Dehydrogenative Synthesis of Quinolines, 2-Aminoquinolines and Quinazolines using Singlet Di-radical Ni(II)-Catalysts

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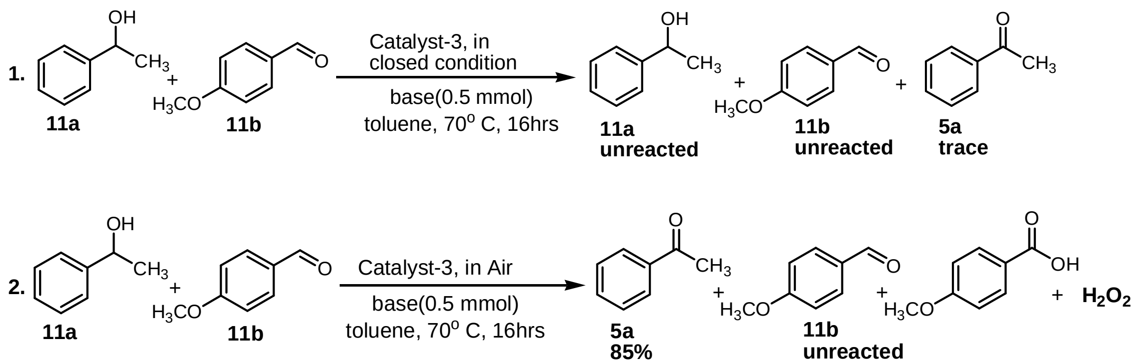
Intermolecular Transfer Hydrogenation Experiments using 3 as the catalyst.



Scheme S1. Intermolecular Transfer Hydrogenation Experiments using **3** as the catalyst.

Detection of Hydrogen Peroxide During the Catalytic Alcohol Oxidation Reaction.[1] During catalytic alcohol oxidation reaction H_2O_2 was produced and it was detected spectrophotometrically following the gradual development of the characteristic peak of I_3^- at λ_{max}= 351 nm, upon reaction with KI. A mixture of 1.0 mmol 1-phenylethanol, 0.5 mmol KO^{t}Bu and catalyst **3** (4 mol%) in a 5.0 ml dry toluene was placed in a 50 ml round-bottom flask fitted with a stir bar and a condenser and stirred in a preheated oil bath at 70°C for 16h. To this mixture an equal volume of water was added and the total reaction mixture was extracted three times with dichloromethane. The separated aqueous layer was acidified with H_2SO_4 to pH=2 to stop further oxidation. Then 1.0 mL of a10% solution of KI and a few drops of a 3% solution of ammoniummolybdate was added to it. Produced hydrogen peroxide oxidizes I^- to I_2, which reacts with excess I^- to form I^{3-} according to the following reactions: (i) $H_2O_2 + 2I^- + 2H^+ \rightarrow 2H_2O + I_2$, (ii) $I_2\,(aq) + I^- \rightarrow I_3^-$. (Fig: S1).

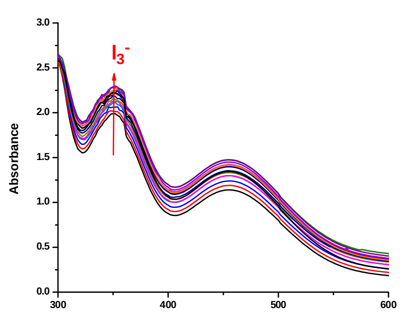
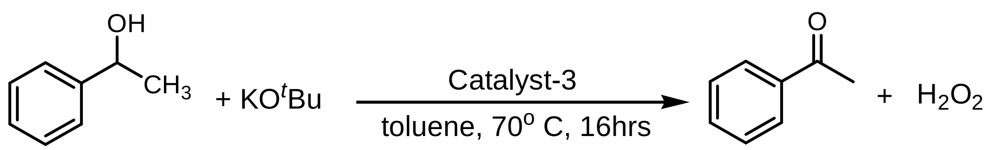


Figure S1: Detection of H_2O_2. Absorption spectral changes during formation of I_3^- in presence of H_2O_2.

Quantification of Hydrogen Peroxide During the Catalytic Alcohol Oxidation Reaction. Hydrogen Peroxide was quantified iodometrically using standard sodium thiosulphate solution. At first (N/20) sodium thiosulphate solution was standardized by standard (N/20) potassium dichromate solution ($S_{dichromate}$ = 0.611/0.6129 (N/20) = 0.0498 (N)) using 1% starch solution as indicator. Strength of sodium thiosulphate solution was 0.0517 (N).



Scheme S2. Reaction for quantification of H_2O_2 using **3** as the catalyst.

Serial No.	Amount of 1-phenyl ethanol	Amount of KO^{t}Bu	Amount of catalyst **3**	Amount of H_2O_2 (w.r.t. alcohol)
1	1.0 mmol	0.5 mmol	4.0 mol%	0.68 equiv.
2	1.0 mmol	1.0 mmol	4.0 mol%	0.48 equiv.
3	0.1 mmol	0.1 mmol	0.1 mmol	0.82 equiv.

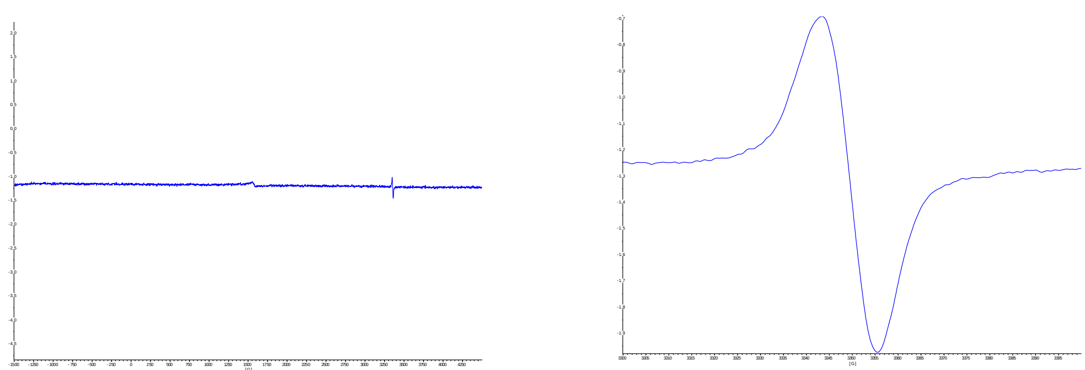


Figure S2. EPR spectra (left full spectrum, right zoom) of the reaction mixture containing catalyst **3** and KO^{t}Bu recorded at RT.

Figures of ^{1}H and ^{13}C NMR spectra

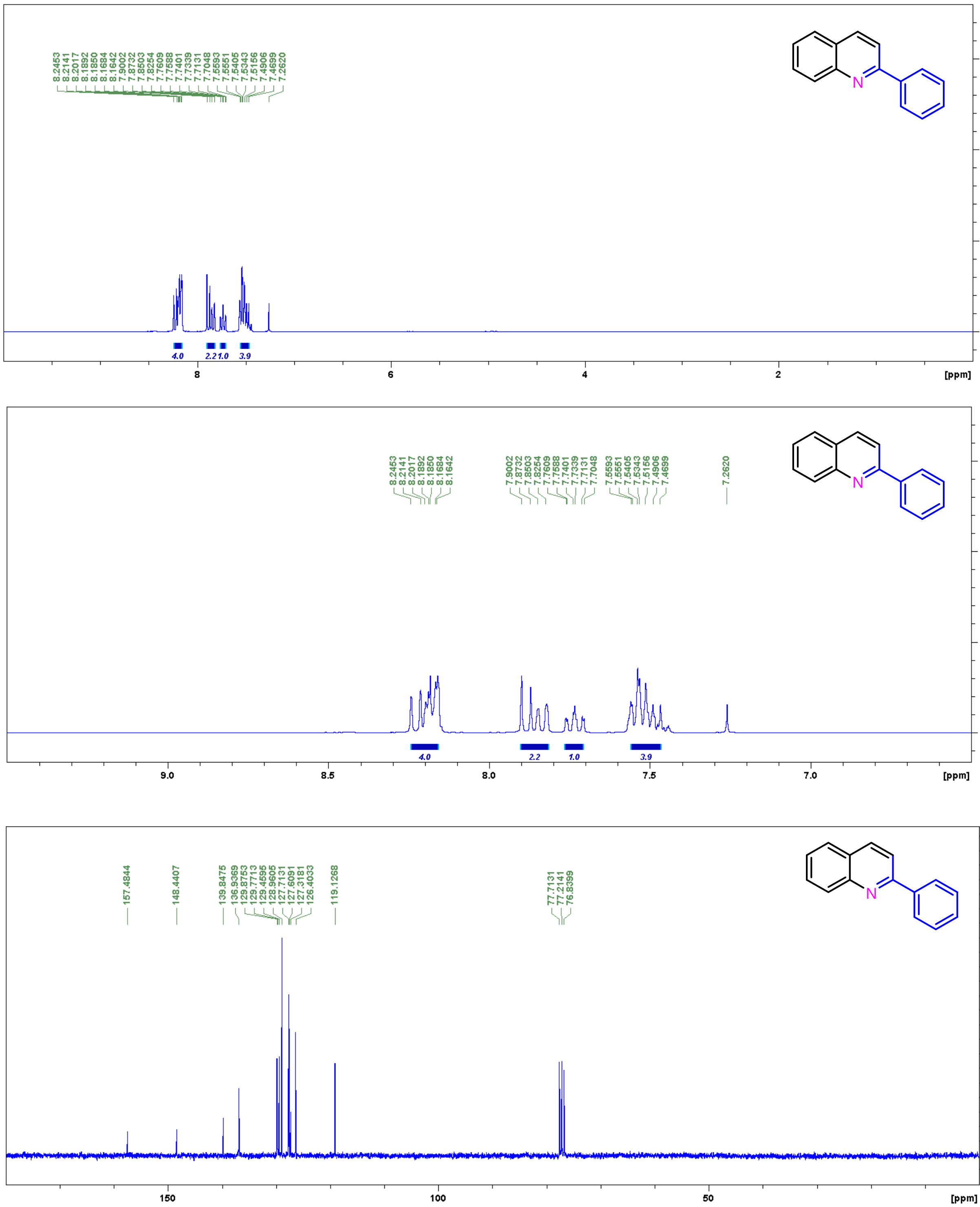


Figure S3. ^{1}H and ^{13}C NMR spectra of compound **8aa** in $CDCl_3$.

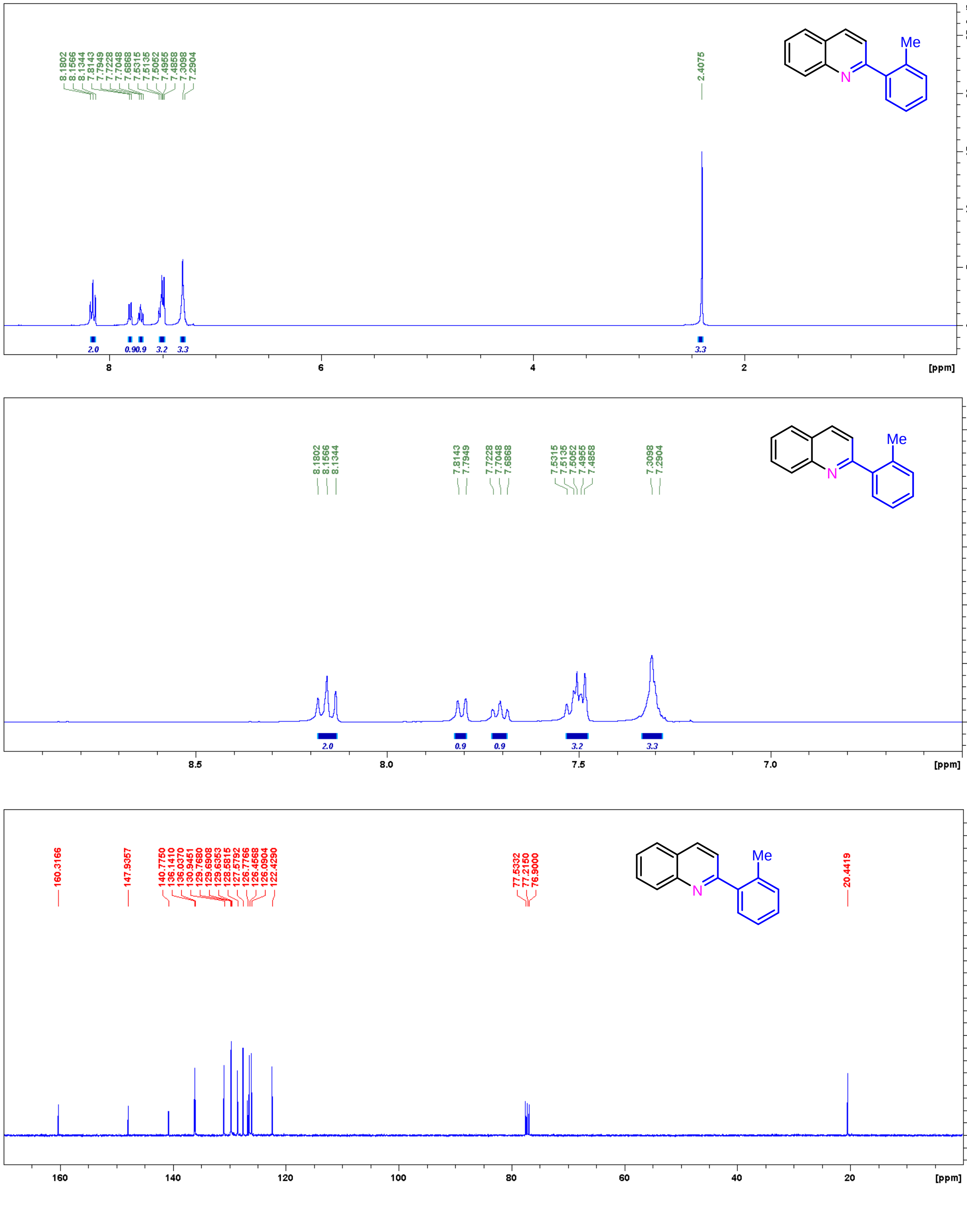
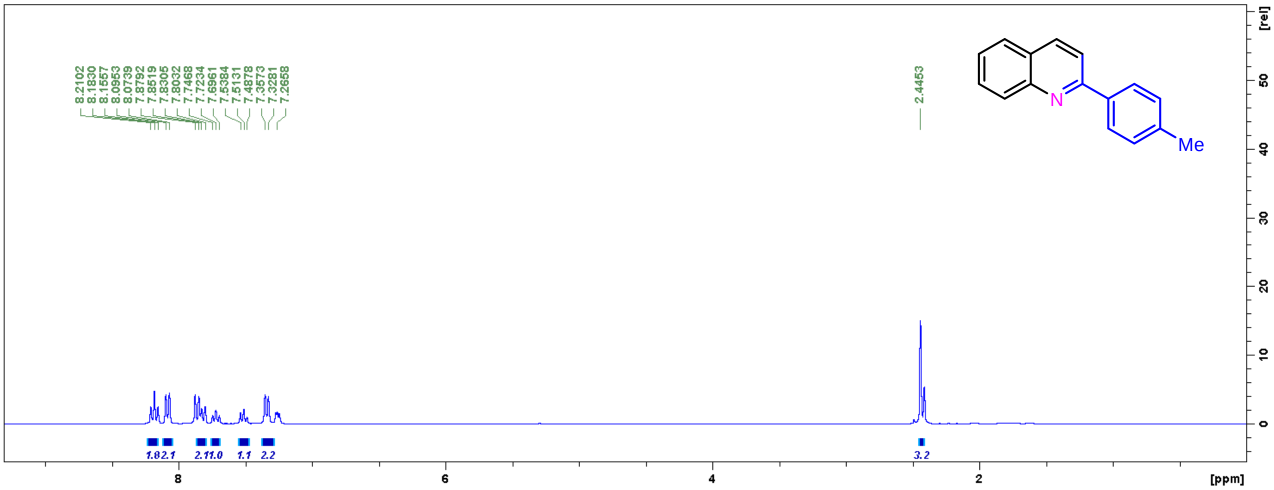
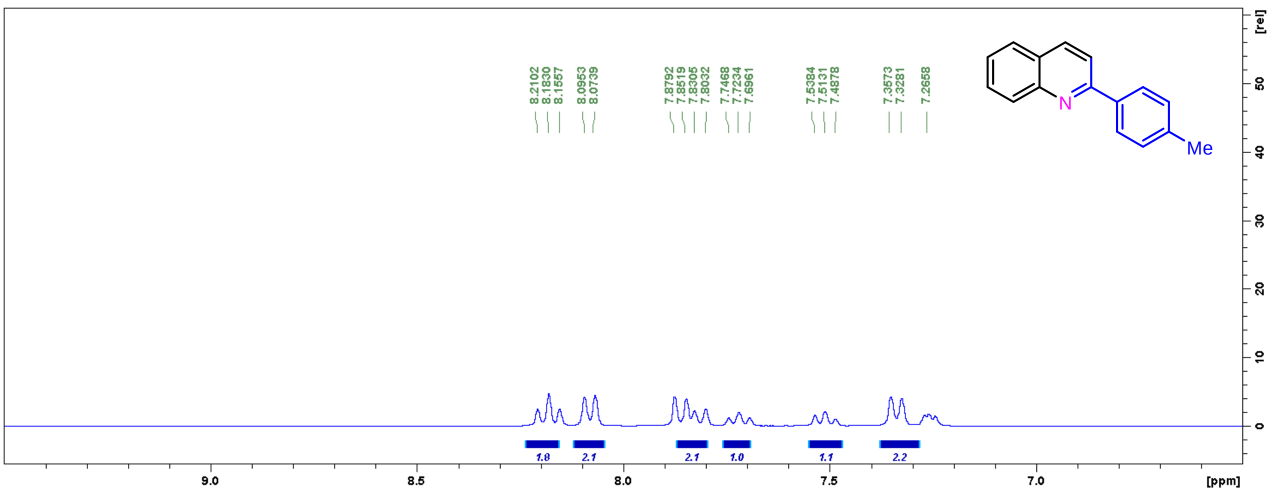


Figure S4. ^{1}H and ^{13}C NMR spectra of compound **8ab** in $CDCl_3$.





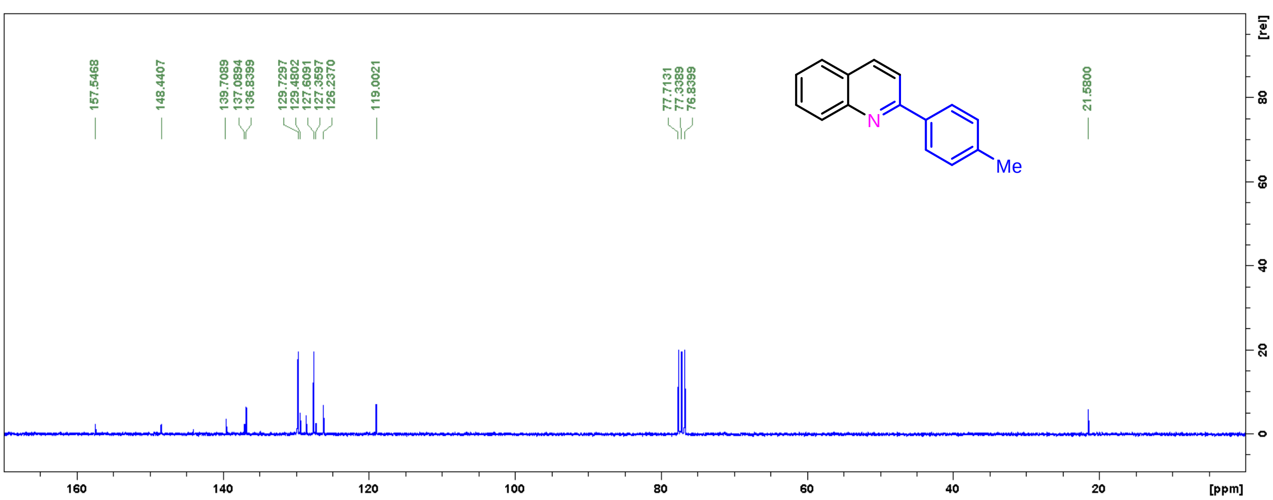


Figure S5. ^{1}H and ^{13}C NMR spectra of compound **8ac** in $CDCl_3$.

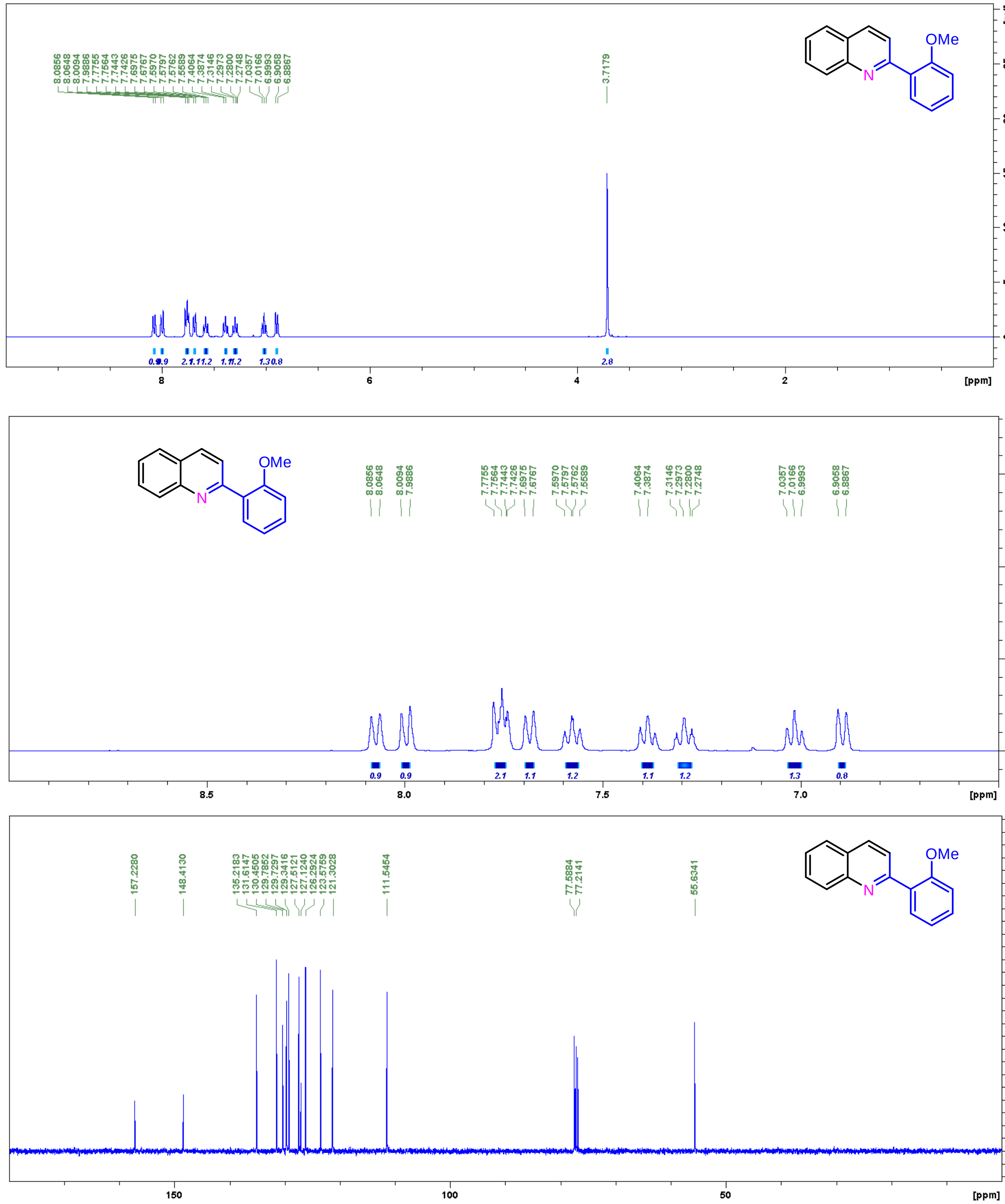


Figure S6. ^{1}H and ^{13}C NMR spectra of compound **8ad** in $CDCl_3$.

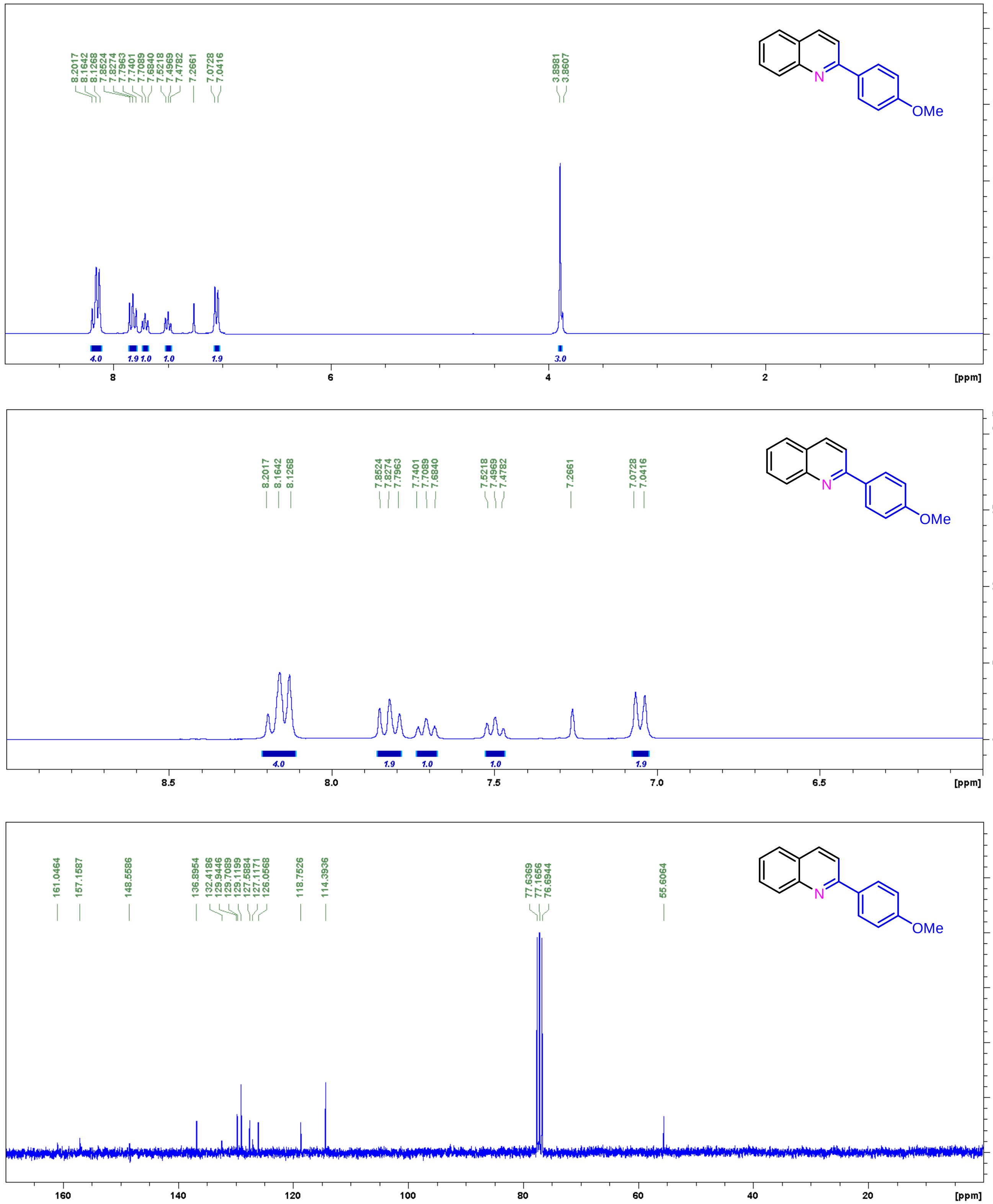


Figure S7. ^{1}H and ^{13}C NMR spectra of compound **8ae** in $CDCl_3$.

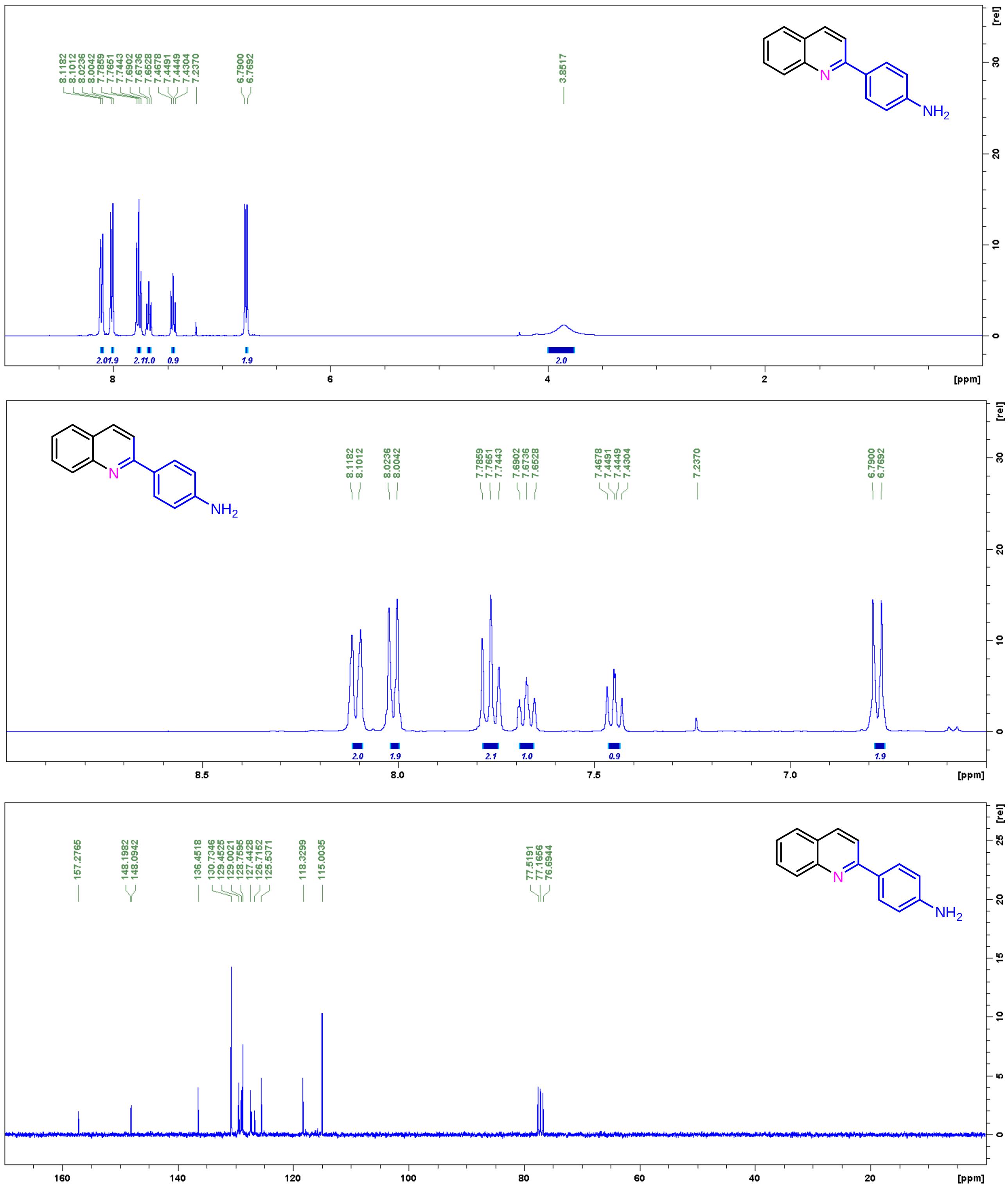
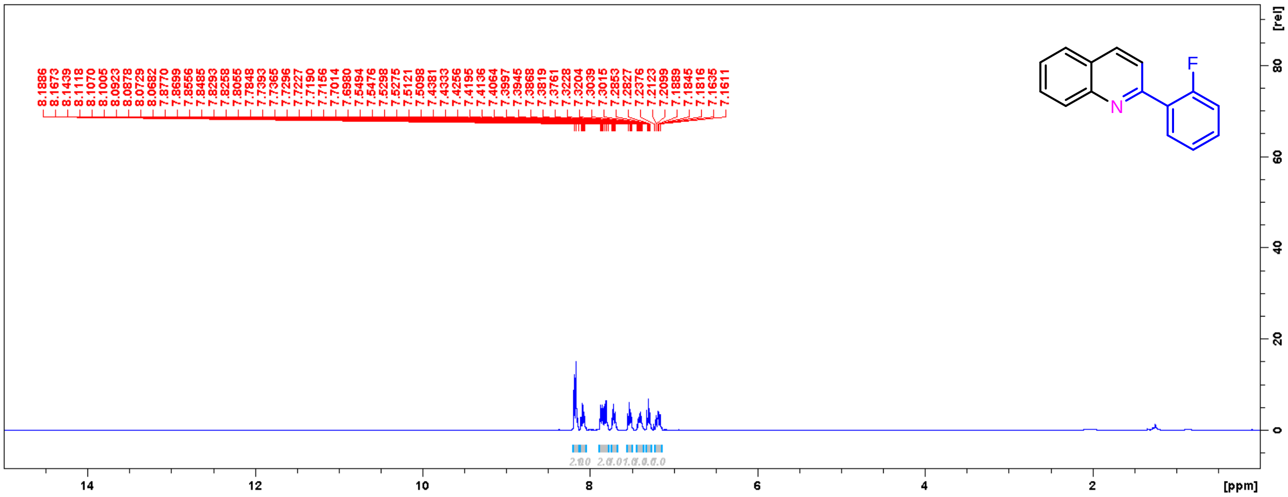
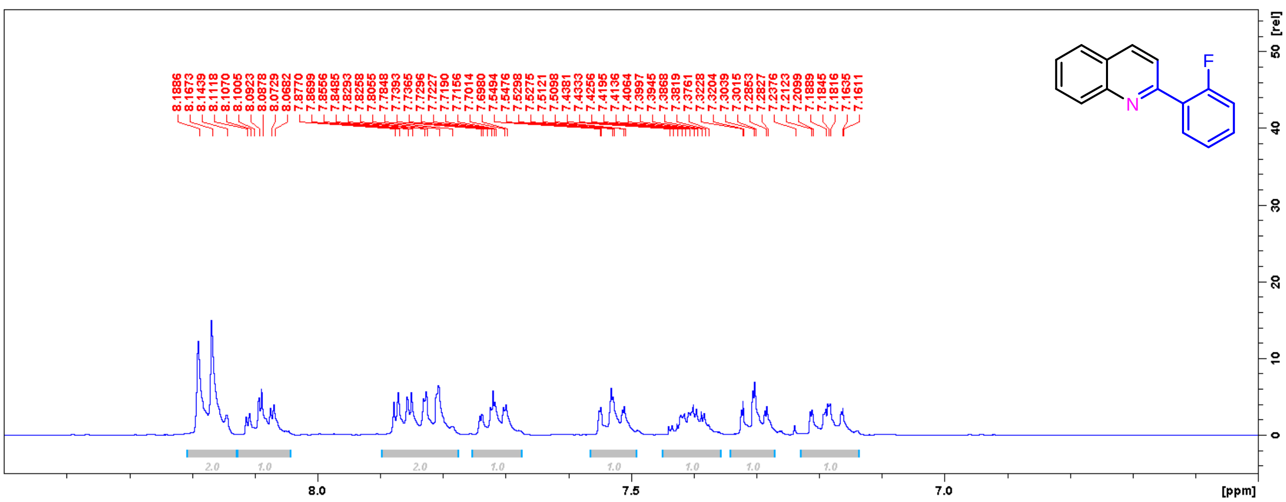


Figure S8. ^{1}H and ^{13}C NMR spectra of compound **8af** in $CDCl_3$.





