Supporting Information

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

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## References

## Crystallographic results of $\mathbf{1}^{-}$

Table S1. X-ray Crystallographic Data

|  | [TBA][1] ${ }^{\text {THF }}$ |
| :---: | :---: |
| Empirical formula | $\mathrm{C}_{43} \mathrm{H}_{58} \mathrm{Fe}_{2} \mathrm{NO}_{6} \mathrm{PS}_{2}$ |
| Formula weight | 891.69 |
| $T, \mathrm{~K}$ | 150(2) |
| Crystal system | Monoclinic |
| Space group | C2/c |
| $a, \AA$ | 38.787(2) |
| $b, \AA$ | 10.9018(7) |
| $c, \AA$ | 23.5032(15) |
| $\alpha,{ }^{\circ}$ | 90 |
| $\beta,{ }^{\circ}$ | 115.228(2) |
| $\gamma,{ }^{\circ}$ | 90 |
| $V, \AA^{3}$ | 8990.3(10) |
| Z | 8 |
| $\rho_{\text {calcd, }} \mathrm{Mg} \mathrm{m}^{-3}$ | 1.318 |
| $\mu, \mathrm{mm}^{-1}$ | 0.819 |
| $F(000)$ | 3760 |
| Reflections collected | 26721 |
| Independent reflections | 7904 |
| $R_{\text {int }}$ | 0.0818 |
| Goodness-of-fit on $\mathrm{F}^{2}$ | 1.171 |
| R1 $[I>2 \sigma(I)]\left(\right.$ all data) ${ }^{\text {a }}$ | 0.0850 (0.1095) |
| wR2 $[I>2 \sigma(I)]$ (all data) ${ }^{\text {b }}$ | 0.1776 (0.1881) |

${ }^{\mathrm{a}} \mathrm{R} 1=\left(\Sigma| | F_{\mathrm{o}}\left|-\left|F_{\mathrm{c}}\right|\right|\right) /\left(\Sigma\left|F_{\mathrm{o}}\right|\right) .{ }^{\mathrm{b}} \mathrm{wR} 2=\left[\Sigma w\left(F_{\mathrm{o}}^{2}-F_{\mathrm{c}}{ }^{2}\right)^{2} / \Sigma w\left(F_{\mathrm{o}}{ }^{2}\right)^{2}\right]^{1 / 2}$.

## 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 $6-31 \mathrm{G}(\mathrm{d}, \mathrm{p})$ basis set was used for $\mathrm{O}, \mathrm{S}, \mathrm{P}, \mathrm{C}$, and H atoms. All structure optimization and thermochemical properties were calculated under the solvent effect by using the polarizable continuum model (PCM) for $\mathrm{CH}_{2} \mathrm{Cl}_{2}$. $^{5-7}$

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 ( $\left.E^{\text {cal }}\right)$ of the related species, and the calculated $\mathrm{p} K_{\mathrm{a}}$ values.

## Estimation of $\mathbf{p} K_{\mathrm{a}}$ values, redox potentials and equilibrium constants

The estimation of $\mathrm{p} K_{\mathrm{a}}$ values of key intermediates $\left(\mathrm{AH}^{+}\right)$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 $\mathrm{p} K_{\mathrm{a}}$ value.

$$
\mathrm{AH}^{+}+\mathrm{A}_{\mathrm{ref}} \rightarrow \mathrm{~A}+\mathrm{A}_{\mathrm{ref}} \mathrm{H}^{+}
$$

The calculated $\mathrm{p} K_{\mathrm{a}}$ can be expressed as:

$$
\mathrm{p} K_{\mathrm{a}}^{\mathrm{cal}}=\frac{\Delta G_{r}^{0}}{\ln (0) R T}+\mathrm{p} K_{a}(\mathrm{ref})
$$

where $\mathrm{p} K_{\mathrm{a}}($ ref $)$ is the known $\mathrm{p} K_{\mathrm{a}}$ of the reference species. $\Delta G_{r}^{0}$ 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.

$$
\Delta G_{r}^{0}=\Delta G_{\mathrm{gas}}^{0}+\Delta G_{s}^{0}(A)+\Delta G_{s}^{0}\left(\mathrm{~A}_{\mathrm{ref}} \mathrm{H}^{+}\right)-\Delta G_{s}^{0}\left(\mathrm{AH}^{+}\right)-\Delta G_{s}^{0}\left(\mathrm{~A}_{\mathrm{ref}}\right)
$$

The $\mathrm{p} K_{\mathrm{a}}$ of $\mathrm{H}\left(\mathrm{OEt}_{2}\right)_{2}{ }^{+}$is defined to be 0 as suggested that the weak coordinated proton can be treated as a reference. ${ }^{9}$ The $\mathrm{p} K_{\mathrm{a}}{ }^{\text {cal }}$ (in $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ solution) of $\mathrm{PhNH}_{3}{ }^{+}$is estimated to be 12.11 , which is consistent with the measured value in MeCN solution ( $\mathrm{p} K_{\mathrm{a}}{ }^{\mathrm{MeCN}}=10.7$ ). The estimated $\mathrm{p} K_{\mathrm{a}}{ }^{\text {cal }}$ values for the protonated species are listed in Table S 2 . The $\mathrm{p} K_{\mathrm{a}}{ }^{\mathrm{cal}}$ of $\mathbf{1} \boldsymbol{\mu} \mathbf{H}$ is 22.44 . The values for $\mathbf{1} \boldsymbol{\mu} \mathbf{H S H}^{+}$and $\mathbf{1} \boldsymbol{\mu} \mathbf{H S H}$ concerning the dissociation of the S-proton are 4.28 and 18.38 , respectively.

The theoretical reduction potentials of reactions and $\mathrm{Fc}^{+} / \mathrm{Fc}$ couple are estimated from the relationship and equations in Table S 3 where $n$ is the number of electron involved, and $F$ the

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

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

$$
K_{\mathrm{eq}}=10^{-(p K a(A c i d)-p K a(\text { Catalyst }))}
$$

For the protonation reaction of $\mathbf{1} \boldsymbol{\mu} \mathbf{H}^{-}$by HOTf, the $\mathrm{p} K_{\mathrm{a}}($ Catalyst $)$ is $\mathrm{p} K_{\mathrm{a}}\left(\mathbf{1} \boldsymbol{\mu} \mathbf{H S H}{ }^{+}\right)$. For the protonation reaction of $\mathbf{1}^{-}$by TFA or TCA, the $\mathrm{p} K_{\mathrm{a}}$ (Catalyst) is $\mathrm{p} K_{\mathrm{a}}(\mathbf{1} \boldsymbol{\mu} \mathbf{H})$.

Table S2. Calculated $\mathrm{p} K_{\mathrm{a}}$ values for selected species in $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ solution.

| Species | $\mathrm{p} K_{\mathrm{a}}{ }^{\mathrm{cal}}$ |
| :---: | :---: |
| $\mathrm{PhNH}_{3}{ }^{+}$ | $12.11(10.7)^{\diamond}$ |
| $\mathbf{1} \boldsymbol{\mu} \mathbf{~}$ | 22.44 |
| $\mathbf{1} \boldsymbol{\mathbf { H S H }}$ |  |
|  |  |
| $\mathbf{1} \boldsymbol{\mu} \mathbf{H S H}$ | $4.28(\mathrm{SH})$ |
|  | $18.38(\mathrm{SH})$ |

${ }^{\circ}$ Value 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

$$
\begin{gathered}
\Delta H_{g}^{0, \text { redox }}=d \varepsilon_{S C F}+d \varepsilon_{\text {trans }}+d \varepsilon_{\text {rot }}+d \varepsilon_{v i b}+d \varepsilon_{Z P E} \\
\Delta G_{g}^{0, \text { redox }}=\Delta H_{g}^{0, \text { redox }}-T \Delta S_{g}^{0, \text { redox }} \\
\Delta G_{s}^{0}=\left(\varepsilon_{S C F}+G_{\text {corr }}\right)_{\text {solv }}-\left(\varepsilon_{S C F}+G_{\text {corr }}\right)_{\text {gas }}
\end{gathered}
$$

Estimation of reduction potential

$$
\begin{gathered}
\Delta G_{\text {solv }}^{0, \text { redox }}=\Delta G_{g}^{0, \text { redox }}+\Delta G_{s}^{0}(\text { Red })-\Delta G_{s}^{0}(O x) \\
E_{\text {calc }}^{0}=-\Delta G_{\text {solv }}^{0, \text { redox }} / n F
\end{gathered}
$$

Table S4. Computed thermodynamic parameters and reduction potentials ( $\mathrm{vs} . \mathrm{Fc}^{+} / \mathrm{Fc}$ ) for selected species.

| Reaction | $\mathrm{S}-\mathrm{H}(\AA \AA)$ | $\Delta G_{g}^{0, \text { redox }}$ <br> $\left(\mathrm{kcal} \mathrm{mol}^{-1}\right)$ | $\Delta G_{s}^{0}($ Red $)$ <br> $\left(\mathrm{kcal} \mathrm{mol}^{-1}\right)$ | $\Delta G_{s}^{0}(O x)$ <br> $\left(\mathrm{kcal} \mathrm{mol}^{-1}\right)$ | $E^{\text {cal }}$ <br> $(\mathrm{V})$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| $\mathbf{1} \boldsymbol{\mu} \mathbf{H S H}^{+/ 0}$ | 1.35 | -123.646 | -6.722 | -32.939 | -1.22 |
| $\mathbf{1} \boldsymbol{\mu} \mathbf{H S H N H}_{\mathbf{2}} \mathbf{P h}^{+/ 0}$ | 2.135 | -106.272 | -16.603 | -36.366 | -1.69 |

## Evaluation of the intra-molecular route for $\mathbf{H}_{\mathbf{2}}$ 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 $\mathbf{1} \boldsymbol{\mu} \mathbf{H S H}$ is formed, it readily reacts to produce molecular hydrogen and $\mathbf{1} \boldsymbol{\mu} \mathbf{H}$. The detailed is described below.

