

Supporting Information

for

In situ synthesis of hexadentate cyclometalated Ir(III) complexes as photocatalysts for the oxidation of sulfides into sulfoxides in water

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S1. NMR and MS Figures for Ir(III) Complexes

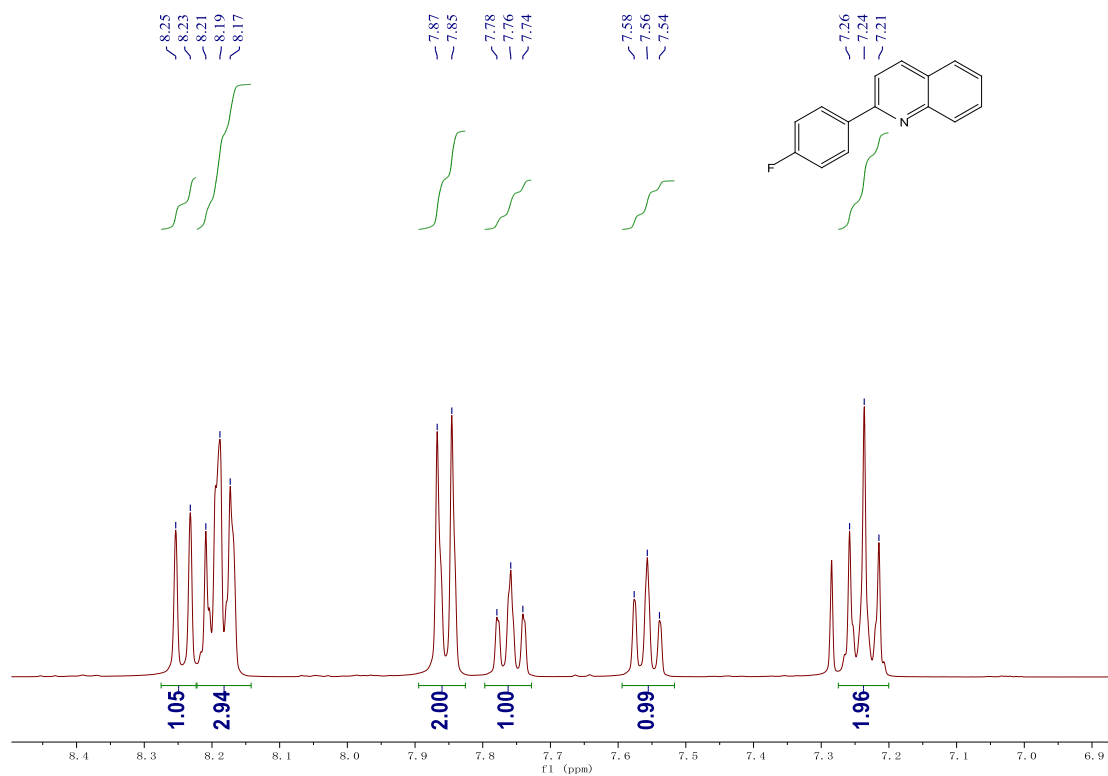


Figure S1. ¹H NMR spectra of fpq in CDCl₃.

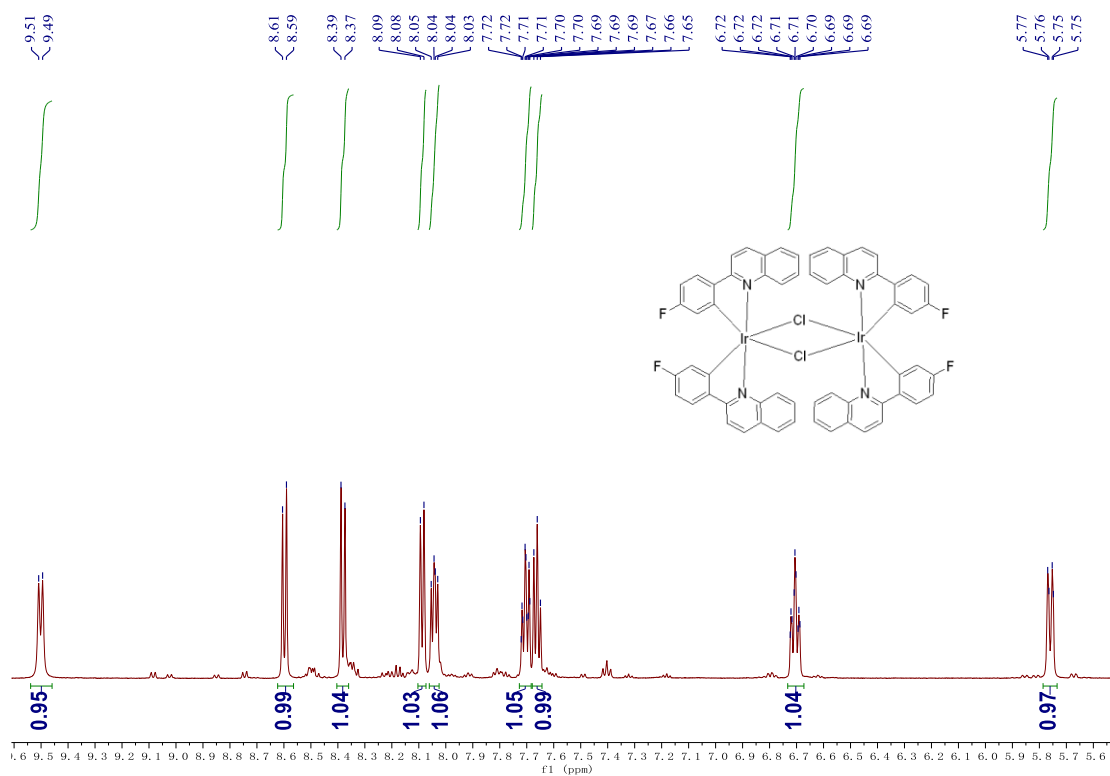


Figure S2. ¹H NMR spectra of [Ir(fpq)₂Cl]₂ in DMSO-*d*₆.

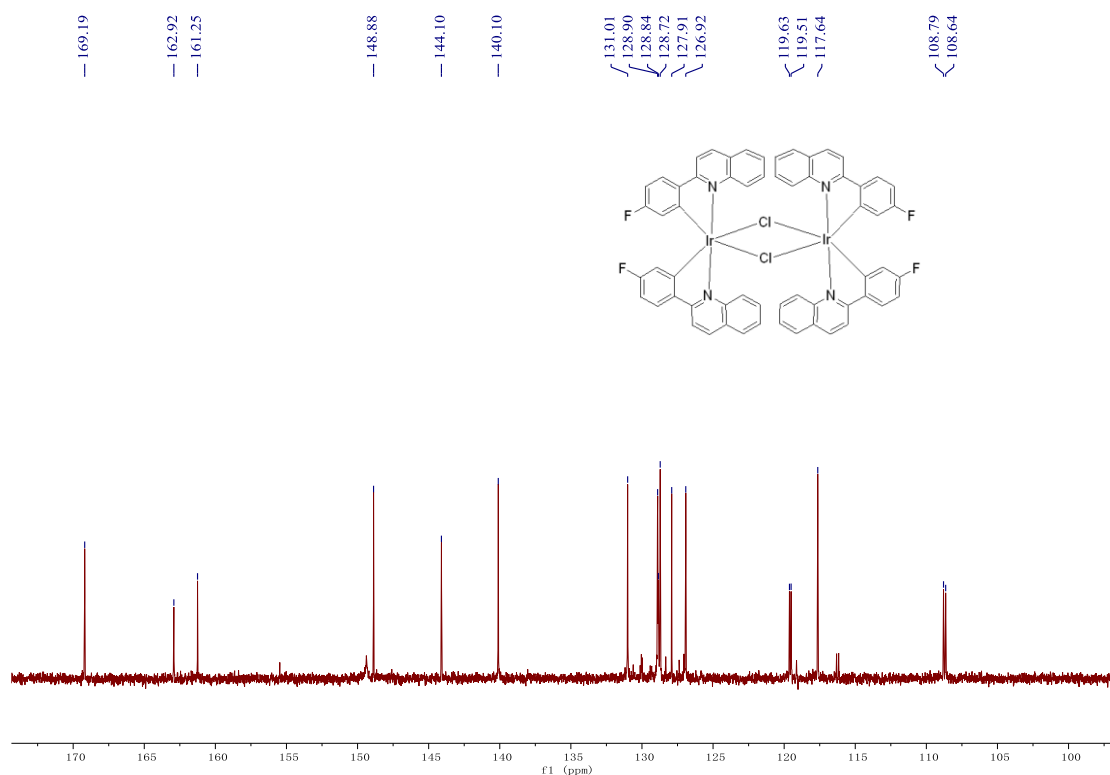
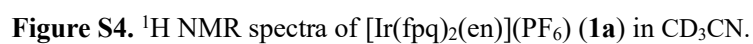


Figure S3. ¹³C NMR spectra of [Ir(fpq)₂Cl]₂ in DMSO-*d*₆.



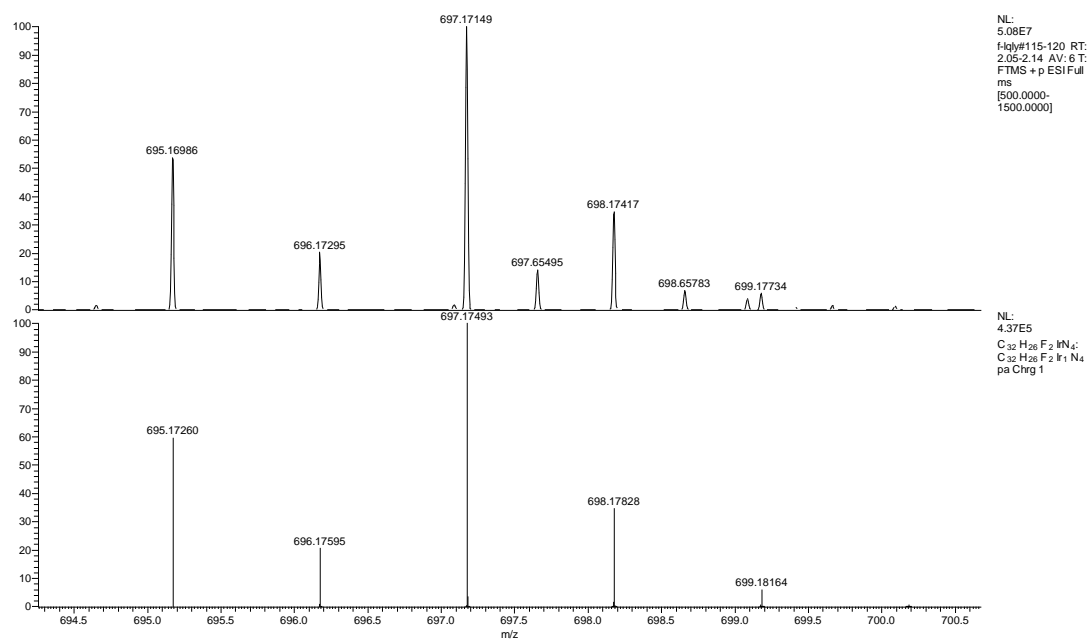


Figure S6. HRMS of $[\text{Ir}(\text{fpq})_2(\text{en})](\text{PF}_6)$ (up) and calculated for $[\text{Ir}(\text{fpq})_2(\text{en})]^+$ (down).

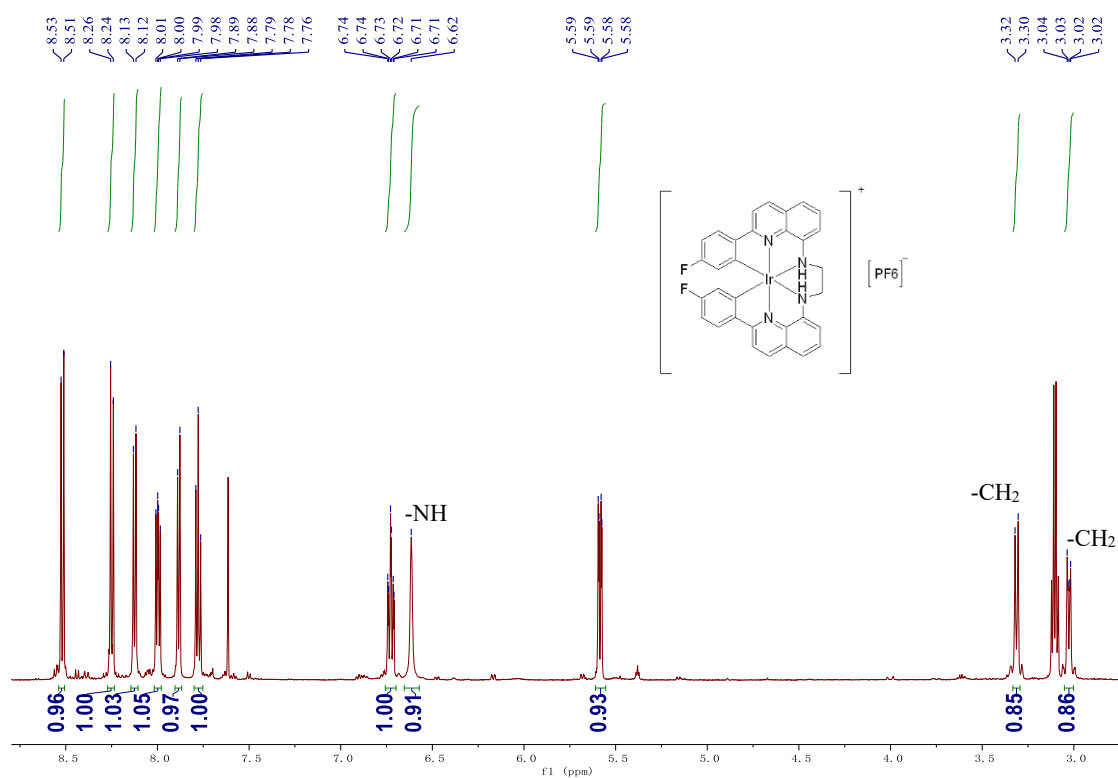


Figure S7. ¹H NMR spectra of [Ir(bfpqen)](PF₆) (1) in CD₃CN.

