Supporting information for

Synthesis, structural characterization and reactivity of heteroazuliporphyrins.

Timothy D. Lash,* Jessica A. El-Beck and Gregory M. Ferrence

Department of Chemistry, Illinois State University, Normal, Illinois 61790-4160

E-mail: tdlash@ilstu.edu

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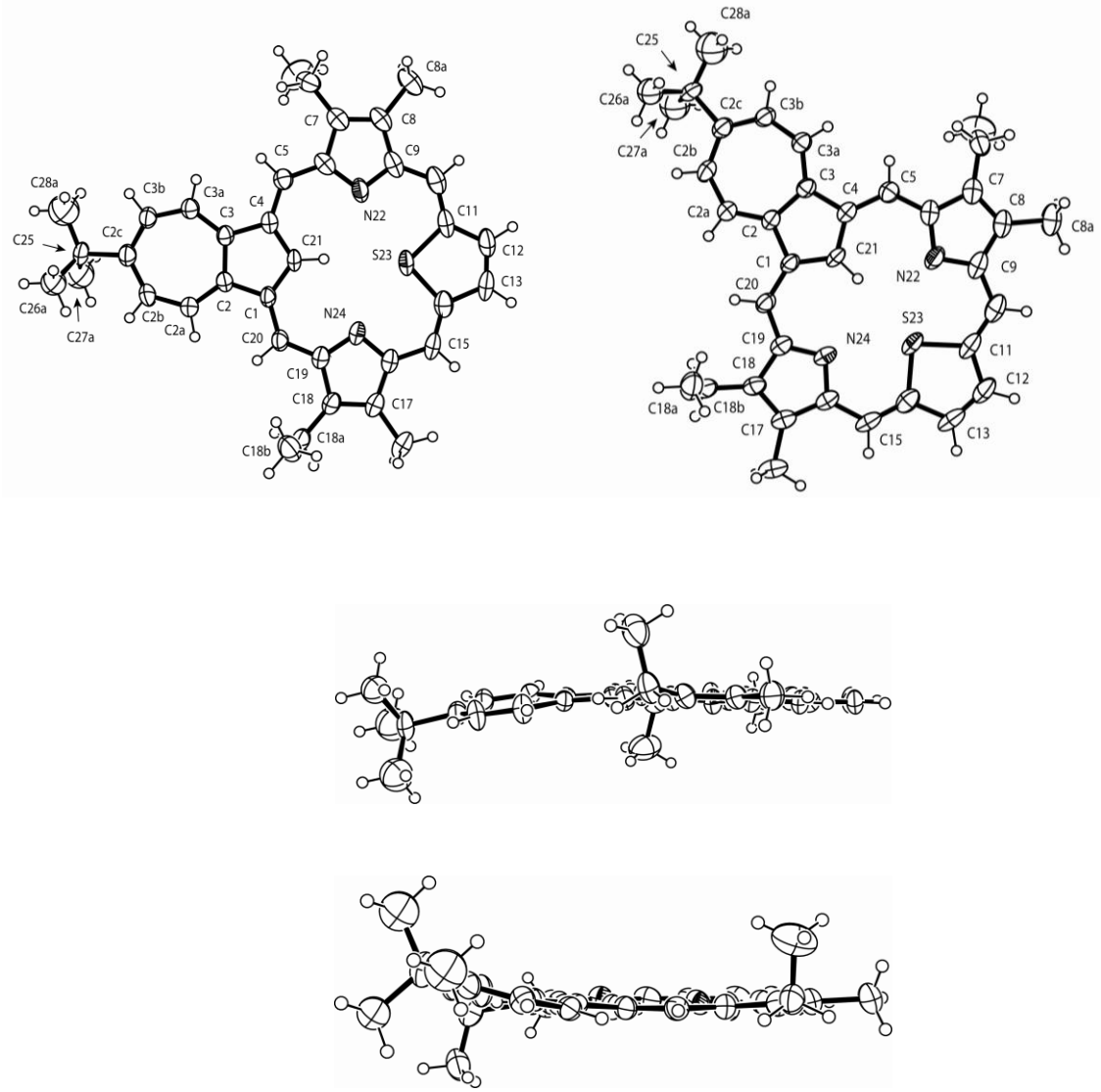

Figure S1. ORTEP-III drawings (50% probability level, hydrogens drawn arbitrarily small) of thia-azuliporphyrin **8b** showing several different views.

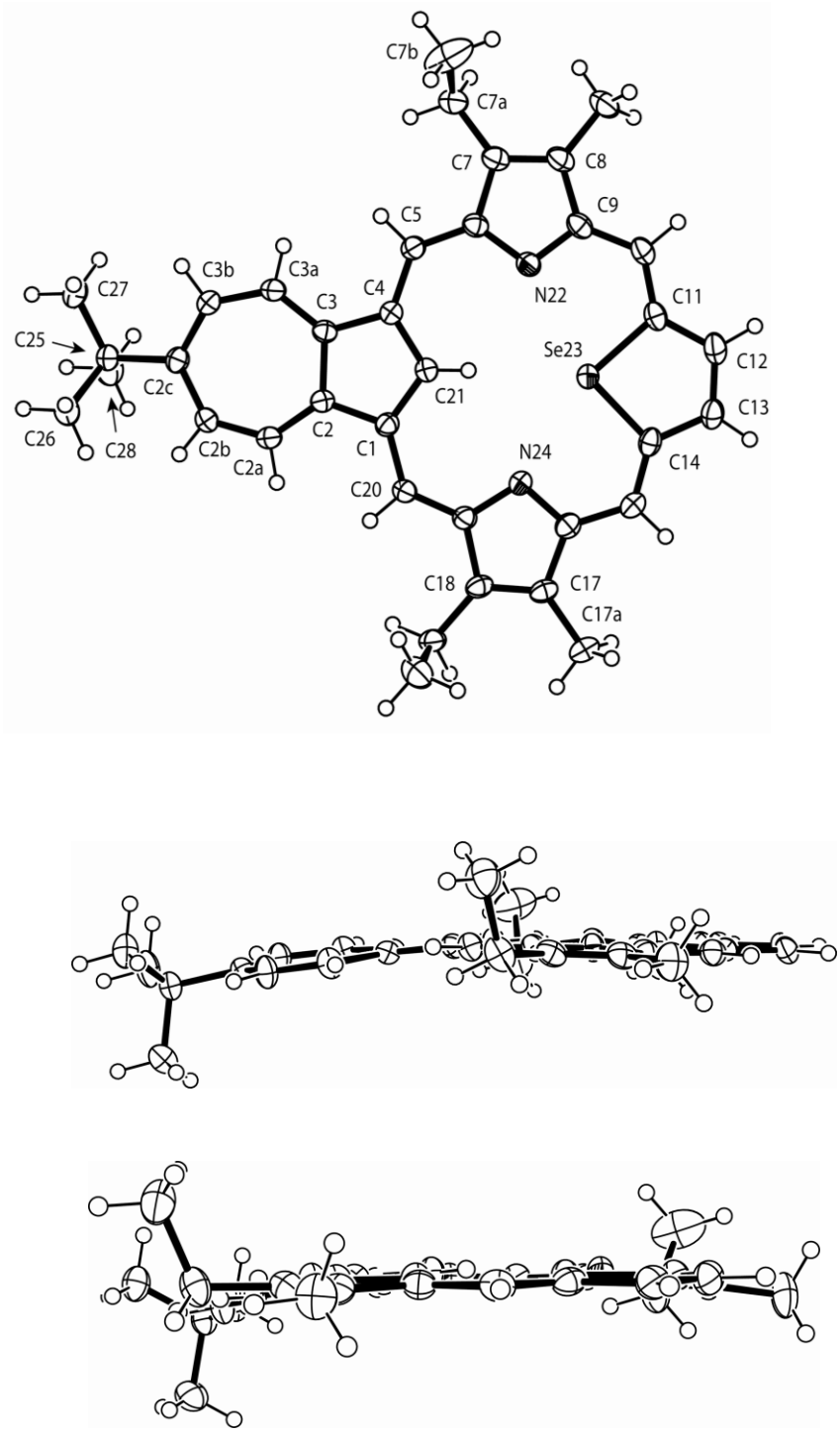

Figure S2. ORTEP-III drawings (50% probability level, hydrogens drawn arbitrarily small) of selena-azuliporphyrin **9b** showing several different views.

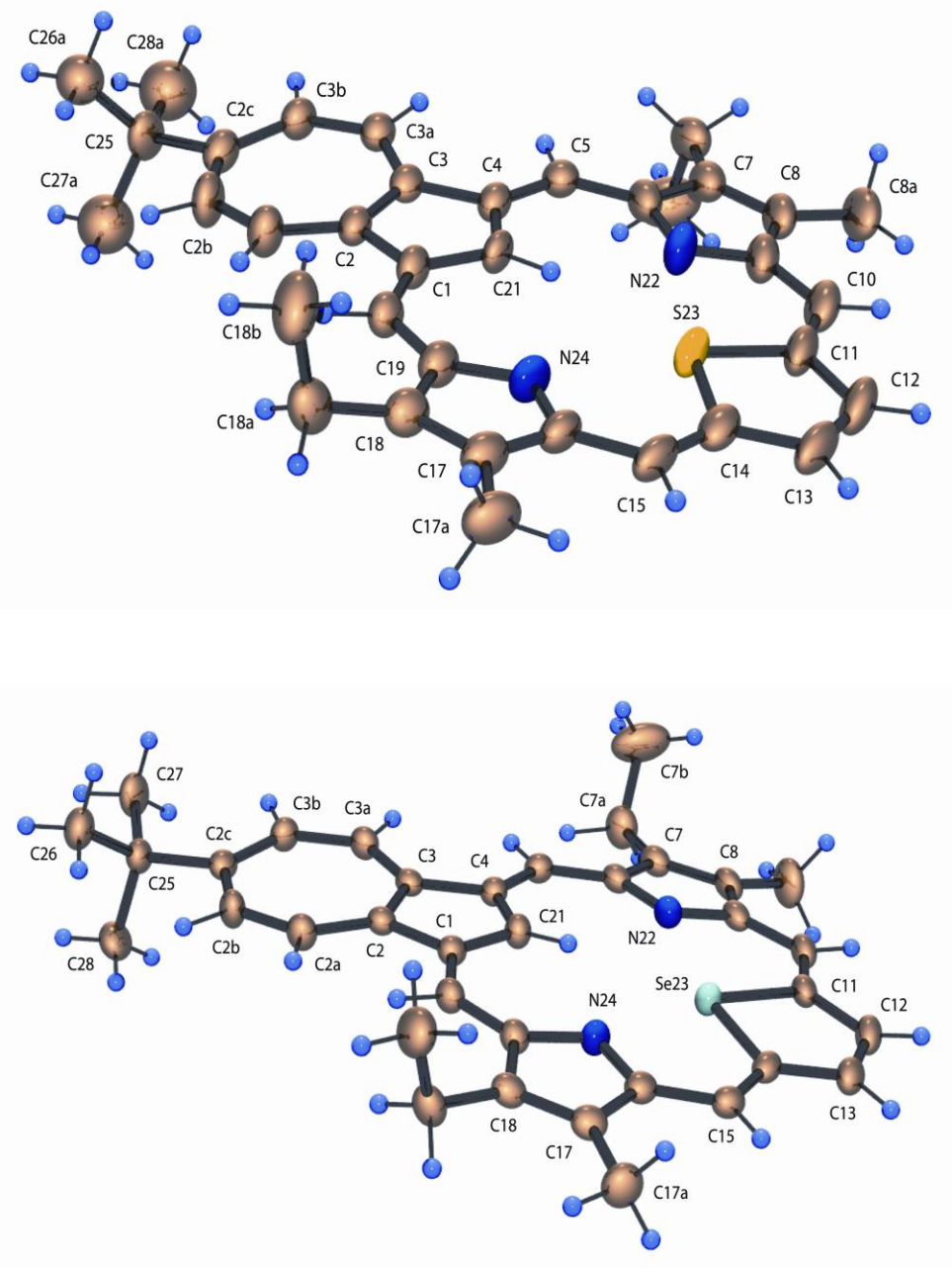

Figure S3. Color ORTEP-III drawings rendered in POV-Ray (50% probability level, hydrogen atoms drawn arbitrarily small) for thia-azuliporphyrin **8b** and selena-azuliporphyrin **9b**.

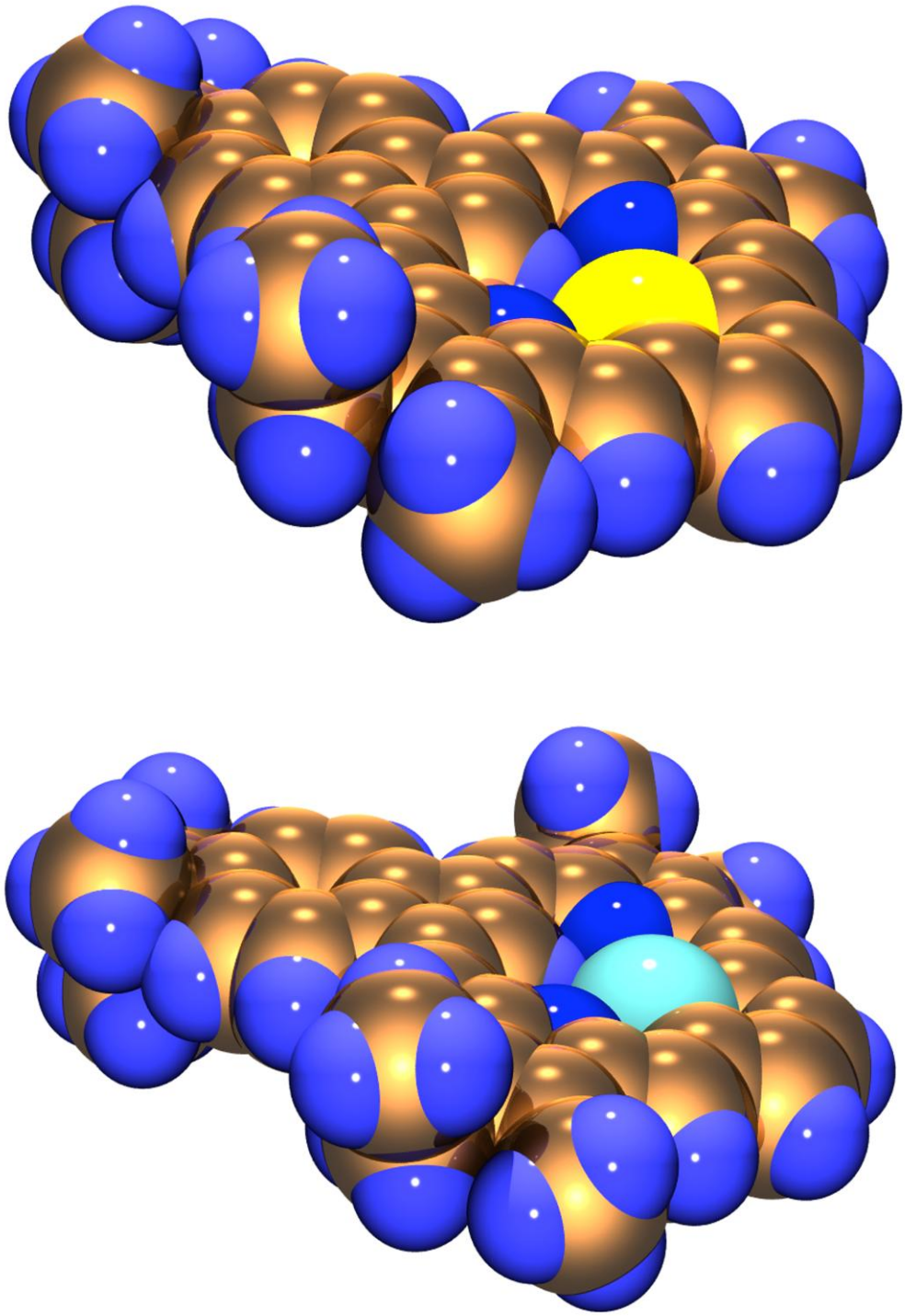

Figure S4. Space filling representations of the X-ray crystal structures for thia-azuliporphyrin **8b** and selena-azuliporphyrin **9b** generated with POV-Ray.

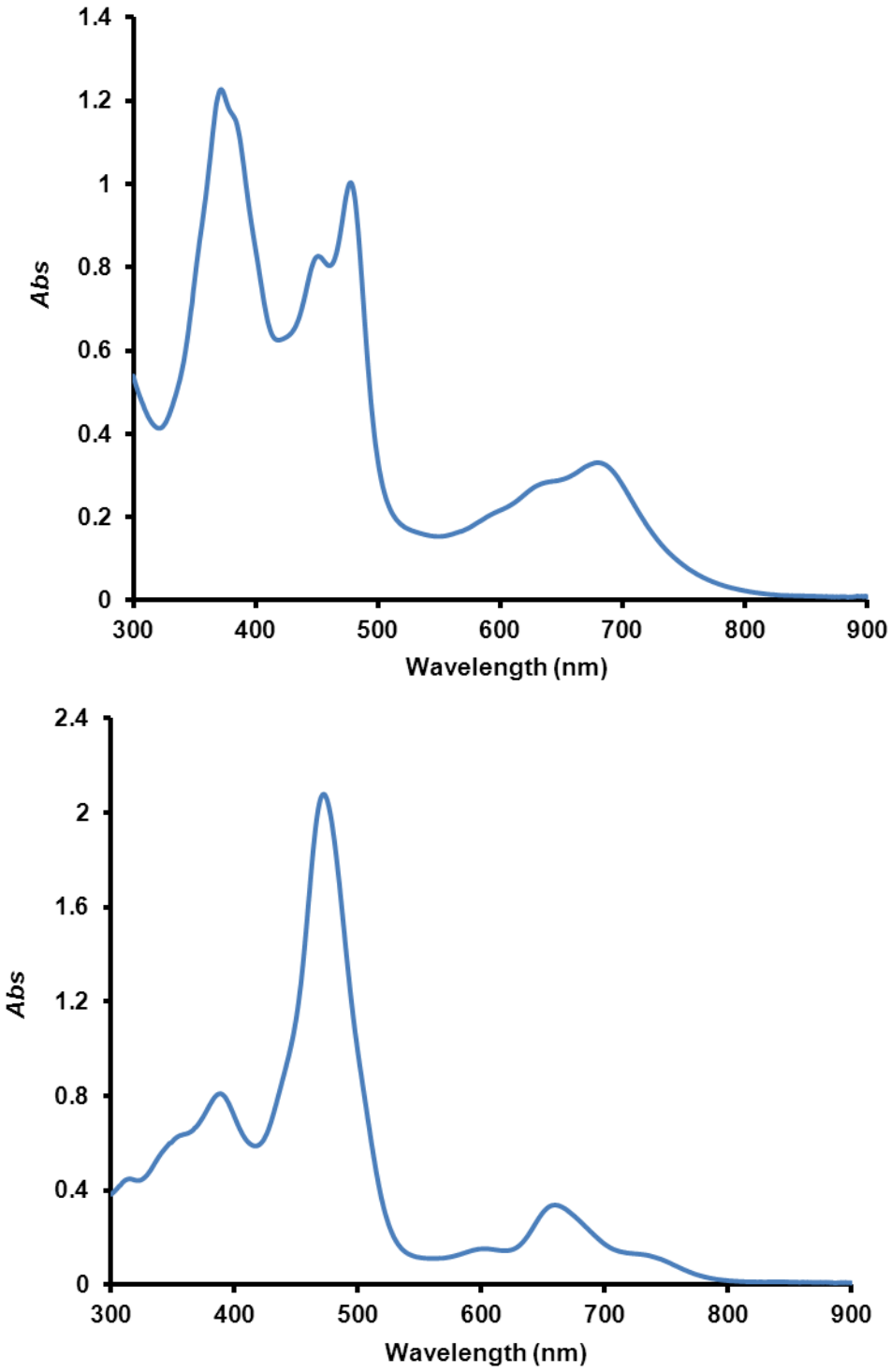

Figure S5. UV-vis spectra of thia-azuliporphyrin **8b**. Upper spectrum: **8b** in 1% Et_3N-chloroform. Lower spectrum: **8b**H_2^{2+} in 1% TFA-chloroform.

