

# DFT Investigations on the Ring-Opening Polymerization of Trimethylene Carbonate Catalysed by Heterocyclic Nitrogen Bases

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## 1. Quantum chemical calculations

All calculations in this study were conducted with the Gaussian 16 program package.[29] Geometries of the chemical relevant species were obtained by density functional theory (DFT) from optimizations using the hybrid meta-GGA exchange–correlation functional M06-2X [30] together with the 6-31+G(d,p) basis set. In all calculations solvent effects were taken into account by using the SMD continuum solvation model [33] with the parameters of dichloromethane. Frequency analysis confirmed optimized geometries as energy minimum by the non-existence of imaginary frequencies or as transition states by the existence of a sole imaginary frequency that links reactants and products along the reaction coordinate.

## Coordinates of selected structures of the H-bond / alcohol activation pathway of the TBD catalysed ring-opening polymerization of TMC

### TS1

O	-1.903523000	-0.330567000	-1.260954000
C	-2.202886000	-0.972302000	-0.094736000
C	-2.534616000	0.929097000	-1.530911000
H	-2.066643000	1.694119000	-0.903188000
H	-2.318477000	1.138113000	-2.580321000
O	-3.495993000	-0.912675000	0.326886000
O	-1.558625000	-1.982505000	0.182723000
C	-4.209481000	0.318571000	0.152749000
H	-5.251773000	0.079791000	0.371651000
H	-3.835011000	1.039212000	0.887505000
C	-4.023265000	0.838238000	-1.259236000
H	-4.495100000	0.156444000	-1.975182000
H	-4.485579000	1.824605000	-1.361534000
N	0.850463000	0.981602000	0.450669000
C	1.325902000	2.343441000	0.633427000
C	1.693962000	0.015840000	0.121611000
N	2.999994000	0.250674000	-0.139704000
C	3.543474000	1.610843000	-0.176075000
N	1.228015000	-1.251528000	0.065362000
C	3.955431000	-0.811951000	-0.464612000

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H	4.138861000	-0.804316000	-1.547456000
H	4.898204000	-0.565096000	0.034841000
C	3.454533000	-2.175982000	-0.019418000
H	3.499076000	-2.257201000	1.071792000
C	2.016455000	-2.345185000	-0.479608000
H	4.092129000	-2.952503000	-0.448960000
H	1.969372000	-2.356659000	-1.577581000
H	1.586488000	-3.279091000	-0.112245000
H	0.215115000	-1.388649000	0.136438000
H	0.476305000	3.016056000	0.487212000
H	1.690924000	2.491207000	1.660356000
H	4.253351000	1.654632000	-1.008721000
C	2.441973000	2.642643000	-0.356064000
H	4.102170000	1.797903000	0.750376000
H	2.851458000	3.643018000	-0.193914000
H	2.047029000	2.594173000	-1.376793000
O	-1.497294000	0.443632000	1.062914000
C	-1.528410000	0.017070000	2.393032000
H	-0.272693000	0.711218000	0.715464000
H	-2.437097000	0.367631000	2.907142000
H	-1.500973000	-1.082422000	2.464120000
H	-0.661392000	0.407569000	2.951202000

# INT1

O	-1.877341000	-0.426536000	-1.103136000
C	-2.059470000	-0.561768000	0.302188000
C	-2.768430000	0.473592000	-1.757612000
H	-2.566233000	1.502617000	-1.432153000
H	-2.542547000	0.396570000	-2.824709000
O	-3.411550000	-0.891685000	0.595389000
O	-1.251555000	-1.432226000	0.805308000
C	-4.380361000	-0.003298000	0.048179000
H	-5.355556000	-0.415840000	0.320528000
H	-4.282401000	0.990128000	0.509249000
C	-4.211086000	0.095183000	-1.460210000
H	-4.438478000	-0.874716000	-1.917166000
H	-4.895128000	0.843565000	-1.874369000
N	0.993081000	1.038008000	0.255169000
C	1.516225000	2.391516000	0.359959000
C	1.778434000	-0.032036000	0.039192000
N	3.096082000	0.138801000	-0.183911000
C	3.714072000	1.463213000	-0.295913000
N	1.224434000	-1.239235000	0.050218000
C	4.012487000	-0.998742000	-0.311547000
H	4.251806000	-1.142768000	-1.372942000
H	4.937663000	-0.728880000	0.207852000
C	3.413592000	-2.264167000	0.280627000
H	3.389197000	-2.192268000	1.373224000
C	1.997219000	-2.434848000	-0.247383000
H	4.035069000	-3.120208000	0.006781000
H	2.017702000	-2.619447000	-1.329724000
H	1.493701000	-3.279592000	0.227236000
H	0.177482000	-1.317725000	0.320454000

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H	0.704983000	3.078919000	0.112463000
H	1.842240000	2.602335000	1.387101000
H	4.460162000	1.405846000	-1.094984000
C	2.684295000	2.538310000	-0.602077000
H	4.241061000	1.688164000	0.640455000
H	3.148094000	3.521996000	-0.497297000
H	2.324404000	2.433309000	-1.630919000
O	-1.833528000	0.801857000	0.785872000
C	-1.917705000	0.915123000	2.194110000
H	-0.012446000	0.884106000	0.371338000
H	-2.930343000	0.689776000	2.550167000
H	-1.209801000	0.237878000	2.685271000
H	-1.669657000	1.949463000	2.447264000

