Supporting Information for

The Copper-catalyzed Reaction of 2-(1-Hydroxyprop-2-yn-1-yl)phenols with Sulfonyl Azides Leading to C3-Unsubstituted *N*-Sulfonyl-2-iminocoumarins

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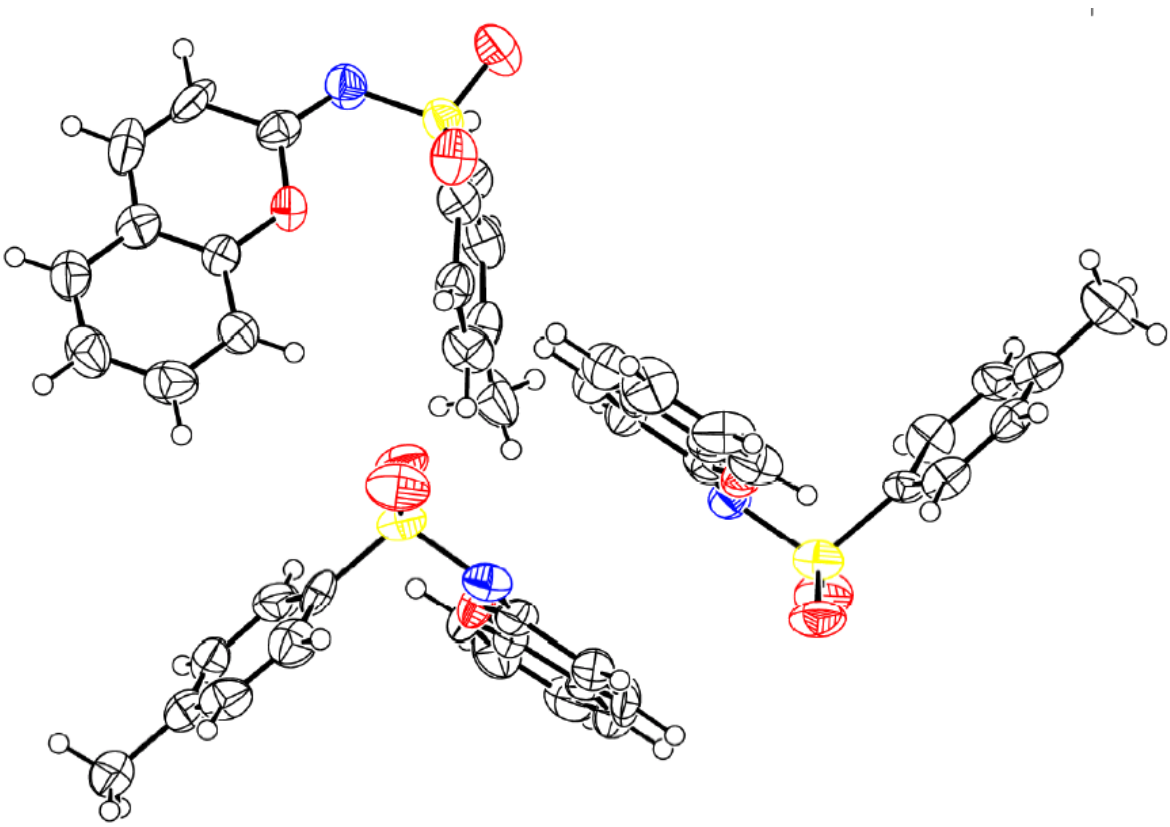


Figure S1: Molecular structure of compound **8a** (CCDC 2043700) and showing the relative orientations of the molecules within the unit cell. Atomic displacement parameters shown at 50% probability level (crystal grown from ethyl acetate/60–90 petroleum ether by slow evaporation).

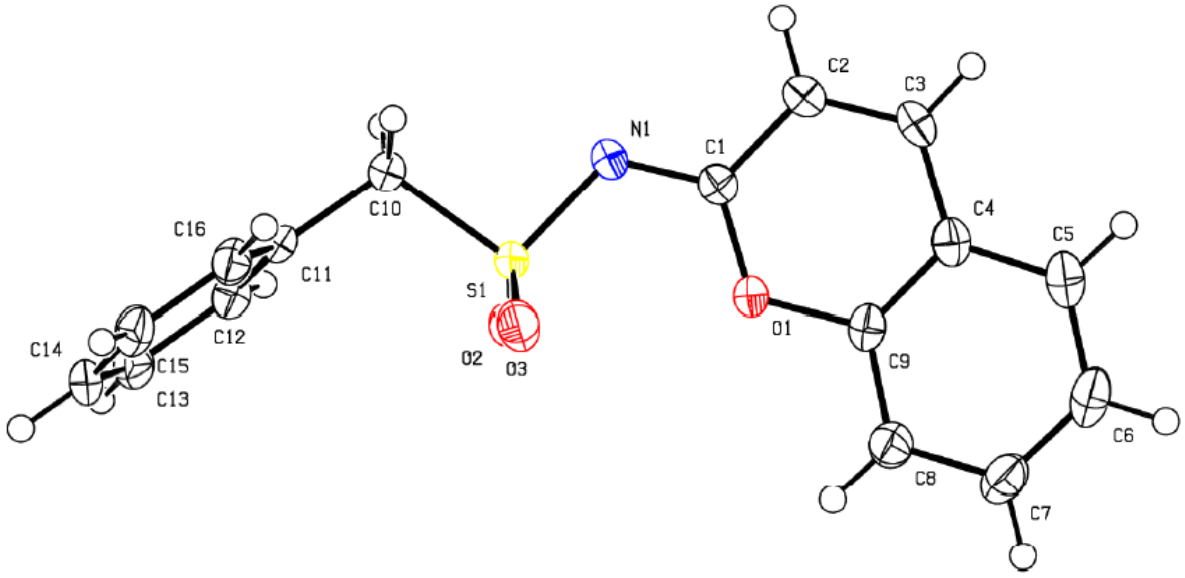


Figure S2: Molecular structure of compound **8j** (CCDC 2060954). Atomic displacement parameters shown at 50% probability level (crystal grown from ethyl acetate/60–90 petroleum ether by slow evaporation).

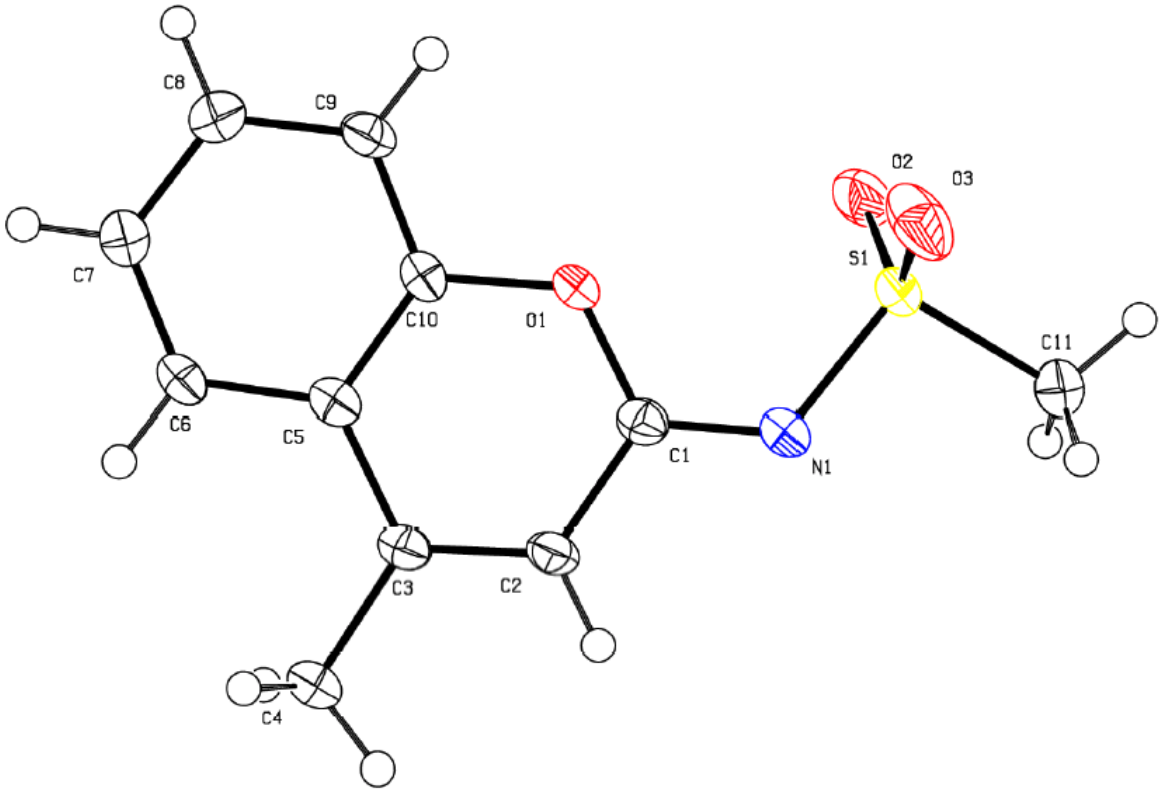
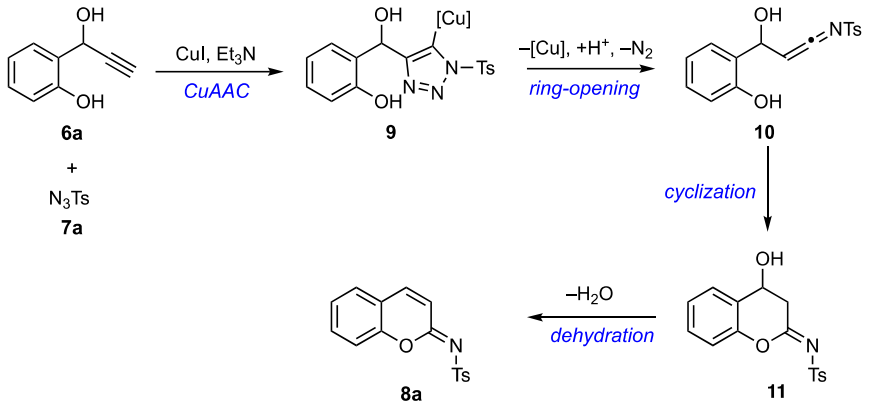


Figure S3: Molecular structure of compound **8q** (CCDC 2060955). Atomic displacement parameters shown at 50% probability level (crystal grown from ethyl acetate/60–90 petroleum ether by slow evaporation).



Scheme S1: A possible pathway for the formation of the *N*-sulfonyl-2-iminocoumarin **8a** from precursors **6a** and **7a**.

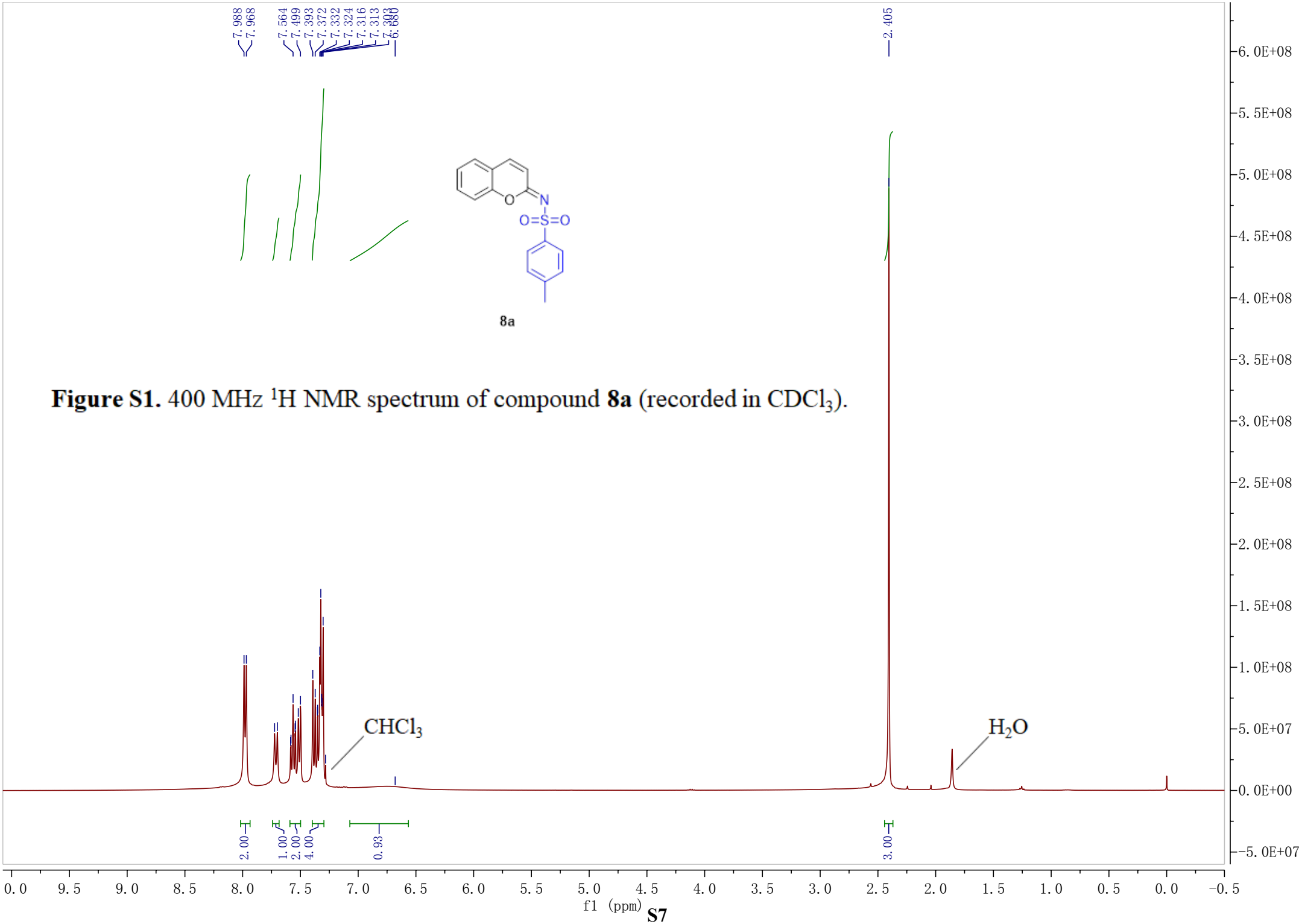


Figure S1. 400 MHz ^{1}H NMR spectrum of compound **8a** (recorded in $CDCl_3$).

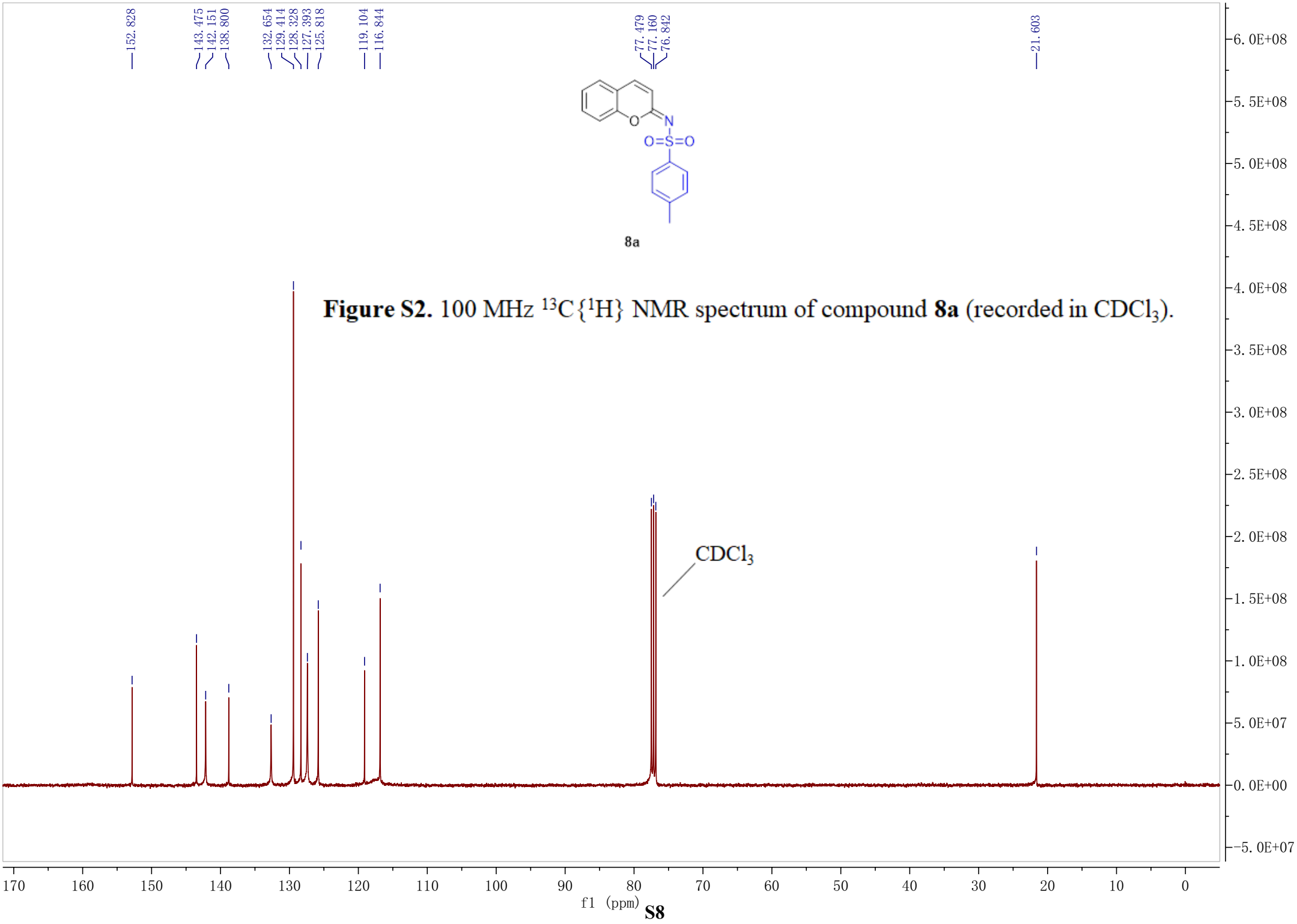


Figure S2. 100 MHz $^{13}C\{^{1}H\}$ NMR spectrum of compound **8a** (recorded in $CDCl_3$).