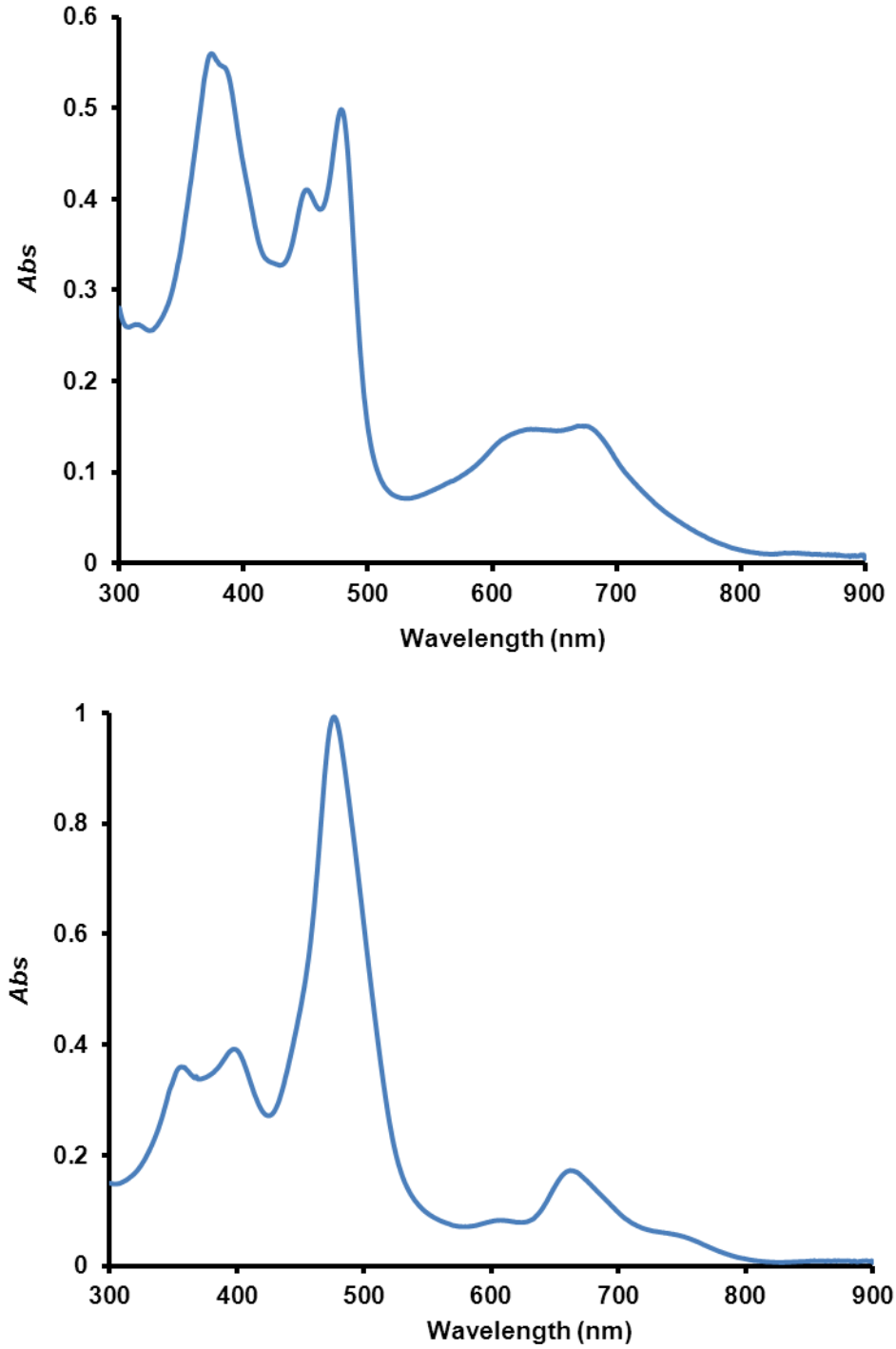

Figure S6. UV-vis spectra of thia-azuliporphyrin **8c**. Upper spectrum: **8c** in 1% Et_3N-chloroform. Lower spectrum: **8c**H_2^{2+} in 1% TFA-chloroform.

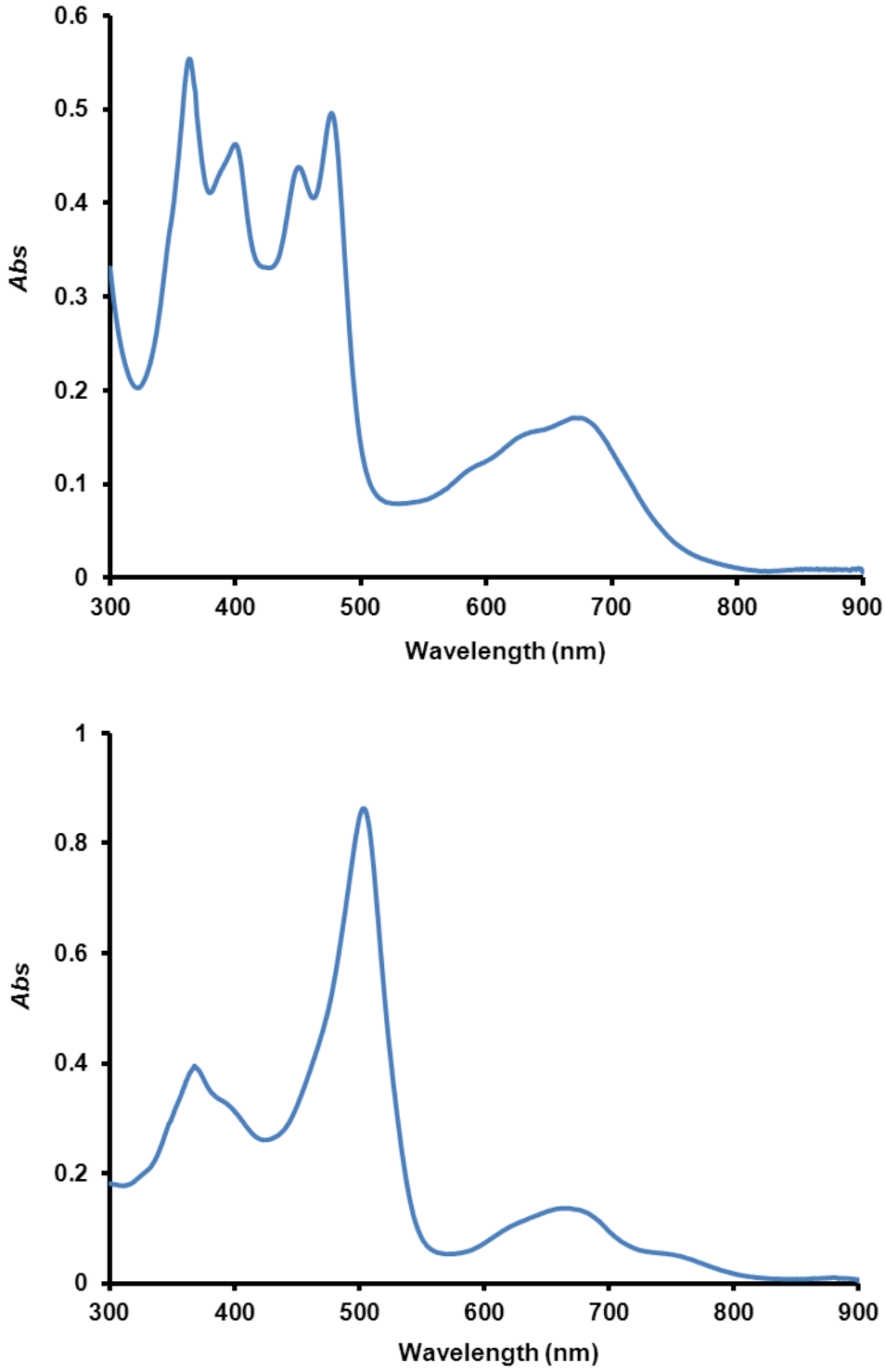

Figure S7. UV-vis spectra of selena-azuliporphyrin **9b**. Upper spectrum: **9b** in 1% Et_3N-chloroform. Lower spectrum: **9b**H_2^{2+} in 1% TFA-chloroform.

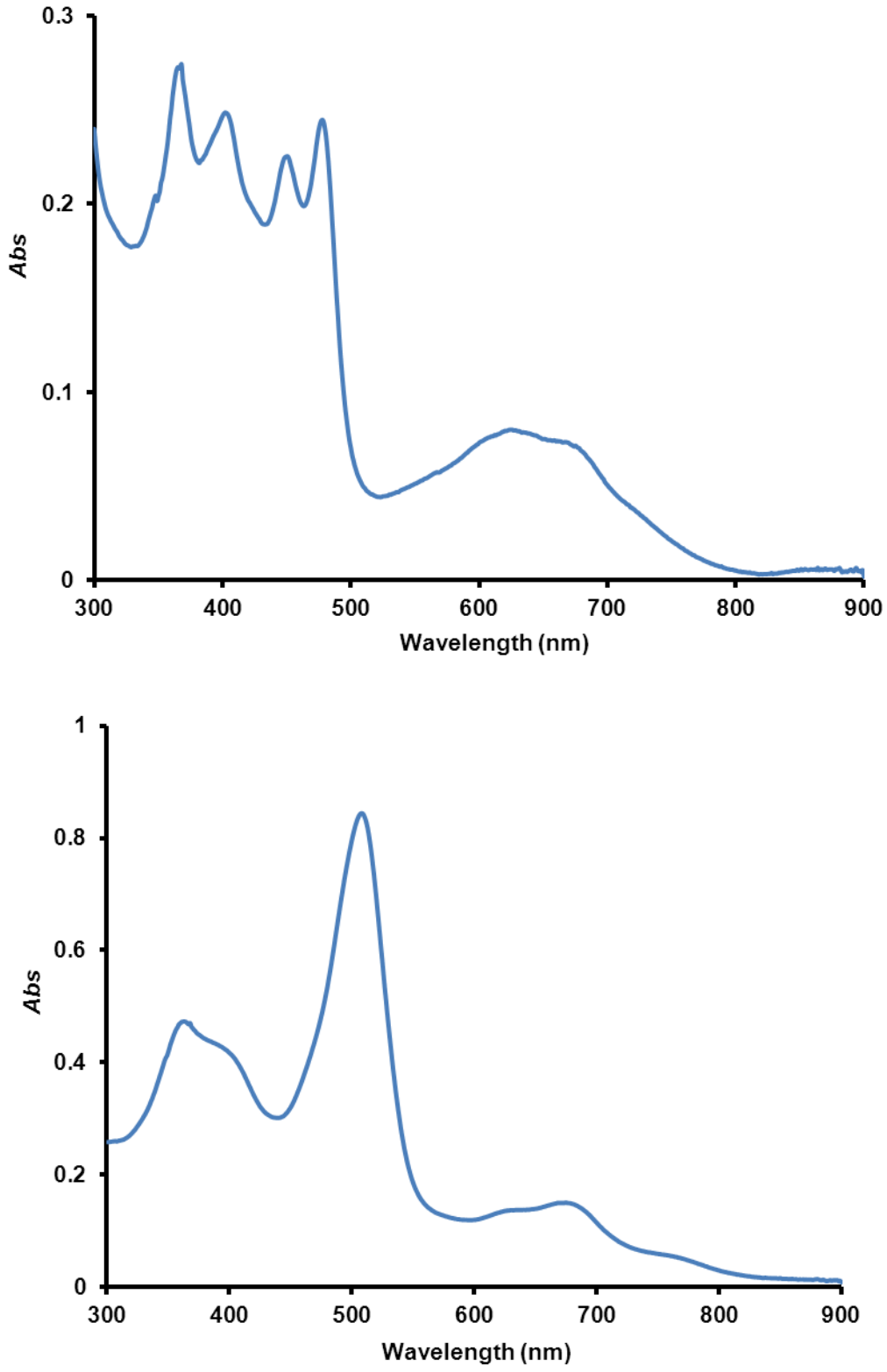

Figure S8. UV-vis spectra of selena-azuliporphyrin **9c**. Upper spectrum: **9c** in 1% Et_3N-chloroform. Lower spectrum: **9c**H_2^{2+} in 1% TFA-chloroform.

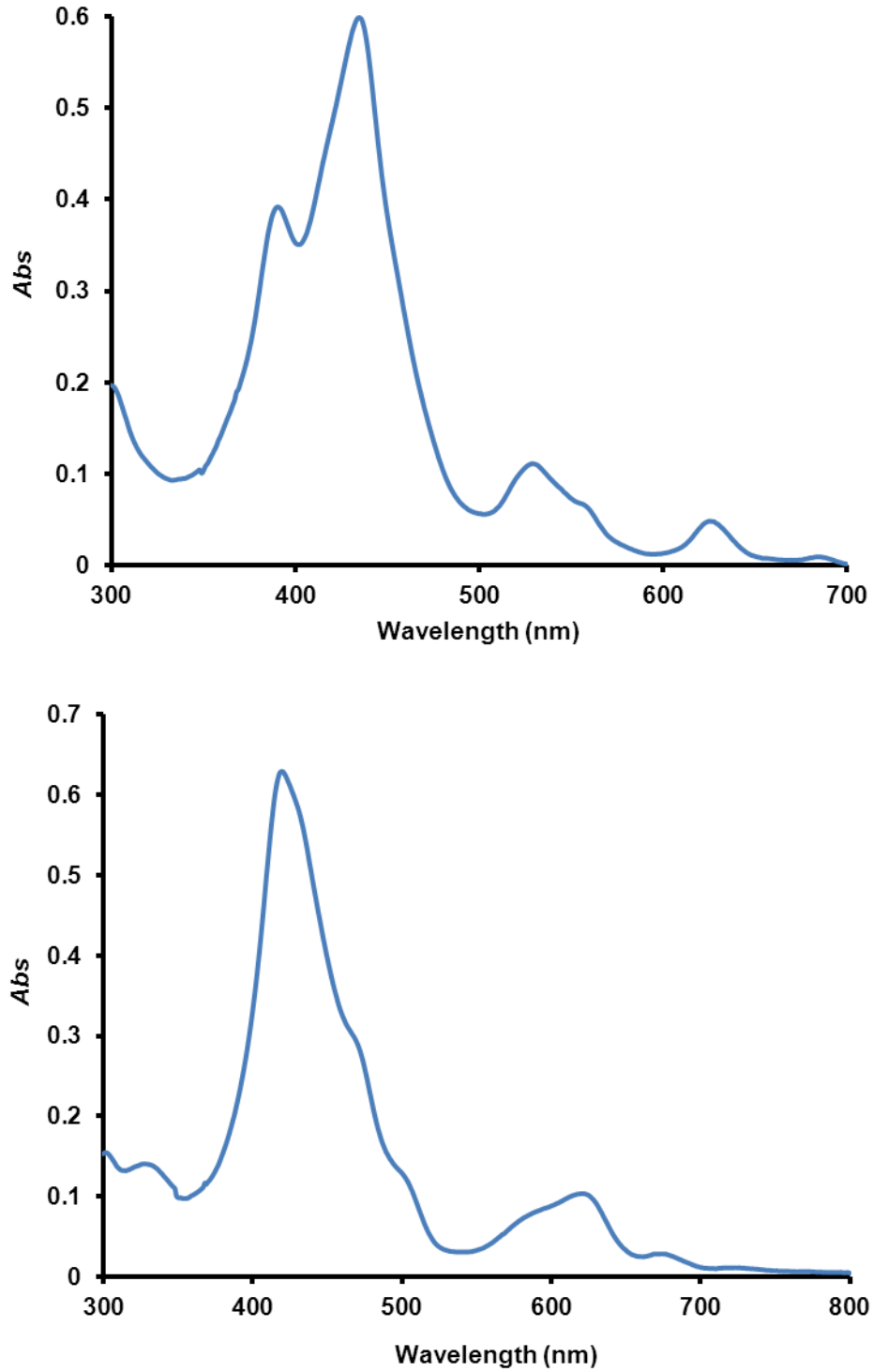

Figure S9. UV-vis spectra of thiacarbaporphyrin **15a**. Upper spectrum: **15a** in 1% Et_3N-chloroform. Lower spectrum: **15a**H^+ in 1% TFA-chloroform.

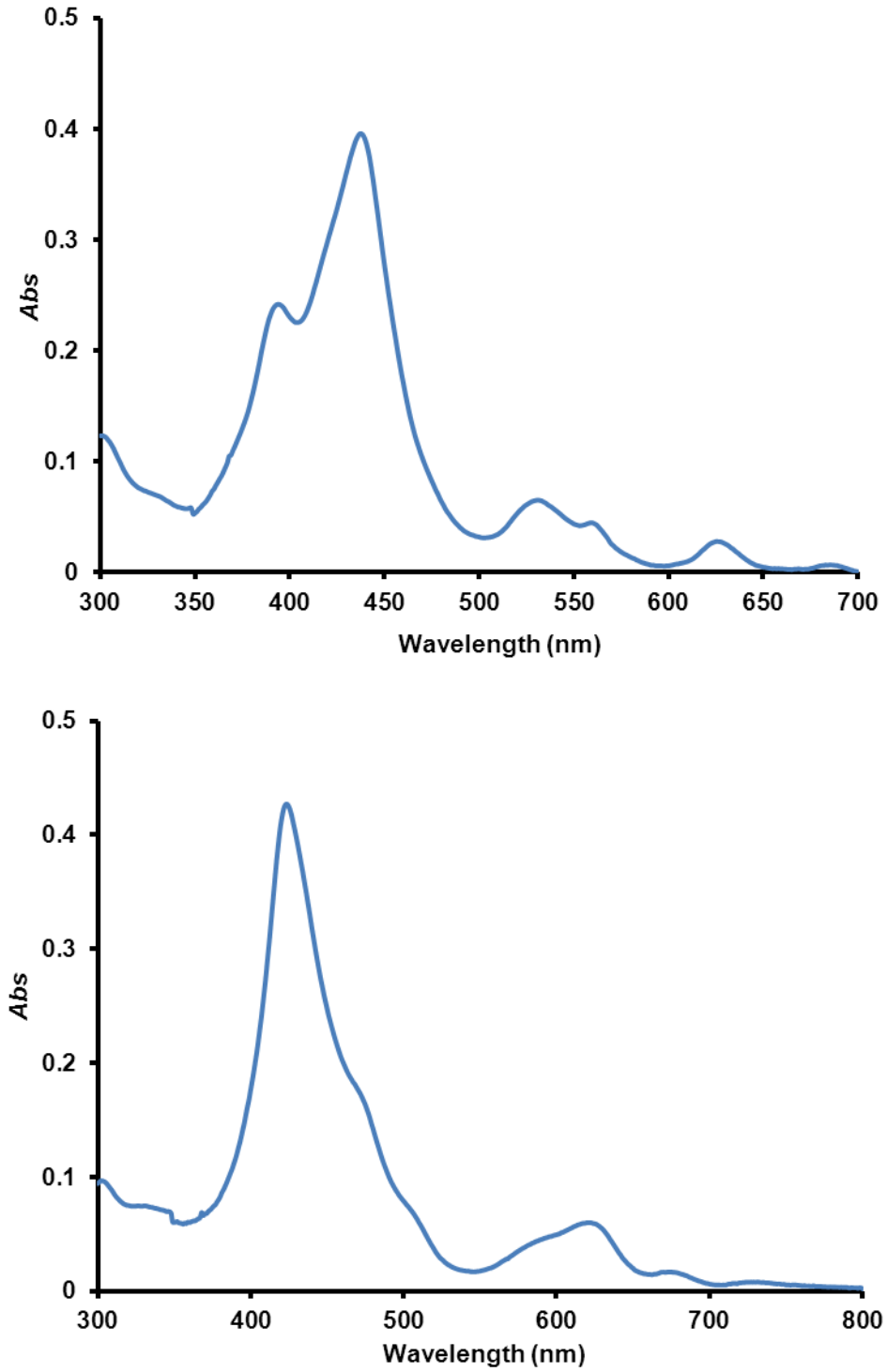

Figure S10. UV-vis spectra of thiacarbaporphyrin **15b**. Upper spectrum: **15b** in 1% Et_3N-chloroform. Lower spectrum: **15b**H^+ in 1% TFA-chloroform.

