Supporting Information for

Kinetics And Mechanistic Studies Of Photochemical And Oxidative Stability Of Galaxolide

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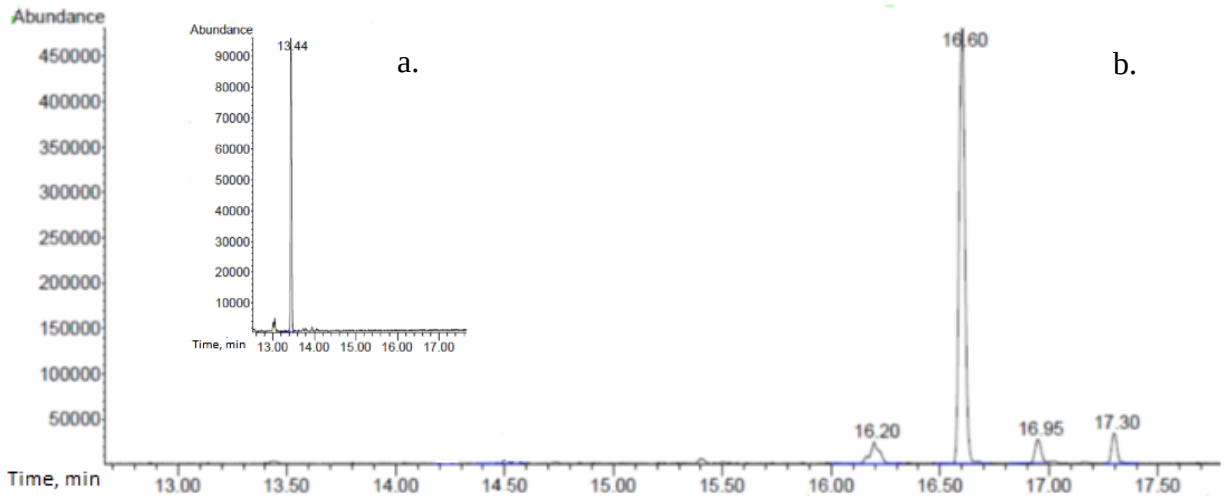
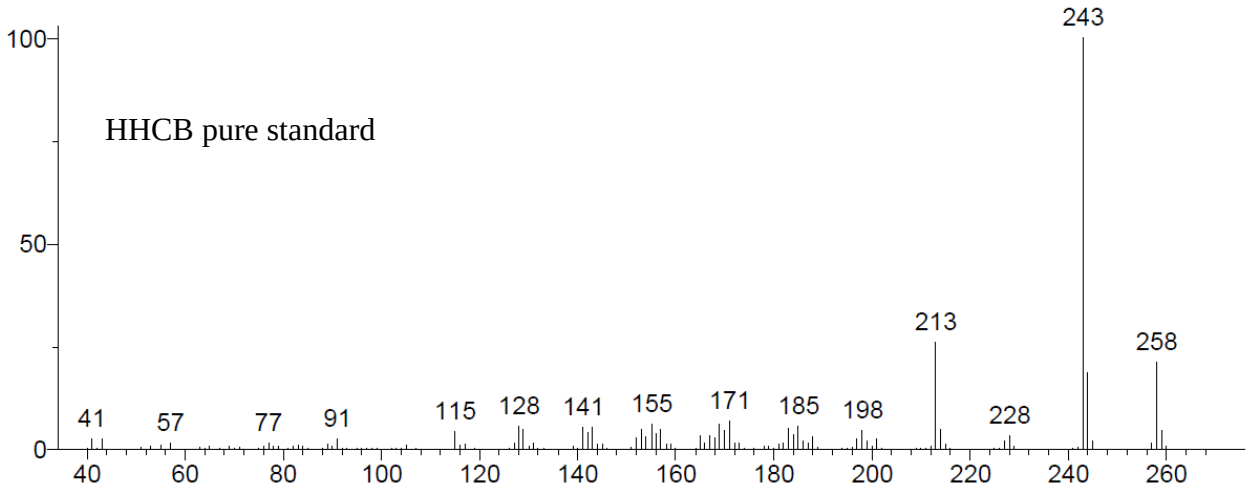


Figure S1. Chromatographic characterization of (a) HHCB pure standard and transformation products of HHCB after 100 min of irradiation (small insert).

a.



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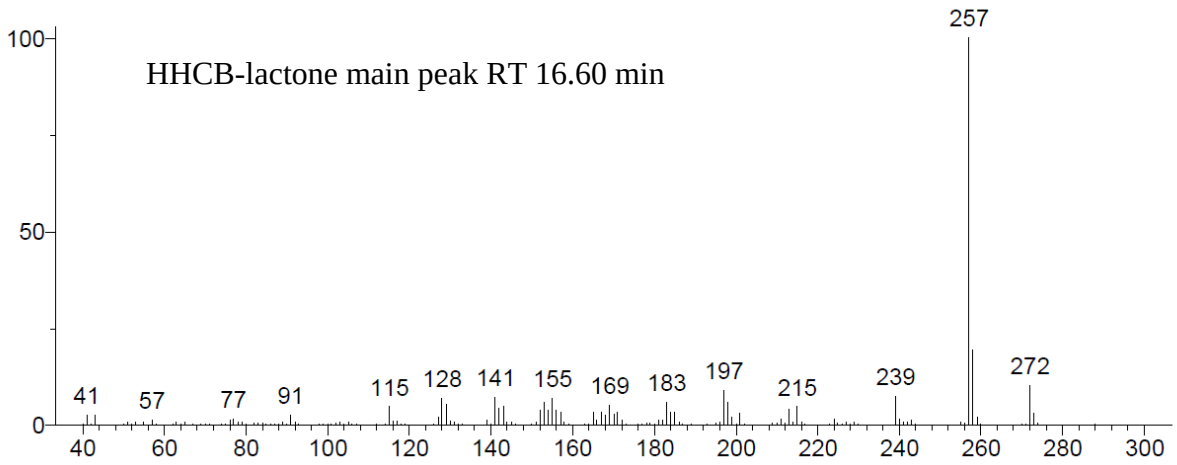
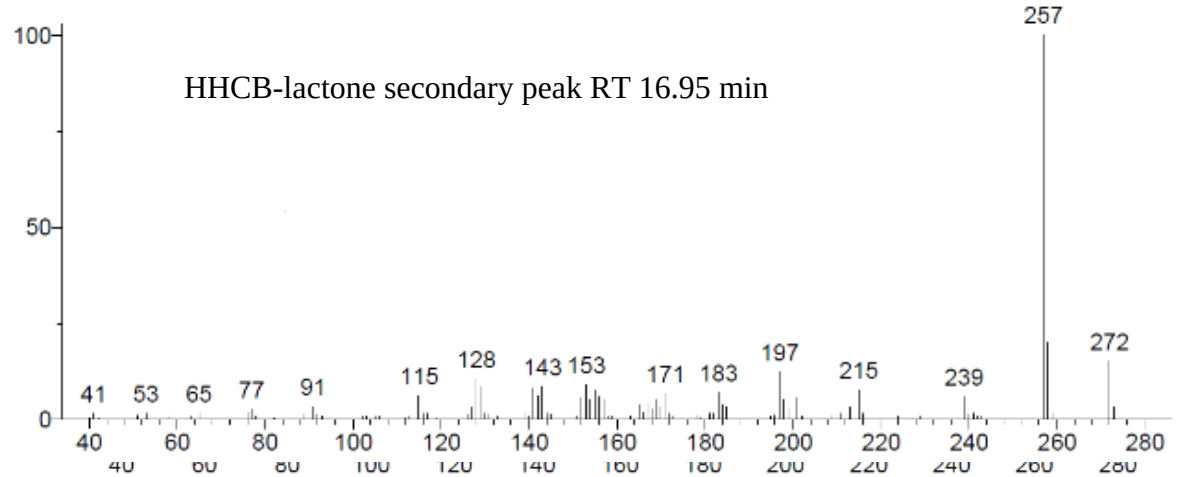
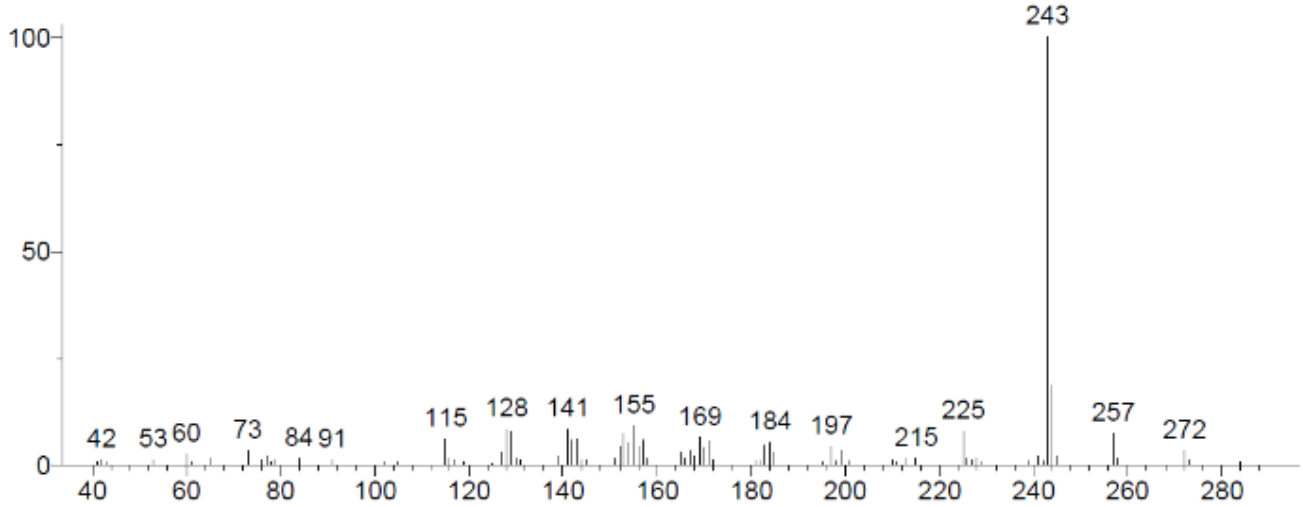

HHCB-lactone main peak RT 16.60 min
100
50
0
257
272
239
215
197
183
169
155
141
128
115
91
77
57
41
40
60
80
100
120
140
160
180
200
220
240
260
280
300

c.


HHCB-lactone secondary peak RT 16.95 min
100
50
0
257
272
239
215
197
183
171
153
143
128
115
91
77
65
53
41
40
60
80
100
120
140
160
180
200
220
240
260
280

d.


100
50
0
243
272
257
225
215
197
184
169
155
141
128
115
91
84
73
60
53
42
40
60
80
100
120
140
160
180
200
220
240
260
280

e.

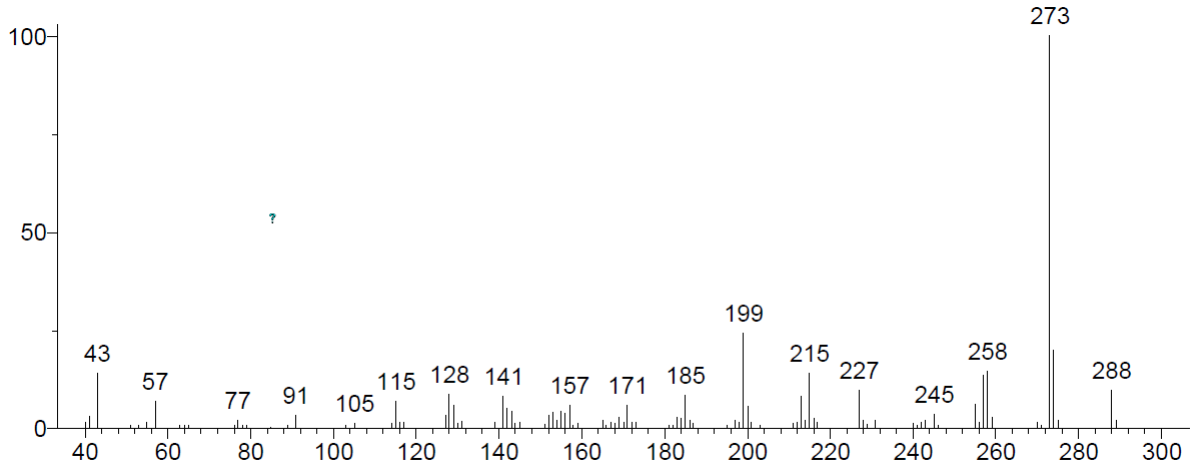
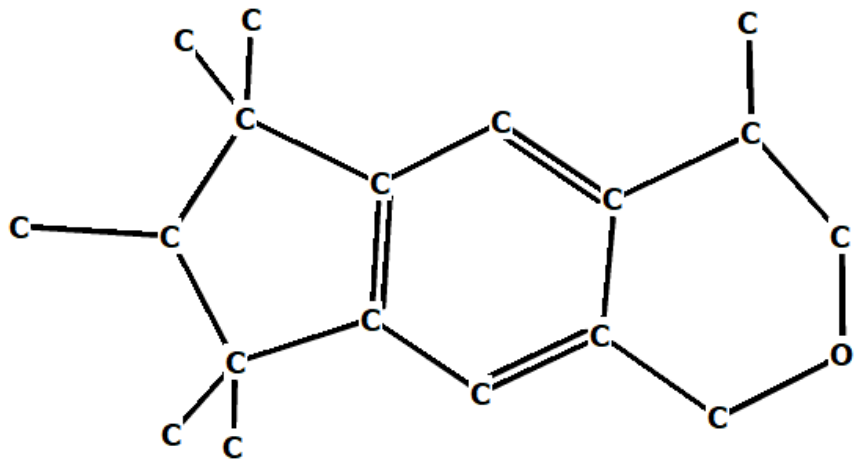


Figure S2. Mass spectra of HHCB pure standard (5x10-5 mol L-1) (a) and two HHCB-lactones; (b) HHCB-lactone main peak; RT 16.60 min, (c) HHCB-lactone secondary peak; RT 16.95; (d) not identified peak; RT 16.20; (e) not identified; RT 17.30. 1-under full scan conditions, 2-standart mass spectrum.

All reaction geometries and frequencies were calculated at CPCM/M06-2X/cc-pVDZ level of theory. Geometries are in angstroms, frequencies in cm^{-1}.

Galaxolide

Figure S3. The optimized structure of galaxolide.



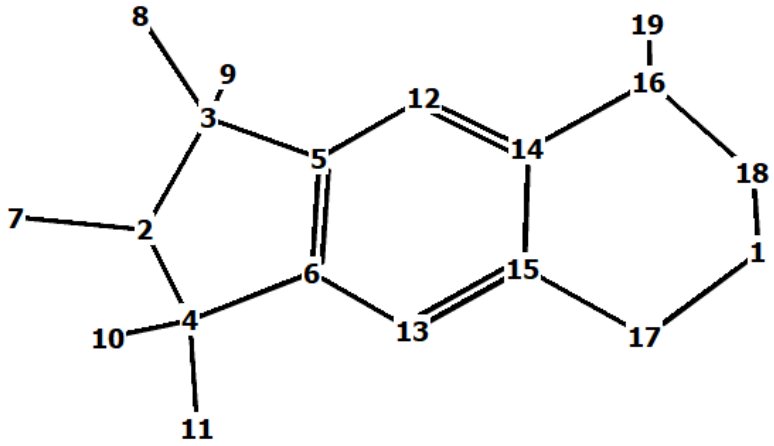


Table S1. Geometry (Å) of galaxolide.

Atom	x	y	z
O	4.050355	-1.21284	0.479631
C	-2.90717	0.16158	-0.45196
C	-1.97296	1.304385	0.057164
C	-2.19356	-1.19556	-0.15777
C	-0.61677	0.62199	0.034771
C	-0.73963	-0.7645	-0.08552
C	-4.3546	0.249055	0.011221
C	-2.2936	1.780233	1.482338
C	-2.02892	2.510248	-0.88509
C	-2.61166	-1.84194	1.172263
C	-2.44464	-2.19742	-1.28822
C	0.640211	1.208727	0.140149
C	0.398364	-1.56372	-0.09016
C	1.797902	0.416109	0.127179
C	1.665698	-0.97867	0.020022
C	3.181965	1.038628	0.240084
C	2.893161	-1.86453	0.004302
C	4.235898	0.021613	-0.18374
C	3.342199	2.321483	-0.57402
H	-2.9022	0.255564	-1.55218
H	-4.44298	0.161836	1.103784
H	-4.80276	1.209062	-0.28776
H	-4.95845	-0.55299	-0.44023
H	-1.53717	2.511105	1.807763
H	-3.27748	2.272562	1.52102
H	-2.29224	0.952207	2.205451
H	-1.36868	3.318669	-0.53451
H	-1.72045	2.229122	-1.90316
H	-3.05329	2.91271	-0.93199
H	-2.47788	-1.1604	2.024484
H	-3.66632	-2.156	1.142596

H	-1.99806	-2.73694	1.359156
H	-3.52275	-2.4009	-1.38701
H	-2.07629	-1.80764	-2.24885
H	-1.94117	-3.15609	-1.08843
H	0.727645	2.294129	0.233288
H	0.315019	-2.652	-0.17326
H	3.364913	1.270425	1.303984
H	2.734388	-2.73959	0.649811
H	3.066836	-2.2365	-1.02538
H	4.193087	-0.12681	-1.28201
H	5.2424	0.377016	0.075869
H	3.097874	2.141864	-1.63248
H	2.694768	3.127884	-0.2058
H	4.381108	2.679819	-0.51631

Table S2. Frequencies (cm^{-1}) of galaxolide.

43	61	92	113	144	151	201	230
238	243	248	260	262	273	276	288
307	316	331	333	351	374	380	389
415	457	483	516	525	550	560	589
629	679	690	723	772	785	823	832
902	911	919	931	944	944	953.	960
983	991	1003	1016	1025	1027	1069	1091
1105	1122	1146	1155	1161	1182	1208	1212
1216	1233	1246	1254	1259	1295	1302	1311
1326	1340	1350	1351	1371	1374	1376	1380
1384	1387	1390	1396	1412	1438	1444	1448
1450	1454	1456	1458	1462	1462	1467	1469
1470	1476	1478	1493	1544	1660	1704	3003
3006	3036	3039	3045	3046	3046	3052	3053
3055	3119	3119	3121	3125	3125	3126	3127
3129	3132	3136	3143	3145	3146	3151	3180
3198							

TS1

Figure S4. The optimized structure of the TS1 transition state.

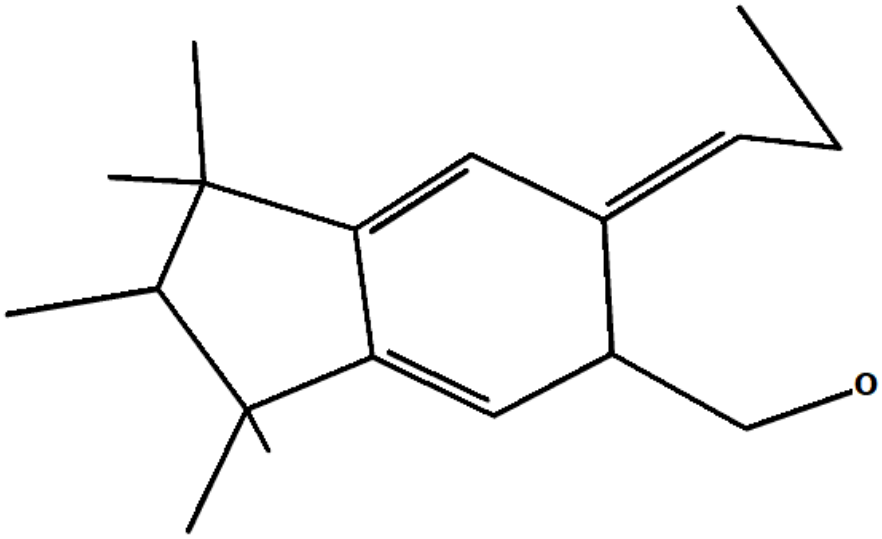


Table S3. Geometry (Å) of the TS1 transition state.

Atom	x	y	z
O	3.988673	-1.40978	1.021008
C	-2.86492	0.185545	-0.46105
C	-1.97159	1.312957	0.146052
C	-2.16508	-1.17834	-0.16742
C	-0.613	0.637383	0.177299
C	-0.71837	-0.75106	0.0034
C	-4.33911	0.254689	-0.08763
C	-2.3819	1.730521	1.566688
C	-1.97911	2.553608	-0.75127
C	-2.65687	-1.86719	1.115352
C	-2.34256	-2.14518	-1.3413
C	0.632442	1.211051	0.369651
C	0.4113	-1.55716	0.050104
C	1.781063	0.394912	0.36511
C	1.687604	-1.00511	0.240475
C	3.110401	1.012678	0.489791
C	4.19053	0.58519	-0.27135
C	3.483214	2.000902	-1.06446
H	-2.79088	0.317027	-1.55505
H	-4.4967	0.130184	0.993318
H	-4.77049	1.224273	-0.38015
H	-4.91039	-0.53177	-0.60398
H	-1.64985	2.448388	1.967748
H	-3.36768	2.220461	1.56247
H	-2.42417	0.87413	2.25443
H	-1.35166	3.353421	-0.32788
H	-1.60176	2.314265	-1.7567
H	-3.00242	2.949014	-0.84952

H	-2.57918	-1.21259	1.995079
H	-3.70596	-2.18358	1.010793
H	-2.05052	-2.76532	1.309507
H	-3.41199	-2.34573	-1.51217
H	-1.91668	-1.7262	-2.26514
H	-1.85035	-3.10902	-1.13957
H	0.7351	2.292967	0.496486
H	0.319439	-2.64558	-0.03504
H	3.293685	1.734322	1.289399
H	4.052209	-0.19679	-1.0118
H	5.204349	0.845069	0.023316
H	2.858847	1.608865	-1.86864
H	2.983466	2.838495	-0.56121
H	4.451867	2.38739	-1.40475
C	2.910711	-1.93469	0.423042
H	3.078658	-2.3469	-0.62186
H	2.467824	-2.82671	0.951154

Table S4. Frequencies (cm^{-1}) of the TS1 transition state.

45	50	81	107	125	136	163	167
181	225	232	238	242	253	264	272
283	284	305	312	329	330	344	368
381	410	428	488	523	549	551	572
592	622	671	709	718	750	780	824
831	850	909	916	925	936	944.	947
954	978	993	1000	1005	1012	1026	1036
1089	1092	1105	1113	1142	1161	1163	1208
1210	1217	1220	1245	1251	1256	1275	1295
1299	1311	1348	1349	1351	1371	1374	1384
1389	1396	1400	1400	1411	1433	1438	1439
1443	1446	1454	1455	1460	1461	1468	1472
1476	1480	1529	1599	1643	1696	2684	2786
3031	3040	3042	3046	3050	3055	3095	3120
3123	3123	3125	3130	3130	3133	3140	3140
3158	3162	3174	3181	3212	3215	3246	3335
-591							

IM1

Figure S5. The optimized structure of IM1.

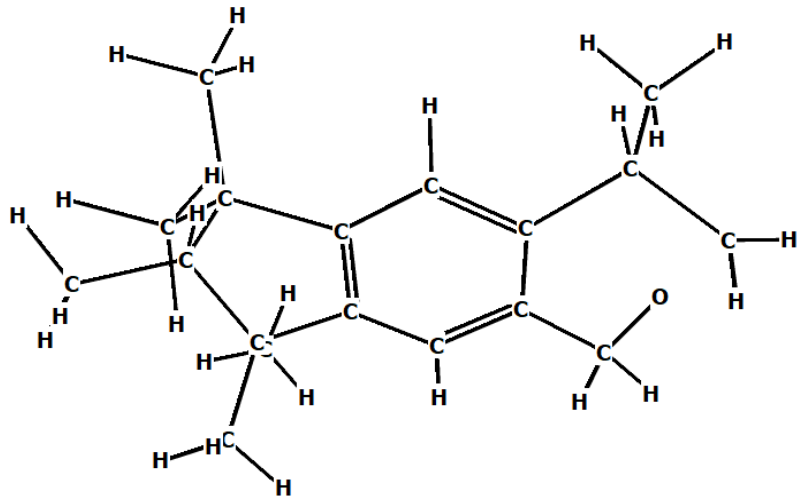


Table S5. Geometry (Å) of IM1.

Atom	x	y	z
O	3.9242	-1.68105	-0.72329
C	-2.89564	-0.01567	-0.34367
C	-1.99382	1.256029	-0.2542
C	-2.09382	-1.206	0.273311
C	-0.60846	0.64043	-0.17871
C	-0.66457	-0.71997	0.116679
C	-4.31382	0.154144	0.182779
C	-2.24989	2.112136	0.995732
C	-2.16975	2.135773	-1.49486
C	-2.40064	-1.45908	1.757534
C	-2.35416	-2.49742	-0.50762
C	0.624648	1.267632	-0.33455
C	0.516807	-1.44347	0.251653
C	1.825869	0.556081	-0.2032
C	1.763152	-0.82344	0.093084
C	3.124087	1.333178	-0.44403
C	4.240839	0.992345	0.488801
C	3.548639	1.241394	-1.91602
H	-2.96416	-0.24341	-1.422
H	-4.32855	0.379022	1.258944
H	-4.82901	0.974165	-0.34057
H	-4.9018	-0.76257	0.02256
H	-1.51087	2.926811	1.044971
H	-3.25209	2.566387	0.961736
H	-2.16633	1.526595	1.92241
H	-1.535	3.03363	-1.43829
H	-1.90721	1.583719	-2.40962
H	-3.21523	2.472	-1.58039
H	-2.25841	-0.55748	2.370144
H	-3.43621	-1.8078	1.890658

H	-1.72906	-2.23934	2.147896
H	-3.42382	-2.75805	-0.47007
H	-2.06157	-2.38486	-1.56222
H	-1.7897	-3.34052	-0.07992
H	0.670841	2.337203	-0.56194
H	0.483174	-2.51323	0.47953
H	2.855086	2.387815	-0.24697
H	4.132867	1.167759	1.560388
H	5.163926	0.541762	0.121915
H	3.797771	0.202329	-2.169
H	2.735283	1.581068	-2.57366
H	4.429877	1.874642	-2.09841
C	2.987674	-1.69895	0.27223
H	2.68717	-2.74655	0.476927
H	3.552258	-1.40556	1.18703

Table S6. Frequencies (cm^{-1}) of IM1.

48	55	96	120	134	140	153	195
218	221	229	237	253	256	270	274
280	282	292	298	302	313	329	344
356	378	401	425	429	459	512	543
550	556	589	606	624	684	712	728
752	791	820	833	894	919	923.	928
938	943	948	953	989	995	1003	1027
1028	1076	1091	1103	1114	1141	1157	1160
1162	1201	1209	1216	1223	1243	1252	1294
1299	1318	1327	1331	1348	1351	1355	1370
1372	1373	1374	1384	1390	1395	1434	1440
1444	1447	1451	1453	1454	1459	1461	1466
1467	1474	1477	1480	1544	1656	1700	2961
3011	3018	3033	3040	3041	3046	3052	3055
3056	3117	3119	3125	3126	3132	3133	3136
3138	3138	3143	3150	3165	3168	3170	3172
3288							

P1 (G3)

Figure S6. The optimized structure of P1(G3).

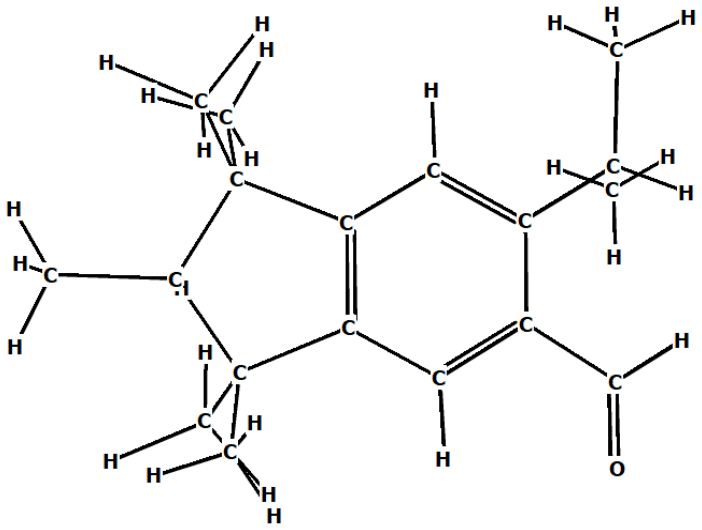


Table S7. Geometry (Å) of P1(G3).

