

Supplementary Information

Selective and efficient catalytic oxygenation of alkyl aromatics employing H₂O₂ catalyzed by simple porphyrin iron(II) under mild conditions

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S1. Experimental section

S2. Characterizations

S3. Experiment data

S4. ¹H NMR spectra of porphyrins

S5. ¹³C NMR spectra of porphyrins

S6. ESI-MS spectra of metalloporphyrins

S7. Qualitative characterization of mechanism experiment

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S1 Experimental section

S1.1 General

All ^1H nuclear magnetic resonance (NMR) spectra were recorded on a Bruker AVANCE III 500MHz NMR spectrometer to determine the structure of porphyrins with CDCl_3 as solvent and tetramethylsilane as internal standard. The ESI-MS data of porphyrins and metalloporphyrins were performed on an Agilent 6210 LC/TOF mass spectrometer through direct injection technique. The UV-vis data were collected on a HITACHI U-3900 spectrometer using a quartz cuvette in DMF solution. The thermal stability of metalloporphyrins was studied through thermal gravimetric analysis (TGA) on a PerkinElmer Diamond TG/DTA instrument under air atmosphere from room temperature to 800 °C with the ramping speed of 10 °C/min. The redox potentials of representative metalloporphyrins were measured on a ZAHNER Zennium electrochemical workstation through three-electrode system in which a glassy carbon was employed as working electrode, a platinum wire was used as counter electrode and Ag/AgCl was employed as the reference electrode in the presence of tetrabutylammonium hexafluorophosphate (TBAPF₆) (0.025 mol/L in DMF) as supporting electrolyte. All the electrochemical measurements were conducted under the atmosphere of nitrogen at 25 °C.

S1.2 Materials

The aromatic aldehydes used for synthesizing porphyrins were brought from Energy Chemical Co. Ltd. China, Xilong Chemical Reagent Co. Ltd. China, Adamas Reagent Co. Ltd. China and Macklin Biochemical Co. Ltd. China respectively and used as received. Pyrrole was purchased from Xilong Chemical Reagent Co. Ltd. China and distilled prior to use. The metal acetates in the syntheses of metalloporphyrins were purchased from Energy Chemical Co. Ltd. China and Adamas Reagent Co. Ltd. China. Ethylbenzene and its derivatives as well as their oxidation products were acquired from Energy Chemical Co. Ltd. China, Adamas Reagent Co. Ltd. China, and Macklin

Biochemical Co. Ltd. China. all the reagents are used without further purification unless otherwise noted.

2-methoxybenzaldehyde in 99% purity, 3-methoxybenzaldehyde in 99% purity, 4-methoxybenzaldehyde in 99% purity, 2-methyl benzaldehyde in 98% purity, 3-methyl benzaldehyde in 98% purity, 4-methyl benzaldehyde in 98% purity, benzaldehyde in 98% purity, 2-chlorobenzaldehyde in 99% purity, 3-chlorobenzaldehyde in 96% purity, 4-chlorobenzaldehyde in 98% purity, 4-formyl benzoic acid in 98% purity, 2-nitrobenzaldehyde in 99% purity, 3-nitrobenzaldehyde in 99% purity, 4-nitrobenzaldehyde in 99% purity, 2, 3, 6-trichlorobenzaldehyde in 97% purity, 2, 6-dichlorobenzaldehyde in 98% purity, pyrrole in 99% purity anhydrous iron (II) acetate in 98% purity and acetonitrile in 99% purity were purchased from Shanghai Energy Chemical Co. Ltd., China. Anhydrous cobalt (II) acetate and manganese (II) acetate in 98% purity were purchased from Adamas Reagent Co. Ltd., China. Zinc (II) acetate dihydrate in 99% purity was purchased from Xilong Chemical Reagent Co. Ltd., China. Propionic acid in 99% purity was purchased from Shanghai Macklin Biochemical Co. Ltd., China. ethylbenzene in 99% purity, 1-Phenylethanol in 97% purity, acetophenone in 99% purity. Triphenylphosphine and triphenylphosphine oxide in 99% purity were purchased from Adamas Reagent Co. Ltd., China. All the other common reagents were analytical grade. All of the other reagents were used as received without further purification unless otherwise noted.

S1.3 Synthesis of porphyrins

S1.3.1 Adler-Longo method

Firstly, substituted benzaldehyde (150 mmol) was dissolved in propionic acid (550 mL). Then the solution was heated to refluxing under the nitrogen atmosphere with redistilled pyrrole (150 mmol) injecting slowly in. After that, the solution was kept stirring with refluxing for another 2.0 h. When the solution was cooled to the room temperature, methanol (800 mL) was poured into the mixture. A lot of precipitate would appear when methanol was added, which was collected through filtration. The

precipitate was washed with methanol (100 mL) three times until the filtrate is transparent. Finally, the crude products were purified using silica column with eluent of cyclohexane and dichloromethane (10 : 1 ~ 4 : 1, volume / volume).

Tetrakis(3-methoxyphenyl)porphyrin T(3-OCH₃)PP: Silica column (200-300 mesh), eluent ($V_{\text{cyclohexane}} : V_{\text{dichloromethane}} = 2 : 1$), purple red powder 5.73 g in the yield of 20.7%. ¹H NMR (500 MHz, CDCl₃): $\delta = 8.88$ (s, 4H), 7.81 (d, $J = 7.3$ Hz, 2H), 7.78 (s, 2H), 7.67 – 7.62 (m, 2H), 7.33 (d, $J = 8.4$ Hz, 2H), 4.00 – 3.94 (m, 6H), -2.83 (s, 1H).

Tetrakis(4-methoxyphenyl)porphyrin T(4-OCH₃)PP: Silica column (200-300 mesh), eluent ($V_{\text{cyclohexane}} : V_{\text{dichloromethane}} = 2 : 1$), purple red powder 5.91 g in the yield of 21.5%. ¹H NMR (500 MHz, CDCl₃): $\delta = 8.88$ (s, 4H), 8.14 (d, $J = 6.5$ Hz, 4H), 7.31 (d, $J = 4.6$ Hz, 4H), 4.11 (s, 6H), -2.75 (s, 1H).

Tetrakis(2-methylphenyl)porphyrin (T(2-CH₃)PP): Silica column (200-300 mesh), eluent ($V_{\text{cyclohexane}} : V_{\text{dichloromethane}} = 4 : 1$), purple red powder 5.07 g in the yield of 20.1%. ¹H NMR (500 MHz, CDCl₃): $\delta = 8.65$ (s, 4H), 8.08 – 7.90 (m, 2H), 7.67 (t, $J = 7.6$ Hz, 2H), 7.59 (d, $J = 7.1$ Hz, 2H), 7.52 (d, $J = 6.2$ Hz, 2H), 2.01 (s, 6H), -2.65 (s, 1H).

Tetrakis(3-methylphenyl)porphyrin (T(3-CH₃)PP): Silica column (200-300 mesh), eluent ($V_{\text{cyclohexane}} : V_{\text{dichloromethane}} = 3 : 1$), purple red powder 3.77 g in the yield of 15.7%. ¹H NMR (500 MHz, CDCl₃): $\delta = 8.86$ (s, 4H), 8.04 (s, 4H), 7.64 (t, $J = 7.6$ Hz, 2H), 7.59 (d, $J = 7.8$ Hz, 2H), 2.65 (s, 6H), -2.77 (s, 1H).

Tetrakis(4-methylphenyl)porphyrin (T(4-CH₃)PP): Silica column (200-300 mesh), eluent ($V_{\text{cyclohexane}} : V_{\text{dichloromethane}} = 4 : 1$), purple red powder 5.23 g in the yield of 20.8%. ¹H NMR (500 MHz, CDCl₃): $\delta = 8.87$ (s, 4H), 8.11 (d, $J = 7.8$ Hz, 4H), 7.57 (d, $J = 7.7$ Hz, 4H), 2.72 (s, 6H), -2.75 (s, 1H).

Tetrakis benzene porphyrin (TPP): Silica column (200-300 mesh), eluent ($V_{\text{cyclohexane}} : V_{\text{dichloromethane}} = 3 : 1$), purple red powder 5.68 g in the yield of 24.7%. ¹H NMR (500 MHz, CDCl₃): $\delta = 8.85$ (s, 4H), 8.22 (d, $J = 9.1$ Hz, 4H), 7.77 (t, $J = 6.9$ Hz, 6H), -2.76 (s, 1H).

Tetrakis(3-chlorophenyl)porphyrin (T(3-Cl)PP): Silica column (200-300

mesh), eluent ($V_{\text{cyclohexane}} : V_{\text{dichloromethane}} = 4 : 1$), purple red powder 5.64 g in the yield of 21.9%. ^1H NMR (500 MHz, CDCl_3): $\delta = 8.85$ (s, 4H), 8.21 (s, 2H), 8.10 (d, $J = 7.3$ Hz, 2H), 7.79 (d, $J = 6.2$ Hz, 2H), 7.69 (t, $J = 7.8$ Hz, 2H), -2.91 (s, 1H).

Tetrakis(4-chlorophenyl)porphyrin (T(4-Cl)PP): Silica column (200-300 mesh), eluent ($V_{\text{cyclohexane}} : V_{\text{dichloromethane}} = 6 : 1$), purple red powder 5.10 g in the yield of 19.6%. ^1H NMR (500 MHz, CDCl_3): $\delta = 8.86$ (s, 4H), 8.16 (d, $J = 8.3$ Hz, 4H), 7.78 (d, $J = 8.3$ Hz, 4H), -2.84 (s, 1H).

S1.3.2 Lindsay method

Aromatic aldehyde (6.0 mmol) and pyrrole (6.0 mmol) which had been redistilled, were dissolved in dry dichloromethane (600 mL) under the nitrogen atmosphere, and the obtained solution was stirred at ambient temperature for 15 min in the shield from ambient light. $\text{BF}_3 \cdot \text{OEt}_2$ (2.0 mmol) was added to the reaction mixture in one portion, and the resultant reaction solution was kept stirring for 3.0 h at ambient temperature followed by the addition of *p*-chloranil (6.0 mmol) and stirring for another 3.0 h. Then the reaction was quenched through addition of triethylamine (2.0 mL). After evaporation of solvent, the crude products were passed through neutral alumina column for purification with dichloromethane as eluent and all of the eluent from black to red was collected. The crude products obtained from concentrating the collected eluent were purified further through silica column chromatography using the eluent of cyclohexane and dichloromethane in the volume ratio of 4 : 1 ~ 1 : 1.

Tetrakis(2, 6-dichlorophenyl)porphyrin (T(2, 6-di Cl)PP): Silica column (200-300 mesh), eluent ($V_{\text{cyclohexane}} : V_{\text{dichloromethane}} = 6 : 1$), purple red powder 0.27 g in the yield of 20.7%. ^1H NMR (500 MHz, CDCl_3): $\delta = 8.67$ (s, 4H), 7.79 (d, $J = 8.2$ Hz, 4H), 7.73 – 7.67 (m, 2H), -2.54 (s, 1H).

Tetrakis(2, 3, 6-trichlorophenyl)porphyrin (T(2, 3, 6-tri Cl)PP): Silica column (200-300 mesh), eluent ($V_{\text{cyclohexane}} : V_{\text{dichloromethane}} = 5 : 1$), purple red powder 0.37 g in the yield of 23.0%. ^1H NMR (500 MHz, CDCl_3): $\delta = 8.68$ (s, 4H), 7.91 (d, $J = 17.6$ Hz, 2H), 7.77 (d, $J = 16.2$ Hz, 2H), -2.54 (s, 1H).

S1.4 Synthesis of metalloporphyrins

metal acetate (2.0 mmol) and porphyrin (0.20 mmol) were dissolved in DMF (100 mL) and heated to refluxing under nitrogen atmosphere. DMF was evaporated with rotary evaporation after 24.0 h. Then the obtained solid residue was dissolved in dichloromethane (60 mL) and washed with water four times (4×200 mL) until the upper water layer became clear and colorless. The crude products were purified further using silica column with eluent of cyclohexane and dichloromethane ($4 : 1 \sim 1 : 1$, volume / volume). The metalloporphyrins were dried at $80\text{ }^{\circ}\text{C}$ for 8.0 h under the conditions of vacuum before used.

Tetraphenylporphyrin iron (II) (TPPFe): Silica column (200-300 mesh), eluent ($V_{\text{cyclohexane}} : V_{\text{dichloromethane}} = 1 : 1$), dark red powder 0.0984 g in the yield of 34.8%. MS (ESI): m/z : 668.2 $[\text{M}+\text{H}]^{+}$.

Tetrakis(2, 6-dichlorophenyl)porphyrin iron (II) (T(2, 6-di Cl)PPFe): Silica column (200-300 mesh), eluent ($V_{\text{cyclohexane}} : V_{\text{dichloromethane}} = 1 : 1$), dark red powder 0.0984 g in the yield of 34.8%. MS (ESI): m/z : 943.9 $[\text{M}+\text{H}]^{+}$.

Tetrakis(4-chlorophenyl)porphyrin iron (II) (T(4-Cl)PPFe): Silica column (200-300 mesh), eluent ($V_{\text{cyclohexane}} : V_{\text{dichloromethane}} = 1 : 1$), dark red powder 0.1845 g in the yield of 76.3%. MS (ESI): m/z : 806.0 $[\text{M}+\text{H}]^{+}$.

Tetrakis(3-chlorophenyl)porphyrin iron (II) (T(3-Cl)PPFe): Silica column (200-300 mesh), eluent ($V_{\text{cyclohexane}} : V_{\text{dichloromethane}} = 1 : 1$), dark red powder 0.2145 g in the yield of 87.5%. MS (ESI): m/z : 806.0 $[\text{M}+\text{H}]^{+}$.

Tetrakis(4-bromophenyl)porphyrin iron (II) (T(4-Br)PPFe): Silica column (200-300 mesh), eluent ($V_{\text{cyclohexane}} : V_{\text{dichloromethane}} = 1 : 1$), dark red powder 0.2145 g in the yield of 87.5%. MS (ESI): m/z : 983.8 $[\text{M}+\text{H}]^{+}$.

Tetrakis(3-fluoro-4-bromophenyl)porphyrin iron (II) (T(3-F-4-Br)PPFe): Silica column (200-300 mesh), eluent ($V_{\text{cyclohexane}} : V_{\text{dichloromethane}} = 1 : 1$), dark red powder 0.2145 g in the yield of 87.5%. MS (ESI): m/z : 1055.8 $[\text{M}+\text{H}]^{+}$.

Tetrakis(3-Methoxyphenyl)porphyrin iron (II) (T(3-OCH₃)PPFe): Silica column (200-300 mesh), eluent ($V_{\text{cyclohexane}} : V_{\text{dichloromethane}} = 1 : 1$), dark red powder

0.2145 g in the yield of 87.5%. MS (ESI): m/z : 788.2 $[M+H]^+$.

Tetrakis(4-chlorophenyl)porphyrin zinc (II) (T(4-Cl)PPZn): Silica column (200-300 mesh), eluent ($V_{\text{cyclohexane}} : V_{\text{dichloromethane}} = 1 : 1$), dark red powder 0.1929 g in the yield of 78.9%. MS (ESI): m/z : 815.0 $[M+H]^+$.

Tetrakis(4-methylphenyl)porphyrin nickel (II) (T(4-CH₃)PPNi): Silica column (200-300 mesh), eluent ($V_{\text{cyclohexane}} : V_{\text{dichloromethane}} = 1 : 1$), dark red powder 0.1842 g in the yield of 84.5%. MS (ESI): m/z : 726.5 $[M+H]^+$.

S1.5 Catalytic oxidation of secondary benzylic C-H bonds

Initially, the catalytic efficiency of the metalloporphyrins was investigated towards ethylbenzene oxidation at 70 °C, in acetonitrile, and the best condition was applied to the other substrates. A typical reaction was carried out in a 35 mL reaction tube, where 0.01 mmol of catalyst; 0.1 mmol of substrate; 0.8 mmol of H₂O₂ and CH₃CN to complete 1 mL of volume, were sequentially mixed and stirred under nitrogen atmosphere, under a thermostated bath. After stirring for 6.0 h, the resultant mixture was transferred to a volumetric flask with the capacity of 5 mL using acetonitrile as solvent. In succession, the conversion and selectivity in the autoxidation of secondary benzylic C-H bonds was analyzed by GC and HPLC.

S1.6 Products analyses

The oxidation products were analyzed in a Thermo Trace 1300 gas chromatographer with Flame Ionization Detector and TG-5MS capillary column (30 m \times 0.32 mm \times 0.25 μ m). Aromatic carboxylic acids were analyzed in a Thermo Ultimate 3000 HPLC chromatographer with Photodiode Array Detector and Amethyst C18-H liquid chromatography column (250 mm \times 4.6 mm \times 0.25 μ m). Internal calibration technique was carried out for quantification, where calibration curves for all substrates and products were used to determine the respective response factor. Naphthalene was the internal standard of GC analyses and 2-naphthalenecarboxylic acid was the internal standard of HPLC analyses. For a reliable determination of the alkyl hydroperoxides,

the samples were analyzed before and after addition of triphenylphosphine, which converts the hydroperoxide to the corresponding alcohol. The method can calculate the real yield of the hydroperoxide. All the data were the average values from three experiments.

S2 Characterizations

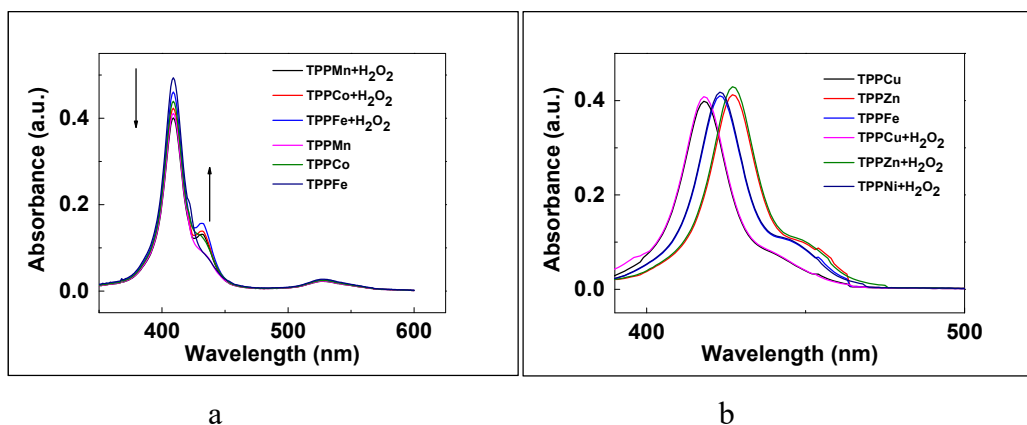


Fig. S1. The UV–Vis absorption spectra of representative porphyrins with H_2O_2 (a, b).