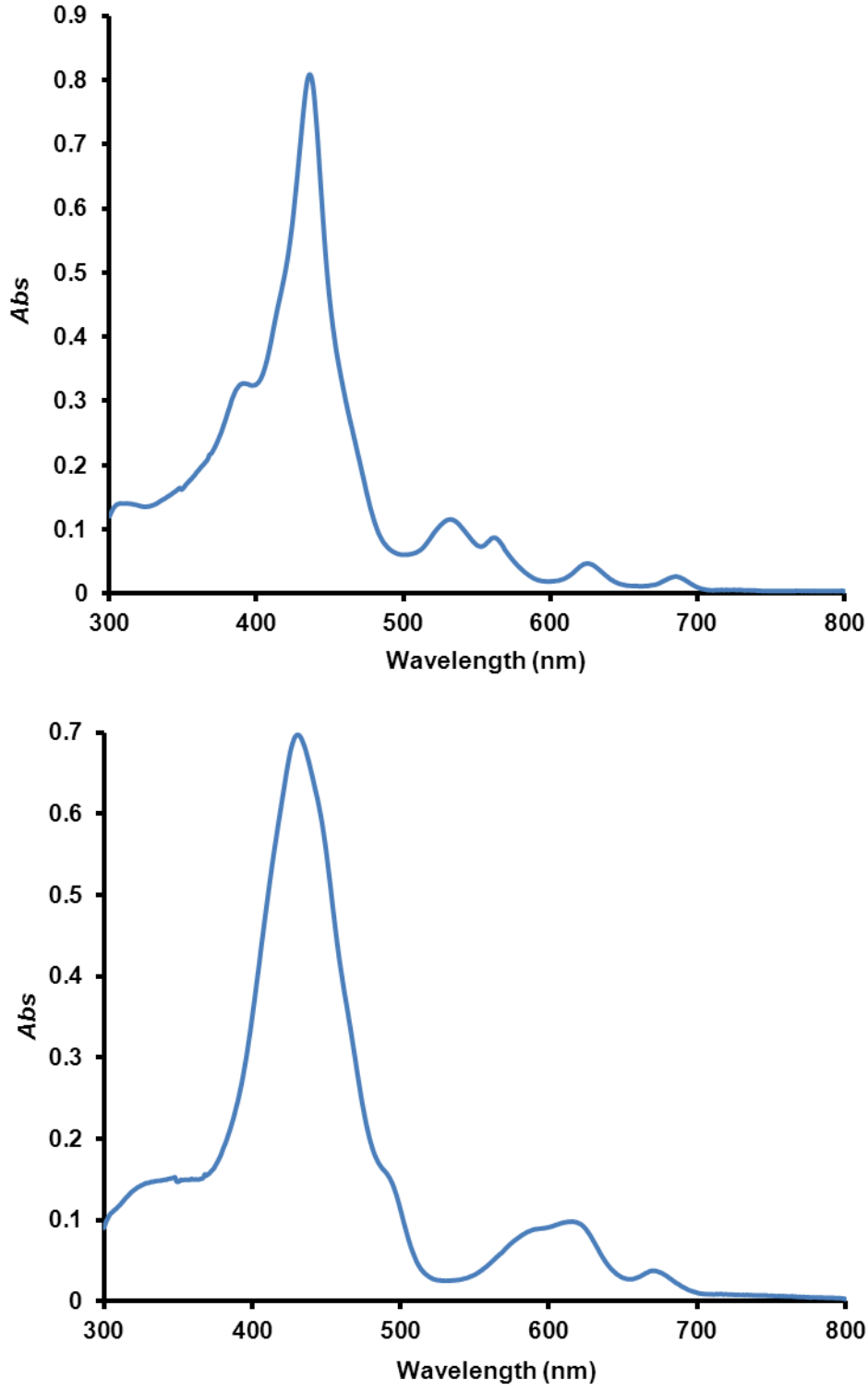

Figure S11. UV-vis spectra of thiacarbaporphyrin **16b**. Upper spectrum: **16b** in 1% Et_3N-chloroform. Lower spectrum: **16b**H^+ in 1% TFA-chloroform.

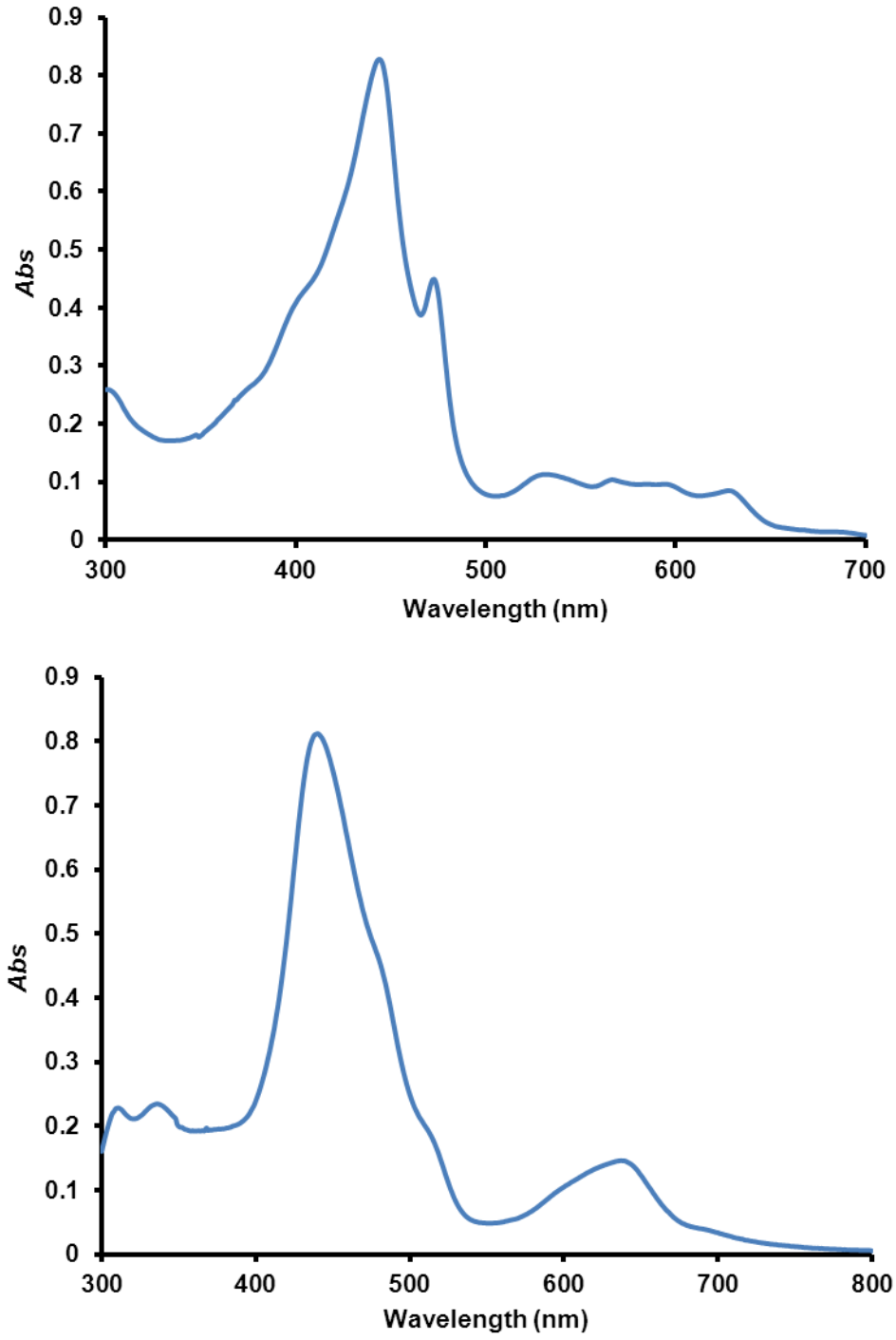

Figure S12. UV-vis spectra of selenacarbaporphyrin **15c**. Upper spectrum: **15c** in 1% Et_3N-chloroform. Lower spectrum: **15c**H^+ in 1% TFA-chloroform.

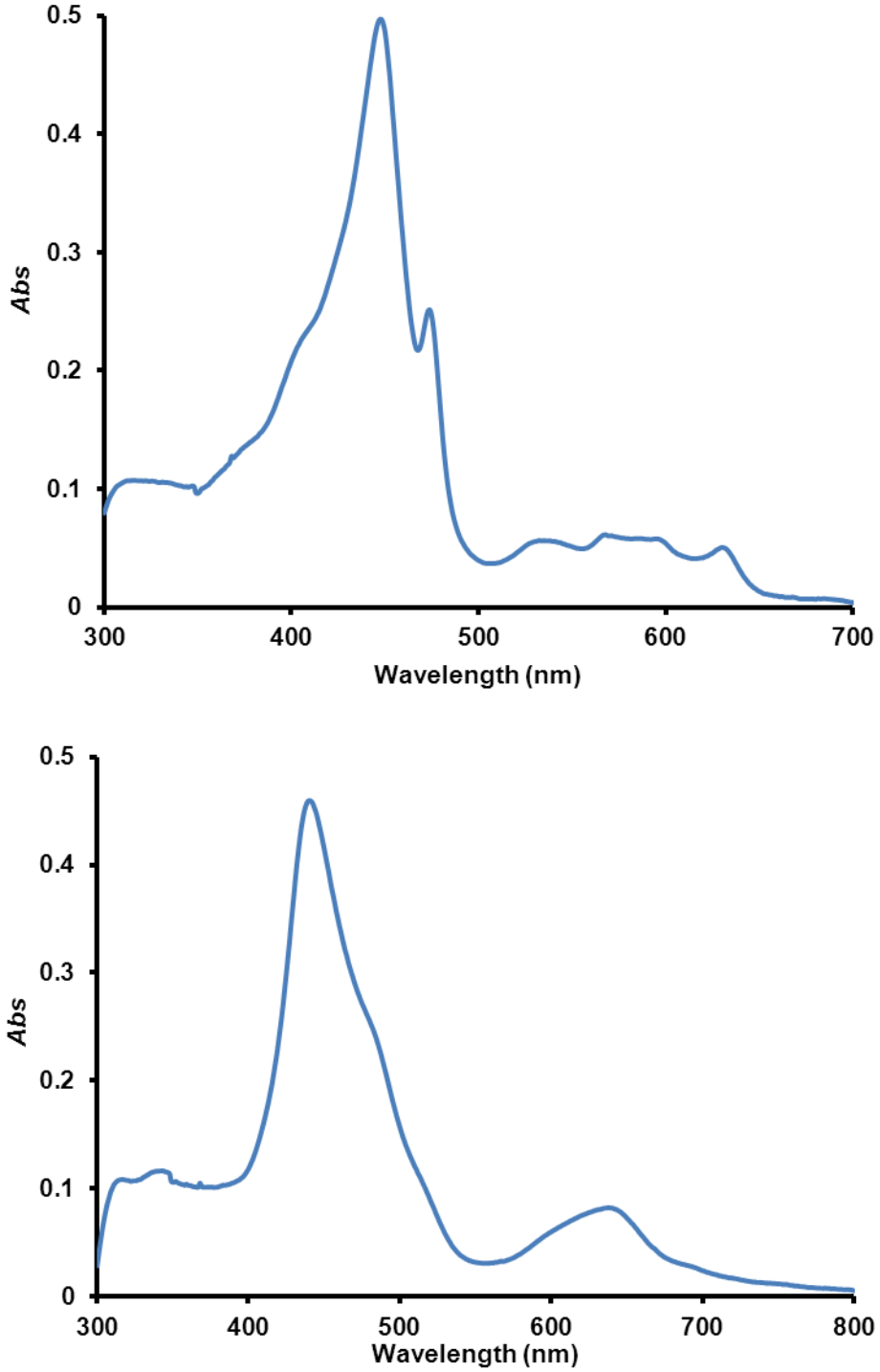

Figure S13. UV-vis spectra of selenacarbaporphyrin **15d**. Upper spectrum: **15d** in 1% Et_3N-chloroform. Lower spectrum: **15d**H^+ in 1% TFA-chloroform.

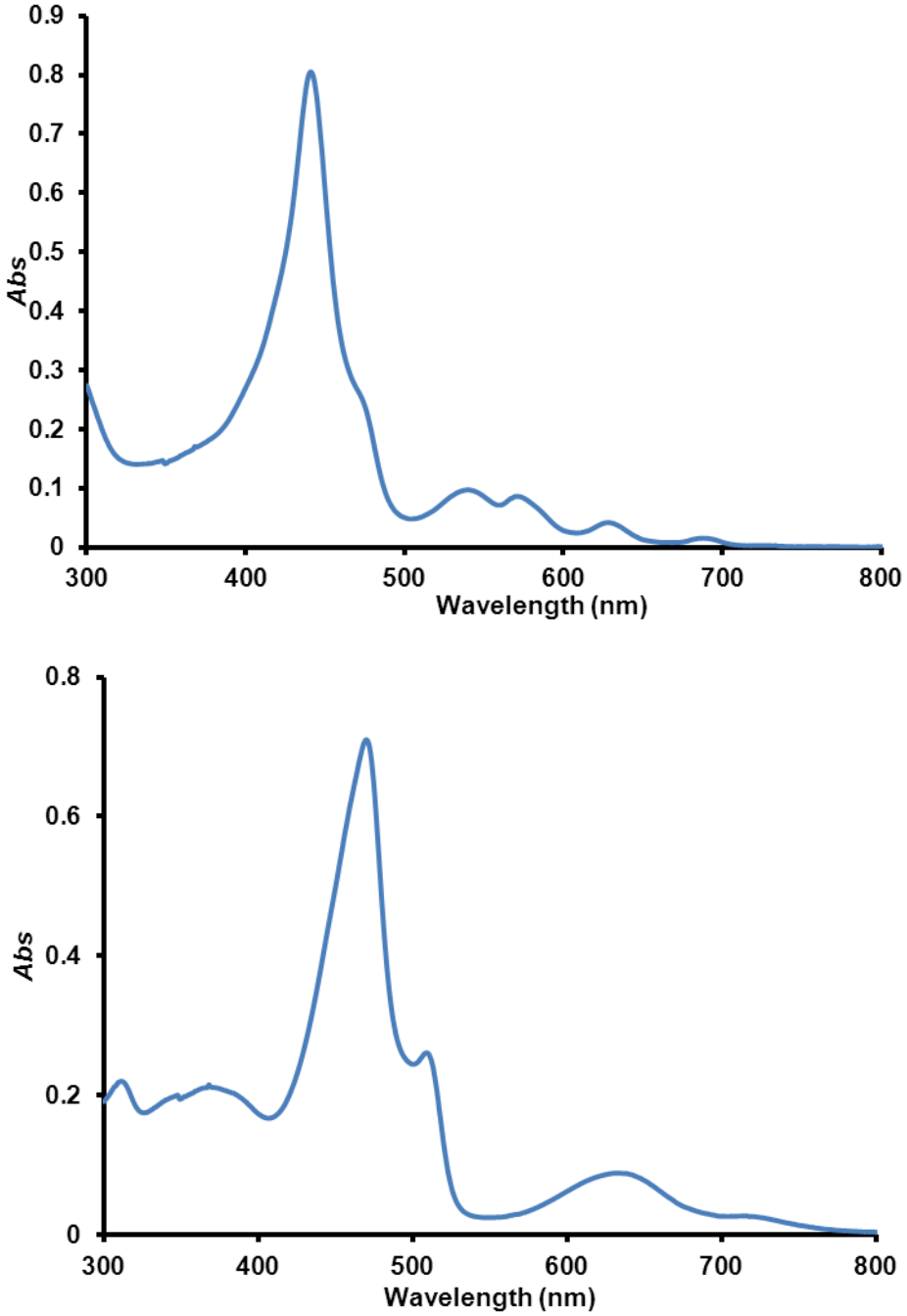

Figure S14. UV-vis spectra of selenacarbaporphyrin **16d**. Upper spectrum: **16d** in 1% Et_3N-chloroform. Lower spectrum: **16d**H^+ in 1% TFA-chloroform.

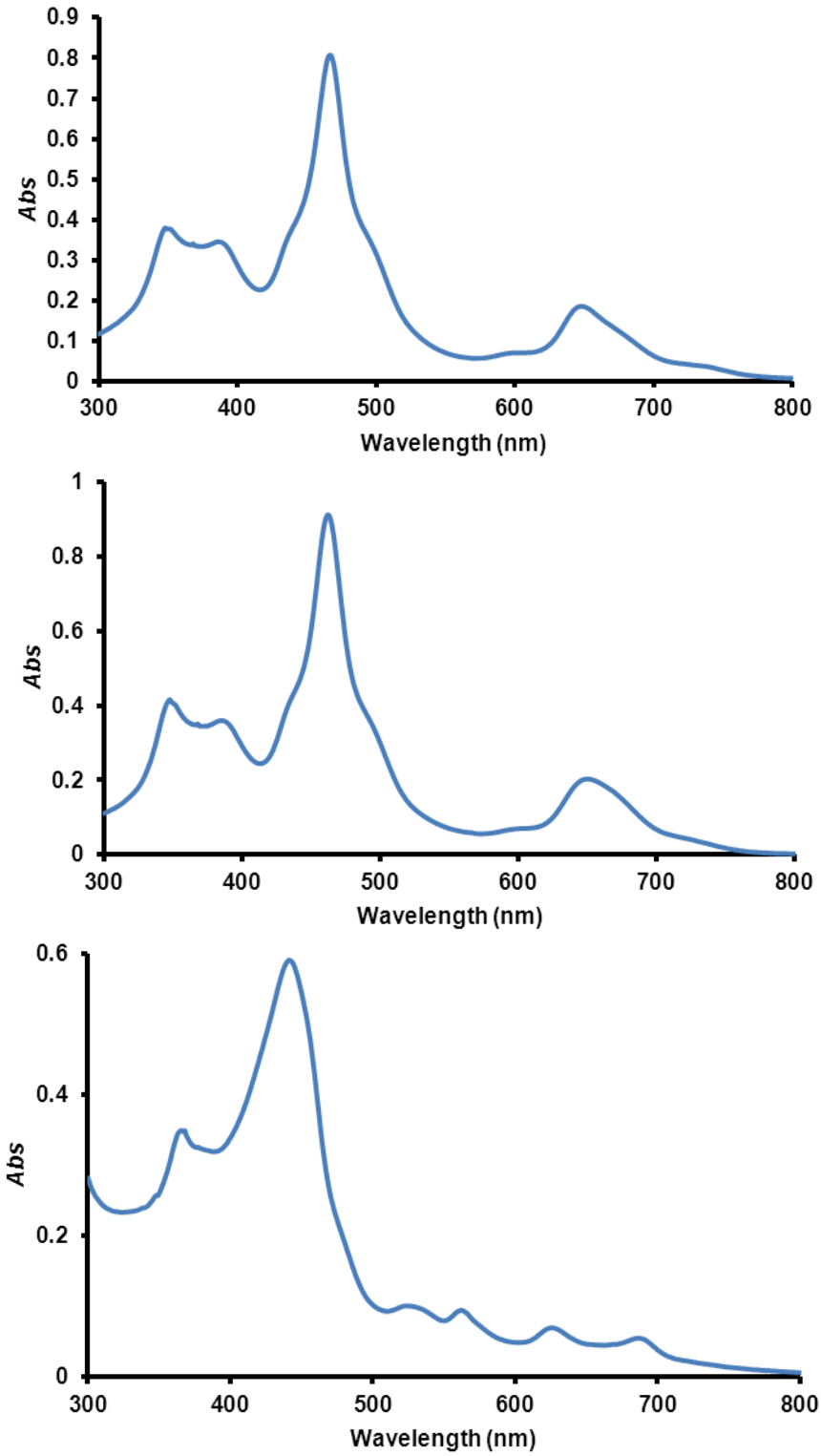

Figure S15. UV-vis spectra of oxa-azuliporphyrin **12a**.2HCl in chloroform (upper spectrum), 1% TFA-chloroform (middle spectrum) and 2% DBU-chloroform (free base **12a**, lower spectrum).

