

# Computational Study on Non-Enzymatic Peptide Bond Cleavage at Asparagine and Aspartic Acid-Supporting Information

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## Table of Contents

*Table T1:* Cartesian coordinates and energy of B3LYP/6-31+G\*\* optimized conformation for compound (TS1) S-2

*Table T2:* Cartesian coordinates and energy of B3LYP/6-31+G\*\* optimized conformation for compound (TS1-H<sub>2</sub>O) S-3

*Table T3:* Cartesian coordinates and energy of B3LYP/6-31+G\*\* optimized conformation for compound (TS2-H<sub>2</sub>O) S-4

*Table T4:* Cartesian coordinates and energy of B3LYP/6-31+G\*\* optimized conformation for compound (TS3-H<sub>2</sub>O) S-5

*Table T5:* Cartesian coordinates and energy of B3LYP/6-31+G\*\* optimized conformation for compound (TS4-H<sub>2</sub>O) S-6

*Table T6:* Cartesian coordinates and energy of B3LYP/6-31+G\*\* optimized conformation for compound (TS5-H<sub>2</sub>O) S-7

*Table T7:* Cartesian coordinates and energy of B3LYP/6-31+G\*\* optimized conformation for compound (TS6-H<sub>2</sub>O) S-8

*Table T8:* Cartesian coordinates and energy of B3LYP/6-31+G\*\* optimized conformation for compound (TS7-H<sub>2</sub>O) S-9

*Table T9:* Cartesian coordinates and energy of B3LYP/6-31+G\*\* optimized conformation for compound (Asp-TS1) S-10

*Table T10:* Cartesian coordinates and energy of B3LYP/6-31+G\*\* optimized conformation for compound (Asp-TS1-H<sub>2</sub>O) S-11

*Table T11:* Cartesian coordinates and energy of B3LYP/6-31+G\*\* optimized conformation for compound (Asp-TS2-H<sub>2</sub>O) S-12

Table T1: Cartesian coordinates and energy of B3LYP/6-31+G\*\* optimized conformation for compound (TS1)

Standard orientation:

| Center<br>Number                             | Atomic<br>Number | Atomic<br>Type | Coordinates (Angstroms) |           |           |
|--|------------------|----------------|-------------------------|-----------|-----------|
|  |                  |                | X                       | Y         | Z         |
| 1  | 6                | 0              | 3.641761                | -1.374336 | .404240   |
| 2  | 6                | 0              | 2.390537                | -.767213  | -.194674  |
| 3  | 8                | 0              | 2.429601                | -.075591  | -1.218205 |
| 4  | 7                | 0              | 1.214808                | -1.029684 | .445693   |
| 5  | 6                | 0              | -.078561                | -.609321  | -.098489  |
| 6  | 6                | 0              | -1.222221               | -1.521776 | .338337   |
| 7  | 6                | 0              | -2.537719               | -.929695  | -.212945  |
| 8  | 8                | 0              | -3.439665               | -1.666900 | -.629054  |
| 9  | 6                | 0              | -.337382                | .863259   | .257906   |
| 10   | 7                | 0              | .339172                 | 1.759050  | -.434904  |
| 11   | 6                | 0              | .338998                 | 3.197261  | -.193604  |
| 12   | 8                | 0              | -.780034                | 1.228103  | 1.469267  |
| 13   | 7                | 0              | -2.490782               | .416813   | -.158552  |
| 14   | 1                | 0              | 4.064703                | -2.080000 | -.317029  |
| 15   | 1                | 0              | 3.464894                | -1.895207 | 1.348915  |
| 16   | 1                | 0              | 4.378970                | -.582639  | .560408   |
| 17   | 1                | 0              | 1.220975                | -1.572954 | 1.297385  |
| 18   | 1                | 0              | .007679                 | -.653072  | -1.188318 |
| 19   | 1                | 0              | -1.275944               | -1.590302 | 1.433455  |
| 20   | 1                | 0              | -1.078014               | -2.529123 | -.057814  |
| 21   | 1                | 0              | -3.289817               | .839547   | -.631814  |
| 22   | 1                | 0              | -1.739303               | .943779   | 1.387015  |
| 23   | 1                | 0              | .932767                 | 1.389352  | -1.177172 |
| 24   | 1                | 0              | -.040823                | 3.717726  | -1.078000 |
| 25   | 1                | 0              | -.296742                | 3.415358  | .662322   |
| 26   | 1                | 0              | 1.356574                | 3.540313  | .014291   |
| Sum of electronic and zero-point Energies=   |                  |                | -664.328582             |           |           |
| Sum of electronic and thermal Energies=      |                  |                | -664.314837             |           |           |
| Sum of electronic and thermal Enthalpies=    |                  |                | -664.313893             |           |           |
| Sum of electronic and thermal Free Energies= |                  |                | -664.369875             |           |           |

