Supporting Information

Cu(I)-catalysed Asymmetric Intramolecular Tandem Oxaziridination/Rearrangement Reaction: Theoretical Insight into Mechanism, Enantioselectivity, Ligand Effect, and Comparison with the Corresponding Lewis-acid-promoted Reaction

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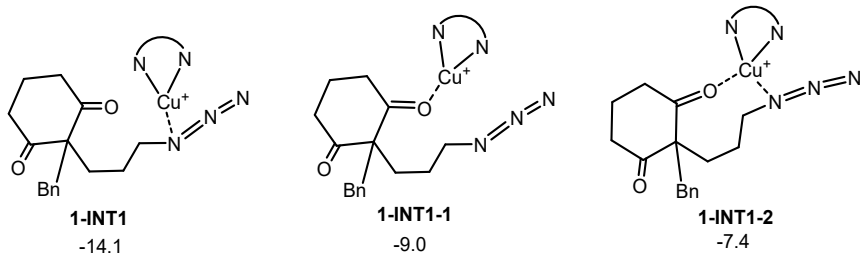
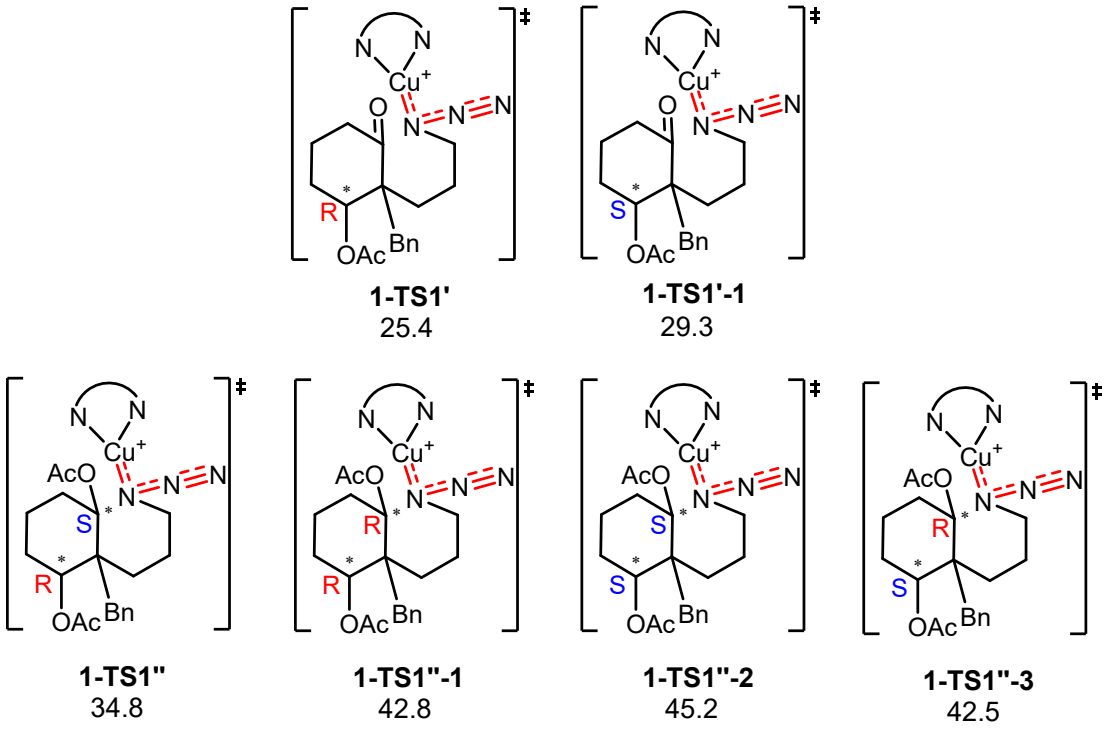
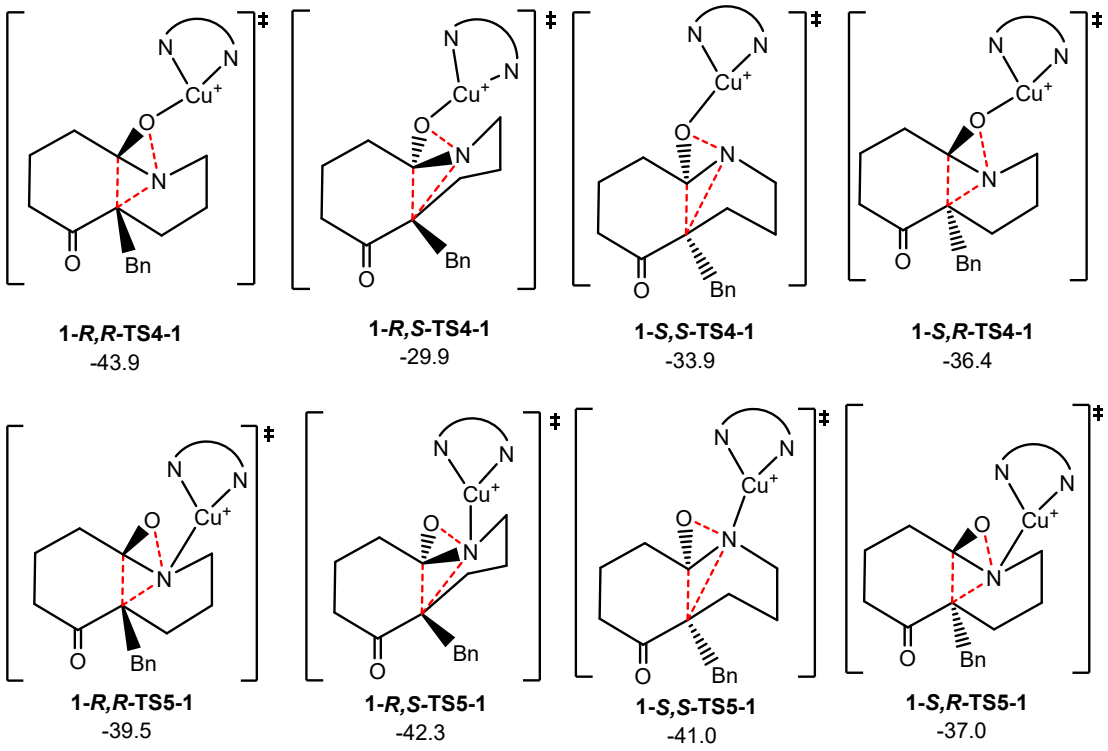
Section 1. Other possible isomers for key species



