Supporting Information

The Pd(0) and Pd(II) cocatalyzed isomerization of alkynyl epoxides to furans: a mechanistic investigation using DFT calculations

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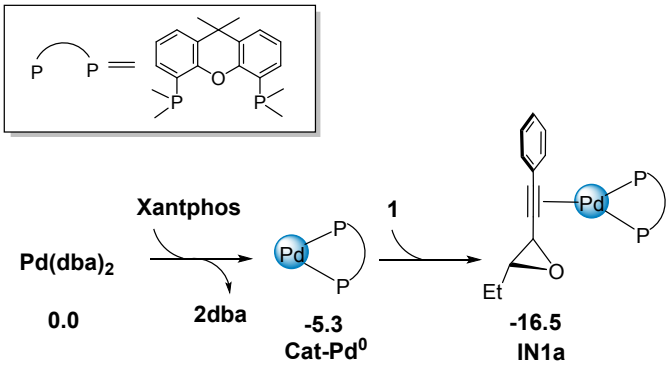


Scheme S1 Energies of **Cat-Pd^0** and **IN1a** relative to catalyst precursor. Values shown are relative free energies in kcal/mol.

Section 2. Comparison between real and model Xantphos systems

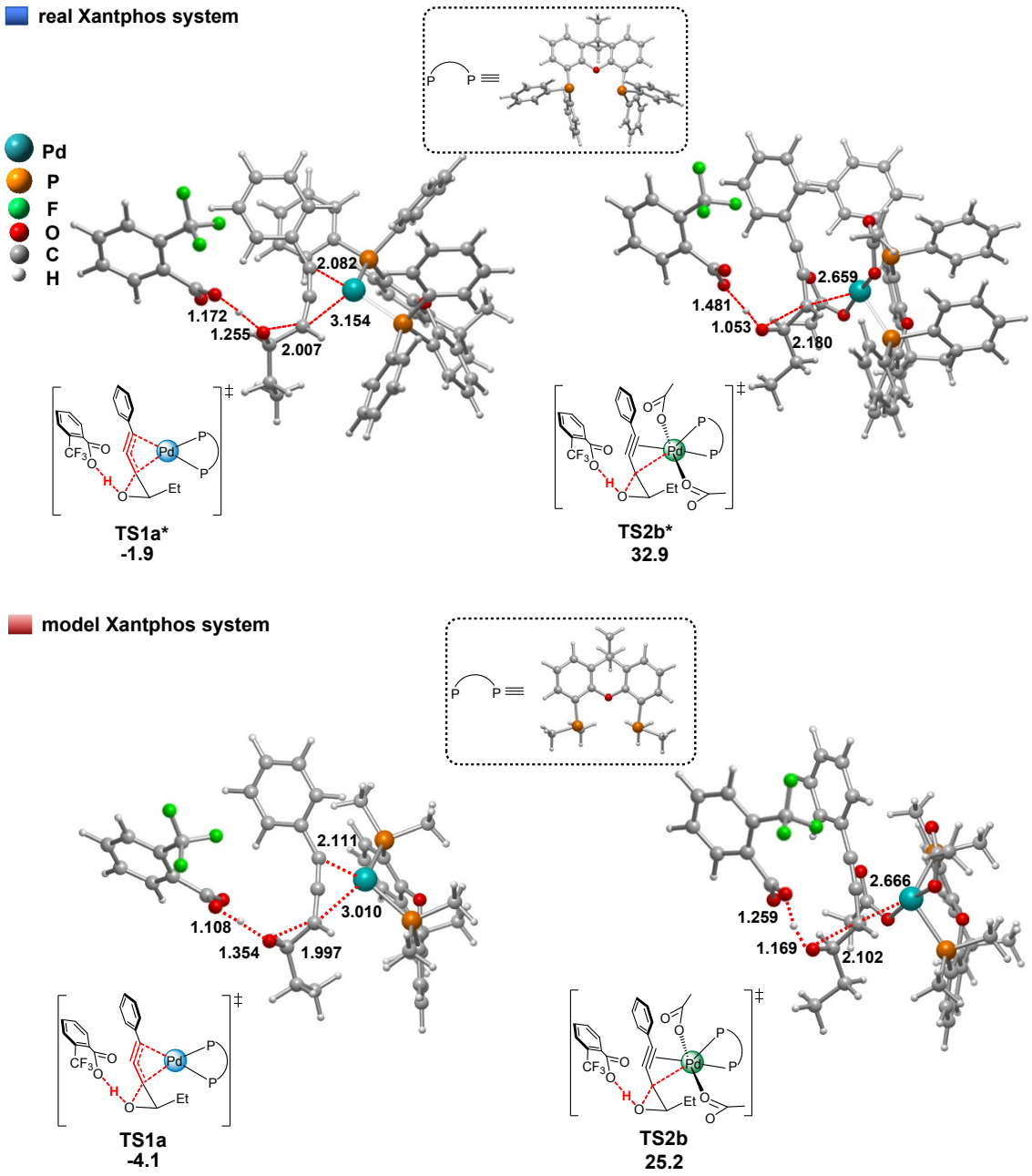


Fig. S1. Optimized structures of key transition states in Stage I. Key bond lengths are given in Å. Values shown are relative free energies in kcal/mol.

