Supporting Information for

A computational mechanistic investigation into reduction of Pt(IV) prodrugs with two axial chlorides by biological reductants

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Contents:

Benchmark calculations. To realize which methods are more accurate, the single-point calculations were carried out at the M06/BS2, M06-D3/BS2, and B3LYP-D3-CPCM/BS2 levels using the SMD, IEFPMC, and CPMC solvation models for structures **1**, **3**, **13**, HAsc⁻ and **TS$_{13\text{-prod}}$** (see the following results). These calculations show that the overall activation energies are highly sensitive to the solvation model. The CPCM and IEFPCM models significantly underestimate activation barriers. In contrast, the results obtained from the SMD solvation model are in good agreement with the experimental data; $\Delta H^{\ddagger}$ and $\Delta G^{\ddagger}$ for reduction of **1** by ascorbate at pH 7.12 were measured by Dong et al. to be 13.4 ± 0.5 and 13.4 ± 0.5 + 2.7 ± 0.9 kcal/mol, respectively (for details see ref 6e). To this end, all the energies discussed in the text are from the B3LYP-D3-SMD/BS2//B3LYP-CPCM/BS1 calculations and, for the sake of comparison, the results obtained from the M06-D3-SMD/BS2//B3LYP-CPCM/BS1 calculations are reported in Fig. S4-S6.
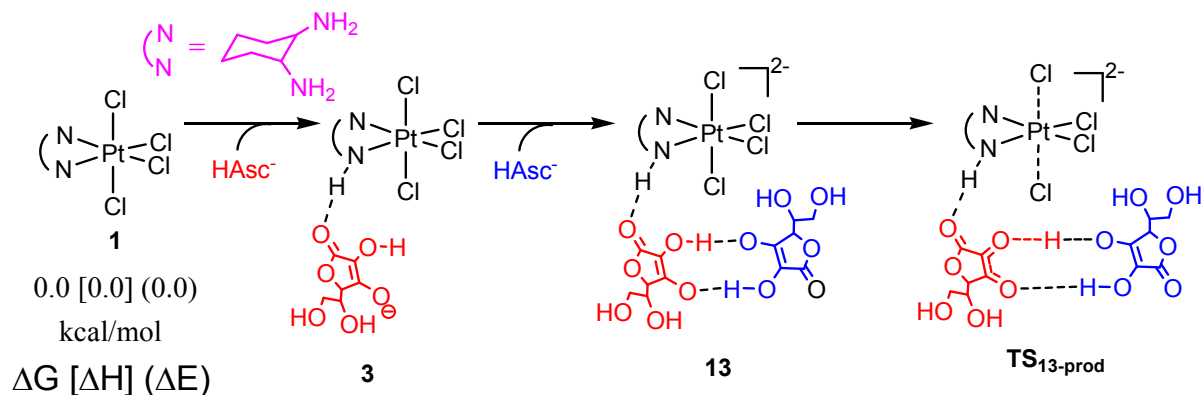
method (solvation model)	3	13	TS$_{13\text{-prod}}$	$\Delta G^{\ddagger}$	$\Delta H^{\ddagger}$	$\Delta E^{\ddagger}$
B3LYP-D3 (SMD)	3.5	4.6	13.0	13.0	11.3	14.3
	[-8.0]	[-20.4]	[-9.1]			
	(-9.3)	(-22.7)	(-8.4)			
M06-D3 (SMD)	1.4	3.0	12.5	12.5	12.3	15.3
	[-10.1]	[-22.0]	[-9.7]			
	(-11.4)	(-24.2)	(-8.9)			
B3LYP-D3 (IEFPCM)	-0.1	-1.1	3.8	4.9	7.8	10.8
	[-11.7]	[-26.1]	[-18.4]			
	(-13.0)	(-28.4)	(-17.6)			
M06 (IEFPCM)	1.2	2.6	7.8	7.8	8.1	11.1
	[-10.3]	[-22.4]	[-14.3]			
	(-11.6)	(-24.7)	(-13.6)			
B3LYP-D3 (CPCM)	-0.2	-1.3	3.6	4.9	7.8	10.9
	[-11.7]	[-26.3]	[-18.5]			
	(-13.0)	(-28.6)	(-17.7)			
M06 (CPCM)	1.2	2.3	7.7	7.7	8.2	11.2
	[-10.3]	[-22.7]	[-14.5]			
	(-11.6)	(-24.9)	(-13.7)			
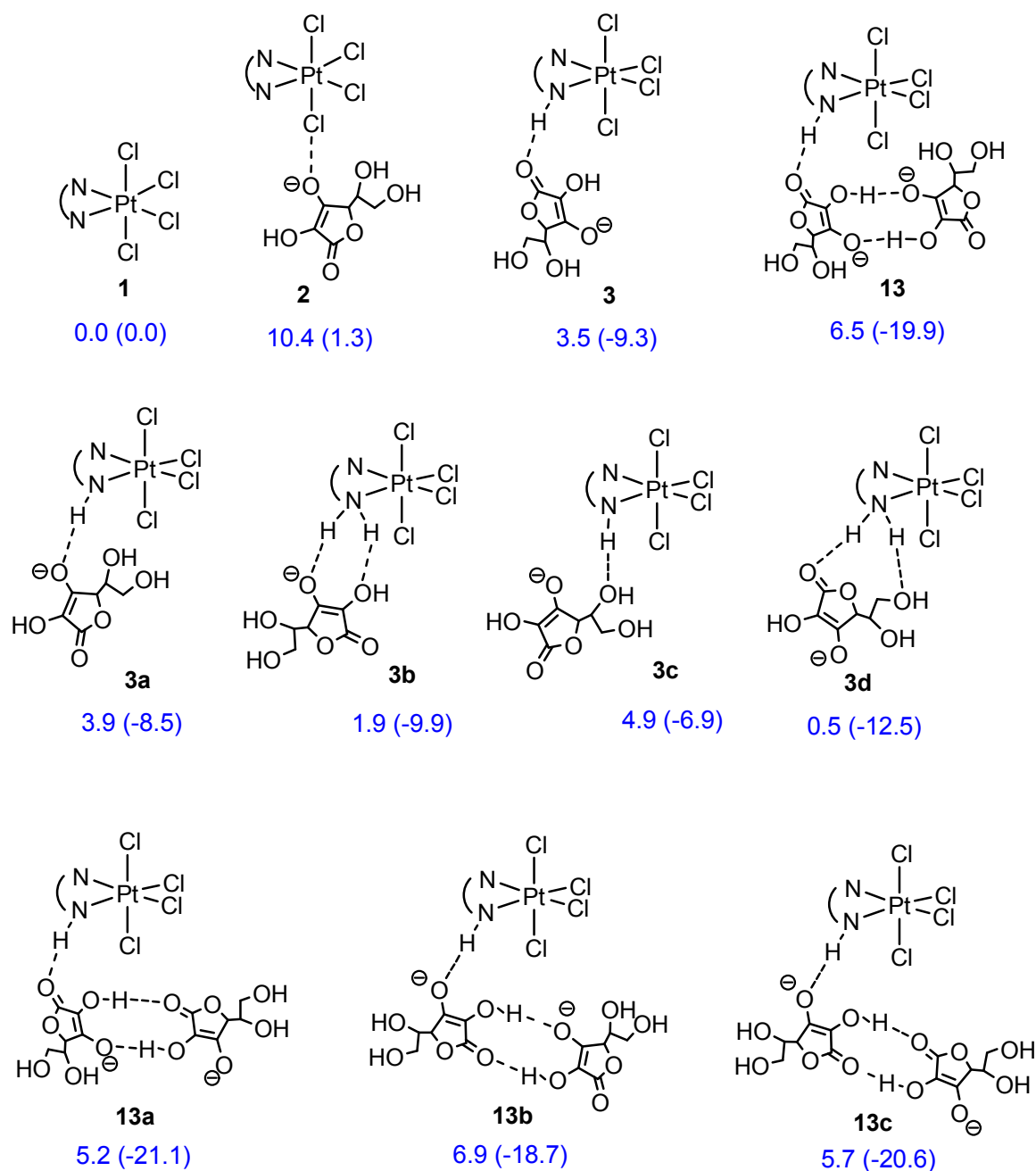
Fig S1. Relative stability of other possible outer-sphere complexes. The relative Gibbs and electronic energies (in parentheses) calculated at the B3LYP-D3-SMD/BS2//B3LYP-CPCM/BS1 level in water are given in kcal/mol. The calculations show that all the outer-sphere complexes are higher in energy than the reference point and thus their energies are not likely to affect the overall activation energies.

(a)