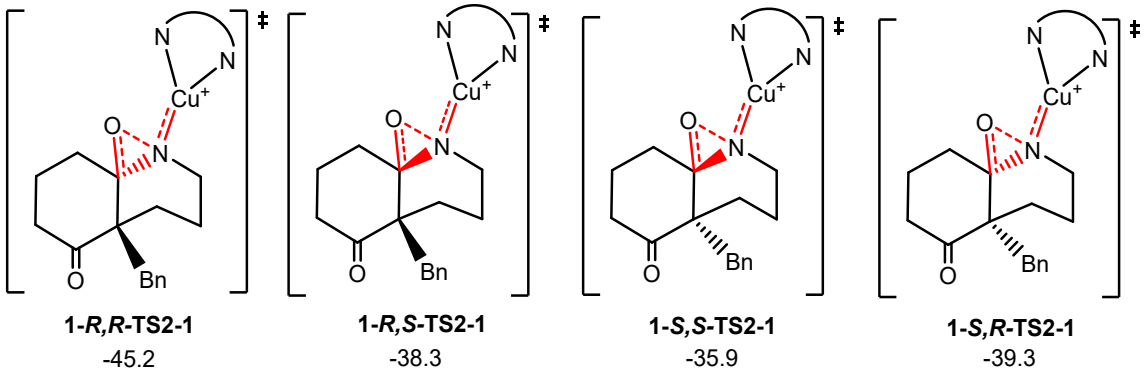
Scheme S1 Other possible isomers of intermediate **1-INT1**. Values shown are relative free energies in kcal/mol.



Scheme S2 Other stereoisomeric modes of transition states **1-TS1'** and **1-TS1"**. Values shown are relative free energies in kcal/mol.



Scheme S3 Other possible isomers of transition states **1-TS4** and **1-TS5**. Values shown are relative free energies in kcal/mol.



Scheme S4 Other possible conformers of transition states **1-TS2**. Values shown are relative free energies in kcal/mol.

Section 2. Other possible Cu-catalyzed pathways to afford 2-*S* and 2-*R*

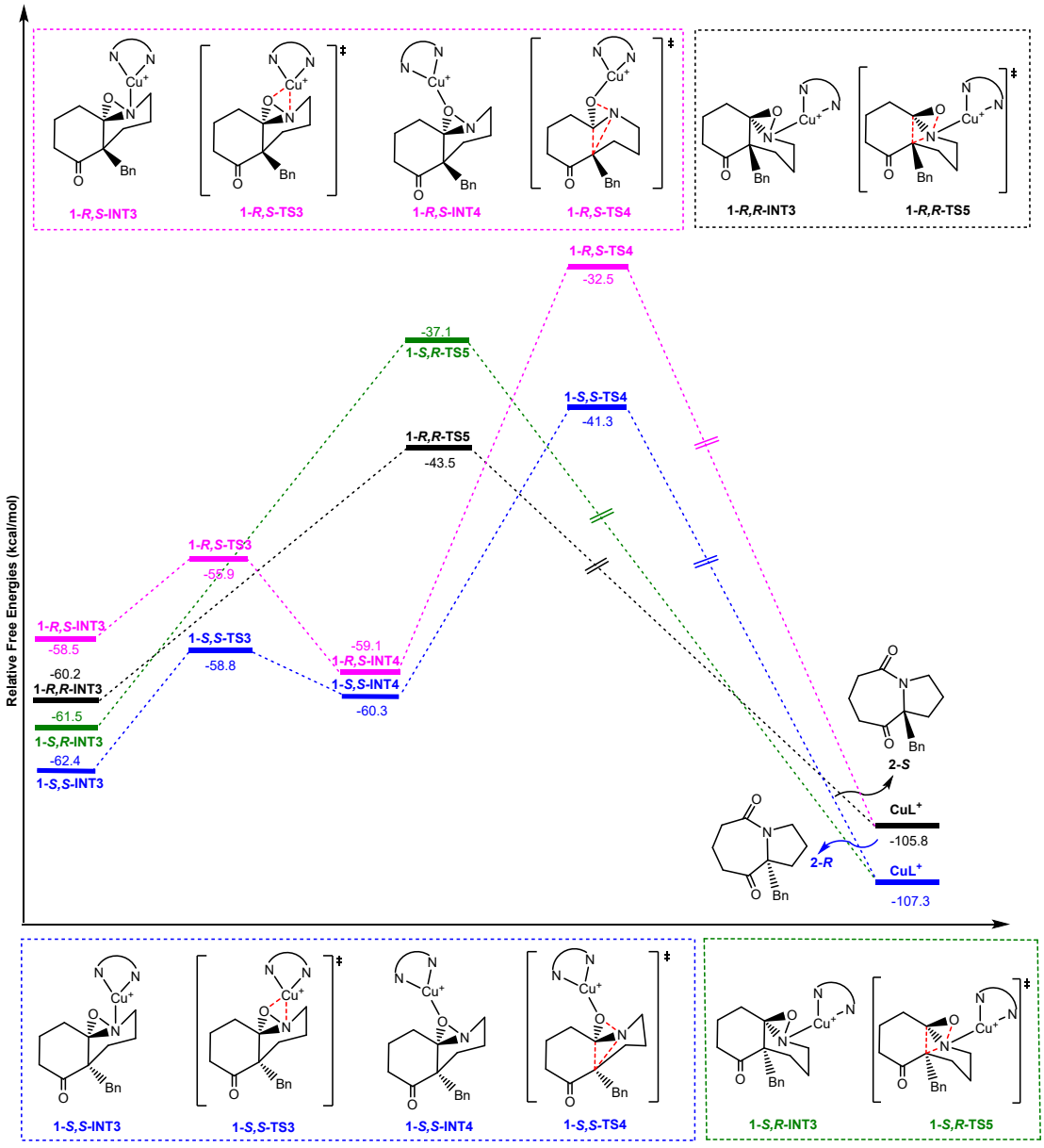


Fig. S1 Calculated energy profiles for other possible rearrangement processes from **1-*R*,*R*-INT3**, **1-*R*,*S*-INT3**, **1-*S*,*S*-INT3** and **1-*S*,*R*-INT3**, respectively. Values shown are relative free energies in kcal/mol.

