Electronic Supplementary Information

Synergistic effects of CH$_3$CO$_2$H and Ca$^{2+}$ on C-H bond activation by MnO$_4^-$

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Experimental details

Materials

KMnO₄ and Ca(OTf)₂ were purchased from Sigma-Aldrich and used as received. Reagent grade cyclohexane and acetic acid were obtained from Sigma-Aldrich and were purified according to standard methods.¹ Acetonitrile (RCI Labscan), toluene (VWR Chemicals), cyclohexanol (Johnson Matthey Electronics) and d₁₂-cyclohexane (Cambridge Isotope Laboratories) were of analytical grade and were used as received.

Instrumentations

Gas chromatographic analyses were performed on a HP 6890 gas chromatograph with a HP-5MS (25 m × 0.2 mm × 0.33 um) or a HP-FFAP (25 m × 0.2 mm × 0.33 um) column equipped with FID detector. GC-MS measurements were carried out on a HP 6890 gas chromatograph interfaced to a HP 5970 mass selective detector. UV-Vis spectroscopy was performed on an Agilent 8453 photodiode-array spectrophotometer. Elemental analysis was conducted with an Elementar Carbon-Hydrogen-Nitrogen micro-Analysers. ICP-AES was performed with a PerkinElmer Optima 6000 Spectrometer. Magnetic susceptibility was conducted with Sherwood Scientific Magnetic Susceptibility Balance (MK1) and the balance was calibrated with both Hg[Ca(SCN)₄] and (NH₄)₂FeSO₄. X-ray photoelectron spectroscopy was carried out with a PHI 5800 X-ray Photoelectron Spectrometer. Liquid Infrared spectra were recorded on a Nicolet iS50 FTIR spectrometer with a 1 mm KBr liquid cell.

Stoichiometric oxidation of cyclohexane by KMnO₄

(1) Stoichiometric oxidation of cyclohexane by KMnO₄-AcOH in CH₃CN

In a typical experiment, 0.031 mmol of KMnO₄ was added to a solution of CH₃CN containing cyclohexane (0.314 ml), acetic acid (0.1-1.5 ml) and chlorobenzene (1 uL, as internal standard) at 23 °C (Total volume = 3.1 ml). 1 uL of the reaction mixture was withdrawn at different reaction times and analyzed with GC until the amount of product formed from the reaction became steady.

(2) Stoichiometric oxidation of cyclohexane by KMnO₄-Ca(OTf)₂ in CH₃CN

In a typical experiment, 0.031 mmol of KMnO₄ was added to a solution of CH₃CN containing cyclohexane (0.314 ml), Ca(OTf)₂ (0.5 to 4 equivalents with respect to KMnO₄) and chlorobenzene (1 uL, as internal standard) at 23 °C (Total volume = 3.1 ml). 1 uL of the reaction mixture was withdrawn at different reaction times and analyzed with GC.

(3) Stoichiometric oxidation of cyclohexane by KMnO₄-Ca(OTf)₂-AcOH in CH₃CN

In a typical experiment, 0.031 mmol of KMnO₄ was added to a solution of CH₃CN containing cyclohexane (0.314 ml), Ca(OTf)₂ (0.5 to 4 equivalents), AcOH (0.1 ml to 1.5 ml) and chlorobenzene (1 uL, as internal standard) at 23 °C (Total volume = 3.1 ml). 1 uL of the reaction mixture was withdrawn at different reaction times and analyzed with GC.

Determination of KIE

(1) Stoichiometric oxidation of cyclohexane by KMnO₄-AcOH in CH₃CN

0.031 mmol of KMnO₄ was added to a solution of CH₃CN containing cyclohexane (0.157 ml), d₁₂-cyclohexane (0.157 ml), acetic acid (0.5 ml) and chlorobenzene(1 uL, as internal standard) at 23 °C (total volume = 3.1 ml). The reaction mixture was analyzed by GC fitted with a HP5MS column. The deuterated products were well separated and corresponding areas were used to calculate the KIE.
(2) Stoichiometric oxidation of cyclohexane by KMnO₄-Ca(OTf)₂ in CH₃CN

0.031 mmol of KMnO₄ was added to a solution of CH₃CN containing cyclohexane (0.157 ml), d₁₂-cyclohexane (0.157 ml), Ca(OTf)₂ (1 equivalent) and chlorobenzene (1 uL, as internal standard) at 23 °C (Total volume = 3.1 ml). The reaction mixture was analyzed by GC fitted with HP5MS column.

(3) Stoichiometric oxidation of cyclohexane by KMnO₄-Ca(OTf)₂-AcOH in CH₃CN

0.031 mmol of KMnO₄ was added to a solution of CH₃CN containing cyclohexane (0.157 ml), d₁₂-cyclohexane (0.157 ml), Ca(OTf)₂ (1 equivalent), AcOH (0.5 ml) and chlorobenzene (1 uL, as internal standard) at 23 °C (Total volume = 3.1 ml). The reaction mixture was analyzed by GC fitted with HP5MS column.

### Determination of the oxidation state of the manganese product
dation

(1) Oxidation of cyclohexane by KMnO₄ in the presence of Ca(OTf)₂ and acetic acid in CH₃CN

0.031 mmol of KMnO₄ was dissolved in solution containing 1.69 ml of CH₃CN, 1 ml of acetic acid, 0.031 mmol of Ca(OTf)₂ and 0.31 ml of cyclohexane. The reaction was allowed to react in room temperature (23 °C) until the amount of cyclohexanone formed was constant based on GC analysis. 114 mg of N(Bu)₄I and 1 ml of CH₃CN was added to the resulting solution. The solution turned brown immediately. 5 uL of the brown solution was withdrawn by 5 uL-syringe and added to 4 ml of solution in a 1 cm cuvette. The absorbance at 363 nm of the diluted solution was taken by a UV-vis spectrophotometer.

(2) Oxidation of cyclohexane by KMnO₄ in the presence of Ca(OTf)₂ in CH₃CN

Similar method as that of (1), except that 2.69 ml of CH₃CN was used for the oxidation.

(3) Oxidation of cyclohexane by KMnO₄ in the presence of AcOH in CH₃CN

Similar method as that of (1), except no Ca(OTf)₂ was added to the reaction mixture for the oxidation.

### Stoichiometric oxidation of toluene by KMnO₄-Ca(OTf)₂-AcOH in CH₃CN

0.031 mmol of KMnO₄ was added to a solution of CH₃CN containing toluene (0.33 ml), (1 equivalent), acetic acid (0.5 ml) and chlorobenzene (1 uL, as internal standard) at 23 °C (Total volume = 3.1 ml). 50 uL of the reaction mixture was withdrawn and then added to 50 uL of isopropanol to quench the reaction at different reaction time, 1 ul of the resulting solution was withdrawn and analyzed by GC. The yield was taken when the amount of product determined from the GC analysis became steady.

### Analysis of manganese product (brown solid)

| Experimental results | MW   | Ca (%) | Mn (%) | C (%) | N (%) | H (%) |
|----------------------|------|--------|--------|-------|-------|-------|
| Ca₃Mn₆O₁₀(CF₃SO₃)₆(CH₃CN)₁₃H₂O | 1368 | 5.84   | 20.10  | 5.26  | 1.02  | 2.12  |
| Ca₃Mn₅O₁₄(CF₃SO₃)₆(CH₃CN)₁₀H₂O | 1885 | 6.37   | 20.42  | 6.37  | 1.49  | 1.38  |
| Ca₃Mn₃O₁₆(CF₃SO₃)₆(CH₃CN)₂₀H₂O | 2125 | 5.65   | 20.71  | 5.65  | 1.32  | 2.16  |
DFT Calculations.

The structures and energies of all molecular species were calculated at the B3LYP-D3(BJ) level\(^2\) with the def2-SVPD basis sets\(^3-4\). The polarizable continuum model (PCM)\(^5-6\) was used to account for the solvent effect in acetonitrile and the D3 version\(^7\) of Grimme’s dispersion with Becke-Johnson damping were included. All calculations were performed with Gaussian 16 package of program.\(^8\)

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Figures and Tables

**Fig. S1** UV-Vis spectra of KMnO$_4$ in CH$_3$CN, KMnO$_4$ and 3 M AcOH in CH$_3$CN (using 3 M AcOH as background), and KMnO$_4$, 3 M AcOH and 1 eq. Ca(OTf)$_2$ in CH$_3$CN (using 3 M AcOH as background). In spectrum of KMnO$_4$, 3 M AcOH and 1 eq. Ca(OTf)$_2$ in CH$_3$CN (blue), the absorbance at 527 nm decreased as the KMnO$_4$ decayed slightly after addition of Ca(OTf)$_2$. 

![UV-Vis spectra](image.png)
Fig. S2 Solution IR spectra (950-500 cm\(^{-1}\)) of KMnO\(_4\) (2.5 mM), Ca(OTf)\(_2\) (2.5 mM) and KMnO\(_4\)+Ca(OTf)\(_2\) (2.5 mM) in CH\(_3\)CN measured with a 1 mm KBr IR cell. The IR spectra show that upon addition of 1 equiv. Ca(OTf)\(_2\) to KMnO\(_4\) in CH\(_3\)CN the stretching frequency of Mn=O at 904 cm\(^{-1}\) is not shifted.

Fig. S3 Time trace for the oxidation of toluene by KMnO\(_4\) in acetonitrile with 1 equivalent of Ca(OTf)\(_2\) and 2.8M acetic acid, Temperature: 22\(^\circ\)C. Conditions: KMnO\(_4\) (0.01M), Ca(OTf)\(_2\) (0.01M), AcOH (2.8M), toluene (1M), solvent: CH\(_3\)CN

Assuming KMnO\(_4\) also acted as a 3-electron oxidant as that for the oxidation in cyclohexane, the yield for the oxidation of toluene is 30.7%.

\(k_{\text{obs}}\) for the reaction 0.31 min\(^{-1}\). The oxidation of cyclohexane under the same conditions: \(k_{\text{obs}} = 0.054\) min\(^{-1}\) (yield: 57\%). Therefore, the ratio of \(k_{\text{obs}}\) of toluene to cyclohexane = 5.75:1.
**Fig. S4** UV-Vis monitoring the reaction of KMnO$_4$ (0.0003 M), Ba(OTf)$_2$ (0.0003 M), AcOH (3 M) and cyclohexane (1 M) in CH$_3$CN at 25 °C. 3 M AcOH in CH$_3$CN was used as background in measurement.