The free energy change of $\mathrm{H}_{2}$ elimination from $\mathbf{1} \mu \mathbf{H S H}$ was calculated from the thermodynamic cycle as shown in Table S5. The reduction potentials of $\mathbf{1} \boldsymbol{\mu} \mathbf{H S H}^{+}$and $\mathbf{1}$ were taken from experiments to be -1 and -0.6 V vs. $\mathrm{Fc}^{+} / \mathrm{Fc}$, respectively. The NHE potential $E^{\mathrm{o}}\left(\mathrm{H}^{+} / \mathrm{H}_{2}\right)$ is 0.14 V vs. $\mathrm{Fc}^{+} / \mathrm{Fc}$ from the experimental measurement in acetonitrile. ${ }^{12}$ The $\mathrm{p} K_{\mathrm{a}}$ of $\mathbf{1} \boldsymbol{\mu} \mathbf{H S H}^{+}$and $\mathbf{1} \boldsymbol{\mu} \mathbf{H}$ are taken from the calculated values (vide supra). The pathway of $\mathrm{H}_{2}$ elimination from $\mathbf{1} \boldsymbol{\mu} \mathbf{H S H}$ is slightly unfavored by $6.11 \mathrm{kcal} \mathrm{mol}^{-1}$.

Moreover, two energy barriers ( 13.3 and $13.4 \mathrm{kcal} \mathrm{mol}^{-1}$ for $\mathrm{TS}_{1}$ and $\mathrm{TS}_{2}$, respectively) are to be overcome for proton relay from the S site of $\mathbf{1} \mu \mathbf{H S H}$ to the Fe center, followed by hydrogen evolution, shown in the Scheme $S 1$. The final product in this route is $\mathbf{1}$, which is inconsistent with the experimental result in which $\mathbf{1} \boldsymbol{\mu} \mathbf{H}$ 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 $\mathbf{1} \mu \mathbf{H S H}$ generate two $\mathbf{1} \mu \mathbf{H}$ with liberation of molecular hydrogen. This is favored in thermodynamics $\left(\Delta G_{2}{ }^{0}=-14.02 \mathrm{kcal} \mathrm{mol}^{-1}\right)$.

Table S5. Thermodynamic cycles for the calculation of the free energy by intra-molecular $\mathrm{H}_{2}$ elimination and homolytic fashion from $\mathbf{1} \boldsymbol{\mu} \mathbf{H S H}$.

| Intra-molecular $\mathrm{H}_{2}$ elimination |  |
| :---: | :---: |
| Reaction | Free energy |
| $\mathbf{1} \boldsymbol{\mu H S H} \rightarrow \mathbf{1} \boldsymbol{\mu} \mathbf{H S H}{ }^{+}+\mathrm{e}^{-}$ | $F E^{0}$ |
| $\mathbf{1} \mu \mathbf{H S H}^{+} \rightarrow \mathbf{1} \mu \mathrm{H}+\mathrm{H}^{+}$ | $2.3 R T \mathrm{p} K_{\text {a }}$ |
| $\mathbf{1} \boldsymbol{\mu} \mathbf{H} \rightarrow \mathbf{1}^{-}+\mathrm{H}^{+}$ | $2.3 R T \mathrm{p} K_{\mathrm{a}}$ |
| $\mathbf{1}^{-} \rightarrow \mathbf{1}+\mathrm{e}^{-}$ | $F E^{0}$ |
| $2 \mathrm{H}^{+}+2 \mathrm{e}^{-} \rightarrow \mathrm{H}_{2}$ | $-2 F E^{0}\left(\mathrm{H}^{+} / \mathrm{H}_{2}\right)$ |
| $\mathbf{1} \boldsymbol{\mu} \mathbf{H S H} \rightarrow \mathbf{1}+\mathrm{H}_{2}$ | $\Delta G_{1}{ }^{0}$ |
| Homolytic $\mathrm{H}_{2}$ elimination |  |
| Reaction | Free energy |
| $\mathbf{1} \boldsymbol{\mu H S H} \rightarrow \mathbf{1} \boldsymbol{\mu} \mathbf{H S H}^{+}+\mathrm{e}^{-}$ | $F E^{0}$ |
| $\mathbf{1} \boldsymbol{\mu} \mathbf{H S H}^{+} \rightarrow \mathbf{1} \boldsymbol{\mu} \mathbf{H}+\mathrm{H}^{+}$ | $2.3 R T \mathrm{p} K_{\mathrm{a}}$ |
| $\mathrm{H}^{+}+\mathrm{e}^{-} \rightarrow 0.5 \mathrm{H}_{2}$ | $-F E^{0}\left(\mathrm{H}^{+} / \mathrm{H}_{2}\right)$ |
| $\mathbf{1} \mu \mathbf{H S H} \rightarrow \mathbf{1} \boldsymbol{\mu H}+0.5 \mathrm{H}_{2}$ | $\Delta G_{2}{ }^{0}$ |

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


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

| Species | $\Delta G_{\text {solv }}$ (hartree) | $\Delta G_{\text {gas }}($ hartree $)$ |
| :---: | :---: | :---: |
| $1{ }^{-}$ | -2645.669149 | -2645.610236 |
| 1 | -2645.525386 | NA |
| $1 \mu \mathrm{H}$ | -2646.119996 | -2646.109649 |
| $1 \mu \mathrm{H}^{-}$ | -2646.240978 | NA |
| $1 \mu \mathrm{HSH}^{+}$ | -2646.531071 | -2646.478578 |
| $1 \mu \mathrm{HSH}$ | -2646.682896 | -2646.672183 |
| $1 \mu \mathrm{HSH} *$ | -2646.681467 | NA |
| $1 \mu \mathrm{HSHNH}_{2} \mathrm{Ph}^{+}$ | -2934.062753 | -2934.004799 |
| $1 \mu \mathrm{HSHNH} 2 \mathrm{Ph}$ | -2934.197124 | -2934.170666 |
| $\mathrm{PhNH}_{2}$ | -287.524176 | -287.528423 |
| $\mathrm{PhNH}_{3}{ }^{+}$ | -287.952437 | -287.87111 |
| $\mathrm{OEt}_{2}$ | -233.572668 | -233.570308 |
| $\mathrm{H}\left(\mathrm{OEt}_{2}\right)_{2}{ }^{+}$ | -467.547176 | -467.489869 |
| Fc | -510.393960 | -510.390633 |
| $\mathrm{Fc}^{+}$ | -510.193857 | -510.131014 |
| TS ${ }_{1}$ | -2646.661710 | NA |
| $\mathrm{TS}_{2}$ | -2646.660069 | NA |

## Chemical reduction of $1 \mu \mathbf{H S H}^{+}$and $1 \mu \mathrm{H}$


(c)

Response_


Time

Figure S1. FTIR spectra of (a) $\mathbf{1} \boldsymbol{\mu} \mathbf{H S H}^{+}$alone (black) and the species after the reaction with $\mathrm{Cp}_{2} \mathrm{Co}$ (red). (b) $1 \mu \mathbf{H}$ alone (red) and the species after the reaction with $\mathrm{Cp}{ }_{2} \mathrm{Co}$ (blue). The IR profile of $\mathbf{1}^{-}$is shown in a dotted curve. (c) Gas chromatogram of the gaseous content in headspace of the chemical reduction of $\mathbf{1 \mu} \mathbf{H S H}^{+}$by $\mathrm{Cp}_{2} \mathrm{Co}$, and standard $\mathrm{H}_{2}$ with different volume. (inset: calibration curve used to calculate the amount of hydrogen generated.) Conditions: column and injector temperature: $120^{\circ} \mathrm{C}$ and detector temperature: $220^{\circ} \mathrm{C}$. Gas flow: $30 \mathrm{~mL} \mathrm{~min}{ }^{-1}$. Carrier gas: nitrogen.

## Evaluation of the uni-molecular (heterolytic) and bi-molecular (homolytic) pathways for $\mathbf{H}_{\mathbf{2}}$ evolution by chemical reduction

We designed experiments to examine the validity of the heterolytic pathways (Scheme S 2 , eqs. S1-S2, S6-S7) and homolytic pathways (Scheme S2, eqs. S3-S5, S8-S10) for the reduction of $\mathbf{1} \mu \mathbf{H}$ and $\mathbf{1} \boldsymbol{\mu} \mathbf{H S H}^{+}$in the presence of limited amount of acid.
$\mathbf{1} \boldsymbol{\mu} \mathbf{H}$ was reduced by 1 equiv. of $\mathrm{Cp}^{*}{ }_{2} \mathrm{Co}$ in the presence of 3 equiv. of TFA in solution. If the heterolytic pathway occurred, complex 1 would be observed because the generated $\mathbf{1}$ did not react with acid and no reducing agent was available to convert $\mathbf{1}$ back to $\mathbf{1}^{-}$. The FTIR spectral results indicated that $\mathbf{1} \mu \mathbf{H}$ and acid were detected in solution after the reaction, and the formation of $\mathrm{H}_{2}$ gas was confirmed by GC ( $84 \%$ yield based on the formation of 0.5 equiv. of $\mathrm{H}_{2}$ ). The results suggest that the $\mathrm{H}_{2}$ evolution reaction proceeded via the homolytic pathway. If $\mathbf{1}$ disproportionated to $\mathbf{1}^{-}$and $\mathbf{1}^{+}$, only $50 \% \mathbf{1}^{-}$was regenerated. In addition, $\mathbf{1}^{+}$was unstable and readily decayed. From the FTIR results, $\mathbf{1}^{-}$was regenerated quantitatively. Therefore, the disproportionation reaction was not observed.

The same conclusion was made for the catalysis involving $\mathbf{1} \mu \mathbf{H S H}^{+}$. When $\mathbf{1} \mu \mathbf{H S H}^{+}$was reduced by 1 equiv. of $\mathrm{Cp}_{2} \mathrm{Co}$ in the presence of 8 equiv. of HOTf in solution, $\mathbf{1} \boldsymbol{\mu} \mathbf{H S H}^{+}$was detected after the catalysis. Neither $\mathbf{1} \boldsymbol{\mu} \mathbf{H}^{+}$or $\mathbf{1 S H}{ }^{+}$was observed. The yield of $\mathrm{H}_{2}$ gas was $91 \%$ yield based on the formation of 0.5 equiv. of $\mathrm{H}_{2}$.