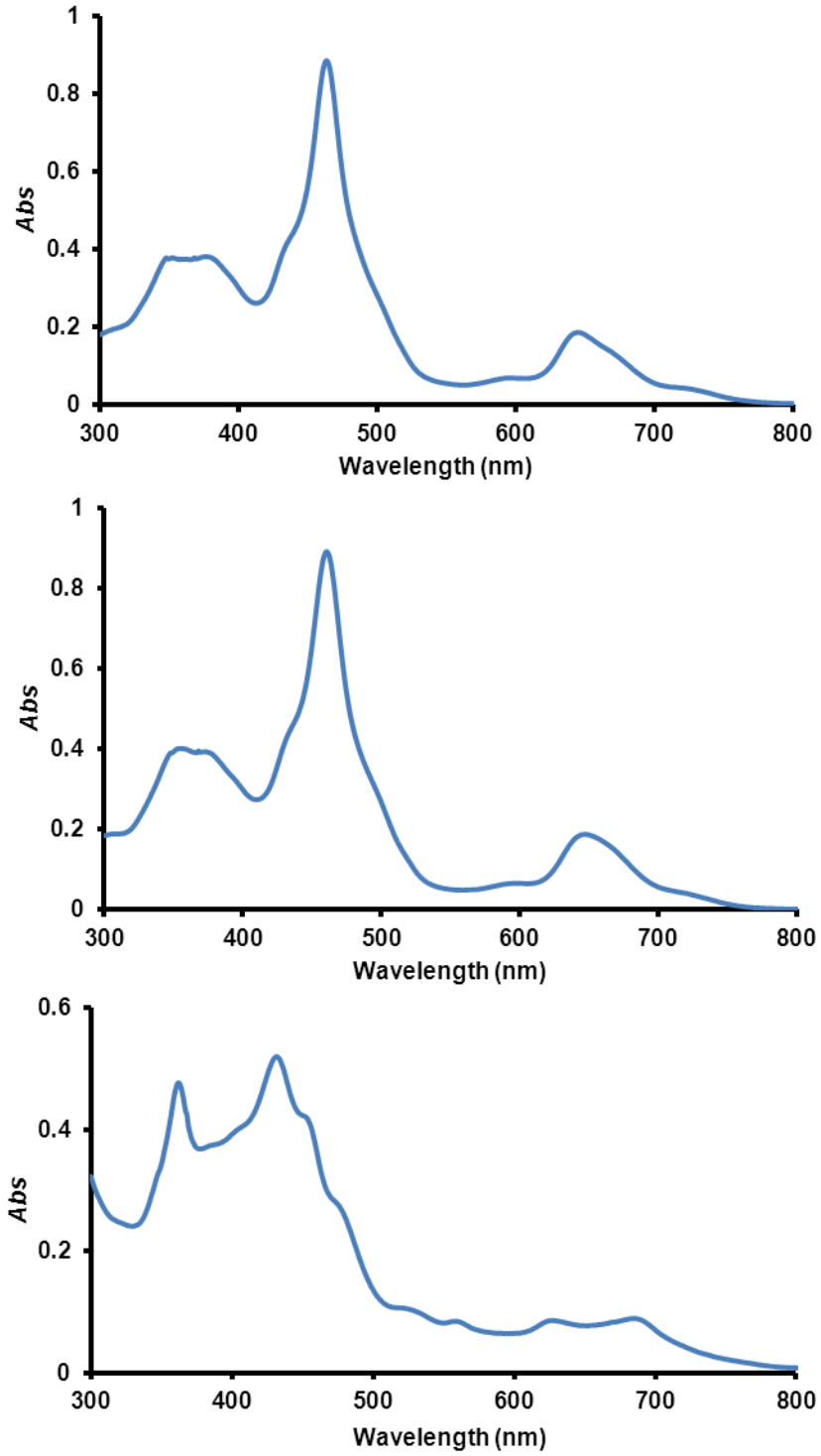

Figure S16. UV-vis spectra of oxa-azuliporphyrin **12b**.2HCl in chloroform (upper spectrum), 1% TFA-chloroform (middle spectrum) and 2% DBU-chloroform (free base **12b**, lower spectrum).

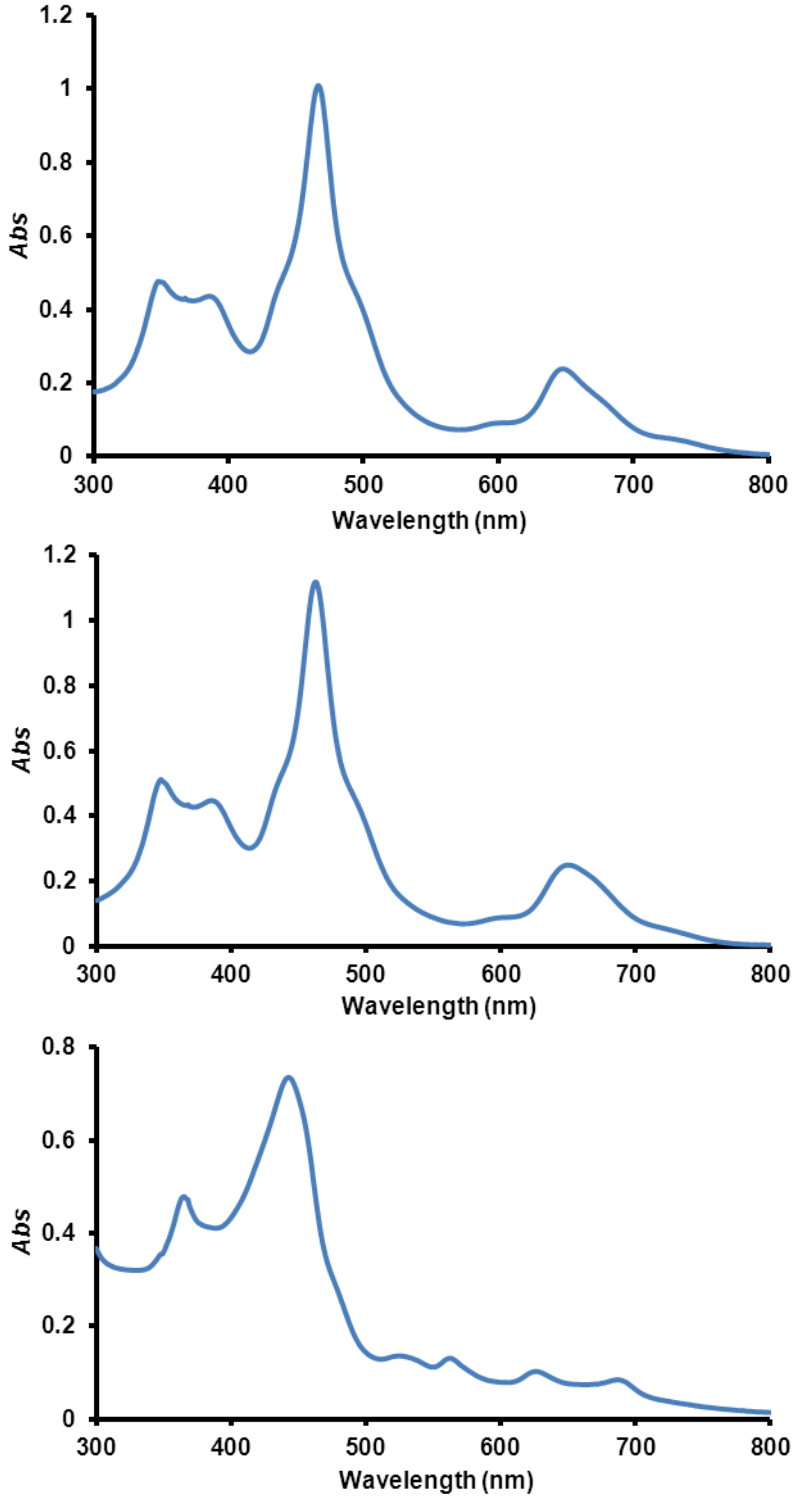

Figure S17. UV-vis spectra of oxa-azuliporphyrin **12c**.2HCl in chloroform (upper spectrum), 1% TFA-chloroform (middle spectrum) and 2% DBU-chloroform (free base **12c**, lower spectrum).

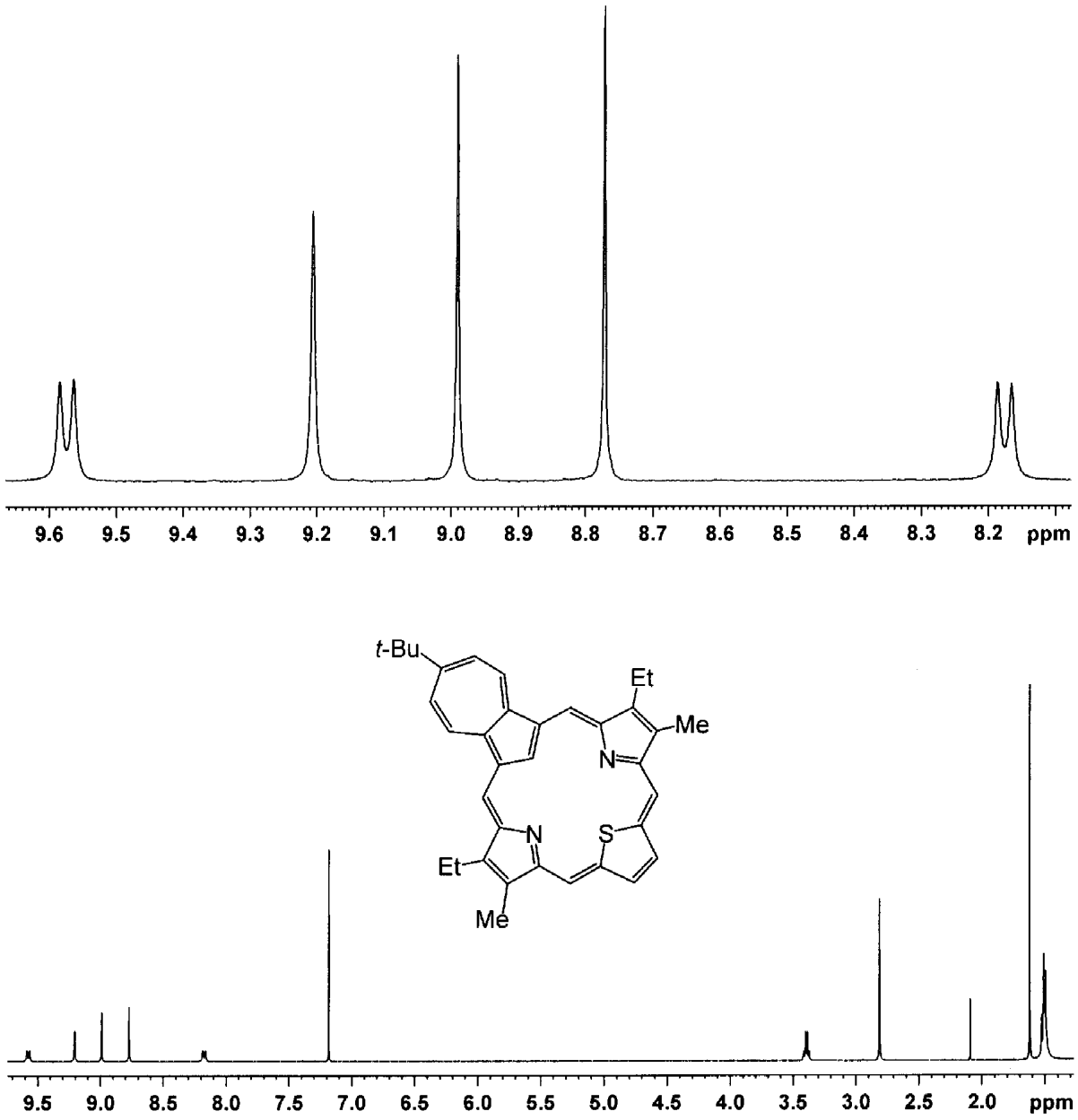

Figure S18. 500 MHz proton NMR spectrum of thia-azuliporphyrin **8b** in $CDCl_3$.

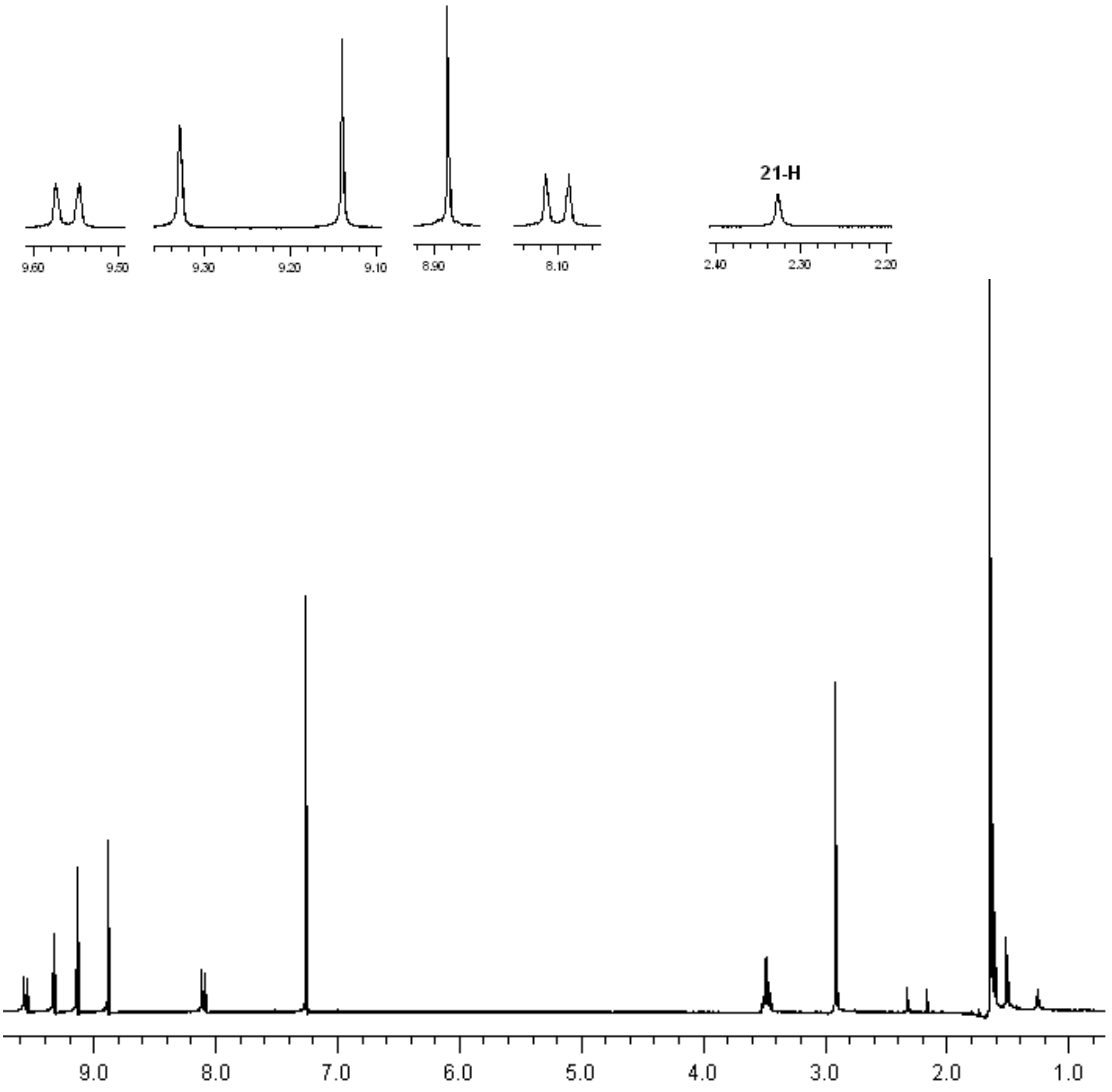

Figure S19. 400 MHz proton NMR spectrum of thia-azuliporphyrin **8b** in $CDCl_3$ showing the 21-H resonance near 2.3 ppm.

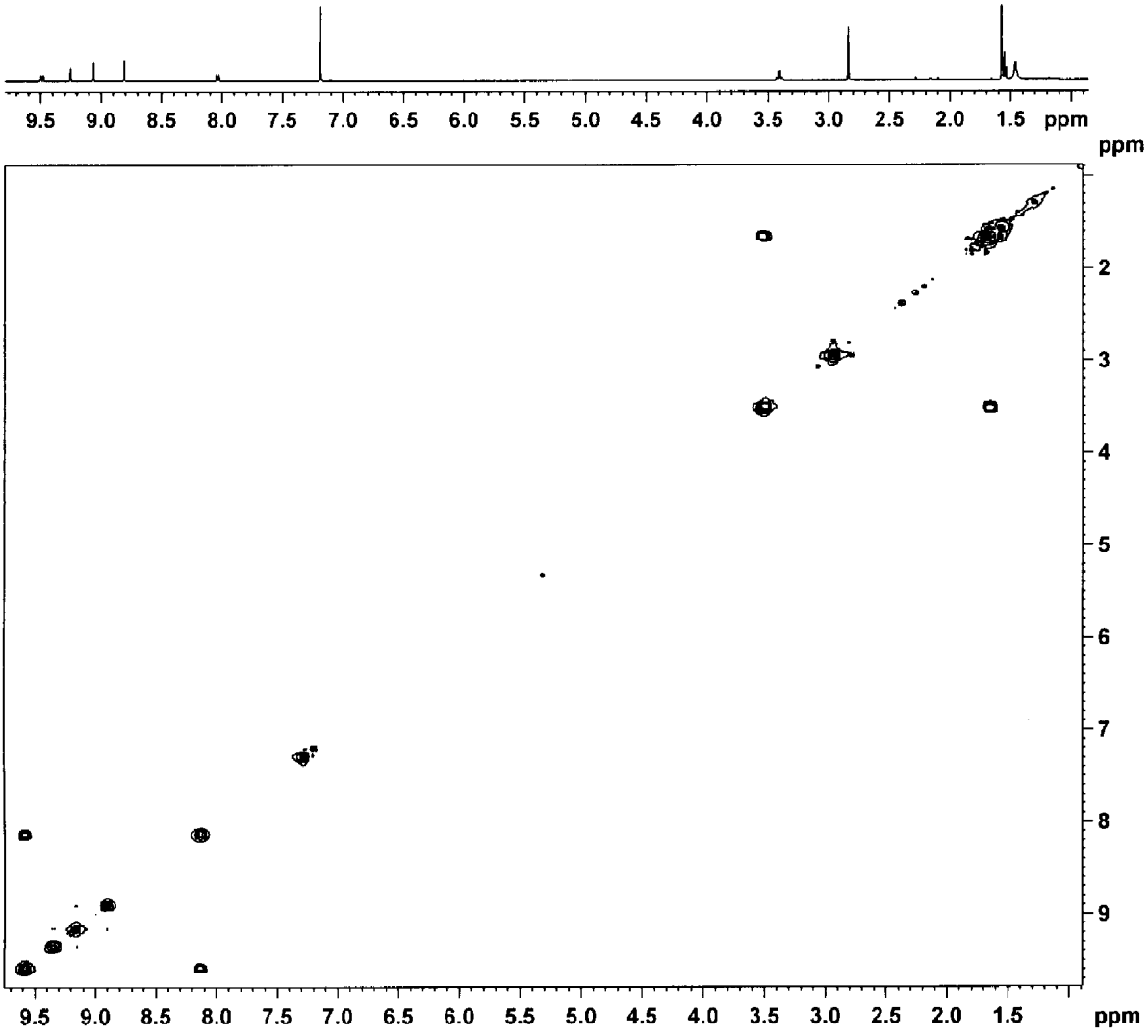

Figure S20. ^{1}H-^{1}H COSY NMR spectrum of thia-azuliporphyrin **8b** in $CDCl_3$.

