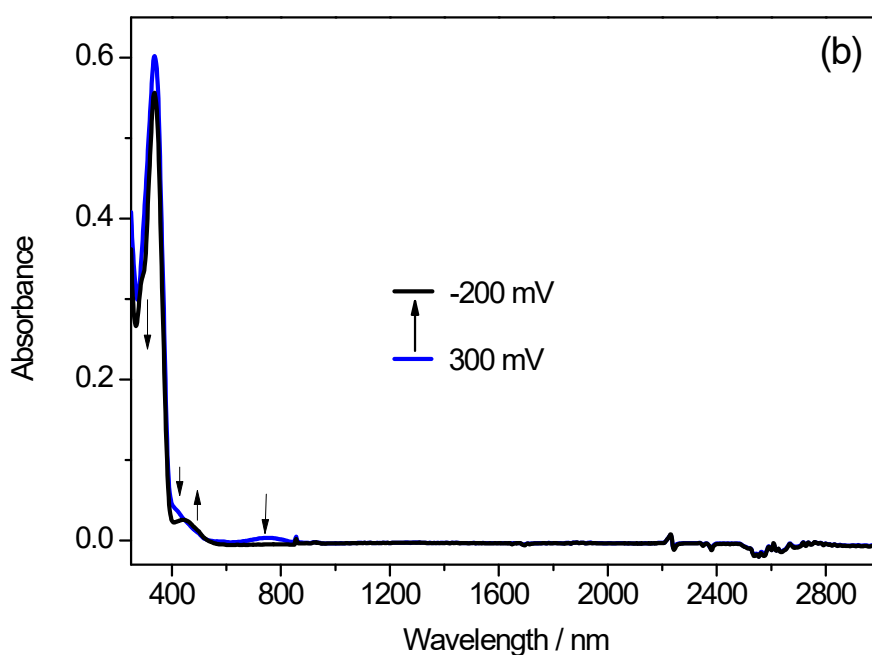
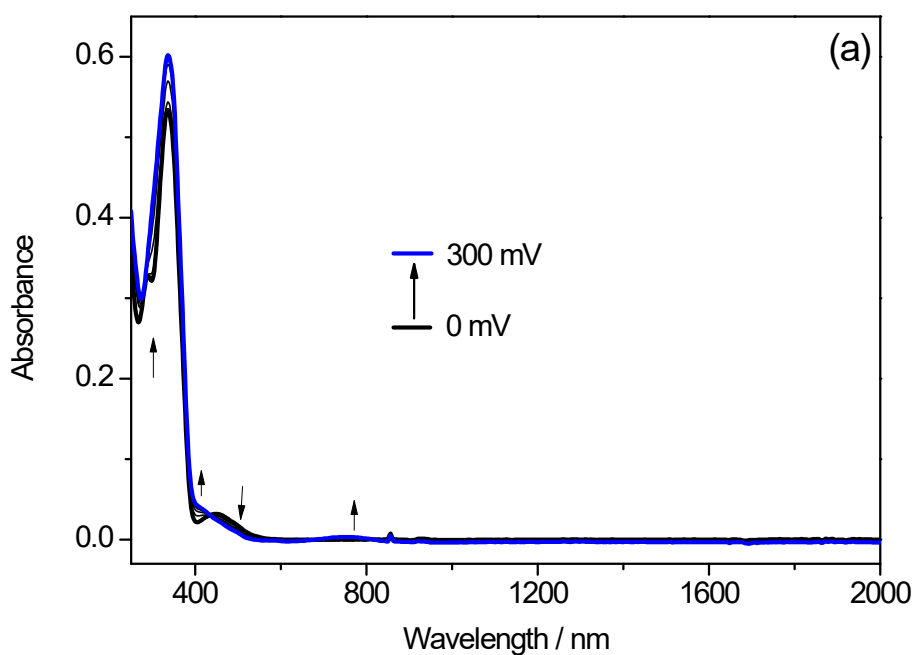


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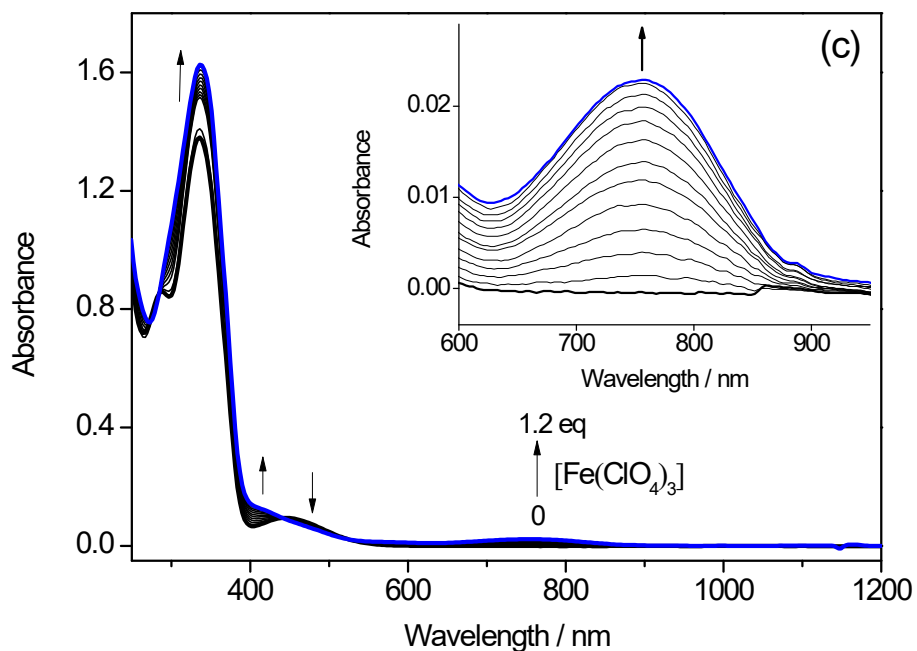
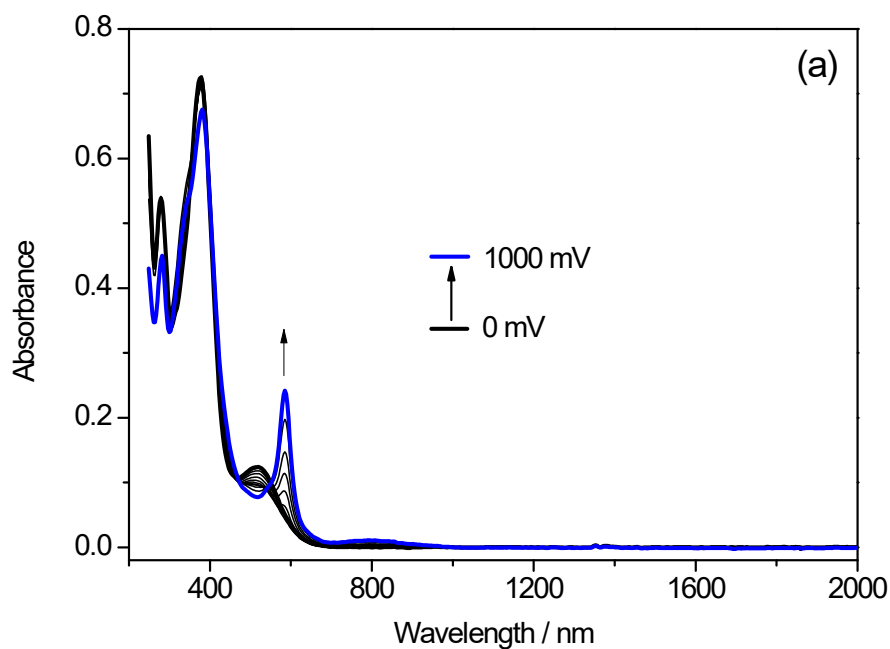


Figure S1. (a) UV/Vis/NIR absorption spectral change of **13** ($1 \times 10^{-3} \text{ mol L}^{-1}$) in 0.1 mol L^{-1} TBAPF₆- dichloromethane at rising potentials (0 to 300 mV versus Ag/AgCl) and (b) subsequent electrolysis at -200 mV versus Ag/AgCl. (c) UV/Vis/NIR absorption spectra change of **13** ($5.1 \times 10^{-5} \text{ mol L}^{-1}$) in chloroform upon addition of Fe(ClO₄)₃ (0 → 1.2 equiv), The inset shows the absorbance change at 600-1000 nm. Arrows indicate areas of increasing and decreasing of absorptions.



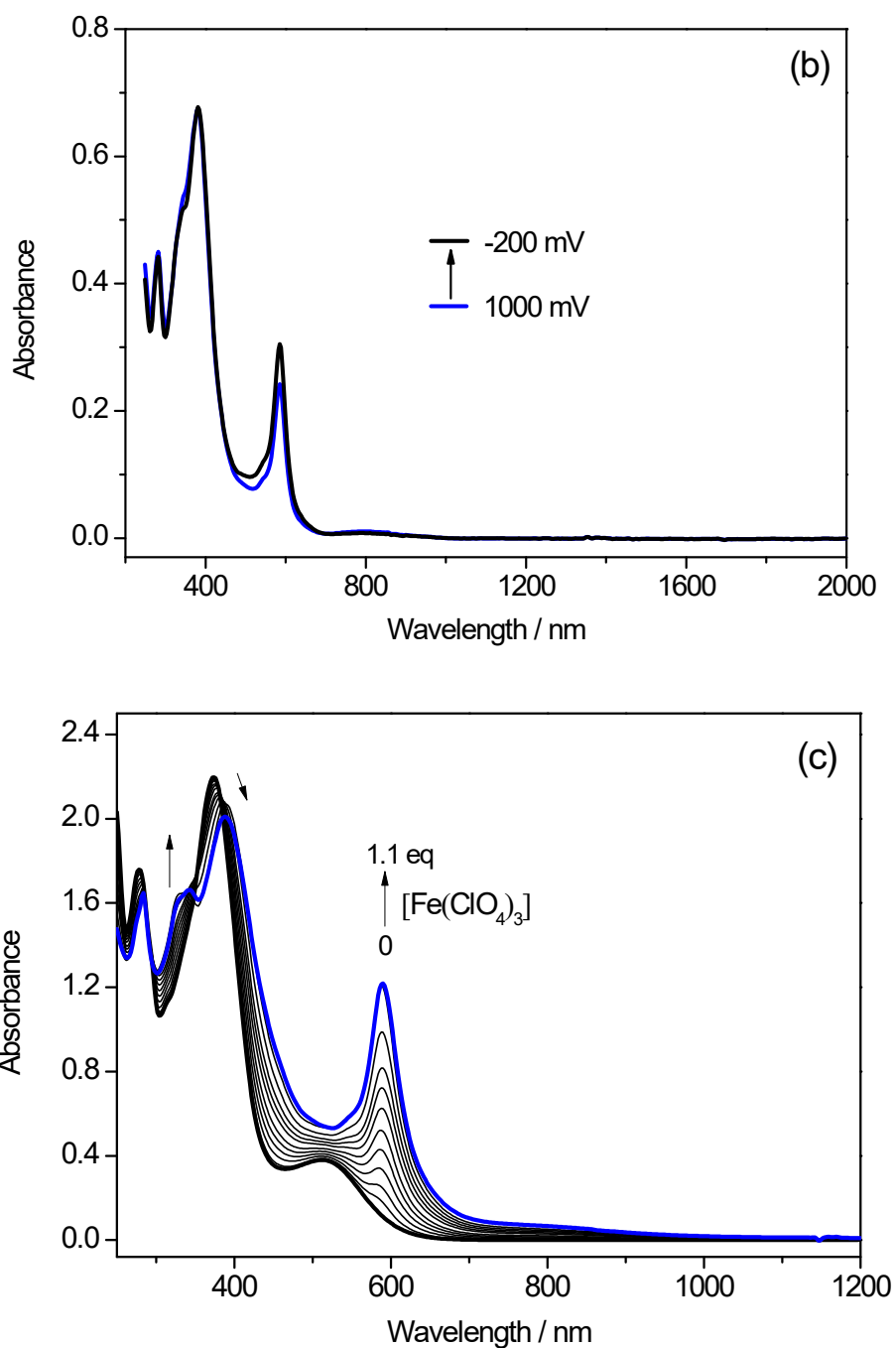
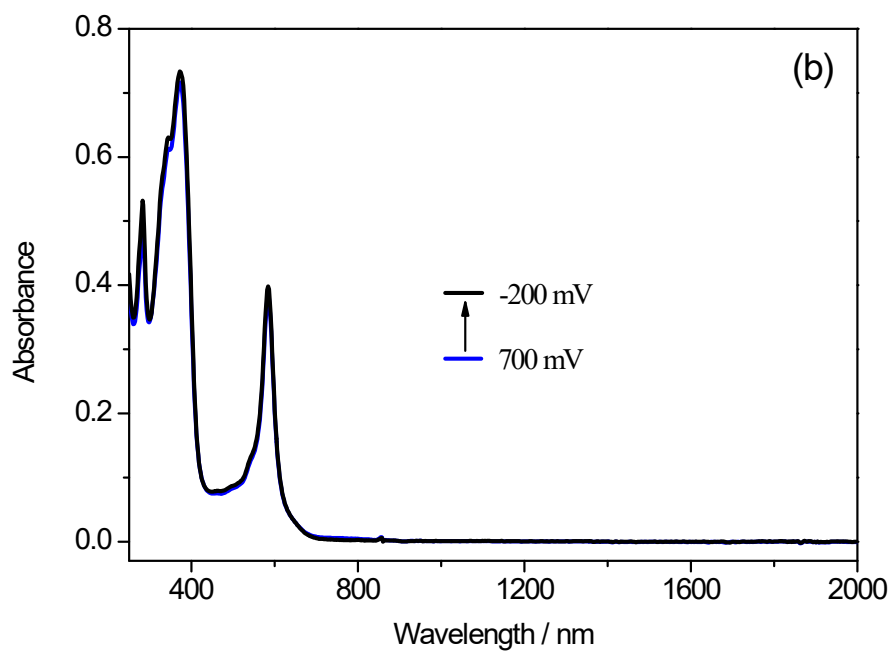
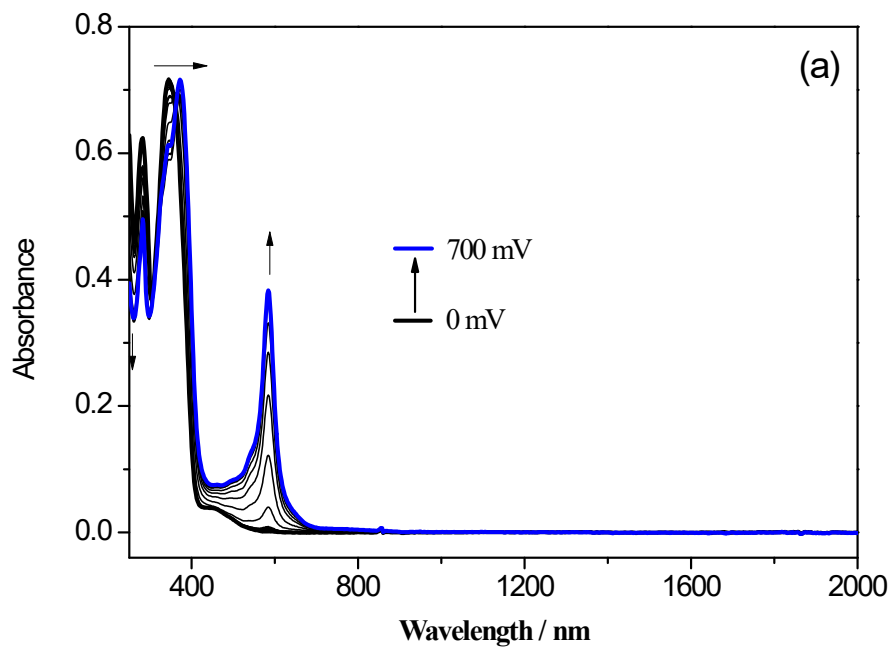


Figure S2. (a) UV/Vis/NIR absorption spectral change of **14** ($1 \times 10^{-3} \text{ mol L}^{-1}$) in 0.1 mol L^{-1} TBAPF₆ - dichloromethane at rising potentials (0 to 1000 mV versus Ag/AgCl) and (b) subsequent electrolysis at -200 mV versus Ag/AgCl. (c) UV/Vis/NIR absorption spectra change of **14** ($5.6 \times 10^{-5} \text{ mol L}^{-1}$) in chloroform upon addition of Fe(ClO₄)₃ (0 → 1.1 equiv), The inset shows the absorbance change at 600-1000 nm. Arrows indicate areas of increasing and decreasing of absorptions.



