

## Supporting Information for:

# Stereoselectivity predictions for the Pd-catalyzed 1,4-conjugate addition using Q2MM

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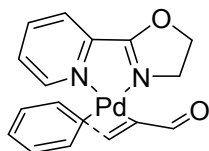
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**Table S1 QM structures in Training Set**



TS 1.

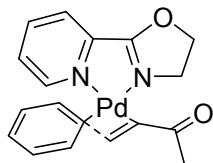
Gibbs Free Energy: -1043.630127 (Hartrees)

Imaginary Frequency: -253.28 cm<sup>-1</sup>

Cartesian coordinates and point charges:

Pd	0.041817	-0.684382	0.182160	-0.253110
C	4.592934	0.602094	-0.110789	-0.027170
C	4.018355	0.428767	1.148175	-0.083900
C	2.781911	-0.204419	1.273404	-0.213940
C	2.122801	-0.650881	0.126470	0.279800
C	2.700522	-0.499305	-1.136000	-0.159160
C	3.934685	0.139005	-1.250587	-0.099990
H	5.564199	1.084422	-0.203757	0.101060
H	4.536170	0.778104	2.040073	0.115500
H	2.338302	-0.346097	2.260034	0.153390
H	2.194039	-0.874951	-2.027065	0.117500
H	4.386879	0.263606	-2.233321	0.120900
C	-0.045238	-2.779528	0.368967	0.014560
C	1.355797	-2.611047	0.412379	-0.150220
H	-0.615344	-2.961413	1.284703	0.118120
C	-0.688635	-3.195637	-0.897966	0.422420
O	-1.854321	-3.510309	-0.986584	-0.461170
H	-0.018542	-3.191154	-1.791502	0.038090
H	1.939140	-2.918943	-0.455684	0.094350
H	1.873242	-2.707110	1.364049	0.134140
C	-0.629045	4.223928	-0.333258	0.055490
C	-1.676275	3.311452	-0.207451	-0.164700
C	-1.359861	1.971141	-0.056430	0.240120
C	0.906923	2.390922	-0.148572	0.210430
C	0.677395	3.758408	-0.303327	-0.167990
H	-0.837528	5.284760	-0.454131	0.123700
H	-2.717389	3.625087	-0.225710	0.136850
H	1.917364	1.984403	-0.119686	0.025650
H	1.520934	4.437400	-0.398063	0.140160
C	-2.372597	0.921774	0.086519	0.340610
C	-4.387036	-0.022032	0.139209	0.253100
C	-3.301836	-1.073852	0.409078	-0.029930
H	-5.144318	0.064655	0.921370	0.053090
H	-4.873200	-0.136227	-0.835186	0.046710
H	-3.343132	-1.932556	-0.270161	0.084450
H	-3.322407	-1.459905	1.437500	0.069380
O	-3.655479	1.241449	0.100776	-0.358020

N	-2.058702	-0.319074	0.210819	-0.098170
N	-0.088212	1.515304	-0.025859	-0.222100



TS 2.

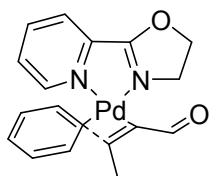
Gibbs Free Energy: -1082.89913 (Hartrees)

Imaginary Frequency: -254.32 cm<sup>-1</sup>

Cartesian coordinates and point charges:

Pd	-0.024175	-0.538439	-0.257068	-0.239250
C	-4.638681	0.532780	-0.044464	-0.064690
C	-4.005545	0.448356	-1.284536	-0.061860
C	-2.741749	-0.130862	-1.388807	-0.226330
C	-2.107052	-0.609793	-0.239982	0.304050
C	-2.742399	-0.542330	1.002192	-0.201830
C	-4.007994	0.036548	1.096134	-0.068650
H	-5.631653	0.971842	0.031550	0.110840
H	-4.499625	0.823911	-2.179211	0.109990
H	-2.257259	-0.209869	-2.363113	0.153950
H	-2.260622	-0.937667	1.897496	0.131270
H	-4.503200	0.091157	2.064413	0.113370
C	0.159971	-2.605440	-0.613296	-0.119720
C	-1.249241	-2.507392	-0.589813	-0.061810
H	0.670363	-2.667334	-1.579587	0.137460
C	0.972921	-3.150791	0.518127	0.609750
O	2.148882	-3.400390	0.320491	-0.534330
H	-1.797893	-2.898492	0.265480	0.067110
H	-1.786030	-2.576447	-1.533468	0.108640
C	0.385425	4.357058	0.588468	0.058240
C	1.476491	3.516446	0.371192	-0.163550
C	1.229551	2.172412	0.141406	0.240620
C	-1.051793	2.454587	0.324856	0.208650
C	-0.893656	3.819935	0.565286	-0.178260
H	0.538774	5.418067	0.773520	0.123010
H	2.498804	3.886996	0.378713	0.134080
H	-2.038100	1.992156	0.298154	0.027910
H	-1.770307	4.440811	0.731318	0.143380
C	2.297040	1.198019	-0.096863	0.352100
C	4.367348	0.405536	-0.290183	0.232270
C	3.345066	-0.708260	-0.557235	-0.035140
H	5.070462	0.585250	-1.106605	0.059440
H	4.917412	0.278559	0.647855	0.048700
H	3.479216	-1.586476	0.082132	0.094670
H	3.345549	-1.057912	-1.598449	0.077880

O	3.553965	1.607682	-0.142788	-0.356890
N	2.060806	-0.053638	-0.275416	-0.117470
N	-0.014135	1.646877	0.116855	-0.230850
C	0.323152	-3.389299	1.852161	-0.278920
H	-0.253930	-2.518269	2.190477	0.072940
H	-0.367899	-4.242093	1.794690	0.111560
H	1.095385	-3.622071	2.590178	0.107660



TS 3.

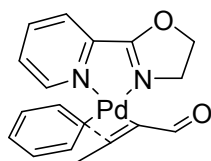
Gibbs Free Energy: -1082.891641 (Hartrees)

Imaginary Frequency: -281.08  $\text{cm}^{-1}$

Cartesian coordinates and point charges:

Pd	-0.090039	-0.554965	-0.110601	-0.307880
C	-4.169071	1.765390	0.332337	-0.031750
C	-3.702103	1.453884	-0.944758	-0.108920
C	-2.676268	0.523379	-1.107042	-0.132450
C	-2.115568	-0.091375	0.015828	0.289460
C	-2.590485	0.211998	1.296197	-0.160190
C	-3.611585	1.147618	1.452302	-0.113540
H	-4.977635	2.483711	0.454749	0.107520
H	-4.140141	1.931544	-1.819939	0.116980
H	-2.319740	0.279912	-2.108965	0.114810
H	-2.167514	-0.281625	2.173586	0.115140
H	-3.980280	1.383635	2.449191	0.124290
C	-0.544268	-2.596003	-0.115632	-0.130710
C	-1.908477	-2.211970	-0.204309	0.144090
H	-0.043741	-3.001919	-1.002518	0.125690
C	0.016620	-3.006181	1.189668	0.464880
O	1.088353	-3.557131	1.319178	-0.471220
H	-0.618489	-2.763498	2.075980	0.016310
H	-2.480068	-2.287777	0.723534	0.036240
C	1.751338	4.066598	0.148601	0.059960
C	2.543201	2.923512	0.042069	-0.181810
C	1.908271	1.695112	-0.050244	0.261080
C	-0.185957	2.655494	0.063560	0.215680
C	0.370488	3.931376	0.159564	-0.176030
H	2.213261	5.048545	0.225755	0.122390
H	3.629318	2.976011	0.033218	0.140900
H	-1.265209	2.503923	0.068842	0.018630
H	-0.281455	4.797322	0.241791	0.141960
C	2.636296	0.427379	-0.154653	0.315260
C	4.366173	-0.972516	-0.165942	0.202670

C	3.054682	-1.748127	-0.359956	-0.015630
H	5.102441	-1.113400	-0.960391	0.064180
H	4.836537	-1.146068	0.807426	0.059830
H	2.899045	-2.540508	0.380952	0.083850
H	2.962819	-2.198309	-1.357880	0.066290
O	3.958834	0.428915	-0.192739	-0.348240
N	2.032636	-0.706180	-0.211318	-0.056980
N	0.563913	1.560910	-0.041619	-0.228040
C	-2.673347	-2.472908	-1.461959	-0.188150
H	-2.854995	-3.556492	-1.518731	0.102050
H	-3.643579	-1.968706	-1.478759	0.048200
H	-2.101788	-2.191240	-2.354944	0.093190



TS 4.

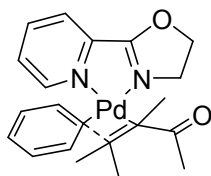
Gibbs Free Energy: -1082.889348 (Hartrees)

Imaginary Frequency: -278.93  $\text{cm}^{-1}$

Cartesian coordinates and point charges:

Pd	-0.091902	-0.504839	-0.206403	-0.396710
C	-4.109640	1.950733	0.288410	-0.092130
C	-3.665332	1.697403	-1.008954	-0.036130
C	-2.640628	0.776715	-1.230319	-0.298750
C	-2.068518	0.105212	-0.146444	0.559120
C	-2.519070	0.353062	1.155168	-0.242060
C	-3.530150	1.285729	1.370805	-0.068150
H	-4.915743	2.662481	0.456651	0.117300
H	-4.121598	2.210809	-1.853973	0.109450
H	-2.298233	0.579824	-2.247569	0.138930
H	-2.085569	-0.183222	2.001961	0.122690
H	-3.874611	1.485601	2.384230	0.116620
C	-0.707667	-2.492823	-0.491888	-0.085520
C	-2.020040	-1.982221	-0.682420	0.000610
H	-0.120119	-2.749893	-1.380682	0.130430
C	-0.278533	-3.175692	0.745034	0.471960
O	0.748815	-3.818372	0.813516	-0.486490
H	-0.928951	-3.050548	1.639980	0.022310
H	-2.261124	-1.758073	-1.723297	0.105410
C	2.059604	3.957415	0.229086	0.055540
C	2.772554	2.760651	0.166641	-0.173220
C	2.057324	1.579342	0.050878	0.248630
C	0.032786	2.686419	0.063665	0.188750
C	0.673544	3.920507	0.177315	-0.163370
H	2.585687	4.905473	0.318236	0.121870
H	3.858938	2.735949	0.205454	0.140340

H	-1.053450	2.610404	0.019713	0.019630
H	0.081704	4.831237	0.222715	0.141970
C	2.699580	0.263850	-0.029386	0.321000
C	4.330919	-1.250362	0.016322	0.250250
C	2.979190	-1.932335	-0.245968	-0.084980
H	5.083629	-1.419278	-0.757310	0.056590
H	4.755766	-1.480394	0.998557	0.046230
H	2.732983	-2.716094	0.479393	0.107200
H	2.906921	-2.378828	-1.246955	0.080550
O	4.019361	0.175438	0.014259	-0.362890
N	2.023888	-0.822998	-0.146738	-0.024290
N	0.707898	1.540815	-0.001273	-0.208380
C	-3.204950	-2.396187	0.138352	-0.154910
H	-4.071289	-1.755532	-0.056499	0.028500
H	-3.464317	-3.422035	-0.166043	0.108110
H	-3.016877	-2.411041	1.216068	0.068000



TS 5.

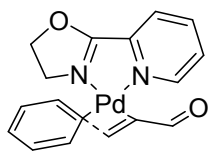
Gibbs Free Energy: -1200.6682 (Hartrees)

Imaginary Frequency: -288.46  $\text{cm}^{-1}$

Cartesian coordinates and point charges:

Pd	-0.078818	-0.234803	-0.090490	-0.498300
C	-3.262539	3.199692	-0.129832	-0.046900
C	-2.854988	2.591359	-1.318228	-0.120230
C	-2.186741	1.370613	-1.282250	-0.187010
C	-1.905791	0.753569	-0.054869	0.478570
C	-2.297275	1.379543	1.133187	-0.216890
C	-2.978106	2.596761	1.094467	-0.096070
H	-3.805775	4.142570	-0.159030	0.110710
H	-3.065260	3.064276	-2.276308	0.119680
H	-1.883570	0.899638	-2.218548	0.132890
H	-2.076961	0.924688	2.099201	0.124030
H	-3.288388	3.070465	2.024750	0.115820
C	-1.140963	-2.031386	-0.327288	0.223570
C	-2.379656	-1.347050	-0.021950	0.031100
C	-0.432867	-2.915678	0.683211	0.582940
O	0.100207	-3.932615	0.273873	-0.520720
C	2.978459	3.699274	0.270676	0.058060
C	3.427097	2.386712	0.131016	-0.181500
C	2.479725	1.377727	0.042002	0.218040
C	0.730505	2.868117	0.220429	0.165440
C	1.613460	3.943976	0.315102	-0.165730

H	3.692313	4.516918	0.343826	0.119090
H	4.486351	2.144628	0.090932	0.138110
H	-0.348846	3.014536	0.254811	0.027050
H	1.222725	4.952802	0.422110	0.139920
C	2.839419	-0.035041	-0.118975	0.347810
C	4.164053	-1.817400	-0.292769	0.145490
C	2.689899	-2.229314	-0.418973	0.025810
H	4.782764	-2.080326	-1.154206	0.077630
H	4.643261	-2.174427	0.624479	0.067000
H	2.389534	-2.991946	0.308582	0.067370
H	2.434585	-2.615890	-1.414869	0.067650
O	4.120364	-0.364270	-0.214061	-0.338800
N	1.964266	-0.974207	-0.187844	-0.095990
N	1.151677	1.612431	0.087316	-0.142170
C	-0.290876	-2.562072	2.144764	-0.396370
H	-0.329762	-1.485300	2.349672	0.103860
H	-1.069601	-3.064569	2.734348	0.133850
H	0.670820	-2.960358	2.488005	0.130680
C	-3.029260	-1.480995	1.333550	-0.281290
H	-3.374720	-2.522361	1.433860	0.114210
H	-2.383648	-1.267536	2.185478	0.096260
H	-3.912853	-0.838025	1.403013	0.090720
C	-0.901166	-2.478454	-1.752753	-0.440440
H	0.122478	-2.841446	-1.877295	0.146160
H	-1.564611	-3.315301	-2.020277	0.120680
H	-1.070171	-1.671412	-2.474930	0.155740
C	-3.435747	-1.305175	-1.098905	-0.146010
H	-3.888272	-2.310248	-1.138717	0.110940
H	-4.227933	-0.590579	-0.850341	0.039500
H	-3.064839	-1.081026	-2.100485	0.048030



TS 6.

