Supporting Information

Vitrimerization of Crosslinked Elastomers: A Mechanochemical Approach for Recycling Thermoset Polymers

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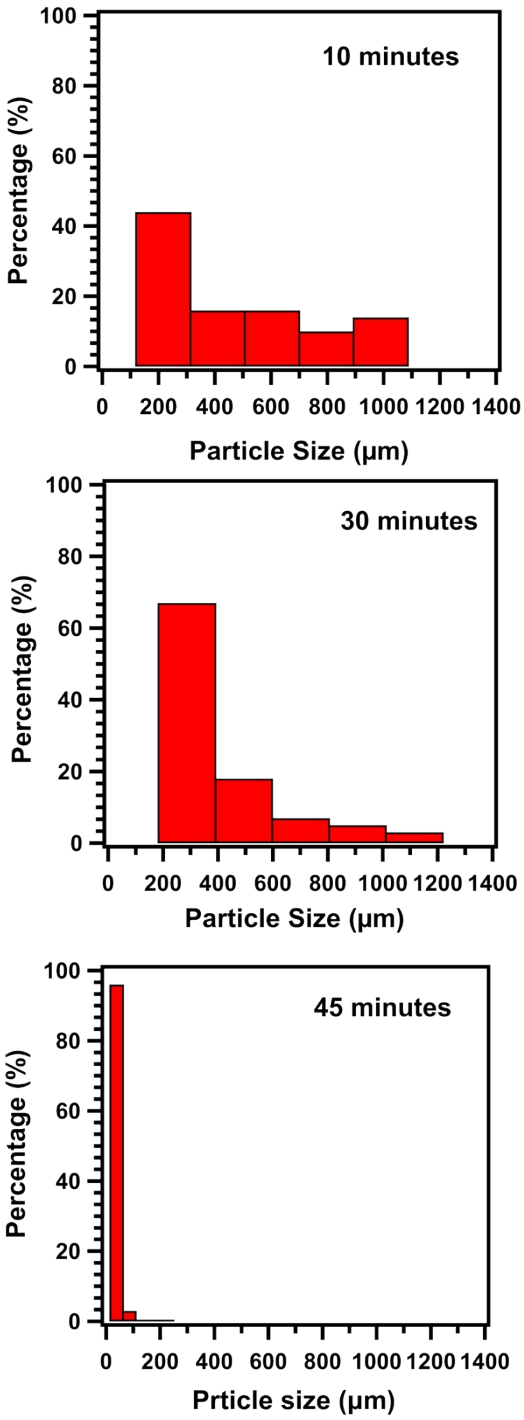


Figure S1. Particle size distribution of crosslinked EVA powders after cryomilling for 10, 30, and 45 minutes, (the particle size larger than 1 mm is related to the agglomoration of some powders under microscope)