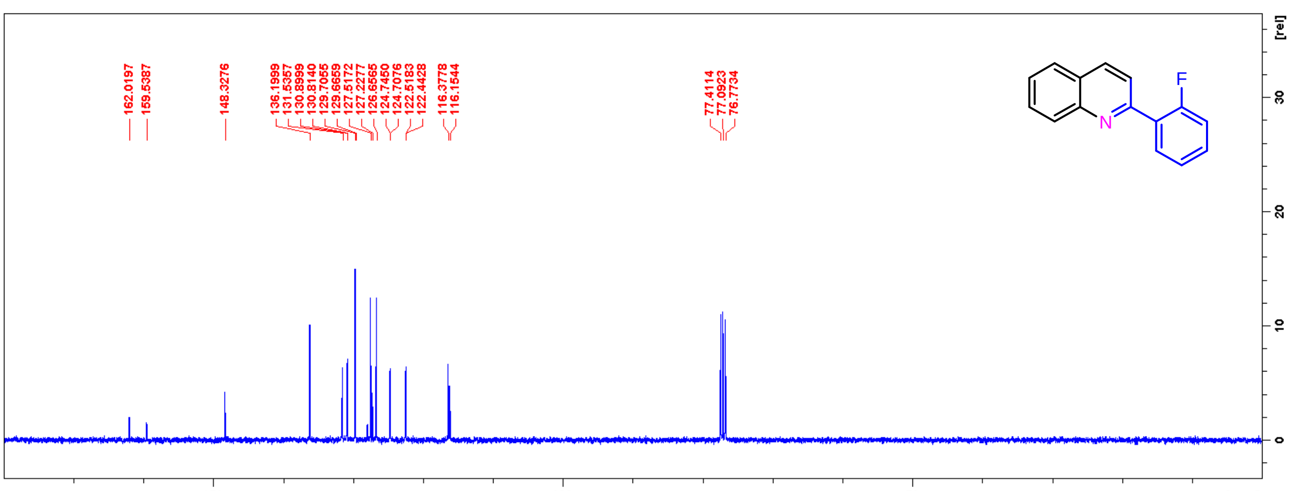


Figure S9. [1]H and [13]C NMR spectra of compound **8ag** in $CDCl_3$.

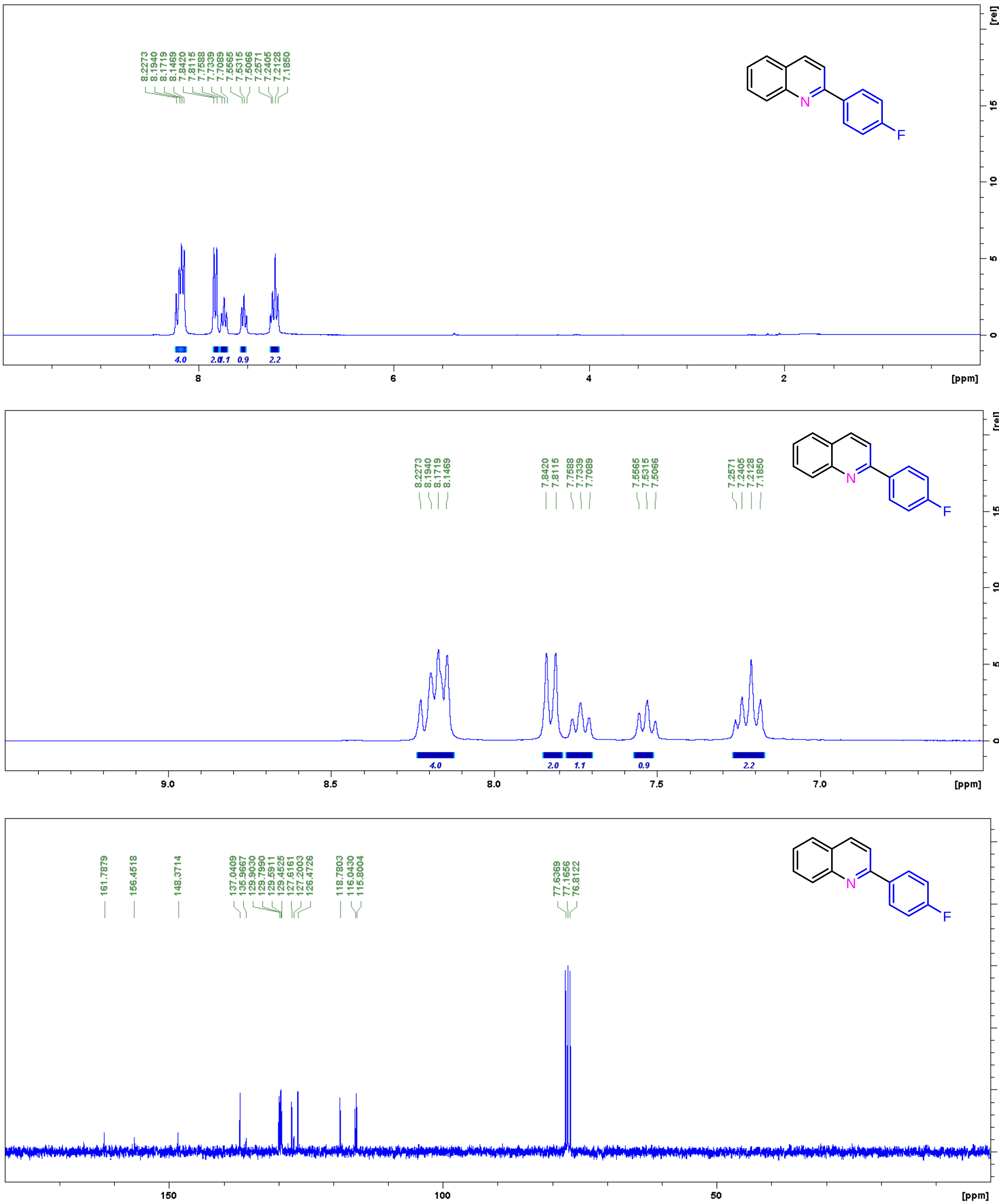


Figure S10. ^{1}H and ^{13}C NMR spectra of compound **8ah** in $CDCl_3$.

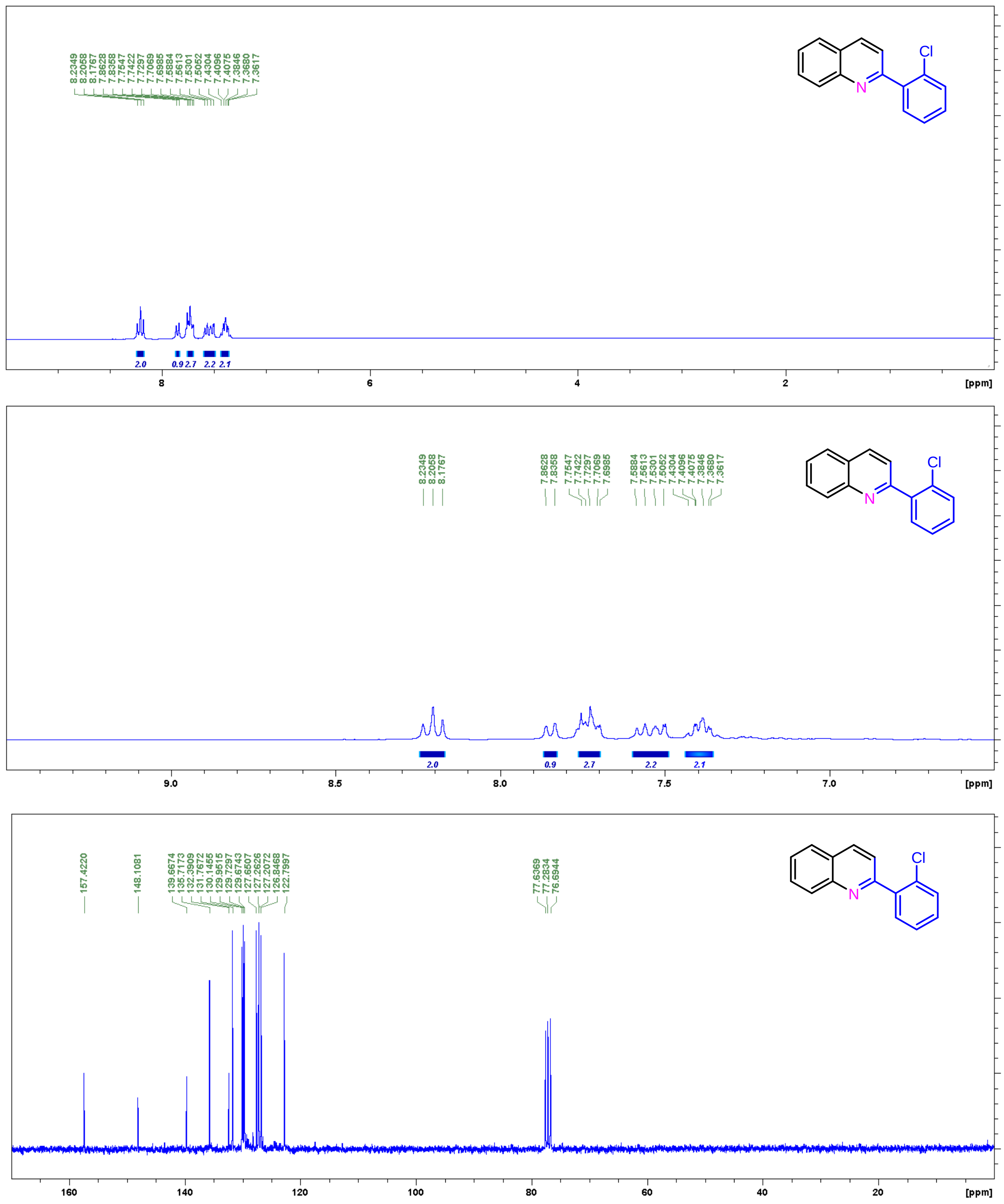
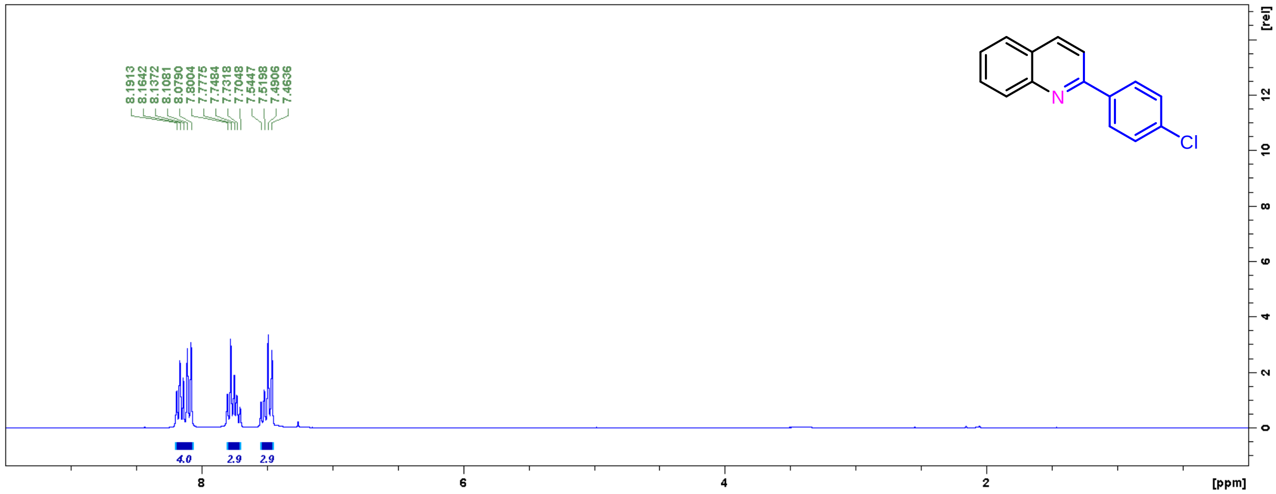
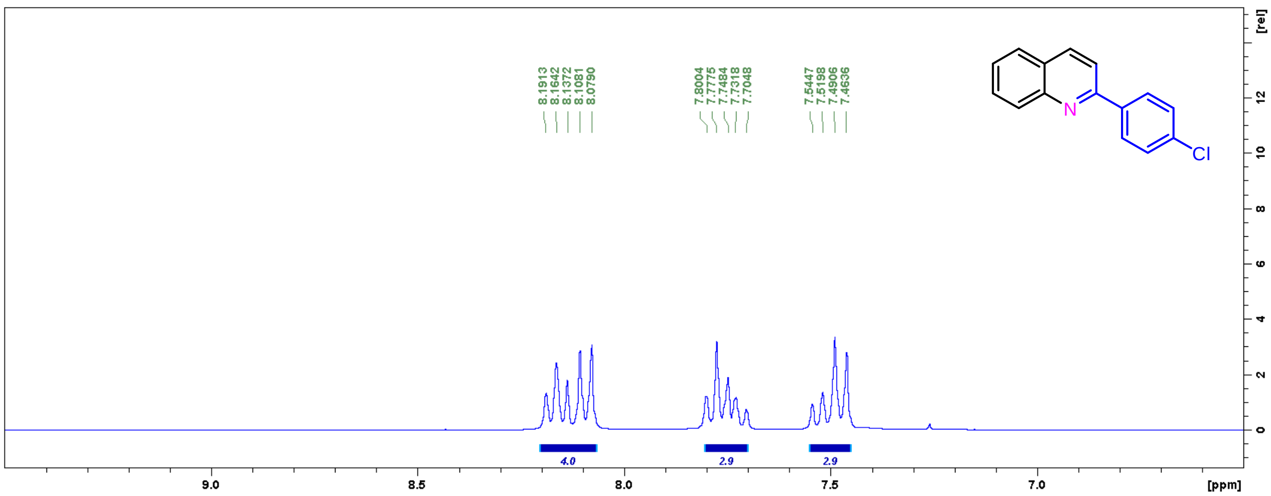


Figure S11. ^1H and ^{13}C NMR spectra of compound **8ai** in $CDCl_3$.





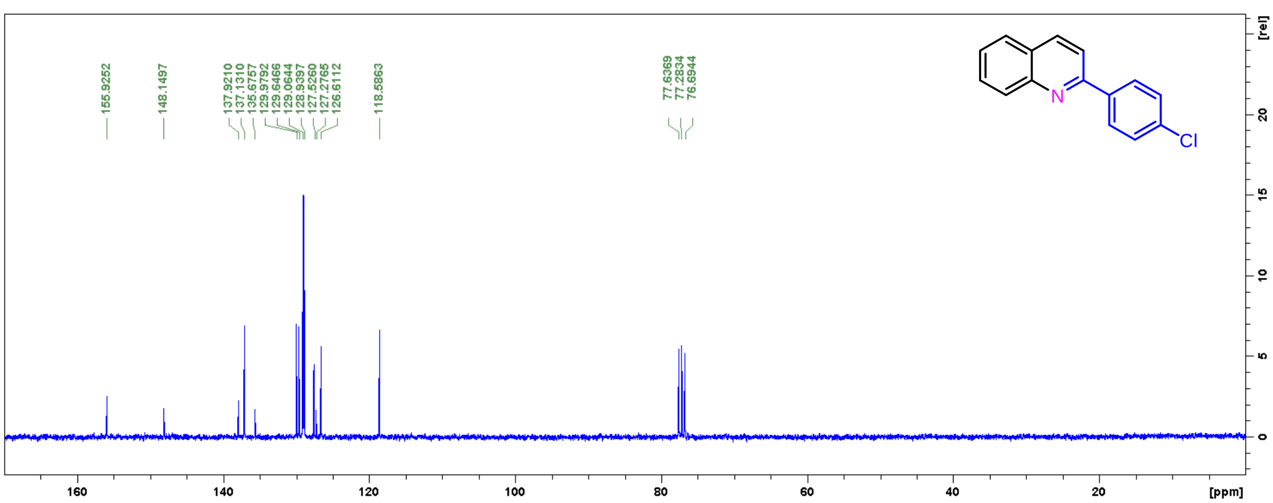
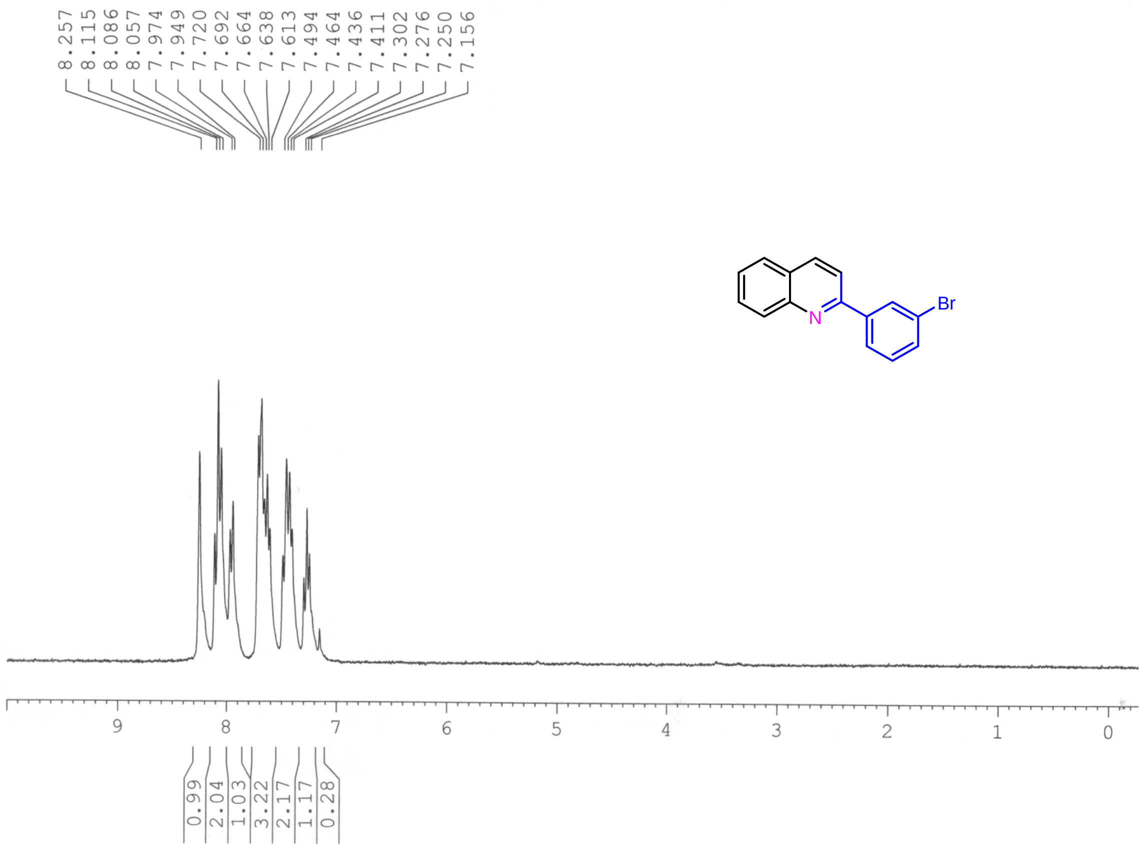


Figure S12. ^{1}H and ^{13}C NMR spectra of compound **8aj** in $CDCl_3$.



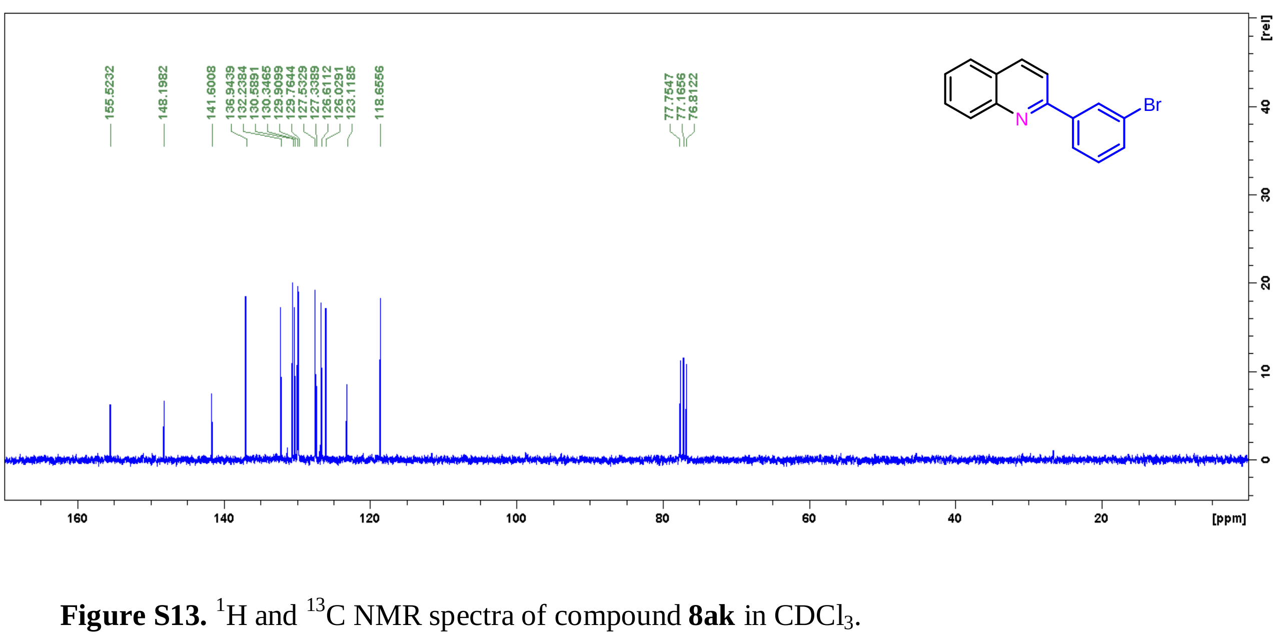
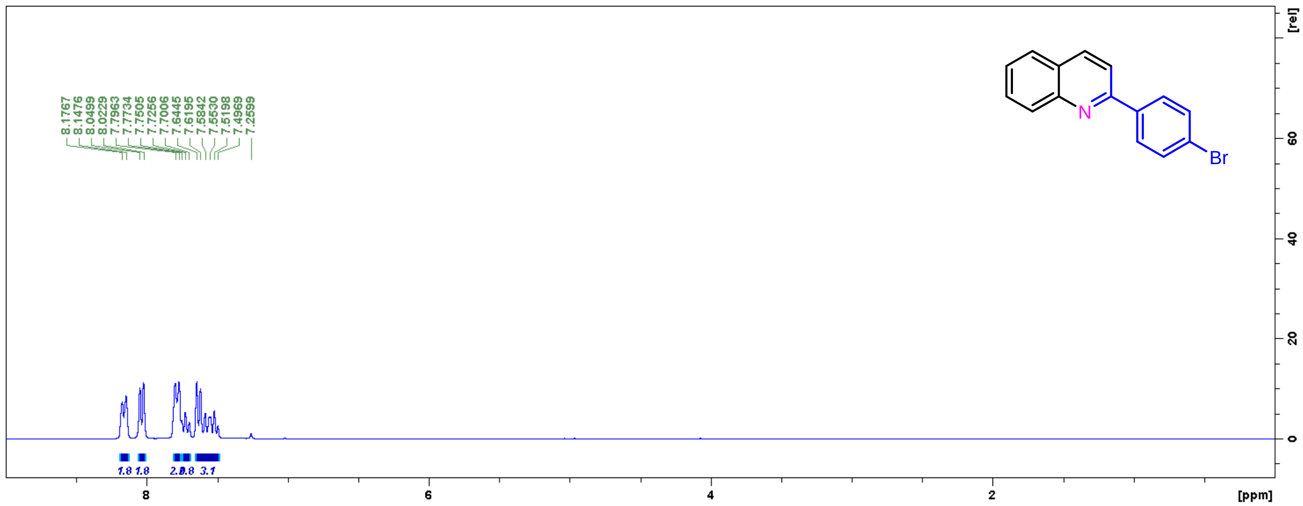
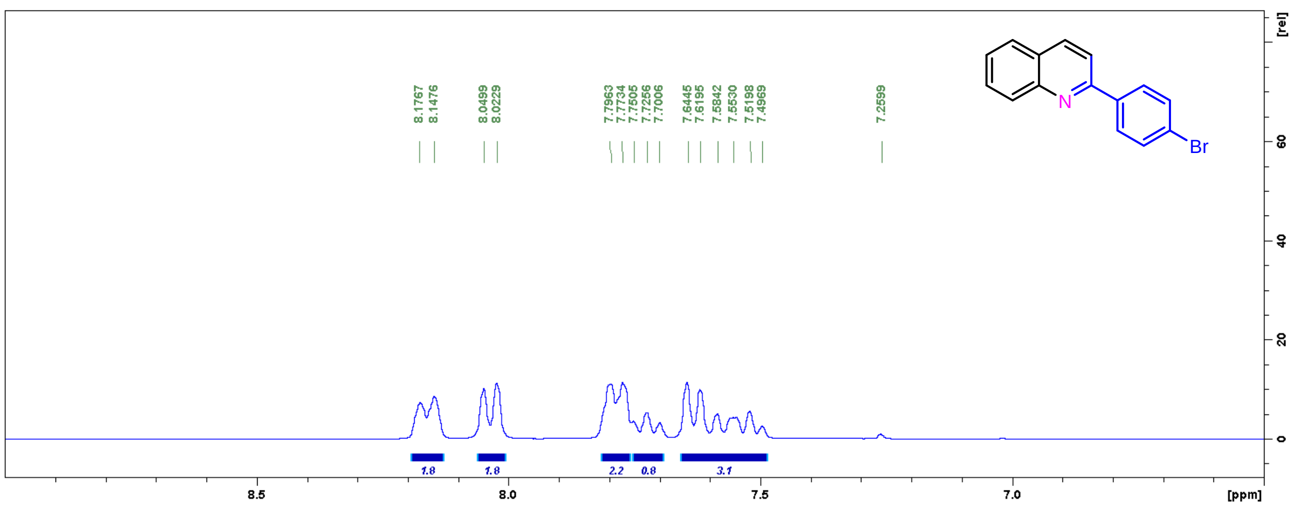


Figure S13. ^{1}H and ^{13}C NMR spectra of compound **8ak** in $CDCl_3$.





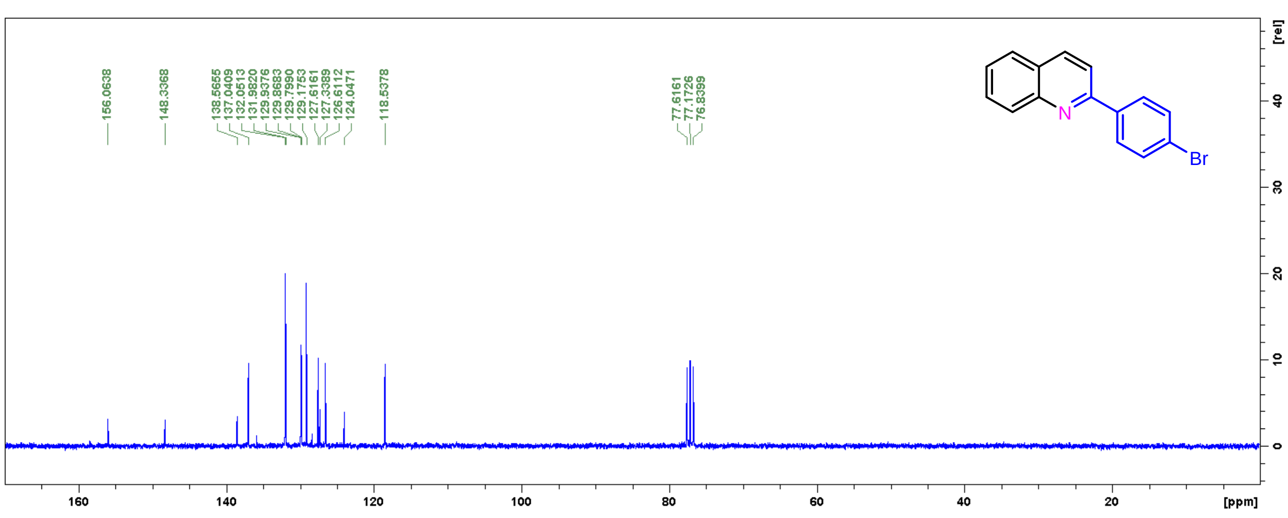


Figure S14. ^{1}H and ^{13}C NMR spectra of compound **8al** in $CDCl_3$.