Scheme S2. The uni- and bi-molecular pathways for $\mathrm{H}_{2}$ evolution involving $\mathbf{1} \boldsymbol{\mu} \mathbf{H}$ and $\mathbf{1} \boldsymbol{\mu} \mathbf{H S H}^{+}$. For $\mathbf{1} \boldsymbol{\mu} \mathbf{H}^{0 /-}$ :
Heterolytic pathway:

$$
\begin{align*}
& 1 \mu \mathrm{H}+\mathrm{e}^{-} \rightleftharpoons 1 \mu \mathrm{H}^{-}  \tag{S1}\\
& 1 \mu \mathrm{H}^{-}+\mathrm{H}^{+} \longrightarrow 1+\mathrm{H}_{2} \tag{S2}
\end{align*}
$$

Homolytic pathway:

$$
\begin{align*}
1 \mu \mathrm{H}+\mathrm{e}^{-} & \longmapsto 1 \mu \mathrm{H}^{-}  \tag{S3}\\
1 \mu \mathrm{H}^{-}+1 \mu \mathrm{H}^{-} & \longrightarrow 1^{-}+1^{-}+\mathrm{H}_{2}  \tag{S4}\\
1^{-}+\mathrm{H}^{+} & \longrightarrow 1 \mu \mathrm{H} \tag{S5}
\end{align*}
$$

For $\mathbf{1} \boldsymbol{\mu} \mathbf{H S H}^{+/ 0}$ :
Heterolytic pathway:

$$
\begin{gather*}
1 \mu \mathrm{HSH}^{+}+\mathrm{e}^{-} \rightleftharpoons 1 \mu \mathrm{HSH}  \tag{S6}\\
1 \mu \mathrm{HSH}+\mathrm{H}^{+} \longrightarrow 1 \mu \mathrm{H}^{+}\left(\text {or } 1 \mathrm{SH}^{+}\right)+\mathrm{H}_{2} \tag{S7}
\end{gather*}
$$

Homolytic pathway:

$$
\begin{align*}
& 1 \mu \mathrm{HSH}^{+}+\mathrm{e}^{-} \longmapsto 1 \mu \mathrm{HSH}  \tag{S8}\\
& 1 \mu \mathrm{HSH}+1 \mu \mathrm{HSH} \longrightarrow 1 \mu \mathrm{H}+1 \mu \mathrm{H}+\mathrm{H}_{2}  \tag{S9}\\
& 1 \mu \mathrm{H}+\mathrm{H}^{+} \longrightarrow 1 \mu \mathrm{HSH}^{+} \tag{S10}
\end{align*}
$$

## Cyclic voltammograms and simulation of cyclic voltammograms



Figure S2. (a) Cyclic voltammogram of $\mathbf{1}^{-}$in THF solution $\left(1 \mathrm{mM}, v=0.1 \mathrm{~V} \mathrm{~s}^{-1}, 1 \mathrm{~mm}\right.$ vitreous carbon electrode, 295 K ). $E_{1 / 2}{ }^{\mathrm{ox}}=-0.62 \mathrm{~V}$ and $E_{1 / 2}{ }^{\mathrm{red}}=-2.37 \mathrm{~V}$. (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 $\mathbf{1}^{-}$. The experimental $D$ value is estimated to be $4.74 \times$ $10^{-6} \mathrm{~cm}^{2} \mathrm{~s}^{-1}$.


Figure S4. Cyclic voltammograms of $\mathbf{1}^{-}$at $v=0.1$ and $0.2 \mathrm{~V} \mathrm{~s}^{-1}(0.5 \mathrm{mM}, 1 \mathrm{~mm}$ vitreous carbon electrode, 292 K). Simulated cyclic voltammograms are displayed in circles. Optimized simulation parameters: $\alpha=0.6, k_{\mathrm{s}}=0.01 \mathrm{~cm} \mathrm{~s}^{-1}, k_{\mathrm{f}}=0.07, k_{\mathrm{b}}=0.035, D\left(\mathbf{1}^{-}\right)=4.76 \times 10^{-6} \mathrm{~cm}^{2} \mathrm{~s}^{-1}$.

## Determination of the diffusion coefficient of $\left[\mathrm{PhNH}_{3}\right]\left[\mathrm{BArF}_{24}\right]$

The diffusion coefficient of $\left[\mathrm{PhNH}_{3}\right]\left[\mathrm{BArF}_{24}\right]$ was estimated by ${ }^{1} \mathrm{H}$-DOSY NMR spectroscopy. The pulse width was varied until null peaks were observed for anilinium peaks, with the calibrated $90^{\circ}$ pulse found to be $11.9 \mu \mathrm{~s}$. The anilinium protons were allowed to sufficiently relax for accurate measurements. The DOSY data were processed in the VNMRJ software. The $D$ value of $\left[\mathrm{PhNH}_{3}\right]\left[\mathrm{BArF}_{24}\right]$ was estimated to be $1 \times 10^{-5} \mathrm{~cm}^{2} \mathrm{~s}^{-1}$. This value was also used for the rest of the acids in the simulations.


Figure S5. ${ }^{1} \mathrm{H}$-DOSY NMR spectrum of $\left[\mathrm{PhNH}_{3}\right]\left[\mathrm{BArF}_{24}\right]$ in $\mathrm{CD}_{2} \mathrm{Cl}_{2}$ solution.

## Digital simulation for the $1 \mu \mathrm{HSH}^{+/ 0}$ process via the bi-molecular pathway

The HOTf case:


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


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

Table S7. Digital simulation parameters for Figure S7.

| $E^{0}(\mathrm{~V})$ | $\alpha$ | $k_{\mathrm{s}}{ }^{\prime}\left(\mathrm{cm} \mathrm{s}^{-1}\right)$ | $k_{\mathrm{pT}}{ }^{\prime}\left(\mathrm{s}^{-1} \mathrm{M}^{-1}\right)$ | $k_{\mathrm{rxn}}{ }^{\prime}\left(\mathrm{s}^{-1} \mathrm{M}^{-1}\right)$ | $K_{\mathrm{eq}}{ }^{\prime}\left(\mathrm{M}^{-1}\right)$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| -1.160 | 0.5 | 0.029 | $2.2 \times 10^{5}$ | $1.92 \times 10^{10}$ | 47.86 |
| $D\left(\mathbf{1} \boldsymbol{\mu} \mathbf{H S H}^{+}\right)$ | $D(\mathbf{1} \boldsymbol{\mu} \mathbf{H S H})$ | $D(\mathbf{1} \mathbf{H})$ | $D\left(\mathrm{H}_{2}\right)$ | $D\left(\mathrm{H}^{+}\right)$ |  |
| $2.1 \times 10^{-5}$ | $4.76 \times 10^{-6}$ | $4.76 \times 10^{-6}$ | $1 \times 10^{-5}$ | $1 \times 10^{-5}$ |  |

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

The TFA case:


Figure S8. Experimental (solid line) and simulated (hollow dots) catalytic responses of $\mathbf{1}^{-}$with different [TFA] ( $2,3,4$ and 5 mM ) in $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ solution under $\mathrm{N}_{2}$. Potentials were calibrated with the $\mathrm{Fc}^{+} / \mathrm{Fc}$ redox pair as an internal standard $\left(\left[\mathbf{1}^{-}\right] 1 \mathrm{mM}, v=0.1 \mathrm{~V} \mathrm{~s}^{-1}, 1 \mathrm{~mm}\right.$ vitreous carbon, 295 $\mathrm{K})$. Background CV is shown as a dashed trace.

Table S8. Digital simulation parameters for Figure S8.

| $E^{0}(\mathrm{~V})$ | $\alpha$ | $k_{\mathrm{s}}{ }^{\prime \prime}\left(\mathrm{cm} \mathrm{s}^{-1}\right)$ | $k_{\mathrm{PT}}{ }^{\prime \prime}\left(\mathrm{s}^{-1} \mathrm{M}^{-1}\right)$ | $k_{\mathrm{rxn}}{ }^{\prime \prime}\left(\mathrm{s}^{-1} \mathrm{M}^{-1}\right)$ | $K_{\mathrm{eq}}{ }^{\prime \prime}\left(\mathrm{M}^{-1}\right)$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| -1.566 | 0.5 | 0.0162 | 3495 | $3.84 \times 10^{6}$ | $5.5 \times 10^{9}$ |
| $D\left(\mathbf{1}^{-}\right)$ | $D\left(\mathbf{1} \boldsymbol{\mu} \mathbf{H}^{-}\right)$ | $D(\mathbf{1} \mathbf{\mu} \mathbf{H})$ | $D\left(\mathrm{H}_{2}\right)$ | $D\left(\mathrm{H}^{+}\right)$ |  |
| $4.76 \times 10^{-6}$ | $4.76 \times 10^{-6}$ | $4.76 \times 10^{-6}$ | $1 \times 10^{-5}$ | $1 \times 10^{-5}$ |  |

The TCA case:


Figure S9. Cyclic voltammograms of $\mathbf{1}^{-}$in $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ solution with increments of TCA ([1-] 1 mM , $v=0.1 \mathrm{~V} \mathrm{~s}^{-1}, 1 \mathrm{~mm}$ vitreous carbon electrode). Background CV is shown as a dashed trace.


Figure S10. Experimental (solid line) and simulated (hollow dots) catalytic responses of $\mathbf{1}^{-}$with different [TCA] ( $2.6,3.4$ and 4.2 mM ) in $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ solution under $\mathrm{N}_{2}$. Potentials were calibrated with the $\mathrm{Fc}^{+} / \mathrm{Fc}$ redox pair as an internal standard $\left(\left[1^{-}\right] 1 \mathrm{mM}, v=0.1 \mathrm{~V} \mathrm{~s}^{-1}, 1 \mathrm{~mm}\right.$ vitreous carbon, $295 \mathrm{~K})$. Background CV is shown as a dashed trace.

