Supporting Information

Dioxygen-Promoted Catalytic Deformylation of Aldehydes via Hydrogen Atom Abstraction by $[Fe(TPP)]_2O$

Kai-Chun Hsu[a,b,c], Bhakyaraj Kasi[a,d,e], Tanmoy Pain[a] Chen-Hsiung Hung[a]*

General Information

All chemicals were obtained from commercial suppliers and used without further purification unless otherwise specified. Reactions requiring an inert atmosphere were carried out under N_2 using standard Schlenk techniques or in an N_2-filled glovebox. Dichloromethane was purified using an AWS-1000 solvent purification system (Asiawong Ent. Co. LTD). Deuterated solvents for NMR were purchased from Sigma-Aldrich. Triethylamine was distilled from CaH_2, degassed by repeated freeze-pump-thaw cycles, and stored in an N_2-filled glovebox prior to use. The syntheses of $TPPH_2$, Fe(TPP)Cl, and $[Fe(TPP)]_2O$ followed reported procedures. UV-Vis spectra were recorded on an Agilent 8453 spectrophotometer. ^1H NMR spectra were collected on a Bruker AV400 spectrometer. Catalytic products were analyzed using a PerkinElmer GC-MS system. Anaerobic samples were prepared in a nitrogen-filled glovebox (Innovative Technology).

Synthesis of Tetraphenylporphyrin ($TPPH_2$)

$TPPH_2$ was prepared according to a reported method.[1] Pyrrole (10 mL, 0.16 mol) and benzaldehyde (16 mL, 0.16 mol) were added to propionic acid (100 mL) in a 250 mL round-bottom flask and refluxed for 45 min. After cooling, the precipitate was collected and washed sequentially with hot methanol and hot water to afford a crude purple solid. The crude product was purified by

column chromatography on silica gel using dichloromethane/hexane (1:1) as the eluent, affording $TPPH_2$ as the first fraction. After drying, pure $TPPH_2$ was obtained in 78% yield (19 g).

UV-Vis [(CH_2Cl_2, λ_{max} ,nm (ε, 10^5 M^{-1} cm^{-1})]: 407 (3.67), 514 (0.18), 549 (0.075), 589 (0.055), 646 (0.051).

^1H NMR (400 MHz, $CDCl_3$): δ 8.85 (s, 8H), 8.23 (s, 8H), 7.77 (s, 12H), -2.76 (s, 2H). (**Fig. S4**)

Synthesis of [Fe^{III}(TPP)Cl] (1)

Compound **1** was prepared according to reported methods.[2-4] $TPPH_2$ (500 mg, 0.81 mmol) and $FeCl_2 \cdot 4H_2O$ (970 mg, 4.9 mmol) were dissolved in DMF (81 mL) at room temperature. The solution was refluxed for 30 min and then cooled to room temperature. After filtration through a glass funnel, the filtrate was extracted with DCM. The organic phase was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The product was precipitated from DCM/hexane to afford a purple solid (530 mg, 93% yield).

UV-Vis [(CH_2Cl_2, λ_{max} ,nm (ε, 10^5 M^{-1} cm^{-1})]: 377 (0.82), 416 (1.45), 510 (0.17), 579 (0.035), 690 (0.041). (**Fig. S1**)

ESI-MS: $[M\text{-}Cl]^+$ $[Fe^{III}(TPP)]^+$, m/z 668.1648. (**Fig. S2**)

^1H NMR (400 MHz, CD_2Cl_2): δ 80.42 (s, 8H), 12.81 (d, J = 464 Hz, 8H), 6.41-8.00 (m, 12H). (**Fig. S5**)

Synthesis of [Fe^{III}(TPP)]$_2$O (2)

Compound **2** was prepared according to reported procedures.

Method A: Compound 1 (800 mg) in dry DCM (50 mL) was shaken with three successive portions of aqueous NaOH (2 M, 100 mL each). The dark brown organic layer was separated, dried over anhydrous Na_2CO_3, and concentrated to ~25% of the original volume on a rotary evaporator.

Methanol was then added to precipitate the product. The resulting crystals were collected by filtration and dried at 80 °C for 2 h, affording >90% yield. The UV-Vis spectrum of **2** displayed characteristic bands at 408, 570, and 610 nm.

Method B: Compound 1 (10 mg, 14 μmol) and triethylamine (0.2 mL, 1.4 mmol) were dissolved in CH_2Cl_2 (10 mL) under N_2 in a glovebox. After stirring for 10 min at room temperature, the solution was evaporated under vacuum to afford a solid product containing **2**.

UV-Vis [(CH_2Cl_2, λ_{max} ,nm (ε, 10^5 M^{-1} cm^{-1})]: 407 (1.39), 570 (0.112), 611 (0.052). (**Fig. S1**)

ESI-MS: $[M + Na]^+$ $\{[Fe^{III}(TPP)]_2O \cdot Na\}^+$, m/z 1375.3176. (**Fig. S3**)

^1H NMR (400 MHz, CD_2Cl_2): δ 13.51 (s, 16H), 7.65 (s, 40H). (**Fig. S6**)

Hydrogen Atom Abstraction (HAA)

For a typical NMR-scale reaction, a solution of **1** or **2** (3 μmol) and 2-phenylpropanol (2-PPA, 40 mg, 0.30 mmol) in CD_2Cl_2 (1.0 mL) was prepared inside a glovebox under an inert atmosphere. The mixture was stirred at ambient temperature for 24 h. After completion of the reaction period, the solution was transferred to a J. Young NMR tube for analysis.

For optical absorption spectroscopy, solutions of 1 or 2 (6 μM) and 2-phenylpropanol (2-PPA, 12 mM) in dichloromethane (3.0 mL) were prepared in a 1 cm path-length quartz cuvette inside a glovebox under an inert atmosphere. After preparation, the cuvette was sealed and removed from the glovebox. Immediately before measurement, 1.0 mL of O_2 gas was injected through the septum to initiate the HAA reaction.

Kinetic Measurements

Time-resolved UV-Vis spectroscopy was employed to evaluate the HAA reactivity of 2. Stock

solutions of the μ-oxo dimer **2** (5 μM) with varying concentrations of 2-PPA (10, 20, 30, 40, and 50 mM) were prepared in dichloromethane under an inert (N_2) atmosphere. For each run, 3.0 mL of the reaction solution was transferred to a quartz cuvette fitted with a septum, sealed, and removed from the glovebox. Immediately after removal, 1.0 mL of O_2 gas was injected through the septum to initiate the reaction, and spectral acquisition was started simultaneously. Under these conditions, the concentrations of both 2-PPA and O_2 remained effectively constant during the kinetic measurements, allowing the decay of **2** at 570 nm to be treated as a pseudo-first-order process.

EPR Study

A solution of **2** (4 mg, 3 μmol), 2-PPA (40 mg, 0.30 mmol), and 5,5-dimethyl-1-pyrroline N-oxide (DMPO, 4 mg, 0.04 mmol) in dichloromethane (1.0 mL) was prepared under an inert atmosphere in a glovebox. The mixture was stirred at ambient temperature for 10 min and then transferred to a J. Young EPR tube for analysis. Spectra were recorded using the following instrument settings: microwave power, 20 mW; modulation frequency, 100 kHz; modulation amplitude, 1 G; response time, 0.5 s; and sweep rate, 12.5 G min^{-1}.