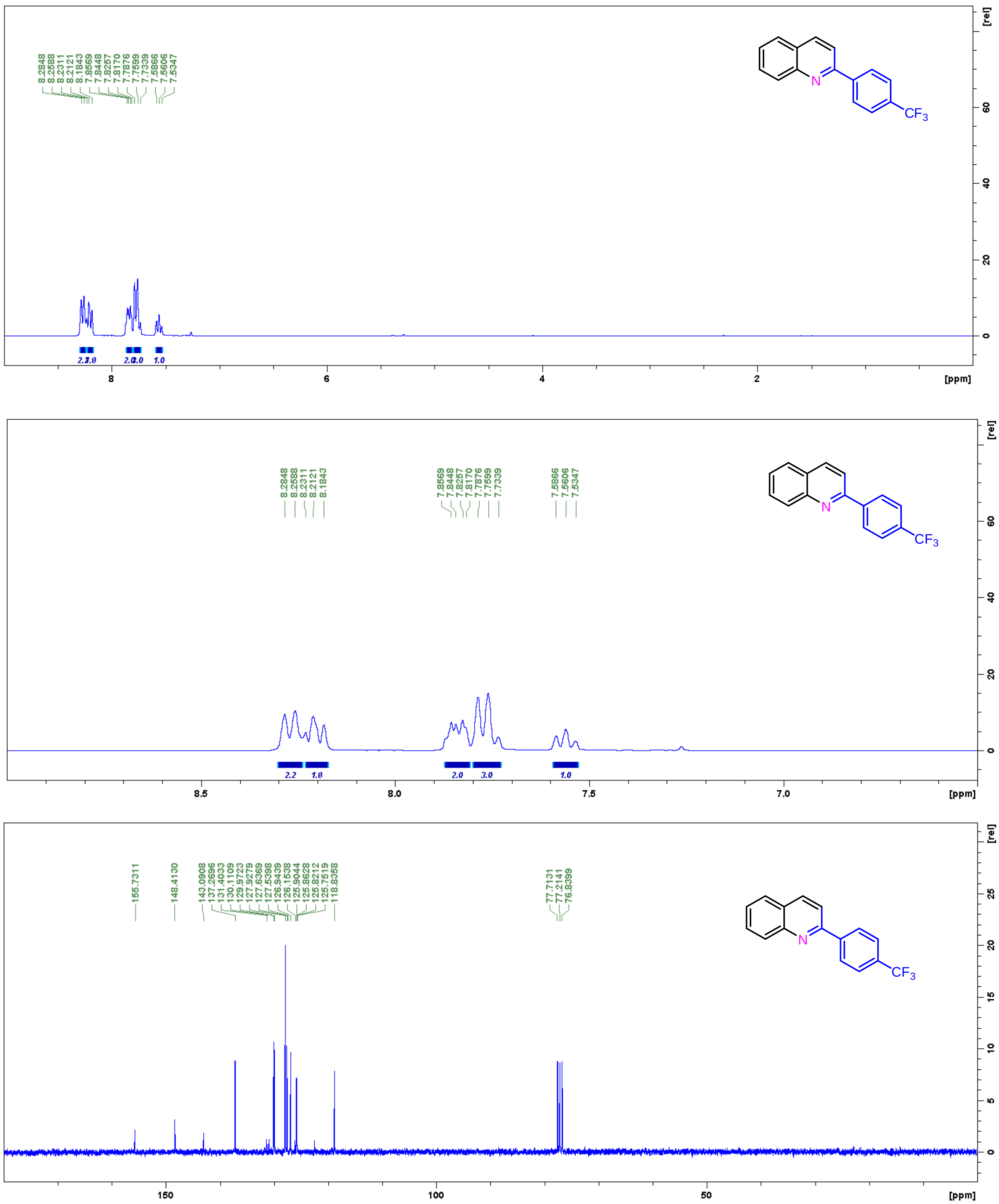
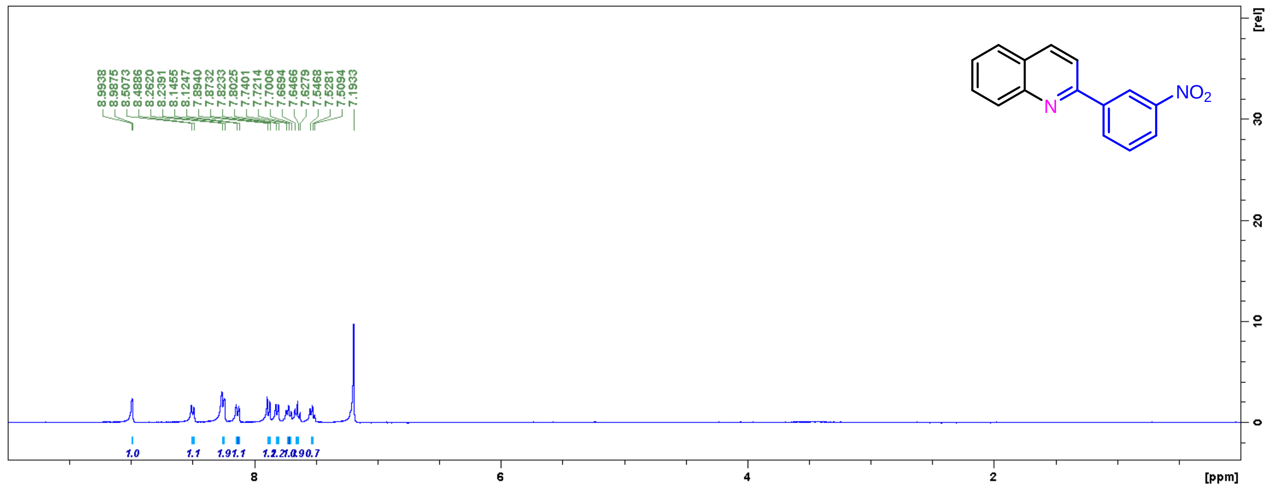
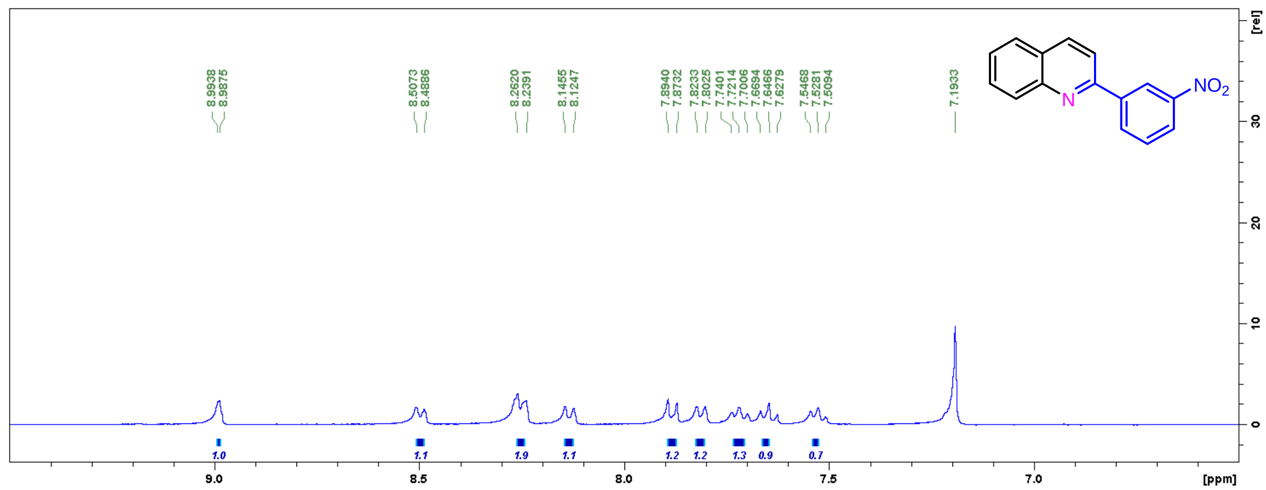


Figure S15. ^{1}H and ^{13}C NMR spectra of compound **8am** in $CDCl_3$.





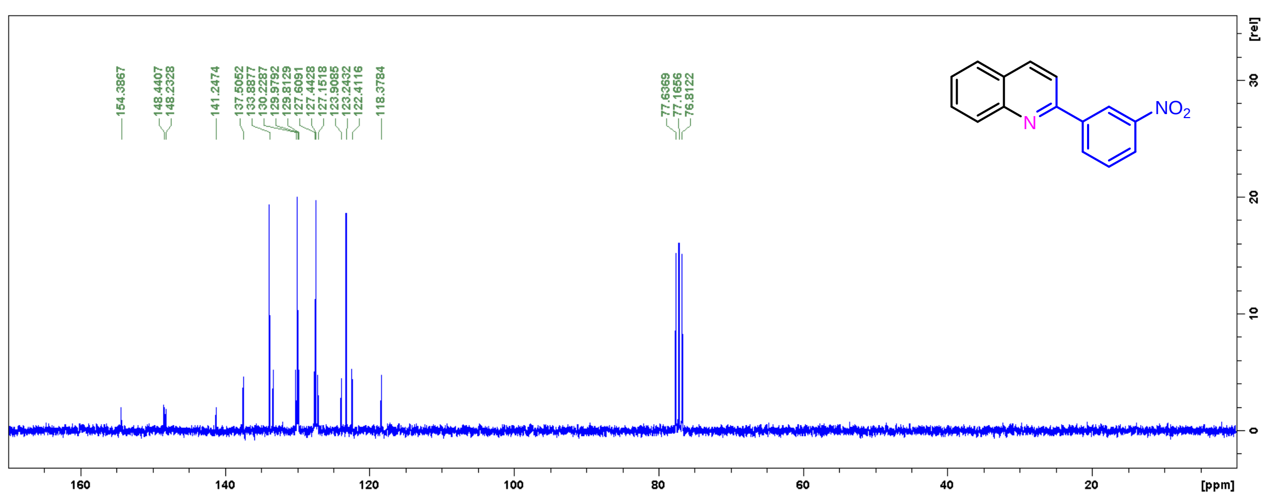
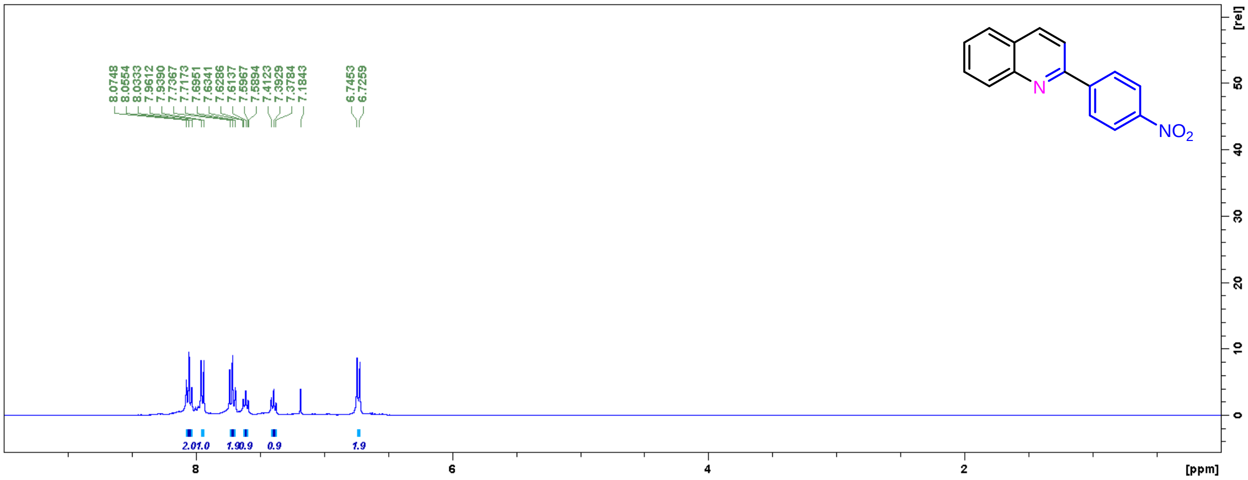
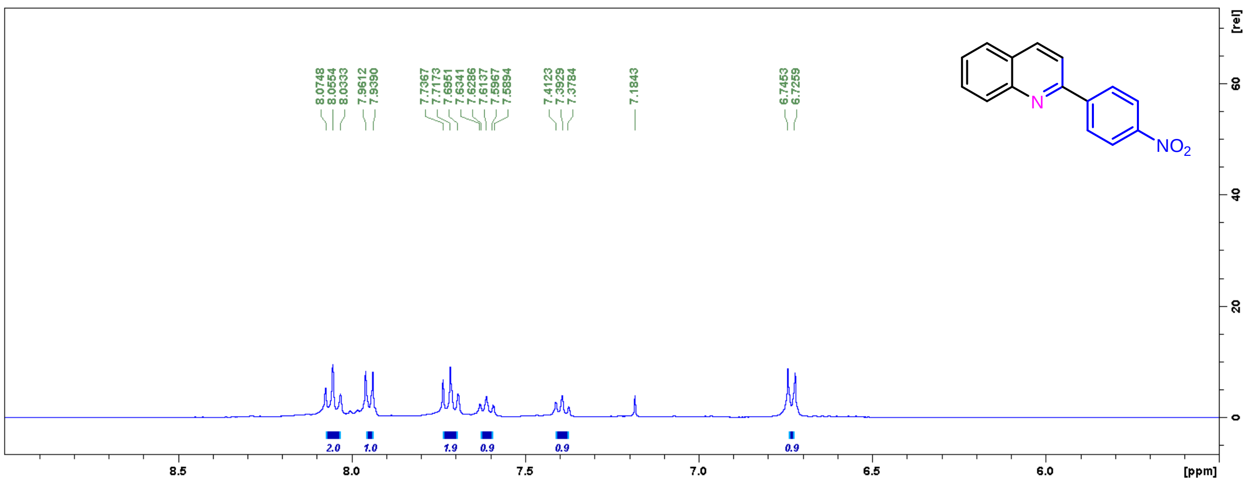


Figure S16. ^{1}H and ^{13}C NMR spectra of compound **8an** in $CDCl_3$.





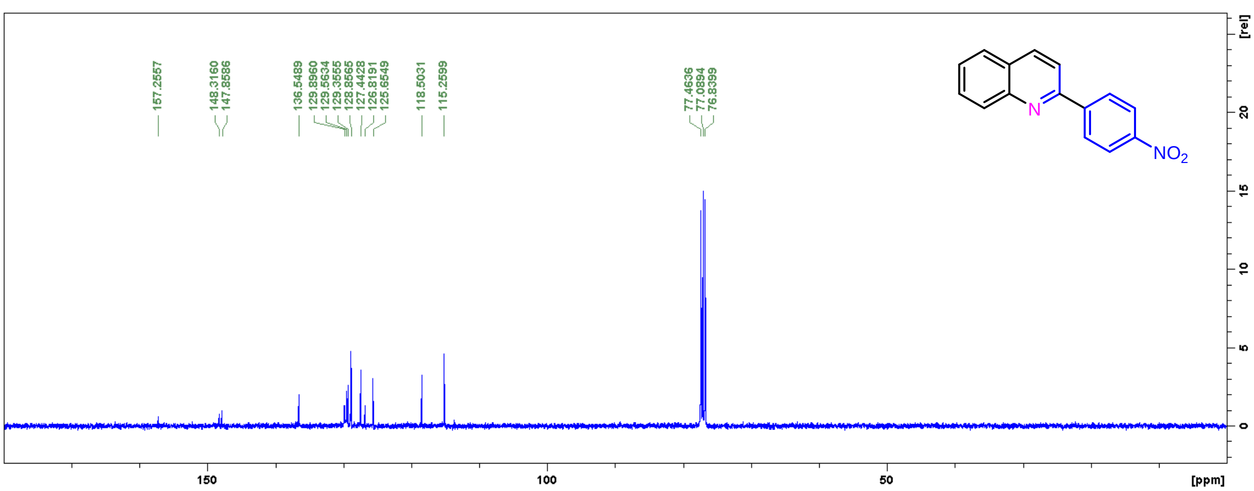
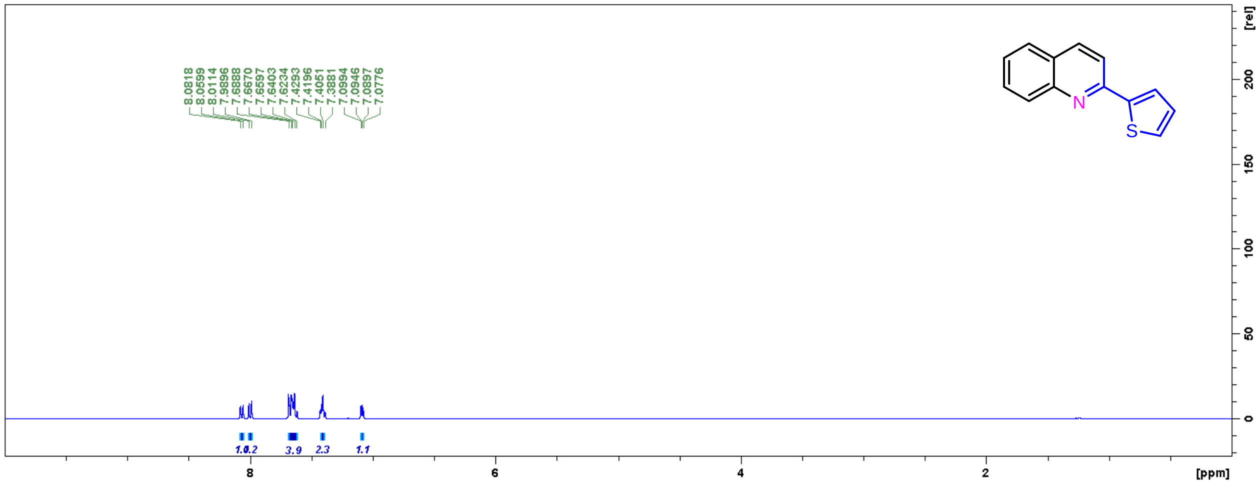


Figure S17. ^{1}H and ^{13}C NMR spectra of compound **8ao** in $CDCl_3$.



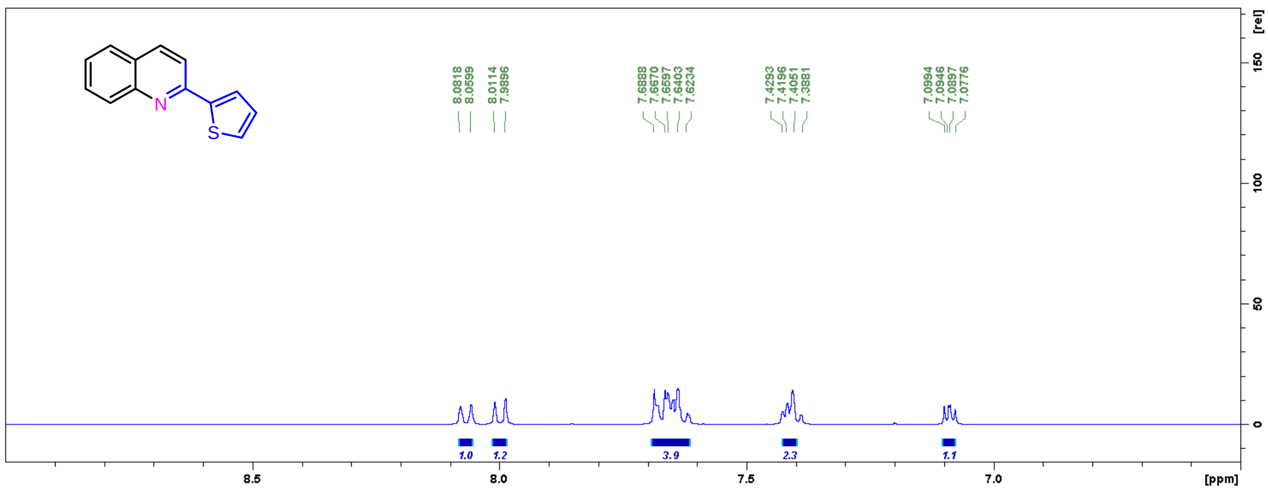


Figure S18. ^{1}H NMR spectum of compound **8ap** in $CDCl_3$.

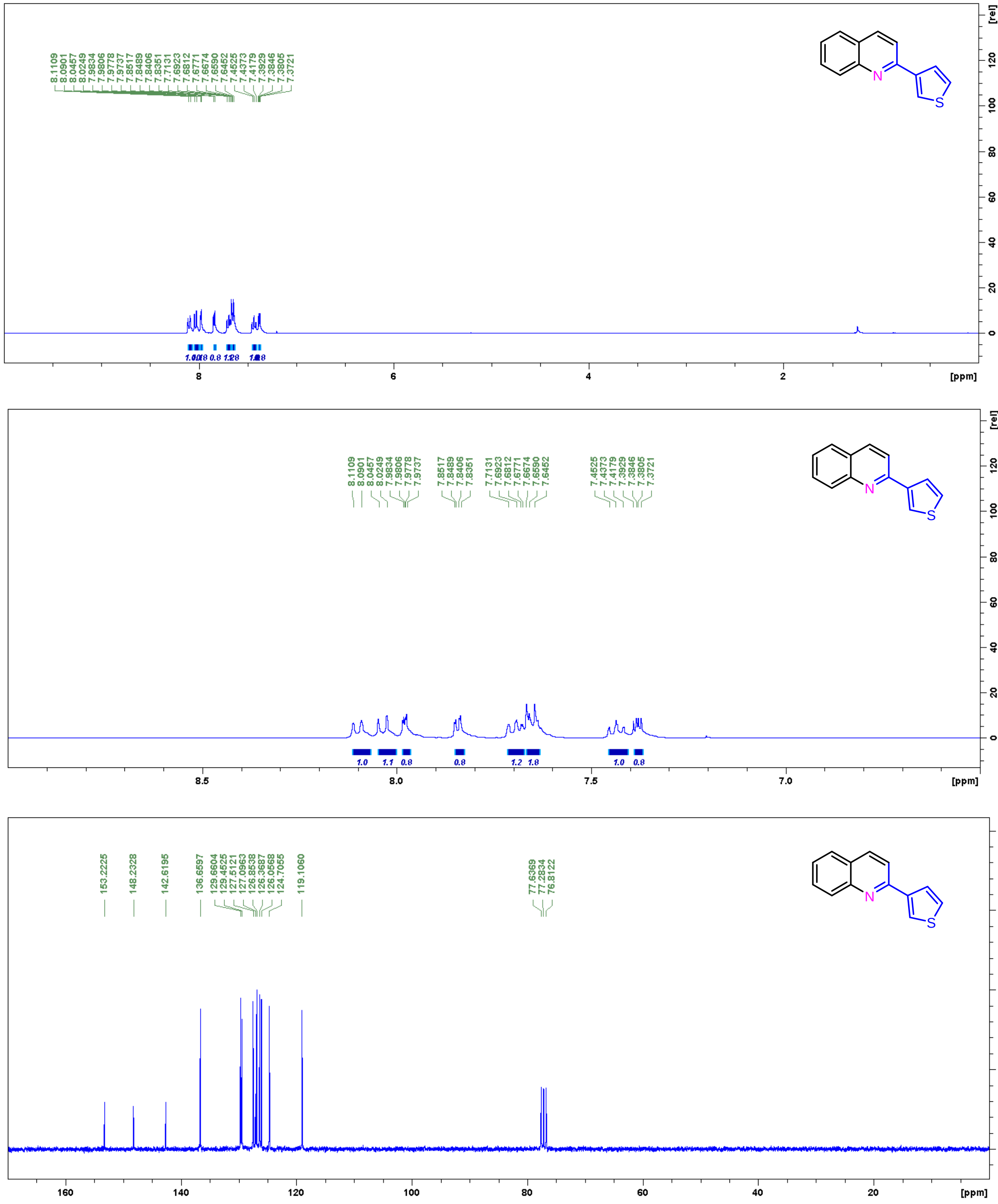


Figure S19. ^{1}H and ^{13}C NMR spectra of compound **8aq** in $CDCl_3$.

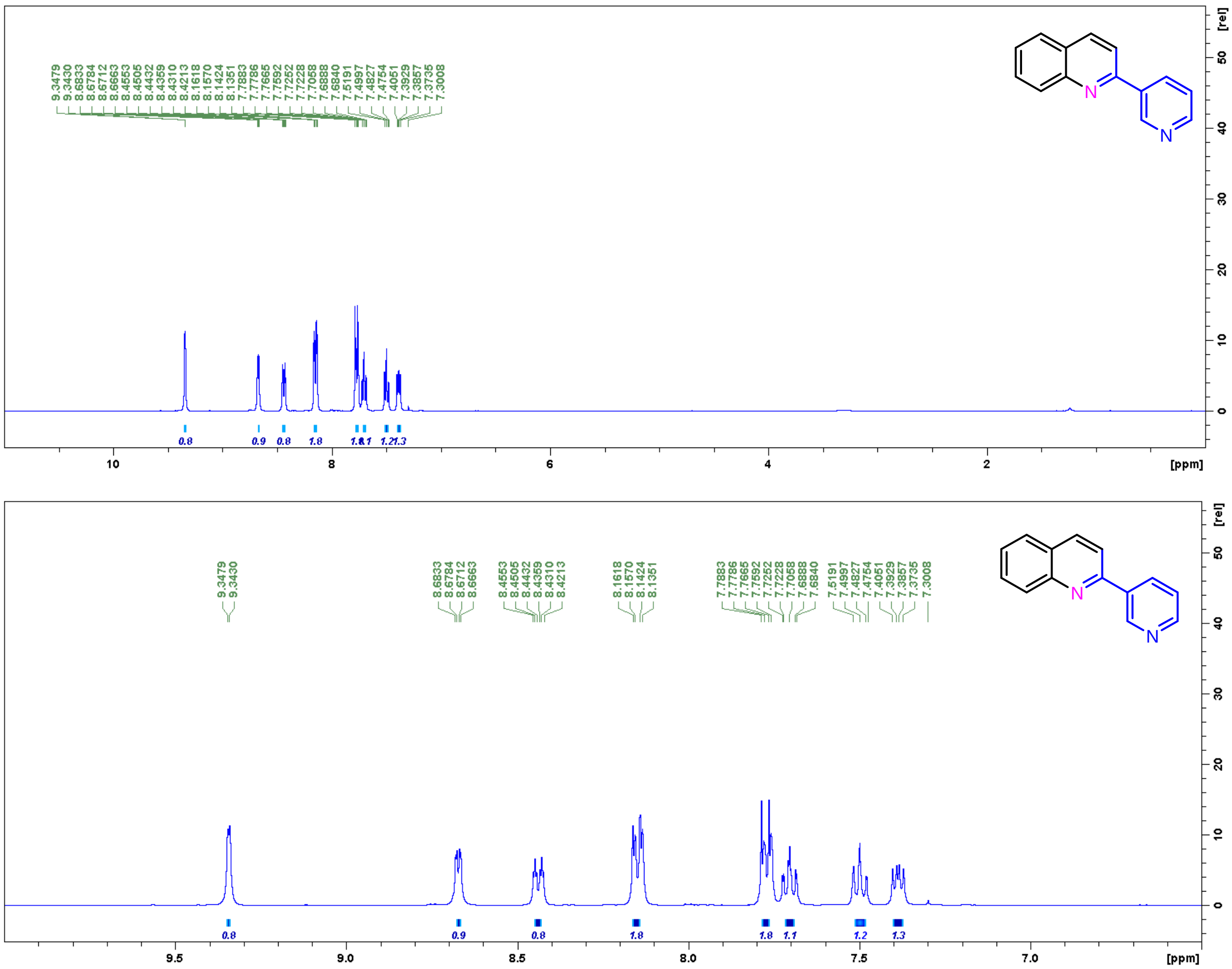
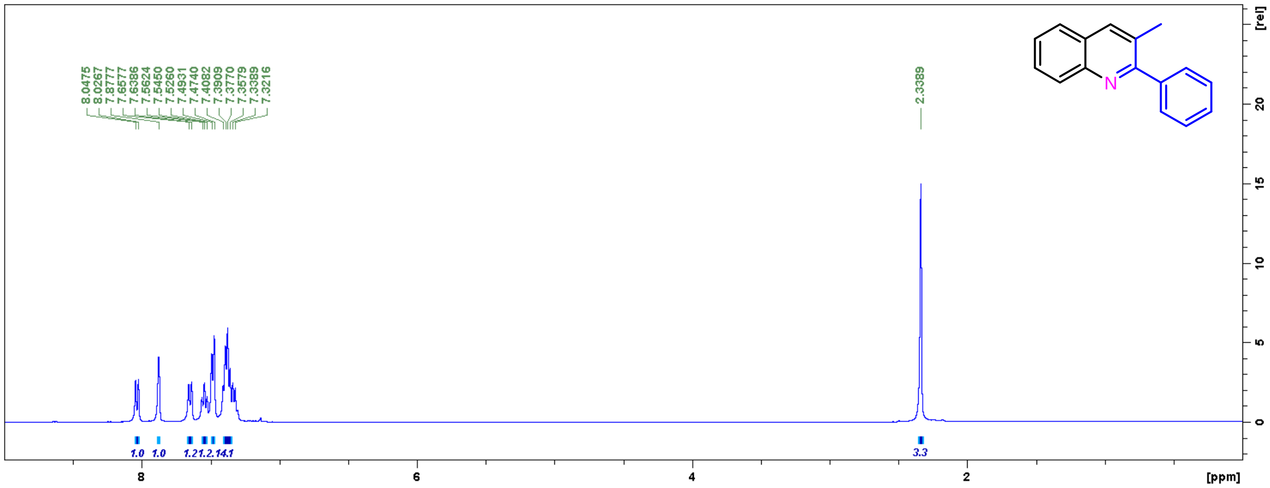
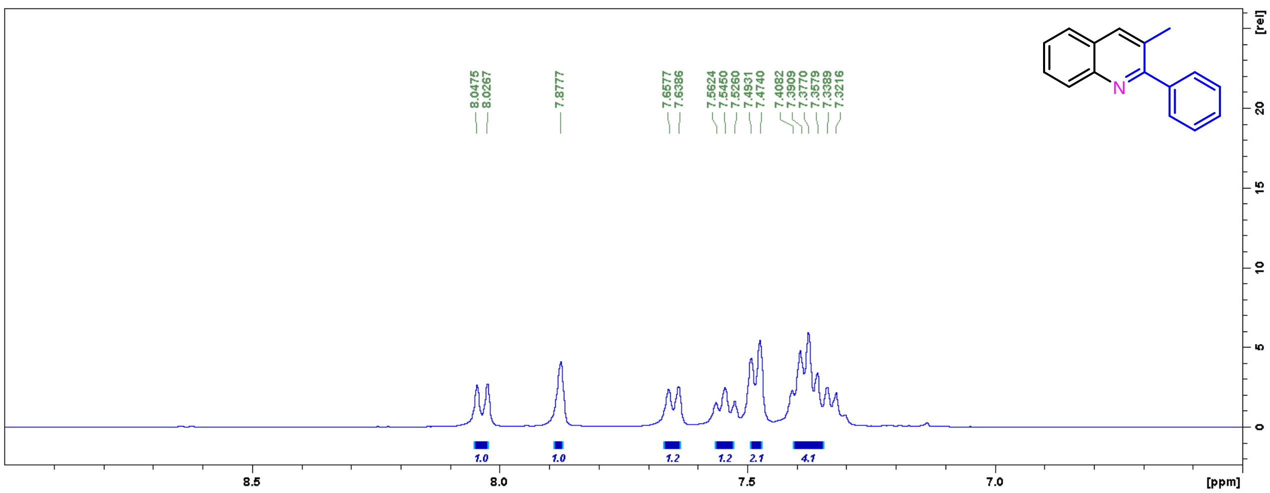


Figure S20. ^{1}H NMR spectrum of compound **8ar** in $CDCl_3$.





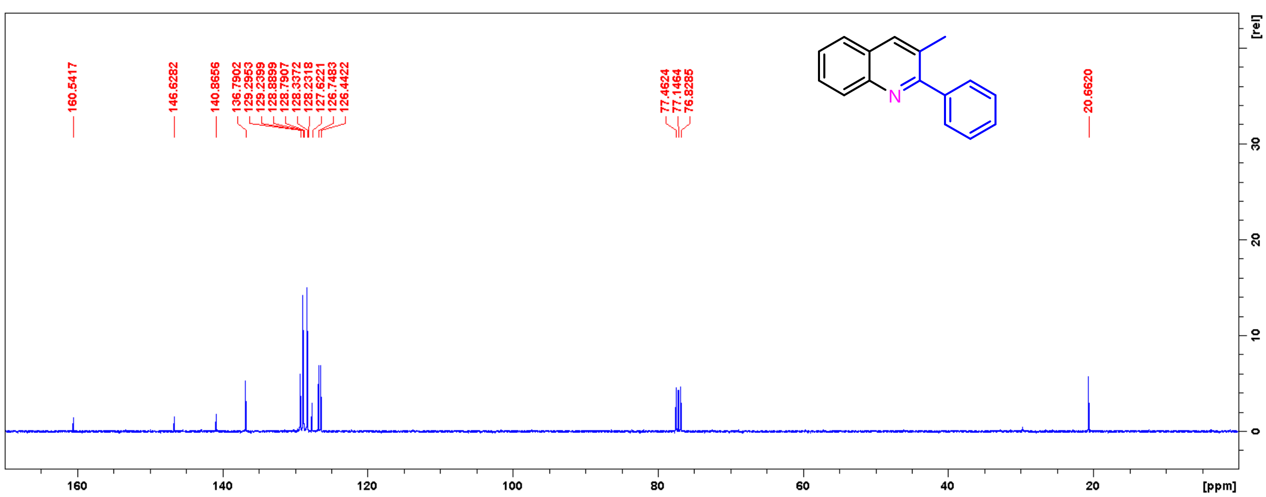
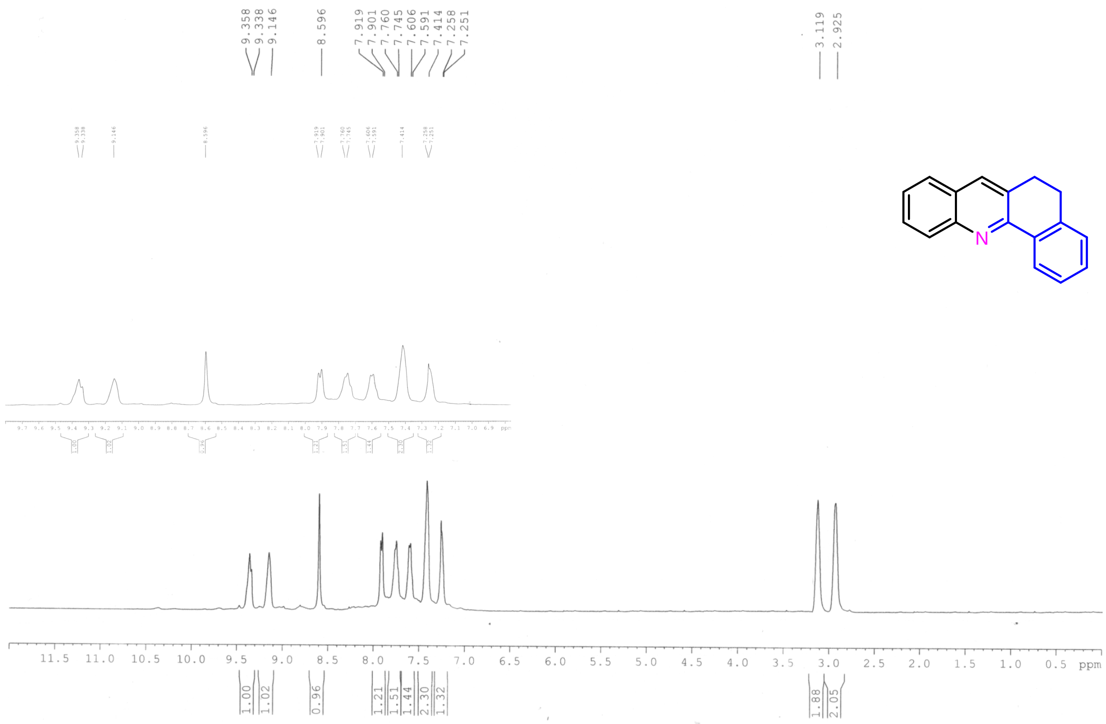


Figure S21. ^{1}H and ^{13}C NMR spectra of compound **8as** in $CDCl_3$.



