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Cyclopentadienone iron complexes as efficient and selective catalysts for the electroreduction of CO_2 to CO

Supporting Information

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Content

1. Experimental Part

1.1. General procedures

All reactions we are carried out using Schlenk techniques under atmosphere of dry Argon. Solvents and reagents for the synthesis of complexes and electrochemical reactions were dried and degassed prior to use by freeze-pump-thaw procedure (4 times). CO_2 tanks (>99.998%) were purchased from Linde and used as received. Complexes **1a-d** were prepared using known literature protocols.[1] Reagents were used as received from commercial sources unless otherwise stated. Solvents for NMR spectroscopy were dried over molecular sieves. NMR spectra were recorded on a 400 MHz and 300 MHz Bruker spectrometers. Chemical shifts are reported in δ units, parts per million relative to the residual solvent. Analyses of the headspace of the bulk electrolysis experiments were performed using a gas chromatograph equipped with a TCD detector (Agilent Technologies 6890N, carboxen 1000, external calibration).

1.1.1. Preparation of complex 2b and reactivity experiments with CO_2

Synthesis of hydride species 2b.

The synthesis of **2b** was carried out according to previously reported protocols.[1a] To a solution of complex **1b** (124 mg, 0.30 mmol) in 5 mL of THF was added 3 mL of a 1 M solution of NaOH. After 2.5 h of vigorously stirring, 0.10 mL of H_3PO_4 were added and the product was extracted into Et_2O (3 x 5 mL), the extracts were dried over Na_2SO_4 and filtered, and the solvent was removed in vacuo to give the product as a brown solid (96 mg, 0.25 mmol, 82%). ^{1}H NMR (400 MHz, C_6D_6): δ 3.72 (s, 1H), 2.18 (m, 4H), 1.34 (m, 4H), 0.30 (s, 18H), -11.62 (s, 1H). ^{13}C NMR (100 MHz, C_6D_6): δ 216.95, 145.52, 102.97, 70.14, 25.48, 23.03, 0.85.

Reaction between complex 2b and CO_2.

Complex **2b** (19.6 mg, 50 µmol) was weighted inside a glovebox and transferred to a J. Young NMR tube. CH_3CN (0.5 mL) and benzene-d_6 (0.1 mL) were added and the resulting solution was degassed by 3 freeze-pump-thaw cycles, filling the atmosphere with CO_2 in the last cycle. The NMR tube was kept under dark conditions for 30 min and a ^{13}C NMR spectrum was recorded (see Figure S1).

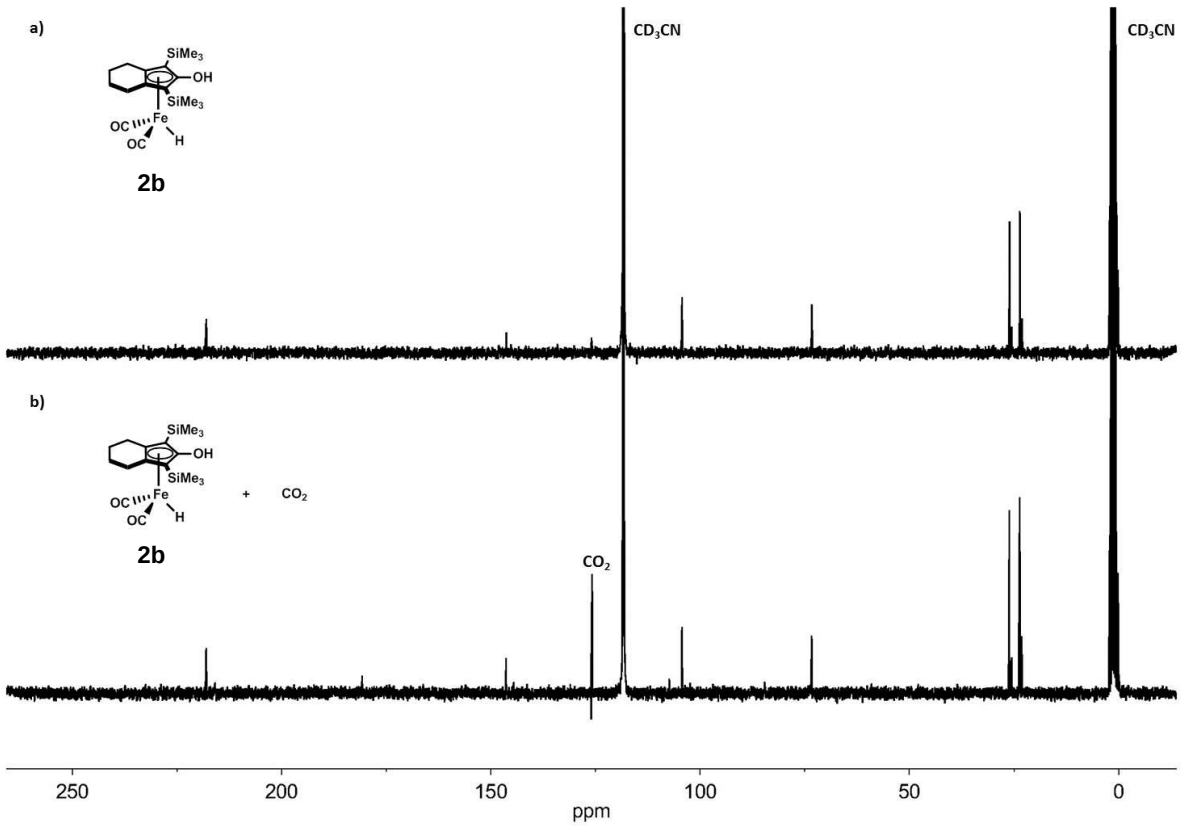


Figure S1: ^{13}C NMR spectra of the experiments with iron hydride **2b** and CO_2. (a) Solution of complex **2b** in CD_3CN under Ar atmosphere. (b) Solution of complex **2b** in CD_3CN under 1 atm of CO_2 after 30 min of reaction in dark conditions.

1.1.2. Cyclic voltammetry

The experiments were carried out in a conventional three electrode cell using a Parstat 4000 (Princeton Applied Research). A glassy carbon disc (diameter: 0.16 mm) served as working electrode and a platinum wire as counter electrode. The glassy carbon disc was polished using polishing alumina (0.05 µm) prior to each experiment. As reference a $Ag/AgNO_3$ electrode (silver wire in 0.1 M NBu_4ClO_4/CH_3CN solution; c($AgNO_3$) = 0.01 M; E_0 = −87 mV vs. ferrocene redox couple and +548 mV vs. NHE)[2] was used and this compartment separated from the rest of the cell with a Vycor frit. As electrolyte, 0.1 M NBu_4ClO_4 (Sigma Aldrich, electrochemical grade) was employed in dry acetonitrile unless it is stated otherwise. Although catalysts **1a-d** are air-stable, the electrolyte solutions containing the iron complexes were prepared under Schlenk conditions in order to guarantee a constantly low water content (the water content of a freshly prepared electrolyte was typically determined to be 10 – 20 ppm using Karl Fischer coulometry). After transferring the solution into the pre-dried and argon-flushed cell, it was purged with argon for at least five minutes prior to recording the CVs. For the estimation of reduction potentials, the average value of three different measurements was formed (typical deviation within the range of ±10 mV).

1.1.3. Controlled potential electrolysis

Bulk electrolysis was carried out in a gastight H-type cell equipped with a fine-porous glass frit as a separator (frit diameter: 0.8 cm, pore size: 10 - 16 µm / P16 according to ISO 479)

and an additional inlet sealed with a stop-cock and a septum for taking headspace samples. The cathodic compartment was fitted with a glassy carbon plate or a glassy carbon disk as the working electrode and the same $Ag/AgNO_3$ reference electrode as described in section 1.1.2. The potential of the reference was checked vs. ferrocene in a separate cell prior to and after electrolysis and was generally found to be stable within a range of ±10 mV after 24 – 48 h. A platinum sheet served as the counter electrode in the cathodic compartment. Both anolyte and catholyte were based on 0.2 M NBu_4ClO_4 in dry CH_3CN, the catholyte solution containing the catalyst with c = 0.5 mM.

The electrolysis was carried out as follows: Under CO_2 or Ar atmosphere, 5 mL of anolyte and 5 mL of catholyte were transferred simultaneously from Schlenk flasks to the corresponding cell compartment with syringes. After addition of the solutions, it was purged with CO_2 or Ar for 10 min. The electrolyses were carried out at E = –1.65 V vs. NHE under stirring. Gas samples were taken using a Gastight Hamilton syringe equipped with a PTFE luer lock valve. The products were analyzed using a calibrated GC and Karl Fischer coulometry. Calculations of TONs for carbon monoxide were performed using its van der Waals volume (24.44323 mol/L) at 25 °C and 1.01325 bar.

1.2. Cyclic voltammetry studies

1.2.1. Voltammetry under Ar

A selection of 4 iron complexes **1a-d** with different cyclopentadienyl ligands was studied using cyclic voltammetry (see Figure S2). By recording a voltammogram of the blank electrolyte (blue dashed line) it was confirmed that all signals in the studied potential range correspond to the conversion of the catalysts. In the cathodic scan between 0.55 and – 1.95 V vs. NHE, the four complexes exhibit very similar behavior with two reduction events in each case at similar potentials. Applying a scan rate of 100 mV s^{-1}, a reduction signal appears at $E_{p,red}(1)$ = −1.4 V for **1a-c**, whereas for **1d** a comparable peak is found at −1.25 V. In the case of **1b**–**d**, a reduction event of minor intensity and unknown origin occurs in the cathodic scan prior to the first major signal (indicated with an asterisk). The reduction at −1.4 V is followed by a less pronounced reversible reduction event centered around −1.5 V in the case of **1a-c** and −1.4 V for **1d**. In contrast to **1b**–**d**, **1a** exhibits a weakly pronounced reoxidation peak at $E_{p,ox}(2)$ = 1.2 V coupled to the event at $E_{p,red}(1)$ = −1.4 V.

In the anodic scan with catalyst **1a**, three minor oxidation peaks appear at −1.2 V, −0.6 V, 0.1 V and 0.4 V. Reversing the scan at −1.5 V (right after the first reduction event) reveals that all three oxidation signals are related to the process occurring at −1.32 V (see Figure S2, top left, dashed line). Catalysts **1b**–**d** exhibit comparable oxidation signals with low intensity in the reverse scan (see Table S1).

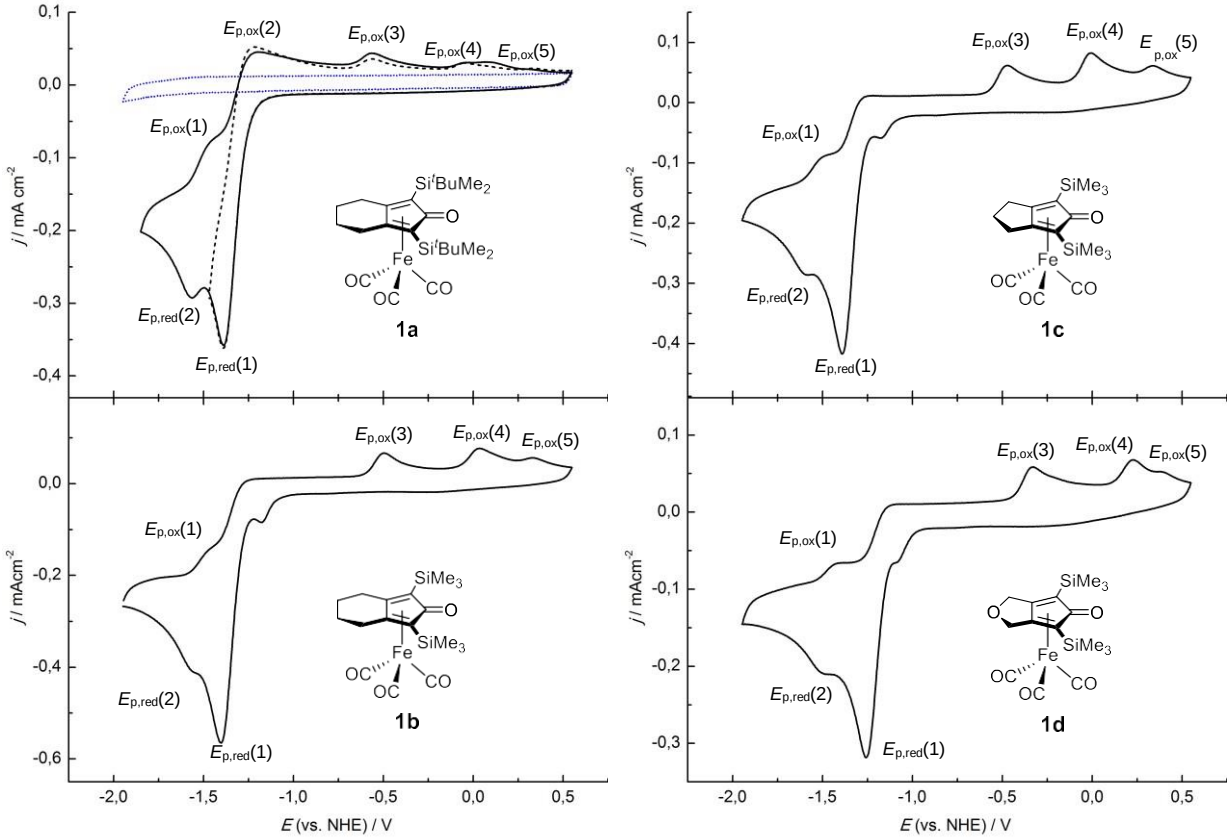


Figure S2: Cyclic voltammetry of catalysts **1a−d** under Ar atmosphere; conditions: v = 100 mV s^{-1}, WE = glassy carbon disc, c(**1**) = 1 mM; electrolyte: 0.1 M NBu_4ClO_4 in dry acetonitrile; blue dotted line (top left): blank electrolyte under Ar atmosphere.

Table S1: Summary of peak potentials $E_{p,red}$ and $E_{p,ox}$ vs. NHE for the studied catalysts **1a**–**d** (experimental conditions: see 1.1.2).

Catalyst	$E_{p,red}(1)$ [mV]	$E_{p,red}(2)$ [mV]	$E_{p,ox}(1)$ [mV]	$E_{p,ox}(2)$ [mV]	$E_{p,ox}(3)$ [mV]	$E_{p,ox}(4)$ [mV]	$E_{p,ox}(5)$ [mV]
1a	−1.40	−1.57	−1.45	−1.20	−0.58	0.13	0.36
1b	−1.40	−1.55	−1.46	-	−0.49	0.04	0.34
1c	−1.40	−1.58	−1.47	-	−0.46	0	0.34
1d	−1.25	−1.46	−1.39	-	−0.33	0.23	0.38

1.2.2. Voltammetry under CO_2

After recording CVs with catalysts **1a**–**d** under Ar (Figure S2 and Figure S3, black lines), the electrolyte was saturated with CO_2 and the scans were repeated (Figure S3, red lines). Whereas the feature observed under Ar at $E_{p,red}(1)$ is retained with a similar current density, the feature at the second reduction potential $E_{p,red}(2)$ is significantly enhanced. This increase in current density is ascribed to the catalytic turnover of CO_2, whereby the peaked shape of the CV indicates a current limitation by the rate determining step of the catalytic cycle at potentials more positive than $E_{p,cat}$ and diffusion of CO_2 to the electrode at potentials more negative than $E_{p,cat}$. The ratio between the catalytic current $i_{p,cat}$ and the peak current density

in absence of CO_2 $i_{p,red}(1)$ can be considered as a measure for the catalytic activity and allows for a comparison between the differently substituted catalysts. The ratio $i_{p,cat}/i_{p,red}(1)$ is increasing in the order **1d**<**1c**<**1b**<**1a** (Table S2). With respect to $E_{p,red}(2)$, the peak potential $E_{p,cat}$ is shifted cathodically in all cases, which can be assigned to a pronounced *iR* drop (uncompensated resistance) at high current densities.[3]

Table S2: Current density $i_{p,red}(1)$ at the first reduction event under Ar, catalytic current density $i_{p,cat}$ and the ratio $i_{p,cat}$ / $i_{p,red}(1)$ as a measure for comparison of catalytic activities.