Atom	x	y	z
O	1.397296	-1.42224	-4.05188
C	-2.72532	0.59688	0.570699
C	-1.39376	0.591387	1.386177
C	-2.5138	-0.31326	-0.6807
C	-0.38144	0.229544	0.315482
C	-1.00459	-0.27253	-0.83049
C	-3.9839	0.309605	1.377313
C	-1.35491	-0.45692	2.509234
C	-1.12219	1.970327	1.994126
C	-2.98056	-1.76296	-0.47986
C	-3.22798	0.268154	-1.90388
C	1.006419	0.331019	0.389535
C	-0.2278	-0.67263	-1.90691
C	1.812006	-0.06124	-0.68727
C	1.17052	-0.56563	-1.8431
C	3.324398	0.114025	-0.62825
C	1.92781	-1.01027	-3.03997
C	3.737485	1.369781	-1.40893
C	3.879024	0.178583	0.794838
H	-2.81193	1.622141	0.169956
H	-3.97622	-0.70149	1.809498
H	-4.09018	1.028125	2.204213
H	-4.8806	0.397721	0.745033
H	-0.35591	-0.46844	2.971611
H	-2.08775	-0.21244	3.292999
H	-1.56691	-1.47052	2.141034
H	-0.18844	1.971047	2.577279
H	-1.04216	2.738311	1.210514
H	-1.94026	2.253431	2.6748

H	-2.52415	-2.22708	0.40569
H	-4.0746	-1.81017	-0.3698
H	-2.70165	-2.36647	-1.35722
H	-4.31177	0.332832	-1.71864
H	-2.85495	1.277171	-2.13478
H	-3.07756	-0.36823	-2.78981
H	1.466972	0.723159	1.297504
H	-0.67114	-1.07296	-2.82137
H	3.788741	-0.75936	-1.11037
H	3.287307	2.262827	-0.94756
H	4.831068	1.488563	-1.39696
H	3.578701	1.106824	1.30378
H	3.541562	-0.67376	1.401719
H	4.977582	0.164702	0.760789
H	3.035141	-0.95925	-2.98366
H	3.405485	1.329796	-2.45682

Table S8. Frequencies (cm^{-1}) of P1(G3).

37	61	64	101	135	137	149	184
218	232	240	244	250	257	260	271
273	288	302	311	321	328	342	351
361	399	408	442	484	505	526	537
554	601	632	672	708	725	784	794
826	845	914	916	926	940	946.	948
952	958	968	993	1006	1012	1029	1044
1082	1091	1105	1126	1147	1149	1163	1191
1211	1217	1230	1246	1254	1296	1313	1334
1348	1351	1355	1369	1373	1374	1384	1387
1391	1393	1400	1440	1444	1445	1447	1451
1456	1457	1458	1461	1462	1463	1470	1476
1478	1481	1483	1538	1653	1696	1812	3031
3032	3044	3045	3046	3048	3053	3054	3058
3087	3124	3126	3127	3128	3131	3134	3134
3135	3136	3137	3143	3143	3144	3156	3200
3207							

TS2

Figure S7. The optimized structure of TS2.

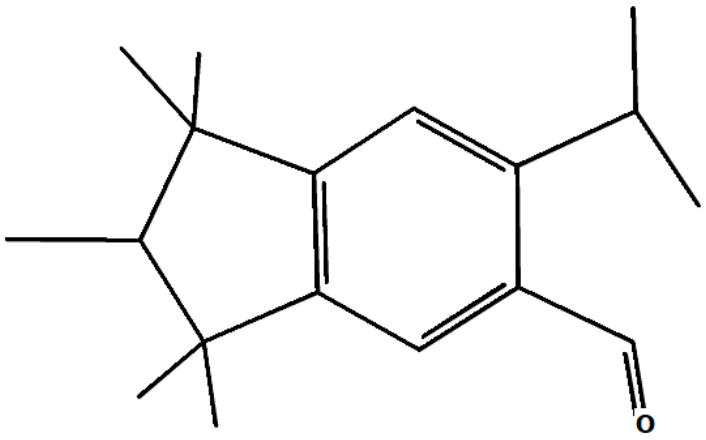


Table S9. Geometry (Å) of TS2.

Atom	x	y	z
O	2.067804	-0.21576	-3.92122
C	-2.74385	0.530361	0.655987
C	-1.46547	0.42881	1.546021
C	-2.43715	-0.19713	-0.69082
C	-0.38105	0.21896	0.504512
C	-0.92156	-0.1279	-0.73715
C	-4.0423	0.118862	1.33572
C	-1.47978	-0.75711	2.523603
C	-1.25792	1.718377	2.345331
C	-2.89251	-1.66456	-0.72275
C	-3.08371	0.540732	-1.86671
C	1.000477	0.333423	0.680393
C	-0.08604	-0.37629	-1.82583
C	1.840746	0.075366	-0.40166
C	1.293323	-0.2896	-1.63991
C	3.354083	0.216134	-0.41807
C	2.269145	-0.57017	-2.74763
C	3.713878	0.597206	-1.82954
C	3.893339	1.234755	0.592223
H	-2.82749	1.599582	0.393312
H	-4.03657	-0.94268	1.621649
H	-4.21116	0.713129	2.246767
H	-4.9015	0.283926	0.6678
H	-0.50951	-0.82351	3.039751
H	-2.26092	-0.62508	3.28783
H	-1.65389	-1.71454	2.012262
H	-0.36166	1.653601	2.981381
H	-1.14527	2.583471	1.674968
H	-2.12104	1.900656	3.00495
H	-2.4808	-2.2459	0.114441
H	-3.99035	-1.73492	-0.68625

H	-2.55492	-2.13749	-1.65792
H	-4.17813	0.569115	-1.74501
H	-2.71519	1.575287	-1.93248
H	-2.8666	0.034451	-2.82001
H	1.412111	0.639263	1.645041
H	-0.48584	-0.63823	-2.80855
H	3.806063	-0.76569	-0.19378
H	3.365414	1.577458	-2.17111
H	4.660151	0.256284	-2.25589
H	3.425413	2.218095	0.435964
H	3.684779	0.908362	1.621064
H	4.981584	1.342416	0.486539
H	2.959806	-1.42314	-2.54561

Table S10. Frequencies (cm^{-1}) of TS2.

46	61	98	110	134	146	181	219
222	234	242	248	259	268	270	279
291	308	328	333	342	357	373	394
416	426	486	508	531	544	556	590
616	636	656	712	729	780	798	821
836	881	911	915	926	937	941.	942
946	952	986	991	1004	1009	1027	1056
1090	1099	1113	1142	1158	1160	1169	1206
1214	1226	1240	1243	1292	1307	1312	1349
1349	1351	1361	1373	1374	1376	1378	1385
1389	1395	1436	1439	1444	1446	1450	1453
1456	1458	1460	1463	1466	1473	1476	1488
1530	1599	1664	1696	2942	3038	3040	3043
3048	3050	3052	3054	3061	3117	3121	3125
3128	3129	3137	3137	3138	3140	3142	3144
3149	3160	3184	3187	3252			
3207	-411						

TS2A_v1

Figure S8. The optimized structure of TS2A_v1.

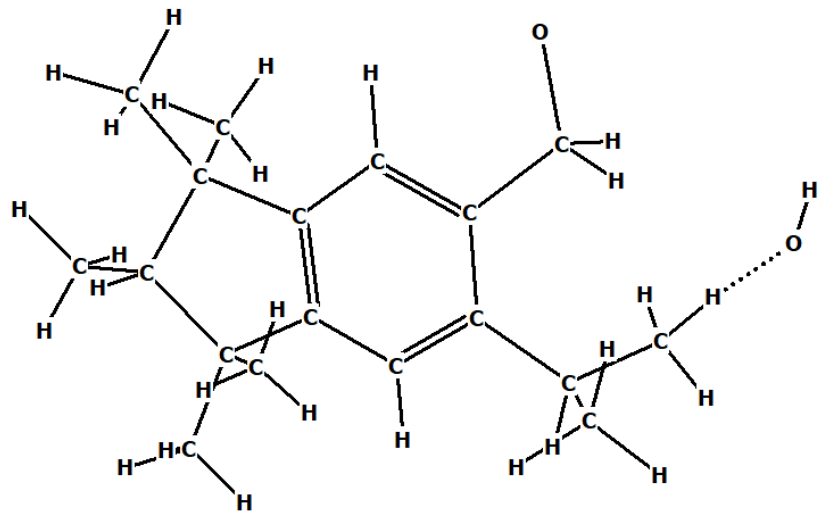


Table S11. Geometry (Å) of TS2a_v1.

Atom	x	y	z
O	2.587108	-3.10698	0.468914
C	-2.80671	0.205303	-0.86744
C	-1.8719	1.427029	-0.5974
C	-2.1578	-1.04273	-0.18965
C	-0.54166	0.740267	-0.3473
C	-0.70045	-0.62541	-0.11876
C	-4.27781	0.42887	-0.54719
C	-2.26957	2.252985	0.635672
C	-1.82512	2.355338	-1.81428
C	-2.68768	-1.32928	1.223944
C	-2.35818	-2.29421	-1.04935
C	0.727942	1.308119	-0.29731
C	0.410585	-1.41401	0.16219
C	1.862836	0.531057	-0.01881
C	1.69034	-0.85006	0.214053
C	3.21073	1.24154	-0.05794
C	4.148244	0.979047	1.119731
C	3.926583	1.012761	-1.39732
H	-2.72601	0.017227	-1.9526
H	-4.44158	0.624596	0.522441
H	-4.67439	1.287389	-1.11057
H	-4.87536	-0.45351	-0.82305
H	-1.51051	3.028283	0.822789
H	-3.23563	2.756567	0.477507
H	-2.34619	1.633484	1.540528
H	-1.16198	3.215293	-1.63235
H	-1.46098	1.820234	-2.70402
H	-2.82997	2.749998	-2.0335
H	-2.59308	-0.45722	1.886516

H	-3.74685	-1.62784	1.193899
H	-2.11576	-2.15574	1.673286
H	-3.43197	-2.50891	-1.16984
H	-1.91642	-2.16035	-2.04805
H	-1.89176	-3.17448	-0.58048
H	0.855318	2.379249	-0.48059
H	0.3072	-2.48625	0.339708
H	2.972626	2.31703	-0.00855
H	3.640584	0.706925	2.055367
H	4.823196	1.828215	1.292908
H	4.170581	-0.05096	-1.5395
H	3.293737	1.337029	-2.23513
H	4.869002	1.580119	-1.42988
C	2.847614	-1.77341	0.551169
H	3.759889	-1.57126	-0.04896
H	3.218638	-1.58624	1.584953
O	5.883666	-0.86025	0.519492
H	5.891801	-1.2708	1.408624
H	4.888816	0.111262	0.845883

Table S12. Frequencies (cm^{-1}) of TS2a_v1.

38	45	72	93	104	120	139	145
148	179	211	227	236	241	253	258
263	270	274	279	290	295	312	319
331	341	355	360	399	409	435	455
502	526	551	555	571	593	635	658
710	724	734	767	792	820	837.	913
921	937	940	944	948	953	959	973
990	1001	1002	1025	1040	1070	1084	1091
1106	1127	1144	1152	1156	1162	1197	1212
1218	1235	1244	1251	1295	1305	1309	1317
1340	1349	1350	1356	1366	1372	1373	1384
1384	1388	1396	1398	1412	1441	1444	1447
1449	1456	1456	1461	1464	1466	1468	1475
1477	1479	1491	1545	1661	1705	2957	2996
3030	3044	3044	3046	3048	3049	3050	3059
3094	3121	3122	3123	3126	3127	3133	3135
3139	3139	3141	3151	3156	3163	3169	3194
3700	-861						

TS2A_v2

Figure S9. The optimized structure of TS2a_v2.

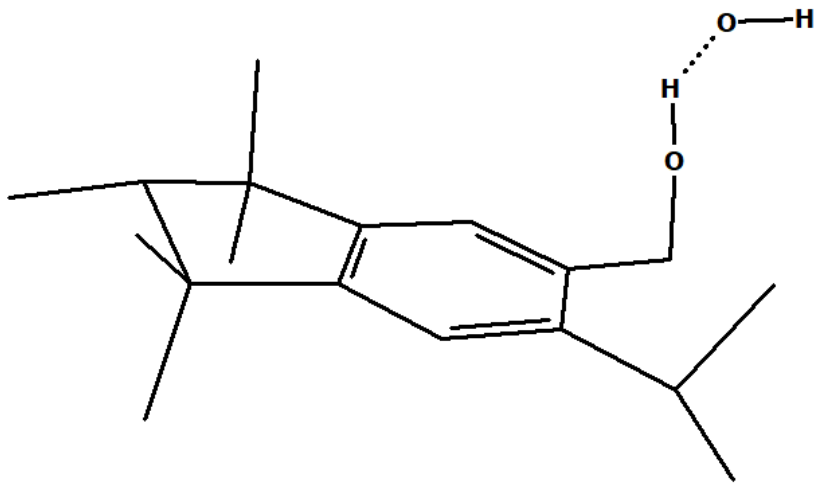


Table S13. Geometry (Å) of TS2a_v2.

Atom	x	y	z
O	-4.35215	2.033717	-0.13747
C	1.873841	-1.01051	1.763308
C	1.288428	-1.48413	0.394544
C	0.688692	-0.45804	2.617231
C	0.020968	-0.65637	0.307106
C	-0.31319	-0.08444	1.538737
C	2.771457	-2.01698	2.469552
C	0.944903	-2.98167	0.351871
C	2.262524	-1.17571	-0.74673
C	0.072676	-1.49684	3.566862
C	1.132422	0.753625	3.44132
C	-0.80318	-0.44933	-0.80119
C	-1.4542	0.684947	1.657243
C	-1.96208	0.324942	-0.72807
C	-2.30758	0.917153	0.535746
C	-2.78888	0.579982	-1.9795
C	-3.44407	1.730045	0.807525
C	-2.4817	1.977194	-2.53708
C	-2.59972	-0.47001	-3.07469
H	2.489683	-0.12633	1.521243
H	2.229588	-2.93516	2.739192
H	3.617292	-2.30431	1.826319
H	3.188333	-1.5879	3.393728
H	0.44908	-3.22038	-0.60192
H	1.854493	-3.59797	0.422866
H	0.265283	-3.27255	1.165246
H	1.850924	-1.49672	-1.71638
H	2.474623	-0.09748	-0.80205
H	3.214158	-1.7098	-0.59523
H	-0.24316	-2.40711	3.037475

H	0.788405	-1.78437	4.352503
H	-0.81498	-1.06863	4.057414
H	1.940479	0.471119	4.134859
H	1.500622	1.559624	2.789122
H	0.299944	1.149658	4.043641
H	-0.52916	-0.90577	-1.7545
H	-1.72254	1.13176	2.618964
H	-3.84842	0.56072	-1.68688
H	-1.43157	2.025264	-2.86833
H	-3.12494	2.199004	-3.40281
H	-1.59627	-0.41511	-3.52388
H	-2.74814	-1.4901	-2.69071
H	-3.32775	-0.29633	-3.88028
H	-3.54823	2.09396	1.838724
H	-2.64445	2.75558	-1.77912
O	-6.25331	3.178924	0.411111
H	-5.3892	2.372778	0.23332
H	-6.56628	3.448156	-0.48464

Table S14. Frequencies (cm^{-1}) of TS2a_v2.

33	52	66	87	98	117	123	140
182	192	211	221	229	238	248	256
264	269	277	288	294	303	316	327
336	342	356	372	400	410	417	451
467	489	522	550	559	592	611	635
677	709	722	750	774	802.	824	842
887	903	914	926	936	943	947	954
972	991	1003	1010	1026	1076	1084	1090
1108	1116	1144	1160	1164	1175	1211	1214
1217	1240	1243	1270	1297	1308	1309	1338
1349	1350	1365	1372	1374	1377	1384	1388
1390	1395	1401	1439	1443	1444	1446	1446
1452	1454	1459	1461	1465	1466	1468	1475
1477	1478	1483	1532	1594	1668	3030	3039
3042	3042	3047	3050	3052	3053	3082	3120
3121	3121	3122	3125	3126	3127	3134	3135
3136	3137	3142	3152	3154	3154	3177	3206
3626	-2757						

IM2A_v1

Figure S10. The optimized structure of IM2_v1.

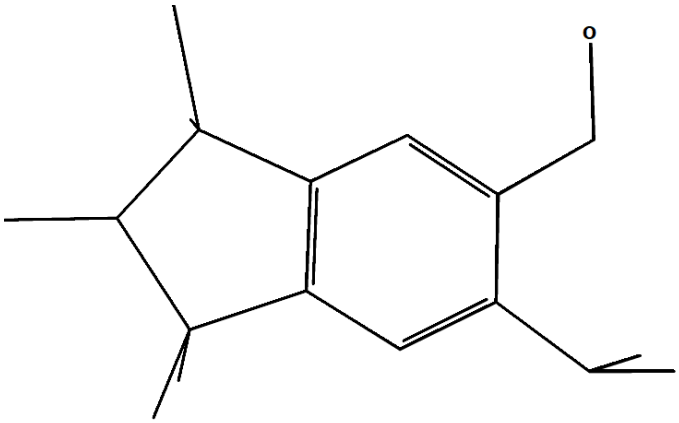


Table S15. Geometry (Å) of IM2_v1.

Atom	x	y	z
O	-3.75965	1.581876	1.277158
C	2.748612	-0.25027	-0.43818
C	1.801962	-1.22653	0.329522
C	2.097665	1.168178	-0.40259
C	0.464937	-0.54562	0.173623
C	0.62642	0.840679	-0.20826
C	4.212214	-0.30443	-0.02172
C	2.145297	-1.37206	1.824681
C	1.832693	-2.62045	-0.30618
C	2.591376	2.046172	0.758526
C	2.350072	1.913622	-1.71559
C	-0.82088	-1.15758	0.145428
C	-0.45799	1.627425	-0.4097
C	-1.94705	-0.39982	-0.04522
C	-1.76933	1.091635	0.040907
C	-3.32236	-0.95955	-0.31709
C	-3.92547	-0.27714	-1.55166
C	-3.35044	-2.47757	-0.45561
H	2.690497	-0.56992	-1.49388
H	4.355296	-0.00564	1.026827
H	4.613533	-1.32273	-0.13788
H	4.821297	0.365155	-0.64791
H	1.382431	-1.99391	2.317466
H	3.121985	-1.86307	1.95636
H	2.173599	-0.40277	2.341585
H	1.190015	-3.32468	0.243857
H	1.494159	-2.58527	-1.35252
H	2.85732	-3.02387	-0.28605
H	2.452679	1.563963	1.73639
H	3.658703	2.287805	0.640901
H	2.026652	2.990727	0.767189
H	3.431433	2.047683	-1.87811

H	1.935959	1.357585	-2.56967
H	1.888698	2.913023	-1.69782
H	-0.88319	-2.24834	0.171043
H	-0.37506	2.65299	-0.78124
H	-3.95344	-0.66885	0.539783
H	-3.31576	-0.48414	-2.44591
H	-4.94515	-0.64709	-1.73532
H	-2.72807	-2.80849	-1.3026
H	-2.98343	-2.97689	0.452904
H	-4.37954	-2.82055	-0.63599
H	-3.97101	0.811665	-1.40526
H	-4.07137	1.849446	2.152184
C	-2.35369	1.774174	1.248108
H	-2.1003	2.8498	1.212182
H	-1.881	1.354713	2.162874

Table S16. Frequencies (cm^{-1}) of IM2_v1.

30	49	67	76	106	122	138	165
179	218	227	235	243	248	257	259
266	276	279	297	301	308	331	335
340	346	369	377	415	427	447	486
539	553	568	603	636	662	693	703
746	804	812	833	887	894	916.	936
941	945	947	949	966	990	996	1003
1027	1067	1086	1089	1092	1108	1130	1148
1152	1169	1179	1195	1211	1214	1224	1237
1259	1280	1287	1309	1315	1328	1346	1356
1357	1366	1372	1376	1383	1387	1390	1399
1403	1433	1438	1442	1444	1452	1452	1456
1459	1460	1460	1462	1465	1467	1474	1477
1478	1553	1668	2963	3031	3041	3044	3046
3048	3048	3049	3052	3055	3064	3119	3124
3125	3127	3128	3130	3132	3132	3136	3137
3139	3140	3144	3160	3185	3200	3846	

IM2A_v2

Figure S11. The optimized structure of IM2_v2.

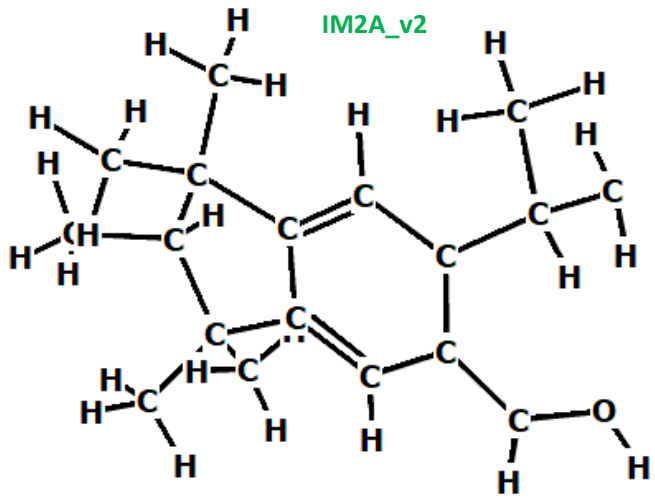


Table S17. Geometry (Å) of IM2_v2.

Atom	x	y	z
O	-2.54262	2.896489	-0.24773
C	3.199831	-0.05769	-0.44176
C	2.346172	-1.29597	-0.02029
C	2.383797	1.222751	-0.07706
C	0.945096	-0.71199	-0.01962
C	0.966402	0.680603	-0.05263
C	4.643796	-0.06749	0.039793
C	2.685716	-1.83851	1.37642
C	2.499325	-2.43142	-1.03631
C	2.738125	1.815838	1.295474
C	2.568924	2.307923	-1.14152
C	-0.27251	-1.38441	0.034724
C	-0.22899	1.392248	-0.03362
C	-1.49214	-0.68958	0.054483
C	-1.45629	0.721865	0.016357
C	-2.76699	-1.52734	0.068318
C	-3.79495	-1.14584	1.140565
C	-3.40884	-1.60392	-1.32309
H	3.216002	-0.08307	-1.54564
H	4.71254	-0.03895	1.13691
H	5.1655	-0.97263	-0.30718
H	5.191698	0.802518	-0.35353
H	1.978493	-2.63854	1.644914
H	3.701049	-2.26364	1.396832
H	2.621018	-1.06001	2.149941
H	1.898212	-3.30733	-0.74683
H	2.179615	-2.10864	-2.0384
H	3.55118	-2.7536	-1.0946

H	2.647106	1.074683	2.102171
H	3.766395	2.208839	1.301057
H	2.056488	2.648977	1.526665
H	3.627912	2.6041	-1.20753
H	2.246643	1.948193	-2.13005
H	1.984643	3.207747	-0.89425
H	-0.2917	-2.47807	0.060479
H	-0.23226	2.483251	-0.06621
H	-2.4341	-2.54789	0.3141
H	-3.31119	-0.93847	2.106757
H	-4.49813	-1.97917	1.285922
H	-3.75664	-0.61839	-1.66924
H	-2.6909	-1.98603	-2.06296
H	-4.27927	-2.27712	-1.3056
C	-2.71444	1.575892	0.040395
H	-3.52128	1.167923	-0.60046
H	-3.17527	1.565891	1.055929
H	-4.39679	-0.27105	0.857853

Table S18. Frequencies (cm^{-1}) of IM2_v2.

40	60	78	105	135	140	152	177
217	222	233	242	250	256	259	266
276	284	293	303	316	321	330	347
360	398	402	421	463	500	525	549
553	592	633	656	661	725	745	763
797	819	836	912	918	928.	938	944
944	948	954	971	990	1000	1004	1026
1076	1088	1091	1106	1130	1145	1151	1158
1162	1191	1212	1218	1236	1244	1252	1294
1312	1319	1338	1343	1349	1351	1370	1372
1373	1380	1384	1385	1389	1395	1397	1440
1444	1448	1449	1454	1455	1458	1462	1463
1468	1470	1474	1478	1478	1489	1545	1660
1704	2952	3020	3027	3041	3042	3045	3048
3054	3056	3059	3073	3121	3121	3122	3125
3129	3131	3132	3132	3134	3138	3139	3149
3151	3155	3167	3199				

P3A

Figure S12. The optimized structure of P3A product.

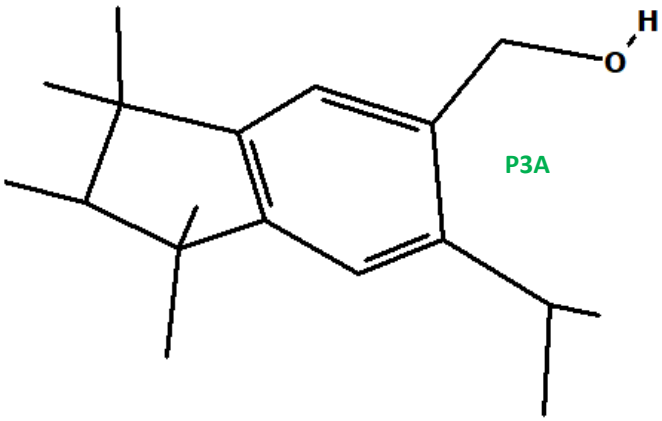


Table S19. Geometry (Å) of P3A product.

Atom	x	y	z
O	-3.75965	1.581876	1.277158
C	2.748612	-0.25027	-0.43818
C	1.801962	-1.22653	0.329522
C	2.097665	1.168178	-0.40259
C	0.464937	-0.54562	0.173623
C	0.62642	0.840679	-0.20826
C	4.212214	-0.30443	-0.02172
C	2.145297	-1.37206	1.824681
C	1.832693	-2.62045	-0.30618
C	2.591376	2.046172	0.758526
C	2.350072	1.913622	-1.71559
C	-0.82088	-1.15758	0.145428
C	-0.45799	1.627425	-0.4097
C	-1.94705	-0.39982	-0.04522
C	-1.76933	1.091635	0.040907
C	-3.32236	-0.95955	-0.31709
C	-3.92547	-0.27714	-1.55166
C	-3.35044	-2.47757	-0.45561
H	2.690497	-0.56992	-1.49388
H	4.355296	-0.00564	1.026827
H	4.613533	-1.32273	-0.13788
H	4.821297	0.365155	-0.64791
H	1.382431	-1.99391	2.317466
H	3.121985	-1.86307	1.95636
H	2.173599	-0.40277	2.341585
H	1.190015	-3.32468	0.243857
H	1.494159	-2.58527	-1.35252
H	2.85732	-3.02387	-0.28605
H	2.452679	1.563963	1.73639
H	3.658703	2.287805	0.640901
H	2.026652	2.990727	0.767189

H	3.431433	2.047683	-1.87811
H	1.935959	1.357585	-2.56967
H	1.888698	2.913023	-1.69782
H	-0.88319	-2.24834	0.171043
H	-0.37506	2.65299	-0.78124
H	-3.95344	-0.66885	0.539783
H	-3.31576	-0.48414	-2.44591
H	-4.94515	-0.64709	-1.73532
H	-2.72807	-2.80849	-1.3026
H	-2.98343	-2.97689	0.452904
H	-4.37954	-2.82055	-0.63599
H	-3.97101	0.811665	-1.40526
H	-4.07137	1.849446	2.152184
C	-2.35369	1.774174	1.248108
H	-2.1003	2.8498	1.212182
H	-1.881	1.354713	2.162874

Table S20. Frequencies (cm^{-1}) of P3A product.

30	49	67	76	106	122	138	165
179	218	227	235	243	248	257	259
266	276	279	297	301	308	331	335
340	346	369	377	415	427	447	486
539	553	568	603	636	662	693	703
746	804	812	833	887	894.	916	936
941	945	947	949	966	990	996	1003
1027	1067	1086	1089	1092	1108	1130	1148
1152	1169	1179	1195	1211	1214	1224	1237
1259	1280	1287	1309	1315	1328	1346	1356
1357	1366	1372	1376	1383	1387	1390	1399
1403	1433	1438	1442	1444	1452	1452	1456
1459	1460	1460	1462	1465	1467	1474	1477
1478	1553	1668	2963	3031	3041	3044	3046
3048	3048	3049	3052	3055	3064	3119	3124
3125	3127	3128	3130	3132	3132	3136	3137
3139	3140	3144	3160	3185	3200	3846	

TS4A (OH departure)

Figure S13. The optimized structure of TS4A.

