

Supporting Information

Intermediates involved in the Reduction of SO₂: Insight into the mechanism of Sulfite Reductases

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Experimental Procedures

1. Materials:

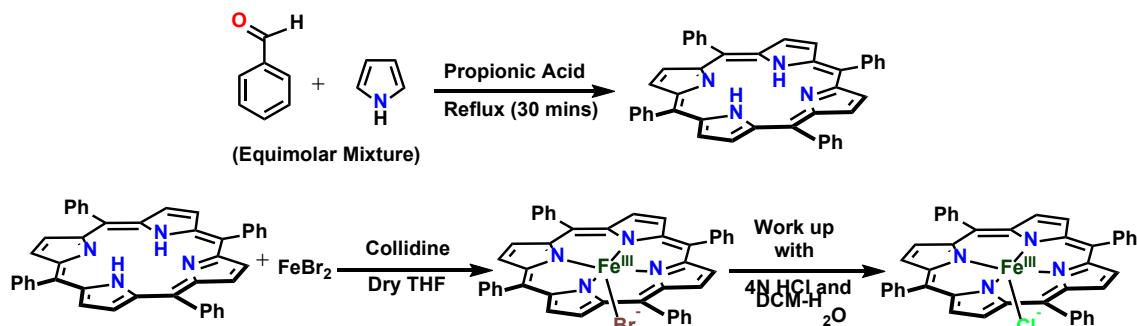
All the reagents used were of the best commercially available quality. H₂SO₄ (98%, Merck), Na₂SO₃ (anhydrous, Merck), Silica (Merck), Na₂SO₄ (Merck), CD₃OD (Merck), all were bought from respective vendors and used without further purification. Benzaldehyde (Spectrochem), Pyrrole (Spectrochem), Glacial Acetic acid (Spectrochem), Na₂S (Spectrochem) were bought from respective vendors. 2,4,6-Trimethylpyridine (Sigma-Aldrich), Ferrous Bromide (anhydrous, Sigma-Aldrich), HCl (37%, Merck), were used for Fe^{III}TPP synthesis. Na₂³⁴SO₃ isotope was bought from Icon Isotopes and used for ³⁴SO₂ generation. Tetrahydrofuran, Methanol, Hexane were sourced from Finar Chemicals and used only after subjecting them to adequate drying and distilling procedures. Dry and pure SO₂ gas was passed through a solution of conc. H₂SO₄ to remove any moisture and tested using GC-MS prior to use. The solubility of SO₂ in THF (after 20 mins purging) is assumed to be 0.3-0.5 M as is the case for commercial sources of the same (<https://www.sigmaaldrich.com/catalog/product/aldrich/901592>). All solvents used were dried and degassed before use. Absorption spectra were obtained by a UV-Vis diode array spectrophotometer (Agilent 8453). EPR experiments were performed at 77 K in a liquid nitrogen finger Dewar. EPR spectra were obtained by a JEOL FA200 spectrophotometer with the following parameters- modulation width: 10 gauss; amplitude: 20; time constant: 300 ms; power: 2 mW; frequency: 9.25 GHz. Resonance Raman (rR) data were collected using 413.1 nm excitation from a Kr⁺ ion source (Sabre Coherent Inc.) and a Trivista 555 triple spectrophotometer (gratings used in the three stages were 900, 900, and 2400 grooves/mm) fit with an electronically cooled Pixis CCD camera (Princeton Instruments). The irradiation power kept at the sample is 8-10 mW, so that photodegradation does not take place. All the data were collected at 77 K in a liquid N₂ cooled finger Dewar after preparing the reaction mixtures at their respective reaction temperature and freezing them after a stipulated time.

2. Methods:

2 a) Synthesis:

Synthesis of Tetraphenylporphyrin (TPP):

Freshly distilled pyrrole (56 ml, 0.8 mol) and 80 ml (0.8 mol) of reagent grade benzaldehyde are added to 3 lit. of refluxing reagent grade propionic acid. (Note: crystalline material is not directly obtained if acetic acid is used.) After refluxing for 30 min, the solution is cooled to room temperature and filtered, and the filter cake is washed thoroughly with methanol. After a hot water wash, the resulting purple crystals are air dried, and finally dried in vacuo to remove adsorbed acid to yield 25 g (20%, yield) of TPP. Spectrophotometric analysis shows that only 1% of the TPP yield remains in the filtrate and also that the filtered material is about 3% tetraphenylporphyrin (TPP) by weight. This method was developed by Adler *et al.*¹



