

DFT Studies on the Directing Group Dependent Arene-Alkene Cross-Couplings: Arene Activation vs. Alkene Activation

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Table S1. Cartesian coordinates of all the stationary points in the catalytic cycles, calculated at the B3LYP-IDSCRF/DZVP level of theory.

Names	Cartesian Coordinates							
1a	C	-1.13187	-1.20741	0.24743	H	-2.99963	-2.15834	-0.26450
	C	-0.44458	0.00302	0.43679	C	1.01235	0.00642	0.82985
	C	-1.13540	1.21008	0.23930	H	1.25743	-0.87740	1.42701
	C	-2.48393	1.20853	-0.13440	H	1.25670	0.89902	1.41409
	C	-3.16072	-0.00352	-0.31882	S	2.08045	-0.00424	-0.68109
	C	-2.48032	-1.21235	-0.12631	C	3.72685	0.00194	0.11413
	H	-0.60898	-2.15074	0.39612	H	4.47068	-0.00264	-0.68674
	H	-0.61533	2.15593	0.38168	H	3.86862	0.90023	0.72194
	H	-3.00602	2.15205	-0.27884	H	3.86981	-0.88836	0.73330
	H	-4.20960	-0.00604	-0.60748				
Pd(OAc)₂	H	4.29269	-0.02702	-1.05808	O	-1.79140	1.09233	-0.01877
	C	3.96257	0.00226	-0.01378	C	-2.46702	0.00060	-0.01706
	C	2.46706	0.00091	0.01681	O	-1.79308	-1.09213	-0.01813
	H	4.35131	-0.88251	0.49477	C	-3.96254	0.00181	0.01344
	H	4.34955	0.91364	0.44641	H	-4.29270	0.00326	1.05814
	O	1.79341	-1.09200	0.01894	H	-4.34967	0.90000	-0.47210
	O	1.79116	1.09248	0.01836	H	-4.35109	-0.89683	-0.47011
	Pd	0.00002	-0.00080	0.00038				
TS-1a	C	2.64784	0.62217	-0.72267	H	0.25903	-0.45395	4.06541
	C	2.83765	0.00281	0.52371	H	-0.69537	0.71260	3.09358
	C	3.89988	-0.90392	0.67533	H	-1.53419	-4.24240	-0.71643
	C	4.75739	-1.18286	-0.39429	C	-2.33133	-3.62919	-1.15101
	C	4.56186	-0.55867	-1.63260	C	-2.11097	-2.19804	-0.75441
	C	3.50438	0.34456	-1.79371	H	-2.29105	-3.73675	-2.23729
	H	1.82770	1.32446	-0.85857	H	-3.28985	-3.98319	-0.76595
	H	4.05855	-1.39117	1.63599	O	-1.34811	-1.45047	-1.49182
	H	5.57875	-1.88355	-0.26050	O	-2.61597	-1.69119	0.28800
	H	5.22954	-0.77296	-2.46425	Pd	-1.45156	0.21466	-0.31681
	H	3.34612	0.83438	-2.75207	O	-1.63313	1.96008	0.75710
	C	1.91168	0.29538	1.67853	C	-1.19017	2.70816	-0.20070
	H	1.50974	1.31123	1.62103	O	-0.83346	2.13487	-1.27763
	H	2.42938	0.17926	2.63561	C	-1.13595	4.19683	-0.02919
	S	0.48577	-0.88604	1.67891	H	-2.06449	4.62960	-0.41760
	C	-0.38145	-0.32985	3.18783	H	-1.04820	4.45827	1.02737

	H	-1.26591	-0.96162	3.29731	H	-0.30128	4.61114	-0.59884
INT-1a	C	2.82074	0.73729	-0.27378	H	-0.25179	-1.77942	3.52083
	C	2.68205	-0.39566	0.54387	H	-0.82714	-0.11674	3.16744
	C	3.46502	-1.53148	0.27760	H	-2.23007	-3.39199	-2.43837
	C	4.37104	-1.53421	-0.78731	C	-3.04871	-2.87110	-1.93198
	C	4.50417	-0.40027	-1.59872	C	-2.48289	-1.94998	-0.85940
	C	3.72853	0.73539	-1.33856	H	-3.58226	-2.28765	-2.68769
	H	2.22323	1.62394	-0.07265	H	-3.72275	-3.60123	-1.48149
	H	3.36841	-2.41457	0.90731	O	-1.72974	-0.99655	-1.35062
	H	4.97474	-2.41799	-0.98115	O	-2.72117	-2.11665	0.34589
	H	5.21054	-0.40147	-2.42592	Pd	-0.98332	0.42515	-0.09367
	H	3.83044	1.62043	-1.96264	O	-0.39629	2.19981	0.85311
	C	1.70462	-0.39388	1.69092	C	-1.08279	2.92096	0.03041
	H	1.46511	0.61776	2.02719	O	-1.72782	2.32778	-0.89448
	H	2.07897	-0.97511	2.53987	C	-1.13040	4.41244	0.19009
	S	0.11181	-1.21944	1.20696	H	-2.01245	4.67478	0.78466
	C	-0.77678	-1.14443	2.80234	H	-0.24156	4.77188	0.71234
	H	-1.77646	-1.53288	2.60919	H	-1.22341	4.89284	-0.78634
TS-2a	C	1.75018	-0.07930	-0.09383	H	-1.47926	-3.27051	2.18034
	C	2.10207	-1.36550	0.40591	H	-1.61812	-1.49805	2.43072
	C	3.26326	-2.00323	-0.03803	H	-4.68029	1.06113	-1.73992
	C	4.08745	-1.38495	-0.98853	C	-4.70114	0.28156	-0.97164
	C	3.73829	-0.13921	-1.52257	C	-3.29564	-0.28327	-0.78137
	C	2.57621	0.49950	-1.08264	H	-5.04938	0.74766	-0.04527
	H	1.42623	0.91998	0.74392	H	-5.39149	-0.50771	-1.27384
	H	3.52002	-2.99146	0.33842	O	-2.45088	0.59094	-0.31337
	H	4.99105	-1.88819	-1.32571	O	-3.03576	-1.46789	-1.05916
	H	4.36873	0.33003	-2.27440	Pd	-0.39612	0.24276	-0.14814
	H	2.31968	1.47758	-1.48514	O	1.38251	2.12979	1.33367
	C	1.11939	-2.06313	1.30469	C	0.60202	2.84743	0.61452
	H	0.95116	-1.51228	2.23612	O	-0.17825	2.37159	-0.27116
	H	1.40273	-3.09301	1.53604	C	0.62603	4.34454	0.83040
	S	-0.47496	-2.07411	0.35337	H	0.39283	4.55965	1.87720
	C	-1.68370	-2.30848	1.70322	H	1.63483	4.71986	0.63499
	H	-2.66606	-2.32329	1.23300	H	-0.09136	4.84386	0.17940
INT-2a	C	1.86144	0.43429	-0.09466	H	0.44988	-4.19822	1.11809
	C	2.82291	-0.57300	0.14328	H	-0.12571	-2.75856	2.02285
	C	4.18982	-0.27877	0.01747	H	-4.73509	-0.24101	-1.03991
	C	4.60751	1.00994	-0.32873	C	-4.46943	-1.14965	-0.48939
	C	3.65502	2.00840	-0.56174	C	-2.95805	-1.33896	-0.49479
	C	2.28717	1.72036	-0.45141	H	-4.82696	-1.02464	0.53773
	H	-2.74814	1.03211	0.27874	H	-4.96444	-2.00728	-0.94716
	H	4.92847	-1.06023	0.18970	O	-2.28425	-0.35939	0.06273
	H	5.66856	1.23030	-0.42246	O	-2.43195	-2.34788	-0.98199

	H	3.97251	3.01280	-0.83578	Pd	-0.11268	-0.00224	-0.01669
	H	1.55784	2.50354	-0.63571	O	-2.89256	2.05713	0.40575
	C	2.35837	-1.94473	0.55048	C	-1.75050	2.69677	0.31482
	H	2.23461	-2.01841	1.63614	O	-0.64524	2.14477	0.14193
	H	3.02845	-2.74365	0.22064	C	-1.86109	4.19462	0.42638
	S	0.69211	-2.20751	-0.20882	H	-2.39792	4.57910	-0.44695
	C	-0.10708	-3.25973	1.05361	H	-2.44473	4.45875	1.31240
	H	-1.11946	-3.44584	0.69675	H	-0.87106	4.64688	0.47539
TS-3a	C	-1.48231	0.73321	0.21171	O	2.57491	-2.13317	1.14992
	C	-2.55959	-0.13664	0.53432	O	2.06962	-1.35381	-0.90363
	C	-3.86746	0.26016	0.22615	Pd	0.28262	-0.33611	-0.26673
	C	-4.12269	1.48452	-0.40482	C	1.27028	0.97222	1.10656
	C	-3.05766	2.31325	-0.76959	C	-0.06637	1.12907	1.60066
	C	-1.74659	1.94039	-0.45547	H	1.90257	0.20280	1.54452
	H	-4.69409	-0.41104	0.45251	H	-0.45202	2.13619	1.69494
	H	-5.14641	1.77422	-0.63031	H	-0.36648	0.46261	2.40522
	H	-3.24273	3.25440	-1.28241	C	2.04473	2.08028	0.49372
	H	-0.92514	2.60867	-0.69665	O	3.25256	2.03118	0.30084
	C	-2.28515	-1.54188	0.99166	O	1.28911	3.16218	0.18517
	H	-3.20224	-2.10800	1.17450	C	1.99335	4.27499	-0.41287
	H	-1.66412	-1.59004	1.89266	H	2.44890	3.97187	-1.35832
	S	-1.26482	-2.42425	-0.28769	H	1.23627	5.04095	-0.58009
	C	-2.39294	-2.42427	-1.72601	H	2.76711	4.64205	0.26517
	H	-1.83537	-2.87167	-2.55146	C	1.17968	-0.39535	-3.92685
	H	-3.27264	-3.03527	-1.50864	O	0.27058	-0.04622	-3.17683
	H	-2.68740	-1.40994	-1.99857	O	2.27813	-1.03112	-3.50830
	H	4.72379	-1.87269	-1.05319	H	2.23122	-1.16900	-2.50505
	C	4.05253	-2.65723	-0.68837	C	1.17984	-0.15525	-5.41893
	C	2.81781	-2.02059	-0.06124	H	2.05918	0.43241	-5.69982
	H	3.77064	-3.27233	-1.54851	H	1.24430	-1.11089	-5.94832
	H	4.57975	-3.26994	0.04454	H	0.27227	0.37113	-5.71447
INT-3a	C	-0.76207	-1.26556	0.84718	O	0.48240	1.82282	-2.90762
	C	-2.14052	-0.95067	1.06636	O	1.53319	2.12124	-0.92610
	C	-2.53270	-0.49038	2.32394	Pd	0.43695	0.66647	0.20929
	C	-1.61411	-0.32962	3.37669	C	0.73725	-0.91457	-1.07651
	C	-0.27376	-0.63164	3.17872	C	-0.23146	-1.91466	-0.44335
	C	0.15327	-1.09515	1.91965	H	0.41811	-0.49206	-2.02768
	H	-3.58237	-0.26116	2.49696	H	0.25450	-2.86372	-0.20072
	H	-1.96244	0.02245	4.34484	H	-1.04433	-2.11756	-1.14079
	H	0.44663	-0.52677	3.98603	C	2.19539	-1.23061	-1.12164
	H	1.17397	-1.44914	1.80130	O	2.96409	-0.82359	-1.98313
	C	-3.19255	-1.14251	0.00145	O	2.60012	-2.03474	-0.10352
	H	-4.18442	-1.15465	0.46134	C	4.00488	-2.37221	-0.08329
	H	-3.05754	-2.08879	-0.53185	H	4.61227	-1.46855	0.00784

