Electronic Supplementary Material (ESI) for Polymer Chemistry
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Phosphoric and Phosphoramidic Acids as Bifunctional Catalysts for the Ring-Opening Polymerization of ε-Caprolactone: A Combined Experimental and Theoretical Study

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Synthesis of phosphoramidic acid PAA: Diphenylphosphochloridate (1.1 mL, 5.3 mmol, 1 equiv.) was dissolved in DCM (20 mL). Triethylamine NEt_3 (5.1 mL, 36.8 mmol, 7 equiv.) was added at 0°C. DMAP (1.28 g, 10.5 mmol, 2 equiv.) and trifluoromethanesulfonamide $TfNH_2$ (940 mg, 6.3 mmol, 1.2 equiv.) were then added to the reaction mixture at 0°C. The cold bath was removed and the reaction mixture was stirred for 2 hours at room temperature, and then heated at reflux for 1 hour. The total conversion of phosphochloridate was monitored by ^{31}P NMR spectroscopy: disappearance of the signal for the starting material at 7.2 ppm and appearance of a new singlet at –12.9 ppm. DCM (15mL) was then added and the organic layer was washed with water (20 mL). The organic layer was washed with a hydrochloric acid solution (37%) until no traces of triethylamine and DMAP were observed in the ^{1}H NMR spectrum. The organic layer was then dried over Na_2SO_4, filtered and the solvent was removed under vacuum. The resulting white solid was dissolved in DCM and cooled to –30°C to give white crystals (m = 0.89 g, Yield = 60%). ^{19}F NMR ($CDCl_3$, 282 MHz): –76.9 (s) ppm. ^{31}P NMR ($CDCl_3$, 203 MHz): –16.4 (s) ppm. ^{1}H NMR ($CDCl_3$, 300 MHz): 8.30 (br s, 1H, NH), 7.10 (m, 2 x 5H, C_6H_5) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): 130.0 (2 x CH), 126.4 (CH), 120.0 (2 x CH), 118.9 (q, $^{1}J_{C\text{-}F}$ = 322.0 Hz, CF_3) ppm. Mp = 93–94°C.

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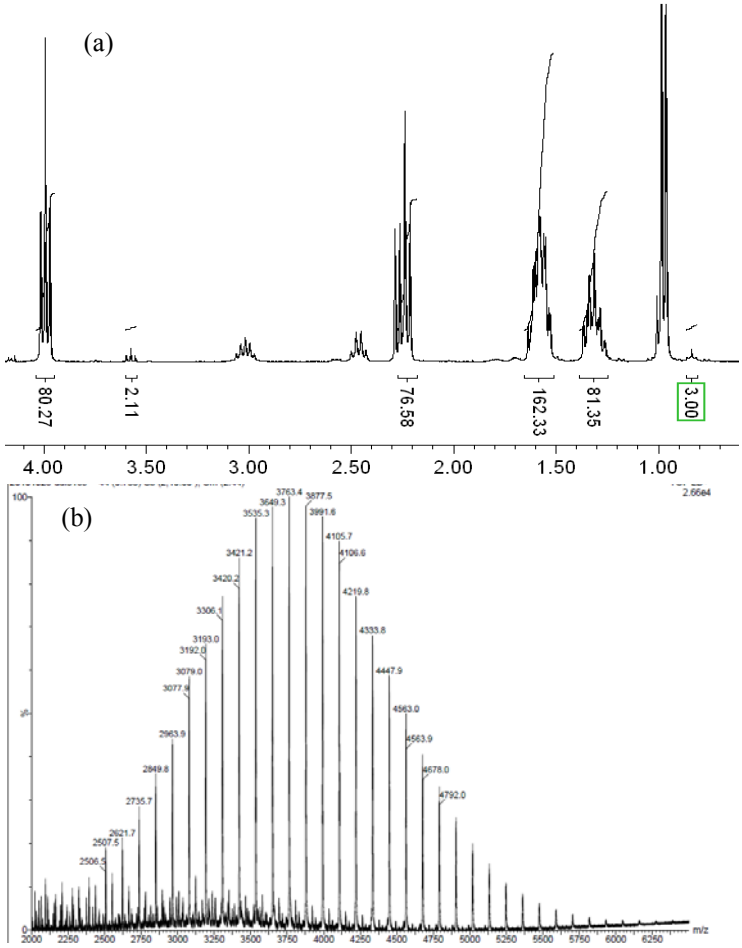

Figure S1 (a) ^{1}H NMR spectrum ($CDCl_3$, 300 MHz) and (b) MALDI-TOF MS (region m/z 1000 to 6000 g/mol) of a PCL ($[\varepsilon\text{-CL}]_0/[n\text{-PentOH}]_0/[PA]$ = 40/1/1, $[\varepsilon\text{-CL}]_0$ = 0.9 mol/L, toluene, 30°C).

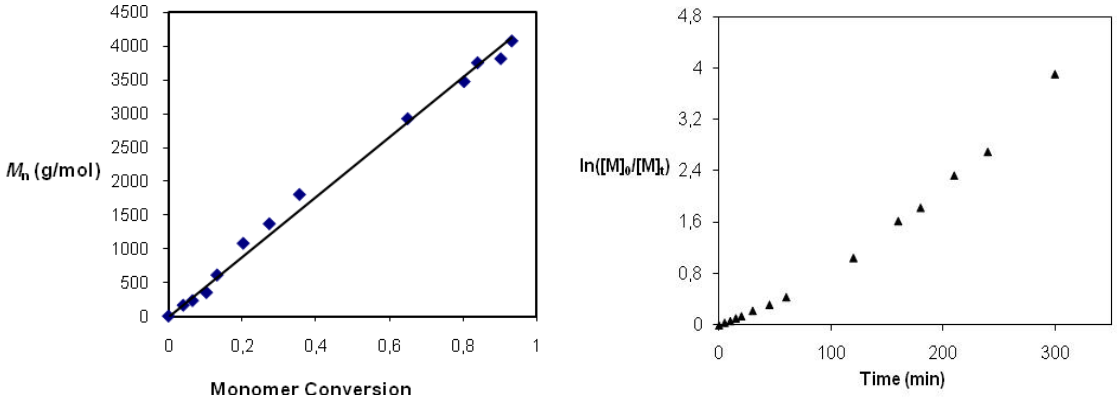

Figure S2. (a) Plot of $M_{n(SEC)}$ (estimated by SEC and a correction factor of 0.56) *vs* ε-CL conversion ($[\varepsilon\text{-CL}]_0/[n\text{-PentOH}]_0/[PA]$ = 40/1/1, toluene, 30°C). (b) Semi-logarithmic plot ($[\varepsilon\text{-CL}]_0/[n\text{-PentOH}]_0/[PA]$ = 40/1/1, toluene, 30°C).

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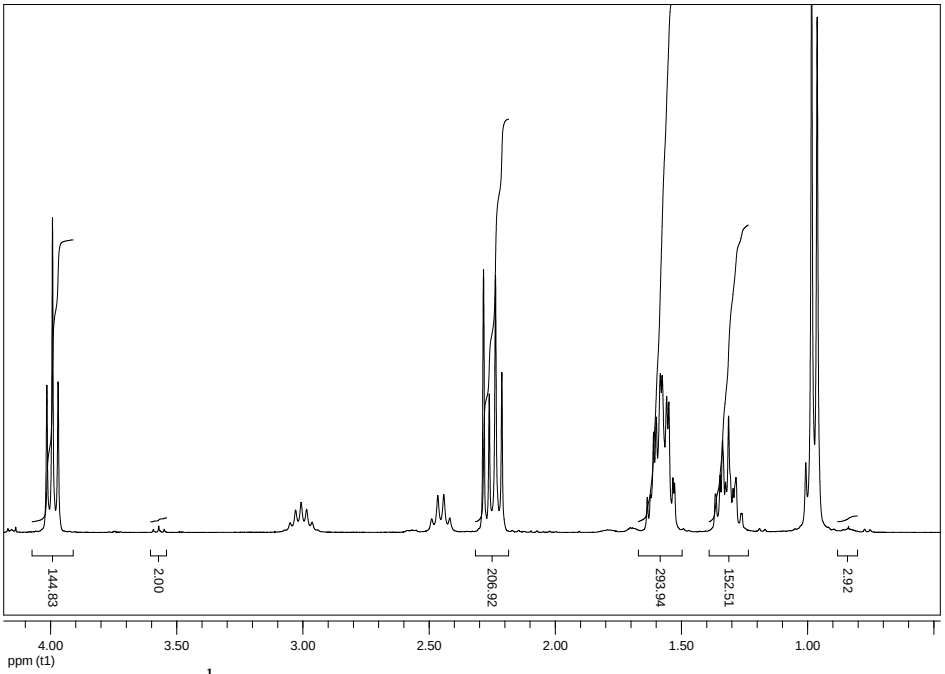

Figure S3 (a) ^{1}H NMR spectrum ($CDCl_3$, 300 MHz) of a PCL ([ε-CL]$_0$/[*n*-PentOH]$_0$/[PAA] = 80/1/1, ([ε-CL]$_0$ = 0.9 mol/L, toluene, 30°C).

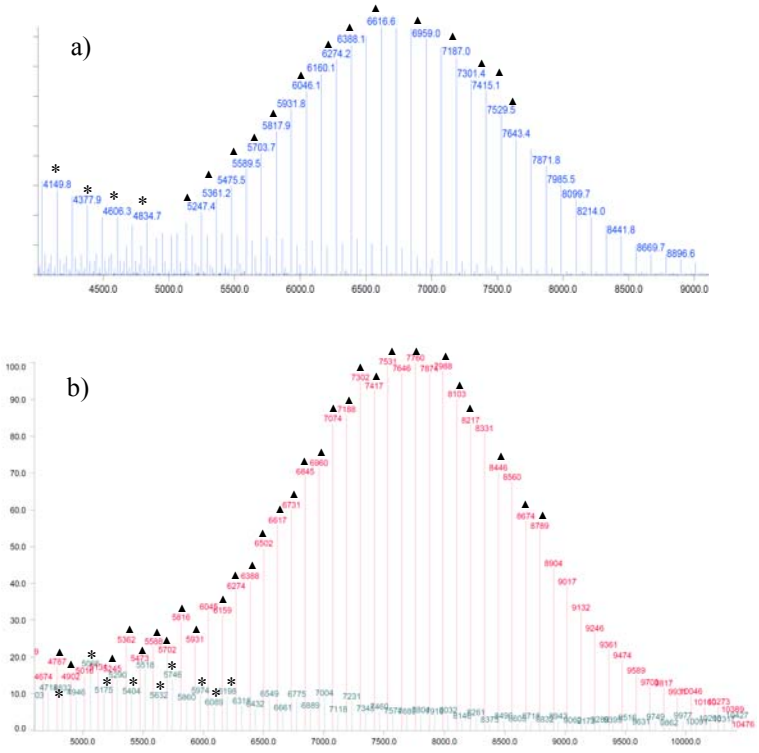

Figure S4 (a) MALDI-TOF MS (region m/z 4 000 to 9 500 g/mol) of a PCL ([ε-CL]$_0$/[*n*-PentOH]$_0$/[PA] = 80/1/1, toluene, 30°C, [ε-CL]$_0$ = 0.9 mol/L) and (b) MALDI-TOF MS (region m/z 5 000 to 12 000 g/mol) of a PCL ([ε-CL]$_0$/[*n*-PentOH]$_0$/[PAA] = 80/1/1, toluene, 30°C, [ε-CL]$_0$ = 0.9 mol/L). ▲Main population M = n×114 ($M_{ε\text{-CL}}$) + 18 (M_{PentOH}) + 23 (M_{Na+}) g/mol. * Second population M = n×114 ($M_{ε\text{-CL}}$) + 18 (M_{H2O}) + 23 (M_{Na+}) g/mol

