Supporting Information

Novel 7-(1*H*-Pyrrol-1-yl)spiro[chromeno[4,3-*b*]quinoline-6,1'-cycloalkanes]: Synthesis, Cross-Coupling Reactions and Photophysical Properties

Letícia B. Silva, Felipe S. Stefanello, Sarah C. Feitosa, Clarissa P. Frizzo, Marcos A. P. Martins, Nilo Zanatta, Bernardo A. Iglesias[b], Helio G. Bonacorso[a*]

[a]*Núcleo de Química de Heterociclos (NUQUIMHE), Departamento de Química, Universidade Federal de Santa Maria, 97105-900 – Santa Maria, RS – Brazil.*

[b]*Laboratório de Bioinorgânica e Materiais Porfirínicos, Departamento de Química, Universidade Federal de Santa Maria, 97105-900 – Santa Maria, RS – Brazil.*

Email: helio.bonacorso@ufsm.br

1. General

^{1}H and ^{13}C NMR spectra were acquired on Bruker DPX 400 MHz (**3a-g**, **3i-k**) or on a Bruker Avance III 600 MHz (**3h**, **4**, **5**, **6**) spectrometers for one-dimensional experiments, with 5-mm sample tubes, 298 K, and digital resolution of 0.01 ppm, in $CDCl_3$ as solvent, and using TMS as the internal reference. All spectra can be found in Figures S1–S33 in the *Supplementary information*. All results are reported with the chemical shift (δ), multiplicity, integration, and coupling constant (Hz). The following abbreviations were used to explain multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, and dd = double doublet. All NMR chemical shifts were reported in parts per million, which is relative to the internal reference. The CHN elemental analyses were performed on a Perkin–Elmer 2400 CHN elemental analyzer (University of São Paulo, USP, Brazil). The HRMS analyses were performed on a a hybrid high-resolution and high-accuracy (5μL/L) micrOTOF-Q mass spectrometer (Bruker Scientific®, Billerica, MA, USA) at (Caxias do Sul University, UCS, Brazil).

For mass spectrometry, the fractions were dissolved in a solution consisting of 50% (v/v) chromatographic grade acetonitrile (Tedia, Fairfild, OH, USA) and 50% (v/v) deionized water, to which 0.1% formic acid and 0.1% ammonium formate had been added, for analysis in positive ESI(+). The individual solutions were infused directly into the ESI source via a syringe pump (Harvard Apparatus, Hamilton, Reno, NV, USA), at a flow rate of 180μL/min. The ESI(+)-and ESI(-) mass spectrometric (MS) and tandem MS-MS profiles were acquired using a hybrid high-resolution and high-accuracy (5μL/L) micrOTOF-Q mass spectrometer (Bruker Scientific®, Billerica, MA, USA) under the following conditions: capillary and cone voltages were set to +3500 and +40V, respectively, with a desolvation temperature of 200°C. The collision-induced dissociation energy (CID) for the ESI (+) MS-MS was optimized for each component. For data acquisition and processing, time-of-flight (TOF) control and data analysis software (Bruker Scientific®) was used. The data were collected in the 70–800 *m/z* range, at a rate of two scans/s, providing 50,000 full width at half maximum (FWHM) resolution at 200 *m/z*. No important ions were observed below 90 *m/z* and above 1000 *m/z*, so the ESI(+)-MS data are shown for the range of 90–1000 *m/z.* [1]

Electronic UV-Vis absorption analysis of compounds in CH_3CN, CH_2Cl_2 and DMSO solutions were done with a Shimadzu UV2600 spectrophotometer (data interval of 1.0 nm) at 250 to 500 nm range. Steady-state emission fluorescence analysis of samples

in CH_3CN, CH_2Cl_2 and DMSO solutions were measured with a Varian Cary50 fluorescence spectrophotometer (slit of 5.0 mm; em/exc) and corrected according to the manufacturer's instructions. Fluorescence quantum yield values (Φ_{fl}) of the compounds in solution were determined by comparing the corrected fluorescence spectra with that of 9,10-diphenylanthracene (DPA) in chloroform (Φ_{fl} = 0.65, λ_{ex} = 366 nm) as the standard for the fluorescence yield. All spectra can be found in Figures S34–S48 in the *Supplementary information*.