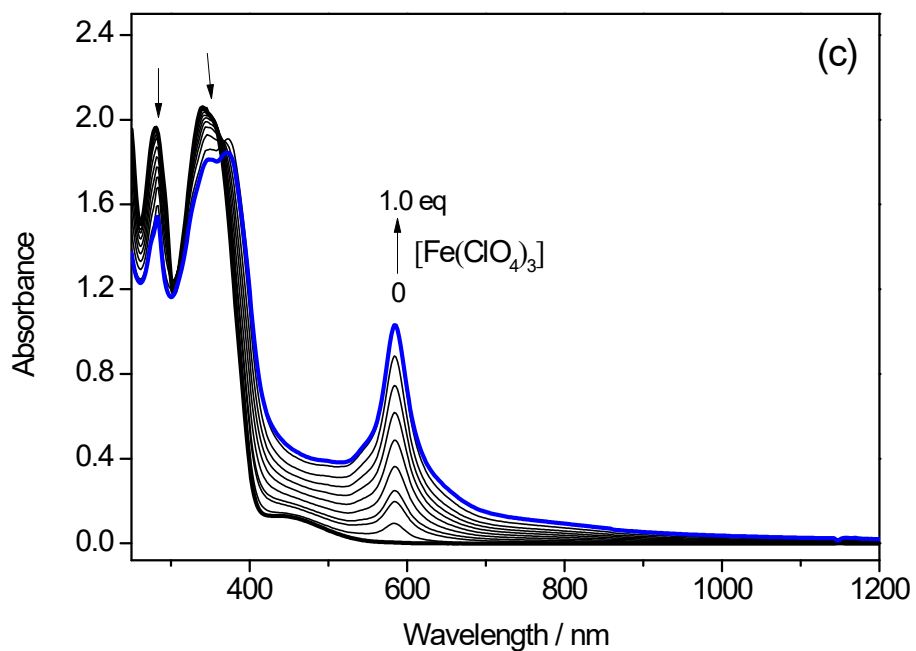
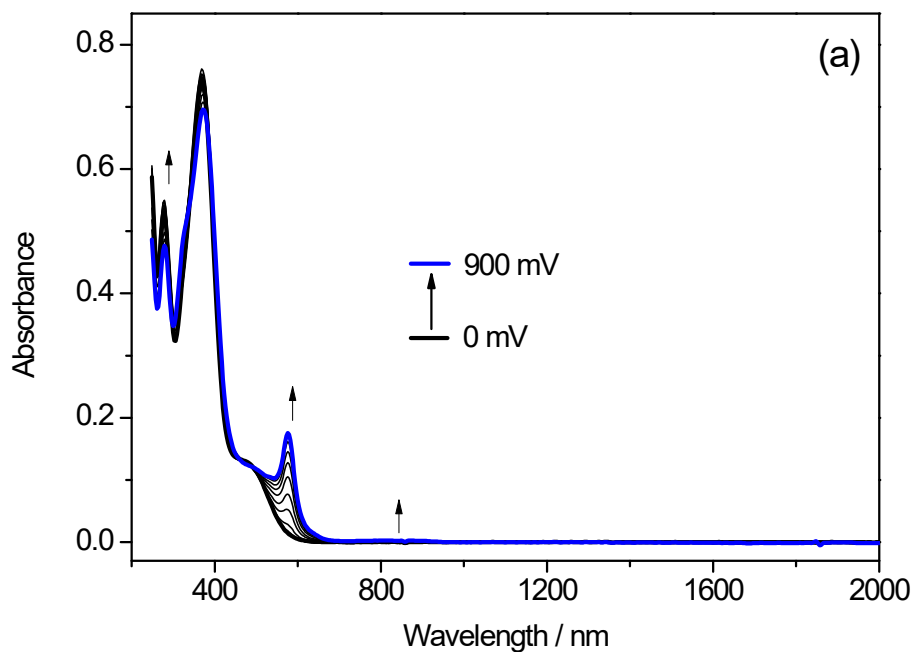


Figure S3. (a) UV/Vis/NIR absorption spectral change of **15** ($1 \times 10^{-3} \text{ mol L}^{-1}$) in 0.1 mol L^{-1} TBAPF₆ - dichloromethane at rising potentials (0 to 700 mV versus Ag/AgCl) and (b) subsequent electrolysis at -200 mV versus Ag/AgCl. (c) UV/Vis/NIR absorption spectra change of **15** ($4.6 \times 10^{-5} \text{ mol L}^{-1}$) in chloroform upon addition of Fe(ClO₄)₃ (0 → 1.1 equiv), The inset shows the absorbance change at 600-1000 nm. Arrows indicate areas of increasing and decreasing of absorptions.



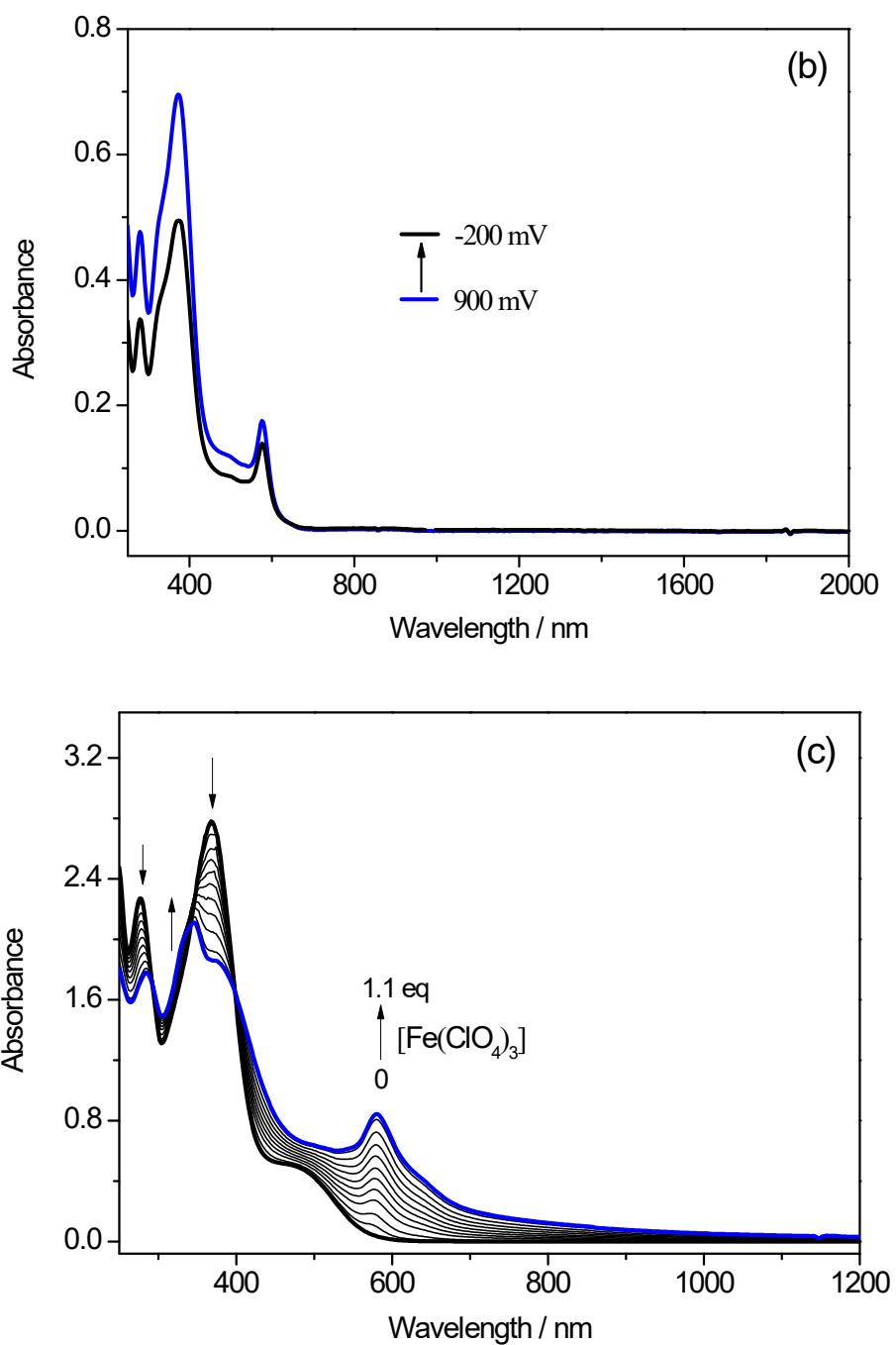
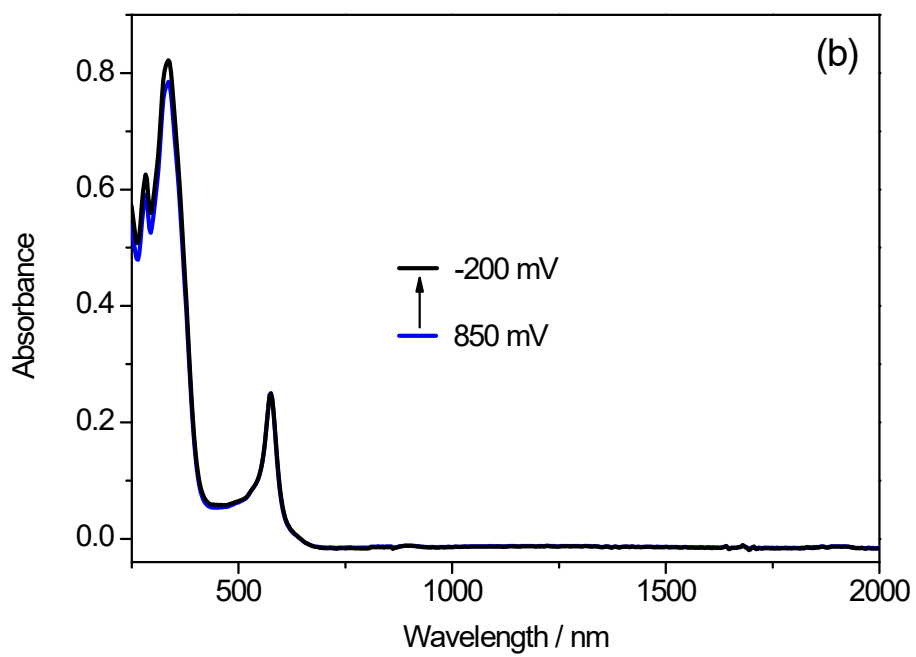
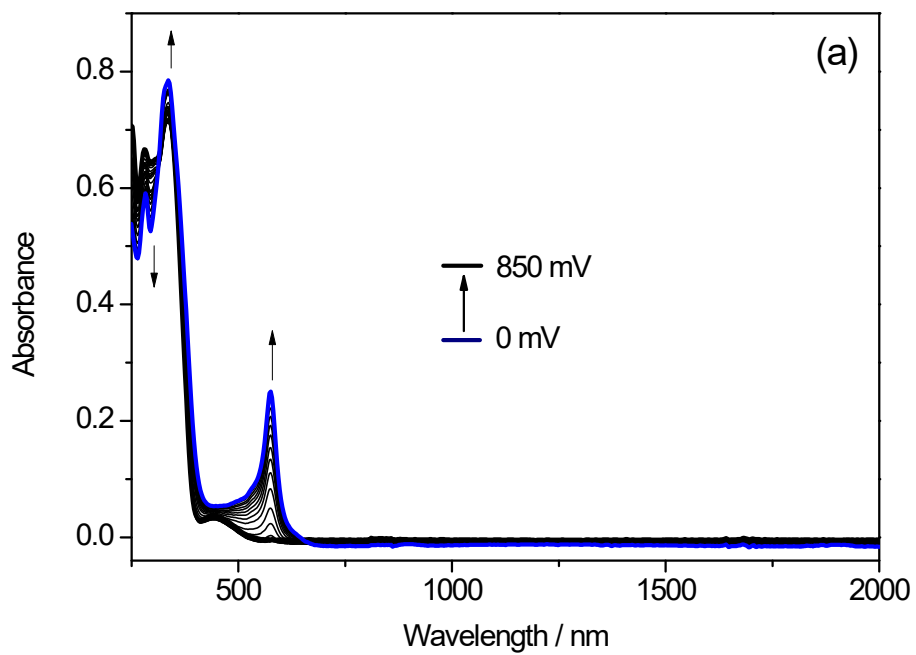


Figure S4. (a) UV/Vis/NIR absorption spectral change of **16** ($1 \times 10^{-3} \text{ mol L}^{-1}$) in 0.1 mol L^{-1} TBAPF₆ - dichloromethane at rising potentials (0 to 900 mV versus Ag/AgCl) and (b) subsequent electrolysis at -200 mV versus Ag/AgCl. (c) UV/Vis/NIR absorption spectra change of **16** ($5.7 \times 10^{-5} \text{ mol L}^{-1}$) in chloroform upon addition of Fe(ClO₄)₃ (0 → 1.1 equiv), The inset shows the absorbance change at 600-1000 nm. Arrows indicate areas of increasing and decreasing of absorptions.



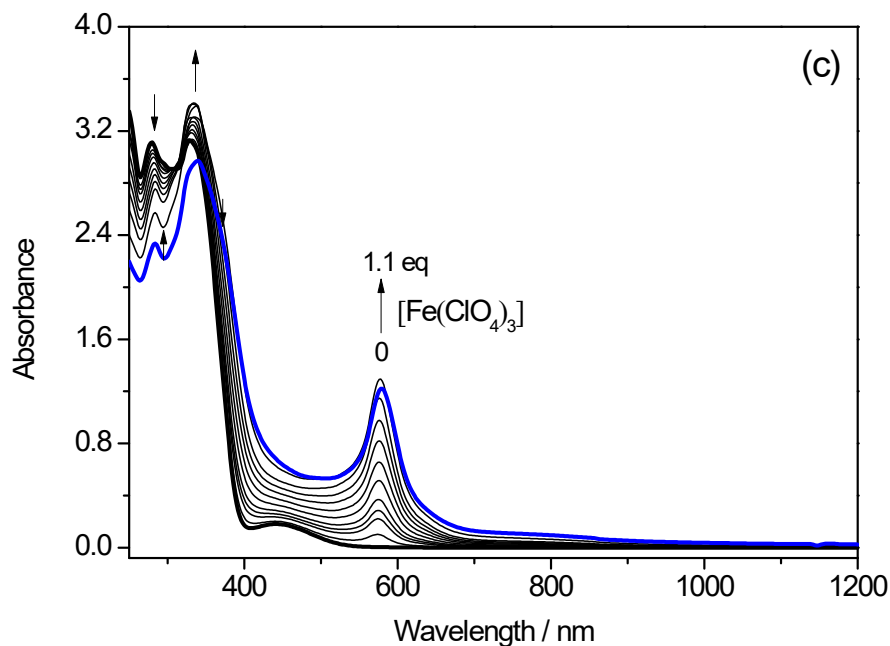


Figure S5. (a) UV/Vis/NIR absorption spectral change of **17** ($1 \times 10^{-3} \text{ mol L}^{-1}$) in 0.1 mol L^{-1} TBAPF₆- dichloromethane at rising potentials (0 to 850 mV versus Ag/AgCl) and (b) subsequent electrolysis at -200 mV versus Ag/AgCl. (c) UV/Vis/NIR absorption spectra change of **17** ($7.0 \times 10^{-5} \text{ mol L}^{-1}$) in chloroform upon addition of Fe(ClO₄)₃ (0 → 1.1 equiv), The inset shows the absorbance change at 600-1000 nm. Arrows indicate areas of increasing and decreasing of absorptions.