W= -336.5227

Table T2: Cartesian coordinates and energy of B3LYP/6-31+G\*\* optimized conformation for compound (TS1-H<sub>2</sub>O)

Standard orientation:

| Center<br>Number                             | Atomic<br>Number | Atomic<br>Type | Coordinates (Angstroms) |           |           |
|--|------------------|----------------|-------------------------|-----------|-----------|
|  |                  |                | X                       | Y         | Z         |
| 1  | 6                | 0              | -.533231                | .395573   | -.328194  |
| 2  | 6                | 0              | .671483                 | -.599375  | -.184830  |
| 3  | 7                | 0              | 1.926921                | .440752   | -.255430  |
| 4  | 6                | 0              | 1.404960                | 1.804284  | -.299488  |
| 5  | 6                | 0              | -.019417                | 1.758340  | .185549   |
| 6  | 7                | 0              | .794925                 | -1.440759 | -1.355627 |
| 7  | 6                | 0              | 1.457490                | -2.734156 | -1.162579 |
| 8  | 8                | 0              | .701723                 | -1.212781 | 1.005017  |
| 9  | 8                | 0              | 2.058289                | 2.729481  | -.709249  |
| 10   | 7                | 0              | -1.659786               | -.144638  | .392170   |
| 11   | 6                | 0              | -2.953493               | .113445   | .040538   |
| 12   | 8                | 0              | -3.242137               | .849341   | -.902785  |
| 13   | 6                | 0              | -4.016551               | -.564031  | .886898   |
| 14   | 8                | 0              | 2.641874                | -.249656  | 2.002727  |
| 15   | 1                | 0              | -4.649202               | -1.171744 | .233800   |
| 16   | 1                | 0              | -4.651832               | .205923   | 1.333825  |
| 17   | 1                | 0              | -3.606594               | -1.195368 | 1.679916  |
| 18   | 1                | 0              | -1.417838               | -.764206  | 1.158510  |
| 19   | 1                | 0              | -.818161                | .509269   | -1.379074 |
| 20   | 1                | 0              | -.015897                | 1.766656  | 1.283662  |
| 21   | 1                | 0              | -.590193                | 2.615428  | -.173076  |
| 22   | 1                | 0              | 2.524352                | .255173   | -1.063022 |
| 23   | 1                | 0              | 1.712678                | -.845488  | 1.706423  |
| 24   | 1                | 0              | -.108727                | -1.555535 | -1.801936 |
| 25   | 1                | 0              | 1.428554                | -3.275975 | -2.111467 |
| 26   | 1                | 0              | 2.510462                | -2.582130 | -.902230  |
| 27   | 1                | 0              | 1.000994                | -3.343487 | -.373819  |
| 28   | 1                | 0              | 2.504470                | .237753   | .752453   |
| 29   | 1                | 0              | 3.397071                | -.819318  | 2.195204  |
| Sum of electronic and zero-point Energies=   |                  |                | -740.750873             |           |           |
| Sum of electronic and thermal Energies=      |                  |                | -740.735539             |           |           |
| Sum of electronic and thermal Enthalpies=    |                  |                | -740.734594             |           |           |
| Sum of electronic and thermal Free Energies= |                  |                | -740.794749             |           |           |

W= -1097.4924

Table T3: Cartesian coordinates and energy of B3LYP/6-31+G\*\* optimized conformation for compound (TS2-H<sub>2</sub>O)

Standard orientation:

| Center<br>Number                             | Atomic<br>Number | Atomic<br>Type | Coordinates (Angstroms) |           |           |
|--|------------------|----------------|-------------------------|-----------|-----------|
|  |                  |                | X                       | Y         | Z         |
| 1  | 6                | 0              | 1.569581                | -1.448360 | .172184   |
| 2  | 6                | 0              | .706205                 | -1.126374 | 1.383195  |
| 3  | 6                | 0              | -.236322                | .013349   | .956562   |
| 4  | 6                | 0              | .596551                 | .815546   | -.105595  |
| 5  | 7                | 0              | 1.286420                | -.329599  | -.862474  |
| 6  | 7                | 0              | -1.472179               | -.527771  | .416825   |
| 7  | 6                | 0              | -2.541442               | .271728   | .180171   |
| 8  | 6                | 0              | -3.790449               | -.413564  | -.327932  |
| 9  | 7                | 0              | 1.535670                | 1.673463  | .556091   |
| 10   | 6                | 0              | 2.434496                | 2.479668  | -.270117  |
| 11   | 8                | 0              | -.140634                | 1.510499  | -1.046699 |
| 12   | 8                | 0              | 2.578872                | -2.100656 | .097542   |
| 13   | 8                | 0              | -.074461                | -2.287125 | -.964407  |
| 14   | 8                | 0              | -2.509603               | 1.497604  | .388722   |
| 15   | 1                | 0              | -.478501                | .696592   | 1.773205  |
| 16   | 1                | 0              | -1.356886               | -1.428962 | -.079059  |
| 17   | 1                | 0              | -4.546319               | -.390386  | .464008   |
| 18   | 1                | 0              | -3.614078               | -1.451427 | -.619489  |
| 19   | 1                | 0              | -4.185207               | .149229   | -1.177241 |
| 20   | 1                | 0              | 2.017901                | 1.219760  | 1.324068  |
| 21   | 1                | 0              | 1.841697                | 3.071175  | -.969204  |
| 22   | 1                | 0              | 3.175350                | 1.896564  | -.843959  |
| 23   | 1                | 0              | 2.982892                | 3.163699  | .381648   |
| 24   | 1                | 0              | 1.374765                | -.809191  | 2.193163  |
| 25   | 1                | 0              | .174356                 | -2.015531 | 1.720704  |
| 26   | 1                | 0              | 2.129773                | -.058765  | -1.368408 |
| 27   | 1                | 0              | -.949730                | 1.847450  | -.600073  |
| 28   | 1                | 0              | .112132                 | -3.187986 | -1.256448 |
| 29   | 1                | 0              | .607363                 | -.929393  | -1.448080 |
| Sum of electronic and zero-point Energies=   |                  |                | -740.723216             |           |           |
| Sum of electronic and thermal Energies=      |                  |                | -740.708424             |           |           |
| Sum of electronic and thermal Enthalpies=    |                  |                | -740.707480             |           |           |
| Sum of electronic and thermal Free Energies= |                  |                | -740.764109             |           |           |

W= -408.8202

Table T1: Cartesian coordinates and energy of B3LYP/6-31+G\*\* optimized conformation for compound (TS3-H<sub>2</sub>O)

Standard orientation:

| Center<br>Number | Atomic<br>Number | Atomic<br>Type | Coordinates (Angstroms) |           |           |
|------------------|------------------|----------------|-------------------------|-----------|-----------|
|                  |                  |                | X                       | Y         | Z         |
| 1                | 6                | 0              | .033039                 | -.321350  | .901092   |
| 2                | 6                | 0              | -.239134                | 1.156493  | 1.254205  |
| 3                | 6                | 0              | -1.020691               | 1.676663  | .069797   |
| 4                | 7                | 0              | -1.555201               | .658376   | -.577069  |
| 5                | 6                | 0              | -1.142146               | -.691701  | -.092237  |
| 6                | 8                | 0              | -1.589004               | 2.882230  | -.004809  |
| 7                | 7                | 0              | -2.178696               | -1.373577 | .644432   |
| 8                | 6                | 0              | -3.431526               | -1.643813 | -.061993  |
| 9                | 8                | 0              | -.792868                | -1.414766 | -1.221703 |
| 10               | 7                | 0              | 1.365766                | -.475047  | .337770   |
| 11               | 6                | 0              | 1.889376                | -1.686670 | .038152   |
| 12               | 8                | 0              | 1.208016                | -2.726764 | .046724   |
| 13               | 6                | 0              | 3.360961                | -1.712771 | -.316652  |
| 14               | 8                | 0              | .610747                 | 2.662703  | -.895937  |
| 15               | 8                | 0              | 2.771730                | 2.013696  | .296257   |
| 16               | 1                | 0              | -.058046                | -.983158  | 1.768063  |
| 17               | 1                | 0              | 1.975445                | .348076   | .295341   |
| 18               | 1                | 0              | 3.882882                | -2.331889 | .419609   |
| 19               | 1                | 0              | 3.812073                | -.718421  | -.337896  |
| 20               | 1                | 0              | 3.479718                | -2.193753 | -1.291391 |
| 21               | 1                | 0              | -2.346349               | -.934240  | 1.544848  |
| 22               | 1                | 0              | -3.213437               | -2.211830 | -.968212  |
| 23               | 1                | 0              | -3.998080               | -.739435  | -.338858  |
| 24               | 1                | 0              | -4.067158               | -2.258811 | .579935   |
| 25               | 1                | 0              | -.898481                | 1.232275  | 2.128970  |
| 26               | 1                | 0              | .657823                 | 1.739835  | 1.459185  |
| 27               | 1                | 0              | -.254611                | -2.175043 | -.902380  |
| 28               | 1                | 0              | -2.174277               | .788879   | -1.367527 |
| 29               | 1                | 0              | .613963                 | 2.475241  | -1.844850 |
| 30               | 1                | 0              | -.792306                | 3.409228  | -.322416  |
| 31               | 1                | 0              | 2.007849                | 2.399137  | -.257592  |
| 32               | 1                | 0              | 3.581670                | 2.487745  | .080796   |