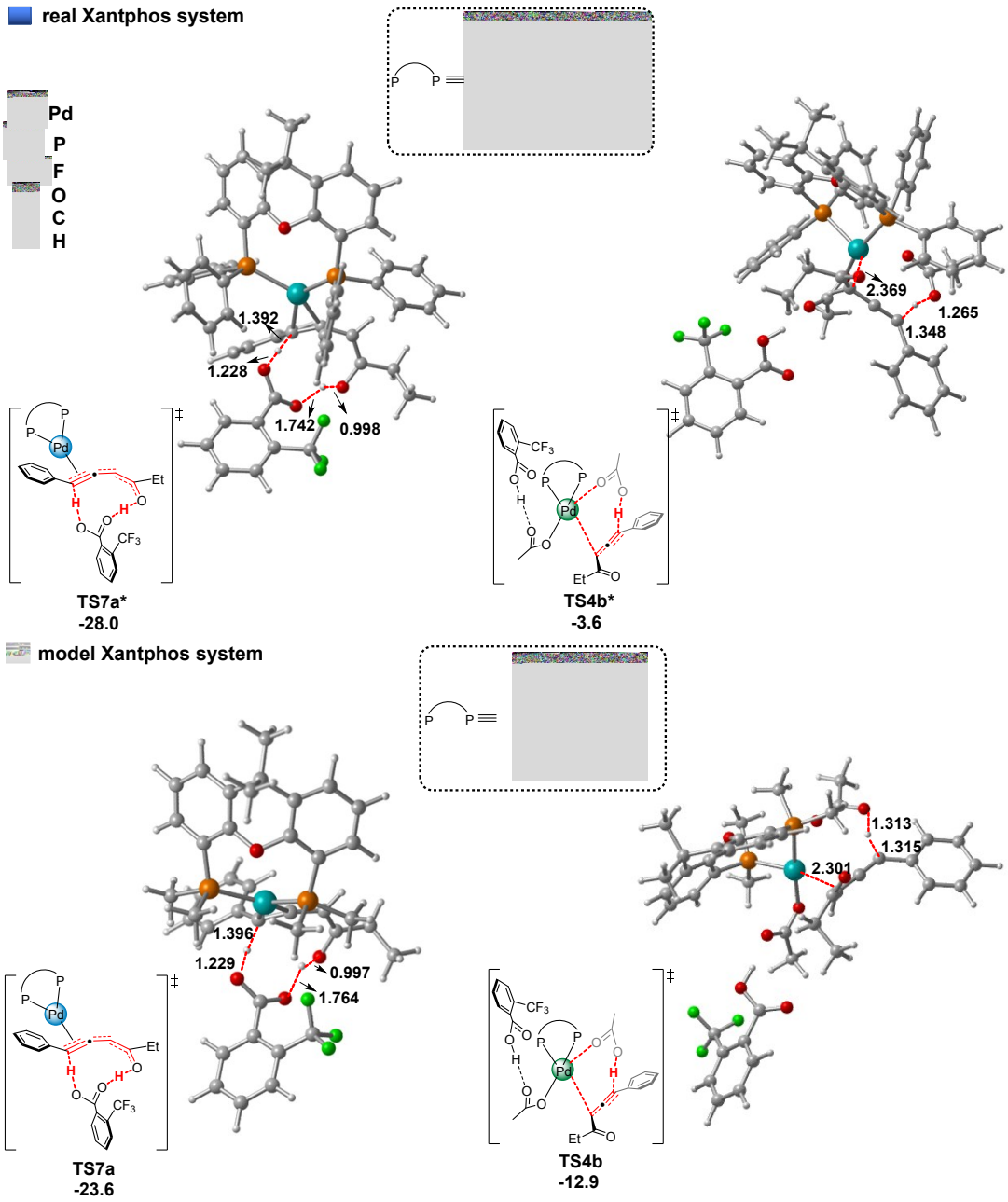
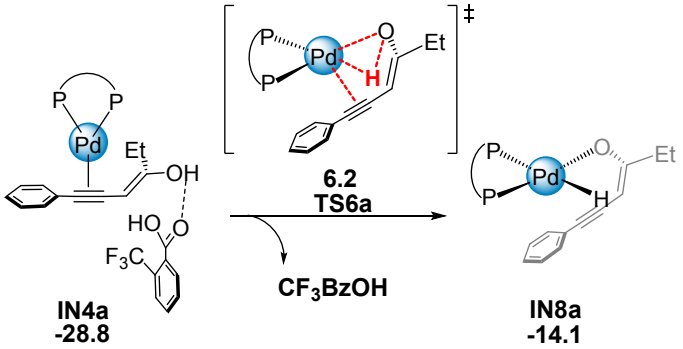


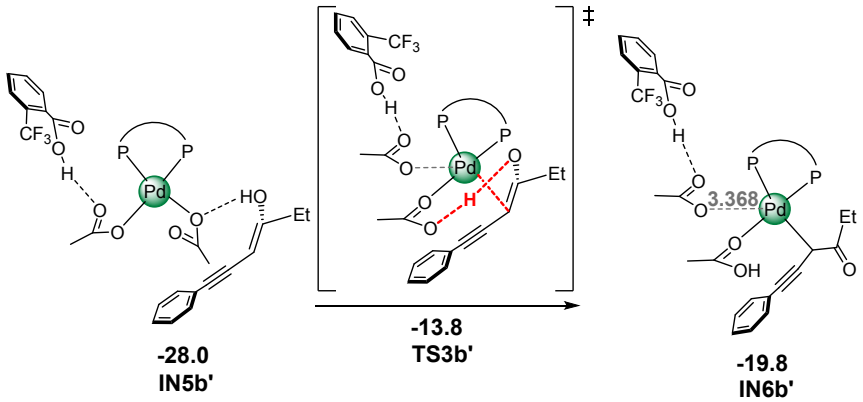
Fig. S2. Optimized structures of key transition states in Stage II. Key bond lengths are given in Å. Values shown are relative free energies in kcal/mol.