*al.*¹

Scheme 1. Synthesis of TPP and Fe^{III}TPP by the reported procedure of Adler *et al.*¹

Synthesis of Fe^{III}TPP:

The synthesized 100mg, 0.162 mmol TPP was dissolved in dry degassed THF solvent inside a glove box and then stirred with 98.6 mg, 0.810 mmol 2,4,6-trimethyl pyridine (Collidine) for 30 minutes for the purpose of deprotonation of the pyrrolic protons. Then 350 mg, 1.62 mmol FeBr₂ metallic salt was added into the solution and left under stirring condition and the reaction was followed by TLC until disappearance of the TPP spot and appearance of a new spot. The reaction mixture was taken out of the glove box, the THF was removed from the reaction mixture *in vacuo* and the reaction was worked up with DCM and water after treating with 4N HCl to remove excess FeBr₂. The organic layer was dried with Na₂SO₄ and evaporated through a rotary evaporator. The solid compound was purified by column chromatography using 5:95 MeOH-DCM solution to afford the Fe^{III}TPP-Cl (HCl being the source of Cl⁻ in the resulting compound) (Scheme 1).

2 b) Generation of ³⁴SO₂ for isotopic shift studies:

80 mg of Na₂³⁴SO₃ (Icon Isotopes) was taken in an anaerobic vial and sparged with N₂ to remove traces of Oxygen. In another anaerobic vial H₃PO₄ was taken and purged with N₂ to ensure removal of traces of Oxygen. In the vial containing Na₂³⁴SO₃, the H₃PO₄ was added to generate ³⁴SO₂ and it was bubbled into another vial containing dry degassed THF, to generate ³⁴SO₂ bubbled THF solution. That solution was injected into Fe^{II}TPP solution and subjected to different spectroscopic techniques like resonance Raman and EPR.

2 c) Sample Preparation for EPR and Raman Spectroscopy:

Fe^{III}TPP was reduced to Fe^{II}TPP inside the glovebox using 0.5eq. Na₂S dissolved in dry degassed MeOH and/or CD₃OD². XylH⁺Cl⁻ was dissolved in dry degassed MeOH to prepare its 10mM stock solution. In EPR Tubes, 20 μL, 5 mM solution of Fe^{II}TPP were taken, in presence or absence of XylH⁺Cl⁻ and maintained at different temperatures like -40^oC, -80^oC, RT. Then they were injected with an 80 μL saturated solution of dry and pure SO₂ gas in THF (or ³⁴SO₂ bubbled THF) to afford a 100 μL solution of 1 mM concentration reaction mixture. The reaction mixtures were allowed to progress for required time before freezing them in liq. N₂ for EPR analysis and resonance Raman analysis.

2 d) DFT Calculations:

The density functional calculations are performed using Gaussian 16 G16, B3LYP, 6-311g*) software package. Geometry optimisation was done with the B3LYP functional with an unrestricted formalism. For MeOH bound SO complex a mixed basis set with 6-311g* on Fe and 6-31g* on C, H, N, S, O have been used for optimization and frequency calculations.³ Tight SCF convergence and the 6-311+g* basis set has been used on all the atoms for a single point energy calculation using the PCM model and convergence criterion of 10⁻¹⁰ Hartree.⁴ Mulliken orbital populations are calculated using QMForge, and molecular orbital contours are generated using Gaussview software. The ground state wave function of Fe^{III}-LS-SO₂⁻ complexes have been calculated using the contribution of Fe and S, O in the unoccupied molecular orbitals.

