Electronic Supplementary Material (ESI) for Dalton Transactions

Supporting Information

A Computational Insight into a Metal Mediated Pathway for the Ring-Opening Polymerization (ROP) of Lactides by an Ionic $\{(NHC)_2Ag\}^+X^-$ (X = halide) Type N-heterocyclic Carbene (NHC) Complex

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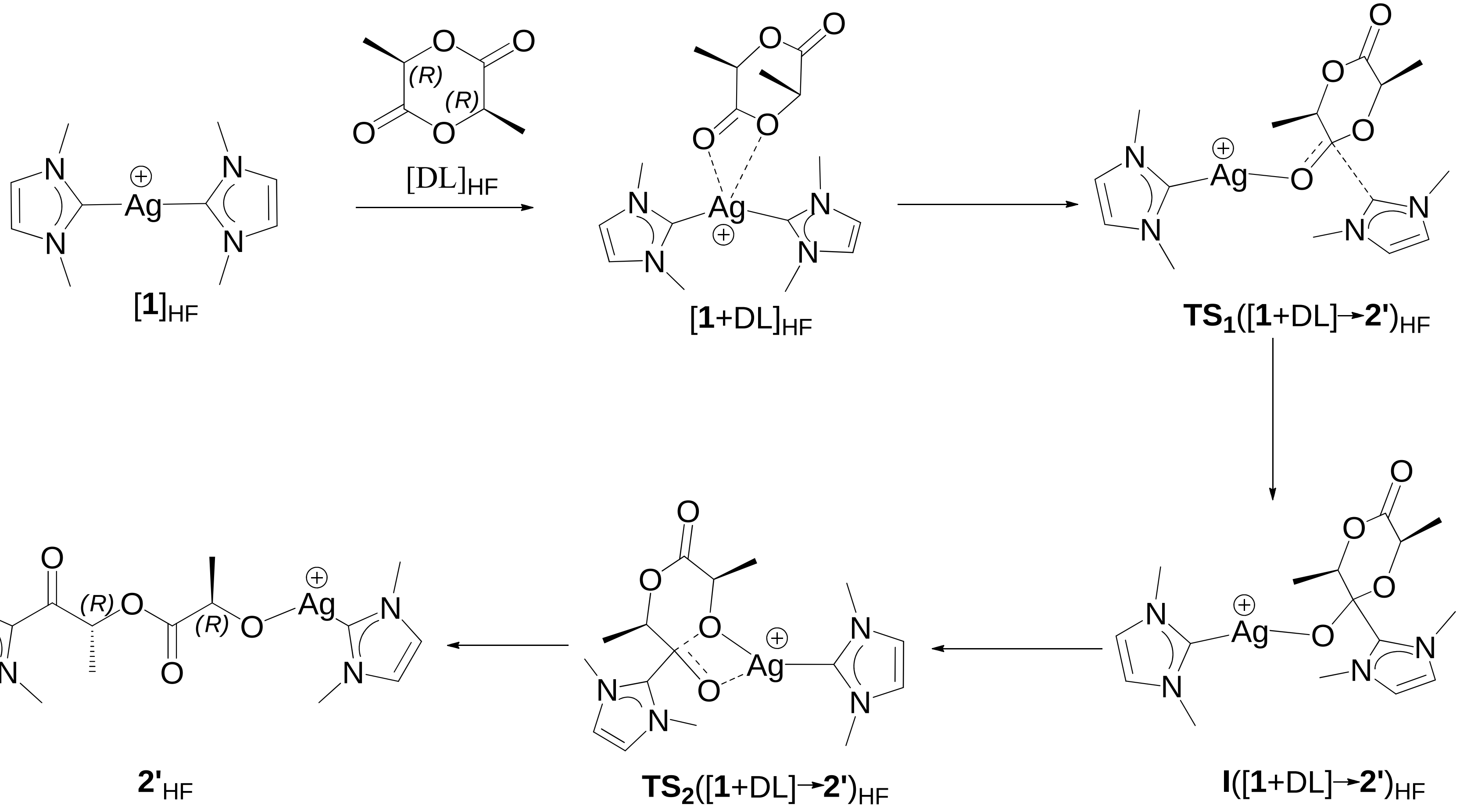
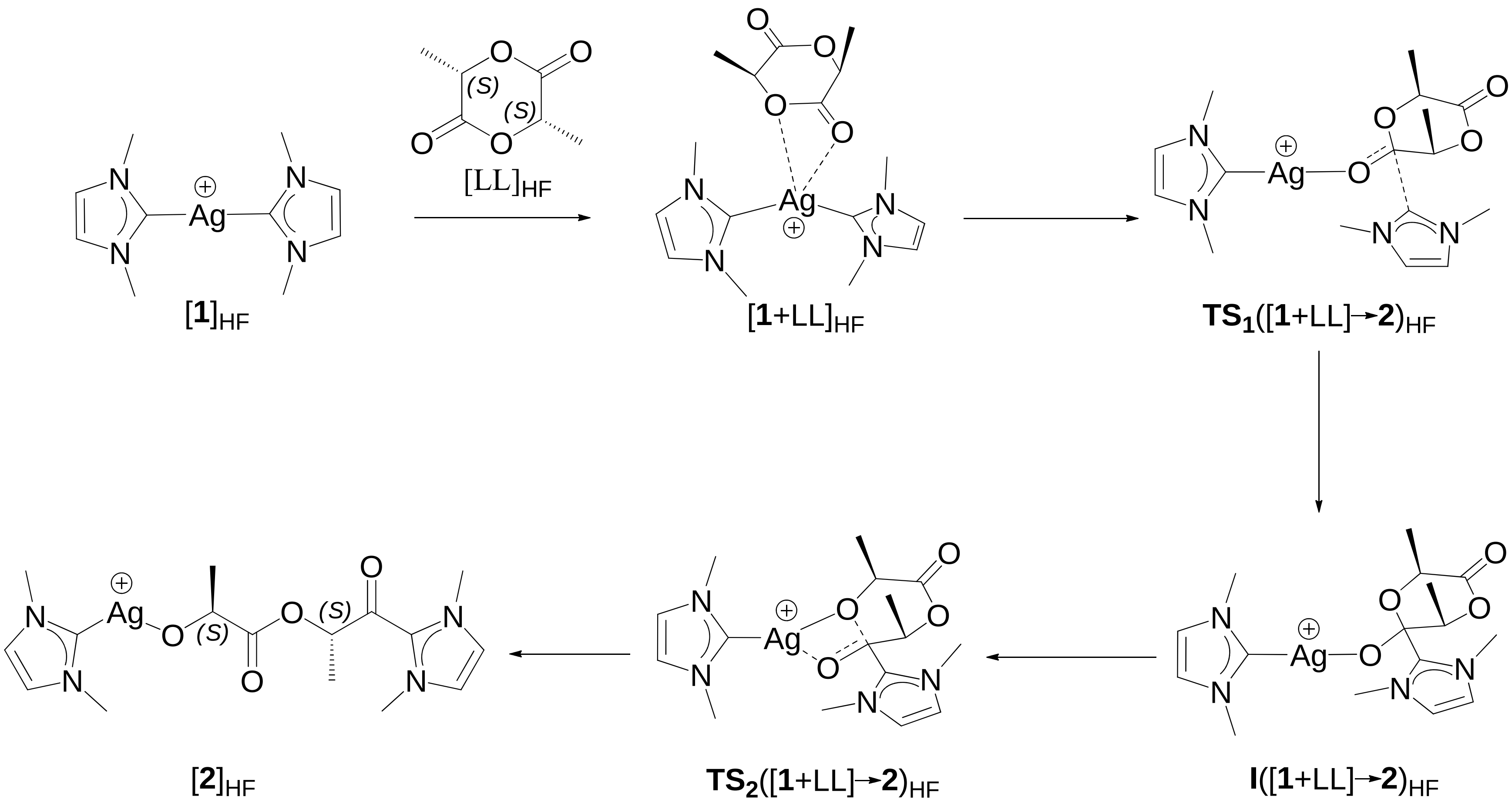


Scheme S1. (initiation step for ROP of D-Lactide)



Scheme S2. (initiation step for ROP of L-Lactide)

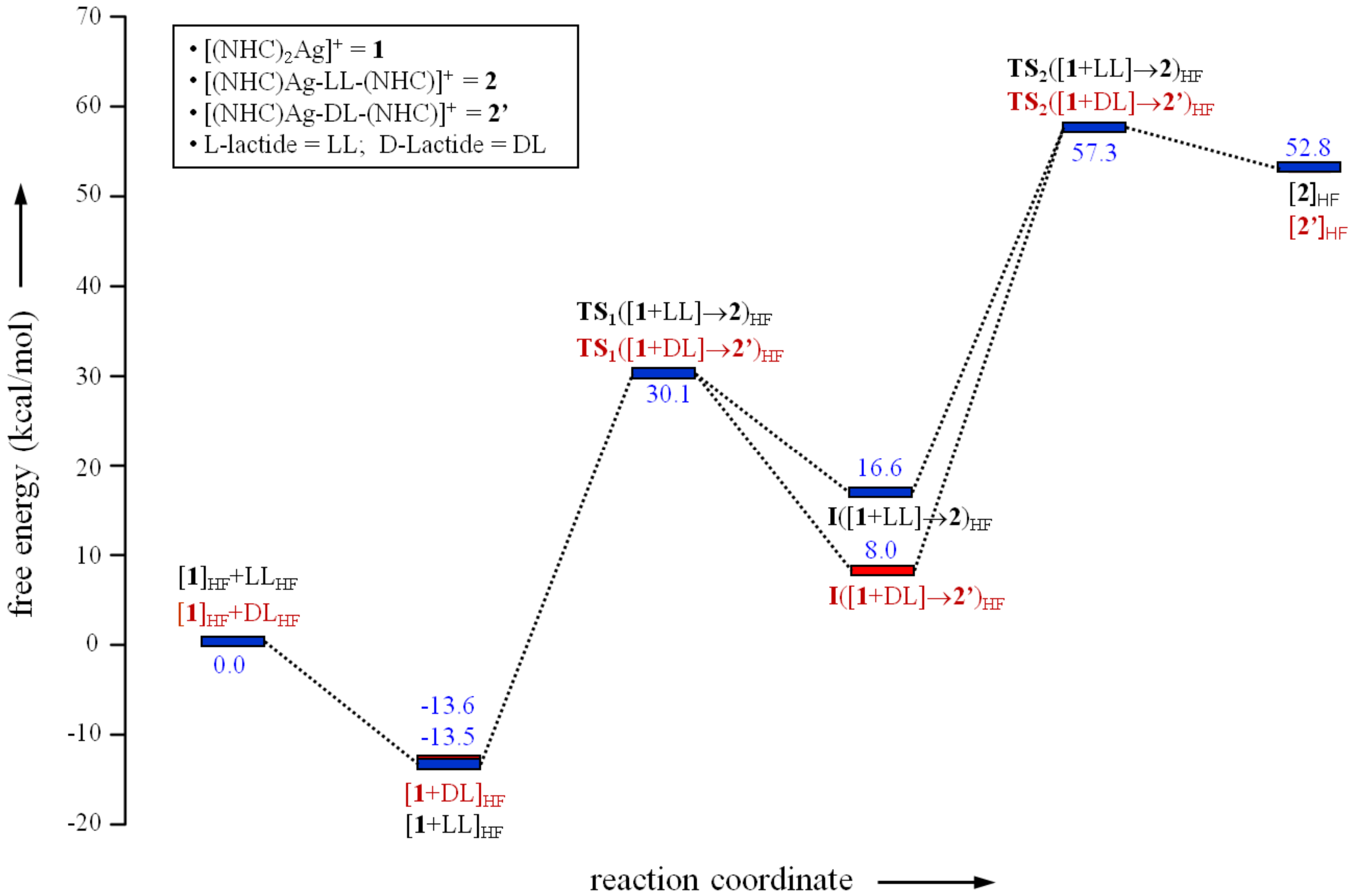


Figure S1. Free energy profile for the first ring-opening polymerization (ROP) of D- and L-lactide by **1** (computed at HF/STO3G, LANL1MB).

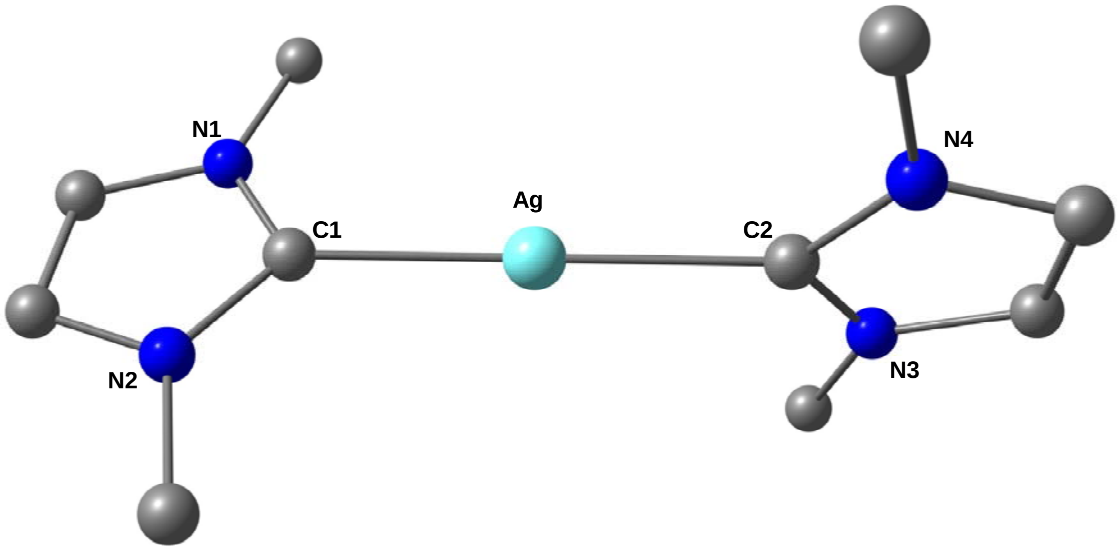


Figure S2. Computed structure of [**1**]$_{HF}$. Selected bond lengths (Å) and angles (°): Ag-C1 2.209, Ag-C2 2.209, C1-Ag-C2 180.0.

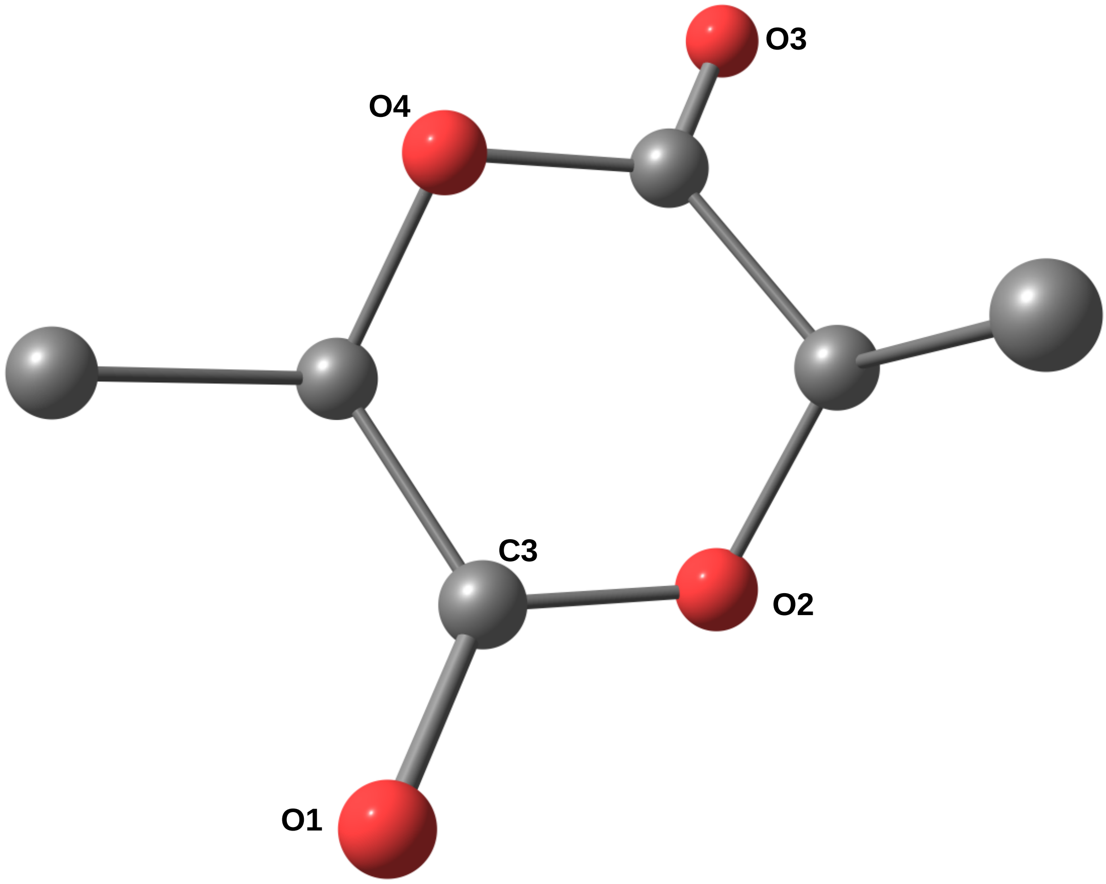


Figure S3. Computed structure of DL_{HF}. Selected bond lengths (Å) and angles (°): O1-C3 1.213, O2-C3 1.406, O1-C3-O2 119.9.

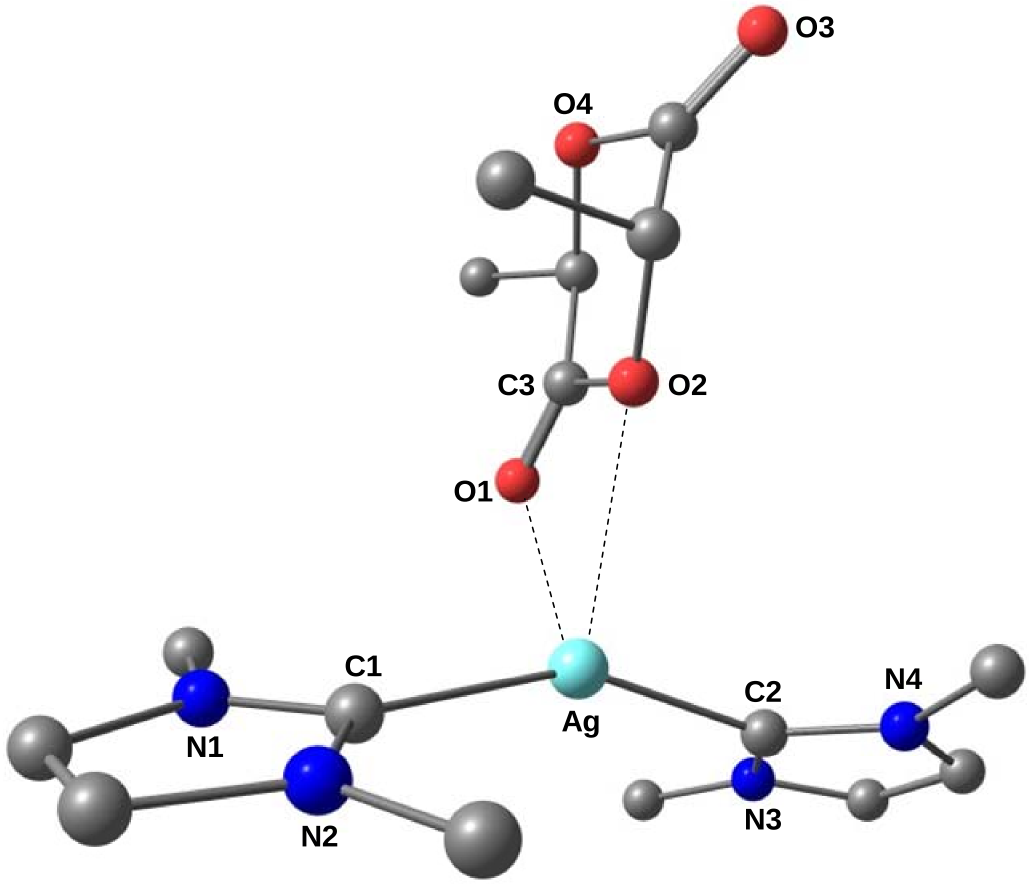


Figure S4. Computed structure of [**1**+DL]$_{HF}$. Selected bond lengths (Å) and angles (°): Ag-C1 2.270, Ag-C2 2.275, Ag···O1 2.627, Ag···O2 2.715, O1-C3 1.218, C3-O2 1.394, C1-Ag-C2 154.22.

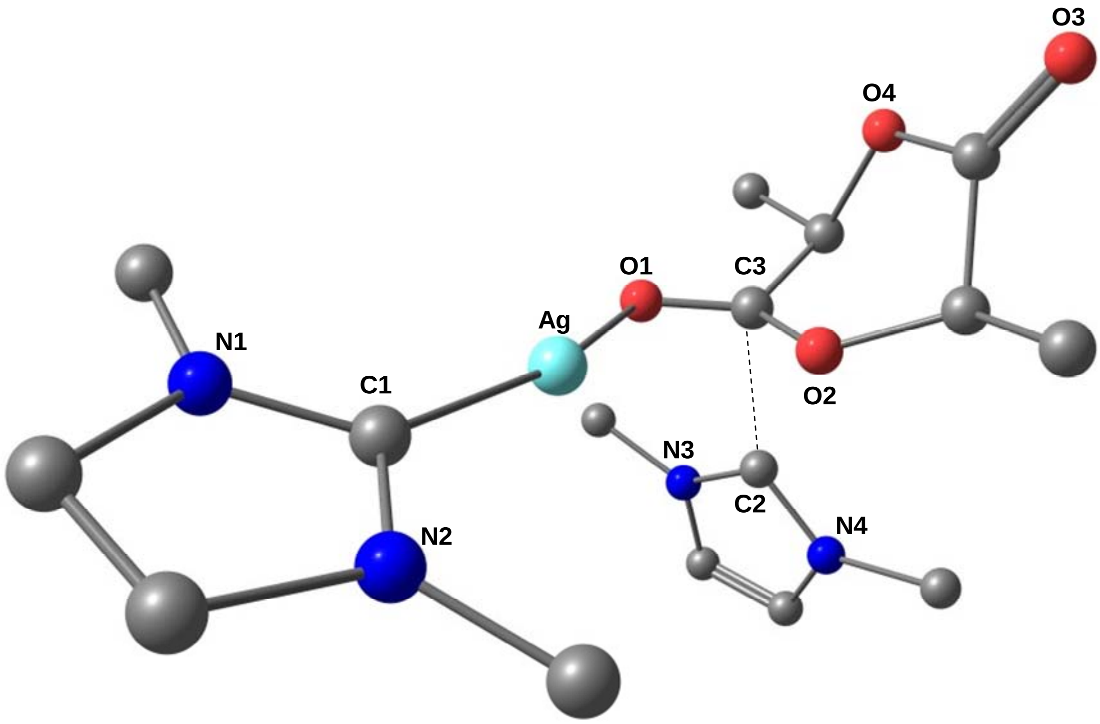


Figure S5. Computed structure of $\mathbf{TS_1}$([**1**+DL]→**2'**)$_{\mathrm{HF}}$. Selected bond lengths (Å) and angles (°): Ag-C1 2.217, Ag···C2 4.074, Ag-O1 2.168, Ag···O2 2.668, O1-C3 1.245, C3-O2 1.398, C2···C3 2.313, C1-Ag-O1 167.28, Ag-O1-C3 110.08, C1-Ag-O1-C3 167.60, Ag-O1-C3-O2 -1.43.

