## Supporting information for:

# Nucleophilic Aromatic Substitution Reactions Described by the Local Electron Attachment Energy

*Joakim H. Stenlid and Tore Brinck**

Applied Physical Chemistry, School of Chemical Science and Engineering, KTH Royal Institute of Technology, SE-100 44 Stockholm, Sweden

*E-mail: tore@kth.se

**Summary of Content:**

Additional $E_{S,min}$ values for serie **1**, energies, xyz-coordinates and number of imaginary frequencies (NumIM) for the compounds and transition-states of series **1-6**. The energies and coordinates are sorted into gas-phase or condensed phase (piperidine), as well as into ground state (GS) or transition state (TS) and according to the corrections employed – i.e. electronic energy ($E_{el}$) or Gibbs free energies ($G$). If not otherwise reported the energies obtained at the B3LYP/6-31G(d) level in gas phase and given in Hartrees (a.u.) without any thermal corrections.

# Table of Contents

# Additional Descriptor values ($E_{S,min}$ - Series 1)

Included here are additional $E_{S,min}$ values for the H-substituted ortho and para positions with respect to the $NO_2$ group of the series **1** compounds are includes in Table S1. These positions will not participate in the $S_NAr$ reaction studied in the main text, but may be active in e.g. the VNS reaction. See also Figure S1 for depiction of the sites.

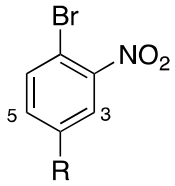


**Figure S1.** Generic figure of the series **1** compounds including site identification used in Table S1.

**Table S1.** Gas phase $E_{S,min}$ values (in eV) calculated at the 0.004 a.u. isosurface for the position 3 (ortho with respect to the $NO_2$ group) and 5 (para) of the series **1** compounds.

| | **Ortho** (Position 3) | **Para** (Position 5) |
|---|---|---|
| **Br** | -1.18 | -1.06 |
| **Cl** | -1.20 | -1.07 |
| **COOH** | -1.19 | -1.09 |
| **EtO** | -0.85 | -0.64 |
| **F** | -1.01 | -0.92 |
| **H** | -0.95 | -0.84 |
| **I** | -1.33 | -1.2 |
| **Me** | -0.83 | -0.79 |
| **$NH_2$** | -0.59 | -0.52 |
| **$NMe_2$** | -0.61 | -0.53 |
| **$NO_2$** | -1.73 | -1.6 |
| **OH** | -0.66 | -0.56 |
| **OMe** | -0.86 | -0.65 |
| **tBu** | -0.88 | -0.69 |

# Energies of the optimized structures

The energies of the various structures are reported here.

## *Series 1*

**Table S2.** SCF energies ($E_{el}$) in a.u. and number of imaginary vibrational frequencies (NumIM) at the B3LYP/6-31G(d) level of theory for the optimized structures of the series **1** compounds. Included are energies of the structures in gas phase and in piperidine solvent represented by a polarizable continuum model [implicit], and by explicit piperidine solvent molecules in combination with the polarizable continuum model solvation [explicit].

| | $E_{el}$ **(gas phase)** | $E_{el}$ **(piperidine)** [implicit] | $E_{el}$ **(piperidine)** [explicit] | **NumIM** |
|---|---|---|---|---|
| **Br** | -5578.9434560 | -5578.94892373 | (-) | 0 |
| **Cl** | -3467.4345235 | -3467.4399933 | (-) | 0 |
| **COOH** | -3196.4128609 | -3196.42122573 | -3448.35204321 | 0 |
| **EtO** | -3161.6840150 | -3161.69100861 | (-) | 0 |
| **F** | -3107.0723833 | -3107.07788846 | (-) | 0 |
| **H** | -3007.8422759 | -896.338185968 | (-) | 0 |
| **I** | -3018.30523351 | -3018.31091671 | (-) | 0 |
| **Me** | -3047.1611310 | -3047.16717398 | (-) | 0 |
| **$NH_2$** | -3063.1968840 | -3063.20639891 | -3315.12371034 | 0 |
| **$NMe_2$** | -3141.8118648 | -3141.81949974 | (-) | 0 |
| **$NO_2$** | -3212.3370687 | -3212.34500804 | (-) | 0 |
| **OH** | -3083.0571534 | -3083.0662433 | -3334.99436052 | 0 |
| **OMe** | -3122.3644271 | -3122.37163317 | (-) | 0 |
| **tBu** | -3165.0987077 | -3165.10452223 | (-) | 0 |

**Table S3.** Energies used in the transition state calculations for the compounds of series **1** reported in a.u. Electronic energies $E_{el}$ corresponds to SCF energies obtained at the level of theory of the optimizations [i.e. M06-2X/6-31+G(d,p)]. The Gibbs free energies are given at 298.15 K and were obtained at the M06-2X/6-311+G(3df,2p)//M06-2X/6-31+G(d,p) level of theory. Note that no concentrations corrections have been added to the Gibbs free energies in this table. The electronic core states of the iodine atoms were represented by effective core potentials as specified in the main article. Energies are reported in implicit (PCM) and explicit piperidine solvation.

| R= | $E_{el}$ (implicit) | $\Delta G$ (implicit) | $E_{el}^{\dagger}$ (implicit) | $\Delta G^{\dagger}$ (implicit) | $E_{el}$ (explicit) | $\Delta G$ (explicit) | $E_{el}^{\dagger}$ (explicit) | $\Delta G^{\dagger}$ (explicit) | NumIM GS (TS) |
|---|---|---|---|---|---|---|---|---|---|
| **Br** | -5578.98210616 | -5583.81502358 | -5830.78253721 | -5835.51413541 | (-) | (-) | (-) | (-) | 0 (1) |
| **Cl** | -3467.34586225 | -3469.84470275 | -3719.14466837 | -3721.54319257 | (-) | (-) | (-) | (-) | 0 (1) |
| **COOH** | -3196.29868236 | -3198.80723819 | -3448.10792707 | -3702.24828667 | -3448.13341789 | -3450.548827 | -3699.93043086 | -3702.24828667 | 0 (1) |
| **EtO** | -3161.56072759 | -3164.00728688 | -3413.35558346 | -3415.69809088 | (-) | (-) | (-) | (-) | 0 (1) |
| **F** | -3106.98882682 | -3109.48430261 | -3358.78485646 | -3361.17935338 | (-) | (-) | (-) | (-) | 0 (1) |
| **H** | -3007.77981617 | -3010.23011629 | -3259.57792873 | -3261.92675721 | (-) | (-) | (-) | (-) | 0 (1) |
| **I** | -3018.01510792 | -3020.97472032 | -3269.73401541 | -3272.67309668 | (-) | (-) | (-) | (-) | 0 (1) |
| **Me** | -3047.07868329 | -3049.51525358 | -3298.87699936 | -3301.20973001 | (-) | (-) | (-) | (-) | 0 (1) |
| **$NH_2$** | -3063.12052125 | -3065.57910255 | -3314.91635952 | -3568.99403581 | -3314.94227251 | -3317.30732588 | -3566.72818584 | -3568.99403581 | 0 (1) |
| **$NMe_2$** | -3141.69331628 | -3144.11969044 | -3393.48925223 | -3395.80723689 | (-) | (-) | (-) | (-) | 0 (1) |
| **$NO_2$** | -3212.21099326 | -3214.73358926 | -3464.01909295 | -3466.44249149 | (-) | (-) | (-) | (-) | 0 (1) |
| **OH** | -3082.97913073 | -3085.45978985 | -3334.77591360 | -3588.8843469 | -3334.81082814 | -3337.19815765 | -3586.59630317 | -3588.8843469 | 0 (1) |
| **OMe** | -3122.26214299 | -3124.72329165 | -3374.05556196 | -3376.41287555 | (-) | (-) | (-) | (-) | 0 (1) |
| **tBu** | -3164.96236699 | -3167.35353341 | -3416.76542510 | -3419.04887812 | (-) | (-) | (-) | (-) | 0 (1) |
| **Piperidine** | -251.867739853 | -251.735583853 | (-) | (-) | (-) | (-) | (-) | (-) | 0 (-) |

**Table S4.** SCF energies ($E_{el}$) and Gibbs free energies ($G$) in a.u. for the full $S_NAr$ mechanism of the **H**, **$NH_2$** and **$NO_2$** compound of series **1** with the piperidine nucleophile. $E_{el}$ corresponds to SCF energies obtained at the level of theory of the optimizations [i.e. M06-2X/6-31+G(d,p)]. The Gibbs free energies are given at 298.15 K without concentration corrections and were obtained at the M06-2X/6-311+G(3df,2p)//M06-2X/6-31+G(d,p) Products* indicates the product···HBr super-complex. NumIM = 0 for GS structures and NumIM = 1 for TS structures.

| | | R=H | R=$NH_2$ | R=$NO_2$ | Piperidine | HBr |
|---|---|---|---|---|---|---|
| **Reactants** | $E_{el}$ | -3007.77981617 | -3314.94227251 | -3212.21099326 | -251.867739853 | (-) |
| | $G$ | -3010.23011629 | -3317.30732588 | -3214.73358926 | -251.735583853 | (-) |
| **TS1** | $E_{el}$ | -3259.57792873 | -3566.72818584 | -3464.01909295 | (-) | (-) |
| | $G$ | -3261.92675721 | -3568.99403581 | -3466.44249149 | (-) | (-) |
| **Intermediate** | $E_{el}$ | -3259.6298085 | -3566.79310202 | -3464.05712878 | (-) | (-) |
| | $G$ | -3261.98832495 | -3569.06507534 | -3466.49040399 | (-) | (-) |
| **$TS_{DP}$** | $E_{el}$ | -3259.59948953 | -3566.75907131 | -3464.03807841 | (-) | (-) |
| | $G$ | -3261.96799764 | -3569.04087229 | -3466.47743459 | (-) | (-) |
| **Products*** | $E_{el}$ | -3259.60374408 | -3566.75990080 | -3464.04095907 | (-) | (-) |
| | $G$ | -3261.96578862 | -3569.04082162 | -3466.47676273 | (-) | (-) |
| **Products** | $E_{el}$ | -687.197560643 | -994.351140037 | -891.634180573 | (-) | -2574.77257513 |
| | $G$ | -687.19397189 | -994.266599590 | -891.704346525 | (-) | -2574.78574913 |

## *Series 2*

**Table S5.** SCF energies ($E_{el}$) in a.u. and number of imaginary vibrational frequencies (NumIM) at the B3LYP/6-31G(d) level of theory for the optimized structures of the series **2** compounds.

| | $E_{el}$ | NumIM |
|---|---|---|
| **2a** | -1104.79815214 | 0 |
| **2b** | -1005.57831368 | 0 |
| **2c** | -661.254416700 | 0 |
| **2d** | -744.430047700 | 0 |
| **2e** | -1104.79969674 | 0 |
| **2f** | -661.202890874 | 0 |
| **2g** | -982.239863805 | 0 |
| **2h** | -1220.04943057 | 0 |
| **2i** | -661.261044095 | 0 |
| **2j'** | -545.997399704 | 0 |
| **2k'** | -1465.16924538 | 0 |
| **2l'** | -645.213787642 | 0 |
| **2m'** | -645.198779025 | 0 |
| **2n'** | -1104.79065236 | 0 |
| **2o'** | -1465.16370843 | 0 |
| **2p'** | -1825.52881240 | 0 |
| **2q'** | -1465.15107825 | 0 |
| **2r'** | -578.093241014 | 0 |

## *Series 3*

**Table S6.** SCF energies ($E_{el}$) in a.u. and number of imaginary vibrational frequencies (NumIM) at the B3LYP/6-31G(d) level of theory for the optimized structures of the series **3** compounds.

| | $E_{el}$ | NumIM |
|---|---|---|
| **3a** | -866.9209242 | 0 |
| **3b** | -1303.2142959 | 0 |
| **3c** | -966.1599634 | 0 |
| **3d** | -813.6284252 | 0 |
| **3e** | -1303.2064468 | 0 |
| **3f** | -820.6145849 | 0 |
| **3g** | -813.6244706 | 0 |

## *Series 4*

**Table S7.** SCF energies ($E_{el}$) in a.u. and number of imaginary vibrational frequencies (NumIM) at the B3LYP/6-31G(d) level of theory for the optimized structures of the series **4** compounds.

| | $E_{el}$ | NumIM |
|---|---|---|
| **4a** | -629.1634303 | 0 |
| **4b** | -629.1580881 | 0 |
| **4c** | -629.1640897 | 0 |
| **4d** | -728.3810287 | 0 |
| **4e** | -1187.9666378 | 0 |
| **4f** | -827.5969420 | 0 |
| **4g** | -2629.4249140 | 0 |
| **4h** | -2269.0656304 | 0 |
| **4i** | -1548.3361124 | 0 |
| **4j** | -1908.7054332 | 0 |

## *Series 5*

**Table S8.** SCF energies ($E_{el}$) in a.u. and number of imaginary vibrational frequencies (NumIM) at the B3LYP/6-31G(d) level of theory for the optimized structures of the series **5** compounds.

| | $E_{el}$ | NumIM |
|---|---|---|
| **Br** | -3007.85352929 | 0 |
| **$cC_3O_2H_5$** | -703.903391598 | 0 |
| **$CF_3$** | -773.784743027 | 0 |
| **Cl** | -896.344821083 | 0 |
| **CN** | -528.989055338 | 0 |
| **COOiPr** | -743.265637217 | 0 |
| **F** | -535.983354282 | 0 |
| **H** | -436.750584748 | 0 |
| **I** | -447.517465314 | 0 |
| **iPr** | -554.696264537 | 0 |
| **OMe** | -551.275860223 | 0 |
| **OPh** | -743.016311376 | 0 |
| **SMe** | -874.252725858 | 0 |
| **SPh** | -1065.98395474 | 0 |
| **tBu** | -594.006677747 | 0 |

## *Series 6*

**Table S9.** SCF energies ($E_{el}$) in a.u. and number of imaginary vibrational frequencies (NumIM) at the B3LYP/6-31G(d) level of theory for the optimized structures of the series **6** compounds.

| | $E_{el}$ | NumIM |
|---|---|---|
| **6a** | -452.782669753 | 0 |
| **6b** | -912.367480486 | 0 |
| **6c** | -606.619854708 | 0 |
| **6d** | -567.313762432 | 0 |
| **6e** | -453.981761183 | 0 |
| **6f** | -453.983678193 | 0 |
| **6g** | -470.026296289 | 0 |
| **6h** | -470.027456287 | 0 |
| **6i** | -470.013517830 | 0 |

# Optimized geometries

Below are all the optimized geometries used in the current study presented. All structures were optimized at the B3LYP/6-31G(d) level of theory, expect for the structures used in the calculations of the transition state barriers and the $S_NAr$ mechanism of series 1. The geometries of latter two studies were identified at the M06-2X/6-31+G(d,p) level of theory. Effective core potentials were used to represent the iodine core electrons as specified in the main article.

## *Series 1*

Ground-state structures for descriptor calculations (gas phase):

**Br**

| | | | |
|---|---|---|---|
| C | 0.87995 | 0.84025 | -0.00122 |
| C | -0.50933 | 0.70008 | 0.01282 |
| C | -1.10727 | -0.56682 | 0.01046 |
| C | -0.27800 | -1.69223 | 0.00308 |
| C | 1.10778 | -1.56536 | 0.01496 |
| C | 1.68077 | -0.29348 | 0.01177 |
| H | 1.30649 | 1.83472 | -0.02144 |
| H | -0.73147 | -2.67672 | -0.01488 |
| H | 1.73594 | -2.44913 | 0.01989 |
| N | -1.27785 | 1.96101 | 0.04048 |
| O | -2.34537 | 1.97285 | 0.64307 |
| O | -0.77078 | 2.92828 | -0.52598 |
| Br | -2.97681 | -0.86859 | -0.06317 |
| Br | 3.57452 | -0.10797 | 0.01989 |

**Cl**

| | | | |
|---|---|---|---|
| C | 1.48355 | 0.79577 | 0.00599 |
| C | 0.09194 | 0.68303 | 0.01626 |
| C | -0.53212 | -0.57106 | 0.01286 |
| C | 0.27424 | -1.71315 | 0.00838 |
| C | 1.66203 | -1.61557 | 0.02417 |
| C | 2.26103 | -0.35484 | 0.02175 |
| H | 1.93129 | 1.78118 | -0.01401 |
| H | -0.19963 | -2.68797 | -0.01034 |
| H | 2.27360 | -2.51119 | 0.03132 |
| N | -0.65063 | 1.95946 | 0.04147 |
| O | -1.71859 | 1.99377 | 0.64231 |
| O | -0.12297 | 2.91565 | -0.52510 |
| Br | -2.40716 | -0.83430 | -0.06675 |
| Cl | 4.00520 | -0.21873 | 0.03323 |

**COOH**

| | | | |
|---|---|---|---|
| C | 1.23470 | 0.79122 | 0.00227 |
| C | -0.15458 | 0.67984 | 0.01438 |

| | | | |
|---|---|---|---|
| C | -0.77354 | -0.57863 | 0.01135 |
| C | 0.03094 | -1.72340 | 0.00609 |
| C | 1.41549 | -1.61577 | 0.02057 |
| C | 2.02763 | -0.35592 | 0.01785 |
| H | 1.67978 | 1.77767 | -0.01772 |
| H | -0.44536 | -2.69688 | -0.01257 |
| H | 2.04049 | -2.50243 | 0.02665 |
| N | -0.90481 | 1.95068 | 0.04189 |
| O | -1.95872 | 1.98598 | 0.66785 |
| O | -0.39602 | 2.90318 | -0.54749 |
| Br | -2.64751 | -0.83804 | -0.06604 |
| C | 3.51546 | -0.29399 | 0.02480 |
| O | 4.24045 | -1.26689 | 0.02714 |
| O | 3.98743 | 0.97458 | 0.02855 |
| H | 4.96014 | 0.90355 | 0.02973 |

**EtO**

| | | | |
|---|---|---|---|
| C | 0.95793 | 1.02470 | -0.00140 |
| C | -0.40704 | 0.76431 | 0.01253 |
| C | -0.89595 | -0.55112 | 0.01101 |
| C | 0.03184 | -1.59086 | 0.00044 |
| C | 1.40488 | -1.34643 | 0.01154 |
| C | 1.87927 | -0.02817 | 0.01019 |
| H | 1.30918 | 2.04877 | -0.01918 |
| H | -0.33043 | -2.61273 | -0.01952 |
| H | 2.08684 | -2.18818 | 0.01437 |
| N | -1.28526 | 1.95073 | 0.04560 |
| O | -2.33744 | 1.87208 | 0.67117 |
| O | -0.88295 | 2.95644 | -0.53868 |
| Br | -2.73681 | -1.01357 | -0.06409 |
| C | 4.18773 | -0.69194 | 0.02346 |
| H | 4.07241 | -1.32538 | -0.86712 |
| H | 4.06037 | -1.32562 | 0.91226 |
| O | 3.18700 | 0.33227 | 0.01685 |
| C | 5.54180 | -0.00613 | 0.03273 |
| H | 5.64980 | 0.62275 | 0.92163 |
| H | 6.33992 | -0.75596 | 0.03762 |
| H | 5.66144 | 0.62367 | -0.85400 |

**F**

| | | | |
|---|---|---|---|
| C | 1.85003 | 0.71563 | 0.01532 |
| C | 0.45548 | 0.65420 | 0.02078 |
| C | -0.21424 | -0.57681 | 0.01609 |
| C | 0.54780 | -1.74990 | 0.01422 |
| C | 1.93847 | -1.70593 | 0.03429 |
| C | 2.57071 | -0.46677 | 0.03324 |

| | | | |
|---|---|---|---|
| H | 2.35078 | 1.67523 | -0.00353 |
| H | 0.03535 | -2.70485 | -0.00583 |
| H | 2.53031 | -2.61484 | 0.04317 |
| N | -0.23966 | 1.95700 | 0.04220 |
| O | -1.30908 | 2.03132 | 0.63677 |
| O | 0.32653 | 2.89311 | -0.52095 |
| Br | -2.09944 | -0.77037 | -0.07078 |
| F | 3.91248 | -0.41219 | 0.04642 |

**H**

| | | | |
|---|---|---|---|
| C | 2.26463 | 0.21545 | 0.03074 |
| C | 0.88703 | 0.44880 | 0.02798 |
| C | -0.01813 | -0.62092 | 0.02118 |
| C | 0.48446 | -1.92471 | 0.02620 |
| C | 1.85794 | -2.15660 | 0.05461 |
| C | 2.75328 | -1.08535 | 0.05595 |
| H | 2.92976 | 1.07058 | 0.01578 |
| H | -0.21454 | -2.75310 | 0.00383 |
| H | 2.22474 | -3.17873 | 0.06822 |
| H | 3.82432 | -1.26001 | 0.07273 |
| N | 0.46953 | 1.86300 | 0.04496 |
| O | -0.55948 | 2.15779 | 0.64402 |
| O | 1.20995 | 2.66422 | -0.52598 |
| Br | -1.90372 | -0.42160 | -0.07770 |

**I**

| | | | |
|---|---|---|---|
| C | 0.36832 | 0.84242 | -0.00479 |
| C | -1.02232 | 0.70253 | 0.01103 |
| C | -1.62036 | -0.56466 | 0.00937 |
| C | -0.78874 | -1.68823 | 0.00097 |
| C | 0.59855 | -1.56121 | 0.01087 |
| C | 1.17294 | -0.28906 | 0.00720 |
| H | 0.78224 | 1.84199 | -0.02544 |
| H | -1.24067 | -2.67347 | -0.01642 |
| H | 1.21745 | -2.45171 | 0.01466 |
| N | -1.78803 | 1.96546 | 0.03865 |
| O | -2.86359 | 1.97380 | 0.62584 |
| O | -1.27002 | 2.93620 | -0.51172 |
| Br | -3.48884 | -0.87543 | -0.05973 |
| I | 3.29595 | -0.07105 | 0.01371 |

**Me**

| | | | |
|---|---|---|---|
| C | 1.81825 | 0.70731 | 0.00997 |
| C | 0.42216 | 0.65154 | 0.01886 |
| C | -0.24472 | -0.57853 | 0.01582 |
| C | 0.52438 | -1.74532 | 0.00958 |

| | | | |
|---|---|---|---|
| C | 1.91389 | -1.68273 | 0.02494 |
| C | 2.58934 | -0.45360 | 0.02633 |
| H | 2.28584 | 1.68521 | -0.00920 |
| H | 0.01853 | -2.70411 | -0.01316 |
| H | 2.48220 | -2.60958 | 0.02729 |
| N | -0.27585 | 1.95010 | 0.04133 |
| O | -1.34111 | 2.02623 | 0.64507 |
| O | 0.28043 | 2.88847 | -0.53022 |
| C | 4.09731 | -0.39012 | 0.05517 |
| H | 4.45963 | 0.61317 | -0.18707 |
| H | 4.48503 | -0.65249 | 1.04771 |
| H | 4.53886 | -1.09204 | -0.66102 |
| Br | -2.13078 | -0.77885 | -0.06790 |

**$NH_2$**

| | | | |
|---|---|---|---|
| C | 1.83382 | 0.70502 | 0.02035 |
| C | 0.44146 | 0.64795 | 0.02495 |
| C | -0.23796 | -0.57623 | 0.02187 |
| C | 0.53084 | -1.74355 | 0.01947 |
| C | 1.91841 | -1.69829 | 0.03818 |
| C | 2.59955 | -0.46726 | 0.03790 |
| H | 2.30648 | 1.68047 | 0.00606 |
| H | 0.02308 | -2.70145 | -0.00216 |
| H | 2.48269 | -2.62730 | 0.05115 |
| N | -0.24774 | 1.95272 | 0.04265 |
| O | -1.32000 | 2.03411 | 0.63228 |
| O | 0.32072 | 2.89046 | -0.51904 |
| N | 3.98567 | -0.41208 | 0.10941 |
| H | 4.47847 | -1.23163 | -0.22065 |
| H | 4.41152 | 0.44766 | -0.21192 |
| Br | -2.12544 | -0.77013 | -0.07340 |

**$NMe_2$**

| | | | |
|---|---|---|---|
| C | -1.15951 | 0.81570 | -0.03650 |
| C | 0.22693 | 0.68429 | -0.03231 |
| C | 0.84620 | -0.57060 | -0.02640 |
| C | 0.01458 | -1.69243 | -0.02523 |
| C | -1.36869 | -1.57995 | -0.05213 |
| C | -2.00076 | -0.31393 | -0.06693 |
| H | -1.55709 | 1.81992 | -0.01244 |
| H | 0.46924 | -2.67656 | 0.00410 |
| H | -1.95656 | -2.48956 | -0.05342 |
| N | 0.98130 | 1.95338 | -0.04662 |
| O | 2.06394 | 1.97718 | -0.62301 |
| O | 0.45653 | 2.92363 | 0.50273 |
| N | -3.37507 | -0.18513 | -0.11178 |

| | | | |
|---|---|---|---|
| C | -4.21083 | -1.36745 | 0.01699 |
| H | -4.07458 | -1.88005 | 0.98192 |
| H | -5.25828 | -1.07399 | -0.06757 |
| H | -4.00337 | -2.08747 | -0.78425 |
| C | -3.97817 | 1.12921 | 0.04625 |
| H | -3.64498 | 1.81383 | -0.74331 |
| H | -5.06230 | 1.03559 | -0.03397 |
| H | -3.74203 | 1.58749 | 1.01855 |
| Br | 2.72011 | -0.86464 | 0.08054 |

**$NO_2$**

| | | | |
|---|---|---|---|
| C | 1.24683 | 0.82881 | 0.00346 |
| C | -0.13875 | 0.69289 | 0.01490 |
| C | -0.73838 | -0.57612 | 0.00967 |
| C | 0.08267 | -1.71037 | 0.00370 |
| C | 1.46677 | -1.59006 | 0.01901 |
| C | 2.03007 | -0.31579 | 0.01820 |
| H | 1.69971 | 1.81135 | -0.01613 |
| H | -0.37942 | -2.69040 | -0.01546 |
| H | 2.10909 | -2.46201 | 0.02451 |
| N | -0.90879 | 1.95426 | 0.04145 |
| O | -1.96171 | 1.97083 | 0.66830 |
| O | -0.41285 | 2.91057 | -0.54994 |
| Br | -2.60497 | -0.86219 | -0.06571 |
| N | 3.49645 | -0.17497 | 0.02623 |
| O | 4.16028 | -1.20967 | 0.02581 |
| O | 3.95625 | 0.96409 | 0.03325 |