Results and Discussion

3. Figures:

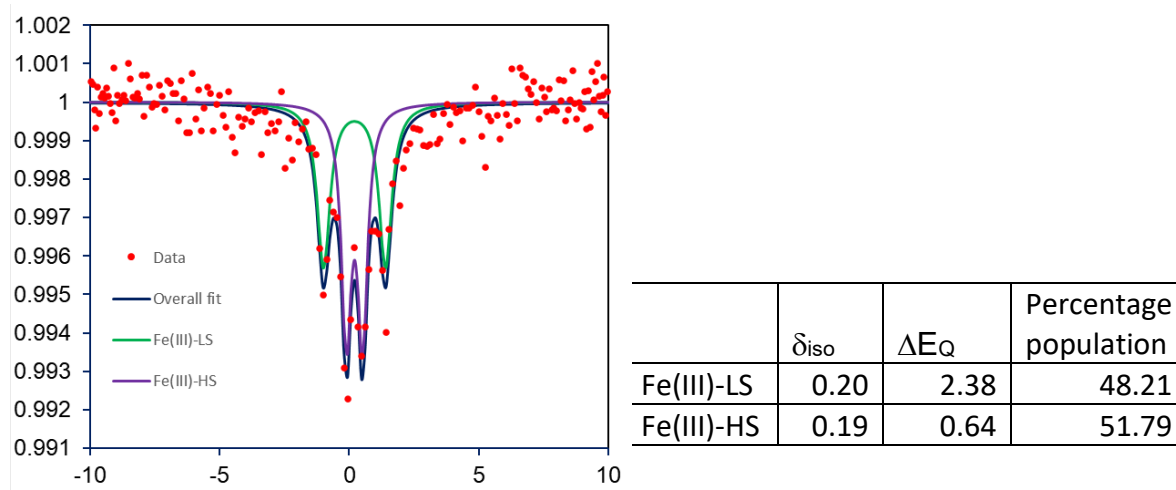


Fig. S1. Mössbauer data of Int-I collected at 90K using ^{55}Fe enriched samples. The spectra can be fitted with a HS Fe(III) and a LS Fe(III) component having almost equal population.

Table 1: Experimental and theoretically calculated vibrations of the Fe-S-O unit						
Species	Fe-S (Å)	Fe-S (³⁴ S) (cm ⁻¹)		S-O (Å)	S-O (³⁴ S) (cm ⁻¹)	
		Expt.	Theo.		Expt.	Theo.
Fe ³⁺ -SO ₂ ²⁻ (Int-1)	2.33	340 (337)	339 (337)	1.50	984 (970)	994 (987)
Fe ³⁺ -SO (Int-2)	2.24	206 (204) 382 (377)	215 ^s (214) 349 ^b (347)	1.52	1014 (1005)	1053 (1044)
s. Fe-SO stretch b. Fe-S-O bend						

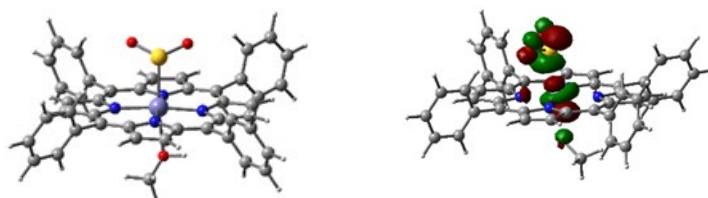


Figure S2. (left) DFT optimized structure of [Fe(III)TPP-SO₂]⁻ species being proposed as Int-I, (right) contour of the anti-bonding d_{z²} orbital showing interaction with the SO₂²⁻ ligand.

4. DFT Coordinates:

MeOH-LS-Fe^{III}-³²S³²O₂²⁻-TPP

Fe	3.32396500	9.29041700	6.74064600
N	5.13932300	9.32432200	5.85541800
N	2.46630600	9.14491200	4.91381300
N	1.51050500	9.46017100	7.56611600
N	4.18566100	9.55761100	8.52554500
C	6.55726100	9.36024700	7.87682900
C	4.48646500	9.12009600	3.47742000
C	3.10069300	9.09046200	3.68789600
C	1.11542400	9.11748400	4.62909200
C	6.85957000	9.14494800	4.30636700
C	7.43394600	9.19221500	5.53740600
C	6.36242600	9.30296500	6.49526900