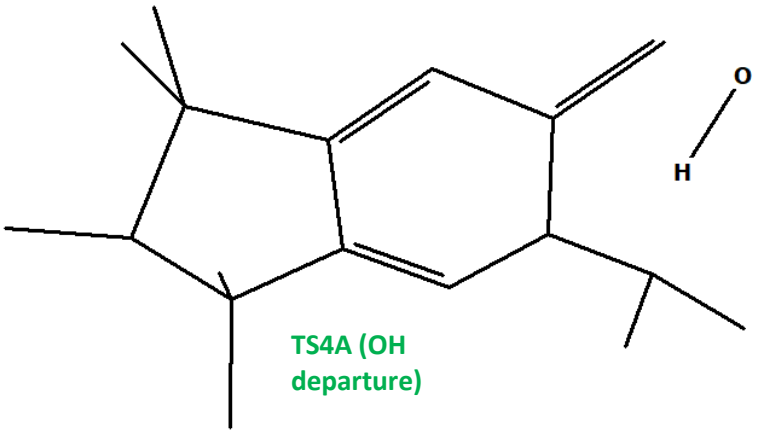


Table S21. Geometry (Å) of TS4A.

Atom	x	y	z
C	-2.71202	0.026228	-0.57421
C	-1.80305	1.244763	-0.21532
C	-2.06779	-1.24788	0.057598
C	-0.47398	0.580379	0.020839
C	-0.60897	-0.84581	0.166001
C	-4.19447	0.215389	-0.28475
C	-2.24365	2.002811	1.052335
C	-1.75082	2.24303	-1.37927
C	-2.60804	-1.58365	1.457616
C	-2.26349	-2.46543	-0.84875
C	0.813138	1.196784	0.093018
C	0.478284	-1.62609	0.365486
C	1.946201	0.464484	0.294007
C	1.818874	-1.01868	0.497863
C	3.324161	1.082271	0.343035
C	3.311665	2.597825	0.524674
H	-2.5996	-0.1039	-1.66484
H	-4.39171	0.355026	0.787741
H	-4.58538	1.095666	-0.8173
H	-4.77198	-0.65905	-0.62122
H	-1.50372	2.781441	1.293174
H	-3.21415	2.496208	0.889959
H	-2.33238	1.339596	1.923809
H	-1.11763	3.109205	-1.13377
H	-1.35307	1.76808	-2.28831
H	-2.76209	2.620616	-1.5979
H	-2.50163	-0.7441	2.159011
H	-3.67171	-1.86151	1.408769
H	-2.05086	-2.43812	1.870416

H	-3.33686	-2.66806	-0.98862
H	-1.80996	-2.29789	-1.83669
H	-1.80839	-3.36482	-0.40662
H	0.879756	2.279976	-0.02605
H	0.403439	-2.71264	0.449207
H	3.838355	0.647105	1.218628
H	2.887707	3.101194	-0.35798
H	2.727246	2.897008	1.406549
H	4.340348	2.963939	0.650786
C	2.905487	-1.85316	0.717635
H	2.71767	-2.85122	1.113779
O	3.178376	-2.5363	-1.03243
H	3.893634	-1.43929	0.908202
H	2.713959	-1.87231	-1.57411
C	4.134144	0.711453	-0.91181
H	5.164364	1.087423	-0.82377
H	4.169889	-0.37392	-1.07567
H	3.672815	1.1786	-1.79661

Table S22. Frequencies (cm^{-1}) of TS4A.

24	58	81	92	110	123	145	160
185	212	222	235	240	246	257	272
275	279	290	300	303	321	329	334
346	359	381	396	416	457	465	499
514	546	575	593	644	673	691	715
739	813	821	829	858	893.	898	905
927	933	943	946	949	963	972	991
1000	1002	1012	1023	1075	1086	1091	1112
1136	1143	1147	1182	1209	1213	1233	1242
1268	1281	1301	1318	1342	1348	1353	1365
1369	1373	1376	1385	1388	1391	1394	1400
1411	1437	1444	1444	1455	1455	1458	1460
1463	1465	1466	1469	1477	1478	1488	1537
1618	1718	3036	3042	3044	3046	3047	3048
3051	3052	3056	3123	3124	3126	3129	3129
3129	3129	3131	3136	3142	3144	3148	3150
3155	3168	3201	3210	3270	3749	-824	

P4A

Figure S14. The optimized structure of P4A.

Table S23. Geometry (Å) of P4A.

Atom	x	y	z
C	-2.78837	0.164683	-0.62265
C	-1.8026	1.300645	-0.20322
C	-2.18286	-1.18779	-0.13253
C	-0.49701	0.539507	-0.08152
C	-0.70598	-0.8439	-0.04438
C	-4.24568	0.399411	-0.25052
C	-2.15127	1.961978	1.140148
C	-1.7395	2.389149	-1.27939
C	-2.69752	-1.63561	1.244241
C	-2.45609	-2.30467	-1.14325
C	0.797726	1.058818	0.017348
C	0.369815	-1.70285	0.084166
C	1.904732	0.222404	0.141923
C	1.701378	-1.20193	0.175671
C	3.313217	0.788427	0.195176
C	3.377398	2.244295	0.656001
H	-2.72761	0.124272	-1.72456
H	-4.39031	0.455543	0.838238
H	-4.61325	1.341002	-0.68674
H	-4.88208	-0.41298	-0.63307
H	-1.36013	2.675458	1.417801
H	-3.09858	2.518298	1.06992
H	-2.24078	1.227429	1.952784
H	-1.04557	3.193496	-0.98961
H	-1.40481	1.973223	-2.24154
H	-2.73341	2.841775	-1.42349
H	-2.55718	-0.86121	2.011834
H	-3.76796	-1.88877	1.200521
H	-2.15031	-2.53382	1.569616
H	-3.54035	-2.45558	-1.26555
H	-2.02724	-2.06004	-2.12657
H	-2.02264	-3.25895	-0.80565
H	0.939023	2.141434	-0.00559
H	0.218912	-2.78564	0.116629
H	3.881185	0.191553	0.927142
H	2.940585	2.923391	-0.09197
H	2.845486	2.392734	1.607025
H	4.426066	2.542827	0.796792
C	2.765021	-2.12208	0.299692
H	2.550544	-3.19057	0.321837
H	3.804514	-1.81373	0.382732
C	3.998589	0.641791	-1.17153
H	5.041761	0.988835	-1.12181
H	3.995532	-0.4021	-1.51651

H	3.469155	1.250274	-1.92192

Table S24. Frequencies (cm^{-1}) of P4A.

45	63	92	115	140	147	202	216
224	234	239	249	255	267	276	282
298	303	310	324	328	349	357	383
408	418	452	480	511	517	536	551
582	603	654	704	721	739	763	786
822	841	909	911	922	933.	938	944
948	955	971	987	994	1002	1019	1027
1083	1090	1107	1116	1148	1159	1163	1210
1215	1218	1227	1243	1272	1297	1313	1320
1335	1349	1352	1367	1372	1372	1380	1384
1390	1395	1397	1436	1437	1440	1446	1448
1454	1455	1458	1462	1464	1466	1468	1474
1479	1480	1486	1526	1598	1661	3033	3037
3041	3046	3047	3053	3058	3058	3063	3119
3121	3125	3127	3128	3130	3130	3135	3138
3138	3138	3143	3143	3154	3187	3192	3214
3295							

TS5A

Figure S15. The optimized structure of TS5A transition state.

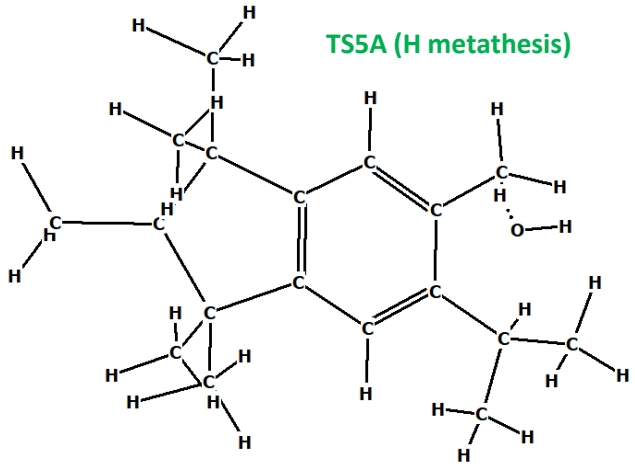


Table S25. Geometry (Å) of TS5A transition state.

Atom	x	y	z
C	-2.73451	-0.05678	-0.94338
C	-2.01603	0.877113	0.081023
C	-1.88832	-1.36273	-1.06209

C	-0.58847	0.366034	0.006369
C	-0.51783	-0.87305	-0.62865
C	-4.22356	-0.26357	-0.70373
C	-2.54357	0.747376	1.518278
C	-2.12857	2.342545	-0.34915
C	-2.35728	-2.49321	-0.13319
C	-1.88846	-1.88203	-2.50245
C	0.566484	0.967245	0.504968
C	0.712338	-1.50793	-0.7696
C	1.813044	0.346476	0.367223
C	1.885197	-0.9051	-0.29083
C	3.08083	1.015226	0.874281
C	2.855708	1.901353	2.100105
H	-2.62134	0.447815	-1.91918
H	-4.42343	-0.7625	0.255718
H	-4.75537	0.700355	-0.69663
H	-4.666	-0.87968	-1.50152
H	-1.92981	1.361788	2.195102
H	-3.58288	1.103354	1.587506
H	-2.50799	-0.28937	1.881855
H	-1.61871	3.006067	0.366435
H	-1.68259	2.497549	-1.34288
H	-3.18602	2.648283	-0.39169
H	-2.4077	-2.17209	0.916895
H	-3.35141	-2.8601	-0.43161
H	-1.65312	-3.33752	-0.19362
H	-2.91477	-2.12013	-2.8239
H	-1.47465	-1.13096	-3.19192
H	-1.28945	-2.80153	-2.59278
H	0.495978	1.934459	1.008073
H	0.77991	-2.48088	-1.26496
H	3.773944	0.215612	1.174877
H	2.277093	2.803352	1.848106
H	2.32071	1.361591	2.895127
H	3.82365	2.236452	2.500318
C	3.733969	1.831618	-0.24989
H	4.684064	2.271029	0.089979
H	3.937192	1.217031	-1.13912
H	3.06472	2.651996	-0.55452
C	3.188468	-1.61652	-0.46206
H	3.094321	-2.52014	-1.07711
H	3.995967	-0.98228	-0.85063
O	4.359785	-2.11336	1.833218
H	5.221614	-1.90267	1.41998
H	3.561367	-1.97551	0.575283

Table S26. Frequencies (cm^{-1}) of TS5A transition state.

38	48	76	83	101	117	142	148
192	208	209	236	239	251	255	262
267	274	289	291	297	312	321	332
335	349	354	377	408	415	469	493
519	525	552	580	603	649	687	723
734	762	792	823	836	908.	914	917
928	936	947	948	955	967	983	993
1004	1007	1026	1063	1083	1091	1092	1107
1133	1148	1157	1162	1203	1212	1217	1243
1251	1253	1296	1314	1329	1342	1349	1352
1356	1369	1374	1376	1386	1388	1389	1396
1404	1433	1440	1444	1444	1447	1455	1456
1457	1461	1462	1466	1469	1476	1479	1481
1489	1539	1642	1682	1718	3040	3042	3044
3046	3047	3049	3052	3055	3102	3108	3119
3120	3120	3125	3126	3130	3132	3135	3137
3138	3140	3142	3142	3154	3178	3183	3196
3718	-789						

Product P5 (G1)

Figure S16. The optimized structure of product P5(G1).

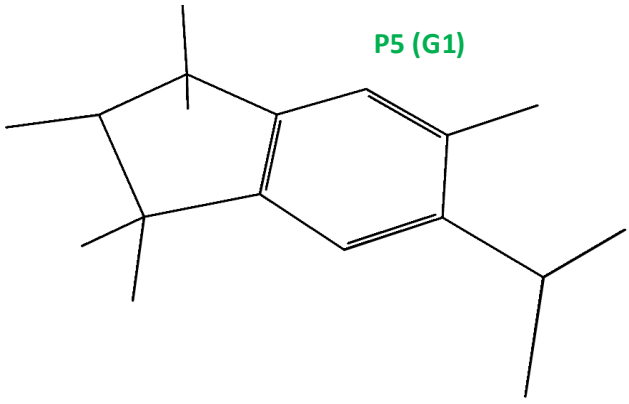


Table S27. Geometry (Å) of product P5(G1).

Atom	x	y	z
C	2.836752	-0.16229	-0.51394
C	1.856574	-1.30591	-0.10301
C	2.195129	1.188964	-0.06761

C	0.535086	-0.56081	-0.03557
C	0.723538	0.819207	-0.01157
C	4.286233	-0.366	-0.09531
C	2.174194	-1.93358	1.263149
C	1.844391	-2.41594	-1.15773
C	2.667304	1.676268	1.310878
C	2.474273	2.288768	-1.09581
C	-0.75279	-1.08996	0.028616
C	-0.37738	1.668377	0.07874
C	-1.86988	-0.24904	0.112954
C	-1.67719	1.151492	0.138866
C	-3.27628	-0.82807	0.113207
C	-3.81092	-0.90588	-1.32387
C	-3.37972	-2.19718	0.786366
H	2.808043	-0.14295	-1.61778
H	4.400349	-0.39941	0.998068
H	4.682117	-1.30923	-0.50239
H	4.920621	0.449687	-0.47443
H	1.385171	-2.65281	1.53225
H	3.131253	-2.47682	1.234463
H	2.228038	-1.18089	2.06237
H	1.153758	-3.22519	-0.87324
H	1.533451	-2.02496	-2.13821
H	2.848728	-2.85642	-1.26234
H	2.522383	0.915871	2.091452
H	3.733551	1.949497	1.288138
H	2.09523	2.57051	1.603
H	3.55846	2.457125	-1.19466
H	2.075108	2.01454	-2.08393
H	2.01521	3.242134	-0.79077
H	-0.89126	-2.17369	0.009978
H	-0.23663	2.753062	0.100181
H	-3.92223	-0.13661	0.675983
H	-3.19943	-1.60812	-1.91286
H	-4.85189	-1.26311	-1.33553
H	-2.87135	-2.97633	0.197973
H	-2.93861	-2.18643	1.793882
H	-4.43565	-2.49175	0.873938
H	-3.77572	0.073015	-1.82425
C	-2.84624	2.101351	0.243528
H	-3.59313	1.924239	-0.5441
H	-3.3666	1.992146	1.208037
H	-2.50548	3.141529	0.161053

Table S28. Frequencies (cm^{-1}) of product P5(G1).

43	63	86	112	140	147	200	209
219	225	235	243	254	259	267	269
278	288	293	302	323	328	349	356
379	407	414	466	493	517	526	552
582	604	652	703	726	754	789	823
835	907	917	920	929.	938	944	947
957	969	992	1002	1003	1017	1027	1046
1082	1090	1106	1127	1146	1158	1162	1198
1212	1218	1242	1248	1258	1297	1324	1329
1343	1349	1354	1370	1371	1374	1380	1384
1389	1391	1397	1398	1437	1440	1441	1445
1446	1451	1454	1457	1460	1461	1463	1465
1467	1473	1476	1480	1492	1547	1658	1704
3029	3038	3040	3044	3048	3050	3052	3058
3060	3075	3119	3119	3122	3125	3126	3129
3129	3130	3133	3133	3134	3139	3140	3144
3156	3161	3186	3205				

.

P2

Figure S17. The optimized structure of product P2.

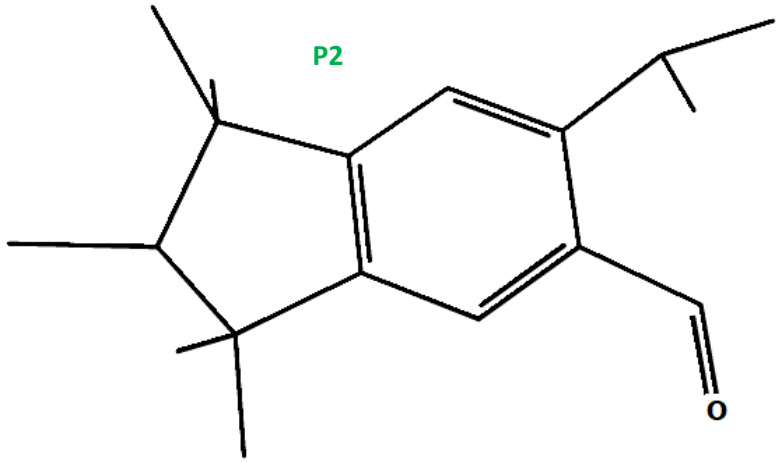


Table S29. Geometry (Å) of product P2.

Atom	x	y	z
O	2.900736	-2.918	0.017497
C	-2.84696	0.10619	-0.47927
C	-1.96189	1.300404	-0.00067
C	-2.08672	-1.21224	-0.13072
C	-0.58189	0.671238	0.016897

C	-0.65218	-0.72306	-0.05641
C	-4.30119	0.155141	-0.03296
C	-2.31181	1.811161	1.405906
C	-2.04887	2.470878	-0.98436
C	-2.4949	-1.82957	1.215925
C	-2.28077	-2.26033	-1.23009
C	0.650057	1.313038	0.118574
C	0.515904	-1.4699	-0.03085
C	1.842769	0.579234	0.14605
C	1.761839	-0.82949	0.064937
C	3.160564	1.341718	0.227558
C	4.039544	0.885722	1.348853
C	3.892413	1.358997	-1.12315
H	-2.8336	0.16318	-1.58188
H	-4.39879	0.098815	1.060792
H	-4.78109	1.087671	-0.36713
H	-4.86889	-0.68311	-0.46487
H	-1.58483	2.578339	1.713789
H	-3.31241	2.269481	1.41555
H	-2.29138	1.007861	2.155871
H	-1.42961	3.317948	-0.6515
H	-1.71313	2.168654	-1.98748
H	-3.08839	2.826912	-1.05911
H	-2.3977	-1.11585	2.046184
H	-3.53627	-2.18439	1.184617
H	-1.84988	-2.69344	1.438856
H	-3.34746	-2.51558	-1.33063
H	-1.92027	-1.88545	-2.19945
H	-1.73582	-3.18713	-0.99327
H	0.697861	2.403741	0.179468
H	0.501982	-2.56055	-0.08786
H	2.875957	2.391836	0.438639
H	3.599656	0.629368	2.314079
H	5.11495	1.064347	1.297931
H	4.197748	0.347361	-1.42945
H	3.241708	1.770664	-1.90744
H	4.795109	1.983714	-1.05731
C	2.962814	-1.70635	0.066443
H	3.950157	-1.20187	0.119156

Table S30. Frequencies (cm^{-1}) of product P2.

43	56	65	100	136	142	150	185
205	221	232	235	244	254	258	264
274	276	288	303	312	324	330	348
363	395	407	421	484	492	514	533

553	575	598	649	672	712	724	788
793	822	845	910	924	937	943	945
951	952	957	991	1002	1005	1025	1026
1044	1090	1104	1112	1153	1158	1161	1189
1208	1216	1222	1243	1250	1293	1300	1312
1344	1351	1354	1371	1373	1374	1379	1385
1390	1396	1426	1434	1440	1444	1448	1451
1455	1459	1462	1463	1464	1468	1477	1478
1482	1538	1650	1696	1812	2994	3032	3043
3044	3048	3051	3053	3056	3060	3122	3124
3125	3128	3132	3132	3136	3140	3143	3144
3150	3152	3157	3181	3198	3271		

TS3

Figure S18. The optimized structure of transition state TS3.

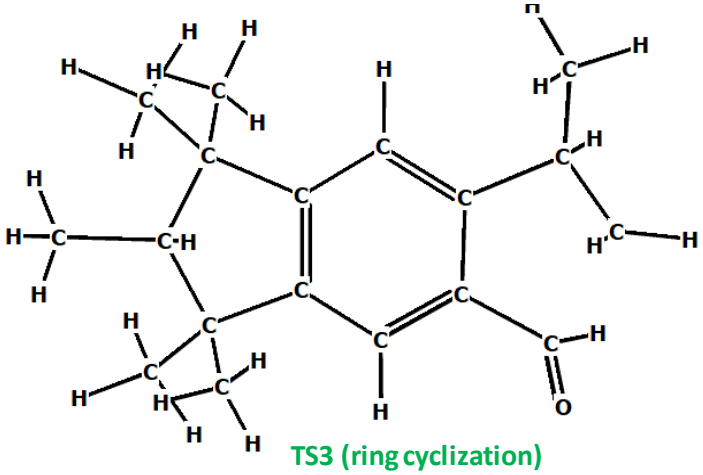


Table S31. Geometry (Å) of transition state TS3.

Atom	x	y	z
O	2.067804	-0.21576	-3.92122
C	-2.74385	0.530361	0.655987
C	-1.46547	0.42881	1.546021
C	-2.43715	-0.19713	-0.69082
C	-0.38105	0.21896	0.504512
C	-0.92156	-0.1279	-0.73715
C	-4.0423	0.118862	1.33572
C	-1.47978	-0.75711	2.523603
C	-1.25792	1.718377	2.345331
C	-2.89251	-1.66456	-0.72275
C	-3.08371	0.540732	-1.86671
C	1.000477	0.333423	0.680393

C	-0.08604	-0.37629	-1.82583
C	1.840746	0.075366	-0.40166
C	1.293323	-0.2896	-1.63991
C	3.354083	0.216134	-0.41807
C	2.269145	-0.57017	-2.74763
C	3.713878	0.597206	-1.82954
C	3.893339	1.234755	0.592223
H	-2.82749	1.599582	0.393312
H	-4.03657	-0.94268	1.621649
H	-4.21116	0.713129	2.246767
H	-4.9015	0.283926	0.6678
H	-0.50951	-0.82351	3.039751
H	-2.26092	-0.62508	3.28783
H	-1.65389	-1.71454	2.012262
H	-0.36166	1.653601	2.981381
H	-1.14527	2.583471	1.674968
H	-2.12104	1.900656	3.00495
H	-2.4808	-2.2459	0.114441
H	-3.99035	-1.73492	-0.68625
H	-2.55492	-2.13749	-1.65792
H	-4.17813	0.569115	-1.74501
H	-2.71519	1.575287	-1.93248
H	-2.8666	0.034451	-2.82001
H	1.412111	0.639263	1.645041
H	-0.48584	-0.63823	-2.80855
H	3.806063	-0.76569	-0.19378
H	3.365414	1.577458	-2.17111
H	4.660151	0.256284	-2.25589
H	3.425413	2.218095	0.435964
H	3.684779	0.908362	1.621064
H	4.981584	1.342416	0.486539
H	2.959806	-1.42314	-2.54561

Table S32. Frequencies (cm^{-1}) of transition state TS3.

46	61	98	110	134	146	181	219
222	234	242	248	259	268	270	279
291	308	328	333	342	357	373	394
416	426	486	508	531	544	556	590
616	636	656	712	729	780	798	821
836	881	911	915	926	937	941	942
946	952	986	991	1004	1009	1027	1056
1090	1099	1113	1142	1158	1160	1169	1206
1214	1226	1240	1243	1292	1307	1312	1349
1349	1351	1361	1373	1374	1376	1378	1385

1389	1395	1436	1439	1444	1446	1450	1453
1456	1458	1460	1463	1466	1473	1476	1488
1530	1599	1664	1696	2942	3038	3040	3043
3048	3050	3052	3054	3061	3117	3121	3125
3128	3129	3137	3137	3138	3140	3142	3144
3149	3160	3184	3187	3252	-411		

P3

Figure S19. The optimized structure of product P3.

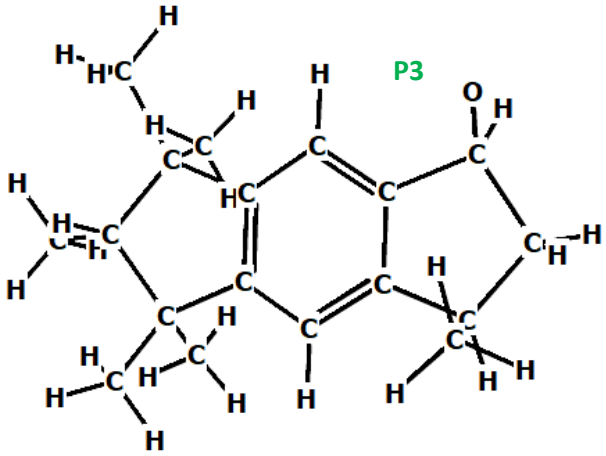


Table S33. Geometry (Å) of product P3.

Atom	x	y	z
O	3.642455	-1.79291	-0.80479
C	-2.79174	0.045791	-0.52114
C	-1.97022	1.283674	-0.04279
C	-2.00762	-1.23247	-0.08857
C	-0.5701	0.704135	0.059058
C	-0.59242	-0.69699	0.03809
C	-4.26712	0.060921	-0.14632
C	-2.40714	1.827132	1.326712
C	-2.05183	2.418543	-1.06765
C	-2.46727	-1.81961	1.255298
C	-2.11562	-2.32274	-1.15876
C	0.631053	1.40408	0.18532
C	0.588714	-1.43087	0.151982
C	1.812728	0.671485	0.30485
C	1.781228	-0.72606	0.298607
C	3.240432	1.181123	0.371916
C	3.201505	-1.26186	0.386058
C	4.007128	-0.04891	0.901162

C	3.728858	1.590227	-1.02084
H	-2.72609	0.065382	-1.62326
H	-4.41318	0.038406	0.943109
H	-4.7594	0.965876	-0.53413
H	-4.78729	-0.80952	-0.57461
H	-1.72256	2.629563	1.642546
H	-3.42251	2.249181	1.275507
H	-2.39411	1.049885	2.104024
H	-1.47384	3.295407	-0.73705
H	-1.66175	2.095504	-2.04443
H	-3.09718	2.739651	-1.20026
H	-2.4393	-1.07681	2.065165
H	-3.49286	-2.21254	1.181276
H	-1.80649	-2.65266	1.541119
H	-3.16833	-2.61232	-1.30563
H	-1.71555	-1.97021	-2.12108
H	-1.55944	-3.22566	-0.86272
H	0.648525	2.497556	0.18881
H	0.58205	-2.52401	0.133274
H	3.327539	2.035366	1.059013
H	5.048985	-0.09502	0.556669
H	3.996899	-0.05477	2.000024
H	3.707958	0.715715	-1.69293
H	3.08732	2.37104	-1.45492
H	4.761161	1.96736	-0.97869
H	3.27901	-2.12778	1.081396

Table S34. Frequencies (cm^{-1}) of product P3.

53	59	103	124	142	158	176	225
230	242	244	262	269	272	277	290
296	320	329	336	352	377	383	417
427	474	516	549	551	586	602	682
704	710	718	777	792	816	826	848
895	905	920	933	935	941	943	952
956	989	1004	1010	1027	1027	1061	1088
1090	1096	1100	1138	1152	1162	1194	1203
1206	1216	1230	1244	1260	1271	1292	1312
1326	1350	1352	1360	1363	1374	1376	1380
1386	1389	1395	1436	1439	1443	1446	1451
1454	1456	1458	1460	1462	1467	1473	1476
1491	1527	1668	1699	2963	3037	3039	3041
3044	3045	3046	3050	3073	3087	3120	3120
3121	3122	3124	3126	3134	3135	3136	3140
3141	3143	3146	3168	3173			

Transition State TS4

Figure S20. The optimized structure of TS4 transition state.

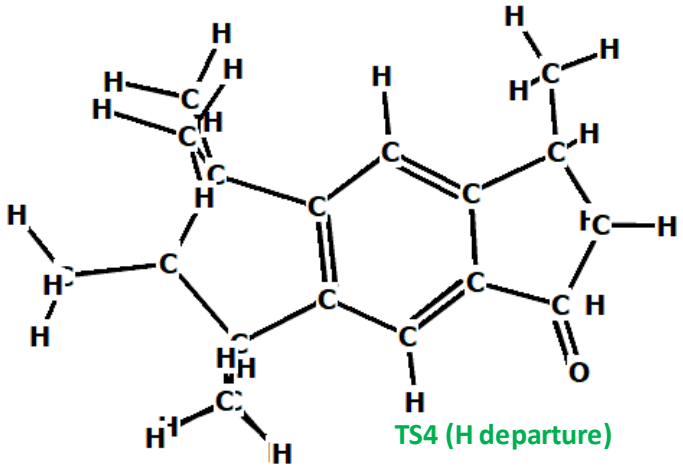


Table S35. Geometry (Å) of TS4 transition state.