Section 3. Deprotonation processes without the assistance of CF_3BzOH in Stage II catalyzed by Pd(0)

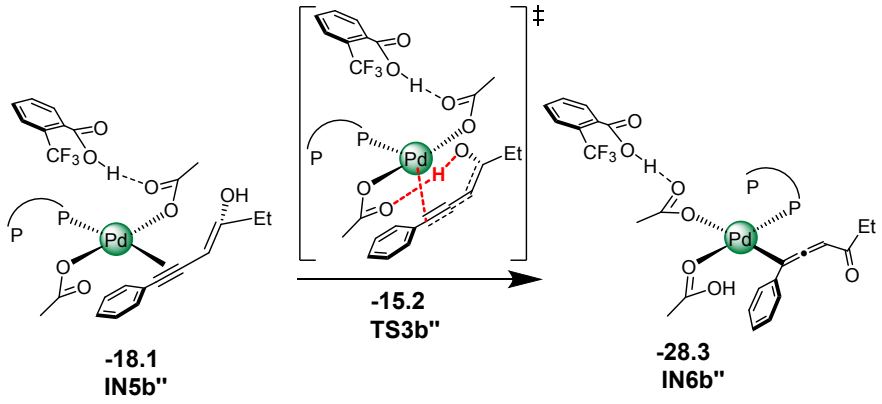


Scheme S2 Deprotonation processes via **TS6a**. Values shown are relative free energies in kcal/mol.

Section 4. Other O−H deprotonation processes in Stage II catalyzed by Pd(II)

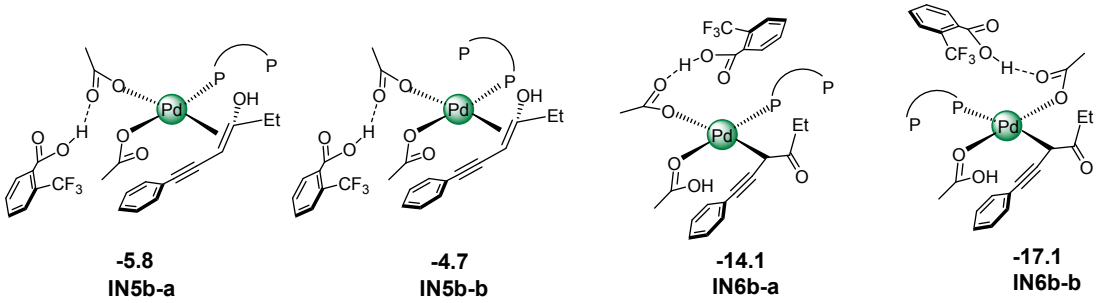


Scheme S3 O−H deprotonation via **TS3b′**. Values shown are relative free energies in kcal/mol.



Scheme S4 O−H deprotonation via **TS3b′′**. Values shown are relative free energies in kcal/mol.

Section 5. Isomers of IN5b and IN6b



Scheme S5 Isomers of **IN5b** and **IN6b**. Values shown are relative free energies in kcal/mol.

Section 6. Processes from IN7b to allenyl ketone and alkynyl ketone with monodentate coordination of Xantphos ligand