	S	-3.13715	0.23292	-1.23110	H	4.13769	-3.01247	0.78886
	C	-4.44603	-0.34000	-2.37091	H	4.28127	-2.90581	-0.99567
	H	-4.51974	0.40307	-3.16900	C	0.46476	3.48307	1.75832
	H	-4.18946	-1.30744	-2.81209	O	-0.04985	2.35758	1.67737
	H	-5.41157	-0.40898	-1.86181	O	1.37988	3.93842	0.91855
	H	1.96281	3.71508	-3.78086	H	1.53391	3.26299	0.16978
	C	2.23790	3.47266	-2.75326	C	0.08820	4.46431	2.83684
	C	1.32170	2.38724	-2.20110	H	0.98888	4.83550	3.33362
	H	3.27425	3.12082	-2.72670	H	-0.41271	5.32426	2.38074
	H	2.18401	4.37457	-2.13548	H	-0.57706	3.99377	3.56005
TS-4a	C	1.87382	1.39312	-0.72671	O	-0.83396	-0.53373	2.64739
	C	3.19257	1.50779	-0.23243	O	-2.22695	-1.07806	0.95267
	C	3.58289	2.70617	0.39012	Pd	-1.20051	0.28806	-0.35903
	C	2.70372	3.78323	0.52750	C	0.55008	-0.75359	-0.38427
	C	1.40482	3.67897	0.02159	C	1.33128	0.12469	-1.35976
	C	1.01018	2.49470	-0.60505	H	0.92977	-0.76481	0.63626
	H	4.59842	2.79322	0.77215	H	0.67495	0.39502	-2.20708
	H	3.03424	4.69833	1.01335	H	2.12178	-0.47676	-1.82624
	H	0.70998	4.51168	0.10128	C	0.23016	-2.14511	-0.83759
	H	0.01183	2.44760	-1.04997	O	0.23135	-3.13032	-0.11475
	C	4.21234	0.39924	-0.35283	O	-0.06915	-2.19605	-2.15977
	H	5.22159	0.82116	-0.34239	C	-0.40168	-3.50148	-2.68487
	H	4.09505	-0.16285	-1.28425	H	-1.28289	-3.90096	-2.17755
	S	4.07163	-0.78518	1.05999	H	-0.60641	-3.34518	-3.74381
	C	5.38128	-1.96639	0.58124	H	0.43764	-4.18846	-2.55334
	H	5.41386	-2.73937	1.35319	C	-4.23030	1.22380	-0.23783
	H	5.15628	-2.43703	-0.38009	O	-3.07892	1.53771	-0.57877
	H	6.35671	-1.47394	0.53267	O	-4.52683	0.11284	0.41629
	H	-2.32909	-2.03430	4.09994	H	-3.68827	-0.41196	0.63505
	C	-2.56883	-2.16669	3.04377	C	-5.42161	2.09325	-0.53414
INT-4a	C	-1.79123	-1.16817	2.19611	H	-5.82870	2.47718	0.40670
	H	-2.28881	-3.18005	2.73710	H	-5.13076	2.92543	-1.17443
	H	-3.64592	-2.06259	2.88678	H	-6.20540	1.50024	-1.01335
	C	1.87691	1.45905	-0.30598	O	-2.04889	0.36767	2.54965
	C	3.27680	1.28321	-0.22081	O	-2.96685	-0.47371	0.66440
	C	4.05926	2.33569	0.28254	Pd	-1.43755	0.38011	-0.55670
	C	3.48634	3.54261	0.69122	C	0.25469	-0.44746	0.24351
	C	2.10200	3.71443	0.59942	C	0.97273	0.34644	-0.80529
	C	1.31154	2.67627	0.10056	H	0.35198	-0.11647	1.27542
	H	5.13726	2.20297	0.35272	H	0.17021	0.87353	-1.46583
	H	4.11662	4.34222	1.07357	H	1.44058	-0.30315	-1.54636
	H	1.63989	4.64920	0.90814	C	0.15429	-1.93494	0.14800
	H	0.23378	2.81583	0.02167	O	-0.08529	-2.66096	1.10118
	C	3.96625	0.00296	-0.63119	O	0.32868	-2.39402	-1.11403

	H	5.02925	0.19102	-0.80554	C	0.20229	-3.82340	-1.29021
	H	3.54596	-0.41387	-1.55226	H	-0.79791	-4.15365	-1.00044
	S	3.81044	-1.27085	0.69948	H	0.37216	-4.00104	-2.35193
	C	4.63467	-2.67270	-0.13444	H	0.94855	-4.34686	-0.68826
	H	4.60461	-3.51901	0.55637	C	-4.25277	1.24281	-1.74689
	H	4.11048	-2.94763	-1.05423	O	-3.02527	1.43130	-1.76847
	H	5.67868	-2.43818	-0.36074	O	-4.85730	0.41484	-0.91293
	H	-4.06538	-0.63477	3.77051	H	-4.18804	0.00012	-0.27022
	C	-4.08592	-0.92118	2.71807	C	-5.18856	1.95787	-2.68322
	C	-2.93116	-0.26990	1.96929	H	-4.62340	2.54827	-3.40351
	H	-4.00190	-2.00958	2.63548	H	-5.82209	1.23188	-3.20040
	H	-5.04422	-0.63392	2.27472	H	-5.84688	2.61256	-2.10332
TS-5a	C	-1.30293	-1.09894	0.49535	O	2.60531	-1.54837	2.50921
	C	-2.52773	-1.27550	-0.19663	O	3.56617	-0.70328	0.65110
	C	-3.30979	-2.40491	0.08971	Pd	1.70980	-0.40693	-0.44823
	C	-2.89730	-3.35784	1.02299	C	0.57155	0.54906	1.09535
	C	-1.67627	-3.19359	1.68868	C	-0.48642	0.11775	0.25764
	C	-0.88829	-2.07613	1.42286	H	0.83490	-0.00138	1.99287
	H	-4.25454	-2.53927	-0.43317	H	0.37366	-0.17704	-1.26559
	H	-3.52024	-4.22650	1.22388	H	-0.95265	0.89665	-0.33692
	H	-1.33906	-3.93495	2.40916	C	1.00084	1.97888	1.14937
	H	0.06572	-1.97040	1.93233	O	1.69018	2.42920	2.05261
	C	-3.03108	-0.29872	-1.23337	O	0.54141	2.71985	0.11839
	H	-3.77115	-0.78873	-1.87176	C	0.92282	4.11547	0.12112
	H	-2.22624	0.06776	-1.87917	H	2.01028	4.21003	0.08030
	S	-3.84205	1.15216	-0.42175	H	0.46654	4.54102	-0.77214
	C	-4.30692	2.10388	-1.91135	H	0.54459	4.60947	1.01885
	H	-4.81824	3.00615	-1.56654	C	3.93763	-1.49813	-2.39158
	H	-3.42316	2.39518	-2.48585	O	2.72766	-1.25082	-2.22889
	H	-4.98957	1.53123	-2.54537	O	4.85447	-1.37028	-1.45622
	H	5.55204	-0.55735	2.44917	H	4.43271	-1.08667	-0.56106
	C	5.01532	-1.50782	2.36686	C	4.46620	-1.98549	-3.71395
	C	3.60760	-1.25726	1.84422	H	4.84308	-3.00641	-3.59581
	H	5.57308	-2.13670	1.66525	H	3.67838	-1.96895	-4.46627
	H	4.98048	-1.99337	3.34317	H	5.30637	-1.36064	-4.02935
INT-5a	C	1.50399	0.84886	0.80266	O	-2.08961	0.62738	2.76454
	C	2.41646	1.42192	-0.12524	O	-2.33976	0.76819	0.52996
	C	2.81387	2.75391	0.05046	Pd	-0.91583	-0.65457	-0.41194
	C	2.32759	3.52353	1.11095	C	0.15258	-1.24863	1.41352
	C	1.42157	2.96279	2.01921	C	1.12114	-0.56633	0.67004
	C	1.01369	1.64010	1.86323	H	-0.44450	-0.74725	2.17186
	H	3.51225	3.19559	-0.65749	H	-0.09204	-1.68623	-1.19899
	H	2.65278	4.55511	1.22602	H	1.79504	-1.18284	0.08395
	H	1.03754	3.55389	2.84722	C	0.12617	-2.73794	1.54042

	H	0.30698	1.21677	2.56952	O	-0.66250	-3.32035	2.27113
	C	2.96471	0.65584	-1.30595	O	1.06498	-3.36561	0.80467
	H	3.29352	1.35518	-2.07956	C	1.07151	-4.80990	0.88258
	H	2.21356	-0.00567	-1.74839	H	0.11726	-5.21191	0.53431
	S	4.42154	-0.36497	-0.79628	H	1.88381	-5.13017	0.23081
	C	4.80528	-1.15329	-2.40015	H	1.25266	-5.13307	1.91006
	H	5.67077	-1.80074	-2.23828	C	-3.01404	0.40181	-2.50550
	H	3.96756	-1.76284	-2.75016	O	-2.04679	-0.35653	-2.27450
	H	5.06039	-0.40449	-3.15514	O	-3.57154	1.18347	-1.61632
	H	-4.78395	1.44576	1.40489	H	-3.11469	1.07796	-0.67704
	C	-3.92720	1.92389	1.89102	C	-3.62656	0.47062	-3.87922
	C	-2.69400	1.03839	1.76557	H	-3.56346	1.49672	-4.25381
	H	-3.75487	2.87913	1.38436	H	-3.11305	-0.20755	-4.55989
	H	-4.16068	2.10578	2.94096	H	-4.68720	0.20930	-3.81804
TS-6a	C	0.82198	-2.16010	1.56213	O	-0.88702	1.17692	-2.04859
	C	0.24302	-2.52389	2.80775	O	-1.71429	-0.82553	-1.55105
	C	-0.18918	-3.84450	2.99846	Pd	-1.03316	0.51466	0.12969
	C	-0.06979	-4.80377	1.99008	C	1.69041	-0.24247	0.15947
	C	0.49541	-4.44720	0.75951	C	1.31484	-0.79234	1.34573
	C	0.93518	-3.14182	0.55446	H	1.63699	-0.78532	-0.77986
	H	-0.63089	-4.12313	3.95327	H	-0.61409	1.67336	1.03746
	H	-0.41333	-5.82114	2.16312	H	1.44170	-0.17366	2.22895
	H	0.59916	-5.18579	-0.03191	C	2.34729	1.07807	0.03212
	H	1.39103	-2.88604	-0.39803	O	2.80222	1.49634	-1.02675
	C	0.05926	-1.53946	3.93903	O	2.41841	1.76936	1.19196
	H	-0.72259	-1.89642	4.61512	C	3.06240	3.06031	1.12029
	H	-0.23882	-0.55221	3.57635	H	2.52616	3.71590	0.43012
	S	1.62192	-1.37208	4.91574	H	3.02443	3.45922	2.13389
	C	1.06035	-0.15877	6.16226	H	4.09827	2.95196	0.79012
	H	1.90671	0.03244	6.82681	C	-3.33381	-1.01798	1.49764
	H	0.76111	0.78148	5.69064	O	-2.39491	-0.24033	1.73122
	H	0.23057	-0.55723	6.75295	O	-3.61285	-1.52314	0.30457
	H	-2.73221	-0.45168	-4.01675	H	-2.96261	-1.23305	-0.39621
	C	-1.67940	-0.18808	-3.87806	C	-4.27262	-1.48087	2.57703
	C	-1.41344	0.08390	-2.41793	H	-4.05184	-0.96786	3.51213
	H	-1.08231	-1.04706	-4.20043	H	-5.30603	-1.29020	2.27419
	H	-1.42920	0.68047	-4.48884	H	-4.16317	-2.56168	2.71026
INT-6a	H	-4.66153	0.17465	-0.47177	C	2.81779	0.19715	0.15694
	C	-4.10641	0.51653	0.40725	O	1.76177	0.48399	-0.42640
	C	-2.62698	0.32066	0.18454	O	2.93380	-0.77577	1.04861
	H	-4.32712	1.56797	0.59858	H	2.06484	-1.23712	1.18342
	H	-4.43336	-0.08932	1.25826	C	4.09878	0.93190	-0.11012
	O	-2.20659	-0.87517	-0.08034	H	4.63200	1.11509	0.82526
	O	-1.80616	1.28078	0.25475	H	4.73667	0.30463	-0.74222

	Pd -0.19242 -0.33035 -0.24333 H 0.37658 -1.73408 -0.55665	H 3.89000 1.86747 -0.62751
INT-7a	H 5.08428 -0.22033 -0.06480 C 4.49315 0.42558 -0.72095 C 3.06838 -0.05172 -0.75046 H 4.53336 1.45466 -0.36597 H 4.92543 0.35789 -1.72376 O 2.94081 -1.31120 -1.17927 O 2.10824 0.64488 -0.41268 Pd -0.01405 0.03236 -0.41007 H 1.97501 -1.55352 -1.17219	C -3.07148 0.03430 0.11419 O -2.13402 -0.58735 -0.39176 O -2.91829 1.20890 0.73324 H -1.95567 1.46186 0.70219 C -4.49411 -0.45003 0.09995 H -4.85169 -0.56951 1.12718 H -5.13293 0.29393 -0.38516 H -4.55829 -1.40003 -0.42922
2	C 1.95518 -1.75997 0.95561 C 1.99049 -2.03131 -0.35646 H 2.57779 -0.98254 1.39186 H 1.36986 -2.80732 -0.79582 H 2.64752 -1.47655 -1.02185 C 1.09328 -2.46142 1.93982	O 1.08500 -2.18863 3.13448 O 0.32178 -3.42604 1.39452 C -0.53801 -4.14164 2.30949 H -1.23804 -3.45473 2.79103 H -1.07377 -4.86614 1.69648 H 0.05631 -4.65002 3.07245
3a	C -0.05527 -3.25706 0.15238 C 0.13887 -4.62915 -0.16019 C 1.43079 -5.17140 -0.08115 C 2.52695 -4.39205 0.29462 C 2.33980 -3.03862 0.60322 C 1.06398 -2.48452 0.53142 H 1.57789 -6.22227 -0.32284 H 3.51817 -4.83654 0.34797 H 3.18359 -2.42226 0.90474 H 0.92993 -1.43821 0.79231 C -0.99291 -5.53725 -0.58389 H -0.59566 -6.38442 -1.14989 H -1.72023 -5.02308 -1.21827 S -1.87446 -6.20235 0.90042 C -3.15348 -7.20330 0.06157	H -3.75852 -7.66941 0.84334 H -3.79979 -6.57611 -0.55888 H -2.70076 -7.98863 -0.55034 C -1.69871 -1.34544 0.08950 C -1.39709 -2.66174 0.08873 H -0.94452 -0.56422 0.12173 H -2.24104 -3.34571 0.04220 C -3.10452 -0.89650 0.02970 O -4.09508 -1.61632 -0.02990 O -3.17747 0.45869 0.04527 C -4.50713 1.01974 -0.01037 H -5.09670 0.69021 0.84858 H -4.36794 2.10050 0.01377 H -5.01003 0.71903 -0.93273
1b	C 0.49802 1.05243 0.00032 C 0.09142 -0.28847 0.00022 C 1.07005 -1.29658 -0.00010 C 2.42972 -0.97128 -0.00028 C 2.83129 0.37178 -0.00018 C 1.86132 1.37956 0.00011 H -0.25252 1.83682 0.00054 H 0.76807 -2.34363 -0.00022 H 3.17511 -1.76395 -0.00054 H 3.88879 0.62738 -0.00034	H 2.16365 2.42503 0.00017 C -1.37084 -0.68565 0.00065 H -1.58608 -1.30593 0.88662 H -1.58602 -1.30815 -0.88378 C -3.58860 0.12089 -0.00015 H -4.15125 1.05738 -0.00141 H -3.85837 -0.46240 -0.89295 H -3.85816 -0.45987 0.89436 O -2.20754 0.46166 -0.00080
TS-1b	C 2.51198 1.04460 0.18072 C 2.32500 -0.16470 0.86628	H -0.85703 -0.04755 3.41850 H -2.52015 -4.12377 -1.16927

