Supporting Information

Theoretical Insights into the Mechanism and Ligand-Controlled Selectivity of Multicomponent Carbonylation toward γ-Butenolide and Ynone

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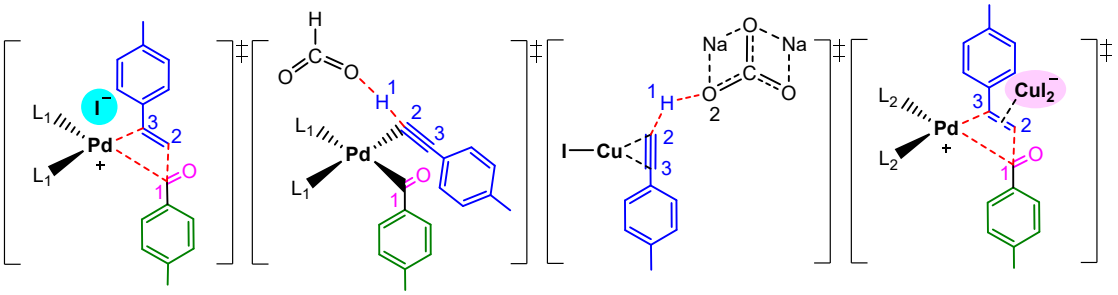
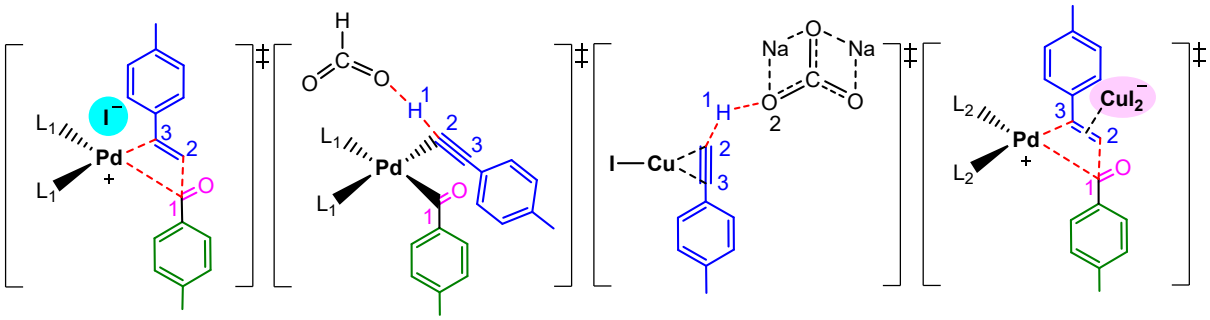
Section 1. Comparison of Computational Methods and Entropy Corrections

Table S1. Relative Gibbs energies (in kcal·mol^{-1}) for the chemo-determining transition states with M06 and BP86 methods.



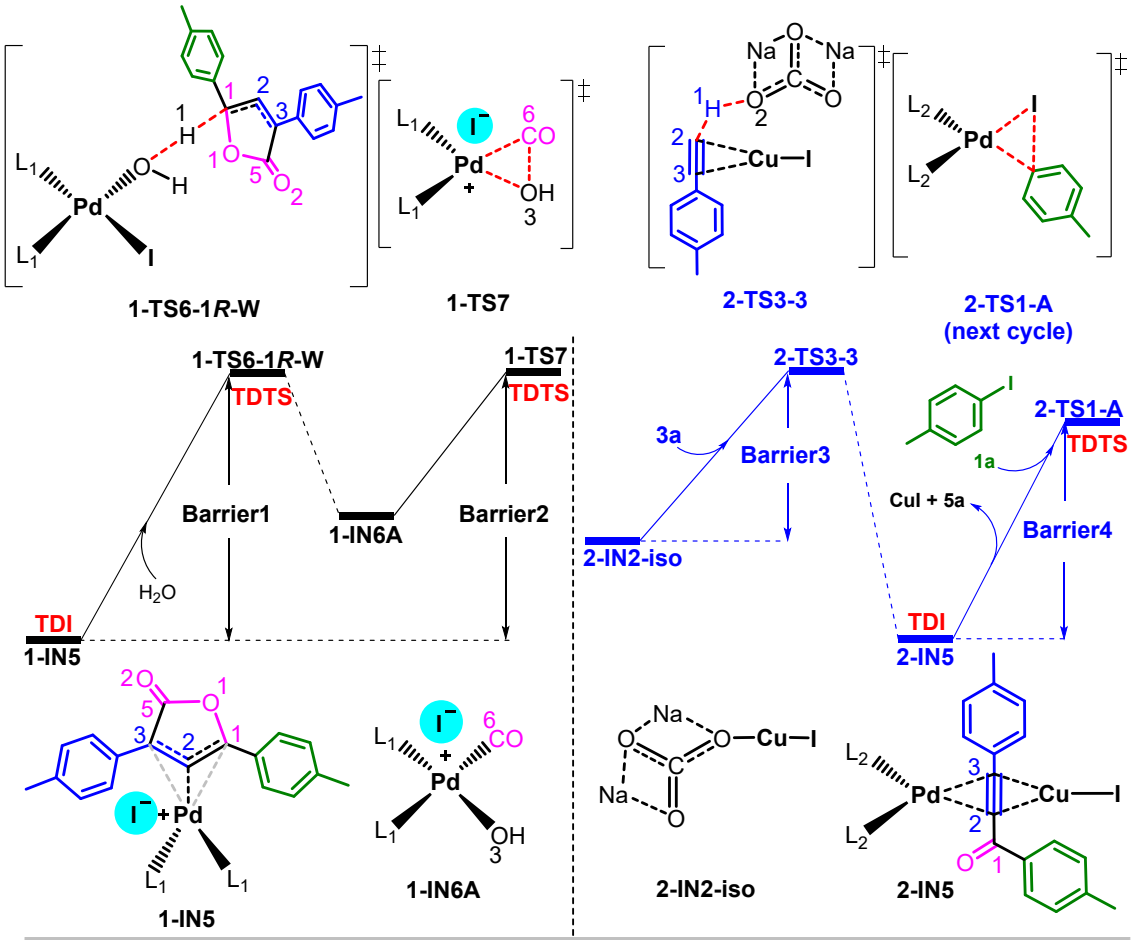
Species	△△ *G*
1-TS3-M06	0.0
1-TS3-1-M06	3.9
2-TS3-3-M06	0.0
2-TS3-2-M06	11.7
1-TS3-BP86	0.0
1-TS3-1-BP86	5.1
2-TS3-3-BP86	0.0
2-TS3-2-BP86	10.1

Table S2. Relative Gibbs energies (in kcal·mol^{-1}) of the chemo-determining transition states under standard RRHO, Martin-type condensed-phase, and Grimme quasi-RRHO corrections.



1-TS3 **1-TS3-1** **2-TS3-3** **2-TS3-2**

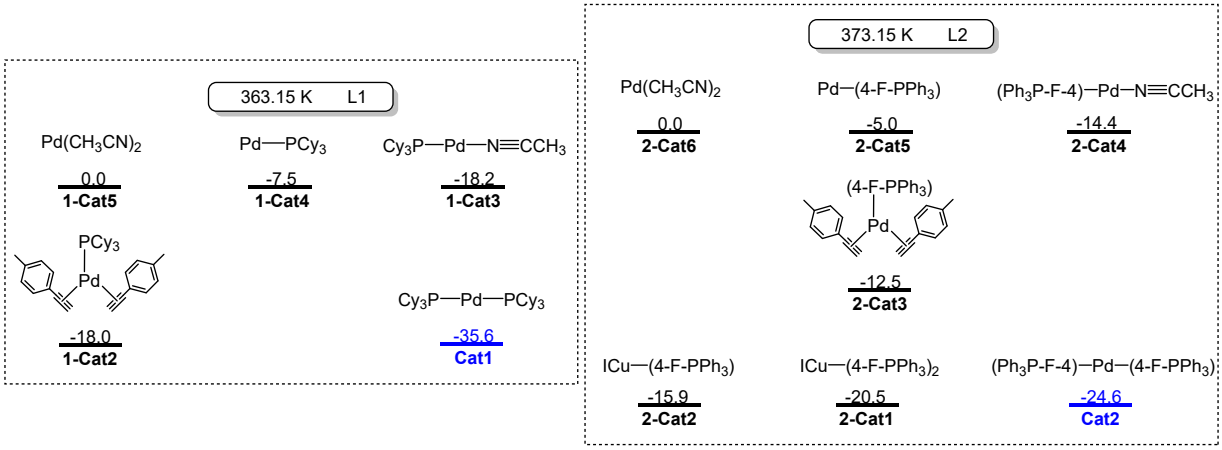
Species Name	RRHO △△ *G*	Martin-type △△ *G*	Grimme-type △△ *G*
1-TS3	0.0	0.0	0.0
1-TS3-1	3.0	2.9	3.4
2-TS3-3	0.0	0.0	0.0
2-TS3-2	12.2	15.3	15.0



Barrier Name	RRHO barrier	Martin-type barrier	Grimme-type barrier
Barrier1	25.5	21.2	28.0
Barrier2	25.5	21.2	27.9
Barrier3	17.8	13.4	19.9
Barrier4	27.4	27.4	30.3

Fig. S1 Identification of turnover-determining transition states and comparison of key barriers under standard RRHO, Martin-type condensed-phase, and Grimme quasi-RRHO corrections. Relative free energies are given in kcal·mol^{-1}.

Section 2. Potential Active Pd-catalysts



Scheme S1. All plausible active Pd catalysts under the γ-butenolide- and ynone-forming conditions. Relative free energies are given in kcal·mol^{-1}.

Section 3. Alternative Mechanistic Pathways for CO Formation

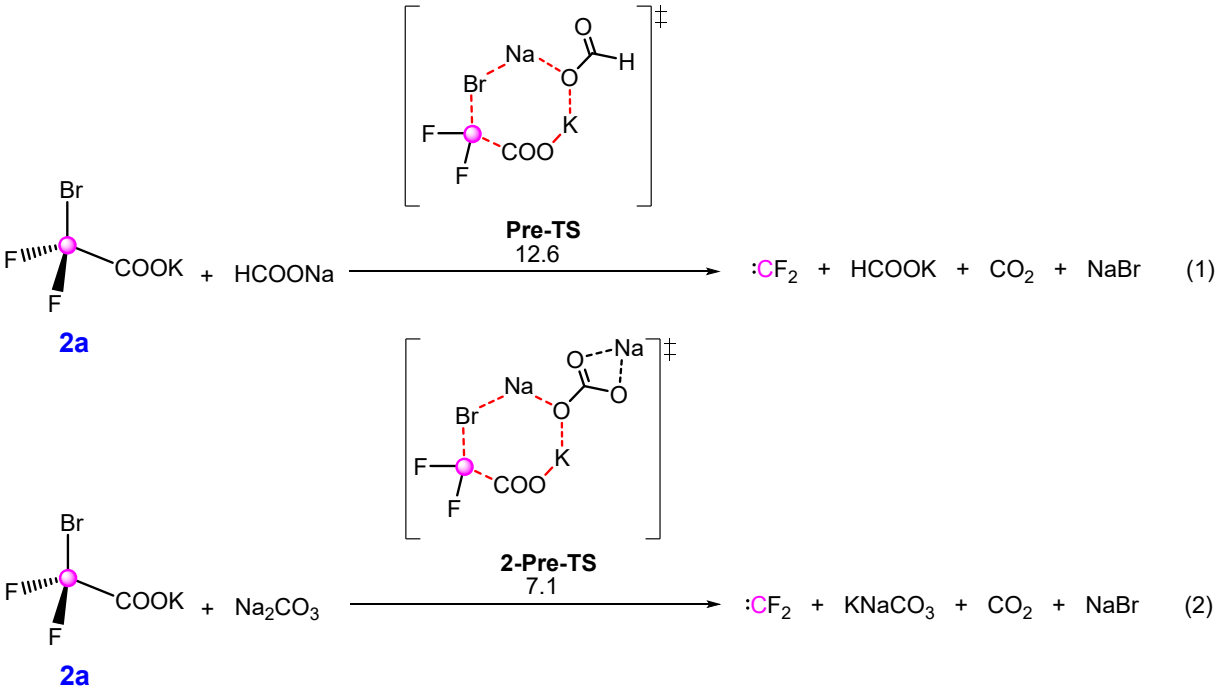


Fig. S2 Calculated free-energy profiles for difluorocarbene formation under the γ-butenolide-forming (eq 1) and ynone-forming (eq 2) conditions. Relative free energies are given in kcal·mol^{-1}.