Table S9. Digital simulation parameters for Figure S10.

| $E^{0}(\mathrm{~V})$ | $\alpha$ | $k_{\mathrm{s}}{ }^{\prime \prime}\left(\mathrm{cm} \mathrm{s}^{-1}\right)$ | $k_{\mathrm{PT}}{ }^{\prime \prime}\left(\mathrm{s}^{-1} \mathrm{M}^{-1}\right)$ | $k_{\mathrm{rxn}}{ }^{\prime \prime}\left(\mathrm{s}^{-1} \mathrm{M}^{-1}\right)$ | $K_{\mathrm{eq}}{ }^{\prime \prime}\left(\mathrm{M}^{-1}\right)$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| -1.550 | 0.5 | 0.02194 | 4198 | $5.55 \times 10^{6}$ | $6.9 \times 10^{11}$ |
| $D\left(\mathbf{1}^{-}\right)$ | $D\left(\mathbf{1} \boldsymbol{\mu} \mathbf{H}^{-}\right)$ | $D(\mathbf{1} \boldsymbol{\mu} \mathbf{H})$ | $D\left(\mathrm{H}_{2}\right)$ | $D\left(\mathrm{H}^{+}\right)$ |  |
| $4.76 \times 10^{-6}$ | $4.76 \times 10^{-6}$ | $4.76 \times 10^{-6}$ | $1 \times 10^{-5}$ | $1 \times 10^{-5}$ |  |

## Digital simulation for the $\mathbf{1} \mu \mathrm{H}-\mathrm{PhNH}_{3}{ }^{+}$system with the PCET pathways





Figure S11. Experimental (solid line) and simulated (hollow dots) catalytic responses of $\mathbf{1}^{-}$with $2 \mathrm{mM}\left[\mathrm{PhNH}_{3}\right]\left[\mathrm{BArF}_{24}\right]$ in $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ solution at various scan rates under $\mathrm{N}_{2}$ : (a) $v=0.1,0.2$ and 0.4 $\mathrm{V} \mathrm{s}^{-1}$. (b) $v=0.625,0.9$ and $1.6 \mathrm{~V} \mathrm{~s}^{-1}$. (c) Experimental (solid line, $v=0.4 \mathrm{~V} \mathrm{~s}^{-1}$ ) and simulated (hollow dots) catalytic responses of $\mathbf{1}^{-}$with different concentration of $\left[\mathrm{PhNH}_{3}\right]\left[\mathrm{BArF}_{24}\right]$ (2, 3, 4 and 5 mM ) in $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ solution under $\mathrm{N}_{2}$. Potentials were calibrated with the $\mathrm{Fc}^{+} / \mathrm{Fc}$ redox pair as an internal standard. ([1-] $1 \mathrm{mM}, 1 \mathrm{~mm}$ vitreous carbon, 295 K ). Background CVs are shown as dashed traces.

Table S10. Digital simulation parameters for Figure S11.

| $E^{0}(\mathrm{~V})$ | $\alpha$ | $k_{\text {PCET }}\left(\mathrm{cm} \mathrm{s}^{-1}\right)$ | $k_{\mathrm{rxn}}{ }^{\prime}\left(\mathrm{s}^{-1} \mathrm{M}^{-1}\right)$ |
| :---: | :---: | :---: | :---: |
| -0.986 | 0.316 | 0.63 | $1.92 \times 10^{10}$ |
| $D(\mathbf{1} \boldsymbol{\mu} \mathbf{H S H})\left(\mathrm{cm}^{2} \mathrm{~s}^{-1}\right)$ | $D(\mathbf{1} \boldsymbol{\mu} \mathbf{H})\left(\mathrm{cm}^{2} \mathrm{~s}^{-1}\right)$ | $D\left(\mathrm{H}_{2}\right)\left(\mathrm{cm}^{2} \mathrm{~s}^{-1}\right)$ |  |
| $4.76 \times 10^{-6}$ | $4.76 \times 10^{-6}$ | $1 \times 10^{-5}$ |  |
| $D\left(\mathrm{PhNH}_{3}{ }^{+}\right)\left(\mathrm{cm}^{2} \mathrm{~s}^{-1}\right)$ |  | $D\left(\mathrm{PhNH}_{2}\right)\left(\mathrm{cm}^{2} \mathrm{~s}^{-1}\right)$ |  |
| $1 \times 10^{-5}$ | $1 \times 10^{-5}$ |  |  |

## 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 $j_{\mathrm{cat}}$ 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 $1 \mu \mathrm{H}-\mathrm{PhNH}_{3}{ }^{+}$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 $k_{\mathrm{rxn}}$ ' in the PCET pathways listed in Table S 10 were used. $E^{0}$ is the redox potential of the $1 \mu \mathbf{H}^{0 /-}$ pair, -1.5 V . The proton transfer rate $k_{\mathrm{PT}}$ '" was initially assumed to be the maximum diffusion rate $k_{\text {Max-diff }}$ between $\mathbf{1} \boldsymbol{\mu} \mathbf{H}^{-}$and $\mathrm{PhNH}_{3}{ }^{+}$. The $k_{\text {Max-diff }}$ value was estimated by the Debye-Smoluchowski method, as shown in the following equation. ${ }^{13,14}$

$$
k_{\text {Max-diff }}=4 \pi N_{A}\left(D_{1 \mu \mathrm{H}^{-}}+D_{\mathrm{PhNH}_{3}^{+}}\right) \beta
$$

where $N_{\mathrm{A}}$ is Avogadro constant, $D_{1 \mu \mathrm{H}^{-}}$and $D_{\mathrm{PhNH}_{3}^{+}}$are diffusion coefficients for the species $\mathbf{1} \mu \mathbf{H}^{-}$ and $\mathrm{PhNH}_{3}{ }^{+}$, respectively, and $\beta$ is the effective reaction radius. The $D_{1 \mu \mathrm{H}^{-}}$value was assumed to be equal to the $D_{1^{-}}$value ( $4.76 \times 10^{-6} \mathrm{~cm}^{2} \mathrm{~s}^{-1}$ ) obtained from the electrochemical measurement. $D_{\mathrm{PhNH}_{3}^{+}}$was assumed to be $1 \times 10^{-5} \mathrm{~cm}^{2} \mathrm{~s}^{-1}$. The effective reaction radius $\beta$ was calculated from the sum of the radii of $\mathbf{1 \mu} \mathbf{H}^{-}$and $\mathrm{PhNH}_{3}{ }^{+}$by Gaussion09, by which a $\beta$ value of $6.55 \AA$ was estimated. The resulting $k_{\text {Max-diff }}$ of $7.8 \times 10^{9} \mathrm{~s}^{-1} \mathrm{M}^{-1}$ was therefore obtained, and this value was employed to the electroanalytical simulation.

With the values of $D, k_{\mathrm{rxn}}{ }^{\prime}, k_{\mathrm{PT}}{ }^{\prime \prime \prime}$ and $E^{0}$ at hand, we could simulate the voltammograms via adjusting transfer coefficient $\alpha$ and heterogeneous ET rate $k_{\mathrm{s}}{ }^{\prime \prime}$. First, $k_{\mathrm{s}}{ }^{\prime \prime}$ was varied with a fixed value of $\alpha$ at a certain scan rate. As shown in Figures S13a and S13c, the increase of $k_{\mathrm{s}}$ " led to the anodic shift of the simulated peak potential. At fast ET rates, the peak potential approached the limiting value of $\sim-1.35 \mathrm{~V}$, which was too negative compared to the observed catalytic potential. The similar procedures were applied by varying $\alpha$ (Figures S13b and S13d). In the simulations, the resulting peak potential displayed insignificant variation upon changing $\alpha$. In the scenarios via adjusting $k_{\mathrm{s}}$ " or $\alpha$, 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 $k_{\mathrm{s}}{ }^{\prime \prime}>10 \mathrm{~cm} \mathrm{~s}^{-1}$ 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 $k_{\mathrm{pT}}{ }^{\prime \prime \prime}$. In fact, the maximum diffusion rate could be faster as both $\mathbf{1} \boldsymbol{\mu} \mathbf{H}^{-}$and $\mathrm{PhNH}_{3}{ }^{+}$are charged species carrying
opposite signs. The corrected maximum diffusion rate $k_{\text {Max-diff }}^{\text {Corr }}$ was obtained with consideration of the electrostatic interaction between these two charged species.

$$
\begin{gathered}
k_{\text {Max }- \text { diff }}^{\text {Corr }}=4 \pi N_{A}\left(D_{1 \mu \mathbf{H}^{-}}+D_{\mathrm{PhNH}_{3}^{+}}\right) \beta^{\prime} \\
\beta^{\prime}=\frac{R_{C}}{\left(\exp \left(R_{C} / \beta\right)-1\right)} \exp \left(R_{C} \kappa\right) \\
R_{C}=\left(z_{1} z_{2} e^{2} / 4 \pi \varepsilon_{r} \varepsilon_{0} k_{B} T\right) \\
\kappa=\sqrt{\frac{2000 e^{2} N_{A}}{\varepsilon_{r} \varepsilon_{0} k_{B} T}}
\end{gathered}
$$

The effective reaction radius was modified to the corrected value $\beta^{\prime}$, and in the equations $z_{1}$ and $z_{2}$ are the respective charges of the two species $\mathbf{1} \mu \mathbf{H}^{-}$and $\mathrm{PhNH}_{3}{ }^{+}, e$ is the elementary charge, $\varepsilon_{\mathrm{r}}$ is the relative permittivity of the solvent ( 8.81 for $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ ), $\varepsilon_{0}$ is the permittivity of vacuum, $k_{\mathrm{B}}$ is the Boltzmann constant, and $T$ is temperature. The electrostatic modified diffusion rate $k_{\text {Max-diff }}^{\text {Corr }}$ was estimated to be $2.15 \times 10^{15} \mathrm{~s}^{-1} \mathrm{M}^{-1}$. With the employment of $k_{\mathrm{Max}-\text { diff }}^{\mathrm{Corr}}$, the simulated peak potential could approach the experimental data upon varying $\alpha$ or $k_{\mathrm{s}}$ " 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 $\alpha$ and $k_{\mathrm{s}}$ " were optimized in the simulations. It is concluded that the stepwise ETPT reaction is not an appropriate description for the catalysis in the $\mathbf{1} \mu \mathbf{H}-\mathrm{PhNH}_{3}{ }^{+}$system.


Figure S13. Experimental and simulated catalytic responses of $\mathbf{1}^{-}$with $2 \mathrm{mM}\left[\mathrm{PhNH}_{3}\right]\left[\mathrm{BArF}_{24}\right]$ in $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ solution under $\mathrm{N}_{2}$ at various scan rates: (a)(b)(e)(f) $0.3 \mathrm{~V} \mathrm{~s}^{-1}$, (c)(d)(g)(h) $0.4 \mathrm{~V} \mathrm{~s}^{-1}$. For (a)-(d), $k_{\mathrm{PT}}{ }^{\prime \prime \prime}=k_{\text {Max-diff }}\left(7.8 \times 10^{9} \mathrm{~s}^{-1} \mathrm{M}^{-1}\right)$. For (e)-(h): $k_{\mathrm{PT}}{ }^{\prime \prime \prime}=k_{\mathrm{Max}-\text { diff }}^{\text {Corr }}\left(2.15 \times 10^{15} \mathrm{~s}^{-1} \mathrm{M}^{-1}\right)$. The simulations were based on the hypothetical stepwise mechanism and performed by varying one parameter at a time ( $k_{\mathrm{s}}$ or $\alpha$ ). Potentials are calibrated with the $\mathrm{Fc}^{+} / \mathrm{Fc}$ redox pair as an internal standard ( $\left[1^{-}\right] 1 \mathrm{mM}, 1 \mathrm{~mm}$ vitreous carbon, 295 K ).