(b)
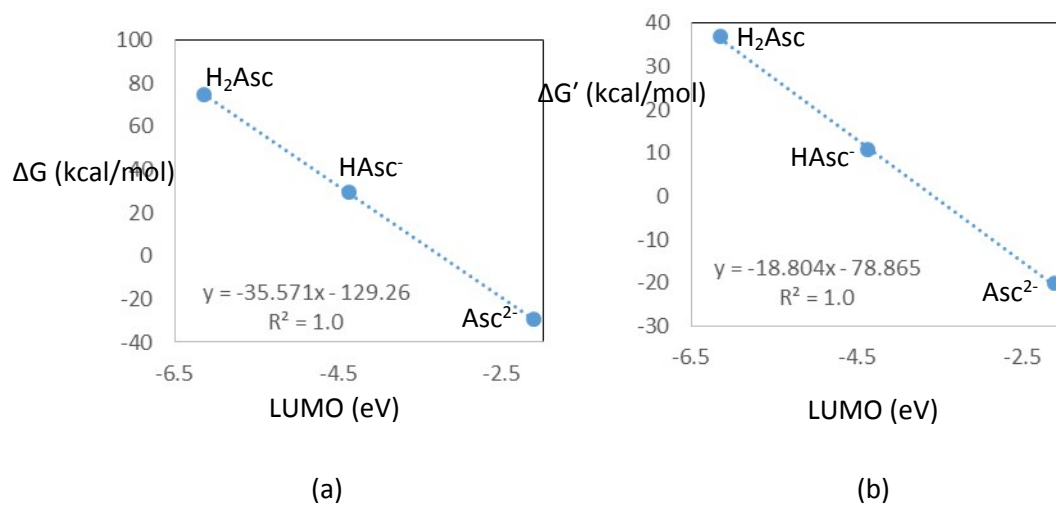
Fig. S2 Plots of the HOMO energies of H_2Asc, $HAsc^-$ and Asc^{2-} vs (a) ΔG_n and (b) $\Delta G_n'$ based on the reactions given in Scheme 2.
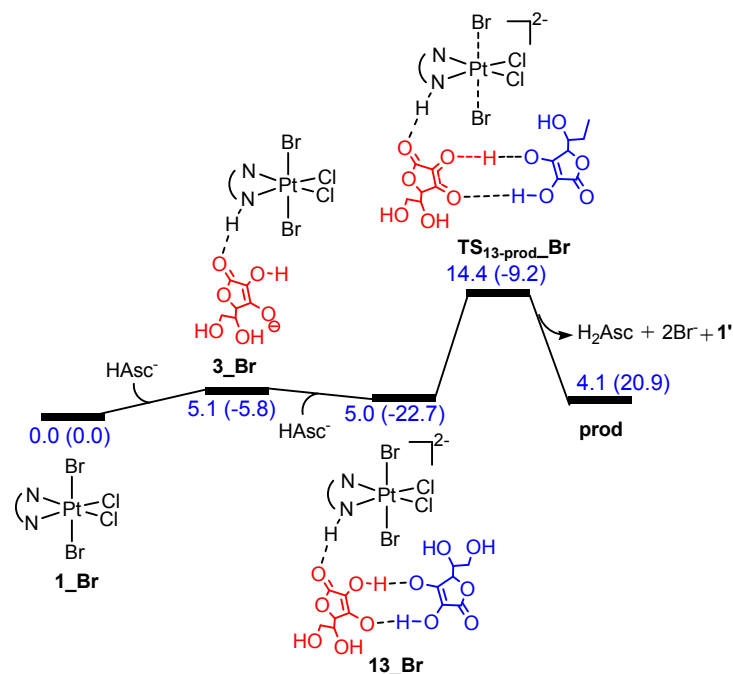
Fig. S3 Calculated energy profiles for reduction of the Pt(IV) complex **1_Br** by HAsc⁻ via base-assisted outer sphere mechanism where base is HAsc⁻. The relative Gibbs and electronic energies (in parentheses) calculated at the B3LYP-D3-SMD/BS2//B3LYP-CPCM/BS1 level in water are given in kcal/mol. Dong et al found that $\Delta H^{\ddagger}$ for reduction of cis,cis,trans-[Pt(NH₃)₂Cl₂Br₂] by ascorbate is about 0.8 kcal/mol lower in energy than that of cis-[Pt(NH₃)₂Cl₄].[6e] In good agreement with this experimental finding, the replacement of two axial chlorides in **1** with two bromides results in lowering the activation potential energy by 0.9 kcal/mol where base is a second HAsc⁻ (Fig. S3). This slight decrease in the activation energies can be ascribed to the fact that the LUMO of trans,cis-[Pt(dach)Br₂Cl₂] is about 0.01 eV lower in energy than that of [Pt(dach)Cl₄].
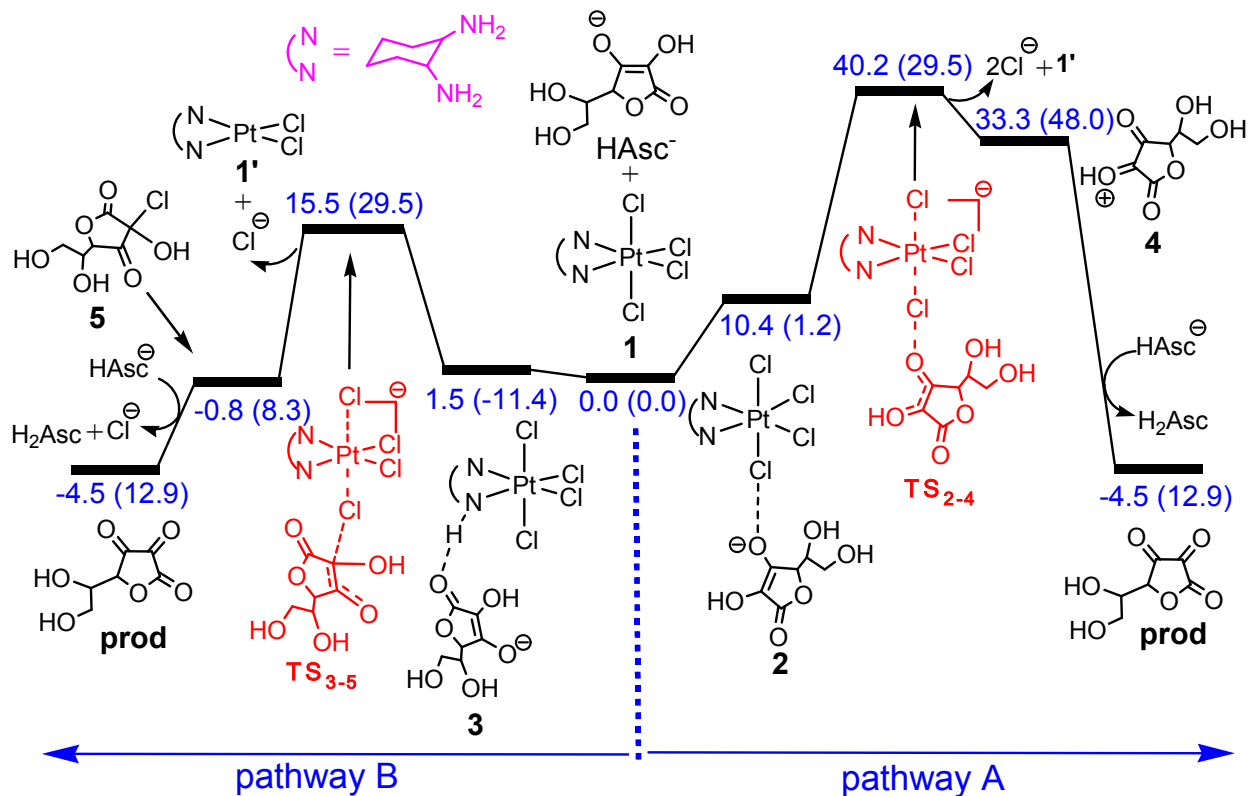
Fig. S4 Calculated energy profiles for Pt(IV) reduction by HAsc⁻ via inner sphere pathways A and B. The relative Gibbs and electronic energies (in parentheses) calculated at the M06-D3-SMD/BS2//B3LYP-CPCM/BS1 level in water are given in kcal/mol.
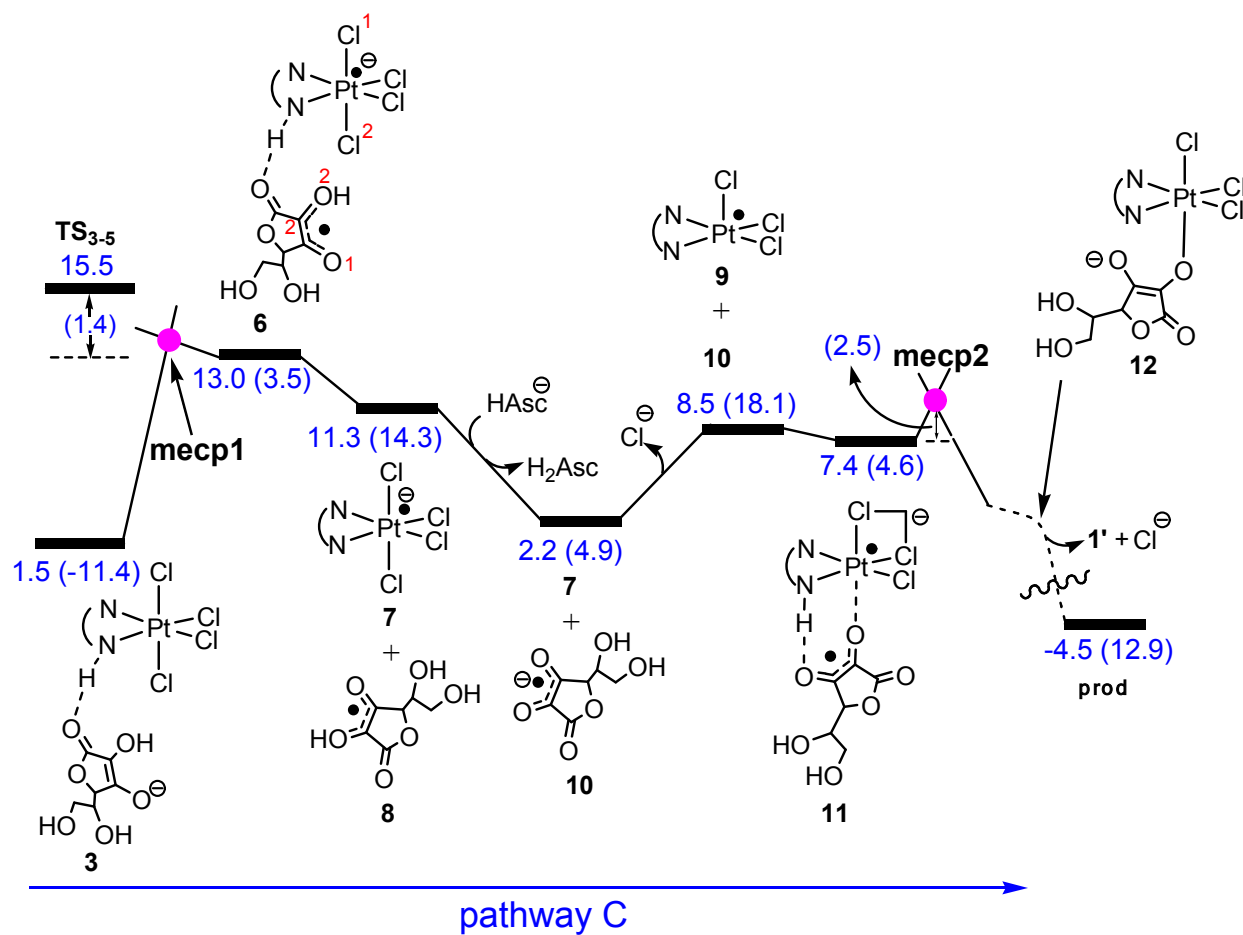
Fig. S5 Calculated energy profile for Pt(IV) reduction by HAsc⁻ via outer sphere mechanism (pathway C). The relative Gibbs and electronic energies (in parentheses) calculated at the M06-D3-SMD/BS2//B3LYP-CPCM/BS1 level in water are given in kcal/mol.
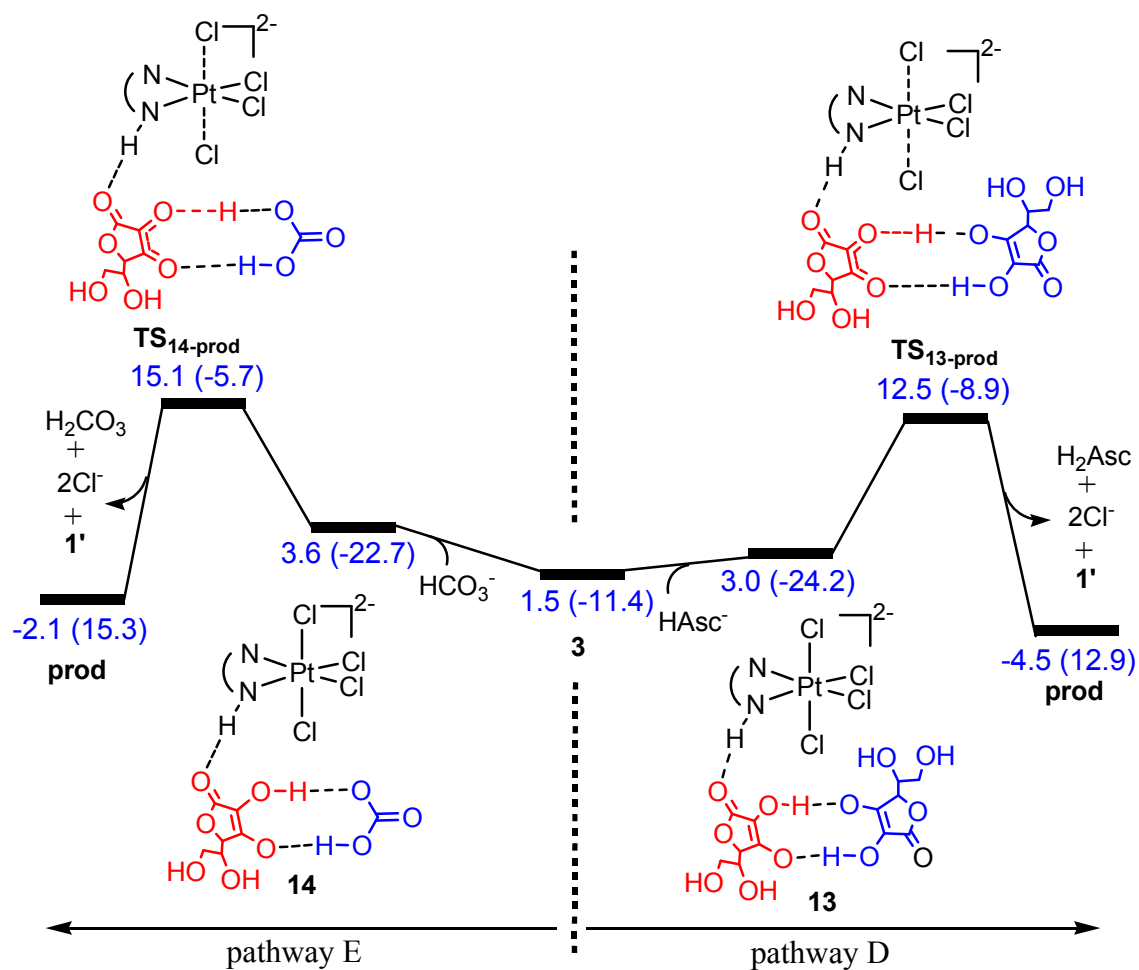
Fig. S6 Calculated energy profiles for Pt(IV) reduction by HAsc⁻ via base-assisted outer sphere mechanism where base is HAsc⁻ (pathway D) or HCO_3^- (pathway E). The relative Gibbs and electronic energies (in parentheses) calculated at the M06-D3-SMD/BS2//B3LYP-CPCM/BS1 level in water are given in kcal/mol.
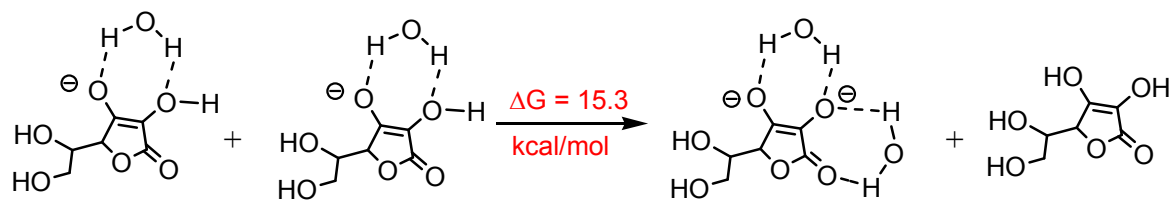
Scheme S1 Calculated reaction Gibbs energy for deprotonation of HAsc[-] by another HAsc[-] in the presence of explicit water molecules. The hydrogen-bond interaction of water molecules with the negatively charged enolate oxygen atoms of HAsc[-] and Asc[2-] leads to a decrease in the calculated Gibbs energy from 21.8 kcal/mol (Scheme 4) to 15.3 kcal/mol which is closer to the experimental value of 10 kcal/mol; the experimental value was estimated based on pKa values of H_2Asc (3.95) and HAsc[-] (11.24). The improvement of the reaction energy by considering explicit solvation effects is consistent with the results of Cramer, Truhlar et al who found that a more accurate value for pKa is obtained in the aqueous phase if the strong solute-solvent hydrogen bond interactions are taken into account (see: C. P. Kelly, C. J. Cramer, D. G. Truhlar *J. Phys. Chem. A* 2006, **110**, 2493). In addition, we have to note that the apparent discrepancy between the experimental and theoretical data on deprotonation energies can be partly attributed to the inability of the solvation model to predict an accurate solvation energy for the highly charged small molecule Asc[2-].

Computational details. Gaussian 09 [S1] was used to fully optimize all the structures reported in this paper at the B3LYP level of theory.[S2] The effective-core potential of Hay and Wadt with a double-ξ valence basis set (LANL2DZ) was chosen to describe Pt.[S3] The 6-31G(d) basis set was used for other atoms.[S4] Polarization functions were also added for Pt ($\xi_f = 0.993$).[S5] This basis set combination will be referred to as BS1. Frequency calculations were carried out at the same level of theory as those for the structural optimization. Transition structures were located using the Berny algorithm. Intrinsic reaction coordinate (IRC) calculations were used to confirm the connectivity between transition structures and minima.[S6] To further refine the energies obtained from the B3LYP-CPCM/BS1 calculations and to consider dispersive interactions,[S7] we carried out single-point energy calculations using the B3LYP-D3 functional for all of the structures with a larger basis set (BS2). BS2 utilizes the def2-QZVP basis set [S8] on Pt and 6-311+G(2d,p) on the other atoms. Effective core potentials including scalar relativistic effects were used for the platinum atom. The potential and Gibbs free energies obtained from the B3LYP-D3-CPCM/BS2//B3LYP-CPCM/BS1 calculations are used for interpreting the obtained results. For all the calculations solvent effects were considered with water as the solvent (the CPCM solvation model [S9a] for optimizations and the SMD solvation model[S9b] for single points). The benchmark calculations show that the activation energies obtained from the SMD solvation model are in better agreement with experiment when compared to other models such as CPCM and PCM (vide supra). The atomic orbital populations were calculated on the basis of natural bond orbital (NBO) analyses.[S10] Minimum energy crossing points (MECPs) between closed shell singlet and triplet states were located using the code of Harvey et al [S11] at the B3LYP-D3-CPCM/BS2 level. Since the MECPs do not correspond to stationary points, their energies are reported uncorrected. To estimate more accurately the relative energies of the MECPs in Figure 2, the stationary points **TS$_{3-5}$** and **11** are also optimized using B3LYP-D3-CPCM/BS2. To assess how sensitive the relative energies of the MECPs to the solvation model are, B3LYP-D3-SMD/BS2 was used to calculate **mecp1** and to optimize **TS$_{3-5}$**. The results show that there is no significant dependence of the relative energies on the solvation model. Using B3LYP-D3-CPCM/BS2, **mecp1** is calculated to be 1.4 kcal/mol lower in energy than **TS$_{3-5}$** while using B3LYP-D3-SMD/BS2, **mecp1** is about 1.7 kcal/mol more stable than **TS$_{3-5}$**.