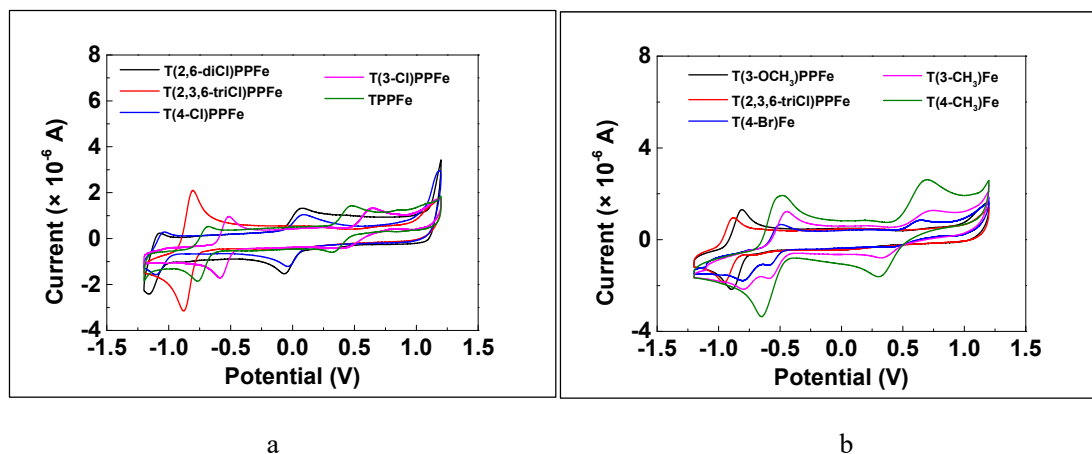
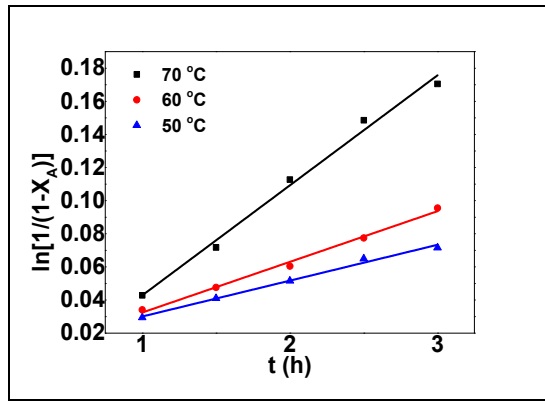
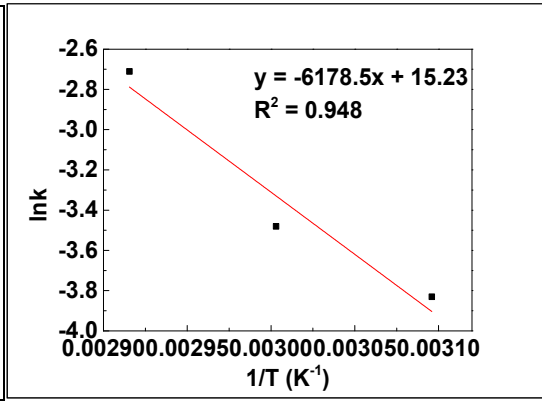


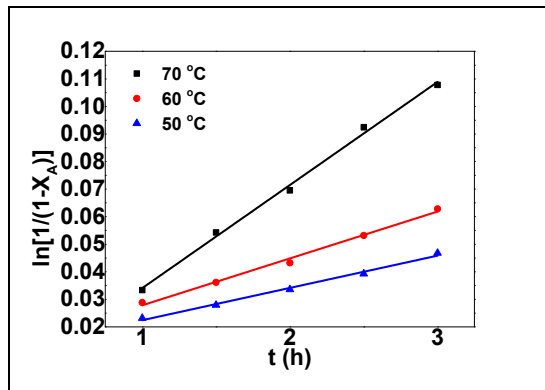
Fig. S2. Cyclic voltammetric curves for metalloporphyrins (a, b).



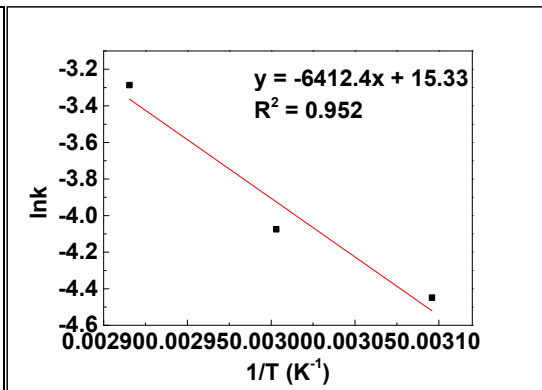
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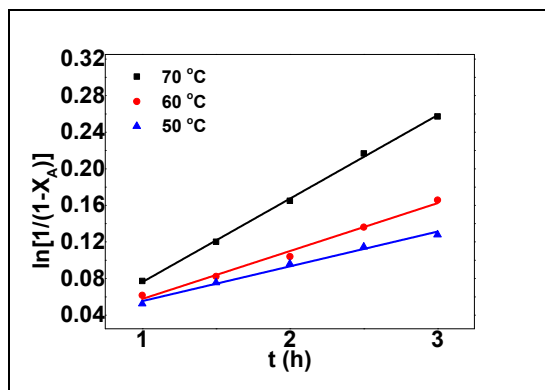
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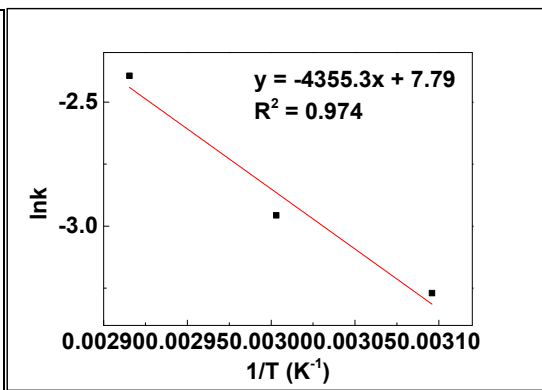
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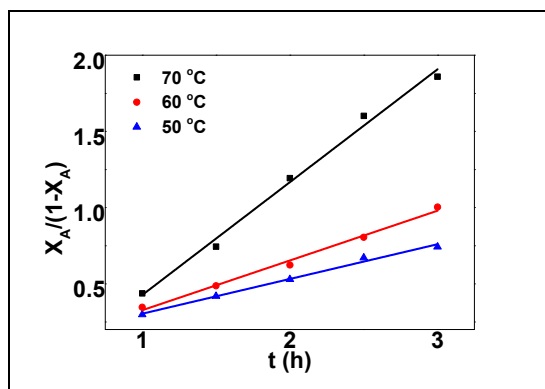
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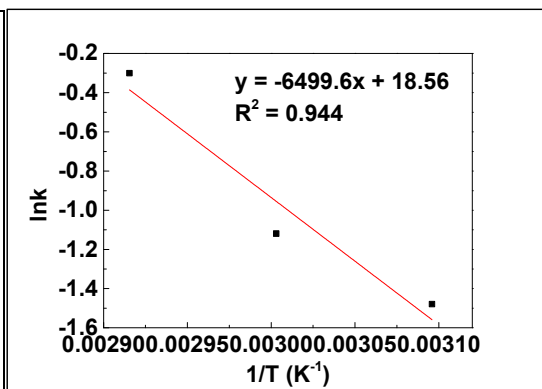
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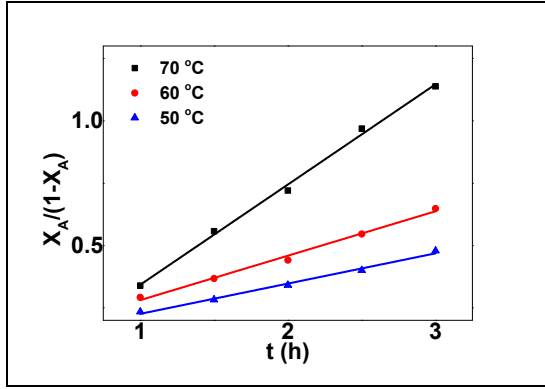
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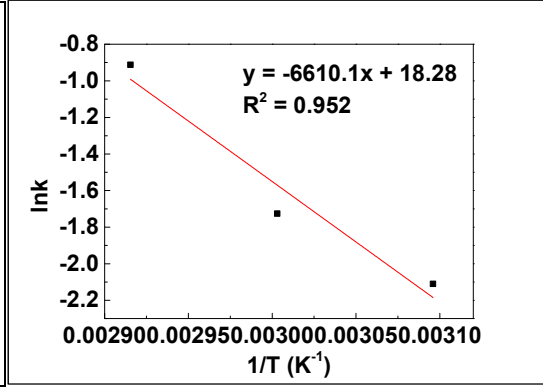
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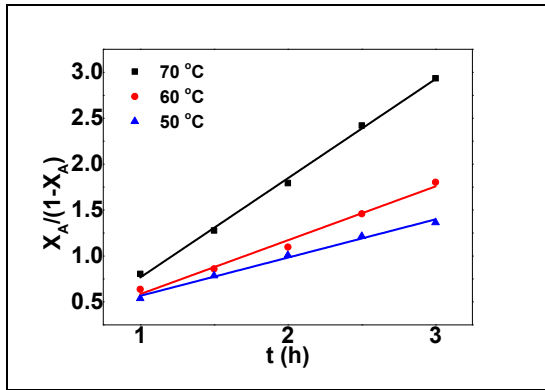
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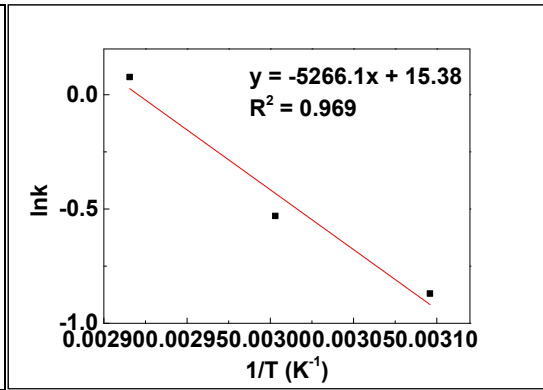
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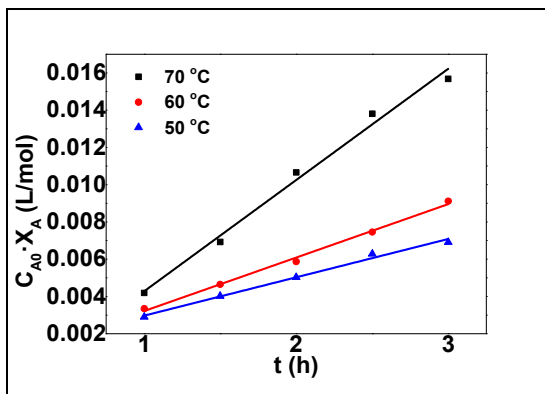
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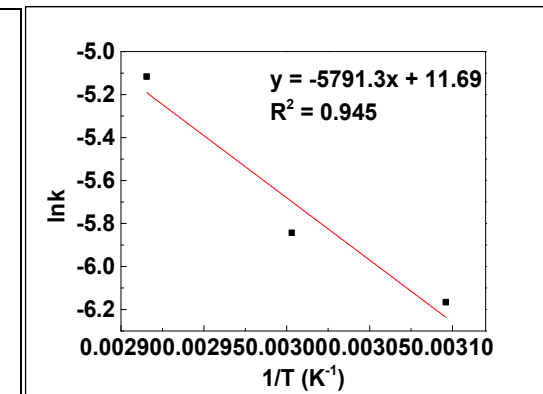
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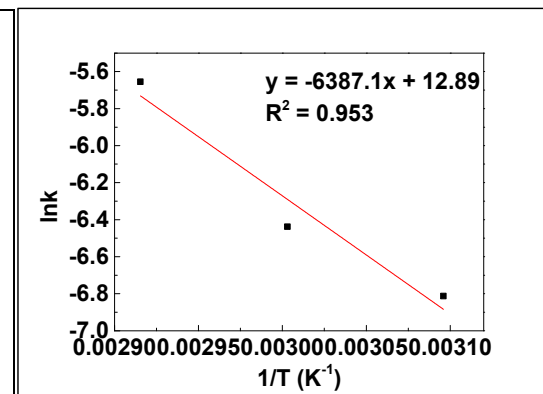
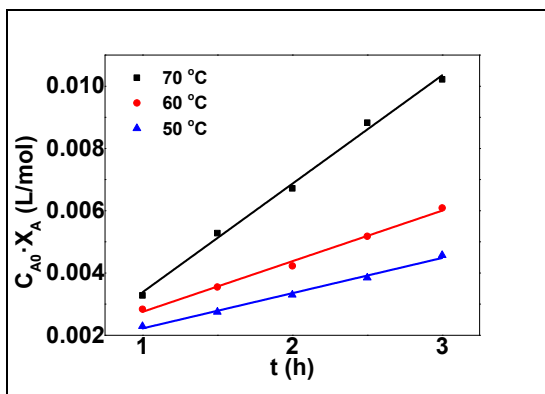
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m



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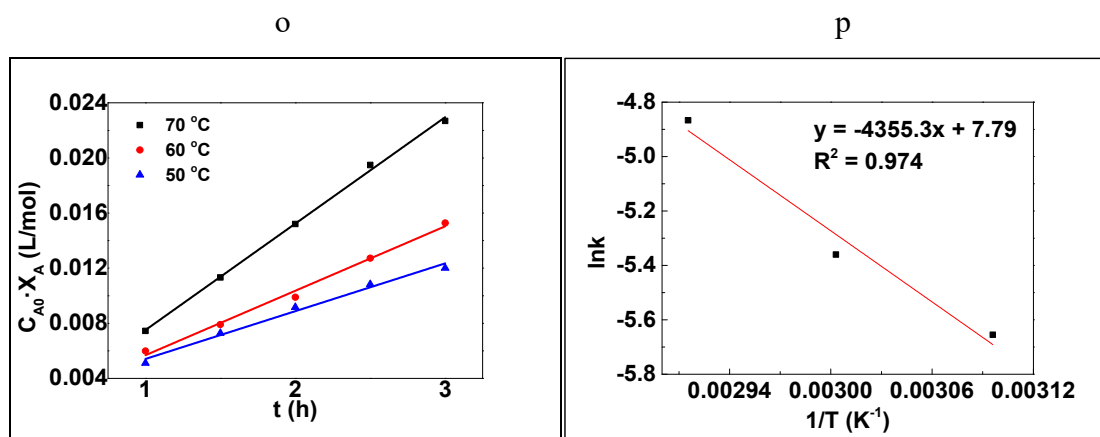


Figure S3. Pseudo-first-order fits for oxygenation of ethylbenzene with H_2O_2 catalyzed by TPPFe (a, b), T(4-Br)PPFe (c, d), T(2,6-diCl)PPFe (e, f), pseudo-second-order fits for oxygenation of ethylbenzene with H_2O_2 catalyzed by TPPFe (g, h), T(4-Br)PPFe (i, j), T(2,6-diCl)PPFe (k, l) and pseudo-zero-order fits for the oxidation of ethylbenzene with H_2O_2 catalyzed by TPPFe (m, n), T(4-Br)PPFe (o, p), T(2,6-diCl)PPFe (q, r).

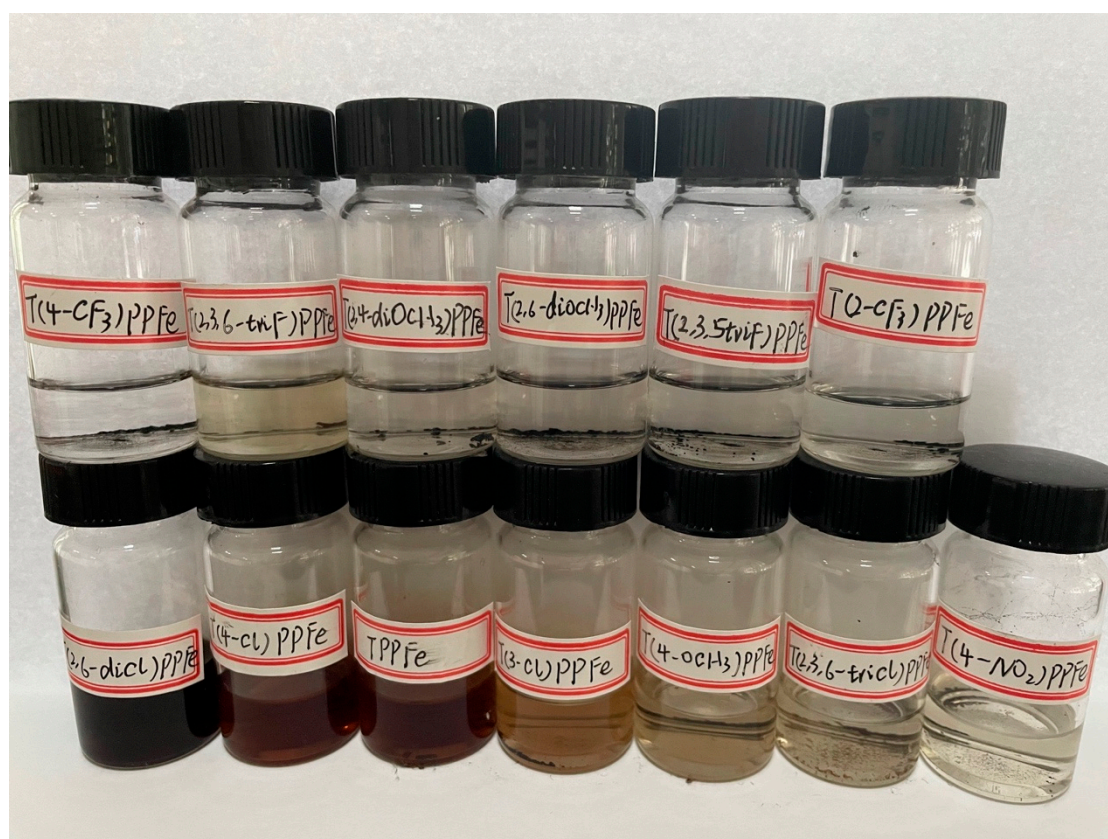


Fig. S4. Porphyrins of different structure dissolved in 10 mL acetonitrile, the darker the color, the higher the solubility (from left to right).

Hit 1 : Benzene, (1-bromoethyl)-
C₈H₉Br; MF: 906; RMF: 908; Prob 52.9%; CAS: 585-71-7; Lib: replib; ID: 15088.

