Electronic supplementary information

Electron transfer and binding affinities in an electrochemically controlled ligand transfer system containing zinc porphyrin and a meso-phenylenediamine substituent

Hsu-Chun Cheng,[a] Peter Ping Yu Chen*[b] and Yuhlong Oliver Su*[a]

[a] Department of Applied Chemistry, National Chi Nan University, 1, University Road, Puli, Nantou, 545, Taiwan
[b] Department of Chemistry, National Chung Hsing University, 250, Kuo Kuang Road, Taichung, 402, Taiwan

* To whom correspondence should be addressed.
E-mail: yosu@ncnu.edu.tw ; pychen@dragon.nchu.edu.tw

Supporting information

Electrochemical and spectral results

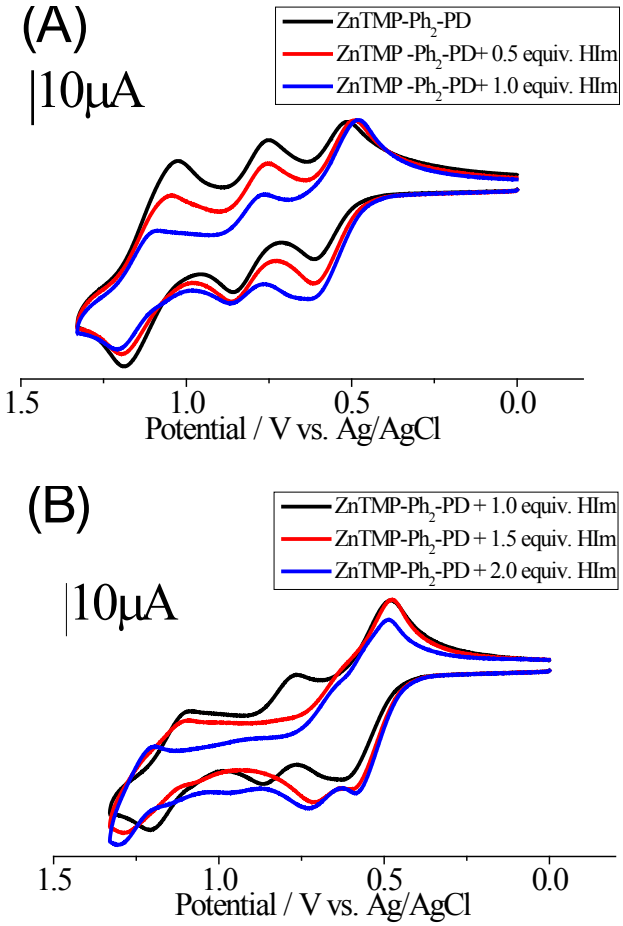


Fig S1 Cyclic voltammgrams of 1.0×10^{-3} M ZnTMP-Ph_2-PD in CH_2Cl_2 containing 0.1 M TBAP in the presence of (A) 0.0–1.0 equiv. and (B) 1.0–2.0 equiv. of HIm. Working electrode: glassy carbon. Scan rate: 0.1 Vs^{-1}.

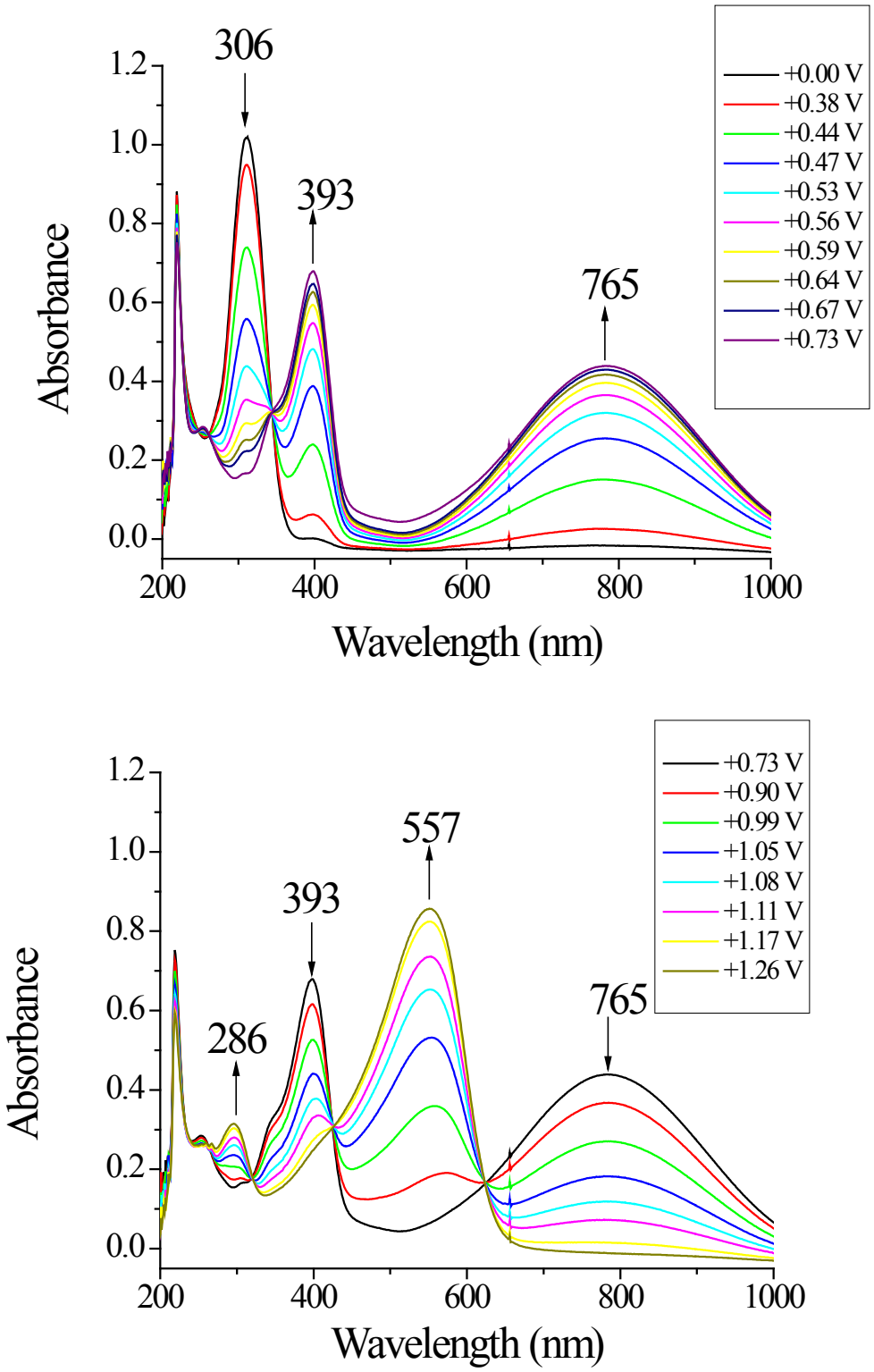


Fig S2 Spectral changes of 2.0×10^{-4} M **PD** in CH_2Cl_2 containing 0.1 M TBAP at various applied potentials (0.00V~1.26V).

