Electronic Supplementary Information

Synergistic effects of CH_3CO_2H and Ca^{2+} on C-H bond activation by MnO_4^-

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Experimental details

Materials

$KMnO_4$ 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 d_{12}-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 $(NH_4)_2FeSO_4$. 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 $KMnO_4$

(1) Stoichiometric oxidation of cyclohexane by $KMnO_4$-AcOH in CH_3CN

In a typical experiment, 0.031 mmol of $KMnO_4$ was added to a solution of CH_3CN containing cyclohexane (0.314 ml), acetic acid (0.1-1.5 ml) and chlorobenzene (1 uL, as internal standard) at 23 ^oC (Total volume = 3.1 ml). 1 uL of the reaction mixture was withdrawn at different reaction times and analyzed with GC until the amount of product formed from the reaction became steady.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 $KMnO_4$-$Ca(OTf)_2$ in CH_3CN

In a typical experiment, 0.031 mmol of $KMnO_4$ was added to a solution of CH_3CN containing cyclohexane (0.314 ml), $Ca(OTf)_2$ (0.5 to 4 equivalents with respect to $KMnO_4$) and chlorobenzene (1 uL, as internal standard) at 23 ^oC (Total volume = 3.1 ml). 1 uL of the reaction mixture was withdrawn at different reaction times and analyzed with GC.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 $KMnO_4$-$Ca(OTf)_2$-AcOH in CH_3CN

In a typical experiment, 0.031 mmol of $KMnO_4$ was added to a solution of CH_3CN 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 ^oC (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 $KMnO_4$-AcOH in CH_3CN

0.031 mmol of $KMnO_4$ was added to a solution of CH_3CN containing cyclohexane (0.157 ml), d_{12}-cyclohexane (0.157 ml), acetic acid (0.5 ml) and chlorobenzene(1 uL, as internal standard) at 23 ^oC (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 $KMnO_4$-$Ca(OTf)_2$ in CH_3CN

0.031 mmol of $KMnO_4$ was added to a solution of CH_3CN containing cyclohexane (0.157 ml), d_{12}-cyclohexane (0.157 ml), $Ca(OTf)_2$ (1 equivalent) and chlorobenzene (1 uL, as internal standard) at 23 °C (Total volume = 3.1ml). The reaction mixture was analyzed by GC fitted with HP5MS column.

(3) Stoichiometric oxidation of cyclohexane by $KMnO_4$-$Ca(OTf)_2$-AcOH in CH_3CN

0.031 mmol of $KMnO_4$ was added to a solution of CH_3CN containing cyclohexane (0.157 ml), d_{12}-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 = 3.1ml). 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 $KMnO_4$ in the presence of $Ca(OTf)_2$ and acetic acid in CH_3CN

0.031mmol of $KMnO_4$ was dissolved in solution containing 1.69 ml of CH_3CN, 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 CH_3CN 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 $KMnO_4$ in the presence of $Ca(OTf)_2$ in CH_3CN

Similar method as that of (1), except that 2.69 ml of CH_3CN was used for the oxidation.

(3) Oxidation of cyclohexane by $KMnO_4$ in the presence of AcOH in CH_3CN

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 $KMnO_4$-$Ca(OTf)_2$-AcOH in CH_3CN

0.031 mmol of $KMnO_4$ was added to a solution of CH_3CN 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)

	MW	Ca (%)	Mn (%)	C (%)	N (%)	H (%)
Experimental results		6.25	22.45	6.82	1.59	3.15
$Ca_2Mn_5O_{10}(CF_3SO_3)_4(CH_3CN).13H_2O$	1368	5.84	20.10	5.26	1.02	2.12
$Ca_3Mn_7O_{14}(CF_3SO_3)_6(CH_3CN)_2.10H_2O$	1885	6.37	20.42	6.37	1.49	1.38
$Ca_3Mn_8O_{16}(CF_3SO_3)_6(CH_3CN)_2.20H_2O$	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

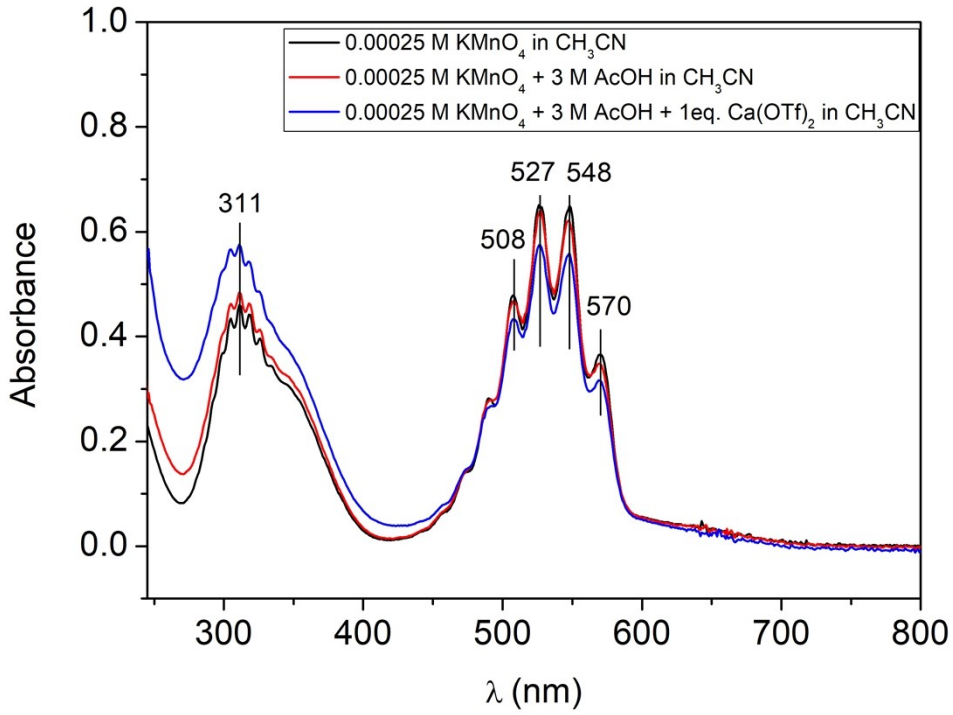


Fig. S1 UV-Vis spectra of $KMnO_4$ in CH_3CN, $KMnO_4$ and 3 M AcOH in CH_3CN (using 3 M AcOH as background), and $KMnO_4$, 3 M AcOH and 1 eq. $Ca(OTf)_2$ in CH_3CN (using 3 M AcOH as background). In spectrum of $KMnO_4$, 3 M AcOH and 1 eq. $Ca(OTf)_2$ in CH_3CN (blue), the absorbance at 527 nm decreased as the $KMnO_4$ decayed slightly after addition of $Ca(OTf)_2$.

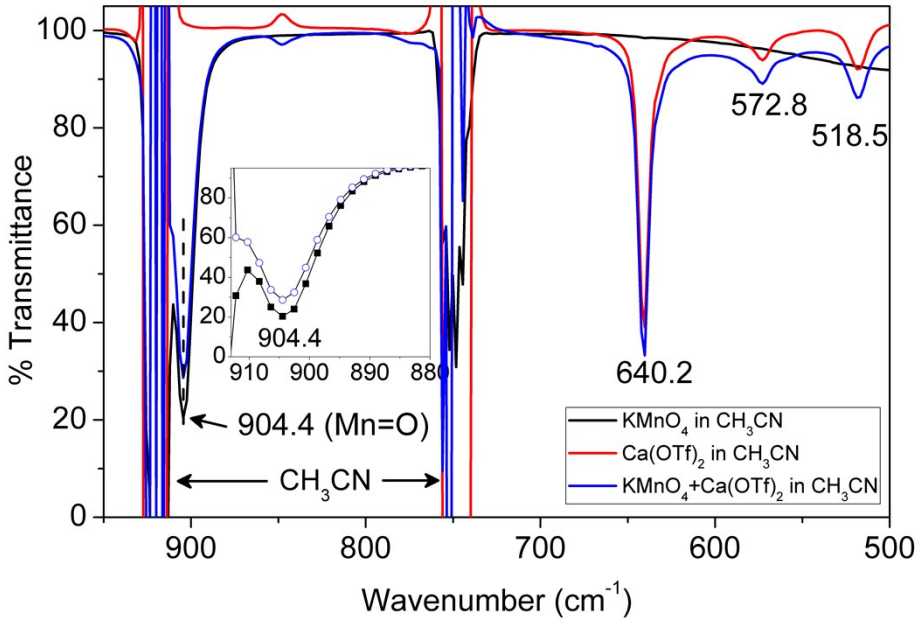


Fig. S2 Solution IR spectra (950-500 cm^{-1}) of $KMnO_4$ (2.5 mM), $Ca(OTf)_2$ (2.5 mM) and $KMnO_4$+$Ca(OTf)_2$ (2.5 mM) in CH_3CN measured with a 1 mm KBr IR cell. The IR spectra show that upon addition of 1 equiv. $Ca(OTf)_2$ to $KMnO_4$ in CH_3CN the stretching frequency of Mn=O at 904 cm^{-1} is not shifted.