(S1) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A.; , Jr., Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev,

O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian 09, Revision D.01; Gaussian, Inc.: Wallingford, CT, **2009**.

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Table S1. Cartesian coordinates and total energies for all of the calculated structures in water.

1
E (B3LYP-CPCM/BS1) = -2306.691272 au
H (B3LYP-CPCM/BS1) = -2306.456888 au
G (B3LYP-CPCM/BS1) = -2306.517752 au
E (B3LYP-D3-CPCM/BS2//B3LYP-CPCM/BS1) = -2307.243049 au
E (B3LYP-D3-SMD/BS2//B3LYP-CPCM/BS1) = -2307.250981 au
E (M06-D3-SMD/BS2//B3LYP-CPCM/BS1) = -2306.776719 au

```
 Pt                 -0.79434400    -0.00012700    -0.00008300
 N                   0.75959300    -0.76048500     1.15432000
 N                   0.75946900     0.76039100    -1.15442500
 Cl                 -2.42861900    -0.96080000     1.44051400
 Cl                 -2.42915600     0.96046300    -1.44020900
 Cl                 -0.72520800    -1.99299400    -1.31913100
 C                   2.04336900     0.66712500    -0.37711200
 C                   2.04353300    -0.66685000     0.37725900
 C                   3.28787800     0.80571500    -1.25969700
 H                   2.00358100     1.48826100     0.34512000
 C                   3.28790300    -0.80525600     1.25992800
 H                   2.00392900    -1.48787600    -0.34507900
 C                   4.55643600     0.65704400    -0.39803300
 C                   4.55656100    -0.65622500     0.39848600
 H                   3.27600800    -1.77706800     1.76481700
 H                   3.27091600    -0.02966300     2.03725000
 H                   5.43680500     0.70431700    -1.04790700
 H                   4.62619800     1.50795900     0.29252600
 H                   5.43687300    -0.70326400     1.04846200
 H                   4.62663800    -1.50710500    -0.29207400
 H                   0.80062800    -0.21040100     2.01857800
 H                   0.55391100    -1.72731000     1.41967100
 H                   0.80094200     0.21034200    -2.01860400
 H                   0.55357300     1.72730700    -1.41937400
 H                   3.27120500     0.02996600    -2.03689400
 H                   3.27588900     1.77741000    -1.76477700
 Cl                 -0.72677100     1.99323600     1.31885400
```

HAsc⁻
E (B3LYP-CPCM/BS1) = -684.2839657 au
H (B3LYP-CPCM/BS1) = -684.134372 au
G (B3LYP-CPCM/BS1) = -684.184998 au
E (B3LYP-D3-SMD/BS2//B3LYP-CPCM/BS1) = -684.600352 au
E (M06-D3-SMD/BS2//B3LYP-CPCM/BS1) = -684.211553 au

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 H                   2.83151500     0.75899700     1.51363300
 H                   1.10293300     1.14356300     1.62535700
 O                   2.64764700    -0.49704700    -0.87780900
 H                   2.07720900    -1.26842700    -1.04364500
 O                   1.51961200    -0.84518700     1.71031500
 H                   2.13228400    -1.45541700     1.26670300
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O                     -2.86475400      0.51009500      0.72339500
O                     -0.63389300      2.46722100     -0.18264200
H                      0.49117100      0.66178200     -2.04684200
H                     -3.27276100     -0.36903400      0.82258100
C                      1.77941500      0.50976600     -0.33788900
O                     -0.03382800     -0.99349800     -0.94717100
C                     -1.66573600      0.27423900      0.06215500
C                     -0.71173100      1.21922200     -0.31349800
C                      0.39363600      0.38726000     -0.98823400
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C                     -1.26633400     -1.03497800     -0.29036200
C                      1.82494000      0.44457500      1.19463600
H                      2.18783100      1.48320300     -0.63490100
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2

E (B3LYP-CPCM/BS1) = -2990.978764 au

H (B3LYP-CPCM/BS1) = -2990.592598 au

G (B3LYP-CPCM/BS1) = -2990.691764 au

E (B3LYP-D3-CPCM/BS2//B3LYP-CPCM/BS1) = -2991.828839 au

E (B3LYP-D3-SMD/BS2//B3LYP-CPCM/BS1) = -2991.849282 au

E (M06-D3-SMD/BS2//B3LYP-CPCM/BS1) = -2990.986308 au

```
Cl                    -0.23778900     -0.11076900     -0.49253800
Pt                     1.99951900     -0.84297200      0.06162800
Cl                     1.16957300     -2.22593900      1.82180400
Cl                     1.88856900     -2.59552600     -1.55559100
Cl                     4.33043700     -1.40084500      0.62124200
N                      2.14268700      0.79644200      1.33316900
N                      2.73714100      0.49461600     -1.34922400
C                      2.62124300      1.89170400     -0.81141600
C                      2.98133700      1.85757900      0.67785800
C                      3.48826600      2.90148400     -1.56932400
H                      1.56390200      2.15356600     -0.91550700
C                      2.81085100      3.23747500      1.32060400
H                      4.01554500      1.51705500      0.78884800
C                      3.34201100      4.29718900     -0.93436600
C                      3.66328300      4.27659900      0.56790200
H                      3.10080500      3.19101000      2.37595900
H                      1.75175100      3.52689900      1.28361000
H                      4.00433600      4.99880700     -1.45289800
H                      2.31594400      4.65786100     -1.08673200
H                      3.49118100      5.26604200      1.00515400
H                      4.72714800      4.04604900      0.71382800
H                      1.19050200      1.12999500      1.51342100
H                      2.54246300      0.50965300      2.23032000
H                      3.71391900      0.24025300     -1.52729600
H                      2.22724500      0.39400900     -2.23047200
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H                      3.19234000      2.92338600     -2.62378900
H                     -6.48335600      3.05422000     -0.98663500
H                     -5.48307000      1.76365600     -1.68091000
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O              -6.22230800     2.24098300     1.57274500
H              -6.53402900     1.36993500     1.87482100
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H              -7.77653100     1.33461700    -0.09678900
O              -3.84652500    -2.05031300    -1.58373700
O              -2.87176200     0.82412800    -1.04589900
H              -3.88318400     0.87896400     1.60441600
H              -4.37511200    -2.85203300    -1.41473800
C              -5.33994800     1.98086100     0.47381900
O              -5.46346600    -0.35414000     1.14934100
C              -4.24820900    -1.13582100    -0.63739100
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C              -4.54717800     0.69513100     0.75051000
O              -5.94098500    -2.46433300     0.42091900
C              -5.27843100    -1.43510900     0.29940200
C              -6.13212900     2.02098700    -0.83932800
H              -4.61474800     2.80277500     0.44283300
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3

E (B3LYP-CPCM/BS1) = -2990.994019 au

H (B3LYP-CPCM/BS1) = -2990.608018 au

G (B3LYP-CPCM/BS1) = -2990.701124 au

E (B3LYP-D3-CPCM/BS2//B3LYP-CPCM/BS1) = -2991.849508 au

E (B3LYP-D3-SMD/BS2//B3LYP-CPCM/BS1) = -2991.866156 au

E (M06-D3-SMD/BS2//B3LYP-CPCM/BS1) = -2991.006437 au

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Cl              0.65459600    -1.68762800    -1.15475700
Pt              2.19272700    -0.22226200    -0.06081300
Cl              2.84866200    -1.93210900     1.46854500
Cl              3.86695600    -0.82697100    -1.67024000
Cl              3.70332500     1.32828500     0.97126600
N               0.72075200     0.46581900     1.23577100
N               1.48598100     1.30502800    -1.27794100
C               0.17445500     1.80234800    -0.73115000
C               0.30287700     1.83850200     0.79446000
C              -0.22256600     3.16633100    -1.30191600
H              -0.56836100     1.04647100    -1.00373500
C              -0.99119000     2.31777500     1.46515400
H               1.12555800     2.50885100     1.06459700
C              -1.52931700     3.64316900    -0.64153400
C              -1.40449300     3.68538900     0.88917300
H              -0.83166400     2.38957300     2.54721500
H              -1.78718800     1.58796900     1.29196500
H              -1.78570100     4.63529900    -1.02931400
H              -2.34399300     2.96630000    -0.92999400
H              -2.35872100     3.98558900     1.33659000
H              -0.66628800     4.44718800     1.17548200
H              -0.09525300    -0.20044900     1.26624900
H               1.11799400     0.49834200     2.17821400
H               2.19321500     2.04671700    -1.28955500
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```
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H              -0.34125500      3.09351800     -2.38863600
H              -6.56910600      0.73129600      0.54345000
H              -5.51057400     -0.58082700      1.11282900
O              -4.69490400      1.60199500     -1.30033600
H              -4.45507600      2.10589400     -0.49847500
O              -4.74533400      1.35407800      1.33244500
H              -5.32867700      1.80901700      1.95820300
O              -3.05538400     -3.66029100      1.02715200
O              -4.94278300     -2.74809100     -1.23475300
H              -3.36245600     -0.52970600     -1.98515900
H              -2.32457000     -3.56474600      1.66323900
C              -4.95536600      0.28899500     -0.81252100
O              -2.65894100     -0.24261900     -0.07164200
C              -3.16214800     -2.43422100      0.39252700
C              -4.05108600     -2.10161000     -0.63963800
C              -3.73451700     -0.62758700     -0.95825800
O              -1.44873100     -1.24843600      1.58019900
C              -2.35016400     -1.33452300      0.71793400
C              -5.52834700      0.39389000      0.61040700
H              -5.72232400     -0.16088100     -1.45490800
```

4

E (B3LYP-CPCM/BS1) = -683.9141946 au

H (B3LYP-CPCM/BS1) = -683.762569 au

G (B3LYP-CPCM/BS1) = -683.809029 au

E (B3LYP-D3-CPCM/BS2//B3LYP-CPCM/BS1) = -684.1801163 au

E (B3LYP-D3-SMD/BS2//B3LYP-CPCM/BS1) = -684.2097785 au

E (M06-D3-SMD/BS2//B3LYP-CPCM/BS1) = -683.8197394 au

```
H               1.84152600      0.31639400      2.19017200
H               1.20434800      1.80102700      1.42080300
O               2.70981000     -0.85693200      0.04665000
H               2.15583600     -1.65243000      0.12675100
O              -0.13016900      0.24953700      1.52306100
H              -0.19541900     -0.57055800      2.06033300
O              -2.35222400      0.62795200      0.62337400
O              -0.62903100      2.18040200     -1.16998900
H               1.19340100      0.25568700     -2.10498300
H              -2.90454800     -0.13482800      0.90146900
C               1.90433000      0.28587000     -0.00834400
O               0.20457500     -1.18768200     -0.99544600
C              -1.16832900      0.23491400      0.23441400
C              -0.36161200      1.08490600     -0.76564700
C               0.79761200      0.15462100     -1.09698300
O              -1.67224700     -2.12411800     -0.12050600
C              -0.94840500     -1.18475400     -0.29425100
C               1.29257500      0.71859000      1.34044300
H               2.56212500      1.10656000     -0.30949400
```

Cl⁻

E (B3LYP-CPCM/BS1) = -460.3659217 au
H (B3LYP-CPCM/BS1) = -460.363561 au
G (B3LYP-CPCM/BS1) = -460.380944 au
E (B3LYP-D3-CPCM/BS2//B3LYP-CPCM/BS1) = -460.414794 au
E (B3LYP-D3-SMD/BS2//B3LYP-CPCM/BS1) = -460.407712 au
E (M06-D3-SMD/BS2//B3LYP-CPCM/BS1) = -460.366135 au

1'
E (B3LYP-CPCM/BS1) = -1386.293882 au
H (B3LYP-CPCM/BS1) = -1386.066017 au
G (B3LYP-CPCM/BS1) = -1386.119861 au
E (B3LYP-D3-CPCM/BS2//B3LYP-CPCM/BS1) = -1386.752583 au
E (B3LYP-D3-SMD/BS2//B3LYP-CPCM/BS1) = -1386.755940 au
E (M06-D3-SMD/BS2//B3LYP-CPCM/BS1) = -1386.35977 au

```
 Pt                 0.93581400      -0.00001400       0.00003800
 N                 -0.61033300       1.37222400       0.06406200
 N                 -0.61032400      -1.37228100      -0.06403900
 Cl                 2.55998400       1.74860700       0.04659400
 Cl                 2.56013500      -1.74850000      -0.04672800
 C                 -1.89608000      -0.69799800       0.31633300
 C                 -1.89606200       0.69796800      -0.31632600
 C                 -3.14502800      -1.48947900      -0.08307700
 H                 -1.86069600      -0.59056400       1.40645500
 C                 -3.14501600       1.48947000       0.08303900
 H                 -1.86067300       0.59050200      -1.40644700
 C                 -4.41543500      -0.70796000       0.29905700
 C                 -4.41542000       0.70797000      -0.29912600
 H                 -3.13309600       2.47002300      -0.40622900
 H                 -3.12912500       1.66675500       1.16778900
 H                 -5.29791900      -1.26149900      -0.04042700
 H                 -4.48458500      -0.64380300       1.39357100
 H                 -5.29790800       1.26151500       0.04033800
 H                 -4.48454800       0.64381700      -1.39364200
 H                 -0.67506400       1.75241900       1.01255500
 H                 -0.42585400       2.16952000      -0.54850400
 H                 -0.67504400      -1.75241100      -1.01255400
 H                 -0.42591100      -2.16962400       0.54849000
 H                 -3.12911500      -1.66675300      -1.16782700
 H                 -3.13314200      -2.47003400       0.40618700
```