# *INT2*

O	1.991242000	0.575542000	-0.797213000
C	2.132032000	-0.691138000	-0.079239000
C	2.772888000	1.650994000	-0.286154000
H	3.840728000	1.421050000	-0.407629000
H	2.536808000	2.523996000	-0.902090000
O	1.836229000	-0.455339000	1.290644000
O	1.332934000	-1.561983000	-0.598928000
C	2.605631000	0.564787000	1.921850000
H	2.232298000	0.630491000	2.947449000
H	3.662171000	0.269383000	1.954575000
C	2.444421000	1.883452000	1.180786000
H	1.408353000	2.232595000	1.274494000
H	3.106718000	2.644738000	1.606713000
N	-0.889231000	0.878108000	-0.636258000
C	-1.376617000	2.200198000	-0.997706000
C	-1.698709000	-0.103118000	-0.200489000
N	-3.007535000	0.145367000	-0.001034000
C	-3.589128000	1.482140000	-0.153677000
N	-1.174358000	-1.302620000	0.025058000
C	-3.944555000	-0.915021000	0.382461000
H	-4.158165000	-0.827663000	1.455526000
H	-4.877534000	-0.735252000	-0.161345000
C	-3.389706000	-2.291955000	0.055222000
H	-3.391386000	-2.448839000	-1.028711000
C	-1.964773000	-2.390021000	0.578829000
H	-4.023853000	-3.054760000	0.513456000
H	-1.962041000	-2.347575000	1.676299000
H	-1.493631000	-3.328205000	0.278427000
H	-0.121460000	-1.430352000	-0.186288000
H	-0.544050000	2.899675000	-0.895944000
H	-1.710512000	2.217796000	-2.043349000
H	-4.327284000	1.606729000	0.644937000
C	-2.526578000	2.566043000	-0.073071000
H	-4.120132000	1.531324000	-1.113149000
H	-2.964773000	3.523579000	-0.364279000
H	-2.155620000	2.653307000	0.953743000
O	3.513635000	-1.030031000	-0.102029000

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C	3.984106000	-1.376217000	-1.389307000
H	0.108545000	0.671266000	-0.734455000
H	3.448823000	-2.246524000	-1.782889000
H	3.873036000	-0.541453000	-2.093159000
H	5.044437000	-1.617673000	-1.283514000

TS2

O	1.642038000	0.837268000	-0.665473000
C	2.332451000	-0.911462000	-0.095741000
C	2.183747000	1.869387000	0.108550000
H	3.262000000	1.975458000	-0.109333000
H	1.715522000	2.835861000	-0.144916000
O	2.054740000	-0.822482000	1.231151000
O	1.670883000	-1.690138000	-0.785225000
C	2.636790000	0.258900000	1.979076000
H	2.441976000	0.005317000	3.023564000
H	3.719492000	0.274029000	1.818607000
C	2.006837000	1.587847000	1.601097000
H	0.936144000	1.562013000	1.842912000
H	2.471279000	2.379337000	2.202209000
N	-0.872130000	0.923398000	-0.666010000
C	-1.479046000	2.202481000	-0.999840000
C	-1.627714000	-0.083098000	-0.245400000
N	-2.955488000	0.058580000	-0.031177000
C	-3.618153000	1.364153000	-0.093638000
N	-1.049964000	-1.279104000	-0.034759000
C	-3.827122000	-1.062374000	0.330132000
H	-4.056145000	-1.000162000	1.402413000
H	-4.766256000	-0.935547000	-0.218991000
C	-3.189508000	-2.401974000	0.000416000
H	-3.174197000	-2.557088000	-1.083535000
C	-1.764979000	-2.410256000	0.531827000
H	-3.777843000	-3.202806000	0.454991000
H	-1.770523000	-2.358207000	1.629064000
H	-1.233007000	-3.317550000	0.239429000
H	-0.059028000	-1.385346000	-0.280640000
H	-0.697267000	2.964206000	-0.946140000
H	-1.862106000	2.192425000	-2.030061000
H	-4.317467000	1.416502000	0.747975000
C	-2.613923000	2.503359000	-0.031699000
H	-4.205269000	1.417748000	-1.019669000
H	-3.114231000	3.440291000	-0.289758000
H	-2.210437000	2.596590000	0.982680000
O	3.639609000	-0.642118000	-0.339519000
C	3.996073000	-0.669574000	-1.717705000
H	0.277803000	0.839987000	-0.661718000
H	3.902845000	-1.680860000	-2.121862000
H	3.353376000	0.016369000	-2.275959000
H	5.035538000	-0.343246000	-1.767557000

**Coordinates of selected structures of the nucleophilic mechanism of the TBD catalysed ring-opening polymerization of TMC**

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*TS1*

O	1.842261000	-0.845312000	-0.841875000
C	1.783981000	0.561015000	-0.758193000
C	3.102128000	-1.354811000	-0.376162000
H	3.121457000	-2.408935000	-0.656856000
H	3.909018000	-0.840226000	-0.909561000
O	2.433573000	1.016828000	0.373476000
O	1.873948000	1.238019000	-1.776571000
C	2.408426000	0.111071000	1.477458000
H	2.823895000	0.656078000	2.326360000
H	1.364772000	-0.141251000	1.696064000
C	3.215323000	-1.144958000	1.134825000
H	4.267374000	-1.029296000	1.411914000
H	2.811180000	-2.000934000	1.683909000
N	-0.010048000	0.760398000	-0.167583000
C	-0.339964000	2.173406000	-0.267463000
C	-0.998976000	-0.099126000	-0.029011000
N	-2.302302000	0.279400000	0.098716000
C	-2.687940000	1.676154000	0.299343000
N	-0.720924000	-1.429095000	0.015727000
C	-3.411898000	-0.673446000	0.134675000
H	-3.738630000	-0.814068000	1.174944000
H	-4.244455000	-0.221882000	-0.415758000
C	-3.023879000	-2.005693000	-0.481078000
H	-2.883212000	-1.894577000	-1.561679000
C	-1.726422000	-2.469130000	0.159195000
H	-3.821046000	-2.733243000	-0.308712000
H	-1.897804000	-2.696777000	1.220080000
H	-1.344323000	-3.372403000	-0.320598000
H	0.225122000	-1.663672000	-0.258530000
H	0.562525000	2.736570000	-0.016371000
H	-0.611566000	2.437599000	-1.299826000
H	-3.445945000	1.700983000	1.090982000
C	-1.484270000	2.522509000	0.671942000
H	-3.154837000	2.053287000	-0.620346000
H	-1.744651000	3.581819000	0.596719000
H	-1.183265000	2.317770000	1.705805000