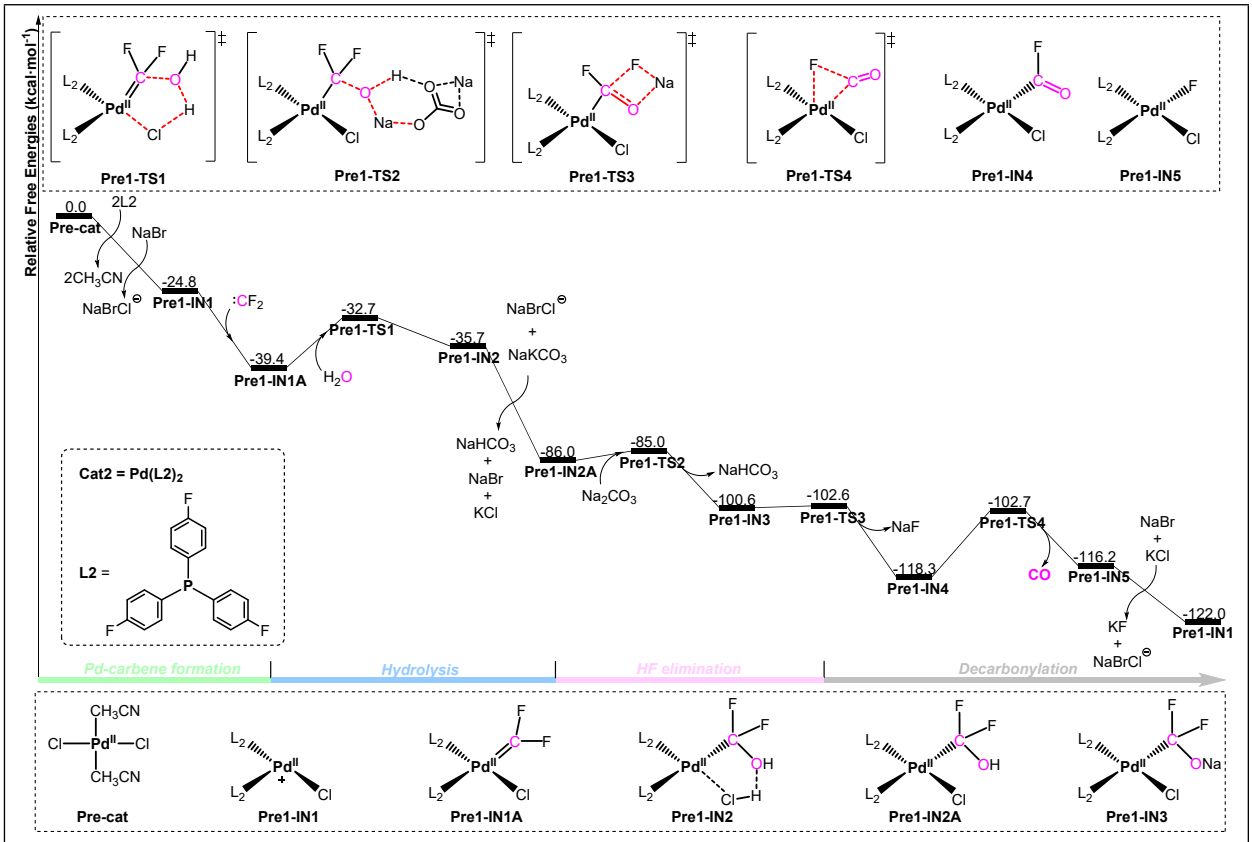
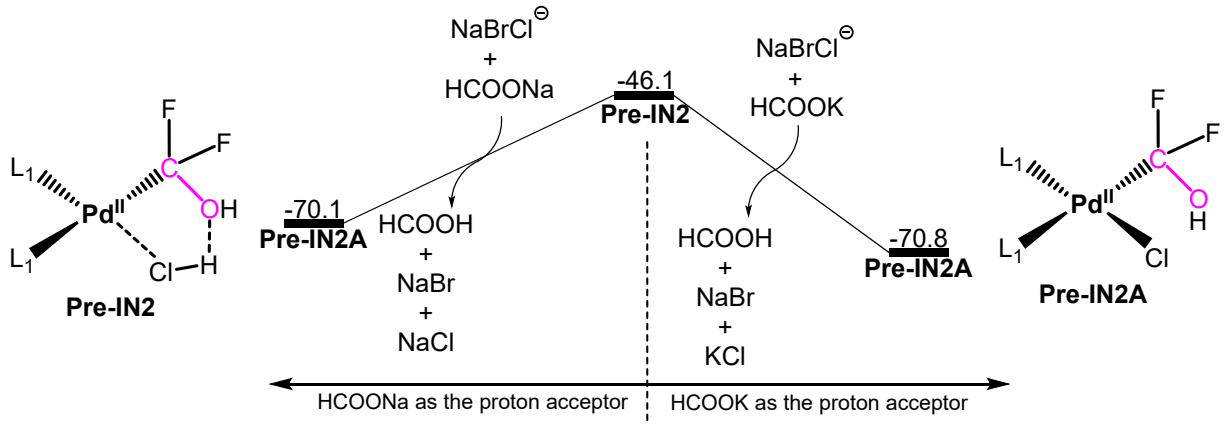
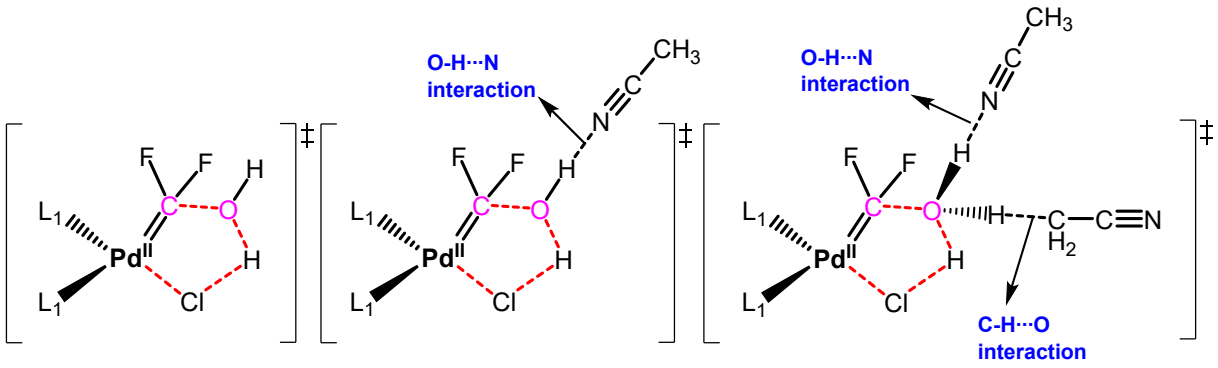


Fig. S3 Calculated free-energy profile for the carbon monoxide formation pathway under the **5a**-forming conditions. Relative free energies are given in kcal·mol^{-1}.



Scheme S2. Comparison of **Pre-IN2A** formation using HCOONa versus HCOOK as the proton acceptor in the presence of $NaBrCl^-$. Relative free energies (kcal·mol^{-1}) are shown.

Table S3. Relative Gibbs energies (in kcal·mol^{-1}) for the potential hydrogen-bonding network with MeCN in hydrolysis process.



Species	△△ *G*
Pre-TS1	0.0
Pre-TS1-1	3.4
Pre-TS1-2	8.7

Section 4. Alternative Pathways for Oxidative Addition

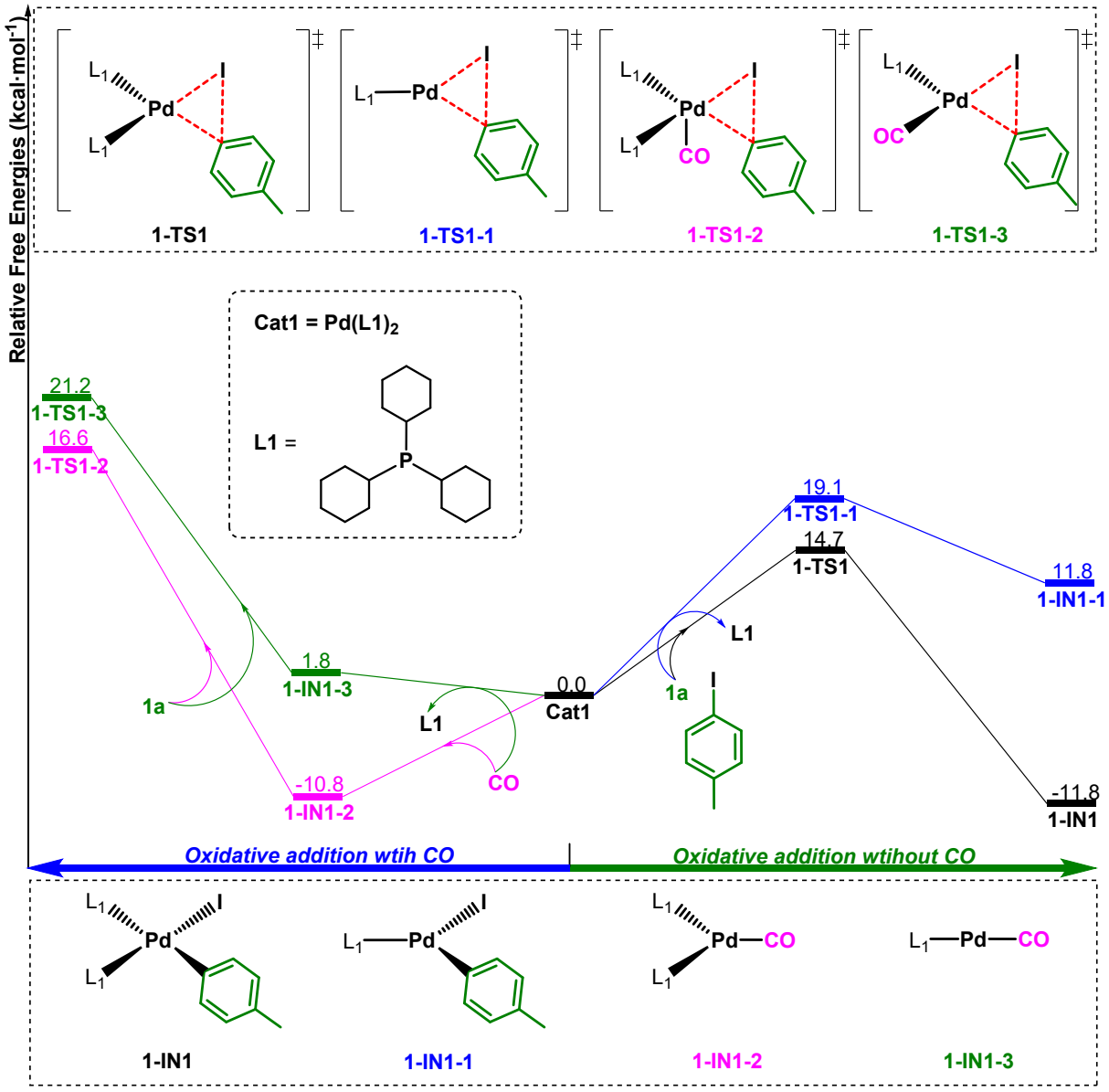
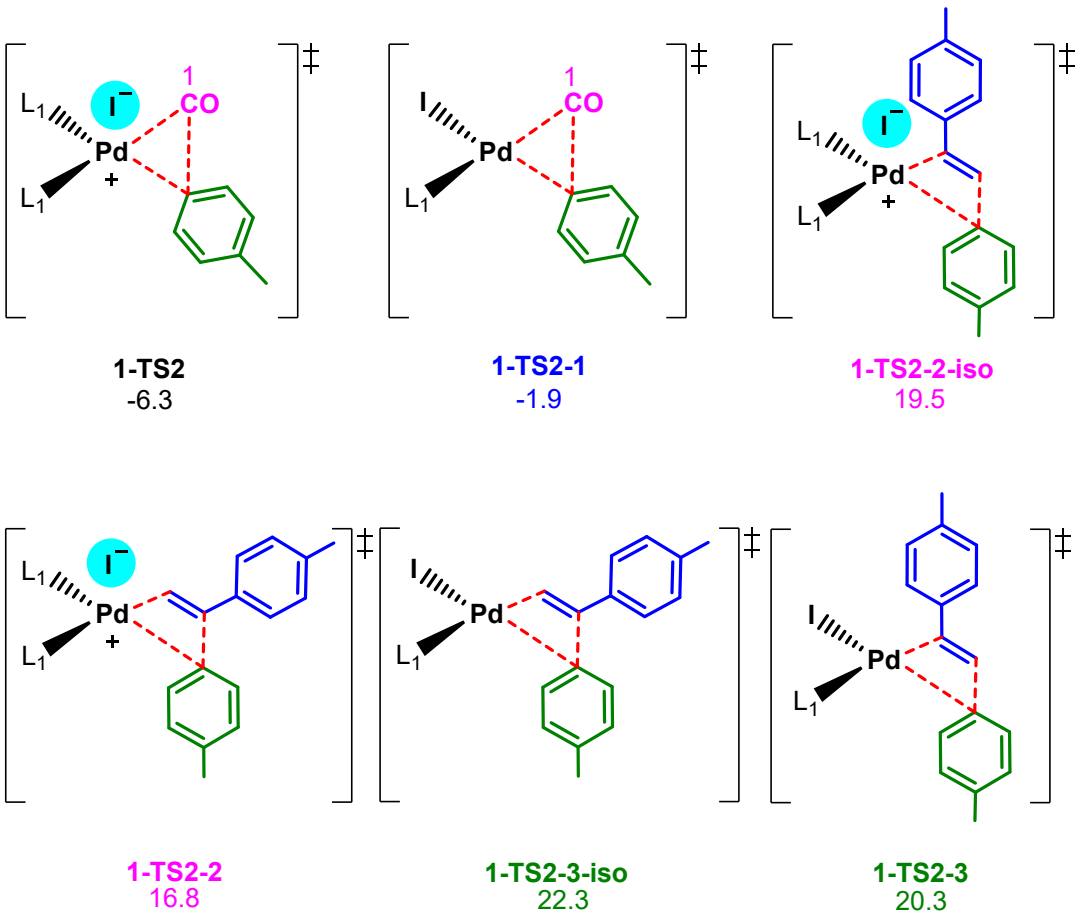