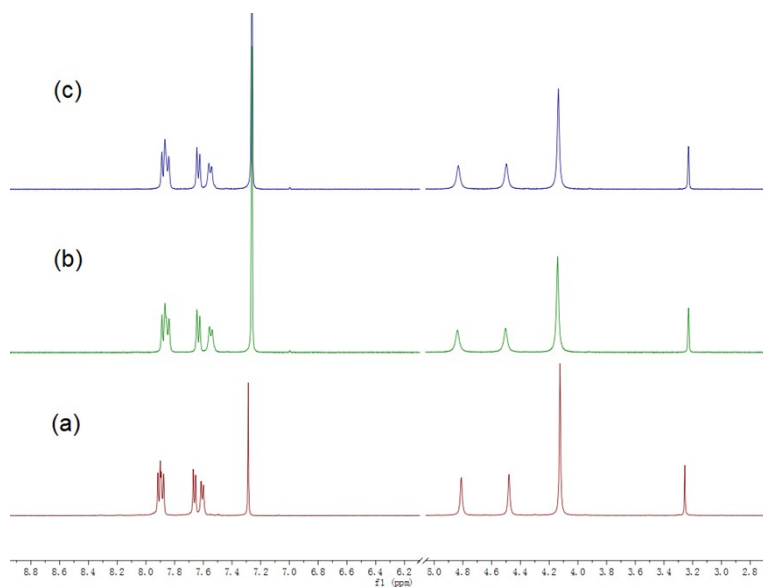


Figure S6. ¹H NMR spectra change of **12** in CDCl₃: (a) original spectrum of *trans*-**12**; (b) after irradiation with 550 nm for 60 min; (c) subsequent irradiation at 365 nm for 60 min.

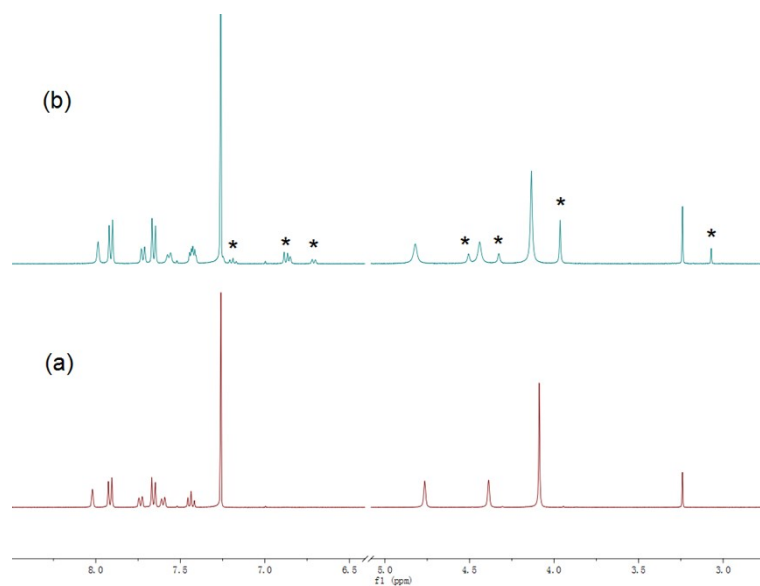


Figure S7. ^1H NMR spectra change of **13** in CDCl_3 : (a) original spectrum of *trans*-**13**; (b) after irradiation with 550 nm for 30 min. The signals marked with asterisks are corresponding to the *cis* form.

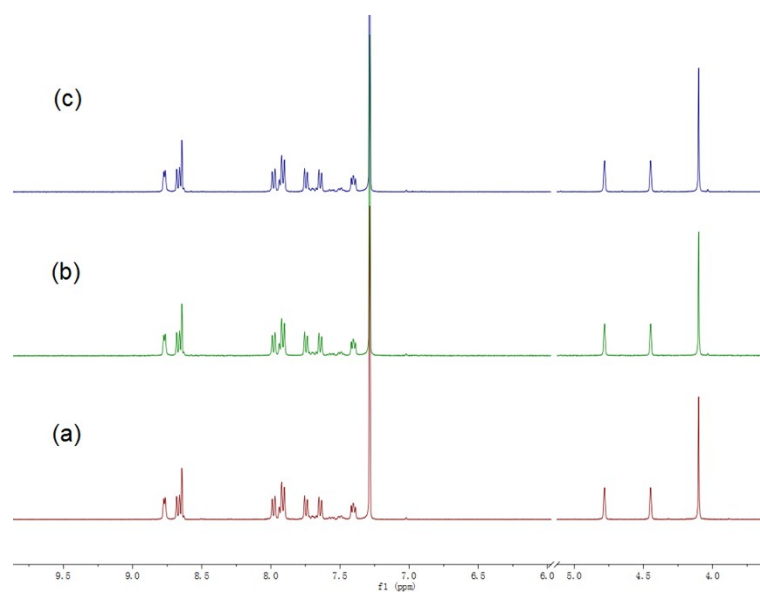


Figure S8. ^1H NMR spectra change of **14** in CDCl_3 : (a) original spectrum of *trans*-**14**; (b) after irradiation with 550 nm for 60 min; (c) subsequent irradiation at 365 nm for 60 min.

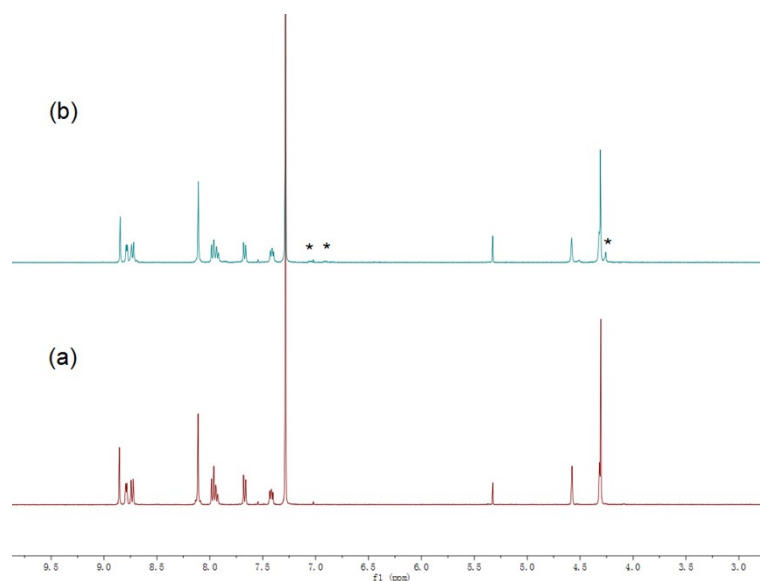


Figure S9. ^1H NMR spectra change of **16** in CDCl_3 : (a) original spectrum of *trans*-**16**; (b) after irradiation with 550 nm for 30 min. The signals marked with asterisks are corresponding to the *cis* form.

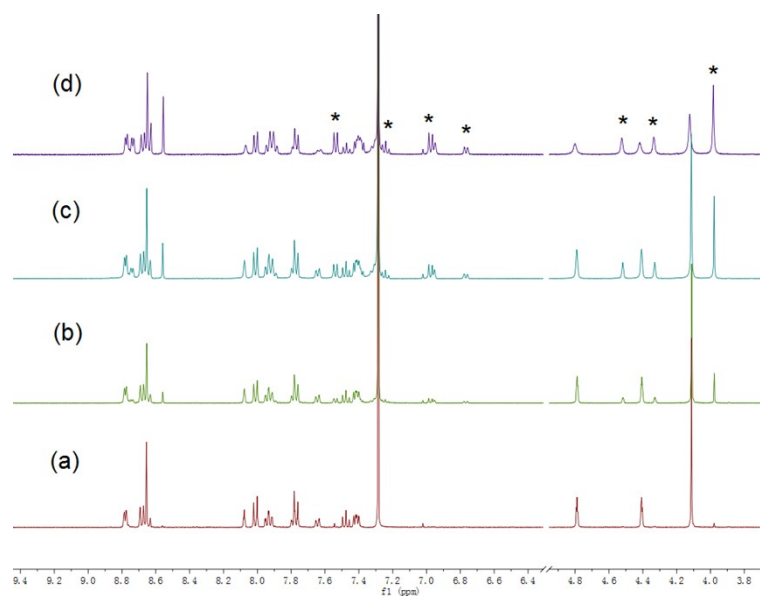


Figure S10. ^1H NMR spectra change of **17** in CDCl_3 : (a) original spectrum of *trans*-**17**; (b) after irradiation with 550 nm for 60 min; (c, d) subsequent irradiation at 365 nm for 30 min and 95 min, respectively. The signals marked with asterisks are corresponding to the *cis* form.

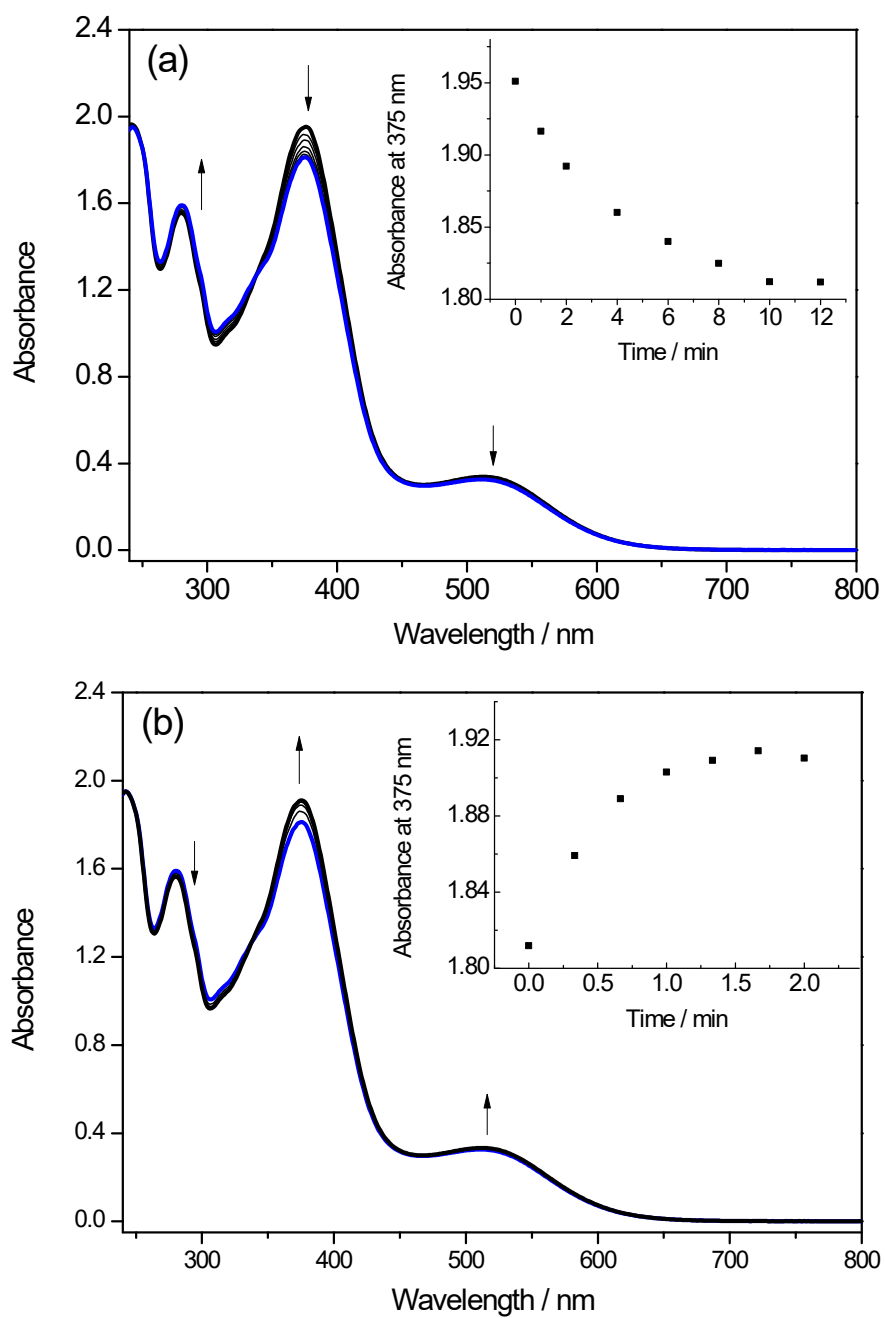
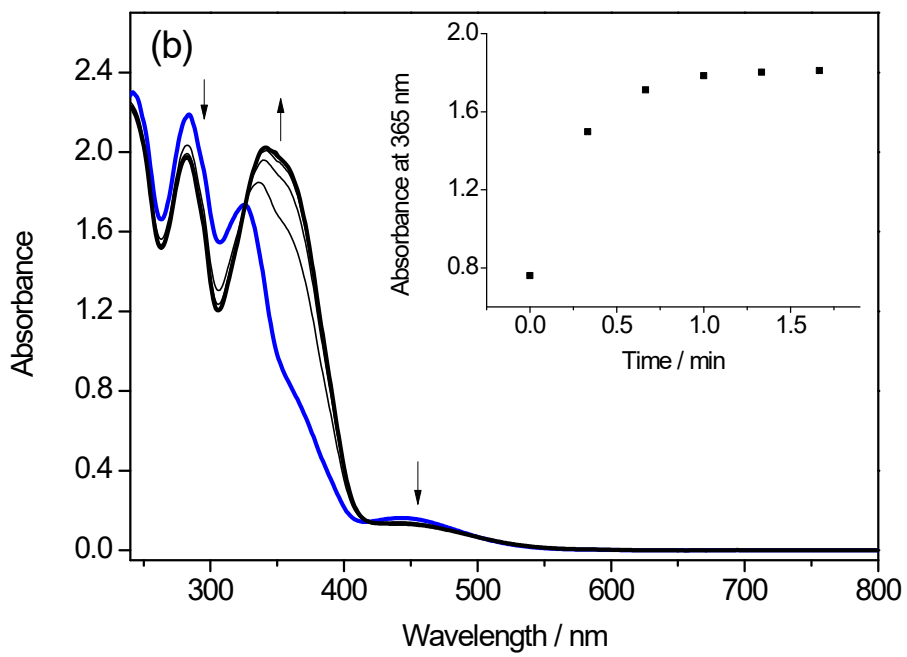
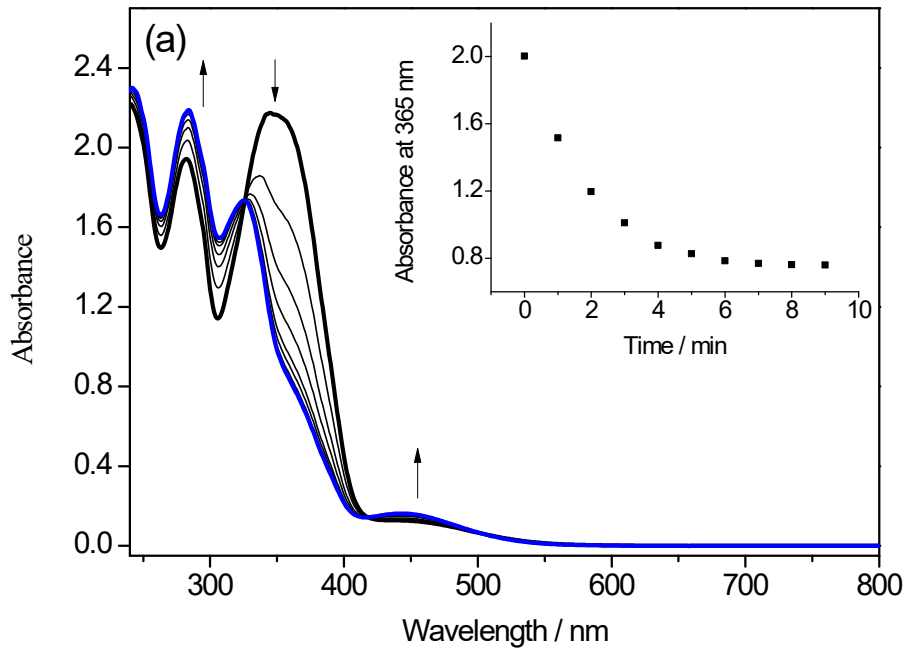


Figure S11. (a) UV/Vis spectral changes of **14** ($5.0 \times 10^{-5} \text{ mol L}^{-1}$) in chloroform upon irradiation at 365 nm for 12 min and (b) subsequent irradiation at 435 nm for 120 s. The inset shows the absorbance change at 375 nm with irradiation time.



