Supporting Information

Energy-Efficient Hydrogen Evolution by Fe-S Electrocatalysts: Mechanistic Investigations

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List of symbols in electrochemical study

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Crystallographic results of 1⁻

Table	S1 .	X-rav	Crvstal	lograp	hic	Data
1 4010	~ .	11 100	CI J Diai	10 Brap	1110	Dain

	[TBA][1]·THF
Empirical formula	$C_{43}H_{58}Fe_2NO_6PS_2$
Formula weight	891.69
<i>Т</i> , К	150(2)
Crystal system	Monoclinic
Space group	C2/c
<i>a</i> , Å	38.787(2)
<i>b</i> , Å	10.9018(7)
<i>c</i> , Å	23.5032(15)
α, °	90
β , °	115.228(2)
γ, °	90
<i>V</i> , Å ³	8990.3(10)
Z	8
$ ho_{\text{calcd}}$, Mg m ⁻³	1.318
μ , mm ⁻¹	0.819
F (000)	3760
Reflections collected	26721
Independent reflections	7904
R _{int}	0.0818
Goodness-of-fit on F ²	1.171
R1 [$I > 2\sigma(I)$] (all data) ^a	0.0850 (0.1095)
wR2 [$I > 2\sigma(I)$] (all data) ^b	0.1776 (0.1881)

^a R1 = $(\Sigma ||F_o| - |F_c||)/(\Sigma |F_o|)$. ^b wR2 = $[\Sigma w (F_o^2 - F_c^2)^2 / \Sigma w (F_o^2)^2]^{1/2}$.

Computational methods

All DFT calculations were performed using a hybrid functional B3LYP^{1,2} on *Gaussian 09*.³ The effective core potential and associated basis set of LANL2DZ were used for the Fe atom,⁴ and the 6-31G(d,p) basis set was used for O, S, P, C, and H atoms. All structure optimization and thermochemical properties were calculated under the solvent effect by using the polarizable continuum model (PCM) for CH_2Cl_2 .⁵⁻⁷

Computational results are summarized in Tables S2-S6, which include the solvent corrected free energy, the thermodynamic parameters for the calculation of the reduction potentials (E^{cal}) of the related species, and the calculated p K_a values.

Estimation of pK_a values, redox potentials and equilibrium constants

The estimation of pK_a values of key intermediates (AH⁺) was based on the method reported in literature.⁸ The following equation describes the deprotonation reaction with respect to a reference species having the known pK_a value.

$$AH^+ + A_{ref} \rightarrow A + A_{ref}H^+$$

The calculated pK_a can be expressed as:

$$pK_{a}^{cal} = \frac{\Delta G_{r}^{0}}{\ln(0)RT} + pK_{a}(ref)$$

where $pK_a(ref)$ is the known pK_a of the reference species. ΔG_r^0 is the free energy change for the corresponding reaction, which is calculated from Born–Haber thermodynamic cycle based on the energies in gas and solution phase.

$$\Delta G_r^0 = \Delta G_{\text{gas}}^0 + \Delta G_s^0(A) + \Delta G_s^0(A_{\text{ref}} \text{H}^+) - \Delta G_s^0(A \text{H}^+) - \Delta G_s^0(A_{\text{ref}})$$

The p K_a of H(OEt₂)₂⁺ is defined to be 0 as suggested that the weak coordinated proton can be treated as a reference.⁹ The p K_a^{cal} (in CH₂Cl₂ solution) of PhNH₃⁺ is estimated to be 12.11, which is consistent with the measured value in MeCN solution (p $K_a^{MeCN} = 10.7$). The estimated p K_a^{cal} values for the protonated species are listed in Table S2. The p K_a^{cal} of **1µH** is 22.44. The values for **1µHSH**⁺ and **1µHSH** concerning the dissociation of the S-proton are 4.28 and 18.38, respectively.

The theoretical reduction potentials of reactions and Fc^+/Fc couple are estimated from the relationship and equations in Table S3 where *n* is the number of electron involved, and *F* the

Faraday constant.^{10,11} The calibrated potentials was obtained with $E_{calc}(Ox/Red) = E_{calc}^{0}(Ox/Red) - E_{calc}^{0}(Fc^{+}/Fc)$.

The equilibrium constant of the protonation reaction was calculated from the following equation:

$$K_{\rm eq} = 10^{-(pKa(Acid) - pKa(Catalyst))}$$

For the protonation reaction of $1\mu H^-$ by HOTf, the $pK_a(\text{Catalyst})$ is $pK_a(1\mu HSH^+)$. For the protonation reaction of 1^- by TFA or TCA, the $pK_a(\text{Catalyst})$ is $pK_a(1\mu H)$.

Table S2.	Calculated pK	a values for	selected species	in CH ₂ Cl ₂ solution.
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Species	$\mathrm{p}K_\mathrm{a}^\mathrm{cal}$
PhNH ₃ ⁺	12.11 (10.7)
1µH	22.44
$1 \mu HSH^+$	4.28 (SH)
1µHSH	18.38 (SH)

^oValue in parentheses is measured in MeCN solution from experiments.

Table S3. Thermodynamic relationships and equations for theoretical estimation of the reduction potential.

Thermodynamic cycle used to calculate Gibbs free energy				
$\Delta H_g^{0,redox} = d\varepsilon_{SCF} + d\varepsilon_{trans} + d\varepsilon_{rot} + d\varepsilon_{vib} + d\varepsilon_{ZPE}$				
$\Delta G_g^{0,redox} = \Delta H_g^{0,redox} - T\Delta S_g^{0,redox}$				
$\Delta G_s^0 = (\varepsilon_{SCF} + G_{corr})_{solv} - (\varepsilon_{SCF} + G_{corr})_{gas}$				
Estimation of reduction potential				
$\Delta G_{solv}^{0,redox} = \Delta G_g^{0,redox} + \Delta G_s^0(Red) - \Delta G_s^0(Ox)$				
$E_{calc}^{0} = -\Delta G_{solv}^{0,redox} / nF$				

Reaction	S-H (Å)	$\Delta G_g^{0,redox}$ (kcal mol ⁻¹)	$\Delta G_s^0(Red)$ (kcal mol ⁻¹)	$\Delta G_s^0(Ox)$ (kcal mol ⁻¹)	$E^{ m cal}$ (V)
1µHSH ^{+/0}	1.35	-123.646	-6.722	-32.939	-1.22
1µHSHNH2Ph ^{+/0}	2.135	-106.272	-16.603	-36.366	-1.69

Table S4. Computed thermodynamic parameters and reduction potentials (vs. Fc⁺/Fc) for selected species.

Evaluation of the intra-molecular route for H₂ evolution by calculation

According to our experimental and computational results, the possibility of the intramolecular reaction in which a sulfur-proton reacts with a Fe-hydride for hydrogen evolution is eliminated. In such case, when the thermodynamically disfavored species 1μ HSH is formed, it readily reacts to produce molecular hydrogen and 1μ H. The detailed is described below.

The free energy change of H₂ elimination from **1µHSH** was calculated from the thermodynamic cycle as shown in Table S5. The reduction potentials of **1µHSH**⁺ and **1** were taken from experiments to be -1 and -0.6 V vs. Fc⁺/Fc, respectively. The NHE potential $E^{\circ}(H^+/H_2)$ is -0.14 V vs. Fc⁺/Fc from the experimental measurement in acetonitrile.¹² The p*K*_a of **1µHSH**⁺ and **1µHSH** are taken from the calculated values (vide supra). The pathway of H₂ elimination from **1µHSH** is slightly unfavored by 6.11 kcal mol⁻¹.

Moreover, two energy barriers (13.3 and 13.4 kcal mol⁻¹ for TS₁ and TS₂, respectively) are to be overcome for proton relay from the S site of **1µHSH** to the Fe center, followed by hydrogen evolution, shown in the Scheme S1. The final product in this route is **1**, which is inconsistent with the experimental result in which **1µH** is the end product of the catalysis (see the discussion in *Determination of the Intermediates and Dominant Reaction Pathways*). The most possible route is a bi-molecular pathway where two **1µHSH** generate two **1µH** with liberation of molecular hydrogen. This is favored in thermodynamics ($\Delta G_2^0 = -14.02$ kcal mol⁻¹).

Intra-molecular H ₂ elimina	ation
Reaction	Free energy
$1\mu HSH \rightarrow 1\mu HSH^+ + e^-$	FE^0
$1 \mu HSH^+ \rightarrow 1 \mu H + H^+$	2.3 <i>RT</i> p <i>K</i> _a
$1\mu\mathrm{H} ightarrow 1^- + \mathrm{H^+}$	2.3 <i>RT</i> p <i>K</i> _a
$1^- \rightarrow 1 + e^-$	FE^0
$2H^+ + 2e^- \rightarrow H_2$	$-2FE^{0}(H^{+}/H_{2})$
$1\mu HSH \rightarrow 1 + H_2$	$\Delta G_1{}^0$
Homolytic H ₂ elimination	on
Reaction	Free energy
$1\mu HSH \rightarrow 1\mu HSH^+ + e^-$	FE^0
$1\mu HSH^+ \rightarrow 1\mu H + H^+$	2.3 <i>RT</i> p <i>K</i> _a
$\mathrm{H^{+}} + \mathrm{e^{-}} \rightarrow 0.5 \mathrm{~H_{2}}$	$-FE^{0}(H^{+}/H_{2})$
$1\mu HSH \rightarrow 1\mu H + 0.5 H_2$	ΔG_2^0

Table S5. Thermodynamic cycles for the calculation of the free energy by intra-molecular H_2 elimination and homolytic fashion from $1\mu HSH$.

Scheme S1. The computed intra-molecular pathway including the free energy changes, optimized intermediates and transition states.