Fig. S4 Calculated free-energy profiles for the oxidative addition pathways. The blue, green, and pink lines correspond to the monophosphine-ligated pathway, the monophosphine/CO-ligated pathway, and the diphosphine/CO-ligated pathway, respectively. Relative free energies are given in kcal·mol^{-1}.

Section 5. Alternative Pathways in the CO Insertion Process



Scheme S3. Potential transition-state structures for the CO insertion step. Relative free energies are given in kcal·mol^{-1}.

Section 6. IGMH Analysis around the Iodide Anion

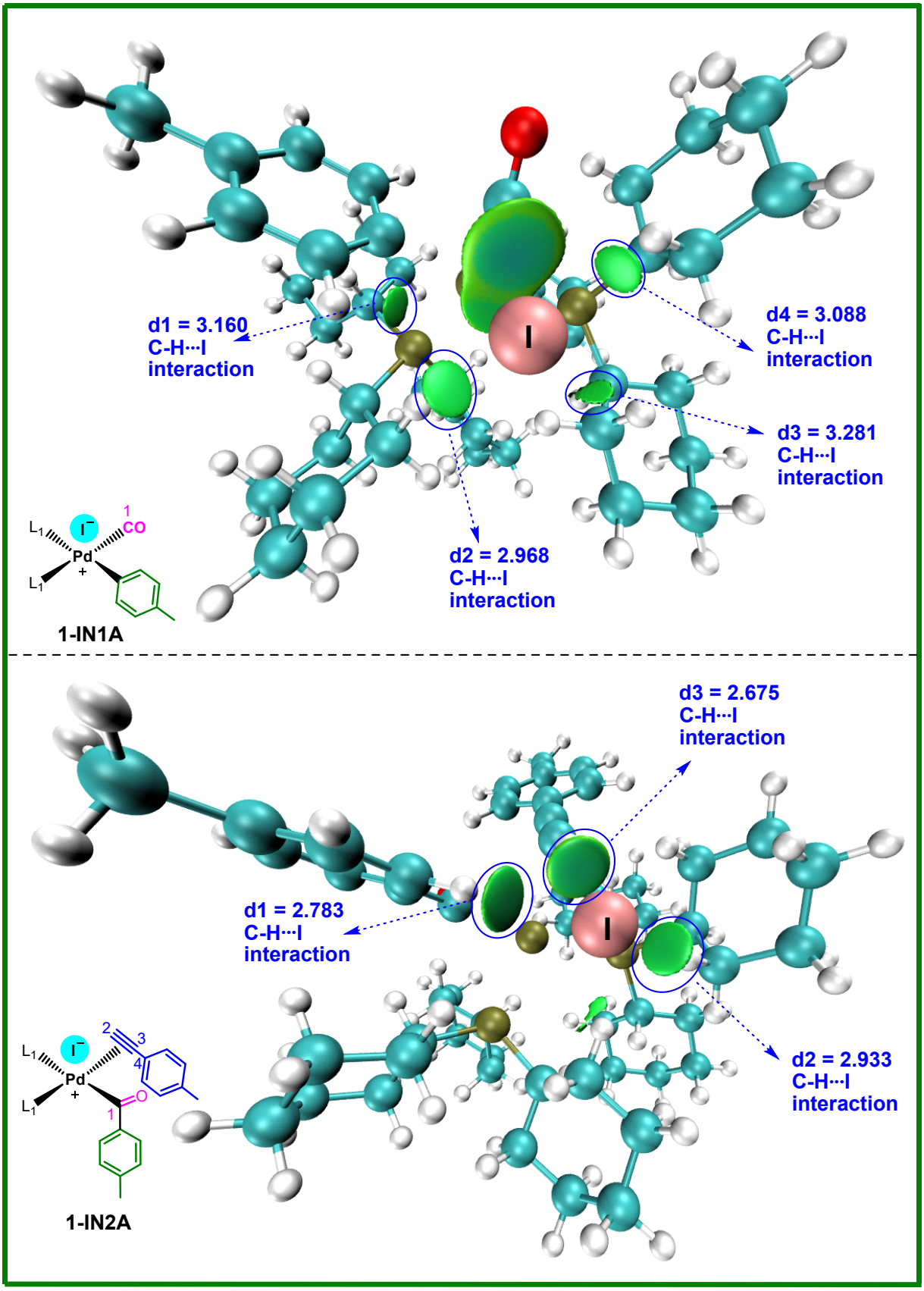
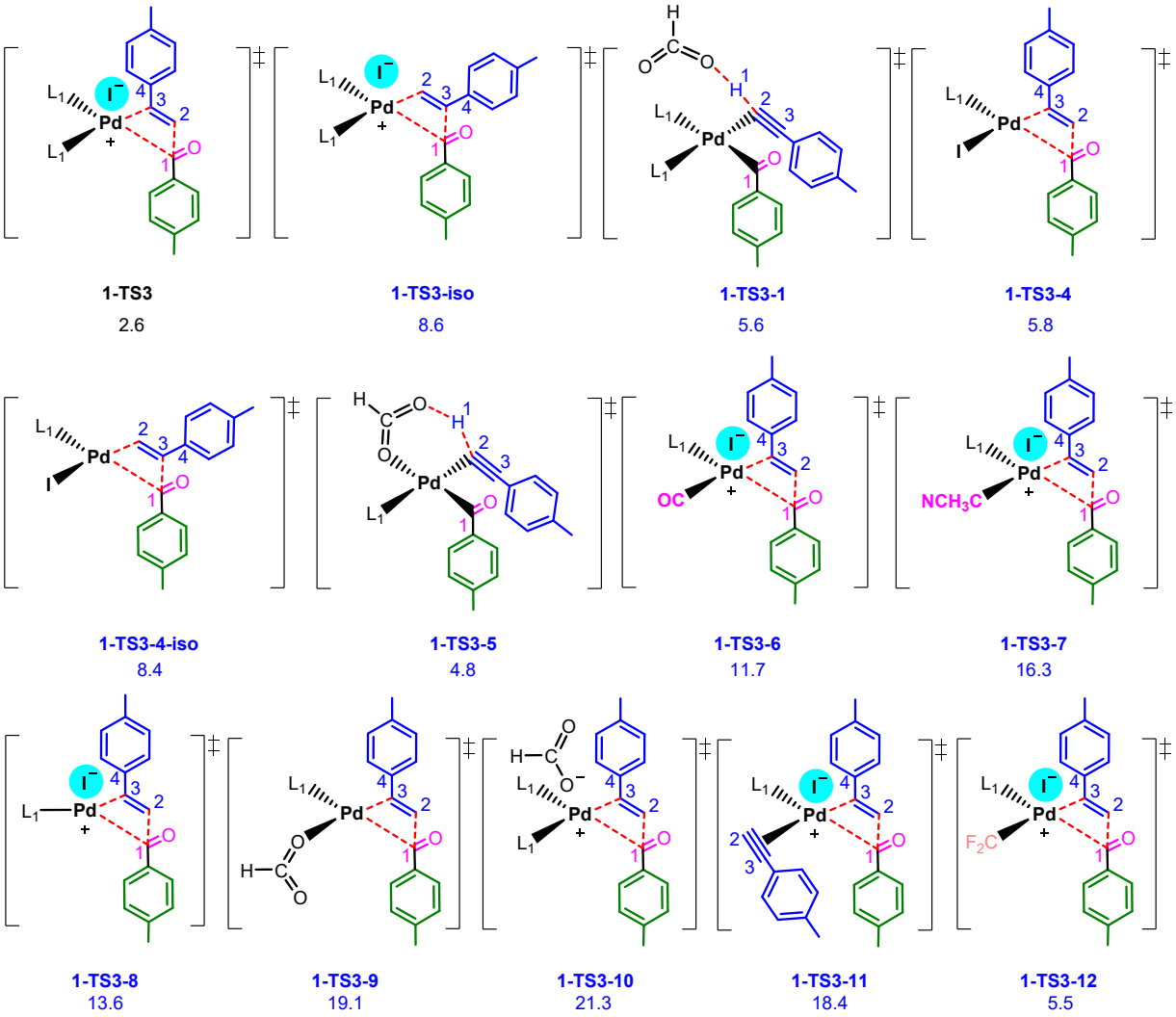


Fig. S5 IGMH isosurfaces around the iodide anion in **1-IN1A** and **1-IN2A**.

Section 7. Alternative Transition States for Alkyne Insertion



Scheme S4. Possible transition states for the alkyne insertion step during the formation of **4a**.

Relative free energies are given in kcal·mol^{-1}.