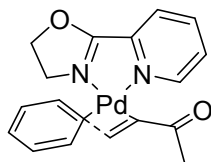
Gibbs Free Energy: -1043.630149 (Hartrees)

Imaginary Frequency: -258.57  $\text{cm}^{-1}$

Cartesian coordinates and point charges:

Pd	-0.132984	-0.599264	-0.171545	-0.268600
C	-0.085500	-2.698225	-0.457888	0.081170
C	-1.480641	-2.501905	-0.504878	-0.204240
C	-2.212701	-0.535880	-0.131613	0.337190
N	-0.067723	1.529392	0.044795	-0.198140
N	2.027516	-0.172637	-0.127091	-0.171580
C	-2.865963	-0.034885	-1.257794	-0.210290
C	-4.663403	0.735309	0.164390	-0.113770
C	-4.095136	0.604860	-1.102329	-0.064990

C	-2.781295	-0.427930	1.138290	-0.174200
C	-4.007980	0.218276	1.282023	-0.048260
H	-5.628798	1.224599	0.279504	0.123070
H	-4.612061	0.995070	-1.977793	0.117580
H	-2.424906	-0.141258	-2.250015	0.142120
H	-2.276635	-0.846624	2.010953	0.113160
H	-4.456840	0.307187	2.270181	0.112780
H	0.483756	-2.839511	-1.381465	0.091160
C	0.531717	-3.208084	0.782345	0.410930
O	1.684191	-3.577638	0.853893	-0.461800
C	1.123908	2.007321	0.079104	0.394150
C	2.305259	1.149077	-0.022543	0.177730
C	3.046715	-1.028888	-0.209959	0.227030
O	1.265437	3.315998	0.215867	-0.340190
C	3.595523	1.650663	-0.002665	-0.142650
C	4.655902	0.749595	-0.099924	0.048370
C	4.376688	-0.603984	-0.202927	-0.192880
C	-0.079304	3.862566	0.350012	0.141320
C	-1.005183	2.647888	0.155475	0.166250
H	3.758134	2.722001	0.088942	0.128950
H	5.683300	1.106780	-0.089482	0.127320
H	-0.143988	4.313453	1.344762	0.071230
H	-0.191138	4.638950	-0.411068	0.072820
H	-1.613249	2.709953	-0.756055	0.006970
H	5.170347	-1.343382	-0.273613	0.157050
H	2.798723	-2.089744	-0.254308	0.075070
H	-1.687092	2.483810	0.998659	-0.006370
H	-1.993032	-2.535398	-1.463345	0.141310
H	-2.078588	-2.836474	0.343005	0.093030
H	-0.137901	-3.222075	1.675467	0.040200



TS 7.

Gibbs Free Energy: -1082.896544 (Hartrees)

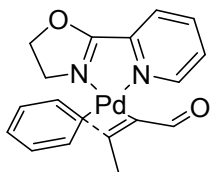
Imaginary Frequency: -260.29  $\text{cm}^{-1}$

Cartesian coordinates and point charges:

Pd	-0.129216	-0.456686	-0.249796	-0.227390
C	-0.056604	-2.532945	-0.663151	-0.068540
C	-1.456603	-2.353966	-0.659992	-0.090710
C	-2.212432	-0.421069	-0.247264	0.305660
N	-0.097623	1.652746	0.153708	-0.228980
N	2.025296	0.016552	-0.222899	-0.189570
C	-2.817412	0.119754	-1.383331	-0.211050



C	-4.671270	0.858037	-0.018364	-0.146490
C	-4.047641	0.763781	-1.262245	-0.017120
C	-2.837849	-0.346864	0.998293	-0.179530
C	-4.067771	0.300745	1.108278	-0.046340
H	-5.637964	1.350205	0.070421	0.129770
H	-4.522933	1.184227	-2.147281	0.102150
H	-2.338018	0.036507	-2.359812	0.137850
H	-2.376092	-0.787975	1.882808	0.118360
H	-4.557846	0.361359	2.078900	0.113030
H	0.461529	-2.593421	-1.625550	0.112970
C	0.690859	-3.179483	0.455274	0.581300
O	1.848549	-3.515022	0.264174	-0.518150
C	1.085366	2.147633	0.213814	0.413720
C	2.279465	1.327292	0.007454	0.176370
C	3.059354	-0.799412	-0.433782	0.235780
O	1.207904	3.441341	0.468445	-0.340950
C	3.559158	1.854572	0.042938	-0.159940
C	4.634977	0.994095	-0.175534	0.062620
C	4.380080	-0.346058	-0.418183	-0.199850
C	-0.145461	3.962538	0.611009	0.124660
C	-1.051276	2.733581	0.407001	0.188430
H	3.701690	2.915140	0.236905	0.132880
H	5.654541	1.372703	-0.154216	0.122440
H	-0.216320	4.409269	1.606539	0.075150
H	-0.272619	4.739906	-0.147639	0.073500
H	-1.732533	2.837956	-0.446515	-0.003660
H	5.185421	-1.055307	-0.591377	0.157150
H	2.831909	-1.853178	-0.596246	0.075540
H	-1.658675	2.492542	1.288475	-0.003280
H	-1.979972	-2.353106	-1.613529	0.113190
H	-2.044279	-2.738849	0.171691	0.058180
C	0.008231	-3.410883	1.773456	-0.269030
H	0.743347	-3.769242	2.498910	0.097680
H	-0.462215	-2.494127	2.153948	0.079260
H	-0.779393	-4.170761	1.673551	0.112950



TS 8.

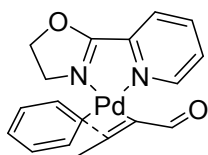
Gibbs Free Energy: -1082.891922 (Hartrees)

Imaginary Frequency: -283.92  $\text{cm}^{-1}$

Cartesian coordinates and point charges:

Pd	-0.110425	-0.470045	-0.080490	-0.309560
C	-0.422696	-2.545720	-0.212485	-0.094280

C	-1.808753	-2.256917	-0.309317	0.067650
C	-2.163965	-0.167137	0.015725	0.317010
N	0.272595	1.639681	-0.013201	-0.205360
N	2.086270	-0.367308	-0.101528	-0.107310
C	-2.754897	0.463544	-1.081496	-0.097240
C	-4.353697	1.509900	0.399459	-0.115230
C	-3.850299	1.302818	-0.885011	-0.079890
C	-2.670541	0.033098	1.303733	-0.200320
C	-3.762789	0.877375	1.493157	-0.057810
H	-5.216684	2.156496	0.546931	0.126420
H	-4.314752	1.792411	-1.739925	0.112410
H	-2.366461	0.304423	-2.088476	0.100070
H	-2.221456	-0.473922	2.160145	0.124110
H	-4.161517	1.028341	2.495100	0.117960
H	0.116422	-2.853362	-1.116516	0.104660
C	0.130535	-3.025474	1.067055	0.478800
O	1.221007	-3.547045	1.173880	-0.480060
C	1.522613	1.932359	-0.021467	0.427520
C	2.560042	0.901202	-0.089582	0.124310
C	2.963554	-1.370847	-0.142053	0.184090
O	1.863865	3.210340	0.044963	-0.356820
C	3.910905	1.203098	-0.125689	-0.135410
C	4.821970	0.148289	-0.179574	0.050480
C	4.341783	-1.151746	-0.185129	-0.182880
C	0.619146	3.965597	0.110901	0.174370
C	-0.482342	2.889054	0.081630	0.150040
H	4.233738	2.241403	-0.109627	0.130640
H	5.891023	0.347123	-0.209873	0.122800
H	0.646569	4.553404	1.032530	0.063260
H	0.606216	4.638820	-0.750775	0.063630
H	-1.154181	2.984218	-0.780245	-0.007800
H	5.014708	-2.004882	-0.214866	0.153430
H	2.556407	-2.381699	-0.108105	0.095970
H	-1.104894	2.875547	0.985514	0.004260
H	-0.524307	-2.870859	1.958174	0.008960
H	-2.388797	-2.423184	0.601180	0.052840
C	-2.531830	-2.496993	-1.594737	-0.126450
H	-3.536385	-2.064851	-1.602343	0.022770
H	-1.967780	-2.123384	-2.458211	0.079130
H	-2.631804	-3.585977	-1.716437	0.098820



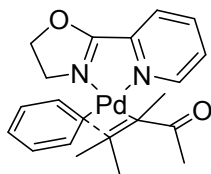
TS 9.

Gibbs Free Energy: -1082.888104 (Hartrees)

Imaginary Frequency: -283.19 cm<sup>-1</sup>

Cartesian coordinates and point charges:

Pd	-0.103953	-0.424806	-0.182276	-0.379290
C	-0.529811	-2.469650	-0.504663	-0.052520
C	-1.880634	-2.080158	-0.708020	0.001970
C	-2.129243	-0.013118	-0.148082	0.525530
N	0.383818	1.646950	0.019395	-0.210930
N	2.101631	-0.445014	-0.100086	-0.072030
C	-2.731444	0.622911	-1.235995	-0.271090
C	-4.325603	1.645847	0.265112	-0.129120
C	-3.834987	1.449325	-1.025225	-0.057140
C	-2.621187	0.178919	1.147063	-0.213460
C	-3.714535	1.016723	1.351170	-0.048520
H	-5.192747	2.283804	0.425306	0.129490
H	-4.315413	1.935247	-1.873220	0.120000
H	-2.349943	0.471887	-2.247209	0.136930
H	-2.159901	-0.329898	1.996064	0.117930
H	-4.098478	1.169079	2.358759	0.113330
H	0.084514	-2.654337	-1.393507	0.103230
C	-0.064947	-3.147849	0.717033	0.455070
O	1.002734	-3.725689	0.778522	-0.480150
C	1.646752	1.874933	0.066146	0.462330
C	2.634299	0.796085	-0.003902	0.100660
C	2.930365	-1.487878	-0.153814	0.168340
O	2.047606	3.131441	0.186541	-0.379270
C	3.998204	1.032200	0.033978	-0.129770
C	4.859288	-0.063265	-0.030277	0.044860
C	4.318383	-1.336066	-0.123164	-0.175890
C	0.840087	3.942410	0.271553	0.240340
C	-0.310336	2.931562	0.105616	0.057890
H	4.369825	2.051089	0.113758	0.130880
H	5.936911	0.082688	-0.003016	0.123050
H	0.856811	4.440927	1.245076	0.053200
H	0.898055	4.691044	-0.522842	0.049920
H	-0.899146	3.096362	-0.805555	0.033360
H	4.950854	-2.219161	-0.165694	0.152140
H	2.472968	-2.477245	-0.198207	0.098550
H	-1.005804	2.923135	0.953952	0.011260
H	-2.125535	-1.859936	-1.748642	0.103370
H	-0.724448	-3.086045	1.611198	0.024470
C	-3.035379	-2.611606	0.086604	-0.169840
H	-3.953660	-2.051969	-0.119846	0.032610
H	-3.192594	-3.653891	-0.231749	0.114000
H	-2.866903	-2.619241	1.167611	0.064260



TS 10.

