

Supporting Information

Palladium Porphyrin Complexes for Photodynamic Cancer Therapy: Effect of Porphyrin Units and Metal

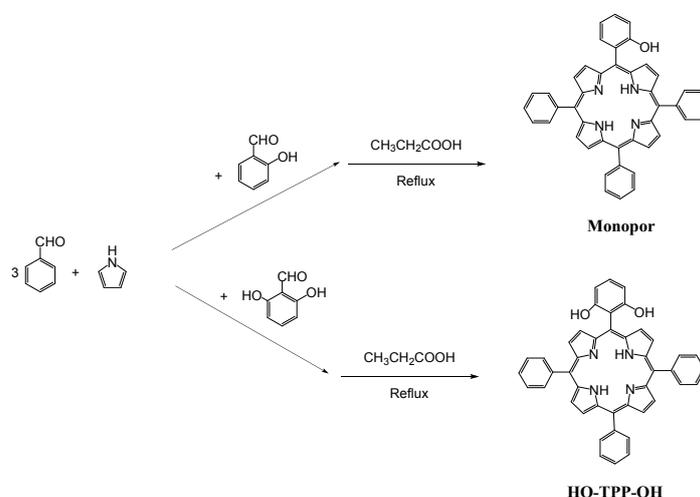
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Experiment sections

General

All chemicals were reagent grade, purchased from Aladdin (China) and used without further purification. The ^1H NMR and ^{13}C NMR spectra were recorded on the Varian Mercury-VX 400 spectrometer (400 MHz) at room temperature using CDCl_3 (with 1wt% TMS as internal reference) as a solvent. The UV-vis spectra were obtained through an UV-vis spectrophotometer (Shimadzu, UV-1900). The fluorescence spectra were recorded on the fluorescence spectrometer (PE LS-55). The silica gel plates for TLC was 300-400 mesh and the silica gel for column chromatography was 200-300 mesh.



Scheme S1. Synthetic routes of Monopor and HO-TPP-OH.

Synthesis of Monopor

The Monopor was synthesized according to the method reported in the literature with minor modification.¹ A solution of benzaldehyde (5.3 mL, 81 mmol) and 2-hydroxybenzaldehyde (5.5 mL, 52 mmol) in 250 mL of propionic acid was heated to reflux with intense stirring. Then 7.5 mL (108 mmol) of freshly distilled pyrrole in 80 mL propionic acid was added slowly to the solution in 30 min. The reaction mixture was continued to reflux for 1 hour and then cooled down to room temperature. Later the solvent was concentrated to about 150 mL and the same amount of methanol was added to precipitate the title compound. Filtration gave the crude products in about 1.8 g. Purification was processed on silica gel with dichloromethane as eluent. The desired product was obtained with the yield of 8%. ¹H-NMR (400 MHz, CDCl₃) δ 8.88-8.96 (m, 6H), 8.84 (d, 2H, *J*=4.8 Hz), 8.55 (d, 2H, *J*=8.4 Hz), 8.41 (d, 2H, *J*=7.2 Hz), 8.23-8.27 (m, 6H), 7.75-7.89 (m, 9H), -2.84 (s, 2H). HRMS (ESI): *m/z* calcd for C₄₄H₃₀N₄O 630.2415 [M+H]⁺, found 630.5682.

Synthesis of HO-TPP-OH

The synthetic procedure of HO-TPP-OH was similar with that of Monopor by replacing 2-hydroxybenzaldehyde with 2,6-dihydroxybenzaldehyde. After the reaction, the crude compound was purified by silica gel column chromatography (EtOH in CH₂Cl₂, 0-8% v/v) to get the desired product, yield 6%. ¹H-NMR (400 MHz, CDCl₃) δ 8.89-9.02 (m, 6H), 8.87 (d, 2H, *J*=5.4 Hz), 8.53-8.46 (m, 4H), 8.27-8.35 (m, 6H), 7.79-7.92 (m, 8H), -2.92 (s, 2H). HRMS (ESI): *m/z* calcd for C₄₄H₃₀N₄O₂ 646.2468 [M+H]⁺, found 646.6345.

UV-vis absorption and fluorescence spectra

The UV-vis absorption spectrum and fluorescence spectrum of six porphyrin compounds at 10 μM were measured in DMF solution.

Fluorescence quantum yield

Fluorescence quantum yield (ϕ_f) of an unknown sample is calculated by using Eq. (1)

$$\phi_f = \phi_f^R \frac{I_f}{I_f^R} \frac{A^R}{A} \left(\frac{n}{n^R}\right)^2 \quad (1)$$

ϕ_f^R is the known fluorescence quantum yield of the reference sample (referred by the superscript 'R'). I_f and I_f^R are the integrated fluorescence intensities of the unknown sample and

reference sample, respectively. A and A^R are the absorbances of the unknown sample and reference sample, respectively. n and n^R are the refractive indices of the solvents for the unknown sample and reference sample, respectively. The unknown sample and reference sample are excited at the same wavelength for measuring I_f and I_f^R , respectively. The fluorescence quantum yield of the synthesized porphyrins was measured at 298 K in DMF solution with tetraphenylporphyrin (TPP) as a reference ($\phi_f^{R_{TPP}}=0.052$ in THF, $n_{DMF}=1.42817$, $n_{THF}^R=1.407$).²