5
E (B3LYP-CPCM/BS1) = -1144.341313 au
H (B3LYP-CPCM/BS1) = -1144.187723 au
G (B3LYP-CPCM/BS1) = -1144.242412 au
E (B3LYP-D3-CPCM/BS2//B3LYP-CPCM/BS1) = -1144.659068 au
E (B3LYP-D3-SMD/BS2//B3LYP-CPCM/BS1) = -1144.670091 au
E (M06-D3-SMD/BS2//B3LYP-CPCM/BS1) = -1144.249118 au

```
Cl                    2.80175800      -0.46771600     -0.77961800
H                    -3.44900800      -0.56205300      1.33803400
H                    -1.76215200      -0.27235700      1.80984700
O                    -2.93575700      -0.48550600     -1.33578700
H                    -3.12183100       0.46145700     -1.18434900
O                    -2.65395800       1.25264100      0.68239100
H                    -3.31225600       1.63468800      1.28253000
O                     1.92079700       0.30654100      1.66263800
O                     0.39758400      -2.08705900      0.99814900
H                    -0.43952400      -1.17235100     -1.64336900
H                     2.24936700       1.22778500      1.68598900
C                    -2.07461900      -0.85207300     -0.27838400
O                    -0.32334800       0.77056700     -0.95016700
C                     1.44998500       0.05290800      0.42292200
C                     0.41968900      -1.07656900      0.34095300
C                    -0.60505700      -0.63867700     -0.70218100
O                     1.06787600       2.37934100     -0.19118200
C                     0.74015500       1.22198200     -0.26447700
C                    -2.49822900      -0.12865500      1.00691900
H                    -2.17156700      -1.93168300     -0.11803800
```

TS₂₋₄

E (B3LYP-CPCM/BS1) = -2990.962577 au

H (B3LYP-CPCM/BS1) = -2990.578031 au

G (B3LYP-CPCM/BS1) = -2990.673074 au

E (B3LYP-D3-CPCM/BS2//B3LYP-CPCM/BS1) = -2991.801721 au

E (B3LYP-D3-SMD/BS2//B3LYP-CPCM/BS1) = -2991.808474 au

E (M06-D3-SMD/BS2//B3LYP-CPCM/BS1) = -2990.941234 au

```
Cl                    0.58723700      -0.41049800     -0.76534500
Pt                   -1.76155900      -0.98745300     -0.00146700
Cl                   -1.94643400      -2.86181600     -1.47337100
Cl                   -0.94243700      -2.32871700      1.79492100
Cl                   -4.72541100      -0.44002100      1.56210200
N                    -2.46761000       0.30264700     -1.46957200
N                    -1.80298400       0.72382100      1.15892000
C                    -1.88792200       1.92766900      0.27131500
C                    -2.88784800       1.60132800     -0.84365500
C                    -2.29374300       3.20314100      1.01719300
H                    -0.89012500       2.05220600     -0.16268900
C                    -3.00247700       2.75091600     -1.84867800
H                    -3.86064700       1.39711600     -0.38554500
C                    -2.42459300       4.37529000      0.02620000
C                    -3.39642900       4.04832900     -1.11823200
H                    -3.74335300       2.50041500     -2.61630000
H                    -2.03883900       2.89031800     -2.35797800
H                    -2.76169100       5.26820800      0.56429200
H                    -1.43484700       4.61073300     -0.38849900
H                    -3.42493200       4.87431100     -1.83749700
H                    -4.41328200       3.94246100     -0.71657000
H                    -1.70449200       0.44584900     -2.13790200
```

```
H            -3.23970600   -0.12148600   -1.98848500
H            -2.67273200    0.61196800    1.70706900
H            -1.00772200    0.78109000    1.79832500
H            -3.25304500    3.03452800    1.52465700
H            -1.55138300    3.43204400    1.79019800
C             3.46991500    0.51914200   -0.37269600
O             4.20747600   -2.58907300   -0.41059800
H             3.97311200    3.65766000    0.05499100
O             3.51152900    2.97273400   -0.46982500
C             3.83687700    1.78507100    0.05746700
C             4.10377100   -0.46009400    0.61642700
C             4.71380400    1.67547200    1.21489600
O             4.84789700    0.36598300    1.55419300
O             5.23934600    2.58983400    1.82769200
H             3.32578600   -0.98122400    1.18610700
C             5.04629700   -1.52856100    0.03581300
H             5.68250000   -1.86296000    0.87082300
C             5.93877200   -1.03324800   -1.11180700
H             5.30607900   -0.72231100   -1.94740500
H             6.56414700   -1.87115500   -1.45780000
O             6.72987800    0.09569100   -0.76292100
H             7.32544400   -0.16716500   -0.04245400
H             4.77809900   -3.32417700   -0.68754800
O             2.77620100    0.17718300   -1.38322400
```

TS$_{3-5}$

E (B3LYP-CPCM/BS1) = -2990.987589 au

H (B3LYP-CPCM/BS1) = -2990.602480 au

G (B3LYP-CPCM/BS1) = -2990.696284 au

E (B3LYP-D3-CPCM/BS2//B3LYP-CPCM/BS1) = -2991.830799 au

E (B3LYP-D3-SMD/BS2//B3LYP-CPCM/BS1) = -2991.843164 au

E (M06-D3-SMD/BS2//B3LYP-CPCM/BS1) = -2990.98231 au

```
Cl            0.33518600   -1.40598900    0.00483100
Pt           -2.06419300   -0.46593200    0.11459000
Cl           -2.83064400   -2.05090500   -1.51116900
Cl           -2.73396000   -1.82898700    1.96718500
Cl           -4.34515000    1.01369700    0.11893300
N            -1.35949100    0.81918000   -1.36726600
N            -1.37361700    1.02919700    1.37896100
C            -0.46150400    1.94536400    0.61809200
C            -1.07574200    2.16639200   -0.76854100
C            -0.20030200    3.27638100    1.32982400
H             0.47949200    1.39734300    0.50777900
C            -0.16393200    3.03078700   -1.64593100
H            -2.05474600    2.64143600   -0.65086000
C             0.71435800    4.16075800    0.46191200
C             0.13269900    4.36947700   -0.94493600
H            -0.64201100    3.20301100   -2.61702900
H             0.77249400    2.48810800   -1.83352800
H             0.86136000    5.12670500    0.95774300
```

```
H                      1.70392700      3.68967700      0.38528100
H                      0.82828900      4.95271000     -1.55866400
H                     -0.79405500      4.95530300     -0.87415100
H                     -0.50317100      0.40680600     -1.75342200
H                     -2.03727000      0.89543600     -2.12852300
H                     -2.21117500      1.52572600      1.69961300
H                     -0.90711100      0.64215100      2.20207800
H                     -1.15524300      3.78974200      1.50832100
H                      0.25770200      3.08971600      2.30785400
H                      7.00194000     -0.37004700      0.73868000
H                      5.88986800     -1.32580600     -0.26445000
O                      5.04974600      1.14237200      1.86259500
H                      5.22399400      1.70320700      1.08323800
O                      5.91502300      0.73327800     -0.65847500
H                      6.78243500      0.86961900     -1.06886300
O                      2.56130000     -2.65809100     -1.86554900
O                      3.68776900     -2.92462300      0.93424400
H                      2.84993000     -0.29463200      1.76233600
H                      2.23122600     -2.21635300     -2.67287000
C                      4.95380200     -0.17092600      1.33623900
O                      3.07310300      0.42370700     -0.15424500
C                      2.68377100     -1.71596600     -0.91719300
C                      3.31897200     -1.89767400      0.36121800
C                      3.50725900     -0.47432800      0.90613000
O                      2.29190400      0.22564200     -2.27827300
C                      2.65926700     -0.29313400     -1.23399700
C                      6.01975400     -0.36434200      0.25073000
H                      5.16742200     -0.87368800      2.14965700
```

H$_2$Asc
E (B3LYP-CPCM/BS1) = -684.7486471 au
H (B3LYP-CPCM/BS1) = -684.586226 au
G (B3LYP-CPCM/BS1) = -684.637248 au
E (B3LYP-D3-CPCM/BS2//B3LYP-CPCM/BS1) = -685.0390767 au
E (B3LYP-D3-SMD/BS2//B3LYP-CPCM/BS1) = -685.0541063 au
E (M06-D3-SMD/BS2//B3LYP-CPCM/BS1) = -684.6637682 au
```
O                      0.82240300     -1.68024900      1.44224900
C                      1.78675500     -0.69212400      1.10783100
C                      1.82666000     -0.34636600     -0.38870900
O                      2.77210600      0.68911400     -0.63203700
C                      0.49595900      0.16903100     -0.97124900
O                     -0.39977100     -0.94705300     -1.17574100
C                     -1.56706000     -0.72088500     -0.50303400
O                     -2.49367800     -1.50980400     -0.49341200
C                     -1.50003400      0.58223300      0.14394400
O                     -2.52492200      1.09520500      0.87271100
C                     -0.29765800      1.12695600     -0.12127500
O                      0.24257900      2.30561600      0.23597900
H                     -0.39687800      2.80138600      0.77817000
H                     -3.25012100      0.44390300      0.84235000
```

```
 H                    0.71741900      0.60411200     -1.95269900
 H                    2.07971100     -1.25071800     -0.96396100
 H                    1.52397500      0.20342200      1.67822500
 H                    2.79887000     -0.99745400      1.41746200
 H                    1.05936600     -2.49984300      0.97872000
 H                    3.65019400      0.35947800     -0.38130700
```

prod

E (B3LYP-CPCM/BS1) = -683.5101495 au

H (B3LYP-CPCM/BS1) = -683.371985 au

G (B3LYP-CPCM/BS1) = -683.421923 au

E (B3LYP-D3-CPCM/BS2//B3LYP-CPCM/BS1) = -683.8021355 au

E (B3LYP-D3-SMD/BS2//B3LYP-CPCM/BS1) = -683.8108747 au

E (M06-D3-SMD/BS2//B3LYP-CPCM/BS1) = -683.4234063 au

```
 C                   -0.14575700      1.14494500     -0.36194100
 O                    2.89992900      0.04281300     -0.78961500
 O                   -2.43134000      1.35459500      0.53148500
 C                   -1.55642400      0.69579800      0.03361600
 C                    0.53395800     -0.07948800     -0.96913300
 C                   -1.64270800     -0.78106800     -0.36975300
 O                   -0.47226400     -1.13067200     -0.97936000
 O                   -2.55682400     -1.54304500     -0.21890800
 H                    0.82909300      0.11564700     -2.00511100
 C                    1.77577000     -0.59574300     -0.21130100
 H                    1.79541000     -1.68234200     -0.39629100
 C                    1.68469400     -0.31601200      1.29785200
 H                    1.86365500      0.74902600      1.46404400
 H                    2.45778500     -0.88087100      1.84060200
 O                    0.38474700     -0.58268800      1.81563100
 H                    0.22745400     -1.54091200      1.79944800
 H                    3.69966800     -0.26014900     -0.33166600
 O                    0.32946900      2.24512400     -0.22011600
```

mecp1
```
Energy of singlet state calculated at B3LYP-D3-CPCM/BS2: -2991.8347154000
Energy of triplet state calculated at B3LYP-D3-CPCM/BS2: -2991.8347259600
 17      0.0456504     -1.7086118     -0.8279813
 78      2.0787150     -0.2874962     -0.0933510
 17      2.7896355     -1.8740112      1.5223270
 17      3.4111705     -1.2087860     -1.8331451
 17      3.9177497      1.4279666      0.5877517
  7      0.8725061      0.6713866      1.3110213
  7      1.3307521      1.1856155     -1.3615903
  6      0.1320741      1.8124743     -0.7174397
  6      0.4525152      2.0022607      0.7624758
  6     -0.2795976      3.1270362     -1.3730400
  1     -0.6737455      1.0817362     -0.8080677
  6     -0.7270367      2.6092380      1.5180758
  1      1.3260133      2.6524483      0.8491950
  6     -1.4710354      3.7382287     -0.6227254
  6     -1.1530865      3.9305968      0.8643019
```

```
1      -0.4491742       2.7641820       2.5636207
1      -1.5593496       1.9030749       1.4986011
1      -1.7373676       4.6932963      -1.0805957
1      -2.3379372       3.0783300      -0.7321860
1      -2.0243675       4.3301530       1.3884505
1      -0.3496329       4.6678576       0.9722856
1       0.0523061       0.0956524       1.5345405
1       1.3976222       0.7954965       2.1746971
1       2.0720212       1.8731213      -1.5043747
1       1.0914823       0.7927689      -2.2705388
1       0.5675125       3.8216461      -1.3481101
1      -0.5298933       2.9527742      -2.4221955
1      -6.7306875       0.2308119      -0.0627478
1      -5.7300160      -1.1061141       0.5356017
8      -4.6954629       1.5054128      -1.3250647
1      -4.5816799       1.9795870      -0.4883822
8      -5.2423679       0.7839782       1.2822759
1      -5.9943937       1.0597497       1.8173983
8      -2.5429002      -3.3907277       1.1649424
8      -3.9985505      -2.8393072      -1.4106269
1      -2.8576914      -0.2736114      -1.7855050
1      -2.0068935      -3.2369197       1.9624502
6      -4.8128530       0.1270195      -0.9951941
8      -2.6834086       0.0348728       0.2394540
6      -2.7545123      -2.2291660       0.5565711
6      -3.4534933      -2.0258260      -0.6628444
6      -3.4252109      -0.5128678      -0.8849078
8      -1.6552683      -0.7572981       2.0871401
6      -2.2997136      -0.9594455       1.0705456
6      -5.7164235      -0.0565721       0.2235842
1      -5.2955320      -0.3682372      -1.8413216
```