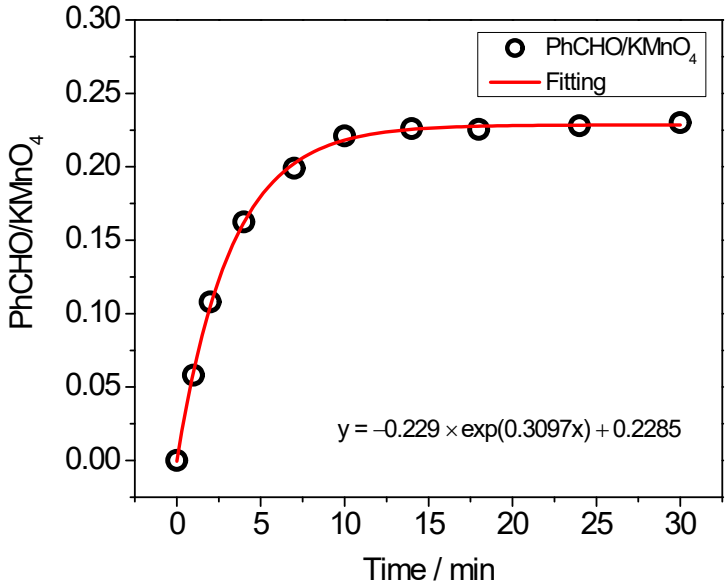


Fig. S3 Time trace for the oxidation of toluene by $KMnO_4$ in acetonitrile with 1 equivalent of $Ca(OTf)_2$ and 2.8M acetic acid, Temperature: 22°C. Conditions: $KMnO_4$ (0.01M), $Ca(OTf)_2$ (0.01M), AcOH (2.8M), toluene (1M), solvent: CH_3CN

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_{obs} for the reaction 0.31 min^{-1}. The oxidation of cyclohexane under the same conditions: k_{obs} = 0.054 min^{-1} (yield: 57 %). Therefore, the ratio of k_{obsd} of toluene to cyclohexane = 5.75:1.

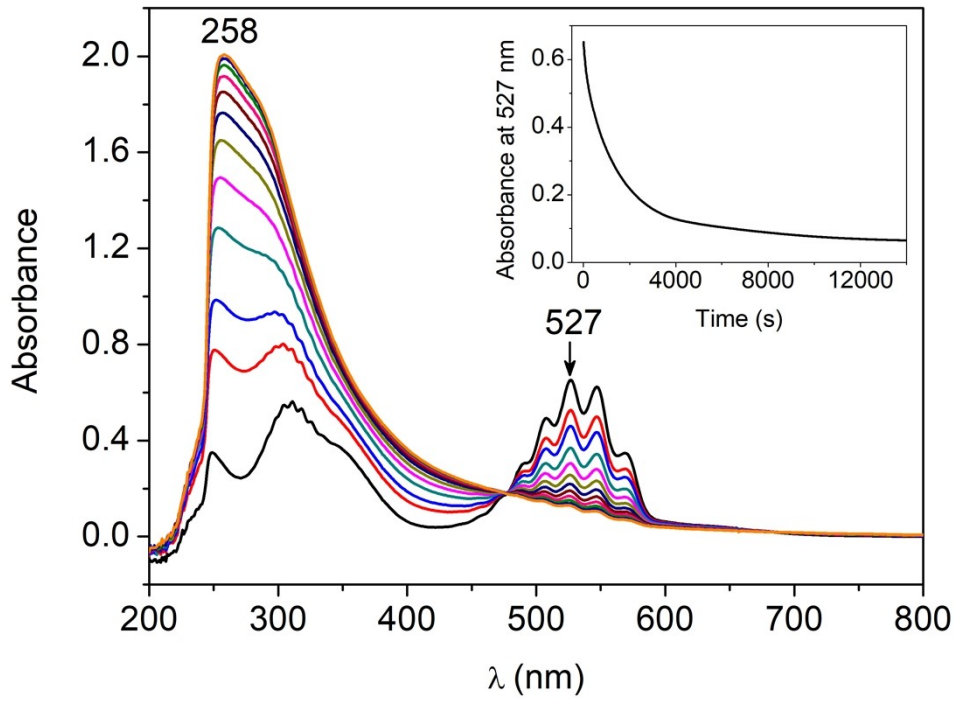


Fig. S4 UV-Vis monitoring the reaction of $KMnO_4$ (0.0003 M), $Ba(OTf)_2$ (0.0003 M), AcOH (3 M) and cyclohexane (1 M) in CH_3CN at 25 °C. 3 M AcOH in CH_3CN was used as background in measurement.

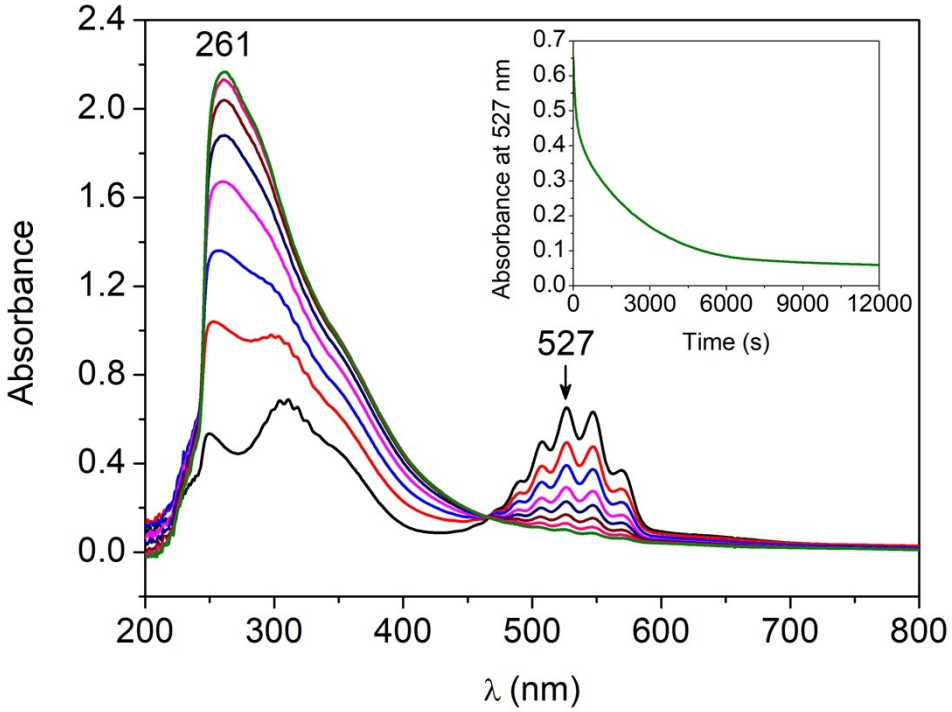


Fig. S5 UV-Vis monitoring the reaction of $KMnO_4$ (0.0003 M), $Mg(OTf)_2$ (0.0003 M), AcOH (3 M) and cyclohexane (1 M) in CH_3CN at 25 °C. 3 M AcOH in CH_3CN was used as background in measurement.