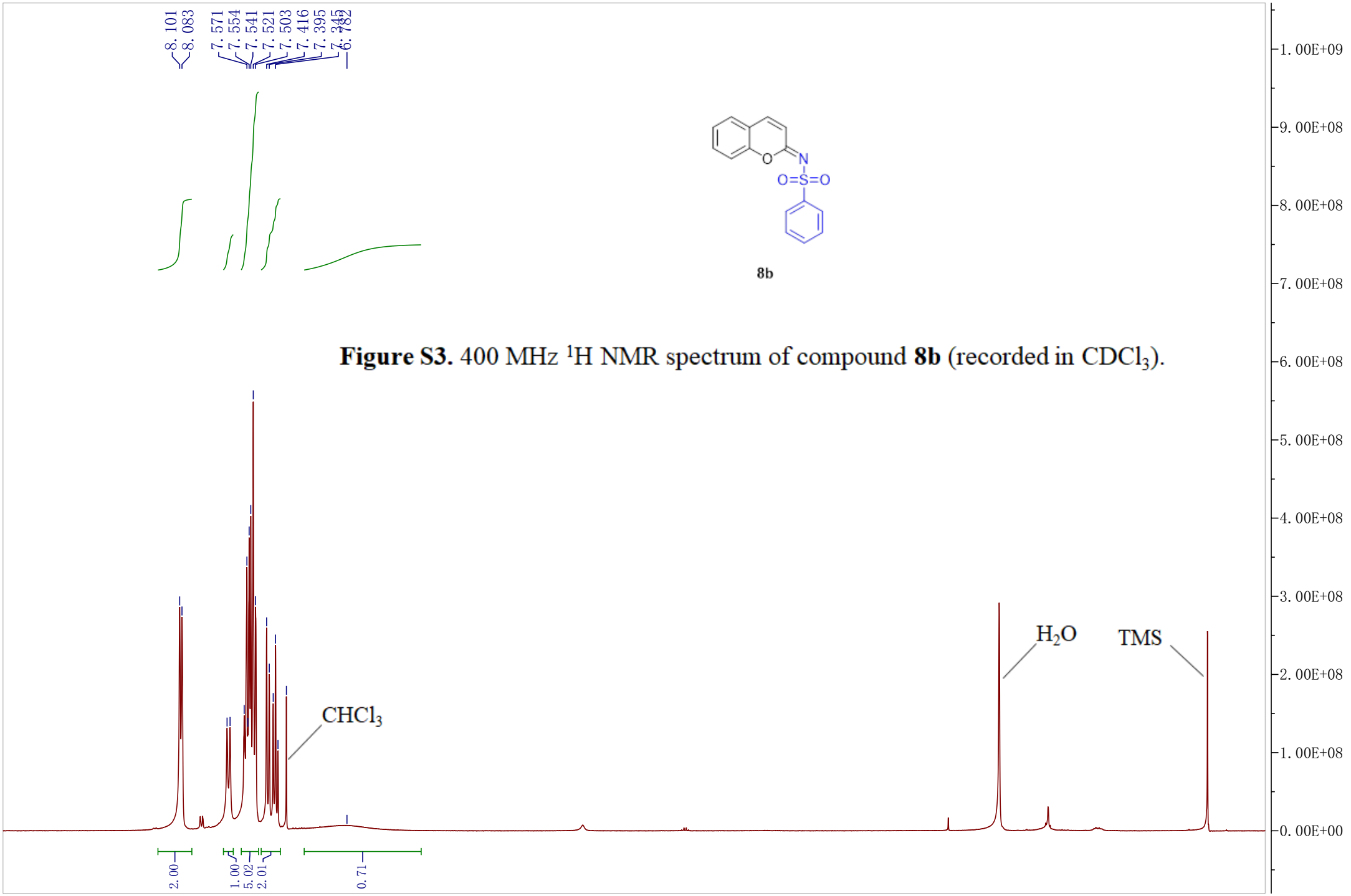


Figure S3. 400 MHz ^{1}H NMR spectrum of compound **8b** (recorded in $CDCl_3$).

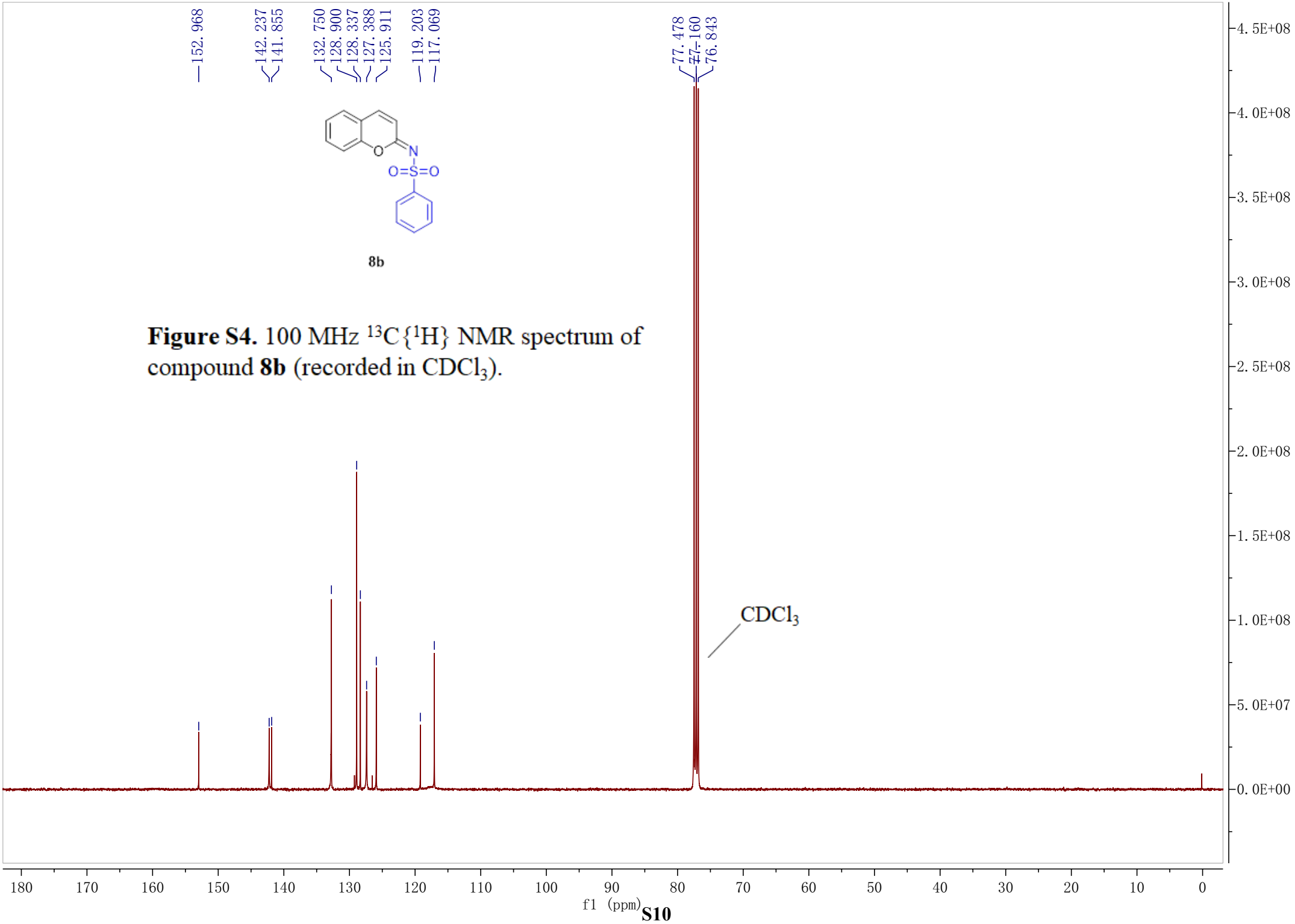


Figure S4. 100 MHz $^{13}C\{^{1}H\}$ NMR spectrum of compound **8b** (recorded in $CDCl_3$).

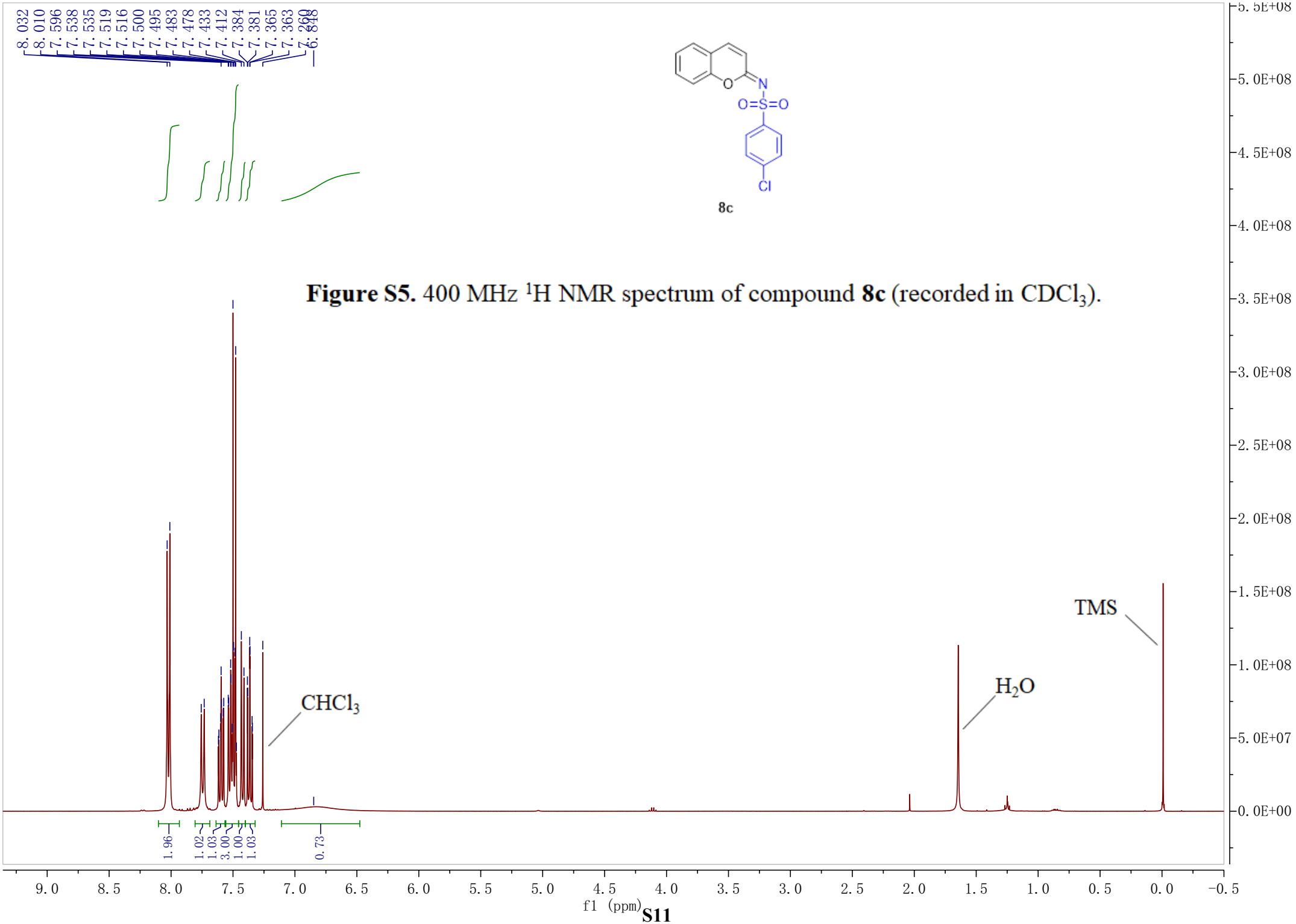


Figure S5. 400 MHz ^{1}H NMR spectrum of compound **8c** (recorded in $CDCl_3$).

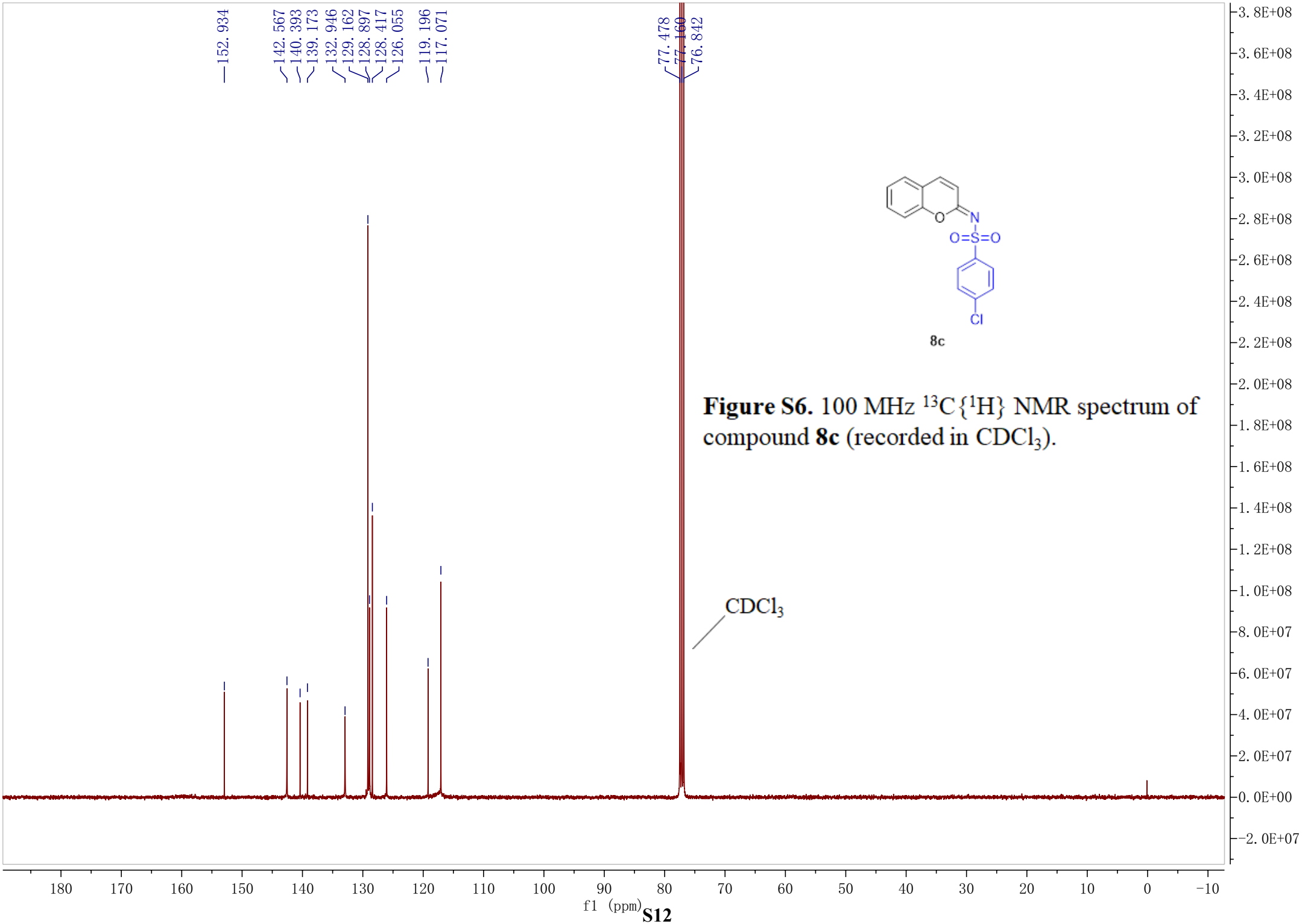


Figure S6. 100 MHz $^{13}C\{^{1}H\}$ NMR spectrum of compound **8c** (recorded in $CDCl_3$).

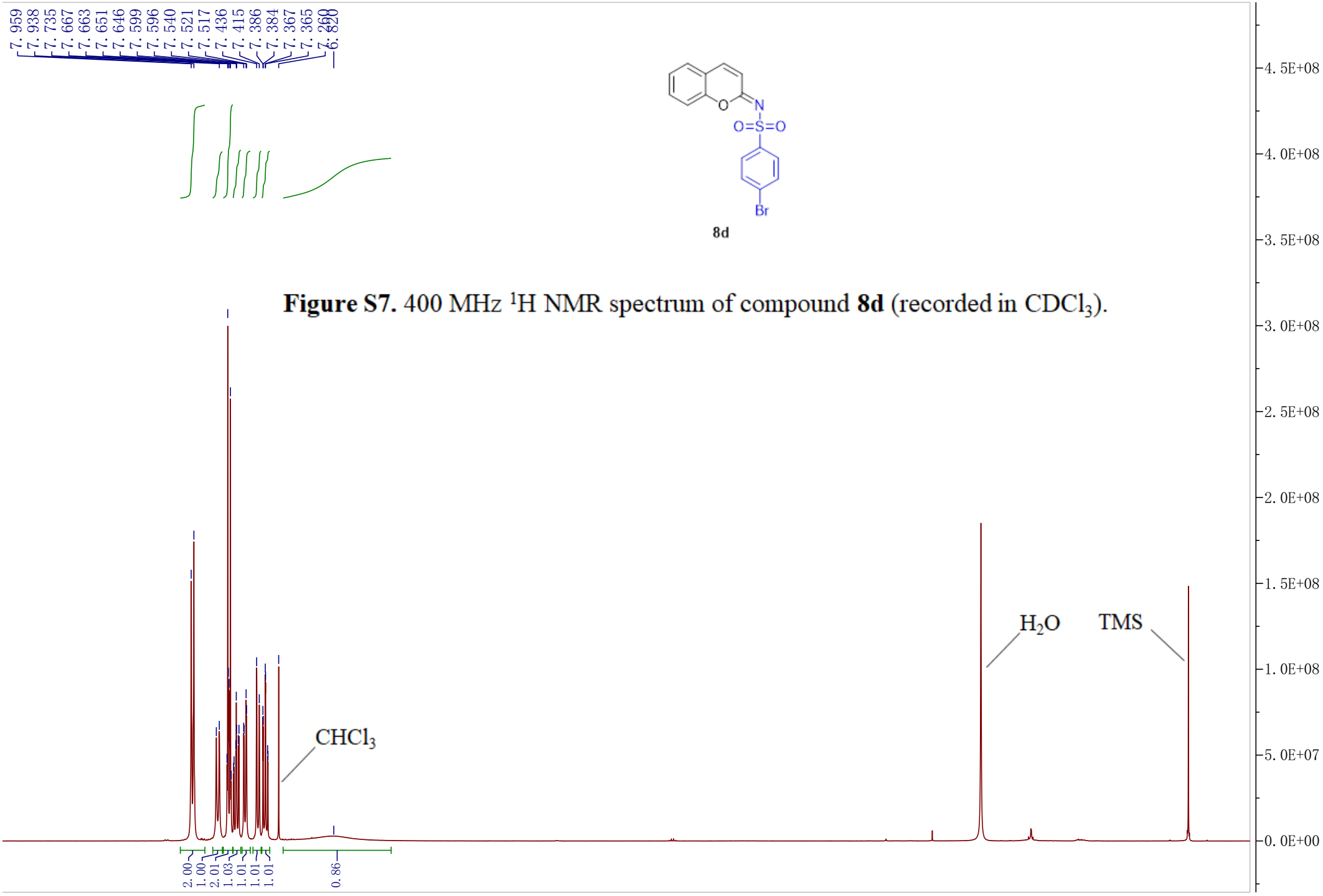


Figure S7. 400 MHz ^{1}H NMR spectrum of compound **8d** (recorded in $CDCl_3$).