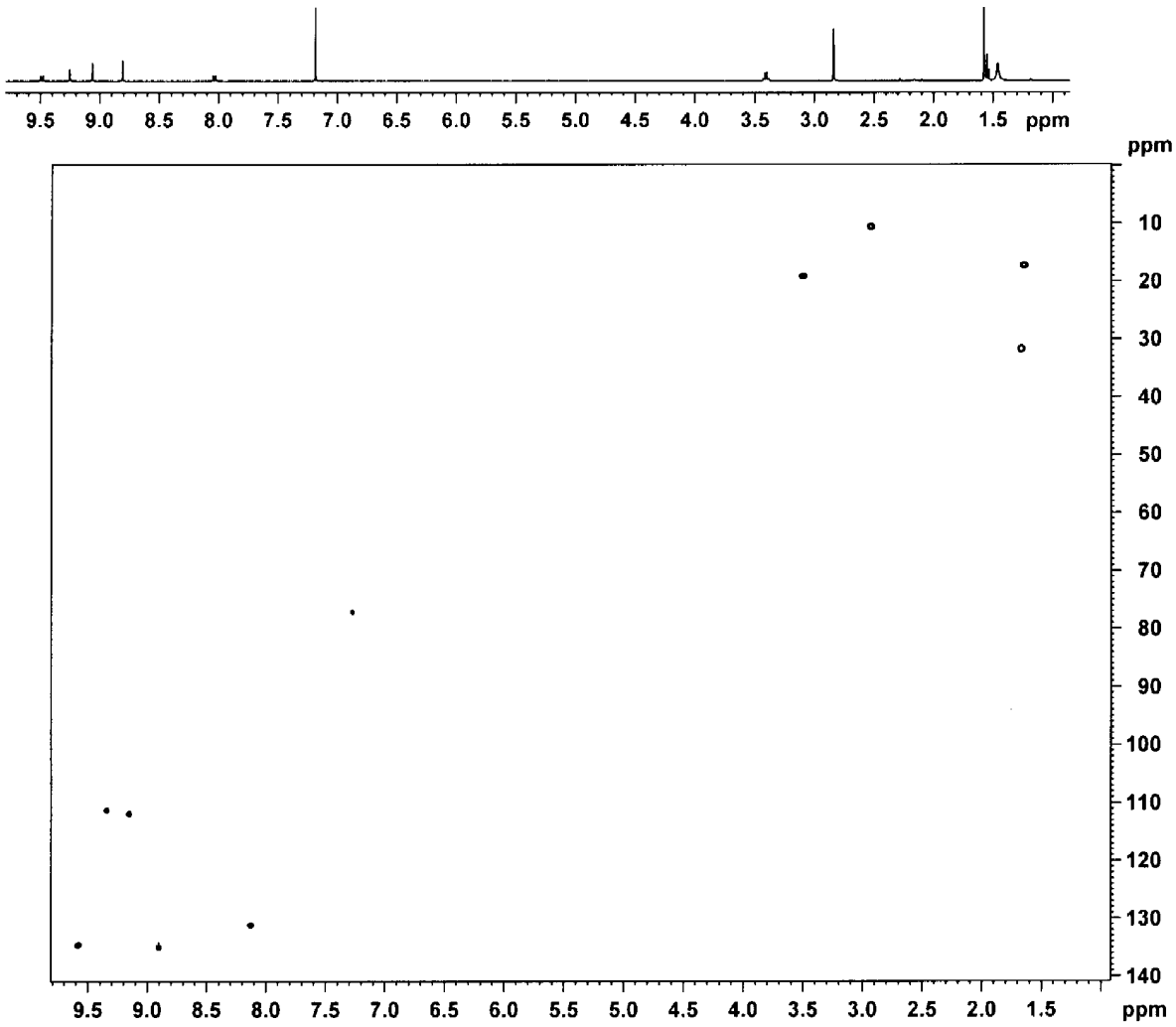

Figure S21. HSQC NMR spectrum of thia-azuliporphyrin **8b** in $CDCl_3$.

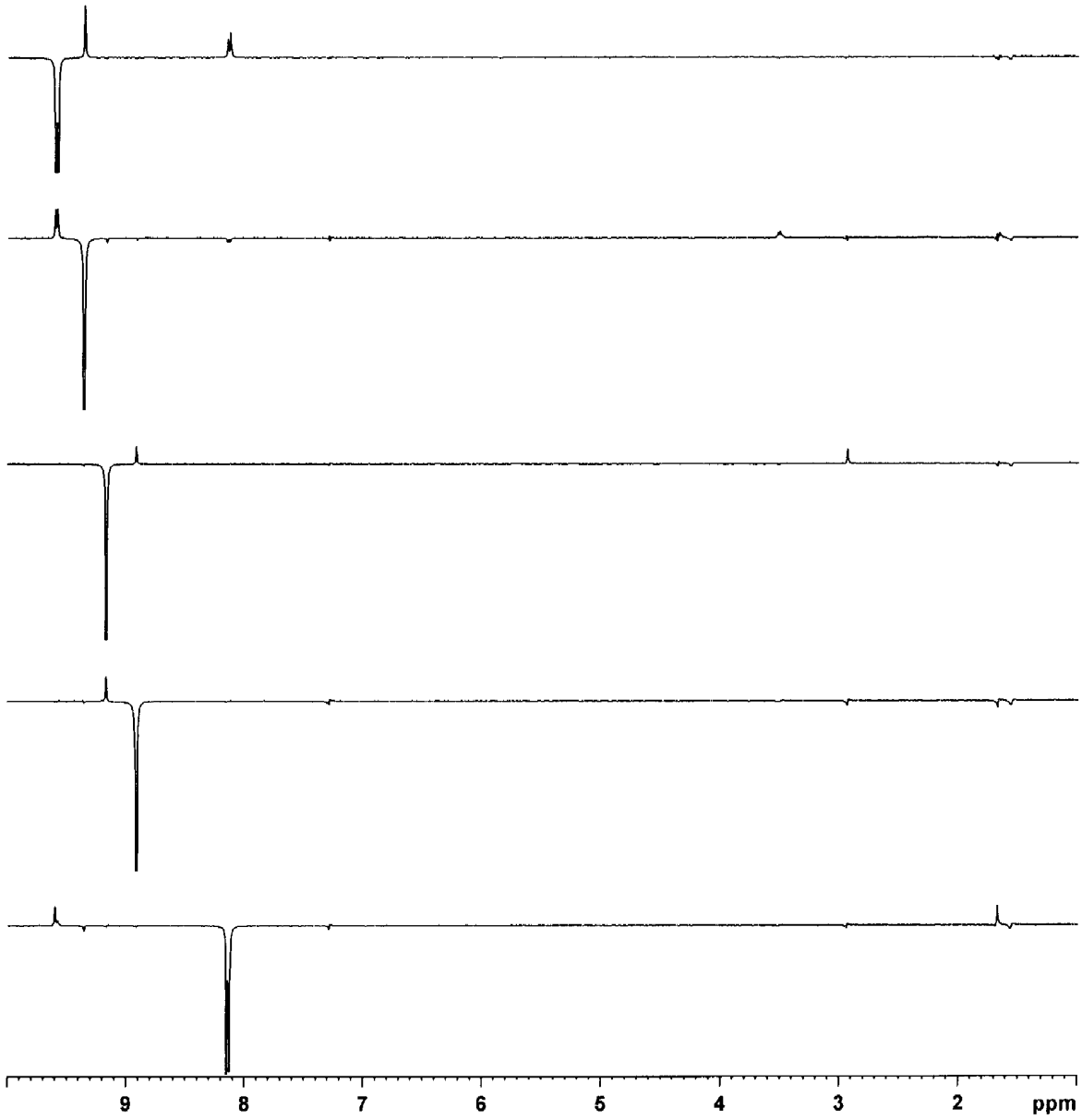

Figure S22. Selected nOe difference proton NMR spectra of thia-azuliporphyrin **8b** in $CDCl_3$.

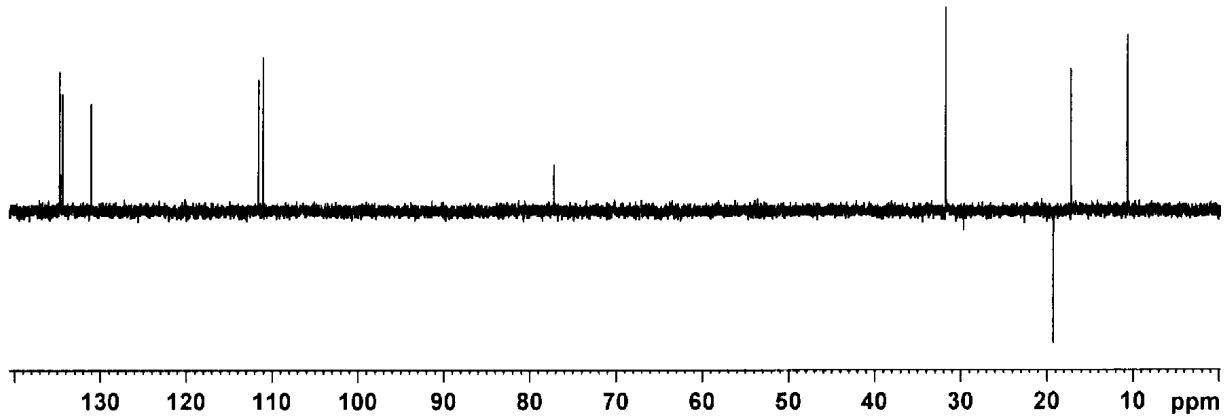

Figure S23. DEPT-135 NMR spectrum of thia-azuliporphyrin **8b** in $CDCl_3$.

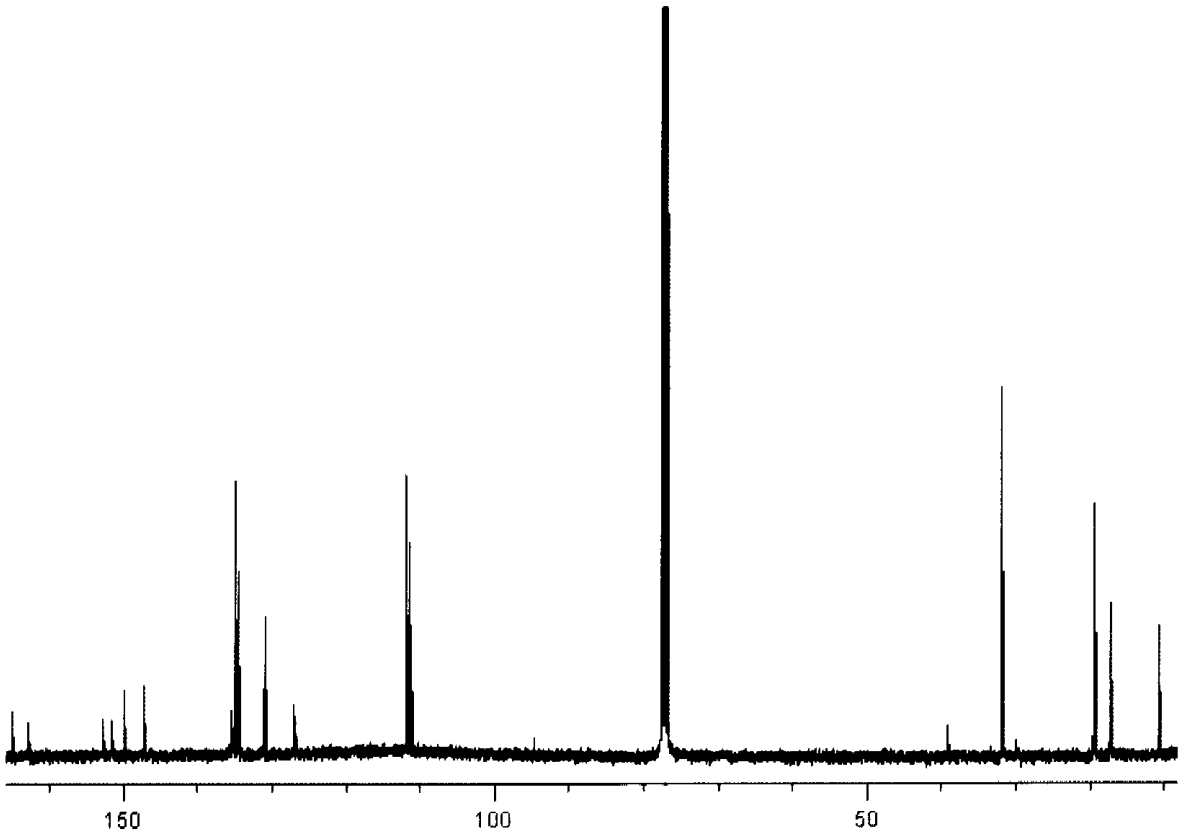

Figure S24. 100 MHz carbon-13 NMR spectrum of thia-azuliporphyrin **8b** in $CDCl_3$.

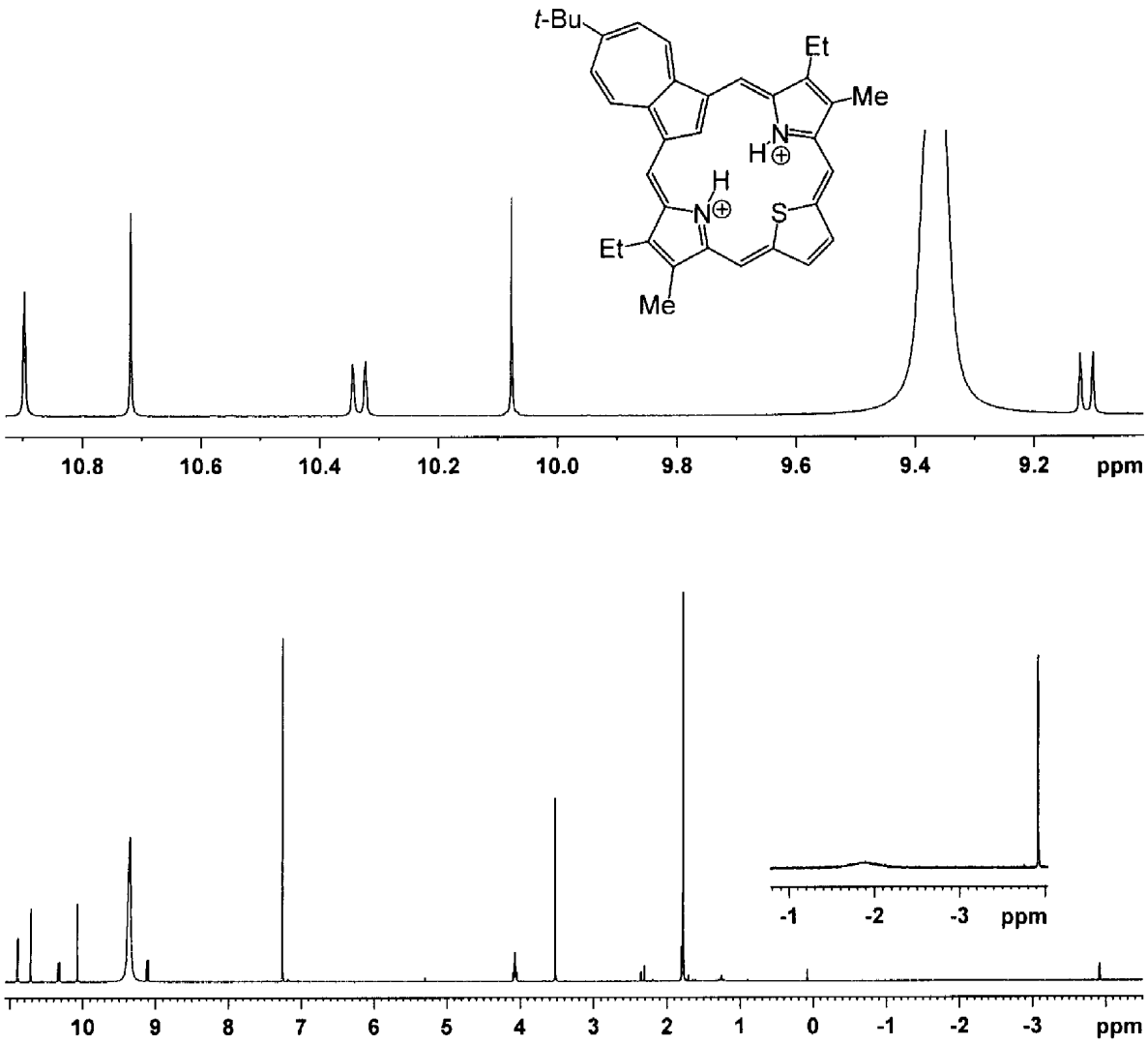

Figure S25. 500 MHz proton NMR spectrum of thia-azuliporphyrin **8b**H_2^{2+} in TFA-$CDCl_3$.

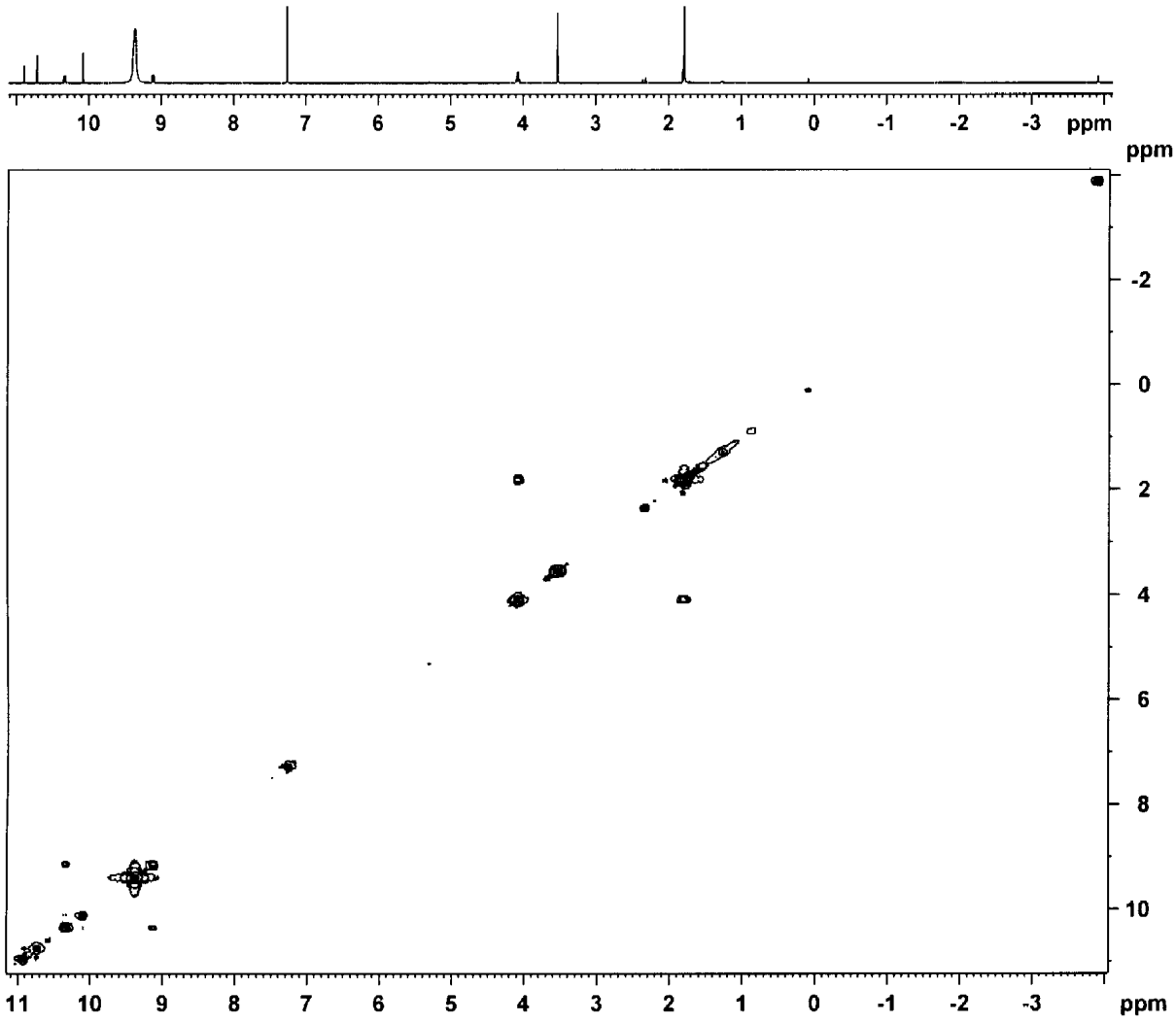

Figure S26. ^{1}H-^{1}H COSY NMR spectrum of thia-azuliporphyrin **8b**H_2^{2+} in TFA-$CDCl_3$.