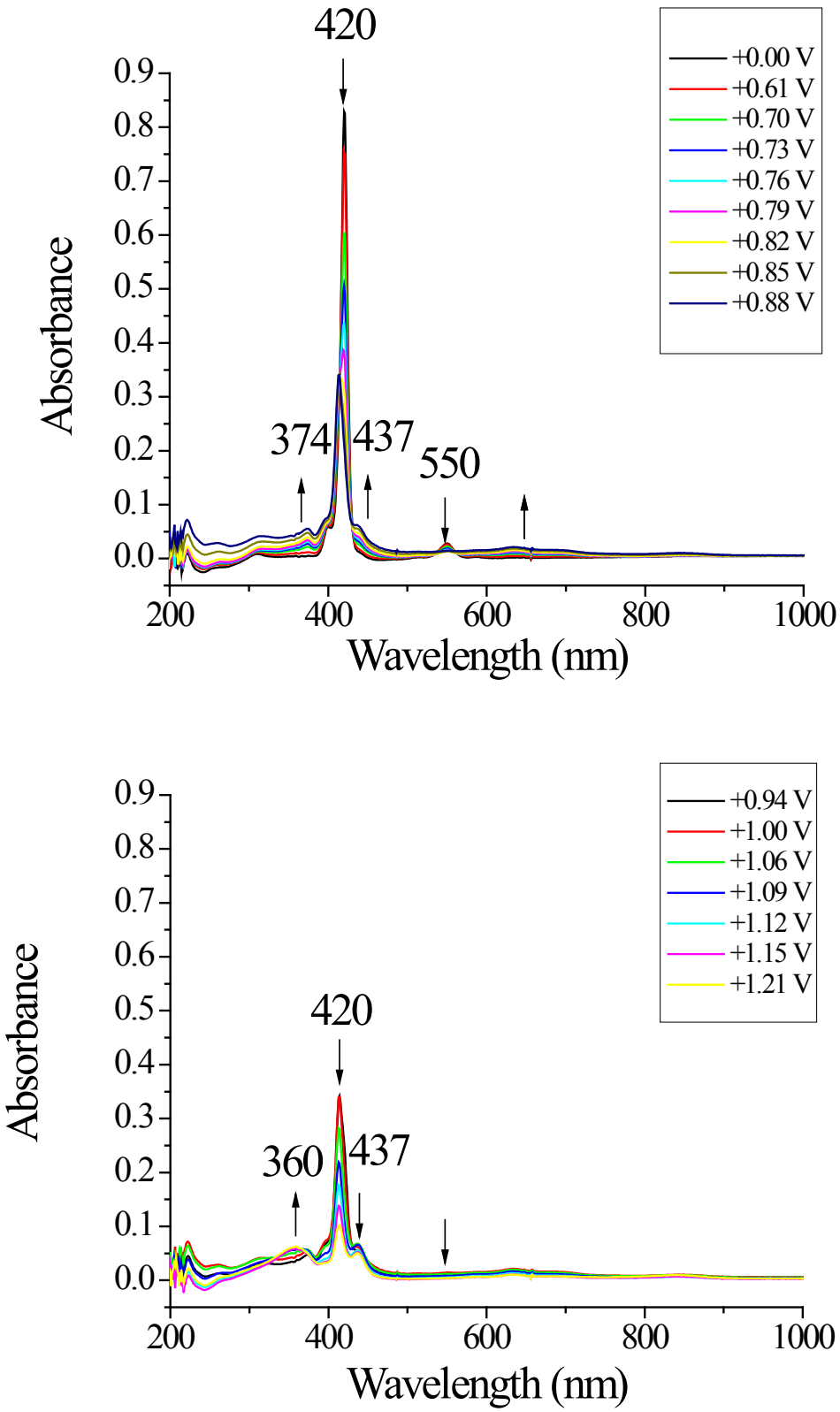


Fig S3 Spectral changes of 2.0×10^{-4} M **ZnTMP** in CH_2Cl_2 containing 0.1 M TBAP at various applied potentials (0.00V~1.21V).

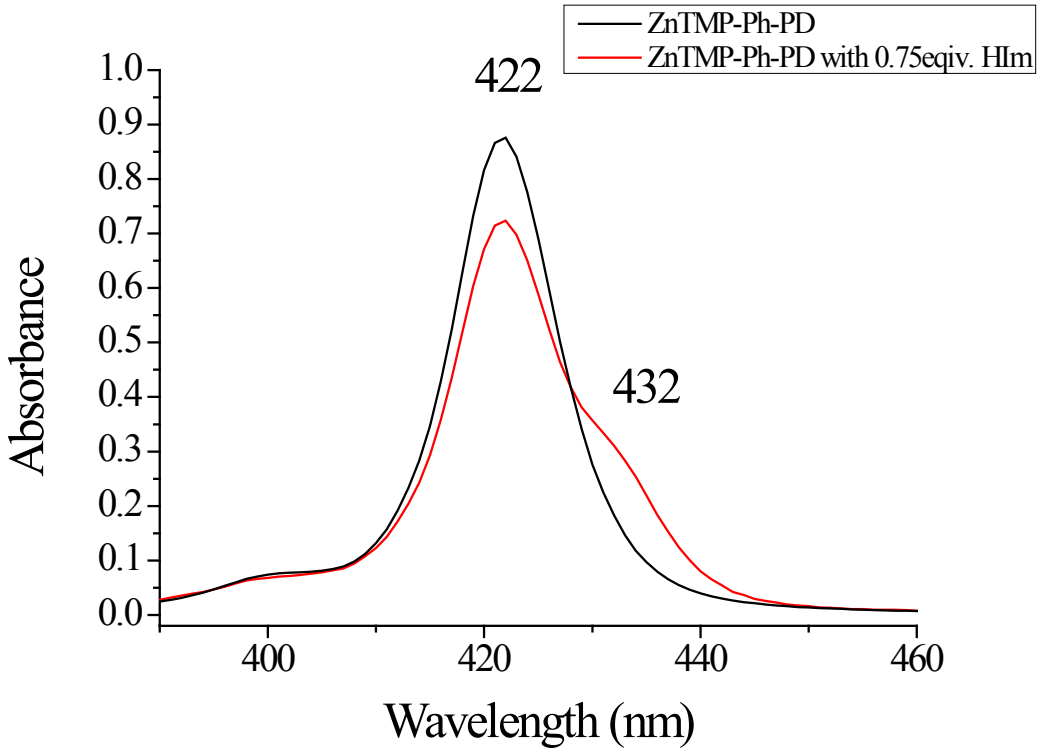


Fig S4 The absorption spectra of 4.0×10^{-5} M **ZnTMP-Ph-PD** in presence of 0.75 equiv. in CH_2Cl_2 containing 0.1 M TBAP.

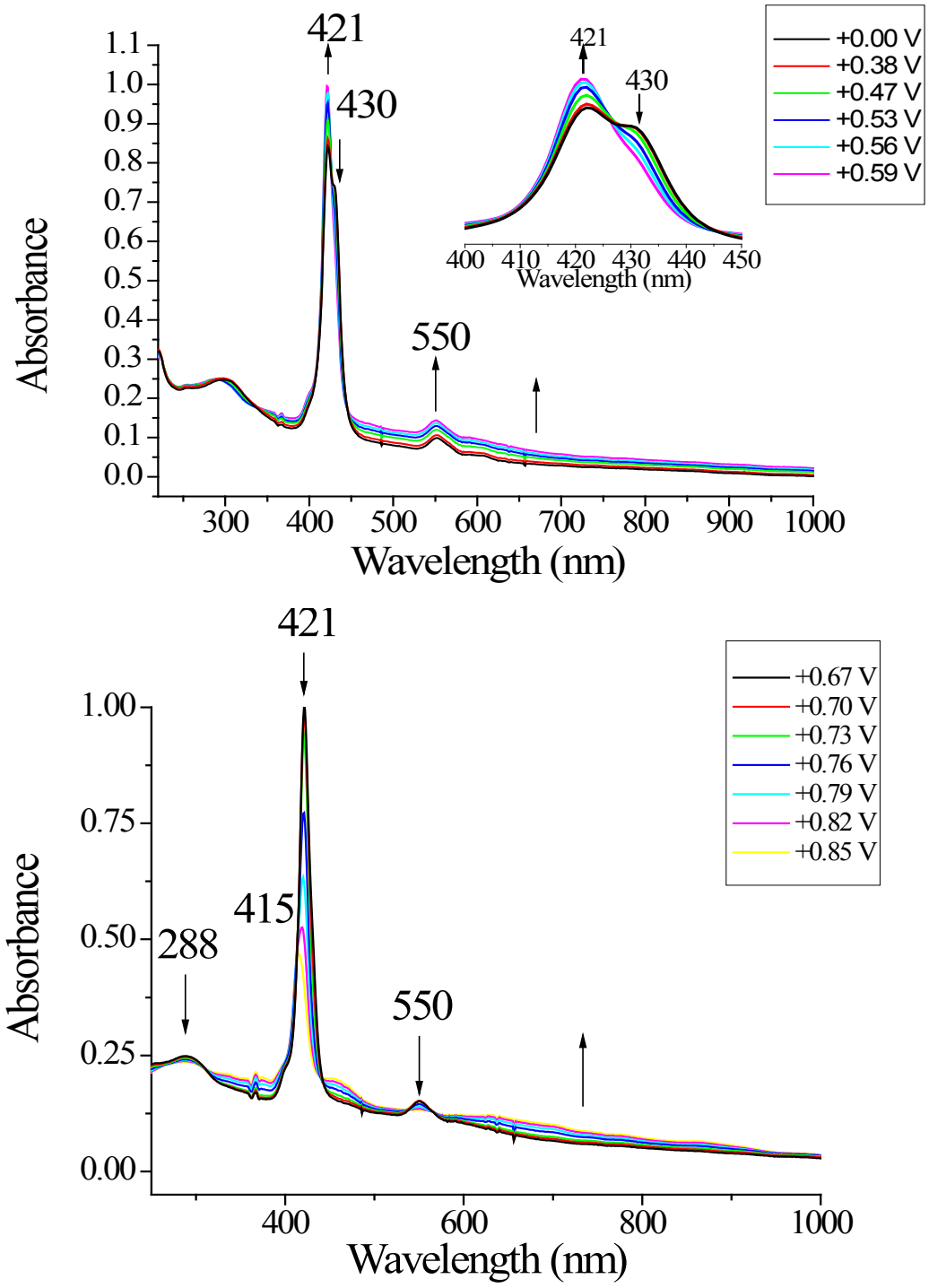
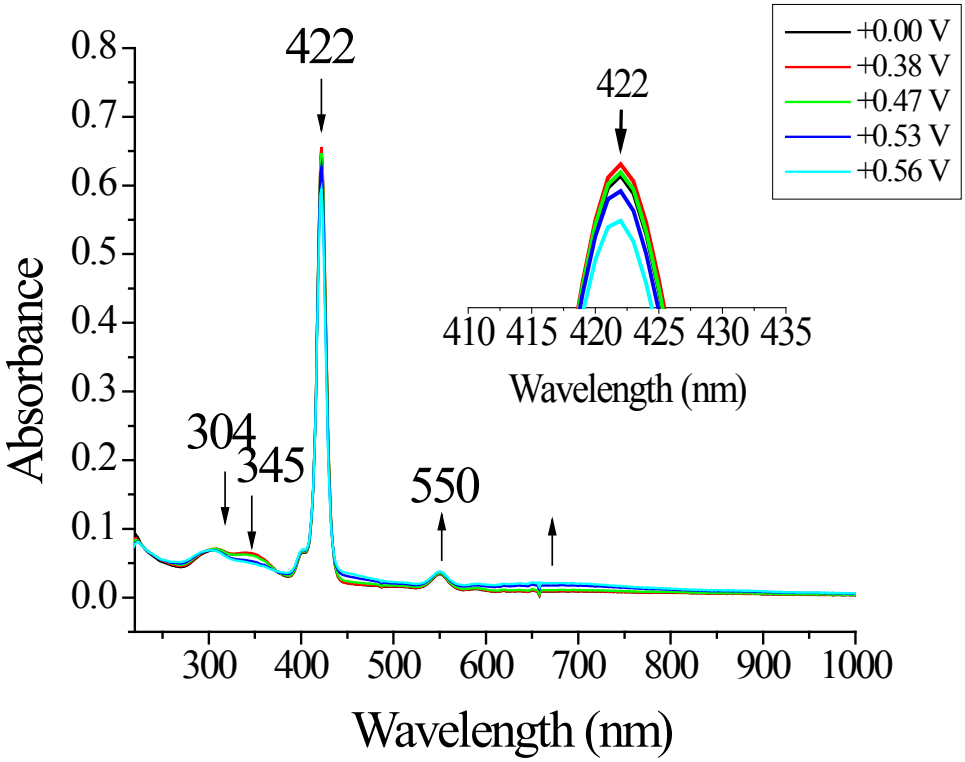


