Supporting Information for “Role of Acid in the Co-Oligomerization of Formaldehyde and Pyrrole”

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Part 1: Free Energy Data

In the data tables below, the (electronic) potential energy of the optimized gas-phase structures and the solvation energy are designated $E_{pot}$ and $E_{solv}$ respectively. The combined ZPE and enthalpy corrections to 298 K are designated $H_{corr}$ and the corresponding gas-phase free energy correction to 298 K is designated $G_{corr}$. The entropy correction, designated $-0.5TS_{corr}$, is calculated by $0.5 \times (G_{corr} - H_{corr})$. The free energy of each species, designated $G_{298}$, is the sum of $E_{elec}$, $E_{solv}$, $H_{corr}$ and $-0.5TS_{corr}$. $DG$ values can be calculated from the difference in $G_{298}$ between the reactants and products, and therefore include the zero-point energy, enthalpic and entropic corrections to 298 K for a reaction in aqueous solution. The rightmost column ($DG_{r}$) is the relative free energy of each species with respect to formaldehyde, (neutral or protonated) pyrrole and water as the reference states. Using this choice of reference states, formaldehyde and pyrrole are assigned $DG_{r} = 0.0$ and water molecules are added where necessary to ensure the reactions are stoichiometrically balanced. This allows us to quickly and easily visualize a map of the energy landscape, for the myriad reactions that can take place.

Table S1. Energies of Neutral Species. All energies are in kcal/mol except where indicated ($E_{pot}$ is in a.u.).

|       | $E_{pot}$ (a.u.) | $E_{solv}$ | $H_{corr}$ | $G_{corr}$ | $-0.5TS_{corr}$ | $G_{298}$ | $DG_{r}$ |
|-------|-----------------|------------|------------|------------|-----------------|-----------|---------|
| H$_2$O | -76.44744       | -8.66      | 15.75      | 2.30       | -6.73           | -47971.14 | 0.0     |
| CH$_2$O| -114.53629      | -2.75      | 19.01      | 3.44       | -7.79           | -71864.15 | 0.0     |
| pyrrole (1)| -210.22604 | -4.36      | 54.70      | 35.05      | -9.83           | -131878.34 | 0.0     |
| 2     | -324.78386      | -7.26      | 77.00      | 53.11      | -11.95          | -203747.20 | -4.7    |
| 3     | -324.78937      | -8.24      | 77.15      | 53.33      | -11.91          | -203751.45 | -9.0    |
| 4     | -324.78613      | -9.68      | 77.12      | 53.11      | -12.01          | -203750.98 | -8.5    |
| 5     | -248.30186      | -4.78      | 57.72      | 36.69      | -10.52          | -155769.38 | -2.0    |
| 6     | -458.58102      | -6.71      | 115.48     | 86.85      | -14.32          | -287669.54 | -19.8   |
| 7     | -573.14416      | -11.14     | 137.89     | 104.61     | -16.64          | -359543.35 | -29.5   |
| 8     | -496.65779      | -9.93      | 117.75     | 88.86      | -14.45          | -311564.16 | -21.5   |
| 9     | -706.93575      | -9.54      | 176.20     | 137.81     | -19.20          | -443461.50 | -40.5   |
| 10    | -821.49904      | -13.71     | 198.64     | 156.08     | -21.28          | -515334.88 | -49.7   |
| 11    | -745.01305      | -12.19     | 178.52     | 140.76     | -18.88          | -467355.39 | -41.3   |
| 12    | -955.29053      | -12.24     | 236.37     | 190.92     | -22.73          | -599252.57 | -60.2   |
| 13    | -1069.85854     | -13.56     | 259.50     | 210.31     | -24.60          | -671125.16 | -68.6   |
Table S2. Energies of Protonated Species. All energies are in kcal/mol except where indicated (\(E_{\text{pot}}\) is in a.u.).

|   | \(E_{\text{pot}}\) (a.u.) | \(E_{\text{solv}}\) | \(H_{\text{corr}}\) | \(G_{\text{corr}}\) | -0.5\(TS_{\text{corr}}\) | \(G_{298}\) | \(\Delta G_r\) |
|---|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| 1a | -210.57371 | -61.03 | 62.65 | 42.81 | -9.92 | -132145.32 | 0.0 |
| 1b | -210.56470 | -61.84 | 62.19 | 42.30 | -9.95 | -132140.97 | +4.4 |
| 1c | -210.54073 | -66.62 | 62.97 | 43.53 | -9.72 | -132129.70 | +15.7 |
| 2a | -325.13644 | -58.25 | 84.70 | 60.28 | -12.21 | -204012.00 | -2.5 |
| 2b | -325.10611 | -62.43 | 85.13 | 61.36 | -11.89 | -203996.39 | +13.1 |
| 3a | -325.15201 | -58.59 | 84.66 | 60.76 | -11.95 | -204021.89 | -12.4 |
| 3b | -325.13756 | -61.16 | 84.97 | 61.10 | -11.94 | -204015.07 | -5.6 |
| 3c | -325.11402 | -62.87 | 85.29 | 61.27 | -12.01 | -204001.76 | +7.7 |
| 3d | -325.13918 | -56.93 | 83.50 | 55.58 | -13.96 | -204015.35 | -5.9 |
| 4a | -325.14289 | -62.30 | 84.70 | 60.57 | -12.07 | -204019.95 | -10.5 |
| 4b | -325.13899 | -62.45 | 84.78 | 60.76 | -12.01 | -204017.52 | -8.1 |
| 5a | -248.67585 | -57.28 | 66.35 | 45.17 | -10.59 | -156048.00 | -9.7 |
| 6a | -458.94783 | -55.21 | 123.17 | 94.35 | -14.41 | -287940.62 | -23.5 |
| 6b | -458.93213 | -58.31 | 123.36 | 94.53 | -14.42 | -287933.68 | -16.5 |
| 7a | -573.50749 | -60.48 | 145.62 | 112.40 | -16.61 | -359812.93 | -31.6 |
| 8a | -497.04679 | -53.73 | 126.89 | 96.51 | -15.19 | -311843.66 | -33.5 |
| 9a | -707.30103 | -58.09 | 183.73 | 145.35 | -19.19 | -443731.74 | -42.7 |
| 10a | -821.86410 | -62.15 | 206.16 | 163.49 | -21.34 | -515604.94 | -51.8 |
| 11a | -745.40111 | -56.02 | 187.39 | 147.13 | -20.13 | -467635.11 | -53.1 |
| 12a | -955.65653 | -59.82 | 243.87 | 198.33 | -22.77 | -599522.37 | -61.5 |
| 13a | -1070.24302 | -51.31 | 267.06 | 218.68 | -24.19 | -671396.21 | -71.2 |
| 14a | -993.76290 | -53.60 | 248.04 | 199.32 | -24.36 | -623425.68 | -71.8 |
| 15a | -993.78752 | -52.53 | 249.48 | 206.39 | -21.55 | -623435.80 | -81.9 |
| TSdimer | -458.91762 | -50.68 | 121.91 | 92.45 | -14.73 | -287918.71 | -1.55 |
| TSdehyd1 | -478.08408 | -57.84 | 118.84 | 86.13 | -16.36 | -299957.70 | -5.96 |
| TSdehyd2 | -478.06891 | -67.93 | 116.60 | 85.93 | -15.34 | -299959.50 | -7.75 |

Table S3. Energies of Organic Acid Transition States. All energies are in kcal/mol except where indicated (\(E_{\text{pot}}\) is in a.u.). Reference states are CH\(_2\)O, pyrrole, H\(_2\)O, and the organic acid.