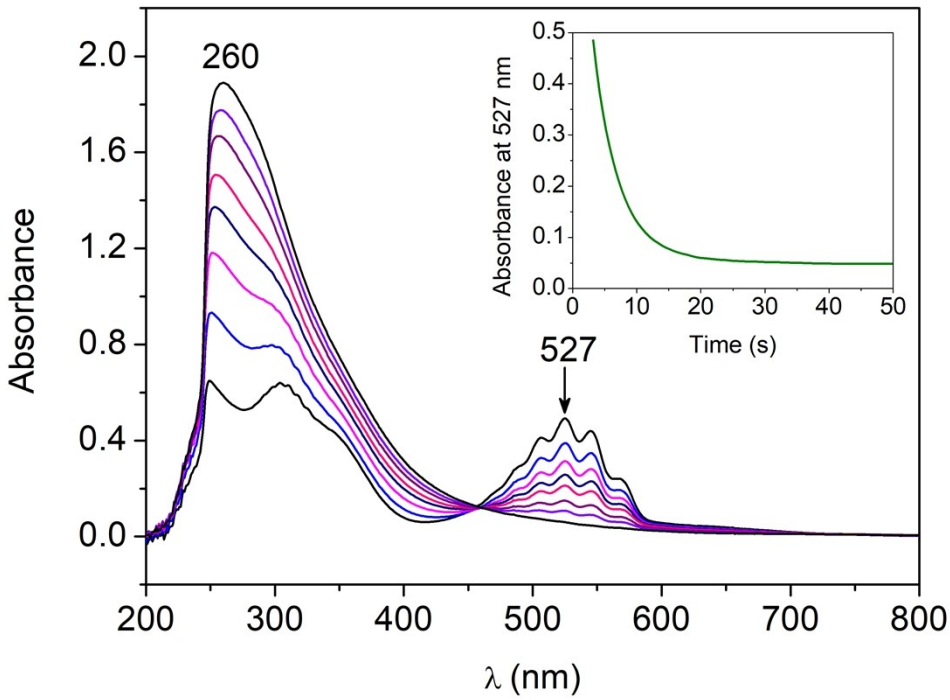


Fig. S6 UV-Vis monitoring the reaction of $KMnO_4$ (0.0003 M), $Sc(OTf)_3$ (0.0003 M), AcOH (3 M) and cyclohexane (1 M) in CH_3CN at 25 °C. 3 M AcOH in CH_3CN was used as background in measurement.

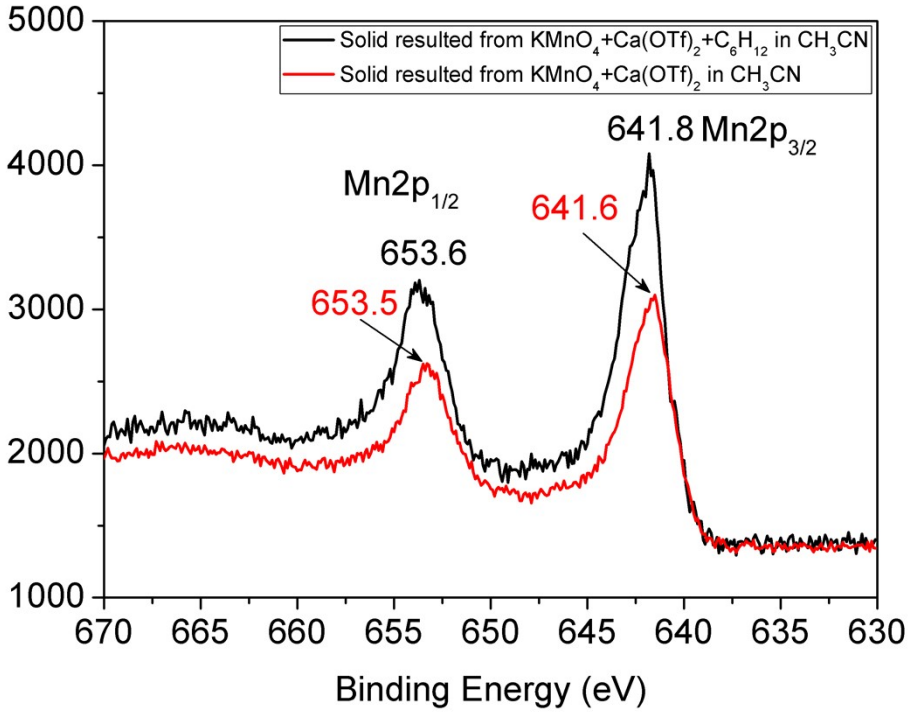


Fig. S7 Mn2p XPS spectra of **1** and **2**.

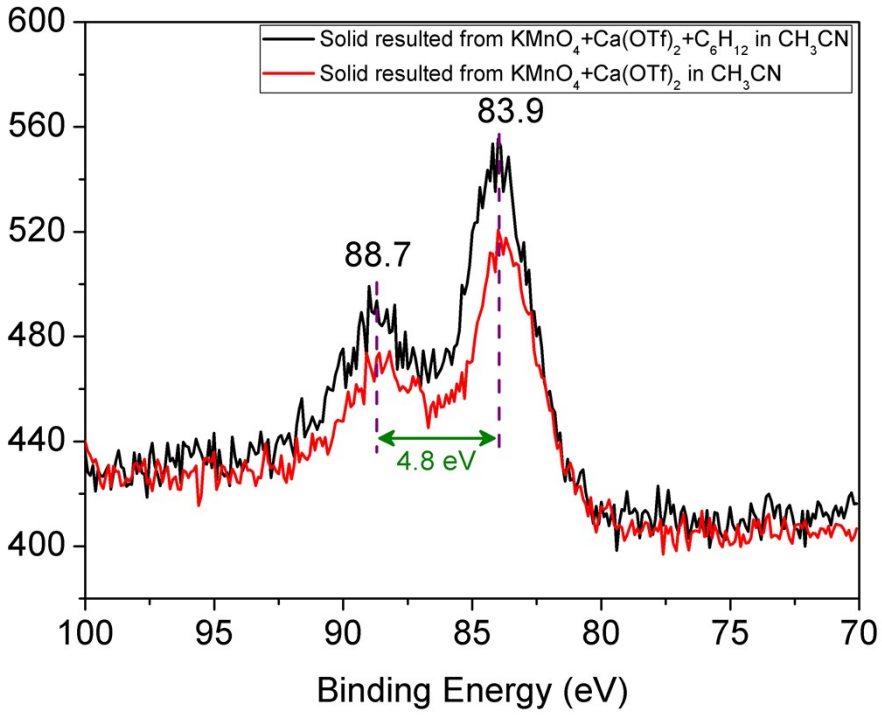


Fig. S8 Mn3s XPS spectra of **1** and **2**.