Calculated imaginary frequency along the bond C2···C3 is i167.

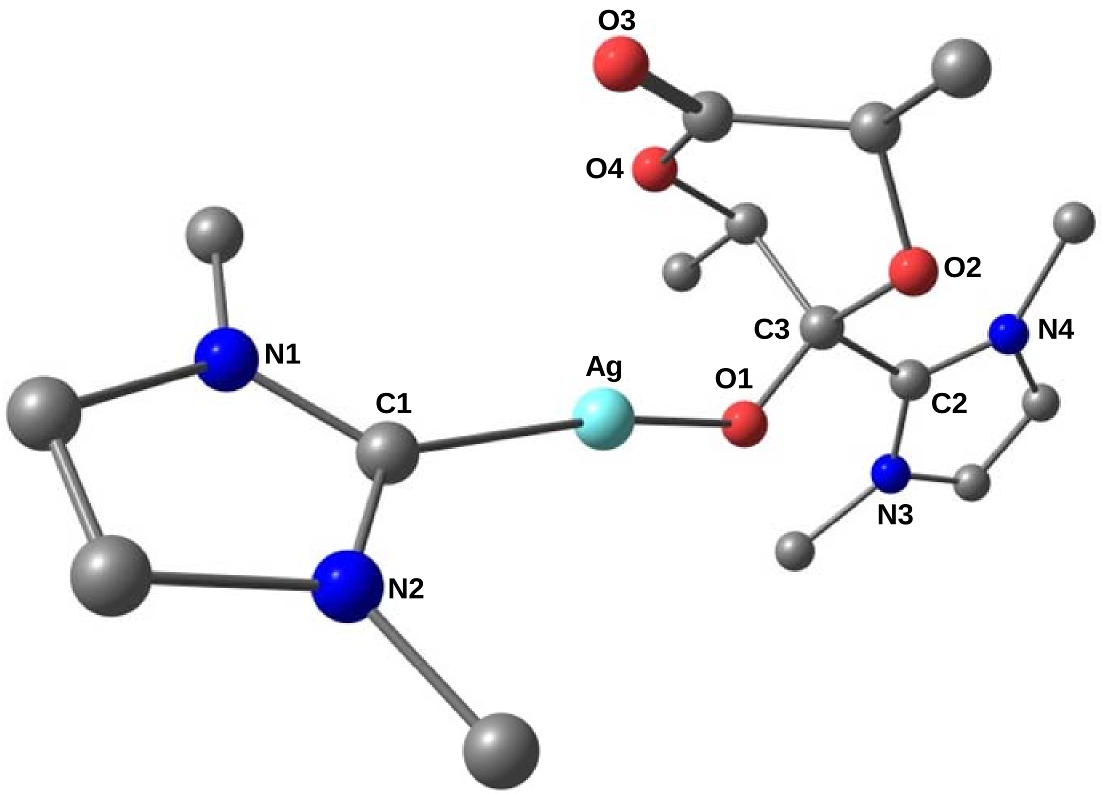


Figure S6. Computed structure of **I**([**1**+DL]→**2'**)$_{HF}$. Selected bond lengths (Å) and angles (°): Ag-C1 2.208, Ag-O1 2.052, O1-C3 1.363, C3-O2 1.456, C2-C3 1.603, C1-Ag-O1 171.43, Ag-O1-C3 123.67, O1-C3-C2 109.24, C1-Ag-O1-C3 -175.56, Ag-O1-C3-O2 51.39, Ag-O1-C3-C2 165.72.

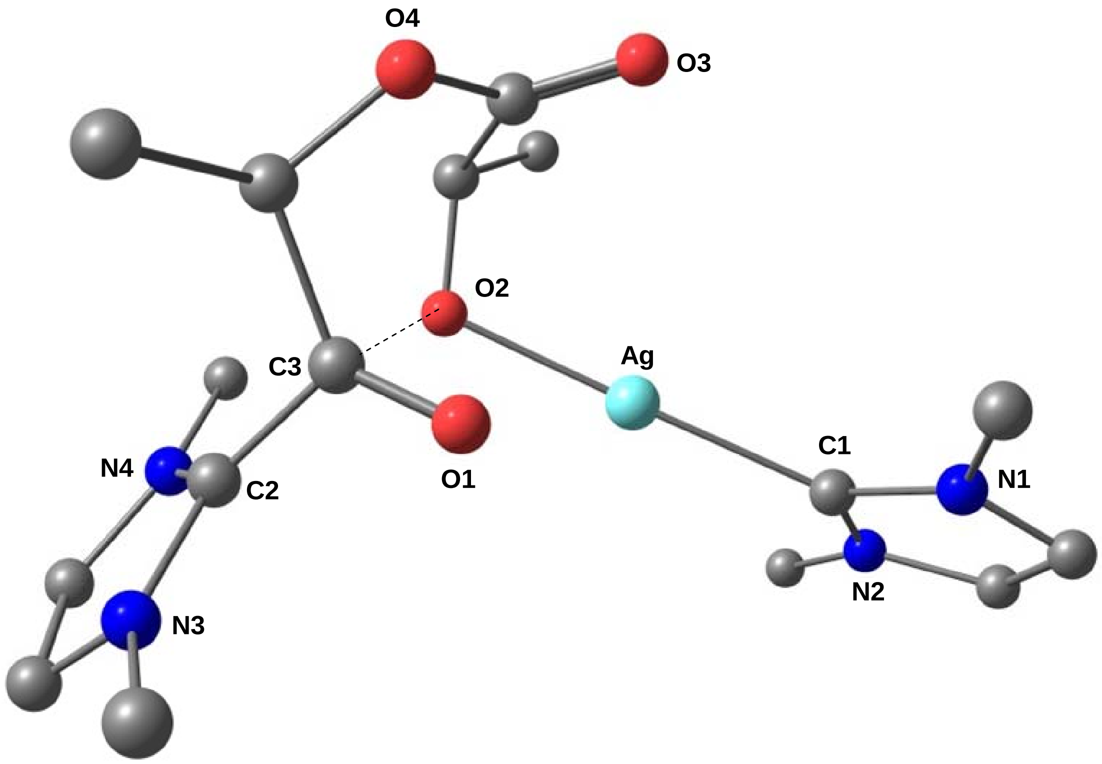


Figure S7. Computed structure of **TS$_2$**([**1**+DL]→**2'**)$_{HF}$. Selected bond lengths (Å) and angles (°): Ag-C1 2.228, Ag···O1 2.690, Ag-O2 2.137, O1-C3 1.227, C3···O2 2.161, C2-C3 1.567, C1-Ag-O2 177.03, O1-C3-C2 117.54.

Calculated imaginary frequency along the bond C3···O2 is i227.

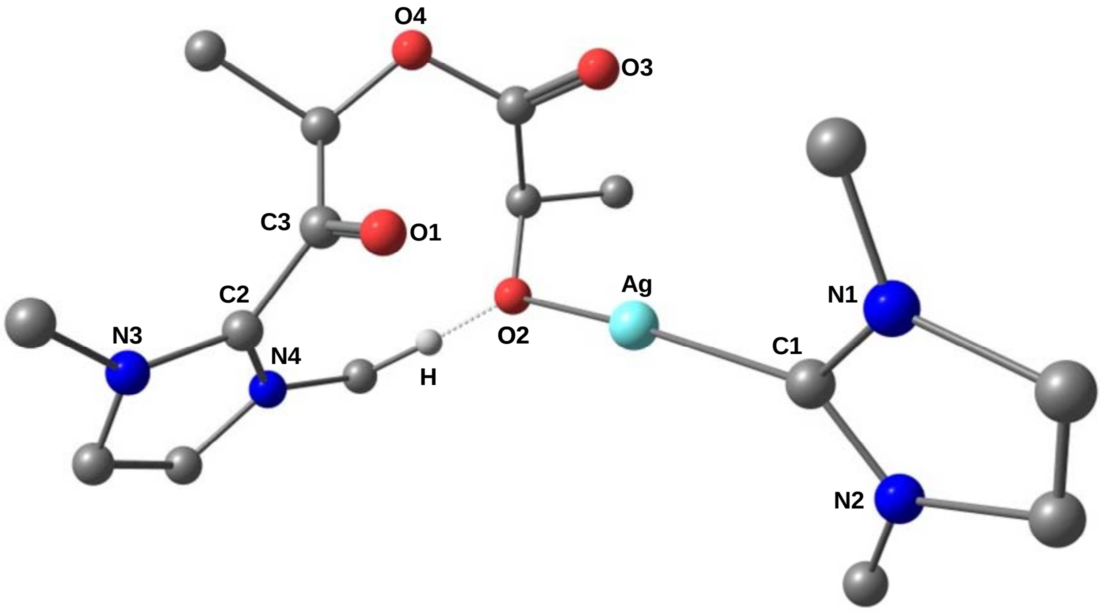


Figure S8. Computed structure of **2'**$_{HF}$. Selected bond lengths (Å) and angles (°): Ag-C1 2.221, Ag···O1 3.013, Ag-O2 2.091, O1-C3 1.218, C3···O2 2.792, C2-C3 1.549, O2-H 1.395, C1-Ag-O2 175.27, O1-C3-C2 119.22.

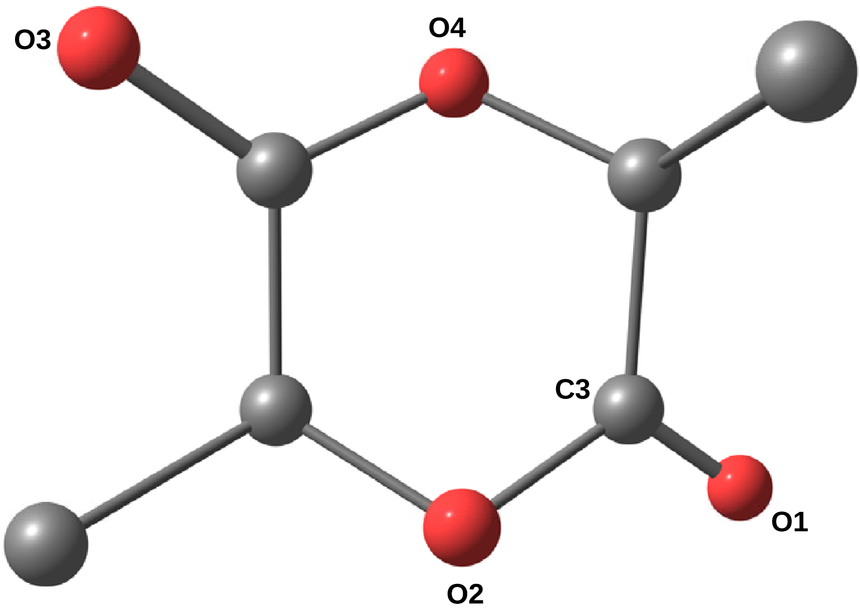


Figure S9. Computed structure of LL_{HF}. Selected bond lengths (Å) and angles (°): O1-C3 1.213, O2-C3 1.406, O1-C3-O2 120.2.

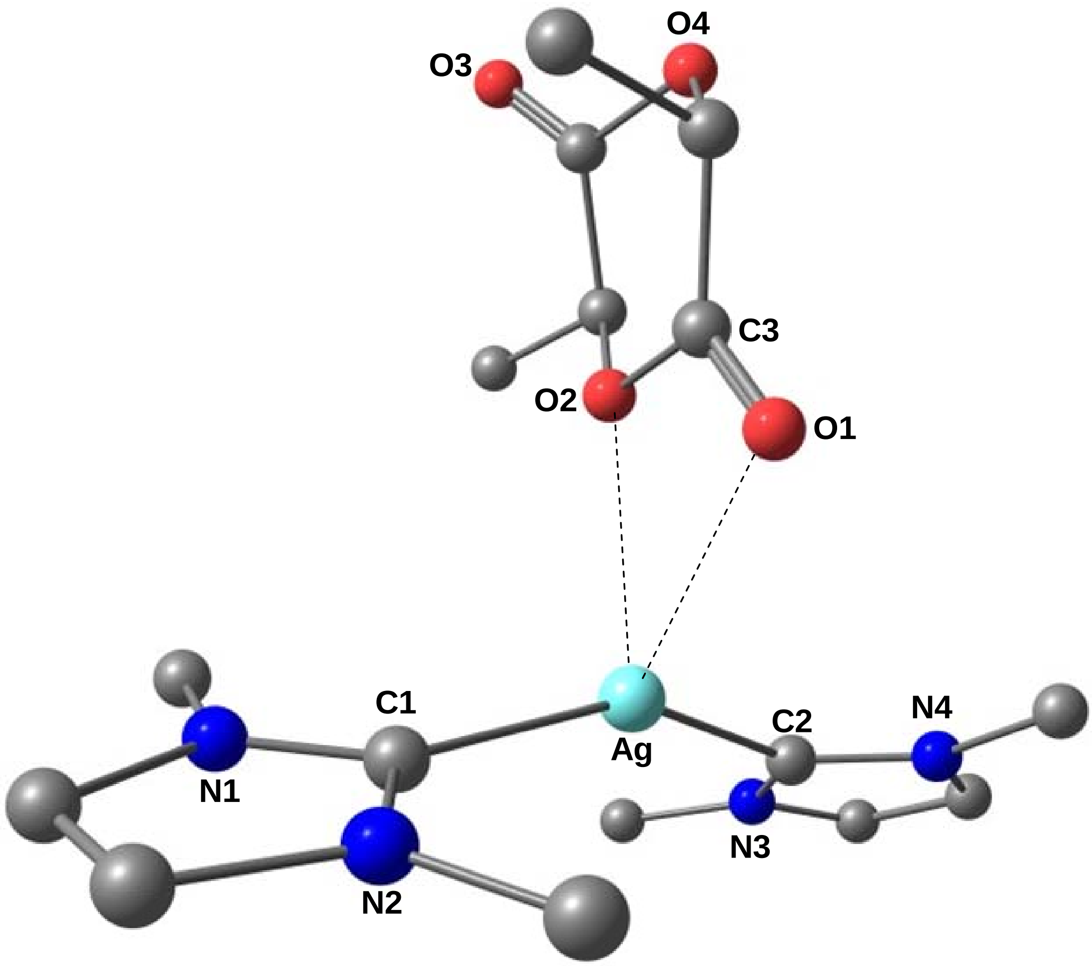


Figure S10. Computed structure of [**1**+LL]$_{HF}$. Selected bond lengths (Å) and angles (°): Ag-C1 2.274, Ag-C2 2.271, Ag···O1 2.647, Ag···O2 2.687, O1-C3 1.217, C3-O2 1.395, C1-Ag-C2 154.29.

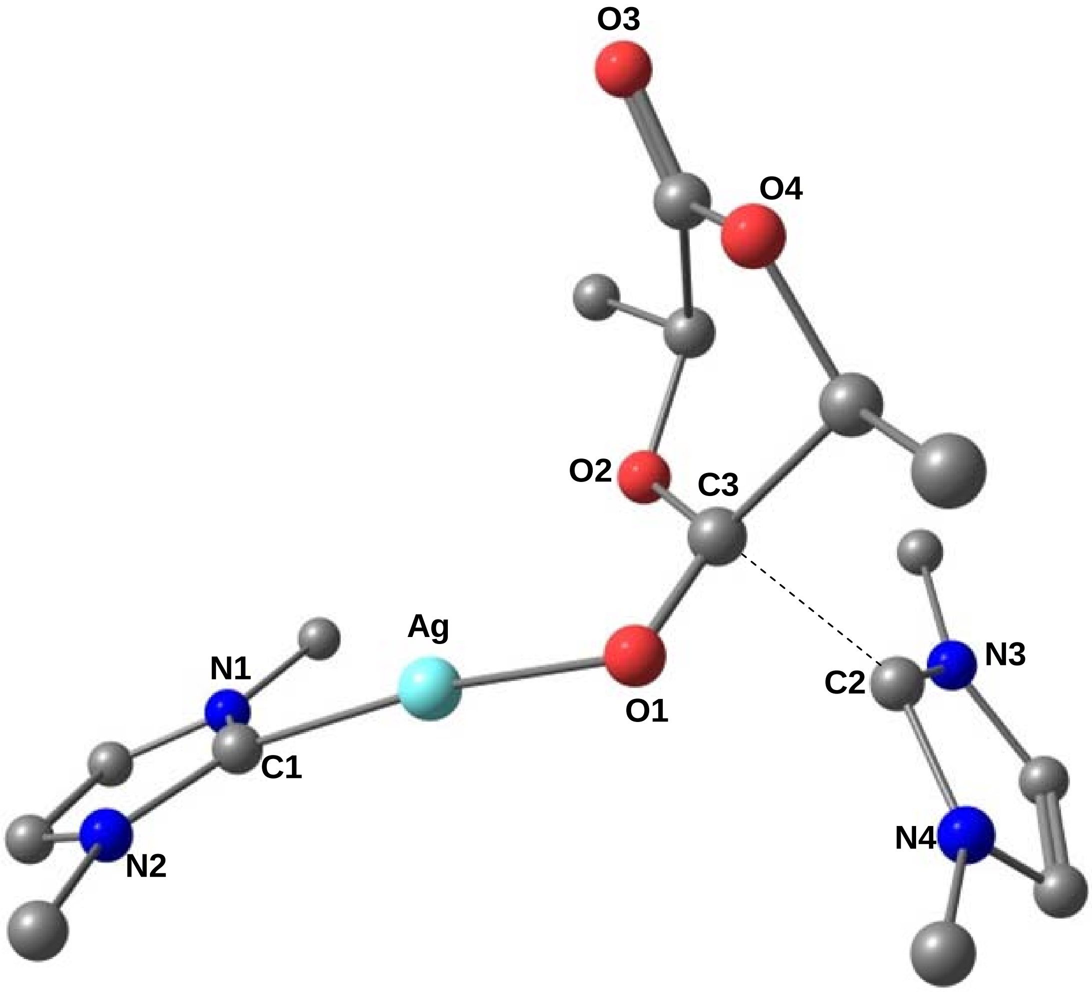


Figure S11. Computed structure of **TS₁**([**1**+LL]→**2**)$_{HF}$. Selected bond lengths (Å) and angles (°): Ag-C1 2.217, Ag-O1 2.168, Ag···O2 2.668, O1-C3 1.225, C3-O2 1.398, C2···C3 2.313, C1-Ag-O1 138.92, Ag-O1-C3 110.07, C1-Ag-O1-C3 -167.59, Ag-O1-C3-O2 1.423.

Calculated imaginary frequency along the bond C2···C3 is i167.

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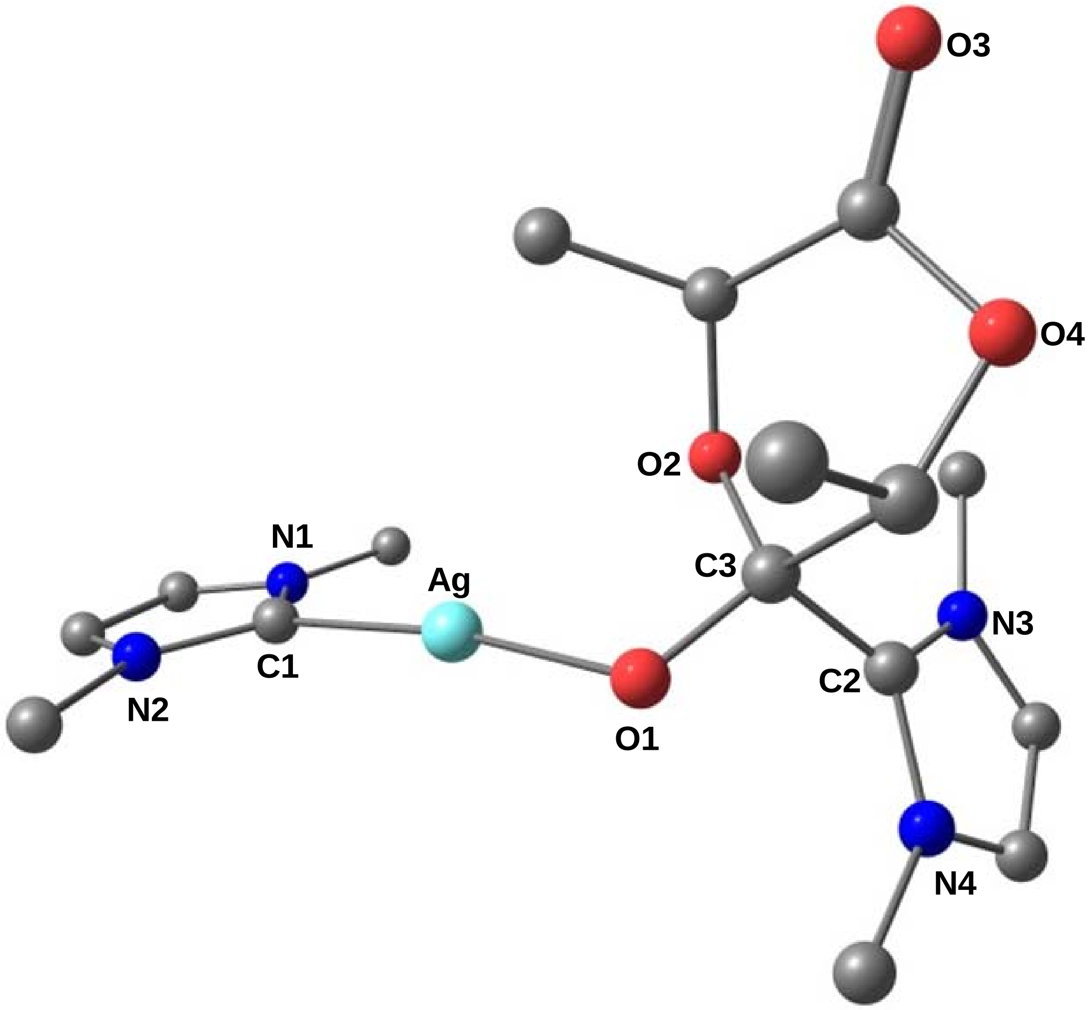


Figure S12. Computed structure of **I**([**1**+LL]→**2**)$_{HF}$. Selected bond lengths (Å) and angles (°): Ag-C1 2.213, Ag-O1 2.051, Ag···O2 2.862, O1-C3 1.361, C3-O2 1.449, C2-C3 1.608, C1-Ag-O1 170.20, Ag-O1-C3 117.43, O1-C3-C2 108.78, C1-Ag-O1-C3 -175.29, Ag-O1-C3-O2 6.67, Ag-O1-C3-C2 -106.12.