Atom	x	y	z
O	3.403172	-2.46211	0.188937
C	-2.80431	0.175264	-0.69901
C	-1.94439	1.405243	-0.27144
C	-2.06475	-1.10742	-0.20717
C	-0.56426	0.788434	-0.1359
C	-0.63297	-0.61509	-0.09812
C	-4.27948	0.255607	-0.33303
C	-2.36482	2.022974	1.071823
C	-1.98446	2.495715	-1.34616
C	-2.54329	-1.61671	1.161739
C	-2.2067	-2.24112	-1.22696
C	0.653767	1.464102	-0.03498
C	0.522735	-1.37671	0.041338
C	1.815469	0.70561	0.106828
C	1.734487	-0.69116	0.136449
C	3.250939	1.179418	0.261922
C	3.112712	-1.26511	0.230883
C	4.073674	-0.09352	-0.00818
C	3.619846	2.36061	-0.62789
H	-2.73365	0.144178	-1.80046
H	-4.43131	0.288977	0.755352
H	-4.74071	1.156401	-0.7659
H	-4.8252	-0.61681	-0.72354

H	-1.6567	2.817873	1.352341
H	-3.3665	2.472984	0.997646
H	-2.37668	1.282282	1.883814
H	-1.38215	3.368732	-1.0513
H	-1.60077	2.11777	-2.30548
H	-3.01914	2.841158	-1.49798
H	-2.48947	-0.83957	1.937167
H	-3.58183	-1.97657	1.103818
H	-1.91174	-2.45822	1.485797
H	-3.26851	-2.50013	-1.36377
H	-1.79253	-1.94708	-2.20274
H	-1.6826	-3.14776	-0.88735
H	0.692129	2.555742	-0.06738
H	0.503405	-2.469	0.065682
H	3.393774	1.472005	1.317781
H	4.341318	-0.14489	-1.07826
H	4.996868	-0.1787	0.577062
H	3.457972	2.109523	-1.68735
H	3.01376	3.245748	-0.38744
H	4.67749	2.629137	-0.49367
H	3.04282	-1.00494	1.872633

Table S36. Frequencies (cm^{-1}) of TS4 transition state.

45	63	104	106	133	152	183	222
224	239	240	250	254	262	273	282
296	310	330	332	346	348	382	389
402	459	504	511	542	551	554	579
588	600	631	651	710	729	764	794
819	823	895	906	916	933	935	944
944	952	970	990	1002	1026	1032	1070
1083	1091	1099	1133	1141	1158	1171	1185
1203	1216	1230	1234	1245	1258	1292	1296
1332	1351	1352	1364	1371	1373	1374	1384
1387	1390	1396	1420	1440	1444	1447	1454
1455	1457	1461	1462	1464	1468	1476	1477
1496	1519	1660	1691	1705	3037	3039	3042
3043	3047	3051	3052	3054	3056	3119	3124
3125	3128	3130	3131	3134	3138	3140	3142
3144	3148	3151	3187	3190	-992		

Product P4 (G2)

Figure S21. The optimized structure of product P4 (G2).

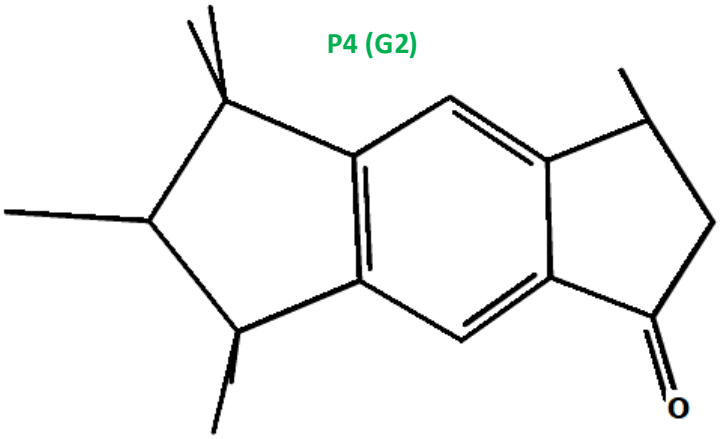


Table S37. Geometry (Å) of product P4 (G2).

Atom	x	y	z
O	3.434281	-2.51373	0.413555
C	-2.79094	0.030419	-0.53993
C	-1.95049	1.258086	-0.06968
C	-2.02764	-1.25653	-0.09893
C	-0.5583	0.662066	0.03361
C	-0.60305	-0.74509	0.017892
C	-4.26594	0.071839	-0.1665
C	-2.37294	1.81455	1.299505
C	-2.01645	2.388834	-1.1004
C	-2.48837	-1.82182	1.253941
C	-2.1589	-2.35525	-1.15749
C	0.645636	1.354611	0.154856
C	0.565403	-1.48782	0.127002
C	1.823241	0.610763	0.263269
C	1.768034	-0.78428	0.247321
C	3.246661	1.123902	0.393129
C	3.13449	-1.33756	0.375165
C	4.101992	-0.16039	0.449937
C	3.633431	2.055992	-0.75515
H	-2.7243	0.041492	-1.64204
H	-4.41498	0.066928	0.922821
H	-4.74542	0.977575	-0.56809
H	-4.79699	-0.79712	-0.58392
H	-1.67695	2.609928	1.607488
H	-3.38258	2.249585	1.248332
H	-2.36748	1.042382	2.081624
H	-1.42933	3.260815	-0.77349
H	-1.63035	2.056555	-2.07552
H	-3.05823	2.719897	-1.23416
H	-2.44104	-1.0723	2.056551

H	-3.5215	-2.19601	1.190138
H	-1.84108	-2.66407	1.543021
H	-3.21767	-2.62452	-1.29809
H	-1.75445	-2.02132	-2.12449
H	-1.62026	-3.26578	-0.85276
H	0.665639	2.447361	0.16726
H	0.566178	-2.58059	0.119134
H	3.336363	1.677924	1.340517
H	4.800025	-0.23036	-0.39873
H	4.702754	-0.24551	1.366438
H	3.553356	1.527733	-1.71789
H	2.97557	2.93635	-0.7906
H	4.668665	2.407251	-0.6374

Table S38. Frequencies (cm^{-1}) of product P4 (G2)

36	53	64	106	132	148	183	222
224	240	242	246	259	272	274	280
297	313	331	334	346	360	387	401
452	503	523	544	548	566	588	611
619	660	708	724	763	794	819	825
890	914	917	934	939	944	946	954
974	991	1002	1027	1033	1075	1082	1092
1100	1124	1142	1159	1187	1195	1204	1217
1225	1235	1246	1262	1294	1298	1333	1351
1352	1365	1372	1374	1382	1382	1385	1392
1398	1409	1438	1443	1446	1454	1456	1457
1461	1462	1463	1468	1476	1478	1501	1521
1665	1700	1832	3040	3041	3043	3048	3053
3055	3055	3078	3084	3119	3124	3126	3129
3130	3130	3131	3137	3139	3142	3146	3150
3151	3187	3192					

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TS1B

Figure S22. The optimized structure of TS1B transition state.

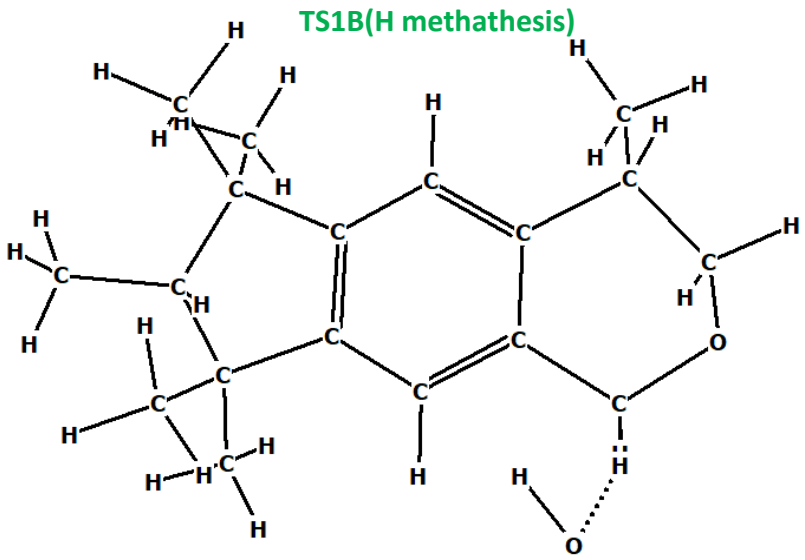


Table S39. Geometry (Å) of TS1B transition state.

Atom	x	y	z
O	3.854985	1.096535	0.034557
C	-3.17874	-0.04545	-0.60221
C	-2.59526	0.244285	0.817325
C	-2.00439	-0.55095	-1.49937
C	-1.12806	0.476292	0.502617
C	-0.80295	0.037832	-0.78462
C	-4.43225	-0.9088	-0.62711
C	-2.73954	-0.92926	1.79864
C	-3.25613	1.480441	1.433753
C	-1.87841	-2.08141	-1.55649
C	-2.14315	-0.01843	-2.92797
C	-0.15072	1.023148	1.328692
C	0.503201	0.145326	-1.24455
C	1.172498	1.142022	0.879935
C	1.490401	0.695507	-0.41514
C	2.26427	1.736261	1.75571
C	2.894184	0.813477	-0.93799
C	3.439225	2.157931	0.882032
C	1.795948	2.917712	2.603182
H	-3.44648	0.94494	-1.01046
H	-4.24554	-1.91754	-0.23093
H	-5.23237	-0.45278	-0.02432
H	-4.8111	-1.01663	-1.65493
H	-2.21277	-0.69526	2.736497
H	-3.798	-1.1089	2.041
H	-2.31414	-1.86006	1.397711
H	-2.84658	1.692483	2.433621
H	-3.10127	2.367295	0.801254

H	-4.34005	1.318792	1.545175
H	-1.80297	-2.53056	-0.55611
H	-2.74338	-2.52647	-2.07149
H	-0.97203	-2.35725	-2.11781
H	-3.08042	-0.37831	-3.38118
H	-2.1531	1.0817	-2.9386
H	-1.31165	-0.3632	-3.56213
H	-0.41579	1.362681	2.332566
H	0.78206	-0.21352	-2.23967
H	2.631388	0.941347	2.428352
H	3.198093	-0.19699	-1.41548
H	2.952331	1.52382	-1.78681
H	3.160067	3.039928	0.272834
H	4.308617	2.422546	1.498047
H	1.352262	3.700361	1.968646
H	1.049221	2.616984	3.349543
H	2.647028	3.354167	3.146869
O	3.089067	-1.56725	-1.97501
H	2.445901	-1.86084	-1.29729

Table S40. Frequencies (cm^{-1}) of TS1B transition state.

31	37	55	87	100	114	146	157
204	227	230	236	244	249	256	268
270	276	279	294	308	326	330	338
358	378	383	413	454	480	513	524
549	562	587	626	673	691	717	725
775	796	825	838	879	900.	909	922
937	944	946	956	963	991	992	1007
1012	1028	1063	1083	1092	1104	1122	1154
1158	1163	1188	1212	1216	1219	1232	1245
1260	1278	1296	1303	1311	1335	1351	1352
1358	1374	1375	1378	1387	1391	1392	1397
1398	1410	1438	1442	1444	1450	1453	1456
1459	1460	1466	1466	1470	1474	1475	1489
1542	1643	1690	1709	3015	3017	3039	3041
3045	3046	3048	3052	3056	3064	3120	3125
3127	3128	3132	3133	3134	3135	3139	3140
3143	3151	3154	3178	3203	3722	-899	

P1B

Figure S23. The optimized structure of P1B.

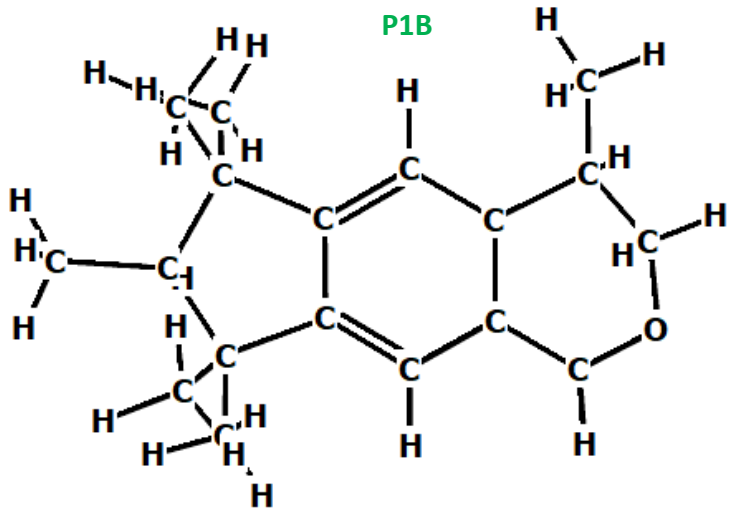


Table S41. Geometry (Å) of P1B.

Atom	x	y	z
O	4.147568	-1.32532	-0.11155
C	-2.83469	0.146656	-0.48935
C	-1.89194	1.294661	-0.00945
C	-2.13512	-1.20835	-0.15331
C	-0.54382	0.60029	-0.00867
C	-0.67492	-0.79281	-0.09514
C	-4.28342	0.260058	-0.03503
C	-2.21845	1.819563	1.397938
C	-1.93438	2.473428	-0.98696
C	-2.56133	-1.80546	1.196566
C	-2.40014	-2.24176	-1.25144
C	0.724274	1.185235	0.089505
C	0.443536	-1.60859	-0.10545
C	1.86591	0.392612	0.094102
C	1.739346	-1.02778	-0.02432
C	3.27146	0.935091	0.252075
C	2.897681	-1.83079	-0.04609
C	4.223999	0.039167	-0.53023
C	3.439466	2.387172	-0.18157
H	-2.82479	0.209492	-1.59185
H	-4.37836	0.201889	1.058953
H	-4.72043	1.216525	-0.36041
H	-4.89377	-0.54715	-0.46842
H	-1.45455	2.550261	1.706244
H	-3.19565	2.32671	1.411779
H	-2.23541	1.015709	2.147498
H	-1.2706	3.287157	-0.65545
H	-1.62075	2.160782	-1.99417
H	-2.9552	2.882497	-1.05239

H	-2.42153	-1.09662	2.024987
H	-3.61925	-2.10898	1.175953
H	-1.95656	-2.69928	1.413909
H	-3.48114	-2.43162	-1.34614
H	-2.02406	-1.88816	-2.22316
H	-1.91203	-3.20125	-1.01983
H	0.816532	2.271171	0.167992
H	0.350082	-2.695	-0.18793
H	3.556443	0.846441	1.316894
H	2.872646	-2.91922	-0.00532
H	3.987364	0.090632	-1.60845
H	5.268553	0.335586	-0.3773
H	3.112745	2.522616	-1.22421
H	2.851773	3.064461	0.451791
H	4.493342	2.691133	-0.10534

Table S42. Frequencies (cm^{-1}) of P1B.

46	63	103	119	146	174	205	229
237	241	246	256	257	272	277	287
308	318	328	343	351	361	379	400
417	449	487	518	533	548	562	587
641	667	693	716	720	772	802	823
846	885	896	919	935	943.	945	953
962	986	990	1004	1028	1028	1064	1091
1102	1111	1152	1153	1160	1187	1203	1211
1216	1242	1260	1264	1280	1294	1316	1320
1336	1349	1352	1361	1370	1373	1383	1386
1390	1391	1397	1430	1439	1443	1447	1454
1456	1458	1460	1463	1467	1468	1471	1476
1478	1522	1539	1604	1661	3030	3035	3040
3041	3045	3050	3053	3053	3060	3118	3121
3122	3127	3131	3132	3132	3137	3139	3143
3149	3152	3154	3183	3193	3246		

TS2B (OH addition)

Figure S24. The optimized structure of transition state TS2B.

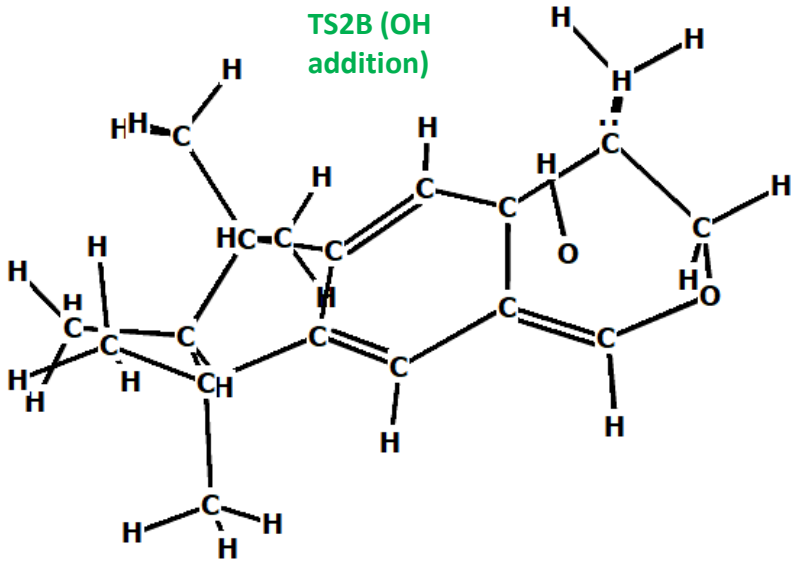


Table S43. Geometry (Å) of transition state TS2B.

Atom	x	y	z
O	3.335791	-2.25689	-1.35615
C	-3.14137	0.403817	-0.15766
C	-1.93148	1.379251	-0.00632
C	-2.63516	-1.03384	0.178396
C	-0.76027	0.455345	-0.20462
C	-1.15294	-0.92848	-0.13688
C	-4.41244	0.830014	0.563391
C	-1.84602	2.063476	1.371595
C	-1.98137	2.47381	-1.08177
C	-2.8174	-1.42176	1.654875
C	-3.33769	-2.07796	-0.69267
C	0.624614	0.817389	-0.34255
C	-0.2504	-1.92526	-0.30256
C	1.567864	-0.14728	-0.49785
C	1.144537	-1.56674	-0.6184
C	2.104975	-2.54478	-0.87072
C	3.460514	1.506297	-0.91683
H	-3.36197	0.385923	-1.23935
H	-4.27265	0.878592	1.652922
H	-4.74018	1.82351	0.22111
H	-5.23134	0.123202	0.360181
H	-0.91895	2.653723	1.436442
H	-2.69355	2.750887	1.517491
H	-1.84196	1.337685	2.196475
H	-1.12857	3.163408	-0.98519
H	-1.96048	2.034931	-2.09031
H	-2.90451	3.065962	-0.97892
H	-2.33925	-0.70337	2.335697

H	-3.88525	-1.48643	1.91346
H	-2.36329	-2.40784	1.835289
H	-4.42305	-2.06494	-0.50644
H	-3.16549	-1.88017	-1.76095
H	-2.97167	-3.09098	-0.46562
H	0.911218	1.870328	-0.2945
H	-0.52024	-2.98088	-0.23492
H	1.804217	-3.57062	-1.08473
H	2.997589	1.849538	-1.85446
H	3.150819	2.186968	-0.11259
H	4.552106	1.581112	-1.01874
C	3.053897	0.071899	-0.60848
H	3.523739	-0.23644	0.34482
C	3.580052	-0.88633	-1.67622
H	4.668273	-0.7994	-1.78229
H	3.106332	-0.65573	-2.64746
O	2.337004	-2.94666	0.945304
H	2.520224	-2.07157	1.333006

Table S44. Frequencies (cm^{-1}) of transition state TS2B.

33	58	88	102	110	140	164	176
203	224	229	236	244	250	259	260
273	284	290	303	322	330	346	349
354	383	390	417	443	457	505	524
540	561	579	636	649	689	698	708
779	806	815	822	858	885.	900	930
941	944	947	959	982	987	998	1017
1020	1052	1059	1081	1089	1100	1130	1146
1151	1162	1183	1201	1212	1232	1250	1257
1266	1280	1300	1311	1324	1344	1348	1350
1363	1373	1375	1385	1388	1388	1395	1397
1421	1439	1443	1446	1453	1454	1458	1462
1464	1466	1468	1468	1477	1479	1549	1628
1716	3018	3037	3040	3043	3046	3050	3053
3057	3057	3120	3124	3124	3126	3130	3131
3135	3138	3142	3144	3147	3149	3154	3186
3199	3224	3759	-852				

P2B

Figure S25. The optimized structure of product P2B.

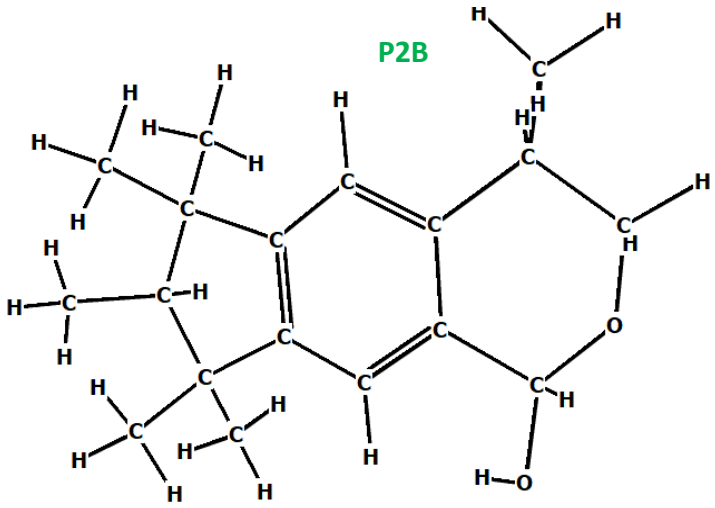


Table S45. Geometry (Å) of product P2B.

Atom	x	y	z
O	3.512622	-2.14432	-0.28445
C	-3.12778	0.442101	-0.11364
C	-1.93129	1.423158	0.096309
C	-2.61364	-0.99879	0.197263
C	-0.74259	0.498123	-0.09473
C	-1.12276	-0.84537	-0.04111
C	-4.42234	0.836205	0.583474
C	-1.88189	2.052748	1.497278
C	-1.96092	2.54685	-0.94319
C	-2.86805	-1.45019	1.643681
C	-3.24822	-2.01939	-0.75133
C	0.591582	0.846581	-0.28158
C	-0.16282	-1.84255	-0.1731
C	1.570643	-0.14671	-0.42524
C	1.180064	-1.49595	-0.36546
C	2.202347	-2.61107	-0.5199
C	3.260605	1.373761	-1.58153
H	-3.31858	0.450448	-1.20126
H	-4.31256	0.860587	1.677388
H	-4.75352	1.834173	0.257836
H	-5.22696	0.125223	0.341256
H	-0.95991	2.644914	1.604902
H	-2.73693	2.727983	1.653998
H	-1.88832	1.295707	2.294176
H	-1.11639	3.239407	-0.80321
H	-1.90972	2.140758	-1.96453
H	-2.89007	3.130794	-0.84842
H	-2.45757	-0.74271	2.378082
H	-3.94625	-1.56175	1.835399
H	-2.39102	-2.42751	1.814996

H	-4.3431	-2.02572	-0.63001
H	-3.01675	-1.78027	-1.80004
H	-2.88324	-3.03653	-0.53986
H	0.879397	1.900039	-0.31474
H	-0.4364	-2.8994	-0.12372
H	2.150046	-3.03296	-1.54129
H	2.80791	1.156073	-2.56117
H	2.830896	2.31144	-1.206
H	4.338345	1.539996	-1.72858
C	3.035309	0.212967	-0.61458
H	3.442866	0.490978	0.373054
C	3.801948	-1.01597	-1.08903
H	4.885207	-0.84813	-1.02508
H	3.549133	-1.22942	-2.14714
O	1.959676	-3.68132	0.333919
H	1.878142	-3.31776	1.229648

Table S46. Frequencies (cm^{-1}) of product P2B.

42	62	73	106	132	140	188	215
225	236	242	250	255	261	263	272
281	295	318	326	342	352	369	382
386	418	438	465	485	513	522	549
576	590	614	648	684	698	726	776
808	825	840	910	920	932.	934	945
947	956	961	987	991	1002	1027	1048
1070	1092	1104	1124	1135	1149	1160	1165
1184	1204	1212	1217	1231	1246	1254	1283
1296	1303	1319	1325	1346	1351	1353	1369
1372	1374	1377	1385	1391	1393	1398	1413
1437	1438	1441	1446	1450	1454	1458	1461
1462	1468	1468	1473	1474	1481	1489	1544
1662	1706	3013	3029	3033	3038	3044	3045
3046	3051	3053	3061	3116	3122	3124	3125
3129	3133	3134	3135	3137	3138	3144	3150
3167	3184	3187	3791				

TS3B_v1

Figure S27. The optimized structure of TS3B_v1.

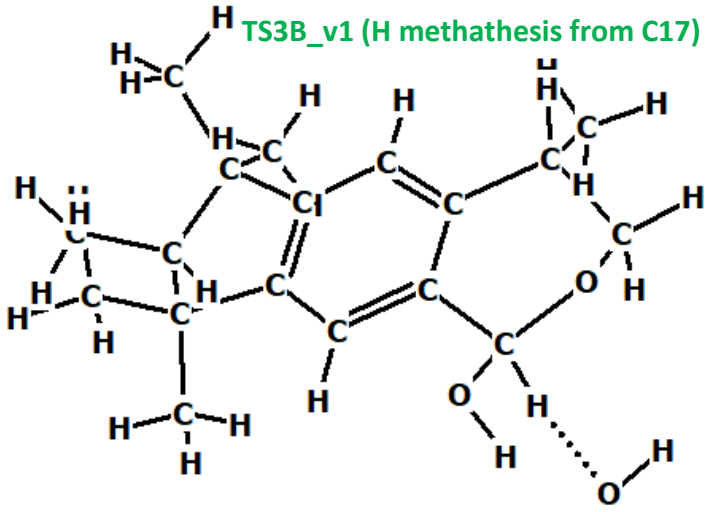


Table S47. Geometry (Å) of TS3B_v1.

Atom	x	y	z
O	3.879158	-0.36695	-0.53478
C	-3.23321	0.151117	-0.34631
C	-2.38216	1.252911	0.361265
C	-2.3338	-1.11644	-0.49172
C	-0.96957	0.805982	0.030662
C	-0.94447	-0.50729	-0.44688
C	-4.6102	-0.09268	0.255317
C	-2.5705	1.300025	1.88525
C	-2.69866	2.635619	-0.21592
C	-2.4964	-2.12921	0.652206
C	-2.60749	-1.82981	-1.81827
C	0.210911	1.530993	0.167603
C	0.265325	-1.09811	-0.79085
C	1.439629	0.955201	-0.18093
C	1.45259	-0.3689	-0.65429
C	2.751972	-1.01214	-1.06115
C	2.648143	3.184603	-0.45437
H	-3.37967	0.519062	-1.37713
H	-4.55021	-0.46058	1.289889
H	-5.20303	0.834832	0.262759
H	-5.16708	-0.83707	-0.33394
H	-1.86868	2.026549	2.322807
H	-3.59203	1.61828	2.143324
H	-2.38264	0.324996	2.356268
H	-2.10841	3.419818	0.283025
H	-2.48124	2.671337	-1.29394
H	-3.76364	2.875162	-0.06892
H	-2.33934	-1.6715	1.639194
H	-3.50037	-2.58008	0.63531

H	-1.7598	-2.93931	0.53636
H	-3.65677	-2.16107	-1.86578
H	-2.41514	-1.16268	-2.67166
H	-1.97139	-2.722	-1.92658
H	0.180373	2.55491	0.546881
H	0.312643	-2.12459	-1.16014
H	2.855168	-0.9431	-2.21441
H	2.285019	3.26174	-1.49075
H	1.970347	3.758018	0.190862
H	3.638792	3.659722	-0.39863
C	2.743026	1.721222	-0.02431
H	3.026897	1.683744	1.041868
C	3.846444	1.025725	-0.81182
H	4.832606	1.423354	-0.54182
H	3.693602	1.184845	-1.89847
O	3.907112	-1.60717	-3.20924
H	4.653977	-1.1481	-2.77151
O	2.785512	-2.34893	-0.73168
H	3.400201	-2.75534	-1.36544

Table S48. Frequencies (cm^{-1}) of TS3B_v1.