**Fig. S5** UV-Vis monitoring the reaction of KMnO$_4$ (0.0003 M), Mg(OTf)$_2$ (0.0003 M), AcOH (3 M) and cyclohexane (1 M) in CH$_3$CN at 25 °C. 3 M AcOH in CH$_3$CN was used as background in measurement.
Fig. S6 UV-Vis monitoring the reaction of KMnO₄ (0.0003 M), Sc(OTf)₃ (0.0003 M), AcOH (3 M) and cyclohexane (1 M) in CH₃CN at 25 °C. 3 M AcOH in CH₃CN was used as background in measurement.

Fig. S7 Mn2p XPS spectra of 1 and 2.
Fig. S8 Mn3s XPS spectra of 1 and 2.
Fig. S9 PESs for cyclohexane oxidation by $[\text{MnO}_4^-]/[\text{MnO}_4(\text{AcOH})^-]/[\text{MnO}_4(\text{AcOH})_3^-]/[\text{MnO}_4(\text{CaOTf})]/[\text{MnO}_4(\text{CaOTf})(\text{AcOH})]/[\text{MnO}_4(\text{CaOTf})(\text{AcOH})_3]$ at the B3LYP-D3(BJ)/def2-SVPD level. Relative 298 K Gibbs free energies in acetonitrile are given in kcal mol$^{-1}$. 
**Fig. S10** PES and structures for cyclohexane oxidation by $[\text{MnO}_4(\text{AcOH})]^{-}$ at the B3LYP-D3(BJ)/def2-SVPD level. Relative 298 K Gibbs free energies in acetonitrile are given in kcal mol$^{-1}$. 
Fig. S11 PES and structures for cyclohexane oxidation by [MnO₄(CaOTf)(AcOH)] at the B3LYP-D3(BJ)/def2-SVPD level. Relative 298 K Gibbs free energies in acetonitrile are given in kcal mol⁻¹.
Fig. S12 Arrhenius plot of the reaction of KMnO$_4$ (0.00025 M) with cyclohexane (1.0 M) in CH$_3$CN in the presence of AcOH (3.0 M) and Ca(OTf)$_2$ (0.00025 M). Rate constants in temperature range of 20-50 °C were obtained by Pseudo-first-order reaction fitting of the absorbance of KMnO$_4$ at 527 nm. $\Delta G^\ddagger = 10.4 \pm 0.6$ kcal/mol.
Table S1 Transition state of hydroxylation of cyclohexane by KMnO$_4$ via rebound mechanism of KMnO$_4$/AcOH/Ca(OTf)$_2$ system.

|               | TS for hydroxylation via rebound mechanism and $\Delta G^{\ddagger}_{298}$ | $\Delta G^{\ddagger}_{298}$ (current TS2) |
|---------------|---------------------------------------------------------------------------|-------------------------------------------|
| MnO$_4^-$     | ![diagram](image1)                                                         | 20.3                                      |
| $\Delta G^{\ddagger}_{298}$=22.9                                        |                                            |
| MnO$_4^-$/AcOH | ![diagram](image2)                                                         | 17.6                                      |
| $\Delta G^{\ddagger}_{298}$=19.6                                        |                                            |
| MnO$_4^-$/(CaOTf)$^+$ | ![diagram](image3)                                                     | 8.2                                       |
| $\Delta G^{\ddagger}_{298}$=11.6                                        |                                            |
| Table S2. XYZ coordinates of molecular species |
|----------------------------------------------|
| **MnO$_4$** |
| **INT1** |
| Mn    | 2.12609400 | 0.00049900 | -0.09710400 |
| O     | 1.87185700 | 0.30097000 | 1.44750600 |
| O     | 3.67796400 | -0.29002900 | -0.33224700 |
| O     | 1.68427200 | 1.26195600 | -0.96636200 |
| O     | 1.27491700 | -1.27192800 | -0.53694900 |
| H     | -0.63005200 | -0.60018500 | 1.62509800 |
| C     | -2.07510000 | -1.40634400 | 0.21775500 |
| C     | -1.63117100 | -0.35654000 | 1.24258200 |
| C     | -1.62487300 | 1.05063400 | 0.63586200 |
| C     | -2.98072600 | 1.40559500 | 0.01465300 |
| C     | -3.41422100 | 0.35504200 | -1.01494600 |
| C     | -3.43061700 | -1.05164400 | -0.40444200 |
| H     | -1.34797500 | 1.79180100 | 1.40093800 |
| H     | -2.32053700 | -0.37607700 | 2.10478000 |
| H     | -1.31127600 | 1.46462500 | -0.57396700 |
| H     | -2.11876700 | 2.40103700 | 0.68739800 |
| H     | -3.74220000 | 1.46330200 | 0.81135000 |
| H     | -2.93743800 | 2.40140900 | -0.45204700 |
| H     | -4.40441100 | 0.60606100 | -1.42487200 |
| H     | -2.70749800 | 0.37025700 | -1.86232700 |
| H     | -4.21038700 | 1.09495100 | 0.37542900 |
| H     | -3.70740000 | -1.79513800 | -1.16729200 |
| H     | -0.84624600 | 1.09849200 | -0.14126300 |
| **TS1** |
| Mn    | 2.26040200 | 0.01045000 | -0.02087900 |
| O     | 1.52489400 | 0.64207300 | 1.28056900 |
| O     | 3.35692500 | -1.06023800 | 0.43404300 |
| O     | 2.80262300 | 1.17458700 | -0.97001100 |
| O     | 0.95845000 | -0.78996200 | -0.78231100 |
| H     | -0.08339800 | 0.55142300 | -0.15713000 |
| C     | -2.14352500 | -1.38877400 | -0.20104300 |
| C     | -1.25148400 | -0.30181100 | 0.35669400 |
| C     | -1.61861800 | 1.09199000 | -0.09575900 |
| C     | -3.09516700 | 1.38872600 | 0.24474800 |
| C     | -4.02460000 | 0.31063900 | -0.32194300 |
| C     | -3.61735800 | -1.08888900 | 0.14990000 |
| H     | -0.95685100 | 1.83477300 | 0.36716600 |
| H     | -1.08019900 | -0.38099700 | 1.43694200 |
| H     | -2.04353900 | -1.42215500 | -1.29844800 |
| H     | -1.85074500 | -2.37501900 | 0.18460700 |
| H     | -3.20970000 | 1.43055500 | 1.34033000 |
| H     | -3.36917600 | 2.38108800 | -0.14289000 |
| H     | -5.06568300 | 0.51865700 | -0.03251100 |
| H     | -3.98892200 | 0.34495900 | -1.42389100 |
| H     | -3.74882800 | -1.15922100 | 1.24203600 |
| H     | -4.26531100 | -1.85537500 | -0.30047700 |
|   |   |   |   |
|---|---|---|---|
| H | -1.48632800 | 1.16994200 | -1.18767300 |

**INT2**

|   |   |   |   |
|---|---|---|---|
| Mn | 2.34567700 | 0.02630100 | -0.04767800 |
| O  | 1.63579600 | 0.55633000 | 1.31246100 |
| O  | 3.53743200 | -0.97827600 | 0.30079700 |
| O  | 2.70627900 | 1.25102800 | -1.00502600 |
| O  | 1.02135000 | -0.90347300 | -0.78381700 |
| H  | 0.21498000 | -0.76959000 | -0.22956800 |
| C  | -2.31019500 | -1.42345200 | -0.04239400 |
| C  | -1.47363800 | -0.38415000 | 0.63528700 |
| C  | -1.64843400 | 1.02696700 | 0.17243300 |
| C  | -3.14505800 | 1.42252300 | 0.20938400 |
| C  | -4.00543600 | 0.40191300 | -0.54328000 |
| C  | -3.80494000 | 1.01780000 | -0.00246000 |
| H  | -1.04312300 | 1.71789000 | 0.77202300 |
| H  | -1.09628900 | -0.57005100 | 1.64208400 |
| H  | -2.01675100 | -1.50338600 | -1.10534600 |
| H  | -2.16585500 | -2.41386900 | 0.40945200 |
| H  | -3.47591700 | 1.47544300 | 1.25922500 |
| H  | -3.27163000 | 2.42793100 | -0.21851100 |
| H  | -5.06730300 | 0.68275500 | -0.47791500 |
| H  | -3.73737600 | 0.42221700 | -1.61332900 |
| H  | -4.16176600 | -1.06624300 | 1.03890700 |
| H  | -4.39851000 | -1.74133400 | -0.58057300 |
| H  | -1.30302500 | 1.11983300 | -0.87363200 |

**TS2**

|   |   |   |   |
|---|---|---|---|
| Mn | 2.21293000 | 0.03453900 | -0.03645600 |
| O  | 1.15172900 | 0.07087500 | 1.21511000 |
| O  | 3.40467000 | -0.98672400 | 0.26339500 |
| O  | 2.58694500 | 1.50951600 | -0.51192200 |
| O  | 1.07902700 | -0.69516300 | 1.21115700 |
| H  | 0.24665700 | -0.76619200 | -0.70577500 |
| C  | -1.99230600 | -1.38002600 | 0.02458400 |
| C  | -1.29777400 | -0.25299700 | 0.72901900 |
| C  | -1.54656000 | 1.11488800 | 0.18476300 |
| C  | -3.07121700 | 1.39163100 | 0.15260000 |
| C  | -3.82264900 | 0.27416600 | -0.57956600 |
| C  | -3.51963700 | -1.10277600 | 0.02099700 |
| H  | -1.02567000 | 1.87652900 | 0.77775400 |
| H  | -1.14312000 | -0.35367900 | 1.80171700 |
| H  | -1.67471300 | -1.44604300 | -1.03064400 |
| H  | -1.77592200 | -2.34761400 | 0.49619800 |
| H  | -3.44296200 | 1.46453200 | 1.18741600 |
| H  | -3.25926400 | 2.36449700 | -0.32518800 |
| H  | -4.90551500 | 0.46692000 | -0.55155200 |
| H  | -3.52752800 | 0.27614400 | -1.64249200 |
| H  | -3.89488600 | -1.14459200 | 1.05595900 |
| H  | -4.03406800 | -1.89599100 | -0.54147700 |
H       -1.16435600  1.18471300  -0.84828500