	C	2.95487	-1.32462	0.38460	C	-1.57536	-3.63414	-1.41469
	C	3.75184	-1.27603	-0.76260	C	-1.55533	-2.24020	-0.84800
	C	3.93232	-0.06293	-1.44140	H	-0.76030	-4.20951	-0.96212
	C	3.31251	1.09799	-0.96707	H	-1.42269	-3.61699	-2.49603
	H	2.03674	1.95173	0.54985	O	-0.83698	-1.34337	-1.46360
	H	2.81929	-2.26753	0.91154	O	-2.17494	-1.91725	0.19533
	H	4.23525	-2.18023	-1.12632	Pd	-1.09995	0.22829	-0.21573
	H	4.55516	-0.02416	-2.33254	O	-1.43949	1.98262	0.82550
	H	3.45025	2.04276	-1.48832	C	-1.24931	2.72164	-0.21584
	C	1.46008	-0.22531	2.09958	O	-0.93685	2.13425	-1.30239
	H	1.29600	0.77890	2.51359	C	-1.42305	4.20829	-0.13851
	H	1.93810	-0.84020	2.87534	H	-1.27891	4.55777	0.88586
	C	-0.62825	-1.00933	2.94025	H	-0.72494	4.70462	-0.81631
	H	-1.54970	-1.48483	2.60393	H	-2.44195	4.46011	-0.45269
	H	-0.11857	-1.65996	3.66356	O	0.18671	-0.82359	1.77573
INT-1b	C	2.83374	1.01940	0.13979	H	-0.62650	-0.25004	3.32502
	C	2.49970	-0.24136	0.65722	H	-1.43091	-3.61896	-1.96471
	C	2.98005	-1.39622	0.01668	C	-2.36496	-3.17430	-1.61311
	C	3.77603	-1.29081	-1.12656	C	-2.09659	-2.00745	-0.67310
	C	4.10657	-0.02795	-1.63731	H	-2.90883	-2.80572	-2.48951
	C	3.63617	1.12649	-1.00227	H	-2.97688	-3.92442	-1.10895
	H	2.46776	1.91884	0.63090	O	-1.09201	-1.25704	-1.05802
	H	2.72817	-2.37775	0.41419	O	-2.78685	-1.80009	0.33536
	H	4.14295	-2.18965	-1.61704	Pd	-0.72588	0.39694	0.05921
	H	4.72991	0.05385	-2.52512	O	-0.51950	2.36836	0.78144
	H	3.89144	2.10834	-1.39453	C	-1.19542	2.80806	-0.21864
	C	1.64576	-0.36034	1.88969	O	-1.60828	1.94694	-1.07555
	H	1.55429	0.59788	2.41346	C	-1.51377	4.26407	-0.36609
	H	2.04941	-1.10738	2.58285	H	-2.49005	4.45902	0.09140
	C	-0.50009	-1.13878	2.69658	H	-0.76369	4.87022	0.14582
	H	-1.46200	-1.48619	2.32195	H	-1.57168	4.53359	-1.42286
	H	0.00034	-1.93045	3.26418	O	0.30346	-0.82391	1.52963
TS-1b	C	1.71629	-0.08666	-0.01321	H	-1.36997	-1.94951	2.62800
	C	2.01160	-1.37800	0.50033	H	-4.90836	1.34146	-0.52470
	C	3.12341	-2.08451	0.03709	C	-4.63507	0.31360	-0.78711
	C	3.95359	-1.52710	-0.94572	C	-3.11930	0.22001	-0.91620
	C	3.64973	-0.27851	-1.49774	H	-5.00035	-0.33727	0.01163
	C	2.53137	0.42688	-1.04251	H	-5.11150	0.05266	-1.73387
	H	1.42387	0.99314	0.75693	O	-2.49382	0.20897	0.23196
	H	3.33681	-3.07930	0.42351	O	-2.56318	0.17494	-2.02562
	H	4.82029	-2.08229	-1.29760	Pd	-0.41653	0.17920	0.10638
	H	4.27860	0.14249	-2.27892	O	1.38171	2.25093	1.20343
	H	2.30911	1.40480	-1.46529	C	0.48405	2.85047	0.51874
	C	1.03071	-2.00769	1.44962	O	-0.36885	2.24762	-0.21409

	H	1.01321	-1.50189	2.42470	C	0.43351	4.35982	0.57614
	H	1.22722	-3.07387	1.60328	H	0.22748	4.66702	1.60582
	C	-1.35323	-2.41878	1.63822	H	1.41082	4.76494	0.30006
	H	-2.28219	-2.20655	1.11251	H	-0.33859	4.74954	-0.08665
	H	-1.20013	-3.49886	1.73259	O	-0.28548	-1.86919	0.83305
INT-2b	C	1.82633	0.48938	-0.02783	H	-0.01569	-3.04578	1.85888
	C	2.71449	-0.56634	0.25178	H	-4.80082	-0.12564	-0.57964
	C	4.09611	-0.35145	0.13865	C	-4.49218	-1.13307	-0.28142
	C	4.58683	0.90206	-0.24123	C	-2.98300	-1.28713	-0.41729
	C	3.69642	1.94581	-0.51817	H	-4.78435	-1.26542	0.76550
	C	2.31256	1.74019	-0.41512	H	-5.00881	-1.86893	-0.89936
	H	-2.70119	0.96117	0.48168	O	-2.27922	-0.41605	0.27379
	H	4.78910	-1.16588	0.34596	O	-2.48130	-2.17996	-1.11109
	H	5.65941	1.06058	-0.32697	Pd	-0.10637	0.02102	0.08728
	H	4.07424	2.92089	-0.81960	O	-2.84471	2.00190	0.55449
	H	1.62336	2.55134	-0.63118	C	-1.75353	2.65108	0.24232
	C	2.16130	-1.89012	0.69579	O	-0.65649	2.11104	-0.02481
	H	2.18428	-1.98551	1.79072	C	-1.89296	4.14990	0.21121
	H	2.70493	-2.73905	0.26323	H	-2.55421	4.42942	-0.61531
	C	0.07164	-3.10595	0.76777	H	-2.36060	4.49554	1.13710
	H	-0.90852	-3.09399	0.29473	H	-0.92003	4.62162	0.07780
	H	0.61826	-4.01287	0.48556	O	0.78090	-1.95735	0.25657
TS-3b	C	1.79474	0.61511	0.27628	O	-2.36682	-0.13691	-0.10487
	C	2.68820	-0.41325	-0.09512	Pd	-0.24968	0.28946	-0.03845
	C	3.86690	-0.56267	0.65252	C	-0.30271	1.65925	-1.66917
	C	4.16566	0.28299	1.72691	C	1.07581	1.77849	-1.38065
	C	3.27710	1.30597	2.07240	H	-0.63410	1.03589	-2.49611
	C	2.09863	1.47859	1.33780	H	1.42917	2.68174	-0.89909
	H	4.56158	-1.35814	0.38651	H	1.78027	1.29863	-2.05047
	H	5.08825	0.14521	2.28616	C	-1.26917	2.74756	-1.32560
	H	3.50034	1.97470	2.90104	O	-2.32583	2.91485	-1.91405
	H	1.42108	2.29127	1.59107	O	-0.83700	3.54478	-0.32303
	C	2.41291	-1.35549	-1.25460	C	-1.71413	4.63607	0.04076
	H	3.29320	-1.99191	-1.42354	H	-2.68048	4.24992	0.37269
	H	2.23240	-0.79427	-2.17758	H	-1.20818	5.15470	0.85466
	C	1.40598	-3.20259	-0.12004	H	-1.85930	5.30555	-0.81018
	H	0.47801	-3.77865	-0.12478	C	-1.18137	-1.31732	2.58675
	H	2.24307	-3.86391	-0.38758	O	-0.22483	-0.95679	1.88280
	H	1.57021	-2.79534	0.88453	O	-2.44935	-1.14948	2.25606
	H	-4.99017	-0.12192	-0.61517	H	-2.51878	-0.73031	1.32216
	C	-4.42517	-1.00199	-0.93809	C	-0.98174	-1.99578	3.91686
	C	-2.96862	-0.62233	-1.17246	H	-1.49465	-1.42797	4.69884
	H	-4.49836	-1.74723	-0.13909	H	-1.43133	-2.99307	3.88917
	H	-4.86582	-1.40502	-1.85119	H	0.08058	-2.07274	4.14615

	O	-2.42916	-0.75902	-2.27502	O	1.24761	-2.16757	-1.09167
INT-3b	C	1.47824	1.54127	-0.39161	O	-1.76773	-1.39948	0.43031
	C	2.62181	0.91393	-0.97764	Pd	-0.06264	-0.09677	0.33731
	C	3.67517	0.52914	-0.15143	C	-0.91873	1.31631	-0.89421
	C	3.64092	0.73524	1.24147	C	0.32816	2.13997	-1.21867
	C	2.53359	1.33374	1.82469	H	-1.29993	0.70192	-1.70792
	C	1.45164	1.73321	1.01393	H	0.20335	3.19434	-0.95779
	H	4.55295	0.06372	-0.59634	H	0.54056	2.06956	-2.28506
	H	4.48587	0.42699	1.85285	C	-2.04858	1.95550	-0.15783
	H	2.49463	1.50777	2.89709	O	-3.22465	1.64036	-0.28752
	H	0.64346	2.31348	1.45255	O	-1.64668	2.94436	0.68322
	C	2.74402	0.72772	-2.48166	C	-2.69078	3.59372	1.44183
	H	3.73586	0.31454	-2.71437	H	-3.20761	2.86887	2.07535
	H	2.66489	1.69487	-2.98970	H	-2.18483	4.34273	2.05108
	C	1.85145	-1.47152	-2.74547	H	-3.41042	4.06852	0.77077
	H	1.03558	-1.98551	-3.25691	C	0.53721	-2.56546	2.31050
	H	2.81513	-1.86739	-3.09790	O	1.02690	-1.64277	1.64185
	H	1.76157	-1.65351	-1.66654	O	-0.74619	-2.88643	2.29702
	H	-4.30454	-2.26745	0.19643	H	-1.24138	-2.31901	1.60921
	C	-3.51703	-2.83351	-0.31120	C	1.37005	-3.43260	3.21738
	C	-2.35472	-1.90349	-0.63882	H	0.92501	-3.46114	4.21594
	H	-3.19455	-3.62660	0.37086	H	1.37467	-4.45712	2.83175
	H	-3.91768	-3.27635	-1.22432	H	2.39066	-3.05473	3.26861
	O	-2.02565	-1.65671	-1.80196	O	1.72428	-0.08534	-3.06161
TS-4b	C	-2.04615	-1.01054	-0.84127	O	2.15856	0.83009	1.08043
	C	-3.23636	-1.00106	-0.08075	Pd	1.07969	-0.19090	-0.46962
	C	-3.72415	-2.20584	0.44195	C	-0.56274	1.00834	-0.39349
	C	-3.05160	-3.41418	0.22292	C	-1.43774	0.26504	-1.39951
	C	-1.87935	-3.43059	-0.53557	H	-0.91279	0.99242	0.63785
	C	-1.39104	-2.23144	-1.06531	H	-0.83535	0.02401	-2.29313
	H	-4.63916	-2.19147	1.02480	H	-2.20746	0.95063	-1.78414
	H	-3.44839	-4.33744	0.63951	C	-0.11532	2.38722	-0.77037
	H	-1.35257	-4.36344	-0.72271	O	-0.04307	3.32975	0.00473
	H	-0.49790	-2.25408	-1.69272	O	0.20810	2.47948	-2.08350
	C	-3.97921	0.29946	0.15980	C	0.66544	3.77506	-2.53566
	H	-4.23335	0.77010	-0.80546	H	1.56565	4.07007	-1.99163
	H	-3.33423	1.01274	0.69895	H	0.88072	3.65261	-3.59685
	C	-5.87699	1.27519	1.16663	H	-0.11433	4.52546	-2.38585
	H	-6.76561	1.00233	1.74014	C	3.98086	-1.47146	-0.35415
	H	-5.27007	1.97922	1.75397	O	2.82945	-1.58561	-0.80370
	H	-6.18689	1.76739	0.23327	O	4.35050	-0.52163	0.48896
	H	2.16133	1.48035	4.31209	H	3.56179	0.06083	0.74478
	C	2.56742	1.57221	3.30376	C	5.08632	-2.42172	-0.72483
	C	1.66080	0.86589	2.30334	H	5.38694	-2.98685	0.16326