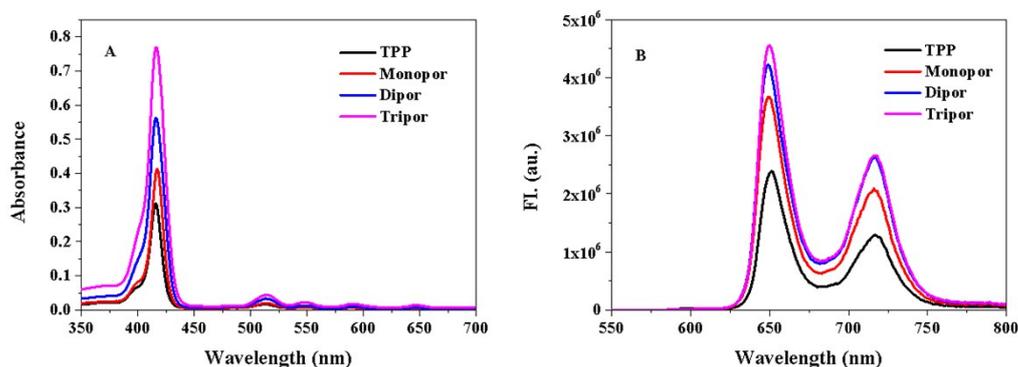


Figure S1. UV-Vis absorption spectrum of free base porphyrins at the same concentration. (b) Fluorescence spectra of free base porphyrins at the same concentration.

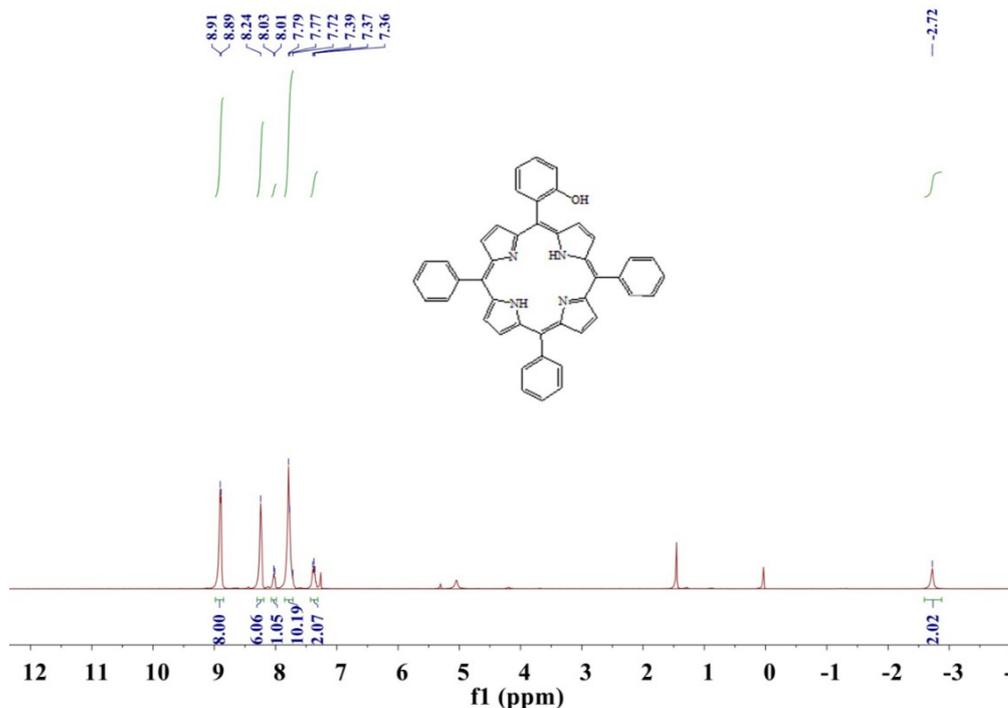


Figure S2. ^1H NMR spectrum of Monopor.

