**Supporting Information**

**for**

# Asymmetric Diels–Alder reaction with >C=P– functionality of the 2-phosphaindolizine-$\eta^1$-P-aluminium(O-menthoxy) dichloride complex: experimental and theoretical results

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**Cartesian coordinates of the geometries optimized (Table S1) and total energies of reactants, transition structures and products in the gas phase and in methylene chloride (Table S2) at the B3LYP/6-31+G* level.**

**Table S1:** Cartesian coordinates of the geometries optimized at the B3LYP/6-31+g* level.

**7a**

| | | | |
|---|---|---|---|
| C | 6.122176000 | 1.316326000 | -0.858090000 |
| C | 5.947601000 | 1.431747000 | 0.546560000 |
| C | 4.803422000 | 0.987149000 | 1.147044000 |
| N | 3.792853000 | 0.415655000 | 0.390484000 |
| C | 3.929939000 | 0.284985000 | -1.006005000 |
| C | 5.124908000 | 0.750907000 | -1.612779000 |
| C | 2.587736000 | -0.073449000 | 0.870639000 |
| C | 2.211283000 | -0.054946000 | 2.284567000 |
| O | 2.883552000 | 0.378869000 | 3.211340000 |
| C | 2.820314000 | -0.312323000 | -1.633807000 |
| C | 2.738942000 | -0.560763000 | -3.115894000 |
| P | 1.632351000 | -0.698925000 | -0.437137000 |
| Al | -0.719934000 | -1.699670000 | -0.485162000 |
| O | -1.750207000 | -0.504426000 | 0.172474000 |
| O | 0.990673000 | -0.601283000 | 2.435106000 |
| C | 0.466171000 | -0.681148000 | 3.773820000 |
| Cl | -0.488115000 | -3.459160000 | 0.690477000 |
| Cl | -0.845332000 | -2.018837000 | -2.607220000 |
| H | 6.718039000 | 1.874003000 | 1.169205000 |
| H | 4.604145000 | 1.042083000 | 2.207838000 |
| H | 7.034926000 | 1.671845000 | -1.325977000 |
| H | 5.222205000 | 0.645164000 | -2.687819000 |
| H | 1.786216000 | -1.020899000 | -3.387475000 |
| H | 2.831155000 | 0.375413000 | -3.681932000 |
| H | 3.540498000 | -1.232273000 | -3.450325000 |
| H | -0.511587000 | -1.148346000 | 3.663475000 |
| H | 1.122090000 | -1.292319000 | 4.399083000 |
| H | 0.375739000 | 0.320040000 | 4.202970000 |
| C | -2.510553000 | 0.571198000 | -0.364385000 |
| C | -1.687410000 | 1.867101000 | -0.301969000 |
| H | -2.742046000 | 0.361354000 | -1.421140000 |
| C | -2.456804000 | 3.098276000 | -0.809974000 |
| H | -1.379717000 | 2.027478000 | 0.742517000 |
| H | -0.765545000 | 1.733340000 | -0.885758000 |
| C | -3.785840000 | 3.229832000 | -0.048029000 |
| C | -1.608266000 | 4.372875000 | -0.714850000 |
| H | -2.697814000 | 2.931443000 | -1.872887000 |
| C | -4.614068000 | 1.937741000 | -0.116437000 |
| H | -3.571850000 | 3.472909000 | 1.004890000 |
| H | -4.367302000 | 4.071061000 | -0.450858000 |
| C | -3.837759000 | 0.714455000 | 0.414324000 |
| H | -5.543567000 | 2.067497000 | 0.451222000 |
| H | -4.912152000 | 1.761288000 | -1.160408000 |
| H | -3.550162000 | 0.927751000 | 1.457401000 |
| C | -4.666552000 | -0.598805000 | 0.450846000 |
| H | -2.154193000 | 5.244095000 | -1.098758000 |
| H | -1.333288000 | 4.584411000 | 0.327395000 |
| H | -0.679406000 | 4.278722000 | -1.292055000 |
| H | -3.967795000 | -1.379524000 | 0.776199000 |
| C | -5.789634000 | -0.537029000 | 1.500642000 |
| C | -5.235971000 | -1.025190000 | -0.914241000 |
| H | -5.679208000 | -2.026290000 | -0.843264000 |
| H | -6.025367000 | -0.343460000 | -1.256638000 |
| H | -4.466290000 | -1.065782000 | -1.693515000 |
| H | -6.285455000 | -1.511675000 | 1.593180000 |
| H | -5.397617000 | -0.268349000 | 2.490277000 |
| H | -6.562103000 | 0.196056000 | 1.235309000 |