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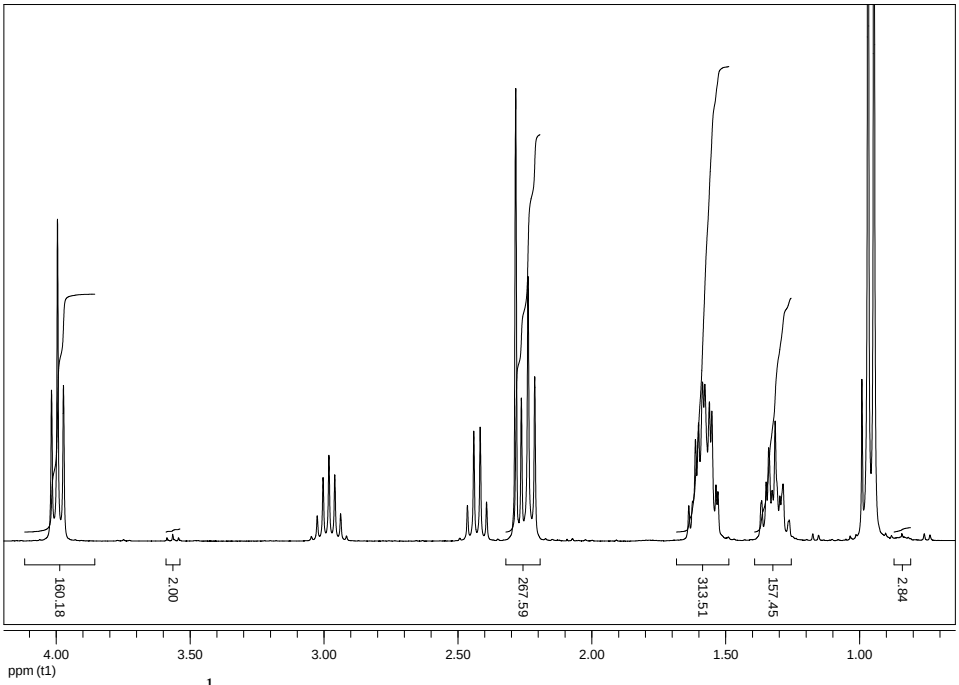

Figure S5 (a) ^{1}H NMR spectrum ($CDCl_3$, 300 MHz) of a PCL ($[\varepsilon\text{-CL}]_0/[n\text{-PentOH}]_0/[PAA]$ = 80/1/3, $[\varepsilon\text{-CL}]_0$ = 2.7 mol/L, toluene, 60°C).

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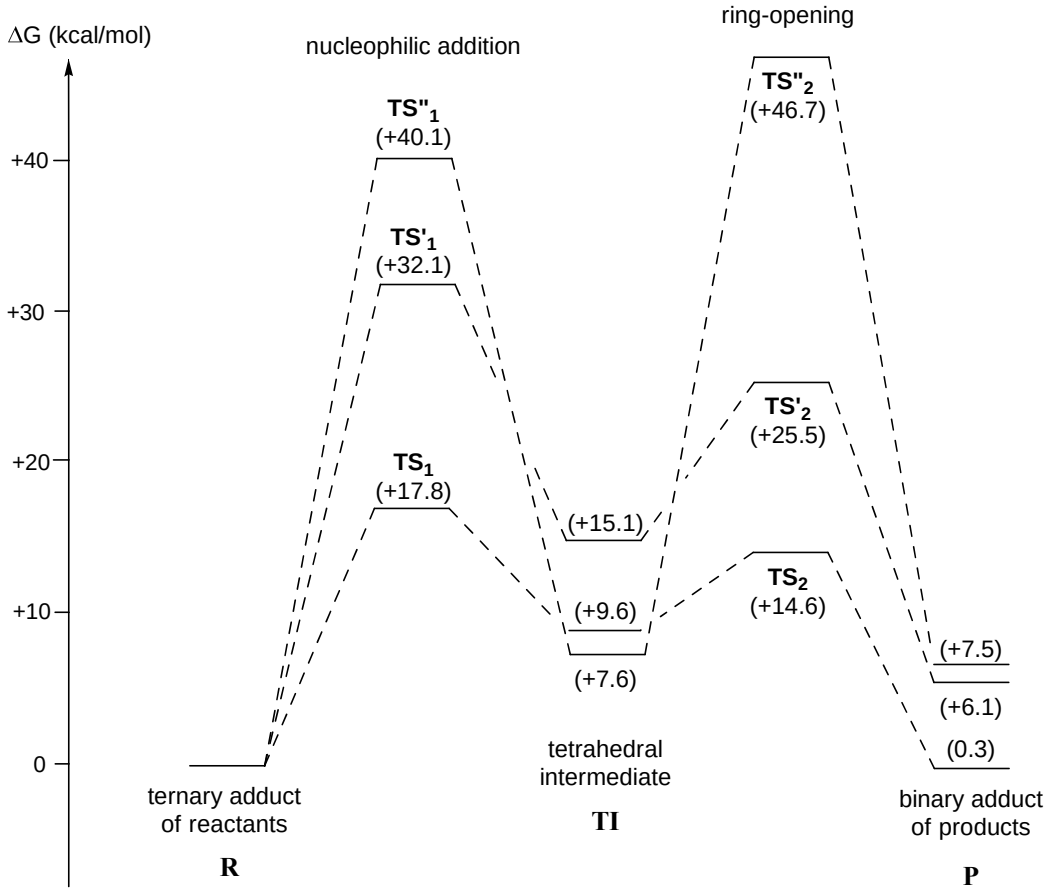
Reaction of ε-CL with methanol catalyzed by phosphoric acid PA



Ternary adduct of reactant R

Energy: -1271.451416 H

C	-1.887155	0.076960	2.598362	H	-2.268667	0.097043	6.110968
C	-2.840937	1.008760	2.998683	H	1.665348	1.956962	2.326023
C	-4.180833	0.876833	2.646183	H	2.923624	0.710071	2.400792
C	-4.574596	-0.214108	1.875274	H	2.875956	1.989528	3.629944
C	-3.636866	-1.163927	1.470591	H	-0.144792	0.270783	7.432873
C	-2.300218	-1.015166	1.835760	H	0.278096	-1.227188	8.242519
P	-1.850336	2.047851	5.230146	H	2.050790	0.057114	6.101641
O	-2.743805	0.987878	6.031436	H	2.158144	0.508467	7.786827
C	-3.600978	3.935478	5.831037	H	3.849530	-1.233349	7.022776
C	-4.424373	3.576450	6.893789	H	2.957432	-1.647556	8.474990
C	-5.725458	4.073742	6.936543	H	3.243173	-3.471785	6.596330
C	-6.191306	4.920202	5.931018	H	2.133555	-1.809184	4.805371
C	-5.350641	5.271170	4.874888	H	1.697311	-3.350963	7.401615
C	-4.048095	4.779103	4.818708	H	1.728539	-3.535306	4.818301
O	-0.356088	1.863614	5.309030	H	-4.043420	2.914487	7.663375
O	-1.506621	-1.259683	6.054553	H	-6.375695	3.797689	7.761831
C	-0.302758	-1.421780	6.233692	H	-7.205473	5.306888	5.971283
O	0.272646	-2.360832	5.493881	H	-5.707067	5.931826	4.089559
C	1.692862	-2.613567	5.402815	H	-3.375814	5.037121	4.007624
C	2.385671	-2.805024	6.744295	H	-4.891430	1.626073	2.979343
C	2.851121	-1.494049	7.393841	H	-5.618966	-0.323208	1.596451
C	1.907579	-0.322436	7.118528	H	-3.947553	-2.016628	0.873835
C	0.427003	-0.651400	7.316848	H	-1.564470	-1.751982	1.526713
O	1.446844	0.462813	3.776872	H	-0.843314	0.195872	2.874952
C	2.255010	1.327929	3.008051	O	-2.479206	2.152271	3.711158
H	0.822833	1.010590	4.293446	O	-2.271429	3.515698	5.814493

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Bifunctional pathway involving the acidic proton and the basic P=O moiety of PA

Tetrahedral intermediate

Energy: -1271.436182 H

C	-3.270501	0.581305	1.187902	H	-0.941529	-0.293845	5.165334
C	-3.581439	0.779597	2.529101	H	2.482541	2.356027	4.205740
C	-4.285935	-0.170720	3.262151	H	3.293552	0.790302	4.497838
C	-4.686024	-1.345793	2.629053	H	2.676836	1.759526	5.870255
C	-4.387642	-1.561140	1.283965	H	0.914103	0.992016	7.073837
C	-3.681276	-0.596325	0.566590	H	-0.015916	-0.467997	7.316707
P	-1.998879	2.038213	4.198074	H	3.038572	-0.436955	7.189997
O	-2.093532	1.030857	5.323806	H	2.156084	-0.252278	8.695003
C	-3.204643	4.121193	5.302743	H	3.038665	-2.644069	7.970051
C	-3.677419	3.557889	6.485687	H	1.484053	-2.489924	8.764593
C	-4.761541	4.156142	7.126438	H	1.381462	-4.032341	6.814097
C	-5.353822	5.303500	6.600826	H	2.869569	-3.027919	5.168106
C	-4.859834	5.856923	5.419914	H	0.251118	-2.700013	6.700191
C	-3.783488	5.265876	4.762807	H	1.211408	-3.053100	4.532413
O	-0.662071	2.010393	3.326442	H	-3.203944	2.666004	6.880847
O	-0.197495	-0.878646	4.896108	H	-5.139408	3.721035	8.047481
C	0.978124	-0.380635	5.393820	H	-6.195121	5.764994	7.109485
O	2.027746	-1.220686	5.037789	H	-5.315272	6.750687	5.002872
C	1.863258	-2.615240	5.298086	H	-3.384798	5.675248	3.840471
C	1.318573	-2.944580	6.682625	H	-4.503419	0.015697	4.307761
C	2.026362	-2.239970	7.843985	H	-5.234876	-2.095002	3.192560
C	2.107536	-0.706696	7.698188	H	-4.704658	-2.478331	0.796266
C	0.936436	-0.092846	6.927337	H	-3.443930	-0.759354	-0.480842
O	1.226220	0.845357	4.675957	H	-2.716586	1.345555	0.653090
C	2.496934	1.460443	4.830173	O	-3.228926	1.998267	3.112057
H	0.064486	1.504643	3.806926	O	-2.088014	3.612743	4.641776