**OH**

| | | | |
|---|---|---|---|
| C | 1.83635 | 0.73002 | 0.01404 |
| C | 0.44610 | 0.65613 | 0.02021 |
| C | -0.21929 | -0.57780 | 0.01702 |
| C | 0.55527 | -1.73915 | 0.01459 |
| C | 1.94569 | -1.67983 | 0.03426 |
| C | 2.59503 | -0.44037 | 0.03297 |
| H | 2.32329 | 1.69688 | -0.00466 |
| H | 0.05584 | -2.70119 | -0.00581 |
| H | 2.52241 | -2.60206 | 0.04327 |
| N | -0.26163 | 1.95202 | 0.04395 |
| O | -1.31598 | 2.02141 | 0.66648 |
| O | 0.27697 | 2.88886 | -0.54453 |
| O | 3.94909 | -0.30456 | 0.04666 |
| H | 4.36366 | -1.18145 | 0.05364 |
| Br | -2.10484 | -0.78331 | -0.07261 |

**OMe**

| | | | |
|---|---|---|---|
| C | 1.35075 | 1.04215 | 0.00564 |
| C | -0.01184 | 0.76989 | 0.01543 |
| C | -0.48933 | -0.54989 | 0.01192 |
| C | 0.44714 | -1.58183 | 0.00366 |
| C | 1.81810 | -1.32547 | 0.01899 |
| C | 2.27974 | -0.00341 | 0.01958 |
| H | 1.69370 | 2.06908 | -0.01113 |
| H | 0.09369 | -2.60675 | -0.01773 |
| H | 2.50763 | -2.16128 | 0.02351 |
| N | -0.90032 | 1.94895 | 0.04558 |
| O | -1.95431 | 1.86078 | 0.66665 |
| O | -0.50387 | 2.95804 | -0.53662 |
| O | 3.58533 | 0.36879 | 0.03022 |
| C | 4.57891 | -0.64875 | 0.03733 |
| H | 4.51444 | -1.27841 | -0.85920 |
| H | 5.53666 | -0.12679 | 0.04426 |
| H | 4.50141 | -1.27854 | 0.93286 |
| Br | -2.32581 | -1.02792 | -0.06826 |

**tBu**

| | | | |
|---|---|---|---|
| C | 0.90519 | 0.79163 | -0.00120 |
| C | -0.48388 | 0.67853 | 0.01199 |
| C | -1.10062 | -0.57975 | 0.01315 |
| C | -0.27965 | -1.70557 | 0.00882 |
| C | 1.10956 | -1.58367 | 0.02102 |
| C | 1.73941 | -0.33179 | 0.01446 |
| H | 1.31597 | 1.79367 | -0.02225 |
| H | -0.73908 | -2.68762 | -0.00794 |
| H | 1.69818 | -2.49389 | 0.02836 |
| N | -1.23501 | 1.94767 | 0.04050 |
| O | -2.30545 | 1.97493 | 0.63933 |
| O | -0.71642 | 2.91372 | -0.52083 |
| Br | -2.97622 | -0.86179 | -0.06443 |
| C | 3.26689 | -0.15166 | 0.01807 |
| C | 3.68432 | 0.65985 | 1.26757 |
| H | 4.77183 | 0.79720 | 1.28208 |
| H | 3.22446 | 1.65359 | 1.28236 |
| H | 3.39490 | 0.14213 | 2.18906 |
| C | 4.00802 | -1.50170 | 0.04681 |
| H | 3.77858 | -2.11393 | -0.83291 |
| H | 5.08926 | -1.32661 | 0.05060 |
| H | 3.76662 | -2.08307 | 0.94417 |
| C | 3.69410 | 0.61193 | -1.25806 |
| H | 4.78109 | 0.75434 | -1.26647 |
| H | 3.41716 | 0.05588 | -2.16080 |
| H | 3.22879 | 1.60135 | -1.31825 |

Ground-state structures for descriptor calculations (piperidine solvent - implicit):

**Br**

| | | | |
|---|---|---|---|
| C | 0.88170 | 0.84133 | -0.00021 |
| C | -0.50769 | 0.69948 | 0.01426 |
| C | -1.10533 | -0.56817 | 0.01216 |
| C | -0.27792 | -1.69364 | 0.00336 |
| C | 1.10856 | -1.56596 | 0.01413 |
| C | 1.68026 | -0.29381 | 0.01143 |
| H | 1.31123 | 1.83446 | -0.01270 |
| H | -0.72774 | -2.67949 | -0.01529 |
| H | 1.73388 | -2.45138 | 0.01829 |
| N | -1.27631 | 1.95455 | 0.04150 |
| O | -2.33678 | 1.97625 | 0.65980 |
| O | -0.78681 | 2.92203 | -0.54240 |
| Br | -2.97746 | -0.86782 | -0.06423 |
| Br | 3.57540 | -0.10609 | 0.01992 |

**Cl**

| | | | |
|---|---|---|---|
| C | 1.48521 | 0.79803 | 0.00718 |
| C | 0.09350 | 0.68321 | 0.01754 |
| C | -0.52985 | -0.57188 | 0.01398 |
| C | 0.27491 | -1.71376 | 0.00705 |
| C | 1.66341 | -1.61513 | 0.02190 |
| C | 2.26037 | -0.35396 | 0.02110 |
| H | 1.93594 | 1.78198 | -0.00400 |
| H | -0.19492 | -2.69014 | -0.01306 |
| H | 2.27242 | -2.51205 | 0.02758 |
| N | -0.64962 | 1.95391 | 0.04201 |
| O | -1.71277 | 1.99669 | 0.65443 |
| O | -0.13749 | 2.91159 | -0.53863 |
| Br | -2.40733 | -0.83461 | -0.06695 |
| Cl | 4.00631 | -0.21593 | 0.03409 |

**COOH**

| | | | |
|---|---|---|---|
| C | 1.23708 | 0.79073 | 0.00299 |
| C | -0.15232 | 0.67925 | 0.01509 |
| C | -0.77275 | -0.57933 | 0.01244 |
| C | 0.02951 | -1.72403 | 0.00607 |
| C | 1.41485 | -1.61587 | 0.01956 |
| C | 2.02878 | -0.35724 | 0.01731 |
| H | 1.68450 | 1.77588 | -0.00953 |
| H | -0.44360 | -2.69871 | -0.01301 |
| H | 2.03383 | -2.50626 | 0.02513 |

| | | | |
|---|---|---|---|
| N | -0.90072 | 1.94590 | 0.04252 |
| O | -1.95237 | 1.98998 | 0.67507 |
| O | -0.40298 | 2.90089 | -0.55484 |
| Br | -2.64887 | -0.83717 | -0.06642 |
| C | 3.51746 | -0.29144 | 0.02484 |
| O | 4.24199 | -1.26760 | 0.02843 |
| O | 3.98415 | 0.97366 | 0.02699 |
| H | 4.95886 | 0.92103 | 0.02952 |

**EtO**

| | | | |
|---|---|---|---|
| C | 0.95852 | 1.02955 | -0.00003 |
| C | -0.40659 | 0.76574 | 0.01507 |
| C | -0.89333 | -0.55086 | 0.01487 |
| C | 0.03507 | -1.58957 | 0.00345 |
| C | 1.40752 | -1.34228 | 0.01308 |
| C | 1.88165 | -0.02293 | 0.01064 |
| H | 1.31017 | 2.05354 | -0.00996 |
| H | -0.32194 | -2.61311 | -0.01653 |
| H | 2.08996 | -2.18307 | 0.01582 |
| N | -1.28601 | 1.94487 | 0.04700 |
| O | -2.33487 | 1.87418 | 0.68328 |
| O | -0.90122 | 2.95126 | -0.55066 |
| Br | -2.73675 | -1.01590 | -0.06615 |
| C | 4.19147 | -0.69213 | 0.02366 |
| H | 4.07192 | -1.32403 | -0.86576 |
| H | 4.06183 | -1.32071 | 0.91405 |
| O | 3.18626 | 0.33692 | 0.01623 |
| C | 5.54454 | -0.00621 | 0.02987 |
| H | 5.65673 | 0.62268 | 0.91844 |
| H | 6.33895 | -0.75950 | 0.03537 |
| H | 5.66628 | 0.61973 | -0.85951 |

**F**

| | | | |
|---|---|---|---|
| C | 1.85190 | 0.71852 | 0.01611 |
| C | 0.45707 | 0.65512 | 0.02205 |
| C | -0.21165 | -0.57708 | 0.01773 |
| C | 0.54923 | -1.74985 | 0.01414 |
| C | 1.94033 | -1.70456 | 0.03308 |
| C | 2.57082 | -0.46486 | 0.03276 |
| H | 2.35622 | 1.67617 | 0.00603 |
| H | 0.04066 | -2.70655 | -0.00662 |
| H | 2.53011 | -2.61446 | 0.04128 |
| N | -0.23921 | 1.95181 | 0.04286 |
| O | -1.30562 | 2.03329 | 0.64596 |
| O | 0.31259 | 2.89158 | -0.53100 |
| Br | -2.09925 | -0.77162 | -0.07126 |

| | | | |
|---|---|---|---|
| F | 3.91326 | -0.40818 | 0.04651 |

**H**

| | | | |
|---|---|---|---|
| C | -0.83689 | -1.60644 | 0.05239 |
| C | 0.08035 | -0.55219 | 0.02144 |
| C | -0.36289 | 0.77958 | -0.01166 |
| C | -1.73628 | 1.03192 | -0.00482 |
| C | -2.64862 | -0.02062 | 0.05138 |
| C | -2.20132 | -1.34299 | 0.07937 |
| H | -0.45806 | -2.62115 | 0.06605 |
| H | -2.08072 | 2.05912 | -0.04822 |
| H | -3.71165 | 0.19872 | 0.06602 |
| H | -2.90845 | -2.16473 | 0.11941 |
| N | 1.50105 | -0.92389 | 0.03720 |
| O | 2.29477 | -0.18800 | 0.61885 |
| O | 1.80981 | -1.98108 | -0.51657 |
| Cl | 0.70875 | 2.15367 | -0.14180 |

**I**

| | | | |
|---|---|---|---|
| C | 0.36991 | 0.84330 | -0.00376 |
| C | -1.02088 | 0.70171 | 0.01252 |
| C | -1.61886 | -0.56606 | 0.01136 |
| C | -0.78915 | -1.68974 | 0.00136 |
| C | 0.59890 | -1.56185 | 0.01014 |
| C | 1.17260 | -0.28958 | 0.00691 |
| H | 0.78663 | 1.84156 | -0.01685 |
| H | -1.23731 | -2.67636 | -0.01687 |
| H | 1.21482 | -2.45401 | 0.01302 |
| N | -1.78647 | 1.95894 | 0.03979 |
| O | -2.85481 | 1.97725 | 0.64359 |
| O | -1.28585 | 2.92974 | -0.52895 |
| Br | -3.49003 | -0.87435 | -0.06098 |
| I | 3.29702 | -0.06989 | 0.01374 |

**Me**

| | | | |
|---|---|---|---|
| C | 1.82085 | 0.71123 | 0.00950 |
| C | 0.42404 | 0.65309 | 0.01961 |
| C | -0.24185 | -0.57868 | 0.01804 |
| C | 0.52646 | -1.74452 | 0.01003 |
| C | 1.91670 | -1.67962 | 0.02356 |
| C | 2.59203 | -0.45006 | 0.02503 |
| H | 2.29182 | 1.68736 | -0.00178 |
| H | 0.02470 | -2.70523 | -0.01307 |
| H | 2.48511 | -2.60575 | 0.02524 |
| N | -0.27578 | 1.94457 | 0.04217 |
| O | -1.33796 | 2.02720 | 0.65529 |

| | | | |
|---|---|---|---|
| O | 0.26428 | 2.88758 | -0.54016 |
| C | 4.09933 | -0.38727 | 0.05541 |
| H | 4.46223 | 0.61638 | -0.18293 |
| H | 4.48185 | -0.65402 | 1.04849 |
| H | 4.53859 | -1.09016 | -0.66058 |
| Br | -2.13113 | -0.78068 | -0.06853 |

**$NH_2$**

| | | | |
|---|---|---|---|
| C | 1.83601 | 0.71211 | 0.01854 |
| C | 0.44342 | 0.64981 | 0.02530 |
| C | -0.23372 | -0.57669 | 0.02457 |
| C | 0.53641 | -1.74233 | 0.01876 |
| C | 1.92398 | -1.69337 | 0.03528 |
| C | 2.60569 | -0.46037 | 0.03630 |
| H | 2.31135 | 1.68611 | 0.01109 |
| H | 0.03396 | -2.70287 | -0.00478 |
| H | 2.48886 | -2.62130 | 0.04342 |
| N | -0.25130 | 1.94543 | 0.04396 |
| O | -1.31435 | 2.03222 | 0.65471 |
| O | 0.29137 | 2.88678 | -0.53908 |
| N | 3.98652 | -0.40365 | 0.11241 |
| H | 4.48354 | -1.22653 | -0.20475 |
| H | 4.41704 | 0.45293 | -0.21286 |
| Br | -2.12480 | -0.77337 | -0.07441 |

**$NMe_2$**

| | | | |
|---|---|---|---|
| C | 1.16169 | 0.82120 | 0.01403 |
| C | -0.22436 | 0.68440 | 0.02289 |
| C | -0.84208 | -0.57227 | 0.02365 |
| C | -0.01000 | -1.69349 | 0.01572 |
| C | 1.37304 | -1.57819 | 0.03036 |
| C | 2.00630 | -0.30977 | 0.03303 |
| H | 1.56304 | 1.82413 | 0.00080 |
| H | -0.46029 | -2.67973 | -0.00729 |
| H | 1.96222 | -2.48666 | 0.03250 |
| N | -0.98326 | 1.94412 | 0.04858 |
| O | -2.04486 | 1.97585 | 0.66781 |
| O | -0.49520 | 2.91420 | -0.53600 |
| N | 3.37286 | -0.18138 | 0.05372 |
| C | 4.21480 | -1.36903 | 0.02067 |
| H | 4.06565 | -1.95440 | -0.89744 |
| H | 5.26058 | -1.06431 | 0.06251 |
| H | 4.01952 | -2.02290 | 0.88024 |
| C | 3.98100 | 1.14001 | -0.01453 |
| H | 3.67906 | 1.76532 | 0.83579 |
| H | 5.06563 | 1.03468 | 0.01556 |

| | | | |
|---|---|---|---|
| H | 3.71394 | 1.66795 | -0.94062 |
| Br | -2.72110 | -0.86516 | -0.07508 |

**$NO_2$**

| | | | |
|---|---|---|---|
| C | 1.24787 | 0.82887 | 0.00485 |
| C | -0.13725 | 0.69251 | 0.01619 |
| C | -0.73799 | -0.57685 | 0.01092 |
| C | 0.08105 | -1.71144 | 0.00442 |
| C | 1.46532 | -1.59148 | 0.01902 |
| C | 2.02933 | -0.31722 | 0.01820 |
| H | 1.70078 | 1.81088 | -0.00789 |
| H | -0.37793 | -2.69249 | -0.01490 |
| H | 2.10104 | -2.46772 | 0.02432 |
| N | -0.90483 | 1.95041 | 0.04254 |
| O | -1.95787 | 1.97523 | 0.67162 |
| O | -0.41639 | 2.90998 | -0.55257 |
| Br | -2.60541 | -0.86152 | -0.06651 |
| N | 3.49142 | -0.17568 | 0.02571 |
| O | 4.16313 | -1.20647 | 0.02876 |
| O | 3.95732 | 0.96288 | 0.02806 |

**OH**

| | | | |
|---|---|---|---|
| C | 1.83868 | 0.73088 | 0.01450 |
| C | 0.44756 | 0.65704 | 0.02153 |
| C | -0.21744 | -0.57743 | 0.01961 |
| C | 0.55646 | -1.73885 | 0.01520 |
| C | 1.94692 | -1.68042 | 0.03303 |
| C | 2.59766 | -0.44034 | 0.03203 |
| H | 2.32772 | 1.69672 | 0.00478 |
| H | 0.06002 | -2.70223 | -0.00565 |
| H | 2.52173 | -2.60280 | 0.04115 |
| N | -0.25917 | 1.94753 | 0.04436 |
| O | -1.31456 | 2.02492 | 0.66853 |
| O | 0.26963 | 2.88923 | -0.54845 |
| O | 3.94850 | -0.30275 | 0.04571 |
| H | 4.37090 | -1.17729 | 0.05533 |
| Br | -2.10611 | -0.78410 | -0.07279 |

**OMe**

| | | | |
|---|---|---|---|
| C | 1.35170 | 1.04651 | 0.00604 |
| C | -0.01113 | 0.77121 | 0.01735 |
| C | -0.48679 | -0.54950 | 0.01524 |
| C | 0.45007 | -1.58067 | 0.00551 |
| C | 1.82041 | -1.32187 | 0.01882 |
| C | 2.28223 | 0.00117 | 0.01867 |
| H | 1.69509 | 2.07331 | -0.00276 |

| | | | |
|---|---|---|---|
| H | 0.10146 | -2.60706 | -0.01596 |
| H | 2.51023 | -2.15681 | 0.02252 |
| N | -0.90033 | 1.94327 | 0.04683 |
| O | -1.95113 | 1.86316 | 0.67856 |
| O | -0.52074 | 2.95309 | -0.54822 |
| O | 3.58486 | 0.37224 | 0.02832 |
| C | 4.58318 | -0.64953 | 0.03738 |
| H | 4.51668 | -1.27700 | -0.85893 |
| H | 5.53918 | -0.12560 | 0.04487 |
| H | 4.50164 | -1.27551 | 0.93353 |
| Br | -2.32583 | -1.02989 | -0.06956 |

**tBu**

| | | | |
|---|---|---|---|
| C | 0.90739 | 0.79482 | -0.00325 |
| C | -0.48208 | 0.67878 | 0.01189 |
| C | -1.09773 | -0.58089 | 0.01460 |
| C | -0.27784 | -1.70598 | 0.00826 |
| C | 1.11204 | -1.58131 | 0.01905 |
| C | 1.74151 | -0.32906 | 0.01229 |
| H | 1.32085 | 1.79580 | -0.01761 |
| H | -0.73296 | -2.68980 | -0.00930 |
| H | 1.70025 | -2.49135 | 0.02596 |
| N | -1.23520 | 1.94036 | 0.04181 |
| O | -2.29587 | 1.97606 | 0.66196 |
| O | -0.73945 | 2.90731 | -0.54069 |
| Br | -2.97692 | -0.86206 | -0.06561 |
| C | 3.26888 | -0.14964 | 0.01837 |
| C | 3.68373 | 0.65780 | 1.27155 |
| H | 4.77123 | 0.79383 | 1.28609 |
| H | 3.22440 | 1.65186 | 1.28924 |
| H | 3.39380 | 0.13537 | 2.19021 |
| C | 4.00833 | -1.50061 | 0.04366 |
| H | 3.77837 | -2.10997 | -0.83776 |
| H | 5.08927 | -1.32435 | 0.04827 |
| H | 3.76586 | -2.08365 | 0.93950 |
| C | 3.69741 | 0.61824 | -1.25486 |
| H | 4.78456 | 0.75796 | -1.25988 |
| H | 3.42115 | 0.06487 | -2.15948 |
| H | 3.23459 | 1.60919 | -1.31113 |

<u>Ground-state for descriptor calculations (piperidine solvent – explicit):</u>

**COOH**

| | | | |
|---|---|---|---|
| C | 0.72022 | 0.43278 | -0.27753 |
| C | 2.09715 | 0.60039 | -0.13329 |
| C | 2.94161 | -0.50788 | 0.03175 |

| | | | |
|---|---|---|---|
| C | 2.37801 | -1.78618 | 0.03906 |
| C | 1.00793 | -1.95423 | -0.13170 |
| C | 0.16724 | -0.84663 | -0.28977 |
| H | 0.08948 | 1.30498 | -0.38879 |
| H | 3.02286 | -2.64534 | 0.18353 |
| H | 0.57323 | -2.94778 | -0.13617 |
| N | 2.58892 | 1.98518 | -0.17942 |
| O | 3.68043 | 2.20253 | -0.70022 |
| O | 1.85325 | 2.85639 | 0.28699 |
| Br | 4.81161 | -0.38156 | 0.33448 |
| C | -1.30846 | -1.06707 | -0.46141 |
| O | -1.79133 | -2.19425 | -0.47646 |
| O | -1.99834 | 0.05275 | -0.58679 |
| H | -3.03066 | -0.16264 | -0.70651 |
| C | -5.03725 | -1.20755 | 0.30510 |
| C | -4.97357 | -0.31876 | 1.54975 |
| C | -5.77048 | 0.97862 | 1.34328 |
| C | -5.31445 | 1.69802 | 0.06424 |
| C | -5.36886 | 0.75762 | -1.14282 |
| H | -5.35617 | -0.87740 | 2.41197 |
| H | -6.07010 | -1.55694 | 0.14641 |
| H | -4.39217 | -2.08393 | 0.41373 |
| H | -6.84058 | 0.73841 | 1.26233 |
| H | -5.65934 | 1.63846 | 2.21182 |
| H | -5.94198 | 2.57488 | -0.13399 |
| H | -4.28520 | 2.05987 | 0.18985 |
| H | -6.41476 | 0.48137 | -1.35324 |
| H | -4.96676 | 1.24379 | -2.03766 |
| H | -3.92356 | -0.07742 | 1.76202 |
| N | -4.56014 | -0.45416 | -0.87870 |
| H | -4.59846 | -1.06716 | -1.69315 |

**$NH_2$**

| | | | |
|---|---|---|---|
| C | 0.70134 | 1.47574 | -0.35659 |
| C | 1.94683 | 0.90434 | -0.10227 |
| C | 2.15661 | -0.47658 | -0.21353 |
| C | 1.06880 | -1.26616 | -0.59576 |
| C | -0.16983 | -0.70722 | -0.87704 |
| C | -0.38834 | 0.68409 | -0.76161 |
| H | 0.59234 | 2.54841 | -0.24599 |
| H | 1.20149 | -2.34000 | -0.66870 |
| H | -0.98653 | -1.35113 | -1.18926 |
| N | 3.01313 | 1.84346 | 0.27406 |
| O | 4.16311 | 1.60238 | -0.08844 |
| O | 2.68732 | 2.84423 | 0.91727 |
| N | -1.60367 | 1.23965 | -1.07986 |

| | | | |
|---|---|---|---|
| H | -2.43609 | 0.63230 | -1.04645 |
| H | -1.76770 | 2.18167 | -0.74839 |
| Br | 3.78233 | -1.36944 | 0.22308 |
| C | -4.10559 | -1.58763 | -0.04040 |
| C | -4.06173 | -1.01749 | 1.38039 |
| C | -5.23581 | -0.05485 | 1.61717 |
| C | -5.29145 | 1.01914 | 0.51947 |
| C | -5.28563 | 0.37863 | -0.87218 |
| H | -4.08241 | -1.83945 | 2.10611 |
| H | -5.00402 | -2.22242 | -0.15024 |
| H | -3.23271 | -2.22243 | -0.22960 |
| H | -6.17611 | -0.62530 | 1.61148 |
| H | -5.15652 | 0.41169 | 2.60654 |
| H | -6.18724 | 1.64184 | 0.63174 |
| H | -4.42181 | 1.68401 | 0.60966 |
| H | -6.22217 | -0.19185 | -1.01265 |
| H | -5.25036 | 1.14648 | -1.65297 |
| H | -3.11150 | -0.48488 | 1.51940 |
| N | -4.10241 | -0.48862 | -1.02318 |
| H | -4.10418 | -0.88504 | -1.96225 |

**OH**

| | | | |
|---|---|---|---|
| C | -0.55120 | 1.28495 | -0.18922 |
| C | -1.86610 | 0.85289 | -0.03673 |
| C | -2.19455 | -0.51027 | -0.06266 |
| C | -1.15805 | -1.42647 | -0.24559 |
| C | 0.16325 | -1.00996 | -0.37516 |
| C | 0.48956 | 0.35862 | -0.34818 |
| H | -0.32944 | 2.34467 | -0.17266 |
| H | -1.39416 | -2.48399 | -0.29002 |
| H | 0.94462 | -1.75184 | -0.50494 |
| N | -2.86713 | 1.91039 | 0.16772 |
| O | -3.81491 | 1.68253 | 0.91692 |
| O | -2.68199 | 2.98390 | -0.40896 |
| O | 1.73764 | 0.83099 | -0.46785 |
| H | 2.43926 | 0.09142 | -0.56273 |
| Br | -3.96913 | -1.19592 | 0.03503 |
| C | 4.87769 | -0.14271 | -1.30687 |
| C | 5.24621 | 1.03601 | -0.40108 |
| C | 5.60812 | 0.55170 | 1.01161 |
| C | 4.49296 | -0.33642 | 1.58474 |
| C | 4.15658 | -1.47835 | 0.62131 |
| H | 6.08221 | 1.58605 | -0.84902 |
| H | 5.76318 | -0.78050 | -1.46586 |
| H | 4.54073 | 0.20863 | -2.28763 |
| H | 6.54388 | -0.02427 | 0.96941 |

| | | | |
|---|---|---|---|
| H | 5.79273 | 1.40680 | 1.67249 |
| H | 4.78824 | -0.75507 | 2.55401 |
| H | 3.58979 | 0.26509 | 1.75092 |
| H | 5.02443 | -2.15202 | 0.52529 |
| H | 3.31655 | -2.07244 | 0.99697 |
| H | 4.39469 | 1.72653 | -0.34996 |
| N | 3.77667 | -0.92670 | -0.69932 |
| H | 3.54316 | -1.69719 | -1.32517 |

TS structures in piperidine solvent (M06-2X):

**Br**

| | | | |
|---|---|---|---|
| C | -0.43309 | -0.67066 | -0.44425 |
| C | 0.23737 | -0.07644 | -1.56243 |
| C | 1.53410 | 0.36152 | -1.47991 |
| C | 2.28639 | 0.16542 | -0.30299 |
| C | 1.72693 | -0.48566 | 0.76500 |
| C | 0.39100 | -0.91552 | 0.69007 |
| H | -0.30230 | 0.00864 | -2.49874 |
| H | 1.99660 | 0.82262 | -2.34670 |
| H | 2.28048 | -0.67961 | 1.67609 |
| N | -0.16487 | -1.52101 | 1.86232 |
| O | 0.59128 | -1.93898 | 2.73447 |
| O | -1.39212 | -1.56377 | 1.96410 |
| H | -1.63434 | 3.44701 | 2.03173 |
| C | -2.17571 | 2.69439 | 1.45035 |
| C | -1.18583 | 1.63348 | 0.97142 |
| H | -2.90216 | 2.22427 | 2.12567 |
| C | -3.55671 | 2.25262 | -0.59659 |
| N | -1.82990 | 0.61862 | 0.12736 |
| H | -0.71603 | 1.12834 | 1.81872 |
| H | -0.39238 | 2.09045 | 0.36324 |
| C | -2.52459 | 1.20834 | -1.02490 |
| H | -4.35792 | 1.75640 | -0.03393 |
| H | -4.01145 | 2.68640 | -1.49271 |
| H | -2.45762 | 0.03399 | 0.68305 |
| H | -2.98586 | 0.39964 | -1.59713 |
| H | -1.75640 | 1.68083 | -1.65111 |
| Br | -1.70929 | -2.05860 | -0.99343 |
| C | -2.90414 | 3.33229 | 0.26724 |
| H | -3.65573 | 4.04394 | 0.62145 |
| H | -2.18531 | 3.89830 | -0.34054 |
| Br | 4.08289 | 0.73857 | -0.24296 |

