Supporting Information

Phosphine- and Water-Cocatalyzed [3+2] Cycloaddition Reactions of 2-Methyl-2,3-butadienoate with Fumarates: A Computational and Experimental Study

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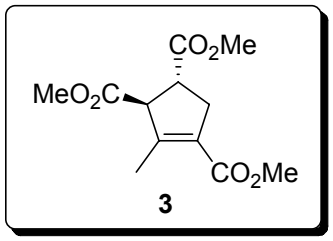
Content

1. Copies of NMR Spectra



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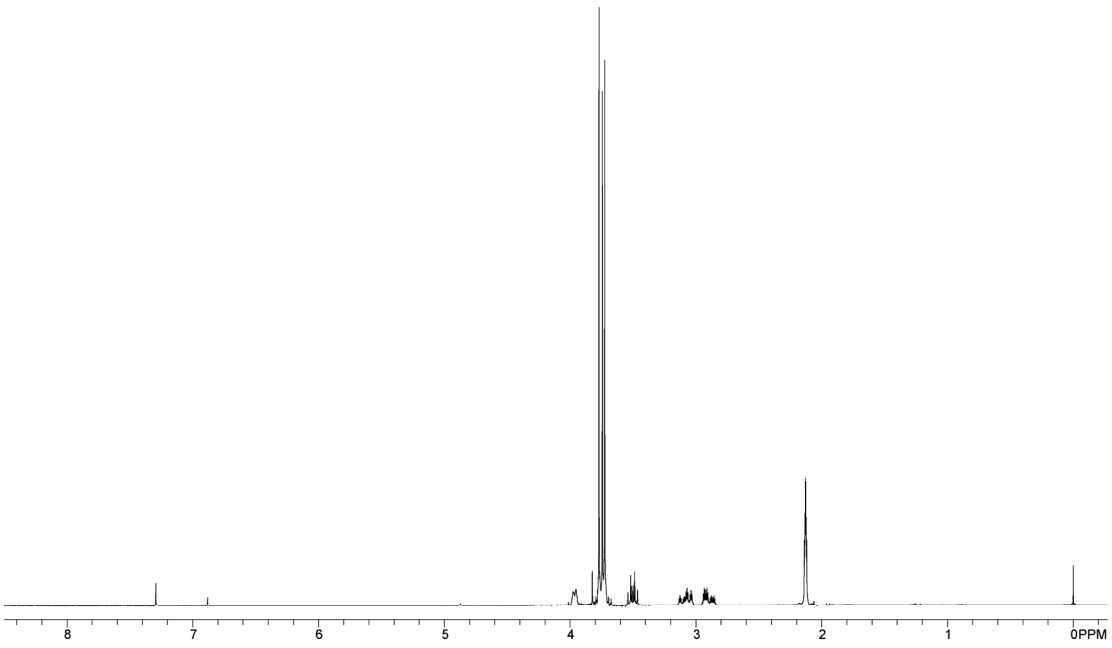