Ring-opened product

Energy: -1271.450962 H

C	-3.402984	-3.568003	3.084326	C	1.805736	1.683628	5.162133
C	-3.980044	-2.304335	3.182527	H	-3.709116	-5.669047	3.395344
C	-5.280918	-2.135081	3.647299	H	1.912297	1.120300	7.857644
C	-6.019966	-3.256375	4.018038	H	-1.716803	-0.109375	5.584074
C	-5.458388	-4.529766	3.930440	H	1.090768	-0.303993	8.488959
C	-4.152009	-4.679480	3.466196	H	3.579828	-0.484584	7.906244
O	-3.300977	-1.168597	2.745275	H	3.138660	-0.476900	6.207794
P	-1.920419	-0.691115	3.500099	H	3.572410	-2.728928	7.211718
O	-2.411527	-0.011709	4.854771	H	2.204261	-2.521570	8.285888
O	-1.543037	0.601600	2.561207	H	1.688703	-4.008281	6.411766
C	-1.079375	0.406148	1.260969	H	0.630763	-2.611025	6.359869
C	-1.886504	0.849744	0.217454	H	1.612853	-3.413744	4.131022
C	-1.422777	0.745981	-1.091999	H	3.171030	-2.781903	4.672254
C	-0.167030	0.197886	-1.351189	H	2.366226	2.084896	6.011306
C	0.626422	-0.244541	-0.293371	H	2.386618	0.925423	4.633899
C	0.179129	-0.142236	1.023001	H	1.544595	2.498547	4.486895
O	-0.851423	-1.753658	3.601582	H	-2.384404	-3.662216	2.725682
O	-0.631495	-0.296424	6.735876	H	-5.694763	-1.134030	3.709517
C	0.447504	0.268347	6.589732	H	-7.036583	-3.131118	4.380075
O	1.755459	-1.358357	4.343023	H	-6.036630	-5.401785	4.221899
C	2.084177	-2.665533	4.783535	H	0.789035	-0.486286	1.851215
C	1.673393	-2.924322	6.233724	H	-2.860891	1.268798	0.445505
C	2.577157	-2.268200	7.283838	H	-2.048030	1.091894	-1.910336
C	2.780826	-0.749904	7.203033	H	1.605548	-0.672786	-0.489102
C	1.563095	0.113783	7.595781	H	0.191983	0.116487	-2.373075
O	0.558422	1.113313	5.566347	H	0.804226	-1.384207	4.111344

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Transition state for the nucleophilic addition TS_1

Energy: -1271.423062 H

C	-2.757494	0.580621	1.327239	H	-1.224997	-0.384888	5.101968
C	-3.560678	0.952181	2.403582	H	2.650456	0.945387	2.484627
C	-4.805715	0.365146	2.611103	H	3.269923	-0.200232	3.702188
C	-5.253638	-0.610403	1.723421	H	2.721988	1.428079	4.198522
C	-4.459810	-0.999373	0.644536	H	1.009019	1.358327	5.767857
C	-3.214119	-0.403271	0.452086	H	0.008087	0.483951	6.896800
P	-1.853573	1.752811	4.235004	H	3.034321	0.089234	6.593538
O	-2.104419	0.499804	5.127861	H	2.308137	1.138944	7.796734
C	-3.109312	3.537418	5.808542	H	3.040413	-1.292526	8.487655
C	-3.961665	2.650701	6.465765	H	1.550626	-0.630032	9.128127
C	-5.052142	3.160652	7.169180	H	1.296288	-2.998029	8.397909
C	-5.286875	4.533208	7.228594	H	2.648320	-3.143119	6.352303
C	-4.419594	5.406418	6.572672	H	0.163282	-1.904866	7.639960
C	-3.330893	4.912726	5.859207	H	0.940022	-3.446217	5.957529
O	-0.526498	1.830835	3.484291	H	-3.765941	1.584967	6.423734
O	-0.402455	-1.192220	5.060058	H	-5.720135	2.472065	7.679743
C	0.757595	-0.752744	5.335187	H	-6.137915	4.919575	7.781781
O	1.775466	-1.651399	5.331847	H	-4.591358	6.478641	6.610211
C	1.651662	-2.694439	6.317858	H	-2.647182	5.573686	5.336365
C	1.226810	-2.168856	7.683379	H	-5.403766	0.683166	3.458696
C	2.031663	-0.969396	8.202765	H	-6.225667	-1.070135	1.879352
C	2.149515	0.218569	7.223674	H	-4.811361	-1.762196	-0.044128
C	0.933726	0.415182	6.315099	H	-2.591754	-0.700162	-0.387575
O	1.248293	0.028837	3.680427	H	-1.794323	1.060946	1.192454
C	2.540655	0.589357	3.514212	O	-3.171374	1.973322	3.261144
H	0.530200	0.743189	3.550766	O	-1.973827	3.134876	5.124530

Transition state for the ring-opening TS_2

Energy: -1271.428167 H

C	-3.027294	-3.643104	2.200696	C	2.140293	1.068679	4.618114
C	-3.228442	-2.520674	3.000722	H	-3.308121	-5.765224	2.026939
C	-3.855179	-2.626644	4.242458	H	2.042314	1.150789	7.357626
C	-4.274098	-3.880506	4.684772	H	-1.301609	0.185236	5.697682
C	-4.080623	-5.012695	3.893827	H	0.968157	0.120441	8.276737
C	-3.459935	-4.888528	2.650749	H	3.472021	-0.579318	8.055606
O	-2.853784	-1.285991	2.496570	H	3.091110	-1.044266	6.407959
P	-1.664580	-0.429401	3.275819	H	2.863423	-3.065926	7.626291
O	-2.170425	0.151817	4.600839	H	2.162911	-2.270480	9.023234
O	-1.559955	0.835910	2.221252	H	0.491932	-3.657180	7.845246
C	-1.279017	0.720980	0.872157	H	0.011958	-1.976052	7.933856
C	-1.836384	1.703721	0.054263	H	-0.532533	-2.853387	5.744874
C	-1.566984	1.696176	-1.311347	H	1.121885	-3.445187	5.497853
C	-0.748791	0.710914	-1.863690	H	2.860635	1.407873	5.370260
C	-0.198136	-0.264483	-1.034481	H	2.463897	0.114512	4.196709
C	-0.451738	-0.266470	0.336586	H	2.068677	1.814911	3.827132
O	-0.375061	-1.282528	3.293667	H	-2.540647	-3.522130	1.238441
O	-0.659128	0.113184	6.546032	H	-4.004233	-1.732041	4.837567
C	0.589159	0.145000	6.205359	H	-4.764078	-3.968085	5.650832
O	0.919532	-1.421505	5.361476	H	-4.416530	-5.985484	4.241409
C	0.521150	-2.659852	5.974526	H	-0.017059	-1.014567	0.990123
C	0.739692	-2.654417	7.476314	H	-2.475058	2.457590	0.503169
C	2.155470	-2.283162	7.926002	H	-2.004077	2.462724	-1.945464
C	2.660592	-0.926528	7.405483	H	0.443450	-1.035284	-1.453512
C	1.578628	0.157624	7.369715	H	-0.542324	0.704283	-2.929979
O	0.826183	0.962032	5.158074	H	0.363421	-1.325611	4.444547

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Bifunctional pathway involving the acidic proton and oxygen atom of the P−OH moiety of PA

Tetrahedral intermediate

Energy: -1271.427333 H

C	2.097174	-3.365864	5.495070	P	-2.748504	1.287285	6.713280
C	1.823673	-3.643930	6.976075	O	-2.298930	0.555572	7.940619
C	1.070936	-2.509343	7.701365	O	-4.130836	0.685428	6.075603
C	0.141307	-1.706621	6.787679	O	-3.213209	2.860231	6.927752
C	0.899727	-0.738796	5.832518	C	-0.780704	5.600933	6.874484
O	2.273973	-0.906305	5.852513	C	-0.405775	5.653995	8.217037
C	2.821604	-2.057434	5.206317	C	-0.957350	4.752930	9.128005
O	0.457277	-0.819620	4.518266	C	-1.883093	3.800133	8.705966
C	1.167453	1.024028	7.500847	C	-2.246795	3.762976	7.361634
H	0.617056	0.526426	8.306173	H	-2.007465	4.586852	5.398944
O	0.691230	0.627613	6.215109	H	-0.353408	6.299553	6.160672
H	-0.769347	1.124291	5.800974	H	0.312177	6.396752	8.552602
H	-0.507630	-0.785636	4.519239	H	-0.669591	4.790903	10.174969
H	0.993154	2.098962	7.568321	H	-2.321641	3.086072	9.394574
H	2.237199	0.818617	7.580982	C	-4.766857	1.284159	4.989037
H	2.852738	-1.882987	4.123807	C	-4.366109	0.972759	3.693411
H	3.852140	-2.097211	5.574494	C	-5.068562	1.515354	2.619013
H	1.153953	-3.372214	4.938017	C	-6.160163	2.353747	2.841299
H	2.701373	-4.177053	5.069329	C	-6.550618	2.651648	4.146714
H	1.235901	-4.568367	7.037455	C	-5.855025	2.117645	5.229133
H	2.765377	-3.849168	7.500209	H	-3.514961	0.319259	3.539921
H	0.482741	-2.931296	8.524009	H	-4.760310	1.277807	1.604750
H	1.790678	-1.823232	8.158461	H	-6.705930	2.771787	2.000483
H	-0.456889	-2.392815	6.176775	H	-7.401053	3.303152	4.326768
H	-0.574105	-1.124200	7.377930	H	-6.139114	2.337037	6.252592
O	-1.703081	1.328766	5.481606	C	-1.702293	4.651071	6.437988