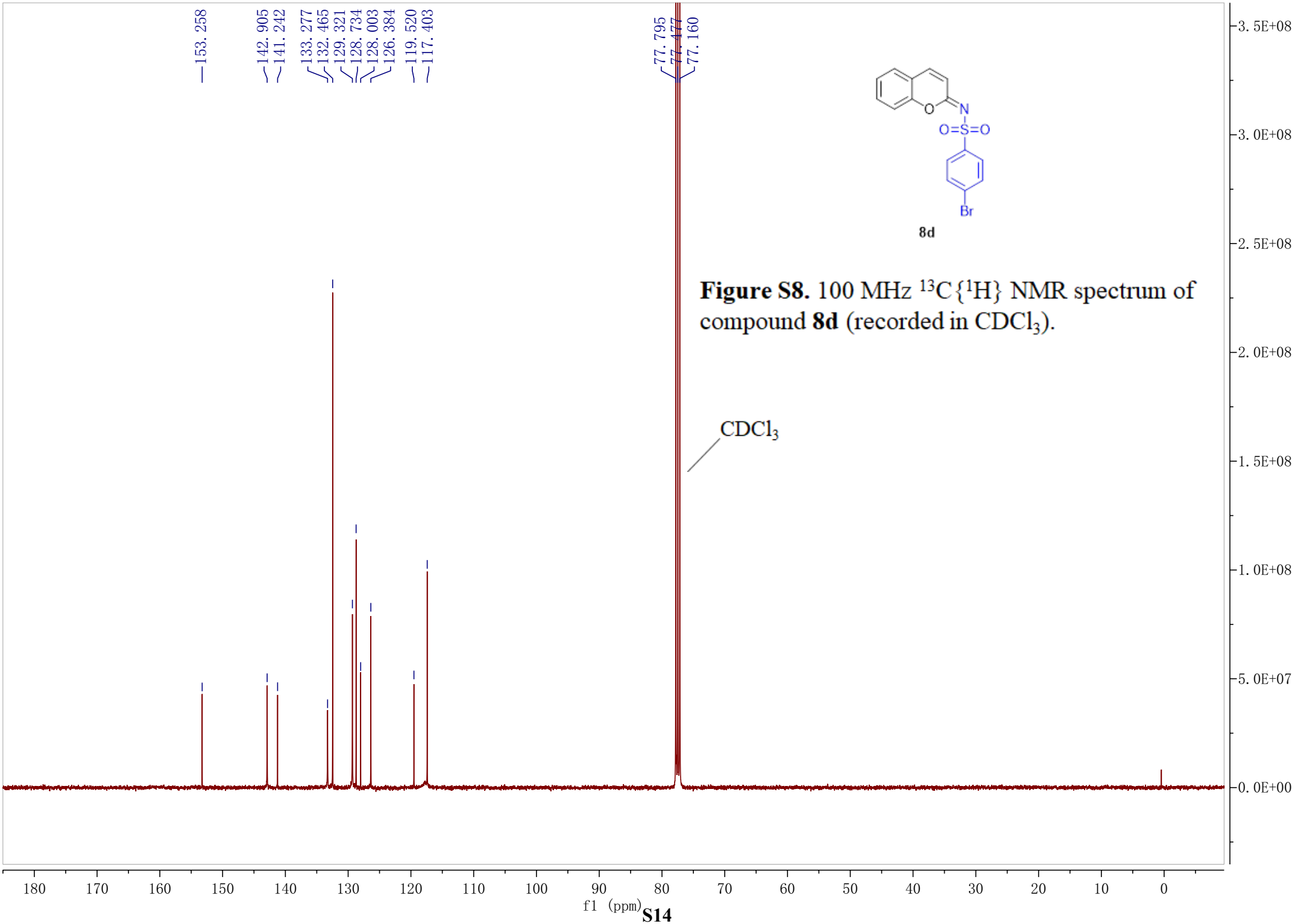


Figure S8. 100 MHz $^{13}C\{^{1}H\}$ NMR spectrum of compound **8d** (recorded in $CDCl_3$).

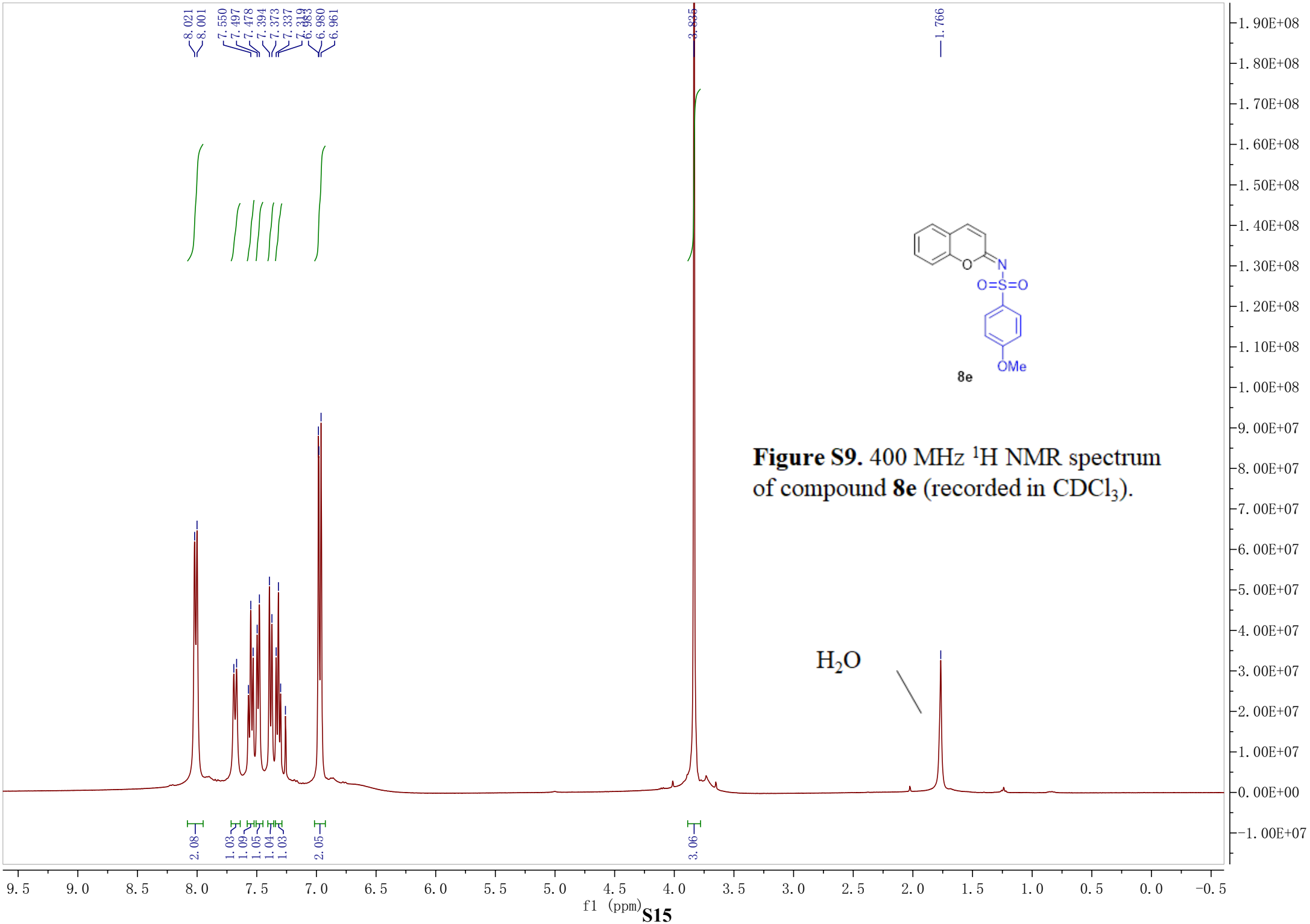


Figure S9. 400 MHz ^{1}H NMR spectrum of compound **8e** (recorded in $CDCl_3$).

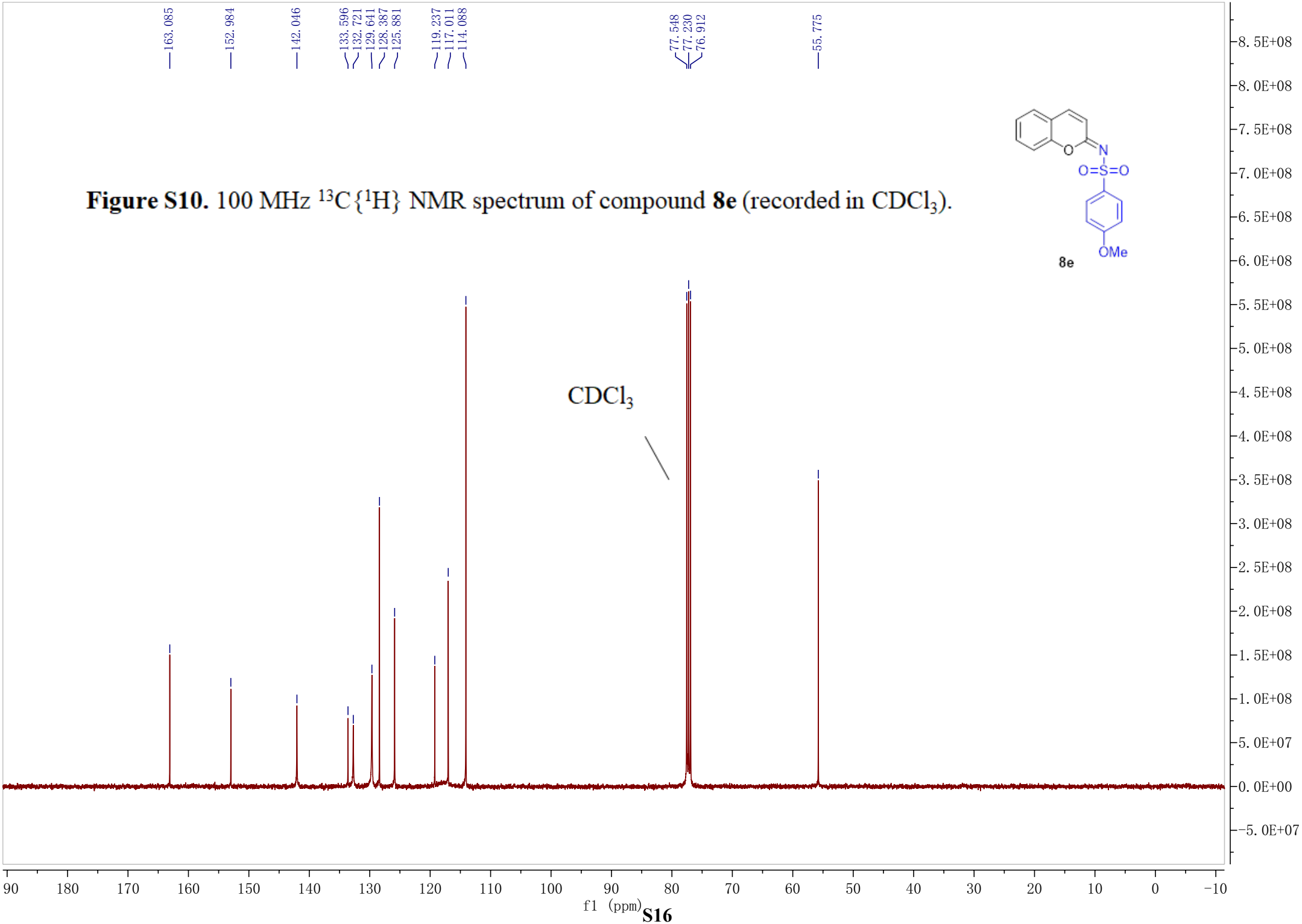


Figure S10. 100 MHz $^{13}C\{^{1}H\}$ NMR spectrum of compound **8e** (recorded in $CDCl_3$).

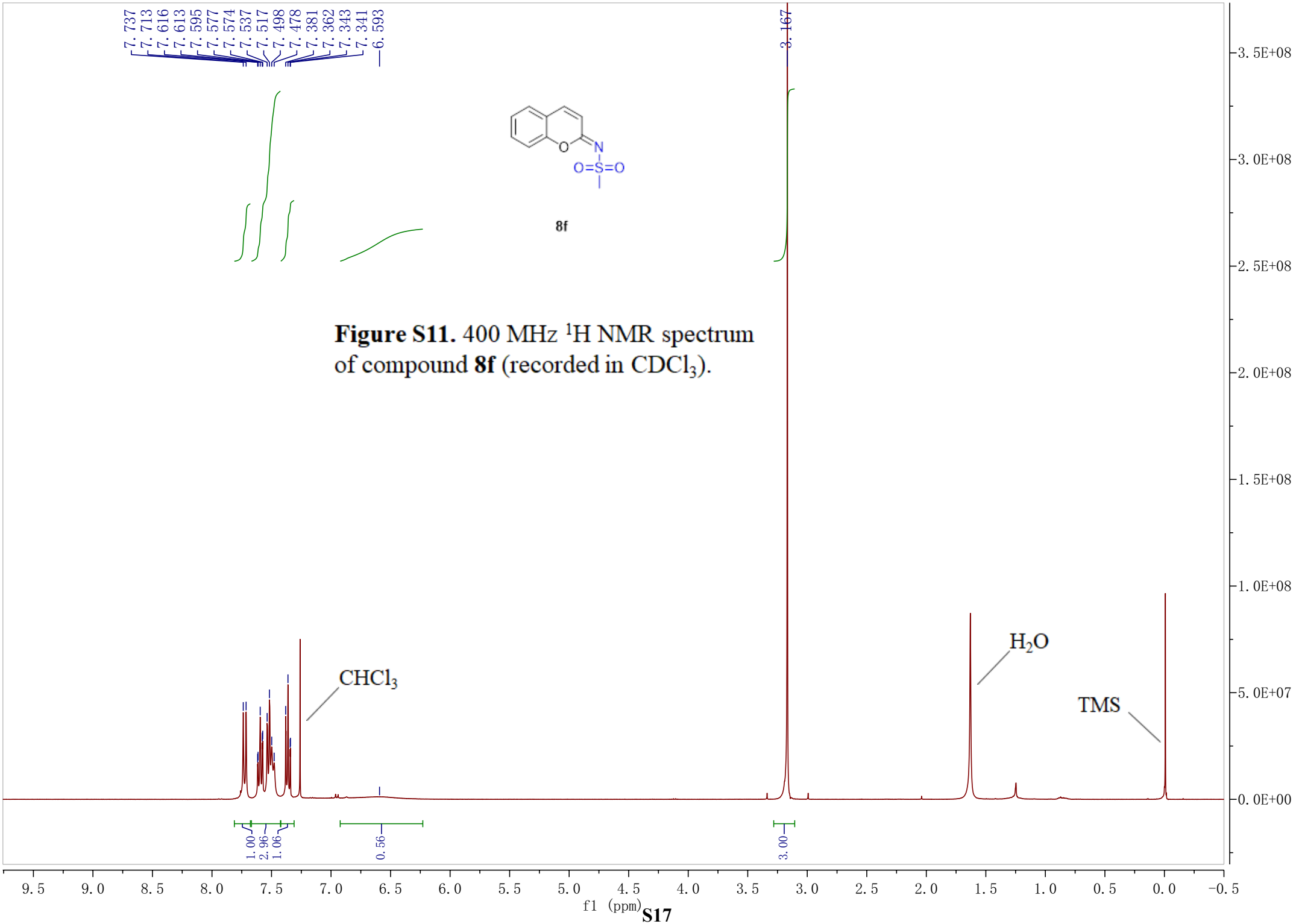


Figure S11. 400 MHz ^{1}H NMR spectrum of compound **8f** (recorded in $CDCl_3$).

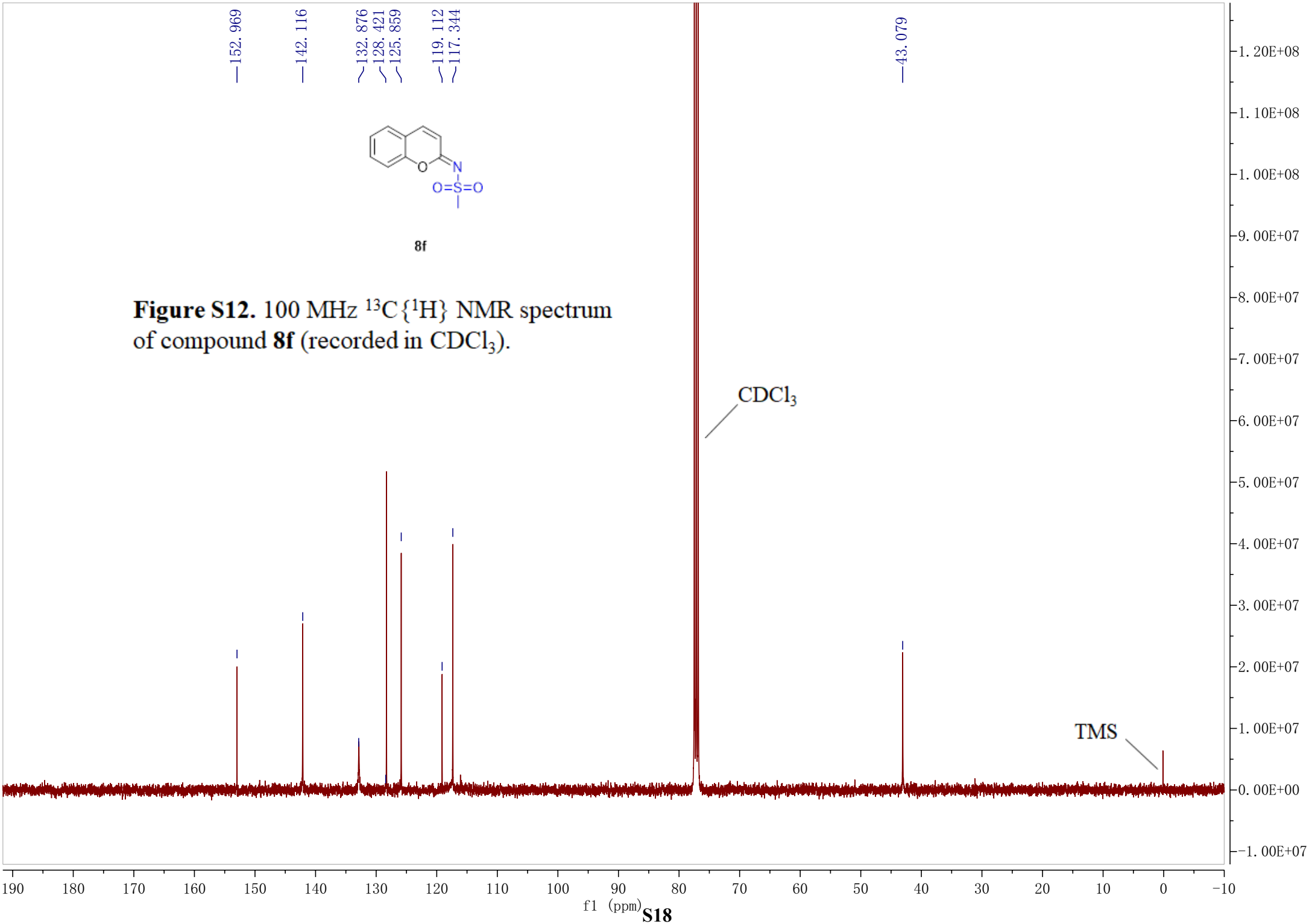


Figure S12. 100 MHz $^{13}C\{^{1}H\}$ NMR spectrum of compound **8f** (recorded in $CDCl_3$).