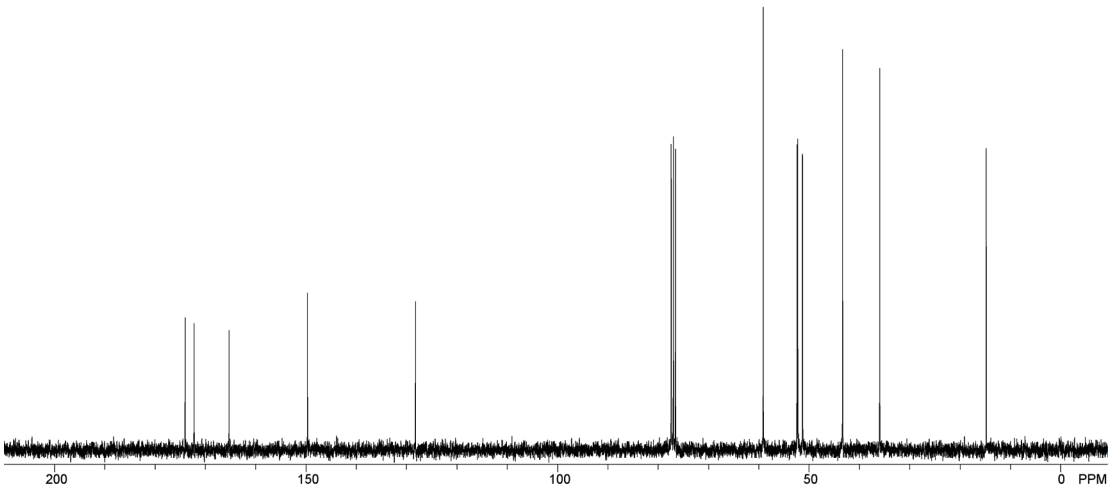

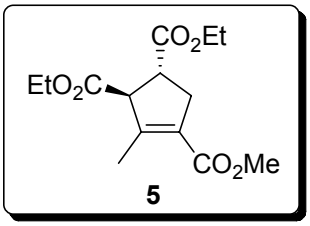

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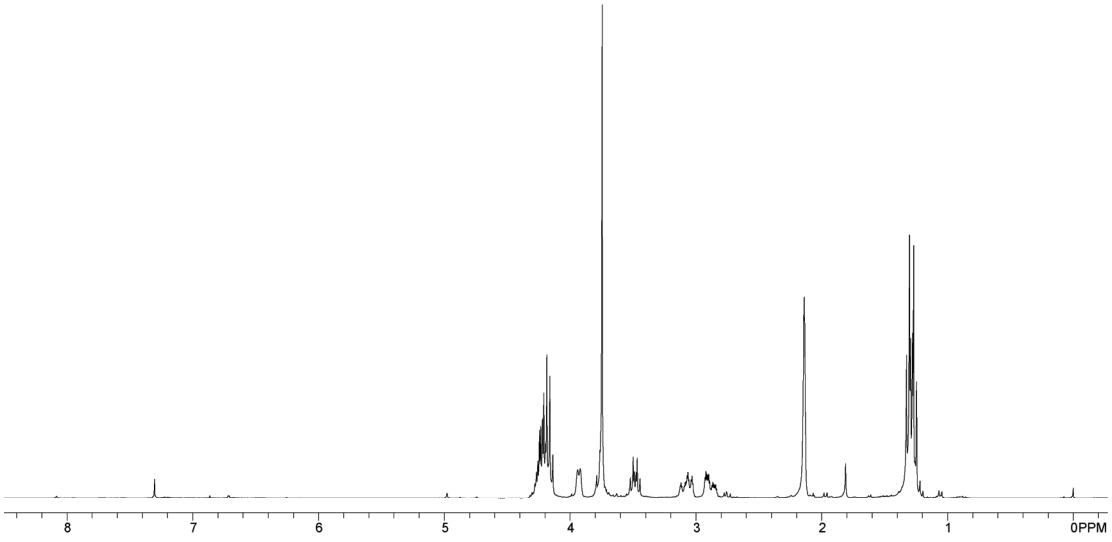