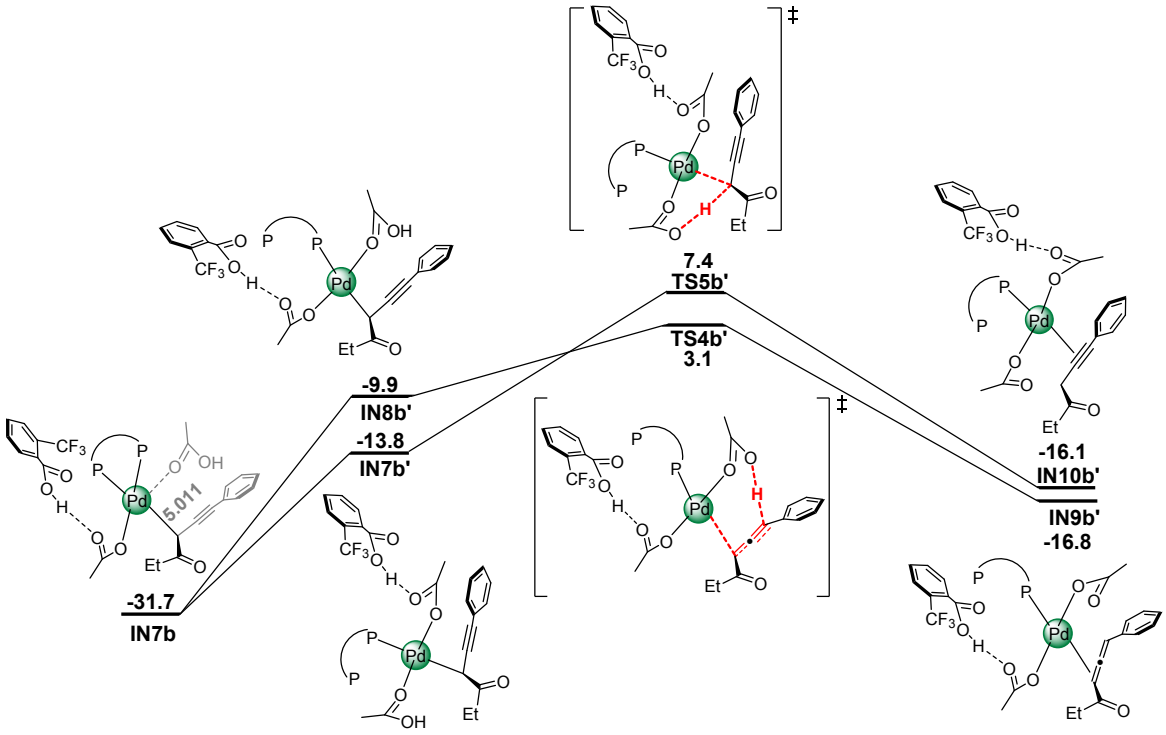


Fig. S3. Calculated energy profiles started form **IN7b** to allenyl ketone and alkynyl ketone with monodentate coordination of Xantphos ligand. Values shown are relative free energies in kcal/mol.

Section 7. Processes from IN7b to IN12b

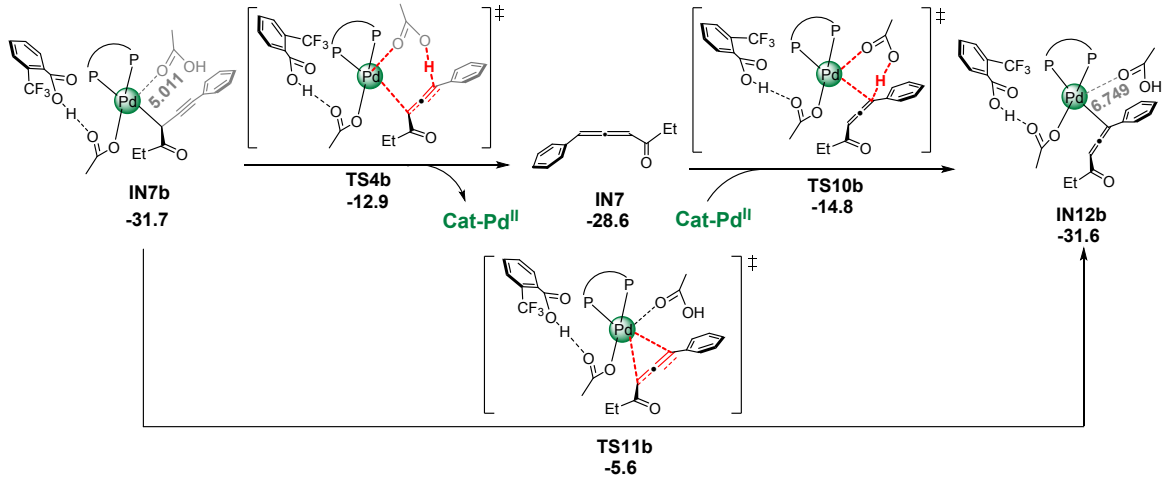
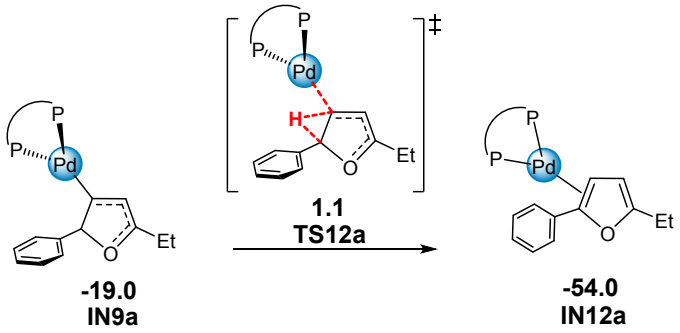


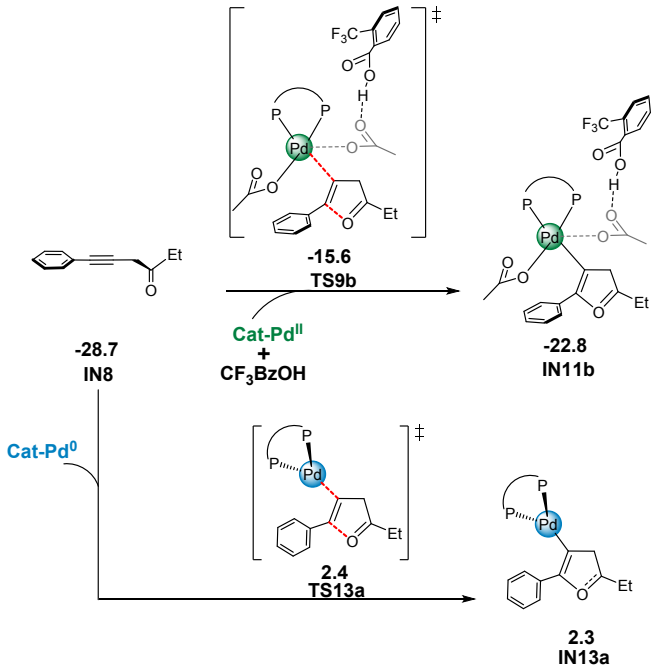
Fig. S4. Calculated energy profiles started form **IN7b** to **IN12b**. Values shown are relative free energies in kcal/mol.