General Catalytic Aldehyde Deformylation

Reactions were performed at 298 K under 1 atm of O_2. A stock solution containing 2-PPA (30 μmol) and NEt_3 (30 μmol) in DCM (1 mL) was prepared inside a glovebox under an inert atmosphere. For each run, 1.0 mL of this stock solution was added to a vial containing the iron catalyst (1.5 μmol) to dissolve the catalyst completely. The resulting mixture was gently stirred, transferred to a sealed reaction vessel, and removed from the glovebox. Immediately afterward,

1.0 mL of O_2 gas was introduced through the septum to initiate the reaction. After 24 h at 298 K, a 5 μL aliquot of the reaction mixture was withdrawn and analyzed by GC-MS.

References

1. K.-Y. Li, P.-H. Lu, B.-H. Wu and S.-P. Wu, *Dyes and Pigments*, 2022, **205**, 110521.
2. D. Zhang, L. E. Rosch, M. R. Crawley and T. R. Cook, *Inorg. Chem. Front.*, 2024, **11**, 5557-5565.
3. M. L. Pegis, D. J. Martin, C. F. Wise, A. C. Brezny, S. I. Johnson, L. E. Johnson, N. Kumar, S. Raugei and J. M. Mayer, *JACS*, 2019, **141**, 8315-8326.
4. J. Rosenthal, B. J. Pistorio, L. L. Chng and D. G. Nocera, *J. Org. Chem.*, 2005, **70**, 1885-1888.
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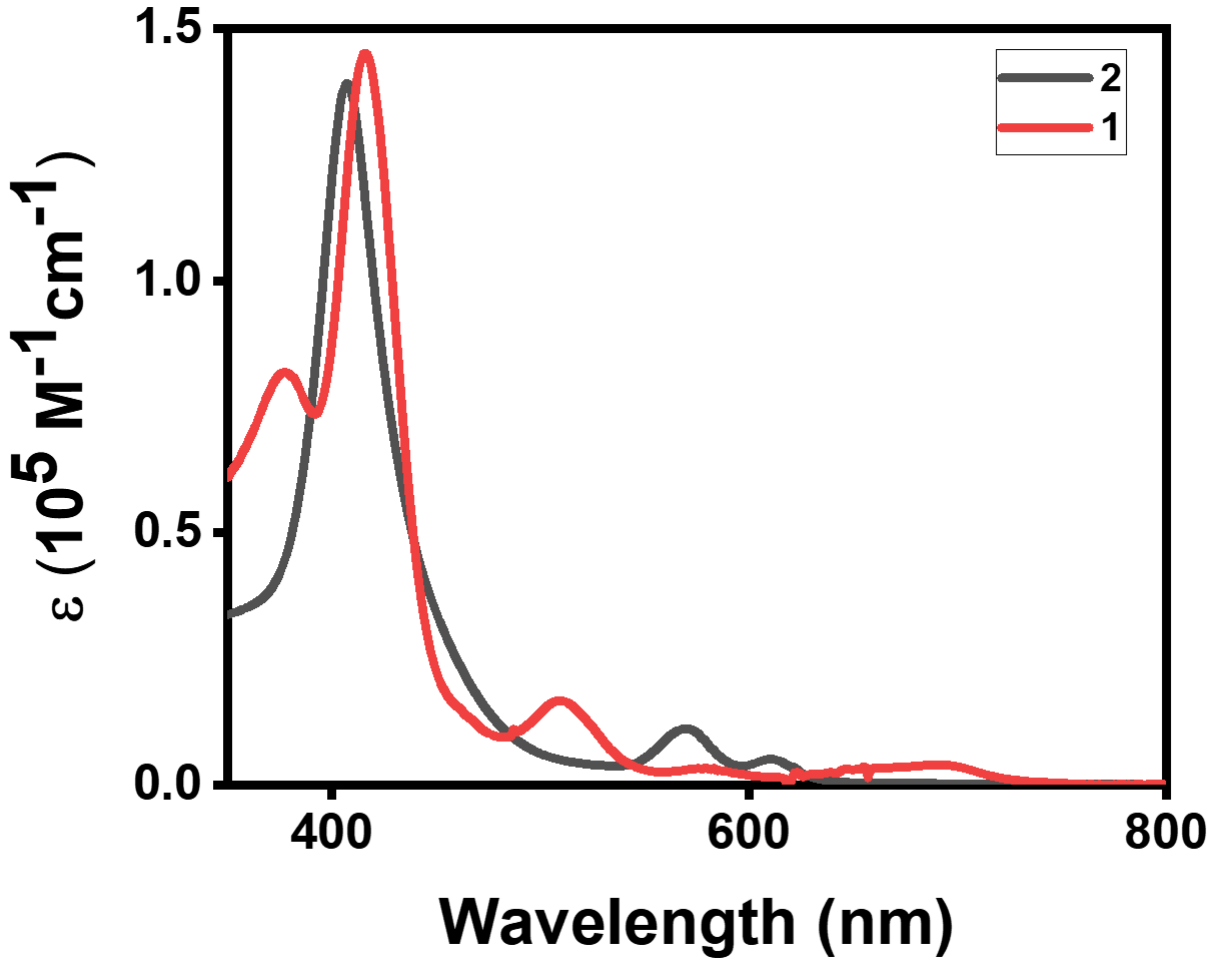

Fig. S1 UV-Vis absorption spectra of compounds **1** and **2** in dichloromethane.

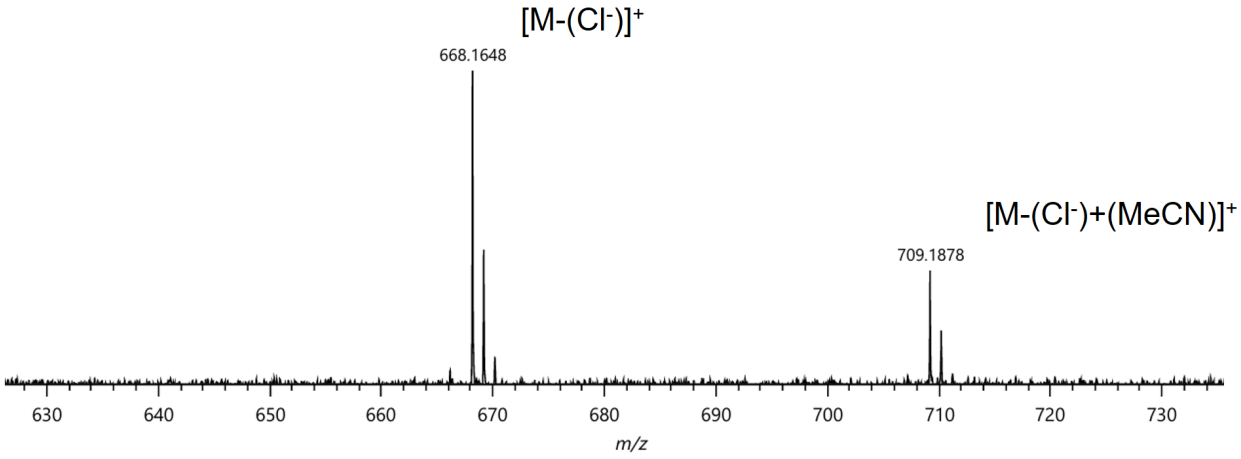

Fig. S2 ESI-MS spectrum of **1** in CH_2Cl_2/MeCN (1:1) with $NaBF_4$, showing $[Fe^{III}(TPP)]^+$ at m/z 668.1648.