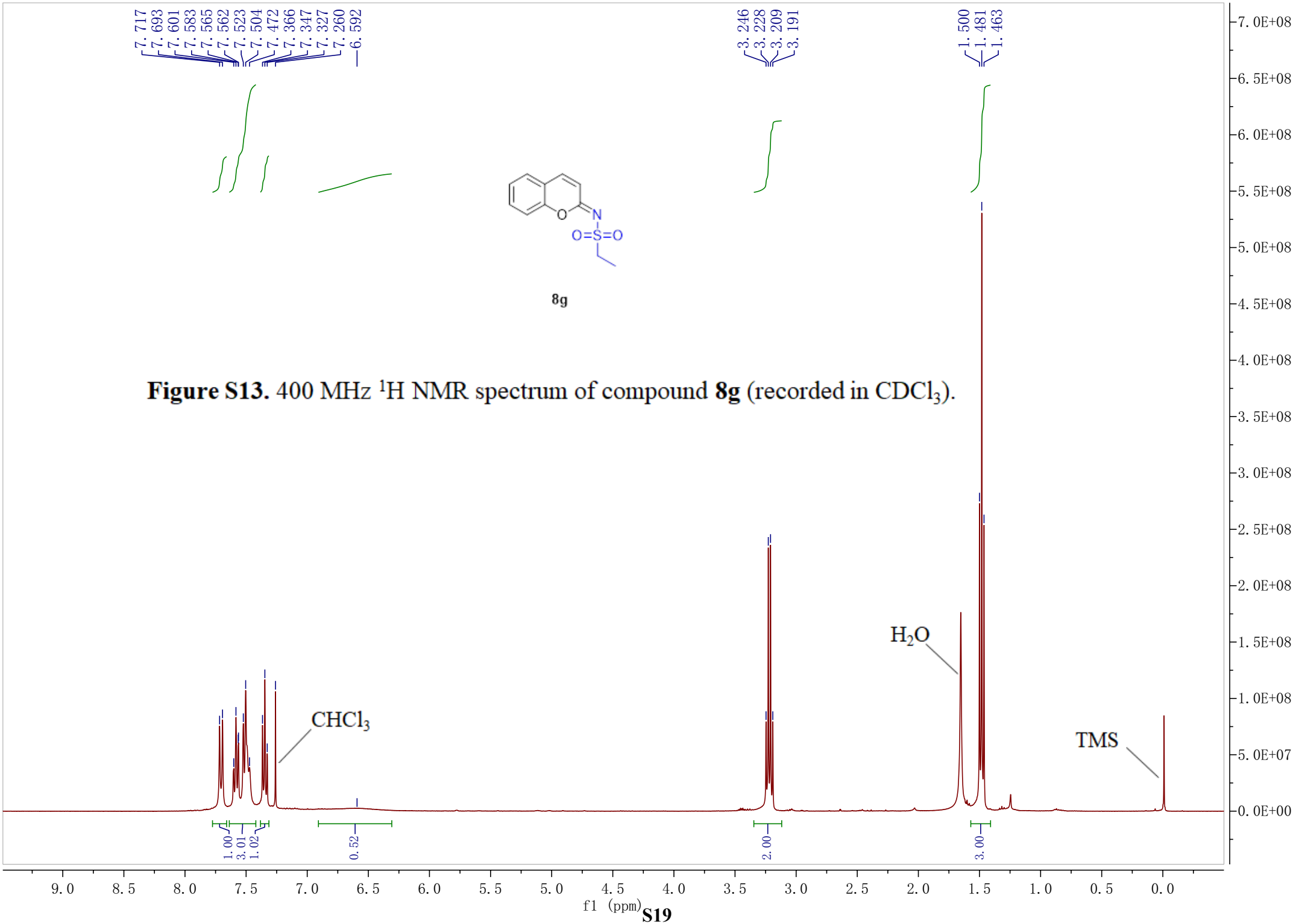


Figure S13. 400 MHz ^{1}H NMR spectrum of compound **8g** (recorded in $CDCl_3$).

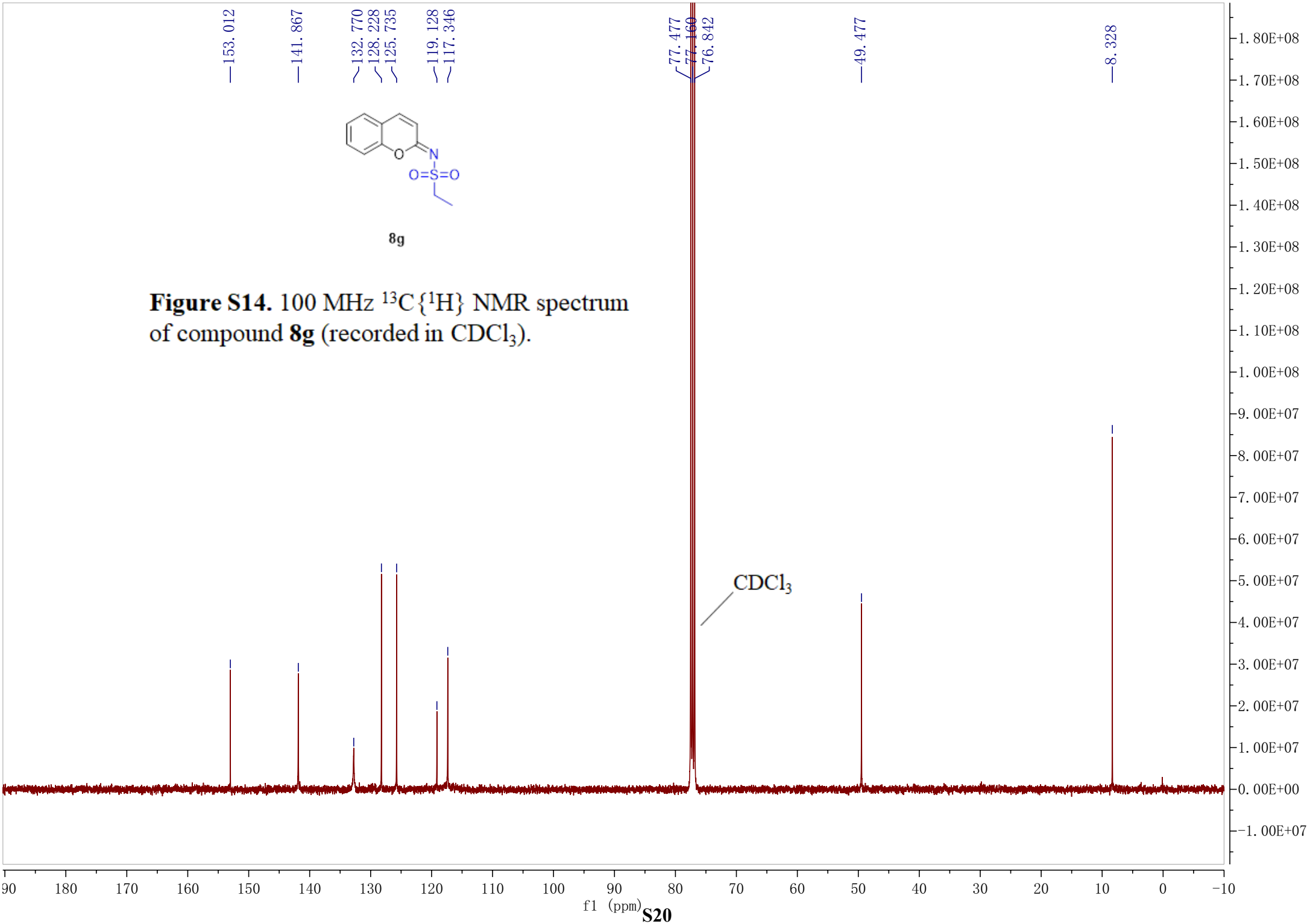


Figure S14. 100 MHz $^{13}C\{^{1}H\}$ NMR spectrum of compound **8g** (recorded in $CDCl_3$).

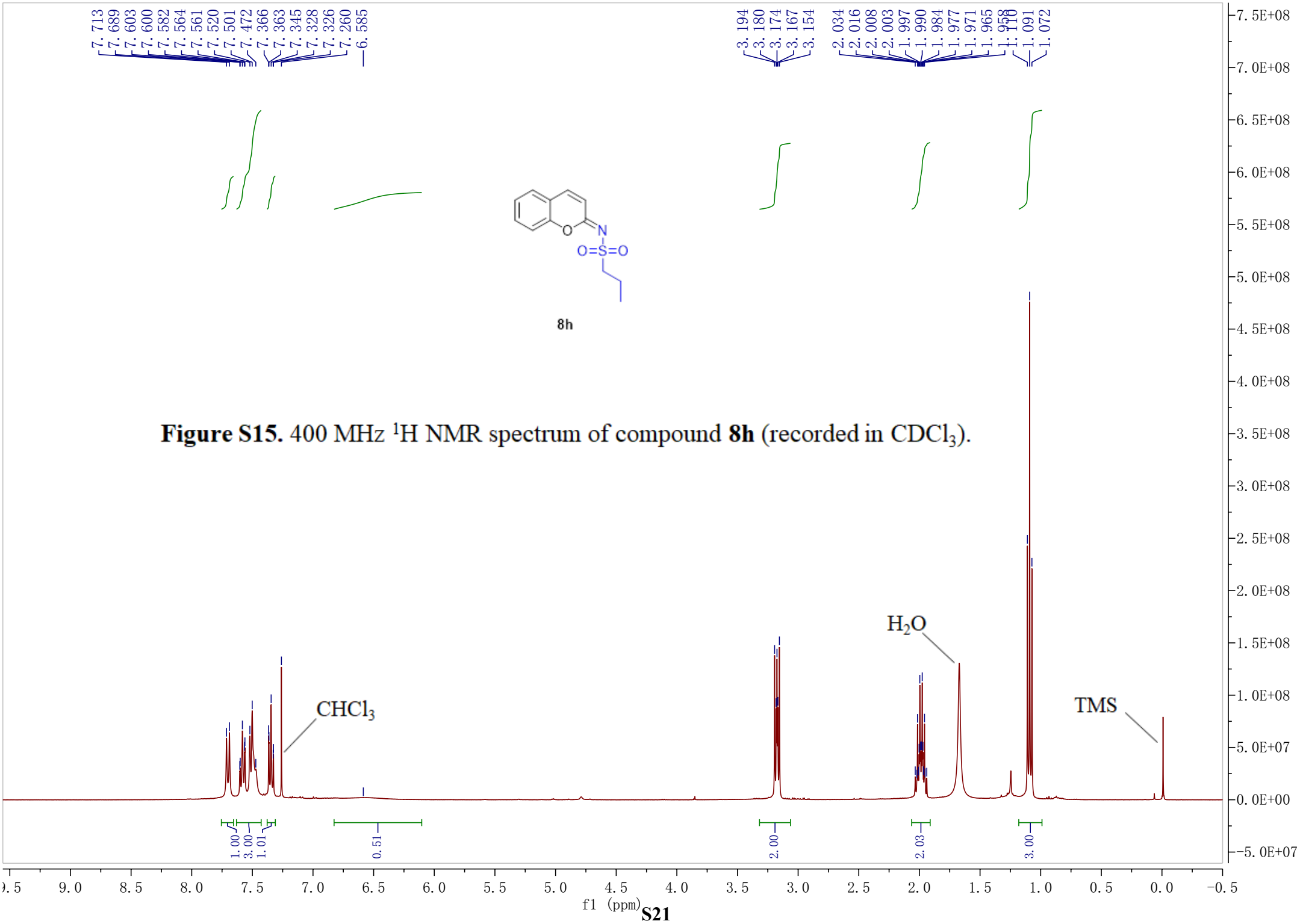


Figure S15. 400 MHz ^{1}H NMR spectrum of compound **8h** (recorded in $CDCl_3$).

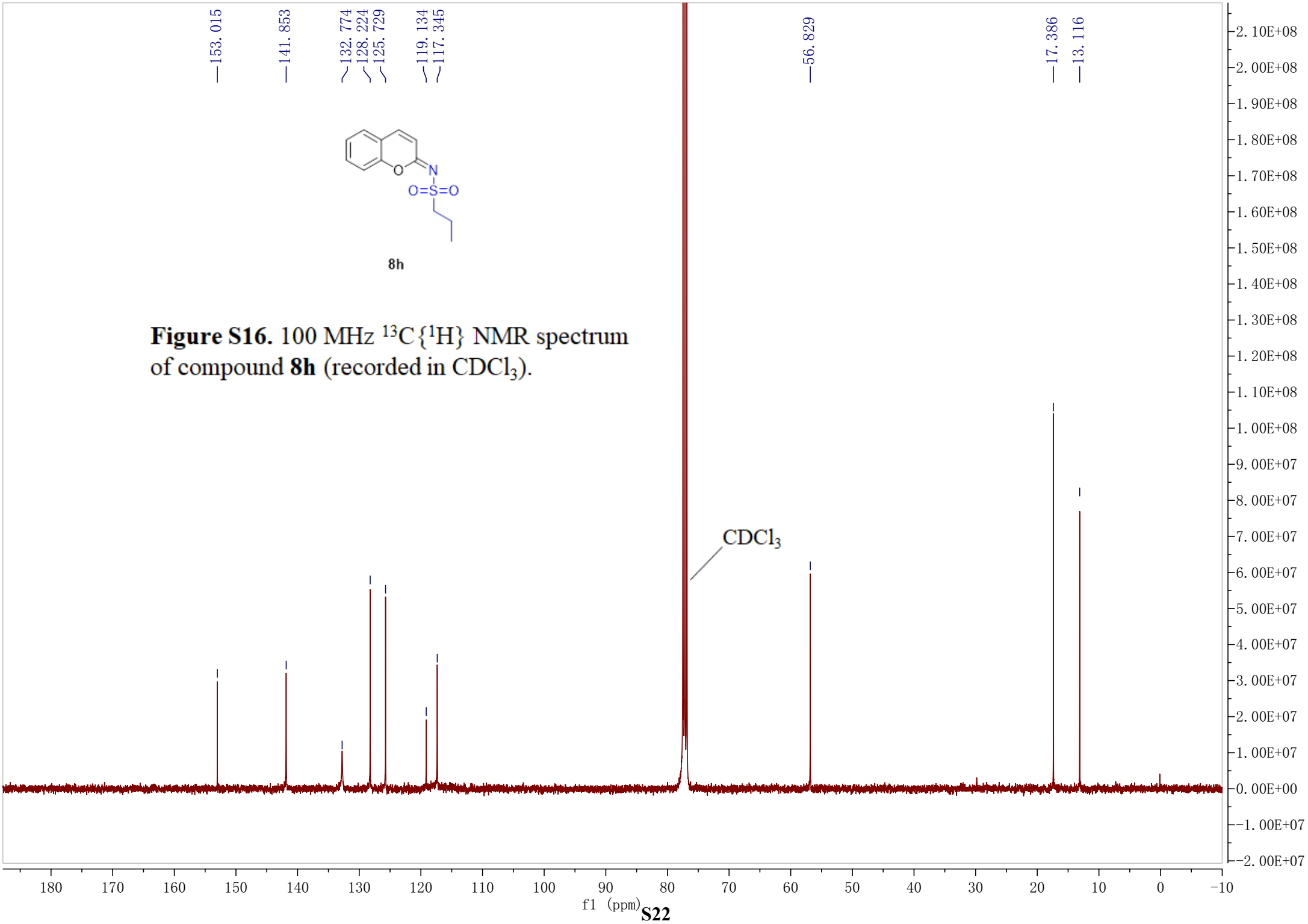


Figure S16. 100 MHz $^{13}C\{^{1}H\}$ NMR spectrum of compound **8h** (recorded in $CDCl_3$).

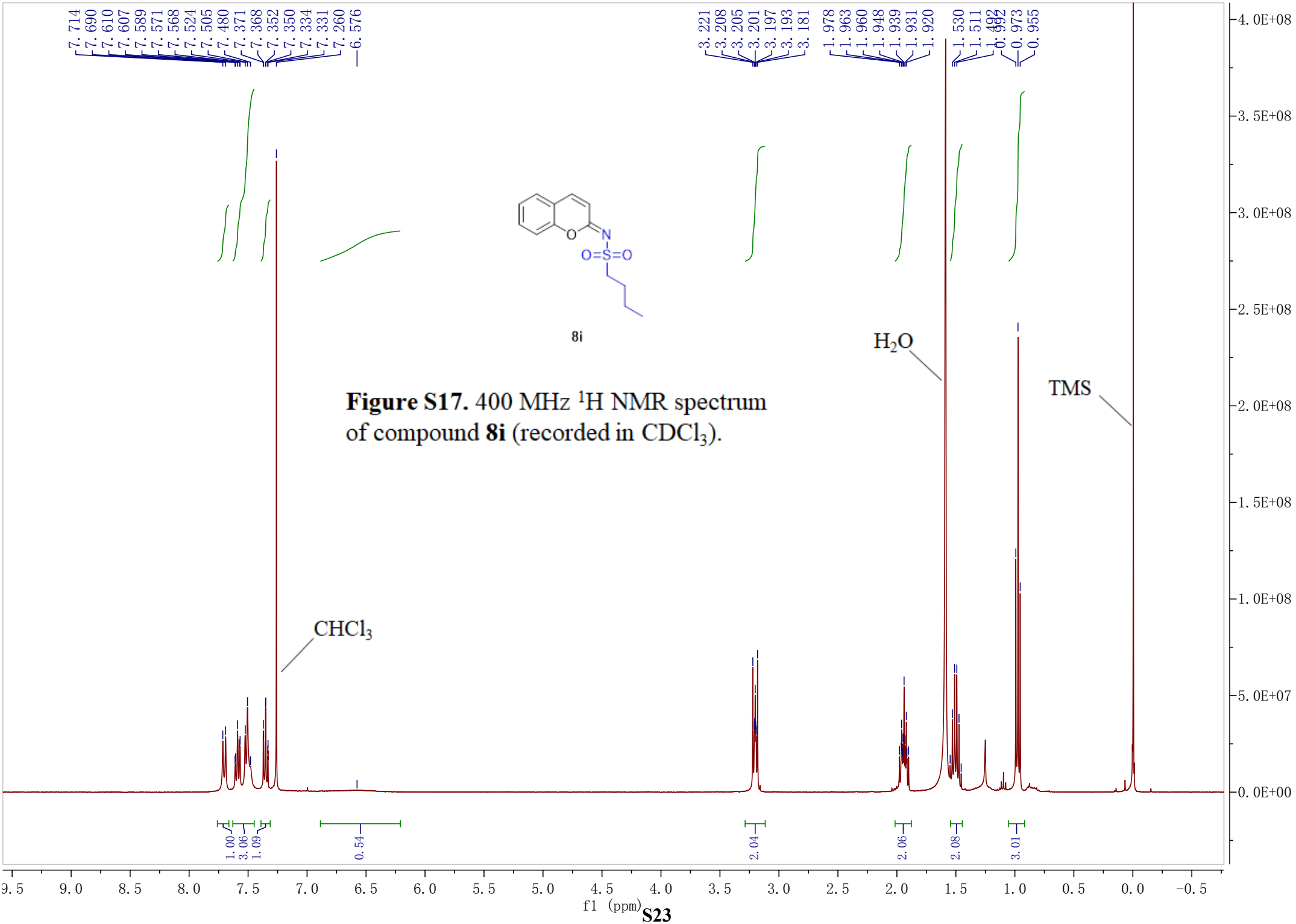


Figure S17. 400 MHz ^{1}H NMR spectrum of compound **8i** (recorded in $CDCl_3$).