Section 8. Other processes via 1,2 hydrogen migration from IN9a



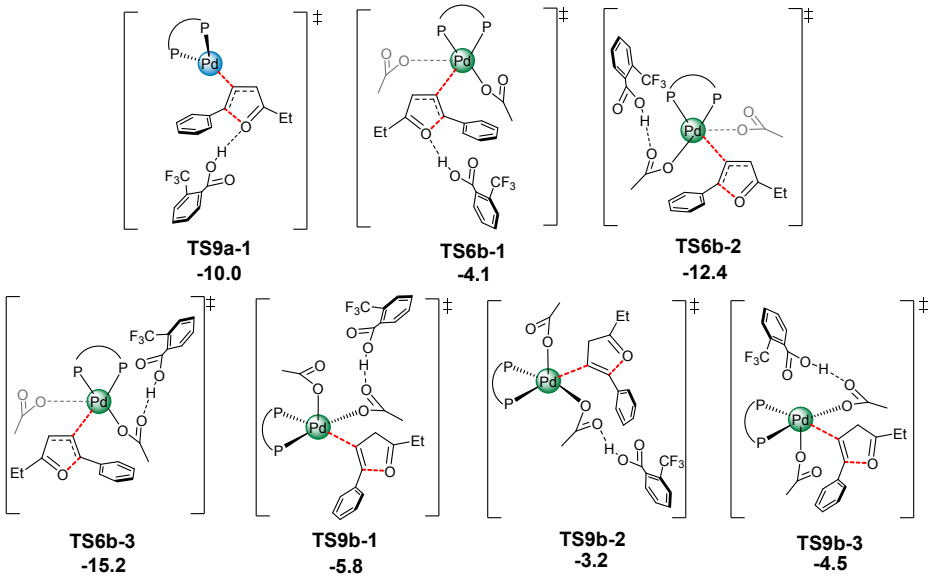
Scheme S6 Calculated energy profiles for 1,2 hydrogen migration from **IN9a**. Values shown are relative free energies in kcal/mol.

Section 9. Stage III started from IN8



Scheme S7 Stage III started from **IN8**. Values shown are relative free energies in kcal/mol.

Section 10. Isomers of TS9a, TS6b and TS9b



Scheme S8 Isomers of **TS9a, TS6b** and **TS9b**. Values shown are relative free energies in kcal/mol.

Section 11. Optimization with D3 dispersion correction

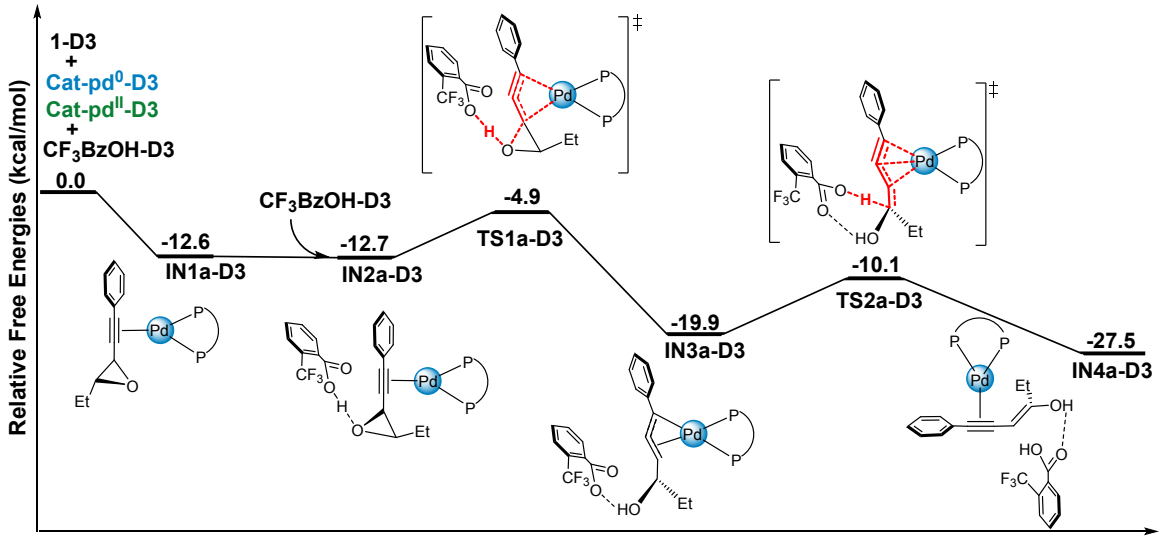
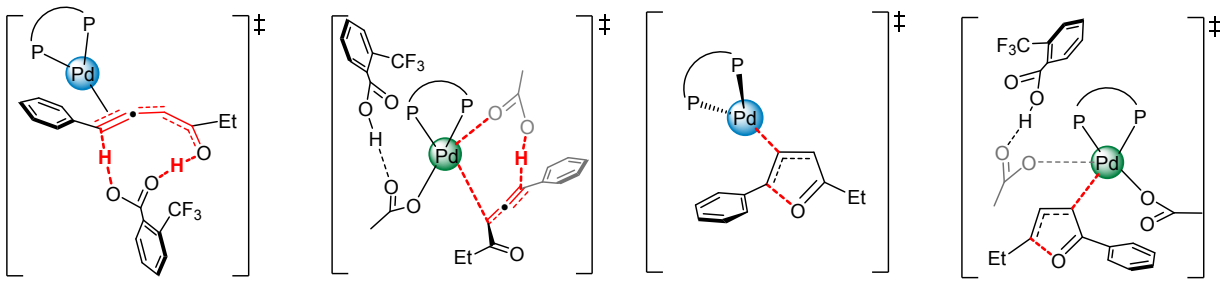
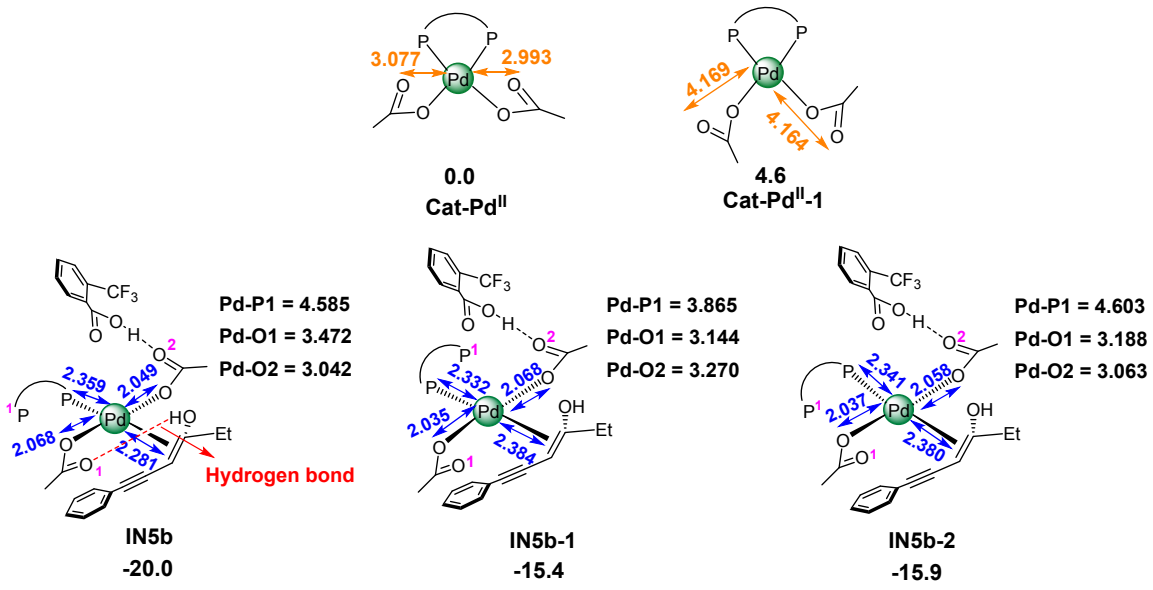