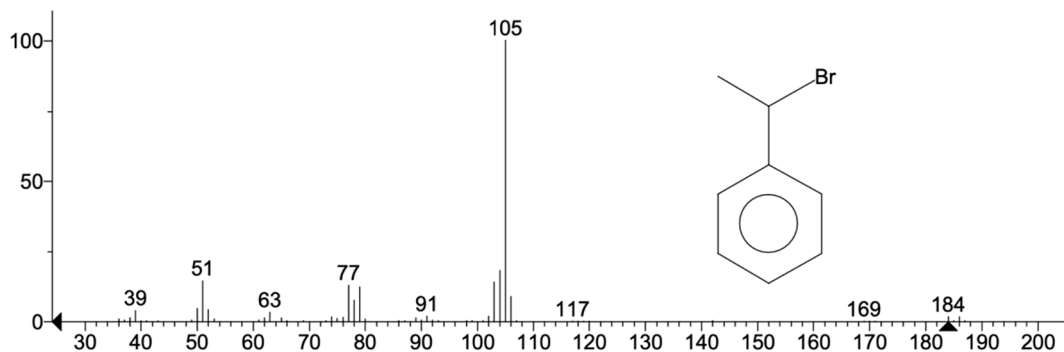


Fig. S5. (1-Bromoethyl)benzene was detected by GC-MS in mechanism experiments.

Hit 1 : 2-Propanol, 2-methyl-
C₄H₁₀O; MF: 819; RMF: 832; Prob 52.6%; CAS: 75-65-0; Lib: replib; ID: 6826.

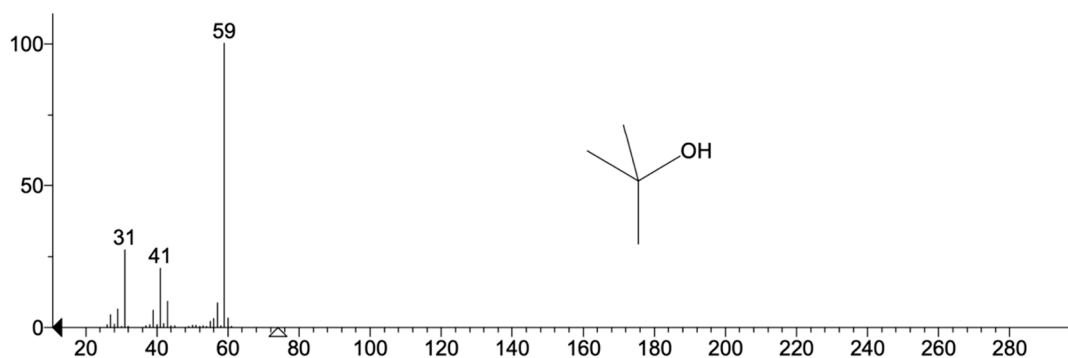


Fig. S6. Tert-Butanol was detected by GC-MS in mechanism experiments.

Hit 1 : Benzene, (1-chloroethyl)-
C₈H₉Cl; MF: 923; RMF: 925; Prob 63.4%; CAS: 672-65-1; Lib: replib; ID: 15216.

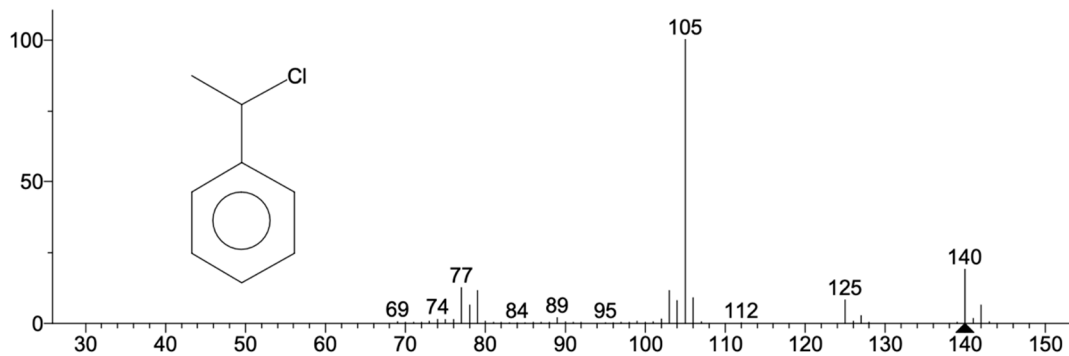
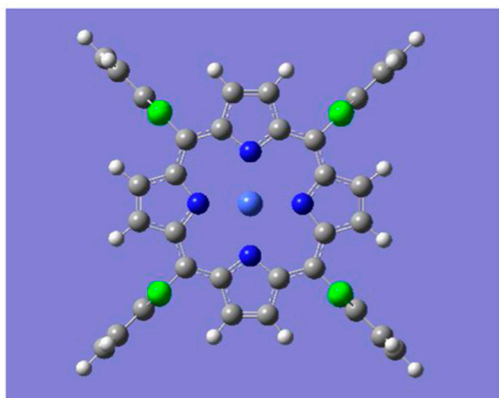
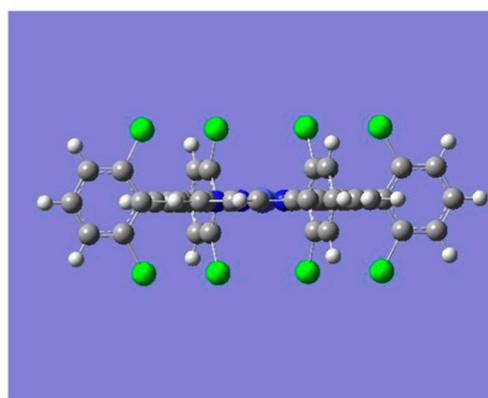


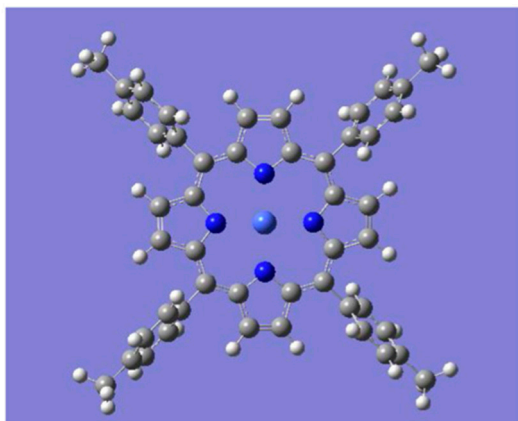
Fig. S7. (1-Chloroethyl)benzene was detected by GC-MS in mechanism experiments.



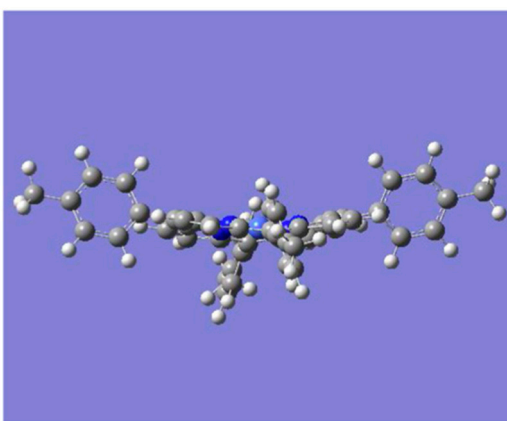
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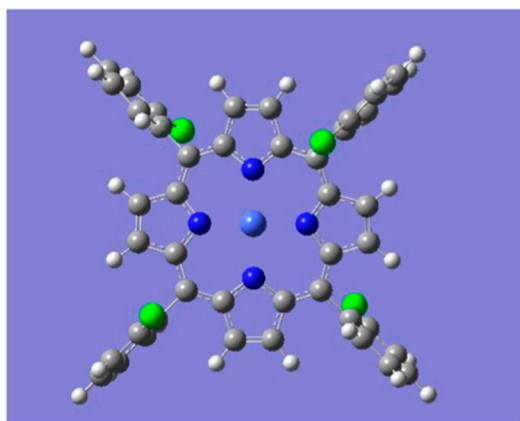
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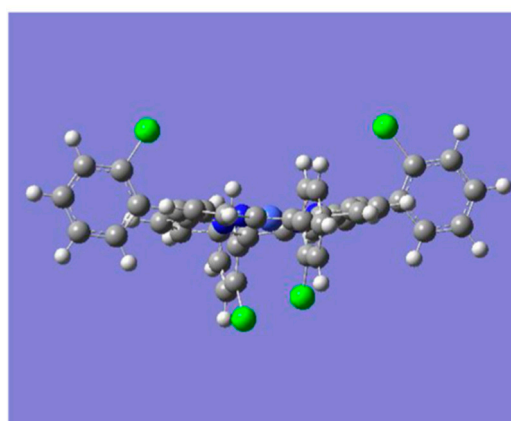
c



d



e

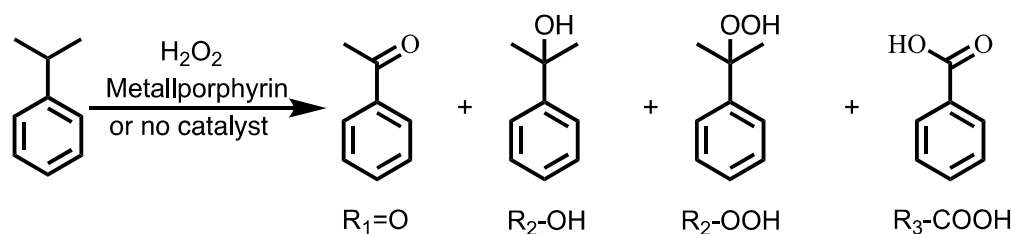


f

Fig. S8. Optimized conformations of representative metalloporphyrins T(2,6-diCl)PPFe (a, b), T(4-CH₃)PPFe (c, d), T(2-Cl)PPFe (e, f).

S3 Experiment data

Table S1 Effect of temperature on catalytic oxidation of tertiary benzylic C-H bonds^a.



Entry	Catalysts	Temp. (°C)	Conversion (%)	Selectivity (%)			
				R ₁ =O	R ₂ -OH	R ₂ -OOH	R ₃ -COOH
1	-	50	<1%	-	-	-	-
2	-	55	<1%	-	-	-	-
3	-	60	<1%	-	-	-	-
4	-	65	<1%	-	-	-	-
5	-	70	<1%	-	-	-	-
6	TPPFe	50	18.26	62.92	37.08	N.D. ^b	N.D.
7	TPPFe	55	19.48	63.13	36.87	N.D.	N.D.
8	TPPFe	60	19.99	66.69	33.31	N.D.	N.D.
9	TPPFe	65	21.30	64.71	35.29	N.D.	N.D.
10	TPPFe	70	23.22	65.29	34.71	N.D.	N.D.
11	T(4-Br)PPFe	50	9.98	63.57	36.43	N.D.	N.D.
12	T(4-Br)PPFe	55	10.66	64.01	35.99	N.D.	N.D.
13	T(4-Br)PPFe	60	12.44	64.42	35.58	N.D.	N.D.
14	T(4-Br)PPFe	65	13.30	68.64	31.36	N.D.	N.D.
15	T(4-Br)PPFe	70	15.63	63.39	36.61	N.D.	N.D.
16	TPPFe ^c	70	22.68	64.59	35.41	N.D.	N.D.
17	T(4-Br)PPFe ^c	70	15.06	64.35	35.65	N.D.	N.D.
18	TPP	70	<1%	-	-	-	-
19	T(4-Br)PP	70	<1%	-	-	-	-
20	Fe(OAc) ₂	70	<1%	-	-	-	-

^a Reaction tube (35 mL), cumene (0.1 mmol, 0.0120 g), H₂O₂ (0.8 mmol), 6.0 h, 550 rpm.

^b No obvious product detected.

^c Sample were analyzed after addition of triphenylphosphine.

Table S2 Effect of central metal on catalytic oxidation of secondary benzylic C-H bonds^a.

$\text{R}_1=\text{O}$ R_1-OH R_1-OOH R_2-COOH

Entry	Catalyst	Conversion (%)	Selectivity (%)			
			R ₁ -OOH	R ₁ -OH	R ₁ =O	R ₂ -COOH
1	T(4-CH ₃)PPFe	20.52	78.32	21.68	N.D. ^b	N.D.
2	T(4-CH ₃)PPCo	<1%	-	-	-	-
3	T(4-CH ₃)PPMn	<1%	-	-	-	-
4	T(4-CH ₃)PPNi	<1%	-	-	-	-
5	T(4-CH ₃)PPCu	<1%	-	-	-	-
6	T(4-CH ₃)PPZn	<1%	-	-	-	-
7	T(4-Cl)PPFe	20.84	82.38	17.62	N.D.	N.D.
8	T(4-Cl)PPCo	<1%	-	-	-	-
9	T(4-Cl)PPMn	<1%	-	-	-	-
10	T(4-Cl)PPNi	<1%	-	-	-	-
11	T(4-Cl)PPCu	<1%	-	-	-	-
12	T(4-Cl)PPZn	<1%	-	-	-	-

^a Reaction tube (35 mL), ethylbenzene (0.1 mmol, 0.0106 g), H₂O₂ (0.8 mmol), metalloporphyrins (10%, mol/mol), 70 °C, 6.0 h, 550 rpm.

^b No obvious product detected.

Table S3 Effect of central metal on catalytic oxidation of tertiary benzylic C-H bonds^a.

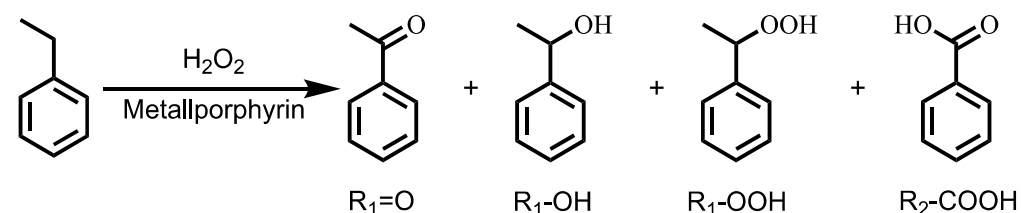
Entry	Catalyst	Conversion (%)	Selectivity (%)			
			R ₁ -OOH	R ₂ -OH	R ₂ =O	R ₃ -COOH
1	TPPFe	23.22	65.29	34.71	N.D. ^b	N.D.
2	TPPCo	<1%	-	-	-	-
3	TPPMn	<1%	-	-	-	-
4	TPPNi	<1%	-	-	-	-
5	TPPCu	<1%	-	-	-	-
6	TPPZn	<1%	-	-	-	-
7	T(4-Br)PPFe	15.63	63.39	36.61	N.D.	N.D.
8	T(4-Br)PPCo	<1%	-	-	-	-
9	T(4-Br)PPMn	<1%	-	-	-	-
10	T(4-Br)PPNi	<1%	-	-	-	-
11	T(4-Br)PPCu	<1%	-	-	-	-
12	T(4-Br)PPZn	<1%	-	-	-	-
13	T(4-CH ₃)PPFe	21.59	74.80	25.20	N.D.	N.D.
14	T(4-CH ₃)PPCo	<1%	-	-	-	-
15	T(4-CH ₃)PPMn	<1%	-	-	-	-
16	T(4-CH ₃)PPNi	<1%	-	-	-	-
17	T(4-CH ₃)PPCu	<1%	-	-	-	-
18	T(4-CH ₃)PPZn	<1%	-	-	-	-
19	T(4-Cl)PPFe	21.47	71.00	29.00	N.D.	N.D.
20	T(4-Cl)PPCo	<1%	-	-	-	-

21	T(4-Cl)PPMn	<1%	-	-	-	-
22	T(4-Cl)PPNi	<1%	-	-	-	-
23	T(4-Cl)PPCu	<1%	-	-	-	-
24	T(4-Cl)PPZn	<1%	-	-	-	-

^a Reaction tube (35 mL), cumene (0.1 mmol, 0.0120 g), H₂O₂ (0.8 mmol), metalloporphyrins (10%, mol/mol), 70 °C, 6.0 h, 550 rpm.

^b No obvious product detected.

Table S4 Effect of porphyrin structures on catalytic oxidation of secondary benzylic C-H bonds^a.

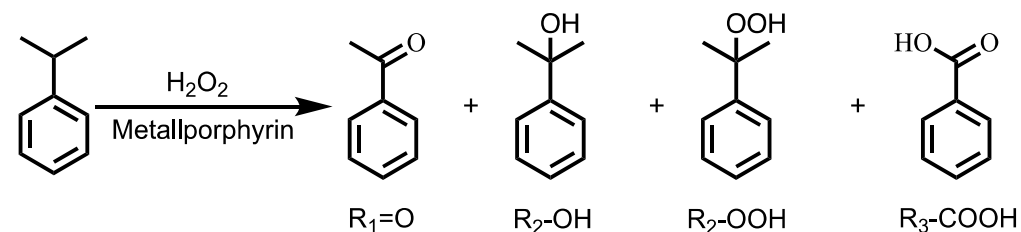


Entry	Catalysts	Conversion (%)	Selectivity (%)			
			R ₁ -OOH	R ₁ -OH	R ₁ =O	R ₂ -COOH
1	T(2,3-diF-4-Br)PPFe	13.49	58.58	41.42	N.D.	N.D. ^b
2	T(2,5-diF-4-Br)PPFe	14.73	61.89	38.11	N.D.	N.D.
3	T(2,6-diF-4-Br)PPFe	14.13	62.80	37.20	N.D.	N.D.

^a Reaction tube (35 mL), ethylbenzene (0.1 mmol, 0.0106 g), H₂O₂ (0.8 mmol), metalloporphyrins (10%, mol/mol), 70 °C, 6.0 h, 550 rpm.

^b No obvious product detected.

Table S5 Effect of porphyrin structures on catalytic oxidation of tertiary benzylic C-H bonds^a.



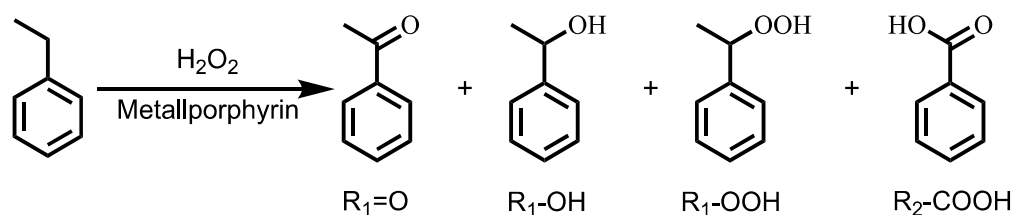
Entry	Catalysts	Conversion (%)	Selectivity (%)			
			R ₁ -OOH	R ₂ -OH	R ₂ =O	R ₃ -COOH
1	TPPFe	23.22	65.29	34.71	N.D.	N.D. ^b
2	T(2-Cl)PPFe	<1%	-	-	-	-
3	T(3-Cl)PPFe	17.50	75.68	24.32	N.D.	N.D.
4	T(4-Cl)PPFe	21.47	71.00	29.00	N.D.	N.D.
5	T(2,6-diCl)PPFe	24.18	17.44	82.56	N.D.	N.D.
6	T(2-CH ₃)PPFe	<1%	-	-	-	-
7	T(3-CH ₃)PPFe	15.88	80.07	19.93	N.D.	N.D.
8	T(4-CH ₃)PPFe	21.59	74.80	25.20	N.D.	N.D.
9	T(3-OCH ₃)PPFe	14.74	76.08	23.92	N.D.	N.D.
10	T(4-OCH ₃)PPFe	<1%	-	-	-	-
11	T(4-Br)PPFe	15.63	63.39	36.61	N.D.	N.D.
12	T(4-Br-3F)PPFe	15.21	54.36	45.64	N.D.	N.D.
13	T(4-Br-2F)PPFe	14.78	60.79	39.21	N.D.	N.D.
14	T(4-Br-2Cl)PPFe	14.86	63.87	36.13	N.D.	N.D.
15	T(4-Br-3Cl)PPFe	15.52	65.74	34.26	N.D.	N.D.
16	T(4-Br-2,3-diF)PPFe	13.49	58.58	41.42	N.D.	N.D.
17	T(4-Br-2,5-diF)PPFe	14.73	61.89	38.11	N.D.	N.D.
18	T(4-Br-2,6-diF)PPFe	14.13	62.80	37.20	N.D.	N.D.
23	T(2,3,6-3Cl) PPFe	6.32	61.30	38.70	N.D.	N.D.
24	T(2,3,5-3Cl) PPFe	6.05	62.48	37.52	N.D.	N.D.
25	T(2,3,6-3F) PPFe	5.46	65.11	34.89	N.D.	N.D.
26	T(2,3,5-3F) PPFe	5.08	61.22	38.78	N.D.	N.D.