	H	2.64431	2.63090	3.03632	H	4.74874	-3.10845	-1.50028
	H	3.57771	1.15338	3.27155	H	5.96012	-1.86052	-1.06721
	O	0.56689	0.39702	2.62757	O	-5.16394	0.07065	0.90496
INT-4b	C	1.96520	1.62688	-0.36990	O	-2.53589	-0.87669	0.87815
	C	3.35869	1.44912	-0.22397	Pd	-1.24952	0.25988	-0.38423
	C	4.12816	2.49965	0.29207	C	0.59355	-0.49211	0.09307
	C	3.53573	3.71220	0.66320	C	1.10248	0.50014	-0.91067
	C	2.15726	3.88718	0.52080	H	0.78740	-0.28516	1.14401
	C	1.38230	2.84411	0.00387	H	0.18339	1.01784	-1.40119
	H	5.19832	2.35943	0.40270	H	1.53236	0.00206	-1.78390
	H	4.15186	4.51537	1.06157	C	0.62025	-1.95794	-0.19671
	H	1.68616	4.82513	0.80536	O	0.61471	-2.82156	0.66832
	H	0.30767	2.98037	-0.11303	O	0.64287	-2.23092	-1.52227
	C	4.00583	0.13405	-0.61251	C	0.63792	-3.63220	-1.88199
	H	3.80101	-0.09009	-1.67350	H	-0.26513	-4.11614	-1.50321
	H	3.56599	-0.68903	-0.02369	H	0.65597	-3.65128	-2.97131
	C	6.04588	-1.04483	-0.74102	H	1.51968	-4.13121	-1.47366
	H	7.11192	-0.91459	-0.54247	C	-4.24872	1.01593	-1.09130
	H	5.66468	-1.87887	-0.13438	O	-3.04946	1.30338	-1.24183
	H	5.90332	-1.28514	-1.80460	O	-4.68133	0.04828	-0.30271
	H	-3.19796	-1.59127	4.03004	H	-3.90563	-0.38900	0.18707
	C	-3.36513	-1.68924	2.95654	C	-5.34453	1.76067	-1.80380
	C	-2.33605	-0.87432	2.18491	H	-4.91939	2.48179	-2.50098
	H	-3.28595	-2.74237	2.66883	H	-5.98811	1.05341	-2.33446
	H	-4.37901	-1.35941	2.70958	H	-5.96575	2.27949	-1.06688
	O	-1.40671	-0.28912	2.74554	O	5.40580	0.18015	-0.39675
TS-5b	C	1.84513	1.11813	0.57316	O	-2.89454	-0.16082	0.62608
	C	2.99320	1.48526	-0.17261	Pd	-0.96777	-0.16478	-0.38421
	C	3.55852	2.75070	0.02683	C	0.26810	-0.80019	1.24646
	C	3.00287	3.65088	0.94048	C	1.26094	-0.23527	0.40723
	C	1.86016	3.29681	1.66692	H	-0.12557	-0.25331	2.09711
	C	1.28653	2.04129	1.47932	H	0.42145	-0.19164	-1.14671
	H	4.43743	3.02792	-0.54475	H	1.86728	-0.95793	-0.13045
	H	3.45849	4.62883	1.08016	C	0.10566	-2.27887	1.38377
	H	1.41700	3.99545	2.37252	O	-0.53602	-2.79491	2.28672
	H	0.38895	1.78379	2.03460	O	0.74777	-2.98248	0.42595
	C	3.60290	0.53391	-1.18575	C	0.62460	-4.42202	0.50559
	H	2.83407	0.21391	-1.91013	H	-0.42466	-4.71622	0.43122
	H	3.96781	-0.37642	-0.68088	H	1.19228	-4.80734	-0.34087
	C	5.28104	0.29250	-2.82675	H	1.04230	-4.78621	1.44688
	H	6.08622	0.85711	-3.30161	C	-3.26417	0.42369	-2.46297
	H	5.70185	-0.60172	-2.34488	O	-2.03814	0.38949	-2.24541
	H	4.55970	-0.02332	-3.59404	O	-4.18693	0.19160	-1.55384
	H	-5.17393	0.91368	1.50015	H	-3.76249	0.02158	-0.63172

	C	-4.54453	0.42027	2.24797	C	-3.80884	0.74565	-3.82864
	C	-3.09163	0.41562	1.79317	H	-4.40376	1.66259	-3.77400
	H	-4.64439	0.93474	3.20479	H	-2.99464	0.87349	-4.54104
	H	-4.90271	-0.60943	2.34621	H	-4.47535	-0.05734	-4.15658
	O	-2.19166	0.90688	2.48550	O	4.67432	1.15811	-1.87139
INT-5b	C	1.37637	-1.17145	-0.76399	O	-2.45140	-0.58685	-0.45920
	C	2.21982	-1.82559	0.17517	Pd	-0.83252	0.64512	0.43528
	C	2.44413	-3.19953	0.04588	C	0.27900	1.06094	-1.41363
	C	1.85541	-3.92966	-0.99265	C	1.16746	0.28023	-0.66623
	C	1.02369	-3.29022	-1.91889	H	-0.38453	0.62003	-2.15410
	C	0.78544	-1.92302	-1.80165	H	0.13076	1.57250	1.19532
	H	3.08383	-3.69733	0.76638	H	1.90780	0.83166	-0.09529
	H	2.04795	-4.99712	-1.07719	C	0.43659	2.53870	-1.57359
	H	0.56589	-3.85335	-2.72866	O	-0.28414	3.20083	-2.30625
	H	0.13495	-1.43292	-2.51872	O	1.45876	3.05882	-0.86414
	C	2.85340	-1.05581	1.31885	C	1.63975	4.49038	-0.96740
	H	2.07145	-0.54586	1.90593	H	0.74706	5.01094	-0.61308
	H	3.52065	-0.27142	0.92321	H	2.49490	4.71957	-0.33221
	C	4.21261	-1.23937	3.23841	H	1.84284	4.77300	-2.00268
	H	4.75276	-1.98641	3.82393	C	-3.02039	-0.08391	2.57763
	H	4.92244	-0.48225	2.87524	O	-1.95624	0.52094	2.32138
	H	3.46636	-0.74818	3.87923	O	-3.70521	-0.78074	1.70685
	H	-4.96444	-0.94949	-1.33698	H	-3.25273	-0.75772	0.76076
	C	-4.17900	-1.56259	-1.79111	C	-3.60964	-0.05122	3.96282
	C	-2.83605	-0.85152	-1.68679	H	-3.69471	-1.07280	4.34527
	H	-4.14498	-2.50949	-1.24246	H	-2.98689	0.54599	4.62795
	H	-4.42784	-1.75545	-2.83553	H	-4.61975	0.36680	3.91845
	O	-2.17840	-0.56415	-2.69528	O	3.59251	-1.92830	2.15654
TS-6b	C	-1.21665	0.62991	1.39661	O	1.74478	-2.30551	0.35511
	C	-2.53671	0.60654	0.87211	Pd	1.12925	-0.59500	-0.97558
	C	-3.52301	-0.13389	1.53372	C	1.16516	1.38543	0.98157
	C	-3.22915	-0.84458	2.70209	C	-0.17132	1.41009	0.72216
	C	-1.93224	-0.82128	3.22822	H	1.59961	0.74084	1.74028
	C	-0.94103	-0.08943	2.57891	H	1.02223	0.52150	-2.01754
	H	-4.52785	-0.15053	1.12573	H	-0.49457	2.11401	-0.03945
	H	-4.01230	-1.41051	3.20208	C	2.13936	2.33328	0.39509
	H	-1.69802	-1.36442	4.14074	O	3.31073	2.38925	0.75213
	H	0.05789	-0.06279	3.00544	O	1.61530	3.14479	-0.55141
	C	-2.87855	1.35849	-0.40094	C	2.52921	4.09136	-1.14815
	H	-2.23108	1.01437	-1.22225	H	3.35449	3.56780	-1.63632
	H	-2.69019	2.43665	-0.26443	H	1.93864	4.64126	-1.88079
	C	-4.60178	1.86558	-1.92977	H	2.92548	4.76958	-0.38870
	H	-5.65514	1.64963	-2.12167	C	-1.31414	-2.47445	-1.27757
	H	-4.47343	2.95004	-1.80045	O	-0.89412	-1.34774	-1.58273

	H	-4.00287	1.53853	-2.79193	O	-0.63223	-3.36219	-0.56583
	H	3.75222	-4.06853	0.48507	H	0.25705	-3.01519	-0.27501
	C	4.02766	-3.02426	0.65850	C	-2.67736	-2.95714	-1.68801
	C	2.98609	-2.11467	0.05438	H	-3.14285	-2.23791	-2.36034
	H	4.05498	-2.86857	1.74197	H	-2.59608	-3.93528	-2.16998
	H	5.01395	-2.82141	0.23880	H	-3.29627	-3.07928	-0.79361
	O	3.32365	-1.16512	-0.71589	O	-4.24022	1.15735	-0.74834
3b	C	0.67247	-1.02867	0.08365	H	3.00467	3.49479	0.65129
	C	1.90079	-0.39688	0.41410	H	2.73480	3.05826	2.36412
	C	3.08413	-1.14511	0.39447	C	-1.83768	-0.75386	0.04159
	C	3.07454	-2.50024	0.04938	C	-0.58044	-0.26350	0.10232
	C	1.86910	-3.12854	-0.28530	H	-2.05808	-1.81620	-0.01139
	C	0.68475	-2.39546	-0.26744	H	-0.50429	0.81924	0.17640
	H	4.01734	-0.65687	0.65331	C	-2.99975	0.15700	0.06026
	H	4.00618	-3.06192	0.03787	O	-2.96200	1.38105	0.12380
	H	1.85457	-4.17976	-0.56362	O	-4.16078	-0.54260	-0.00149
	H	-0.24374	-2.88677	-0.54574	C	-5.37267	0.24311	0.01086
	C	1.93947	1.07152	0.80046	H	-5.39919	0.91731	-0.84866
	H	1.28614	1.25115	1.66960	H	-6.18752	-0.47863	-0.04456
	H	1.55198	1.68981	-0.02626	H	-5.43994	0.82657	0.93229
	C	3.34185	2.84559	1.47228	O	3.26563	1.47047	1.10977
	H	4.38998	3.06026	1.69216				
TS2-1	H	4.36083	-1.85607	1.30016	H	-2.67393	3.39577	0.04945
	C	3.93454	-1.90326	0.29555	C	-2.28159	-0.31504	2.24669
	C	2.70554	-1.05004	0.21620	C	-3.15976	-0.43453	3.25217
	H	4.67829	-1.51690	-0.41000	H	-1.47126	0.40778	2.28213
	H	3.70094	-2.93504	0.02537	H	-3.97287	-1.15444	3.21987
	O	1.71734	-1.38715	-0.54113	H	-3.07916	0.19315	4.13623
	O	2.59887	0.04143	0.86758	C	-2.31729	-1.13245	1.01235
	Pd	0.62758	0.30391	-0.06133	O	-1.49128	-1.02855	0.10355
	O	-0.18170	2.06912	0.50541	O	-3.33216	-2.00731	0.95940
	C	-0.91199	2.35381	-0.54089	C	-3.40998	-2.83408	-0.22753
	O	-0.91293	1.57449	-1.52108	H	-2.50866	-3.44330	-0.32314
	C	-1.74056	3.60995	-0.48257	H	-4.28658	-3.46391	-0.08012
	H	-1.21349	4.39581	0.06364	H	-3.52803	-2.20955	-1.11555
	H	-1.98381	3.94465	-1.49282				
INT2-1	H	5.13456	-0.79880	-0.14004	H	-1.11657	4.50128	-0.86571
	C	4.41939	-1.53524	0.23431	C	-2.44216	-0.36423	1.44240
	C	3.02701	-0.99047	0.14793	C	-3.58448	-0.53163	2.12499
	H	4.49776	-2.46664	-0.32925	H	-1.60123	0.18095	1.85813
	H	4.65781	-1.73453	1.28475	H	-4.43012	-1.07196	1.70862
	O	2.03451	-1.72573	-0.19438	H	-3.69181	-0.12584	3.12771
	O	2.77817	0.23800	0.43541	C	-2.22974	-0.90153	0.08727
	Pd	0.73989	-0.06453	0.04744	O	-1.14868	-0.84257	-0.53247