C	5.43078900	9.21709200	4.50888700
C	0.90136800	9.05213500	3.20241100
C	2.12896900	9.04128700	2.61965200
C	2.17001400	9.66860400	9.93739100
C	3.55340500	9.66288700	9.74118600
C	1.22902300	9.58733000	8.90720000
C	0.07901600	9.21623800	5.56626900
C	4.52269200	9.71572100	10.81345600
C	5.52857400	9.50553500	8.81186500
C	5.74765100	9.61606800	10.23702000
C	-0.78551900	9.48069900	7.91151800
C	-0.19856700	9.61123100	9.12824700
C	0.28469600	9.38766300	6.94170500
H	7.34911300	9.04519900	3.34827800
H	8.48536100	9.14875300	5.78437200
H	-0.06369500	9.04081200	2.71632000
H	2.36189700	9.01703300	1.56477600
H	4.28359600	9.80325600	11.86380000
H	6.71529100	9.61132900	10.71867200
H	-1.84062300	9.43886700	7.68272100
H	-0.67690400	9.70746400	10.09262200
C	7.94782800	9.15506400	8.39705700
C	8.86070100	10.20941400	8.53487100
C	8.35067900	7.85906400	8.75794700
C	10.14957000	9.97738300	9.02316800
H	8.55405400	11.21503700	8.25853100
C	9.63759300	7.62749200	9.24604300
H	7.63654900	7.04783200	8.64307200
C	10.54101000	8.68561500	9.38037400
H	10.84624800	10.80664400	9.12552700
H	9.93599500	6.61837400	9.52088800
H	11.54374900	8.50422000	9.76098700
C	-1.32957400	9.14124200	5.06396500
C	-2.17441200	10.26292800	5.09774400
C	-1.84313700	7.94331400	4.53993700
C	-3.48647000	10.19130200	4.62623600
H	-1.79004700	11.19724500	5.49756100
C	-3.15390900	7.86925400	4.06543200
C	-3.98187500	8.99329200	4.10680000
H	-4.12058800	11.07444100	4.66068200
H	-3.53022900	6.92923300	3.66832600
H	-5.00359100	8.93599600	3.73866000
C	1.66276400	9.67615100	11.34747600
C	1.26101000	8.46919100	11.94210100
C	1.58171700	10.85662200	12.09953100
C	0.78691100	8.44689600	13.25474600
H	1.33689200	7.55554500	11.35880000
C	1.10779600	10.83488000	13.41383000
H	1.89214400	11.79417200	11.64571400
C	0.70797000	9.62975400	13.99486800
H	0.48226500	7.50324700	13.70155800
H	1.04982800	11.76044200	13.98253400
H	0.33894600	9.61187100	15.01794000
C	4.98941300	9.02369200	2.07079100
C	4.82269800	7.84612700	1.32262400
C	5.64454400	10.10560900	1.45945700
C	5.29016700	7.75466900	0.01056500
H	4.32618400	6.99818300	1.78548000
C	6.11563400	10.01647000	0.14834500
H	5.78039300	11.02379900	2.02440800
C	5.93912300	8.83985900	-0.58286000
H	5.15276100	6.83064200	-0.54641800

H	6.61707100	10.86948500	-0.30347300
H	6.30493300	8.76874400	-1.60451600
H	-1.20271900	7.06633300	4.51438400
S	3.47129200	7.02963700	7.27299800
O	4.90754100	6.59399700	7.40984400
O	3.51634900	11.61537700	6.42500500
H	4.32100800	11.45987400	5.90315100
C	2.56910000	12.32571700	5.63660600
H	1.63121500	12.31912700	6.19583800
H	2.88281600	13.36927700	5.48132900
H	2.39744900	11.84732100	4.66538400
O	2.58073800	6.67009000	8.43272300

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C	8.86070100	10.20941400	8.53487100
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H	7.63654900	7.04783200	8.64307200
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H	11.54374900	8.50422000	9.76098700
C	-1.32957400	9.14124200	5.06396500
C	-2.17441200	10.26292800	5.09774400
C	-1.84313700	7.94331400	4.53993700
C	-3.48647000	10.19130200	4.62623600

H	-1.79004700	11.19724500	5.49756100
C	-3.15390900	7.86925400	4.06543200
C	-3.98187500	8.99329200	4.10680000
H	-4.12058800	11.07444100	4.66068200
H	-3.53022900	6.92923300	3.66832600
H	-5.00359100	8.93599600	3.73866000
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C	1.26101000	8.46919100	11.94210100
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C	1.10779600	10.83488000	13.41383000
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C	0.70797000	9.62975400	13.99486800
H	0.48226500	7.50324700	13.70155800
H	1.04982800	11.76044200	13.98253400
H	0.33894600	9.61187100	15.01794000
C	4.98941300	9.02369200	2.07079100
C	4.82269800	7.84612700	1.32262400
C	5.64454400	10.10560900	1.45945700
C	5.29016700	7.75466900	0.01056500
H	4.32618400	6.99818300	1.78548000
C	6.11563400	10.01647000	0.14834500
H	5.78039300	11.02379900	2.02440800
C	5.93912300	8.83985900	-0.58286000
H	5.15276100	6.83064200	-0.54641800
H	6.61707100	10.86948500	-0.30347300
H	6.30493300	8.76874400	-1.60451600
H	-1.20271900	7.06633300	4.51438400
S(Iso=34)	3.47129200	7.02963700	7.27299800
O	4.90754100	6.59399700	7.40984400
O	3.51634900	11.61537700	6.42500500
H	4.32100800	11.45987400	5.90315100
C	2.56910000	12.32571700	5.63660600
H	1.63121500	12.31912700	6.19583800
H	2.88281600	13.36927700	5.48132900
H	2.39744900	11.84732100	4.66538400
O	2.58073800	6.67009000	8.43272300