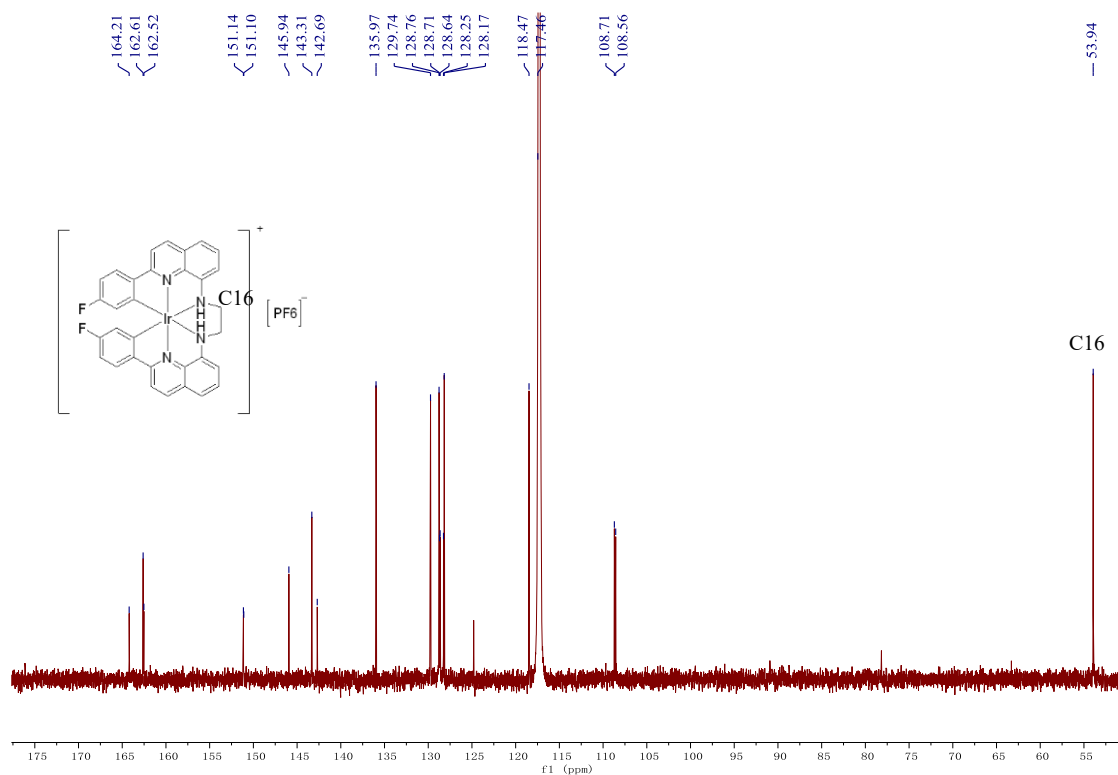


Figure S8. ¹³C NMR spectra of [Ir(bfpqen)](PF₆) (1) in CD₃CN.

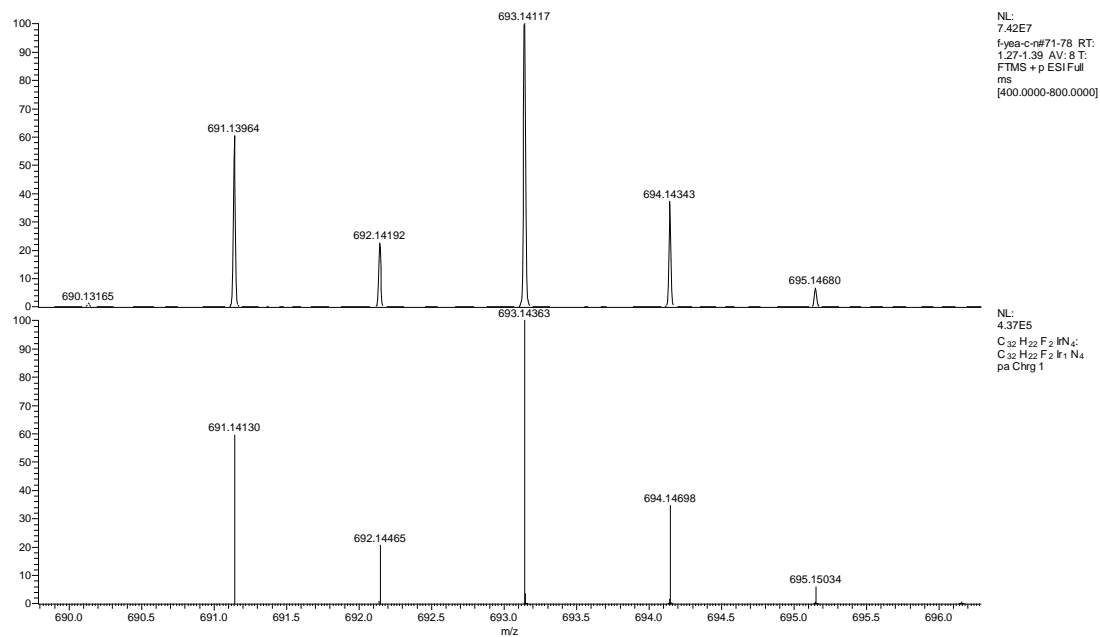


Figure S9. HRMS of $[\text{Ir}(\text{bfpqen})](\text{PF}_6)$ (up) and calculated for $[\text{Ir}(\text{bfpqen})]^+$ (down).

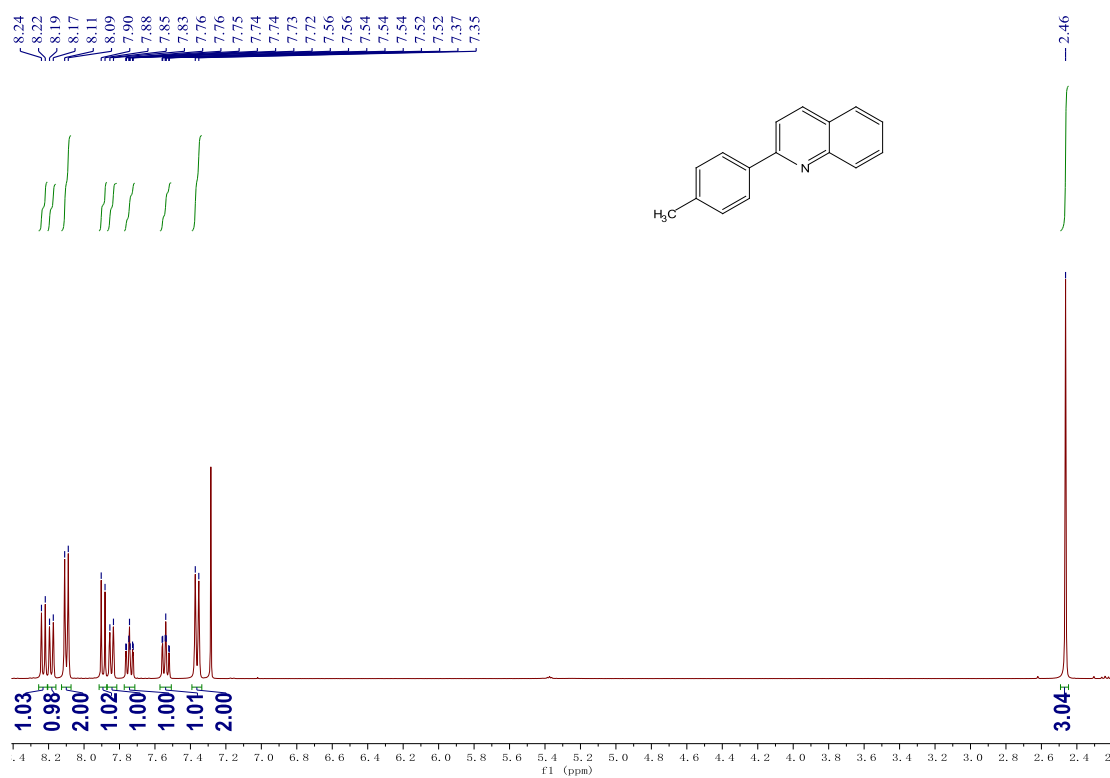


Figure S10. ^1H NMR spectra of **tq** in CDCl_3 .

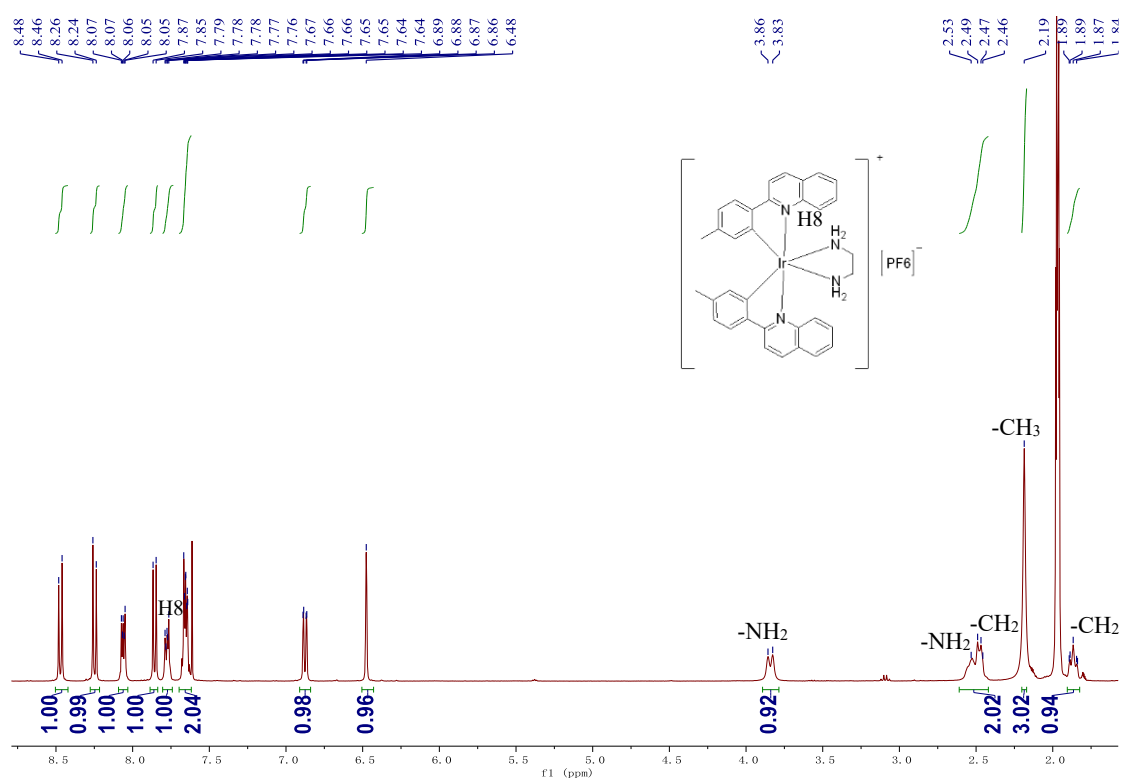


Figure S11. ¹H NMR spectra of [Ir(tq)₂(en)](PF₆) (**2a**) in CD₃CN.

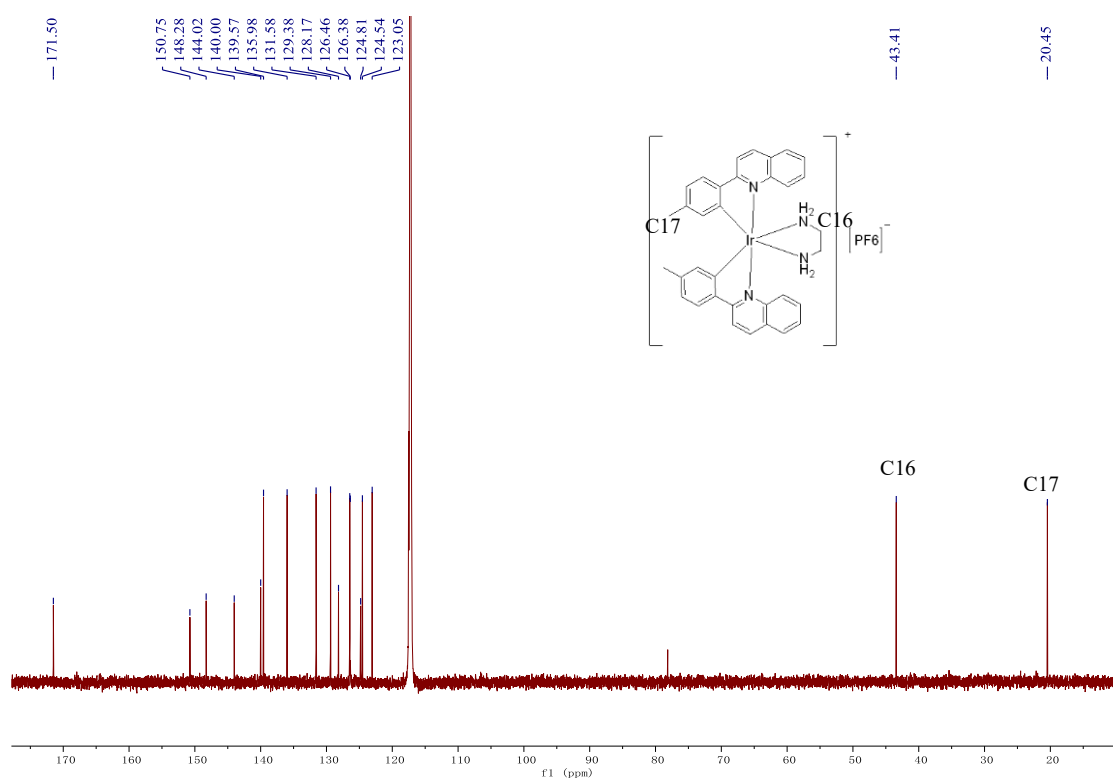


Figure S12. ¹³C NMR spectra of [Ir(tq)₂(en)](PF₆) (**2a**) in CD₃CN.