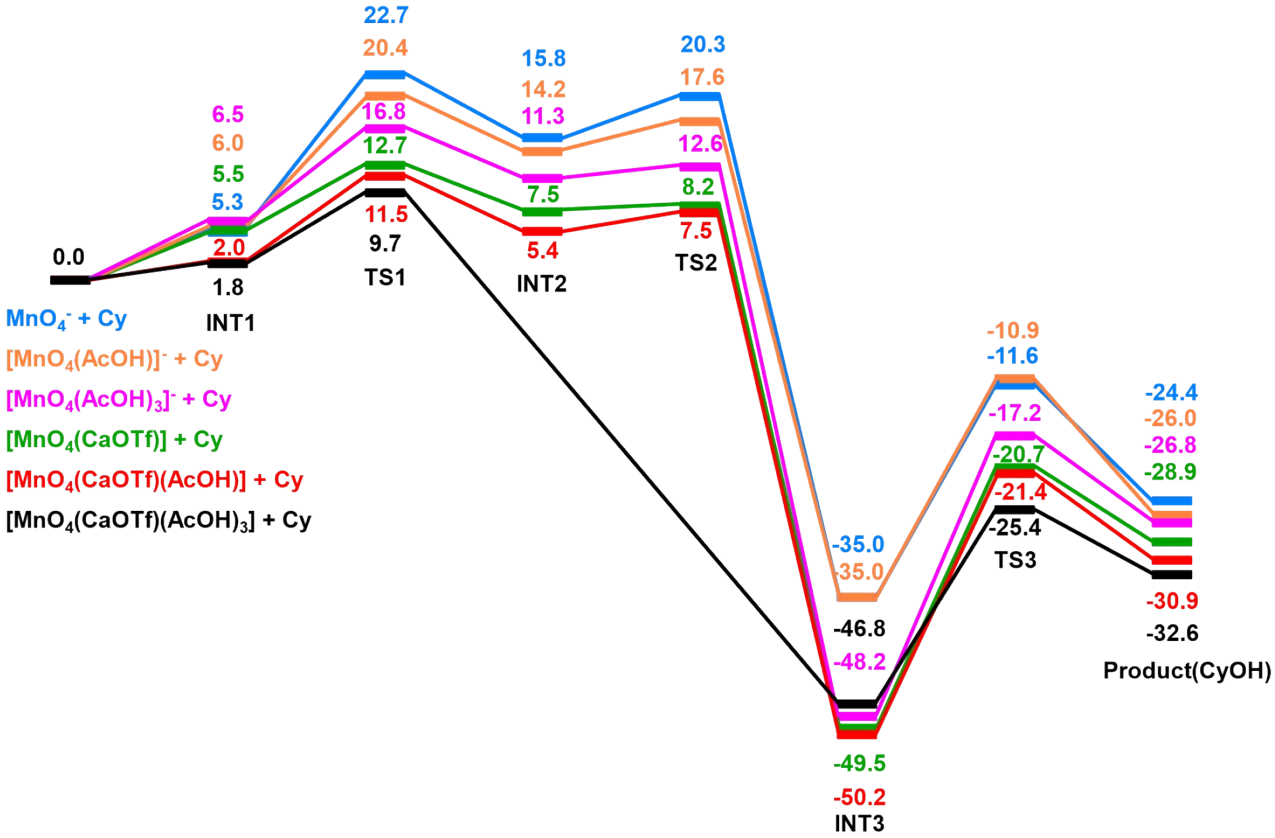


Fig. S9 PESs for cyclohexane oxidation by $[MnO_4]^-$/$[MnO_4(AcOH)]^-$/$[MnO_4(AcOH)_3]^-$/ $[MnO_4(CaOTf)]$/$[MnO_4(CaOTf)(AcOH)]$/ $[MnO_4(CaOTf)(AcOH)_3]$ at the B3LYP-D3(BJ)/def2-SVPD level. Relative 298 K Gibbs free energies in acetonitrile are given in kcal mol^{-1}.

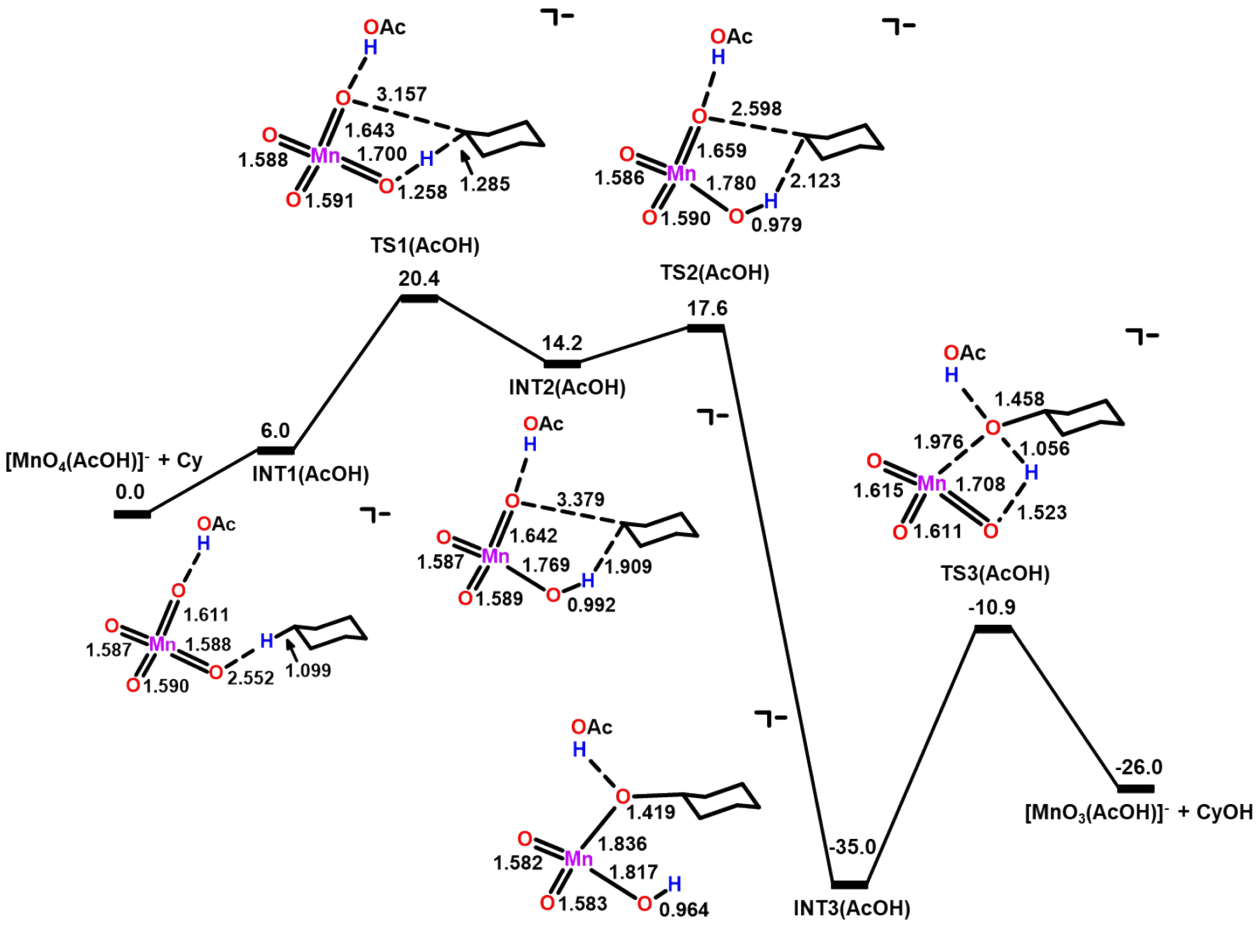


Fig. S10 PES and structures for cyclohexane oxidation by $[MnO_4(AcOH)]^-$ at the B3LYP-D3(BJ)/def2-SVPD level. Relative 298 K Gibbs free energies in acetonitrile are given in kcal mol^{-1}.

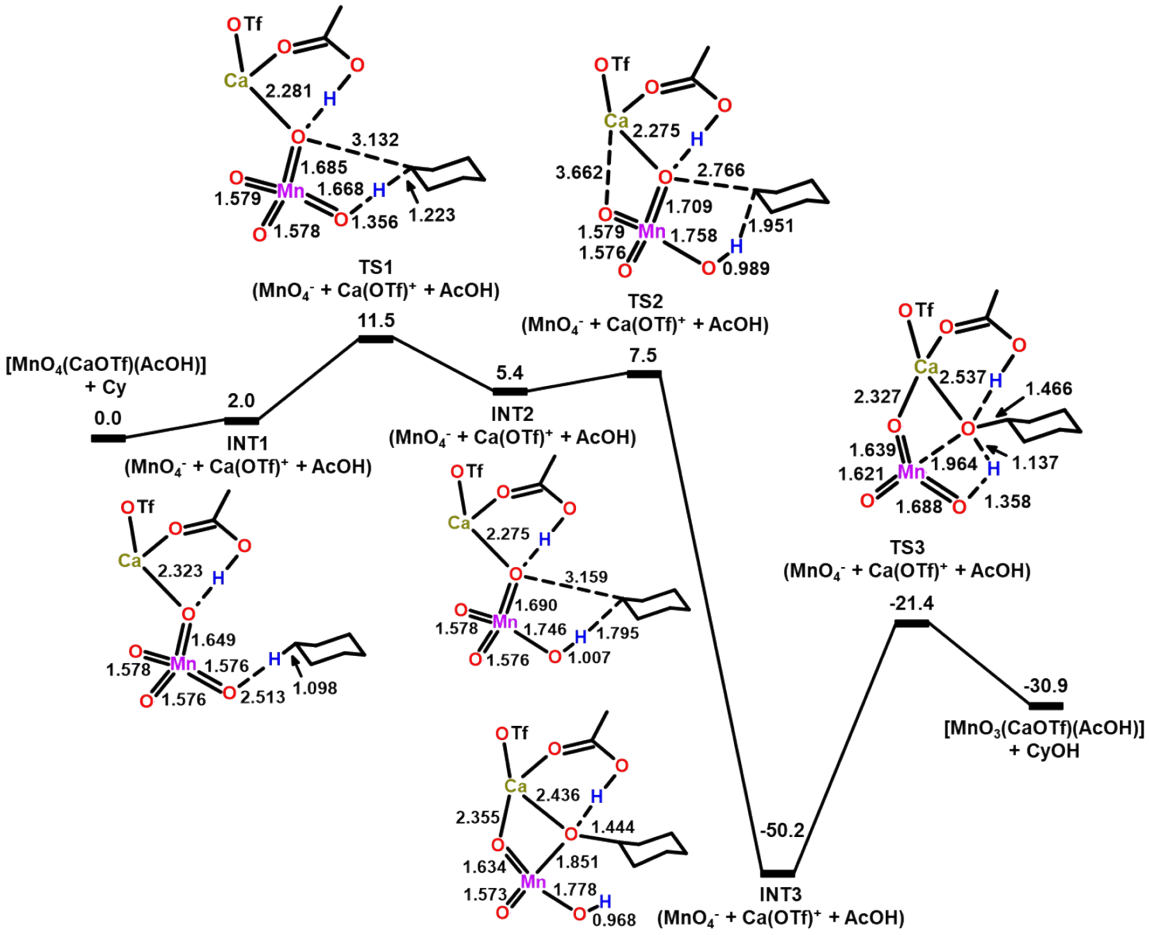


Fig. S11 PES and structures for cyclohexane oxidation by [MnO_4(CaOTf)(AcOH)] at the B3LYP-D3(BJ)/def2-SVPD level. Relative 298 K Gibbs free energies in acetonitrile are given in kcal mol^{-1}.