Gibbs Free Energy: -1200.665558 (Hartrees)

Imaginary Frequency: -303.83  $\text{cm}^{-1}$

Cartesian coordinates and point charges:

Pd	-0.071803	-0.163110	-0.098565	-0.536860
C	-0.743027	-2.147678	-0.364699	0.342080
C	-2.111811	-1.735908	-0.140846	-0.109050
C	-2.066002	0.413409	-0.053849	0.532070
N	0.639955	1.871094	0.079099	-0.146340
N	2.170668	-0.376776	-0.135495	-0.082490
C	-2.488875	1.026069	-1.241128	-0.215650
C	-3.895342	2.527746	0.023554	-0.132490
C	-3.398504	2.079260	-1.200928	-0.058650
C	-2.549907	0.883410	1.171474	-0.221050
C	-3.464839	1.934156	1.208978	-0.060350
H	-4.621755	3.337960	0.052888	0.130310
H	-3.726741	2.544638	-2.129266	0.108790
H	-2.111293	0.683727	-2.205540	0.138840
H	-2.220240	0.432296	2.107630	0.128790
H	-3.844363	2.285721	2.167391	0.111920
C	0.051697	-2.875914	0.694478	0.456350
O	0.786328	-3.781909	0.332172	-0.499750
C	1.917140	1.979080	0.052199	0.398710
C	2.803376	0.817579	-0.061894	0.150140
C	2.921827	-1.474715	-0.232932	0.151680
O	2.444357	3.194739	0.132628	-0.362840
C	4.183512	0.947564	-0.085960	-0.151860
C	4.957192	-0.207103	-0.190489	0.050850
C	4.316123	-1.433980	-0.263904	-0.183030
C	1.327100	4.117279	0.273413	0.186140
C	0.079966	3.218286	0.185240	0.110020
H	4.633346	1.935455	-0.020828	0.131430
H	6.042772	-0.141756	-0.211759	0.123210
H	1.444331	4.618968	1.238683	0.058100
H	1.409937	4.852633	-0.531325	0.062070
H	-0.544958	3.427591	-0.692693	0.008400
H	4.874192	-2.363638	-0.342323	0.149150
H	2.400407	-2.431359	-0.277364	0.114940
H	-0.563209	3.285129	1.071307	0.002240
C	-2.811636	-2.052341	1.157829	-0.218150
H	-3.801786	-1.586011	1.188938	0.077480
H	-2.959964	-3.143818	1.191543	0.115600
H	-2.272102	-1.770801	2.061881	0.062330

C	-3.074168	-1.869383	-1.293574	-0.111220
H	-4.017024	-1.352512	-1.084832	0.036740
H	-2.689981	-1.524782	-2.255172	0.033900
H	-3.294829	-2.944591	-1.400778	0.108640
C	0.062436	-2.481481	2.151997	-0.212250
H	1.084727	-2.625408	2.520837	0.068250
H	-0.244372	-1.445564	2.339962	0.071320
H	-0.580248	-3.157125	2.732713	0.104380
C	-0.337500	-2.536059	-1.770940	-0.352830
H	0.743539	-2.678543	-1.846584	0.089930
H	-0.798329	-3.492209	-2.063492	0.102040
H	-0.631483	-1.781458	-2.509547	0.138020

**Table S2: TSFF Parameters added to the Standard MM3 Force Field**

C Carbonyl bond OPT

9 Pd.C2-C2=O2

-2

1 3 4            1.2080 12.5120 2.7884

1 2 3            1.5000 4.6494 -0.1043

-3

C Palladium 1,4-conj\_add OPT

9 N2.Pd-C2.C2=C2.2

-2

2 H1 4 H1        114.7060 0.3167

2 H1 4 C0        116.4597 0.7008

2 C0 4 C0        111.5649 1.6814

2 H1 5 H1        116.1335 0.4271

2 H1 5 C0        116.4352 0.6303

2 C0 5 C0        113.6399 1.1304

-3

C Palladium 1,4-conj\_add OPT

9 N2.Pd(-C2.C2=C2.2)(.N2)

-2

aA 1 2 3        180.0000 45.0000

1 AA 3            1.4008 4.0520 -0.5205

1 C0 4            1.4986 4.6388 0.3874

1 H1 4            1.0887 5.6177 0.5626

1 C3 5            1.4919 5.4066 -0.6529

1 H1 5            1.0940 5.3908 0.7706

1 2 3            2.0808 2.0591 -3.0514

1 2 5            2.1051 1.8988 -3.1035

1 3 4            2.1200 2.2151 -0.5741

1 4 5            1.4186 5.6388 0.6100

2 1 2 3          93.4906 0.0381

a2 1 2 3        171.7862 0.6146

2 1 2 5        174.5624 0.1644

a2 1 2 5        96.8402 0.8644

2 1 2 6	76.4398	2.7049	
2 3 2 5	91.3167	0.7108	
2 2 3 00	115.9518	1.0480	
2 4 3 00	111.8124	0.9574	
2 2 3 4	68.0653	0.3880	
2 3 4 5	113.6471	0.0397	
2 3 4 H1	88.6724	0.5462	
2 3 4 C0	99.7976	1.2805	
2 5 4 H1	116.9272	0.6223	
2 5 4 C3	121.7670	0.4535	
2 2 5 4	83.9894	0.0347	
2 2 5 H1	104.4516	0.3705	
2 2 5 C0	101.6436	1.3981	
4 00 00 3 2	0.0000	0.0000	0.0000
4 00 00 3 4	0.0000	0.0000	0.0000
4 00 00 4 3	0.0000	0.0000	0.0000
4 C0 1 2 3	0.0000	5.8459	0.0000
a4 C0 1 2 3	0.0000	0.0000	0.0000
4 00 1 2 5	0.0000	0.0000	0.0000
a4 00 1 2 5	0.0000	2.3843	0.0000
4 C0 1 2 5	0.0000	0.0000	0.0000
a4 C0 1 2 5	0.0000	0.1258	0.0000
4 00 1 2 6	0.0000	0.0000	0.0000
4 1 2 3 00	0.0000	0.4832	0.0000
a4 1 2 3 00	0.0000	0.0000	0.0000
4 1 2 3 4	0.0000	2.0523	0.0000
a4 1 2 3 4	0.0000	0.0000	0.0000
4 5 2 3 00	0.0000	0.0000	0.0000
4 5 2 3 4	0.0000	1.8405	0.0000
4 1 2 5 00	0.0000	0.0000	0.0000
a4 1 2 5 00	0.0000	0.0000	0.0000
4 1 2 5 4	0.0000	0.0000	0.0000
a4 1 2 5 4	0.0000	1.9308	-0.9674
4 1 2 5 H1	0.0000	0.0000	0.0000
a4 1 2 5 H1	0.0000	0.5019	0.0000
4 1 2 5 C0	0.0000	0.0000	0.0000
a4 1 2 5 C0	0.0000	0.0000	0.8621
4 3 2 5 00	0.0000	0.0000	0.0000
4 3 2 5 4	0.0000	0.0000	0.0000
4 3 2 5 H1	0.0000	0.0000	0.0000
4 3 2 5 C0	0.0000	0.0000	0.0000
4 00 3 4 5	0.0000	0.0000	0.0000
4 00 3 4 H1	0.0000	0.0000	0.0000
4 00 3 4 C3	0.0000	0.0000	0.0000
4 2 3 4 5	0.0000	2.6837	0.0000
4 2 3 4 H1	0.0000	0.0000	0.0000
4 2 3 4 C3	0.0000	0.0000	0.0000
4 C0 4 5 C0	0.0000	3.3284	0.0000

4 C0 4 5 H1	0.0000	0.0000	0.0000
4 H1 4 5 C0	0.0000	0.0000	0.0000
4 H1 4 5 H1	0.0000	0.0000	0.0000
4 3 4 5 2	0.0000	0.0000	0.0000
4 3 4 5 H1	0.0000	0.0000	0.0000
4 3 4 5 C0	0.0000	0.0000	0.0000
4 00 4 5 2	0.0000	0.0000	0.0000
4 C0 4 5 2	0.0000	0.0000	0.0000
4 C0 4 C3 C0	0.0000	0.0000	0.0000
4 C0 4 C3 O3	0.0000	0.0000	0.0000
4 C0 4 C3 H1	0.0000	0.0000	0.0000
4 H1 4 C3 C0	0.0000	0.0000	0.0000
4 H1 4 C3 O3	0.0000	0.0000	0.0000
4 H1 4 C3 H1	0.0000	0.0000	0.0000
4 3 4 C3 C0	0.0000	0.0000	0.0000
4 3 4 C3 O3	0.0000	0.0000	0.0000
4 3 4 C3 H1	0.0000	0.0000	0.0000
4 5 4 C3 C0	0.0000	0.0000	0.0000
4 5 4 C3 O3	0.0000	0.0000	0.0000
4 5 4 C3 H1	0.0000	0.0000	0.0000
4 C0 5 C3 C0	0.0000	0.0000	0.0000
4 C0 5 C3 O3	0.0000	0.0000	0.0000
4 C0 5 C3 H1	0.0000	0.0000	0.0000
4 H1 5 C3 C0	0.0000	0.0000	0.0000
4 H1 5 C3 O3	0.0000	0.0000	0.0000
4 H1 5 C3 H1	0.0000	0.0000	0.0000
4 2 5 C0 C0	0.0000	0.2597	0.0000
4 2 5 C2 O2	0.0000	0.1172	0.0000
4 2 5 C0 H1	0.0000	0.0000	0.0000
4 4 5 C0 C0	0.0000	3.3193	0.1910
4 4 5 C3 O3	0.0000	0.0000	0.0000
4 4 5 C3 H1	0.0000	0.0000	0.0000
4 1 3 5 6	0.0000	5.9082	0.0000
a4 1 3 5 6	0.0000	5.9474	0.0000
5 3 2 00 00	0.0000	0.0000	
5 5 4 00 00	0.0000	0.0000	
5 4 5 00 00	0.0000	0.0000	

-3

C Palladium pyridine-extra OPT

9 Pd.N2\*AA

-2

4 AA 2 3 00	0.0000	1.0955	0.0000
4 1 2 3 00	0.0000	2.8000	0.0000

-3

C Palladium pyridine OPT

9 Pd.N2\*AA

-2

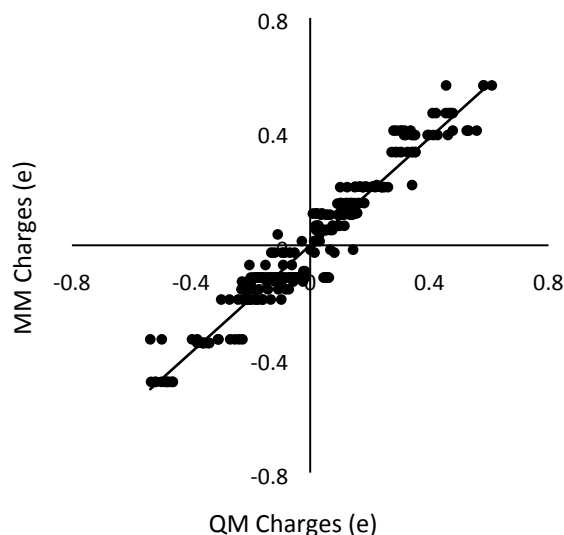
1 1 2	2.2313	2.8324	-4.2389
-------	--------	--------	---------

1 2 3	1.3367	4.5093	-1.7661
1 H1 3	1.1010	4.9903	0.3633
2 1 2 3	120.9121	0.6009	
4 1 2 3 H1	0.0000	0.9804	0.0000
4 1 2 3 C2	0.0000	2.9074	0.0000
-3			
C Palladium oxazoline			
9 Pd.N2=C2-O3-C3-C3-2			
-2			
1 1 2	2.1500	2.6731	-3.3365
1 2 3	1.2712	3.1754	-1.8439
1 2 6	1.4724	3.5244	-1.0506
1 3 4	1.3235	3.3790	0.0991
1 3 C2	1.4600	3.5563	0.4945
1 4 5	1.4373	4.9151	-2.2650
2 1 2 3	114.6086	0.0044	
2 1 2 6	139.7180	0.5554	
2 3 2 6	106.8071	1.0023	
2 2 3 4	118.3343	1.5946	
2 2 3 C0	126.4541	0.5074	
2 4 3 C0	118.5661	0.9830	
2 3 4 5	112.6583	0.5091	
2 4 5 6	104.1000	0.6197	
4 1 2 3 4	0.0000	2.5492	0.0000
4 1 2 3 C2	0.0000	3.6985	0.0000
4 1 2 6 00	0.0000	0.0000	0.0000
5 2 00 00 00	0.0000	0.0000	0.0000
-3			

## Details of Force Field Parameterization

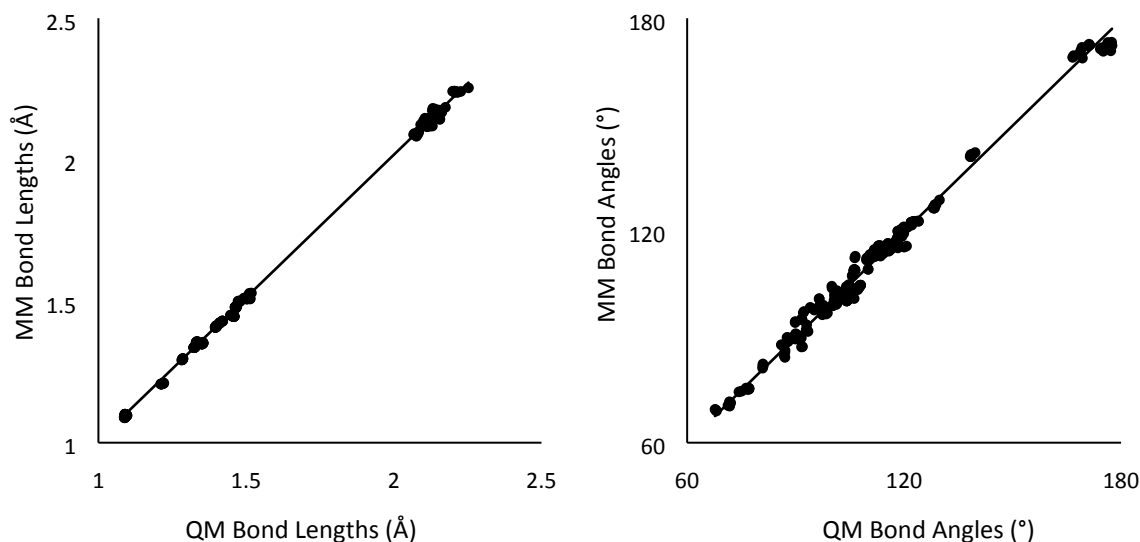
The bond dipoles were the first value parameterized in the force field. The values were optimized using a penalty function only based on the point charge data. After the values were optimized, the point charge values were determined MM and compared to the QM point charge data (Figure S). These values will not be a perfect fit since point charges are not an observable piece of data. Electrostatic fitting methods fit point charges based on the overall charge on the molecule. The MM3 forcefield uses bond dipoles which will give the same point charges for the same type of interaction. This leads to horizontal bands in the graph in which the QM will have different charges for a given type of interaction while MM will give the same point charge.