*INT1*

O	1.739296000	-0.920659000	-0.777374000
C	1.588517000	0.519522000	-0.730063000
C	3.042611000	-1.332347000	-0.366428000
H	3.147992000	-2.376945000	-0.667033000
H	3.789596000	-0.741243000	-0.907571000
O	2.311543000	0.987772000	0.416256000
O	1.865688000	1.146788000	-1.778534000
C	2.322185000	0.080275000	1.509411000
H	2.721540000	0.624922000	2.368143000
H	1.293873000	-0.223825000	1.748370000
C	3.177419000	-1.139694000	1.146501000
H	4.228141000	-0.977938000	1.407519000
H	2.824496000	-2.021766000	1.691018000
N	0.055144000	0.743444000	-0.314429000

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C	-0.258450000	2.172625000	-0.380150000
C	-0.946714000	-0.119158000	-0.108012000
N	-2.210803000	0.320321000	0.114721000
C	-2.543386000	1.720918000	0.385603000
N	-0.729135000	-1.447441000	-0.109476000
C	-3.362300000	-0.584051000	0.207694000
H	-3.636313000	-0.700316000	1.264872000
H	-4.196847000	-0.090181000	-0.300770000
C	-3.076023000	-1.936053000	-0.416566000
H	-3.003663000	-1.845652000	-1.505417000
C	-1.759392000	-2.442409000	0.142790000
H	-3.889836000	-2.625183000	-0.179019000
H	-1.855960000	-2.633274000	1.219670000
H	-1.445399000	-3.369378000	-0.340029000
H	0.219170000	-1.721990000	-0.347293000
H	0.675948000	2.707148000	-0.215521000
H	-0.624601000	2.433887000	-1.381289000
H	-3.229996000	1.734880000	1.239269000
C	-1.293117000	2.525327000	0.670142000
H	-3.077100000	2.129159000	-0.482013000
H	-1.526858000	3.592362000	0.636971000
H	-0.900940000	2.290114000	1.666088000

#### TS2

O	1.687940000	-0.827592000	-1.116190000
C	1.336265000	0.830085000	-0.210509000
C	2.700971000	-1.536758000	-0.447381000
H	2.270291000	-2.195545000	0.334442000
H	3.225389000	-2.192621000	-1.158096000
O	1.600014000	0.360684000	1.053832000
O	2.034295000	1.684617000	-0.743414000
C	3.004132000	0.203283000	1.320745000
H	3.459513000	1.188095000	1.467937000
H	3.028710000	-0.341569000	2.267923000
C	3.699204000	-0.589452000	0.215063000
H	4.099103000	0.084329000	-0.547505000
H	4.532629000	-1.154586000	0.646382000
N	-0.103284000	0.895832000	-0.407961000
C	-0.678581000	2.200003000	-0.746058000
C	-0.964158000	-0.119011000	-0.086759000
N	-2.255827000	0.162735000	0.160640000
C	-2.794227000	1.518099000	0.319507000
N	-0.497829000	-1.353829000	-0.092444000
C	-3.241042000	-0.910655000	0.337794000
H	-3.439568000	-1.029909000	1.410422000
H	-4.168002000	-0.578808000	-0.140366000
C	-2.760463000	-2.219559000	-0.267702000
H	-2.768022000	-2.152087000	-1.360751000
C	-1.343100000	-2.495528000	0.213695000
H	-3.437201000	-3.023797000	0.031070000
H	-1.340141000	-2.689420000	1.294101000
H	-0.915064000	-3.368229000	-0.283686000
H	0.499485000	-1.355949000	-0.592669000

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H	0.143844000	2.909935000	-0.796662000
H	-1.154632000	2.151271000	-1.733126000
H	-3.369406000	1.540538000	1.251545000
C	-1.696462000	2.566919000	0.322267000
H	-3.490683000	1.696704000	-0.509114000
H	-2.135756000	3.547881000	0.123767000
H	-1.195141000	2.604375000	1.294951000

### TS3

O	-3.089645000	-1.823565000	-0.007389000
C	-0.928972000	0.404063000	-0.691890000
O	-0.183750000	2.047373000	-1.213302000
C	-1.002768000	3.139219000	-0.879691000
C	-3.967095000	-1.051213000	0.795125000
H	-4.687104000	-0.512177000	0.160322000
H	-4.535465000	-1.760790000	1.404977000
O	-1.184293000	0.675095000	0.627152000
O	-1.846614000	0.167550000	-1.487504000
C	-2.514124000	1.069316000	0.999182000
H	-2.382137000	1.915130000	1.679587000
H	-3.064669000	1.408340000	0.117359000
C	-3.261394000	-0.056039000	1.709794000
H	-2.564887000	-0.582284000	2.373729000
H	-4.028220000	0.407133000	2.344076000
N	0.297352000	-0.354609000	-0.795690000
C	0.247349000	-1.672767000	-1.429224000
C	1.435658000	-0.007282000	-0.098381000
N	2.327193000	-0.976214000	0.200924000
C	2.094128000	-2.412744000	0.022210000
N	1.615942000	1.261585000	0.186569000
C	3.631636000	-0.639035000	0.779823000
H	3.607819000	-0.863839000	1.853929000
H	4.373787000	-1.298250000	0.317316000
C	3.986104000	0.820778000	0.546401000
H	4.229711000	0.983207000	-0.509151000
C	2.791584000	1.685324000	0.927774000
H	4.864878000	1.078209000	1.143284000
H	2.606787000	1.613489000	2.008520000
H	2.974874000	2.736963000	0.695032000
H	-2.694548000	-1.218978000	-0.662140000
H	-0.767946000	-1.830396000	-1.787186000
H	0.919543000	-1.692618000	-2.296203000
H	2.340331000	-2.911469000	0.966405000
C	0.666786000	-2.712226000	-0.402045000
H	2.798829000	-2.772162000	-0.738650000
H	0.619734000	-3.720622000	-0.821361000
H	-0.015532000	-2.661787000	0.452885000
H	0.766961000	1.902273000	-0.477186000
H	-2.020532000	2.974161000	-1.255979000
H	-1.049392000	3.301327000	0.207395000
H	-0.615171000	4.053812000	-1.345689000