INT3
Mn     1.87704900  0.03326300  -0.01681500
O      0.49522300  -0.38674400  0.03007900
O      3.08569300  -0.97497800  0.30174400
O      2.20230700   1.60567600  0.08976600
O      1.21985400  -0.32348100  -1.66984900
H      0.56244200  -1.03025900  -1.62186000
C     -1.55815500  -1.34195700  0.12235600
C     -0.89000400  -0.17459200  0.85852600
C     -1.22464800   1.16199400  0.18982100
C     -2.74135900   1.36451000  0.08976600
C     -3.41771700   0.19634200  -0.63649200
C     -3.07561500  -1.14206600  0.02753100
H     -0.75839000   1.97665400   0.76040800
H     -1.32277400   -0.14753600  1.87741100
H     -1.14908300   -1.41334600  -0.89814400
H     -3.13219000   -2.28177900  0.63661300
H     -3.16489100   1.45244100  1.10440100
H     -2.95853300   2.31266300  -0.42344900
H     -4.50780400   0.34212100  -0.66210100
H     -3.07482500   0.17622100  -1.68492000
H     -3.50752400  -1.16503200  1.10110100
H     -3.37944700   1.19456900  1.18291900

TS3
Mn     1.86194100  0.08682100  -0.21355100
O      0.49382500  -0.16553100   1.15742400
O      1.25458400  0.15767500  -1.70421200
O      2.90792400   1.21812200  0.24857900
O      2.17012600  -1.51048100  0.35550500
H     -1.01398800  -1.12155300  1.10110100
C     -1.34743600   1.23481200   0.43662800
C     -0.93043300  -0.14344000  0.93393300
C     -1.38123800  -1.24859300  -0.01649000
C     -2.89861300  -1.18836200  -0.23281000
C     -3.33559700   0.19278700  -0.73390000
C     -2.86324500   1.30070400  0.21429500
H     -1.08535500  -2.22810900  0.38586600
H     -1.37926000  -0.31790400  1.92604100
H     -0.82434400   1.42748100  -0.51263200
H     -1.02044500   1.99888900  1.15570100
H     -3.41302000  -1.40995000   0.71662600
H     -3.20161400  -1.97002800  -0.94420800
H     -4.42903300   0.22867000  -0.84696100
H     -2.90531900   0.36627900  -1.73429600
H     -3.37944700   1.19456900  1.18291900
H     -3.13651300   2.28930600  -0.18100200
H  -1.52620300 -0.96955800  1.86927300
H  -1.12085700  0.59466200  1.15026700
H  -3.38780100 -1.54840900 -1.67081000
H  -3.76229200 -3.10875300 -0.92534600
H  -4.95057000 -1.20421200  0.22300300
H  -3.85755200 -2.05569100  1.32033500
H  -3.27879800  0.60096200 -0.10496900
H  -3.58413500  0.39177600  1.62465500
H  -1.62275300 -3.07857400  0.32480800
C  -1.68825200  3.77793300 -0.36642000
H  -1.77651300  4.97649000  0.45232300
H  -2.59401200  3.15593400 -0.40925100
H  -1.60388500  4.29967700 -1.32845300
C  -0.49527900  2.88370000 -0.15118800
O   0.16590700  2.86201700  0.87431000
O  -0.25051400  2.09985200 -1.19172100
H   0.51316300  1.45621300 -1.01401200
Mn  2.46110500  0.57298800  0.05941300

INT2
O  3.70702600 -1.42371100 -0.67521800
O  1.74247800  0.32677700 -0.98765200
O  1.29368400 -1.77260300  0.54166600
O  2.98509100  0.20785500  1.35654600
C  1.69926800 -0.35039000  0.91032400
C  1.32109500 -0.97038800 -0.39661800
C  2.05741000 -2.21620700 -0.76914000
C  3.58317600 -1.93348900 -0.75573700
C  4.02275600 -1.31821300  0.57786100
C  3.22093000 -0.05731100  0.91933800
H  1.74618700 -2.59336100 -1.75227500
H  0.95173600 -0.32189200 -1.19160100
H  0.43629000 -1.51111800  0.11697000
H  1.48757000 -1.05587700  1.73296200
H  1.12493200  0.56088700  1.11034100
H  3.82227400 -1.23788700 -1.57605100
H  4.13269900 -2.86570300 -0.95304900
H  5.09719200 -1.08413000 -0.54588600
H  3.88404300 -2.06074800  1.38138400
H  3.43829600  0.72943700  0.17933900
H  3.51420600  0.33720100  1.90326300
H  1.85366400 -3.00982600 -0.02878900
C  1.57608900  3.74601000 -0.39239900
H  1.69275100  4.45132100  0.43527200
H  2.47710600  3.11996600 -0.46967600
H  1.46709600  4.28241000 -1.34352200
C  0.38872700  2.85062200  0.15363000
O  0.21294900  2.78194000  0.90560700
O  0.07060200  2.11841500 -1.21506600
H  0.66538600  1.46005900 -1.02108700
Mn       2.55647100  -0.62455000  0.07534300

TS2
O       3.07182500  -2.02597500  -0.82177800
O       1.11291500  -0.20391600  -0.75634700
O       2.44186000  -0.75550500    1.50400900
C       -1.61856300   0.12249600    0.78032900
C       -1.47450500  -0.39444100  -0.61199800
C       -2.36296800  -1.53817900  -0.99303200
C       -3.83959400  -1.11285900  -0.76595600
C       -4.05086400  -0.61976100    0.66932400
C       -3.09646200   0.52583100   1.02333700
H       -2.20489000  -1.84432400  -2.03512000
H       -1.20637400   0.31202600  -1.39471800
H       -0.14708500  -1.95932000  -0.06877600
H       -1.35572100  -0.66584100    1.50580400
H       -0.94940400    0.97005800    0.96429900
H       -4.09435900  -0.30877700  -1.47440600
H       -4.50084000  -1.96285000  -0.98963400
H       -5.09365300  -0.29660600    0.80551200
H       -3.88459300  -1.45796000   1.36671600
H       -3.33272300   1.40497000    0.40277300
H       -3.22404100   0.82984500   2.07249500
H       -2.17747000  -2.41813000  -0.35358100
C       0.44548600   4.53400700    0.89778000
H       0.48292000   5.17524000    0.96429900
H       -0.55348200   4.57825700    0.89778000
H       1.16192700   4.89194700  -1.19470500
C       0.77191300   3.10953400  -0.07297900
O       1.05968400   2.74776600    1.05683300
O       0.71356700   2.28730200  -1.11019900
H       0.92383300   1.32303200  -0.85995400
Mn     1.97893000  -1.32956300    0.10017100

INT3
O       0.64180700  -2.79074000  -1.26541300
O       0.23317000  -0.27929300  -0.20074200
O      -1.61243400  -2.34248100    0.24361300
O       0.84726700  -2.38160100    1.48345800
C      -1.44156500   0.86752200   1.18870300
C      -0.75383900   0.74015200  -0.17282300
C      -1.75379200   0.63683600  -1.32787100
C      -2.73484900   1.81554300  -1.30584500
C      -3.43810500   1.93178300    0.05137400
C      -2.42428000   2.04456600    1.19561400
H      -1.19888300   0.60335700  -2.27582600
H      -0.18541200   1.67482500  -0.32244300
H      -2.10565900  -1.51897700    0.15049600
H      -1.98245900  -0.05973800    1.43127100
H  -0.67027600  0.99213600  1.96090600
H  -2.18258000  2.74844800 -1.50737800
H  -3.47171400  1.70520900 -2.11417700
H  -4.11512500  2.79863500  0.05570000
H  -4.06552900  1.03851000  0.21104100
H  -1.86109500  2.98640300  1.08780900
H  -2.94063400  2.09581600  2.16485900
H  -2.31917700 -0.30586300 -1.26538900
C   4.32927300  2.09358000 -0.25061500
H   4.56169500  3.00952400  0.30049700
H   4.45419500  2.26290600 -1.32922100
H   5.02845800  1.29569400  0.03575500
C   2.91479800  1.65269300  0.03202100
O   2.15420400  2.25325800  0.77766500
O   2.58064400  0.54971000 -0.61407300
H   1.61558600  0.24571600 -0.40499800
Mn  0.17982000 -2.09334200  0.07846800
TS3  2.53515400 -1.59634100  0.24141400
O   0.03820100 -0.32740700 -0.56031600
O   0.47285500 -2.40320900 -1.50944400
O   0.19613900 -2.68131900  1.27416500
C  -2.29218800 -0.77673000  0.10255800
C  -1.15919000  0.23945100  0.04861900
C  -1.54979600  1.48919200 -0.73252600
C  -2.81245900  2.12517600 -0.13718700
C  -3.96647300  1.12044000 -0.06268800
C  -3.55180900 -0.13997600  0.70352800
H  -0.71905300  2.20591300 -0.72624100
H  -0.84866000  0.51950200  1.06325700
H  -0.10570700 -1.00282600 -1.35931400
H  -2.50528700 -1.12172000 -0.92245600
H  -1.97594800 -1.64980800  0.68586800
H  -2.58451900  2.49442100  0.87625000
H  -3.09804300  3.00202300 -0.73482500
H  -4.84332700  1.58399500  0.41213900
H  -4.26867700  0.83923300 -1.08526300
H  -3.35589100  0.12153200  1.75661600
H  -4.36767600 -0.87605000  0.70928700
H  -1.73203600  1.20437000 -1.78110900
C  3.22660300  3.29163200  0.13260300
H  3.25241500  3.89680400  1.04312100
H  3.04202000  3.92752200 -0.74354100
H  4.20020100  2.80387600 -0.01728100
C  2.15782600  2.23974300  0.23840700
O  1.49429600  2.02197100  1.23574500
O  2.00441800  1.54792400 -0.89200000
H  1.31345600  0.85071100 -0.76559500
Mn  0.97412600 -1.95304100  0.06050800
### MnO<sub>4</sub>/3AcOH