34	42	62	75	97	119	141	155
190	216	225	235	241	245	256	260
267	278	292	310	317	323	329	344
354	356	381	394	422	432	478	495
503	521	548	571	578	604	626	662
694	705	725	764	794	810.	825	846
909	920	933	939	946	948	957	958
988	993	1006	1029	1055	1078	1092	1106
1124	1132	1154	1161	1173	1187	1212	1217
1226	1240	1247	1270	1287	1296	1304	1321
1350	1351	1353	1363	1371	1373	1375	1386
1387	1392	1400	1411	1427	1441	1445	1448
1452	1456	1460	1460	1463	1466	1470	1471
1478	1480	1492	1545	1660	1703	2090	3011
3036	3043	3045	3050	3051	3052	3055	3062
3121	3125	3125	3128	3131	3132	3137	3138
3141	3144	3146	3148	3159	3192	3195	3722
3752	-808						

TS3B_v2

Figure S28. The optimized structure of TS3B_v2 transition state.

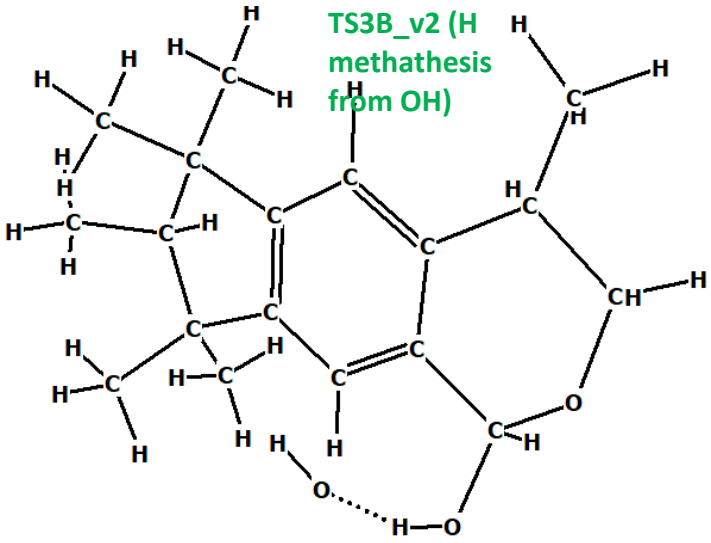


Table S49. Geometry (Å) of TS3B_v2 transition state.

Atom	x	y	z
O	3.404072	-2.40215	-0.03238
C	-3.13429	0.451066	-0.1142
C	-1.90982	1.372761	0.186829
C	-2.6918	-1.02137	0.15548
C	-0.75101	0.407946	0.011303
C	-1.18752	-0.9199	-0.01042
C	-4.44032	0.868329	0.547348
C	-1.89938	1.943389	1.613496
C	-1.84736	2.535536	-0.80752
C	-3.02097	-1.5229	1.570563
C	-3.32261	-1.97585	-0.8617
C	0.603384	0.706998	-0.09853
C	-0.26439	-1.95175	-0.13359
C	1.549483	-0.32027	-0.22732
C	1.100854	-1.65092	-0.22897
C	2.087136	-2.80828	-0.29238
C	3.361864	1.156946	-1.24133
H	-3.27821	0.512131	-1.20734
H	-4.37676	0.831169	1.644492
H	-4.71157	1.895867	0.261005
H	-5.26418	0.208106	0.236035
H	-0.96299	2.495871	1.785824
H	-2.73708	2.642043	1.760225
H	-1.96934	1.15493	2.376136
H	-0.98851	3.191821	-0.59795
H	-1.75765	2.166816	-1.8402
H	-2.75994	3.148188	-0.73632
H	-2.61695	-0.86122	2.349902

H	-4.10924	-1.60416	1.714596
H	-2.58408	-2.52271	1.719874
H	-4.42098	-1.94117	-0.78722
H	-3.03553	-1.70422	-1.88826
H	-3.00837	-3.01491	-0.67801
H	0.935291	1.747733	-0.07793
H	-0.583	-2.99748	-0.13641
H	2.033097	-3.27175	-1.30332
H	2.946612	0.994539	-2.24783
H	2.95995	2.101576	-0.85261
H	4.45201	1.274599	-1.3317
C	3.035535	-0.02268	-0.3275
H	3.40244	0.200402	0.689621
C	3.766449	-1.27068	-0.8058
H	4.852494	-1.15298	-0.69963
H	3.541801	-1.45261	-1.87537
O	1.754888	-3.83676	0.560059
H	1.725561	-3.45734	1.581758
O	1.470679	-2.67614	2.52994
H	0.656184	-2.21746	2.240036

Table S50. Frequencies (cm^{-1}) of TS3B_v2 transition state.

27	38	56	80	102	116	138	154
197	204	224	229	241	250	256	260
264	269	277	285	294	326	330	338
346	370	382	396	428	447	467	485
516	523	550	576	589	612	644	682
697	725	764	779	814	825.	840	904
911	922	930	940	946	950	956	959
992	996	1006	1026	1050	1072	1092	1106
1123	1129	1152	1160	1164	1192	1200	1213
1216	1228	1246	1255	1282	1291	1295	1301
1319	1334	1348	1350	1359	1373	1376	1383
1388	1391	1394	1398	1411	1438	1443	1446
1446	1455	1459	1460	1461	1463	1468	1469
1474	1475	1478	1489	1540	1656	1701	2959
3022	3039	3044	3045	3049	3050	3053	3057
3066	3124	3127	3128	3129	3133	3135	3140
3140	3144	3148	3149	3151	3153	3198	3204
3703	-1640						

P3B_v1

Figure S29. The optimized structure of P3B_v1.

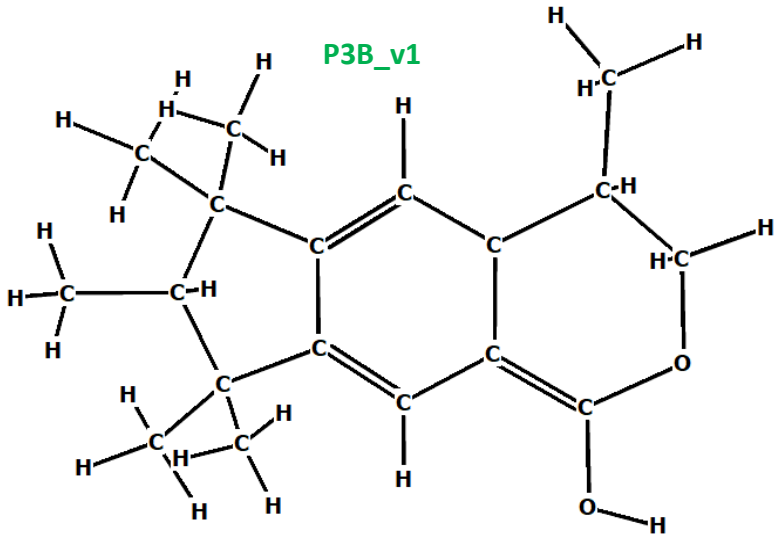


Table S51. Geometry (Å) of P3B_v1.

Atom	x	y	z
O	4.06548	-0.94369	0.109104
C	-2.9834	0.074669	-0.51503
C	-2.12542	1.287196	-0.03344
C	-2.20679	-1.22774	-0.14533
C	-0.73717	0.679434	0.00576
C	-0.77704	-0.72093	-0.0595
C	-4.44546	0.102399	-0.09167
C	-2.51677	1.809354	1.358856
C	-2.22348	2.447423	-1.02954
C	-2.62426	-1.83671	1.202409
C	-2.38091	-2.29003	-1.2344
C	0.493679	1.343997	0.129918
C	0.383599	-1.4727	-0.02051
C	1.679886	0.62978	0.184887
C	1.641826	-0.80543	0.08999
C	2.845251	-1.51403	0.120648
C	3.137887	2.711516	-0.09249
H	-2.95437	0.123125	-1.61796
H	-4.55777	0.060319	1.001377
H	-4.93734	1.021783	-0.44479
H	-4.99242	-0.7519	-0.51955
H	-1.80691	2.590353	1.673428
H	-3.52447	2.253658	1.348343
H	-2.49718	1.014186	2.117717
H	-1.61165	3.302932	-0.70289
H	-1.87851	2.138194	-2.02761
H	-3.26514	2.796741	-1.11426
H	-2.54319	-1.11304	2.026055
H	-3.66166	-2.20357	1.165041

H	-1.9714	-2.69049	1.440623
H	-3.44429	-2.55677	-1.34462
H	-2.01269	-1.92283	-2.20399
H	-1.83031	-3.20958	-0.98222
H	0.515355	2.434784	0.191318
H	0.36053	-2.56223	-0.08056
H	2.837337	2.805705	-1.14732
H	2.489868	3.363684	0.507424
H	4.168011	3.08148	0.010954
C	3.044057	1.261075	0.369122
H	3.307076	1.212167	1.442053
C	4.07483	0.409859	-0.36426
H	5.094381	0.771512	-0.18934
H	3.868133	0.406834	-1.44846
O	2.875119	-2.85655	0.169238
H	3.787702	-3.14043	-0.00268

Table S52. Frequencies (cm^{-1}) of P3B_v1.

42	64	96	109	135	151	186	224
228	237	239	244	250	258	262	276
287	294	321	330	335	341	344	366
380	400	430	448	477	495	505	543
551	576	590	641	674	696	714	736
763	818	826	860	900	914.	929	939
942	950	958	975	988	1000	1024	1043
1061	1090	1098	1111	1116	1147	1157	1165
1198	1208	1215	1228	1240	1248	1268	1293
1303	1314	1322	1348	1350	1360	1370	1372
1374	1382	1387	1392	1394	1425	1439	1442
1443	1446	1455	1456	1459	1462	1466	1467
1472	1474	1476	1481	1525	1582	1642	1656
3030	3039	3040	3042	3042	3046	3049	3059
3065	3117	3119	3120	3121	3124	3129	3135
3137	3138	3141	3148	3162	3162	3182	3194
3798							

P3B_v2

Figure S30. The optimized structure of P3B_v2.

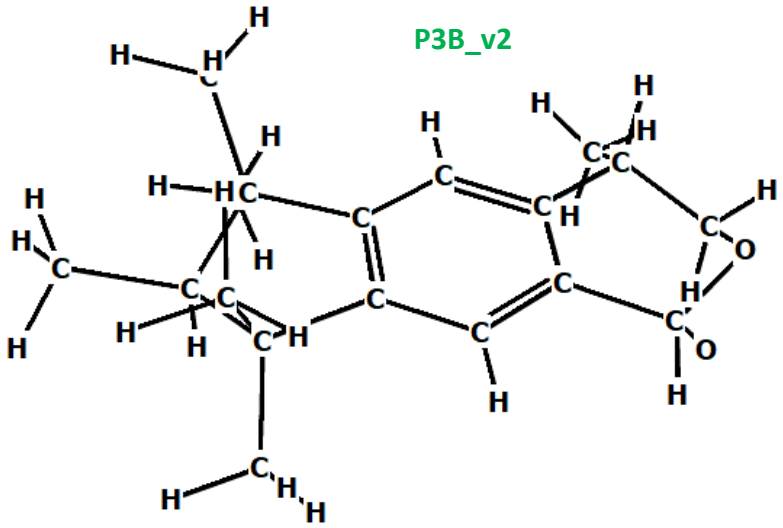


Table S53. Geometry (Å) of P3B_v2.

Atom	x	y	z
O	3.408819	-2.34018	-0.03869
C	-3.15313	0.4833	-0.15293
C	-1.93439	1.416875	0.132492
C	-2.70966	-0.97911	0.165326
C	-0.7716	0.45059	-0.00543
C	-1.20364	-0.87821	0.008857
C	-4.46713	0.91744	0.480953
C	-1.93609	2.029249	1.541897
C	-1.86699	2.550994	-0.8939
C	-3.05542	-1.437	1.590715
C	-3.32924	-1.96495	-0.82881
C	0.58217	0.751899	-0.11412
C	-0.2763	-1.91009	-0.08134
C	1.534543	-0.27344	-0.21108
C	1.082582	-1.60236	-0.18923
C	2.094309	-2.75605	-0.29837
C	3.329544	1.220297	-1.236
H	-3.28575	0.511046	-1.24878
H	-4.41354	0.925724	1.579252
H	-4.74432	1.930371	0.151169
H	-5.28306	0.239194	0.18816
H	-1.00089	2.58711	1.704535
H	-2.77397	2.732707	1.662586
H	-2.01041	1.264171	2.327586
H	-1.00731	3.211265	-0.70073
H	-1.7754	2.153271	-1.91565
H	-2.7786	3.166934	-0.84208
H	-2.65732	-0.75406	2.354581
H	-4.14552	-1.50935	1.725021

H	-2.6252	-2.4337	1.77373
H	-4.42844	-1.93096	-0.76597
H	-3.03299	-1.72354	-1.8605
H	-3.01447	-2.99735	-0.61099
H	0.908706	1.794158	-0.12445
H	-0.58731	-2.95665	-0.06232
H	2.03417	-3.15881	-1.34628
H	2.908808	1.059735	-2.24053
H	2.92443	2.16034	-0.84015
H	4.418214	1.345354	-1.33322
C	3.018732	0.034296	-0.32522
H	3.395272	0.2565	0.688218
C	3.75488	-1.20582	-0.81556
H	4.841218	-1.07922	-0.72354
H	3.519365	-1.38781	-1.88292
O	1.742066	-3.78716	0.473487

Table S54. Frequencies (cm^{-1}) of P3B_v2.

43	61	72	107	133	140	188	214
224	234	241	248	252	259	264	270
281	297	319	327	339	350	370	381
386	422	457	470	501	520	549	566
588	594	635	680	691	723	752	787
822	826	907	918	927	932.	944	945
956	958	976	991	1002	1026	1034	1065
1091	1097	1104	1124	1130	1146	1154	1161
1174	1200	1210	1216	1227	1246	1249	1274
1296	1299	1307	1327	1350	1351	1361	1369
1372	1374	1384	1391	1394	1398	1412	1438
1441	1446	1449	1454	1458	1461	1462	1468
1469	1473	1474	1480	1487	1540	1660	1704
2824	3023	3032	3040	3043	3046	3049	3051
3053	3060	3118	3123	3124	3125	3129	3133
3135	3136	3137	3138	3147	3150	3167	3192
3198							

TS4B_v1

Figure S31. The optimized structure of TS4B_v1 transition state.

TS4B_v1 (H methathesis from O)

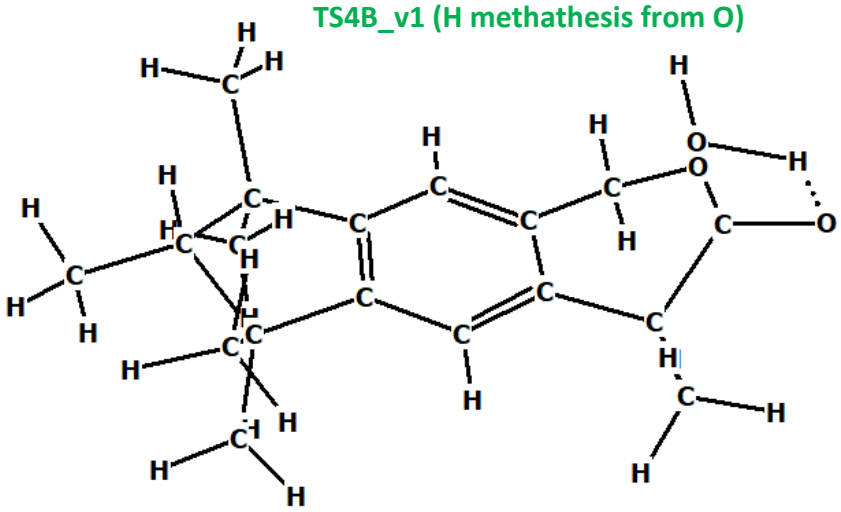


Table S55. Geometry (Å) of TS4B_v1 transition state.

Atom	x	y	z
O	3.576819	-1.57555	-0.32045
C	-3.16705	0.326634	-0.46429
C	-2.19445	1.333925	0.224777
C	-2.60059	-1.10873	-0.22858
C	-0.90373	0.53564	0.259264
C	-1.12923	-0.81889	0.008212
C	-4.63947	0.510788	-0.12547
C	-2.60686	1.717489	1.654555
C	-2.0594	2.613576	-0.60547
C	-3.19663	-1.81908	0.996806
C	-2.82602	-1.98981	-1.46061
C	0.383693	1.010804	0.513781
C	-0.06369	-1.71922	0.007484
C	1.451053	0.112665	0.528658
C	1.221147	-1.24706	0.275056
C	2.89384	0.505451	0.755356
C	2.423522	-2.14451	0.329297
C	3.759992	-0.23603	-0.25646
C	3.174291	1.999112	0.732204
H	-3.04841	0.507898	-1.54709
H	-4.84058	0.351903	0.943883
H	-4.97395	1.527769	-0.38145
H	-5.26233	-0.19611	-0.69462
H	-1.82391	2.341837	2.1118
H	-3.54197	2.298169	1.649963
H	-2.75032	0.836193	2.295326
H	-3.03777	3.109982	-0.70357
H	-1.37066	3.326904	-0.12686
H	-1.68086	2.39056	-1.61417

H	-3.08952	-1.22491	1.915385
H	-4.26585	-2.03131	0.844026
H	-2.68018	-2.77831	1.155403
H	-3.90334	-2.08394	-1.67006
H	-2.33574	-1.56083	-2.34721
H	-2.42854	-3.00426	-1.30133
H	0.553311	2.074214	0.694024
H	-0.22216	-2.78077	-0.20136
H	3.21844	0.091874	1.730268
H	2.703311	-2.34995	1.375889
H	2.242464	-3.10131	-0.17296
H	2.850048	2.429635	-0.2259
H	2.642019	2.507539	1.546565
H	4.249797	2.175345	0.849722
O	4.988196	0.15204	-0.49473
H	4.421732	0.483643	-1.56159
O	3.240486	0.400809	-1.77912
H	3.049463	-0.35672	-2.35841

Table S56. Frequencies (cm^{-1}) of TS4B_v1 transition state.

46	51	85	116	125	145	173	200
212	229	236	245	250	257	269	276
279	289	301	308	330	333	349	364
369	392	402	443	475	488	515	530
545	557	569	590	640	647	654	696
725	772	797	807	833	838.	868	884
916	924	938	946	948	957	992	996
1003	1005	1028	1043	1085	1092	1101	1106
1130	1158	1164	1176	1212	1218	1234	1234
1246	1259	1272	1287	1297	1311	1338	1347
1353	1361	1372	1374	1377	1385	1387	1391
1397	1420	1440	1444	1448	1454	1456	1457
1459	1463	1464	1469	1471	1478	1481	1499
1504	1548	1670	1709	2036	3027	3029	3041
3045	3049	3053	3058	3070	3071	3122	3122
3128	3128	3131	3133	3142	3142	3144	3157
3157	3158	3171	3185	3198	3784	-1667	

TS4B_v2

Figure S32. The optimized structure of TS4B_v2 transition state.

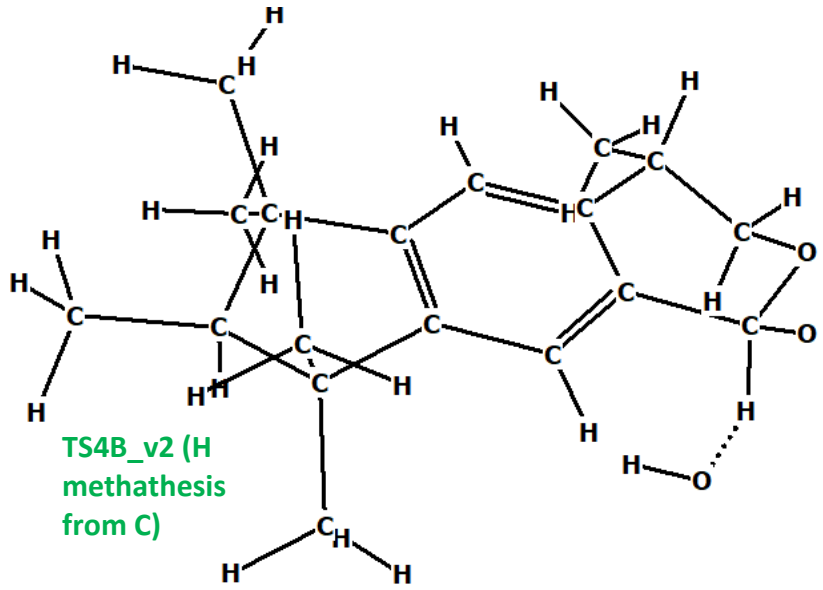


Table S57. Geometry (Å) of TS4B_v2 transition state.

Atom	x	y	z
O	4.002443	-0.38071	-0.38233
C	-3.13023	0.135556	-0.45293
C	-2.3034	1.248531	0.266366
C	-2.23964	-1.14559	-0.5162
C	-0.8817	0.776289	0.026234
C	-0.84814	-0.55113	-0.40819
C	-4.53701	-0.07859	0.087328
C	-2.56769	1.341835	1.777443
C	-2.57046	2.618028	-0.36482
C	-2.47634	-2.12726	0.642347
C	-2.4465	-1.88886	-1.83854
C	0.295635	1.502254	0.193712
C	0.372663	-1.16296	-0.66357
C	1.538925	0.908593	-0.05443
C	1.554697	-0.43272	-0.47982
C	2.889518	-1.11593	-0.78355
C	2.720513	3.148888	-0.34675
H	-3.22112	0.475469	-1.4995
H	-4.52779	-0.42141	1.13185
H	-5.11785	0.855309	0.043739
H	-5.07352	-0.8312	-0.51034
H	-1.88176	2.074621	2.229713
H	-3.59742	1.677814	1.971878
H	-2.41519	0.379674	2.286427
H	-1.99519	3.408774	0.141009
H	-2.29939	2.619809	-1.43112
H	-3.63795	2.874559	-0.27783

H	-2.37013	-1.64555	1.624665
H	-3.48257	-2.56859	0.579773
H	-1.74345	-2.94712	0.589126
H	-3.49537	-2.21078	-1.93481
H	-2.20153	-1.24421	-2.69561
H	-1.81578	-2.78971	-1.89074
H	0.248472	2.545856	0.510777
H	0.428652	-2.19747	-1.00869
H	2.962768	-1.27652	-1.93602
H	2.317838	3.23511	-1.36746
H	2.06795	3.713509	0.331193
H	3.711005	3.626491	-0.32367
C	2.840994	1.683766	0.066688
H	3.176483	1.634421	1.116788
C	3.901015	0.982117	-0.77192
H	4.892249	1.424188	-0.61452
H	3.649555	1.04231	-1.84784
O	2.816289	-2.2999	-0.14366
O	2.771614	-0.86072	-3.38168
H	1.906814	-0.43122	-3.21799

Table S58. Frequencies (cm^{-1}) of TS4B_v2 transition state.

34	36	61	66	102	109	132	142
185	210	226	230	237	241	252	256
260	264	274	280	290	318	328	328
346	370	378	384	416	442	461	500
524	537	552	569	587	625	639	685
704	722	753	774	797	824	831	908
914	917	936	944	945	953	958	982
990	1006	1028	1044	1071	1091	1104	1122
1133	1143	1161	1162	1173	1204	1212	1215
1224	1243	1249	1272	1294	1300	1308	1327
1350	1352	1358	1365	1374	1377	1388	1389
1392	1397	1407	1440	1444	1446	1447	1454
1458	1458	1462	1467	1469	1472	1475	1476
1482	1533	1643	1684	1726	3038	3041	3047
3047	3048	3050	3054	3061	3065	3121	3122
3127	3129	3130	3136	3138	3140	3142	3147
3150	3157	3169	3195	3198	3718	-1169	

ProductB

Figure S33. The optimized structure of ProductB.

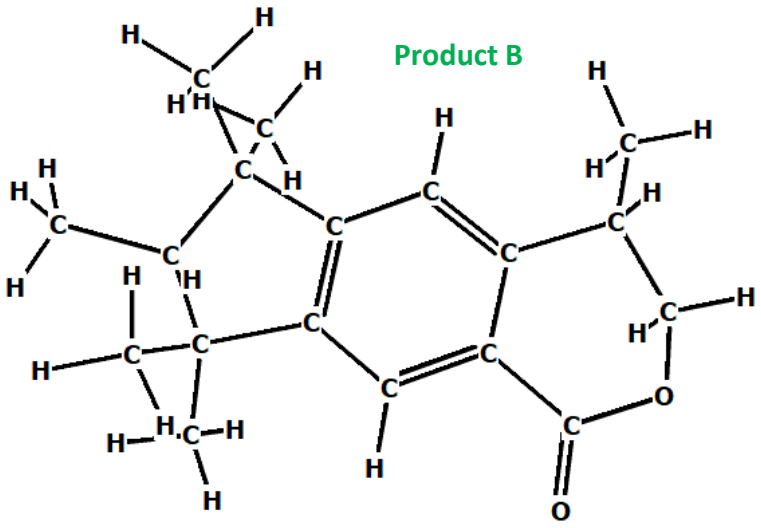


Table S59. Geometry (Å) of ProductB.

Atom	x	y	z
O	3.340787	-2.45583	-0.44268
C	-3.14807	0.455329	-0.17332
C	-1.93444	1.406476	0.072325
C	-2.70123	-0.98771	0.219448
C	-0.76636	0.441292	-0.00512
C	-1.1942	-0.88831	0.074482
C	-4.46617	0.91502	0.433023
C	-1.94553	2.087997	1.449795
C	-1.86144	2.486629	-1.01072
C	-3.05854	-1.38041	1.661628
C	-3.30442	-2.02301	-0.73396
C	0.587531	0.754006	-0.11785
C	-0.26312	-1.91794	0.042019
C	1.535819	-0.27182	-0.15924
C	1.095494	-1.60547	-0.08356
C	2.072272	-2.72966	-0.08425
C	3.401692	1.296246	-0.92453
H	-3.27498	0.428941	-1.26979
H	-4.41779	0.968869	1.530091
H	-4.74165	1.912609	0.058288
H	-5.27945	0.223762	0.164441
H	-1.01477	2.659082	1.58939
H	-2.78879	2.79066	1.529751
H	-2.02051	1.361389	2.271049
H	-1.00858	3.162267	-0.8431
H	-1.75702	2.037203	-2.00944
H	-2.77758	3.097673	-0.99922
H	-2.67176	-0.66078	2.39705
H	-4.14948	-1.45249	1.788182

H	-2.62548	-2.36505	1.896008
H	-4.40431	-1.99225	-0.68408
H	-2.9983	-1.8279	-1.7724
H	-2.98601	-3.04193	-0.46478
H	0.904786	1.796562	-0.17881
H	-0.55737	-2.96713	0.108553
H	2.933281	1.39289	-1.91582
H	3.083605	2.147567	-0.30907
H	4.491939	1.36323	-1.04656
C	3.0262	-0.03069	-0.27334
H	3.458827	-0.06505	0.742279
C	3.620524	-1.1883	-1.05601
H	4.714174	-1.12574	-1.09427
H	3.226731	-1.19602	-2.08613
O	1.79032	-3.86042	0.239362

Table S60. Frequencies (cm^{-1}) of ProductB.

44	62	87	111	134	146	193	220
227	232	240	242	251	258	264	273
281	297	326	330	338	347	370	384
404	433	484	494	525	532	549	583
607	642	663	707	721	758	780	820
822	826	909	918	930	944.	945	949
956	965	978	991	1002	1026	1072	1084
1092	1102	1119	1144	1150	1161	1176	1207
1216	1224	1239	1244	1262	1277	1295	1324
1329	1352	1352	1367	1372	1374	1377	1385
1391	1396	1397	1427	1440	1444	1447	1454
1455	1458	1463	1463	1468	1472	1477	1478
1479	1499	1537	1658	1702	1836	3039	3042
3044	3047	3052	3054	3060	3062	3079	3120
3124	3125	3128	3130	3130	3137	3140	3143
3149	3151	3158	3169	3201	3206		

Figure S34. The optimized structure of TS1C_v1 transition state.

