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CATALYSIS

Supporting Information

Efficient Photocatalytic Water Reduction Using In Situ Generated Knölker's Iron Complexes

Yuan-Yuan Sun,[a] Hai Wang,[b] Nan-Yu Chen,[a] Alastair J J Lennox,[a, c] Aleksej Friedrich,[d] Liang-Min Xia,[a] Stefan Lochbrunner,*[d] Henrik Junge,[c] Matthias Beller,*[c] Shaolin Zhou,*[b] and Shu-Ping Luo*[a]

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General methods

Compounds **1a-1g** and Cu(Xantphos)(2,9-dimethyl-4,7-diphenyl- 1,10-phenanthroline)PF_6 (CuPS) were synthesized according to literature procedures and stored under normal temperature and atmosphere.[1-3] All catalytic experiments were carried out under an argon atmosphere with exclusion of air. THF, TEA, and doubly distilled water were degassed and purified by standard laboratory methods prior to use. The amount of gas liberated was measured by a gas burette. Details on the equipment and the experimental set-up have been published elsewhere. The relative composition of the evolved gas was determined by GC (gas chromatograph Fuli 9790II, carboxen 1000, TCD, external calibration). The light source was a 300W Xe lamp.

Typical procedure for light-driven water reduction. A double-walled thermostatically controlled reaction vessel is evacuated and purged with argon. The copper photosensitizer, Knölker's Iron and the base are added as solids. The corresponding solvent mixture (THF/TEA/H_2O, 4:3:1) is added and the system is taken to 25 ℃ before switching on the light source. It is then stirred at 25 ℃ until no further gas evolution is observed. All given values are the averages of at least two experiments. The results differ between 1 and 17% except for volumes <10 mL (up to 40%).

The turnover number (TON) was calculated from the amount of hydrogen produced using the following equations:

Supplementary Equation 1

$$TON = \frac{V_{H_2}}{24.48 * n_{cat}} * 1000$$

V_{H2}: the volume of H_2.

n_{cat}: amount of catalyst (metal atom, [μmol])

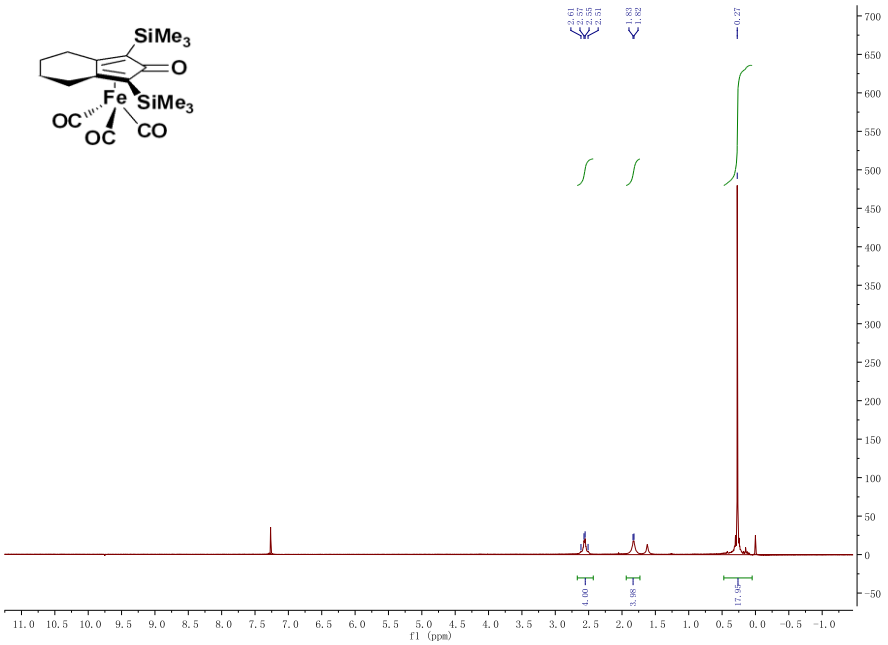
Supplementary Equation 2

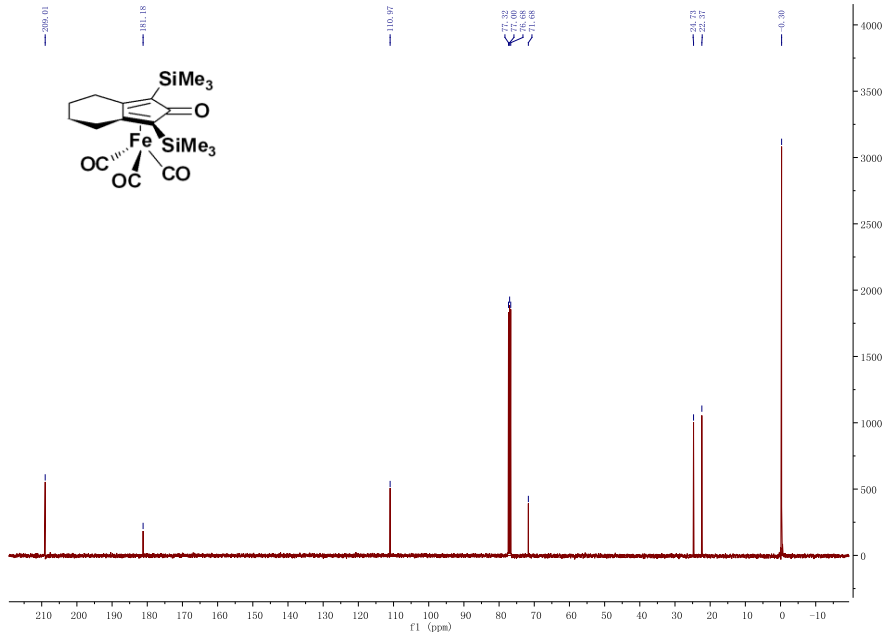
$$V_{m,H_2,25.0°C} = \frac{RT}{p} + b - \frac{a}{RT} = 24.48 \frac{mL}{mmol}$$

R: 8.3145 x 10^6 cm^3 Pa mol^{-1} K^{-1}
T: 298.15 K
p: 101325 Pa
b: 26.6 cm^3 mol^{-1}
a: 24.7 x 10^9 cm^6 Pa mol^{-2}

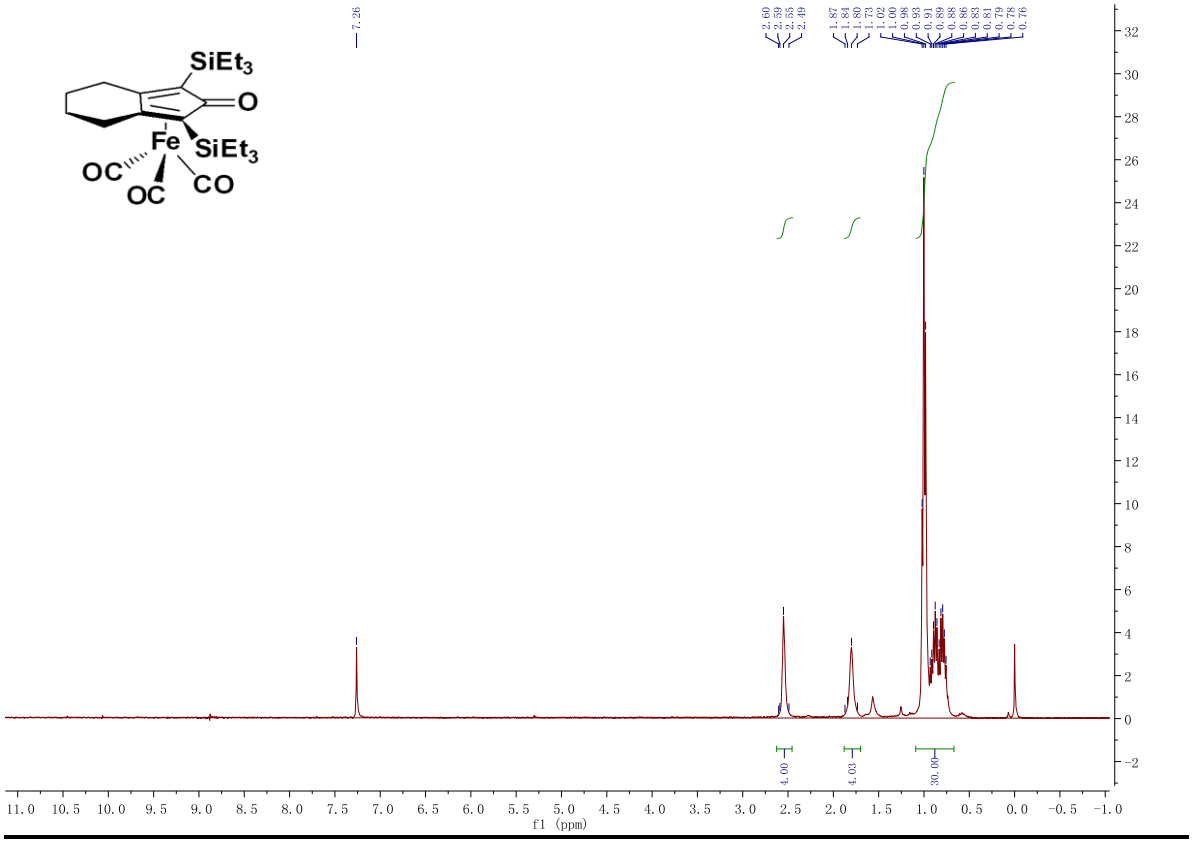
The characterization of compounds 1a-1g:

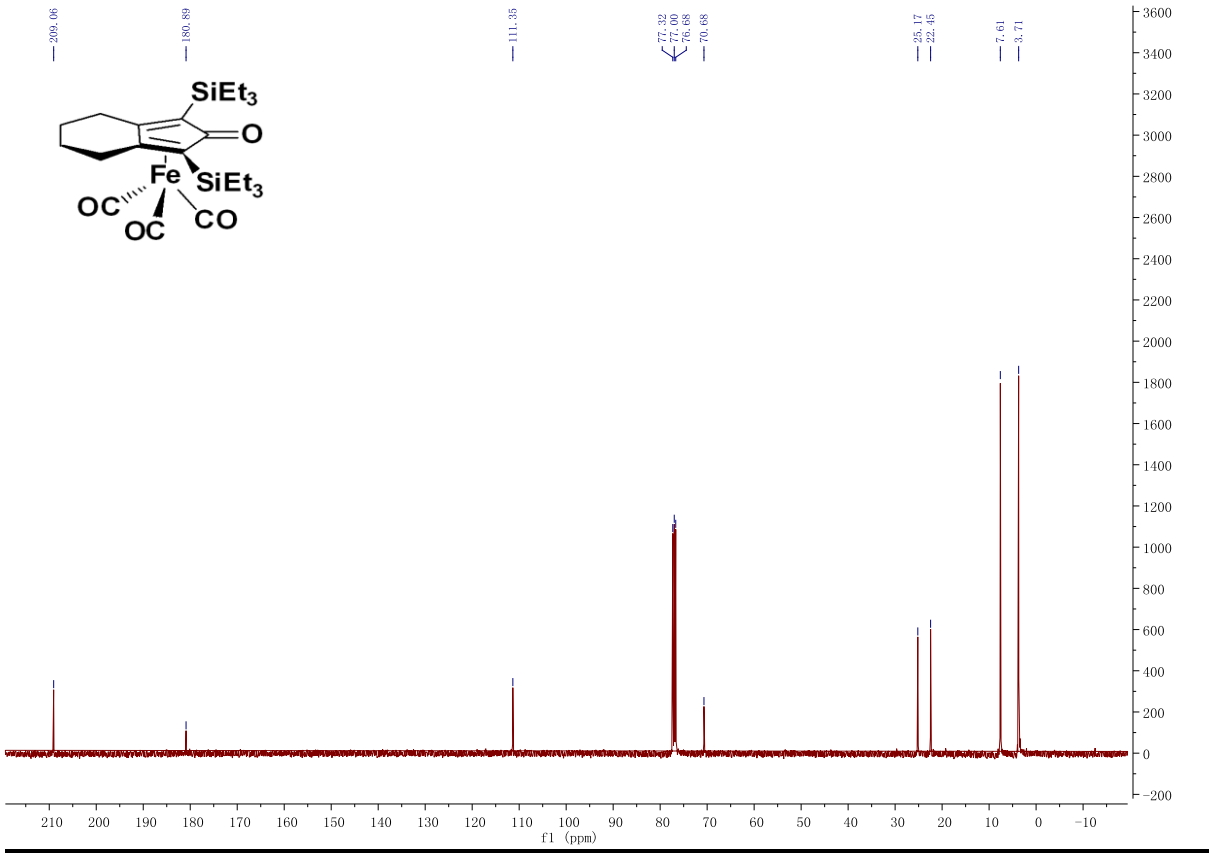
1a: **^{1}H NMR** (400 MHz, $CDCl_3$): δ 0.27 (s, 18H), 1.83-1.82 (m, 4H), 2.61-2.51 (m, 4H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ = -0.30, 22.37, 24.73, 71.68, 110.97, 181.18, 209.01. **HRMS (ESI-TOF/MS, m/z)** calcd. for $C_{18}H_{27}Fe_2O_4Si_2$ $(M+H)^+$, 419.07922; found 419.07996.