2. NMR Spectra

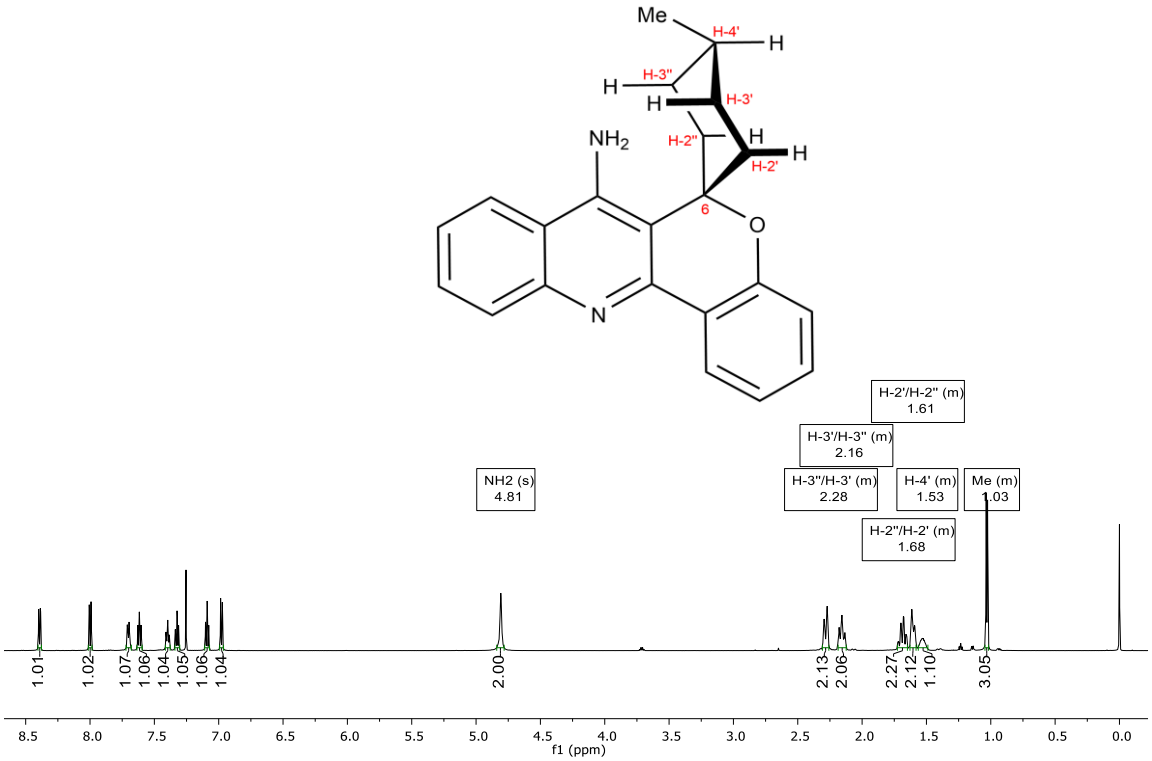

Figure S1. ^{1}H NMR spectra at 600 MHz in $CDCl_3$ of compound **1d**

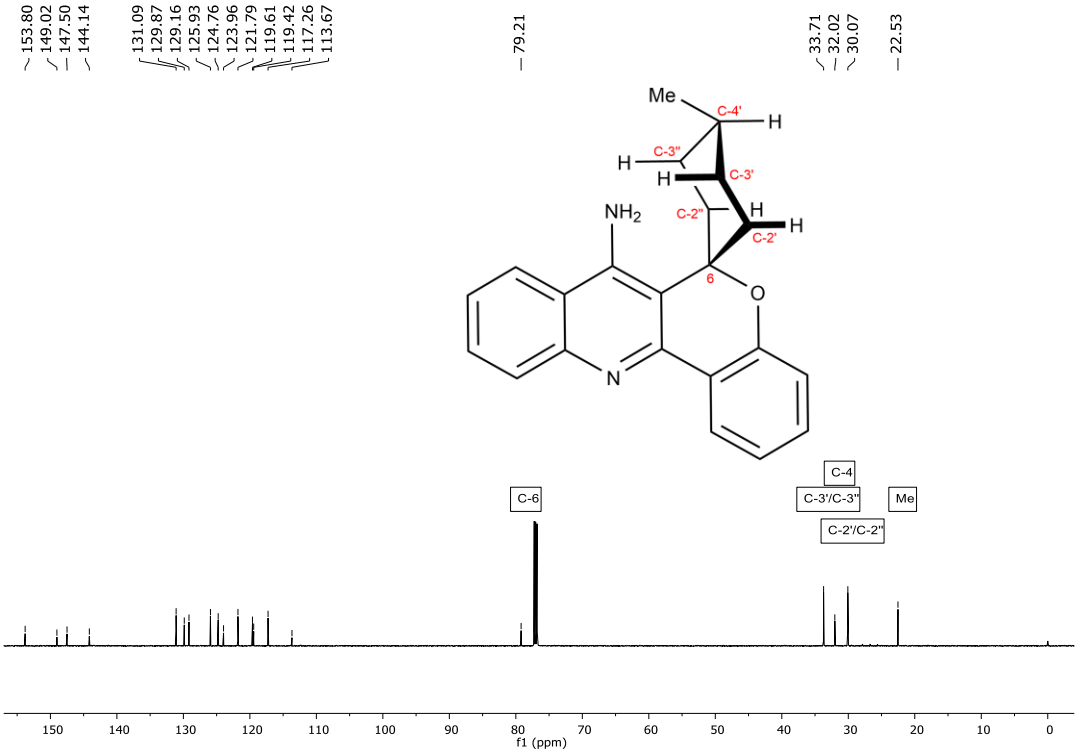

Figure S2. ^{13}C NMR spectra at 150 MHz in $CDCl_3$ of compound **1d.**

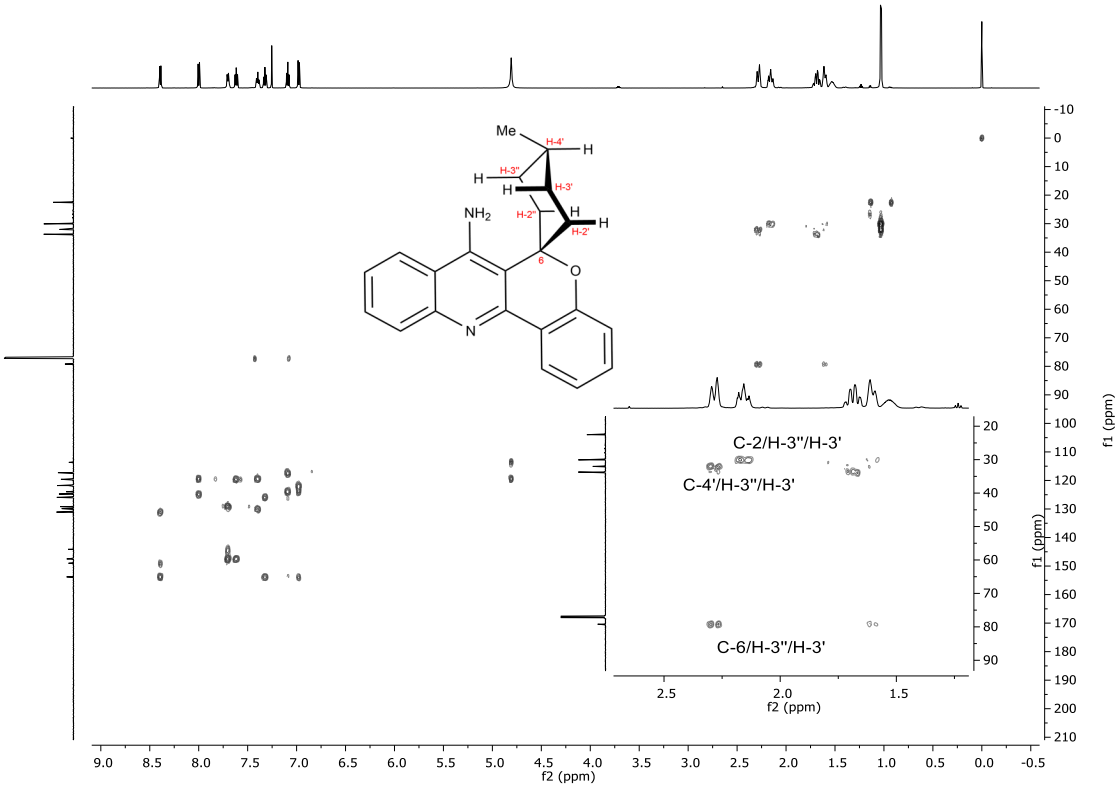

Figure S3. ^{13}C-^{1}H HMBC spectra at 150 MHz in $CDCl_3$ of compound **1d.**

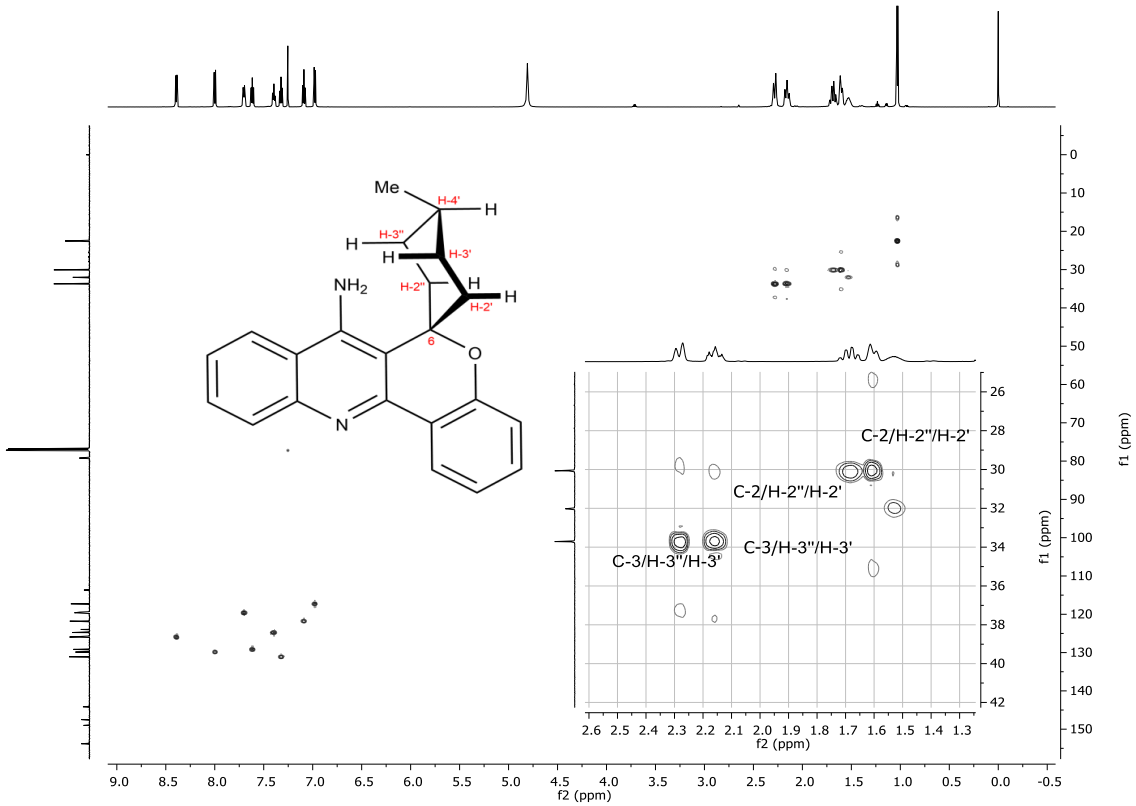

Figure S4. ^{13}C-^{1}H HSQC spectra at 150 MHz in $CDCl_3$ of compound **1d.**

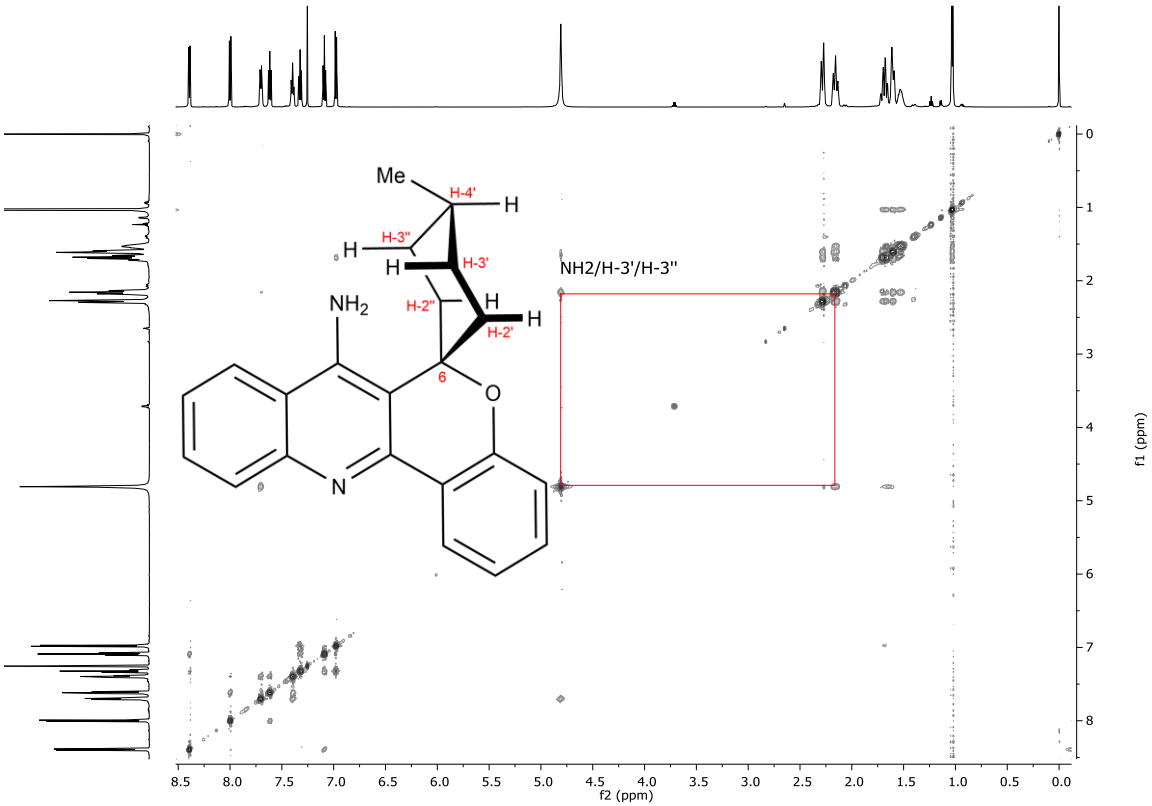

Figure S5. ^{1}H-^{1}H NOESY spectra at 600 MHz in $CDCl_3$ of compound **1d.**

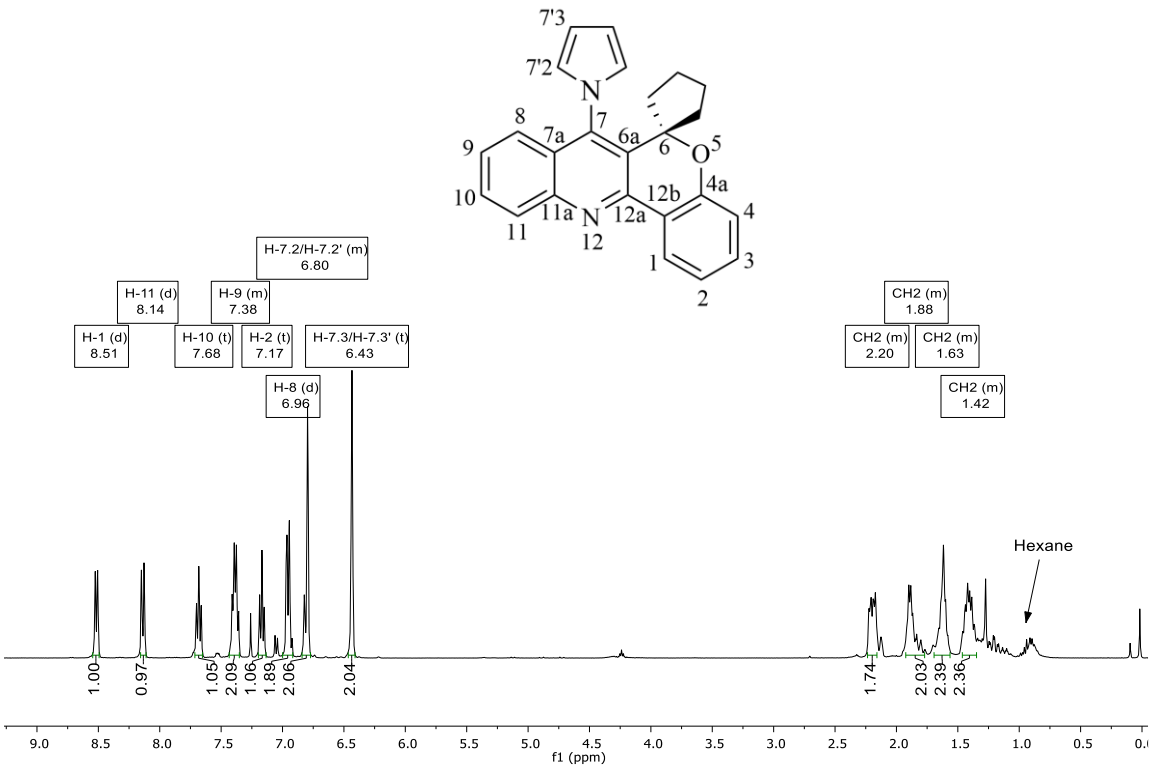

Figure S6. ^{1}H NMR spectra at 400 MHz in $CDCl_3$ of compound **3a.**

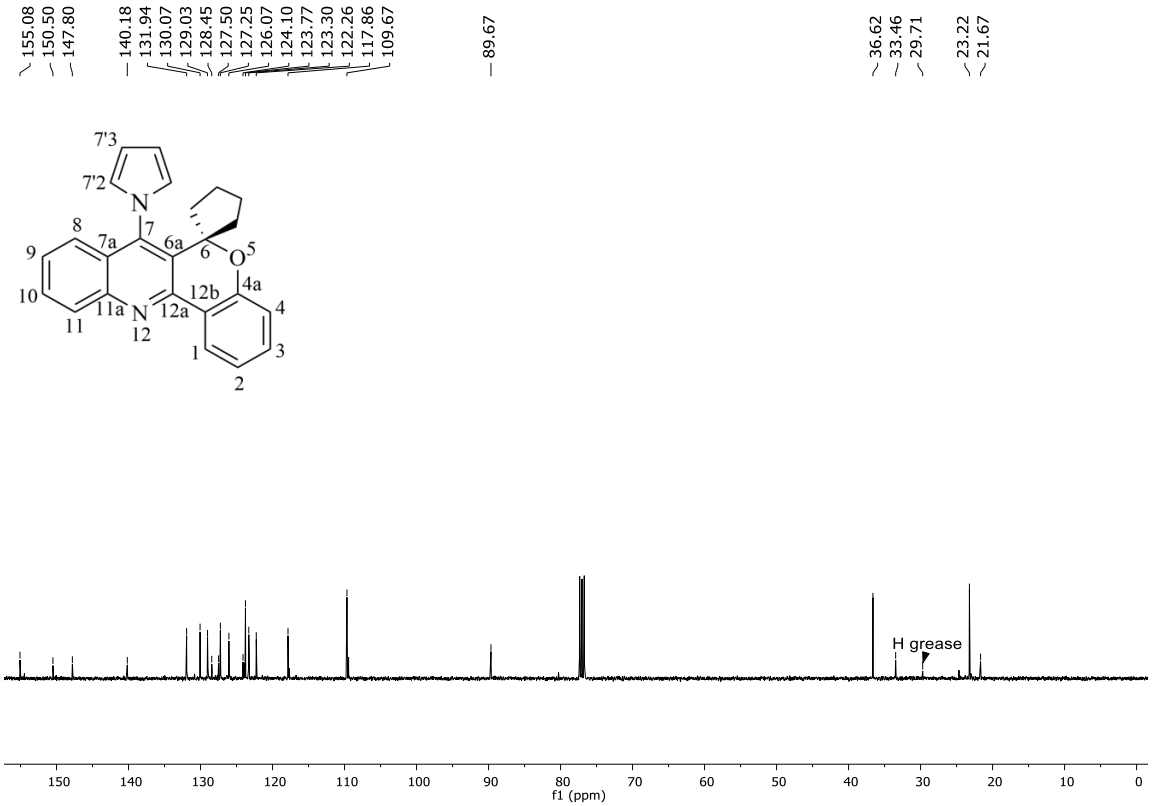