Ring-opened product

Energy: -1271.441782 H

C	-2.321021	1.091040	5.680271	C	3.124045	-2.504253	5.078207
C	-2.921973	-0.055322	5.162943	H	-4.946533	2.239306	7.520817
C	-4.236467	-0.388034	5.479793	H	3.910289	-3.184834	5.417594
C	-4.963457	0.444208	6.327828	H	-0.115492	-3.217250	3.357422
C	-4.377543	1.593061	6.858758	H	2.758884	-1.907313	5.912017
C	-3.058965	1.909566	6.534215	H	3.483541	-1.845226	4.286616
O	-2.261804	-0.875050	4.253617	H	1.286084	-1.234169	0.297734
P	-0.855349	-1.614054	4.682736	H	3.048614	-1.234587	0.349818
O	0.202001	-0.742174	5.287825	H	1.336497	-3.706191	0.915748
O	-1.402562	-2.848926	5.641837	H	1.941457	-3.293645	-0.677205
C	-0.820018	-3.197961	6.851466	H	3.379104	-4.983554	0.350799
C	-0.580835	-2.263930	7.857076	H	4.247935	-3.505181	-0.006714
C	-0.067861	-2.703420	9.076108	H	5.074186	-4.326590	2.036308
C	0.194044	-4.055720	9.293359	H	4.185097	-2.858016	2.403163
C	-0.056512	-4.977552	8.277555	H	3.054215	-5.691291	2.757091
C	-0.561114	-4.552188	7.050886	H	3.964021	-4.851711	4.017015
O	-0.571303	-2.324933	3.263212	H	1.269806	-1.561161	2.495409
O	0.917029	-4.469948	3.185704	H	-4.669552	-1.288039	5.055808
C	2.004048	-4.113778	3.634508	H	-5.990168	0.189881	6.575767
C	3.305565	-4.703408	3.154045	H	-2.597173	2.804310	6.942528
C	4.066835	-3.894688	2.079470	H	-1.293542	1.318205	5.420053
C	3.485906	-3.934375	0.658875	H	-0.761642	-5.250848	6.245099
C	2.160720	-3.207318	0.395872	H	0.141093	-6.034091	8.436729
C	2.155167	-1.723571	0.760049	H	0.587252	-4.389156	10.249373
O	2.174509	-1.483023	2.159437	H	0.121298	-1.978726	9.863252
O	1.973998	-3.220520	4.617772	H	-0.784230	-1.214792	7.677529

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Transition state for the nucleophilic addition TS'$_1$

Energy: -1271.400205 H

C	1.581077	-3.231368	6.182023
C	1.871723	-2.801196	7.626070
C	1.581874	-1.318979	7.941781
C	0.379545	-0.719573	7.203873
C	0.613043	-0.685396	5.690774
O	1.876271	-0.941367	5.302565
C	2.183218	-2.341960	5.103496
O	-0.319148	-1.088317	4.884889
C	1.366279	2.062807	5.976328
H	1.069488	2.156641	7.025713
O	0.573416	1.109499	5.271128
H	-0.415929	1.263783	5.366719
H	-1.193593	-0.542988	5.116469
H	1.258125	3.033981	5.486870
H	2.402432	1.730314	5.901225
H	1.829584	-2.642391	4.111271
H	3.275839	-2.371741	5.113711
H	0.497199	-3.280116	6.026083
H	1.951675	-4.250195	6.016702
H	1.266515	-3.436874	8.283094
H	2.918171	-3.013734	7.877147
H	1.407003	-1.213231	9.018024
H	2.465461	-0.715218	7.711445
H	-0.542747	-1.281447	7.380650
H	0.172113	0.280474	7.591488
O	-1.959402	0.654588	5.363412
P	-3.033960	0.636914	6.512576
O	-2.857118	-0.321021	7.658277
O	-4.526984	0.450122	5.830614
O	-3.198660	2.247086	6.971618
C	-0.731083	4.835112	7.695898
C	-0.139972	4.346616	8.861688
C	-0.567791	3.127630	9.389878
C	-1.578388	2.395720	8.766508
C	-2.157093	2.892032	7.593743
H	-2.210675	4.473460	6.150757
H	-0.412505	5.787652	7.280646
H	0.638393	4.916650	9.360808
H	-0.124318	2.747029	10.306390
H	-1.936055	1.453871	9.169472
C	-4.914697	1.195154	4.727511
C	-4.545182	0.792073	3.446364
C	-5.017405	1.504824	2.346247
C	-5.852443	2.607590	2.524251
C	-6.215739	2.998436	3.812820
C	-5.747721	2.294734	4.920545
H	-3.895596	-0.067854	3.327174
H	-4.732203	1.192979	1.345143
H	-6.221119	3.157300	1.662879
H	-6.868046	3.855065	3.959474
H	-6.016296	2.580329	5.931941
C	-1.734483	4.109679	7.055877

Transition state for the ring-opening TS'$_2$

Energy: -1271.410796 H

C	-2.323216	1.125069	5.728281
C	-2.938940	0.045491	5.094119
C	-4.306690	-0.182300	5.238316
C	-5.066614	0.679225	6.025426
C	-4.464588	1.758766	6.671419
C	-3.095316	1.973561	6.520054
O	-2.251380	-0.798755	4.239965
P	-0.834376	-1.532407	4.693186
O	0.228001	-0.619615	5.253397
O	-1.479887	-2.595618	5.817175
C	-0.775611	-3.087260	6.895028
C	-0.064741	-2.262179	7.769439
C	0.559255	-2.829055	8.879698
C	0.473306	-4.199045	9.128089
C	-0.247295	-5.009729	8.251914
C	-0.869709	-4.458850	7.134261
O	-0.494350	-2.379694	3.416674
O	0.879388	-4.535283	3.140005
C	1.982762	-3.901005	3.463766
C	3.268515	-4.530826	2.957644
C	4.198603	-3.654217	2.110314
C	3.787013	-3.578062	0.633986
C	2.287869	-3.374423	0.404145
C	1.691014	-2.187035	1.137918
O	1.803418	-2.289827	2.572221
O	1.936350	-3.405659	4.696020
C	2.983653	-2.568750	5.196827
H	-5.058673	2.428153	7.287044
H	3.958075	-3.060061	5.110590
H	0.116278	-3.941006	3.423801
H	2.735941	-2.407816	6.244159
H	2.976153	-1.617009	4.665437
H	0.629809	-2.082711	0.887885
H	2.203275	-1.259523	0.852646
H	1.732016	-4.275896	0.684393
H	2.102857	-3.225022	-0.666605
H	4.087751	-4.504438	0.128348
H	4.351425	-2.769990	0.152063
H	5.211403	-4.067241	2.174981
H	4.246004	-2.650444	2.542089
H	2.969755	-5.423213	2.399457
H	3.795916	-4.884641	3.850747
H	0.829691	-2.135311	2.966642
H	-4.753323	-1.030682	4.729913
H	-6.132939	0.501651	6.136607
H	-2.618430	2.813779	7.017958
H	-1.257015	1.275218	5.601725
H	-1.438939	-5.073092	6.443583
H	-0.327691	-6.077769	8.436259
H	0.956685	-4.629169	10.000682
H	1.108730	-2.186544	9.563139
H	-0.003524	-1.200976	7.560850

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Monofunctional pathway: activation by the acidic proton of PA

Tetrahedral intermediate

Energy: -1271.439277 H

C	-1.689669	-6.476389	6.765889	H	-3.982050	-6.954328	-0.745046
C	-2.514005	-6.326181	5.654144	H	-6.288858	-3.955146	0.714201
C	-3.802005	-6.856198	5.630338	H	-2.803696	-7.173676	-2.802375
C	-4.257763	-7.560306	6.743431	H	-4.030906	-5.671735	1.285526
C	-3.445827	-7.722353	7.865119	H	-7.193679	-4.029276	-0.825623
C	-2.162989	-7.176138	7.873211	H	-5.841930	-2.878475	-0.629906
P	-1.988070	-6.038758	3.041821	H	-2.401182	-6.199711	-0.525675
C	-0.235212	-8.014200	3.440991	H	-4.040571	-5.973775	-3.105512
C	-1.106354	-9.099883	3.376904	H	-1.604580	-5.533175	-3.982492
C	-0.703860	-10.314980	3.929109	H	-1.164476	-5.284646	-2.309469
C	0.550152	-10.448026	4.522940	H	-2.690778	-3.485000	-4.175925
C	1.412198	-9.352727	4.566756	H	-1.523542	-3.083537	-2.929132
C	1.022261	-8.128893	4.028676	H	-4.504490	-3.690403	-2.642149
O	-1.680538	-4.668797	2.277122	H	-3.651857	-2.188676	-2.272470
O	-3.196461	-6.822111	2.579125	H	-2.076289	-8.984185	2.906139
O	-3.936762	-4.777577	0.898840	H	-1.379730	-11.164512	3.887459
C	-4.035886	-4.841023	-0.506682	H	0.855499	-11.400420	4.946118
O	-3.411605	-3.646276	-0.890920	H	2.393199	-9.446925	5.023968
C	-3.562852	-3.280649	-2.260860	H	1.676398	-7.263245	4.049994
C	-2.396365	-3.711041	-3.142140	H	-4.419733	-6.726449	4.749800
C	-1.997791	-5.194173	-3.017005	H	-5.259853	-7.979881	6.731104
C	-3.107048	-6.149042	-2.556906	H	-3.811780	-8.268965	8.729285
C	-3.360257	-6.103796	-1.046697	H	-1.523365	-7.295154	8.743143
O	-5.374444	-4.900261	-0.902971	H	-0.695166	-6.043073	6.750542
C	-6.211338	-3.877659	-0.374454	O	-2.021572	-5.546160	4.609414
H	-2.446987	-4.484735	1.663738	O	-0.534647	-6.783966	2.863442

Ring-opened product

Energy: -1271.439550 H

C	-2.288276	5.372897	6.930206	O	2.204848	-1.901754	4.244087
C	-1.680970	6.486987	7.505828	H	0.618667	1.140930	8.280902
C	-1.358279	6.490878	8.862831	H	-0.604597	1.687166	5.715356
C	-1.646659	5.374914	9.647935	H	1.316729	-1.547460	4.101073
C	-2.259171	4.255594	9.086786	H	1.797599	1.966681	7.222786
C	-2.573108	4.270921	7.730404	H	2.150406	0.319381	7.791429
O	-3.248617	3.194526	7.156613	H	1.789153	-3.646355	3.189659
P	-2.417291	1.805007	6.864340	H	3.135636	-3.686532	4.329760
O	-3.593600	0.920825	6.152294	H	0.185272	-3.492231	5.126647
C	-4.100553	1.261926	4.897595	H	1.082030	-4.994186	5.008281
C	-3.503184	0.724543	3.761690	H	1.001841	-4.404656	7.329279
C	-4.062706	1.000216	2.515798	H	2.659798	-4.255322	6.777928
C	-5.201162	1.799761	2.413502	H	2.132723	-2.462126	8.301382
C	-5.785299	2.326949	3.564726	H	2.451434	-1.792781	6.702984
C	-5.236937	2.059916	4.818047	H	-0.452936	-2.381099	7.291370
O	-1.385589	2.282847	5.707686	H	0.251035	-1.126355	8.296647
O	-1.815395	1.091029	8.037932	H	-2.544690	5.342371	5.876556
O	-0.456055	-0.952397	5.194065	H	-1.457564	7.353018	6.889154
C	0.153146	-0.696905	6.212042	H	-0.885062	7.361633	9.307327
O	0.707752	0.544504	6.291897	H	-1.398315	5.373465	10.705609
C	1.356949	1.005033	7.487625	H	-2.491594	3.376163	9.677638
C	0.365288	-1.659213	7.349436	H	-2.619075	0.104354	3.868202
C	1.737029	-2.385582	7.282099	H	-3.605153	0.586097	1.621715
C	1.663121	-3.800507	6.692912	H	-5.633465	2.009268	1.439306
C	1.187501	-3.925822	5.241078	H	-6.673459	2.948274	3.490969
C	2.113029	-3.314683	4.189627	H	-5.673342	2.457669	5.727848