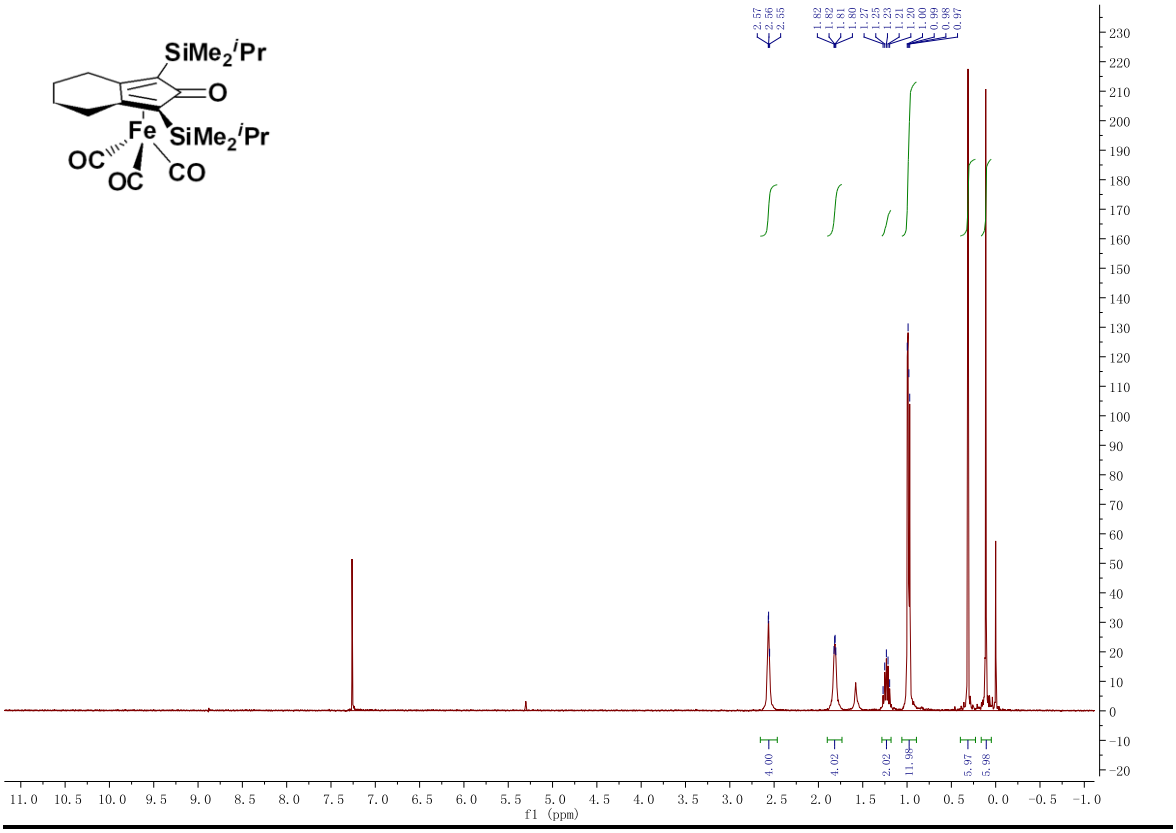
1b: **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 0.76-1.02 (m, 30 H), 1.73-1.87 (m, 4 H), 2.49-2.60 (m, 4 H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 3.71, 7.61, 22.45, 25.17, 70.68, 111.35, 180.89, 209.06. **HRMS (ESI-TOF/MS, m/z)** calcd. for $C_{24}H_{39}FeO_4Si_2$ $(M+H)^+$, 503.1731; found 503.1740.

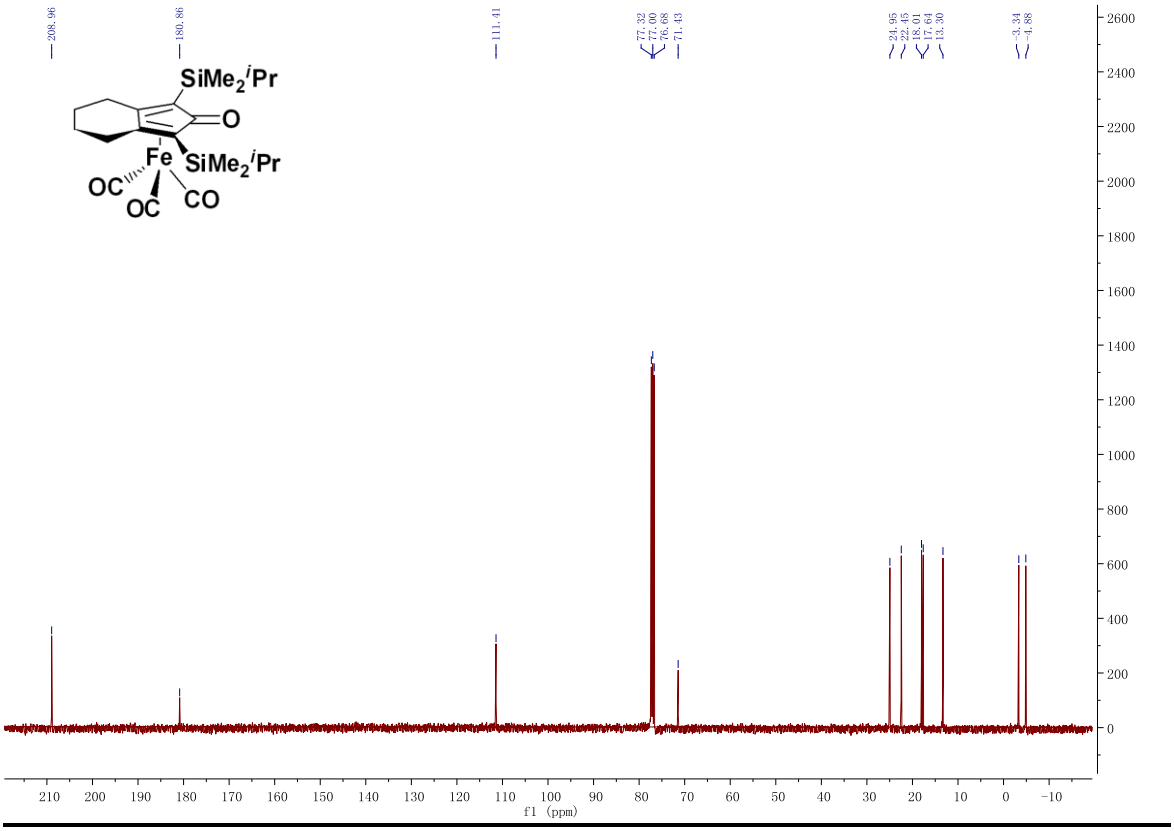




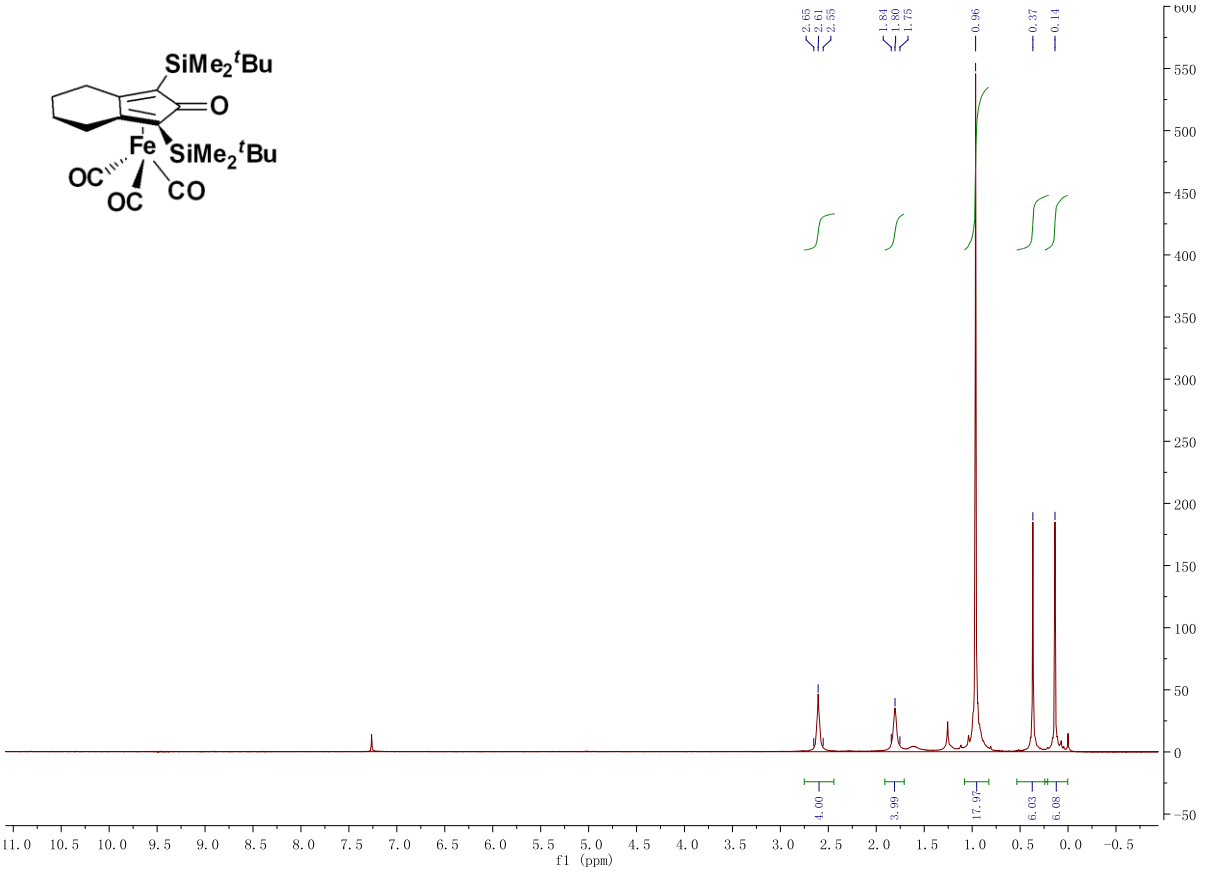
1c: **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 0.11 (s, 6 H), 0.31 (s, 6 H), 1.00(d, J=4.0Hz, 6H), 0.98 (d, J=4.0Hz, 6H), 1.20-1.27(m, 2 H), 1.80-1.82 (m, 4 H), 2.55-2.57 (m, 4H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ = -4.88, -3.34, 13.31,