|    | \(E_{\text{pot}}\) (a.u.) | \(E_{\text{solv}}\) | \(H_{\text{corr}}\) | \(G_{\text{corr}}\) | -0.5\(TS_{\text{corr}}\) | \(G_{298}\) | \(\Delta G_r\) |
|---|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| TS2aa | -553.91466 | -7.87 | 115.97 | 84.04 | -15.97 | -347494.63 | 21.47 |
| TS3aa | -553.90391 | -19.64 | 116.44 | 83.88 | -16.28 | -347499.50 | 16.60 |
| TS4aa | -553.89444 | -21.31 | 116.59 | 84.13 | -16.23 | -347495.03 | 21.08 |
|       | E   | ZPE | TH   |   S  |   TD  |   TOT  |
|-------|-----|-----|------|-----|------|--------|
| TS5aa | -553.92554 | -12.68 | 116.92 | 83.76 | -16.58 | -347505.93 | 10.17 |
| TS6aa | -687.69727 | -8.66  | 155.40 | 119.43 | -17.99 | -431407.88 | 15.92 |
| TS6faa| -802.25722 | -17.60 | 178.65 | 138.40 | -20.13 | -503283.18 | 4.76  |
| TS2fa | -514.57973 | -9.74  | 97.97  | 69.06  | -14.46 | -322829.95 | 16.86 |
| TS3fa | -514.57017 | -19.41 | 98.26  | 68.59  | -14.84 | -322833.71 | 13.10 |
| TS4fa | -514.56084 | -21.71 | 98.51  | 69.03  | -14.74 | -322829.81 | 17.00 |
| TS5fa | -514.59193 | -13.18 | 98.82  | 68.90  | -14.96 | -322840.69 | 6.11  |
| TS6fa | -648.36400 | -9.43  | 137.93 | 103.23 | -17.35 | -406743.48 | 11.01 |
| TS6faa| -762.93080 | -18.26 | 164.95 | 127.72 | -18.62 | -478618.33 | 0.32  |
| TS2faa| -653.16810 | -11.60 | 112.46 | 79.69  | -16.39 | -409784.78 | 17.01 |
| TS3f aa| -653.16010 | -20.73 | 112.77 | 79.01  | -16.88 | -409789.07 | 12.72 |
| TS4f aa| -653.15006 | -23.89 | 113.20 | 79.84  | -16.68 | -409785.30 | 16.49 |
| TS5f aa| -653.18144 | -15.20 | 113.41 | 79.54  | -16.94 | -409796.35 | 5.44  |
| TS6f aa| -786.95546 | -9.98  | 152.42 | 114.25 | -19.09 | -493698.75 | 10.74 |
| TS6f aa| -901.51375 | -19.12 | 174.94 | 133.81 | -20.57 | -565573.28 | 0.36  |
| TS2faa| -851.71482 | -9.62  | 103.90 | 68.17  | -17.87 | -534382.81 | 14.42 |
| TS3faa| -851.70884 | -19.00 | 103.65 | 68.89  | -17.38 | -534388.20 | 9.03  |
| TS4faa| -851.70048 | -21.57 | 104.62 | 68.45  | -18.09 | -534385.26 | 11.97 |
| TS5faa| -851.73083 | -13.33 | 104.74 | 67.71  | -18.52 | -534396.38 | 0.85  |
| TS6faa| -985.50457 | -8.39  | 143.54 | 102.53 | -20.51 | -618298.93 | 5.99  |
| TSe6faa| -1100.06390 | -16.01 | 165.55 | 123.36 | -21.10 | -690172.21 | -3.14 |
| TSp3faa| -514.58050 | -15.30 | 99.20  | 70.97  | -14.12 | -322834.42 | +12.4 |
| TSp6faa| -648.37054 | -13.54 | 137.03 | 103.17 | -16.93 | -406752.18 | +2.3  |
| S3ts1 | -630.37581 | -14.12 | 132.71 | 98.03  | -17.34 | -395465.62 | 21.62 |
| S3ts2 | -630.37249 | -20.47 | 132.26 | 95.00  | -18.63 | -395471.63 | 15.61 |
Part 2: Additional Transition State Structures

Figure S1. Dimerization Transition State (TSdimer)

Figure S2. Dehydration Transition State Structures (TSdehyd1 and TSdehyd2)

Figure S3. Acetic Acid Proxy Catalyst with Additional Water (S3TS1 and S3TS2)
Figure S4a. Transition State Structures with Acetic Acid Catalyst

Figure S4b. Additional Proton Transfer Transition States with Formic Acid
Part 3:
In the main text, we discussed two challenges when calculating transition states. (1) When an additional proton is added to the system, cleanly optimizing an unconstrained transition state with the appropriate eigenvectors representing the bond-making/bond-breaking reaction coordinate was largely unsuccessful, with the exception of $1 + 5a \rightarrow 6a$. (2) When using a neutral carboxylic acid as a proxy, while good transition states could be optimized, acetic acid had noticeably higher barriers than for water alone in some cases, and that fluoroacetic acid, with its lower pKa, essentially showed similar results to formic acid.

One reviewer made the very reasonable suggestion that these problems might be an artifact of B3LYP, and that we should try more modern functionals to see if this resolves the issue. Of the available functionals in Jaguar, we chose two commonly used more modern functionals, PBE0 (Perdew-Burke-Ernzehof with HF exact exchange in a 3:1 ratio) and M06-2X (Minnesota with 54% HF exchange recommended for main group kinetics). Unfortunately, this did not resolve the issues. (1) Optimizing cationic transition states was similarly problematic. (2) For neutral proxy acids, while acetic acid no longer had a higher barrier than water alone in most cases, other artifacts were introduced. The results and brief discussion are below.

**Figure S5a. Proxy Acid Catalyst Barriers with PBE0 Functional.** All energies are in kcal/mol.

Figure S5a is analogous to Figure 4 in the main text except that the PBE0 functional was used. Acetic acid no longer has a higher barrier than water alone in four of the six cases; for TS6aa the barrier was similar to water, and for TSe6aa the barrier was higher than water. Formic acid may still not scale with the other three acids. In four cases, there is a (non-monotonic) trend of decreasing barrier with decreasing pKa, but this was not the case for TS3fa and TS6fa. The hydration barriers (TS5xx) are marginally higher for the acids, but significantly higher for water at +24.4 kcal/mol. The dimerization barriers are significantly reduced and two have unrealistic “negative” barriers. The main general trend is similar compared to B3LYP results in the main paper: The proxy acid significantly stabilizes C–C bond formation (versus C–N) when adding CH$_2$O to pyrrole. (Oddly though the barriers for adding to the nitrogen and the alpha-carbon in the water-only case are both ~19 kcal/mol.) The main difference compared to B3LYP is that the
acid also now stabilizes the dehydration step. Unfortunately, the dimerization barriers look unrealistically low.

**Figure S5b. Proxy Acid Catalyst Barriers with M06-2X Functional.** All energies are in kcal/mol.

In Figure S5b we show the analogous results using the M06-2X functional. For CH$_2$O addition, the water-only barriers are in-line with B3LYP, with a slightly higher barrier for addition to nitrogen. Except for the oddly low TS4fa, CH$_2$O addition catalyzed by proxy acid shows a uniform decreasing barrier as pKa decreases. With M06-2X, the dehydration barriers have been pushed higher – they might be unrealistically high, but there isn’t sufficient experimental data to conclude this since the azafulvene is challenging to isolate. The dimerization barriers show the same artifacts as PBE0.

We have encountered negative barriers in previous work for the isomerization reaction of an amidic acid to an amide. One possibility we investigated (see *J. Phys. Chem. A* 2018, 122, 6769-6779) was that the “half-entropy” approximation was suspect for certain classes of reactions. However, the other results do not, on the whole, show improvement over B3LYP and new artifacts are introduced. It may be that our protocol, with its many approximations, works particularly well for B3LYP for the types of reactions we have studied thus far where only water was used as a proton-transfer catalyst. Not having tested PBE0 or M06-2X against experimental results may suggest that the hoped-for “error cancelation” when a computational chemist uses multiple approximations does not pan out – at least with our current protocol. We might need to modifications to our protocol as we consider acid-catalyzed reactions. This is alluded to in the main text as future work we plan to carry out since it is beyond the scope of the present manuscript.
Part 4a: XYZ coordinates of structures from Table S2
(Coordinates for structures in Table S1 can be found in our previous work.)

**1a**

|   |   |   |   |
|---|---|---|---|
| N1 | -1.1507929066 | -0.0786737204 | 0.0012652404 |
| C2 | -0.4553716246 | -1.1851278926 | -0.0003685135 |
| C3 | 0.9499040167 | -0.8949603738 | -0.0019022962 |
| C4 | 1.0788804768 | 0.4534325813 | -0.0010919348 |
| C5 | -0.2672062414 | 1.0848291016 | 0.0012384719 |
| H6 | -2.1630297906 | -0.0273645122 | 0.0026796061 |
| H7 | -0.9343131669 | -2.1569453452 | -0.0004573788 |
| H8 | 1.7306498087 | -1.6398639750 | -0.0033378770 |
| H9 | 1.9979855925 | 1.02911392 | -0.0016287341 |
| H10 | -0.4482771038 | 1.704990264 | 0.8881641347 |
| H11 | -0.4510986788 | 1.7071020475 | -0.8831982096 |

**1b**

|   |   |   |   |
|---|---|---|---|
| C1 | -1.1725264412 | -0.0886074743 | 0.0011151755 |
| N2 | -0.45288772201 | -1.1694600285 | -0.0000504368 |
| C3 | 0.9474064525 | -0.8853323781 | -0.0013694851 |
| C4 | 1.095582125 | 0.4446988870 | -0.0016942939 |
| C5 | -0.261722947 | 1.0768486990 | 0.0008903771 |
| H6 | -2.2543779413 | -0.1063136537 | 0.0024432442 |
| H7 | -0.8353345712 | -2.1120743731 | -0.0000097407 |
| H8 | 1.6564494144 | -1.6976558710 | -0.0026980022 |
| H9 | 2.0287618192 | 0.9864134905 | -0.0019571279 |
| H10 | -0.4465575073 | 1.7177796778 | 0.8761164358 |
| H11 | -0.4494979061 | 1.7223751084 | -0.8700610607 |