**Cl**

| | | | |
|---|---|---|---|
| C | 0.15288 | -0.57486 | -0.44862 |
| C | 0.62887 | 0.10998 | -1.61496 |
| C | 1.80024 | 0.82243 | -1.61111 |
| C | 2.62799 | 0.83687 | -0.46825 |
| C | 2.26583 | 0.12706 | 0.64643 |
| C | 1.05451 | -0.58813 | 0.65248 |
| H | 0.04334 | 0.04175 | -2.52464 |
| H | 2.11435 | 1.34277 | -2.51038 |
| H | 2.88458 | 0.10420 | 1.53567 |
| N | 0.69293 | -1.24959 | 1.86872 |
| O | 1.55459 | -1.44354 | 2.72210 |
| O | -0.48676 | -1.57027 | 2.02470 |
| H | -1.91140 | 3.25044 | 1.95450 |
| C | -2.27435 | 2.36952 | 1.41612 |
| C | -1.07236 | 1.55062 | 0.94234 |
| H | -2.85320 | 1.76961 | 2.13010 |
| C | -3.56401 | 1.53383 | -0.56627 |
| N | -1.48022 | 0.38531 | 0.14616 |
| H | -0.48151 | 1.19661 | 1.79086 |
| H | -0.41826 | 2.15587 | 0.29938 |
| C | -2.32218 | 0.75541 | -0.99930 |
| H | -4.20469 | 0.88269 | 0.04214 |
| H | -4.13632 | 1.81180 | -1.45668 |
| H | -1.93896 | -0.31139 | 0.73595 |
| H | -2.58752 | -0.15725 | -1.53801 |
| H | -1.70618 | 1.38111 | -1.65800 |
| Br | -0.79860 | -2.23072 | -0.90716 |
| C | -3.16325 | 2.77028 | 0.23833 |
| H | -4.05142 | 3.29923 | 0.59650 |
| H | -2.61460 | 3.46434 | -0.41236 |
| Cl | 4.11625 | 1.74856 | -0.49625 |

**COOH**

| | | | |
|---|---|---|---|
| C | -0.12168 | -0.68951 | -0.50820 |
| C | 0.44868 | -0.04445 | -1.64998 |
| C | 1.70361 | 0.50435 | -1.60377 |
| C | 2.52300 | 0.37438 | -0.45754 |
| C | 2.04063 | -0.33727 | 0.62753 |
| C | 0.75804 | -0.88151 | 0.59632 |
| H | -0.13732 | -0.00287 | -2.56092 |
| H | 2.10192 | 1.01553 | -2.47490 |
| H | 2.64039 | -0.47846 | 1.51964 |
| N | 0.28794 | -1.52862 | 1.79588 |
| O | 1.11006 | -1.94461 | 2.60282 |

| | | | |
|---|---|---|---|
| O | -0.92607 | -1.60226 | 1.97119 |
| H | -1.37622 | 3.39706 | 2.10026 |
| C | -1.91999 | 2.63409 | 1.53463 |
| C | -0.92359 | 1.60508 | 1.00041 |
| H | -2.60308 | 2.13641 | 2.23517 |
| C | -3.37846 | 2.17080 | -0.45365 |
| N | -1.57207 | 0.58294 | 0.17302 |
| H | -0.40499 | 1.10495 | 1.82209 |
| H | -0.16902 | 2.09264 | 0.36634 |
| C | -2.33698 | 1.15978 | -0.93789 |
| H | -4.13804 | 1.64729 | 0.14126 |
| H | -3.88656 | 2.60069 | -1.32268 |
| H | -2.15256 | -0.03160 | 0.74574 |
| H | -2.80163 | 0.34244 | -1.49586 |
| H | -1.61482 | 1.66005 | -1.59713 |
| Br | -1.38048 | -2.10011 | -0.97034 |
| C | -2.71709 | 3.26072 | 0.39055 |
| H | -3.47051 | 3.94995 | 0.78330 |
| H | -2.04076 | 3.84995 | -0.24333 |
| C | 3.85832 | 0.99597 | -0.45597 |
| O | 4.32340 | 1.63314 | -1.38086 |
| O | 4.53687 | 0.79958 | 0.68935 |
| H | 5.39798 | 1.23829 | 0.60592 |

**EtO**

| | | | |
|---|---|---|---|
| C | -0.34411 | -0.68716 | -0.45485 |
| C | 0.37025 | -0.21341 | -1.60587 |
| C | 1.72579 | -0.01127 | -1.57989 |
| C | 2.49590 | -0.33856 | -0.43775 |
| C | 1.86801 | -0.86960 | 0.65816 |
| C | 0.47042 | -1.06268 | 0.65131 |
| H | -0.18915 | -0.03864 | -2.51798 |
| H | 2.23300 | 0.35315 | -2.46941 |
| H | 2.43110 | -1.14866 | 1.54131 |
| N | -0.13207 | -1.54877 | 1.84741 |
| O | 0.57642 | -2.05984 | 2.71351 |
| O | -1.35142 | -1.40643 | 1.98657 |
| H | -0.88226 | 3.58390 | 1.98173 |
| C | -1.53735 | 2.89380 | 1.44105 |
| C | -0.70453 | 1.71572 | 0.93390 |
| H | -2.27703 | 2.52001 | 2.16078 |
| C | -3.06465 | 2.59562 | -0.52859 |
| N | -1.51006 | 0.77930 | 0.13881 |
| H | -0.25762 | 1.16445 | 1.76517 |

| | | | |
|---|---|---|---|
| H | 0.10774 | 2.06290 | 0.27993 |
| C | -2.17944 | 1.43864 | -0.99068 |
| H | -3.88774 | 2.19870 | 0.07953 |
| H | -3.51192 | 3.07161 | -1.40681 |
| H | -2.18033 | 0.28867 | 0.73396 |
| H | -2.75447 | 0.68512 | -1.53330 |
| H | -1.39078 | 1.81750 | -1.65338 |
| Br | -1.83561 | -1.88003 | -0.95828 |
| C | -2.25004 | 3.60068 | 0.28647 |
| H | -2.89630 | 4.39588 | 0.66968 |
| H | -1.50530 | 4.07612 | -0.36586 |
| O | 3.86286 | -0.18193 | -0.46042 |
| C | 4.29271 | 1.15624 | -0.18829 |
| H | 3.83772 | 1.83952 | -0.91848 |
| H | 3.94421 | 1.44387 | 0.81292 |
| C | 5.80267 | 1.19101 | -0.27637 |
| H | 6.13456 | 0.90631 | -1.27806 |
| H | 6.16711 | 2.19881 | -0.06139 |
| H | 6.24215 | 0.49976 | 0.44713 |

**F**

| | | | |
|---|---|---|---|
| C | 0.49911 | -0.34864 | -0.45486 |
| C | 0.68410 | 0.32314 | -1.71097 |
| C | 1.55918 | 1.36921 | -1.85193 |
| C | 2.36563 | 1.76071 | -0.76836 |
| C | 2.30725 | 1.11142 | 0.42841 |
| C | 1.39020 | 0.04979 | 0.58159 |
| H | 0.12015 | -0.02871 | -2.56726 |
| H | 1.66906 | 1.86930 | -2.80884 |
| H | 2.93764 | 1.39421 | 1.26263 |
| N | 1.30649 | -0.55614 | 1.87001 |
| O | 2.20394 | -0.35544 | 2.68610 |
| O | 0.30982 | -1.23640 | 2.12993 |
| H | -2.64227 | 2.77478 | 1.74542 |
| C | -2.70046 | 1.77218 | 1.31082 |
| C | -1.31356 | 1.37151 | 0.80790 |
| H | -2.99703 | 1.08744 | 2.11589 |
| C | -3.70931 | 0.34645 | -0.49079 |
| N | -1.32842 | 0.05895 | 0.14800 |
| H | -0.59512 | 1.33356 | 1.63030 |
| H | -0.94506 | 2.09201 | 0.06473 |
| C | -2.29532 | -0.00013 | -0.95692 |
| H | -4.05442 | -0.42054 | 0.21457 |
| H | -4.38222 | 0.31977 | -1.35346 |

| | | | |
|---|---|---|---|
| H | -1.49925 | -0.68231 | 0.83007 |
| H | -2.25092 | -0.99891 | -1.39752 |
| H | -1.96416 | 0.72649 | -1.70991 |
| Br | 0.15580 | -2.27536 | -0.70401 |
| C | -3.72985 | 1.71968 | 0.18123 |
| H | -4.72900 | 1.94113 | 0.56797 |
| H | -3.49388 | 2.49132 | -0.56383 |
| F | 3.23059 | 2.78903 | -0.94460 |

**H**

| | | | |
|---|---|---|---|
| C | 0.67112 | 0.17863 | 0.52249 |
| C | 0.54763 | -0.01072 | 1.93750 |
| C | 1.02089 | -1.14298 | 2.55383 |
| C | 1.72141 | -2.14364 | 1.84128 |
| C | 1.94352 | -1.94983 | 0.49904 |
| C | 1.44810 | -0.80592 | -0.15456 |
| H | 0.08250 | 0.77745 | 2.51901 |
| H | 0.88292 | -1.24401 | 3.62666 |
| H | 2.49207 | -2.67009 | -0.09719 |
| N | 1.64920 | -0.71066 | -1.56524 |
| O | 2.50165 | -1.41707 | -2.09980 |
| O | 0.92896 | 0.05948 | -2.20662 |
| H | -3.15508 | -2.56069 | -0.98782 |
| C | -2.92495 | -1.49186 | -0.94027 |
| C | -1.50930 | -1.31524 | -0.39095 |
| H | -2.95774 | -1.10779 | -1.96806 |
| C | -3.53782 | 0.72021 | 0.06982 |
| N | -1.15141 | 0.10013 | -0.22893 |
| H | -0.77370 | -1.78005 | -1.05184 |
| H | -1.41437 | -1.77627 | 0.60213 |
| C | -2.11164 | 0.82962 | 0.60933 |
| H | -3.59539 | 1.22391 | -0.90377 |
| H | -4.21394 | 1.24957 | 0.74861 |
| H | -1.03380 | 0.54889 | -1.13900 |
| H | -1.78522 | 1.87033 | 0.67473 |
| H | -2.05913 | 0.38699 | 1.61233 |
| Br | 0.95678 | 2.07281 | 0.05177 |
| C | -3.94389 | -0.74643 | -0.07782 |
| H | -4.94325 | -0.82552 | -0.51593 |
| H | -3.98933 | -1.21141 | 0.91618 |
| H | 2.09626 | -3.02639 | 2.34438 |

**I**

| | | | |
|---|---|---|---|
| C | -0.90648 | -0.76583 | -0.48080 |

| | | | |
|---|---|---|---|
| C | -0.20241 | -0.19732 | -1.57577 |
| C | 1.12955 | 0.14973 | -1.47309 |
| C | 1.85642 | -0.12403 | -0.29409 |
| C | 1.22347 | -0.74376 | 0.76262 |
| C | -0.14047 | -1.06806 | 0.66927 |
| H | -0.72764 | -0.05275 | -2.51089 |
| H | 1.62301 | 0.60302 | -2.32490 |
| H | 1.73851 | -0.98354 | 1.68384 |
| N | -0.75416 | -1.62040 | 1.83457 |
| O | -0.03289 | -2.17967 | 2.70050 |
| O | -2.00192 | -1.49163 | 1.97465 |
| H | -1.53957 | 3.54515 | 2.07055 |
| C | -2.20062 | 2.89626 | 1.48751 |
| C | -1.42716 | 1.64352 | 1.05270 |
| H | -3.02565 | 2.59501 | 2.14586 |
| C | -3.60875 | 2.69437 | -0.59529 |
| N | -2.22823 | 0.76844 | 0.18305 |
| H | -1.10448 | 1.06356 | 1.92063 |
| H | -0.53331 | 1.92895 | 0.47874 |
| C | -2.78955 | 1.45726 | -0.98822 |
| H | -4.49735 | 2.37761 | -0.03439 |
| H | -3.95735 | 3.20012 | -1.50137 |
| H | -2.90704 | 0.21119 | 0.70191 |
| H | -3.38848 | 0.74104 | -1.55610 |
| H | -1.94144 | 1.76851 | -1.61352 |
| Br | -2.41251 | -1.94643 | -1.01637 |
| C | -2.76120 | 3.64003 | 0.26705 |
| H | -3.35579 | 4.50095 | 0.58726 |
| H | -1.92812 | 4.02822 | -0.33494 |
| I | 3.88870 | 0.38564 | -0.16331 |

**Me**

| | | | |
|---|---|---|---|
| C | 0.46615 | -0.38405 | -0.45573 |
| C | 0.69338 | 0.30987 | -1.68978 |
| C | 1.63122 | 1.30420 | -1.79162 |
| C | 2.49116 | 1.65990 | -0.71785 |
| C | 2.35106 | 0.94999 | 0.44969 |
| C | 1.37727 | -0.06383 | 0.58822 |
| H | 0.11170 | 0.01565 | -2.55642 |
| H | 1.74602 | 1.80784 | -2.74925 |
| H | 2.97909 | 1.15647 | 1.31008 |
| N | 1.25247 | -0.69234 | 1.85960 |
| O | 2.16048 | -0.57507 | 2.68232 |
| O | 0.21327 | -1.31467 | 2.10613 |

| | | | |
|---|---|---|---|
| H | -2.48833 | 2.90328 | 1.76001 |
| C | -2.60624 | 1.90741 | 1.32196 |
| C | -1.24529 | 1.42354 | 0.82044 |
| H | -2.94673 | 1.23974 | 2.12398 |
| C | -3.69781 | 0.54914 | -0.48251 |
| N | -1.33729 | 0.11682 | 0.15565 |
| H | -0.53099 | 1.33918 | 1.64302 |
| H | -0.83146 | 2.12238 | 0.08036 |
| C | -2.30726 | 0.11711 | -0.94763 |
| H | -4.09029 | -0.19494 | 0.22254 |
| H | -4.37040 | 0.56421 | -1.34580 |
| H | -1.54437 | -0.61812 | 0.83452 |
| H | -2.32275 | -0.88198 | -1.38898 |
| H | -1.93328 | 0.82329 | -1.69990 |
| Br | 0.01064 | -2.28396 | -0.75300 |
| C | -3.63411 | 1.92097 | 0.18942 |
| H | -4.61819 | 2.20654 | 0.57284 |
| H | -3.34628 | 2.67577 | -0.55493 |
| C | 3.50120 | 2.76579 | -0.87658 |
| H | 4.11747 | 2.86212 | 0.02023 |
| H | 4.16593 | 2.57552 | -1.72543 |
| H | 3.01003 | 3.72816 | -1.05444 |

**$NH_2$**

| | | | |
|---|---|---|---|
| C | -0.46896 | 0.36277 | -0.43723 |
| C | -0.70808 | -0.30670 | -1.68472 |
| C | -1.65055 | -1.29022 | -1.80999 |
| C | -2.51268 | -1.65370 | -0.73813 |
| C | -2.36601 | -0.98073 | 0.44853 |
| C | -1.37046 | 0.01657 | 0.60458 |
| H | -0.12660 | -0.00235 | -2.54792 |
| H | -1.76979 | -1.77936 | -2.77380 |
| H | -2.99294 | -1.20065 | 1.30543 |
| N | -1.23021 | 0.61083 | 1.88349 |
| O | -2.11205 | 0.44384 | 2.72975 |
| O | -0.20120 | 1.25787 | 2.12318 |
| H | 2.55301 | -2.87446 | 1.72961 |
| C | 2.64632 | -1.87676 | 1.28993 |
| C | 1.27133 | -1.42360 | 0.79920 |
| H | 2.97850 | -1.20098 | 2.08871 |
| C | 3.69448 | -0.49734 | -0.52424 |
| N | 1.33302 | -0.11352 | 0.13585 |
| H | 0.56151 | -1.35410 | 1.62670 |
| H | 0.86681 | -2.12974 | 0.06134 |

| | | | |
|---|---|---|---|
| C | 2.29140 | -0.09529 | -0.97825 |
| H | 4.07706 | 0.25571 | 0.17668 |
| H | 4.35958 | -0.49896 | -1.39341 |
| H | 1.53740 | 0.62172 | 0.81542 |
| H | 2.28147 | 0.90347 | -1.42049 |
| H | 1.92540 | -0.81065 | -1.72544 |
| Br | -0.04267 | 2.28234 | -0.71748 |
| C | 3.66536 | -1.86945 | 0.14953 |
| H | 4.65841 | -2.13269 | 0.52569 |
| H | 3.38845 | -2.63122 | -0.59175 |
| N | -3.42505 | -2.71357 | -0.91175 |
| H | -4.16282 | -2.71987 | -0.21753 |
| H | -3.83296 | -2.74110 | -1.83913 |

**$NMe_2$**

| | | | |
|---|---|---|---|
| C | -0.12638 | -0.62006 | -0.39163 |
| C | 0.44659 | -0.04481 | -1.57520 |
| C | 1.67968 | 0.54356 | -1.56659 |
| C | 2.51743 | 0.54699 | -0.41169 |
| C | 2.02614 | -0.06043 | 0.71995 |
| C | 0.73176 | -0.63827 | 0.73849 |
| H | -0.12859 | -0.08671 | -2.49351 |
| H | 2.03769 | 1.00602 | -2.48203 |
| H | 2.59213 | -0.10993 | 1.64098 |
| N | 0.26112 | -1.15741 | 1.97308 |
| O | 1.05360 | -1.32068 | 2.90325 |
| O | -0.94672 | -1.40331 | 2.08507 |
| H | -2.00092 | 3.44958 | 1.73514 |
| C | -2.39861 | 2.56559 | 1.22707 |
| C | -1.23286 | 1.66450 | 0.81679 |
| H | -3.02289 | 2.02858 | 1.95289 |
| C | -3.68756 | 1.71281 | -0.74946 |
| N | -1.69291 | 0.48649 | 0.06906 |
| H | -0.67627 | 1.31939 | 1.69148 |
| H | -0.53596 | 2.20202 | 0.15898 |
| C | -2.47973 | 0.85144 | -1.11708 |
| H | -4.37587 | 1.12261 | -0.13091 |
| H | -4.22351 | 1.98175 | -1.66504 |
| H | -2.21492 | -0.14341 | 0.68158 |
| H | -2.77907 | -0.06806 | -1.62516 |
| H | -1.81399 | 1.41565 | -1.78241 |
| Br | -1.20700 | -2.22638 | -0.80604 |
| C | -3.23964 | 2.96029 | 0.01236 |
| H | -4.10615 | 3.55032 | 0.32521 |

| | | | |
|---|---|---|---|
| H | -2.64003 | 3.59516 | -0.65358 |
| N | 3.77233 | 1.20246 | -0.48338 |
| C | 4.67349 | 0.65165 | -1.49580 |
| H | 4.17561 | 0.58132 | -2.46349 |
| H | 5.53482 | 1.31542 | -1.60382 |
| H | 5.03271 | -0.35220 | -1.21448 |
| C | 4.45877 | 1.35890 | 0.78731 |
| H | 3.80828 | 1.86383 | 1.50586 |
| H | 4.78169 | 0.39533 | 1.21867 |
| H | 5.34708 | 1.97487 | 0.62986 |

**$NO_2$**

| | | | |
|---|---|---|---|
| C | -0.06940 | -0.72140 | -0.52163 |
| C | 0.48567 | -0.04221 | -1.64731 |
| C | 1.71386 | 0.56490 | -1.58409 |
| C | 2.49311 | 0.43934 | -0.41973 |
| C | 2.04756 | -0.29528 | 0.66225 |
| C | 0.79331 | -0.88557 | 0.59832 |
| H | -0.08882 | -0.01592 | -2.56574 |
| H | 2.10978 | 1.10103 | -2.43874 |
| H | 2.65440 | -0.41052 | 1.55270 |
| N | 3.79076 | 1.07502 | -0.35506 |
| O | 4.15478 | 1.73268 | -1.32166 |
| O | 4.45998 | 0.93032 | 0.65951 |
| N | 0.33161 | -1.57031 | 1.78962 |
| O | 1.16447 | -1.99301 | 2.57766 |
| O | -0.87842 | -1.65750 | 1.96301 |
| H | -1.42610 | 3.36320 | 2.13818 |
| C | -1.95783 | 2.60396 | 1.55630 |
| C | -0.95117 | 1.57950 | 1.03080 |
| H | -2.65383 | 2.09946 | 2.23908 |
| C | -3.37777 | 2.15648 | -0.46583 |
| N | -1.58083 | 0.56526 | 0.18315 |
| H | -0.44443 | 1.07480 | 1.85774 |
| H | -0.18745 | 2.07788 | 0.41537 |
| C | -2.32667 | 1.14733 | -0.93521 |
| H | -4.14993 | 1.62903 | 0.10899 |
| H | -3.86739 | 2.59455 | -1.34143 |
| H | -2.16674 | -0.06046 | 0.73721 |
| H | -2.78045 | 0.33265 | -1.50681 |
| H | -1.59459 | 1.65307 | -1.58008 |
| Br | -1.30199 | -2.12863 | -0.98828 |
| C | -2.73292 | 3.23877 | 0.40125 |
| H | -3.49422 | 3.92483 | 0.78435 |

| | | | |
|---|---|---|---|
| H | -2.04438 | 3.83359 | -0.21417 |

**OH**

| | | | |
|---|---|---|---|
| C | -0.47721 | 0.34667 | -0.44105 |
| C | -0.70357 | -0.32689 | -1.68761 |
| C | -1.62888 | -1.33030 | -1.81367 |
| C | -2.46574 | -1.70204 | -0.73455 |
| C | -2.34642 | -1.03103 | 0.45268 |
| C | -1.37725 | -0.01261 | 0.60065 |
| H | -0.13187 | -0.01037 | -2.55268 |
| H | -1.74699 | -1.81603 | -2.77945 |
| H | -2.97822 | -1.27546 | 1.29805 |
| N | -1.25498 | 0.59349 | 1.88082 |
| O | -2.14218 | 0.42266 | 2.71730 |
| O | -0.23475 | 1.25025 | 2.12263 |
| H | 2.59862 | -2.81538 | 1.75211 |
| C | 2.67334 | -1.81948 | 1.30489 |
| C | 1.28992 | -1.39647 | 0.81142 |
| H | 2.99241 | -1.13173 | 2.09871 |
| C | 3.69402 | -0.43512 | -0.52111 |
| N | 1.32624 | -0.09047 | 0.13741 |
| H | 0.57995 | -1.33392 | 1.63925 |
| H | 0.89871 | -2.11572 | 0.07913 |
| C | 2.28342 | -0.06459 | -0.97811 |
| H | 4.06184 | 0.33150 | 0.17297 |
| H | 4.35869 | -0.43111 | -1.39053 |
| H | 1.52050 | 0.65319 | 0.81078 |
| H | 2.25396 | 0.92955 | -1.42987 |
| H | 1.93016 | -0.79377 | -1.71809 |
| Br | -0.09001 | 2.27503 | -0.72172 |
| C | 3.69218 | -1.80160 | 0.16460 |
| H | 4.69017 | -2.04120 | 0.54334 |
| H | 3.43130 | -2.57529 | -0.57006 |
| O | -3.39821 | -2.70134 | -0.84347 |
| H | -3.40933 | -3.05323 | -1.74155 |

**OMe**

| | | | |
|---|---|---|---|
| C | 0.15872 | -0.50843 | -0.41945 |
| C | 0.79296 | 0.24422 | -1.45802 |
| C | 2.01978 | 0.84187 | -1.29011 |
| C | 2.75632 | 0.67934 | -0.09274 |
| C | 2.22336 | -0.10466 | 0.90165 |
| C | 0.95669 | -0.70071 | 0.74352 |
| H | 0.28978 | 0.32070 | -2.41535 |

| | | | |
|---|---|---|---|
| H | 2.42752 | 1.40765 | -2.12050 |
| H | 2.76350 | -0.26644 | 1.82694 |
| N | 0.43789 | -1.44115 | 1.84466 |
| O | 1.19179 | -1.77188 | 2.75888 |
| O | -0.77072 | -1.70028 | 1.85519 |
| H | -2.01885 | 3.07021 | 2.18676 |
| C | -2.33938 | 2.26655 | 1.51673 |
| C | -1.10628 | 1.48740 | 1.05695 |
| H | -2.98369 | 1.59730 | 2.10158 |
| C | -3.44637 | 1.70056 | -0.66320 |
| N | -1.45768 | 0.42916 | 0.09835 |
| H | -0.59580 | 1.02514 | 1.90508 |
| H | -0.39200 | 2.14825 | 0.54705 |
| C | -2.17735 | 0.95361 | -1.07092 |
| H | -4.14872 | 0.99268 | -0.20475 |
| H | -3.92750 | 2.09709 | -1.56266 |
| H | -1.99117 | -0.30890 | 0.56206 |
| H | -2.39959 | 0.11723 | -1.73729 |
| H | -1.49210 | 1.63724 | -1.58807 |
| Br | -0.81736 | -2.08954 | -1.14899 |
| C | -3.11679 | 2.82153 | 0.32248 |
| H | -4.03290 | 3.31340 | 0.66270 |
| H | -2.51059 | 3.58424 | -0.18440 |
| O | 3.97991 | 1.24718 | 0.14040 |
| C | 4.52734 | 2.06123 | -0.88095 |
| H | 5.47448 | 2.43380 | -0.49343 |
| H | 4.71161 | 1.48438 | -1.79473 |
| H | 3.87025 | 2.90874 | -1.10892 |

