

Supporting Information

Theoretical Insights into Pd-Catalyzed Dual γ -1,1-C(sp³)-H Activation of Aliphatic Carboxylic Acids: Mechanistic Pathways, Substituent Influence on Product Selectivity, Diastereoselectivity, and Additive Effects

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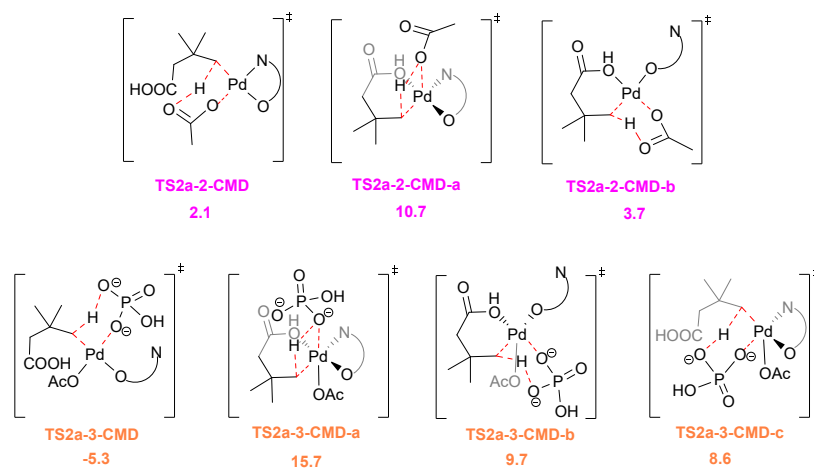
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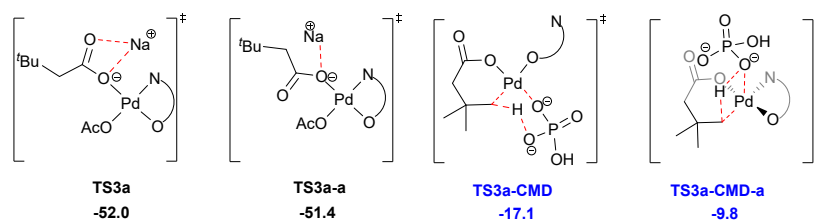
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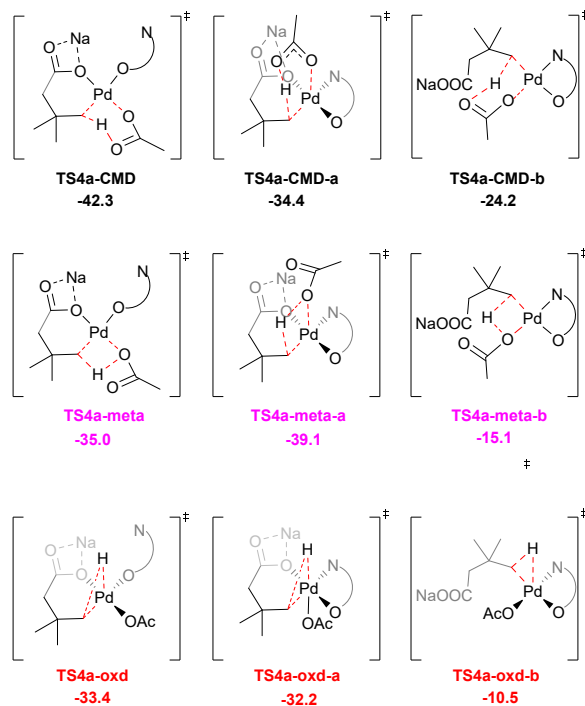
Section 1. Other Possible Isomers



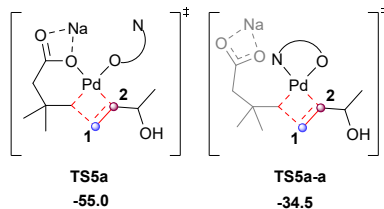
Scheme S1 Other possible isomers of transition states **TS2a-2-CMD** and **TS2a-3-CMD** with relative free energies in kcal/mol.



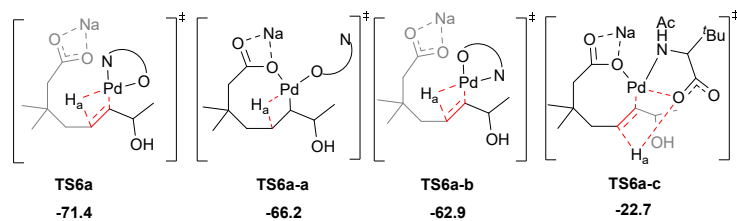
Scheme S2 Other possible isomers of transition states **TS3a** and **TS3a-CMD** with relative free energies in kcal/mol.



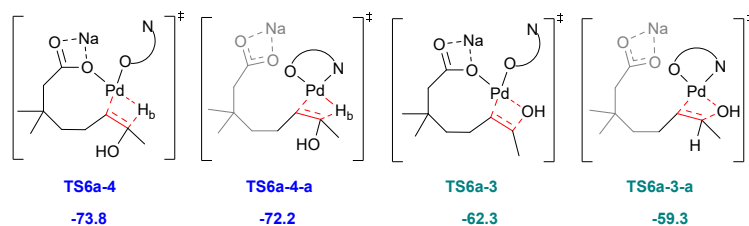
Scheme S3 Other possible isomers of transition states **TS4a** with relative free energies in kcal/mol.



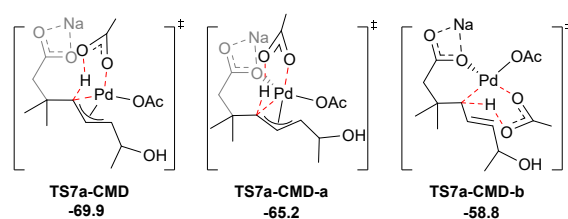
Scheme S4 Other possible isomers of transition state **TS5a** with relative free energies in kcal/mol.



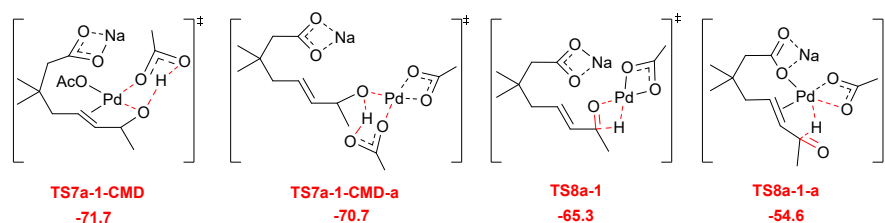
Scheme S5 Other possible isomers of transition states **TS6a** with relative free energies in kcal/mol.



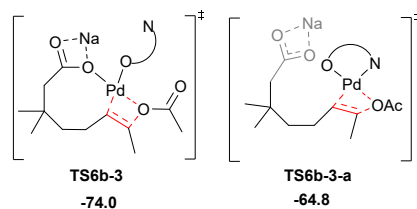
Scheme S6 Other possible isomers of transition states **TS6a-3** and **TS6a-4** with relative free energies in kcal/mol.



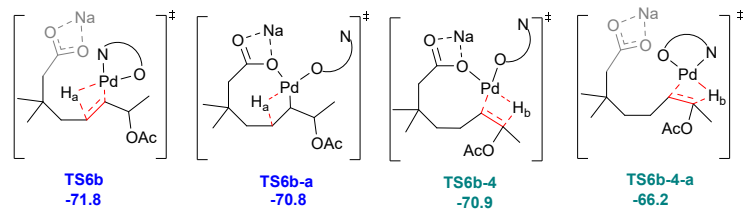
Scheme S7 Other possible isomers of transition states **TS7a-CMD** with relative free energies in kcal/mol.



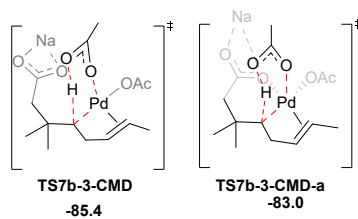
Scheme S8 Other possible isomers of transition states **TS7a-1-CMD** and **TS8a-3** with relative free energies in kcal/mol.



Scheme S9 Other possible isomers of transition states **TS6b-3** with relative free energies in kcal/mol.