Figure S7. ^{13}C NMR spectra at 150 MHz in $CDCl_3$ of compound **3a.**

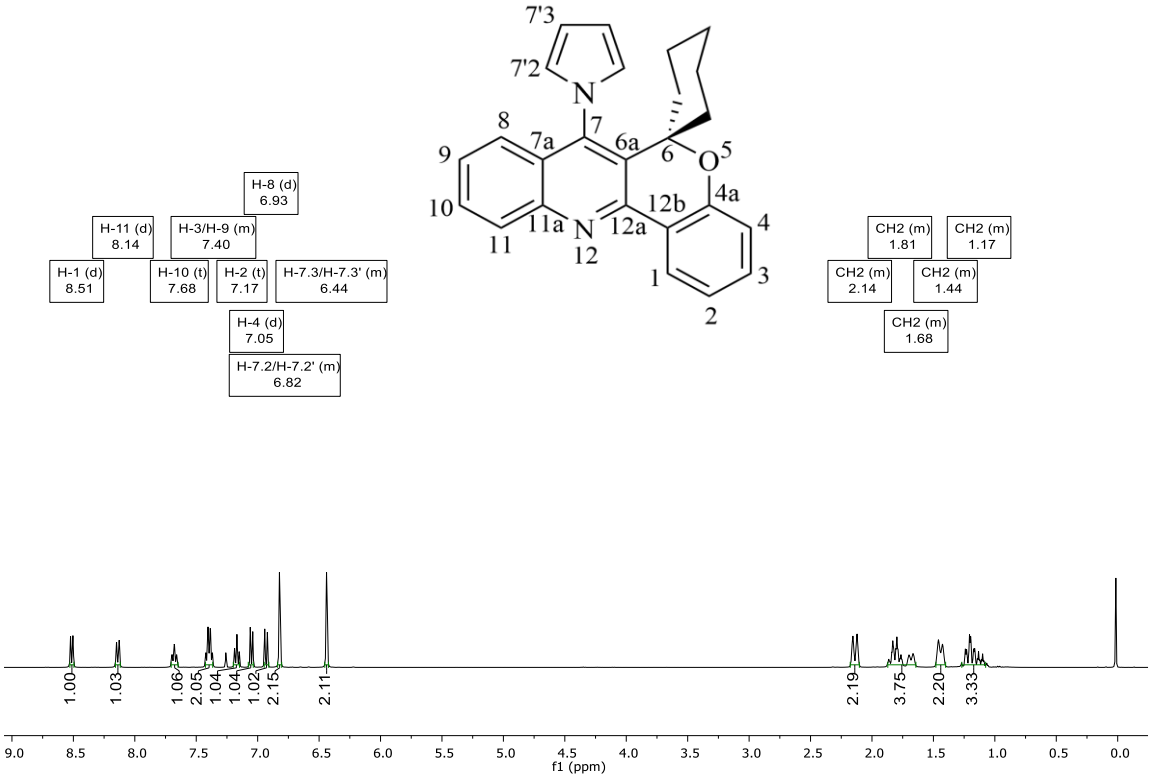

Figure S8. ^{1}H NMR spectra at 400 MHz in $CDCl_3$ of compound **3b**

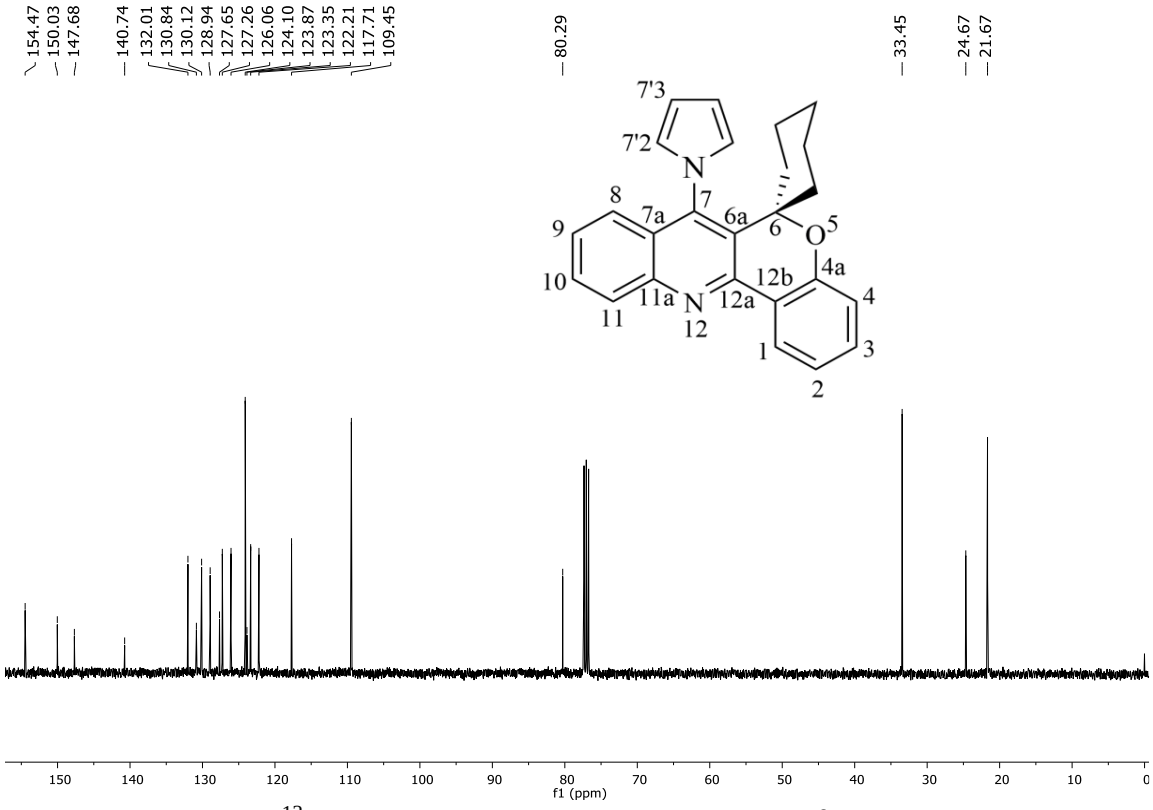

Figure S9. ^{13}C NMR spectra at 100 MHz in $CDCl_3$ of compound **3b**

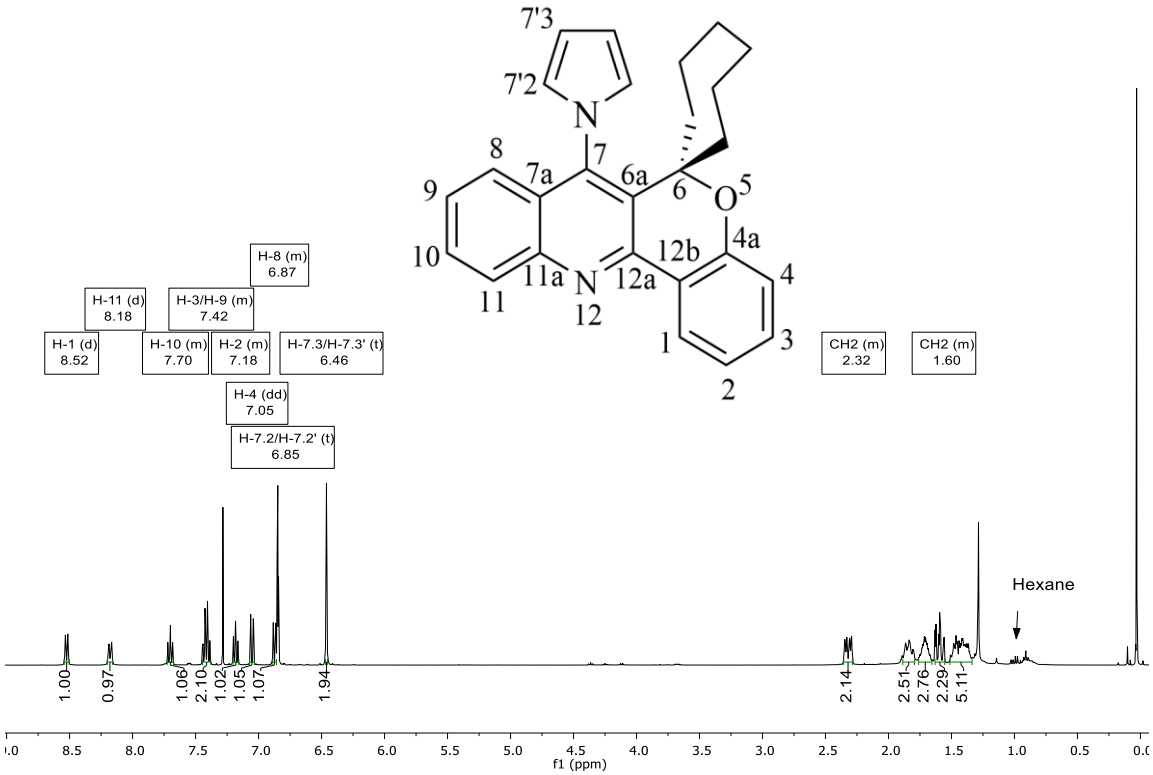

Figure S10. ^{1}H NMR spectra at 400 MHz in $CDCl_3$ of compound **3c**

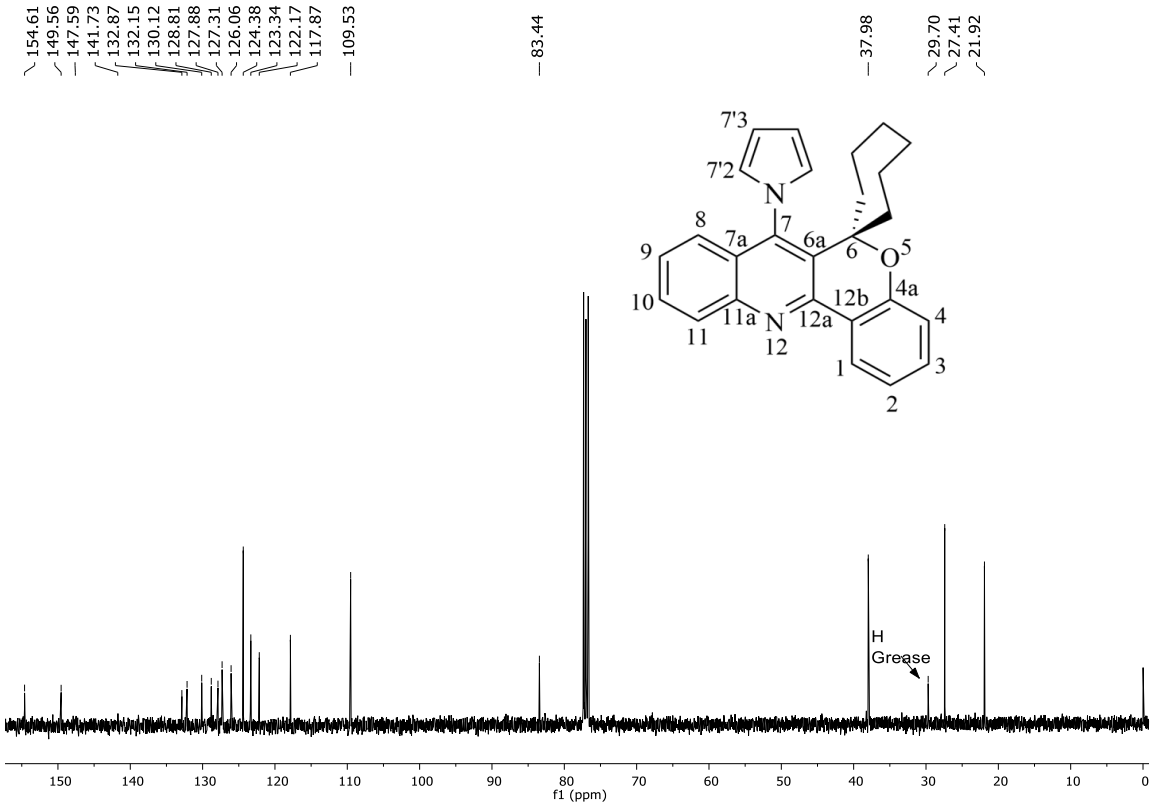

Figure S11. ^{13}C NMR spectra at 100 MHz in $CDCl_3$ of compound **3c**

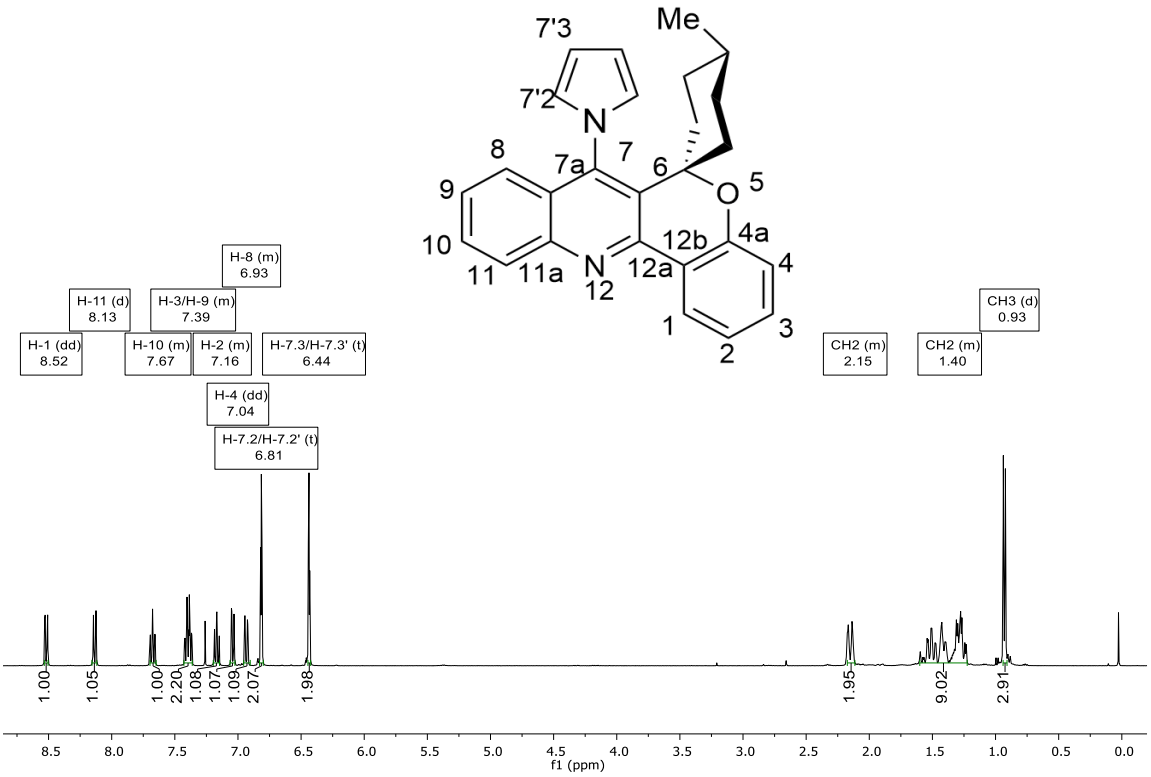

Figure S12. ^{1}H NMR spectra at 400 MHz in $CDCl_3$ of compound **3d**

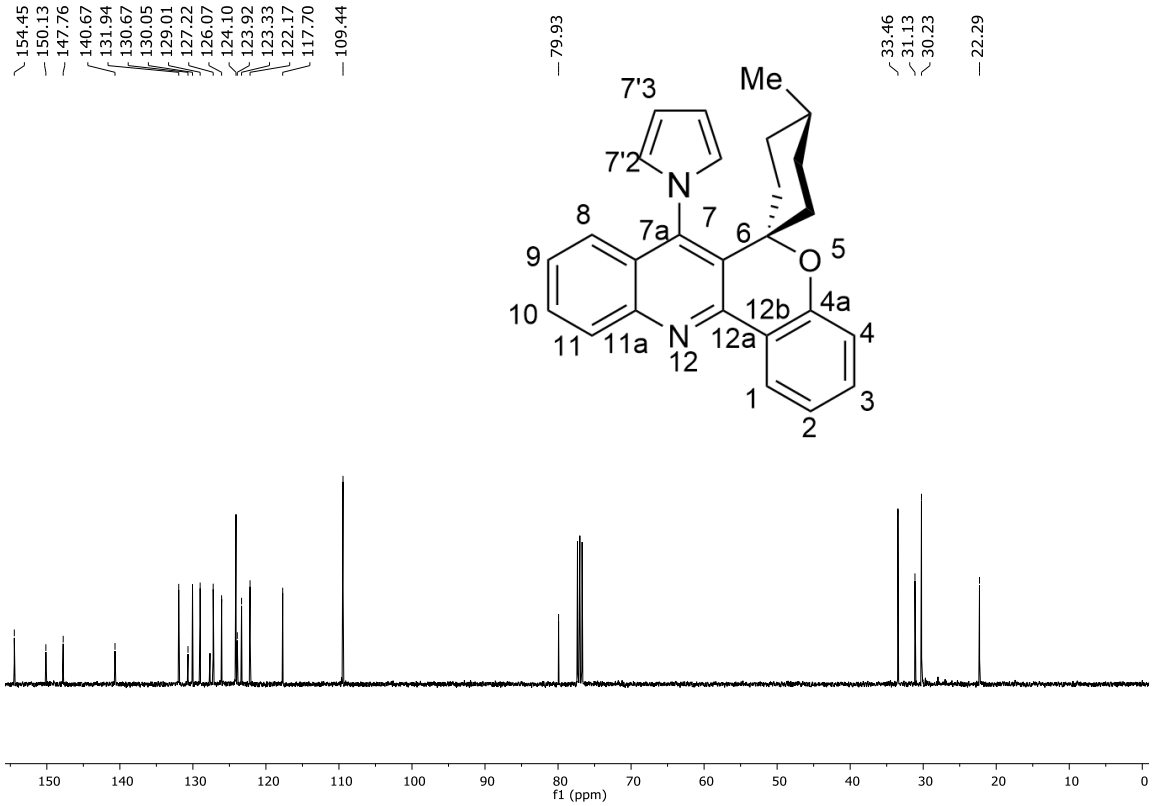

Figure S13. ^{13}C NMR spectra at 100 MHz in $CDCl_3$ of compound **3d**