**INT1**

| Element | X          | Y          | Z          |
|---------|------------|------------|------------|
| O       | 2.18118500 | 2.83931900 | 0.38453900 |
| O       | 3.59252100 | 0.73329800 | -0.31486300|
| O       | 1.10984500 | 0.47618000 | 0.40467500 |
| O       | 1.68077900 | 1.60752400 | -1.84941800|
| H       | 1.79838600 | -4.55029600 | -0.82836500|
| C       | 2.15233300 | -3.92627600 | -0.00295400|
| H       | 2.98117700 | -4.41476100 | 0.52396800 |
| H       | 1.33762400 | -3.77225000 | 0.71833500 |
| C       | 2.57209700 | -2.57658000 | -0.51841300|
| O       | 2.29290400 | -2.13901100 | -1.61761000|
| O       | 3.28058900 | -1.88467000 | 0.37801000 |
| H       | 3.46075500 | -0.97261800 | 0.03969300 |
| C       | -1.46627200| -1.50104600 | -1.51586100|
| C       | -1.47822800| 0.01829000  | -1.31939700|
| C       | -2.72993300| 0.65784400  | -1.92756300|
| C       | -4.00063000| 0.01413000  | -1.37319900|
| C       | -4.00016600| -1.50634500 | -1.57553000|
| C       | -2.74525200| -2.14561600 | -0.96871200|
| H       | -2.72781400| 1.73913300  | -1.73211200|
| H       | -2.72781400| 1.73913300  | -1.73211200|
| H       | -1.45627900| 0.23772100  | -0.24279900|
| H       | -0.57018300| 0.46490200  | -1.74674200|
| H       | -0.57986000| 0.19372390  | -1.03726700|
| H       | -4.07591200| 0.23216800  | -0.29417400|
| H       | -0.24279900| -1.34322200 | -1.37319900|
| H       | -0.24279900| -1.34322200 | -1.37319900|
| C       | -1.53880700| -2.93742800 | 2.71359900 |
| H       | -2.51110500| -2.81349400 | 3.19732900 |
| H       | -0.81676800| -3.36948300 | 3.42451400 |
| H       | -1.61948800| -3.63829700 | 1.87197000 |
| C       | -1.03421900| -1.16117700 | 2.21682000|
| O       | -1.60892700| -0.54948300 | 2.36424500|
| O       | 0.13371300 | -1.72161900 | 1.58336400|
| H       | 0.43058900 | -0.85180200 | 1.22071400|
| C       | -2.55546000| 2.61882300  | 1.43662800|
| H       | -3.36571100| 2.76190000  | 0.71693700 |
| H       | -2.75853300| 3.18618500  | 2.35475200|
| H       | -2.47299400| 1.55923200  | 1.71416400|
| C       | -1.25032600| 3.06029400  | 0.83928100|
| O       | -1.10361500| 3.46110000  | -0.29934900|
| O       | -0.23323800| 2.95699600  | 1.70298600|
| H       | 0.62070200 | 3.10735900  | 1.23291000|
| Mn      | 2.14556200 | 1.41862700  | -0.35078300|
| Element | X-coord     | Y-coord     | Z-coord     |
|---------|-------------|-------------|-------------|
| H       | -4.92738800 | 1.61694100  | 0.05120600  |
| C       | -4.54754800 | 0.78243500  | 0.64769400  |
| O       | -3.88847500 | 1.16740400  | 1.43842600  |
| O       | -2.82278200 | 2.93035400  | -0.66658000 |
| C       | -2.01200300 | 1.41873000  | -1.99269800 |
| C       | 2.44430300  | 2.87395100  | -1.69989500 |
| C       | 3.27857500  | 3.14717400  | -2.36260800 |
| C       | 2.53574900  | 2.93035400  | -2.09429200 |
| C       | 2.08988100  | -2.77824300 | 0.69754700  |
| Mn      | -0.22279700 | -2.28532800 | -0.64884400 |
INT2
O  0.65478700  -3.52703600  -0.33305400
O  -1.94139100  -2.79321500  -0.79596900
O  -0.30537100  -1.26920400   0.59919600
O   0.10549100  -1.39916500  -1.96540200
H  -4.68432100   2.04536500  -0.13027900
C  -4.41479900   1.19331200   0.50024500
H  -5.30656400   0.76786900   0.97707600
H  -3.73300900   1.52456500   1.29599300
C  -3.70046100   0.15130300  -0.31498900
O  -3.23903600   0.34273400  -1.42574300
O  -3.60323300  -1.01778200   0.31710800
H  -3.03556600  -1.65193900  -0.20028600
C  -0.19025000   2.05180800  -1.20914600
C   0.98908400   1.15299400  -1.02725100
C   2.17042200   1.43860800  -1.89570100
C   2.62196400   2.90340900  -1.65055400
C   1.45725800   3.88320400  -1.83488000
C   0.25603700   3.51565100  -0.95668100
H   2.98964700   0.73990800  -1.69009800
H   1.17569500   0.74965800  -0.03208100
H   0.40704600  -0.49990800  -1.64397900
H  -0.56086800   1.98217700  -2.24557300
H  -1.01878400   1.77817900  -0.54883000
H   3.01056500   2.98542600  -0.62294200
H   3.45104300   3.15159600  -2.32947200
H   1.78915900   4.90735700  -1.60839300
H   1.14450700   3.87806200  -2.89234400
H   0.53030500   3.62611600   0.10429100
H  -0.58845700   4.19490100  -1.14336500
H   1.89421400   1.33991300  -2.95976600
C  -0.97085400   2.89542900   2.90046500
H  -0.21485800   3.47672100   3.43491400
H  -1.81382600   2.66300900   3.56394100
H  -1.36799200   3.48386800   2.06153900
C  -0.36997800   1.62353900   2.36600800
O   0.81511700   1.34655600   2.41903400
O  -1.27911300   0.82977600   1.80834300
H  -0.86066600   0.02603400   1.38407800
C   3.69720600  -0.56952500   1.96304000
H   4.53616300   0.00295600   1.55627900
H   4.00154400  -1.12217700   2.86011500
H   2.88873700   0.12102800   2.24712400
C   3.14949300  -1.49927400   0.91767200
O   3.32355700  -1.36581400  -0.28014000
O   2.41355600  -2.48353400   1.43599400
H   1.89851700  -2.93984200   0.71966400
Mn -0.41031500  -2.35920500  -0.59767600

TS2
| X          | Y          | Z          |
|------------|------------|------------|
| -1.4227750 | -3.1582520 | 0.1773620  |
| 1.3034000  | -3.1540420 | 0.5947940  |
| 0.0463460  | -1.0277080 | -0.3675710 |
| -0.3293550 | -1.4850460 | 2.0755490  |
| 4.5201510  | 1.3335480  | 0.1075760  |
| 4.2182740  | 0.5049400  | -0.5388500 |
| 5.0944800  | 0.0827410  | -1.0485530 |
| 3.5259960  | 0.8605070  | -1.3145750 |
| 3.5295230  | -0.5612830 | 0.2683760  |
| 3.2930280  | -0.4800720 | 1.4604760  |
| 3.1894680  | -1.6168510 | -0.4681370 |
| 2.5867090  | -2.2240760 | 0.0444350  |
| 0.8760190  | 1.8364970  | 0.8711920  |
| -0.5048820 | 1.2829300  | 0.9477300  |
| -1.2965630 | 1.6276080  | 2.1681370  |
| -1.3748030 | 3.1757450  | 2.2749680  |
| 0.0248490  | 3.7978670  | 2.2526550  |
| 0.8087980  | 3.3811670  | 1.0043960  |
| -2.2992780 | 1.1877010  | 2.1255360  |
| -1.0420370 | 1.1296770  | 0.0156860  |
| -0.3558690 | -0.5333190 | 1.8120340  |
| 1.4936260  | 1.4417190  | 1.6924790  |
| 1.3668750  | 1.5580220  | -0.0661550 |
| -1.9648600 | 3.5624930  | 1.4292410  |
| -1.9119670 | 3.4475600  | 3.1952820  |
| -0.0499760 | 4.8944120  | 2.3010770  |
| 0.5769870  | 3.4768190  | 3.1516060  |
| 0.3182830  | 3.7933640  | 0.1083900  |
| 1.8301200  | 3.7875240  | 1.0282750  |
| -0.7971630 | 1.2597350  | 3.0803880  |
| 1.0586980  | 2.1438020  | -3.8076210 |
| 0.3834560  | 2.9010740  | -4.2152350 |
| 1.4565760  | 1.5140450  | -4.6143690 |
| 1.9158730  | 2.6312450  | -3.3220110 |
| 0.3387720  | 1.2913650  | -2.7973270 |
| -0.8037960 | 1.4893870  | -2.4223770 |
| 1.0929430  | 0.2950580  | -2.3444670 |
| 0.6288950  | -0.2297220 | -1.6256010 |
| -3.9971380 | 0.5987850  | -1.5015950 |
| -4.6154570 | 1.3042670  | -0.9392080 |
| -4.5605420 | 0.1786630  | -2.3444510 |
| -3.1178180 | 1.1164100  | -1.9117600 |
| -3.5051560 | -0.4961400 | -0.5969900 |
| -3.5656710 | -0.4632970 | 0.6196110  |
| -2.9645650 | -1.5111520 | -1.2690900 |
| -2.4999440 | -2.1392250 | -0.6506540 |
| -0.0901460 | -2.3575640 | 0.5696120  |

**INT3**

| X          | Y          | Z          |
|------------|------------|------------|
| 0.7843160  | -0.5201490 | -2.3738970 |
\[
\begin{align*}
\text{O} & : 0.27900700 \quad 1.17144100 \quad -0.10348000 \\
\text{O} & : -0.37322900 \quad 2.14636300 \quad -2.06129300 \\
\text{H} & : -5.89147100 \quad 1.62160300 \quad 1.19428300 \\
\text{C} & : -5.42811800 \quad 0.64383500 \quad 1.03343200 \\
\text{H} & : -6.16824200 \quad -0.07715800 \quad 0.66382600 \\
\text{H} & : -5.04480500 \quad 0.26179100 \quad 1.99101500 \\
\text{C} & : -4.27776600 \quad 0.76242500 \quad 0.06867500 \\
\text{O} & : -3.77762900 \quad 1.82105900 \quad -0.27109600 \\
\text{O} & : -3.85211900 \quad -0.41769600 \quad -0.36710100 \\
\text{H} & : -3.00682600 \quad -0.31917100 \quad -0.90532900 \\
\text{C} & : 1.62809500 \quad 1.53106000 \quad 1.87145300 \\
\text{C} & : 1.62789100 \quad 1.01276300 \quad 0.43782100 \\
\text{C} & : 2.65939100 \quad 1.72637900 \quad -0.42522000 \\
\text{C} & : 4.05635900 \quad 1.57532400 \quad 0.19056100 \\
\text{C} & : 4.09171600 \quad 2.08160100 \quad 1.63623000 \\
\text{H} & : 5.08882700 \quad 1.92197000 \quad 2.07167700 \\
\text{C} & : 3.26877000 \quad 0.31536100 \quad 2.57388500 \\
\text{H} & : 3.01897300 \quad 1.79171400 \quad 3.51053100 \\
\text{H} & : 2.39452300 \quad 2.79424300 \quad -0.49138300 \\
\text{C} & : -2.43494300 \quad -1.77231500 \quad 2.62383900 \\
\text{C} & : -2.12557800 \quad -2.77641600 \quad 2.92658800 \\
\text{H} & : -3.33020700 \quad -1.83703400 \quad 1.98934300 \\
\text{H} & : -2.69346300 \quad -1.16657000 \quad 3.50148100 \\
\text{C} & : -1.34587000 \quad -1.10869600 \quad 1.82892700 \\
\text{O} & : -0.36623300 \quad -1.67789100 \quad 1.38462600 \\
\text{O} & : -1.57408700 \quad 0.19188300 \quad 1.63853000 \\
\text{H} & : -0.89480800 \quad 0.56715900 \quad 1.02456000 \\
\text{C} & : 1.80637900 \quad -4.15118700 \quad 0.23306400 \\
\text{H} & : 2.66769500 \quad -4.37607400 \quad 0.86892800 \\
\text{H} & : 1.61000100 \quad -4.97792400 \quad -0.46024700 \\
\text{H} & : 0.91479500 \quad -4.01618600 \quad 0.86226100 \\
\text{C} & : 2.03178500 \quad -2.86609900 \quad -0.51441600 \\
\text{O} & : 2.87239900 \quad -2.03636300 \quad -0.21138800 \\
\text{O} & : 1.19866600 \quad -2.71485400 \quad -1.53935500 \\
\text{H} & : 1.25253900 \quad -1.79305800 \quad -1.92877000 \\
\text{Mn} & : -0.24270700 \quad 0.46674000 \quad -1.84627600 \\
\end{align*}
\]