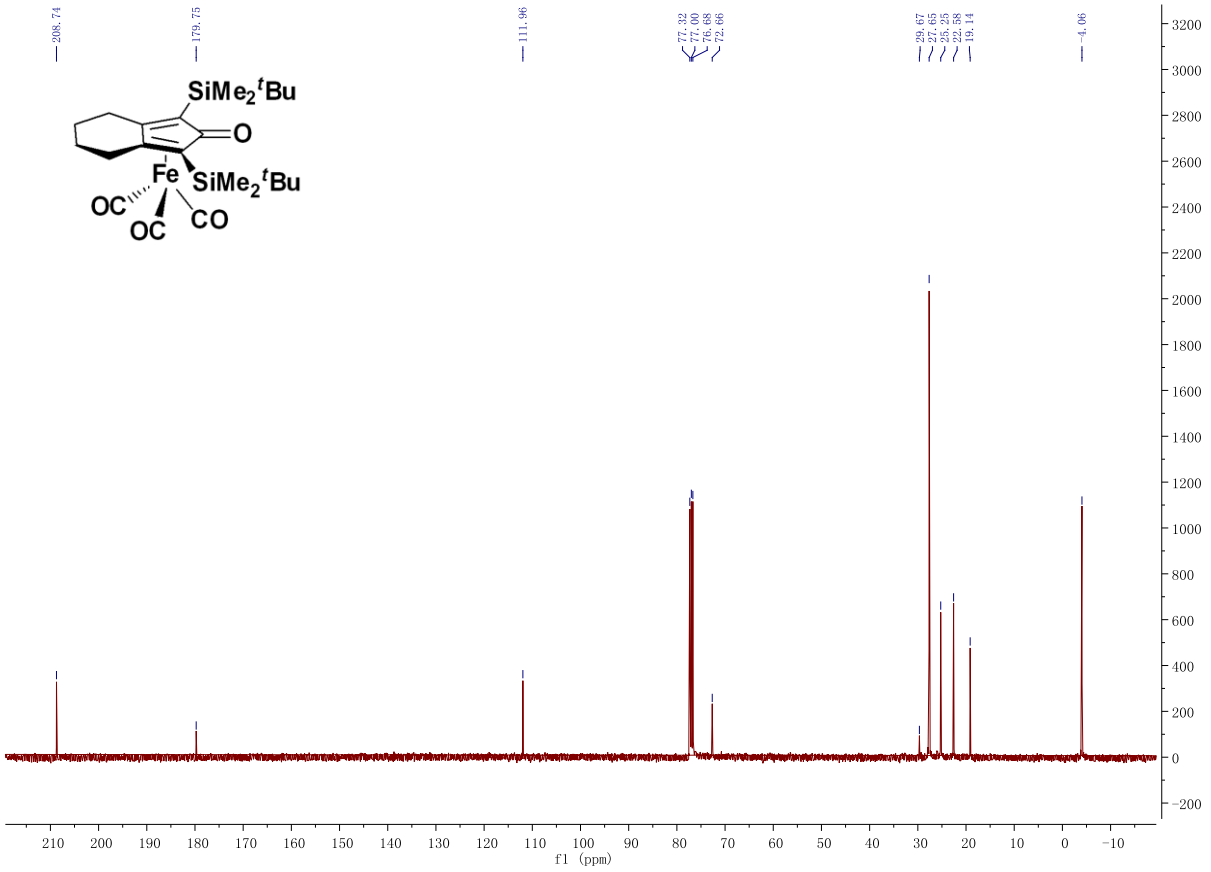
17.64, 18.01, 22.45, 24.95, 71.43, 111.41, 180.86, 208.96. **HRMS (ESI-TOF/MS, m/z)** calcd. for $C_{22}H_{35}FeO_4Si_2$ $(M+H)^+$, 475.1418; found 475.1423.



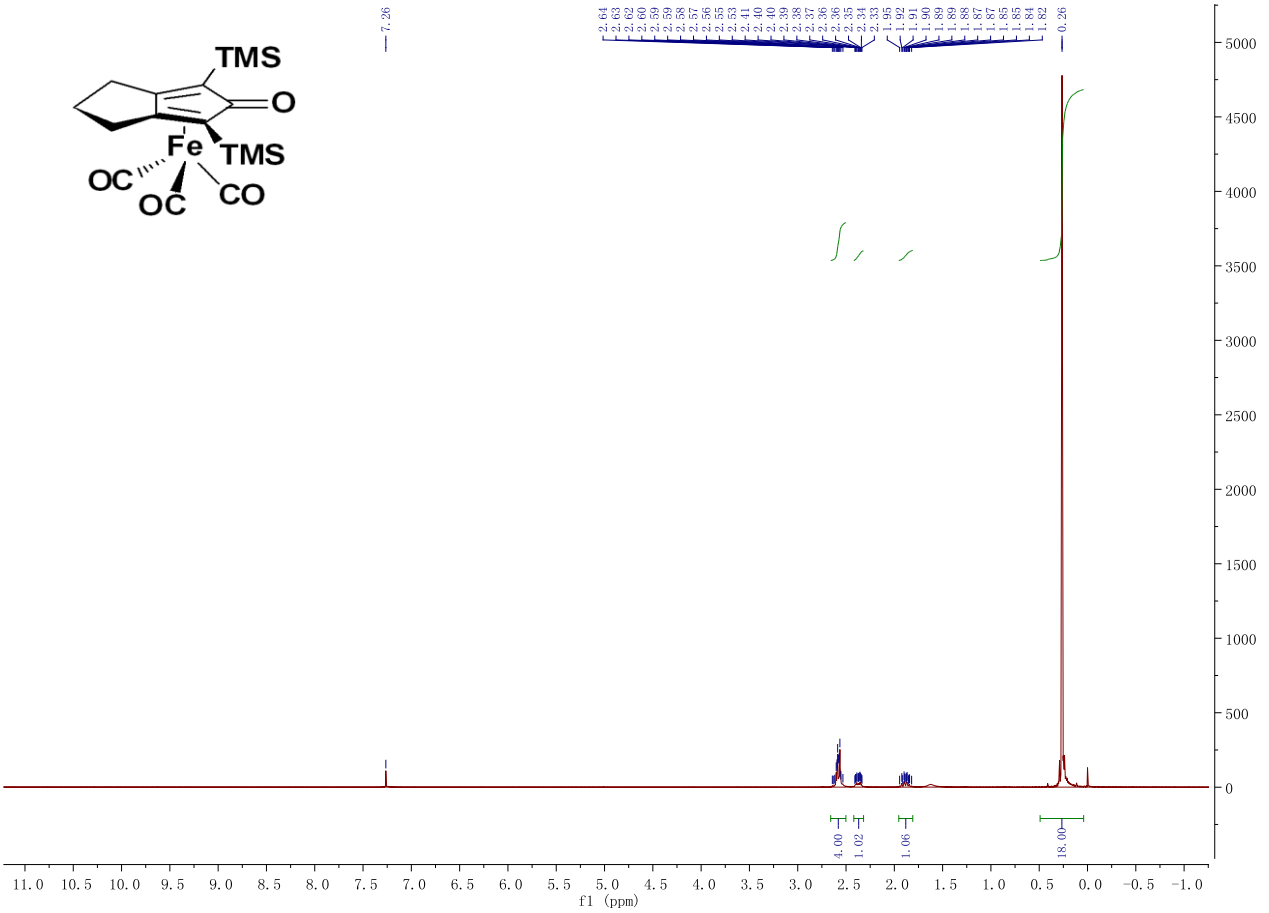


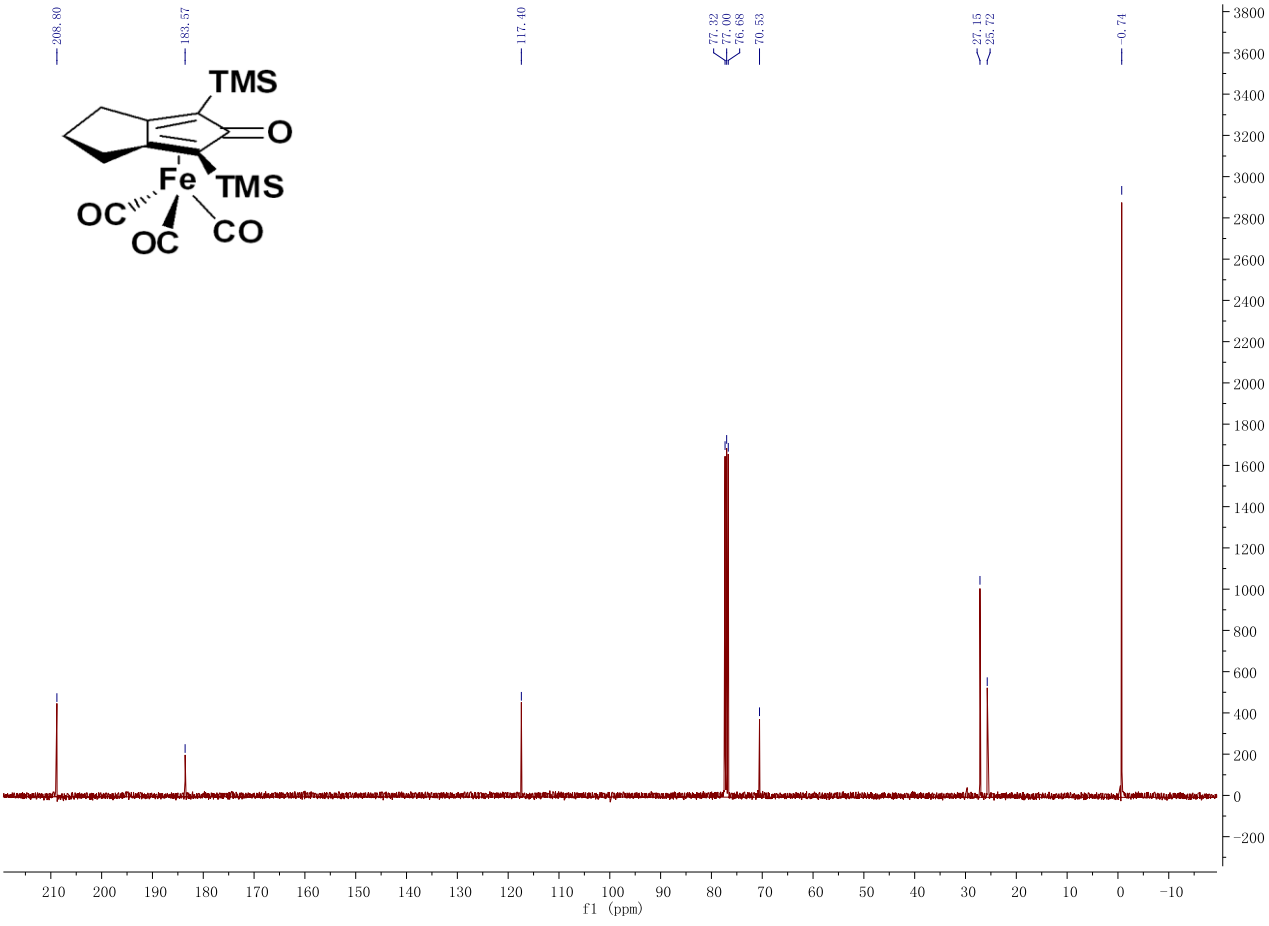
1d: **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 0.14 (s, 6 H), 0.37 (s, 6 H), 0.96 (s, 18 H), 1.75-1.84 (s, 4H), 2.55-2.65 (s, 4 H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ = -4.06, 19.14, 22.58, 25.25, 27.65, 29.67, 72.66, 111.96, 179.75, 208.74. **HRMS (ESI-TOF/MS, m/z)** calcd. for $C_{24}H_{39}FeO_4Si_2$ $(M+H)^+$, 503.1731; found 503.1740.