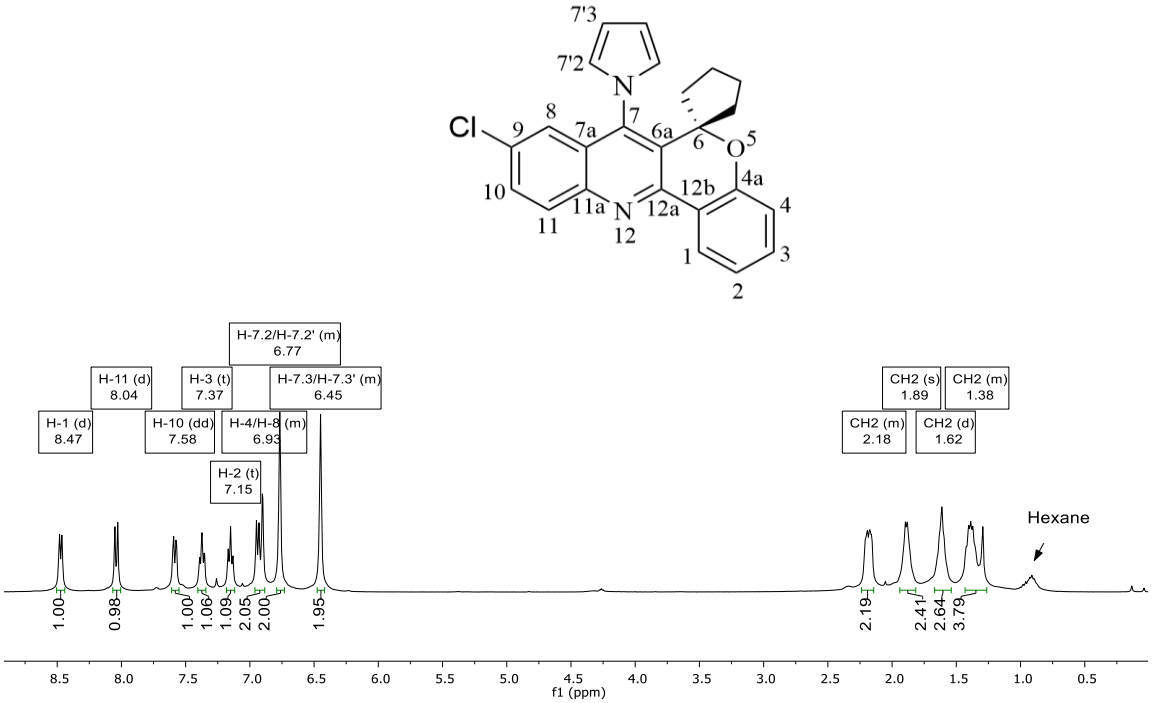

Figure S14. ^{1}H NMR spectra at 400 MHz in $CDCl_3$ of compound **3e**

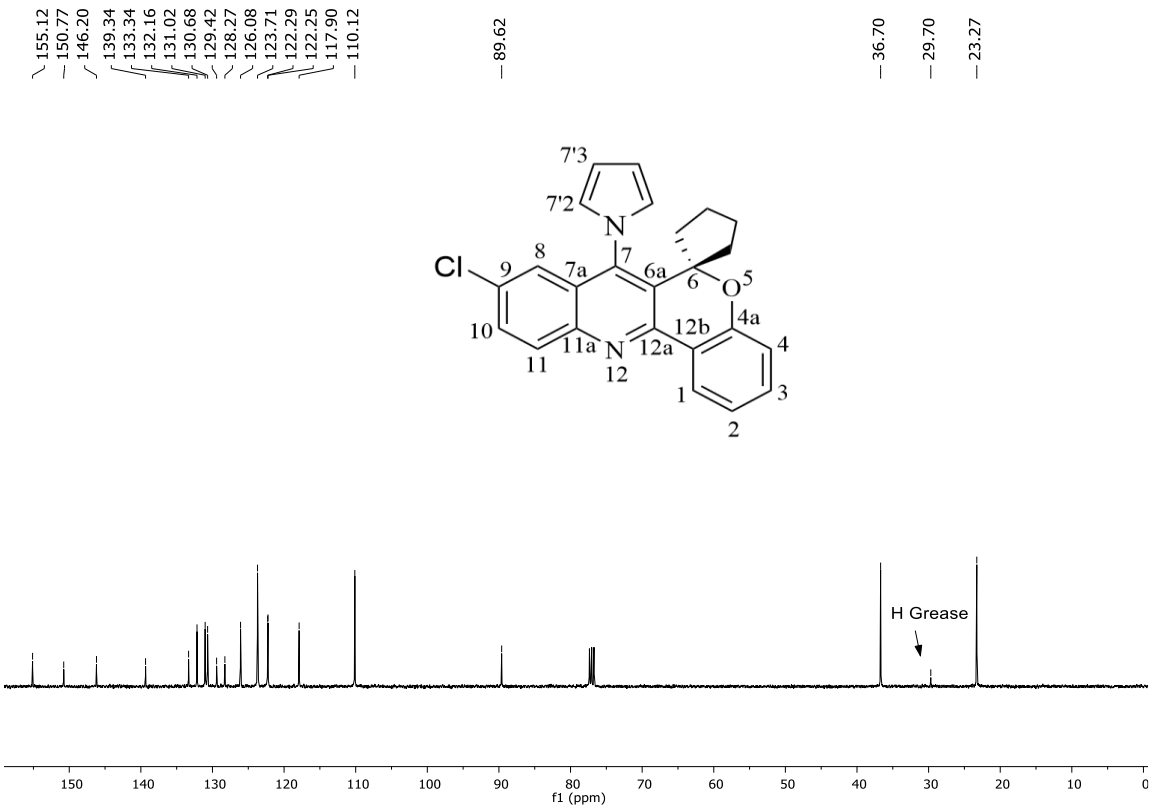

Figure S15. ^{13}C NMR spectra at 100 MHz in $CDCl_3$ of compound **3e**

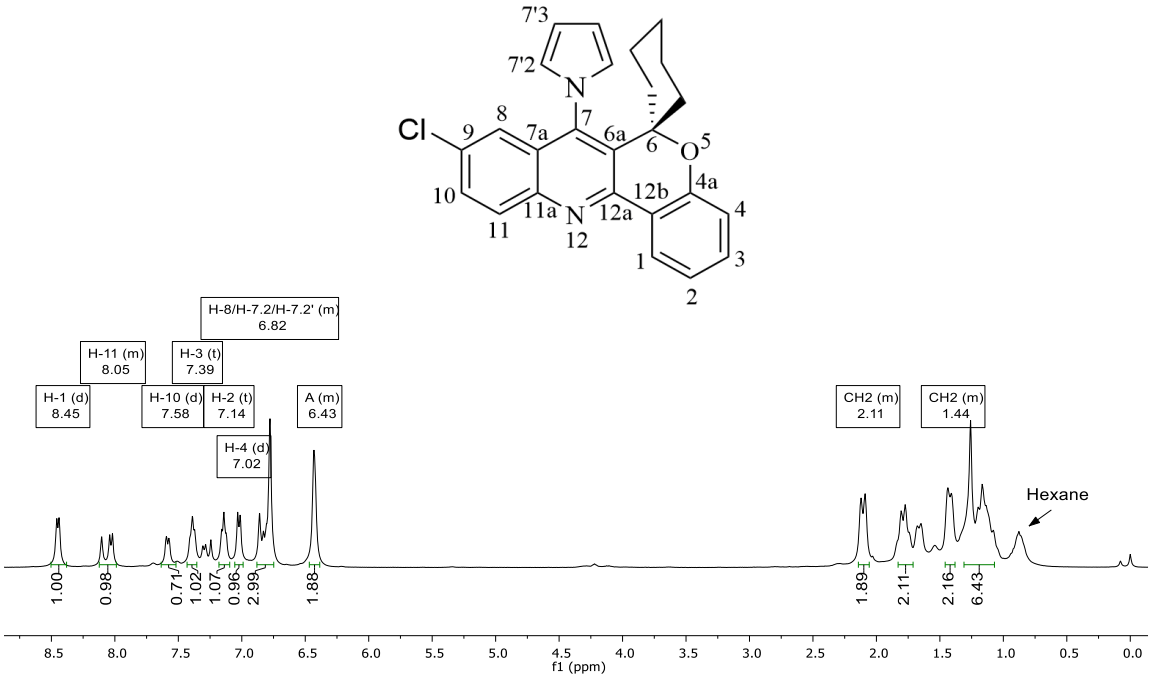

Figure S16. ^{1}H NMR spectra at 400 MHz in $CDCl_3$ of compound **3f**

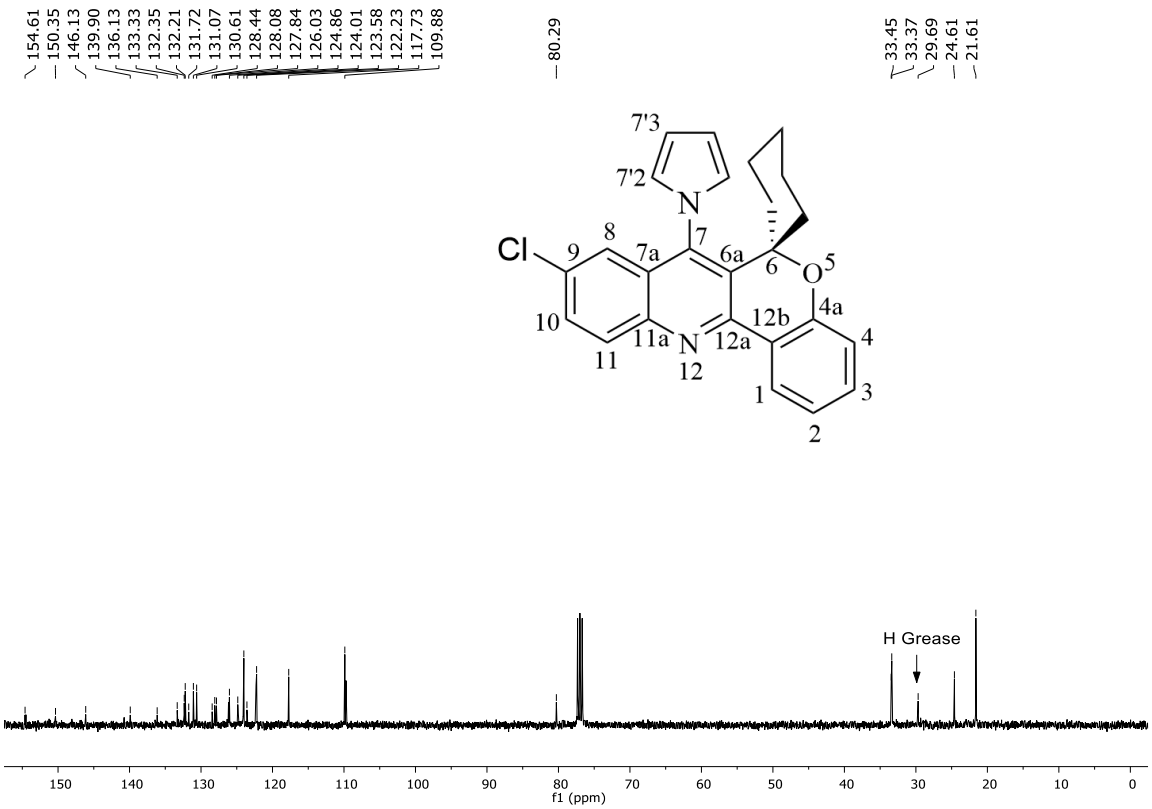

Figure S17. ^{13}C NMR spectra at 100 MHz in $CDCl_3$ of compound **3f**

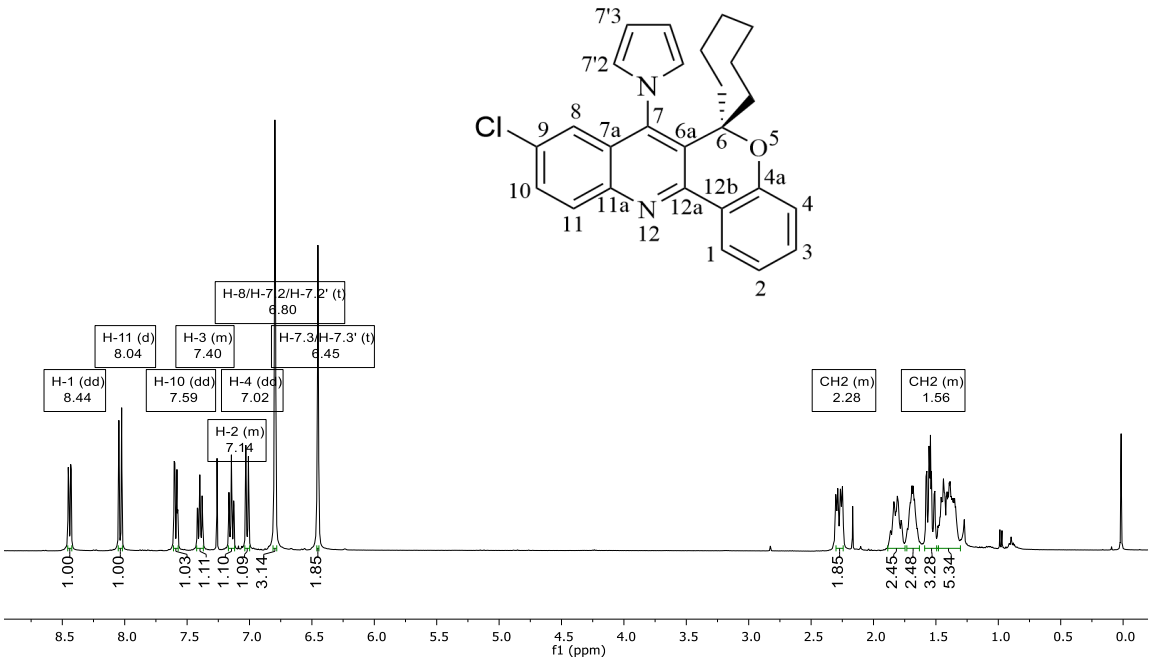

Figure S18. ^{1}H NMR spectra at 400 MHz in $CDCl_3$ of compound **3g**

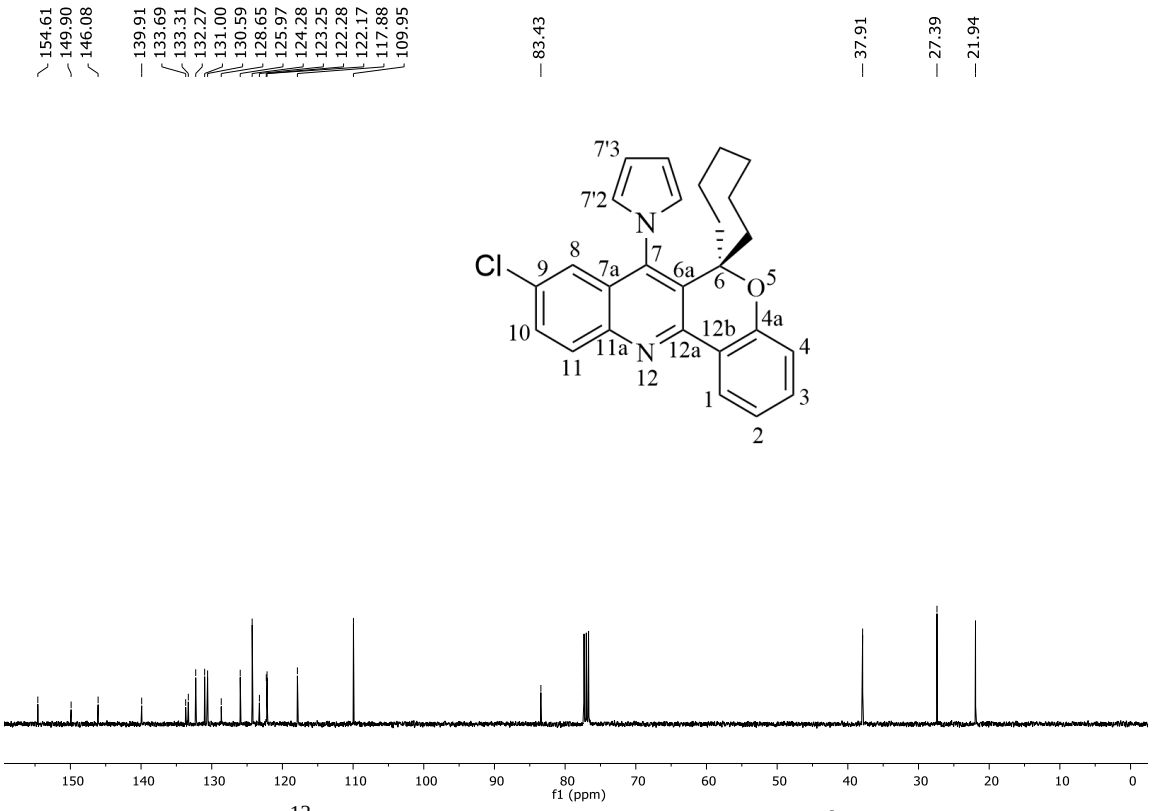

Figure S19. ^{13}C NMR spectra at 100 MHz in $CDCl_3$ of compound **3g**

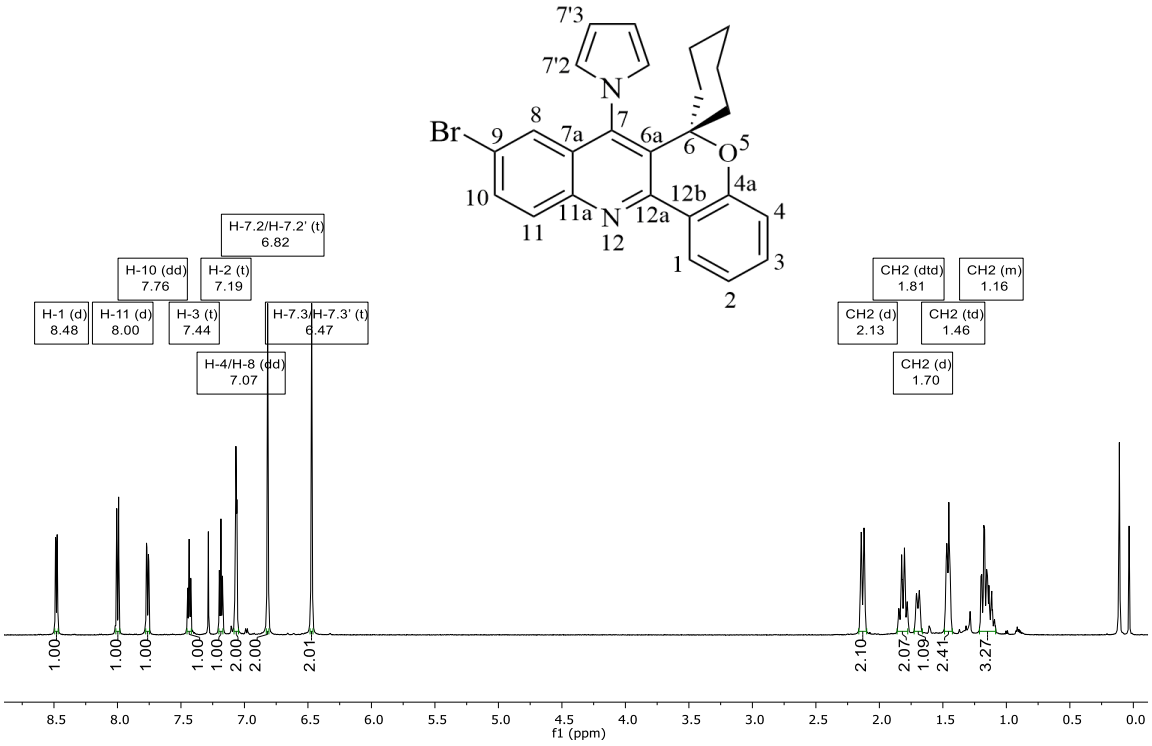