**9**

| | | | |
|---|---|---|---|
| C | -0.326701000 | 0.652114000 | 0.000000000 |
| C | 0.326701000 | 1.826242000 | 0.000000000 |
| C | 0.326701000 | -0.652114000 | 0.000000000 |
| C | -0.326701000 | -1.826242000 | 0.000000000 |
| H | -0.202963000 | 2.774563000 | 0.000000000 |
| H | 1.414155000 | 1.872857000 | 0.000000000 |
| H | -1.417538000 | 0.646904000 | 0.000000000 |
| H | 1.417538000 | -0.646904000 | 0.000000000 |
| H | 0.202963000 | -2.774563000 | 0.000000000 |
| H | -1.414155000 | -1.872857000 | 0.000000000 |

**TS1**

| | | | |
|---|---|---|---|
| C | 4.069116000 | 3.448220000 | -0.508837000 |
| C | 3.848461000 | 3.302569000 | 0.893590000 |
| C | 3.169909000 | 2.215223000 | 1.362428000 |
| N | 2.681258000 | 1.258592000 | 0.497397000 |
| C | 2.874216000 | 1.360504000 | -0.899780000 |
| C | 3.598351000 | 2.501227000 | -1.375525000 |
| C | 2.053738000 | 0.063310000 | 0.889890000 |
| C | 1.248487000 | 0.001104000 | 2.120974000 |
| O | 1.154647000 | 0.871195000 | 2.972606000 |
| C | 2.305058000 | 0.341271000 | -1.651161000 |
| C | 2.398463000 | 0.230483000 | -3.149219000 |
| P | 1.607183000 | -0.864329000 | -0.579786000 |
| Al | -0.756520000 | -1.678227000 | -0.813724000 |
| O | -1.737042000 | -0.543752000 | 0.020634000 |
| O | 0.630506000 | -1.196882000 | 2.200121000 |
| C | -0.289107000 | -1.385583000 | 3.295340000 |
| Cl | -0.681012000 | -3.639003000 | 0.059632000 |
| Cl | -0.943049000 | -1.723244000 | -2.960815000 |
| H | 4.208583000 | 4.043167000 | 1.598818000 |
| H | 2.947785000 | 2.048693000 | 2.406586000 |
| H | 4.615943000 | 4.308707000 | -0.883759000 |
| H | 3.761716000 | 2.587361000 | -2.444045000 |
| H | 1.634849000 | -0.446159000 | -3.543454000 |
| H | 2.245837000 | 1.202481000 | -3.634239000 |
| H | 3.379518000 | -0.149274000 | -3.474590000 |
| H | -0.677067000 | -2.394810000 | 3.163285000 |
| H | 0.234356000 | -1.283396000 | 4.249408000 |
| H | -1.096160000 | -0.653113000 | 3.229461000 |
| C | -2.582926000 | 0.524834000 | -0.391286000 |
| C | -1.797038000 | 1.845171000 | -0.360434000 |
| H | -2.916501000 | 0.347304000 | -1.426529000 |
| C | -2.652827000 | 3.069370000 | -0.728210000 |
| H | -1.383657000 | 1.975404000 | 0.651340000 |
| H | -0.941507000 | 1.765930000 | -1.045556000 |
| C | -3.893202000 | 3.125963000 | 0.178075000 |
| C | -1.836079000 | 4.366775000 | -0.670100000 |
| H | -3.004180000 | 2.937513000 | -1.764997000 |
| C | -4.687339000 | 1.811652000 | 0.138359000 |
| H | -3.572794000 | 3.331163000 | 1.211883000 |
| H | -4.538526000 | 3.963935000 | -0.121183000 |
| C | -3.824861000 | 0.591641000 | 0.525267000 |
| H | -5.553568000 | 1.884552000 | 0.807638000 |
| H | -5.090771000 | 1.672939000 | -0.875141000 |
| H | -3.436139000 | 0.768801000 | 1.542179000 |
| C | -4.609196000 | -0.748259000 | 0.584815000 |
| H | -2.444375000 | 5.233072000 | -0.960372000 |