Fig. S5. Calculated energy profiles for Stage I as catalyzed by Pd(0). All species are optimized with D3 dispersion correction. Values shown are relative free energies in kcal/mol.



Scheme S9 Key transition states optimized with D3 dispersion corrections. Values shown are relative free energies in kcal/mol.

Section 12. Isomers of Cat-Pd^{II} and IN5b



Scheme S10 Isomers of **Cat-Pd^{II}** and **IN5b**. Values shown are relative free energies in kcal/mol. Key bond lengths are given in Å.

Section 13. Table of energy values

Table S1 Energies (in Hartree) for all TS and intermediates.

Geometry	E_0	E	$H_{313.15}$	$G_{313.15}$	$E_{(sol,M06)}$
1	-539.428970	-539.415592	-539.414600	539.472641	-539.2185525
Cat-Pd^0	-1622.834526	-1622.807780	-1622.806789	-1622.890868	-1623.694
Cat-Pd^{II}	-2079.733568	-2079.695473	-2079.694481	-2079.804658	-2080.513903
CF_3BzOH	-757.726347	-757.714768	-757.713775	-757.765921	-757.6179039
IN1a	-2162.289999	-2162.248208	-2162.247217	-2162.367814	-2162.930475
IN2a	-2920.029832	-2919.974664	-2919.973673	-2920.126627	-2920.548454
TS1a	-2920.016810	-2919.961700	-2919.960708	-2920.114451	-2920.537061
IN3a	-2920.025720	-2919.970591	-2919.969600	-2920.120749	-2920.561595
TS2a	-2920.017922	-2919.963071	-2919.962080	-2920.113858	-2920.539869
IN4a	-2920.051570	-2919.996007	-2919.995015	-2920.150397	-2920.57634
TS3a	-2162.245453	-2162.204211	-2162.203219	-2162.319906	-2162.890868
IN5a	-2162.276988	-2162.235941	-2162.234949	-2162.350691	-2162.916903
TS4a	-2162.239465	-2162.197984	-2162.196992	-2162.317208	-2162.87349