Figure S20. ^{1}H NMR spectra at 600 MHz in $CDCl_3$ of compound **3h**

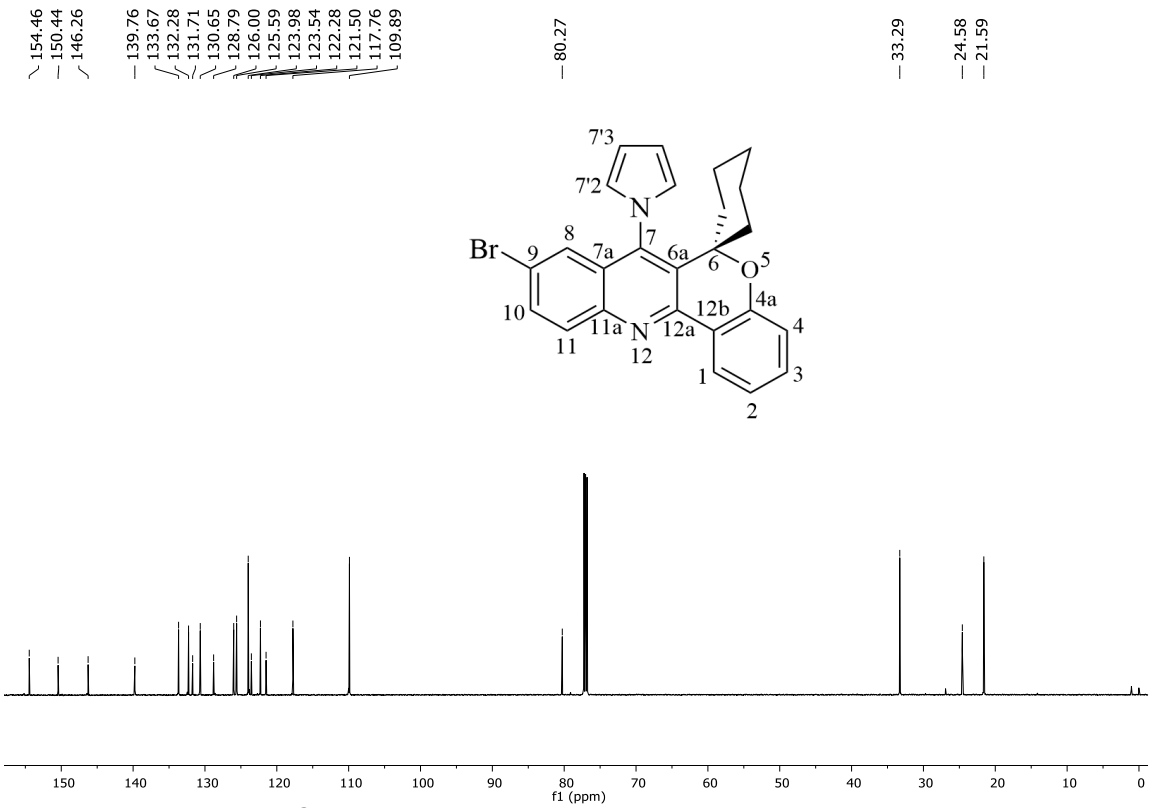

Figure S21. ^{13}C NMR spectra at 150 MHz in $CDCl_3$ of compound **3h**

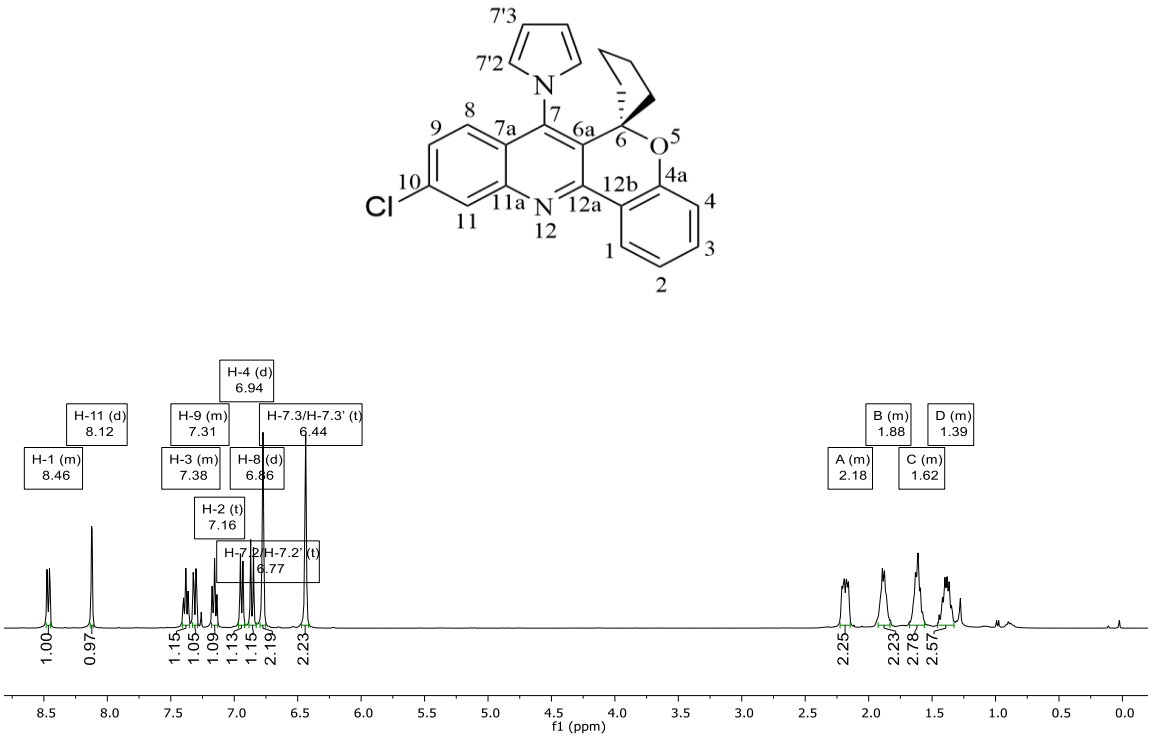

Figure S22. ^{1}H NMR spectra at 400 MHz in $CDCl_3$ of compound **3i**

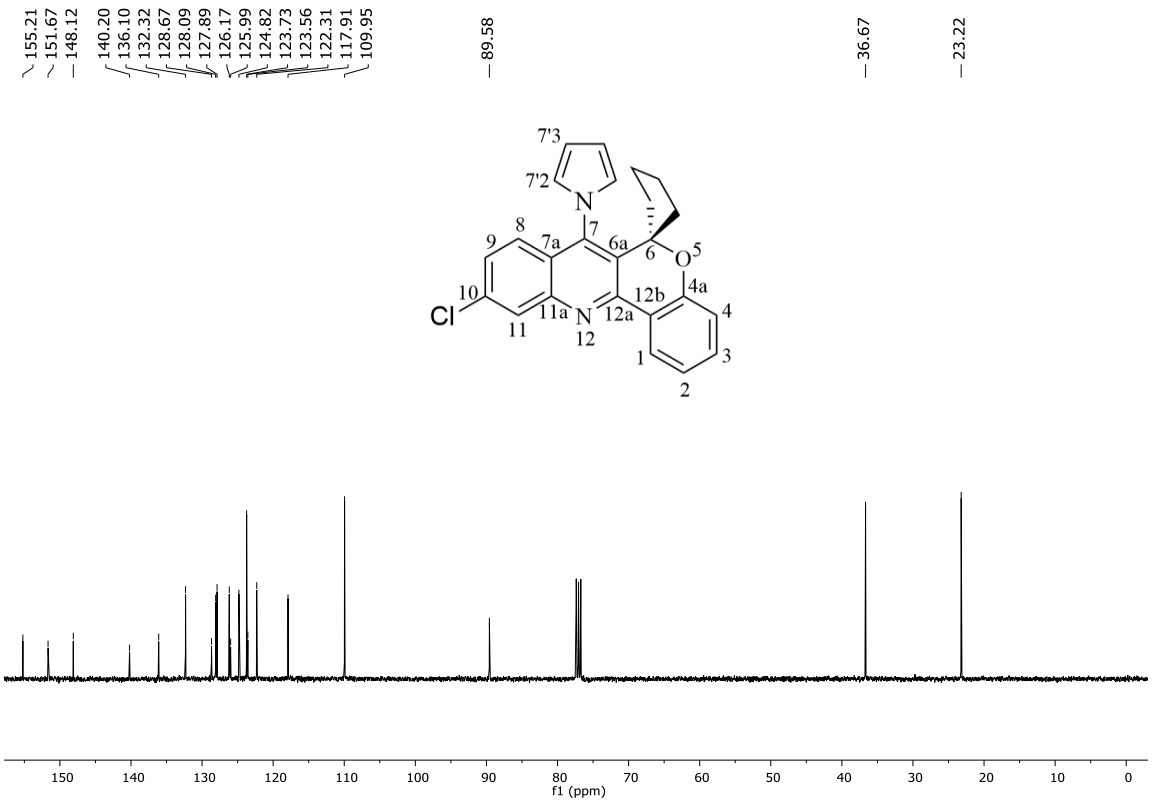

Figure S23. ^{13}C NMR spectra at 100 MHz in $CDCl_3$ of compound **3i**

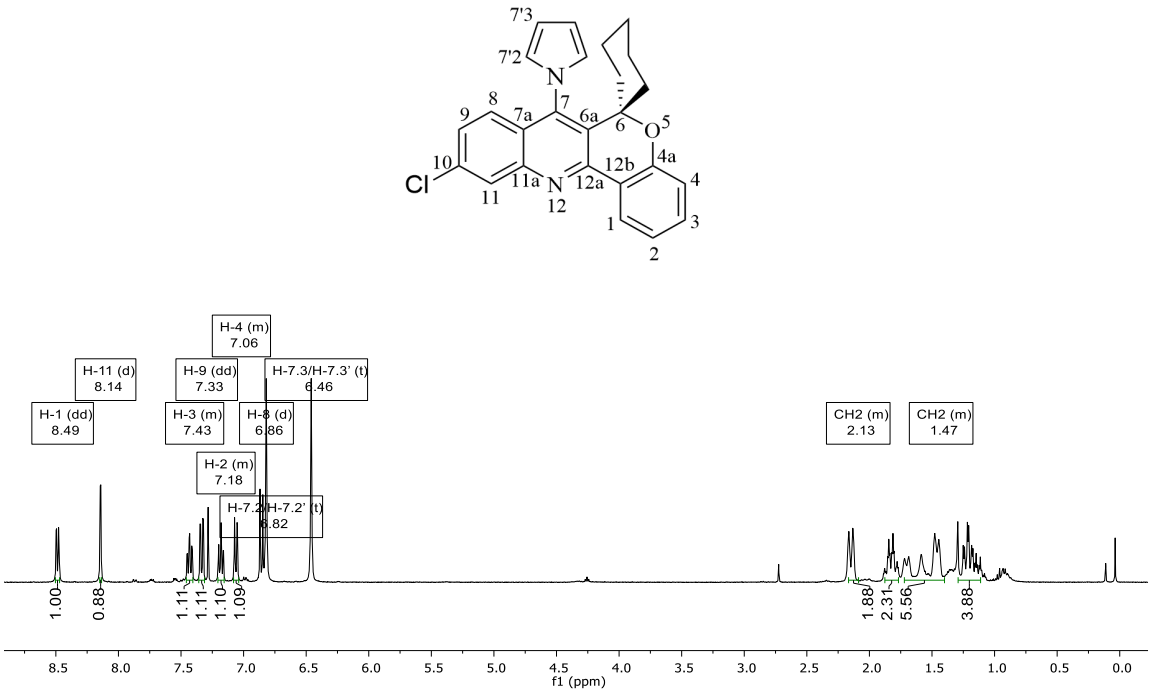

Figure S24. ^{1}H NMR spectra at 400 MHz in $CDCl_3$ of compound **3j**

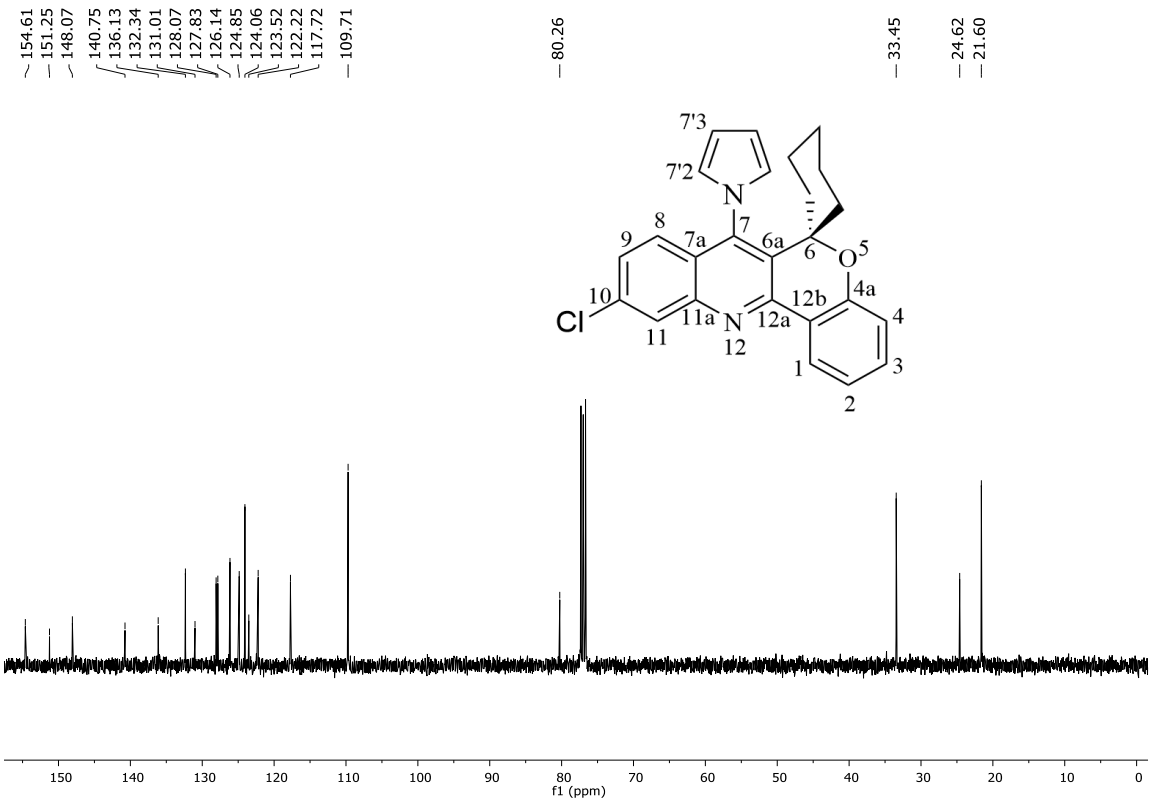

Figure S25. ^{13}C NMR spectra at 100 MHz in $CDCl_3$ of compound **3j**

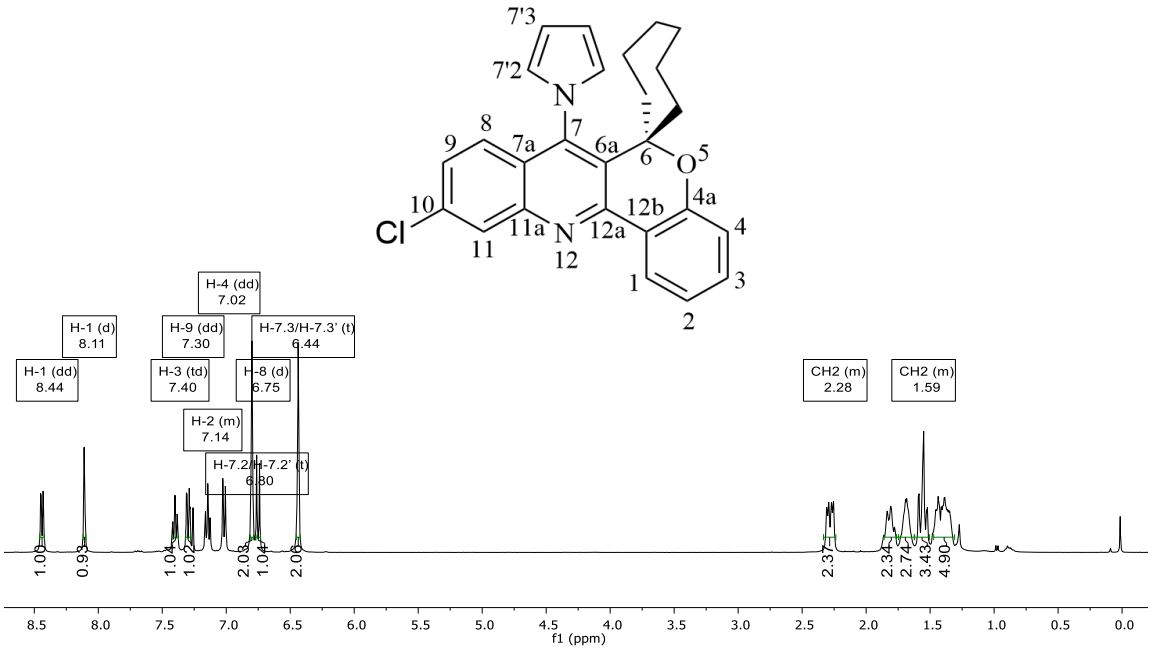

Figure S26. ^{1}H NMR spectra at 400 MHz in $CDCl_3$ of compound **3k**

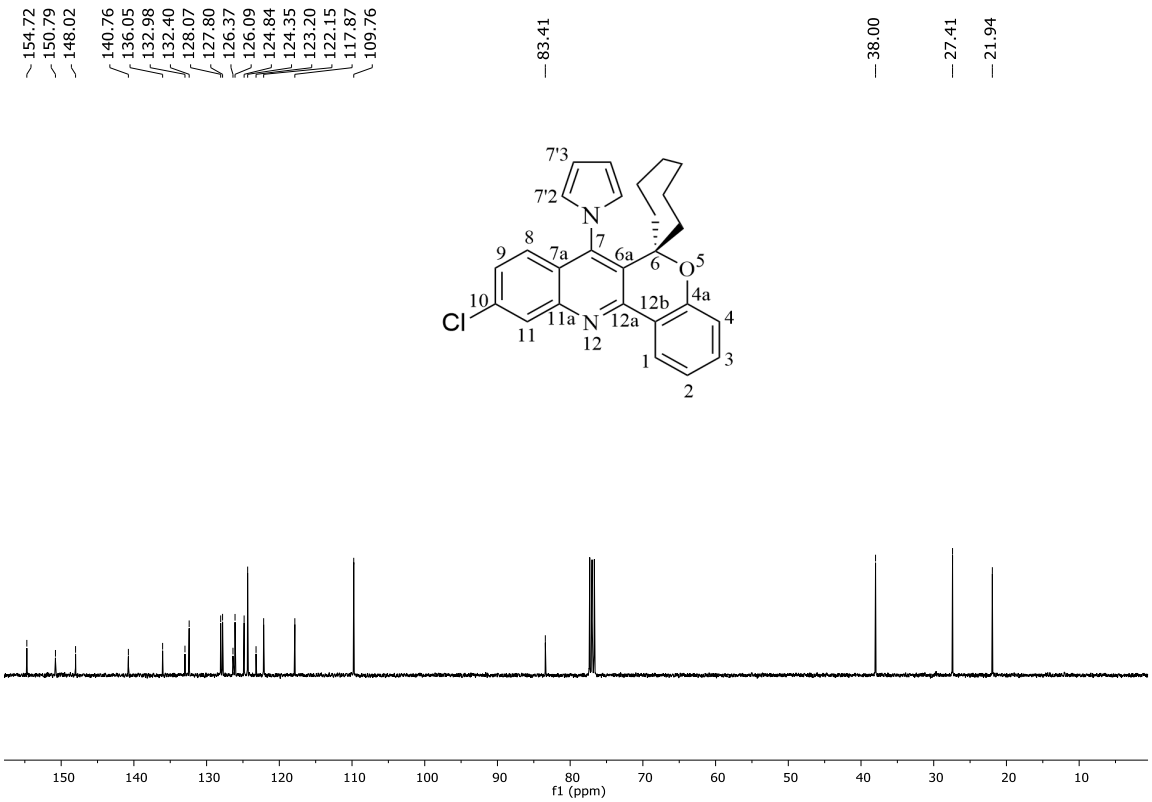