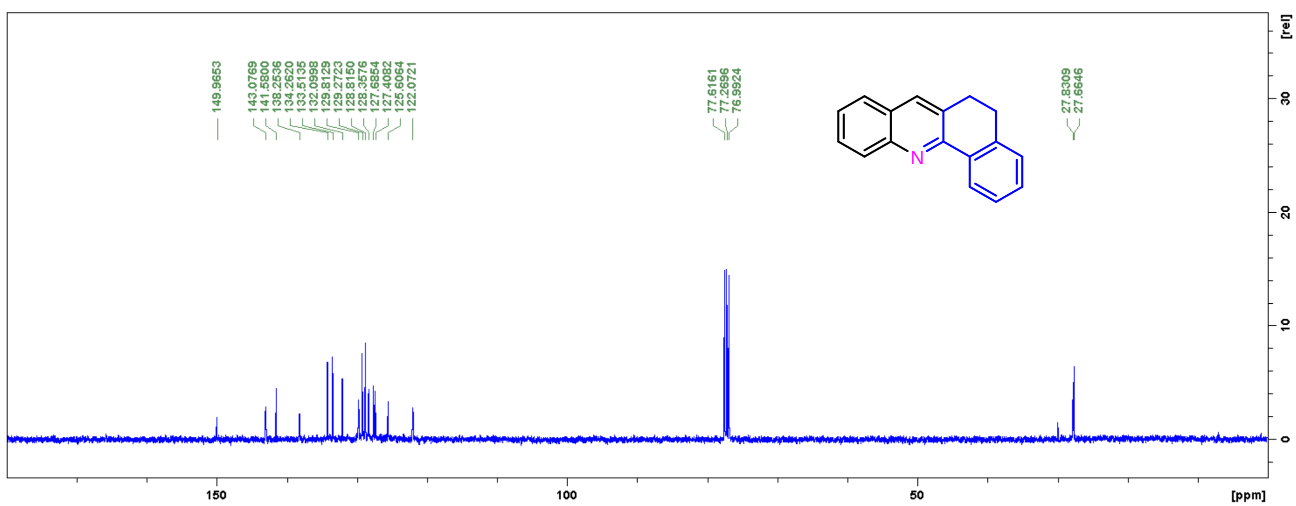
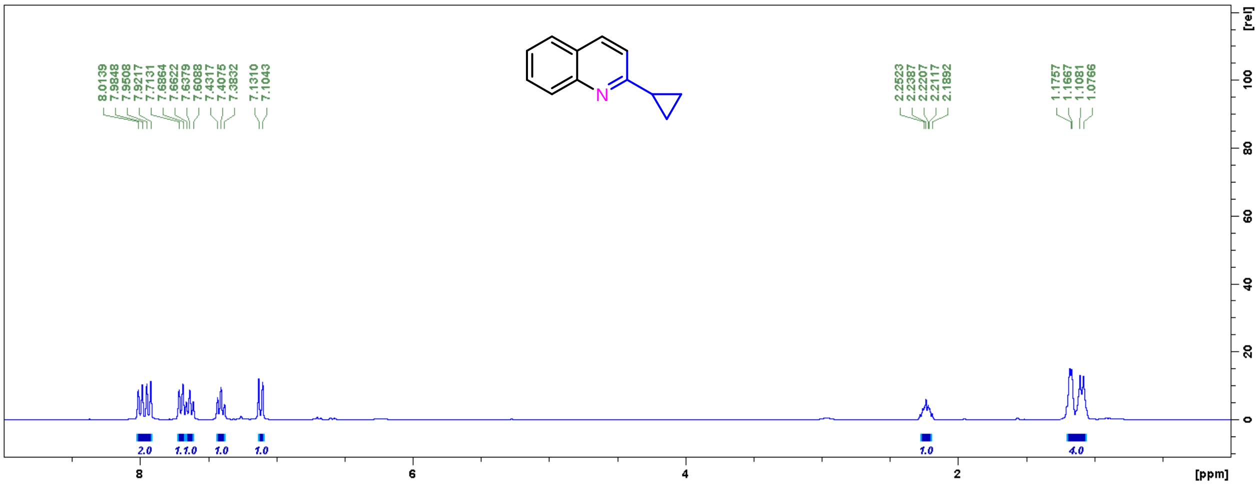
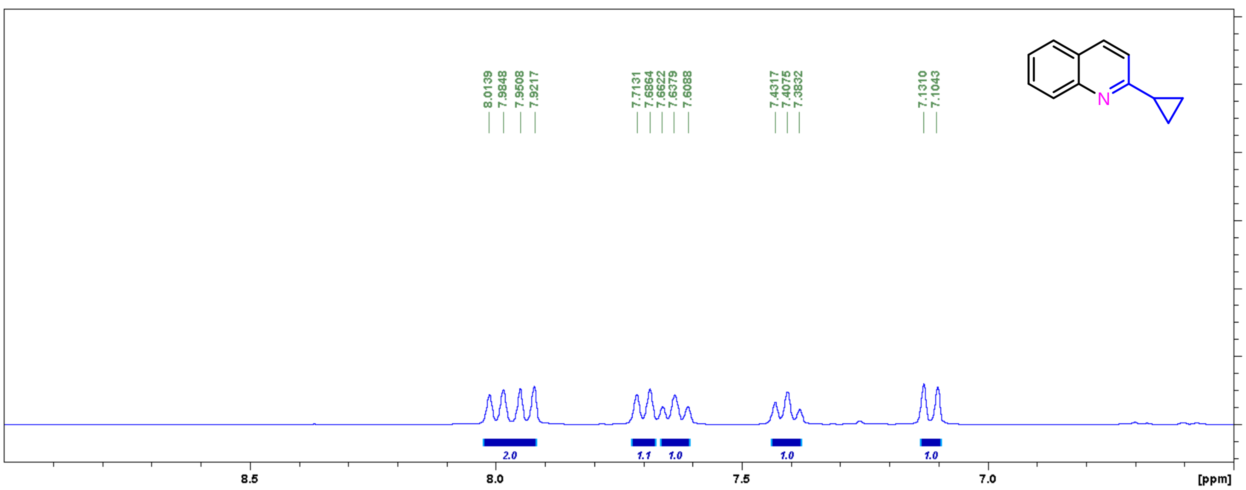


Figure S22. ^{1}H and ^{13}C NMR spectra of compound **8at** in $CDCl_3$.





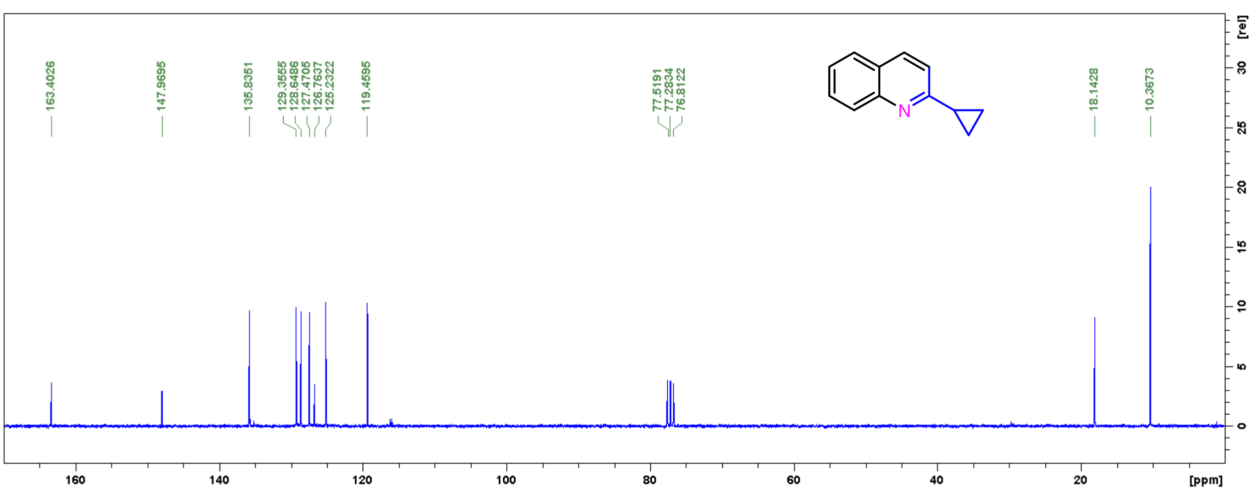


Figure S23. ^{1}H and ^{13}C NMR spectra of compound **8au** in $CDCl_3$.

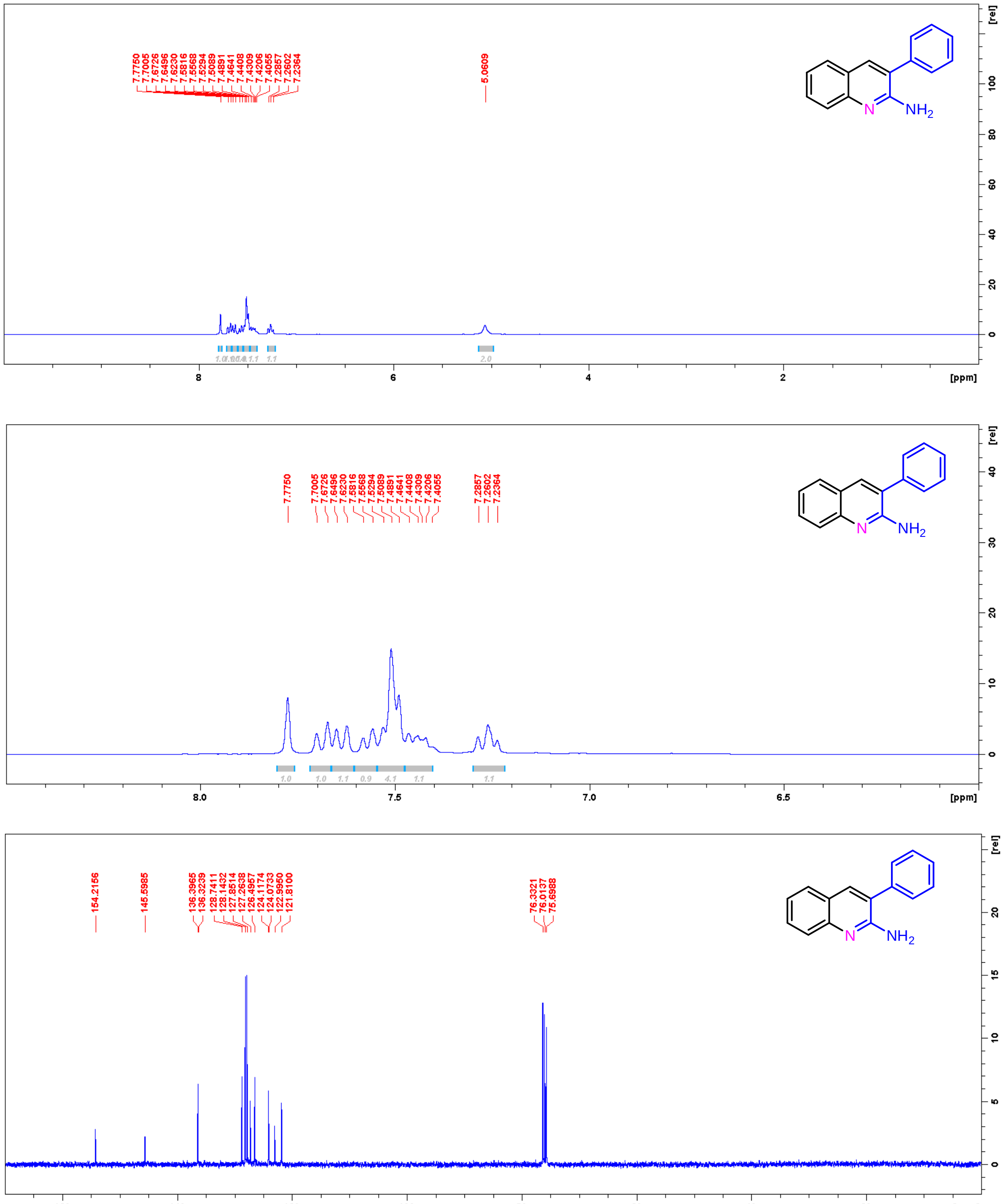
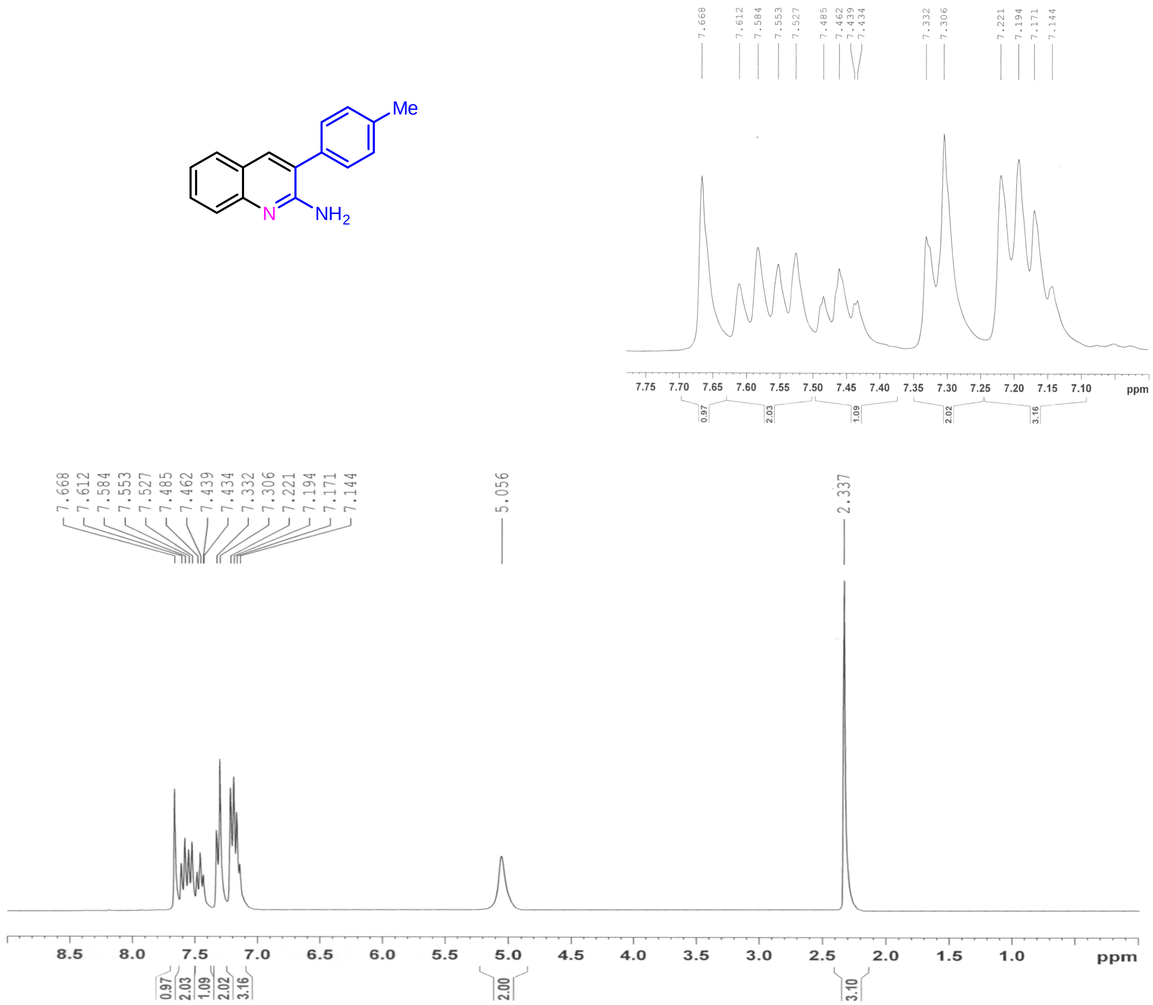


Figure S24. [1]H and [13]C NMR spectra of compound **9aa** in $CDCl_3$.



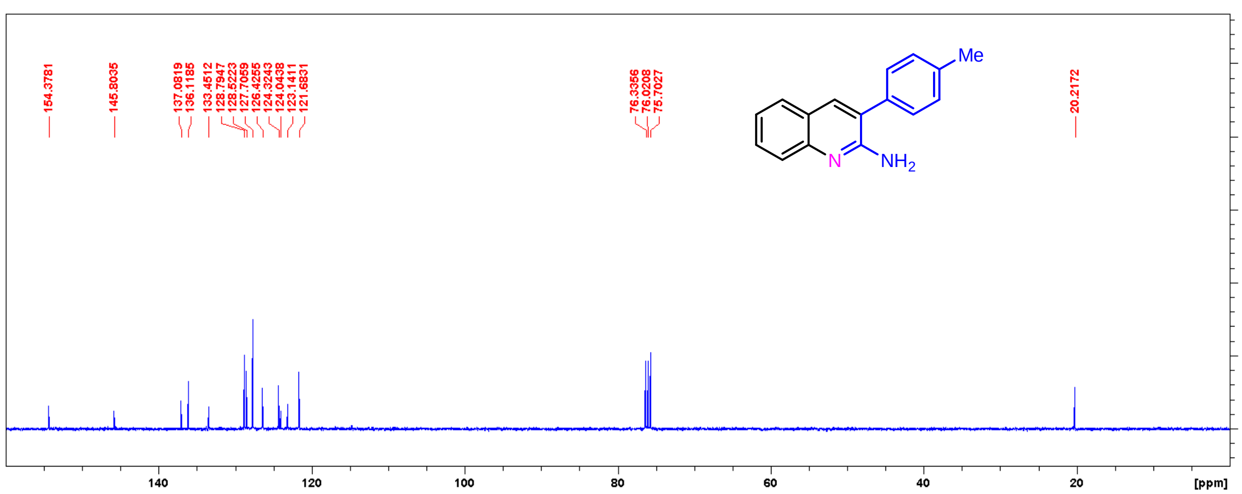
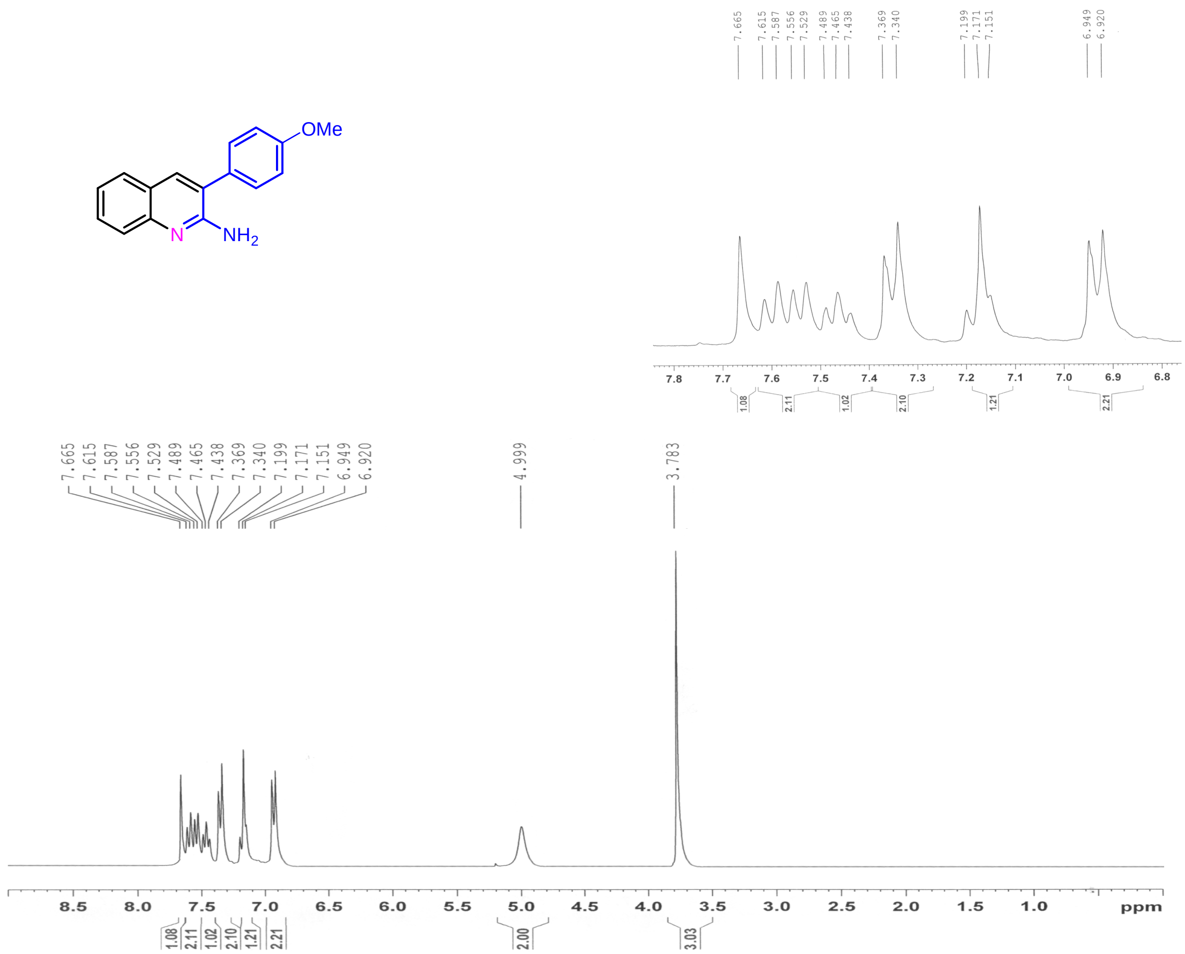


Figure S25. ^{1}H and ^{13}C NMR spectra of compound **9ab** in $CDCl_3$.



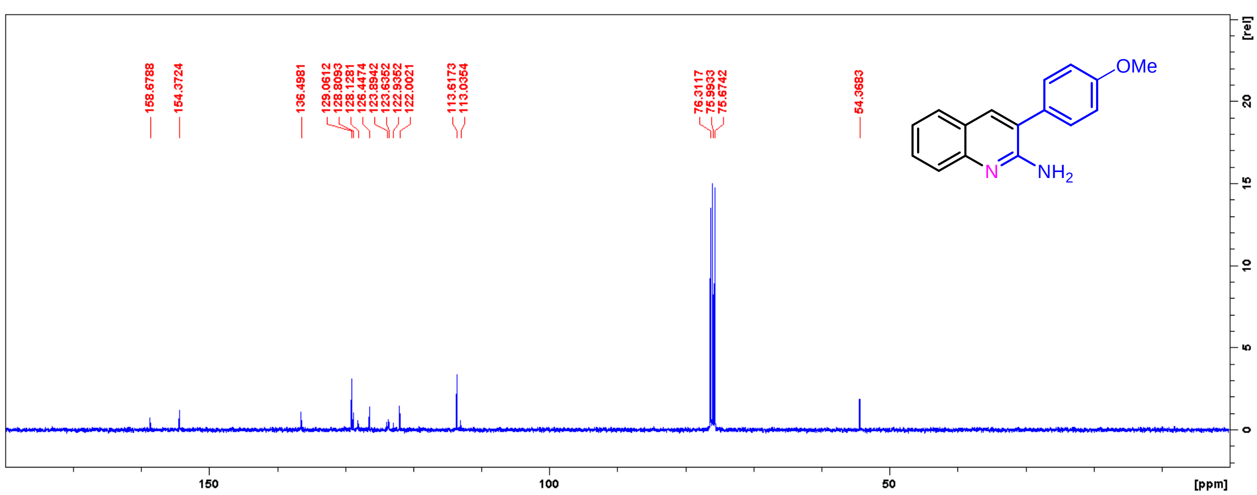
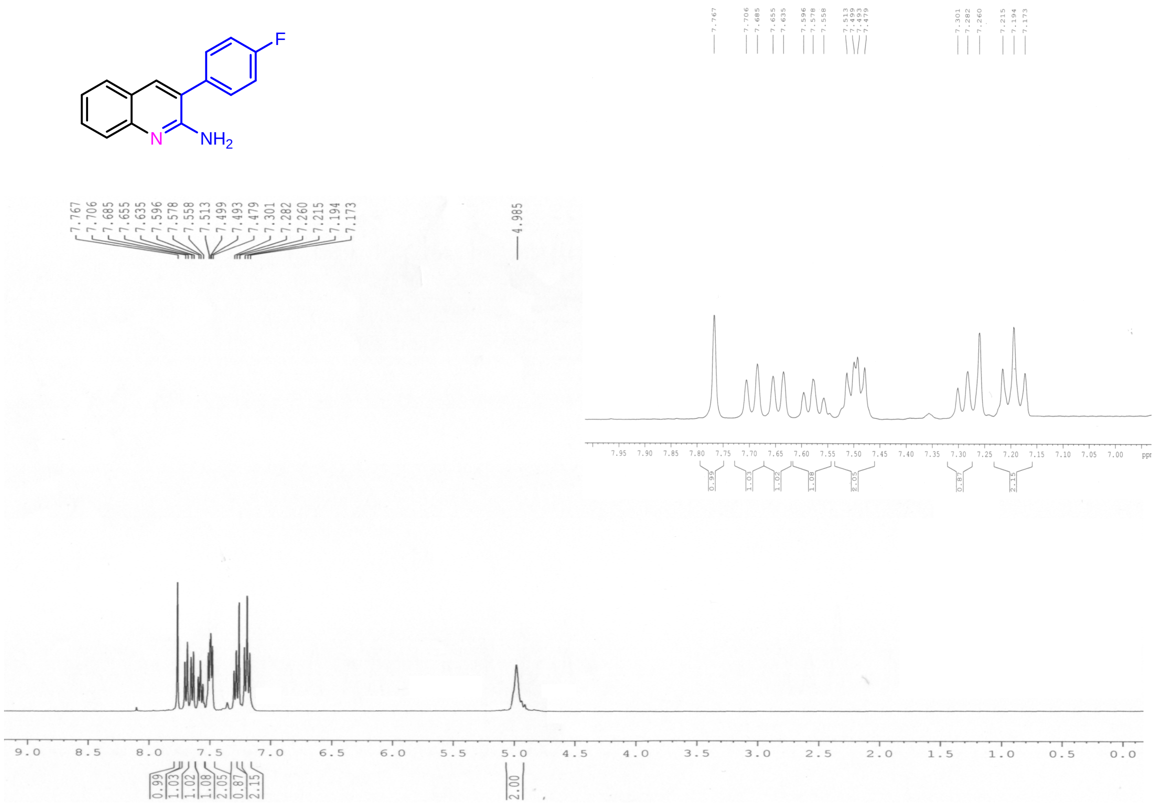


Figure S26. ^{1}H and ^{13}C NMR spectra of compound **9ac** in $CDCl_3$.



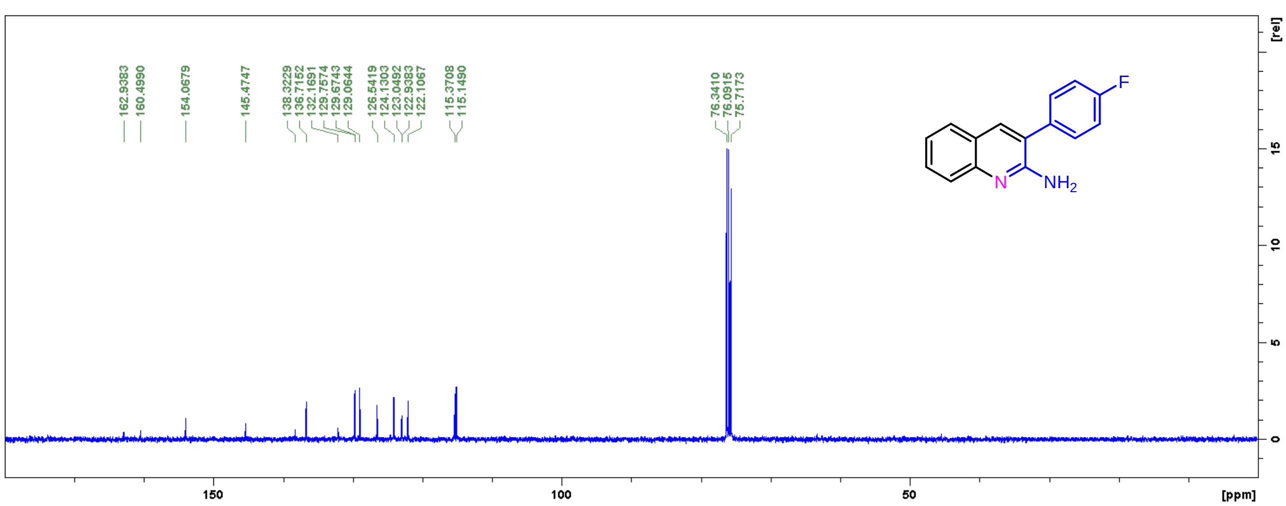
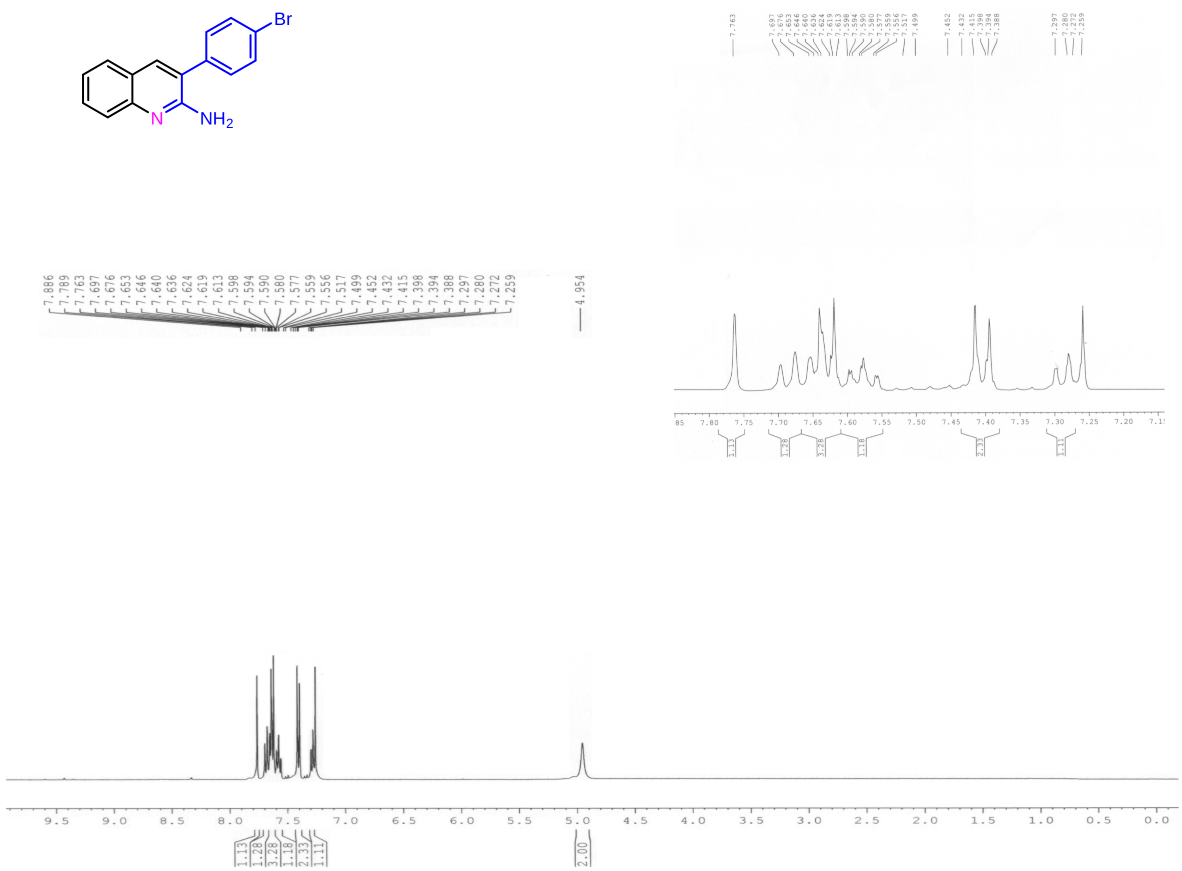


Figure S27. ^{1}H and ^{13}C NMR spectra of compound **9ad** in $CDCl_3$.