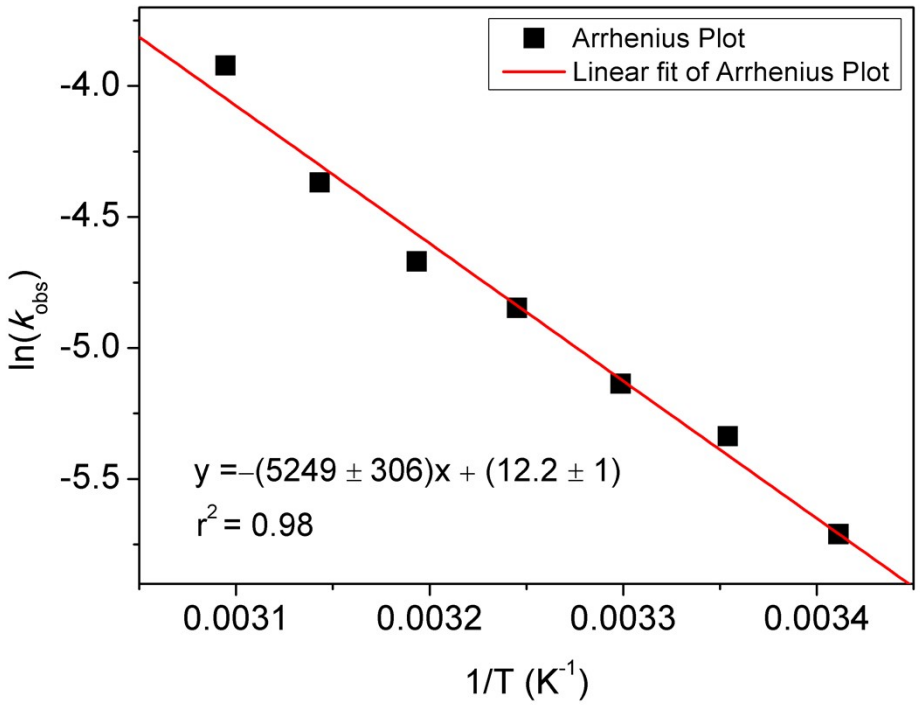


Fig. S12 Arrhenius plot of the reaction of $KMnO_4$ (0.00025 M) with cyclohexane (1.0 M) in CH_3CN in the presence of AcOH (3.0 M) and $Ca(OTf)_2$ (0.00025 M). Rate constants in temperature range of 20-50 °C were obtained by Pseudo-first-order reaction fitting of the absorbance of $KMnO_4$ at 527 nm. $\Delta G^{\ddagger}$ = 10.4 ± 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.

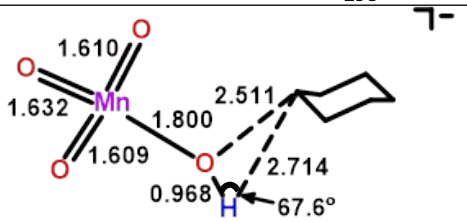
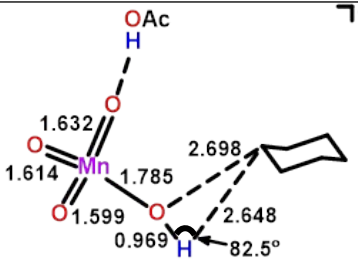
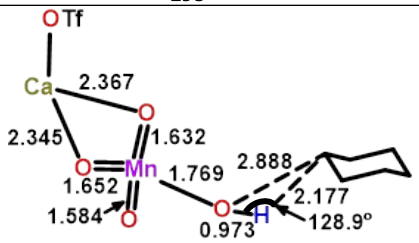
	TS for hydroxylation via rebound mechanism and $\Delta G_{298}^{\ddagger}$	$\Delta G_{298}^{\ddagger}$ (current TS2)
MnO_4^-	 $\Delta G_{298}^{\ddagger}$=22.9	20.3
MnO_4^-/AcOH	 $\Delta G_{298}^{\ddagger}$=19.6	17.6
MnO_4^-/ $(CaOTf)^+$	 $\Delta G_{298}^{\ddagger}$=11.6	8.2

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	1.11488000	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	1.05351700
O	3.08569300	-0.97497800	0.30174400
O	2.20230700	1.60567600	0.03007900
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	-1.31321900	-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	-1.68475200
H	-3.50752400	-1.16503200	1.04188100
H	-3.53086800	-1.97562000	-0.52653000
H	-0.78037700	1.17274300	-0.81648100

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	-0.23328100
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	-0.86045800	-1.11390100	-0.97587500

MnO_4^-/AcOH
INT1

O	4.15503300	-0.32071600	-0.22542500
O	1.79448400	0.54212400	-0.93114500
O	2.13273900	-1.94808900	-0.22466700
O	2.28698600	-0.07571100	1.55976100
C	-1.20980400	-0.83730300	0.72287900
C	-1.25582300	-1.32057400	-0.72983200
C	-2.40581200	-2.30883300	-0.95412000
C	-3.74938000	-1.70907800	-0.52065300
C	-3.70482000	-1.22522600	0.93408900
C	-2.55147000	-0.24078800	1.16059000
H	-2.44767500	-2.61410600	-2.01052200
H	-1.39369700	-0.44966900	-1.38996900
H	-0.29263800	-1.77480800	-1.00087500
H	-0.96258800	-1.69007500	1.37808100
H	-0.40542700	-0.10422000	0.85618900
H	-3.98769600	-0.85351500	-1.17570800
H	-4.55823300	-2.44343900	-0.65408500
H	-4.66373600	-0.76232600	1.21189600
H	-3.57016700	-2.09548900	1.59860000
H	-2.74523400	0.67475900	0.57799100
H	-2.50693800	0.06407500	2.21667800
H	-2.21499600	-3.22468500	-0.36893700
C	-2.07064900	3.46089200	-0.39598500
H	-2.46492800	3.87369900	0.53680400
H	-2.81668700	2.81313200	-0.87424600
H	-1.84925700	4.27869600	-1.09606800
C	-0.80768200	2.68718100	-0.12658600
O	-0.22355900	2.67385800	0.94171500
O	-0.38291200	2.01852900	-1.19602300
H	0.43771600	1.49103200	-0.99204600
Mn	2.59490600	-0.45362600	0.05000800

TS1

O	3.58927600	-1.38027700	-0.72042000
O	1.62708600	0.37010700	-0.99618800
O	1.25823300	-1.65109300	0.58876400
O	2.96947500	0.29388700	1.28928600
C	-1.64859200	-0.34825800	0.96733700
C	-1.07341600	-1.07302300	-0.22643400
C	-1.74770300	-2.39077100	-0.52685100
C	-3.25752800	-2.14654900	-0.75443200
C	-3.88904200	-1.40640500	0.42969400
C	-3.15463400	-0.09742600	0.73830000
H	-1.30257200	-2.87167200	-1.40842400
H	-0.95744500	-0.43388300	-1.10787800
H	0.13557000	-1.35255600	0.10687500