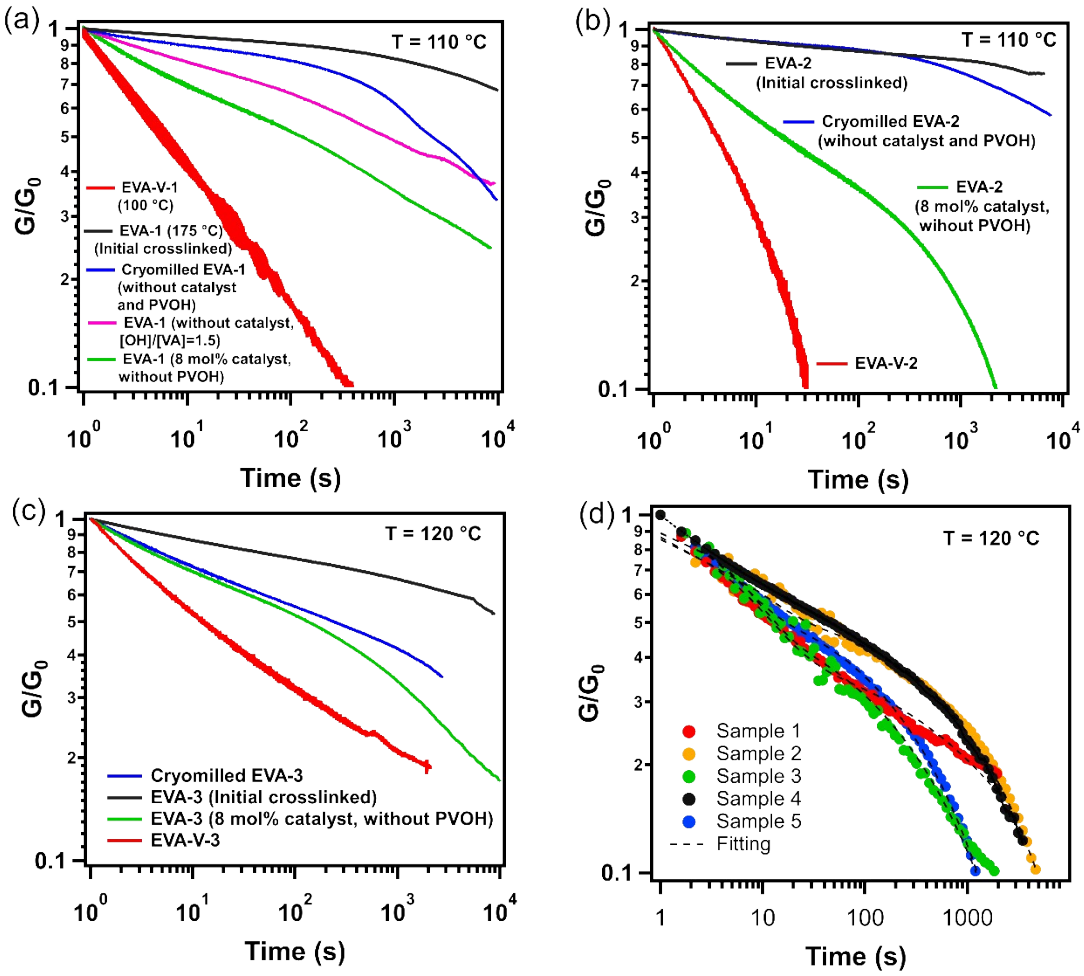


Figure S2. Stress relaxation curves of initial crosslinked EVAs, vitrimerized EVAs with addition of either catalyst or PVOH for (a) EVA-1, (b) EVA-2, (c) EVA-3. (d) Stress relaxation curves of EVA-3 at 120 °C on five separate samples. The G_0 is considered as initial stress at time equal to one second (t = 1s). The mol% of catalyst is with respect to VA.

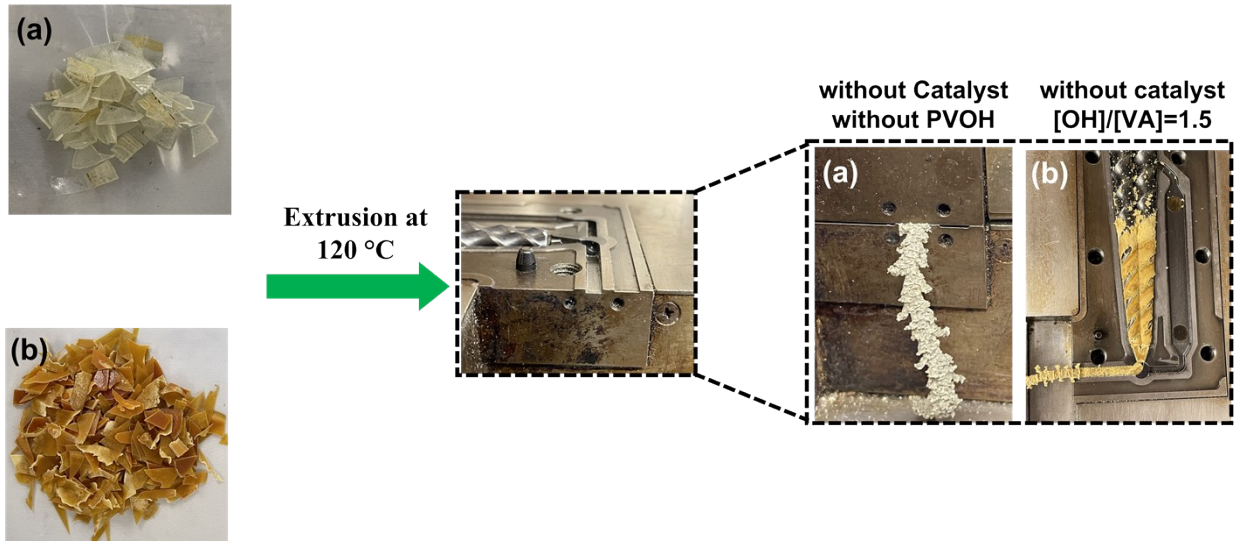


Figure S3. Unsuccessful reprocessing of compression molded EVA powders (a) without addition of catalyst and PVOH (b) with PVOH and without addition of catalyst.

Table S1. Swelling ratio of initial crosslinked and vitrimerized EVAs in toluene and water.

Solvent	EVA1	EVA2	EVA3	EVA-V-1	EVA-V-2	EVA-V-3
Toluene (100 °C)	504	569	347	1901	2080	980
Water (100 °C)	4	25	26	50	42	70
~~Water (25 °C)~~	~~2~~	~~11~~	~~24~~	~~6~~	~~13~~	~~40~~

Table S2. Crystallinity and melting temperature of initial crosslinked and vitrimerized EVAs.