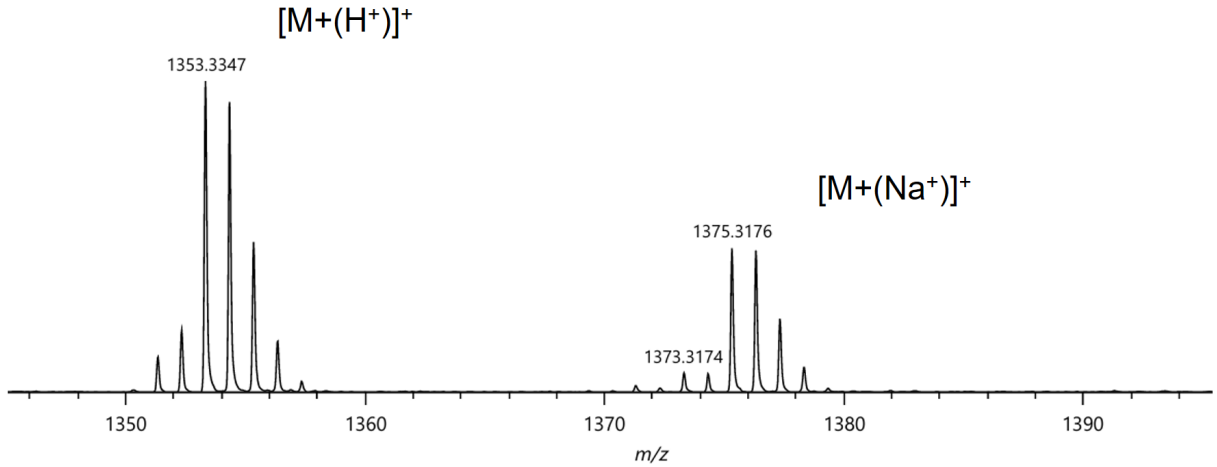

Fig. S3 ESI-MS spectrum of **2** in the CH_2Cl_2/MeCN (1:1) in the presence of $NaBF_4$, with the major ion assigned as $\{[Fe^{III}(TPP)]_2O(Na^+)\}^+$ at m/z 1375.3176.

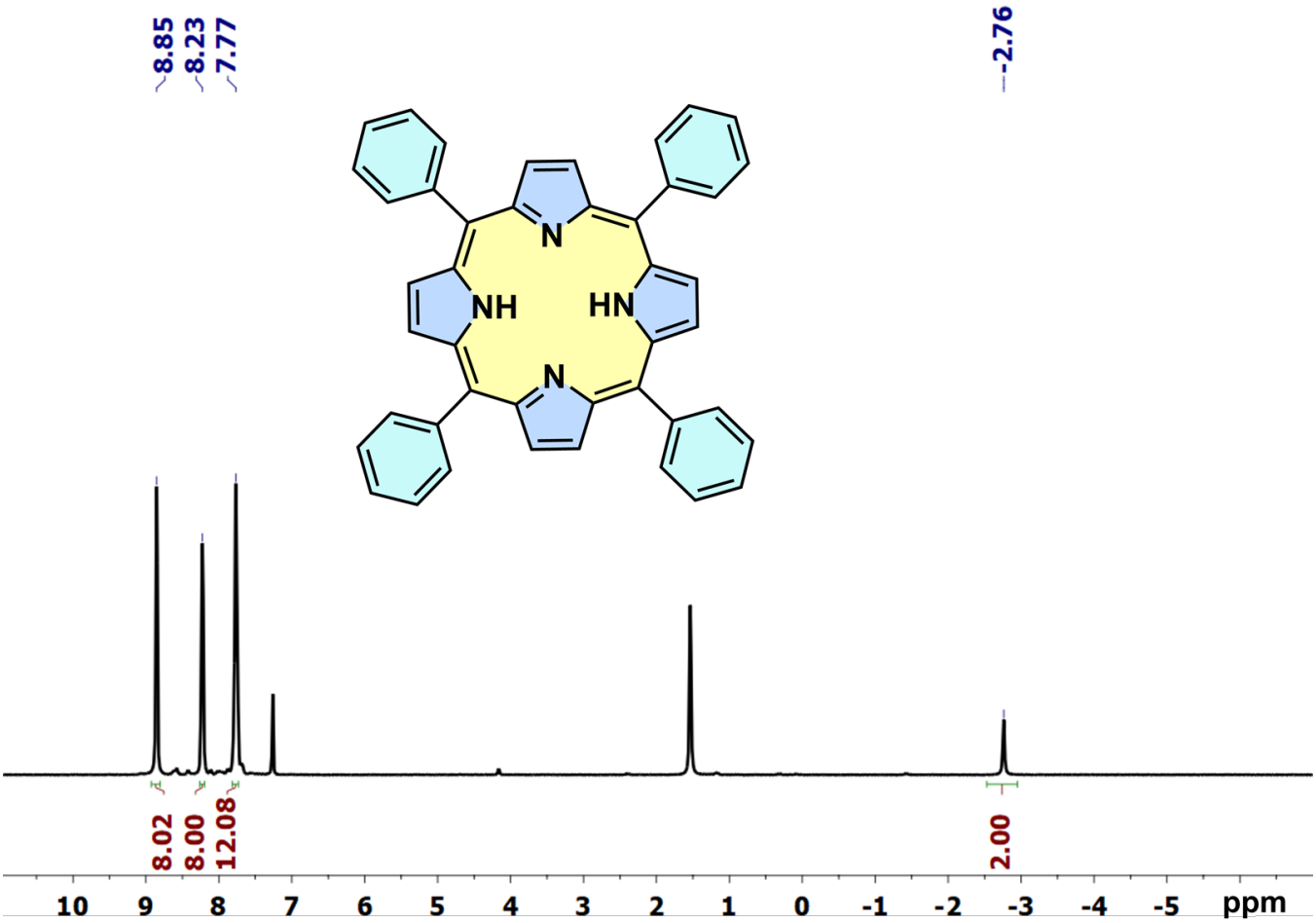

Fig. S4 ^{1}H NMR spectrum (400 MHz, CD_2Cl_2) of $TPPH_2$.