mecp1
```
Energy of singlet state calculated at B3LYP-D3-SMD/BS2: -2991.8456594600
Energy of triplet state calculated at B3LYP-D3-SMD/BS2: -2991.8456496400
 17      0.0205083      -1.7633399      -0.7725844
 78      2.0794399      -0.2621326      -0.1039042
 17      2.8559242      -1.7992565       1.5360433
 17      3.3975954      -1.1933466      -1.8520834
 17      3.9077149       1.5491143       0.5041544
  7      0.8839708       0.6999150       1.3020537
  7      1.2680009       1.1598999      -1.3866318
  6      0.0824574       1.7892584      -0.7247448
  6      0.4425705       2.0144134       0.7386518
  6     -0.3457618       3.0877363      -1.3974007
  1     -0.7218689       1.0545168      -0.7812672
  6     -0.7072089       2.6408609       1.5190157
  1      1.3162183       2.6671802       0.7826605
  6     -1.5094310       3.7223132      -0.6255732
  6     -1.1488991       3.9467683       0.8464882
  1     -0.3882899       2.8200520       2.5488909
  1     -1.5433008       1.9388047       1.5480206
```

```
1     -1.7859288      4.6684996     -1.0965440
1     -2.3819262      3.0647048     -0.6902292
1     -2.0035312      4.3623688      1.3856072
1     -0.3383454      4.6809643      0.9127515
1      0.0732422      0.1190316      1.5276005
1      1.4063247      0.8447463      2.1649629
1      1.9829236      1.8646859     -1.5724554
1      0.9998798      0.7424424     -2.2770911
1      0.5070894      3.7756469     -1.4150280
1     -0.6276174      2.8858204     -2.4335905
1     -6.6850399      0.2397271     -0.1796347
1     -5.7239919     -1.1324141      0.4028120
8     -4.5878849      1.5573001     -1.2837627
1     -4.4066179      2.0143043     -0.4487479
8     -5.3033337      0.7010873      1.3041863
1     -6.1060396      0.9874372      1.7555118
8     -2.6154475     -3.4565439      1.1400054
8     -3.8828115     -2.7694137     -1.4646443
1     -2.6964080     -0.1984287     -1.6504147
1     -2.1498689     -3.3843764      1.9928776
6     -4.7130294      0.1685295     -0.9905624
8     -2.6804142      0.0186616      0.3964430
6     -2.7621601     -2.2562285      0.5965557
6     -3.3815860     -1.9842411     -0.6514295
6     -3.3349657     -0.4708550     -0.8082962
8     -1.7597843     -0.8443792      2.2631039
6     -2.3367119     -1.0092470      1.2006128
6     -5.6922081     -0.0668454      0.1547326
1     -5.1350045     -0.3019672     -1.8817499
```

TS$_{3-5}$ (optimizeb at the B3LYP-D3-CPCM/BS2 level of theory)
E (B3LYP-D3-CPCM/BS2) = -2991.832353 au
```
Cl                 -0.37201300    -1.39072900     0.23718000
Pt                  2.01571300    -0.49659700    -0.09868300
Cl                  2.95119700    -1.96602200     1.49775000
Cl                  2.48145000    -1.90657400    -1.93407200
Cl                  4.31705900     1.31079800    -0.40147200
N                   1.51059700     0.87192200     1.38476600
N                   1.17976700     0.93714400    -1.34553400
C                   0.31319300     1.84050500    -0.52759100
C                   1.06549800     2.16216500     0.76014900
C                  -0.10603700     3.11181100    -1.25807100
H                  -0.57718700     1.26130000    -0.28047100
C                   0.20732500     3.00822600     1.69605200
H                   1.98496900     2.69177600     0.50329900
C                  -0.97733800     3.97222800    -0.33212500
C                  -0.25483000     4.28728400     0.98255800
H                   0.77509100     3.25141800     2.59706300
H                  -0.66483200     2.42219300     2.00699700
H                  -1.25243200     4.89706800    -0.84349600
```

H	-1.90790100	3.43588400	-0.11795600
H	-0.90942300	4.85587800	1.64671300
H	0.61544700	4.91997500	0.77737800
H	0.76367700	0.46938400	1.95137100
H	2.30528600	1.03518600	2.00072100
H	1.96413800	1.45484300	-1.74653300
H	0.65544200	0.52237400	-2.11432600
H	0.78600700	3.67110500	-1.56063900
H	-0.65111500	2.84741600	-2.16732200
H	-6.67423000	-0.02203300	-1.18674900
H	-5.75219500	-1.49052500	-0.79912500
O	-4.64236000	1.60505800	-1.52994100
H	-4.64740800	1.94537700	-0.62468000
O	-5.70337600	0.00184300	0.66265600
H	-6.51431500	-0.27793000	1.10186600
O	-2.72277300	-2.80851400	1.62122400
O	-3.36115200	-2.63231800	-1.29009600
H	-2.42407300	0.06234000	-1.61141500
H	-2.52717200	-2.54356900	2.53520800
C	-4.57211200	0.18617700	-1.45015300
O	-2.92365600	0.49945900	0.33786500
C	-2.64143100	-1.73165300	0.83367000
C	-3.08407000	-1.70682900	-0.54233100
C	-3.19554200	-0.22415100	-0.89631700
O	-2.61801300	-0.01585900	2.51465800
C	-2.72931900	-0.36576800	1.36232100
C	-5.76511300	-0.40004900	-0.70965600
H	-4.61744000	-0.18240000	-2.47676900

TS$_{3-5}$ (optimizeb at the B3LYP-D3-SMD/BS2 level of theory)
E (B3LYP-D3-SMD/BS2) = -2991.842659 au

Cl	-0.32105500	-1.51429100	0.17315700
Pt	2.02964400	-0.44742100	-0.08751800
Cl	3.06540700	-1.87785800	1.48166100
Cl	2.63692700	-1.77594300	-1.94064100
Cl	4.22621600	1.75063600	-0.43593500
N	1.40315000	0.84032600	1.41961000
N	1.12132400	0.96072800	-1.30484500
C	0.18432700	1.77883700	-0.48017400
C	0.88988400	2.11780800	0.82533800
C	-0.31530400	3.03040200	-1.18881900
H	-0.66480800	1.13567000	-0.25477100
C	-0.04546200	2.86814800	1.76599100
H	1.77307600	2.71885300	0.60342700
C	-1.26075800	3.80202100	-0.25855400
C	-0.58634500	4.12934700	1.07848400
H	0.48671600	3.12494100	2.68518400
H	-0.87524900	2.20568400	2.03785700
H	-1.59066800	4.72034000	-0.74983900
H	-2.15498700	3.19533900	-0.07697900
H	-1.29168400	4.63237300	1.74425200

```
H              0.24174100     4.82513700     0.90442800
H              0.66013500     0.38323500     1.95071000
H              2.16276500     1.03977800     2.06876900
H              1.87595800     1.54810600    -1.66772600
H              0.63163400     0.54396400    -2.09578900
H              0.54091900     3.65678800    -1.46204300
H             -0.82619600     2.74497400    -2.11186200
H             -6.59164200    -0.00824300    -1.21782000
H             -5.69790200    -1.33053300    -0.44318100
O             -4.45537200     1.57167800    -1.63987000
H             -4.50289400     2.01962800    -0.78277900
O             -5.76617800     0.45890700     0.63370800
H             -6.68215200     0.45556600     0.93770100
O             -2.57061000    -3.15151100     1.34581000
O             -3.26990600    -2.64034600    -1.47941400
H             -2.34037500     0.08659600    -1.47561600
H             -2.35370300    -3.02899000     2.28570200
C             -4.47872000     0.16577000    -1.40136000
O             -2.91312200     0.28454900     0.49842700
C             -2.49992400    -1.97375200     0.71026300
C             -2.99519400    -1.79194400    -0.64261300
C             -3.13497400    -0.28477600    -0.82599000
O             -2.52119400    -0.45337800     2.58696700
C             -2.64212900    -0.68071900     1.40208000
C             -5.71401300    -0.24904300    -0.61316100
H             -4.54895000    -0.31274700    -2.38063700
```

6

E (B3LYP-CPCM/BS1) = -2990.9987 au

H (B3LYP-CPCM/BS1) = -2990.612456 au

G (B3LYP-CPCM/BS1) = -2990.711144 au

E (B3LYP-D3-CPCM/BS2//B3LYP-CPCM/BS1) = -2991.83533 au

E (B3LYP-D3-SMD/BS2//B3LYP-CPCM/BS1) = -2991.842354 au

E (M06-D3-SMD/BS2//B3LYP-CPCM/BS1) = -2990.982673 au

```
Cl             0.09448100    -1.76577300    -1.16066200
Pt             2.17242100    -0.31583100    -0.05717000
Cl             2.76180600    -1.97690700     1.58056000
Cl             3.68223900    -1.19672400    -1.71647400
Cl             4.00630100     1.53619500     0.82765700
N              0.87106100     0.61267000     1.27554400
N              1.53987000     1.19500100    -1.33148600
C              0.29404800     1.81614900    -0.77221200
C              0.50240300     1.96606300     0.73755600
C             -0.06926600     3.15041300    -1.43103800
H             -0.49901300     1.08305100    -0.94821000
C             -0.72107700     2.57768800     1.42869700
H              1.38131800     2.59618900     0.90738400
C             -1.31208300     3.75168500    -0.74980700
C             -1.09811700     3.91420900     0.76295800
H             -0.50320300     2.72529500     2.49291200
```

```
H          −1.56441100     1.88118300     1.36067100
H          −1.54138400     4.72129800    −1.20616100
H          −2.17774700     3.10067300    −0.93378700
H          −2.00521700     4.30975900     1.23396200
H          −0.30186600     4.64989900     0.94239000
H           0.03436200     0.03096700     1.42542000
H           1.33868200     0.70637100     2.17943600
H           2.30010000     1.87928200    −1.38925800
H           1.37612000     0.82458500    −2.26985300
H           0.77584500     3.84697200    −1.33896900
H          −0.24903900     2.99783400    −2.50149300
H          −6.77961400     0.69556700     0.16725400
H          −5.94527400    −0.78496700     0.68294200
O          −4.62991500     1.72371000    −1.13314200
H          −4.49558300     2.10962700    −0.24622100
O          −5.12943300     1.00608400     1.40583300
H          −5.79395500     1.31486500     2.04039100
O          −2.91518900    −3.49997000     1.02101500
O          −4.61056300    −2.70995700    −1.34299800
H          −3.13581100    −0.31849400    −1.83511800
H          −2.28716300    −3.42283600     1.77088500
C          −4.94335700     0.36388500    −0.88492700
O          −2.74725600    −0.06501900     0.16911100
C          −3.06461500    −2.31208000     0.46958500
C          −3.88039100    −1.98524400    −0.66835700
C          −3.65930700    −0.48560200    −0.88907700
O          −1.61344200    −1.02575200     1.88401600
C          −2.38686400    −1.10895300     0.94235200
C          −5.79659000     0.26204100     0.38532400
H          −5.53691900    −0.00568900    −1.72912000
```

7

E (B3LYP-CPCM/BS1) = -2306.859855 au
H (B3LYP-CPCM/BS1) = -2306.626154 au
G (B3LYP-CPCM/BS1) = -2306.691414 au
E (B3LYP-D3-CPCM/BS2//B3LYP-CPCM/BS1) = -2307.409394 au
E (B3LYP-D3-SMD/BS2//B3LYP-CPCM/BS1) = -2307.405634 au
E (M06-D3-SMD/BS2//B3LYP-CPCM/BS1) = -2306.932068 au

```
Cl          0.52104800     2.73744500    −0.00377500
Pt          0.83286600    −0.00009500    −0.00005000
Cl          2.47847700     0.03478900    −1.75515600
Cl          2.47849100    −0.03425600     1.75514100
Cl          0.52451400    −2.73573100     0.00397500
N          −0.72434800     0.07443700    −1.37362900
N          −0.72425000    −0.07408300     1.37373200
C          −2.00588600     0.31447800     0.69861000
C          −2.00569400    −0.31526000    −0.69867200
C          −3.25417700    −0.08643800     1.49041800
H          −1.95924600     1.40318700     0.59558900
C          −3.25424800     0.08500000    −1.49043100
```

```
H                 -1.95847000     -1.40397400     -0.59591400
C                 -4.52294500      0.29887500      0.70743400
C                 -4.52275100     -0.30120000     -0.70746000
H                 -3.24223800     -0.40425900     -2.47103900
H                 -3.24171600      1.16964800     -1.66694800
H                 -5.40673300     -0.03753500      1.26086600
H                 -4.58872200      1.39350100      0.64143200
H                 -5.40677700      0.03461300     -1.26087500
H                 -4.58777500     -1.39587200     -0.64147400
H                 -0.76219500      1.04382200     -1.70419700
H                 -0.53655100     -0.52436300     -2.18026600
H                 -0.76192500     -1.04283300      1.70616100
H                 -0.53636300      0.52613400      2.17929700
H                 -3.24095300     -1.17105700      1.66706300
H                 -3.24246400      0.40294600      2.47096800
```

8

E (B3LYP-CPCM/BS1) = -684.1303047 au

H (B3LYP-CPCM/BS1) = -683.980133 au

G (B3LYP-CPCM/BS1) = -684.031117 au

E (B3LYP-D3-CPCM/BS2//B3LYP-CPCM/BS1) = -684.411066 au

E (B3LYP-D3-SMD/BS2//B3LYP-CPCM/BS1) = -684.4237291 au

E (M06-D3-SMD/BS2//B3LYP-CPCM/BS1) = -684.0333879 au

```
H                  2.80187400      0.41770600      1.63871700
H                  1.28200500      1.32841700      1.59156000
O                  2.69240700     -0.61714900     -0.78119600
H                  2.16908100     -1.43678200     -0.77415900
O                  1.01882100     -0.66814600      1.77983900
H                  1.52522800     -1.48491200      1.64330100
O                 -2.75852000      0.58690900      0.61834800
O                 -0.57070300      2.45901000     -0.27672500
H                  0.63479200      0.60186500     -2.06294500
H                 -3.24446700     -0.25121600      0.77561400
C                  1.85856300      0.42317600     -0.28485700
O                 -0.00928700     -1.00859500     -0.95351400
C                 -1.61850700      0.30347800      0.01890600
C                 -0.60441400      1.23411900     -0.39027600
C                  0.49500000      0.36266400     -1.00508900
O                 -1.83254100     -2.07971600     -0.11272800
C                 -1.21061300     -1.05797400     -0.32277300
C                  1.77597600      0.41472700      1.24673100
H                  2.33404300      1.36528500     -0.58012400
```