^a Reaction tube (35 mL), cumene (0.1 mmol, 0.0120 g), H₂O₂ (0.8 mmol), metalloporphyrins, 70 °C, 6.0 h, 550 rpm.

^b No obvious product detected.

Table S6 Effect of catalyst amount on oxidation of secondary benzylic C-H bonds

employing ethylbenzene as model substrate^a.

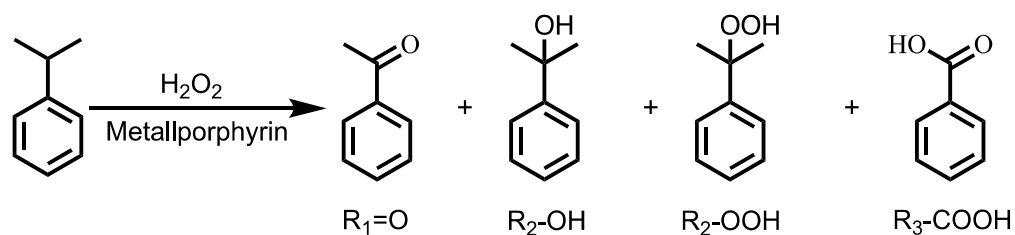


Entry	Catalysts	Catalyst amount (%, mol/mol)	Conversion (%)	Selectivity (%)			
				R ₁ =O	R ₁ -OH	R ₁ -OOH	R ₂ -COOH
1	T(4-Br)PPFe	0.005	13.81	91	9	N.D. ^b	N.D.
2	T(4-Br)PPFe	0.010	14.35	93	7	N.D.	N.D.
3	T(4-Br)PPFe	0.015	14.65	94	6	N.D.	N.D.
4	T(4-Br)PPFe	0.020	14.89	92	8	N.D.	N.D.
5	T(4-Br)PPFe	0.025	15.32	93	7	N.D.	N.D.

^a Reaction tube (35 mL), ethylbenzene (0.1 mmol, 0.0106 g), H₂O₂ (0.8 mmol), metalloporphyrins, 70 °C, 6.0 h, 550 rpm.

^b No obvious product detected.

Table S7 Effect of catalyst amount on catalytic oxidation of tertiary benzylic C-H bonds^a.



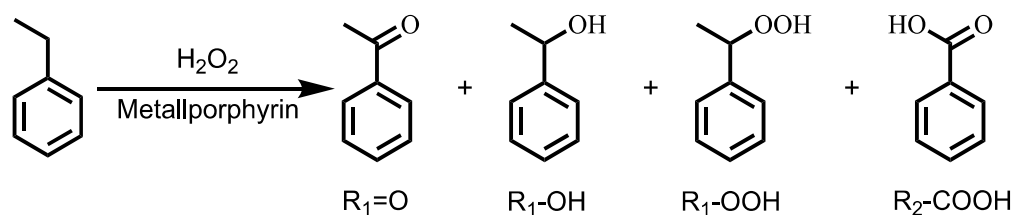
Entry	Catalysts	Catalyst amount (%, mol/mol)	Conversion (%)	Selectivity (%)			
				R ₁ =O	R ₂ -OH	R ₂ -OOH	R ₃ -COOH
1	TPPFe	0.005	22.46	65.47	34.53	N.D. ^b	N.D.
2	TPPFe	0.010	23.22	65.29	34.71	N.D.	N.D.
3	TPPFe	0.015	23.73	67.83	32.17	N.D.	N.D.
4	TPPFe	0.020	23.89	66.36	33.64	N.D.	N.D.

5	TPPFe	0.025	24.08	66.91	33.09	N.D.	N.D.
6	T(4-Br)PPFe	0.005	14.83	62.54	37.46	N.D.	N.D.
7	T(4-Br)PPFe	0.010	15.63	63.39	36.61	N.D.	N.D.
8	T(4-Br)PPFe	0.015	15.89	63.14	36.86	N.D.	N.D.
9	T(4-Br)PPFe	0.020	16.01	63.93	36.07	N.D.	N.D.
10	T(4-Br)PPFe	0.025	16.29	64.50	35.50	N.D.	N.D.

^a Reaction tube (35 mL), cumene (0.1 mmol, 0.0120 g), H₂O₂ (0.8 mmol), metalloporphyrins, 70 °C, 6.0 h, 550 rpm.

^b No obvious product detected.

Table S8 Effect of oxidant amount on oxidation of secondary benzylic C-H bonds employing ethylbenzene as model substrate^a.



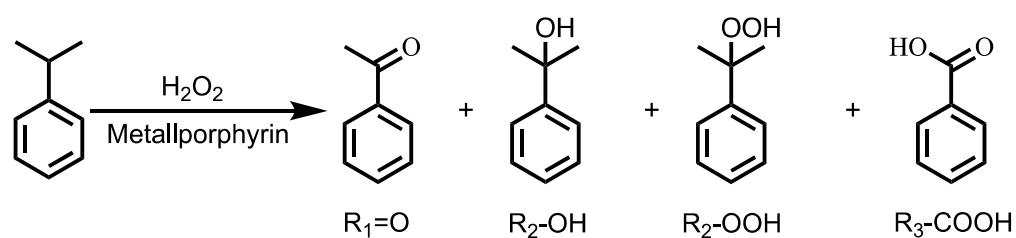
Entry	Catalysts	Mole ratio (H ₂ O ₂ : substrate)	Conversion (%)	Selectivity (%)			
				R ₁ =O	R ₁ -OH	R ₁ -OOH	R ₂ -COOH
7	T(4-Br)PPFe	4	5.56	89	11	N.D. ^b	N.D.
8	T(4-Br)PPFe	6	9.41	90	10	N.D.	N.D.
9	T(4-Br)PPFe	8	14.35	93	7	N.D.	N.D.
10	T(4-Br)PPFe	10	17.83	88	7	N.D.	5
11	T(4-Br)PPFe	12	18.39	84	6	N.D.	10
12	T(4-Br)PPFe	14	19.07	83	7	N.D.	10

^a Reaction tube (35 mL), ethylbenzene (0.1 mmol, 0.0106 g), H₂O₂, metalloporphyrins (10%, mol/mol), 70 °C, 6.0 h, 550 rpm.

^b No obvious product detected.

Table S9 Effect of oxidant amount on catalytic oxidation of tertiary benzylic C-H

bonds^a.

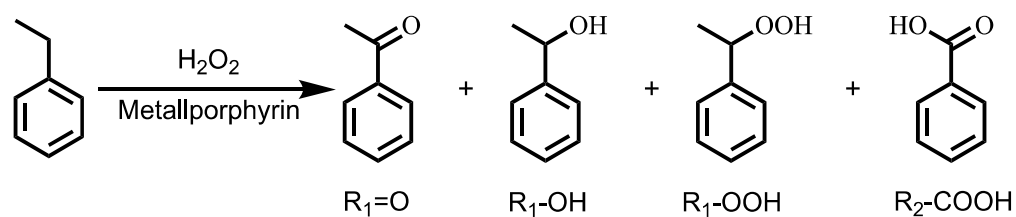


Entry	Catalysts	Mole ratio (H ₂ O ₂ : substrate)	Conversion (%)	Selectivity (%)			
				R ₁ =O	R ₂ -OH	R ₂ -OOH	R ₃ -COOH
1	TPPFe	4	8.69	64.13	35.87	N.D. ^b	N.D.
2	TPPFe	6	16.45	64.76	35.24	N.D.	N.D.
3	TPPFe	8	23.22	65.29	34.71	N.D.	N.D.
4	TPPFe	10	23.43	64.58	35.42	N.D.	N.D.
5	TPPFe	12	23.71	65.24	34.76	N.D.	N.D.
6	TPPFe	14	24.13	66.11	33.89	N.D.	N.D.
7	T(4-Br)PPFe	4	4.38	65.71	34.29	N.D.	N.D.
8	T(4-Br)PPFe	6	9.46	62.14	37.86	N.D.	N.D.
9	T(4-Br)PPFe	8	15.63	63.39	36.61	N.D.	N.D.
10	T(4-Br)PPFe	10	16.87	66.02	33.98	N.D.	N.D.
11	T(4-Br)PPFe	12	17.02	65.49	34.51	N.D.	N.D.
12	T(4-Br)PPFe	14	17.16	66.38	33.62	N.D.	N.D.

^a Reaction tube (35 mL), ethylbenzene (0.1 mmol, 0.0106 g), H₂O₂, metalloporphyrins (10%, mol/mol), 70 °C, 6.0 h, 550 rpm.

^b No obvious product detected.

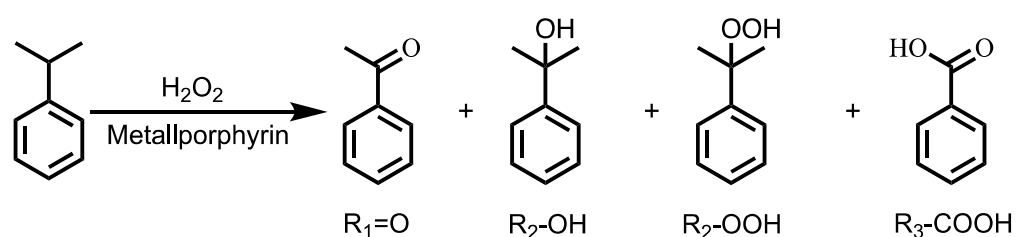
Table S10 Effect of reaction time on oxidation of secondary benzylic C-H bonds employing ethylbenzene as model substrate^a.



Entry	Catalysts	Time (h)	Conversion (%)	Selectivity (%)			
				R ₁ =O	R ₁ -OH	R ₁ -OOH	R ₂ -COOH
1	TPPFe	2	11.28	74	26	-	-
2	TPPFe	4	18.45	78	22	-	-
3	TPPFe	6	19.71	79	21	-	-
4	TPPFe	8	20.09	75	25	-	-
5	TPPFe	10	20.30	76	24	-	-
6	TPPFe	12	20.87	79	21	-	-
7	T(4-Br)PPFe	2	9.48	88	12	-	-
8	T(4-Br)PPFe	4	13.15	90	10	-	-
9	T(4-Br)PPFe	6	14.35	93	7	-	-
10	T(4-Br)PPFe	8	14.47	94	6	-	-
11	T(4-Br)PPFe	10	14.58	93	7	-	-
12	T(4-Br)PPFe	12	14.62	93	7	-	-
13	T(2,6-diCl)PPFe	2	16.11	83	17	-	-
14	T(2,6-diCl)PPFe	4	24.43	85	15	-	-
15	T(2,6-diCl)PPFe	6	27.44	85	15	-	-
16	T(2,6-diCl)PPFe	8	28.67	85	15	-	-
17	T(2,6-diCl)PPFe	10	28.87	85	15	-	-
18	T(2,6-diCl)PPFe	12	28.90	86	14	-	-

^a Reaction tube (35 mL), ethylbenzene (0.1 mmol, 0.0106 g), H₂O₂ (0.8 mmol), metalloporphyrins (10%, mol/mol), 70 °C, 550 rpm.

Table S11 Effect of reaction time on catalytic oxidation of tertiary benzylic C-H bonds^a.



Entry	Catalysts	Time (h)	Conversion (%)	Selectivity (%)			
				R ₁ =O	R ₂ -OH	R ₂ -OOH	R ₃ -COOH
1	TPPFe	2	12.43	62.88	37.12	N.D.	N.D.
2	TPPFe	4	19.67	64.42	35.58	N.D.	N.D.
3	TPPFe	6	23.22	65.29	34.71	N.D.	N.D.
4	TPPFe	8	23.55	66.17	33.83	N.D.	N.D.
5	TPPFe	10	23.89	62.56	37.44	N.D.	N.D.
6	TPPFe	12	24.12	66.35	33.65	N.D.	N.D.
7	T(4-Br)PPFe	2	8.40	61.31	38.69	N.D.	N.D.
8	T(4-Br)PPFe	4	10.51	62.57	37.43	N.D.	N.D.
9	T(4-Br)PPFe	6	15.63	63.39	36.61	N.D.	N.D.
10	T(4-Br)PPFe	8	15.69	64.06	35.94	N.D.	N.D.
11	T(4-Br)PPFe	10	15.75	63.85	36.15	N.D.	N.D.
12	T(4-Br)PPFe	12	15.89	63.73	36.27	N.D.	N.D.

^a Reaction tube (35 mL), cumene (0.1 mmol, 0.0120 g), H₂O₂ (0.8 mmol), metalloporphyrins (10%, mol/mol), 70 °C, 550 rpm.

^b No obvious product detected.

Table S12 The pseudo-zero-order kinetic parameters for catalytic oxidation of ethylbenzene.

Entry	Catalysts	Temp. (°C)	k (h ⁻¹)	R ²	Average intercepts	E _a (kJ/mol)
1	TPPFe	50	0.0021	0.9915	-0.0001	48.15
2		60	0.0029	0.9954		
3		70	0.0060	0.9899		
4	T(4-Br)PPFe	50	0.0011	0.9935	0.0067	53.10
5		60	0.0016	0.9944		
6		70	0.0035	0.9960		

7	T(2, 6-di Cl)PPFe	50	0.0035	0.9886	0.0009	36.21
8		60	0.0047	0.9930		
9		70	0.0077	0.9984		

Table S13 The pseudo-second-order kinetic parameters for catalytic oxidation of ethylbenzene.

Entry	Catalysts	Temp. (°C)	k (h ⁻¹)	R ²	Average intercepts	Ea (kJ/mol)
1	TPPFe	50	0.1213	0.9924	-0.0789	54.04
2		60	0.1781	0.9929		
3		70	0.4019	0.9966		
4	T(4-Br)PPFe	50	0.2279	0.9925	0.0497	54.96
5		60	0.3265	0.9927		
6		70	0.7404	0.9927		
7	T(2, 6-di Cl)PPFe	50	0.4164	0.9925	-0.0557	43.78
8		60	0.5865	0.9877		
9		70	1.0806	0.9978		