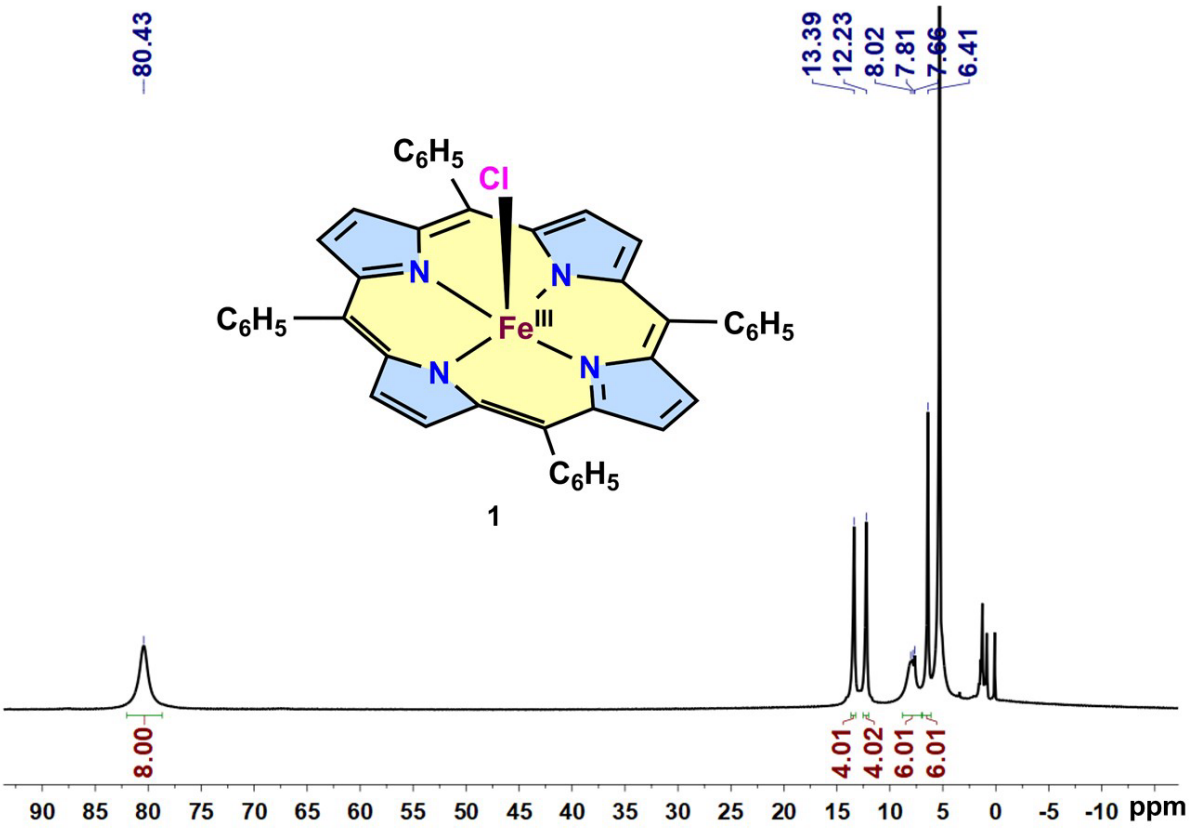

Fig. S5 ^{1}H NMR spectrum (400 MHz, CD_2Cl_2) of compound **1.**

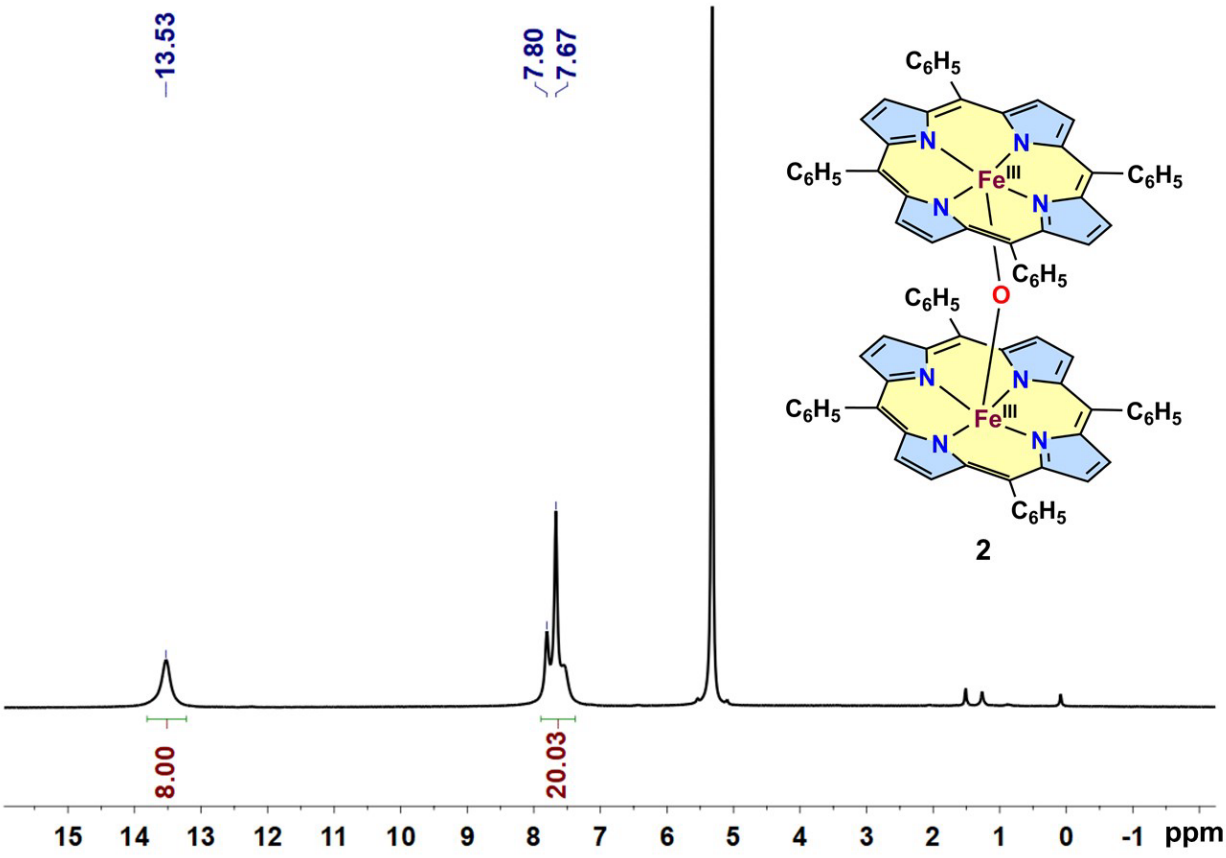

Fig. S6 ^{1}H NMR spectrum (400 MHz, CD_2Cl_2) of compound **2**.