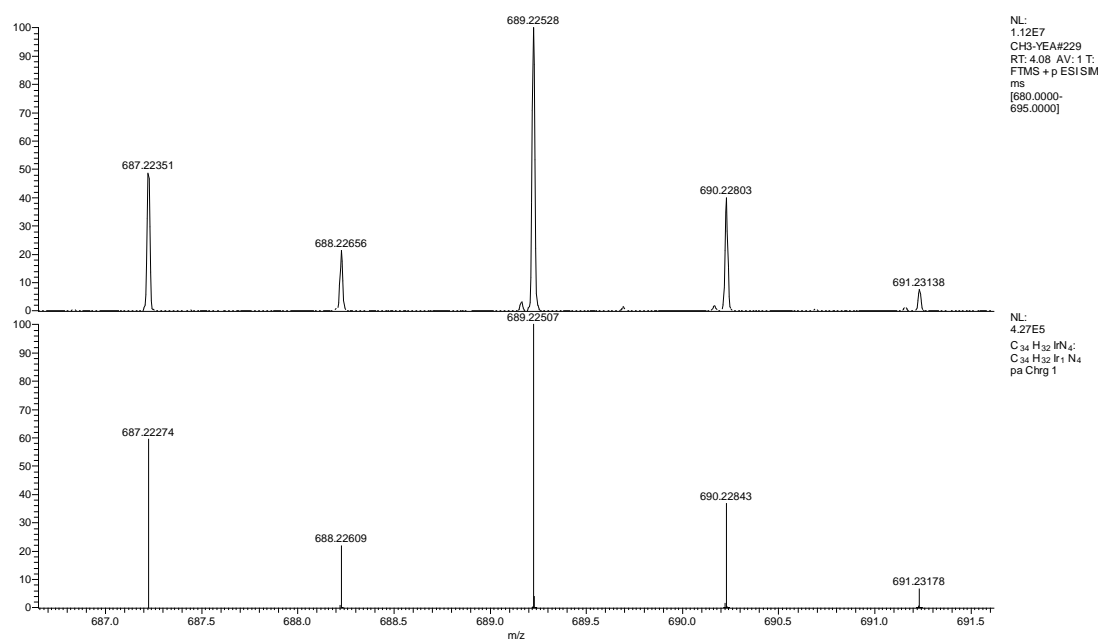


Figure S13. HRMS of $[\text{Ir}(\text{tq})_2(\text{en})](\text{PF}_6)$ (up) and calculated for $[\text{Ir}(\text{tq})_2(\text{en})]^+$ (down).

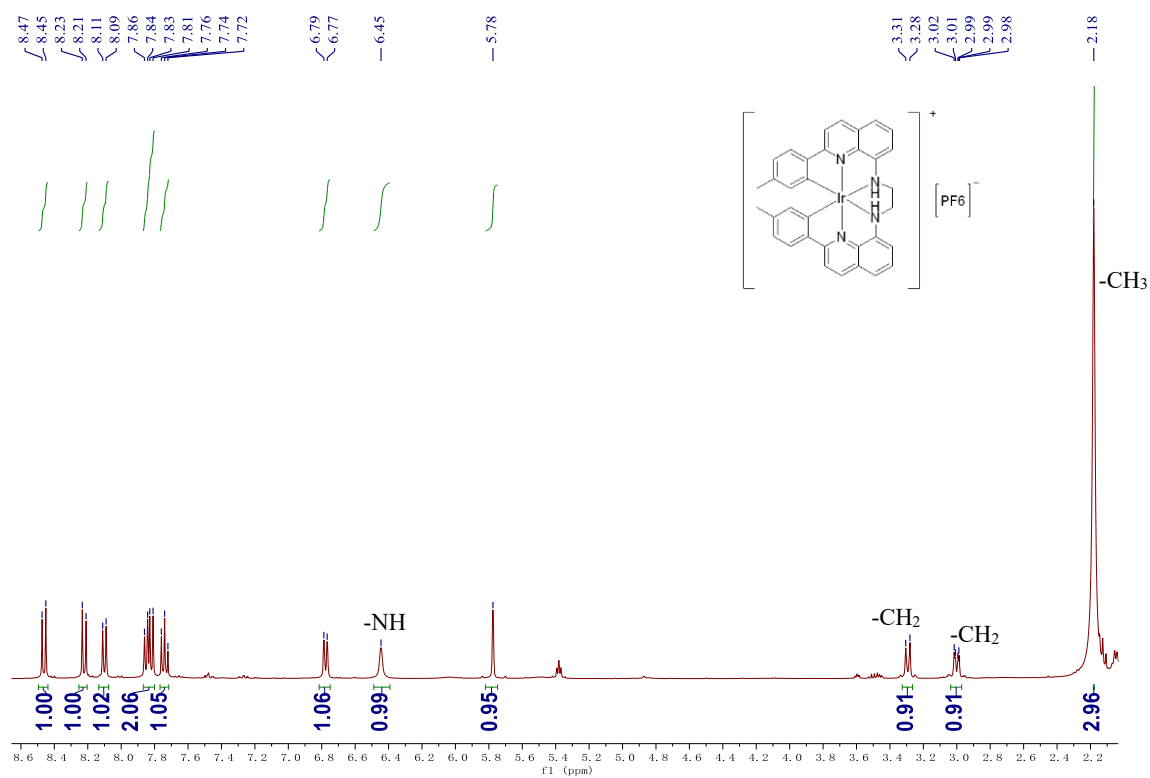


Figure S14. ^1H NMR spectra of $[\text{Ir}(\text{btqen})](\text{PF}_6)$ (2) in CD_3CN .

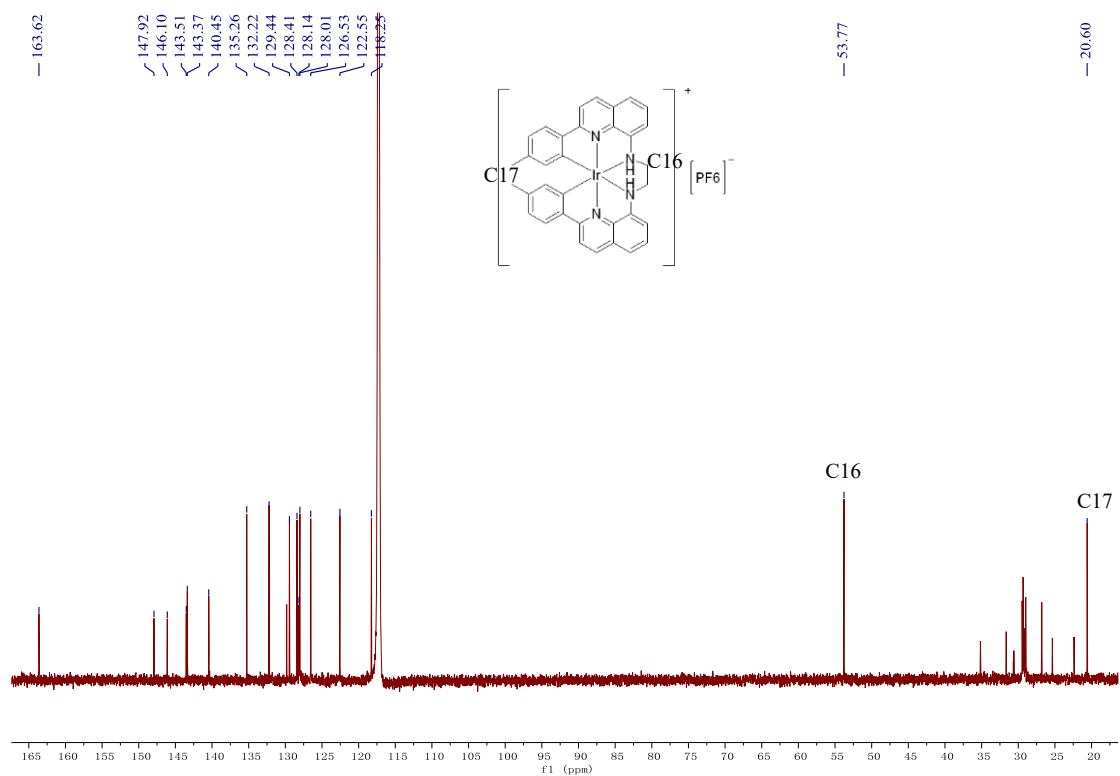


Figure S15. ^{13}C NMR spectra of $[\text{Ir}(\text{btqen})](\text{PF}_6)$ (2) in CD_3CN .

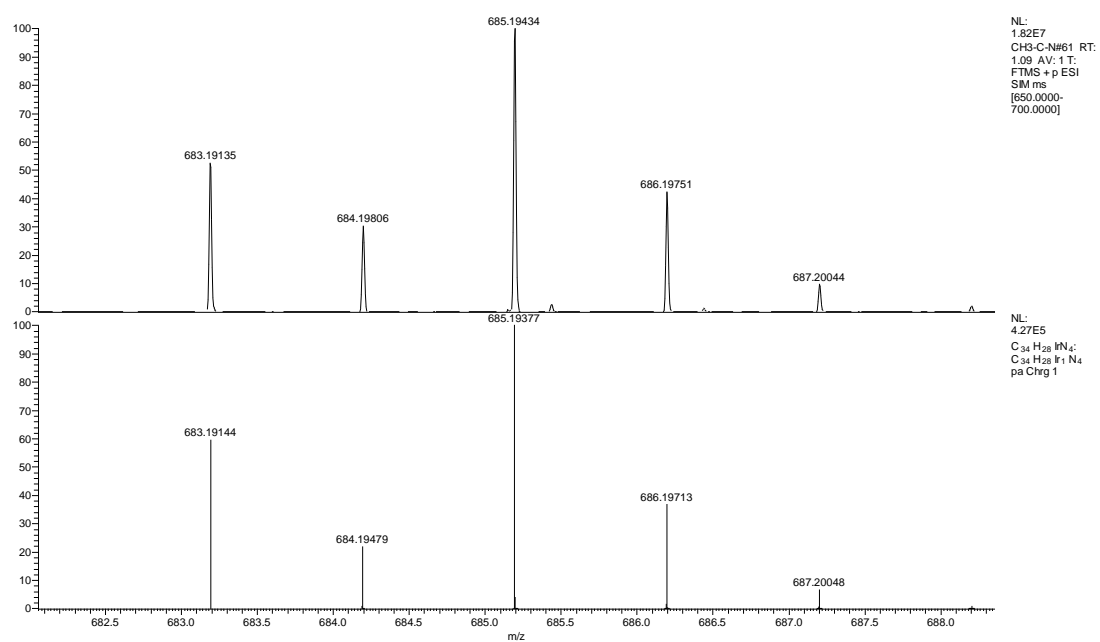


Figure S16. HRMS of $[\text{Ir}(\text{btqen})](\text{PF}_6)$ (up) and calculated for $[\text{Ir}(\text{btqen})]^+$ (down).

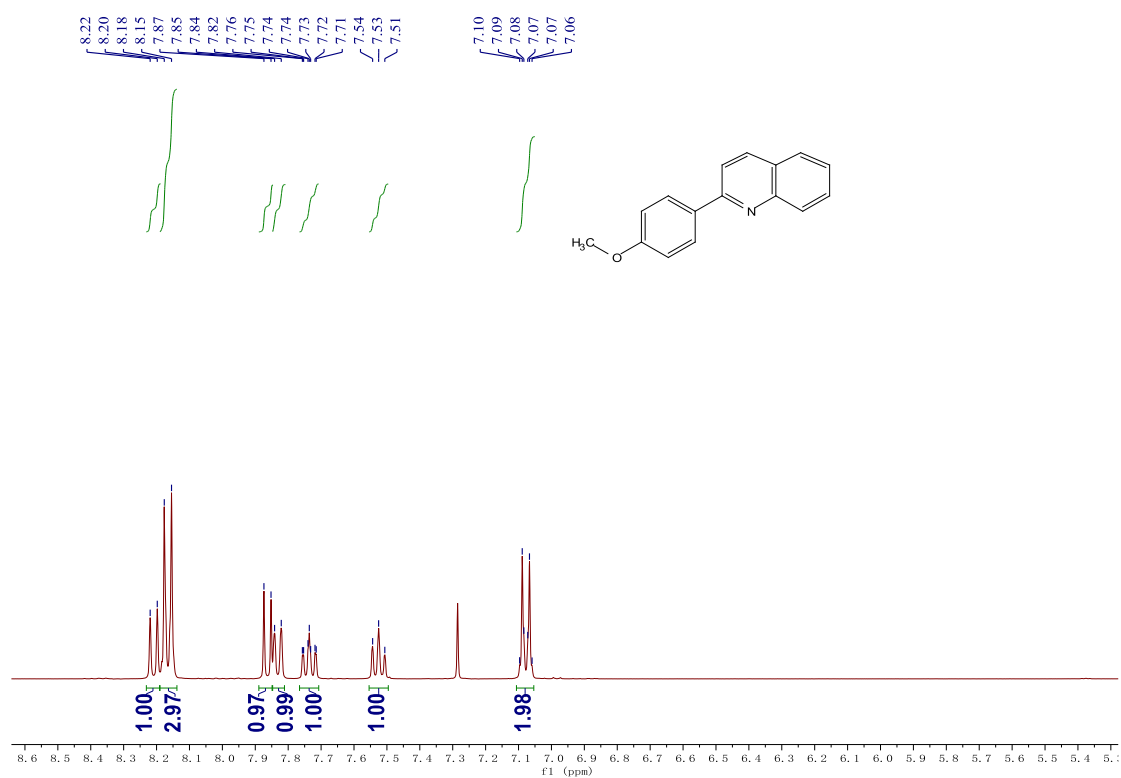


Figure S17. ¹H NMR spectra of **mpq** in CDCl₃.