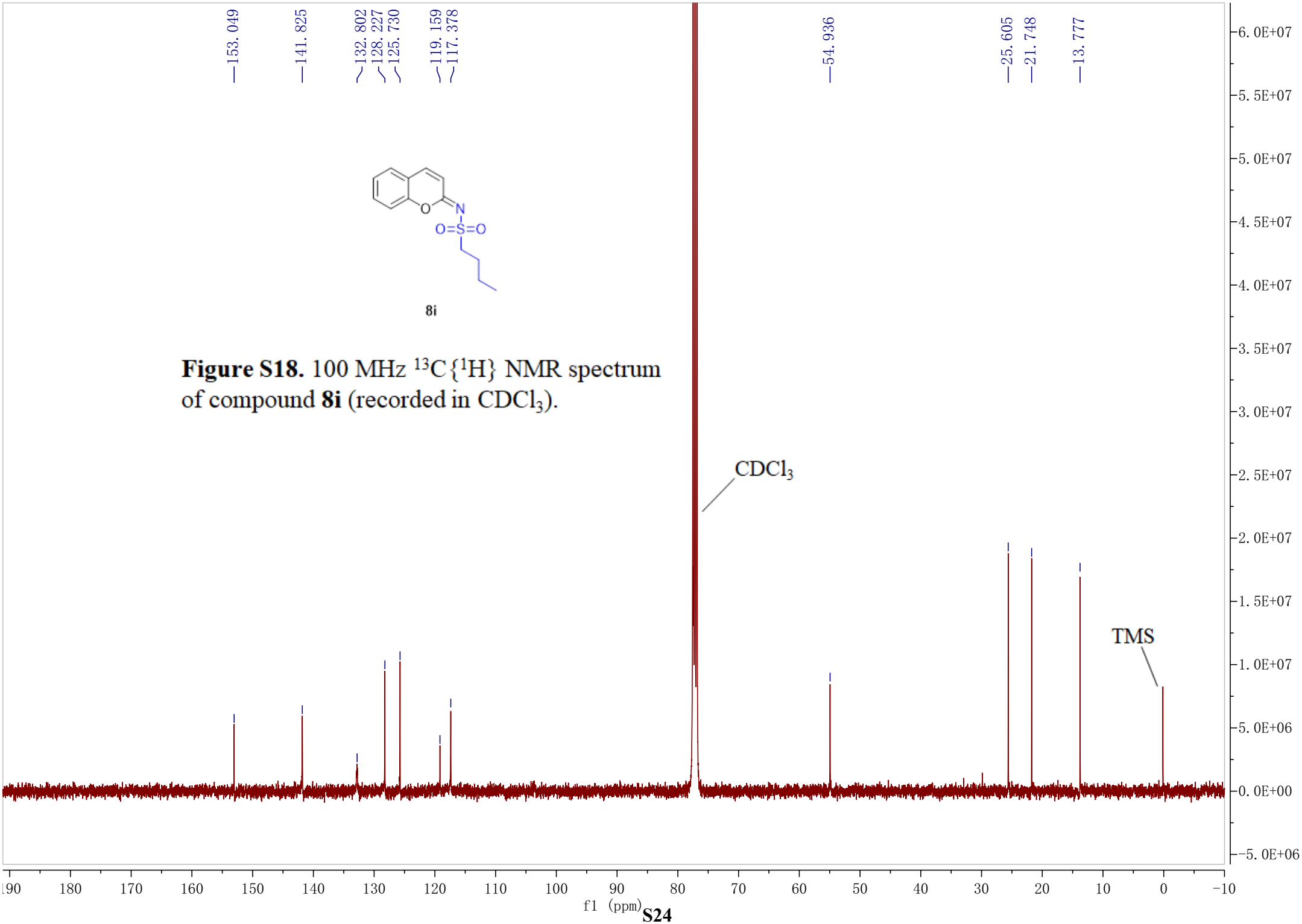


Figure S18. 100 MHz $^{13}C\{^{1}H\}$ NMR spectrum of compound **8i** (recorded in $CDCl_3$).

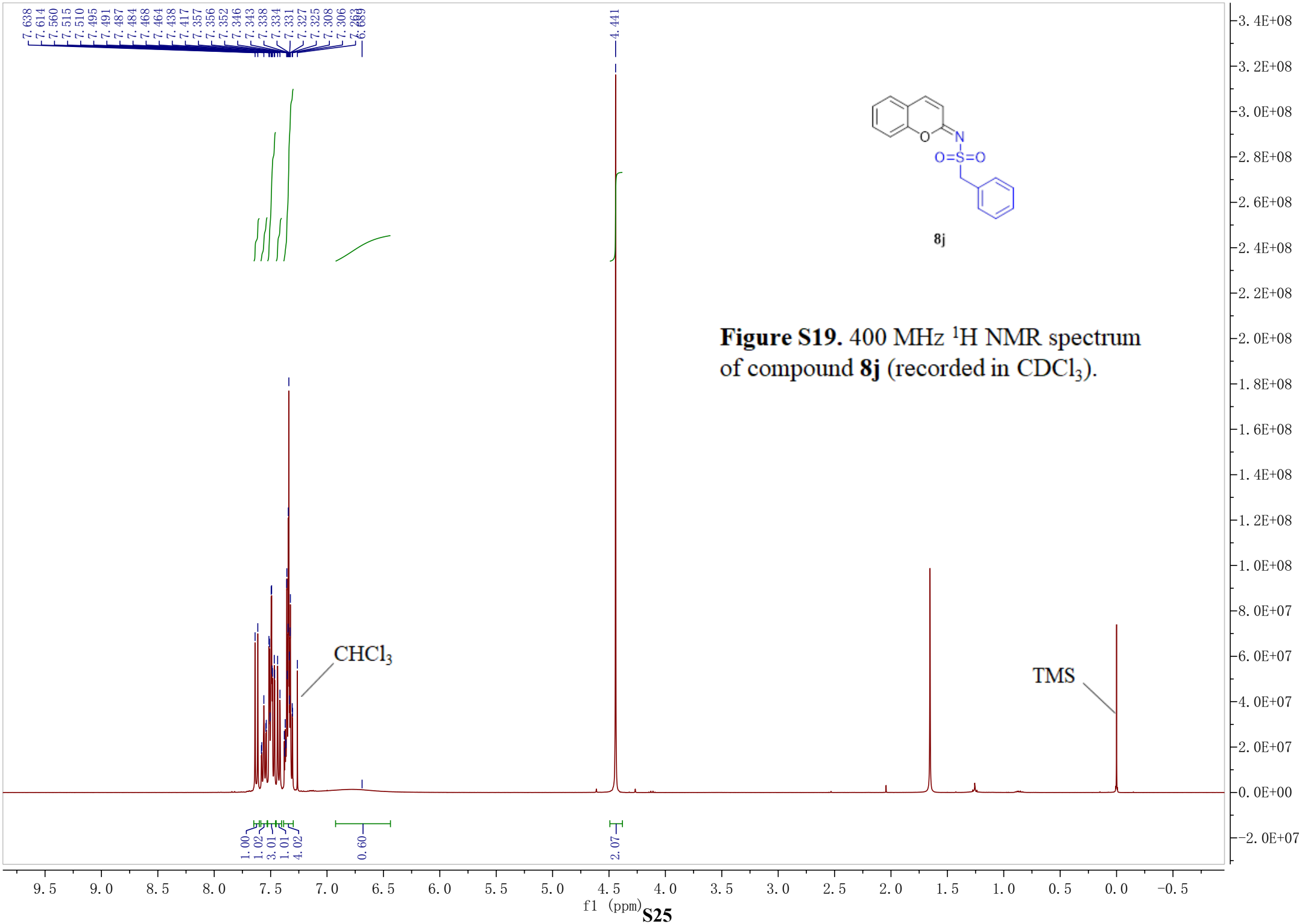


Figure S19. 400 MHz ^{1}H NMR spectrum of compound **8j** (recorded in $CDCl_3$).

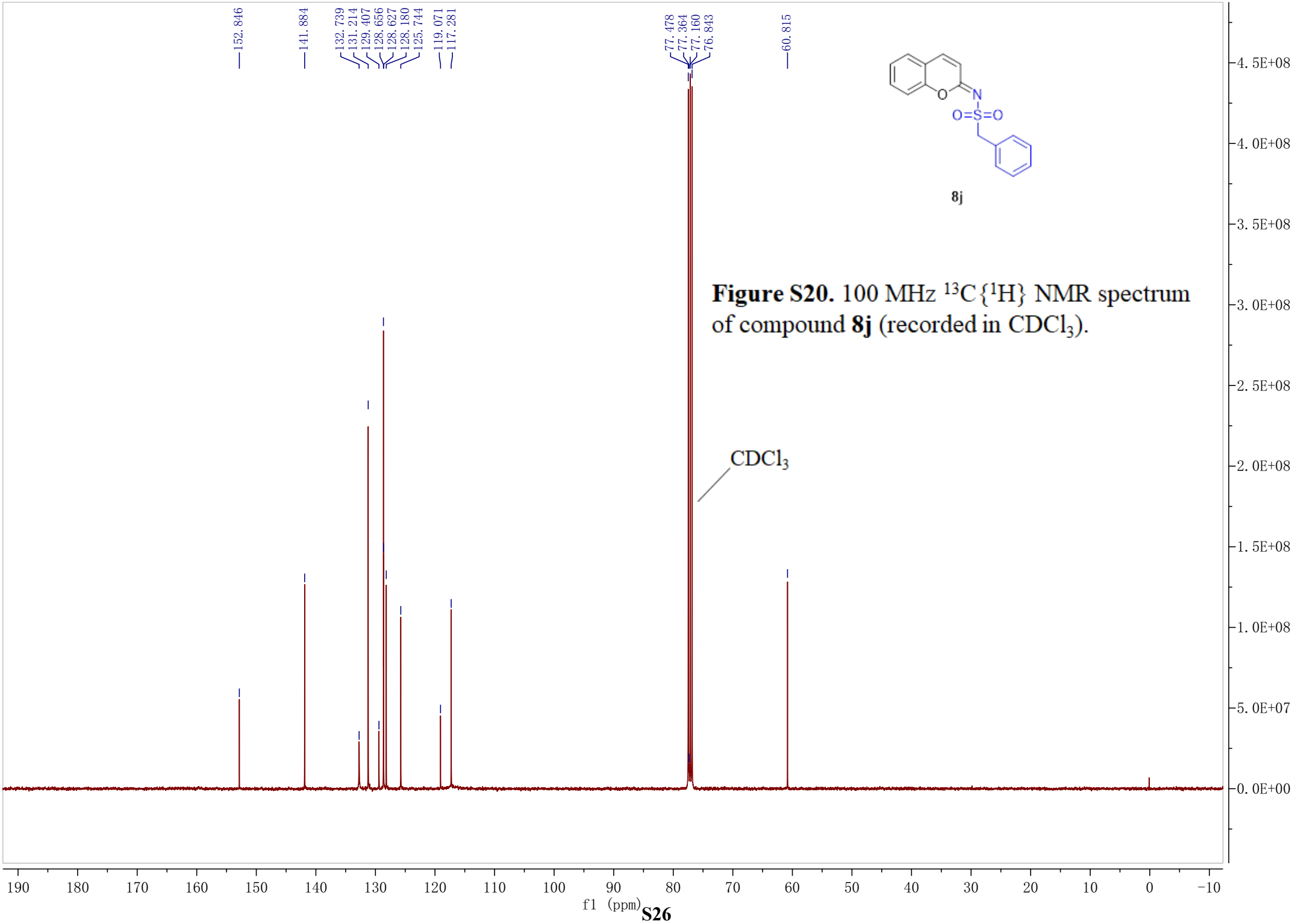


Figure S20. 100 MHz $^{13}C\{^{1}H\}$ NMR spectrum of compound **8j** (recorded in $CDCl_3$).

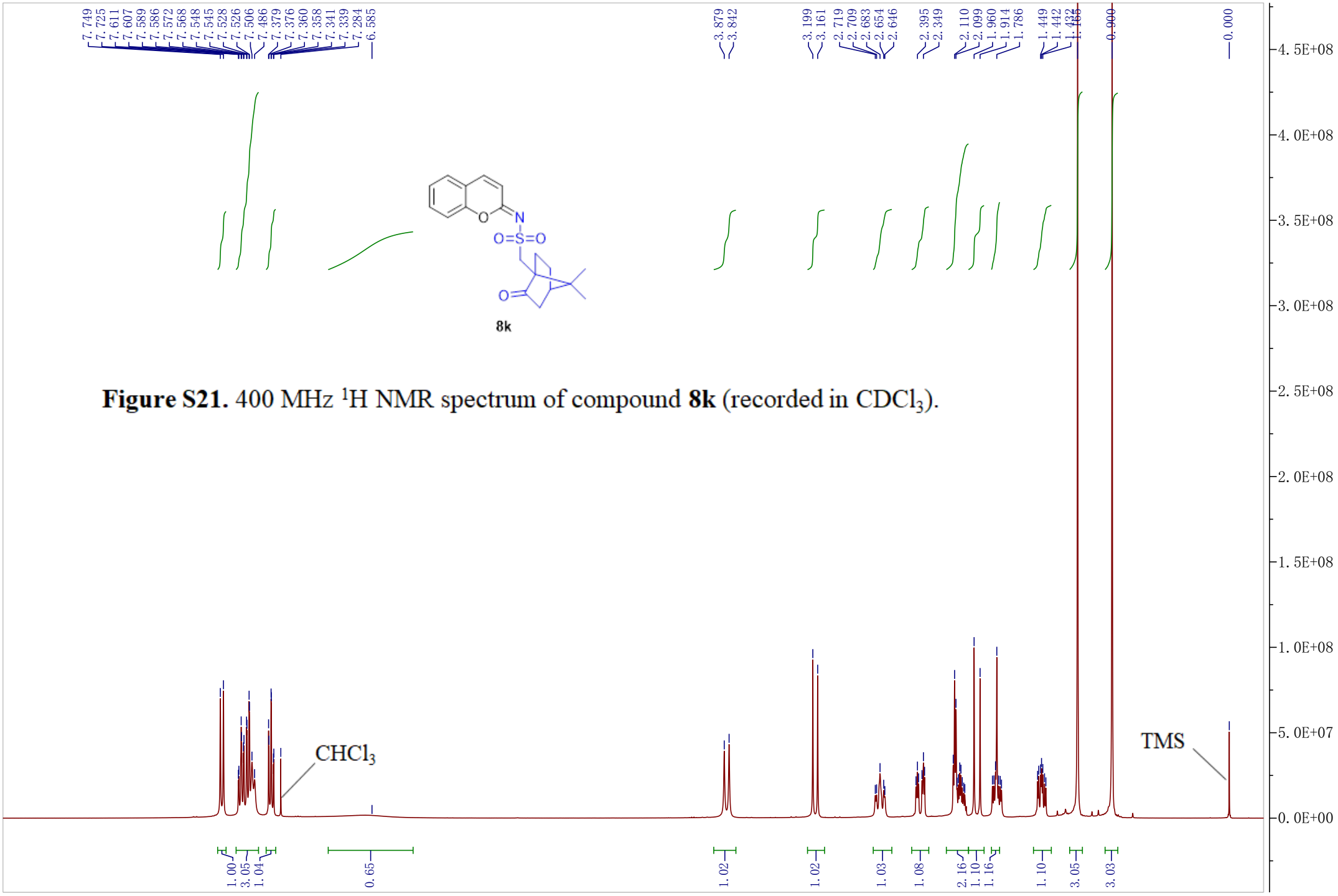
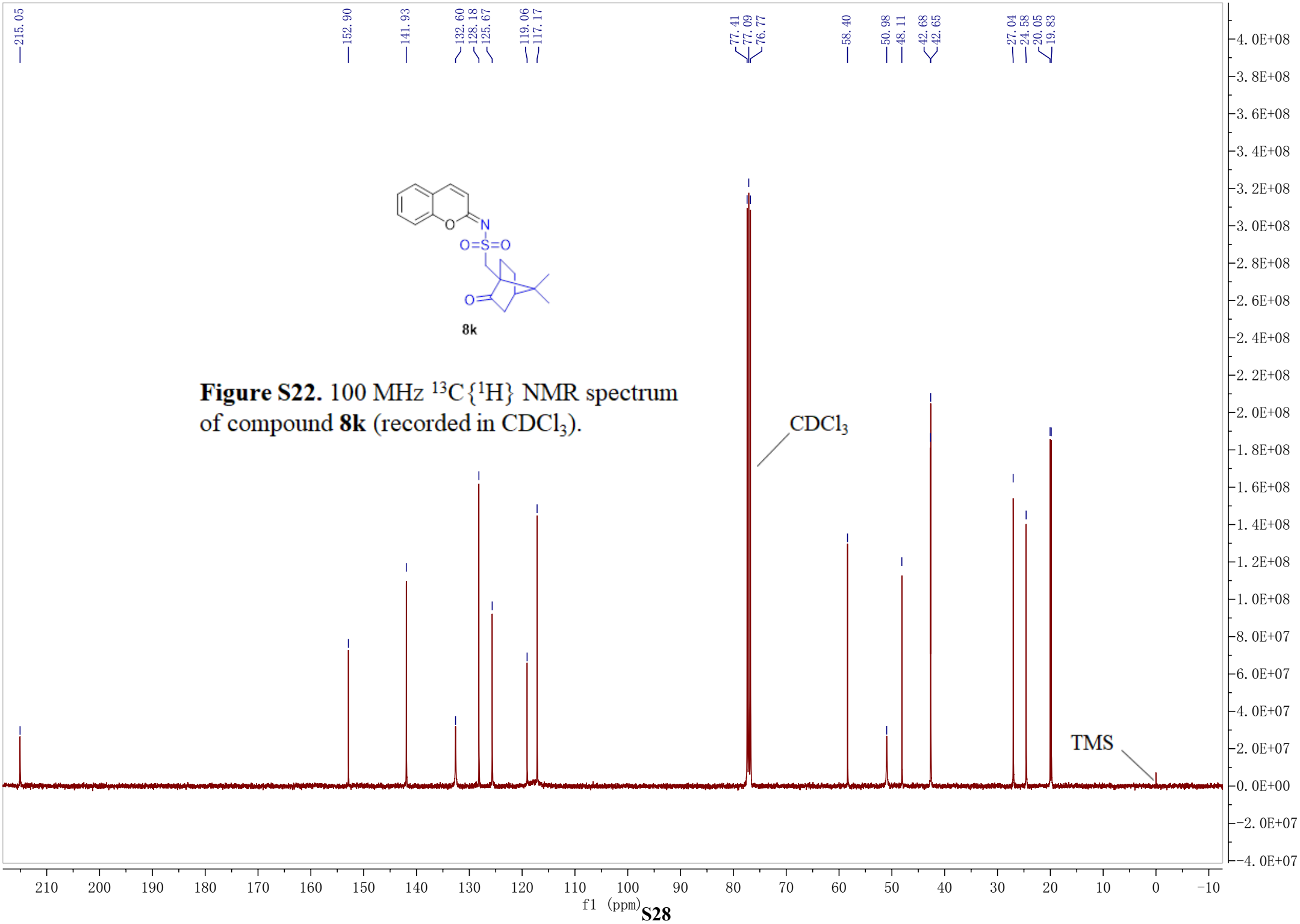


Figure S21. 400 MHz ^{1}H NMR spectrum of compound **8k** (recorded in $CDCl_3$).