**Figure S1.** Comparison of point charges between QM and MM methods after parameterization of bond dipoles in force field

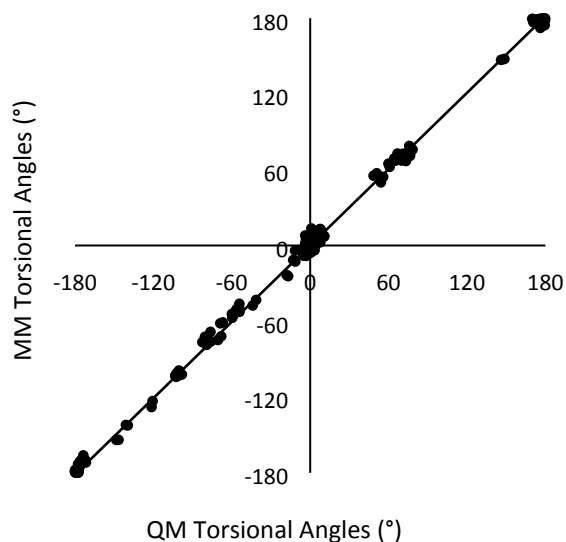
The next parameter that was optimized was the bond and angle force constants. Since force constants are the second derivative of energy, they are described by fitting to Hessian elements. The MM eigenmatrix is compared to an unmodified QM eigenmatrix. The MM eigenmatrix is diagonalized from the MM Hessian and QM eigenvectors. Once the force constants were parameterized, the bond lengths and angles were compared between the QM and MM structures. These data types showed good agreement between the QM and MM structures (Figure S). Therefore, the force field is able to accurately reproduce the structural information of the reference structures.



**Figure S2.** Comparison of bond lengths and angles between QM and MM methods after parameterization of the bond and angle force constants.

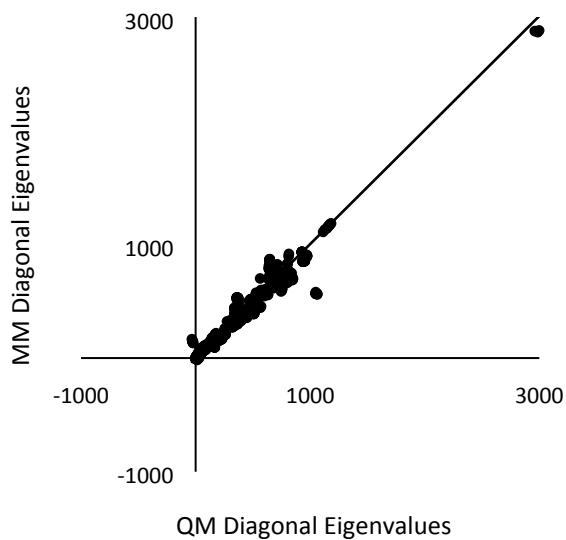
Torsional parameters are typically the last parameter altered in the force field. Since we are fitting to a TS, only a few torsional terms are parameterized. The torsional terms used in this force field were those need to keep the square planarity around the metal center. All torsional terms that are not parameterized are set to zero. For the TSFF, there was a high linear dependence seen with no significant deviations between

the QM and MM structures (Figure 6). This internal validation showed that the torsions sampled were able to keep the geometry of the TS around the metal center.



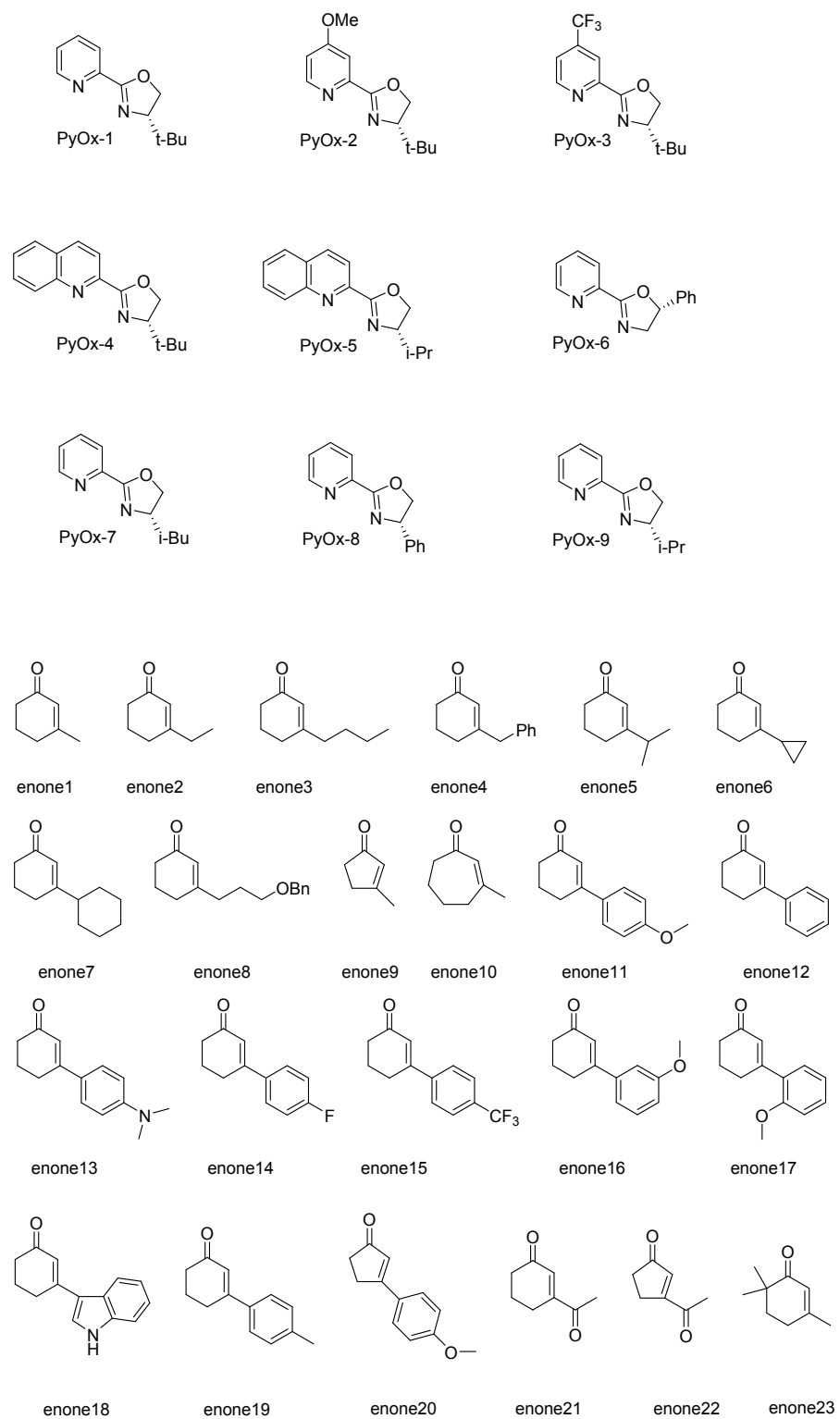
**FigureS3.** Comparison of torsion angles between QM and MM methods after the parametrization of torsional constants

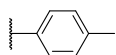
The last internal validation of the force field needed was to test how well it is able to reproduce the Hessian matrix. Since the eigenvectors are the same between the two methods, the diagonal eigenvalues were compared (Figure 6). There was a strong linear dependence between the MM eigenvalues and the QM eigenvalues. This validation, was used to prove that we can accurately reproduce the energies of the structures with the TSFF. With the TSFF able to reproduce the structural and electronic aspects of the QM data, its accuracy underwent an external validation by reproducing structures from the literature.



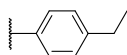
**Figure S4.** Comparison of Hessian diagonal eigenvalues from QM and MM methods after parameterization of all force constants.

**Figure S5: Structures of the Validation Set**

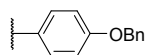




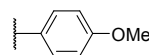
Aryl1



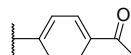
Aryl2



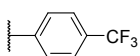
Aryl3



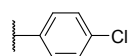
Aryl4



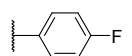
Aryl5



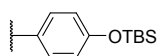
Aryl6



Aryl7



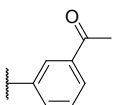
Aryl8



Aryl9



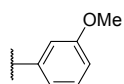
Aryl10



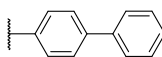
Aryl11



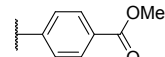
Aryl12



Aryl13



Aryl14



Aryl15



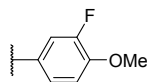
Aryl16



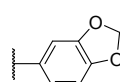
Aryl17



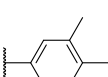
Aryl18



Aryl19



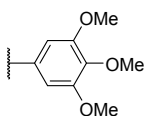
Aryl20



Aryl21



Aryl22



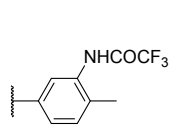
Aryl23



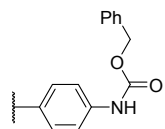
Aryl24



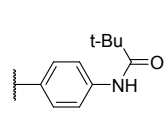
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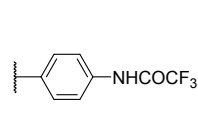
Aryl26



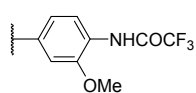
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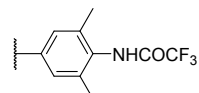
Aryl28



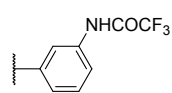
Aryl29



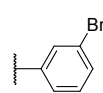
Aryl30



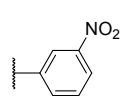
Aryl31



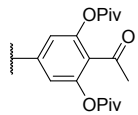
Aryl32



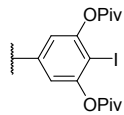
Aryl33



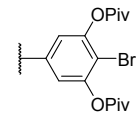
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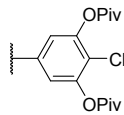
Aryl35



Aryl36



Aryl37



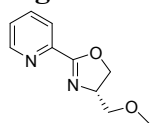
Aryl38

**Table S3: Results for Validation Set**

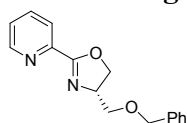
	Ligand	enone	aryl	Abs. Conf.	temp (K)	% ee (exp.)	ln(er) (exp.)	ln(er) (calc.)
enone001	PyOx-1	enone1	aryl12	R	333	93	3.32	2.69
enone002	PyOx-2	enone1	aryl12	R	333	78	2.09	2.67
enone003	PyOx-3	enone1	aryl12	R	333	81	2.25	2.52
enone004	PyOx-4	enone1	aryl12	R	333	20	0.41	0.57
enone005	PyOx-5	enone1	aryl12	R	333	0	0.00	-0.09
enone006	PyOx-6	enone1	aryl12	R	333	2	0.04	0.06
enone007	PyOx-7	enone1	aryl12	R	333	24	0.49	0.92
enone008	PyOx-8	enone1	aryl12	R	333	52	1.15	3.08
enone009	PyOx-9	enone1	aryl12	R	333	40	0.85	1.45
enone010	PyOx-1	enone1	aryl1	R	333	87	2.67	2.62
enone011	PyOx-1	enone1	aryl2	R	333	85	2.51	2.50
enone012	PyOx-1	enone1	aryl3	R	333	74	1.90	2.74
enone013	PyOx-1	enone1	aryl4	R	333	69	1.70	2.55
enone014	PyOx-1	enone1	aryl5	R	333	96	3.89	1.87
enone015	PyOx-1	enone1	aryl6	R	333	96	3.89	2.09
enone016	PyOx-1	enone1	aryl7	R	333	95	3.66	2.11
enone017	PyOx-1	enone1	aryl8	R	333	92	3.18	2.27
enone018	PyOx-1	enone1	aryl9	R	333	82	2.31	3.04
enone019	PyOx-1	enone1	aryl10	R	333	91	3.06	2.59
enone020	PyOx-1	enone1	aryl11	R	333	95	3.66	2.24
enone021	PyOx-1	enone2	aryl12	R	333	92	3.18	3.08
enone022	PyOx-1	enone3	aryl12	R	333	91	3.06	3.19
enone023	PyOx-1	enone4	aryl12	R	333	91	3.06	2.60
enone024	PyOx-1	enone5	aryl12	R	333	79	2.14	2.03
enone025	PyOx-1	enone6	aryl12	R	333	88	2.75	2.42
enone026	PyOx-1	enone7	aryl12	R	333	85	2.51	1.93
enone027	PyOx-1	enone8	aryl12	R	333	91	3.06	3.57
enone028	PyOx-1	enone9	aryl12	R	333	91	3.06	2.63
enone029	PyOx-1	enone10	aryl12	R	333	93	3.32	3.97
enone030	PyOX-1	enone11	aryl1	S	353	-87	-2.67	-2.90
enone031	PyOx-1	enone11	aryl12	S	353	-87	-2.67	-2.97
enone032	PyOx-1	enone11	aryl14	S	353	-90	-2.94	-2.41
enone033	PyOx-1	enone11	aryl7	R	353	83	2.38	2.38
enone034	PyOx-1	enone11	aryl8	R	353	91	3.06	2.57
enone035	PyOx-1	enone11	aryl15	S	353	-87	-2.67	-2.29
enone036	PyOx-1	enone11	aryl6	S	353	-82	-2.31	-2.31
enone037	PyOx-1	enone11	aryl10	R	353	90	2.94	2.87
enone038	PyOx-1	enone11	aryl13	R	353	90	2.94	2.73
enone039	PyOx-1	enone11	aryl16	R	353	85	2.51	2.20