Section 8. Alternative Pathways for the Second CO Insertion

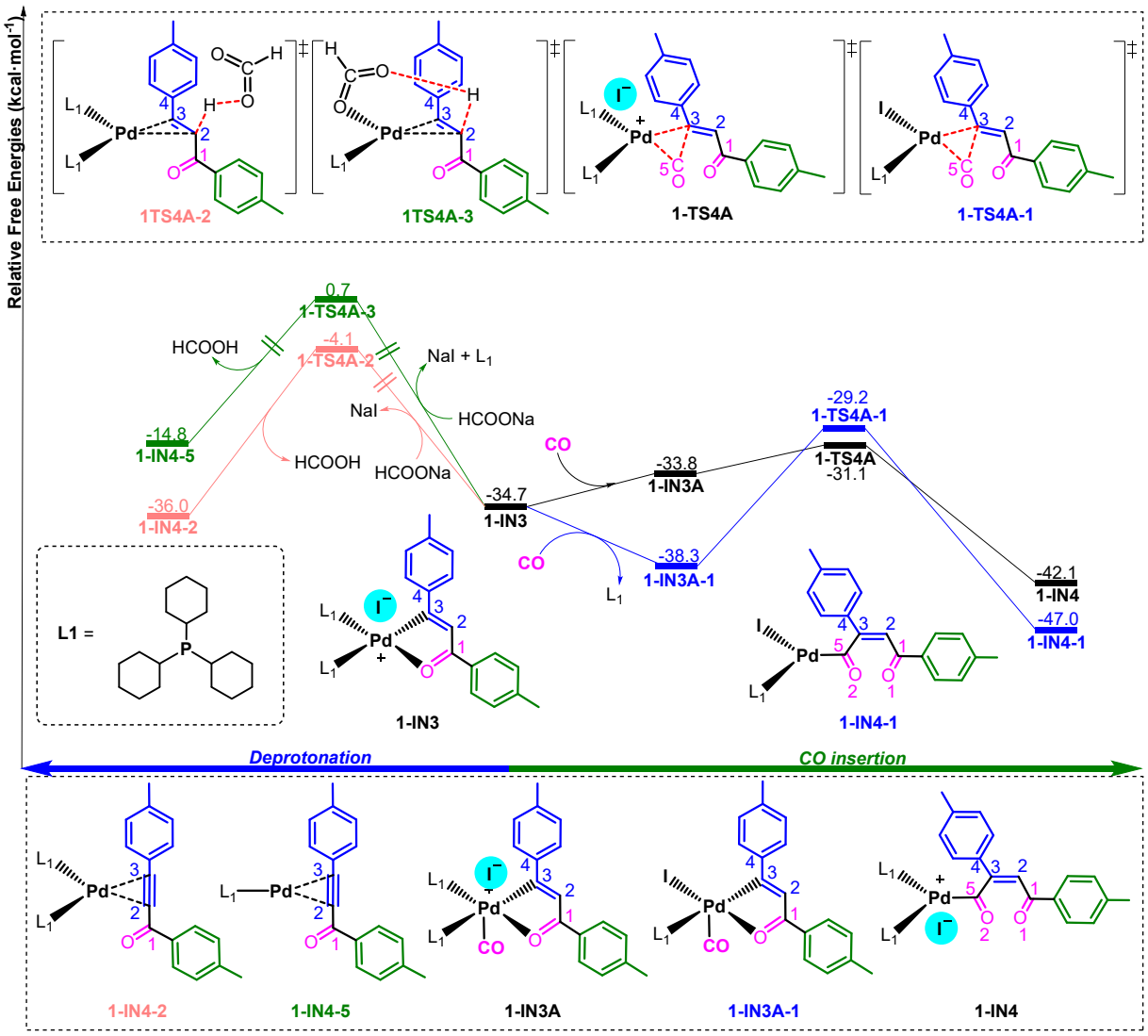
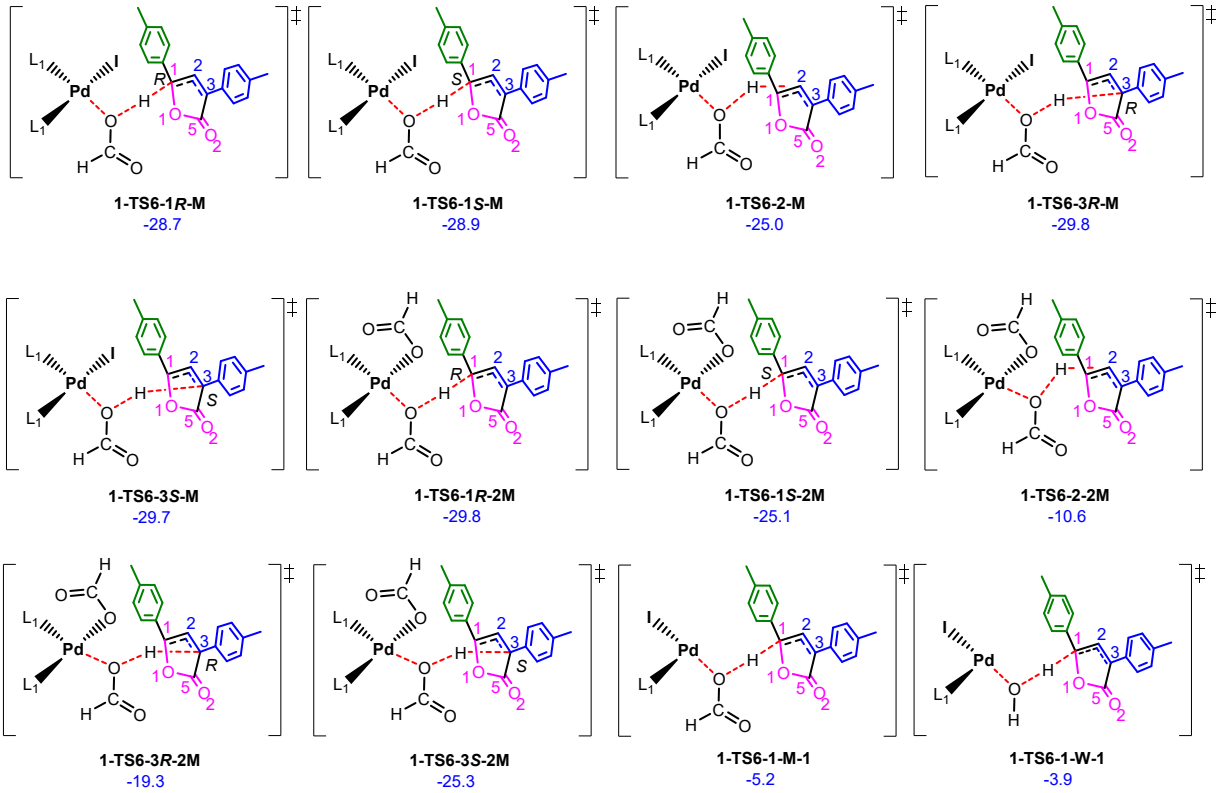


Fig. S6 Calculated free-energy profiles for the possible reactions originating from **1-IN3**. The blue, green, and orange lines correspond to the iodide-coordination pathway, the monophosphine-ligated pathway leading to **5a**, and the diphosphine-ligated pathway leading to **5a**, respectively. Relative free energies are given in kcal·mol^{-1}.

Section 9. Alternative Pathways for Protonation



Scheme S5. Possible transition states for the protonation step during the formation of **4a**. Relative free energies are given in kcal·mol^{-1}.

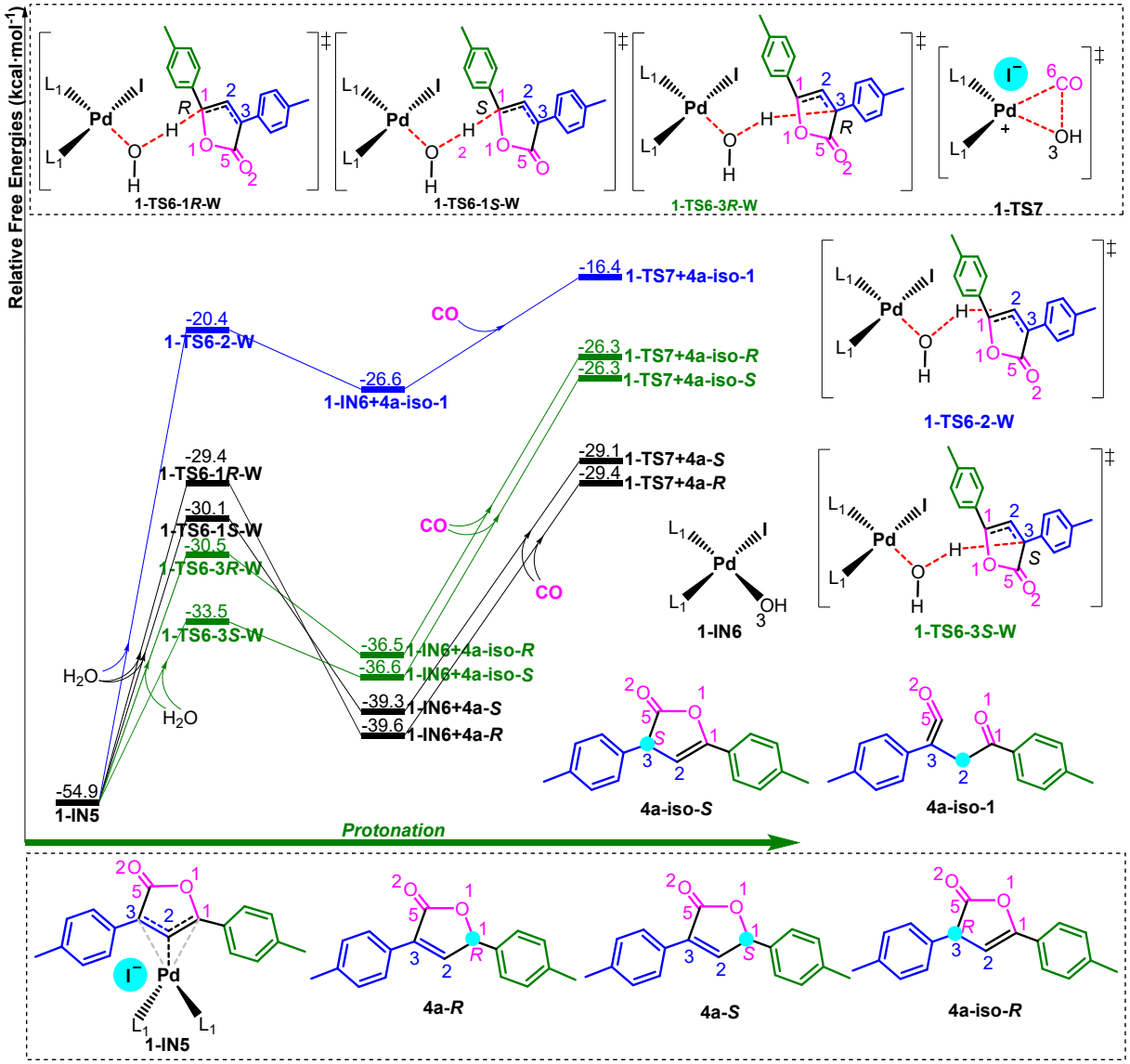


Fig. S7 Calculated free-energy profiles for all potential protonation pathways. The black, green, and blue lines correspond to protonation at the C1, C3, and C2 sites, respectively. Relative free energies are given in kcal·mol^{-1}.

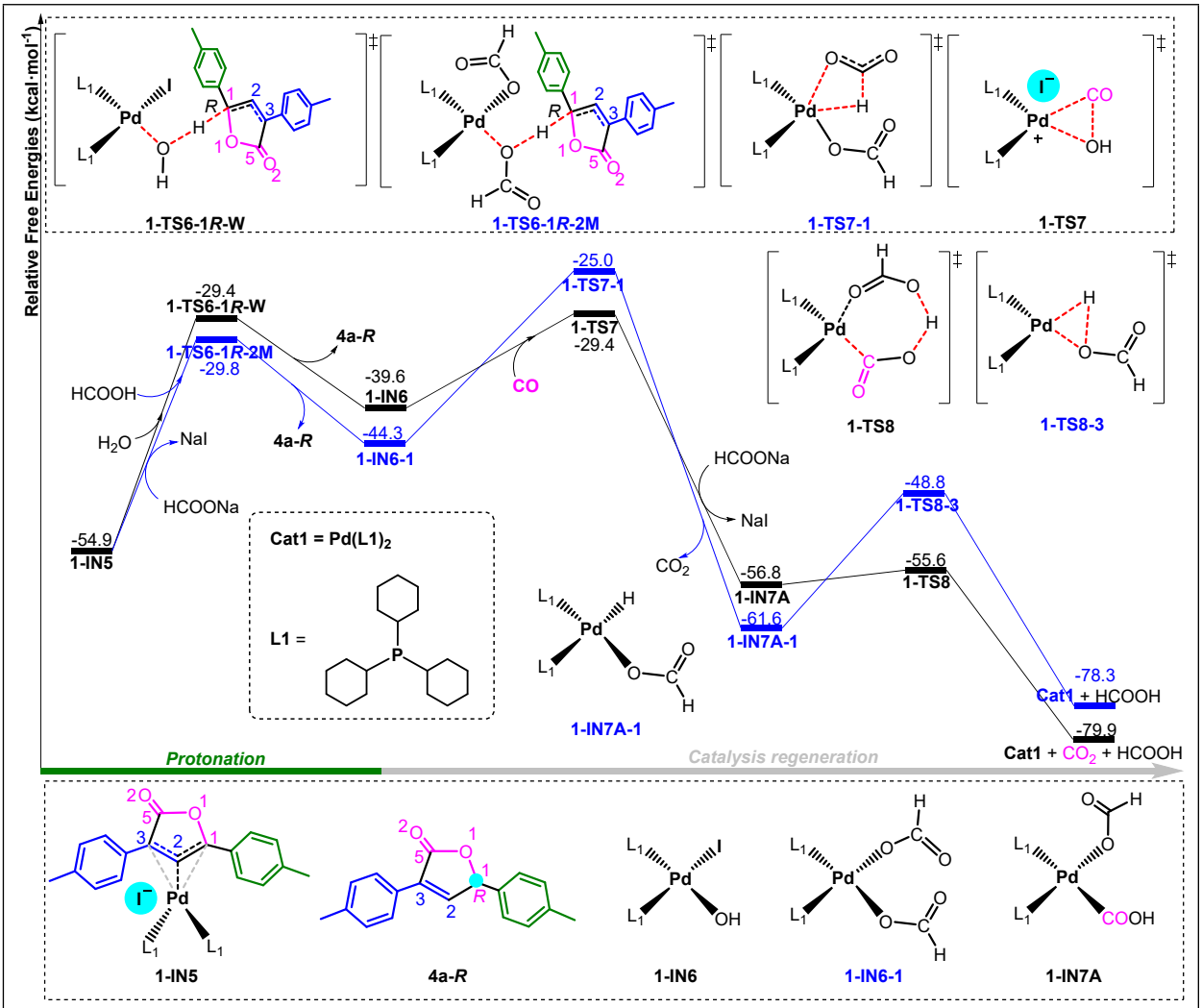


Fig. S8 Calculated free-energy profiles for alternative protonation pathways. The black and blue lines correspond to pathways using water and formic acid as the proton source, respectively. Relative free energies are given in kcal·mol^{-1}.