Catalyst	$i_{p,red}(1)$ [mA cm^{-2}]	$i_{p,cat}$ [mA cm^{-2}]	$i_{p,cat}$ / $i_{p,red}(1)$
1a	0.36	7.74	21.5
1b	0.58	8.16	14.1
1c	0.41	2.57	6.2
1d	0.32	0.87	2.7

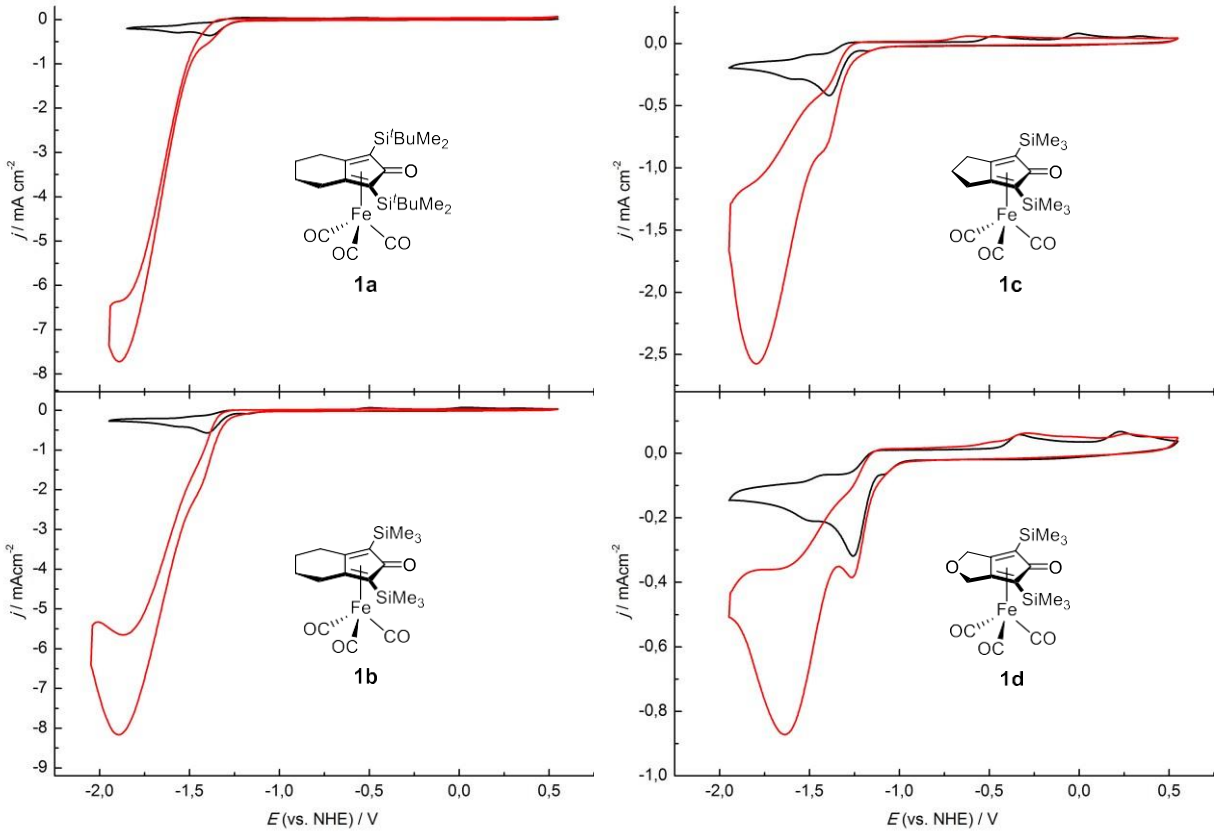


Figure S3: Cyclic voltammetry of catalysts **1a−d** under Ar atmosphere (black lines) and CO_2 atmosphere (red lines); conditions: v = 100 mV s^{-1}, WE = glassy carbon disc, c(**1**) = 1 mM; electrolyte: 0.1 M NBu_4ClO_4 in dry acetonitrile; blue dotted line (top left): blank electrolyte under Ar atmosphere.

1.2.3. Influence of electrode material and solvent

The voltammety of **1a** on platinum differs slightly from glassy carbon. Under Ar atmosphere, both reduction events described above are shifted for about 300 mV in the cathodic direction (see Figure S4). Since in this potential range direct CO_2 reduction on platinum would be the predominant reaction (leading to a mixture of oxalate, formate and carbon monoxide),[4] we decided to continue our studies on the homogeneous catalysts with glassy carbon working electrodes.

Furthermore, we investigated the solvent effect on the voltammetry and the catalytic performance of **1a**. Replacing acetonitrile by DMF leads to similar voltammetric profiles for **1a** under Ar and CO_2 (Figure S5). However, the catalytic activity is relatively low in this solvent ($i_{p,cat}$ / $i_{p,red}$(1) = 3.5) and therefore, acetonitrile was selected for further studies.

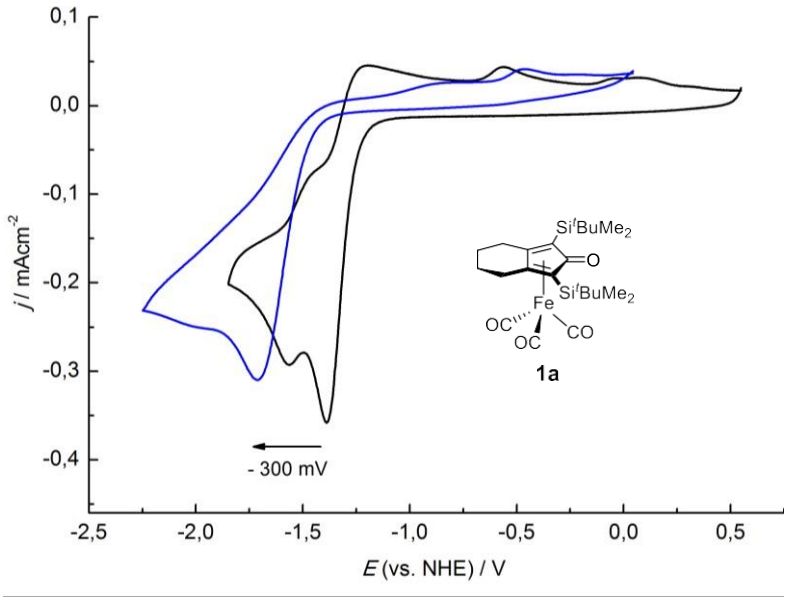


Figure S4: Cyclic voltammetry of catalyst **1a** under Ar atmosphere on glassy carbon (black line) and on platinum (blue line); conditions: v = 100 mV s^{-1}, WE = glassy carbon disc, c(**1a**) = 1 mM; electrolyte: 0.1 M NBu_4ClO_4 in dry acetonitrile.

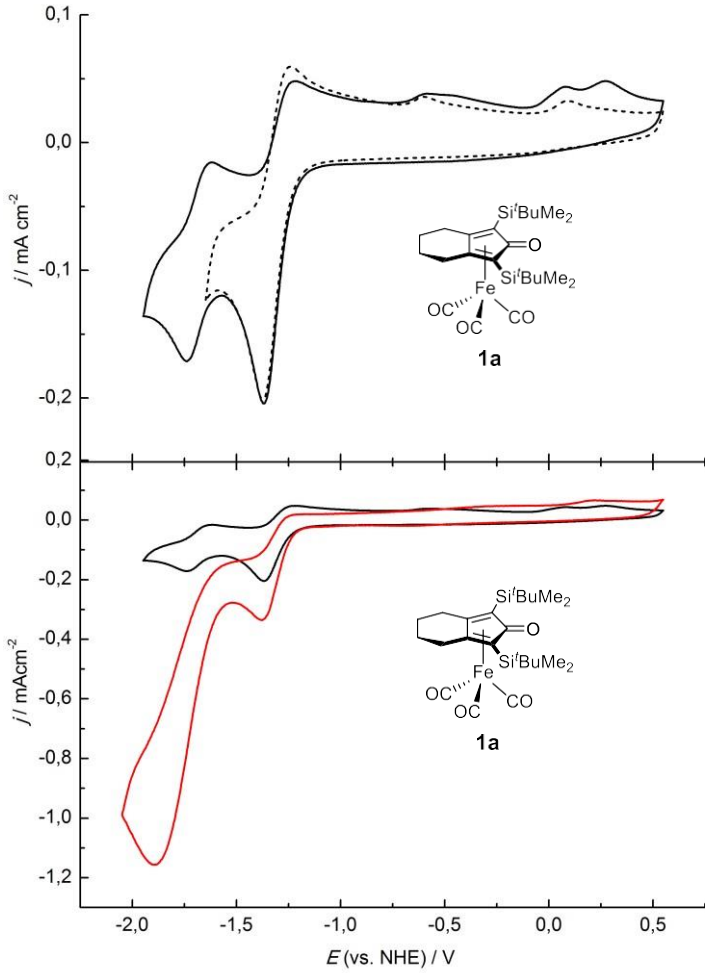


Figure S5: Cyclic voltammetry of catalyst **1a** under Ar atmosphere (black lines) and CO_2 atmosphere (red line); conditions: v = 100 mV s^{-1}, WE = glassy carbon disc, c(**1a**) = 0.5 mM; electrolyte: 0.1 M NBu_4ClO_4 in dry DMF.

1.3. Catalyst benchmarking

In order to calculate the turnover frequency (*TOF*) of catalyst **1a** during bulk electrolysis, the TOF-overpotential relationship (1) reported by Savéant and Costentin has been used.[5]

$$TOF = \frac{k_{cat}}{1 + \exp[\frac{F}{RT}(E - E^0_{cat})]} \quad (1)$$

$$k_{cat} = \frac{j^2 \cdot (1 + \exp[\frac{F}{RT}(E - E^0)])^2}{D(Fc)^2_{cat}} \quad (2)$$

Here, k_{cat} represents the overall rate constant of the catalytic reaction and can be calculated using equation (2). *F* is the Faraday's constant, *R* the universal gas constant and *T* the temperature (with 298 K). *E* represents the applied potential, E^0_{cat} the standard potential of the catalyst, *D* the diffusion constant of **1a**, whereas *j* represents the stable current density during electrolysis (whereby the Faradaic efficiency of 95% has been taken into account) and c_{cat} the concentration of the catalyst. For the relationships (1) and (2) fast electrode kinetics are assumed (limitation of the current by the catalytic reaction and diffusion of the catalyst).
The *TOF*s mentioned in the text (354 s^{-1} and 728 s^{-1}) were calculated from the data obtained from a prolonged electrolysis at E = −1.65 V vs. NHE (see Figure 3) and are based on the initial current density of 3.0 mA cm^{-2} (mean value of the first hour) and the mean value of the 15th hour (4.3 mA cm^{-2}), the period with the highest average current density. The potential of the second redox couple of **1a** (E_2 = −1.5 V), which represents the generation of the active form of the catalyst, has been used as E^0_{cat} Based on cyclic voltammetry data, the diffusion constant was determined to be 1.04×10^{-5} cm^2 s^{-1} using the Randles-Sevcik treatment according to equation (3),

$$j_p = 0.4463 \cdot nFc\sqrt{\frac{nFDv}{RT}} \quad (3)$$

Where *n* represents the number of transferred electrons (n = 1) and *v* the scan rate.[3] The peak current density j_p at $E_{p,red}(1)$ = −1.40 V was used for the calculations and found to be linearly dependent on $v^{0.5}$ in the range of 0.01 V s^{-1} < v < 0.2 V s^{-1}, indicating diffusion control of the electron transfer process. For calculation of *D*, the slope of the linear fit of the data in the range between 0.01 and 0.1 V s^{-1} has been used (see Figure S6), whereby the concentration of **1a** was 1 mM and the temperature T = 298 K.

Table S3 contains benchmark data of a selection of catalysts reported elsewhere for the electroreduction of CO_2 to CO. We note that due to a number of differences between electrolysis parameters (catalyst concentration, electrolyte, applied overpotential with respect to E^0_{cat}, etc.), a quantitative comparison between the reported catalysts is very difficult. When the *TOF* of **1a** is compared to FeTDHPP and Re(bipy)$(CO)_3$Cl (728 s^{-1} vs. 1632 s^{-1} and 1871 s^{-1}, respectively), it is important to keep in mind that in contrast to **1a**, the latter ones were obtained at electrolysis potentials around or less negative than E^0_{cat} (compare Table S3). In this low-overpotential regime, side-phenomena such as substrate consumption, self-inhibition and deactivation of the catalyst are less pronounced and the obtained *TOF* values are therefore typically higher compared to electrolysis at higher overpotentials.[5] In the case of FeTDHPP and Re(bipy)$(CO)_3$Cl, the presented *TOF* values reflect the performance of the catalyst under low stress (low current density), whereas at higher overpotentials (as in our case of **1a**) a higher strain was applied in order to obtain reasonable current densities.

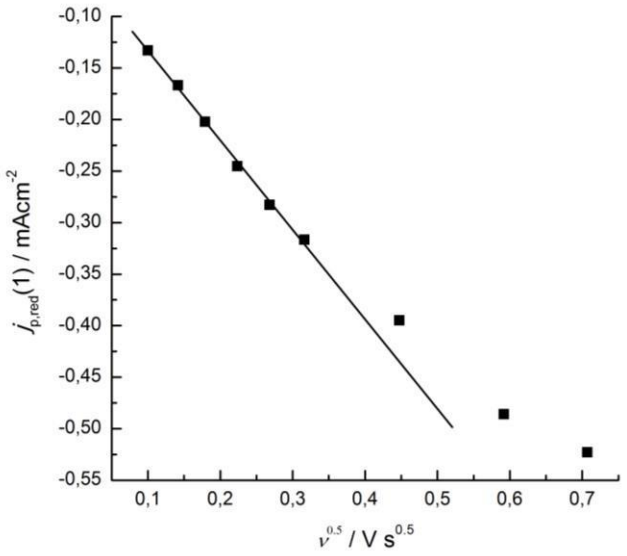


Figure S6: Plot of the peak current density $j_{p,red}(1)$ for the first reduction event at $E_{p,red}(1)$ = −1.40 V versus the square root of the scan rate ν (for catalyst **1a**); slope of the linear fit: −0.868; R^2 = 0.996.

Table S3: Comparison of different homogeneous catalysts for the electrochemical reduction of CO_2 to CO in CPE experiments.

catalyst	*MW* [g mol^{-1}]	c_{cat} [mmol]	solvent / H^+ source	E[a] (E^0_{cat}) [V]	j[b] [mA cm^{-2}]	*TOF* [s^{-1}]	*FE* [%]	ref.
1a	503	0.5	CH_3CN -	−1.65 −1.5	4.3 3.0	728 (354)	96	this work
Mn(mesbpy)$(CO)_3Br$	611	0.5	CH_3CN 0.3 M TFE	−1.57 −0.92	3.5	469	98[c]	[6]
Mn(bpy-^{t}Bu)$(CO)_3Br$	487	5	CH_3CN 1.3 M TFE	−1.95 −1.31	26.3	270	100[d]	[7]
FeTDHPP	797	1	DMF 2 M H_2O	−1.16 −1.33	0.3	1632	94[e]	[5]
Re(bipy)$(CO)_3$Cl	462	0.1	DMF 10% H_2O	−1.25 −1.25	0.5	1871	98	[8,9]
Ni(cyclam)	259	1	CH_3CN 20% H_2O	−1.21 −1.21	1.8	125	90[e]	[10]
Ru(tpy)(bpy)(CH_3CN)	532	1	CH_3CN[f]	−1.52 (−1.3)	1.4	32	76	[11]

[a]Electrolysis potential. [b]Stable electrolysis current density. [c]The *FE* refers only to the first 70 min of catalysis and gradually decreases in the course of electrolysis. [d]*FE* and *j* refer to the first three hours of electrolysis. [e]*FE* was determined after 2 hours. [f]Carbonate was detected as second product.

Calculation of the TOF values of other catalysts:

Mn(mesbpy) (CO)$_3$Br:[6] The electrolysis was carried out under CO_2 atmosphere in CH_3CN / 0.3 M TFE at −2.2 V vs. Fc/Fc^+, which converts to −1.57 V vs. NHE. E^0_{cat} was reported to be −1.55 V vs. Fc/Fc^+ (−0.92 V vs. NHE) and the diffusion coefficient $D = 1.1 \times 10^{-5}$ cm^2 s^{-1}. The Faradaic efficiency of the electrolysis was 98% for CO production at a catalyst concentration c_{cat} = 0.5 mmol and a stable electrolysis current density of 3.5 mA cm^{-2}.