	O	-0.09174	1.72276	0.52490	O	-3.28463	-1.48351	-0.46636
	C	-0.21946	2.58571	-0.45981	C	-3.11828	-2.04394	-1.79765
	O	0.09364	2.36623	-1.63582	H	-2.35342	-2.82236	-1.78092
	C	-0.78025	3.92521	-0.00198	H	-4.09200	-2.46088	-2.04936
	H	-1.60242	3.78572	0.70422	H	-2.83740	-1.25734	-2.50011
	H	0.00820	4.48448	0.51285				
TS2-2	H	4.98105	0.07744	1.32615	H	0.77812	4.37735	0.59732
	C	4.49844	-0.84740	1.64158	C	-0.29742	-2.58567	-1.46394
	C	3.13345	-0.98767	1.00947	C	0.92271	-2.22764	-0.99959
	H	5.11371	-1.71187	1.38192	H	-0.43358	-3.33289	-2.24490
	H	4.37616	-0.83844	2.72947	H	1.47830	-2.02514	0.18988
	O	2.52700	-2.10454	1.09473	H	1.78220	-2.68598	-1.49682
	O	2.64420	0.03994	0.42035	C	-1.48540	-1.84794	-1.01427
	Pd	0.66171	-0.22521	-0.12479	O	-1.38654	-0.75372	-0.41062
	O	0.22027	1.65831	0.57314	O	-2.65208	-2.37614	-1.32635
	C	0.15454	2.56642	-0.36834	C	-3.84582	-1.63424	-0.94079
	O	0.32850	2.34190	-1.57576	H	-3.83787	-0.65243	-1.41708
	C	-0.13689	3.96516	0.15856	H	-4.67811	-2.23683	-1.29940
	H	-0.45885	4.61219	-0.65927	H	-3.87858	-1.52727	0.14475
	H	-0.89730	3.93826	0.94290				
INT2-2	H	-4.10262	-2.45741	0.69419	H	-2.22988	3.51356	-0.85039
	C	-4.27145	-1.53228	0.14444	C	2.13981	-2.34767	0.86819
	C	-2.97358	-0.80245	-0.06957	C	0.79407	-2.23311	0.81716
	H	-4.72691	-1.75063	-0.82621	H	2.68426	-3.21272	1.24396
	H	-4.96392	-0.88814	0.69430	H	-2.15447	0.81185	-0.79679
	O	-3.07724	0.32952	-0.71625	H	0.10673	-3.01202	1.15453
	O	-1.89847	-1.28436	0.35574	C	2.84688	-1.17988	0.36130
	Pd	0.09043	-0.53396	0.10162	O	2.21322	-0.18394	-0.07704
	O	-0.75359	1.28979	-0.75003	O	4.17085	-1.20881	0.38011
	C	-0.36634	2.50759	-0.41788	C	4.86710	-0.03431	-0.12054
	O	0.56815	2.74341	0.35290	H	4.58753	0.84254	0.46610
	C	-1.16518	3.61902	-1.08375	H	5.92519	-0.26154	-0.00103
	H	-0.81430	4.59607	-0.74832	H	4.61971	0.12518	-1.17164
	H	-1.06316	3.54616	-2.17130				
TS2-3a	C	-1.27592	1.44771	-1.28725	C	-5.21415	0.41054	1.43856
	C	-2.57213	1.11302	-1.00329	H	-5.13868	1.26019	2.12143
	C	-3.17075	0.89237	0.32719	H	-6.25105	0.24654	1.14579
	H	3.28795	-2.86780	1.69877	H	-4.80535	-0.48053	1.92114
	C	2.63778	-2.38000	2.43227	C	0.08660	3.54946	-1.60099
	C	2.04645	-1.10462	1.84107	C	-0.34972	2.83508	-0.40413
	H	1.83563	-3.08463	2.67602	C	0.69466	2.07813	0.32173
	H	3.20895	-2.15632	3.33472	C	1.97400	1.89726	-0.29063
	O	2.21215	-0.00320	2.38469	C	2.26703	2.48391	-1.51498
	O	1.37178	-1.28080	0.73257	C	1.32841	3.34461	-2.14851

	Pd	0.09448	0.17892	-0.36178	H	-0.62982	4.21109	-2.08336
	C	-0.38196	-2.89769	-1.33468	H	0.60829	1.96163	1.40075
	O	-0.68713	-1.70124	-1.47117	H	2.72958	1.34622	0.26017
	O	0.50694	-3.34178	-0.46799	H	3.24422	2.32921	-1.96643
	H	0.91159	-2.55750	0.07705	H	1.60782	3.85890	-3.06521
	C	-1.01590	-3.98082	-2.17059	C	-1.35562	3.58831	0.45837
	H	-1.74128	-3.55123	-2.86101	H	-1.69839	2.96450	1.28285
	H	-0.24025	-4.51459	-2.72808	H	-2.21540	3.89666	-0.14396
	H	-1.50711	-4.70823	-1.51729	S	-0.54158	5.09001	1.16362
	O	-2.59144	0.87063	1.40916	C	-1.83743	5.57802	2.35658
	H	-1.03094	1.53929	-2.34527	H	-1.99645	4.79664	3.10476
	H	-3.25292	0.95326	-1.83886	H	-1.48303	6.48210	2.85801
	O	-4.50707	0.68659	0.20943	H	-2.77882	5.80269	1.84759
INT2-3a	C	1.56220	0.15538	-1.18959	C	1.70928	3.48735	2.47380
	C	1.44250	1.35525	-0.49943	H	2.77577	3.42628	2.70231
	C	1.78006	1.70179	0.91365	H	1.37677	4.52489	2.46632
	H	-4.70294	-1.14892	1.69792	H	1.14367	2.90646	3.20586
	C	-4.09007	-0.50428	2.33632	C	1.80040	-2.21710	-1.81314
	C	-2.63024	-0.58039	1.90089	C	1.91260	-1.25514	-0.64702
	H	-4.46491	0.51815	2.22113	C	0.80198	-1.45298	0.39671
	H	-4.19674	-0.81420	3.37708	C	-0.09601	-2.58010	0.28717
	O	-1.74456	-0.96502	2.67555	C	-0.08444	-3.39673	-0.80786
	O	-2.41676	-0.21984	0.65722	C	0.87446	-3.19580	-1.88038
	Pd	-0.45036	0.09624	-0.32052	H	2.52548	-2.08461	-2.61536
	C	-2.88370	1.96216	-1.61356	H	1.03816	-1.11222	1.40319
	O	-1.66718	1.72419	-1.58860	H	-0.79065	-2.74450	1.10519
	O	-3.76801	1.36400	-0.83407	H	-0.78473	-4.22637	-0.87588
	H	-3.29730	0.70141	-0.19936	H	0.84955	-3.86178	-2.74021
	C	-3.48890	2.97726	-2.55023	C	3.35610	-1.30013	-0.08355
	H	-4.27075	2.50515	-3.15234	H	3.44246	-0.60457	0.75035
	H	-3.96202	3.77396	-1.96775	H	4.05370	-0.99966	-0.87417
	H	-2.72114	3.39965	-3.19803	S	3.80318	-2.98433	0.51741
	O	2.29159	0.98585	1.76292	C	5.26901	-2.53935	1.51455
	H	1.47385	0.23660	-2.27284	H	4.99999	-1.86141	2.32923
	H	1.22676	2.23215	-1.10620	H	5.65829	-3.46802	1.93958
	O	1.45364	2.99448	1.13808	H	6.04598	-2.08352	0.89447
TS2-3b	C	-1.22414	1.39308	-1.24229	C	-5.30573	0.46592	1.29140
	C	-2.53844	1.09517	-1.02796	H	-5.19966	1.27952	2.01304
	C	-3.19906	0.86018	0.26863	H	-6.34063	0.38249	0.95978
	H	3.31419	-2.97855	1.68836	H	-4.97199	-0.46911	1.74806
	C	2.65072	-2.51762	2.42731	C	0.11757	3.53391	-1.41914
	C	2.05285	-1.23250	1.86411	C	-0.30334	2.74982	-0.26389
	H	1.85346	-3.23694	2.64254	C	0.74341	1.96092	0.41502
	H	3.20933	-2.31283	3.34202	C	2.02735	1.83110	-0.20642

	O	2.20123	-0.14490	2.44011	C	2.31536	2.49228	-1.39008
	O	1.39311	-1.38476	0.74344	C	1.36323	3.37714	-1.97259
	Pd	0.11232	0.09368	-0.31304	H	-0.60905	4.21473	-1.85345
	C	-0.39314	-2.96781	-1.32625	H	0.66856	1.79154	1.48914
	O	-0.69625	-1.76900	-1.44084	H	2.78608	1.25074	0.30912
	O	0.50998	-3.42664	-0.48128	H	3.29474	2.37817	-1.84880
	H	0.92300	-2.65176	0.06907	H	1.63869	3.95115	-2.85467
	C	-1.04504	-4.03836	-2.16447	C	-1.26862	3.45441	0.68669
	H	-0.28128	-4.56767	-2.74226	H	-0.69071	4.25253	1.18143
	H	-1.52736	-4.77229	-1.51182	C	-3.19434	4.81280	0.81496
	H	-1.78099	-3.59767	-2.83648	H	-4.01012	5.18470	0.19131
	O	-2.66153	0.75386	1.36711	H	-3.61208	4.21950	1.64064
	H	-0.93126	1.52769	-2.28324	H	-2.64237	5.66552	1.23598
	H	-3.19260	1.00471	-1.89466	O	-2.35854	4.01936	-0.02333
	O	-4.54090	0.74523	0.09884	H	-1.61796	2.76312	1.46063
INT2-3b	C	1.58318	0.22923	-1.03277	C	1.58592	3.72932	2.46788
	C	1.41564	1.45430	-0.40509	H	2.64550	3.68216	2.72956
	C	1.70718	1.86962	0.99963	H	1.25280	4.76447	2.39979
	H	-4.75489	-1.33363	1.46213	H	1.00039	3.18424	3.21179
	C	-4.26601	-0.60325	2.11490	C	1.83317	-2.17393	-1.54001
	C	-2.77220	-0.55590	1.81149	C	1.89896	-1.15350	-0.42031
	H	-4.72319	0.37093	1.91207	C	0.75769	-1.30956	0.59598
	H	-4.43722	-0.87316	3.15817	C	-0.06237	-2.50238	0.56797
	O	-1.92771	-0.81074	2.67968	C	0.02834	-3.40589	-0.45052
	O	-2.48421	-0.23961	0.56984	C	0.97541	-3.21486	-1.53642
	Pd	-0.47891	0.19630	-0.23223	H	2.54895	-2.04505	-2.34855
	C	-2.86843	1.98345	-1.68963	H	0.95669	-0.88885	1.58100
	O	-1.64839	1.82105	-1.54489	H	-0.76741	-2.64046	1.38186
	O	-3.78659	1.30163	-1.02460	H	-0.60814	-4.28816	-0.45474
	H	-3.34015	0.65262	-0.36398	H	0.99293	-3.93568	-2.35127
	C	-3.44138	2.99335	-2.65140	C	3.29867	-1.24191	0.23631
	H	-4.13664	2.49991	-3.33674	H	3.45646	-2.27565	0.58271
	H	-4.01001	3.74433	-2.09402	C	5.60032	-0.94821	-0.21682
	H	-2.64203	3.47742	-3.21194	H	6.27526	-0.64828	-1.02188
	O	2.19440	1.19799	1.89749	H	5.72759	-0.26468	0.63484
	H	1.52599	0.26130	-2.11998	H	5.85544	-1.96787	0.10647
	H	1.20730	2.29929	-1.05780	O	4.27570	-0.88740	-0.73665
	O	1.36897	3.17031	1.15182	H	3.35129	-0.56906	1.09783
TS2-hom	C	-0.81844	1.19162	-1.38765	H	4.12105	2.92568	0.09009
	C	-2.08059	0.87847	-1.74112	H	3.36448	4.12220	-1.01231
	C	-3.09034	0.27673	-0.84089	H	3.43747	4.43654	0.75266
	H	3.62732	-1.89638	2.77923	C	1.09707	-2.54058	-1.64663
	C	2.62418	-2.31485	2.90786	O	0.33614	-1.56071	-1.55611
	C	1.58768	-1.34155	2.36280	O	2.04863	-2.82020	-0.77839

	H	2.58998	-3.25682	2.35075	H	2.02316	-2.15459	0.00155
	H	2.44206	-2.51129	3.96535	C	0.98805	-3.52355	-2.78129
	O	0.70855	-0.85428	3.07941	H	1.97376	-3.69572	-3.22169
	O	1.73415	-1.07259	1.07895	H	0.63111	-4.48174	-2.38971
	Pd	0.35231	0.12662	-0.05572	H	0.29258	-3.15598	-3.53514
	C	0.39826	1.79322	1.25866	O	-2.94013	0.02421	0.34862
	C	-0.63824	2.22537	0.39121	H	-0.17609	1.68982	-2.11533
	H	0.14700	1.33208	2.21060	H	-2.40976	1.07618	-2.76110
	H	-0.44741	3.08726	-0.24138	O	-4.24512	0.04771	-1.50730
	H	-1.65828	2.07938	0.72759	C	-5.31608	-0.53936	-0.73282
	C	1.76282	2.40510	1.23188	H	-5.59640	0.12249	0.08993
	O	2.54036	2.34719	2.17120	H	-6.14560	-0.65758	-1.42946
	O	2.03137	3.04288	0.07214	H	-5.00820	-1.50826	-0.33288
	C	3.33148	3.67230	-0.02053				
INT2-hom	C	-1.26216	1.78595	-1.30403	H	4.16721	1.10709	-0.94474
	C	-2.28655	1.00920	-0.79544	H	3.81857	2.13364	-2.37427
	C	-2.95332	1.21704	0.52780	H	4.14750	2.88419	-0.77889
	H	3.67577	-1.43195	1.80493	C	-0.50344	-2.93274	-1.61358
	C	2.82298	-2.10843	1.92507	O	-1.12886	-1.90226	-1.31697
	C	1.55243	-1.35493	1.56551	O	0.75960	-3.14848	-1.28596
	H	2.98080	-2.95693	1.25325	H	1.11091	-2.38977	-0.71140
	H	2.78206	-2.45252	2.95969	C	-1.13523	-4.06110	-2.38252
	O	0.74549	-0.98095	2.42056	H	-0.50218	-4.33377	-3.23136
	O	1.41416	-1.12877	0.26845	H	-1.20938	-4.93931	-1.73308
	Pd	-0.30270	-0.00997	-0.34210	H	-2.12848	-3.77405	-2.72594
	C	0.40037	1.81958	0.37991	O	-2.64348	2.03823	1.37742
	C	-0.43416	2.76812	-0.49401	H	-1.03543	1.67784	-2.36401
	H	0.12017	1.80319	1.43210	H	-2.81946	0.34549	-1.47231
	H	0.18679	3.36769	-1.16022	O	-3.99563	0.36947	0.64870
	H	-1.05999	3.42179	0.11584	C	-4.74705	0.46244	1.88286
	C	1.88650	1.85327	0.22502	H	-5.18571	1.45773	1.98349
	O	2.67500	1.78448	1.15729	H	-5.52608	-0.29489	1.80314
	O	2.27564	1.99110	-1.06484	H	-4.09653	0.25932	2.73639
	C	3.70160	2.03087	-1.29552				

Table S2. Frequencies (cm^{-1}) of all the stationary points in the catalytic cycles, computed at the B3LYP-IDSCRF/DZVP level of theory.