**1c**

|   |   |   |   |
|---|---|---|---|
| C1 | 0.0000000000 | 1.1806473277 | -0.2628382845 |
| C2 | 0.0000000000 | 0.7337698804 | 0.9933509033 |
| C3 | 0.0000000000 | -0.7337698804 | 0.9933509033 |
| C4 | 0.0000000000 | -1.1806473277 | -0.2628382845 |
| N5 | 0.0000000000 | 0.0000000000 | -1.1646785007 |
| H6 | 0.0000000000 | 2.1641201762 | -0.7043589152 |
| H7 | 0.0000000000 | 1.3568791787 | 1.8755704511 |
| H8 | 0.0000000000 | -1.3568791787 | 1.8755704511 |
| H9 | 0.0000000000 | -2.1641201762 | -0.7043589152 |
| H10 | 0.8263545727 | 0.0000000000 | -1.7780746198 |
| H11 | -0.8263545727 | 0.0000000000 | -1.7780746198 |

**2a**

|   |   |   |   |
|---|---|---|---|
| N1 | -1.1114632986 | 0.0946370777 | -0.3327834235 |
| C2 | -0.6582386686 | -1.0962223963 | -0.0449826777 |
| C3 | 0.7429392323 | -1.0556897369 | 0.2689034108 |
C4  1.1306161958  0.2378838076  0.1858172867
C5  -0.0324986453  1.0789569387  -0.1996848422
H6  -1.3072998570  -1.9637260607  -0.0527276987
H7  1.3391127175  -1.9166290435  0.5294009154
H8  2.1183563086  0.6387962652  0.3665191671
H9  -0.3092230736  1.8175796278  0.5610855759
H10  0.1164514571  1.6121294578  -1.1462182428
C11 -2.5041049958  0.4639097785  -0.6294921853
H12 -2.5279098120  0.9120132807  -1.6289550107
H13 -3.0834060869  -0.4652761781  -0.6306674426
O14 -2.8868354021  1.3524250746  0.3760256768
H15 -3.6118304989  1.9080582990  0.0675534891

2b
C1  -1.1387942505  -0.2591960013  -0.0146549666
C2  -0.3218045310  -1.3159102219  0.00090617398
C3  1.0655951440  -0.8472131146  0.0681549547
C4  1.0736742328  0.4884884323  0.0841520962
N5  -0.3189534454  0.9651079685  0.0155871509
H6  -2.2117031461  -0.1627164412  -0.0278832843
H7  -0.6325088419  -2.3500747858  -0.0086860037
H8  1.9398387750  -1.4805540449  0.0982174629
H9  1.8695071463  1.2145860501  0.1286302314
H10 -0.5576611755  1.5139999574  0.8522448941
C11 -0.572551260  1.9303310758  -1.2029329888
H12 -0.3473082460  1.3342517302  -2.0871904229
H13  0.1422605640  2.7373386005  -1.0640072148
O14 -1.8472050055  2.4222141081  -1.1236604556
H15 -2.4466366691  1.9573732769  -1.7190630790

3a
N1  -0.9244593858  -0.2122382338  -0.4524118380
C2  -0.1641453157  -1.2189022415  -0.1135670783
C3  1.0873102835  -0.7269253301  0.4194898881
C4  1.0378197064  0.6217031168  0.3821800148
C5  -0.2682641667  1.0623544893  -0.1851401979
H6  -1.8488696778  -0.3483675534  -0.8511541825
H7  1.8940057513  -1.3504420078  0.7744539808
H8  1.8049718196  1.3112051627  0.7056700182
H9  -0.8587281479  1.6619630463  0.5174051152
H10 -0.1587398192  1.6418955351  -1.1092720179
C11 -0.6225232169  -2.6229158790  -0.2984855427
H12 -0.5952371678  -3.1189452331  0.6834022992
H13  0.1081154498  -3.1332524122  -0.9440288822
O14 -1.9117648277  -2.5643969292  -0.8560653007
H15 -2.2611444899  -3.4507490591  -0.9954474112
3b
N1  -1.0457672825  0.1242059589  0.5835706983
C2  -0.6791926366  -0.9781891787  -0.007736819
C3  0.5855256864  -0.8011020026  -0.6647443882
C4  0.9574623969  0.4824351452  -0.4642981447
C5  -0.0683334011  1.1969454107  0.3534229975
H6  -1.9184049446  0.2496649775  1.0825218926
H7  -1.2856867575  -1.8749335565  0.0337585346
H8  1.1047615777  -1.5711095382  -1.2138917461
H9  1.8566291069  0.9635531786  -0.8231715996
H10  0.3529480538  1.5053051926  1.3197175860
C11 -0.7083125743  2.4274270553  -0.3201150535
H12  0.0875993133  3.1676472111  -0.4679014716
H13 -1.4494939664  2.8581464127  0.3662694676
O14 -1.2788900752  1.9761995950  -1.5237191218
H15 -1.6683194313  2.7182199782  -1.9984491591

3c
C1  -1.0326913418  -0.1281221733  -0.2804741318
C2  -0.5074808613  -1.2560579030  0.2017601488
C3  0.9305753139  -1.0745419040  0.4261422713
C4  1.2827021295  0.1731714824  0.1032603484
N5  0.0526911574  0.8707852901  -0.3709337089
H6  -2.0272623653  0.1580508070  -0.5808567501
H7  -1.0535020520  -2.1698931956  0.3835177167
H8  1.6032450354  -1.8421176104  0.7790729399
H9  -0.1469581460  1.7009225569  0.2014017551
H10  0.2334713955  1.2219637772  -1.3237148749
H11  2.5451126742  0.9681450546  0.0302889874
H12  2.6882486462  1.5526292922  0.9499825101
H13  3.3917020859  0.2820770764  -0.0753185914
O14  2.3735402320  1.8195494864  -1.0994334759
H15  3.1487911274  2.3793490435  -1.2160648676

3d
C1  0.8405314751  0.2538732778  1.0452474438
C2  0.2602358646  -0.2685536408  -0.1663510657
C3  0.8012190861  -0.7275265934  1.9987938062
C4  0.1945147841  -1.8667587209  1.4002418519
N1  -0.1179647870  -1.5952971651  0.1417472103
H12  1.2362386408  1.2533256813  1.1461488573
H13  1.1554800100  -0.6798645712  3.0160166285
H15  -0.0170289366  -2.3304537572  1.8396321593
H6  -0.5683649239  -2.2339800993  -0.5010120718
C5  0.0847766724  0.3111772722  -1.3702837012
H2  -0.3487610458  -0.2183366750  -2.2064339636
H3  0.4013318895  1.3314079716  -1.5355305474
O1  -2.3291448433  1.2209915193  -1.7799786242
H1  -2.8671612203  1.6625683020  -1.1138301244
H18  -2.6355452641  1.5836171786  -2.6189665154

4a
N1  -1.1366566655  -0.1042685314  -0.1508836413
C2  -0.4082155650  -1.1622834695  0.1114625792
C3  0.9615764490  -0.8086022177  0.2783927378
C4  1.0606078095  -0.5389320734  0.1063221558
C5  -0.2998358554  1.0933147137  -0.1857595602
H6  -2.1367456388  -0.1074972270  -0.3083004082
H7  -0.8514518974  -2.1484771762  0.1788806394
H8  1.7677607463  -1.4888141624  0.5003192007
H9  -0.6385533635  1.8147905302  0.5659705622
H10  -0.3645093122  1.5726755780  -1.1688181425
C11  2.3046779301  1.3503370772  0.1899247625
H12  2.1650023836  2.1214058661  0.9652173041
H13  2.4371753490  1.8832859073  -0.7658294836
O14  3.3679089107  0.4794851212  0.4769523529
H15  4.1887770925  0.9786114952  0.5380384166

4b
N1  -1.1250644368  -0.0657639034  -0.1583998495
C2  -0.4614154328  -1.1913812120  -0.1042531495
C3  0.9364898655  -0.9514148194  0.1222564683
C4  1.0899056797  0.3955714824  0.2040343731
C5  -0.2225939000  1.0681421400  0.0300512294
H6  -2.1237407953  0.0136498066  -0.3094027613
H7  -0.9634009465  -2.1448017249  -0.2229357999
H8  -0.5267118522  1.6550184060  0.9052102754
H9  -0.2563179873  1.7304826164  -0.8434308253
H10  2.0223808880  0.9146069075  0.3707470658
C11  2.0091607173  -1.9916588954  0.2434647327
H12  2.0326396977  -2.5926418842  -0.6774458061
H13  1.7611001334  -2.6685429422  1.0741862915
O14  3.2139622468  -1.2962966841  0.4602997877
H15  3.9386016805  -1.9242740686  0.5454118918