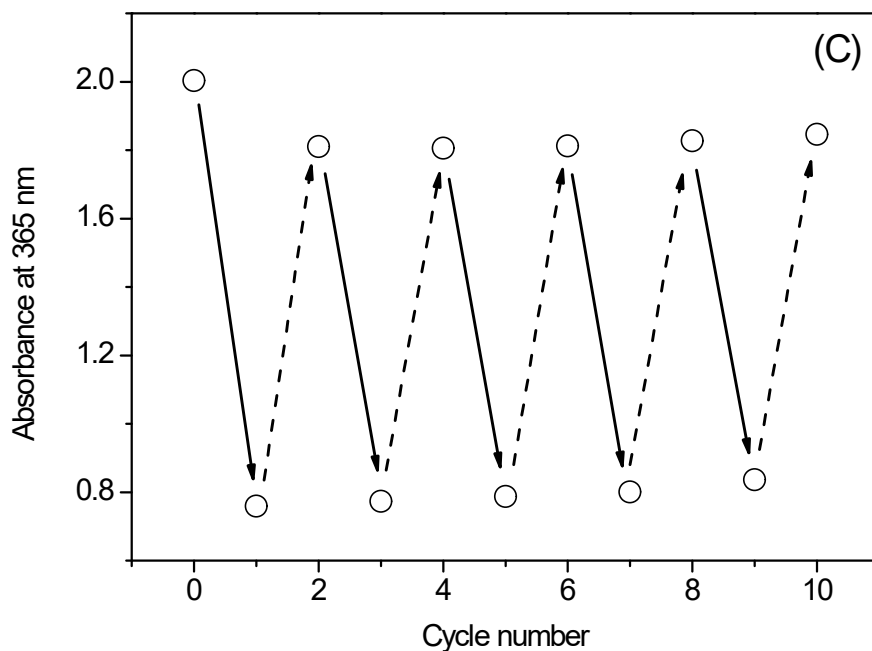
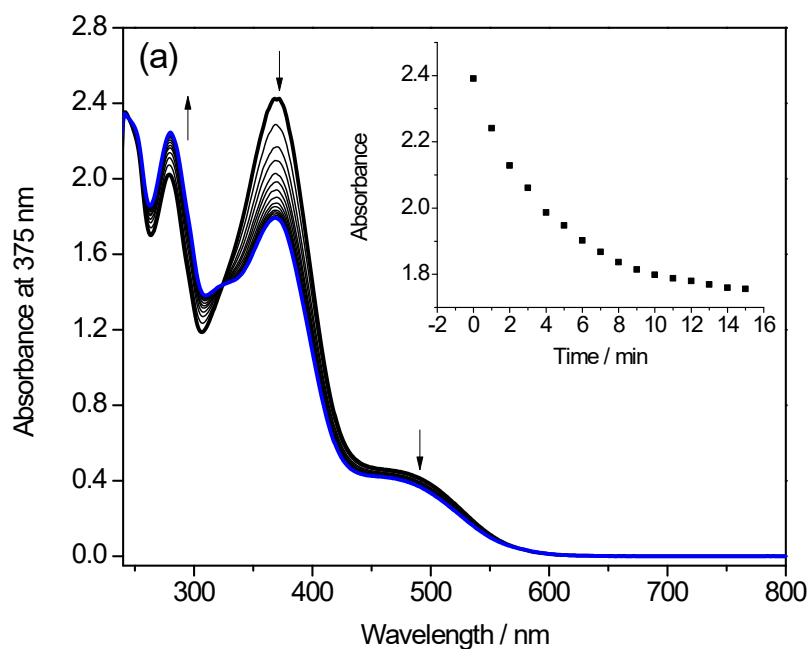


Figure S12. (a) UV/Vis spectral changes of **15** ($5.0 \times 10^{-5} \text{ mol L}^{-1}$) in chloroform upon irradiation at 365 nm for 9 min and (b) subsequent irradiation at 435 nm for 100 s. (c) Reversible isomerization cycles of **15** were repeated several times between two photostationary states. Solid line shows the *trans*-to-*cis* isomerization upon irradiation at 365 nm, while the dash line shows the *cis*-to-*trans* isomerization upon irradiation at 435 nm. The inset shows the absorbance change at 365 nm with irradiation time.



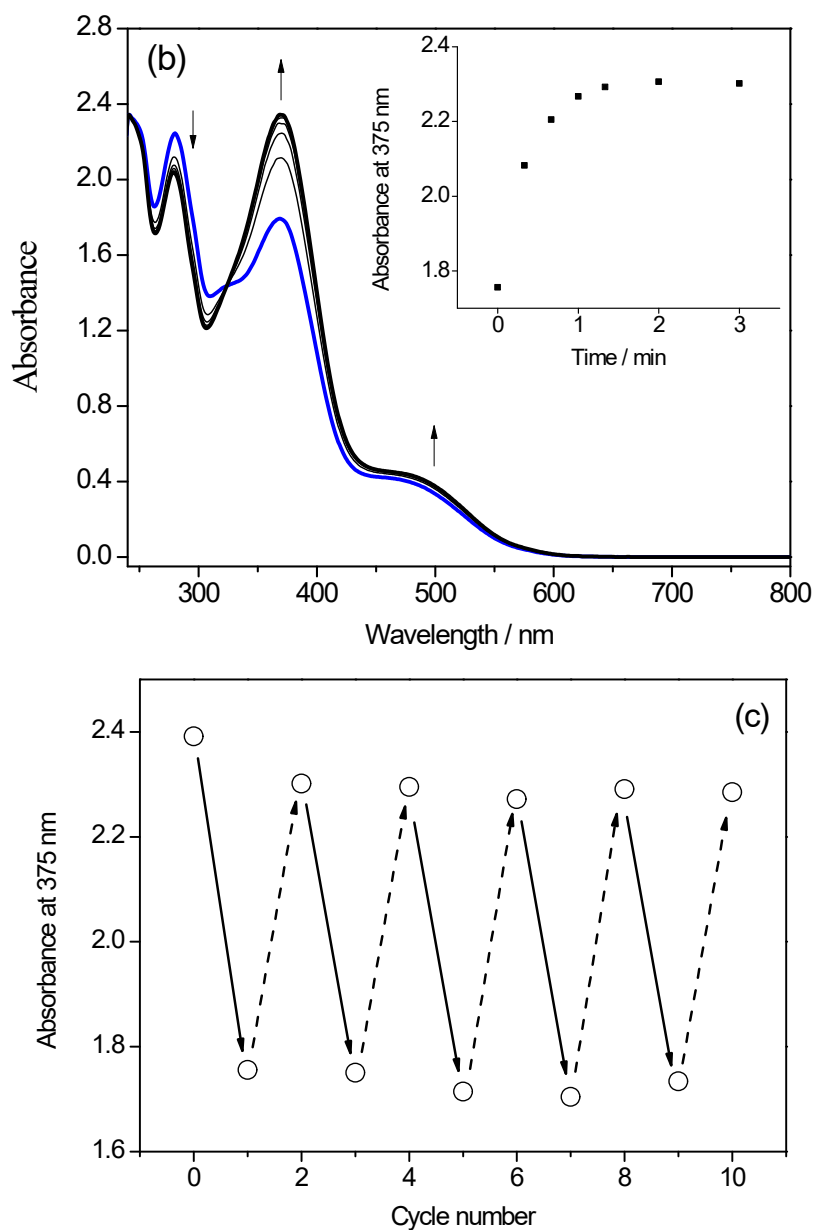
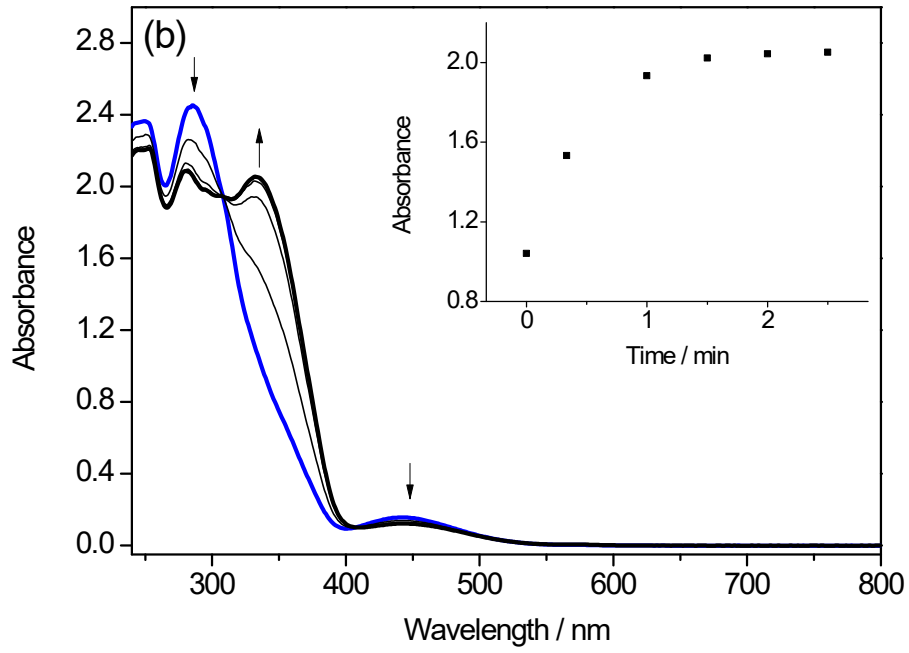
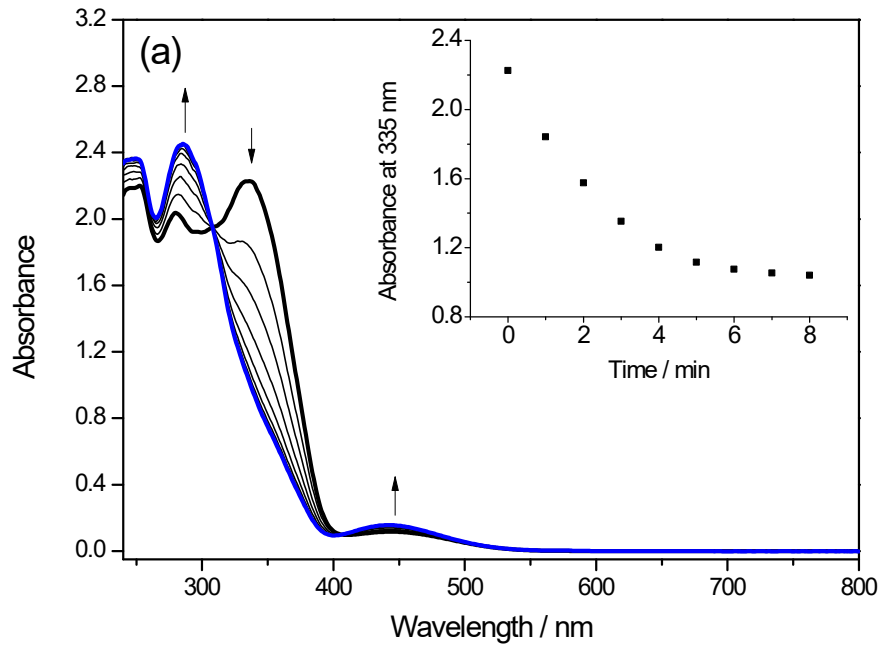


Figure S13. (a) UV/Vis spectral changes of **16** ($5.0 \times 10^{-5} \text{ mol L}^{-1}$) in chloroform upon irradiation at 365 nm for 15 min and (b) subsequent irradiation at 435 nm for 180 s. (c) Reversible isomerization cycles of **16** were repeated several times between two photostationary states. Solid line shows the *trans*-to-*cis* isomerization upon irradiation at 365 nm, while the dash line shows the *cis*-to-*trans* isomerization upon irradiation at 435 nm. The inset shows the absorbance change at 375 nm with irradiation time.