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Transition state for the nucleophilic addition TS"$_1$

Energy: -1271.387485 H

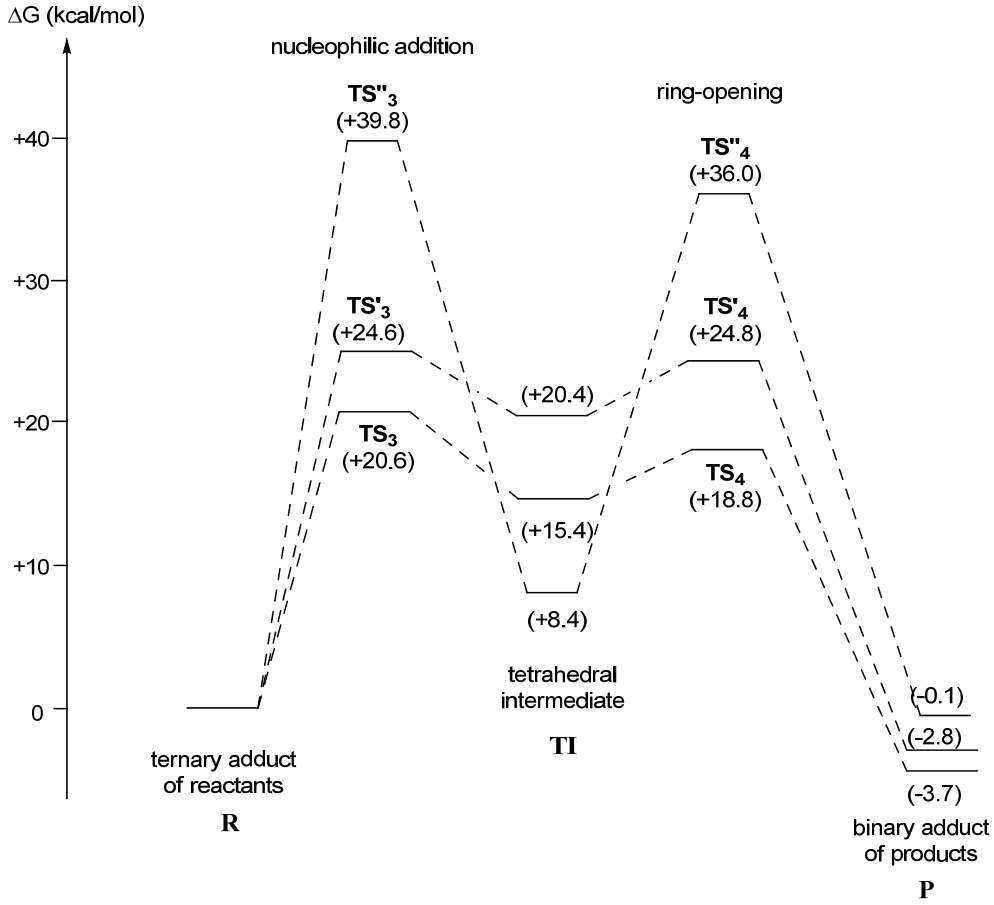
C	-2.390946	-7.280014	6.715023	H	-5.935855	-4.942253	0.003060
C	-3.109091	-7.220145	5.523344	H	-3.016824	-2.378388	-1.961729
C	-3.722000	-8.353931	4.992484	H	-5.924627	-7.259494	-0.735384
C	-3.597497	-9.565510	5.669626	H	-4.405773	-2.827830	0.017752
C	-2.881049	-9.642926	6.863351	H	-4.437712	-1.309275	-2.081463
C	-2.281560	-8.496784	7.384089	H	-4.334782	-2.750717	-3.113353
P	-2.800686	-5.674084	3.380071	H	-4.728918	-5.892095	0.866943
C	-0.149835	-6.183195	3.609442	H	-5.416894	-6.288974	-2.095420
C	-0.193337	-7.491871	3.129957	H	-4.057527	-8.474800	-1.544731
C	0.934981	-8.298515	3.272642	H	-3.461915	-7.606081	-0.140641
C	2.094591	-7.810888	3.871862	H	-2.749242	-7.263684	-3.048867
C	2.124063	-6.496340	4.337022	H	-1.729323	-7.119742	-1.626014
C	1.004203	-5.679701	4.210168	H	-3.707186	-5.066064	-2.741224
O	-3.459463	-4.236643	3.212608	H	-1.943483	-4.968791	-2.739315
O	-3.125338	-6.752237	2.379142	H	-1.095728	-7.859707	2.655690
O	-3.778876	-3.562431	0.736995	H	0.901014	-9.320607	2.905145
C	-3.932736	-4.392041	-0.300940	H	2.967958	-8.448182	3.974932
O	-2.782257	-4.624997	-0.942595	H	3.021589	-6.101685	4.805414
C	-2.806609	-5.350300	-2.187612	H	1.005006	-4.654898	4.567403
C	-2.712531	-6.855894	-2.029677	H	-4.269590	-8.276569	4.060560
C	-3.826602	-7.473532	-1.164912	H	-4.070158	-10.453945	5.259772
C	-5.104574	-6.630760	-1.100392	H	-2.792627	-10.590753	7.386337
C	-4.983882	-5.467380	-0.113047	H	-1.722135	-8.546992	8.314029
O	-4.796566	-3.081741	-1.123474	H	-1.931885	-6.375692	7.100719
C	-4.102381	-2.350843	-2.120409	O	-3.259020	-5.970625	4.935365
H	-3.584681	-3.992208	2.241164	O	-1.196567	-5.283367	3.494940

Transition state for the ring-opening TS"$_2$

Energy: -1271.376948 H

C	-2.502002	5.463040	6.909845	O	1.932132	-1.379610	4.853543
C	-1.957823	6.657144	7.377475	H	1.077468	0.290287	8.073823
C	-1.349876	6.710868	8.631642	H	-0.439310	1.685392	5.701862
C	-1.290632	5.563509	9.421860	H	0.961364	-1.130763	4.108353
C	-1.838490	4.363475	8.971285	H	1.821648	1.684372	7.262538
C	-2.437236	4.329513	7.714212	H	2.557356	0.069594	7.059503
O	-3.056602	3.171604	7.248725	H	2.909444	-2.847448	3.860460
P	-2.160402	1.818431	6.982924	H	3.283840	-2.752909	5.581612
O	-3.309032	0.838683	6.347973	H	0.519067	-3.547577	4.571226
C	-3.936183	1.141630	5.137802	H	1.795250	-4.740142	4.725144
C	-3.375068	0.683411	3.949725	H	0.225880	-4.602403	6.722399
C	-4.053824	0.919714	2.755517	H	1.937247	-4.521884	7.100127
C	-5.271477	1.600005	2.754667	H	0.537837	-2.905432	8.397358
C	-5.817059	2.048082	3.957268	H	1.861879	-2.156319	7.538014
C	-5.150438	1.820360	5.159746	H	-0.907531	-2.281114	6.262655
O	-1.200589	2.305499	5.773543	H	-0.562789	-1.052758	7.468495
O	-1.491858	1.175484	8.161845	H	-2.973978	5.393495	5.935407
O	-0.139245	-0.790813	4.452473	H	-2.006111	7.546533	6.755431
C	0.426924	-0.795332	5.629752	H	-0.925323	7.643401	8.991954
O	0.827086	0.458267	6.004182	H	-0.820091	5.599459	10.400517
C	1.618350	0.616490	7.182354	H	-1.802539	3.459675	9.569909
C	-0.096715	-1.711215	6.725236	H	-2.427117	0.153956	3.971293
C	0.902146	-2.664202	7.392535	H	-3.625340	0.567721	1.821262
C	1.117348	-3.970497	6.621383	H	-5.795020	1.778545	1.819764
C	1.430312	-3.789153	5.132191	H	-6.766346	2.576513	3.963346
C	2.462771	-2.700889	4.852373	H	-5.553704	2.159000	6.107974

Reaction of ε-CL with methanol catalyzed by the phosphoramidic acid PAA



Ternary adduct of reactant R

Energy: -1910.461700 H

C	0.950360	-6.089364	5.122928
C	0.021355	-6.890113	4.461591
C	0.417015	-7.811889	3.495651
C	1.773809	-7.911723	3.185896
C	2.717514	-7.116470	3.831879
C	2.299955	-6.207378	4.804108
O	-1.298885	-6.711969	4.870511
P	-2.634380	-7.140930	4.023497
O	-3.763957	-6.911953	5.181927
C	-3.686932	-7.617921	6.386592
C	-3.500955	-6.877069	7.548507
C	-3.489448	-7.540892	8.773081
C	-3.654965	-8.925068	8.825673
C	-3.837964	-9.648307	7.647793
C	-3.860980	-8.998174	6.414587
N	-2.973285	-5.838404	2.955304
O	-2.625285	-8.438256	3.280220
O	-4.543799	-6.466766	0.833526
C	-4.353423	-6.014004	-0.286652
O	-4.888038	-2.877687	-0.144462
C	-5.117074	-1.484670	-0.089196
O	-3.138406	-5.539219	-0.572696
C	-2.904539	-4.888511	-1.836371
C	-2.688929	-5.903102	-2.950021
C	-3.732044	-7.025640	-2.930673
C	-5.166725	-6.534731	-2.714548
C	-5.457055	-5.929274	-1.314418
H	-3.505336	-6.117328	2.084108
H	-5.702141	-4.861323	-1.379393
H	-4.250531	-0.931348	0.299912
H	-5.844681	-7.380532	-2.865627
H	-4.710168	-3.182032	0.757587
H	-5.993212	-1.227529	0.523133
H	-5.306382	-1.140938	-1.110198
H	-6.315868	-6.415227	-0.848905
H	-5.420952	-5.800332	-3.487988
H	-3.678078	-7.582687	-3.872524
H	-3.475711	-7.745363	-2.142902
H	-2.731498	-5.359171	-3.902455
H	-1.684754	-6.334918	-2.875877
H	-3.734957	-4.208208	-2.039517
H	-2.015518	-4.278220	-1.667245
H	-0.320422	-8.438763	3.007509
H	2.089069	-8.627851	2.432112
H	3.770788	-7.205731	3.582992
H	3.025347	-5.582844	5.317789
H	0.601522	-5.385793	5.871595
H	-4.006039	-9.541352	5.486806
H	-3.969124	-10.726023	7.684072
H	-3.642931	-9.438531	9.782658
H	-3.347020	-6.972893	9.688037
H	-3.370957	-5.802751	7.473784
S	-3.106139	-4.249724	3.357503
O	-4.221475	-3.666051	2.618055
O	-2.925245	-4.042470	4.780387
C	-1.588504	-3.523754	2.546075
F	-1.522818	-2.235621	2.856098
F	-0.495743	-4.129726	2.972967
F	-1.672301	-3.645611	1.231078