Fig S5 The absorption spectra of 4.0×10^{-5} M **ZnTMP-PD** in presence of 0.75 equiv. in CH_2Cl_2 containing 0.1 M TBAP..



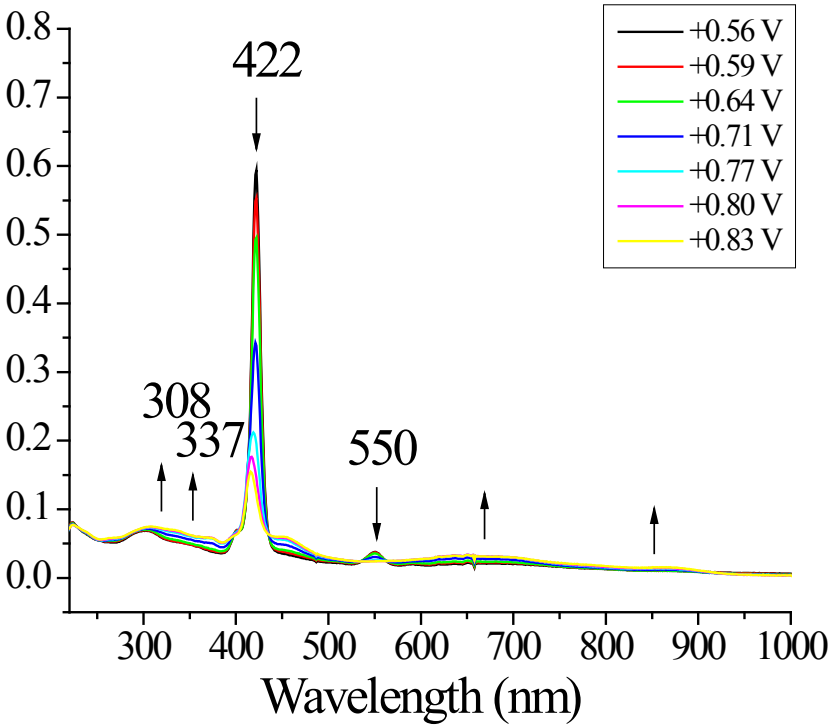


Fig S6 Spectral changes of 4.0×10^{-5} M **ZnTMP-Ph$_2$-PD** in CH_2Cl_2 containing 0.1 M TBAP at $E_{appl.}$ = +0.00V~+0.83V

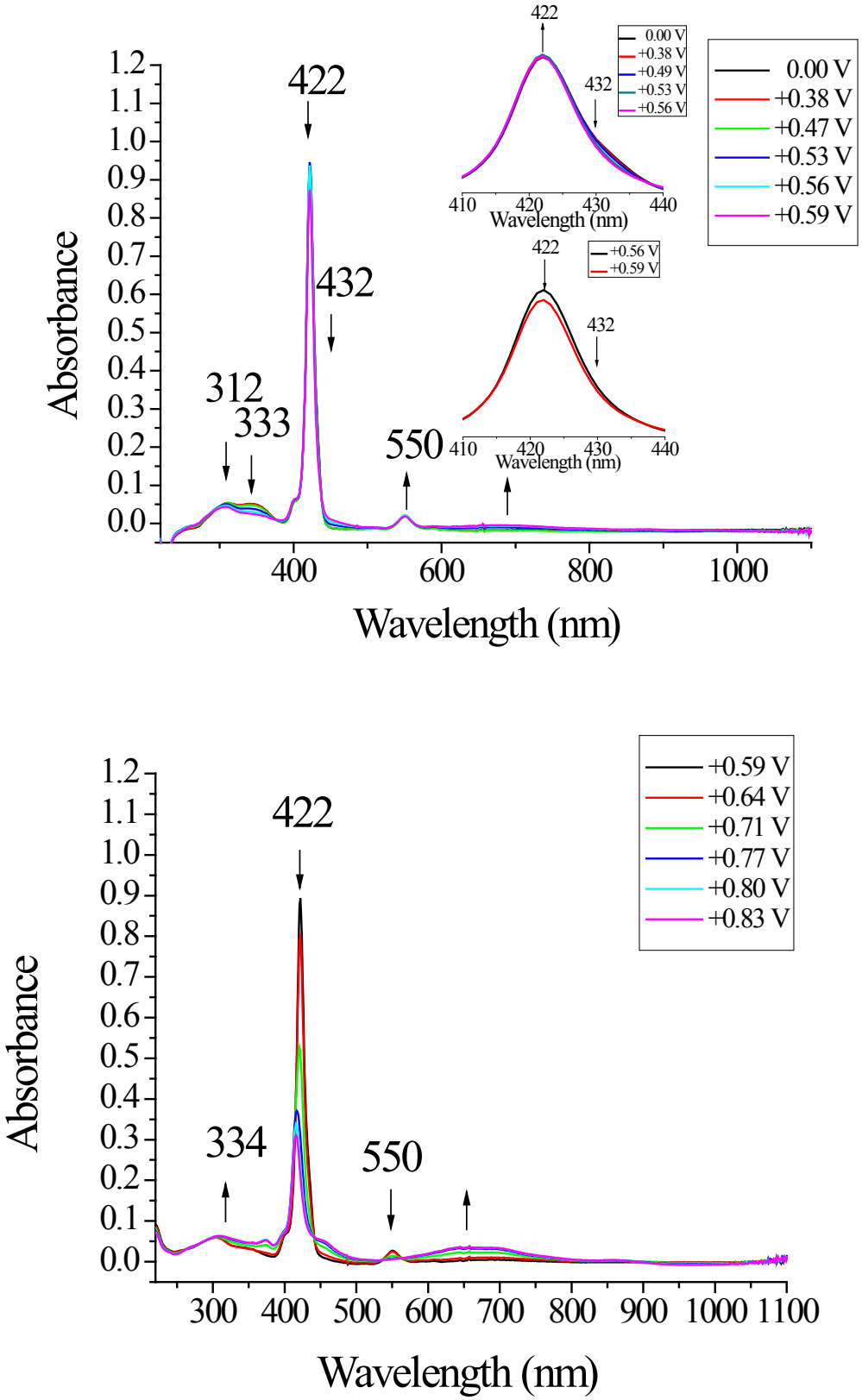


Fig S7 Spectral changes of 4.0×10^{-5} M **ZnTMP-Ph$_2$-PD** in presence of 0.75 equiv. in CH_2Cl_2 containing 0.1 M TBAP at $E_{appl.}$ = +0.00V~+0.83V