Mn(bpy-^{t}Bu)(CO)$_3$Br:[7] The electrolysis was performed under CO_2 atmosphere in CH_3CN / 1.3 M TFE at −2.2 V vs. SCE, which converts to −1.95 V vs. NHE. The second reduction potential at −1.56 V vs. SCE (−1.31 V vs. NHE) was used as E^0_{cat} and the diffusion coefficient assumed to be $D = 1.1 \times 10^{-5}$ cm^2 s^{-1}. The Faradaic efficiency of the electrolysis was reported to be 100% for CO production at a catalyst concentration c_{cat} = 5 mmol and with a stable electrolysis current density of 26.3 mA cm^{-2}.

FeTDHPP:[5] An electrolysis under CO_2 atmosphere in DMF / 2 M H_2O at −1.16 V vs. NHE (E^0_{cat} = −1.333 V vs. NHE) rendered a Faradaic efficiency of FE = 94% for CO production (6% for H_2 production). The diffusion coefficient is assumed to be $D = 0.5 \times 10^{-6}$ cm^2 s^{-1}. A stable electrolysis current of 0.31 mA cm^{-2} was obtained at a catalyst concentration c_{cat} = 1 mmol.

Re(bipy)(CO)$_3$Cl:[8] The electrolysis was conducted under CO_2 atmosphere in DMF / 10% H_2O at −1.25 V vs. NHE, approximately the second reduction potential of the catalyst in the same electrolyte system.[9] The diffusion coefficient is assumed to be $D = 0.5 \times 10^{-6}$ cm^2 s^{-1}. The Faradaic efficiency of the electrolysis was reported to be 98% for CO production at a catalyst concentration c_{cat} = 0.1 mmol. A stable electrolysis current density of 0.5 mA cm^{-2} is assumed based on the data provided in the paper (259 C passed in 14h; electrode size: 10 cm^2).

Ni(cyclam):[10] The electrolysis was performed under CO_2 atmosphere in CH_3CN / H_2O (4:1) at E = −1.21 V vs. NHE, the reduction potential of the catalyst in the same electrolyte system. The diffusion coefficient is again assumed to be $D = 0.5 \times 10^{-6}$ cm^2 s^{-1}. After one hour of electrolysis (c_{cat} = 1 mM), a Faradaic yield of 90% for CO production was obtained at an average current density of 1.8 mA cm^{-2}.

Ru(tpy)(bpy) (CH_3CN):[11] The electrolysis was carried out under CO_2 atmosphere with a catalyst concentration c_{cat} = 1 mM at E = −1.52 V vs. NHE (E^0_{cat} = −1.3 V vs. NHE). The stable current density according to the data provided in the paper (1.8 C passed in 5 h, electrode size: 0.071 cm^2) was calculated to be j = 1.41 mA cm^{-2}. The Faradaic efficiency was determined to be 76% for CO production after 5 h and the diffusion coefficient is assumed to be $D = 0.5 \times 10^{-6}$ cm^2 s^{-1}.

2. Computational part

2.1 Computational details

All presented calculations were conducted with the ORCA program package (version 3.0.3) and employed Kohn-Sham density functional theory (DFT) using the hybrid density functional B3LYP.[12] If not stated otherwise, the calculations were performed on the iron complex **1b**. Scalar relativistic effects were approximated within the zeroth order regular approximation (ZORA).[13] Accordingly the scalar relativistic recontraction of the def2-TZVP(-f) basis set and the def2-TZVP basis set was used during geometry optimizations and final single point calculations, respectively.[13] The generation of Coulomb and exchange integrals was accelerated with the resolution of identity (RI) and the chain-of-spheres (COSX) approximations together with the def2-TZV/J basis set.[15] Accurate numerical integration was ensured by choosing a dense integration grid (ORCA Grid 4). Dispersion energies were accounted for using Grimme's semiempirical pairwise dispersion correction in its formulation from 2010 with Becke-Johnson damping (D3BJ).[16] The effects of the acetonitrile solvent were simulated with the conductor-like screening model (COSMO) employing a dielectric constant of 36.6 and a refractive index of $\eta = 1.344$.[17]
All investigated geometries were fully optimized without symmetry constraints. Harmonic vibrational frequencies were calculated numerically to verify the nature of the stationary points. Minimum energy points correspond to exclusively positive eigenvalues of the Hessian matrix while transition states feature one negative eigenvalue. Thermochemical contributions were calculated using the ideal gas, rigid rotor and harmonic oscillator approximations at a temperature of 298.15 K. With the resulting Gibbs free enthalpies at hand redox potentials and pK_a values were calculated on the basis of widely accepted thermodynamic cycles illustrated in Figure S7.

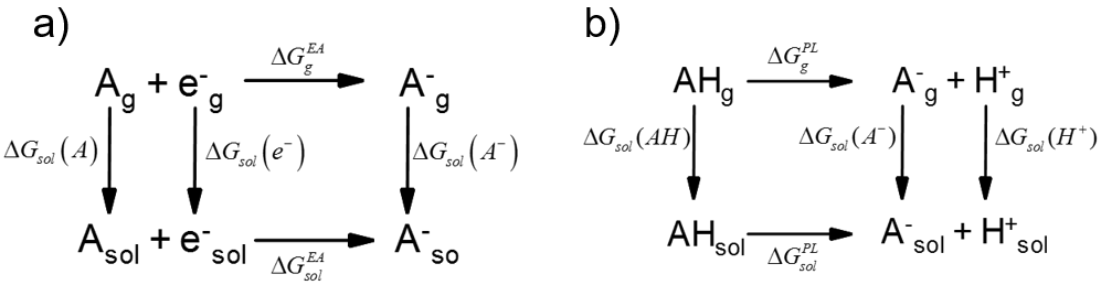


Figure S7: Thermodynamic cycle for the evaluation of redox potentials (a) and pK_a values (b) on the basis of calculated gas-phase reaction free enthalpies.

Assuming a shift of -4.48 V for the redox potential of the NHE in acetonitrile, a value of -6.28 kcal/mol for the formation free enthalpy of a proton in the gas phase as well as a solvation free enthalpy of -260.2 kcal/mol the redox potentials and pK_a values become[18,19,20]

(4)
$$E^0(NHE) = -\frac{\left(\Delta G^{EA}_{g} + \Delta G_{sol}\left(A^-\right) - \Delta G_{sol}\left(A\right)\right)}{F} - 4.48V$$

$$pK_a = -\frac{\Delta G^{PL}_{g} + \Delta G_{Sol}\left(A^-\right) + \Delta G_{Sol}\left(H^+\right) - \Delta G^{PL}_{Sol}\left(AH\right) - 1.89\ kcal/mol}{2.303RT}$$

Note, that a shift of 1.89 kcal/mol was applied to account for the change in standard states from gas phase to condensed phase.[19,20] Furthermore, particle inconsistencies and energy contributions due to an electrode potential were modeled by adding an artificial term $-e\phi$.[21] To this end we would like to note, that for the majority of investigated structures calculations with an increased total spin were performed in order to verify the low-spin nature of the electronic ground state. Indeed, for all investigated cases such states are fairly well separated from the low-spin electronic ground state. This leads to the conclusion that higher spin states do not play a role in the catalytic cycle.

2.2 Calculated redox potentials and pK_a values

Table S4: Calculated redox potentials.

Redox pair	E^0 / V
1b/1b$^-$	-1.88
1b$^-$/1b^{2-}	-2.12
3$^-$/3^{2-}	-2.25
5/5$^-$	-1.67
8/8$^-$	-0.27
9/9$^-$	-0.12
6/6$^-$	-0.72
10$^-$/10^{2-}	-1.42
4/4$^-$	-1.68

Table S5: Calculated pK_a values.

Acid/Base pair	pK_a
4/1b$^-$	18.1
4$^-$/1b^{2-}	25.6
5/3$^-$	21.7
5$^-$/3^{2-}	31.5
8/3$^-$	9.0
6$^-$/10^{2-}	38.1
6/10$^-$	19.8
9/10$^-$	11.8
9$^-$/10^{2-}	33.8
2b/5$^-$	32.1
2b/8$^-$	21.2
7/9$^-$	19.5
7/6$^-$	15.2

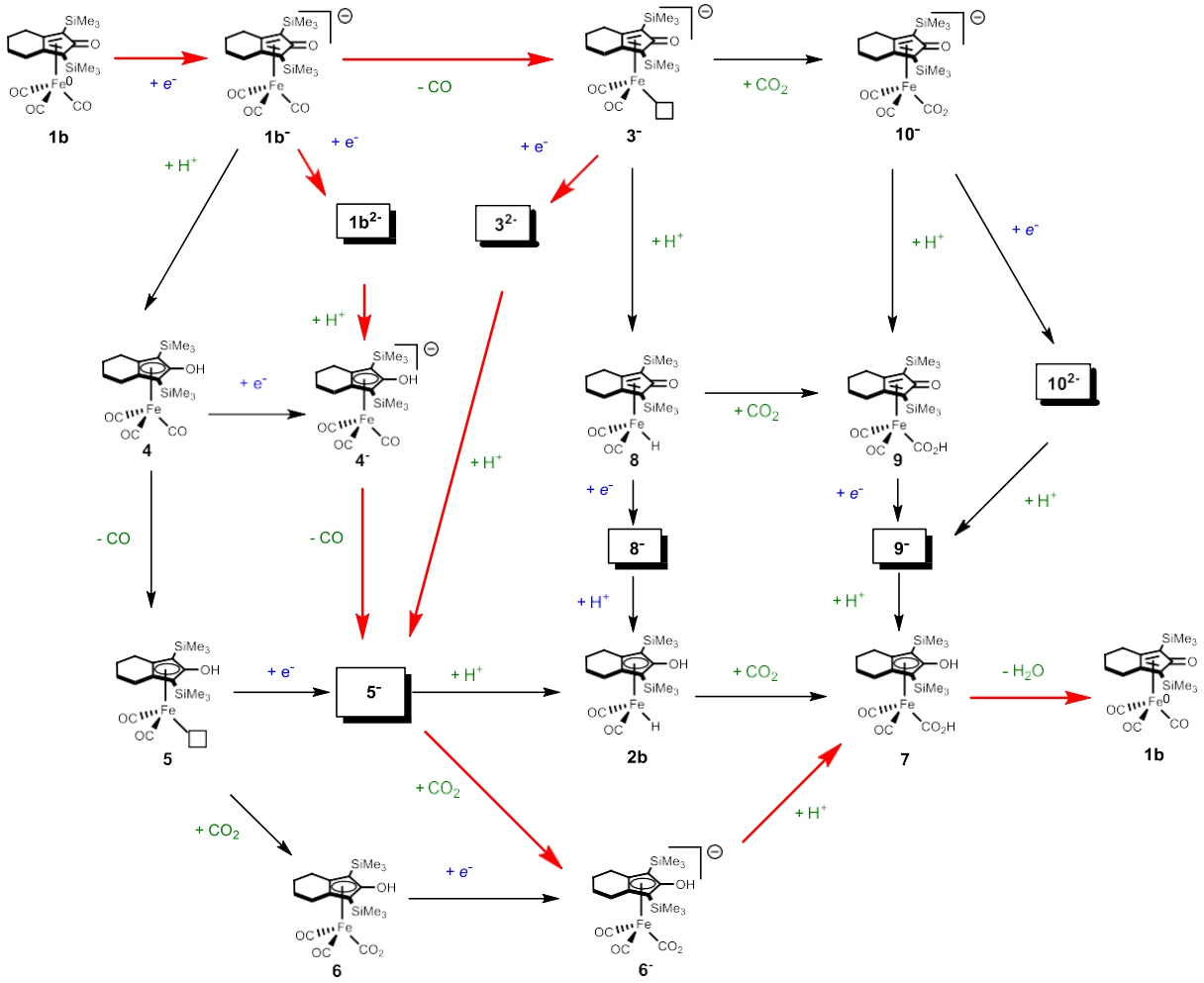
2.3 CO_2 binding energies

Table S6: Calculated binding energies of CO_2 in kcal mol^{-1}.

Molecule	η^1-CO_2	η^1-OCO	η^2-OCO[a]
3/10		4	
3^-/10^-	19.7	10.7	
3^{2-}/10^{2-}	-3.8		
5/6	9.28	9.48	
5^-/6^-	-12.2	10.1	

[a] No stable η^2 structures could be identified

2.4 Alternative pathways and reaction energy profiles



Scheme S1: Summary of alternative reaction pathways for the catalytic reduction of CO_2 by **1b**. The two most likely pathways are highlighted in red.

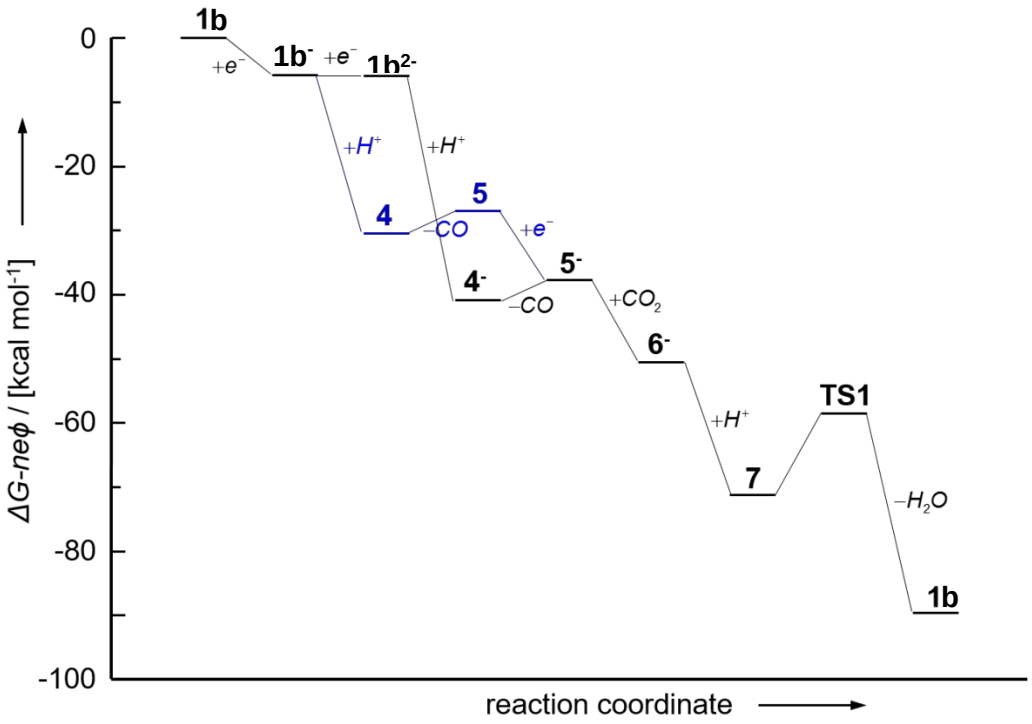


Figure S8: Alternative reaction profile for the catalytic reduction of CO_2 by **1b**.