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Bifunctional pathway involving the acidic proton and the basic P=O moiety of PAA

Tetrahedral intermediate

Energy: -1910.457321 H

C	-3.531518	-3.541184	3.552087	C	2.966448	-0.652313	7.161609
C	-4.036921	-2.339352	3.064756	C	1.734768	0.152935	7.628114
C	-5.400625	-2.148687	2.862124	O	0.572317	1.060715	5.640014
C	-6.279816	-3.185912	3.162212	C	1.750556	1.727653	5.182707
C	-5.797659	-4.395360	3.662704	H	-4.044700	-5.506075	4.241264
C	-4.428120	-4.565657	3.855669	H	2.047797	1.177411	7.864010
O	-3.217367	-1.271198	2.690621	H	-1.673605	-0.177712	5.748781
P	-1.893570	-0.803567	3.520839	H	1.338926	-0.280386	8.550562
N	-2.400437	-0.098172	4.983207	H	3.794261	-0.346537	7.812966
S	-3.451183	1.176420	5.135627	H	3.248510	-0.366708	6.145434
O	-2.831713	2.250953	5.889924	H	3.852311	-2.591697	7.131378
O	-1.431041	0.477418	2.621650	H	2.535236	-2.445062	8.276884
C	-1.014740	0.279967	1.297468	H	1.983390	-3.963978	6.448404
C	-1.860620	0.714554	0.283331	H	0.868355	-2.611384	6.431361
C	-1.437701	0.597865	-1.038848	H	1.782398	-3.414972	4.167605
C	-0.189456	0.048892	-1.332178	H	3.331836	-2.702461	4.626081
C	0.641488	-0.381145	-0.298425	H	2.324782	2.158089	6.007487
C	0.237223	-0.266505	1.031199	H	2.358897	1.024372	4.610803
O	-0.851942	-1.856630	3.794289	H	1.395245	2.530752	4.536870
O	-4.151660	1.386693	3.881486	H	-2.463200	-3.664953	3.689508
C	-4.680516	0.407768	6.313380	H	-5.749887	-1.193828	2.484065
F	-4.062523	0.024635	7.420672	H	-7.345554	-3.043020	3.008426
F	-5.268119	-0.637661	5.758473	H	-6.486226	-5.201006	3.899528
F	-5.598695	1.313225	6.617561	H	0.875871	-0.593921	1.845591
O	-0.481949	-0.379505	6.896695	H	-2.825685	1.136150	0.543040
C	0.556380	0.237970	6.688300	H	-2.088436	0.935362	-1.840404
O	1.844355	-1.349704	4.336458	H	1.614976	-0.807643	-0.522773
C	2.247583	-2.634307	4.786031	H	0.135706	-0.041717	-2.364477
C	1.915778	-2.884129	6.258023	H	0.881595	-1.404770	4.189766
C	2.841569	-2.178446	7.256057				

Ring-opened product

Energy: -1271.450962 H

C	-3.402984	-3.568003	3.084326	C	1.805736	1.683628	5.162133
C	-3.980044	-2.304335	3.182527	H	-3.709116	-5.669047	3.395344
C	-5.280918	-2.135081	3.647299	H	1.912297	1.120300	7.857644
C	-6.019966	-3.256375	4.018038	H	-1.716803	-0.109375	5.584074
C	-5.458388	-4.529766	3.930440	H	1.090768	-0.303993	8.488959
C	-4.152009	-4.679480	3.466196	H	3.579828	-0.484584	7.906244
O	-3.300977	-1.168597	2.745275	H	3.138660	-0.476900	6.207794
P	-1.920419	-0.691115	3.500099	H	3.572410	-2.728928	7.211718
O	-2.411527	-0.011709	4.854771	H	2.204261	-2.521570	8.285888
O	-1.543037	0.601600	2.561207	H	1.688703	-4.008281	6.411766
C	-1.079375	0.406148	1.260969	H	0.630763	-2.611025	6.359869
C	-1.886504	0.849744	0.217454	H	1.612853	-3.413744	4.131022
C	-1.422777	0.745981	-1.091999	H	3.171030	-2.781903	4.672254
C	-0.167030	0.197886	-1.351189	H	2.366226	2.084896	6.011306
C	0.626422	-0.244541	-0.293371	H	2.386618	0.925423	4.633899
C	0.179129	-0.142236	1.023001	H	1.544595	2.498547	4.486895
O	-0.851423	-1.753658	3.601582	H	-2.384404	-3.662216	2.725682
O	-0.631495	-0.296424	6.735876	H	-5.694763	-1.134030	3.709517
C	0.447504	0.268347	6.589732	H	-7.036583	-3.131118	4.380075
O	1.755459	-1.358357	4.343023	H	-6.036630	-5.401785	4.221899
C	2.084177	-2.665533	4.783535	H	0.789035	-0.486286	1.851215
C	1.673393	-2.924322	6.233724	H	-2.860891	1.268798	0.445505
C	2.577157	-2.268200	7.283838	H	-2.048030	1.091894	-1.910336
C	2.780826	-0.749904	7.203033	H	1.605548	-0.672786	-0.489102
C	1.563095	0.113783	7.595781	H	0.191983	0.116487	-2.373075
O	0.558422	1.113313	5.566347	H	0.804226	-1.384207	4.111344

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Transition state for the nucleophilic addition TS_3

Energy: -1910.428890 H

C	-2.071489	4.571573	4.951446
C	-2.740688	3.741530	5.846284
C	-3.812791	4.198616	6.605399
C	-4.221603	5.522650	6.463186
C	-3.568662	6.370636	5.568453
C	-2.498532	5.891457	4.814050
O	-2.314449	2.433388	6.073720
P	-2.302450	1.301713	4.886861
O	-3.783728	1.580812	4.237845
C	-4.333506	0.828430	3.203648
C	-5.712383	0.641469	3.262145
C	-6.345561	-0.063195	2.242130
C	-5.606486	-0.580031	1.177774
C	-4.228275	-0.380040	1.135431
C	-3.578921	0.332468	2.143470
N	-2.202233	-0.157045	5.667817
O	-1.155224	1.454957	3.895434
O	-0.092271	-1.478035	5.208625
C	0.952764	-0.856590	5.600204
C	0.892711	0.139526	6.754170
C	2.183779	0.124084	7.575768
C	2.415465	-1.187510	8.357084
C	1.868721	-2.451359	7.679360
C	2.318822	-2.660341	6.240527
O	2.124586	-1.482527	5.416389
O	1.188388	0.323198	4.046273
C	2.228787	1.284922	4.000249
H	0.292659	0.767434	3.954539
H	-1.000160	-0.942692	5.427564
H	2.205554	1.806297	3.037440
H	3.175013	0.748831	4.091902
H	2.149968	2.026755	4.805883
H	0.685204	1.143248	6.374625
H	0.025718	-0.132900	7.367541
H	3.028094	0.312441	6.905871
H	2.153075	0.961006	8.281451
H	3.489238	-1.300133	8.549643
H	1.934899	-1.112564	9.339252
H	2.170987	-3.337256	8.250614
H	3.393589	-2.845976	6.172816
H	0.772329	-2.441427	7.714246
H	1.783876	-3.498819	5.781540
H	-4.305202	3.512141	7.285945
H	-5.057405	5.889912	7.051958
H	-3.892939	7.401408	5.459225
H	-1.987137	6.547232	4.114955
H	-1.241000	4.180452	4.373330
H	-2.509471	0.508349	2.111032
H	-3.645334	-0.774789	0.307986
H	-6.102685	-1.133661	0.386186
H	-7.420623	-0.212888	2.285470
H	-6.263259	1.042872	4.106126
S	-3.112801	-0.584230	6.942093
O	-2.239040	-1.092256	7.999552
O	-4.197887	0.341129	7.243797
C	-3.933907	-2.113370	6.258116
F	-4.667570	-2.679457	7.207308
F	-4.716342	-1.807069	5.234947
F	-3.016180	-2.984247	5.850308

Transition state for the ring-opening TS_4

Energy: -1910.431671 H

C	-2.593366	-3.585262	2.977965
C	-3.351309	-2.422716	2.857150
C	-4.727536	-2.426823	3.064935
C	-5.354548	-3.621486	3.411897
C	-4.612149	-4.794384	3.549524
C	-3.235228	-4.771458	3.331537
O	-2.776198	-1.227548	2.435756
P	-1.620961	-0.454909	3.311209
N	-2.134452	0.140727	4.753522
S	-3.383598	1.177438	4.854221
O	-2.965946	2.448309	5.432448
O	-1.368198	0.831684	2.326248
C	-1.288274	0.696510	0.941118
C	-2.303803	1.266681	0.180657
C	-2.213871	1.215444	-1.208317
C	-1.125268	0.596150	-1.823003
C	-0.119686	0.027079	-1.042822
C	-0.191919	0.077109	0.348518
O	-0.379154	-1.343167	3.486611
O	-4.271538	1.143907	3.693480
C	-4.329293	0.338858	6.226558
F	-3.567908	0.217985	7.310311
F	-4.734628	-0.870270	5.859654
F	-5.394318	1.068473	6.533778
O	-0.409487	0.044359	6.744632
C	0.823488	0.083042	6.318733
O	1.089170	-1.436639	5.456553
C	0.731241	-2.691228	6.080392
C	1.047985	-2.710763	7.562754
C	2.490055	-2.348320	7.927084
C	2.959822	-0.981627	7.398419
C	1.869249	0.093826	7.432589
O	0.982522	0.924167	5.278506
C	2.266674	1.084695	4.680127
H	-2.653340	-5.684187	3.427530
H	2.321034	1.091678	7.407629
H	-1.079518	0.162455	5.973008
H	1.306923	0.042518	8.369293
H	3.801124	-0.635742	8.009272
H	3.340775	-1.082850	6.378690
H	3.176524	-3.125602	7.569571
H	2.566095	-2.354569	9.021301
H	0.823735	-3.721465	7.924418
H	0.349738	-2.045465	8.080890
H	-0.335015	-2.875490	5.914214
H	1.302648	-3.460063	5.546506
H	3.004697	1.450304	5.401327
H	2.610002	0.145428	4.239890
H	2.128194	1.830610	3.898140
H	-1.525710	-3.547293	2.793886
H	-5.277693	-1.498107	2.959108
H	-6.428000	-3.631580	3.577971
H	-5.105552	-5.723166	3.820836
H	0.580215	-0.359708	0.972857
H	-3.142342	1.731902	0.687912
H	-3.001633	1.658171	-1.811228
H	0.729969	-0.456925	-1.516437
H	-1.061137	0.557199	-2.906527
H	0.474132	-1.335526	4.598735

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Bifunctional pathway involving the acidic proton and the basic S=O moiety of PAA