Sum of electronic and zero-point Energies= -817.156318  
Sum of electronic and thermal Energies= -817.138872  
Sum of electronic and thermal Enthalpies= -817.137927  
Sum of electronic and thermal Free Energies= -817.200673

W= -382.2281

Table T1: Cartesian coordinates and energy of B3LYP/6-31+G\*\* optimized conformation for compound (TS4-H<sub>2</sub>O)

Standard orientation:

| Center<br>Number                             | Atomic<br>Number | Atomic<br>Type | Coordinates (Angstroms) |           |           |
|--|------------------|----------------|-------------------------|-----------|-----------|
|  |                  |                | X                       | Y         | Z         |
| 1  | 6                | 0              | -.376473                | .187364   | .990270   |
| 2  | 6                | 0              | .704725                 | -.794444  | 1.484980  |
| 3  | 6                | 0              | 1.700375                | -1.057896 | .314715   |
| 4  | 7                | 0              | 1.078699                | -.196806  | -.830917  |
| 5  | 6                | 0              | .327826                 | .959576   | -.170816  |
| 6  | 8                | 0              | 1.822613                | -2.339384 | -.114481  |
| 7  | 8                | 0              | 2.965005                | -.541492  | .627609   |
| 8  | 7                | 0              | 1.186625                | 1.980739  | .357688   |
| 9  | 6                | 0              | 1.964985                | 2.765271  | -.602393  |
| 10   | 8                | 0              | -.511974                | 1.472484  | -1.149858 |
| 11   | 7                | 0              | -1.567578               | -.520024  | .537842   |
| 12   | 6                | 0              | -2.724696               | .160825   | .314684   |
| 13   | 8                | 0              | -2.818276               | 1.384602  | .496904   |
| 14   | 6                | 0              | -3.907034               | -.667439  | -.140163  |
| 15   | 8                | 0              | -.321299                | -2.246016 | -1.283473 |
| 16   | 1                | 0              | -.679481                | .908842   | 1.750528  |
| 17   | 1                | 0              | -1.410304               | -1.390873 | .010823   |
| 18   | 1                | 0              | -4.638040               | -.705408  | .674128   |
| 19   | 1                | 0              | -3.629591               | -1.688005 | -.414151  |
| 20   | 1                | 0              | -4.384021               | -.171292  | -.988923  |
| 21   | 1                | 0              | 1.781244                | 1.625637  | 1.099688  |
| 22   | 1                | 0              | 1.290030                | 3.214852  | -1.331969 |
| 23   | 1                | 0              | 2.735184                | 2.187125  | -1.140768 |
| 24   | 1                | 0              | 2.471447                | 3.567960  | -.061029  |
| 25   | 1                | 0              | 1.259756                | -.377921  | 2.328172  |
| 26   | 1                | 0              | .270133                 | -1.742467 | 1.805899  |
| 27   | 1                | 0              | -1.301308               | 1.834986  | -.697750  |
| 28   | 1                | 0              | 1.797296                | .113817   | -1.484960 |
| 29   | 1                | 0              | .375134                 | -.923462  | -1.313153 |
| 30   | 1                | 0              | 3.605804                | -1.175686 | .269988   |
| 31   | 1                | 0              | -.574735                | -2.722576 | -2.081345 |
| 32   | 1                | 0              | .920434                 | -2.563986 | -.638757  |
| Sum of electronic and zero-point Energies=   |                  |                | -817.166356             |           |           |
| Sum of electronic and thermal Energies=      |                  |                | -817.150436             |           |           |
| Sum of electronic and thermal Enthalpies=    |                  |                | -817.149491             |           |           |
| Sum of electronic and thermal Free Energies= |                  |                | -817.208383             |           |           |