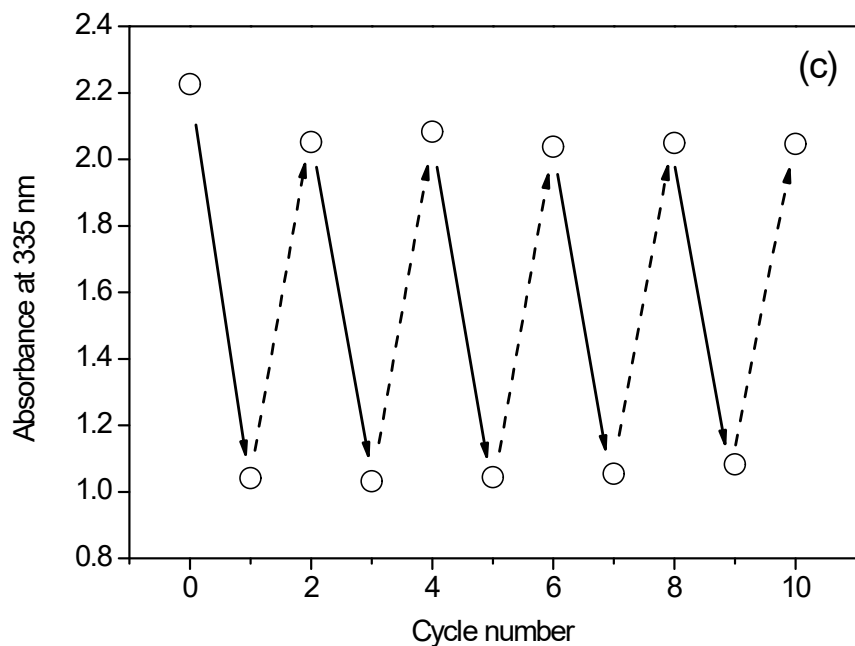
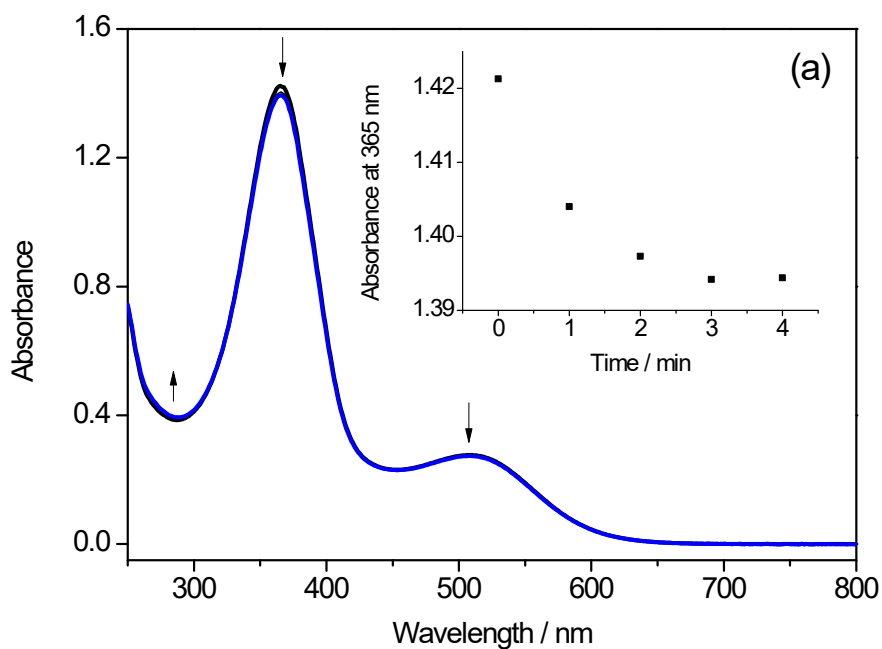
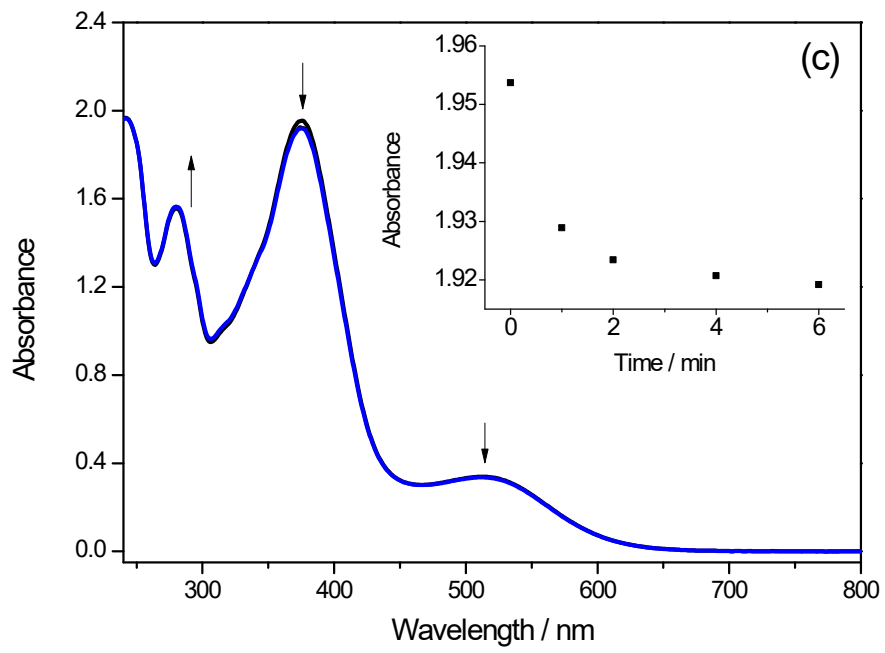
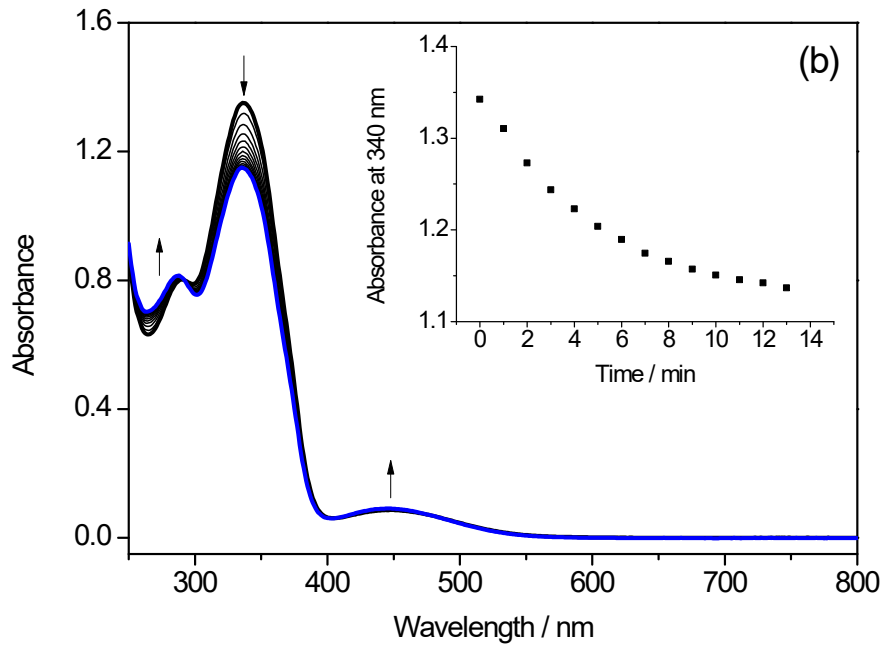
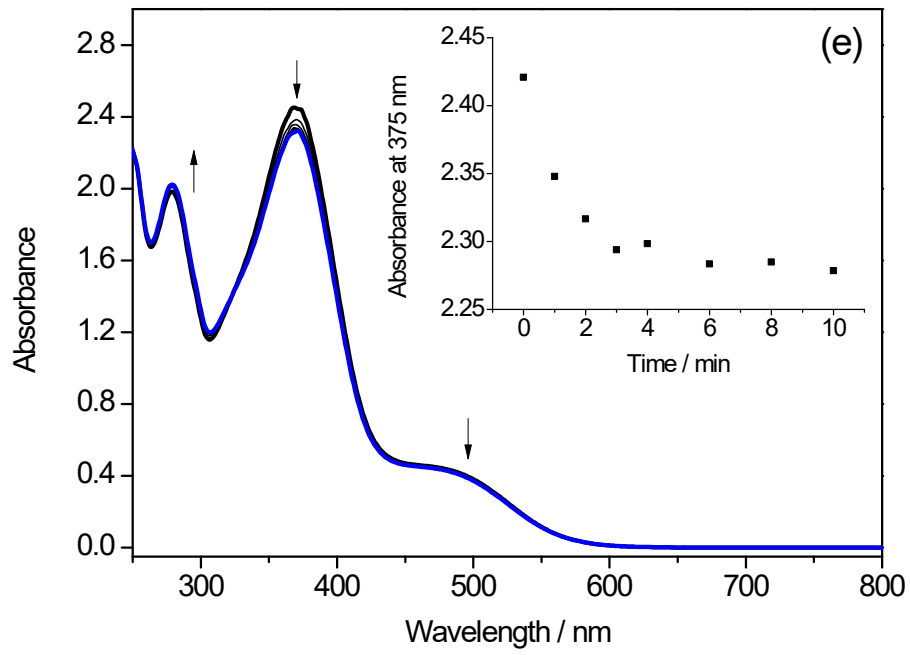
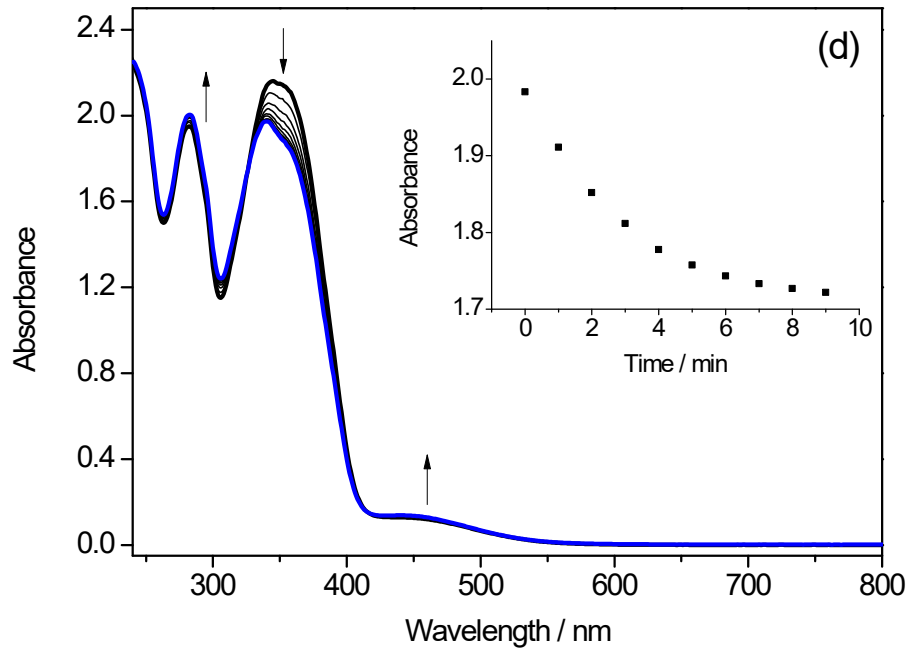


Figure S14. (a) UV/Vis spectral changes of **17** ($5.0 \times 10^{-5} \text{ mol L}^{-1}$) in chloroform upon irradiation at 365 nm for 15 min and (b) subsequent irradiation at 435 nm for 180 s. (c) Reversible isomerization cycles of **17** were repeated several times between two photostationary states. Solid line shows the *trans*-to-*cis* isomerization upon irradiation at 365 nm, while the dash line shows the *cis*-to-*trans* isomerization upon irradiation at 435 nm. The inset shows the absorbance change at 335 nm with irradiation time.







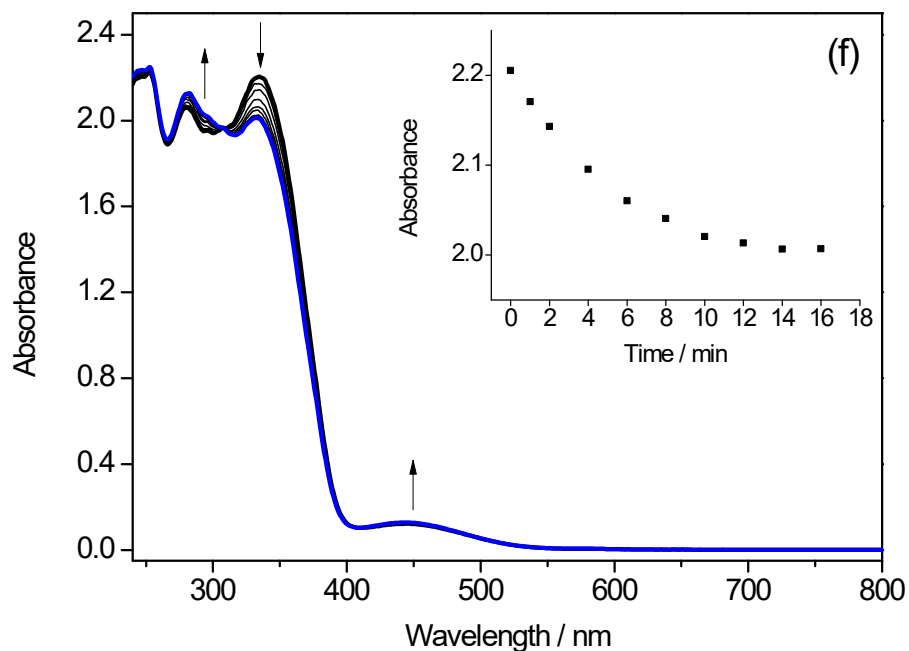


Figure S15. (a) UV/Vis spectra changes of **12** ($5.0 \times 10^{-5} \text{ mol L}^{-1}$) in chloroform upon irradiation at 550 nm for 4 min. The inset shows the absorbance change at 365 nm with irradiation time. (b) UV/Vis spectra changes of **13** ($5.0 \times 10^{-5} \text{ mol L}^{-1}$) in chloroform upon irradiation at 550 nm for 13 min. The inset shows the absorbance change at 340 nm with irradiation time. (c) UV/Vis spectra changes of **14** ($5.0 \times 10^{-5} \text{ mol L}^{-1}$) in chloroform upon irradiation at 550 nm for 6 min. The inset shows the absorbance change at 375 nm with irradiation time. (d) UV/Vis spectra changes of **15** ($5.0 \times 10^{-5} \text{ mol L}^{-1}$) in chloroform upon irradiation at 550 nm for 9 min. The inset shows the absorbance change at 365 nm with irradiation time. (e) UV/Vis spectra changes of **16** ($5.0 \times 10^{-5} \text{ mol L}^{-1}$) in chloroform upon irradiation at 550 nm for 10 min. The inset shows the absorbance change at 375 nm with irradiation time. (f) UV/Vis spectra changes of **17** ($5.0 \times 10^{-5} \text{ mol L}^{-1}$) in chloroform upon irradiation at 550 nm for 16 min. The inset shows the absorbance change at 335 nm with irradiation time.

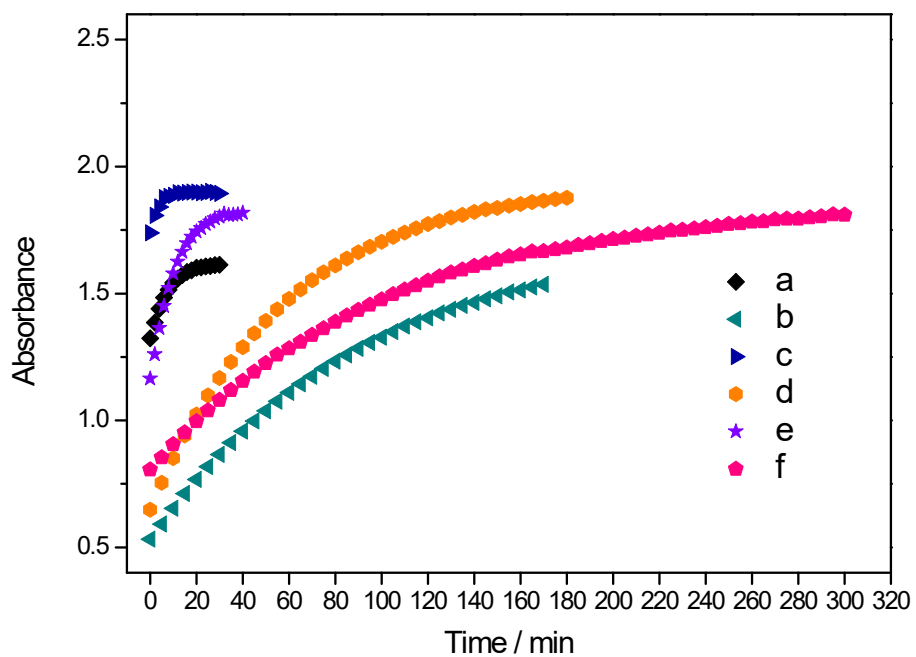


Figure S16. Thermal *cis*-to-*trans* isomerization of **12-17** ($5.0 \times 10^{-5} \text{ mol L}^{-1}$) in toluene at $55 \text{ }^\circ\text{C}$: (a) Absorbance at 365 nm versus time for **12**; (b) Absorbance at 340 nm versus time for **13**; (c) Absorbance at 375 nm versus time for **14**; (d) Absorbance at 365 nm versus time for **15**; (e) Absorbance at 375 nm versus time for **16**; (f) Absorbance at 335 nm versus time for **17**.