5a
N1  -1.0900523107  -0.2298271729  0.3781403552
C2  -0.4208786328  -1.2499679451  -0.1305614581
C3  0.9673592665  -0.9255397348  -0.2137346726
C4  1.1122020285  0.3422871828  0.2690993337
C5  -0.1937844117  0.8313898478  0.6638124907
H6 -2.0895234035 -0.2081225190 0.5398197346
H7 -0.9175273349 -2.1665580610 -0.4195512897
H8 1.7317532886 -1.5848711184 -0.5932809232
H9 2.0238302785 0.9143393715 0.3575316464
C11 -0.5522913500 2.0132638980 1.1899477269
H11 0.1964943662 2.7728416616 1.3781317302
H12 -1.5803080655 2.2489545281 1.4414187165

6a
N1 0.3164948740 -0.1049522620 -0.7090819120
C2 -0.9216745666 -0.5024561021 -0.5689908428
C3 -1.3079110946 -0.3672050154 0.8221478044
C4 0.8879500289 0.3371298315 0.5576157806
H6 0.7888750137 -0.1313853098 -1.6123376595
H7 -2.2805604686 -0.6254421224 1.2132268648
H8 -0.1972447626 0.3600577036 2.5518566819
H9 1.2061791475 1.3840883319 0.4945444163
H10 1.7676214075 -0.2642088530 0.8151542215
C11 -1.7390500118 -1.0296094853 -1.7089628847
H12 -2.7164330717 -0.5350239019 -1.6753473343
H13 -1.9514790432 -2.0822042418 -1.4746338407
C14 -0.0189650519 -1.5907778388 -3.5949597019
C15 0.2335373245 -1.0455613596 -4.8827556285
C16 -0.6812084275 -0.0395767701 -5.0880791571
N17 -1.4699691889 0.0516228302 -3.9696956651
C18 -1.0868871063 -0.8985121821 -3.0486520448
H19 -2.2491657755 0.6835546469 -3.8722032140
H20 0.9857829311 -1.3689726977 -5.5837628145
H21 -0.8393882741 0.6079719851 -5.9347218766
H22 0.4874964150 -2.4317796724 -3.1438001996

6b
N1 1.4196212418 -0.3089384735 -0.5547881597
C2 0.4557880399 -1.1822782237 -0.7205553008
C3 -0.7794666920 -0.5088593422 -0.9765791588
C4 -0.5215921047 0.8241726322 -0.9395654145
C5 0.9133189064 1.0608035135 -0.6465640024
H6 2.3842337548 -0.5454509728 -0.3572233489
H7 0.6343920311 -2.2481582438 -0.6521713159
H8 -1.7238012390 -1.0006021445 -1.1515296265
H9 -1.2266110689 1.6312877770 -1.0786130480
H10 1.4124645374 1.5727680937 -1.4760533748
C11 1.2061153730 1.9037369914 0.6682372542
H12 2.2909373647 1.9119453955 0.7950980487
H13 0.7776964495 1.3632063914 1.5161111737
C14  1.2223752180  4.4044870131  -0.0529705999
C15  0.3093868286  5.4743125889  0.1132359087
C16  -0.7593880339  4.9934142944  0.8369266426
N17  -0.5332512932  3.6653210250  1.0968734077
C18  0.6921903665  3.2918465407  0.5773850191
H19  -1.0994050975  3.1059677680  1.7154293882
H20  0.4236795301  6.4834698530  -0.2476727672
H21  -1.6455196320  5.4891755523  1.1983266000
H22  2.1691508829  4.4440366565  -0.5707091060

7a
N1  -0.6483717421  0.0469809244  0.9660140106
C2  -0.2488426319  -1.913052050  0.7552241392
C3  -0.0127704705  -1.3661295919  -0.6622257393
C4  -0.2694336588  -0.1951519177  -1.2792245983
C5  -0.7056498964  0.8175957939  -0.2751105040
H6  -0.8394451669  0.4384287400  1.8793452183
H7  0.3055108048  -2.2959101564  -1.1073497463
H8  -0.1851666324  0.0204071507  -2.3348911671
H9  -0.0311945360  1.6798814804  -0.2198992731
H10  -1.7187591867  1.951176053  -0.4571156905
C11  -0.1412806388  -2.2360209747  1.8176005988
H12  -0.2437892316  -1.7918427681  2.8126355159
H13  0.8514885396  -2.6898180530  1.7626438745
C14  -1.0467770193  -4.5313663611  0.9457004708
C15  -2.3338763665  -5.1182056082  0.8934916180
C16  -3.2235209356  -4.2226757979  1.4597124111
N17  -2.5137179860  -3.1142970161  1.8354680238
C18  -1.1753079503  -3.2897731641  1.5448268713
H19  -2.9579138869  -2.3295585751  2.2895876668
H20  -2.5808396442  -6.0946291866  0.5075211650
H21  -0.1231905776  -4.9723232919  0.6019861523
C22  -4.6860112872  -4.3023042538  1.7899624205
H23  -5.1876765538  -4.9963937730  1.1086004925
H24  -4.8211785455  -4.6881774860  2.8045672813
O25  -5.2857709212  -3.0066947150  1.7913909330
H26  -5.5053907986  -2.7754175369  0.8830346883

8a
N1  -0.6401840772  -0.6151807485  -0.2267975151
C2  -0.4078685692  -1.3120567722  0.8838675328
C3  0.4608138417  -0.5320487804  1.7278867481
C4  0.7196601023  0.6405379519  1.0923930725
C5  0.0317154027  0.6317732246  -0.1848237923
H6  -1.2309520781  -0.9227376249  -0.9878569414
H7  0.8253682750  -0.8575728266  2.6892219023
H8  1.3271152652  1.4610442438  1.4435364874
C9  -0.0153685102  1.5627630693  -1.1495451911
H10  0.5191491079  2.4959937334  -1.0280880842
H11  -0.5781171208  1.4218839329  -2.0647615428
C12  -0.9248222410  -2.6899403320  1.1238470490
H13  -1.4294530454  -2.7192098382  2.0942422743
H14  -1.6650187162  -2.9684752269  0.3691289546
C15  1.1328184749  -3.9179544923  0.0702176081
C16  2.1159182122  -4.7943110689  0.5819858879
C17  1.8379317018  -4.9885667594  1.9190500382
N18  0.7264971123  -4.2505583744  2.2339782617
C19  0.2655109486  -3.6054645066  1.1084652228
H20  0.2639054148  -4.2689167709  3.1295659632
H21  2.9300734012  -5.2424431663  0.0362576775
H22  2.3273987138  -5.6014550422  2.6582594680
H23  1.0544087666  -0.9472008720

9a
N1  0.0286059152  -1.0592357102  2.0843129062
C2  -1.0116043446  -0.2966946163  1.8693468459
C3  -0.7308152119  1.0372860364  2.3661375301
C4  0.5171752383  1.0323422307  2.8774641479
C5  1.1076834302  -0.3296854982  2.7389136667
H6  0.0302045842  -2.0451373073  1.8213548955
H7  -1.4215852411  1.8654285200  2.3149362107
H8  2.0139450563  -0.3423646838  2.1225007807
H9  1.3541654572  -0.7883020087  3.7035837615
C11  -2.2691804341  -0.8044081458  1.2312374863
H12  -2.5640535096  -0.8590966912  1.4580976362
H13  -3.0534660023  -0.7265973665  1.9978072068
C14  -2.0881795884  -3.4089337919  1.3620317728
C15  -1.9555713684  -4.4302526462  0.3811679243
C16  -1.9598066824  -3.8287844466  -0.8591759234
N17  -2.0835126680  -2.4726216222  -0.6523147938
C18  -2.1691364197  -2.1984984579  0.6982233352
H19  -2.1366385892  -1.7891109341  -1.3920063110
H20  -1.8743222510  -5.4906083135  0.5557771164
H21  -2.1692333753  -3.5524045237  2.4300274035
C22  -1.8495345366  -4.4054559801  -2.2482877824
H23  -0.9261196160  -4.0498637732  -2.7185848474
H24  -2.6697450865  -4.0122215244  -2.8656460203
C25  -0.7987642898  -6.7821674756  -2.506951926
C26  -1.3251577932  -8.1020550044  -2.4396858444
C27  -2.6713967367  -7.9929564705  -2.1851447784
N28  -2.9749233735  -6.6555025576  -2.0967891841
N1  -1.0398067656 -0.1044944409  0.9562730685
C2   -0.7810108325 -1.2268568538  0.2829253340
C3   0.6428562514 -1.4387570540  0.3030948679
C4   1.2080888254 -0.4276818626  1.0137516380
C5   0.1555931766  0.4682808028  1.4539389414
H6   -1.9646524782  0.2698155993 -1.1195505781
H7    1.1403637723 -2.265989798  -0.1778112428
H8   2.2547219284 -0.2808744522  1.2332510424
C9   0.2249723209  1.5926820878  2.1837159307
H10  1.1829186694  1.9501658715  2.5378663420
C12  -1.8190014269 -2.0315689434  1.2805111517
H13  -1.7124064963 -3.0848486173 -0.4172699064
H14  -2.8255839308 -1.7216589459 -0.1283154120
C15  -1.6623039767 -0.6723134967 -2.6538691731
C16  -1.2556185417 -0.9947946082 -3.9678822566
C17  -0.9031070646 -2.3337588987 -3.9854061420
H18  -1.0743281688 -2.8138763932 -2.7088822808
C19  -1.5665403991  1.8251476677 -1.8868112585
H20  -0.9724763362 -3.7883461591 -2.4510700617
H21  -1.2140092429 -0.3337819794 -4.81692600669
H22  -1.9982454949  0.2923759538 -2.3049775600
C23  -0.4132689078 -3.2150823101 -5.1044981176
H24  -1.0828144842 -4.0812083590 -5.2079343525
H25  0.5647651738 -3.6275196516 -4.8311138284
C26  0.8383455082 -1.9607603566 -7.0229340881
C27  0.4241108254 -1.3979279246 -8.2613985566
C28  -0.9273166226 -1.6202633104 -8.3806775887
N29  -1.3423589407 -2.2942592125 -7.2569745383
C30  -0.2711253014 -2.5133949593 -6.4182518220
H31  -2.2853798030 -2.6049559601 -7.0899063840
H32  1.0474709057 -0.8969359230 -8.9846082812
H33  -1.6191059156 -1.3688220856 -9.1678235620
H34  1.8399000846 -1.9674662039 -6.6204213948