9

E (B3LYP-CPCM/BS1) = -1846.480294 au

H (B3LYP-CPCM/BS1) = -1846.249138 au

G (B3LYP-CPCM/BS1) = -1846.307850 au

E (B3LYP-D3-CPCM/BS2//B3LYP-CPCM/BS1) = -1846.983950 au

E (B3LYP-D3-SMD/BS2//B3LYP-CPCM/BS1) = -1846.98395 au

E (M06-D3-SMD/BS2//B3LYP-CPCM/BS1) = -1846.544868 au

```
Cl            -0.80368700      0.17265900      2.37866300
Pt            -0.86072700     -0.01294100     -0.21879200
Cl            -2.48103600     -1.76833000     -0.30946200
Cl            -2.48255000      1.68883900     -0.59794400
N              0.69317900     -1.37750500     -0.02386500
N              0.69698800      1.37164500     -0.23558400
C              1.97695600      0.69494500      0.16819800
C              1.97682300     -0.71509300     -0.43115300
C              3.22884400      1.47717700     -0.23957600
H              1.92632400      0.61169900      1.25856100
C              3.22276600     -1.50034100     -0.00938500
H              1.93815600     -0.64161600     -1.52395700
C              4.49418100      0.69876100      0.16617600
C              4.49406600     -0.72741500     -0.40588400
H              3.20976800     -2.49072300     -0.47776300
H              3.20370500     -1.65266400      1.07865800
H              5.37912300      1.24448500     -0.17893800
H              4.55644200      0.65511800      1.26192900
H              5.37405900     -1.27627700     -0.05316500
H              4.56560800     -0.68471300     -1.50112200
H              0.72319500     -1.66240700      0.96029100
H              0.51989900     -2.22156700     -0.57468700
H              0.77368700      1.77393500     -1.17394800
H              0.48032800      2.14348400      0.39918300
H              3.22122300      1.63385900     -1.32721500
H              3.21587400      2.46579500      0.23245900
```

10

E (B3LYP-CPCM/BS1) = -683.680502 au
H (B3LYP-CPCM/BS1) = -683.543097 au
G (B3LYP-CPCM/BS1) = -683.593108 au
E (B3LYP-D3-CPCM/BS2//B3LYP-CPCM/BS1) = -683.9732618 au
E (B3LYP-D3-SMD/BS2//B3LYP-CPCM/BS1) = -683.985039 au
E (M06-D3-SMD/BS2//B3LYP-CPCM/BS1) = -683.596226 au

```
H              2.82262100      0.68132700      1.50038800
H              1.15346500      1.27852400      1.57402500
O              2.59980100     -0.55567700     -0.85712800
H              2.01930000     -1.32745800     -0.97922300
O              1.31351600     -0.73668400      1.74878800
H              1.88036600     -1.44280600      1.39700400
O             -2.82143500      0.52268200      0.72786800
O             -0.67535200      2.45099600     -0.23306800
H              0.46945000      0.63201600     -2.06413200
C              1.76231300      0.48872900     -0.35065900
O             -0.07432100     -0.99765900     -0.93524000
C             -1.73817400      0.28153200      0.11744600
C             -0.72666700      1.20997700     -0.33876700
C              0.37062600      0.38126600     -1.00084400
O             -1.79613600     -2.16324800     -0.06127300
```

```
C                  -1.27541800    -1.07800400    -0.25389800
C                   1.78854300     0.47904900     1.18189000
H                   2.19888300     1.43982800    -0.67864200
```

11

E (B3LYP-CPCM/BS1) = -2530.185067 au

H (B3LYP-CPCM/BS1) = -2529.814646 au

G (B3LYP-CPCM/BS1) = -2529.905436 au

E (B3LYP-D3-CPCM/BS2//B3LYP-CPCM/BS1) = -2530.977274 au

E (B3LYP-D3-SMD/BS2//B3LYP-CPCM/BS1) = -2530.986769 au

E (M06-D3-SMD/BS2//B3LYP-CPCM/BS1) = -2530.162623 au

```
Cl                 -4.09054700     0.43865500    -0.55649400
Pt                 -1.66133500    -0.58565000    -0.02154100
Cl                 -2.48062500    -2.16092800     1.60669700
Cl                 -1.69093300    -2.18971300    -1.80900800
N                  -1.51141700     0.90869100     1.40968700
N                  -0.90635100     0.87805800    -1.27259900
C                  -0.96422300     2.20659600    -0.58276800
C                  -0.60252300     1.98242800     0.88937200
C                  -0.05699500     3.25909700    -1.22950200
H                  -2.00915100     2.52975500    -0.63956100
C                  -0.67462900     3.28338700     1.69361900
H                   0.40737600     1.56320100     0.94923000
C                  -0.10956600     4.57255900    -0.42790000
C                   0.23285000     4.34995300     1.05316000
H                  -0.37779100     3.09492200     2.73160700
H                  -1.71323300     3.64148900     1.71121100
H                   0.58345500     5.29636900    -0.87122900
H                  -1.11545800     5.00698700    -0.50962600
H                   0.13621300     5.28900600     1.60935100
H                   1.28131200     4.03468500     1.14423700
H                  -2.45625800     1.27185600     1.56943400
H                  -1.17223400     0.53016700     2.29661600
H                   0.07336300     0.60521200    -1.49981200
H                  -1.44257700     0.89833700    -2.14206900
H                   0.97245900     2.87819900    -1.25982300
H                  -0.37011600     3.42724800    -2.26638900
H                   5.16564100     2.09326000    -0.14335100
H                   3.43744000     1.70429000    -0.21800700
O                   6.08381500    -0.31615100    -0.77123200
H                   6.02166600    -1.00505300    -0.08696500
O                   4.39082500     0.87178600     1.36290600
H                   5.28752400     0.58142200     1.59652500
O                   0.62558000    -1.21410700     0.81376100
O                   1.74253300     0.04671900    -1.76903900
H                   3.99021500    -1.64593500    -1.86299800
C                   4.75799800     0.16753200    -0.98337000
O                   4.04486100    -1.85133400     0.18193000
C                   1.79337100    -1.24124900     0.30478500
C                   2.30816100    -0.66334700    -0.90692600
```

```
C                        3.78266600   -1.02707300   -0.98310400
O                        2.93976700   -2.55490100    2.01874100
C                        2.92458700   -1.94479900    0.97005600
C                        4.42646500    1.29252000    0.00354100
H                        4.73641400    0.60006400   -1.99041600
```

mecp2
Energy of singlet state calculated at B3LYP-D3-CPCM/BS2: -2530.9758875900
Energy of triplet state calculated at B3LYP-D3-CPCM/BS2: -2530.9759023200
```
17      -3.7255158   -1.1400960   -1.2065441
78      -1.3345501   -0.9077769   -0.1393016
17      -1.5564037   -2.7311257    1.3608297
17      -0.1930369   -2.1808656   -1.7736972
 7      -2.1834099    0.3971711    1.2380119
 7      -1.1321005    0.8138608   -1.2734641
 6      -1.9569945    1.9006726   -0.6668247
 6      -1.8215453    1.7982795    0.8497136
 6      -1.5693711    3.2887170   -1.1688208
 1      -2.9934036    1.6844145   -0.9378121
 6      -2.6655958    2.8531248    1.5579365
 1      -0.7688245    1.9115044    1.1180660
 6      -2.4159130    4.3589935   -0.4671728
 6      -2.2941650    4.2563235    1.0571150
 1      -2.5214997    2.7748529    2.6380860
 1      -3.7247373    2.6585799    1.3559144
 1      -2.1060427    5.3502516   -0.8054300
 1      -3.4649714    4.2375813   -0.7583965
 1      -2.9378942    4.9949920    1.5396168
 1      -1.2659131    4.4863497    1.3566844
 1      -3.1956592    0.2659934    1.2249634
 1      -1.8580456    0.1847334    2.1800175
 1      -0.1254221    1.0582641   -1.2820142
 1      -1.4208381    0.6432168   -2.2349087
 1      -0.5073877    3.4598786   -0.9632546
 1      -1.7037062    3.3359643   -2.2522322
 1       5.3561674    2.8048469    0.2341216
 1       3.6201241    2.4784410    0.3224127
 8       6.0726823    0.5304932   -0.9248198
 1       6.1480923   -0.2051881   -0.3027847
 8       4.7206348    1.3867473    1.6234194
 1       5.6318013    1.0942120    1.7434907
 8       0.7595151   -0.2287452    1.1734687
 8       1.6792022    1.1566292   -1.3375594
 1       3.8111654   -0.5912034   -1.8503173
 6       4.7491374    1.0605988   -0.8381525
 8       4.0311354   -1.0644613    0.1387039
 6       1.8679394   -0.3184100    0.5733478
 6       2.2966883    0.3455374   -0.6267497
 6       3.7256788   -0.0822990   -0.8877054
 8       3.0605377   -1.9098679    1.9803755
 6       2.9940304   -1.1741226    1.0215759
```

```
6        4.6067731        2.0147392        0.3470455
1        4.5996458        1.6556408       -1.7426844
```

11 (optimizeb at the B3LYP-D3-CPCM/BS2 level of theory)
E (B3LYP-D3-CPCM/BS2) = −2530.97980032 au
```
Cl              -3.96255400      0.92655100     -0.46047900
Pt              -1.75862400     -0.45800900     -0.03513000
Cl              -2.72177100     -1.91220800      1.57383600
Cl              -2.06905500     -1.97532700     -1.82605600
N               -1.29191500      0.94019800      1.42948100
N               -0.82351700      0.90379400     -1.28306500
C               -0.61409800      2.18857700     -0.55004200
C               -0.23427700      1.85093100      0.88939600
C                0.43505800      3.08053800     -1.20896200
H               -1.58150800      2.69650100     -0.53952000
C               -0.03430200      3.10929200      1.72601900
H                0.68434400      1.26170400      0.88779700
C                0.66903200      4.34470100     -0.37157700
C                1.03226500      4.00322300      1.07788500
H                0.25488600      2.83290400      2.74260600
H               -0.98369100      3.65247600      1.79190300
H                1.46072100      4.94188100     -0.82918600
H               -0.23812200      4.95845600     -0.38272600
H                1.14715800      4.91711700      1.66452800
H                1.99798600      3.48666700      1.10240000
H               -2.13830300      1.46146200      1.66085700
H               -0.97257000      0.47282900      2.27653300
H                0.07893000      0.47680800     -1.56277700
H               -1.38062200      1.05703600     -2.12116400
H                1.36896100      2.51833000     -1.30571200
H                0.11081900      3.33866900     -2.21978000
H                5.03190300      1.83409800     -0.40862700
H                3.30989100      1.47909100     -0.57925300
O                5.95190200     -0.59035300     -0.83912100
H                5.96042100     -1.11695400     -0.02846800
O                4.10452500      0.81477500      1.15827000
H                4.97014700      0.63023900      1.54139100
O                0.49055500     -1.33145300      0.84105700
O                1.62418600     -0.34132300     -1.82232500
H                3.84963300     -2.05235800     -1.73653800
C                4.61345100     -0.15163800     -1.07433800
O                3.90439900     -2.03248400      0.31699800
C                1.65434400     -1.41929800      0.35605600
C                2.18152800     -0.96485200     -0.90030700
C                3.64915700     -1.34044200     -0.93299400
O                2.78777900     -2.54501800      2.19522000
C                2.78120600     -2.05134100      1.09103100
C                4.26212700      1.07544500     -0.23606800
H                4.57747200      0.16255200     -2.12055200
```

13
```
```

E (B3LYP-CPCM/BS1) = -3675.306912 au
H (B3LYP-CPCM/BS1) = -3674.769717 au
G (B3LYP-CPCM/BS1) = -3674.891990 au
E (B3LYP-D3-CPCM/BS2//B3LYP-CPCM/BS1) = -3676.460138 au
E (B3LYP-D3-SMD/BS2//B3LYP-CPCM/BS1) = -3676.487864 au
E (M06-D3-SMD/BS2//B3LYP-CPCM/BS1) = -3675.238466 au

```
Cl        5.11112200      -0.84514000       1.74030900
Pt        3.88060600       0.05760500      -0.10496800
Cl        4.21909000       2.27026500       0.71713300
Cl        5.87729800       0.13260500      -1.43711000
Cl        2.60222900       0.86453100      -1.95311000
N         2.14703100      -0.19769200       1.00793300
N         3.46989700      -1.87901100      -0.73863400
C         2.49621400      -2.50532600       0.21777200
C         1.44713100      -1.45080100       0.57325400
C         1.84197200      -3.77719100      -0.32579900
H         3.08579400      -2.74296300       1.10875400
C         0.48546900      -1.97997800       1.64282400
H         0.87263900      -1.16582200      -0.31327700
C         0.86509900      -4.33496800       0.72706800
C        -0.17191700      -3.28857100       1.16416700
H        -0.27872800      -1.22262600       1.84077300
H         1.03929200      -2.15361900       2.57634900
H         0.36179300      -5.21791100       0.31748700
H         1.43806700      -4.67539300       1.60048600
H        -0.79037700      -3.69256000       1.97398600
H        -0.85519100      -3.05586700       0.33906800
H         2.44916200      -0.27082700       1.98408100
H         1.49027900       0.62326300       0.94321500
H         3.08222900      -1.81501300      -1.68569100
H         4.33788000      -2.41791300      -0.80045900
H         1.30226500      -3.54344600      -1.25323700
H         2.61092600      -4.51837200      -0.57030700
O        -3.61262600       2.39721000       2.21357700
C        -4.33096700       3.15072800       1.24431500
C        -3.46326100       4.17021500       0.49509800
O        -4.25757100       4.86856100      -0.46442700
C        -2.27198100       3.57840500      -0.27787300
O        -1.13202600       3.47036800       0.59903500
C        -0.61502200       2.19329300       0.49324700
O         0.39626400       1.92286400       1.16695600
C        -1.37750900       1.42326500      -0.42469600
O        -1.06313300       0.12518200      -0.75574200
C        -2.43795600       2.19139000      -0.90513100
O        -3.38455900       1.91913500      -1.70270400
H        -6.04362800      -0.20835300       2.71255100
H        -4.81697500       0.03383900       1.45631200
O        -6.98897800      -2.52586600       1.75670800
H        -7.39968700      -2.62564100       0.87906500
O        -6.72940800       0.18292600       0.78461500
```

```
H            -7.57807400    -0.25804500     0.95632700
O            -3.74345200    -0.55716400    -2.64912600
O            -2.92759100    -1.49146300     0.18790800
H            -4.88046000    -3.51863400     0.29904100
H            -3.53208000     0.34696800    -2.27642200
H            -1.80796400    -0.48457400    -0.45892100
C            -5.70222500    -1.94422800     1.50848700
O            -6.22750000    -2.44188500    -0.81538000
C            -4.44787200    -1.26678400    -1.70322000
C            -4.01718700    -1.67634100    -0.45037600
C            -5.16756000    -2.46750700     0.16160700
O            -6.56916100    -1.52956900    -2.86224700
H            -2.02012100     4.30454500    -1.06192800
C            -5.79950400    -1.69065100    -1.92135700
H            -3.03547000     4.87892700     1.22374100
C            -5.78720300    -0.42327900     1.66296900
H            -4.73848500     2.42994700     0.53217200
H            -5.17751100     3.68593000     1.70561000
H            -3.23815400     3.01888600     2.85844900
H            -4.97947900     5.30780200     0.01393300
H            -5.02569700    -2.30965900     2.29094700
```