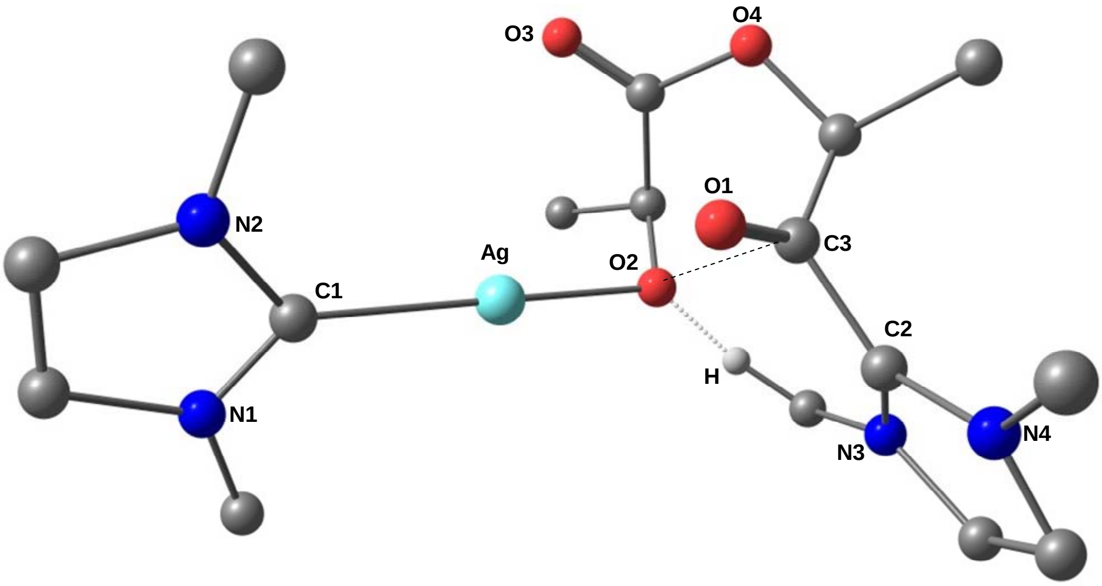


Figure S13. Computed structure of **TS**$_2$([**1**+LL]→**2**)$_{HF}$. Selected bond lengths (Å) and angles (°): Ag-C1 2.228, Ag···O1 2.690, Ag-O2 2.137, O1-C3 1.227, C3···O2 2.162, C2-C3 1.567, C1-Ag-O2 177.03, O1-C3-C2 117.54.

Calculated imaginary frequency along the bond C3···O2 is i227.

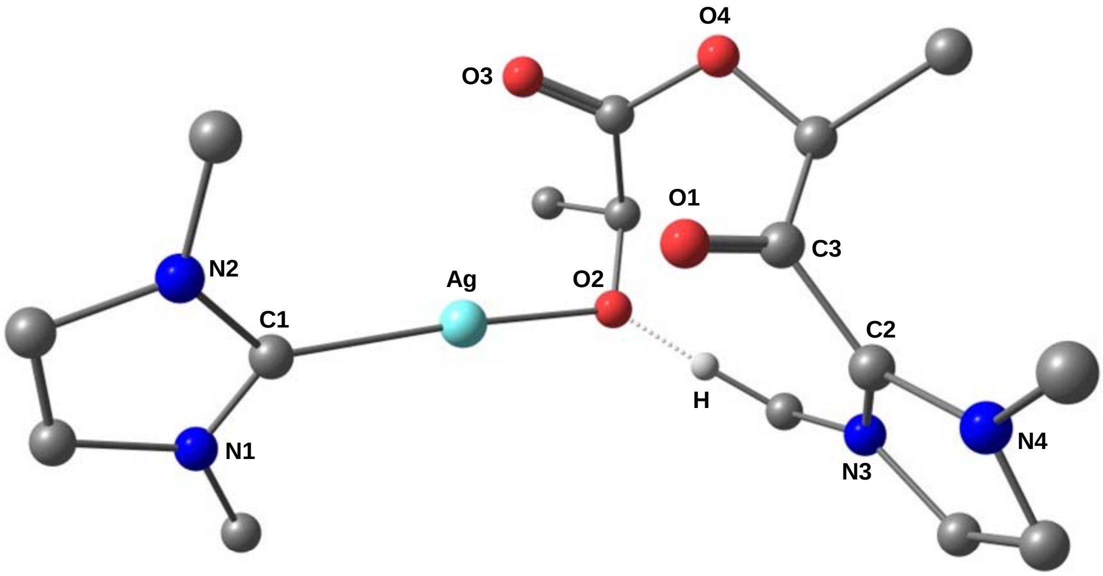


Figure S14. Computed structure of $\mathbf{2}_{HF}$. Selected bond lengths (Å) and angles (°): Ag-C1 2.221, Ag···O1 3.013, Ag-O2 2.091, O1-C3 1.218, C3···O2 2.792, C2-C3 1.549, O2-H 1.395, C1-Ag-O2 175.27, O1-C3-C2 119.22.

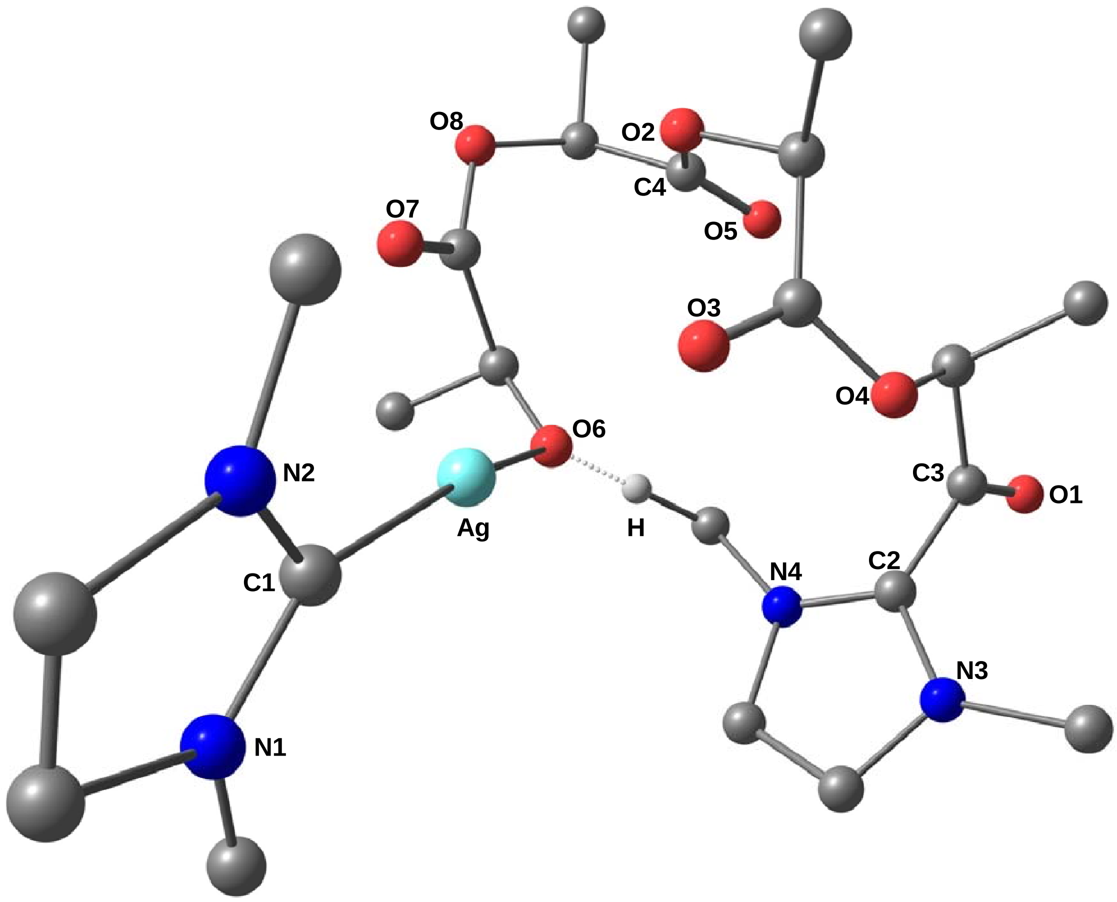


Figure S15. Computed structure of $\mathbf{3}_{HF}$. Selected bond lengths (Å) and angles (°): Ag-C1 2.250, Ag-O6 2.121, O1-C3 1.216, C2-C3 1.546, O6···H 1.307, O2-C4 1.396, C4-O5 1.216, C1-Ag-O6 168.1, O1-C3-C2 120.3, O2-C4-O5 123.2.

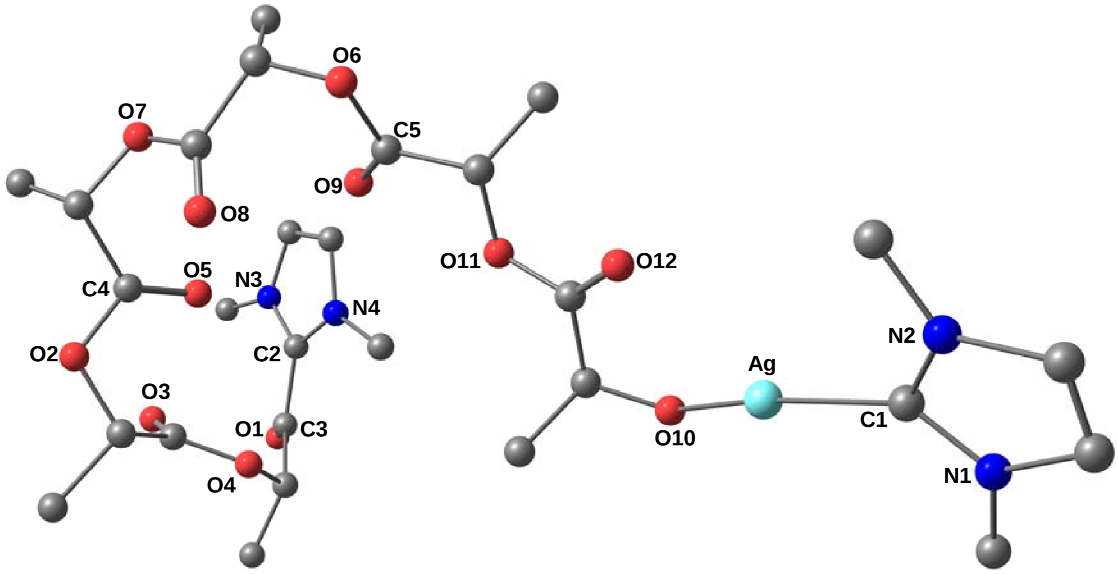


Figure S16. Computed structure of $\mathbf{4}_{HF}$. Selected bond lengths (Å) and angles (°): Ag-C1 2.209, Ag-O10 1.995, O1-C3 1.219, C2-C3 1.544, O2-C4 1.394, C4-O5 1.216, C5-O6 1.389, C5-O9 1.217, C1-Ag-O10 168.9, O1-C3-C2 117.3, O2-C4-O5 122.8, O6-C5-O9 123.8.

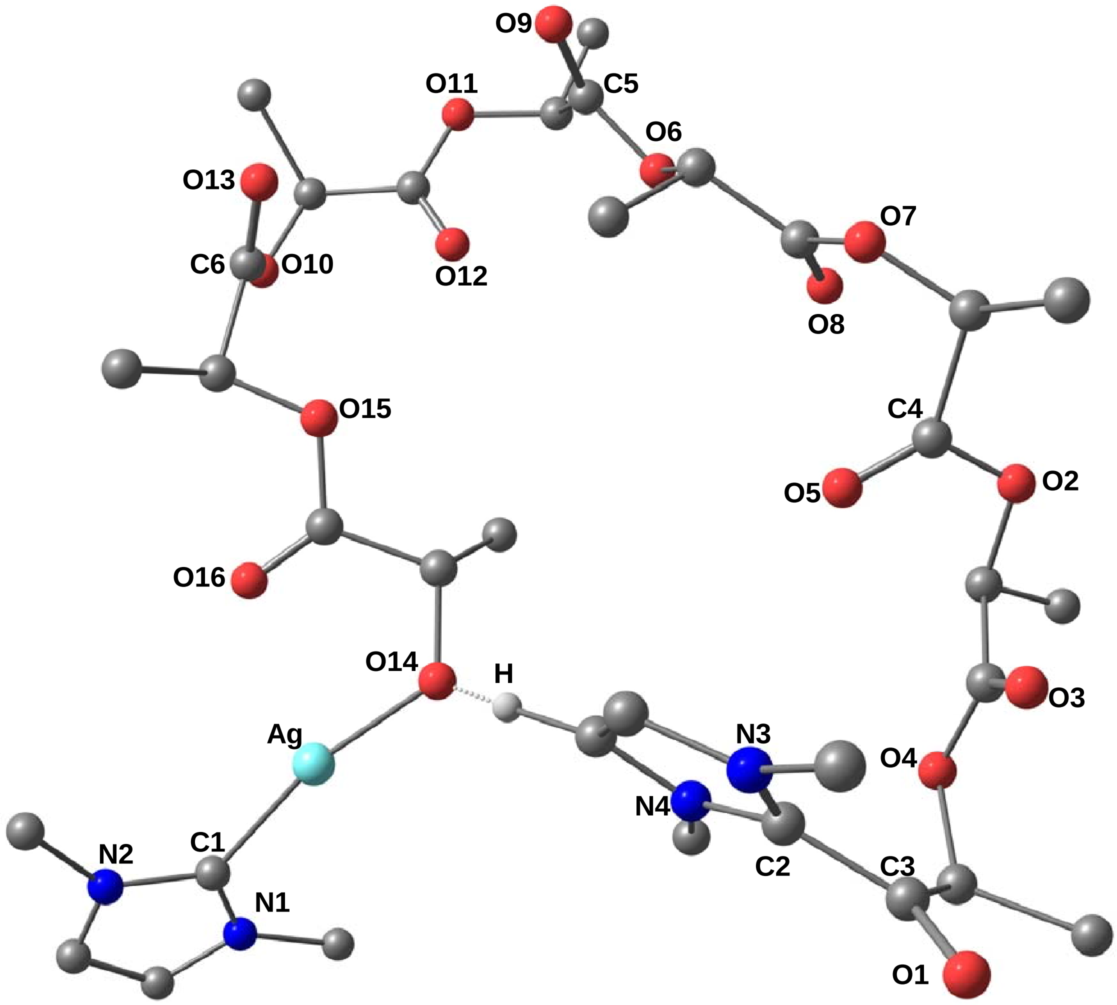


Figure S17. Computed structure of $\mathbf{5}_{HF}$. Selected bond lengths (Å) and angles (°): Ag-C1 2.232, Ag-O14 2.120, O1-C3 1.220, C2-C3 1.534, O2-C4 1.395, C4-O5 1.215, C5-O6 1.394, C5-O9 1.214, C6-O10 1.394, C6-O13 1.214, O14…H 1.144, C1-Ag-O14 168.2, O1-C3-C2 118.5, O2-C4-O5 123.1, O6-C5-O9 124.0, O10-C6-O13 125.0.

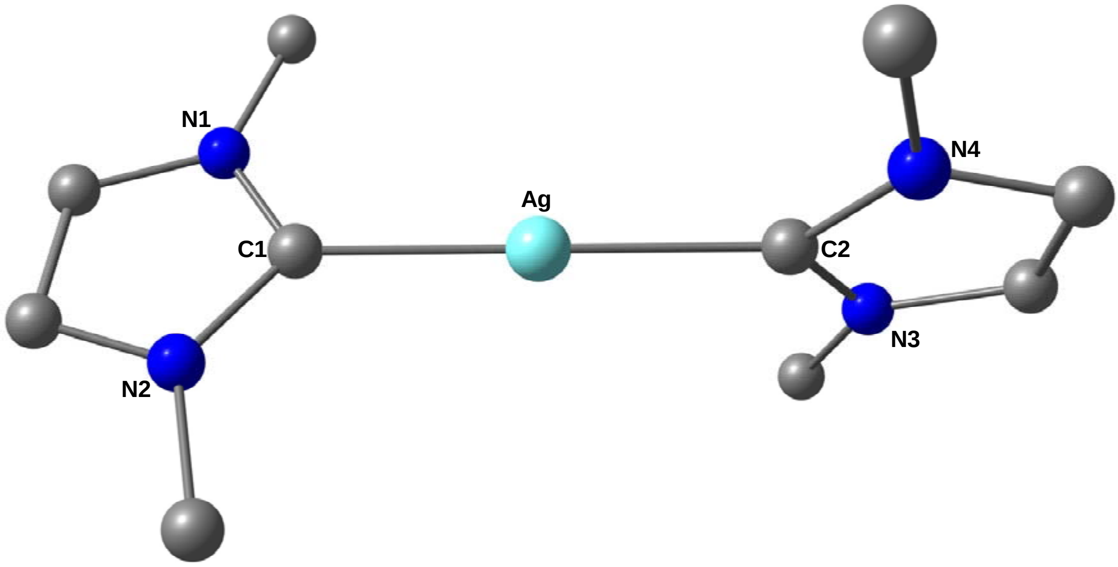


Figure S18. Computed structure of **1**. Selected bond lengths (Å) and angles (°): Ag-C1 2.114, Ag-C2 2.114, C1-Ag-C2 180.0.

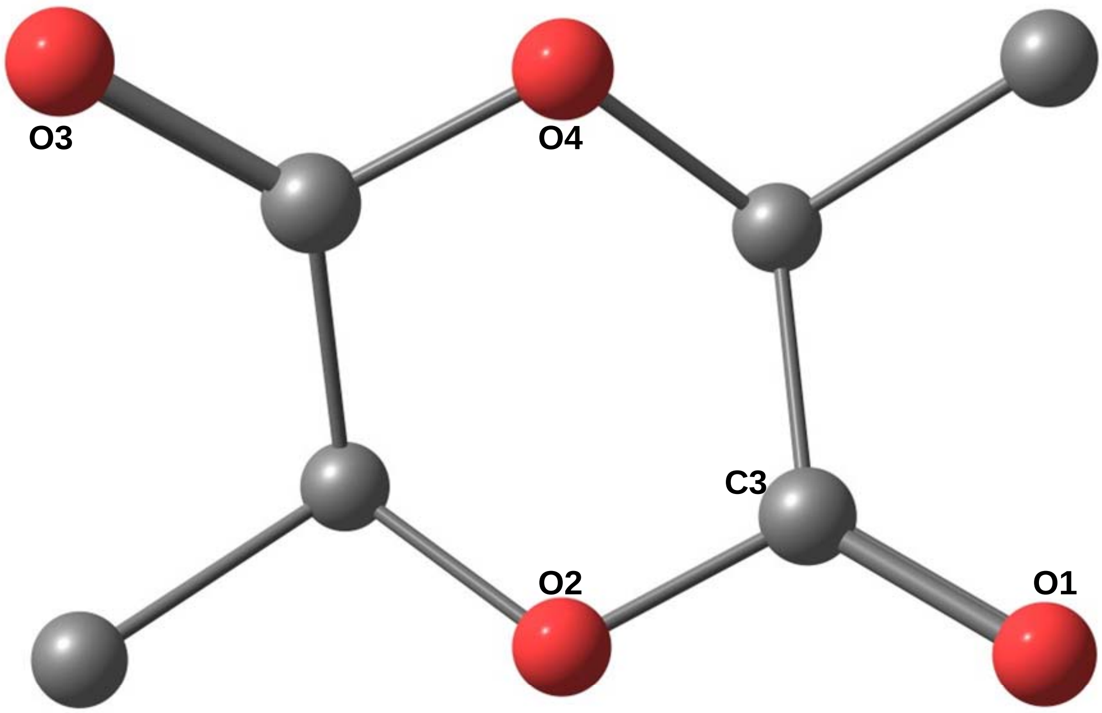


Figure S19. Computed structure of LL. Selected bond lengths (Å) and angles (°): O1-C3 1.204, O2-C3 1.354, O1-C3-O2 121.0.

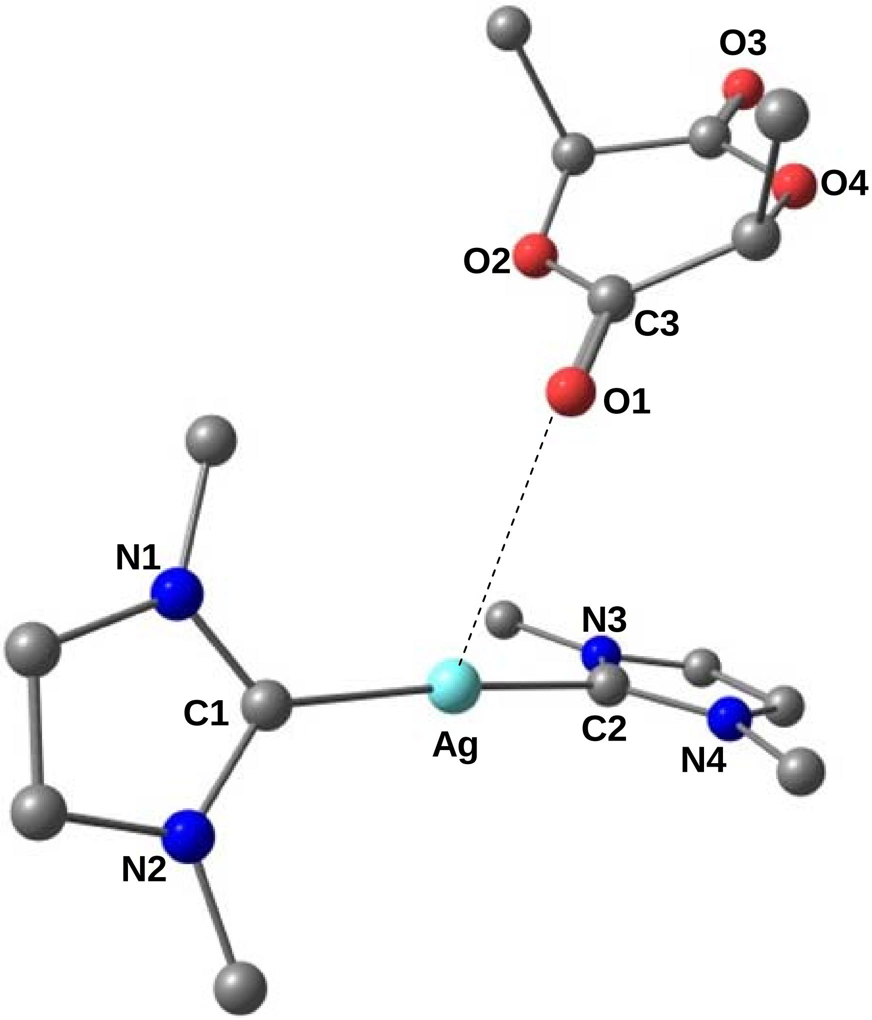


Figure S20. Computed structure of [**1** +LL]. Selected bond lengths (Å) and angles (°): Ag-C1 2.117, Ag-C2 2.119, Ag···O1 3.260, O1-C3 1.215, C3-O2 1.339, C1-Ag-C2 175.21.