12a
N1  -3.3293689434 -4.1541283222 -4.1235249576
C2  -2.9599804443 -3.5635493306 -5.2301394148
C3  -3.3898426368 -4.3647761596 -6.3603525179
C4  -4.0228992162 -5.4529850216 -5.8771276664
C5  -4.0373074370 -5.4010603253 -4.3867168005
H6  -3.1353585876 -3.7415311406 -3.2105620145
H7  -3.2123374585 -4.1053795487 -7.3930976863
H8  -4.4613626746 -6.2615350210 -6.4457688654
H9  -5.0509735025 -5.3662003588 -3.9703400607
H10 -3.5161424430 -6.2475478188 -3.9245233042
| Atom | X-C | Y-C | Z-C |
|------|-----|-----|-----|
| C1   | -2.4290112414 | 0.1040971617 | -2.9210804161 |
| H12  | -2.9299316831 | -0.2604258691 | -2.0180017439 |
| H13  | -3.2047214644 | 0.4960444054 | -2.0180017439 |
| C14  | -0.0801667771 | 2.6079940197 | -1.4511772434 |
| C15  | 0.0192188933 | 2.8582593534 | -2.8071826247 |
| N17  | -0.8016071952 | 1.9588754761 | 3.4451459307 |
| C18  | -1.4391147110 | 1.1546094788 | -2.519835836 |
| H19  | -0.9585927623 | 1.9681005344 | -4.4422962551 |
| H20  | 0.4398934003 | 3.1466987956 | -0.6747421944 |
| H21  | -1.3047970321 | 1.1073641808 | -0.3311725296 |
| C22  | 0.8358098147 | 3.8753236340 | -3.5671300311 |
| H23  | 1.8965861471 | 3.6144290878 | -3.5059139531 |
| C25  | 0.3970826091 | 4.0136007946 | -7.2822139323 |
| N28  | -0.7886342169 | 4.3494651530 | -5.4395204543 |
| C29  | 0.4798268986 | 3.9919371439 | -5.0184091653 |
| H30  | -1.5366237322 | 4.6380247211 | -4.8285672190 |
| C31  | 0.6771820121 | 3.9284765360 | -8.3207714065 |
| C35  | 2.2680791192 | 3.4775865908 | -6.1667190083 |
| C36  | -2.1297539014 | 4.6317862181 | -7.5479280164 |
| H34  | -1.8863801755 | 4.3718351271 | -6.8182196393 |
| C38  | -2.6591249209 | 5.4818667461 | -7.0977691242 |
| C39  | -2.7667426652 | 2.0875272549 | -7.426336952 |
| C40  | -3.9818093550 | 3.9614764697 | -7.6376553126 |
| C41  | -4.9629706419 | 2.2939979269 | -7.9083119690 |
| N39  | -4.3832145762 | 3.5345436097 | -7.8659436877 |
| C40  | -3.0398530584 | 3.4286182451 | -7.5799438491 |
| H41  | -4.8650604037 | 4.3993846765 | -8.0545078160 |
| H42  | -6.0088474196 | 2.1699740512 | -8.1399519317 |
| H43  | -1.7861671694 | 1.6755250146 | -7.2405165742 |
| C44  | -4.1656401284 | -0.1129137791 | -7.5788058266 |
| H45  | -5.0704509437 | -0.4250436434 | -8.1059850652 |
| H46  | -3.3203928577 | -0.6399387973 | -8.0240013757 |
| O47  | -4.2338434838 | -0.6353977603 | -6.2097224095 |
| H48  | -4.9894140688 | -0.2216192891 | -5.7767911765 |

**14a**

| Atom | X-C | Y-C | Z-C |
|------|-----|-----|-----|
| N1   | 0.6120530213 | 2.3875451518 | 0.1265405606 |
| C2   | -0.3421949752 | 1.5846580886 | 0.5702865404 |
| C3   | -0.5000425772 | 1.8014628555 | 1.9867128454 |
| C4   | 0.3893228665 | 2.761209680 | 2.3581511929 |
| C5   | 1.1359307507 | 3.1694510165 | 1.1816345217 |
| H6   | 0.9037329829 | 2.3864491123 | -0.8496371025 |
|   |  C   |  H   |  N   |  C   |  H   |  N   |  C   |  H   |  N   |  C   |  H   |  N   |  C   |  H   |  N   |
|---|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|
| C6 | 18.9526614035 | -2.9959161986 | 12.2338061558 |
| H7 | 19.1780611587 | -2.0615480176 | 12.7237321230 |
| N8 | 20.1457896463 | -7.3019053748 | 12.2241319564 |
| C9 | 18.8686815362 | -7.5758652256 | 12.1391997688 |
| C10| 20.9571836986 | -8.5014113970 | 12.4308471471 |
| H12| 20.1317003787 | -10.6077598674 | 12.5942700963 |
| N15| 22.9239827598 | -6.6362087209 | 10.1709711832 |
| C16| 22.9914439227 | -7.5246072900 | 11.2269284794 |
| C17| 23.8730410870 | -5.6525155525 | 11.8874897179 |
| N22| 21.8673219200 | -3.3738966615 | 9.6468211675 |
| C23| 20.6900913621 | -3.0525603383 | 9.0071383444 |
| C24| 22.7145160202 | -4.0444508390 | 8.7912039516 |
| C25| 22.0601988750 | -4.1597626569 | 7.5836406608 |
| H26| 22.4642137018 | -4.6145561968 | 6.6918676186 |
| C27| 20.7838292012 | -3.5341085485 | 7.7196999325 |
| H28| 20.0344907878 | -3.4226145658 | 6.9506928541 |
| C29| 17.8049288684 | -6.5368054067 | 11.9482588050 |
| C30| 19.5640851927 | -2.3878930406 | 9.7459627290 |
| C31| 24.0338695496 | -4.5818093888 | 9.2630995396 |
| C32| 22.0643234031 | -8.6873963477 | 11.3359005412 |
| H33| 17.2186178990 | -6.8289916780 | 11.0666536084 |
| H34| 19.8712068056 | -1.4198864146 | 10.1539229220 |
| C35| 24.5730265257 | -4.9768839055 | 8.3957913810 |
| H36| 21.5734442521 | -8.8845905929 | 10.3790911356 |
| H37| 18.6508786130 | -4.9696207123 | 9.7546814872 |
| H38| 20.5167869205 | -6.3563506776 | 12.1837629973 |
| H39| 22.3186086306 | -6.7064898327 | 9.3662796093 |
| H40| 22.0793821077 | -3.1482668583 | 10.6063521038 |
| H41| 17.1081208803 | -6.6432861316 | 12.7889170184 |
| H42| 18.7580583154 | -2.1791577272 | 9.0356895493 |
| H43| 24.6630079191 | -3.7867675559 | 9.6758187851 |
| H44| 22.6079532507 | -9.5953986829 | 11.6087459112 |
| H45| 21.4566315258 | -8.4175765431 | 13.4030446206 |