Solvent	EVA1	EVA2	EVA3	EVA-V-1	EVA-V-2	EVA-V-3
Crystallinity (%)	15	10	22	11	5	20
Melting point (°C)	80	77	94	86	78	98

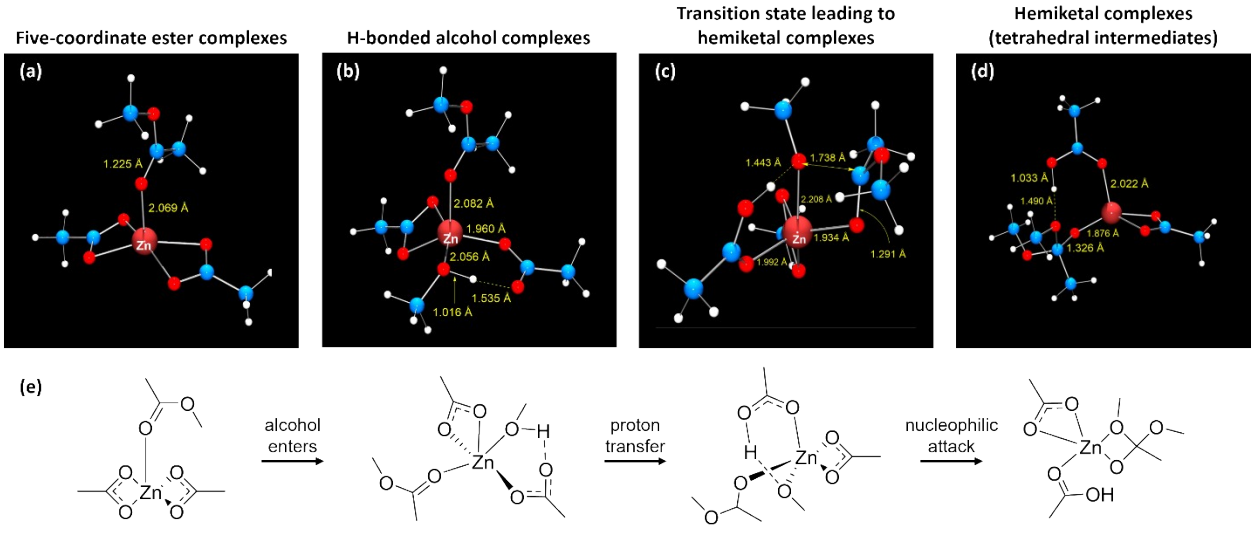


Figure S4. Optimized geometries for the methyl acetate complex; (a) five-coordinate ester complex; (b) hydrogen-bonded alcohol complex were alcohol complexes to zinc; (c) transition state leading indicating a proton transfer prior to forming tetrahedral carbon; (d) hemiketal complex (tetrahedral intermediate); (e) step-by-step formation of hemiketal complex. Legend: large red spheres (zinc), small red spheres (oxygen), blue spheres (carbon), and white spheres (hydrogen).