| | | | |
|---|---|---|---|
| H | -1.459659000 | 4.548074000 | 0.345692000 |
| H | -0.970414000 | 4.324178000 | -1.343401000 |
| H | -3.856798000 | -1.523492000 | 0.776893000 |
| C | -5.598888000 | -0.778907000 | 1.762796000 |
| C | -5.327925000 | -1.117774000 | -0.725127000 |
| H | -5.759129000 | -2.123795000 | -0.649543000 |
| H | -6.150906000 | -0.426597000 | -0.947393000 |
| H | -4.648828000 | -1.118869000 | -1.585630000 |
| H | -6.047402000 | -1.775214000 | 1.865025000 |
| H | -5.100161000 | -0.539551000 | 2.711162000 |
| H | -6.421496000 | -0.064740000 | 1.627996000 |
| C | 2.849628000 | -2.678202000 | -0.489314000 |
| H | 2.312089000 | -3.061608000 | 0.378113000 |
| H | 2.584545000 | -3.212607000 | -1.400378000 |
| C | 3.810164000 | -1.288971000 | 1.871108000 |
| H | 2.988031000 | -1.949108000 | 2.120109000 |
| H | 4.148156000 | -0.637111000 | 2.672473000 |
| C | 4.637599000 | -1.555683000 | 0.789508000 |
| H | 5.612115000 | -1.073444000 | 0.739354000 |
| C | 4.191917000 | -2.266288000 | -0.334157000 |
| H | 4.844543000 | -2.302843000 | -1.204558000 |

**TS2**

| | | | |
|---|---|---|---|
| N | -2.701732000 | 1.306231000 | -0.533652000 |
| C | -2.893296000 | 1.541222000 | 0.848154000 |
| C | -3.576437000 | 2.743786000 | 1.217113000 |
| C | -3.998110000 | 3.634202000 | 0.268108000 |
| C | -3.770658000 | 3.361003000 | -1.113243000 |
| C | -3.140132000 | 2.208528000 | -1.483633000 |
| C | -2.357724000 | 0.573007000 | 1.688249000 |
| C | -2.436040000 | 0.613697000 | 3.192145000 |
| C | -2.121448000 | 0.059345000 | -0.812012000 |
| C | -1.381731000 | -0.185288000 | -2.058053000 |
| O | -1.370175000 | 0.523757000 | -3.054362000 |
| P | -1.672101000 | -0.742032000 | 0.733456000 |
| C | -3.003575000 | -2.465031000 | 0.901946000 |
| C | -3.033367000 | -3.134074000 | -0.347458000 |
| Al | 0.680194000 | -1.530917000 | 1.050106000 |
| Cl | 0.587297000 | -3.587693000 | 0.429757000 |
| O | 1.668613000 | -0.515358000 | 0.082570000 |
| C | 2.562388000 | 0.557544000 | 0.353991000 |
| C | 3.731930000 | 0.531195000 | -0.655185000 |
| C | 4.647582000 | 1.750545000 | -0.417170000 |
| C | 3.880936000 | 3.079789000 | -0.488266000 |
| C | 2.710841000 | 3.116325000 | 0.507949000 |
| C | 1.804109000 | 1.892889000 | 0.289521000 |
| C | 4.479441000 | -0.830635000 | -0.682209000 |
| C | 5.372382000 | -0.967907000 | -1.927807000 |
| C | 1.919862000 | 4.427977000 | 0.419789000 |
| Cl | 0.897637000 | -1.328097000 | 3.187294000 |
| C | 5.289462000 | -1.132557000 | 0.591169000 |
| O | -0.707132000 | -1.347596000 | -1.955838000 |
| C | 0.127015000 | -1.720352000 | -3.069472000 |
| C | -4.039847000 | -1.243103000 | -1.517254000 |
| C | -3.550487000 | -2.539536000 | -1.505793000 |
| H | -3.742923000 | 2.927091000 | 2.272872000 |
| H | -4.509215000 | 4.546272000 | 0.562614000 |
| H | -4.091894000 | 4.054164000 | -1.882673000 |
| H | -2.919693000 | 1.938735000 | -2.506708000 |
| H | -1.703356000 | -0.061460000 | 3.643094000 |