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*TS4*

O	-3.749022000	-1.302411000	-0.331440000
C	-1.210281000	1.281801000	-0.318057000
O	-0.507729000	2.407983000	-0.671321000
C	-0.339047000	2.568012000	-2.072117000
C	-3.545170000	-1.547496000	1.051032000
H	-4.407988000	-1.178013000	1.627875000
H	-3.501589000	-2.633548000	1.189694000
O	-1.262488000	1.314760000	1.056077000
O	-2.165507000	0.876054000	-0.999605000
C	-2.368527000	0.628070000	1.646291000
H	-2.373184000	0.974790000	2.681133000
H	-3.290809000	0.978268000	1.168738000
C	-2.267846000	-0.905686000	1.578967000
H	-1.435467000	-1.183773000	0.924146000
H	-2.048831000	-1.311379000	2.572216000
N	0.155445000	-0.028070000	-0.602990000
C	-0.183059000	-1.110735000	-1.507725000
C	1.345613000	-0.007037000	-0.044584000
N	2.273585000	-0.989222000	-0.219276000
C	1.957465000	-2.215676000	-0.951654000
N	1.694357000	1.060757000	0.726757000
C	3.612305000	-0.960095000	0.374683000
H	3.634673000	-1.650360000	1.229600000
H	4.312702000	-1.342146000	-0.376170000
C	4.013936000	0.436593000	0.817019000
H	4.237551000	1.061858000	-0.053778000
C	2.861585000	1.051061000	1.592451000
H	4.911524000	0.374877000	1.437331000
H	2.676275000	0.477347000	2.512079000
H	3.076480000	2.083778000	1.873629000
H	-3.257718000	-0.495663000	-0.586867000
H	-1.273212000	-1.190734000	-1.528633000
H	0.143216000	-0.872905000	-2.532583000
H	2.425310000	-3.048547000	-0.415360000
C	0.456241000	-2.416869000	-1.057082000
H	2.411748000	-2.166551000	-1.950479000
H	0.242404000	-3.221150000	-1.766180000
H	0.048105000	-2.705640000	-0.081377000
H	0.940301000	1.702843000	0.930346000
H	0.172115000	1.698288000	-2.499614000
H	-1.304362000	2.702486000	-2.567181000
H	0.275727000	3.458863000	-2.205034000

**Coordinates of selected structures of the H-bond / alcohol activation pathway of the DMAP catalysed ring-opening polymerization of TMC**

*INT1*

O	2.264023000	-1.234598000	0.577769000
C	2.653920000	-0.947540000	-0.666165000
C	2.957799000	-0.707978000	1.729133000
H	2.549402000	0.285888000	1.932359000
H	2.702958000	-1.386796000	2.543349000



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O	3.852872000	-0.403320000	-0.879587000
O	1.961719000	-1.273229000	-1.605546000
C	4.633242000	0.160533000	0.195889000
H	5.661496000	0.143806000	-0.166401000
H	4.301902000	1.193925000	0.333242000
C	4.442925000	-0.645389000	1.459559000
H	4.854916000	-1.652989000	1.339653000
H	4.952682000	-0.155694000	2.293597000
N	-0.716763000	0.927913000	0.117038000
C	-1.730956000	1.678711000	0.571984000
C	-1.036411000	-0.284252000	-0.365457000
C	-2.325475000	-0.785284000	-0.414573000
C	-3.399888000	0.003487000	0.067307000
H	-0.204259000	-0.881558000	-0.734009000
H	-1.464903000	2.659649000	0.959548000
C	-3.056513000	1.282192000	0.574552000
H	-3.807399000	1.958232000	0.963853000
O	1.926712000	1.606242000	-0.083915000
C	2.051458000	2.106912000	-1.400239000
H	0.969196000	1.381170000	0.058894000
H	1.726831000	1.370908000	-2.148278000
H	1.472608000	3.030000000	-1.541182000
H	3.106506000	2.334836000	-1.581817000
H	-2.488116000	-1.775560000	-0.821096000
N	-4.682379000	-0.438549000	0.045001000
C	-4.985852000	-1.760661000	-0.478078000
H	-6.060534000	-1.926895000	-0.417071000
H	-4.681871000	-1.851817000	-1.527406000
H	-4.480474000	-2.544322000	0.099115000
C	-5.747174000	0.398143000	0.572847000
H	-5.815550000	1.346668000	0.027417000
H	-6.694710000	-0.127607000	0.465767000
H	-5.591745000	0.618598000	1.635868000