Section 10. Alternative Pathways Leading to 5a with the L1 Ligand

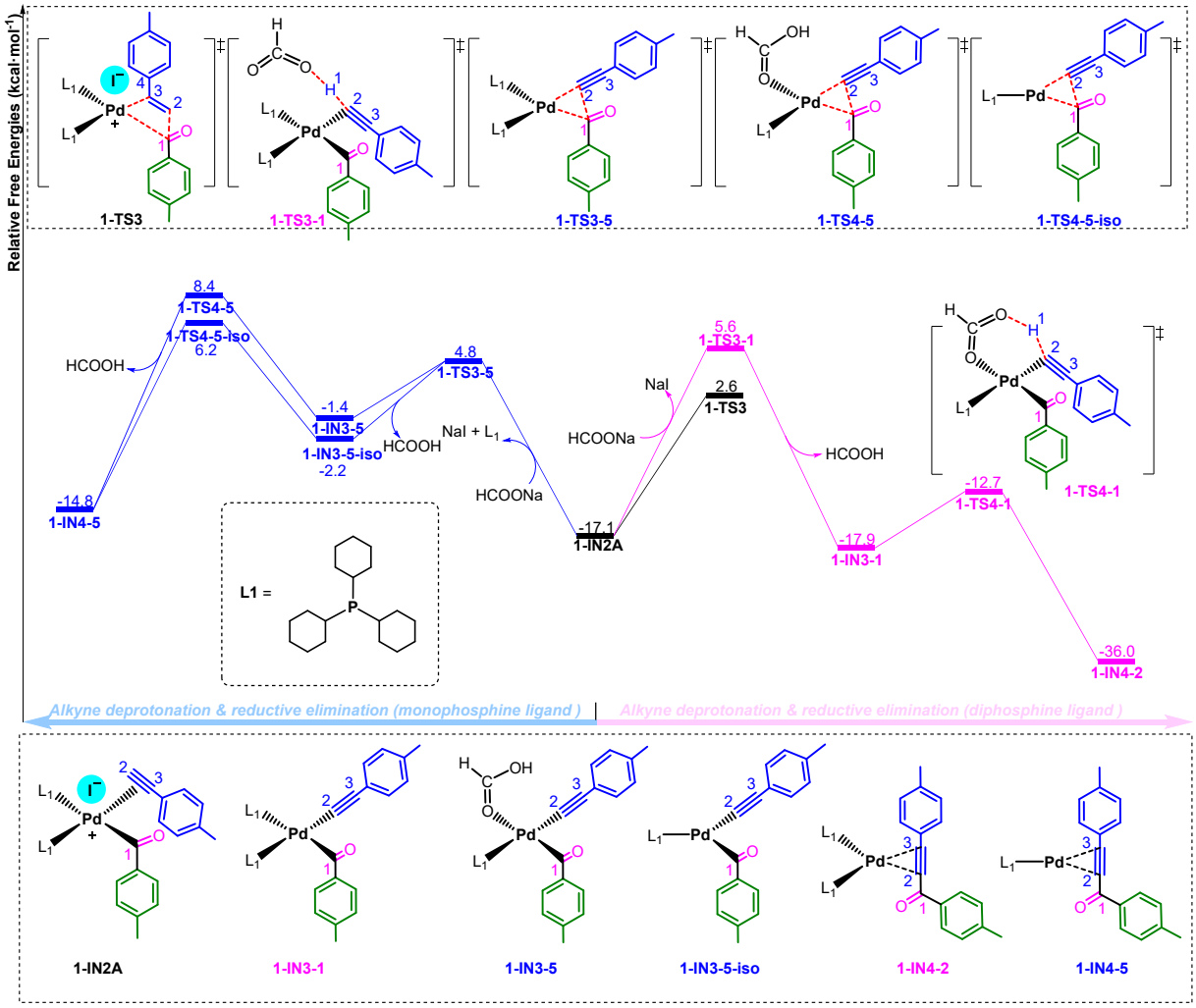


Fig. S9 Calculated free-energy profiles for alternative pathways leading to **5a** from **1-IN2A**. The blue and pink lines correspond to the alkyne deprotonation/reductive elimination pathways with diphosphine and monophosphine ligation, respectively. Relative free energies are given in kcal·mol^{-1}.

Section 11. Alternative Pathways Leading to 5a with the L2 Ligand

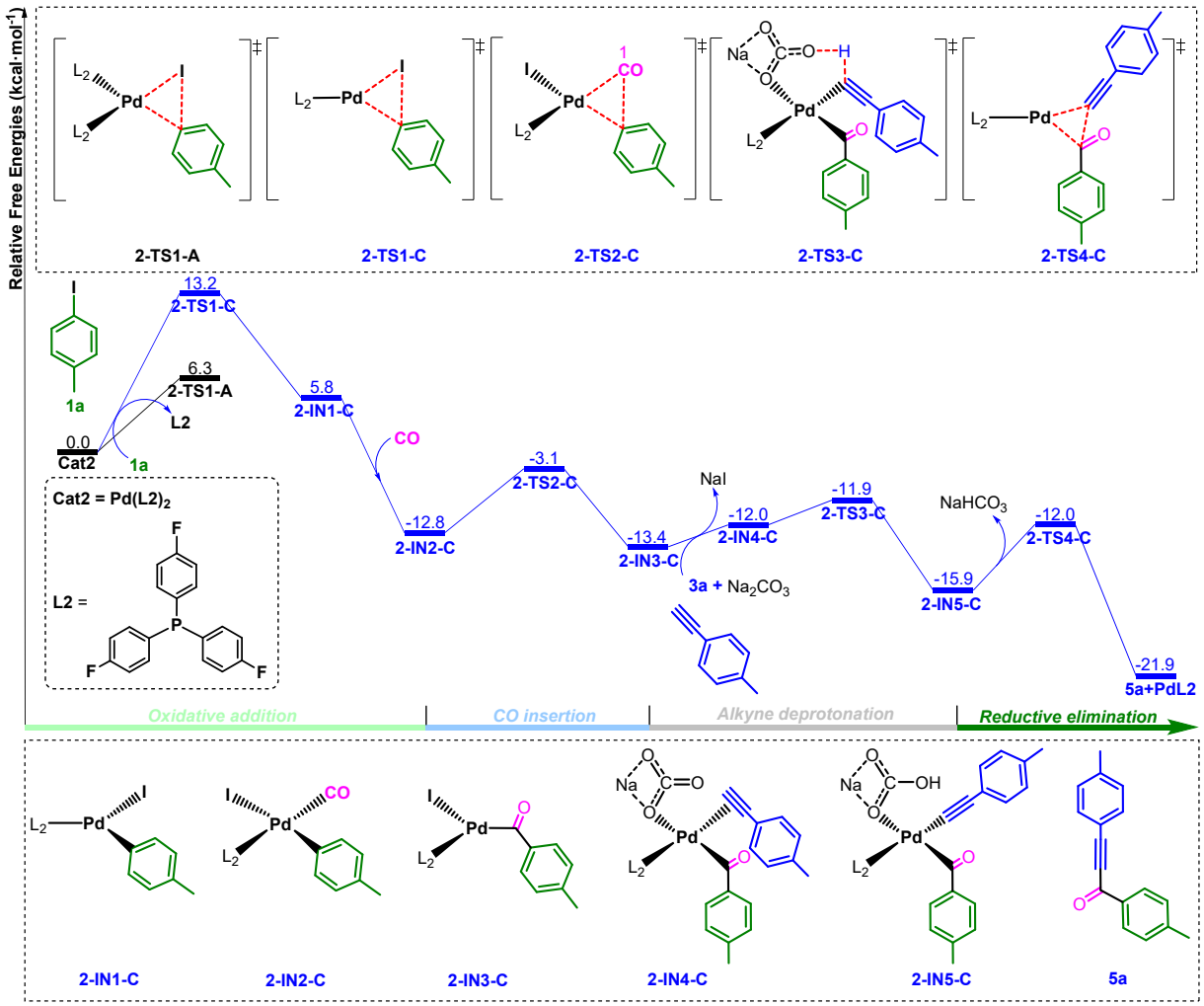


Fig. S10 Calculated free-energy profile for the proposed monophosphine-ligated pathway leading to **5a** in the absence of CuI. The pathway consists of four steps: oxidative addition, CO insertion, alkyne deprotonation, and reductive elimination. Relative free energies are given in kcal·mol^{-1}.

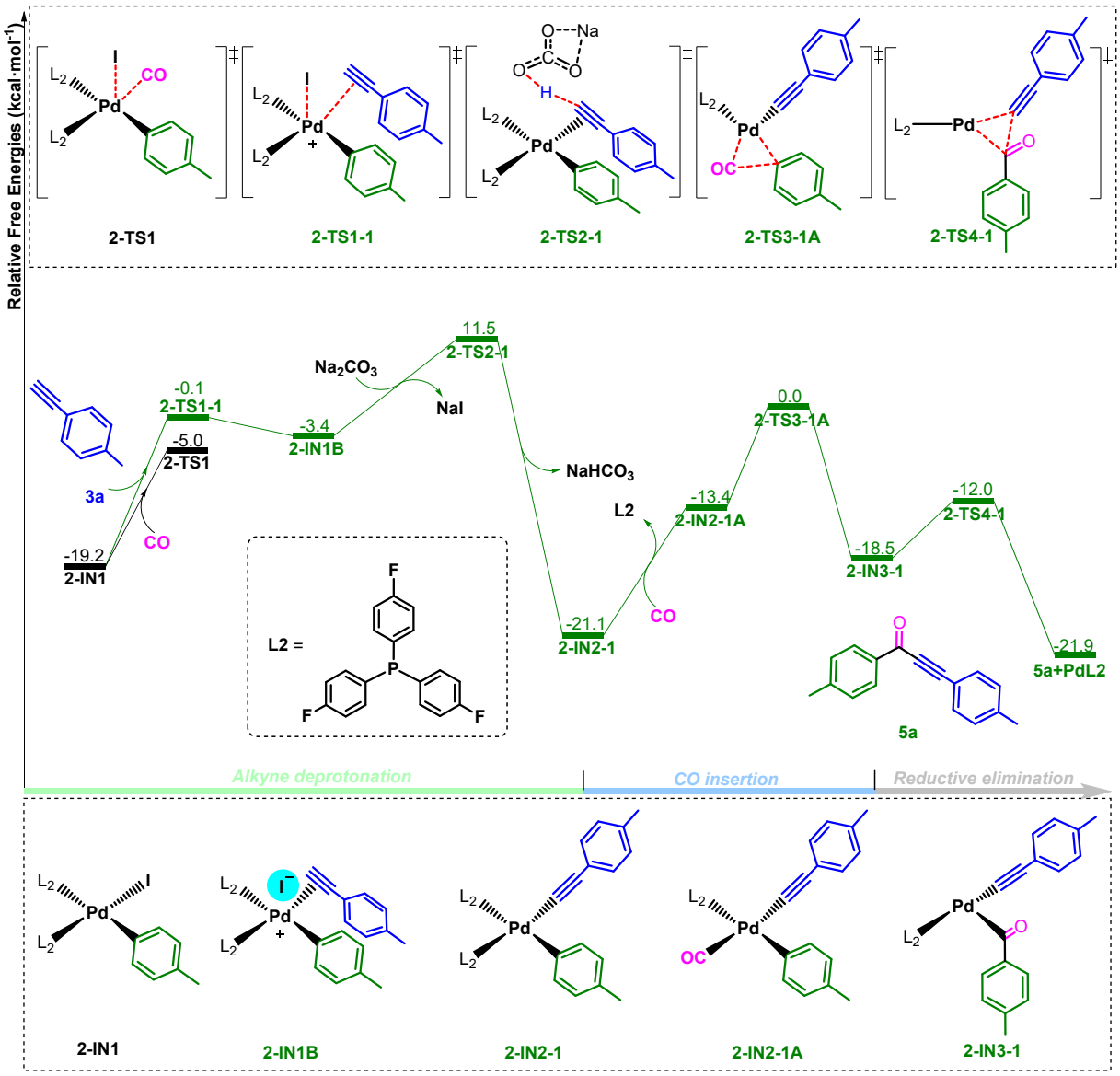


Fig. S11 Calculated free-energy profile for the proposed pathway leading to **5a** in the absence of CuI, in which alkyne deprotonation precedes CO insertion. Relative free energies are given in kcal·mol^{-1}.