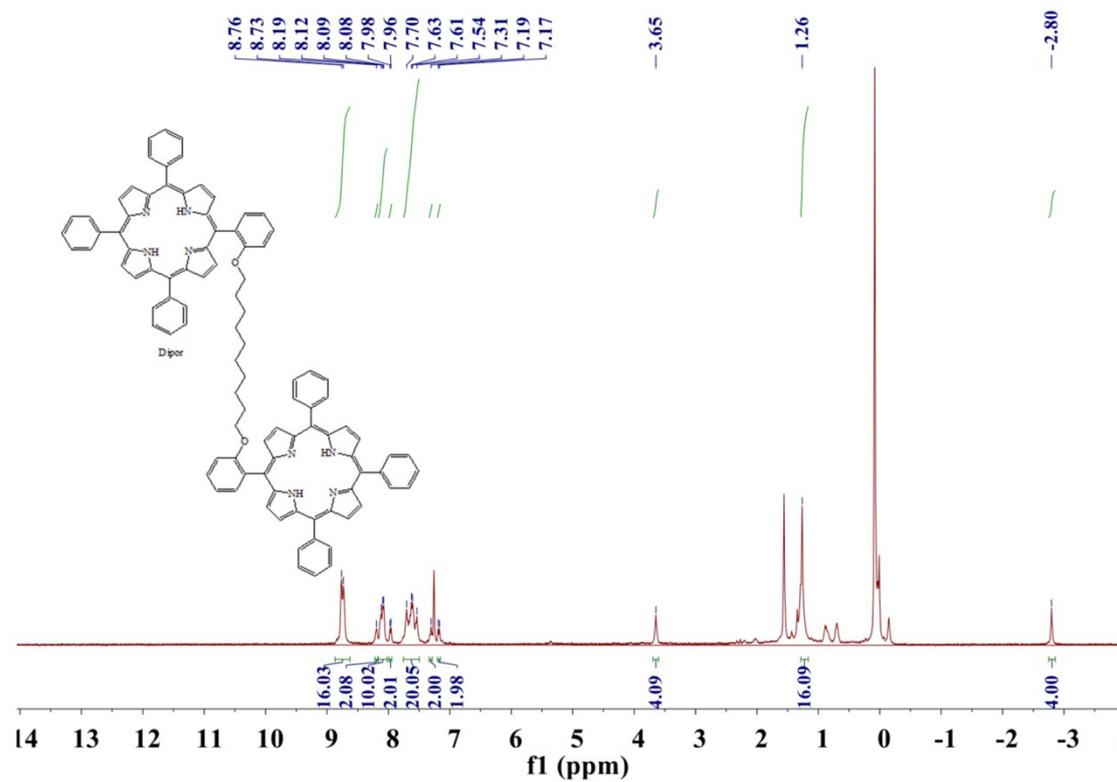


Figure S3. ^1H NMR spectrum of Dipor.

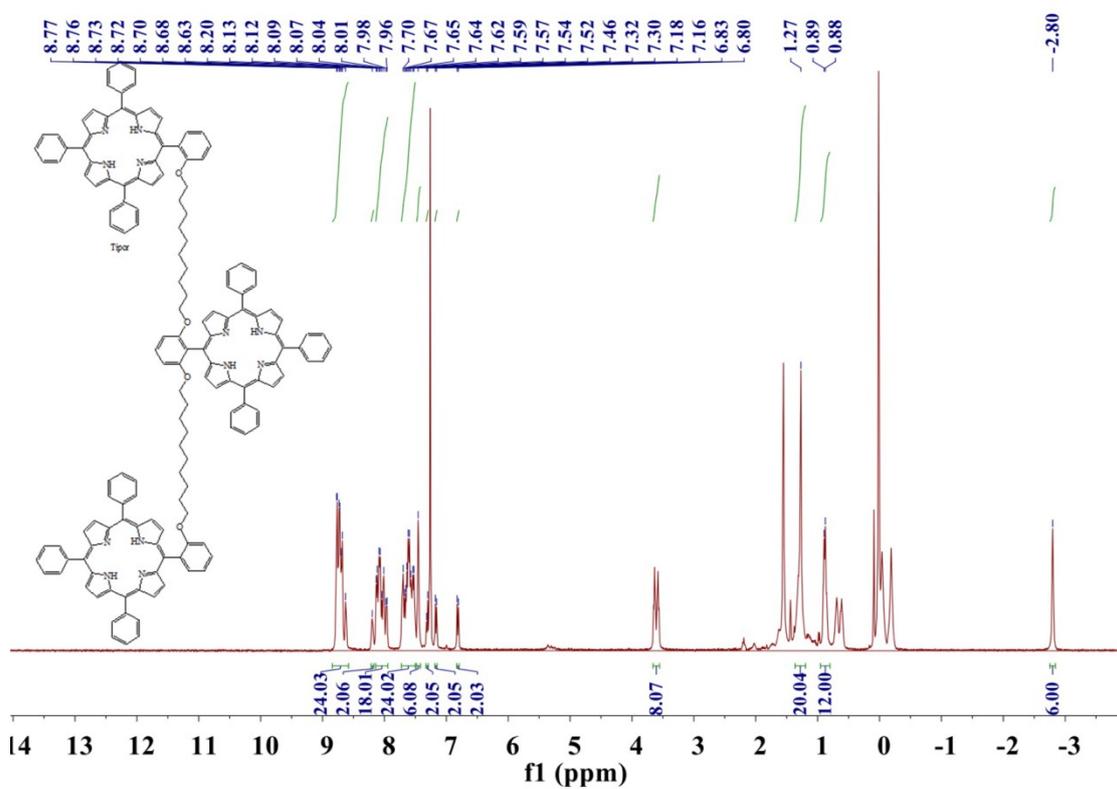


Figure S4. ^1H NMR spectrum of Tripor.