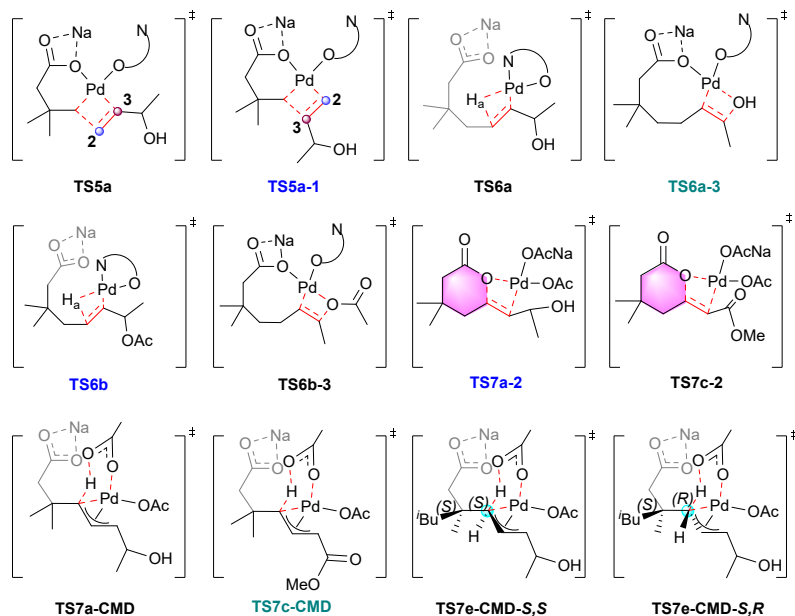
Scheme S10 Other possible isomers of transition states **TS6b** and **TS6b-4** with relative free energies in kcal/mol.



Scheme S11 Other possible isomers of transition states **TS7b-3-CMD** with relative free energies in kcal/mol.

Section 2. Optimization with BP86 and M06 Methods

Table S1. Relative Gibbs energies (in kcal/mol) for key transition states using BP86 and M06 methods.



Species	$\Delta\Delta G(\text{B3LYP})$	$\Delta\Delta G(\text{BP86})$	$\Delta\Delta G(\text{M06})$
TS5a	0.0	0.0	0.0
TS5a-1	4.8	3.8	5.7
TS6a	0.0	0.0	0.0
TS6a-3	9.1	7.2	8.4
TS6b-3	0.0	0.0	0.0
TS6b	2.6	3.6	2.0
TS7a-CMD	0.0	0.0	0.0
TS7a-2	5.4	5.8	4.0
TS7c-2	0.0	0.0	0.0
TS7c-CMD	2.1	2.9	3.7
TS7e-CMD-SR	0.0	0.0	0.0
TS7e-CMD-SS	3.6	2.7	3.4

Section 3. Relaxed Potential Energy Surface Scan

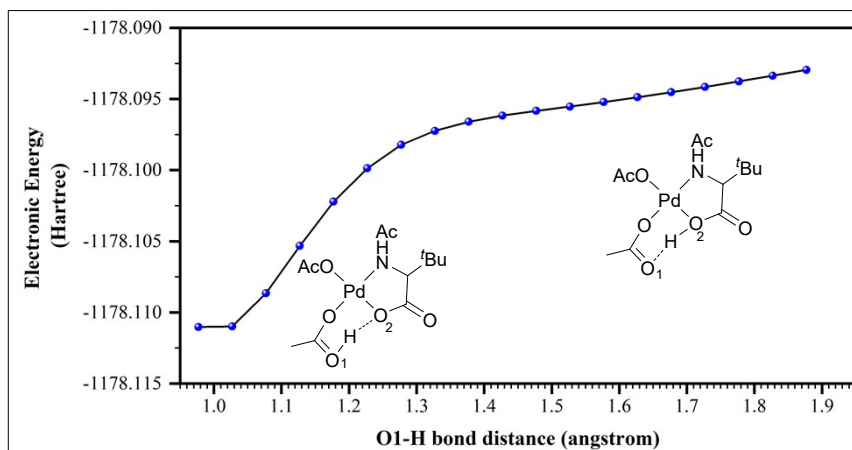


Fig. S1 Relaxed potential energy surface scan of the **O1-H** distance for the CMD transition state from **IN2a** to **IN1a** along the IRC curve.

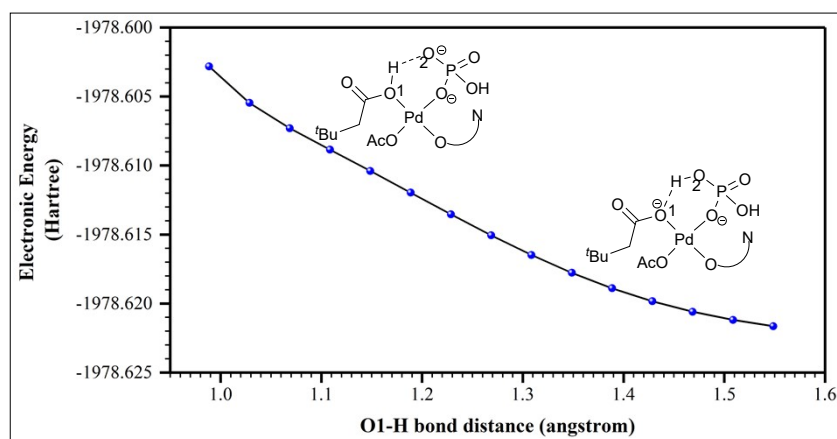


Fig. S2 Relaxed potential energy surface scan of the **O1-H** distance for the CMD transition state from **IN4a** to **IN5a** along the IRC curve.

Section 4. Complete Free-Energy Profiles for the Formation of 3b

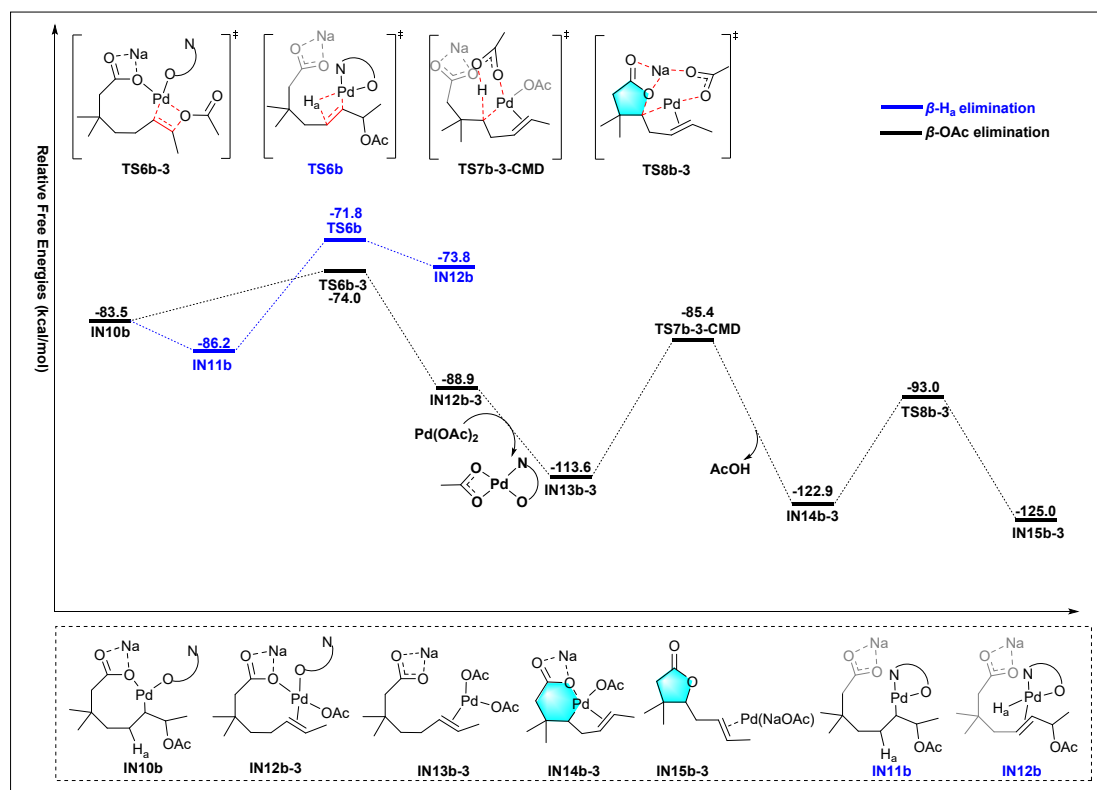


Fig. S3 Calculated free-energy profiles for the process from **IN10b** to **IN15b-3** with relative free energies in kcal/mol. The β -H_a elimination mechanism is shown in blue.