## Alternative pathway for the $1 \mu \mathrm{H}^{\mathbf{0 / -}}$ process in the simulation

The TFA/TCA case:

$$
\begin{align*}
& 1 \mu \mathrm{H}+\mathrm{e}^{-} \xrightarrow{k_{\mathrm{s}^{\prime \prime}}} \mathbf{1} \mu \mathrm{H}^{-}  \tag{S11}\\
& 1 \mu \mathrm{H}^{-}+\mathrm{H}^{+} \xrightarrow{k_{\mathrm{PT}^{\prime \prime \prime \prime}}} \mathbf{1} \mu \mathrm{HSH}  \tag{S12}\\
& \mathbf{1} \mu \mathrm{HSH}+1 \mu \mathrm{HSH} \xrightarrow{k_{\mathrm{rxn}}{ }^{\prime}} \mathbf{1} \mu \mathrm{H}+1 \mu \mathrm{H}+\mathrm{H}_{2} \tag{S13}
\end{align*}
$$

We also evaluated the possibility of an alternative route involving the hydride-acid pathway. In this alternative pathway, upon the formation of $\mathbf{1 \mu} \mathbf{H}^{-}$, it reacts with acid to yield $\mathbf{1} \boldsymbol{\mu} \mathbf{H S H}$. The following decay to $\mathbf{1} \boldsymbol{\mu} \mathbf{H}$ and $\mathrm{H}_{2}$ completes the catalysis. For the mechanism, the step invloving the intra-molecular $\mathrm{H}_{2}$ evolution $\left(\mathbf{1} \boldsymbol{\mu} \mathbf{H S H} \rightarrow \mathbf{1}+\mathrm{H}_{2}\right)$ was not considered because this intra-molecular process is unfavored according to the calculated results (see the previous section, SI). Here we took the $\mathbf{1} \boldsymbol{\mu} \mathbf{H}^{0 /-}$ process in the presence of TCA for this evaluation. The result from the catalysis involving $\mathbf{1}^{-}(1 \mathrm{mM})$ and TCA $(2.6 \mathrm{mM})$ in $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ solution was chosen for the simulation. Experimental details are available in Figure S10.

The parameters $\alpha, D\left(\mathbf{1} \mu \mathbf{H}, \mathbf{1} \mu \mathbf{H}^{-}, \mathbf{1} \mu \mathbf{H S H}\right)$ and $k_{\mathrm{s}}$ " 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 $\mathrm{H}_{2}$ evolution reaction, the rate $k_{\mathrm{rxn}}{ }^{\prime}$ in the HOTf catalysis was used as an initial guess. When $k_{\mathrm{rxn}}$ ' was fixed to $1.92 \times 10^{10} \mathrm{~s}^{-1} \mathrm{M}^{-1}$, the $k_{\mathrm{PT}} "$ " was optimized to $1.60 \times 10^{5} \mathrm{~s}^{-1} \mathrm{M}^{-1}$ in the simulation. The best simulated result displayed a quasi-reversible process with $i_{\mathrm{pa}} i_{\mathrm{pc}}=0.4$, 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 $1 \mu \mathbf{H}^{0 /-}$, it is realzed that more catalysis occurred and the resulting $\mathbf{1} \boldsymbol{\mu} \mathrm{H}$ was increased. Because $\mathbf{1} \boldsymbol{\mu} \mathbf{H S H}$ reacts to yield $\mathbf{1} \boldsymbol{\mu} \mathbf{H}$, the catalysis at the fast $k_{\mathrm{rxn}}$ rate is limitted by the formation of $\mathbf{1} \boldsymbol{\mu} \mathbf{H S H}$, i.e. the $k_{\mathrm{PT}} "$ rate. For comparison, the resulting curve exhibitted the similar peak amplitude relative to the experimental wave, and the better reversible behavior when $k_{\mathrm{PT}}$ "" was manually set to $5.00 \times 10^{3}$ $\mathrm{s}^{-1} \mathrm{M}^{-1}$ (Figure S14b).

We then fixed $k_{\mathrm{PT}} " "=1.60 \times 10^{5} \mathrm{~s}^{-1} \mathrm{M}^{-1}$ to perform the next simulation. An optimized $k_{\mathrm{rxn}}{ }^{\prime}$ of $4.04 \times 10^{3} \mathrm{~s}^{-1} \mathrm{M}^{-1}$ was obtained. The simulated result displayed a nearly irreversible process $\left(i_{\mathrm{pa}} / i_{\mathrm{pc}}=0.3\right)$ with the peak amplitude similar to the experimental data (Figure S 14 c$)$. The observation of the anodic return wave of the $\mathbf{1} \mu \mathbf{H}^{0 /-}$ event indicated that $\mathbf{1} \mu \mathbf{H S H}$ depleted to $\mathbf{1} \mu \mathbf{H}$ at a rate higher than it should be. For the sake of comparison, the $k_{\mathrm{rxn}}$ ' rate was manually changed
to $1.00 \times 10^{3} \mathrm{~s}^{-1} \mathrm{M}^{-1}$, 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 $\mathbf{1} \boldsymbol{\mu} \mathbf{H S H}$.

We also plotted simulated curves with $k_{\mathrm{PT}} " 1=5.00 \times 10^{3} \mathrm{~s}^{-1} \mathrm{M}^{-1}, k_{\mathrm{rxn}}{ }^{\prime}=4.00 \times 10^{3} \mathrm{~s}^{-1} \mathrm{M}^{-}$ ${ }^{1}$ (Figure S14e), and $k_{\mathrm{PT}}{ }^{\prime \prime \prime}=2.15 \times 10^{15} \mathrm{~s}^{-1} \mathrm{M}^{-1}, k_{\mathrm{rxn}}{ }^{\prime}=1.00 \times 10^{3} \mathrm{~s}^{-1} \mathrm{M}^{-1}$ (Figure S 14 f ). In the latter case, the electrostatic modified diffusion rate $k_{\text {Max-diff }}^{\text {Corr }}$ was used for $k_{\mathrm{PT}}$ "". The results were inconsistent with the measured one.

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 $1 \mu \mathbf{H}^{-}$and the formation of $\mathrm{H}_{2}$ (eqs. (S12) and (S13)). Because the decay reaction determines the catalytic response and the amount of $\mathbf{1} \mu \mathbf{H}$ 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 $\mathbf{1}^{-}$with 2.6 mM TCA in $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ solution under $\mathrm{N}_{2}$ with different $k_{\mathrm{rxn}}{ }^{\prime}$ and $k_{\mathrm{PT}}{ }^{\prime \prime \prime}$ : (a) $k_{\mathrm{rxn}}{ }^{\prime}=1.92 \times 10^{10} \mathrm{~s}^{-1}$ $\mathrm{M}^{-1}, k_{\mathrm{PT}} " \mathrm{"}=1.60 \times 10^{5} \mathrm{~s}^{-1} \mathrm{M}^{-1}$; (b) $k_{\mathrm{rxn}}{ }^{\prime}=1.92 \times 10^{10} \mathrm{~s}^{-1} \mathrm{M}^{-1}, k_{\mathrm{PT}} " \mathrm{"}=5.00 \times 10^{3} \mathrm{~s}^{-1} \mathrm{M}^{-1}$; (c) $k_{\mathrm{rxn}}{ }^{\prime}$ $=4.04 \times 10^{3} \mathrm{~s}^{-1} \mathrm{M}^{-1}, k_{\mathrm{PT}} " \mathrm{"}=1.60 \times 10^{5} \mathrm{~s}^{-1} \mathrm{M}^{-1}$; (d) $k_{\mathrm{rxn}}{ }^{\prime}=1.00 \times 10^{3} \mathrm{~s}^{-1} \mathrm{M}^{-1}, k_{\mathrm{PT}} " 1=1.60 \times 10^{5}$ $\mathrm{s}^{-1} \mathrm{M}^{-1}$; (e) $k_{\mathrm{rxn}}{ }^{\prime}=4.00 \times 10^{3} \mathrm{~s}^{-1} \mathrm{M}^{-1}, k_{\mathrm{PT}} " 1=5.00 \times 10^{3} \mathrm{~s}^{-1} \mathrm{M}^{-1}$; (f) $k_{\mathrm{rxn}}=1.00 \times 10^{3} \mathrm{~s}^{-1} \mathrm{M}^{-1}, k_{\mathrm{PT}}{ }^{\prime \prime} "$ $=2.15 \times 10^{15} \mathrm{~s}^{-1} \mathrm{M}^{-1}$. Potentials were calibrated with the $\mathrm{Fc}^{+} / \mathrm{Fc}$ redox pair as an internal standard.

## The deuterium experiments

Table S11. Experimental data of cyclic voltammetry of $\mathbf{1}^{-}$in the presence of anilinium acid and D8-anilinium.

| $\left[\mathrm{H}^{+}\right.$or $\left.\mathrm{D}^{+}\right]$, <br> mM | Current density $-\mathrm{H}^{+}$, <br> mA cm | Current density $-\mathrm{D}^{+}$, <br> mA cm |
| :---: | :---: | :---: |
| 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-]: $1 \mathrm{mM}, \mathrm{H}^{+}=$anilinium acid, $\mathrm{D}^{+}=\mathrm{D} 8$-anilinium acid, $v=0.1 \mathrm{~V} \mathrm{~s}^{-1}$, 297 K.

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

The molecular structure of $[T B A][\mathbf{1}]$ displayed in Figure S 15 , reveals three $\mathrm{S} \cdots \mathrm{H}$ short contacts in the crystal packing. Two of them measured to be 2.797 and $2.898 \AA$ are the distances from the hydrogen atoms $(\mathrm{H} 38 \mathrm{~b}, \mathrm{H} 36 \mathrm{~b})$ of one $\left[n \mathrm{Bu} u_{4} \mathrm{~N}\right]^{+}$cation to the terminal S 2 atom. The third one is from H36a' of the different cation nearby, measured to be $2.934 \AA$. These distances are shorter than the van der Waals radii sum of $3.0 \AA$. None of such short contact is found for the bridging thiolate S 1 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 $\left[\left(\mu, \kappa^{2}-\mathrm{bdt}\right)\left(\mu-\mathrm{PPh}_{2}\right) \mathrm{Fe}_{2}(\mathrm{CO})_{5}\right]^{-}\left(\mathbf{1}^{-}\right)$and two nearby $\left[n \mathrm{Bu} \mathrm{u}_{4}\right]^{+}$ 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 $\mathbf{1} \mu \mathrm{H}-\mathrm{PhNH}_{3}{ }^{+}$system


Figure S16. (a) IR spectra of $\mathbf{1 \mu H}$ 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 $\mathbf{1} \mu \mathrm{H}$ alone (black) and the H-bond pair (red). (c) The DFT-optimized structure of anilinium acid- $\mathbf{1} \boldsymbol{\mu} \mathbf{H}$ hydrogen-bond pair.