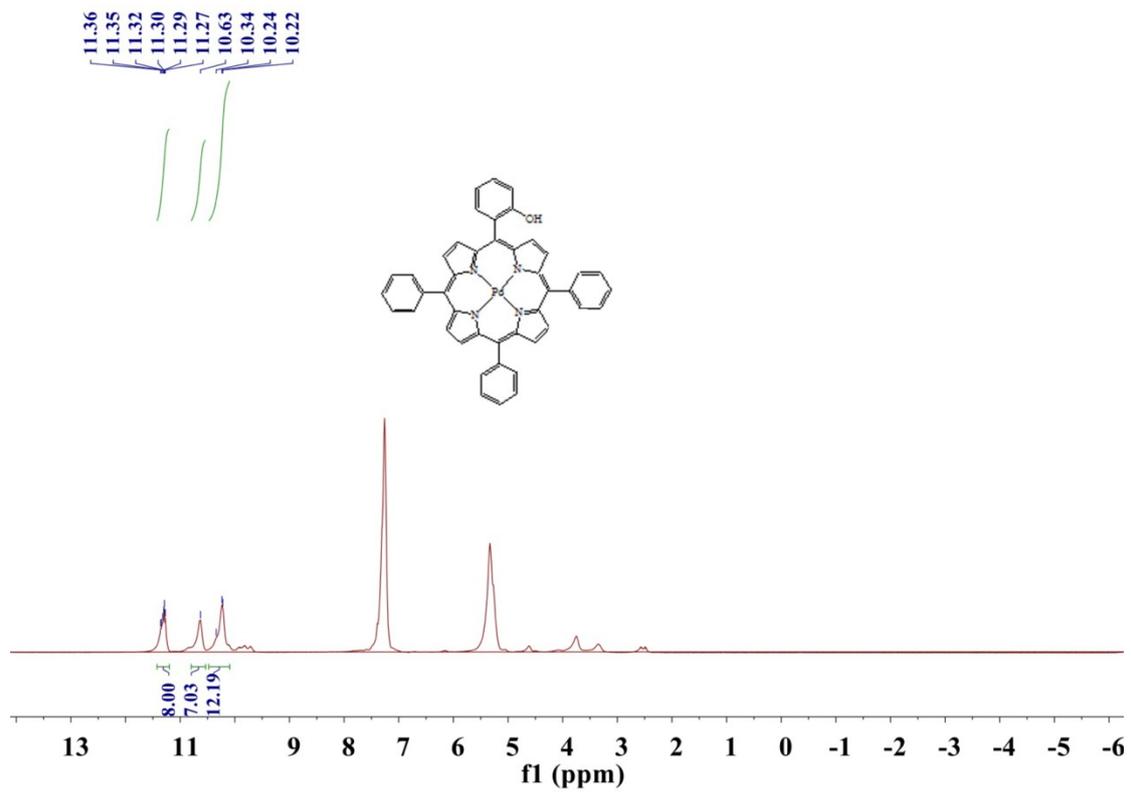


Figure S5. ^1H NMR spectrum of Pd-Monopor.

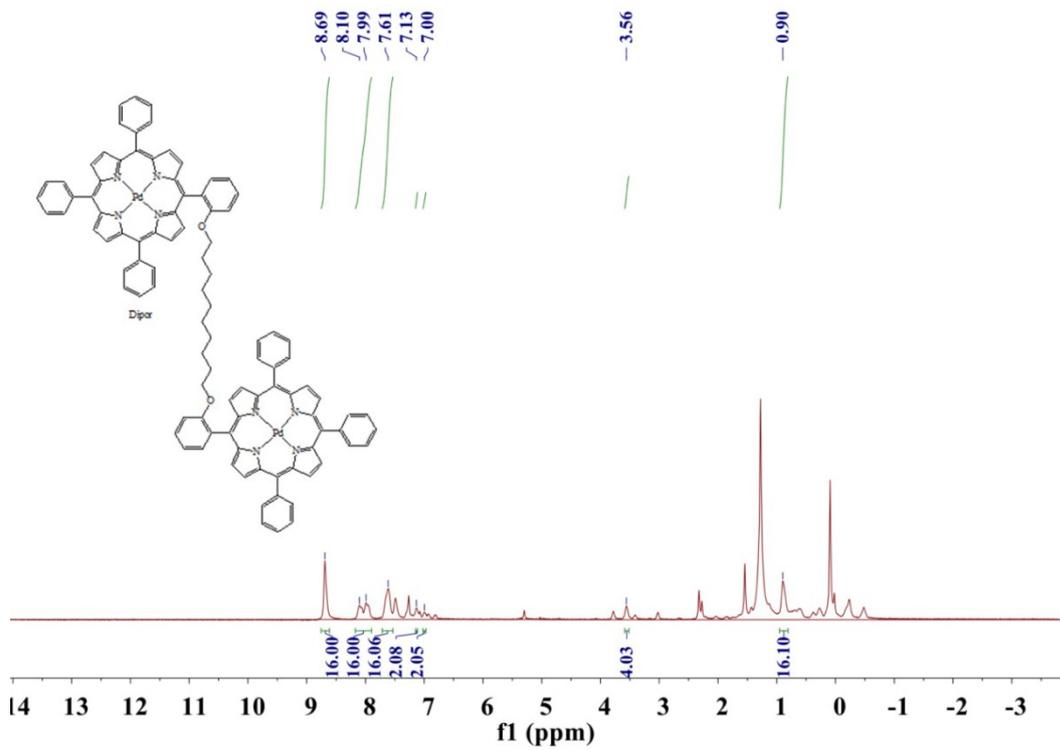


Figure S6. ^1H NMR spectrum of Pd-Dipor.