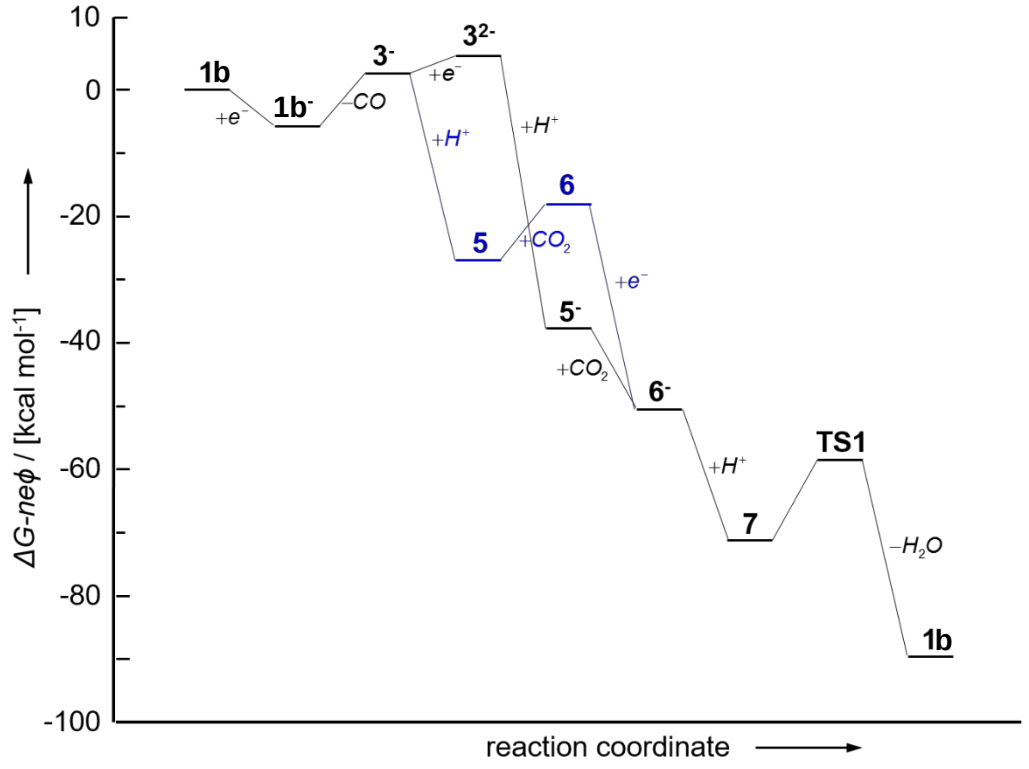


Figure S9: Alternative reaction profile for the catalytic reduction of CO_2 by **1b**.

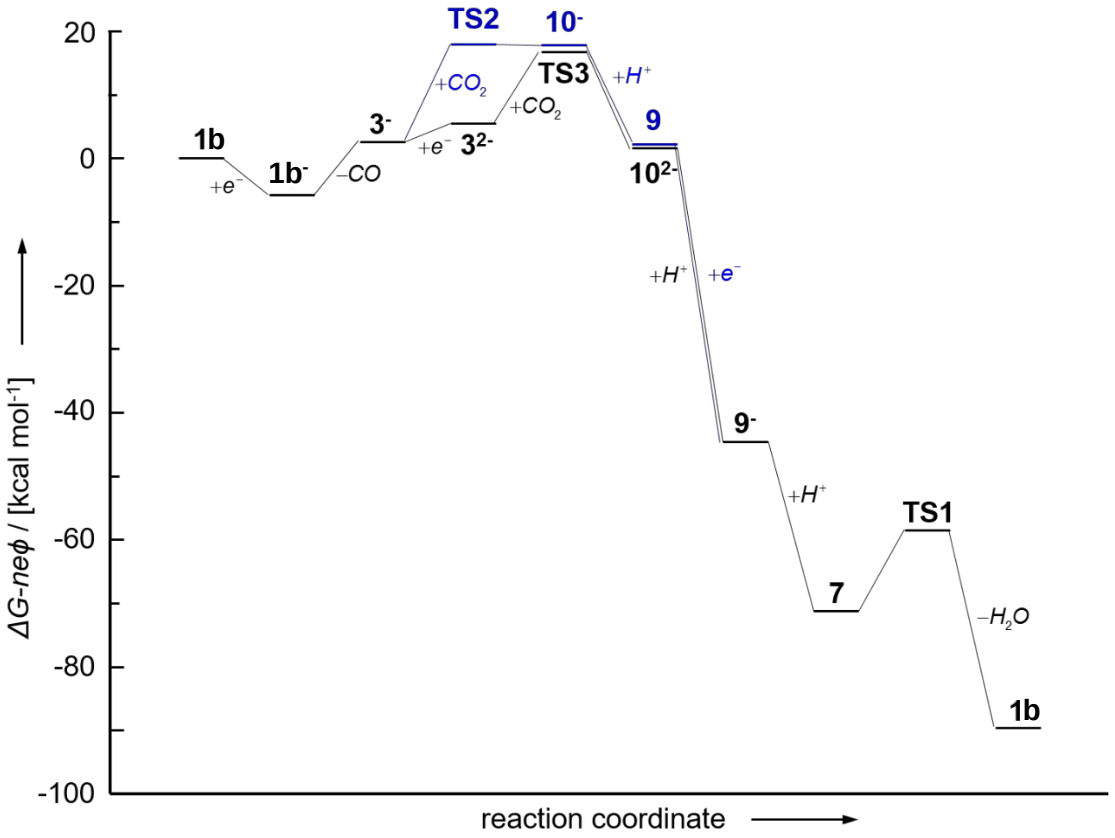


Figure S10: Alternative reaction profile for the catalytic reduction of CO_2 by **1b**.

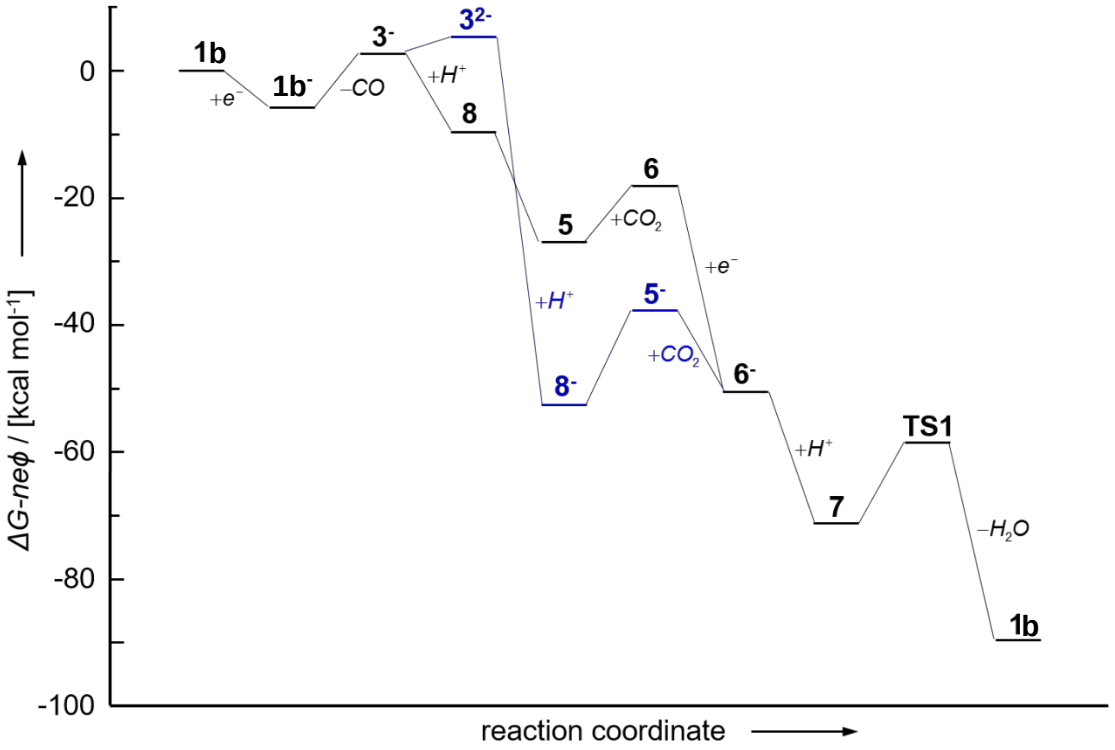


Figure S11: Alternative reaction profile for the catalytic reduction of CO_2 by **1b**.

2.5 Discussion of CO_2 insertion

Scheme S1 and Table S5 reveal that on the basis of thermodynamic arguments intermediate **2** might be a valid candidate as intermediate in the presented electrochemical reduction of CO_2 by **1b**. In the case of the analogous photochemical process **2b** was identified as one of the key intermediates.[22] However, as pointed out previously, its formation might be kinetically hindered[19] and for **2b** to be part of the catalytic cycle an insertion of CO_2 into the Fe-H bond is required.[23] Such an insertion is not observed experimentally as we have described in the present manuscript. In order to verify the experimental results, possible insertion pathways were computationally investigated. The simplest pathway includes addition of CO_2 to **2b** resulting in a fourfold-coordinated intermediate or transition state. However, no corresponding stable structure could be optimized and lowering the Fe-CO_2 distance in a relaxed surface scan results in unphysical structures that are up to 27 kcal/mol higher in energy than the separated compounds. An alternative pathway features cleavage of a CO ligand prior to the CO_2 attack which according to our computational results corresponds to an energy cost of at least 40 kcal/mol. Of course, an energy penalty of this magnitude renders this pathway highly unlikely. Another way for a successful CO_2 insertion corresponds to a rearrangement of the cyclopentadienol ligand. However, our results indicate that even when the binding mode of the cyclopentadienol is altered no stable structure with a Fe-C bond can be obtained. Taken together, we can conclude that based on our findings an insertion into the Fe-H bond of **2b** is improbable which agrees well with the experimental observations. We believe that the main reasons for this behavior are i) the coordinative saturation of the Fe center, ii) the steric demand of the ligand environment and iii) the Fe oxidation state.

2.6 Additional discussion of the bond formation between CO_2 and $5^-/3^{2-}$

As outlined in the manuscript the addition of CO_2 to $\mathbf{5}^-$ proceeds barrierless owing to its ability to form a hydrogen bond between CO_2 and the ligand-based OH group. The structure presented in Figure S12 which was obtained from a relaxed surface scan of the Fe-C bond distance, nicely demonstrates the arrangement of the three involved atoms.

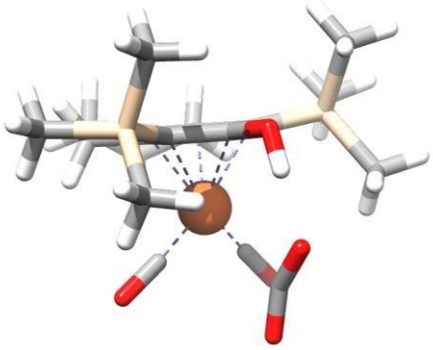


Figure S12: Ball and stick representation of a structure obtained from a relaxed surface scan of the Fe-C bond in $\mathbf{6}^-$.

In contrast, the strong repulsion between the electronegative oxygen atoms of CO_2 and the cyclopentadienone in $\mathbf{3}^{-/2-}$ do not allow a straightforward approach of CO_2. Instead the

substrate is forced into an almost perpendicular position and pushed towards one of the bulky TMS groups (cf. Figure S13). As a result, high barriers of 15.3 kcal mol^{-1} and11.5 kcal mol^{-1} for the binding of CO_2 have been predicted for $\mathbf{3}^-$ and $\mathbf{3}^{2-}$, respectively (compare TS2 and TS3 in Figure S10).

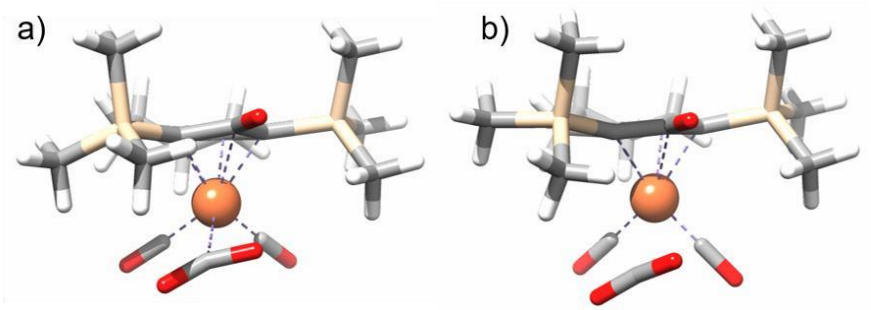
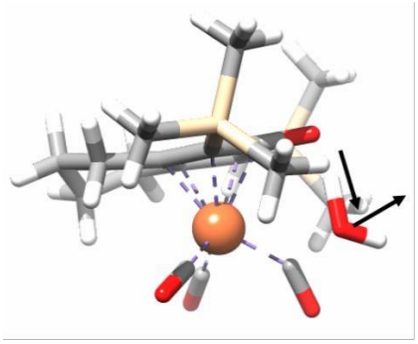


Figure S13: Ball and stick representation of **TS2** (a) and **TS3** (b).

2.7 Additional discussion of the final dehydration step

After CO_2 is successfully bound to the catalyst, the last step of the catalytic cycle involves further protonation of the carboxylic group and elimination of water. In previous studies of catalytic CO_2 reduction with Re and Ni this step was identified as the rate determining step.[19,20] This observation is comprehensible as it involves the simultaneous breaking of a C-O bond and formation of a O-H bond. The required second proton can either be provided by an external source such as water or from the cyclopentadienol in species **7**. The high predicted pK_a values for the acid-base pairs **7**/**9**$^-$ and **7**/**6**$^-$ of 19.5 and 15.2 indicate that protonation of **9**$^-$ and **6**$^-$ is likely to occur at the cyclopentadienone ligand instead of the carboxylic residue thus favoring an intramolecular pathway. The corresponding transition state for such an intramolecular protonation, **TS1**, could be identified and its corresponding reaction coordinate is depicted in Figure S14. It is dominated by a stretching of the C-O bond and a simultaneous movement of the proton from the cyclopentadienol towards the released oxygen atom. Hence, the transition state connects the desired minima on the potential energy surface. The calculated reaction barrier of 12.8 kcal mol^{-1} is about 7 kcal mol^{-1} lower than for the aforementioned reduction with Re and Ni catalysts and weak proton donors.[19,20] This significant reduction of the reaction barrier is likely due to the beneficial arrangement of the carboxylic group and the proton in intermediate **7**. It features a stable hydrogen bond between the carboxylic group and the alcohol and already resembles the cyclic structure of the transition state. Thus preorganization of the carboxylic group and the required proton appears to efficiently facilitate the simultaneous bond breaking/formation process.



TS1

Figure S14: The transition state for water release from species **7**. The black arrows represent the main characteristics of the corresponding vibrational mode with an imaginary frequency.

2.8 Optimized geometries

6$^-$

C	0.68745616280860	-0.03560045734005	3.50705101759490
C	0.85389271388263	0.77940521100520	4.75315612078929
C	0.88683595685039	2.19051688477603	4.73375690421536
C	0.78878888937831	3.00064892375905	3.47040666569249
C	0.81033424083202	2.12174996581391	2.20916126269632
C	0.06182589657187	0.80048588288400	2.38827031538832
C	1.06932695897412	2.67073429020295	6.08460876423431
C	1.18829532469443	1.50378737419471	6.89911468321778
C	1.02661403408931	0.32278048561784	6.11458605490023
Fe	-0.74332232496587	1.51870217069160	5.95101530477375
C	-1.80631635243250	2.82708569740724	5.49742743949460
O	-2.47990951676726	3.70180125207080	5.17030149905237
Si	1.39622820901989	-1.36100440533185	6.84630152286671
C	0.10739485184730	-1.85889446128230	8.11378614083518
Si	1.52993672517028	4.34551006483923	6.78609233834122
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O	1.34251528946394	1.51982228248174	8.23075591909978
C	-1.70549964490775	1.53458418354103	7.74603316544858
O	-2.95417911397720	1.53722275259569	7.76831154947718
C	-1.84715539284658	0.24357335293760	5.49316404692794
O	-2.55064079931622	-0.60578952671256	5.16250720755929
O	-1.01469992585559	1.54162650672132	8.82879580632983
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6

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C	0.90417998141785	3.02548522370124	3.39604180296847

C	0.98252527570866	2.12894902421490	2.15013187403568
C	0.21373005574837	0.81697925277399	2.31066556676215
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C	1.18717750184190	1.56981481994958	6.84508087476878
C	1.02954729187425	0.37854049179752	6.08905037898018
Fe	-0.72922998328175	1.59238874366527	5.85997663663845
C	-1.86823985648446	2.88207452966505	5.49623857288185
O	-2.59670134269794	3.71448616538780	5.17042139064255
Si	1.34281797689883	-1.32207959340779	6.82468894827829
C	0.04435509600112	-1.74444371927530	8.11329509392535
Si	1.58634683268871	4.41420935759987	6.70186390240046
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H	0.62973074089587	1.38405913495489	8.68883950735397