**TSDimer**

|   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| N1 | 0.5418848514 | 0.1174733094 | -0.1334688971 |
| C2 | -0.8112383368 | 0.4169591353 | -0.2054285962 |
| C3 | -1.3997386952 | -0.1383626906 | 0.9488793572 |
| C4 | -0.4093477617 | -0.8335178739 | 1.6471484523 |
| Element | X          | Y          | Z          |
|---------|------------|------------|------------|
| C5      | 0.7881416785 | -0.6470480352 | 0.9569689415 |
| H6      | 1.2430496665 | 0.4475447780 | -0.7785216937 |
| H7      | -2.4412435464 | -0.500448289 | 1.2183685792 |
| H8      | -0.5281729135 | -1.4054797149 | 2.5531817973 |
| H10     | 1.7781554192 | -1.0178328634 | 1.1728815879 |
| C11     | -1.5787586251 | -1.1671550057 | -1.7135167988 |
| H12     | -2.6143008948 | -0.9593184843 | -1.4786049666 |
| H13     | -1.0948010033 | 1.2924676984 | -1.1189044950 |
| C14     | 0.1205153026 | -1.3161430525 | -3.5989912793 |
| C15     | 0.1520290706 | -0.7978918519 | -4.8845305134 |
| C16     | -1.0298843068 | -0.0616917902 | 1.2183685792 |
| N1      | -1.7543827088 | -0.1206393603 | -3.9327096757 |
| C2      | -1.0896516538 | -0.9030125763 | -2.9823697776 |
| H19     | -2.6671095696 | 0.2940059910 | -3.8107042332 |
| H20     | 0.9183150425 | -0.9030125763 | -5.6302461498 |
| H21     | -1.3812517920 | 0.4754729236 | -5.9305185111 |
| H22     | 0.8610477647 | -1.9482355273 | -3.1331086155 |
| H24     | -1.1552380141 | 1.2440186801 | -0.8052474026 |

**TSdehyd1**

| Element | X          | Y          | Z          |
|---------|------------|------------|------------|
| N1      | -0.2419627178 | 0.2408558159 | -0.2331740344 |
| C2      | -0.3789197091 | -1.0489940542 | 0.2833285891 |
| C3      | 0.3638537124 | -1.0823783614 | 1.4829341313 |
| C4      | 0.9208184067 | 0.1777032408 | 1.6780191672 |
| C5      | 0.5280507250 | 0.9703303133 | 0.5941218515 |
| H6      | -0.6302080771 | 0.5782481105 | -1.1119568947 |
| H7      | 0.4494523889 | -1.9398337661 | 2.1335474242 |
| H8      | 1.5299320624 | 0.5037427583 | 2.5054008903 |
| H9      | 0.7529701709 | 2.0047051374 | 0.3851148348 |
| H10     | -0.5229615875 | 1.8322761566 | -3.3554747664 |
| C11     | -1.1323920005 | -2.0630718796 | -0.3167304402 |
| H12     | -1.9009624925 | -1.8112684253 | -1.0367764263 |
| H13     | -1.3275125330 | -2.9520702652 | 0.2672696906 |
| O14     | -0.1515324705 | -3.0074796733 | -1.6339595822 |
| H15     | 0.7897241703 | -2.9797266448 | -1.4114869257 |
| O19     | -0.8080480559 | 1.5437925498 | -3.6664671688 |
| H20     | -0.2917229247 | -2.4863351487 | -2.4781314466 |
| H21     | -1.0028061514 | -1.8357320545 | -4.5621488672 |
| O22     | -1.1018928853 | 1.1632723661 | -2.9684693634 |
| H23     | -0.8680315951 | -0.5734888196 | -3.6323462025 |
| H24     | -1.9985859205 | 1.5040544065 | -3.0827334067 |

**TSdehyd2**

| Element | X          | Y          | Z          |
|---------|------------|------------|------------|
| N1      | -1.0654710196 | 0.3499575585 | 0.4487547342 |
| C2      | -0.6098288913 | -0.8801002916 | 0.2031879555 |
| C3      | 0.6535956074 | -0.7877326394 | -0.4007136722 |

S21
Part 4b: XYZ coordinates of formic and acetic transition state structures from Table S3

**TS2fa**

C1 -0.0622160195 -1.4393596316 0.1666208137
C2 -0.7694934254 -0.8017531470 -0.9277331177
C3 -0.7490012871 0.5318046769 -0.7093255073
N4 -0.0775189712 0.7925584857 0.5153174972
C5 0.3606169116 -0.4660136156 1.0041387980
H6 0.6673047376 1.5936189498 0.5094999159
H7 -1.2345911173 -1.3026308127 -1.7631054756
H8 -1.1742726667 1.3546817964 -1.2596126431
H9 0.1034304815 -2.4993039697 0.2872469809
H10 0.9379639626 -0.5151473549 1.9134655307
C11 -1.2194626374 1.6555538526 1.6628612660
O12 -1.5438070694 2.7880878752 1.1431019826
H13 -0.5390861833 1.6565010123 2.5217951053
H14 -2.0007792069 0.8955811410 1.7016112239
C15 1.4180992350 3.8717662724 1.0568044235
O16 1.6725212706 2.7226388376 0.6362852927
H17 2.2551466710 4.5891135585 1.0992447347
O18 0.3025565978 4.3238156002 1.4538872431
H19 -0.7015025103 3.5367072464 1.294509321

**TS3fa**

C1 0.6155676608 -0.6871899046 -0.4893112419
C2 -0.7603056280 -0.8094779991 -0.4128260255
C3 -1.2287982281 0.3092275982 0.2991745243
| Atom | X       | Y       | Z       |
|------|---------|---------|---------|
| N4   | -0.1878 | 0.5643  | 0.1876  |
| C5   | 1.0213  | 0.8376  | 0.1366  |
| H6   | 0.4237  | 0.9643  | 0.6187  |
| H7   | 0.1366  | 0.6187  | 0.4237  |
| H8   | 0.6187  | 0.1366  | 0.4237  |
| H9   | 0.0213  | 0.9643  | 0.6187  |
| H10  | 0.2136  | 1.0213  | 0.8376  |
| C11  | 0.5643  | 0.8376  | 0.1366  |
| C15  | 4.3754  | 1.6509  | 1.1915  |

**TS4fa**

| Atom | X       | Y       | Z       |
|------|---------|---------|---------|
| C1   | 1.0294  | -0.2342 | -0.8741 |
| C2   | -0.2319 | -0.9209 | -0.5964 |
| C3   | -0.9092 | -0.0572 | 0.3054  |
| N4   | -0.1698 | 1.0342  | 0.5041  |
| C5   | 1.0327  | 0.9486  | -0.2151 |
| H6   | -0.4505 | 1.8300  | 1.0591  |
| H7   | -0.2391 | -2.0296 | -0.4086 |
| H8   | -1.8963 | -0.1719 | 0.7258  |
| H9   | 1.8212  | -0.6096 | -1.5036 |
| H10  | 1.7566  | 1.7455  | -0.1633 |
| C11  | -1.3195 | -1.0739 | -2.0240 |
| O12  | -2.4720 | -1.6566 | -0.8740 |
| H13  | -1.3887 | -0.8642 | -2.4042 |
| H14  | -0.6699 | 1.7409  | 2.6392  |
| C15  | -1.2128 | -4.4515 | -0.8032 |
| O16  | -0.2992 | -3.7740 | -0.2965 |
| H17  | -1.1640 | -5.5511 | -0.6662 |
| O18  | -2.2112 | -4.0483 | -1.4736 |
| H19  | -2.3703 | -2.7172 | -1.5654 |

**TS5fa**

| Atom | X       | Y       | Z       |
|------|---------|---------|---------|
| N1   | 1.0104  | -0.5334 | 0.0085  |
| C2   | 0.5622  | 0.6272  | 0.6368  |
| C3   | -0.8249 | 0.7625  | 0.3408  |
| C4   | -1.1768 | -0.2974 | -0.4686 |
| C5   | -0.0090 | -1.0857 | -0.6350 |
| C6   | 1.3868  | 1.4062  | 1.4142  |
| H7   | 1.0011  | 2.3275  | 1.8271  |
C5  1.0040221779  0.0195592000  -0.0554958298
H6  0.5823941435  1.9076638634  0.7485241069
H7  -2.1134815104  -1.0307163179  -0.6386199040
H8  -1.9069758377  1.3727890495  0.6244999984
H9  0.4079555573  -1.8608655395  -1.0812095151
C10  2.3505515017  1.7396294751  0.0247937402
H11  2.2268327423  0.7312986946  -1.6667110251
H12  3.1151313517  -0.2437932470  -0.4830918698
O13  2.6894958913  1.9076638634  0.7485241069
H14  3.1343543042  1.5544775933  -0.6386199040
N1  3.6414382526  -2.1503983839  1.4295769249
C16  2.2532950566  1.3959167930
C17  1.8435026888  1.1116341685
C4  2.9899595488  -4.2519951263  0.9971470069
C19  4.0833863893  -3.3961858021  1.2083221344
C6  1.4862142931  1.6213169788
H21  0.8190683545  -3.7969197690  1.0124684491
H22  3.0451493073  -5.3106110375  0.7971330980
H10  5.1391407090  -3.6194170770  1.2286751701
H24  0.4694921410  -1.1214858884  1.9687975783
H25  2.0263050394  -0.1436604335  2.0650395255
C26  4.8066219311  2.6556917536
O27  3.6626474503  2.4013997954
H28  5.466726544  3.2906535078
O29  5.2840136325  -0.2990563682  2.2797428235
H30  4.2753295940  -1.3281981349  1.7254319322