| | | | |
|---|---|---|---|
| H | -3.429873000 | 0.326059000 | 3.566832000 |
| H | -2.220688000 | 1.619138000 | 3.574985000 |
| H | 0.899023000 | -0.963061000 | -3.221972000 |
| H | -0.475193000 | -1.826215000 | -3.975841000 |
| H | 0.574010000 | -2.670362000 | -2.778898000 |
| H | 1.320227000 | 1.965462000 | -0.696591000 |
| H | 1.000491000 | 1.882641000 | 1.039073000 |
| H | 1.472090000 | 4.549487000 | -0.575872000 |
| H | 1.106797000 | 4.454796000 | 1.156549000 |
| H | 2.566720000 | 5.295656000 | 0.602884000 |
| H | 3.135379000 | 3.045516000 | 1.523018000 |
| H | 2.970913000 | 0.444838000 | 1.371311000 |
| H | 3.488415000 | 3.223790000 | -1.507401000 |
| H | 4.564454000 | 3.918581000 | -0.295064000 |
| H | 5.122230000 | 1.669046000 | 0.571353000 |
| H | 5.462957000 | 1.755930000 | -1.151164000 |
| H | 6.146197000 | -0.455278000 | 0.700610000 |
| H | 4.680627000 | -1.053487000 | 1.499325000 |
| H | 5.685799000 | -2.154960000 | 0.553846000 |
| H | 5.791981000 | -1.979852000 | -1.993172000 |
| H | 6.216879000 | -0.266991000 | -1.909192000 |
| H | 4.804868000 | -0.782835000 | -2.849307000 |
| H | 3.696572000 | -1.595135000 | -0.761673000 |
| H | 3.270735000 | 0.651130000 | -1.649949000 |
| H | -2.580006000 | -3.014760000 | 1.741140000 |
| H | -3.877636000 | -1.877338000 | 1.177750000 |
| H | -2.447547000 | -4.043208000 | -0.453879000 |
| H | -3.382371000 | -3.042598000 | -2.455513000 |
| H | -4.301131000 | -0.760323000 | -2.455122000 |
| H | -4.457633000 | -0.785109000 | -0.627218000 |

**TS3**

| | | | |
|---|---|---|---|
| C | 6.424331000 | -0.366843000 | 0.509786000 |
| C | 6.195760000 | 0.800455000 | -0.278275000 |
| C | 4.921503000 | 1.145058000 | -0.624522000 |
| N | 3.845866000 | 0.385971000 | -0.212267000 |
| C | 4.023144000 | -0.778546000 | 0.569816000 |
| C | 5.367311000 | -1.133590000 | 0.914796000 |
| C | 2.510247000 | 0.609855000 | -0.589013000 |
| C | 2.023372000 | 1.968025000 | -0.876748000 |
| O | 2.703678000 | 2.975337000 | -0.991038000 |
| C | 2.853222000 | -1.429169000 | 0.937611000 |
| C | 2.800508000 | -2.689831000 | 1.758320000 |
| P | 1.477293000 | -0.639033000 | 0.184367000 |
| Al | -0.589966000 | -0.007042000 | 1.433856000 |
| O | -1.793479000 | 0.039525000 | 0.200996000 |
| O | 0.681707000 | 1.948041000 | -1.039523000 |
| C | 0.037731000 | 3.223678000 | -1.238655000 |
| Cl | -0.087794000 | 1.835377000 | 2.408890000 |
| Cl | -0.783849000 | -1.664326000 | 2.803053000 |
| H | 7.017872000 | 1.426094000 | -0.607302000 |
| H | 4.670960000 | 2.025029000 | -1.199027000 |
| H | 7.438330000 | -0.646582000 | 0.780918000 |
| H | 5.517785000 | -2.029120000 | 1.507209000 |
| H | 1.805533000 | -2.841720000 | 2.186119000 |
| H | 3.046094000 | -3.582127000 | 1.161676000 |
| H | 3.506381000 | -2.650846000 | 2.596926000 |
| H | -1.016968000 | 2.988105000 | -1.373595000 |
| H | 0.181469000 | 3.850094000 | -0.355523000 |
| H | 0.447808000 | 3.721277000 | -2.121055000 |