TS_{13-prod}

E (B3LYP-CPCM/BS1) = -3675.297955 au

H (B3LYP-CPCM/BS1) = -3674.765623 au

G (B3LYP-CPCM/BS1) = -3674.892410 au

E (B3LYP-D3-CPCM/BS2//B3LYP-CPCM/BS1) = -3676.442816 au

E (B3LYP-D3-SMD/BS2//B3LYP-CPCM/BS1) = -3676.465011 au

E (M06-D3-SMD/BS2//B3LYP-CPCM/BS1) = -3675.214034 au

```
Cl            5.48246000    -1.40861000     0.52564300
Pt            3.40211900    -0.16501700    -0.47746500
Cl            4.41209700     1.99214400    -0.17029700
Cl            4.18079800    -0.35709100    -2.74472400
Cl            1.15522400     0.89273200    -1.08693900
N             2.61999700    -0.17010300     1.45429400
N             2.46255300    -2.01451400    -0.59207200
C             2.12392000    -2.48623900     0.79224600
C             1.61480400    -1.27592400     1.57559200
C             1.09701000    -3.62293300     0.80131500
H             3.07084000    -2.82696700     1.22249800
C             1.29127800    -1.63924500     3.02715000
H             0.70599900    -0.89411300     1.10114500
C             0.73803900    -4.00025100     2.25091900
C             0.25949500    -2.78184600     3.05661100
H             0.90340000    -0.75226300     3.53950700
H             2.20872900    -1.94878800     3.54742900
H            -0.03609000    -4.77574600     2.24067700
H             1.61911800    -4.44005300     2.73842800
H             0.06337200    -3.07075400     4.09543800
H            -0.68983000    -2.41540300     2.64289000
```

```
H          3.40689900    -0.31087500     2.09382100
H          2.15721300     0.72492600     1.68210400
H          1.61498600    -1.89316800    -1.15393700
H          3.05941300    -2.68782400    -1.07705500
H          0.19276000    -3.29584100     0.26930400
H          1.49626400    -4.49017300     0.26313500
O         -2.67714000     3.99514300     2.35140600
C         -3.21514000     4.43970900     1.11221200
C         -2.14513900     4.74775800     0.05419100
O         -2.76294300     5.09766300    -1.18064600
C         -1.19269600     3.57938600    -0.25853400
O         -0.14815900     3.53791900     0.74182500
C         -0.08489600     2.29172400     1.30116900
O          0.75428300     2.03138000     2.15965000
C         -1.10866100     1.43124600     0.71997600
O         -1.32413900     0.22237700     1.17833800
C         -1.80611100     2.17943800    -0.27143200
O         -2.75264900     1.83735500    -1.02288300
H         -7.55973200     0.31860400     0.73564800
H         -5.87728000     0.46327600     0.19071700
O         -7.63583100    -2.38766800     0.57625300
H         -7.48493700    -2.85585300    -0.26393100
O         -7.14876600    -0.23162900    -1.23080000
H         -7.93219200    -0.80549800    -1.26525600
O         -2.63679300    -0.74784500    -1.84739700
O         -3.51361700    -0.80187400     1.13806800
H         -5.04882000    -3.12784000     0.91449900
H         -2.66477700     0.19485200    -1.53703700
H         -2.35314100    -0.21056300     1.01578600
C         -6.49509100    -1.54230300     0.75848800
O         -5.49491500    -2.80567600    -1.06581900
C         -3.66208800    -1.41295400    -1.22263200
C         -4.00611000    -1.40749900     0.10701400
C         -5.23920300    -2.27494000     0.25103800
O         -4.64705400    -2.51937400    -3.14783400
H         -0.71868900     3.79433800    -1.22222100
C         -4.58217100    -2.24493200    -1.95924200
H         -1.50728300     5.57095800     0.41509100
C         -6.77093200    -0.16495700     0.13878600
H         -3.85728300     3.63366300     0.74716700
H         -3.84316400     5.33501800     1.24580200
H         -2.10889600     4.70051000     2.70130300
H         -3.30559600     5.88819400    -1.02761600
H         -6.37035700    -1.39851200     1.83823700
```

HCO$_3^-$
E (B3LYP-CPCM/BS1) = -264.525027 au
H (B3LYP-CPCM/BS1) = -264.494320 au
G (B3LYP-CPCM/BS1) = -264.524535 au
E (B3LYP-D3-CPCM/BS2//B3LYP-CPCM/BS1) = -264.6598533 au

E (B3LYP-D3-SMD/BS2//B3LYP-CPCM/BS1) = -264.6685879 au
E (M06-D3-SMD/BS2//B3LYP-CPCM/BS1) = -264.5405472 au

```
O            -1.02751100    -0.74631800     0.00017900
H            -1.75675800    -0.10402600    -0.00131100
C             0.14294900     0.06285000     0.00002500
O            -0.06749200     1.29919400     0.00005100
O             1.20738600    -0.58701000    -0.00008500
```

H_2CO_3
E (B3LYP-CPCM/BS1) = -264.9968892 au
H (B3LYP-CPCM/BS1) = -264.953160 au
G (B3LYP-CPCM/BS1) = -264.983798 au
E (B3LYP-D3-CPCM/BS2//B3LYP-CPCM/BS1) = -265.1131001 au
E (B3LYP-D3-SMD/BS2//B3LYP-CPCM/BS1) = -265.118002 au
E (M06-D3-SMD/BS2//B3LYP-CPCM/BS1) = -264.989014 au

```
O            -1.28572400     0.11853600     0.00000500
H            -1.61151800    -0.79961400     0.00001400
C             0.05304900     0.12689600    -0.00002300
O             0.55096400    -1.12587800     0.00000100
O             0.70604900     1.14434300     0.00000700
H             1.52291400    -1.05777100     0.00002300
```

14
E (B3LYP-CPCM/BS1) = -3255.545733 au
H (B3LYP-CPCM/BS1) = -3255.128432 au
G (B3LYP-CPCM/BS1) = -3255.230788 au
E (B3LYP-D3-CPCM/BS2//B3LYP-CPCM/BS1) = -3256.52914 au
E (B3LYP-D3-SMD/BS2//B3LYP-CPCM/BS1) = -3256.55156 au
E (M06-D3-SMD/BS2//B3LYP-CPCM/BS1) = -3255.56504 au

```
Cl           -4.29336600    -0.47969800     1.00354700
Pt           -2.26412300    -0.73999400    -0.26182100
Cl           -2.16874000    -3.05412700     0.31889100
Cl           -3.52256800    -1.16086500    -2.26255100
Cl           -0.21977800    -0.91291600    -1.48454700
N            -1.20903400    -0.18854200     1.43791400
N            -2.24730800     1.30572300    -0.63527700
C            -1.98710100     2.02941700     0.65505400
C            -0.87033600     1.27178700     1.37020100
C            -1.59602400     3.49625000     0.44821300
H            -2.91785500     1.95577400     1.22514000
C            -0.58081400     1.87408700     2.74711400
H             0.04413600     1.32573700     0.77581700
C            -1.29001300     4.14030800     1.81515000
C            -0.21244100     3.36100600     2.58598200
H             0.24201300     1.32001000     3.20953500
H            -1.46342500     1.76869700     3.39364800
H            -0.96685400     5.17586100     1.65924100
H            -2.21178400     4.18373800     2.41178700
```

```
H          -0.05963000      3.80731600      3.57531400
H           0.74334100      3.42651700      2.05135500
H          -1.81676600     -0.39317400      2.23668700
H          -0.31663700     -0.72570200      1.55199900
H          -1.49492700      1.48565000     -1.30983000
H          -3.12831100      1.59527700     -1.06740900
H          -0.70646000      3.53786000     -0.19438300
H          -2.40840600      4.03211000     -0.05621500
O           5.36915400     -1.43395200      2.29654600
C           6.03343500     -1.42531400      1.03976900
C           5.29692100     -2.20319700     -0.06096100
O           6.05353400     -2.16436500     -1.26987700
C           3.89559700     -1.67509100     -0.40983900
O           2.94900400     -2.15928200      0.56593900
C           2.23774900     -1.08090800      1.06462300
O           1.32823300     -1.30305700      1.88628900
C           2.72299900      0.12692300      0.50162200
O           2.25385600      1.36420900      0.86243500
C           3.71601900     -0.15312100     -0.43608600
O           4.36576600      0.61379800     -1.20530900
O           1.44944100      2.68438200     -1.22470700
H           2.02664800      1.88561400      0.02414200
C           2.20787700      3.46398300     -1.90385400
H           3.62363200     -2.10596900     -1.38164400
H           5.16233000     -3.24605100      0.27267300
H           6.12276000     -0.37717400      0.74156100
H           7.05304700     -1.83730200      1.12744300
H           5.21954200     -2.36007700      2.54612800
H           6.91597800     -2.57259800     -1.09029200
O           1.87492400      4.50679200     -2.48966000
H           3.70037800      2.22174300     -1.58653000
O           3.53930000      3.11246600     -1.99607000
```

TS_{14-prod}

TS$_{14\text{-prod}}$

E (B3LYP-CPCM/BS1) = -3255.540354 au

H (B3LYP-CPCM/BS1) = -3255.125543 au

G (B3LYP-CPCM/BS1) = -3255.234278 au

E (B3LYP-D3-CPCM/BS2//B3LYP-CPCM/BS1) = -3256.514317 au

E (B3LYP-D3-SMD/BS2//B3LYP-CPCM/BS1) = -3256.529512 au

E (M06-D3-SMD/BS2//B3LYP-CPCM/BS1) = -3255.537909 au

```
Cl         -4.64240200     -0.41173000      0.69850600
Pt         -2.24055100     -0.74340800     -0.32571000
Cl         -2.11982600     -3.02494900      0.41699700
Cl         -3.06063600     -1.35113200     -2.50425700
Cl          0.23393600     -0.75622600     -0.98814300
N          -1.49713500     -0.02341900      1.48364800
N          -2.28215300      1.27393000     -0.82206000
C          -2.16888300      2.09369700      0.43122800
C          -1.12677500      1.42111900      1.32599000
C          -1.80790200      3.55794200      0.16146100
```

```
H                -3.15185200      2.02814900      0.90804200
C                -0.97061600      2.15255500      2.66227800
H                -0.15962500      1.41735200      0.81468100
C                -1.63668000      4.31316700      1.49288000
C                -0.60881100      3.62728400      2.40657000
H                -0.18999600      1.65714400      3.24983500
H                -1.90705400      2.08943600      3.23405200
H                -1.33090500      5.34484500      1.28566800
H                -2.60660600      4.36780200      2.00613900
H                -0.53889900      4.15815800      3.36267900
H                 0.38508100      3.67499200      1.94102900
H                -2.23468300     -0.14405200      2.18325700
H                -0.66052800     -0.54552900      1.78660300
H                -1.49560200      1.45307000     -1.45272600
H                -3.14032500      1.49426500     -1.33189800
H                -0.86994900      3.60142500     -0.40916000
H                -2.58558400      4.02667100     -0.45235000
O                 5.21040800     -1.06245600      2.27076500
C                 5.80799500     -1.52580000      1.06620100
C                 4.91658800     -2.49506900      0.27648400
O                 5.53590700     -2.83853200     -0.95894100
C                 3.52473800     -1.94216700     -0.08023800
O                 2.64505500     -2.10404900      1.05703700
C                 2.06852500     -0.90798600      1.38011300
O                 1.26470400     -0.82579200      2.30437900
C                 2.54747200      0.13302900      0.47948900
O                 2.22684600      1.39173200      0.67417100
C                 3.45429900     -0.45884900     -0.44779500
O                 4.12131300      0.06456000     -1.36902800
O                 3.15409100      3.26976800     -0.58077200
H                 2.69421000      2.11781100      0.01557900
C                 3.13255400      3.45880300     -1.85553300
H                 3.12722700     -2.55599200     -0.89543600
H                 4.73772600     -3.39684100      0.88436100
H                 6.00010000     -0.63974100      0.45567800
H                 6.77458000     -2.01755700      1.26036500
H                 5.02635500     -1.83474200      2.82980800
H                 6.38540000     -3.26340900     -0.75720300
O                 2.96442100      4.53948400     -2.43165600
H                 3.58696900      1.58392600     -2.08186800
O                 3.32584900      2.35244800     -2.64725800
```