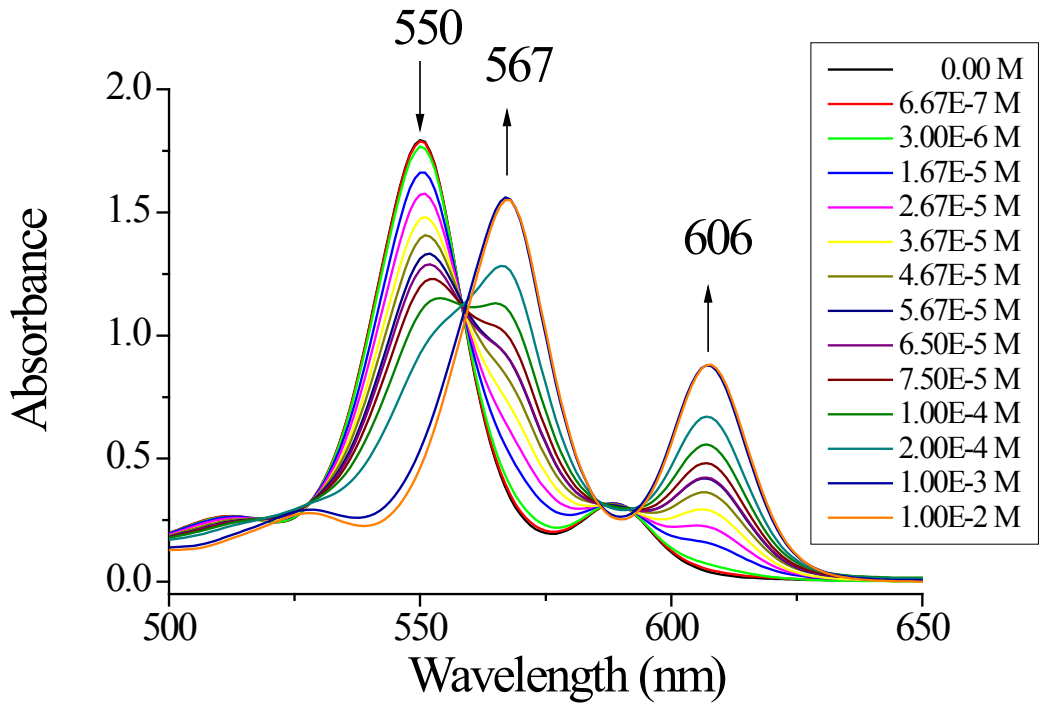


Fig. S8 Absorption spectral change of **ZnTMP-Ph-PD** in the presence of various concentrations of imidazole.

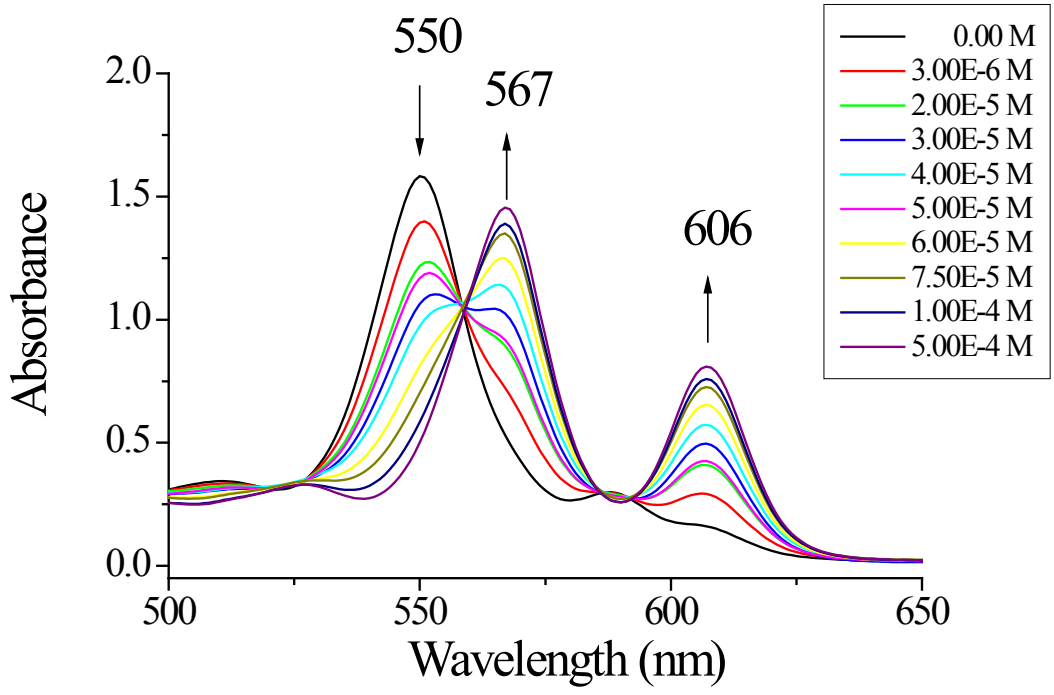


Fig. S9 Absorption spectral change of **ZnTMP-Ph$_2$-PD** in the presence of various concentrations of imidazole.

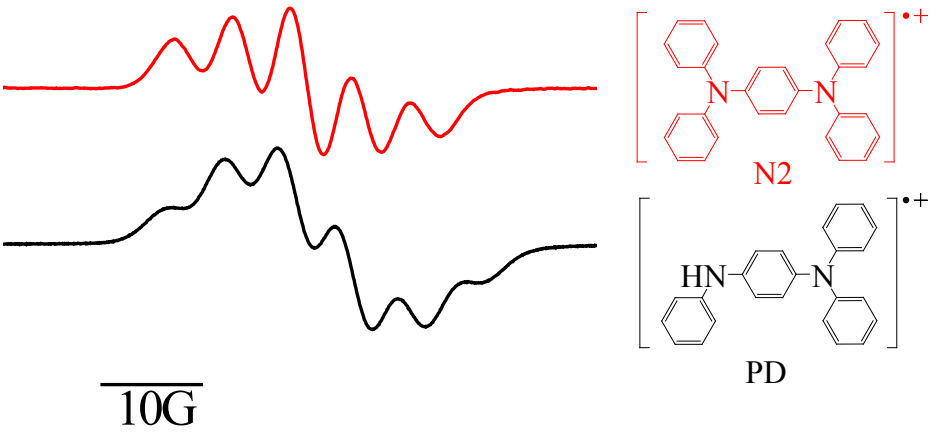


Fig S10 EPR spectra of **N2**$^{+\bullet}$ and **PD**$^{+\bullet}$ at 298K..

Spectral titration methods

According to the following equation, the binding constants would be estimated by photometric titration.[19]

$$ZnP + qL \rightleftharpoons ZnP(L)_q \qquad K_f = \frac{[ZnP(L)_q]}{[ZnP]\,[L]^q}$$

$$\log [\,(A_x - A_i)/(A_\infty - A_x)] = q\log[L] + \log K_f \qquad (1)$$

where $[L]$ is concentration of the free-ligand, A_x is absorbance of zinc porphyrin at various imidazole concentration, A_i is absorption band in absence of imidazole, A_∞ is the absorption band in the presence of saturated imidazole, q is the number of binding ligands, and K_f is a binding constant.

As for the binding constants between HIm and oxidized zinc porphyrins were calculated from the potential shift of CVs as described in the following method.[20]

$$ZnP \overset{-ne^-}{\rightleftharpoons} ZnP^{n+} + pL \rightleftharpoons ZnP^{+\bullet}(L)_p \qquad K_f^{+} = \frac{[ZnP^{+\bullet}(L)_p]}{[ZnP]\,[L]^p}$$

$$(E_{1/2})_u = (E_{1/2})_c - (0.059/n)\,[\,\log (K_f/K_f^{+}) - \log [L]^{n-q}\,] \qquad (2)$$

where $(E_{1/2})_u$ and $(E_{1/2})_c$ are the half potential of uncomplexed and complexed species, $[L]$ is the ligand concentration, p and q are the number of ligation for the neutral and cation radical species, K_f and K_f^{+} are the binding constant of $ZnP(L)_q$ and $ZnP^{+\bullet}(L)_p$, and n is the number of electron transfer in the electrochemical reaction.