| | | | |
|---|---|---|---|
| C | -3.150540000 | -0.397335000 | 0.180919000 |
| C | -3.246173000 | -1.737838000 | -0.563023000 |
| H | -3.502368000 | -0.557952000 | 1.213166000 |
| C | -4.686105000 | -2.267066000 | -0.681530000 |
| H | -2.822210000 | -1.601528000 | -1.570203000 |
| H | -2.615503000 | -2.473077000 | -0.045395000 |
| C | -5.583718000 | -1.195687000 | -1.322239000 |
| C | -4.737610000 | -3.595730000 | -1.446801000 |
| H | -5.062547000 | -2.451264000 | 0.338056000 |
| C | -5.494526000 | 0.143788000 | -0.575925000 |
| H | -5.278783000 | -1.052994000 | -2.371311000 |
| H | -6.625816000 | -1.544208000 | -1.345304000 |
| C | -4.047055000 | 0.671305000 | -0.482887000 |
| H | -6.132546000 | 0.885447000 | -1.072816000 |
| H | -5.904493000 | 0.013765000 | 0.436104000 |
| H | -3.665275000 | 0.782122000 | -1.512037000 |
| C | -3.924442000 | 2.069208000 | 0.183010000 |
| H | -5.763297000 | -3.981761000 | -1.505568000 |
| H | -4.368885000 | -3.471948000 | -2.474346000 |
| H | -4.119375000 | -4.360834000 | -0.960216000 |
| H | -2.848414000 | 2.253168000 | 0.290700000 |
| C | -4.488605000 | 3.182537000 | -0.717065000 |
| C | -4.543070000 | 2.158300000 | 1.589477000 |
| H | -4.300055000 | 3.124074000 | 2.049004000 |
| H | -5.636945000 | 2.076423000 | 1.559478000 |
| H | -4.166015000 | 1.377669000 | 2.260426000 |
| H | -4.286351000 | 4.170704000 | -0.284525000 |
| H | -4.037601000 | 3.157038000 | -1.718107000 |
| H | -5.575915000 | 3.099741000 | -0.841226000 |
| C | 0.679515000 | -1.801414000 | -1.487779000 |
| H | 0.075730000 | -0.964006000 | -1.838309000 |
| H | 0.071068000 | -2.562625000 | -1.002144000 |
| C | 2.403629000 | 0.021097000 | -2.943184000 |
| H | 1.398951000 | 0.420024000 | -2.868705000 |
| H | 3.148308000 | 0.696661000 | -3.355680000 |
| C | 2.628605000 | -1.348173000 | -2.932110000 |
| H | 3.573545000 | -1.730984000 | -3.313359000 |
| C | 1.769082000 | -2.239222000 | -2.275158000 |
| H | 2.084632000 | -3.276884000 | -2.183231000 |

**8a**

| | | | |
|---|---|---|---|
| C | -4.193116000 | 3.351718000 | 0.300067000 |
| C | -4.278908000 | 2.973133000 | -1.075952000 |
| C | -3.684484000 | 1.807297000 | -1.463233000 |
| N | -3.036452000 | 1.001706000 | -0.568307000 |
| C | -2.911286000 | 1.330273000 | 0.793215000 |
| C | -3.533930000 | 2.564730000 | 1.200499000 |
| C | -2.390933000 | -0.258886000 | -0.976513000 |
| C | -1.271296000 | 0.027824000 | -1.999578000 |
| O | -1.025246000 | 1.117340000 | -2.467711000 |
| C | -2.210032000 | 0.453370000 | 1.591320000 |
| C | -1.969224000 | 0.650992000 | 3.067659000 |
| P | -1.665754000 | -0.952803000 | 0.649161000 |
| Al | 0.715337000 | -1.644460000 | 0.713782000 |
| O | 1.618394000 | -0.422180000 | -0.094503000 |
| O | -0.645584000 | -1.109322000 | -2.315239000 |
| C | 0.477472000 | -1.010354000 | -3.224571000 |
| Cl | 0.690552000 | -3.572684000 | -0.249439000 |
| Cl | 1.036849000 | -1.807530000 | 2.844911000 |
| H | -4.782858000 | 3.592993000 | -1.807624000 |