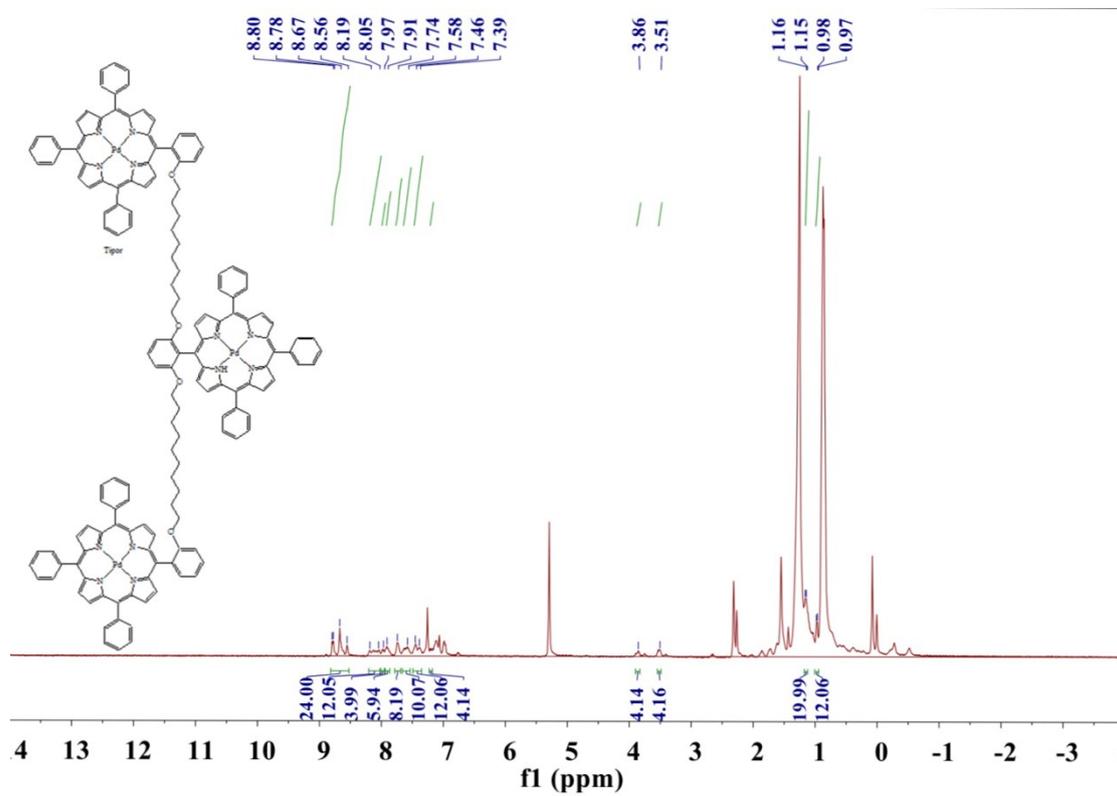


Figure S7. ^1H NMR spectrum of Pd-Tripor.

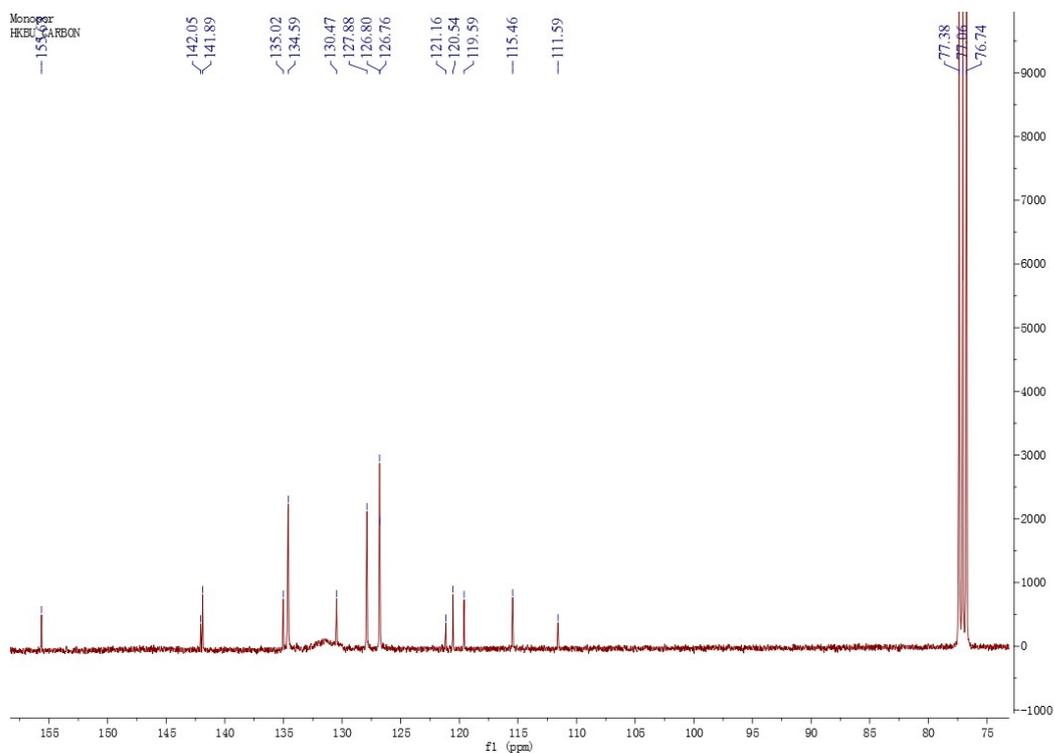


Figure S8. ^{13}C NMR spectrum of Monopor.