Section 5. Complete Free-Energy Profiles for the Formation of 3c

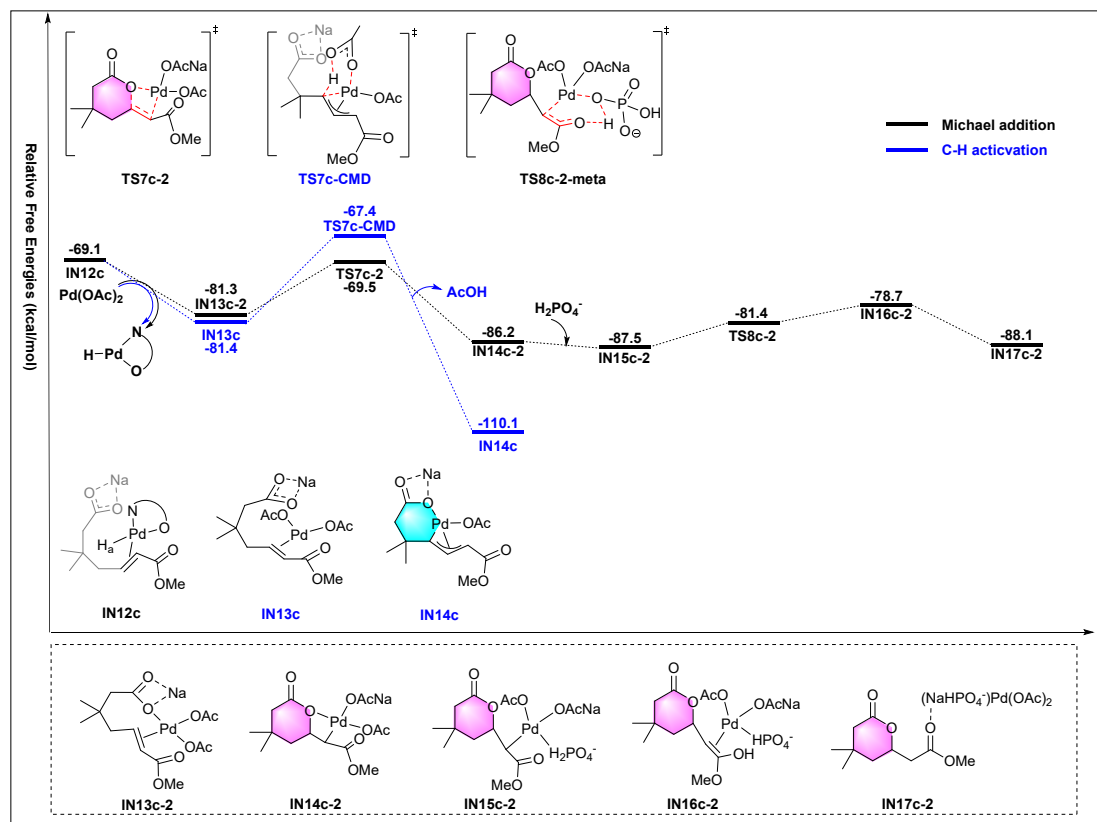


Fig. S4 Calculated free-energy profiles for the process from **IN12c** to **IN17c-2** with relative free energies in kcal/mol. The C–H activation mechanism is shown in blue.

Section 6. Other Possible Pathways

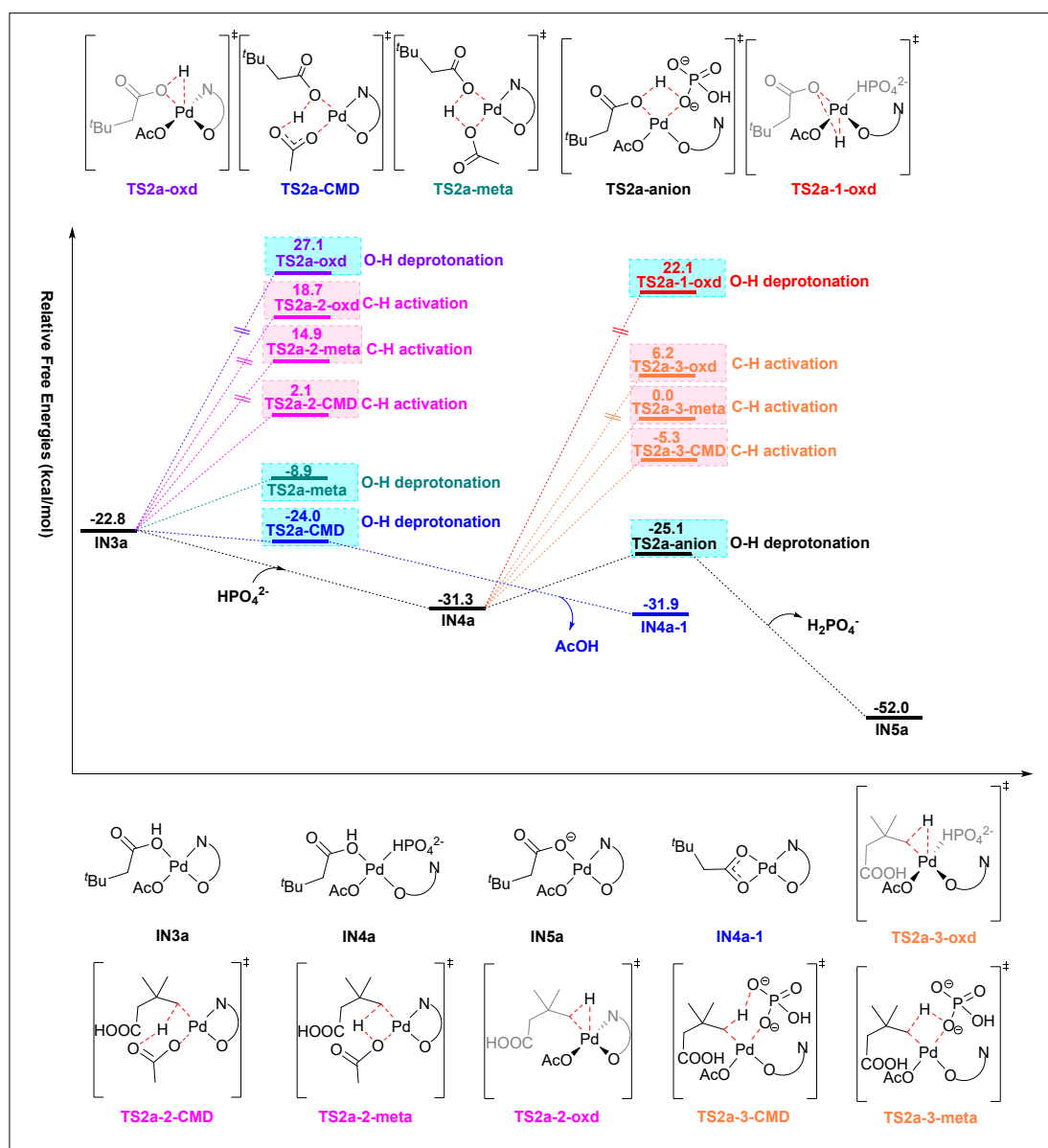


Fig. S5 Calculated free-energy profiles comparing C–H activation and O–H deprotonation from **IN3a**. Relative free energies are provided in kcal/mol.

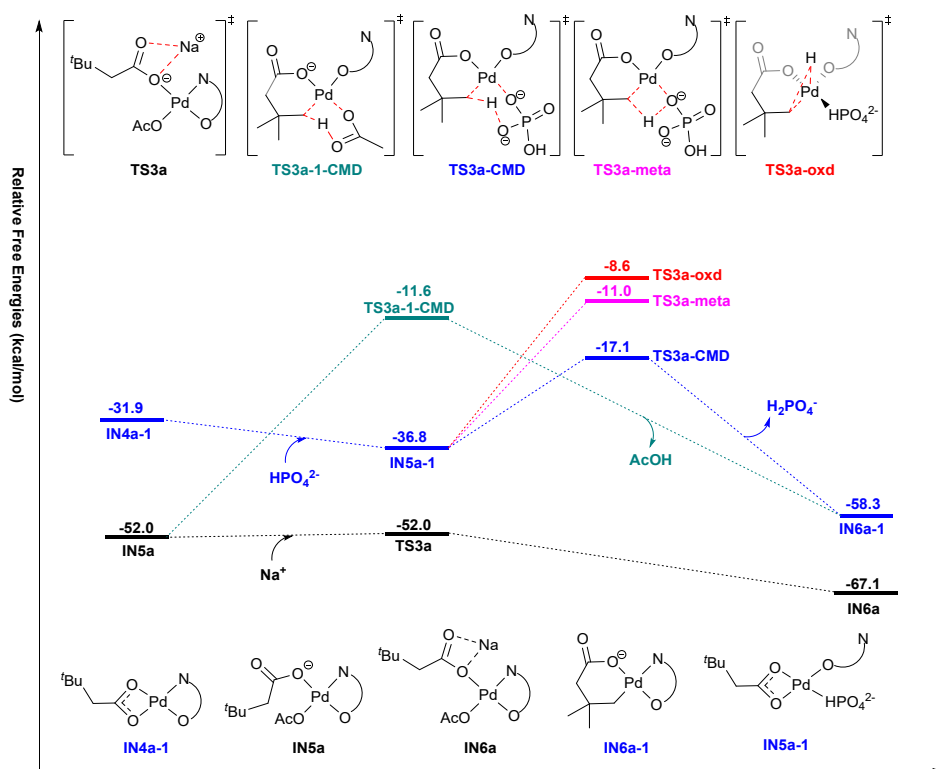


Fig. S6 Calculated free-energy profiles for alternative pathways from IN5a. Relative free energies are provided in kcal/mol.