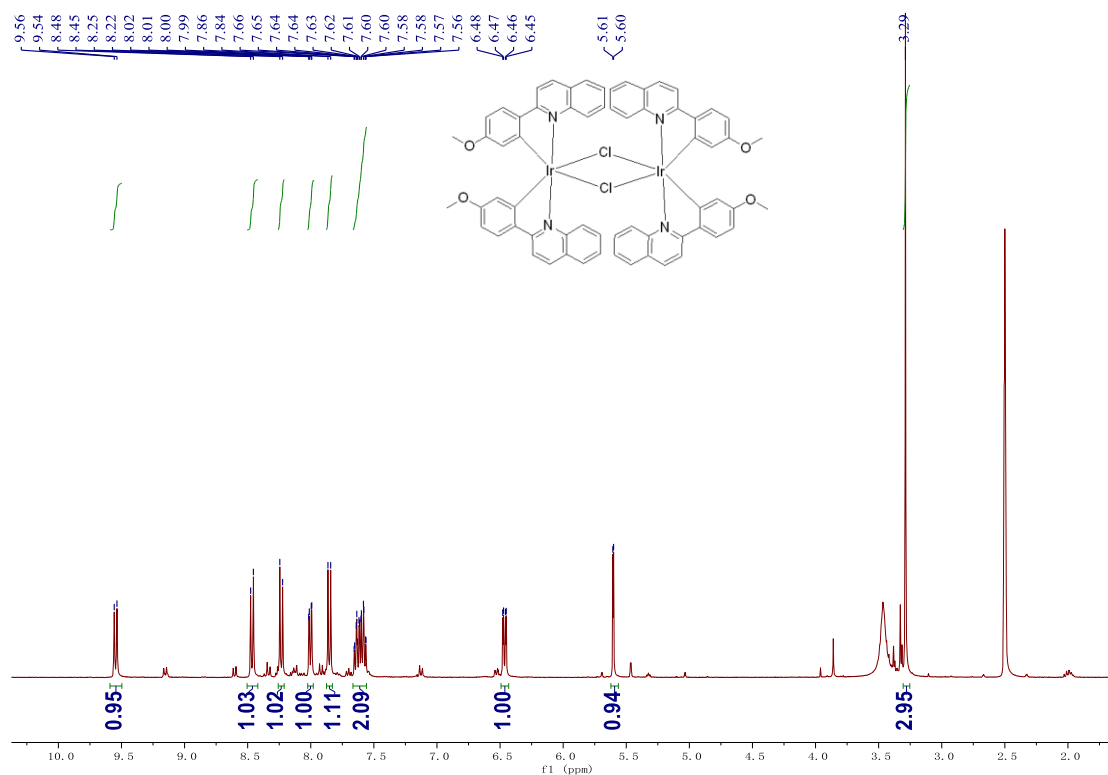


Figure S18. ¹H NMR spectra of [Ir(**mpq**)₂Cl]₂ in DMSO-*d*₆.

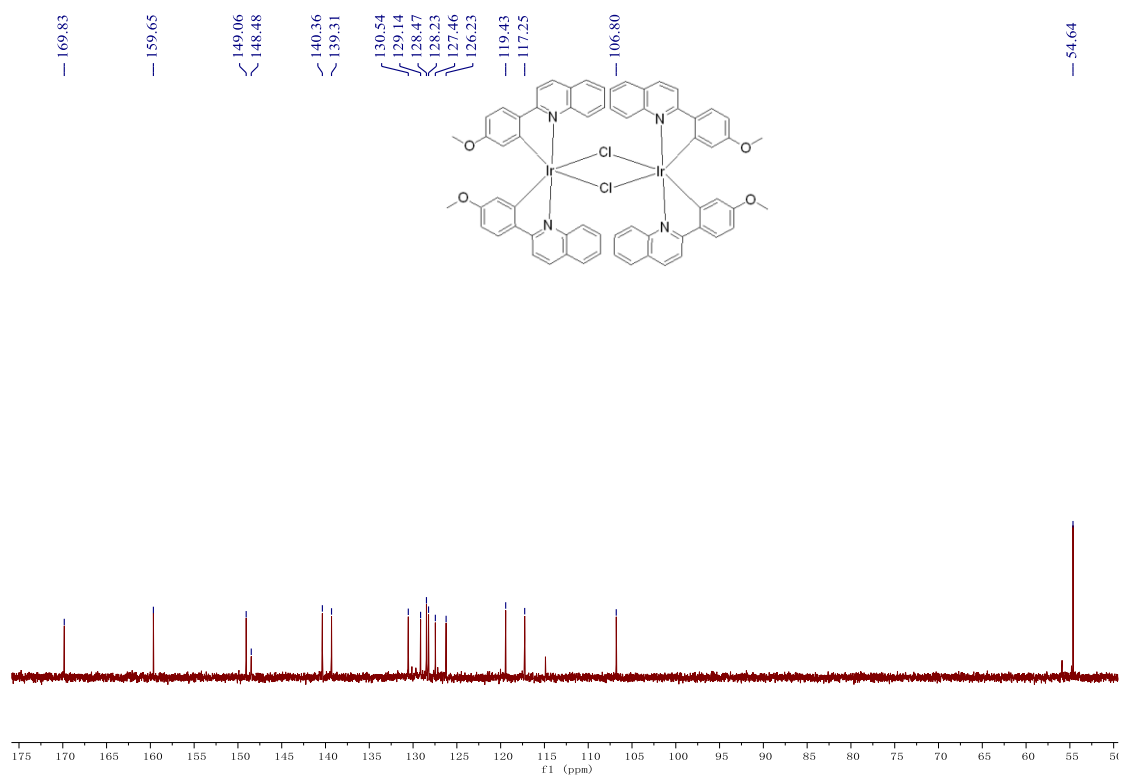


Figure S19. ¹³C NMR spectra of [Ir(mpq)₂Cl]₂ in DMSO-*d*₆.

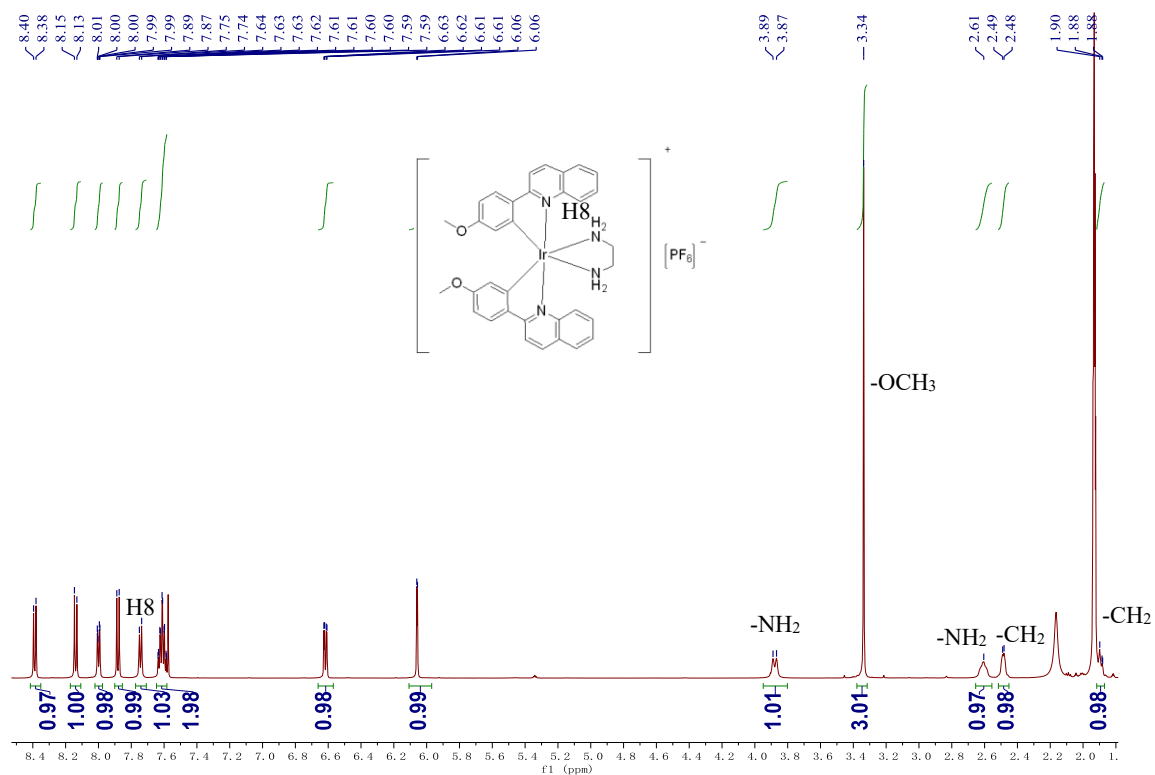


Figure S20. ¹H NMR spectra of [Ir(mpq)₂(en)](PF₆) (**3a**) in CD₃CN.

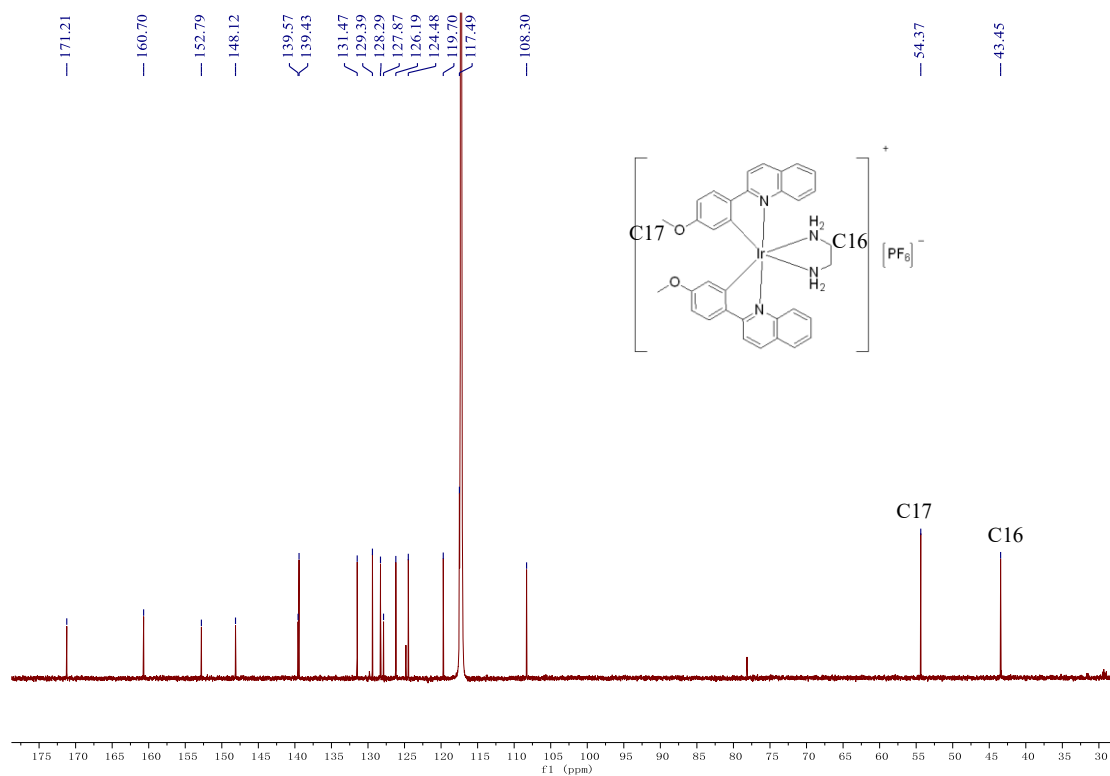


Figure S21. ^{13}C NMR spectra of $[\text{Ir}(\text{mpq})_2(\text{en})](\text{PF}_6)$ (**3a**) in CD_3CN .

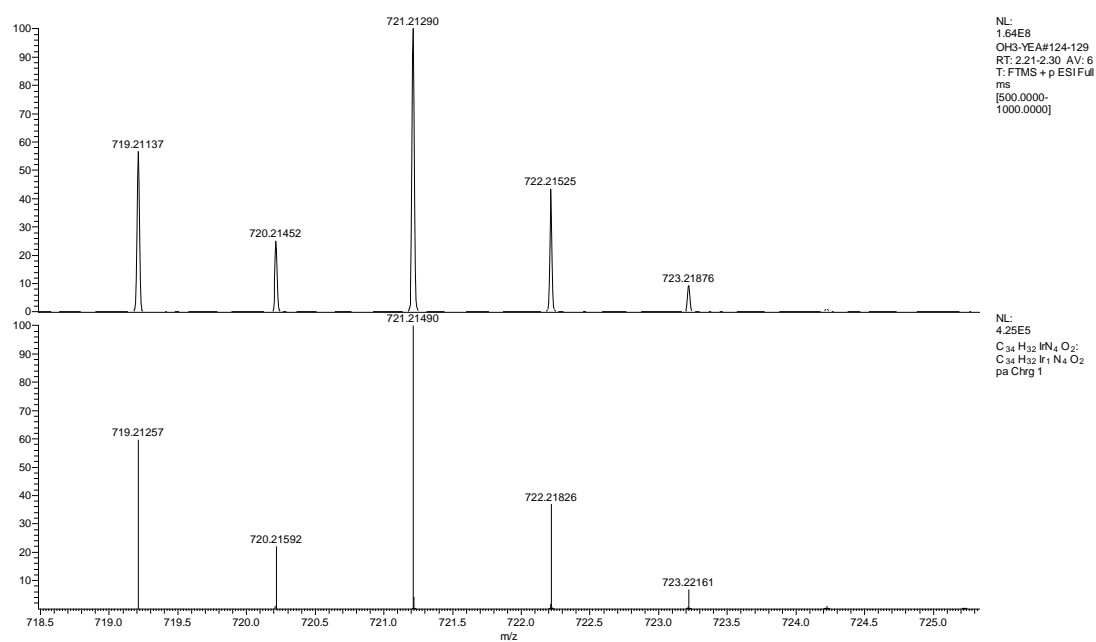


Figure S22. HRMS of $[\text{Ir}(\text{mpq})_2(\text{en})](\text{PF}_6)$ (up) and calculated for $[\text{Ir}(\text{mpq})_2(\text{en})]^+$ (down).