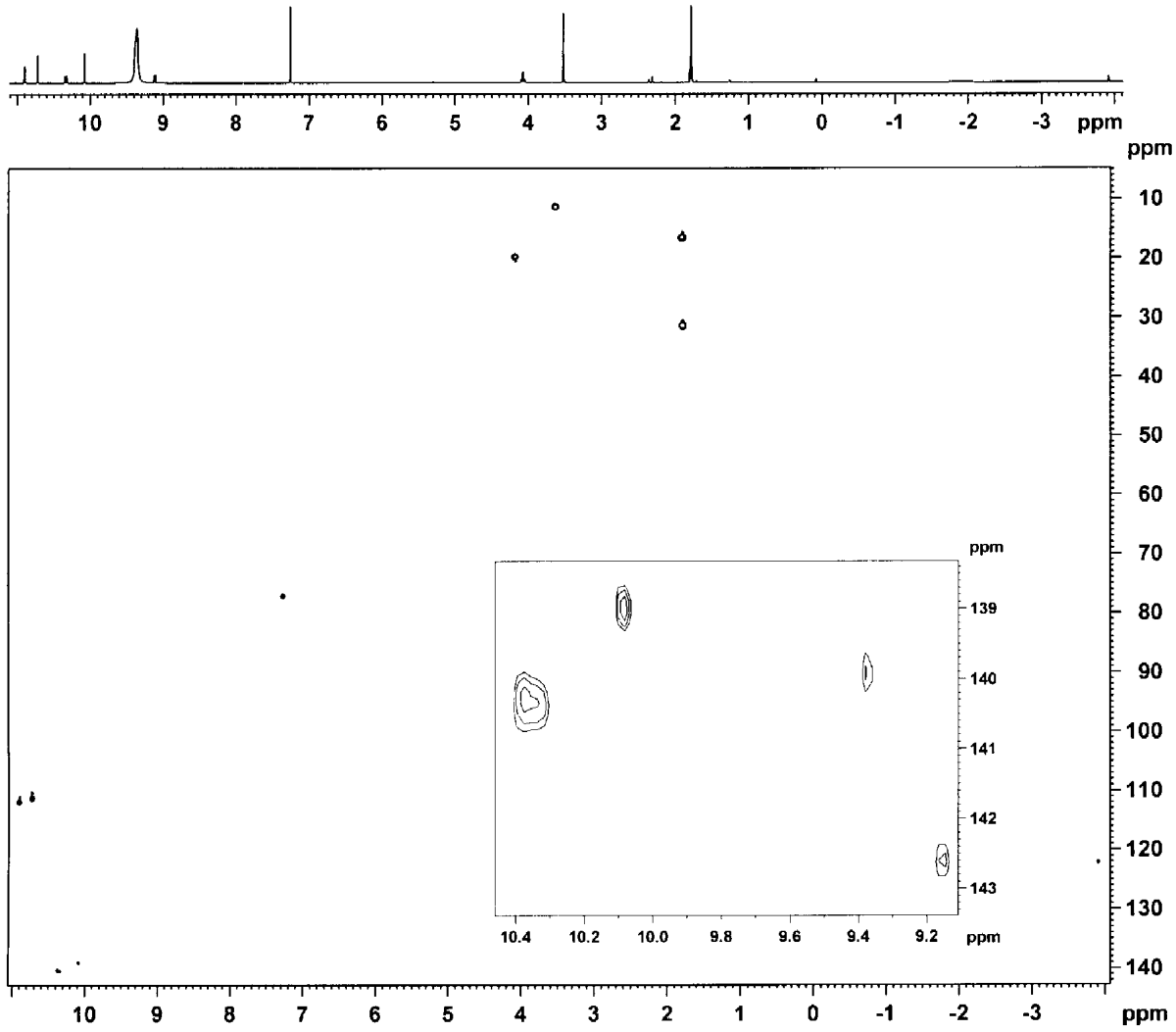

Figure S27. HSQC NMR spectrum of thia-azuliporphyrin **8b**H_2^{2+} in TFA-$CDCl_3$.

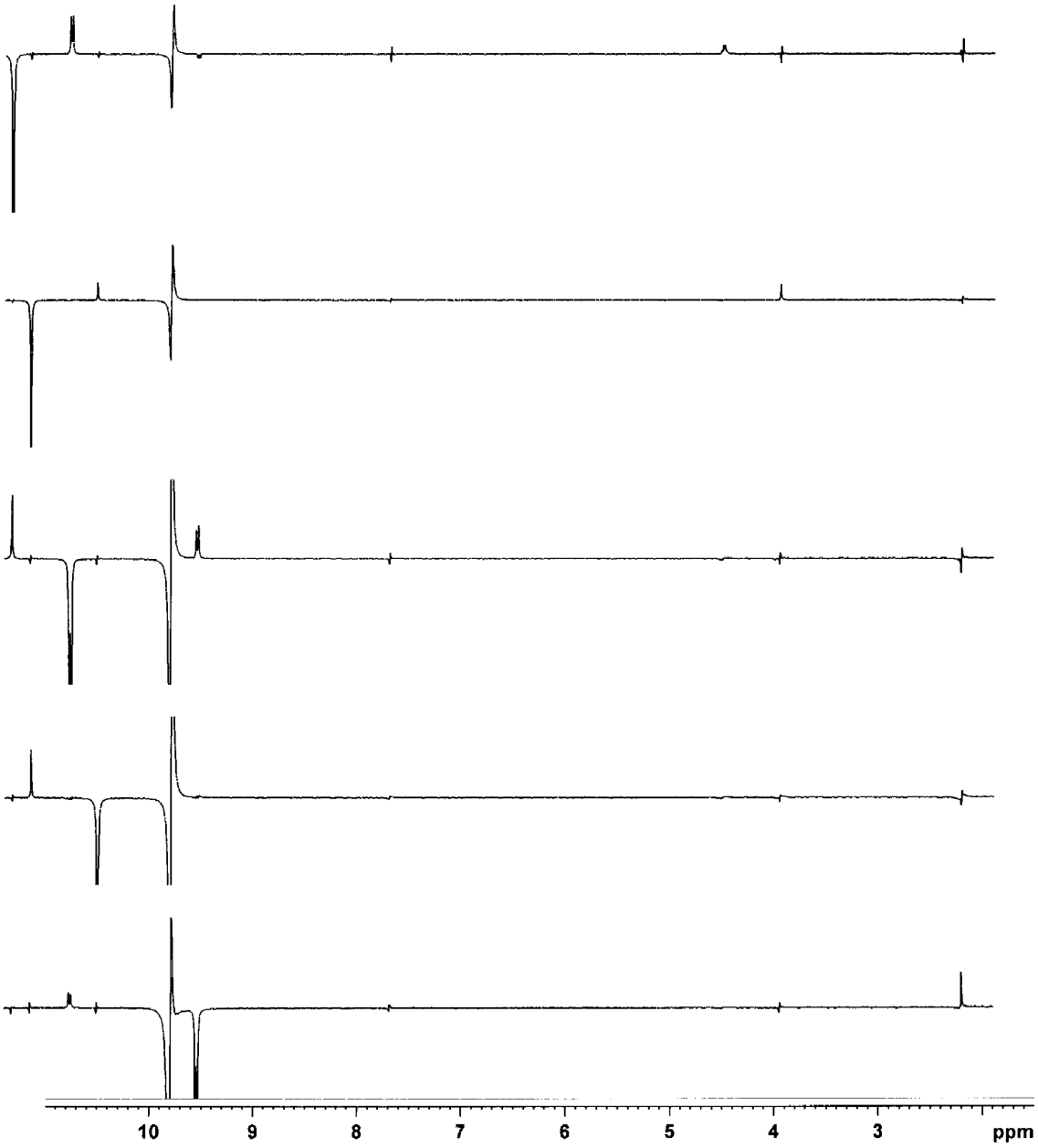

Figure S28. Selected nOe difference proton NMR spectra of thia-azuliporphyrin **8b**H_2^{2+} in $CDCl_3$.

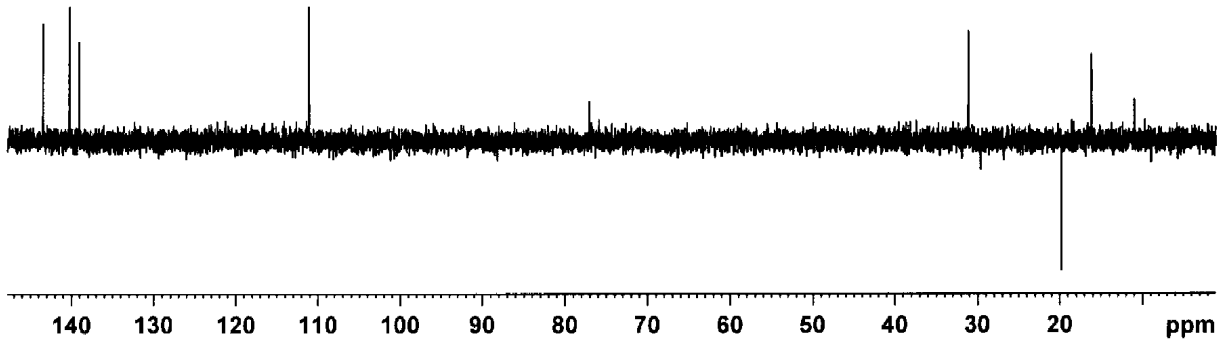

Figure S29. DEPT-135 NMR spectrum of thia-azuliporphyrin **8b**H_2^{2+} in TFA-$CDCl_3$.

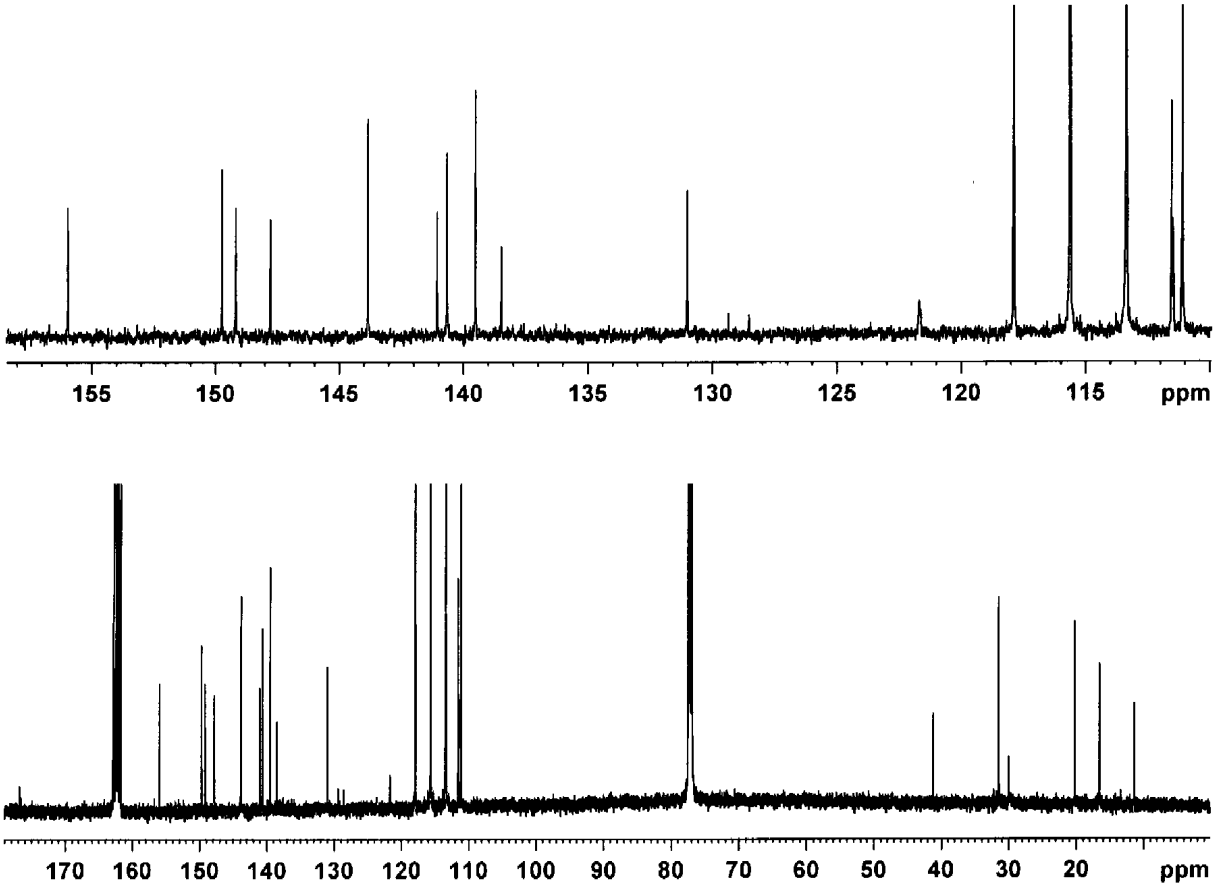

Figure S30. 125 MHz carbon-13 NMR spectrum of thia-azuliporphyrin **8b**H_2^{2+} in $CDCl_3$.

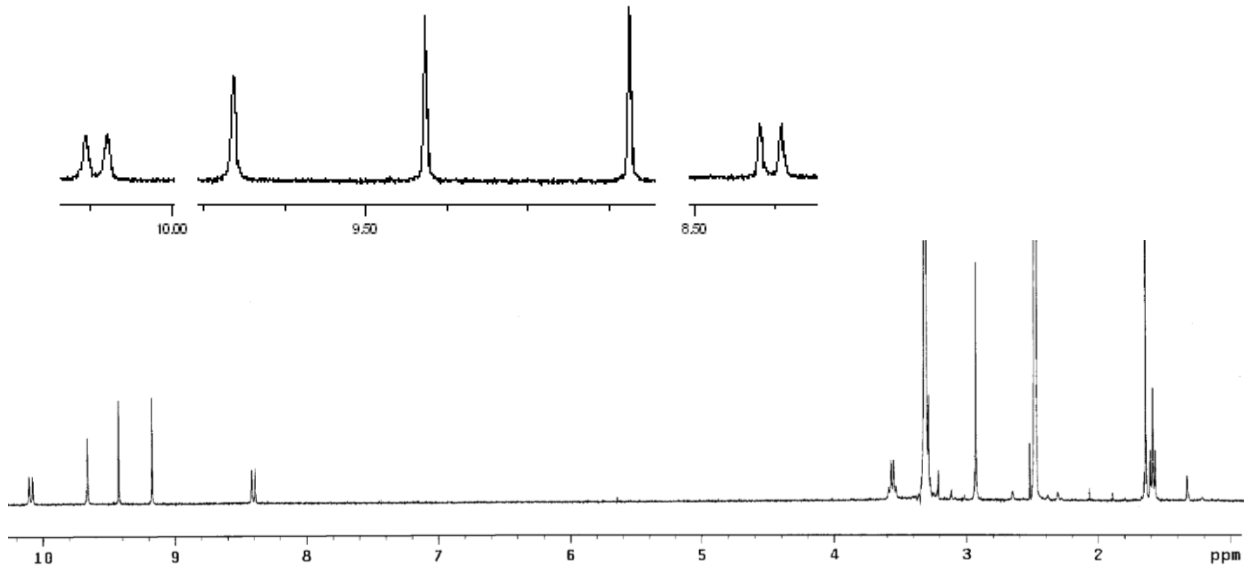

Figure S31. 400 MHz proton NMR spectrum of thia-azuliporphyrin **8b** in DMSO-d_6.

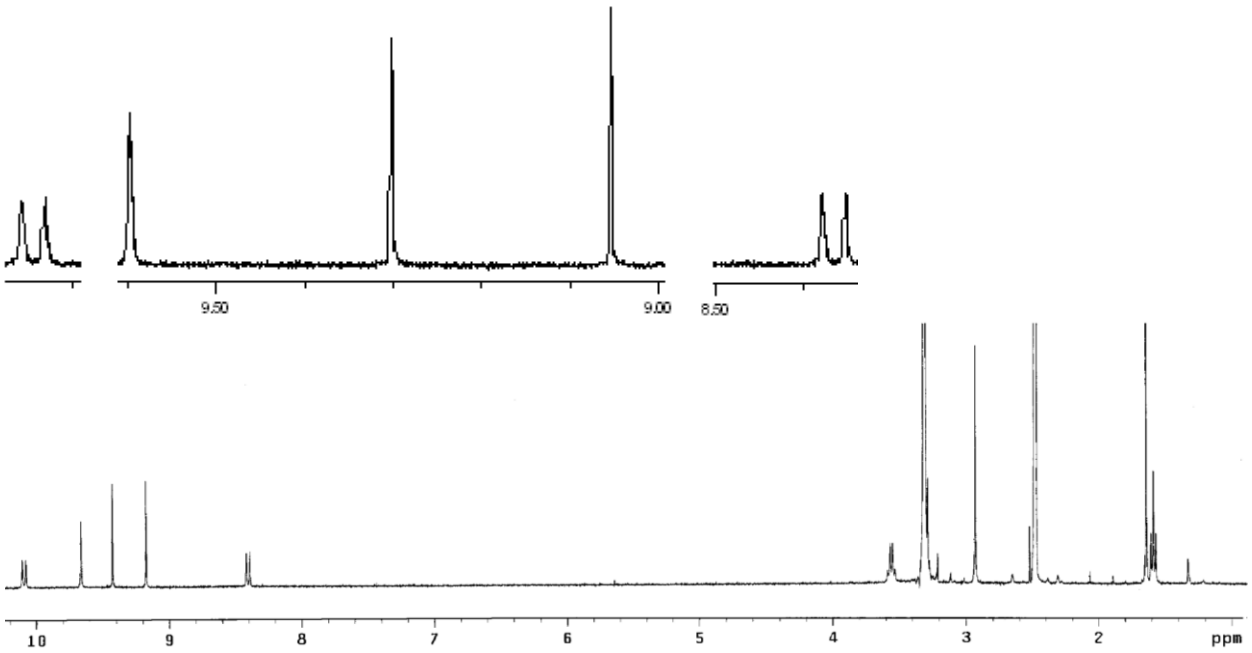

Figure S32. 400 MHz proton NMR spectrum of thia-azuliporphyrin **8b** in acetone-d_6.