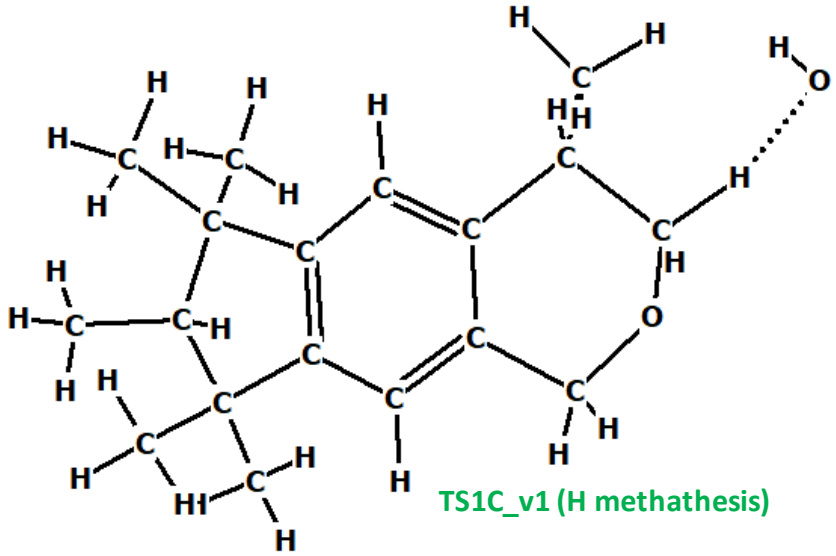


Table S61. Geometry (Å) of TS1C_v1 transition state.

Atom	x	y	z
O	3.782473	0.268871	-0.27314
C	-3.33928	-0.41606	-0.26376
C	-2.69405	0.755605	0.542163
C	-2.24031	-1.50677	-0.47021
C	-1.22112	0.568363	0.22386
C	-0.97029	-0.68701	-0.33593
C	-4.6673	-0.92625	0.277463
C	-2.91619	0.661558	2.059379
C	-3.22383	2.106714	0.053615
C	-2.25927	-2.61787	0.590875
C	-2.36735	-2.14987	-1.85409
C	-0.17685	1.460907	0.443883
C	0.329628	-1.05167	-0.66809
C	1.138593	1.108283	0.109537
C	1.385199	-0.15998	-0.44426
C	2.297698	2.069021	0.345854
C	2.788544	-0.57135	-0.83581
C	3.472228	1.611914	-0.49948
C	1.973291	3.532165	0.056993
H	-3.52656	-0.00276	-1.27047
H	-4.56293	-1.36484	1.280416
H	-5.40174	-0.10889	0.341429
H	-5.0883	-1.69844	-0.38451
H	-2.35661	1.463016	2.566093
H	-3.98149	0.783305	2.308241
H	-2.57228	-0.29837	2.470154
H	-2.77149	2.937245	0.617602
H	-3.00386	2.253864	-1.01432

H	-4.31501	2.164198	0.1938
H	-2.20002	-2.21672	1.61254
H	-3.17484	-3.22318	0.508757
H	-1.39725	-3.28676	0.442828
H	-3.34877	-2.63862	-1.9605
H	-2.26807	-1.39576	-2.64903
H	-1.59369	-2.91837	-2.00754
H	-0.38123	2.441611	0.879757
H	0.539363	-2.03354	-1.10348
H	2.603432	1.973477	1.403013
H	3.003056	-1.588	-0.48023
H	2.882734	-0.5716	-1.93873
H	3.312703	1.820501	-1.57715
H	4.415623	2.237352	-0.21253
H	1.585178	3.65093	-0.96638
H	1.228716	3.933572	0.75653
H	2.890786	4.129999	0.157329
O	5.317419	3.133831	0.456711
H	5.058163	2.864883	1.361359

Table S62. Frequencies (cm^{-1}) of TS1C_v1 transition state.

30	46	72	90	105	118	153	156
207	225	234	236	243	249	255	261
270	275	280	296	301	329	333	346
365	378	387	417	448	474	511	526
549	557	588	626	671	680	723	766
772	785	825	832	885	907.	908	915
936	944	946	956	990	992	1005	1016
1018	1028	1060	1089	1093	1105	1138	1154
1155	1162	1181	1211	1214	1218	1232	1245
1254	1265	1296	1297	1311	1325	1351	1352
1369	1372	1374	1377	1383	1386	1388	1392
1399	1412	1438	1443	1446	1450	1455	1457
1459	1461	1463	1466	1468	1474	1479	1489
1537	1559	1662	1706	3013	3020	3035	3039
3043	3043	3047	3052	3054	3055	3119	3122
3122	3125	3127	3128	3129	3138	3139	3140
3148	3150	3155	3165	3184	3726	-862	

TS1C_v2

Figure S35. The optimized structure of TS1C_v2 transition state.

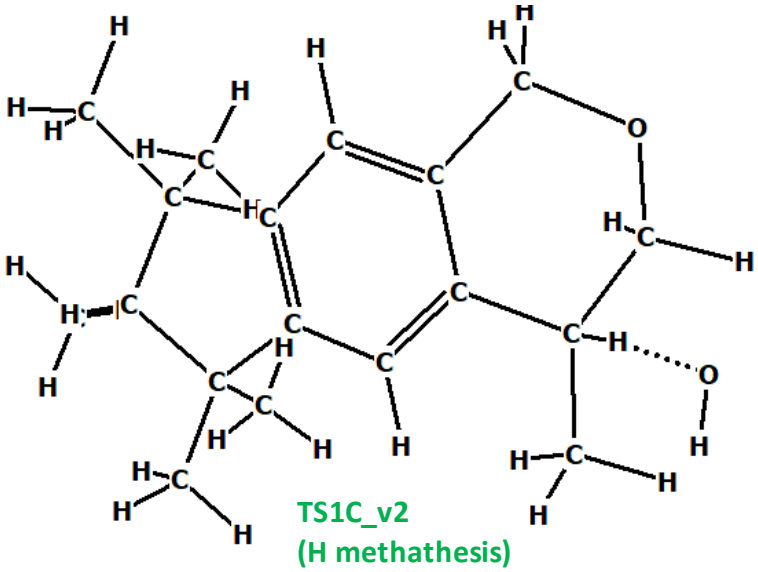


Table S63. Geometry (Å) of TS1C_v2 transition state.

Atom	x	y	z
O	3.57463	-1.96571	-0.07899
C	-3.15054	0.462376	-0.13876
C	-1.98237	1.484311	0.034952
C	-2.60469	-0.94686	0.256037
C	-0.76766	0.581191	-0.08322
C	-1.11433	-0.7678	0.035302
C	-4.46336	0.859576	0.521536
C	-1.97397	2.193589	1.398328
C	-2.02213	2.545433	-1.06793
C	-2.87325	-1.32592	1.720714
C	-3.19606	-2.03329	-0.64643
C	0.560453	0.951046	-0.26207
C	-0.12892	-1.74781	-0.02416
C	1.564513	-0.02757	-0.33235
C	1.209491	-1.38325	-0.20331
C	2.269949	-2.45844	-0.29364
C	3.265518	1.516538	-1.46529
H	-3.32673	0.407994	-1.22747
H	-4.36648	0.940979	1.613719
H	-4.81261	1.83201	0.142185
H	-5.24848	0.118461	0.307179
H	-1.06943	2.815114	1.486776
H	-2.8485	2.853743	1.503046
H	-1.97531	1.482382	2.236471
H	-1.19757	3.266481	-0.95618
H	-1.94376	2.082236	-2.06288
H	-2.96699	3.110071	-1.02245
H	-2.49506	-0.56803	2.421422

H	-3.95172	-1.45461	1.898906
H	-2.37443	-2.27899	1.954777
H	-4.29208	-2.06337	-0.54127
H	-2.95433	-1.8436	-1.7029
H	-2.80815	-3.02767	-0.37542
H	0.823945	2.007537	-0.35006
H	-0.38895	-2.80636	0.071797
H	2.093608	-3.22946	0.46842
H	2.212406	-2.94857	-1.28598
H	2.85567	1.303906	-2.46504
H	2.80674	2.445466	-1.10134
H	4.346717	1.693529	-1.56583
O	4.52164	1.187714	1.452477
H	4.504068	2.085195	1.062499
C	3.013538	0.345088	-0.52642
H	3.421694	0.632473	0.509653
C	3.842612	-0.86689	-0.92386
H	4.91197	-0.6387	-0.82342
H	3.634967	-1.13311	-1.98086

Table S64. Frequencies (cm^{-1}) of TS1C_v2 transition state.

33	46	69	87	100	120	141	153
191	212	221	231	241	242	253	262
270	275	278	297	319	328	333	344
373	378	389	412	447	481	515	525
547	560	583	626	633	681	691	722
770	787	824	834	878	908.	912	934
941	944	947	956	976	991	992	1005
1021	1027	1035	1091	1102	1104	1124	1151
1158	1163	1193	1212	1216	1230	1244	1252
1255	1272	1292	1298	1323	1328	1350	1352
1367	1374	1376	1381	1387	1388	1391	1397
1412	1436	1442	1446	1449	1452	1455	1456
1459	1462	1465	1467	1470	1475	1476	1491
1541	1655	1702	1897	3007	3011	3042	3044
3045	3046	3050	3054	3061	3122	3124	3126
3126	3128	3132	3133	3136	3138	3140	3141
3142	3146	3156	3163	3183	3724	-543	

P2C_v1

Figure S36. The optimized structure of P2C_v1.

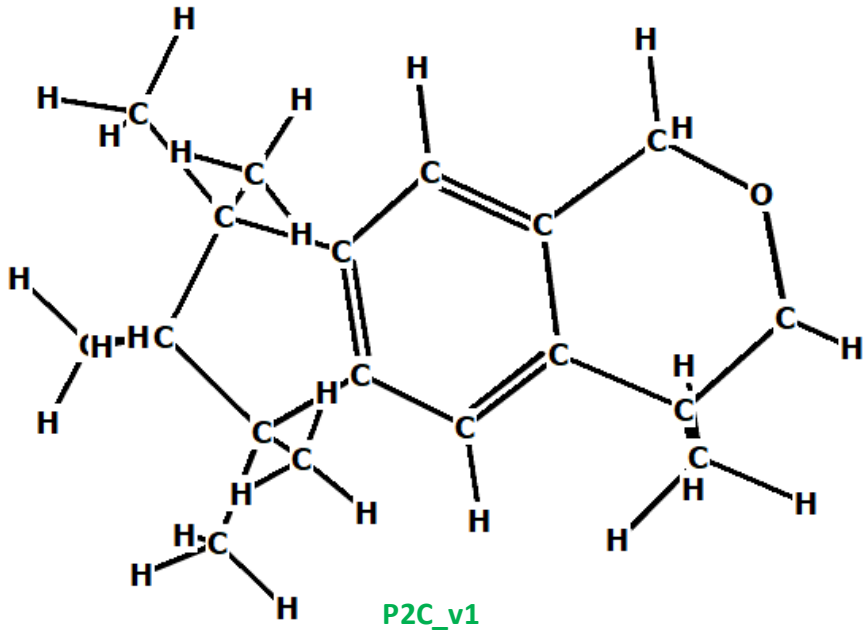


Table S65. Geometry (Å) of P2C_v1.

Atom	x	y	z
O	3.901266	-1.2057	0.882491
C	-2.87626	0.197928	-0.40719
C	-1.96031	1.321231	0.172429
C	-2.13363	-1.16048	-0.21247
C	-0.59046	0.67131	0.089013
C	-0.68713	-0.70558	-0.12893
C	-4.32142	0.22546	0.070248
C	-2.27422	1.690418	1.630554
C	-2.05007	2.588321	-0.68282
C	-2.5217	-1.90184	1.076342
C	-2.37911	-2.09057	-1.40382
C	0.656351	1.278309	0.233187
C	0.463919	-1.48816	-0.20144
C	1.816255	0.503143	0.142736
C	1.713863	-0.87815	-0.07622
C	3.203252	1.10529	0.23228
C	3.004818	-1.65019	-0.13371
C	4.172063	0.130875	0.856999
C	3.671678	1.580219	-1.15936
H	-2.88236	0.3673	-1.49835
H	-4.40109	0.071954	1.156226
H	-4.79333	1.191246	-0.16735
H	-4.91051	-0.56135	-0.42522
H	-1.52684	2.409672	1.999798
H	-3.26539	2.162348	1.711713
H	-2.25261	0.814354	2.294108

H	-1.40182	3.38374	-0.2837
H	-1.74895	2.384879	-1.72133
H	-3.08277	2.971394	-0.69037
H	-2.38989	-1.27558	1.970229
H	-3.57037	-2.23446	1.037854
H	-1.88833	-2.79465	1.19503
H	-3.454	-2.30989	-1.5032
H	-2.03077	-1.63123	-2.34094
H	-1.85428	-3.04966	-1.273
H	0.738167	2.354862	0.41114
H	0.399473	-2.56964	-0.35217
H	3.161125	1.99387	0.881924
H	2.84096	-2.71973	0.042713
H	3.496632	-1.53014	-1.11631
H	4.790541	0.425362	1.705356
H	3.698231	0.738911	-1.86876
H	2.986651	2.345092	-1.55517
H	4.682562	2.008488	-1.09542

Table S66. Frequencies (cm^{-1}) of P2C_v1.

57	61	93	114	147	157	177	216
230	235	250	261	262	268	286	291
300	312	318	330	350	356	373	391
416	456	492	517	535	553	561	576
607	651	701	714	757	779	805	821
842	909	914	922	934	945.	946	954
965	991	1002	1010	1021	1026	1037	1065
1091	1100	1102	1149	1160	1187	1208	1215
1222	1246	1250	1268	1287	1296	1304	1317
1342	1350	1352	1366	1367	1372	1374	1374
1384	1390	1396	1429	1439	1443	1448	1452
1453	1454	1458	1462	1463	1469	1473	1476
1481	1501	1540	1666	1704	3032	3040	3041
3041	3048	3050	3051	3054	3076	3117	3118
3122	3128	3130	3135	3135	3138	3140	3144
3146	3148	3149	3176	3185	3216		

P2C_v2

Figure S37. The optimized structure of P2C_v2.

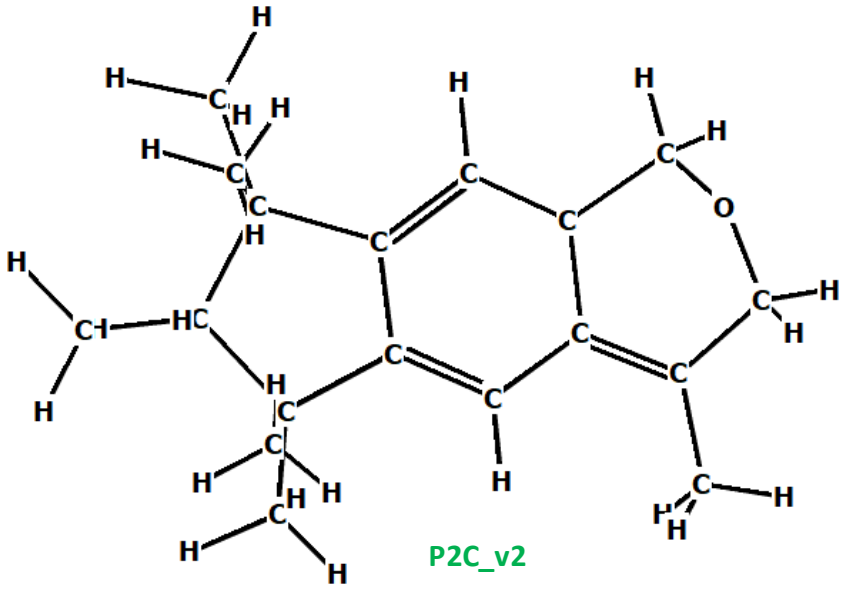


Table S67. Geometry (Å) of P2C_v2.

Atom	x	y	z
O	3.978328	-1.34982	0.502257
C	-2.88653	0.135483	-0.45258
C	-1.90922	1.28595	-0.05557
C	-2.18136	-1.2166	-0.11891
C	-0.56515	0.579926	-0.11325
C	-0.72036	-0.81132	-0.14617
C	-4.30762	0.275343	0.075043
C	-2.14645	1.840754	1.357149
C	-1.99761	2.441896	-1.05572
C	-2.54373	-1.78316	1.263509
C	-2.5071	-2.27371	-1.17858
C	0.6967	1.156064	-0.10618
C	0.406317	-1.64209	-0.16827
C	1.853362	0.331363	-0.13452
C	1.677177	-1.08527	-0.16951
C	3.172498	0.85642	-0.14823
C	2.925246	-1.92627	-0.24759
C	4.334335	-0.08319	-0.00879
C	3.462225	2.315953	-0.27767
H	-2.93595	0.168817	-1.55524
H	-4.34588	0.242464	1.17354
H	-4.75225	1.228684	-0.24945
H	-4.9473	-0.53509	-0.30684
H	-1.36384	2.57535	1.602413
H	-3.12044	2.349732	1.420909
H	-2.11767	1.051707	2.122146
H	-1.30973	3.257009	-0.78217

H	-1.74571	2.103741	-2.07199
H	-3.01769	2.85753	-1.07155
H	-2.36149	-1.05798	2.069123
H	-3.6024	-2.08299	1.300144
H	-1.93292	-2.67551	1.470876
H	-3.59185	-2.46288	-1.21012
H	-2.18361	-1.94302	-2.1768
H	-2.00841	-3.22908	-0.95271
H	0.808482	2.242365	-0.07275
H	0.294822	-2.73034	-0.19122
H	2.750176	-2.92906	0.163391
H	3.241009	-2.04047	-1.30443
H	4.846649	-0.19668	-0.99058
H	5.076129	0.33773	0.687861
H	2.880794	2.778648	-1.09008
H	3.207817	2.862445	0.648167
H	4.528715	2.489549	-0.4782

Table S68. Frequencies (cm^{-1}) of P2C_v2.

50	63	96	107	120	146	150	192
227	231	241	244	256	268	272	285
308	311	327	329	348	354	374	392
421	435	474	510	532	550	559	586
628	648	694	721	767	786	820	836
888	910	916	936	942	943.	951	954
988	990	1002	1008	1022	1026	1043	1089
1100	1104	1152	1160	1176	1201	1208	1217
1236	1238	1243	1277	1292	1306	1311	1343
1350	1352	1367	1369	1372	1372	1384	1386
1389	1397	1431	1438	1442	1443	1444	1447
1452	1454	1458	1459	1461	1464	1468	1475
1481	1494	1530	1614	1667	2951	3001	3021
3035	3036	3037	3047	3050	3056	3093	3095
3114	3116	3122	3125	3128	3128	3132	3136
3139	3140	3141	3151	3174	3195		

TS2C_v1

Figure S38. The optimized structure of TS2C_v1 transition state.

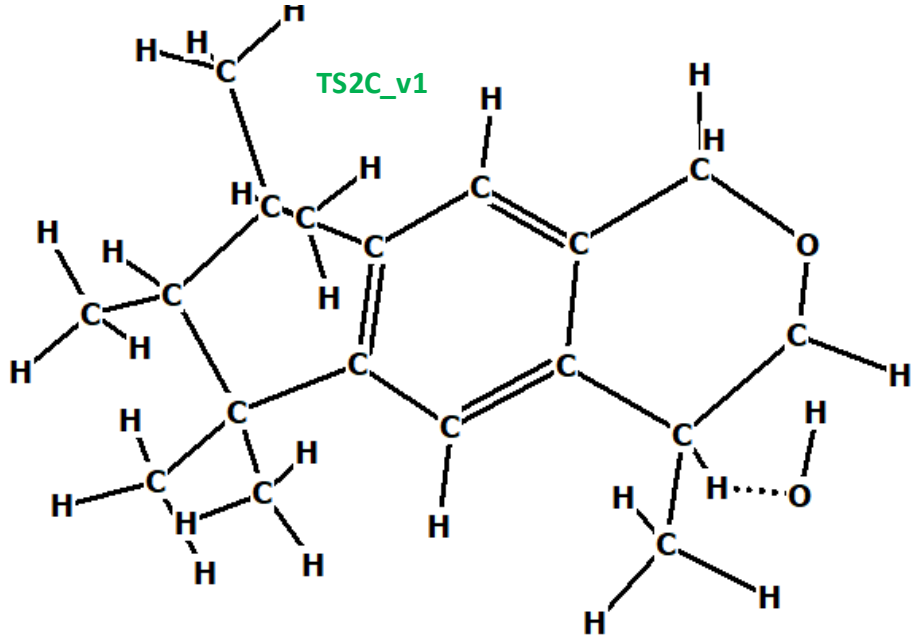


Table S69. Geometry (Å) of TS2C_v1 transition state.

Atom	x	y	z
O	3.662132	-1.8072	-0.30887
C	-3.16143	0.44439	-0.12265
C	-2.02764	1.513399	-0.0195
C	-2.55632	-0.92735	0.313003
C	-0.7841	0.649792	-0.13356
C	-1.07917	-0.70604	0.047111
C	-4.4726	0.819702	0.553412
C	-2.01251	2.276568	1.314042
C	-2.13229	2.526739	-1.16256
C	-2.77211	-1.25899	1.798086
C	-3.13066	-2.0683	-0.53114
C	0.523174	1.059067	-0.36147
C	-0.06257	-1.65278	-0.00146
C	1.559177	0.111666	-0.42079
C	1.25729	-1.24802	-0.23211
C	2.328016	-2.30898	-0.3122
C	3.839976	-0.66411	-1.03769
C	3.226995	1.702522	-1.5623
H	-3.3611	0.340104	-1.20364
H	-4.3571	0.938444	1.640351
H	-4.86131	1.767172	0.149941
H	-5.23681	0.046876	0.378891
H	-1.13309	2.937918	1.352449
H	-2.91136	2.90344	1.416689
H	-1.96175	1.600126	2.179066
H	-1.33207	3.280454	-1.10028

H	-2.06079	2.026504	-2.1399
H	-3.09592	3.058299	-1.11469
H	-2.40641	-0.46094	2.459587
H	-3.83964	-1.42284	2.010384
H	-2.23064	-2.18253	2.054985
H	-4.2223	-2.12905	-0.39823
H	-2.92003	-1.91341	-1.59977
H	-2.70389	-3.03802	-0.23137
H	0.747691	2.11896	-0.4985
H	-0.28261	-2.71521	0.13948
H	2.257756	-2.988	0.547305
H	2.186344	-2.90666	-1.22912
H	4.895442	-0.48812	-1.25993
H	2.849065	1.475627	-2.57214
H	2.734618	2.613716	-1.20089
H	4.304386	1.90782	-1.63546
O	4.281339	0.502714	1.527012
H	4.205104	-0.46773	1.417796
C	2.986133	0.514812	-0.64672
H	3.402842	0.816813	0.416176

Table S70. Frequencies (cm^{-1}) of TS2C_v1 transition state.

32	40	71	82	108	136	146	167
184	212	223	234	238	247	258	267
273	275	288	295	324	330	339	355
378	384	392	414	448	476	488	523
548	558	580	586	650	674	679	723
777	788	805	823	838	868.	912	920
926	939	943	945	954	984	992	1005
1016	1028	1033	1047	1090	1100	1106	1156
1161	1164	1197	1207	1216	1218	1243	1258
1263	1279	1292	1301	1330	1351	1351	1361
1372	1374	1378	1386	1388	1393	1397	1417
1437	1441	1442	1445	1453	1455	1460	1460
1461	1466	1467	1474	1476	1492	1544	1657
1696	1747	3035	3038	3039	3049	3050	3050
3053	3062	3118	3119	3126	3128	3130	3130
3130	3133	3136	3139	3146	3149	3156	3170
3191	3195	3714	-994				

TS2C_v2

Figure S39. The optimized structure of TS2C_v2 transition state.

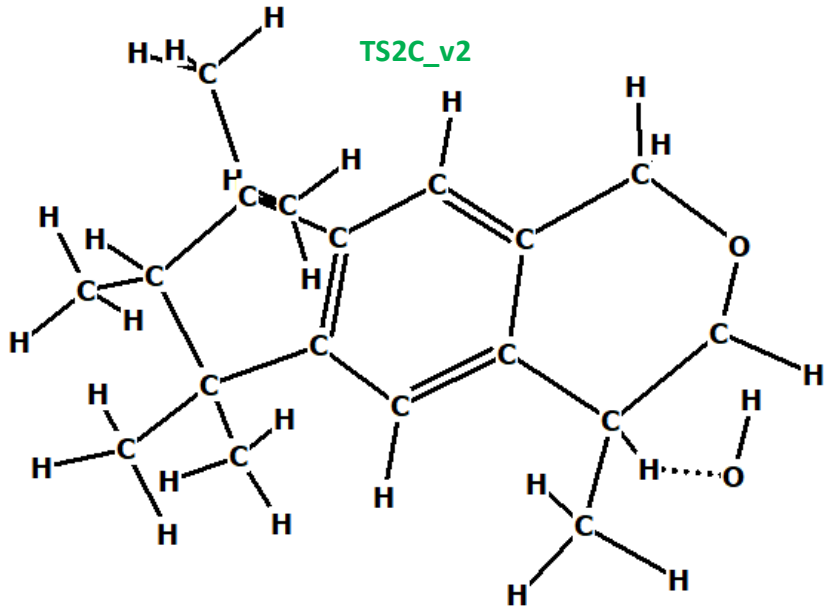


Table S71. Geometry (Å) of TS2C_v2 transition state.

Atom	x	y	z
O	3.662297	-1.80594	-0.31299
C	-3.16218	0.442928	-0.1226
C	-2.0287	1.51227	-0.01928
C	-2.5563	-0.92887	0.311753
C	-0.78486	0.649261	-0.13435
C	-1.07934	-0.70682	0.045443
C	-4.47309	0.817272	0.554519
C	-2.01329	2.274557	1.31475
C	-2.13419	2.526229	-1.16171
C	-2.77125	-1.26126	1.796781
C	-3.1305	-2.06953	-0.53283
C	0.522185	1.059246	-0.36228
C	-0.06237	-1.6531	-0.00407
C	1.558543	0.112299	-0.42263
C	1.257267	-1.24765	-0.23483
C	2.328333	-2.30816	-0.3163
C	3.839443	-0.66211	-1.04079
C	3.225717	1.704888	-1.56278
H	-3.36258	0.339376	-1.20353
H	-4.35705	0.935269	1.641478
H	-4.86234	1.764904	0.151957
H	-5.23713	0.044318	0.379832
H	-1.13429	2.936465	1.35307
H	-2.91246	2.900812	1.418393
H	-1.96152	1.59758	2.179325

H	-1.33435	3.280341	-1.09923
H	-2.06269	2.026577	-2.13935
H	-3.0981	3.057244	-1.1133
H	-2.40596	-0.46297	2.458235
H	-3.83855	-1.42605	2.009491
H	-2.22888	-2.18441	2.053228
H	-4.222	-2.13114	-0.39917
H	-2.92077	-1.91367	-1.60149
H	-2.70285	-3.0392	-0.23414
H	0.746244	2.119334	-0.49856
H	-0.28193	-2.71572	0.136172
H	2.258626	-2.98806	0.542545
H	2.18655	-2.90497	-1.23378
H	4.894703	-0.48559	-1.26357
H	2.847908	1.478889	-2.57287
H	2.732981	2.615526	-1.20046
H	4.303031	1.91067	-1.6357
O	4.280797	0.50253	1.525056
H	4.205682	-0.46784	1.414398
C	2.985299	0.516144	-0.64846
H	3.401973	0.817136	0.414749

Table S72. Frequencies (cm^{-1}) of TS2C_v2 transition state.

32	40	71	82	108	136	146	167
184	212	223	234	238	247	258	267
273	275	288	296	324	330	339	355
378	384	393	414	448	476	488	523
548	558	580	586	650	674	679	723
777	788	805	823	838	868.	912	920
926	939	943	945	954	984	992	1005
1016	1028	1033	1047	1090	1100	1106	1156
1161	1164	1197	1207	1216	1218	1243	1258
1263	1279	1292	1301	1330	1351	1351	1361
1372	1374	1378	1386	1388	1393	1397	1417
1437	1441	1442	1445	1453	1455	1460	1460
1461	1466	1467	1474	1476	1492	1544	1657
1696	1746	3035	3038	3039	3049	3050	3050
3053	3062	3118	3119	3126	3128	3130	3130
3130	3133	3136	3139	3146	3149	3156	3170
3191	3195	3714	-994				

ProductC

Figure S40. The optimized structure of ProductC.