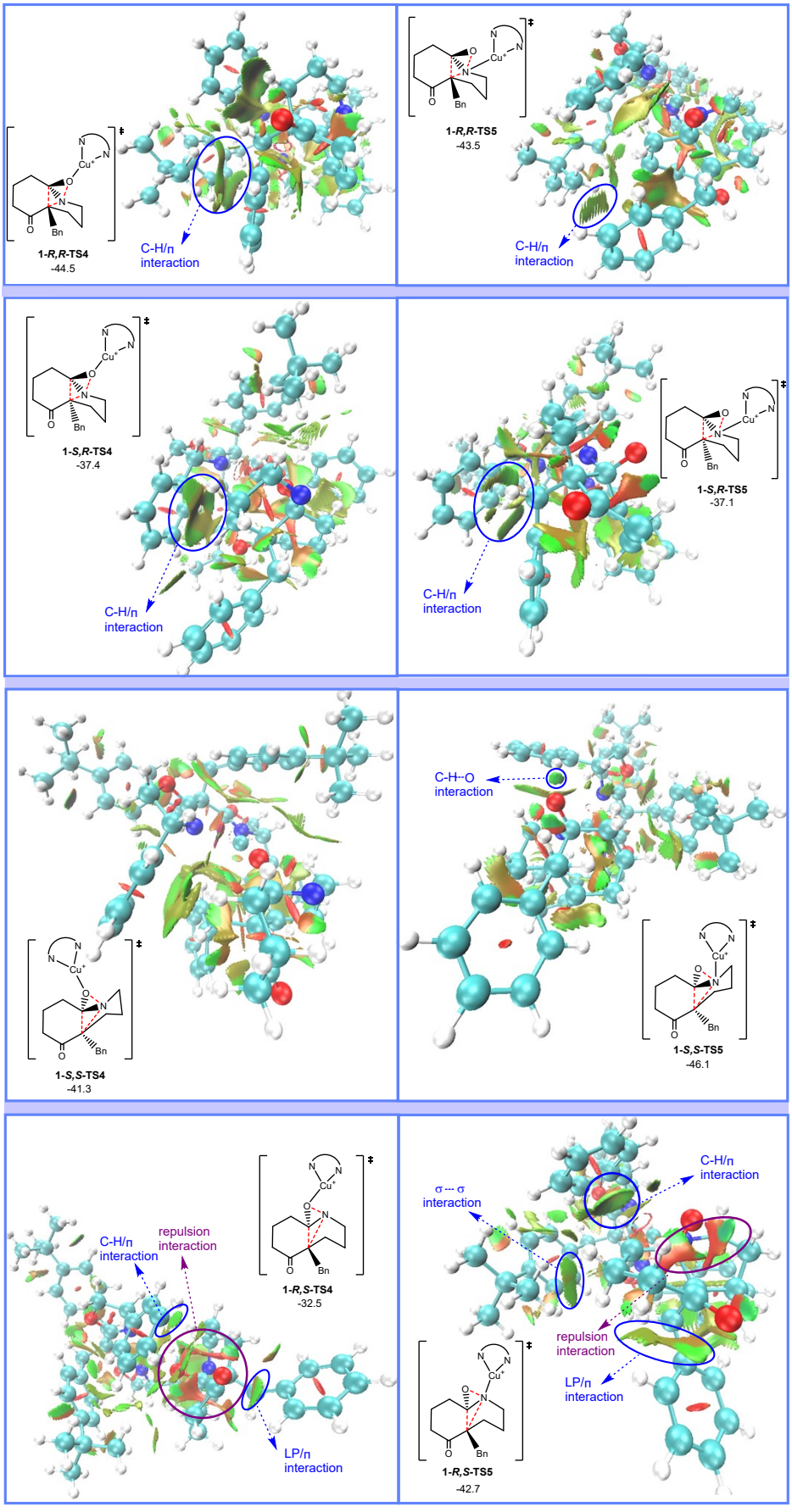


Fig. S2 RDG analyses for the 1,2-alkyl-shift transition states (coordination of oxygen

vs. nitrogen to copper). Distances and free energies are in units of Å and kcal/mol, respectively.

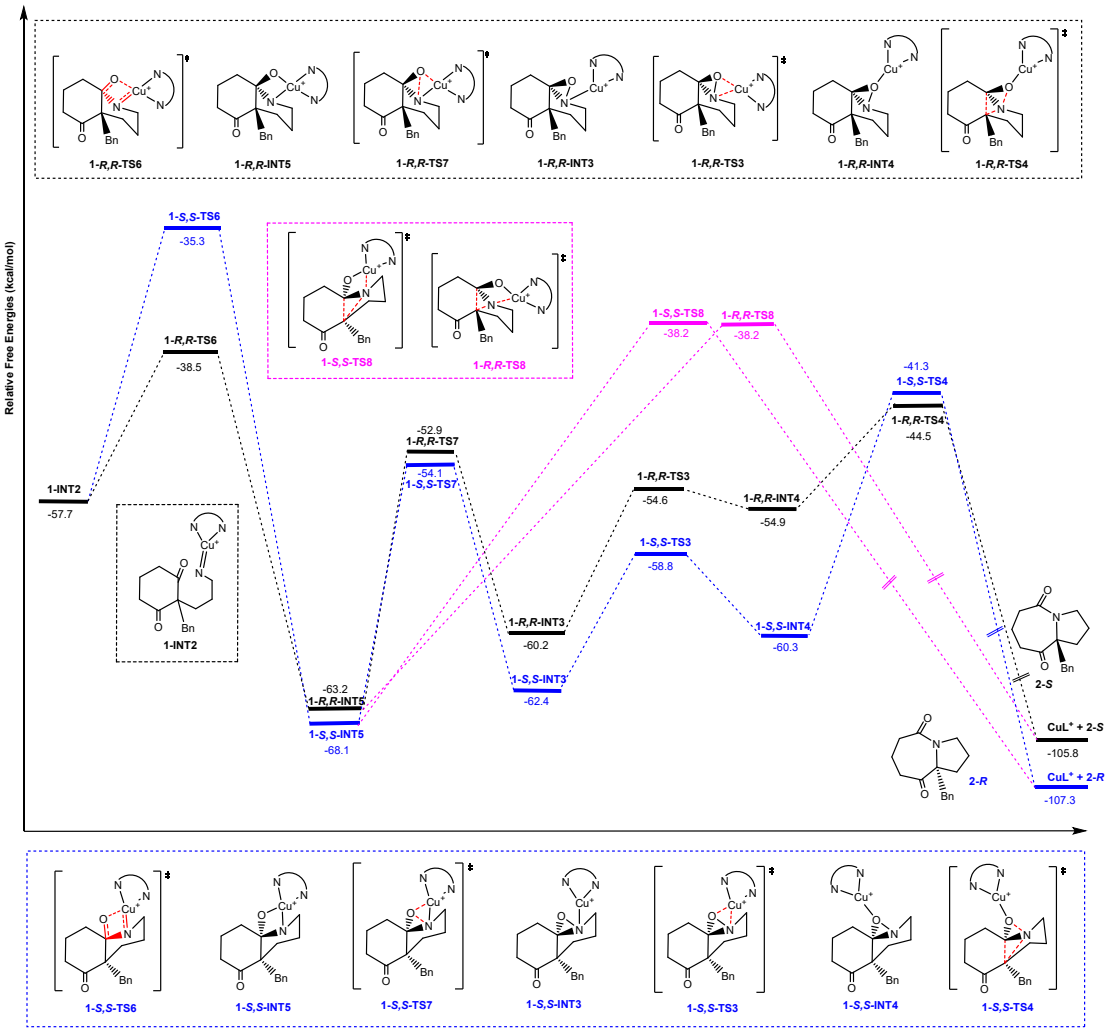


Fig. S3 Calculated energy profiles for other possible pathways affording product **2-*S*** and byproduct **2-*R*** from **1-INT2**. Values shown are relative free energies in kcal/mol.