**tBu**

| | | | |
|---|---|---|---|
| C | -0.42761 | -0.66004 | -0.44423 |
| C | 0.24235 | -0.10595 | -1.58067 |
| C | 1.55251 | 0.30561 | -1.52043 |
| C | 2.36225 | 0.14087 | -0.36690 |
| C | 1.76280 | -0.48336 | 0.70642 |
| C | 0.41854 | -0.89876 | 0.67780 |
| H | -0.30764 | -0.03018 | -2.51213 |
| H | 1.97705 | 0.73520 | -2.42217 |
| H | 2.30250 | -0.66467 | 1.63024 |
| N | -0.12662 | -1.45286 | 1.87343 |
| O | 0.63203 | -1.84178 | 2.76056 |
| O | -1.35610 | -1.49366 | 1.98917 |
| H | -1.59080 | 3.45993 | 1.97361 |
| C | -2.13547 | 2.69466 | 1.41214 |

| | | | |
|---|---|---|---|
| C | -1.14377 | 1.63742 | 0.93075 |
| H | -2.84465 | 2.22732 | 2.10749 |
| C | -3.54915 | 2.21094 | -0.60062 |
| N | -1.79389 | 0.60288 | 0.11246 |
| H | -0.65566 | 1.14828 | 1.77632 |
| H | -0.36477 | 2.09008 | 0.30144 |
| C | -2.51497 | 1.17210 | -1.03576 |
| H | -4.33421 | 1.71465 | -0.01570 |
| H | -4.02562 | 2.62706 | -1.49380 |
| H | -2.40806 | 0.02425 | 0.68957 |
| H | -2.97800 | 0.35144 | -1.58836 |
| H | -1.76177 | 1.64272 | -1.68070 |
| Br | -1.72595 | -2.07430 | -0.95774 |
| C | -2.89224 | 3.30971 | 0.23515 |
| H | -3.64453 | 4.01831 | 0.59396 |
| H | -2.19120 | 3.87449 | -0.39414 |
| C | 3.80829 | 0.63467 | -0.27536 |
| C | 4.73206 | -0.51243 | 0.16754 |
| H | 5.76577 | -0.15632 | 0.23591 |
| H | 4.44922 | -0.90426 | 1.14904 |
| H | 4.69722 | -1.33798 | -0.55069 |
| C | 3.88454 | 1.77348 | 0.75750 |
| H | 4.91065 | 2.15003 | 0.83560 |
| H | 3.23378 | 2.60475 | 0.46502 |
| H | 3.57186 | 1.42962 | 1.74871 |
| C | 4.31334 | 1.16668 | -1.62172 |
| H | 4.27448 | 0.39660 | -2.39982 |
| H | 3.73321 | 2.03206 | -1.95915 |
| H | 5.35480 | 1.48680 | -1.51786 |

**COOH – explicit solvent**

| | | | |
|---|---|---|---|
| C | -2.07731 | -0.72002 | -0.42518 |
| C | -1.46668 | -0.44755 | -1.69277 |
| C | -0.10471 | -0.42935 | -1.83883 |
| C | 0.76119 | -0.76536 | -0.77074 |
| C | 0.20238 | -1.13601 | 0.43639 |
| C | -1.18588 | -1.14283 | 0.60576 |
| H | -2.11468 | -0.26185 | -2.54177 |
| H | 0.33152 | -0.19442 | -2.80508 |
| H | 0.82836 | -1.41874 | 1.27500 |
| N | -1.69034 | -1.45206 | 1.91392 |
| O | -0.96453 | -2.04291 | 2.70683 |
| O | -2.82893 | -1.07933 | 2.19878 |
| H | -1.41176 | 3.72507 | 1.69518 |

| | | | |
|---|---|---|---|
| C | -2.26506 | 3.17069 | 1.29227 |
| C | -1.78460 | 1.79780 | 0.82094 |
| H | -2.98074 | 3.03546 | 2.11362 |
| C | -4.04693 | 3.09475 | -0.47051 |
| N | -2.86116 | 1.01607 | 0.20090 |
| H | -1.37753 | 1.22084 | 1.65503 |
| H | -0.99647 | 1.90255 | 0.06187 |
| C | -3.51059 | 1.73013 | -0.90465 |
| H | -4.85436 | 2.95111 | 0.25924 |
| H | -4.48224 | 3.59627 | -1.34058 |
| H | -3.54072 | 0.71629 | 0.90207 |
| H | -4.30507 | 1.09378 | -1.30266 |
| H | -2.75104 | 1.86338 | -1.68592 |
| Br | -3.80754 | -1.61406 | -0.60718 |
| C | -2.92976 | 3.93626 | 0.14815 |
| H | -3.32344 | 4.89192 | 0.50675 |
| H | -2.17959 | 4.16308 | -0.62127 |
| C | 2.23021 | -0.72554 | -0.98079 |
| O | 2.72406 | -0.40914 | -2.05826 |
| O | 2.94415 | -1.04796 | 0.07898 |
| H | 3.97961 | -0.98254 | -0.14403 |
| C | 5.76417 | 0.26408 | -1.28014 |
| C | 5.29095 | 1.55650 | -0.62242 |
| C | 5.95923 | 1.74717 | 0.74082 |
| C | 5.73006 | 0.51722 | 1.62197 |
| C | 6.19091 | -0.74947 | 0.90690 |
| H | 5.50862 | 2.39981 | -1.28544 |
| H | 6.84344 | 0.32587 | -1.49092 |
| H | 5.22917 | 0.08971 | -2.21578 |
| H | 7.03896 | 1.89288 | 0.59698 |
| H | 5.57730 | 2.64703 | 1.23339 |
| H | 6.26598 | 0.61133 | 2.57172 |
| H | 4.66160 | 0.42540 | 1.85554 |
| H | 7.27957 | -0.70900 | 0.74531 |
| H | 5.96903 | -1.63862 | 1.50370 |
| H | 4.20087 | 1.50872 | -0.50066 |
| N | 5.48674 | -0.87571 | -0.38373 |
| H | 5.77722 | -1.73753 | -0.84130 |

**OH – explicit solvent**

| | | | |
|---|---|---|---|
| C | -0.99927 | -0.41010 | -0.25585 |
| C | -0.26958 | 0.44204 | -1.14884 |
| C | 0.81828 | 1.16370 | -0.73118 |
| C | 1.33957 | 1.04204 | 0.58527 |

| | | | |
|---|---|---|---|
| C | 0.71178 | 0.18127 | 1.44926 |
| C | -0.43546 | -0.54148 | 1.04371 |
| H | -0.59253 | 0.49281 | -2.18282 |
| H | 1.31950 | 1.82350 | -1.43588 |
| H | 1.08278 | 0.04374 | 2.45793 |
| N | -1.08177 | -1.35435 | 2.01165 |
| O | -0.50796 | -1.60731 | 3.07217 |
| O | -2.22487 | -1.76189 | 1.76540 |
| H | -3.99024 | 2.87046 | 1.88577 |
| C | -4.09540 | 2.05858 | 1.15973 |
| C | -2.72831 | 1.40796 | 0.94620 |
| H | -4.77611 | 1.31788 | 1.59901 |
| C | -4.70266 | 1.44286 | -1.19477 |
| N | -2.78408 | 0.34279 | -0.06504 |
| H | -2.34833 | 0.97826 | 1.87606 |
| H | -1.99579 | 2.14322 | 0.58607 |
| C | -3.31562 | 0.81909 | -1.34914 |
| H | -5.41376 | 0.66763 | -0.88124 |
| H | -5.03476 | 1.81154 | -2.17021 |
| H | -3.31594 | -0.45608 | 0.28701 |
| H | -3.32682 | -0.02268 | -2.04535 |
| H | -2.61242 | 1.57274 | -1.72548 |
| Br | -1.62685 | -2.05803 | -1.18081 |
| C | -4.67125 | 2.57012 | -0.16173 |
| H | -5.67511 | 2.97665 | -0.00757 |
| H | -4.04521 | 3.39015 | -0.53834 |
| O | 2.43156 | 1.75641 | 0.97515 |
| H | 3.13222 | 1.68294 | 0.24524 |
| C | 5.59567 | 1.44856 | -0.28605 |
| C | 5.68875 | 0.39270 | 0.81209 |
| C | 5.43762 | -1.00446 | 0.23968 |
| C | 4.10504 | -1.03930 | -0.51251 |
| C | 4.06306 | 0.05794 | -1.57184 |
| H | 6.67468 | 0.44893 | 1.28459 |
| H | 6.40108 | 1.28675 | -1.02130 |
| H | 5.71459 | 2.45346 | 0.12910 |
| H | 6.25009 | -1.26248 | -0.45413 |
| H | 5.44755 | -1.75292 | 1.03833 |
| H | 3.95438 | -2.01098 | -0.99363 |
| H | 3.27528 | -0.89047 | 0.19149 |
| H | 4.84065 | -0.13479 | -2.32959 |
| H | 3.09439 | 0.07034 | -2.08039 |
| H | 4.93952 | 0.61294 | 1.58269 |
| N | 4.27679 | 1.37340 | -0.94110 |

| | | | |
|---|---|---|---|
| H | 4.22023 | 2.09762 | -1.65381 |

**$NH_2$ – explicit solvent**

| | | | |
|---|---|---|---|
| C | 0.78799 | 0.28496 | -0.28123 |
| C | 0.41987 | -0.25430 | -1.55720 |
| C | -0.48384 | -1.27969 | -1.67878 |
| C | -1.16271 | -1.82485 | -0.55824 |
| C | -0.85403 | -1.31279 | 0.67854 |
| C | 0.07739 | -0.26060 | 0.82325 |
| H | 0.84832 | 0.19625 | -2.44558 |
| H | -0.73166 | -1.63726 | -2.67594 |
| H | -1.34722 | -1.68338 | 1.56994 |
| N | 0.34781 | 0.20879 | 2.13497 |
| O | -0.40684 | -0.10323 | 3.05905 |
| O | 1.35632 | 0.90480 | 2.31304 |
| H | 4.34486 | -2.84741 | 1.04432 |
| C | 4.28913 | -1.80378 | 0.71983 |
| C | 2.82370 | -1.43889 | 0.48428 |
| H | 4.67974 | -1.18876 | 1.54092 |
| C | 4.93620 | -0.14139 | -1.04383 |
| N | 2.67711 | -0.06575 | -0.02048 |
| H | 2.24486 | -1.52704 | 1.40637 |
| H | 2.36933 | -2.09847 | -0.26738 |
| C | 3.45274 | 0.16374 | -1.24823 |
| H | 5.35413 | 0.56827 | -0.31845 |
| H | 5.46196 | 0.01559 | -1.99086 |
| H | 2.92149 | 0.60939 | 0.70712 |
| H | 3.29291 | 1.19724 | -1.56406 |
| H | 3.03916 | -0.50307 | -2.01522 |
| Br | 1.00881 | 2.26817 | -0.35804 |
| C | 5.12284 | -1.57322 | -0.54129 |
| H | 6.17920 | -1.77416 | -0.34018 |
| H | 4.80332 | -2.27596 | -1.32244 |
| N | -2.15519 | -2.82081 | -0.68878 |
| H | -2.99417 | -2.50301 | -0.19823 |
| H | -2.38351 | -3.00812 | -1.65864 |
| C | -3.55410 | 0.51278 | 1.07643 |
| C | -3.16412 | 1.15844 | -0.25034 |
| C | -4.35192 | 1.16591 | -1.21598 |
| C | -4.92688 | -0.24507 | -1.36270 |
| C | -5.27498 | -0.82080 | 0.00826 |
| H | -2.80546 | 2.17741 | -0.06672 |
| H | -4.31008 | 1.15036 | 1.57209 |
| H | -2.68673 | 0.44551 | 1.74103 |

| | | | |
|---|---|---|---|
| H | -5.13403 | 1.83099 | -0.82308 |
| H | -4.05377 | 1.56481 | -2.19145 |
| H | -5.81866 | -0.23894 | -1.99855 |
| H | -4.18140 | -0.89573 | -1.84032 |
| H | -6.07884 | -0.20871 | 0.45804 |
| H | -5.65348 | -1.84408 | -0.08683 |
| H | -2.33376 | 0.59320 | -0.69124 |
| N | -4.07657 | -0.84179 | 0.85188 |
| H | -4.30623 | -1.25902 | 1.75015 |

Reactants (used in the TS calculations) in piperidine solvent (M06-2X):

**Br**

| | | | |
|---|---|---|---|
| C | 0.88164 | 0.84649 | 0.01313 |
| C | -0.49899 | 0.68114 | 0.02243 |
| C | -1.10200 | -0.57567 | -0.00557 |
| C | -0.26735 | -1.69291 | -0.01550 |
| C | 1.11491 | -1.55615 | -0.00011 |
| C | 1.68235 | -0.28479 | 0.01198 |
| H | 1.30370 | 1.84497 | 0.01257 |
| H | -0.70884 | -2.68335 | -0.04132 |
| H | 1.74509 | -2.43873 | -0.00230 |
| N | -1.28496 | 1.92609 | 0.03975 |
| O | -2.30160 | 1.95496 | 0.70559 |
| O | -0.84551 | 2.86693 | -0.59888 |
| Br | -2.95161 | -0.85765 | -0.05951 |
| Br | 3.55070 | -0.09347 | 0.02354 |

**Cl**

| | | | |
|---|---|---|---|
| C | 1.47649 | 0.80750 | 0.00969 |
| C | 0.09262 | 0.66891 | 0.01337 |
| C | -0.52985 | -0.57890 | -0.00874 |
| C | 0.28500 | -1.71130 | -0.01583 |
| C | 1.66967 | -1.60019 | 0.00896 |
| C | 2.25758 | -0.33805 | 0.02118 |
| H | 1.91966 | 1.79705 | 0.00978 |
| H | -0.17481 | -2.69327 | -0.04181 |
| H | 2.28755 | -2.49166 | 0.01359 |
| N | -0.66929 | 1.92856 | 0.04023 |
| O | -1.68251 | 1.97142 | 0.71023 |
| O | -0.21355 | 2.86392 | -0.59494 |
| Br | -2.38510 | -0.83007 | -0.06105 |
| Cl | 3.98768 | -0.19000 | 0.04585 |

**COOH**

| | | | |
|---|---|---|---|
| C | 1.22955 | 0.79562 | 0.00231 |

| | | | |
|---|---|---|---|
| C | -0.15275 | 0.66380 | 0.00256 |
| C | -0.77036 | -0.58841 | -0.00948 |
| C | 0.03597 | -1.72752 | -0.01362 |
| C | 1.41854 | -1.60989 | 0.01037 |
| C | 2.01847 | -0.34986 | 0.02087 |
| H | 1.67317 | 1.78514 | -0.00228 |
| H | -0.43098 | -2.70588 | -0.03652 |
| H | 2.04383 | -2.49666 | 0.01647 |
| N | -0.91778 | 1.91969 | 0.04066 |
| O | -1.90315 | 1.96807 | 0.75105 |
| O | -0.48815 | 2.84754 | -0.62279 |
| Br | -2.62605 | -0.82890 | -0.06161 |
| C | 3.50701 | -0.27045 | 0.03131 |
| O | 4.23349 | -1.23801 | 0.03486 |
| O | 3.95775 | 0.99010 | 0.03533 |
| H | 4.93202 | 0.96991 | 0.04067 |

**EtO**

| | | | |
|---|---|---|---|
| C | 0.94702 | 1.04323 | 0.00005 |
| C | -0.40568 | 0.74967 | 0.00623 |
| C | -0.88511 | -0.56190 | -0.00781 |
| C | 0.05281 | -1.58756 | -0.01836 |
| C | 1.41993 | -1.32135 | 0.00525 |
| C | 1.87640 | -0.00003 | 0.01287 |
| H | 1.28527 | 2.07356 | -0.00274 |
| H | -0.28982 | -2.61637 | -0.04342 |
| H | 2.11273 | -2.15408 | 0.00765 |
| N | -1.30898 | 1.91053 | 0.04742 |
| O | -2.27689 | 1.85557 | 0.78178 |
| O | -1.00960 | 2.87292 | -0.63875 |
| Br | -2.70966 | -1.00854 | -0.06200 |
| C | 4.16440 | -0.66675 | 0.01932 |
| H | 4.03827 | -1.27779 | -0.88318 |
| H | 4.02637 | -1.30635 | 0.89997 |
| O | 3.17495 | 0.36452 | 0.02855 |
| C | 5.51967 | 0.00442 | 0.04063 |
| H | 5.63250 | 0.61298 | 0.94193 |
| H | 6.30649 | -0.75498 | 0.03211 |
| H | 5.64483 | 0.64583 | -0.83591 |

**F**

| | | | |
|---|---|---|---|
| C | 1.83732 | 0.74181 | 0.02485 |
| C | 0.44953 | 0.64482 | 0.02140 |
| C | -0.21139 | -0.58334 | -0.00604 |
| C | 0.56767 | -1.74212 | -0.01099 |
| C | 1.95522 | -1.67885 | 0.01971 |

| | | | |
|---|---|---|---|
| C | 2.56394 | -0.43295 | 0.03778 |
| H | 2.32915 | 1.70767 | 0.03002 |
| H | 0.07450 | -2.70756 | -0.04086 |
| H | 2.55901 | -2.57957 | 0.02521 |
| N | -0.27177 | 1.92915 | 0.04036 |
| O | -1.29425 | 2.00496 | 0.69322 |
| O | 0.22430 | 2.85031 | -0.58541 |
| Br | -2.07462 | -0.77753 | -0.06507 |
| F | 3.90415 | -0.36102 | 0.06643 |

**H**

| | | | |
|---|---|---|---|
| C | 2.25187 | 0.29775 | 0.04798 |
| C | 0.86989 | 0.46371 | 0.03336 |
| C | -0.00403 | -0.62419 | 0.00102 |
| C | 0.54907 | -1.90403 | 0.00490 |
| C | 1.92859 | -2.08326 | 0.04822 |
| C | 2.78525 | -0.98371 | 0.06943 |
| H | 2.88618 | 1.17694 | 0.05524 |
| H | -0.11262 | -2.76282 | -0.02780 |
| H | 2.33076 | -3.09118 | 0.05987 |
| H | 3.86051 | -1.12119 | 0.10189 |
| N | 0.39210 | 1.85492 | 0.04371 |
| O | -0.60299 | 2.12108 | 0.69086 |
| O | 1.04720 | 2.67144 | -0.58305 |
| Br | -1.87277 | -0.47212 | -0.07392 |

**I**

| | | | |
|---|---|---|---|
| C | -0.001374 | -0.000368 | 0.026280 |
| C | 0.024960 | 0.000939 | 1.421414 |
| C | 1.228368 | -0.011550 | 2.125772 |
| C | 2.417490 | -0.011540 | 1.400545 |
| C | 2.408240 | 0.010099 | 0.007095 |
| C | 1.193936 | 0.013701 | -0.679235 |
| H | -0.960987 | -0.006223 | -0.473504 |
| H | 3.360084 | -0.034652 | 1.931533 |
| H | 3.348136 | 0.018027 | -0.530090 |
| N | -1.280529 | 0.018592 | 2.074565 |
| O | -1.403870 | 0.626618 | 3.155382 |
| O | -2.223702 | -0.560902 | 1.489868 |
| Br | 1.368654 | -0.102497 | 4.037980 |
| I | 1.161626 | 0.039477 | -2.791796 |

**Me**

| | | | |
|---|---|---|---|
| C | 1.80369 | 0.73811 | 0.01637 |
| C | 0.41408 | 0.64434 | 0.01072 |
| C | -0.23725 | -0.58652 | -0.00712 |

| | | | |
|---|---|---|---|
| C | 0.54900 | -1.73885 | -0.01061 |
| C | 1.93466 | -1.64923 | 0.01936 |
| C | 2.58774 | -0.41117 | 0.03652 |
| H | 2.25887 | 1.72367 | 0.01786 |
| H | 0.06352 | -2.70857 | -0.03881 |
| H | 2.52157 | -2.56409 | 0.02486 |
| N | -0.31629 | 1.91942 | 0.04137 |
| O | -1.31194 | 1.99619 | 0.73648 |
| O | 0.14433 | 2.83944 | -0.61443 |
| C | 4.09087 | -0.33281 | 0.06701 |
| H | 4.43557 | 0.70159 | 0.00138 |
| H | 4.48104 | -0.76457 | 0.99435 |
| H | 4.52496 | -0.89376 | -0.76634 |
| Br | -2.10250 | -0.78853 | -0.06551 |

**$NH_2$**

| | | | |
|---|---|---|---|
| C | 1.81852 | 0.73943 | 0.02295 |
| C | 0.43380 | 0.63788 | 0.01819 |
| C | -0.23051 | -0.58628 | -0.00437 |
| C | 0.56178 | -1.73502 | -0.00783 |
| C | 1.94556 | -1.66092 | 0.02171 |
| C | 2.60239 | -0.41940 | 0.04009 |
| H | 2.27577 | 1.72354 | 0.03162 |
| H | 0.07858 | -2.70616 | -0.03758 |
| H | 2.52765 | -2.57786 | 0.03099 |
| N | -0.29373 | 1.91737 | 0.04267 |
| O | -1.28497 | 2.00085 | 0.74280 |
| O | 0.16144 | 2.83167 | -0.62488 |
| N | 3.98003 | -0.34222 | 0.13565 |
| H | 4.49357 | -1.15627 | -0.17867 |
| H | 4.40258 | 0.52248 | -0.17913 |
| Br | -2.09666 | -0.78131 | -0.06867 |

**$NMe_2$**

| | | | |
|---|---|---|---|
| C | 1.15438 | 0.83037 | 0.01453 |
| C | -0.22290 | 0.66522 | 0.01136 |
| C | -0.83726 | -0.58394 | -0.00525 |
| C | 0.00413 | -1.69606 | -0.01526 |
| C | 1.38310 | -1.56708 | 0.01316 |
| C | 2.00267 | -0.29515 | 0.03846 |
| H | 1.54525 | 1.83967 | 0.01082 |
| H | -0.43546 | -2.68777 | -0.04802 |
| H | 1.98156 | -2.46983 | 0.01104 |
| N | -1.00656 | 1.91104 | 0.04324 |
| O | -1.98456 | 1.95312 | 0.76571 |
| O | -0.60914 | 2.84201 | -0.63807 |

| | | | |
|---|---|---|---|
| N | 3.36088 | -0.15777 | 0.08343 |
| C | 4.20357 | -1.33755 | 0.01558 |
| H | 4.05502 | -1.89037 | -0.92179 |
| H | 5.24692 | -1.02955 | 0.07116 |
| H | 4.00412 | -2.01336 | 0.85516 |
| C | 3.95156 | 1.16559 | 0.00412 |
| H | 3.63300 | 1.79097 | 0.84654 |
| H | 5.03609 | 1.07176 | 0.04585 |
| H | 3.68310 | 1.67550 | -0.93091 |
| Br | -2.69474 | -0.85741 | -0.06594 |

**$NO_2$**

| | | | |
|---|---|---|---|
| C | 1.24053 | 0.83698 | -0.00008 |
| C | -0.13726 | 0.67789 | 0.00553 |
| C | -0.73590 | -0.58484 | -0.01064 |
| C | 0.08956 | -1.71158 | -0.01862 |
| C | 1.47115 | -1.58288 | 0.00270 |
| C | 2.01925 | -0.30678 | 0.01378 |
| H | 1.68590 | 1.82520 | -0.00443 |
| H | -0.36167 | -2.69708 | -0.04177 |
| H | 2.11351 | -2.45535 | 0.00780 |
| N | -0.92237 | 1.92384 | 0.04005 |
| O | -1.91456 | 1.95204 | 0.74023 |
| O | -0.49898 | 2.85753 | -0.61729 |
| Br | -2.58284 | -0.85487 | -0.05951 |
| N | 3.48125 | -0.15592 | 0.03399 |
| O | 4.15194 | -1.17219 | 0.03860 |
| O | 3.93229 | 0.97505 | 0.04435 |

**OH**

| | | | |
|---|---|---|---|
| C | 1.82098 | 0.75946 | 0.02056 |
| C | 0.43821 | 0.64559 | 0.01794 |
| C | -0.21399 | -0.58692 | -0.00568 |
| C | 0.58250 | -1.73052 | -0.00924 |
| C | 1.96908 | -1.64661 | 0.02044 |
| C | 2.59434 | -0.39827 | 0.03669 |
| H | 2.29189 | 1.73614 | 0.02362 |
| H | 0.10611 | -2.70475 | -0.03765 |
| H | 2.56175 | -2.55732 | 0.02668 |
| N | -0.30164 | 1.91834 | 0.04362 |
| O | -1.28653 | 1.99375 | 0.75304 |
| O | 0.13962 | 2.83204 | -0.63246 |
| O | 3.93908 | -0.24065 | 0.06625 |
| H | 4.38597 | -1.10108 | 0.07908 |
| Br | -2.07767 | -0.79254 | -0.06789 |

**OMe**

| | | | |
|---|---|---|---|
| C | 1.33687 | 1.06195 | 0.00751 |
| C | -0.01291 | 0.75566 | 0.00969 |
| C | -0.48038 | -0.56026 | -0.00872 |
| C | 0.46812 | -1.57625 | -0.01740 |
| C | 1.83302 | -1.29855 | 0.00718 |
| C | 2.27505 | 0.02705 | 0.02093 |
| H | 1.66578 | 2.09529 | 0.00792 |
| H | 0.13501 | -2.60820 | -0.04401 |
| H | 2.53419 | -2.12444 | 0.00923 |
| N | -0.92707 | 1.90821 | 0.04746 |
| O | -1.89846 | 1.84351 | 0.77635 |
| O | -0.63302 | 2.87391 | -0.63633 |
| O | 3.57049 | 0.40421 | 0.04223 |
| C | 4.55812 | -0.61797 | 0.04627 |
| H | 4.48731 | -1.23099 | -0.85838 |
| H | 5.51705 | -0.10281 | 0.06601 |
| H | 4.46084 | -1.24962 | 0.93563 |
| Br | -2.29972 | -1.02456 | -0.06570 |

**tBu**

| | | | |
|---|---|---|---|
| C | 0.90304 | 0.79718 | -0.01025 |
| C | -0.47802 | 0.66109 | -0.00480 |
| C | -1.09149 | -0.59226 | -0.01096 |
| C | -0.26775 | -1.71166 | -0.01842 |
| C | 1.11930 | -1.57809 | 0.00030 |
| C | 1.73701 | -0.32435 | 0.00900 |
| H | 1.31330 | 1.80225 | -0.01489 |
| H | -0.71741 | -2.69878 | -0.04032 |
| H | 1.71492 | -2.48410 | 0.00595 |
| N | -1.24920 | 1.91165 | 0.03956 |
| O | -2.23326 | 1.95367 | 0.75376 |
| O | -0.83157 | 2.84771 | -0.62218 |
| Br | -2.95000 | -0.85160 | -0.05887 |
| C | 3.25320 | -0.13356 | 0.02553 |
| C | 3.64628 | 0.68394 | 1.26848 |
| H | 4.73281 | 0.82198 | 1.29331 |
| H | 3.18311 | 1.67609 | 1.26661 |
| H | 3.34371 | 0.16759 | 2.18602 |
| C | 3.99553 | -1.47291 | 0.06827 |
| H | 3.77729 | -2.08628 | -0.81298 |
| H | 5.07437 | -1.28752 | 0.08422 |
| H | 3.74299 | -2.04845 | 0.96591 |
| C | 3.67805 | 0.62301 | -1.24499 |
| H | 4.76415 | 0.76726 | -1.24592 |
| H | 3.40456 | 0.05892 | -2.14324 |

| | | | |
|---|---|---|---|
| H | 3.20843 | 1.61015 | -1.30675 |

**COOH – explicit solvent**

| | | | |
|---|---|---|---|
| C | 0.65796 | 0.43230 | -0.33039 |
| C | 2.02771 | 0.57776 | -0.15110 |
| C | 2.86161 | -0.52430 | 0.04453 |
| C | 2.29189 | -1.79699 | 0.05194 |
| C | 0.92593 | -1.95386 | -0.14556 |
| C | 0.10470 | -0.84309 | -0.33846 |
| H | 0.03364 | 1.30794 | -0.46858 |
| H | 2.92734 | -2.65924 | 0.21815 |
| H | 0.48016 | -2.94299 | -0.14426 |
| N | 2.54334 | 1.95287 | -0.20848 |
| O | 3.58150 | 2.15177 | -0.81050 |
| O | 1.87146 | 2.81847 | 0.32652 |
| Br | 4.70600 | -0.38407 | 0.35791 |
| C | -1.37454 | -1.04511 | -0.51726 |
| O | -1.86861 | -2.16380 | -0.45188 |
| O | -2.04516 | 0.05381 | -0.73283 |
| H | -3.12423 | -0.17238 | -0.82219 |
| C | -4.94023 | -1.19178 | 0.30070 |
| C | -4.69104 | -0.34649 | 1.54601 |
| C | -5.42086 | 0.99538 | 1.44683 |
| C | -5.03364 | 1.71873 | 0.15510 |
| C | -5.28032 | 0.82503 | -1.05641 |
| H | -5.01633 | -0.90488 | 2.42911 |
| H | -6.00699 | -1.45025 | 0.22866 |
| H | -4.35497 | -2.11378 | 0.32647 |
| H | -6.50528 | 0.81893 | 1.45165 |
| H | -5.19277 | 1.61902 | 2.31659 |
| H | -5.60395 | 2.64565 | 0.04069 |
| H | -3.97080 | 1.99016 | 0.18850 |
| H | -6.35502 | 0.61032 | -1.15135 |
| H | -4.94591 | 1.30865 | -1.97816 |
| H | -3.61176 | -0.17348 | 1.64931 |
| N | -4.52646 | -0.43700 | -0.90190 |
| H | -4.66982 | -1.01994 | -1.72503 |