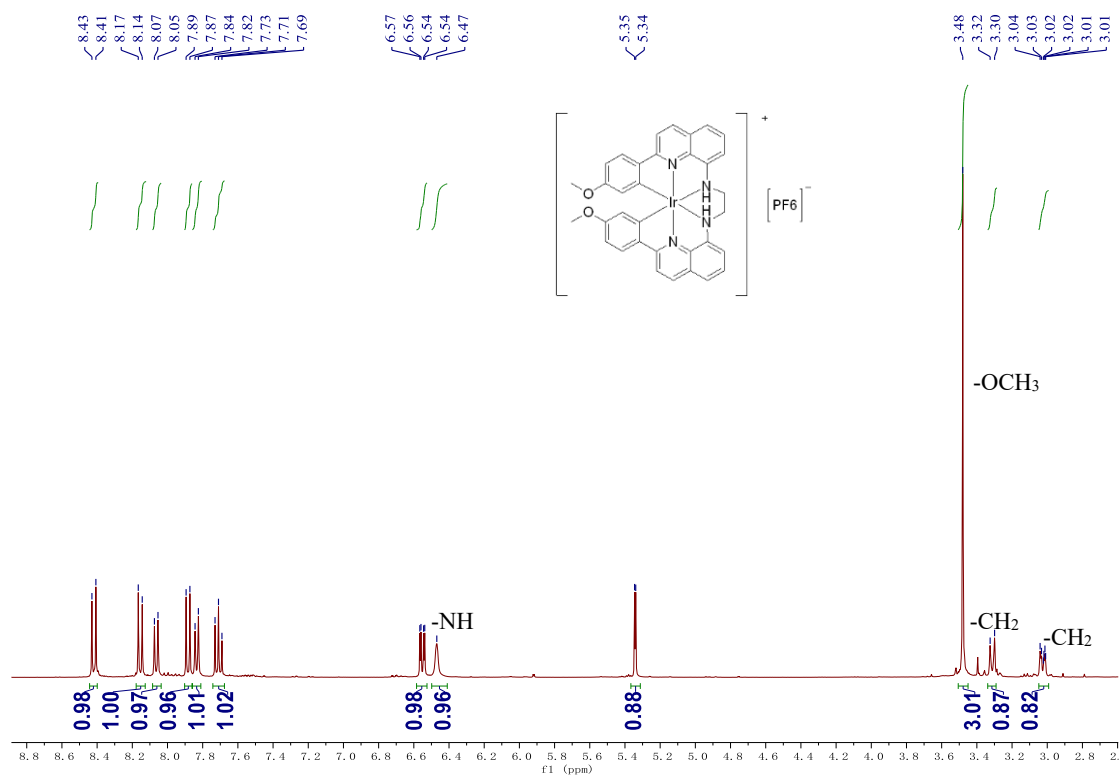


Figure S23. ^1H NMR spectra of $[\text{Ir}(\text{bmpqen})](\text{PF}_6)$ (**3**) in CD_3CN .

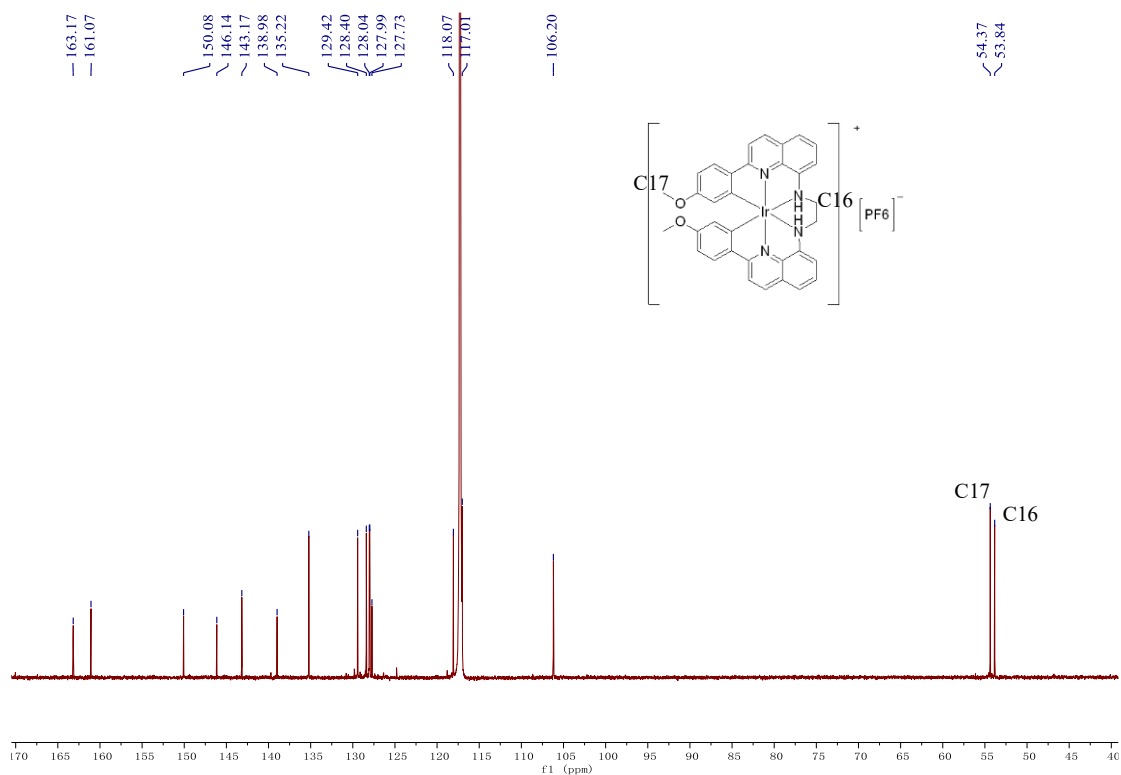


Figure S24. ^{13}C NMR spectra of $[\text{Ir}(\text{bmpqen})](\text{PF}_6)$ (**3**) in CD_3CN .

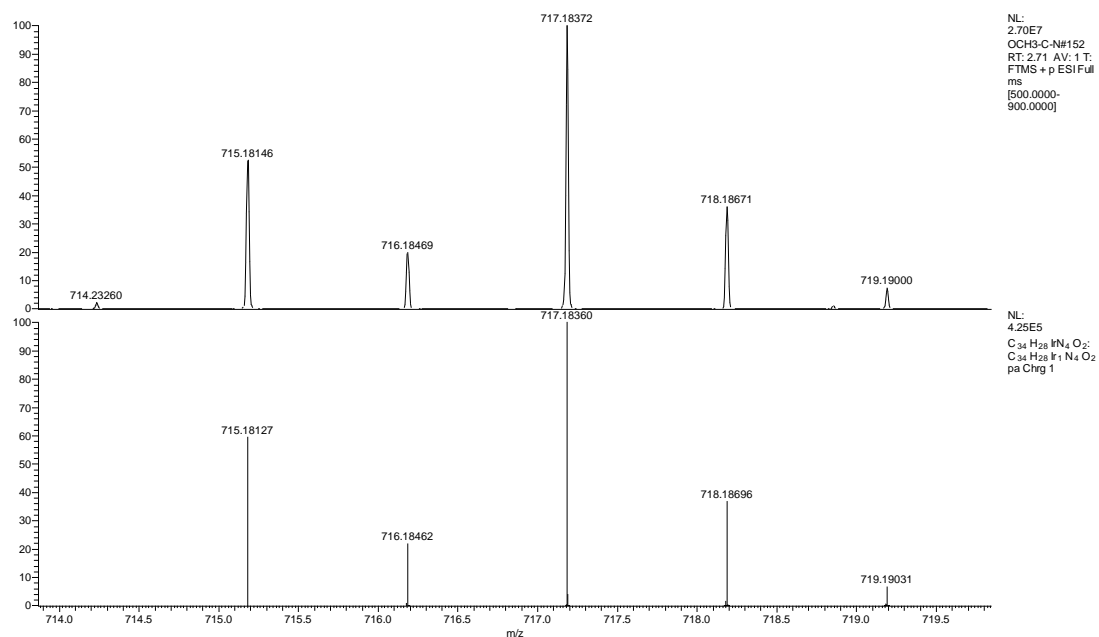


Figure S25. HRMS of [Ir(bmpqen)](PF₆) (up) and calculated for [Ir(bmpqen)]⁺ (down).

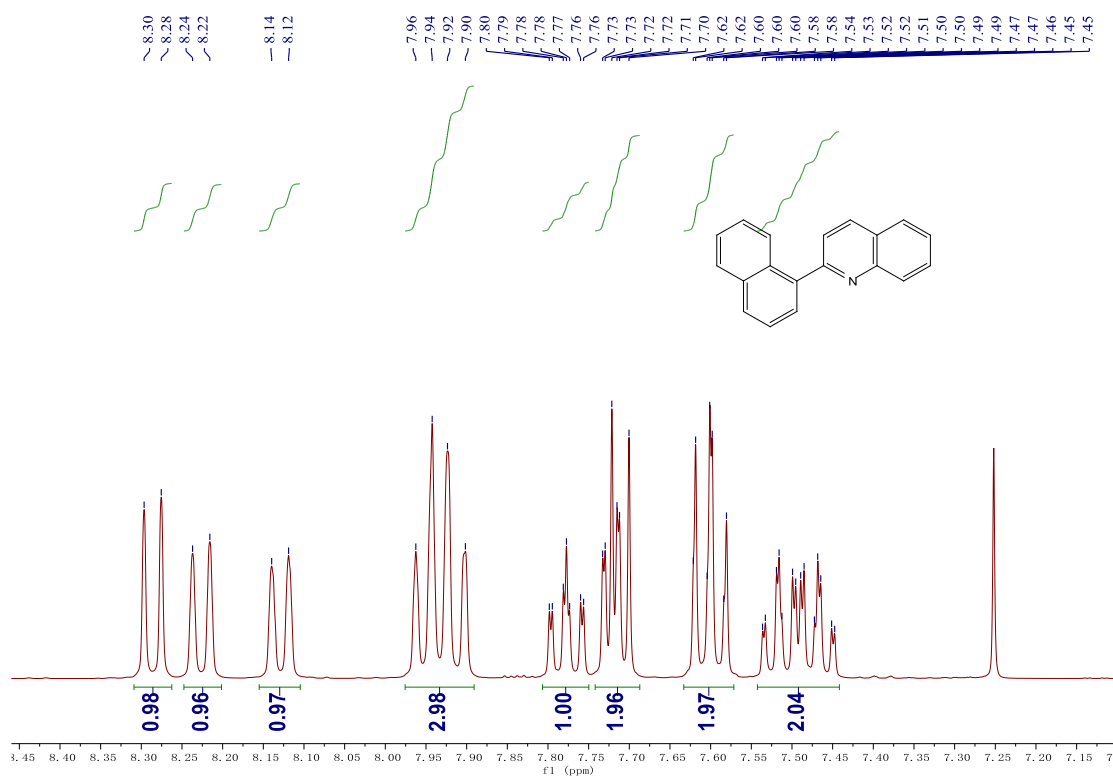


Figure S26. ¹H NMR spectra of **nq** in CDCl₃.

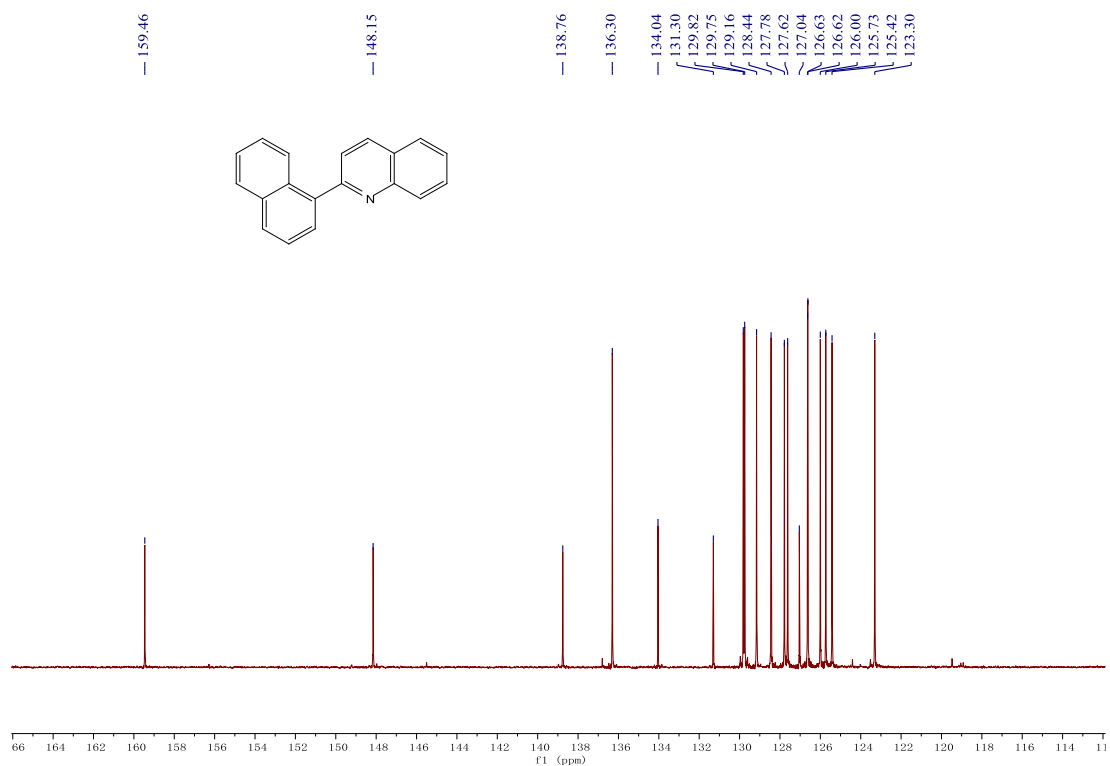


Figure S27. ¹³C NMR spectra of **nq** in CDCl₃.