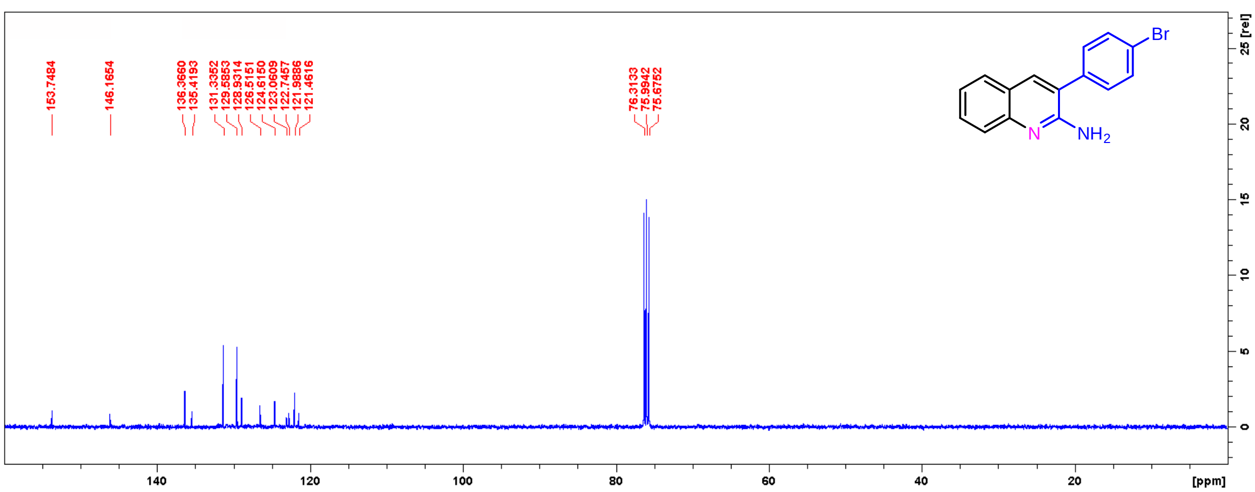
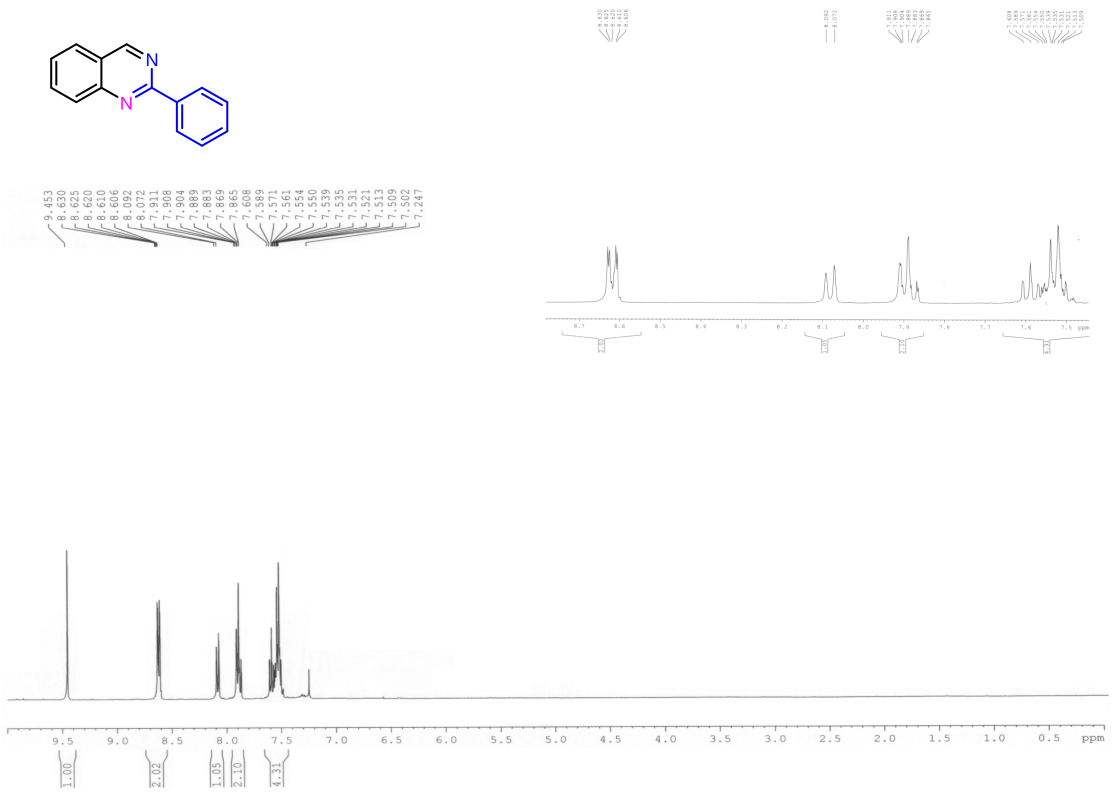


Figure S28. ^{1}H and ^{13}C NMR spectra of compound **9ae** in $CDCl_3$



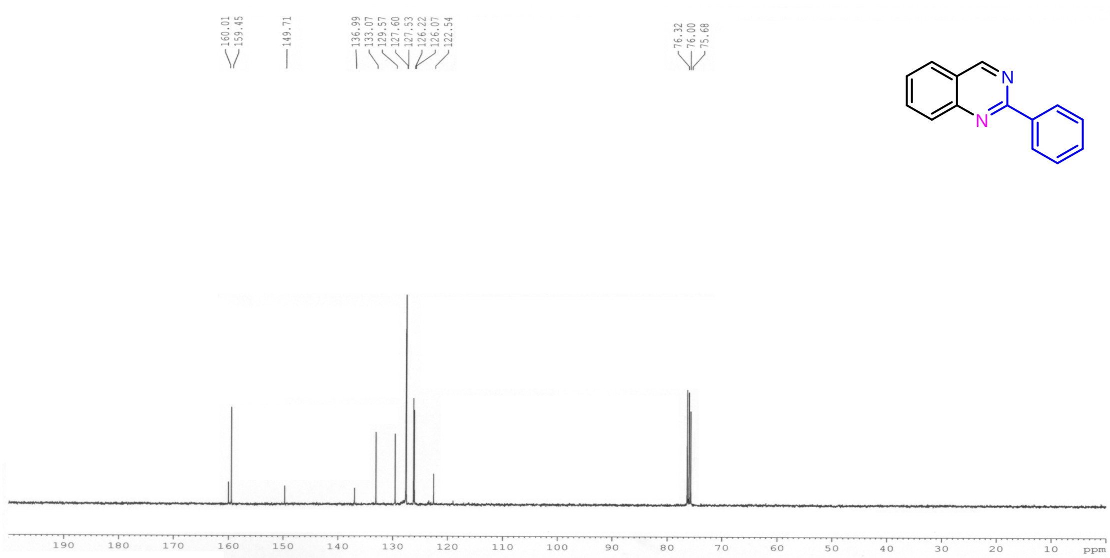


Figure S29. ^{1}H and ^{13}C NMR spectra of compound **10aa** in $CDCl_3$.

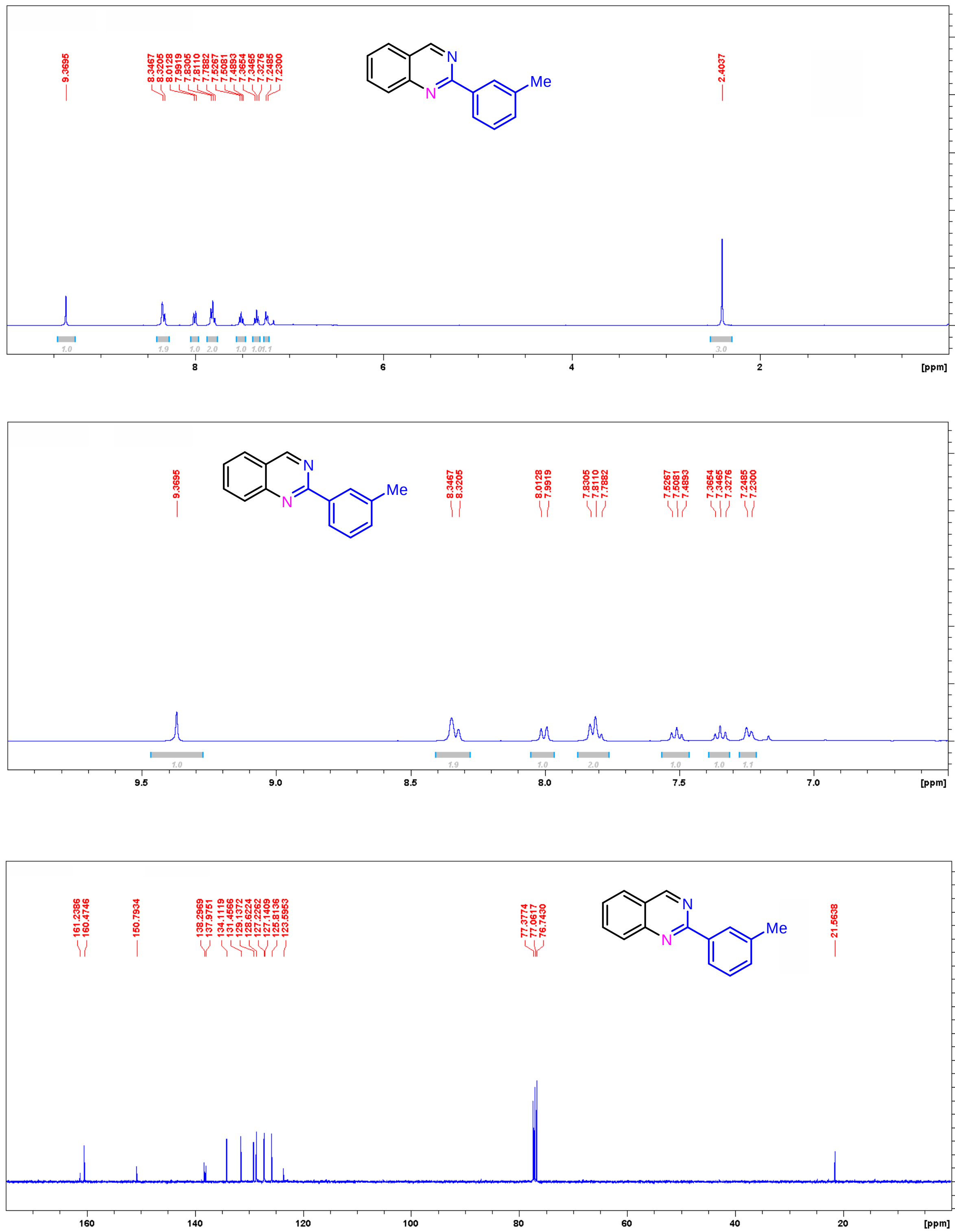
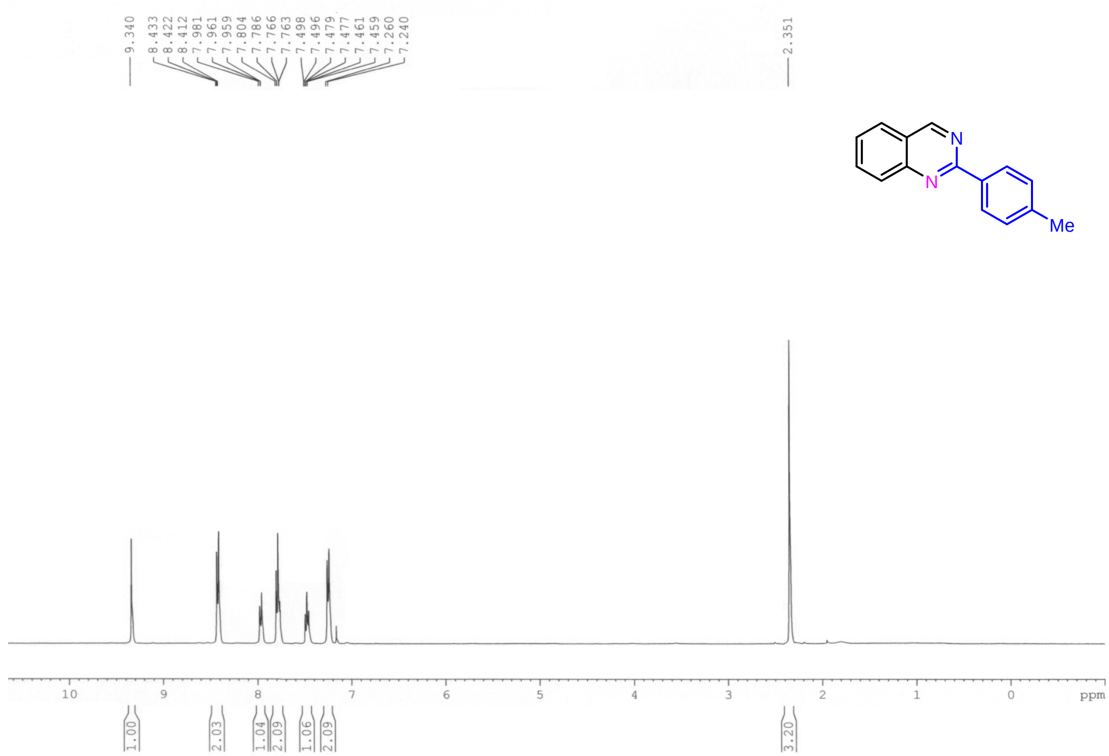


Figure S30. ^{1}H and ^{13}C NMR spectra of compound **10ab** in $CDCl_3$.



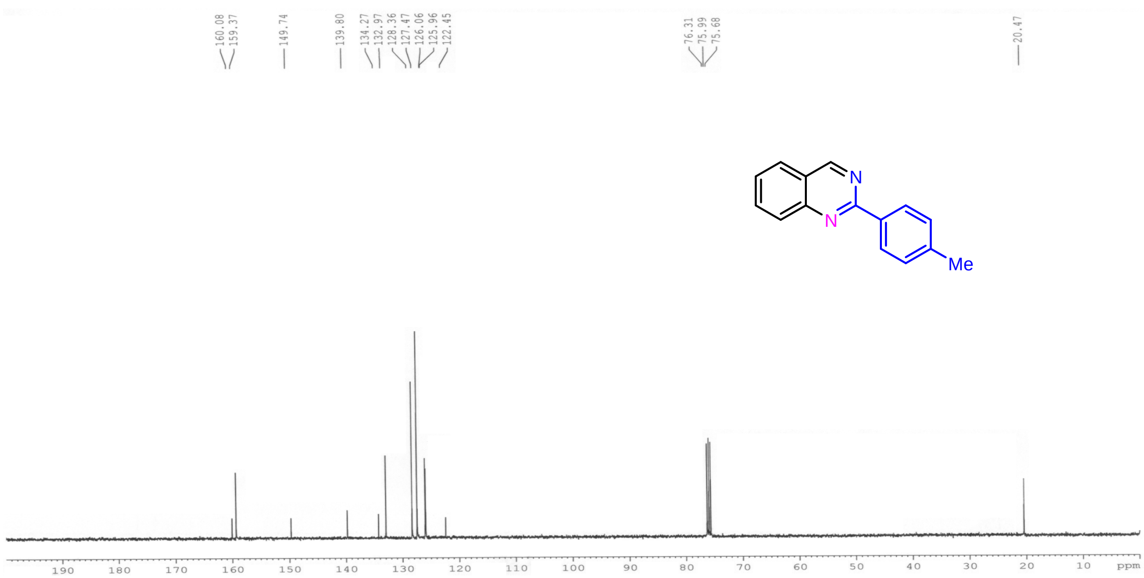
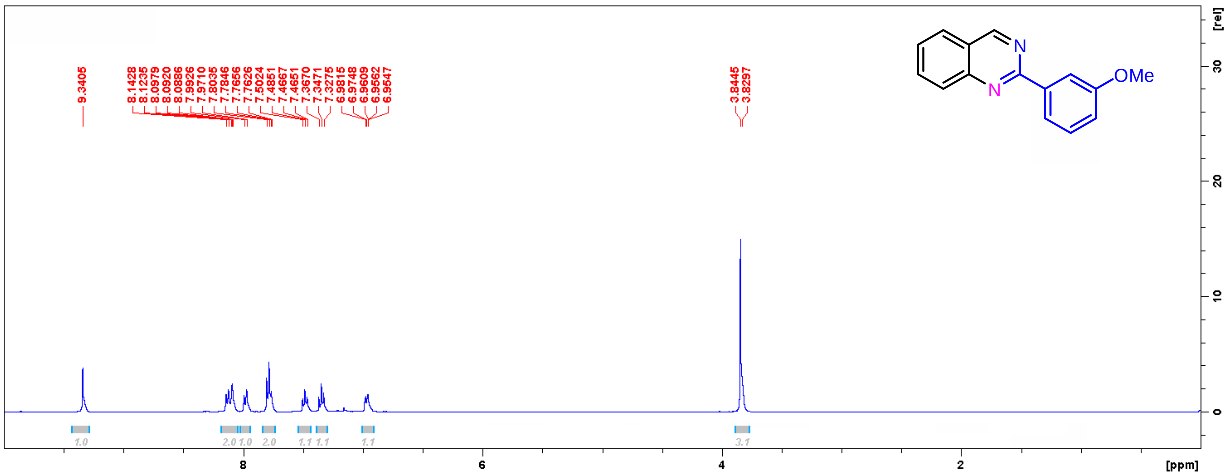
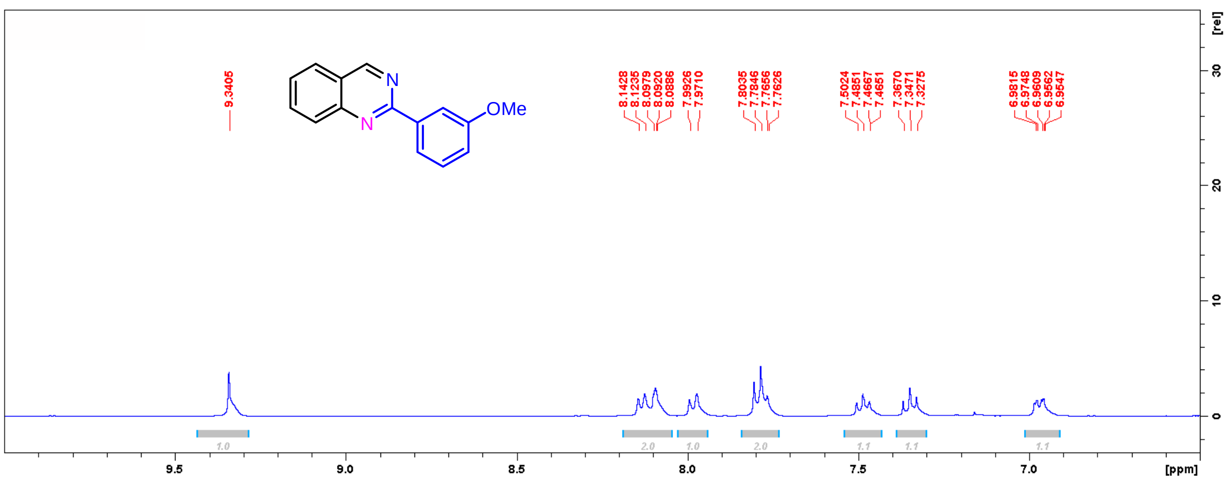


Figure S31. ^{1}H and ^{13}C NMR spectra of compound **10ac** in $CDCl_3$.





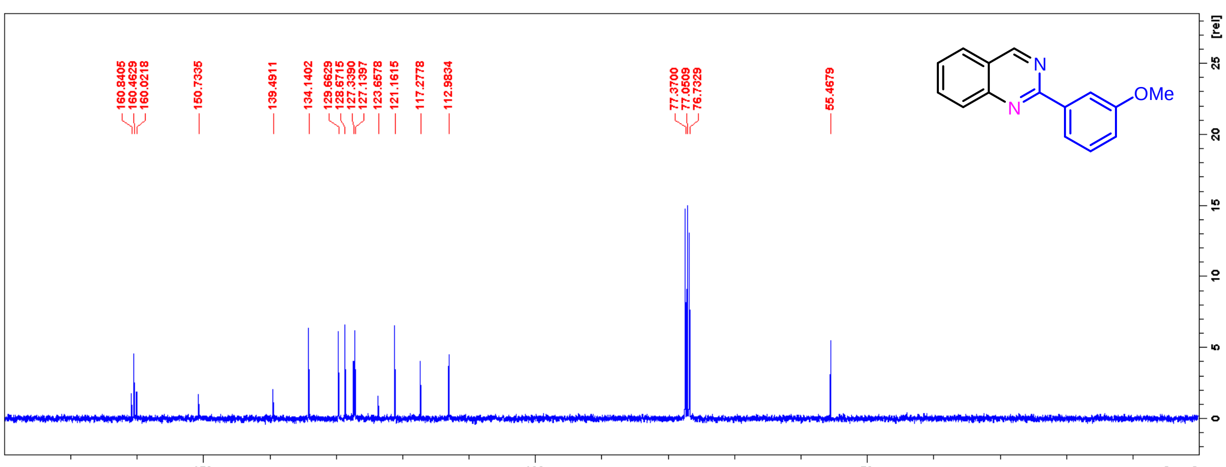
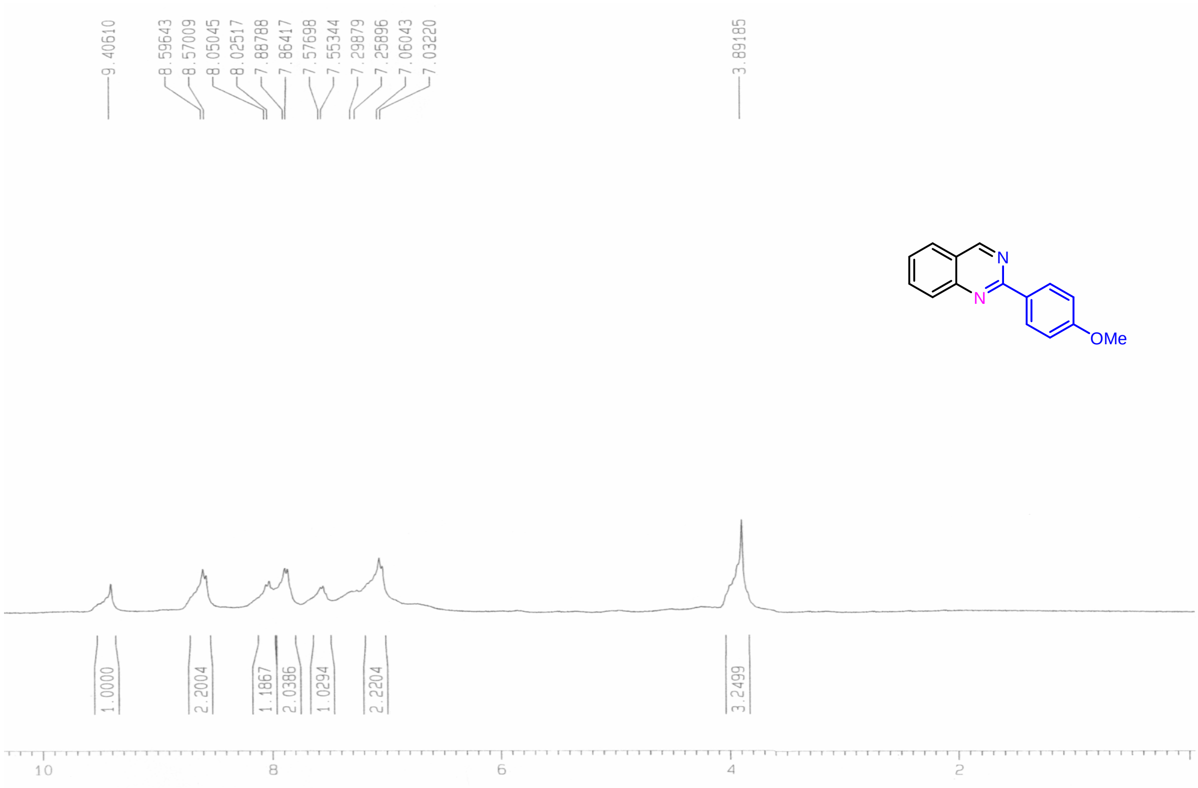


Figure S32. ^{1}H and ^{13}C NMR spectra of compound **10ad** in $CDCl_3$.



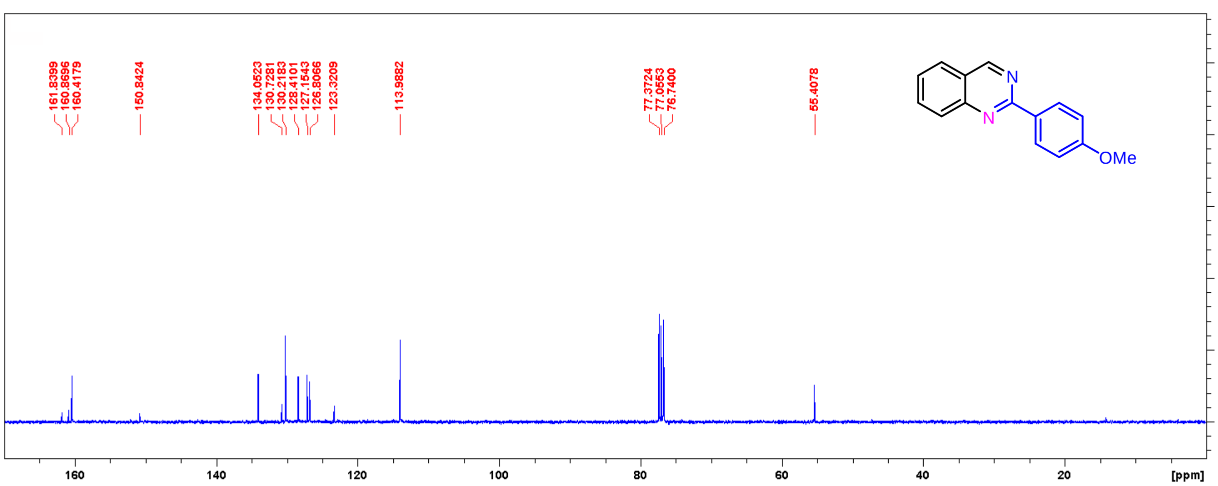
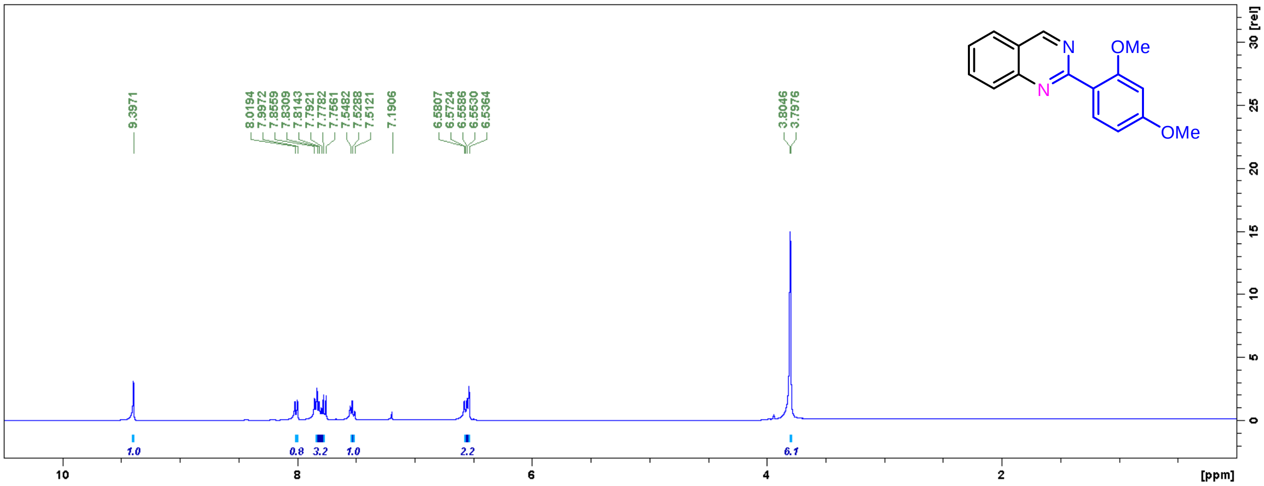
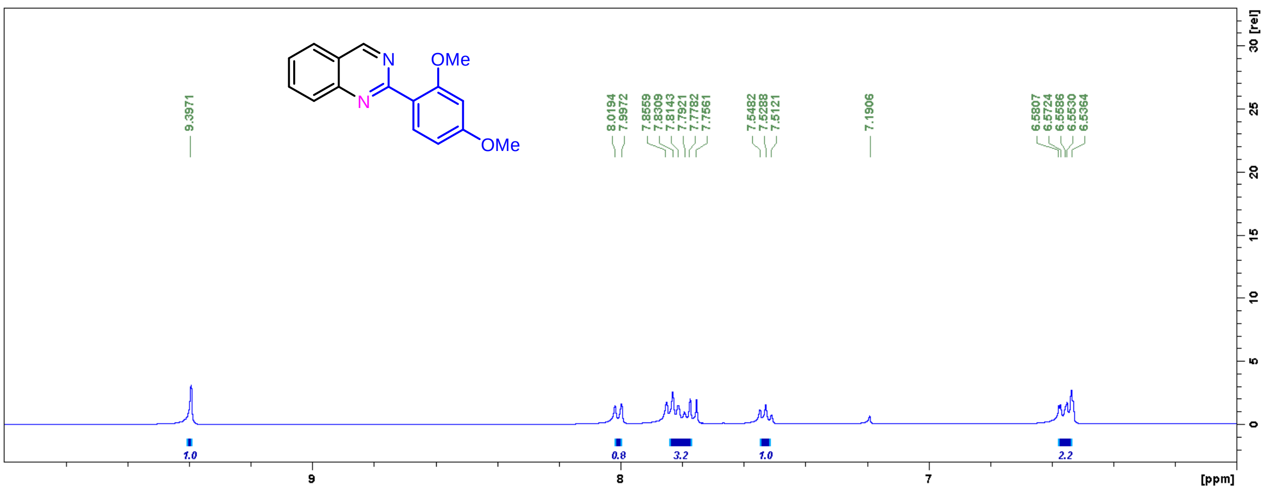


Figure S33. ^{1}H and ^{13}C NMR spectra of compound **10ae** in $CDCl_3$.





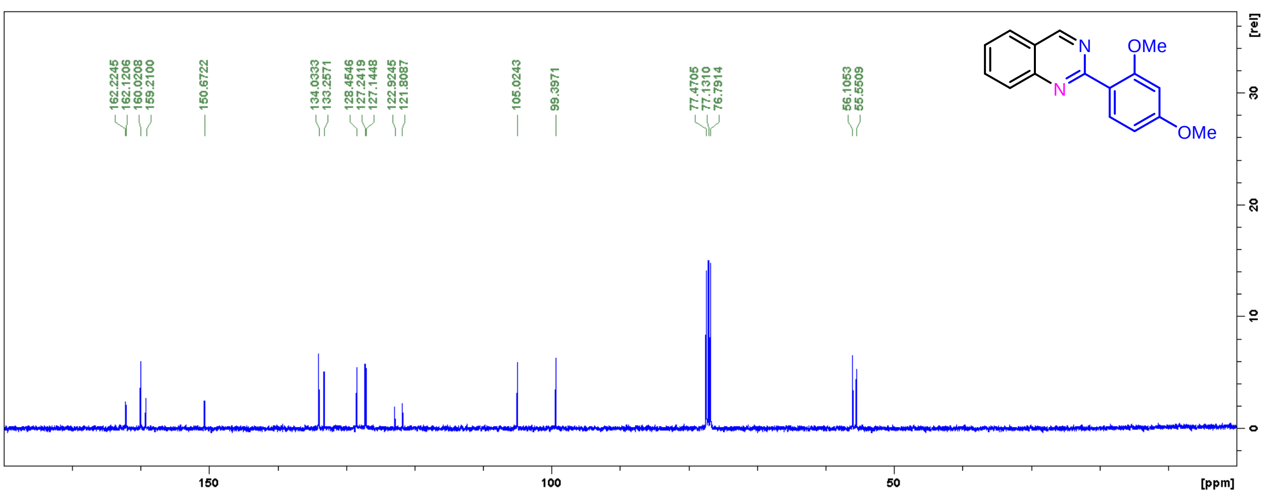
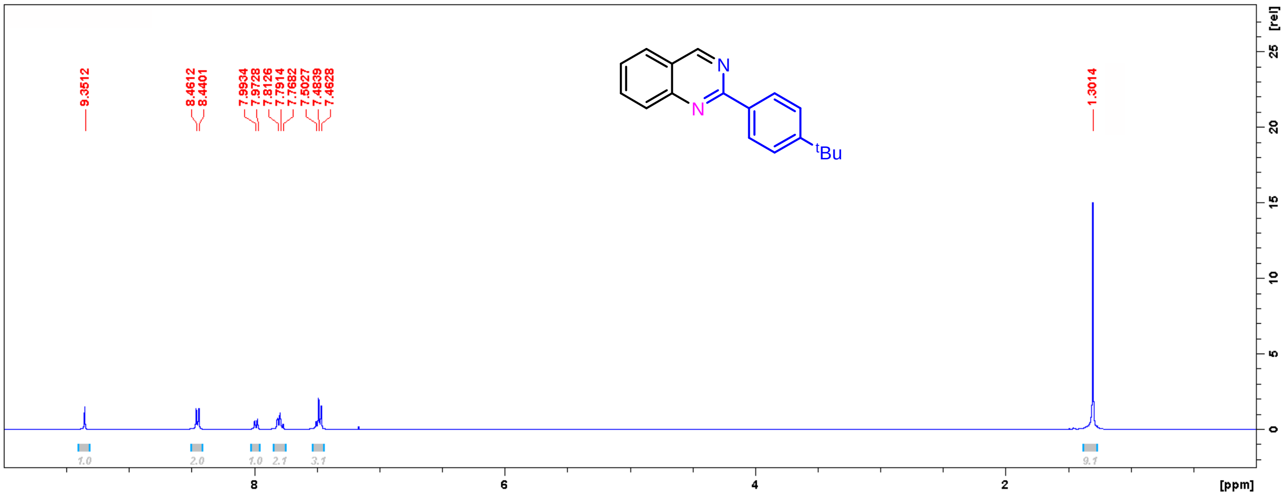


Figure S34. ^{1}H and ^{13}C NMR spectra of compound **10af** in $CDCl_3$.