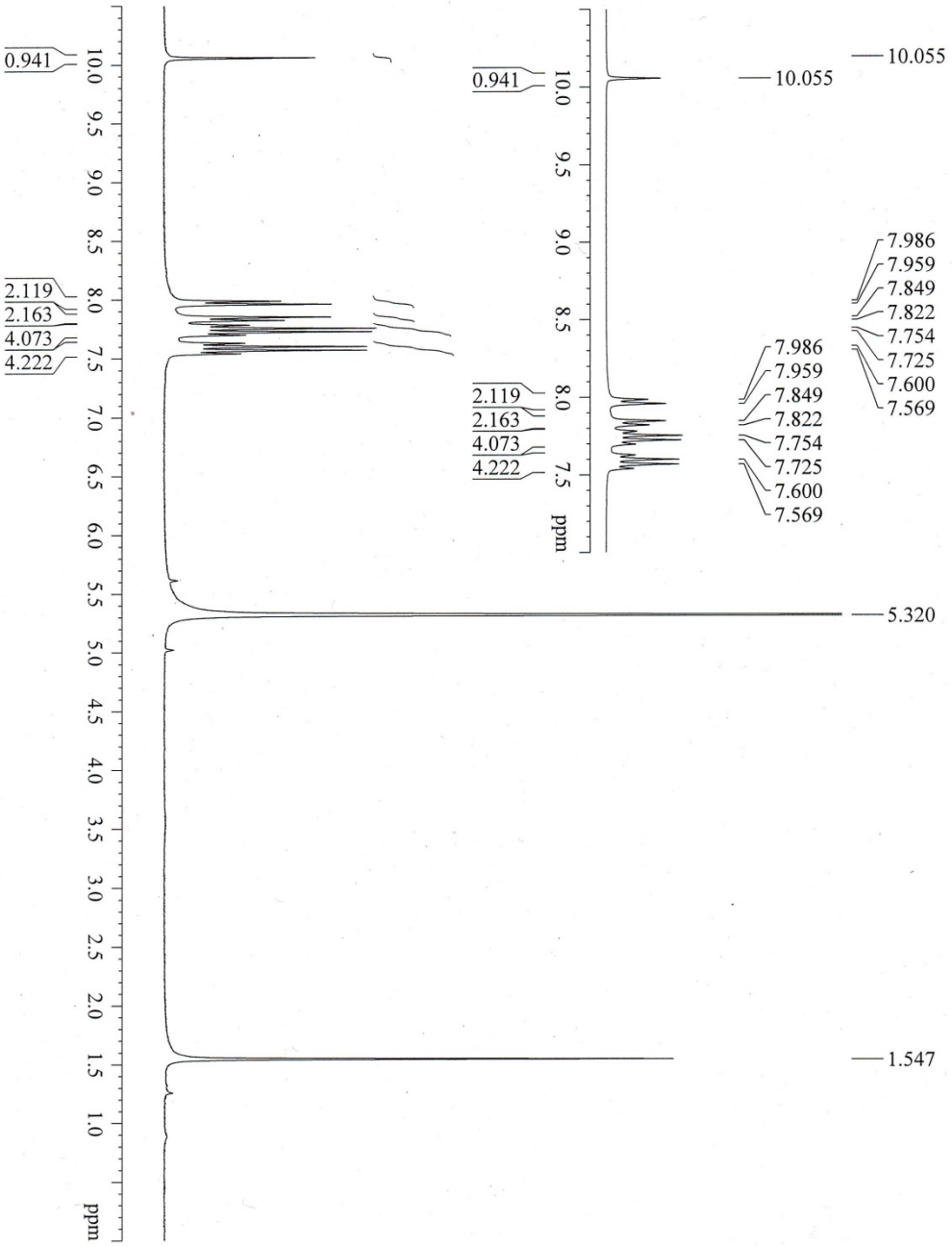


Figure S11. H^1 NMR spectra for 4′-bromo-4-triphenylbenzaldehyde.

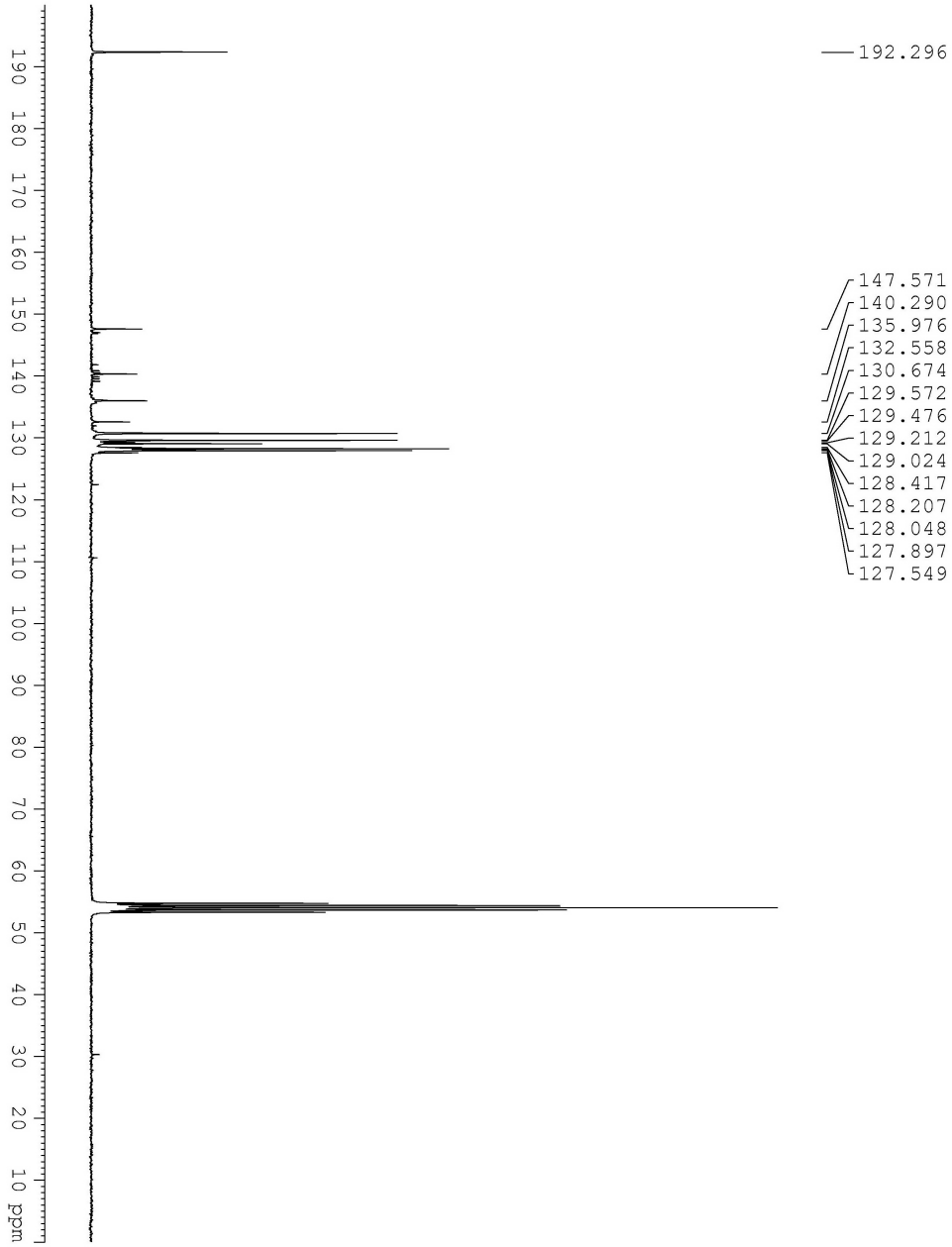


Figure S12. C^{13} NMR spectra for 4′-bromo-4-triphenylbenzaldehyde.

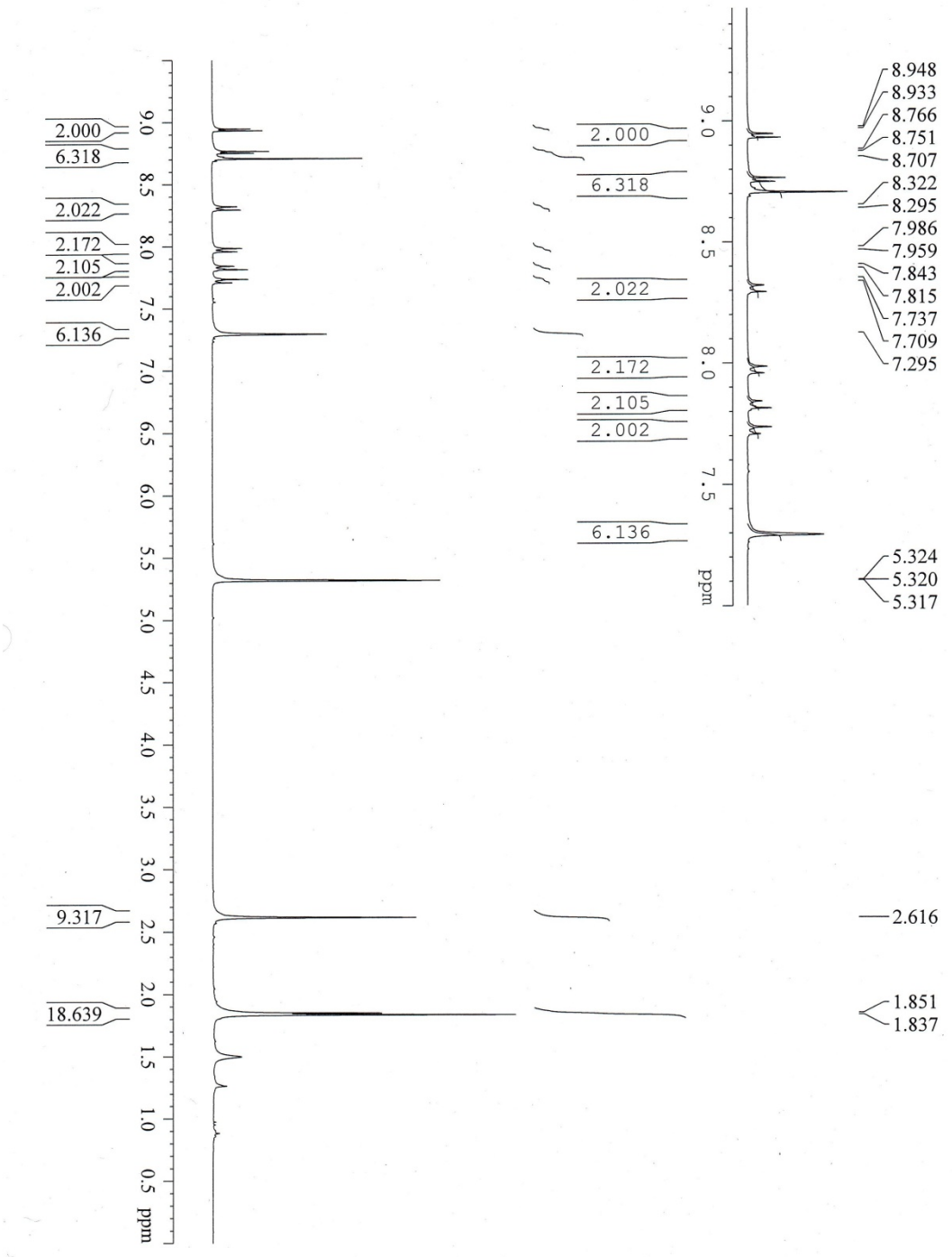


Figure S13. H^1 NMR spectra for $Zn(Ph_2\text{-}Br)(mesityl)_3P$.