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C	0.95535667584033	-0.10034762114533	3.59679508436232
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C	0.95202009584721	2.03963304864237	2.24927890078983
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C	1.47527106188374	1.59148839287369	6.96548701310253
C	1.25328098759308	0.36320535192899	6.18371742978350
Fe	-0.63781975937777	1.36374091679577	5.94954876972561
C	-1.86545503563518	1.92937995157853	4.83081990124484
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Si	1.76110159837213	-1.26968632072048	6.93985437946664
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C	0.79101055736748	4.83185397158253	8.37763806712621
O	1.85281270419689	1.65664930794783	8.15564638705282
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O	-1.36531303700147	2.01993809514979	8.23867356347598
C	-1.54871605043327	-0.14740912119333	6.24689380287038
O	-2.11592990537794	-1.13824169378944	6.36867978748272
O	-2.01189963304965	3.80680250666881	6.98191683301520
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C	0.90207542882152	5.75499536661165	5.43372970929044
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10^{2-}

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C	0.98080161050746	2.18041190483125	4.68894710250321
C	0.79880804101464	2.90508591586541	3.38091851933925
C	0.87460340238964	1.95576693723156	2.17449522979733
C	0.21887578762358	0.59929255155573	2.43494298694657
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C	1.31095794347211	0.41982357599217	6.16810263709943
Fe	-0.56205692017454	1.46938675353018	5.93585900229316
C	-1.77118307165113	2.48353964880014	5.22149022641878
O	-2.56783316604123	3.15095181617799	4.70769636215609
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Si	1.52142802191306	4.48308195815023	6.55195985992109
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C	-1.34592402662411	1.86196447816789	7.78557518079521
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C	-1.51665103850740	0.02916327431681	5.88864637744611
O	-2.12247042902683	-0.96233029887339	5.83553298240561

O	-2.10264292447887	2.87117375770053	7.90744816709205
C	3.36572577792378	4.57630211679179	6.95352570152235
C	1.17572005484914	5.78336261842528	5.22470728489749
C	3.58378275762963	-1.11125282526794	7.40853333670825
C	1.53420258010269	-2.66106626810027	5.76974742921376
H	0.33662375781584	-1.02425376174103	3.86072859176272
H	1.88942738283512	-0.46868642083430	3.27848103894700
H	0.28219941479711	-0.01725098645581	1.53431177337549
H	-0.84171568485329	0.73784916757005	2.66673849091428
H	0.41820178571098	2.43755343398597	1.30570774140328
H	1.92556370920833	1.78064683709387	1.91998909260368
H	1.57574486399217	3.66626927796591	3.28020307702855
H	-0.14684722096042	3.45033457368908	3.36874509537453
H	4.19761610228331	-0.95764920391972	6.51656764486496
H	3.92526159639682	-2.01995321869611	7.91202347006013
H	3.73547359437549	-0.25825187872915	8.07239167180059
H	2.13073137283842	-2.54980843898368	4.86225484736138
H	0.48964342091081	-2.78600420334588	5.47463258426270
H	1.85363596848188	-3.57821826161686	6.27432230449971
H	-0.26896486166790	-1.85551743555052	8.21039099929612
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H	1.19569143798222	-2.28161784516599	9.12446625212224
H	3.65402519634977	5.55038285122678	7.35936220609435
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H	3.59836049267166	3.80259170757510	7.68696376183238
H	1.38952284234955	6.77504321085387	5.63529339386089
H	0.13650493191762	5.77063364871046	4.88713034235992
H	1.81358040171487	5.64035600311008	4.34992511956573
H	0.77316636911666	5.89638310192972	8.46962221380199
H	0.76872245573758	4.15573353930187	8.85782372040039
H	-0.53306793722528	4.81659980772605	7.88963632304204

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C	0.93256222241624	-0.18991737501375	3.58367807889080
C	1.07406713116657	0.71550192215859	4.76609397371183
C	1.00662770155366	2.13846682872636	4.64389067383640
C	0.78634961819130	2.83118178104993	3.32606329455522
C	0.86611244501949	1.86849085449860	2.13183509569418
C	0.23340634137254	0.50683293614445	2.41558636952266
C	1.26687389612770	2.72191346309802	5.92455393237974
C	1.66536427132546	1.63085245856868	6.82883535346286
C	1.37112897713335	0.37353699229572	6.12082284740605
Fe	-0.45520330368179	1.46741782674778	5.96451322739964
C	-1.60541998154745	2.72423655647485	5.45030819464098
O	-2.28931257007380	3.56158514361600	5.07134226952822
Si	1.79848258750245	-1.25562933971579	6.94371971360003
C	0.74630833115087	-1.47807011345932	8.48128863394010
Si	1.52457220930266	4.49025174780124	6.48123469695647
C	0.33488614355992	4.83006355300183	7.89230726518732
O	2.01498105608838	1.74429917464304	8.01810096213499
C	-1.63903708560926	2.18393901934724	8.77187229833064
O	-0.98943944466443	1.50067003790264	8.08643194224531
C	-1.51442074470423	0.10473976358293	5.54319952692501
O	-2.13758388321113	-0.79391342031440	5.20271507467252
O	-2.28444694069319	2.84870018560648	9.45918332490129
C	3.30980415265213	4.62588012063307	7.04933659753454
C	1.24078289913473	5.74233560630890	5.11069293245702
C	3.61942522601068	-1.14760880165107	7.39917123293416
C	1.54679885632237	-2.71978713849431	5.79295886874896
H	0.41760582078906	-1.10987655698644	3.85443355173280
H	1.94127152546129	-0.48593210540780	3.27427902423825
H	0.30706362768088	-0.12500872432817	1.52870549840975
H	-0.83074370663641	0.62557597294675	2.64168356251167

H	0.38949965595550	2.33473313762074	1.26751331089719
H	1.91586717659135	1.71015933415213	1.86706370236479
H	1.53859907638741	3.61240782684662	3.21242655785495
H	-0.17435127451564	3.34702326729654	3.32377614007398
H	4.22681228561494	-0.96260983914571	6.50932884817145
H	3.96485923421218	-2.07444234964976	7.86433792267864
H	3.78224844512833	-0.32446947614073	8.09606845697731
H	2.14536901487454	-2.62916163836442	4.88480870642610
H	0.50203398989086	-2.84828257024675	5.50194803294933
H	1.86354459906659	-3.62891249854750	6.31243451847099
H	-0.29662771427238	-1.66765173967471	8.21631888485115
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H	1.10538988152317	-2.32175500934598	9.07631427389972
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H	3.50595003415393	3.89533464094852	7.83421451055477
H	1.42691781785051	6.74114853227641	5.51587620230402
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H	1.92664112497597	5.58889234529155	4.27545617606058
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H	0.47567634172658	4.09102035783950	8.68317299969425
H	-0.69919120352994	4.78152647890184	7.54125647371374

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C	1.52105208641818	0.04429447844167	6.03104317651661
C	1.29570750952547	0.66237258541805	4.68488045057760
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C	1.39419817594247	3.05114928763334	5.61913277750528
C	1.35824500705370	2.35826885446201	6.99110820941965
C	2.13423205304305	1.04322960229614	7.01274011756340
C	1.04762650296648	2.28998877641191	3.08675855891767
C	0.53084875634169	1.01025683201589	2.60366277659397
C	0.63515179936671	0.00821431893791	3.54046018556333
Fe	3.16054479818483	1.62719009842472	3.47269804338645
C	3.37040735314509	0.77086709785263	1.95136694973114
O	3.59960098475651	0.28946252127841	0.91239390035458
Si	0.49991059938063	-1.81092347426393	3.27518603392747
C	2.19489544882217	-2.55025936575717	2.89262801000011
Si	0.70789604291738	3.87326825908090	2.16633212217535
C	1.73706240542214	3.97223371041523	0.59186424072806
O	0.12835882399314	0.91424338333783	1.30475324528336
C	4.02650554026712	3.14207946882282	3.64112130594856
O	4.68276674395517	4.10937862527600	3.69354165392543
C	4.26356100041817	0.63468439555424	4.37511987897978
O	4.93110412291283	-0.08738986153312	5.00224938139580
C	-1.11784976047192	3.92582722803018	1.68486132818324
C	1.06758413426390	5.39866187147881	3.20891132600399
C	-0.64294379009284	-2.14549912046392	1.80523757949212
C	-0.24302431969004	-2.68102473765924	4.77562996227301
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H	0.55577330270208	-0.29633220842822	6.42672417975850
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H	3.17809311772030	1.22867458825389	6.74928592543461
H	1.74566369778476	3.03947189241836	7.75265117346177
H	0.31846823935998	2.14254752427779	7.26041837220367
H	0.52808985214026	3.71393190532832	5.54412262036195
H	2.27160498797260	3.69356926306055	5.54641766022033
H	-1.58397088215525	-1.59670481770602	1.89436969212460
H	-0.88678319616633	-3.20994491891807	1.75617367854037
H	-0.17642561942953	-1.89458438275465	0.84611040524804
H	-1.17951641742654	-2.20283548546585	5.07285781586551
H	0.43470374350320	-2.65264659612245	5.63001089532452
H	-0.45584527630229	-3.72807448039708	4.54237158409116

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H	2.13109493185609	-3.61027457421892	2.62997995240201
H	-1.37017358253804	4.86851958507336	1.19117876549175
H	-1.75260192898967	3.82075299653502	2.56845550467374
H	-1.35445457495767	3.10813711334020	1.00200963970846
H	0.88761015391504	6.29055818402288	2.60160413980744
H	2.10190872888775	5.42264622916996	3.55564146683317
H	0.41664955783148	5.45256476516058	4.08249988659277
H	1.40363596183329	4.79120264937593	-0.05126898401075
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H	-0.12201129533193	0.00171898800897	1.11081019461971

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C	1.54733458487278	0.14049612428249	6.09457153801686
C	1.31244309543315	0.72215887773936	4.73337371741094
C	1.23388249612666	2.12544042229915	4.52010519991844
C	1.41104827883461	3.13546743104623	5.62014101046079
C	1.44625714695851	2.47851195514181	7.00729473488054
C	2.21805203199555	1.16020412077422	7.01684589167265
C	0.96411151645261	2.35268735818177	3.14200362020189
C	0.70610593838627	1.03422162789585	2.58958340968513
C	0.87692763728971	0.01470281772914	3.53474580681127
Fe	2.91512766704735	1.29751947150368	3.32239768348692
C	3.45869671983667	1.14542832802383	1.62769673391653
O	3.78542347739627	1.03241879853744	0.53357086387570
Si	0.60643983476223	-1.82001277466514	3.30936248392901
C	2.20726175785804	-2.76763070295142	3.03996171148527
Si	0.58210601982757	3.92086914892789	2.17834987457625
C	1.70790516149585	4.04617484774459	0.68081577583625
O	0.32130290467042	0.92370106740756	1.29631416280555
C	4.04638068107486	2.69377172338022	3.85622330805705
O	4.83974846274040	3.45319345727063	4.18206386420052
C	3.95116809097014	-0.00464853523586	3.94959507047965
O	4.60375832919077	-0.83480541400051	4.40088936824430
C	-1.21200759210898	3.81862585622413	1.62592484478221
C	0.79306477423394	5.45887337031667	3.23434706604034
C	-0.46002841376666	-2.07577966249919	1.77319145015804
C	-0.28191635096795	-2.51008447812032	4.81478032593701
H	2.12982579812961	-0.78053681329987	6.03652042713044
H	0.57759962393601	-0.13809006782265	6.52103597439110
H	2.25879423738939	0.75868886160067	8.03118904713238
H	3.24932227489405	1.33147383128035	6.69274139316237
H	1.87876586930769	3.17741181843626	7.72567111540770
H	0.42182548675030	2.27874518938288	7.33746278511596
H	0.58850085990804	3.85006158310286	5.58221061128390
H	2.31936138064571	3.72194854684849	5.46442089385368
H	-1.35784516468995	-1.45454532943283	1.76924720497599
H	-0.78276464302728	-3.11945901761110	1.73700355599158
H	0.10066164163996	-1.90320467394606	0.84755442034187
H	-1.17102394579252	-1.92325381628652	5.05459308894438
H	0.37002016846951	-2.51406086443129	5.68949331937155
H	-0.59586930847185	-3.53943628088379	4.62228132272676
H	2.80865310687805	-2.81772248725233	3.94863246314618
H	2.81270845529945	-2.29999439639921	2.26094722181675
H	1.98013561979484	-3.78955624361364	2.72382567390997
H	-1.51246989202416	4.74264067499411	1.12514043331194
H	-1.87125118656201	3.66286033417759	2.48328420193661
H	-1.35820671193722	2.98996338703017	0.93166986503870
H	0.57847953478789	6.33181761246741	2.61141996331699
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H	0.09983169332725	5.47459052039368	4.07654376502599

H	1.40400457118771	4.87930764596640	0.04201512558703
H	1.67607548858559	3.13074895857039	0.08828706277927
H	2.74165418277471	4.21460660536241	0.99221302379652
H	0.21436531625900	-0.00675370085851	1.05661365799311

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C	0.85338157327290	-0.01760872424414	3.56834570894740
C	1.18014482571970	0.66839672496461	4.74468508870746
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C	1.19861542208730	2.30077837900004	3.08890156191682
C	0.80727350196510	0.98948913277919	2.49538823791755
C	1.29117424550549	3.11144810458361	5.60697623467495
C	1.10981261291997	2.47817271515246	6.99720371691681
C	1.81342979018843	1.13069933299942	7.13879810741289
C	1.26345152628477	0.11481878495158	6.13613896119384
Fe	3.14032737966646	1.46017786684674	3.60335781862457
C	4.07559267290401	3.00623737469843	3.76833318888702
O	4.65559897118417	3.99799804085122	3.89347058529411
Si	0.80112372411800	3.84693500961501	2.12584034459949
C	-1.04622246735106	3.83914284219551	1.72400923095339
O	0.49347002755528	0.79387925073237	1.30402964839656
Si	0.57209539395653	-1.80641743568363	3.19309117425524
C	-1.03463532945650	-1.98207543670967	2.21853694188454
C	4.10187046191664	0.43341326058439	4.68393690120276
O	4.76927902009106	-0.23813275675939	5.35224367774777
C	1.13081377596761	5.43489570097516	3.08851364008250
C	1.76122866436900	3.90521616838980	0.50889917839311
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C	2.00344673937971	-2.46259742213615	2.15401328687023
C	3.78769324568319	0.79096419454864	2.09531319317658
H	1.85345894440897	-0.80209255486267	6.15211447630944
H	0.25165472381315	-0.17465499864406	6.44064082621903
H	1.67264203030025	0.74381237781843	8.15100008417710
H	2.88813264808823	1.25789423534587	6.98612449024152
H	1.46893500057133	3.17142630686900	7.76113436888057
H	0.04199161127946	2.32673932282233	7.18741428636512
H	0.45464231993848	3.79147082509572	5.42926105472858
H	2.18644670131680	3.73510844510557	5.59442909951341
H	-1.88860804512239	-1.69380013966648	2.83724002836700
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H	-1.00600704007392	-1.32048382716885	1.35240732681954
H	-0.31528038503683	-2.47567661551813	5.43873207670997
H	1.38270129739864	-2.93744336277114	5.27907254116312
H	0.12922471674288	-3.88020090408750	4.46253344269557
H	2.92602049712068	-2.46791553757441	2.73986597513799
H	2.16154751057293	-1.81416436971634	1.29018321046049
H	1.81693916363158	-3.47827759140883	1.79306501462738
H	-1.30256440596381	4.64664216151627	1.03247308284300
H	-1.64232017114463	3.97594637636943	2.63027831352626
H	-1.33008895642865	2.89026857517982	1.26409625839596
H	0.88448499603575	6.28737910986225	2.44833298372090
H	2.17251723837772	5.53105837455016	3.40040983124895
H	0.50269342515933	5.49922920610620	3.97777952298035
H	1.37121099318466	4.68672029336017	-0.14876679375512
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H	2.82141812109897	4.10124357860269	0.68381181549745
O	4.25131888272485	0.34382574928601	1.13494180363073

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C	1.10502226233495	0.61258980545727	4.75846469201173
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C	1.20350307770784	2.24126253811745	3.09199951919080