8k

Figure S22. 100 MHz $^{13}C\{^{1}H\}$ NMR spectrum of compound **8k** (recorded in $CDCl_3$).

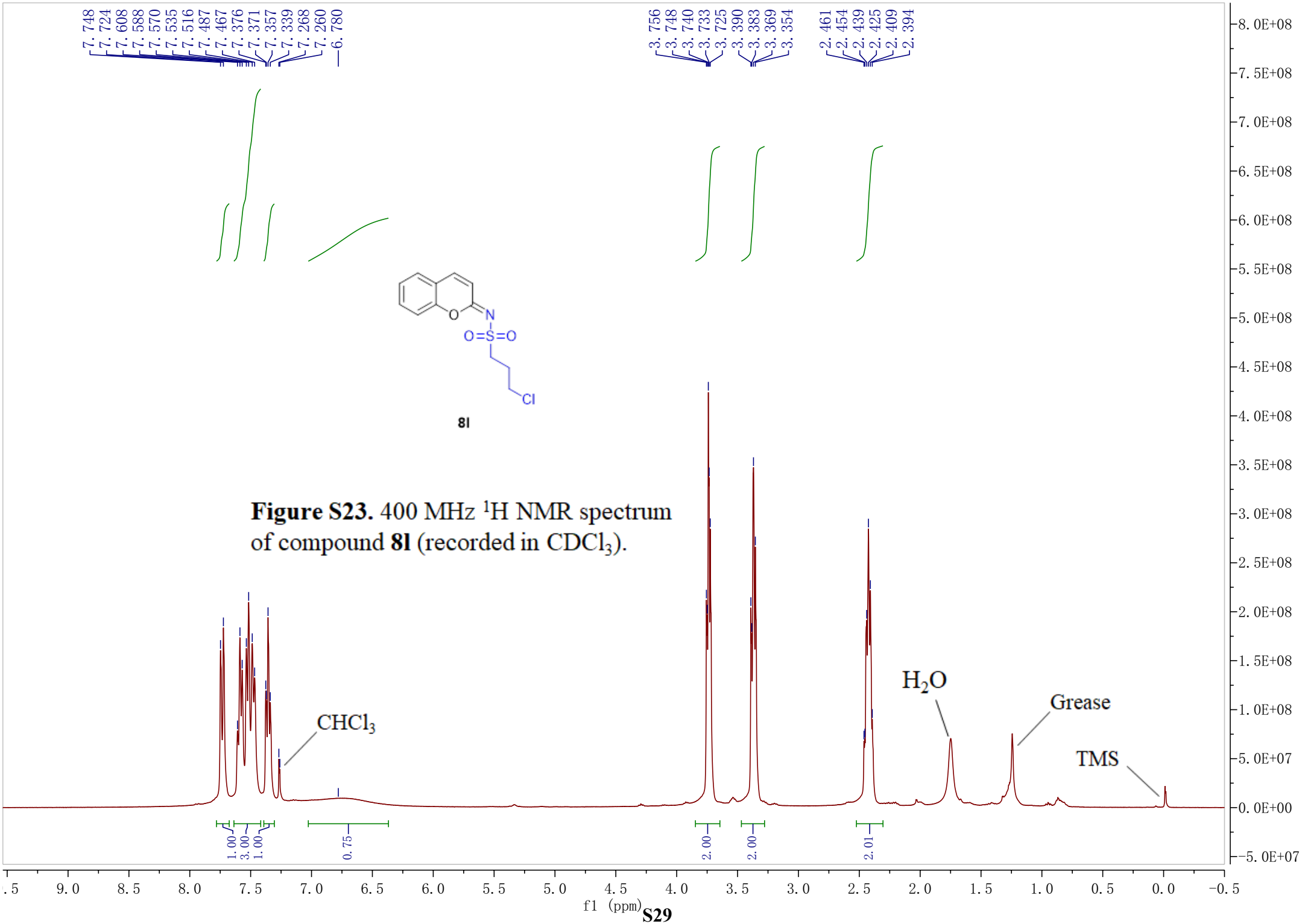


Figure S23. 400 MHz ^{1}H NMR spectrum of compound **8l** (recorded in $CDCl_3$).

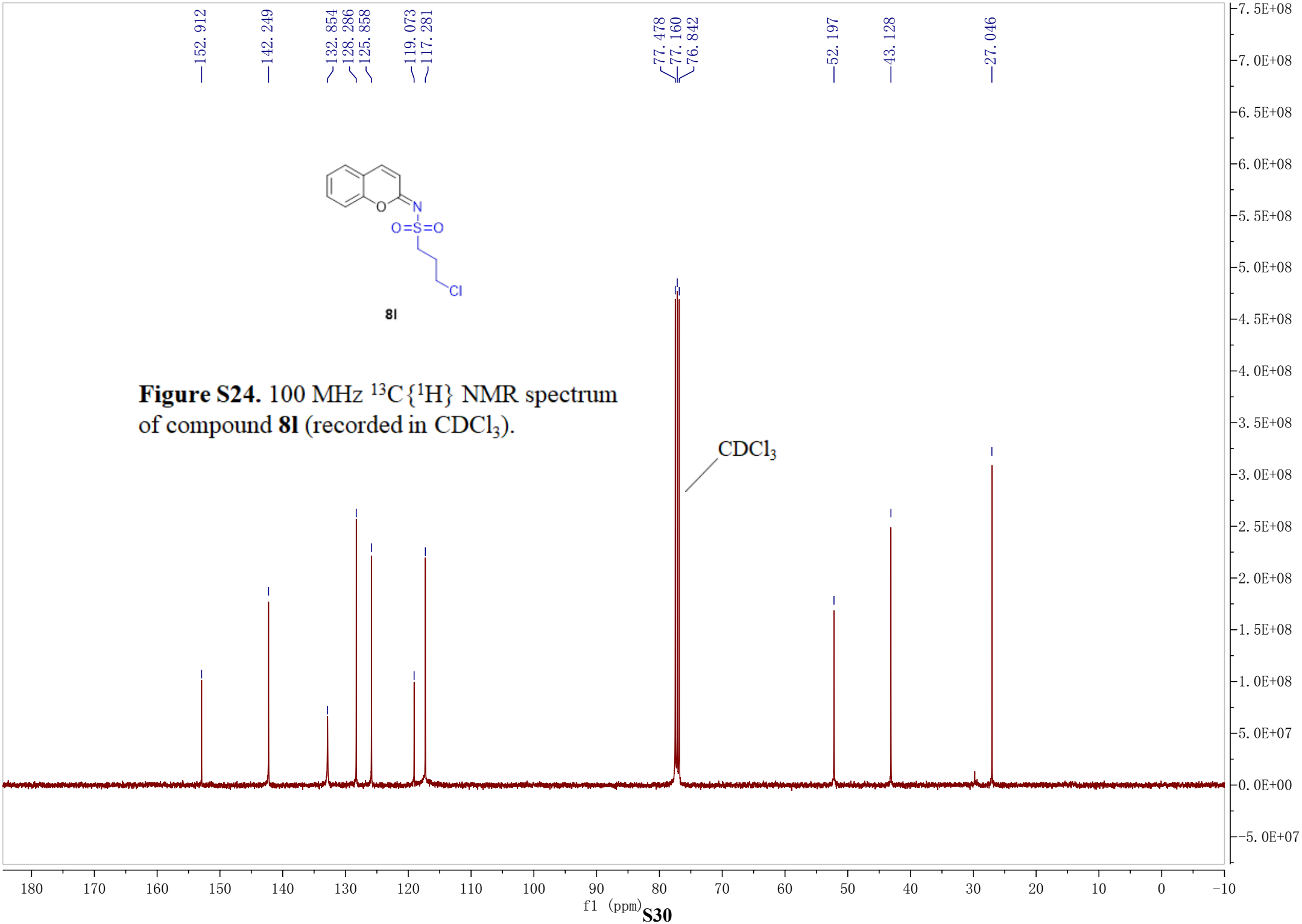


Figure S24. 100 MHz $^{13}C\{^{1}H\}$ NMR spectrum of compound **8l** (recorded in $CDCl_3$).

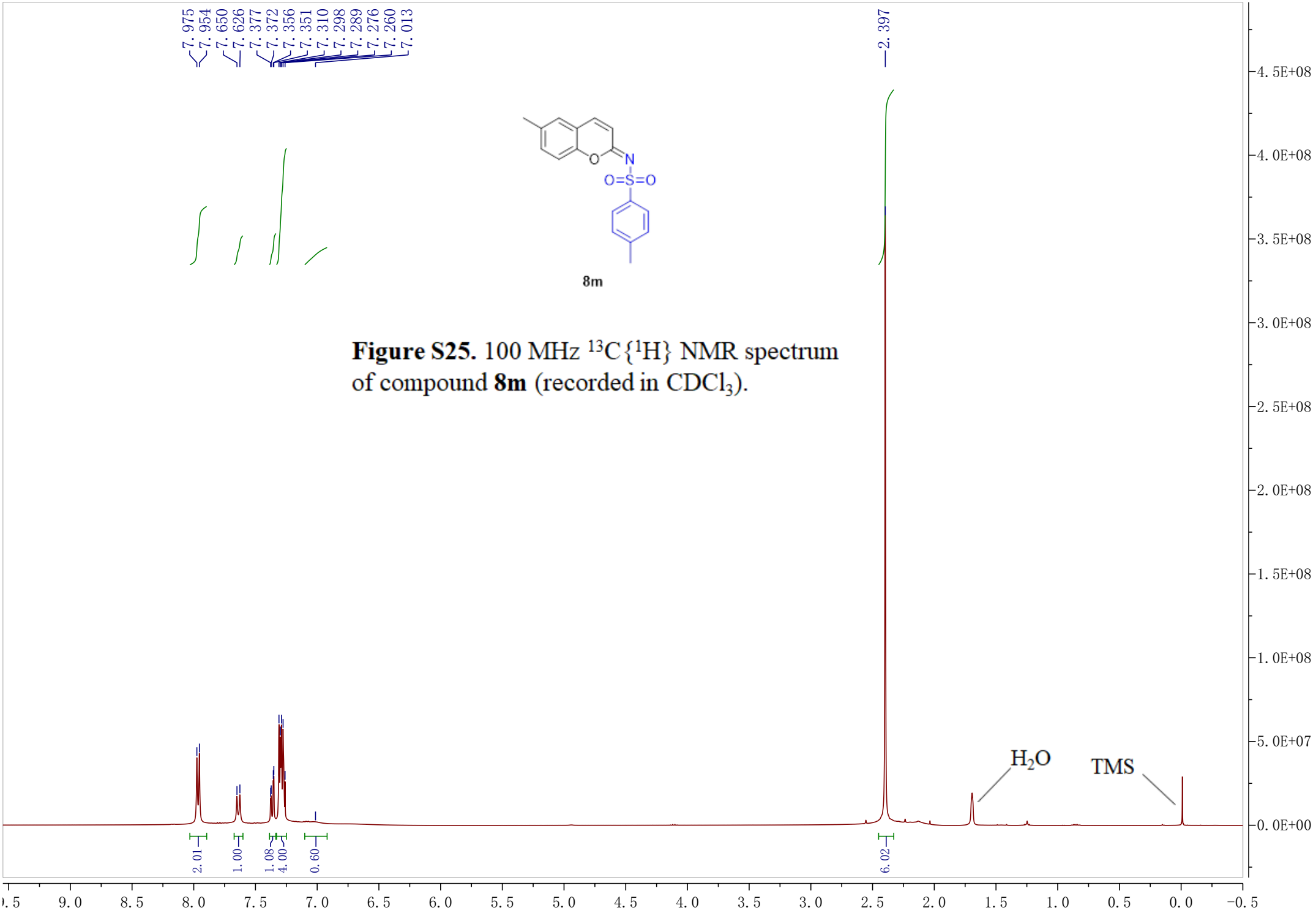
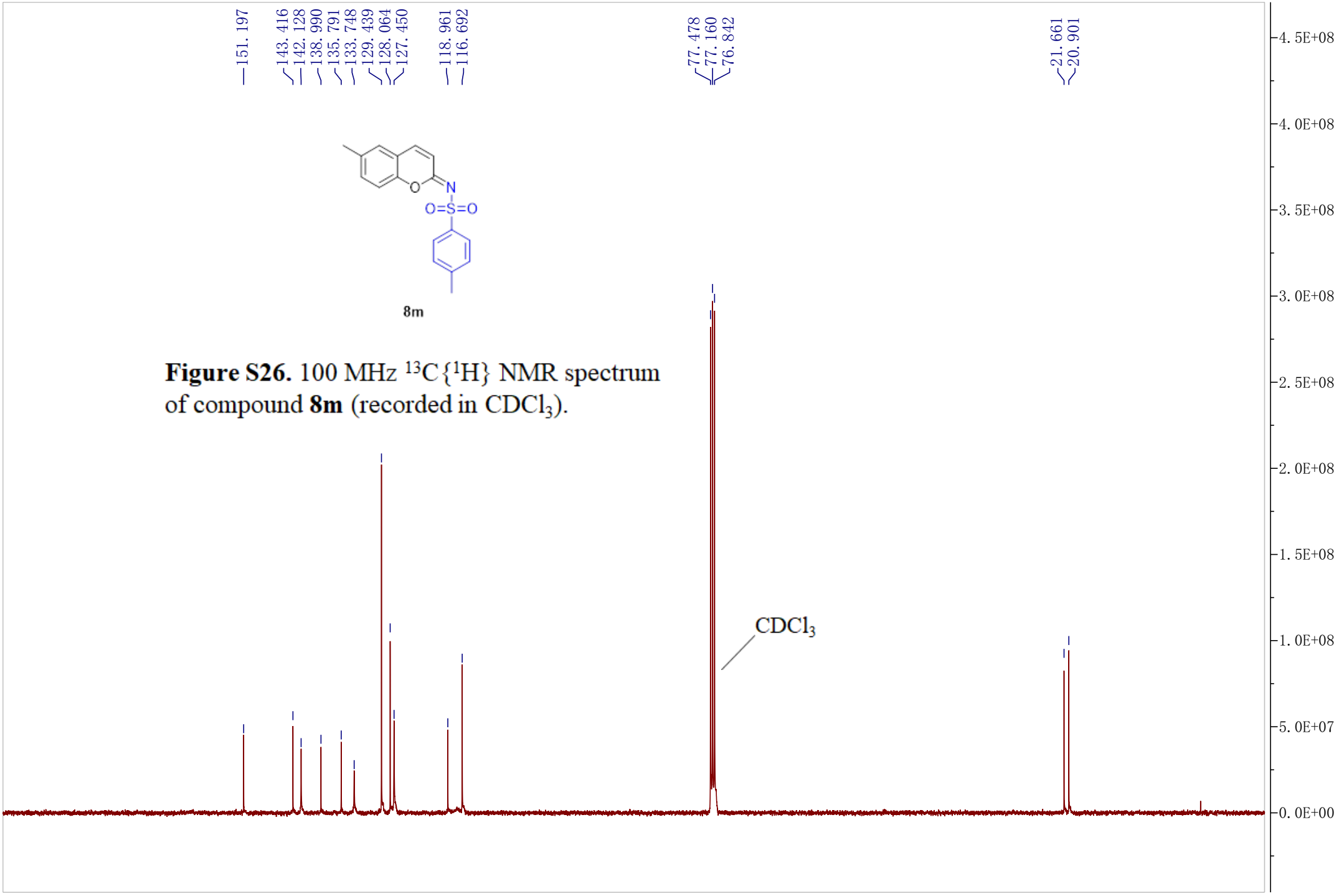


Figure S25. 100 MHz $^{13}C\{^{1}H\}$ NMR spectrum of compound **8m** (recorded in $CDCl_3$).



8m

Figure S26. 100 MHz $^{13}C\{^{1}H\}$ NMR spectrum of compound **8m** (recorded in $CDCl_3$).