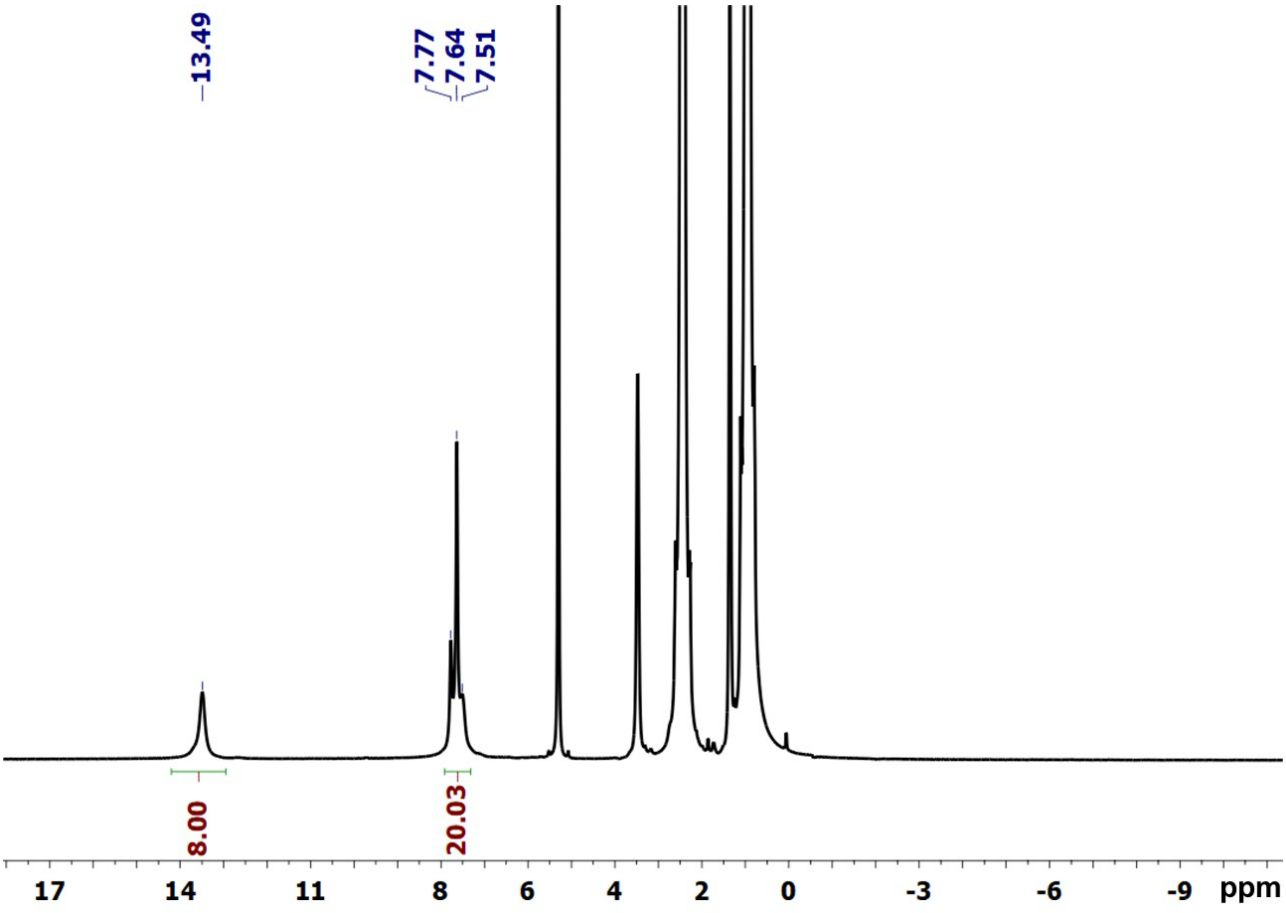

Fig. S7 ^{1}H NMR spectrum (400 MHz, CD_2Cl_2) of compound **2** generated from **1** with triethylamine.

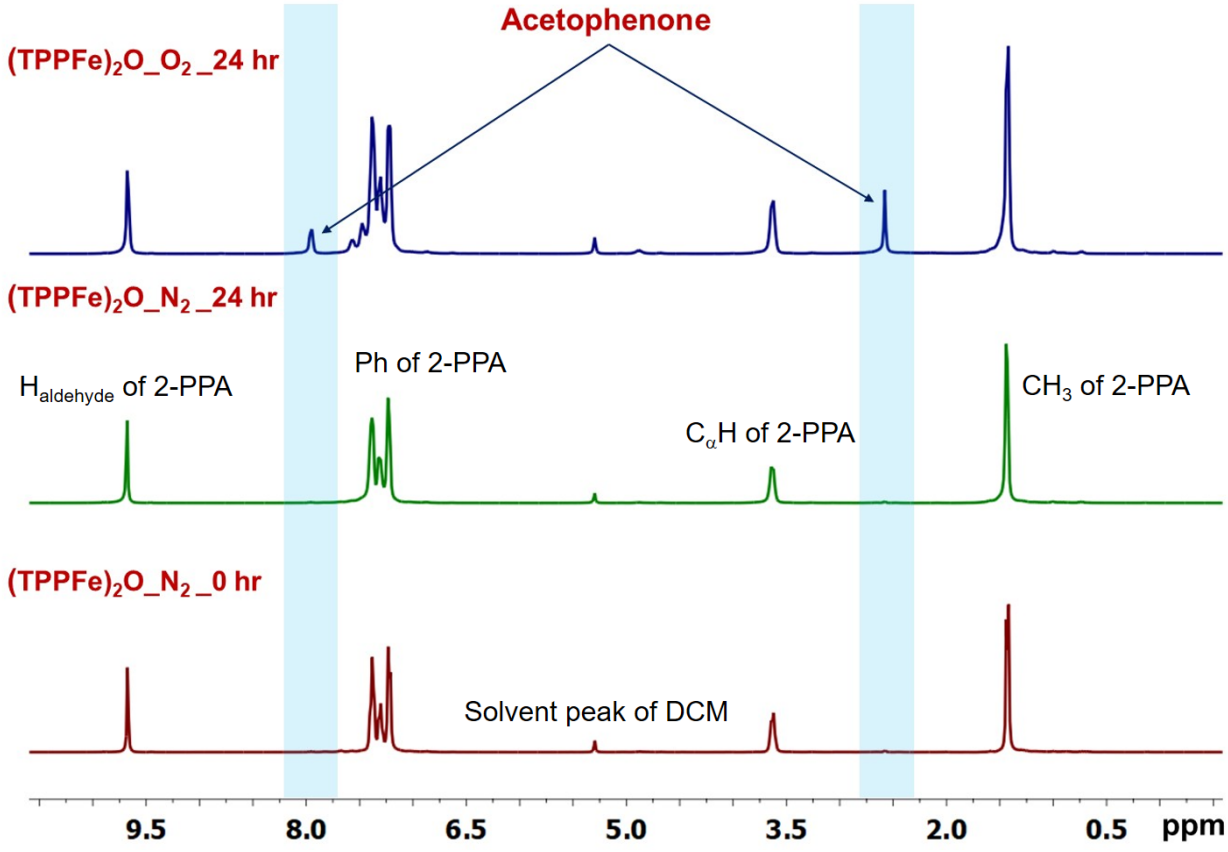

Fig. S8 ^{1}H NMR of HAA by compound **2** under aerobic and anaerobic condition.

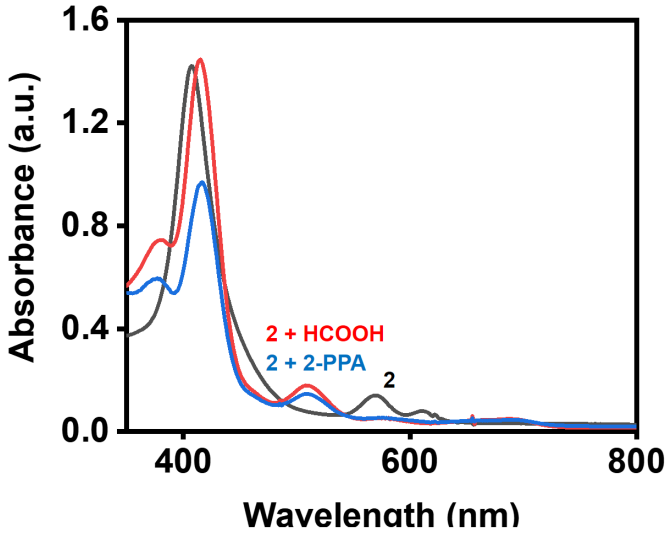

Fig. S9 UV-Vis spectra of [Fe^{III}(TPP)(HCOO)] formed upon addition of formic acid (50 mM) or 2-PPA (50 mM) to the solution of μ-oxo dimer **2** (5 μM).