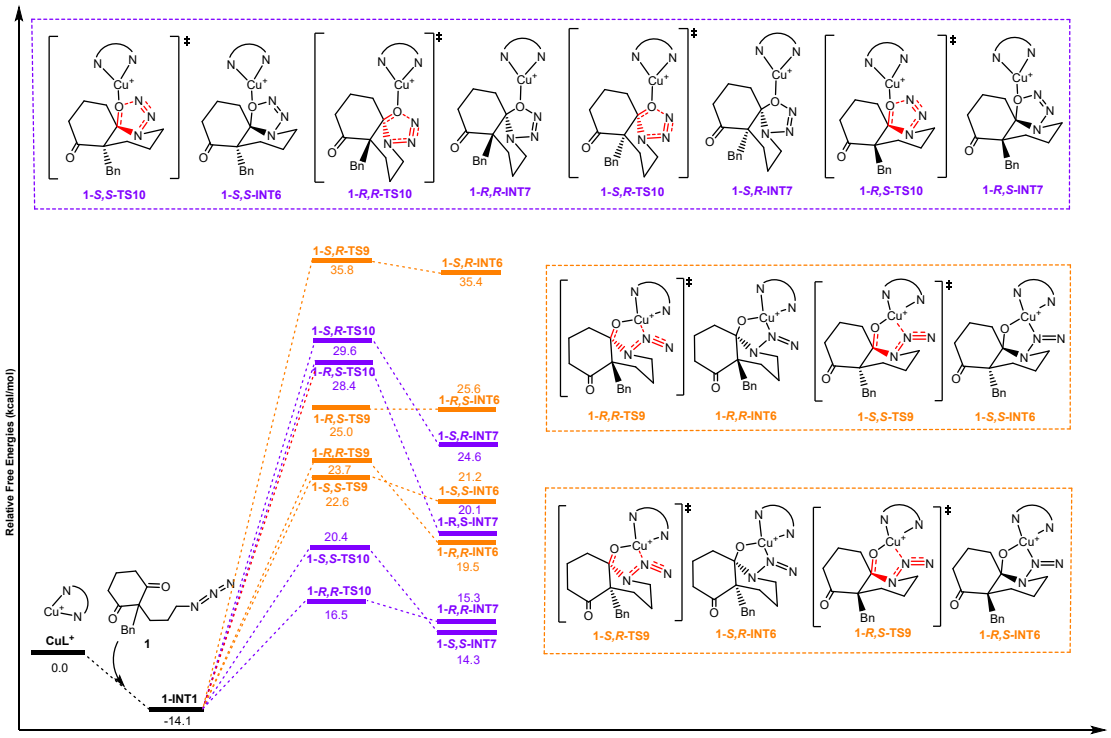


Fig. S4 Calculated energy profiles for the process in which the C−N-bond forming is the first step. Values shown are relative free energies in kcal/mol.

Section 3. Ligand effect

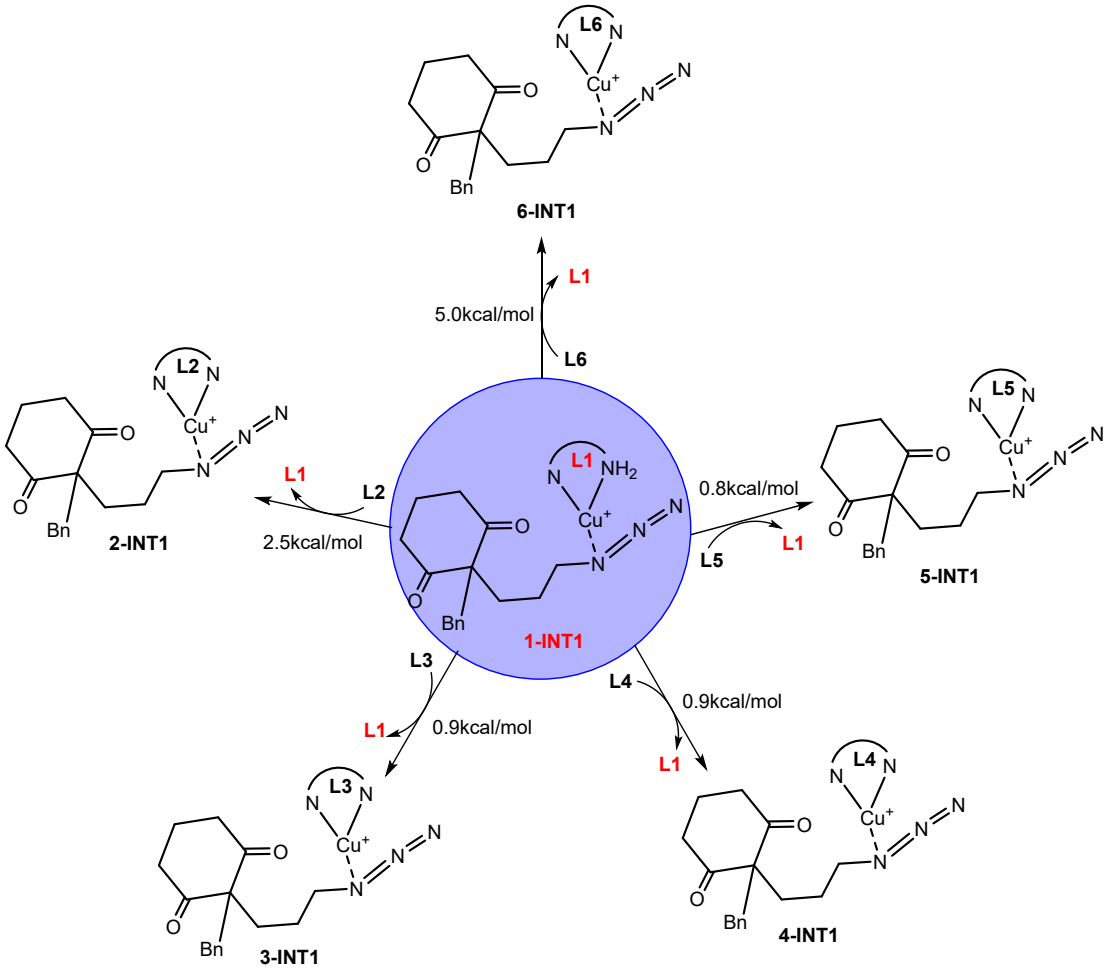


Fig. S5 Ligand exchange energies of intermediate **1-INT1** for ligands **L2**–**L6**. Values shown are relative free energies in kcal/mol.