**MnO$_4$-(CaOTf)$_2$**

**INT1**

\[
\begin{align*}
\text{C} & : 0.15745400 \quad 3.46301300 \quad 1.09043300 \\
\text{C} & : -0.36743800 \quad 2.18271500 \quad 0.43276400 \\
\end{align*}
\]

S26
C  -0.35552200  2.28767100  -1.09457800
C   1.03477100  2.66178100  -1.62099500
C   1.55182800  3.82807700   0.56793400
H   -0.68596200  1.33981100  -1.54092900
H    0.26471400  1.33574200   0.73608000
H   -1.38363400  1.96054300  -1.40550100
H   -0.53769300  4.29180800   0.87280800
H    0.17610300  3.34866700   2.18469400
H    1.72544400  1.83264600  -1.40550100
H    1.00924500  2.77788600  -2.71521100
H    2.57497900  4.16825400  -1.32168300
H    0.92301900  4.79255000  -1.26079500
H    2.26529900  3.04424600   0.87318200
H    1.89784700  4.76810700   1.02390500
H   -1.08380800  3.05389100  -1.40964500
Mn  -3.34793300 -0.32492500   0.21424300
O   -3.07369000 -1.08228500  -1.18089100
O   -4.59473900 -0.94582400   0.95141200
O   -3.57336900  1.21483300  -0.02535600
O   -2.00420200 -0.56143500   1.07741800
Ca  -0.84983800 -1.91437300  -0.54297200
C    2.78442700 -0.74751800   0.94989400
S    2.16316400 -1.66410900  -0.57394800
F    1.76592300 -0.48851600   1.77014600
F    3.35562800  0.39961600   0.58748000
F    3.67832300 -1.49901800   1.59091100
O    1.16919800 -0.71705100  -1.18859600
O    3.36604400 -1.96353200  -1.35904500
O    1.40420100 -2.83182900  -0.00700600
TS1
C    0.40818200  3.12281000  -0.86403300
C    0.38374800  2.00173400   0.14763700
C   -0.04367000  2.41962700   1.53567400
C   -1.44657300  3.06375200   1.45831000
C   -1.47482100  4.21233600   0.44525700
C   -0.99808500  3.76088000  -0.93864100
H   -0.06065600  1.55532100   2.21153300
H   -0.15003900  1.11646000  -0.20589200
H    1.54237600  1.60186300   0.27049500
H    1.13397000  3.89255500  -0.55780300
H    0.71374000  2.75321800  -1.85188900
H   -2.17449800  2.29315300   1.16303200
H   -1.73901100  3.41737900   2.45777300
H   -2.49168200  4.62670700   0.37528100
H   -0.82459500  5.02750700   0.80354400
H   -1.70420300  3.02042600  -1.34669100
H   -0.97676800  4.60773100  -1.63995500
H    0.66633200  3.15543200   1.94458600
| Atom | X       | Y       | Z       |
|------|---------|---------|---------|
| Mn   | 3.09277500 | -0.27548800 | -0.19244200 |
| O    | 3.17040000 | -1.43094200 | 0.93350900  |
| O    | 4.28523400 | -0.19087800 | -1.22264400 |
| O    | 2.80439100 | 1.21129900  | 0.50700000  |
| O    | 1.66978400 | -0.57917700 | -0.9610900  |
| Ca   | 0.94870400 | -2.29806000 | 0.44432200  |
| C    | -2.58913500 | -0.66168500 | -0.93576500 |
| S    | -2.03843600 | -1.69424000 | 0.41880000  |
| F    | -1.54862500 | -0.40998200 | -1.72965900 |
| F    | -3.10522600 | 0.49335700  | -0.51568400 |
| F    | -3.51407400 | -1.32634300 | -1.62689300 |
| O    | -0.94403200 | -0.88079800 | 1.17289900  |
| O    | -2.65567500 | -1.89753700 | 1.33661200  |
| O    | -1.42261900 | -2.91212100 | -0.08752000 |

| Atom | X       | Y       | Z       |
|------|---------|---------|---------|
| C    | 0.03779000 | 3.16409200 | 0.92528300 |
| C    | -0.02829900 | 2.03571600 | -0.04949700 |
| C    | 0.32946600 | 2.35819900 | -1.46404600 |
| C    | 1.76188600 | 2.95095400 | -1.49278100 |
| C    | 1.88444500 | 4.31628300 | -0.52916400 |
| C    | 1.47143900 | 3.76000700 | 0.89793600  |
| H    | 0.27392800 | 1.46216400 | -2.09887700 |
| H    | 0.17339300 | 1.02995400 | 0.31228800  |
| H    | -1.78688600 | 1.70768900 | -0.26866500 |
| H    | -0.66752700 | 3.96167000 | 0.63552800  |
| H    | -0.22470600 | 2.83795900 | 1.93990100  |
| H    | 2.47691400 | 2.16508300 | -1.20604800 |
| H    | 2.00914000 | 3.25554300 | -2.52008200 |
| H    | 2.91695800 | 4.51577900 | -0.53174000 |
| H    | 1.24325000 | 4.95966500 | -0.88539000 |
| H    | 2.17334200 | 3.01214700 | 1.29883100  |
| H    | 1.51613900 | 4.63591100 | 1.56129300  |
| H    | -0.36203600 | 3.11073600 | -1.87230800 |
| Mn   | -3.17735600 | -0.05127700 | 0.19338900  |
| O    | -3.29192400 | -1.15659900 | -0.97756900 |
| O    | -4.36171200 | 0.09006600 | 1.22344400  |
| O    | -2.75257700 | 1.50367000 | -0.46389600 |
| O    | -1.76748800 | -0.44831000 | 0.95275900  |
| Ca   | -1.14127800 | -2.17015800 | -0.49245800 |
| C    | 2.50315400 | -0.91347800 | 0.96164500  |
| S    | 1.87143300 | -1.84812700 | -0.54723600 |
| F    | 1.48812700 | -0.62923400 | 1.77768400  |
| F    | 3.08669300 | 0.22230400 | 0.58019400  |
| F    | 3.39033100 | -1.66282600 | 1.61399900  |
| O    | 0.85016800 | -0.92097100 | -1.14782800 |
| O    | 3.06675900 | -2.12586400 | -1.35264900 |
| O    | 1.14789300 | -3.02870100 | 0.03611700  |

TS2
| Atom | X       | Y       | Z       |
|------|---------|---------|---------|
| C    | 1.52922200 | 2.69438600 | -0.84852300 |
| C    | 0.63117700  | 1.78896100 | -0.08070900 |
| C    | 0.11923700  | 2.29479700  | 1.22740400  |
| C    | -0.64440400  | 3.62299400  | 0.95862200  |
| C    | 0.24129100  | 4.62114300  | 0.20739200  |
| C    | 0.11923700  | 2.29479700  | 1.22740400  |
| C    | -0.64440400  | 3.62299400  | 0.95862200  |
| C    | 0.24129100  | 4.62114300  | 0.20739200  |
| H    | -0.53372300  | 1.56024600  | 1.71110000  |
| H    | -0.00260100  | 1.10635900  | -0.63878900 |
| H    | 1.91465900  | 0.76882100  | 0.91711000  |
| H    | 2.43768100  | 2.91883500  | -0.26547700 |
| H    | 1.84109000  | 2.23924500  | -1.79567900 |
| H    | -1.54467700  | 3.40339600  | 0.36495200  |
| H    | -0.98251500  | 4.39047000  | 1.91836800  |
| H    | -0.02324300  | 5.54041900  | -0.00155300 |
| H    | 1.08871100  | 4.90953900  | 0.85103400  |
| H    | -0.03909100  | 3.84427800  | -1.79112300 |
| H    | 1.45707100  | 4.73771400  | -1.60040500 |
| H    | 0.95002000  | 2.52518000  | 1.91486500  |
| Mn   | 2.98589800  | -1.01794400  | 0.11854200 |
| O    | 2.44507200  | -2.45442700  | 0.62665800 |
| O    | 4.43306700  | -0.87663200  | -0.48829800 |
| O    | 2.66076900  | 0.23576900  | 1.29572300  |
| O    | 1.82137400  | -0.53734700  | -0.96464800 |
| Ca   | 0.36939300  | -2.31133700  | -0.58996700 |
| C    | -3.06690800  | 0.08028000  | -0.43531300 |
| S    | -2.34402400  | -1.41431400  | 0.45224800 |
| F    | -2.27061800  | 0.44317800  | -1.44204500 |
| F    | -3.18077400  | 1.09795000  | 0.41734900 |
| F    | -4.26998300  | -0.22091500  | -0.92038100 |
| O    | -1.00446000  | -0.93767700  | -0.93946100 |
| O    | -3.33678100  | -1.75847100  | 1.47801800 |
| O    | -2.11988500  | -2.41851400  | -0.64292800 |