**OH – explicit solvent**

| | | | |
|---|---|---|---|
| C | -0.55270 | 1.39454 | -0.19014 |
| C | -1.82378 | 0.86320 | -0.03109 |
| C | -2.08216 | -0.50462 | -0.11213 |
| C | -0.99764 | -1.34771 | -0.34419 |
| C | 0.28963 | -0.84327 | -0.47487 |

| | | | |
|---|---|---|---|
| C | 0.53281 | 0.53763 | -0.40292 |
| H | -0.39948 | 2.46602 | -0.13679 |
| H | -1.16739 | -2.41574 | -0.42349 |
| H | 1.11501 | -1.52554 | -0.64916 |
| N | -2.89182 | 1.83869 | 0.24016 |
| O | -3.71050 | 1.56766 | 1.09853 |
| O | -2.87187 | 2.87942 | -0.39543 |
| O | 1.74906 | 1.07160 | -0.53142 |
| H | 2.47463 | 0.35946 | -0.70230 |
| Br | -3.79756 | -1.26114 | 0.02886 |
| C | 4.88143 | 0.31599 | -1.13000 |
| C | 5.08895 | 1.09969 | 0.16351 |
| C | 5.28595 | 0.14893 | 1.34740 |
| C | 4.13174 | -0.85387 | 1.42725 |
| C | 3.96947 | -1.58341 | 0.09738 |
| H | 5.95329 | 1.76099 | 0.04844 |
| H | 5.79404 | -0.25107 | -1.37165 |
| H | 4.66918 | 0.98956 | -1.96489 |
| H | 6.22937 | -0.39932 | 1.21892 |
| H | 5.36783 | 0.71379 | 2.28103 |
| H | 4.30479 | -1.58432 | 2.22347 |
| H | 3.19771 | -0.32648 | 1.66196 |
| H | 4.87490 | -2.17365 | -0.11476 |
| H | 3.12298 | -2.27568 | 0.13094 |
| H | 4.21157 | 1.73366 | 0.34130 |
| N | 3.73457 | -0.60261 | -0.97874 |
| H | 3.59124 | -1.09640 | -1.85764 |

**$NH_2$ – explicit solvent**

| | | | |
|---|---|---|---|
| C | 0.51277 | 1.50716 | -0.53159 |
| C | 1.71627 | 0.90762 | -0.18188 |
| C | 1.92260 | -0.46792 | -0.25994 |
| C | 0.86160 | -1.24113 | -0.73430 |
| C | -0.33623 | -0.66332 | -1.11962 |
| C | -0.54279 | 0.72589 | -1.01859 |
| H | 0.41257 | 2.58216 | -0.42836 |
| H | 0.98754 | -2.31604 | -0.80516 |
| H | -1.13403 | -1.28721 | -1.51072 |
| N | 2.76926 | 1.82547 | 0.28035 |
| O | 3.91492 | 1.60719 | -0.06653 |
| O | 2.42506 | 2.77395 | 0.96709 |
| N | -1.73268 | 1.27821 | -1.43192 |
| H | -2.54592 | 0.65388 | -1.36365 |
| H | -1.91003 | 2.22686 | -1.13177 |

| | | | |
|---|---|---|---|
| Br | 3.49918 | -1.34660 | 0.26142 |
| C | -3.61674 | -1.62285 | 0.13728 |
| C | -3.18708 | -0.82772 | 1.36682 |
| C | -4.31774 | 0.10094 | 1.81738 |
| C | -4.78378 | 0.98209 | 0.65507 |
| C | -5.13789 | 0.12875 | -0.56148 |
| H | -2.90556 | -1.51520 | 2.17110 |
| H | -4.46608 | -2.27522 | 0.40848 |
| H | -2.80512 | -2.26899 | -0.21091 |
| H | -5.16335 | -0.50785 | 2.16677 |
| H | -3.99737 | 0.71846 | 2.66263 |
| H | -5.65273 | 1.58107 | 0.94647 |
| H | -3.98251 | 1.68079 | 0.38194 |
| H | -6.01314 | -0.49883 | -0.31720 |
| H | -5.40815 | 0.76080 | -1.41287 |
| H | -2.29740 | -0.23493 | 1.11390 |
| N | -3.98493 | -0.69864 | -0.94297 |
| H | -4.21748 | -1.23029 | -1.77783 |

**Piperidine**

| | | | |
|---|---|---|---|
| N | 1.38006 | -0.00207 | -0.32255 |
| C | 0.74635 | -1.21005 | 0.20714 |
| H | 1.28922 | -2.08263 | -0.17018 |
| H | 0.79050 | -1.24003 | 1.31313 |
| C | 0.74999 | 1.20775 | 0.20724 |
| H | 1.29554 | 2.07874 | -0.16992 |
| H | 0.79407 | 1.23747 | 1.31323 |
| H | 2.36851 | -0.00356 | -0.08234 |
| C | -0.71245 | 1.25922 | -0.22893 |
| C | -0.71635 | -1.25708 | -0.22884 |
| C | -1.45362 | 0.00223 | 0.23531 |
| H | -1.50771 | 0.00235 | 1.33384 |
| H | -2.48519 | 0.00381 | -0.13457 |
| H | -1.18790 | 2.16027 | 0.17537 |
| H | -0.75105 | 1.32607 | -1.32403 |
| H | -1.19449 | -2.15660 | 0.17567 |
| H | -0.75537 | -1.32397 | -1.32392 |

Structures from mechanistic study (piperidine):

**H – Reactant**

| | | | |
|---|---|---|---|
| C | 2.25187 | 0.29775 | 0.04798 |
| C | 0.86989 | 0.46371 | 0.03336 |
| C | -0.00403 | -0.62419 | 0.00102 |
| C | 0.54907 | -1.90403 | 0.00490 |

| | | | |
|---|---|---|---|
| C | 1.92859 | -2.08326 | 0.04822 |
| C | 2.78525 | -0.98371 | 0.06943 |
| H | 2.88618 | 1.17694 | 0.05524 |
| H | -0.11262 | -2.76282 | -0.02780 |
| H | 2.33076 | -3.09118 | 0.05987 |
| H | 3.86051 | -1.12119 | 0.10189 |
| N | 0.39210 | 1.85492 | 0.04371 |
| O | -0.60299 | 2.12108 | 0.69086 |
| O | 1.04720 | 2.67144 | -0.58305 |
| Br | -1.87277 | -0.47212 | -0.07392 |

**H – TS1**

| | | | |
|---|---|---|---|
| C | 0.67112 | 0.17863 | 0.52249 |
| C | 0.54763 | -0.01072 | 1.93750 |
| C | 1.02089 | -1.14298 | 2.55383 |
| C | 1.72141 | -2.14364 | 1.84128 |
| C | 1.94352 | -1.94983 | 0.49904 |
| C | 1.44810 | -0.80592 | -0.15456 |
| H | 0.08250 | 0.77745 | 2.51901 |
| H | 0.88292 | -1.24401 | 3.62666 |
| H | 2.49207 | -2.67009 | -0.09719 |
| N | 1.64920 | -0.71066 | -1.56524 |
| O | 2.50165 | -1.41707 | -2.09980 |
| O | 0.92896 | 0.05948 | -2.20662 |
| H | -3.15508 | -2.56069 | -0.98782 |
| C | -2.92495 | -1.49186 | -0.94027 |
| C | -1.50930 | -1.31524 | -0.39095 |
| H | -2.95774 | -1.10779 | -1.96806 |
| C | -3.53782 | 0.72021 | 0.06982 |
| N | -1.15141 | 0.10013 | -0.22893 |
| H | -0.77370 | -1.78005 | -1.05184 |
| H | -1.41437 | -1.77627 | 0.60213 |
| C | -2.11164 | 0.82962 | 0.60933 |
| H | -3.59539 | 1.22391 | -0.90377 |
| H | -4.21394 | 1.24957 | 0.74861 |
| H | -1.03380 | 0.54889 | -1.13900 |
| H | -1.78522 | 1.87033 | 0.67473 |
| H | -2.05913 | 0.38699 | 1.61233 |
| Br | 0.95678 | 2.07281 | 0.05177 |
| C | -3.94389 | -0.74643 | -0.07782 |
| H | -4.94325 | -0.82552 | -0.51593 |
| H | -3.98933 | -1.21141 | 0.91618 |
| H | 2.09626 | -3.02639 | 2.34438 |

**H – Intermediate**

| | | | |
|---|---|---|---|
| C | -0.71608 | -1.03321 | -0.16666 |
| C | -1.11515 | -2.06660 | -1.00277 |
| C | -2.46818 | -2.30763 | -1.24178 |
| C | -3.43844 | -1.50836 | -0.65090 |
| C | -3.05464 | -0.47646 | 0.19901 |
| C | -1.70726 | -0.24388 | 0.43772 |
| H | -0.37578 | -2.69022 | -1.48958 |
| H | -2.75211 | -3.12185 | -1.89902 |
| H | -3.78635 | 0.15806 | 0.68382 |
| N | -1.40089 | 0.81285 | 1.41766 |
| O | -2.23103 | 1.68106 | 1.58281 |
| O | -0.34899 | 0.73786 | 2.03522 |
| H | 3.00457 | -1.57259 | 2.45551 |
| C | 2.63689 | -1.02687 | 1.58220 |
| C | 1.24460 | -1.54314 | 1.25538 |
| H | 2.56373 | 0.03045 | 1.86715 |
| C | 2.98735 | -0.53050 | -0.85659 |
| N | 0.71012 | -0.78791 | 0.05903 |
| H | 0.54296 | -1.39648 | 2.07348 |
| H | 1.25473 | -2.59898 | 0.96675 |
| C | 1.58255 | -1.04031 | -1.14958 |
| H | 2.94328 | 0.55774 | -0.73116 |
| H | 3.60294 | -0.73185 | -1.73774 |
| H | 0.79036 | 0.24951 | 0.20637 |
| H | 1.11528 | -0.51487 | -1.98332 |
| H | 1.59140 | -2.11710 | -1.33268 |
| Br | 0.40033 | 2.19356 | -0.88853 |
| C | 3.57717 | -1.19571 | 0.38798 |
| H | 4.55502 | -0.76282 | 0.61430 |
| H | 3.73194 | -2.26557 | 0.19723 |
| H | -4.49092 | -1.68786 | -0.83753 |

**H – $TS_{DP}$ (deprotonation)**

| | | | |
|---|---|---|---|
| C | 0.96379 | 0.14926 | 2.01930 |
| C | 2.33076 | 0.05237 | 2.22802 |
| C | 3.14111 | -0.68768 | 1.36196 |
| C | 2.55260 | -1.31648 | 0.27750 |
| C | 1.17974 | -1.19487 | 0.05477 |
| H | 0.36038 | 0.69342 | 2.73595 |
| H | 2.76882 | 0.55084 | 3.08736 |
| H | 3.14460 | -1.87440 | -0.43853 |
| N | 0.72141 | -1.70351 | -1.23778 |
| O | 1.29996 | -2.67680 | -1.70581 |

| | | | |
|---|---|---|---|
| O | -0.17660 | -1.11469 | -1.82000 |
| H | -3.64369 | -2.12479 | -0.54978 |
| C | -3.03456 | -1.22493 | -0.41453 |
| C | -1.84493 | -1.55740 | 0.47768 |
| H | -2.66149 | -0.91804 | -1.39808 |
| C | -2.96680 | 1.10234 | 0.51857 |
| N | -1.03242 | -0.36627 | 0.73338 |
| H | -1.23069 | -2.34362 | 0.03857 |
| H | -2.21143 | -1.94113 | 1.44622 |
| C | -1.77335 | 0.70572 | 1.38692 |
| H | -2.57950 | 1.52401 | -0.41760 |
| H | -3.53181 | 1.88886 | 1.02971 |
| H | 0.14610 | 1.99304 | -2.16107 |
| H | -1.11217 | 1.56698 | 1.50639 |
| H | -2.11812 | 0.39305 | 2.38908 |
| Br | 0.81604 | 2.10694 | -0.91586 |
| C | -3.85989 | -0.09986 | 0.21304 |
| H | -4.68135 | 0.19180 | -0.44885 |
| H | -4.31192 | -0.46095 | 1.14761 |
| H | 4.21005 | -0.76252 | 1.52361 |

**H – Product¨HBr complex**

| | | | |
|---|---|---|---|
| C | 1.17333 | 0.02924 | 2.04234 |
| C | 2.53123 | 0.16498 | 2.28935 |
| C | 3.47454 | -0.14238 | 1.30678 |
| C | 3.02612 | -0.57250 | 0.06910 |
| C | 1.65809 | -0.68118 | -0.18853 |
| H | 0.47616 | 0.23398 | 2.84459 |
| H | 2.85603 | 0.50291 | 3.26852 |
| H | 3.71990 | -0.79685 | -0.73203 |
| N | 1.31204 | -0.99554 | -1.57747 |
| O | 2.13976 | -1.59983 | -2.24863 |
| O | 0.23985 | -0.61473 | -2.01981 |
| H | -2.75079 | -2.80278 | -1.00207 |
| C | -2.45510 | -1.82331 | -0.61260 |
| C | -1.11278 | -1.94681 | 0.09446 |
| H | -2.33890 | -1.14002 | -1.46237 |
| C | -3.01357 | 0.02840 | 0.97371 |
| N | -0.67933 | -0.63992 | 0.60807 |
| H | -0.35888 | -2.36510 | -0.56880 |
| H | -1.20969 | -2.63956 | 0.94927 |
| C | -1.62075 | -0.10429 | 1.59178 |
| H | -2.97103 | 0.79865 | 0.19447 |
| H | -3.70427 | 0.38033 | 1.74711 |

| | | | |
|---|---|---|---|
| H | -0.40947 | 3.58093 | -0.98675 |
| H | -1.27427 | 0.88391 | 1.90403 |
| H | -1.66140 | -0.75328 | 2.48517 |
| Br | -0.43644 | 2.20293 | -0.64736 |
| C | -3.50064 | -1.28541 | 0.36436 |
| H | -4.46249 | -1.13715 | -0.13621 |
| H | -3.66135 | -2.02443 | 1.16145 |
| H | 4.53643 | -0.04584 | 1.50018 |

**H – Product**

| | | | |
|---|---|---|---|
| C | -0.55491 | -0.65134 | 0.00954 |
| C | -1.07922 | -1.95851 | 0.08894 |
| C | -2.44547 | -2.20314 | 0.12462 |
| C | -3.36583 | -1.15388 | 0.10621 |
| C | -2.89000 | 0.14553 | 0.02774 |
| C | -1.51821 | 0.38523 | -0.04675 |
| H | -0.39470 | -2.79478 | 0.15698 |
| H | -2.79385 | -3.22925 | 0.19048 |
| H | -3.56590 | 0.99175 | -0.01090 |
| N | -1.14510 | 1.78292 | -0.28110 |
| O | -1.86058 | 2.64947 | 0.20422 |
| O | -0.17048 | 2.02493 | -0.97381 |
| H | 3.07967 | 1.76514 | 1.28759 |
| C | 2.68205 | 1.09684 | 0.51696 |
| C | 1.36431 | 0.50481 | 0.99943 |
| H | 2.48707 | 1.69494 | -0.38115 |
| C | 3.05388 | -1.01331 | -0.78213 |
| N | 0.81090 | -0.41385 | -0.00490 |
| H | 0.64620 | 1.29198 | 1.22714 |
| H | 1.53251 | -0.05893 | 1.93479 |
| C | 1.70713 | -1.53365 | -0.28097 |
| H | 2.89644 | -0.52028 | -1.74890 |
| H | 3.72047 | -1.86559 | -0.94983 |
| H | 1.25308 | -2.16410 | -1.04892 |
| H | 1.85662 | -2.15069 | 0.62426 |
| C | 3.67409 | -0.02371 | 0.20313 |
| H | 4.60497 | 0.38553 | -0.20147 |
| H | 3.93030 | -0.54910 | 1.13374 |
| H | -4.43191 | -1.34443 | 0.14445 |

**$NO_2$ – Reactant**

| | | | |
|---|---|---|---|
| C | 1.24053 | 0.83698 | -0.00008 |
| C | -0.13726 | 0.67789 | 0.00553 |
| C | -0.73590 | -0.58484 | -0.01064 |

| | | | |
|---|---|---|---|
| C | 0.08956 | -1.71158 | -0.01862 |
| C | 1.47115 | -1.58288 | 0.00270 |
| C | 2.01925 | -0.30678 | 0.01378 |
| H | 1.68590 | 1.82520 | -0.00443 |
| H | -0.36167 | -2.69708 | -0.04177 |
| H | 2.11351 | -2.45535 | 0.00780 |
| N | -0.92237 | 1.92384 | 0.04005 |
| O | -1.91456 | 1.95204 | 0.74023 |
| O | -0.49898 | 2.85753 | -0.61729 |
| Br | -2.58284 | -0.85487 | -0.05951 |
| N | 3.48125 | -0.15592 | 0.03399 |
| O | 4.15194 | -1.17219 | 0.03860 |
| O | 3.93229 | 0.97505 | 0.04435 |

**$NO_2$ – TS1**

| | | | |
|---|---|---|---|
| C | -0.06940 | -0.72140 | -0.52163 |
| C | 0.48567 | -0.04221 | -1.64731 |
| C | 1.71386 | 0.56490 | -1.58409 |
| C | 2.49311 | 0.43934 | -0.41973 |
| C | 2.04756 | -0.29528 | 0.66225 |
| C | 0.79331 | -0.88557 | 0.59832 |
| H | -0.08882 | -0.01592 | -2.56574 |
| H | 2.10978 | 1.10103 | -2.43874 |
| H | 2.65440 | -0.41052 | 1.55270 |
| N | 3.79076 | 1.07502 | -0.35506 |
| O | 4.15478 | 1.73268 | -1.32166 |
| O | 4.45998 | 0.93032 | 0.65951 |
| N | 0.33161 | -1.57031 | 1.78962 |
| O | 1.16447 | -1.99301 | 2.57766 |
| O | -0.87842 | -1.65750 | 1.96301 |
| H | -1.42610 | 3.36320 | 2.13818 |
| C | -1.95783 | 2.60396 | 1.55630 |
| C | -0.95117 | 1.57950 | 1.03080 |
| H | -2.65383 | 2.09946 | 2.23908 |
| C | -3.37777 | 2.15648 | -0.46583 |
| N | -1.58083 | 0.56526 | 0.18315 |
| H | -0.44443 | 1.07480 | 1.85774 |
| H | -0.18745 | 2.07788 | 0.41537 |
| C | -2.32667 | 1.14733 | -0.93521 |
| H | -4.14993 | 1.62903 | 0.10899 |
| H | -3.86739 | 2.59455 | -1.34143 |
| H | -2.16674 | -0.06046 | 0.73721 |
| H | -2.78045 | 0.33265 | -1.50681 |
| H | -1.59459 | 1.65307 | -1.58008 |
| Br | -1.30199 | -2.12863 | -0.98828 |

| | | | |
|---|---|---|---|
| C | -2.73292 | 3.23877 | 0.40125 |
| H | -3.49422 | 3.92483 | 0.78435 |
| H | -2.04438 | 3.83359 | -0.21417 |

**$NO_2$ – Intermediate**

| | | | |
|---|---|---|---|
| C | 0.23725 | -0.74377 | -0.03794 |
| C | 0.96882 | -1.72723 | 0.61662 |
| C | 2.35524 | -1.64565 | 0.71116 |
| C | 2.98953 | -0.55323 | 0.14783 |
| C | 2.30142 | 0.44925 | -0.51588 |
| C | 0.92371 | 0.34641 | -0.60058 |
| H | 0.46825 | -2.57265 | 1.07004 |
| H | 2.92671 | -2.41401 | 1.21685 |
| H | 2.81841 | 1.29083 | -0.96012 |
| N | 4.45824 | -0.45699 | 0.23278 |
| O | 5.04482 | -1.35510 | 0.80750 |
| O | 4.98916 | 0.51133 | -0.27673 |
| N | 0.26486 | 1.39300 | -1.41131 |
| O | 0.83188 | 2.45922 | -1.50124 |
| O | -0.77908 | 1.10711 | -1.97182 |
| H | -3.46104 | -1.88750 | -2.47859 |
| C | -3.15924 | -1.38880 | -1.55353 |
| C | -1.65730 | -1.56294 | -1.39652 |
| H | -3.38038 | -0.32049 | -1.67296 |
| C | -3.38224 | -1.34424 | 0.94916 |
| N | -1.21544 | -0.86023 | -0.12926 |
| H | -1.10044 | -1.13242 | -2.22543 |
| H | -1.37409 | -2.61331 | -1.27289 |
| C | -1.87230 | -1.50128 | 1.07450 |
| H | -3.62798 | -0.27735 | 0.99787 |
| H | -3.83578 | -1.82239 | 1.82177 |
| H | -1.56928 | 0.14120 | -0.08651 |
| H | -1.47403 | -0.99036 | 1.95241 |
| H | -1.59507 | -2.55774 | 1.08420 |
| Br | -1.60250 | 1.92762 | 1.13526 |
| C | -3.90600 | -1.96177 | -0.34834 |
| H | -4.97783 | -1.77136 | -0.44506 |
| H | -3.77107 | -3.05076 | -0.32181 |

**$NO_2$ – $TS_{DP}$ (deprotonation)**

| | | | |
|---|---|---|---|
| C | 0.09976 | -0.35335 | -0.78643 |
| C | -0.67181 | 0.45074 | -1.67123 |
| C | -2.04437 | 0.51714 | -1.59599 |
| C | -2.71620 | -0.21893 | -0.61490 |

| | | | |
|---|---|---|---|
| C | -2.02305 | -0.99126 | 0.29915 |
| C | -0.63984 | -1.03706 | 0.22167 |
| H | -0.17138 | 0.98408 | -2.46883 |
| H | -2.60921 | 1.11397 | -2.30224 |
| H | -2.54102 | -1.51594 | 1.09247 |
| N | 0.00939 | -1.65498 | 1.37878 |
| O | -0.56169 | -2.59005 | 1.92028 |
| O | 1.05655 | -1.17329 | 1.77930 |
| H | 4.02195 | -2.50991 | -0.08047 |
| C | 3.51283 | -1.54140 | -0.11056 |
| C | 2.15863 | -1.72133 | -0.78570 |
| H | 3.35850 | -1.20927 | 0.92147 |
| C | 3.55683 | 0.79060 | -1.01609 |
| N | 1.44622 | -0.44458 | -0.92017 |
| H | 1.53810 | -2.44645 | -0.26111 |
| H | 2.31234 | -2.11333 | -1.80445 |
| C | 2.19332 | 0.56438 | -1.67046 |
| H | 3.39120 | 1.22970 | -0.02429 |
| H | 4.11049 | 1.52212 | -1.61336 |
| H | 1.29703 | 1.84469 | 2.28149 |
| H | 1.63409 | 1.50106 | -1.65401 |
| H | 2.31548 | 0.24595 | -2.71857 |
| Br | 0.44731 | 2.13871 | 1.18378 |
| C | 4.34180 | -0.51233 | -0.87960 |
| H | 5.29531 | -0.33147 | -0.37454 |
| H | 4.57449 | -0.90463 | -1.87928 |
| N | -4.16345 | -0.15502 | -0.53045 |
| O | -4.72150 | -0.80746 | 0.34014 |
| O | -4.75281 | 0.54998 | -1.33756 |

**$NO_2$ – Product···HBr complex**

| | | | |
|---|---|---|---|
| C | -0.79663 | -0.60220 | 1.59691 |
| C | -2.16628 | -0.71450 | 1.51571 |
| C | -2.85912 | 0.02147 | 0.55102 |
| C | -2.19207 | 0.84047 | -0.34043 |
| C | -0.81035 | 0.92978 | -0.25805 |
| H | -0.28257 | -1.14361 | 2.37961 |
| H | -2.71104 | -1.35019 | 2.20345 |
| H | -2.72577 | 1.37387 | -1.11720 |
| N | -4.30650 | -0.08055 | 0.46899 |
| O | -4.87316 | -0.81064 | 1.26929 |
| O | -4.88350 | 0.56712 | -0.39184 |
| N | -0.17899 | 1.64367 | -1.37132 |
| O | -0.80624 | 2.55273 | -1.89360 |

| | | | |
|---|---|---|---|
| O | 0.91758 | 1.26628 | -1.75047 |
| H | 3.73390 | 2.69155 | 0.23094 |
| C | 3.31029 | 1.68309 | 0.26713 |
| C | 1.90473 | 1.75558 | 0.84714 |
| H | 3.25077 | 1.30242 | -0.75866 |
| C | 3.49867 | -0.60876 | 1.25171 |
| N | 1.29091 | 0.42001 | 0.90828 |
| H | 1.27203 | 2.44296 | 0.29052 |
| H | 1.95531 | 2.13600 | 1.88061 |
| C | 2.05378 | -0.50998 | 1.74623 |
| H | 3.49400 | -1.10089 | 0.27220 |
| H | 4.05122 | -1.25584 | 1.94047 |
| H | 1.03478 | -3.21099 | -1.89355 |
| H | 1.59530 | -1.49805 | 1.68046 |
| H | 2.02645 | -0.17854 | 2.79711 |
| Br | 1.05758 | -1.92647 | -1.28506 |
| C | 4.16881 | 0.75886 | 1.13089 |
| H | 5.17013 | 0.65009 | 0.70381 |
| H | 4.28793 | 1.20275 | 2.12865 |