IN6a	-2162.297594	-2162.256101	-2162.255109	-2162.375075	-2162.932539
TS5a	-2162.199844	-2162.157825	-2162.156833	-2162.280003	-2162.832009
IN7a	-2162.300023	-2162.259599	-2162.258607	-2162.374102	-2162.937218
IN1b	-2619.129805	-2619.075288	-2619.074296	-2619.227463	-2619.698156
TS1b	-2619.098369	-2619.044588	-2619.043596	-2619.195063	-2619.65319
IN2b	-2619.107215	-2619.053968	-2619.052976	-2619.200438	-2619.656536
IN3b	-3376.894178	-3376.825781	-3376.824789	-3377.016829	-3377.336007
TS2b	-3376.851446	-3376.784100	-3376.783108	-3376.964159	-3377.310126
IN4b	-3376.853804	-3376.786998	-3376.786007	-3376.960408	-3377.311478
TS6a	-2162.268105	-2162.225764	-2162.224772	-2162.348048	-2162.902634
IN8a	-2162.301312	-2162.259190	-2162.258198	-2162.380001	-2162.934964
TS7a	-2920.050408	-2919.995489	-2919.994497	-2920.145959	-2920.568046
IN7	-539.478282	-539.464644	-539.463652	-539.522213	-539.2640567
TS8a	-2920.039782	-2919.985293	-2919.984301	-2920.136863	-2920.559645
IN8	-539.471565	-539.457467	-539.456475	-539.517346	-539.2642741
IN5b	-3376.937187	-3376.869957	-3376.868965	-3377.050909	-3377.382253
TS3b	-3376.937399	-3376.870372	-3376.869381	-3377.052584	-3377.381821
IN6b	-3376.933796	-3376.866103	-3376.865111	-3377.049479	-3377.383161
IN7b	-3376.948694	-3376.881151	-3376.880159	-3377.062701	-3377.400142
TS4b	-3376.924822	-3376.858136	-3376.857144	-3377.038497	-3377.370934
TS5b	-3376.890274	-3376.824539	-3376.823547	-3376.999754	-3377.339992
TS9a	-2162.300331	-2162.259065	-2162.258073	-2162.379263	-2162.9332
IN9a	-2162.307567	-2162.266511	-2162.265519	-2162.385083	-2162.942779
TS10a	-2920.044342	-2919.990242	-2919.989250	-2920.137886	-2920.556353
IN10a	-2920.072997	-2920.018775	-2920.017783	-2920.167389	-2920.59573
TS11a	-2920.064979	-2920.010715	-2920.009723	-2920.161478	-2920.582673
IN11a	-2920.090644	-2920.035962	-2920.034970	-2920.187649	-2920.604986
TS6b	-3376.938947	-3376.873574	-3376.872582	-3377.047949	-3377.382074
IN8b	-3376.946558	-3376.880506	-3376.879514	-3377.058810	-3377.058810
TS7b	-3376.948831	-3376.884887	-3376.883895	-3377.055577	-3377.390316
IN9b	-3376.988794	-3376.923109	-3376.922117	-3377.099339	-3377.433079
TS8b	-3376.958015	-3376.892563	-3376.891571	-3377.067614	-3377.402797
IN10b	-3376.966156	-3376.900176	-3376.899184	-3377.075803	-3377.411482
2	-539.516611	-539.504351	-539.503359	-539.557625	-539.2976172
Pd(dba)2	-1589.167508	-1589.130394	-1589.129402	-1589.245969	-1589.743914
dba	-731.187095	-731.170344	-731.169352	-731.235943	-730.8737958
Xantphos	-1496.031907	-1496.006509	-1496.005518	-1496.087488	-1495.689293
Cat-Pd^{0}(real)	-2389.559436	-2389.518073	-2389.517081	-2389.639299	-2390.048572
Cat-Pd^{II}(real)	-2846.439869	-2846.387193	-2846.386201	-2846.532316	-2846.859502
TS1a*	-3686.729093	-3686.660300	-3686.659308	-3686.844521	-3686.888083