| INT3  | C       | X       | Y       | Z       |
|-------|---------|---------|---------|
| C     | 2.45876600  | 1.80426000  | -0.88455400 |
| C     | 1.19922200  | 1.09470700  | -0.39674300 |
| C     | 0.74237900  | 1.63295500  | 0.95770700  |
| C     | 0.49003100  | 3.14326000  | 0.87506600  |
| C     | 1.73264900  | 3.88566600  | 0.37098800  |
| C     | 2.21884100  | 3.31716100  | -0.96720700 |
| H     | -0.15645200  | 1.09436700  | 1.28029800  |
| H     | 0.39882100  | 1.28847400  | -1.12882600 |
| H     | 2.37587000  | -0.29351600  | 2.16256500  |
| H     | 3.28110400  | 1.59863200  | -0.18218200 |
| H     | 2.75391100  | 1.39923000  | -1.86107800 |
| H     | -0.35252400  | 3.33079300  | 0.19018700  |
| H     | 0.18518600  | 3.52337200  | 1.86000000  |
| H     | 1.52016700  | 4.95993400  | 0.27178100  |
| H     | 2.53783500  | 3.78825400  | 1.11809900  |
| H     | 1.46363500  | 3.52059200  | -1.74425800 |
| Element | X            | Y            | Z            |
|---------|--------------|--------------|--------------|
| H       | 3.14201700   | 3.82095500   | -1.28641100  |
| H       | 1.53122600   | 1.44720700   | 1.70342200   |
| Mn      | 2.77935200   | -1.32176900  | 0.09763600   |
| O       | 1.96930900   | -2.75417200  | 0.07518000   |
| O       | 3.97204700   | -1.13423800  | -0.91465800  |
| O       | 3.12839500   | -0.73170800  | 1.73923800   |
| O       | 1.32901300   | -0.33011600  | -0.38584900  |
| Ca      | -0.19627500  | -2.07124600  | -0.46879500  |
| C       | -3.16158600  | 0.87415100   | -0.25529300  |
| S       | -2.92676000  | -0.91976300  | 0.26480500   |
| F       | -2.10592700  | 1.28742200   | -0.95760600  |
| F       | -3.29345500  | 1.64412200   | 0.82415600   |
| F       | -4.25450400  | 0.98611100   | -1.00891200  |
| O       | -1.68342700  | -0.89033200  | 1.11078200   |
| O       | -4.17753300  | -1.28353200  | 0.94316800   |
| O       | -2.61377500  | -1.63400200  | -1.01836200  |

TS3
| Element | X            | Y            | Z            |
|---------|--------------|--------------|--------------|
| C       | -2.59102900  | 1.92484700   | 0.19299200   |
| C       | -1.30396400  | 1.17662500   | -0.12462100  |
| C       | -0.48369200  | 1.88286800   | -1.19765200  |
| C       | -0.16455800  | 3.31960600   | -0.76471900  |
| C       | -1.43870600  | 4.09887400   | -0.42443500  |
| C       | -2.27360200  | 3.36155400   | 0.62785300   |
| H       | 0.43690800   | 1.32021100   | -1.39193200  |
| H       | -0.70737800  | 1.06859000   | 0.79047400   |
| H       | -2.45973700  | -0.36804400  | -1.22930400  |
| H       | -3.22678300  | 1.93719800   | -0.70650800  |
| H       | -3.14584600  | 1.39877500   | 0.98049200   |
| H       | 0.49347900   | 3.29156500   | 0.11838900   |
| H       | 0.39927000   | 3.82404700   | -1.56145900  |
| H       | -1.18305500  | 5.10641200   | -0.06654700  |
| H       | -2.04027400  | 4.22802500   | -1.33924300  |
| H       | -1.71773800  | 3.33317500   | 1.57941900   |
| H       | -3.21074300  | 3.89918100   | 0.82692000   |
| H       | -1.06796700  | 1.89404400   | -2.13150300  |
| Mn      | -2.79094000  | -1.44147100  | 0.38356000   |
| O       | -1.67507300  | -2.67040100  | 0.43835800   |
| O       | -3.54181400  | -1.00686300  | 1.70912000   |
| O       | -3.54955100  | -1.19855100  | -1.11109900  |
| O       | -1.56591400  | -0.18623200  | -0.57124500  |
| Ca      | 0.16375900   | -2.00295100  | -0.72583800  |
| C       | 3.00000700   | 0.70286400   | 0.75037400   |
| S       | 2.96243400   | -0.87162000  | -0.28156300  |
| F       | 1.77173700   | 0.99620700   | 1.17957100   |
| F       | 3.45633200   | 1.71504600   | 0.01433900   |
| F       | 3.79746200   | 0.53158600   | 1.80310400   |
| O       | 2.05689400   | -0.53683900  | -1.43386700  |
| O       | 4.36832200   | -1.14574000  | -0.60402400  |
| O       | 2.26122700   | -1.86542800  | 0.60171900   |

S30
MnO₄⁻/(CaOTf)⁺/AcOH

INT1

| Atom | X       | Y       | Z       |
|------|---------|---------|---------|
| C    | -0.5173 | 1.7670  | 0.8120  |
| C    | -0.8407 | 2.1686  | -0.6284 |
| C    | -1.7439 | 3.4044  | -0.6752 |
| C    | -1.1333 | 4.5725  | 0.1089  |
| C    | -0.8085 | 4.1695  | 1.5529  |
| C    | 0.0934  | 2.9306  | 1.5986  |
| H    | -1.9324 | 3.7013  | -1.7181 |
| H    | 0.1028  | 2.3775  | -1.1557 |
| H    | -1.3158 | 1.3267  | -1.1495 |
| H    | -1.4430 | 1.4396  | 1.3124  |
| H    | 0.1649  | 0.9109  | 0.8122  |
| H    | -0.2034 | 4.8937  | -0.3909 |
| H    | -1.8123 | 5.4386  | 0.0983  |
| H    | -0.3364 | 5.0083  | 2.0866  |
| H    | -1.7501 | 3.9470  | 2.0835  |
| H    | 1.0755  | 3.1811  | 1.1640  |
| H    | 0.2783  | 2.6293  | 2.6406  |
| H    | -2.7235 | 3.1468  | -0.2398 |
| Mn   | -3.4238 | -0.8516 | -0.3144 |
| O    | -4.0941 | -0.9045 | 1.1106  |
| O    | -1.7956 | -1.0449 | -0.1371 |
| O    | -3.6990 | 0.5474  | -0.9865 |
| O    | -3.9908 | -2.0040 | -1.2305 |
| Ca   | -0.1358 | -2.0298 | -1.4301 |
| H    | 1.5182  | -1.5421 | 3.6296  |
| C    | 1.2964  | -2.4448 | 3.0469  |
| H    | 0.7524  | -3.1371 | 3.7052  |
| H    | 2.2187  | -2.9147 | 2.6968  |
| C    | 0.4207  | -2.0960 | 1.8857  |
| O    | 0.6512  | -2.4642 | 0.7329  |
| O    | -0.6276 | -1.3660 | 2.1958  |
| H    | -1.1589 | -1.1709 | 1.3700  |
| C    | 3.4136  | -0.1701 | 0.3297  |
| S    | 2.7297  | 0.2634  | -1.3728 |
| F    | 3.5778  | -1.4892 | 0.4464  |
| F    | 2.5831  | 0.2445  | 1.2916  |
| F    | 4.5972  | 0.4242  | 0.5026  |
| O    | 1.3446  | -0.3183 | -1.3240 |
| O    | 2.7412  | 1.7383  | -1.4051 |
| O    | 3.6320  | -0.4326 | 2.3141  |

TS1

| Atom | X       | Y       | Z       |
|------|---------|---------|---------|
| C    | -0.4379 | 1.9957  | 1.4867  |
| C    | -0.7743 | 2.1388  | 0.0197  |
| C    | -0.8446 | 3.5719  | -0.4628 |
| C    | 0.4922  | 4.2844  | -0.1604 |
| C    | 0.8401  | 4.1864  | 1.3277  |
C          0.88805000  2.72849300  1.79146900
H         -1.06470400  3.61097700 -1.53831500
H         -0.16327300  1.49472400 -0.62068800
H         -1.90665400  1.70421900 -0.13423700
H         -1.23954700  2.44065200  2.09770800
H         -0.36005500  0.93883800  1.76525900
H          1.28984500  3.81019600 -0.75148900
H          0.42409600  5.33496800 -0.47933900
H          1.80792000  4.67315200  1.52062700
H         -1.65664400  4.10227200  0.05961700
Mn         -3.46482300 -0.23492000 -0.27585100
O         -4.27878700 -0.67264500  1.00257500
O         -1.87839400 -0.78729200 -0.14103200
O         -3.22539400  1.41552300 -0.26139400
O         -4.06752600 -0.68291200 -1.66447300
Ca         -0.55267200 -1.94948100 -1.58833500
H          1.42111700 -2.31338900  3.24332700
C          0.82859500 -3.10240500  2.76012000
H          0.15422200 -3.51703200  3.52068400
H          1.49156800 -3.87861200  2.36983900
C          0.02701300 -2.49470100  1.65113000
O          0.19033800 -2.79622900  0.46442700
O         -0.85680800 -1.60868400  2.03619400
H         -1.33972200 -1.22723200  1.21932900
C          3.08145400 -0.65382200  0.28206200
S          2.51567600  0.06580400 -1.36654900
F          3.16244700 -1.98337000  0.20912700
F          2.22104300 -0.33034900  1.25279900
F          4.28468100 -0.16858600  0.59777200
O          1.07856000 -0.37543400 -1.43037300
O          2.66279500  1.52456500 -1.20139400
O          3.38284300 -0.58761100 -2.36852000
INT2
C         -0.21951100  2.05408300  1.46919300
C         -0.42326700  2.16442800 -0.00497400
C         -0.41576800  3.54403000 -0.57836700
C          0.91772600  4.24106100 -0.19531200
C          1.14011400  4.20006000  1.31991600
C          1.10413200  2.76611200  1.85646000
H         -0.54153600  3.52747200 -1.66876600
H         -0.08844500  1.33914800 -0.62941800
H         -2.16791300  1.79864800 -0.21210500
H         -1.04436900  2.55576500  2.00420700
H         -0.20211700  1.00803400  1.79283300
H          1.74322100  3.71942500 -0.70069700
H          0.90350700  5.27777300 -0.56196200