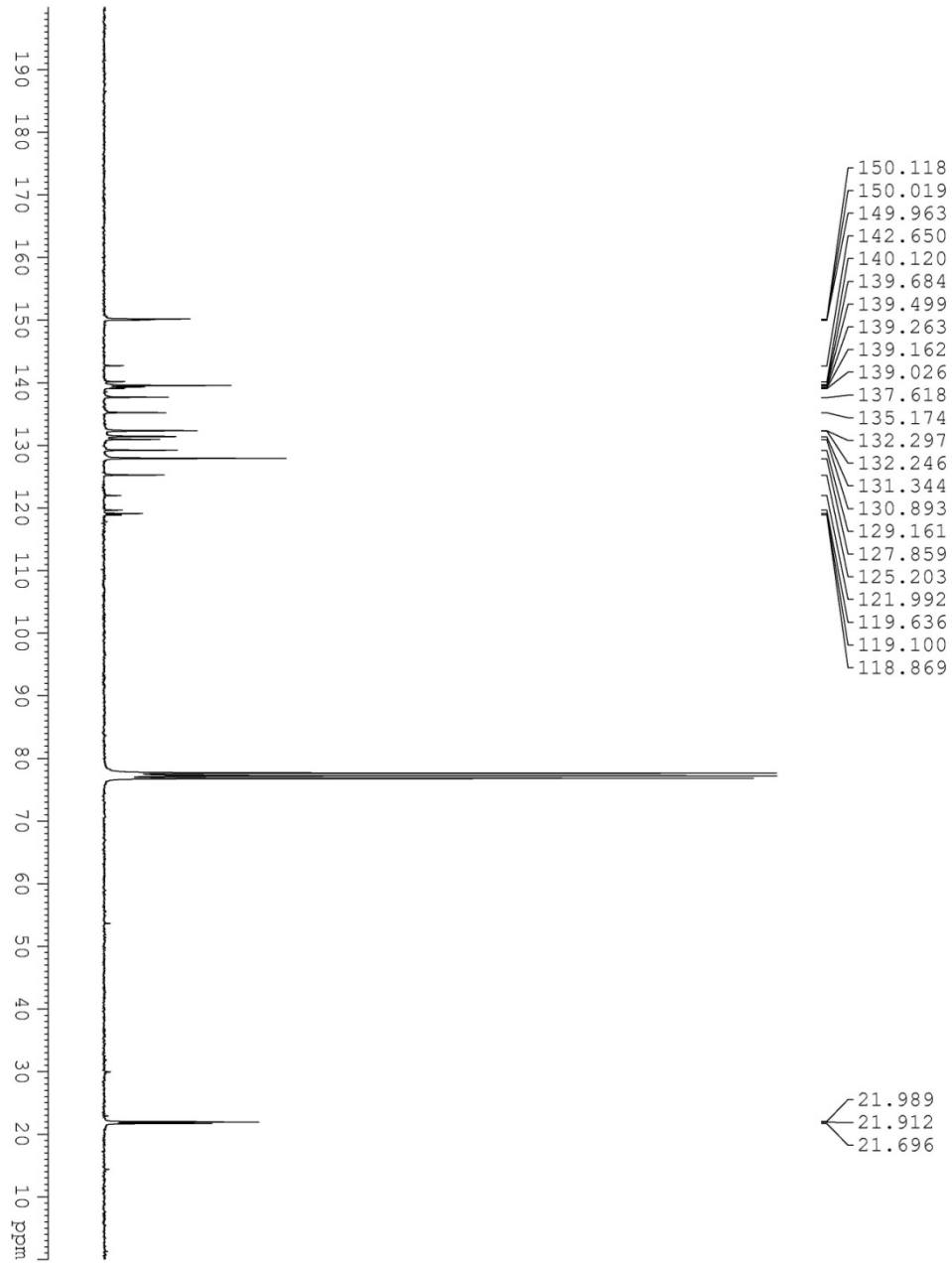


Figure S14. C^{13} NMR spectra for $Zn(Ph_2\text{-}Br)(mesityl)_3P$.

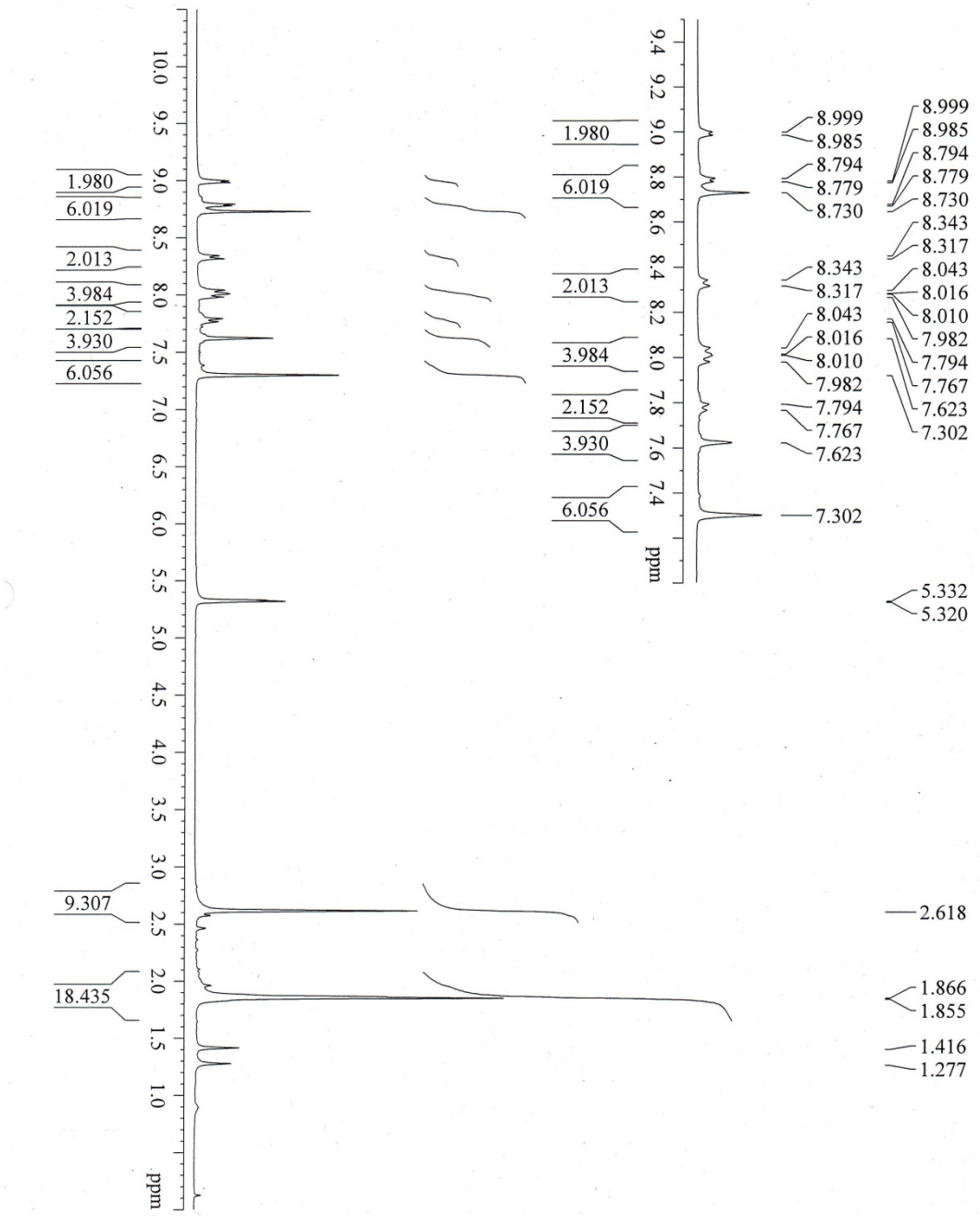


Figure S15. H^1 NMR spectra for $Zn(Ph_3\text{-}Br)(mesityl)_3P$.