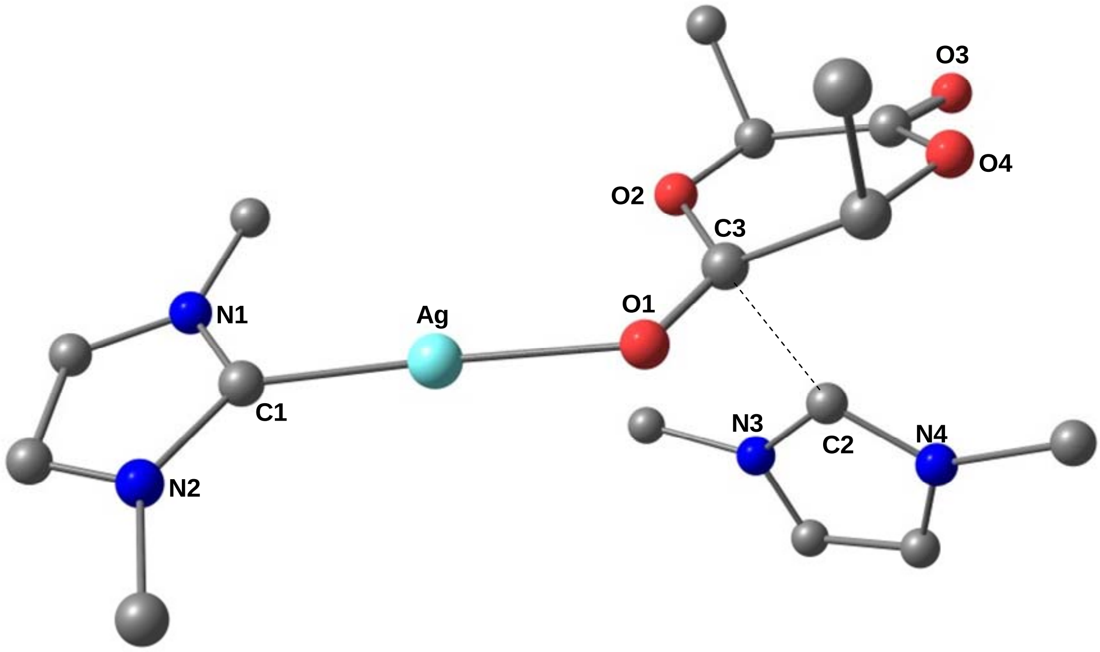


Figure S21. Computed structure of **TS$_1$**([**1**+LL]→**2**). Selected bond lengths (Å) and angles (°): Ag-C1 2.083, Ag-O1 2.128, Ag···O2 3.258, O1-C3 1.249, C3-O2 1.339, C2···C3 2.480, C1-Ag-O1 175.01, Ag-O1-C3 129.00, C1-Ag-O1-C3 -157.38, Ag-O1-C3-O2 -1.55.

Calculated imaginary frequency along the bond C2···C3 is i67.

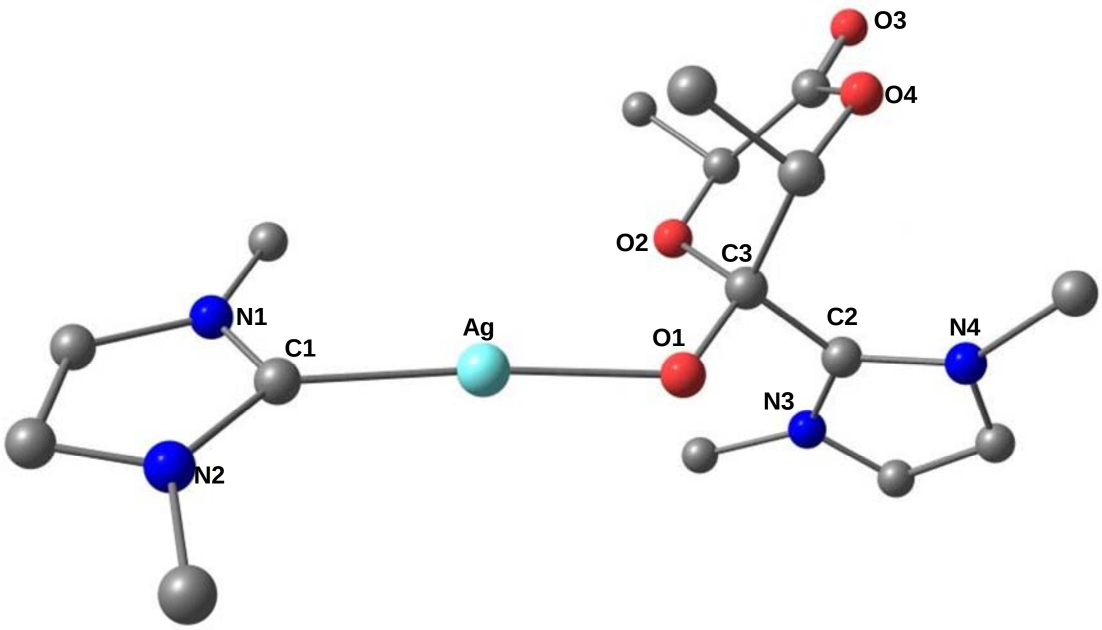


Figure S22. Computed structure of **I**([**1**+LL]→**2**). Selected bond lengths (Å) and angles (°): Ag-C1 2.081, Ag-O1 2.089, Ag···O2 3.183, O1-C3 1.333, C3-O2 1.456, C2-C3 1.570, C1-Ag-O1 174.73, Ag-O1-C3 125.73, O1-C3-C2 105.58, C1-Ag-O1-C3 -174.47, Ag-O1-C3-O2 -30.47, Ag-O1-C3-C2 -146.13.

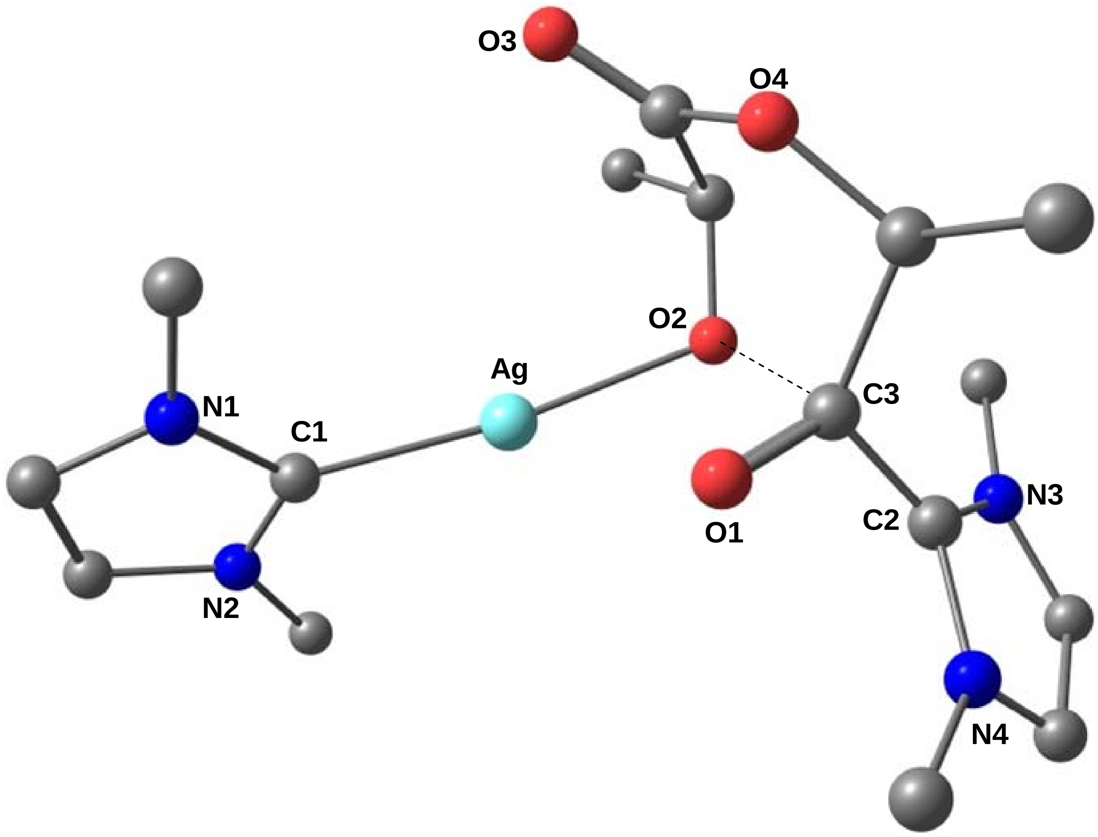


Figure S23. Computed structure of **TS$_2$**([**1**+LL]→**2**). Selected bond lengths (Å) and angles (°): Ag-C1 2.090, Ag···O1 2.831, Ag-O2 2.165, O1-C3 1.232, C3···O2 2.092, C2-C3 1.525, C1-Ag-O2 172.94, O1-C3-C2 115.30.

Calculated imaginary frequency along the bond C3···O2 is i26.

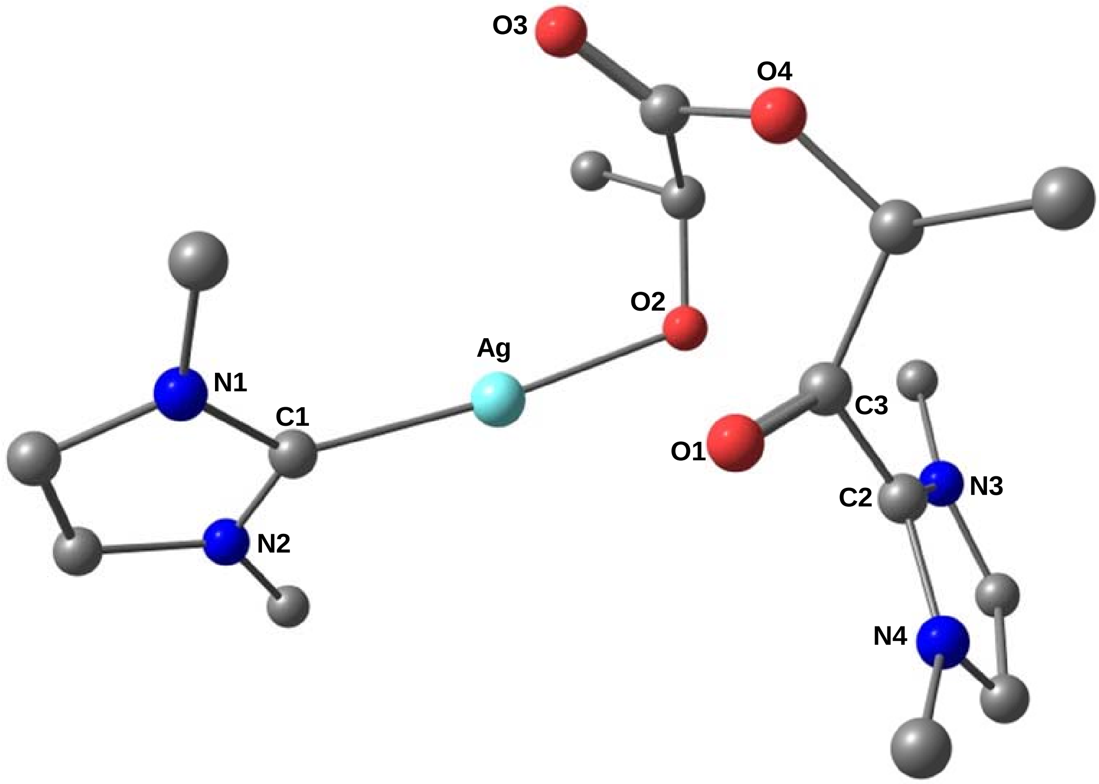


Figure S24. Computed structure of **2**. Selected bond lengths (Å) and angles (°): Ag-C1 2.088, Ag···O1 2.928, Ag-O2 2.148, O1-C3 1.227, C3···O2 2.182, C2-C3 1.522, C1-Ag-O2 173.90, O1-C3-C2 115.64.

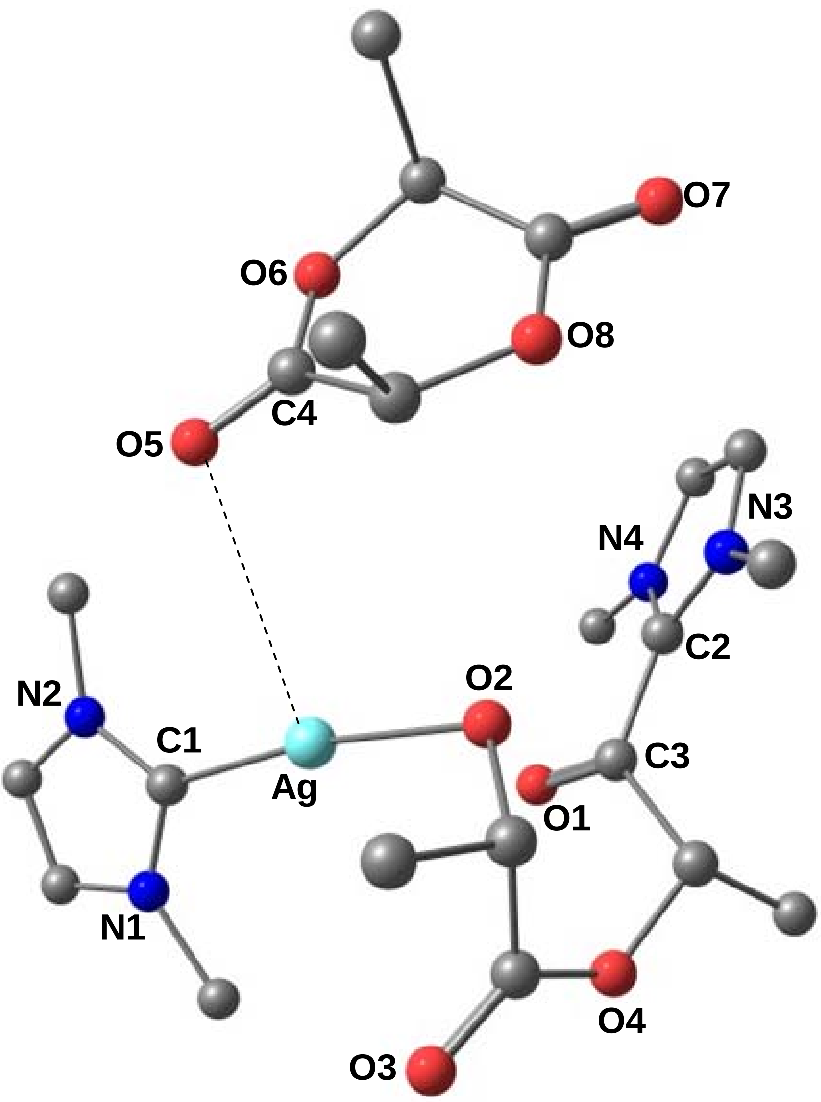


Figure S25. Computed structure of [**2**+LL]. Selected bond lengths (Å) and angles (°): Ag-C1 2.094, Ag-O2 2.153, Ag···O1 3.052, O1-C3 1.220, C3···O2 2.451, C2-C3 1.511, Ag···O5 3.428, C4-O5 1.210, C4-O6 1.346, C1-Ag-O2 171.78.

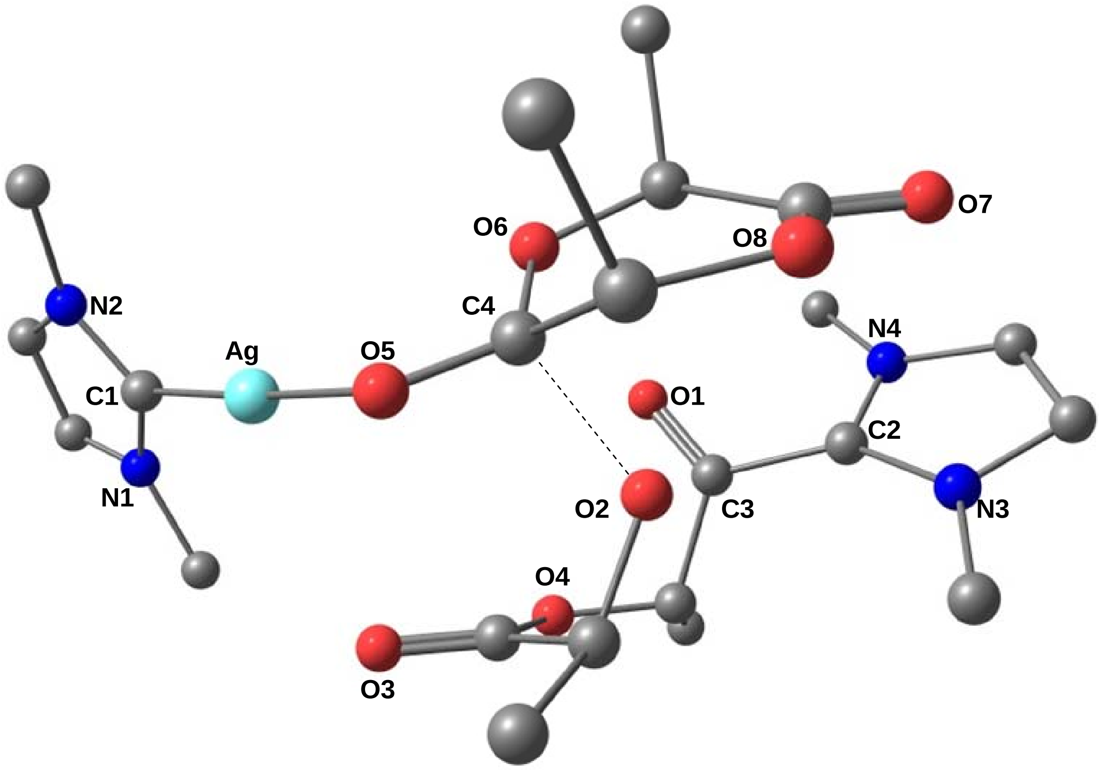


Figure S26. Computed structure of $\mathbf{TS_1}$([**2**+LL]→**3**). Selected bond lengths (Å) and angles (°): Ag-C1 2.091, Ag···O3 2.867, Ag-O5 2.144, Ag···O6 3.181, O1-C3 1.216, C3···O2 2.679, C2-C3 1.515, C4-O5 1.259, C4-O6 1.362, O2···C4 1.936, C1-Ag-O5 173.68, Ag-O5-C4 125.15, C1-Ag-O5-C4 -128.65, Ag-O5-C4-O6 24.19.

Calculated imaginary frequency along the bond C4···O2 is i174.

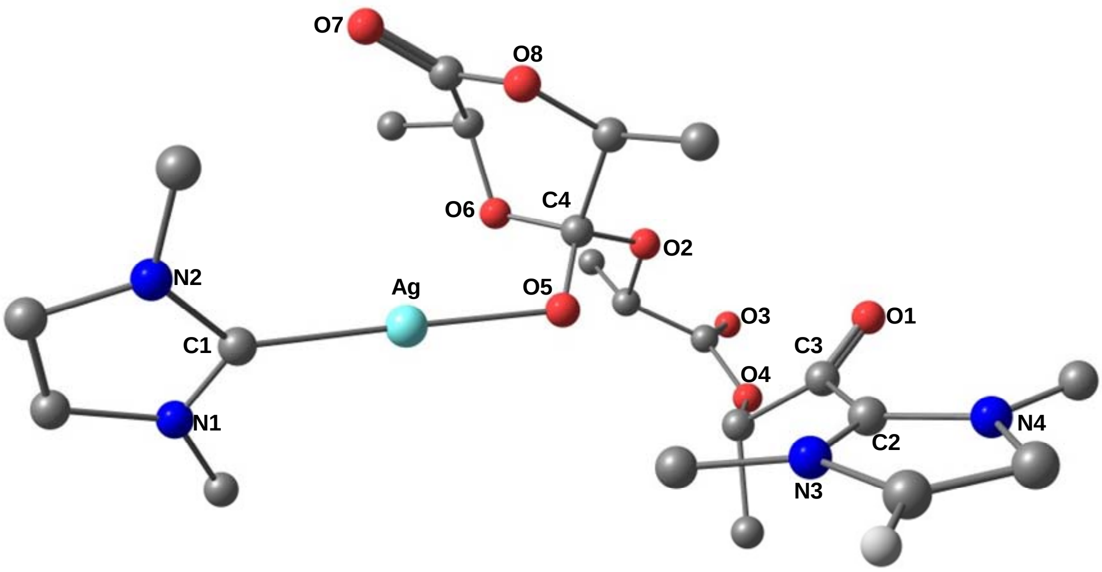


Figure S27. Computed structure of **I**([**2**+LL]→**3**). Selected bond lengths (Å) and angles (°): Ag-C1 2.083, Ag-O5 2.131, Ag···O6 2.768, O1-C3 1.212, C2-C3 1.516, C4-O5 1.347, C4-O6 1.451, O2-C4 1.430, C1-Ag-O5 176.49, Ag-O5-C4 111.87, O5-C4-O2 112.46, C1-Ag-O5-C4 -133.53, Ag-O5-C4-O6 -29.02, Ag-O5-C4-O2 -150.08.

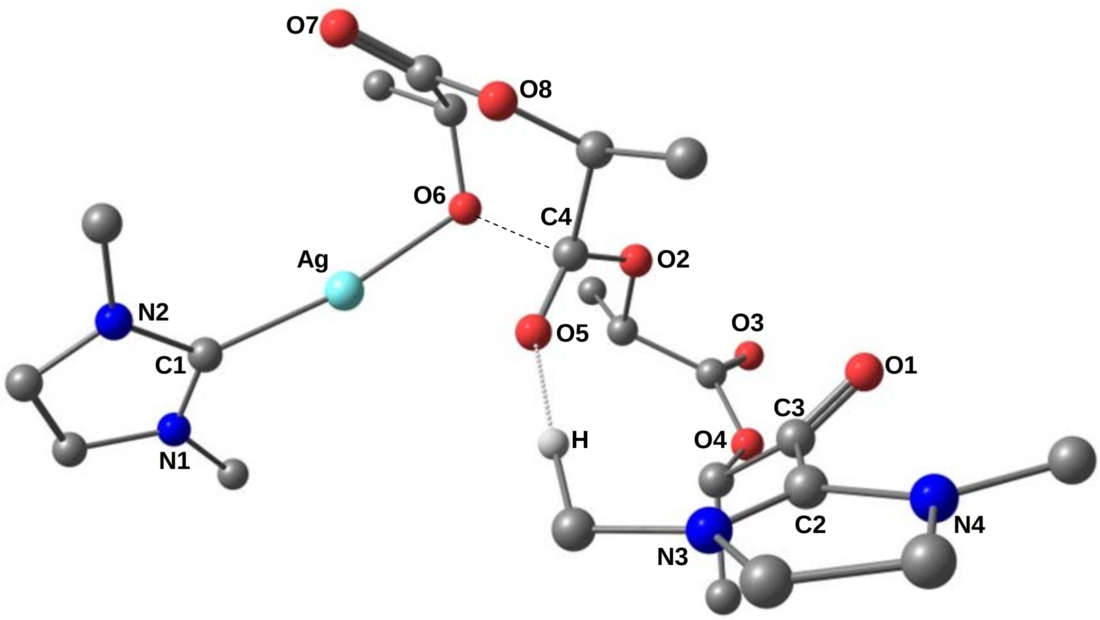


Figure S28. Computed structure of **TS$_2$**([**2**+LL]$\rightarrow$**3**). Selected bond lengths (Å) and angles (°): Ag-C1 2.088, Ag···O5 2.863, Ag-O6 2.140, C4-O5 1.248, C4···O6 1.949, O2-C4 1.379, O1-C3 1.213, C2-C3 1.514, C1-Ag-O6 170.24, O5-C4-O2 121.15.