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	4.49764900	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	0.33701200	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	-0.07960200	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	0.60465400	-2.43620400	0.33798000
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	-0.44237700
H	0.48292000	5.17524000	0.44293800
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	0.54897100	-0.61407300
H	1.61558600	0.24571600	-0.40499800
Mn	0.17982000	-2.09334200	0.07846800

TS3

O	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_4^-/3AcOH
INT1

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	-3.77222500	0.71833500
C	2.57209700	-2.57865800	-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	-2.72999300	0.65784400	-1.92756300
C	-4.00623000	0.01413000	-1.37319900
C	-4.00016600	-1.50635400	-1.57553000
C	-2.74525200	-2.14561600	-0.96871200
H	-2.72781400	1.73913300	-1.73211200
H	-1.45627900	0.23772100	-0.24279900
H	-0.57018300	0.46490200	-1.74674200
H	-1.38226900	-1.72576900	-2.59268300
H	-0.57986000	-1.93723900	-1.03726700
H	-4.07591200	0.23216800	-0.29417400
H	-4.89630500	0.45907900	-1.84342200
H	-4.90559100	-1.95393000	-1.13892100
H	-4.02973500	-1.72550200	-2.65629500
H	-2.77691800	-2.01204800	0.12414100
H	-2.73765100	-3.23015000	-1.15425700
H	-2.70806500	0.53172800	-3.02366300
C	-1.53880700	-2.93742800	2.71359900
H	-2.51110500	-2.81349400	3.19732900
H	-0.81676800	-3.36094800	3.42451400
H	-1.61948800	-3.63829700	1.87197000
C	-1.03421900	-1.61117700	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

TS1

O	0.93252100	-3.37807000	-0.43618400
O	-1.70528700	-2.86674300	-0.86178000
O	-0.22541600	-1.27261300	0.61857800
O	0.18039300	-1.26377100	-1.91870400
H	-4.92738800	1.61694100	0.05120600
C	-4.54754800	0.78243500	0.64769400
H	-5.37295200	0.24334900	1.12871500
H	-3.88847500	1.16740400	1.43842600
C	-3.73784100	-0.14380000	-0.21683600
O	-3.31083400	0.14322500	-1.32073800
O	-3.51322400	-1.32305600	0.36156000
H	-2.89246200	-1.87391600	-0.19013900
C	-0.35926200	1.98752200	-1.30445000
C	0.83079400	1.07778200	-1.11532500
C	2.01200300	1.41873000	-1.99269800
C	2.44430300	2.87395100	-1.69989500
C	1.27409800	3.84850900	-1.86816400
C	0.07203900	3.44232100	-1.00992900
H	2.84090300	0.72643700	-1.80556700
H	1.10788600	0.93631700	-0.06557100
H	0.47818400	-0.07492900	-1.46908500
H	-0.71436300	1.92469500	-2.34484000
H	-1.19306800	1.69227600	-0.66005500
H	2.82278200	2.93035400	-0.66658000
H	3.27857500	3.14717400	-2.36260800
H	1.59376200	4.86917700	-1.61005600
H	0.97023700	3.86976500	-2.92775500
H	0.33934500	3.52822800	0.05499000
H	-0.77932300	4.11666000	-1.18226900
H	1.72900300	1.33608100	-3.05412900
C	-1.16571800	2.90483400	2.80294200
H	-0.45780100	3.54585900	3.33485200
H	-1.99814000	2.62557700	3.46166300
H	-1.59314700	3.45044400	1.95009100
C	-0.47275300	1.66872900	2.29624300
O	0.72815000	1.47423400	2.36968900
O	-1.31716100	0.80794100	1.73861800
H	-0.84108800	0.02404700	1.33480900
C	3.67637300	-0.39215700	2.18069200
H	4.52502700	0.22371300	1.86766400
H	3.92895100	-0.98113300	3.07027500
H	2.82842100	0.26319100	2.43178000
C	3.23588900	-1.27834500	1.05008200
O	3.44949200	-1.04664500	-0.12628000
O	2.54648100	-2.34191900	1.46469200
H	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

O	-1.42277500	-3.15825200	0.17736200
O	1.30340000	-3.15404200	0.59479400
O	0.04634600	-1.02770800	-0.36757100
O	-0.32935500	-1.48504600	2.07554900
H	4.52015100	1.33354800	0.10757600
C	4.21827400	0.50494000	-0.53885000
H	5.09448000	0.08274100	-1.04855300
H	3.52599600	0.86050700	-1.31457500
C	3.52952300	-0.56128300	0.26837600
O	3.29302800	-0.48007200	1.46047600
O	3.18946800	-1.61685100	-0.46813700
H	2.58670900	-2.22407600	0.04443500
C	0.87601900	1.83649700	0.87119200
C	-0.50488200	1.28293000	0.94773000
C	-1.29656300	1.62760800	2.16813700
C	-1.37480300	3.17574500	2.27496800
C	0.02484900	3.79786700	2.25265500
C	0.80879800	3.38116700	1.00439600
H	-2.29927800	1.18770100	2.12553600
H	-1.04203700	1.12967700	0.01568600
H	-0.35586900	-0.53331900	1.81203400
H	1.49362600	1.44171900	1.69247900
H	1.36687500	1.55802200	-0.06615500
H	-1.96486000	3.56249300	1.42924100
H	-1.91196700	3.44756000	3.19528200
H	-0.04997600	4.89441200	2.30107700
H	0.57698700	3.47681900	3.15160600
H	0.31828300	3.79336400	0.10839000
H	1.83012000	3.78752400	1.02827500
H	-0.79716300	1.25973500	3.08038800
C	1.05869800	2.14380200	-3.80762100
H	0.38345600	2.90107400	-4.21523500
H	1.45657600	1.51404500	-4.61436900
H	1.91587300	2.63124500	-3.32201100
C	0.33877200	1.29136500	-2.79732700
O	-0.80379600	1.48938700	-2.42237700
O	1.09294300	0.29505800	-2.34446700
H	0.62889500	-0.22972200	-1.62560100
C	-3.99713800	0.59878500	-1.50159500
H	-4.61545700	1.30426700	-0.93920800
H	-4.56054200	0.17866300	-2.34445100
H	-3.11781800	1.11641000	-1.91176000
C	-3.50515600	-0.49614000	-0.59699000
O	-3.56567100	-0.46329700	0.61961100
O	-2.96456500	-1.51115200	-1.26900900
H	-2.49994400	-2.13922500	-0.65065400
Mn	-0.09014600	-2.35756400	0.56961200

INT3

O	0.78431600	-0.52014900	-2.37389700

O	-1.08346400	-2.20729200	-1.26100200
O	-0.28239700	-0.09047500	0.19479400
O	-1.87968500	0.28575100	-2.10619400
H	-5.82829300	-0.77540700	1.18762800
C	-4.97716500	-1.40969600	1.45056000
H	-5.30501900	-2.44031600	1.63550400
H	-4.51711300	-1.03882000	2.37791200
C	-3.94576800	-1.37711100	0.35784000
O	-3.98533600	-0.58186000	-0.57501800
O	-2.99217100	-2.27505800	0.51471500
H	-2.27881900	-2.22498100	-0.20383700
C	-1.75301900	1.68549200	0.98084600
C	-0.32416500	1.26842900	0.63992200
C	0.33267700	2.23741900	-0.34033600
C	0.30614700	3.66471200	0.21846200
C	-1.12103300	4.10258800	0.56635800
C	-1.78338300	3.11537700	1.53410600
H	1.35960300	1.91158700	-0.54436500
H	0.27633400	1.26589000	1.56403600
H	-2.69282800	0.02959000	-1.60843400
H	-2.36453800	1.62493900	0.07082900
H	-2.17281900	0.97580800	1.70681600
H	0.93140900	3.71060900	1.12571300
H	0.75569100	4.35673800	-0.50794900
H	-1.11587600	5.11427400	0.99825000
H	-1.71707400	4.15435700	-0.36011500
H	-1.25117700	3.14331700	2.49947300
H	-2.82148000	3.41365000	1.73918600
H	-0.22008600	2.20704200	-1.29096600
C	3.15343500	-2.26150800	2.67756500
H	3.94448700	-1.77447300	3.25476200
H	3.60314100	-2.84249900	1.85937700
H	2.59368400	-2.96271500	3.30916200
C	2.22809400	-1.23183500	2.08563600
O	2.46727700	-0.03534500	2.06304900
O	1.12570500	-1.76303800	1.57445200
H	0.57979400	-1.06987000	1.08102000
C	5.09126400	-0.24057400	-0.12918000
H	5.85194300	0.53494200	-0.25843000
H	5.49404700	-1.22597300	-0.39273300
H	4.78142900	-0.27172300	0.92480700
C	3.87826300	0.07933700	-0.96039800
O	3.64048100	1.17942200	-1.42947700
O	3.07428500	-0.96719000	-1.12039700
H	2.24127000	-0.72210400	-1.61971100
Mn	-0.54367500	-0.68351100	-1.47537700