enone040	PyOx-1	enone11	aryl17	R	353	84	2.44	2.34
enone041	PyOx-1	enone11	aryl18	R	353	81	2.25	1.90
enone042	PyOx-1	enone11	aryl19	R	353	88	2.75	2.15
enone043	PyOx-1	enone11	aryl20	R	353	90	2.94	2.55
enone044	PyOx-1	enone11	aryl21	R	353	85	2.51	2.79
enone045	PyOx-1	enone11	aryl22	R	353	90	2.94	2.80
enone046	PyOx-1	enone11	aryl23	R	353	78	2.09	2.46
enone047	PyOx-1	enone12	aryl1	R	353	87	2.67	2.83
enone048	PyOx-1	enone13	aryl1	S	353	-91	-3.06	-2.97
enone049	PyOx-1	enone14	aryl1	S	353	-89	-2.84	-2.79
enone050	PyOx-1	enone15	aryl1	S	353	-90	-2.94	-2.78
enone051	PyOx-1	enone16	aryl1	S	353	-93	-3.32	-2.98
enone052	PyOx-1	enone17	aryl1	S	353	-80	-2.20	-2.51
enone053	PyOx-1	enone18	aryl1	S	353	-77	-2.04	-3.60
enone054	PyOx-1	enone12	aryl10	R	353	88	2.75	2.86
enone055	PyOx-1	enone19	aryl12	S	353	-88	-2.75	-3.00
enone056	PyOx-1	enone12	aryl4	R	353	80	2.20	2.77
enone057	PyOx-1	enone20	aryl1	S	353	-87	-2.67	-2.85
enone058	PyOX-1	enone21	aryl7	S	333	-96	-3.89	-2.24
enone059	PyOx-1	enone21	aryl8	S	333	-90	-2.94	-2.41
enone060	PyOX-1	enone21	aryl10	S	333	-92	-3.18	-2.61
enone061	PyOX-1	enone21	aryl26	S	333	-91	-3.06	-1.37
enone062	PyOX-1	enone22	aryl12	S	333	-93	-3.32	-2.63
enone063	PyOX-1	enone22	aryl10	S	333	-90	-2.94	-2.48
enone064	PyOX-1	enone22	aryl8	S	333	-92	-3.18	-2.32
enone065	PyOX-1	enone1	aryl27	R	333	76	1.99	1.80
enone066	PyOX-1	enone1	aryl28	R	333	78	2.09	2.44
enone067	PyOX-1	enone1	aryl29	R	333	89	2.84	2.75
enone068	PyOX-1	enone1	aryl30	R	333	88	2.75	2.16
enone069	PyOX-1	enone1	aryl31	R	333	90	2.94	3.60
enone070	PyOX-1	enone1	aryl32	R	333	92	3.18	0.51
enone071	PyOX-1	enone1	aryl26	R	333	88	2.75	1.43
enone072	PyOX-1	enone1	aryl25	R	333	37	0.78	1.41
enone073	PyOX-1	enone1	aryl24	R	333	22	0.45	2.18
enone074	PyOx-1	enone1	aryl16	R	333	97	4.18	1.76
enone075	PyOx-1	enone1	aryl33	R	333	86	2.59	1.69
enone076	PyOx-1	enone1	aryl34	R	333	77	2.04	1.04
enone077	PyOx-1	enone1	aryl18	R	333	77	2.04	1.81
enone078	PyOx-1	enone1	aryl35	R	323	94	3.48	3.60
enone079	PyOx-1	enone1	aryl36	R	323	92	3.18	3.64
enone080	PyOx-1	enone1	aryl37	R	323	99	5.29	3.68
enone081	PyOx-1	enone1	aryl38	R	323	99	5.29	3.66
enone082	PyOx-1	enone23	aryl12	R	333	90	3.04	1.56

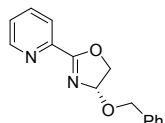
**Figure S6: Structures in Ligand Screen**



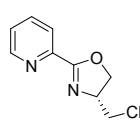
PyOx-10



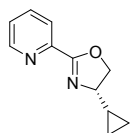
PyOx-11



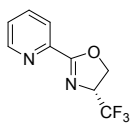
PyOx-12



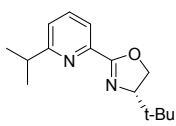
PyOx-13



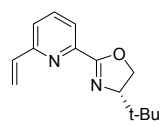
PyOx-14



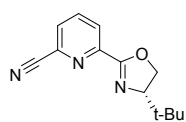
PyOx-15



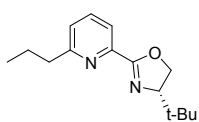
PyOx-16



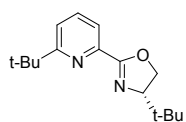
PyOx-17



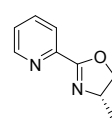
PyOx-18



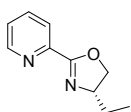
PyOx-19



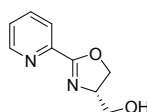
PyOx-20



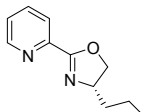
PyOx-21



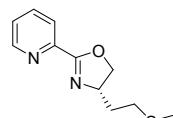
PyOx-22



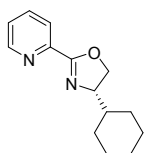
PyOx-23



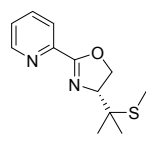
PyOx-24



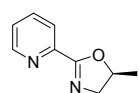
PyOx-25



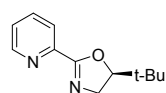
PyOx-26



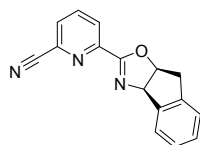
PyOx-27



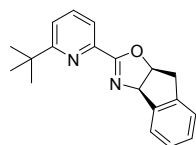
PyOx-28



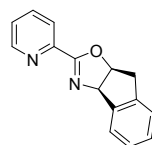
PyOx-29



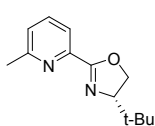
PyOx-30



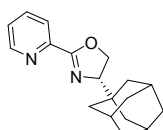
PyOx-31



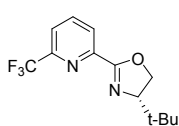
PyOx-32



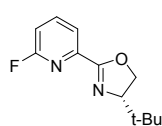
PyOx-33



PyOx-34



PyOx-35



PyOx-36

**Table S4: Results for Ligand Screen**

	Ligand	Enone	Aryl	Abs. Conf.	Temp. (K)	ee (calc.)	ln(er) (calc.)
enone082	PyOx10	enone1	aryl12	R	333	56.8	1.29
enone083	PyOx11	enone1	aryl12	R	333	58.1	1.33
enone084	PyOx12	enone1	aryl12	R	333	94.3	3.53
enone085	PyOx13	enone1	aryl12	R	333	69.2	1.70
enone086	PyOx14	enone1	aryl12	R	333	64.8	1.54
enone087	PyOx15	enone1	aryl12	R	333	91	3.06
enone088	PyOx16	enone1	aryl12	R	333	33.4	0.69
enone089	PyOx17	enone1	aryl12	S	333	-71.5	-1.79
enone090	PyOx18	enone1	aryl12	S	333	-98.9	-5.20
enone091	PyOx19	enone1	aryl12	S	333	-30.5	-0.63
enone092	PyOx20	enone1	aryl12	S	333	-99.9	-7.60
enone093	PyOx21	enone1	aryl12	R	333	32.1	0.67
enone094	PyOx22	enone1	aryl12	R	333	54.1	1.21
enone095	PyOx23	enone1	aryl12	R	333	49.7	1.09
enone096	PyOx24	enone1	aryl12	R	333	48.5	1.06
enone097	PyOx25	enone1	aryl12	R	333	65.5	1.57
enone098	PyOx26	enone1	aryl12	R	333	46.4	1.00
enone099	PyOx27	enone1	aryl12	R	333	89.9	2.93
enone100	PyOx28	enone1	aryl12	S	333	-14.1	-0.28
enone101	PyOx29	enone1	aryl12	R	333	2.8	0.06
enone102	PyOx30	enone1	aryl12	R	333	99.6	6.21
enone103	PyOx31	enone1	aryl12	R	333	99.9	7.60
enone104	PyOx32	enone1	aryl12	S	333	-61.2	-1.42
enone105	PyOx33	enone1	aryl12	R	333	20.8	0.42
enone106	PyOx34	enone1	aryl12	R	333	76.2	2.00
enone107	PyOx35	enone1	aryl12	S	333	-87.6	-2.72
enone108	PyOx36	enone1	aryl12	R	333	6.7	0.13

**Table S5 Coordinates of the 4 TS catalyzed by the PyrOx ligand containing a t-Bu group in the 6 position(enone092) optimized by MM****TS A**

FF Calculated Energy: 508.58 kJ/mol

Pd	-0.361842	0.879731	0.195272
C	-1.968645	0.563009	-1.163812
C	-2.849828	1.513574	-0.568412
C	-1.838233	1.928898	1.321041
N	1.549718	0.437077	1.370293
N	1.015808	-0.022882	-1.223745
C	-4.235741	1.096739	-0.099207
C	-1.681866	3.323018	1.483518



C	-2.856886	3.226535	3.594444
C	-2.212748	3.967278	2.602737
C	-2.419619	1.186963	2.375217
C	-2.948670	1.838083	3.491693
H	-3.272378	3.739756	4.479570
H	-2.118882	5.062775	2.710320
H	-1.169294	3.914025	0.709107
H	-2.465123	0.089216	2.306983
H	-3.428132	1.257970	4.300374
H	-4.315664	1.114821	1.006015
H	-4.995854	1.826676	-0.459961
C	-4.619583	-0.297506	-0.612471
H	-4.812893	-0.251718	-1.709843
H	-5.572232	-0.625705	-0.135777
C	-3.519373	-1.317946	-0.335885
H	-3.841392	-2.320221	-0.700910
H	-3.346233	-1.415891	0.758819
H	-1.499901	0.817593	-2.118469
C	-2.236819	-0.912846	-1.023216
O	-1.458922	-1.719234	-1.479738
C	-2.881384	2.898625	-1.184934
H	-3.400621	3.638201	-0.536748
H	-1.858906	3.283593	-1.393068
H	-3.421016	2.882348	-2.158176
C	1.932704	-0.715690	-0.649772
C	2.266836	-0.546540	0.772461
C	2.074569	0.904753	2.567037
O	2.675222	-1.507655	-1.426887
C	3.208668	-1.341342	1.424760
C	3.543609	-1.030787	2.733946
C	3.005543	0.128171	3.281924
C	2.027631	-1.600481	-2.713464
C	1.174127	-0.324842	-2.676598
H	3.702391	-2.182289	0.909068
H	4.290701	-1.627798	3.286721
H	2.770715	-1.651306	-3.532210
H	1.394639	-2.513860	-2.741900
H	0.181237	-0.555130	-3.128189
C	1.774407	0.871569	-3.445125
C	3.186937	1.238211	-2.941915
H	3.605020	2.105150	-3.500049
H	3.186162	1.520567	-1.866125
H	3.908607	0.401823	-3.065068
C	1.843069	0.554948	-4.955561
H	2.190491	1.434407	-5.541975
H	2.543929	-0.276194	-5.184366
H	0.848035	0.266662	-5.361442
H	3.370591	0.448487	4.270404

C	0.863847	2.107033	-3.265206
H	1.260209	2.991973	-3.810715
H	-0.162371	1.923542	-3.652444
H	0.768675	2.404277	-2.197651
C	1.760593	2.317513	3.055999
C	1.598737	3.272982	1.855570
H	1.299711	4.295499	2.176180
H	2.549347	3.374406	1.285605
H	0.837729	2.924962	1.132222
C	0.507373	2.273502	3.940515
H	0.688810	1.711440	4.883500
H	0.160118	3.290939	4.225312
H	-0.322644	1.756574	3.426411
C	2.895824	2.929008	3.917193
H	2.692319	3.996886	4.155562
H	3.021552	2.417480	4.896032
H	3.877040	2.898827	3.392433

### TS B

FF Calculated Energy: 534.61 kJ/mol

Pd	0.327501	0.465640	0.768308
C	2.391576	-0.075355	0.684196
C	2.731884	1.165165	0.055724
C	0.965752	2.430586	0.333621
N	-1.871138	0.539002	0.279551
N	-0.397208	-1.585303	0.937035
C	3.823478	2.048470	0.646694
C	0.545910	2.971569	-0.901201
C	0.753330	5.207284	-0.006496
C	0.475946	4.355080	-1.076655
C	1.142278	3.302708	1.430409
C	1.063299	4.685293	1.250313
H	0.691658	6.301046	-0.145952
H	0.187794	4.778821	-2.055330
H	0.297980	2.299668	-1.737378
H	1.373013	2.893721	2.425302
H	1.239153	5.368638	2.100397
H	4.581969	2.283934	-0.134589
H	3.419817	3.032057	0.960056
C	4.545443	1.395887	1.834812
H	5.168297	2.155595	2.361360
H	5.248444	0.615692	1.459222
C	3.563603	0.754934	2.811047
H	2.866071	1.513422	3.227459
H	4.122661	0.326211	3.674236
H	2.350661	-0.987784	0.079449
C	2.792652	-0.334347	2.108495
O	2.576270	-1.410436	2.611112