Calculated imaginary frequency along the bond C4···O6 is i92.

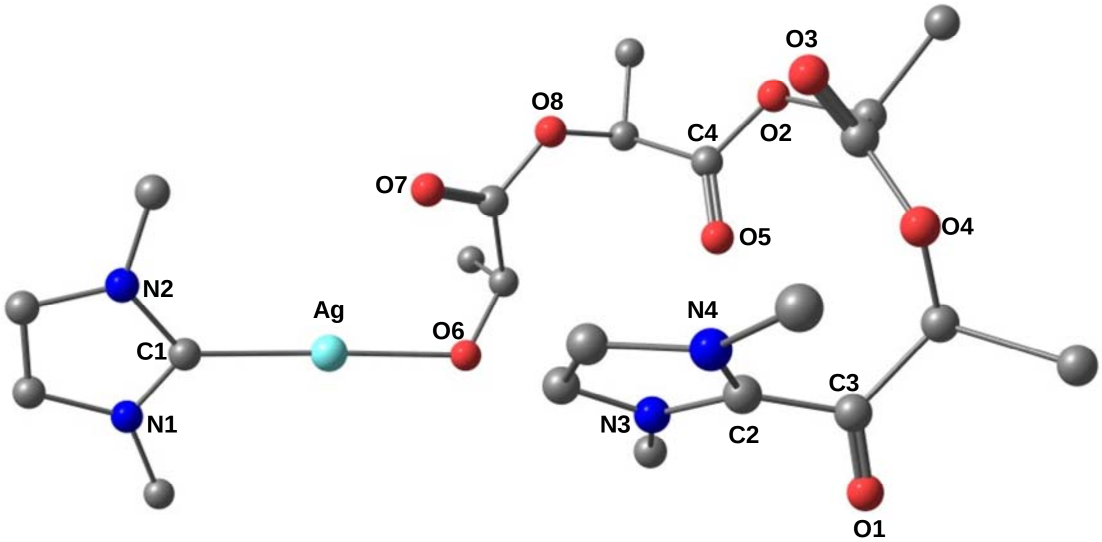


Figure S29. Computed structure of **3**. Selected bond lengths (Å) and angles (°): Ag-C1 2.081, Ag-O6 2.087, C4-O5 1.220, O2-C4 1.338, O1-C3 1.214, C2-C3 1.503, C1-Ag-O6 178.27, O5-C4-O2 122.70.

The Hartree-Fock (HF) and Density Functional Theory (DFT) computation studies on the reactant, product, transition state and the intermediate species, were carried out using GAUSSIAN 03[1] suite of quantum chemical programs.

Table S1: HF/STO-3G, LANL1MB level optimized coordinates of $\mathbf{1}_{HF}$.

Ground state electronic energy = -635.683476182 Hartree/Particle.

C	2.208617000	-0.000001000	0.000076000
N	3.044392000	0.771342000	0.754274000
N	3.044806000	-0.770993000	-0.754022000
C	4.396327000	0.476919000	0.466220000
H	5.208499000	0.986208000	0.964187000
C	4.396583000	-0.476055000	-0.465754000
H	5.209029000	-0.985019000	-0.963606000
N	-3.044476000	0.754272000	-0.771204000
N	-3.044722000	-0.754023000	0.771132000
C	-2.208617000	-0.000007000	-0.000030000
C	-4.396380000	0.466327000	-0.476527000
H	-5.208607000	0.964358000	-0.985665000
C	-4.396531000	-0.465645000	0.476448000
H	-5.208921000	-0.963417000	0.985580000
Ag	0.000000000	-0.000391000	-0.000124000
C	2.634272000	-1.787997000	-1.748502000
H	3.022168000	-2.765092000	-1.458013000
H	1.547136000	-1.826280000	-1.785874000
H	3.022093000	-1.519414000	-2.731873000
C	2.633312000	1.788176000	1.748703000
H	1.546156000	1.826167000	1.785774000
H	3.020933000	1.519637000	2.732165000
H	3.021030000	2.765390000	1.458379000
C	-2.634073000	-1.748560000	1.788033000
H	-1.546933000	-1.785877000	1.826242000
H	-3.021921000	-1.458162000	2.765173000
H	-3.021862000	-2.731931000	1.519401000
C	-2.633511000	1.748719000	-1.788066000
H	-1.546360000	1.785887000	-1.826086000
H	-3.021230000	1.458347000	-2.765266000
H	-3.021212000	2.732150000	-1.519529000

Table S2: HF/STO-3G, LANL1MB level optimized coordinates of DL_{HF}.

Ground state electronic energy = -524.475629734 Hartree/Particle.

O	-0.163294000	1.343571000	-0.832983000
C	-1.332260000	0.732828000	-0.249888000
C	-1.256888000	-0.825849000	-0.178726000
O	-0.061307000	-1.355415000	0.338782000
C	1.101207000	-0.759916000	-0.274292000
C	1.035883000	0.802405000	-0.338203000
O	-2.192973000	-1.557777000	-0.424598000
O	1.978943000	1.530638000	-0.109266000
C	2.341095000	-1.230340000	0.514084000
H	3.240966000	-0.824163000	0.063114000
H	2.282513000	-0.895074000	1.544846000
H	2.392112000	-2.314592000	0.499543000
H	1.180937000	-1.107312000	-1.315152000
C	-1.615848000	1.303441000	1.165564000
H	-1.656921000	2.387426000	1.119190000
H	-2.567572000	0.929552000	1.530423000
H	-0.835562000	1.011934000	1.862765000
H	-2.166564000	0.988682000	-0.911452000

Table S3: HF/STO-3G, LANL1MB level optimized coordinates of [**1**+DL]$_{HF}$.

Ground state electronic energy = -1160.197617 Hartree/Particle.

O	1.609643000	-0.139445000	-0.538761000
C	2.544710000	-0.804163000	-1.424770000
C	4.034908000	-0.526456000	-1.051785000
O	4.345807000	-0.768085000	0.301516000
C	3.513136000	0.026822000	1.164557000
C	1.989985000	-0.057044000	0.800272000
O	4.893486000	-0.248278000	-1.859569000
O	1.092223000	0.061289000	1.614378000
C	-1.114884000	2.459487000	-0.077096000
N	-1.416872000	3.327310000	0.933527000
N	-0.885515000	3.270993000	-1.152071000
C	-1.374509000	4.668409000	0.483877000
H	-1.585883000	5.497499000	1.142816000
C	-1.046974000	4.633756000	-0.806010000
H	-0.908039000	5.425441000	-1.527160000
N	-1.960547000	-2.813630000	1.029438000

N	-2.532418000	-2.521429000	-1.025964000
C	-1.905227000	-1.898801000	0.016127000
C	-2.619731000	-3.994794000	0.614124000
H	-2.761764000	-4.832470000	1.280728000
C	-2.972459000	-3.814550000	-0.656864000
H	-3.491512000	-4.459518000	-1.350273000
Ag	-1.018616000	0.190386000	0.055645000
C	-0.532153000	2.818336000	-2.513612000
H	0.413660000	3.266665000	-2.820001000
H	-0.433455000	1.734654000	-2.506463000
H	-1.314017000	3.106579000	-3.217558000
C	-1.751358000	2.950334000	2.323611000
H	-1.757629000	1.864733000	2.400287000
H	-1.008015000	3.358430000	3.009628000
H	-2.737187000	3.336990000	2.584293000
C	-2.752853000	-1.947315000	-2.370272000
H	-2.387996000	-0.922233000	-2.376967000
H	-2.215758000	-2.531252000	-3.118986000
H	-3.818203000	-1.951866000	-2.603050000
C	-1.434610000	-2.622647000	2.398185000
H	-0.967277000	-1.642573000	2.462337000
H	-2.249766000	-2.683837000	3.120168000
H	-0.695380000	-3.392733000	2.621399000
C	3.747933000	-0.430081000	2.620838000
H	3.126264000	0.151824000	3.294429000
H	3.506041000	-1.482778000	2.730165000
H	4.792345000	-0.280491000	2.876899000
H	3.782621000	1.089769000	1.070292000
C	2.277536000	-2.329976000	-1.444367000
H	1.238734000	-2.517184000	-1.702155000
H	2.913094000	-2.801360000	-2.188088000
H	2.489152000	-2.770184000	-0.473976000
H	2.362419000	-0.386680000	-2.419972000

Table S4: HF/STO-3G, LANL1MB level optimized coordinates of $\mathbf{TS_1}$([**1**+DL]→**2'**)$_{HF}$.

Ground state electronic energy = -1160.13442 Hartree/Particle.

Calculated imaginary frequency along the bond C2···C3 is i167.

O	1.225867000	-0.119834000	-0.619828000
C	2.375597000	-0.053446000	-1.495338000
C	3.665743000	-0.459263000	-0.705632000
O	3.794621000	0.087623000	0.581134000
C	2.834533000	1.126903000	0.857565000

C	1.405258000	0.515770000	0.612386000
O	4.511095000	-1.219397000	-1.123771000
O	0.659115000	0.091641000	1.513671000
C	0.274293000	2.467640000	0.101095000
N	-0.390798000	3.167691000	1.081010000
N	0.020002000	3.229271000	-1.020346000
C	-1.018272000	4.335055000	0.577466000
H	-1.579998000	5.000763000	1.215080000
C	-0.762401000	4.374271000	-0.724416000
H	-1.048542000	5.081641000	-1.487920000
N	-2.643199000	-3.911406000	1.357918000
N	-2.604043000	-3.562421000	-0.770529000
C	-2.085934000	-3.107994000	0.406989000
C	-3.504407000	-4.864562000	0.767789000
H	-4.039593000	-5.592141000	1.360359000
C	-3.480668000	-4.648840000	-0.547208000
H	-3.990407000	-5.145484000	-1.359767000
Ag	-0.651093000	-1.448992000	0.731850000
C	0.496534000	2.930164000	-2.385367000
H	1.540172000	3.225226000	-2.511063000
H	0.393336000	1.865866000	-2.588533000
H	-0.110077000	3.483402000	-3.100102000
C	-0.478650000	2.787969000	2.507293000
H	-0.026240000	1.808422000	2.637691000
H	0.041014000	3.520106000	3.127287000
H	-1.524204000	2.746487000	2.813177000
C	-2.310006000	-3.020460000	-2.115285000
H	-1.636429000	-2.171992000	-2.011559000
H	-1.836464000	-3.788174000	-2.728691000
H	-3.235269000	-2.693179000	-2.590957000
C	-2.398657000	-3.834183000	2.815929000
H	-1.749606000	-2.984594000	3.019947000
H	-3.345750000	-3.700514000	3.339634000
H	-1.917008000	-4.750524000	3.159706000
C	3.032767000	1.569035000	2.320400000
H	2.434268000	2.449105000	2.528121000
H	4.080681000	1.809203000	2.473799000
H	2.748007000	0.770922000	2.998926000
C	2.136450000	-0.995200000	-2.690256000
H	2.993844000	-0.959111000	-3.355655000
H	1.249989000	-0.683497000	-3.234684000
H	2.006418000	-2.016696000	-2.344144000
H	2.974916000	1.979624000	0.183338000
H	2.496285000	0.975955000	-1.854765000

Table S5: HF/STO-3G, LANL1MB level optimized coordinates of **I**([**1**+DL]→**2'**)$_{HF}$.

Ground state electronic energy = -1160.175897 Hartree/Particle.

O	-1.593088000	0.911241000	-1.120447000
C	-1.061521000	2.230214000	-0.865689000
C	-0.031624000	2.190985000	0.304049000
O	-0.486141000	1.607574000	1.493293000
C	-1.813258000	1.059795000	1.367090000
C	-1.785851000	0.118140000	0.085708000
O	1.125406000	2.555738000	0.233795000
O	-0.849770000	-0.866423000	0.200570000
C	-3.229123000	-0.546795000	-0.121046000
N	-4.353864000	0.021355000	-0.636202000
N	-3.551832000	-1.819298000	0.206304000
C	-5.396535000	-0.925768000	-0.620649000
H	-6.382123000	-0.681300000	-0.990991000
C	-4.903316000	-2.056345000	-0.102974000
H	-5.362948000	-3.017758000	0.079229000
N	4.241207000	0.093843000	0.788997000
N	4.175707000	-1.048072000	-1.038802000
C	3.374085000	-0.511827000	-0.073272000
C	5.576301000	-0.057821000	0.350004000
H	6.407487000	0.356878000	0.900688000
C	5.536447000	-0.766489000	-0.777525000
H	6.324738000	-1.109503000	-1.430858000
Ag	1.170065000	-0.537787000	0.056560000
C	-2.598040000	-2.815038000	0.775362000
H	-1.628411000	-2.299710000	0.714283000
H	-2.891676000	-3.049156000	1.798365000
H	-2.623951000	-3.713134000	0.160323000
C	-4.504956000	1.402749000	-1.164251000
H	-4.640460000	2.106722000	-0.341343000
H	-3.616533000	1.655924000	-1.739253000
H	-5.383118000	1.422068000	-1.807231000
C	3.716916000	-1.824265000	-2.211028000
H	2.633680000	-1.916555000	-2.167069000
H	4.001248000	-1.310224000	-3.129955000
H	4.166934000	-2.817488000	-2.195108000
C	3.859081000	0.858602000	1.997261000
H	2.860093000	0.556041000	2.305157000
H	4.566514000	0.639998000	2.796672000
H	3.864623000	1.928639000	1.784091000
C	-2.120533000	0.296325000	2.669533000

H	-1.964033000	0.954667000	3.518104000
H	-1.461627000	-0.561002000	2.765908000
H	-3.152391000	-0.040972000	2.677563000
C	-0.402800000	2.744601000	-2.161638000
H	-0.028435000	3.752471000	-2.009832000
H	-1.133002000	2.754150000	-2.965048000
H	0.423533000	2.099265000	-2.444692000
H	-2.545507000	1.865956000	1.236423000
H	-1.869083000	2.917807000	-0.579133000

Table S6: HF/STO-3G, LANL1MB level optimized coordinates of **TS$_2$**([**1**+DL]→**2'**)$_{HF}$.

Ground state electronic energy = -1160.094952 Hartree/Particle.

Calculated imaginary frequency along the bond C3···O2 is i227.

O	-0.977367000	1.181467000	-0.776907000
C	-0.956146000	2.572075000	-0.497826000
C	-0.439489000	2.712983000	0.969141000
O	-1.308721000	2.311182000	2.005995000
C	-2.353970000	1.425095000	1.588590000
C	-1.755015000	0.125487000	0.941242000
O	0.690401000	3.042520000	1.275317000
O	-0.677068000	-0.370320000	1.252390000
C	-2.800151000	-0.800522000	0.230641000
N	-3.170329000	-2.013779000	0.722388000
N	-3.510992000	-0.588353000	-0.898100000
C	-4.145799000	-2.566429000	-0.125185000
H	-4.585291000	-3.533518000	0.077142000
C	-4.351764000	-1.692409000	-1.120996000
H	-5.006084000	-1.734829000	-1.981059000
N	3.947257000	-0.484217000	0.299291000
N	3.806903000	-0.876510000	-1.815821000
C	3.081539000	-0.419406000	-0.754047000
C	5.207970000	-0.973828000	-0.113204000
H	6.027349000	-1.093331000	0.579996000
C	5.120638000	-1.218786000	-1.419774000
H	5.846302000	-1.600523000	-2.122441000
Ag	0.996558000	0.365838000	-0.720925000
C	-3.323640000	0.583997000	-1.807278000
H	-4.119988000	1.304769000	-1.623448000
H	-2.300082000	0.963806000	-1.537927000
H	-3.381735000	0.221996000	-2.831041000
C	-2.657116000	-2.673234000	1.954973000
H	-1.740234000	-2.173979000	2.263396000

H	-3.408613000	-2.609420000	2.744267000
H	-2.448516000	-3.718446000	1.726930000
C	3.319340000	-0.999751000	-3.206520000
H	2.287801000	-0.655829000	-3.246723000
H	3.931856000	-0.386410000	-3.868314000
H	3.369187000	-2.041407000	-3.525875000
C	3.651868000	-0.060223000	1.686137000
H	2.579376000	0.095393000	1.786160000
H	3.971939000	-0.838414000	2.379013000
H	4.175931000	0.869242000	1.913727000
C	-3.155506000	1.056714000	2.863091000
H	-3.989217000	0.405235000	2.618495000
H	-3.544498000	1.966426000	3.309666000
H	-2.511817000	0.564361000	3.585842000
C	-0.087164000	3.420243000	-1.454966000
H	-0.208869000	4.478957000	-1.245696000
H	-0.390381000	3.229257000	-2.480261000
H	0.964944000	3.167789000	-1.345069000
H	-3.033782000	1.891533000	0.868036000
H	-1.979295000	2.976526000	-0.551164000

Table S7: HF/STO-3G, LANL1MB level optimized coordinates of **2’**$_{HF}$.

Ground state electronic energy = -1160.100071 Hartree/Particle.

O	-0.492698000	0.774030000	-1.387690000
C	-0.716796000	2.160141000	-1.227628000
C	-0.603380000	2.474497000	0.303163000
O	-1.763955000	2.489594000	1.113744000
C	-2.741779000	1.506328000	0.754930000
C	-2.123293000	0.067300000	0.765335000
O	0.468015000	2.626052000	0.861670000
O	-1.060652000	-0.228019000	1.283006000
C	-2.965423000	-1.039227000	0.083070000
N	-3.601290000	-2.054457000	0.725939000
N	-3.186948000	-1.176985000	-1.239957000
C	-4.250046000	-2.849117000	-0.233208000
H	-4.824846000	-3.719715000	0.051617000
C	-3.994012000	-2.311316000	-1.436007000
H	-4.295871000	-2.618309000	-2.428187000
N	4.210040000	-1.312220000	-0.487799000
N	3.821577000	-0.413359000	1.432651000
C	3.264348000	-0.610246000	0.202157000

C	5.350677000	-1.546203000	0.314575000
H	6.208325000	-2.086165000	-0.058089000
C	5.110742000	-0.990378000	1.501078000
H	5.712229000	-0.936005000	2.396210000
Ag	1.310159000	0.141497000	-0.539118000
C	-2.617098000	-0.308730000	-2.331679000
H	-3.387540000	0.410604000	-2.608440000
H	-1.631354000	0.191212000	-1.944525000
H	-2.431841000	-0.967952000	-3.175950000
C	-3.627859000	-2.299164000	2.193546000
H	-2.833361000	-1.721971000	2.663778000
H	-4.597234000	-2.002077000	2.598920000
H	-3.463107000	-3.361876000	2.372557000
C	3.198588000	0.318456000	2.557613000
H	2.206820000	0.648942000	2.256476000
H	3.117428000	-0.338823000	3.423980000
H	3.805757000	1.187029000	2.815026000
C	4.096776000	-1.766874000	-1.890573000
H	4.175494000	-2.853701000	-1.934695000
H	3.130420000	-1.455838000	-2.282053000
H	4.891136000	-1.319635000	-2.489163000
C	-3.886587000	1.610580000	1.794684000
H	-4.675864000	0.899959000	1.567851000
H	-4.300737000	2.613513000	1.762273000
H	-3.508103000	1.424231000	2.795288000
C	0.268890000	3.059924000	-2.014524000
H	-0.016062000	4.105461000	-1.940203000
H	0.258735000	2.767262000	-3.060078000
H	1.279221000	2.946824000	-1.628969000
H	-3.156396000	1.677058000	-0.244897000
H	-1.732547000	2.409694000	-1.571054000

Table S8: HF/STO-3G, LANL1MB level optimized coordinates of LL_{HF}.

Ground state electronic energy = -524.475629721 Hartree/Particle.

O	0.163160000	1.343584000	-0.833017000
C	1.332191000	0.733087000	-0.249772000
H	1.656142000	2.387404000	1.119829000
H	2.166658000	0.989207000	-0.911037000
C	1.615325000	1.303396000	1.165894000
H	2.567071000	0.929644000	1.530837000
H	0.834982000	1.011512000	1.862871000
C	1.257089000	-0.825604000	-0.178831000

O	2.193271000	-1.557377000	-0.424762000
O	0.061571000	-1.355395000	0.338650000
C	-1.101074000	-0.760043000	-0.274295000
H	-1.180825000	-1.107463000	-1.315143000
C	-2.340826000	-1.230627000	0.514224000
H	-2.281963000	-0.895688000	1.545074000
H	-2.391959000	-2.314873000	0.499368000
H	-3.240760000	-0.824219000	0.063601000
C	-1.035988000	0.802288000	-0.338261000
O	-1.979207000	1.530376000	-0.109515000

Table S9: HF/STO-3G, LANL1MB level optimized coordinates of [**1**+LL]$_{HF}$.

Ground state electronic energy = -1160.197812 Hartree/Particle.

O	-1.095717000	-1.249175000	0.230334000
C	-1.459087000	-2.470269000	0.919658000
C	-2.903185000	-2.939918000	0.551273000
O	-3.117204000	-3.090742000	-0.832657000
C	-2.816893000	-1.883334000	-1.554509000
C	-1.489644000	-1.183390000	-1.106469000
O	-3.741542000	-3.275099000	1.358579000
O	-0.827190000	-0.468738000	-1.836227000
C	-1.303575000	-2.235324000	2.433687000
H	-0.770045000	-3.263851000	0.595301000
H	-1.533445000	-3.151472000	2.969189000
H	-1.981236000	-1.455349000	2.767642000
H	-0.280667000	-1.943420000	2.655398000
C	-3.980537000	-0.856859000	-1.467917000
H	-4.114862000	-0.506043000	-0.448567000
H	-4.898235000	-1.334508000	-1.798194000
H	-3.770682000	-0.007849000	-2.111517000
H	-2.681004000	-2.176979000	-2.601765000
C	-0.400871000	2.554888000	0.179144000
N	-0.611034000	3.509188000	-0.775223000
N	-1.066223000	3.029872000	1.273847000
C	-1.402801000	4.568324000	-0.271488000
H	-1.674551000	5.416929000	-0.881667000
C	-1.683019000	4.272964000	0.996019000
H	-2.254238000	4.805322000	1.741964000
N	3.290374000	-1.250484000	-1.104136000
N	3.532308000	-0.852190000	0.998161000
C	2.700309000	-0.601652000	-0.056377000
C	4.480717000	-1.898300000	-0.697224000
H	5.087736000	-2.462384000	-1.389734000

C	4.629821000	-1.652873000	0.602711000
H	5.396112000	-1.954729000	1.301202000
Ag	0.796116000	0.636608000	-0.061252000
C	-1.132383000	2.371098000	2.594889000
H	-2.173424000	2.210376000	2.877288000
H	-0.621910000	1.412144000	2.532549000
H	-0.645394000	2.992905000	3.347345000
C	-0.095465000	3.472765000	-2.160718000
H	0.546639000	2.601295000	-2.273029000
H	-0.924524000	3.406477000	-2.866501000
H	0.481944000	4.375550000	-2.362360000
C	3.348840000	-0.360414000	2.380037000
H	2.484826000	0.300534000	2.404211000
H	3.186322000	-1.199727000	3.057705000
H	4.234214000	0.192959000	2.694657000
C	2.793770000	-1.277296000	-2.496678000
H	1.873893000	-0.699702000	-2.553700000
H	3.538039000	-0.840156000	-3.163255000
H	2.596311000	-2.306025000	-2.800314000

Table S10: HF/STO-3G, LANL1MB level optimized coordinates of **TS$_1$**([**1**+LL]→**2**)$_{HF}$.