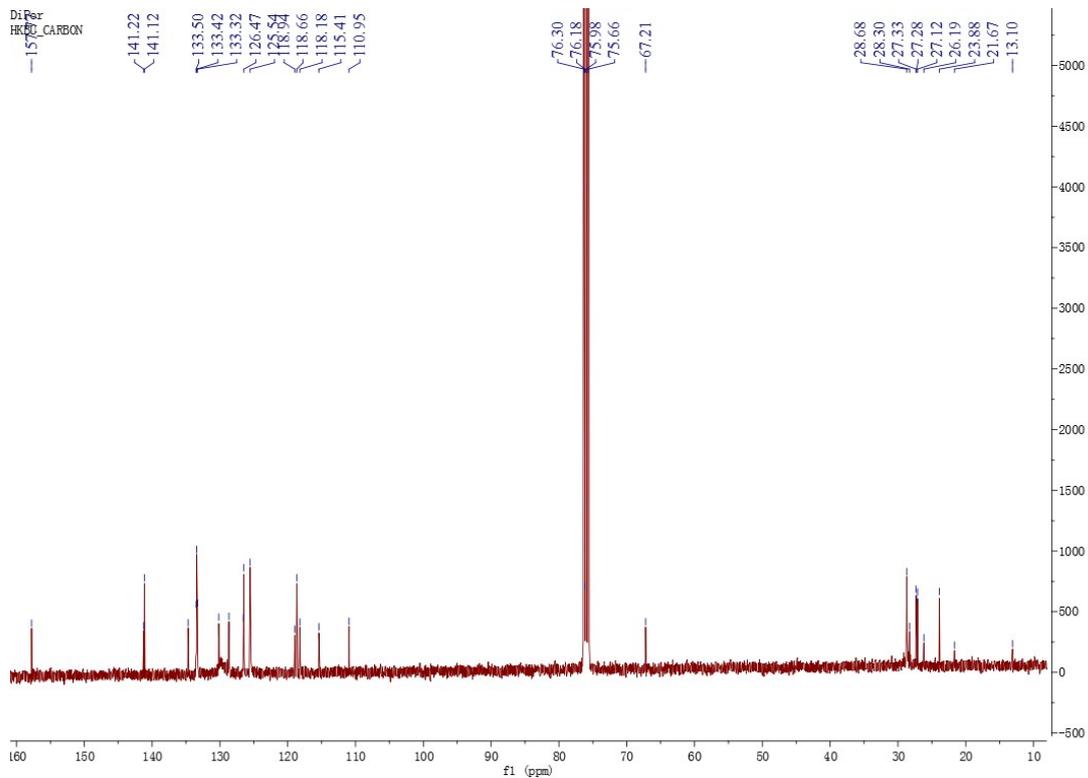


Figure S9. ¹³C NMR spectrum of Dipor.