## ${ }^{1} \mathrm{H}-\mathrm{NMR}$ results

${ }^{1} \mathrm{H}$-NMR, 193 K

$\left[\mathrm{PhNH}_{3}\right]\left[\mathrm{BArF}_{24}\right]$ in $\mathrm{CD}_{2} \mathrm{Cl}_{2}$


Figure S17. Low field ${ }^{1} \mathrm{H}$-NMR spectra of the H -bond pair $\left\{\mathrm{PhNH}_{3}{ }^{+} \boldsymbol{\bullet} \boldsymbol{1} \boldsymbol{1} \mathbf{\mu} \mathbf{H}\right\}$ (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 $\mathrm{CD}_{2} \mathrm{Cl}_{2}$ solution at 193 K .


Figure S18. Full-range ${ }^{1} \mathrm{H}-\mathrm{NMR}$ spectra of the H -bond pair $\left\{\mathrm{PhNH}_{3}{ }^{+} \boldsymbol{\bullet} \boldsymbol{1} \boldsymbol{1} \mathbf{\mu} \mathbf{H}\right\}$ 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 $-14.13(J=52 \mathrm{~Hz}) \mathrm{ppm}$, 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 $\mathrm{CD}_{2} \mathrm{Cl}_{2}$ solution.

## CPE experiments

The potentials for the CPE of $\mathbf{1}^{-}$in the presence of anilinium acid (for the PCET reaction) and TFA (for the non-PCET reaction) were -1.1 and $-1.6 \mathrm{~V} \mathrm{vs}. \mathrm{Fc}^{+} / \mathrm{Fc}$, respectively. $\mathrm{H}_{2}$ generated in the CPE experiments at both potentials was confirmed by GC. Faradaic yield, $\mathrm{H}_{2}$ yield and TON were calculated from the experiments at each potential. The results are summarized in Tables S12S15. 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 $\mathrm{t}>7,000 \mathrm{~s}$ (Figure S22). The major solution species at the end of the experiment was $\mathbf{1} \boldsymbol{\mu} \mathbf{H}$. 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, $\left[(\mu\right.$-bdt $\left.) \mathrm{Fe}_{2}(\mathrm{CO})_{5}\left(\mathrm{PPh}_{2} \mathrm{H}\right)\right]$ and $\left[\left(\mu, \mu, \kappa_{2} \text {-bdt) }\right)_{4}(\mu\right.$ $\left.\left.\mathrm{PPh}_{2}\right)_{4} \mathrm{Fe}_{8}(\mathrm{CO})_{18}\right]$ (Figure S23). $\mathbf{1} \boldsymbol{\mu} \mathbf{H}$ was reported to slowly convert to $\left[(\mu-b d t) \mathrm{Fe}_{2}(\mathrm{CO})_{5}\left(\mathrm{PPh}_{2} \mathrm{H}\right)\right]$ in solution. ${ }^{15}$ It was reported that $\left[\left(\mu, \mu, \kappa_{2}-\mathrm{bdt}\right)_{4}\left(\mu-\mathrm{PPh}_{2}\right)_{4} \mathrm{Fe}_{8}(\mathrm{CO})_{18}\right]$ was generated from oxidation of $\mathbf{1}^{-16}$


Figure S19. CPE of 30 equiv. of anilinium acid in $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ 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 $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ 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 $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ 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 | $2.39 \pm 0.19$ | $93.2 \pm 8.66$ |

Table S13. Coulombs passed and Faradaic efficiency from the CPE of 30 equiv. of anilinium acid in $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ solution at -1.1 V for 1 hr at 298 K in the presence of $1 \mathrm{mM} \mathbf{1}^{-}$.

|  | Coulombs <br> Passed (C) | Corrected Coulombs <br> Passed (C) | TON | Faradaic Efficiency (\%) |
| :--- | :--- | :--- | :--- | :--- |
| 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 | $8.94 \pm 0.31$ | $6.55 \pm 0.31$ | $1.41 \pm 0.07$ | $96.99 \pm 1.55$ |

Table S14. Coulombs passed and Faradaic efficiency from the CPE of 30 equiv. of TFA in $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ 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 | $2.55 \pm 0.09$ | $85.81 \pm 10.10$ |

Table S15. Coulombs passed and Faradaic efficiency from the CPE of 30 equiv. of TFA in $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ solution at -1.6 V for 1 hr at 298 K in the presence of $1 \mathrm{mM} \mathbf{1}^{-}$.

|  | Coulombs <br> Passed (C) | Corrected Coulombs <br> Passed (C) | TON | Faradaic Efficiency (\%) |
| :--- | :--- | :--- | :--- | :--- |
| 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 | $10.56 \pm 0.18$ | $8.01 \pm 0.18$ | $1.72 \pm 0.04$ | $96.26 \pm 3.41$ |



Figure S21. IR profile changes of the CPE experiments in $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ solution at 273 K . (a) $\mathbf{1}^{-}$with 30 equiv. of TFA before (black) and 2 hrs after the electrolysis (red). The potential was set at -1.6 V vs. $\mathrm{Fc}^{+} / \mathrm{Fc}$. (b) $\mathbf{1}^{-}$with 10 equiv. of $\left[\mathrm{PhNH}_{3}\right]\left[\mathrm{BArF}_{24}\right]$ before (black) and 3 hrs after the electrolysis (red). The potential was set at -1.1 V vs. $\mathrm{Fc}^{+} / \mathrm{Fc}$.


Figure S22. A current-time plot for the CPE of $\mathbf{1}^{-}(1 \mathrm{mM})$ in the presence of 30 equiv. of $\left[\mathrm{PhNH}_{3}\right]\left[\mathrm{BArF}_{24}\right]$ in $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ solution at $298 \mathrm{~K}\left(E=-1.1 \mathrm{~V}\right.$ vs. $\left.\mathrm{Fc}^{+} / \mathrm{Fc}\right)$.


Figure S23. IR profile changes of the prolonged CPE experiment in $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ solution. $\mathbf{1}^{-}$with 30 equiv. of $\left[\mathrm{PhNH}_{3}\right]\left[\mathrm{BArF}_{24}\right]$ before (blue) and 12 hrs after the electrolysis (red). The potential was set at -1.1 V vs. $\mathrm{Fc}^{+} / \mathrm{Fc}$. The major species in solution was $1 \mu \mathrm{H}$ after the catalysis. The daughter species generated from the prolonged CPE are indicated as asterisks: [( $\mu-\mathrm{bdt}) \mathrm{Fe}_{2}(\mathrm{CO})_{5}\left(\mathrm{PPh}_{2} \mathrm{H}\right)$ ] (black) and $\left[\left(\mu, \mu, \kappa_{2}-\text { bdt }\right)_{4}\left(\mu-\mathrm{PPh}_{2}\right)_{4} \mathrm{Fe}_{8}(\mathrm{CO})_{18}\right]$ (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.


Time
(b)

Response_


Time
(c)

Response_


Time


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 $1 \mathrm{mM} \mathbf{1}^{-}$in $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ solution for 1 hr . Gas chromatograms of the corresponding background CPE (without $\mathbf{1}^{-}$) are shown in (b) and (d). Standard gas $\mathrm{H}_{2}$ (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 $\mathrm{H}_{2}$.

## List of symbols in electrochemical study

$\alpha-\operatorname{transfer}$ coefficient.
$v$ - scan rate.
$E_{\text {cat }}$ - potential of catalytic event.
$E^{0}-$ standard redox potential.
$K_{\text {eq }}{ }^{\prime}$ - equilibrium constant for protonation of $\mathbf{1} \boldsymbol{\mu} \mathbf{H}^{-}$by HOTf.
$K_{\mathrm{eq}}{ }^{\prime \prime}$ - equilibrium constant for protonation of $\mathbf{1}^{-}$by TFA or TCA.
$k_{\mathrm{rxn}}{ }^{\prime}$ - reaction rate of the conversion from $\mathbf{1} \boldsymbol{\mu} \mathbf{H S H}$ to $\mathbf{1} \boldsymbol{\mu} \mathbf{H}$.
$k_{\text {rxn }}{ }^{\prime \prime}$ - reaction rate of the conversion from $\mathbf{1 \mu} \mathbf{H}^{-}$to $\mathbf{1}^{-}$.
$k_{\mathrm{PT}^{\prime}}$ - proton transfer rate of the conversion from $\mathbf{1} \mu \mathbf{H}$ to $\mathbf{1} \mu \mathbf{H S H}{ }^{+}$.
$k_{\mathrm{PT}}{ }^{\prime \prime}$ - proton transfer rate of the conversion from $\mathbf{1}^{-}$to $\mathbf{1} \mu \mathbf{H}$.
$k_{\mathrm{PT}}{ }^{\prime \prime \prime}-$ proton transfer rate of the conversion from $\mathbf{1} \boldsymbol{\mu} \mathbf{H}^{-}$to $\mathbf{1} \mu \mathbf{H S H}$ in the $\mathbf{1} \boldsymbol{\mu} \mathbf{H}-\mathrm{PhNH}_{3}{ }^{+}$system.
$k_{\mathrm{PT}}{ }^{\prime \prime \prime \prime}$ - proton transfer rate of the conversion from $\mathbf{1} \mu \mathrm{H}^{-}$to $\mathbf{1} \mu \mathrm{HSH}$ in the $\mathbf{1} \boldsymbol{\mu} \mathbf{H}-\mathrm{TFA} / \mathrm{TCA}$ system.
$k_{\mathrm{s}}{ }^{\prime}$ - electron transfer rate in the $\mathbf{1} \boldsymbol{\mu} \mathbf{H S H}^{+/ 0}$ process.
$k_{\mathrm{s}}{ }^{\prime \prime}$ - electron transfer rate in the $\mathbf{1} \boldsymbol{\mu} \mathbf{H}^{0 /-}$ process.
$k_{\text {PCET }}$ - apparent heterogeneous rate constant of the PCET event in the $\mathbf{1} \boldsymbol{\mu} \mathbf{H}-\mathrm{PhNH}_{3}{ }^{+}$system. $D$ - diffusion coefficient.