C	0.67867174218390	0.96956894933889	2.54151461865872
C	1.31255630165123	3.02513632632429	5.61873313108127
C	1.17743568653332	2.37293160870728	7.00835280483104
C	1.90708058620226	1.03611903657364	7.10947635863717
C	1.31480944344599	0.02677307593614	6.12422592167840
Fe	3.26986640789327	1.88645628228999	3.44441499452086
C	4.05423948716297	3.42274544454054	3.64433118672524
O	4.76001100545800	4.37056090180107	3.74741635113292
Si	0.85826147966952	3.79534424277239	2.15430510534289
C	-0.98056391986760	3.87016830088725	1.68812602509580
O	0.33912012462292	0.77220582273535	1.35399862584582
Si	0.46437213693570	-1.82090420978412	3.27647215783600
C	-0.91914570813158	-2.13917907775450	2.03719805064944
C	4.07092605791508	0.67581266594435	4.37769167281911
O	4.63069257773876	-0.14263371425605	5.01952210724529
C	1.18979300915242	5.37603393848593	3.13306135032599
C	1.83516478404496	3.86210464413080	0.54153666839771
C	0.08657899767402	-2.85111963527591	4.81750293202322
C	2.09550761463904	-2.43391805732074	2.54130133536879
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H	0.35341118285677	-0.33194171405379	6.50788682483761
H	1.82411851357748	0.63896640519771	8.12524042417436
H	2.96893510528454	1.17587166346791	6.89522048458059
H	1.54032067619595	3.06071450736820	7.77694415954256
H	0.11800180455928	2.19407479662183	7.22598531359124
H	0.42269898353483	3.64090233974290	5.44757103267104
H	2.15794771356127	3.71112839227496	5.60828036778381
H	-1.88519526666124	-1.85891983461614	2.46804575165111
H	-0.96707493488768	-3.19232248793887	1.74426976515343
H	-0.75240662390143	-1.52430877505869	1.15263984061980
H	-0.74874648562495	-2.42483626153972	5.37885797051871
H	0.94485172889249	-2.90771321087278	5.48968704449877
H	-0.18904104871277	-3.86994474316133	4.52798179071271
H	2.88833329850208	-2.34103691065892	3.28862759090828
H	2.37687837801207	-1.80560276355889	1.69362869021565
H	2.04965756457407	-3.47567138416002	2.20869160818430
H	-1.19129483700965	4.69403334536032	0.99990153765697
H	-1.60122775990150	4.01040887420143	2.57782473647427
H	-1.27757301194278	2.93624488548746	1.20609388055723
H	0.95277393160559	6.23928558648429	2.50348661197656
H	2.22924849546971	5.45123556508521	3.45282163670368
H	0.55637907733979	5.42714650549562	4.02011161150011
H	1.46575303346116	4.64287137819885	-0.12938653304026
H	1.75033608953432	2.89599519655657	0.04021341857324
H	2.89241352211368	4.03909876659177	0.74702053288523
O	3.78884962662863	0.65527246554069	0.85542663137426

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C	1.02985479846337	0.01514588499130	3.55896983374414
C	1.14906849606927	0.73235082400475	4.79405093006188
C	1.16386378435063	2.13444034588151	4.51929254634517
C	1.07784125370623	2.33140147549086	3.10470688725269
C	0.73005614288384	1.01761259279408	2.50895116960175
C	1.17175330955682	3.18022507637376	5.60266213783161
C	0.97639416229958	2.58631237361284	7.00654899048215
C	1.66808054861857	1.23667933547308	7.19026152024850
C	1.14138754270113	0.20189729477244	6.19415354198279
Fe	2.82345869854637	1.18137477870501	3.62371917305873
C	3.92516940078050	2.52209146147257	4.03258568563741
O	4.63114028341477	3.37477734580502	4.31192309769703
Si	0.83063803369044	3.89385281362636	2.08054890525476
C	-0.98408034368266	3.93571925512476	1.59327670706938

O	0.37815012865594	0.79895979923421	1.34437919026116
Si	0.76770975522242	-1.80960863170690	3.18604091196698
C	-0.99477562403763	-1.98566650983989	2.56016023153937
C	3.82392965049665	0.03766312587477	4.55921041635609
O	4.45118516523004	-0.68166146599732	5.18633107120655
C	1.20739397362438	5.45465073766979	3.05481783142004
C	1.92038051764290	3.80635550755709	0.55663336230750
C	0.97985074772646	-2.89185140509401	4.70688626989316
C	1.99222092569512	-2.33042882344594	1.86484703561548
C	3.42891283011584	0.84532031167345	1.96174972978577
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H	0.10396768054552	-0.04650362336257	6.44337190139192
H	1.49822671539976	0.87099723070262	8.20451507305935
H	2.74926418279613	1.35225833815137	7.06529620591289
H	1.34049968356904	3.29855271308408	7.74855080616869
H	-0.09353056106418	2.45504968743429	7.19249132843023
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H	2.09086320715681	3.76505233378687	5.56097576271390
H	-1.71154410552127	-1.70928144123866	3.33734375946673
H	-1.19680453575644	-3.01680221275820	2.25826715475577
H	-1.15199438737245	-1.33274256435272	1.70139905067334
H	0.28549447793056	-2.61696768247766	5.50252214396907
H	1.99372739589855	-2.86112964437781	5.11170826728262
H	0.76437231349804	-3.92545543083356	4.42052431209776
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H	1.79245729650551	-3.35170959755340	1.53106132687124
H	-1.17446809481058	4.76023155081641	0.90154124565387
H	-1.61947294573295	4.07959024587329	2.47034392967852
H	-1.27134245586632	3.00332052554398	1.10493831272911
H	1.04442385253942	6.31477337066928	2.39932145825463
H	2.23677484037167	5.49531996615115	3.41623184997375
H	0.53963298973053	5.56333738567857	3.90993901393545
H	1.66930695469999	4.60971536140705	-0.14017970051888
H	1.78365913541667	2.85114255203158	0.04767112716214
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O	3.78897551078517	0.63756416868339	0.90074534778800

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C	0.96419188426291	0.02045222325689	3.58808945551357
C	1.13322586451529	0.73497555066761	4.84333179879086
C	1.11243076402575	2.12025750027085	4.58559279995973
C	0.96003399682310	2.32373121532611	3.15381853386568
C	0.73269979797628	1.01451190247058	2.54524309374717
C	1.19355920790315	3.16360867456920	5.66773515334320
C	1.09134937232647	2.54696780877531	7.07067944656427
C	1.82624576302703	1.21243017664644	7.19087777266278
C	1.24883862176099	0.17398580254921	6.22687223505173
Fe	2.73303785348201	1.22395678235536	3.57373947526679
C	3.81122147906253	2.59601574911658	3.60746855994927
O	4.47016636578159	3.54853406674585	3.70560754616882
Si	0.75069969685384	3.86465663858474	2.13109564254760
C	-1.04256236039925	3.95449875723757	1.55638874836027
O	0.50705805965653	0.78544162336053	1.31551950273017
Si	0.71971307261925	-1.78592403225305	3.21748320513573
C	-0.89346904520240	-1.97131427063609	2.25715685049959
C	3.92178494787868	0.03341330320574	4.05975915580018
O	4.69123128082209	-0.75281205079656	4.43618171126133
C	1.11102718436963	5.43665625646135	3.10607487964865
C	1.87139825940684	3.81571899837992	0.62035119579939
C	0.57420713040962	-2.82592800179700	4.78474273484596
C	2.14523593933435	-2.45803500607334	2.18641516790754
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H	0.25379556762160	-0.12802172405146	6.57688369717626
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H	1.47560169207208	3.25573095164587	7.80802927306648
H	0.03634514446204	2.38027612517411	7.31299840010048
H	0.38363705736441	3.88547910922948	5.53884125695420
H	2.11845927301464	3.73676683655540	5.57400306190359
H	-1.74260854085597	-1.67589581293804	2.87971938901757
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H	-0.17649763409918	-2.42094534008824	5.46617900841516
H	1.52037897448972	-2.89291907202523	5.32570765510383
H	0.26746983564237	-3.84055662088823	4.51287728521857
H	3.05712860612051	-2.50955892322960	2.78508666778569
H	2.33407272024373	-1.79683628793998	1.33829262558477
H	1.92850385950163	-3.45905663410049	1.80208717832136
H	-1.18463257684357	4.74737603246172	0.81707699923002
H	-1.71133715551859	4.15314330125903	2.39778174280261
H	-1.33008992185558	3.00398356786276	1.10169969904833
H	0.95571108680136	6.30170763550978	2.45475786827260
H	2.13807923714933	5.46696059189049	3.47576361572435
H	0.44043088932889	5.53914152371978	3.96038348444113
H	1.62754614603699	4.61716430394837	-0.08217520827226
H	1.75097069448192	2.85552323664647	0.11608005597181
H	2.91851848634320	3.92432687615611	0.91376296611052

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C	1.16134765241986	2.14009234003984	4.61584210730951
C	1.04541940400268	2.34592753878034	3.18951493052981
C	0.82733752069588	1.04175470751955	2.56001175813428
C	1.22050399398079	3.17051526249266	5.71340620690926
C	1.01313233961592	2.54321367786924	7.10066295653186
C	1.71409118114438	1.19301193183399	7.25248857262034
C	1.18605705179824	0.17304670208343	6.24166713294937
Fe	2.80449848080409	1.23377731526543	3.67455368225492
C	3.98200645006909	2.32058276266287	3.08704176470883
O	4.78939776606996	3.12474341081891	2.73364897073646
Si	0.76826233634281	3.86862791291288	2.17838059817609
C	-1.04635362155430	3.89699080797405	1.64142759091474
O	0.55653836419098	0.83722964802843	1.31953477200268
Si	0.73911982098866	-1.74033104784269	3.22036565213736
C	-0.86103266652879	-1.93786048012048	2.23001517266481
C	3.96244848672911	0.09432394861498	4.21101298180280
O	4.74598563119007	-0.71556771824867	4.58658480974865
C	1.06883729966051	5.46920314727571	3.13739469201728
C	1.83045430689097	3.89428882484908	0.62304351986597
C	0.55872716693836	-2.81022273083659	4.77066916874023
C	2.17298227385990	-2.44338658047173	2.21646903978816
H	1.79088084099348	-0.73441102130700	6.27263953349558
H	0.17126246495992	-0.12890240882238	6.53701506047225
H	1.56694846070192	0.81255710558601	8.26802172710770
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H	1.35908383080084	3.23620462782511	7.87285170695434
H	-0.05960447194391	2.39418163767931	7.27072191015866
H	0.44901767491852	3.93047559018731	5.55726993359592
H	2.17403554014520	3.70322183289089	5.68257497709869
H	-1.72461874729033	-1.69562665642749	2.85667195937096
H	-0.99112051463223	-2.95264357245098	1.84208838478193
H	-0.83652498509336	-1.23002339786976	1.40028706734254
H	-0.20376545043727	-2.41363219250787	5.44446856785745
H	1.49455172078276	-2.88226952626176	5.32932750675559

H	0.25732407384494	-3.82180708451625	4.48015360859111
H	3.07776010776529	-2.45662235058150	2.82817635424190
H	2.36176457819887	-1.79879693040174	1.35596307447021
H	1.97277836958748	-3.45834555663751	1.85826316461057
H	-1.23910090501035	4.66905266536864	0.89102901548212
H	-1.70413084513451	4.08433778763613	2.49460865280915
H	-1.30143996781950	2.92491909758644	1.21261479078684
H	0.88114034804867	6.32566086884885	2.48273066361456
H	2.09354803077912	5.53639746490676	3.51010133193336
H	0.39472109972787	5.55039391582525	3.99172262375622
H	1.52050819014006	4.68587171329082	-0.06501399445221
H	1.72855116689992	2.92847920561298	0.12494797887046
H	2.88179878761751	4.04245421693331	0.87857782135879

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C	0.95376973180356	0.00512976627840	3.59336361960916
C	1.17673254248247	0.71632205073453	4.80475996887902
C	1.16247305702429	2.12709204587189	4.54091294727748
C	0.95563636230153	2.34469030256950	3.15128753697789
C	0.78526279849765	1.01587604042253	2.54011337585584
C	1.30931041984211	3.15294593230500	5.62964915903172
C	1.19718956723252	2.54430811706804	7.03196020035791
C	1.92766944791220	1.20931358657864	7.14532903952791
C	1.33149817054590	0.17472982301638	6.18934766754115
Fe	2.69002942384768	1.18039170350107	3.41534419132104
C	3.82940556885223	2.53838227134815	3.51817141884037
O	4.51565196411888	3.44587273394247	3.65094243426033
Si	0.69187156543321	3.91395328563968	2.14345266861714
C	-1.08284550967939	3.86362629912738	1.53347117704926
O	0.81534807371566	0.78005271076319	1.30641749926711
Si	0.68854745971128	-1.82287172216653	3.23483180896797
C	-0.86414052021574	-1.93466538249849	2.18393245816990
C	3.84803024615109	-0.04463223206366	3.98427378274936
O	4.55093276978536	-0.83889087783467	4.41645376860614
C	0.90888333217006	5.46716769617514	3.17633949861043
C	1.88346447882556	3.95037661011336	0.69538029218277
C	0.41054421840586	-2.77345815597731	4.83218769993099
C	2.17115641383248	-2.52989363829213	2.32093023854015
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H	0.33308287177247	-0.10517330892589	6.54280400347549
H	1.85617547742465	0.82978425645972	8.16605368156602
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H	1.58914276979103	3.25404596155414	7.76224148944073
H	0.14134212782608	2.38912784273100	7.27454767231113
H	0.53931301814325	3.91270908778950	5.49778305583927
H	2.26218872828854	3.67373815758753	5.52111427319841
H	-1.72625217799768	-1.55276517378564	2.73651845511180
H	-1.06902106256363	-2.97049867354736	1.90158447396471
H	-0.74897492918229	-1.33964913512794	1.27756759468873
H	-0.35616054764355	-2.29938880751958	5.44794500436585
H	1.32161953119296	-2.85741606735062	5.42687422874723
H	0.06986598039602	-3.78447046614961	4.59242917078918
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H	-1.29342380281715	2.92626618574233	1.01488855993872
H	0.73024691997496	6.33132748485639	2.53006031149365
H	1.91236339099763	5.55910973290610	3.59648460607727
H	0.19032847174768	5.51524230108856	3.99548072253725
H	1.62376155997452	4.76028859936218	0.00926229043934
H	1.84455337673201	3.00527534294160	0.15233803436720

H	2.90891362384146	4.11373520621628	1.03610308796650

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C	1.68413959073775	0.08175006410180	6.10350591859175
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C	1.49914205937976	3.09548381791296	5.71192736358541
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C	2.38314005148613	1.09372376986960	7.01548695499340
C	0.92657413212934	2.36989115571032	3.22246843718165
C	0.75920434471824	1.09537229369367	2.60903039383054
C	1.02538798310716	0.04523854998052	3.53111152748686
Fe	2.75724260927478	1.26979691368419	3.29253381183657
C	4.00239628297976	0.09699169339927	3.40119146508915
O	4.85333231766601	-0.71425933266783	3.50312014529354
Si	0.65760114182829	-1.76406446430436	3.29661710987529
C	2.06848368876809	-2.92320416241218	3.73805984655532
Si	0.47645515090898	3.94044874982392	2.31806086445152
C	1.51918796225580	4.14616201001330	0.76880375335507
O	0.26357761454149	0.97860636917551	1.32342299925662
C	3.87980477111510	2.44470835865661	2.75016240197522
O	4.66822968747806	3.26217394717684	2.42106660446393
C	-1.33780220184697	3.79863740431702	1.82323690384822
C	0.66007989489626	5.47364909971991	3.39332997103718
C	0.17319635069401	-2.13432288369627	1.51039283741874
C	-0.81018903263558	-2.14440217758682	4.41271944903608
H	2.30624731175773	-0.80419848032665	5.96737390053560
H	0.76250184569746	-0.25775653296012	6.59354648364762
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H	3.38347246334839	1.29614278161857	6.62233494290027
H	2.02958555152962	3.08147282329618	7.80807477708518
H	0.57701877067929	2.16894717872259	7.43362107895645
H	0.67979600703678	3.81789454928922	5.73268003866608
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H	-0.54125256962573	-1.98268309540810	5.45942404628194
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H	0.38725610170268	6.35291014465561	2.80265663926231
H	1.68311243355354	5.60524199346046	3.75217862656526
H	0.00008048643707	5.43779581907461	4.26202767449218
H	1.11967596684158	4.93859846304290	0.13027841064467
H	1.52525782869022	3.21270631085050	0.20364254089625
H	2.55094955230491	4.39215037252918	1.02655838504000
H	0.61192413731007	0.17068179010261	0.92925059535427