S32
| Atom | X         | Y         | Z         |
|------|-----------|-----------|-----------|
| O    | -3.286593 | 1.486954  | -0.598621 |
| O    | -4.095582 | -0.920840 | 1.623903  |
| Ca   | -0.555895 | -1.859397 | -1.567113 |
| H    | 1.207888  | -2.230150 | 3.352529  |
| C    | 0.610289  | -2.994707 | 2.837625  |
| H    | -0.129998 | -3.369501 | 3.556751  |
| H    | 1.256976  | -3.806591 | 1.677299  |
| O    | 0.110554  | -2.704204 | 0.506438  |
| O    | -0.934802 | -1.413789 | 1.996240  |
| H    | -1.357103 | -1.017745 | 1.143687  |
| C    | 3.026332  | -0.580045 | 0.452551  |
| F    | 3.089629  | -1.906716 | 0.568684  |
| F    | 2.039039  | -0.127677 | 1.234275  |
| F    | 4.178952  | -0.056460 | 0.874929  |
| O    | 1.323906  | -0.586418 | -1.583729 |
| O    | 2.809572  | 1.389200  | -1.328757 |
| O    | 3.751211  | -0.814192 | -2.105980 |

**INT3**

| Atom | X         | Y         | Z         |
|------|-----------|-----------|-----------|
| C    | -1.907377 | 1.722856  | 1.491180  |
| C    | -1.012659 | 1.256018  | 0.347165  |
| C    | -1.004504 | 2.235262  | -0.821789 |
| C    | -0.576116 | 3.627502  | -0.340946 |
| C    | -1.459885 | 4.120559  | 0.809523  |
| C    | -1.478190 | 3.116131  | 1.966991  |
| H    | -0.322188 | 1.870690  | -1.598208 |
| H    | 0.018590  | 1.192934  | 0.724278  |
| H    | -3.486656 | 1.238191  | -1.226470 |
| H    | -2.951628 | 1.756220  | 1.147098  |
| H    | -1.861419 | 0.998436  | 2.314989  |
| H    | 0.472115  | 3.575967  | -0.008826 |
| H    | -0.606207 | 4.332749  | -1.182928 |
| H    | -1.109485 | 5.100607  | 1.163462  |
| H    | -2.488991 | 4.265027  | 0.440613  |
| H    | -0.470668 | 3.051597  | 2.409142  |
| H    | -2.152547 | 3.457290  | 2.764659  |
| H    | -2.007575 | 2.308122  | -1.270633 |
| Mn   | -2.982734 | -0.863132 | -0.264952 |
| O    | -3.453369 | -1.337757 | 1.159077  |
| O    | -1.310620 | -0.095689 | -0.065656 |
| O    | -3.969154 | 0.442218  | -0.961409 |
| O    | -2.511895 | -1.975350 | -1.365506 |
| Ca   | -0.276749 | -1.405257 | -1.840024 |
| H    | 1.600489  | -3.001533 | 2.959983  |
| C    | 1.138816  | -3.530762 | 2.119125  |
| H    | 0.386295  | -4.221667 | 2.527273  |
| H    | 1.882248  | -4.105081 | 1.559644  |
| C    | 0.443025  | -2.568422 | 1.211061  |
O  0.41413000 -2.69912700 -0.01384400
O  -0.16155300 -1.57467000  1.82166800
H  -0.63474100 -1.00185500  1.14736700
C   3.19304600  0.08865800  0.69118500
S   2.78405400  0.64042900 -1.06242700
F   3.23292800 -1.24620500  0.76362700
F   2.26910100  0.53288400  1.54832000
F   4.38233400  0.57222200  1.05529400
O   1.45622900 -0.01957600 -1.29333000
O   2.69945200  2.11137600 -0.96811300
O   3.87610600  0.08381800  1.88719100

TS3
C  -1.81907300  2.10737400  0.91958700
C  -0.87350100  1.41185900 -0.04798400
C  -0.11618900  2.41076400 -0.91569500
C   0.66897500  3.39030200 -0.03530800
C  -0.24552100  4.09795400  0.96881800
C  -1.03363100  3.08433400  1.80454400
H   0.55622300  1.87325100 -1.59195900
H  -0.16487900  0.79021600  0.50992300
H  -2.41646400  0.96893100 -1.53485100
H  -2.58324600  2.65278200  0.34464600
H  -2.34092300  1.36630000  1.53455900
H   1.45194700  2.83549700  0.50335500
H   1.18477900  4.11919700 -0.67536000
H   0.34470400  4.75309200  1.62536800
H  -0.95232200  4.74546500  0.42411000
H  -0.33505500  2.51213500  2.43689700
H  -1.72714600  3.59635800  2.48548200
H  -0.84601900  2.96305400 -1.52897600
Mn  -3.19147700 -0.55233600 -0.62275000
O  -3.55972400 -0.58274400  0.95578700
O  -1.56169200  0.49058700 -0.95676500
O  -3.73936500  0.67907800 -1.63749400
O  -2.64848100 -1.92643300 -1.33158700
Ca  -0.34069500 -1.67028700 -1.48144000
H   0.97934200 -1.32092500  3.37976500
C   0.46309000 -2.22448700  3.02324800
H   0.01142300 -2.72232300  3.88750200
H   1.19625000 -2.86862500  2.53075000
C  -0.58610100 -1.79764200  2.04347100
O  -0.37365800 -1.71853300  0.83290300
O  -1.73698400 -1.48524100  2.58482000
H  -2.42475000 -1.16723900  1.91333500
C   3.18065500 -0.36558900  0.67022900
S   3.00921400 -0.08807000 -1.18403100
F   2.99872400 -1.65577800  0.96228600
F   2.27607500  0.35695800  1.33850100
F  4.40037400 -0.00327500  1.07381300
O 1.56318300 -0.42639600 -1.41831000
O 3.30943000 1.34379300 -1.37490600
O 3.94863400 -1.05554500 -1.78686200
MnO\textsubscript{4-}/(CaOTf\textsuperscript{+}/3AcOH)

INT1
C 2.39425300 -1.95284800 -3.08507500
C 1.36016800 -1.64171200 -1.99798200
C 1.56255600 -2.51409500 -0.75671800
C 2.99490100 -2.41757500 -0.22252700
C 4.02642600 -2.73133400 -1.31219700
C 3.82425700 -1.83925400 -2.54317000
H 0.85591900 -2.21226600 0.02312800
H 1.44870400 -0.58671300 -1.70115800
H 0.34398300 -1.78120300 -2.39350300
H 2.23090200 -2.97806600 -3.45826300
H 2.25590600 -1.28022600 -3.94462000
H 3.15974200 -1.39578000 0.15042100
H 3.12416500 -3.09342800 0.63606300
H 5.04667500 -2.61193800 -0.91757200
H 3.92673800 -3.47879530 -1.61378600
H 4.01791100 -0.79105100 -2.26160900
H 4.55198400 -2.09785600 -3.32716300
H 1.33423000 -3.56396000 -1.00678800
Mn -2.26545100 -2.08580500 -0.43793300
O -3.79270600 -1.74130900 -0.13051100
O -1.38525700 -0.73076400 -2.47693500
H -1.73159000 -3.14180000 0.62543500
Ca -1.01654500 1.04250700 1.31141200
H -0.65624800 4.11247400 -2.42014600
C -0.75538500 3.15423500 -2.93535900
H 0.11876600 2.96688800 -3.57202700
H -1.63923700 3.16614200 -3.58765000
C -0.89898700 2.04682900 -1.94134100
O -0.98292500 2.22871800 -0.72926000
O -0.93907500 0.84289700 -2.47693500
H -1.05736000 0.16314500 -1.76438200
C -4.54023700 3.01600700 -0.20053700
H -4.37760900 3.64201300 0.68185000
H -5.57540400 3.08189800 -0.55078700
H -3.87963000 3.37276900 -1.00515100
C -4.15823400 1.60152400 0.10170400
O -3.30603300 1.29160500 0.93024900
O -4.78835400 0.69925600 -0.61989900
H -4.44547500 -0.21133300 -0.41571300
C 1.25572800 -1.33985400 3.98955700
H 0.90057900 -0.67458500 4.78354900
H 2.03623600 -0.80576200 3.42670000
H 1.68085100 -2.25873100 4.40368400
| Atom | X        | Y        | Z        |
|------|----------|----------|----------|
| C    | 0.13796100 | -1.62968300 | 3.04058500 |
| O    | -0.70534800 | -0.79788600 | 2.71192400 |
| O    | 0.13325300 | -2.85199100 | 2.55236100 |
| H    | -0.58641400 | -2.95328700 | 1.87742600 |
| C    | 2.86160000 | 2.28402100 | -0.15883100 |
| S    | 2.02196500 | 1.49089600 | 0.75140100 |
| O    | -0.70534800 | -0.79788600 | 2.71192400 |
| O    | 0.13325300 | -2.85199100 | 2.55236100 |
| H    | -0.58641400 | -2.95328700 | 1.87742600 |
| C    | 2.86160000 | 2.28402100 | -0.15883100 |
| S    | 2.02196500 | 1.49089600 | 0.75140100 |
| F    | 1.99609000 | 2.58224400 | -1.01259200 |
| F    | 3.75755700 | 1.43601700 | -0.66496600 |
| F    | 3.48370800 | 3.40196600 | 0.21645500 |
| O    | 1.27252800 | 0.32804900 | 0.75140100 |
| O    | 3.13516500 | 1.16406800 | 2.23528500 |
| O    | 1.03546300 | 2.50857000 | 1.81792000 |
| TS1  | C      | -1.62013300 | 2.24093200 | -2.93292300 |
| C    | -1.09112400 | 1.98201000 | -1.54237000 |
| C    | -1.81543600 | 2.72336700 | -0.44467500 |
| C    | -3.30981400 | 2.33084200 | -0.48376000 |
| C    | -3.90817500 | 2.56534500 | -1.87370800 |
| C    | -3.11458700 | 1.83720500 | -2.96255300 |
| H    | -1.38757700 | 2.47934900 | 0.53398500 |
| H    | -1.00738700 | 0.91687400 | -1.31343300 |
| H    | 0.05864700 | 2.40212900 | -1.51495000 |
| H    | -1.52961200 | 3.30830500 | -3.18603500 |
| H    | -1.05754600 | 1.66856400 | -3.68220600 |
| H    | -3.39817800 | 1.26806300 | -0.21633100 |
| H    | -3.85407600 | 2.90464100 | 0.28009800 |
| H    | -4.95709000 | 2.23330700 | -1.89105400 |
| H    | -3.91456100 | 3.64608600 | -2.09079300 |
| H    | -3.19174900 | 0.74959200 | -2.80640900 |
| H    | -3.52647900 | 2.05180700 | -3.95344400 |
| H    | -1.72079300 | 3.80985800 | -0.59427100 |
| Mn   | 2.15773400 | 2.11139900 | -0.20529500 |
| O    | 3.61160400 | 1.74433700 | -0.75791400 |
| O    | 1.25957000 | 0.73163300 | -0.15242400 |
| O    | 1.28866300 | 2.99394800 | -1.30810300 |
| O    | 2.13343800 | 2.82981500 | 1.21884700 |
| Ca   | 1.02857600 | -1.11109000 | 1.28158500 |
| H    | 0.73099700 | -3.85219200 | -2.74562800 |
| C    | 0.83926400 | -2.83831300 | -3.13817900 |
| H    | -0.00625800 | -2.58300700 | -3.78901300 |
| H    | 1.75302000 | -2.76744300 | -3.74448300 |
| C    | 0.92977800 | -1.85524600 | -2.01485900 |
| O    | 1.01683700 | -2.18612200 | -0.83265800 |
| O    | 0.92313300 | -0.59511000 | -2.39165100 |
| H    | 1.02616400 | -0.00293500 | -1.58709700 |
| C    | 4.52424600 | -3.03515300 | -0.32733100 |
| H    | 4.54392900 | -3.59209700 | 0.61400600 |
| H    | 5.50217600 | -3.05145600 | -0.81973900 |
| H    | 3.79275100 | -3.50953900 | -0.99892600 |
|  | X    | Y    | Z    |
|---|------|------|------|
| C | 4.06405400 | -1.63198400 | -0.08132400 |
| O | 3.33871400 | -1.31432700 | 0.85837700 |
| O | 4.47758100 | -0.76704800 | -0.98281200 |
| H | 4.12272000 | 0.15180400 | -0.82716800 |
| C | -1.38090000 | 1.14440700 | 4.07064600 |
| H | -1.18782700 | 0.38952800 | 4.83978700 |
| H | -2.16193700 | 0.75103400 | 3.40286700 |
| H | -1.73025900 | 2.08168800 | 4.51394400 |
| C | -0.14980900 | 1.35158700 | 3.24741800 |
| O | 0.63410900 | 0.44358700 | 2.97135800 |
| O | 0.02120300 | 2.57941100 | 0.76125500 |
| H | 0.82683100 | 2.64907700 | 2.22554900 |
| C | -2.83979500 | -2.26056500 | -0.27513600 |
| S | -2.03364300 | -1.53550200 | 1.26591000 |
| F | -1.93023000 | -2.48800600 | -1.22251300 |
| F | -3.74543500 | -1.40158100 | -0.74685900 |
| F | -3.44596000 | -3.40913100 | 0.02690000 |
| O | -1.30738300 | -0.32646600 | 0.76125500 |
| O | -0.02120300 | 2.57941100 | 0.76125500 |
| H | 0.82683100 | 2.64907700 | 2.22554900 |