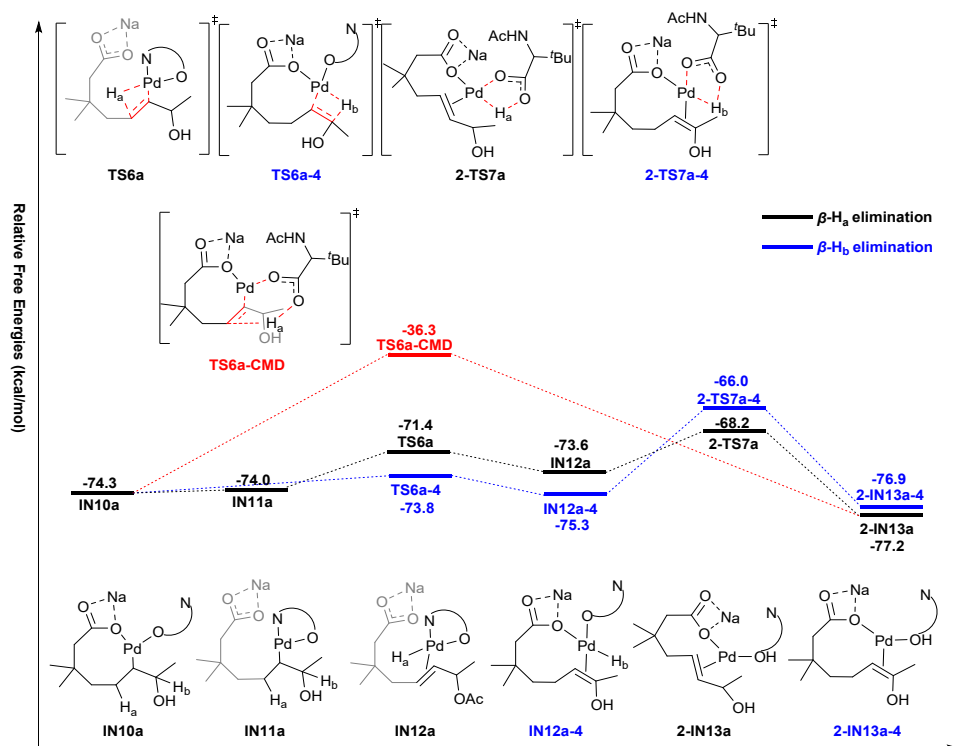


Fig. S7 Calculated free-energy profiles for the reductive elimination pathways from IN10a to 2-IN13a. Relative free energies are provided in kcal/mol.

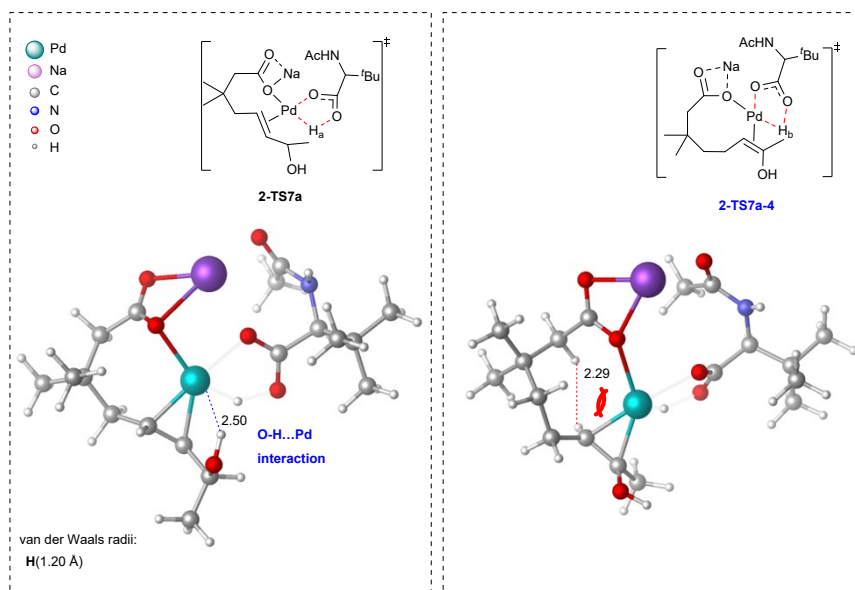


Fig. S8 Optimized structures of transition states **2-TS7a**, **2-TS7a-4** with distances in Å.

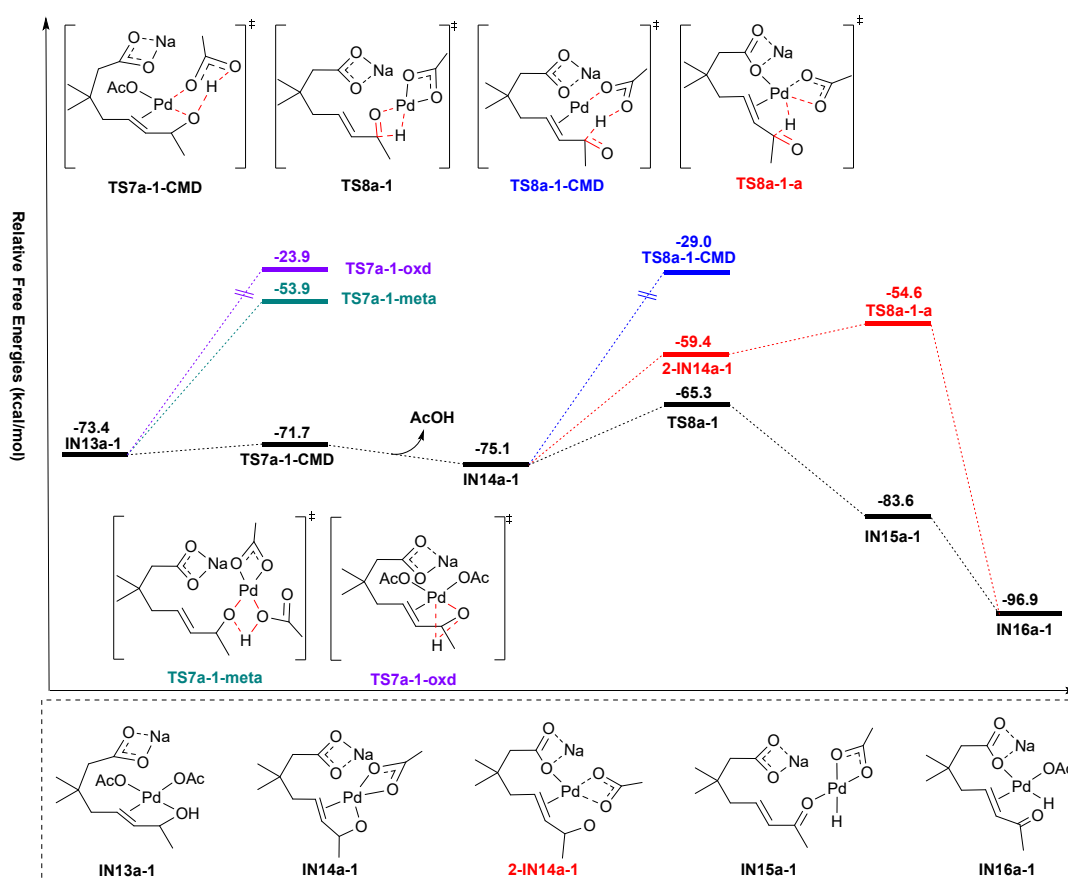


Fig. S9 Calculated free-energy profiles for the process from **IN13a-1**. Relative free energies are provided in kcal/mol.