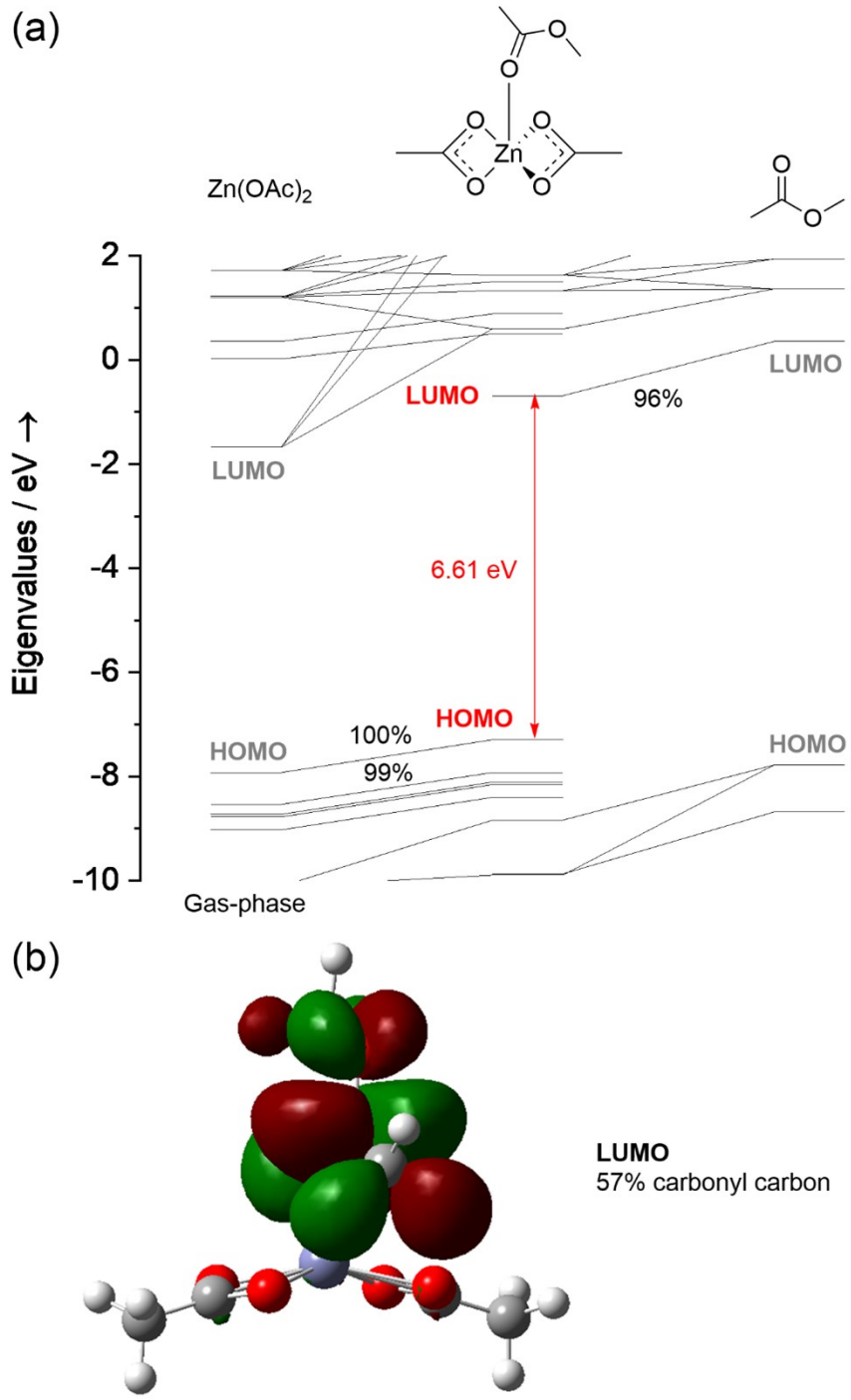


Figure S5. (a) Partial Kohn-Sham orbital energy level diagram of a five-coordinate zinc acetate complex with methyl acetate. (b) Depiction of the LUMO. Contour level 0.02 a.u. Percentages are of orbital density. The corresponding diagram for the isopropyl acetate complex is similar.

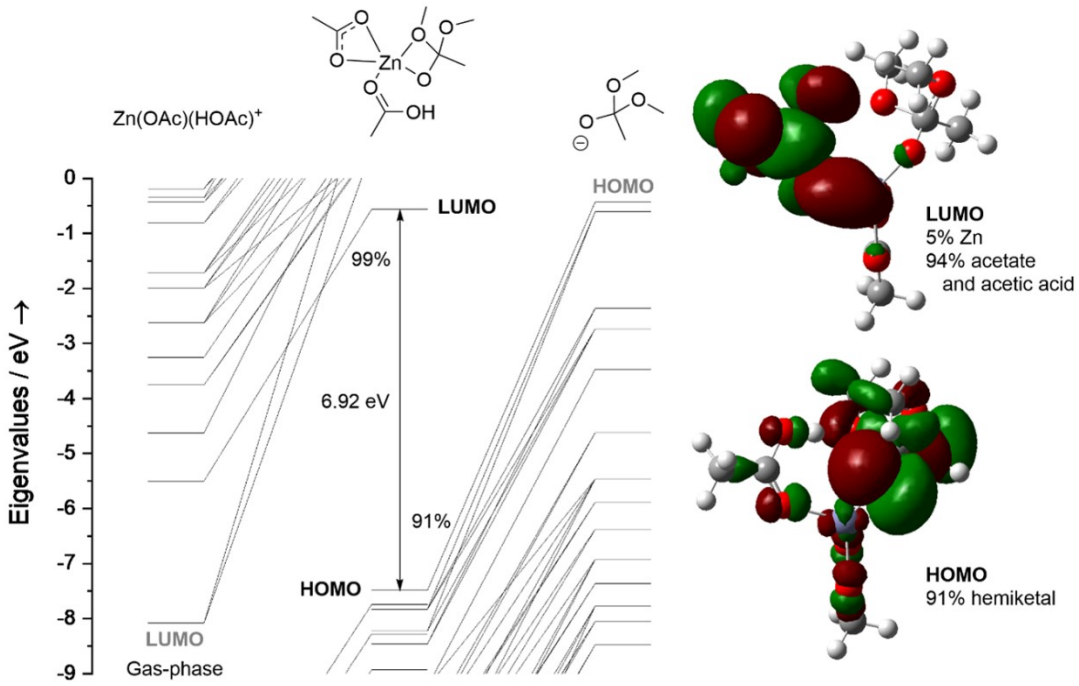


Figure S6. (a) Partial Kohn-Sham orbital energy level diagram of the hemiketal zinc complex formed with methanol and methyl acetate. (b) Depiction of frontier orbitals. Contour level 0.02 a.u. Percentages are of orbital density. The corresponding diagram for the isopropyl analogue is similar.