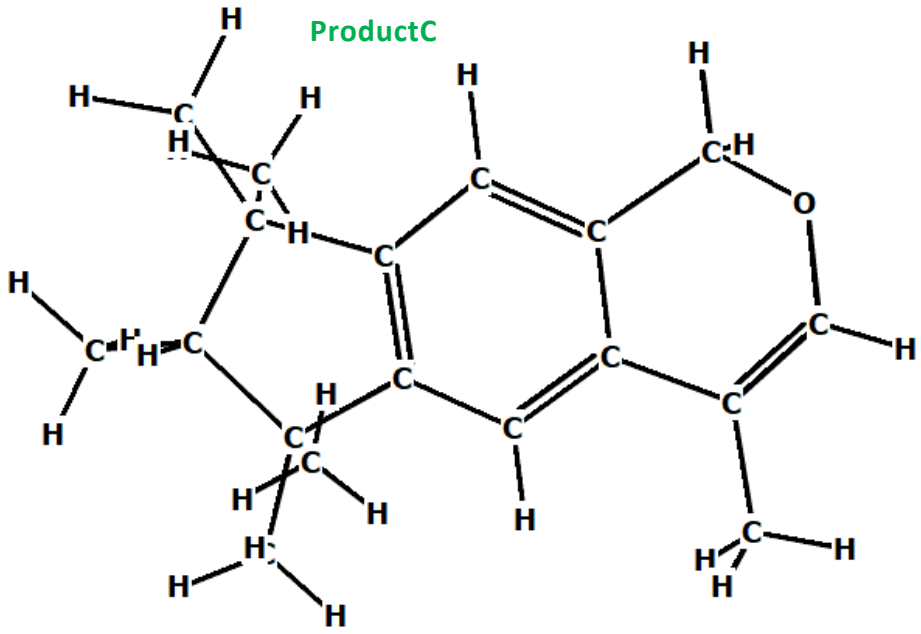


Table S73. Geometry (Å) of ProductC.

Atom	x	y	z
O	4.064634	-0.96924	0.600213
C	-2.90048	0.024774	-0.44561
C	-1.99562	1.26092	-0.1458
C	-2.12241	-1.24891	0.011986
C	-0.61461	0.629738	-0.12675
C	-0.68599	-0.76112	-0.03903
C	-4.33316	0.127728	0.058491
C	-2.28408	1.927747	1.207854
C	-2.13269	2.314057	-1.24884
C	-2.46725	-1.71009	1.436738
C	-2.37231	-2.41242	-0.95178
C	0.619048	1.279357	-0.15834
C	0.484597	-1.52202	0.009405
C	1.799058	0.525304	-0.11359
C	1.718632	-0.87991	-0.04205
C	3.140486	1.133581	-0.07604
C	3.022372	-1.62811	-0.11823
C	4.166862	0.35888	0.321208
C	3.322672	2.600201	-0.3393
H	-2.9388	-0.0424	-1.54716
H	-4.38204	0.189585	1.155273
H	-4.82752	1.021488	-0.3521
H	-4.92099	-0.74892	-0.25418
H	-1.54603	2.723406	1.393819
H	-3.2846	2.386707	1.213643
H	-2.22593	1.214086	2.042063

H	-1.49602	3.188909	-1.04451
H	-1.84667	1.899375	-2.22704
H	-3.17411	2.667296	-1.3134
H	-2.33886	-0.90617	2.175282
H	-3.50657	-2.06861	1.492135
H	-1.80734	-2.54192	1.728151
H	-3.44397	-2.66605	-0.97532
H	-2.0551	-2.15328	-1.97291
H	-1.8233	-3.31366	-0.63748
H	0.668289	2.36927	-0.21531
H	0.442028	-2.61326	0.069804
H	2.941924	-2.63488	0.307797
H	3.339374	-1.71467	-1.17548
H	5.171063	0.745913	0.508362
H	2.950223	2.874988	-1.33813
H	2.766275	3.207841	0.391635
H	4.382542	2.879857	-0.27769

Table S74. Frequencies (cm^{-1}) of ProductC.

52	62	101	135	145	164	215	221
230	233	249	254	259	267	276	282
306	325	331	344	349	373	390	398
432	474	504	520	544	561	576	599
654	681	712	730	782	808	825	846
898	917	921	935	942	944.	955	986
991	994	1003	1022	1027	1041	1054	1090
1102	1109	1153	1161	1194	1209	1217	1236
1244	1252	1278	1289	1305	1332	1350	1351
1358	1370	1373	1377	1385	1390	1396	1401
1421	1438	1441	1442	1446	1452	1454	1455
1460	1461	1467	1468	1476	1479	1493	1546
1656	1702	1740	3022	3033	3035	3036	3048
3051	3052	3058	3115	3116	3121	3124	3125
3126	3128	3133	3138	3140	3148	3149	3153
3179	3193	3218					

TS2D

Figure S41. The optimized structure of TS2D transition state.

TS2D (OH addition)

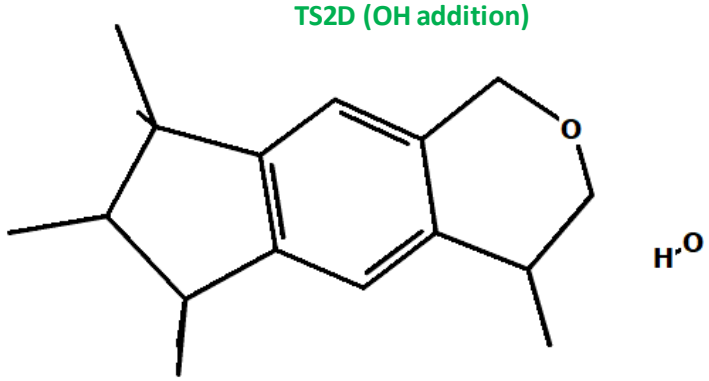


Table S75. Geometry (Å) of TS2D transition state.

Atom	x	y	z
O	3.334732	-0.69239	-1.42067
C	-2.9609	0.081939	-0.60364
C	-2.06602	1.2761	-0.1423
C	-2.32147	-1.22896	-0.04535
C	-0.7461	0.602035	0.095184
C	-0.86113	-0.83236	0.089083
C	-4.45024	0.24598	-0.33286
C	-2.55455	1.969846	1.144954
C	-1.96762	2.338361	-1.24818
C	-2.86711	-1.63585	1.33275
C	-2.51921	-2.39319	-1.01794
C	0.522156	1.254364	0.455487
C	1.641023	0.49762	0.609922
C	1.562634	-0.9429	0.280214
C	3.143492	2.526411	0.968991
H	-2.82598	0.025558	-1.698
H	-4.66986	0.322524	0.741787
H	-4.83581	1.154667	-0.81968
H	-5.01559	-0.60991	-0.73199
H	-1.81895	2.723835	1.465042
H	-3.50872	2.488798	0.966341
H	-2.695	1.261584	1.972995
H	-1.32782	3.177805	-0.93486
H	-1.54758	1.907468	-2.16927
H	-2.96616	2.743613	-1.47739
H	-2.74708	-0.83575	2.077059
H	-3.9349	-1.89466	1.269759
H	-2.32192	-2.51897	1.698446
H	-3.59225	-2.59667	-1.16054
H	-2.07431	-2.16681	-1.99828
H	-2.05316	-3.31234	-0.63085
H	0.544003	2.332732	0.625996

H	2.791482	3.015508	0.044731
H	2.548291	2.937161	1.802875
H	4.19667	2.784558	1.12335
C	2.980975	1.040859	0.861322
H	3.580047	0.441242	1.553037
C	3.396994	0.601823	-1.16517
H	3.94708	1.166275	-1.92826
O	5.168909	0.799509	-0.14831
H	5.260763	-0.09204	0.238407
C	2.752396	-1.5367	-0.39384
H	2.508434	-2.48077	-0.89444
H	3.563711	-1.73166	0.331795
C	0.230314	-1.61767	0.256124
H	0.167923	-2.70537	0.334852

Table S76. Frequencies (cm^{-1}) of TS2D transition state.

32	43	61	69	104	128	137	189
198	202	211	218	226	230	247	254
259	266	271	283	296	298	309	316
328	330	351	375	396	429	458	469
493	532	549	562	586	628	640	664
674	695	752	768	806	817.	826	848
882	910	929	938	943	944	947	976
988	999	1019	1021	1042	1054	1089	1092
1120	1140	1147	1156	1173	1193	1208	1214
1217	1242	1251	1264	1284	1310	1333	1347
1350	1358	1367	1370	1374	1386	1389	1399
1413	1422	1437	1441	1443	1444	1447	1450
1455	1457	1459	1462	1466	1473	1473	1638
1683	3024	3027	3036	3040	3046	3050	3056
3060	3087	3123	3126	3130	3130	3131	3132
3135	3143	3147	3151	3157	3163	3167	3176
3187	3197	3747	-1152				

P2D

Figure S42. The optimized structure of P2D.

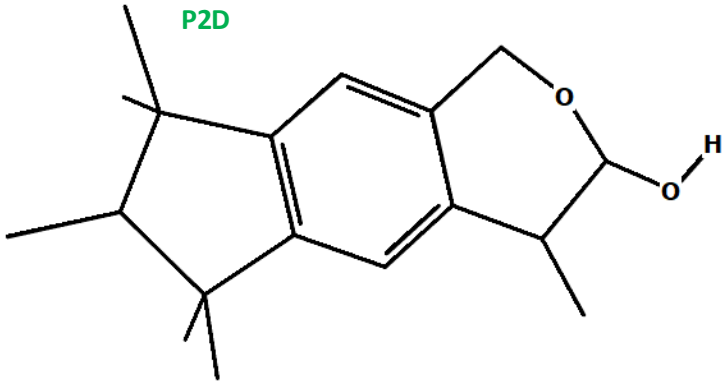


Table S77. Geometry (Å) of P2D.

Atom	x	y	z
O	3.742947	-1.36955	0.634087
C	-3.12674	0.213094	-0.48093
C	-2.15901	1.332468	0.017755
C	-2.47081	-1.16223	-0.13942
C	-0.82965	0.599011	0.036683
C	-1.00335	-0.78441	-0.0493
C	-4.57798	0.366508	-0.04802
C	-2.48625	1.854321	1.425172
C	-2.15267	2.516277	-0.9536
C	-2.93836	-1.75906	1.197204
C	-2.73748	-2.18191	-1.25023
C	0.44651	1.141844	0.147008
C	0.103579	-1.62516	-0.01185
C	1.573413	0.307014	0.178631
C	1.389141	-1.08396	0.10567
C	2.975286	0.889526	0.296448
C	4.000415	-0.17252	-0.0723
C	3.186998	2.148815	-0.5424
H	-3.09792	0.278908	-1.58281
H	-4.6902	0.307383	1.044252
H	-4.98249	1.336126	-0.37663
H	-5.20429	-0.42157	-0.49346
H	-1.71028	2.566383	1.746141
H	-3.45282	2.381044	1.434156
H	-2.52622	1.045006	2.168058
H	-1.46878	3.307752	-0.60983
H	-1.8372	2.199391	-1.95892
H	-3.16011	2.955518	-1.02888
H	-2.79525	-1.06194	2.035104
H	-4.00336	-2.03393	1.153645
H	-2.3629	-2.67151	1.417973
H	-3.82033	-2.34825	-1.3652
H	-2.33717	-1.82951	-2.21249

H	-2.2736	-3.1531	-1.0177
H	0.572055	2.225308	0.210938
H	-0.01819	-2.71135	-0.06861
H	3.17135	1.124955	1.357328
H	3.948455	-0.39026	-1.16177
H	2.940947	1.95569	-1.59832
H	2.564065	2.982323	-0.19343
H	4.237906	2.46086	-0.47942
O	5.258398	0.28353	0.29769
H	5.907091	-0.36477	-0.01263
C	2.58655	-2.0077	0.134214
H	2.780295	-2.40075	-0.88347
H	2.391321	-2.86683	0.789728

Table S78. Frequencies (cm^{-1}) of P2D.

43	52	83	113	138	141	194	223
227	239	243	254	262	264	273	279
290	299	306	327	332	339	349	356
371	398	438	454	477	510	536	549
557	571	614	633	681	724	744	776
788	827	834	895	912	920.	933	944
946	954	990	992	1004	1010	1027	1045
1064	1091	1105	1114	1137	1154	1161	1162
1186	1201	1212	1216	1224	1244	1250	1268
1282	1296	1314	1318	1333	1351	1351	1372
1374	1377	1381	1385	1386	1390	1396	1406
1439	1444	1448	1448	1454	1456	1458	1461
1462	1468	1469	1473	1477	1479	1497	1544
1662	1706	2984	3014	3036	3040	3046	3047
3052	3054	3056	3059	3120	3123	3123	3126
3129	3129	3133	3137	3141	3144	3148	3151
3160	3180	3199	3841				

TS3D_v1

Figure S43. The optimized structure of TS3d_v1 transition state.

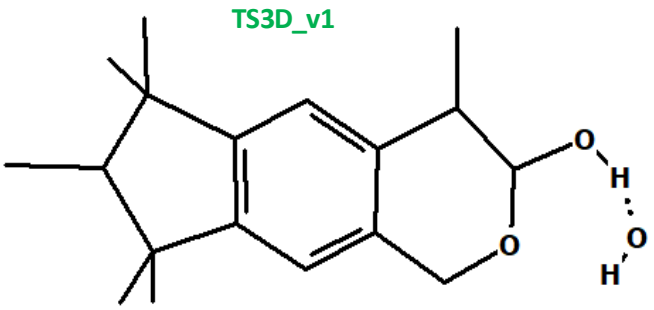


Table S79. Geometry (Å) of TS3d_v1 transition state.

Atom	x	y	z
O	3.650308	-2.11258	-0.25243
C	-2.99996	0.473446	-0.17017
C	-1.80367	1.44656	0.074804
C	-2.49672	-0.97476	0.124578
C	-0.61496	0.51958	-0.10621
C	-1.00041	-0.82309	-0.07946
C	-4.30366	0.860119	0.513805
C	-1.77747	2.056596	1.484658
C	-1.81086	2.583567	-0.95089
C	-2.78039	-1.45277	1.557403
C	-3.11568	-1.97496	-0.85606
C	0.724091	0.86337	-0.25922
C	-0.04126	-1.82235	-0.19796
C	1.702327	-0.13426	-0.38602
C	1.307618	-1.48125	-0.34918
C	3.403227	1.435612	-1.46777
H	-3.17338	0.500685	-1.26034
H	-4.20991	0.856934	1.60931
H	-4.62278	1.867544	0.205607
H	-5.10851	0.159993	0.242345
H	-0.85681	2.645951	1.616316
H	-2.63464	2.730143	1.637816
H	-1.79774	1.286461	2.2688
H	-0.96811	3.272796	-0.78633
H	-1.74057	2.189721	-1.97583
H	-2.74052	3.168382	-0.86681
H	-2.38072	-0.76132	2.312831
H	-3.86239	-1.56298	1.72723
H	-2.31125	-2.4353	1.720786
H	-4.21303	-1.97555	-0.75961
H	-2.85891	-1.7184	-1.89458
H	-2.76223	-2.99816	-0.65512
H	1.015661	1.91575	-0.2778
H	-0.32783	-2.87797	-0.17038
H	2.951964	1.256645	-2.45566

H	2.967742	2.353566	-1.05334
H	4.480458	1.602266	-1.59851
C	3.170319	0.239839	-0.54596
H	3.588402	0.459649	0.451081
C	3.943726	-0.9815	-1.05112
H	3.661109	-1.20328	-2.10177
C	2.335886	-2.57914	-0.49805
H	2.277712	-3.01764	-1.51269
H	2.150137	-3.38273	0.225964
O	5.288146	-0.71412	-0.92851
H	5.850742	-1.54869	-1.37258
O	5.996105	-2.7329	-1.68787
H	5.374562	-3.16257	-1.06319

Table S80. Frequencies (cm^{-1}) of TS3d_v1 transition state.

31	48	76	89	106	116	137	151
198	221	230	232	241	253	260	261
274	280	286	289	300	330	333	346
352	368	377	397	404	442	455	472
508	534	548	557	569	609	633	680
722	739	749	779	794	828.	833	884
905	913	921	933	944	945	953	990
990	1002	1009	1026	1050	1072	1091	1104
1114	1142	1156	1160	1165	1173	1199	1212
1216	1228	1244	1257	1268	1284	1295	1316
1323	1350	1351	1362	1371	1373	1376	1379
1384	1390	1390	1395	1399	1439	1444	1447
1452	1455	1458	1459	1462	1463	1467	1472
1476	1477	1490	1545	1587	1662	1706	3004
3026	3037	3039	3043	3045	3053	3055	3062
3068	3118	3120	3125	3126	3128	3130	3135
3141	3142	3148	3149	3154	3164	3176	3202
3680	-1649						

TS3D_v2

Figure S44. The optimized structure of TS3D_v2 transition state.

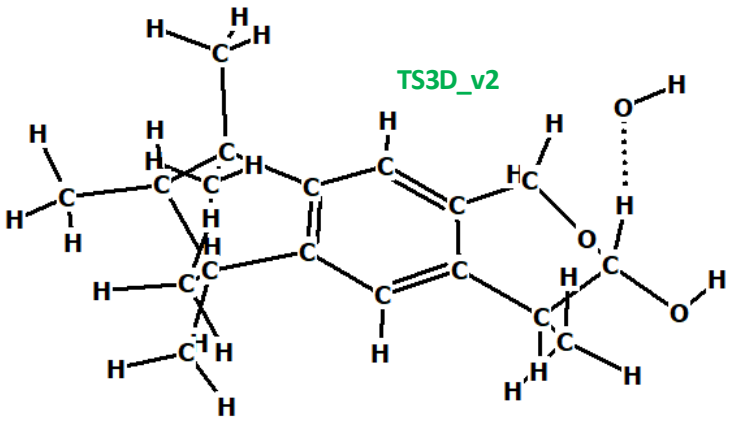


Table S81. Geometry (Å) of TS3D_v2 transition state.

Atom	x	y	z
O	3.803582	-1.88846	0.550889
C	-2.92071	0.266276	-0.50913
C	-1.82475	1.331705	-0.19096
C	-2.38928	-1.11708	-0.01581
C	-0.57546	0.47163	-0.12173
C	-0.88907	-0.88622	-0.02555
C	-4.32719	0.62376	-0.04913
C	-2.03335	2.058099	1.147009
C	-1.74522	2.377376	-1.30666
C	-2.85228	-1.48939	1.401197
C	-2.80836	-2.23353	-0.97652
C	0.751942	0.887634	-0.12482
C	0.129658	-1.82704	0.076346
C	1.789889	-0.05078	-0.03358
C	1.466856	-1.41313	0.074291
C	3.549431	1.475417	-1.0771
H	-2.93797	0.191765	-1.61074
H	-4.39133	0.715117	1.044713
H	-4.64884	1.581404	-0.48619
H	-5.04917	-0.14434	-0.36621
H	-1.17124	2.711627	1.351793
H	-2.93499	2.688796	1.114665
H	-2.13105	1.358163	1.988956
H	-0.97316	3.131801	-1.08983
H	-1.50668	1.906135	-2.27176
H	-2.70705	2.904973	-1.40615
H	-2.60401	-0.71135	2.13693
H	-3.9401	-1.65567	1.427123
H	-2.35997	-2.42145	1.718833
H	-3.9066	-2.29572	-1.03476
H	-2.41743	-2.04932	-1.98841
H	-2.43649	-3.21173	-0.63399

H	0.988112	1.951804	-0.19821
H	-0.10161	-2.89334	0.159542
H	3.291498	1.109948	-2.08285
H	2.989248	2.39931	-0.88579
H	4.620534	1.717022	-1.05587
C	3.243216	0.399289	-0.03629
H	3.498581	0.7789	0.969427
C	4.151451	-0.80215	-0.2569
H	4.014114	-1.1179	-1.35656
C	2.56295	-2.44967	0.154953
H	2.682754	-2.9342	-0.83097
H	2.318334	-3.21872	0.898415
O	3.482226	-1.59492	-2.79002
H	4.196169	-2.25914	-2.88586
O	5.457732	-0.44839	0.005476
H	6.003291	-1.24208	-0.10513

Table S82. Frequencies (cm^{-1}) of TS3D_v2 transition state.

31	42	59	72	103	117	137	144
180	220	222	232	240	250	256	259
266	274	278	285	297	302	316	328
336	345	356	372	398	439	454	474
510	536	550	559	570	609	631	652
684	722	744	776	789	826.	834	901
911	919	936	944	946	954	989	990
1004	1013	1027	1033	1056	1092	1103	1113
1119	1135	1155	1162	1184	1192	1206	1213
1217	1240	1246	1266	1283	1295	1300	1311
1326	1339	1349	1351	1373	1374	1379	1380
1383	1385	1389	1395	1411	1440	1444	1446
1450	1452	1455	1458	1458	1462	1465	1468
1475	1476	1494	1546	1665	1706	1874	3036
3042	3043	3045	3048	3050	3053	3056	3058
3120	3121	3128	3131	3133	3136	3140	3140
3142	3144	3145	3152	3157	3170	3192	3713
3821	-446						

P3D_v1

Figure S45. The optimized structure of P3D_v1.

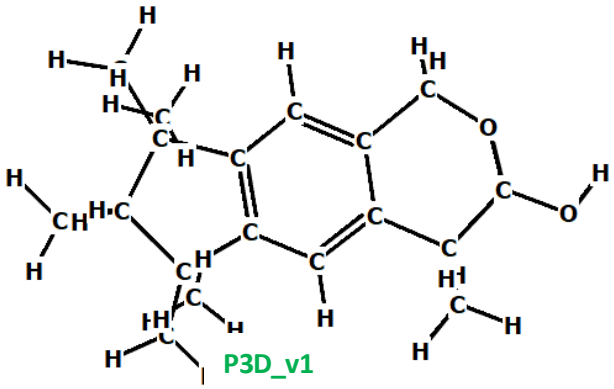


Table S83. Geometry (Å) of P3D_v1.

Atom	x	y	z
O	3.40383	-2.31992	0.047958
C	-3.14726	0.492369	-0.15749
C	-1.92788	1.420986	0.141541
C	-2.70677	-0.97482	0.144905
C	-0.76675	0.45346	-0.00338
C	-1.19923	-0.87511	-0.00137
C	-4.4624	0.920416	0.47817
C	-1.93414	2.018688	1.556784
C	-1.85623	2.565578	-0.87326
C	-3.06123	-1.45071	1.562402
C	-3.32178	-1.9466	-0.86603
C	0.587611	0.75189	-0.10616
C	-0.27104	-1.90616	-0.08893
C	1.533575	-0.27967	-0.20748
C	1.093971	-1.6116	-0.18754
C	3.305659	1.187868	-1.31161
H	-3.27689	0.532907	-1.25328
H	-4.41388	0.903037	1.576555
H	-4.7305	1.942211	0.168683
H	-5.28186	0.254518	0.167136
H	-1.00239	2.580124	1.726351
H	-2.77655	2.715554	1.684716
H	-2.00466	1.244071	2.333554
H	-0.99569	3.221958	-0.67105
H	-1.76221	2.177869	-1.89861
H	-2.7668	3.183048	-0.81832
H	-2.66635	-0.77734	2.336432
H	-4.15204	-1.52348	1.690549
H	-2.63328	-2.45014	1.736698
H	-4.42131	-1.91052	-0.81081
H	-3.01798	-1.69195	-1.89227
H	-3.01133	-2.98283	-0.66052
H	0.916468	1.793712	-0.10619

H	-0.59399	-2.95158	-0.07519
H	2.864098	0.966705	-2.29516
H	2.895144	2.142216	-0.95829
H	4.3899	1.308772	-1.43097
C	3.012968	0.060345	-0.32635
H	3.395023	0.331392	0.671693
C	3.805122	-1.22291	-0.73373
H	3.578316	-1.41766	-1.8136
C	2.095627	-2.73857	-0.28667
H	2.085567	-3.16638	-1.30806
H	1.835376	-3.54447	0.411617
O	5.106782	-0.98753	-0.61666

Table S84. Frequencies (cm^{-1}) of P3D_v1.

38	50	79	111	138	139	193	225
227	237	243	251	262	263	273	279
289	306	325	331	332	345	349	373
397	432	444	466	503	528	550	555
567	599	636	678	719	724	767	783
816	833	851	910	917	933.	945	946
954	956	986	993	1004	1008	1027	1060
1074	1091	1103	1108	1139	1154	1155	1161
1168	1201	1212	1217	1229	1246	1253	1268
1284	1296	1310	1327	1346	1351	1352	1372
1375	1380	1383	1390	1390	1391	1397	1439
1444	1448	1452	1456	1458	1461	1462	1464
1468	1469	1477	1478	1489	1543	1663	1704
2883	3024	3036	3041	3046	3048	3053	3055
3073	3076	3120	3123	3124	3127	3130	3131
3138	3140	3144	3149	3151	3157	3169	3183
3200							

P3D_v2

Figure S46. The optimized structure of P3D_v2.

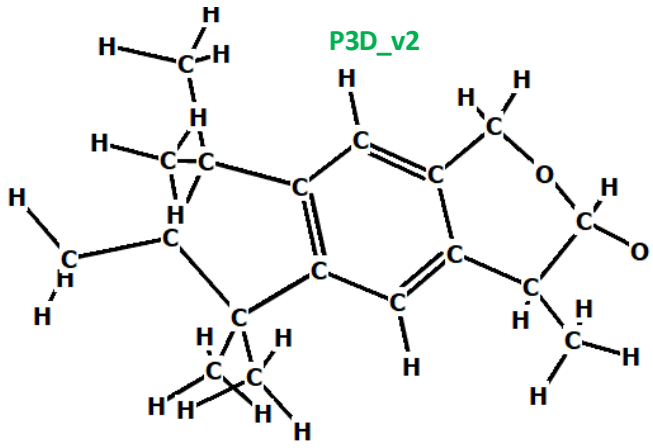


Table S85. Geometry (Å) of P3D_v2.

Atom	x	y	z
O	3.761692	-1.34465	0.564671
C	-3.11515	0.216485	-0.44287
C	-2.15158	1.322545	0.092021
C	-2.43035	-1.1641	-0.19458
C	-0.81112	0.611884	0.033052
C	-0.96617	-0.76805	-0.12592
C	-4.55688	0.323392	0.033439
C	-2.44678	1.760031	1.534883
C	-2.18999	2.558477	-0.81139
C	-2.84979	-1.8385	1.120954
C	-2.71404	-2.12771	-1.35028
C	0.459197	1.167268	0.143148
C	0.152397	-1.59348	-0.15942
C	1.595855	0.348127	0.090731
C	1.432843	-1.03747	-0.05156
C	3.218121	2.066521	-0.84076
H	-3.11589	0.342955	-1.53983
H	-4.64105	0.207621	1.123733
H	-4.98446	1.301737	-0.23466
H	-5.18221	-0.45117	-0.43635
H	-1.67371	2.467168	1.873271
H	-3.42105	2.268297	1.599383
H	-2.45242	0.910769	2.232818
H	-1.50626	3.339463	-0.44424
H	-1.90152	2.302734	-1.84186
H	-3.20498	2.986107	-0.83147
H	-2.6924	-1.18421	1.990232
H	-3.91148	-2.12794	1.092928
H	-2.25476	-2.75194	1.275784
H	-3.79717	-2.30502	-1.44374
H	-2.34624	-1.71906	-2.30324

H	-2.22993	-3.10231	-1.18238
H	0.577917	2.246499	0.27426
H	0.043563	-2.67736	-0.26304
H	3.095533	1.660451	-1.85595
H	2.515001	2.899401	-0.70746
H	4.239842	2.45853	-0.74285
C	2.981943	0.961537	0.194718
H	3.08667	1.405929	1.205759
C	4.042938	-0.0975	0.060888
C	2.647054	-1.93393	-0.093
H	2.922829	-2.16056	-1.13779
H	2.447746	-2.87987	0.425621
O	5.276445	0.331887	0.44272
H	5.877504	-0.42813	0.398576

Table S86. Frequencies (cm^{-1}) of P3D_v2.