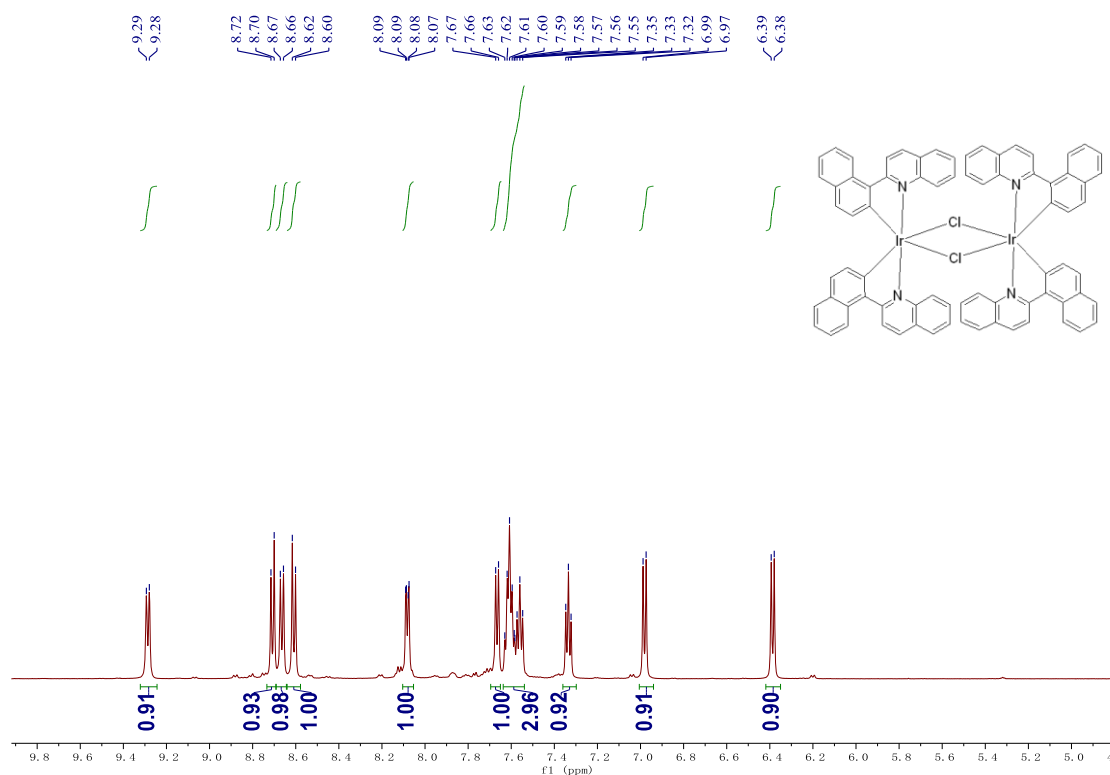


Figure S28. ¹H NMR spectra of **[Ir(nq)₂Cl]₂** in DMSO-*d*₆.

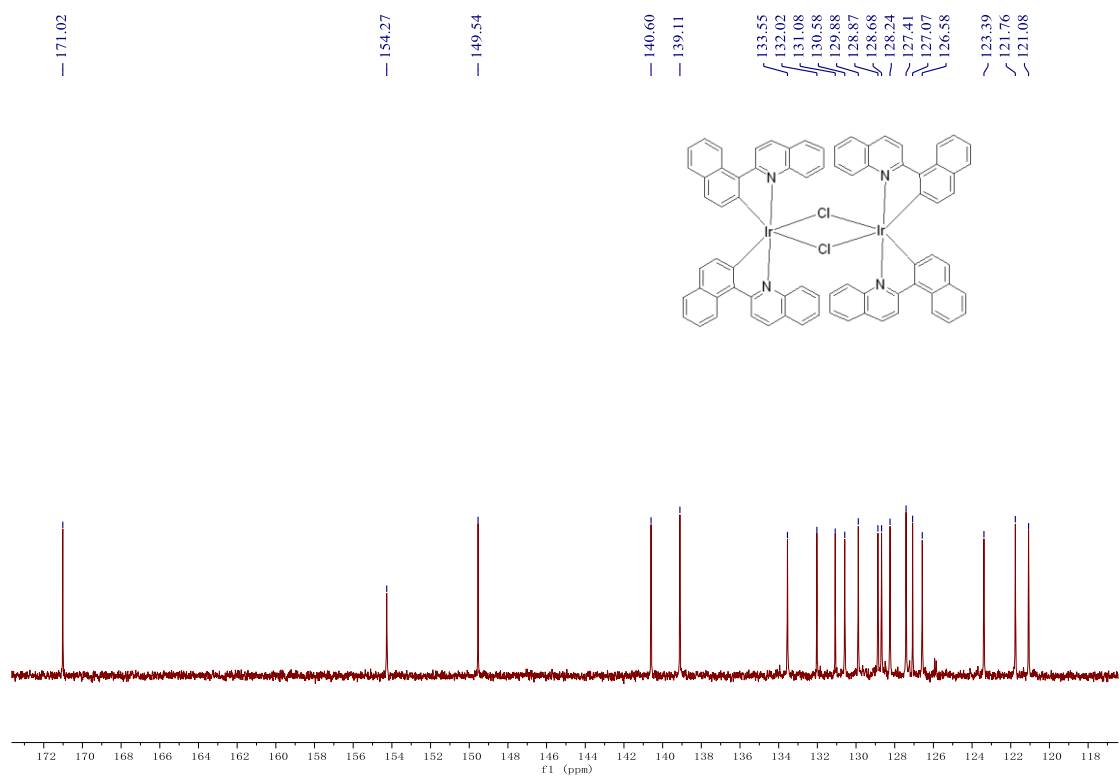


Figure 29. ¹³C NMR spectra of [Ir(nq)₂Cl]₂ in DMSO-*d*₆.

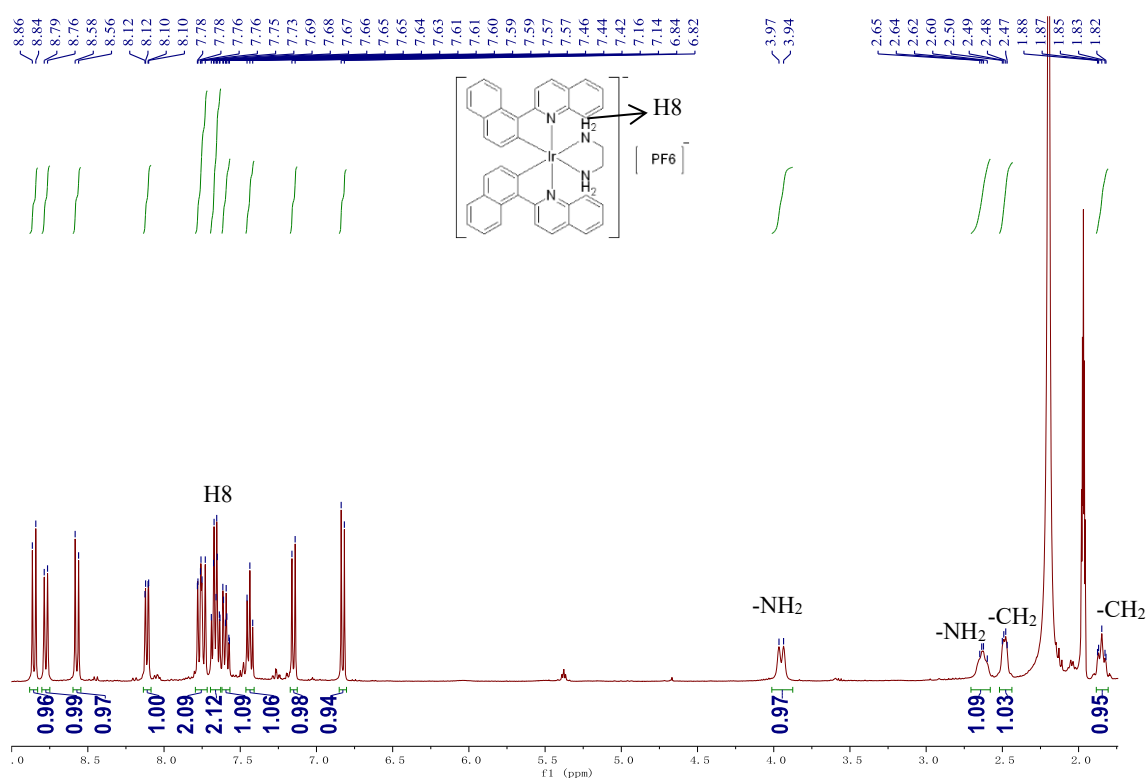


Figure S30. ¹H NMR spectra of [Ir(nq)₂(en)](PF₆) (**4a**) in CD₃CN.

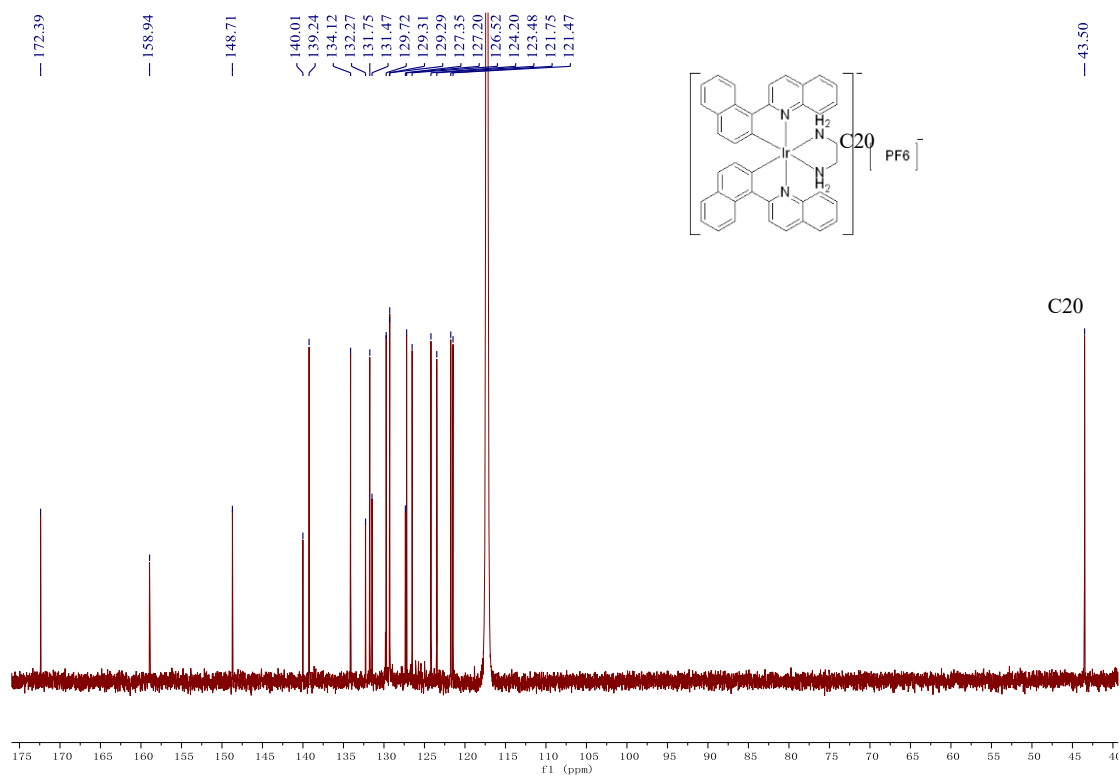


Figure S31. ^{13}C NMR spectra of $[\text{Ir}(\text{nq})_2(\text{en})](\text{PF}_6)$ (**4a**) in CD_3CN .

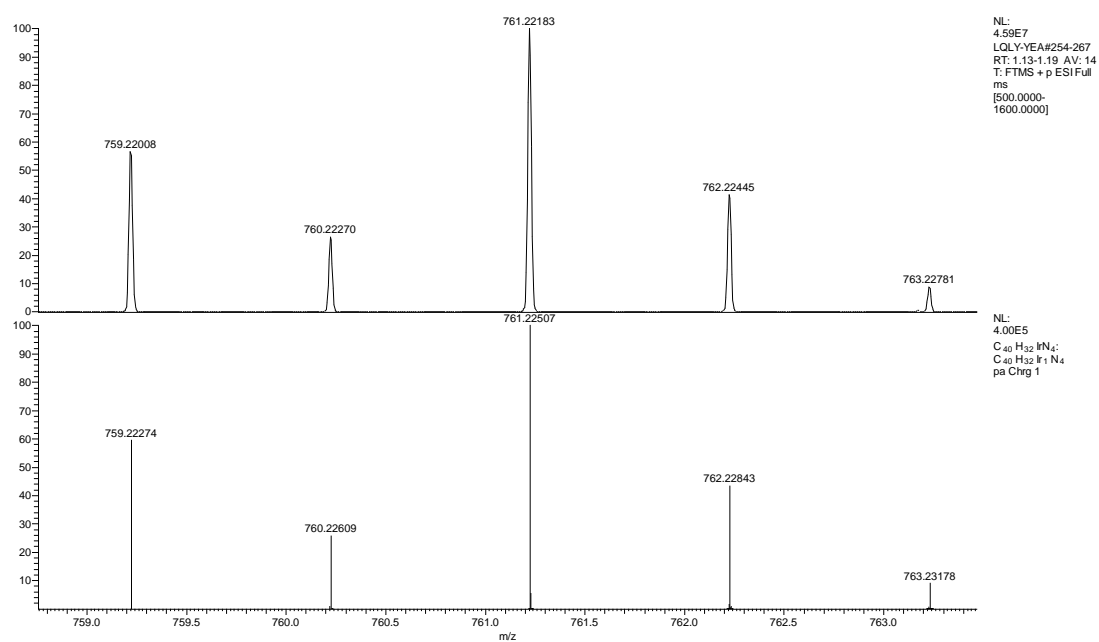


Figure S32. HRMS of $[\text{Ir}(\text{nq})_2(\text{en})](\text{PF}_6)$ (up) and calculated for $[\text{Ir}(\text{nq})_2(\text{en})]^+$ (down).