Figure S27. ^{13}C NMR spectra at 100 MHz in $CDCl_3$ of compound **3k**

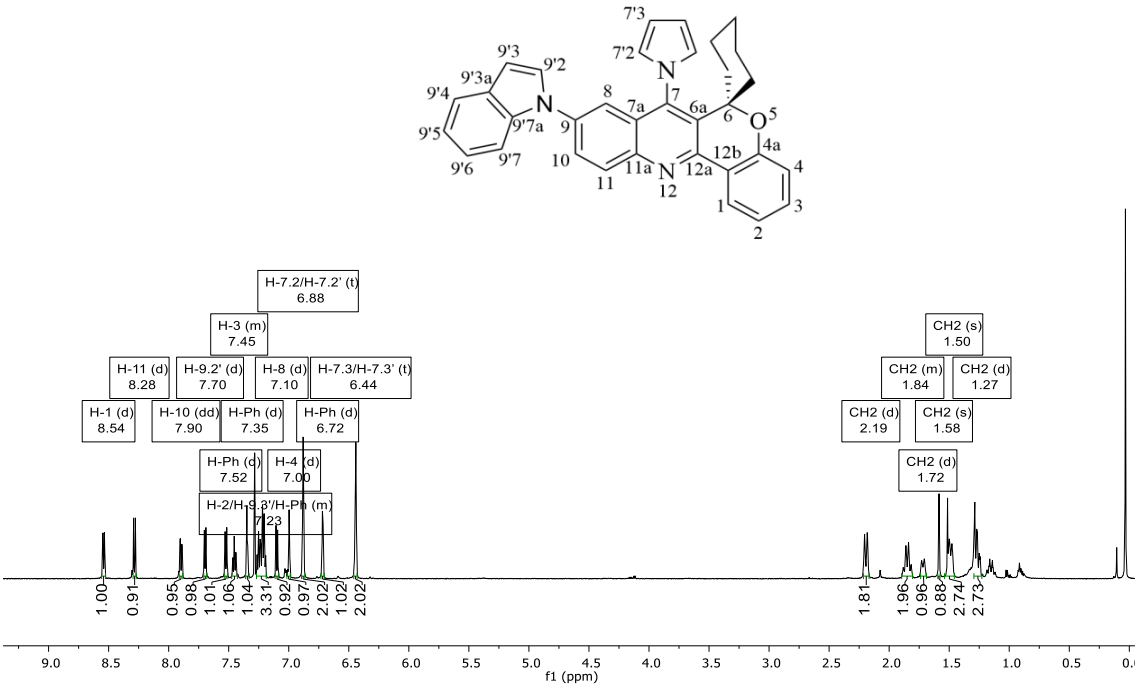

Figure S28. ^{1}H NMR spectra at 600 MHz in $CDCl_3$ of compound **4**

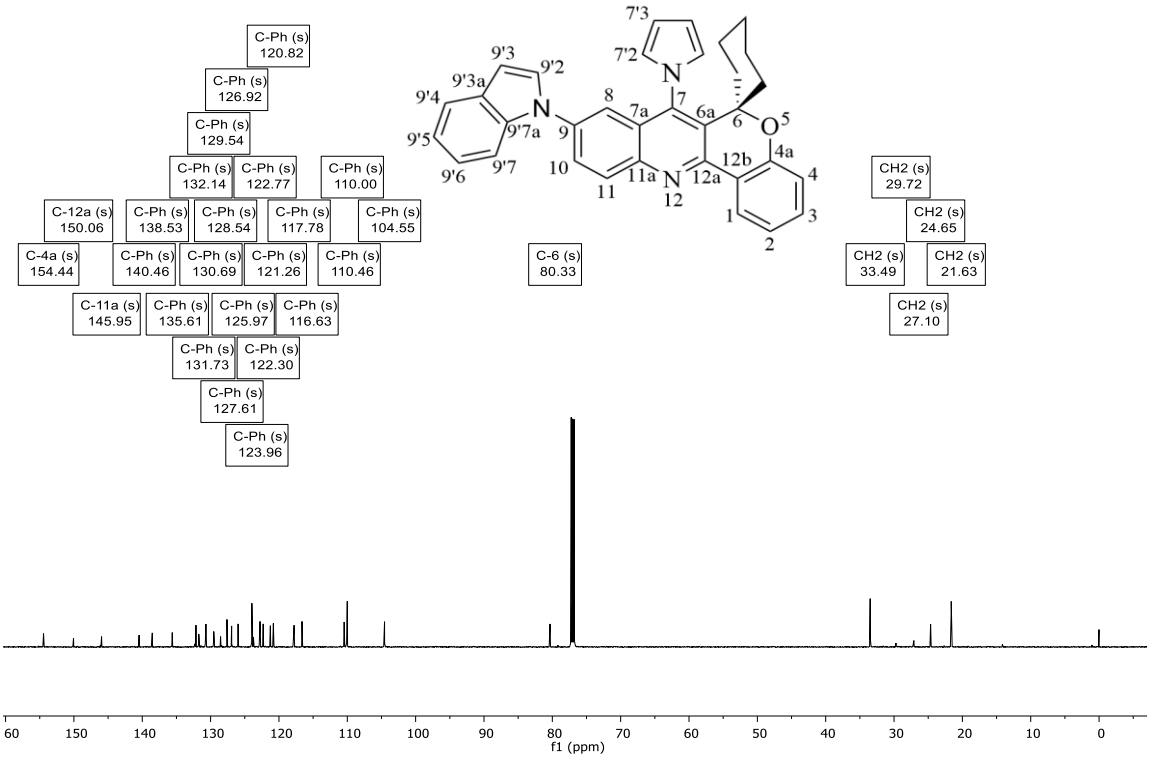

Figure S29. ^{13}C NMR spectra at 150 MHz in $CDCl_3$ of compound **4**

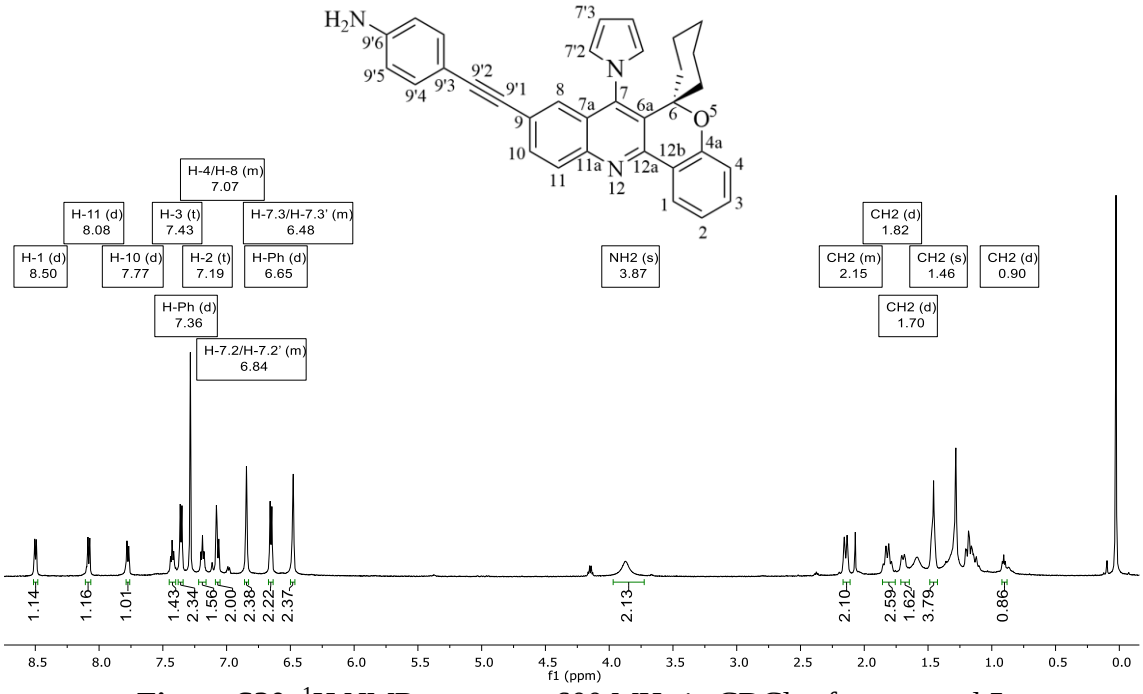

Figure S30. ^{1}H NMR spectra at 600 MHz in $CDCl_3$ of compound **5**

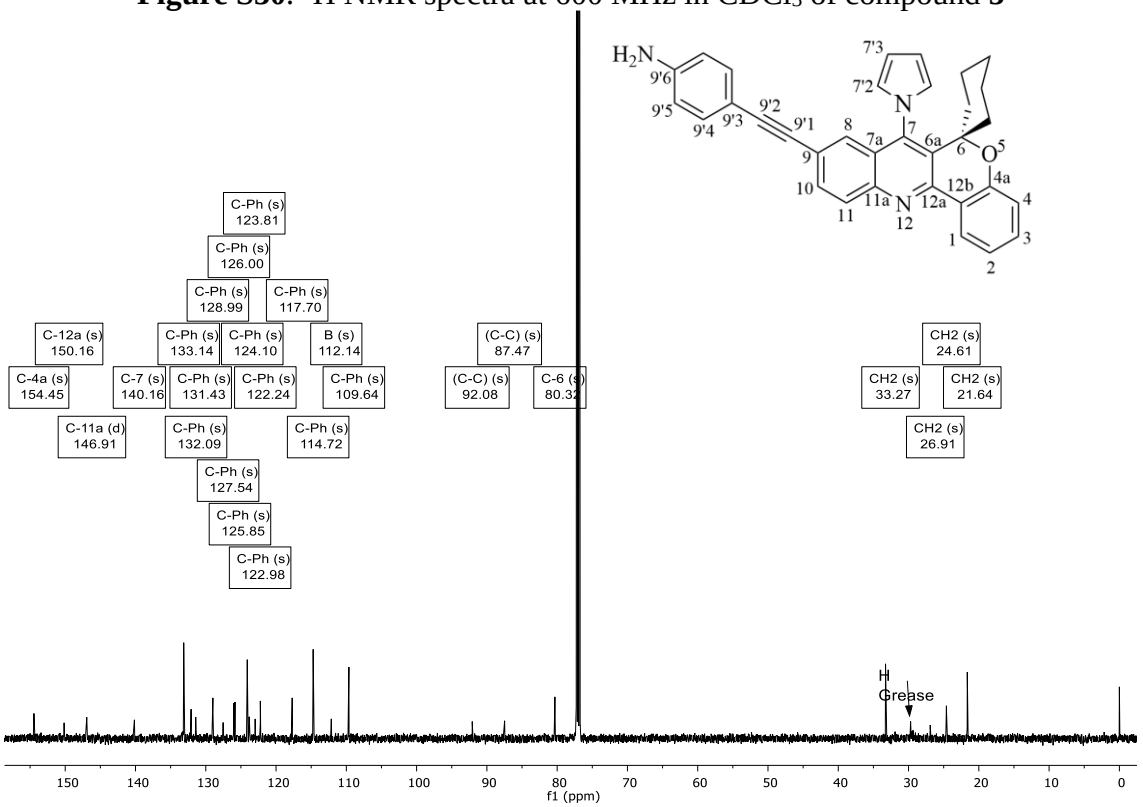

Figure S31. ^{13}C NMR spectra at 150 MHz in $CDCl_3$ of compound **5**

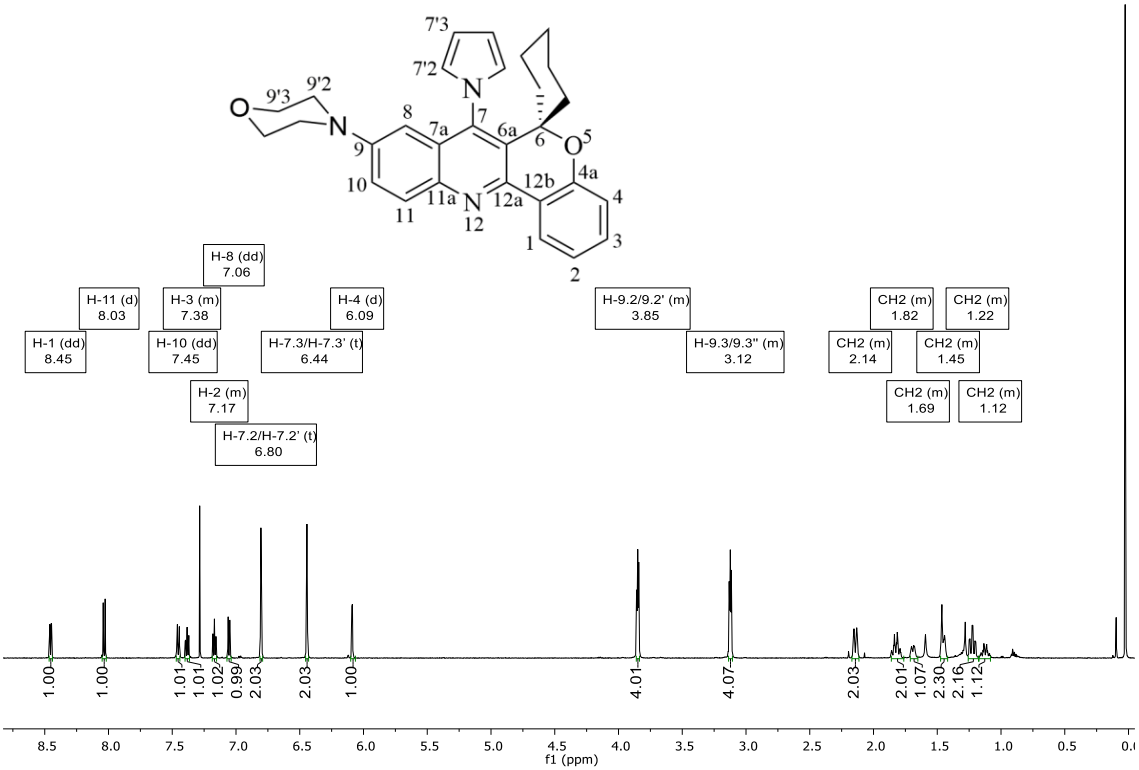

Figure S32. ^{1}H NMR spectra at 600 MHz in $CDCl_3$ of compound **6**

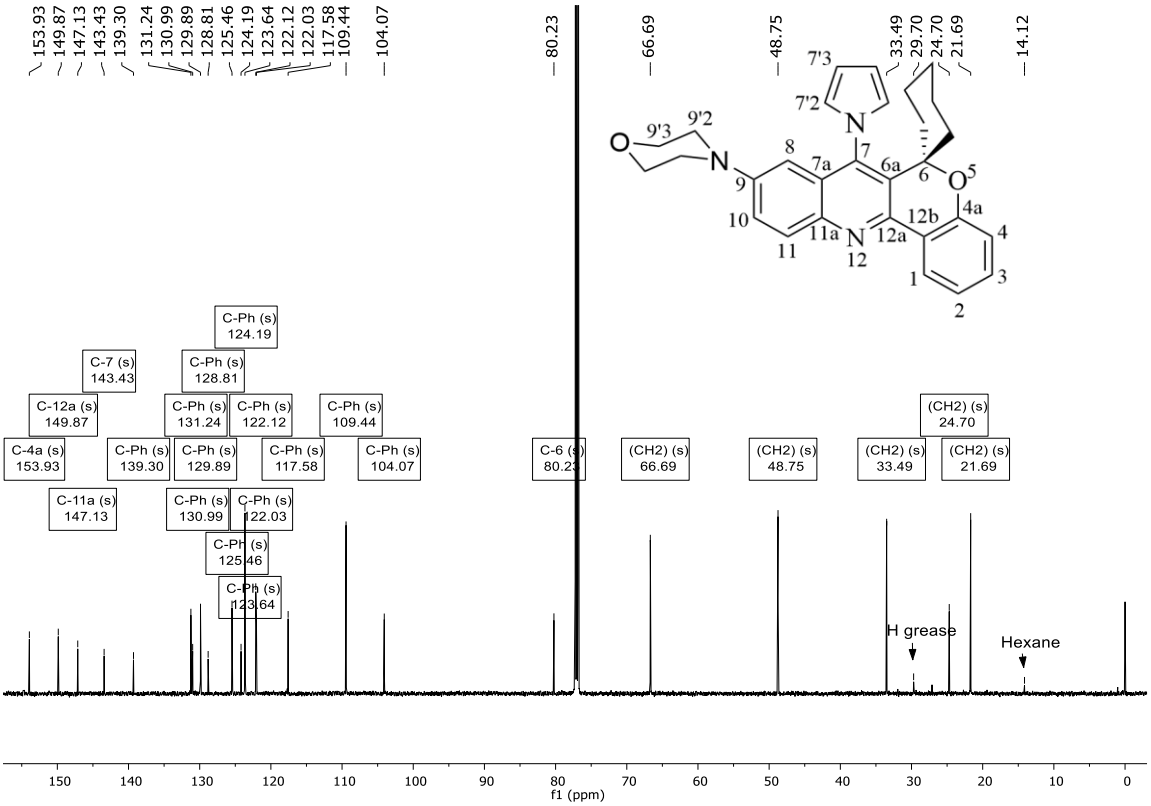

Figure S33. ^{13}C NMR spectra at 150 MHz in $CDCl_3$ of compound **6**