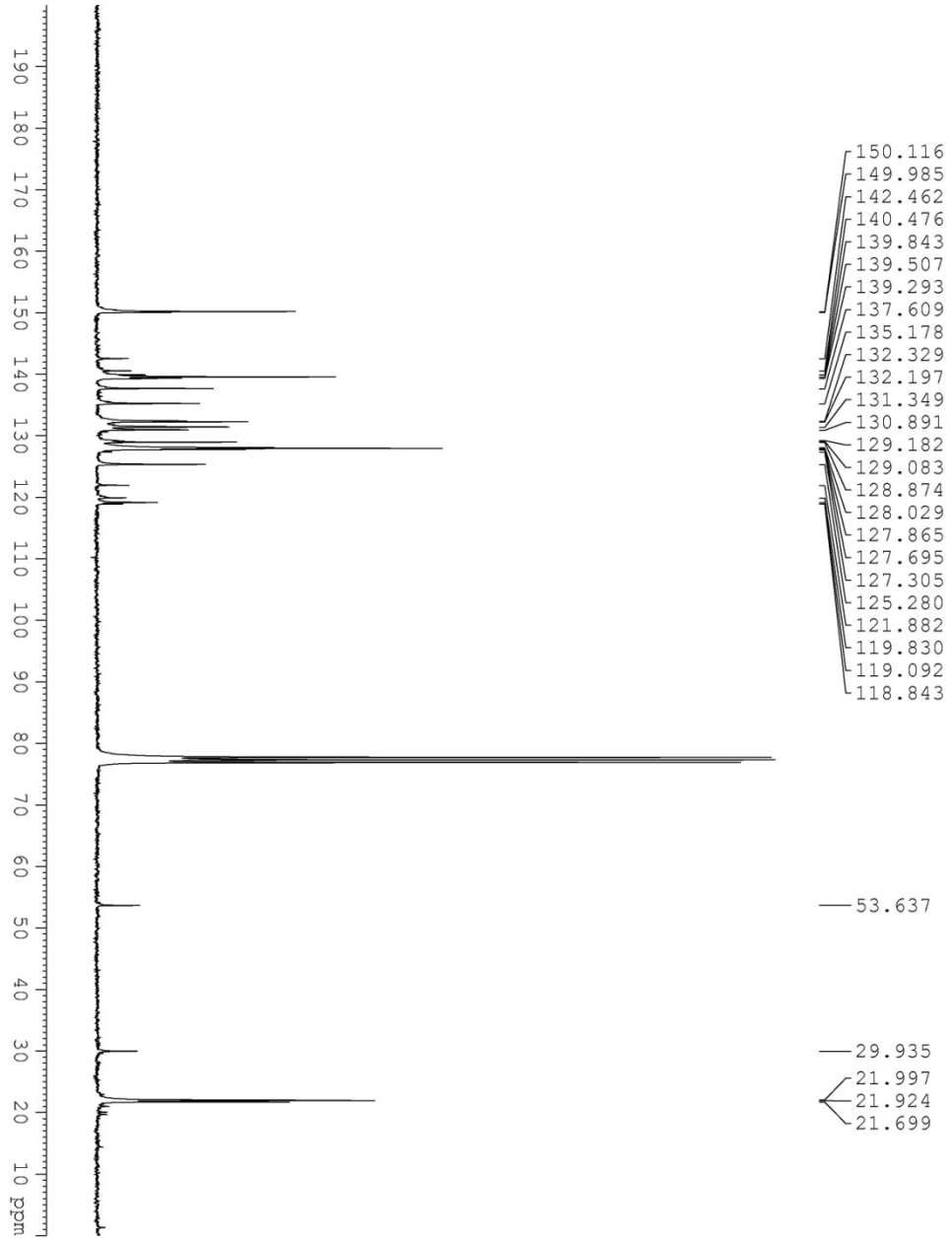


Figure S16. C^{13} NMR spectra for $Zn(Ph_3\text{-}Br)(mesityl)_3P$.

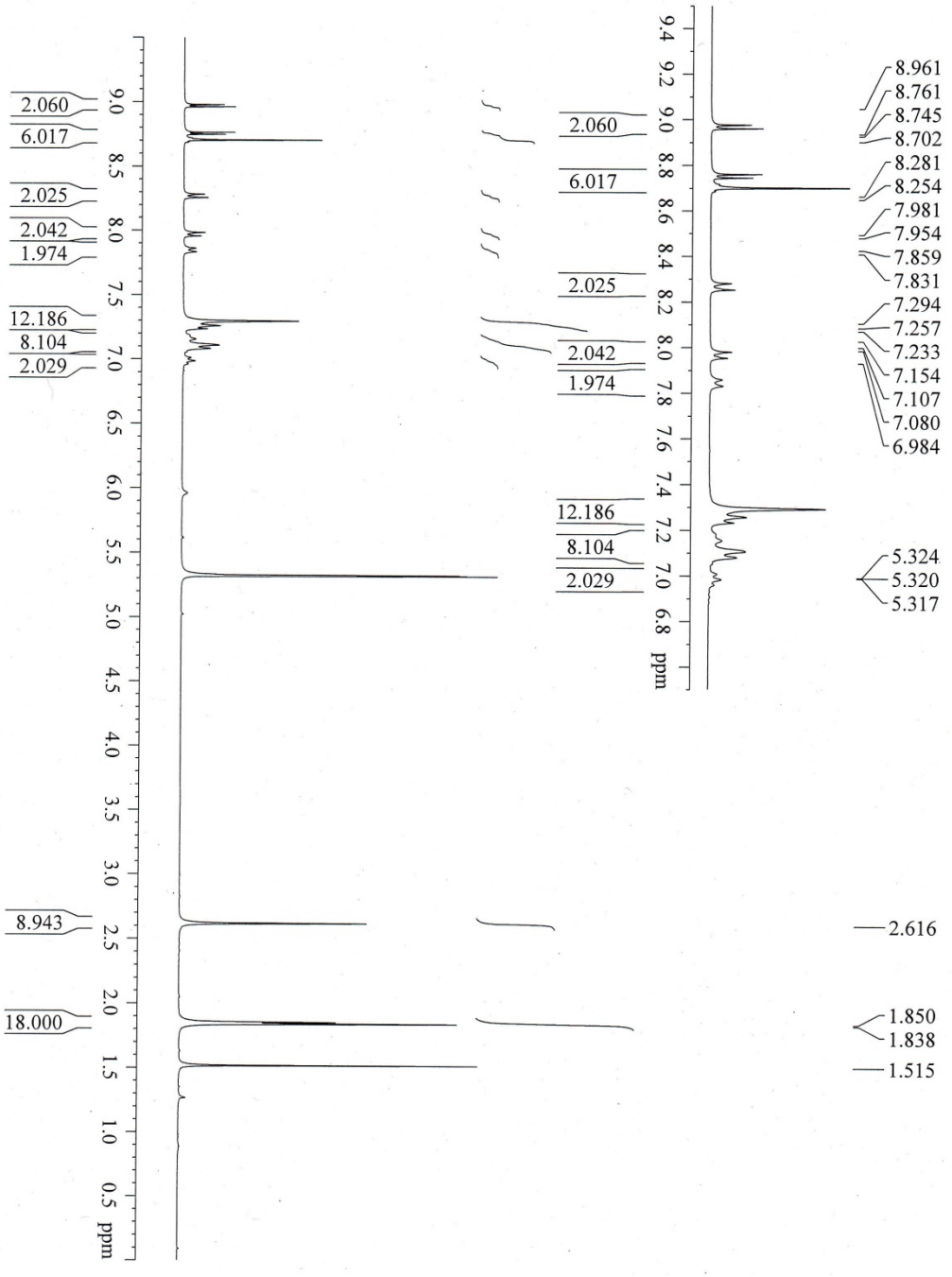


Figure S17. H^1 NMR spectra for ZnTMP-Ph-PD.