# TS1

O	2.038302000	-1.233756000	0.306766000
C	2.483194000	-0.432604000	-0.746290000
C	2.565475000	-0.977350000	1.610648000
H	2.144484000	-0.041106000	1.996605000
H	2.216753000	-1.803918000	2.234387000
O	3.858292000	-0.212501000	-0.743372000
O	1.973932000	-0.664810000	-1.851041000
C	4.468068000	0.114907000	0.505659000
H	5.543892000	0.118330000	0.315542000
H	4.157912000	1.123280000	0.808563000
C	4.080585000	-0.902412000	1.563327000
H	4.494314000	-1.883123000	1.303426000
H	4.476036000	-0.605329000	2.539878000
N	-0.527257000	0.634032000	-0.041106000
C	-1.368120000	1.377504000	0.698018000
C	-1.011635000	-0.411670000	-0.736794000
C	-2.345103000	-0.749775000	-0.721715000
C	-3.259197000	0.017397000	0.052067000

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H	-0.270357000	-0.964218000	-1.308231000
H	-0.923974000	2.206740000	1.240262000
C	-2.716170000	1.115809000	0.775642000
H	-3.338585000	1.752853000	1.389949000
O	1.913182000	1.082288000	-0.149421000
C	2.181451000	2.120531000	-1.067528000
H	0.654162000	0.865728000	-0.083697000
H	2.042333000	1.771095000	-2.098440000
H	1.496828000	2.956262000	-0.879324000
H	3.211041000	2.478532000	-0.947744000
H	-2.673170000	-1.602348000	-1.301511000
N	-4.572774000	-0.280834000	0.098728000
C	-5.091071000	-1.413006000	-0.657084000
H	-6.162729000	-1.490369000	-0.482523000
H	-4.921622000	-1.280681000	-1.731424000
H	-4.618473000	-2.348813000	-0.339014000
C	-5.477140000	0.525871000	0.906292000
H	-5.481767000	1.568774000	0.570607000
H	-6.485387000	0.127619000	0.808258000
H	-5.193159000	0.497305000	1.964179000

INT2

O	2.153726000	-0.891953000	-0.632548000
C	2.406422000	0.547627000	-0.479250000
C	2.822085000	-1.747800000	0.293123000
H	2.441694000	-1.570289000	1.307563000
H	2.573101000	-2.772307000	-0.000607000
O	3.824159000	0.747436000	-0.521429000
O	1.786046000	1.213940000	-1.361143000
C	4.576042000	-0.008117000	0.419346000
H	5.625965000	0.242037000	0.241021000
H	4.316494000	0.296377000	1.443472000
C	4.320774000	-1.496887000	0.232141000
H	4.704154000	-1.812266000	-0.745075000
H	4.834521000	-2.073767000	1.008847000
N	-0.581489000	-0.545385000	-0.439833000
C	-1.370496000	-1.585732000	-0.109596000
C	-1.086123000	0.698292000	-0.571442000
C	-2.421481000	0.941506000	-0.381125000
C	-3.299001000	-0.127876000	-0.035357000
H	-0.351084000	1.451689000	-0.839182000
H	-0.881927000	-2.549103000	-0.019236000
C	-2.714646000	-1.422684000	0.098532000
H	-3.307294000	-2.288592000	0.360337000
O	1.977614000	0.767359000	0.892664000
C	2.053206000	2.123452000	1.271045000
H	0.442341000	-0.690297000	-0.570799000
H	1.430758000	2.753281000	0.624106000
H	1.690559000	2.192786000	2.300247000
H	3.086044000	2.495502000	1.229996000
H	-2.783083000	1.953879000	-0.499397000
N	-4.612220000	0.072862000	0.155001000
C	-5.180688000	1.406294000	-0.007517000

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H	-6.251853000	1.355486000	0.177274000
H	-4.736048000	2.110746000	0.703227000
H	-5.019059000	1.778670000	-1.024503000
C	-5.481295000	-1.042148000	0.512884000
H	-5.164483000	-1.497749000	1.456781000
H	-6.496770000	-0.670046000	0.632708000
H	-5.479219000	-1.808202000	-0.270002000

*TS2*

O	-1.954346000	0.900459000	-0.597249000
C	-2.501207000	-0.685823000	-0.545347000
C	-2.455216000	1.758455000	0.434583000
H	-2.077084000	1.420044000	1.407755000
H	-2.080954000	2.769173000	0.239467000
O	-3.884614000	-0.521227000	-0.561553000
O	-2.007790000	-1.298432000	-1.499695000
C	-4.453327000	0.270268000	0.484051000
H	-5.534444000	0.205885000	0.340585000
H	-4.202105000	-0.163252000	1.459601000
C	-3.972613000	1.710306000	0.392873000
H	-4.324462000	2.152678000	-0.545767000
H	-4.385746000	2.292161000	1.223476000
N	0.504073000	0.604358000	-0.378409000
C	1.367150000	1.615541000	-0.187778000
C	0.987771000	-0.650480000	-0.396920000
C	2.323906000	-0.942176000	-0.227856000
C	3.253681000	0.112575000	-0.023165000
H	0.247983000	-1.428382000	-0.565435000
H	0.942105000	2.615320000	-0.180225000
C	2.720957000	1.429936000	-0.008631000
H	3.352430000	2.295796000	0.141896000
O	-2.047905000	-0.973245000	0.766614000
C	-2.217206000	-2.344473000	1.091883000
H	-0.798656000	0.785207000	-0.514882000
H	-1.624819000	-2.981834000	0.426756000
H	-1.872600000	-2.468167000	2.120351000
H	-3.271805000	-2.640668000	1.025994000
H	2.640162000	-1.976546000	-0.260470000
N	4.572380000	-0.124064000	0.147450000
C	5.073788000	-1.490736000	0.140299000
H	6.145832000	-1.473691000	0.329266000
H	4.594523000	-2.089590000	0.922568000
H	4.898245000	-1.973564000	-0.827982000
C	5.495703000	0.986776000	0.327181000
H	5.263774000	1.552041000	1.237189000
H	6.507360000	0.593640000	0.413265000
H	5.462002000	1.670242000	-0.528672000