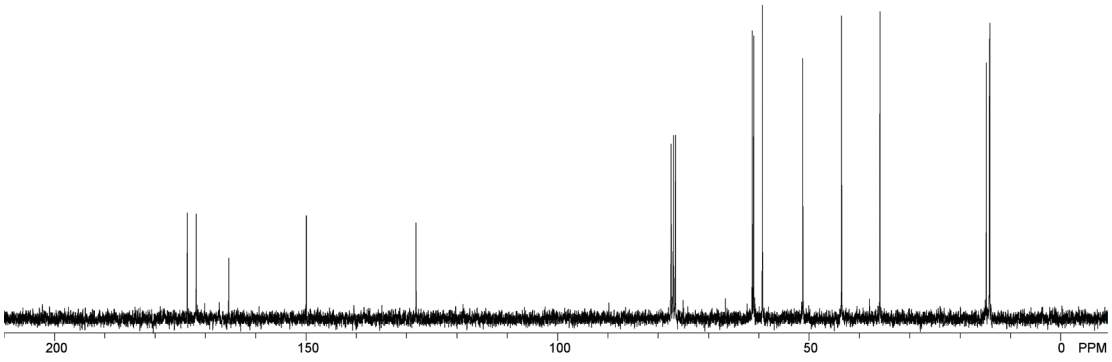

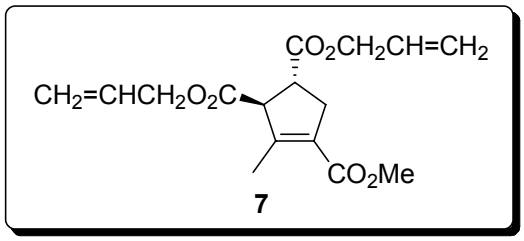
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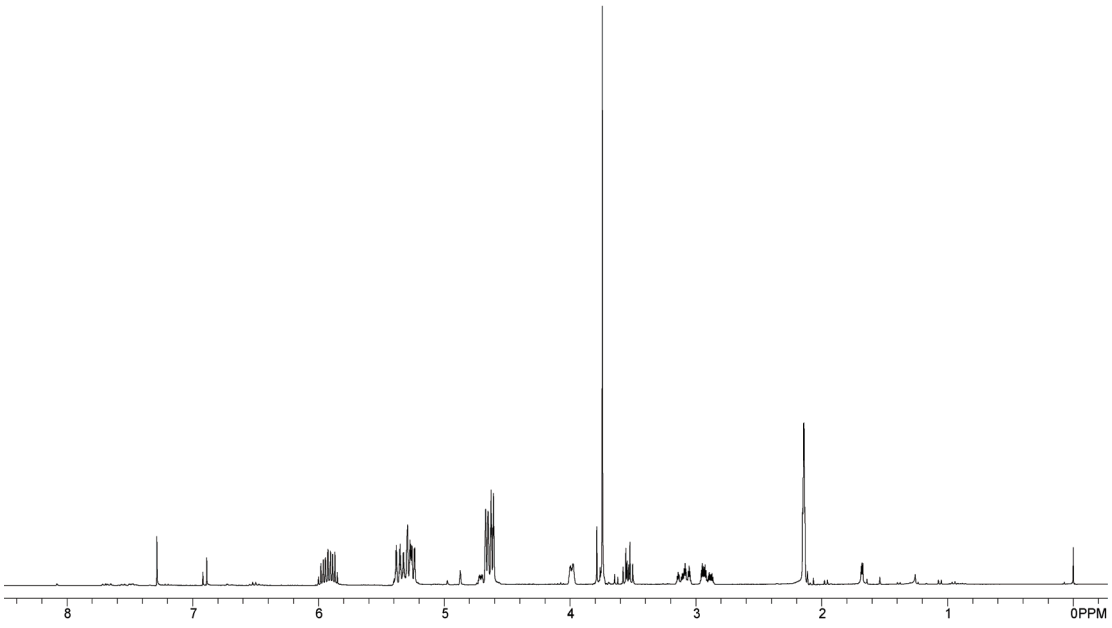
CO2Me

7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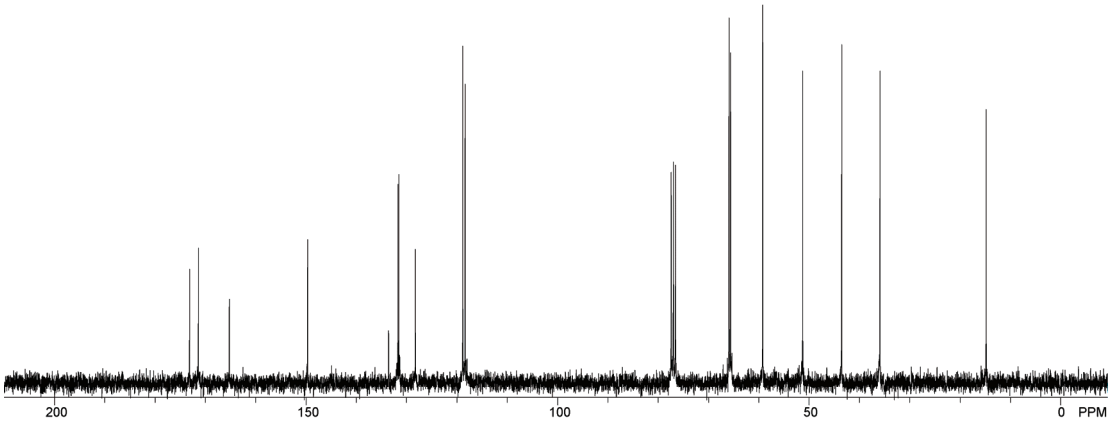
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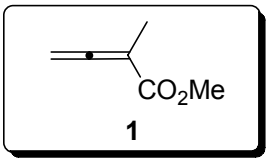
2. Coordinates of All Stationary Points