39	50	78	110	138	138	190	216
225	235	242	248	259	263	271	278
288	292	310	323	332	347	353	373
386	398	437	450	480	508	534	552
556	566	606	633	682	722	748	766
785	820	835	872	912	920.	932	945
947	954	982	993	1004	1013	1027	1037
1064	1090	1093	1106	1124	1154	1160	1170
1201	1206	1214	1218	1243	1248	1272	1280
1295	1301	1327	1330	1351	1352	1372	1374
1378	1380	1385	1391	1396	1401	1429	1439
1444	1448	1451	1456	1457	1461	1462	1463
1468	1469	1477	1480	1499	1544	1664	1706
2985	3034	3042	3046	3047	3051	3052	3055
3061	3119	3122	3122	3127	3131	3138	3138
3141	3141	3148	3149	3152	3153	3183	3187
3812							

TS4D_v1

Figure S47. The optimized structure of TS4D_v1 transition state.

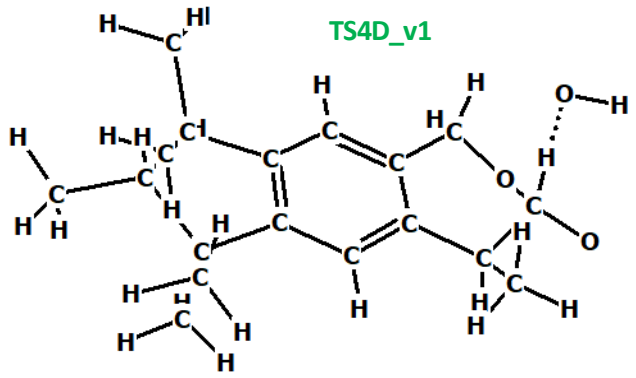


Table S87. Geometry (Å) of TS4D_v1 transition state.

Atom	x	y	z
O	3.73957	-1.88633	0.68595
C	-2.94845	0.27359	-0.50951
C	-1.85019	1.335367	-0.18593
C	-2.42675	-1.11077	-0.00837
C	-0.60564	0.46977	-0.10551
C	-0.92579	-0.88668	-0.00727
C	-4.35603	0.638288	-0.05899
C	-2.06465	2.065017	1.149253
C	-1.75702	2.37764	-1.30385
C	-2.90093	-1.47689	1.406702
C	-2.84315	-2.22854	-0.96852
C	0.722508	0.881442	-0.09794
C	0.087293	-1.83056	0.112073
C	1.754492	-0.0632	0.00462
C	1.426315	-1.42215	0.12091
C	3.518758	1.418174	-1.10308
H	-2.95857	0.196171	-1.6109
H	-4.42542	0.732793	1.034209
H	-4.67109	1.595715	-0.50119
H	-5.07901	-0.12797	-0.37795
H	-1.2024	2.716837	1.358212
H	-2.96447	2.697779	1.109921
H	-2.16925	1.366883	1.991744
H	-0.98226	3.128272	-1.08338
H	-1.51448	1.902372	-2.26601
H	-2.71526	2.909982	-1.41123
H	-2.65807	-0.69653	2.141801
H	-3.9891	-1.6415	1.423862
H	-2.41282	-2.40841	1.732209
H	-3.94119	-2.28621	-1.03373
H	-2.44492	-2.04922	-1.97837
H	-2.4779	-3.20719	-0.62023
H	0.962274	1.944731	-0.16874

H	-0.14809	-2.89493	0.204663
H	3.336215	0.961229	-2.08631
H	2.898409	2.317682	-1.00788
H	4.571372	1.725562	-1.04811
C	3.203833	0.409983	0.001095
H	3.439515	0.842571	0.987997
C	4.122174	-0.83965	-0.14956
H	3.988781	-1.19446	-1.2588
C	2.517077	-2.45793	0.245907
H	2.681445	-2.96204	-0.72399
H	2.248936	-3.21814	0.989558
O	5.369262	-0.4326	0.109269
O	3.823432	-1.53237	-2.68132
H	4.757561	-1.34748	-2.91053

Table S88. Frequencies (cm^{-1}) of TS4D_v1 transition state.

26	39	52	75	94	108	136	143
196	224	226	230	238	246	252	255
264	269	281	286	302	316	328	332
344	348	372	397	438	449	462	503
519	531	555	563	598	629	674	687
719	727	769	784	810	832	843	874
915	921	935	943	945	954	969	990
995	1004	1015	1027	1066	1091	1095	1106
1111	1153	1158	1163	1174	1191	1210	1217
1223	1241	1245	1255	1276	1281	1295	1307
1325	1351	1352	1372	1375	1379	1383	1387
1390	1391	1393	1394	1440	1444	1446	1453
1456	1457	1459	1461	1465	1466	1468	1473
1476	1489	1545	1664	1704	3041	3041	3042
3047	3050	3054	3057	3064	3076	3120	3120
3130	3131	3133	3134	3137	3139	3143	3151
3152	3163	3176	3183	3205	3706	-1180	

TS4D_v2

Figure S48. The optimized structure of TS4D_v2 transition state.

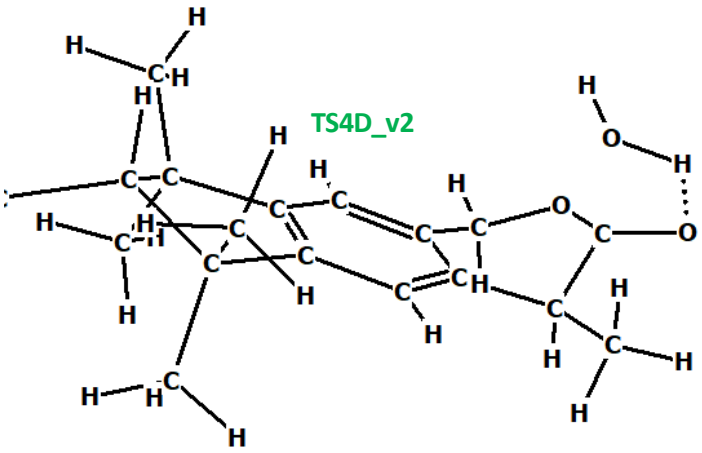


Table S89. Geometry (Å) of TS4D_v2 transition state.

Atom	x	y	z
O	3.73957	-1.88633	0.68595
C	-2.94845	0.27359	-0.50951
C	-1.85019	1.335367	-0.18593
C	-2.42675	-1.11077	-0.00837
C	-0.60564	0.46977	-0.10551
C	-0.92579	-0.88668	-0.00727
C	-4.35603	0.638288	-0.05899
C	-2.06465	2.065017	1.149253
C	-1.75702	2.37764	-1.30385
C	-2.90093	-1.47689	1.406702
C	-2.84315	-2.22854	-0.96852
C	0.722508	0.881442	-0.09794
C	0.087293	-1.83056	0.112073
C	1.754492	-0.0632	0.00462
C	1.426315	-1.42215	0.12091
C	3.518758	1.418174	-1.10308
H	-2.95857	0.196171	-1.6109
H	-4.42542	0.732793	1.034209
H	-4.67109	1.595715	-0.50119
H	-5.07901	-0.12797	-0.37795
H	-1.2024	2.716837	1.358212
H	-2.96447	2.697779	1.109921
H	-2.16925	1.366883	1.991744
H	-0.98226	3.128272	-1.08338
H	-1.51448	1.902372	-2.26601
H	-2.71526	2.909982	-1.41123
H	-2.65807	-0.69653	2.141801
H	-3.9891	-1.6415	1.423862
H	-2.41282	-2.40841	1.732209
H	-3.94119	-2.28621	-1.03373
H	-2.44492	-2.04922	-1.97837

H	-2.4779	-3.20719	-0.62023
H	0.962274	1.944731	-0.16874
H	-0.14809	-2.89493	0.204663
H	3.336215	0.961229	-2.08631
H	2.898409	2.317682	-1.00788
H	4.571372	1.725562	-1.04811
C	3.203833	0.409983	0.001095
H	3.439515	0.842571	0.987997
C	4.122174	-0.83965	-0.14956
H	3.988781	-1.19446	-1.2588
C	2.517077	-2.45793	0.245907
H	2.681445	-2.96204	-0.72399
H	2.248936	-3.21814	0.989558
O	5.369262	-0.4326	0.109269
O	3.823432	-1.53237	-2.68132
H	4.757561	-1.34748	-2.91053

Table S90. Frequencies (cm^{-1}) of TS4D_v2 transition state.

24	40	58	64	103	112	136	143
191	222	229	233	241	250	255	262
268	270	282	292	300	316	328	331
342	347	373	398	436	445	464	504
514	531	554	561	597	627	669	689
709	722	770	785	801	831	833	856
912	919	936	944	946	954	968	990
992	1004	1012	1028	1065	1090	1092	1105
1112	1153	1158	1162	1192	1202	1215	1218
1237	1245	1260	1268	1284	1292	1295	1307
1325	1350	1350	1353	1373	1374	1382	1384
1389	1390	1392	1396	1440	1444	1446	1451
1455	1458	1458	1462	1462	1466	1468	1474
1476	1490	1545	1666	1704	3040	3042	3044
3048	3051	3054	3057	3060	3074	3120	3121
3130	3133	3133	3137	3137	3141	3142	3152
3152	3162	3174	3176	3200	3715	-1243	

ProductD

Figure S49. The optimized structure of ProductD.

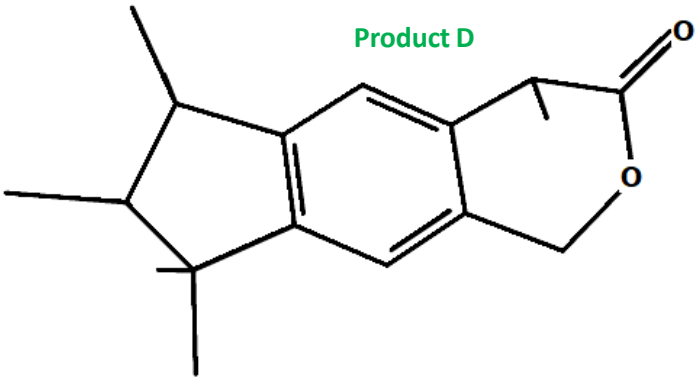


Table S91. Geometry (Å) of ProductD.

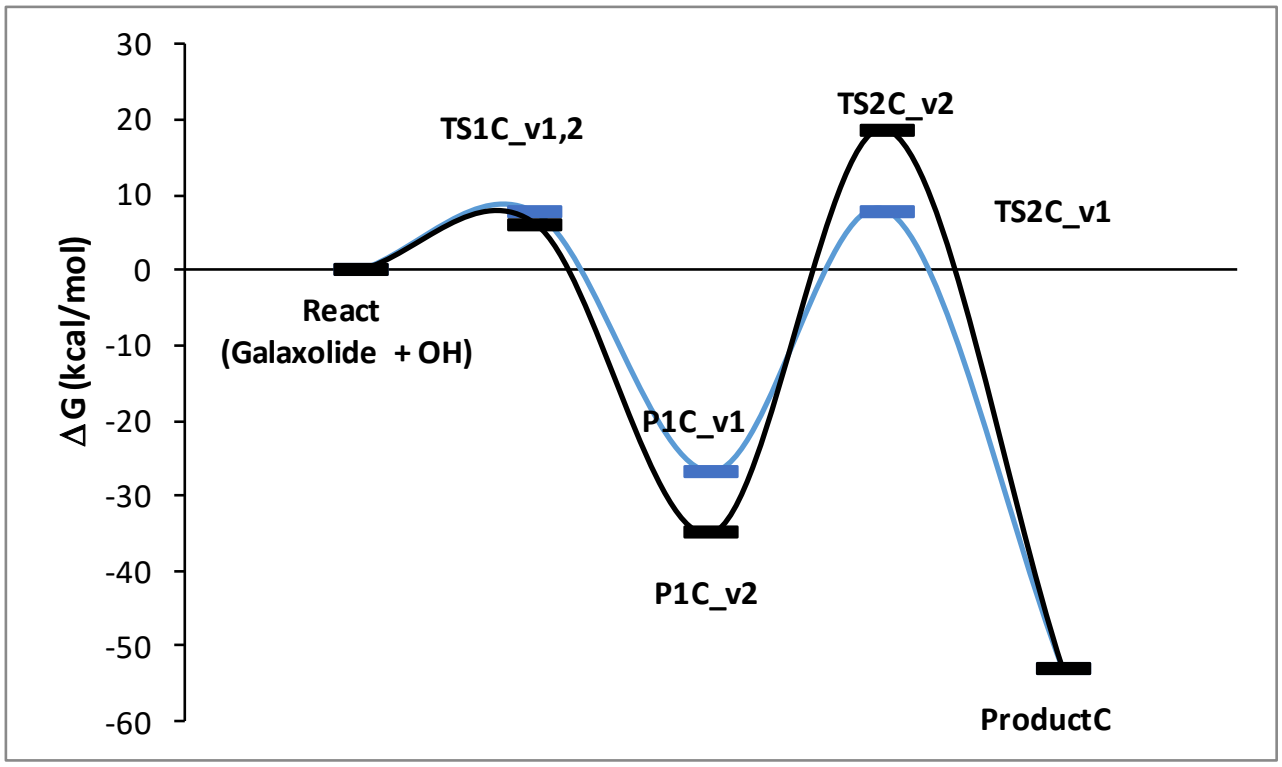
Atom	x	y	z
O	3.40492	-2.1545	0.239935
C	-3.16901	0.524526	-0.10033
C	-1.98026	1.466896	0.266325
C	-2.68582	-0.94441	0.107846
C	-0.78938	0.5484	0.058439
C	-1.18129	-0.7906	-0.02986
C	-4.50017	0.871095	0.551477
C	-2.00608	1.96527	1.719281
C	-1.94125	2.680383	-0.66688
C	-3.02641	-1.52319	1.489992
C	-3.27051	-1.86638	-0.96594
C	0.557864	0.896752	-0.01371
C	-0.22878	-1.79538	-0.18663
C	1.514067	-0.10608	-0.1909
C	1.120121	-1.44503	-0.27565
C	3.396783	0.363426	-1.80934
H	-3.29441	0.633087	-1.19201
H	-4.45955	0.786208	1.64712
H	-4.79857	1.901601	0.30491
H	-5.29633	0.201423	0.191991
H	-1.0907	2.539398	1.930626
H	-2.86789	2.628327	1.889668
H	-2.05771	1.1378	2.440929
H	-1.1037	3.348973	-0.41446
H	-1.83129	2.368251	-1.71611
H	-2.87177	3.262313	-0.57395
H	-2.65392	-0.8912	2.308503
H	-4.11461	-1.63852	1.608642
H	-2.5677	-2.51822	1.59857
H	-4.37053	-1.86615	-0.91176
H	-2.97282	-1.53751	-1.97273
H	-2.93042	-2.90421	-0.82621
H	0.875217	1.940727	0.061654

H	-0.52425	-2.84683	-0.24
H	3.171585	-0.54066	-2.39336
H	2.839236	1.201669	-2.24831
H	4.472718	0.572762	-1.88526
C	2.9852	0.197727	-0.33378
H	3.237226	1.122313	0.201563
C	3.839181	-0.88273	0.302803
C	2.201052	-2.46928	-0.47935
H	2.45503	-2.57491	-1.54647
H	1.892517	-3.45283	-0.10719
O	4.892495	-0.65552	0.845409

Table S92. Frequencies (cm^{-1}) of ProductD.

47	50	82	110	138	142	166	196
213	233	236	238	255	261	267	277
292	292	312	318	332	352	359	377
401	445	450	507	530	556	558	569
613	652	689	713	750	761	777	803
811	841	858	916	922	934	946	946
955	968	992	1002	1005	1027	1032	1060
1086	1091	1104	1129	1152	1161	1197	1210
1216	1223	1246	1250	1265	1278	1295	1303
1305	1348	1353	1360	1368	1373	1374	1379
1385	1390	1397	1419	1440	1444	1448	1452
1454	1455	1458	1462	1464	1470	1474	1478
1483	1506	1545	1673	1707	1854	3040	3041
3045	3049	3050	3056	3059	3076	3112	3117
3119	3120	3129	3130	3131	3136	3141	3142
3150	3153	3157	3158	3190	3194		

Figure S50. Energy profile of the proposed 2-nd channel of the reaction mechanism under oxidative conditions.



Energy profile of the proposed 2-nd channel of the reaction mechanism under oxidative conditions. (in terms of ΔG values, kcal/mol). To be comparable with galaxolide + OH, ΔG values were corrected with the values appropriate for species gained/lost during the course of the reaction. Species are pictured in Figure S51.

Figure S51: The optimized (at the M06-2X/cc-pVDZ level) geometries of the species involved in the reaction scheme from Figure S50.

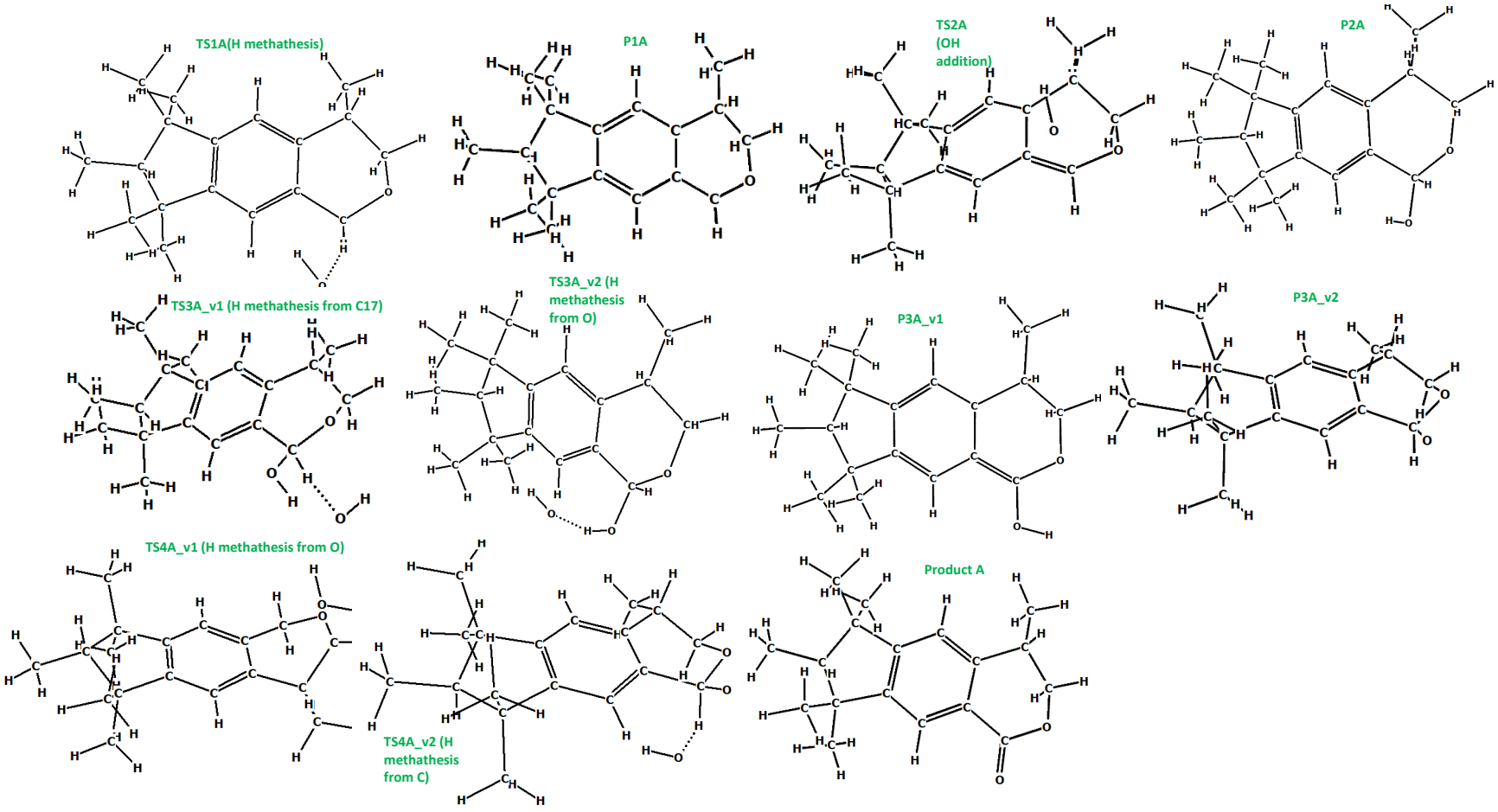
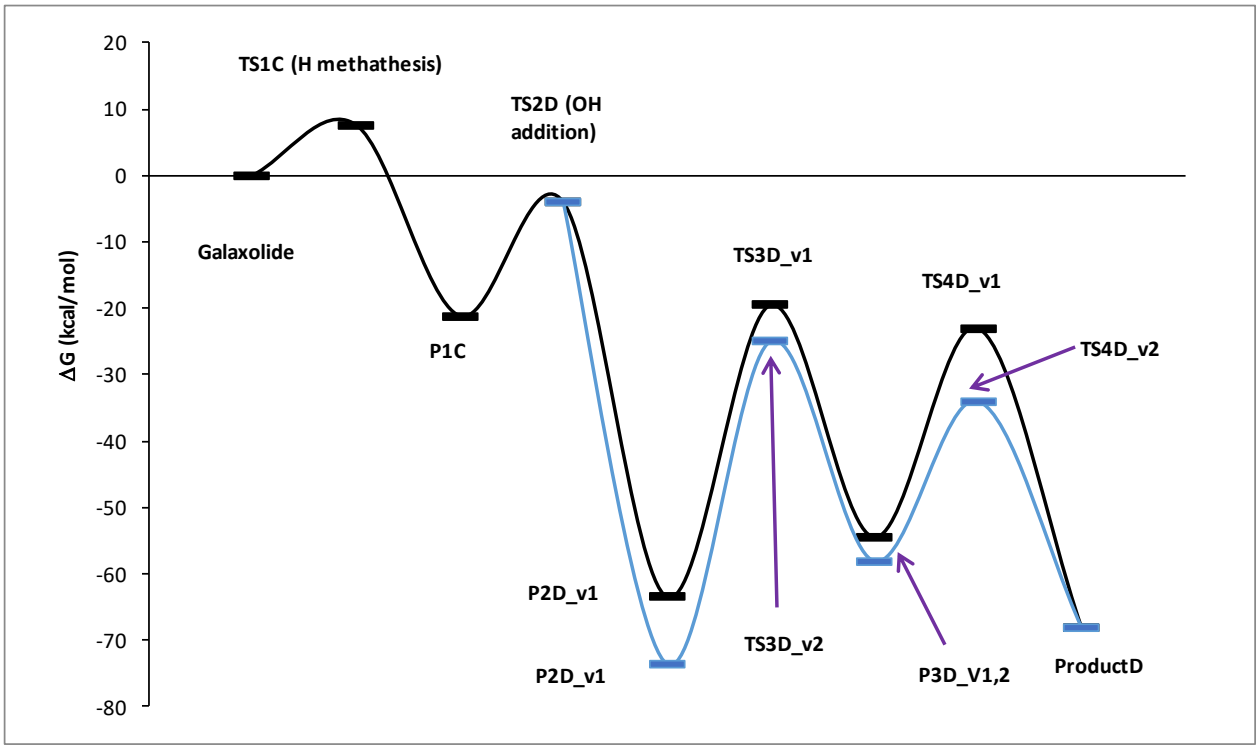


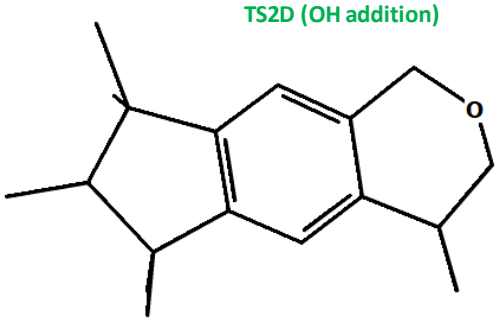
Figure S52: Energy profile of the proposed 3-rd channel of the reaction mechanism under oxidative condition.



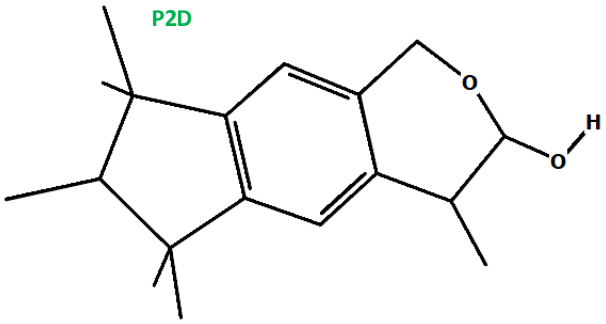
Energy profile of the proposed 3-rd channel of the reaction mechanism under oxidative conditions. (in terms of ΔG values, kcal/mol). To be comparable with galaxolide + OH, ΔG values were corrected with the values appropriate for species gained/lost during the reaction. Species are pictured in Figure S53.

Figure S53. The optimized (at the M06-2X/cc-pVDZ level) geometries of the species involved in the reaction scheme from Figure S52.

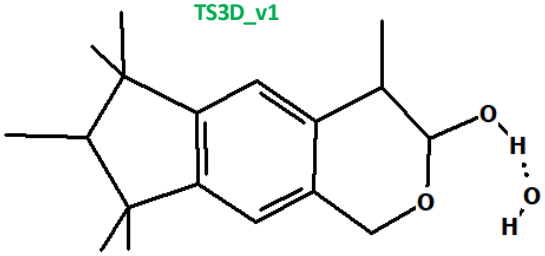
TS2D (OH addition)



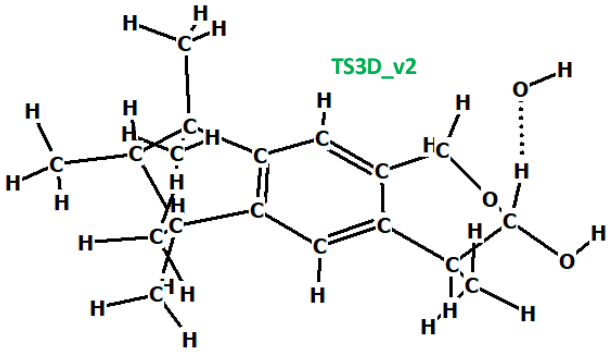
P2D

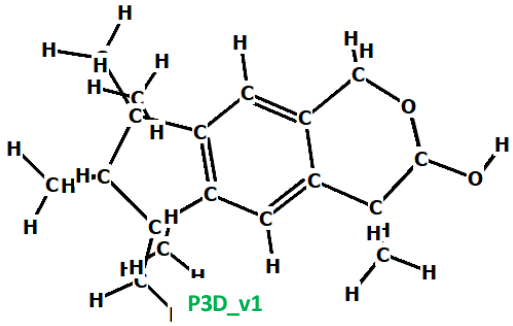


TS3D_v1

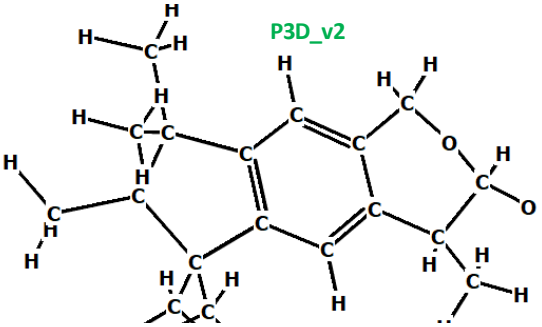


TS3D_v2



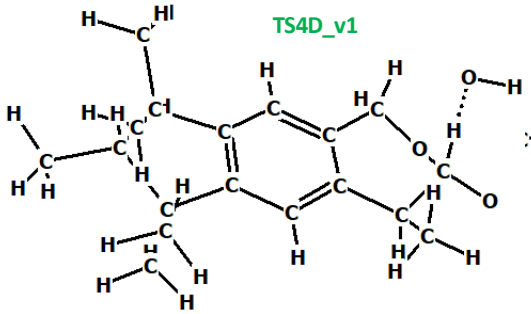


P3D_v2

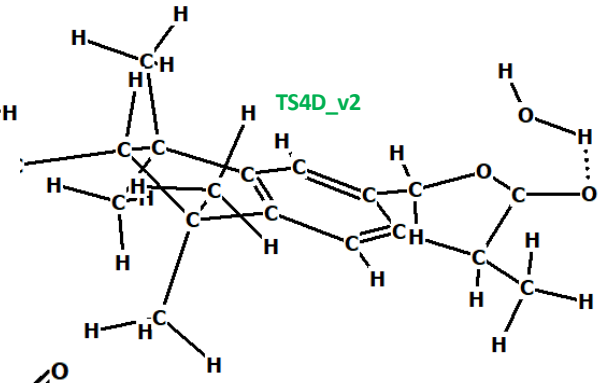


P3D_v1

TS4D_v1



TS4D_v2



Product D