Species	$\Delta G_{\rm solv}$ (hartree)	$\Delta G_{\rm gas}$ (hartree)
1-	-2645.669149	-2645.610236
1	-2645.525386	NA
1µH	-2646.119996	-2646.109649
1μH [_]	-2646.240978	NA
1µHSH ⁺	-2646.531071	-2646.478578
1µHSH	-2646.682896	-2646.672183
1µHSH*	-2646.681467	NA
1µHSHNH₂Ph⁺	-2934.062753	-2934.004799
1µHSHNH2Ph	-2934.197124	-2934.170666
PhNH ₂	-287.524176	-287.528423
PhNH ₃ ⁺	-287.952437	-287.87111
OEt ₂	-233.572668	-233.570308
$H(OEt_2)_2^+$	-467.547176	-467.489869
Fc	-510.393960	-510.390633
Fc^+	-510.193857	-510.131014
TS_1	-2646.661710	NA
TS_2	-2646.660069	NA

Table S6. Computed free energies for all species in this work.

Chemical reduction of $1\mu HSH^{\scriptscriptstyle +}$ and $1\mu H$





Figure S1. FTIR spectra of (a) 1μ HSH⁺ alone (black) and the species after the reaction with Cp₂Co (red). (b) 1μ H alone (red) and the species after the reaction with Cp*₂Co (blue). The IR profile of 1^- is shown in a dotted curve. (c) Gas chromatogram of the gaseous content in headspace of the chemical reduction of 1μ HSH⁺ by Cp₂Co, and standard H₂ with different volume. (inset: calibration curve used to calculate the amount of hydrogen generated.) Conditions: column and injector temperature: 120 °C and detector temperature: 220 °C. Gas flow: 30 mL min⁻¹. Carrier gas: nitrogen.

Evaluation of the uni-molecular (heterolytic) and bi-molecular (homolytic) pathways for H₂ evolution by chemical reduction

We designed experiments to examine the validity of the heterolytic pathways (Scheme S2, eqs. S1-S2, S6-S7) and homolytic pathways (Scheme S2, eqs. S3-S5, S8-S10) for the reduction of 1μ H and 1μ HSH⁺ in the presence of limited amount of acid.

1μH was reduced by 1 equiv. of Cp*₂Co in the presence of 3 equiv. of TFA in solution. If the heterolytic pathway occurred, complex 1 would be observed because the generated 1 did not react with acid and no reducing agent was available to convert 1 back to 1⁻. The FTIR spectral results indicated that 1μH and acid were detected in solution after the reaction, and the formation of H₂ gas was confirmed by GC (84 % yield based on the formation of 0.5 equiv. of H₂). The results suggest that the H₂ evolution reaction proceeded via the homolytic pathway. If 1 disproportionated to 1⁻ and 1⁺, only 50% 1⁻ was regenerated. In addition, 1⁺ was unstable and readily decayed. From the FTIR results, 1⁻ was regenerated quantitatively. Therefore, the disproportionation reaction was not observed.

The same conclusion was made for the catalysis involving $1\mu HSH^+$. When $1\mu HSH^+$ was reduced by 1 equiv. of Cp₂Co in the presence of 8 equiv. of HOTf in solution, $1\mu HSH^+$ was detected after the catalysis. Neither $1\mu H^+$ or $1SH^+$ was observed. The yield of H₂ gas was 91 % yield based on the formation of 0.5 equiv. of H₂.

Scheme S2. The uni- and bi-molecular pathways for H₂ evolution involving 1µH and 1µHSH⁺.

For **1**µ**H**^{0/–}:

Heterolytic pathway:

$$\mathbf{1}\mu\mathbf{H} + \mathbf{e}^{-} \underbrace{\qquad} \mathbf{1}\mu\mathbf{H}^{-} \tag{S1}$$

$$\mathbf{1}\mu\mathbf{H}^{-} + \mathbf{H}^{+} \longrightarrow \mathbf{1} + \mathbf{H}_{2}$$
(S2)

Homolytic pathway:

$$1\mu H + e^{-} = 1\mu H^{-}$$
 (S3)

 $1\mu H^{-} + 1\mu H^{-} \longrightarrow 1^{-} + 1^{-} + H_{2}$ (S4)

 $\mathbf{1}^{-} + \mathbf{H}^{+} \longrightarrow \mathbf{1} \boldsymbol{\mu} \mathbf{H}$ (S5)

For **1µHSH**^{+/0}:

Heterolytic pathway:

$$1\mu HSH^+ + e^- \longrightarrow 1\mu HSH$$
 (S6)

$$\mathbf{1}\mu\mathbf{HSH} + \mathbf{H}^{+} \longrightarrow \mathbf{1}\mu\mathbf{H}^{+} \text{ (or } \mathbf{1SH}^{+} \text{)} + \mathbf{H}_{2}$$
 (S7)

Homolytic pathway:

$$1\mu HSH^+ + e^- - 1\mu HSH$$
 (S8)

$$1\mu HSH + 1\mu HSH \longrightarrow 1\mu H + 1\mu H + H_2$$
(S9)

$$\mathbf{1}\mu\mathbf{H} + \mathbf{H}^{+} \longrightarrow \mathbf{1}\mu\mathbf{H}\mathbf{S}\mathbf{H}^{+}$$
(S10)

Cyclic voltammograms and simulation of cyclic voltammograms



Figure S2. (a) Cyclic voltammogram of 1⁻ in THF solution (1 mM, v = 0.1 V s⁻¹, 1 mm vitreous carbon electrode, 295 K). $E_{1/2}^{ox} = -0.62$ V and $E_{1/2}^{red} = -2.37$ V. (b) Linear dependence of the peak currents of the oxidation wave on the square root of scan rates. Background CV is shown as a dashed trace.



Figure S3. Chronocoulometric result of 1⁻. The experimental *D* value is estimated to be 4.74×10^{-6} cm² s⁻¹.



Figure S4. Cyclic voltammograms of 1⁻ at v = 0.1 and 0.2 V s⁻¹ (0.5 mM, 1 mm vitreous carbon electrode, 292 K). Simulated cyclic voltammograms are displayed in circles. Optimized simulation parameters: $\alpha = 0.6$, $k_s = 0.01$ cm s⁻¹, $k_f = 0.07$, $k_b = 0.035$, $D(1^-) = 4.76 \times 10^{-6}$ cm² s⁻¹.

Determination of the diffusion coefficient of [PhNH₃][BArF₂₄]

The diffusion coefficient of $[PhNH_3][BArF_{24}]$ was estimated by ¹H-DOSY NMR spectroscopy. The pulse width was varied until null peaks were observed for anilinium peaks, with the calibrated 90° pulse found to be 11.9 µs. The anilinium protons were allowed to sufficiently relax for accurate measurements. The DOSY data were processed in the VNMRJ software. The *D* value of $[PhNH_3][BArF_{24}]$ was estimated to be 1×10^{-5} cm² s⁻¹. This value was also used for the rest of the acids in the simulations.



Figure S5. ¹H-DOSY NMR spectrum of [PhNH₃][BArF₂₄] in CD₂Cl₂ solution.

Digital simulation for the 1µHSH^{+/0} process via the bi-molecular pathway

The HOTf case:



Figure S6. (a) Catalytic responses of 1^- with 2 mM HOTf in CH₂Cl₂ solution at various scan rates under N₂. Potentials were calibrated with the Fc⁺/Fc redox pair as an internal standard ([1^-] 1 mM, 1 mm vitreous carbon, 295 K). (b) The corresponding *j*_{cat}- $v^{0.5}$ plot. Background CV is shown as a dashed trace.



Figure S7. Experimental (solid line) and simulated (hollow dots) catalytic responses of 1^- with 4 mM HOTf in CH₂Cl₂ solution at various scan rates under N₂. Potentials were calibrated with the Fc⁺/Fc redox pair as an internal standard ([1⁻] 1 mM, 1 mm vitreous carbon, 295 K). (a) v = 0.05, 0.1, 0.4 and 0.9 V s⁻¹. (b) v = 2, 3 and 5 V s⁻¹. Background CVs are shown as dashed traces.

$E^{0}\left(\mathrm{V}\right)$	α	$k_{\rm s}' ({\rm cm \ s^{-1}})$	$k_{\rm PT}' ({ m s}^{-1} { m M}^{-1})$	$k_{\rm rxn}' ({\rm s}^{-1} { m M}^{-1})$	$K_{\rm eq}'({\rm M}^{-1})$
-1.160	0.5	0.029	2.2×10^{5}	1.92×10^{10}	47.86
<i>D</i> (1µH	SH ⁺)	D(1µHSH)	$D(1\mu H)$	$D(\mathrm{H}_2)$	$D(\mathrm{H}^{+})$
2.1 ×	10 ⁻⁵	4.76×10^{-6}	4.76×10^{-6}	1×10^{-5}	1×10^{-5}

 Table S7. Digital simulation parameters for Figure S7.

Digital simulation for the $1\mu H^{0/-}$ process via the bi-molecular pathway

The TFA case:



Figure S8. Experimental (solid line) and simulated (hollow dots) catalytic responses of 1^- with different [TFA] (2, 3, 4 and 5 mM) in CH₂Cl₂ solution under N₂. Potentials were calibrated with the Fc⁺/Fc redox pair as an internal standard ([1^-] 1 mM, v = 0.1 V s⁻¹, 1 mm vitreous carbon, 295 K). Background CV is shown as a dashed trace.

$E^{0}\left(\mathrm{V} ight)$	α	$k_{\rm s}'' ({\rm cm}~{\rm s}^{-1})$	$k_{\rm PT}'' ({ m s}^{-1}~{ m M}^{-1})$	$k_{\rm rxn}$ " (s ⁻¹ M ⁻¹)	$K_{\mathrm{eq}}^{\prime\prime}(\mathrm{M}^{-1})$
-1.566	0.5	0.0162	3495	3.84×10^{6}	5.5×10^{9}
D(1 ⁻)		$D(1\mu H^{-})$	$D(1\mu H)$	$D(H_2)$	$D(\mathrm{H}^{+})$
4.76×10^{-10})-6	4.76×10^{-6}	4.76×10^{-6}	1×10^{-5}	1×10^{-5}

Table S8. Digital simulation parameters for Figure S8.