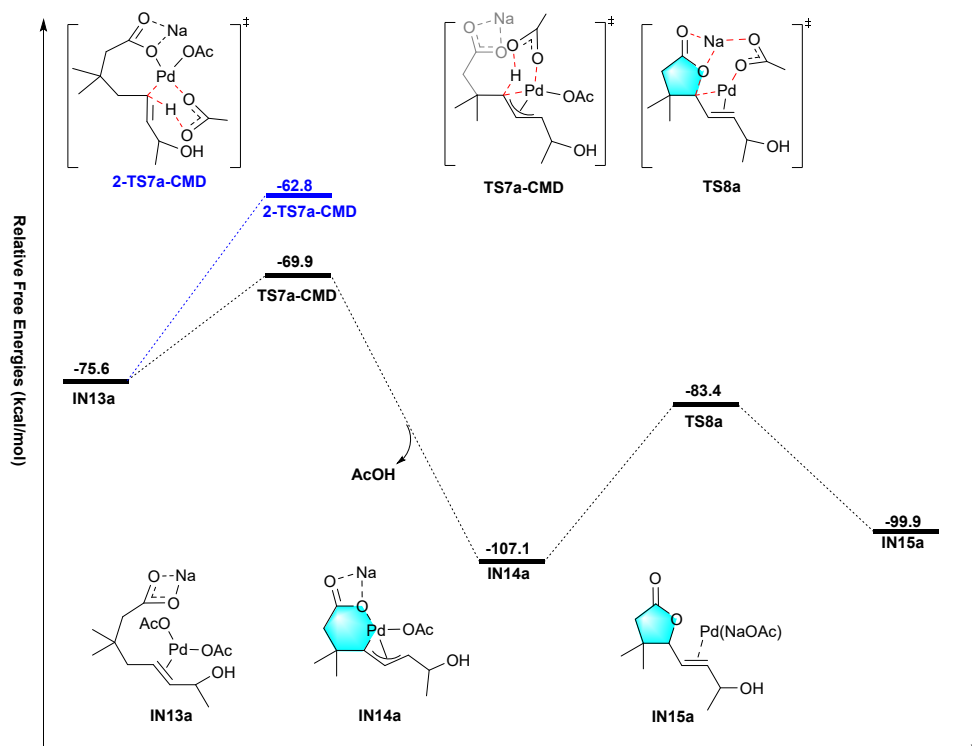


Fig. S10 Calculated free-energy profiles for the process from **IN13a**. Relative free energies are provided in kcal/mol.

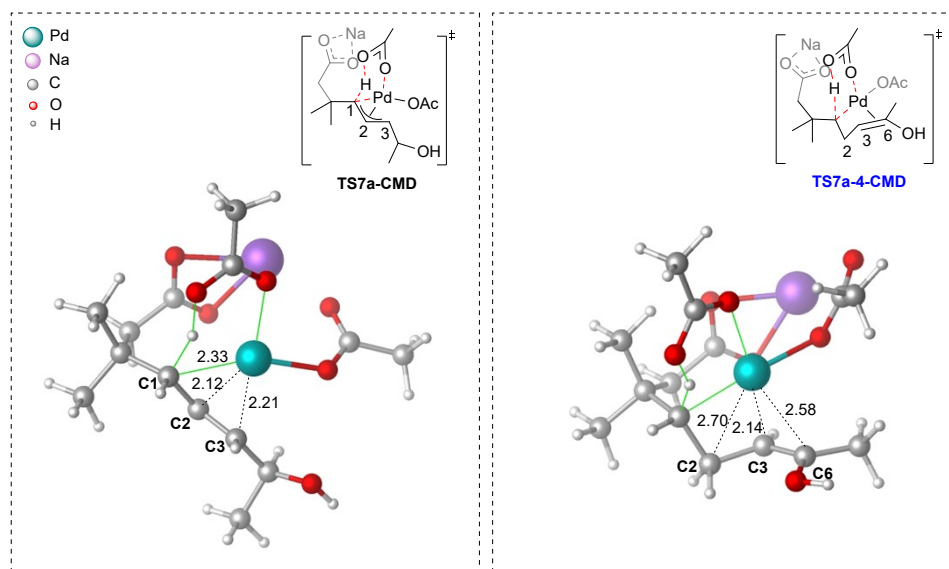


Fig. S11 Optimized structures of transition states **TS7a-CMD**, **TS7a-4-CMD** with distances in Å.

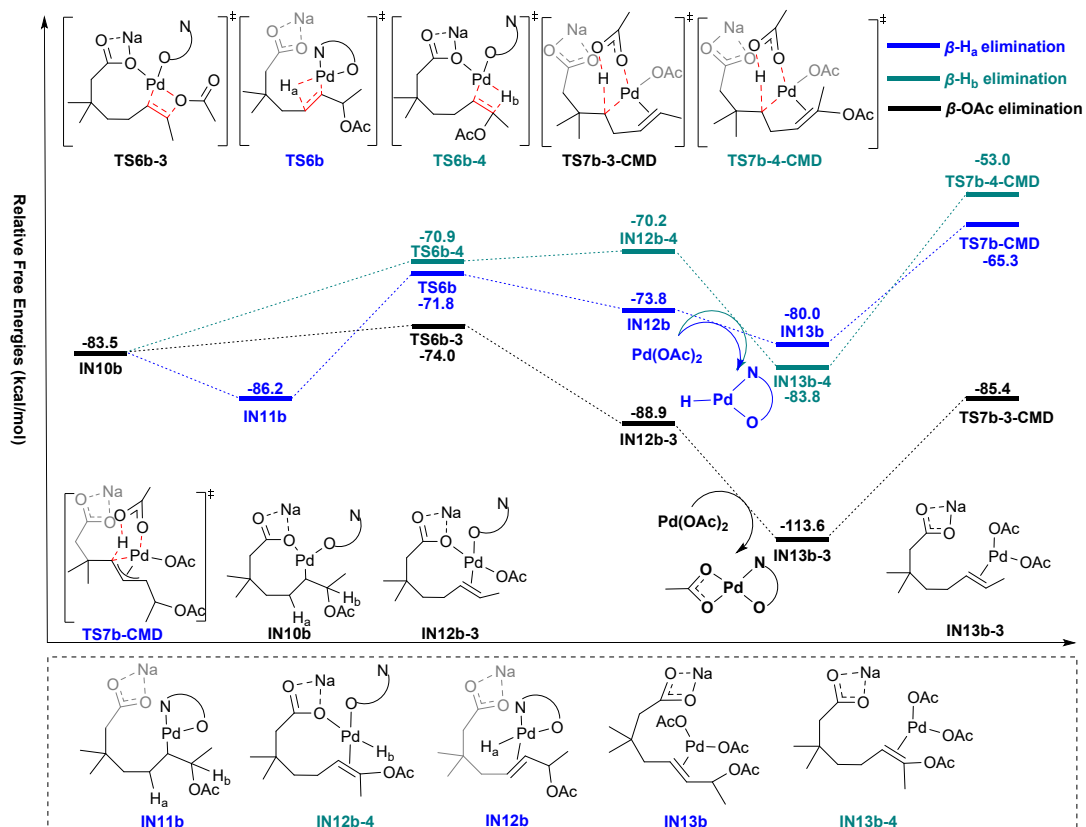


Fig. S12 Calculated free-energy profiles for the three pathways: β -H_a elimination (blue), β -H_b elimination (green), and β -OAc elimination (black). Relative free energies are provided in kcal/ mol.

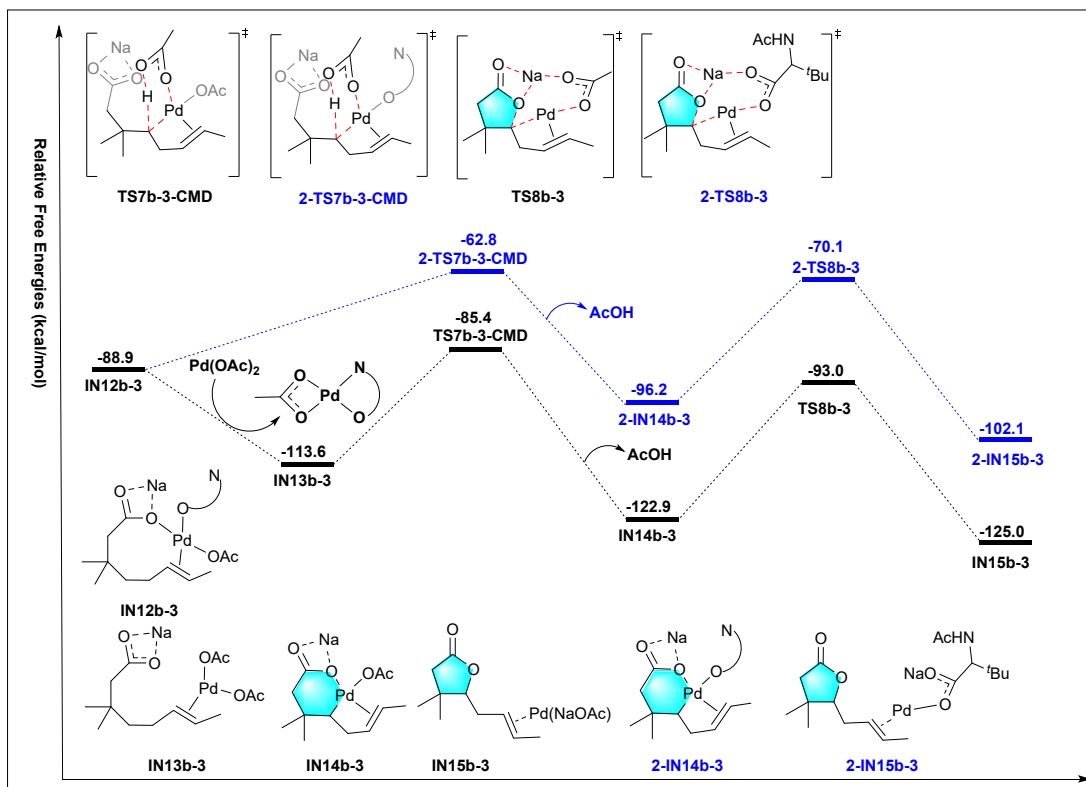


Fig. S13 Calculated free-energy profiles comparing C(sp²)-H and C(sp³)-H activation from IN12b-3. Relative free energies are provided in kcal/mol.