S4 ¹H NMR spectra of porphyrins

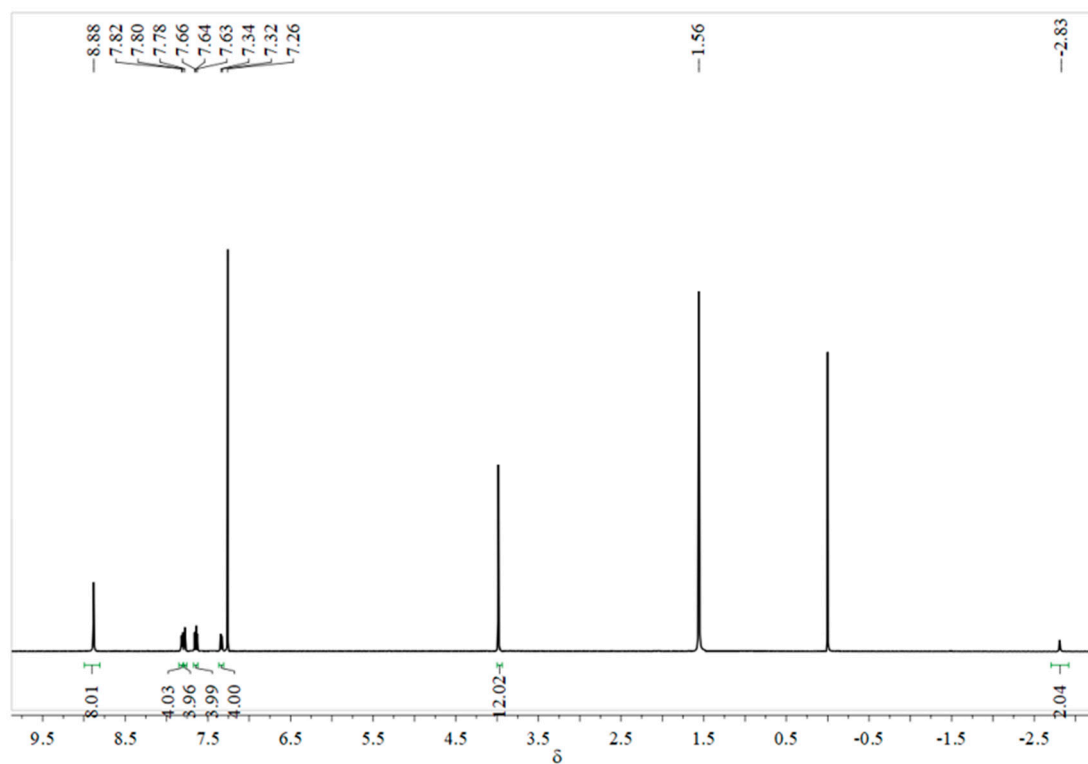


Fig. S9. ¹H NMR spectrum of T(3-OCH₃)PP in CDCl₃

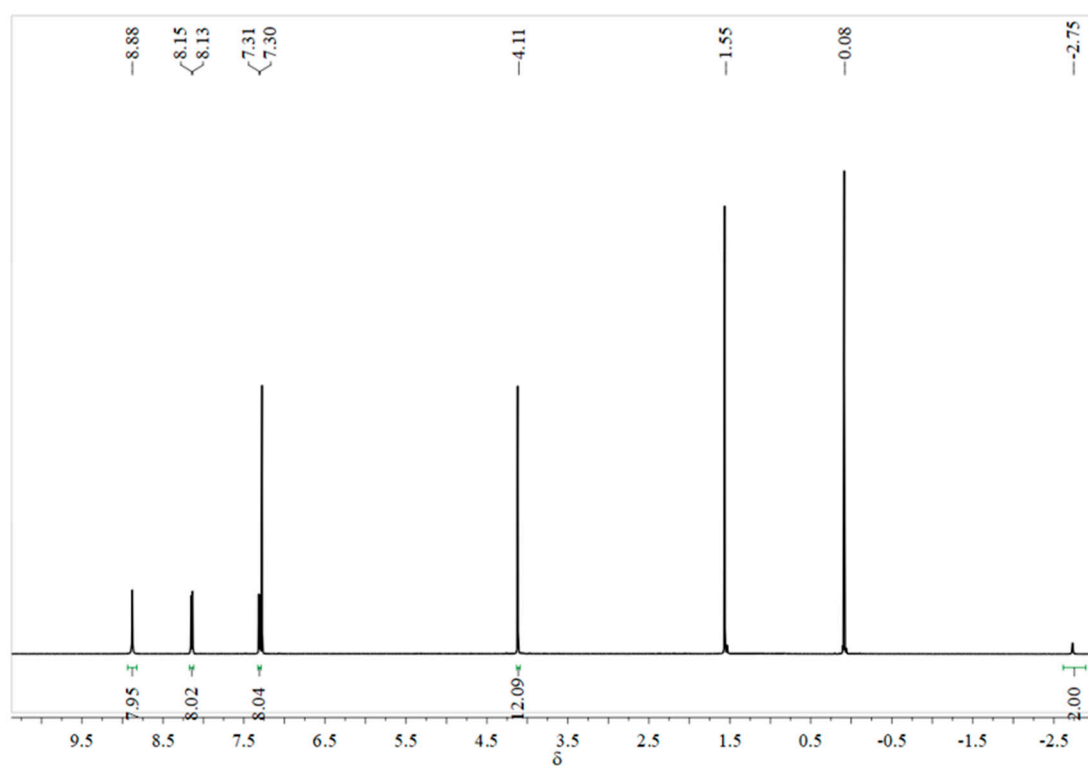


Fig. S10. ¹H NMR spectrum of T(4-OCH₃)PP in CDCl₃

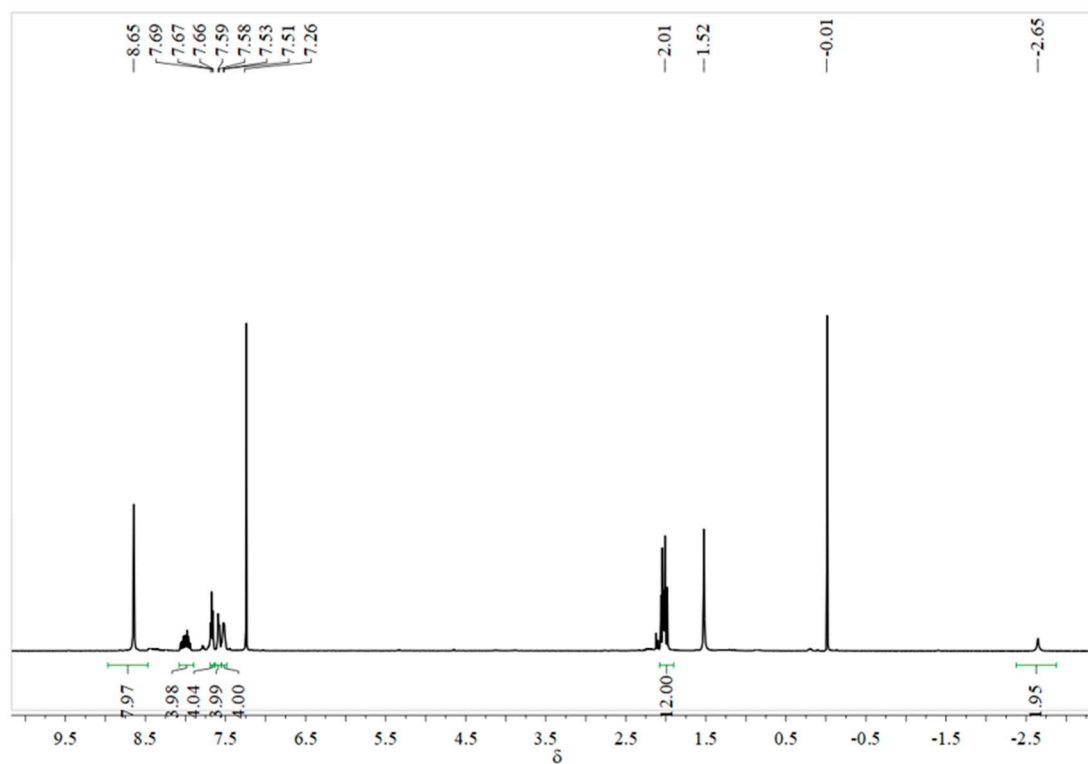


Fig. S11. ¹H NMR spectrum of T(2-CH₃)PP in CDCl₃

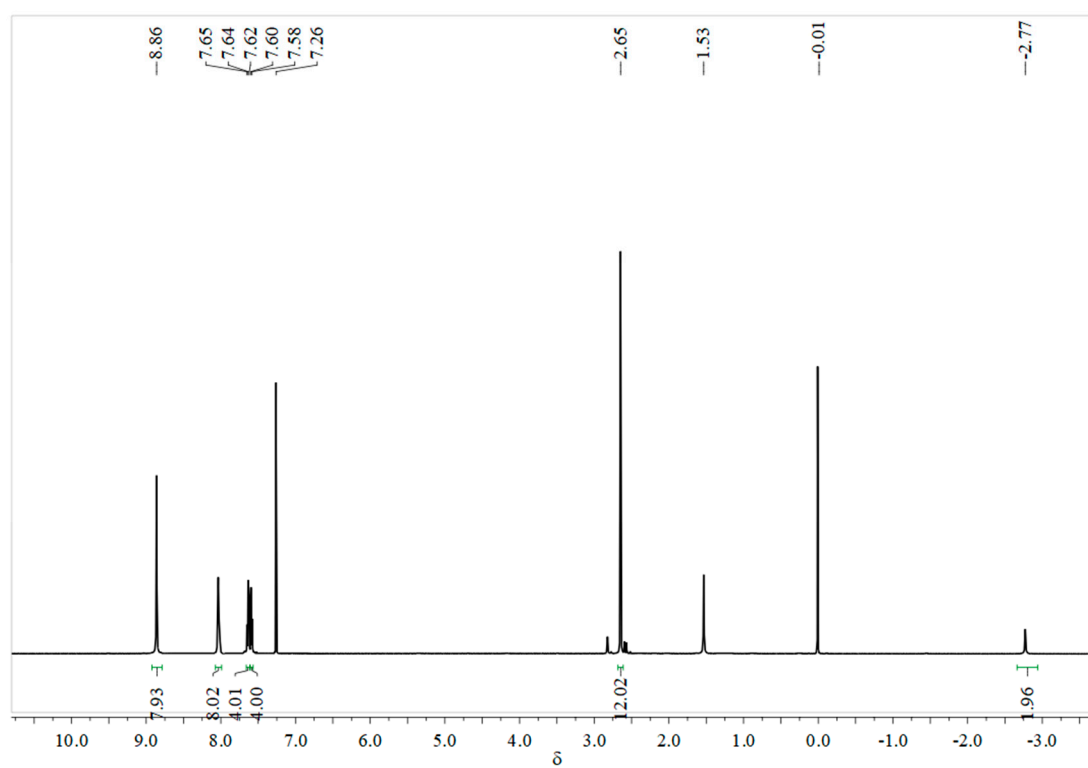


Fig. S12. ¹H NMR spectrum of T(3-CH₃)PP in CDCl₃

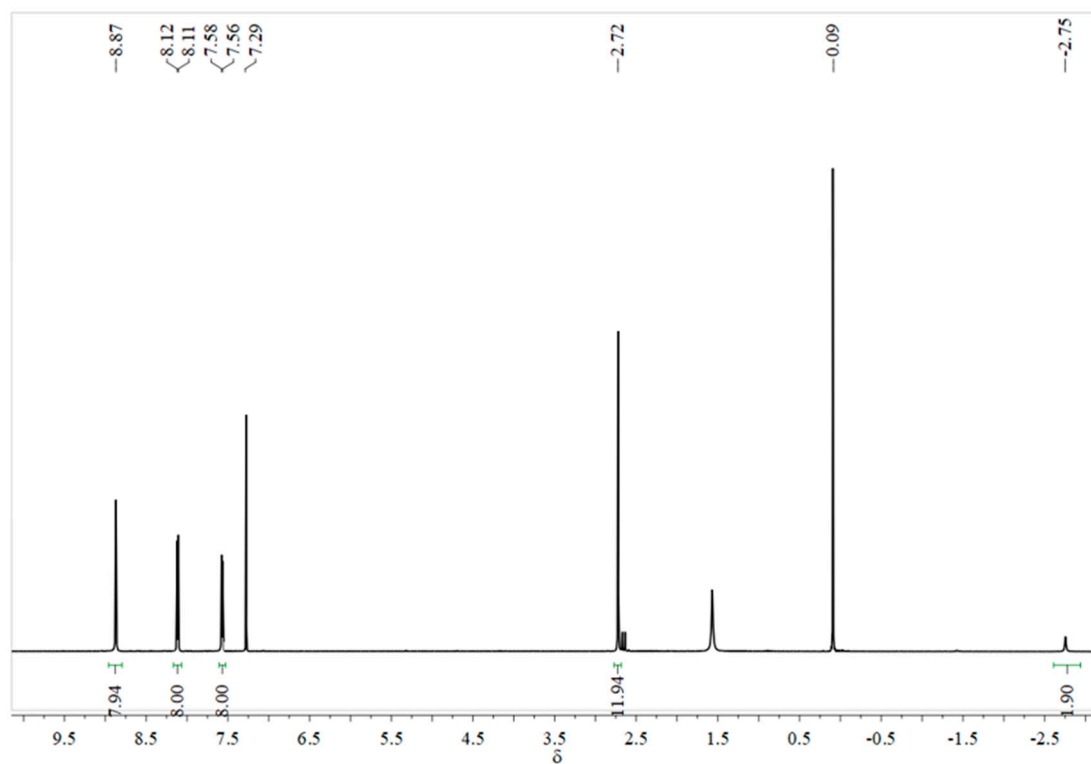


Fig. S13. ^1H NMR spectrum of T(4-CH₃)PP in CDCl₃

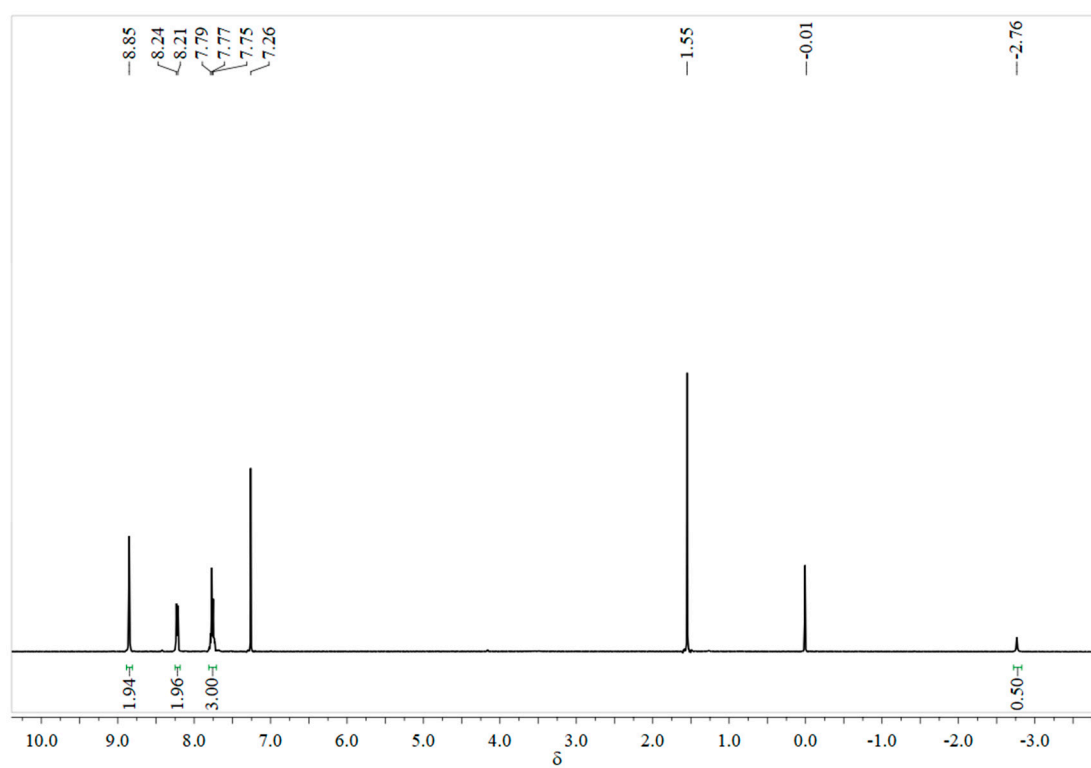


Fig. S14. ^1H NMR spectrum of TPP in CDCl₃

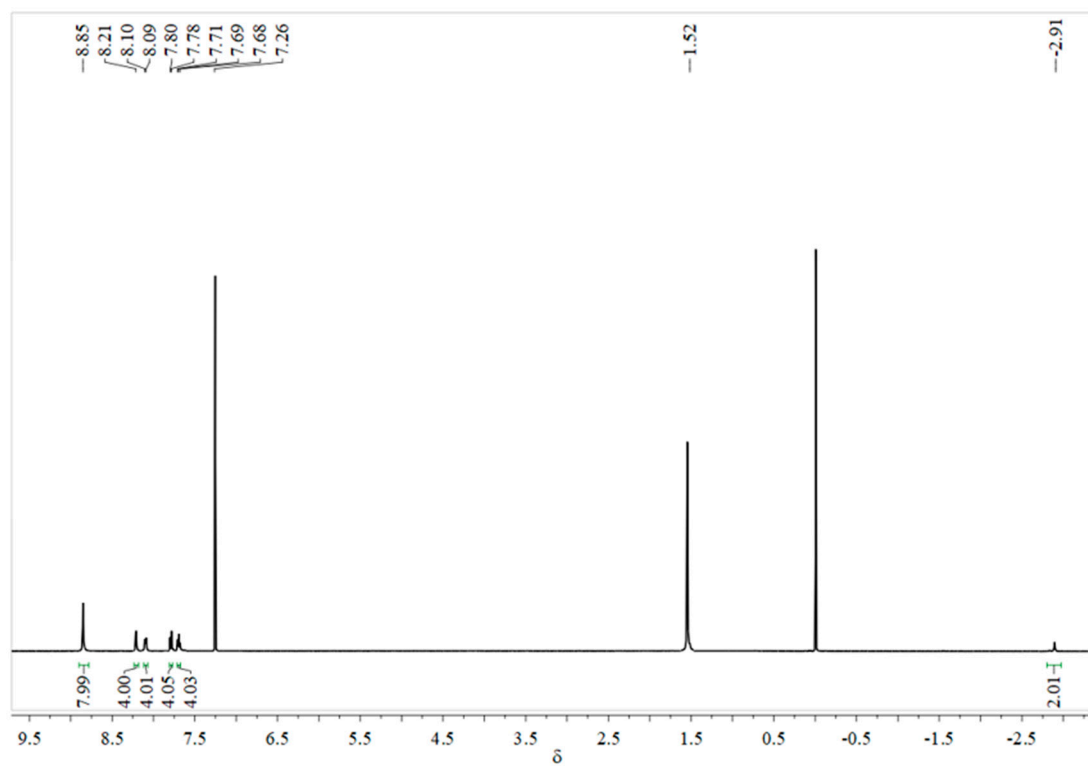


Fig. S15. ¹H NMR spectrum of T(3-Cl)PP in CDCl₃

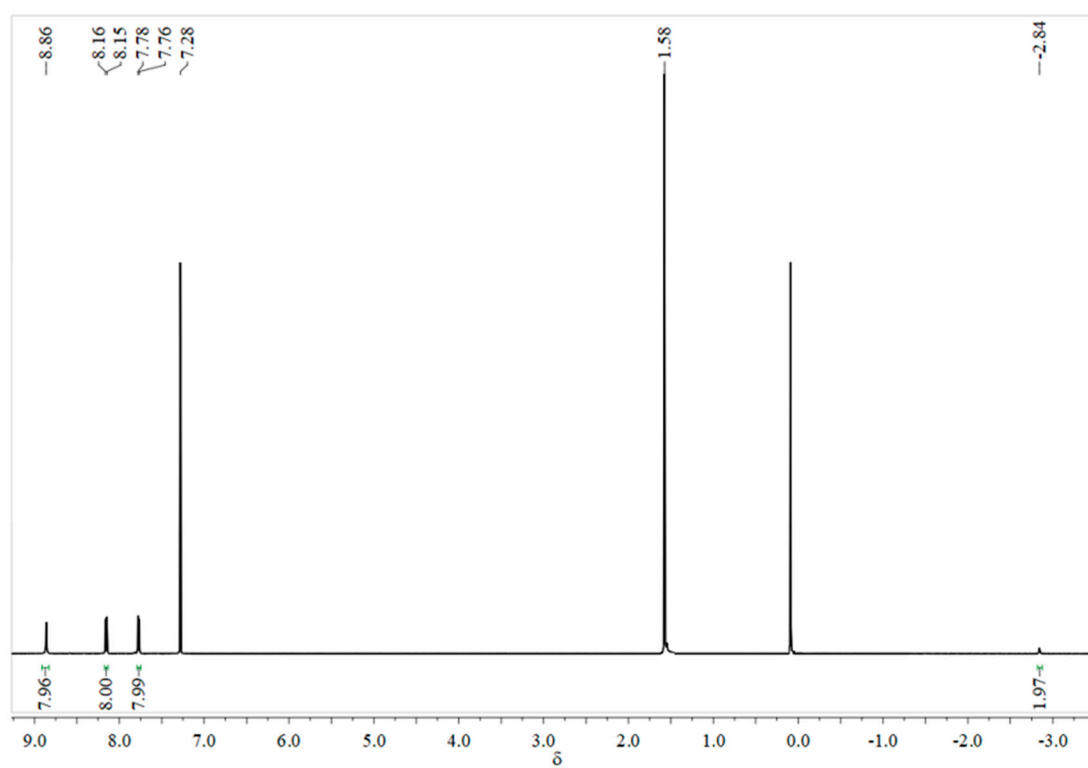