C	2.819047	1.146927	-1.458666
H	2.898870	2.169286	-1.889008
H	3.716342	0.580655	-1.794654
H	1.936045	0.650649	-1.918248
C	-1.396198	-1.749025	0.133499
C	-2.258166	-0.625990	-0.278817
C	-2.803406	1.547695	0.306724
O	-1.694639	-3.003703	-0.213529
C	-3.311094	-0.722127	-1.187232
C	-4.095888	0.404497	-1.407042
C	-3.869984	1.524778	-0.609632
C	-0.613885	-3.850148	0.241933
C	-0.045509	-2.970147	1.364300
H	-3.538254	-1.671909	-1.700009
H	-4.949734	0.371394	-2.107172
H	-0.983396	-4.845329	0.555096
H	0.121745	-3.981958	-0.581218
H	1.061506	-3.092926	1.394525
C	-0.626892	-3.316973	2.759776
C	-2.172504	-3.321368	2.776794
H	-2.566852	-3.579043	3.784780
H	-2.596169	-2.326809	2.515809
H	-2.604207	-4.064674	2.072541
C	-0.122637	-4.707156	3.208527
H	-0.455768	-4.948724	4.242342
H	-0.493895	-5.525306	2.554889
H	0.988580	-4.763117	3.204357
H	-4.591393	2.357301	-0.653351
C	-0.159136	-2.287713	3.812550
H	-0.651740	-2.455338	4.795968
H	0.933274	-2.352286	3.997189
H	-0.390268	-1.242390	3.510840
C	-2.853816	2.531397	1.486365
C	-4.287110	2.584381	2.075543
H	-4.330515	3.218259	2.989094
H	-5.031107	3.010475	1.368584
H	-4.648626	1.572470	2.366207
C	-1.940801	2.092780	2.650145
H	-2.021067	2.781880	3.519842
H	-2.198805	1.074322	3.017495
H	-0.872558	2.075617	2.364375
C	-2.486346	3.951169	1.027006
H	-2.484263	4.674506	1.872226
H	-1.479709	3.975794	0.571038
H	-3.195678	4.339690	0.263323

### TS C

FF Calculated Energy: 519.01 kJ/mol

Pd	-0.308398	0.696295	-0.001449
C	-1.542424	0.883425	-1.741115
C	-1.774497	2.261595	-1.432499
C	-0.377555	2.796932	0.147871
N	0.322074	0.018352	1.989019
N	0.260183	-1.467404	-0.301379
C	-3.114070	2.641107	-0.828615
C	0.793763	3.419386	-0.342973
C	0.653250	5.108832	1.375263
C	1.302417	4.566092	0.267490
C	-1.006206	3.353110	1.279748
C	-0.497465	4.505973	1.881352
H	1.053307	6.019553	1.854847
H	2.218381	5.045261	-0.122166
H	1.321177	2.980668	-1.204174
H	-1.919940	2.898754	1.682127
H	-1.004873	4.946854	2.758152
H	-3.035995	3.579424	-0.238131
H	-3.828057	2.866307	-1.654302
C	-3.704345	1.511380	0.025380
H	-4.691410	1.825882	0.436751
H	-3.051962	1.300480	0.900648
C	-3.868278	0.231199	-0.785011
H	-4.676155	0.367701	-1.540107
H	-4.194376	-0.595820	-0.113149
H	-0.877795	0.643517	-2.570860
C	-2.596218	-0.165581	-1.501380
O	-2.422266	-1.291394	-1.907108
C	-1.358020	3.279349	-2.476387
H	-1.338790	4.311764	-2.062631
H	-0.349136	3.063890	-2.890956
H	-2.064811	3.281295	-3.335781
C	0.594646	-1.247485	2.003235
C	0.367764	-2.137256	0.857720
C	0.612936	-2.176927	-1.430766
O	1.320905	-1.692975	3.034594
C	0.246641	-3.522673	0.949076
C	0.203350	-4.254519	-0.231778
C	0.454280	-3.575872	-1.422683
C	1.866670	-0.534630	3.702520
C	0.778993	0.483744	3.338372
H	0.224794	-4.032163	1.927022
H	0.115956	-5.355432	-0.214658
H	2.014046	-0.721577	4.782989
H	2.844530	-0.268536	3.245098
H	1.238709	1.496299	3.248148
C	-0.335873	0.539871	4.416503
C	-0.952128	-0.841544	4.732085

H	-1.757468	-0.761214	5.495626
H	-1.412725	-1.308967	3.834254
H	-0.206455	-1.557851	5.139349
C	0.229271	1.139300	5.725828
H	-0.569372	1.285717	6.486648
H	0.998030	0.490471	6.196838
H	0.699172	2.133269	5.554788
H	0.614196	-4.166620	-2.339441
C	-1.479879	1.457896	3.954160
H	-2.299142	1.508551	4.705165
H	-1.122995	2.498218	3.801482
H	-1.934416	1.096473	3.006754
C	1.358047	-1.531671	-2.612066
C	0.480994	-1.494950	-3.880358
H	-0.464545	-0.937447	-3.730955
H	1.010818	-1.012664	-4.731553
H	0.195476	-2.516729	-4.214745
C	1.900828	-0.122692	-2.288855
H	1.101372	0.625946	-2.141499
H	2.526308	-0.122171	-1.368306
H	2.537599	0.270788	-3.111866
C	2.615320	-2.379499	-2.947823
H	3.234250	-1.900006	-3.738549
H	3.271793	-2.509282	-2.058177
H	2.368356	-3.394733	-3.325840

### TS D

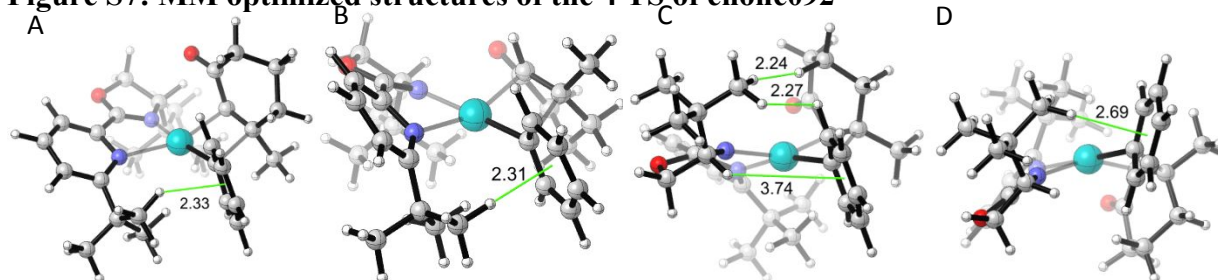
FF Calculated Energy: 488.00 kJ/mol

Pd	0.413562	0.515421	0.785143
C	2.302214	0.319988	-0.190370
C	2.692817	1.551107	0.432806
C	0.902322	2.502767	1.229311
N	-1.148644	0.154965	2.250358
N	-0.434272	-1.493192	0.252373
C	3.585965	1.479981	1.657799
C	0.379917	3.459046	0.332409
C	0.197024	5.066277	2.126578
C	0.044346	4.737779	0.779319
C	0.999262	2.835504	2.599412
C	0.661693	4.117315	3.037727
H	-0.070916	6.078667	2.477047
H	-0.349389	5.489228	0.071680
H	0.236993	3.191573	-0.726289
H	1.341288	2.088162	3.329403
H	0.754829	4.383900	4.105696
H	4.650415	1.482533	1.327489
H	3.468012	2.384835	2.292214

C	3.337106	0.209461	2.479743
H	2.299982	0.200020	2.882625
H	4.017243	0.192432	3.362692
C	3.557597	-1.041300	1.636643
H	3.256860	-1.941218	2.221006
H	4.643367	-1.153566	1.412893
H	2.058521	0.316165	-1.255000
C	2.795126	-1.005419	0.329545
O	2.592420	-2.012236	-0.308476
C	3.160114	2.657003	-0.494296
H	3.218587	3.637620	0.027649
H	4.173719	2.437477	-0.897519
H	2.486597	2.780838	-1.370182
C	-1.389787	-1.114286	2.358860
C	-1.002298	-2.088223	1.318366
C	-0.500313	-2.164635	-0.945807
O	-2.093796	-1.506170	3.422063
C	-1.192922	-3.466089	1.400768
C	-0.940107	-4.230618	0.266920
C	-0.649886	-3.563815	-0.922753
C	-2.172846	-0.393053	4.340083
C	-1.885597	0.776541	3.385248
H	-1.574100	-3.938210	2.321657
H	-1.086040	-5.325460	0.278648
H	-3.156104	-0.362417	4.847345
H	-1.375193	-0.493770	5.107882
H	-1.222936	1.506681	3.906637
C	-3.151158	1.523323	2.912055
C	-4.174228	0.579107	2.244809
H	-5.074536	1.134278	1.899645
H	-3.750585	0.069869	1.351358
H	-4.534598	-0.211568	2.937805
C	-3.824527	2.237557	4.104909
H	-4.691256	2.853062	3.776347
H	-4.210738	1.524858	4.864656
H	-3.119030	2.922356	4.625863
H	-0.607556	-4.148067	-1.856509
C	-2.755745	2.602333	1.882459
H	-3.639932	3.174438	1.523937
H	-2.049386	3.340352	2.318699
H	-2.269725	2.163527	0.983627
C	-0.576027	-1.422209	-2.290479
C	-1.763724	-1.981207	-3.117702
H	-1.907767	-1.414685	-4.064504
H	-1.624973	-3.043376	-3.413107
H	-2.721295	-1.917179	-2.553627
C	-0.854785	0.088755	-2.136399
H	-1.052790	0.571608	-3.118880

H	-1.743629	0.283919	-1.495651
H	0.000222	0.637882	-1.698029
C	0.708118	-1.630892	-3.118118
H	0.649570	-1.115551	-4.102444
H	1.609299	-1.240058	-2.604146
H	0.897361	-2.707095	-3.326276

**Figure S7: MM optimized structures of the 4 TS of enone092**



**Table S6 coordinates of the 4 TS catalyzed by the PyrOx ligand containing a t-Bu group in the 6 position(enone092) optimized by QM**

**TS A**

Gibbs Free Energy: -1513.599622 (Hartrees)

Imaginary Frequency: -283.67  $\text{cm}^{-1}$

Cartesian coordinates

Pd	-0.00717900	-0.67148000	-0.15491900
C	0.58526800	-2.46724900	0.75598600
C	-0.76773500	-2.86208300	1.00006100
C	-1.82832800	-1.58196900	-0.45430900
N	-0.25219400	2.03043800	0.15149900
N	1.89929200	0.27119500	-0.05755100
C	-1.36033800	-2.49697000	2.33375600
C	-1.83515600	-2.11598700	-1.74931800
C	-4.20842000	-1.70045900	-1.89169000
C	-3.02304200	-2.15064400	-2.47515200
C	-3.01106200	-1.12773800	0.12805800
C	-4.20243000	-1.19250600	-0.59380700
H	-5.14130200	-1.74971500	-2.45053500
H	-3.02567600	-2.54604900	-3.48959900
H	-0.91651400	-2.50494600	-2.19439800
H	-3.01522500	-0.70386600	1.13268400
H	-5.12485500	-0.82860100	-0.14251000
H	-2.45527700	-2.47692000	2.27598600
H	-1.12385100	-3.35377000	2.99216200
C	-0.77720100	-1.23159800	2.94049800
H	-1.23328300	-1.03945000	3.91922000
H	-1.01904700	-0.35977200	2.30660900
C	0.73221300	-1.37416200	3.08826300
H	0.97051900	-2.04046300	3.93330400
H	1.22250300	-0.41679900	3.31767700

H	1.14743900	-3.02297800	-0.00372700
C	1.42203500	-1.97151000	1.88710100
O	2.63835500	-2.10309600	1.85062900
C	-1.26487800	-4.14586400	0.40564400
H	-2.35914700	-4.17436900	0.34260700
H	-0.83539700	-4.34915800	-0.58002900
H	-0.94406300	-4.95423600	1.08156300
C	1.98720200	1.38442100	0.57355000
C	0.82362000	2.19773500	0.94914900
C	-1.32001000	2.80610200	0.35166400
O	3.20726800	1.84068100	0.83889700
C	0.87170300	3.07784100	2.01713500
C	-0.28138400	3.81296200	2.29173700
C	-1.37129500	3.68666600	1.44948000
C	4.12422000	0.80480000	0.38077200
C	3.25087300	-0.13734700	-0.46340600
H	1.77411800	3.17309000	2.61644700
H	-0.31340100	4.49436700	3.13917400
H	4.92942600	1.30696500	-0.16251000
H	4.53020300	0.31570600	1.27288500
H	3.41176400	-1.18078600	-0.15336700
C	3.42306500	-0.04658700	-1.99597700
C	3.19061300	1.37454400	-2.50678300
H	3.32579400	1.40567100	-3.59674500
H	2.16752300	1.71911400	-2.29286600
H	3.89517400	2.09844200	-2.07239800
C	4.83851600	-0.50762100	-2.34469200
H	4.97747300	-0.50530400	-3.43460200
H	5.61229800	0.14577900	-1.91821500
H	5.02268400	-1.53064400	-1.98515900
H	-2.26153700	4.28730600	1.62504700
C	2.42442300	-0.99001300	-2.66799800
H	2.59433200	-1.00952900	-3.75362700
H	2.52855200	-2.01979700	-2.29277000
H	1.38480600	-0.66852600	-2.50174500
C	-2.45010100	2.79738300	-0.66886600
C	-2.18090800	1.82302700	-1.81124300
H	-2.99520100	1.89347900	-2.54597400
H	-1.23565300	2.04994300	-2.32324100
H	-2.13946000	0.78362800	-1.46587600
C	-3.77280300	2.44171900	0.01919800
H	-4.06855000	3.19593900	0.76057000
H	-4.57704300	2.37570500	-0.72737000
H	-3.70760700	1.47182200	0.53003600
C	-2.55365600	4.20918200	-1.26775300
H	-3.35464700	4.23180200	-2.01988300
H	-2.78731400	4.96916700	-0.51074700
H	-1.61502400	4.49727100	-1.76201600