Tetrahedral intermediate

Energy: -1910.422948 H

C	-0.315362	5.632852	8.531632
C	0.415637	5.478426	7.357939
C	1.669144	6.063384	7.196993
C	2.197926	6.812666	8.246997
C	1.479193	6.983024	9.429363
C	0.222526	6.393579	9.567170
O	-0.192303	4.769385	6.321247
P	0.542646	3.452689	5.654051
N	-0.664743	2.838880	4.658018
S	-2.120887	2.530658	5.099383
C	-2.414076	0.812571	4.432548
F	-2.204681	0.793665	3.127994
O	0.656386	2.524385	7.011558
C	1.203580	1.243363	6.997710
C	2.423855	0.960773	6.387740
C	2.924108	-0.338460	6.464522
C	2.225659	-1.332560	7.147997
C	1.011148	-1.026056	7.761420
C	0.492107	0.264543	7.687457
O	1.810819	3.690803	4.888196
O	-3.109995	3.324391	4.211709
O	-2.528261	2.520253	6.492282
F	-1.587198	-0.029482	5.025603
F	-3.662078	0.452228	4.682871
O	-2.395035	4.569909	2.258025
C	-3.165822	5.763058	2.098338
C	-1.014875	4.556445	1.736873
C	-0.146664	5.576986	2.526343
C	0.269929	6.787248	1.686152
C	1.347578	6.470304	0.629774
C	1.278704	5.046105	0.070340
C	-0.081532	4.627807	-0.472219
O	-1.182691	4.890727	0.407923
O	-0.602026	3.259040	1.846350
H	-0.704810	5.905097	3.409321
H	0.735844	5.057283	2.913526
H	0.641573	7.569978	2.357200
H	-0.617123	7.197512	1.193253
H	2.341404	6.603772	1.073864
H	1.277400	7.200856	-0.185627
H	2.005814	4.931174	-0.743288
H	1.581232	4.332053	0.843771
H	-0.070908	3.560524	-0.721659
H	-0.333833	5.190671	-1.376510
H	-0.357734	3.069106	2.775411
H	-2.692963	3.854090	3.341438
H	-3.240551	6.003864	1.037531
H	-4.155641	5.544470	2.502371
H	-2.726363	6.601854	2.649031
H	-0.452710	0.527954	8.151515
H	0.460092	-1.793131	8.298158
H	2.626325	-2.340418	7.204368
H	3.872730	-0.569190	5.987851
H	2.956620	1.745084	5.861768
H	-1.285874	5.155121	8.615505
H	-0.342045	6.519551	10.486700
H	1.896649	7.572078	10.240702
H	3.177525	7.268609	8.134012
H	2.214513	5.920022	6.270388

Ring-opened product

Energy: -1910.455762 H

C	4.269495	11.910394	0.752316
C	4.716134	10.716401	1.310968
C	5.717632	10.687558	2.275390
C	6.285148	11.889965	2.690883
C	5.858414	13.098476	2.140162
C	4.855345	13.104014	1.171815
O	4.121267	9.497456	0.974911
P	4.155694	8.951445	-0.566776
O	3.311874	9.646309	-1.587789
N	3.640193	7.328709	-0.369557
S	4.238235	6.232555	0.699388
C	4.859313	4.914875	-0.468498
F	5.823917	5.395269	-1.231301
O	3.136382	5.585940	1.405907
O	5.400692	6.754923	1.390262
F	5.327668	3.900662	0.243742
F	3.866358	4.487994	-1.233563
O	5.777615	8.910841	-0.789895
C	6.408069	8.548697	-1.979373
C	5.825628	8.698129	-3.235402
C	6.561425	8.323338	-4.359906
C	7.855293	7.822271	-4.234453
C	8.423749	7.693158	-2.967095
C	7.702200	8.054314	-1.832942
O	0.286035	5.569170	2.081095
C	0.044698	4.191749	1.831343
C	-0.260829	3.889354	0.365062
C	-1.647461	4.342092	-0.106850
C	-2.001977	5.827453	0.042743
C	-1.244485	6.793507	-0.892982
C	0.182811	7.138955	-0.539648
O	0.458524	8.051098	0.392382
C	-0.519028	8.547525	1.309893
O	1.130767	6.664698	-1.155194
H	-3.066037	5.940469	-0.198358
H	-0.078742	9.445555	1.743494
H	2.651523	7.130239	-0.692922
H	1.216855	5.738921	1.875429
H	-1.807497	7.731568	-0.968080
H	-1.197226	6.367878	-1.899066
H	-1.883174	6.133644	1.084589
H	-1.776887	4.052885	-1.158819
H	-2.402139	3.772828	0.453750
H	-0.194717	2.802771	0.217822
H	0.525376	4.329412	-0.258235
H	0.902478	3.589954	2.161511
H	-0.808470	3.902826	2.459603
H	-0.692163	7.799775	2.086278
H	-1.454538	8.812503	0.809676
H	8.118865	7.955187	-0.836118
H	9.432486	7.305614	-2.856183
H	8.418687	7.536478	-5.117743
H	6.112512	8.433176	-5.343094
H	4.824096	9.103630	-3.326187
H	6.033387	9.731833	2.679930
H	7.067174	11.879375	3.444784
H	6.306264	14.033025	2.465074
H	4.519199	14.042372	0.739892
H	3.485296	11.893994	0.002730

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Transition state for the nucleophilic addition TS'$_3$

Energy: -1910.422566 H

C	-2.625006	1.096244	4.825839
F	-2.426556	0.843995	3.536708
S	-2.312263	2.900646	5.173551
O	-3.231218	3.569810	4.218014
N	-0.809862	3.069916	4.658819
O	-2.550225	3.085376	6.596640
F	-1.811870	0.339167	5.543382
F	-3.879739	0.795921	5.132570
O	-0.529289	3.163949	2.101109
C	-0.821812	4.344090	1.675344
C	-0.497055	5.570157	2.526748
C	-0.103995	6.771480	1.663857
C	1.253946	6.603365	0.947173
C	1.613536	5.158981	0.573987
C	0.558965	4.419353	-0.235997
O	-0.766073	4.512925	0.342867
O	-2.698096	4.254535	1.734530
C	-3.496276	5.362462	1.329218
H	-1.339151	5.808836	3.181547
H	0.325180	5.281339	3.192108
H	-0.064554	7.658367	2.305108
H	-0.892739	6.955777	0.928233
H	2.053168	6.979001	1.596309
H	1.265087	7.236165	0.051509
H	2.541846	5.148639	-0.009807
H	1.832663	4.586964	1.483755
H	0.819116	3.360610	-0.341532
H	0.433078	4.853450	-1.231004
H	-0.557145	3.107665	3.147239
H	-2.921447	3.979414	2.669347
H	-3.223944	5.594067	0.299177
H	-4.550330	5.073816	1.371406
H	-3.335558	6.240165	1.965800
P	0.480579	3.597407	5.585080
O	1.682561	3.844619	4.711438
O	-0.125149	4.908973	6.375776
O	0.706785	2.611981	6.888591
C	0.559856	5.495227	7.436823
C	1.223304	1.324566	6.803783
C	0.720885	0.412144	7.729692
C	1.216160	-0.888808	7.741787
C	2.201841	-1.276537	6.833998
C	2.694316	-0.349967	5.917118
C	2.215917	0.960048	5.896186
H	-0.050939	0.734690	8.420718
H	0.824590	-1.601758	8.461979
H	2.583820	-2.293144	6.842982
H	3.465551	-0.641426	5.209371
H	2.599886	1.693045	5.195212
C	-0.125229	5.616195	8.642028
C	0.494807	6.261153	9.709635
C	1.786188	6.770615	9.572524
C	2.457656	6.636239	8.358099
C	1.847066	6.002690	7.276795
H	-1.124704	5.201765	8.721498
H	-0.033493	6.359844	10.653836
H	2.267131	7.269456	10.408908
H	3.463995	7.029939	8.245104
H	2.354030	5.889351	6.324354

Transition state for the ring-opening TS'$_4$

Energy: -1910,422245 H

C	5.196496	12.105092	0.252902
C	5.362729	11.135994	1.240223
C	6.327777	11.273216	2.234565
C	7.147224	12.399240	2.234344
C	7.005948	13.374627	1.247502
C	6.031966	13.220969	0.262305
O	4.545927	10.014003	1.331892
P	4.024705	9.184645	0.014572
O	3.155692	9.904780	-0.976870
N	3.251320	7.826550	0.615801
S	3.526229	7.064531	1.970759
C	5.163708	6.181707	1.788342
F	6.163636	7.049213	1.810979
O	2.594248	5.890851	2.011553
O	3.647311	7.833471	3.199570
F	5.317152	5.325262	2.789838
F	5.200671	5.509479	0.644149
O	5.512937	8.717601	-0.561896
C	5.705119	7.996571	-1.728337
C	4.829180	8.027794	-2.813710
C	5.138545	7.279529	-3.949622
C	6.304763	6.519765	-4.013521
C	7.175651	6.510124	-2.923890
C	6.879908	7.245279	-1.779788
O	0.664900	5.514019	0.504995
C	1.156760	4.744792	-0.624619
C	0.175694	4.763607	-1.779916
C	-1.274853	4.431325	-1.418337
C	-1.898137	5.340088	-0.340279
C	-1.393810	6.786767	-0.379419
C	-0.007905	7.058924	0.207910
O	0.070393	7.587366	1.447821
C	-0.728709	7.055045	2.503962
O	0.805779	7.660425	-0.631998
H	-2.985201	5.355204	-0.475352
H	-0.503775	7.672504	3.372720
H	1.672672	7.878839	-0.176227
H	1.471431	5.702739	1.143357
H	-2.086334	7.442029	0.159526
H	-1.363758	7.160362	-1.406897
H	-1.718954	4.921368	0.653666
H	-1.865218	4.510939	-2.338977
H	-1.354656	3.386213	-1.095965
H	0.542945	4.042481	-2.519756
H	0.225414	5.742944	-2.266129
H	2.126272	5.149018	-0.931387
H	1.301723	3.731918	-0.234393
H	-0.458652	6.017619	2.715304
H	-1.796903	7.124996	2.274494
H	7.543335	7.249039	-0.921194
H	8.091431	5.926480	-2.960263
H	6.536815	5.945016	-4.905422
H	4.458233	7.304266	-4.796876
H	3.935268	8.639812	-2.766607
H	6.418226	10.500652	2.991099
H	7.901289	12.510146	3.008661
H	7.649140	14.249811	1.248159
H	5.911345	13.978102	-0.507621
H	4.427965	11.978568	-0.502238

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Monofunctional pathway: activation by the acidic proton of PAA