| | | | |
|---|---|---|---|
| H | -3.684464000 | 1.469898000 | -2.491518000 |
| H | -4.658348000 | 4.276533000 | 0.631247000 |
| H | -3.467780000 | 2.843871000 | 2.245923000 |
| H | -1.191115000 | -0.023359000 | 3.437059000 |
| H | -1.631507000 | 1.672307000 | 3.288882000 |
| H | -2.873762000 | 0.467463000 | 3.667469000 |
| H | 0.831426000 | -2.033764000 | -3.340169000 |
| H | 0.146007000 | -0.592583000 | -4.178263000 |
| H | 1.248012000 | -0.384441000 | -2.773038000 |
| C | 2.543269000 | 0.565467000 | 0.356481000 |
| C | 1.852894000 | 1.937954000 | 0.371411000 |
| H | 2.855719000 | 0.327541000 | 1.385823000 |
| C | 2.791466000 | 3.084835000 | 0.784813000 |
| H | 1.451033000 | 2.134143000 | -0.633904000 |
| H | 0.990726000 | 1.892795000 | 1.051046000 |
| C | 4.038513000 | 3.084891000 | -0.113560000 |
| C | 2.069034000 | 4.438215000 | 0.767394000 |
| H | 3.126762000 | 2.894051000 | 1.817847000 |
| C | 4.737792000 | 1.717472000 | -0.115129000 |
| H | 3.740694000 | 3.347364000 | -1.141167000 |
| H | 4.739336000 | 3.864448000 | 0.217078000 |
| C | 3.794383000 | 0.575693000 | -0.550260000 |
| H | 5.613312000 | 1.752392000 | -0.775389000 |
| H | 5.121213000 | 1.515251000 | 0.895587000 |
| H | 3.428811000 | 0.817642000 | -1.562799000 |
| C | 4.485178000 | -0.812220000 | -0.654786000 |
| H | 2.736723000 | 5.249359000 | 1.085442000 |
| H | 1.709092000 | 4.677484000 | -0.242307000 |
| H | 1.200276000 | 4.436256000 | 1.437982000 |
| H | 3.685226000 | -1.526108000 | -0.888547000 |
| C | 5.488779000 | -0.865557000 | -1.820078000 |
| C | 5.154473000 | -1.285290000 | 0.647900000 |
| H | 5.519189000 | -2.313639000 | 0.533239000 |
| H | 6.017696000 | -0.661663000 | 0.913457000 |
| H | 4.462209000 | -1.279620000 | 1.497646000 |
| H | 5.866878000 | -1.886524000 | -1.957412000 |
| H | 5.024127000 | -0.552843000 | -2.764525000 |
| H | 6.357680000 | -0.218331000 | -1.645217000 |
| C | -2.766222000 | -2.440372000 | 0.980428000 |
| H | -2.314966000 | -3.275941000 | 0.427038000 |
| H | -2.663659000 | -2.677989000 | 2.044777000 |
| C | -3.424020000 | -1.266284000 | -1.587534000 |
| H | -2.855322000 | -2.140883000 | -1.923804000 |
| H | -3.861008000 | -0.817923000 | -2.486678000 |
| C | -4.501587000 | -1.667224000 | -0.610337000 |
| H | -5.538352000 | -1.490534000 | -0.885398000 |
| C | -4.193909000 | -2.201806000 | 0.578793000 |
| H | -4.979078000 | -2.455880000 | 1.287686000 |

**8a′**

| | | | |
|---|---|---|---|
| Al | 0.599319000 | -1.604377000 | 0.967303000 |
| O | 1.496761000 | -0.471832000 | 0.030562000 |
| O | -0.722439000 | -1.343682000 | -2.160310000 |
| C | -1.219056000 | -0.126259000 | -1.936855000 |
| H | 3.037753000 | 2.963306000 | 1.687479000 |
| N | -2.868660000 | 1.148718000 | -0.607013000 |
| C | -2.818287000 | 1.514505000 | 0.750987000 |
| C | -2.266746000 | 0.606399000 | 1.628523000 |
| P | -1.766362000 | -0.870528000 | 0.770057000 |
| C | -2.374411000 | -0.204713000 | -0.916805000 |