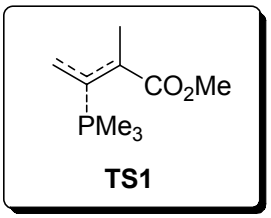
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.511441	1.816519	0.000046
2	1	0	1.196846	2.387334	0.880963
3	6	0	2.281673	-1.767501	-0.000006
4	6	0	1.566811	-0.674804	0.000014
5	1	0	2.601122	1.732582	0.000114
6	1	0	1.196954	2.387309	-0.880926
7	1	0	2.586358	-2.247354	0.928804
8	1	0	2.586725	-2.247080	-0.928837
9	6	0	-0.622767	0.419794	-0.000154
10	8	0	-1.304600	1.429258	-0.000003
11	6	0	0.870221	0.444244	0.000033
12	1	0	-2.987250	-0.423854	0.891628
13	6	0	-2.577485	-0.906467	0.000049
14	8	0	-1.141399	-0.827110	-0.000024
15	1	0	-2.804782	-1.972962	0.000077
16	1	0	-2.987338	-0.423874	-0.891500

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	15	0	-0.000524	-0.000549	-0.605642
2	6	0	0.459499	1.577630	0.279874
3	1	0	1.464428	1.892352	-0.024061
4	1	0	-0.235590	2.376423	-0.003128
5	1	0	0.442065	1.467894	1.372459
6	6	0	1.138131	-1.185734	0.280334
7	1	0	0.899553	-2.214844	-0.011709

8	1	0	2.175594	-0.991610	-0.015164
9	1	0	1.063949	-1.104634	1.373003
10	6	0	-1.596898	-0.391177	0.280738
11	1	0	-2.369749	0.326646	-0.017192
12	1	0	-1.945666	-1.389199	-0.008584
13	1	0	-1.491116	-0.359109	1.373332

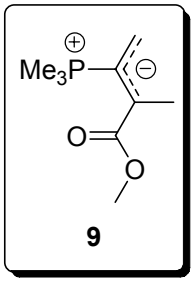


TS1

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.165538	1.469019	-0.352662
2	15	0	-1.718245	-0.317927	0.143334
3	6	0	-2.158703	-1.267814	-1.374717
4	1	0	-1.259759	-1.772061	-1.737688
5	1	0	-2.501352	-0.573565	-2.149793
6	1	0	-2.950476	-2.001751	-1.179561
7	6	0	-1.337432	-1.622086	1.398299
8	1	0	-0.472588	-2.194750	1.054949
9	1	0	-2.190674	-2.295995	1.548315
10	1	0	-1.086826	-1.153385	2.356314
11	6	0	-3.378193	0.293714	0.715160
12	1	0	-3.783393	1.015914	-0.001585
13	1	0	-4.098174	-0.528750	0.818655
14	1	0	-3.276485	0.796742	1.682698
15	1	0	-2.004619	2.458732	-0.809629
16	6	0	-0.927584	2.394915	-0.931356
17	1	0	-0.461543	3.137207	-1.578434
18	6	0	1.115896	1.180144	0.032743
19	6	0	1.913138	2.160361	0.876244
20	1	0	2.230844	1.719884	1.830981
21	1	0	1.313971	3.050658	1.088989
22	1	0	2.825051	2.482686	0.356844
23	6	0	1.632152	-0.134311	-0.257323
24	8	0	0.995699	-1.058864	-0.778765
25	1	0	2.961976	-2.374654	0.448872

26	6	0	3.498475	-1.593990	-0.099709
27	1	0	3.470561	-1.828937	-1.168018
28	8	0	2.925997	-0.306373	0.153520
29	1	0	4.530346	-1.526893	0.249962