Fig. S16. ¹H NMR spectrum of T(4-Cl)PP in CDCl₃

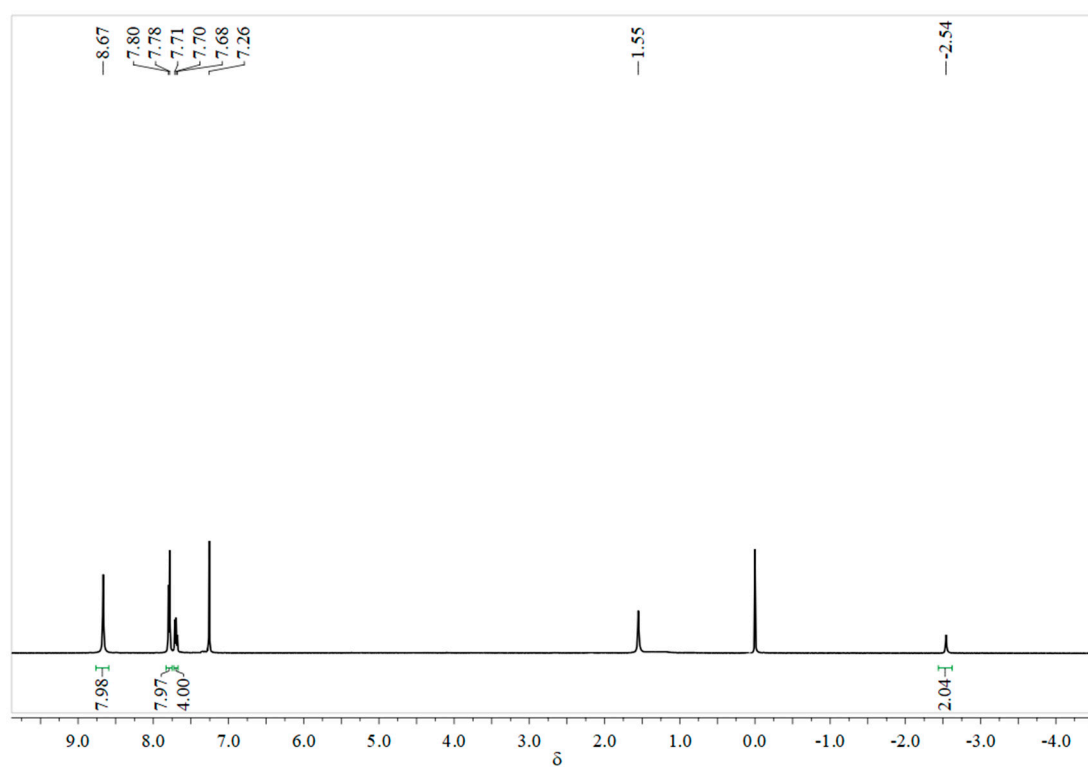


Fig. S17. ¹H NMR spectrum of T(2, 6-di Cl)PP in CDCl₃

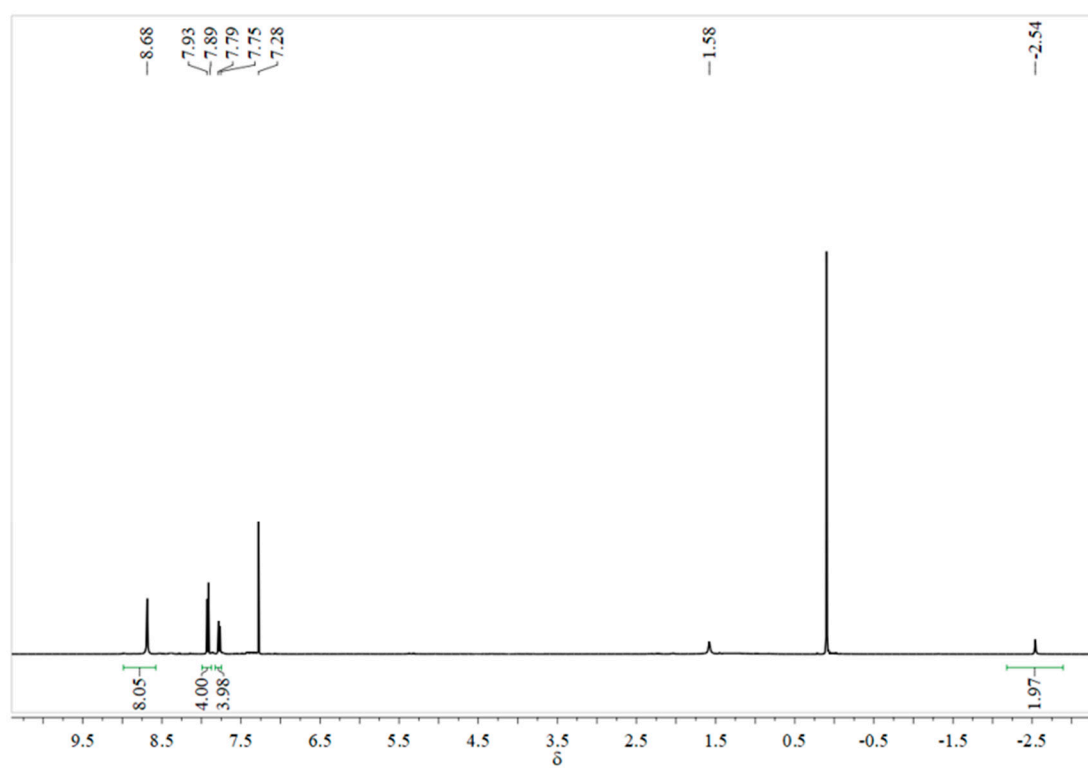


Fig. S18. ¹H NMR spectrum of T(2, 3, 6-tri Cl)PP in CDCl₃

S5 ^{13}C NMR spectra of porphyrins

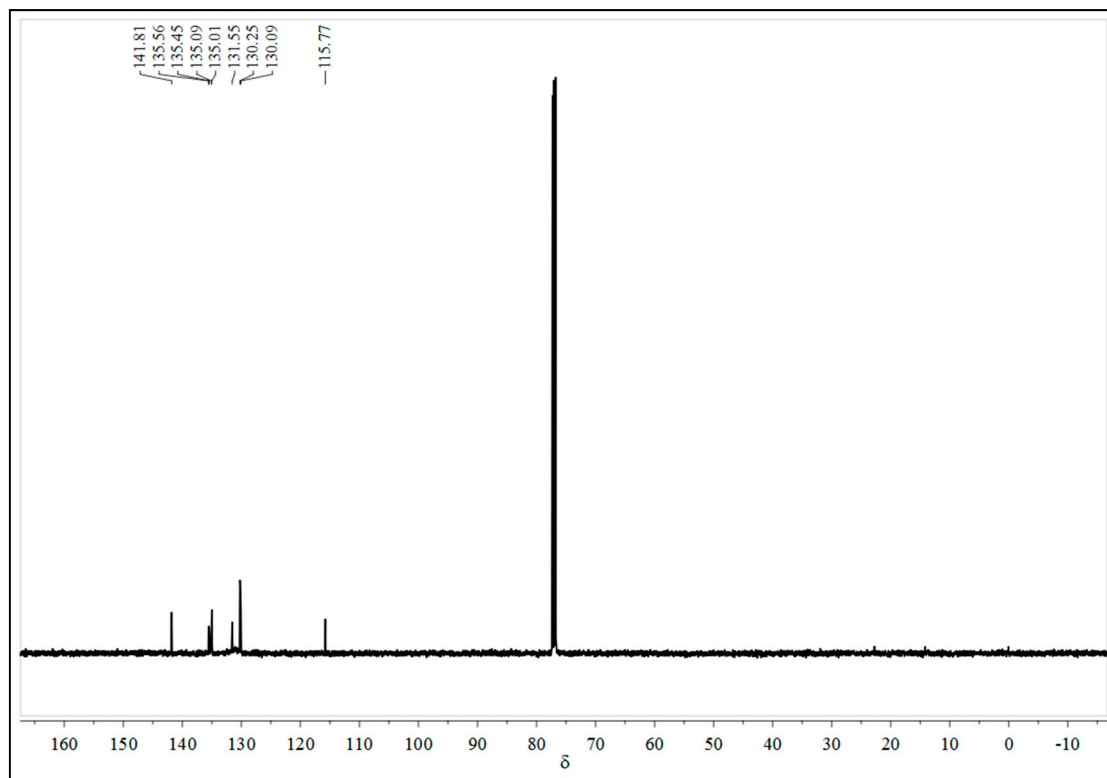


Fig. S19. ^{13}C NMR spectrum of T(2, 5-diCl)PP in CDCl_3

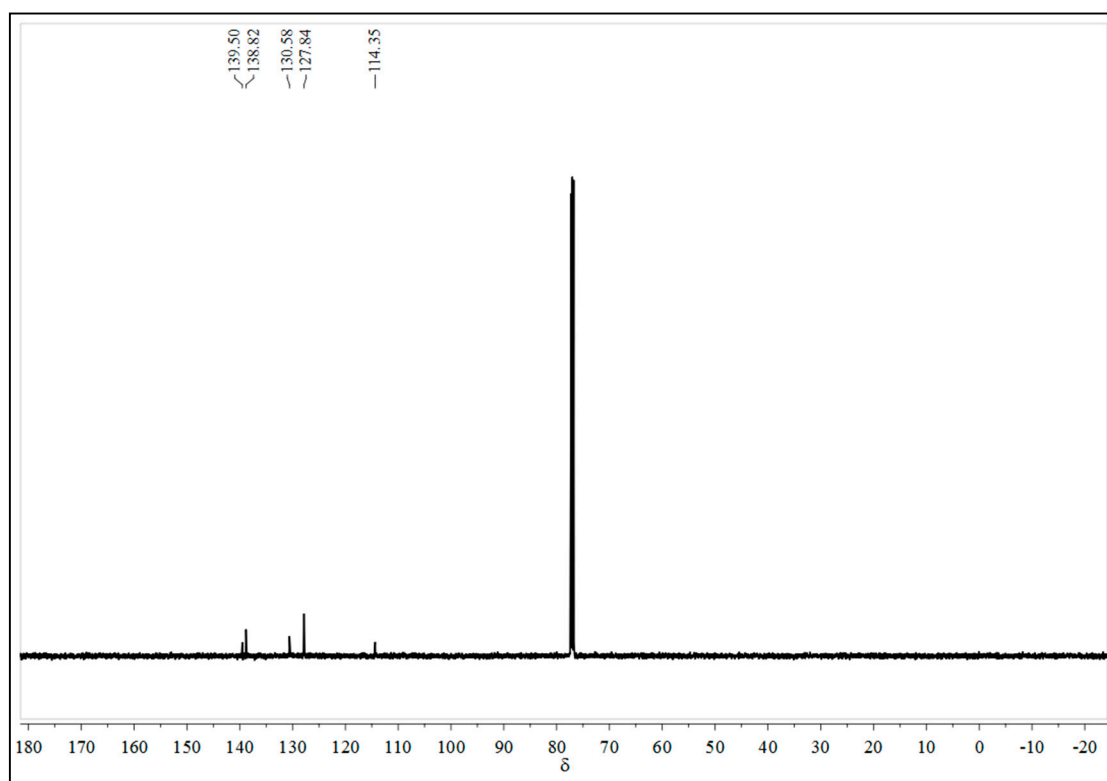


Fig. S20. ^{13}C NMR spectrum of T(2, 6-diCl)PP in CDCl_3

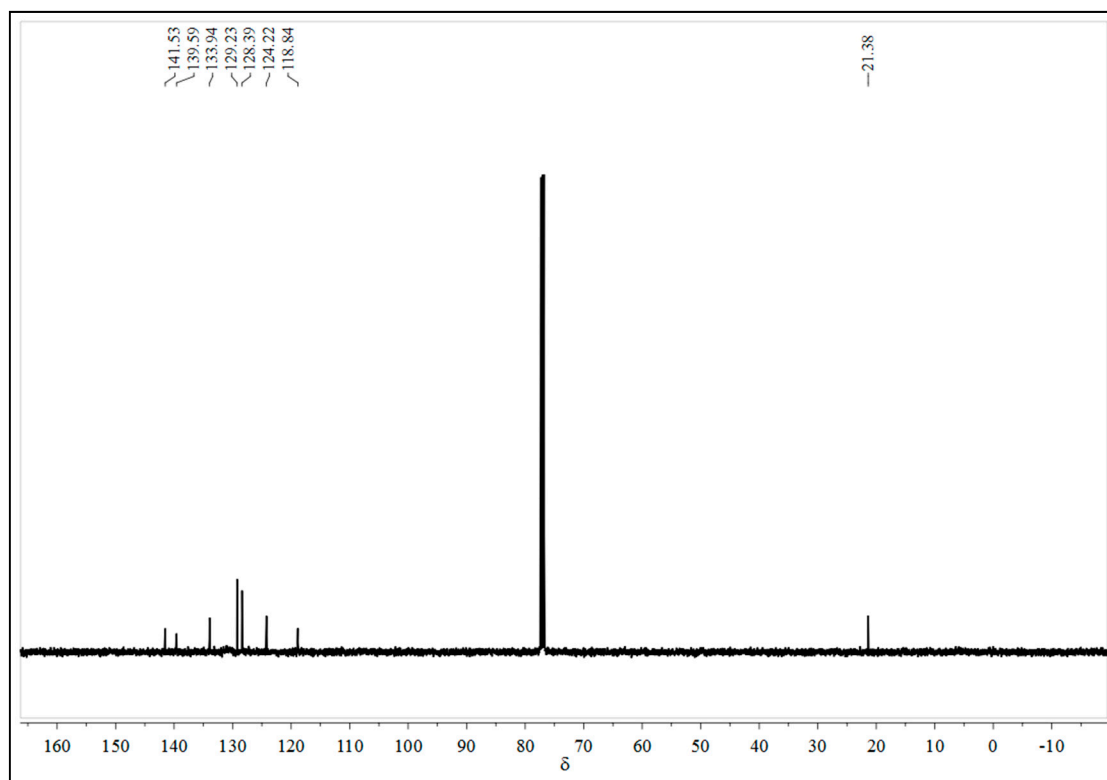


Fig. S21. ^{13}C NMR spectrum of T(2-CH₃)PP in CDCl₃

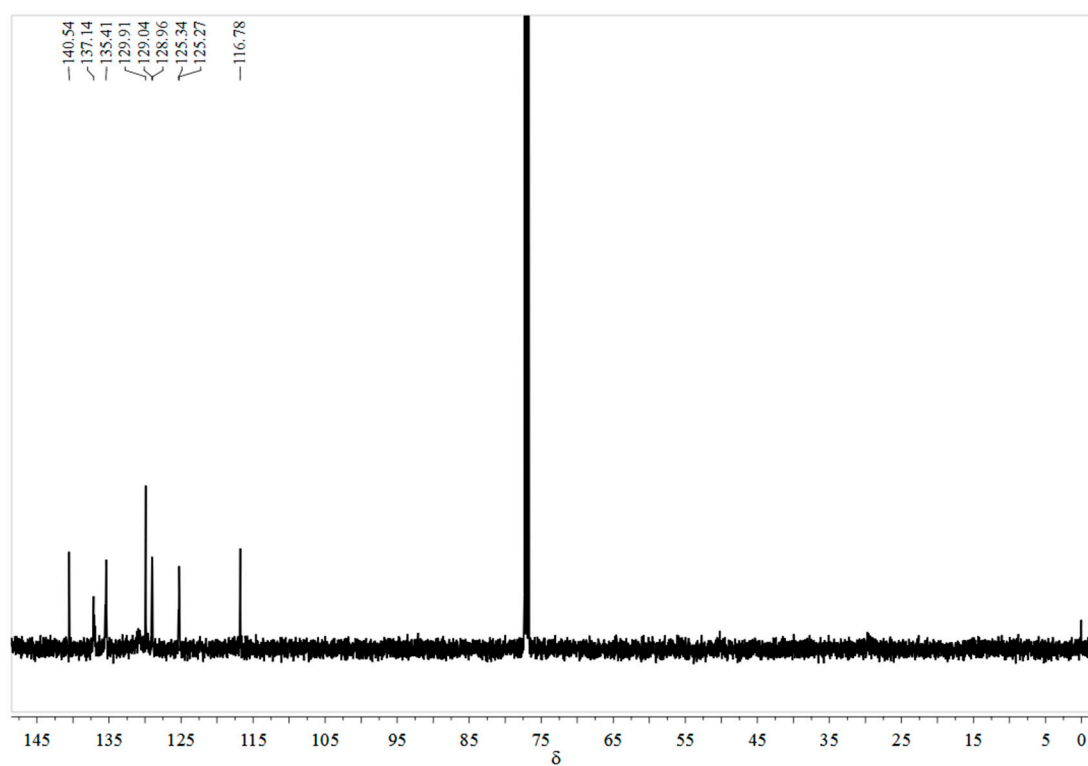


Fig. S22. ^{13}C NMR spectrum of T(2-Cl)PP in CDCl₃

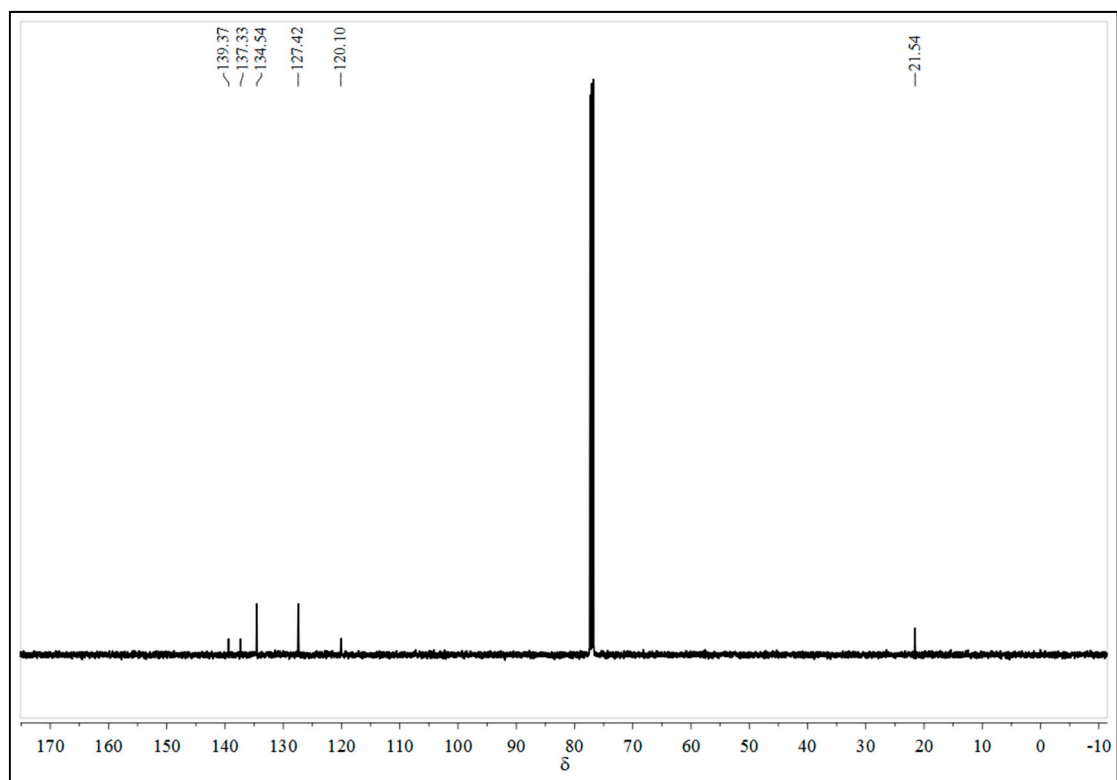