Ground state electronic energy = -1160.134420 Hartree/Particle.

Calculated imaginary frequency along the bond C2···C3 is i167.

O	-0.461845000	6.541495000	-0.052414000
C	-0.578220000	7.926295000	0.349569000
C	-2.088532000	8.338010000	0.396972000
O	-2.958356000	7.411395000	0.993844000
C	-2.272018000	6.347044000	1.682594000
C	-1.304596000	5.669212000	0.642863000
O	-2.530765000	9.365480000	-0.067785000
O	-1.558805000	4.616009000	0.030443000
C	0.203150000	8.794990000	-0.653800000
H	-0.152228000	8.047552000	1.353185000
H	0.122098000	9.839208000	-0.367056000
H	-0.205326000	8.675118000	-1.653266000
H	1.250121000	8.506503000	-0.655312000
C	-3.338356000	5.366068000	2.207259000
H	-3.828051000	4.861460000	1.380192000
H	-4.079116000	5.924492000	2.771860000
H	-2.879466000	4.629659000	2.857640000
H	-1.677256000	6.738832000	2.515769000
C	0.262211000	4.179384000	-3.905483000

N	-0.244036000	3.299637000	-4.816545000
N	1.333245000	4.744007000	-4.534435000
C	0.512939000	3.322130000	-6.010245000
H	0.266194000	2.692603000	-6.852710000
C	1.487737000	4.214163000	-5.835991000
H	2.282655000	4.537775000	-6.491827000
N	0.185208000	3.565486000	2.600744000
N	1.427741000	5.305600000	2.728593000
C	0.276638000	4.851119000	2.119664000
C	1.239617000	3.248223000	3.493822000
H	1.315862000	2.280115000	3.965212000
C	2.008782000	4.327011000	3.574471000
H	2.912552000	4.520180000	4.132210000
Ag	-0.512061000	4.588086000	-1.868303000
C	2.230333000	5.773923000	-3.966059000
H	1.918969000	5.984906000	-2.944833000
H	3.257442000	5.407142000	-3.963797000
H	2.170378000	6.686461000	-4.560683000
C	-1.426493000	2.430019000	-4.623882000
H	-1.793271000	2.554111000	-3.606649000
H	-2.210187000	2.708823000	-5.329534000
H	-1.145095000	1.388570000	-4.782997000
C	2.014785000	6.649351000	2.556705000
H	1.970242000	6.941520000	1.509177000
H	1.488676000	7.388921000	3.163573000
H	3.057387000	6.621513000	2.868316000
C	-0.865633000	2.584753000	2.254219000
H	-1.493539000	3.005176000	1.473084000
H	-0.405558000	1.665209000	1.891946000
H	-1.472359000	2.353414000	3.131049000

Table S11: HF/STO-3G, LANL1MB level optimized coordinates of **I**([**1**+LL]→**2**)$_{HF}$.

Ground state electronic energy = -1160.160859 Hartree/Particle.

O	-1.143341000	0.645452000	0.812125000
C	-1.347527000	2.063627000	0.986082000
C	-2.716746000	2.592973000	0.438082000
O	-3.496416000	1.685718000	-0.296838000
C	-2.695127000	0.919126000	-1.213018000
C	-1.614952000	0.047309000	-0.420304000
O	-3.148737000	3.692847000	0.707895000
O	-0.568455000	-0.351031000	-1.193536000

C	-0.153275000	2.918831000	0.491548000
H	-1.403161000	2.202427000	2.072831000
H	-0.370998000	3.969472000	0.661893000
H	0.044586000	2.768840000	-0.564238000
H	0.736472000	2.653466000	1.056090000
C	-2.094327000	1.762508000	-2.362853000
H	-1.502264000	2.591973000	-1.996264000
H	-2.902982000	2.159849000	-2.968651000
H	-1.465068000	1.129468000	-2.979569000
H	-3.395020000	0.212683000	-1.669751000
C	3.457649000	-0.186892000	0.153783000
N	4.514489000	0.012375000	-0.686454000
N	4.030454000	-0.358767000	1.380963000
C	5.738014000	-0.034908000	0.020942000
H	6.687929000	0.101676000	-0.474446000
C	5.439123000	-0.264790000	1.298486000
H	6.069207000	-0.373962000	2.168700000
N	-2.535064000	-2.380917000	-0.659637000
N	-3.083260000	-1.475337000	1.244392000
C	-2.411692000	-1.255684000	0.083923000
C	-3.299904000	-3.328106000	0.047070000
H	-3.517231000	-4.302061000	-0.368566000
C	-3.635520000	-2.772901000	1.216510000
H	-4.212119000	-3.154785000	2.047117000
Ag	1.310488000	-0.219368000	-0.381320000
C	3.307499000	-0.615667000	2.644877000
H	2.239699000	-0.640089000	2.437762000
H	3.618751000	-1.574632000	3.060888000
H	3.521321000	0.178213000	3.361546000
C	4.430675000	0.253174000	-2.143872000
H	3.386786000	0.207898000	-2.448038000
H	4.835846000	1.237808000	-2.380454000
H	4.997070000	-0.511570000	-2.676329000
C	-3.275020000	-0.517337000	2.366535000
H	-2.308589000	-0.246126000	2.790376000
H	-3.790263000	0.372397000	2.002724000
H	-3.886329000	-1.010079000	3.120368000
C	-1.975861000	-2.557485000	-2.029820000
H	-2.789990000	-2.546310000	-2.755421000
H	-1.287317000	-1.715421000	-2.162030000
H	-1.448042000	-3.508864000	-2.074353000

Table S12: HF/STO-3G, LANL1MB level optimized coordinates of **TS**$_2$([**1**+LL]$\rightarrow$**2**)$_{HF}$.

Ground state electronic energy = -1160.094952 Hartree/Particle.

Calculated imaginary frequency along the bond C3···O2 is i227.

O	-0.938940000	0.140074000	1.244425000
C	-1.208738000	1.313833000	1.993827000
C	-0.794816000	2.514426000	1.084962000
O	-1.609989000	2.795249000	-0.032498000
C	-2.437479000	1.702284000	-0.447958000
C	-1.562996000	0.446669000	-0.802229000
O	0.231751000	3.154322000	1.210164000
O	-0.422070000	0.500410000	-1.249435000
C	-0.486632000	1.401723000	3.358183000
H	-2.288880000	1.382996000	2.198211000
H	-0.827037000	2.268950000	3.916326000
H	0.588933000	1.483699000	3.219693000
H	-0.700571000	0.507573000	3.936432000
C	-3.203285000	2.182321000	-1.707175000
H	-2.505852000	2.446779000	-2.496330000
H	-3.785600000	3.061922000	-1.451183000
H	-3.878184000	1.410324000	-2.064749000
H	-3.165168000	1.414890000	0.318062000
C	3.353374000	-0.262515000	0.572550000
N	4.200875000	-1.189735000	1.105902000
N	4.168116000	0.569620000	-0.139444000
C	5.538167000	-0.927883000	0.727764000
H	6.355323000	-1.554336000	1.053135000
C	5.518021000	0.160874000	-0.039675000
H	6.313950000	0.698032000	-0.533786000
N	-2.510632000	-1.454816000	-2.256133000
N	-3.059333000	-1.629317000	-0.148447000
C	-2.369880000	-0.876404000	-1.032834000
C	-3.318172000	-2.597683000	-2.125422000
H	-3.563524000	-3.214656000	-2.978942000
C	-3.651671000	-2.705675000	-0.831170000
H	-4.246462000	-3.442479000	-0.308689000
Ag	1.153920000	-0.051300000	0.859956000
C	3.734015000	1.772803000	-0.883945000
H	2.648831000	1.763855000	-0.966142000
H	4.050341000	2.674235000	-0.356969000
H	4.173712000	1.760148000	-1.881245000
C	3.808560000	-2.320700000	1.974208000
H	2.731544000	-2.287555000	2.125555000
H	4.081313000	-3.264158000	1.499859000
H	4.312594000	-2.238665000	2.937828000
C	-3.071339000	-1.399276000	1.329064000
H	-2.157183000	-0.768149000	1.503635000
H	-4.003070000	-0.904599000	1.602283000

H	-3.011410000	-2.369739000	1.816015000
C	-1.929502000	-0.979283000	-3.542088000
H	-2.712224000	-0.522446000	-4.150730000
H	-1.146291000	-0.254829000	-3.325764000
H	-1.504952000	-1.834793000	-4.067311000

Table S13: HF/STO-3G, LANL1MB level optimized coordinates of $\mathbf{2}_{HF}$.

Ground state electronic energy = -1160.100071 Hartree/Particle.

O	0.492565000	0.773763000	-1.387629000
C	0.716732000	2.159888000	-1.227816000
C	0.603546000	2.474440000	0.302942000
O	1.764312000	2.489884000	1.113273000
C	2.742036000	1.506457000	0.754608000
C	2.123471000	0.067478000	0.765250000
O	-0.467773000	2.625849000	0.861627000
O	1.060906000	-0.227767000	1.283114000
C	-0.269033000	3.059599000	-2.014701000
H	1.732448000	2.409349000	-1.571412000
H	0.015982000	4.105135000	-1.940597000
H	-1.279305000	2.946610000	-1.628964000
H	-0.259061000	2.766768000	-3.060210000
C	3.886856000	1.610775000	1.794335000
H	3.508372000	1.424625000	2.794976000
H	4.301094000	2.613667000	1.761749000
H	4.676064000	0.900044000	1.567608000
H	3.156654000	1.676965000	-0.245260000
C	-3.264420000	-0.610304000	0.202233000
N	-4.210354000	-1.311983000	-0.487681000
N	-3.821484000	-0.413359000	1.432799000
C	-5.351024000	-1.545629000	0.314742000
H	-6.208855000	-2.085323000	-0.057890000
C	-5.110845000	-0.989932000	1.501256000
H	-5.712257000	-0.935440000	2.396432000
N	3.601437000	-2.054280000	0.726001000
N	3.186838000	-1.177207000	-1.240022000
C	2.965486000	-1.039167000	0.083003000
C	4.250052000	-2.849134000	-0.233067000
H	4.824916000	-3.719666000	0.051835000
C	3.993880000	-2.311570000	-1.435945000
H	4.295651000	-2.618747000	-2.428095000
Ag	-1.310203000	0.141311000	-0.538992000
C	-3.198207000	0.318216000	2.557758000
H	-2.205890000	0.647376000	2.256989000

H	-3.804459000	1.187631000	2.814504000
H	-3.118273000	-0.338798000	3.424437000
C	-4.097396000	-1.766378000	-1.890564000
H	-3.130065000	-1.457534000	-2.281371000
H	-4.178685000	-2.852994000	-1.935071000
H	-4.890337000	-1.317051000	-2.489483000
C	2.616833000	-0.309142000	-2.331807000
H	1.631144000	0.190805000	-1.944578000
H	3.387200000	0.410197000	-2.608761000
H	2.431491000	-0.968481000	-3.175969000
C	3.628070000	-2.298680000	2.193661000
H	4.597417000	-2.001403000	2.598961000
H	2.833512000	-1.721485000	2.663784000
H	3.463447000	-3.361373000	2.372899000

Table S14: HF/STO-3G, LANL1MB level optimized coordinates of $\mathbf{3}_{\mathrm{HF}}$.

Ground state electronic energy = -1684.6050804 Hartree/Particle.

H	-4.615591000	-3.315388000	-1.073070000
H	-5.404205000	-1.976652000	-1.942375000
H	4.137312000	-0.165689000	2.957444000
C	-4.582155000	-2.244548000	-1.277695000
H	4.063480000	-1.920379000	2.809568000
H	-6.671281000	-2.168719000	0.608138000
H	-3.637090000	-1.992672000	-1.753577000
H	1.610366000	1.057979000	4.143874000
C	4.285273000	-0.999163000	2.279337000
H	5.325090000	-1.013636000	1.966581000
O	0.005641000	-0.009803000	1.416591000
C	-5.820016000	-1.544482000	0.834319000
N	-4.689784000	-1.485657000	-0.014933000
O	1.982036000	-1.025658000	1.336428000
C	1.210642000	0.121165000	1.544816000
H	2.917624000	1.440132000	2.036633000
C	1.293866000	1.818827000	3.436274000
C	3.378891000	-0.864514000	1.028636000
H	0.209155000	1.864652000	3.422093000
H	3.568572000	0.089220000	0.517863000
H	2.836729000	-0.517425000	-2.060020000
C	1.827244000	1.489351000	2.021480000
H	1.683818000	2.781148000	3.753757000
C	-5.579764000	-0.724273000	1.854951000
C	-3.748089000	-0.627628000	0.478527000
H	-6.174374000	-0.471621000	2.719986000

C	3.712443000	-2.014088000	0.023510000
C	1.876882000	-0.934049000	-2.353900000
Ag	-1.795645000	0.025394000	-0.428750000
N	-4.301479000	-0.158928000	1.636202000
H	3.573340000	-4.739588000	0.899836000
H	0.925383000	-0.252757000	-2.039104000
O	1.383891000	2.539864000	1.140011000
O	3.166141000	2.018969000	-0.216357000
O	4.837399000	-2.388516000	-0.245657000
H	1.905675000	-1.165821000	-3.416891000
C	2.486600000	-2.707677000	-0.613477000
N	1.750345000	-2.256361000	-1.641623000
O	-0.108469000	0.443441000	-1.644230000
H	-0.594184000	1.297515000	-4.178288000
C	2.197496000	2.715029000	0.019216000
N	1.985879000	-3.915358000	-0.227623000
C	0.737101000	-3.194227000	-1.905054000
C	2.483268000	-4.746985000	0.898135000
H	0.022880000	-3.032384000	-2.700464000
H	-1.912178000	1.898606000	-3.170120000
H	2.126653000	-5.765538000	0.753193000
C	0.880728000	-4.210954000	-1.038795000
C	-3.681475000	0.826403000	2.547445000
C	-0.857302000	2.014987000	-3.407143000
H	0.319306000	-5.126398000	-0.915305000
C	0.008240000	1.753712000	-2.141354000
H	2.105084000	-4.355574000	1.844909000
H	-4.325498000	1.701671000	2.638084000
H	-2.720992000	1.127025000	2.135321000
H	-3.534041000	0.379910000	3.531501000
H	1.057077000	1.943722000	-2.411201000
C	1.677548000	3.905034000	-0.850633000
H	-0.693826000	3.017455000	-3.792697000
H	3.298193000	5.254450000	-0.315656000
H	2.064280000	3.756448000	-1.866151000
H	1.868941000	5.396375000	0.723269000
C	-0.435528000	2.781466000	-1.040020000
C	2.212322000	5.247955000	-0.296038000
O	0.241628000	3.995478000	-0.834686000
O	-1.431141000	2.584329000	-0.362454000
H	1.842597000	6.061657000	-0.912420000

Table S15: HF/STO-3G, LANL1MB level optimized coordinates of $\mathbf{4}_{\mathrm{HF}}$.

Ground state electronic energy = -2209.0913563 Hartree/Particle.

H	9.238410000	-2.875188000	-0.531465000
H	8.843419000	-3.140488000	1.184985000
H	-3.606487000	-5.064605000	1.810143000
C	8.544814000	-2.624483000	0.271874000
H	-5.200692000	-4.599933000	1.196683000
H	10.649112000	-0.917660000	1.038368000
H	7.539688000	-2.933973000	-0.006686000
H	-4.428095000	-2.530940000	4.197358000
C	-4.171289000	-4.804129000	0.920288000
H	-4.153580000	-5.643937000	0.233190000
O	-5.589805000	-1.991437000	0.899125000
C	9.695022000	-0.436347000	0.885676000
N	8.545411000	-1.163803000	0.498312000
O	-3.358055000	-2.462089000	1.154969000
C	-4.553119000	-1.820908000	1.509716000
H	-3.220300000	-0.808598000	2.854258000
C	-4.895681000	-1.565825000	4.026216000
C	-3.520947000	-3.569324000	0.249371000
H	-5.967827000	-1.701284000	3.918888000
H	-2.500082000	-3.833630000	-0.052418000
H	-1.127652000	-1.998627000	-1.611605000
C	-4.308414000	-0.909719000	2.754584000
H	-4.705333000	-0.925631000	4.882180000
C	9.327867000	0.838489000	0.995710000
C	7.464280000	-0.339323000	0.368335000
H	9.889311000	1.719816000	1.266199000
C	-4.307915000	-3.197943000	-1.047518000
C	-1.682179000	-1.224278000	-1.079150000
Ag	5.398397000	-0.890498000	-0.187509000
N	7.951302000	0.899350000	0.675732000
H	-6.443438000	-2.521797000	-3.387979000
H	-1.853297000	-1.511662000	-0.042662000
O	-4.915833000	0.390110000	2.627450000
O	-3.962279000	0.517989000	0.545894000
O	-5.088125000	-3.961340000	-1.589660000
H	-1.147590000	-0.273648000	-1.120163000
C	-4.101018000	-1.814261000	-1.701623000
N	-3.006112000	-1.015539000	-1.741510000
O	-0.612196000	3.944635000	-0.153879000
H	-2.073634000	5.264085000	-1.988264000
C	-4.509148000	1.070162000	1.481077000
N	-5.073136000	-1.206530000	-2.430912000
C	-3.305690000	0.121089000	-2.506368000
C	-6.458086000	-1.710185000	-2.658336000
H	-2.570727000	0.905581000	-2.631247000

H	-2.840697000	3.672105000	-1.934438000
H	-7.052326000	-0.879714000	-3.036156000
C	-4.574115000	0.004852000	-2.930838000
C	7.167271000	2.152068000	0.683390000
C	-2.688525000	4.597474000	-1.390795000
H	-5.185742000	0.659791000	-3.535148000
C	-1.993641000	4.343349000	-0.030628000
H	-6.872512000	-2.065173000	-1.714026000
H	7.159489000	2.578536000	1.687123000
H	6.148404000	1.927671000	0.376068000
H	7.608013000	2.867347000	-0.011761000
H	-1.949064000	5.294578000	0.514773000
C	-4.892273000	2.580219000	1.577627000
H	-3.651647000	5.067090000	-1.220591000
H	-6.993699000	2.210923000	1.972953000
H	-4.674337000	2.895490000	2.605850000
H	-6.625500000	2.480324000	0.262388000
C	-2.772163000	3.342437000	0.883839000
C	-6.394448000	2.790415000	1.276958000
O	-4.144695000	3.368401000	0.632925000
O	-2.268817000	2.638108000	1.736286000
H	-6.643715000	3.841408000	1.386538000
C	-0.425101000	2.672213000	-0.679301000
O	-1.335698000	1.945196000	-1.031096000
O	1.138460000	0.889168000	-0.848408000
C	2.401191000	0.357339000	-0.573730000
O	3.358031000	1.068362000	-0.323208000
C	2.426850000	-1.207405000	-0.616130000
H	1.751614000	-1.496723000	-1.444884000
O	3.696928000	-1.701175000	-0.840479000
C	1.789273000	-1.718645000	0.714812000
H	1.772046000	-2.804021000	0.709337000
H	2.387079000	-1.389187000	1.561233000
H	0.775521000	-1.349087000	0.839143000
C	1.089625000	2.327255000	-0.764201000
H	1.575803000	2.685203000	0.151428000
C	1.731011000	3.027746000	-1.990264000
H	1.576748000	4.099983000	-1.917910000
H	2.797458000	2.827786000	-2.011349000
H	1.284904000	2.665432000	-2.911641000

Table S16: HF/STO-3G, LANL1MB level optimized coordinates of $\mathbf{5}_{HF}$.

Ground state electronic energy = -2733.62293275 Hartree/Particle.