**TS B**Gibbs Free Energy: -1513.594515 (Hartrees)

Imaginary Frequency: -314.13 cm<sup>-1</sup>

Cartesian coordinates

Pd	0.00106900	0.55193300	-0.12664400
C	0.57608100	2.44221600	-0.81469500
C	-0.72155100	3.01636200	-0.60819900
C	-1.95049600	1.25271100	-0.40923400
N	-0.50774600	-1.77973000	0.00305800
N	1.84185200	-0.51012000	-0.53113700
C	-0.92317600	3.78043900	0.67289000
C	-2.35725700	0.72107800	-1.64432100
C	-4.65696800	0.76688300	-0.91750400
C	-3.70100600	0.45225200	-1.88473800
C	-2.90854300	1.52375100	0.56982700
C	-4.25953500	1.30101300	0.30655800
H	-5.71267700	0.59227500	-1.11797600
H	-4.00349000	0.02264300	-2.83850500
H	-1.62487700	0.52489600	-2.43111200
H	-2.62172300	1.91712700	1.54440500
H	-4.99971400	1.53051900	1.07187300
H	-0.60479400	4.81318700	0.43628800
H	-1.98872200	3.86093500	0.91590800
C	-0.08205400	3.25969500	1.82500100
H	-0.35241400	2.21391600	2.05400800
H	-0.27820700	3.84086100	2.73391000
C	1.39159900	3.34447600	1.45528600
H	2.03556000	2.81771200	2.17325300
H	1.72811700	4.39403100	1.46668200
H	0.88440200	2.25711900	-1.85081700
C	1.70409100	2.82379300	0.07607000
O	2.85589000	2.75845100	-0.33709300
C	-1.45541900	3.56492600	-1.79715000
H	-2.52979300	3.67209600	-1.60425200
H	-1.04391000	4.56805800	-1.99082200
H	-1.30382900	2.96502500	-2.69970300
C	1.52100300	-1.57173500	-1.18163200
C	0.19557600	-2.19700100	-1.07689300
C	-1.61419000	-2.44208200	0.35016600
O	2.47038600	-2.17750800	-1.88615100
C	-0.23917100	-3.18295700	-1.94213700
C	-1.47719900	-3.76872700	-1.67023600
C	-2.14463300	-3.42378300	-0.50851700
C	3.63522000	-1.30655700	-1.78577700
C	3.30323900	-0.36340400	-0.62077000
H	0.36710700	-3.48054000	-2.79391100
H	-1.88793900	-4.52293600	-2.33779600
H	4.50608300	-1.94887200	-1.63113600

H	3.73080000	-0.78585900	-2.74477500
H	3.54902800	0.67833700	-0.86902900
C	3.96857200	-0.71341100	0.73266500
C	3.68576200	-2.15690700	1.14878000
H	4.18263300	-2.36891200	2.10557400
H	2.60921800	-2.33419100	1.29502000
H	4.06064300	-2.89018700	0.42052400
C	5.47446900	-0.49163600	0.59201000
H	5.97340000	-0.67365600	1.55397000
H	5.93480600	-1.16564700	-0.14404200
H	5.69393400	0.54332000	0.29051500
H	-3.06780700	-3.93480200	-0.24375600
C	3.43776700	0.22714200	1.81444200
H	3.92621300	0.00846100	2.77430900
H	3.64578000	1.27579600	1.55766000
H	2.35218000	0.11189100	1.95509000
C	-2.18872700	-2.25011800	1.74681800
C	-1.91877400	-3.56623500	2.49987500
H	-2.28771900	-3.47922700	3.53136900
H	-2.42403400	-4.42249000	2.03392500
H	-0.84183300	-3.78395900	2.54046300
C	-1.49401900	-1.13017400	2.51581300
H	-1.90317500	-1.08694000	3.53420100
H	-0.41026300	-1.29672400	2.58972000
H	-1.65452100	-0.15033800	2.05041500
C	-3.69686400	-1.99616900	1.70105600
H	-4.07805000	-1.85273300	2.72158500
H	-3.93266200	-1.09522300	1.12077900
H	-4.24864000	-2.83753600	1.26161400

## TS C

Gibbs Free Energy: -1513.583918 (Hartrees)

Imaginary Frequency: -388.55 cm<sup>-1</sup>

Cartesian coordinates

Pd	0.24326400	-0.45194000	-0.24952600
C	0.54718900	-2.51066900	-0.39761400
C	1.42860800	-2.68940800	0.72024300
C	1.67096800	-0.61680300	1.23947600
N	0.08485900	1.71516000	-0.05789300
N	-2.43852700	0.42305400	0.05965200
C	2.85395100	-3.17161400	0.47657200
C	1.11143200	-0.29052900	2.48286900
C	3.09245400	0.97912000	3.03071600
C	1.82303500	0.51012600	3.37263500
C	2.93818100	-0.13097900	0.89611100
C	3.65183500	0.65688600	1.79335400
H	3.64874500	1.59776000	3.73274000
H	1.38429300	0.76698800	4.33529600

H	0.11783600	-0.64741300	2.75590000
H	3.37973600	-0.36925700	-0.07160100
H	4.63859500	1.02819400	1.52006900
H	3.58768300	-2.41296000	0.76686000
H	3.02432700	-4.00792200	1.17022600
C	3.10721800	-3.63659800	-0.95552400
H	2.64206000	-4.62202900	-1.11056000
H	4.18415600	-3.77332200	-1.11056600
C	2.53970100	-2.66024500	-1.97927800
H	2.73716600	-2.97382800	-3.01083200
H	2.99170300	-1.66186500	-1.85744300
H	-0.48980000	-2.84527300	-0.27372900
C	1.05035700	-2.54940600	-1.79565400
O	0.26479700	-2.50829900	-2.73595700
C	0.81709400	-3.22377500	1.98076500
H	1.46803100	-3.06751500	2.84848400
H	-0.17643300	-2.81434800	2.18914200
H	0.70449300	-4.31065100	1.84249500
C	-0.99416500	2.31747000	0.29075100
C	-2.33860300	1.72495100	0.36081700
C	-3.64519000	-0.15825000	0.11026100
O	-0.89386800	3.61228800	0.60292500
C	-3.42170400	2.52416400	0.71573000
C	-4.67673100	1.93002500	0.74458100
C	-4.78956200	0.58139100	0.44123800
C	0.52204700	3.91360700	0.60741100
C	1.15905700	2.72368500	-0.12120000
H	-3.27880700	3.57394300	0.95584800
H	-5.55779500	2.51227300	1.00621000
H	0.65224300	4.88407900	0.12125000
H	0.83648300	3.98680800	1.65540100
H	2.02390200	2.34723500	0.44360300
C	1.62375000	3.00716100	-1.56952600
C	0.48344700	3.54715600	-2.43103400
H	0.84860200	3.74686900	-3.44786400
H	-0.33923000	2.82274400	-2.51417400
H	0.07276400	4.49043600	-2.04412100
C	2.76333300	4.02617800	-1.50341200
H	3.16526700	4.20619400	-2.50995300
H	2.44282400	4.99833400	-1.10431600
H	3.58770500	3.65601500	-0.87474300
H	-5.76542400	0.10494800	0.46458000
C	2.17262500	1.73087400	-2.20626700
H	2.52970300	1.94406300	-3.22347700
H	3.02331000	1.33514400	-1.63212500
H	1.41121200	0.93968200	-2.28311400
C	-3.69423700	-1.65491800	-0.16761500
C	-3.08669300	-1.93713600	-1.54454500

H	-2.07657800	-1.52553400	-1.65470300
H	-3.02694900	-3.02159200	-1.71615500
H	-3.71044700	-1.50228700	-2.33863200
C	-2.89760000	-2.34931900	0.94374200
H	-1.90147800	-1.90037700	1.05062200
H	-3.41080500	-2.25153000	1.91124000
H	-2.78173400	-3.42161300	0.72620600
C	-5.11707300	-2.21053300	-0.15522100
H	-5.08302400	-3.28787800	-0.36644300
H	-5.60585900	-2.08551400	0.82097300
H	-5.74872600	-1.74486100	-0.92476200

## TS D

Gibbs Free Energy: -1513.599826 (Hartrees)

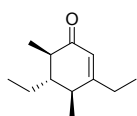
Imaginary Frequency: -339.60 cm<sup>-1</sup>

Cartesian coordinates

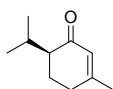
Pd	0.03622500	-0.52366700	0.17106300
C	1.00563100	-2.37057400	-0.19755000
C	-0.23624400	-3.00035200	-0.54768000
C	-1.65613200	-1.69743300	0.33173400
N	-0.92862300	1.37813800	-0.37156600
N	1.71663200	0.99438700	0.11391600
C	-0.60526700	-3.02875800	-2.01055200
C	-1.85590600	-1.98886800	1.68899500
C	-4.24404800	-1.92342900	1.35213300
C	-3.14720600	-2.08872800	2.19843000
C	-2.75871700	-1.50811200	-0.50716700
C	-4.04925000	-1.63094200	0.00215900
H	-5.25413300	-2.02026700	1.74645100
H	-3.29618700	-2.30817300	3.25436600
H	-1.00234300	-2.15285500	2.34978900
H	-2.62422500	-1.25986300	-1.55999700
H	-4.90407300	-1.48694800	-0.65741100
H	-0.13172300	-3.94813500	-2.40194900
H	-1.68389300	-3.18619400	-2.13075700
C	-0.08965400	-1.84192900	-2.80479500
H	-0.55475400	-0.90728100	-2.44788900
H	-0.37048500	-1.94592300	-3.86016700
C	1.42387500	-1.75624200	-2.67332800
H	1.82927600	-0.81145000	-3.06261100
H	1.89944400	-2.55319500	-3.26866500
H	1.50573200	-2.71776100	0.71311700
C	1.94434000	-1.93633000	-1.26809800
O	3.13246100	-1.77306900	-1.01791600
C	-0.63827900	-4.23532100	0.20990200
H	-1.70884700	-4.44993600	0.10449100
H	-0.07749400	-5.07630200	-0.22705400
H	-0.37944100	-4.18326600	1.27177100

C	-0.06014200	2.01766600	-1.07203600
C	1.38739100	1.82730300	-0.90654200
C	2.98541200	0.93095000	0.52928100
O	-0.50394900	2.92996200	-1.93241000
C	2.32221900	2.50225400	-1.66590200
C	3.66782200	2.30964700	-1.34252500
C	3.99235800	1.55991000	-0.22805000
C	-1.95439800	2.80688200	-1.91400100
C	-2.24941000	1.94041700	-0.67728500
H	2.01007300	3.15452500	-2.47725100
H	4.44852400	2.78460000	-1.93231900
H	-2.36691000	3.81898700	-1.88119000
H	-2.24692000	2.32502400	-2.85339500
H	-2.93425200	1.11801000	-0.93565000
C	-2.84359100	2.67793300	0.54291100
C	-1.99140400	3.88097400	0.94322500
H	-2.43279700	4.37104400	1.82205200
H	-0.96943100	3.57934700	1.21507300
H	-1.92718500	4.63908400	0.14972300
C	-4.25755700	3.12824700	0.17740700
H	-4.72761900	3.63185600	1.03329400
H	-4.27129400	3.83544500	-0.66429900
H	-4.88766100	2.26709500	-0.09261600
H	5.03221500	1.46819200	0.07719800
C	-2.92410300	1.70845700	1.72192600
H	-3.41972900	2.19512800	2.57369900
H	-3.50409100	0.80946300	1.46412700
H	-1.92676300	1.38424400	2.05044300
C	3.32545100	0.33014600	1.89015400
C	3.89535100	1.48969800	2.73098000
H	4.11733300	1.12772100	3.74429200
H	4.82559800	1.89435600	2.31236900
H	3.17113100	2.31250100	2.81469600
C	2.10387200	-0.20394000	2.63192700
H	2.40781800	-0.51176400	3.64139800
H	1.31621400	0.55640200	2.73291700
H	1.66903700	-1.08365500	2.14133200
C	4.37735000	-0.77716700	1.77995700
H	4.65119700	-1.11761000	2.78817800
H	3.99379000	-1.63067200	1.20843900
H	5.29577900	-0.43004800	1.28759900

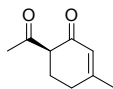
**Figure S8 Structures in Enone Screen**



enone24



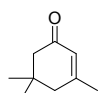
enone25



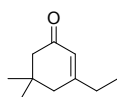
enone26



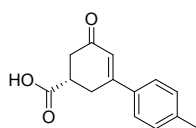
enone27



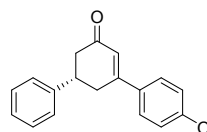
enone28



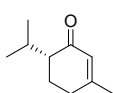
enone29



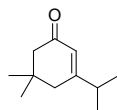
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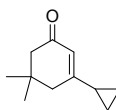
enone31



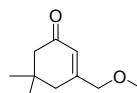
enone32



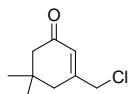
enone33



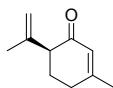
enone34



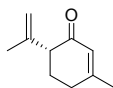
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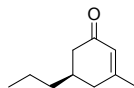
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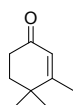
enone37