TS2aa
C1  -0.0937720088  -1.4618987667  0.2127269427
C2  -0.7528900641  -0.8331927413  -0.9159206151
C3  -0.7305855273  0.5026145879  -0.7127026568
N4  -0.1003770063  0.7753373633  0.5306470432
C5  0.3031388847  -0.4805826233  1.0540088543
H6  0.6707341226  1.5683374972  0.5275728935
H7  -1.1892152300  -1.3408692190  -1.7625462751
H8  -1.1303316425  1.3216279044  -1.2870448659
H9  0.0586855995  -2.5213152406  0.3530584133
H10  0.8430604291  -0.5230698464  1.9863587960
C11  -1.2441073261  1.6874973700  1.6098843984
O12  -1.5180610568  2.8162462083  1.0522851544
H13  -0.5965086760  1.6915593124  2.4949800031
H14  -2.0513851831  0.9539947115  1.6481567465
C15  1.4819927391  3.8232786835  0.9984206246
O16  1.6873368877  2.6381638077  0.6336632769
O17  0.3582237479  4.3040116519  1.3573407947
H18  -0.6419418695  3.5484072961  1.2023048245
|  |  |  |  |
|---|---|---|---|
| H20 | 3.5913788099 | 4.2420091861 | 1.1020570500 |
| H21 | 2.6651511179 | 5.3123017996 | 0.0382624838 |
| C22 | 2.6526685998 | 4.7842207423 | 0.9965253980 |
| H22 | 2.5384691493 | 5.5266515367 | 1.7861813642 |

**TS3aa**

|  |  |  |  |
|---|---|---|---|
| C1 | 0.6320206348 | -0.6988702728 | -0.4841213732 |
| C2 | -0.7366953298 | -0.8628300166 | -0.3776607200 |
| C3 | -1.2263127540 | 0.2545339775 | 0.3232492428 |
| N4 | -0.2043227085 | 1.0533146381 | 0.6328468942 |
| C5 | 1.0146525073 | 0.5447771808 | 0.1165867152 |
| H6 | -0.2707640793 | 1.9016535986 | 1.1751197428 |
| H7 | -1.3403614629 | -1.6663610399 | -0.7689087492 |
| H8 | -2.2432401300 | 0.5017211973 | 0.5917058705 |
| H9 | 1.3316845613 | -1.3359217949 | -1.0036148288 |
| H10 | 1.8905443216 | 0.6561807324 | 0.7970753708 |
| C11 | 1.6956500237 | 1.6033156843 | -1.1388370869 |
| O12 | 2.8293880564 | 1.1002703373 | -1.5652883872 |
| H13 | 0.8946863133 | 1.6364108332 | -1.8848078903 |
| H14 | 1.7639926880 | 2.5392688279 | -0.5643062583 |
| C15 | 4.3622745624 | 1.6391546084 | 1.2047623209 |
| O16 | 3.2836934742 | 1.2841473116 | 1.7205619904 |
| O17 | 4.5968197500 | 1.7535234731 | -0.0481590581 |
| H18 | 3.6725498170 | 1.3925074798 | -0.8421670336 |
| C19 | 5.5410565281 | 1.9663559037 | 2.1107871172 |
| H21 | 6.2923548012 | 1.1776090906 | 2.0130048111 |
| H22 | 6.0087622053 | 2.9002038960 | 1.7932289664 |
| H23 | 5.2216083365 | 2.0317438708 | 3.1499979740 |

**TS4aa**

|  |  |  |  |
|---|---|---|---|
| C1 | 1.0229878575 | -0.2308480659 | -0.8770270884 |
| C2 | -0.2454746683 | -0.9133883325 | -0.6220980983 |
| C3 | -0.9210849868 | -0.0636188095 | 0.2937299311 |
| N4 | -0.1710387658 | 1.0138577044 | 0.5269999963 |
| C5 | 1.0351237631 | 0.9340584148 | -0.1865934355 |
| H6 | -0.4461423082 | 1.7970762942 | 1.1019611508 |
| H7 | -0.2528957027 | -0.207967168 | -0.4360122905 |
| H8 | -1.9126664133 | -0.1790160441 | 0.7034013702 |
| H9 | 1.8151287872 | -0.5980610726 | -1.5109531060 |
| H10 | 1.7675749240 | 1.7209782174 | -0.1086962371 |
| C11 | -1.3211848347 | -1.1081626175 | -2.0436326432 |
| O12 | -2.4705999224 | -1.6345833411 | -1.6761064851 |
| H13 | -1.3976390547 | -0.0888308977 | -2.4289104606 |
| H14 | -0.6688373573 | -1.7367283651 | -2.6623331128 |
| C15 | -1.2035028691 | -4.4526354320 | -0.8013587086 |
| O16 | -0.3068501217 | -3.7373722552 | -0.3033229139 |
O17 -2.1990526119 -4.0444804025 -1.4853587622
H18 -2.3579622895 -2.7356508363 -1.5782384120
C19 -1.1333684142 -5.9597463865 -0.5890053598
H20 -0.2144101830 -6.2358996586 -0.0739045487
H21 -1.9971149058 -6.2796317518 -0.0000858814
H22 -1.1946271228 -6.4689947065 -1.5534161740

TS5aa
N1  1.0123156077 -0.5367335551  0.0106116004
C2  0.5507677009  0.6228025347  0.6299945244
C3  -0.8407057616  0.7344774993  0.3467249661
C4  -1.1836937911 -0.3395917857 -0.4485615500
C5  -0.0051843349 -1.1111982993 -0.6169293131
C6  1.3714612520  1.4211997378  1.3942523641
H7  0.9757036261  2.3410669455  1.8009787898
H8  2.0295401832 -0.9676264087  0.1785154878
H9  0.1245612760 -2.0406395094 -1.1522151759
H10 -1.4822782972  1.5335387272  0.6862866985
H11 -2.1508360347 -0.5671335395 -0.8684710302
H12  2.4443740495  1.3326465371  1.3065429955
O13  1.5376620542  0.4906696559  3.2512903043
H14  1.9605425846  1.0806882648  3.8884884632
C15  3.9294975704 -1.4897967355  1.4891342899
C16  3.3088304238 -1.5711780386  0.3899786831
C17  3.5767599292 -0.8255946831  2.5002369995
H18  2.2946126666 -0.1287845186  2.9483221992
C19  5.2236730786 -2.2837892525  1.6068513366
H20  5.9667478925 -1.7106218165  2.1632098668
H21  5.0220025185 -3.1976541814  2.1739793243
H22  5.6043391991 -2.5584626616  0.6237729857

TS6aa
N1  4.4716789584  3.3525121417 -0.3164046313
C2  3.1121057469  3.6602058357 -0.3110116145
C3  2.7436033014  3.9087226779 -1.6614398524
C4  3.8736963939  3.7334891522 -2.4426623279
C5  4.9291478117  3.3964172923 -1.5669030387
C6  2.3762771957  3.6825628127  0.8595011819
H8  1.7502701117  4.1685959829 -1.993264933
H9  3.9540078805  3.8266520433 -3.5139171319
H10  5.9645976840  3.1918227237 -1.7938536898
H11  1.3066515410  3.8217529340  0.8201341530
H12  2.8189909302  3.2655074721  1.7514245260
C1  0.8099318997  5.9969368489  3.1034078692
C13  1.5280921954  6.2305079820  1.9253049653
C14  2.8145358081  5.6802440138  2.1050552882
| Atom | x      | y      | z      |
|------|--------|--------|--------|
| N4   | 2.8835963634 | 5.1892132211 | 3.3872043390 |
| C16  | 1.6844045747  | 5.3480482413  | 3.9825911050 |
| H17  | 3.7422123111  | 4.6889710726  | 3.7919395498 |
| H18  | 1.1787834889  | 6.7260326600  | 1.0320199432 |
| H19  | 3.7146728208  | 5.8162000669  | 1.5308387718 |
| H20  | -0.216963913  | 6.256571026  | 3.3072779594 |
| H21  | 1.5118368348  | 4.9880535060  | 4.9853460910 |
| C22  | 5.5879540228  | 3.3174279592  | 3.3641605231 |
| O23  | 5.0260313824  | 3.9225405043  | 4.3076056277 |
| C24  | 6.8942358757  | 2.5839149961  | 3.6545087706 |
| O25  | 5.1433465021  | 3.2708245042  | 2.1775491558 |
| H26  | 4.9903523900  | 3.199051590  | 0.5824228714 |
| H27  | 7.6900076796  | 2.995110695  | 3.0269728475 |
| H28  | 7.1711943484  | 2.6760409334  | 4.704223833 |
| H29  | 6.7873416146  | 1.528356183  | 3.3894834839 |