Section 4. Other possible acid-promoted pathways to afford 2-*S* and 2-*R*

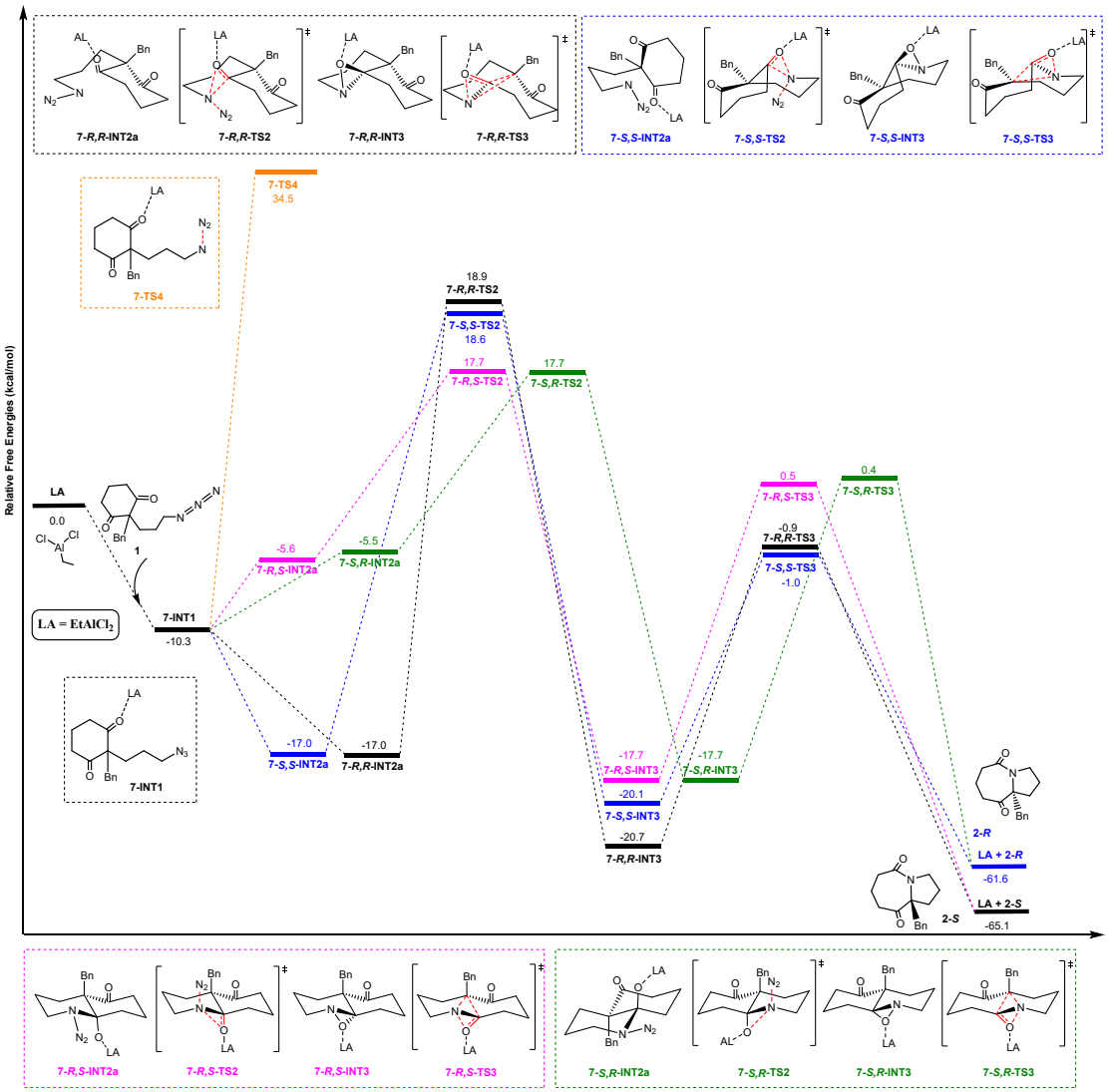
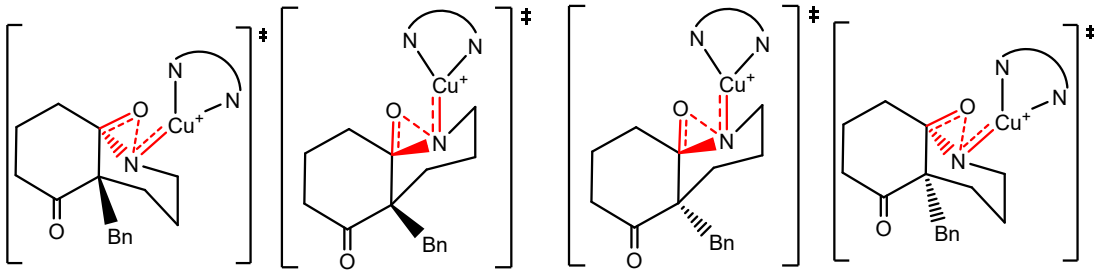


Fig. S6 Calculated energy profiles for the other possible pathways of Lewis-acid-promoted asymmetric Schmidt reaction. Values shown are relative free energies in kcal/mol.

Section 5. Optimization with M06-D3 and ωB97XD methods

Table S1 Calculated free energy barriers (in kcal/mol) for the asymmetric oxaziridination step with M06-D3 and ωB97XD methods



Species	ΔΔ G
1-*R*,*R*-TS2-M06-D3	0.0
1-*R*,*S*-TS2-M06-D3	1.3
1-*S*,*S*-TS2-M06-D3	2.8
1-*S*,*R*-TS2-M06-D3	2.5
1-*R*,*R*-TS2-wB97XD	0.0
1-*R*,*S*-TS2-wB97XD	4.6
1-*S*,*S*-TS2-wB97XD	4.7
1-*S*,*R*-TS2-wB97XD	4.3

Section 6. Energies (in hartree) of All TSs and Intermediates

Solvent=dichloromethane:

Geometry	E_0	E	$H_{353.15}$	$G_{353.15}$	$E_{(sol,M06-D3)}$
CuL^+	-2045.447061	-2045.404318	-2045.403374	-2045.527444	-2046.465952
CuCl	-656.421168	-656.418414	-656.417470	-656.444676	-657.6563139
AgCl	-606.027028	-606.024190	-606.023246	-606.051502	-607.2477728
$BArF^-$	-3647.563630	-3647.517060	-3647.516116	-3647.653715	-3647.405246
AgSbF6	-750.401864	-750.391015	-750.390071	-750.441132	-751.6485904
NaBArF	-3809.792515	-3809.740924	-3809.739979	-3809.890536	-3809.5992998
NaSbF6	-766.993718	-766.983427	-766.982483	-767.030032	-767.0012536
L	-1849.360791	-1849.319611	-1849.318667	-1849.439317	-1849.1767851
N_2	-109.510010	-109.507649	-109.506705	-109.528459	-109.5546816
1	-935.502803	-935.483307	-935.482363	-935.553228	-935.422538

2-*S*	-826.080658	-826.064485	-826.063541	-826.124825	-826.0230453
2-*R*	-826.084870	-826.068895	-826.067950	-826.128656	-826.0266094
1-INT1	-2980.988147	-2980.924991	-2980.924046	-2981.090091	-2981.9424057
1-INT1-1	-2980.994599	-2980.931413	-2980.930468	-2981.095402	-2981.932478
1-INT1-2	-2980.993802	-2980.930345	-2980.929401	-2981.097598	-2981.9320647
1-TS1	-2980.963779	-2980.900745	-2980.899800	-2981.064030	-2981.903828
1-INT2	-2871.470842	-2871.409987	-2871.409042	-2871.569730	-2872.436077
1-*R,R*-TS2	-2871.461247	-2871.401401	-2871.400457	-2871.558442	-2872.402155
1-*R,S*-TS2	-2871.451713	-2871.392543	-2871.391599	-2871.546505	-2872.415156
1-S,S-TS2	-2871.453400	-2871.393867	-2871.392923	-2871.550435	-2872.4139793
1-*S,R*-TS2	-2871.450701	-2871.390844	-2871.389900	-2871.547480	-2872.4122424
1-*R,R*-TS2-1	-2871.459410	-2871.399832	-2871.398888	-2871.555018	-2872.4196612
1-*R,S*-TS2-1	-2871.445759	-2871.386573	-2871.385629	-2871.541747	-2872.409747
1-*S,S*-TS2-1	-2871.444988	-2871.385617	-2871.384673	-2871.540999	-2872.405549
1-*S,R*-TS2-1	-2871.449315	-2871.389401	-2871.388457	-2871.547039	-2872.407723
1-*R,R*-INT3	-2871.492559	-2871.433197	-2871.432253	-2871.586643	-2872.444441
1-*R,S*-INT3	-2871.480197	-2871.420279	-2871.419335	-2871.578774	-2872.441294
1-*S,S*-INT3	-2871.486149	-2871.426494	-2871.425550	-2871.584167	-2872.448416
1-*S,R*-INT3	-2871.486676	-2871.426787	-2871.425842	-2871.584096	-2872.447253
1-*R,R*-TS3	-2871.479591	-2871.420226	-2871.419282	-2871.577068	-2872.4352909
1-*R,S*-TS3	-2871.478806	-2871.419148	-2871.418204	-2871.578764	-2872.4339103
1-*S,S*-TS3	-2871.484683	-2871.425255	-2871.424311	-2871.583228	-2872.4401382
1-*S,R*-TS3	-2871.479744	-2871.420644	-2871.419700	-2871.575947	-2872.4345895
1-*R,R*-INT4	-2871.476159	-2871.415982	-2871.415038	-2871.575519	-2872.4339869
1-*R,S*-INT4	-2871.486780	-2871.426987	-2871.426043	-2871.585158	-2872.4424948
1-*S,S*-INT4	-2871.488335	-2871.428708	-2871.427764	-2871.585586	-2872.4453902
1-*S,R*-INT4	-2871.473877	-2871.414424	-2871.413480	-2871.573172	-2872.4285157
1-*R,R*-TS4	-2871.462875	-2871.403768	-2871.402824	-2871.555947	-2872.4221385
1-*R,S*-TS4	-2871.442649	-2871.382976	-2871.382032	-2871.540231	-2872.3963796
1-*S,S*-TS4	-2871.459012	-2871.399409	-2871.398465	-2871.556438	-2872.4113639
1-*S,R*-TS4	-2871.460498	-2871.401658	-2871.400713	-2871.552944	-2872.4116197
1-*R,R*-TS4-1	-2871.465136	-2871.405906	-2871.404962	-2871.557323	-2872.421007
1-*R,S*-TS4-1	-2871.441448	-2871.381775	-2871.380831	-2871.538953	-2872.3931238
1-*S,S*-TS4-1	-2871.448066	-2871.388179	-2871.387235	-2871.544299	-2872.4005347
1-*S,R*-TS4-1	-2871.456608	-2871.397446	-2871.396502	-2871.549864	-2872.4077921
1-*R,R*-TS5	-2871.458145	-2871.399034	-2871.398090	-2871.552354	-2872.4200164
1-*R,S*-TS5	-2871.456443	-2871.397050	-2871.396106	-2871.552355	-2872.4159746
1-*S,S*-TS5	-2871.466075	-2871.407156	-2871.406212	-2871.561269	-2872.4240111
1-*S,R*-TS5	-2871.450749	-2871.391399	-2871.390455	-2871.546644	-2872.4076727
1-*R,R*-TS5-1	-2871.455463	-2871.396444	-2871.395500	-2871.550110	-2872.4132084
1-*R,S*-TS5-1	-2871.457764	-2871.398486	-2871.397542	-2871.552681	-2872.4168418
1-*S,S*-TS5-1	-2871.454799	-2871.395470	-2871.394526	-2871.553391	-2872.4106774
1-*S,R*-TS5-1	-2871.453972	-2871.394623	-2871.393679	-2871.551199	-2872.4051702