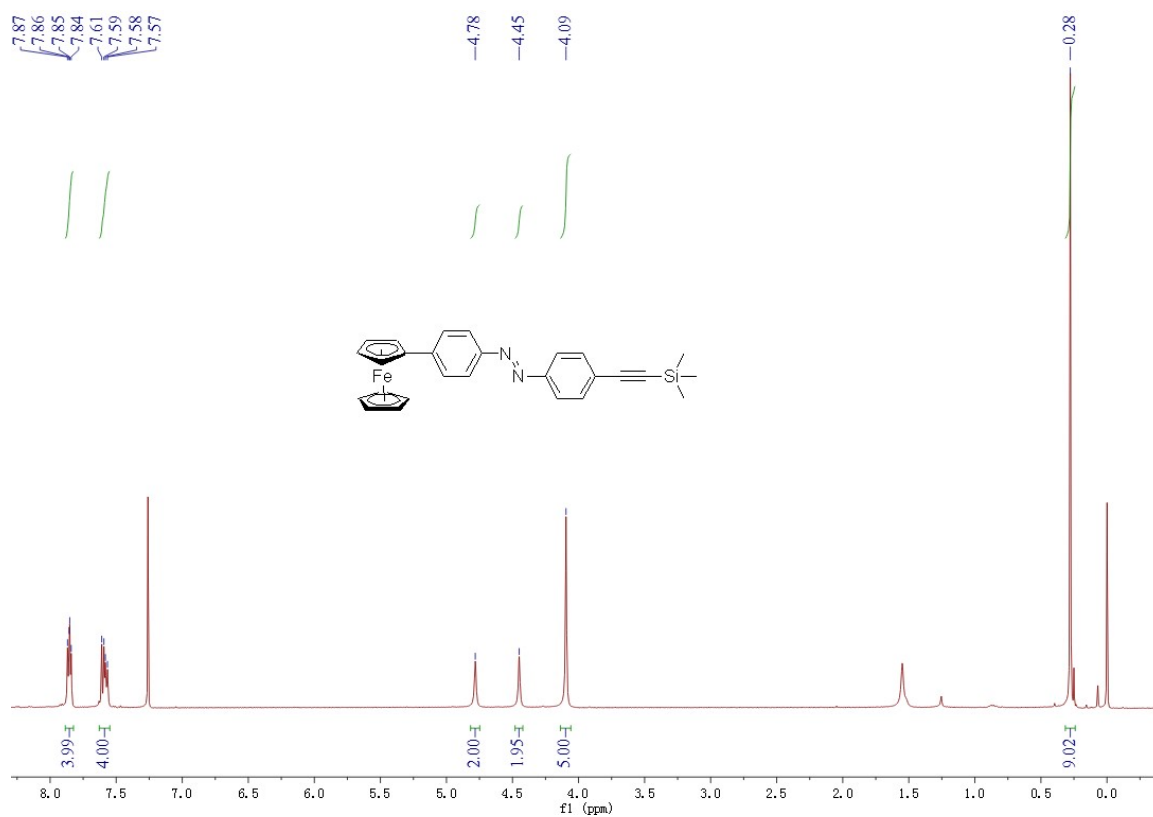


Figure S17. ^1H NMR spectrum of compound **3** (CDCl_3)

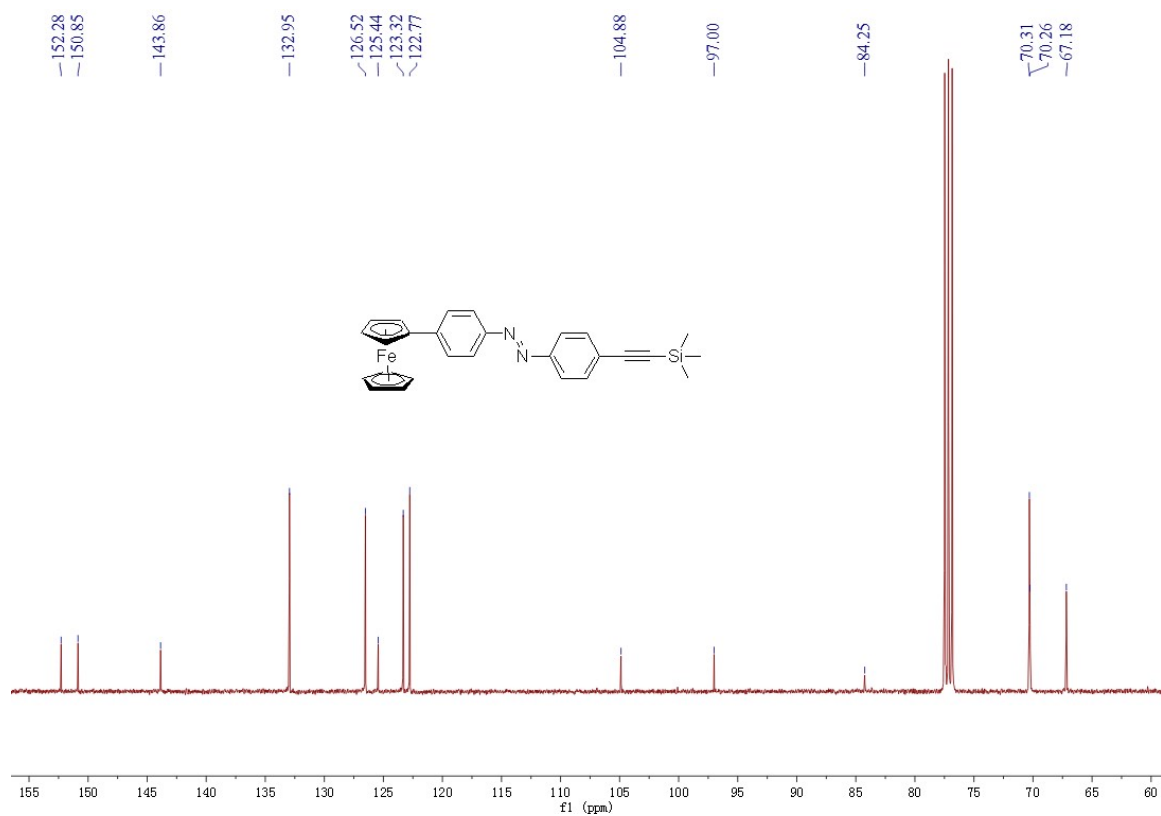


Figure S18. ¹³C NMR spectrum of compound 3 (CDCl₃)

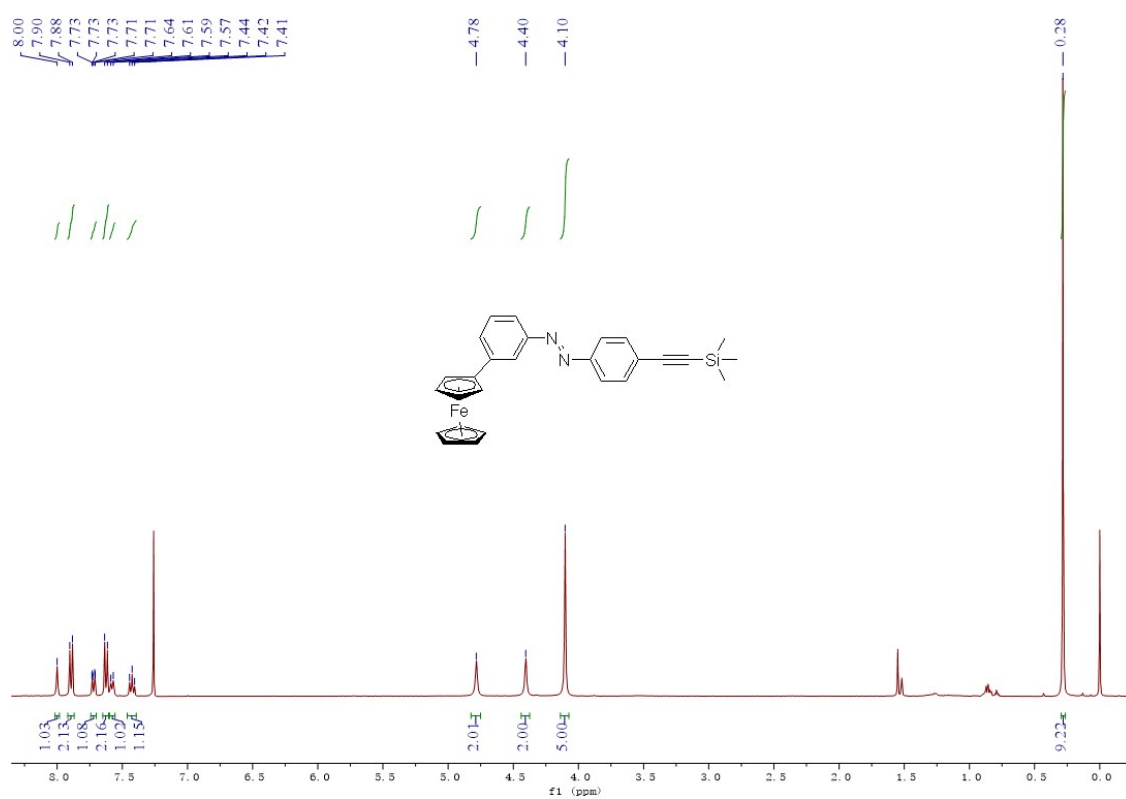


Figure S19. ¹H NMR spectrum of compound 4 (CDCl₃)

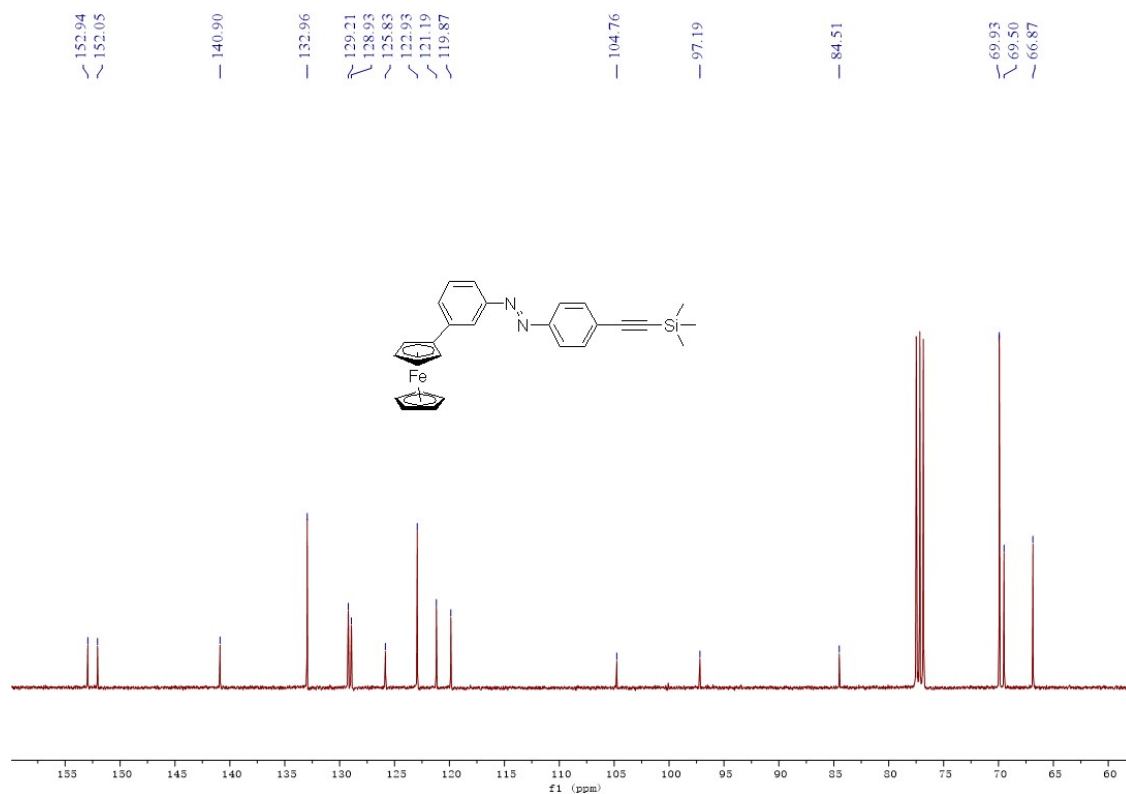


Figure S20. ^{13}C NMR spectrum of compound 4 (CDCl_3)

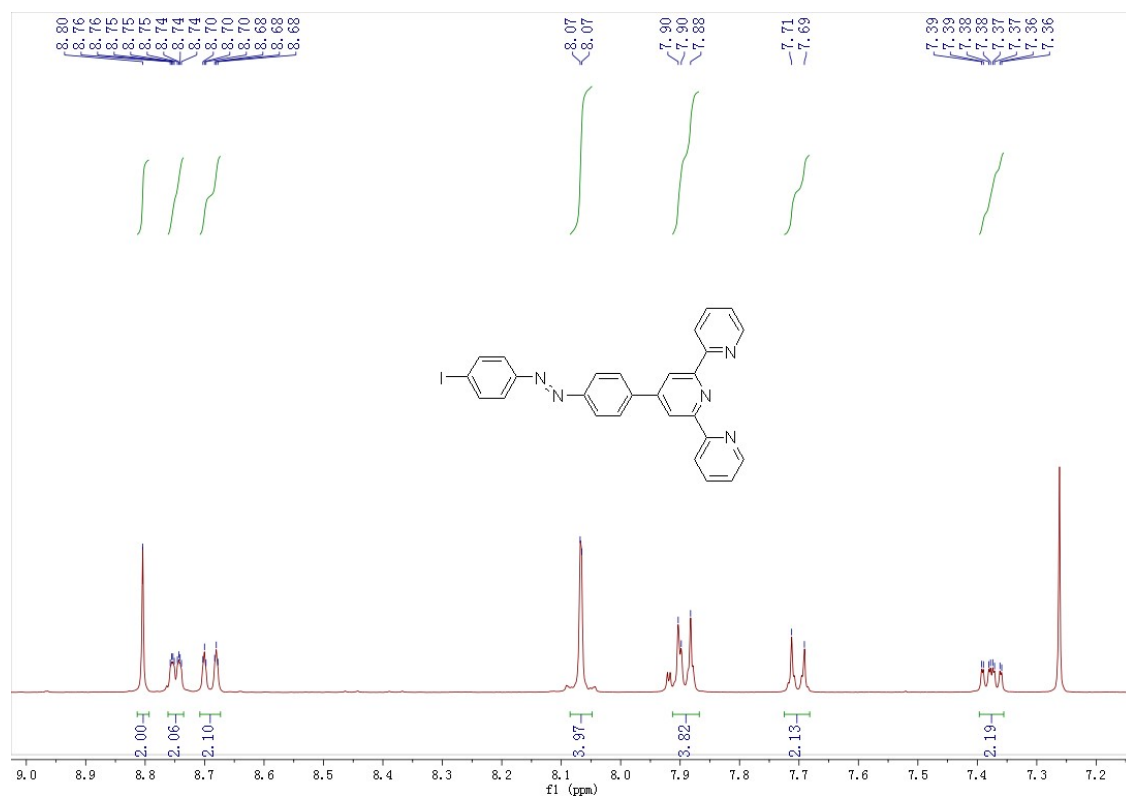


Figure S21. ^1H NMR spectrum of compound 9 (CDCl_3)