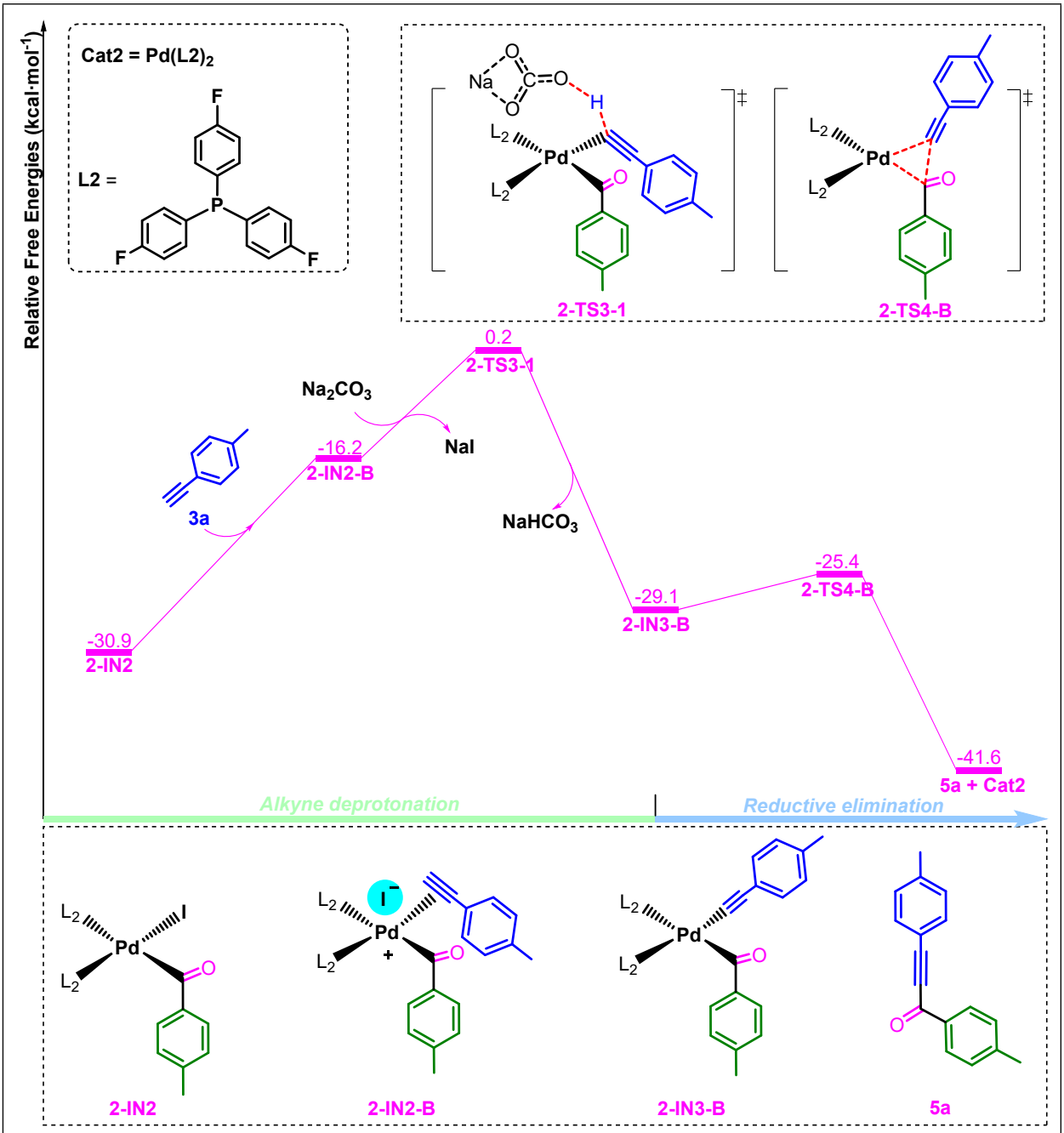


Fig. S12 Calculated free-energy profile for the proposed pathway leading to **5a** from **2-IN2** in the absence of CuI. Relative free energies are given in kcal·mol^{-1}.

Section 12. Potential Pathways Leading to 4a with the L2 Ligand

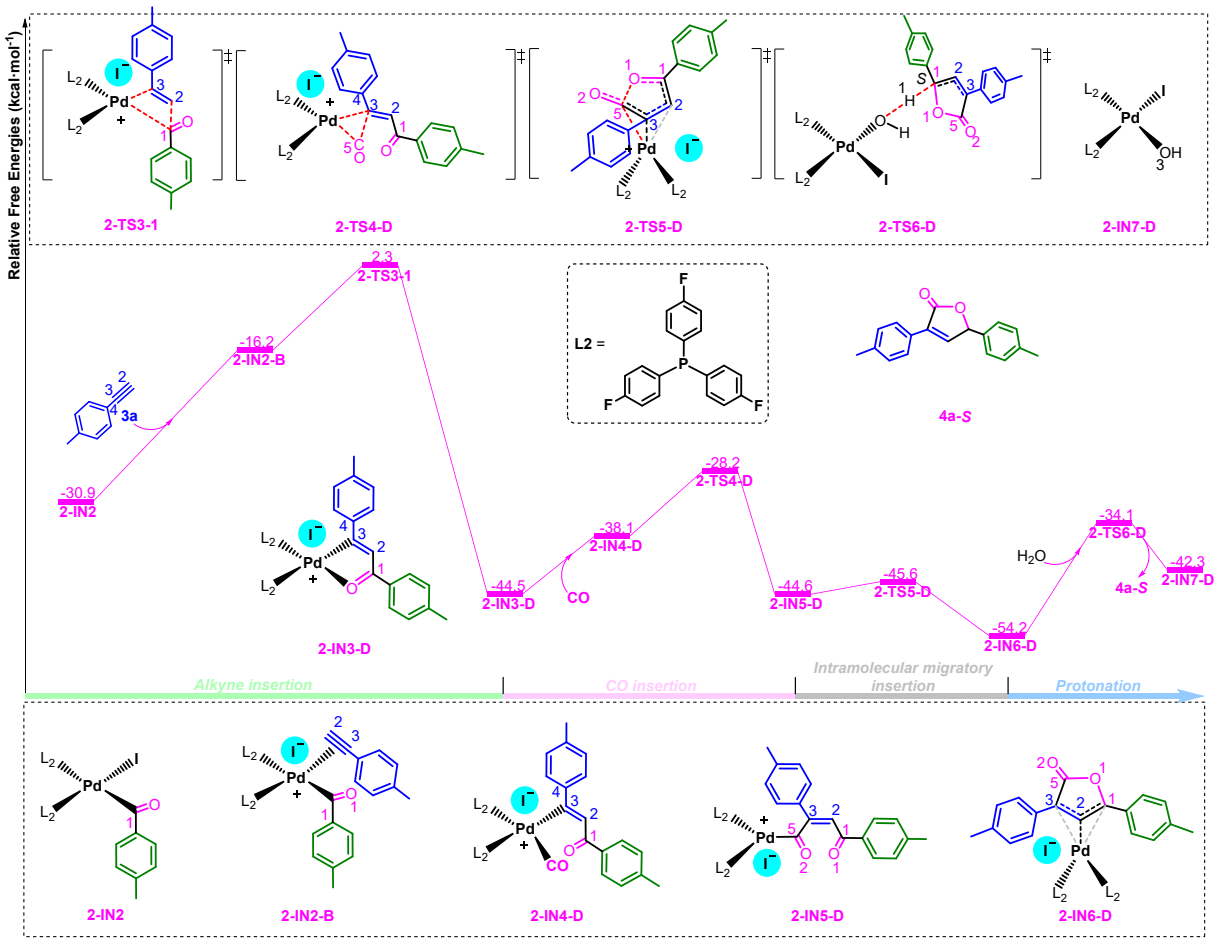


Fig. S13 Calculated free-energy profile for the proposed pathway leading to **4a** under the ynone-forming conditions in the absence of CuI. Relative free energies are given in kcal·mol^{-1}.

Section 13. Energies (in hartree) of All TSs and Intermediates

Solvent = *N*, *N*-Dimethylformamide:

Geometry	E_0	E	$H_{363.15}$	$G_{363.15}$	$E_{(sol,M06)}$
1a	-282.231956	-282.221038	-282.219888	-282.276760	-282.204172
1-Cat2	-1868.866985	-1868.808219	-1868.807068	-1868.973169	-1869.866699
1-Cat3	-1306.340566	-1306.302576	-1306.301426	-1306.420160	-1307.483438
1-Cat4	-1173.512033	-1173.481301	-1173.480151	-1173.579818	-1174.745241
1-Cat5	-392.233361	-392.219458	-392.218308	-392.283763	-393.353303
1-TS1	-2502.550183	-2502.476570	-2502.475420	-2502.667686	-2503.834592
1-TS1-1	-1455.779794	-1455.736297	-1455.735147	-1455.869154	-1456.986775
1-TS1-2	-2615.861385	-2615.783341	-2615.782191	-2615.987454	-2617.129589
1-TS1-3	-1569.102727	-1569.055490	-1569.054340	-1569.192908	-1570.290658
1-IN1	-2502.586495	-2502.512404	-2502.511254	-2502.706659	-2503.876645
1-IN1-1	-1455.792629	-1455.748105	-1455.746955	-1455.883677	-1456.997276
1-IN1-2	-2333.649844	-2333.584570	-2333.583420	-2333.760322	-2334.939003
1-IN1-3	-1286.875123	-1286.840487	-1286.839337	-1286.950192	-1288.087331
1-TS1A	-2615.883238	-2615.807141	-2615.805991	-2616.003180	-2617.159525
1-IN1A	-2615.896230	-2615.818812	-2615.817661	-2616.018940	-2617.179595
1-TS2	-2615.891447	-2615.814795	-2615.813645	-2616.012814	-2617.174356
1-TS2-1	-1569.131939	-1569.085390	-1569.084240	-1569.222184	-1570.329002
1-TS2-2	-2850.147178	-2850.061447	-2850.060297	-2850.279499	-2851.391324
1-TS2-2-iso	-2850.136668	-2850.050163	-2850.049013	-2850.268849	-2851.388790
1-TS2-3	-1803.387656	-1803.330832	-1803.329682	-1803.490135	-1804.546033
1-TS2-3-iso	-1803.386336	-1803.329455	-1803.328305	-1803.490552	-1804.540485
1-TS2A	-2963.515210	-2963.425447	-2963.424297	-2963.653256	-2964.738626
1-IN2	-2615.921047	-2615.844679	-2615.843529	-2616.041348	-2617.197226
1-IN2A	-2963.517981	-2963.427759	-2963.426609	-2963.657701	-2964.749214
1-TS3	-2963.474738	-2963.385205	-2963.384055	-2963.611940	-2964.719257
1-TS3-M06	-2961.579117	-2961.489572	-2961.488422	-2961.712485	-2964.726585
1-TS3-BP86	-2963.618971	-2963.527345	-2963.526195	-2963.756326	-2964.706711
1-TS3-iso	-2963.461877	-2963.372033	-2963.370883	-2963.601026	-2964.706854
1-TS3-1	-3141.222532	-3141.130661	-3141.129511	-3141.363644	-3142.429730
1-TS3-1-M06	-3139.267861	-3139.177260	-3139.176110	-3139.402747	-3142.436089
1-TS3-1-BP86	-3141.340517	-3141.246550	-3141.245400	-3141.481062	-3142.413503
1-TS3-4	-1916.731562	-1916.672283	-1916.671133	-1916.837349	-1917.876048
1-TS3-4-iso	-1916.731085	-1916.671925	-1916.670775	-1916.837194	-1917.871819
1-TS3-5	-2094.472411	-2094.410496	-2094.409346	-2094.581956	-2095.591535
1-TS3-6	-2030.040775	-2029.977649	-2029.976499	-2030.151285	-2031.169658
1-TS3-7	-2049.442584	-2049.376300	-2049.375150	-2049.558871	-2050.583339
1-TS3-8	-1916.672032	-1916.611908	-1916.610758	-1916.784181	-1917.855107
1-TS3-9	-2094.448249	-2094.386767	-2094.385617	-2094.555835	-2095.574743