Tetrahedral intermediate

Energy: -1910.448314 H

C	0.736654	-6.024689	4.154107
C	-0.357039	-6.770328	3.723851
C	-0.253529	-7.674860	2.670367
C	0.976663	-7.812385	2.027945
C	2.082356	-7.069355	2.438379
C	1.959165	-6.179035	3.504725
O	-1.530690	-6.618535	4.463512
P	-3.009120	-6.426218	3.789626
O	-3.928892	-6.505632	5.139292
C	-3.872062	-7.634172	5.963780
C	-3.396719	-7.457887	7.258369
C	-3.393565	-8.548006	8.125650
C	-3.853419	-9.792837	7.695503
C	-4.323800	-9.947426	6.392233
C	-4.341884	-8.864426	5.514418
N	-3.175328	-4.779150	3.361239
O	-3.377847	-7.304814	2.632351
O	-4.814645	-4.145025	1.183467
C	-4.490996	-4.641441	-0.109568
O	-5.049307	-3.828274	-1.096135
C	-4.679906	-2.452423	-1.043989
O	-3.097248	-4.585681	-0.074997
C	-2.435924	-4.836351	-1.316768
C	-1.978573	-6.279347	-1.479825
C	-3.068380	-7.334794	-1.214611
C	-4.511387	-6.872177	-1.457179
C	-5.074568	-6.043292	-0.297281
H	-3.743178	-4.605401	2.506023
H	-6.158449	-5.923597	-0.418347
H	-4.933410	-2.010437	-0.075966
H	-5.148488	-7.758882	-1.555420
H	-5.763956	-4.256059	1.316918
H	-5.249766	-1.960477	-1.834183
H	-3.609294	-2.311843	-1.226297
H	-4.893348	-6.584147	0.637612
H	-4.608189	-6.327063	-2.404510
H	-2.859558	-8.216156	-1.832207
H	-2.997891	-7.667629	-0.173141
H	-1.603087	-6.368760	-2.508348
H	-1.123860	-6.468478	-0.821091
H	-3.097352	-4.545158	-2.140191
H	-1.571576	-4.164296	-1.333600
H	-1.120592	-8.248693	2.364834
H	1.067919	-8.515197	1.204490
H	3.036691	-7.187190	1.933619
H	2.815778	-5.598892	3.835699
H	0.613984	-5.339721	4.986149
H	-4.707206	-8.962264	4.497648
H	-4.684831	-10.914294	6.053328
H	-3.846596	-10.639896	8.375186
H	-3.026250	-8.422622	9.140169
H	-3.040727	-6.479243	7.561858
S	-3.024780	-3.470387	4.367141
O	-4.219609	-2.648266	4.291510
O	-2.420317	-3.884797	5.619600
C	-1.716173	-2.507964	3.444091
F	-1.504575	-1.365301	4.081543
F	-0.585582	-3.192634	3.395870
F	-2.122868	-2.251070	2.212131

Ring-opened product

Energy: -1910.461865 H

C	-0.497079	-8.364597	3.097647
C	-0.456056	-7.423271	4.123226
C	0.752573	-6.934740	4.613417
C	1.944611	-7.391038	4.057270
C	1.926604	-8.324822	3.021132
C	0.707015	-8.805238	2.548271
O	-1.597921	-6.959116	4.773894
P	-3.028923	-6.646728	4.041792
N	-2.916673	-5.098061	3.324825
S	-2.411174	-3.704731	4.053773
O	-1.874989	-3.986360	5.372471
O	-3.935656	-6.334560	5.365827
C	-4.113646	-7.313224	6.348413
C	-4.816487	-8.481175	6.068954
C	-5.026191	-9.396893	7.099133
C	-4.548720	-9.138534	8.383324
C	-3.851658	-7.958056	8.641104
C	-3.625843	-7.036773	7.620829
O	-3.542278	-7.641031	3.044532
C	-0.940097	-3.306989	2.974555
F	-0.036851	-4.269690	3.031188
O	-3.356043	-2.634695	3.788066
F	-1.331833	-3.161806	1.710147
F	-0.393742	-2.172248	3.385075
O	-4.620599	-4.782140	1.273059
C	-4.469860	-5.289502	0.166603
O	-5.397417	-5.179174	-0.778544
C	-6.511697	-4.336987	-0.456306
C	-3.303490	-6.164518	-0.202953
C	-3.080879	-6.502601	-1.680097
C	-2.274526	-5.499829	-2.520945
C	-2.959356	-4.181921	-2.934998
C	-2.631660	-2.971292	-2.076409
O	-3.176149	-3.160161	-0.781387
H	-3.573411	-4.963791	2.502456
H	-3.459844	-7.084753	0.376187
H	-7.018846	-4.696469	0.441455
H	-2.533767	-7.452806	-1.706281
H	-2.889909	-2.448288	-0.199918
H	-7.174382	-4.385011	-1.320006
H	-6.163660	-3.315272	-0.290892
H	-2.415947	-5.694849	0.231265
H	-4.044960	-6.699063	-2.162201
H	-1.986530	-6.029944	-3.437035
H	-1.330643	-5.274644	-2.004468
H	-4.047433	-4.311290	-2.962509
H	-2.652584	-3.927934	-3.957424
H	-3.051034	-2.067168	-2.546021
H	-1.538577	-2.840972	-2.029169
H	-1.451833	-8.737037	2.744734
H	0.684416	-9.538456	1.746795
H	2.857783	-8.678335	2.588308
H	2.889351	-7.011656	4.436190
H	0.738923	-6.205513	5.416479
H	-5.183119	-8.660664	5.063942
H	-5.571189	-10.313895	6.893882
H	-4.720483	-9.854430	9.181795
H	-3.477402	-7.751882	9.639814
H	-3.083761	-6.112435	7.789561

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Transition state for the nucleophilic addition TS"$_3$

Energy: -1910.398275 H

C	0.699056	-5.900618	4.184154
C	-0.383606	-6.673931	3.774526
C	-0.265063	-7.602138	2.742823
C	0.966357	-7.735694	2.102078
C	2.060166	-6.964276	2.492048
C	1.923130	-6.050328	3.536513
O	-1.557085	-6.529761	4.511778
P	-3.038730	-6.340448	3.836293
O	-3.960048	-6.511771	5.176616
C	-3.883940	-7.683893	5.934532
C	-3.369522	-7.584901	7.222520
C	-3.346917	-8.723129	8.025288
C	-3.826534	-9.939294	7.538383
C	-4.336321	-10.016547	6.243065
C	-4.373374	-8.884689	5.429818
N	-3.247544	-4.686742	3.478484
O	-3.365467	-7.181817	2.637808
O	-4.754708	-4.273712	1.287288
C	-4.343749	-4.796223	0.130204
O	-5.259742	-3.532036	-0.691677
C	-4.554048	-2.449453	-1.276173
O	-3.035781	-4.605475	-0.093445
C	-2.480370	-4.971103	-1.371348
C	-2.006330	-6.409672	-1.451129
C	-3.099526	-7.456661	-1.166010
C	-4.527481	-6.953978	-1.403420
C	-5.041823	-6.086834	-0.252172
H	-3.852803	-4.498373	2.632180
H	-6.095850	-5.830107	-0.387300
H	-3.584326	-2.284285	-0.790005
H	-5.200406	-7.816835	-1.465196
H	-5.297409	-3.493187	0.535408
H	-5.160455	-1.544813	-1.165961
H	-4.399751	-2.633915	-2.344783
H	-4.976297	-6.673162	0.673496
H	-4.619563	-6.440201	-2.368871
H	-2.910054	-8.345010	-1.778549
H	-3.027140	-7.779845	-0.121717
H	-1.613061	-6.536335	-2.468723
H	-1.159921	-6.551125	-0.771008
H	-3.218732	-4.753294	-2.149525
H	-1.641061	-4.284480	-1.508125
H	-1.123434	-8.197369	2.454584
H	1.069372	-8.459015	1.297783
H	3.016178	-7.079477	1.989744
H	2.770586	-5.448675	3.852428
H	0.566258	-5.199021	5.000556
H	-4.769672	-8.921184	4.420710
H	-4.713568	-10.960686	5.860410
H	-3.805002	-10.824003	8.168009
H	-2.949407	-8.657783	9.034084
H	-2.999693	-6.626764	7.571509
S	-3.071137	-3.416477	4.521246
O	-4.262995	-2.587827	4.510580
O	-2.423423	-3.862546	5.741684
C	-1.796765	-2.423436	3.583747
F	-1.563632	-1.295786	4.239838
F	-0.664500	-3.099691	3.471945
F	-2.247530	-2.133978	2.371241

Transition state for the ring-opening TS"$_4$

Energy: -1910.404412 H

C	-0.574586	-8.543320	3.183111
C	-0.480807	-7.555824	4.160778
C	0.752429	-7.111885	4.630614
C	1.917242	-7.661479	4.100908
C	1.846653	-8.642478	3.111810
C	0.602261	-9.077420	2.659039
O	-1.602189	-7.009936	4.783016
P	-2.940579	-6.513193	3.978465
N	-2.621314	-4.964020	3.337201
S	-2.072447	-3.646153	4.169179
O	-1.598351	-4.039591	5.483776
O	-3.894161	-6.157321	5.259534
C	-4.198394	-7.133148	6.212287
C	-4.934186	-8.263043	5.867670
C	-5.266352	-9.174513	6.869019
C	-4.877209	-8.949051	8.188696
C	-4.145012	-7.806357	8.511461
C	-3.796677	-6.890679	7.521270
O	-3.489613	-7.410564	2.910364
C	-0.551922	-3.263600	3.154573
F	0.314167	-4.261870	3.209066
O	-2.952656	-2.511794	3.949849
F	-0.894581	-3.060324	1.887396
F	0.019836	-2.166618	3.628235
O	-3.973168	-4.308419	1.132548
C	-3.864871	-4.958734	-0.027422
O	-5.015959	-5.362788	-0.613176
C	-6.224898	-4.750164	-0.157660
C	-2.743614	-5.935157	-0.277472
C	-2.569759	-6.326121	-1.747855
C	-2.278463	-5.183829	-2.737770
C	-3.470984	-4.258847	-3.044694
C	-3.653068	-3.110232	-2.051788
O	-3.318548	-3.548243	-0.735516
H	-3.169588	-4.733951	2.454279
H	-2.950449	-6.821545	0.333395
H	-6.353559	-4.898336	0.915676
H	-1.740778	-7.042064	-1.797040
H	-3.680195	-3.321796	0.354489
H	-7.024208	-5.242932	-0.711833
H	-6.236890	-3.676836	-0.373766
H	-1.830877	-5.475279	0.111803
H	-3.462011	-6.868549	-2.083014
H	-1.963242	-5.646160	-3.680608
H	-1.422185	-4.592227	-2.387984
H	-4.384617	-4.860272	-3.085631
H	-3.348088	-3.809120	-4.037324
H	-4.675784	-2.714063	-2.086555
H	-2.961135	-2.290763	-2.277166
H	-1.549453	-8.875086	2.844921
H	0.539361	-9.846870	1.894516
H	2.756755	-9.068390	2.699725
H	2.881886	-7.317992	4.463541
H	0.778643	-6.345201	5.397579
H	-5.230922	-8.417373	4.835665
H	-5.837800	-10.062202	6.612876
H	-5.144518	-9.661312	8.963813
H	-3.838168	-7.626245	9.537813
H	-3.222138	-5.996877	7.739873

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