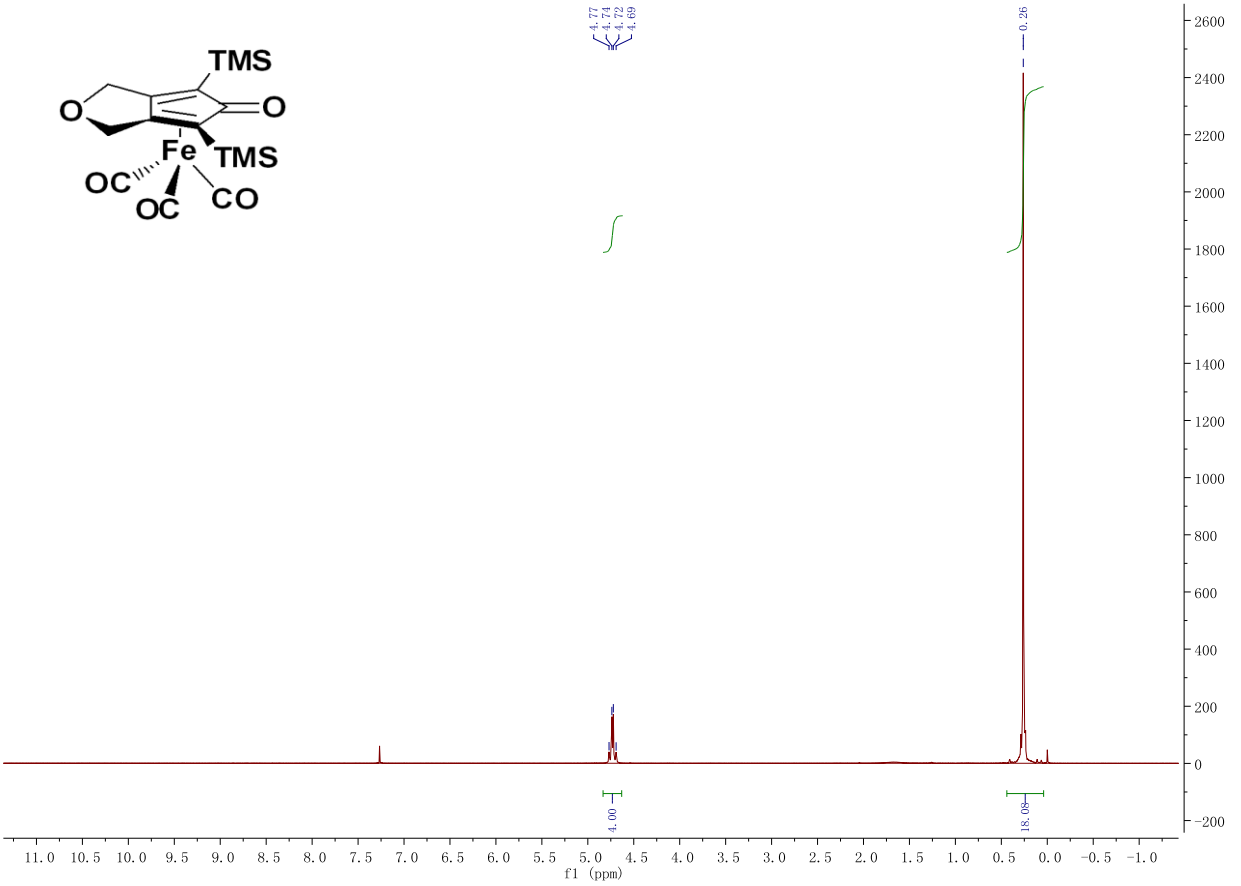


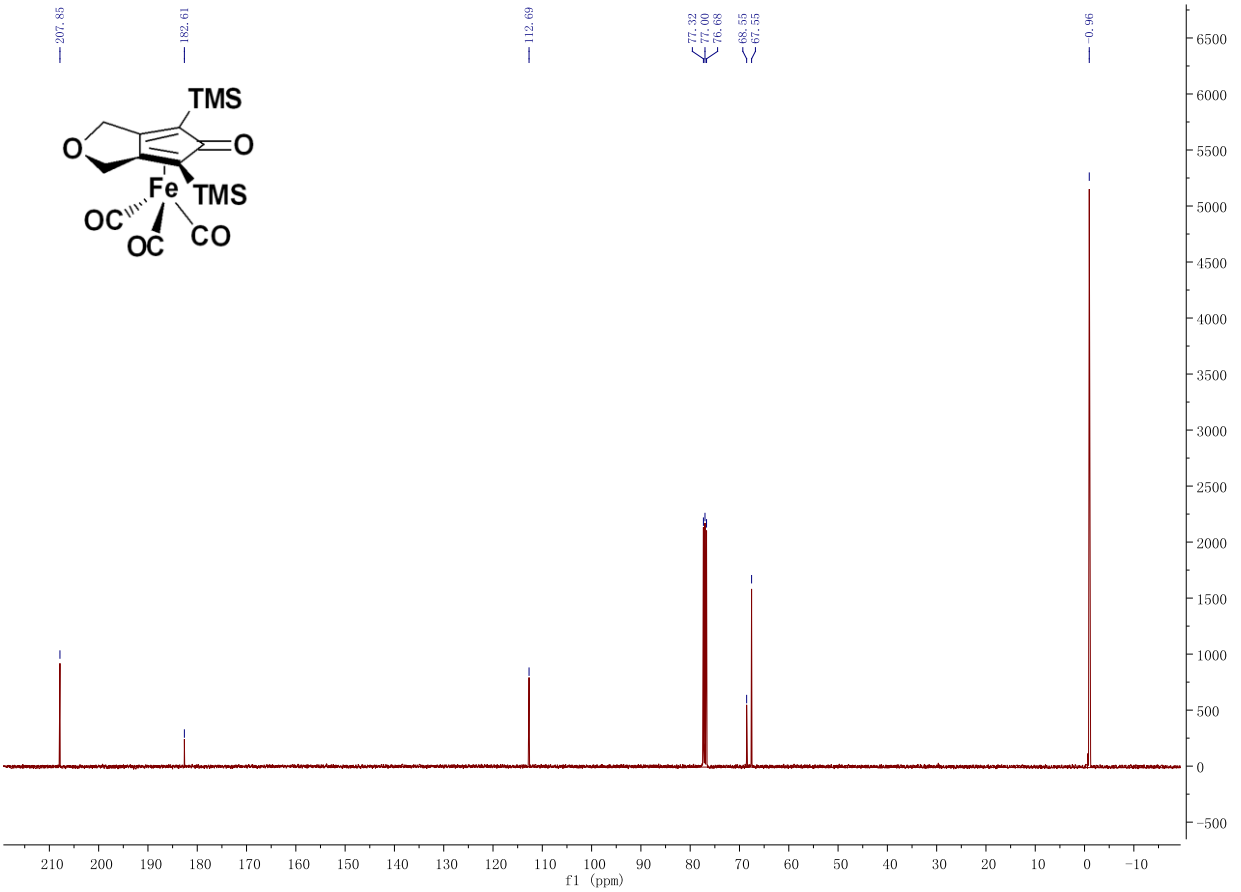
1e:^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.26 (s, 18H), 1.82-1.95 (m, 1H), 2.33-2.41 (m, 1H), 2.53-2.64 (m, 4H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ = -0.74, 25.72, 27.15, 70.53, 117.40, 183.57, 208.80. **HRMS (ESI-TOF/MS, m/z)** calcd. for $C_{17}H_{25}FeO_4Si_2$ $(M+H)^+$, 405.0636; found 405.0645