3. UV-Vis analysis

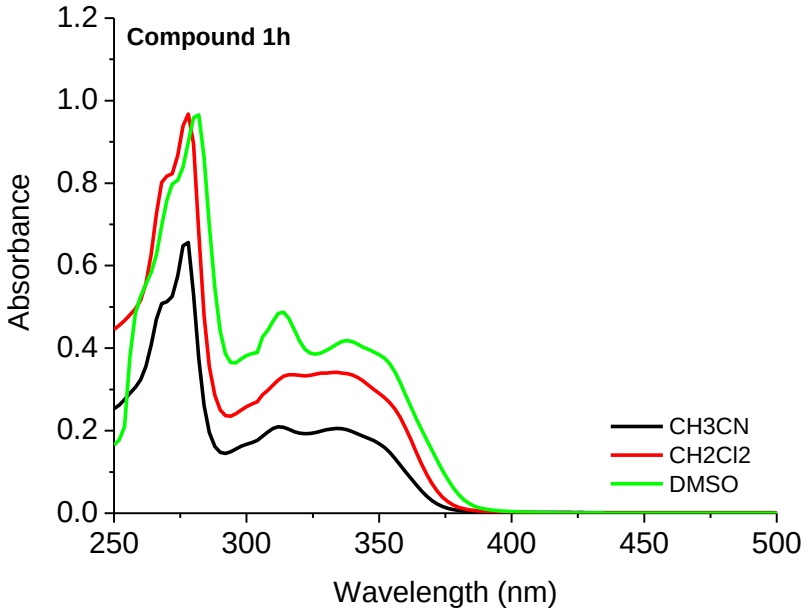

Figure S34. UV-Vis ([ ] = 10^{-5} M range) spectra of derivative **1h**.

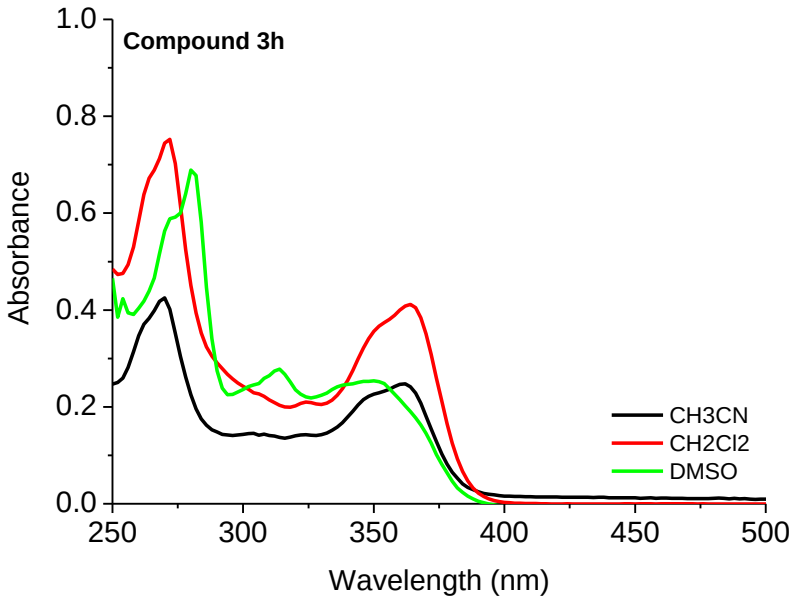

Figure S35. UV-Vis ([ ] = 10^{-5} M range) spectra of derivative **3h**.

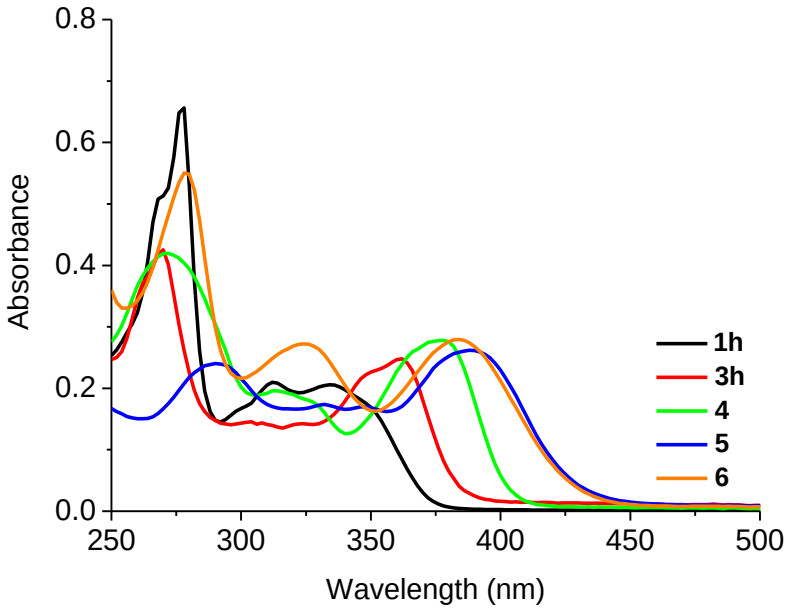

Figure S36. UV-Vis ([ ] = 10^{-5} M range) spectra of derivatives **4**, **5**, and **6** in CH_3CN solution, respectively.

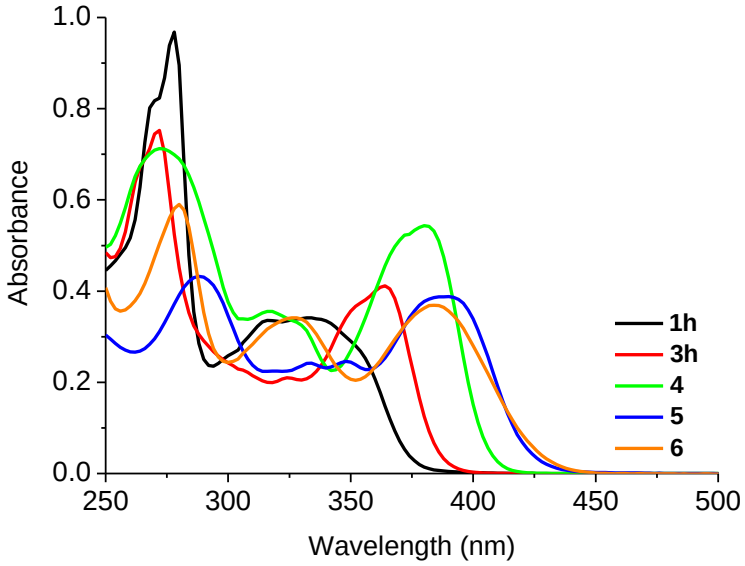

Figure S37. UV-Vis ([ ] = 10^{-5} M range) spectra of derivatives **4**, **5**, and **6** in CH_2Cl_2 solution, respectively.

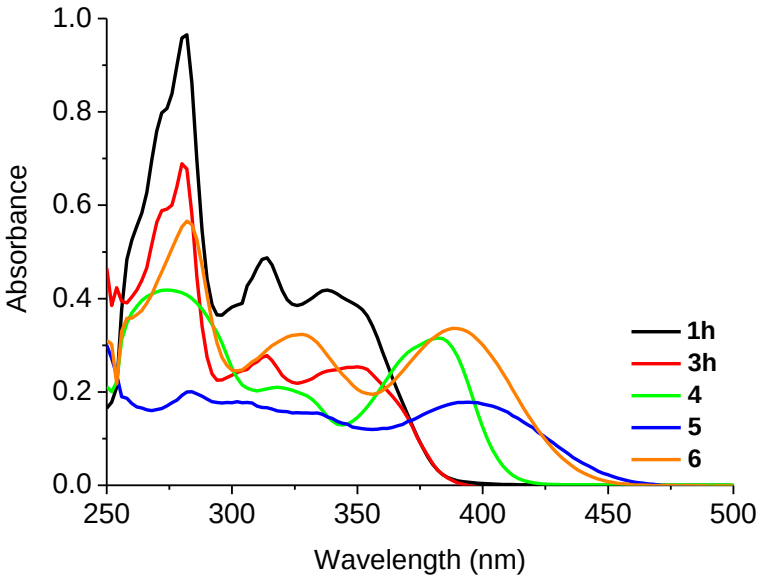

Figure S38. UV-Vis ([ ] = 10^{-5} M range) spectra of derivatives **4**, **5**, and **6** in DMSO solution, respectively.