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C	1.49620353530737	0.10096007026390	6.11297574727744
C	1.19671071705472	0.71082029400264	4.77687859575883
C	1.12364515900496	2.09975672569681	4.57533986476968
C	1.29917369335369	3.10594774532067	5.67956659038722
C	1.39844084471782	2.42860090384530	7.05566375661702
C	2.19211427389833	1.12218213162689	7.01641008722086
C	0.83748750250044	2.35046355457730	3.16835138342715
C	0.64446659750251	1.06745853960925	2.58844571181596

C	0.92513007605587	0.02435333884564	3.51428507740860
Fe	2.67387042657721	1.26362401582874	3.35402786945230
C	3.93431934171924	0.12054244372210	3.80239681520157
O	4.74715461095902	-0.60781496912098	4.17674361975122
Si	0.69127780981229	-1.82762038695124	3.26325522983867
C	2.31092277335688	-2.74574473993687	3.02887585330259
Si	0.57732430324909	3.94279811505476	2.19422662180494
C	1.64619621652753	3.91738380630994	0.64771563487697
O	0.29906517437297	0.94961554693567	1.27594113723778
C	3.73554245555290	2.66159477318636	3.34522307457817
O	4.37904415834051	3.61540606206003	3.43688465338467
C	-1.23505973022959	4.04493535299315	1.71051220785857
C	1.01154171602347	5.44506892885258	3.22947155904961
C	-0.35204839677097	-2.09008894674911	1.71427250809106
C	-0.22345951922087	-2.52567259471927	4.74891210708055
H	2.10605570837046	-0.79723795821042	6.00069366166331
H	0.56056228719321	-0.21696984404585	6.58486269096192
H	2.29028802862420	0.71260887419422	8.02385659545094
H	3.20147202577422	1.31369755546273	6.64023398873609
H	1.84660375569582	3.12433839046265	7.76748437239325
H	0.39091257370392	2.20634444233980	7.42136780903121
H	0.45417049636212	3.79731925729054	5.67678542807493
H	2.18681448635799	3.71571344481025	5.50023477632632
H	-1.26277320072026	-1.48801066991432	1.71031562920732
H	-0.65261378577098	-3.14015054156942	1.66932201505408
H	0.21157865533832	-1.89587387027512	0.79547623547198
H	-1.10128037184587	-1.92500511096045	4.99565425562622
H	0.42041045072186	-2.56584329069792	5.62834638831435
H	-0.56004368531318	-3.54253635380296	4.53019436770570
H	2.90195636348613	-2.76950413113924	3.94601841515911
H	2.91547710873284	-2.28050742055365	2.24837729865655
H	2.10564641779505	-3.77754224344602	2.72968458032080
H	-1.40362520527807	4.89391857896728	1.04320982598372
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H	-1.55058647322233	3.13785799771719	1.19118345666303
H	0.84263403719389	6.34244957956702	2.62806099222672
H	2.05590932694852	5.44106200125272	3.54682824120965
H	0.38527499006587	5.51586406998632	4.11929483702172
H	1.38376289947556	4.74895660764725	-0.01099421008262
H	1.50972533735742	2.98550440766101	0.09745122587293
H	2.70307940573213	4.01207195485836	0.90653731191720
H	0.28293946856906	0.01788356703378	1.01956485870234

8

C	0.94665262918672	0.01870091924739	3.55098389048528
C	1.09209850886669	0.77825159986315	4.83500723689615
C	1.13448620923057	2.19203470331564	4.87542681812602
C	1.08111036539898	3.05250261862351	3.64127933914317
C	1.10461919616994	2.22534146772477	2.34408135985949
C	0.34349874423995	0.90414199438600	2.45838981456322
C	1.31358042037497	2.61244169016882	6.24371170796682
C	1.55571102852217	1.40838617776479	7.04570745573785
C	1.25931522749092	0.26781439065767	6.17568012049258
Fe	-0.49862097839746	1.47435140610046	5.97128377823382
H	-1.03972242574972	1.45274042920256	7.38455269420075
Si	1.64744245020831	-1.43796657817627	6.79935779045363
C	0.57389752619567	-1.87387197572801	8.27769664839179
Si	1.79713092593813	4.25105491497604	6.97637288373176
C	0.77369928939172	4.62889405171527	8.50538001761933
O	1.89702300580106	1.36580495735287	8.25786365918479
C	-1.60082261320000	2.74934793668818	5.54694819974559
O	-2.33509964030845	3.59157852454786	5.24214890455762
C	-1.61047131682647	0.21700175937087	5.52073047903878

O	-2.34665361802353	-0.62011464260968	5.20736592296244
C	3.61693974131643	4.10740912289486	7.45151745560266
C	1.64743000727674	5.69470850490626	5.77341273659180
C	3.45892403817260	-1.41666149617820	7.32133531416171
C	1.44863717135968	-2.77447321946419	5.48582035273647
H	0.34258668676875	-0.87646648613193	3.69847670022317
H	1.93527704770810	-0.32924681140819	3.22726904422889
H	0.37671105798928	0.37694686720958	1.50190521788325
H	-0.70730663700972	1.10070947784249	2.69127329626675
H	0.69927066906627	2.82546744359272	1.52608402139068
H	2.14284693840608	1.99608913995755	2.08263632226194
H	1.93845654851893	3.72854890904246	3.64636343942437
H	0.20048858989048	3.69737719203549	3.66475558094916
H	4.10115192028004	-1.21192468836660	6.46019215233691
H	3.76699634033023	-2.36865149330010	7.76230368368048
H	3.60878229695382	-0.62130873632890	8.05293782812968
H	2.08351084252375	-2.58070600910498	4.61879998526004
H	0.41728955450641	-2.86408446265156	5.13660051861643
H	1.74652821944275	-3.73624427803006	5.91434039439017
H	-0.46310426280443	-2.03470923892799	7.97248629148154
H	0.60129494271975	-1.05079197818360	8.99364319366392
H	0.93166870324992	-2.78087175169307	8.77319802010494
H	3.98806423765137	5.02603803586801	7.91410000857954
H	4.22477924370521	3.89860284172905	6.56664776930506
H	3.74591575262072	3.28070170685490	8.15150190329204
H	1.93436251955372	6.61514631680879	6.29079102843557
H	0.63092377762647	5.81898731066445	5.39311082429425
H	2.31403007878404	5.57394670860866	4.91727270129833
H	1.19124461530016	5.47355373120096	9.06051672240201
H	0.76428039821087	3.75243346746164	9.15459453836608
H	-0.25666697462862	4.87116552789957	8.23364123325119

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C	0.96095309024944	-0.05142473812549	3.58538510856570
C	1.08416866823763	0.73928446469396	4.85056651222236
C	1.10321068634420	2.18729806024617	4.84280269343851
C	0.91938919421369	2.98517934253983	3.58060250412878
C	1.13252502258786	2.13513159925937	2.32140544929271
C	0.43935971967893	0.77666157599995	2.40784118812055
C	1.33515138279812	2.64747961392831	6.15390195595841
C	1.55078439455944	1.43961750523589	7.00143581891771
C	1.29594979593066	0.25656408665651	6.16053142376374
Fe	-0.46865698467518	1.48077726653858	6.13245832642353
H	-1.11607125084935	0.49305446634366	7.05259102139040
Si	1.67650479429711	-1.46282417564142	6.82615304464488
C	0.48107015162785	-1.93528334652869	8.18745882365526
Si	1.82921400244820	4.32107722980839	6.87590907242757
C	0.77491525178320	4.70872799986579	8.37469156392391
O	1.81804231492260	1.44706850210846	8.22085692039239
C	-1.55310930614957	2.73113049142840	6.78400423497798
O	-2.30036070911629	3.50356481219467	7.17333029999638
C	-1.73881900692207	0.88833059566131	5.04029602670295
O	-2.60097073737536	0.43770025585677	4.43665427289225
C	3.62741674763783	4.10622330120472	7.37392382527365
C	1.70134812760199	5.70722091257413	5.62060461528004
C	3.43023120955230	-1.35566973082973	7.49041100941993
C	1.63492309815416	-2.76404614279080	5.47286922277406
H	0.34687397644873	-0.93683695200595	3.74478276652920
H	1.96408743135670	-0.41822286636345	3.34353030270692
H	0.60800517133365	0.21608784601040	1.48655538180982
H	-0.64065215432137	0.92040148254433	2.49710389932904
H	0.76462731095883	2.68792853839059	1.45511024099228
H	2.20471451582295	1.97838605052809	2.16827223548792

H	1.61265621230785	3.82518552180688	3.57750594641808
H	-0.08322018614982	3.41824829765741	3.56865902937462
H	4.12387014034523	-1.06289257697509	6.69807093899378
H	3.75015416025839	-2.32344230238368	7.88540462034211
H	3.49434746335075	-0.61563690063941	8.28864759936794
H	2.31709993387003	-2.52313212606687	4.65564893116817
H	0.63591613906678	-2.90360030516151	5.05511226896578
H	1.95530413810114	-3.71618279403911	5.90584885177566
H	-0.52197447269449	-2.08958027481443	7.78372570780912
H	0.43118955829330	-1.15193552439911	8.94514047310529
H	0.80533677551106	-2.86173655518524	8.66902882263638
H	4.02711211197340	5.04313583067176	7.77005548479178
H	4.23400296589504	3.80835822090139	6.51518156181685
H	3.72127104618115	3.33685196598555	8.14108812698367
H	1.97683789597725	6.64390753701939	6.11344983986977
H	0.69053071940246	5.81592631670531	5.22209471786536
H	2.38552128779269	5.55888907735839	4.78341160864585
H	1.23280944669411	5.51816686488324	8.94901702355472
H	0.69578605848518	3.83300325420615	9.01976925485870
H	-0.22918830379838	5.02600642513618	8.08859643021746

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C	0.98082173828478	-0.01656070037283	3.56381116700174
C	1.10355105393918	0.72573373616378	4.79928961500942
C	1.06351702405620	2.11220628491576	4.50554013100019
C	0.97814462329974	2.28216571731916	3.07689754677256
C	0.69840724462170	0.95483641787870	2.50249405512473
C	1.03779185337646	3.17936651516059	5.56863164729317
C	1.00430377534442	2.60359617419713	6.99530046658041
C	1.76202421401534	1.28451562580391	7.13758235932278
C	1.18504194847119	0.21600423173627	6.20683076388072
Fe	2.74656890917210	1.20987273180198	3.63806743829560
C	3.64510922152891	1.06525528802665	1.89288987365954
O	4.63533434992051	2.02439556663136	1.67426696027769
Si	0.76874354765887	3.81319474059479	2.03205962429846
C	-1.06068826231415	3.96801620194531	1.60145496817882
O	0.36294390271315	0.70487535562325	1.32263773466948
Si	0.71471051563671	-1.83568944378756	3.25302138422834
C	-1.05379093726334	-2.04167275194845	2.63286064580674
C	3.71630187095149	-0.09107130084860	4.28631864968879
O	4.29812206735583	-0.98722053506622	4.72307871232554
C	3.73267874337775	2.53970974161045	4.21064421840752
O	4.31576408373893	3.43321277388338	4.64724237045392
C	1.28250861234404	5.38522316419510	2.93560501296702
C	1.76725816651585	3.66733722706145	0.44851182950933
C	0.90319557775958	-2.87832510456715	4.81396595192766
C	1.91834622194831	-2.47821039107164	1.96421948544905
O	3.48383333661133	0.24885359699793	1.00475145102910
H	1.77837603290863	-0.69601882869327	6.25760829088723
H	0.17846854446891	-0.05318232089622	6.54806487419918
H	1.70251317658918	0.93722778270662	8.17168405779973
H	2.82019682268860	1.43485476539873	6.90326759549252
H	1.40669059720090	3.34300867250260	7.69109989980277
H	-0.03538919072332	2.42926383782505	7.28878804785138
H	0.14764427755725	3.79353472637203	5.41376714922632
H	1.88262199271383	3.85851449312349	5.45681461609248
H	-1.76944304652692	-1.74592263997254	3.40455463792093
H	-1.26046452653495	-3.07780314039304	2.35062578039507
H	-1.20860312713314	-1.40230069706806	1.76280338339411
H	0.22794490222762	-2.55709027419594	5.60870799472496
H	1.92322540404895	-2.85370547656204	5.20373242270360
H	0.66151219420634	-3.91726107860504	4.56926389209066
H	2.90717899232084	-2.62379580617755	2.40632372374338

H	2.02332100756236	-1.74761825638077	1.16343649905672
H	1.58050317461483	-3.43347025084322	1.55242249498465
H	-1.23781161490401	4.77605803639294	0.88686232920539
H	-1.65519266822419	4.17308554123347	2.49571466843325
H	-1.41536965394111	3.03414004100921	1.16000408382245
H	1.11683293812876	6.24240538145841	2.27674484043959
H	2.33901995126446	5.37124553242097	3.21274302264341
H	0.69567677124277	5.54316702973617	3.84152246766400
H	1.49043885951832	4.45265986543495	-0.25994951291710
H	1.58415815571442	2.69344358961645	-0.00717010639540
H	2.83483381540670	3.74693626410561	0.65982985623930
H	5.00274544418413	1.84218294185666	0.78918506828833

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C	1.04000127690956	-0.10553721943789	3.60513989599347
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C	1.05260484263579	2.20005910098212	2.98148323016539
C	0.81407895468928	0.83152862035041	2.46454149103417
C	0.99211813898617	3.18265077749224	5.41375689621545
C	0.71694563073334	2.66207356236914	6.83573435062312
C	1.45927369435065	1.36635015851841	7.15896258403021
C	1.06094481518635	0.24382562450134	6.20031846729961
Fe	2.82024491631529	1.10170183925123	3.57612398141855
C	3.83998246005539	1.77518229741537	2.04637113800510
O	4.53140978318895	2.93721637814952	2.19889908884212
Si	0.81192011191681	3.74838142866196	1.92846962381134
C	-1.02523531983109	4.14780255484737	1.98728155742474
O	0.53458762232645	0.50101447123417	1.30873066765765
Si	0.74834331353030	-1.95559854123411	3.33565500610763
C	-1.03160814186476	-2.09172805501468	2.75214510418397
C	3.93398086536034	-0.28848226566329	3.73877567970899
O	4.65804792415396	-1.16049901597632	3.85609378315346
C	3.80651770149147	2.07800413872743	4.73144011777998
O	4.46471453866755	2.72581520790957	5.39976866304144
C	1.80538134617631	5.17751216353816	2.62848477164213
C	1.29846193439179	3.41243199878310	0.15077349253010
C	0.96213996182038	-2.94018957300954	4.91837113904476
C	1.91707406176759	-2.58016336524613	2.00967837341621
O	3.87949635841278	1.17310164543213	0.99300303067354
H	1.68985781186568	-0.63373042213942	6.34315476815191
H	0.03552063869062	-0.07212738906689	6.42315548933310
H	1.22981857650515	1.05635739935300	8.18012240971461
H	2.53911935402390	1.52886412503777	7.11319014490799
H	0.98672909980417	3.43734746619556	7.55391928302242
H	-0.35616547250280	2.48390304671438	6.94950072956041
H	0.19132681888300	3.86124684170799	5.11413762849075
H	1.90220342541291	3.78280476176107	5.39775291552296
H	-1.72623882947781	-1.74827964707011	3.52193645787193
H	-1.27070231568907	-3.13139233748771	2.51331284748198
H	-1.18245780081129	-1.48761318584490	1.85717193366004
H	0.28185020193352	-2.60112010353841	5.70065301502082
H	1.98177652940477	-2.89809124326639	5.30680894765050
H	0.72686191257180	-3.98694795738505	4.70470571545967
H	2.92023035312288	-2.74997009297482	2.40458171243702
H	1.98032562093497	-1.86082096732597	1.19246826120820
H	1.55082271301407	-3.52803925773696	1.60725328244153
H	-1.24391413476303	5.01713066615839	1.36226943560343
H	-1.35985575408224	4.36903403840889	3.00331490745488
H	-1.61137102561316	3.30685954419167	1.60928182385932
H	1.67419598021386	6.05575793942668	1.99150690254936
H	2.86763804402327	4.92963352837354	2.65958177510549
H	1.48309765368759	5.44473218309093	3.63585659088858