1_Br
E (B3LYP-CPCM/BS1) = -6529.125995 au
H (B3LYP-CPCM/BS1) = -6528.892118 au
G (B3LYP-CPCM/BS1) = -6528.955821 au
E (B3LYP-D3-CPCM/BS2//B3LYP-CPCM/BS1) = -6535.084315 au
E (B3LYP-D3-SMD/BS2//B3LYP-CPCM/BS1) = -6535.088340 au
```
 Pt               0.68901800      0.00004700     -0.00000500
 Cl               2.32765500     -0.05058500     -1.73195600
 Cl               2.32808900      0.05039400      1.73136600
```

```
N              -0.87006800    -0.03392800    -1.38323200
N              -0.87000500     0.03409000     1.38319000
C              -2.15164100     0.36799700     0.67217500
C              -2.15169700    -0.36788500    -0.67227900
C              -3.39764200     0.02521800     1.49451000
H              -2.10501700     1.44624000     0.49007700
C              -3.39768600    -0.02511000    -1.49451300
H              -2.10512900    -1.44615700    -0.49029700
C              -4.66573600     0.35110000     0.68316500
C              -4.66574000    -0.35123300    -0.68317600
H              -3.38513700    -0.58775800    -2.43407100
H              -3.38255700     1.04295500    -1.75068400
H              -5.54668500     0.05264000     1.26160900
H              -4.73439400     1.43777900     0.53972900
H              -5.54677100    -0.05283400    -1.26151900
H              -4.73424500    -1.43793200    -0.53986500
H              -0.91393200     0.89132200    -1.82227000
H              -0.66714800    -0.71250400    -2.12202000
H              -0.91390300    -0.89108200     1.82240100
H              -0.66736700     0.71276600     2.12188500
H              -3.38230000    -1.04281400     1.75077300
H              -3.38515100     0.58796800     2.43401100
Br              0.61918600     2.53337500    -0.06760800
Br              0.61910100    -2.53345100     0.06794100
```

3_Br
E (B3LYP-CPCM/BS1) = -7213.424381 au
H (B3LYP-CPCM/BS1) = -7213.039394 au
G (B3LYP-CPCM/BS1) = -7213.137914 au
E (B3LYP-D3-CPCM/BS2//B3LYP-CPCM/BS1) = -7219.684637 au
E (B3LYP-D3-SMD/BS2//B3LYP-CPCM/BS1) = -7219.697913 au
```
Pt              2.01462900    -0.55477000     0.02470600
Cl              1.39221800    -2.50639100    -1.20305700
Cl              3.88237500    -1.66650000     1.05337500
N               0.47141900     0.57636100    -0.78583400
N               2.44529400     1.21153600     1.03804800
C               1.72342000     2.34984800     0.37453800
C               0.32977100     1.85001700    -0.00986500
C               1.64564700     3.60551300     1.24699900
H               2.29419800     2.56015500    -0.53528400
C              -0.44730900     2.92258300    -0.77887200
H              -0.22964100     1.58021000     0.89042000
C               0.85305700     4.70016700     0.50654800
C              -0.53437900     4.20611300     0.06712700
H              -1.44656000     2.54217000    -1.00807200
H               0.06095000     3.13273200    -1.73016100
H               0.75507800     5.57528800     1.15834700
H               1.42408500     5.02355600    -0.37423000
H              -1.04534800     4.98564400    -0.50905600
H              -1.15427900     4.00651300     0.95124100
```

```
H            0.74074600     0.77208700    -1.75497800
H           -0.44899000     0.06694100    -0.81303400
H            2.13454100     1.08504100     2.00686700
H            3.45641000     1.36613800     1.05852600
H            1.14743500     3.36114500     2.19490400
H            2.65539700     3.95601000     1.48793100
O           -5.69030600     0.78692900    -2.17738200
C           -6.69658200     0.36612200    -1.26540300
C           -6.46196200    -1.03799800    -0.69026600
O           -7.53261100    -1.38827600     0.18622700
C           -5.17107000    -1.20145100     0.12813800
O           -4.06066700    -1.43552900    -0.76465100
C           -3.04032100    -0.54216900    -0.46451700
O           -1.99338800    -0.60686700    -1.14004600
C           -3.43956400     0.27935000     0.60227400
O           -2.66896900     1.29765500     1.14199700
C           -4.74089300    -0.01778600     1.00692000
O           -5.43051700     0.53952600     1.89666900
H           -3.24356000     1.70268000     1.81814400
H           -5.29866200    -2.10058700     0.74477800
H           -6.39839900    -1.75757500    -1.52385800
H           -6.70032300     1.09183600    -0.44795900
H           -7.69314700     0.38449000    -1.73776400
H           -5.65175100     0.13598000    -2.89668600
H           -8.35767700    -1.34570500    -0.32384000
Br           3.49029900     0.22186500    -1.88964200
Br           0.52873400    -1.21781300     1.96711400
```

13_Br
E (B3LYP-CPCM/BS1) = -7897.741171 au
H (B3LYP-CPCM/BS1) = -7897.204332 au
G (B3LYP-CPCM/BS1) = -7897.329042 au
E (B3LYP-D3-CPCM/BS2//B3LYP-CPCM/BS1) = -7904.301346 au
E (B3LYP-D3-SMD/BS2//B3LYP-CPCM/BS1) = -7904.32507 au
```
Pt          -3.57844200     0.10751800     0.06461400
Cl          -3.75867000     2.23109400    -1.01489800
Cl          -5.70389600     0.37326100     1.16068000
N           -1.73859500    -0.31435600    -0.81270600
N           -3.30840700    -1.75961300     0.93996000
C           -2.25093900    -2.50604400     0.18003900
C           -1.13173600    -1.51671000    -0.15257800
C           -1.72051400    -3.73130700     0.92770000
H           -2.73759000    -2.82078600    -0.74874000
C           -0.05472700    -2.18279200    -1.01688300
H           -0.67257800    -1.14089800     0.76659400
C           -0.63681600    -4.41778000     0.07505400
C            0.48397400    -3.44269000    -0.31318700
H            0.76042000    -1.47489200    -1.18618100
H           -0.48441200    -2.45196400    -1.99230900
H           -0.22555000    -5.26722400     0.63182000
```

```
H        -1.10105500    -4.82883700    -0.83190900
H         1.20387400    -3.93828000    -0.97384900
H         1.04419100    -3.13546500     0.57783400
H        -1.93609600    -0.50819100    -1.79907200
H        -1.07582300     0.50325300    -0.78553400
H        -3.02976100    -1.60052500     1.91362700
H        -4.19441900    -2.27141700     0.95449400
H        -1.29607400    -3.41886700     1.89131000
H        -2.54406700    -4.42227400     1.14018700
O         3.86377700     2.19708400    -2.39386300
C         4.65681900     2.97112200    -1.50177600
C         3.86899100     4.07052900    -0.77816200
O         4.73979200     4.80090600     0.08606600
C         2.70461100     3.57807300     0.09841800
O         1.52602600     3.41171600    -0.71625800
C         1.00453100     2.15393200    -0.48172200
O        -0.02672900     1.83116600    -1.09767800
C         1.78943900     1.46061700     0.47830600
O         1.46716800     0.20479900     0.93992800
C         2.87966300     2.25034900     0.84229200
O         3.85878200     2.03495200     1.61789900
H         6.01758400    -0.53809900    -3.01018700
H         4.94820100    -0.15399600    -1.65091700
O         7.05386000    -2.76891200    -1.95469000
H         7.56634200    -2.79528600    -1.12677900
O         6.92695700     0.02309800    -1.22159400
H         7.74659100    -0.44758500    -1.44698300
O         4.35629200    -0.38819300     2.63260900
O         3.21664500    -1.52475200    -0.01578000
H         5.13448200    -3.58211400    -0.16770000
H         4.09467600     0.49026700     2.23175500
H         2.17244500    -0.44897300     0.64161800
C         5.80997800    -2.14345400    -1.61129200
O         6.60952700    -2.42657800     0.67095200
C         4.94664500    -1.16637700     1.66272600
C         4.37216500    -1.66979700     0.50477000
C         5.43992100    -2.52694100    -0.16602500
O         7.18992500    -1.35433800     2.58191200
H         2.49969400     4.37803700     0.82193700
C         6.31448000    -1.58424600     1.75455000
H         3.42466700     4.74441500    -1.52964800
C         5.88418100    -0.64686800    -1.92204300
H         5.06638600     2.27395400    -0.76774100
H         5.50349500     3.43993200    -2.03029800
H         3.49443200     2.79596700    -3.06289700
H         5.45047200     5.17453200    -0.45982300
H         5.04140400    -2.57059000    -2.26728500
Br       -4.70263400    -1.02049800    -1.91435000
Br       -2.41110800     1.13044000     2.06693900
```

TS_{13-prod_Br}

E (B3LYP-CPCM/BS1) = -7897.733498 au
H (B3LYP-CPCM/BS1) = -7897.200141 au
G (B3LYP-CPCM/BS1) = -7897.327837 au
E (B3LYP-D3-CPCM/BS2//B3LYP-CPCM/BS1) = -7904.287801 au
E (B3LYP-D3-SMD/BS2//B3LYP-CPCM/BS1) = -7904.303677 au

```
Pt           3.13888800    -0.07511700    -0.51688900
Cl           4.13163000     2.10021000    -0.28701900
Cl           3.85875800    -0.30351400    -2.79940700
N            2.39888200    -0.04821600     1.43475100
N            2.21272400    -1.93489600    -0.57050700
C            1.89810900    -2.37985900     0.82914900
C            1.40122600    -1.15626800     1.60080500
C            0.87328500    -3.51717600     0.87846300
H            2.85304100    -2.71169800     1.24889400
C            1.10869800    -1.49394900     3.06485200
H            0.48231000    -0.78706100     1.13654000
C            0.54537500    -3.86977400     2.34155600
C            0.08054900    -2.63835700     3.13513500
H            0.72780700    -0.59932500     3.56913300
H            2.03730800    -1.79181000     3.57172300
H           -0.22672500    -4.64710800     2.36151200
H            1.43782700    -4.29861600     2.81802100
H           -0.09424800    -2.90901600     4.18263900
H           -0.87771100    -2.28133300     2.73379100
H            3.20088800    -0.17504800     2.05867100
H            1.94021500     0.84748200     1.65819700
H            1.35481400    -1.83764400    -1.12115400
H            2.80749800    -2.61557400    -1.04766400
H           -0.04242900    -3.20109300     0.35950700
H            1.26309500    -4.39310300     0.34748000
O           -3.05194400     4.01121800     2.49115600
C           -3.62041000     4.50003300     1.28227000
C           -2.57492000     4.83694100     0.20866800
O           -3.21828500     5.19973400    -1.00885400
C           -1.61726700     3.68272200    -0.13810100
O           -0.54941700     3.64358200     0.83789300
C           -0.45136700     2.39365900     1.38142800
O            0.40603000     2.13328400     2.21773300
C           -1.47204700     1.52206100     0.80435000
O           -1.66529400     0.31362700     1.28065000
C           -2.21888500     2.27591800    -0.14956100
O           -3.19480000     1.93739600    -0.85893200
H           -7.98220800    -0.36411600     0.93935100
H           -6.36322300     0.06787100     0.35734700
O           -7.66683600    -3.03136700     0.60201100
H           -7.47707700    -3.43208200    -0.26475200
O           -7.57384600    -0.71796300    -1.07194200
H           -8.25443700    -1.40965100    -1.12303700
O           -3.01414400    -0.58774900    -1.87706700
O           -3.78996900    -0.89225900     1.11990800
```

```
H               -4.99079600   -3.40172400    0.80252600
H               -3.10117600    0.31642400   -1.48254100
H               -2.61689900   -0.15366600    1.05110800
C               -6.65287800   -2.03947700    0.80069000
O               -5.56234400   -3.03075700   -1.13613100
C               -3.93179500   -1.40505300   -1.26190400
C               -4.23104500   -1.50693400    0.07756200
C               -5.32877400   -2.54706900    0.20264900
O               -4.82257600   -2.53167400   -3.22012700
H               -1.16762200    3.91096000   -1.11006600
C               -4.75595000   -2.30974700   -2.01952700
H               -1.93731700    5.65988700    0.57019300
C               -7.15479900   -0.68339000    0.28652100
H               -4.27441800    3.70858700    0.90690000
H               -4.24059800    5.39256000    1.46194400
H               -2.47322100    4.70243800    2.85197500
H               -3.76574300    5.98231900   -0.83383900
H               -6.50217600   -1.94482300    1.88266000
Br               5.38147200   -1.35787500    0.57338700
Br               0.72072500    1.01503900   -1.09083300
```

Br⁻

E (B3LYP-CPCM/BS1) = -2571.575216 au
H (B3LYP-CPCM/BS1) = -2571.572855 au
G (B3LYP-CPCM/BS1) = -2571.591391 au
E (B3LYP-D3-CPCM/BS2//B3LYP-CPCM/BS1) = -2574.335797 au
E (B3LYP-D3-SMD/BS2//B3LYP-CPCM/BS1) = -2574.317418 au

Asc²⁻

E (B3LYP-CPCM/BS1) = -683.7515307 au
H (B3LYP-CPCM/BS1) = -683.615654 au
G (B3LYP-CPCM/BS1) = -683.66434 au
E (B3LYP-D3-CPCM/BS2//B3LYP-CPCM/BS1) = -684.0827972
E (B3LYP-D3-SMD/BS2//B3LYP-CPCM/BS1) = -684.1125564
E (M06-D3-SMD/BS2//B3LYP-CPCM/BS1) = -683.7236793
```
O                1.26880800   -2.16068300    0.75505900
C                1.70053900   -0.82248200    0.98655900
C                1.80998400   -0.01998600   -0.32082100
O                2.57892200    1.16889200   -0.13886700
C                0.43521700    0.36697700   -0.91184600
O               -0.28809900   -0.87143200   -1.08088300
C               -1.51730500   -0.75123700   -0.34202400
O               -2.24245500   -1.76221500   -0.33937000
C               -1.65178300    0.55049300    0.25566400
O               -2.69377100    0.94359500    0.95051700
C               -0.48146600    1.28554000   -0.09445500
O               -0.18292200    2.50439100    0.13633100
H                0.62120400    0.80322700   -1.90662700
H                2.30412600   -0.68052500   -1.05443500
```

```
H          1.02705600    -0.29756300    1.68162900
H          2.69259200    -0.87827400    1.45416000
H          0.57170100    -2.07125700    0.07266000
H          3.48834700     0.88817200    0.05185000
```

pK_a values of L-cysteine. The pK_a values of L-cysteine at 25°C are as follows: pK_{a1} = 1.92 (for –COOH), pK_{a2} = 8.37 (for –SH), and pK_{a3} = 10.7 (for –NH$_3^+$)R. M. Smith, A. E. Martell, Critical Stability Constants; Plenum Press: New York, 1989; Vol. 6, 2nd Suppl., p 20.