## DFT results

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

| Species $\mathbf{1}^{-}$ |  |  |  |
| :---: | :---: | :---: | :---: |
| Symbol | X | 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 |
| P | 1.319638 | 0.155122 | -0.014579 |
| C | 0.212355 | -2.266182 | -1.30238 |
| C | -0.297738 | -0.070936 | -2.723232 |
| C | -1.865038 | -0.996258 | 2.024833 |
| C | 0.074373 | 0.743474 | 2.857659 |
| C | 0.511511 | -1.832946 | 1.865416 |
| C | -3.203931 | 0.817358 | -0.11396 |
| C | -4.087373 | 1.775643 | 0.408577 |
| H | -3.682614 | 2.676264 | 0.862551 |
| C | -5.464251 | 1.578212 | 0.350238 |
| H | -6.139675 | 2.324083 | 0.758609 |
| C | -5.965461 | 0.411209 | -0.242724 |
| H | -7.038064 | 0.244508 | -0.295937 |
| C | -5.097155 | -0.538338 | -0.769993 |
| H | -5.49333 | -1.43937 | $-1.230111$ |
| C | -3.697673 | -0.357346 | -0.721046 |
| C | 2.941729 | -0.72314 | -0.040664 |
| C | 3.45439 | $-1.232375$ | -1.244344 |
| H | 2.877787 | -1.130574 | -2.158984 |
| C | 4.69675 | -1.869446 | -1.27579 |
| H | 5.078229 | -2.260336 | -2.214894 |
| C | 5.444028 | -2.005843 | -0.10375 |
| H | 6.40913 | -2.503751 | -0.127206 |
| C | 4.944526 | -1.501853 | 1.099611 |
| H | 5.519547 | -1.607098 | 2.015321 |
| C | 3.702235 | -0.865268 | 1.131227 |
| H | 3.319966 | -0.479151 | 2.071725 |
| C | 1.855315 | 1.912149 | -0.261175 |
| C | 2.192352 | 2.724849 | 0.833048 |
| H | 2.101522 | 2.337654 | 1.842642 |
| C | 2.635006 | 4.035244 | 0.638998 |
| H | 2.887226 | 4.650791 | 1.498059 |
| C | 2.74706 | 4.554432 | -0.652695 |
| H | 3.087359 | 5.574949 | -0.803487 |
| C | 2.414801 | 3.75591 | -1.74927 |


| H | 2.494385 | 4.152946 | -2.757482 |
| :--- | ---: | ---: | ---: |
| C | 1.972523 | 2.445534 | -1.555019 |
| H | 1.709115 | 1.839114 | -2.415363 |
| O | 0.625244 | -3.337537 | -1.452937 |
| O | -0.179225 | 0.304205 | -3.814532 |
| O | -2.870988 | -1.437784 | 2.38715 |
| O | 0.339346 | 1.365705 | 3.802525 |
| O | 1.039609 | -2.825713 | 2.161769 |

## Species 1

| Symbol | X | Y | Z |
| :---: | :---: | :---: | :---: |
| 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 |
| P | 1.313345 | 0.150364 | 0.050825 |
| C | 0.278148 | -2.056659 | -1.775774 |
| C | -0.050104 | 0.434884 | -2.645195 |
| C | -1.956799 | -1.020659 | 2.108895 |
| C | 0.103393 | 0.568626 | 2.940109 |
| C | 0.456075 | -1.952047 | 1.880461 |
| C | -3.243836 | 0.736032 | -0.135905 |
| C | -4.193458 | 1.589551 | 0.445435 |
| H | -3.86292 | 2.467478 | 0.992315 |
| C | -5.550532 | 1.305872 | 0.320489 |
| H | -6.283687 | 1.965735 | 0.773668 |
| C | -5.966039 | 0.172138 | -0.391762 |
| H | -7.024539 | -0.047746 | -0.493076 |
| C | -5.029703 | -0.67356 | -0.976682 |
| H | -5.35194 | -1.54857 | -1.532818 |
| C | -3.653407 | -0.401097 | -0.85751 |
| C | 2.896465 | -0.78247 | 0.029418 |
| C | 3.427401 | -1.294409 | -1.164994 |
| H | 2.892367 | -1.162307 | -2.099807 |
| C | 4.651546 | -1.96706 | -1.164762 |
| H | 5.049737 | -2.357865 | -2.096311 |
| C | 5.357644 | -2.136038 | 0.02735 |
| H | 6.307301 | -2.662534 | 0.027542 |
| C | 4.840576 | -1.624789 | 1.220375 |
| H | 5.386655 | -1.751145 | 2.150451 |
| C | 3.619213 | -0.95043 | 1.223013 |
| H | 3.229654 | -0.552744 | 2.155578 |
| C | 1.869737 | 1.901648 | -0.104911 |
| C | 1.299926 | 2.931589 | 0.660316 |


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

## Species $\mathbf{1} \boldsymbol{\mu} \mathbf{H}$

| Symbol | X | 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 |
| P | 1.35092 | 0.102842 | -0.132695 |
| C | 0.22072 | -2.461229 | -1.287367 |
| C | -0.451803 | -0.366204 | -2.723997 |
| C | -1.833751 | -0.427729 | 2.39581 |
| C | 0.182252 | 1.419103 | 2.360166 |
| C | 0.649453 | -1.255719 | 2.482727 |
| C | -3.218709 | 0.681009 | -0.143535 |
| C | -4.107518 | 1.661659 | 0.328457 |
| H | -3.715191 | 2.616459 | 0.666832 |
| C | -5.474559 | 1.41049 | 0.365933 |
| H | -6.157211 | 2.169286 | 0.735063 |
| C | -5.958801 | 0.171691 | -0.077468 |
| H | -7.024812 | -0.035466 | -0.052515 |
| C | -5.085622 | -0.797378 | -0.556835 |
| H | -5.470135 | -1.751734 | -0.904302 |
| C | -3.694718 | -0.563275 | -0.605717 |
| C | 2.930547 | -0.824973 | 0.009702 |
| C | 3.448361 | -1.451369 | -1.136788 |
| H | 2.901634 | -1.403813 | -2.073725 |
| C | 4.665747 | -2.131219 | -1.083407 |
| H | 5.051964 | -2.612524 | -1.976861 |
| C | 5.381989 | -2.193345 | 0.114109 |
| H | 6.327465 | -2.725604 | 0.156038 |
|  |  |  |  |


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

## Species $\mathbf{1} \boldsymbol{\mu} \mathbf{H}^{-}$

| Symbol | X | 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 |
| P | 1.355745 | 0.122273 | -0.026497 |
| C | 0.212288 | -2.309933 | -1.414061 |
| C | -0.414885 | -0.098051 | -2.660243 |
| C | -1.7314 | -0.623213 | 2.416497 |
| C | 0.267945 | 1.126381 | 2.638566 |
| C | 0.796994 | -1.591814 | 2.630425 |
| C | -3.325497 | 0.766322 | -0.299288 |
| C | -4.268454 | 1.689765 | 0.186788 |
| H | -3.92284 | 2.661626 | 0.529861 |
| C | -5.626344 | 1.378891 | 0.232779 |
| H | -6.33627 | 2.107167 | 0.614929 |
| C | -6.06212 | 0.126098 | -0.211898 |
| H | -7.117137 | -0.132585 | -0.179927 |
| C | -5.137972 | -0.797953 | -0.69581 |
| H | -5.47633 | -1.771719 | -1.040164 |
| C | -3.763203 | -0.499663 | -0.749158 |


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

## Species $\mathbf{1} \boldsymbol{\mu} \mathbf{H S H}^{+}$

| Symbol | X | 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 |
| P | 1.356903 | 0.1207 | -0.097756 |
| C | 0.31717 | -2.414424 | -1.351289 |
| C | -0.269998 | -0.237799 | -2.736458 |
| C | -1.886498 | -0.492931 | 2.365581 |
| C | 0.143517 | 1.331156 | 2.415131 |
| C | 0.584928 | -1.334025 | 2.453155 |
| C | -3.215834 | 0.696286 | -0.146708 |
| C | -4.099488 | 1.648255 | 0.381673 |
| H | -3.710167 | 2.586903 | 0.762552 |


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

## Species $\mathbf{1} \boldsymbol{\mu} \mathbf{H S H}$

| Symbol | X | 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 |
| P | 1.313572 | 0.13449 | -0.004672 |


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

## Species $\mathbf{1} \boldsymbol{\mu} \mathbf{H S H} *$

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


| O | 0.756853 | -3.3058 | -1.503156 |
| :--- | ---: | ---: | ---: |
| O | -0.096017 | 0.364926 | -3.736061 |
| O | -2.770813 | -0.69684 | 2.988256 |
| O | 0.779218 | 1.886507 | 3.370885 |
| O | 1.148573 | -2.674406 | 2.97734 |
| H | -0.797009 | -1.312928 | 0.48769 |
| H | -2.718663 | -2.594462 | -0.539692 |