**$NO_2$ – Product**

| | | | |
|---|---|---|---|
| C | 0.22880 | -0.49623 | 0.04505 |
| C | -0.55388 | -1.68343 | 0.03935 |
| C | -1.93151 | -1.65599 | 0.02525 |
| C | -2.59652 | -0.42756 | 0.02176 |
| C | -1.89539 | 0.76454 | -0.00603 |
| C | -0.51051 | 0.72038 | -0.02701 |
| H | -0.05723 | -2.64201 | 0.10886 |
| H | -2.50177 | -2.57689 | 0.05004 |
| H | -2.41066 | 1.71612 | -0.05521 |
| N | -4.04843 | -0.39277 | 0.02930 |
| O | -4.64627 | -1.45912 | 0.00852 |
| O | -4.59918 | 0.69807 | 0.05764 |
| N | 0.13565 | 2.01138 | -0.27845 |
| O | -0.38905 | 3.00974 | 0.19016 |
| O | 1.13315 | 2.02894 | -0.97974 |
| H | 4.20068 | 1.40264 | 1.11963 |
| C | 3.67136 | 0.74918 | 0.41918 |
| C | 2.32850 | 0.36175 | 1.02333 |
| H | 3.49706 | 1.31214 | -0.50409 |
| C | 3.67765 | -1.46609 | -0.75106 |
| N | 1.58570 | -0.54295 | 0.13335 |
| H | 1.72746 | 1.23524 | 1.26925 |
| H | 2.49792 | -0.18169 | 1.96763 |

| | | | |
|---|---|---|---|
| C | 2.30984 | -1.78468 | -0.14430 |
| H | 3.52028 | -1.01240 | -1.73688 |
| H | 4.21491 | -2.40757 | -0.90293 |
| H | 1.73520 | -2.37932 | -0.85531 |
| H | 2.42770 | -2.36882 | 0.78324 |
| C | 4.48546 | -0.51212 | 0.12777 |
| H | 5.43054 | -0.25695 | -0.36078 |
| H | 4.73534 | -1.00958 | 1.07490 |

**$NH_2$ – reactant**

| | | | |
|---|---|---|---|
| C | 0.51277 | 1.50716 | -0.53159 |
| C | 1.71627 | 0.90762 | -0.18188 |
| C | 1.92260 | -0.46792 | -0.25994 |
| C | 0.86160 | -1.24113 | -0.73430 |
| C | -0.33623 | -0.66332 | -1.11962 |
| C | -0.54279 | 0.72589 | -1.01859 |
| H | 0.41257 | 2.58216 | -0.42836 |
| H | 0.98754 | -2.31604 | -0.80516 |
| H | -1.13403 | -1.28721 | -1.51072 |
| N | 2.76926 | 1.82547 | 0.28035 |
| O | 3.91492 | 1.60719 | -0.06653 |
| O | 2.42506 | 2.77395 | 0.96709 |
| N | -1.73268 | 1.27821 | -1.43192 |
| H | -2.54592 | 0.65388 | -1.36365 |
| H | -1.91003 | 2.22686 | -1.13177 |
| Br | 3.49918 | -1.34660 | 0.26142 |
| C | -3.61674 | -1.62285 | 0.13728 |
| C | -3.18708 | -0.82772 | 1.36682 |
| C | -4.31774 | 0.10094 | 1.81738 |
| C | -4.78378 | 0.98209 | 0.65507 |
| C | -5.13789 | 0.12875 | -0.56148 |
| H | -2.90556 | -1.51520 | 2.17110 |
| H | -4.46608 | -2.27522 | 0.40848 |
| H | -2.80512 | -2.26899 | -0.21091 |
| H | -5.16335 | -0.50785 | 2.16677 |
| H | -3.99737 | 0.71846 | 2.66263 |
| H | -5.65273 | 1.58107 | 0.94647 |
| H | -3.98251 | 1.68079 | 0.38194 |
| H | -6.01314 | -0.49883 | -0.31720 |
| H | -5.40815 | 0.76080 | -1.41287 |
| H | -2.29740 | -0.23493 | 1.11390 |
| N | -3.98493 | -0.69864 | -0.94297 |
| H | -4.21748 | -1.23029 | -1.77783 |

**$NH_2$ – TS1**

| | | | |
|---|---|---|---|
| C | 0.78799 | 0.28496 | -0.28123 |
| C | 0.41987 | -0.25430 | -1.55720 |
| C | -0.48384 | -1.27969 | -1.67878 |
| C | -1.16271 | -1.82485 | -0.55824 |
| C | -0.85403 | -1.31279 | 0.67854 |
| C | 0.07739 | -0.26060 | 0.82325 |
| H | 0.84832 | 0.19625 | -2.44558 |
| H | -0.73166 | -1.63726 | -2.67594 |
| H | -1.34722 | -1.68338 | 1.56994 |
| N | 0.34781 | 0.20879 | 2.13497 |
| O | -0.40684 | -0.10323 | 3.05905 |
| O | 1.35632 | 0.90480 | 2.31304 |
| H | 4.34486 | -2.84741 | 1.04432 |
| C | 4.28913 | -1.80378 | 0.71983 |
| C | 2.82370 | -1.43889 | 0.48428 |
| H | 4.67974 | -1.18876 | 1.54092 |
| C | 4.93620 | -0.14139 | -1.04383 |
| N | 2.67711 | -0.06575 | -0.02048 |
| H | 2.24486 | -1.52704 | 1.40637 |
| H | 2.36933 | -2.09847 | -0.26738 |
| C | 3.45274 | 0.16374 | -1.24823 |
| H | 5.35413 | 0.56827 | -0.31845 |
| H | 5.46196 | 0.01559 | -1.99086 |
| H | 2.92149 | 0.60939 | 0.70712 |
| H | 3.29291 | 1.19724 | -1.56406 |
| H | 3.03916 | -0.50307 | -2.01522 |
| Br | 1.00881 | 2.26817 | -0.35804 |
| C | 5.12284 | -1.57322 | -0.54129 |
| H | 6.17920 | -1.77416 | -0.34018 |
| H | 4.80332 | -2.27596 | -1.32244 |
| N | -2.15519 | -2.82081 | -0.68878 |
| H | -2.99417 | -2.50301 | -0.19823 |
| H | -2.38351 | -3.00812 | -1.65864 |
| C | -3.55410 | 0.51278 | 1.07643 |
| C | -3.16412 | 1.15844 | -0.25034 |
| C | -4.35192 | 1.16591 | -1.21598 |
| C | -4.92688 | -0.24507 | -1.36270 |
| C | -5.27498 | -0.82080 | 0.00826 |
| H | -2.80546 | 2.17741 | -0.06672 |
| H | -4.31008 | 1.15036 | 1.57209 |
| H | -2.68673 | 0.44551 | 1.74103 |
| H | -5.13403 | 1.83099 | -0.82308 |
| H | -4.05377 | 1.56481 | -2.19145 |

| | | | |
|---|---|---|---|
| H | -5.81866 | -0.23894 | -1.99855 |
| H | -4.18140 | -0.89573 | -1.84032 |
| H | -6.07884 | -0.20871 | 0.45804 |
| H | -5.65348 | -1.84408 | -0.08683 |
| H | -2.33376 | 0.59320 | -0.69124 |
| N | -4.07657 | -0.84179 | 0.85188 |
| H | -4.30623 | -1.25902 | 1.75015 |

**$NH_2$ – Intermediate**

| | | | |
|---|---|---|---|
| C | -1.11769 | 1.22490 | -0.10967 |
| C | -0.78524 | 2.16771 | -1.07192 |
| C | 0.48653 | 2.72752 | -1.13108 |
| C | 1.48019 | 2.34694 | -0.21925 |
| C | 1.13060 | 1.43444 | 0.79051 |
| C | -0.13362 | 0.88302 | 0.83102 |
| H | -1.51401 | 2.46046 | -1.81838 |
| H | 0.71526 | 3.44498 | -1.91280 |
| H | 1.86643 | 1.13200 | 1.52654 |
| N | -0.37843 | -0.07221 | 1.92596 |
| O | 0.58460 | -0.56464 | 2.47427 |
| O | -1.53825 | -0.30288 | 2.24284 |
| H | -5.39153 | 0.98206 | 1.54354 |
| C | -4.67874 | 0.43966 | 0.91618 |
| C | -3.43668 | 1.30269 | 0.75992 |
| H | -4.40592 | -0.47570 | 1.45666 |
| C | -4.24121 | -0.53046 | -1.36307 |
| N | -2.43569 | 0.58640 | -0.11692 |
| H | -2.94835 | 1.49946 | 1.71229 |
| H | -3.65096 | 2.25186 | 0.25864 |
| C | -3.01233 | 0.35798 | -1.49333 |
| H | -3.92567 | -1.50930 | -0.98099 |
| H | -4.64601 | -0.69144 | -2.36604 |
| H | -2.26974 | -0.37269 | 0.25283 |
| H | -2.22262 | -0.10682 | -2.08450 |
| H | -3.27860 | 1.33339 | -1.90797 |
| Br | -0.81949 | -2.17244 | -0.49249 |
| C | -5.29039 | 0.09674 | -0.44310 |
| H | -6.13206 | -0.58864 | -0.31378 |
| H | -5.68477 | 1.01098 | -0.90513 |
| N | 2.76131 | 2.84616 | -0.24808 |
| H | 3.45135 | 2.18234 | 0.11690 |
| H | 3.03712 | 3.29847 | -1.10911 |
| C | 3.86446 | -0.81863 | 1.22264 |
| C | 2.86635 | -1.46796 | 0.26904 |

| | | | |
|---|---|---|---|
| C | 3.49437 | -1.70558 | -1.10420 |
| C | 4.09453 | -0.40269 | -1.63793 |
| C | 5.08644 | 0.17291 | -0.63011 |
| H | 2.49960 | -2.40413 | 0.70239 |
| H | 4.67648 | -1.53719 | 1.43459 |
| H | 3.38018 | -0.57847 | 2.17538 |
| H | 4.29103 | -2.45878 | -1.02159 |
| H | 2.74579 | -2.10163 | -1.79766 |
| H | 4.59792 | -0.56559 | -2.59689 |
| H | 3.29232 | 0.32996 | -1.80376 |
| H | 5.92437 | -0.53637 | -0.50620 |
| H | 5.50535 | 1.11827 | -0.99264 |
| H | 1.98998 | -0.82245 | 0.15135 |
| N | 4.40750 | 0.42419 | 0.64863 |
| H | 5.08005 | 0.81337 | 1.30557 |

**$NH_2$ – $TS_{DP}$ (deprotonation)**

| | | | |
|---|---|---|---|
| C | -0.73200 | -1.75854 | 0.23264 |
| C | 0.42228 | -1.06899 | 0.60946 |
| C | 1.39571 | -0.62050 | -0.31005 |
| C | 1.07400 | -0.85730 | -1.66174 |
| C | -0.09427 | -1.49017 | -2.05268 |
| C | -1.02923 | -1.95261 | -1.11171 |
| H | -1.43328 | -2.07302 | 0.99810 |
| H | 1.77110 | -0.54473 | -2.43030 |
| H | -0.29095 | -1.62896 | -3.11259 |
| N | 0.46858 | -0.70005 | 2.02245 |
| O | 0.95003 | 0.38793 | 2.33230 |
| O | -0.02388 | -1.46093 | 2.83923 |
| Br | 0.17058 | 2.50556 | -0.16443 |
| N | 2.55550 | 0.03676 | 0.07490 |
| C | 3.30165 | 0.82836 | -0.89941 |
| H | 2.60428 | 1.24237 | -1.63062 |
| H | 3.72581 | 1.68313 | -0.35214 |
| C | 3.41226 | -0.52872 | 1.12010 |
| H | 2.82465 | -1.16536 | 1.78209 |
| H | 3.80227 | 0.29995 | 1.72692 |
| H | 0.78163 | 1.69003 | 0.84272 |
| C | 4.56365 | -1.34335 | 0.52084 |
| C | 4.44155 | 0.04953 | -1.55971 |
| C | 5.36892 | -0.51791 | -0.48327 |
| H | 5.86410 | 0.31129 | 0.04110 |
| H | 6.15781 | -1.12769 | -0.93476 |
| H | 5.20415 | -1.70557 | 1.33227 |

| | | | |
|---|---|---|---|
| H | 4.14137 | -2.22384 | 0.01782 |
| H | 4.98851 | 0.71140 | -2.23965 |
| H | 4.03229 | -0.77449 | -2.15844 |
| N | -2.20859 | -2.60416 | -1.47912 |
| H | -2.98165 | -2.32773 | -0.86703 |
| H | -2.45264 | -2.47145 | -2.45307 |
| C | -3.77685 | -0.21575 | 1.43041 |
| C | -2.91612 | 0.88132 | 0.81015 |
| C | -3.66393 | 1.58541 | -0.32165 |
| C | -4.15687 | 0.55593 | -1.34096 |
| C | -4.99740 | -0.51434 | -0.64870 |
| H | -2.61042 | 1.59536 | 1.58309 |
| H | -4.64751 | 0.24854 | 1.92841 |
| H | -3.21319 | -0.76095 | 2.19510 |
| H | -4.52661 | 2.12845 | 0.08994 |
| H | -3.01459 | 2.32558 | -0.80160 |
| H | -4.74909 | 1.03649 | -2.12702 |
| H | -3.29237 | 0.07754 | -1.82179 |
| H | -5.90454 | -0.04092 | -0.23110 |
| H | -5.32288 | -1.27628 | -1.36526 |
| H | -2.00426 | 0.43152 | 0.40206 |
| N | -4.20703 | -1.17132 | 0.40005 |
| H | -4.77281 | -1.89376 | 0.83850 |

**$NH_2$ – Product···HBr complex**

| | | | |
|---|---|---|---|
| C | 1.34568 | -0.94291 | -0.63382 |
| C | 0.97871 | -1.13163 | -1.97863 |
| C | -0.29488 | -1.52947 | -2.35914 |
| C | -1.28578 | -1.79947 | -1.40382 |
| C | -0.94213 | -1.65819 | -0.06087 |
| C | 0.32276 | -1.20509 | 0.30354 |
| H | 1.72114 | -0.96588 | -2.75087 |
| H | -0.52381 | -1.63946 | -3.41588 |
| H | -1.68485 | -1.83897 | 0.70744 |
| N | 0.46494 | -0.88894 | 1.73056 |
| O | -0.20873 | -1.53211 | 2.52640 |
| O | 1.19725 | 0.02945 | 2.06001 |
| H | 5.00091 | -1.10834 | 2.06455 |
| C | 4.40804 | -0.46646 | 1.40458 |
| C | 3.39110 | -1.31689 | 0.65419 |
| H | 3.86490 | 0.25271 | 2.02884 |
| C | 4.46113 | 1.06231 | -0.58407 |
| N | 2.61092 | -0.49021 | -0.26891 |
| H | 2.72318 | -1.82469 | 1.35166 |

| | | | |
|---|---|---|---|
| H | 3.91640 | -2.10276 | 0.07999 |
| C | 3.43743 | 0.16156 | -1.27543 |
| H | 3.91605 | 1.85708 | -0.05951 |
| H | 5.09391 | 1.53403 | -1.34351 |
| H | -0.07716 | 3.33863 | -0.75465 |
| H | 2.79241 | 0.76377 | -1.92096 |
| H | 3.95836 | -0.58102 | -1.90999 |
| Br | 0.30627 | 1.99694 | -0.49087 |
| C | 5.30853 | 0.27190 | 0.41320 |
| H | 5.99985 | 0.93706 | 0.94050 |
| H | 5.91963 | -0.46020 | -0.13358 |
| N | -2.56673 | -2.23003 | -1.74553 |
| H | -3.25398 | -1.94085 | -1.04763 |
| H | -2.85094 | -1.98176 | -2.68467 |
| C | -3.79286 | -0.20355 | 1.75863 |
| C | -2.81651 | 0.92763 | 1.44277 |
| C | -3.43407 | 1.91584 | 0.45318 |
| C | -3.91030 | 1.16744 | -0.79281 |
| C | -4.89190 | 0.06806 | -0.39467 |
| H | -2.52612 | 1.42881 | 2.37232 |
| H | -4.65259 | 0.21426 | 2.31341 |
| H | -3.31622 | -0.95124 | 2.40182 |
| H | -4.29251 | 2.41691 | 0.92300 |
| H | -2.71264 | 2.69555 | 0.18801 |
| H | -4.38964 | 1.85013 | -1.50246 |
| H | -3.04620 | 0.70989 | -1.29636 |
| H | -5.78287 | 0.53267 | 0.06552 |
| H | -5.23031 | -0.48903 | -1.27540 |
| H | -1.90637 | 0.50872 | 0.99914 |
| N | -4.23799 | -0.86937 | 0.52568 |
| H | -4.89563 | -1.60424 | 0.77484 |

**$NH_2$ – Product**

| | | | |
|---|---|---|---|
| C | 1.49400 | 0.65997 | -0.24579 |
| C | 1.10991 | 2.00498 | -0.14218 |
| C | -0.15342 | 2.45330 | -0.50482 |
| C | -1.12070 | 1.56546 | -1.00225 |
| C | -0.76759 | 0.21701 | -1.11224 |
| C | 0.50145 | -0.20565 | -0.73814 |
| H | 1.82639 | 2.72109 | 0.24700 |
| H | -0.39886 | 3.50674 | -0.40063 |
| H | -1.48935 | -0.50888 | -1.47138 |
| N | 0.72996 | -1.65025 | -0.81675 |
| O | -0.21272 | -2.38205 | -0.53874 |

| | | | |
|---|---|---|---|
| O | 1.82779 | -2.05659 | -1.15414 |
| H | 5.72845 | -0.66797 | -1.23664 |
| C | 4.97875 | -0.65926 | -0.43820 |
| C | 3.76794 | 0.14923 | -0.89109 |
| H | 4.65855 | -1.69471 | -0.26896 |
| C | 4.47766 | 0.05754 | 1.91609 |
| N | 2.76221 | 0.19533 | 0.18148 |
| H | 3.31194 | -0.29835 | -1.77478 |
| H | 4.07949 | 1.17971 | -1.15032 |
| C | 3.29463 | 0.85615 | 1.37471 |
| H | 4.12316 | -0.93616 | 2.21515 |
| H | 4.87092 | 0.55473 | 2.80930 |
| H | 2.49568 | 0.92345 | 2.11910 |
| H | 3.63711 | 1.88441 | 1.15114 |
| C | 5.56509 | -0.07781 | 0.84918 |
| H | 6.38738 | -0.70144 | 1.21476 |
| H | 5.98505 | 0.91569 | 0.63755 |
| N | -2.37960 | 1.98165 | -1.40860 |
| H | -3.09333 | 1.25573 | -1.28756 |
| H | -2.66471 | 2.88105 | -1.04382 |
| C | -3.75905 | -1.57678 | -0.13713 |
| C | -3.04027 | -1.25784 | 1.17025 |
| C | -3.96495 | -0.49497 | 2.12058 |
| C | -4.53444 | 0.74222 | 1.42263 |
| C | -5.21971 | 0.34814 | 0.11639 |
| H | -2.68840 | -2.18910 | 1.62616 |
| H | -4.58505 | -2.28079 | 0.07082 |
| H | -3.07517 | -2.06739 | -0.83760 |
| H | -4.79439 | -1.14885 | 2.42538 |
| H | -3.42975 | -0.21065 | 3.03252 |
| H | -5.24874 | 1.26196 | 2.06994 |
| H | -3.71857 | 1.44304 | 1.19894 |
| H | -6.09049 | -0.29185 | 0.34628 |
| H | -5.59036 | 1.23449 | -0.40965 |
| H | -2.15415 | -0.64932 | 0.94954 |
| N | -4.26349 | -0.34370 | -0.75672 |
| H | -4.72289 | -0.57890 | -1.63298 |

**Piperidine**

| | | | |
|---|---|---|---|
| N | 1.38006 | -0.00207 | -0.32255 |
| C | 0.74635 | -1.21005 | 0.20714 |
| H | 1.28922 | -2.08263 | -0.17018 |
| H | 0.79050 | -1.24003 | 1.31313 |
| C | 0.74999 | 1.20775 | 0.20724 |

| | | | |
|---|---|---|---|
| H | 1.29554 | 2.07874 | -0.16992 |
| H | 0.79407 | 1.23747 | 1.31323 |
| H | 2.36851 | -0.00356 | -0.08234 |
| C | -0.71245 | 1.25922 | -0.22893 |
| C | -0.71635 | -1.25708 | -0.22884 |
| C | -1.45362 | 0.00223 | 0.23531 |
| H | -1.50771 | 0.00235 | 1.33384 |
| H | -2.48519 | 0.00381 | -0.13457 |
| H | -1.18790 | 2.16027 | 0.17537 |
| H | -0.75105 | 1.32607 | -1.32403 |
| H | -1.19449 | -2.15660 | 0.17567 |
| H | -0.75537 | -1.32397 | -1.32392 |

**HBr**

| | | | |
|---|---|---|---|
| Br | 0.00000 | 0.00000 | 0.00000 |
| H | 1.41507 | 0.00000 | 0.00000 |

## *Series 2*

Ground state structures (gas phase):

**2a**

| | | | |
|---|---|---|---|
| C | -1.26321 | -1.12923 | 0.00001 |
| C | 0.12917 | -1.19832 | 0.00001 |
| C | 0.84664 | -0.00001 | 0.00001 |
| C | 0.12919 | 1.19832 | 0.00002 |
| C | -1.26320 | 1.12924 | 0.00004 |
| N | -1.93765 | 0.00002 | 0.00002 |
| F | -1.95487 | -2.26758 | -0.00002 |
| F | 0.75394 | -2.37557 | -0.00001 |
| F | 0.75397 | 2.37556 | -0.00001 |
| F | -1.95483 | 2.26761 | -0.00003 |
| Cl | 2.57106 | -0.00002 | -0.00000 |

**2b**

| | | | |
|---|---|---|---|
| C | -1.48058 | -1.02198 | 0.00000 |
| C | -0.15996 | -1.45816 | 0.00001 |
| C | 0.82230 | -0.46652 | 0.00002 |
| C | 0.43988 | 0.87422 | 0.00002 |
| C | -0.92731 | 1.15558 | 0.00004 |
| N | -1.87046 | 0.23963 | 0.00001 |
| F | -2.45271 | -1.93798 | -0.00002 |
| F | 1.33668 | 1.86254 | -0.00001 |
| F | -1.30488 | 2.43271 | -0.00002 |
| Cl | 2.50746 | -0.87530 | -0.00001 |

| | | | |
|---|---|---|---|
| H | 0.08849 | -2.51157 | 0.00001 |

**2c**

| | | | |
|---|---|---|---|
| C | -1.12392 | 0.69981 | 0.00001 |
| C | -1.12392 | -0.69981 | 0.00001 |
| N | 0.00000 | -1.38363 | 0.00000 |
| C | 1.12392 | -0.69981 | -0.00001 |
| C | 1.12392 | 0.69981 | -0.00001 |
| N | 0.00000 | 1.38363 | 0.00000 |
| F | -2.27427 | -1.36562 | -0.00000 |
| F | -2.27427 | 1.36562 | -0.00000 |
| F | 2.27427 | 1.36562 | 0.00000 |
| F | 2.27427 | -1.36562 | 0.00000 |

**2d**

| | | | |
|---|---|---|---|
| C | 1.13108 | -0.97049 | 0.00000 |
| C | 1.20311 | 0.42081 | 0.00001 |
| C | 0.00000 | 1.12538 | 0.00000 |
| C | -1.20311 | 0.42082 | 0.00002 |
| C | -1.13108 | -0.97049 | 0.00004 |
| N | -0.00000 | -1.64341 | 0.00002 |
| F | 2.26766 | -1.66469 | -0.00001 |
| F | -2.37029 | 1.06818 | -0.00001 |
| F | -2.26767 | -1.66468 | -0.00003 |
| F | 2.37028 | 1.06818 | -0.00001 |
| F | 0.00001 | 2.45387 | -0.00000 |

**2e**

| | | | |
|---|---|---|---|
| C | -0.54747 | 1.27968 | -0.00001 |
| C | -0.98323 | -0.04822 | 0.00000 |
| C | 0.01349 | -1.02827 | -0.00001 |
| C | 1.35578 | -0.65458 | 0.00001 |
| C | 1.63983 | 0.70863 | 0.00005 |
| N | 0.71746 | 1.64701 | 0.00002 |
| F | -1.45387 | 2.25212 | -0.00001 |
| F | 2.31995 | -1.57754 | -0.00001 |
| F | 2.91399 | 1.09157 | -0.00003 |
| F | -0.30135 | -2.31690 | 0.00001 |
| Cl | -2.65889 | -0.47740 | -0.00001 |

**2f**

| | | | |
|---|---|---|---|
| N | 1.67151 | -0.74473 | 0.00000 |
| C | 1.32942 | 0.51842 | 0.00000 |
| C | 0.00000 | 0.98272 | 0.00000 |
| C | -0.98257 | 0.01913 | 0.00000 |
| C | -0.54422 | -1.31907 | 0.00000 |

| | | | |
|---|---|---|---|
| N | 0.71204 | -1.68567 | 0.00000 |
| F | 2.30307 | 1.42358 | 0.00000 |
| F | -0.28390 | 2.27928 | 0.00000 |
| F | -2.27336 | 0.32827 | 0.00000 |
| F | -1.46810 | -2.27496 | 0.00000 |

**2g**

| | | | |
|---|---|---|---|
| C | -0.01450 | -1.32566 | 0.00027 |
| C | -0.52895 | -0.02273 | -0.00001 |
| C | 0.42883 | 0.99617 | 0.00004 |
| C | 1.78767 | 0.68103 | -0.00006 |
| C | 2.13647 | -0.66517 | -0.00027 |
| N | 1.26013 | -1.64898 | 0.00001 |
| F | -0.87778 | -2.33966 | 0.00046 |
| F | 2.70830 | 1.64685 | 0.00012 |
| F | 3.42514 | -0.98680 | -0.00025 |
| F | 0.09452 | 2.28086 | 0.00039 |
| C | -2.02343 | 0.19814 | -0.00008 |
| F | -2.58828 | -0.36322 | 1.08688 |
| F | -2.34458 | 1.50206 | -0.00145 |
| F | -2.58815 | -0.36539 | -1.08609 |

**2h**

| | | | |
|---|---|---|---|
| C | 1.13987 | 1.46068 | -0.00368 |
| C | 1.20053 | 0.06062 | -0.01549 |
| C | -0.04053 | -0.57524 | -0.00770 |
| C | -1.24337 | 0.14511 | -0.00698 |
| C | -1.10824 | 1.53500 | -0.00449 |
| N | 0.04300 | 2.18174 | -0.00229 |
| F | 2.28313 | 2.13648 | 0.00734 |
| F | -2.18698 | 2.30598 | -0.00273 |
| F | -0.11595 | -1.90095 | -0.00024 |
| C | 2.54039 | -0.63899 | -0.00183 |
| F | 3.19096 | -0.39538 | 1.15336 |
| F | 2.42384 | -1.96895 | -0.13484 |
| F | 3.31804 | -0.19283 | -1.00710 |
| C | -2.55385 | -0.60972 | 0.00106 |
| F | -2.63877 | -1.42242 | -1.07179 |
| F | -2.64747 | -1.38323 | 1.10195 |
| F | -3.61678 | 0.20607 | -0.01809 |