W= -296.6738

Table T1: Cartesian coordinates and energy of B3LYP/6-31+G\*\* optimized conformation for compound (TS5-H<sub>2</sub>O)

| Standard orientation:                        |                  |                |                         |           |           |  |
|--|------------------|----------------|-------------------------|-----------|-----------|--|
| Center<br>Number                             | Atomic<br>Number | Atomic<br>Type | Coordinates (Angstroms) |           |           |  |
|  |                  |                | X                       | Y         | Z         |  |
| 1  | 6                | 0              | -2.086580               | 3.076049  | -.713536  |  |
| 2  | 6                | 0              | -1.376506               | 2.026816  | .118205   |  |
| 3  | 8                | 0              | -1.090267               | 2.218408  | 1.302619  |  |
| 4  | 7                | 0              | -1.075384               | .858108   | -.520923  |  |
| 5  | 6                | 0              | -.343865                | -.215851  | .131732   |  |
| 6  | 6                | 0              | -.835809                | -1.566680 | -.423183  |  |
| 7  | 6                | 0              | -2.296445               | -1.807323 | -.115827  |  |
| 8  | 8                | 0              | -2.502690               | -2.024792 | 1.210402  |  |
| 9  | 6                | 0              | 1.206670                | -.074381  | -.042940  |  |
| 10   | 7                | 0              | 1.852240                | -1.061388 | 1.173521  |  |
| 11   | 7                | 0              | 1.616365                | 1.249988  | .218934   |  |
| 12   | 6                | 0              | 3.001309                | 1.654035  | .003939   |  |
| 13   | 8                | 0              | 1.662232                | -.599893  | -1.189311 |  |
| 14   | 8                | 0              | -3.199683               | -1.813533 | -.923751  |  |
| 15   | 8                | 0              | 3.705619                | -1.556783 | -.380744  |  |
| 16   | 1                | 0              | -.581806                | -.129704  | 1.195645  |  |
| 17   | 1                | 0              | -1.191325               | .808904   | -1.523919 |  |
| 18   | 1                | 0              | -2.423971               | 2.705824  | -1.685278 |  |
| 19   | 1                | 0              | -1.405020               | 3.918062  | -.870080  |  |
| 20   | 1                | 0              | -2.945826               | 3.446263  | -.149175  |  |
| 21   | 1                | 0              | 1.132535                | 1.700845  | .988406   |  |
| 22   | 1                | 0              | 3.311200                | 1.363222  | -1.001456 |  |
| 23   | 1                | 0              | 3.716462                | 1.214088  | .715134   |  |
| 24   | 1                | 0              | 3.057613                | 2.742867  | .082802   |  |
| 25   | 1                | 0              | -.693007                | -1.598825 | -1.503976 |  |
| 26   | 1                | 0              | -.252787                | -2.388038 | .003813   |  |
| 27   | 1                | 0              | -3.458486               | -2.148740 | 1.339221  |  |
| 28   | 1                | 0              | 2.007710                | -.515946  | 2.019304  |  |
| 29   | 1                | 0              | 1.254198                | -1.852973 | 1.405947  |  |
| 30   | 1                | 0              | 2.694512                | -1.068313 | -1.010609 |  |
| 31   | 1                | 0              | 3.982588                | -2.432079 | -.675959  |  |
| 32   | 1                | 0              | 2.828537                | -1.435658 | .665389   |  |
| Sum of electronic and zero-point Energies=   |                  |                | -817.175114             |           |           |  |
| Sum of electronic and thermal Energies=      |                  |                | -817.157225             |           |           |  |
| Sum of electronic and thermal Enthalpies=    |                  |                | -817.156280             |           |           |  |
| Sum of electronic and thermal Free Energies= |                  |                | -817.222245             |           |           |  |

W= -1032.6757

Table T1: Cartesian coordinates and energy of B3LYP/6-31+G\*\* optimized conformation for compound (TS6-H<sub>2</sub>O)

Standard orientation:

| Center<br>Number | Atomic<br>Number | Atomic<br>Type | Coordinates (Angstroms) |           |           |
|------------------|------------------|----------------|-------------------------|-----------|-----------|
|                  |                  |                | X                       | Y         | Z         |
| 1                | 7                | 0              | -2.328666               | .271927   | -.219662  |
| 2                | 6                | 0              | -.921749                | .489383   | .050603   |
| 3                | 6                | 0              | -.345970                | -.947944  | -.195584  |
| 4                | 6                | 0              | -1.470081               | -1.845037 | .347888   |
| 5                | 6                | 0              | -2.729224               | -1.020181 | .120877   |
| 6                | 7                | 0              | .975845                 | -1.168048 | .334317   |
| 7                | 6                | 0              | 2.034591                | -1.422575 | -.503474  |
| 8                | 6                | 0              | 3.375216                | -1.571046 | .188444   |
| 9                | 7                | 0              | -.329927                | 1.450104  | -.995584  |
| 10               | 6                | 0              | -.982832                | 2.786551  | -1.052433 |
| 11               | 8                | 0              | -.745631                | 1.024510  | 1.291500  |
| 12               | 8                | 0              | -3.886425               | -1.378237 | .219719   |
| 13               | 8                | 0              | 1.900292                | -1.562545 | -1.719967 |
| 14               | 8                | 0              | 1.668145                | 1.097201  | 1.918263  |
| 15               | 1                | 0              | -.264828                | -1.110582 | -1.274570 |
| 16               | 1                | 0              | 1.197632                | -.799215  | 1.257401  |
| 17               | 1                | 0              | 3.522694                | -2.624288 | .452544   |
| 18               | 1                | 0              | 3.438107                | -.971225  | 1.100480  |
| 19               | 1                | 0              | 4.166733                | -1.286374 | -.507058  |
| 20               | 1                | 0              | -.375964                | 1.000858  | -1.912060 |
| 21               | 1                | 0              | -1.010561               | 3.191911  | -.041228  |
| 22               | 1                | 0              | -1.992312               | 2.703172  | -1.459710 |
| 23               | 1                | 0              | -.379464                | 3.437805  | -1.686404 |
| 24               | 1                | 0              | -1.530479               | -2.818855 | -.141790  |
| 25               | 1                | 0              | -1.365082               | -2.008875 | 1.426413  |
| 26               | 1                | 0              | -2.988953               | 1.011500  | -.004756  |
| 27               | 1                | 0              | .266634                 | 1.078450  | 1.615932  |
| 28               | 1                | 0              | 1.902328                | 1.609426  | 2.701313  |
| 29               | 1                | 0              | .762527                 | 1.635770  | -.747984  |
| 30               | 1                | 0              | 2.010324                | 1.652319  | .809477   |
| 31               | 8                | 0              | 2.042813                | 2.052963  | -.263536  |
| 32               | 1                | 0              | 2.826639                | 1.734280  | -.727259  |

Sum of electronic and zero-point Energies= -817.202771  
Sum of electronic and thermal Energies= -817.185898  
Sum of electronic and thermal Enthalpies= -817.184954  
Sum of electronic and thermal Free Energies= -817.247538

W= -596.9971



Table T1: Cartesian coordinates and energy of B3LYP/6-31+G\*\* optimized conformation for compound (TS7-H<sub>2</sub>O)

Standard orientation:

| Center<br>Number                             | Atomic<br>Number | Atomic<br>Type | Coordinates (Angstroms) |           |           |
|--|------------------|----------------|-------------------------|-----------|-----------|
|  |                  |                | X                       | Y         | Z         |
| 1  | 6                | 0              | .129897                 | 3.381388  | .188865   |
| 2  | 6                | 0              | .087234                 | 2.033577  | -.498143  |
| 3  | 8                | 0              | -.183693                | 1.906256  | -1.699429 |
| 4  | 7                | 0              | .384745                 | .961827   | .296792   |
| 5  | 6                | 0              | .391175                 | -.400866  | -.218398  |
| 6  | 6                | 0              | 1.488242                | -1.212753 | .495386   |
| 7  | 6                | 0              | 2.880583                | -.700335  | .203727   |
| 8  | 8                | 0              | 3.159542                | -.719961  | -1.127456 |
| 9  | 6                | 0              | -.985888                | -1.145780 | -.068145  |
| 10   | 7                | 0              | -1.083994               | -2.249787 | -.979906  |
| 11   | 7                | 0              | -2.082884               | -.068195  | -.443256  |
| 12   | 6                | 0              | -3.412867               | -.633172  | -.767787  |
| 13   | 8                | 0              | -1.274781               | -1.550563 | 1.202093  |
| 14   | 8                | 0              | 3.686554                | -.329220  | 1.028682  |
| 15   | 8                | 0              | -1.820397               | .692373   | 1.992978  |
| 16   | 1                | 0              | .616487                 | -.317996  | -1.285576 |
| 17   | 1                | 0              | .195110                 | 1.071630  | 1.291463  |
| 18   | 1                | 0              | 1.167020                | 3.730959  | .238978   |
| 19   | 1                | 0              | -.261487                | 3.322360  | 1.208661  |
| 20   | 1                | 0              | -.451662                | 4.097250  | -.393194  |
| 21   | 1                | 0              | -1.735014               | .525573   | -1.205646 |
| 22   | 1                | 0              | -3.750107               | -1.230277 | .080242   |
| 23   | 1                | 0              | -3.343428               | -1.262044 | -1.654578 |
| 24   | 1                | 0              | -4.108808               | .191892   | -.934054  |
| 25   | 1                | 0              | 1.334366                | -1.193077 | 1.574866  |
| 26   | 1                | 0              | 1.435649                | -2.258185 | .172112   |
| 27   | 1                | 0              | 4.063194                | -.378585  | -1.237243 |
| 28   | 1                | 0              | -.304652                | -2.343070 | -1.619898 |
| 29   | 1                | 0              | -1.246892               | -3.111092 | -.471177  |
| 30   | 1                | 0              | -1.519228               | -.647959  | 1.763365  |
| 31   | 1                | 0              | -2.474069               | .868692   | 2.678854  |
| 32   | 1                | 0              | -2.149588               | .503582   | .489438   |
| Sum of electronic and zero-point Energies=   |                  |                | -817.186258             |           |           |
| Sum of electronic and thermal Energies=      |                  |                | -817.168717             |           |           |
| Sum of electronic and thermal Enthalpies=    |                  |                | -817.167773             |           |           |
| Sum of electronic and thermal Free Energies= |                  |                | -817.232656             |           |           |