Table S3. Parameters obtained from fitting stress relaxation curves to experimental data for EVA-1 using equation 1.

Temperature (°C)	τ_{net} (seconds)	τ_{ex} (seconds)	β_{net}	β_{ex}	A_{net}	A_{ex}	Adjusted R^2
80	73594±337	20.0±0.05	0.33±0.00	0.48±0.00	0.61±0.00	0.39±0.00	0.9926
85	1360±34	10.0±0.03	0.30±0.00	0.70±0.00	0.53±0.00	0.47±0.00	0.9924
90	113±3	5.0±0.02	0.41±0.00	0.97±0.01	0.46±0.00	0.54±0.01	0.9903
100	123±5	5.0±0.23	0.40±0.01	0.90±0.01	0.47±0.00	0.53±0.01	0.9878

Table S4. Parameters obtained from fitting stress relaxation curves to experimental data for EVA-2 using equation 1.

Temperature (°C)	τ_{net} (seconds)	τ_{ex} (seconds)	β_{net}	β_{ex}	A_{net}	A_{ex}	Adjusted R^2
80	50870±20956	24.59±0.03	0.99±0.00	0.44±0.00	0.69±0.00	0.31±0.00	0.9963
90	85061±605	7.80±0.02	0.24±0.00	0.72±0.00	0.62±0.00	0.38±0.00	0.9903
100	42±0	3.87±0.01	0.81±0.01	1.00±0.01	0.39±0.00	0.62±0.01	0.9968
110	27±0	3.80±0.01	1.00±0.01	1.00±0.01	0.36±0.00	0.64±0.05	0.9860

Table S5. Parameters obtained from fitting stress relaxation curves to experimental data for EVA-3 using equation 1.

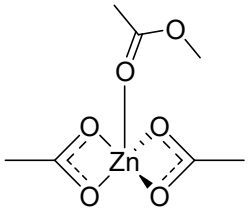
Temperature (°C)	τ_{net} (seconds)	τ_{ex} (seconds)	β_{net}	β_{ex}	A_{net}	A_{ex}	Adjusted R^2
80	53007±383	48.35±0.07	0.37±0.01	0.47±0.00	0.71±0.00	0.29±0.01	0.9959
100	6766±77	9.87±0.02	0.29±0.00	0.71±0.00	0.60±0.00	0.40±0.00	0.9940
110	1114±15	6.48±0.02	0.33±0.00	0.88±0.00	0.59±0.00	0.41±0.00	0.9927
120	1546±42	6.87±0.02	0.32±0.00	0.78±0.01	0.49±0.00	0.51±0.00	0.9880

Table S6. Parameters obtained from fitting stress relaxation curves to experimental data (repeated for five times) measured at 120 °C for EVA-3.

Temperature (°C)	τ_{net} (seconds)	τ_{ex} (seconds)	β_{net}	β_{ex}	A_{net}	A_{ex}	Adjusted R^2
120	297±2	4.87±0.01	0.43±0.00	1.00±0.01	0.65±0.00	0.35±0.00	0.9969
120	270±6	6.71±0.02	0.39±0.00	1.00±0.01	0.61±0.00	0.39±0.00	0.9809
120	1445±10	4.98±0.02	0.46±0.00	0.73±0.01	0.57±0.00	0.43±0.00	0.9814
120	1546±42	6.87±0.02	0.32±0.00	0.78±0.01	0.49±0.00	0.51±0.00	0.9880
120	713±4	5.90±0.01	0.37±0.00	1.00±0.00	0.72±0.00	0.28±0.00	0.9970

Table S7. Optimized Cartesian coordinates (Å) in .xyz format.