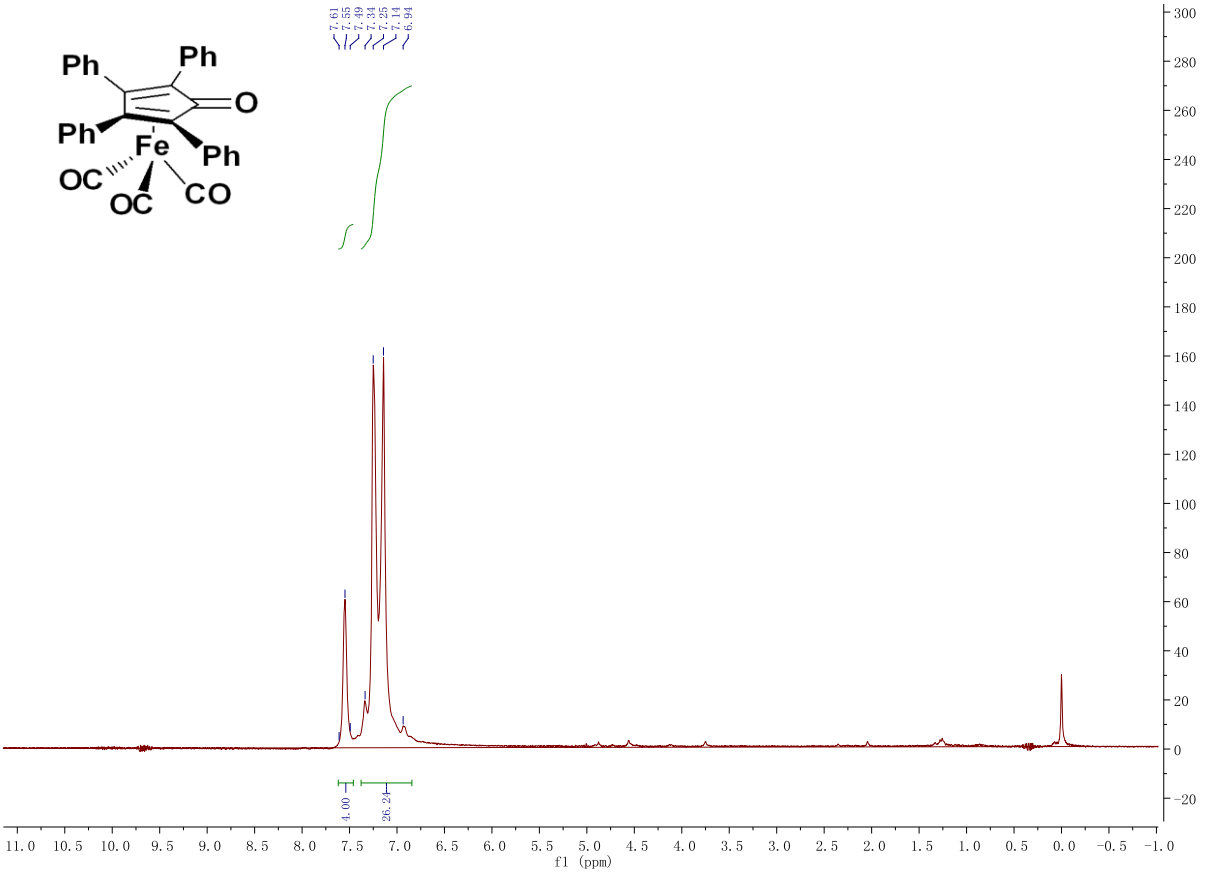


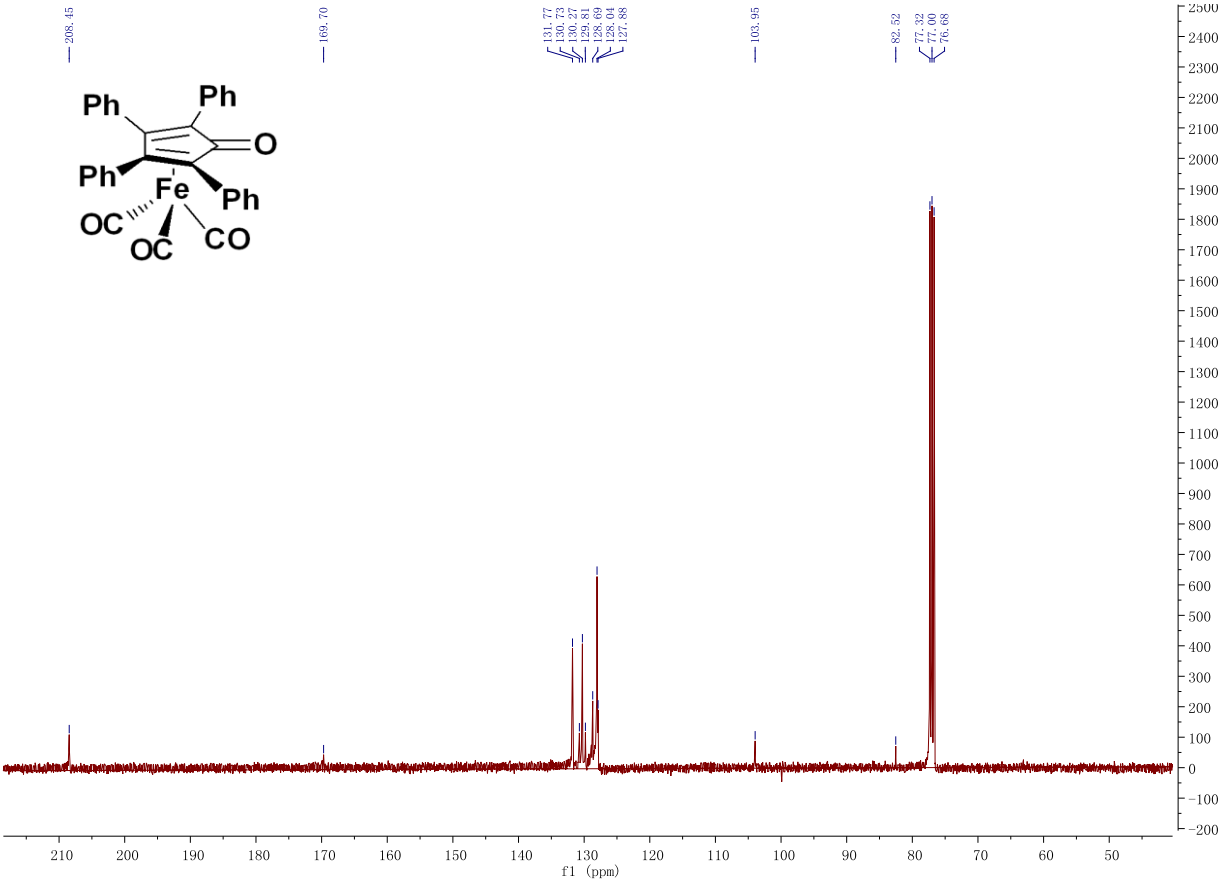
1f: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.26 (s, 18H), 4.73 (AB system, J = 20.0 Hz, 4H); **^{3}C NMR** (75 MHz, $CDCl_3$): δ = -0.96, 67.55, 68.55, 112.69, 182.61, 207.85. **HRMS (ESI-TOF/MS, m/z)** calcd. For $C_{16}H_{23}FeO_5Si_2$ $(M+H)^+$, 407.0428; found 407.0438.

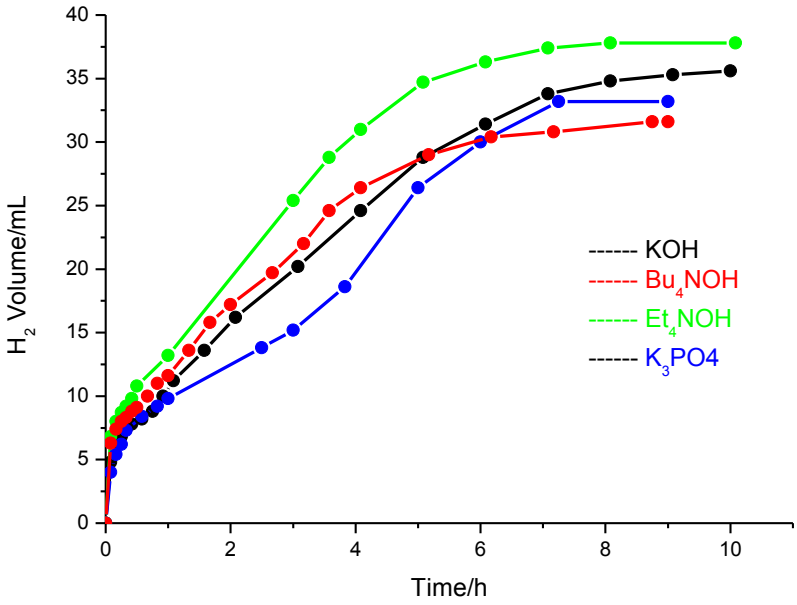




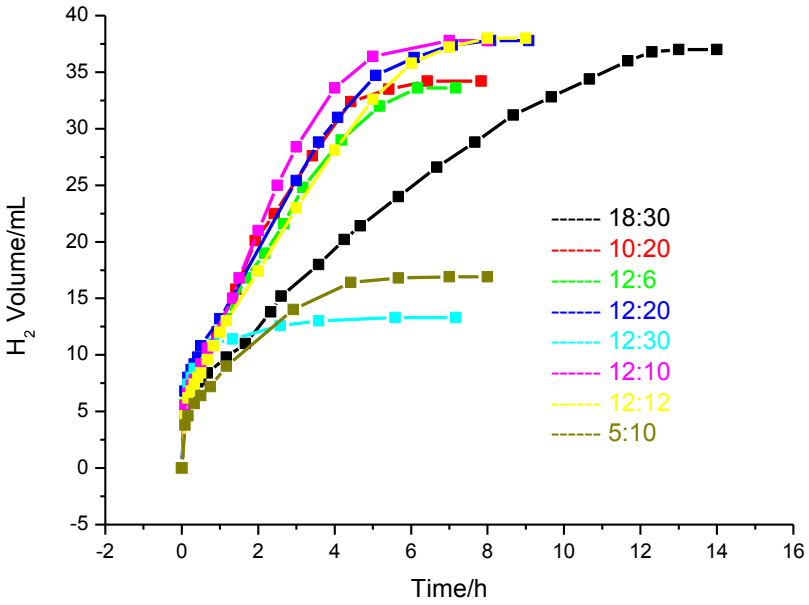
1g : ^{1}H NMR (400 MHz, $CDCl_3$):δ 6.94-7.34 (m, 16H), 7.49-7.61 (m, 4H); **^{13}C NMR** (75 MHz, $CDCl_3$); δ = 82.52, 103.95, 127.88, 128.04, 128.69, 129.81, 130.27, 130.73, 131.77, 169.70, 208.45.



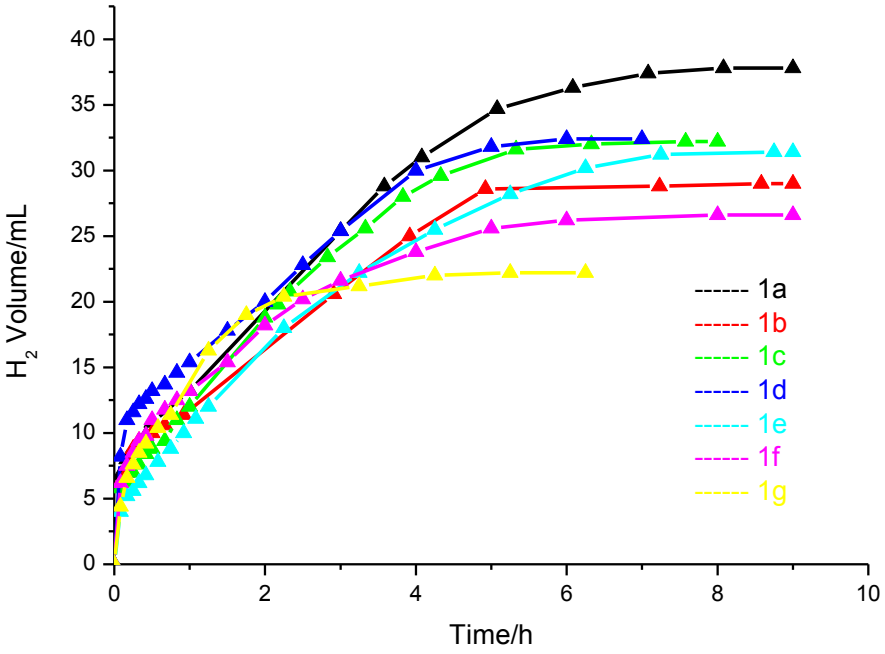




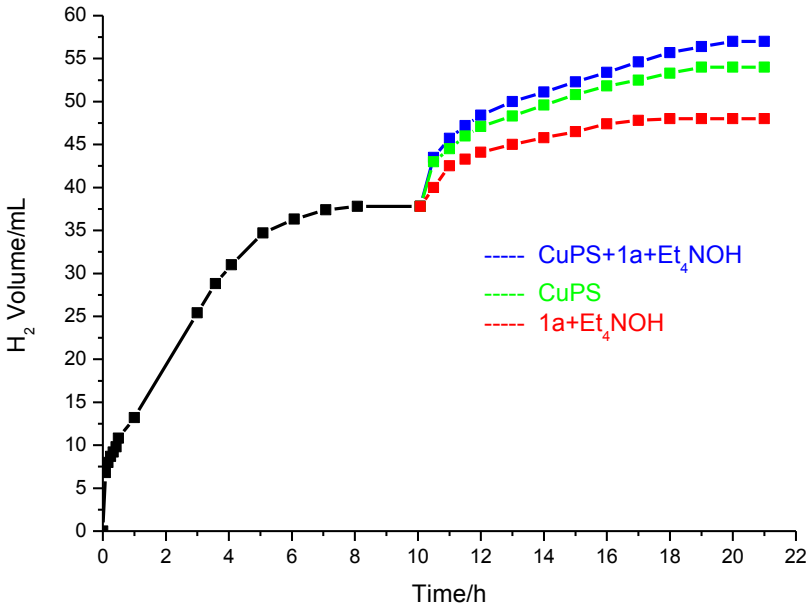
Supplementary Figure 1 Screening of bases (Cu PS 3.5 μmol, Cat. 12 μmol, base 12 μmol, 10 mL THF/TEA/H_2O (4/3/1), 25 ℃, Xe-light irradiation (output 1.5 W), without light filter).



Supplementary Figure 2 Screening of the amount effect of cat. and base (Cat. :base, μmol).