H	-5.857217000	-4.722355000	-2.473608000
H	-6.047642000	-3.296214000	-3.523633000
H	4.254430000	-6.930765000	-1.826654000
C	-5.743914000	-3.639395000	-2.533790000
H	4.774054000	-6.449627000	-0.204763000
H	-8.518286000	-3.798345000	-2.095234000
H	-4.703247000	-3.373292000	-2.361298000
H	4.911576000	-3.950152000	-3.425175000
C	3.930191000	-6.779385000	-0.801645000
H	3.569635000	-7.722223000	-0.403423000
O	4.423396000	-3.954493000	0.367656000
C	-7.977052000	-3.166470000	-1.406963000
N	-6.576538000	-2.991338000	-1.498428000
O	3.127053000	-4.507323000	-1.446799000
C	4.098092000	-3.747420000	-0.784241000
H	3.773028000	-2.114733000	-2.154918000
C	5.501641000	-3.238134000	-2.856256000
C	2.786785000	-5.735742000	-0.773751000
H	6.369970000	-3.742139000	-2.442510000
H	1.940786000	-6.136407000	-1.343417000
H	-0.348953000	-5.127351000	-1.067677000
C	4.642290000	-2.627814000	-1.724165000
H	5.839350000	-2.447594000	-3.519231000
C	-8.392476000	-2.434728000	-0.374565000
C	-6.125224000	-2.149105000	-0.523340000
H	-9.377877000	-2.284801000	0.040918000
C	2.303649000	-5.504391000	0.694147000
C	0.011553000	-4.098238000	-1.080154000
Ag	-4.051139000	-1.420572000	-0.137867000
N	-7.249414000	-1.805470000	0.170734000
H	2.095410000	-4.769031000	3.863019000
H	0.838860000	-4.002217000	-1.783761000
O	5.472873000	-1.710191000	-0.995286000
O	2.793651000	5.757744000	0.812855000
O	2.595373000	-6.259847000	1.606350000
H	-0.799077000	-3.436295000	-1.376833000
C	1.432881000	-4.280716000	1.006921000
N	0.445144000	-3.687503000	0.278172000
O	-2.403381000	5.268668000	-0.338507000
H	-2.504789000	7.973954000	0.006344000
C	2.729488000	5.252995000	-0.289911000
N	1.495678000	-3.618655000	2.180664000
C	-0.148710000	-2.616607000	0.991300000
C	2.434571000	-3.899059000	3.298074000
H	-1.142012000	-1.846770000	0.522969000

H	-1.078537000	7.488513000	0.933301000
H	2.452547000	-3.023536000	3.944655000
C	0.525886000	-2.597781000	2.164870000
C	-7.300334000	-0.905507000	1.343767000
C	-1.486555000	7.603476000	-0.064655000
H	0.432969000	-1.949269000	3.020575000
C	-1.480024000	6.259099000	-0.834947000
H	3.431964000	-4.084472000	2.898575000
H	-7.996609000	-0.089181000	1.149754000
H	-6.306449000	-0.498696000	1.517837000
H	-7.626227000	-1.461023000	2.224078000
H	-1.816752000	6.451722000	-1.861223000
C	2.185686000	5.942141000	-1.583043000
H	-0.887273000	8.324400000	-0.611382000
H	4.111716000	6.655303000	-2.285604000
H	2.109696000	5.165246000	-2.353335000
H	3.242850000	7.814745000	-1.270123000
C	-0.057889000	5.623280000	-0.940400000
C	3.135022000	7.067858000	-2.050953000
O	0.894410000	6.547495000	-1.354730000
O	0.193941000	4.455460000	-0.714411000
H	2.730839000	7.542913000	-2.939654000
C	-2.096246000	4.768951000	0.926175000
O	-1.296157000	5.261486000	1.694790000
O	-1.948016000	2.412219000	0.882039000
C	-2.506990000	1.198698000	0.562036000
O	-3.710959000	0.977064000	0.588145000
C	-1.429309000	0.161120000	0.140755000
H	-0.614826000	0.232307000	0.877474000
O	-1.970903000	-1.145421000	0.162607000
C	-0.873935000	0.555905000	-1.254704000
H	-0.092486000	-0.137895000	-1.547953000
H	-1.667279000	0.522542000	-1.998384000
H	-0.459886000	1.559680000	-1.225105000
C	-2.898794000	3.459351000	1.198791000
H	-3.754632000	3.412907000	0.515946000
C	-3.368834000	3.375615000	2.668541000
H	-4.070795000	4.178087000	2.872881000
H	-3.862664000	2.426057000	2.851529000
H	-2.518914000	3.473584000	3.336951000
O	3.556398000	-1.035820000	0.076859000
O	3.164939000	3.961627000	-0.583163000
H	1.993411000	3.643944000	1.956060000
C	4.749404000	-0.905996000	-0.114078000
H	1.720874000	2.235532000	0.924878000
C	2.464718000	2.781137000	1.497080000

C	3.623849000	3.237002000	0.573778000
H	4.332235000	3.839274000	1.157211000
C	5.698045000	0.129358000	0.566804000
H	2.858798000	2.137500000	2.277005000
H	6.990361000	-1.370650000	1.456983000
H	6.435074000	0.431830000	-0.187272000
H	5.700586000	-0.809326000	2.531023000
C	4.383288000	2.003033000	0.008279000
C	6.420908000	-0.503653000	1.778330000
O	4.957880000	1.265027000	1.047247000
O	4.475975000	1.680957000	-1.158423000
H	7.099099000	0.221473000	2.217639000

Table S17: B3LYP/6-31G*, SDD level optimized coordinates of **1**.

Ground state electronic energy = -756.5363493 Hartree/Particle.

C	2.114387000	-0.000022000	0.000017000
N	2.946550000	-0.761294000	-0.760081000
N	2.946539000	0.761282000	0.760093000
C	4.273401000	-0.480476000	-0.479756000
H	5.089032000	-0.980634000	-0.979150000
C	4.273393000	0.480520000	0.479728000
H	5.089018000	0.980705000	0.979107000
N	-2.946577000	-0.760488000	0.760862000
N	-2.946516000	0.760476000	-0.760927000
C	-2.114390000	-0.000018000	-0.000010000
C	-4.273418000	-0.479970000	0.480190000
H	-5.089066000	-0.979600000	0.980085000
C	-4.273378000	0.480007000	-0.480313000
H	-5.088986000	0.979641000	-0.980270000
Ag	-0.000003000	-0.000014000	0.000011000
C	2.523769000	1.751536000	1.748842000
H	2.901469000	2.740215000	1.474268000
H	1.433962000	1.777083000	1.774275000
H	2.901380000	1.478417000	2.737957000
C	2.523807000	-1.751570000	-1.748815000
H	1.434001000	-1.776800000	-1.774583000
H	2.901799000	-1.478696000	-2.737854000
H	2.901138000	-2.740320000	-1.473987000
C	-2.523698000	1.749673000	-1.750714000
H	-1.433890000	1.775124000	-1.776208000
H	-2.901360000	1.475554000	-2.739532000
H	-2.901323000	2.738661000	-1.477152000

C	-2.523857000	-1.749590000	1.750783000
H	-1.434052000	-1.775736000	1.775665000
H	-2.900784000	-1.474883000	2.739724000
H	-2.902276000	-2.738427000	1.477782000

Table S18: B3LYP/6-31G*, SDD level optimized coordinates of LL.

Ground state electronic energy = -534.360449782 Hartree/Particle.

O	-0.257716000	1.353781000	-0.108355000
C	-1.264781000	0.465326000	0.436720000
H	-2.737785000	2.031288000	0.416977000
H	-1.162658000	0.466529000	1.532783000
C	-2.622715000	1.012180000	0.038509000
H	-3.410244000	0.378994000	0.453118000
H	-2.724450000	1.021068000	-1.049847000
C	-1.038493000	-0.965338000	-0.055233000
O	-1.923921000	-1.716041000	-0.376100000
O	0.257632000	-1.353784000	-0.107431000
C	1.264766000	-0.465361000	0.436569000
H	1.163103000	-0.465397000	1.532767000
C	2.622631000	-1.012455000	0.038242000
H	2.723260000	-1.023005000	-1.050212000
H	2.738184000	-2.031021000	0.418002000
H	3.410294000	-0.378429000	0.451191000
C	1.038523000	0.965284000	-0.055870000
O	1.924093000	1.716312000	-0.375414000

Table S19: B3LYP/6-31G*, SDD level optimized coordinates of [**1** +LL].

Ground state electronic energy = -1290.89487660 Hartree/Particle.

O	-2.494545000	-1.183538000	-0.729833000
C	-3.881675000	-1.258921000	-1.164040000
C	-4.845648000	-0.404108000	-0.346052000
O	-4.452022000	0.013341000	0.878295000
C	-3.286738000	-0.544665000	1.514055000
C	-2.174149000	-0.913041000	0.541597000
O	-5.918048000	-0.090768000	-0.792129000
O	-1.015431000	-0.962740000	0.903982000
C	-4.332956000	-2.715902000	-1.259637000

H	-3.869907000	-0.820158000	-2.164061000
H	-5.341694000	-2.750501000	-1.680102000
H	-4.347698000	-3.203201000	-0.279915000
H	-3.655733000	-3.269754000	-1.915667000
C	-3.667095000	-1.715409000	2.425465000
H	-4.060605000	-2.562412000	1.855467000
H	-4.436237000	-1.385838000	3.128959000
H	-2.789140000	-2.048010000	2.986750000
H	-2.893145000	0.269504000	2.126742000
C	2.959049000	-1.262715000	-0.054376000
N	2.596883000	-2.550942000	-0.293439000
N	4.297461000	-1.324704000	0.186321000
C	3.687324000	-3.399903000	-0.207383000
H	3.605308000	-4.464029000	-0.367034000
C	4.761018000	-2.626858000	0.098442000
H	5.795261000	-2.886043000	0.265193000
N	0.324400000	3.097770000	0.891572000
N	0.191064000	2.941433000	-1.248318000
C	0.669346000	2.295403000	-0.151116000
C	-0.352216000	4.225144000	0.453467000
H	-0.710738000	4.985509000	1.130313000
C	-0.437120000	4.126034000	-0.897932000
H	-0.885855000	4.782070000	-1.628052000
Ag	1.742457000	0.469352000	-0.080945000
C	5.151458000	-0.187460000	0.520128000
H	5.986572000	-0.129056000	-0.183224000
H	4.558967000	0.725292000	0.450546000
H	5.539271000	-0.291399000	1.537618000
C	1.250363000	-2.994164000	-0.656394000
H	0.520611000	-2.269666000	-0.293279000
H	1.166790000	-3.097493000	-1.742819000
H	1.056804000	-3.962072000	-0.187609000
C	0.322798000	2.473169000	-2.626211000
H	0.782860000	1.484655000	-2.614807000
H	-0.663233000	2.407021000	-3.094026000
H	0.952281000	3.159037000	-3.200279000
C	0.642965000	2.838240000	2.293908000
H	1.025200000	1.820839000	2.382336000
H	1.399100000	3.544579000	2.649073000
H	-0.259173000	2.937282000	2.903273000

Table S20: B3LYP/6-31G*, SDD level optimized coordinates of **TS$_1$**([**1**+LL]$\rightarrow$**2**).

Ground state electronic energy = -1290.84942799 Hartree/Particle.

Calculated imaginary frequency along the bond C2···C3 is i67.

O	-1.143110000	-1.273287000	-0.433207000
C	-2.318602000	-1.766131000	-1.134562000
C	-3.626118000	-1.717782000	-0.348071000
O	-3.613413000	-1.386398000	0.963291000
C	-2.410891000	-0.982456000	1.632929000
C	-1.303291000	-0.560455000	0.688569000
O	-4.662572000	-1.995362000	-0.893214000
O	-0.306119000	0.013787000	1.173528000
C	-2.019823000	-3.179080000	-1.625941000
H	-2.463192000	-1.089163000	-1.981647000
H	-2.863643000	-3.535008000	-2.221431000
H	-1.866487000	-3.865869000	-0.787583000
H	-1.120079000	-3.176617000	-2.248193000
C	-1.927785000	-2.126836000	2.532856000
H	-1.614031000	-2.992034000	1.939986000
H	-2.748673000	-2.434111000	3.186269000
H	-1.088355000	-1.793764000	3.149396000
H	-2.678826000	-0.117948000	2.241022000
C	3.730560000	0.036502000	-0.009350000
N	4.713420000	0.757216000	0.591846000
N	4.361817000	-0.662590000	-0.988890000
C	5.939908000	0.512386000	-0.003305000
H	6.849285000	0.988357000	0.330215000
C	5.718486000	-0.382850000	-0.999917000
H	6.397234000	-0.839389000	-1.703926000
N	-1.959795000	2.100962000	-1.231397000
N	-3.631085000	2.084694000	0.102642000
C	-2.587529000	1.309404000	-0.312627000
C	-2.588462000	3.330988000	-1.379702000
H	-2.243415000	4.083392000	-2.072672000
C	-3.646280000	3.319526000	-0.532712000
H	-4.403604000	4.063287000	-0.336470000
Ag	1.709027000	0.003159000	0.490261000
C	3.722936000	-1.597436000	-1.913143000
H	2.657635000	-1.640900000	-1.684444000
H	3.859388000	-1.257877000	-2.943539000
H	4.157247000	-2.594000000	-1.796476000
C	4.531966000	1.671154000	1.719099000
H	3.481409000	1.663817000	2.010983000
H	5.142518000	1.344947000	2.565199000
H	4.819626000	2.685335000	1.429149000
C	-4.624236000	1.708588000	1.108397000
H	-5.587231000	2.150234000	0.841909000
H	-4.730269000	0.625250000	1.128482000

H	-4.330069000	2.074908000	2.097765000
C	-0.776080000	1.724343000	-1.993398000
H	0.078042000	2.348689000	-1.709631000
H	-0.542442000	0.680711000	-1.789355000
H	-0.963702000	1.848197000	-3.064585000

Table S21: B3LYP/6-31G*, SDD level optimized coordinates of **I**([**1**+LL]→**2**).

Ground state electronic energy = -1290.88262309 Hartree/Particle.

O	1.570407000	0.868891000	-1.099578000
C	1.037644000	2.202371000	-1.014222000
C	0.112354000	2.364066000	0.192478000
O	0.586543000	1.849570000	1.352027000
C	1.850889000	1.152464000	1.307949000
C	1.769247000	0.116786000	0.134619000
O	-0.961832000	2.917441000	0.165086000
O	0.859256000	-0.835797000	0.326203000
C	0.338924000	2.521033000	-2.325675000
H	1.868911000	2.913989000	-0.862575000
H	-0.027971000	3.550354000	-2.316266000
H	-0.509912000	1.849046000	-2.477886000
H	1.038379000	2.399461000	-3.157908000
C	2.053848000	0.536244000	2.679482000
H	1.275930000	-0.205761000	2.876801000
H	2.003019000	1.313688000	3.446852000
H	3.036826000	0.057194000	2.749107000
H	2.641545000	1.888990000	1.106823000
C	-3.283964000	-0.509413000	-0.061415000
N	-4.113474000	-1.263003000	-0.832023000
N	-4.107500000	0.350537000	0.593055000
C	-5.434200000	-0.881960000	-0.659444000
H	-6.246977000	-1.354378000	-1.189130000
C	-5.428784000	0.134439000	0.241448000
H	-6.237869000	0.717285000	0.653675000
N	3.460316000	-1.823475000	0.297290000
N	4.243819000	-0.043851000	-0.677270000
C	3.144070000	-0.564765000	-0.081676000
C	4.763235000	-2.096815000	-0.070722000
H	5.222067000	-3.051744000	0.130996000
C	5.253668000	-0.986595000	-0.680157000
H	6.220768000	-0.786220000	-1.113710000
Ag	-1.214434000	-0.628607000	0.105345000

C	-3.671830000	1.345581000	1.577807000
H	-3.477024000	0.863760000	2.540199000
H	-2.771801000	1.851389000	1.224426000
H	-4.467456000	2.082733000	1.701060000
C	-3.691933000	-2.330209000	-1.735088000
H	-2.605627000	-2.413355000	-1.690153000
H	-4.141055000	-3.279761000	-1.430403000
H	-3.994312000	-2.096170000	-2.759705000
C	4.391533000	1.278856000	-1.301166000
H	3.756501000	1.344085000	-2.183292000
H	4.124835000	2.065899000	-0.595333000
H	5.439425000	1.396900000	-1.578694000
C	2.609139000	-2.829104000	0.961852000
H	3.272744000	-3.607194000	1.342869000
H	2.053127000	-2.369925000	1.773678000
H	1.904170000	-3.245935000	0.243677000

Table S22: B3LYP/6-31G*, SDD level optimized coordinates of **TS**$_2$([**1**+LL]→**2**).

Ground state electronic energy = -1290.85755148 Hartree/Particle.

Calculated imaginary frequency along the bond C3···O2 is i26.

O	0.847938000	0.606275000	-1.041555000
C	0.820664000	2.004046000	-1.306274000
C	0.460731000	2.708892000	0.006921000
O	1.308214000	2.485948000	1.054722000
C	2.393206000	1.566315000	0.920942000
C	1.838295000	0.141696000	0.741881000
O	-0.525538000	3.382066000	0.186985000
O	0.932771000	-0.285542000	1.459063000
C	-0.133206000	2.378141000	-2.436026000
H	1.831045000	2.336823000	-1.604626000
H	-0.098775000	3.455260000	-2.628056000
H	-1.166718000	2.116898000	-2.185778000
H	0.154356000	1.846010000	-3.348434000
C	3.200009000	1.662330000	2.215047000
H	2.569336000	1.392987000	3.066691000
H	3.555080000	2.687349000	2.351183000
H	4.071162000	0.997438000	2.186254000
H	3.025090000	1.846237000	0.070888000
C	-3.084551000	-0.573034000	0.043466000
N	-3.901038000	-1.569051000	-0.391484000
N	-3.838149000	0.128713000	0.930614000
C	-5.144227000	-1.493570000	0.216639000

H	-5.938678000	-2.190651000	-0.001330000
C	-5.102628000	-0.423493000	1.051606000
H	-5.852981000	-0.010070000	1.707852000
N	2.988296000	-2.090800000	0.828929000
N	3.557815000	-0.937037000	-0.928391000
C	2.779051000	-0.918146000	0.179388000
C	3.896334000	-2.847155000	0.121800000
H	4.210234000	-3.823068000	0.457389000
C	4.250227000	-2.128073000	-0.978103000
H	4.923828000	-2.361652000	-1.787631000
Ag	-1.115290000	-0.119237000	-0.488961000
C	-3.381050000	1.288971000	1.699590000
H	-3.099413000	0.985235000	2.711953000
H	-2.520557000	1.740634000	1.204595000
H	-4.186374000	2.025213000	1.749983000
C	-3.543778000	-2.578384000	-1.383750000
H	-2.517767000	-2.397535000	-1.705875000
H	-3.616965000	-3.578632000	-0.947248000
H	-4.210196000	-2.509035000	-2.248133000
C	3.624407000	0.074980000	-1.992501000
H	2.602538000	0.342783000	-2.258859000
H	4.182551000	0.949501000	-1.650384000
H	4.143170000	-0.368235000	-2.842828000
C	2.376822000	-2.549905000	2.090224000
H	2.978658000	-3.382700000	2.456210000
H	2.372247000	-1.742367000	2.819338000
H	1.350391000	-2.868717000	1.911517000

Table S23: B3LYP/6-31G*, SDD level optimized coordinates of **2**.

Ground state electronic energy = -1290.85758134 Hartree/Particle.

O	0.815733000	0.624201000	-1.064385000
C	0.806676000	2.022520000	-1.311360000
C	0.496717000	2.717550000	0.020252000
O	1.382620000	2.490738000	1.038292000
C	2.453090000	1.562670000	0.873924000
C	1.884933000	0.138016000	0.774257000
O	-0.482281000	3.387851000	0.243701000
O	0.983107000	-0.248638000	1.511001000
C	-0.168457000	2.437699000	-2.409096000
H	1.815433000	2.340140000	-1.633769000
H	-0.112316000	3.516245000	-2.588638000

H	-1.200958000	2.198712000	-2.133573000
H	0.080958000	1.910858000	-3.335738000
C	3.330874000	1.691649000	2.119790000
H	2.746026000	1.457496000	3.013565000
H	3.700395000	2.717335000	2.201574000
H	4.194021000	1.017993000	2.066061000
H	3.040894000	1.808465000	-0.016490000
C	-3.085060000	-0.565654000	0.056582000
N	-3.910431000	-1.542922000	-0.403850000
N	-3.820828000	0.097692000	0.987147000
C	-5.141069000	-1.494103000	0.231803000
H	-5.939833000	-2.181953000	0.000627000
C	-5.082823000	-0.459859000	1.109871000
H	-5.820506000	-0.073930000	1.796539000
N	2.960708000	-2.128659000	0.840014000
N	3.514890000	-1.001231000	-0.940279000
C	2.771237000	-0.952329000	0.190391000
C	3.822232000	-2.916676000	0.110711000
H	4.114870000	-3.900655000	0.442047000
C	4.166006000	-2.214035000	-1.003581000
H	4.806626000	-2.473391000	-1.831826000
Ag	-1.132427000	-0.087183000	-0.506673000
C	-3.351554000	1.230539000	1.788748000
H	-3.078996000	0.896082000	2.793873000
H	-2.482258000	1.681747000	1.309017000
H	-4.146021000	1.977357000	1.855297000
C	-3.571034000	-2.512047000	-1.441486000
H	-2.568737000	-2.287929000	-1.808086000
H	-3.591095000	-3.526662000	-1.033079000
H	-4.281594000	-2.439042000	-2.269480000
C	3.576208000	0.001564000	-2.014361000
H	2.554326000	0.318746000	-2.224105000
H	4.199127000	0.845763000	-1.709854000
H	4.022082000	-0.473425000	-2.888636000
C	2.370402000	-2.560047000	2.120877000
H	2.946978000	-3.417497000	2.469950000
H	2.424640000	-1.752739000	2.848669000
H	1.325950000	-2.834224000	1.975629000

Table S24: B3LYP/6-31G*, SDD level optimized coordinates of [**2**+LL].

Ground state electronic energy = -1825.22325848 Hartree/Particle.

O	0.090230000	0.798415000	1.104143000
C	0.583704000	1.327606000	2.319202000
C	1.868066000	2.113926000	2.012001000
O	1.753939000	3.204075000	1.187613000
C	0.524234000	3.522555000	0.548213000
C	0.284169000	2.542548000	-0.606420000
O	2.971409000	1.812834000	2.400496000
O	1.202990000	2.091446000	-1.270777000
C	0.837119000	0.274550000	3.397398000
H	-0.154855000	2.042335000	2.732267000
H	1.201212000	0.736644000	4.320867000
H	1.585603000	-0.453286000	3.067439000
H	-0.096415000	-0.254278000	3.616476000
C	0.676932000	4.942150000	-0.008937000
H	1.515115000	4.981383000	-0.710229000
H	0.877033000	5.633779000	0.813759000
H	-0.236016000	5.268026000	-0.520682000
H	-0.301575000	3.498463000	1.262295000
C	3.069739000	-1.690915000	-0.589574000
N	4.371275000	-1.292849000	-0.611217000
N	3.076497000	-2.918679000	-1.173364000
C	5.173824000	-2.253236000	-1.203453000
H	6.240574000	-2.128921000	-1.309066000
C	4.357831000	-3.278884000	-1.557797000
H	4.573841000	-4.224109000	-2.031544000
N	-1.311518000	2.240778000	-2.517244000
N	-2.318793000	2.356279000	-0.586718000
C	-1.103537000	2.385198000	-1.183650000
C	-2.661135000	2.115486000	-2.750533000
H	-3.058098000	1.989247000	-3.745583000
C	-3.291968000	2.180793000	-1.543031000
H	-4.331176000	2.063632000	-1.278369000
Ag	1.493688000	-0.563825000	0.204573000
C	1.903654000	-3.763229000	-1.393667000
H	1.651375000	-3.785487000	-2.458646000
H	2.119882000	-4.779830000	-1.054704000
H	1.061121000	-3.373418000	-0.824115000
C	4.879873000	-0.013012000	-0.113515000
H	4.155158000	0.431553000	0.568628000
H	5.814265000	-0.183179000	0.426667000
H	5.060332000	0.672064000	-0.947200000
C	-2.606941000	2.413036000	0.854971000
H	-1.858700000	1.803831000	1.360922000
H	-2.590368000	3.450303000	1.198148000
H	-3.595143000	1.983064000	1.010162000
C	-0.302143000	2.213217000	-3.590908000

H	0.413593000	3.022094000	-3.453166000
H	0.231087000	1.263041000	-3.576969000
H	-0.831298000	2.342133000	-4.535805000
C	-1.925190000	-2.547223000	0.365950000
O	-0.834728000	-3.070603000	0.411076000
C	-2.337683000	-1.529966000	1.417614000
H	-1.474826000	-0.868413000	1.544678000
C	-2.706151000	-2.177010000	2.752314000
H	-1.854817000	-2.757613000	3.118702000
H	-3.570162000	-2.842391000	2.664951000
H	-2.941885000	-1.397561000	3.482445000
C	-4.249768000	-0.951270000	-0.005050000
O	-3.392711000	-0.630880000	0.976501000
O	-5.083107000	-0.149284000	-0.366420000
C	-4.133370000	-2.330699000	-0.638123000
H	-4.369419000	-2.201953000	-1.696067000
C	-5.102922000	-3.343017000	-0.025915000
H	-6.129649000	-2.985038000	-0.146769000
H	-4.998948000	-4.300369000	-0.543707000
H	-4.911462000	-3.499782000	1.039425000
O	-2.776897000	-2.838568000	-0.634243000

Table S25: B3LYP/6-31G*, SDD level optimized coordinates of **TS$_1$**([**2**+LL]→**3**).