Fig. S23. ^{13}C NMR spectrum of T(4-CH₃)PP in CDCl₃

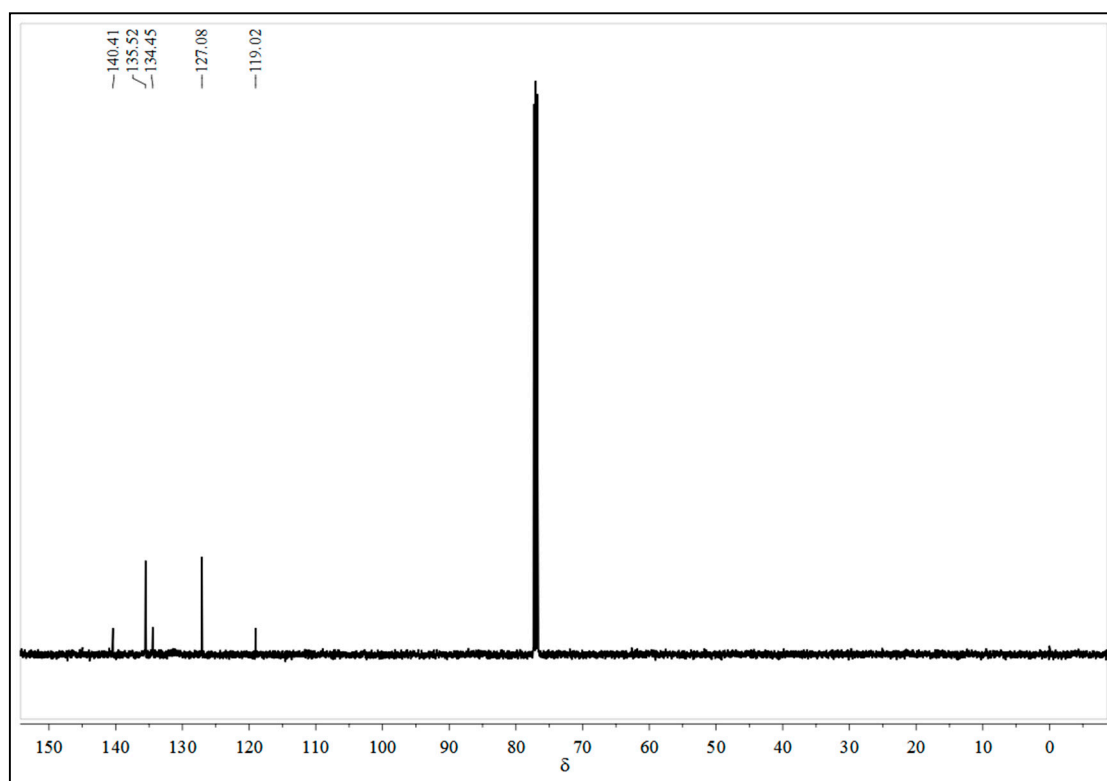


Fig. S24. ^{13}C NMR spectrum of T(4-Cl)PP in CDCl₃

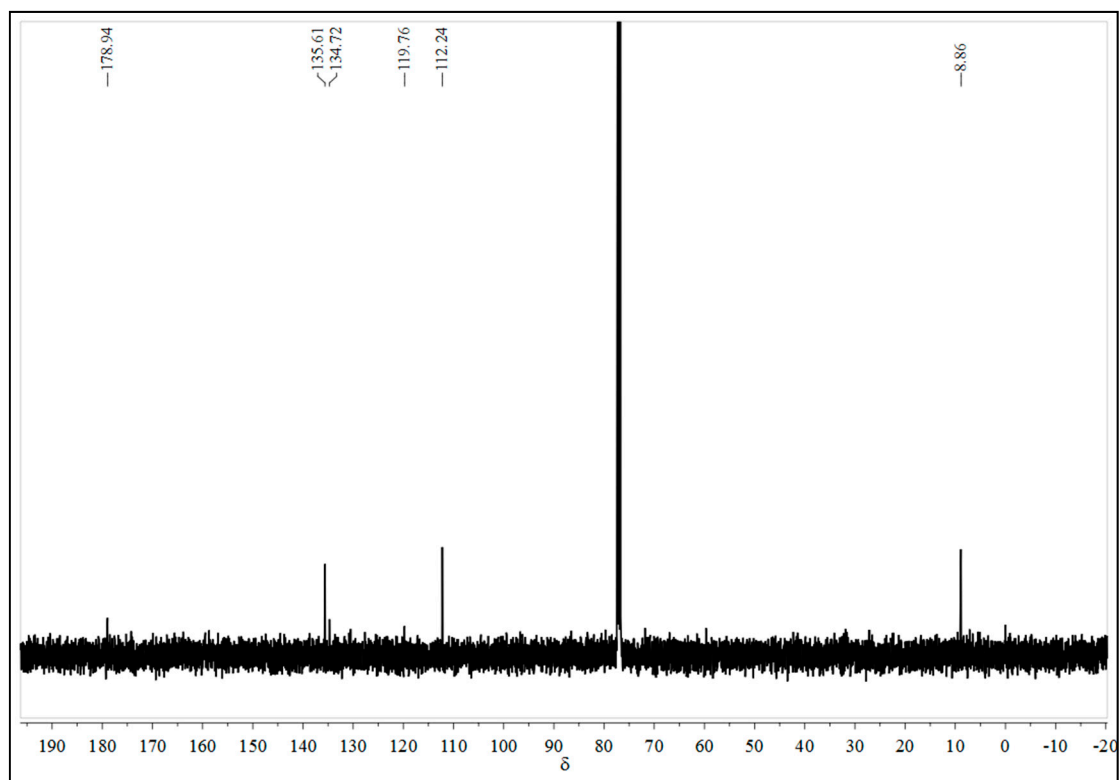


Fig. S25. ^{13}C NMR spectrum of T(4-OCH₃)PP in CDCl₃

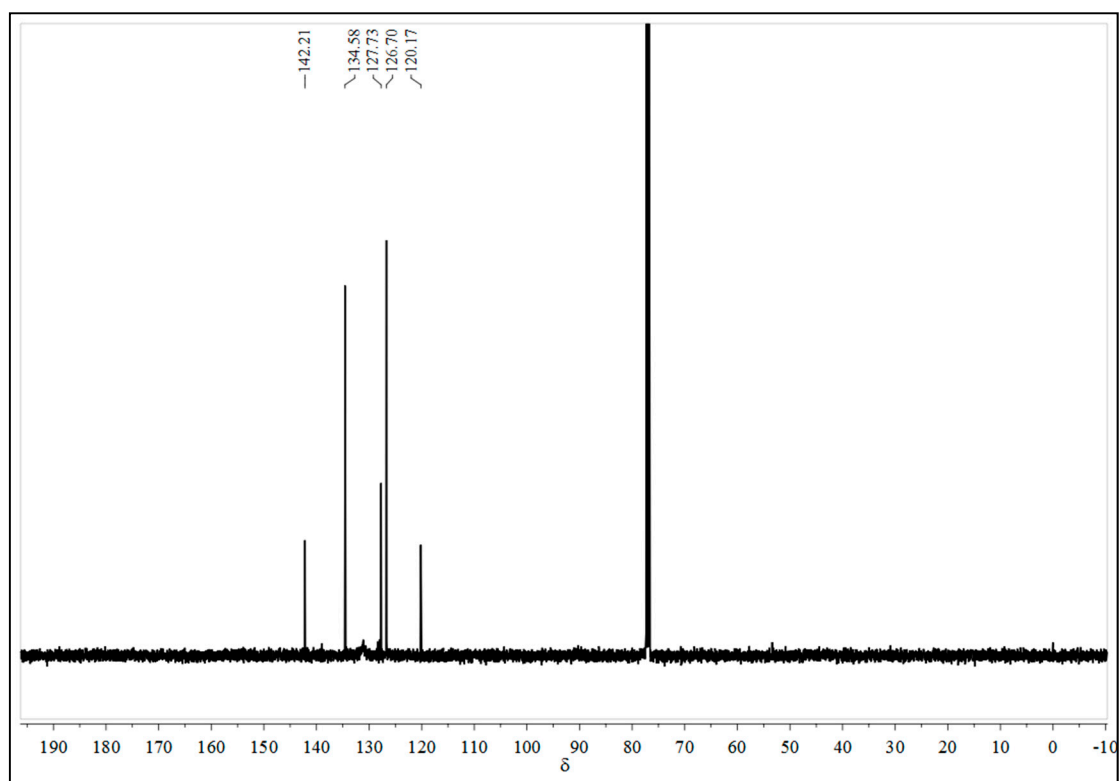


Fig. S26. ^{13}C NMR spectrum of TPP in CDCl₃

S6 ESI-MS spectra of metalloporphyrins

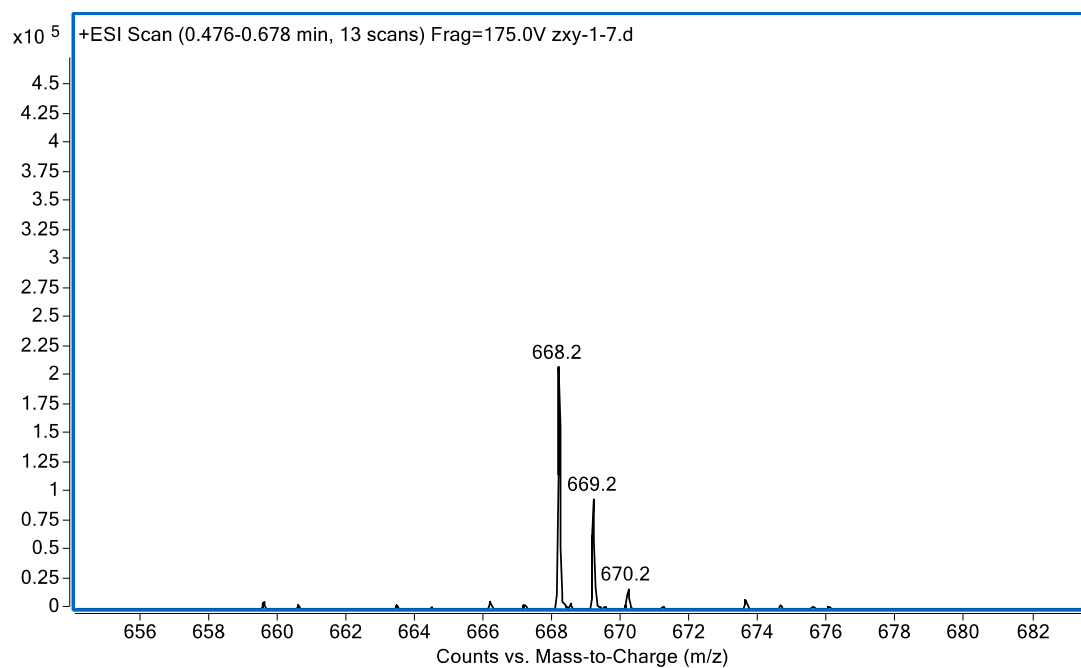


Fig. S27. ESI-MS spectrum of TPPFe

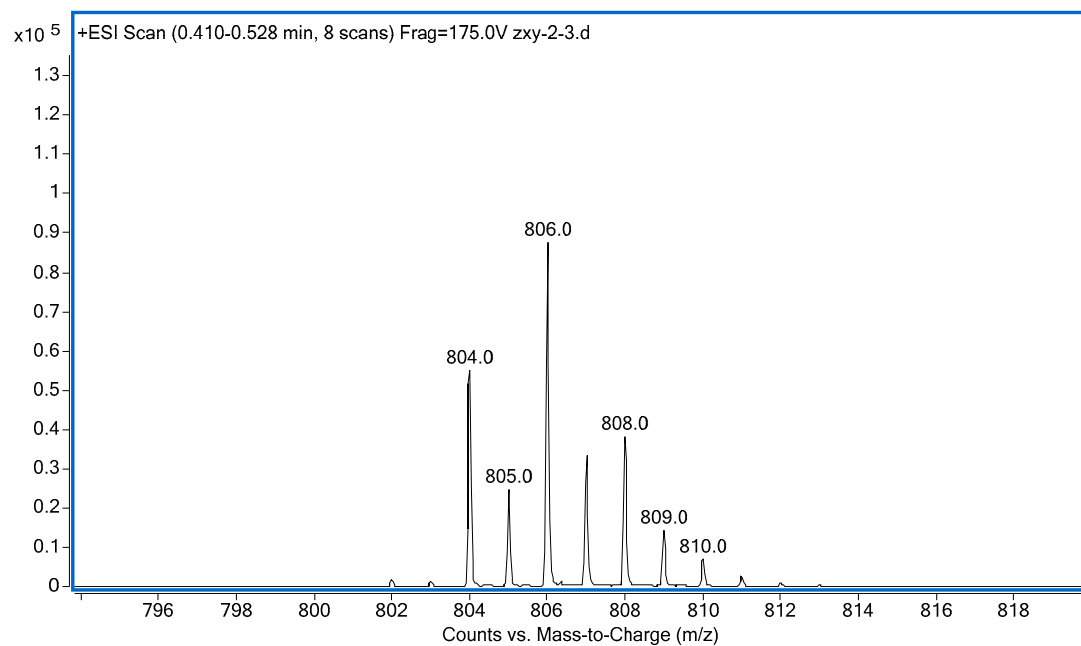


Fig. S28. ESI-MS spectrum of T(3-Cl)PPFe

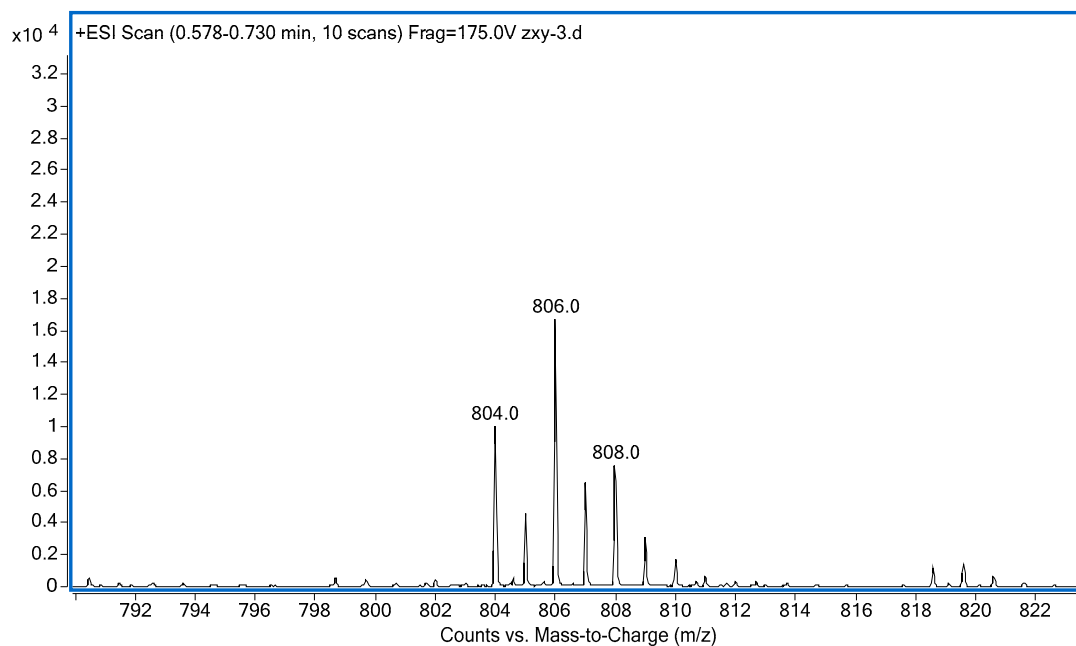


Fig. S29. ESI-MS spectrum of T(4-Cl)PPFe

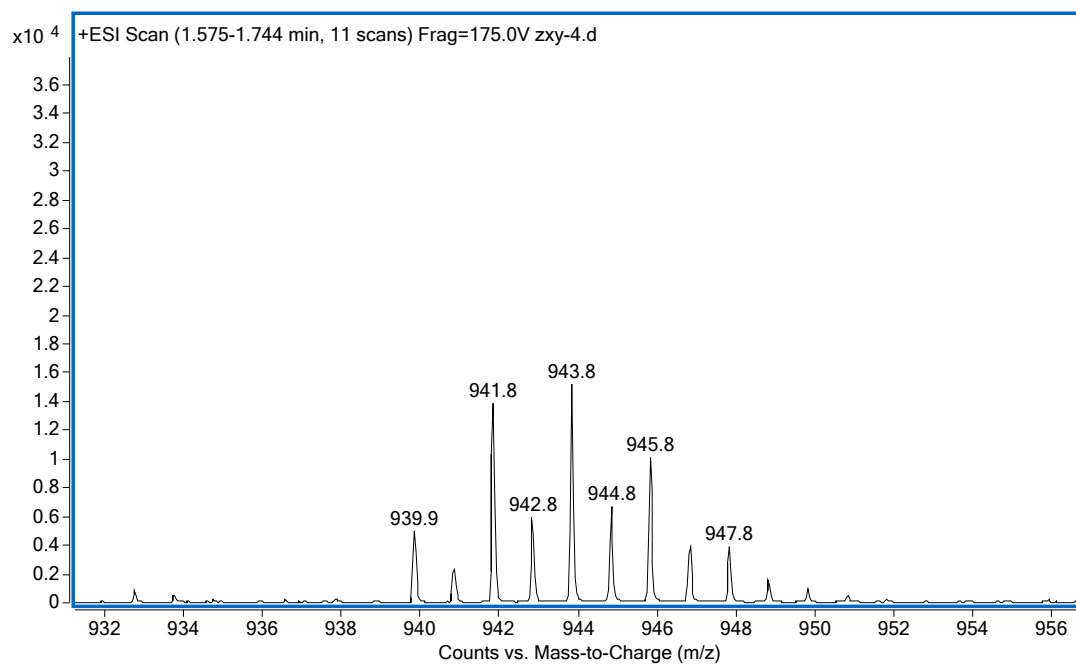


Fig. S30. ESI-MS spectrum of T(2, 6-diCl)PPFe