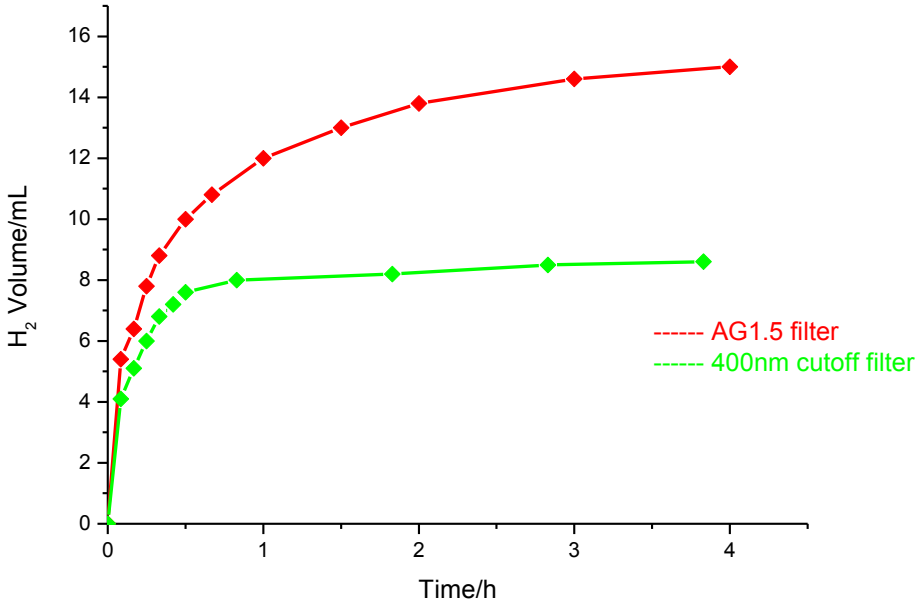
Supplementary Figure 3 Screening of cat..



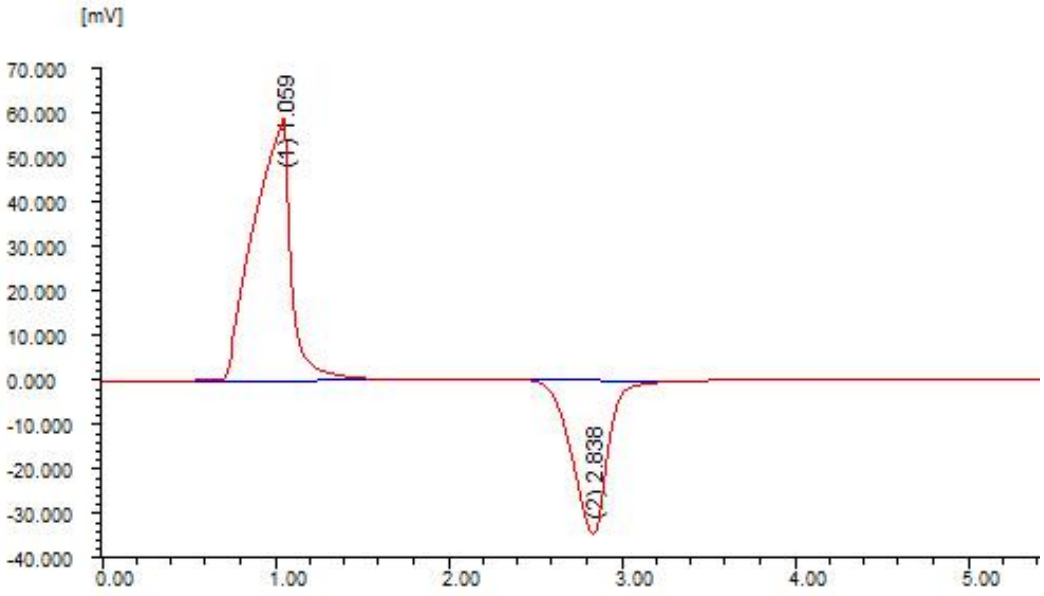
Supplementary Figure 4 Restart of water reduction by adding CuPS or cat.

pH data / Entry	CuPS+ **1a** (dark)	Et_4NOH (dark)	irradiation 1h	irradiation 3h	irradiation 8h
1	11.38	11.49	11.26	10.86	10.71
2	11.33	11.50	11.25	10.74	10.64

Supplementary Table 1 The change of PH in the process of water reduction.



Supplementary Figure 5 Screening of the 400nm cutoff and AG1.5 filter.



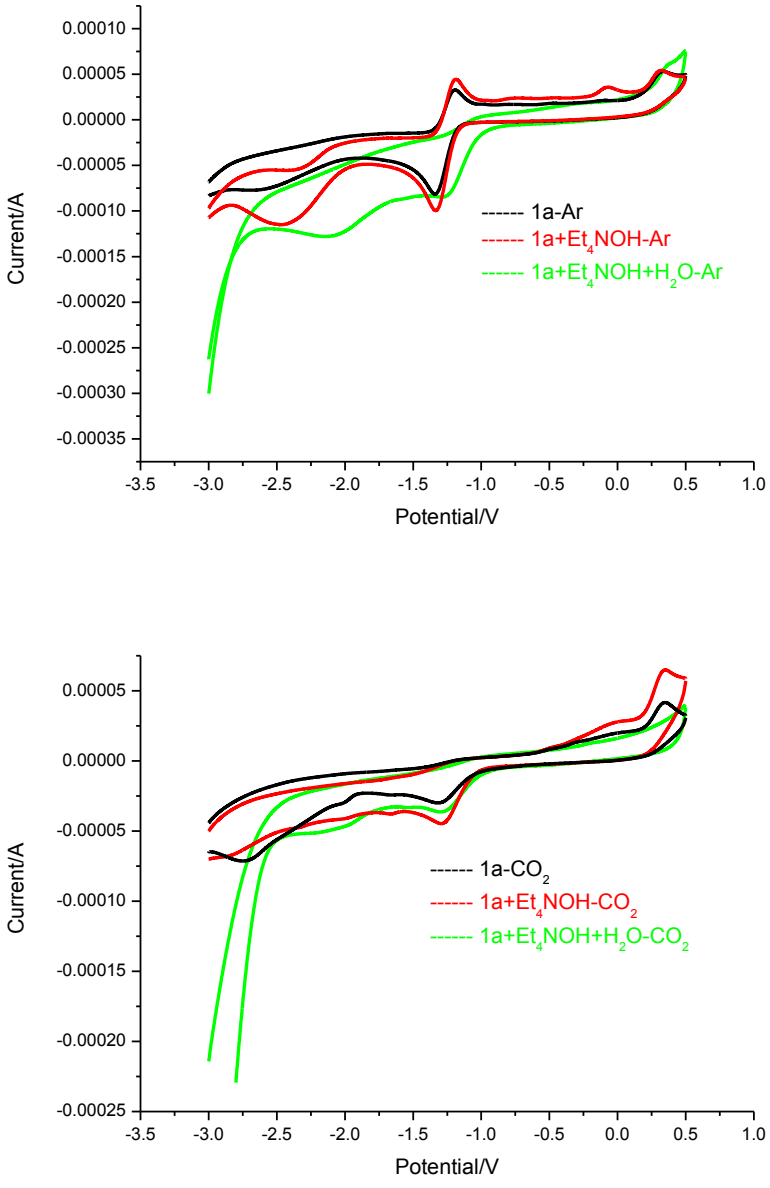
Supplementary Figure 6 GC analysis result of the photocatalytic water reduction

Electrochemical Measurements

General Methods. All studies were performed at room temperature (25 ℃) in dried acetonitrile p.A. (VWR) under Argon atmosphere with 0.1 M Tetrabutylammonium hexafluorophosphate: ($[Bu_4N]PF_6$, Fluka) as conducting salt using an Autolab (PGSTAT 128N, Metrohm). Working electrode was a glassy carbon disk electrode (d=2mm), the counter electrode a Pt-electrode and the reference electrode an Ag/AgCl/LiCl salt in CH_3CN system (all electrodes purchased). All the

potentials were measured with regard to this reference system and were checked by using the ferrocen/ferrocenium internal reference system.

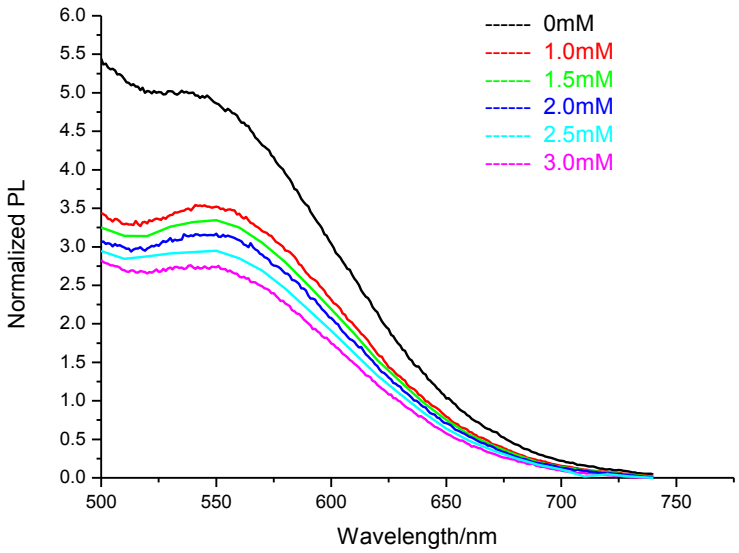
The cyclic voltammetry scans were done three times at a scan rate of 100mVs^{-1}. Differential pulse voltammograms were performed at a scan rate of 5m Vs^{-1}. (step potential 2.5 mV, modulation amplitude 25 mV, modulation time 0.05 s, interval time 0.5 s). Concentrations of 1 mM analyses were used for the measurements.



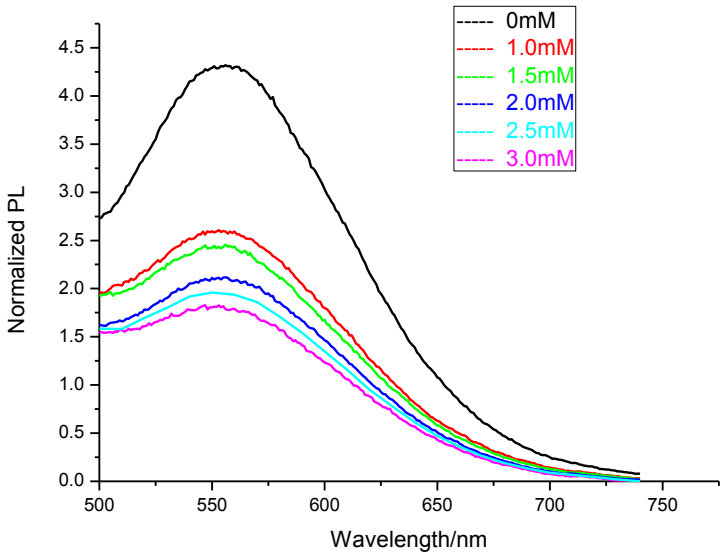
Supplementary Figure 7 Cyclic voltammograms with **1a**, then quenched by H_2O in Ar and CO_2.

Photoluminescence Spectroscopy

General Methods: Luminescence spectra were measured with a spectrofluorometer (FluoroMax-4P, Horiba Scientific). For the streak camera experiments the samples were excited with femtosecond pulses at 360 nm. Luminescence quenching by different concentrations of TEA and **1a** is studied for a $3.5*10^{-4}$ M solution of the CuPS in acetonitrile.



Supplementary Figure 8 Photoluminescence spectra of a $3.5*10^{-4}$ M solution in acetonitrile containing TEA.