H	1.11170135257046	4.30979623905578	-0.44525812163436
H	0.70251738194191	2.59437141591796	-0.25230064891859
H	2.34937363215873	3.13971207023681	0.05140851608481
H	5.00006159777471	3.12320557322824	1.36288528962852

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C	0.94537889982323	0.22756373715810	6.17538896876224
C	1.02264669923321	0.74024352156432	4.77074259919205
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C	0.99129679487216	3.19934074659477	5.51834616395392
C	0.71343487775049	2.63389368048854	6.92102205866492
C	1.40741665670799	1.29438279985733	7.17118125856696
C	1.07278308217061	2.29282432834648	3.03088128570575
C	1.04307484436128	0.97074911049749	2.49975463008402
C	1.05509180561661	-0.00878249170550	3.52940707370949
Fe	2.79294619376632	1.20199661490097	3.71543622790180
C	3.77058189743453	-0.02631258438042	4.46768872078711
O	4.39597286309797	-0.85082145622930	4.97053710970493
Si	0.75737495175820	3.89936059787479	2.10768997124751
C	1.96836065946777	5.23033528180945	2.62045580823527
O	0.98535838638839	0.60810680464380	1.19176998576901
Si	0.94053332540635	-1.84817734580109	3.15237493579455
C	0.76917335100964	-2.85264815215781	4.72881826324021
C	3.93570387507341	2.47372046502727	4.07845254910824
O	4.70381728975734	3.29412924692327	4.32441720842030
H	3.58753113223368	0.96835782902601	2.46502903085215
C	2.46865149258420	-2.38149193382725	2.19967002190143
C	-0.59803097799977	-2.08644415676123	2.10056693223759
C	0.86642177299397	3.62038258476760	0.24990121366736
C	-1.00978994354384	4.41706523244352	2.48947761544164
H	1.53199234760726	-0.68212395158053	6.29320608460570
H	-0.09403660279175	-0.04576856762301	6.38869277738165
H	1.19442422180404	0.95265971096938	8.18629100611807
H	2.49166455263426	1.41935840635903	7.08914712295022
H	1.02748674615496	3.36340863499806	7.66960011623172
H	-0.36485692990401	2.49608129675144	7.04625823574658
H	0.21163304606247	3.91870748493422	5.25940841910235
H	1.92690597982963	3.76034763226211	5.52167897053866
H	-1.49167696311846	-1.78500501478666	2.65262354473751
H	-0.71101157349920	-3.13441287793254	1.81066226290001
H	-0.53794526520755	-1.48325780623759	1.19399313482246
H	-0.04018919868497	-2.48074397598831	5.35892866018678
H	1.68864172585874	-2.85452870560918	5.31751775437561
H	0.53731367180049	-3.88748141685386	4.46176042477749
H	3.34888250496115	-2.38554260082848	2.84453949335070
H	2.65655492422430	-1.69472916051099	1.37297933844785
H	2.34071924591264	-3.38683461154446	1.78977763537892
H	-1.26420609305841	5.32332205539434	1.93433959664043
H	-1.16717974509579	4.61565859792912	3.55125122416371
H	-1.70401322358839	3.63005318792854	2.18516241915716
H	1.74450974985309	6.15611776448567	2.08447891971026
H	2.99280669052445	4.93581671828041	2.38391494245606
H	1.90751716570674	5.43622295910523	3.69056170159849
H	0.65501428221953	4.56910925897194	-0.25050375530660
H	0.11362055744086	2.91205188305396	-0.10533050853580
H	1.85466847486085	3.29124584921475	-0.08286292055220
H	1.20979695425140	1.36187178696363	0.63061017033493

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C	1.03582132506269	-0.02715734691630	3.54816869865952
C	1.01939468161413	0.73144294658635	4.77863605517700
C	1.04834505705856	2.10926618749319	4.46691206244593
C	1.07128764816019	2.27049230292180	3.02695217774954

C	1.02613605556895	0.94461501408526	2.50951291478922
C	1.00234836949382	3.19571543391455	5.50784996798885
C	0.74554105074285	2.64283080050447	6.92017326368431
C	1.42793026626475	1.29758662881518	7.17113111899620
C	0.94169245904412	0.23152450218263	6.18715303172633
Fe	2.80158482624597	1.17290140872413	3.70091395412327
C	3.94142367107403	0.84360142351354	2.13884339375381
O	3.49993802862852	1.48177630494576	0.98539728195206
Si	0.73405565143877	3.86528129310353	2.07948425165894
C	-1.03281073932209	4.35418709895511	2.51033521021273
O	0.96682034263481	0.58894970333701	1.20120216249438
Si	0.87003323396742	-1.86299600945362	3.15834649648517
C	-0.69995759493786	-2.04969666606673	2.14124779540897
C	3.73983664935036	0.03278157835120	4.66713600158250
O	4.32206808266257	-0.69769751027633	5.32717890448662
C	3.85850120758293	2.51551035190769	4.10981108327636
O	4.54540041489638	3.38375130090240	4.40343847938299
C	1.93606953104688	5.20892138387425	2.58317409043761
C	0.81383359319622	3.59886631702848	0.22490636187248
C	0.71376831056002	-2.87212431001323	4.73130881347907
C	2.37335824090913	-2.41047128457697	2.17950660147770
O	4.97354343954108	0.20595610229769	2.05852006792391
H	1.50573046426703	-0.69190577153220	6.30890387862070
H	-0.10287397168427	-0.01731453710512	6.40306889917774
H	1.22216223424063	0.96437374375139	8.19003291371289
H	2.51301487972044	1.40922362479271	7.07983739091867
H	1.08221580037147	3.37476583491542	7.65588816274551
H	-0.33127930161663	2.51828512303405	7.06622619374617
H	0.21213684401913	3.90254875986787	5.24831453313789
H	1.92894134272293	3.77053003699490	5.49452570944960
H	-1.57169213499869	-1.73137953164231	2.71828987791299
H	-0.84888867513579	-3.09085217814911	1.84316424319323
H	-0.64587232030562	-1.43883157121793	1.23957649165489
H	-0.08082873526910	-2.49542110813673	5.37716246568039
H	1.64335094796252	-2.88848710079960	5.30372095139203
H	0.46563096779354	-3.90247488071808	4.46160790744116
H	3.28032457238883	-2.32378592798089	2.78042763614889
H	2.49793302196434	-1.78835695257470	1.29228136725543
H	2.27055914013911	-3.44981441402659	1.85698785143186
H	-1.30653055336853	5.27171059035822	1.98349606739425
H	-1.17481050106899	4.52377083294398	3.57917371186325
H	-1.72527090040732	3.56881227088531	2.19752096354167
H	1.68970466347175	6.13211502142508	2.05215042462669
H	2.95973400650384	4.93055872436245	2.32495556054679
H	1.89298162523223	5.41383009178502	3.65403588735102
H	0.50299202806564	4.52424373228408	-0.26813968336231
H	0.13259617646544	2.80921763581371	-0.09492206479191
H	1.81918441318535	3.35059955436350	-0.11797114594321
H	1.68869220373310	1.04840172240995	0.73298386094387
H	4.11581795912241	1.24698071775457	0.26637270298432

TS1

C	1.03087218339766	0.03200205671909	3.59078166319482
C	1.16701609997923	0.76383253540414	4.82245451398849
C	1.20257796213350	2.15264410342371	4.53742292320831
C	1.08018509920589	2.34016567667720	3.10704094622192
C	0.89847874544911	1.02483892608554	2.54709529294078
C	1.26022188642987	3.20691046495945	5.61051558329528
C	1.10328601239987	2.62626622935160	7.02443883161110
C	1.77569056964667	1.26589537454329	7.19546161891467
C	1.19813032929369	0.23677663608466	6.22322381288839
Fe	2.83178274489375	1.18149907319944	3.58711492695336
C	3.80137699893890	0.53588523541058	2.05031244045350

O	3.01694929138744	0.94187189132525	0.52617734956957
Si	0.71780416746900	3.90429884360973	2.10577262668328
C	-1.09762030871446	3.80695955025730	1.62459863221510
O	0.74718030833351	0.75652724804527	1.28077418367153
Si	0.74035917453385	-1.79440548579971	3.23169000994514
C	-0.87573259641503	-1.90902940558629	2.27928893025349
C	3.84546038884150	0.15144668169315	4.62370326307498
O	4.47287482844669	-0.52368234496240	5.29875238462658
C	3.83684969180159	2.63657477965571	3.70929315205476
O	4.43592277791384	3.60630010161742	3.79958305494866
C	0.95910894545257	5.46556739536615	3.12259658856303
C	1.79233192228023	4.02541346705763	0.57489265866306
C	0.59561882837076	-2.78893068579616	4.81871057976224
C	2.16179956978515	-2.46999166706583	2.20926557345637
O	4.79710666987583	-0.02462082411306	1.80421443005712
H	1.74533444540791	-0.70256714838278	6.27921782315388
H	0.16699435779497	0.00657643998286	6.51081417632468
H	1.63317490931929	0.90870553336682	8.21688823044563
H	2.85388728582004	1.36146837520811	7.03499145518541
H	1.50615906314928	3.33685071376004	7.74780254755544
H	0.03827287691210	2.51620035538109	7.24855476216427
H	0.46003147207096	3.92507973696676	5.43334067103625
H	2.18831514046442	3.77452469803772	5.53419400899096
H	-1.71041075526570	-1.56635388340015	2.89592939994235
H	-1.07605025581322	-2.93980218850036	1.97525799784817
H	-0.82936169898726	-1.28185172430085	1.38902021464697
H	-0.14812017475939	-2.37064119775175	5.49855293192937
H	1.54671541556966	-2.85644596437195	5.35064310683858
H	0.28161791490622	-3.80516472659389	4.56404972855410
H	3.09753621768115	-2.43424175331570	2.77093261522126
H	2.29222295214964	-1.89118288311032	1.29382462650457
H	1.97102237350422	-3.50880597828555	1.92714795439068
H	-1.34759738699468	4.60779175094966	0.92410415247341
H	-1.73577199612111	3.92025946039464	2.50414077029470
H	-1.32875093853588	2.85241422310350	1.14795195187270
H	0.73338376124329	6.31935824596760	2.47712150820662
H	1.98042601731231	5.58012419223073	3.49080710908784
H	0.28109581459868	5.51129281520646	3.97477403414925
H	1.47441077522068	4.88824780880305	-0.01662242345447
H	1.71655806974406	3.13272880244228	-0.04396407710333
H	2.84257337459271	4.16414944311921	0.84074287748358
H	1.89597502522817	0.84760370667378	0.76854896027589
H	3.28634365265680	0.24982428925606	-0.09703008523429

TS2

C	1.04512625119924	-0.14740559672194	3.60579135636425
C	1.13687476586685	0.72835568844457	4.81770347338946
C	1.07907341642939	2.14076597583900	4.74127394091587
C	0.99331826955605	2.88953676028942	3.43930987868413
C	1.07056730192077	1.95849041974577	2.21554044071589
C	0.39933831796429	0.60229214998854	2.43844014328592
C	1.20649980325102	2.68860138659451	6.07490659103595
C	1.58384022488530	1.58172581748531	6.95901483493209
C	1.33453791004416	0.35322261867118	6.19891188600542
Fe	-0.50849168877282	1.40241014324986	5.89525920431108
C	-1.65063605318847	2.40379338166054	5.03275623436302
O	-2.35528354339450	3.06416928301105	4.39666160050796
Si	1.71078391070922	-1.28625262797179	6.99747018346947
C	0.65371948908317	-1.49624650304221	8.53585547012649
Si	1.45554365378528	4.45781076313256	6.58955827963135
C	0.96213096209533	4.75798071499384	8.37742862446662
O	1.94940487012814	1.65290581308870	8.15823787126662
C	-1.59860427901178	2.53986729991500	7.70529367177629

O	-1.22911133327947	1.65741003842649	8.42478638143715
C	-1.49613617134148	-0.05588429426254	5.79442469739795
O	-2.10131909278078	-1.02892430008813	5.65372899890936
O	-2.18399693609523	3.56998301580958	7.56365093692932
C	3.30763366904185	4.76912069062733	6.42268226089659
C	0.49863740138949	5.65671746766272	5.50024722229421
C	3.53660987659460	-1.26127992218524	7.45953415682247
C	1.41005972585793	-2.73853391046725	5.83704562815899
H	0.48527658960692	-1.05499291913141	3.83090831892054
H	2.05170280833055	-0.47233463239130	3.31478516337481
H	0.48200223332197	0.00121892995797	1.52985048953510
H	-0.66634907701712	0.74050426425110	2.64494185645562
H	0.62433711031494	2.46185357484611	1.35471706989108
H	2.12066095216087	1.77862915691945	1.96507082480958
H	1.81614966083568	3.60812011197274	3.39254816549690
H	0.08148578398121	3.48626029056878	3.39854800254560
H	4.15299598841550	-1.11866919895349	6.56791867143947
H	3.84422381610244	-2.19051825513705	7.94632366267517
H	3.72701804105572	-0.42883449003636	8.13880209536010
H	2.02007925089146	-2.67154540341185	4.93441922929301
H	0.36247653192070	-2.80936268078842	5.53525685247127
H	1.67500659163829	-3.66612922023595	6.35333297864299
H	-0.37698767995187	-1.73739635498893	8.26524744923065
H	0.64901737508114	-0.55853691466498	9.09284202566112
H	1.03638888853956	-2.29203164672401	9.18024045845126
H	3.58707991499401	5.78301919273392	6.72189536793473
H	3.63631131486356	4.60696401875033	5.39235389849456
H	3.85002814421093	4.06477737619028	7.05813671786214
H	0.64074163997514	6.67621377372570	5.87018334939647
H	-0.56977202373430	5.43098519359783	5.53144486725188
H	0.82614353696629	5.62735550100663	4.46009197033481
H	1.39281453942338	5.70135572429301	8.72520794018546
H	1.33880568298121	3.94298956765584	8.99453258399121
H	-0.12084933684569	4.81400276609727	8.49304902220061

TS3

C	1.017922	-0.126900	3.459091
C	1.041219	0.722957	4.693326
C	0.913218	2.139856	4.656906
C	0.717001	2.904456	3.371619
C	0.928999	2.020222	2.131498
C	0.358304	0.609193	2.290814
C	1.110171	2.670784	5.987004
C	1.450497	1.557020	6.850169
C	1.298997	0.336561	6.052073
Fe	-0.603783	1.289006	5.816481
C	-1.902753	2.022796	4.991053
O	-2.781744	2.560477	4.407412
Si	1.832632	-1.256514	6.806884
C	0.854526	-1.635031	8.368809
Si	1.497268	4.364843	6.586053
C	0.557275	4.845699	8.148152
O	1.808023	1.615386	8.076500
C	-1.955675	2.704729	8.223259
O	-1.386542	2.178079	9.096775
C	-1.623855	0.283668	6.756682
O	-2.347833	-0.456539	7.342247
O	-2.668540	3.392054	7.597603
C	3.340673	4.396385	7.015905
C	1.220515	5.725629	5.300297
C	3.660152	-1.074675	7.259016
C	1.703770	-2.732975	5.633355
H	0.503159	-1.069560	3.651198

H	2.045453	-0.392171	3.166525
H	0.512783	0.044777	1.365932
H	-0.719715	0.668242	2.469806
H	0.489159	2.508942	1.256839
H	2.003673	1.934539	1.931857
H	1.421720	3.737765	3.324972
H	-0.277548	3.355884	3.338877
H	4.255814	-0.878484	6.362479
H	4.063509	-1.962132	7.754945
H	3.764661	-0.215065	7.923596
H	2.302923	-2.573090	4.733743
H	0.673320	-2.918749	5.320959
H	2.077089	-3.633664	6.130557
H	-0.160625	-1.949729	8.119960
H	0.789229	-0.714745	8.951287
H	1.329795	-2.414073	8.972012
H	3.655771	5.346870	7.456901
H	3.944024	4.209855	6.122793
H	3.534835	3.591490	7.727260
H	1.438206	6.697567	5.754621
H	0.191778	5.741216	4.931655
H	1.881811	5.603489	4.439974
H	1.004079	5.729399	8.614283
H	0.602746	4.013948	8.851504
H	-0.491174	5.064841	7.934649

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