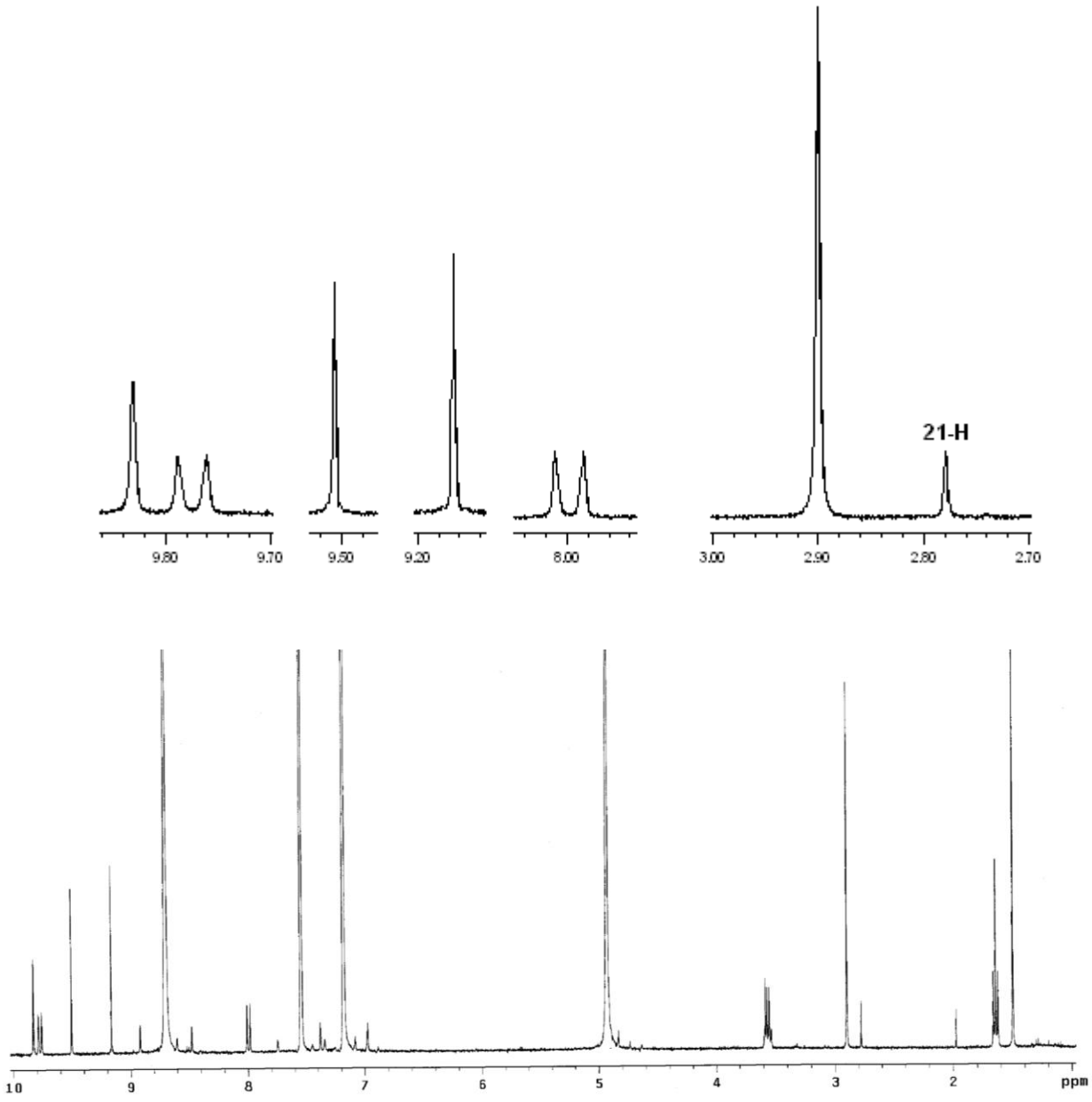

Figure S33. 400 MHz proton NMR spectrum of thia-azuliporphyrin **8b** in pyridine-d_5.

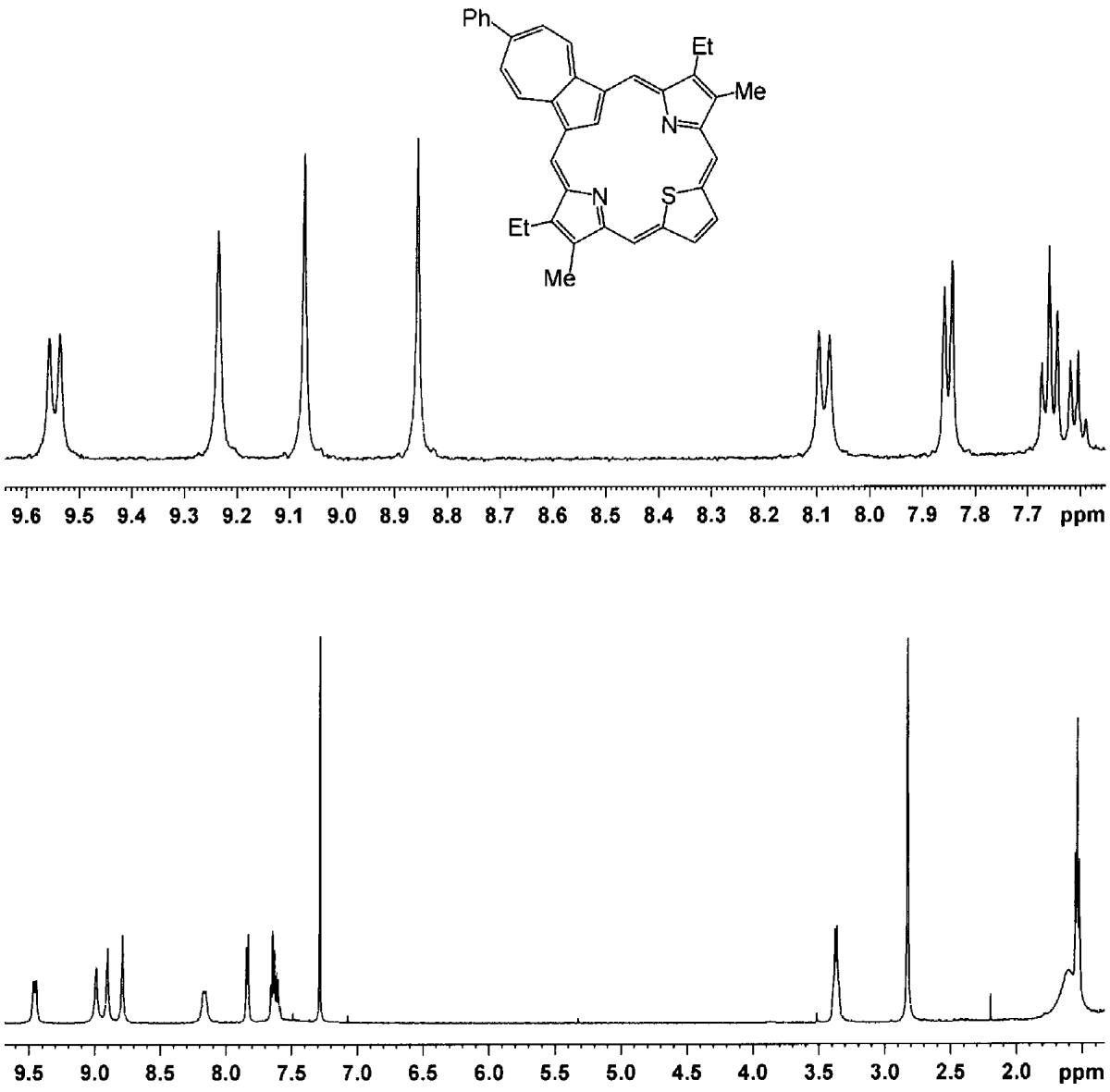

Figure S34. 500 MHz proton NMR spectrum of thia-azuliporphyrin **8c** in $CDCl_3$.

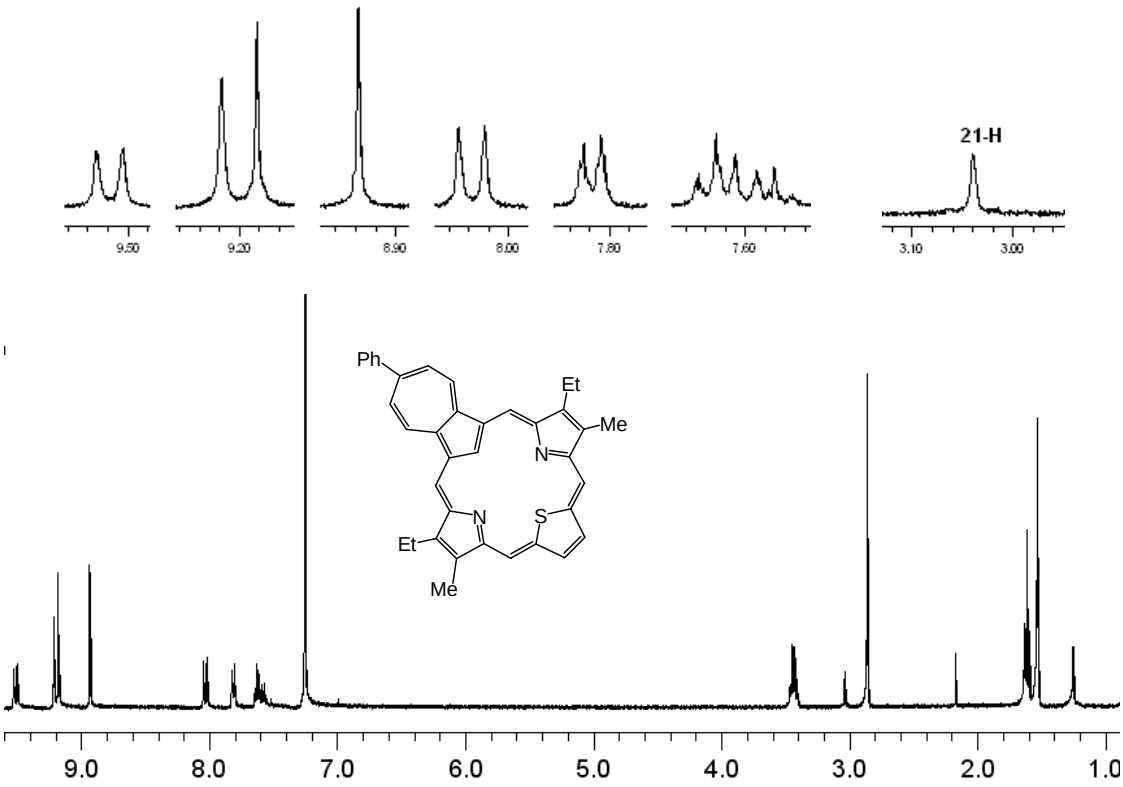

Figure S35. 400 MHz proton NMR spectrum of thia-azuliporphyrin **8c** in $CDCl_3$ showing the 21-H resonance near 3.0 ppm.

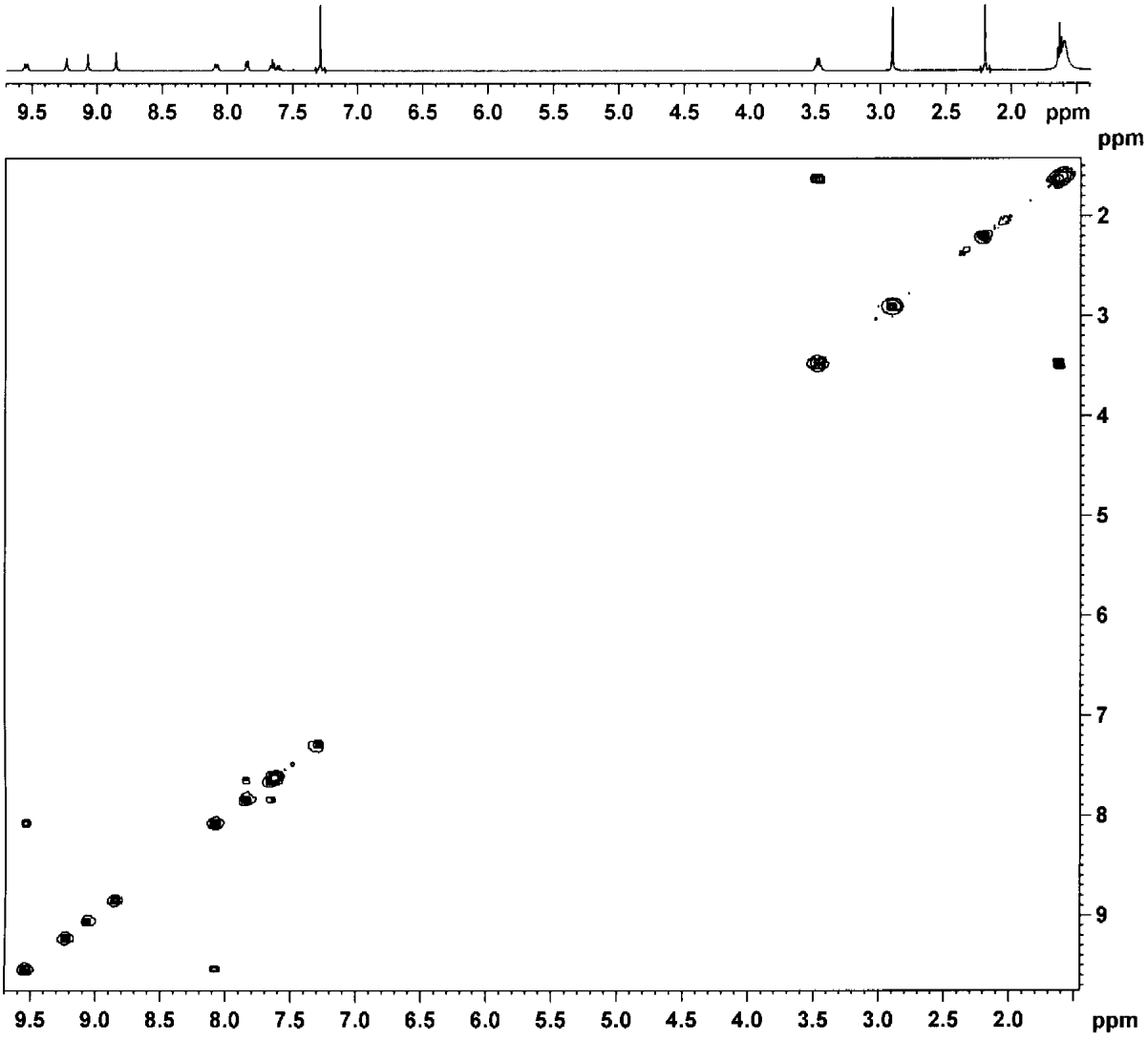

Figure S36. ^{1}H-^{1}H COSY NMR spectrum of thia-azuliporphyrin **8c** in $CDCl_3$.

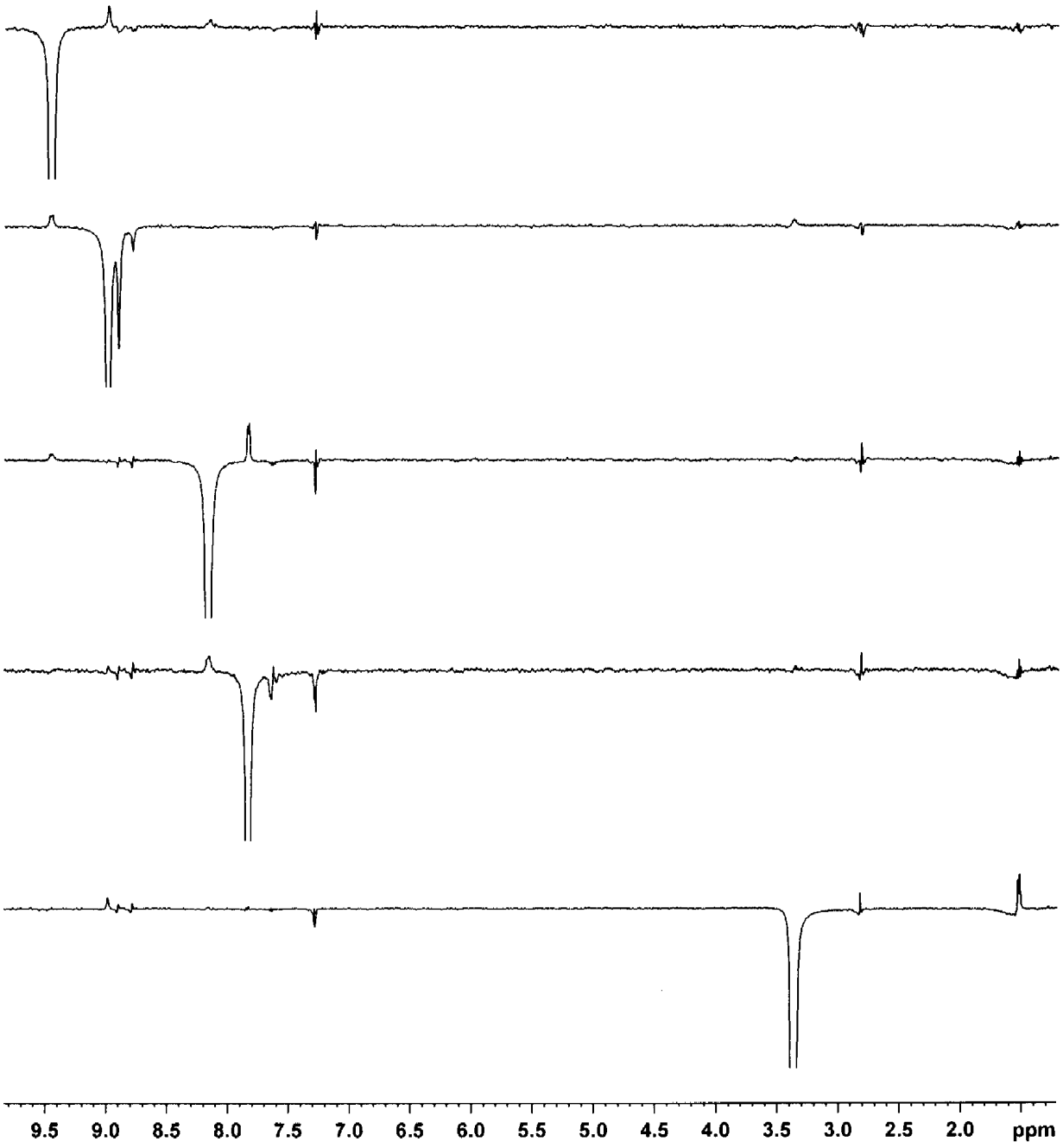

Figure S37. Selected nOe difference proton NMR spectra of thia-azuliporphyrin **8c** in $CDCl_3$.