MeOH-LS-Fe^{III}-³²SO-TPP

Fe	3.36147200	9.27476200	6.73408800
N	5.15450600	9.24609500	5.89696700
N	2.50041100	9.11337000	4.94595000
N	1.55139300	9.38165100	7.56724000
N	4.22871400	9.50253300	8.50414100
C	6.53516800	8.86414800	7.91133100
C	4.49694600	9.46586300	3.51811800
C	3.11107000	9.29897300	3.72277000
C	1.17278600	8.87304800	4.67050600
C	6.85882000	9.20106400	4.33970400
C	7.41492100	8.93050100	5.55446500
C	6.34901300	8.96876900	6.51693300
C	5.44556900	9.36967600	4.55404300
C	0.94178300	8.91706600	3.25288300
C	2.13540500	9.21882100	2.66849900
C	2.22459900	10.03217300	9.86186000
C	3.60733800	9.84158700	9.68451700
C	1.26884000	9.74426900	8.86482800
C	0.14359400	8.76602000	5.62976200
C	4.54614800	9.77088800	10.77532300
C	5.52909200	9.19977000	8.83679300
C	5.72584200	9.33313600	10.25509000

C	-0.72216600	9.21756800	7.95346800
C	-0.15071200	9.68831100	9.09651100
C	0.33500500	9.07249900	6.98982400
H	7.35193600	9.24752200	3.38052000
H	8.45291400	8.74179400	5.78336100
H	-0.01646300	8.78372200	2.77405500
H	2.33622800	9.37058700	1.61909000
H	4.31236200	9.97381000	11.80948700
H	6.64388500	9.11995400	10.78083300
H	-1.76596800	9.01234600	7.77255200
H	-0.64314400	9.94984900	10.02033600
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C	8.70393300	9.30003300	9.13497800
C	8.31558600	7.13193500	8.12004000
C	9.95629700	8.86820900	9.57126100
H	8.37907000	10.31627700	9.33953600
C	9.56189100	6.70108700	8.57335700
H	7.66498600	6.45735100	7.57169500
C	10.38563300	7.56771200	9.29579000
H	10.59753100	9.54914000	10.12341000
H	9.88811100	5.68667200	8.36325000
H	11.35867000	7.23176300	9.64207300
C	-1.21633900	8.39526200	5.14572400
C	-2.29629600	9.29118200	5.22762100
C	-1.42565100	7.12841800	4.57337400
C	-3.55567300	8.92447600	4.75391400
H	-2.14170300	10.28363100	5.64090700
C	-2.69019600	6.76012000	4.11511500
C	-3.75727900	7.65696800	4.20261300
H	-4.37822000	9.63139100	4.81175900
H	-2.84078100	5.77221000	3.68980600
H	-4.74019000	7.37123400	3.83975800
C	1.75753600	10.47236500	11.20825500
C	0.98800900	9.63102600	12.02997600
C	2.11296300	11.74673800	11.68212600
C	0.57882800	10.05978900	13.29248900
H	0.73331800	8.63216300	11.68790200
C	1.68918000	12.17725900	12.93928900
H	2.70924700	12.40360200	11.05515100
C	0.92258800	11.33498500	13.74754500
H	-0.00395500	9.39435100	13.92271800
H	1.95951900	13.17002900	13.28717100
H	0.59867000	11.66841300	14.72905500
C	5.00482500	9.66658000	2.13108300
C	4.82104300	8.68966600	1.13707200
C	5.70197100	10.84296700	1.80530000
C	5.31790400	8.88966800	-0.15049800
H	4.31050000	7.76331600	1.38314600
C	6.18436300	11.04610700	0.51273800
H	5.85179600	11.60482400	2.56519600
C	5.99484500	10.06968300	-0.46770300
H	5.18058600	8.12012600	-0.90450700
H	6.70889100	11.96633200	0.27254300
H	6.37655200	10.22535400	-1.47242300
H	-0.59845800	6.42757900	4.50688800
S	3.34087900	7.04659200	6.95846700
O	4.69072200	6.51682100	7.42893700
O	3.39432200	11.42902900	6.55559200
H	4.30557400	11.73443800	6.42471500
C	2.48781800	12.26533300	5.81661100
H	1.48411300	11.91114200	6.04920000
H	2.58946000	13.30569600	6.14128500