1-*R,R*-TS6	-2871.447763	-2871.387415	-2871.386471	-2871.546172	-2872.4036328
1-*S,S*-TS6	-2871.442890	-2871.383309	-2871.382364	-2871.538887	-2872.426305
1-*R,R*-INT5	-2871.485256	-2871.425983	-2871.425039	-2871.582684	-2872.450385
1-*S,S*-INT5	-2871.493392	-2871.434322	-2871.433378	-2871.589233	-2872.4595202
1-*R,R*-TS7	-2871.476074	-2871.416563	-2871.415619	-2871.574426	-2872.4307725
1-*S,S*-TS7	-2871.480206	-2871.421102	-2871.420157	-2871.575703	-2872.4358409
1-*R,R*-TS8	-2871.447924	-2871.388535	-2871.387591	-2871.543892	-2872.4086629
1-*S,S*-TS8	-2871.447186	-2871.387314	-2871.386370	-2871.545603	-2872.4049657
1-*R,R*-TS9	-2980.944956	-2980.883788	-2980.882844	-2981.043589	-2981.885605
1-*R,S*-TS9	-2980.944878	-2980.883908	-2980.882964	-2981.042740	-2981.8853701
1-*S,S*-TS9	-2980.947943	-2980.886641	-2980.885696	-2981.046008	-2981.888053
1-*S,R*-TS9	-2980.933668	-2980.872738	-2980.871794	-2981.031204	-2981.8681042
1-*R,R*-INT6	-2980.953458	-2980.892551	-2980.891607	-2981.051294	-2981.8955424
1-*R,S*-INT6	-2980.946770	-2980.885908	-2980.884964	-2981.043790	-2981.8933471
1-*S,S*-INT6	-2980.951470	-2980.890128	-2980.889184	-2981.049537	-2981.8918093
1-*S,R*-INT6	-2980.935512	-2980.874855	-2980.873910	-2981.031475	-2981.8728548
1-*R,R*-TS10	-2980.958764	-2980.897286	-2980.896342	-2981.058500	-2981.896382
1-*R,S*-TS10	-2980.945371	-2980.884125	-2980.883181	-2981.044770	-2981.8782312
1-*S,S*-TS10	-2980.953271	-2980.892056	-2980.891112	-2981.052745	-2981.8910771
1-*S,R*-TS10	-2980.943639	-2980.882642	-2980.881698	-2981.042535	-2981.8773601
1-*R,R*-INT7	-2980.966555	-2980.905594	-2980.904650	-2981.065155	-2981.9025826
1-*R,S*-INT7	-2980.961736	-2980.900552	-2980.899608	-2981.061200	-2981.8933471
1-*S,S*-INT7	-2980.969491	-2980.908219	-2980.907274	-2981.068090	-2981.9036945
1-*S,R*-INT7	-2980.953211	-2980.892310	-2980.891366	-2981.052643	-2981.8867345
1-INT1’	-3134.799924	-3134.733501	-3134.732557	-3134.906026	-3135.7513085
1-INT1’-1	-3134.795907	-3134.729746	-3134.728801	-3134.901456	-3135.7477209
1-INT1”	-3288.589025	-3288.519138	-3288.518194	-3288.696711	-3289.5550652
1-INT1”-1	-3288.591042	-3288.521182	-3288.520238	-3288.698782	-3289.5591499
1-INT1”-2	-3288.598243	-3288.528166	-3288.527222	-3288.707204	-3289.5615975
1-INT1”-3	-3288.595522	-3288.525452	-3288.524508	-3288.704897	-3289.5594856
1-TS’	-3134.763227	-3134.696685	-3134.695741	-3134.868412	-3135.7134292
1-TS’-1	-3134.757669	-3134.691523	-3134.690578	-3134.860428	-3135.7041888
1-TS”	-3288.538151	-3288.467719	-3288.466774	-3288.648091	-3289.4910381
1-TS”-1	-3288.532484	-3288.462622	-3288.461678	-3288.639235	-3289.4867166
1-TS”-2	-3288.539278	-3288.468744	-3288.467800	-3288.467800	-3289.4910292
1-TS”-3	-3288.533484	-3288.463802	-3288.462858	-3288.640314	-3289.4902648
2-INT1	-2666.685594	-2666.633378	-2666.632434	-2666.775755	-2667.5900918
2-TS1	-2666.646925	-2666.594351	-2666.593407	-2666.738608	-2666.3584525
3-INT1	-2745.273127	-2745.216962	-2745.216018	-2745.371079	-2746.1833121
3-TS1	-2745.233559	-2745.177469	-2745.176525	-2745.329721	-2744.9507815
4-INT1	-2902.427076	-2902.366378	-2902.365433	-2902.526827	-2903.3549467
4-TS1	-2902.387478	-2902.326728	-2902.325784	-2902.487844	-2902.1235736
5-INT1	-3340.756597	-3340.697118	-3340.696174	-3340.857879	-3341.6634372

5-TS1	-3340.717517	-3340.657979	-3340.657035	-3340.818140	-3340.431068
6-INT1	-2204.715853	-2204.671829	-2204.670885	-2204.796204	-2205.7183373
6-TS1	-2204.675958	-2204.631972	-2204.631027	-2204.756253	-2204.4857495
1-*R,R*-TS2-M06-D3	-2869.423219	-2869.364554	-2869.363609	-2869.513932	-2872.426944
1-*R,S*-TS2-M06-D3	-2869.415228	-2869.356307	-2869.355363	-2869.507598	-2872.4217857
1-*S,S*-TS2-M06-D3	-2869.415399	-2869.356610	-2869.355666	-2869.508319	-2872.4200069
1-*S,R*-TS2-M06-D3	-2869.414118	-2869.354922	-2869.353978	-2869.506825	-2872.4191018
1-*R,R*-TS2-ωB97XD	-2870.497208	-2870.438117	-2870.437173	-2870.592385	-2873.4817107
1-*R,S*-TS2-ωB97XD	-2870.486383	-2870.427614	-2870.426670	-2870.580405	-2873.4762372
1-*S,S*-TS2-ωB97XD	-2870.488752	-2870.429876	-2870.428931	-2870.583763	-2873.4747444
1-*S,R*-TS2-ωB97XD	-2870.486590	-2870.427288	-2870.426343	-2870.583523	-2873.4727143

Solvent=diethylether:

1	-935.500249	-935.480743	-935.479799	-935.551342	-935.419035
LA	-1242.139984	-1242.132326	-1242.131382	-1242.174183	-1242.1464968
2-*S*	-826.084076	-826.068067	-826.067123	-826.128192	-826.0252677
2-*S*-1	-826.066468	-826.050787	-826.049843	-826.109284	-826.006771
2-*R*	-826.077078	-826.061032	-826.060088	-826.121294	-826.0193626
2-*R*-1	-826.057516	-826.041651	-826.040707	-826.101088	-825.9972895
N_2	-109.510368	-109.508007	-109.507063	-109.528817	-109.4855152
7-INT1	-2177.686239	-2177.658127	-2177.657183	-2177.748592	-2177.6083854
7-*R,R*-INT2a	-2177.696668	-2177.668946	-2177.668001	-2177.757438	-2177.620711
7-*R,S*-INT2a	-2177.680975	-2177.653924	-2177.652979	-2177.739632	-2177.6053694
7-*S,S*-INT2a	-2177.696672	-2177.668949	-2177.668005	-2177.757437	-2177.6207143
7-*S,R*-INT2a	-2177.680956	-2177.653918	-2177.652973	-2177.739549	-2177.6053816
7-*R,R*-INT2b	-2177.688083	-2177.660376	-2177.659432	-2177.748490	-2177.6100082
7-*R,S*-INT2b	-2177.682891	-2177.655349	-2177.654405	-2177.742550	-2177.6059601
7-*S,S*-INT2b	-2177.683511	-2177.656362	-2177.655418	-2177.743564	-2177.6053119
7-*S,R*-INT2b	-2177.682876	-2177.655343	-2177.654399	-2177.742488	-2177.6059491
7-*R,R*-TS1a	-2177.657846	-2177.630823	-2177.629879	-2177.717254	-2177.5748026
7-*R,S*-TS1a	-2177.654652	-2177.627804	-2177.626860	-2177.712962	-2177.5710451
7-*S,S*-TS1a	-2177.658510	-2177.631649	-2177.630705	-2177.717165	-2177.5744931
7-*S,R*-TS1a	-2177.654657	-2177.627807	-2177.626863	-2177.712965	-2177.5710476
7-*R,R*-TS1b	-2177.649744	-2177.623019	-2177.622075	-2177.707261	-2177.5631388
7-*R,S*-TS1b	-2177.642990	-2177.615954	-2177.615010	-2177.701670	-2177.5599414
7-*S,S*-TS1b	-2177.650165	-2177.623030	-2177.622086	-2177.709234	-2177.5639089