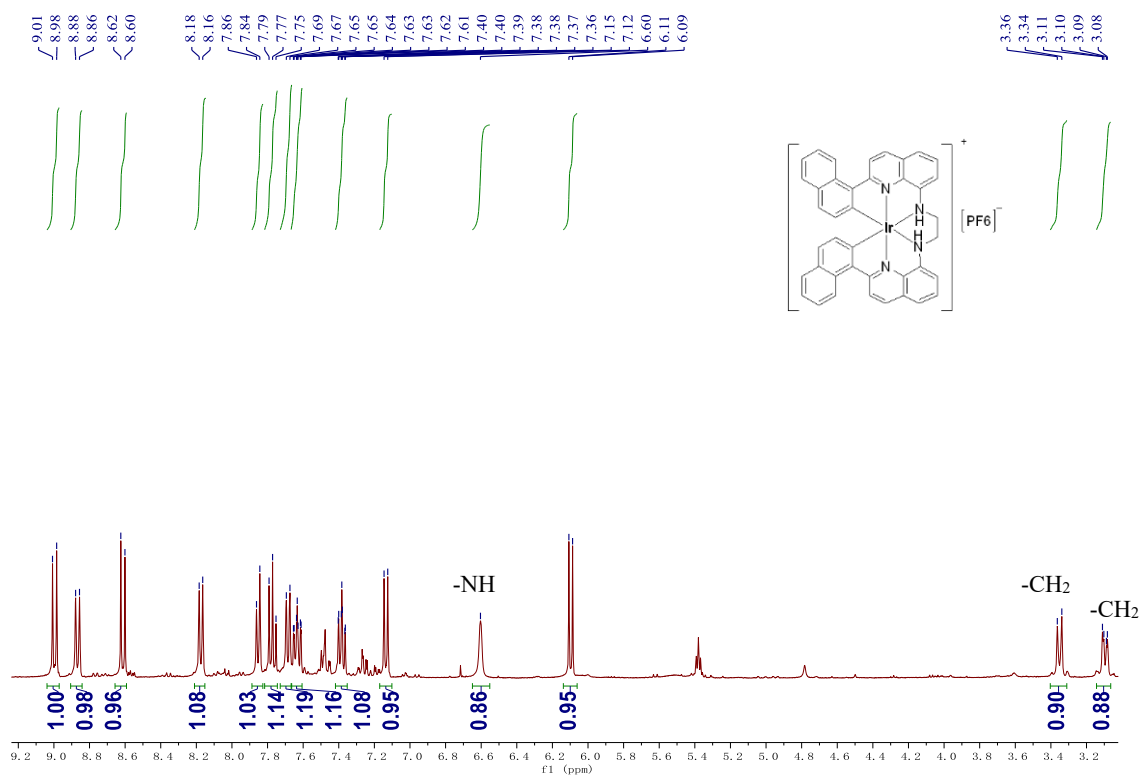


Figure S33. ¹H NMR spectra of [Ir(bnqen)](PF₆) (4) in CD₃CN.

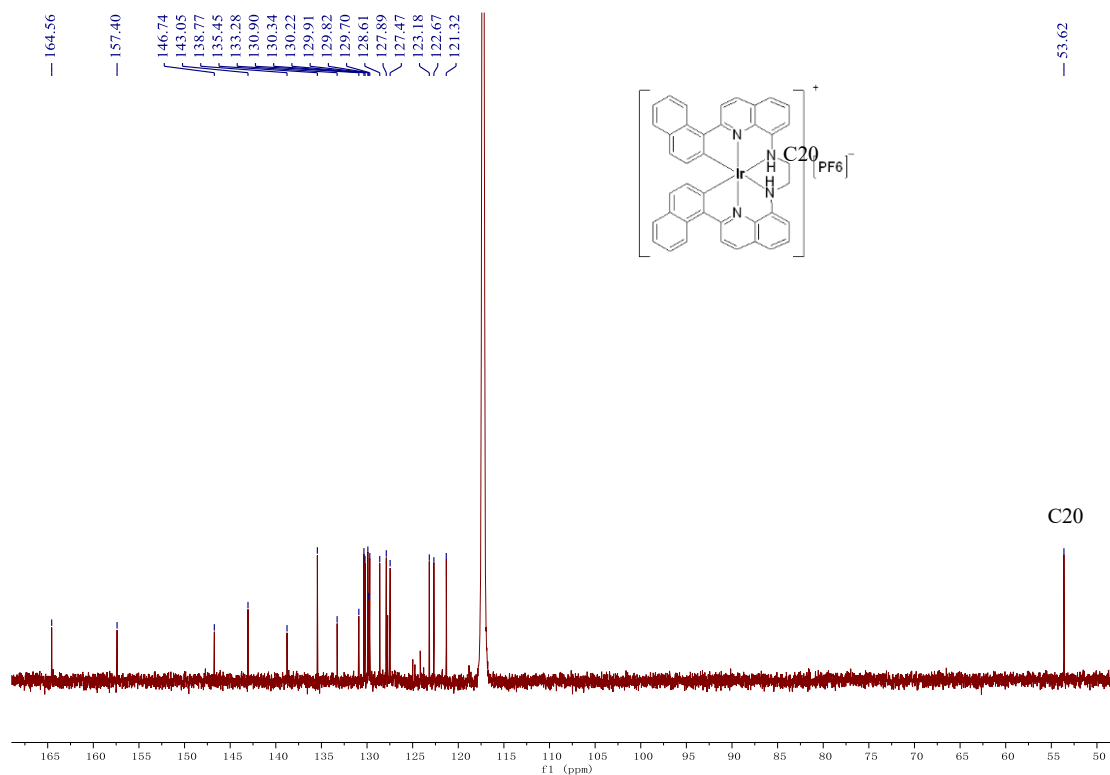


Figure S34. ¹³C NMR spectra of [Ir(bnqen)](PF₆) (4) in CD₃CN.

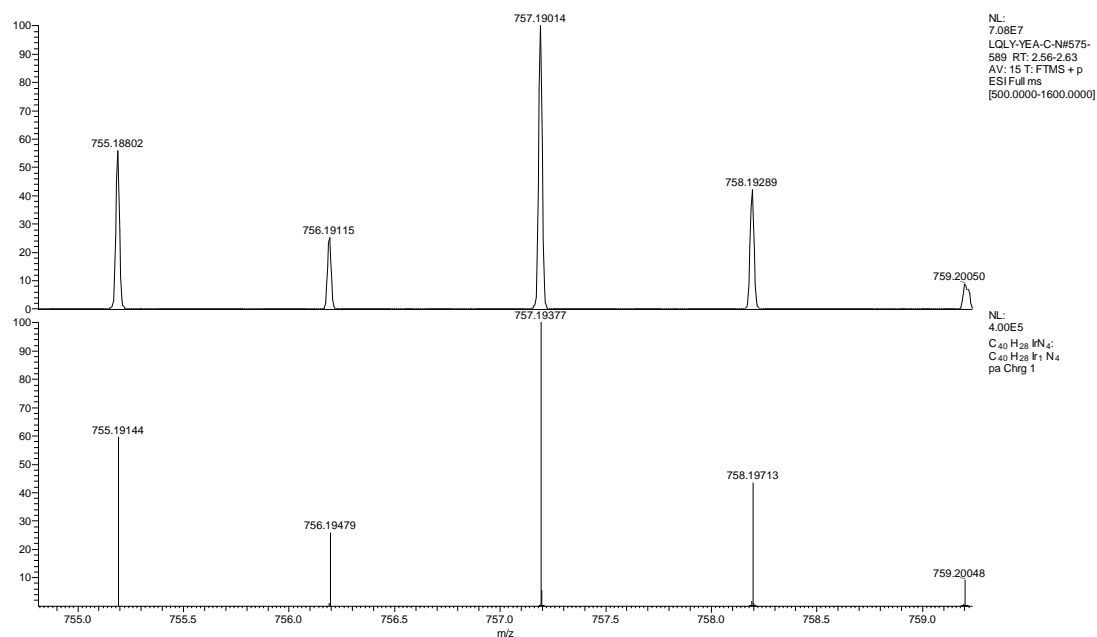


Figure S35. HRMS of $[\text{Ir}(\text{bnqen})](\text{PF}_6)$ (up) and calculated for $[\text{Ir}(\text{bnqen})]^+$ (down).

S2. Photoluminescence diagrams

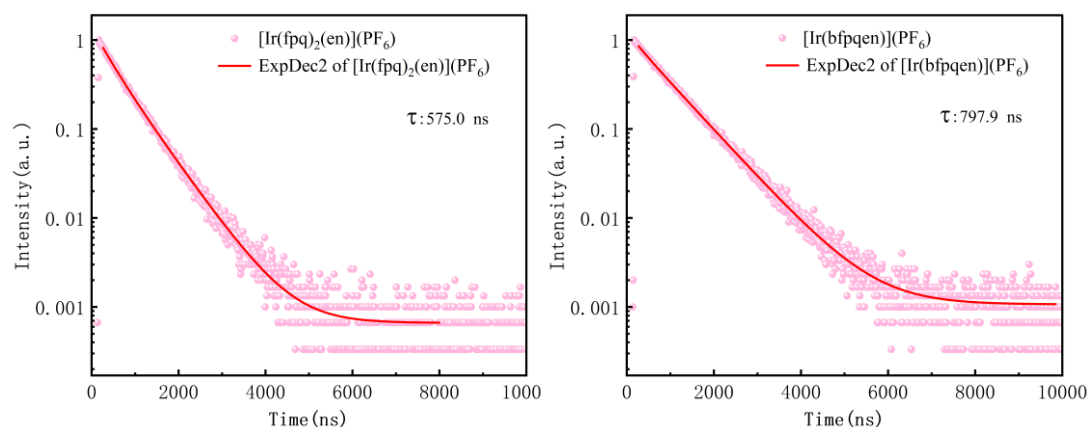


Figure S36. Single-wavelength decay traces for **1a** (left) and **1** (right) in Ar-saturated MeOH at room temperature.

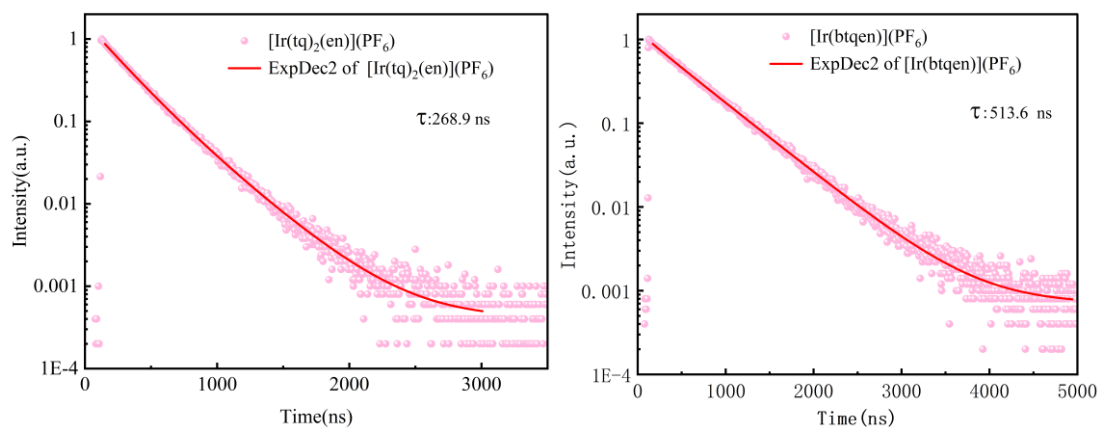


Figure S37. Single-wavelength decay traces for **2a** (left) and **2** (right) in Ar-saturated MeOH at room temperature.

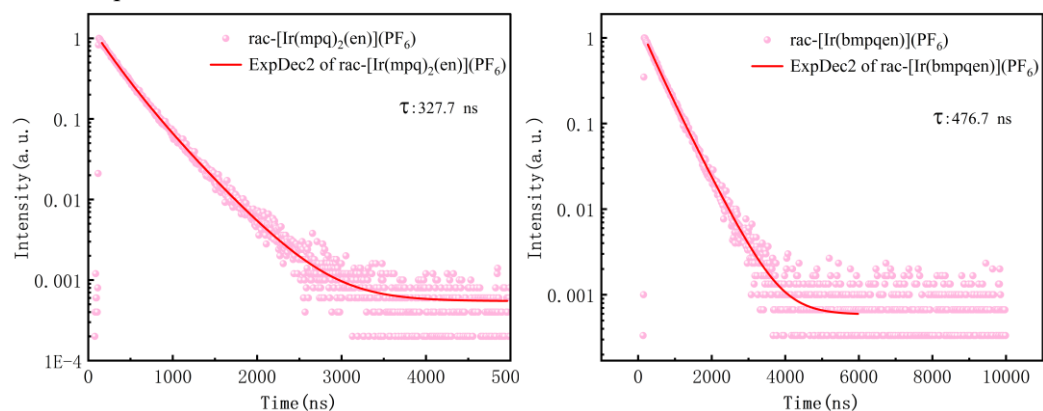


Figure S38. Single-wavelength decay traces for **3a** (left) and **3** (right) in Ar-saturated MeOH at room temperature.

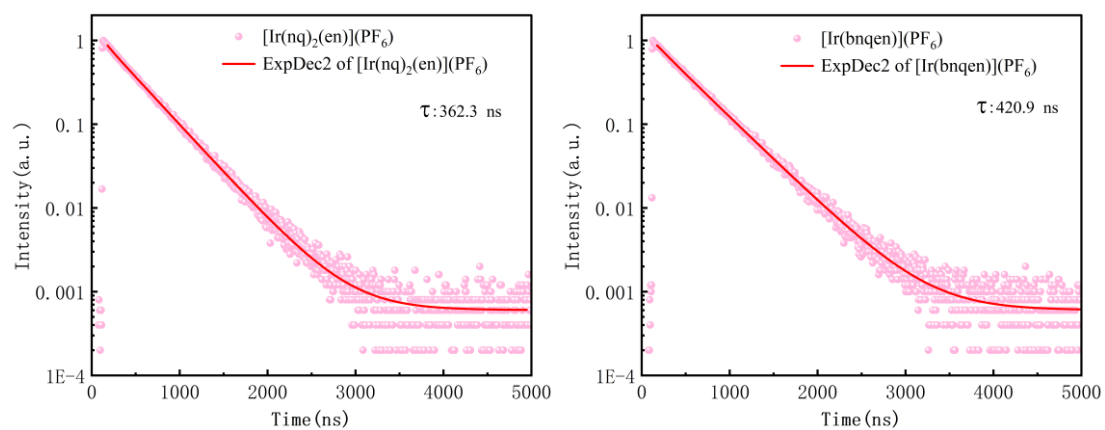


Figure S39. Single-wavelength decay traces for **4a** (left) and **4** (right) in Ar-saturated MeOH at room temperature.