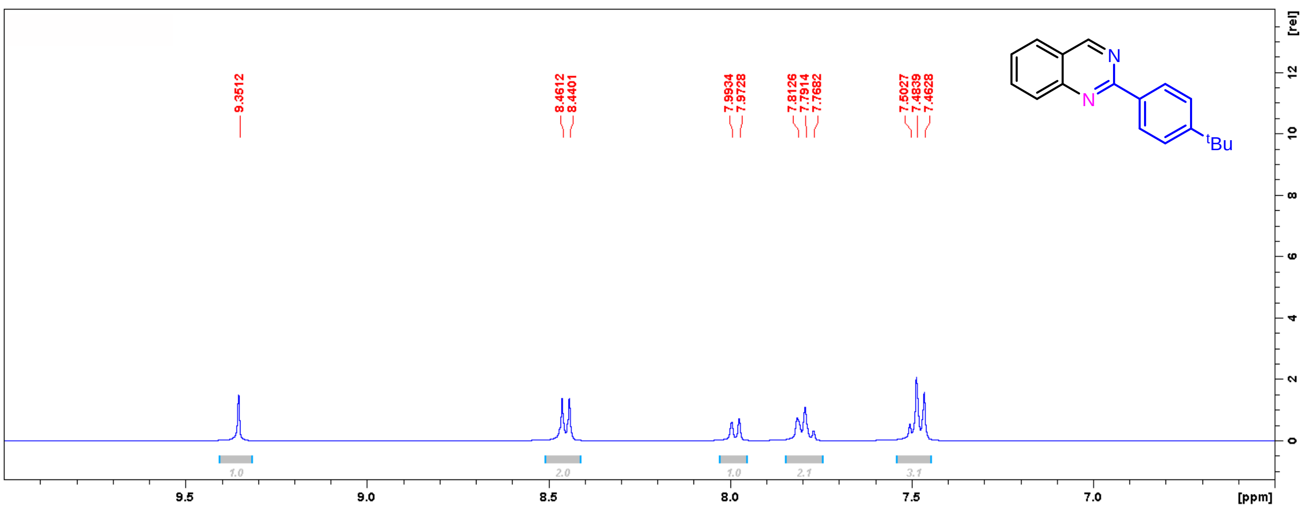
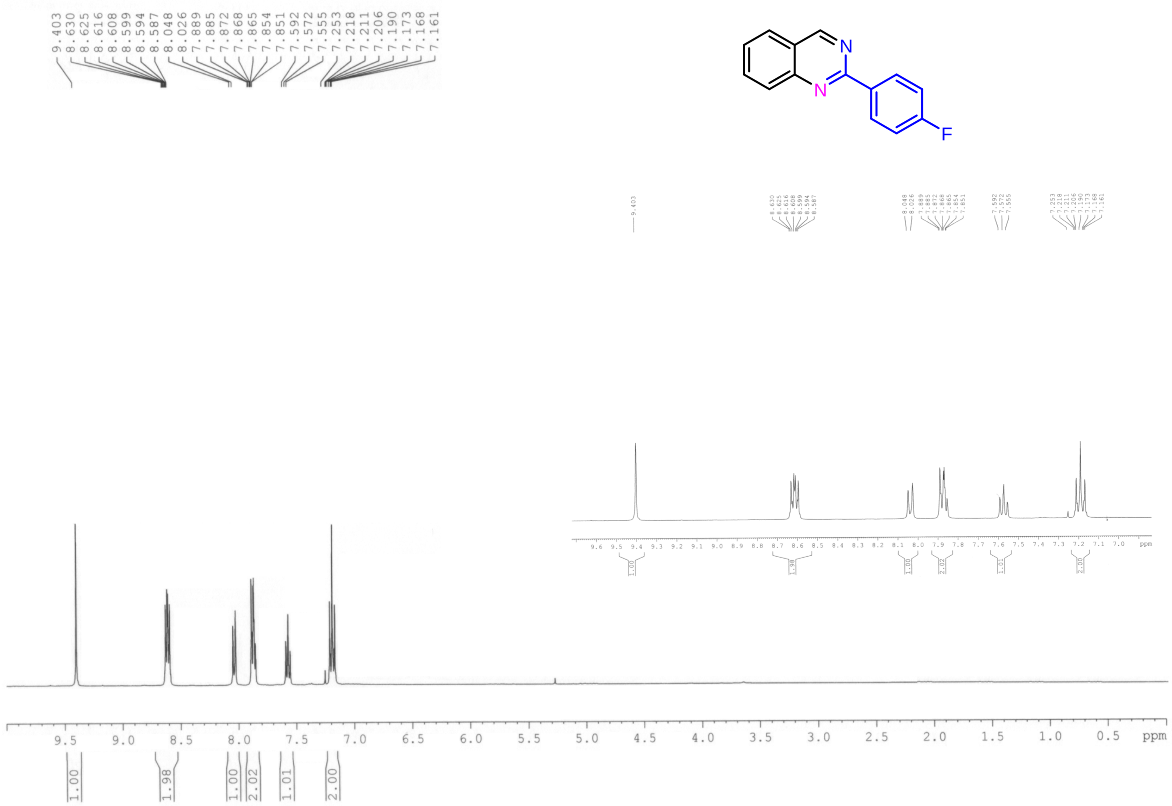


Figure S35. ^{1}H NMR spectrum of compound **10ag** in $CDCl_3$.



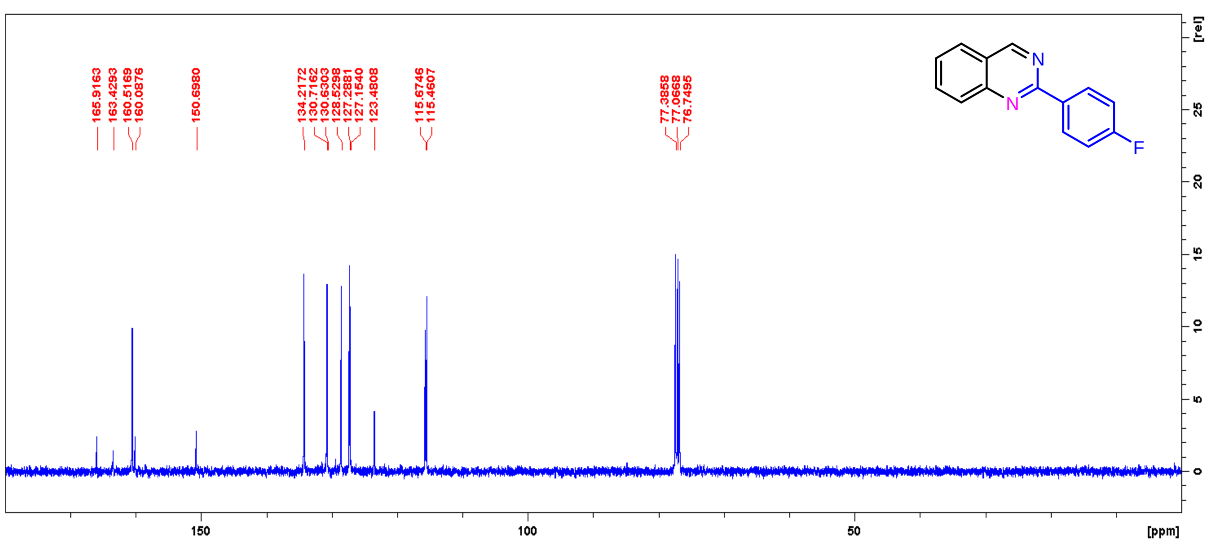


Figure S36. ^{1}H and ^{13}C NMR spectra of compound **10ah** in $CDCl_3$.

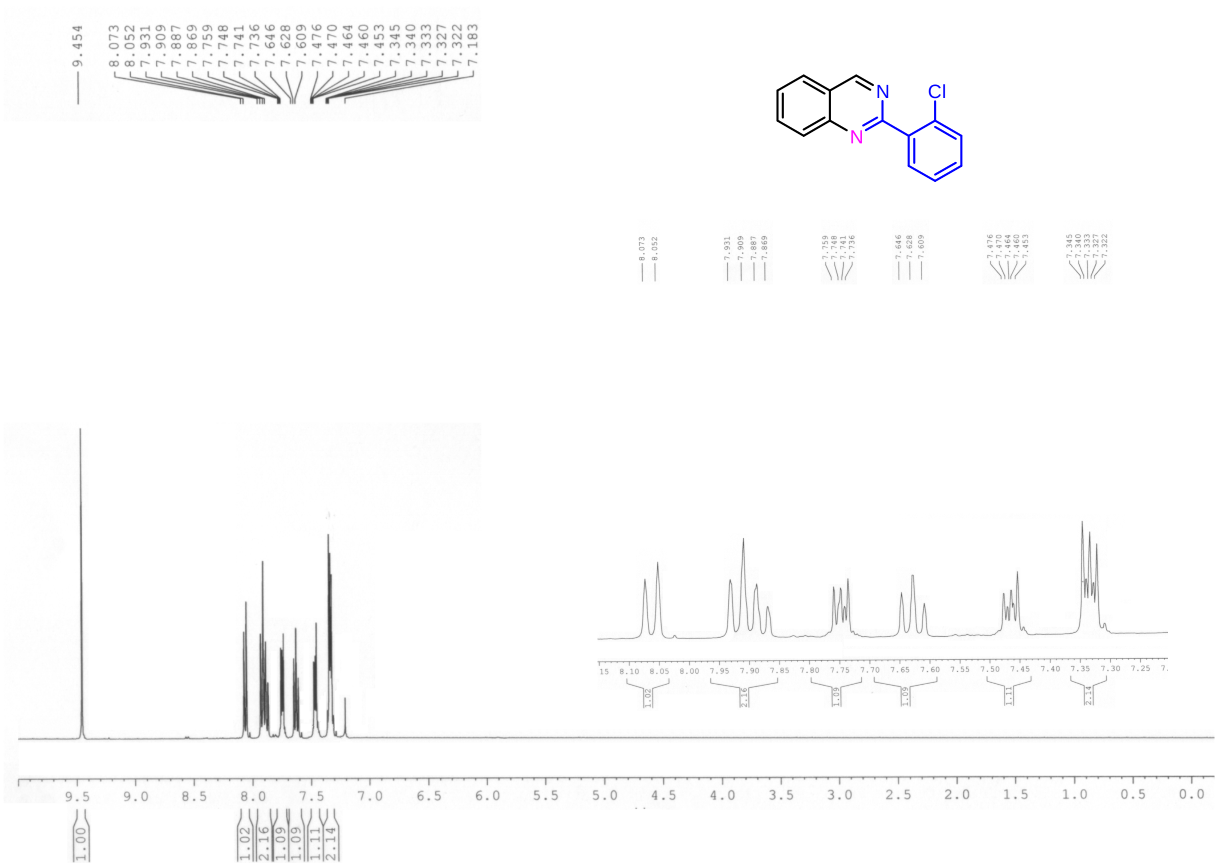
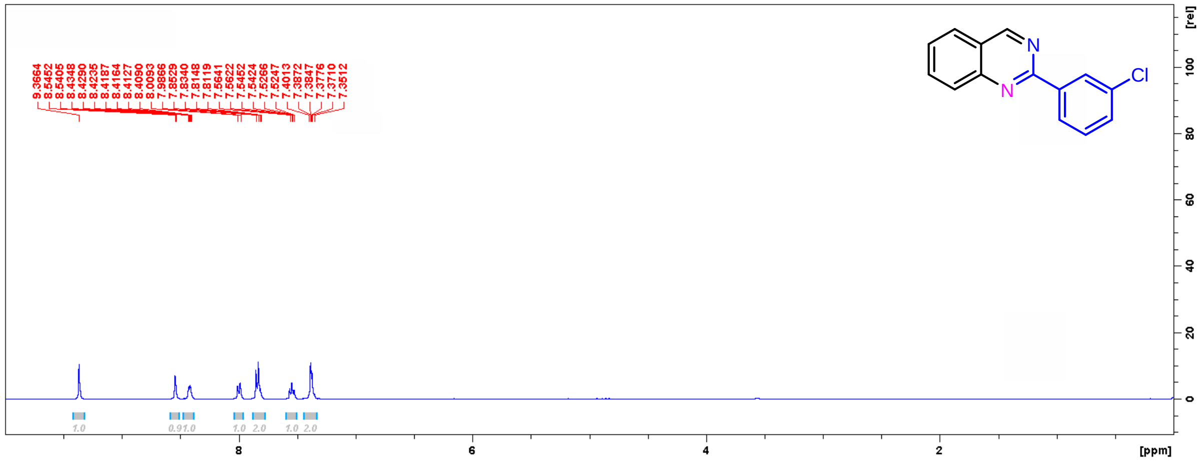
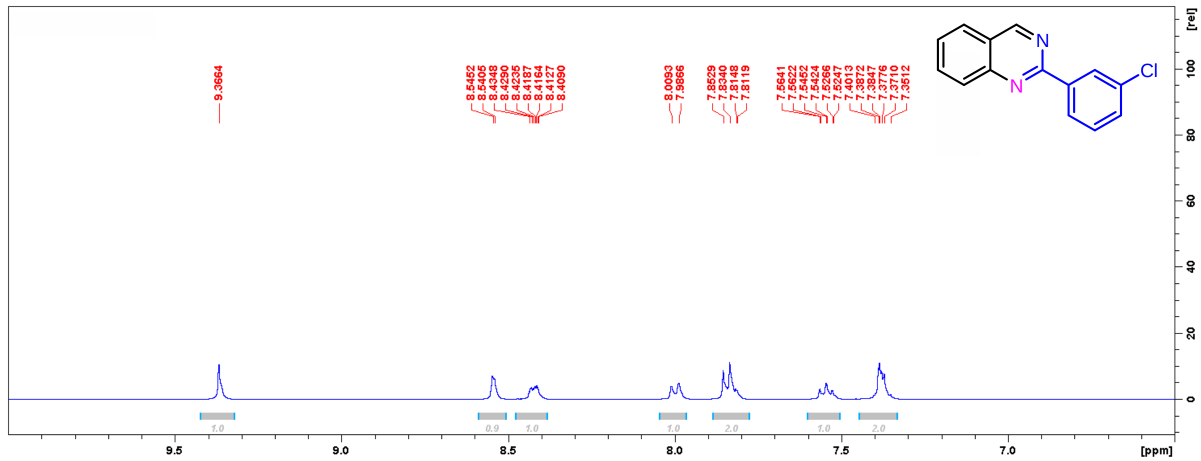


Figure S37. ^{1}H NMR spectrum of compound **10ai** in $CDCl_3$.





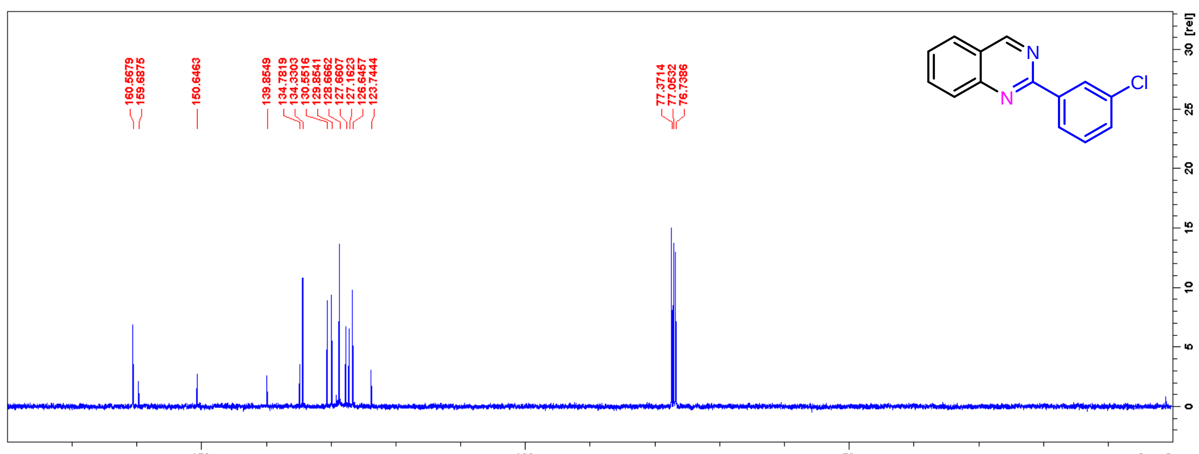
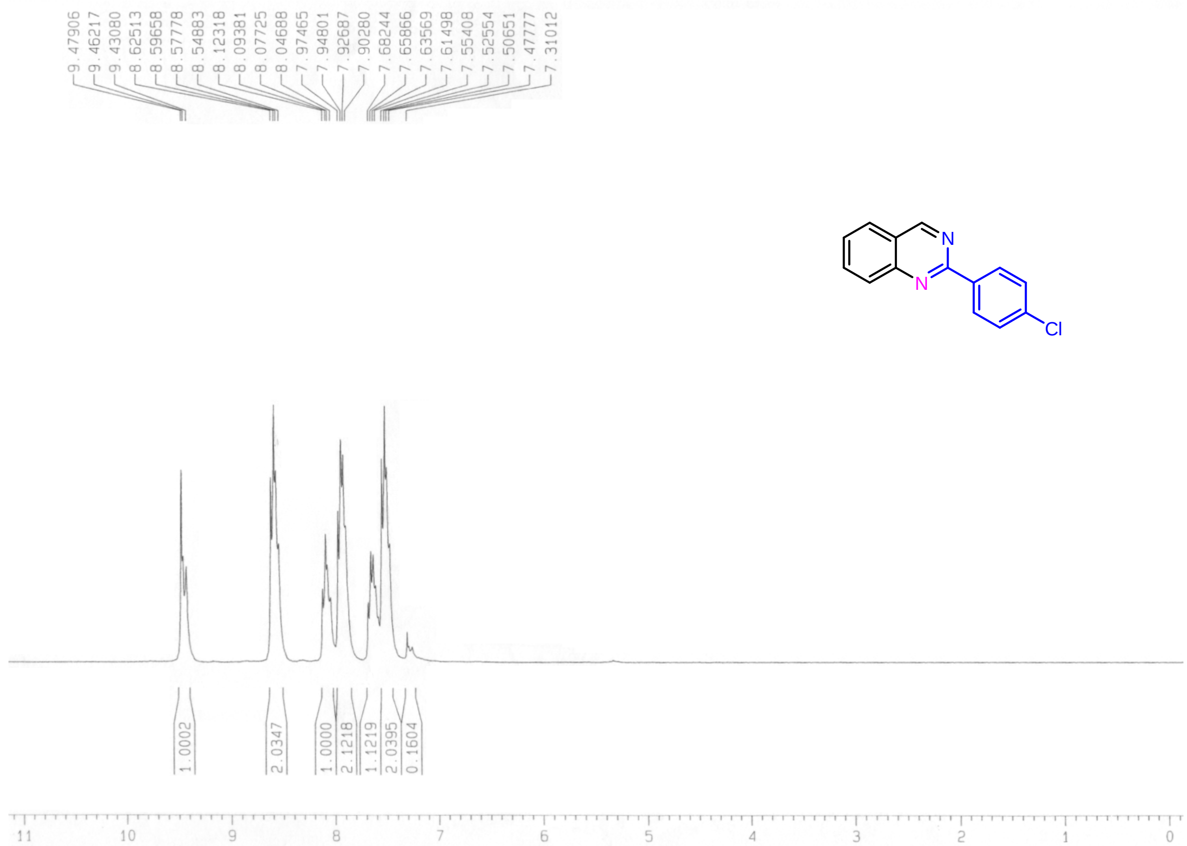


Figure S38. ^{1}H and ^{13}C NMR spectra of compound **10aj** in $CDCl_3$.



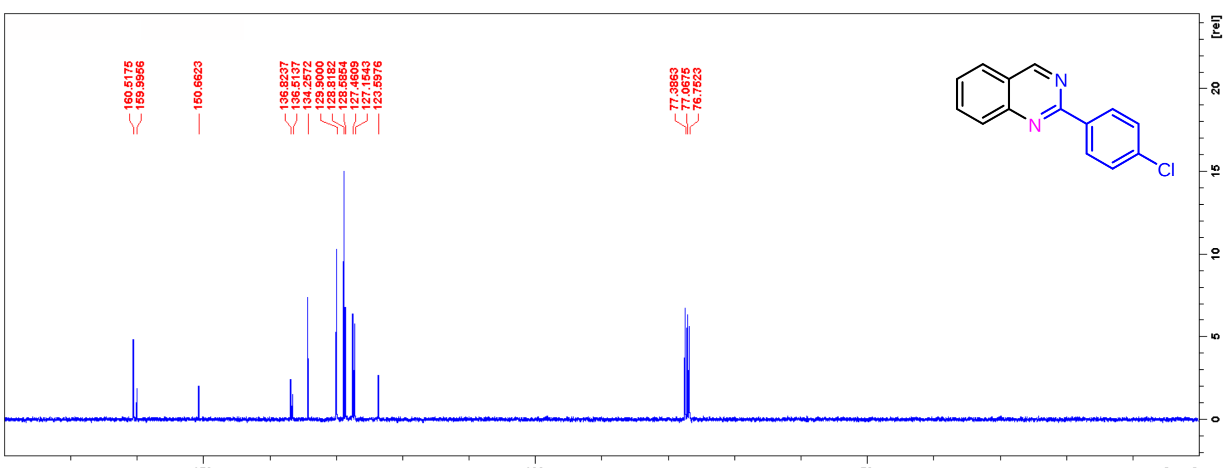


Figure S39. ^{1}H and ^{13}C NMR spectra of compound **10ak** in $CDCl_3$.

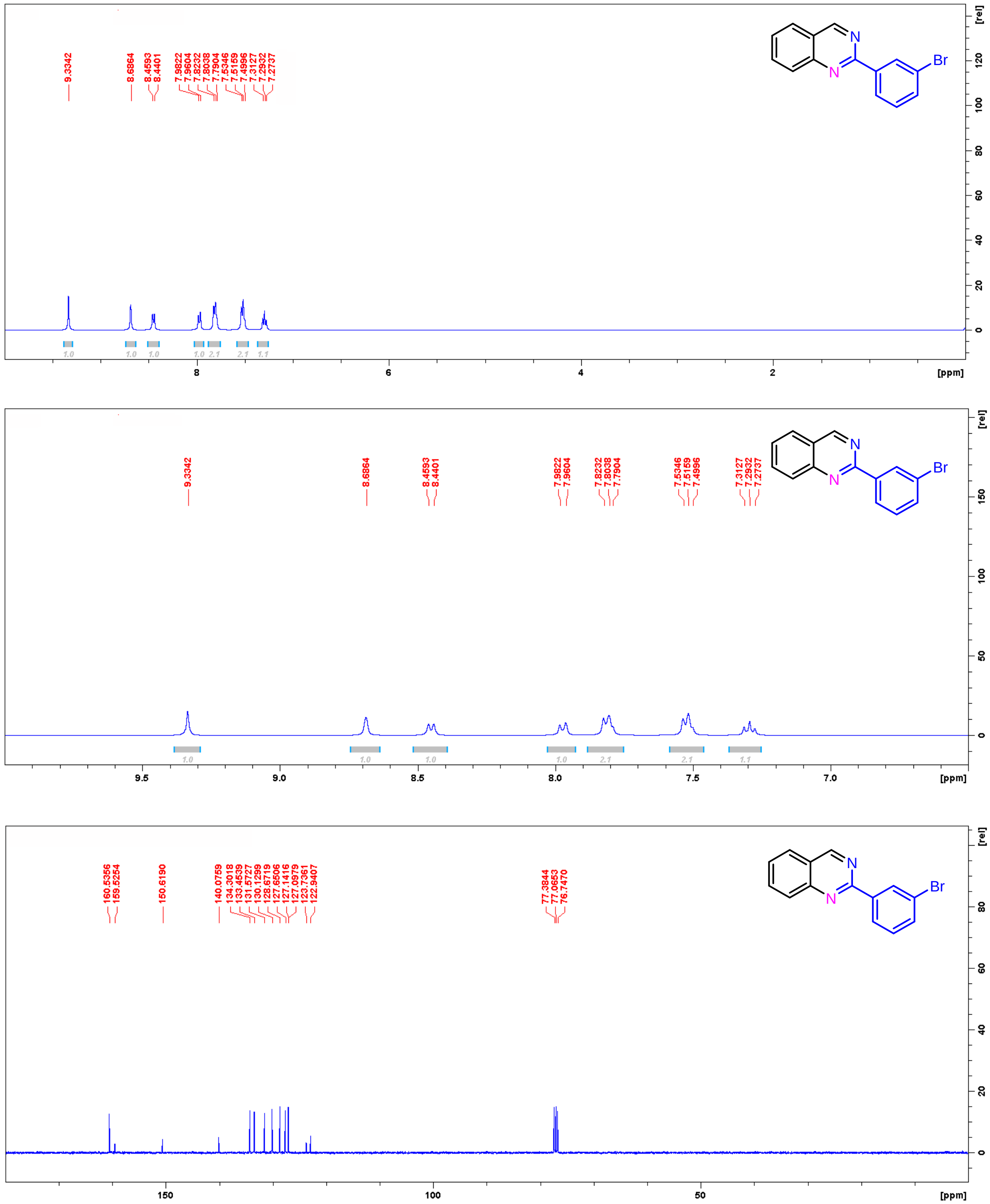


Figure S40. ^{1}H and ^{13}C NMR spectra of compound **10al** in $CDCl_3$.

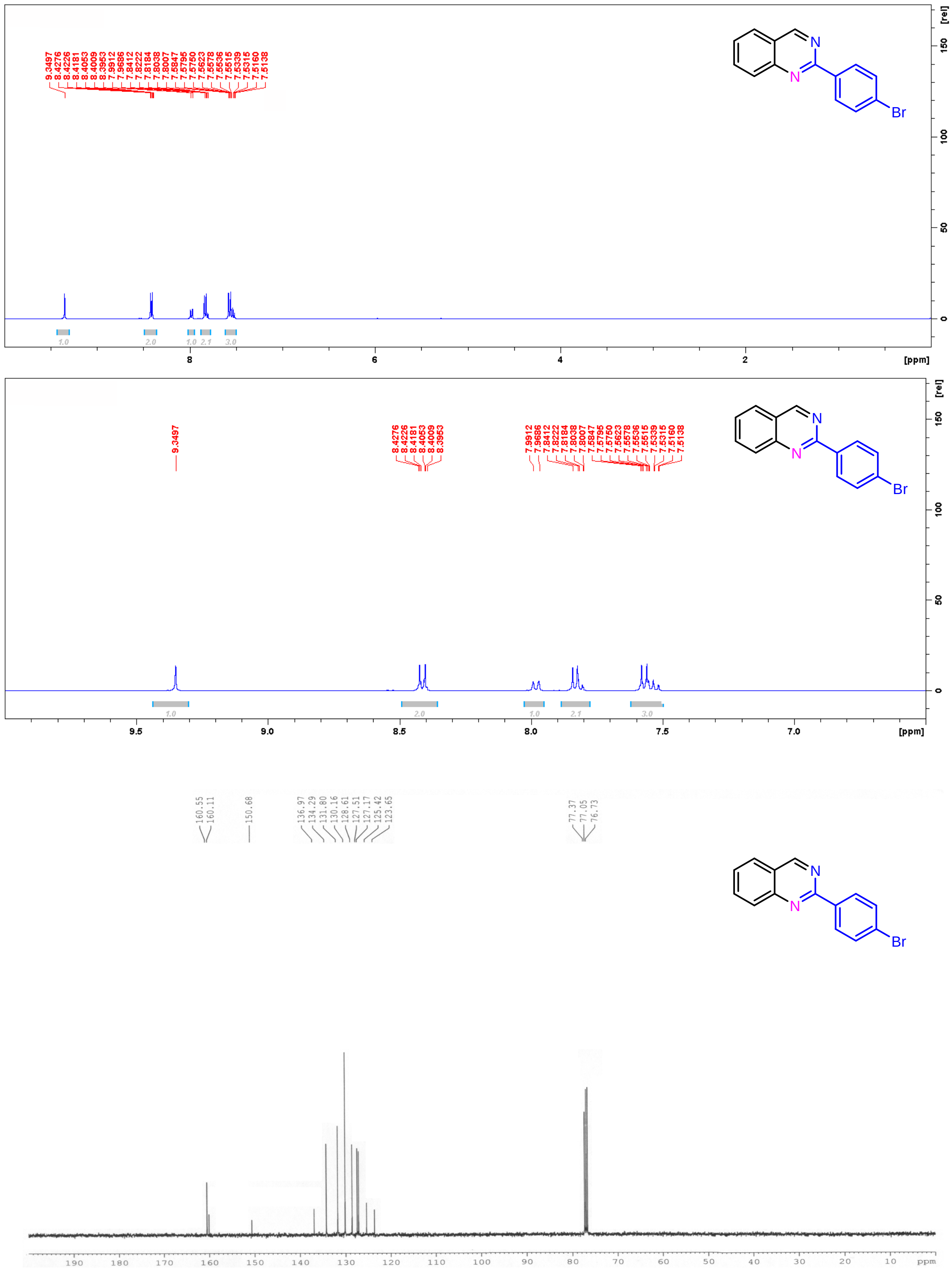
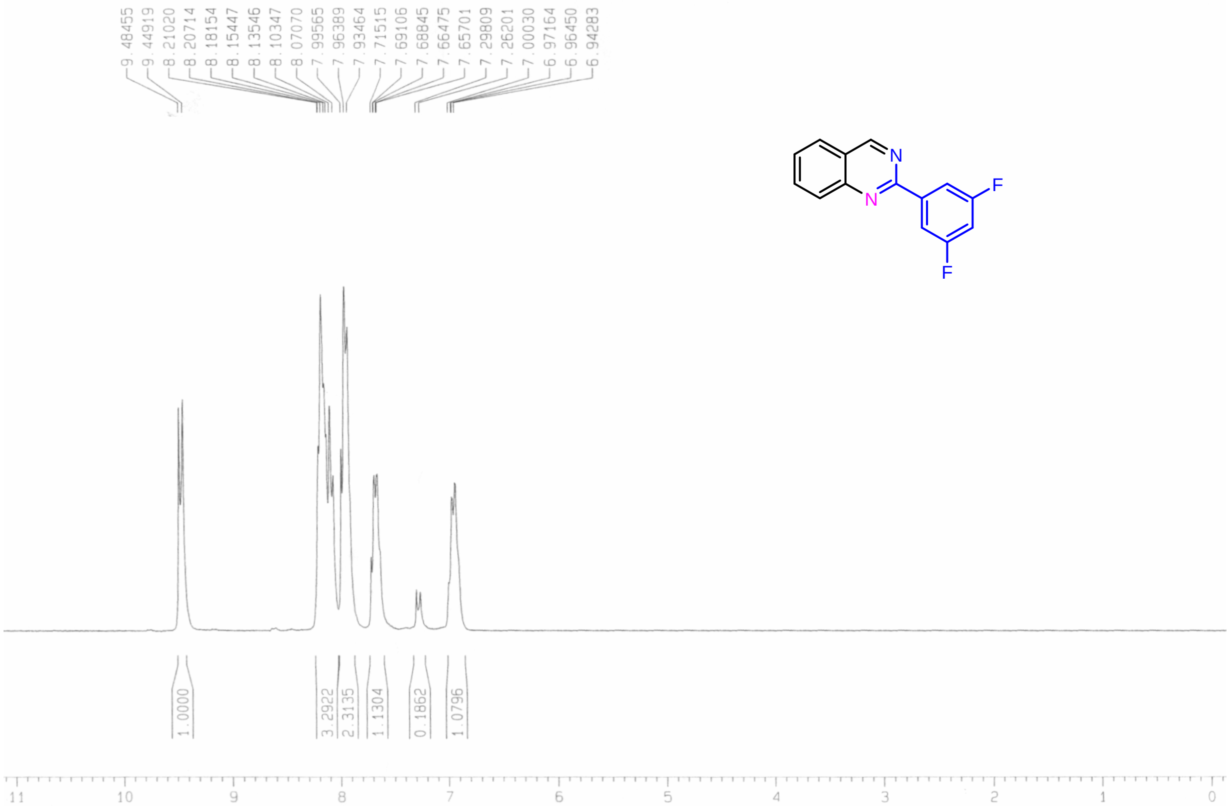


Figure S41. ^{1}H and ^{13}C NMR spectra of compound **10am** in $CDCl_3$.



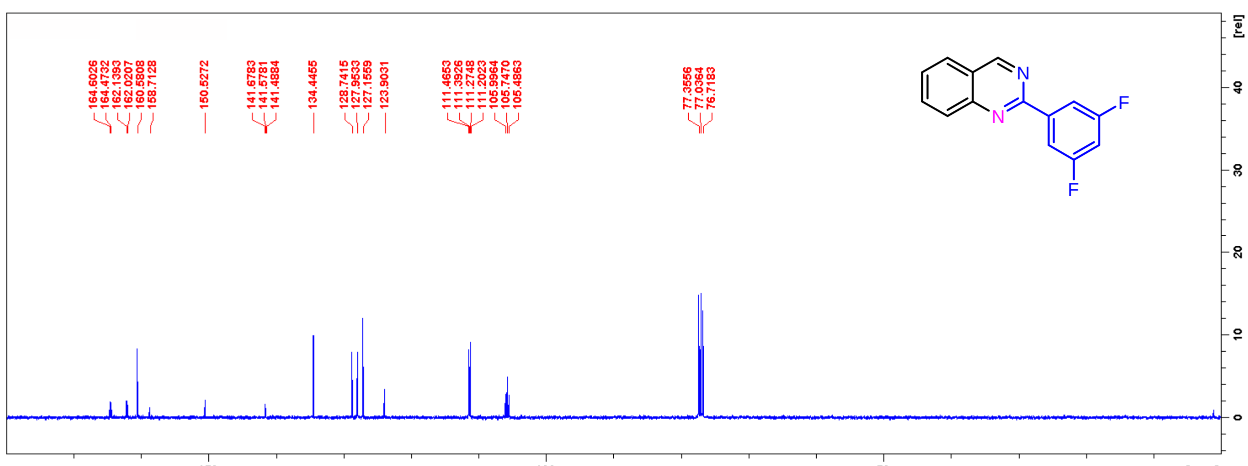
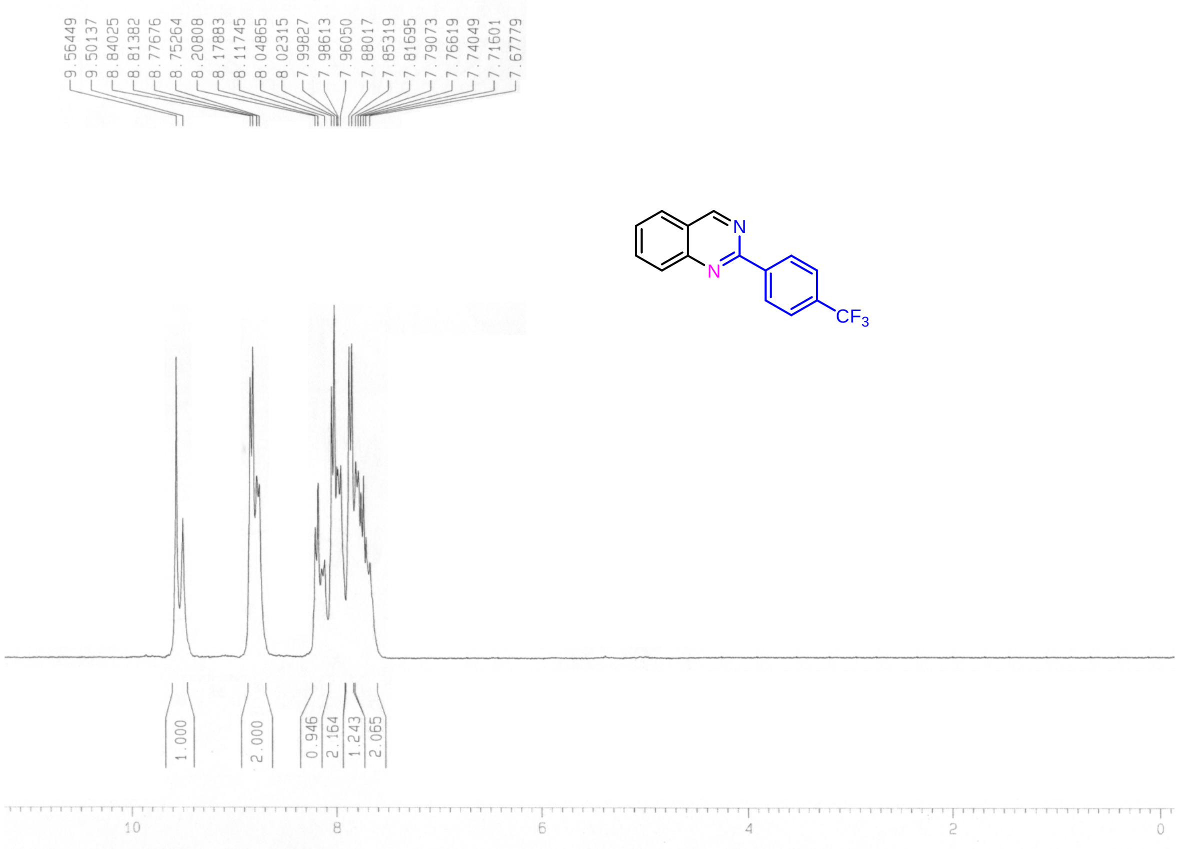


Figure S42. ^{1}H and ^{13}C NMR spectra of compound **10an** in $CDCl_3$.