A. Five-coordinate ester complexes



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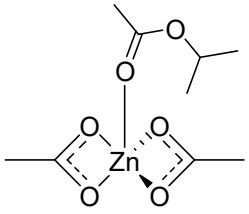
O	-0.466207	1.828632	1.031184
O	-0.992436	1.982150	-1.085262
C	-0.746930	2.534862	0.024714
C	-0.820669	4.025362	0.143363
H	-0.552595	4.497965	-0.800058
H	-1.853673	4.297400	0.375270
H	-0.185847	4.379318	0.953545
O	-1.752452	-1.373719	-1.072816
O	-1.149479	-1.502497	1.024838
C	-1.728351	-2.003508	0.024289
C	-2.415983	-3.329264	0.128113
H	-3.478191	-3.148790	0.312176
H	-2.330209	-3.876270	-0.809711
H	-2.015887	-3.909113	0.957391
Zn	-0.684263	0.146869	-0.237280
O	1.320651	-0.283109	-0.512194
C	2.120068	-0.454715	0.399713
C	1.785924	-0.382712	1.843178
H	2.659426	-0.563316	2.463680
H	1.354311	0.600419	2.047286
H	0.999314	-1.113110	2.049039
O	3.381495	-0.726348	0.146845
C	3.752372	-0.807281	-1.233528
H	3.558828	0.142134	-1.732134
H	4.814891	-1.034590	-1.234978
H	3.187220	-1.595639	-1.730093



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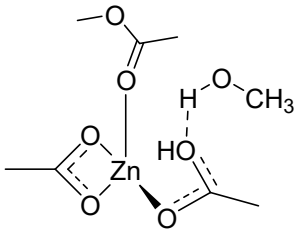
O	7.288787	-0.807449	3.970442
O	6.996545	-0.660897	1.807844
C	7.015617	-1.351674	2.871164
C	6.730990	-2.819469	2.789664
H	5.885117	-2.999810	2.126453
H	7.600466	-3.315708	2.351867
H	6.544737	-3.235431	3.777249
O	8.312449	2.525575	1.703066
O	8.963856	2.155637	3.757184
C	9.049079	2.817997	2.683742
C	10.044429	3.930964	2.571942
H	11.018841	3.494955	2.337347
H	9.770449	4.616862	1.773027
H	10.137044	4.454701	3.522555
Zn	7.471992	1.012959	2.836586
O	5.784848	1.926702	3.583855
C	5.572587	2.135386	4.773942
C	6.470447	1.691544	5.870380
H	6.080682	1.975927	6.843982
H	6.594351	0.608451	5.796112
H	7.458890	2.127320	5.702764
O	4.506502	2.782788	5.177387
C	3.574861	3.271873	4.170858
C	4.092929	4.572570	3.603075
C	2.247367	3.405638	4.873162
H	3.524044	2.514782	3.385995
H	5.054790	4.431071	3.109876
H	3.386556	4.955339	2.863862
H	4.199730	5.318594	4.393868
H	1.926761	2.449792	5.289869
H	2.309822	4.135981	5.682691
H	1.490116	3.743004	4.163285

B. Hydrogen-bonded alcohol complexes.



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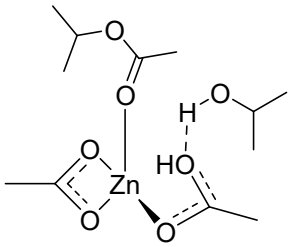
O	7.459567	-0.523440	3.530008
O	6.240241	-1.718444	2.082865
C	6.907394	-1.601678	3.122294
C	7.106221	-2.799733	4.012516
H	6.636013	-3.682042	3.584677
H	8.174490	-2.972139	4.154695
H	6.681065	-2.593364	4.997070
O	8.844712	2.165910	1.516673
O	8.815937	2.456198	3.684226
C	9.329976	2.690311	2.566142
C	10.535627	3.571565	2.440451
H	11.405149	2.941619	2.237913
H	10.418738	4.246684	1.592653
H	10.707317	4.130359	3.357715
O	5.803323	2.174361	3.457843
C	5.634787	2.321525	4.660004
C	6.536257	1.801246	5.717489
H	6.104354	1.930331	6.706358
H	6.756270	0.752280	5.510026
H	7.486747	2.334828	5.636017
O	4.597702	2.991227	5.118370
C	3.707434	3.531582	4.137129
H	3.297956	2.733524	3.518321
H	2.920917	4.026668	4.700287
H	4.233980	4.243432	3.501662
Zn	7.405998	1.185437	2.571008
O	6.278921	0.551852	0.972634
C	6.805049	0.575559	-0.343242
H	7.177336	1.578488	-0.546539
H	7.634218	-0.129362	-0.454781
H	6.021396	0.324752	-1.063162
H	6.157469	-0.405540	1.291159