**Coordinates of selected structures of the nucleophilic mechanism of the DMAP catalysed ring-opening polymerization of TMC**

*TS1*

O	2.483216000	-0.355819000	-1.061244000
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C	2.068114000	0.808432000	-0.395349000
C	3.779759000	-0.778725000	-0.622726000
H	4.099931000	-1.549326000	-1.325556000
H	4.475220000	0.065573000	-0.696377000
O	2.446456000	0.780789000	0.945257000
O	2.118850000	1.906063000	-0.954314000
C	2.571419000	-0.522986000	1.514534000
H	2.773696000	-0.368161000	2.575528000
H	1.614843000	-1.050757000	1.422556000
C	3.693589000	-1.296924000	0.814319000
H	4.652299000	-1.143916000	1.318748000
H	3.467653000	-2.367382000	0.833328000
N	0.312219000	0.358184000	-0.269189000
C	-0.495302000	1.359427000	0.103309000
C	-0.222648000	-0.840004000	-0.538499000
C	-1.575974000	-1.090507000	-0.439242000
C	-2.453919000	-0.051850000	-0.029839000
H	0.475283000	-1.610018000	-0.851000000
H	-1.941042000	-2.080507000	-0.679573000
H	-0.001807000	2.311047000	0.281520000
C	-1.857548000	1.210084000	0.239920000
H	-2.449411000	2.063728000	0.543265000
N	-3.784730000	-0.249964000	0.093201000
C	-4.651498000	0.848807000	0.493496000
H	-5.675048000	0.483408000	0.556355000
H	-4.362578000	1.240283000	1.475088000
H	-4.618124000	1.667879000	-0.234461000
C	-4.361231000	-1.547869000	-0.224925000
H	-4.190898000	-1.811929000	-1.275242000
H	-3.934445000	-2.334010000	0.407672000
H	-5.434736000	-1.509031000	-0.047497000

# INT1

O	2.428694000	-0.325268000	-1.068299000
C	1.943639000	0.795480000	-0.337453000
C	3.758906000	-0.661693000	-0.674391000
H	4.139513000	-1.351938000	-1.429553000
H	4.378916000	0.242406000	-0.691280000
O	2.349263000	0.681671000	1.019869000
O	2.080537000	1.940217000	-0.814695000
C	2.557202000	-0.650399000	1.479453000
H	2.747996000	-0.576366000	2.552060000
H	1.641345000	-1.240235000	1.342169000
C	3.732125000	-1.283370000	0.725189000
H	4.679170000	-1.085066000	1.236564000
H	3.596571000	-2.368294000	0.672539000
N	0.333988000	0.398591000	-0.279515000
C	-0.487432000	1.396725000	0.088329000
C	-0.180067000	-0.814942000	-0.542781000
C	-1.527555000	-1.077686000	-0.442877000
C	-2.422022000	-0.049058000	-0.040039000
H	0.529513000	-1.572523000	-0.851912000
H	-1.877067000	-2.073872000	-0.679500000

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H	0.000330000	2.350738000	0.259128000
C	-1.842850000	1.224415000	0.222309000
H	-2.446198000	2.072001000	0.519123000
N	-3.745776000	-0.264940000	0.082957000
C	-4.629602000	0.821176000	0.485220000
H	-5.646811000	0.439410000	0.549449000
H	-4.343921000	1.216062000	1.466066000
H	-4.608993000	1.638955000	-0.243940000
C	-4.303372000	-1.576279000	-0.218962000
H	-4.129206000	-1.848321000	-1.266132000
H	-3.863410000	-2.346779000	0.423228000
H	-5.377020000	-1.550901000	-0.041097000

#### TS2

O	2.183427000	0.326149000	-0.763476000
C	1.410517000	1.211640000	-0.201097000
C	3.627847000	0.509889000	-0.611305000
H	3.958953000	1.137251000	-1.442835000
H	3.792612000	1.010363000	0.342469000
O	3.561631000	-1.047230000	1.739606000
O	1.700216000	2.290622000	0.246186000
C	3.636214000	-1.711189000	0.563080000
H	4.249598000	-2.649462000	0.596876000
H	2.639495000	-2.061605000	0.178779000
C	4.246047000	-0.866124000	-0.587892000
H	5.319735000	-0.718560000	-0.411139000
H	4.129589000	-1.364450000	-1.560591000
N	0.043138000	0.743435000	-0.175614000
C	-0.932438000	1.624205000	0.196482000
C	-0.280664000	-0.552165000	-0.471828000
C	-1.566691000	-0.989031000	-0.414567000
C	-2.619686000	-0.096493000	-0.032986000
H	0.543336000	-1.201575000	-0.736939000
H	-1.760070000	-2.026355000	-0.649867000
H	-0.593774000	2.627448000	0.422072000
C	-2.236423000	1.250151000	0.271240000
H	-2.964677000	1.993333000	0.565080000
N	-3.884577000	-0.496282000	0.039630000
C	-4.930838000	0.434475000	0.463914000
H	-5.876487000	-0.100496000	0.509459000
H	-4.707010000	0.835911000	1.456398000
H	-5.024339000	1.260142000	-0.248025000
C	-4.244715000	-1.874900000	-0.293804000
H	-3.936656000	-2.114751000	-1.315475000
H	-3.772761000	-2.575512000	0.401654000
H	-5.324682000	-1.980832000	-0.221978000

#### INT2

O	2.152755000	0.219194000	-0.423156000
C	1.350086000	1.185545000	-0.076231000
C	3.588391000	0.505100000	-0.368446000
H	3.783280000	1.323934000	-1.065439000