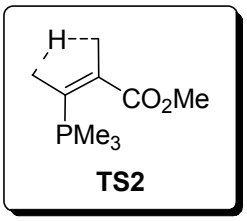


9

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	1	0	1.360998	3.039337	-0.882615
2	6	0	1.611586	2.428040	0.000123
3	1	0	1.360592	3.039417	0.882686
4	1	0	2.691227	2.267685	0.000373
5	6	0	0.872998	1.115665	0.000036
6	8	0	0.971997	-1.250322	-0.000160
7	8	0	2.912351	-0.061815	0.000030
8	6	0	3.599158	-1.312673	-0.000031
9	1	0	3.352888	-1.900930	-0.890345
10	1	0	4.661706	-1.059018	-0.000010
11	1	0	3.352879	-1.901023	0.890220
12	6	0	-0.558444	1.154672	-0.000080
13	6	0	-1.316433	2.302224	-0.000229
14	1	0	-0.831703	3.272326	-0.000323
15	1	0	-2.396890	2.315986	-0.000247
16	6	0	-1.411762	-1.407024	-1.526880
17	1	0	-1.659810	-0.761951	-2.376337
18	1	0	-0.405432	-1.807929	-1.636198
19	1	0	-2.143886	-2.220476	-1.473845
20	15	0	-1.521042	-0.402611	0.000024
21	6	0	-3.313760	0.035645	0.000127
22	1	0	-3.886937	-0.897887	0.000190
23	1	0	-3.584596	0.608524	0.890562
24	1	0	-3.584717	0.608470	-0.890303
25	6	0	-1.411562	-1.406914	1.526986
26	1	0	-2.144015	-2.220094	1.474313

27	1	0	-1.659048	-0.761658	2.376469
28	1	0	-0.405335	-1.808163	1.635988
29	6	0	1.538704	-0.122359	-0.000035



TS2

Standard orientation:

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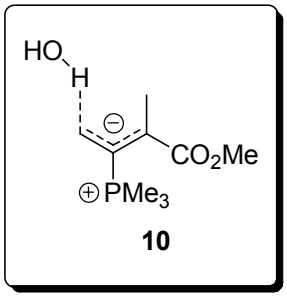
1	6	0	1.375922	2.392203	-0.004777
2	1	0	0.130221	2.811734	-0.660968
3	6	0	-1.139849	2.361033	-0.111678
4	1	0	-1.055785	3.087346	0.704824
5	1	0	-2.120223	2.443329	-0.587165
6	1	0	1.184114	3.132096	0.778543
7	1	0	2.402626	2.458744	-0.368225
8	6	0	0.838813	1.065749	0.165937
9	6	0	1.628801	-0.147029	0.120583
10	8	0	1.166067	-1.291243	0.241263
11	8	0	2.959013	0.050838	-0.064163
12	6	0	3.766851	-1.128274	-0.158003
13	1	0	3.463865	-1.743719	-1.011035
14	1	0	4.787726	-0.767491	-0.294216
15	1	0	3.690256	-1.723954	0.756389
16	6	0	-0.582472	1.037230	0.117093
17	1	0	-1.388764	-0.987469	-2.357706
18	6	0	-1.311327	-1.557415	-1.426238
19	1	0	-0.319615	-2.004234	-1.351839
20	1	0	-2.076500	-2.342224	-1.420634
21	15	0	-1.578756	-0.414732	-0.008566
22	6	0	-3.326006	0.098534	-0.227062
23	1	0	-3.955423	-0.796703	-0.268476
24	1	0	-3.649377	0.728281	0.605107
25	1	0	-3.450659	0.657675	-1.158731
26	6	0	-1.605467	-1.438602	1.509483
27	1	0	-2.300265	-2.276920	1.384508
28	1	0	-1.933472	-0.817355	2.348534

29	1	0	-0.599633	-1.815479	1.700759



10

Standard orientation:

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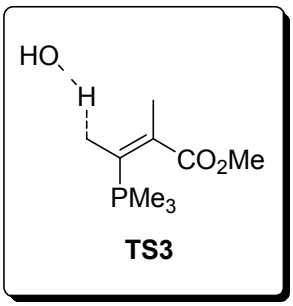
1	6	0	1.353239	1.710878	-1.089012
2	1	0	2.162265	2.019311	0.974313
3	8	0	2.697884	1.765347	1.757666
4	1	0	2.734199	2.550617	2.323791
5	1	0	2.391784	1.493162	-1.296813
6	1	0	1.004380	2.689187	-1.401756
7	6	0	0.450369	0.770743	-0.623419
8	6	0	-0.942125	1.008502	-0.439795
9	6	0	-1.468127	2.379234	-0.780148
10	1	0	-1.283687	2.637571	-1.835552
11	1	0	-0.979227	3.164306	-0.179256
12	1	0	-2.542693	2.442428	-0.602087
13	6	0	-1.788961	-0.013298	0.049778
14	8	0	-1.427357	-1.178266	0.348406
15	8	0	-3.108910	0.339589	0.190359
16	6	0	-3.985138	-0.679652	0.673467
17	1	0	-3.687813	-1.015780	1.672120
18	1	0	-4.973692	-0.216756	0.710650
19	1	0	-3.997166	-1.542463	-0.000430
20	15	0	1.189593	-0.859658	-0.208087
21	6	0	1.170014	-1.293556	1.566275
22	1	0	0.144537	-1.419983	1.909088
23	1	0	1.734815	-2.221902	1.707574
24	1	0	1.668705	-0.479668	2.103354
25	6	0	2.996713	-0.781780	-0.547803
26	1	0	3.198778	-0.565171	-1.599844
27	1	0	3.480023	-0.033575	0.085571
28	1	0	3.418015	-1.764675	-0.309575

29	6	0	0.660717	-2.228969	-1.300912
30	1	0	0.868472	-1.940328	-2.336567
31	1	0	-0.402326	-2.422734	-1.166386
32	1	0	1.243599	-3.124639	-1.058935

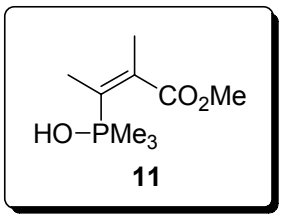


TS3

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.369798	1.921107	-0.646190
2	1	0	1.995742	1.904789	0.392381
3	8	0	2.737205	1.358554	1.602363
4	1	0	3.433311	0.166092	0.044165
5	1	0	1.799645	-0.481627	2.026844
6	15	0	1.255473	-0.800008	-0.229933
7	6	0	1.276175	-1.308738	1.516710
8	1	0	0.264918	-1.454337	1.894689
9	1	0	1.848176	-2.239907	1.603308
10	6	0	0.703935	-2.121119	-1.374692
11	1	0	0.771007	-1.749405	-2.402525
12	1	0	1.388671	-2.969329	-1.266487
13	1	0	-0.315085	-2.435424	-1.157705
14	6	0	3.020168	-0.586715	-0.644247
15	1	0	3.158281	-0.296546	-1.689656
16	1	0	3.514868	-1.550542	-0.477921
17	1	0	2.133086	1.758122	-1.413805
18	1	0	0.900340	2.893500	-0.797765
19	1	0	3.089139	2.041010	2.194685
20	6	0	0.403725	0.821070	-0.499328
21	6	0	-0.951970	1.011468	-0.373851
22	6	0	-1.555627	2.381934	-0.608889
23	6	0	-1.839847	-0.079455	0.050553
24	8	0	-1.479163	-1.226855	0.314155
25	8	0	-3.140709	0.282922	0.143012

26	6	0	-4.053830	-0.738544	0.576537
27	1	0	-3.775206	-1.104960	1.568213
28	1	0	-5.031009	-0.255240	0.605285
29	1	0	-4.058189	-1.574383	-0.128638
30	1	0	-2.637272	2.320428	-0.730627
31	1	0	-1.353240	3.056583	0.234185
32	1	0	-1.133120	2.848291	-1.505506