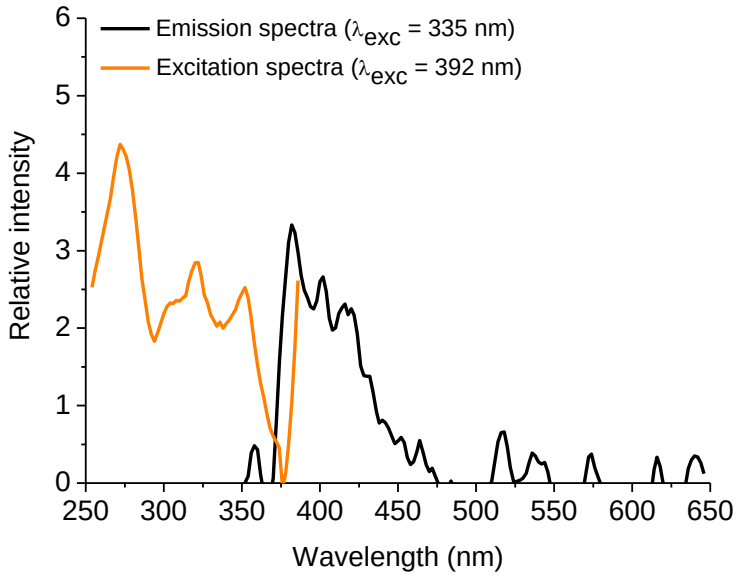

Figure S39. Steady-state emission and excitation spectra ([ ] = 10^{-6} M range) of derivative **1h** in CH_3CN solution.

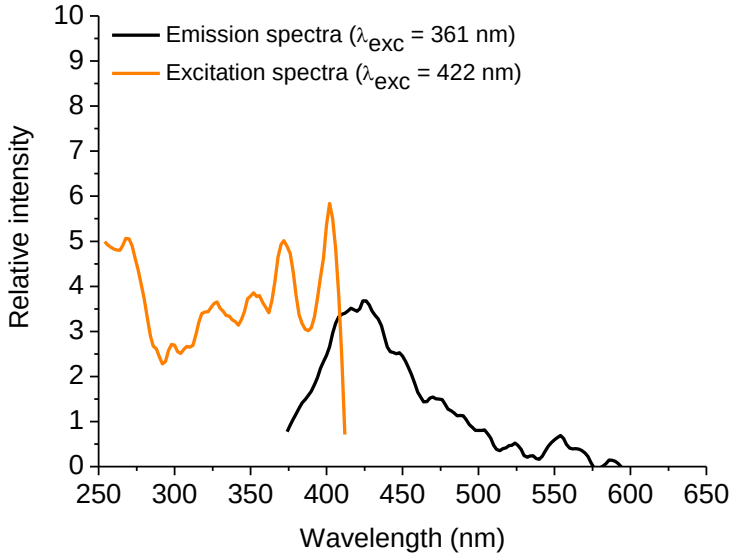

Figure S40. Steady-state emission and excitation spectra ([ ] = 10^{-6} M range) of derivative **3h** in CH_3CN solution.

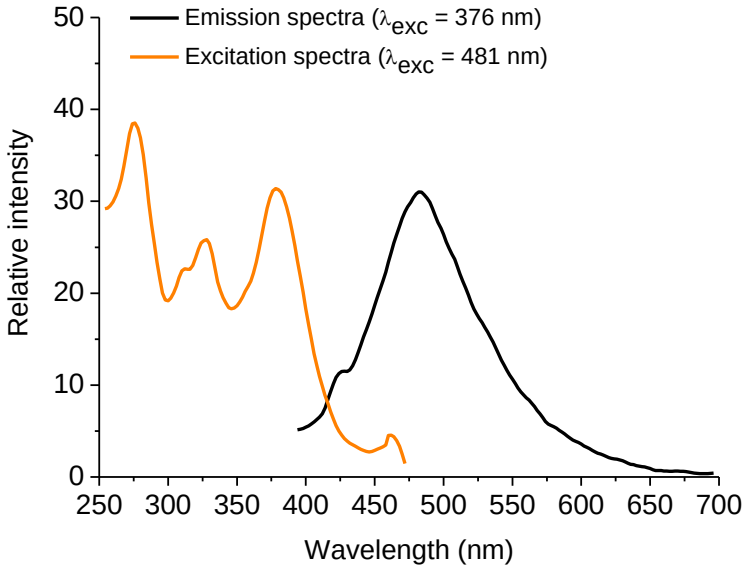

Figure S41. Steady-state emission and excitation spectra ([ ] = 10^{-6} M range) of derivative **4** in CH_3CN solution.

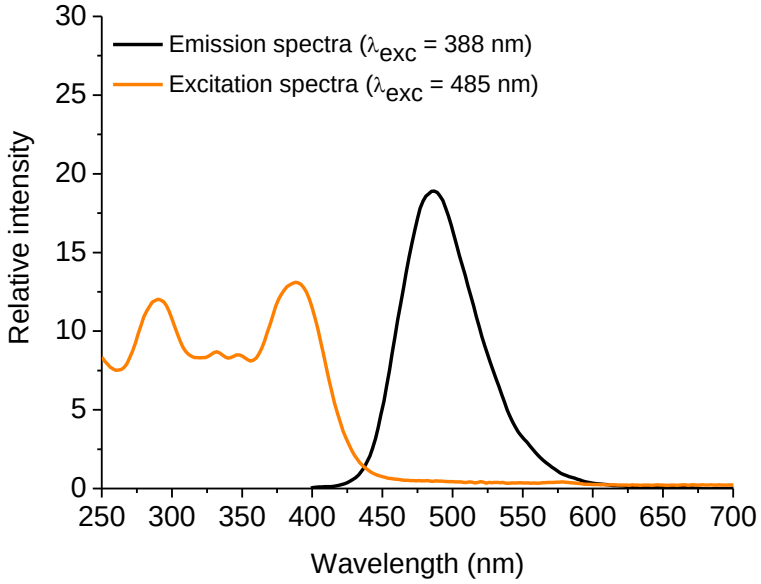

Figure S42. Steady-state emission and excitation spectra ([ ] = 10^{-6} M range) of derivative **5** in CH_3CN solution.

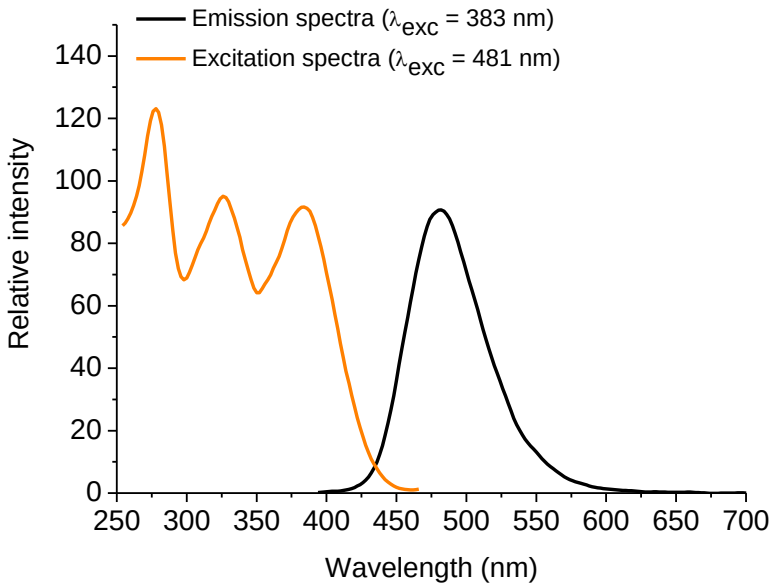

Figure S43. Steady-state emission and excitation spectra ([ ] = 10^{-6} M range) of derivative **6** in CH_3CN solution.

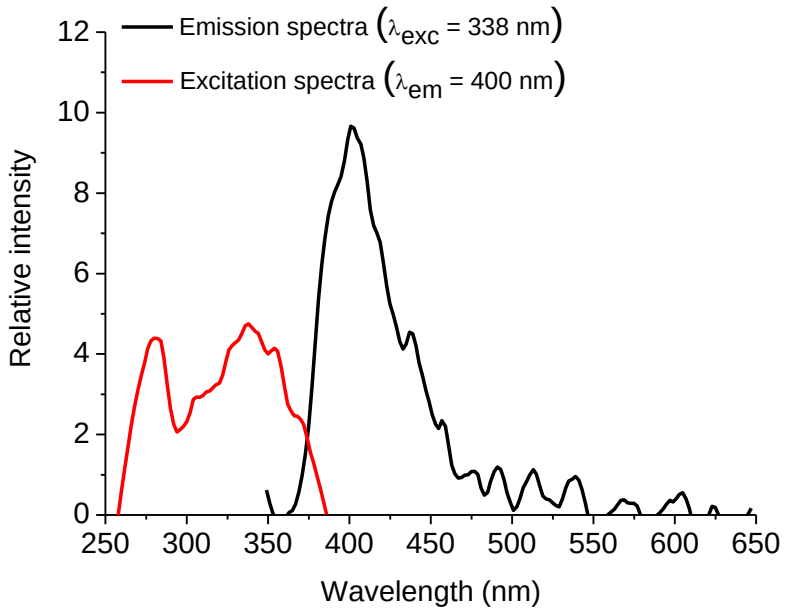

Figure S44. Steady-state emission and excitation spectra ([ ] = 10^{-6} M range) of derivative **1h** in DMSO solution.

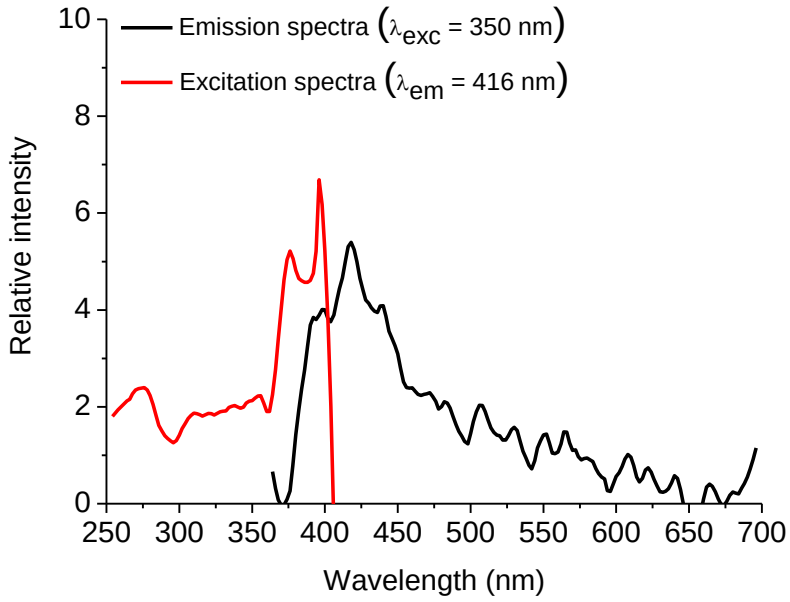

Figure S45. Steady-state emission and excitation spectra ([ ] = 10^{-6} M range) of derivative **3h** in DMSO solution.

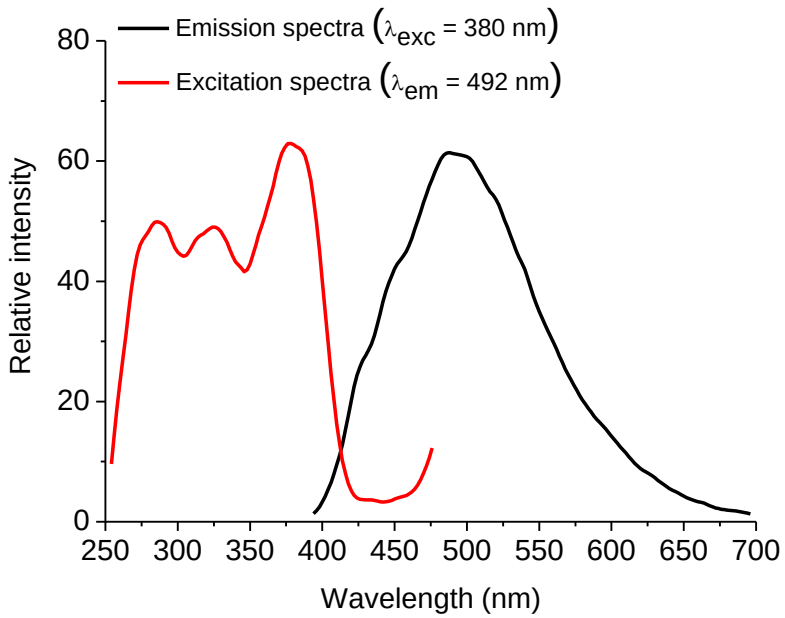

Figure S46. Steady-state emission and excitation spectra ([ ] = 10^{-6} M range) of derivative **4** in DMSO solution.

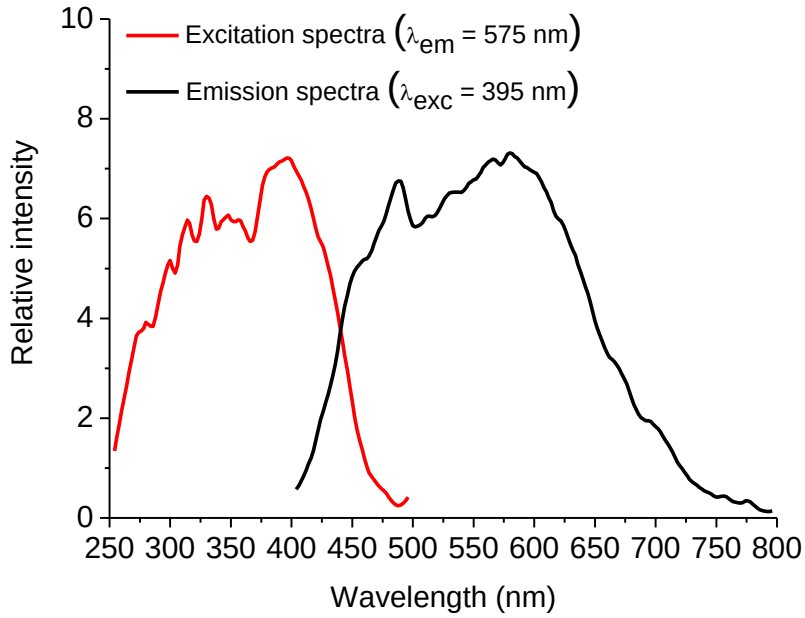

Figure S47. Steady-state emission and excitation spectra ([ ] = 10^{-6} M range) of derivative **5** in DMSO solution.

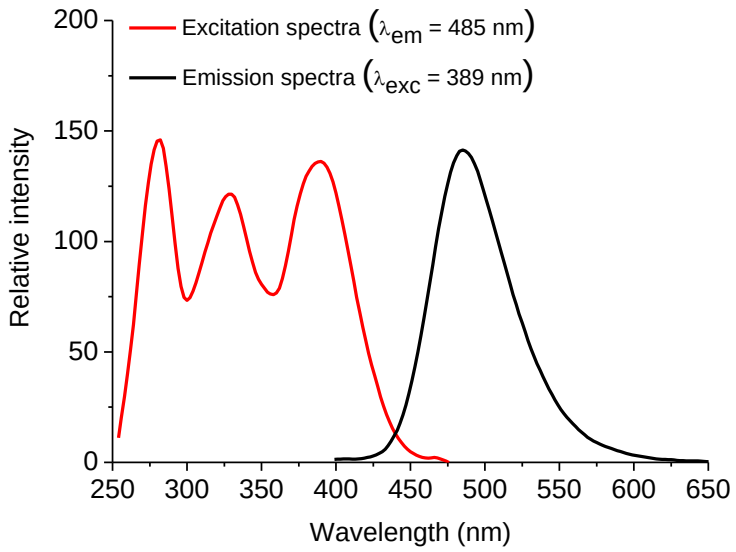

Figure S48. Steady-state emission and excitation spectra ([ ] = 10^{-6} M range) of derivative **6** in DMSO solution.

4. References

(1) Bristow, A. W. T.; Webb, K. S. Intercomparison study on accurate mass measurement of small molecules in mass spectrometry. *J. Am. Soc. Mass Spectrom.* **2003**, *14* (10), 1086–1098. https://doi.org/10.1016/S1044-0305(03)00403-3.