Ground state electronic energy = -1825.19766527 Hartree/Particle.

Calculated imaginary frequency along the bond C4···O2 is i174.

O	1.301600000	0.230558000	1.213082000
C	0.828034000	-0.515948000	2.305841000
C	-0.186223000	-1.524675000	1.755224000
O	0.291091000	-2.514108000	0.931948000
C	1.676538000	-2.655268000	0.642743000
C	2.093790000	-1.694008000	-0.474095000
O	-1.384921000	-1.493526000	1.932416000
O	1.372344000	-1.482931000	-1.430278000
C	0.281374000	0.245121000	3.521523000
H	1.672205000	-1.104499000	2.710063000
H	0.030290000	-0.466568000	4.315916000
H	-0.604401000	0.829931000	3.283321000
H	1.061934000	0.911057000	3.906451000
C	1.871986000	-4.092089000	0.141550000
H	1.253020000	-4.263435000	-0.743451000
H	1.568922000	-4.791337000	0.925303000
H	2.921194000	-4.286210000	-0.108480000

H	2.278418000	-2.506753000	1.540366000
C	-4.318128000	-0.326339000	-0.515685000
N	-4.754710000	-1.609179000	-0.408007000
N	-5.260555000	0.293334000	-1.277386000
C	-5.950519000	-1.785079000	-1.084756000
H	-6.459048000	-2.736315000	-1.118462000
C	-6.270390000	-0.585432000	-1.633834000
H	-7.112289000	-0.285536000	-2.238671000
N	4.160789000	-1.239556000	-1.810460000
N	4.432363000	-0.805262000	0.308944000
C	3.538951000	-1.258355000	-0.602896000
C	5.439066000	-0.769214000	-1.652778000
H	6.118138000	-0.666659000	-2.484363000
C	5.606587000	-0.493002000	-0.329180000
H	6.450523000	-0.082399000	0.201657000
Ag	-2.593003000	0.529264000	0.298807000
C	-5.253442000	1.707900000	-1.639287000
H	-5.470908000	1.824647000	-2.703820000
H	-6.034131000	2.232991000	-1.077702000
H	-4.289381000	2.139224000	-1.371168000
C	-4.099697000	-2.672021000	0.355972000
H	-3.123857000	-2.325319000	0.696521000
H	-4.708739000	-2.936918000	1.224945000
H	-3.963761000	-3.548220000	-0.284201000
C	4.227436000	-0.548097000	1.741648000
H	3.642240000	0.369092000	1.840211000
H	3.756219000	-1.386609000	2.244077000
H	5.206346000	-0.317947000	2.165316000
C	3.606254000	-1.628973000	-3.117572000
H	2.983879000	-2.515810000	-3.013884000
H	3.004719000	-0.814822000	-3.522575000
H	4.446759000	-1.845302000	-3.777985000
C	0.190913000	1.715116000	0.655268000
O	-0.953097000	1.601856000	1.167508000
C	1.107160000	2.796294000	1.224978000
H	1.236672000	2.603714000	2.288122000
C	0.537472000	4.198303000	1.016204000
H	-0.406148000	4.292172000	1.560389000
H	0.348569000	4.407600000	-0.040882000
H	1.243074000	4.941047000	1.399566000
C	2.669250000	2.130585000	-0.503520000
O	2.449379000	2.720355000	0.675461000
O	3.805158000	1.934929000	-0.889516000
C	1.488222000	1.748872000	-1.388191000
H	1.732754000	0.779465000	-1.824905000
C	1.298352000	2.772143000	-2.512563000

H	2.210032000	2.836106000	-3.113639000
H	0.470353000	2.454647000	-3.153313000
H	1.070268000	3.766828000	-2.118694000
O	0.242716000	1.571165000	-0.698265000

Table S26: B3LYP/6-31G*, SDD level optimized coordinates of **I**([**2**+LL]→**3**).

Ground state electronic energy = -1825.20779080 Hartree/Particle.

H	1.312206000	0.068244000	3.673867000
O	-3.122666000	1.356788000	2.856100000
O	-0.978182000	0.778784000	2.677471000
C	-2.028470000	1.589022000	2.395931000
H	-3.475412000	3.874543000	1.702444000
C	1.309551000	0.122469000	2.581180000
H	0.584415000	2.136531000	2.528922000
H	1.050194000	-0.863171000	2.183861000
H	-5.284777000	-1.879696000	2.293696000
H	5.427412000	-4.145570000	1.595780000
H	6.058442000	-0.854535000	1.946901000
H	2.309926000	0.408380000	2.245313000
H	-3.642360000	-2.471380000	1.949876000
C	0.304785000	1.159217000	2.122578000
H	-1.025992000	3.431381000	1.852410000
H	-3.962512000	-0.716204000	2.066072000
H	6.937138000	-2.285741000	1.319470000
C	-4.365143000	-1.677809000	1.741851000
C	-1.702188000	2.696066000	1.391463000
C	-2.941832000	3.402033000	0.873439000
C	4.683470000	-3.528585000	1.116157000
C	6.192984000	-1.521099000	1.095306000
H	-3.618707000	2.692125000	0.390066000
H	2.833184000	-4.723167000	0.802835000
C	3.409539000	-3.814863000	0.720625000
N	4.924549000	-2.214314000	0.797206000
H	-2.656809000	4.171405000	0.150467000
H	6.511757000	-0.937540000	0.232510000
C	0.169217000	1.305309000	0.575135000
H	-6.707074000	-2.401246000	0.386537000
O	-1.046860000	2.043038000	0.290009000
N	-4.681412000	-1.646723000	0.310001000
N	2.889418000	-2.674590000	0.152543000
O	4.409287000	0.531342000	0.435211000

C	3.822688000	-1.695929000	0.200105000
H	0.909583000	-3.313344000	0.185976000
O	1.310589000	2.092678000	0.226912000
O	0.109881000	0.151005000	-0.116503000
H	1.101693000	-1.579312000	-0.178960000
C	-5.893177000	-2.047134000	-0.226964000
Ag	-1.899157000	-0.494618000	-0.412810000
C	1.508567000	-2.581327000	-0.357599000
C	3.763162000	-0.245413000	-0.234829000
C	-3.826523000	-1.242564000	-0.666417000
H	1.327074000	4.697093000	-0.472782000
H	-0.273623000	4.030525000	-0.903817000
H	1.493538000	-2.822637000	-1.423200000
C	1.348840000	2.631577000	-1.105979000
H	1.934133000	0.151940000	-1.281675000
C	-5.798605000	-1.887224000	-1.572357000
C	0.784762000	4.048016000	-1.164640000
C	3.009558000	0.176332000	-1.503679000
N	-4.527822000	-1.394631000	-1.822098000
C	2.824291000	2.656202000	-1.544191000
H	0.790528000	1.967497000	-1.779032000
O	3.439390000	3.671180000	-1.729078000
O	3.470653000	1.475647000	-1.828554000
H	-6.513612000	-2.070811000	-2.359375000
H	3.132430000	-1.768137000	-2.534689000
H	0.898270000	4.461286000	-2.171290000
C	3.356867000	-0.711581000	-2.707808000
H	4.418551000	-0.612541000	-2.953967000
H	-3.009145000	-0.710407000	-3.069130000
C	-4.037364000	-1.062880000	-3.156600000
H	-4.652293000	-0.273475000	-3.598061000
H	2.778155000	-0.377785000	-3.572869000
H	-4.065667000	-1.948085000	-3.798447000

Table S27: B3LYP/6-31G*, SDD level optimized coordinates of **TS$_2$**([**2**+LL]$\rightarrow$**3**).

Ground state electronic energy = -1825.19107756 Hartree/Particle.

Calculated imaginary frequency along the bond C4···O6 is i92.

O	-1.242432000	-2.147285000	0.043081000
C	3.884206000	1.240016000	-0.732618000
N	4.342048000	1.624758000	-1.954420000
N	4.607735000	1.976966000	0.152312000
C	5.335899000	2.583840000	-1.835155000

H	5.833581000	3.012084000	-2.691704000
C	5.501424000	2.806473000	-0.506126000
H	6.168425000	3.471270000	0.021063000
Ag	2.477475000	-0.223586000	-0.244652000
C	4.476886000	1.924584000	1.610116000
H	5.459944000	1.762298000	2.059513000
H	4.057628000	2.863630000	1.983262000
H	3.820648000	1.099554000	1.889185000
C	3.897824000	1.069219000	-3.229140000
H	4.698207000	0.480585000	-3.687045000
H	3.038576000	0.423649000	-3.044029000
H	3.607053000	1.876404000	-3.907261000
C	-0.506519000	-1.123100000	0.599506000
O	-0.367428000	-0.032680000	0.008104000
C	-0.650864000	-1.241077000	2.131999000
H	-0.747952000	-2.301176000	2.380858000
C	-1.873283000	-0.490598000	2.645061000
H	-1.929464000	-0.582646000	3.733288000
H	-2.784950000	-0.907886000	2.208402000
H	-1.794232000	0.572445000	2.393024000
C	1.697688000	-1.284397000	2.707142000
O	0.479373000	-0.678842000	2.815814000
O	2.637886000	-0.818919000	3.310517000
C	1.766575000	-2.424708000	1.686184000
H	1.084461000	-3.235590000	1.988170000
C	3.166701000	-3.011996000	1.565323000
H	3.486986000	-3.446164000	2.517906000
H	3.166011000	-3.795158000	0.801266000
H	3.894594000	-2.243163000	1.284827000
O	1.294912000	-1.856474000	0.473691000
C	-1.175326000	-2.336447000	-1.386245000
C	-2.619285000	-2.470710000	-1.902562000
O	-3.378164000	-1.339504000	-2.117238000
C	-3.063593000	-0.025131000	-1.695649000
C	-3.849572000	0.231423000	-0.401814000
O	-4.466613000	-0.641123000	0.170996000
H	-0.695162000	-1.460212000	-1.832088000
H	-0.314699000	-3.749341000	-2.777003000
C	-3.513663000	0.907287000	-2.830616000
H	-4.557406000	0.703335000	-3.087583000
H	-2.903687000	0.712271000	-3.716297000
H	-3.415816000	1.966163000	-2.572182000
H	-1.997409000	0.100722000	-1.470107000
N	-5.082810000	2.016754000	0.852365000
N	-3.091400000	2.653827000	0.216802000
C	-3.971072000	1.623656000	0.180642000

C	-4.902402000	3.300026000	1.304238000
H	-5.664460000	3.822126000	1.861793000
C	-3.655756000	3.695852000	0.914352000
H	-3.126496000	4.620776000	1.082294000
C	-1.715250000	2.694148000	-0.316661000
H	-1.188522000	1.765894000	-0.073531000
H	-1.742333000	2.853581000	-1.396666000
H	-1.209555000	3.535770000	0.157312000
C	-6.308104000	1.231677000	1.100851000
H	-6.620157000	0.726353000	0.187870000
H	-6.118853000	0.487426000	1.874033000
H	-7.082127000	1.929790000	1.420457000
C	-0.382753000	-3.598953000	-1.694402000
H	0.618666000	-3.492950000	-1.273475000
H	-0.877706000	-4.471147000	-1.261843000
O	-3.116618000	-3.523274000	-2.193845000

Table S28: B3LYP /6-31G*, SDD level optimized coordinates of **3**.

Ground state electronic energy = -1825.21952772 Hartree/Particle.

H	-6.697623000	-2.637957000	-1.162928000
H	-7.271919000	-1.132740000	-1.933856000
H	7.156568000	-1.665396000	-0.319406000
C	-6.472389000	-1.581866000	-1.338061000
H	6.276765000	-3.032306000	0.391360000
H	-8.361442000	-1.125938000	0.669268000
H	-5.529080000	-1.497001000	-1.878285000
H	6.936048000	1.737064000	0.899832000
C	6.280803000	-2.310191000	-0.431062000
H	6.353267000	-2.851772000	-1.377114000
O	3.955259000	0.674998000	2.172396000
C	-7.374479000	-0.725633000	0.843526000
N	-6.340038000	-0.876005000	-0.066570000
O	4.861754000	-0.858884000	0.867810000
C	4.493873000	0.432505000	1.122345000
H	5.186659000	1.178665000	-0.826808000
C	6.050263000	2.367172000	0.769707000
C	5.008163000	-1.466935000	-0.419394000
H	5.748751000	2.759135000	1.744099000
H	5.053704000	-0.710916000	-1.209353000
H	1.846797000	-1.179812000	-2.518550000
C	4.912553000	1.555171000	0.160228000

H	6.308825000	3.198821000	0.108757000
C	-6.872136000	-0.020177000	1.889181000
C	-5.201356000	-0.283271000	0.383591000
H	-7.336800000	0.315834000	2.803458000
C	3.764004000	-2.301891000	-0.781144000
C	1.075291000	-1.818302000	-2.090253000
Ag	-3.341539000	-0.139784000	-0.537942000
N	-5.544145000	0.240564000	1.591563000
H	4.021911000	-3.081457000	2.030115000
H	0.091447000	-1.352829000	-2.203380000
O	3.795464000	2.460685000	-0.006311000
O	2.600479000	0.743487000	-0.822046000
O	3.766605000	-2.962358000	-1.799774000
H	1.110187000	-2.804285000	-2.555390000
C	2.480376000	-2.184379000	-0.009191000
N	1.307160000	-1.953257000	-0.639813000
O	-1.470576000	-0.058350000	-1.457848000
H	-1.752769000	1.933312000	-3.210186000
C	2.679211000	1.919693000	-0.507851000
N	2.228753000	-2.233179000	1.319347000
C	0.314366000	-1.804016000	0.293513000
C	3.154779000	-2.551339000	2.419216000
H	-0.675237000	-1.488269000	-0.014946000
H	-2.512627000	2.473436000	-1.699716000
H	2.626486000	-3.197881000	3.122134000
C	0.888006000	-1.998780000	1.519032000
C	-4.647944000	0.995931000	2.466510000
C	-1.552388000	2.273825000	-2.189860000
H	0.457819000	-1.985836000	2.508136000
C	-0.798127000	1.149870000	-1.440768000
H	3.473747000	-1.626370000	2.900395000
H	-5.029216000	2.012066000	2.603001000
H	-3.659016000	1.040540000	2.008679000
H	-4.576569000	0.502606000	3.440206000
H	0.180105000	1.016195000	-1.929661000
C	1.507211000	2.905806000	-0.632970000
H	-0.992844000	3.217043000	-2.239383000
H	2.623502000	4.731712000	-0.960654000
H	1.145362000	2.824384000	-1.660835000
H	2.170841000	4.446312000	0.734674000
C	-0.532253000	1.622233000	0.010810000
C	1.836915000	4.353167000	-0.301216000
O	0.504795000	2.468607000	0.303359000
O	-1.237832000	1.303157000	0.943716000
H	0.940565000	4.964322000	-0.437817000

Electronic Supplementary Material (ESI) for Dalton Transactions

Table S29. Relative potential and free energies of first four lactide inserted products [**2**]$_{HF}$, [**3**]$_{HF}$, [**4**]$_{HF}$ and [**5**]$_{HF}$ with respect to the initiating species [**1**]$_{HF}$ computed at HF/STO-3G, LANL1MB level of theory.

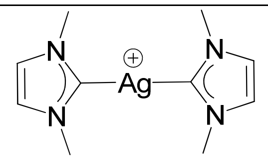
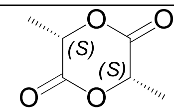
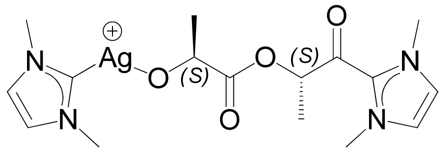
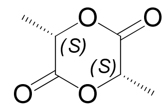
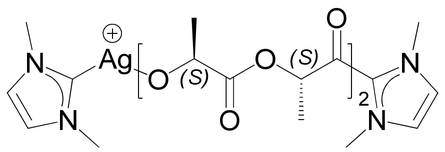
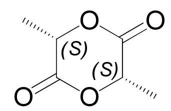
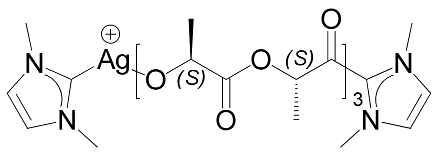
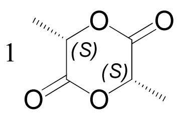
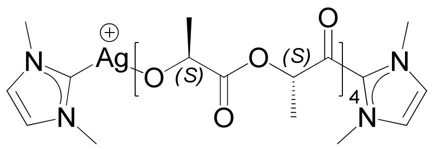
entry	species		relative energy (ΔE) (kcal/mol)	relative free energy (ΔG) (kcal/mol)
	silver-NHC species	free lactide		
1.	 [**1**]$_{HF}$	4  4LL$_{HF}$	0.0	0.0
2.	 [**2**]$_{HF}$	3  3LL$_{HF}$	37.0	52.8
3.	 [**3**]$_{HF}$	2  2LL$_{HF}$	18.6	47.8
4.	 [**4**]$_{HF}$	1  LL$_{HF}$	11.9	54.4
5.	 [**5**]$_{HF}$	-	-23.2	31.9

Table S30: B3LYP/6-311G(d,p), SDD level optimized coordinates of LL.

Ground state electronic energy = -534.507457794 Hartree/Particle.

Sum of electronic and thermal Free Energies= -534.402536 Hartree/Particle.

8	-0.255376000	1.351363000	-0.113295000
6	-1.264029000	0.463205000	0.432456000
1	-2.731190000	2.028102000	0.433319000
1	-1.158237000	0.460321000	1.525918000
6	-2.619183000	1.015867000	0.042944000
1	-3.406225000	0.380385000	0.448724000
1	-2.720238000	1.038970000	-1.042847000
6	-1.041076000	-0.968187000	-0.057589000
8	-1.921154000	-1.716717000	-0.370719000
8	0.255365000	-1.351372000	-0.113258000
6	1.264028000	-0.463204000	0.432450000
1	1.158257000	-0.460309000	1.525914000
6	2.619181000	-1.015865000	0.042930000
1	2.720183000	-1.039095000	-1.042862000
1	2.731253000	-2.028046000	0.433427000
1	3.406229000	-0.380309000	0.448590000
6	1.041082000	0.968183000	-0.057593000
8	1.921158000	1.716724000	-0.370700000

Table S31: B3LYP/6-311G(d,p), SDD level optimized coordinates of **1**.

Ground state electronic energy = -756.695188893 Hartree/Particle.

Sum of electronic and thermal Free Energies= -756.486476 Hartree/Particle.

6	-2.118139000	0.000035000	-0.000036000
7	-2.947765000	0.761101000	0.758083000
7	-2.947819000	-0.761042000	-0.758083000
6	-4.273819000	0.479863000	0.478028000
1	-5.089374000	0.977768000	0.974038000
6	-4.273854000	-0.479827000	-0.477913000
1	-5.089443000	-0.977729000	-0.973870000
7	2.947762000	-0.758192000	0.760996000
7	2.947821000	0.758119000	-0.761002000
6	2.118137000	-0.000033000	-0.000032000
6	4.273818000	-0.478048000	0.479852000
1	5.089371000	-0.974088000	0.977732000
6	4.273856000	0.477981000	-0.479749000
1	5.089447000	0.973995000	-0.977592000

47	-0.000003000	-0.000001000	-0.000047000
6	-2.523801000	-1.752291000	-1.745633000
1	-2.899239000	-1.480918000	-2.733274000
1	-1.436548000	-1.777291000	-1.770078000
1	-2.899761000	-2.738793000	-1.470870000
6	-2.523673000	1.752287000	1.745670000
1	-1.436417000	1.777384000	1.769944000
1	-2.899769000	2.738778000	1.471059000
1	-2.898930000	1.480789000	2.733346000
6	2.523819000	1.745792000	-1.752132000
1	1.436566000	1.769631000	-1.777732000
1	2.898556000	2.733554000	-1.480217000
1	2.900478000	1.471570000	-2.738517000
6	2.523672000	-1.745747000	1.752209000
1	1.436416000	-1.770457000	1.776865000
1	2.899434000	-2.733319000	1.481040000
1	2.899251000	-1.470806000	2.738808000

Table S32: B3LYP/6-311G(d,p), SDD level optimized coordinates of [**1**+LL].

Ground state electronic energy = -1291.20949013 Hartree/Particle.

Sum of electronic and thermal Free Energies= -1290.880187 Hartree/Particle.

8	-3.139803000	-0.954101000	-0.479014000
6	-4.504175000	-1.185665000	-0.942566000
6	-5.395810000	0.051494000	-0.944227000
8	-4.991205000	1.130951000	-0.240294000
6	-3.935109000	1.030659000	0.734609000
6	-2.840895000	0.042053000	0.360471000
8	-6.409105000	0.070614000	-1.577642000
8	-1.722721000	0.144269000	0.807154000
6	-5.130077000	-2.350865000	-0.183285000
1	-4.381688000	-1.458232000	-1.990775000
1	-6.109946000	-2.568399000	-0.610314000
1	-5.256444000	-2.124010000	0.877166000
1	-4.499091000	-3.235468000	-0.279167000
6	-4.506108000	0.754621000	2.126188000
1	-4.982231000	-0.226286000	2.179910000
1	-5.253380000	1.513432000	2.360906000
1	-3.709959000	0.796693000	2.871342000
1	-3.464820000	2.013867000	0.725617000
6	2.371120000	-2.023660000	0.072885000
7	1.406278000	-2.969709000	-0.043992000
7	3.522750000	-2.725541000	0.232321000

6	1.946405000	-4.241269000	0.034816000
1	1.345058000	-5.131303000	-0.035943000
6	3.280871000	-4.088277000	0.211235000
1	4.063429000	-4.818164000	0.328735000
7	1.280454000	2.971905000	0.798265000
7	2.448153000	3.050340000	-1.002341000
6	1.936909000	2.184977000	-0.090506000
6	1.384179000	4.306857000	0.450379000
1	0.933789000	5.093843000	1.030350000
6	2.118997000	4.357526000	-0.687078000
1	2.426754000	5.194973000	-1.289313000
47	2.132373000	0.078815000	-0.013000000
6	4.850267000	-2.143606000	0.417151000
1	5.510179000	-2.446476000	-0.397305000
1	4.756889000	-1.059854000	0.420945000
1	5.272836000	-2.469815000	1.368595000
6	-0.014694000	-2.701540000	-0.271248000
1	-0.255503000	-1.691362000	0.052030000
1	-0.257008000	-2.813902000	-1.329609000
1	-0.608414000	-3.406047000	0.311388000
6	3.237942000	2.676585000	-2.173760000
1	3.341340000	1.593939000	-2.192216000
1	2.734916000	3.004243000	-3.084740000
1	4.227389000	3.133254000	-2.120279000
6	0.575908000	2.477405000	1.984664000
1	-0.101257000	1.671574000	1.703978000
1	1.291247000	2.125325000	2.729068000
1	-0.000751000	3.297248000	2.410840000

[1]. Gaussian 03, Revision C.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, Gaussian, Inc., Wallingford CT, 2004.