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H	3.818316000	0.805459000	0.655862000
O	4.258208000	-1.490289000	1.609601000
O	1.623104000	2.326077000	0.195164000
C	4.028744000	-1.881899000	0.335386000
H	4.645898000	-2.757580000	0.001988000
H	2.971899000	-2.216800000	0.146648000
C	4.307635000	-0.774228000	-0.712782000
H	5.379607000	-0.536844000	-0.703904000
H	4.041909000	-1.097961000	-1.729412000
N	-0.018719000	0.723637000	-0.055804000
C	-1.005640000	1.648263000	0.140888000
C	-0.338928000	-0.598660000	-0.206722000
C	-1.631145000	-1.018732000	-0.180142000
C	-2.695964000	-0.078374000	0.002636000
H	0.490563000	-1.281009000	-0.337991000
H	-1.823174000	-2.076679000	-0.294677000
H	-0.669430000	2.669735000	0.265436000
C	-2.316366000	1.292728000	0.172655000
H	-3.053501000	2.068376000	0.328391000
N	-3.968508000	-0.457330000	0.014274000
C	-5.031858000	0.530253000	0.200207000
H	-5.991449000	0.019421000	0.171365000
H	-4.926388000	1.030886000	1.167194000
H	-5.005621000	1.277192000	-0.598856000
C	-4.321512000	-1.865799000	-0.166428000
H	-3.971690000	-2.226775000	-1.138041000
H	-3.880946000	-2.476527000	0.626709000
H	-5.403693000	-1.962313000	-0.122867000

### TS3

N	0.104105000	1.415726000	-0.341330000
C	-0.025692000	0.243763000	-1.026353000
C	-0.902941000	1.900042000	0.425960000
C	-2.082749000	1.225170000	0.555694000
C	-2.278362000	-0.008790000	-0.136699000
H	-0.702978000	2.843098000	0.919136000
H	-2.849996000	1.651205000	1.187673000
H	0.874006000	-0.125436000	-1.617530000
C	-1.191511000	-0.468215000	-0.938757000
H	-1.254363000	-1.397309000	-1.490714000
N	-3.420270000	-0.697827000	-0.031589000
C	-3.586617000	-1.958648000	-0.749398000
H	-4.582874000	-2.346703000	-0.547175000
H	-3.481557000	-1.807939000	-1.828313000
H	-2.847938000	-2.696191000	-0.419183000
C	-4.500578000	-0.207713000	0.818942000
H	-4.173192000	-0.132705000	1.861070000
H	-4.847185000	0.774508000	0.482245000
H	-5.332692000	-0.906587000	0.765120000
O	2.232121000	-0.900755000	-2.209389000
C	1.348441000	2.211980000	-0.502946000
O	1.342403000	3.370045000	0.112158000
C	2.619550000	-1.541425000	-1.065840000

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H	1.746543000	-1.915719000	-0.462979000
H	3.222031000	-2.457352000	-1.266281000
O	2.451835000	1.432559000	-0.499298000
O	1.281408000	2.792929000	-1.920170000
C	2.687616000	0.464328000	0.539665000
H	3.254315000	0.960440000	1.335314000
H	1.733510000	0.120383000	0.957744000
C	3.452033000	-0.693957000	-0.075865000
H	4.340928000	-0.298813000	-0.585235000
H	3.798666000	-1.330002000	0.751142000
H	1.411529000	3.687911000	-1.196796000
C	2.232143000	2.357178000	-2.926786000
H	2.296411000	1.264530000	-2.865442000
H	1.829696000	2.690121000	-3.883163000
H	3.205731000	2.809831000	-2.733233000

TS4

N	0.112695000	-0.649878000	-0.188239000
C	-0.332575000	0.594355000	-0.525527000
C	-0.748280000	-1.591835000	0.281853000
C	-2.087697000	-1.350248000	0.379113000
C	-2.617429000	-0.082476000	-0.011370000
H	-0.314702000	-2.542342000	0.561136000
H	-2.722447000	-2.143998000	0.749176000
H	0.452297000	1.408037000	-0.740414000
C	-1.671213000	0.885353000	-0.451580000
H	-1.977412000	1.889468000	-0.715586000
N	-3.928596000	0.180106000	0.049272000
C	-4.436025000	1.478664000	-0.383573000
H	-5.523051000	1.461737000	-0.337472000
H	-4.066782000	2.281161000	0.263832000
H	-4.134276000	1.686297000	-1.414619000
C	-4.859104000	-0.819881000	0.563668000
H	-4.585774000	-1.118176000	1.580625000
H	-5.858274000	-0.389411000	0.586544000
H	-4.873666000	-1.707980000	-0.076896000
O	1.470158000	2.619641000	-0.842801000
C	1.586282000	-0.946591000	-0.217386000
O	2.198660000	-0.254352000	-1.231234000
C	2.361518000	2.918956000	0.151687000
H	3.155980000	3.624848000	-0.184220000
H	1.879448000	3.440905000	1.017886000
O	2.179658000	-0.644162000	0.986765000
O	1.662292000	-2.312166000	-0.399072000
C	2.150878000	0.723939000	1.454852000
H	1.118306000	1.091114000	1.409943000
H	2.407474000	0.615129000	2.510343000
C	3.102686000	1.702439000	0.751742000
H	3.847019000	2.057327000	1.477374000
H	3.638037000	1.178420000	-0.043758000
H	1.579868000	0.058694000	-1.907129000
C	2.993443000	-2.833948000	-0.421632000
H	2.894404000	-3.878316000	-0.716982000

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H	3.602970000	-2.300175000	-1.155386000
H	3.450828000	-2.768382000	0.568023000