Section 7. Energies (in Hartree) of all TSs and Intermediates

Geometry	E_0	E	$H_{383.15}$	$G_{383.15}$	$E_{(\text{sol},\text{B3LYP})}$
Pd(OAc)₂	-583.604642	-583.588659	-583.587445	-583.657611	-584.7435698
L1	-594.144466	-594.123141	-594.121928	-594.201070	-594.1698134
IN1a	-1177.807194	-1177.767879	-1177.766665	-1177.891107	-1178.965916
TS1a-meta	-1177.777982	-1177.739224	-1177.738011	-1177.860419	-1178.927695
TS1a-oxd	-1177.736224	-1177.697623	-1177.696410	-1177.817507	-1178.881564
AcOH	-229.026944	-229.020243	-229.019030	-229.063679	-229.0402594
IN2a	-948.753331	-948.722795	-948.721581	-948.823591	-949.901888
1a	-386.177530	-386.162922	-386.161708	-386.224977	-386.2076449
IN3a	-1334.979013	-1334.932451	-1334.931238	-1335.069530	-1336.148016
HPO₄²⁻	-643.169845	-643.162079	-643.160866	-643.209603	-643.218899
IN4a	-1978.215727	-1978.160441	-1978.159228	-1978.314652	-1979.416418
TS2a-CMD	-1334.982370	-1334.936570	-1334.935357	-1335.072089	-1336.149363
TS2a-meta	-1334.953111	-1334.906759	-1334.905546	-1335.044460	-1336.121082
TS2a-oxd	-1334.902578	-1334.855767	-1334.854554	-1334.993120	-1336.063757
TS2a-2-CMD	-1334.923863	-1334.878084	-1334.876871	-1335.011916	-1336.108656
TS2a-2-meta	-1334.903895	-1334.857674	-1334.856460	-1334.991664	-1336.087322
TS2a-2-oxd	-1334.900238	-1334.854176	-1334.852962	-1334.987607	-1336.083684
TS2a-2-CMD-a	-1334.912027	-1334.865398	-1334.864184	-1335.001894	-1336.090733
TS2a-2-CMD-b	-1334.922352	-1334.876091	-1334.874877	-1335.014653	-1336.100016
IN4a-1	-1105.933069	-1105.894758	-1105.893544	-1106.012469	-1497.880219
TS2a-anion	-1978.202033	-1978.146159	-1978.144945	-1978.305394	-1979.397005
TS2a-1-oxd	-1978.133329	-1978.077819	-1978.076605	-1978.231900	-1979.32576
TS2a-3-CMD	-1978.161575	-1978.106211	-1978.104997	-1978.260532	-1979.368794
TS2a-3-meta	-1978.141934	-1978.086134	-1978.084920	-1978.244545	-1979.356645
TS2a-3-oxd	-1978.135394	-1978.080827	-1978.079614	-1978.234223	-1979.35631
TS2a-3-CMD-a	-1978.118815	-1978.063078	-1978.061865	-1978.218672	-1979.334931
TS2a-3-CMD-b	-1978.134095	-1978.078592	-1978.077379	-1978.234345	-1979.342608
TS2a-3-CMD-c	-1978.136513	-1978.081589	-1978.080375	-1978.232889	-1979.350676
H₂PO₄⁻	-643.657399	-643.648987	-643.647774	-643.696685	-643.6994192
IN5a	-1334.545898	-1334.499409	-1334.498196	-1334.636644	-1335.715016
IN5a-1	-1749.155929	-1749.107996	-1749.106782	-1749.250264	-1750.349983
Na⁺	-162.190819	-162.188999	-162.187786	-162.210122	-162.1850646
TS3a	-1496.771344	-1496.723206	-1496.721993	-1496.861965	-1497.92083
TS3a-HFIP	-2286.520669	-2286.456296	-2286.455083	-2286.634456	-2287.6854831
TS3a-a	-1496.766788	-1496.718627	-1496.717413	-1496.859479	-1497.917617
TS3a-CMD	-1749.116817	-1749.069790	-1749.068577	-1749.207920	-1750.315774
TS3a-CMD-a	-1749.110739	-1749.065294	-1749.064080	-1749.195361	-1750.3107413
TS3a-meta	-1749.101290	-1749.053734	-1749.052521	-1749.192443	-1750.305384
TS3a-oxd	-1749.105144	-1749.058805	-1749.057591	-1749.192933	-1750.306989
TS3a-1-CMD	-1334.484565	-1334.438426	-1334.437212	-1334.575134	-1335.663383

TS3a-1-CMD-a	-1749.110739	-1749.065294	-1749.064080	-1749.195361	-1750.310741
IN6a	-1496.799368	-1496.750475	-1496.749261	-1496.892302	-1497.942992
IN6a-1	-1105.483429	-1105.445492	-1105.444279	-1105.562612	-1106.657267
IN7a	-1496.776470	-1496.727312	-1496.726099	-1496.869947	-1497.916011
TS4a-CMD	-1496.754654	-1496.706381	-1496.705168	-1496.848573	-1497.897005
TS4a-CMD-a	-1496.741564	-1496.693418	-1496.692204	-1496.832177	-1497.887376
TS4a-CMD-b	-1496.712443	-1496.664559	-1496.663345	-1496.804005	-1497.871704
TS4a-meta	-1496.737167	-1496.688416	-1496.687203	-1496.832880	-1497.881885
TS4a-meta-a	-1496.751169	-1496.703136	-1496.701923	-1496.840829	-1497.895851
TS4a-meta-b	-1496.668036	-1496.620085	-1496.618872	-1496.758389	-1497.858093
TS4a-oxd	-1496.744670	-1496.696158	-1496.694945	-1496.836416	-1497.885609
TS4a-oxd-a	-1496.738663	-1496.689959	-1496.688746	-1496.830814	-1497.882946
TS4a-oxd-b	-1496.692564	-1496.644284	-1496.643070	-1496.785136	-1497.849403
IN8a	-1267.723122	-1267.682095	-1267.680881	-1267.807268	-1268.862223
2a	-232.322917	-232.313364	-232.312150	-232.362975	-232.3431789
IN9a	-1500.092521	-1500.040634	-1500.039421	-1500.189659	-1501.259404
IN9a-1	-1500.096005	-1500.044633	-1500.043420	-1500.190366	-1501.262439
TS5a	-1500.059944	-1500.009976	-1500.008763	-1500.153355	-1501.230923
TS5a-BP86	-1500.135651	-1500.084626	-1500.083412	-1500.229127	-1501.224918
TS5a-M06	-1499.218492	-1499.168741	-1499.167528	-1499.309699	-1501.235134
TS5a-1	-1500.049238	-1499.998735	-1499.997521	-1500.143159	-1501.221196
TS5a-1-BP86	-1500.124615	-1500.072739	-1500.071526	-1500.219874	-1501.215192
TS5a-1-M06	-1499.207871	-1499.157743	-1499.156530	-1499.299826	-1501.224107
TS5a-a	-1500.020538	-1499.971179	-1499.969965	-1500.111790	-1501.199825
IN10a	-1500.093959	-1500.043758	-1500.042544	-1500.185263	-1501.2648044
IN10a-1	-1500.073214	-1500.022452	-1500.021239	-1500.167518	-1501.242664
IN11a	-1500.089350	-1500.038429	-1500.037216	-1500.182456	-1501.261116
TS6a	-1500.081403	-1500.030636	-1500.029423	-1500.174659	-1501.251764
TS6a-BP86	-1500.158379	-1500.106780	-1500.105566	-1500.251298	-1501.246331
TS6a-M06	-1499.241820	-1499.191194	-1499.189981	-1499.333416	-1501.255634
TS6a-a	-1500.068940	-1500.017809	-1500.016596	-1500.163885	-1501.242334
TS6a-b	-1500.059923	-1500.010071	-1500.008857	-1500.151051	-1501.243511
TS6a-c	-1499.998562	-1499.948071	-1499.946858	-1500.092712	-1501.175071
TS6a-3	-1500.086320	-1500.036365	-1500.035151	-1500.176821	-1501.245481
TS6a-3-BP86	-1500.156882	-1500.105818	-1500.104605	-1500.249033	-1501.239711
TS6a-3-M06	-1499.233005	-1499.183125	-1499.181912	-1499.322208	-1501.248546
TS6a-3-a	-1500.076954	-1500.026555	-1500.025341	-1500.169855	-1501.236985
TS6a-4	-1500.092789	-1500.042832	-1500.041618	-1500.183172	-1501.261033
TS6a-4-a	-1500.083739	-1500.033488	-1500.032274	-1500.177382	-1501.254406
TS6a-CMD	-1500.020280	-1499.969422	-1499.968209	-1500.116914	-1501.1917
IN12a	-1500.088558	-1500.037447	-1500.036233	-1500.183596	-1501.2569822
IN12a-3	-1500.094719	-1500.043603	-1500.042390	-1500.186343	-1501.253424
IN12a-4	-1500.097601	-1500.046693	-1500.045479	-1500.190973	-1501.261496