Names	Frequencies													
TS-1a	110i	10	26	29	37	46	49	53	60	65	69	92	100	
	128	135	160	185	213	227	259	291	334	342	354	414	476	
	483	517	571	605	610	630	684	687	696	707	710	784	819	
	854	901	931	944	947	985	987	999	1002	1013	1014	1015	1048	
	1065	1065	1095	1156	1173	1196	1225	1282	1350	1359	1370	1378	1386	

	1428 1435 1475 1476 1479 1483 1489 1492 1494 1498 1525 1537 1559 1632 1652 3052 3058 3059 3062 3126 3145 3146 3154 3167 3174 3176 3178 3179 3187 3195 3204
INT-1a	17 21 29 38 40 44 60 64 76 92 103 123 137 160 165 184 204 225 267 270 273 327 341 354 413 478 488 523 571 606 614 629 674 682 685 695 707 779 822 854 904 932 933 948 986 994 1003 1007 1013 1016 1025 1048 1062 1065 1097 1169 1175 1195 1226 1290 1325 1352 1359 1360 1384 1397 1439 1474 1475 1479 1482 1483 1488 1488 1498 1524 1531 1632 1651 1661 3059 3059 3062 3069 3142 3146 3146 3168 3174 3175 3178 3181 3190 3198 3201 3206
TS-2a	1290i 29 38 47 49 65 77 83 94 104 126 143 160 171 175 183 204 214 228 258 275 296 302 319 391 449 496 508 531 574 617 629 652 667 679 690 706 757 769 826 882 918 931 936 973 990 1004 1007 1020 1029 1039 1059 1061 1067 1110 1144 1176 1179 1211 1258 1285 1340 1342 1358 1381 1392 1398 1449 1468 1472 1477 1481 1482 1488 1490 1490 1491 1593 1601 1627 1645 3056 3065 3065 3066 3138 3144 3148 3171 3173 3179 3183 3189 3194 3205 3206
INT-2a	25 33 36 45 52 56 71 84 96 105 125 133 159 173 190 197 211 228 239 250 261 294 307 383 435 478 491 500 581 604 607 640 662 678 695 706 737 753 823 866 916 921 935 957 990 992 1009 1028 1037 1038 1060 1062 1068 1079 1130 1163 1175 1218 1257 1308 1316 1331 1359 1365 1404 1420 1458 1474 1474 1479 1483 1483 1487 1494 1495 1538 1603 1622 1668 1689 2448 3053 3059 3064 3064 3129 3132 3146 3169 3171 3173 3178 3194 3197 3203 3209
TS-3a	309i 3 21 32 36 37 42 49 51 55 69 70 78 80 87 98 108 121 135 137 146 156 163 172 192 202 210 221 246 265 295 332 338 391 430 444 446 494 504 548 568 595 609 616 635 644 657 677 706 728 751 766 811 853 868 877 893 898 923 937 966 976 982 984 999 1007 1025 1029 1029 1061 1063 1066 1104 1117 1138 1173 1174 1178 1205 1216 1219 1265 1280 1304 1305 1334 1340 1370 1402 1403 1404 1457 1473 1475 1478 1481 1483 1483 1486 1488 1491 1495 1497 1501 1505 1600 1618 1665 1735 1743 2971 3053 3062 3062 3066 3072 3134 3138 3142 3166 3168 3169 3171 3176 3180 3181 3187 3189 3196 3203 3216 3271
INT-3a	5 23 28 34 36 42 46 51 57 62 73 82 85 103 110 113 129 141 144 156 163 176 181 192 204 215 219 246 262 287 318 348 405 452 468 476 496 504 550 594 602 608 616 633 663 665 697 717 731 759 778 789 838 850 901 909 912 923 925 971 981 983 995 1002 1008 1027 1037 1040 1063 1068 1069 1073 1097 1165 1173 1181 1186 1196 1211 1227 1268 1284 1300 1313 1334 1337 1358 1370 1372 1400 1409 1466 1472

	1474 1482 1482 1485 1486 1490 1492 1496 1499 1504 1506 1511 1611 1631 1685 1703 1733 2842 3045 3054 3059 3065 3070 3083 3120 3135 3143 3146 3155 3158 3166 3172 3172 3179 3192 3193 3194 3203 3211
TS-4a	42i 16 23 25 36 40 45 48 53 58 61 64 84 86 89 94 109 130 134 150 154 165 180 182 197 212 219 229 253 299 323 347 401 420 470 474 486 518 553 571 601 609 615 632 660 687 701 717 742 761 779 790 839 859 860 882 907 908 922 949 954 980 993 995 1013 1025 1036 1050 1057 1063 1069 1071 1105 1167 1172 1178 1191 1208 1213 1238 1252 1285 1290 1294 1322 1327 1352 1372 1382 1397 1401 1463 1465 1473 1476 1482 1482 1482 1487 1493 1494 1496 1504 1510 1522 1622 1649 1678 1697 1746 2962 2979 3045 3056 3057 3060 3065 3071 3098 3117 3140 3143 3147 3157 3167 3172 3174 3177 3191 3195 3196 3205
INT-4a	12 21 28 35 41 44 49 55 61 67 70 78 83 86 94 109 121 139 144 149 158 167 172 184 197 213 222 240 259 307 321 388 435 442 472 477 494 509 549 574 602 608 615 634 664 677 696 716 741 753 778 787 840 855 876 887 909 910 925 960 964 969 979 994 997 1026 1037 1052 1062 1069 1070 1091 1106 1165 1174 1179 1193 1210 1215 1237 1268 1282 1297 1299 1322 1334 1348 1370 1400 1405 1406 1469 1474 1475 1481 1482 1485 1487 1491 1493 1494 1497 1505 1513 1526 1625 1651 1683 1696 1745 2338 2916 3045 3056 3056 3065 3072 3117 3136 3137 3143 3147 3158 3160 3168 3174 3177 3185 3191 3196 3197 3205
TS-5a	456i 18 25 28 38 45 49 49 52 57 63 70 75 84 89 103 121 126 138 144 152 158 169 178 189 210 229 245 249 268 285 330 376 424 455 474 480 494 522 535 584 604 605 612 633 640 671 692 702 716 748 777 787 813 859 875 897 916 917 922 940 980 982 995 1008 1022 1028 1043 1053 1063 1068 1071 1098 1133 1163 1174 1184 1208 1213 1230 1271 1276 1289 1311 1315 1333 1353 1363 1372 1404 1412 1473 1475 1480 1481 1482 1486 1492 1493 1497 1500 1504 1509 1517 1548 1620 1649 1670 1685 1746 1943 2678 3046 3054 3055 3065 3073 3119 3134 3145 3147 3158 3171 3173 3179 3190 3195 3200 3200 3208 3211 3220
INT-5a	15 26 31 31 39 43 47 50 61 63 65 78 86 89 100 108 119 128 138 145 155 168 172 190 212 218 231 244 267 274 326 354 416 426 472 479 492 516 536 555 577 605 606 610 638 677 685 701 715 744 774 782 813 859 867 882 891 915 925 935 953 973 980 994 1005 1029 1040 1051 1061 1068 1069 1077 1093 1100 1166 1173 1184 1210 1214 1238 1282 1287 1310 1315 1319 1339 1369 1370 1371 1404 1425 1473 1475 1480 1481 1483 1486 1493 1495 1497 1504 1510 1514 1551 1577 1616 1647 1657 1688 1745 2129 2339 3047 3053 3061 3065 3073 3121 3132 3146 3147 3158 3170 3174 3180 3180 3192 3194 3199 3204 3214 3225
TS-6a	87i 6 16 20 21 30 35 40 41 57 61 67 74

	78 88 89 98 117 118 137 155 164 172 184 201 202 208 215 246 259 282 311 334 429 452 463 473 511 520 579 582 597 613 616 628 657 685 704 713 721 765 775 783 815 818 862 875 882 897 903 915 941 971 981 994 1001 1018 1022 1035 1063 1066 1068 1071 1102 1166 1174 1182 1209 1212 1241 1274 1282 1288 1297 1324 1343 1367 1372 1377 1385 1440 1450 1466 1476 1478 1480 1482 1486 1487 1494 1498 1505 1515 1516 1556 1612 1639 1655 1691 1731 2179 3046 3058 3066 3068 3070 3127 3140 3144 3148 3157 3166 3177 3178 3188 3194 3198 3198 3206 3210 3218 3272
INT-6a	41 45 52 55 83 112 140 173 228 253 311 471 484 553 592 614 627 661 679 895 910 944 1019 1036 1066 1067 1235 1378 1381 1434 1447 1471 1477 1487 1488 1569 1701 2061 3057 3067 3140 3153 3174 3202 3397
INT-7a	28 32 37 43 65 85 108 138 153 168 238 450 454 549 550 611 614 663 663 890 891 1025 1025 1065 1065 1234 1241 1362 1366 1425 1426 1479 1480 1485 1485 1725 1727 3065 3065 3146 3146 3197 3197 3327 3334
1a	39 53 89 170 209 257 339 412 484 571 629 690 706 714 786 819 850 902 927 978 981 993 999 1013 1047 1092 1155 1172 1193 1226 1282 1349 1358 1370 1479 1481 1493 1497 1523 1631 1651 3044 3056 3119 3141 3156 3173 3175 3185 3193 3203
2	88 153 175 217 333 503 528 627 826 861 984 993 1014 1090 1173 1211 1305 1306 1437 1479 1498 1505 1678 1748 3071 3166 3167 3196 3206 3269
3a	21 35 56 67 86 89 108 143 166 193 202 209 246 259 312 335 414 463 518 521 567 611 686 710 719 724 775 783 809 856 880 893 912 951 968 980 994 999 1017 1038 1070 1099 1163 1174 1181 1196 1209 1215 1243 1283 1317 1331 1345 1368 1371 1475 1479 1481 1493 1497 1504 1514 1516 1613 1645 1677 1738 3046 3066 3069 3124 3144 3157 3164 3178 3187 3194 3197 3199 3206 3210
1b	12 77 151 208 220 340 391 413 471 611 629 706 738 825 854 913 984 989 998 1012 1038 1047 1097 1143 1171 1178 1190 1217 1230 1276 1332 1358 1418 1475 1486 1499 1508 1522 1528 1632 1655 2976 2999 3011 3065 3148 3163 3177 3187 3200 3217
TS-1b	98i 14 28 36 48 49 50 58 63 71 78 113 134 144 151 173 228 249 289 303 321 339 344 348 414 481 503 511 604 608 614 630 681 699 707 758 844 854 919 940 947 957 985 997 1003 1013 1014 1016 1047 1064 1065 1090 1105 1173 1177 1193 1214 1238 1255 1351 1359 1370 1386 1411 1419 1435 1474 1475 1479 1481 1488 1499 1508 1511 1523 1526 1528 1591 1633 1654 3013 3019 3058 3059 3068 3090 3145 3146 3174 3175 3176 3177 3182 3185 3194 3204
INT-1b	18 29 33 35 42 46 63 65 73 91 103 129 144 171 179 201 230 270 275 318 330 341 349 388 411 488

	505 521 605 610 613 629 682 690 704 756 842 853 903 929 945 951 987 990 1006 1013 1014 1022 1038 1049 1060 1065 1108 1174 1177 1196 1216 1240 1262 1325 1353 1361 1387 1396 1407 1440 1472 1473 1482 1482 1489 1503 1507 1509 1511 1517 1527 1633 1654 1663 3041 3051 3058 3059 3112 3131 3143 3147 3174 3177 3179 3181 3189 3197 3198 3206
TS-2b	1350i 29 33 40 45 60 66 74 90 107 127 132 160 172 181 199 211 238 251 274 301 313 326 377 413 453 504 510 537 610 611 632 657 675 690 741 760 842 881 925 927 940 970 1005 1009 1022 1024 1042 1059 1060 1064 1068 1123 1175 1178 1190 1213 1224 1244 1279 1329 1336 1374 1391 1399 1407 1445 1469 1475 1482 1482 1489 1490 1492 1496 1503 1511 1589 1605 1630 1655 3035 3048 3055 3066 3113 3136 3138 3151 3170 3179 3183 3192 3194 3206 3209
INT-2b	27 35 42 44 55 69 73 80 104 111 131 139 153 169 196 216 227 241 247 248 278 307 387 425 444 482 488 504 607 608 614 645 670 676 705 749 836 866 924 930 944 953 991 1026 1028 1039 1041 1056 1062 1068 1085 1116 1136 1173 1180 1226 1229 1253 1284 1306 1327 1371 1403 1409 1423 1463 1472 1475 1482 1485 1486 1494 1500 1514 1517 1535 1604 1628 1653 1686 2289 3022 3038 3052 3065 3084 3123 3131 3147 3168 3172 3180 3195 3199 3205 3209
TS-3b	232i 20 23 33 38 52 54 58 61 70 76 83 85 91 110 117 126 134 141 151 159 172 175 193 208 222 228 246 260 296 312 335 402 428 432 441 470 494 497 549 603 611 614 628 634 645 669 726 747 755 821 853 859 875 911 920 926 939 961 991 996 1005 1018 1028 1030 1039 1062 1063 1068 1085 1112 1113 1136 1174 1175 1177 1208 1210 1213 1236 1278 1281 1308 1312 1343 1345 1397 1400 1402 1410 1456 1474 1477 1478 1482 1483 1487 1493 1498 1501 1504 1505 1505 1515 1518 1601 1620 1684 1700 1754 2736 3011 3026 3053 3064 3073 3095 3098 3133 3145 3154 3169 3170 3172 3179 3187 3191 3193 3197 3199 3203 3294
INT-3b	19 23 32 35 43 47 50 61 65 71 79 84 94 103 108 119 130 140 147 155 165 179 193 201 211 245 251 262 278 320 356 404 430 454 468 477 492 503 565 602 610 612 624 632 663 665 733 752 765 779 842 854 903 909 922 924 929 969 990 1003 1006 1007 1026 1037 1041 1063 1068 1068 1074 1107 1123 1173 1176 1180 1187 1197 1211 1214 1223 1267 1297 1299 1317 1336 1342 1360 1371 1400 1403 1408 1466 1472 1474 1480 1482 1486 1488 1490 1496 1498 1500 1502 1505 1511 1516 1611 1633 1687 1702 1733 2846 3007 3025 3054 3064 3070 3079 3087 3098 3135 3146 3161 3161 3165 3172 3175 3176 3189 3193 3194 3197 3209
TS-4b	28i 15 23 25 37 41 45 48 51 56 64 70 79 81 90 111 126 129 147 152 153 173 183 192 210 226