**TSeбaa**

| Atom | x      | y      | z      |
|------|--------|--------|--------|
| C1   | 0.1753557129 | -1.0164617910 | -0.7408730324 |
| C2   | -1.1289022338 | -0.6027777430 | -0.5165592200 |
| C3   | -1.0583739331 | 0.6293707694  | 0.1569013812 |
| N4   | 0.2293900162  | 0.9425487972  | 0.1434703432 |
| C5   | 1.0705018996  | -0.0716157493 | -0.1434730432 |
| H6   | 0.6348852553  | 1.8056530563  | 0.6762276832 |
| H7   | -2.0369463116 | -1.1238183196 | -0.7766024445 |
| H8   | -1.8528792840 | 1.2654919092  | 0.5165749068 |
| H9   | 0.4916376217  | -1.9421291017 | -1.1971158468 |
| C10  | 2.4204557106  | 0.4544815614  | -0.6646970304 |
| H11  | 2.3048152311  | 0.6724733857  | -1.7309149604 |
| H12  | 3.1861709588  | -0.3210647582 | -0.5574352664 |
| O13  | 2.7499291583  | 1.6501275796  | -0.0152432285 |
| H14  | 3.1990369260  | 1.4462860771  | 0.8541361484 |
| N1   | 3.6901671002  | -2.2609929589 | 1.3214852024 |
| C16  | 2.3022875476  | -2.2557040872 | 1.2946919529 |
| C17  | 1.8855919149  | -3.5754802851 | 1.0134420216 |
| C4   | 3.0287645680  | -4.3614680571 | 0.8940591699 |
| C19  | 4.1261011686  | -3.5082645171 | 1.0979034701 |
| C6   | 1.5402735061  | -1.0830193511 | 1.5242236318 |
| H21  | 0.8592934694  | -3.8988419814 | 0.9209778949 |
| H22  | 3.0795315660  | -5.4206919054 | 0.6958924811 |
| H10  | 5.1813597748  | -3.7346603922 | 1.1105847727 |
| H24  | 0.5223650414  | -1.2239653425 | 1.8694160707 |
| H25  | 2.0848517334  | -0.2547822135 | 1.9766008819 |
| C26  | 4.9115378995  | 0.6684087982  | 2.5365296819 |
| O27  | 3.7440445989  | 1.1158267672 | 2.3240823470 |
| C28  | 5.8417234890  | 1.5415741881  | 3.3712116883 |
| O29  | 5.3574030800  | -0.4301894153 | 2.1178524313 |
H30 4.3344404024 -1.4365215146 1.6072634975
H32 6.0176240995 2.4846122186 2.8465190936
H33 5.3549592384 1.7881791824 4.3179633562
H34 6.7914322715 1.0412654591 3.5566188158

TSpt3fa
C1 0.3980760154 -0.6779683073 -0.6650528128
C2 -0.6691802338 -0.3722546451 0.1382797248
C3 -0.3744168985 0.8796163213 0.7474621203
N4 0.7746042880 1.3343861026 0.3029767777
C5 1.4018340404 0.3689281599 -0.5639340050
H6 1.4078405355 2.0521660180 0.7169844199
H7 -1.5563329847 -0.9596866633 0.3167941944
H8 -0.9394199934 1.4070023377 1.5041847237
H9 0.5052518416 -1.5562041507 -1.2857068594
H10 2.3432311699 0.0559828769 0.1118998088
C11 2.0098585108 0.9499688160 -1.8667799529
O12 3.1682139688 1.7147703385 -1.6857310391
H13 2.2696138969 0.0999129271 -2.5047752213
H14 1.2193827438 1.5219654774 -2.3759395818
C15 3.6998262507 1.3530315076 1.4767455569
O16 3.5042264937 0.1562360794 1.1490432382
O17 3.0874712852 2.3762627482 1.0533722315
H18 3.1412847677 2.1671712017 -0.8221873471
H19 4.4988943482 1.5243796056 2.2244836610

TSpt6fa
C1 0.5482376061 -0.6078533290 -1.0306256950
C2 -0.7547762913 -0.9068690099 -0.7207998053
C3 -1.2020718756 0.1051657929 0.1726532006
N4 -0.2582295440 1.0036720962 0.3539908783
C5 0.9465415009 0.5845526833 -0.3088888532
H6 -0.1011826497 1.6299895301 1.2039116330
H7 -1.3385184349 -1.7523235007 -1.0510403669
H8 -2.1406588395 0.1574944501 0.7081843455
H9 1.2026737719 -1.1540738088 -1.6942774793
H10 1.6187721837 0.3416534544 0.6756401100
C11 1.7550538759 1.7057133159 -1.0005356609
H13 1.1493997764 2.1465317511 -1.7996986780
H14 1.9188693219 2.4897448842 -0.2567014430
C15 1.7856036250 1.4359071121 2.7147866676
O16 2.3113983987 0.5280487920 2.0040181688
O17 0.7717458069 2.1272964538 2.4590888836
C21 4.1657709831 0.6854552546 -0.9204439940
C22 5.1228238875 0.3679799854 -1.9236446593
C23 4.5779605429 0.7084576483 -3.1404227123
S3ts1
C1 -0.1277027683 -1.3449187639 0.8661556618
C2 -0.9004518690 -1.1949785158 -0.3566790211
C3 -0.9324214811 0.1162013603 -0.6674607911
N4 -0.2181977101 0.8538275266 0.3284052144
C5 0.2792181548 -0.1176341516 -0.2491113775
H6 0.5729538154 1.5049299428 -0.0835436008
H7 -1.3738608367 -1.9915421639 -0.9104965084
H8 -1.4256982295 0.6589430925 -1.4563346857
H9 0.0881031384 -2.2738866680 1.3723474628
H10 0.8882588860 0.2023303532 2.0791095409
C11 -1.2707498110 2.0377767779 1.0383135493
O12 -1.6512448080 2.8770507230 0.6193940275
H13 -0.6150704321 2.4285812033 1.826755352
H14 -2.0390213356 1.3589142405 1.4205050522
C15 0.4511818118 5.4678370220 0.5473047609
O16 1.4680017091 4.7540611490 0.4034506174
O17 -0.7615838441 5.0838477347 0.4751961088
H18 -1.1448048716 3.8814914537 0.2340747194
H20 1.6811301277 7.1621907566 1.0785168586
H21 0.3663440308 7.5156564259 -0.0673683733
C22 0.6434894637 6.9491129672 0.8263522497
H22 -0.0218724767 7.2679358538 1.6304748817
O23 1.6680803198 2.3988914451 -0.5177645820
H24 1.7719131570 2.5122170275 -1.4670720357
H25 1.5714050141 3.3408561886 -0.1306631052

S3ts2
C1 -0.0458251006 -1.3439362952 0.1770539477
C2 -0.7915279456 -0.7234376251 -0.9017550928
C3 -0.8696216779 0.6001420158 -0.6389374539
N4 -0.2388202216 0.8655063012 0.6044320959
C5 0.2977488577 -0.3696077191 1.0493375639
H6 0.4546982584 1.6928402988 0.6537886432
H7 -1.2138295739 -1.2279480967 -1.7574546595
H8 -1.3578987528 1.4035626778 -1.1646259672
H9 0.1992610818 -2.3917426622 0.2629661408
H10 0.8829008285 -0.4002583903 1.9541103862
| Atom | X       | Y       | Z       |
|------|---------|---------|---------|
| C11  | -1.5569332781 | 1.4912918992 | 1.7856250196 |
| O12  | -2.1289537895  | 2.5244853866  | 1.2859076616 |
| H13  | -0.8801114061  | 1.6353436477  | 2.6332986520 |
| H14  | -2.1312753623  | 0.5638138004  | 1.7928516743 |
| C15  | 1.9713638367   | 3.8324522285  | 0.7027871567 |
| O16  | 1.6565548448   | 2.6215791124  | 0.8171871494 |
| O17  | 1.2125606482   | 4.8239038847  | 0.9241571171 |
| H18  | 0.0593988270   | 4.5919896711  | 1.5118098601 |
| H20  | 4.0753550256   | 3.8594153207  | 1.0906720408 |
| H21  | 3.6643687390   | 3.5448256256  | -0.5909435173 |
| C22  | 3.3980524737   | 4.4451528307  | 0.2810711154 |
| H22  | 3.5208881441   | 5.2056365176  | 0.0664535654 |
| O23  | -0.9355731802  | 4.4430951392  | 2.0448837720 |
| H24  | -1.5795961048  | 3.4829158114  | 1.6101558817 |
| H25  | -1.3919209618  | 5.2720703001  | 2.0529678008 |