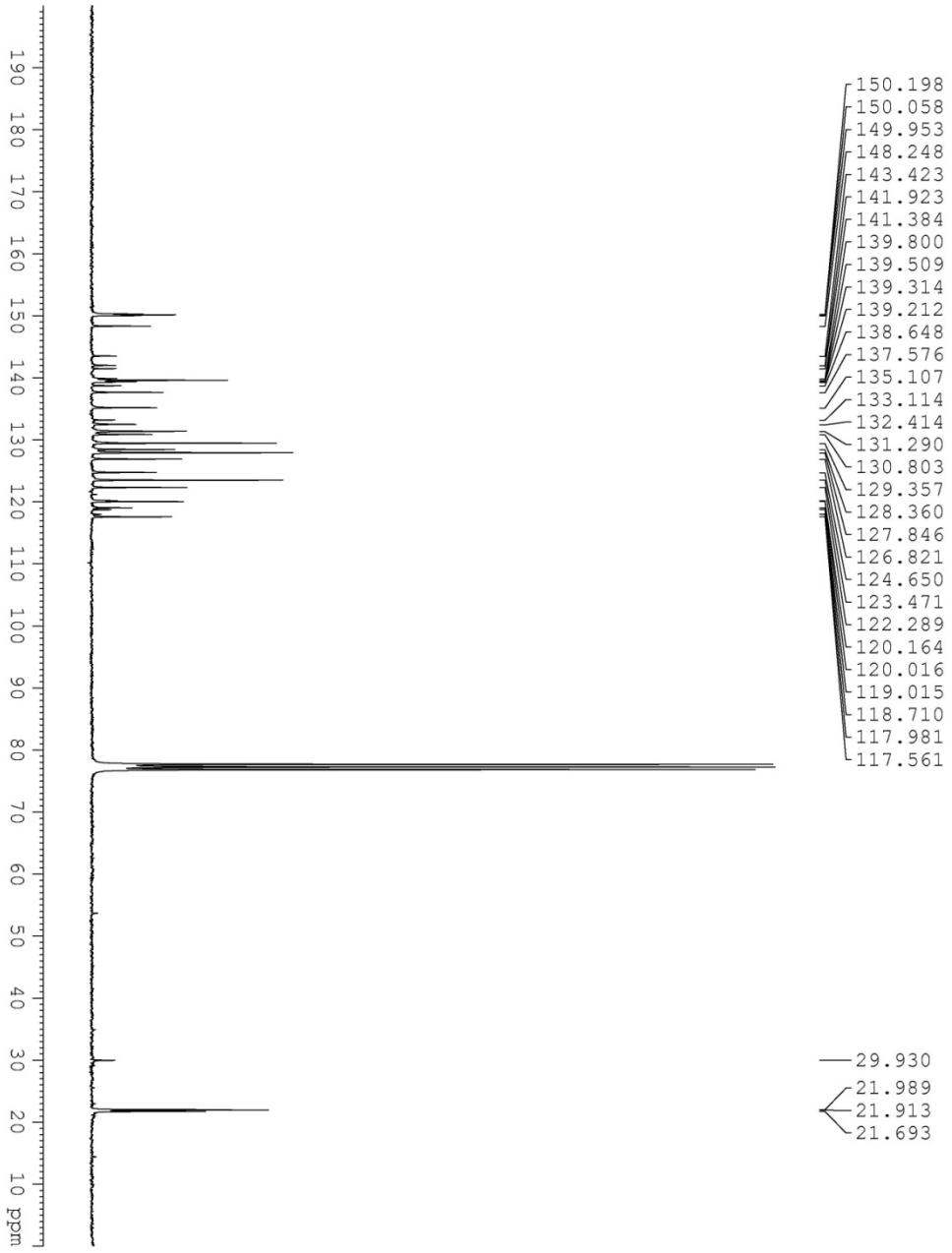


Figure S18. C^{13} NMR spectra for ZnTMP-Ph-PD.

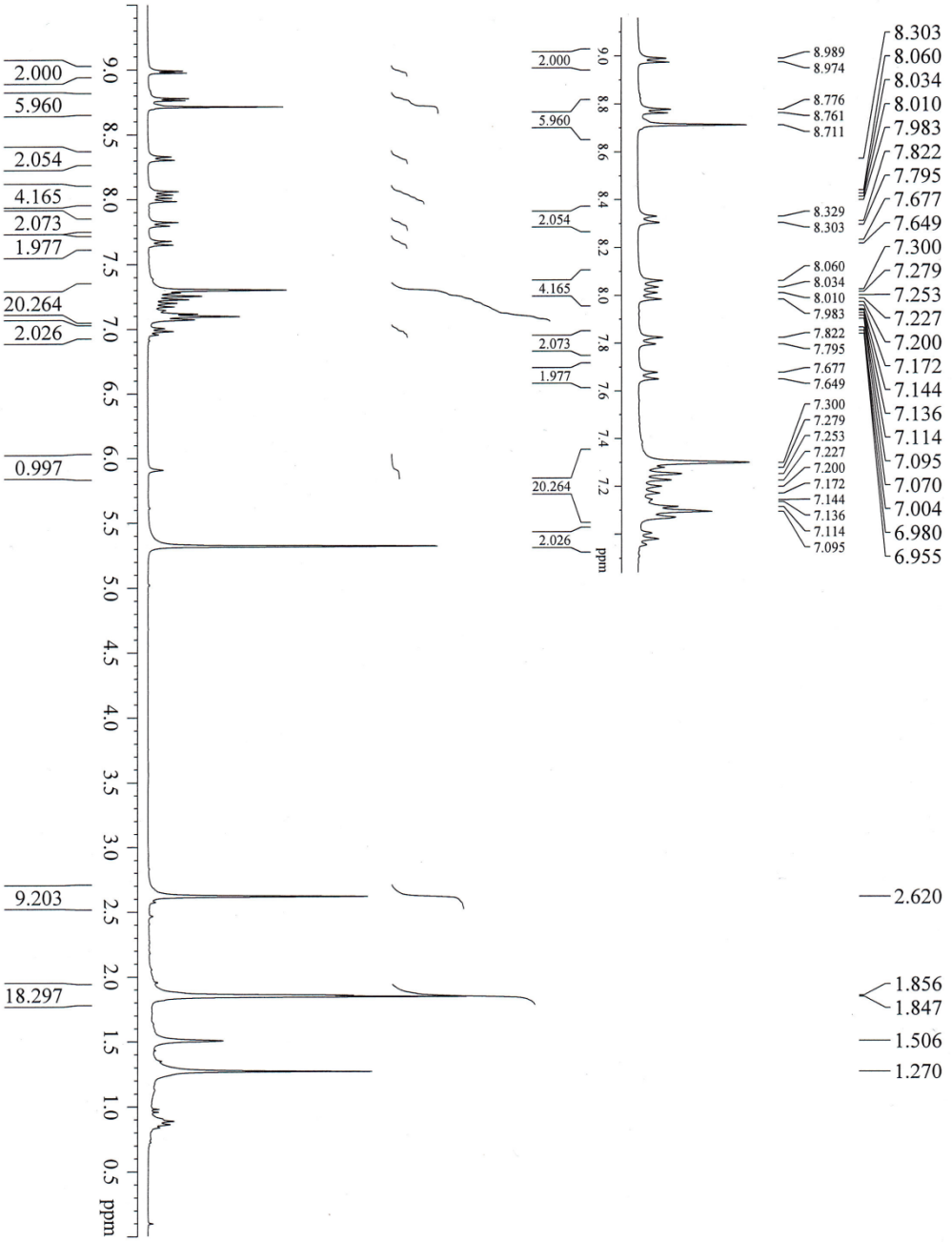


Figure S19. H^1 NMR spectra for ZnTMP-Ph_2-PD.

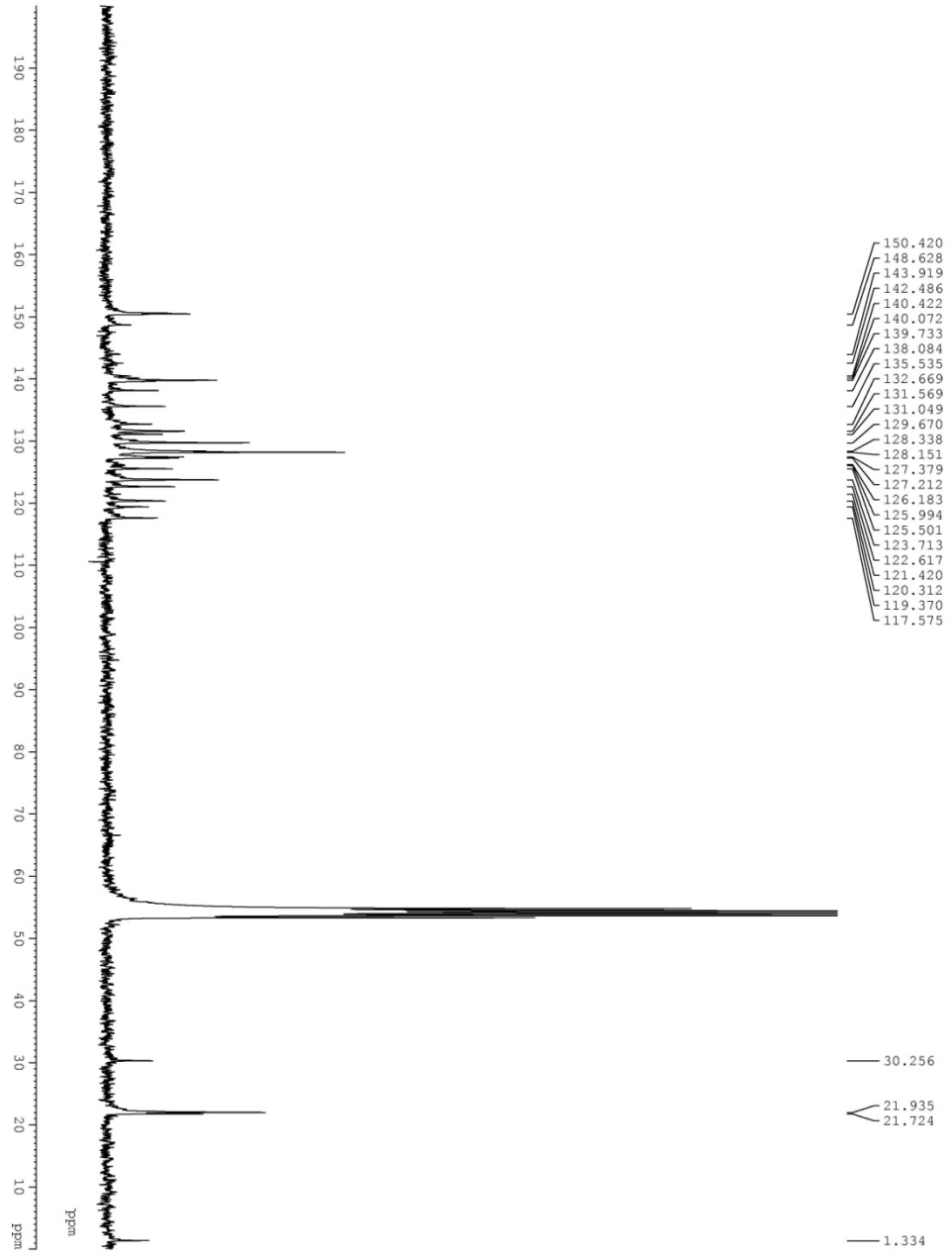


Figure S20. C^{13} NMR spectra for ZnTMP-Ph_2-PD.