| | | | |
|---|---|---|---|
| C | -3.547490000 | -1.094463000 | -1.482755000 |
| C | 2.417750000 | 0.564539000 | 0.365709000 |
| C | 3.588122000 | 0.578500000 | -0.642681000 |
| C | 4.523958000 | 1.765923000 | -0.329983000 |
| C | 3.780102000 | 3.109501000 | -0.319502000 |
| C | 2.612357000 | 3.104589000 | 0.679989000 |
| C | 1.683306000 | 1.913787000 | 0.386623000 |
| C | -3.349139000 | 2.815780000 | 1.070520000 |
| C | -3.863698000 | 3.625189000 | 0.098485000 |
| C | -3.890223000 | 3.201142000 | -1.266489000 |
| C | -3.384924000 | 1.970798000 | -1.572170000 |
| C | 4.316381000 | -0.790015000 | -0.750535000 |
| C | 5.206926000 | -0.866450000 | -2.003427000 |
| C | 1.845087000 | 4.433092000 | 0.676348000 |
| Cl | 0.904847000 | -1.524173000 | 3.104389000 |
| Cl | 0.602890000 | -3.627146000 | 0.235441000 |
| O | -0.850965000 | 0.891732000 | -2.481636000 |
| C | 0.417369000 | -1.431296000 | -3.049035000 |
| C | -2.107845000 | 0.841792000 | 3.110832000 |
| C | 5.125455000 | -1.174809000 | 0.500956000 |
| H | -4.283697000 | 3.834602000 | -2.052298000 |
| H | -3.349518000 | 1.591750000 | -2.584788000 |
| H | -4.259922000 | 4.601777000 | 0.364216000 |
| H | -3.333746000 | 3.127161000 | 2.108759000 |
| H | -1.397491000 | 0.135801000 | 3.550354000 |
| H | -1.720820000 | 1.847626000 | 3.321152000 |
| H | -3.057792000 | 0.735019000 | 3.656273000 |
| H | 0.641769000 | -2.495260000 | -3.109447000 |
| H | 0.159481000 | -1.021746000 | -4.028675000 |
| H | 1.251912000 | -0.884934000 | -2.607792000 |
| H | 2.824327000 | 0.378734000 | 1.372808000 |
| H | 1.196626000 | 2.055492000 | -0.589666000 |
| H | 0.881621000 | 1.867785000 | 1.136697000 |
| H | 3.388772000 | 3.321706000 | -1.327042000 |
| H | 4.478431000 | 3.922950000 | -0.076965000 |
| H | 5.341092000 | 1.802830000 | -1.061219000 |
| H | 4.994963000 | 1.616138000 | 0.652362000 |
| H | 3.132175000 | 0.768755000 | -1.629056000 |
| H | 2.508221000 | 5.275953000 | 0.910585000 |
| H | 1.395927000 | 4.623590000 | -0.307617000 |
| H | 1.035013000 | 4.428080000 | 1.416810000 |
| H | 3.524982000 | -1.540518000 | -0.870968000 |
| H | 5.509515000 | -2.197844000 | 0.403609000 |
| H | 5.989741000 | -0.514118000 | 0.644721000 |
| H | 4.520366000 | -1.140532000 | 1.414232000 |
| H | 5.610520000 | -1.878998000 | -2.130248000 |
| H | 4.643933000 | -0.615895000 | -2.912240000 |
| H | 6.062039000 | -0.181275000 | -1.941740000 |
| C | -3.327868000 | -2.579267000 | -1.354174000 |
| C | -3.069372000 | -3.136738000 | -0.163826000 |
| C | -2.970422000 | -2.291221000 | 1.074286000 |
| H | -2.858094000 | -4.199275000 | -0.082630000 |
| H | -3.355684000 | -3.184990000 | -2.255473000 |
| H | -4.442052000 | -0.793583000 | -0.920717000 |
| H | -3.727039000 | -0.817645000 | -2.527324000 |
| H | -2.608727000 | -2.860524000 | 1.935418000 |
| H | -3.932076000 | -1.837269000 | 1.347558000 |

**10**

| | | | |
|---|---|---|---|
| C | 2.194282000 | -0.396950000 | -2.468349000 |

| | | | |
|---|---|---|---|
| C | 2.389145000 | 0.252233000 | -1.054380000 |
| P | 1.467664000 | -0.762179000 | 0.275797000 |
| C | 0.998747000 | -2.321025000 | -0.668595000 |
| C | 2.047620000 | -2.736954000 | -1.660195000 |
| C | 2.593993000 | -1.851262000 | -2.503404000 |
| N | 3.798103000 | 0.206161000 | -0.622710000 |
| C | 4.799780000 | 0.802143000 | -1.339142000 |
| C | 6.097856000 | 0.765206000 | -0.919348000 |
| C | 6.393611000 | 0.101831000 | 0.312053000 |
| C | 5.401609000 | -0.487132000 | 1.042370000 |
| C | 4.033084000 | -0.463500000 | 0.591842000 |
| C | 2.944706000 | -1.017754000 | 1.228346000 |
| C | 3.009382000 | -1.734357000 | 2.554927000 |
| C | 1.900754000 | 1.715423000 | -1.107169000 |
| O | 0.580315000 | 1.750043000 | -1.310752000 |
| C | -0.028215000 | 3.060752000 | -1.404013000 |
| Al | -0.571000000 | 0.105473000 | 1.371693000 |
| Cl | -0.854815000 | -1.395878000 | 2.907423000 |
| O | 2.621491000 | 2.685520000 | -1.031581000 |
| O | -1.794737000 | 0.085259000 | 0.156268000 |
| C | -3.145151000 | -0.365774000 | 0.156884000 |
| C | -3.226050000 | -1.738298000 | -0.529078000 |
| C | -4.660096000 | -2.286729000 | -0.628325000 |
| C | -5.566058000 | -1.253607000 | -1.318193000 |
| C | -5.494706000 | 0.116740000 | -0.628022000 |
| C | -4.053558000 | 0.663700000 | -0.552250000 |
| C | -4.696967000 | -3.648789000 | -1.333358000 |
| C | -3.949069000 | 2.088347000 | 0.058216000 |
| C | -4.573398000 | 2.225274000 | 1.458201000 |
| Cl | 0.004381000 | 2.018169000 | 2.168213000 |
| C | -4.522278000 | 3.159200000 | -0.886539000 |
| H | 6.869647000 | 1.248811000 | -1.505900000 |
| H | 4.497476000 | 1.313125000 | -2.243381000 |
| H | 7.419676000 | 0.066672000 | 0.668874000 |
| H | 5.617696000 | -0.995159000 | 1.975320000 |
| H | 2.008540000 | -1.922417000 | 2.953717000 |
| H | 3.518945000 | -2.706829000 | 2.479354000 |
| H | 3.542427000 | -1.140469000 | 3.309623000 |
| H | -1.087023000 | 2.865486000 | -1.563839000 |
| H | 0.129680000 | 3.603264000 | -0.470465000 |
| H | 0.406512000 | 3.610992000 | -2.242150000 |
| H | -3.495270000 | -0.485922000 | 1.195072000 |
| H | -2.800467000 | -1.640453000 | -1.540452000 |
| H | -2.589292000 | -2.444080000 | 0.021280000 |
| H | -5.037823000 | -2.428264000 | 0.397542000 |
| H | -5.257642000 | -1.152063000 | -2.371045000 |
| H | -6.604272000 | -1.614138000 | -1.330939000 |
| H | -6.139114000 | 0.829884000 | -1.157464000 |
| H | -5.907413000 | 0.023380000 | 0.386869000 |
| H | -3.670250000 | 0.737543000 | -1.584127000 |
| H | -5.718766000 | -4.047008000 | -1.376861000 |
| H | -4.327129000 | -3.567662000 | -2.364757000 |
| H | -4.072567000 | -4.385257000 | -0.811733000 |
| H | -2.875391000 | 2.288048000 | 0.162211000 |
| H | -4.340829000 | 3.210074000 | 1.881428000 |
| H | -5.666371000 | 2.132411000 | 1.427833000 |
| H | -4.191783000 | 1.473648000 | 2.159003000 |
| H | -4.333326000 | 4.165847000 | -0.492221000 |
| H | -4.067382000 | 3.100065000 | -1.884487000 |
| H | -5.608072000 | 3.058788000 | -1.011125000 |
| H | 0.039968000 | -2.097001000 | -1.157192000 |