The TCA case:



Figure S9. Cyclic voltammograms of 1^- in CH₂Cl₂ solution with increments of TCA ([1^-] 1 mM, $v = 0.1 \text{ V s}^{-1}$, 1 mm vitreous carbon electrode). Background CV is shown as a dashed trace.



Figure S10. Experimental (solid line) and simulated (hollow dots) catalytic responses of 1^- with different [TCA] (2.6, 3.4 and 4.2 mM) in CH₂Cl₂ solution under N₂. Potentials were calibrated with the Fc⁺/Fc redox pair as an internal standard ([1^-] 1 mM, v = 0.1 V s⁻¹, 1 mm vitreous carbon, 295 K). Background CV is shown as a dashed trace.

Table S9. Digital simulation parameters for Figure S10.

$E^{0}\left(\mathrm{V}\right)$	α	$k_{\rm s}''({\rm cm~s^{-1}})$	$k_{\rm PT}'' ({ m s}^{-1} { m M}^{-1})$	$k_{\rm rxn}'' ({\rm s}^{-1}~{\rm M}^{-1})$	$K_{\mathrm{eq}}^{\prime\prime}(\mathrm{M}^{-1})$
-1.550	0.5	0.02194	4198	5.55×10^{6}	6.9×10^{11}
D(1 ⁻)		<i>D</i> (1µH⁻)	$D(1\mu H)$	$D(\mathrm{H}_2)$	$D(\mathrm{H}^{+})$
4.76 × 10)-6	4.76×10^{-6}	4.76×10^{-6}	1×10^{-5}	1×10^{-5}



Digital simulation for the 1µH-PhNH₃⁺ system with the PCET pathways

Figure S11. Experimental (solid line) and simulated (hollow dots) catalytic responses of 1⁻ with 2 mM [PhNH₃][BArF₂₄] in CH₂Cl₂ solution at various scan rates under N₂: (a) v = 0.1, 0.2 and 0.4 V s⁻¹. (b) v = 0.625, 0.9 and 1.6 V s⁻¹. (c) Experimental (solid line, v = 0.4 V s⁻¹) and simulated (hollow dots) catalytic responses of 1⁻ with different concentration of [PhNH₃][BArF₂₄] (2, 3, 4 and 5 mM) in CH₂Cl₂ solution under N₂. Potentials were calibrated with the Fc⁺/Fc redox pair as an internal standard. ([1⁻] 1 mM, 1 mm vitreous carbon, 295 K). Background CVs are shown as dashed traces.

Table S10. Digital	simulation parameters	for Figure S11.
U	1	0

$E^0(\mathbf{V})$	α	$k_{\rm PCET} ({\rm cm}~{\rm s}^{-1})$	$k_{\rm rxn}' ({ m s}^{-1}{ m M}^{-1})$
-0.986	0.316	0.63	1.92×10^{10}
D(1µHSH)	$(cm^2 s^{-1})$	$D(1\mu H) (cm^2 s^{-1})$	$D({ m H_2})~({ m cm^2~s^{-1}})$
4.76 ×	10 ⁻⁶	$4.76 imes 10^{-6}$	$1 imes 10^{-5}$
D(I	$PhNH_{3}^{+}) (cm^{2} s^{-1})$		$D(PhNH_2) (cm^2 s^{-1})$
	1×10^{-5}		1×10^{-5}

Reaction order of acid concentration in the catalysis

The current density is proportional to the square root of the acid concentration. The following figures display the linear relationship. The catalysis therefore is assumed to be pseudo first-order reaction on acid.



Figure S12. Plots of j_{cat} vs. [acid]^{0.5}. (a) HOTf, the first reduction wave, the data from Figure 3(a); (b) TFA, the data from Figure 3(b); (c) anilinium acid, the first reduction wave, the data from Figure 2; (d) TCA, the data from Figure S9.

Digital simulation for the 1μ H-PhNH₃⁺ system with the hypothetical stepwise ETPT pathways

In the simulation on the stepwise mechanism (eqs. (9)-(11) in the article), the values of diffusion coefficients and k_{rxn} ' in the PCET pathways listed in Table S10 were used. E^0 is the redox potential of the $1\mu H^{0/-}$ pair, -1.5 V. The proton transfer rate k_{PT} " was initially assumed to be the maximum diffusion rate $k_{Max-diff}$ between $1\mu H^-$ and PhNH₃⁺. The $k_{Max-diff}$ value was estimated by the Debye–Smoluchowski method, as shown in the following equation.^{13,14}

$$k_{\text{Max-diff}} = 4\pi N_A (D_{1\mu\text{H}^-} + D_{\text{PhNH}_3^+})\beta$$

where N_A is Avogadro constant, $D_{1\mu H^-}$ and $D_{PhNH_3^+}$ are diffusion coefficients for the species $1\mu H^$ and PhNH₃⁺, respectively, and β is the effective reaction radius. The $D_{1\mu H^-}$ value was assumed to be equal to the D_{1^-} value (4.76 × 10⁻⁶ cm² s⁻¹) obtained from the electrochemical measurement. $D_{PhNH_3^+}$ was assumed to be 1 × 10⁻⁵ cm² s⁻¹. The effective reaction radius β was calculated from the sum of the radii of $1\mu H^-$ and PhNH₃⁺ by *Gaussion09*, by which a β value of 6.55 Å was estimated. The resulting $k_{Max-diff}$ of 7.8 × 10⁹ s⁻¹ M⁻¹ was therefore obtained, and this value was employed to the electroanalytical simulation.

With the values of *D*, k_{rxn}' , k_{PT}''' and E^0 at hand, we could simulate the voltammograms via adjusting transfer coefficient α and heterogeneous ET rate k_{s}'' . First, k_{s}'' was varied with a fixed value of α at a certain scan rate. As shown in Figures S13a and S13c, the increase of k_{s}'' led to the anodic shift of the simulated peak potential. At fast ET rates, the peak potential approached the limiting value of ~ -1.35 V, which was too negative compared to the observed catalytic potential. The similar procedures were applied by varying α (Figures S13b and S13d). In the simulations, the resulting peak potential displayed insignificant variation upon changing α . In the scenarios via adjusting k_{s}'' or α , the experimental waves were unable to be reproduced in either peak potential or current amplitude. The decreasing magnitude for the anodic shift of the simulated catalytic wave with the increase of the ET rate and no observable potential shift at $k_{\text{s}}'' > 10$ cm s⁻¹ suggested that the catalysis was hindered by the slow PT process (eq. (10) in the article). In other words, this PT step is the rate-determining step in the hypothetical stepwise mechanism.

In the simulations, we have used $k_{\text{Max-diff}}$ to approximate the PT rate k_{PT} ". In fact, the maximum diffusion rate could be faster as both 1μ H⁻ and PhNH₃⁺ are charged species carrying

opposite signs. The corrected maximum diffusion rate $k_{Max-diff}^{Corr}$ was obtained with consideration of the electrostatic interaction between these two charged species.

$$k_{\text{Max-diff}}^{\text{Corr}} = 4\pi N_A (D_{1\mu\text{H}^-} + D_{\text{PhNH}_3^+})\beta$$
$$\beta' = \frac{R_C}{(\exp(R_C/\beta) - 1)} \exp(R_C\kappa)$$
$$R_C = (z_1 z_2 e^2 / 4\pi \varepsilon_r \varepsilon_0 k_B T)$$
$$\kappa = \sqrt{\frac{2000 e^2 N_A}{\varepsilon_r \varepsilon_0 k_B T}}$$

The effective reaction radius was modified to the corrected value β' , and in the equations z_1 and z_2 are the respective charges of the two species 1μ H⁻ and PhNH₃⁺, *e* is the elementary charge, ε_r is the relative permittivity of the solvent (8.81 for CH₂Cl₂), ε_0 is the permittivity of vacuum, k_B is the Boltzmann constant, and *T* is temperature. The electrostatic modified diffusion rate $k_{Max-diff}^{Corr}$ was estimated to be 2.15×10^{15} s⁻¹ M⁻¹. With the employment of $k_{Max-diff}^{Corr}$, the simulated peak potential could approach the experimental data upon varying α or k_s " but a large deviation on the current amplitude was received (Figures S13e-h). A satisfactory fit that fully reproduced the experimental voltammetric results could not be obtained when both α and k_s " were optimized in the simulations. It is concluded that the stepwise ETPT reaction is not an appropriate description for the catalysis in the 1μ H-PhNH₃⁺ system.



Figure S13. Experimental and simulated catalytic responses of 1⁻ with 2 mM [PhNH₃][BArF₂₄] in CH₂Cl₂ solution under N₂ at various scan rates: (a)(b)(e)(f) 0.3 V s⁻¹, (c)(d)(g)(h) 0.4 V s⁻¹. For (a)-(d), $k_{\text{PT}}^{\prime\prime\prime} = k_{\text{Max-diff}} (7.8 \times 10^9 \text{ s}^{-1} \text{ M}^{-1})$. For (e)-(h): $k_{\text{PT}}^{\prime\prime\prime} = k_{\text{Max-diff}}^{\text{Corr}} (2.15 \times 10^{15} \text{ s}^{-1} \text{ M}^{-1})$. The simulations were based on the hypothetical stepwise mechanism and performed by varying one parameter at a time (k_{s} or α). Potentials are calibrated with the Fc⁺/Fc redox pair as an internal standard ([1⁻] 1 mM, 1 mm vitreous carbon, 295 K).