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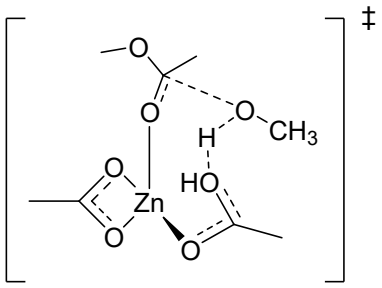
O	-2.222933	-0.595478	1.175870
O	-2.815567	0.757549	-0.504646
C	-3.066981	0.098800	0.522577
C	-4.468621	0.090521	1.069766
H	-5.127830	0.704230	0.460161
H	-4.835238	-0.937323	1.100672
H	-4.456716	0.455906	2.098261
O	1.195904	-1.989141	0.296068
O	0.660959	-1.601090	2.378781
C	1.360869	-2.211771	1.531147
C	2.374382	-3.221355	1.975506
H	3.233830	-3.218917	1.306282
H	2.679190	-3.035866	3.003477
H	1.915644	-4.212151	1.924279
Zn	-0.307210	-0.605543	0.828811
O	0.374101	1.315940	1.248233
C	0.571611	2.242509	0.473826
C	-0.386139	3.372063	0.323048
H	-1.299406	2.965908	-0.121712
H	-0.646430	3.752052	1.311242
H	0.014002	4.164822	-0.303866
O	1.628688	2.338002	-0.291959
C	2.587314	1.241778	-0.298969
C	3.496049	1.352436	0.902329
C	3.310513	1.344613	-1.617482
H	2.022022	0.309987	-0.257857
H	2.930603	1.272306	1.830714
H	4.225484	0.540338	0.878639
H	4.037984	2.301062	0.889974
H	2.607466	1.284189	-2.449372
H	3.859807	2.285931	-1.689978
H	4.021090	0.521185	-1.707561
O	-0.464891	0.078086	-1.155247
H	-1.428309	0.388427	-1.070441

C	-0.279030	-0.764832	-2.293079
C	-0.443794	0.057423	-3.554105
C	-1.215987	-1.954357	-2.245421
H	0.751250	-1.123079	-2.215591
H	0.228584	0.917508	-3.542934
H	-0.223438	-0.543894	-4.438957
H	-1.469906	0.425945	-3.639130
H	-1.047553	-2.539249	-1.339170
H	-2.258193	-1.624422	-2.264780
H	-1.047881	-2.607493	-3.104645

C. Transition states for intramolecular nucleophilic attack.



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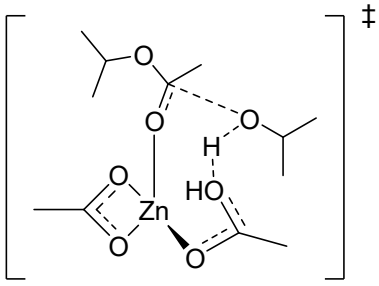
O	7.676586	-0.400839	4.751632
O	7.078032	-1.196310	2.795977
C	7.502131	-1.390388	3.971804
C	7.809821	-2.776605	4.454510
H	7.285668	-2.960451	5.396674
H	7.524272	-3.521914	3.711815
H	8.882051	-2.854211	4.661116
O	8.261877	1.678754	1.961408
O	8.102270	3.799811	2.681566
C	8.506499	2.892030	1.850314
C	9.301627	3.405748	0.692738
H	9.783856	2.579898	0.170396
H	8.624069	3.922131	0.003958
H	10.039458	4.135164	1.035465
Zn	7.010280	0.802552	3.239354
O	6.943538	2.594339	4.527772
C	5.242684	2.298534	4.328305
C	4.883689	1.522954	5.572260
H	4.934160	2.142803	6.469675
H	3.854853	1.172152	5.448504
H	5.543167	0.658149	5.675500
O	4.663669	3.521817	4.372686
C	4.635208	4.237912	3.147009
H	4.134140	3.656839	2.369377
H	4.080689	5.154101	3.355391
H	5.646470	4.491067	2.811793
O	5.286875	1.678333	3.196687
H	7.553622	3.359309	3.466588
C	7.449547	2.971497	5.789750
H	8.460369	3.375889	5.660144

H	6.815864	3.750085	6.232903
H	7.502053	2.107934	6.460823



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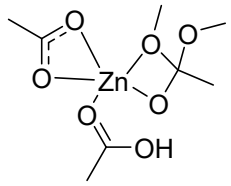
O	7.678699	-0.569543	3.538196
O	6.922433	-1.985124	1.978273
C	7.457992	-1.738290	3.069358
C	7.899021	-2.874763	3.953195
H	7.687976	-3.833427	3.485116
H	8.967578	-2.781100	4.155319
H	7.384285	-2.807816	4.913871
O	8.615001	2.391554	1.773526
O	8.511263	2.588020	3.955234
C	8.988615	2.943973	2.864378
C	10.024494	4.025641	2.774706
H	10.953953	3.595840	2.395355
H	9.704477	4.782762	2.057111
H	10.200519	4.477019	3.748314
Zn	7.330977	1.105945	2.593206
O	6.347979	0.278339	0.996202
H	6.509529	-0.693612	1.242084
O	5.622083	1.913725	3.414618
C	5.370214	2.045197	4.606263
C	6.189399	1.480761	5.707688
H	5.652221	1.503916	6.652437
H	6.504503	0.470301	5.444820
H	7.101183	2.081183	5.771740
O	4.326981	2.730633	5.014209
C	6.604281	0.520405	-0.389568
C	8.028821	0.151454	-0.751902
C	6.285889	1.969898	-0.674064
H	5.910657	-0.117058	-0.952148
H	8.235336	-0.890383	-0.497169
H	8.192075	0.278550	-1.824909