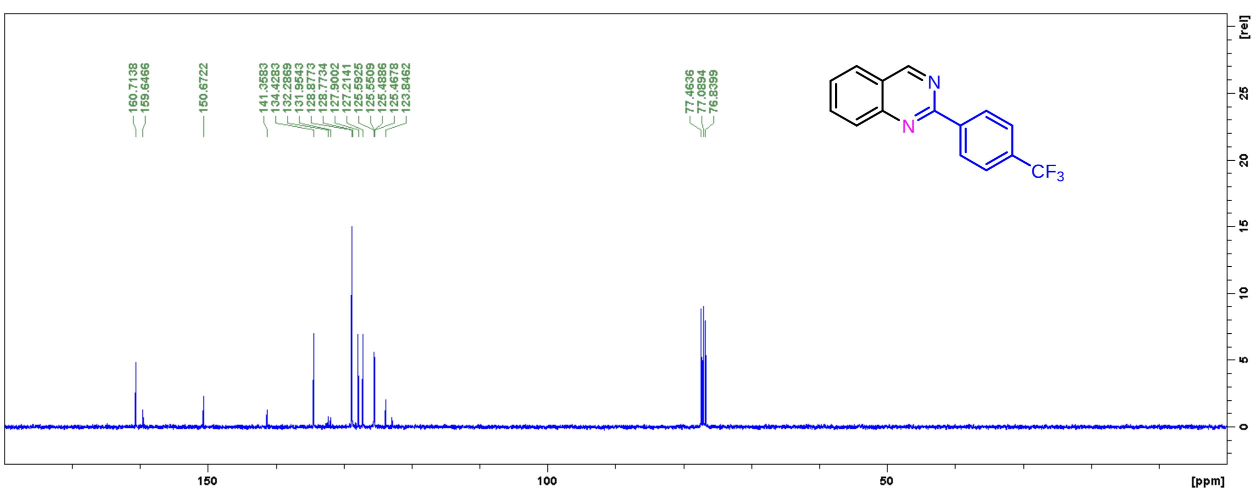
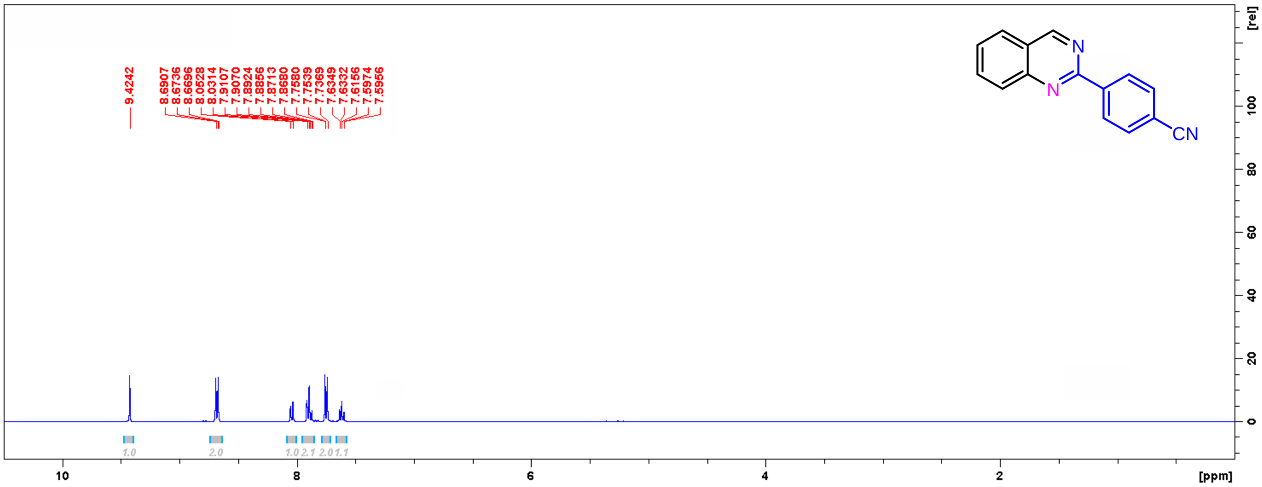
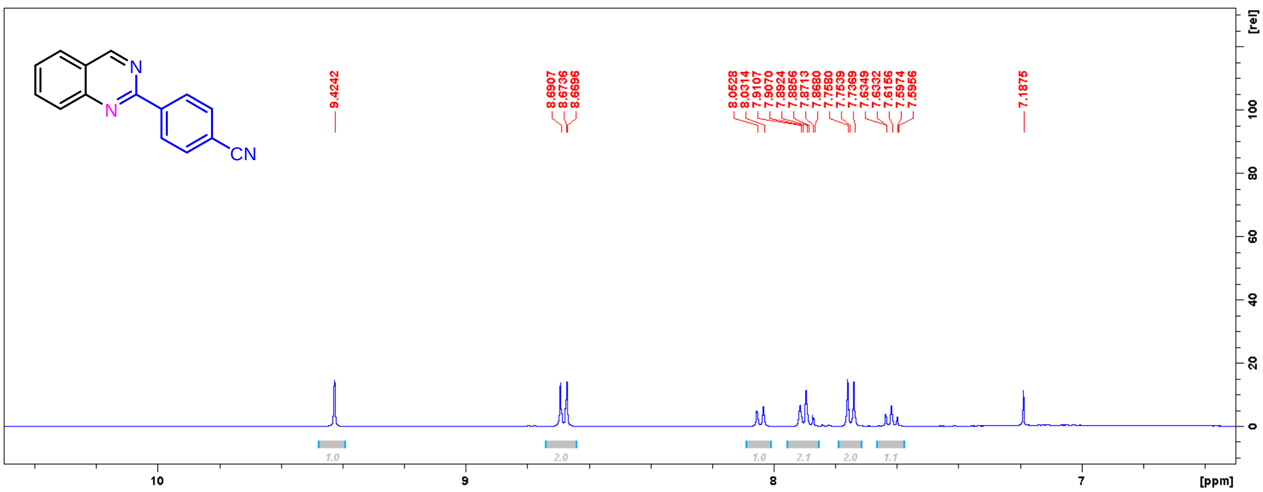


Figure S43. ^{1}H and ^{13}C NMR spectra of compound **10ao** in $CDCl_3$.





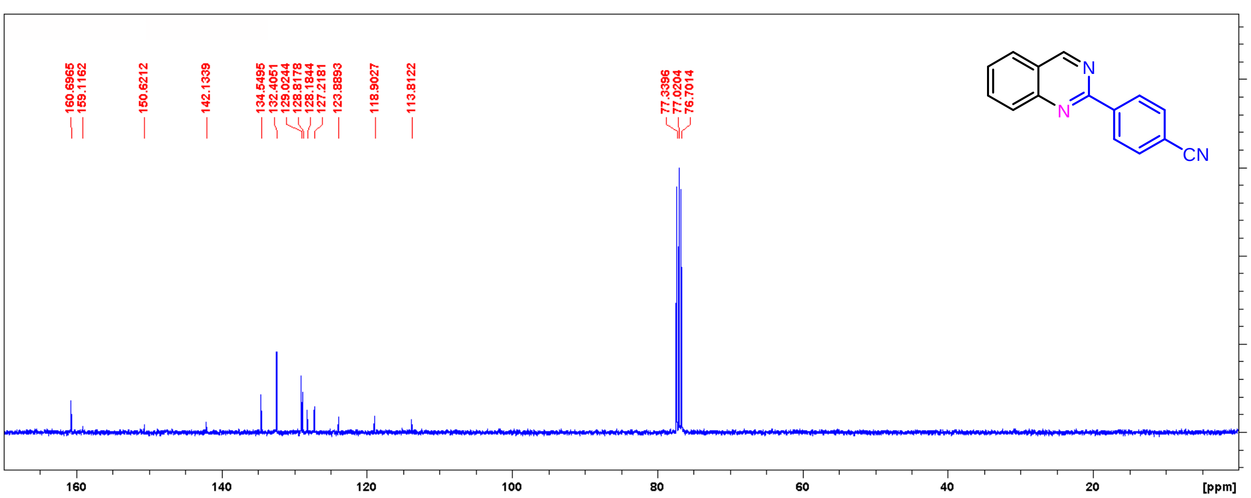
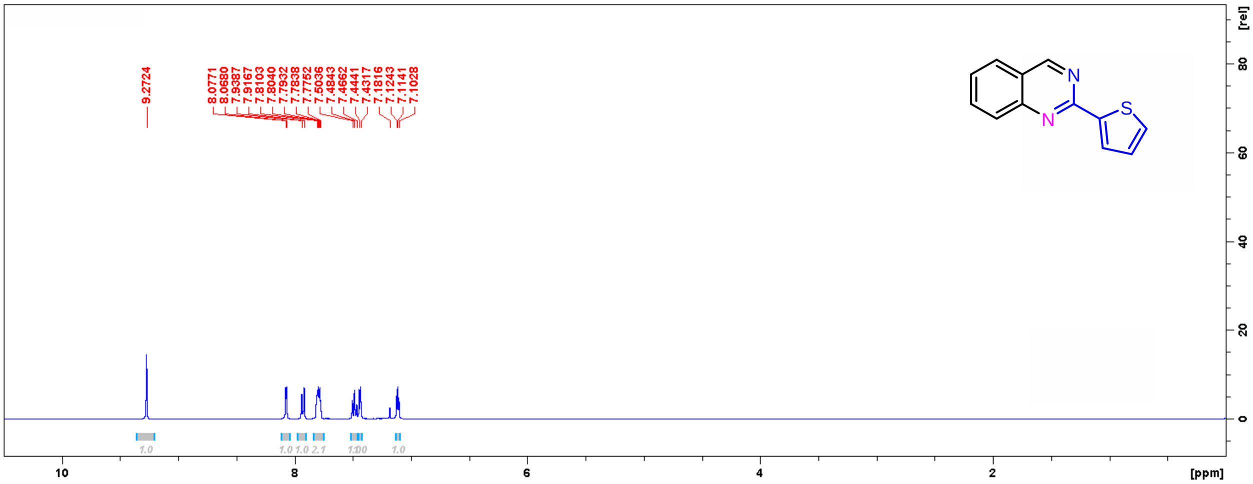
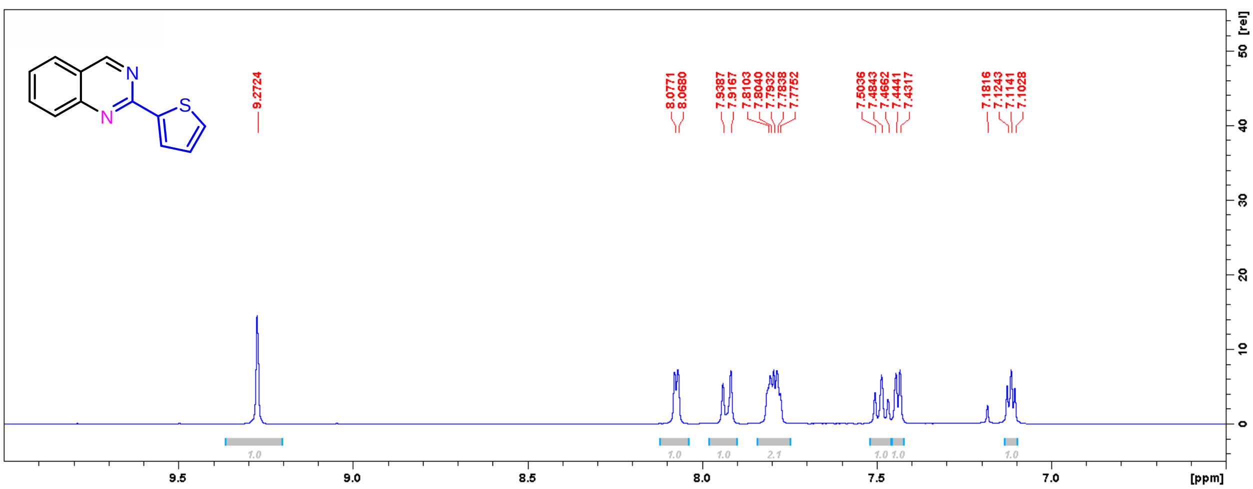


Figure S44. ^{1}H and ^{13}C NMR spectra of compound **10ap** in $CDCl_3$.





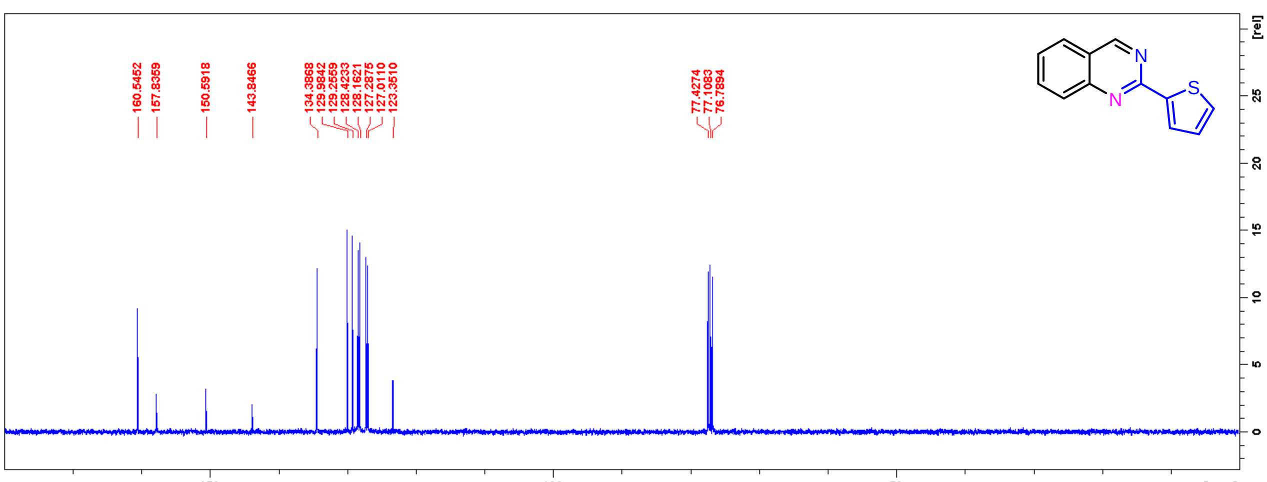


Figure S45. ${}^{1}H$ and ${}^{13}C$ NMR spectra of compound **10aq** in $CDCl_3$.

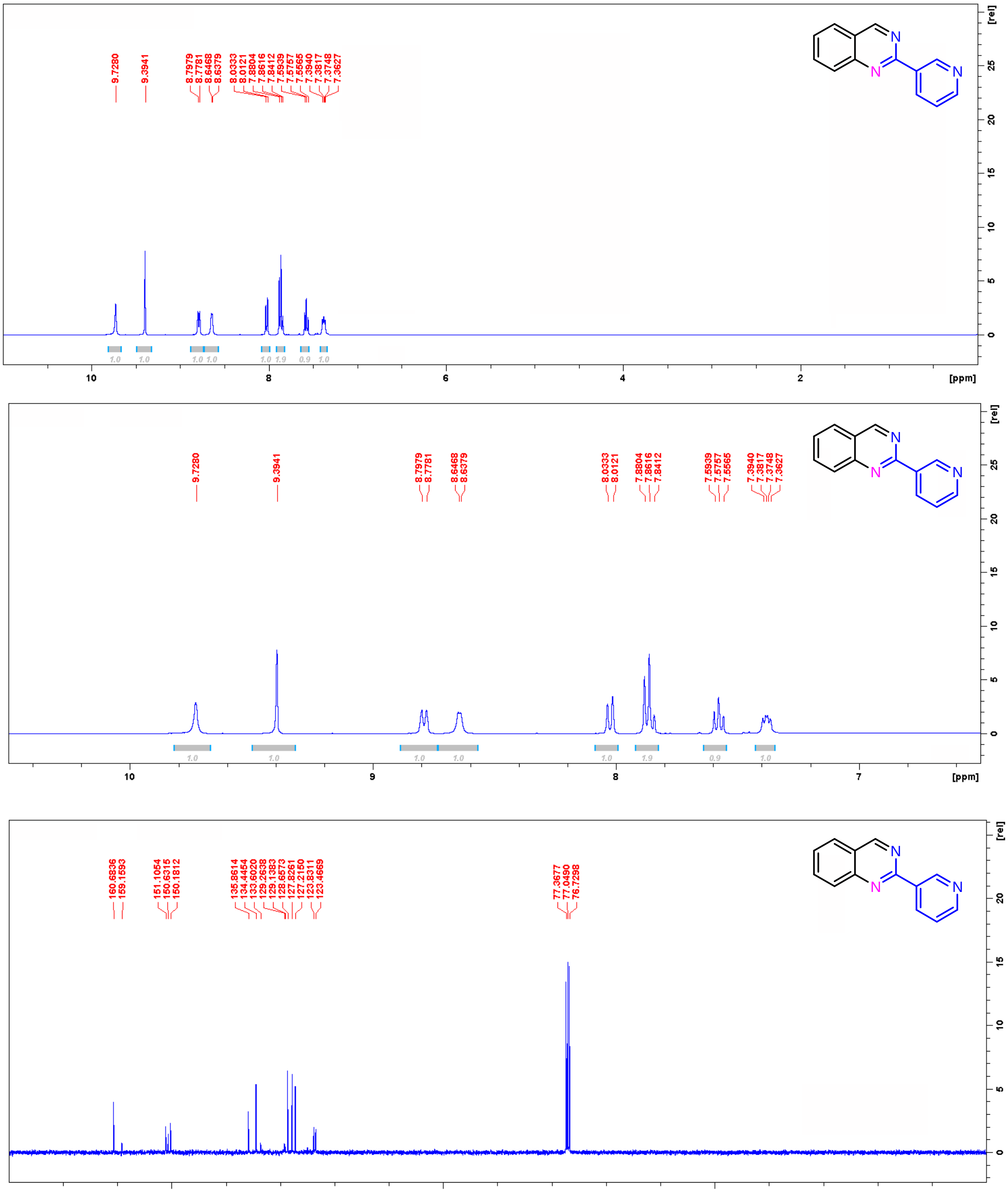
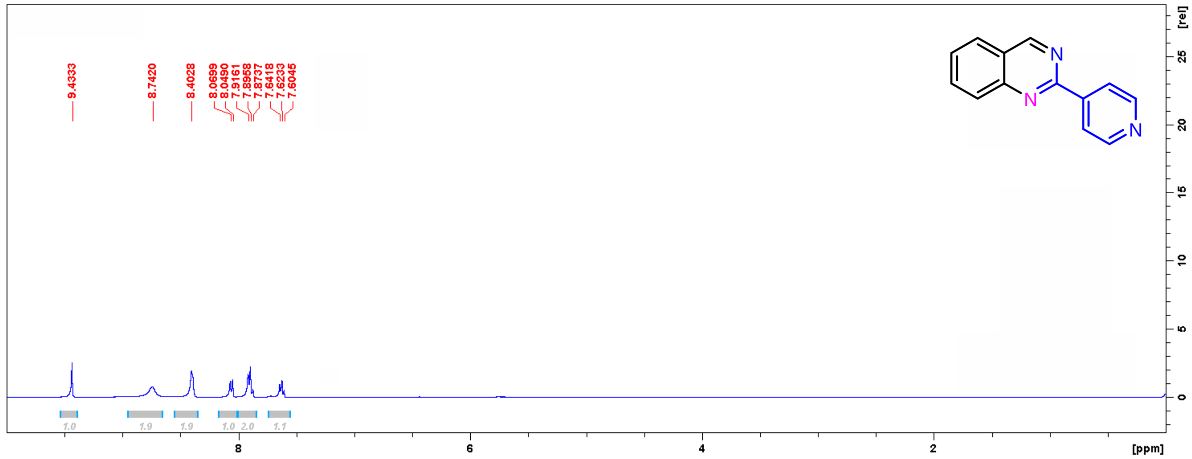


Figure S46. ^{1}H and ^{13}C NMR spectra of compound **10ar** in $CDCl_3$.



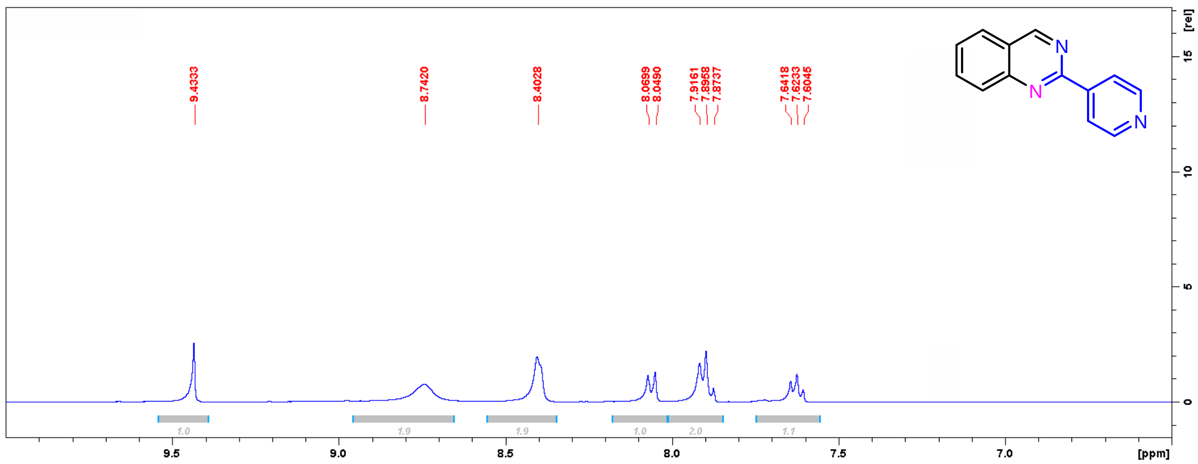


Figure S47. [1]H NMR spectrum of compound **10as** in $CDCl_3$.

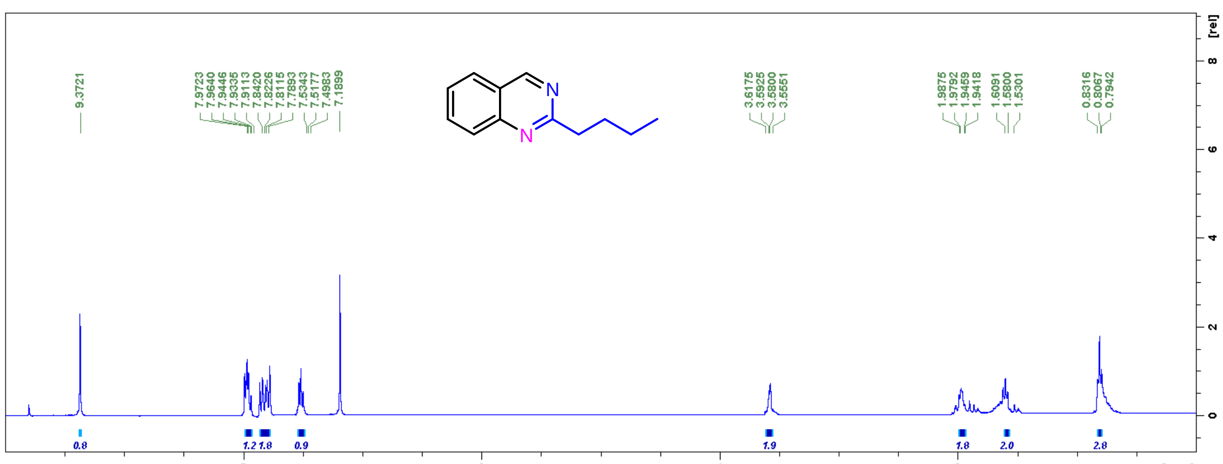
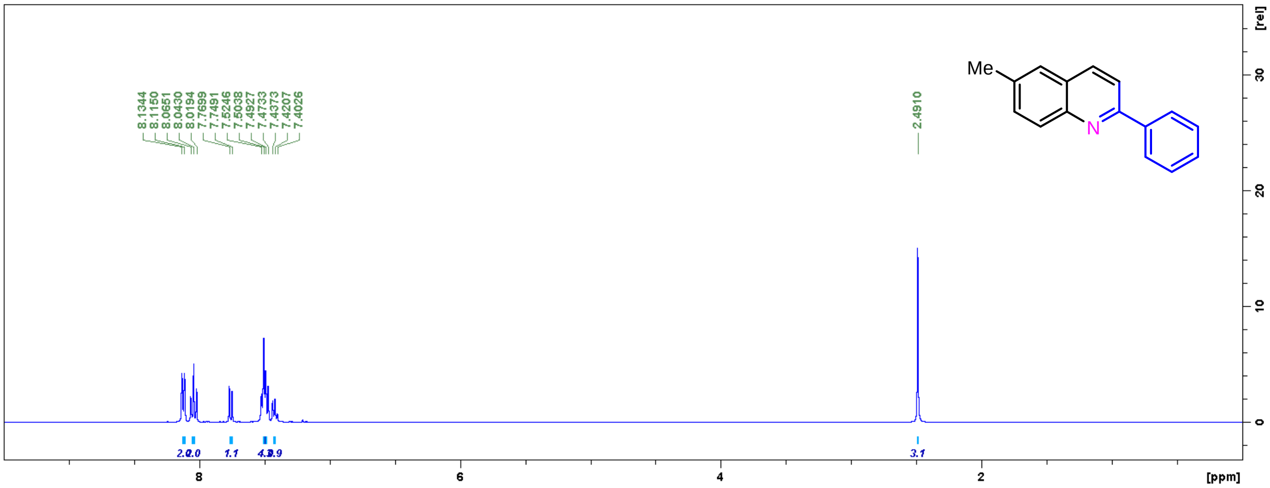


Figure S48. [1]H NMR spectrum of compound **10at** in $CDCl_3$.



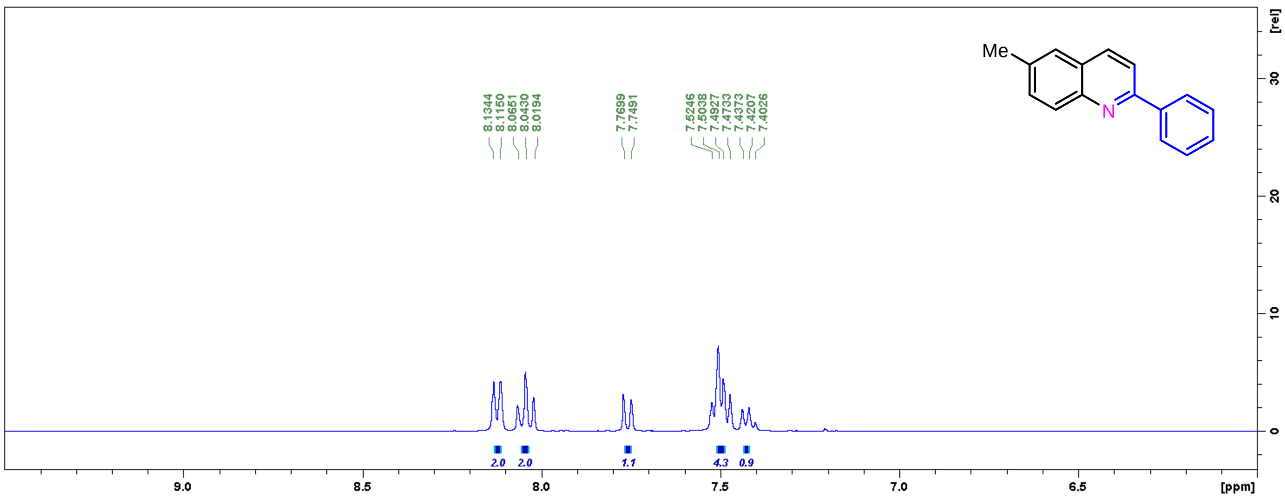
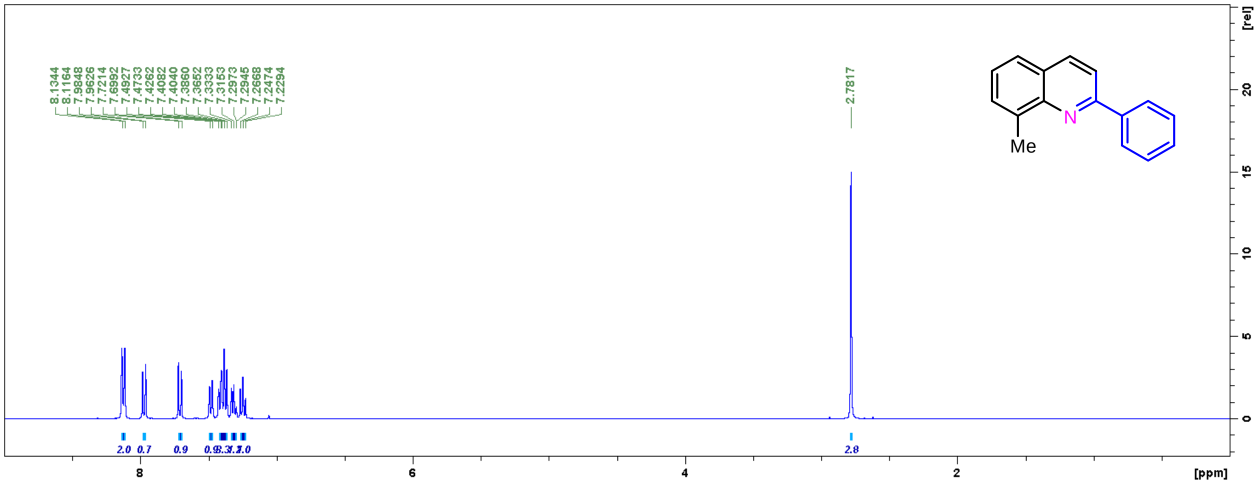


Figure S49. ^{1}H NMR spectrum of compound **8ba** in $CDCl_3$.



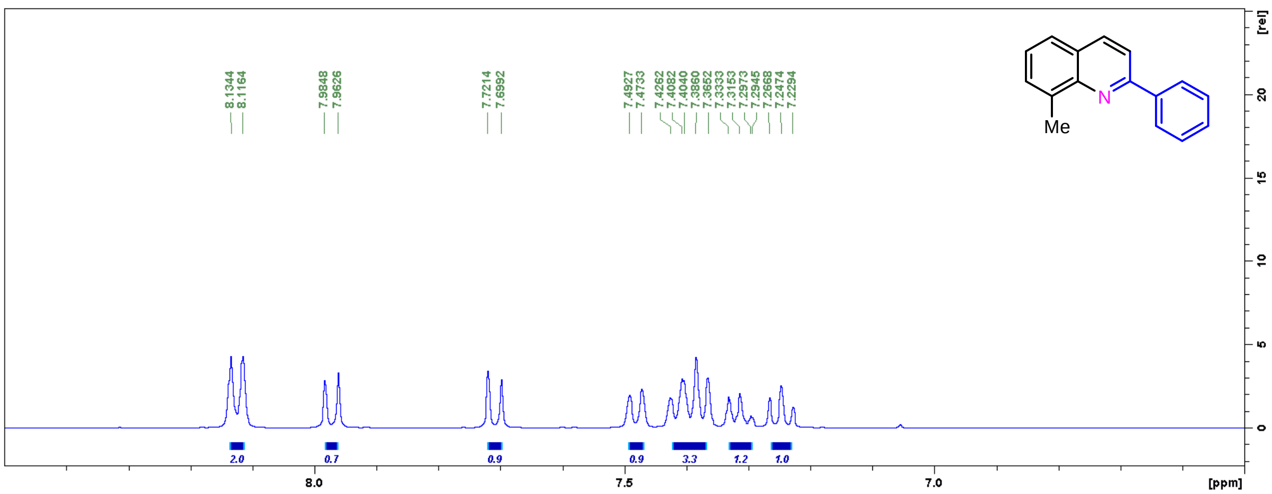
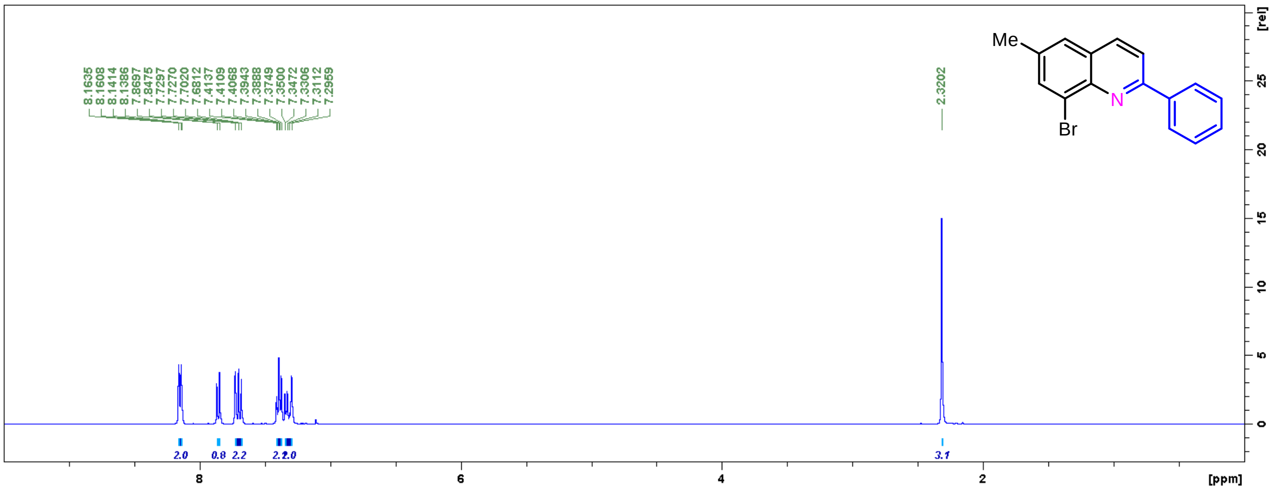


Figure S50. ^{1}H NMR spectrum of compound **8ca** in $CDCl_3$.