TS3

O	1.03165900	-0.26192600	-2.54216200
O	-1.61704100	-0.37253300	-1.68257400

O	0.27900700	1.17144100	-0.10348000
O	-0.37322900	2.14636300	-2.06129300
H	-5.89147100	1.62160300	1.19428300
C	-5.42811800	0.64383500	1.03343200
H	-6.16824200	-0.07715800	0.66382600
H	-5.04480500	0.26179100	1.99101500
C	-4.27776600	0.76242500	0.06867500
O	-3.77762900	1.82105900	-0.27109600
O	-3.85211900	-0.41769600	-0.36710100
H	-3.00682600	-0.31917100	-0.90532900
C	1.62809500	1.53106000	1.87145300
C	1.62789100	1.01276300	0.43782100
C	2.65939100	1.72637900	-0.42522000
C	4.05635900	1.57532400	0.19056100
C	4.09171600	2.08160100	1.63623000
C	3.02543700	1.38693300	2.48889800
H	2.63846500	1.31368000	-1.44063900
H	1.82107500	-0.06471500	0.42968100
H	0.07902800	2.05708700	-0.74410500
H	1.32545100	2.59017500	1.86650700
H	0.88981400	0.97998000	2.46748100
H	4.33899600	0.51094800	0.16935700
H	4.79040200	2.11279900	-0.42593300
H	5.08882700	1.92197000	2.07167700
H	3.91043700	3.16935500	1.64466300
H	3.26877000	0.31536100	2.57388500
H	3.01897300	1.79171400	3.51053100
H	2.39452300	2.79424300	-0.49138300
C	-2.43494300	-1.77231500	2.62383900
H	-2.12557800	-2.77641600	2.92658800
H	-3.33020700	-1.83703400	1.98934300
H	-2.69346300	-1.16665700	3.50148100
C	-1.34587000	-1.10869600	1.82892700
O	-0.36623300	-1.67789100	1.38462600
O	-1.57408700	0.19188300	1.63853000
H	-0.89480800	0.56715900	1.02456000
C	1.80637900	-4.15118700	0.23306400
H	2.66769500	-4.37607400	0.86892800
H	1.61000100	-4.97792400	-0.46024700
H	0.91479500	-4.01618600	0.86226100
C	2.03178500	-2.86609900	-0.51441600
O	2.87239900	-2.03636300	-0.21138800
O	1.19866600	-2.71485400	-1.53935500
H	1.25253900	-1.79305800	-1.92877000
Mn	-0.24270700	0.46674000	-1.84627600

MnO_4^-/$(CaOTf)^+$

INT1

C	0.15745400	3.46301300	1.09043300
C	-0.36743800	2.18271500	0.43276400

C	-0.35552200	2.28767100	-1.09457800
C	1.03477100	2.66178100	-1.62099500
C	1.55989500	3.94266300	-0.96147500
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	0.78543500
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

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	-0.96410900
Ca	0.94870400	-2.29806000	0.44432200
C	-2.58913500	-0.66168500	-0.93576500
S	-2.03843600	-1.69424000	0.54088000
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	-3.25565700	-1.89757300	1.33661200
O	-1.42261900	-2.91212100	-0.08752000

INT2

C	0.03779000	3.16409200	0.92528300
C	-0.02829900	2.03571600	-0.04949700
C	0.32946600	2.35416900	-1.46404600
C	1.76188600	2.95095400	-1.49278100
C	1.88444500	4.13628300	-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	-0.88553900
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	-0.44883100	0.95275900
Ca	-1.14127800	-2.17015800	-0.49248500
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

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	0.77820100	4.03206300	-1.10075400
H	-0.53372300	1.56024600	1.71160200
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	4.03904700	1.91836800
H	-0.32532400	5.54041900	-0.00155300
H	1.08871100	4.90953900	0.85103400
H	-0.05909100	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	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

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

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

MnO_4^-/$(CaOTf)^+$/AcOH

INT1

C	-0.51730100	1.76705500	0.81204300
C	-0.84066100	2.16863700	-0.62849100
C	-1.74392000	3.40445300	-0.67526200
C	-1.13327900	4.57255000	0.10889300
C	-0.80853800	4.16959300	1.55293200
C	0.09346500	2.93061200	1.59869000
H	-1.93239900	3.70127100	-1.71815800
H	0.10279000	2.37745800	-1.15577200
H	-1.31583400	1.32676500	-1.14952900
H	-1.44301700	1.43961600	1.31241500
H	0.16497000	0.91089400	0.81220400
H	-0.20344000	4.89375500	-0.39093400
H	-1.81233900	5.43861100	0.09830500
H	-0.33644500	5.00838100	2.08663200
H	-1.75018000	3.94703700	2.08354800
H	1.07550300	3.18110400	1.16400400
H	0.27833100	2.62931300	2.64063600
H	-2.72347600	3.14684400	-0.23983100
Mn	-3.42384300	-0.85162400	-0.31447900
O	-4.09418400	-0.90446900	1.11062500
O	-1.79565100	-1.04499000	-0.13715100
O	-3.69906800	0.54736600	-0.98653200
O	-3.99083200	-2.00404900	-1.23055900
Ca	-0.13580700	-2.02982600	-1.43018500
H	1.51822400	-1.54211600	3.62961200
C	1.29641400	-2.44482300	3.04697700
H	0.75236800	-3.13714800	3.70522800
H	2.21869900	-2.91466900	2.69680600
C	0.42071100	-2.09606800	1.88570200
O	0.65124700	-2.46424400	0.73289600
O	-0.62761400	-1.36600900	2.19581200
H	-1.15889100	-1.17090700	1.37000700
C	3.41361500	-0.17011500	0.32977900
S	2.72972400	0.26343100	-1.37287300
F	3.57779800	-1.48924300	0.44641200
F	2.58316600	0.24459300	1.29159900
F	4.59727300	0.42425200	0.50256200
O	1.34462300	-0.31835200	-1.32400500
O	2.74121800	1.73839500	-1.40519400
O	3.63208200	-0.43261600	-2.31417500

TS1

C	-0.43793400	1.99571100	1.48672900
C	-0.77434500	2.13888900	0.01970300
C	-0.84462300	3.57199000	-0.46284800
C	0.49223200	4.28448500	-0.16043300
C	0.84010400	4.18647000	1.32777500

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	0.08613600	4.73530600	1.91625600
H	1.70550200	2.21176800	1.27008100
H	1.09583200	2.66479900	2.86949600
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	-1.33997200	-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

H	2.10434600	4.66746600	1.56893700
H	0.35952600	4.79745200	1.81985300
H	1.94487500	2.19797800	1.43420000
H	1.21587400	2.75252900	2.95023200
H	-1.24240400	4.13953000	-0.15416200
Mn	-3.49815800	-0.05776800	-0.29122900
O	-4.29549800	-0.43947900	1.01376300
O	-1.90909000	-0.61914400	-0.16740100
O	-3.16129400	1.65515200	-0.29027400
O	-4.11515400	-0.47698000	-1.68163400
Ca	-0.69600900	-1.97464100	-1.53300500
H	1.26136800	-2.32200300	3.27406200
C	0.54637800	-3.05352500	2.87184200
H	-0.16092800	-3.29622800	3.67492500
H	1.08169700	-3.94786200	2.54295100
C	-0.18019700	-2.42768700	1.72211000
O	-0.02891200	-2.80114800	0.55357700
O	-0.97761300	-1.44297800	2.04866800
H	-1.41288400	-1.05277800	1.20696700
C	2.99430900	-0.83247300	0.27654100
S	2.49039800	-0.12470400	-1.39676900
F	2.98479200	-2.16617900	0.24318700
F	2.15068400	-0.42237600	1.22935300
F	4.22539000	-0.42110200	0.58922400
O	1.03005000	-0.48228600	-1.46933600
O	2.72187900	1.32641300	-1.26611900
O	3.32846300	-0.85451100	-2.37040200