TS2b*	-4143.545977	-4143.464967	-4143.463975	-4143.674735	-4143.64354
TS7a*	-3686.765410	-3686.696096	-3686.695105	-3686.881284	-3686.929697
TS4b*	-4143.611870	-4143.531227	-4143.530236	-4143.742317	-4143.701703
IN5b′	-3376.953069	-3376.886216	-3376.885224	-3377.065793	-3377.395035
TS3b′	-3376.920977	-3376.855010	-3376.854018	-3377.030746	-3377.372396
IN6b'	-3376.924309	-3376.857577	-3376.856585	-3377.033802	-3377.38191
IN5b''	-3376.936657	-3376.869201	-3376.868210	-3377.050550	-3377.379171
TS3b''	-3376.934939	-3376.867925	-3376.866934	-3377.048252	-3377.374639
IN6b''	-3376.949714	-3376.882160	-3376.881168	-3377.063510	-3377.39549
IN5b-a	-3376.918310	-3376.850835	-3376.849843	-3377.032804	-3377.359575
IN5b-b	-3376.915127	-3376.847605	-3376.846613	-3377.031647	-3377.357859
IN6b-a	-3376.935306	-3376.868828	-3376.867837	-3377.047855	-3377.372822
IN6b-b	-3376.936191	-3376.868937	-3376.867945	-3377.048852	-3377.377537
IN7b'	-3376.926979	-3376.858938	-3376.857946	-3377.042684	-3377.37241
IN8b'	-3376.920297	-3376.852345	-3376.851353	-3377.035084	-3377.366068
TS4b'	-3376.903421	-3376.836126	-3376.835134	-3377.019489	-3377.345391
TS5b'	-3376.897563	-3376.829534	-3376.828542	-3377.017715	-3377.338616
IN9b'	-3376.938865	-3376.871268	-3376.870276	-3377.052953	-3377.377096
IN10b'	-3376.939400	-3376.871361	-3376.870369	-3377.053460	-3377.375989
TS10b	-3376.919038	-3376.851732	-3376.850740	-3377.030917	-3377.373869
IN12b	-3376.954373	-3376.886626	-3376.885634	-3377.068341	-3377.400755
TS11b	-3376.896668	-3376.829807	-3376.828815	-3377.011200	-3377.359293
TS12a	-2162.271680	-2162.230554	-2162.229562	-2162.349534	-2162.910744
IN12a	-2162.357026	-2162.315789	-2162.314797	-2162.433666	-2162.998683
TS9b	-3376.931804	-3376.865437	-3376.864445	-3377.044949	-3377.375142
IN11b	-3376.944179	-3376.878016	-3376.877024	-3377.055786	-3377.38673
TS13a	-2162.273943	-2162.232265	-2162.231273	-2162.352383	-2162.908726
IN13a	-2162.274855	-2162.233066	-2162.232074	-2162.353248	-2162.908822
TS9a-1	-2920.042287	-2919.988384	-2919.987392	-2920.138617	-2920.546383
TS6b-1	-3376.913109	-3376.847775	-3376.846783	-3377.021960	-3377.356956
TS6b-2	-3376.924621	-3376.858746	-3376.857754	-3377.034013	-3377.370165
TS6b-3	-3376.931842	-3376.865937	-3376.864945	-3377.041422	-3377.374622
TS9b-1	-3376.906848	-3376.840980	-3376.839988	-3377.017569	-3377.357532
TS9b-2	-3376.909170	-3376.842810	-3376.841818	-3377.021517	-3377.355383
TS9b-3	-3376.909060	-3376.843626	-3376.842635	-3377.016724	-3377.35956
1-D3	-539.428970	-539.415592	-539.414600	-539.472641	-539.2185525
Cat-pd^{0}-D3	-1622.896285	-1622.869626	-1622.868634	-1622.952334	-1623.693992
Cat-pd^{II}-D3	-2079.822087	-2079.784241	-2079.783250	-2079.892608	-2080.513524
CF_3BzOH-D3	-757.726347	-757.714791	-757.713799	-757.765863	-757.6178459
IN1a-D3	-2162.388102	-2162.346848	-2162.345856	-2162.463897	-2162.932756

IN2a-D3	-2920.154514	-2920.100015	-2920.099024	-2920.247013	-2920.550631
TS1a-D3	-2920.145080	-2920.090784	-2920.089793	-2920.237443	-2920.538149
IN3a-D3	-2920.162718	-2920.108467	-2920.107475	-2920.253438	-2920.562107
TS2a-D3	-2920.146427	-2920.091692	-2920.090701	-2920.240929	-2920.546515
IN4a-D3	-2920.175630	-2920.121076	-2920.120084	-2920.269422	-2920.574221
TS7a-D3	-2920.179252	-2920.125081	-2920.124089	-2920.272793	-2920.569899
TS4b-D3	-3377.095413	-3377.030294	-3377.029302	-3377.199933	-3377.374622
TS9a-D3	-2162.399635	-2162.359584	-2162.358593	-2162.473286	-2162.938743
TS6b-D3	-3377.106977	-3377.042296	-3377.041304	-3377.210184	-3377.386819
Cat-PdII-1	-2079.719464	-2079.681534	-2079.680543	-2079.790123	-2080.506531
IN5b-1	-3376.923907	-3376.856126	-3376.855134	-3377.038894	-3377.374833
IN5b-2	-3376.927081	-3376.859335	-3376.858343	-3377.041060	-3377.375703

E_0 = Sum of electronic and zero-point Energies by B3LYP in solvent

E = Sum of electronic and thermal Energies by B3LYP in solvent

$H_{313.15}$ = Sum of electronic and thermal Enthalpies by B3LYP in solvent

$G_{313.15}$ = Sum of electronic and thermal Free Energies by B3LYP in solvent

$E_{(sol, M06)}$ = Single point energies calculated by M06 in solvent

Section 14. Calculated imaginary frequencies of all transition states species

Table S2. Calculated imaginary frequencies of all transition states species

for substrate

Species	Frequency
TS1a	-284.92
TS2a	-1218.49
TS3a	-76.15
TS4a	-403.67
TS5a	-394.28
TS1b	-126.85
TS2b	-646.68

TS6a	-835.06
TS7a	-1269.26
TS8a	-1245.57
TS3b	-586.07
TS4b	-1102.6
TS5b	-1273.11
TS9a	-364.24
TS10a	-1282.06
TS11a	-1303.79
TS6b	-130.96
TS7b	-922.21
TS8b	-1032.44
TS1a*	-689.46
TS2b*	-46.04
TS7a*	-1271.07
TS4b*	-1258.61
TS3b′	-33.34
TS3b''	-818.49
TS4b'	-1335.53
TS5b'	-1273.70
TS10b	-1138.40
TS11b	-145.68
TS12a	-1190.38
TS9b	-195.93
TS13a	-308.31
TS9a-1	-361.91
TS6b-1	-191.63
TS6b-2	-202.64
TS6b-3	-158.69
TS9b-1	-218.77
TS9b-3	-220.41
TS1a-D3	-232.62
TS2a-D3	-1392.33
TS7a-D3	-1457.99
TS4b-D3	-1108.54
TS9a-D3	-412.53
TS6b-D3	-146.24

Section 15. Complete reference for Ref. 8

8 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Jr. Montgomery, J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian 09, Revision E.01; Gaussian, Inc.: Wallingford CT, 2013.