1-TS3-10	-3141.188665	-3141.096652	-3141.095502	-3141.326604	-3142.410261
1-TS3-11	-2264.300065	-2264.227120	-2264.225970	-2264.422850	-2265.411885
1-TS3-12	-2154.416432	-2154.351780	-2154.350630	-2154.530694	-2155.576121
1-IN3	-2963.559142	-2963.470629	-2963.469479	-2963.696111	-2964.783826
1-IN3-1	-2951.502571	-2951.415402	-2951.414252	-2951.640630	-2952.707749
1-IN3-5	-2094.476072	-2094.413352	-2094.412202	-2094.590609	-2095.601633
1-IN3-5-iso	-1904.715484	-1904.658245	-1904.657095	-1904.823435	-1905.843349
1-IN3A	-3076.855171	-3076.762902	-3076.761752	-3076.999170	-3078.083556
1-IN3A-1	-2030.123409	-2030.060577	-2030.059427	-2030.239465	-2031.247063
1-TS4-1	-2951.494951	-2951.408296	-2951.407146	-2951.633408	-2952.697146
1-TS4-5	-2094.455135	-2094.392776	-2094.391626	-2094.569206	-2095.585256
1-TS4-5-iso	-1904.707890	-1904.651535	-1904.650385	-1904.812123	-1905.833097
1-TS4A	-3076.855006	-3076.763736	-3076.762586	-3076.994310	-3078.082954
1-TS4A-1	-2030.108499	-2030.046369	-2030.045219	-2030.224146	-2031.232247
1-TS4A-2	-3141.244878	-3141.153530	-3141.152380	-3141.384654	-3142.446277
1-TS4A-3	-2094.480611	-2094.419568	-2094.418418	-2094.590589	-2095.599340
1-IN4	-3076.863295	-3076.771674	-3076.770524	-3077.005622	-3078.098956
1-IN4-1	-2030.138940	-2030.077231	-2030.076081	-2030.249128	-2031.269185
1-IN4-2	-2951.538015	-2951.451614	-2951.450464	-2951.672964	-2952.740579
1-IN4-5	-1904.742778	-1904.686189	-1904.685039	-1904.846184	-1905.869223
1-TS5	-3076.863787	-3076.773055	-3076.771905	-3077.002610	-3078.100790
1-IN5	-3076.908037	-3076.817800	-3076.816650	-3077.043533	-3078.128974
1-TS6-1*R*-W	-3153.300151	-3153.207043	-3153.205893	-3153.444063	-3154.527401
1-TS6-1*S*-W	-3153.292954	-3153.199820	-3153.198670	-3153.436379	-3154.528954
1-TS6-2-W	-3153.273988	-3153.181094	-3153.179944	-3153.415017	-3154.515250
1-TS6-3*R*-W	-3153.306778	-3153.214967	-3153.213817	-3153.446419	-3154.533712
1-TS6-3*S*-W	-3153.297619	-3153.204406	-3153.203256	-3153.441537	-3154.533634
1-TS6-1*R*-M	-3266.625524	-3266.530224	-3266.529074	-3266.769724	-3267.840203
1-TS6-1*S*-M	-3266.621187	-3266.525830	-3266.524680	-3266.766277	-3267.839422
1-TS6-2-M	-3266.609190	-3266.513654	-3266.512504	-3266.753809	-3267.831951
1-TS6-3*R*-M	-3266.620953	-3266.526720	-3266.525570	-3266.763348	-3267.843028
1-TS6-3*S*-M	-3266.619577	-3266.524021	-3266.522871	-3266.766605	-3267.838199
1-TS6-1*R*-2M	-3444.344579	-3444.247339	-3444.246189	-3444.490875	-3445.561312
1-TS6-1*S*-2M	-3444.359365	-3444.263077	-3444.261927	-3444.506336	-3445.553162
1-TS6-2-2M	-3331.001942	-3330.907435	-3330.906285	-3331.142626	-3332.222775
1-TS6-3*R*-2M	-3444.352071	-3444.257060	-3444.255910	-3444.492817	-3445.550320
1-TS6-3*S*-2M	-3444.342311	-3444.245279	-3444.244129	-3444.486576	-3445.556761
1-TS6-1-M-1	-2219.844059	-2219.778766	-2219.777616	-2219.956075	-2220.964346
1-TS6-1-W-1	-2106.510091	-2106.447135	-2106.445985	-2106.619809	-2107.651299
1-IN6	-2307.540383	-2307.474199	-2307.473049	-2307.648521	-2308.876636
1-IN6-1	-2598.606841	-2598.536080	-2598.534930	-2598.720263	-2599.914232
1-TS6A	-2420.849255	-2420.780178	-2420.779028	-2420.959696	-2422.168666
1-IN6A	-2420.849326	-2420.779546	-2420.778396	-2420.963192	-2422.176404

1-TS7	-2420.818009	-2420.748983	-2420.747833	-2420.931725	-2422.161842
1-TS7-1	-2598.565669	-2598.495351	-2598.494201	-2598.677928	-2599.882241
1-IN7A	-2598.622066	-2598.551313	-2598.550163	-2598.736086	-2599.929967
1-IN7A-1	-2410.035973	-2409.969347	-2409.968197	-2410.144609	-2411.353260
1-TS8	-2598.622524	-2598.551931	-2598.550781	-2598.736446	-2599.922764
1-TS8-1	-2598.569428	-2598.498764	-2598.497614	-2598.682991	-2599.890161
1-TS8-2	-2598.571583	-2598.500792	-2598.499642	-2598.685190	-2599.873556
1-TS8-3	-2410.018243	-2409.950985	-2409.949835	-2410.131877	-2411.323568
1-IN8-1	-2410.027847	-2409.961055	-2409.959905	-2410.137017	-2411.352818
1-IN8-2	-378.261815	-378.254169	-378.253019	-378.300046	-378.268880
2a	-1039.447302	-1039.435691	-1039.434541	-1039.493883	-1039.653353
3a	-347.577298	-347.565373	-347.564223	-347.620657	-347.527533
4a	-845.737905	-845.712625	-845.711475	-845.803538	-845.640190
4a-*R*	-845.737905	-845.712625	-845.711475	-845.803538	-845.640190
4a-*S*	-845.738018	-845.712762	-845.711612	-845.803259	-845.640240
4a-iso-*R*	-845.732464	-845.707004	-845.705854	-845.798793	-845.633955
4a-iso-*S*	-845.732470	-845.707004	-845.705854	-845.798907	-845.633947
4a-iso-1	-845.712470	-845.685823	-845.684673	-845.780072	-845.615194
Cat1	-2220.307857	-2220.246156	-2220.245006	-2220.417573	-2221.614345
:CF_2	-237.679525	-237.675738	-237.674588	-237.709012	-237.675905
CO	-113.301876	-113.298999	-113.297849	-113.325980	-113.281072
CO_2	-188.566144	-188.562749	-188.561599	-188.592255	-188.560625
CH_3CN	-132.706958	-132.702230	-132.701080	-132.737336	-132.703202
HCOOH	-189.710864	-189.706640	-189.705490	-189.741236	-189.733365
HCOONa	-351.491714	-351.486113	-351.484963	-351.525793	-351.494240
HCOOK	-789.095806	-789.089848	-789.088698	-789.131496	-789.124579
HIO	-87.143483	-87.139648	-87.138498	-87.174949	-87.166204
H_2O	-76.385898	-76.382439	-76.381289	-76.408324	-76.426296
HF	-100.409174	-100.406299	-100.405149	-100.429982	-100.456311
KCl	-1060.166147	-1060.162618	-1060.161468	-1060.195585	-1060.210764
KF	-699.749948	-699.746657	-699.745507	-699.777725	-699.839037
NaBr	-175.538110	-175.534619	-175.533469	-175.567836	-175.736504
$NaBrCl^-$	-635.882963	-635.877113	-635.875963	-635.918365	-636.125588
NaCl	-622.556447	-622.553047	-622.551897	-622.584636	-622.578557
$NaCl_2^-$	-1082.898998	-1082.892869	-1082.891719	-1082.932878	-1082.968407
NaF	-262.155286	-262.152110	-262.150960	-262.181859	-262.208573
NaI	-173.756618	-173.753071	-173.751921	-173.787371	-173.776594
$OPCy_3$	-1121.984692	-1121.955221	-1121.954071	-1122.049045	-1122.063880
PCy_3(L1)	-1046.729212	-1046.700902	-1046.699752	-1046.793056	-1046.801594
Pre-cat	-1312.645487	-1312.629161	-1312.628011	-1312.699513	-1313.814774
Pre-IN1	-2680.346317	-2680.283002	-2680.281852	-2680.450342	-2681.712927
Pre-IN1A	-2918.077687	-2918.009334	-2918.008184	-2918.190732	-2919.432117
Pre-TS1	-2994.484253	-2994.414596	-2994.413446	-2994.595218	-2995.862214

Pre-TS1-1	-3259.944279	-3259.860981	-3259.859831	-3260.077468	-3128.579109
Pre-TS1-2	-3127.221646	-3127.146151	-3127.145001	-3127.344704	-3261.295477
Pre-IN2	-2994.489845	-2994.417926	-2994.416776	-2994.606627	-2995.866292
Pre-IN2A	-2994.129356	-2994.059714	-2994.058564	-2994.241196	-2995.466166
Pre-TS2	-3345.690093	-3345.636752	-3345.635808	-3345.777727	-3346.990352
Pre-IN3	-3155.928067	-3155.855932	-3155.854782	-3156.043231	-3157.230334
Pre-TS3	-3155.926781	-3155.855182	-3155.854032	-3156.042166	-3157.229360
Pre-TS3-1	-2994.065447	-2993.995765	-2993.994615	-2994.177310	-2995.406964
Pre-IN4	-2893.712909	-2893.644593	-2893.643443	-2893.825256	-2895.032129
Pre-TS4	-2893.664217	-2893.595952	-2893.594802	-2893.773652	-2894.997344
Pre-TS4-1	-2893.678081	-2893.610205	-2893.609055	-2893.790478	-2894.983406
Pre-IN5	-2780.383782	-2780.318857	-2780.317707	-2780.489081	-2781.723542
Pre-IN5-1	-673.342338	-673.337567	-673.336417	-673.376246	-673.340533
Pre-TS	-1390.984185	-1390.963244	-1390.962094	-1391.048194	-1391.141426

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

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

$H_{363.15}$ = Sum of electronic and thermal enthalpies calculated by B3LYP-D3

$G_{363.15}$ = Sum of electronic and thermal free energies calculated by B3LYP-D3

$E_{(M06)}$ = Single point energies calculated by M06

Geometry	E_0	E	$H_{373.15}$	$G_{373.15}$	$E_{(sol,M06)}$
1a	-282.231956	-282.220509	-282.219327	-282.278334	-282.204172
1-TS3-2	-3171.154160	-3171.054325	-3171.053144	-3171.308678	-3173.623205
1-TS3-3	-906.723545	-906.698337	-906.697155	-906.797041	-907.898307
1-IN2-1	-2615.921047	-2615.840644	-2615.839462	-2616.046852	-2617.197225
1-IN2-2	-3171.175613	-3171.074699	-3171.073517	-3171.333953	-3173.654812
1-IN2-3	-559.152070	-559.140823	-559.139641	-559.200576	-560.383177
2a	-1039.447302	-1039.435222	-1039.434040	-1039.495524	-1039.653353
2-Cat1	-2875.228175	-2875.164617	-2875.163435	-2875.345289	-2876.239392
2-Cat2	-1541.414027	-1541.380619	-1541.379438	-1541.494165	-1542.550011
2-Cat3	-2155.776097	-2155.717226	-2155.716044	-2155.881457	-2156.714930
2-Cat4	-1593.284842	-1593.246957	-1593.245775	-1593.372657	-1594.322512
2-Cat5	-1460.542068	-1460.511563	-1460.510381	-1460.615263	-1461.586474
2-Cat6	-392.200431	-392.185828	-392.184647	-392.252476	-393.352850
2-Pre-TS	-1627.997674	-1627.973665	-1627.972483	-1628.065677	-1628.140264
2-TS1	-3189.955230	-3189.878204	-3189.877023	-3190.085841	-3190.848630
2-TS1-1	-3424.239844	-3424.152240	-3424.151058	-3424.384807	-3425.092223
2-TS1-A	-3076.618817	-3076.544983	-3076.543801	-3076.748704	-3077.520438