H-Pd-L1	-720.881873	-720.858368	-720.857155	-720.942556	-722.0480543
IN13a	-1362.809098	-1362.764973	-1362.763759	-1362.897782	-1363.952267
IN13a-1	-1362.814157	-1362.771092	-1362.769879	-1362.901259	-1363.953524
IN13a-2	-1362.829563	-1362.786315	-1362.785102	-1362.916526	-1363.957398
IN13a-4	-1362.841934	-1362.799387	-1362.798174	-1362.927733	-1363.981751
TS7a-CMD	-1362.800170	-1362.757183	-1362.755970	-1362.885215	-1363.942853
2-TS7a-CMD	-1362.635001	-1362.601433	-1362.600219	-1362.708055	-1363.9284989
TS7a-CMD-BP86	-1362.886429	-1362.842417	-1362.841204	-1362.972886	-1363.937079
TS7a-CMD-M06	-1362.097022	-1362.054254	-1362.053041	-1362.180907	-1363.945656
TS7a-CMD-a	-1362.788411	-1362.744968	-1362.743755	-1362.876172	-1363.931841
TS7a-CMD-b	-1362.779328	-1362.735652	-1362.734439	-1362.869687	-1363.918965
TS7a-meta	-1362.784626	-1362.741259	-1362.740046	-1362.872652	-1363.928517
TS7a-oxd	-1362.776913	-1362.732938	-1362.731725	-1362.866265	-1363.92206
TS7a-1-CMD	-1362.817946	-1362.775810	-1362.774597	-1362.902451	-1363.94844
TS7a-1-CMD-a	-1362.819538	-1362.777114	-1362.775901	-1362.907312	-1363.943344
TS7a-1-meta	-1362.796487	-1362.753766	-1362.752553	-1362.884424	-1363.91573
TS7a-1-oxd	-1362.745437	-1362.702599	-1362.701386	-1362.830293	-1363.869988
TS7a-2	-1362.809344	-1362.767331	-1362.766118	-1362.895102	-1363.939463
TS7a-2-BP86	-1362.888847	-1362.845840	-1362.844627	-1362.975864	-1363.933
TS7a-2-M06	-1362.097733	-1362.055495	-1362.054281	-1362.183606	-1363.942483
TS7a-4-CMD	-1362.792243	-1362.749542	-1362.748329	-1362.877060	-1363.934198
2-TS7a	-1500.081510	-1500.031187	-1500.029973	-1500.175091	-1501.246455
2-TS7a-4	-1500.078781	-1500.028390	-1500.027176	-1500.172344	-1501.243736
2-IN13a	-1500.085663	-1500.034682	-1500.033468	-1500.179628	-1501.265361
2-IN13a-4	-1500.086803	-1500.035846	-1500.034632	-1500.181513	-1501.265153
2-IN14a-1	-1133.717183	-1133.682336	-1133.681123	-1133.793468	-1134.86047
IN14a	-1133.791442	-1133.756891	-1133.755677	-1133.867609	-1134.936661
IN14a-1	-1133.760179	-1133.725659	-1133.724446	-1133.834723	-1134.888395
IN14a-2	-1362.827602	-1362.785071	-1362.783857	-1362.915873	-1363.963428
IN14a-4	-1133.786114	-1133.750769	-1133.749555	-1133.861426	-1134.928124
TS8a	-1133.754972	-1133.719883	-1133.718670	-1133.832691	-1134.8967
TS8a-1	-1133.737940	-1133.703062	-1133.701848	-1133.815078	-1134.864154
TS8a-1-a	-1133.704489	-1133.670118	-1133.668905	-1133.781178	-1134.850015
TS8a-1-CMD	-1133.679437	-1133.644798	-1133.643585	-1133.754717	-1134.807671
IN15a	-1133.778509	-1133.743085	-1133.741871	-1133.857556	-1134.923327
IN15a-1	-1133.772243	-1133.736161	-1133.734948	-1133.852678	-1134.891919
IN16a-1	-1133.778560	-1133.743067	-1133.741853	-1133.856199	-1134.916352
IN16a	-1199.821583	-1199.782100	-1199.780887	-1199.905131	-1200.96697
Pd(NaOAc)	-517.550601	-517.539172	-517.537959	-517.599163	-518.6921551
TS9a-CMD	-1199.822347	-1199.783522	-1199.782309	-1199.904292	-1200.962791
TS9a-meta	-1199.791344	-1199.752378	-1199.751165	-1199.873405	-1200.924368
TS9a-oxd	-1199.733411	-1199.693787	-1199.692574	-1199.817592	-1200.869165
IN17a	-970.767416	-970.736442	-970.735228	-970.839511	-971.90487

TS10a	-970.741759	-970.710521	-970.709308	-970.815345	-971.8776305
IN18a	-970.770007	-970.737640	-970.736426	-970.844378	-971.9020713
IN19a	-970.771368	-970.738502	-970.737289	-970.848428	-971.9125594
TS11a	-970.771601	-970.739881	-970.738668	-970.846453	-971.9124892
IN20a	-970.799327	-970.767144	-970.765931	-970.873369	-971.9517111
2b	-384.949486	-384.935491	-384.934278	-384.996658	-384.9520288
IN10b	-1652.745247	-1652.690306	-1652.689092	-1652.842123	-1653.890425
IN11b	-1652.744520	-1652.689299	-1652.688085	-1652.843678	-1653.891863
TS6b	-1652.711834	-1652.656826	-1652.655613	-1652.809317	-1653.865785
TS6b-BP86	-1652.792238	-1652.730125	-1652.735271	-1652.888620	-1653.85295
TS6b-M06	-1651.779751	-1651.724773	-1651.723560	-1651.875916	-1653.86305
TS6b-a	-1652.703610	-1652.647747	-1652.646534	-1652.804942	-1653.859037
TS6b-3	-1652.732405	-1652.677462	-1652.676248	-1652.829758	-1653.872389
TS6b-3-BP86	-1652.805428	-1652.749298	-1652.748084	-1652.903135	-1653.863918
TS6b-3-M06	-1651.787495	-1651.732669	-1651.731456	-1651.883201	-1653.874015
TS6b-3-a	-1652.712503	-1652.657326	-1652.656112	-1652.811579	-1653.855048
TS6b-4	-1652.709336	-1652.654373	-1652.653160	-1652.807403	-1653.863923
TS6b-4-a	-1652.698048	-1652.642814	-1652.641601	-1652.798635	-1653.853158
AcO-Pd-L1	-948.779817	-948.749394	-948.748181	-948.850225	-949.9260985
IN12b	-1652.719046	-1652.663769	-1652.662556	-1652.817376	-1653.870268
IN12b-3	-1652.750484	-1652.694227	-1652.693013	-1652.850739	-1653.893205
IN12b-4	-1652.711919	-1652.656143	-1652.654929	-1652.814118	-1653.860008
IN13b	-1515.442190	-1515.393465	-1515.392251	-1515.537044	-1516.568664
IN13b-3	-1287.613362	-1287.571573	-1287.570360	-1287.698723	-1288.747539
IN13b-4	-1515.456897	-1515.408502	-1515.407288	-1515.550928	-1516.576818
TS7b-CMD	-1515.421082	-1515.373629	-1515.372416	-1515.512434	-1516.545562
TS7b-3-CMD	-1287.562987	-1287.521796	-1287.520582	-1287.645657	-1288.699617
TS7b-3-CMD-a	-1287.559500	-1287.518528	-1287.517315	-1287.641654	-1288.696379
TS7b-4-CMD	-1515.405399	-1515.357536	-1515.356323	-1515.496423	-1516.525097
IN14b-3	-1058.555707	-1058.522318	-1058.521105	-1058.629063	-1059.694661
TS8b-3	-1058.502449	-1058.468560	-1058.467347	-1058.579607	-1059.64049
IN15b-3	-1058.558611	-1058.526205	-1058.524991	-1058.633586	-1059.697672
2-TS7b-3-CMD	-1652.701419	-1652.645577	-1652.644364	-1652.800177	-1653.847023
2-IN14b-3	-1423.689043	-1423.640879	-1423.639665	-1423.778671	-1424.835052
2-TS8b-3	-1423.644081	-1423.595662	-1423.594449	-1423.736243	-1424.788711
2-IN15b-3	-1423.696653	-1423.648514	-1423.647300	-1423.788602	-1424.843546
2c	-306.374484	-306.364603	-306.363390	-306.416080	-306.3665519
IN12c	-1574.134018	-1574.082695	-1574.081481	-1574.229247	-1575.274324
IN13c	-1436.874767	-1436.830356	-1436.829143	-1436.964736	-1437.985743
IN13c-2	-1436.881070	-1436.836977	-1436.835763	-1436.970430	-1437.986755
TS7c-2	-1436.864916	-1436.822115	-1436.820902	-1436.951056	-1437.971026
TS7c-2-BP86	-1436.949411	-1436.905441	-1436.904228	-1437.038353	-1437.963526
TS7c-2-M06	-1436.131408	-1436.088761	-1436.087547	-1436.216691	-1437.975488