## Species $\mathbf{1} \boldsymbol{\mu} \mathbf{H S H N H}_{\mathbf{2}} \mathbf{P h}^{+}$

| Symbol | X | 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 |
| P | -2.31186 | -0.311688 | 0.214107 |
| C | -0.299304 | -2.273145 | -0.904698 |
| C | 0.329807 | -1.468273 | 1.520687 |
| C | -0.228128 | 2.204991 | -2.270513 |
| C | -2.458817 | 2.591282 | -0.742214 |
| C | -2.3186 | 0.669109 | -2.649437 |
| C | 1.683261 | 1.985268 | 0.15558 |
| C | 2.075491 | 3.306209 | 0.4275 |
| H | 1.372724 | 3.983765 | 0.903985 |
| C | 3.352008 | 3.742574 | 0.087546 |
| H | 3.648918 | 4.765303 | 0.296971 |
| C | 4.245465 | 2.854586 | -0.524023 |
| H | 5.243588 | 3.186259 | -0.794022 |
| C | 3.865074 | 1.542291 | -0.78858 |
| H | 4.564643 | 0.859581 | -1.261737 |
| C | 2.578923 | 1.083083 | -0.448216 |
| C | -3.554828 | -1.531799 | -0.364933 |
| C | -3.446858 | -2.859873 | 0.082226 |
| H | -2.621715 | -3.150044 | 0.725956 |
| C | -4.397958 | -3.810496 | -0.289333 |
| H | -4.30147 | -4.833128 | 0.062504 |
| C | -5.468445 | -3.447184 | -1.110241 |
| H | -6.207228 | -4.187447 | -1.400378 |
| C | -5.587142 | -2.129537 | -1.554932 |
| H | -6.418239 | -1.84008 | -2.190261 |
| C | -4.63731 | -1.174497 | -1.184807 |
| H | -4.752355 | -0.153262 | -1.532271 |
| C | -3.045945 | 0.345602 | 1.768016 |
| C | -4.390924 | 0.759535 | 1.778513 |
| H | -4.998524 | 0.668685 | 0.884059 |


| C | -4.961997 | 1.282828 | 2.937198 |
| :--- | ---: | ---: | ---: |
| H | -6.000772 | 1.598943 | 2.927281 |
| C | -4.202735 | 1.399044 | 4.104834 |
| H | -4.649536 | 1.806185 | 5.006754 |
| C | -2.871362 | 0.982345 | 4.108242 |
| H | -2.277008 | 1.058784 | 5.013712 |
| C | -2.295156 | 0.45707 | 2.949252 |
| H | -1.262839 | 0.131773 | 2.973695 |
| O | -0.384632 | -3.252191 | -1.497733 |
| O | 0.637024 | -1.947526 | 2.520633 |
| O | 0.482217 | 2.80629 | -2.935293 |
| O | -3.152179 | 3.443325 | -0.417534 |
| O | -2.873595 | 0.308762 | -3.585583 |
| H | -0.419475 | -0.019926 | -1.569372 |
| C | 6.203425 | -2.102691 | -0.533193 |
| C | 7.49206 | -1.635472 | -0.795161 |
| C | 8.168491 | -0.865949 | 0.154988 |
| C | 7.558904 | -0.55916 | 1.372939 |
| C | 6.269845 | -1.018929 | 1.649711 |
| C | 5.617043 | -1.785194 | 0.689535 |
| H | 5.672279 | -2.702632 | -1.265729 |
| H | 7.964574 | -1.876654 | -1.741608 |
| H | 9.171202 | -0.507579 | -0.05369 |
| H | 8.08273 | 0.036271 | 2.113185 |
| H | 5.791725 | -0.782981 | 2.59572 |
| N | 4.242884 | -2.253694 | 0.95554 |
| H | 3.516148 | -1.697681 | 0.402835 |
| H | 4.126743 | -3.239682 | 0.702624 |
| H | 4.003535 | -2.168863 | 1.947189 |
|  |  |  |  |

## Species $\mathbf{1} \boldsymbol{\mu} \mathbf{H S H N H} \mathbf{2} \mathbf{P h}$

| Symbol | X | 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 |
| P | -2.137117 | -0.322878 | 0.175906 |
| C | -0.725564 | -0.800665 | -2.390524 |
| C | 0.489575 | -1.939235 | -0.333077 |
| C | -0.553505 | 3.325913 | -0.326034 |
| C | -2.483216 | 2.426804 | 1.295109 |
| C | -2.78116 | 2.290412 | -1.497285 |
| C | 2.147716 | 1.558129 | 0.647981 |
| C | 2.768269 | 2.44342 | 1.54886 |


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


| H | 6.018247 | -0.224906 | 2.25326 |
| :--- | ---: | ---: | ---: |
| H | 3.961335 | -0.703857 | 0.949455 |
| N | 3.772651 | -2.264978 | -1.214718 |
| H | 3.214752 | -1.375084 | -1.441714 |
| H | 3.982788 | -2.726251 | -2.10353 |
| H | 3.132862 | -2.879948 | -0.698254 |

## Species $\mathrm{PhNH}_{2}$

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

## Species $\mathrm{PhNH}_{3}{ }^{+}$

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

## Species $\mathrm{OEt}_{2}$

| Symbol | X | Y | Z |
| :--- | ---: | ---: | ---: |
| O | -0.000002 | -0.265399 | -0.000369 |
| C | -1.18442 | 0.519243 | -0.000349 |
| H | -1.204525 | 1.175611 | -0.886296 |
| H | -1.203977 | 1.175939 | 0.885348 |
| C | -2.38536 | -0.411314 | 0.000289 |
| H | -3.314466 | 0.166544 | 0.000465 |
| H | -2.377883 | -1.052108 | -0.886498 |
| H | -2.377402 | -1.051963 | 0.887181 |
| C | 1.184416 | 0.519241 | 0.000387 |
| H | 1.204121 | 1.17532 | 0.886552 |
| H | 1.204372 | 1.176222 | -0.88509 |
| C | 2.385365 | -0.411312 | -0.000056 |
| H | 2.377708 | -1.051749 | -0.887108 |
| H | 3.314467 | 0.166554 | 0.0002 |
| H | 2.377592 | -1.052321 | 0.88657 |

## Species $\mathrm{H}\left(\mathrm{OEt}_{2}\right)_{2}{ }^{+}$

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


| H | 1.20633 | 0.563296 | -2.578276 |
| :--- | ---: | ---: | ---: |
| H | 1.391677 | -1.088105 | -3.194104 |
| C | 2.916355 | 0.602476 | 1.379677 |
| H | 2.646307 | 1.650914 | 1.229713 |
| H | 3.368546 | 0.500893 | 2.370901 |
| H | 3.67168 | 0.323315 | 0.640633 |
| H | -0.289791 | -0.017074 | 0.058953 |

Species Fc

| Symbol | X | Y | Z |
| :---: | :---: | :---: | :---: |
| Fe | 0 | 0 | 0 |
| C | -0.000898 | -0.008984 | 2.082754 |
| C | 1.341113 | -0.003377 | 1.593769 |
| C | 1.525332 | -1.17416 | 0.79673 |
| C | 0.297044 | -1.903085 | 0.792658 |
| C | -0.6464 | -1.182808 | 1.587213 |
| H | -0.458019 | 0.757794 | 2.693565 |
| H | 2.078171 | 0.768612 | 1.769066 |
| H | 2.426418 | -1.444109 | 0.262725 |
| H | 0.105387 | -2.821889 | 0.255049 |
| H | -1.677833 | -1.460762 | 1.757035 |
| C | 0.000898 | 0.008984 | -2.082754 |
| C | -1.341113 | 0.003377 | -1.593769 |
| C | -1.525332 | 1.17416 | -0.79673 |
| C | -0.297044 | 1.903085 | -0.792658 |
| C | 0.6464 | 1.182808 | -1.587213 |
| H | 0.458019 | -0.757794 | -2.693565 |
| H | -2.078171 | -0.768612 | -1.769066 |
| H | -2.426418 | 1.444109 | -0.262725 |
| H | -0.105387 | 2.821889 | -0.255049 |
| H | 1.677833 | 1.460762 | -1.757035 |

Species Fc ${ }^{+}$

| Symbol | X | Y | Z |
| :--- | ---: | ---: | ---: |
| Fe | 0 | 0 | 0 |
| C | 0.003556 | -0.016175 | 2.096606 |
| C | 1.34702 | -0.010849 | 1.607531 |
| C | 1.531393 | -1.18262 | 0.809406 |
| C | 0.301918 | -1.912314 | 0.805312 |
| C | -0.642421 | -1.191382 | 1.600757 |
| H | -0.457996 | 0.758264 | 2.693181 |
| H | 2.07843 | 0.768696 | 1.769035 |
| H | 2.426442 | -1.443553 | 0.262099 |


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

$\mathrm{TS}_{1}$

| Symbol | X | 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 |
| P | 1.341333 | 0.15278 | 0.016998 |
| C | 0.385417 | -2.276237 | -1.361427 |
| C | -0.208163 | -0.030716 | -2.672675 |
| C | -1.752946 | -0.655806 | 2.424752 |
| C | 0.330138 | 0.99681 | 2.711671 |
| C | 0.719697 | -1.779872 | 2.48145 |
| C | -3.40391 | 0.75101 | -0.279085 |
| C | -4.331662 | 1.657671 | 0.264278 |
| H | -3.97413 | 2.609591 | 0.645187 |
| C | -5.690592 | 1.352588 | 0.312113 |
| H | -6.385555 | 2.071182 | 0.73582 |
| C | -6.157247 | 0.129589 | -0.178271 |
| H | -7.214453 | -0.112968 | -0.140095 |
| C | -5.257385 | -0.790627 | -0.715746 |
| H | -5.609757 | -1.746028 | -1.092367 |
| C | -3.898139 | -0.473541 | -0.763169 |
| C | 2.934588 | -0.74746 | -0.198332 |
| C | 3.467412 | -0.922022 | -1.487855 |
| H | 2.929743 | -0.544329 | -2.352977 |
| C | 4.6834 | -1.580037 | -1.668997 |
| H | 5.079848 | -1.712107 | -2.671419 |
| C | 5.388295 | -2.067566 | -0.564583 |
| H | 6.334688 | -2.580858 | -0.706301 |
| C | 4.873507 | -1.890274 | 0.720124 |
| H | 5.418626 | -2.261261 | 1.583029 |


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

$\mathrm{TS}_{2}$

| Symbol | X | 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 |
| P | 1.315244 | -0.007632 | 0.129916 |
| C | 0.603564 | 0.226499 | -2.806393 |
| C | -0.224237 | 2.296877 | -1.413071 |
| C | -1.882141 | -2.199859 | 1.29456 |
| C | -0.173218 | -0.885337 | 3.043607 |
| C | 0.652559 | -2.694056 | 1.155836 |
| C | -3.278238 | 0.458039 | 0.254174 |
| C | -4.236948 | 0.433919 | 1.2784 |
| H | -3.913254 | 0.546001 | 2.308881 |
| C | -5.591122 | 0.282721 | 0.984964 |
| H | -6.318255 | 0.271048 | 1.790944 |
| C | -6.004826 | 0.154852 | -0.342537 |
| H | -7.057304 | 0.03916 | -0.581862 |
| C | -5.06093 | 0.166111 | -1.368674 |
| H | -5.37794 | 0.051881 | -2.400829 |
| C | -3.697277 | 0.312799 | -1.080092 |
| C | 2.749007 | -0.94953 | -0.541402 |


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

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