W= -263.6103

Table T1: Cartesian coordinates and energy of B3LYP/6-31+G\*\* optimized conformation for compound (**Asp-TS1**)

Standard orientation:

| Center<br>Number | Atomic<br>Number | Atomic<br>Type | Coordinates (Angstroms) |           |           |
|------------------|------------------|----------------|-------------------------|-----------|-----------|
|                  |                  |                | X                       | Y         | Z         |
| 1                | 6                | 0              | 3.642053                | -1.406679 | .411683   |
| 2                | 6                | 0              | 2.406717                | -.756044  | -.172030  |
| 3                | 7                | 0              | 1.215891                | -1.050255 | .425266   |
| 4                | 6                | 0              | -.064881                | -.611158  | -.136033  |
| 5                | 6                | 0              | -.327552                | .850612   | .253416   |
| 6                | 8                | 0              | -.889443                | 1.214705  | 1.407409  |
| 7                | 8                | 0              | 2.469176                | .001335   | -1.147540 |
| 8                | 6                | 0              | -1.217308               | -1.531587 | .245985   |
| 9                | 6                | 0              | -2.544833               | -.894745  | -.247439  |
| 10               | 8                | 0              | -2.460326               | .397765   | -.319948  |
| 11               | 8                | 0              | -3.514614               | -1.607829 | -.484935  |
| 12               | 7                | 0              | .353765                 | 1.765146  | -.394371  |
| 13               | 6                | 0              | .318183                 | 3.200730  | -.125843  |
| 14               | 1                | 0              | 4.082944                | -2.057671 | -.349117  |
| 15               | 1                | 0              | 3.441572                | -1.995383 | 1.310535  |
| 16               | 1                | 0              | 4.375216                | -.629987  | .643956   |
| 17               | 1                | 0              | 1.198286                | -1.665422 | 1.226513  |
| 18               | 1                | 0              | .045456                 | -.616547  | -1.224655 |
| 19               | 1                | 0              | -1.277074               | -1.658050 | 1.336158  |
| 20               | 1                | 0              | -1.081401               | -2.522053 | -.194507  |
| 21               | 1                | 0              | -1.822778               | .898764   | 1.298727  |
| 22               | 1                | 0              | 1.011957                | 1.411320  | -1.092045 |
| 23               | 1                | 0              | .269574                 | 3.733509  | -1.077867 |
| 24               | 1                | 0              | -.561240                | 3.432920  | .471806   |
| 25               | 1                | 0              | 1.217284                | 3.509792  | .415900   |

Sum of electronic and zero-point Energies= -684.226243  
Sum of electronic and thermal Energies= -684.212667  
Sum of electronic and thermal Enthalpies= -684.211723  
Sum of electronic and thermal Free Energies= -684.267485

W= -192.6100

Table T1: Cartesian coordinates and energy of B3LYP/6-31+G\*\* optimized conformation for compound (**Asp-TS1-H<sub>2</sub>O**)

Standard orientation:

| Center<br>Number | Atomic<br>Number | Atomic<br>Type | Coordinates (Angstroms) |           |           |
|------------------|------------------|----------------|-------------------------|-----------|-----------|
|                  |                  |                | X                       | Y         | Z         |
| 1                | 6                | 0              | -.579883                | -1.820401 | .221722   |
| 2                | 6                | 0              | .404448                 | -.717517  | -.151505  |
| 3                | 6                | 0              | -.159776                | .672450   | .156684   |
| 4                | 8                | 0              | -2.109097               | -.320092  | -.813348  |
| 5                | 6                | 0              | -1.960398               | -1.555928 | -.426327  |
| 6                | 7                | 0              | 1.705796                | -.875127  | .499030   |
| 7                | 6                | 0              | 2.846191                | -.370629  | -.056902  |
| 8                | 6                | 0              | 4.145355                | -.684410  | .655728   |
| 9                | 7                | 0              | .240856                 | 1.659523  | -.621174  |
| 10               | 6                | 0              | -.089660                | 3.067161  | -.439610  |
| 11               | 8                | 0              | -.769688                | .914130   | 1.280935  |
| 12               | 8                | 0              | -2.784025               | -2.462203 | -.492435  |
| 13               | 8                | 0              | 2.816494                | .301080   | -1.092817 |
| 14               | 8                | 0              | -3.160447               | 1.156089  | .870656   |
| 15               | 1                | 0              | 4.660233                | .253385   | .880715   |
| 16               | 1                | 0              | 4.784830                | -1.255834 | -.023332  |
| 17               | 1                | 0              | 4.010064                | -1.252230 | 1.580029  |
| 18               | 1                | 0              | 1.753333                | -1.397263 | 1.362437  |
| 19               | 1                | 0              | .585335                 | -.751674  | -1.229021 |
| 20               | 1                | 0              | -.729340                | -1.857364 | 1.308277  |
| 21               | 1                | 0              | -.197732                | -2.794586 | -.094948  |
| 22               | 1                | 0              | -1.820723               | 1.156480  | 1.186109  |
| 23               | 1                | 0              | .880033                 | 1.401247  | -1.368928 |
| 24               | 1                | 0              | .765532                 | 3.672056  | -.746931  |
| 25               | 1                | 0              | -.958313                | 3.341840  | -1.046979 |
| 26               | 1                | 0              | -.307300                | 3.254944  | .612711   |
| 27               | 1                | 0              | -3.018192               | .525546   | .066601   |
| 28               | 1                | 0              | -3.617889               | 1.956294  | .585597   |

Sum of electronic and zero-point Energies= -760.659789  
Sum of electronic and thermal Energies= -760.643983  
Sum of electronic and thermal Enthalpies= -760.643039  
Sum of electronic and thermal Free Energies= -760.703828

W= -160.2097

Table T1: Cartesian coordinates and energy of B3LYP/6-31+G\*\* optimized conformation for compound (**Asp-TS2-H<sub>2</sub>O**)

Standard orientation:

| Center<br>Number | Atomic<br>Number | Atomic<br>Type | Coordinates (Angstroms) |           |           |
|------------------|------------------|----------------|-------------------------|-----------|-----------|
|                  |                  |                | X                       | Y         | Z         |
| 1                | 6                | 0              | 2.214797                | 2.639328  | -.261940  |
| 2                | 7                | 0              | 1.307017                | 1.832424  | .564507   |
| 3                | 6                | 0              | .538930                 | .838024   | -.117584  |
| 4                | 8                | 0              | -.261970                | 1.403322  | -1.101057 |
| 5                | 8                | 0              | 1.393663                | -.108355  | -.830310  |
| 6                | 6                | 0              | -.254984                | -.033648  | .927735   |
| 7                | 7                | 0              | -1.459202               | -.635063  | .377053   |
| 8                | 6                | 0              | -2.593014               | .097936   | .188446   |
| 9                | 6                | 0              | -3.774392               | -.636502  | -.410163  |
| 10               | 6                | 0              | .732484                 | -1.115601 | 1.375850  |
| 11               | 6                | 0              | 1.645447                | -1.463195 | .221779   |
| 12               | 8                | 0              | .415715                 | -2.146401 | -1.045910 |
| 13               | 8                | 0              | 2.708305                | -1.986076 | .171626   |
| 14               | 8                | 0              | -2.657837               | 1.292485  | .500562   |
| 15               | 1                | 0              | -.557520                | .616101   | 1.751304  |
| 16               | 1                | 0              | -1.339551               | -1.504958 | -.133220  |
| 17               | 1                | 0              | -4.615340               | -.567994  | .285857   |
| 18               | 1                | 0              | -3.568326               | -1.688526 | -.622436  |
| 19               | 1                | 0              | -4.070336               | -.131479  | -1.333931 |
| 20               | 1                | 0              | 1.794055                | 1.443390  | 1.365879  |
| 21               | 1                | 0              | 1.635144                | 3.136681  | -1.041160 |
| 22               | 1                | 0              | 3.009893                | 2.050800  | -.738062  |
| 23               | 1                | 0              | 2.665365                | 3.405948  | .373462   |
| 24               | 1                | 0              | 1.379248                | -.756075  | 2.183047  |
| 25               | 1                | 0              | .235312                 | -2.021793 | 1.728993  |
| 26               | 1                | 0              | -1.017120               | 1.827993  | -.651606  |
| 27               | 1                | 0              | .890140                 | -2.840861 | -1.526190 |
| 28               | 1                | 0              | .785707                 | -.948600  | -1.336876 |

Sum of electronic and zero-point Energies= -760.595124  
Sum of electronic and thermal Energies= -760.580160  
Sum of electronic and thermal Enthalpies= -760.579216  
Sum of electronic and thermal Free Energies= -760.636559

W= -1140.5117