INT3

|  | X    | Y    | Z    |
|---|------|------|------|
| C | -0.52543600 | 2.57250800 | -2.08939000 |
| C | -0.52463900 | 1.77035600 | -0.79201400 |
| C | -1.03994200 | 2.59187600 | 0.38205900 |
| C | -2.46180900 | 3.08389400 | 0.08738000 |
| C | -2.52469500 | 3.86766600 | -1.22795700 |
| C | -1.95273600 | 3.05123300 | -2.39197100 |
| H | -1.03159900 | 1.98200500 | 1.29035100 |
| H | -1.20908000 | 0.92390500 | -0.93287800 |
| H | 1.97962500 | 3.56349400 | -1.41865900 |
| H | 0.12694300 | 3.45109200 | -1.98980600 |
| H | -0.14174200 | 1.96011000 | -2.91464100 |
| H | -3.13200200 | 2.21191600 | 0.02859600 |
| H | -2.81745800 | 3.70216300 | 0.92304400 |
| H | -3.56122200 | 4.16267600 | -1.44922200 |
| H | -1.94431200 | 4.79902900 | -1.12237500 |
| H | -2.59368900 | 2.17344500 | -2.57373000 |
| H | -1.95489000 | 3.64242400 | -3.31777300 |
| H | -0.37251900 | 3.44991300 | 0.54593700 |
| Mn | 2.17880100 | 1.97341500 | 0.29164100 |
| O | 3.41760100 | 1.04802200 | -0.16593300 |
| O | 0.75486400 | 1.13706100 | -0.51883100 |
| O | 2.22420000 | 3.56695700 | -0.48162900 |
| O | 1.87201700 | 2.09386400 | 1.86066600 |
| Ca | 0.44839200 | -1.11483800 | 0.60428900 |
| H | 1.47545100 | -3.17411800 | -3.69720000 |
| C | 1.65884400 | -2.11242100 | -3.87905700 |
| H | 1.02883200 | -1.75524500 | -4.70514800 |
| H | 2.70441900 | -1.94890700 | -4.17169400 |
|   | C                  | O                  | O                  | H                  | C                  | H                  | H                  | C                  | O                  | O                  | H                  | C                  | O                  | O                  | H                  | C                  | O                  | O                  | H                  | C                  | O                  | O                  | H                  |
|---|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|
| C | 1.35609500         | -1.31546400        | -2.65057000        | 1.33540600         | 4.09571000         | 3.72859100         | -4.34693200        | 1.33540600         | 0.45013700         | -1.92374200        | 4.09571000         | -3.70838900        | 0.10022600         | 2.54603700         | -2.05875300        | 0.89936200         | 4.27171800         | -1.39484200        | -0.34946800        | 3.88100700         | -0.47239200        | -0.23648100        | 3.23121700         | -0.31688000        | 4.60884000         |
| H | -1.01812100        | -1.32709100        | 4.97306200         | -2.17833000        | -0.35019700        | 4.04918000         |                   | -1.33555800        | 0.39052400         | 5.43708500         |                   |                   |                   |                   |                   |                   |                   |                   |                   |                   |                   |                   |                   |                   |                   |
| F | 2.39008400         | -0.45346100        | 1.00047300         | -3.91023400        | -2.54604600        | -1.48401300        |                   | -1.93998100        | -0.37422600        | 0.95935600         |                   |                   |                   |                   |                   |                   |                   |                   |                   |                   |                   |                   |                   |                   |                   |
| O | -3.68282300        | -2.12482100        | 1.50162500         | -1.47909500        | -2.70333600        | 0.39723200         |                   |                   |                   |                   |                   |                   |                   |                   |                   |                   |                   |                   |                   |                   |                   |                   |                   |                   |                   |

**TS3**

|   | C                  | O                  | O                  | H                  | C                  | C                  | C                  | C                  | C                  | C                  | C                  | C                  | C                  | C                  | C                  | C                  | C                  | C                  | C                  | C                  | C                  | C                  | C                  | C                  | C                  | C                  | C                  |
|---|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|
| C | -2.18712700        | 3.15847500         | -0.54477300        | -1.64522300        | 1.97883300         | 0.25566600         |                   | -2.49640400        | 1.67375300         | 1.47660500         |                   |                   |                   |                   |                   |                   |                   |                   |                   |                   |                   |                   |                   |                   |                   |                   |                   |
| C | -3.94425500        | 1.40014400         | 1.05123100         | -4.52266100        | 2.55949900         | 0.23356300         |                   | -3.63459200        | 2.88204200         | -0.97232800        |                   |                   |                   |                   |                   |                   |                   |                   |                   |                   |                   |                   |                   |                   |                   |                   |                   |
| H | -2.08377200        | 0.80693000         | 2.00432600         | -1.58860000        | 1.08778600         | -0.37742500        |                   | 0.07372100         | 3.13296200         | 1.27366400         |                   |                   |                   |                   |                   |                   |                   |                   |                   |                   |                   |                   |                   |                   |                   |                   |                   |
| H | -2.14705700        | 4.06185100         | 0.08365500         | -1.55224500        | 3.33825200         | -1.42195500        |                   | -3.96875800        | 0.47908600         | 0.44802400         |                   |                   |                   |                   |                   |                   |                   |                   |                   |                   |                   |                   |                   |                   |                   |                   |                   |
| H | -4.55722800        | 1.21022900         | 1.94282300         | -5.54174000        | 2.31733600         | -0.10007100        |                   | -4.60104800        | 3.45255700         | 0.87518000         |                   |                   |                   |                   |                   |                   |                   |                   |                   |                   |                   |                   |                   |                   |                   |                   |                   |
| H | -3.64516900        | 2.03066300         | -1.67174600        | -4.02459100        | 3.74982900         | -1.52197900        |                   | -2.45984700        | 2.53230700         | 2.16543000         |                   |                   |                   |                   |                   |                   |                   |                   |                   |                   |                   |                   |                   |                   |                   |                   |                   |
| O | 0.83698500         | 1.48569800         | 1.99516900         | 2.04873600         | 0.75042800         | 1.13704700         |                   |                   |                   |                   |                   |                   |                   |                   |                   |                   |                   |                   |                   |                   |                   |                   |                   |                   |                   |                   |                   |                   |
| Element | X          | Y          | Z          |
|---------|------------|------------|------------|
| O       | -0.25756900| 2.27184100 | 0.59593700 |
| O       | 0.96169800 | 3.14180200 | 2.28328900 |
| O       | 0.06258000 | 0.62353800 | 3.10341100 |
| Ca      | 1.50329600 | -1.23291500| -0.05931200|
| H       | 2.26131100 | 0.67478100 |-4.15575900 |
| C       | 2.19480800 | 1.61569400 | -3.60374500|
| H       | 1.67699100 | 2.38185900 | -4.19245900|
| H       | 3.20919600 | 1.98589600 | -3.39457600|
| C       | 1.49786300 | 1.39799800 | -2.29747500|
| H       | 1.31550500 | 0.28821800 | -1.80732200|
| O       | 0.96169800 | 3.14180200 | 2.28328900 |
| C       | 2.19480800 | 1.61569400 | -3.60374500|
| H       | 1.67699100 | 2.38185900 | -4.19245900|
| H       | 3.20919600 | 1.98589600 | -3.39457600|
| C       | 1.49786300 | 1.39799800 | -2.29747500|
| H       | 1.31550500 | 0.28821800 | -1.80732200|