S3. ^1H NMR spectra of sulfoxides

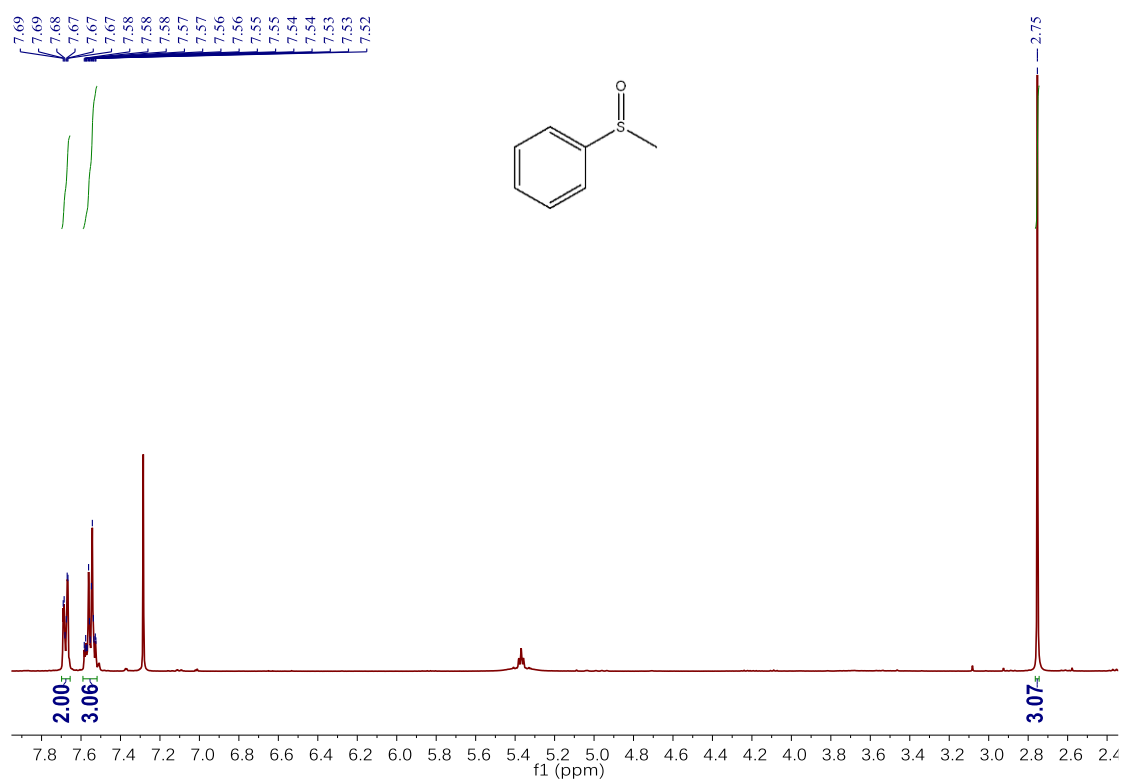


Figure S40. ^1H NMR spectra of methyl phenyl sulfoxide (**6a**) in CDCl₃.

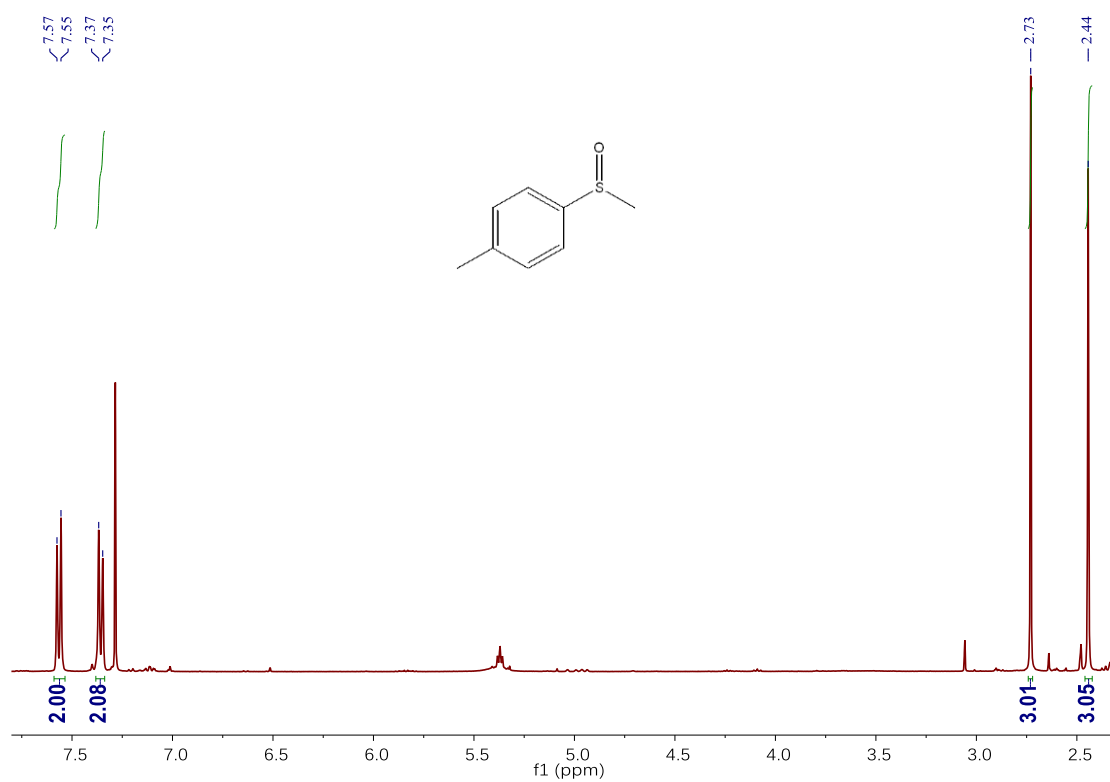


Figure S41. ^1H NMR spectra of methyl 4-methylphenyl sulfoxide (**6b**) in CDCl₃.

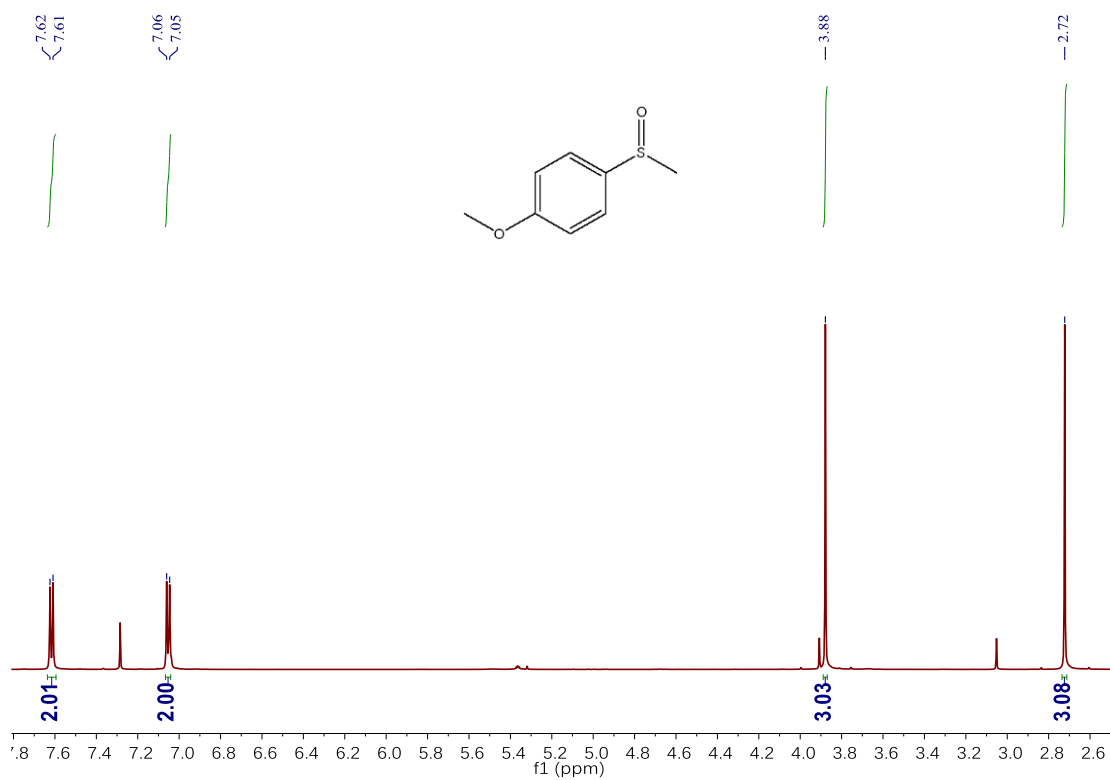


Figure S42. ¹H NMR spectra of methyl 4-methoxyphenyl sulfoxide (**6c**) in CDCl₃.

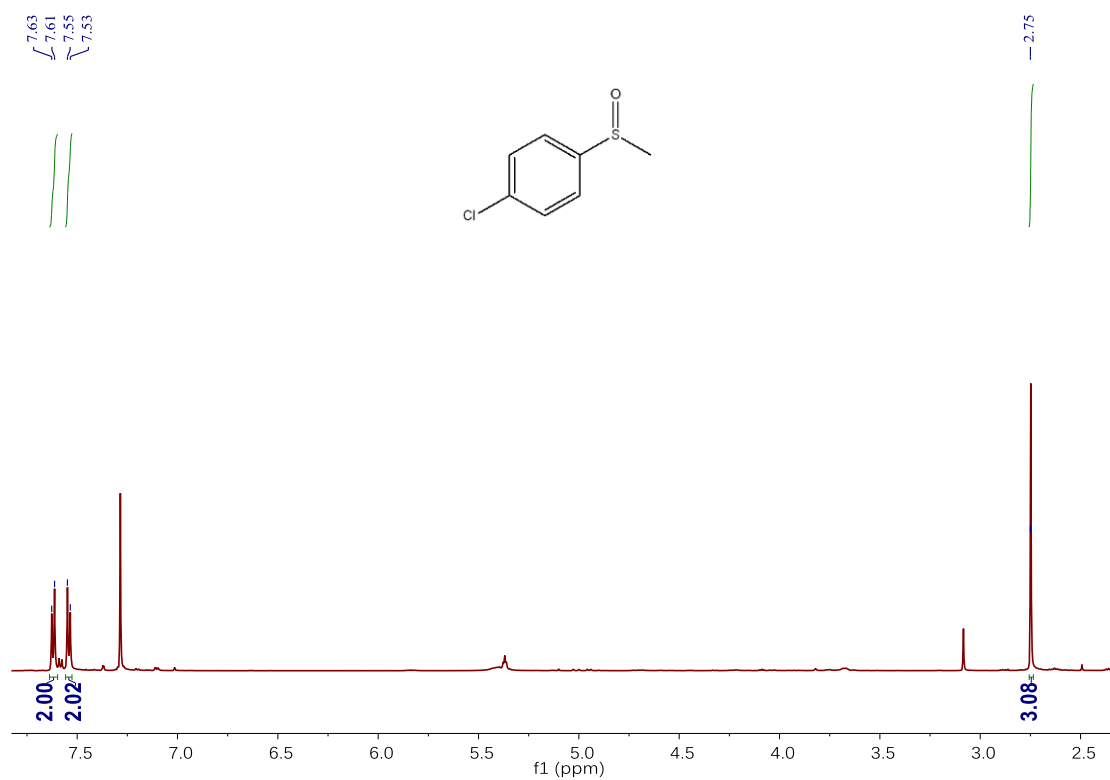


Figure S43. ¹H NMR spectra of methyl 4-chloro-phenyl sulfoxide (**6d**) in CDCl₃.

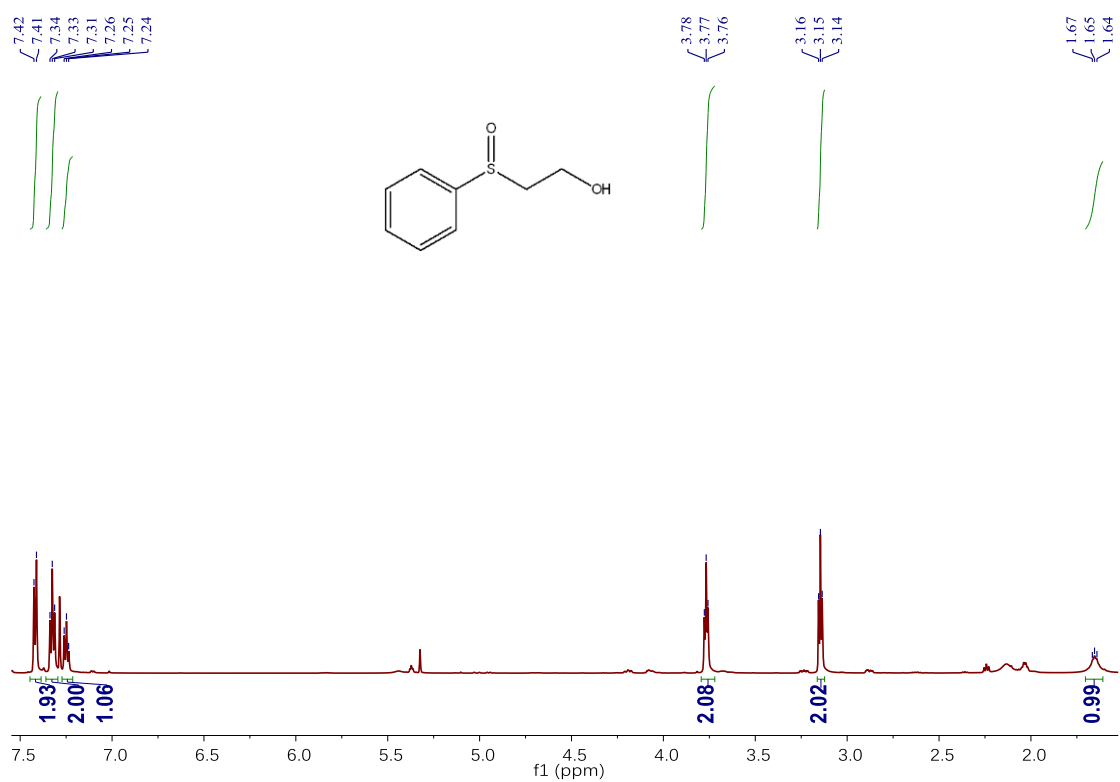


Figure S44. ¹H NMR spectra of 2-(phenylsulfinyl)ethan-1-ol (**6e**) in CDCl₃.