	228 250 285 300 318 360 414 446 459 471 489 524 556 590 601 611 619 632 659 694 737 747 766 805 846 856 863 882 909 922 949 954 994 996 1016 1024 1034 1036 1048 1056 1063 1069 1071 1112 1147 1173 1177 1179 1191 1201 1212 1224 1241 1254 1290 1292 1293 1315 1329 1346 1386 1397 1403 1424 1467 1471 1474 1477 1481 1483 1484 1486 1493 1497 1500 1503 1505 1517 1527 1625 1652 1681 1697 1742 2969 2972 2976 3002 3005 3027 3056 3065 3071 3071 3132 3138 3146 3152 3166 3168 3174 3183 3195 3197 3200 3223
INT-4b	12 22 27 35 38 39 47 53 58 65 69 74 76 88 93 119 121 141 146 154 167 176 190 196 214 229 238 257 282 318 344 384 429 465 472 474 496 510 551 594 601 610 620 635 666 681 731 750 765 800 841 852 875 886 911 924 958 963 964 994 998 1025 1034 1036 1052 1062 1068 1069 1093 1109 1147 1173 1177 1179 1192 1209 1214 1224 1241 1267 1291 1296 1299 1315 1336 1341 1399 1401 1406 1424 1470 1474 1475 1482 1483 1485 1487 1494 1497 1499 1500 1504 1506 1519 1530 1627 1653 1685 1696 1743 2359 2918 2964 2997 3003 3056 3065 3071 3072 3107 3136 3146 3153 3162 3169 3175 3179 3184 3195 3199 3201 3223
TS-5b	455i 17 23 26 34 43 45 50 56 61 75 76 79 87 92 104 123 130 139 150 155 166 177 199 219 230 235 247 253 277 319 351 382 422 461 471 481 494 530 548 597 603 608 615 639 643 671 713 726 751 780 818 858 874 891 916 916 936 977 994 1007 1019 1029 1036 1041 1052 1063 1068 1072 1102 1138 1146 1174 1178 1181 1208 1212 1220 1228 1269 1277 1298 1307 1313 1323 1353 1355 1404 1413 1424 1473 1475 1479 1482 1486 1486 1493 1497 1500 1500 1504 1508 1510 1524 1548 1622 1651 1671 1686 1747 1938 2683 2965 3001 3005 3054 3065 3073 3073 3134 3146 3155 3171 3173 3185 3195 3197 3200 3202 3208 3220 3229
INT-5b	12 19 25 28 44 48 51 59 63 68 76 81 83 92 96 107 127 136 143 154 161 174 195 214 221 231 234 243 274 317 342 358 411 436 470 479 492 518 542 553 595 604 606 615 638 677 710 719 749 777 818 855 860 880 889 925 932 948 973 994 1006 1029 1035 1040 1049 1061 1065 1068 1074 1089 1105 1146 1174 1179 1181 1210 1213 1223 1234 1281 1295 1306 1314 1316 1328 1362 1370 1404 1424 1425 1473 1476 1478 1483 1486 1486 1494 1497 1500 1504 1504 1510 1526 1550 1575 1618 1648 1658 1688 1746 2131 2351 2970 3004 3005 3052 3065 3072 3073 3132 3146 3154 3170 3173 3178 3185 3194 3199 3200 3211 3223 3228
TS-6b	91i 15 19 25 27 34 34 37 41 57 64 68 76 80 87 90 113 119 136 149 155 163 188 198 203 204 218 234 260 278 299 315 353 439 453 454 471 517 534 591 594 598 616 617 626 657 704 717 739 759 778 803 820 861 875 882 888 901 941 969 993 1002 1013 1023 1035 1039 1062 1066 1068 1070 1105 1145 1173 1179 1180 1208 1212 1223 1238

	1271 1283 1296 1302 1315 1338 1365 1377 1383 1425 1438 1450 1466 1476 1477 1478 1485 1486 1488 1497 1500 1505 1506 1513 1529 1555 1613 1637 1656 1694 1731 2157 2977 3003 3024 3058 3066 3070 3071 3140 3148 3152 3166 3176 3183 3194 3194 3199 3202 3207 3213 3225 3296
3b	20 58 66 77 82 100 146 148 191 205 220 233 250 298 318 354 425 452 517 537 589 616 704 729 740 779 815 852 880 886 951 967 993 1001 1012 1037 1038 1070 1104 1144 1173 1179 1179 1196 1209 1215 1223 1242 1297 1314 1318 1349 1366 1424 1475 1478 1485 1497 1500 1504 1507 1514 1528 1616 1645 1676 1737 2977 3003 3014 3069 3071 3152 3163 3182 3189 3193 3193 3203 3209 3227
TS2-1	96i 17 24 32 34 46 52 61 72 81 101 107 132 155 163 179 223 228 287 318 346 349 482 502 511 533 604 608 631 681 699 825 873 937 948 983 1000 1013 1013 1015 1065 1065 1093 1173 1213 1314 1329 1363 1386 1417 1435 1437 1475 1478 1481 1486 1498 1500 1503 1523 1603 1667 1722 3058 3058 3075 3144 3146 3167 3174 3175 3177 3202 3213 3269
INT2-1	14 24 32 38 47 55 62 85 94 108 133 150 156 169 183 192 211 245 271 337 343 398 492 495 522 550 606 612 649 683 691 819 897 927 952 980 1003 1011 1013 1022 1060 1066 1098 1173 1217 1312 1320 1368 1387 1396 1437 1441 1475 1482 1487 1489 1499 1499 1500 1518 1626 1674 1699 3058 3060 3083 3143 3147 3171 3174 3180 3186 3214 3231 3274
TS2-2	1280i 17 43 48 52 59 68 80 113 125 133 150 156 200 209 217 237 280 291 312 340 405 445 507 513 558 611 630 636 678 701 749 823 917 928 946 999 1006 1023 1041 1060 1067 1105 1172 1213 1282 1287 1328 1372 1390 1396 1431 1464 1480 1482 1490 1490 1496 1498 1499 1581 1599 1635 1658 3057 3066 3085 3131 3142 3153 3173 3183 3189 3192 3219
INT2-2	26 29 40 44 62 71 77 86 115 122 139 152 163 184 204 228 239 260 313 336 409 489 491 501 605 606 612 647 667 675 763 808 924 927 932 947 1013 1025 1040 1059 1068 1079 1086 1172 1210 1255 1301 1370 1395 1403 1420 1472 1482 1485 1486 1493 1497 1499 1525 1560 1612 1654 1692 2421 3053 3066 3082 3132 3148 3156 3172 3185 3185 3196 3212
TS2-3a	390i 18 27 29 38 40 43 45 58 65 73 75 77 85 90 101 111 125 127 136 141 156 169 180 181 208 219 231 237 242 264 327 345 359 459 469 485 496 524 547 565 603 605 606 632 674 680 683 709 730 737 769 790 832 858 911 912 914 932 938 964 980 991 996 1005 1011 1019 1025 1028 1035 1057 1063 1067 1068 1144 1169 1173 1177 1190 1192 1209 1227 1287 1321 1324 1338 1352 1372 1375 1403 1416 1446 1467 1472 1476 1482 1483 1487 1493 1494 1497 1503 1505 1531 1532 1542 1626 1667 1697 1717 2546 3047 3051 3063 3069 3076 3130 3144 3146 3146 3158 3164 3169 3169 3172 3175

	3183 3190 3194 3195 3205 3227
INT2-3a	21 23 26 35 38 42 47 55 56 69 71 80 82 96 98 115 122 133 140 149 162 168 173 182 199 217 232 244 249 308 319 334 364 429 462 473 484 492 520 583 596 602 607 628 650 667 698 708 717 736 749 783 830 846 884 909 911 929 932 977 979 984 989 994 1004 1004 1011 1026 1031 1047 1050 1053 1061 1068 1103 1126 1174 1183 1196 1200 1220 1254 1299 1316 1316 1343 1354 1373 1401 1413 1415 1420 1457 1474 1476 1482 1483 1487 1491 1494 1495 1497 1503 1519 1551 1576 1672 1684 1702 1744 2649 3046 3051 3054 3063 3072 3130 3144 3144 3153 3157 3166 3168 3169 3169 3173 3186 3187 3190 3198 3199 3220
TS2-3b	404i 15 23 27 34 40 43 54 57 68 75 76 85 87 104 110 120 124 130 138 146 159 178 182 208 217 235 239 260 283 315 343 353 385 451 466 484 491 530 554 602 604 606 616 632 673 679 682 735 751 811 837 862 913 914 927 935 954 984 992 1008 1012 1017 1025 1027 1031 1034 1054 1061 1068 1078 1135 1159 1172 1174 1177 1190 1193 1206 1218 1229 1269 1309 1325 1336 1350 1369 1403 1415 1429 1447 1464 1472 1476 1483 1483 1487 1494 1497 1500 1504 1511 1529 1530 1537 1552 1629 1666 1697 1719 2558 2993 3005 3051 3064 3069 3073 3100 3130 3144 3148 3154 3158 3163 3169 3170 3187 3191 3194 3200 3213 3227
INT2-3b	23 26 35 41 49 52 57 62 67 72 82 86 90 100 114 116 128 138 143 149 163 169 188 213 227 228 238 263 287 312 341 355 372 429 462 471 485 499 580 587 601 602 610 628 657 666 700 735 747 791 834 847 883 909 927 928 954 968 985 990 994 1008 1012 1016 1024 1028 1040 1056 1061 1068 1108 1116 1140 1162 1174 1180 1193 1199 1217 1220 1240 1277 1299 1315 1341 1355 1402 1404 1412 1421 1427 1456 1474 1476 1482 1482 1487 1493 1497 1499 1503 1512 1513 1531 1563 1583 1672 1685 1704 1747 2700 3001 3007 3052 3064 3072 3072 3112 3131 3145 3149 3161 3162 3169 3170 3179 3189 3191 3192 3199 3202 3221
TS2-hom	287i 19 27 30 39 43 45 52 53 66 75 80 96 99 107 131 138 141 146 157 158 180 203 218 229 242 251 290 322 336 349 442 473 495 502 529 558 602 609 632 636 661 671 731 752 833 855 869 914 916 926 951 997 1012 1015 1027 1036 1042 1063 1068 1098 1123 1166 1172 1174 1197 1210 1220 1231 1285 1305 1336 1349 1402 1408 1412 1473 1473 1477 1482 1486 1492 1497 1497 1500 1503 1503 1508 1609 1682 1693 1735 1755 2742 3054 3065 3072 3074 3134 3147 3150 3165 3168 3171 3172 3174 3195 3198 3199 3200 3282
INT2-hom	21 29 37 39 47 51 54 61 76 80 84 94 101 120 128 141 145 148 157 167 182 203 209 225 247 264 310 320 336 376 427 450 469 492 534 600 605 612 632 661 666 727 756 766 843 863 898 908 922 931 965 969

	1015 1022 1024 1026 1036 1063 1064 1068 1077 1174 1174 1192 1206 1211 1230 1243 1274 1296 1309 1329 1345 1400 1402 1422 1465 1474 1475 1481 1482 1483 1487 1493 1497 1497 1502 1505 1582 1684 1697 1741 1752 2952 3056 3065 3071 3074 3102 3138 3147 3163 3167 3171 3172 3173 3179 3195 3195 3197 3202
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Table S3. The eletron-energies calculated at the B3LYP/DZVP, B3LYP/BS1 and M062x/BS1 levels of theory (BS1 = DZVP_{Pd} + 6-311+G**_{C,H,O,S}), zero-point energies and Gibbs free-energies for all the stationary points (in Hartree), in solution (IDSCRF) at 373K.