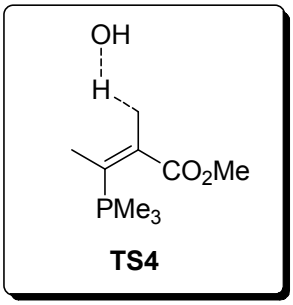


11

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	-1.688140	-0.066651	-1.772943
2	15	0	-1.498436	-0.411781	0.023118
3	6	0	-1.203963	-0.672743	1.903111
4	1	0	-1.946125	-1.370685	2.313954
5	1	0	-1.282364	0.271375	2.457592
6	1	0	-0.208478	-1.093172	2.079140
7	6	0	-3.255235	0.123584	0.243289
8	1	0	-3.676876	0.493632	-0.691711
9	1	0	-3.822364	-0.753796	0.572811
10	1	0	-3.340295	0.881557	1.026545
11	1	0	-0.903427	-0.335698	-2.277519
12	6	0	-1.448927	-2.233506	-0.384299
13	1	0	-1.220105	-2.835591	0.498295
14	1	0	-0.706609	-2.441354	-1.153720
15	1	0	-2.436884	-2.493293	-0.778751
16	6	0	-0.335983	1.078215	-0.002235
17	6	0	-1.107802	2.379190	0.010637
18	1	0	-1.940524	2.336755	-0.695925
19	1	0	-1.526743	2.571853	1.008896
20	1	0	-0.482716	3.235633	-0.252343
21	6	0	1.022541	1.085123	0.000030
22	6	0	1.831889	2.373888	0.017600
23	1	0	1.701386	2.944449	-0.911369
24	1	0	1.534258	3.024916	0.847458

25	1	0	2.895980	2.164836	0.126097
26	6	0	1.751446	-0.202232	-0.034140
27	8	0	1.220679	-1.303099	-0.112098
28	8	0	3.097844	-0.069532	0.024841
29	6	0	3.853586	-1.291932	-0.014629
30	1	0	3.593346	-1.930446	0.833841
31	1	0	4.898729	-0.985146	0.040180
32	1	0	3.657976	-1.832386	-0.944820

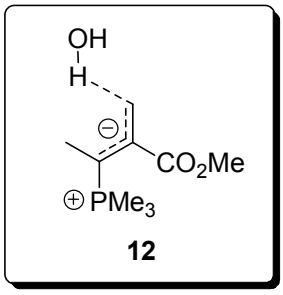


TS4

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.978880	-0.826919	1.772824
2	15	0	1.563726	-0.545121	0.067891
3	6	0	1.858535	-2.103065	-0.857437
4	6	0	0.656088	0.764009	-0.777855
5	6	0	-0.714560	0.854583	-0.677018
6	6	0	-1.482286	-0.392030	-0.383711
7	8	0	-2.808114	-0.227314	-0.364811
8	6	0	-3.591853	-1.387876	-0.039416
9	6	0	-1.431062	2.116866	-0.550665
10	8	0	-0.954129	-1.488769	-0.218291
11	6	0	3.274778	0.087432	0.306737
12	6	0	1.457720	1.980240	-1.204242
13	8	0	-0.794096	1.657274	1.997464
14	1	0	-1.315731	2.149951	0.679010
15	1	0	1.629007	2.679947	-0.373391
16	1	0	-0.924023	2.992266	-0.956695
17	1	0	-1.146846	2.106388	2.782233
18	1	0	-2.484841	2.090406	-0.826322
19	1	0	-3.344938	-1.735032	0.967275
20	1	0	-4.628806	-1.054852	-0.087368
21	1	0	-3.407793	-2.189555	-0.759919

22	1	0	0.366268	-1.726369	1.835961
23	1	0	0.365232	0.060452	2.063980
24	1	0	1.847935	-0.917756	2.432792
25	1	0	0.910435	2.525362	-1.979767
26	1	0	3.258431	1.021363	0.875521
27	1	0	2.430843	1.716706	-1.629343
28	1	0	3.837788	-0.659255	0.876282
29	1	0	3.786520	0.255989	-0.644256
30	1	0	2.347444	-1.866583	-1.808429
31	1	0	2.517618	-2.752131	-0.269580
32	1	0	0.912849	-2.609443	-1.046538

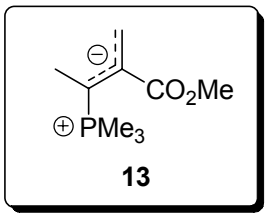


12

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	1	0	-0.664685	2.184457	1.256657
2	8	0	-0.322951	2.301837	2.164978
3	1	0	-0.920849	2.942483	2.577327
4	6	0	-0.805109	0.789156	-0.709907
5	6	0	-1.513089	1.921312	-1.047078
6	1	0	-1.020396	2.818754	-1.401693
7	1	0	-2.595009	1.923244	-1.037649
8	8	0	-2.925909	-0.223914	-0.228256
9	1	0	-3.549682	-2.194757	-0.525851
10	6	0	-3.707361	-1.362795	0.166089
11	1	0	-3.440132	-1.679334	1.178194
12	1	0	-4.743723	-1.024777	0.130782
13	6	0	-1.592256	-0.406778	-0.278570
14	8	0	-1.086795	-1.485966	0.008865
15	6	0	0.628532	0.670705	-0.775105
16	6	0	1.345555	1.860879	-1.385537
17	1	0	0.913868	2.095202	-2.371034
18	1	0	1.243957	2.776724	-0.775836