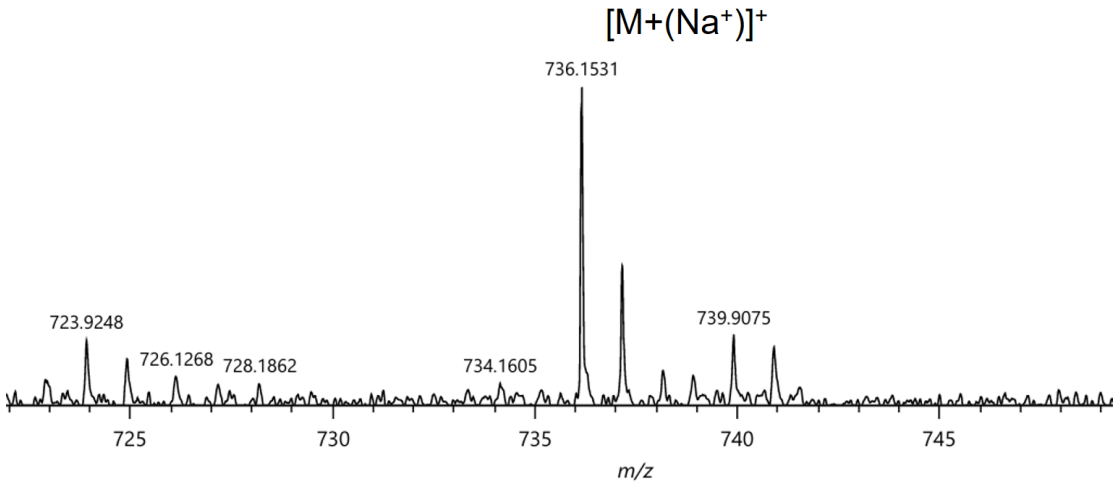

Fig. S10 ESI-MS spectrum of [(TPP)Fe^{III}(HCOO)(Na)]$^+$ in CH_2Cl_2/MeCN (1:1) with $NaBF_4$, obtained after addition of formic acid to a solution of **2**. The major ion was detected as [(TPP)Fe^{III}(HCOO)(Na)]$^+$ at m/z 736.1531.

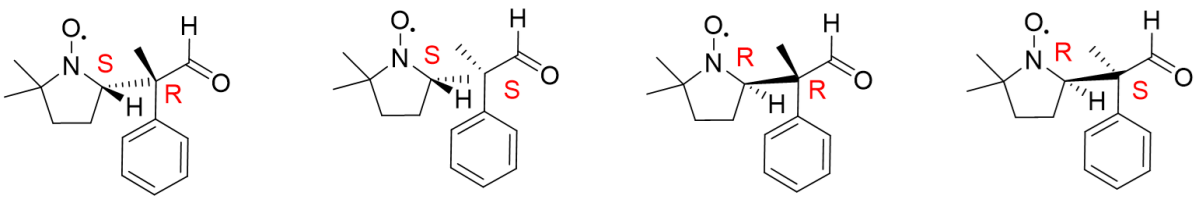

Fig. S11 Diastereomers of DMPO-radical adducts

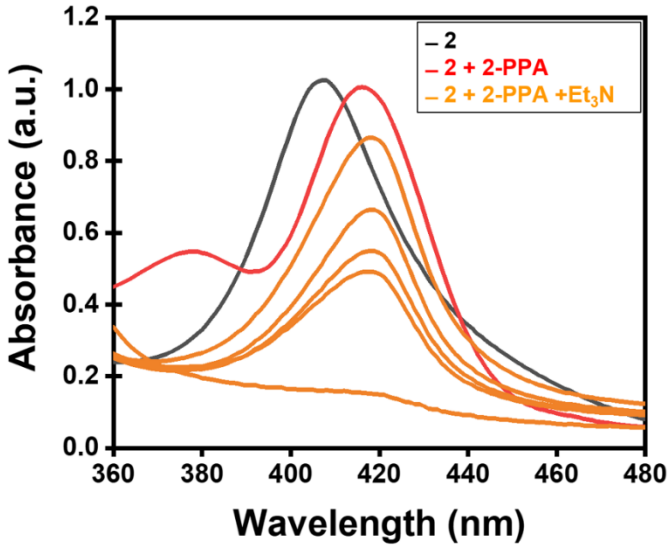

Fig. S12 UV-Vis spectra of **2** (black, 4 μM), [Fe^{III}(TPP)(HCOO)] formed upon addition of 2-PPA (red, 40 mM 2-PPA), and the subsequent decomposition observed after addition of Et_3N (orange, 40 mM Et_3N).

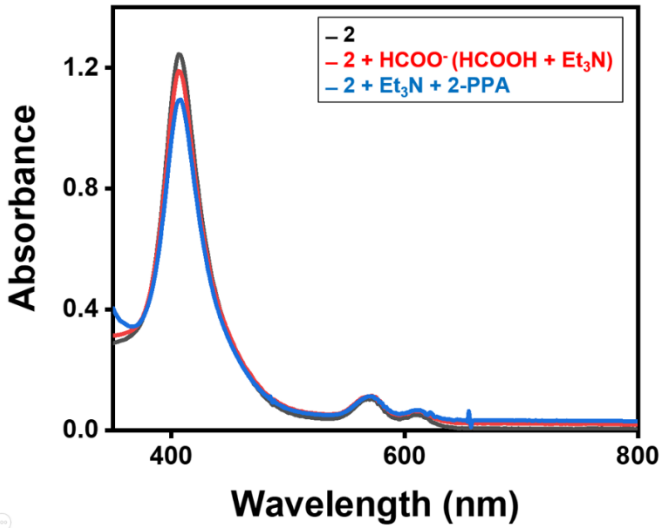

Fig. S13 UV-Vis spectra of **2** (black, 4 μM), upon addition of formate anion generated by mixing 40 mM formic acid and 40 mM Et_3N (red), and upon addition of 40 mM 2-PPA in the presence of 40 mM Et_3N (orange).

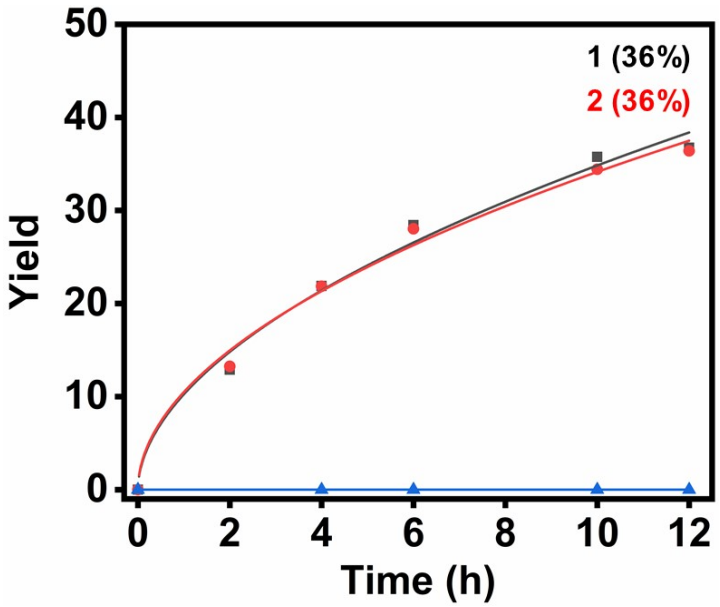

Fig. S14 Time-course of product yield catalyzed by **1** (black squares), **2** (red circles), and in the absence of catalyst (blue triangles). Reactions were performed with 100 equiv of 2-PPA and 20 equiv of Et_3N. After 12 h, maximum yields of 36% were obtained for both **1** and **2**.