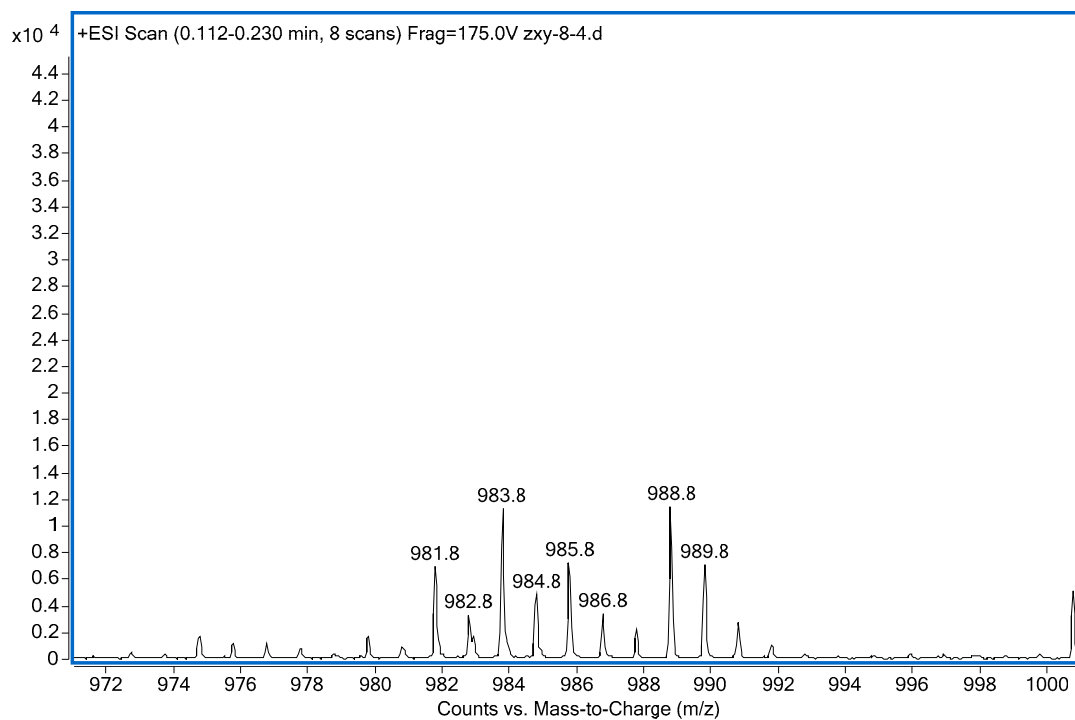


Fig. S31. ESI-MS spectrum of T(4-Br)PPFe

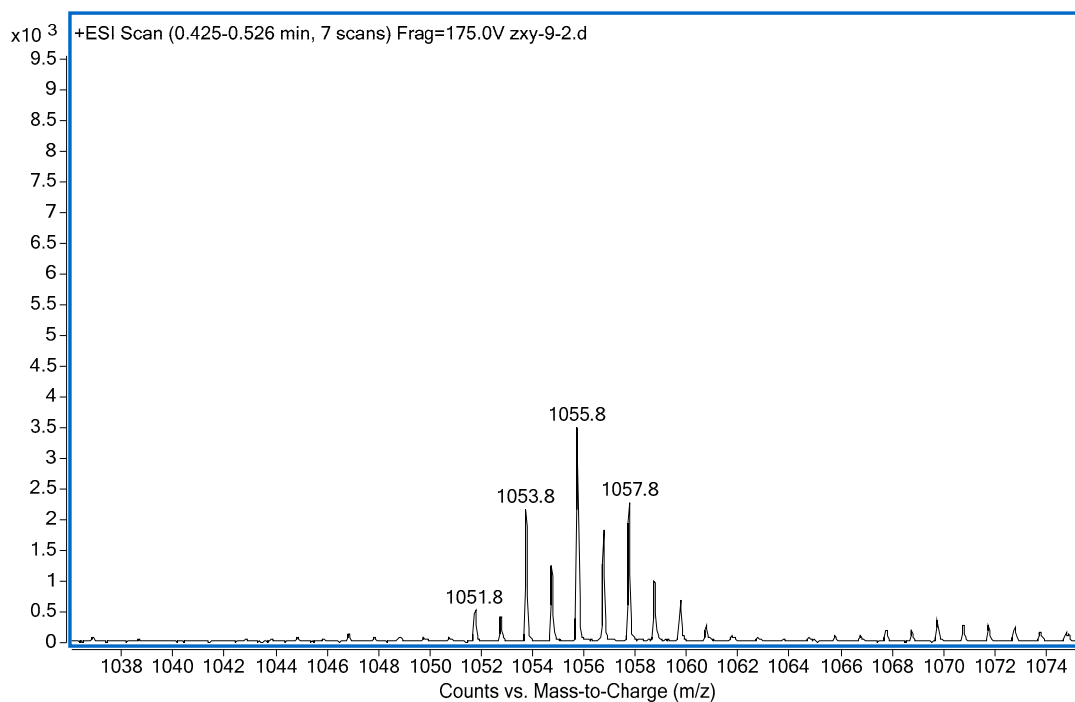


Fig. S32. ESI-MS spectrum of T(3-F-4-Br)PPFe

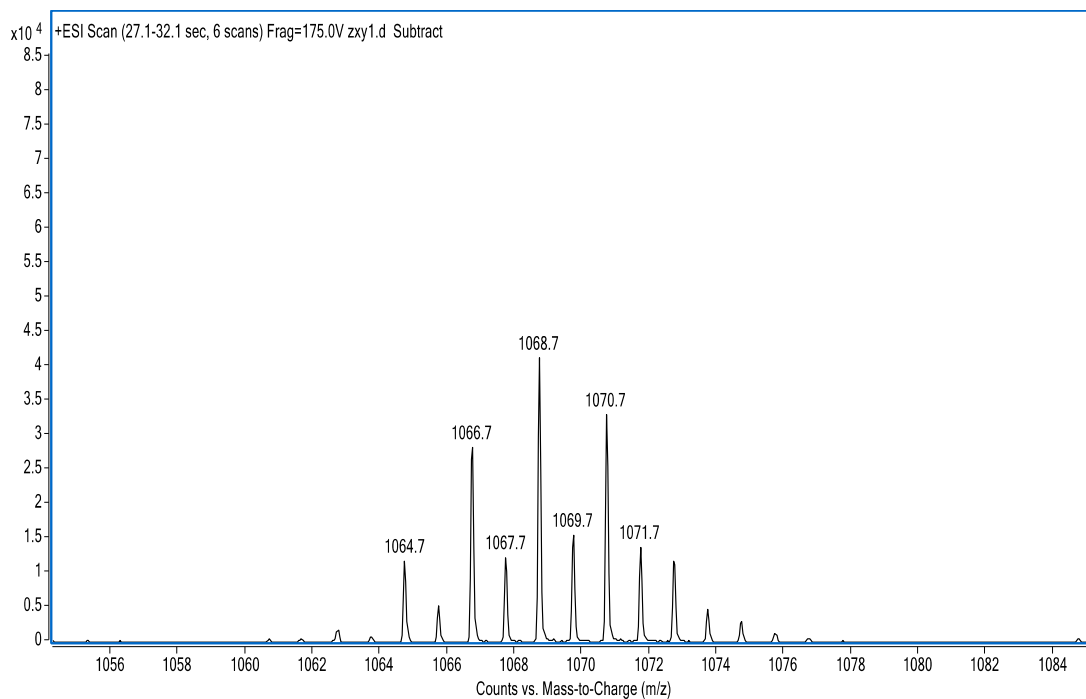


Fig. S33. ESI-MS spectrum of T(2-Cl-4-Br)PPFe

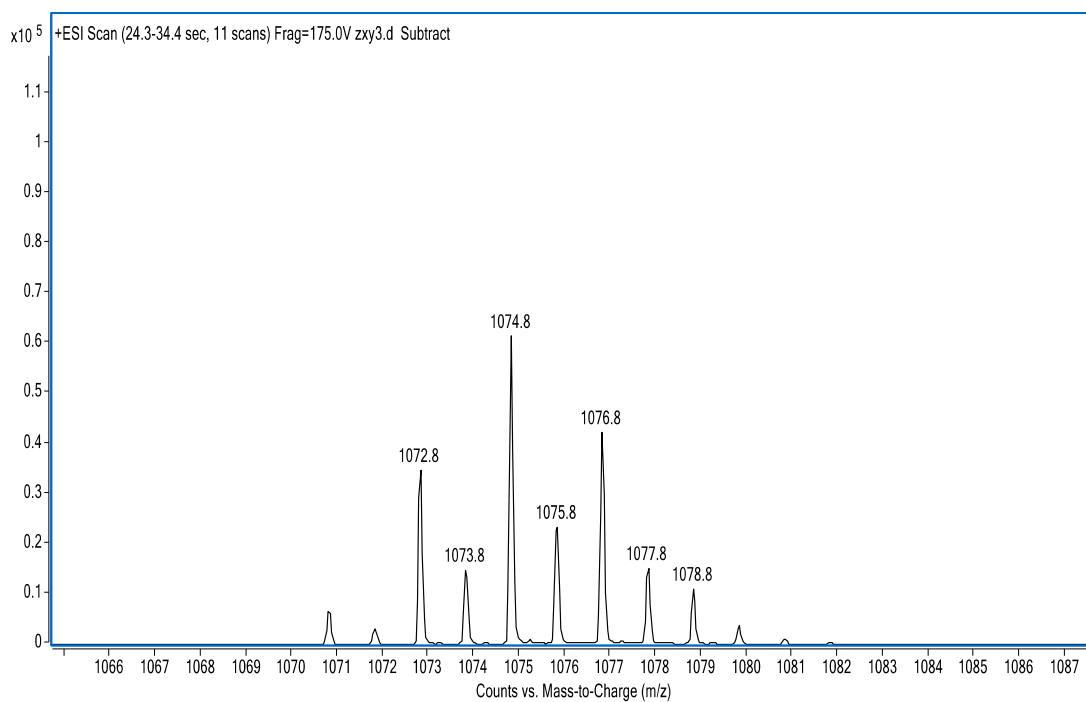


Fig. S34. ESI-MS spectrum of T(2,6-diF-4-Br)PPFe

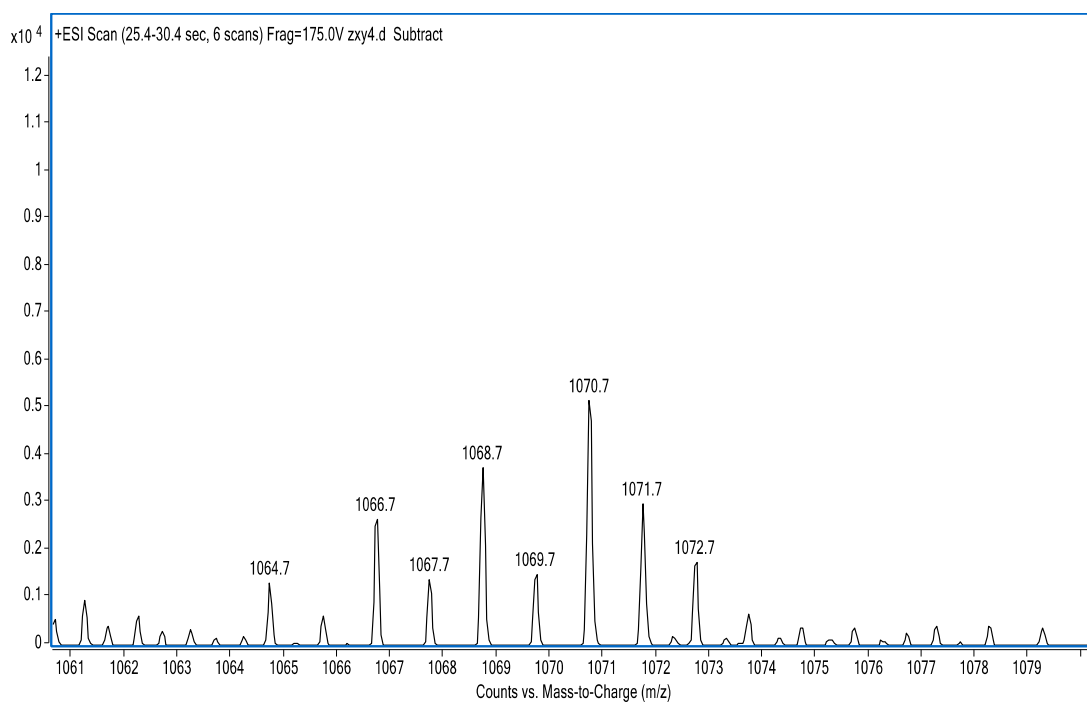


Fig. S35. ESI-MS spectrum of T(2-Cl-4-Br)PPFe

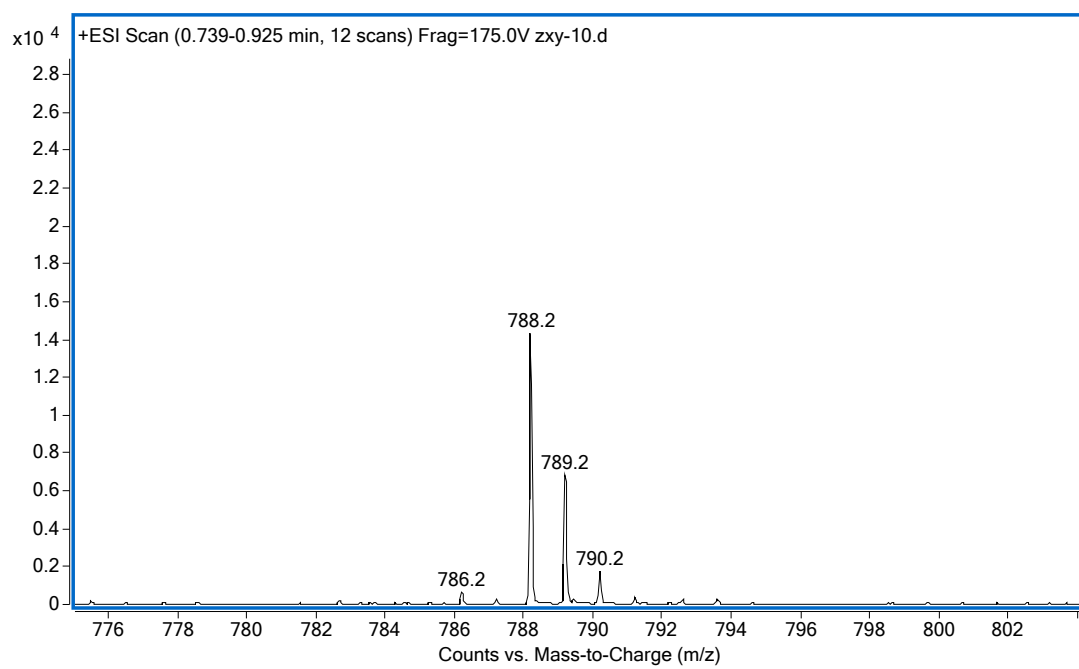


Fig. S36. ESI-MS spectrum of T(3-OCH₃)PPFe

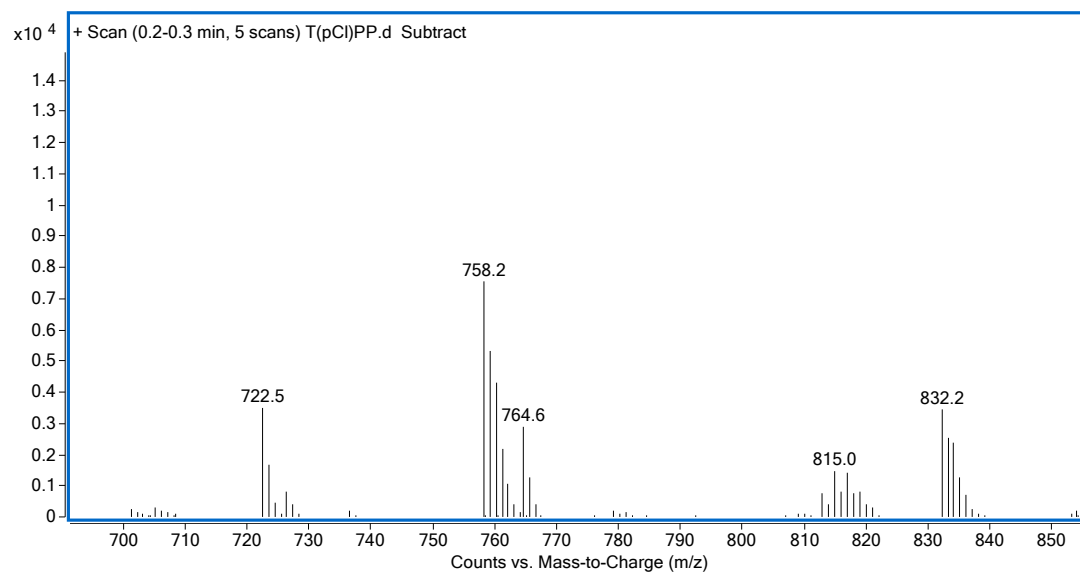


Fig. S37. ESI-MS spectrum of T(4-Cl)PPZn

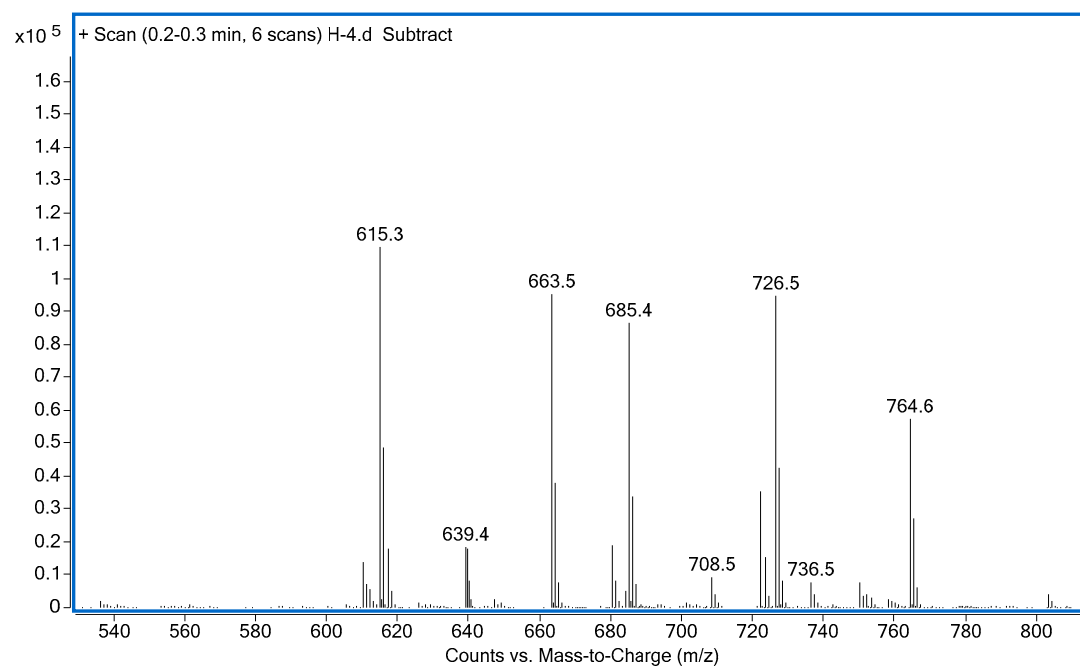


Fig. S38. ESI-MS spectrum of T(4-CH₃)PPNi.