Alternative pathway for the 1µH^{0/-} process in the simulation

The TFA/TCA case:

$$\mathbf{1}\boldsymbol{\mu}\mathbf{H} + \mathbf{e}^{-} \xrightarrow{k_{s}''} \mathbf{1}\boldsymbol{\mu}\mathbf{H}^{-}$$
(S11)

$$\mathbf{1}\boldsymbol{\mu}\mathbf{H}^{-} + \mathbf{H}^{+} \xrightarrow{k_{\mathrm{PT}}''''} \mathbf{1}\boldsymbol{\mu}\mathbf{HSH}$$
(S12)

$$\mathbf{1}\boldsymbol{\mu}\mathbf{HSH} + \mathbf{1}\boldsymbol{\mu}\mathbf{HSH} \xrightarrow{\kappa_{\mathrm{TXN}}} \mathbf{1}\boldsymbol{\mu}\mathbf{H} + \mathbf{1}\boldsymbol{\mu}\mathbf{H} + \mathbf{H}_{2}$$
(S13)

We also evaluated the possibility of an alternative route involving the hydride-acid pathway. In this alternative pathway, upon the formation of 1μ H⁻, it reacts with acid to yield 1μ HSH. The following decay to 1μ H and H₂ completes the catalysis. For the mechanism, the step invloving the intra-molecular H₂ evolution (1μ HSH $\rightarrow 1 + H_2$) was not considered because this intra-molecular process is unfavored according to the calculated results (see the previous section, SI). Here we took the 1μ H^{0/-} process in the presence of TCA for this evaluation. The result from the catalysis involving 1^- (1 mM) and TCA (2.6 mM) in CH₂Cl₂ solution was chosen for the simulation. Experimental details are available in Figure S10.

The parameters α , D (1µH, 1µH⁻, 1µHSH) and k_s " of this case were taken from those values of the bi-molecular reaction because the first ET step is the same in both the bi-molecular and alternative mechanism. For the H₂ evolution reaction, the rate k_{rxn} ' in the HOTf catalysis was used as an initial guess. When k_{rxn} was fixed to $1.92 \times 10^{10} \text{ s}^{-1} \text{ M}^{-1}$, the k_{PT} "" was optimized to $1.60 \times 10^5 \text{ s}^{-1} \text{ M}^{-1}$ in the simulation. The best simulated result displayed a quasi-reversible process with $i_{pa}/i_{pc} = 0.4$, in which the peak amplitude was 1.3 time that of the experimental one (Figure S14a). From the greater peak amplitude and enhanced anodic return wave of 1µH^{0/-}, it is realzed that more catalysis occurred and the resulting 1µH was increased. Because 1µHSH reacts to yield 1µH, the catalysis at the fast k_{rxn} ' rate is limitted by the formation of 1µHSH, i.e. the k_{PT} "" rate. For comparison, the resulting curve exhibited the similar peak amplitude relative to the experimental wave, and the better reversible behavior when k_{PT} "" was manually set to 5.00 × 10³ s⁻¹ M⁻¹ (Figure S14b).

We then fixed k_{PT} "" = 1.60 × 10⁵ s⁻¹ M⁻¹ to perform the next simulation. An optimized k_{rxn} of 4.04 × 10³ s⁻¹ M⁻¹ was obtained. The simulated result displayed a nearly irreversible process ($i_{\text{pa}}/i_{\text{pc}} = 0.3$) with the peak amplitude similar to the experimental data (Figure S14c). The observation of the anodic return wave of the 1µH^{0/-} event indicated that 1µHSH depleted to 1µH at a rate higher than it should be. For the sake of comparison, the k_{rxn} ' rate was manually changed

to 1.00×10^3 s⁻¹ M⁻¹, leading to the diminished anodic return wave and the peak height (Figure S14d). The change of the voltammetric wave from a peaked shape to a plateau suggested that the catalysis was limited by the depletion of **1µHSH**.

In summary, the results suggest that the voltammetric behavior of the alternative route involving the hydride-acid pathway is strongly affected by the reactions concerning the protonation of 1μ H⁻ and the formation of H₂ (eqs. (S12) and (S13)). Because the decay reaction determines the catalytic response and the amount of 1μ H regenerated, the faster the reaction, the larger the anodic return wave, which contradicts the experimental observation. We, therefore, eliminate the possibility of the proposed alternative pathway.



Figure S14. Experimental (soild line) and simulated (hollow dots) catalytic responses of 1^- with 2.6 mM TCA in CH₂Cl₂ solution under N₂ with different k_{rxn}' and k_{PT}''' : (a) $k_{rxn}' = 1.92 \times 10^{10} \text{ s}^{-1}$ M⁻¹, $k_{PT}''' = 1.60 \times 10^5 \text{ s}^{-1} \text{ M}^{-1}$; (b) $k_{rxn}' = 1.92 \times 10^{10} \text{ s}^{-1} \text{ M}^{-1}$, $k_{PT}''' = 5.00 \times 10^3 \text{ s}^{-1} \text{ M}^{-1}$; (c) $k_{rxn}' = 4.04 \times 10^3 \text{ s}^{-1} \text{ M}^{-1}$, $k_{PT}'''' = 1.60 \times 10^5 \text{ s}^{-1} \text{ M}^{-1}$; (d) $k_{rxn}' = 1.00 \times 10^3 \text{ s}^{-1} \text{ M}^{-1}$, $k_{PT}'''' = 1.60 \times 10^5 \text{ s}^{-1} \text{ M}^{-1}$; (e) $k_{rxn}' = 4.00 \times 10^3 \text{ s}^{-1} \text{ M}^{-1}$, $k_{PT}'''' = 5.00 \times 10^3 \text{ s}^{-1} \text{ M}^{-1}$, $k_{PT}'''' = 1.60 \times 10^5 \text{ s}^{-1} \text{ M}^{-1}$; (f) $k_{rxn}' = 1.00 \times 10^3 \text{ s}^{-1} \text{ M}^{-1}$, $k_{PT}'''' = 2.15 \times 10^{15} \text{ s}^{-1} \text{ M}^{-1}$. Potentials were calibrated with the Fc⁺/Fc redox pair as an internal standard.

The deuterium experiments

[H ⁺ or D ⁺], mM	Current density - H^+ , mA cm ⁻²	Current density - D^+ , mA cm ⁻²	
2	0.199	0.229	
3	0.424	0.439	
4	0.639	0.645	
5	0.848	0.849	
6	1.061	1.063	
[1 ⁻]: 1 mM, H ⁺ = anilinium acid, D ⁺ = D8-anilinium acid, $v = 0.1 \text{ V s}^{-1}$, 297 K.			

Table S11. Experimental data of cyclic voltammetry of 1^- in the presence of anilinium acid and D8-anilinium.

The role of the S site: H-bonding interactions in [TBA][1]

The molecular structure of [TBA][1] displayed in Figure S15, reveals three S•••H short contacts in the crystal packing. Two of them measured to be 2.797 and 2.898 Å are the distances from the hydrogen atoms (H38b, H36b) of one $[nBu_4N]^+$ cation to the terminal S2 atom. The third one is from H36a' of the different cation nearby, measured to be 2.934 Å. These distances are shorter than the van der Waals radii sum of 3.0 Å. None of such short contact is found for the bridging thiolate S1 atom. The observation implicates the hydrogen-bonding tendency of the terminal thiolate site while exposed to weak acids which do not readily protonate the Brønsted base.



Figure S15. Molecular structures of $[(\mu,\kappa^2-bdt)(\mu-PPh_2)Fe_2(CO)_5]^-(1^-)$ and two nearby $[nBu_4N]^+$ cations, thermal ellipsoids drawn at the 50% probability level. Some of carbon atoms of the cations and all hydrogen atoms except those involving hydrogen bonds are omitted for clarity.



The role of the S-site for catalysis: H-bonding interaction in the 1µH-PhNH₃⁺ system

Figure S16. (a) IR spectra of 1μ H alone (olive green) and in the presence of 30 equiv. of anilinium acid (blue). The spectra are normalized for clear observation. (b) The computed IR spectra of 1μ H alone (black) and the H-bond pair (red). (c) The DFT-optimized structure of anilinium acid- 1μ H hydrogen-bond pair.

¹H-NMR results



Figure S17. Low field ¹H-NMR spectra of the H-bond pair {PhNH₃⁺•••1 μ H} (top), showing the H-bond proton resonance at 4.54 ppm, and the acid proton resonance of anilinium cations (bottom) at 9.21 ppm. The NMR spectra were recorded in CD₂Cl₂ solution at 193 K.



Figure S18. Full-range ¹H-NMR spectra of the H-bond pair {PhNH₃⁺···1 μ H} at different temperature (left panel). The expanded spectra showing the Fe hydride (inset) and the H-bond proton (right panel) are also displayed. The H-bond proton and Fe hydride resonances were recorded at 4.54 and -14.13 (J = 52 Hz) ppm, respectively, at 193 K. These resonances coalesced at higher temperature. The signals were not observed at temperature higher than 253 K. The NMR spectra were recorded in CD₂Cl₂ solution.

CPE experiments

The potentials for the CPE of 1^- in the presence of anilinium acid (for the PCET reaction) and TFA (for the non-PCET reaction) were -1.1 and -1.6 V vs. Fc⁺/Fc, respectively. H₂ generated in the CPE experiments at both potentials was confirmed by GC. Faradaic yield, H₂ yield and TON were calculated from the experiments at each potential. The results are summarized in Tables S12-S15. The charge-time plots are displayed in Figures S19-S20.