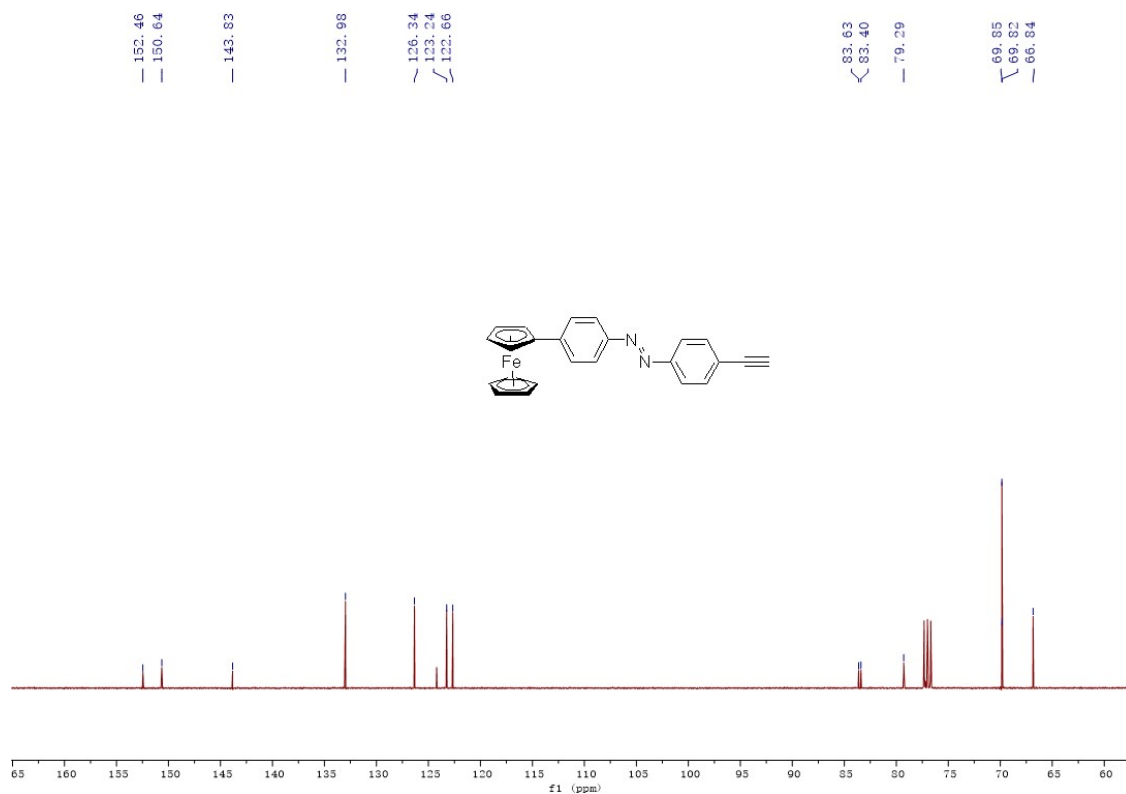


Figure S24. ¹³C NMR spectrum of compound 12 (CDCl₃)

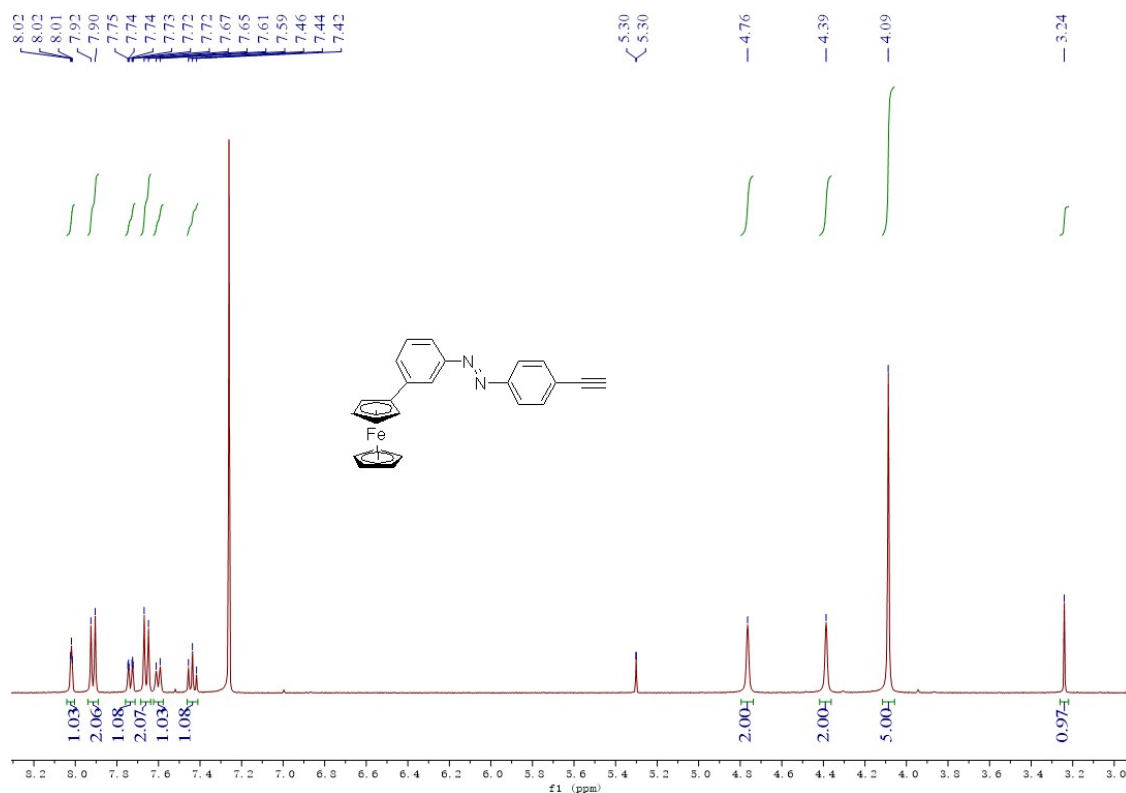


Figure S25. ¹H NMR spectrum of compound 13 (CDCl₃)

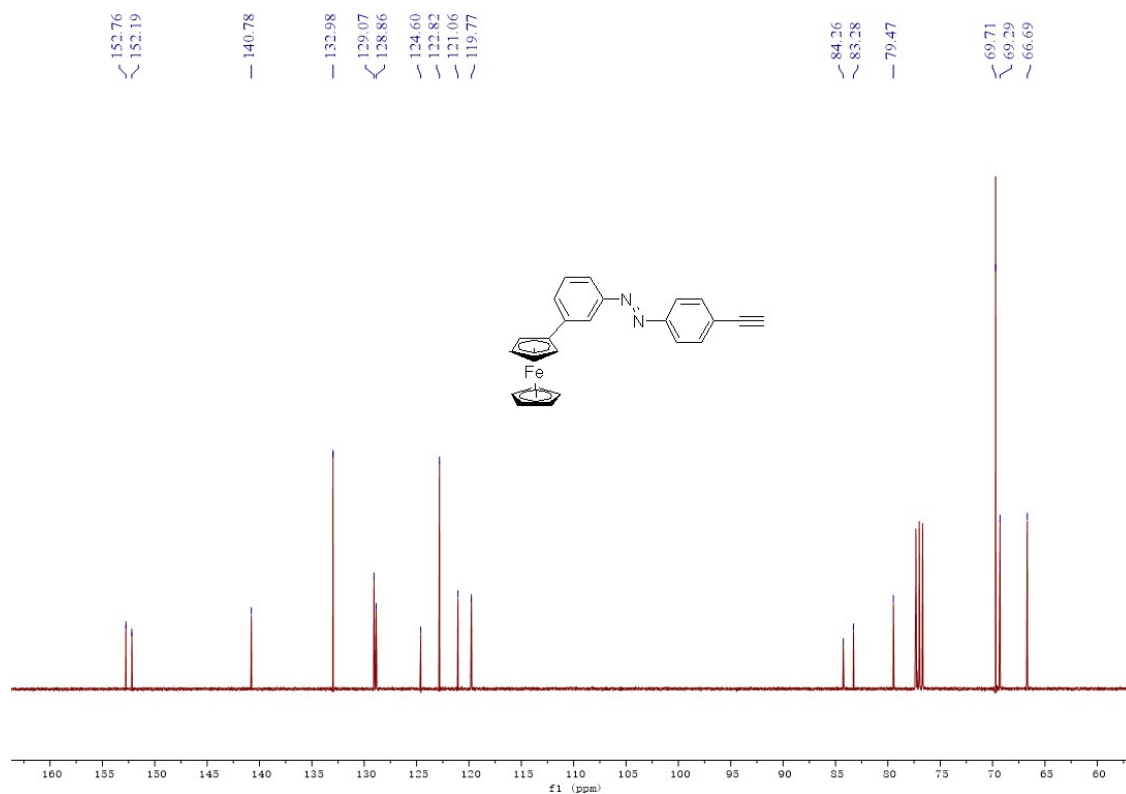


Figure S26. ¹³C NMR spectrum of compound 13 (CDCl₃)

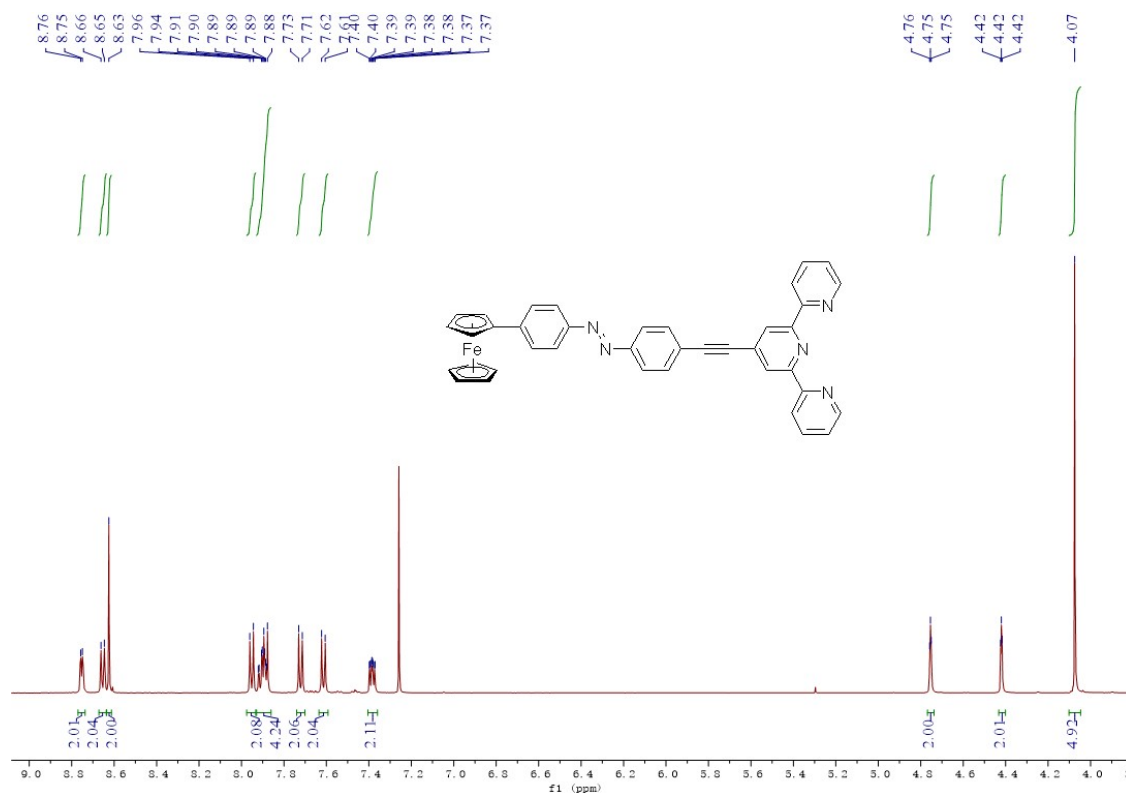


Figure S27. ¹H NMR spectrum of compound 14 (CDCl₃)

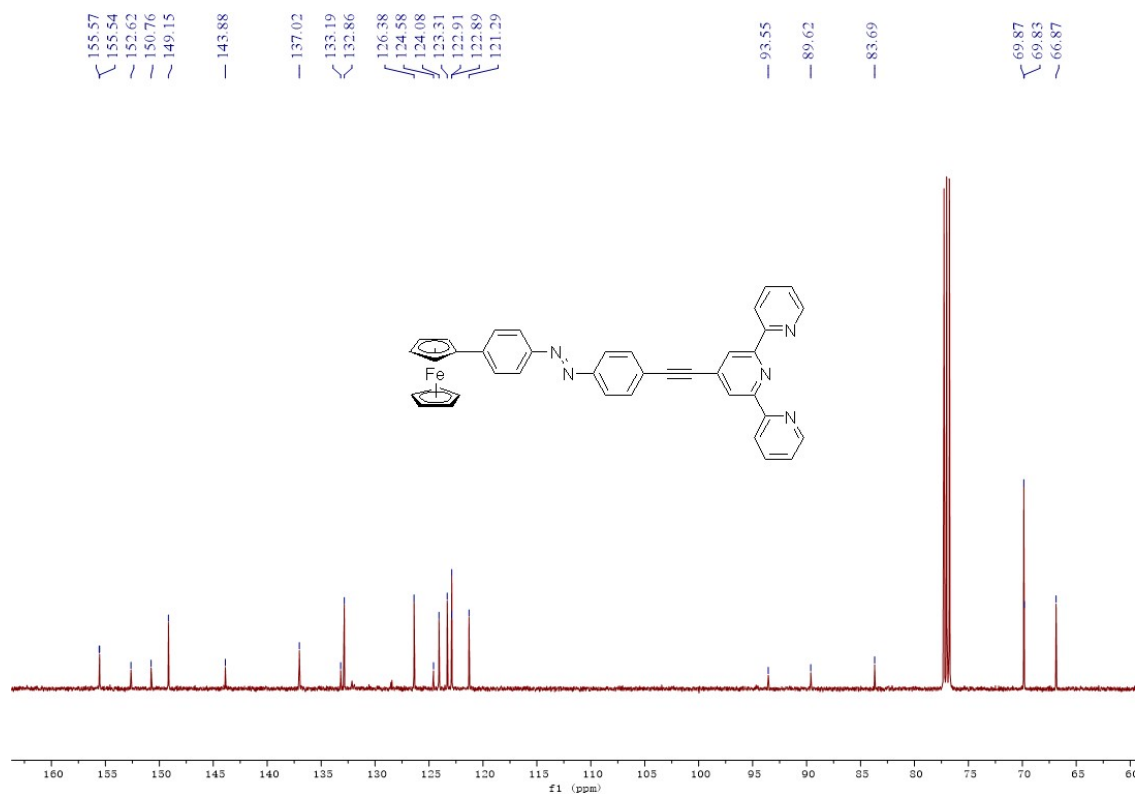


Figure S28. ¹³C NMR spectrum of compound 14 (CDCl₃)

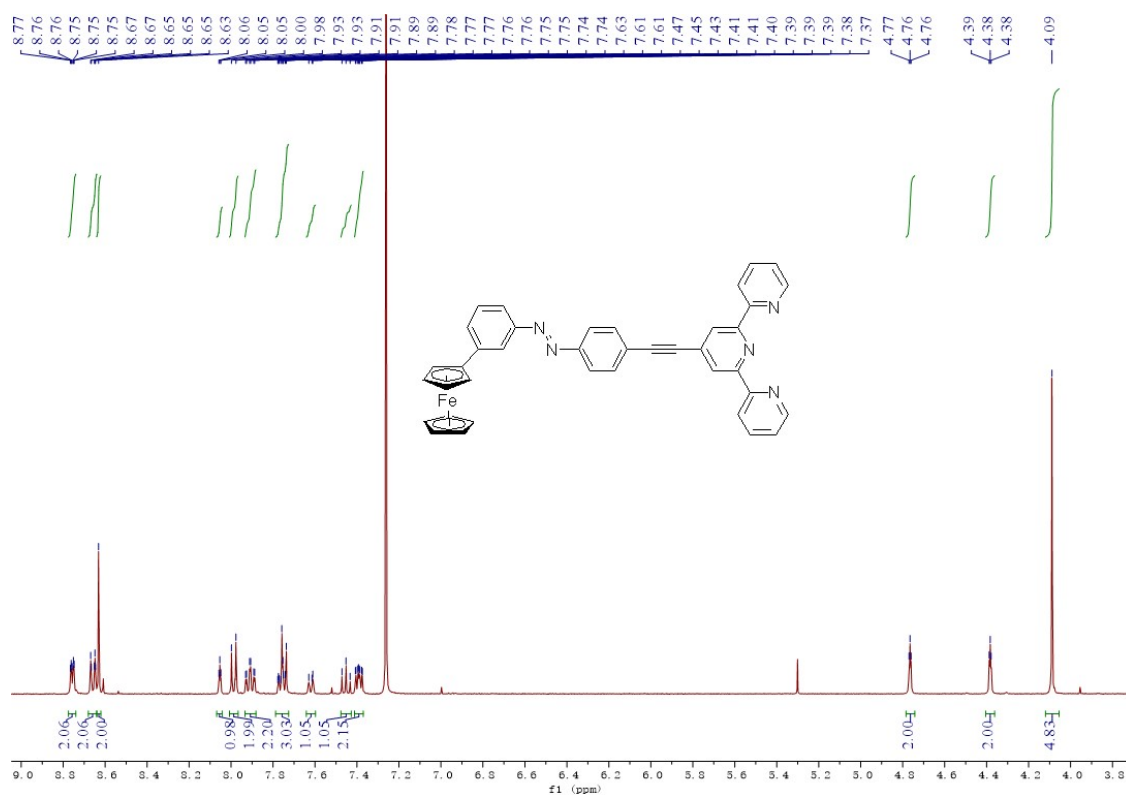


Figure S29. ¹H NMR spectrum of compound 15 (CDCl₃)