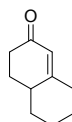
enone38



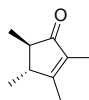
enone39



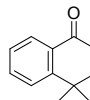
enone40



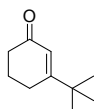
enone41



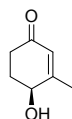
enone42



enone43



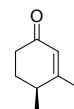
enone44



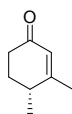
enone45



enone46



enone47



enone48



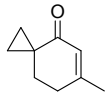
enone49



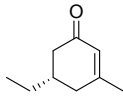
enone50



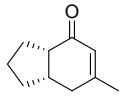
enone51



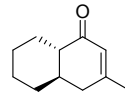
enone52



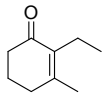
enone53



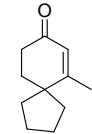
enone54



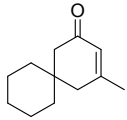
enone55



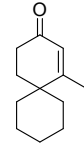
enone56



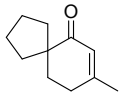
enone57



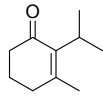
enone58



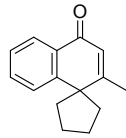
enone59



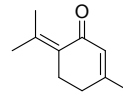
enone60



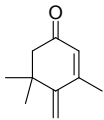
enone61



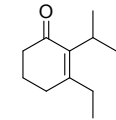
enone62



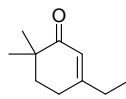
enone63



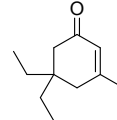
enone64



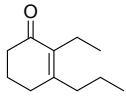
enone65



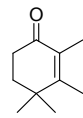
enone66



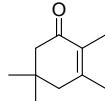
enone67



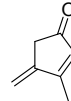
enone68



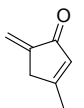
enone69



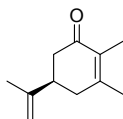
enone70



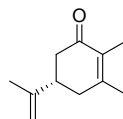
enone71



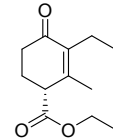
enone72



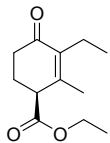
enone73



enone74



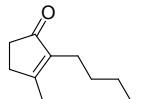
enone75



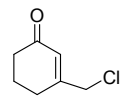
enone76



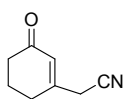
enone77



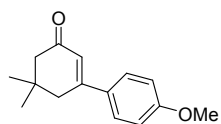
enone78



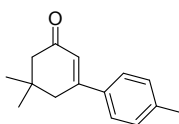
enone79



enone80



enone81



enone82

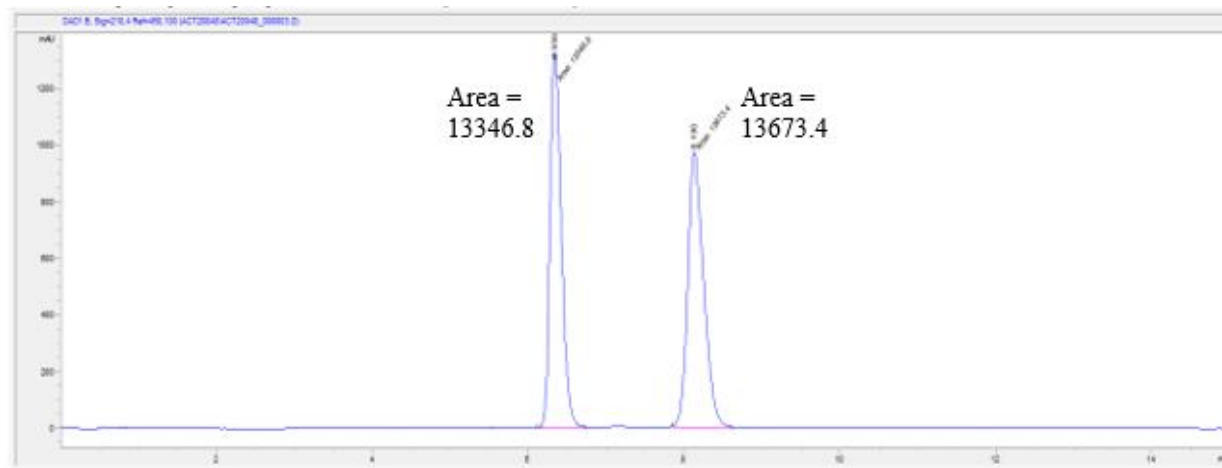
**Table S7: Results for Substrate Screen**

	Ligand	Enone	Aryl	Abs. Conf.	Temp. (K)	ee (calc.)	ln(er) (calc.)
enone109	PyOx1	enone24	aryl12	S	333	-98.3	-4.76
enone110	PyOx1	enone25	aryl12	R	333	49.9	1.10
enone111	PyOx1	enone26	aryl12	R	333	49.4	1.08
enone112	PyOx1	enone27	aryl12	R	333	82.1	2.32
enone113	PyOx1	enone28	aryl12	R	333	97.5	4.37
enone114	PyOx1	enone29	aryl12	R	333	97.8	4.50
enone115	PyOx1	enone30	aryl12	S	333	-57.7	-1.32
enone116	PyOx1	enone31	aryl12	S	333	-87.3	-2.69
enone117	PyOx1	enone32	aryl12	R	333	97.2	4.25
enone118	PyOx1	enone33	aryl12	R	333	98.1	4.65
enone119	PyOx1	enone34	aryl12	R	333	92.5	3.25
enone120	PyOx1	enone35	aryl12	S	333	-97	-4.18
enone121	PyOx1	enone36	aryl12	S	333	-97.3	-4.29
enone122	PyOx1	enone37	aryl12	R	333	72.6	1.84
enone123	PyOx1	enone38	aryl12	R	333	96.8	4.12
enone124	PyOx1	enone39	aryl12	R	333	94.9	3.64
enone125	PyOx1	enone40	aryl12	S	333	-97.8	-4.50
enone126	PyOx1	enone41	aryl12	R	333	98.8	5.11
enone127	PyOx1	enone42	aryl12	S	333	-99.6	-6.21
enone128	PyOx1	enone43	aryl12	R	333	90.3	2.98
enone129	PyOx1	enone44	aryl12	R	333	85.2	2.53
enone130	PyOx1	enone45	aryl12	R	333	99.1	5.40
enone131	PyOx1	enone46	aryl12	S	333	-53.1	-1.18
enone132	PyOx1	enone47	aryl12	S	333	-99.9	-7.60
enone133	PyOx1	enone48	aryl12	R	333	76.8	2.03
enone134	PyOx1	enone49	aryl12	R	333	59.7	1.38
enone135	PyOx1	enone50	aryl12	R	333	82.4	2.34
enone136	PyOx1	enone51	aryl12	R	333	88.3	2.78
enone137	PyOx1	enone52	aryl12	R	333	63.6	1.50
enone138	PyOx1	enone53	aryl12	R	333	77.6	2.07
enone139	PyOx1	enone54	aryl12	R	333	3.7	0.07
enone140	PyOx1	enone55	aryl12	R	333	93.5	3.39
enone141	PyOx1	enone56	aryl12	S	333	-61.7	-1.44
enone142	PyOx1	enone57	aryl12	S	333	-94.6	-3.58
enone143	PyOx1	enone58	aryl12	R	333	97.4	4.33
enone144	PyOx1	enone59	aryl12	S	333	-97.8	-4.50
enone145	PyOx1	enone60	aryl12	R	333	70.1	1.74
enone146	PyOx1	enone61	aryl12	S	333	-81.1	-2.26
enone147	PyOx1	enone62	aryl12	R	333	93.6	3.41
enone148	PyOx1	enone63	aryl12	R	333	58.9	1.35



enone149	PyOx1	enone64	aryl12	R	333	94.6	3.58
enone150	PyOx1	enone65	aryl12	S	333	-76.3	-2.01
enone151	PyOx1	enone66	aryl12	R	333	68.4	1.67
enone152	PyOx1	enone67	aryl12	R	333	97.3	4.29
enone153	PyOx1	enone68	aryl12	S	333	-72.6	-1.84
enone154	PyOx1	enone69	aryl12	R	333	-3.2	-0.06
enone155	PyOx1	enone70	aryl12	S	333	-48.6	-1.06
enone156	PyOx1	enone71	aryl12	S	333	-84.5	-2.48
enone157	PyOx1	enone72	aryl12	R	333	86.2	2.60
enone158	PyOx1	enone73	aryl12	R	333	43.7	0.94
enone159	PyOx1	enone74	aryl12	S	333	-93.3	-3.36
enone160	PyOx1	enone75	aryl12	R	333	99.8	6.91
enone161	PyOx1	enone76	aryl12	S	333	-96.4	-4.00
enone162	PyOx1	enone77	aryl12	S	333	-41.7	-0.89
enone163	PyOx1	enone78	aryl12	S	333	-30.6	-0.63
enone164	PyOx1	enone79	aryl12	S	333	-91.1	-3.07
enone165	PyOx1	enone80	aryl12	S	333	-90.4	-2.99
enone166	PyOx1	enone81	aryl12	S	333	-96.4	-4.00
enone167	PyOx1	enone82	aryl12	S	333	-96.4	-4.00

**Figure S9: Chromatogram of the racemic  $\pm$ 3-methyl-3-phenylcyclohexanone**



**Figure S10: Chromatogram of sample obtained using the (S)-*tert*-butylPyrOx ligand**

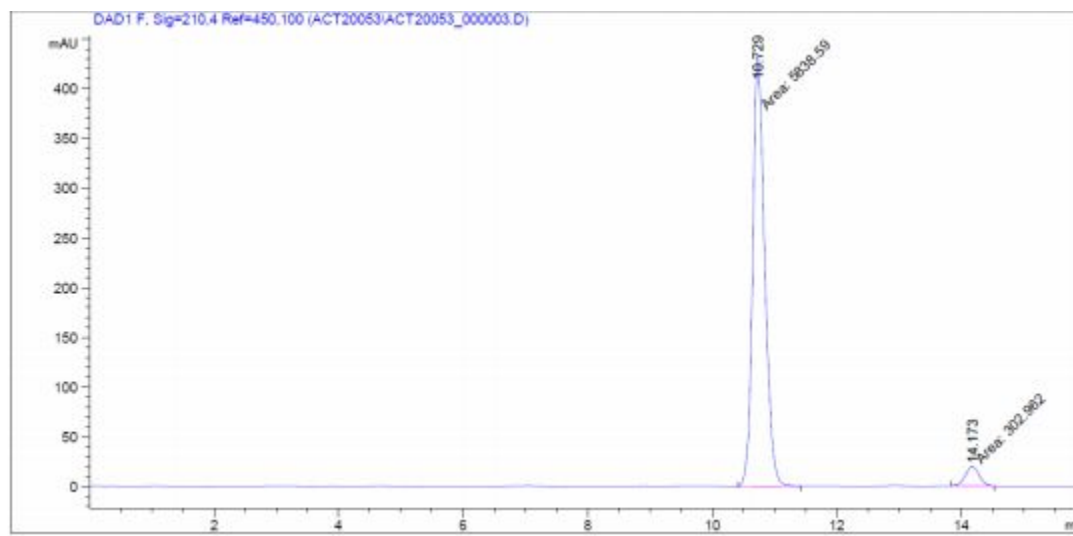


Figure S11: Chromatogram of sample obtained using the CF<sub>3</sub> substituted ligand

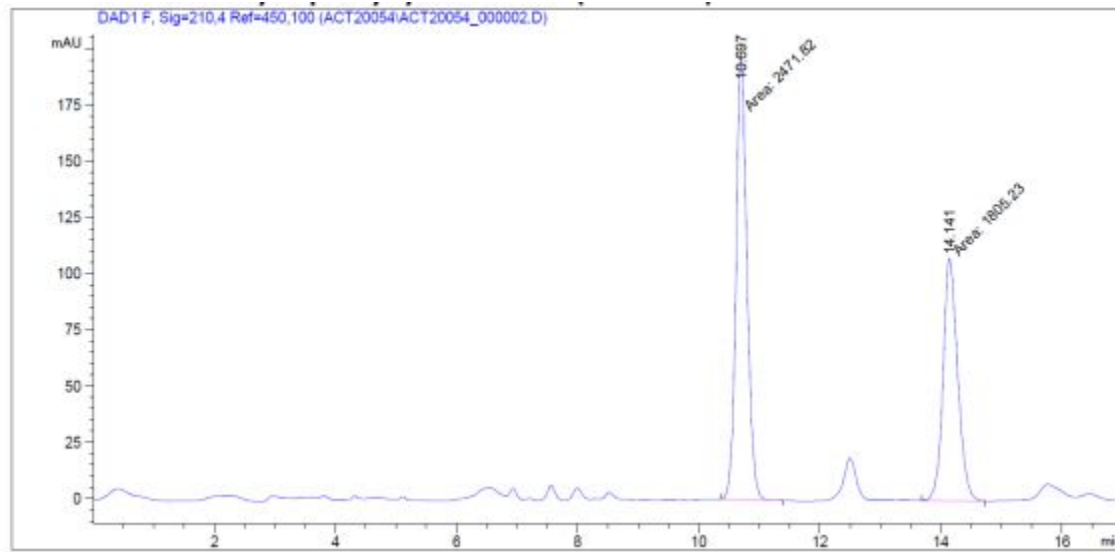


Figure S12: <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) of sample obtained using the CF<sub>3</sub> substituted ligand