TS2

C	-0.68968800	2.06199600	1.46600500
C	-0.45045600	1.84947000	0.01503800
C	-0.40694500	3.06223500	-0.84977800
C	0.72401800	3.98703900	-0.30689100
C	0.51904700	4.28535600	1.18038500
C	0.42903100	2.99968700	2.00633200
H	-0.21836200	2.80469700	-1.89890700
H	0.14138100	0.99492200	-0.29114400
H	-2.31227100	1.64303100	-0.52894800
H	-1.65903700	2.56001000	1.62913100
H	-0.69402700	1.11786500	2.01968000
H	1.68764400	3.48234000	-0.45974700
H	0.73390700	4.91320700	-0.89910800
H	1.34506200	4.90941500	1.55196500
H	-0.40592600	4.87006500	1.31363900
H	1.38918900	2.46440800	1.96306000
H	0.22637400	3.22055600	3.06368500
H	-1.35129600	3.62767200	-0.79545600
Mn	-3.49740900	-0.23773900	-0.33238800
O	-4.18653400	-0.48710700	1.06237900
O	-1.82080500	-0.54318500	-0.20998700

O	-3.28659300	1.48695400	-0.59862100
O	-4.09558200	-0.92084000	-1.62390300
Ca	-0.55589500	-1.85939700	-1.56711300
H	1.20788800	-2.23015000	3.35252900
C	0.61028900	-2.99470700	2.83762500
H	-0.12999800	-3.36950100	3.55675100
H	1.25697600	-3.80659100	2.49582100
C	-0.09343400	-2.36206300	1.67729900
O	0.11055400	-2.70420400	0.50643800
O	-0.93480200	-1.41378900	1.99624000
H	-1.35710300	-1.01774500	1.14368700
C	3.02633200	-0.58004500	0.45255100
S	2.72172300	-0.08376800	-1.34060700
F	3.08962900	-1.90671600	0.56868400
F	2.03903900	-0.12767700	1.23427500
F	4.17895200	-0.05646000	0.87492900
O	1.32390600	-0.58641800	-1.58372900
O	2.80957200	1.38920000	-1.32875700
O	3.75121100	-0.81419200	-2.10598000

INT3

C	-1.90737700	1.72285600	1.49118000
C	-1.01265900	1.25601800	0.34716500
C	-1.00450400	2.23526200	-0.82178900
C	-0.57611600	3.62750200	-0.34094600
C	-1.45988500	4.12055900	0.80952300
C	-1.47819000	3.11613100	1.96699100
H	-0.32218800	1.87069000	-1.59820800
H	0.01859000	1.19293400	0.72427800
H	-3.48665600	1.23819100	-1.22647000
H	-2.95162800	1.75622000	1.14709800
H	-1.86141900	0.99843600	2.31498900
H	0.47211500	3.57596700	-0.00882600
H	-0.60620700	4.33274900	-1.18292800
H	-1.10948500	5.10060700	1.16346200
H	-2.48899100	4.26502700	0.44061300
H	-0.47066800	3.05159700	2.40914200
H	-2.15254700	3.45729000	2.76465900
H	-2.00757500	2.30812200	-1.27063300
Mn	-2.98273400	-0.86313200	-0.26495200
O	-3.45336900	-1.33775700	1.15907700
O	-1.31062000	-0.09568900	-0.06565600
O	-3.96915400	0.44221800	-0.96140900
O	-2.51189500	-1.97535000	-1.36550600
Ca	-0.27674900	-1.40525700	-1.84002400
H	1.60048900	-3.00153300	2.95998300
C	1.13881600	-3.53076200	2.11912500
H	0.38629500	-4.22166700	2.52727300
H	1.88224800	-4.10508100	1.55964400
C	0.44302500	-2.56842200	1.21106100

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	0.67997800	-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	2.53070500
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_4^-/$(CaOTf)^+$/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	-3.78795300	-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	-0.34180300
O	-2.13055000	-2.67196100	-1.88863900
O	-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

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	1.32929000
F	1.96909000	2.58224400	-1.10259200
F	3.75755700	1.43601700	-0.66496600
F	3.48370800	3.40199600	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	-3.95934400
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

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	2.81322800
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	0.02699000
O	-1.30738300	-0.32646600	0.76125500
O	-3.16281700	-1.28953500	2.17798900
O	-1.03131400	-2.56116300	1.70409800

INT3

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	-1.44492200
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	1.35609500	-1.31546400	-2.65057000
O	0.92490000	-1.81192900	-1.61038900
O	1.58828200	-0.02571300	-2.76821900
H	1.33540600	0.45013700	-1.92374200
C	4.09571000	-3.70838900	0.10022600
H	3.72859100	-4.34693200	0.90879700
H	5.19005700	-3.71347400	0.05524900
H	3.71464600	-4.09750800	-0.85632100
C	3.57009500	-2.31631600	0.26487300
O	2.54603700	-2.05875300	0.89936200
O	4.27171800	-1.39484200	-0.34946800
H	3.88100700	-0.47239200	-0.23648100
C	-1.23121700	-0.31688000	4.60884000
H	-1.01812100	-1.32709100	4.97306200
H	-2.17833000	-0.35019700	4.04918000
H	-1.33355800	0.39052400	5.43708500
C	-0.16748400	0.10839300	3.64738800
O	0.38583200	-0.67769900	2.87744400
O	0.11090200	1.39022400	3.65782500
H	0.79359400	1.62319100	2.95693200
C	-3.32334300	-1.42935800	-1.05669400
S	-2.56707900	-1.70016100	0.64565400
F	-2.36711800	-1.08241000	-1.92230800
F	-4.23008400	-0.45346100	-1.00047300
F	-3.91023400	-2.54604600	-1.48401300
O	-1.93998100	-0.37422600	0.95935600
O	-3.68282300	-2.12482100	1.50162500
O	-1.47909500	-2.70333600	0.39723200

TS3

C	-2.18712700	3.15847500	-0.54477300
C	-1.64522300	1.97883300	0.25566600
C	-2.49640400	1.67375300	1.47660500
C	-3.94425500	1.40014400	1.05123100
C	-4.52266100	2.55949900	0.23356300
C	-3.63459200	2.88204200	-0.97232800
H	-2.08377200	0.80693000	2.00432600
H	-1.58860000	1.08778600	-0.37742500
H	0.07372100	3.13296200	1.27366400
H	-2.14705700	4.06185100	0.08365500
H	-1.55224500	3.33825200	-1.42195500
H	-3.96875800	0.47908600	0.44802400
H	-4.55722800	1.21022900	1.94282300
H	-5.54174000	2.31733600	-0.10007100
H	-4.60104800	3.45255700	0.87518000
H	-3.64516900	2.03066300	-1.67174600
H	-4.02459100	3.74982900	-1.52197900
H	-2.45984700	2.53230700	2.16543000
Mn	0.83698500	1.48569800	1.99516900
O	2.04873600	0.75042800	1.13704700

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
O	1.31550500	0.28821800	-1.80732200
O	1.11179000	2.50637500	-1.70224600
H	0.66029000	2.32857000	-0.83269900
C	5.87737600	-0.03997100	-1.36399100
H	6.10609500	-1.05518100	-1.69849300
H	6.68447900	0.35397500	-0.73377000
H	5.78717800	0.62398900	-2.23589500
C	4.58114200	-0.01896000	-0.61477000
O	3.81443000	-0.98255700	-0.56908700
O	4.31539500	1.12566100	-0.02516600
H	3.43263100	1.07512400	0.46597300
C	-0.39920400	-4.17762100	2.69075200
H	0.41659200	-4.87908100	2.49148900
H	-1.15910700	-4.29330700	1.90232000
H	-0.87020600	-4.37853700	3.65836200
C	0.10247000	-2.77007800	2.60968100
O	1.04598400	-2.43841300	1.89011400
O	-0.56829400	-1.91057500	3.33716700
H	-0.26422700	-0.96545400	3.18790400
C	-2.20508300	-1.43418900	-2.20977200
S	-1.31567100	-2.25954700	-0.76867700
F	-1.48248000	-0.41849300	-2.68017700
F	-3.38609600	-0.96886800	-1.79748100
F	-2.40367500	-2.31784500	-3.18737500
O	-1.04115800	-1.13440400	0.18147900
O	-2.24685700	-3.29966900	-0.30365900
O	-0.01837700	-2.74108000	-1.35034400