7-*S,R*-TS1b	-2177.642984	-2177.615950	-2177.615006	-2177.701627	-2177.55994
7-*R,R*-TS2	-2177.647594	-2177.620690	-2177.619745	-2177.706657	-2177.5633642
7-*R,S*-TS2	-2177.649019	-2177.622120	-2177.621176	-2177.708012	-2177.5651394
7-*S,S*-TS2	-2177.647966	-2177.621021	-2177.620076	-2177.707311	-2177.5634141
7-*S,R*-TS2	-2177.649030	-2177.622132	-2177.621187	-2177.707961	-2177.5651452
7-*R,R*-INT3	-2068.183436	-2068.158629	-2068.157685	-2068.240500	-2068.1228291
7-*R,S*-INT3	-2068.179285	-2068.154666	-2068.153722	-2068.235476	-2068.1192798
7-*S,S*-INT3	-2068.182980	-2068.158241	-2068.157297	-2068.239879	-2068.1218851
7-*S,R*-INT3	-2068.179285	-2068.154667	-2068.153723	-2068.235475	-2068.1192799
7-*R,R*-TS3	-2068.151582	-2068.126782	-2068.125838	-2068.209907	-2068.0860164
7-*R,S*-TS3	-2068.150122	-2068.125612	-2068.124668	-2068.205733	-2068.0860731
7-*S,S*-TS3	-2068.151578	-2068.126779	-2068.125835	-2068.209932	-2068.0860165
7-*S,R*-TS3	-2068.150170	-2068.125644	-2068.124699	-2068.205900	-2068.0861041
7-TS4	-2177.613098	-2177.584121	-2177.583177	-2177.676218	-2177.5308883

E_0 = Sum of electronic and zero-point energies calculated by B3LYP-D3 in solvent

E = Sum of electronic and thermal energies calculated by B3LYP-D3 in solvent

$H_{298.15}$ = Sum of electronic and thermal enthalpies calculated by B3LYP-D3 in solvent

$G_{298.15}$ = Sum of electronic and thermal free energies calculated by B3LYP-D3 in solvent

$E_{(M06\text{-}D3)}$ = Single point energies calculated by M06-D3 in solvent

Section 7. Calculated imaginary frequencies of all transition states species.

Species	Frequency
1-TS1	-498.72
1-*R,R*-TS2	-267.54
1-*R,S*-TS2	-211.63
1-*S,S*-TS2	-219.16
1-*S,R*-TS2	-49.34
1-*R,R*-TS2-1	-110.41
1-*R,S*-TS2-1	-130.95
1-*S,S*-TS2-1	-316.37
1-*S,R*-TS2-1	-92.78
1-*R,R*-TS3	-94.25

1-*R,S*-TS3	-84.47
1-*S,S*-TS3	-42.48
1-*S,R*-TS3	-78.21
1-*R,R*-TS4	-540.98
1-*R,S*-TS4	-471.57
1-*S,S*-TS4	-553.75
1-*S,R*-TS4	-586.98
1-*R,R*-TS4-1	-521.34
1-*R,S*-TS4-1	-664.47
1-*S,S*-TS4-1	-654.26
1-*S,R*-TS4-1	-466.09
1-*R,R*-TS5	-643.15
1-*R,S*-TS5	-439.96
1-*S,S*-TS5	-599.77
1-*S,R*-TS5	-652.62
1-*R,R*-TS5-1	-647.01
1-*R,S*-TS5-1	-671.88
1-*S,S*-TS5-1	-498.69
1-*S,R*-TS5-1	-446.62
1-*R,R*-TS6	-57.17
1-*S,S*-TS6	-316.09
1-*R,R*-TS7	-251.63
1-*S,S*-TS7	-177.10
1-*R,R*-TS8	-353.86
1-*S,S*-TS8	-455.83
1-*R,R*-TS9	-235.46
1-*R,S*-TS9	-200.14
1-*S,S*-TS9	-170.23
1-*S,R*-TS9	-100.54
1-*R,R*-TS10	-316.68
1-*R,S*-TS10	-216.26
1-*S,S*-TS10	-300.64
1-*S,R*-TS10	-232.81
1-TS’	-494.09
1-TS’-1	-499.68
1-TS”	-464.56
1-TS”-1	-448.39
1-TS”-2	-466.89
1-TS”-3	-478.29
2-TS1	-503.06
3-TS1	-505.81
4-TS1	-504.96
5-TS1	-505.86

6-TS1	-501.64
7-*R,R*-TS1a	-567.60
7-*R,S*-TS1a	-561.94
7-*S,S*-TS1a	-551.26
7-*S,R*-TS1a	-561.80
7-*R,R*-TS1b	-547.07
7-*R,S*-TS1b	-578.29
7-*S,S*-TS1b	-535.48
7-*S,R*-TS1b	-578.28
7-*R,R*-TS2	-572.87
7-*R,S*-TS2	-566.40
7-*S,S*-TS2	-576.92
7-*S,R*-TS2	-565.69
7-*R,R*-TS3	-670.80
7-*R,S*-TS3	-392.47
7-*S,S*-TS3	-670.66
7-*S,R*-TS3	-389.83
7-TS4	-245.89
1-*R,R*-TS2-M06-D3	-322.74
1-*R,S*-TS2-M06-D3	-304.57
1-*S,S*-TS2-M06-D3	-284.63
1-*S,R*-TS2-M06-D3	-355.00
1-*R,R*-TS2-ωB97XD	-302.13
1-*R,S*-TS2-ωB97XD	-268.83
1-*S,S*-TS2-ωB97XD	-290.35
1-*S,R*-TS2-ωB97XD	-191.37