H 2.66091800 12.18838500 4.73797200

MeOH-LS-Fe^{III}-³⁴SO-TPP

Fe	3.36137500	9.27499900	6.73412900
N	5.15442500	9.24634200	5.89699600
N	2.50035100	9.11372200	4.94593900
N	1.55132100	9.38153700	7.56727600
N	4.22861700	9.50266800	8.50418600
C	6.53508800	8.86441300	7.91135900
C	4.49690800	9.46620800	3.51814000
C	3.11098800	9.29953000	3.72280300
C	1.17271500	8.87346900	4.67045800
C	6.85873700	9.20125000	4.33972800
C	7.41482900	8.93074400	5.55448900
C	6.34892800	8.96907100	6.51695000
C	5.44550000	9.36992000	4.55405300
C	0.94167400	8.91783800	3.25285000
C	2.13531300	9.21955800	2.66851300
C	2.22444700	10.03192600	9.86196500
C	3.60723800	9.84159500	9.68457100
C	1.26872800	9.74382500	8.86497400
C	0.14358700	8.76601000	5.62969900
C	4.54607200	9.77103600	10.77535500
C	5.52903800	9.20001300	8.83682300
C	5.72579600	9.33339900	10.25511500
C	-0.72213800	9.21667200	7.95359500
C	-0.15079300	9.68744000	9.09667700
C	0.33501400	9.07212800	6.98986900
H	7.35184000	9.24761400	3.38053400
H	8.45280900	8.74198900	5.78339500
H	-0.01658700	8.78464500	2.77401200
H	2.33614000	9.37145400	1.61912600
H	4.31228100	9.97393700	11.80952000
H	6.64386200	9.12030900	10.78085700
H	-1.76588100	9.01114900	7.77270300
H	-0.64328300	9.94869300	10.02055000
C	7.87184800	8.43586700	8.40378200
C	8.70378600	9.30023800	9.13517100
C	8.31562100	7.13230700	8.11980200
C	9.95616300	8.86841600	9.57141900
H	8.37884100	10.31641700	9.33992000
C	9.56194100	6.70146100	8.57307500
H	7.66507600	6.45778000	7.57132400
C	10.38559800	7.56800300	9.29570500
H	10.59732500	9.54927800	10.12373700
H	9.88824200	5.68711100	8.36277900
H	11.35864300	7.23204900	9.64196100
C	-1.21628600	8.39514600	5.14557500
C	-2.29643900	9.29080800	5.22780400
C	-1.42532100	7.12849200	4.57270300
C	-3.55573300	8.92401200	4.75395100
H	-2.14205600	10.28313700	5.64145300
C	-2.68978800	6.76008800	4.11431900
C	-3.75706400	7.65666800	4.20216600
H	-4.37843400	9.63072700	4.81205900
H	-2.84015700	5.77230800	3.68863000
H	-4.73991200	7.37086200	3.83919800
C	1.75742800	10.47221800	11.20835000
C	0.98812500	9.63087900	12.03029200
C	2.11269600	11.74672100	11.68198300
C	0.57898300	10.05978500	13.29277000
H	0.73363000	8.63189300	11.68844400

C	1.68893800	12.17738500	12.93910300
H	2.70881500	12.40358700	11.05485300
C	0.92255500	11.33512200	13.74756800
H	-0.00361100	9.39435000	13.92317700
H	1.95914100	13.17025900	13.28679500
H	0.59867100	11.66866800	14.72904900
C	5.00483400	9.66655800	2.13106600
C	4.82089800	8.68944900	1.13727600
C	5.70227700	10.84270500	1.80504300
C	5.31788200	8.88902600	-0.15031100
H	4.31014300	7.76326500	1.38353800
C	6.18478000	11.04543100	0.51245500
H	5.85223100	11.60470800	2.56476500
C	5.99510300	10.06881300	-0.46776100
H	5.18043600	8.11933300	-0.90414300
H	6.70952800	11.96548000	0.27206600
H	6.37690800	10.22415100	-1.47249500
H	-0.59797600	6.42786000	4.50593600
S(Iso=34)	3.34076400	7.04687600	6.95860100
O	4.69085300	6.51717000	7.42839600
O	3.39430700	11.42904900	6.55590200
H	4.30560800	11.73419600	6.42476300
C	2.48782000	12.26562700	5.81721000
H	1.48409700	11.91149200	6.04981400
H	2.58962100	13.30589500	6.14212900
H	2.66080100	12.18892700	4.73853600

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