The catalyst remained stable when the CPEs were conducted at 273 K (Figure S21). When the prolonged CPE concerning anilinium acid was performed at 298 K for 12 hrs, the catalytic current revealed a significant decrease after t > 7,000 s (Figure S22). The major solution species at the end of the experiment was **1µH**. Most of the proton source was consumed, possibly responsible for the catalytic current decay over time. The other plausible explanation is the formation of the daughter species, $[(\mu-bdt)Fe_2(CO)_5(PPh_2H)]$ and $[(\mu,\mu,\kappa_2-bdt)_4(\mu-PPh_2)_4Fe_8(CO)_{18}]$ (Figure S23). **1µH** was reported to slowly convert to $[(\mu-bdt)Fe_2(CO)_5(PPh_2H)]$ in solution.¹⁵ It was reported that $[(\mu,\mu,\kappa_2-bdt)_4(\mu-PPh_2)_4Fe_8(CO)_{18}]$ was generated from oxidation of **1**⁻.¹⁶



Figure S19. CPE of 30 equiv. of anilinium acid in CH_2Cl_2 solution at -1.1 V for 1 hr at 298 K with (left plot) and without (right plot) the catalyst. Various runs of the experiments are indicated in different colors.



Figure S20. CPE of 30 equiv. of TFA in CH_2Cl_2 solution at -1.6 V for 1 hr at 298 K with (left plot) and without (right plot) the catalyst. Various runs of the experiments are indicated in different colors.

Table S12. Coulombs passed and Faradaic efficiency from the CPE of 30 equiv. of anilinium acid in CH_2Cl_2 solution at -1.1 V for 1 hr at 298 K.

	Coulombs Passed (C)	Faradaic Efficiency (%)
Run 1	2.31	80.95
Run 2	2.67	99.69
Run 3	2.21	98.96
Average	2.39 ± 0.19	93.2 ± 8.66

Table S13. Coulombs passed and Faradaic efficiency from the CPE of 30 equiv. of anilinium acid in CH_2Cl_2 solution at -1.1 V for 1 hr at 298 K in the presence of 1mM 1⁻.

	Coulombs	Corrected Coulombs	TON	Faradaic Efficiency (%)
	Passed (C)	Passed (C)		
Run 1	9.39	7	1.51	95.15
Run 2	8.66	6.27	1.35	98.95
Run 3	8.79	6.4	1.38	96.88
Average	8.94 ± 0.31	6.55 ± 0.31	1.41 ± 0.07	96.99 ± 1.55

Table S14. Coulombs passed and Faradaic efficiency from the CPE of 30 equiv. of TFA in CH_2Cl_2 solution at -1.6 V for 1 hr at 298 K.

	Coulombs Passed (C)	Faradaic Efficiency (%)
Run 1	2.65	76.99
Run 2	2.57	80.49
Run 3	2.43	99.96
Average	2.55 ± 0.09	85.81 ± 10.10

Table S15. Coulombs passed and Faradaic efficiency from the CPE of 30 equiv. of TFA in CH_2Cl_2 solution at -1.6 V for 1 hr at 298 K in the presence of 1mM 1⁻.

	Coulombs	Corrected Coulombs	TON	Faradaic Efficiency (%)
	Passed (C)	Passed (C)		
Run 1	10.82	8.27	1.79	99.35
Run 2	10.42	7.87	1.69	97.93
Run 3	10.44	7.89	1.70	91.50
Average	10.56 ± 0.18	8.01 ± 0.18	1.72 ± 0.04	96.26 ± 3.41



Figure S21. IR profile changes of the CPE experiments in CH₂Cl₂ solution at 273 K. (a) 1^- with 30 equiv. of TFA before (black) and 2 hrs after the electrolysis (red). The potential was set at -1.6 V vs. Fc⁺/Fc. (b) 1^- with 10 equiv. of [PhNH₃][BArF₂₄] before (black) and 3 hrs after the electrolysis (red). The potential was set at -1.1 V vs. Fc⁺/Fc.



Figure S22. A current-time plot for the CPE of 1^- (1 mM) in the presence of 30 equiv. of [PhNH₃][BArF₂₄] in CH₂Cl₂ solution at 298 K (E = -1.1 V vs. Fc⁺/Fc).



Figure S23. IR profile changes of the prolonged CPE experiment in CH₂Cl₂ solution. 1⁻ with 30 equiv. of [PhNH₃][BArF₂₄] before (blue) and 12 hrs after the electrolysis (red). The potential was set at -1.1 V vs. Fc⁺/Fc. The major species in solution was **1µH** after the catalysis. The daughter species generated from the prolonged CPE are indicated as asterisks: [(µ-bdt)Fe₂(CO)₅(PPh₂H)] (black) and [(µ,µ,κ₂-bdt)₄(µ-PPh₂)₄Fe₈(CO)₁₈] (pink).

Gas chromatography analysis

The gaseous content in headspace of the electrolysis cell was analyzed by gas chromatography to be molecular hydrogen. Faraday efficiency of at least 96 % was estimated from 3 different experiments at each potential.



(b) Response_





Figure S24. Gas chromatograms of the CPE (a) at -1.1 V of 30 equiv. of anilinium acid, (c) at -1.6 V of 30 equiv. of TFA, with 1 mM 1⁻ in CH₂Cl₂ solution for 1 hr. Gas chromatograms of the corresponding background CPE (without 1⁻) are shown in (b) and (d). Standard gas H₂ (99.999 %) with different volumes were measured in each gas chromatogram for calibration of the amount of hydrogen generated from the CPE experiments. Insets: calibration curves from standard gas H₂.

List of symbols in electrochemical study

 α – transfer coefficient.

v – scan rate.

- E_{cat} potential of catalytic event.
- E^0 standard redox potential.
- K_{eq}' equilibrium constant for protonation of $1\mu H^{-}$ by HOTf.
- K_{eq} " equilibrium constant for protonation of 1⁻ by TFA or TCA.
- k_{rxn}' reaction rate of the conversion from 1µHSH to 1µH.
- $k_{\rm rxn}$ " reaction rate of the conversion from 1μ H⁻ to 1⁻.
- $k_{\rm PT}'$ proton transfer rate of the conversion from 1µH to 1µHSH⁺.
- k_{PT} " proton transfer rate of the conversion from 1[–] to 1µH.
- $k_{\rm PT}$ " proton transfer rate of the conversion from $1\mu H^-$ to $1\mu HSH$ in the $1\mu H$ -PhNH₃⁺ system.
- $k_{\rm PT}$ "" proton transfer rate of the conversion from $1\mu H^-$ to $1\mu HSH$ in the $1\mu H$ -TFA/TCA system.
- $k_{\rm s}'$ electron transfer rate in the 1µHSH^{+/0} process.
- $k_{\rm s}''$ electron transfer rate in the $1\mu {\rm H}^{0/-}$ process.
- k_{PCET} apparent heterogeneous rate constant of the PCET event in the 1µH-PhNH₃⁺ system.
- D diffusion coefficient.

DFT results

 Table S16. Cartesian coordinates of solvent corrected DFT geometry-optimized species.

Species 1⁻

Symbol	Х	Y	Z
Fe	-0.47194	-0.648059	-1.083595
Fe	-0.304439	-0.322833	1.499993
S	-1.447874	1.136388	-0.035243
S	-2.620453	-1.572588	-1.405152
Р	1.319638	0.155122	-0.014579
С	0.212355	-2.266182	-1.30238
С	-0.297738	-0.070936	-2.723232
С	-1.865038	-0.996258	2.024833
С	0.074373	0.743474	2.857659
С	0.511511	-1.832946	1.865416
С	-3.203931	0.817358	-0.11396
С	-4.087373	1.775643	0.408577
Н	-3.682614	2.676264	0.862551
С	-5.464251	1.578212	0.350238
Н	-6.139675	2.324083	0.758609
С	-5.965461	0.411209	-0.242724
Н	-7.038064	0.244508	-0.295937
С	-5.097155	-0.538338	-0.769993
Н	-5.49333	-1.43937	-1.230111
С	-3.697673	-0.357346	-0.721046
С	2.941729	-0.72314	-0.040664
С	3.45439	-1.232375	-1.244344
Н	2.877787	-1.130574	-2.158984
С	4.69675	-1.869446	-1.27579
Н	5.078229	-2.260336	-2.214894
С	5.444028	-2.005843	-0.10375
Н	6.40913	-2.503751	-0.127206
С	4.944526	-1.501853	1.099611
Н	5.519547	-1.607098	2.015321
С	3.702235	-0.865268	1.131227
Н	3.319966	-0.479151	2.071725
С	1.855315	1.912149	-0.261175
С	2.192352	2.724849	0.833048
Н	2.101522	2.337654	1.842642
С	2.635006	4.035244	0.638998
Н	2.887226	4.650791	1.498059
С	2.74706	4.554432	-0.652695
Н	3.087359	5.574949	-0.803487
С	2.414801	3.75591	-1.74927

Н	2.494385	4.152946	-2.757482
С	1.972523	2.445534	-1.555019
Н	1.709115	1.839114	-2.415363
0	0.625244	-3.337537	-1.452937
0	-0.179225	0.304205	-3.814532
0	-2.870988	-1.437784	2.38715
0	0.339346	1.365705	3.802525
0	1.039609	-2.825713	2.161769

Species 1

Symbol	Х	Y	Ζ
Fe	-0.470988	-0.522715	-1.225872
Fe	-0.37174	-0.405286	1.488258
S	-1.510597	1.112969	-0.006247
S	-2.463628	-1.479049	-1.588364
Р	1.313345	0.150364	0.050825
С	0.278148	-2.056659	-1.775774
С	-0.050104	0.434884	-2.645195
С	-1.956799	-1.020659	2.108895
С	0.103393	0.568626	2.940109
С	0.456075	-1.952047	1.880461
С	-3.243836	0.736032	-0.135905
С	-4.193458	1.589551	0.445435
Н	-3.86292	2.467478	0.992315
С	-5.550532	1.305872	0.320489
Н	-6.283687	1.965735	0.773668
С	-5.966039	0.172138	-0.391762
Н	-7.024539	-0.047746	-0.493076
С	-5.029703	-0.67356	-0.976682
Н	-5.35194	-1.54857	-1.532818
С	-3.653407	-0.401097	-0.85751
С	2.896465	-0.78247	0.029418
С	3.427401	-1.294409	-1.164994
Н	2.892367	-1.162307	-2.099807
С	4.651546	-1.96706	-1.164762
Н	5.049737	-2.357865	-2.096311
С	5.357644	-2.136038	0.02735
Н	6.307301	-2.662534	0.027542
С	4.840576	-1.624789	1.220375
Н	5.386655	-1.751145	2.150451
С	3.619213	-0.95043	1.223013
Н	3.229654	-0.552744	2.155578
С	1.869737	1.901648	-0.104911
С	1.299926	2.931589	0.660316