**2i**

| | | | |
|---|---|---|---|
| C | 1.56773 | 0.00000 | 0.00004 |
| N | 0.99261 | 1.19243 | 0.00001 |
| C | -0.32660 | 1.17520 | 0.00000 |
| C | -1.07470 | 0.00000 | -0.00000 |

| | | | |
|---|---|---|---|
| C | -0.32660 | -1.17520 | -0.00001 |
| N | 0.99261 | -1.19243 | 0.00001 |
| F | 2.89102 | 0.00000 | -0.00003 |
| F | -0.95998 | 2.33811 | -0.00001 |
| F | -2.40833 | 0.00000 | -0.00000 |
| F | -0.95998 | -2.33811 | -0.00000 |

**2j'**

| | | | |
|---|---|---|---|
| C | -0.69398 | -1.12032 | -0.00001 |
| C | 0.69397 | -1.21475 | 0.00002 |
| C | 1.37041 | 0.00000 | 0.00001 |
| C | 0.69397 | 1.21475 | 0.00003 |
| C | -0.69398 | 1.12032 | 0.00011 |
| N | -1.39292 | 0.00000 | 0.00003 |
| F | -1.40364 | -2.25203 | -0.00003 |
| F | -1.40364 | 2.25203 | -0.00008 |
| F | 2.70789 | 0.00000 | -0.00002 |
| H | 1.21126 | 2.16513 | -0.00001 |
| H | 1.21126 | -2.16513 | 0.00000 |

**2k'**

| | | | |
|---|---|---|---|
| C | -1.12941 | 1.20768 | 0.00001 |
| C | -1.21374 | -0.18674 | 0.00003 |
| C | 0.00000 | -0.87879 | 0.00003 |
| C | 1.21374 | -0.18674 | 0.00006 |
| C | 1.12941 | 1.20768 | 0.00014 |
| N | 0.00000 | 1.88446 | 0.00005 |
| F | -2.25215 | 1.91765 | -0.00004 |
| F | 2.25215 | 1.91765 | -0.00009 |
| F | 0.00000 | -2.20402 | -0.00001 |
| Cl | 2.72666 | -1.02504 | -0.00003 |
| Cl | -2.72666 | -1.02504 | -0.00001 |

**2l'**

| | | | |
|---|---|---|---|
| C | -1.61913 | -0.04225 | -0.00000 |
| C | -0.94571 | -1.25957 | 0.00002 |
| C | 0.44209 | -1.18318 | 0.00002 |
| C | 1.08203 | 0.05497 | 0.00004 |
| C | 0.26721 | 1.18491 | 0.00009 |
| N | -1.04903 | 1.14840 | 0.00003 |
| F | -2.95466 | -0.05482 | -0.00003 |
| F | 2.41515 | 0.14701 | -0.00002 |
| F | 0.85145 | 2.38213 | -0.00006 |
| F | 1.18216 | -2.29181 | -0.00001 |
| H | -1.46255 | -2.21064 | 0.00000 |

**2m'**

| | | | |
|---|---|---|---|
| C | 0.64058 | -1.70104 | -0.00001 |
| C | 1.36746 | -0.52096 | 0.00001 |
| C | 0.68414 | 0.69915 | 0.00002 |
| C | -0.70417 | 0.68122 | 0.00005 |
| C | -1.33656 | -0.56650 | 0.00012 |
| N | -0.70107 | -1.71222 | 0.00004 |
| F | 2.70625 | -0.52157 | -0.00002 |
| F | -1.39853 | 1.82115 | -0.00004 |
| F | -2.67198 | -0.58688 | -0.00009 |
| F | 1.34676 | 1.85299 | -0.00001 |
| H | 1.15630 | -2.65688 | -0.00004 |

**2n'**

| | | | |
|---|---|---|---|
| C | 1.10684 | -0.40059 | 0.00001 |
| C | 0.63694 | 0.91147 | 0.00003 |
| C | -0.74515 | 1.11314 | 0.00003 |
| C | -1.59407 | 0.01149 | 0.00006 |
| C | -1.00198 | -1.25224 | 0.00013 |
| N | 0.29554 | -1.44856 | 0.00005 |
| F | 1.45348 | 1.96426 | -0.00001 |
| F | -2.91764 | 0.17190 | -0.00003 |
| F | -1.79575 | -2.32211 | -0.00008 |
| F | -1.24177 | 2.34560 | -0.00001 |
| Cl | 2.82534 | -0.68215 | -0.00004 |

**2o'**

| | | | |
|---|---|---|---|
| C | -0.31932 | -1.57747 | -0.00000 |
| C | -0.91374 | -0.31117 | 0.00001 |
| C | -0.04860 | 0.79554 | 0.00001 |
| C | 1.32890 | 0.56814 | 0.00001 |
| C | 1.77928 | -0.75040 | 0.00002 |
| N | 0.97966 | -1.79290 | 0.00001 |
| F | -1.10118 | -2.65339 | -0.00000 |
| F | 2.19713 | 1.57973 | -0.00001 |
| F | 3.09136 | -0.97265 | -0.00002 |
| Cl | -0.62834 | 2.42030 | -0.00000 |
| Cl | -2.63652 | -0.14858 | 0.00000 |

**2p'**

| | | | |
|---|---|---|---|
| C | 1.12620 | 1.42319 | -0.00000 |
| C | 1.21056 | 0.02754 | 0.00001 |
| C | 0.00000 | -0.68548 | 0.00001 |
| C | -1.21056 | 0.02754 | 0.00002 |
| C | -1.12620 | 1.42319 | 0.00004 |
| N | 0.00000 | 2.10246 | 0.00001 |

| | | | |
|---|---|---|---|
| F | 2.24879 | 2.13399 | -0.00001 |
| F | -2.24879 | 2.13399 | -0.00003 |
| Cl | -2.75841 | -0.74830 | -0.00001 |
| Cl | 0.00000 | -2.41075 | -0.00000 |
| Cl | 2.75841 | -0.74830 | -0.00000 |

**2q'**

| | | | |
|---|---|---|---|
| C | 1.14287 | -0.63122 | 0.00001 |
| C | 1.20208 | 0.76371 | 0.00003 |
| C | 0.00000 | 1.46811 | 0.00003 |
| C | -1.20208 | 0.76371 | 0.00005 |
| C | -1.14287 | -0.63122 | 0.00010 |
| N | 0.00000 | -1.29519 | 0.00004 |
| F | 2.35458 | 1.42935 | 0.00000 |
| F | -2.35458 | 1.42935 | -0.00002 |
| F | 0.00000 | 2.79714 | -0.00000 |
| Cl | -2.63103 | -1.53632 | -0.00007 |
| Cl | 2.63103 | -1.53632 | -0.00003 |

**2r'**

| | | | |
|---|---|---|---|
| C | -1.09965 | -0.63524 | 0.00004 |
| C | -0.00034 | 1.26983 | -0.00060 |
| C | 1.09999 | -0.63465 | 0.00067 |
| N | 0.00037 | -1.37454 | 0.00022 |
| F | -2.23905 | -1.29311 | -0.00008 |
| F | 2.23974 | -1.29191 | -0.00044 |
| F | -0.00070 | 2.58533 | 0.00035 |
| N | 1.18998 | 0.68742 | -0.00002 |
| N | -1.19034 | 0.68678 | -0.00009 |

## *Series 3*

Ground state structures (gas phase):

**3a**

| | | | |
|---|---|---|---|
| C | 0.011978 | -0.018275 | 0.012432 |
| C | -0.022491 | -0.045057 | 1.407796 |
| C | 1.202904 | -0.014815 | 2.075848 |
| C | 2.416422 | -0.000270 | 1.394087 |
| C | 2.415468 | 0.013402 | 0.000564 |
| C | 1.209280 | -0.003773 | -0.697314 |
| C | -1.324974 | 0.002349 | 2.159057 |
| H | -2.112051 | -0.493540 | 1.585258 |
| H | -1.219559 | -0.484426 | 3.131951 |
| F | -1.708574 | 1.323983 | 2.372468 |

| | | | |
|---|---|---|---|
| F | -1.135004 | -0.034107 | -0.682695 |
| F | 1.210366 | 0.004562 | -2.034037 |
| F | 3.570648 | 0.030876 | -0.666291 |
| F | 3.574360 | 0.011530 | 2.061885 |
| F | 1.231271 | -0.026971 | 3.416801 |

**3b**

| | | | |
|---|---|---|---|
| C | 0.038573 | 0.147048 | 0.058905 |
| C | 0.002682 | -0.005714 | 1.449276 |
| C | 1.217791 | -0.159378 | 2.114792 |
| C | 2.429997 | -0.160412 | 1.415230 |
| C | 2.461873 | -0.007916 | 0.030059 |
| C | 1.240277 | 0.146035 | -0.634581 |
| C | -1.348784 | 0.005927 | 2.135661 |
| F | -1.984682 | 1.170031 | 1.898940 |
| F | -1.097878 | 0.297742 | -0.626724 |
| F | 1.215486 | 0.295761 | -1.961720 |
| F | 3.543663 | -0.313367 | 2.134286 |
| F | 1.283003 | -0.311418 | 3.438921 |
| C | 3.732243 | 0.001508 | -0.796855 |
| F | -1.255376 | -0.147572 | 3.463562 |
| F | -2.125071 | -0.986921 | 1.659466 |
| F | 4.835102 | -0.153904 | -0.051781 |
| F | 3.847359 | 1.165347 | -1.465961 |
| F | 3.706450 | -0.991384 | -1.707194 |

**3c**

| | | | |
|---|---|---|---|
| C | 0.020574 | 0.086400 | 0.007360 |
| C | -0.002816 | 0.012559 | 1.402826 |
| C | 1.217800 | -0.071521 | 2.070664 |
| C | 2.430219 | -0.082885 | 1.385150 |
| C | 2.426309 | -0.008463 | -0.005117 |
| C | 1.219202 | 0.076654 | -0.698950 |
| C | -1.304726 | 0.023613 | 2.160423 |
| F | -1.990405 | 1.174957 | 1.896534 |
| F | -1.121582 | 0.168837 | -0.679508 |
| F | 1.223548 | 0.147913 | -2.032640 |
| F | 3.586579 | -0.164288 | 2.049234 |
| F | 1.248583 | -0.144505 | 3.411034 |
| F | -2.087515 | -1.022067 | 1.761850 |
| F | 3.578364 | -0.018326 | -0.675384 |
| H | -1.153708 | -0.049164 | 3.239876 |

**3d**

| | | | |
|---|---|---|---|
| C | 0.002348 | 0.000150 | -0.001269 |
| C | -0.012247 | 0.000699 | 1.401956 |
| C | 1.210174 | 0.000070 | 2.091004 |
| C | 2.413576 | -0.001049 | 1.396291 |
| C | 2.428177 | -0.001577 | -0.006880 |
| C | 1.205712 | -0.000976 | -0.695959 |
| F | -1.143644 | 0.000706 | -0.676570 |
| F | 1.193998 | -0.001468 | -2.026070 |
| F | 3.559517 | -0.001638 | 2.071673 |
| F | 1.221985 | 0.000548 | 3.421110 |
| C | 3.663900 | -0.002753 | -0.720305 |
| N | 4.670147 | -0.003716 | -1.301253 |
| C | -1.248019 | 0.001861 | 2.115300 |
| N | -2.254315 | 0.002811 | 2.696165 |

**3e**

| | | | |
|---|---|---|---|
| C | 0.003430 | 0.026880 | 0.021663 |
| C | -0.026636 | -0.022202 | 1.416563 |
| C | 1.203069 | 0.020130 | 2.125858 |
| C | 2.395442 | -0.015854 | 1.400579 |
| C | 2.404867 | -0.005192 | 0.004221 |
| C | 1.207194 | 0.029230 | -0.686123 |
| F | -1.108325 | 0.068821 | -0.717268 |
| F | 1.196129 | 0.059927 | -2.016669 |
| F | 3.592177 | -0.056894 | 1.992114 |
| C | -1.382656 | -0.108375 | 2.113249 |
| C | 1.279082 | 0.092648 | 3.649200 |
| F | 0.293416 | 0.860388 | 4.150382 |
| F | 1.192869 | -1.127625 | 4.209136 |
| F | 2.434358 | 0.644559 | 4.059437 |
| F | -1.318403 | -0.885731 | 3.210382 |
| F | -1.830615 | 1.106258 | 2.479421 |
| F | -2.313523 | -0.658071 | 1.313968 |
| F | 3.562059 | -0.023604 | -0.653040 |

**3f**

| | | | |
|---|---|---|---|
| C | -0.008819 | -0.000347 | 0.007655 |
| C | -0.027918 | -0.000024 | 1.411138 |
| C | 1.196992 | -0.000351 | 2.096406 |
| C | 2.403600 | -0.000961 | 1.405563 |

| | | | |
|---|---|---|---|
| C | 2.398210 | -0.001252 | 0.010552 |
| C | 1.192804 | -0.000961 | -0.691737 |
| F | -1.153835 | -0.000078 | -0.671634 |
| F | 1.199550 | -0.001254 | -2.025600 |
| F | 3.562017 | -0.001266 | 2.066848 |
| F | 3.550338 | -0.001838 | -0.654637 |
| C | -1.263101 | 0.000553 | 2.124170 |
| N | -2.269583 | 0.001009 | 2.705177 |
| F | 1.212739 | -0.000088 | 3.427662 |

**3g**

| | | | |
|---|---|---|---|
| C | -0.012920 | -0.000461 | 0.031173 |
| C | -0.033595 | 0.000102 | 1.427929 |
| C | 1.196154 | -0.000012 | 2.138020 |
| C | 2.395525 | -0.000674 | 1.421880 |
| C | 2.399225 | -0.001221 | 0.026653 |
| C | 1.193614 | -0.001114 | -0.669501 |
| F | -1.150864 | -0.000360 | -0.658443 |
| F | 1.194469 | -0.001642 | -1.998287 |
| F | 3.561650 | -0.000798 | 2.062693 |
| F | 3.549638 | -0.001829 | -0.638344 |
| C | -1.289444 | 0.000810 | 2.107138 |
| N | -2.316289 | 0.001367 | 2.651452 |
| C | 1.235699 | 0.000509 | 3.565231 |
| N | 1.277598 | 0.000945 | 4.726667 |

## *Series 4*

Ground state structures (gas phase):

**4a**

| | | | |
|---|---|---|---|
| C | -0.007238 | 0.000099 | -0.004112 |
| C | 0.005816 | 0.000560 | 1.385632 |
| C | 1.213115 | -0.000015 | 2.082747 |
| C | 2.423262 | -0.001033 | 1.399299 |
| C | 2.410212 | -0.001480 | 0.009588 |
| C | 1.202880 | -0.000928 | -0.687545 |
| H | -0.945804 | 0.000526 | -0.546010 |
| H | 3.361787 | -0.001484 | 1.941268 |
| F | 3.563624 | -0.002484 | -0.676100 |
| F | 1.220129 | -0.001394 | -2.029271 |
| F | 1.195944 | 0.000411 | 3.424478 |

| | | | |
|---|---|---|---|
| F | -1.147639 | 0.001507 | 2.071257 |

**4b**

| | | | |
|---|---|---|---|
| C | -0.005156 | 0.000158 | -0.004242 |
| C | 0.003838 | 0.000585 | 1.384013 |
| C | 1.206813 | 0.000002 | 2.090502 |
| C | 2.412619 | -0.000983 | 1.394371 |
| C | 2.402407 | -0.001397 | -0.000692 |
| C | 1.204722 | -0.000861 | -0.702656 |
| H | -0.956612 | 0.000593 | -0.523997 |
| F | 3.578647 | -0.002397 | -0.647687 |
| F | 1.211131 | 0.000365 | 3.427684 |
| F | -1.144659 | 0.001470 | 2.079017 |
| F | 3.568447 | -0.001563 | 2.066767 |
| H | 1.230434 | -0.001239 | -1.786608 |

**4c**

| | | | |
|---|---|---|---|
| C | -0.014538 | 0.000177 | -0.007080 |
| C | 0.007031 | 0.000583 | 1.382834 |
| C | 1.205771 | -0.000017 | 2.093788 |
| C | 2.404608 | -0.001012 | 1.382914 |
| C | 2.426329 | -0.001428 | -0.006931 |
| C | 1.205937 | -0.000833 | -0.673882 |
| H | -0.953950 | 0.000620 | -0.546112 |
| F | 1.205780 | 0.000335 | 3.433170 |
| F | -1.142483 | 0.001482 | 2.071091 |
| F | 3.554014 | -0.001611 | 2.071400 |
| H | 3.365792 | -0.002218 | -0.545879 |
| F | 1.206023 | -0.001253 | -2.018559 |

**4d**

| | | | |
|---|---|---|---|
| C | -0.010122 | 0.000185 | -0.005762 |
| C | 0.006039 | 0.000595 | 1.383957 |
| C | 1.205831 | -0.000011 | 2.092711 |
| C | 2.411056 | -0.001032 | 1.392298 |
| C | 2.415192 | -0.001440 | -0.001623 |
| C | 1.201543 | -0.000843 | -0.686459 |
| H | -0.948255 | 0.000624 | -0.547429 |
| F | 1.210464 | 0.000340 | 3.430121 |
| F | -1.144141 | 0.001503 | 2.071355 |
| F | 3.567419 | -0.001648 | 2.060079 |
| F | 1.222001 | -0.001293 | -2.026236 |

| | | | |
|---|---|---|---|
| F | 3.575771 | -0.002451 | -0.666261 |

**4e**

| | | | |
|---|---|---|---|
| C | -0.011685 | 0.000093 | -0.006666 |
| C | 0.000253 | 0.000429 | 1.390288 |
| C | 1.205741 | -0.000064 | 2.089194 |
| C | 2.412438 | -0.001098 | 1.393082 |
| C | 2.412104 | -0.001525 | 0.000078 |
| C | 1.204090 | -0.000879 | -0.694616 |
| F | 1.205797 | 0.000455 | 3.424930 |
| F | -1.142025 | 0.001587 | 2.078082 |
| F | 3.567852 | -0.001530 | 2.060369 |
| F | 1.228899 | -0.001141 | -2.027743 |
| F | 3.568898 | -0.002453 | -0.667784 |
| Cl | -1.511493 | 0.000923 | -0.872630 |

**4f**

| | | | |
|---|---|---|---|
| C | 0.000924 | 0.000123 | 0.000591 |
| C | 0.000857 | 0.000477 | 1.394440 |
| C | 1.207906 | -0.000043 | 2.091190 |
| C | 2.415092 | -0.001101 | 1.394626 |
| C | 2.415159 | -0.001506 | 0.000865 |
| C | 1.208035 | -0.000881 | -0.695928 |
| F | 1.208028 | 0.000432 | 3.426775 |
| F | -1.155683 | 0.001564 | 2.062610 |
| F | 3.571416 | -0.001572 | 2.063115 |
| F | 1.208116 | -0.001159 | -2.031517 |
| F | 3.571600 | -0.002453 | -0.667476 |
| F | -1.155502 | 0.000749 | -0.667724 |

**4g**

| | | | |
|---|---|---|---|
| C | 0.019329 | 0.000224 | 0.011234 |
| C | 0.000485 | 0.000671 | 1.405742 |
| C | 1.214236 | 0.000052 | 2.108946 |
| C | 2.431129 | -0.001003 | 1.403903 |
| C | 2.433446 | -0.001442 | -0.002424 |
| C | 1.217639 | -0.000822 | -0.702166 |
| F | -1.133817 | 0.000780 | -0.654601 |
| Cl | -1.536567 | 0.001931 | 2.205143 |
| Cl | 1.201572 | 0.000557 | 3.841842 |
| Cl | 3.933806 | -0.001814 | 2.271617 |
| Cl | 3.927961 | -0.002795 | -0.879661 |

| | | | |
|---|---|---|---|
| Cl | 1.141692 | -0.001344 | -2.432998 |

**4h**

| | | | |
|---|---|---|---|
| C | 0.014918 | 0.000218 | 0.002403 |
| C | -0.002843 | 0.000643 | 1.396602 |
| C | 1.213317 | -0.000001 | 2.078471 |
| C | 2.430943 | -0.001039 | 1.393731 |
| C | 2.435336 | -0.001454 | -0.010854 |
| C | 1.216792 | -0.000822 | -0.709538 |
| F | -1.139129 | 0.000800 | -0.660581 |
| Cl | -1.501649 | 0.001911 | 2.261761 |
| Cl | 3.894569 | -0.001800 | 2.323698 |
| Cl | 3.934789 | -0.002774 | -0.876441 |
| Cl | 1.143512 | -0.001305 | -2.442071 |
| F | 1.210327 | 0.000379 | 3.409396 |

**4i**

| | | | |
|---|---|---|---|
| C | 0.003280 | 0.000182 | 0.006566 |
| C | -0.009138 | 0.000644 | 1.402875 |
| C | 1.207874 | 0.000026 | 2.088924 |
| C | 2.425025 | -0.000995 | 1.403042 |
| C | 2.412795 | -0.001417 | 0.006772 |
| C | 1.208076 | -0.000851 | -0.691576 |
| F | -1.138439 | 0.000694 | -0.680188 |
| Cl | -1.510576 | 0.001883 | 2.265737 |
| Cl | 3.926303 | -0.001758 | 2.266171 |
| F | 1.207800 | 0.000433 | 3.420681 |
| F | 3.554581 | -0.002436 | -0.679876 |
| F | 1.208222 | -0.001307 | -2.027544 |

**4j**

| | | | |
|---|---|---|---|
| C | 0.006291 | 0.000216 | 0.003672 |
| C | -0.008549 | 0.000627 | 1.399966 |
| C | 1.207802 | -0.000009 | 2.085560 |
| C | 2.424201 | -0.001005 | 1.399963 |
| C | 2.410018 | -0.001381 | 0.003729 |
| C | 1.208178 | -0.000795 | -0.707034 |
| F | -1.145715 | 0.000779 | -0.661674 |
| Cl | -1.508770 | 0.001852 | 2.265526 |
| Cl | 3.924045 | -0.001783 | 2.266222 |
| F | 1.208238 | 0.000361 | 3.415894 |
| F | 3.562369 | -0.002368 | -0.661170 |

| | | | |
|---|---|---|---|
| Cl | 1.207705 | -0.001302 | -2.439072 |

## *Series 5*

Ground state structures (gas phase):

**Br**

| | | | |
|---|---|---|---|
| C | -0.28356 | -1.21839 | 0.00022 |
| C | 1.10828 | -1.21917 | 0.00024 |
| C | 1.78362 | 0.00002 | 0.00006 |
| C | 1.10828 | 1.21920 | -0.00014 |
| C | -0.28357 | 1.21842 | -0.00017 |
| C | -0.96599 | 0.00001 | 0.00001 |
| H | -0.83449 | -2.15211 | 0.00048 |
| H | 1.67234 | -2.14366 | 0.00026 |
| H | 1.67232 | 2.14370 | -0.00014 |
| H | -0.83450 | 2.15213 | -0.00045 |
| N | 3.25406 | -0.00000 | 0.00009 |
| O | 3.82423 | -1.09052 | -0.00058 |
| O | 3.82431 | 1.09048 | 0.00040 |
| Br | -2.86985 | -0.00001 | -0.00002 |

**$cC_3O_2H_5$**

| | | | |
|---|---|---|---|
| C | 0.00548 | 1.18638 | -0.35057 |
| C | -1.36667 | 1.21691 | -0.11489 |
| C | -2.05867 | 0.01027 | -0.03351 |
| C | -1.41892 | -1.21939 | -0.18057 |
| C | -0.04767 | -1.23336 | -0.41840 |
| C | 0.67278 | -0.03475 | -0.50274 |
| H | 0.56997 | 2.11048 | -0.40724 |
| H | -1.90289 | 2.14960 | 0.00979 |
| H | -1.99431 | -2.13380 | -0.10543 |
| H | 0.47480 | -2.17835 | -0.52631 |
| N | -3.50820 | 0.03446 | 0.21885 |
| O | -4.04881 | 1.13295 | 0.34683 |
| O | -4.09539 | -1.04533 | 0.28754 |
| C | 2.16723 | -0.07613 | -0.80988 |
| H | 2.32688 | -0.18261 | -1.89120 |
| C | 3.75058 | 0.74466 | 0.66051 |
| C | 3.31767 | -0.66931 | 1.04662 |
| H | 4.76739 | 0.75744 | 0.24688 |
| H | 3.68473 | 1.46433 | 1.48182 |
| H | 4.13398 | -1.31877 | 1.36925 |
| H | 2.53022 | -0.65710 | 1.81338 |
| O | 2.80870 | 1.10972 | -0.35417 |
| O | 2.81497 | -1.17287 | -0.19299 |

**$CF_3$**

| | | | |
|---|---|---|---|
| C | 0.33587 | -1.21376 | -0.03211 |
| C | -1.05579 | -1.21987 | -0.01606 |
| C | -1.72782 | 0.00010 | -0.00713 |
| C | -1.05628 | 1.22027 | -0.01631 |
| C | 0.33546 | 1.21473 | -0.03235 |
| C | 1.02892 | 0.00066 | -0.03938 |
| H | 0.88280 | -2.15007 | -0.04631 |
| H | -1.62137 | -2.14321 | -0.01300 |
| H | -1.62221 | 2.14339 | -0.01341 |
| H | 0.88207 | 2.15118 | -0.04670 |
| N | -3.20332 | -0.00017 | 0.00914 |
| O | -3.77119 | -1.09066 | 0.01531 |
| O | -3.77161 | 1.09009 | 0.01601 |
| C | 2.53728 | 0.00014 | 0.00318 |
| F | 3.05361 | 1.09486 | -0.59335 |
| F | 2.98903 | -0.01094 | 1.27672 |
| F | 3.05275 | -1.08493 | -0.61162 |

**Cl**

| | | | |
|---|---|---|---|
| C | -0.96152 | -1.21887 | 0.00020 |
| C | 0.42998 | -1.21899 | 0.00022 |
| C | 1.10554 | 0.00002 | 0.00006 |
| C | 0.42997 | 1.21903 | -0.00014 |
| C | -0.96153 | 1.21888 | -0.00017 |
| C | -1.64458 | 0.00001 | 0.00000 |
| H | -1.51364 | -2.15210 | 0.00048 |
| H | 0.99414 | -2.14337 | 0.00025 |
| H | 0.99412 | 2.14341 | -0.00014 |
| H | -1.51365 | 2.15211 | -0.00047 |
| N | 2.57583 | -0.00000 | 0.00009 |
| O | 3.14600 | -1.09051 | -0.00055 |
| O | 3.14608 | 1.09047 | 0.00039 |
| Cl | -3.39503 | -0.00001 | -0.00003 |