INT3

N	0.141651000	-0.111123000	-0.629172000
C	0.531788000	0.516842000	0.496779000
C	1.047621000	-0.785400000	-1.362134000
C	2.377477000	-0.822528000	-1.026355000
C	2.832974000	-0.146875000	0.140912000
H	0.659142000	-1.295521000	-2.236505000
H	3.054454000	-1.377738000	-1.661493000
H	-0.256162000	1.003904000	1.059128000
C	1.842224000	0.529355000	0.906273000
H	2.090588000	1.054857000	1.818634000
N	4.127634000	-0.153468000	0.503108000
C	4.549277000	0.527985000	1.720524000
H	5.624777000	0.406601000	1.835607000
H	4.322371000	1.598203000	1.668624000
H	4.053574000	0.103605000	2.600474000
C	5.108251000	-0.873966000	-0.299074000
H	5.135469000	-0.487685000	-1.323451000
H	6.092003000	-0.739770000	0.146587000
H	4.881341000	-1.945346000	-0.330577000
O	-2.384080000	-0.519568000	2.105115000
C	-1.420778000	-0.301631000	-0.950820000
O	-1.870692000	-1.336593000	-0.363136000
C	-3.689655000	-0.015218000	1.909882000
H	-4.335220000	-0.786527000	1.459439000
H	-4.099252000	0.212044000	2.900905000
O	-1.899261000	0.960808000	-0.530541000
O	-1.484868000	-0.401284000	-2.351442000
C	-3.320909000	1.052663000	-0.402813000
H	-3.627597000	1.921121000	-0.997010000
H	-3.791171000	0.159478000	-0.829819000
C	-3.746858000	1.243642000	1.047752000
H	-3.127673000	2.030037000	1.498420000
H	-4.783444000	1.606313000	1.045943000
H	-2.102377000	-0.903001000	1.234708000
C	-1.210706000	0.780345000	-3.091440000
H	-1.121863000	0.473549000	-4.135583000
H	-2.022175000	1.508044000	-2.993637000
H	-0.272771000	1.252894000	-2.775279000

TS5

N	-0.056658000	0.045019000	-0.882497000
C	0.420070000	1.043837000	-0.131154000
C	0.717810000	-1.023707000	-1.109298000
C	1.994632000	-1.140957000	-0.606847000
C	2.529043000	-0.096034000	0.195394000
H	0.267348000	-1.809104000	-1.710528000
H	2.563666000	-2.034773000	-0.826497000
H	-0.252555000	1.881139000	0.025689000
C	1.684247000	1.022847000	0.420889000



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H	2.004957000	1.863842000	1.021552000
N	3.773471000	-0.165249000	0.716298000
C	4.272939000	0.914826000	1.554252000
H	5.279624000	0.665856000	1.885579000
H	4.313819000	1.859162000	0.999522000
H	3.640943000	1.054315000	2.438774000
C	4.602874000	-1.336176000	0.471212000
H	4.775226000	-1.480069000	-0.601324000
H	5.566333000	-1.192212000	0.957344000
H	4.139472000	-2.242876000	0.877025000
O	-1.651358000	-1.269971000	1.426879000
C	-1.750968000	-0.057176000	-1.553381000
O	-2.192168000	-1.177774000	-1.225526000
C	-2.802288000	-0.596077000	1.895146000
H	-3.711683000	-1.168059000	1.649550000
H	-2.722280000	-0.566931000	2.987136000
O	-2.265004000	1.103372000	-1.013183000
O	-1.479373000	0.105592000	-2.894162000
C	-3.358654000	0.987801000	-0.092143000
H	-3.895627000	1.930589000	-0.222130000
H	-4.011831000	0.168280000	-0.409151000
C	-2.961901000	0.831773000	1.377224000
H	-2.048731000	1.406948000	1.574081000
H	-3.762284000	1.295509000	1.968613000
H	-1.763400000	-1.374511000	0.457914000
C	-1.047966000	1.385878000	-3.335440000
H	-0.830401000	1.278908000	-4.399046000
H	-1.827283000	2.138570000	-3.192247000
H	-0.136961000	1.697641000	-2.811983000

*BICY1*

O	-2.707139000	1.414106000	-0.139031000
C	-1.940016000	0.704019000	-1.002261000
C	-3.469123000	0.491751000	0.693095000
H	-3.977300000	1.136481000	1.410684000
H	-4.218161000	0.010073000	0.053440000
O	-0.598885000	-1.642720000	0.429441000
O	-2.365549000	0.245742000	-2.037101000
C	-2.016614000	-1.714356000	0.602389000
H	-2.514988000	-1.825368000	-0.371530000
H	-2.169164000	-2.645113000	1.152731000
C	-2.627941000	-0.554331000	1.424815000
H	-3.314511000	-0.992031000	2.158193000
H	-1.830103000	-0.069141000	1.999660000
N	-0.648219000	0.490102000	-0.545374000
C	-0.043527000	1.309202000	0.405571000
C	-0.126357000	-0.872175000	-0.674592000
C	1.364807000	-0.874632000	-0.645334000
C	2.019233000	0.041608000	0.115763000
H	-0.523582000	-1.284573000	-1.606281000
H	1.869013000	-1.674193000	-1.171620000
H	-0.646157000	2.118941000	0.798285000
C	1.239154000	1.105343000	0.754058000

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H	1.689319000	1.752343000	1.495844000
N	3.395250000	0.016786000	0.354609000
C	4.112506000	1.284725000	0.238023000
H	5.112755000	1.163018000	0.660124000
H	4.210782000	1.596011000	-0.813899000
H	3.607321000	2.077500000	0.788208000
C	4.130494000	-1.079257000	-0.251524000
H	3.689480000	-2.035192000	0.041069000
H	4.141294000	-1.017494000	-1.352353000
H	5.161669000	-1.047893000	0.106324000