19	1	0	2.414282	1.700611	-1.542539
20	15	0	1.566133	-0.553527	0.024897
21	6	0	1.215577	-0.883243	1.804860
22	1	0	1.071665	0.074806	2.314768
23	1	0	2.061673	-1.419227	2.250537
24	1	0	0.311615	-1.483617	1.911048
25	1	0	3.407810	0.965340	0.577449
26	1	0	3.900023	-0.743742	0.636287
27	6	0	3.321595	-0.002306	0.075596
28	1	0	3.746692	0.076433	-0.928595
29	1	0	2.407868	-2.851264	-0.166061
30	1	0	0.752780	-2.695799	-0.823297
31	1	0	2.144255	-2.096530	-1.763006
32	6	0	1.731762	-2.220557	-0.756289



13

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.327491	2.388416	0.000005
2	1	0	1.054067	2.992793	0.881736
3	1	0	2.415619	2.305272	-0.000003
4	1	0	1.054060	2.992819	-0.881704
5	6	0	0.601803	1.055444	-0.000018
6	6	0	-0.843765	1.159979	-0.000003
7	6	0	-1.537504	2.341740	0.000017
8	1	0	-2.619188	2.350500	0.000027
9	1	0	-1.036998	3.301908	0.000025
10	6	0	-1.643476	-0.097139	0.000011
11	8	0	-1.145899	-1.219952	0.000067
12	8	0	-2.980805	0.069928	-0.000043
13	6	0	-3.771103	-1.128275	-0.000010
14	1	0	-3.563457	-1.726659	-0.891657
15	1	0	-3.563505	-1.726578	0.891701
16	1	0	-4.807173	-0.787254	-0.000055
17	15	0	1.519659	-0.409577	-0.000005

18	6	0	1.424843	-1.538298	1.464072
19	1	0	1.687379	-0.965356	2.359394
20	1	0	0.413822	-1.931515	1.570428
21	1	0	2.129180	-2.371406	1.350216
22	6	0	1.424768	-1.538345	-1.464038
23	1	0	0.413742	-1.931565	-1.570335
24	1	0	2.129107	-2.371451	-1.350186
25	1	0	1.687264	-0.965433	-2.359390
26	6	0	3.312205	0.011880	-0.000056
27	1	0	3.585786	0.584265	0.890425
28	1	0	3.881741	-0.923168	-0.000074
29	1	0	3.585733	0.584269	-0.890551

3. Computed Energies

Table S1. Sum of electronic and thermal enthalpies (*H*, in a.u.), sum of electronic and thermal free energies (*G*, in a.u.), thermal correction to Enthalpy (*TCH*, in a.u.), thermal correction to Gibbs free energy (*TCGFE*, in a.u.), total free energy in solution (G_S, in a.u., solvent = benzene)

Structure	*H*	*G*	*TCH*	*TCGFE*	G_S
1	-383.733362	-383.777908	0.137856	0.09331	-383.863326
8	-460.983859	-461.020941	0.120678	0.083596	-461.098449
TS1	-844.689031	-844.75166	0.259098	0.196468	-844.933677
9	-844.717879	-844.777168	0.262085	0.202796	-844.968965
TS2	-844.654657	-844.711794	0.256832	0.199696	-844.902308
H_2O	-76.397698	-76.419138	0.024875	0.003435	-76.428114
10	-921.124674	-921.191531	0.28922	0.222363	-921.403829
TS3	-921.098984	-921.161827	0.28539	0.222546	-921.377874
11	-921.119478	-921.184099	0.290424	0.225803	-921.39986
TS4	-921.081159	-921.143768	0.284795	0.222187	-921.361251
12	-921.114298	-921.18246	0.289487	0.221325	-921.39282
13	-844.710067	-844.769069	0.262347	0.203344	-844.960335