**CN**

| | | | |
|---|---|---|---|
| C | -1.08166 | -1.21959 | 0.00002 |
| C | 0.30848 | -1.22116 | 0.00006 |
| C | 0.97941 | 0.00002 | 0.00001 |
| C | 0.30847 | 1.22119 | -0.00001 |
| C | -1.08168 | 1.21960 | 0.00010 |
| C | -1.78108 | 0.00000 | 0.00007 |
| H | -1.63063 | -2.15501 | 0.00002 |
| H | 0.87551 | -2.14362 | 0.00006 |
| H | 0.87548 | 2.14365 | -0.00004 |

| | | | |
|---|---|---|---|
| H | -1.63064 | 2.15502 | 0.00013 |
| N | 2.45535 | 0.00000 | -0.00003 |
| O | 3.02213 | -1.09076 | -0.00004 |
| O | 3.02220 | 1.09072 | -0.00004 |
| C | -3.21565 | -0.00001 | 0.00007 |
| N | -4.37850 | -0.00001 | -0.00017 |

**COOiPr**

| | | | |
|---|---|---|---|
| C | -0.33421 | -0.90894 | 0.03359 |
| C | -1.70224 | -1.15748 | 0.09184 |
| C | -2.58107 | -0.07871 | 0.01489 |
| C | -2.13730 | 1.23613 | -0.11776 |
| C | -0.76814 | 1.47159 | -0.17443 |
| C | 0.13765 | 0.40449 | -0.09990 |
| H | 0.37152 | -1.72900 | 0.09136 |
| H | -2.09536 | -2.16120 | 0.19448 |
| H | -2.85856 | 2.04188 | -0.17341 |
| H | -0.37961 | 2.47884 | -0.27703 |
| N | -4.03185 | -0.33784 | 0.07586 |
| O | -4.39796 | -1.50670 | 0.19066 |
| O | -4.78696 | 0.63073 | 0.00806 |
| C | 1.59903 | 0.72716 | -0.16685 |
| O | 2.02996 | 1.85844 | -0.27929 |
| O | 2.36671 | -0.37637 | -0.09215 |
| C | 3.81607 | -0.19162 | -0.15349 |
| H | 4.00433 | 0.64275 | -0.83476 |
| C | 4.37690 | -1.48842 | -0.71847 |
| H | 3.95424 | -1.69941 | -1.70572 |
| H | 5.46486 | -1.41180 | -0.81819 |
| H | 4.15129 | -2.33198 | -0.05679 |
| C | 4.34023 | 0.14938 | 1.23734 |
| H | 3.90067 | 1.08328 | 1.59788 |
| H | 4.10556 | -0.65250 | 1.94621 |
| H | 5.42842 | 0.27380 | 1.20614 |

**F**

| | | | |
|---|---|---|---|
| C | -1.39135 | -1.22119 | 0.00030 |
| C | -0.00053 | -1.22062 | 0.00035 |
| C | 0.67530 | 0.00002 | 0.00006 |
| C | -0.00055 | 1.22066 | -0.00026 |
| C | -1.39136 | 1.22120 | -0.00028 |
| C | -2.06188 | 0.00000 | -0.00001 |
| H | -1.95927 | -2.14509 | 0.00066 |
| H | 0.56593 | -2.14345 | 0.00047 |
| H | 0.56589 | 2.14349 | -0.00036 |
| H | -1.95930 | 2.14510 | -0.00068 |

| | | | |
|---|---|---|---|
| N | 2.14365 | 0.00000 | 0.00011 |
| O | 2.71519 | -1.09032 | -0.00085 |
| O | 2.71527 | 1.09028 | 0.00068 |
| F | -3.40447 | -0.00002 | -0.00005 |

**H**

| | | | |
|---|---|---|---|
| C | 1.82074 | -1.21237 | 0.00019 |
| C | 0.42747 | -1.22089 | 0.00015 |
| C | -0.24496 | 0.00002 | -0.00012 |
| C | 0.42748 | 1.22090 | -0.00029 |
| C | 1.82076 | 1.21237 | -0.00014 |
| C | 2.51606 | -0.00001 | 0.00008 |
| H | 2.36335 | -2.15293 | 0.00027 |
| H | -0.14089 | -2.14260 | 0.00031 |
| H | -0.14084 | 2.14263 | -0.00052 |
| H | 2.36337 | 2.15292 | -0.00014 |
| N | -1.71752 | 0.00000 | -0.00022 |
| O | -2.28935 | -1.08985 | -0.00034 |
| O | -2.28941 | 1.08983 | 0.00061 |
| H | 3.60237 | -0.00002 | 0.00015 |

**I**

| | | | |
|---|---|---|---|
| C | 0.41681 | 0.00000 | 0.00006 |
| C | -0.26832 | 1.21776 | 0.00008 |
| C | -1.66153 | 1.21839 | 0.00015 |
| C | -2.33704 | 0.00000 | 0.00019 |
| C | -1.66153 | -1.21839 | 0.00017 |
| C | -0.26832 | -1.21776 | 0.00010 |
| H | -2.22478 | -2.14361 | 0.00020 |
| H | 0.27146 | -2.15786 | 0.00010 |
| N | -3.80831 | 0.00000 | 0.00027 |
| O | -4.37730 | -1.09074 | -0.00031 |
| O | -4.37730 | 1.09074 | -0.00025 |
| H | -2.22478 | 2.14361 | 0.00017 |
| N | 2.55248 | 0.00000 | -0.00004 |
| H | 0.27146 | 2.15786 | 0.00003 |

**iPr**

| | | | |
|---|---|---|---|
| C | -0.65837 | -1.02577 | 0.00100 |
| C | 0.72676 | -1.14704 | 0.00158 |
| C | 1.50138 | 0.01245 | -0.00015 |
| C | 0.92179 | 1.27854 | -0.00242 |
| C | -0.46724 | 1.37591 | -0.00298 |
| C | -1.28155 | 0.23392 | -0.00133 |
| H | -1.26303 | -1.92821 | 0.00235 |
| H | 1.21409 | -2.11429 | 0.00333 |

| | | | |
|---|---|---|---|
| H | 1.55529 | 2.15702 | -0.00375 |
| H | -0.92872 | 2.36004 | -0.00481 |
| N | 2.96572 | -0.10507 | 0.00040 |
| O | 3.44973 | -1.23748 | 0.00254 |
| O | 3.62451 | 0.93537 | -0.00129 |
| C | -2.79748 | 0.36417 | -0.00158 |
| C | -3.42128 | -0.23759 | 1.27256 |
| H | -4.50547 | -0.07698 | 1.27857 |
| H | -3.24482 | -1.31798 | 1.33220 |
| H | -3.00347 | 0.22058 | 2.17541 |
| C | -3.42245 | -0.24918 | -1.26956 |
| H | -4.50652 | -0.08787 | -1.27635 |
| H | -3.00491 | 0.20014 | -2.17696 |
| H | -3.24690 | -1.33022 | -1.31913 |
| H | -3.02890 | 1.43767 | -0.00638 |

**OMe**

| | | | |
|---|---|---|---|
| C | 1.05137 | -0.99691 | -0.00000 |
| C | -0.33426 | -1.12998 | 0.00001 |
| C | -1.13423 | 0.00948 | -0.00000 |
| C | -0.57420 | 1.29134 | -0.00002 |
| C | 0.80325 | 1.42502 | -0.00001 |
| C | 1.62719 | 0.28387 | -0.00002 |
| H | 1.66852 | -1.88720 | -0.00003 |
| H | -0.80195 | -2.10691 | 0.00004 |
| H | -1.22560 | 2.15650 | -0.00005 |
| H | 1.27337 | 2.40274 | -0.00002 |
| N | -2.58855 | -0.13731 | 0.00001 |
| O | -3.05243 | -1.27972 | -0.00002 |
| O | -3.26952 | 0.89033 | 0.00003 |
| O | 2.95989 | 0.52690 | 0.00003 |
| C | 3.85830 | -0.57721 | -0.00000 |
| H | 4.85917 | -0.14354 | -0.00005 |
| H | 3.72927 | -1.19704 | 0.89585 |
| H | 3.72917 | -1.19705 | -0.89584 |

**OPh**

| | | | |
|---|---|---|---|
| C | 1.09236 | 1.72710 | 0.20796 |
| C | 2.40327 | 1.27780 | 0.18314 |
| C | 2.65287 | -0.08059 | -0.02907 |
| C | 1.61320 | -0.98915 | -0.21977 |
| C | 0.29727 | -0.53981 | -0.19633 |
| C | 0.03698 | 0.82066 | 0.02000 |
| H | 0.85889 | 2.77390 | 0.37069 |
| H | 3.23527 | 1.95592 | 0.32698 |
| H | 1.84461 | -2.03390 | -0.38726 |

| | | | |
|---|---|---|---|
| H | -0.51909 | -1.23588 | -0.34798 |
| N | 4.03480 | -0.55877 | -0.05284 |
| O | 4.93204 | 0.26935 | 0.11642 |
| O | 4.22422 | -1.76224 | -0.24075 |
| O | -1.21676 | 1.36339 | 0.04253 |
| C | -2.34050 | 0.53926 | 0.03331 |
| C | -2.72894 | -0.12499 | 1.19692 |
| C | -3.10282 | 0.46831 | -1.13064 |
| C | -3.90221 | -0.88024 | 1.18599 |
| H | -2.12150 | -0.03916 | 2.09261 |
| C | -4.27737 | -0.28663 | -1.12773 |
| H | -2.77562 | 1.00632 | -2.01468 |
| C | -4.67713 | -0.96295 | 0.02646 |
| H | -4.21339 | -1.39894 | 2.08836 |
| H | -4.87904 | -0.34464 | -2.03038 |
| H | -5.59164 | -1.54889 | 0.02450 |

**SMe**

| | | | |
|---|---|---|---|
| C | -0.68466 | 0.99461 | -0.00028 |
| C | 0.69942 | 1.13892 | -0.00020 |
| C | 1.50382 | 0.00237 | 0.00003 |
| C | 0.95084 | -1.28010 | 0.00029 |
| C | -0.42853 | -1.41855 | 0.00026 |
| C | -1.26468 | -0.28437 | -0.00008 |
| H | -1.30240 | 1.88491 | -0.00046 |
| H | 1.16146 | 2.11863 | -0.00031 |
| H | 1.60491 | -2.14332 | 0.00050 |
| H | -0.86753 | -2.41216 | 0.00058 |
| N | 2.95953 | 0.15530 | 0.00001 |
| O | 3.41696 | 1.29981 | 0.00017 |
| O | 3.64376 | -0.86966 | -0.00019 |
| C | -3.75041 | 1.07227 | 0.00048 |
| H | -4.83106 | 0.91070 | 0.00083 |
| H | -3.47688 | 1.63294 | 0.89806 |
| H | -3.47763 | 1.63350 | -0.89698 |
| S | -3.01051 | -0.59403 | -0.00033 |

**SPh**

| | | | |
|---|---|---|---|
| C | -0.86785 | -0.63564 | 1.23889 |
| C | -2.15616 | -0.10719 | 1.22822 |
| C | -2.80842 | 0.04075 | 0.00543 |
| C | -2.21324 | -0.32125 | -1.20117 |
| C | -0.92248 | -0.84427 | -1.17900 |
| C | -0.24229 | -1.00119 | 0.03749 |
| H | -0.34237 | -0.76779 | 2.17887 |
| H | -2.65934 | 0.18481 | 2.14186 |

| | | | |
|---|---|---|---|
| H | -2.75948 | -0.19344 | -2.12770 |
| H | -0.43749 | -1.13528 | -2.10484 |
| N | -4.17342 | 0.59566 | -0.01170 |
| O | -4.66939 | 0.92099 | 1.06617 |
| O | -4.73203 | 0.69956 | -1.10277 |
| S | 1.38891 | -1.74703 | 0.06045 |
| C | 2.50885 | -0.33930 | 0.00717 |
| C | 2.09864 | 0.99488 | -0.07870 |
| C | 3.87674 | -0.64442 | 0.05143 |
| C | 3.05509 | 2.01222 | -0.11814 |
| H | 1.04430 | 1.24719 | -0.11611 |
| C | 4.82116 | 0.37884 | 0.01007 |
| H | 4.20082 | -1.68023 | 0.11774 |
| C | 4.41627 | 1.71303 | -0.07445 |
| H | 2.72517 | 3.04592 | -0.18504 |
| H | 5.87855 | 0.12954 | 0.04512 |
| H | 5.15469 | 2.50913 | -0.10589 |

**tBu**

| | | | |
|---|---|---|---|
| C | -0.28027 | 1.22606 | 0.00011 |
| C | 1.11354 | 1.22549 | 0.00009 |
| C | 1.78550 | 0.00803 | 0.00000 |
| C | 1.09381 | -1.20232 | -0.00008 |
| C | -0.29523 | -1.17761 | -0.00011 |
| C | -1.01739 | 0.03150 | -0.00003 |
| H | -0.79067 | 2.18177 | 0.00023 |
| H | 1.67963 | 2.14897 | 0.00012 |
| H | 1.64601 | -2.13409 | -0.00009 |
| H | -0.82629 | -2.12439 | -0.00020 |
| N | 3.25389 | -0.00365 | -0.00001 |
| O | 3.83629 | 1.08142 | -0.00030 |
| O | 3.81798 | -1.09847 | 0.00029 |
| C | -2.55549 | 0.00365 | -0.00002 |
| C | -3.16925 | 1.41673 | -0.00041 |
| H | -4.26194 | 1.34013 | -0.00030 |
| H | -2.87961 | 1.98972 | 0.88775 |
| H | -2.87976 | 1.98923 | -0.88895 |
| C | -3.05292 | -0.73876 | 1.26373 |
| H | -4.14879 | -0.77159 | 1.27494 |
| H | -2.68925 | -1.77069 | 1.30313 |
| H | -2.71920 | -0.23057 | 2.17541 |
| C | -3.05297 | -0.73955 | -1.26329 |
| H | -2.71916 | -0.23205 | -2.17532 |
| H | -2.68951 | -1.77159 | -1.30196 |
| H | -4.14884 | -0.77221 | -1.27451 |

**H – TS (ortho) [M06-2x/6-31+G(d,p)] (SCFE=-1715.599166) ; NumIM=1**

| | | | |
|---|---|---|---|
| C | 3.066309 | 0.460211 | -0.068949 |
| C | 2.177632 | -0.105687 | 0.875989 |
| C | 2.326306 | -1.503656 | 1.109912 |
| C | 3.154341 | -2.266766 | 0.321014 |
| C | 3.938233 | -1.684847 | -0.708364 |
| C | 3.896550 | -0.322580 | -0.895706 |
| C | 0.135530 | 0.044676 | -0.153982 |
| S | -1.135058 | -0.038671 | 1.016160 |
| N | 3.054899 | 1.868186 | -0.242657 |
| O | 3.830098 | 2.388550 | -1.057177 |
| Cl | 0.052669 | -1.265351 | -1.347828 |
| O | -0.970253 | 1.157903 | 1.869136 |
| O | -1.115780 | -1.362045 | 1.670396 |
| O | 2.256817 | 2.540529 | 0.419849 |
| H | 1.743561 | 0.534674 | 1.631602 |
| H | 4.499829 | 0.166470 | -1.651569 |
| H | 4.576071 | -2.304935 | -1.328220 |
| H | 0.111306 | 1.014750 | -0.649921 |
| H | 1.733356 | -1.964751 | 1.892805 |
| C | -2.752286 | 0.101466 | 0.253090 |
| C | -3.443402 | -1.052609 | -0.111714 |
| C | -3.252015 | 1.371105 | -0.038646 |
| C | -4.665519 | -0.929002 | -0.772911 |
| H | -3.032883 | -2.027029 | 0.132373 |
| C | -4.474771 | 1.482991 | -0.695747 |
| H | -2.692407 | 2.253362 | 0.257297 |
| C | -5.179656 | 0.334483 | -1.063538 |
| H | -5.216688 | -1.819821 | -1.056486 |
| H | -4.879835 | 2.465291 | -0.917078 |
| H | -6.132754 | 0.426473 | -1.574717 |
| H | 3.225075 | -3.335969 | 0.501311 |

**H – TS (para) [M06-2x/6-31+G(d,p)]; (SCFE=-1715.5967522); NumIM=1**

| | | | |
|---|---|---|---|
| C | 2.33804 | 1.51586 | -1.18124 |
| C | 1.57391 | 1.66544 | 0.01313 |
| C | 2.05620 | 1.03844 | 1.19545 |
| C | 3.11856 | 0.16535 | 1.14735 |
| C | 3.78782 | -0.04920 | -0.07190 |
| C | 3.39980 | 0.64388 | -1.23534 |
| C | -0.31490 | 0.45528 | -0.50922 |
| S | -1.64965 | 0.97051 | 0.45781 |
| Cl | 0.11253 | -1.24321 | -0.25926 |
| O | -1.91647 | 2.36689 | 0.04634 |
| O | -1.35355 | 0.71162 | 1.88125 |
| H | 0.90217 | 2.51036 | 0.10131 |

| | | | |
|---|---|---|---|
| H | 3.96347 | 0.50437 | -2.15048 |
| H | -0.52139 | 0.64991 | -1.56132 |
| H | 1.54328 | 1.21225 | 2.13520 |
| C | -3.14446 | 0.04398 | 0.10211 |
| C | -3.43257 | -1.10234 | 0.84150 |
| C | -3.94866 | 0.44059 | -0.96681 |
| C | -4.55599 | -1.85865 | 0.50740 |
| H | -2.79233 | -1.38410 | 1.67100 |
| C | -5.07047 | -0.31953 | -1.28895 |
| H | -3.70131 | 1.33789 | -1.52567 |
| C | -5.37281 | -1.46819 | -0.55387 |
| H | -4.79426 | -2.74957 | 1.07936 |
| H | -5.71028 | -0.01443 | -2.11062 |
| H | -6.24767 | -2.05789 | -0.80831 |
| H | 3.46595 | -0.34128 | 2.04034 |
| N | 4.88715 | -0.94251 | -0.12129 |
| O | 5.22951 | -1.53622 | 0.90930 |
| O | 5.47869 | -1.11196 | -1.19525 |
| H | 2.05144 | 2.06837 | -2.07015 |

## *Series 6*

Ground state structures (gas phase):

**6a**

| | | | |
|---|---|---|---|
| C | -0.46169 | -1.19942 | -0.00067 |
| C | 0.23395 | 0.01064 | -0.00014 |
| C | -0.45082 | 1.22239 | 0.00013 |
| C | -1.84061 | 1.16717 | 0.00022 |
| C | -2.46015 | -0.08597 | 0.00030 |
| N | -1.79641 | -1.24996 | -0.00021 |
| H | 0.09908 | 2.15602 | 0.00026 |
| H | 0.07996 | -2.13985 | -0.00038 |
| H | -2.43509 | 2.07512 | 0.00038 |
| H | -3.54588 | -0.15988 | 0.00016 |
| N | 1.70309 | 0.00630 | 0.00006 |
| O | 2.26803 | -1.08583 | 0.00074 |
| O | 2.27336 | 1.09649 | -0.00053 |

**6b**

| | | | |
|---|---|---|---|
| C | -0.42041 | 0.76036 | -0.01048 |
| C | 0.09475 | -0.54822 | 0.02274 |
| C | -0.79462 | -1.62095 | 0.04226 |
| C | -2.15994 | -1.36396 | 0.07215 |
| C | -2.57146 | -0.03196 | 0.06216 |
| N | -1.72214 | 0.99917 | 0.00600 |

| | | | |
|---|---|---|---|
| H | -0.39605 | -2.62883 | 0.03740 |
| H | -2.88326 | -2.17165 | 0.10135 |
| H | -3.62693 | 0.22826 | 0.09292 |
| N | 1.53082 | -0.87619 | 0.04209 |
| O | 2.29034 | -0.11601 | 0.63001 |
| O | 1.85886 | -1.92448 | -0.51467 |
| Cl | 0.59776 | 2.16845 | -0.15435 |

**6c**

| | | | |
|---|---|---|---|
| C | -2.20324 | -0.37197 | -0.01047 |
| C | -0.96415 | 0.26967 | -0.01158 |
| C | 0.22465 | -0.49589 | -0.01757 |
| C | 0.05608 | -1.89007 | -0.03336 |
| C | -1.23002 | -2.42187 | -0.04669 |
| N | -2.35634 | -1.69657 | -0.03650 |
| H | 0.91018 | -2.55536 | -0.03095 |
| H | -1.35913 | -3.50263 | -0.06075 |
| N | -0.96136 | 1.73367 | -0.02608 |
| O | -1.93588 | 2.29660 | 0.47804 |
| O | -0.01592 | 2.30903 | -0.55884 |
| H | -3.10182 | 0.23744 | 0.00392 |
| O | 1.40767 | 0.12677 | 0.02861 |
| C | 2.61703 | -0.65215 | 0.06804 |
| C | 3.77529 | 0.32598 | 0.12105 |
| H | 2.66906 | -1.28373 | -0.82803 |
| H | 2.60112 | -1.30323 | 0.95173 |
| H | 4.72260 | -0.22292 | 0.14578 |
| H | 3.76972 | 0.97668 | -0.75808 |
| H | 3.71139 | 0.95262 | 1.01543 |

**6d**

| | | | |
|---|---|---|---|
| C | 0.49713 | -1.24840 | 0.00005 |
| C | 1.11286 | 0.00588 | -0.00003 |
| C | 0.32803 | 1.15759 | -0.00006 |
| C | -1.05063 | 1.01418 | -0.00004 |
| C | -1.58223 | -0.29243 | 0.00007 |
| N | -0.82334 | -1.39504 | 0.00015 |
| H | -1.68768 | 1.88951 | -0.00008 |
| N | 2.56689 | 0.10990 | -0.00003 |
| O | 3.21519 | -0.93741 | -0.00026 |
| O | 3.05820 | 1.24036 | 0.00023 |
| H | 1.10085 | -2.15062 | 0.00016 |
| H | 0.80119 | 2.13241 | -0.00003 |
| O | -2.89966 | -0.56529 | 0.00009 |
| C | -3.83034 | 0.51371 | -0.00012 |
| H | -4.81654 | 0.04855 | -0.00062 |

| | | | |
|---|---|---|---|
| H | -3.72105 | 1.13562 | 0.89657 |
| H | -3.72025 | 1.13597 | -0.89646 |

**6e**

| | | | |
|---|---|---|---|
| C | 0.09585 | -0.35698 | 0.00003 |
| C | -0.56970 | -1.57496 | 0.00006 |
| C | -1.94389 | -1.28135 | -0.00001 |
| C | -2.06650 | 0.10158 | -0.00007 |
| N | -0.82844 | 0.67467 | -0.00007 |
| H | -0.08531 | -2.53942 | 0.00009 |
| H | -2.76149 | -1.98830 | -0.00002 |
| H | -2.95023 | 0.72430 | -0.00011 |
| C | -0.59319 | 2.11809 | 0.00010 |
| H | -1.56926 | 2.60765 | 0.00007 |
| H | -0.02947 | 2.41692 | 0.88484 |
| H | -0.02934 | 2.41711 | -0.88449 |
| N | 1.50153 | -0.15760 | -0.00002 |
| O | 1.93527 | 1.00534 | -0.00009 |
| O | 2.21199 | -1.16734 | 0.00003 |

**6f**

| | | | |
|---|---|---|---|
| C | 0.53847 | -0.80887 | -0.01260 |
| C | -0.48439 | 0.12325 | 0.00184 |
| C | 0.07980 | 1.42720 | 0.00288 |
| C | 1.44028 | 1.24503 | -0.01103 |
| N | 1.70934 | -0.11441 | -0.02405 |
| H | -0.46354 | 2.35943 | 0.00354 |
| H | 2.24846 | 1.96228 | -0.01566 |
| C | 3.03947 | -0.70292 | 0.02363 |
| H | 3.70734 | -0.16047 | -0.65088 |
| H | 3.45007 | -0.66816 | 1.03865 |
| H | 2.98348 | -1.74341 | -0.30212 |
| H | 0.49784 | -1.88673 | -0.01664 |
| N | -1.87595 | -0.20292 | 0.00285 |
| O | -2.18574 | -1.40025 | -0.00512 |
| O | -2.68165 | 0.73229 | 0.01301 |

**6g**

| | | | |
|---|---|---|---|
| C | 0.11094 | -0.35362 | 0.00018 |
| C | -0.54704 | -1.56932 | 0.00021 |
| C | -2.04131 | -0.05010 | -0.00021 |
| N | -0.86619 | 0.63047 | -0.00021 |
| H | -2.99134 | 0.46875 | -0.00041 |
| C | -0.72665 | 2.08611 | 0.00017 |
| H | -1.73237 | 2.51145 | -0.00044 |
| H | -0.18393 | 2.41685 | 0.88649 |

| | | | |
|---|---|---|---|
| H | -0.18260 | 2.41717 | -0.88518 |
| N | -1.89052 | -1.36752 | 0.00001 |
| H | -0.09915 | -2.55240 | 0.00041 |
| N | 1.50910 | -0.10157 | -0.00002 |
| O | 2.25115 | -1.08563 | -0.00012 |
| O | 1.89224 | 1.07688 | -0.00005 |

**6h**

| | | | |
|---|---|---|---|
| C | 0.53956 | -0.83064 | -0.00012 |
| C | -0.45765 | 0.11877 | 0.00001 |
| C | 1.33675 | 1.22219 | 0.00001 |
| N | 1.70047 | -0.10494 | -0.00015 |
| H | 2.07490 | 2.01338 | -0.00001 |
| C | 3.05746 | -0.63541 | 0.00008 |
| H | 3.75952 | 0.20058 | -0.00006 |
| H | 3.23077 | -1.24345 | 0.89259 |
| H | 3.23091 | -1.24384 | -0.89215 |
| H | 0.50867 | -1.90817 | -0.00017 |
| N | -1.87126 | -0.17205 | 0.00001 |
| O | -2.17783 | -1.37103 | 0.00010 |
| O | -2.66112 | 0.76511 | -0.00007 |
| N | 0.03511 | 1.38833 | 0.00009 |

**6i**

| | | | |
|---|---|---|---|
| C | -0.54590 | -0.83444 | -0.00003 |
| C | 0.47848 | 0.09964 | -0.00002 |
| N | -1.68621 | -0.11770 | -0.00003 |
| C | -3.05429 | -0.60895 | 0.00002 |
| H | -3.57450 | -0.24877 | 0.89108 |
| H | -3.57485 | -0.24784 | -0.89046 |
| H | -3.03770 | -1.70011 | -0.00056 |
| N | -1.46785 | 1.22685 | 0.00001 |
| C | -0.14841 | 1.36376 | 0.00001 |
| H | 0.31483 | 2.33958 | 0.00004 |
| H | -0.51719 | -1.91315 | -0.00006 |
| N | 1.87769 | -0.18655 | 0.00000 |
| O | 2.65178 | 0.77345 | -0.00002 |
| O | 2.21631 | -1.37444 | 0.00003 |