TS7c-CMD	-1436.847537	-1436.804289	-1436.803076	-1436.933167	-1437.962984
TS7c-CMD-BP86	-1436.941241	-1436.897028	-1436.895814	-1437.027863	-1437.956459
TS7c-CMD-M06	-1436.121735	-1436.078850	-1436.077636	-1436.205894	-1437.965822
IN14c	-1207.843533	-1207.807466	-1207.806253	-1207.924154	-1208.96172
IN14c-2	-1436.885729	-1436.842540	-1436.841327	-1436.973636	-1437.997986
IN15c-2	-2080.590984	-2080.538929	-2080.537716	-2080.689627	-2081.730748
TS8c-2	-2080.588773	-2080.537803	-2080.536589	-2080.685200	-2081.722293
IN16c-2	-2080.578650	-2080.526444	-2080.525231	-2080.678323	-2081.717021
IN17c-2	-2080.596802	-2080.543442	-2080.542229	-2080.700502	-2081.727081
1d	-425.461830	-425.445091	-425.443878	-425.513179	-425.4969734
TS4d-CMD-R	-1536.039284	-1535.988971	-1535.987758	-1536.134538	-1537.186418
TS4d-CMD-S	-1536.040171	-1535.989888	-1535.988675	-1536.135590	-1537.187479
TS7d-CMD-RR	-1402.085330	-1402.039961	-1402.038748	-1402.173978	-1403.232521
TS7d-CMD-RS	-1402.081370	-1402.036266	-1402.035052	-1402.169155	-1403.228773
TS7d-CMD-SR	-1402.084618	-1402.039377	-1402.038164	-1402.173051	-1403.232013
TS7d-CMD-SS	-1402.081331	-1402.036093	-1402.034880	-1402.169637	-1403.22817
1e	-504.032494	-504.011798	-504.010585	-504.087664	-504.0772663
TS4e-CMD-R	-1614.609455	-1614.555059	-1614.553846	-1614.709659	-1615.765938
TS4e-CMD-S	-1614.613481	-1614.559121	-1614.557908	-1614.713411	-1615.76914
TS7e-CMD-SR	-1480.657303	-1480.608056	-1480.606843	-1480.750626	-1481.814007
TS7e-CMD-SR-BP86	-1480.739709	-1480.689349	-1480.688135	-1480.833755	-1481.807807
TS7e-CMD-SR-M06	-1479.849544	-1479.800490	-1479.799276	-1479.941387	-1481.816879
TS7e-CMD-SS	-1480.650356	-1480.600948	-1480.599735	-1480.744097	-1481.807583
TS7e-CMD-SS-BP86	-1480.734694	-1480.683962	-1480.682749	-1480.830511	-1481.800996
TS7e-CMD-SS-M06	-1479.842958	-1479.793749	-1479.792535	-1479.934760	-1481.810919

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

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

$H_{383.15}$ = Sum of electronic and thermal enthalpies calculated by B3LYP-D3

$G_{383.15}$ = Sum of electronic and thermal free energies calculated by B3LYP-D3

$E_{(\text{sol}, \text{B3LYP})}$ = Single point energies calculated by B3LYP-D3 in solvent

Section 8. Calculated Imaginary Frequencies of All Transition States

Species

Species	Frequency
TS1a-meta	-1232.26
TS1a-oxd	-1058.33
TS2a-CMD	-61.91
TS2a-meta	-1167.24
TS2a-oxd	-915.99
TS2a-2-CMD	-1574.26
TS2a-2-meta	-1473.23
TS2a-2-oxd	-578.84
TS2a-2-CMD-a	-1164.63
TS2a-2-CMD-b	-1414.94
TS2a-anion	-1141.67
TS2a-1-oxd	-896.81
TS2a-3-CMD	-1536.03
TS2a-3-meta	-1553.17
TS2a-3-oxd	-673.34
TS2a-3-CMD-a	-945.75
TS2a-3-CMD-b	-1490.44
TS2a-3-CMD-c	-1540.4
TS3a	-285.62
TS3a-HFIP	-10.25
TS3a-a	-296.5
TS3a-CMD	-1501.52
TS3a-CMD-a	-1329.01
TS3a-meta	-1478.84
TS3a-oxd	-267.25
TS3a-1-CMD	-1501.51
TS3a-1-CMD-a	-1329.01
TS4a-CMD	-1433.13
TS4a-CMD-a	-1171.59
TS4a-CMD-b	-1577.90
TS4a-meta	-1543.48
TS4a-meta-a	-1408.34
TS4a-meta-b	-1428.53
TS4a-oxd	-348.11
TS4a-oxd-a	-509.30
TS4a-oxd-b	-537.96
TS5a	-281.93
TS5a-BP86	-261.52

TS5a-M06	-250.47
TS5a-1	-306.60
TS5a-1-BP86	-286.01
TS5a-1-M06	-289.61
TS5a-a	-290.75
TS6a	-573.38
TS6a-BP86	-511.30
TS6a-M06	-426.50
TS6a-a	-819.61
TS6a-b	-594.37
TS6a-c	-279.47
TS6a-3	-192.32
TS6a-3-BP86	-184.90
TS6a-3-M06	-161.04
TS6a-3-a	-259.67
TS6a-4	-556.78
TS6a-4-a	-550.80
TS6a-CMD	-1778.92
TS7a-CMD	-1267.92
2-TS7a-CMD	-1054.71
TS7a-CMD-BP86	-947.68
TS7a-CMD-M06	-1342.56
TS7a-CMD-a	-803.76
TS7a-CMD-b	-1434.15
TS7a-meta	-444.15
TS7a-oxd	-518.78
TS7a-1-CMD	-885.11
TS7a-1-CMD-a	-701.15
TS7a-1-meta	-948.14
TS7a-1-oxd	-943.66
TS7a-2	-297.06
TS7a-2-BP86	-249.69
TS7a-2-M06	-316.12
TS7a-4-CMD	-1420.06
2-TS7a	-828.16
2-TS7a-4	-480.05
TS8a	-233.62
TS8a-1	-632.15
TS8a-1-a	-632.15
TS8a-1-CMD	-197.99
TS9a-CMD	-1012.79
TS9a-meta	-627.42
TS9a-oxd	-948.58

TS10a	-579.11
TS11a	-75.35
TS6b	-584.77
TS6b-BP86	-524.11
TS6b-M06	-397.97
TS6b-a	-832.61
TS6b-3	-298.68
TS6b-3-BP86	-265.09
TS6b-3-M06	-325.43
TS6b-3-a	-330.47
TS6b-4	-551.58
TS6b-4-a	-496.51
TS7b-CMD	-1315.28
TS7b-3-CMD	-1406.25
TS7b-3-CMD-a	-1107.99
TS7b-4-CMD	-1433.86
TS8b-3	-303.58
2-TS7b-3-CMD	-1443.67
2-TS8b-3	-312.52
TS7c-2	-250.88
TS7c-2-BP86	-224.82
TS7c-2-M06	-227.06
TS7c-CMD	-1288.51
TS7c-CMD-BP86	-932.97
TS7c-CMD-M06	-1347.69
TS8c-2	-39.50
TS4d-CMD-R	-1431.78
TS4d-CMD-S	-1448.34
TS7d-CMD-RR	-1298.59
TS7d-CMD-RS	-1237.83
TS7d-CMD-SR	-1320.73
TS7d-CMD-SS	-1270.80
TS4e-CMD-R	-1437.08
TS4e-CMD-S	-1453.56
TS7e-CMD-SR	-1321.88
TS7e-CMD-SR-BP86	-1022.90
TS7e-CMD-SR-M06	-1367.54
TS7e-CMD-SS	-1274.77
TS7e-CMD-SS-BP86	-956.14
TS7e-CMD-SS-M06	-1350.88