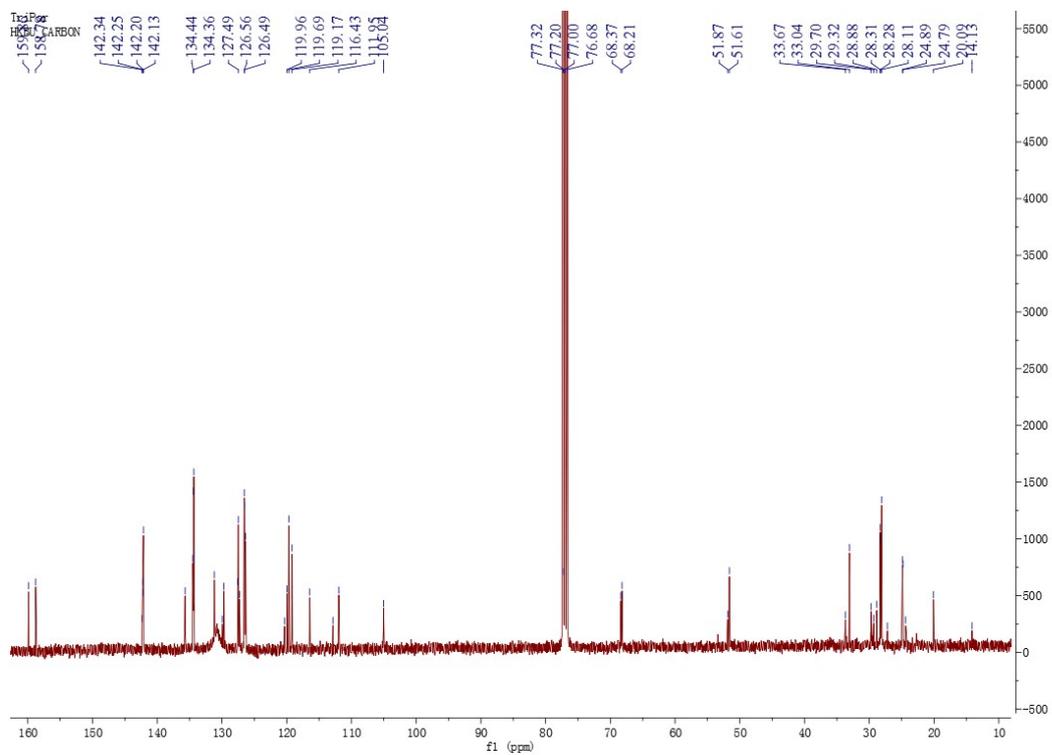


Figure S10. ¹³C NMR spectrum of Tripor.

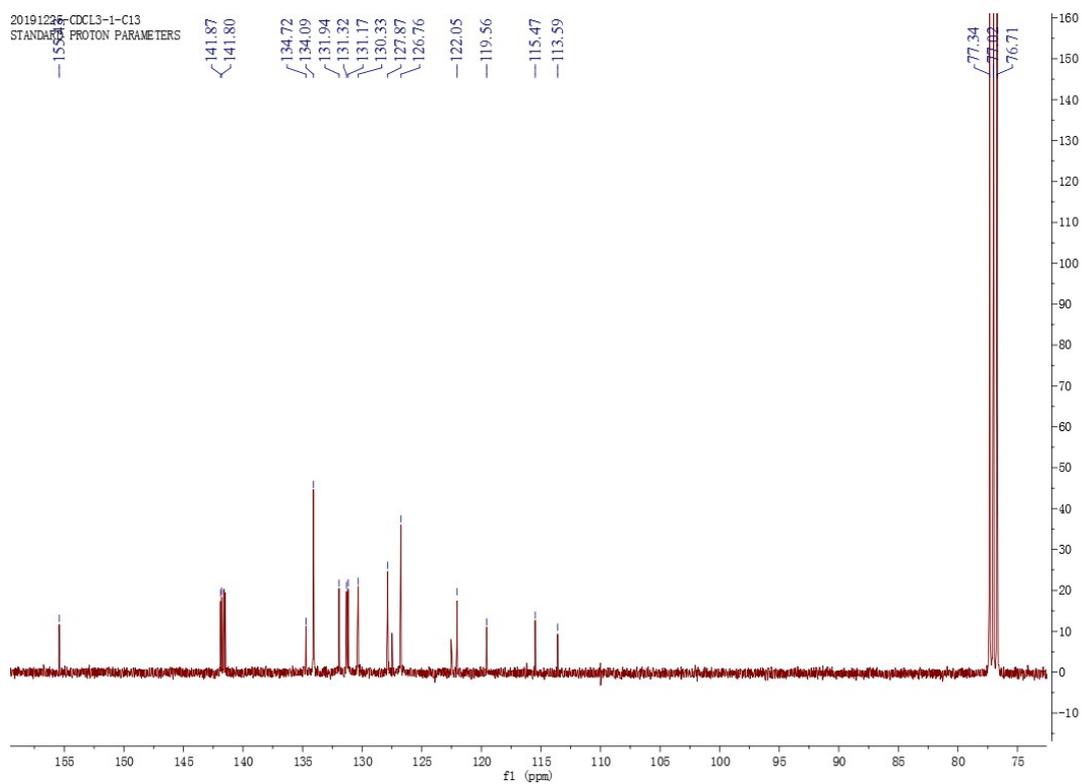


Figure S11. ^{13}C NMR spectrum of Pd-Monopor.