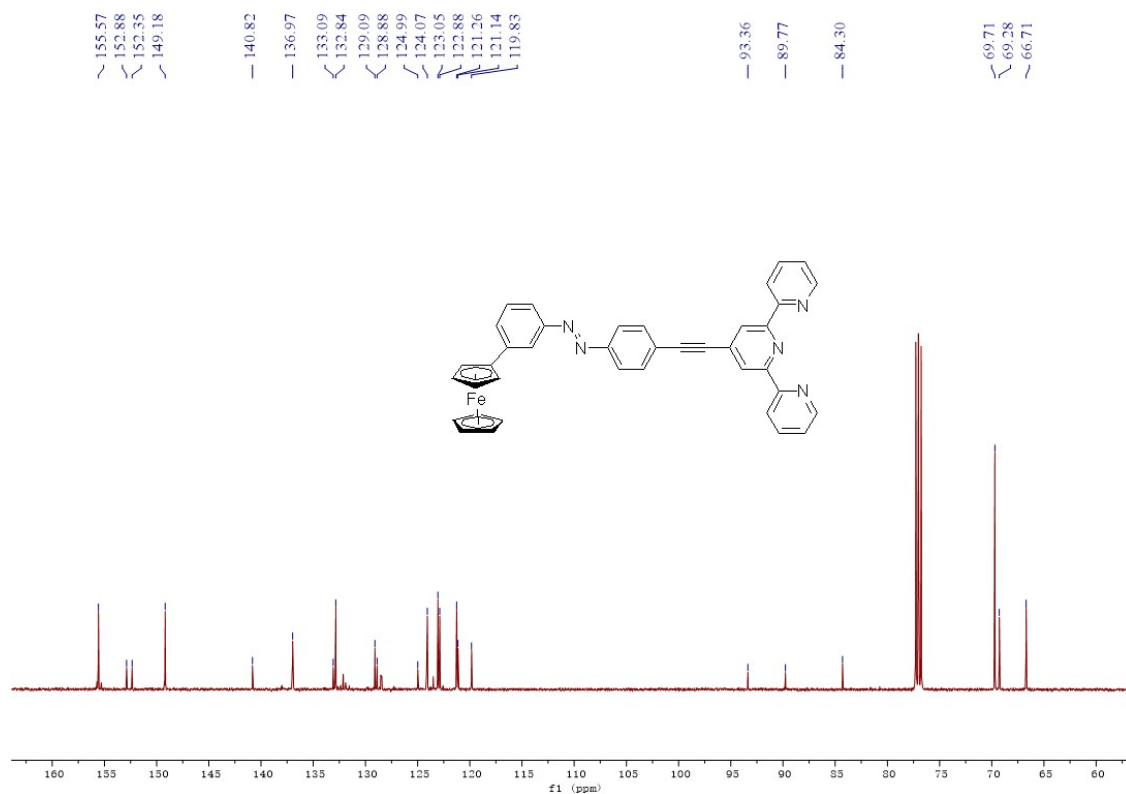


Figure S30. ^{13}C NMR spectrum of compound 15 (CDCl_3)

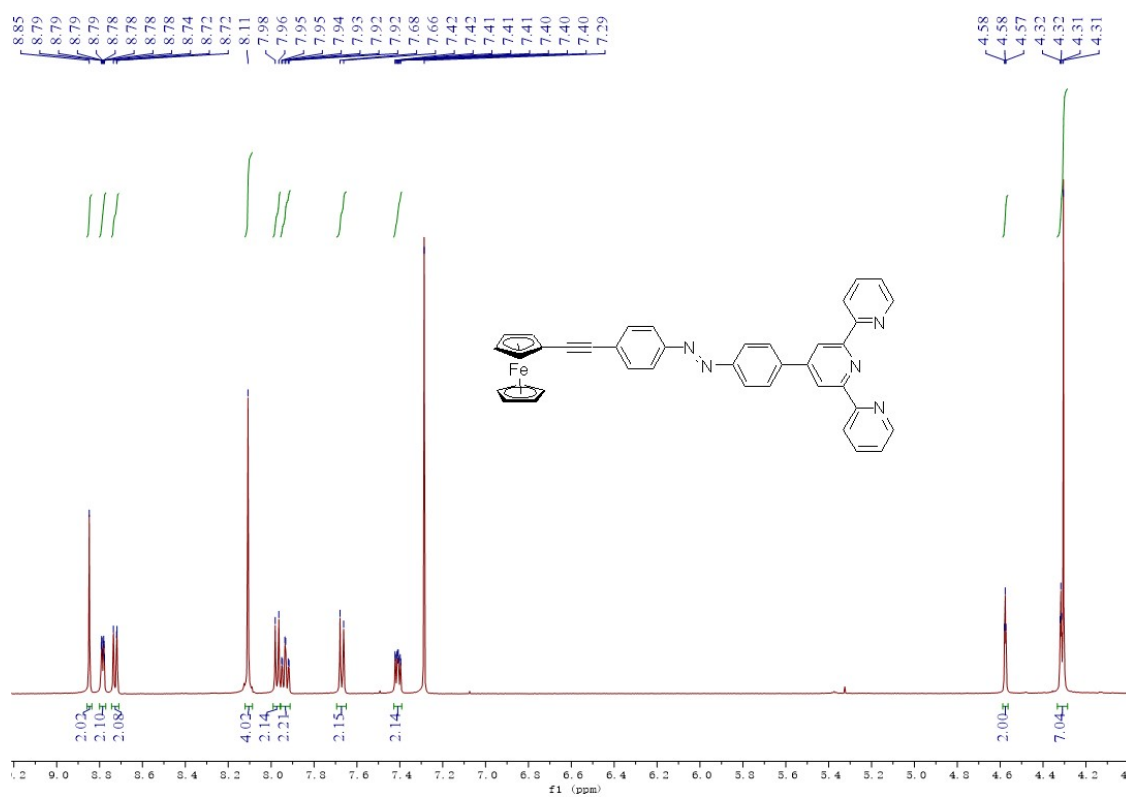


Figure S31. ^1H NMR spectrum of compound 16 (CDCl_3)

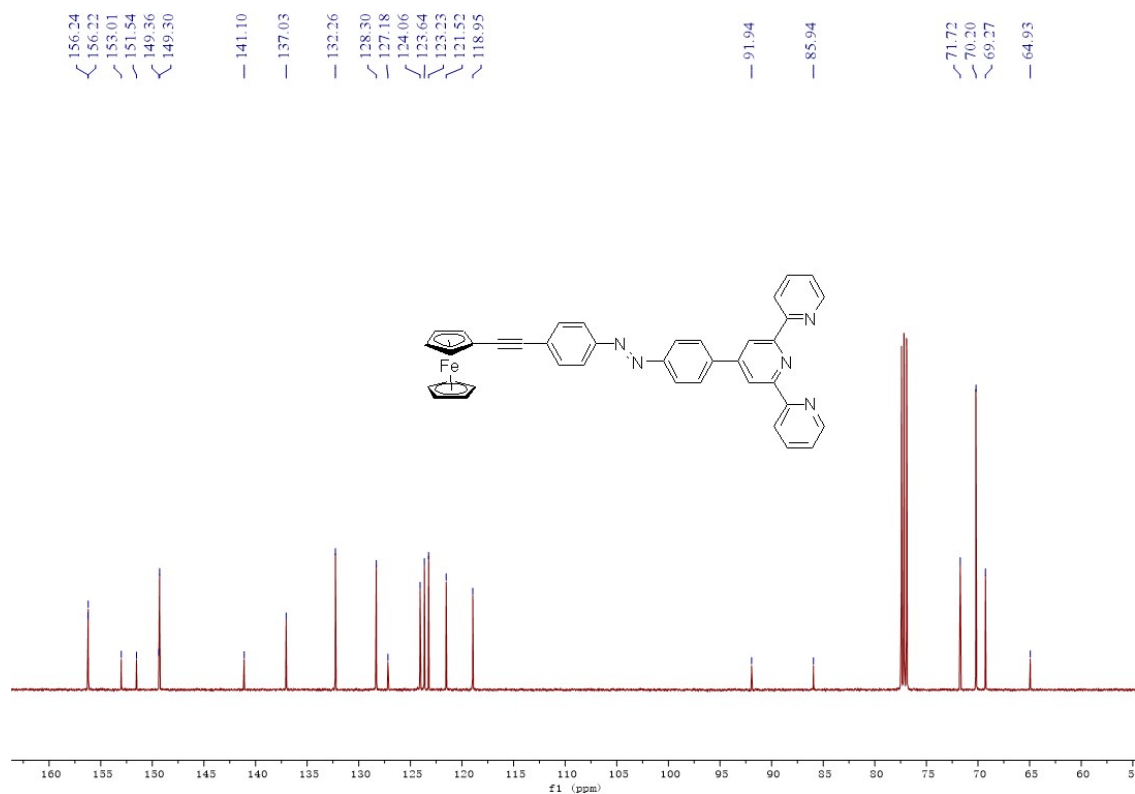


Figure S32. ¹³C NMR spectrum of compound 16 (CDCl₃)

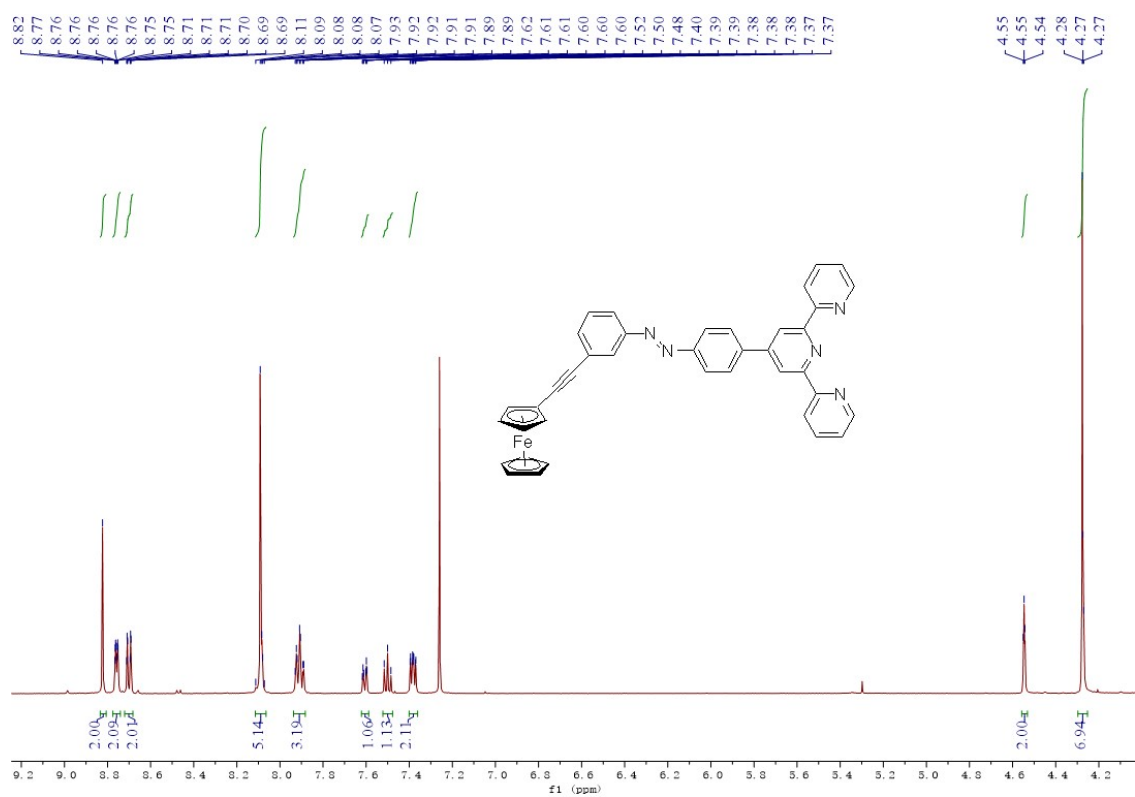


Figure S33. ¹H NMR spectrum of compound 17 (CDCl₃)

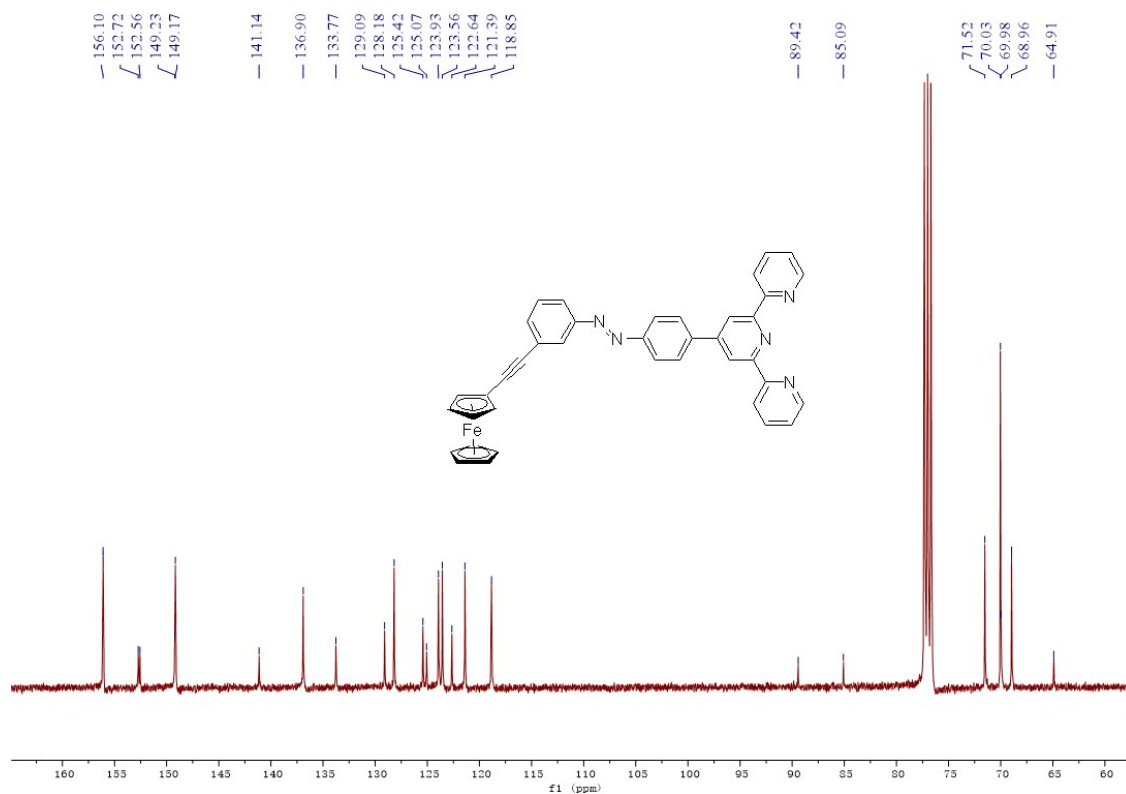


Figure S34. ^{13}C NMR spectrum of compound **17** (CDCl_3)