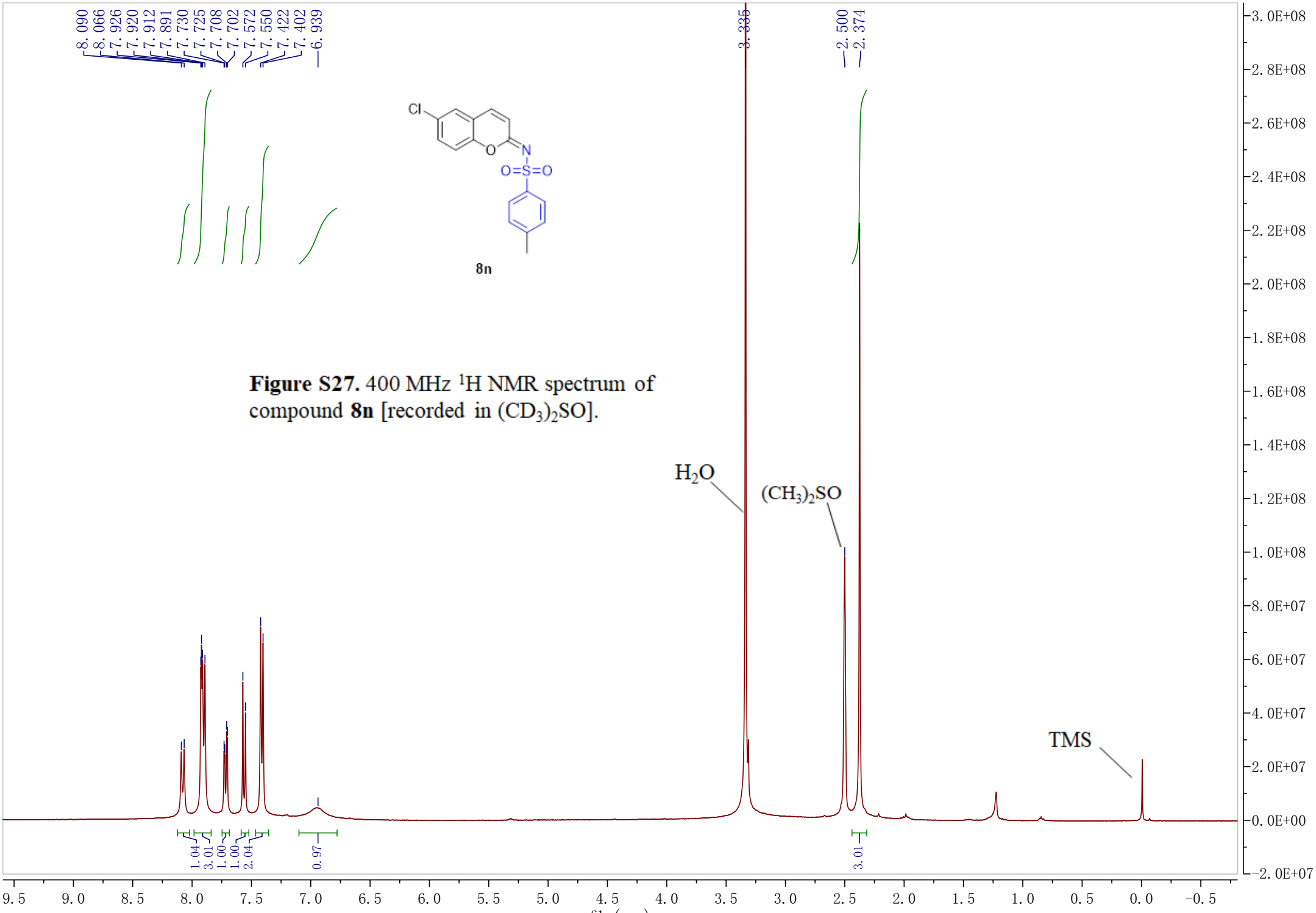


Figure S27. 400 MHz ^{1}H NMR spectrum of compound **8n** [recorded in $(CD_3)_2SO$].

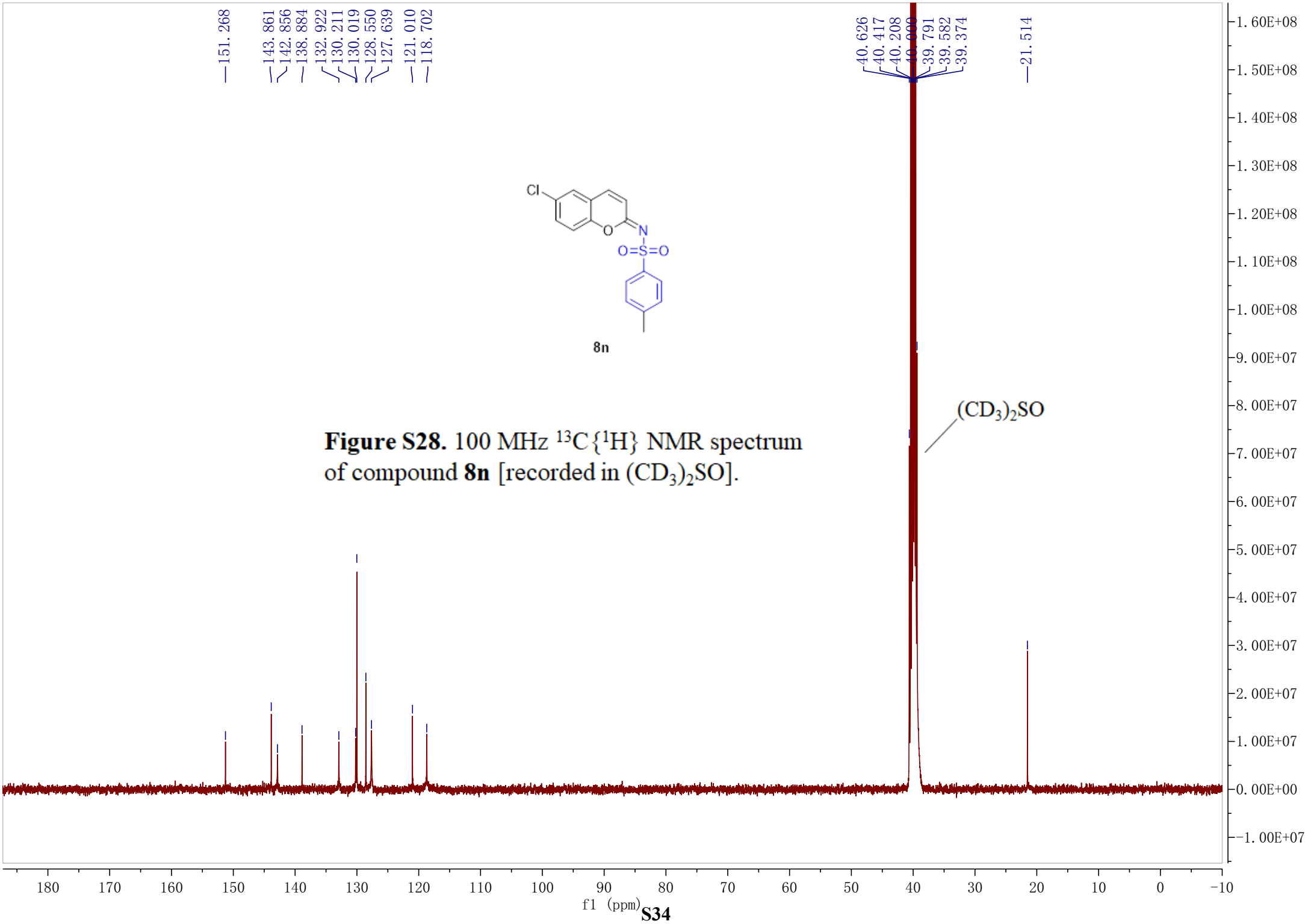


Figure S28. 100 MHz $^{13}C\{^{1}H\}$ NMR spectrum of compound **8n** [recorded in $(CD_3)_2SO$].

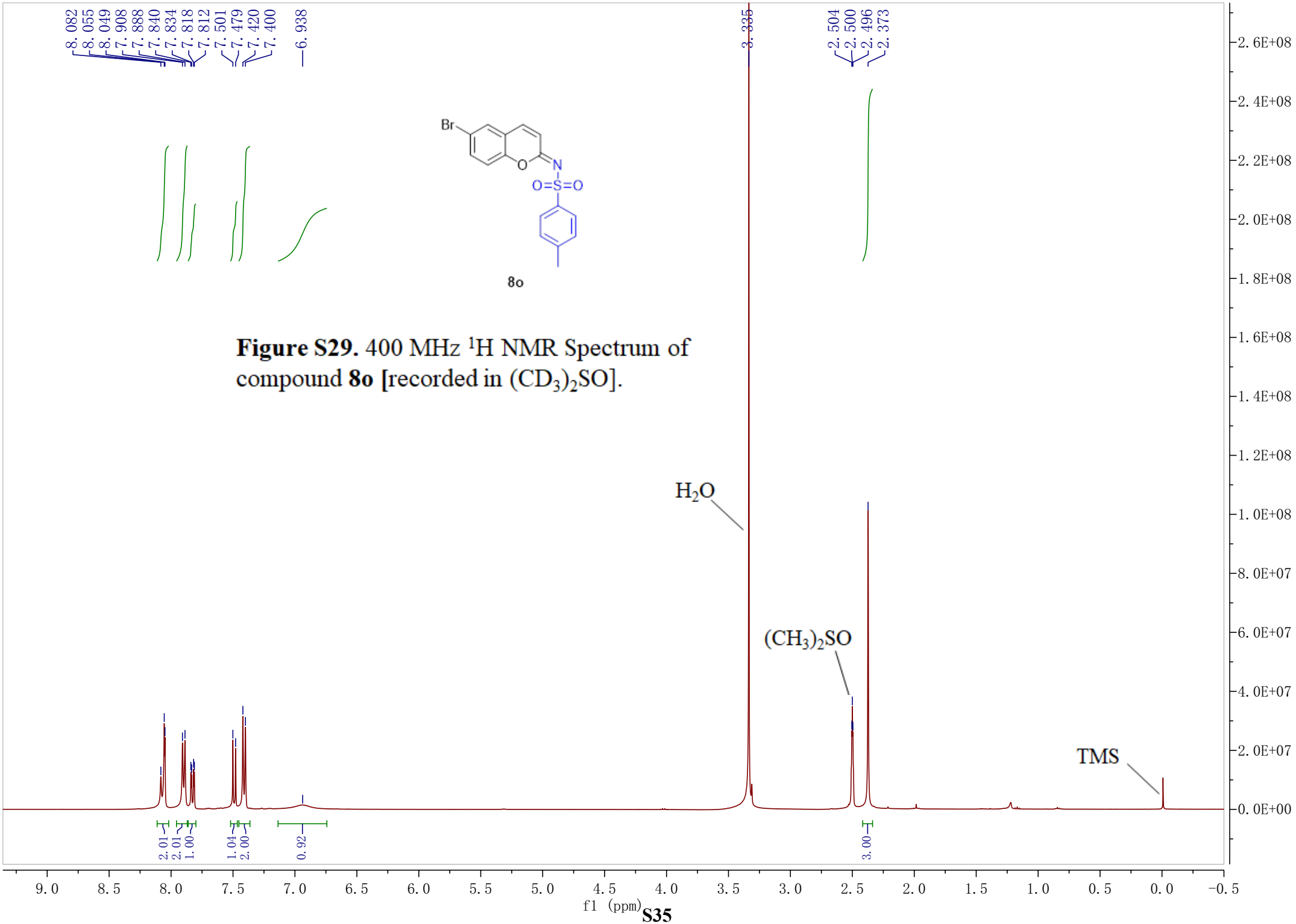


Figure S29. 400 MHz ^{1}H NMR Spectrum of compound **8o** [recorded in $(CD_3)_2SO$].

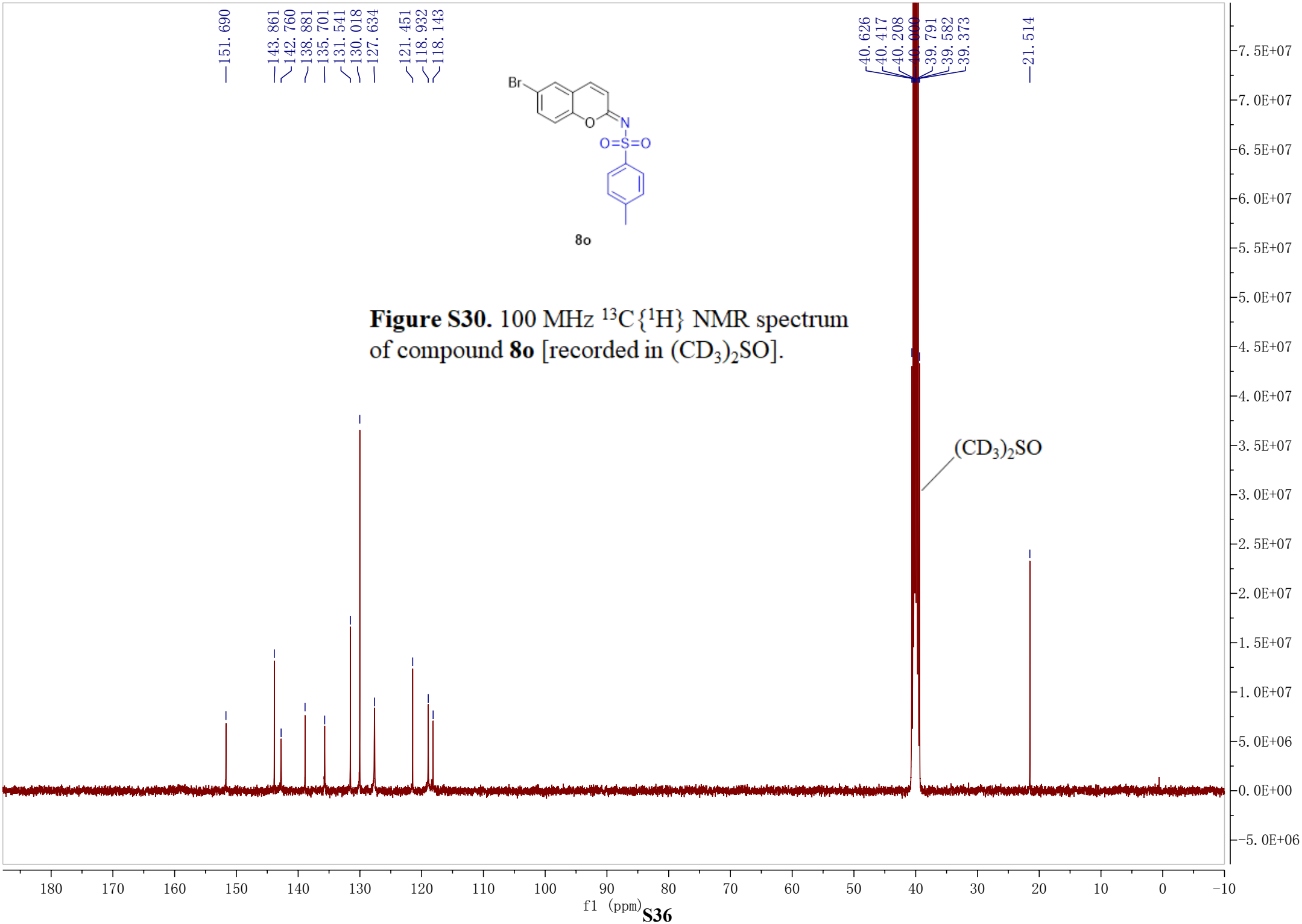


Figure S30. 100 MHz $^{13}C\{^{1}H\}$ NMR spectrum of compound **8o** [recorded in $(CD_3)_2SO$].

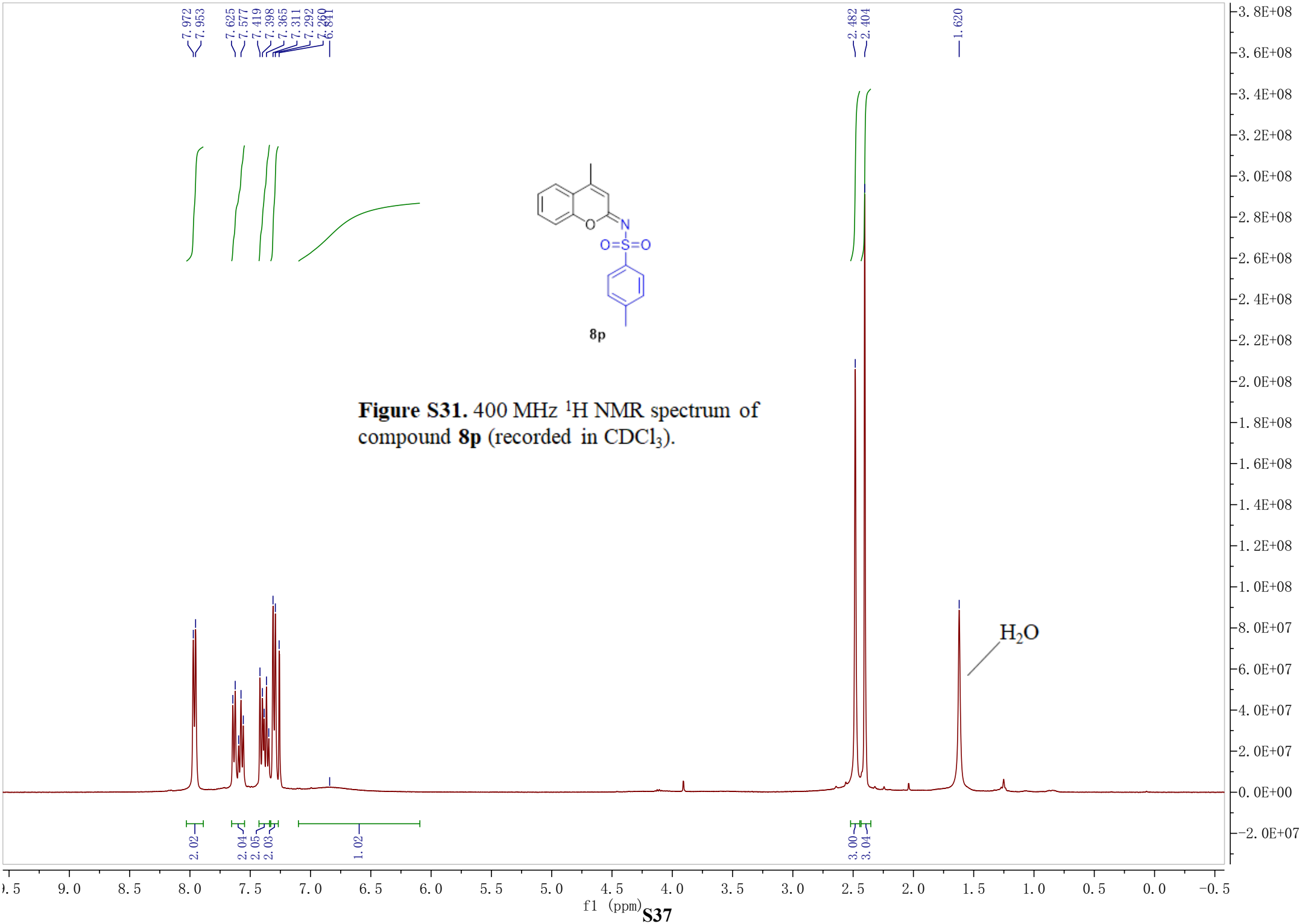


Figure S31. 400 MHz ^{1}H NMR spectrum of compound **8p** (recorded in $CDCl_3$).