Supplementary Figure 9 Photoluminescence spectra of a 3.5µM CuPS solution in acetonitrile containing **1a**

Stern-volmer equation

$F_0/F_n=1+K_D[Q]=1+K_q\ \tau_0[Q]$

F_0: measured luminescence intensity without quenching agent

F_n: measured luminescence intensity with quenching agent

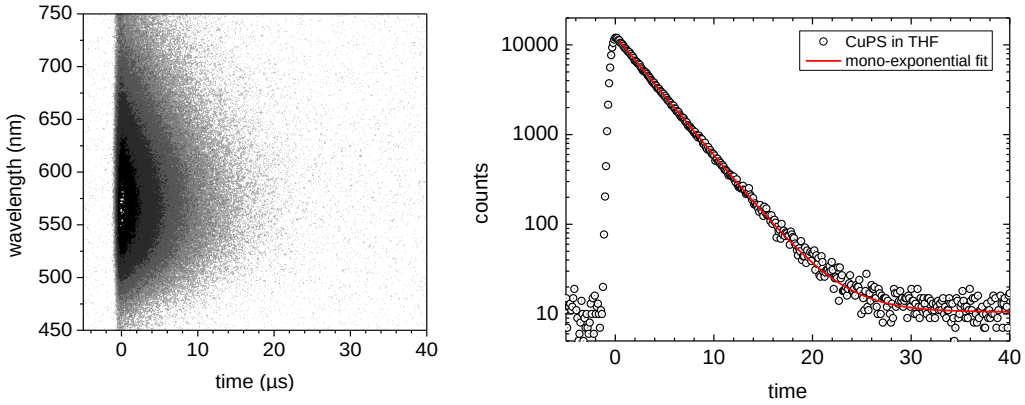
[Q]: The concentration of the quenching agent

K_q: bimolecular quenching rate (about $2*10^{10}$ L $mol^{-1}s^{-1}$)

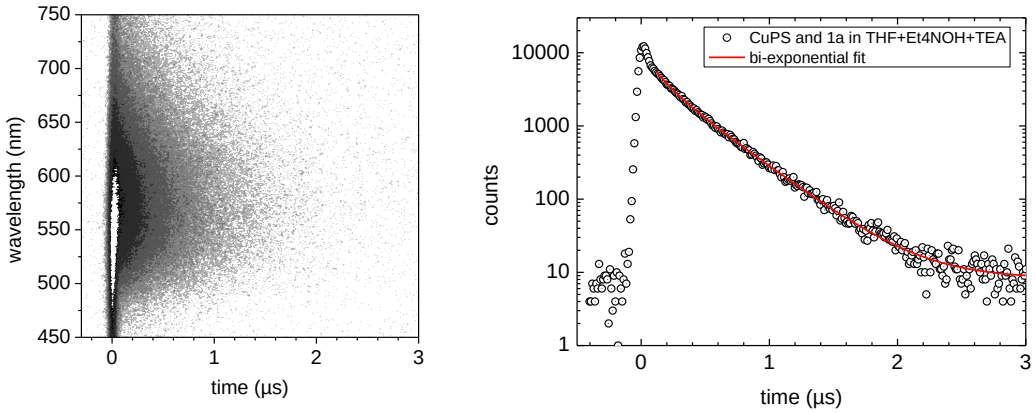
K_D: quenching constant (stern-volmer quenching constant)

τ_0: Luminescence lifetime of CuPS without quencher

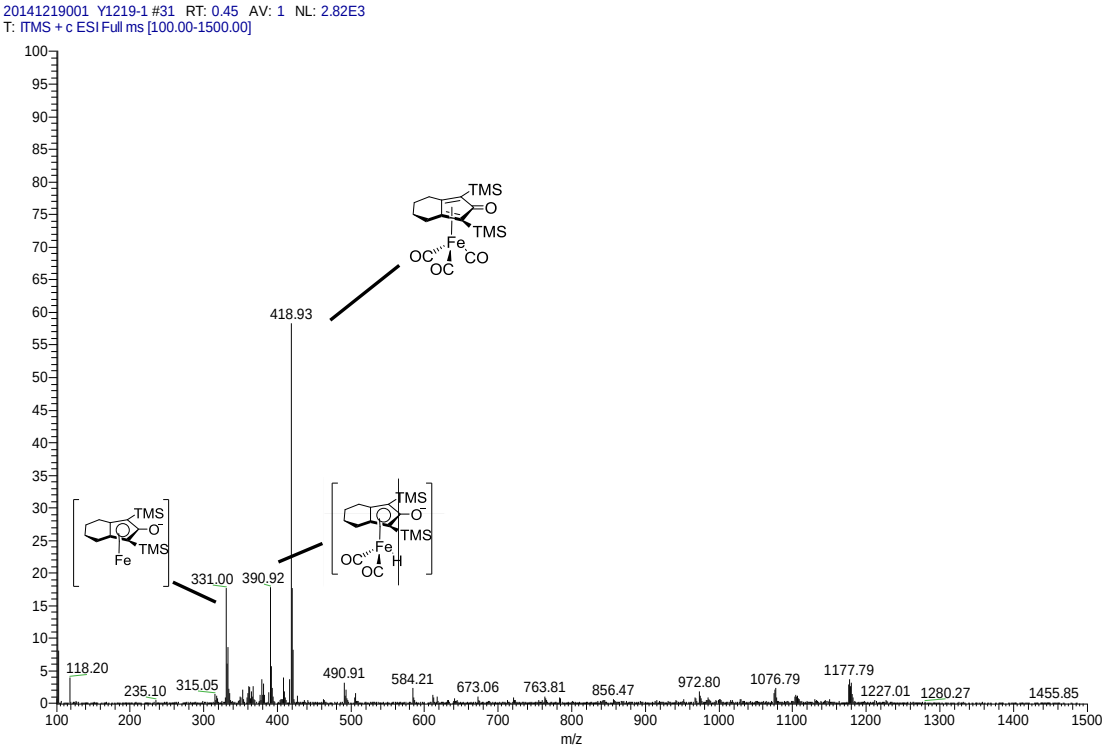
Streak Camera Measurements



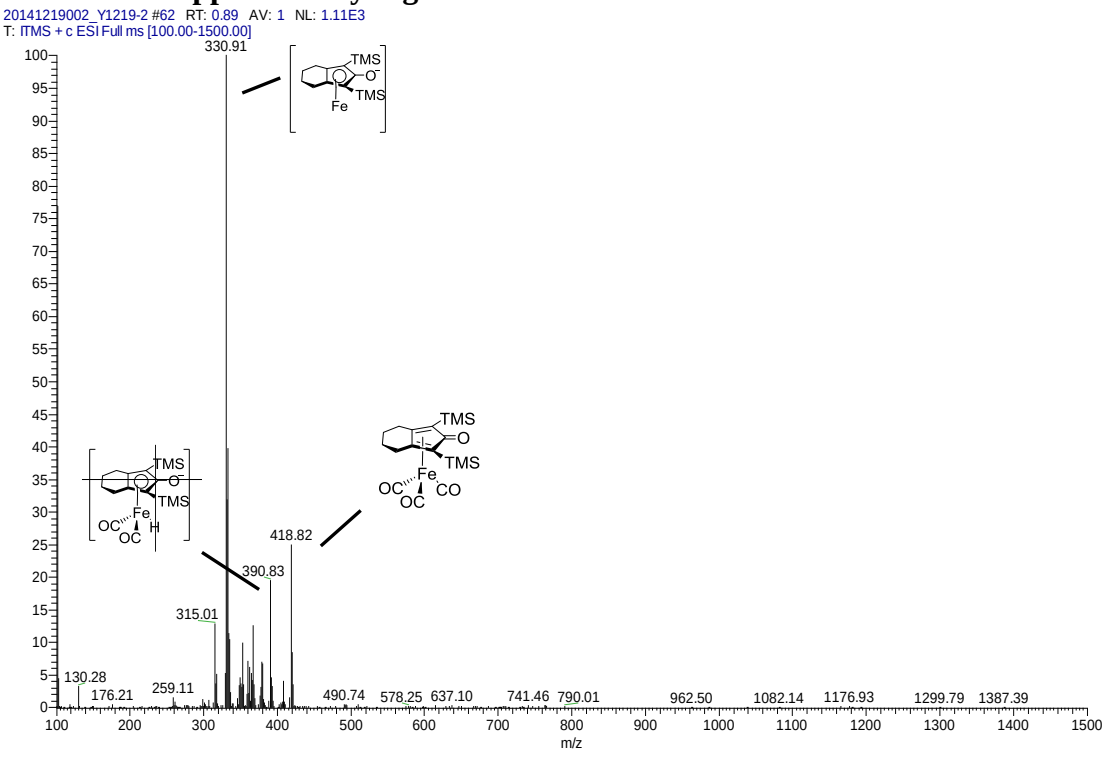
Supplementary Figure10 Example of a streak camera measurement. Spectrally and time resolved photoluminescence of CuPS in pure THF (left) and spectrally integrated luminescence signal with the corresponding fit (right). The fit gives a lifetime of 3.2 µs for the copper sensitizer in THF.



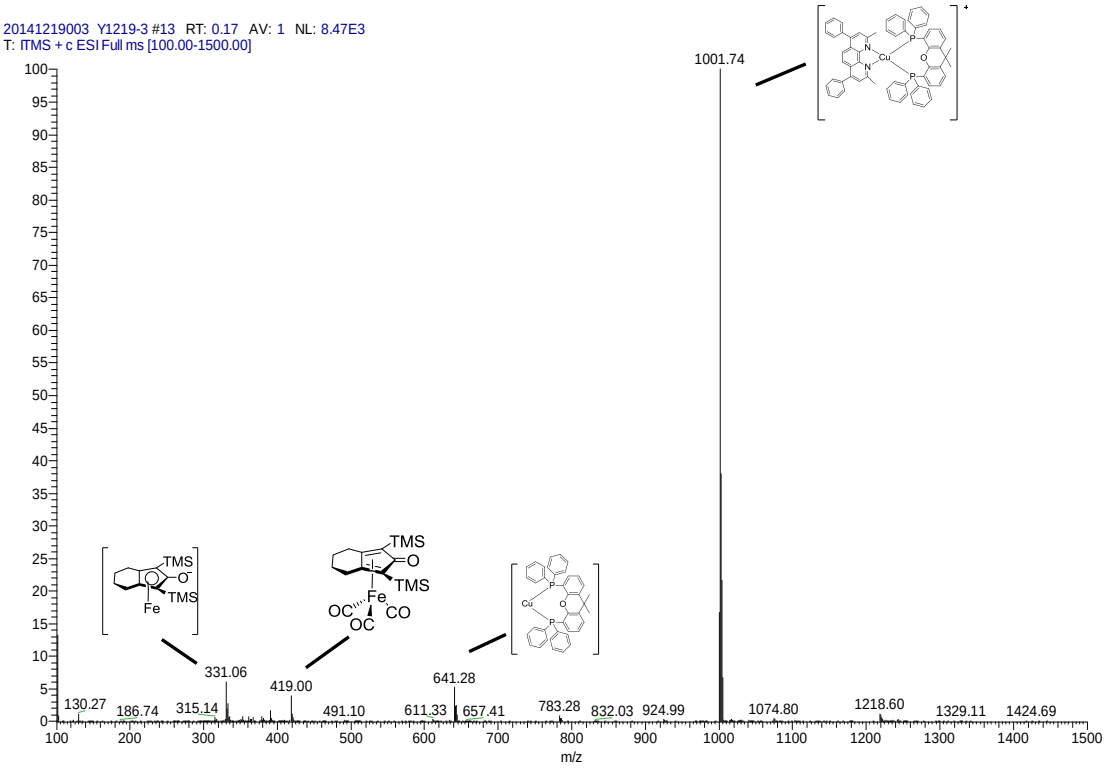
Supplementary Figure 11 Streak camera measurement of the photoluminescence of CuPS in the solvent mixture (THF + Et4NOH) + TEA (5:3). The fit gives two lifetimes: τ_1 = 139 ns (amplitude A_1 = 2540), τ_2 = 351 ns (amplitude A_2 = 3737) with an amplitude weighted average lifetime $\langle\tau\rangle = (\tau_1*A_1+\tau_2*A_2)/(A_1+A_2)$ = 265 ns. At time zero some background fluorescence is observed with a lifetime below the time resolution of the measurement of 60 ns.