Н	0.528699	2.708638	1.387181
С	1.71913	4.253889	0.497352
Н	1.268333	5.035902	1.101193
С	2.714898	4.567238	-0.428269
Н	3.042007	5.595249	-0.552085
С	3.294084	3.549303	-1.19057
Н	4.073448	3.781975	-1.910249
С	2.877664	2.22823	-1.030823
Н	3.347675	1.450454	-1.624191
0	0.710026	-3.060342	-2.134321
0	0.185619	1.065231	-3.57937
0	-2.953561	-1.404872	2.529649
0	0.425135	1.165059	3.870075
0	0.960709	-2.948999	2.155672

Species 1µH

Symbol	Х	Y	Z
Fe	-0.497381	-0.844074	-1.019566
Fe	-0.290268	-0.093975	1.50322
S	-1.480142	1.075804	-0.204982
S	-2.625533	-1.807083	-1.254322
Р	1.35092	0.102842	-0.132695
С	0.22072	-2.461229	-1.287367
С	-0.451803	-0.366204	-2.723997
С	-1.833751	-0.427729	2.39581
С	0.182252	1.419103	2.360166
С	0.649453	-1.255719	2.482727
С	-3.218709	0.681009	-0.143535
С	-4.107518	1.661659	0.328457
Н	-3.715191	2.616459	0.666832
С	-5.474559	1.41049	0.365933
Н	-6.157211	2.169286	0.735063
С	-5.958801	0.171691	-0.077468
Н	-7.024812	-0.035466	-0.052515
С	-5.085622	-0.797378	-0.556835
Н	-5.470135	-1.751734	-0.904302
С	-3.694718	-0.563275	-0.605717
С	2.930547	-0.824973	0.009702
С	3.448361	-1.451369	-1.136788
Н	2.901634	-1.403813	-2.073725
С	4.665747	-2.131219	-1.083407
Н	5.051964	-2.612524	-1.976861
С	5.381989	-2.193345	0.114109
Н	6.327465	-2.725604	0.156038

С	4.879881	-1.568223	1.25696
Н	5.433287	-1.609823	2.190289
С	3.661987	-0.886925	1.206813
Н	3.290358	-0.401149	2.103021
С	1.899474	1.809875	-0.55295
С	2.910771	2.432184	0.202044
Н	3.381934	1.904696	1.025401
С	3.325833	3.728002	-0.100749
Н	4.10689	4.193635	0.492946
С	2.740927	4.424101	-1.162561
Н	3.066333	5.433039	-1.397658
С	1.742683	3.814118	-1.922335
Н	1.288575	4.343123	-2.754889
С	1.324754	2.515375	-1.622143
Н	0.553776	2.05467	-2.226694
0	0.64014	-3.518975	-1.445487
0	-0.449511	-0.062093	-3.833345
0	-2.798414	-0.652125	2.969647
0	0.493711	2.382744	2.89866
0	1.200724	-2.034617	3.120558
Н	-0.661613	-1.387268	0.61987

Species 1µH⁻

Symbol	Х	Y	Z
Fe	-0.501913	-0.735287	-1.010462
Fe	-0.119542	-0.331084	1.683528
S	-1.61325	1.242739	-0.359676
S	-2.635159	-1.704167	-1.401715
Р	1.355745	0.122273	-0.026497
С	0.212288	-2.309933	-1.414061
С	-0.414885	-0.098051	-2.660243
С	-1.7314	-0.623213	2.416497
С	0.267945	1.126381	2.638566
С	0.796994	-1.591814	2.630425
С	-3.325497	0.766322	-0.299288
С	-4.268454	1.689765	0.186788
Н	-3.92284	2.661626	0.529861
С	-5.626344	1.378891	0.232779
Н	-6.33627	2.107167	0.614929
С	-6.06212	0.126098	-0.211898
Н	-7.117137	-0.132585	-0.179927
С	-5.137972	-0.797953	-0.69581
Н	-5.47633	-1.771719	-1.040164
С	-3.763203	-0.499663	-0.749158

С	2.952842	-0.789616	-0.202637
С	3.047295	-2.127967	0.220015
Н	2.191046	-2.614259	0.672404
С	4.231242	-2.849146	0.066109
Н	4.278202	-3.880105	0.405494
С	5.350359	-2.249956	-0.517203
Н	6.273352	-2.81031	-0.634574
С	5.269969	-0.924947	-0.94899
Н	6.131051	-0.447832	-1.408867
С	4.085267	-0.201848	-0.794517
Н	4.046065	0.826441	-1.13605
С	1.872591	1.875106	-0.283385
С	2.662374	2.51491	0.689786
Н	2.961694	1.973927	1.582554
С	3.072092	3.837337	0.521567
Н	3.680241	4.313916	1.285222
С	2.697292	4.547805	-0.622531
Н	3.012676	5.57915	-0.751977
С	1.917114	3.924662	-1.596811
Н	1.623147	4.467233	-2.49079
С	1.510549	2.597416	-1.430305
Н	0.908706	2.127031	-2.198418
0	0.613553	-3.35352	-1.699293
0	-0.394506	0.31235	-3.739558
0	-2.760031	-0.842426	2.891992
0	0.518084	2.051257	3.288396
0	1.340126	-2.375781	3.286464
Н	-0.693225	-1.383809	0.552119

Species 1µHSH⁺

Symbol	Х	Y	Z
Fe	-0.465727	-0.813947	-1.052474
Fe	-0.332252	-0.135199	1.472838
S	-1.469782	1.096058	-0.206134
S	-2.622338	-1.759287	-1.325108
Р	1.356903	0.1207	-0.097756
С	0.31717	-2.414424	-1.351289
С	-0.269998	-0.237799	-2.736458
С	-1.886498	-0.492931	2.365581
С	0.143517	1.331156	2.415131
С	0.584928	-1.334025	2.453155
С	-3.215834	0.696286	-0.146708
С	-4.099488	1.648255	0.381673
Н	-3.710167	2.586903	0.762552

С	-5.468699	1.388534	0.417269
Н	-6.14295	2.131668	0.830256
С	-5.970691	0.179936	-0.070842
Н	-7.035755	-0.023825	-0.039657
С	-5.101294	-0.774709	-0.598594
Н	-5.483727	-1.718347	-0.973586
С	-3.73045	-0.507508	-0.647017
С	2.920711	-0.82603	0.035926
С	3.475226	-1.383604	-1.129245
Н	2.966698	-1.276828	-2.082546
С	4.687435	-2.071241	-1.072505
Н	5.103377	-2.500687	-1.978599
С	5.361495	-2.205396	0.143527
Н	6.303711	-2.742842	0.186393
С	4.824414	-1.643321	1.302758
Н	5.347579	-1.737238	2.249266
С	3.610334	-0.955638	1.252314
Н	3.216916	-0.513327	2.161166
С	1.906321	1.828494	-0.494185
С	2.981453	2.381524	0.227153
Н	3.491808	1.797679	0.986042
С	3.410148	3.682134	-0.031006
Н	4.239839	4.094335	0.534919
С	2.779367	4.449066	-1.014391
Н	3.117788	5.460613	-1.216432
С	1.719503	3.906585	-1.741207
Н	1.23104	4.490367	-2.515221
С	1.284011	2.604887	-1.485377
Н	0.465258	2.203282	-2.067477
0	0.773047	-3.449589	-1.524475
0	-0.146633	0.12423	-3.816881
0	-2.842535	-0.722693	2.946581
0	0.449356	2.267441	2.995959
0	1.109767	-2.133391	3.080961
Н	-0.684218	-1.41278	0.522498
Н	-2.881845	-1.549382	-2.633957

Species 1µHSH

Symbol	Х	Y	Z
Fe	-0.501933	-0.70237	-1.067724
Fe	-0.222015	-0.279244	1.628465
S	-1.627175	1.318412	-0.517026
S	-2.635161	-1.628504	-1.493637
Р	1.313572	0.13449	-0.004672

С	0.274435	-2.301107	-1.294829
С	-0.169809	-0.103508	-2.718197
С	-1.83055	-0.461941	2.425614
С	0.331267	1.082112	2.651407
С	0.570157	-1.719467	2.461335
С	-3.310119	0.801576	-0.329689
С	-4.246646	1.688771	0.237709
Н	-3.914207	2.671852	0.556649
С	-5.57864	1.317788	0.398252
Н	-6.276786	2.020825	0.843158
С	-6.019459	0.049357	0.004817
Н	-7.055727	-0.24242	0.140379
С	-5.111258	-0.844226	-0.559241
Н	-5.431931	-1.834453	-0.867775
С	-3.776824	-0.461859	-0.73108
С	2.88811	-0.818699	-0.110342
С	3.435844	-1.127206	-1.367793
Н	2.918355	-0.825995	-2.274254
С	4.642471	-1.820226	-1.464935
Н	5.050849	-2.055161	-2.443514
С	5.322001	-2.211432	-0.30794
Н	6.260547	-2.752299	-0.384485
С	4.790996	-1.903924	0.945414
Н	5.315185	-2.201701	1.848755
С	3.580772	-1.212366	1.044806
Н	3.181861	-0.97409	2.025083
С	1.909943	1.856828	-0.298491
С	2.935193	2.360277	0.523693
Н	3.370093	1.734284	1.297092
С	3.410169	3.659819	0.353861
Н	4.200854	4.031002	0.99936
С	2.872433	4.480034	-0.642031
Н	3.243553	5.491926	-0.774877
С	1.859728	3.989684	-1.466413
Н	1.438772	4.61653	-2.247093
С	1.38171	2.687243	-1.297764
Н	0.595156	2.327134	-1.949052
0	0.731628	-3.347164	-1.423883
0	0.035652	0.278203	-3.784419
0	-2.846875	-0.597375	2.949988
0	0.711332	1.941408	3.322003
0	1.015328	-2.638081	2.996782
Н	-0.877315	-1.268669	0.446017
Н	-2.850856	-1.29376	-2.786748