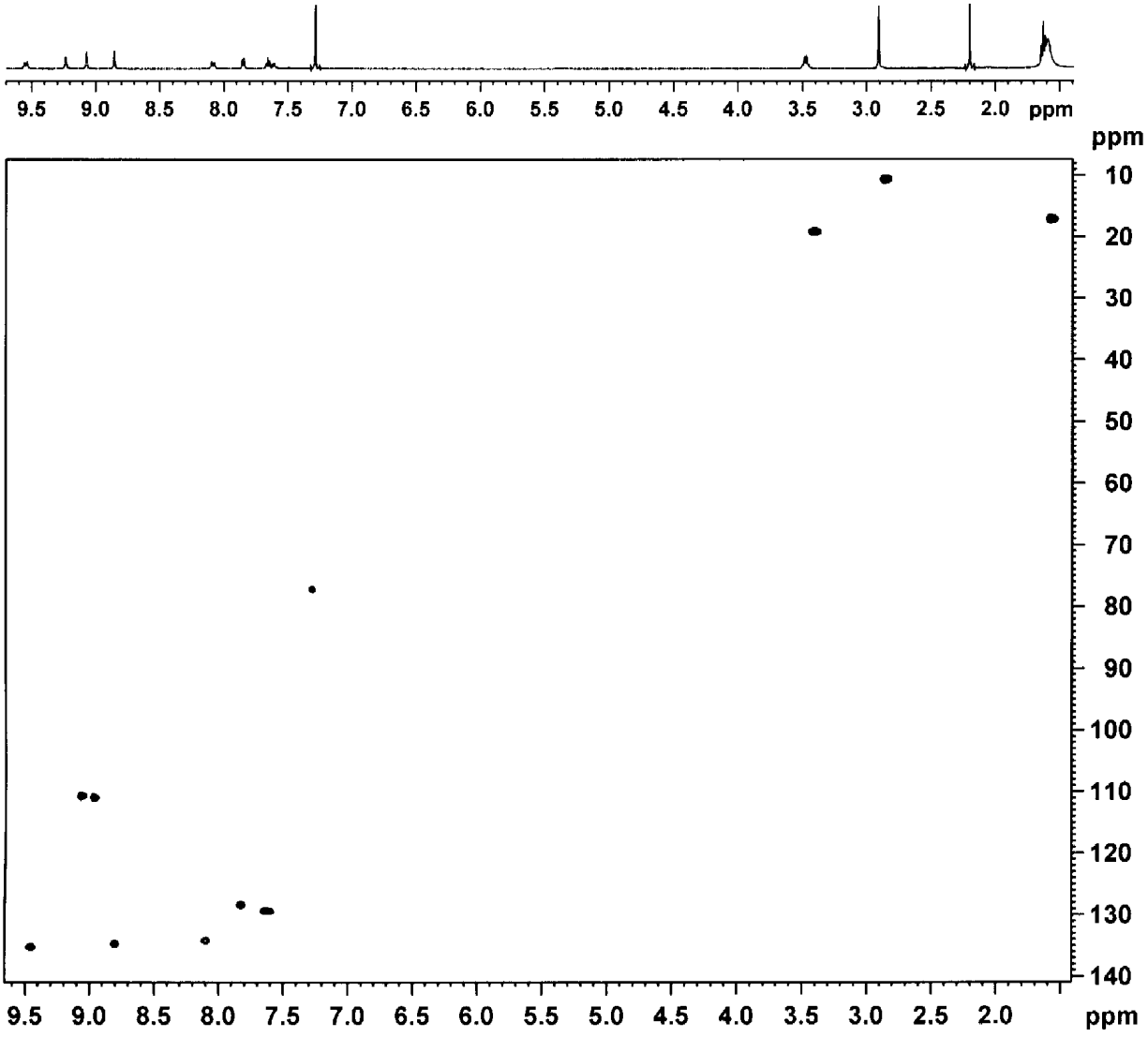

Figure S38. HSQC NMR spectrum of thia-azuliporphyrin **8c** in $CDCl_3$.

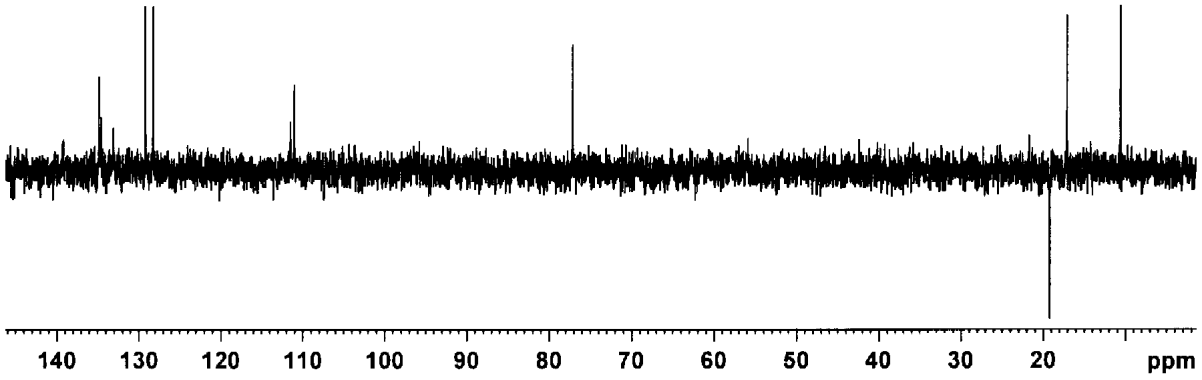

Figure S39. DEPT-135 NMR spectrum of thia-azuliporphyrin **8c** in $CDCl_3$.

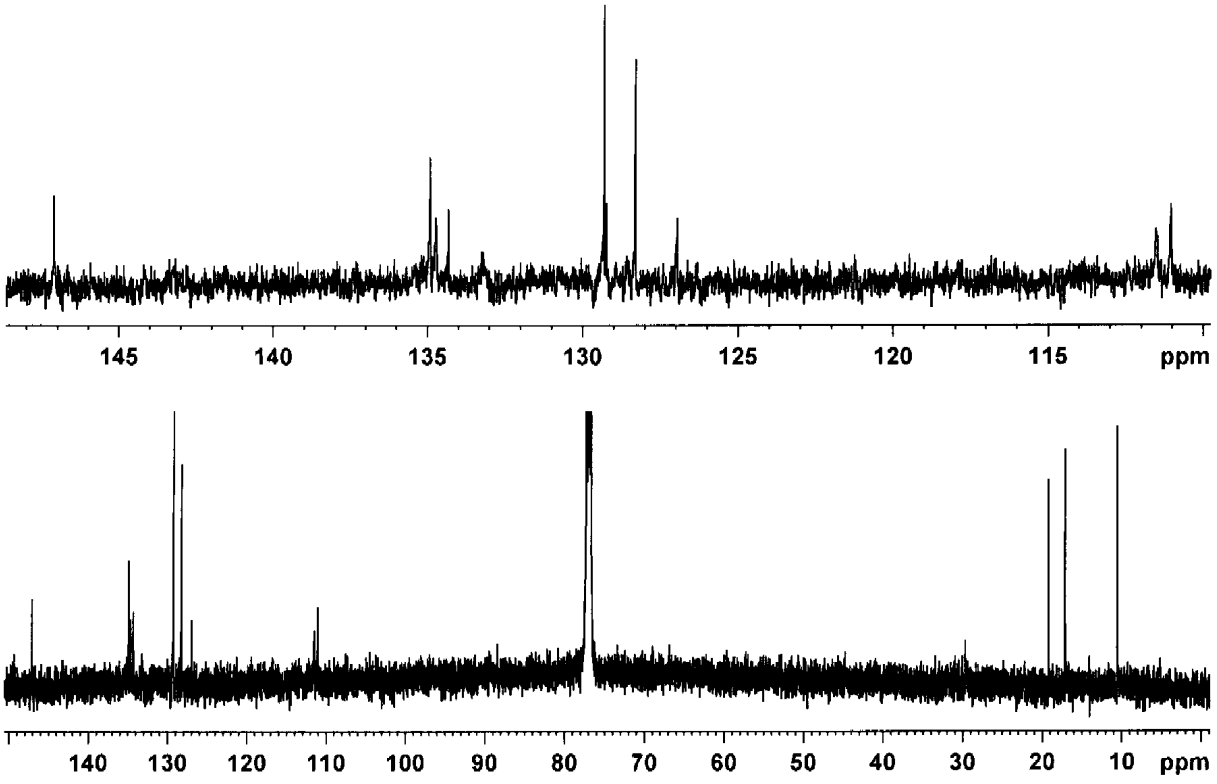

Figure S40. 125 MHz carbon-13 NMR spectrum of thia-azuliporphyrin **8c** in $CDCl_3$.

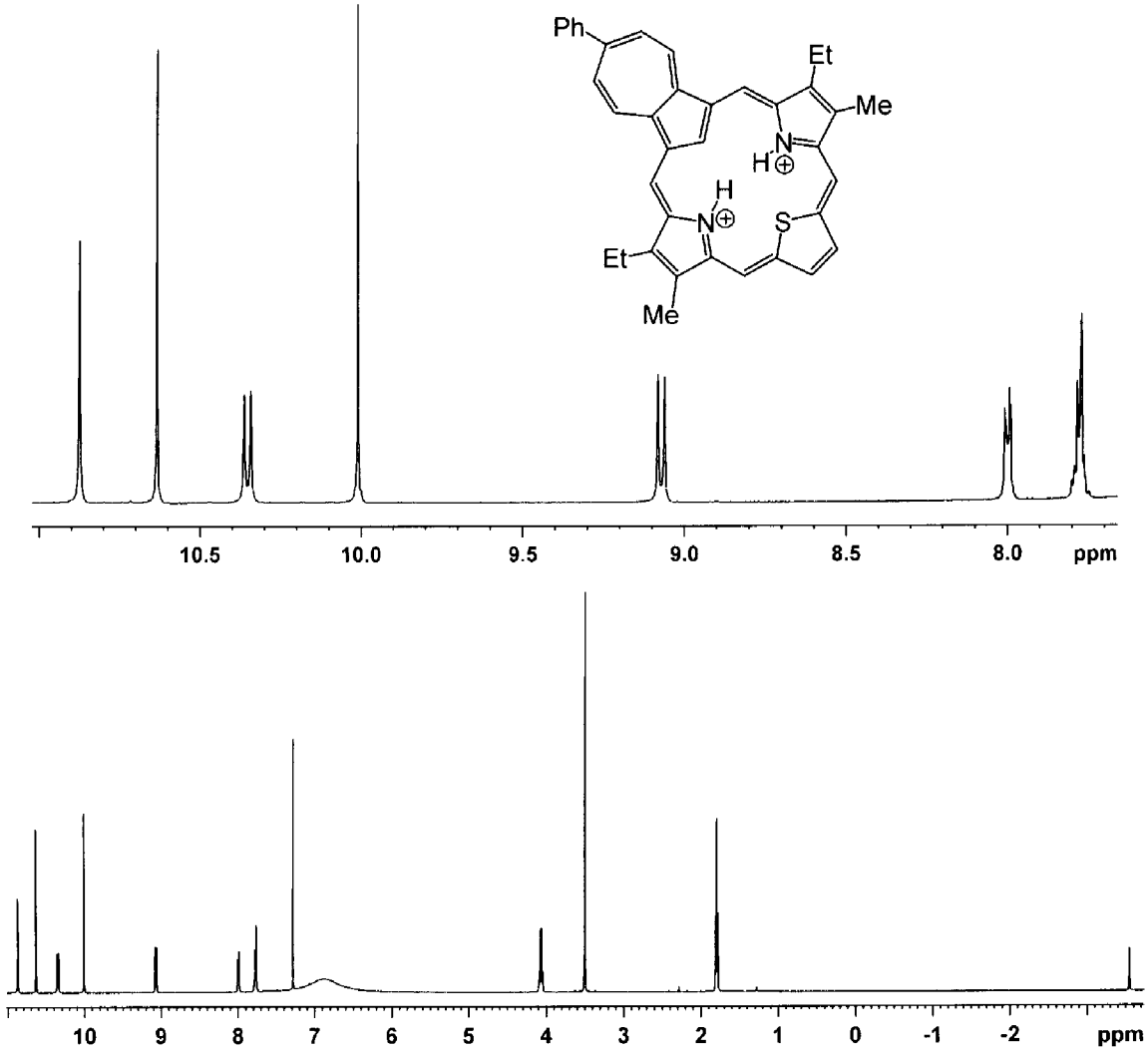

Figure S41. 500 MHz proton NMR spectrum of thia-azuliporphyrin **8c**H_2^{2+} in TFA-$CDCl_3$.

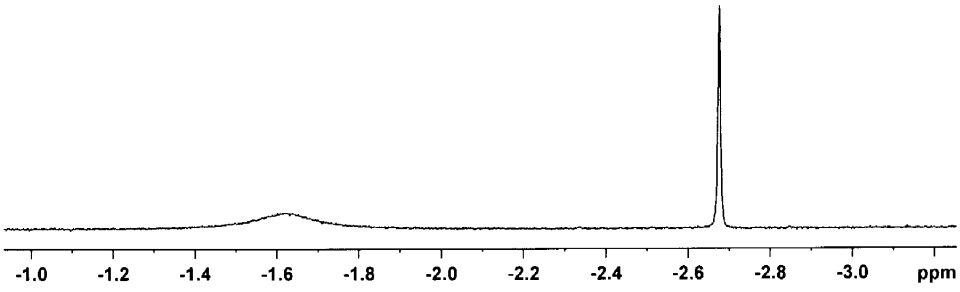

Figure S42. Upfield region for the 500 MHz ^{1}H NMR spectrum of **8c**H_2^{2+} in $CDCl_3$ with a higher concentration of TFA showing the NH resonance.

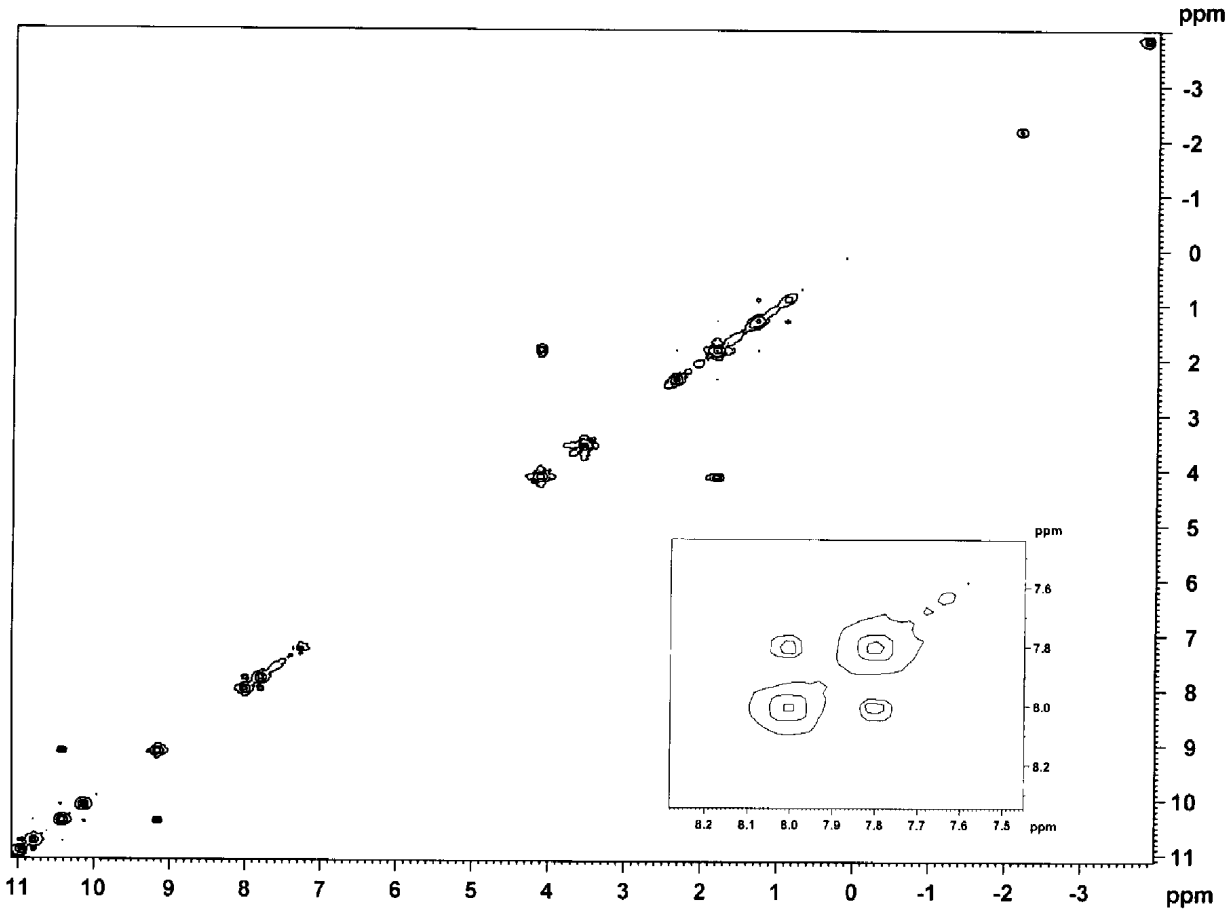

Figure S43. ^{1}H-^{1}H COSY NMR spectrum of thia-azuliporphyrin **8c**H_2^{2+} in TFA-$CDCl_3$.

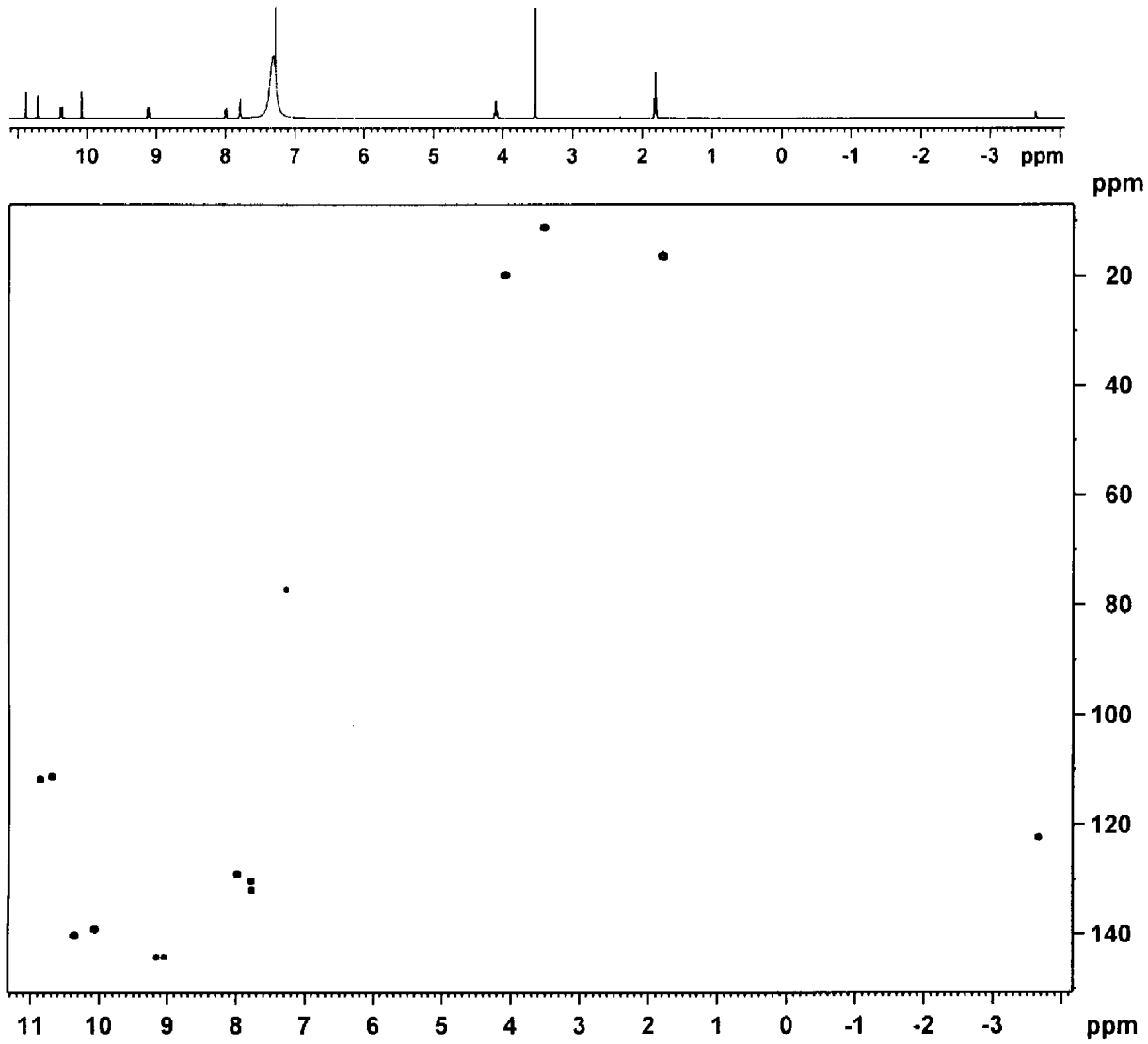

Figure S44. HSQC NMR spectrum of thia-azuliporphyrin **8c**H_2^{2+} in TFA-$CDCl_3$.