| | | | |
|---|---|---|---|
| H | 0.797209000 | -3.094370000 | 0.080049000 |
| H | 1.136632000 | -0.273864000 | -2.730718000 |
| H | 2.764709000 | 0.182632000 | -3.202479000 |
| H | 3.359347000 | -2.159071000 | -3.211348000 |
| H | 2.369723000 | -3.776078000 | -1.667654000 |

**Table S2:** Total energies of reactants, cycloadducts and transition structures in the gas phase and in methylene chloride**.**

| | **Gas-phase** | | | | **$CH_2Cl_2$** | | |
|---|---|---|---|---|---|---|---|
| | **E [a] (a.u.)** | **ZPE[a] (a.u.)** | **$E_{total}$ [b] (a.u.)** | **Relative energy (kcal/mol)** | **E [c] (a.u.)** | **$E_{total}$ [d] (a.u.)** | **Relative energy (kcal/mol)** |
| **7a** | -2564.473593 | 0.467307 | -2564.006286 | | -2564.487286 | -2564.019979 | |
| **9** | -156.001088 | 0.085242 | -155.915846 | | -156.004287 | -155.919045 | |
| **TS1** | -2720.440134 | 0.554126 | -2719.886008 | 22.67 | -2720.455774 | -2719.901648 | 23.45 |
| **TS2** | -2720.441142 | 0.554551 | -2719.886591 | 22.30 | -2720.456779 | -2720.902228 | 23.09 |
| **TS3** | -2720.438421 | 0.554307 | -2719.884114 | 23.86 | -2720.454335 | -2719.900028 | 24.47 |
| **8a** | -2720.485900 | 0.557874 | -2719.928026 | -3.70 | -2720.502533 | -2719.944659 | -3.54 |
| **8a'** | -2720.482467 | 0.557735 | -2719.924732 | -1.63 | -2720.499328 | -2719.941593 | -1.61 |
| **10** | -2720.483562 | 0.557866 | -2719.925696 | -2.24 | -2720.500623 | -2719.942757 | -2.34 |

[a] Energies calculated at the 6-31+G* level in the gas phase
[b] Energies of optimized molecule at the 6-31+G* level + ZPE at the same level
[c] Single-point energies of gas–phase-optimized geometries in $CH_2Cl_2$ at the 6-31+G* level
[d] Single-point energies in $CH_2Cl_2$ at the 6-31+G* level + ZPE in the gas phase at the same level