Species 1µHSH*

Symbol	Х	Y	Z
Fe	-0.517867	-0.701309	-1.02521
Fe	-0.155341	-0.322845	1.663784
S	-1.649713	1.282994	-0.381842
S	-2.6523	-1.625512	-1.476825
Р	1.321742	0.144983	-0.009413
С	0.281567	-2.274126	-1.327691
С	-0.263733	-0.052999	-2.677513
С	-1.753055	-0.539383	2.472183
С	0.396925	1.032043	2.695226
С	0.679469	-1.756268	2.46089
С	-3.347024	0.781953	-0.286397
С	-4.296705	1.682804	0.238066
Н	-3.960475	2.651956	0.593587
С	-5.644364	1.344636	0.307575
Н	-6.35215	2.057348	0.720517
С	-6.091107	0.100249	-0.151315
Н	-7.142656	-0.162704	-0.101005
С	-5.172825	-0.80139	-0.684045
Н	-5.504622	-1.765041	-1.058575
С	-3.815997	-0.464101	-0.733125
С	2.901355	-0.787939	-0.192424
С	3.412528	-1.05091	-1.47541
Н	2.86453	-0.725046	-2.3551
С	4.619911	-1.731491	-1.631827
Н	4.999659	-1.931478	-2.629507
С	5.336869	-2.155421	-0.50935
Н	6.276004	-2.686723	-0.631924
С	4.842508	-1.892715	0.768896
Н	5.395965	-2.215761	1.645735
С	3.631544	-1.213589	0.927652
Н	3.261313	-1.010436	1.926794
С	1.889311	1.879444	-0.289211
С	2.947029	2.372606	0.497455
Н	3.422808	1.732016	1.233995
С	3.402024	3.680647	0.338753
Н	4.218497	4.043636	0.956212
С	2.811283	4.519877	-0.610186
Н	3.166943	5.53839	-0.734536
С	1.765433	4.040165	-1.398655
Н	1.302935	4.682117	-2.142705
С	1.30724	2.729193	-1.241291
Н	0.492779	2.377861	-1.862213

0	0.756853	-3.3058	-1.503156
0	-0.096017	0.364926	-3.736061
0	-2.770813	-0.69684	2.988256
0	0.779218	1.886507	3.370885
0	1.148573	-2.674406	2.97734
Н	-0.797009	-1.312928	0.48769
Н	-2.718663	-2.594462	-0.539692

Species 1µHSHNH₂Ph⁺

Symbol	Х	Y	Z
Fe	-0.102432	-0.722342	-0.026774
Fe	-1.372268	1.238277	-1.240082
S	0.045873	1.474064	0.657814
S	2.126244	-0.600921	-0.791836
Р	-2.31186	-0.311688	0.214107
С	-0.299304	-2.273145	-0.904698
С	0.329807	-1.468273	1.520687
С	-0.228128	2.204991	-2.270513
С	-2.458817	2.591282	-0.742214
С	-2.3186	0.669109	-2.649437
С	1.683261	1.985268	0.15558
С	2.075491	3.306209	0.4275
Н	1.372724	3.983765	0.903985
С	3.352008	3.742574	0.087546
Н	3.648918	4.765303	0.296971
С	4.245465	2.854586	-0.524023
Н	5.243588	3.186259	-0.794022
С	3.865074	1.542291	-0.78858
Н	4.564643	0.859581	-1.261737
С	2.578923	1.083083	-0.448216
С	-3.554828	-1.531799	-0.364933
С	-3.446858	-2.859873	0.082226
Н	-2.621715	-3.150044	0.725956
С	-4.397958	-3.810496	-0.289333
Н	-4.30147	-4.833128	0.062504
С	-5.468445	-3.447184	-1.110241
Н	-6.207228	-4.187447	-1.400378
С	-5.587142	-2.129537	-1.554932
Н	-6.418239	-1.84008	-2.190261
С	-4.63731	-1.174497	-1.184807
Н	-4.752355	-0.153262	-1.532271
С	-3.045945	0.345602	1.768016
С	-4.390924	0.759535	1.778513
Н	-4.998524	0.668685	0.884059

С	-4.961997	1.282828	2.937198
Н	-6.000772	1.598943	2.927281
С	-4.202735	1.399044	4.104834
Н	-4.649536	1.806185	5.006754
С	-2.871362	0.982345	4.108242
Н	-2.277008	1.058784	5.013712
С	-2.295156	0.45707	2.949252
Н	-1.262839	0.131773	2.973695
0	-0.384632	-3.252191	-1.497733
0	0.637024	-1.947526	2.520633
0	0.482217	2.80629	-2.935293
0	-3.152179	3.443325	-0.417534
0	-2.873595	0.308762	-3.585583
Н	-0.419475	-0.019926	-1.569372
С	6.203425	-2.102691	-0.533193
С	7.49206	-1.635472	-0.795161
С	8.168491	-0.865949	0.154988
С	7.558904	-0.55916	1.372939
С	6.269845	-1.018929	1.649711
С	5.617043	-1.785194	0.689535
Н	5.672279	-2.702632	-1.265729
Н	7.964574	-1.876654	-1.741608
Н	9.171202	-0.507579	-0.05369
Н	8.08273	0.036271	2.113185
Н	5.791725	-0.782981	2.59572
Ν	4.242884	-2.253694	0.95554
Н	3.516148	-1.697681	0.402835
Н	4.126743	-3.239682	0.702624
Н	4 003535	-2 168863	1 947189

Species 1µHSHNH₂Ph

Symbol	Х	Y	Z
Fe	-0.093488	-0.341102	-0.789355
Fe	-1.602262	1.871239	-0.154978
S	0.773221	0.580182	1.213086
S	1.952009	0.301957	-1.836067
Р	-2.137117	-0.322878	0.175906
С	-0.725564	-0.800665	-2.390524
С	0.489575	-1.939235	-0.333077
С	-0.553505	3.325913	-0.326034
С	-2.483216	2.426804	1.295109
С	-2.78116	2.290412	-1.497285
С	2.147716	1.558129	0.647981
С	2.768269	2.44342	1.54886

Н	2.379626	2.522536	2.560491
С	3.860552	3.216768	1.160368
Н	4.319088	3.897968	1.871528
С	4.351985	3.120128	-0.145221
Н	5.19671	3.724959	-0.462087
С	3.748191	2.245437	-1.047521
Н	4.124842	2.168904	-2.06382
С	2.652157	1.455528	-0.664921
С	-3.539595	-1.105688	-0.733072
С	-3.434539	-2.438135	-1.167819
Н	-2.518098	-2.99355	-0.988133
С	-4.495484	-3.056287	-1.830316
Н	-4.396876	-4.085829	-2.162459
С	-5.679587	-2.352658	-2.067089
Н	-6.504759	-2.833031	-2.584618
С	-5.797192	-1.030286	-1.636411
Н	-6.714825	-0.477446	-1.815732
С	-4.734234	-0.409929	-0.974431
Н	-4.838468	0.617783	-0.641998
С	-2.423686	-0.956791	1.888127
С	-3.676322	-0.751034	2.495404
Н	-4.466353	-0.240483	1.952774
С	-3.923617	-1.20172	3.791515
Н	-4.897077	-1.031931	4.242657
С	-2.924105	-1.867179	4.507112
Н	-3.116787	-2.217923	5.516778
С	-1.67942	-2.080526	3.914467
Н	-0.897012	-2.600938	4.459564
С	-1.43099	-1.630957	2.614625
Н	-0.458457	-1.806417	2.171414
0	-1.094981	-1.063371	-3.449297
0	0.931536	-2.973167	-0.048564
0	0.099086	4.266755	-0.460131
0	-3.081007	2.786391	2.217426
0	-3.482306	2.577865	-2.368382
Н	-0.541115	1.206408	-1.244803
С	6.204215	-2.548167	-0.854762
С	7.357633	-2.269126	-0.118446
С	7.291542	-1.436872	1.000384
С	6.071328	-0.877337	1.388027
С	4.910313	-1.145454	0.66184
С	5.000666	-1.980152	-0.449424
Н	6.24886	-3.19675	-1.724582
Н	8.303815	-2.703837	-0.423526
Н	8.190718	-1.221944	1.56893

Н	6.018247	-0.224906	2.25326
Н	3.961335	-0.703857	0.949455
Ν	3.772651	-2.264978	-1.214718
Н	3.214752	-1.375084	-1.441714
Н	3.982788	-2.726251	-2.10353
Н	3.132862	-2.879948	-0.698254

Species PhNH₂

Symbol	Х	Y	Z
С	0.24729	1.190681	0.000002
С	-1.147859	1.226103	0.000035
С	-1.880312	0.035883	0.000023
С	-1.208356	-1.187647	0.000003
С	0.18847	-1.220951	-0.00006
С	0.929264	-0.034804	-0.000063
Н	0.816774	2.11677	0.000022
Н	-1.66305	2.18255	0.000063
Н	-2.96599	0.063363	0.000043
Н	-1.76995	-2.117496	-0.000009
Н	0.723709	-2.165338	-0.000128
Ν	2.371866	-0.125737	-0.000106
Н	2.742255	0.373406	-0.807743
Н	2.742208	0.371308	0.808849