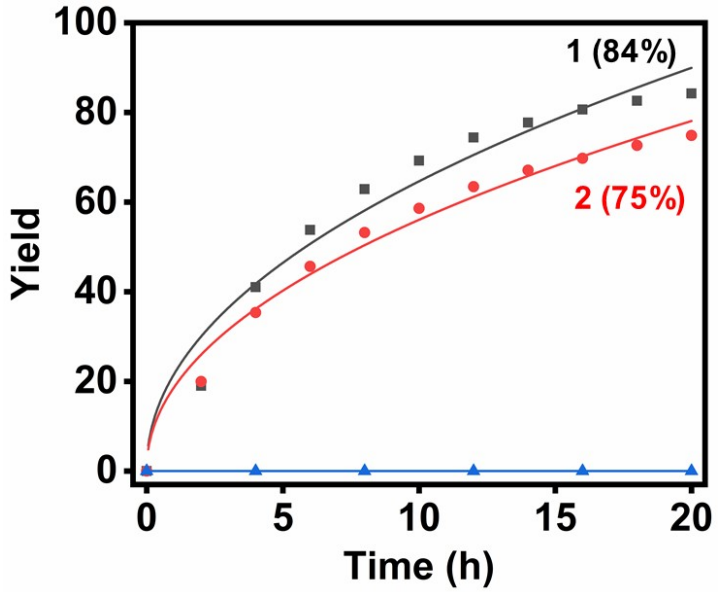

Fig. S15 Time-course of product yield catalyzed by **1** (black squares), **2** (red circles), and in the absence of catalyst (blue triangles). Reactions were conducted with 100 equiv of 2-PPA and 100 equiv of Et_3N. After 20 h, maximum yields of 84% and 75% were obtained for **1** and **2**, respectively.

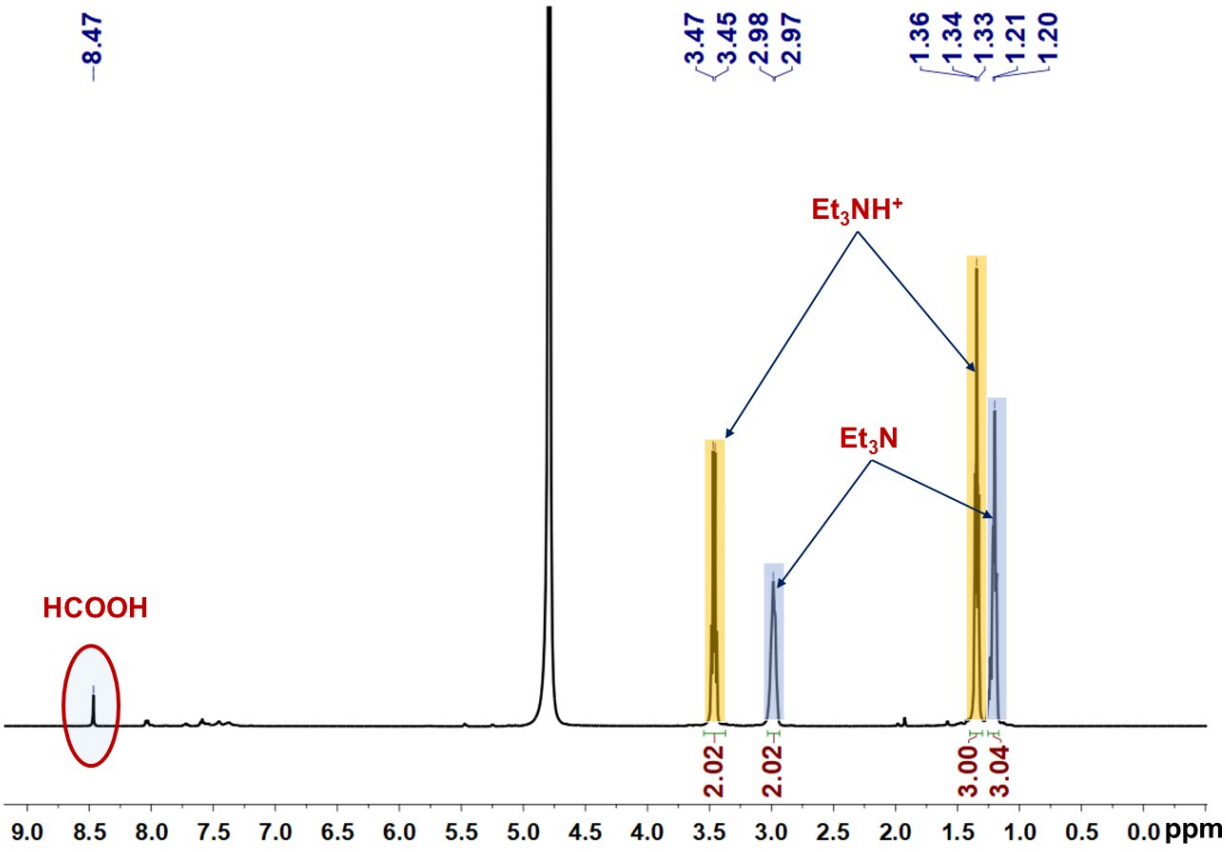

Fig. S16 ^{1}H NMR spectrum (400 MHz) of formic acid obtained in the D_2O after extraction. After catalytic aldehyde deformylation, 1 mL solution is extracted by 0.5 mL D_2O.

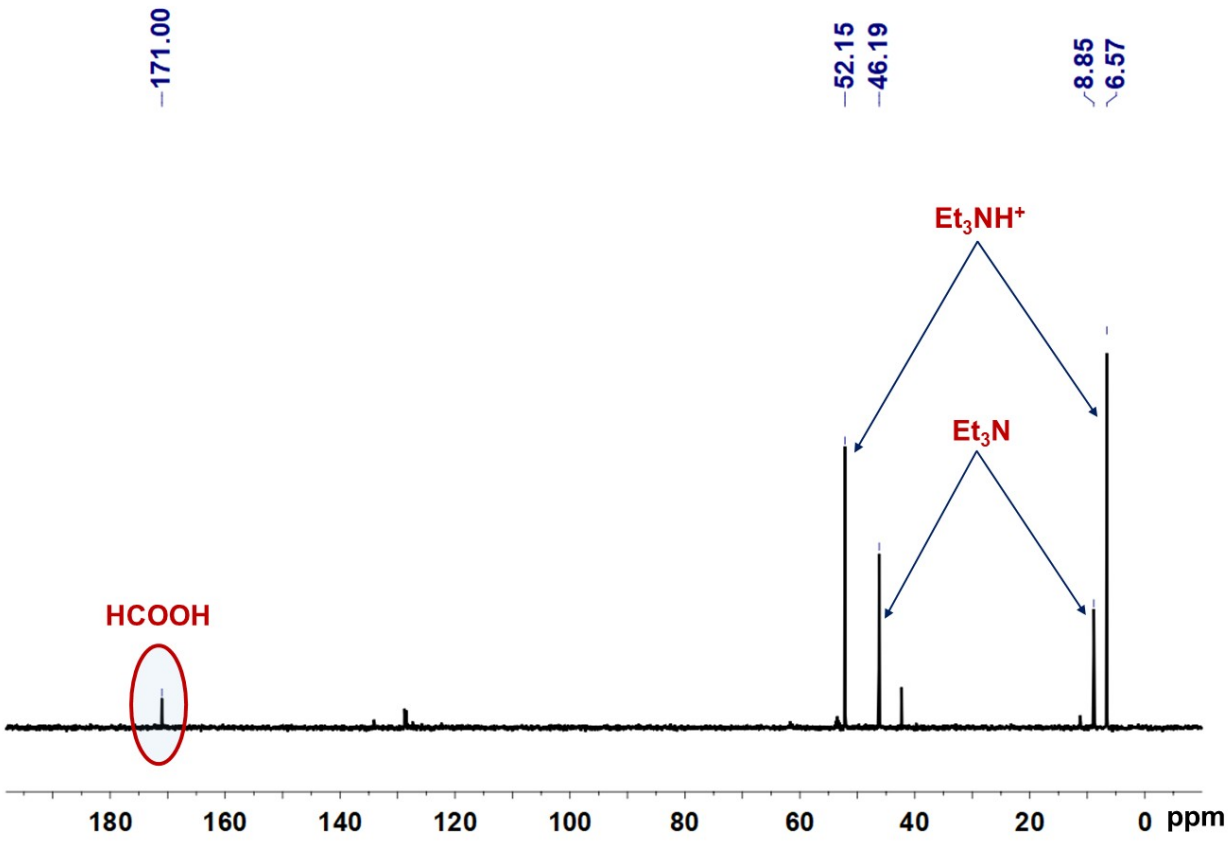

Fig. S17 ^{13}C NMR spectrum (400 MHz) of formic acid obtained in D_2O. After catalytic aldehyde deformylation, 1 mL solution is extracted by 0.5 mL D_2O.