2-TS1-B	-3730.505460	-3730.420536	-3730.419355	-3730.644108	-3731.343708
2-TS1-C	-1742.808613	-1742.764719	-1742.763537	-1742.905264	-1743.823853
2-IN1	-3076.651724	-3076.577550	-3076.576369	-3076.780773	-3077.563988
2-IN1-1	-3730.509277	-3730.422695	-3730.421513	-3730.657318	-3731.351458
2-IN1-C	-1742.819997	-1742.775097	-1742.773915	-1742.917591	-1743.835067
2-IN1A	-3189.966639	-3189.888695	-3189.887513	-3190.099782	-3190.859509
2-IN1B	-3424.239891	-3424.151372	-3424.150190	-3424.387298	-3425.095247
2-TS2	-3189.961806	-3189.885078	-3189.883897	-3190.091760	-3190.851823
2-TS2-1	-3838.958303	-3838.865861	-3838.864679	-3839.105918	-3839.781191
2-TS2-C	-1856.158701	-1856.111881	-1856.110699	-1856.253161	-1857.162107
2-IN2	-3189.995360	-3189.918330	-3189.917149	-3190.129642	-3190.888235
2-IN2-1	-3412.221277	-3412.136320	-3412.135138	-3412.363250	-3413.060425
2-IN2-1A	-2191.725793	-2191.666716	-2191.665534	-2191.840366	-2192.664723
2-IN2-2	-3745.233674	-3745.136695	-3745.135513	-3745.393487	-3747.320165
2-IN2-iso	-796.145172	-796.130890	-796.129709	-796.201496	-797.382015
2-IN2-A	-1143.765370	-1143.736490	-1143.735308	-1143.841062	-1144.922247
2-IN2-B	-3537.590211	-3537.499613	-3537.498431	-3537.736109	-3538.428584
2-IN2-C	-1856.176263	-1856.128402	-1856.127221	-1856.272972	-1857.175637
2-TS3-1	-3952.301675	-3952.206027	-3952.204846	-3952.453569	-3953.104209
2-TS3-1A	-2191.712410	-2191.654444	-2191.653262	-2191.824270	-2192.646062
2-TS3-2	-3745.229094	-3745.132802	-3745.131620	-3745.389217	-3747.301472
2-TS3-3	-1143.746928	-1143.718482	-1143.717300	-1143.822422	-1144.903700
2-TS3-3-M06	-1143.298641	-1143.270569	-1143.269388	-1143.371977	-1144.902103
2-TS3-3-BP86	-1143.868379	-1143.839631	-1143.838450	-1143.944325	-1144.900060
2-TS3-C	-2618.504235	-2618.437910	-2618.436728	-2618.625791	-2619.433222
2-TS3-2-M06	-3743.261618	-3743.166300	-3743.165118	-3743.416638	-3747.305068
2-TS3-2-BP86	-3745.542959	-3745.444625	-3745.443443	-3745.702867	-3747.288191
2-TS3	-3537.561627	-3537.471392	-3537.470210	-3537.708704	-3538.396471
2-IN3	-554.699029	-554.681739	-554.680558	-554.757043	-555.948640
2-IN3-1	-2191.739438	-2191.681465	-2191.680283	-2191.851303	-2192.677785
2-IN3-B	-3525.562000	-3525.474652	-3525.473470	-3525.704160	-3526.384343
2-IN3-C	-1856.166905	-1856.119549	-1856.118367	-1856.264573	-1857.176688
2-IN3-D	-3537.642913	-3537.553378	-3537.552196	-3537.791635	-3538.473981
2-TS4	-3744.754711	-3744.659457	-3744.658276	-3744.912067	-3746.859941
2-TS4-1	-2191.732282	-2191.675041	-2191.673859	-2191.843615	-2192.667033
2-TS4-B	-3525.551149	-3525.463828	-3525.462647	-3525.699614	-3526.370148
2-TS4-C	-2191.732282	-2191.675041	-2191.673859	-2191.843615	-2192.667033
2-TS4-D	-3650.933193	-3650.840970	-3650.839788	-3651.083167	-3651.755134
2-IN4	-3744.762786	-3744.666598	-3744.665416	-3744.922616	-3746.879085
2-IN4-C	-2618.506883	-2618.440212	-2618.439030	-2618.626905	-2619.439157
2-IN4-D	-3650.927164	-3650.833809	-3650.832628	-3651.082427	-3651.765860
2-TS5	-3733.222110	-3733.129396	-3733.128214	-3733.375999	-3735.283085
2-TS5-D	-3650.963873	-3650.872389	-3650.871208	-3651.111834	-3651.786777

2-IN5	-3733.262541	-3733.169961	-3733.168779	-3733.414997	-3735.324813
2-IN5-C	-2618.525336	-2618.458171	-2618.456989	-2618.647402	-2619.445402
2-IN5-D	-3650.960213	-3650.867877	-3650.866695	-3651.108611	-3651.784886
2-IN6-D	-3650.982212	-3650.890815	-3650.889634	-3651.130752	-3651.801968
2-TS6-D	-3727.360074	-3727.265920	-3727.264738	-3727.514714	-3728.212093
2-IN7-D	-2881.601763	-2881.536178	-2881.534996	-2881.718649	-2882.559020
3a	-347.577298	-347.564768	-347.563587	-347.622218	-347.527532
4a	-845.738018	-845.711463	-845.710281	-845.805800	-845.640240
4-F-PPh_3(L2)	-1333.763594	-1333.735711	-1333.734529	-1333.832429	-1333.648276
5a	-731.173659	-731.148734	-731.147552	-731.240210	-731.068840
Cat2	-2794.367429	-2794.306466	-2794.305285	-2794.483460	-2795.293214
:CF_2	-237.679525	-237.675611	-237.674430	-237.709962	-237.675901
CO	-113.301876	-113.298919	-113.297738	-113.326756	-113.281072
CH_3CN	-132.706957	-132.702043	-132.700861	-132.738335	-132.703225
CuI	-207.579318	-207.575647	-207.574465	-207.612130	-208.853162
HCOONa	-351.491708	-351.485896	-351.484714	-351.526908	-351.494231
H_2O	-76.385896	-76.382340	-76.381159	-76.409068	-76.426297
KCl	-1060.166147	-1060.162509	-1060.161328	-1060.196527	-1060.210764
KF	-699.749948	-699.746553	-699.745371	-699.778614	-699.839037
$KNaCO_3$	-1026.081882	-1026.073015	-1026.071833	-1026.124060	-1026.107762
NaBr	-175.538110	-175.534512	-175.533330	-175.568784	-175.736504
$NaBrCl^-$	-635.882961	-635.876927	-635.875746	-635.919532	-636.125546
Na_2CO_3	-588.482396	-588.473845	-588.472664	-588.523079	-588.479664
$Na_2HCO_3^+$	-588.897334	-588.887713	-588.886531	-588.939466	-588.959968
$NaHCO_3$	-426.726084	-426.719141	-426.717959	-426.763486	-426.742743
NaF	-262.155286	-262.152010	-262.150828	-262.182712	-262.208573
NaI	-173.756618	-173.752963	-173.751781	-173.788349	-173.776594
Pre-cat	-1312.645461	-1312.626133	-1312.624951	-1312.710707	-1313.814761
Pre1-IN1	-3254.386784	-3254.324193	-3254.323012	-3254.499754	-3255.377741
Pre1-IN1A	-3492.123843	-3492.056144	-3492.054962	-3492.243760	-3493.103754
Pre1-TS1	-3568.540517	-3568.471216	-3568.470034	-3568.661476	-3569.541479
Pre1-IN2	-3568.544418	-3568.472691	-3568.471509	-3568.672209	-3569.540250
Pre1-IN2A	-3568.195907	-3568.126398	-3568.125217	-3568.317819	-3569.154001
Pre1-TS2	-4156.754194	-4156.675323	-4156.674142	-4156.885708	-4157.661373
Pre1-IN3	-3729.991140	-3729.918985	-3729.917803	-3730.116668	-3730.913103
Pre1-TS3	-3729.990194	-3729.918759	-3729.917577	-3730.114241	-3730.917295
Pre1-IN4	-3467.774050	-3467.706460	-3467.705279	-3467.893315	-3468.710670
Pre1-TS4	-3467.740629	-3467.672424	-3467.671243	-3467.859903	-3468.682886
Pre1-IN5	-3354.440068	-3354.375555	-3354.374373	-3354.554180	-3355.402304

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

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

$H_{373.15}$ = Sum of electronic and thermal enthalpies calculated by B3LYP-D3

$G_{373.15}$ = Sum of electronic and thermal free energies calculated by B3LYP-D3

$E_{(M06)}$ = Single point energies calculated by M06

Section 14. Calculated Imaginary Frequencies of All Transition States Species

Species	Frequency
1-TS1	-113.57
1-TS1-1	-41.72
1-TS1-2	-149.39
1-TS1-3	-183.95
1-TS1A	-112.71
1-TS2	-272.31
1-TS2-1	-296.61
1-TS2-2	-307.66
1-TS2-2-iso	-319.41
1-TS2-3	-186.22
1-TS2-3-iso	-261.47
1-TS2A	-43.21
1-TS3	-290.83
1-TS3-M06	-278.45
1-TS3-BP86	-232.35
1-TS3-iso	-278.39
1-TS3-1	-113.82
1-TS3-2	-205.79
1-TS3-3	-51.26
1-TS3-1-M06	-1401.92
1-TS3-1-BP86	-23.99
1-TS3-4	-224.45
1-TS3-4-iso	-364.08
1-TS3-5	-1044.44
1-TS3-6	-228.19
1-TS3-7	-374.73
1-TS3-8	-197.92
1-TS3-9	-307.92
1-TS3-10	-274.43
1-TS3-11	-185.35
1-TS3-12	-216.63
1-TS4-1	-333.38
1-TS4-5	-270.24
1-TS4-5-iso	-277.27

1-TS4A	-223.72
1-TS4A-1	-282.50
1-TS4A-2	-1239.06
1-TS4A-3	-1242.98
1-TS5	-65.06
1-TS6-1*R*-W	-1100.24
1-TS6-1*S*-W	-1204.47
1-TS6-2-W	-1068.23
1-TS6-3*R*-W	-1068.13
1-TS6-3*S*-W	-1240.99
1-TS6-1*R*-M	-551.20
1-TS6-1*S*-M	-733.68
1-TS6-2-M	-1417.26
1-TS6-3*R*-M	-1086.12
1-TS6-3*S*-M	-881.19
1-TS6-1*R*-2M	-845.78
1-TS6-1*S*-2M	-927.11
1-TS6-2-2M	-715.89
1-TS6-3*R*-2M	-1032.86
1-TS6-3*S*-2M	-232.09
1-TS6-1-M-1	-1421.63
1-TS6-1-W-1	-1208.86
1-TS6A	-31.14
1-TS7	-198.39
1-TS7-1	-350.86
1-TS8	-1004.70
1-TS8-1	-265.44
1-TS8-2	-248.88
1-TS8-3	-724.02
Pre-TS1	-486.14
Pre-TS1-1	-224.66
Pre-TS1-2	-564.14
Pre-TS2	-378.78
Pre-TS3	-83.48
Pre-TS3-1	-503.93
Pre-TS4	-293.40
Pre-TS4-1	-58.13
Pre-TS	-168.81
2-Pre-TS	-168.46
2-TS1	-31.54
2-TS1-1	-30.82
2-TS1-A	-91.91
2-TS1-B	-1110.32

2-TS1-C	-57.80
2-TS2	-203.60
2-TS2-1	-40.81
2-TS2-C	-295.78
2-TS3	-305.26
2-TS3-1	-607.37
2-TS3-1A	-261.50
2-TS3-2	-230.08
2-TS3-2-M06	-296.59
2-TS3-2-BP86	-220.33
2-TS3-3	-919.22
2-TS3-3-M06	-210.42
2-TS3-3-BP86	-276.28
2-TS3-C	-1024.68
2-TS4	-17.90
2-TS4-1	-271.12
2-TS4-B	-331.56
2-TS4-C	-271.12
2-TS4-D	-237.57
2-TS5	-356.74
2-TS5-D	-27.49
2-TS6-D	-1117.15
Pre1-TS1	-556.49
Pre1-TS2	-106.99
Pre1-TS3	-81.56
Pre1-TS4	-141.91