Species PhNH₃⁺

Symbol	Х	Y	Z
С	0.168088	-1.222449	-0.000003
С	-1.226648	-1.210953	0.000016
С	-1.92142	0.001327	-0.000002
С	-1.226997	1.211614	-0.000028
С	0.169295	1.219041	0.000051
С	0.833467	-0.000949	0.000008
Н	0.716285	-2.159448	-0.000035
Н	-1.767263	-2.151088	-0.000001
Н	-3.006276	0.001275	-0.000024
Н	-1.765118	2.153117	-0.000079
Н	0.718415	2.155853	0.000057
Ν	2.31888	0.00007	-0.000001
Н	2.704687	-0.470442	0.826417
Н	2.704688	-0.47114	-0.82604
Н	2.687714	0.955601	-0.000529

Species	OEt ₂
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Symbol	Х	Y	Z
0	-0.000002	-0.265399	-0.000369
С	-1.18442	0.519243	-0.000349
Н	-1.204525	1.175611	-0.886296
Н	-1.203977	1.175939	0.885348
С	-2.38536	-0.411314	0.000289
Н	-3.314466	0.166544	0.000465
Н	-2.377883	-1.052108	-0.886498
Н	-2.377402	-1.051963	0.887181
С	1.184416	0.519241	0.000387
Н	1.204121	1.17532	0.886552
Н	1.204372	1.176222	-0.88509
С	2.385365	-0.411312	-0.000056
Н	2.377708	-1.051749	-0.887108
Н	3.314467	0.166554	0.0002
Н	2.377592	-1.052321	0.88657

Species H(OEt₂)₂⁺

Symbol	Х	Y	Z
0	-1.403405	0.176182	0.032017
С	-2.219043	-0.785282	0.798761
Н	-3.254843	-0.51474	0.587297
Н	-2.015982	-0.627378	1.861842
С	-1.908658	-2.195074	0.346396
Н	-2.576772	-2.879621	0.876303
Н	-2.081321	-2.310725	-0.726366
Н	-0.882225	-2.487843	0.581334
С	-1.745649	1.593627	0.272446
Н	-1.553115	1.806481	1.327971
Н	-2.817186	1.667832	0.079712
С	-0.94294	2.475907	-0.658142
Н	-1.156677	2.242306	-1.703832
Н	-1.227341	3.515536	-0.473357
Н	0.130535	2.380434	-0.480263
0	1.002732	-0.151816	0.022217
С	1.688834	-0.286823	1.306841
Н	1.932561	-1.343894	1.452685
Н	0.951923	0.003455	2.058437
С	1.559771	-0.946901	-1.070745
Н	1.347123	-2.00247	-0.869885
Н	2.641588	-0.80012	-1.055988
С	0.966567	-0.485577	-2.386605
Н	-0.119059	-0.611531	-2.409352

Н	1.20633	0.563296	-2.578276
Н	1.391677	-1.088105	-3.194104
С	2.916355	0.602476	1.379677
Н	2.646307	1.650914	1.229713
Н	3.368546	0.500893	2.370901
Н	3.67168	0.323315	0.640633
Н	-0.289791	-0.017074	0.058953

Species Fc

Symbol	Х	Y	Z
Fe	0	0	0
С	-0.000898	-0.008984	2.082754
С	1.341113	-0.003377	1.593769
С	1.525332	-1.17416	0.79673
С	0.297044	-1.903085	0.792658
С	-0.6464	-1.182808	1.587213
Н	-0.458019	0.757794	2.693565
Н	2.078171	0.768612	1.769066
Н	2.426418	-1.444109	0.262725
Н	0.105387	-2.821889	0.255049
Н	-1.677833	-1.460762	1.757035
С	0.000898	0.008984	-2.082754
С	-1.341113	0.003377	-1.593769
С	-1.525332	1.17416	-0.79673
С	-0.297044	1.903085	-0.792658
С	0.6464	1.182808	-1.587213
Н	0.458019	-0.757794	-2.693565
Н	-2.078171	-0.768612	-1.769066
Н	-2.426418	1.444109	-0.262725
Н	-0.105387	2.821889	-0.255049
Н	1.677833	1.460762	-1.757035
H H H	-2.426418 -0.105387 1.677833	1.444109 2.821889 1.460762	-0.26272 -0.25504 -1.75703

Species Fc⁺

Symbol	Х	Y	Z
Fe	0	0	0
С	0.003556	-0.016175	2.096606
С	1.34702	-0.010849	1.607531
С	1.531393	-1.18262	0.809406
С	0.301918	-1.912314	0.805312
С	-0.642421	-1.191382	1.600757
Н	-0.457996	0.758264	2.693181
Н	2.07843	0.768696	1.769035
Н	2.426442	-1.443553	0.262099

Н	0.105119	-2.821377	0.254313
Н	-1.677944	-1.460196	1.756065
С	-0.003556	0.016175	-2.096606
С	-1.34702	0.010849	-1.607531
С	-1.531393	1.18262	-0.809406
С	-0.301918	1.912314	-0.805312
С	0.642421	1.191382	-1.600757
Н	0.457996	-0.758264	-2.693181
Н	-2.07843	-0.768696	-1.769035
Н	-2.426442	1.443553	-0.262099
Н	-0.105119	2.821377	-0.254313
Н	1.677944	1.460196	-1.756065

TS_1

Symbol	Х	Y	Z
Fe	-0.451102	-0.723652	-1.031379
Fe	-0.141677	-0.376269	1.661232
S	-1.686332	1.223191	-0.366561
S	-2.666051	-1.566926	-1.425628
Р	1.341333	0.15278	0.016998
С	0.385417	-2.276237	-1.361427
С	-0.208163	-0.030716	-2.672675
С	-1.752946	-0.655806	2.424752
С	0.330138	0.99681	2.711671
С	0.719697	-1.779872	2.48145
С	-3.40391	0.75101	-0.279085
С	-4.331662	1.657671	0.264278
Н	-3.97413	2.609591	0.645187
С	-5.690592	1.352588	0.312113
Н	-6.385555	2.071182	0.73582
С	-6.157247	0.129589	-0.178271
Н	-7.214453	-0.112968	-0.140095
С	-5.257385	-0.790627	-0.715746
Н	-5.609757	-1.746028	-1.092367
С	-3.898139	-0.473541	-0.763169
С	2.934588	-0.74746	-0.198332
С	3.467412	-0.922022	-1.487855
Н	2.929743	-0.544329	-2.352977
С	4.6834	-1.580037	-1.668997
Н	5.079848	-1.712107	-2.671419
С	5.388295	-2.067566	-0.564583
Н	6.334688	-2.580858	-0.706301
С	4.873507	-1.890274	0.720124
Н	5.418626	-2.261261	1.583029

С	3.65313	-1.234395	0.903782
Н	3.268745	-1.09526	1.908178
С	1.872786	1.899169	-0.251617
С	2.956009	2.383911	0.505501
Н	3.47118	1.728314	1.201309
С	3.384988	3.703127	0.369024
Н	4.221416	4.059579	0.96308
С	2.743332	4.561331	-0.528382
Н	3.079168	5.58841	-0.636029
С	1.671989	4.089829	-1.287088
Н	1.169841	4.74688	-1.991111
С	1.238296	2.768272	-1.151237
Н	0.401944	2.42538	-1.747447
0	0.871538	-3.297499	-1.557643
0	-0.054383	0.412087	-3.721528
0	-2.778721	-0.855619	2.907936
0	0.660899	1.864572	3.396889
0	1.198474	-2.682435	3.016114
Н	-0.702522	-1.38848	0.476415
Н	-3.358493	-2.579397	-1.970933

 TS_2

Symbol	Х	Y	Z
Fe	-0.378657	0.482123	-1.342048
Fe	-0.363423	-1.222472	1.223397
S	-1.568874	0.784113	0.693602
S	-2.553598	0.315572	-2.466776
Р	1.315244	-0.007632	0.129916
С	0.603564	0.226499	-2.806393
С	-0.224237	2.296877	-1.413071
С	-1.882141	-2.199859	1.29456
С	-0.173218	-0.885337	3.043607
С	0.652559	-2.694056	1.155836
С	-3.278238	0.458039	0.254174
С	-4.236948	0.433919	1.2784
Н	-3.913254	0.546001	2.308881
С	-5.591122	0.282721	0.984964
Н	-6.318255	0.271048	1.790944
С	-6.004826	0.154852	-0.342537
Н	-7.057304	0.03916	-0.581862
С	-5.06093	0.166111	-1.368674
Н	-5.37794	0.051881	-2.400829
С	-3.697277	0.312799	-1.080092
С	2.749007	-0.94953	-0.541402

С	2.530526	-2.003947	-1.446521
Н	1.522675	-2.235037	-1.777362
С	3.594735	-2.767818	-1.923614
Н	3.403341	-3.574577	-2.625126
С	4.899662	-2.495548	-1.504463
Н	5.728931	-3.088158	-1.87896
С	5.128623	-1.457703	-0.599824
Н	6.138045	-1.240258	-0.262829
С	4.06444	-0.691094	-0.119892
Н	4.263186	0.108729	0.584709
С	2.073269	1.511301	0.841403
С	2.761897	2.403812	-0.001613
Н	2.855417	2.183872	-1.061408
С	3.330884	3.568692	0.510062
Н	3.859894	4.245929	-0.153999
С	3.21546	3.866276	1.87161
Н	3.655117	4.776201	2.269085
С	2.53408	2.990006	2.716184
Н	2.442307	3.212357	3.775196
С	1.968701	1.817815	2.2055
Н	1.45144	1.143337	2.876835
0	1.237963	0.083697	-3.75467
0	-0.185815	3.441483	-1.47293
0	-2.839931	-2.835296	1.345873
0	-0.08961	-0.653054	4.167551
0	1.289719	-3.654493	1.178603
Н	-0.611364	-1.089979	-1.245454
Н	-1.566706	-0.709565	-1.875471

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