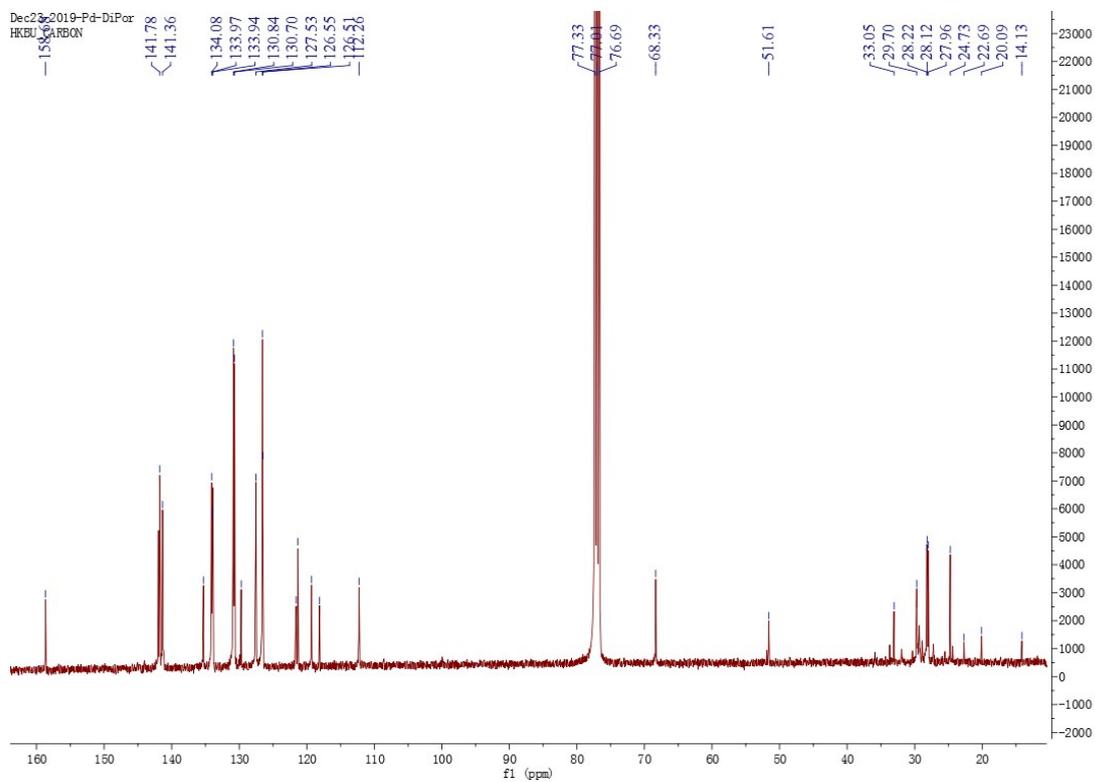


Figure S12. ^{13}C NMR spectrum of Pd-Dipor.

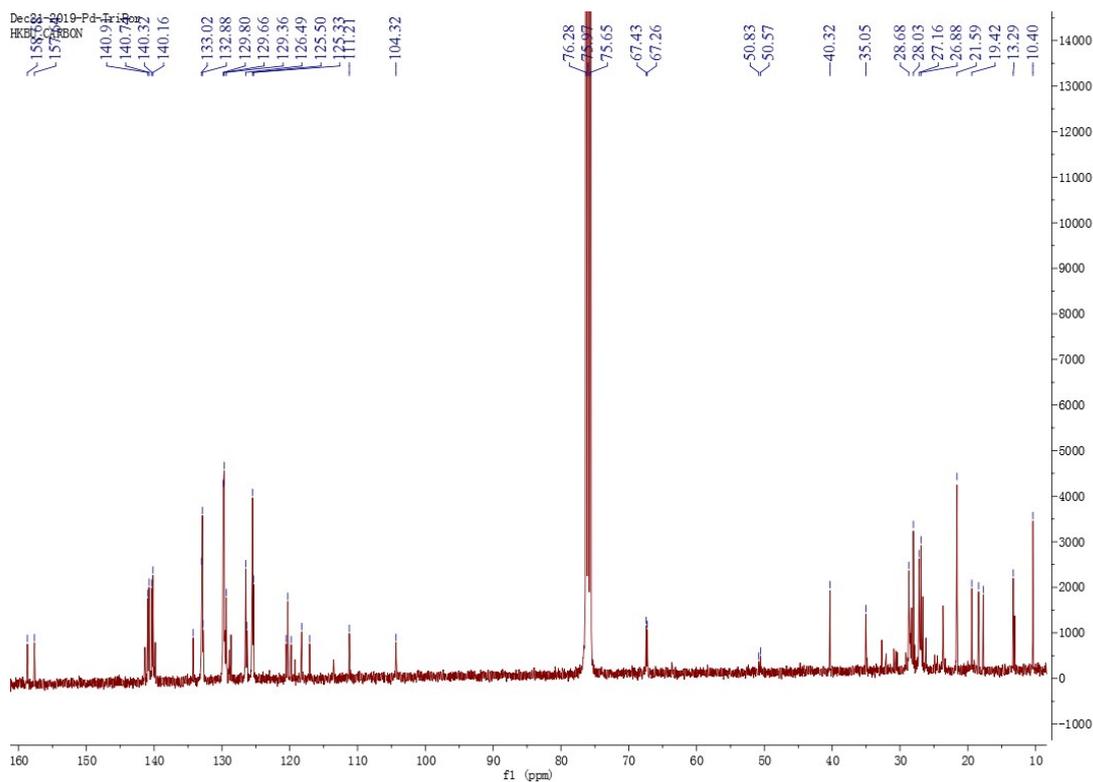


Figure S13. ^{13}C NMR spectrum of Pd-Tripdor.

Reference

1. Venkatasubbaiah, K.; Zhu, X.; Kays, E.; Hardcastle, K. I.; Jones, C. W., Co(III)-Porphyrin-Mediated Highly Regioselective Ring-Opening of Terminal Epoxides with Alcohols and Phenols. *ACS Catal.* **2011**, *1*, 489.
2. Ghosh, M.; Mora, A. K.; Nath, S.; Chandra, A. K.; Hajra, A.; Sinha, S. Photophysics of soret-excited free base tetraphenylporphyrin and its zinc analog in solution, *Spectrochim. Acta. A.* **2013**, *116*, 466.