H	8.732795	0.793347	-0.216896
H	5.262396	2.202502	-0.373424
H	6.973368	2.621177	-0.129048
H	6.389111	2.177141	-1.741239
C	3.497991	3.377927	4.010043
C	4.143482	4.680426	3.597310
C	2.142098	3.551975	4.646382
H	3.441143	2.701173	3.155231
H	5.127202	4.509051	3.159815
H	3.520783	5.178076	2.851195
H	4.246318	5.345182	4.457953
H	1.726100	2.590216	4.949845
H	2.207319	4.196867	5.525341
H	1.457884	4.012801	3.931688

D. Tetrahedral intermediates (hemiketal complexes)



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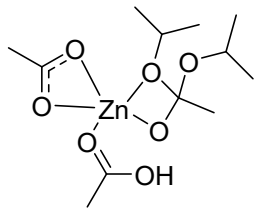
O	7.790005	-0.697004	4.525820
O	6.989497	-1.416532	2.622368
C	7.554866	-1.649652	3.729138
C	7.915870	-3.051591	4.102982
H	8.743835	-3.059019	4.809163
H	7.048582	-3.510314	4.584995
H	8.153469	-3.633262	3.213994
O	8.306671	1.509235	2.023735
O	8.163081	3.631683	2.718383
C	8.584451	2.706639	1.921705
C	9.454650	3.193227	0.811861
H	9.953059	2.356636	0.329621
H	8.823973	3.706948	0.081730
H	10.177081	3.917422	1.187519
H	7.560114	3.281079	3.480652
Zn	6.918289	0.552688	3.139554
O	6.813203	2.871778	4.702973
C	5.407394	2.383891	4.485663
C	4.998959	1.563434	5.692702
H	4.902530	2.177639	6.588164
H	4.030641	1.114268	5.474570
H	5.730759	0.773075	5.867883
O	4.572466	3.490824	4.447108
C	4.620801	4.250291	3.257981
H	4.376965	3.637713	2.388704
H	3.880389	5.040939	3.374160
H	5.605555	4.706608	3.107600
O	5.461328	1.717352	3.340364
C	7.059761	3.655894	5.852562
H	8.003235	4.181638	5.696445
H	6.259837	4.386078	5.996825
H	7.150296	3.026403	6.741321



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O	-1.987583	1.655665	-0.281995
O	-2.944184	-0.347209	-0.020103
C	-2.982306	0.930919	-0.216290
C	-4.353280	1.494622	-0.377966
H	-5.026476	1.071821	0.367444
H	-4.324703	2.578797	-0.310276
H	-4.729114	1.204141	-1.362385
O	1.000745	1.746766	1.208295
O	1.022311	2.872438	-0.665372
C	1.396411	2.740699	0.532476
C	2.330043	3.737689	1.141868
H	2.191186	3.783648	2.220421
H	3.354381	3.411542	0.942868
H	2.192959	4.716951	0.686928
H	-1.983507	-0.702307	0.095411
Zn	-0.038449	1.125748	-0.466665
O	-0.583231	-1.223497	0.325033
O	0.062941	-0.354811	-1.635000
C	0.082306	-1.522945	-1.018015
C	-0.712415	-2.601408	-1.721500
H	-1.749843	-2.285694	-1.828803
H	-0.281826	-2.745876	-2.712125
H	-0.664384	-3.545823	-1.178757
O	1.331027	-2.067417	-0.752474
C	-0.441716	-2.142549	1.419413
C	-1.730542	-2.907685	1.649661
C	-0.019775	-1.350721	2.638099
H	0.353679	-2.837139	1.139201
H	-2.043278	-3.441971	0.751378
H	-1.590139	-3.639476	2.448268
H	-2.538377	-2.235074	1.948895
H	0.894345	-0.788692	2.444751
H	-0.797174	-0.634473	2.917106
H	0.147860	-2.018394	3.486366

C	2.381174	-1.187401	-0.348089
C	3.132518	-0.662172	-1.554697
C	3.278221	-1.980945	0.577030
H	1.956148	-0.349987	0.217388
H	2.461102	-0.123327	-2.221205
H	3.934122	0.010294	-1.238563
H	3.578787	-1.494147	-2.105651
H	2.734177	-2.321441	1.459815
H	3.674334	-2.856660	0.057276
H	4.118658	-1.366986	0.907428