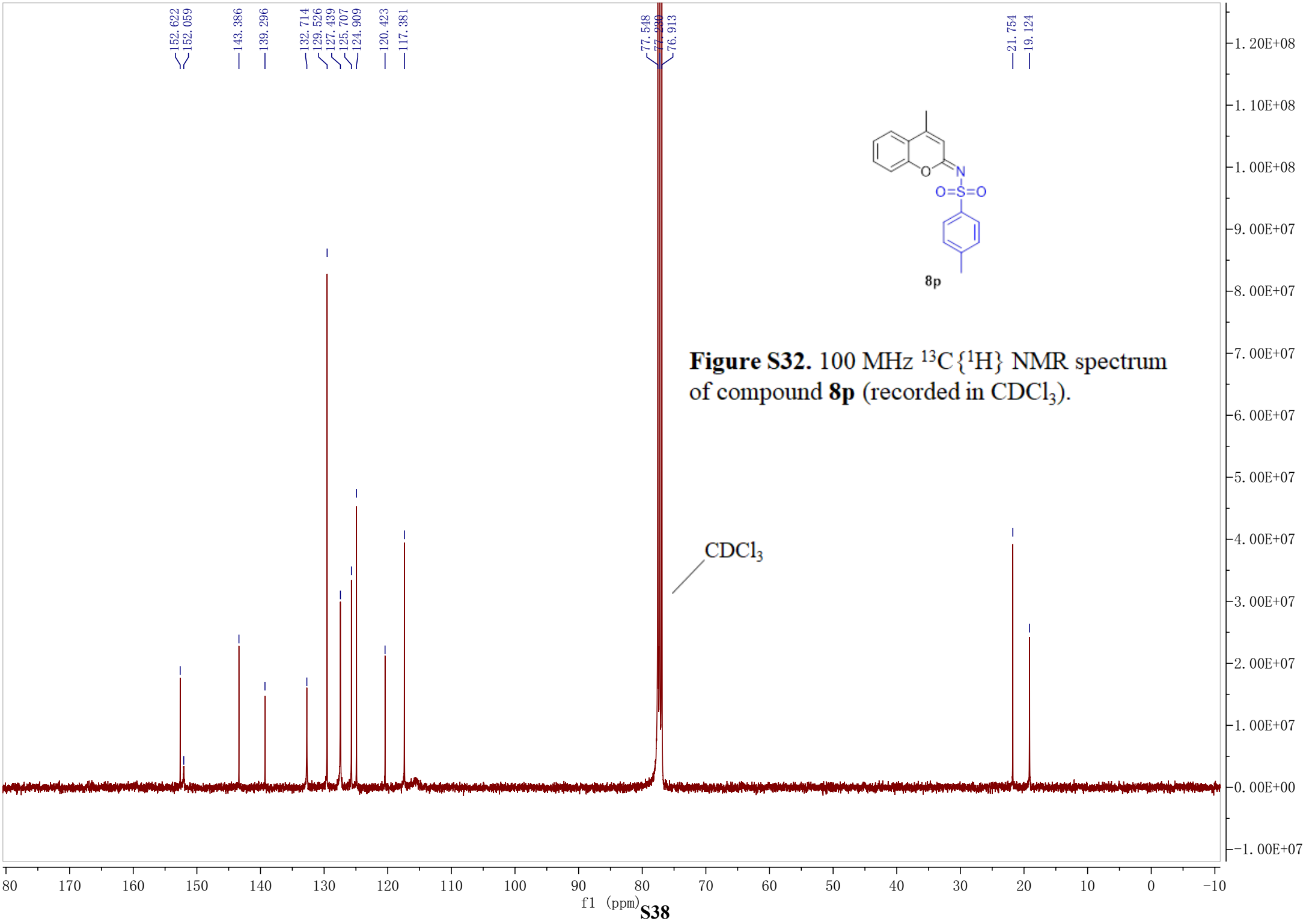


Figure S32. 100 MHz $^{13}C\{^{1}H\}$ NMR spectrum of compound **8p** (recorded in $CDCl_3$).

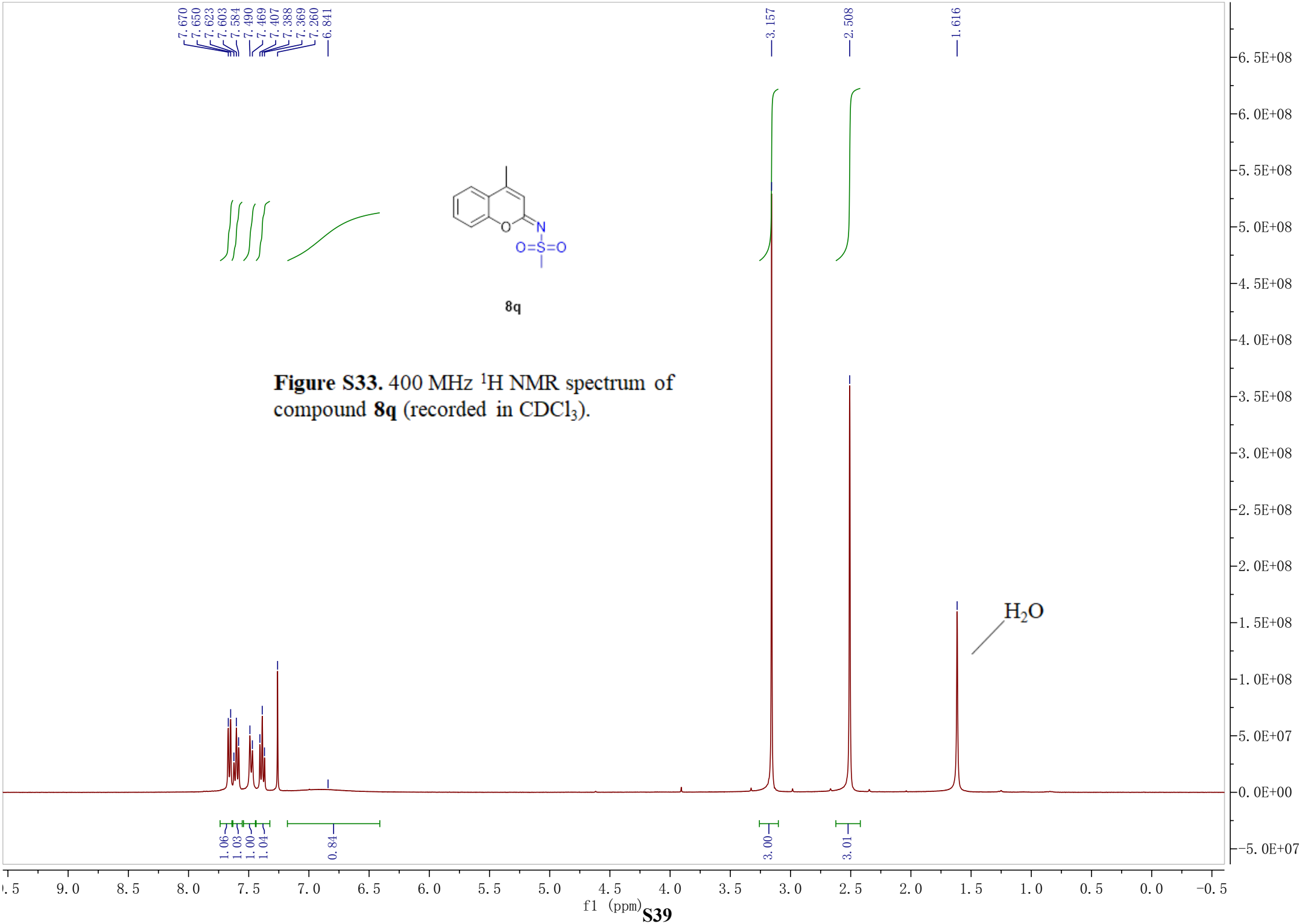


Figure S33. 400 MHz ^{1}H NMR spectrum of compound **8q** (recorded in $CDCl_3$).

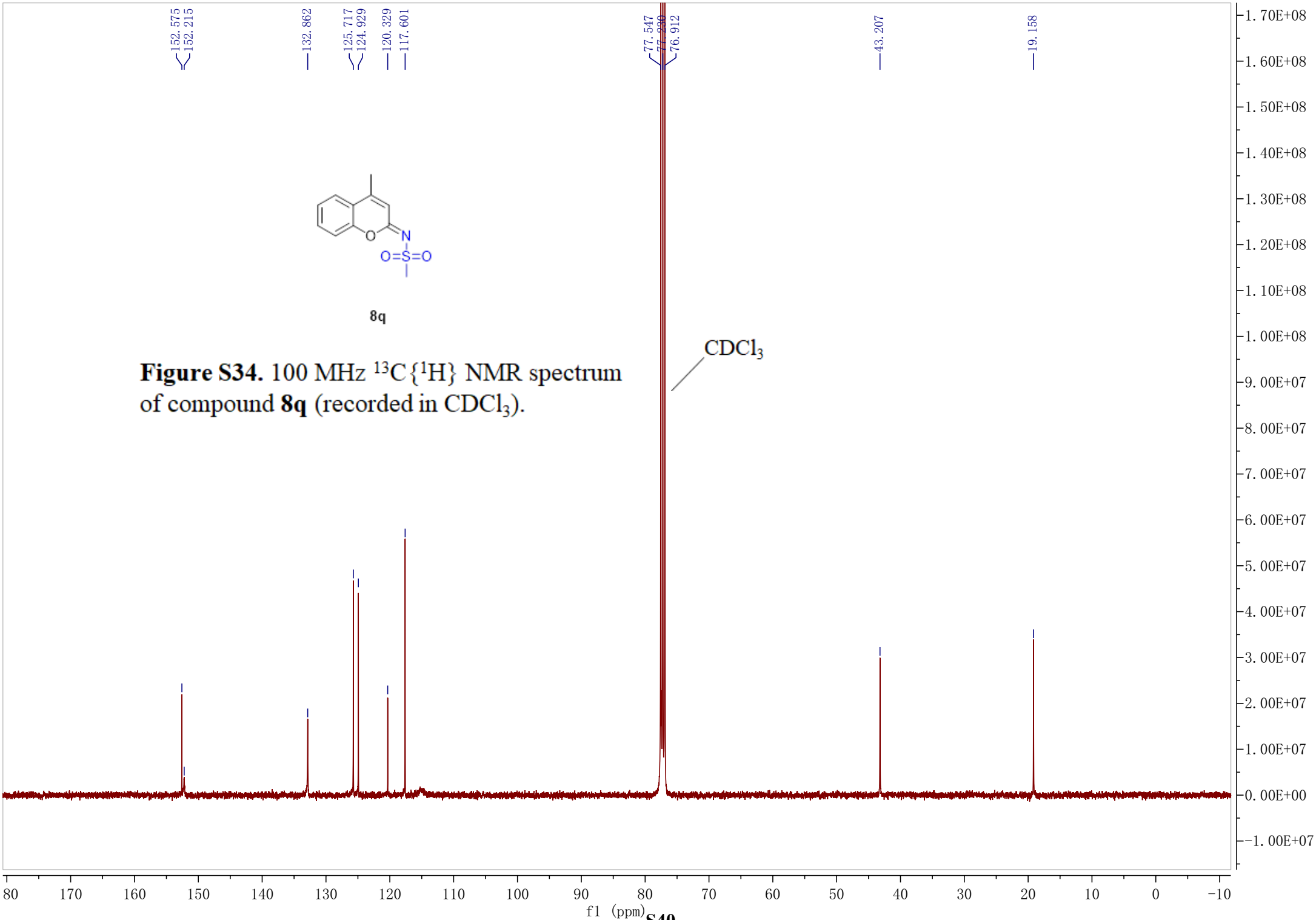


Figure S34. 100 MHz $^{13}C\{^{1}H\}$ NMR spectrum of compound **8q** (recorded in $CDCl_3$).

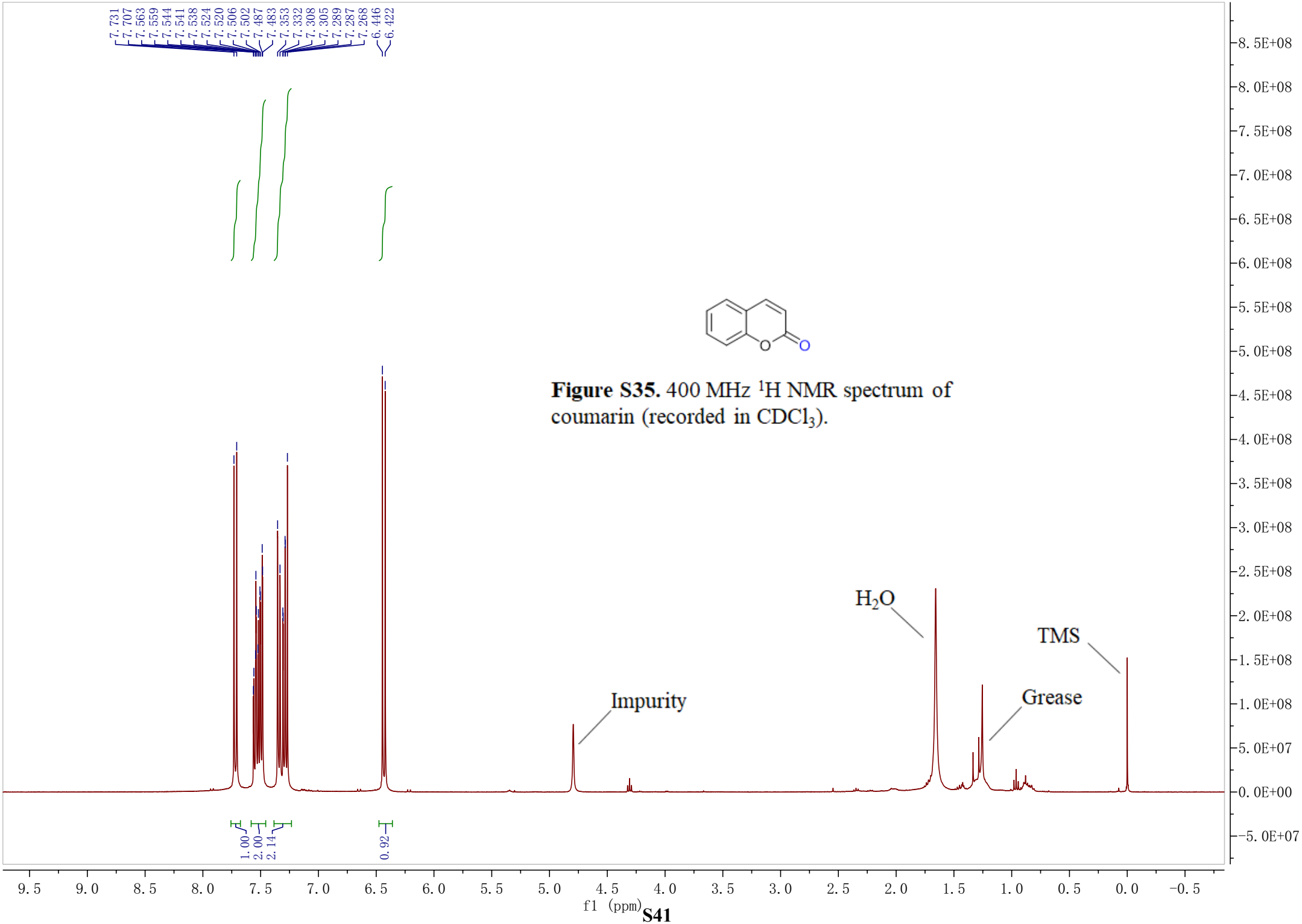


Figure S35. 400 MHz ^{1}H NMR spectrum of coumarin (recorded in $CDCl_3$).

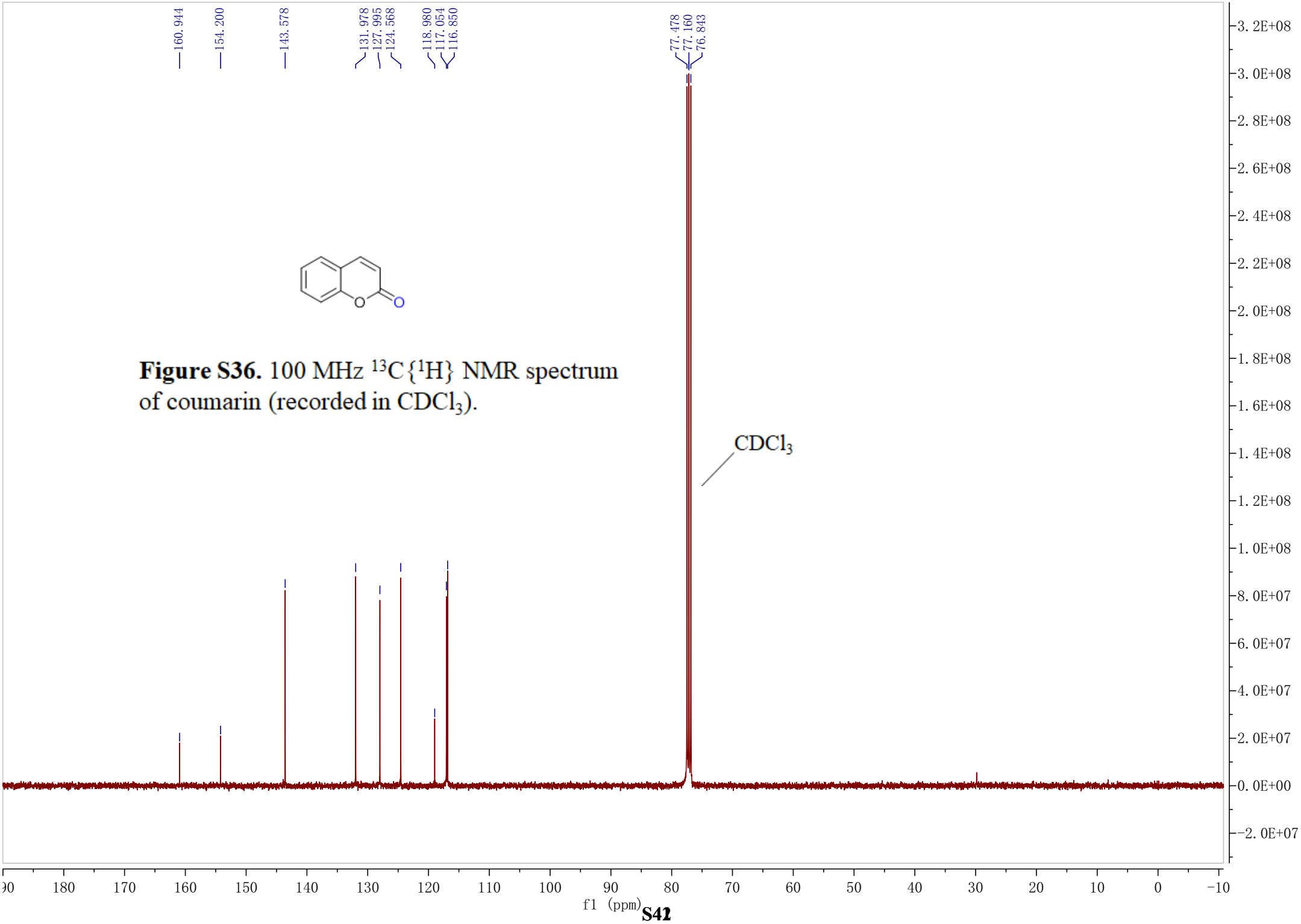


Figure S36. 100 MHz $^{13}C\{^{1}H\}$ NMR spectrum of coumarin (recorded in $CDCl_3$).