Species	Electron-Energies			Zero-Point Energies	Free-Energies (DZVP)
	E(DZVP)	E(BS1)	E(M062x)		
TS-1a	-6105.83817	-6106.01800	-6105.87307	0.260429	-6105.64290
INT-1a	-6105.86349	-6106.04611	-6105.89972	0.261437	-6105.66648
TS-2a	-6105.82358	-6106.01050	-6105.86448	0.256299	-6105.62558
INT-2a	-6105.86715	-6106.05532	-6105.91778	0.261037	-6105.66653
TS-3a	-6412.35367	-6412.58924	-6412.32814	0.357594	-6412.07726
INT-3a	-6412.39358	-6412.62759	-6412.37351	0.360528	-6412.11371
TS-4a	-6412.37897	-6412.61369	-6412.35766	0.359188	-6412.09793
INT-4a	-6412.38469	-6412.62155	-6412.36331	0.358891	-6412.10500
TS-5a	-6412.36958	-6412.60827	-6412.34494	0.355378	-6412.09234
INT-5a	-6412.37468	-6412.61245	-6412.34679	0.356798	-6412.09705
TS-6a	-6412.35179	-6412.58892	-6412.33007	0.355961	-6412.07895
INT-6a	-5397.97152	-5398.04745	-5398.07338	0.121721	-5397.89220
INT-7a	-5397.98806	-5398.06670	-5398.10358	0.124204	-5397.90819
1a	-709.06307	-709.17776	-708.99371	0.157316	-708.93944
2	-306.51760	-306.56721	-306.43022	0.095243	-306.44940
3a	-1014.38871	-1014.54847	-1014.24438	0.233855	-1014.20424
1b	-386.12240			0.161037	-385.99450
Pd(OAc)₂	-5396.77719	-5396.84734	-5396.86994	0.102598	-5396.71366
TS-1b	-5782.89366				-5782.69093
INT-1b	-5782.90451			0.265442	-5782.70175
TS-2b	-5782.86675			0.260135	-5782.66516
INT-2b	-5782.64576			0.264623	-5782.70511
TS-3b	-6089.41435			0.361845	-6089.12733
INT-3b	-6089.45424			0.364631	-6089.16552
TS-4b	-6089.43966			0.362934	-6089.15413
INT-4b	-6089.44440			0.362471	-6089.16084
TS-5b	-6089.42870			0.358993	-6089.14666
INT-5b	-6089.43384			0.360306	-6089.15198
TS-6b	-6089.41147			0.359576	-6089.13179
3b	-691.44847			0.237604	-691.25816

TS2-1	-5703.28691			0.198099	-5703.14896
INT2-1	-5703.29893			0.199130	-5703.16003
TS2-2	-5703.25409			0.194364	-5703.11480
INT2-2	-5703.30650			0.198786	-5703.16415
TS2-3a	-6412.32753			0.356285	-6412.04940
INT2-3a	-6412.34528			0.358428	-6412.06574
TS2-3b	-6089.38883			0.360202	-6089.10562
INT-2a1b	-6089.40907			0.362835	-6089.12149
TS-hom	-6009.81408			0.296060	-6009.59082
INT-hom	-6009.85797			0.299507	-6009.62949

Table S4. The eletron-energies and Gibbs free-energies (in Hartree) of different directing-group systems, calculated at the B3LYP-IDSCRF(DCE) level of theory at 373K. ($E_{\text{PdOAc}} = -5396.77719$ and $G_{\text{PdOAc}} = -5396.71366$)

Names	Simple Molecules		Pd-Complexes		Transition State	
	<i>E</i>	<i>G</i>	<i>E</i>	<i>G</i>	<i>E</i>	<i>G</i>
<i>sp</i>³-P	-692.15550	-691.99761	-6088.98099	-6088.74829	-	-
<i>sp</i>³-N	-405.56254	-405.39504	-5802.36582	-5802.12087	-5802.33713	-5802.09663
<i>sp</i>³-Cl	-731.15286	-731.06177	-6127.92394	-6127.76488	-6127.91328	-6127.7594
<i>sp</i>³-F	-370.84692	-370.75320	-5767.61237	-5767.45148	-5767.61186	-5767.44953
<i>sp</i>³-S	-709.06307	-708.93944	-6105.86349	-6105.66648	-6105.83817	-6105.64290
<i>sp</i>³-O	-386.12240	-385.99450	-5782.90451	-5782.70175	-5782.89366	-5782.69093
<i>sp</i>²-P	-690.91922	-690.78169	-6087.72651	-6087.51550	-6087.69299	-6087.48505
<i>sp</i>²-S	-707.84755	-707.74346	-6104.64307	-6104.46733	-6104.61881	-6104.44401
<i>sp</i>²-N	-404.35686	-404.21397	-5801.16143	-5800.94406	-5801.13082	-5800.91658
<i>sp</i>²-O	-384.94014	-384.83223	-5781.71947	-5781.54142	-5781.70827	-5781.53058

Table S5. The relative eletron-energies (in kcal/mol) of some selected stationary points, calculated at the B3LYP/DZVP, B3LYP/BS1 and M062x/BS1 levels of theory (BS1 = DZVP_{Pd} + 6-311+G**_{C,H,O,S}), respectively, in solution (IDSCRF) at 373 K.

Methods	TS-1a	INT-1a	TS-2a	INT-2a	TS-3a	INT-3a	TS-4a
a	1.3	-14.6	10.5	-16.9	2.6	-22.4	-13.2
b	4.2	-13.2	9.2	-18.9	1.9	-22.1	-13.4
c	-5.9	-22.6	-0.5	-34.0	-21.5	-50.0	-40.0
Methods	INT-4a	TS-5a	INT-5a	TS-6a	INT-6a	INT-7a	
a	-16.8	-7.4	-10.6	3.8	-1.5	-11.9	
b	-18.3	-9.8	-12.4	2.1	-2.3	-14.1	
c	-43.6	-32.0	-33.2	-22.7	-15.0	-33.9	

- B3LYP-IDSCRF/DZVP calculation results
- B3LYP-IDSCRF/DZVP+6-311g(d, p) single point energies
- M062x-IDSCRF/DZVP+6-311g(d, p) single point energies

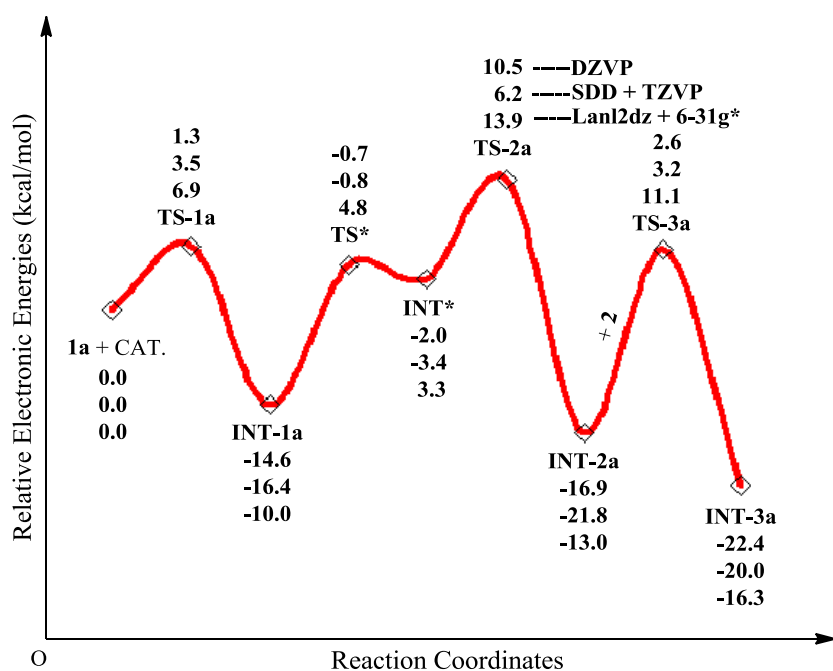


Figure S1. Electronic energy (in kcal/mol) profiles for selected reaction processes (C-H activation and migration insertion), calculated at the B3LYP-IDSCRF level of theory employing DZVP, SDD + TZVP and Lanl2dz + 6-31g* basis sets for comparison. These results indicate that the basis set effect is not evident if the Pd's oxidation state remains the same.

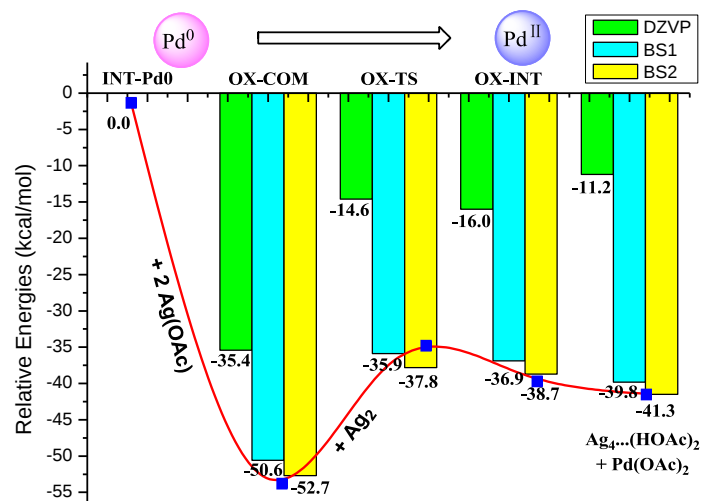


Figure S2. Electronic energy (in kcal/mol) profile of the reoxidation process, characterized at the B3LYP-IDSCRF level of theory employing DZVP, BS1 and BS2 basis sets for comparison. The basis effect is obvious for this $\text{Pd}^0 \rightarrow \text{Pd}^{\text{II}}$ process, which is tightly related to the change of oxidation state of central palladium and the change of bonding character between central palladium and ligands.

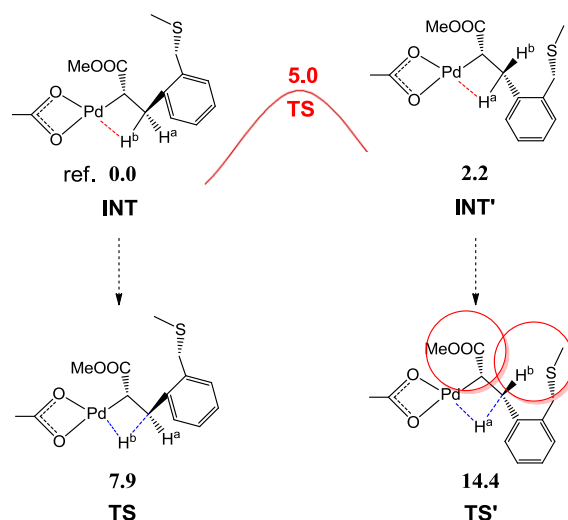


Figure S3. Two possible β -H elimination routes for eliminating H^a (right) or H^b (left) with the calculated free-energies (in kcal/mol) of the involved stationary points. These data surely support that the formation of *trans*-**3a** is more favorable than that of *cis*-**3a**.

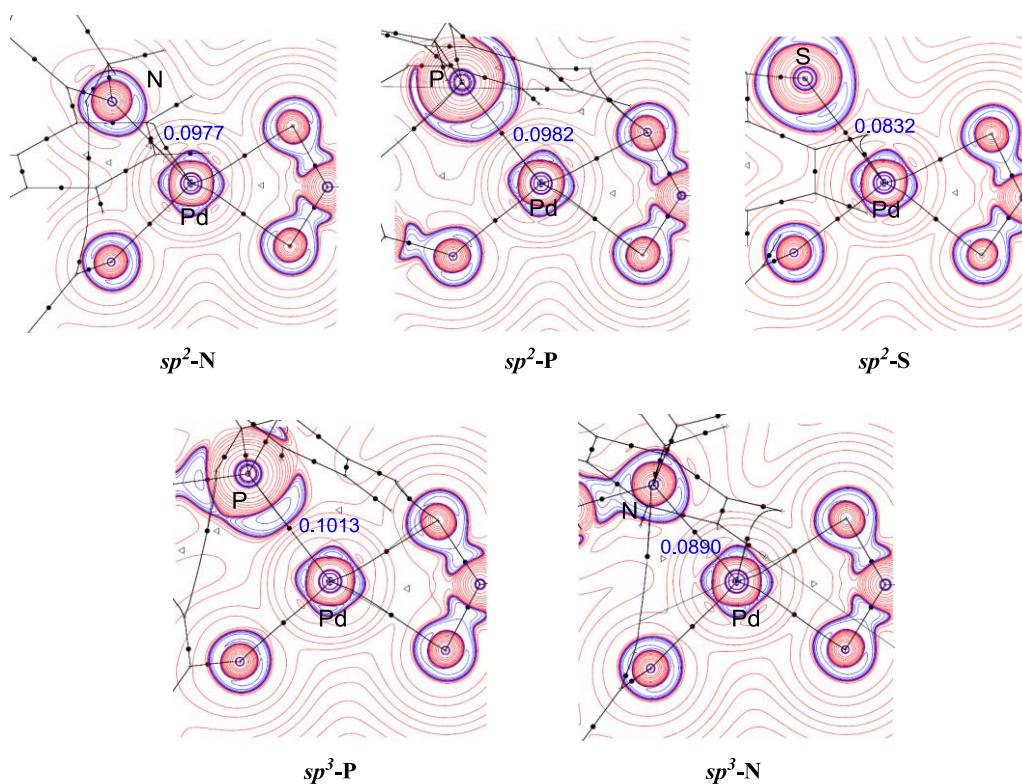


Figure S4. ORTEP plot of complexes formed between catalyst and sp^n -X systems. Depiction of the “onion layer” 2-D isodensity surfaces were provided from the Laplacian of electron densities ($\nabla^2\rho$) in different plane selected, with the bond paths, electron densities (ρ_b in a.u.) and bond critical points are shown in solid black line, blue text and small black dot, respectively.