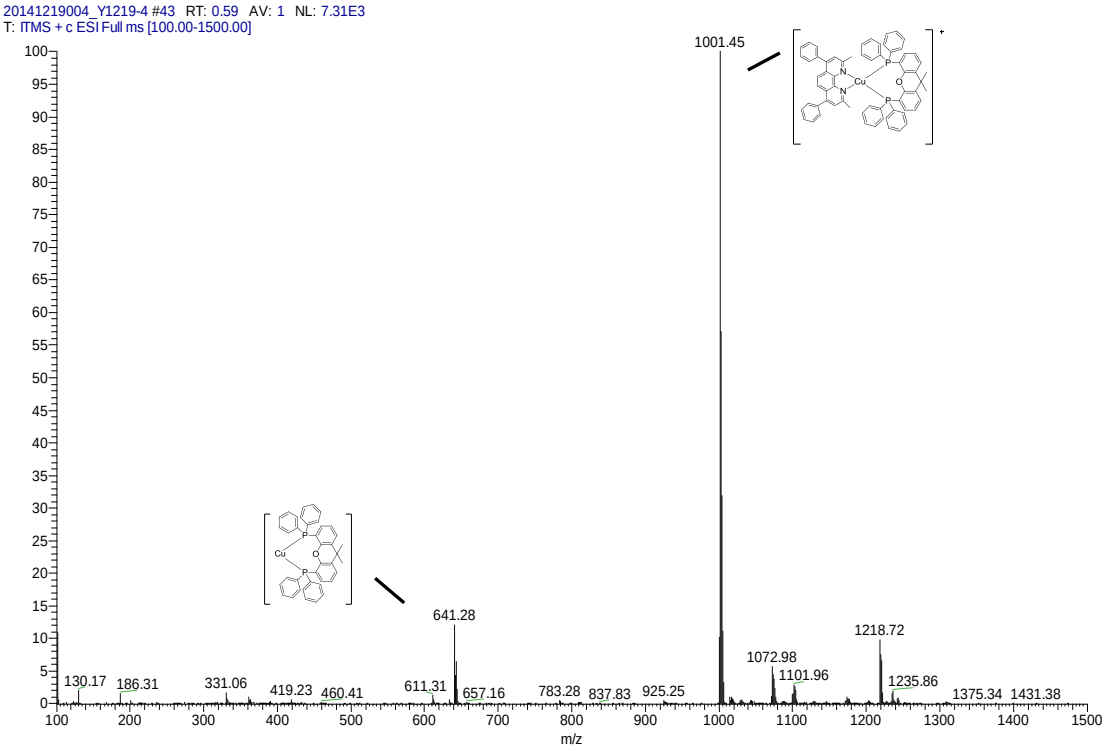
Supplementary Figure 12 The MS of **1a** before irradiation.



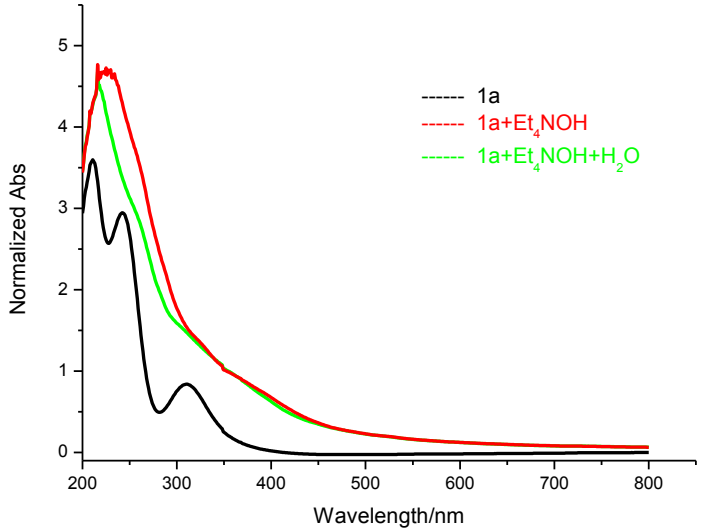
Supplementary Figure 13 The MS of **1a** and Et_4NOH before irradiation.



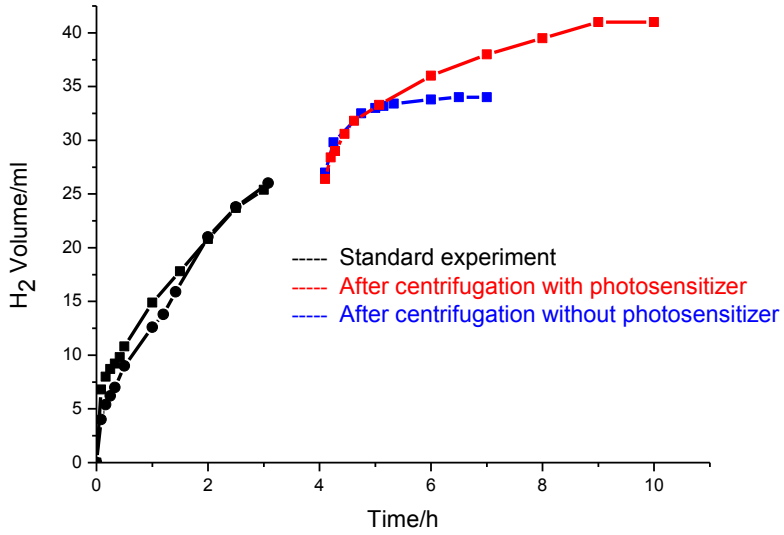
Supplementary Figure 14 The MS of **1a**, Et4NOH and CuPS before irradiation.



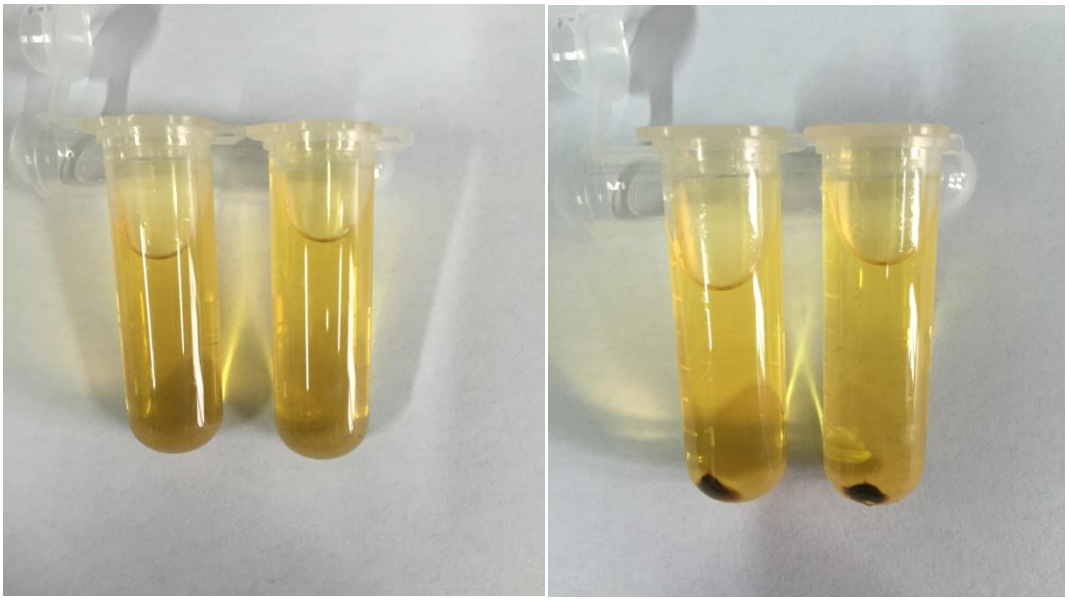
Supplementary Figure 15 The MS of **1a**, Et_4NOH and CuPS after illumination.



Supplementary Figure 16 UV with **1a**, **1a** +Et_4NOH and **1a** +Et_4NOH+H_2O.

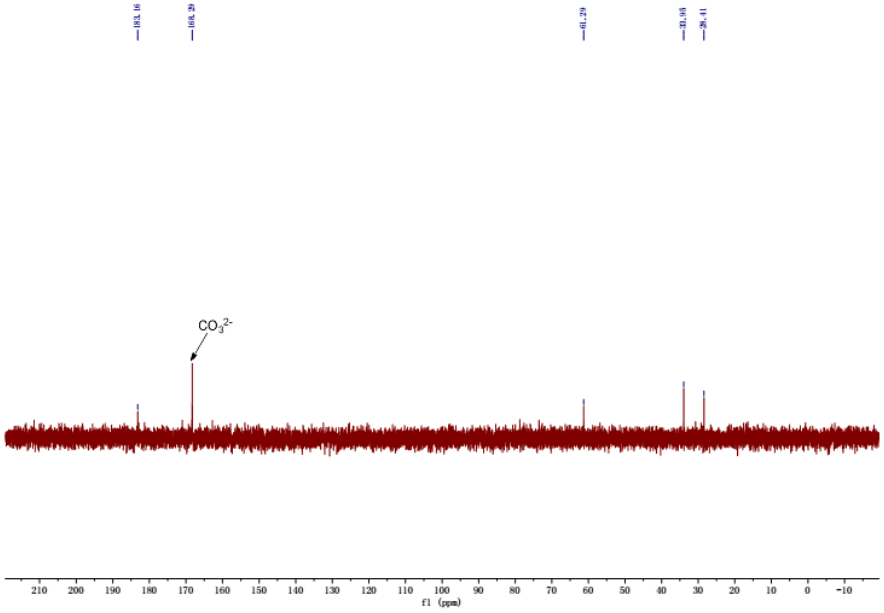


Supplementary Figure 17 Comparison of homogeneous hydrogen production



Supplementary Figure 18 Before and after solution centrifugation.

The reaction is carried out about three hours, then the solvent is injected into a centrifuge tube under the protection of nitrogen. After centrifugation (9000r/min, 5min), the supernatant solution was added to the reaction vessel in order to restart the photocatalytic hydrogen production.



Supplementary Figure 19 ^{13}C NMR of the generation of CO_2

In order to probe the generation of CO_2, we performed the reaction of **1a** (68 mg, 0.16 mmol) with aqueous 1M NaOH (1.33ml) in THF (2.67 ml) at r.t. under argon. After stirring the mixture for 3 h, the organic layer was separated and the aqueous layer was extracted with diethyl ether. The water of the aqueous layer was fully evaporated under reduced pressure and the remaining precipitate was investigated by ^{13}C NMR in D_2O. A single resonance for carbonate at 168.29 ppm was obtained in the ^{13}C NMR spectrum, which is consistent with resonance for sodium carbonate.

References

[1] S. Fleischer, S. Zhou, K. Junge, M. Beller, *Angew, Chem. Int. Ed.*, 2013, **52**, 5210.
[2] A. Pagnoux-Ozherelyeva, S. Gaillard, A. Poater, L. Cavallo, J.-F. Lohier, J.-L.Renaud, *Chem. Eur. J.* 2013, **19**, 17881.
[3] S. P. Luo, E. Mejia, A. Friedrich, A. Pazidis, H. Junge, A. E. Surkus, R. Jackstell, S. Denurra, S. Gladiali, S. Lochbrunner and M. Beller, *Angew. Chem. Int. Edit.*, 2013, **52**, 419.