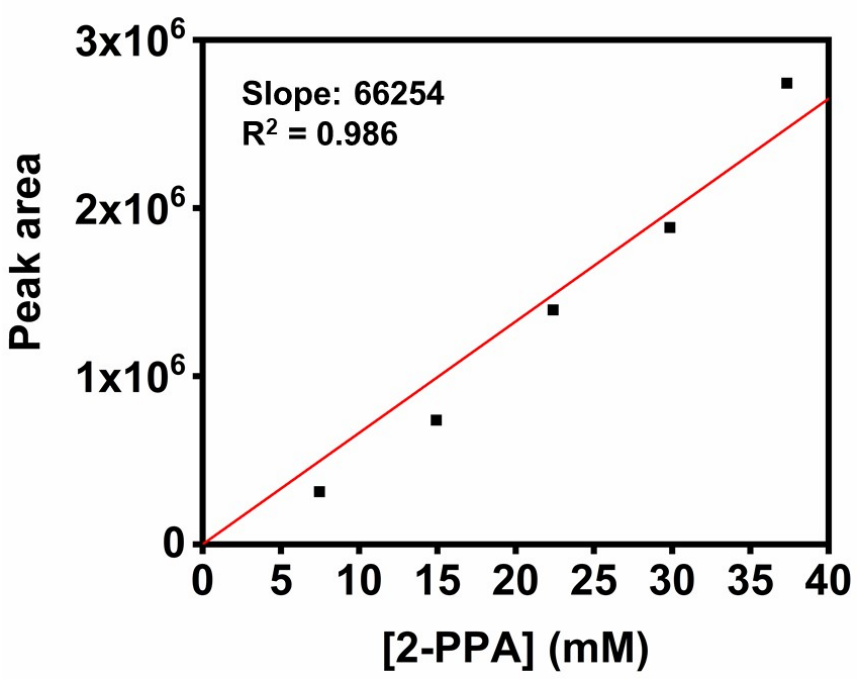

Fig. S18 Calibration curve for 2-PPA.

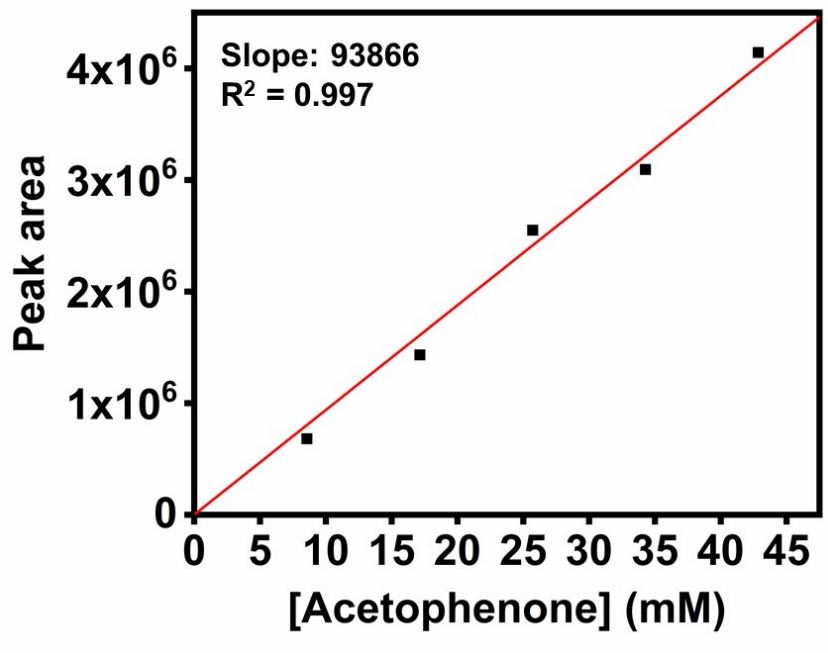

Fig. S19 Calibration curve for acetophenone.

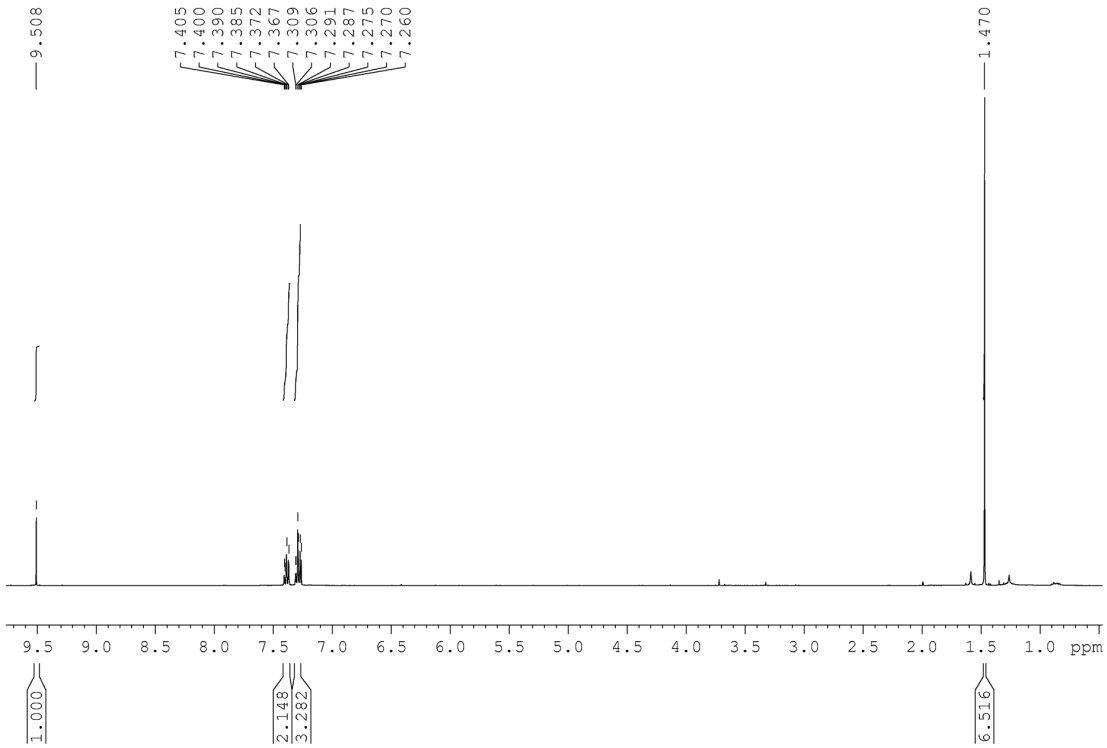

Fig. S20 ^{1}H NMR spectrum (400 MHz, CD_2Cl_2) of 2-methyl-2-phenylpropionaldehyde. The synthesis followed a literature-reported method.[5]