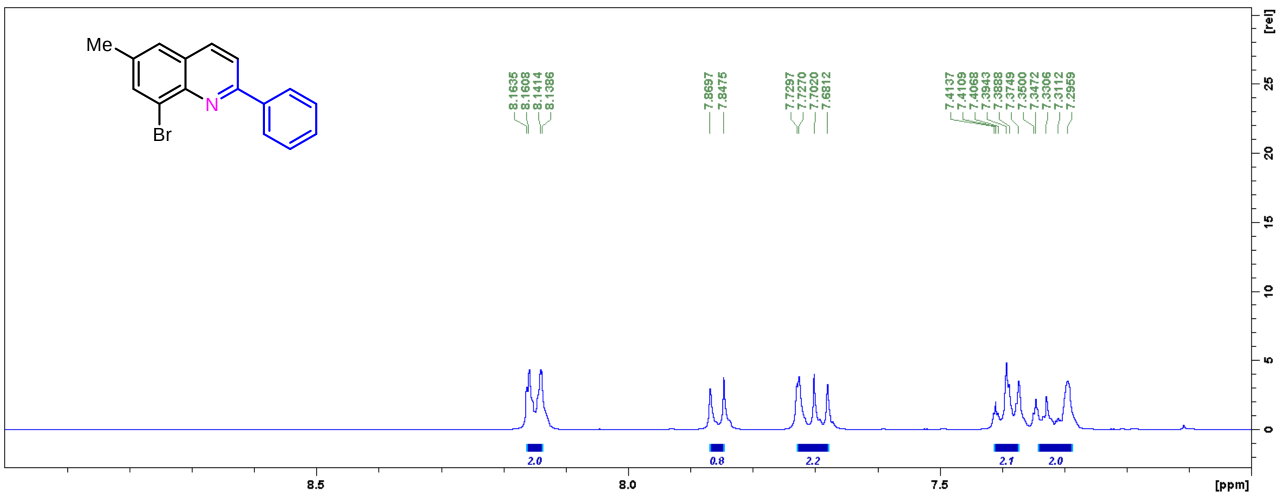
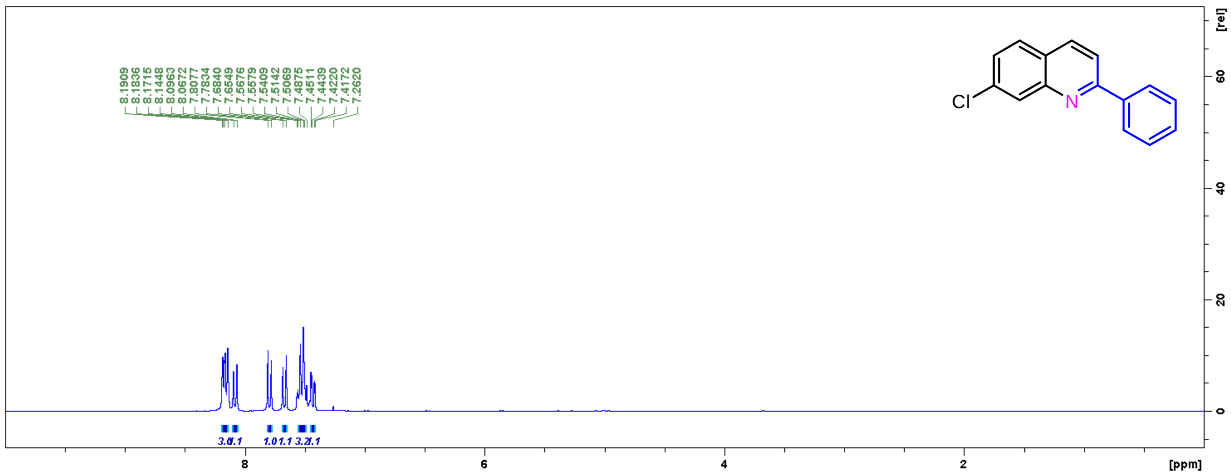
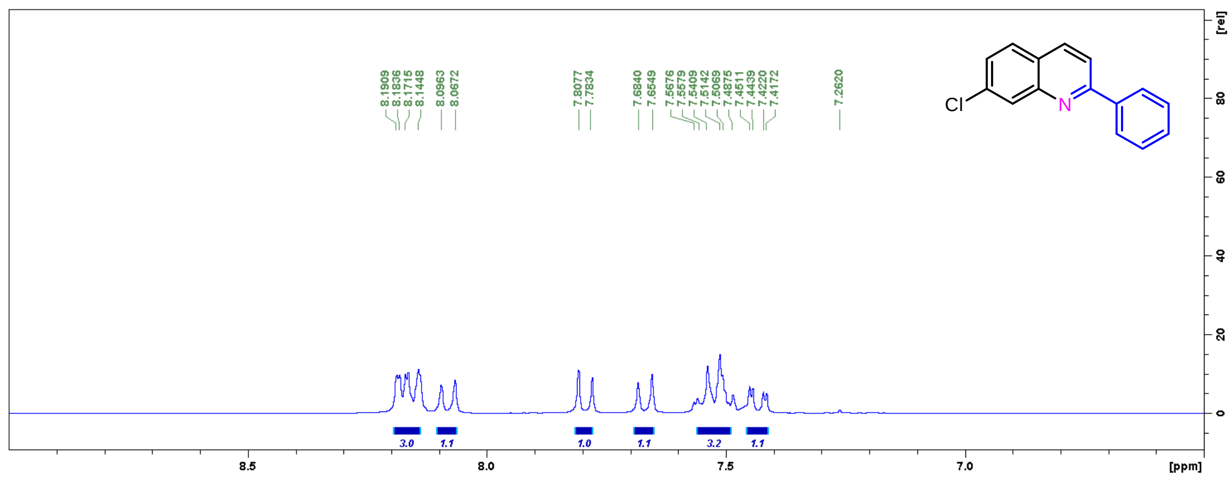


Figure S51. ^{1}H NMR spectrum of compound **8da** in $CDCl_3$.





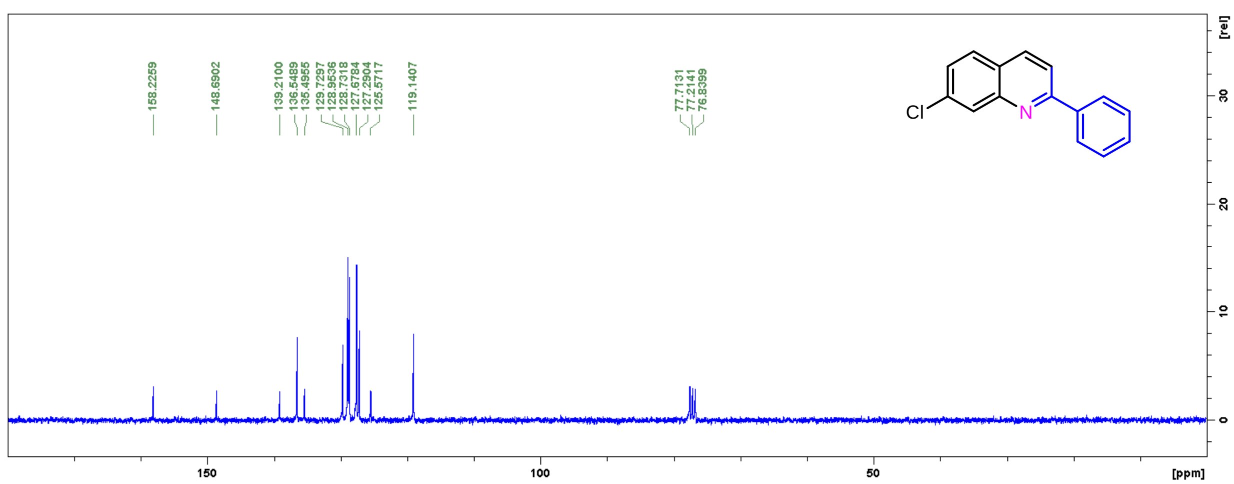
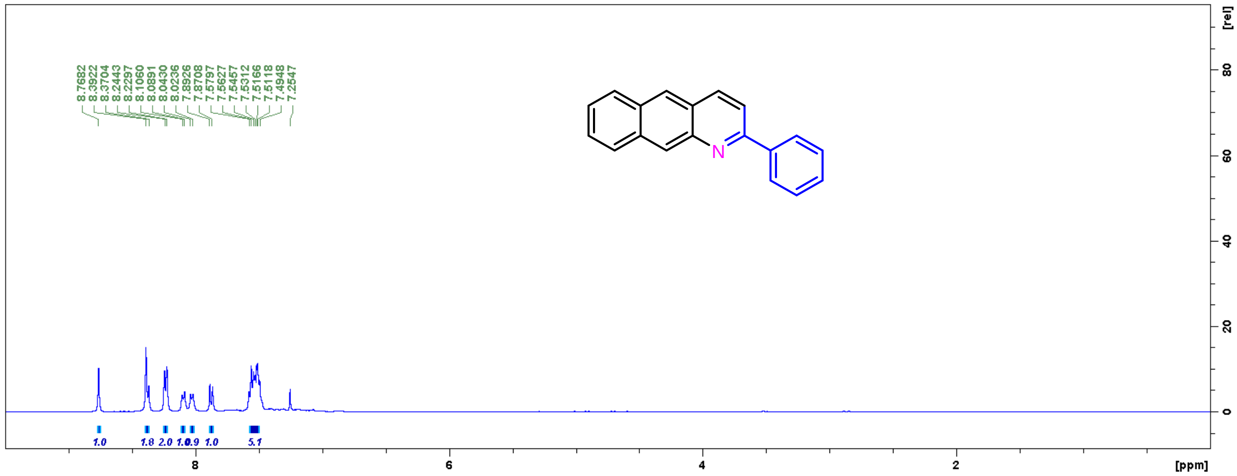


Figure S52. ^{1}H and ^{13}C NMR spectra of compound **8ea** in $CDCl_3$.



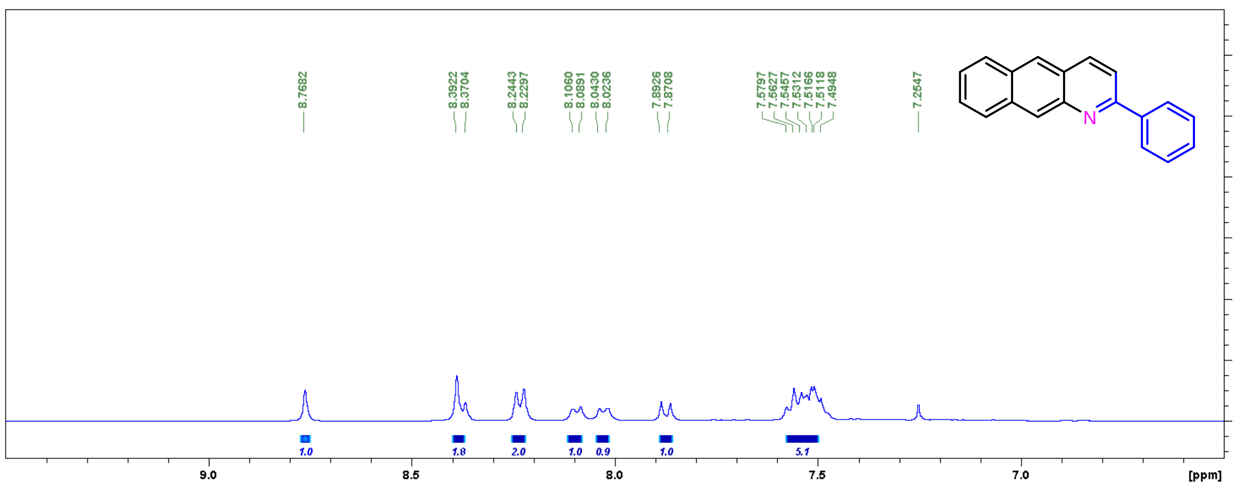
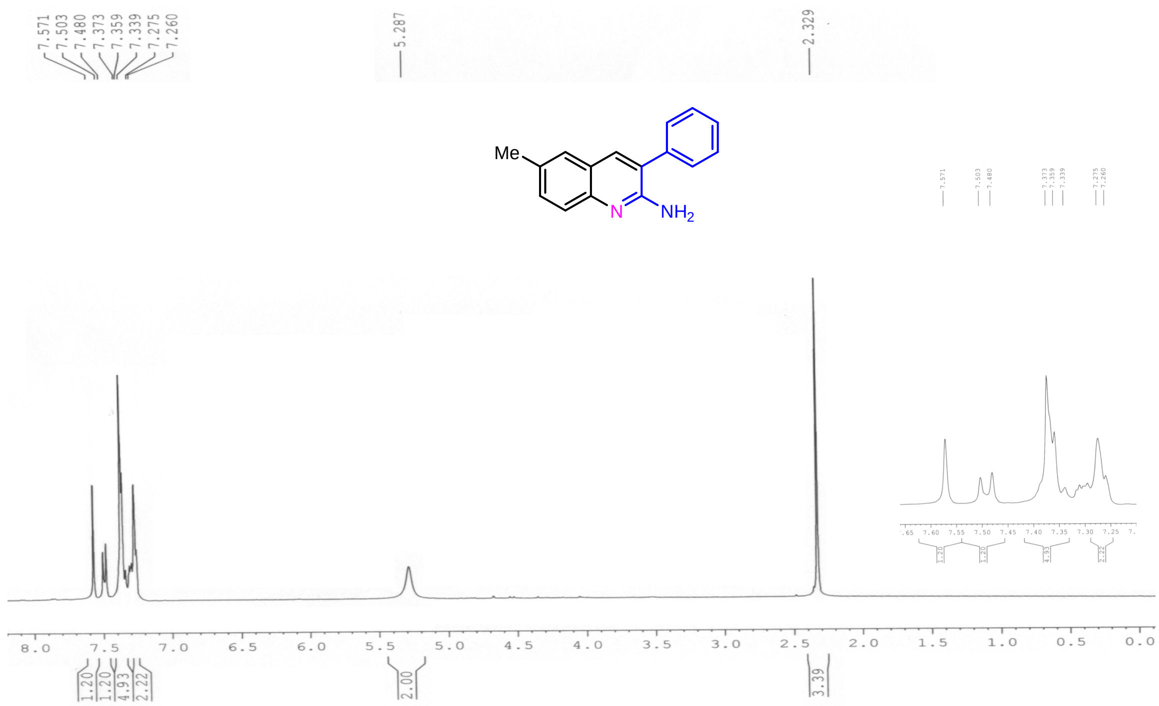


Figure S53. ^{1}H NMR spectrum of compound **8fa** in $CDCl_3$.



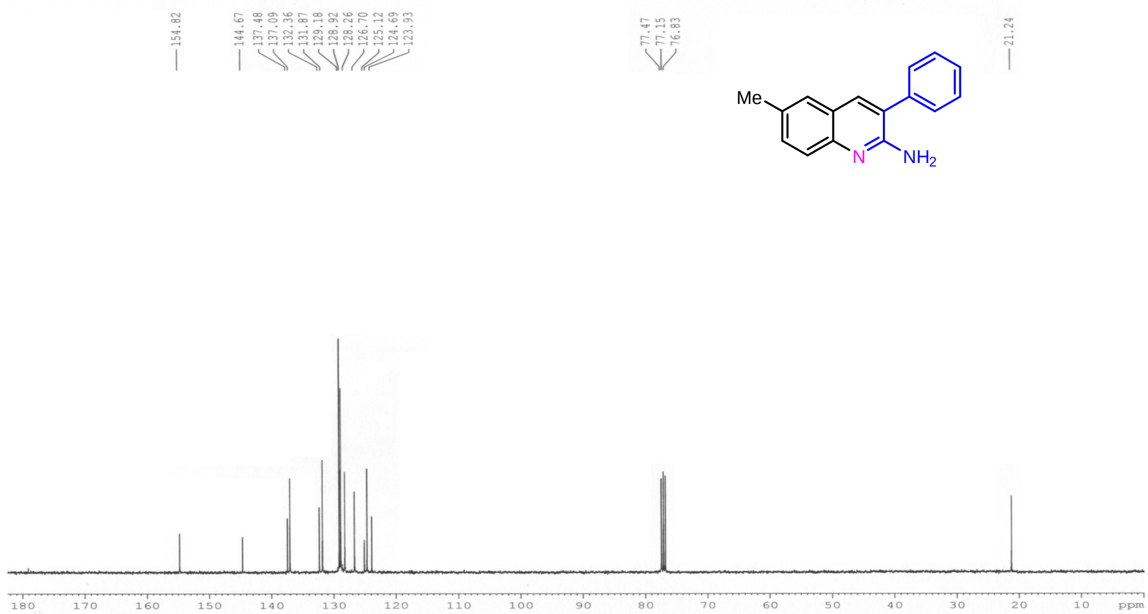
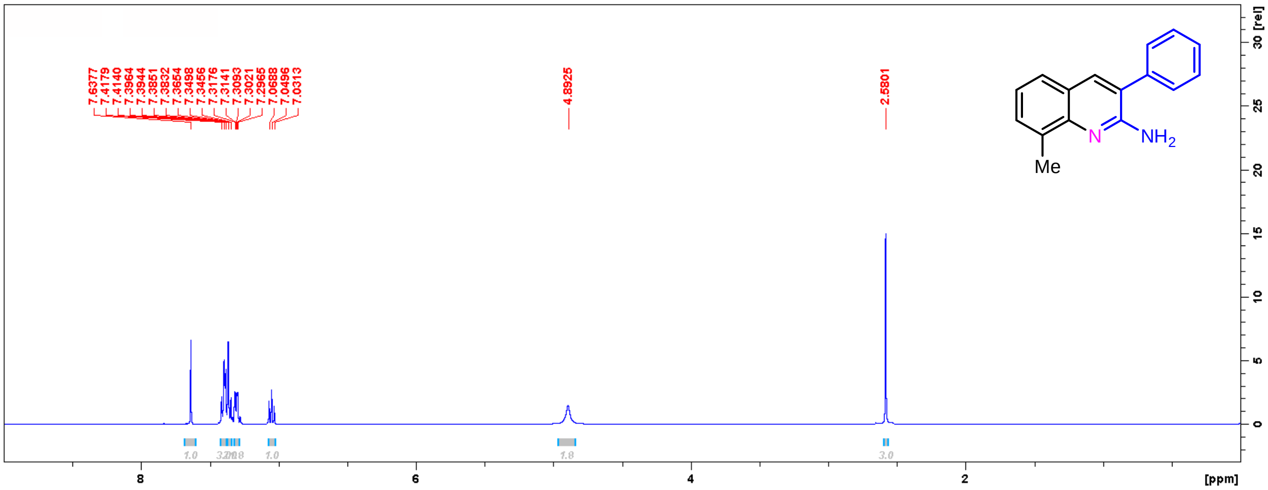
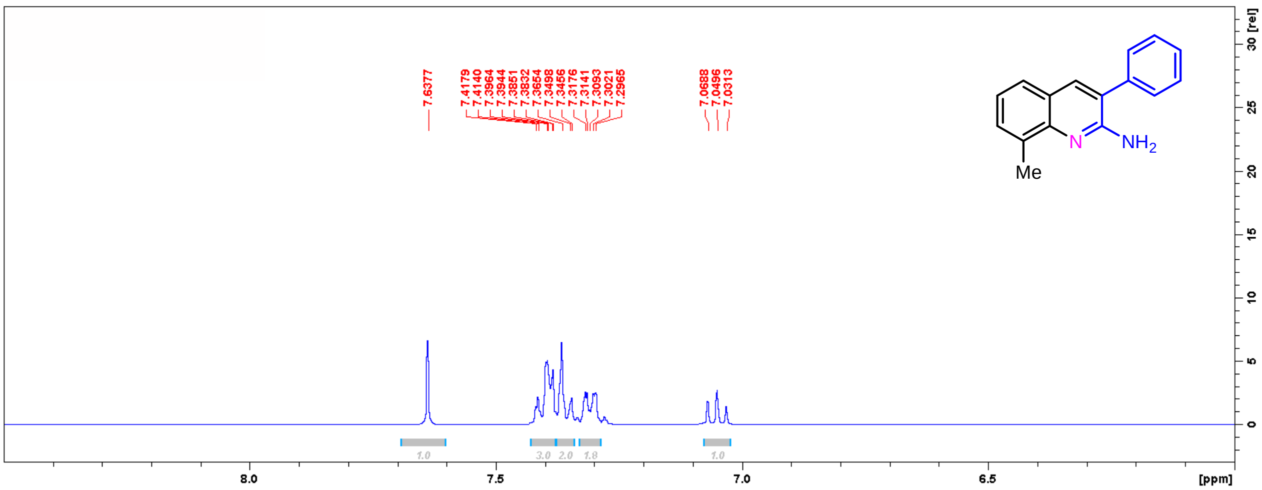


Figure S54. ^{1}H and ^{13}C NMR spectra of compound **9ba** in $CDCl_3$.





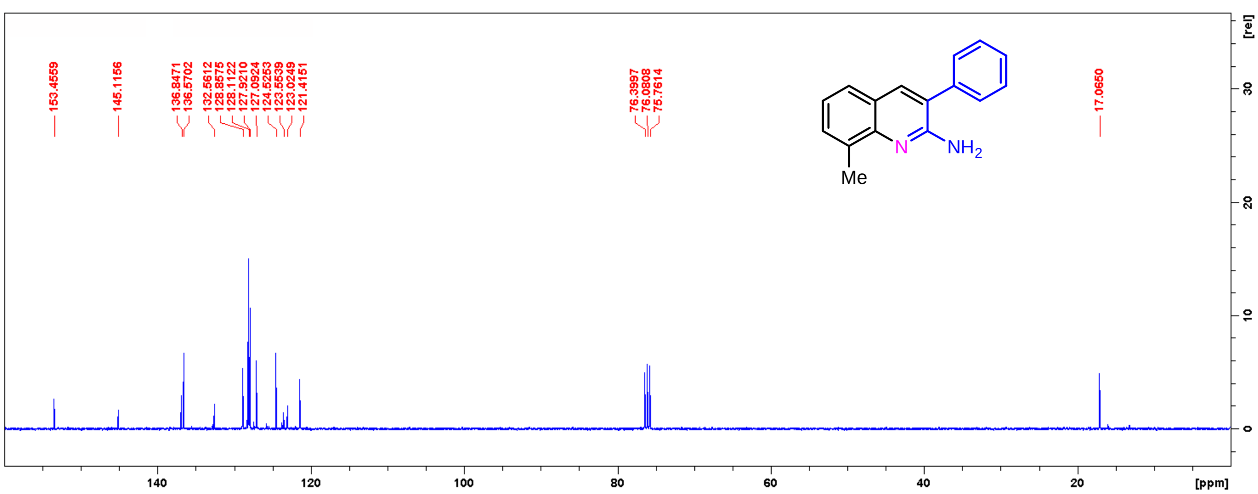
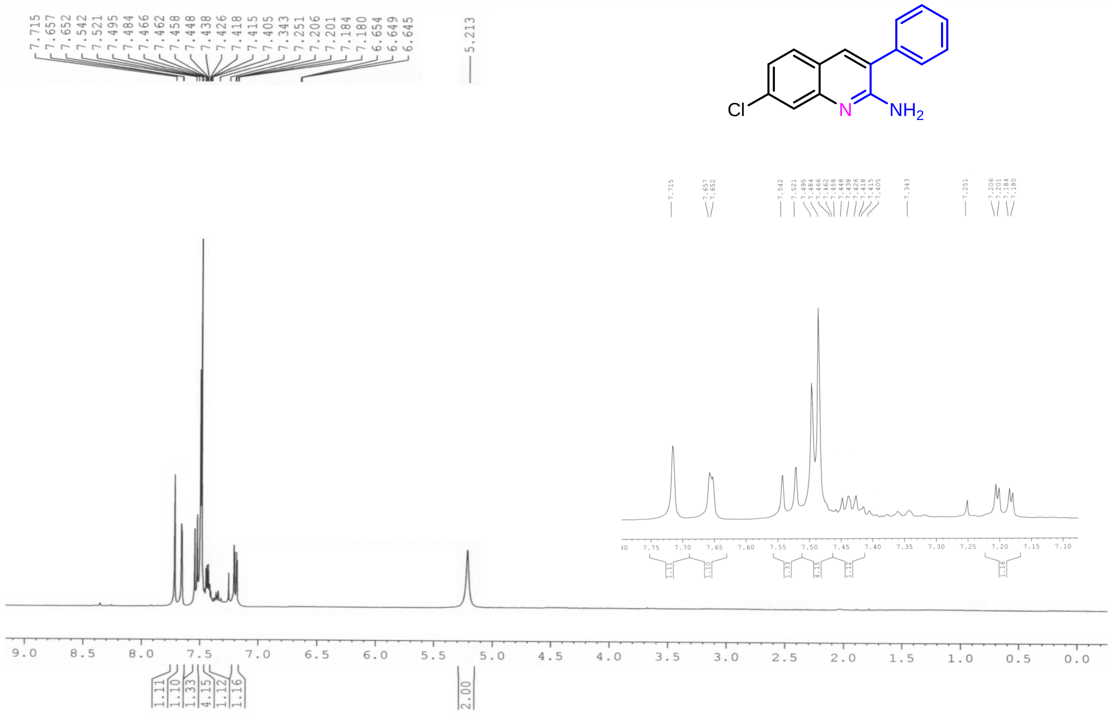


Figure S55. ^{1}H and ^{13}C NMR spectra of compound **9ca** in $CDCl_3$.



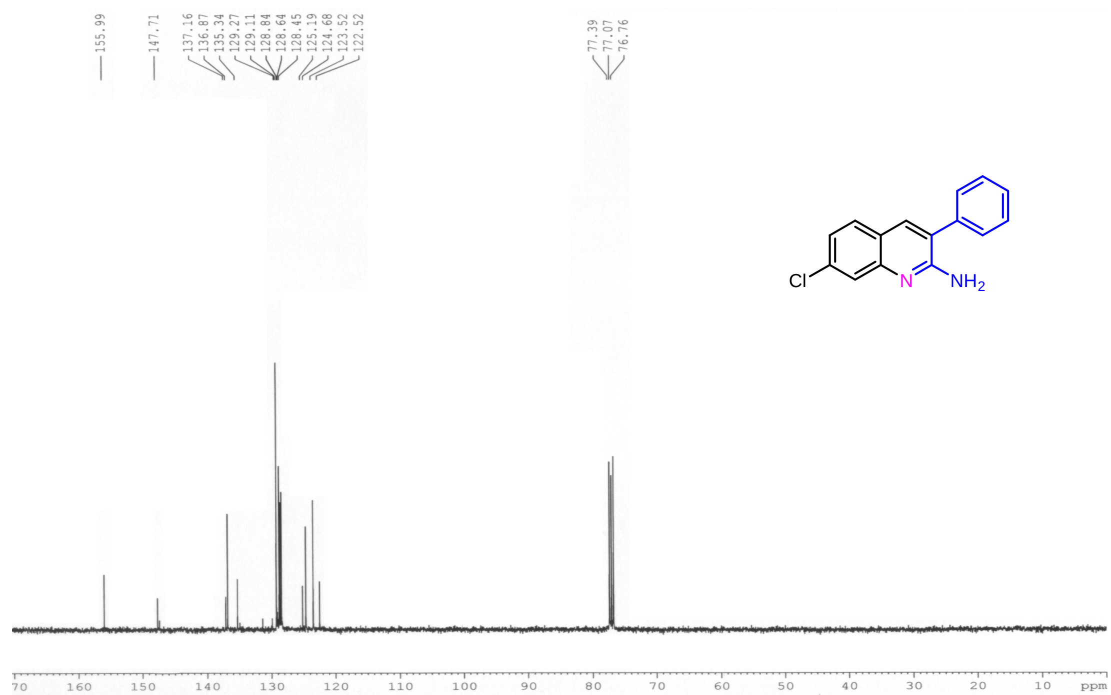
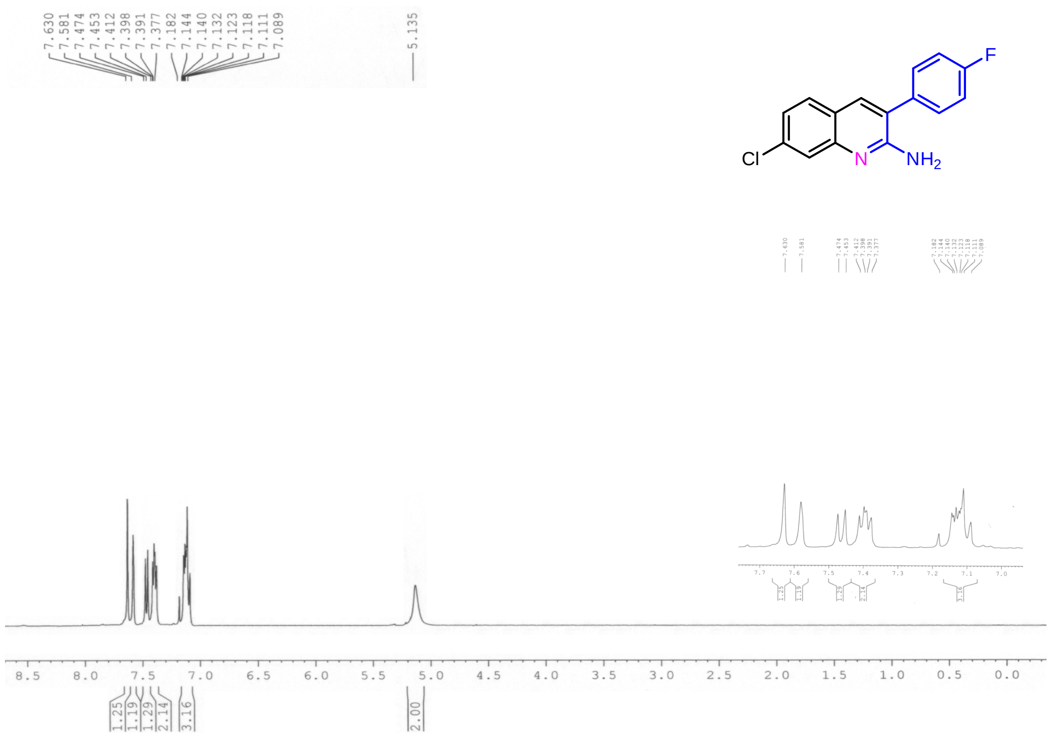


Figure S56. ^{1}H and ^{13}C NMR spectra of compound **9da** in $CDCl_3$.



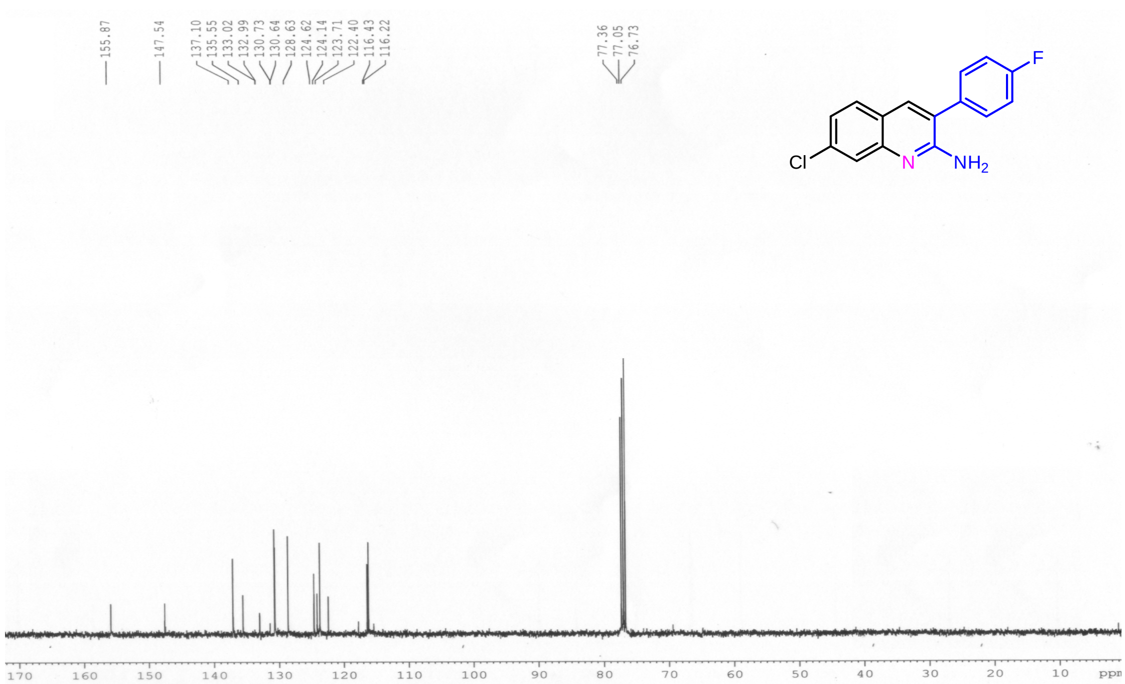
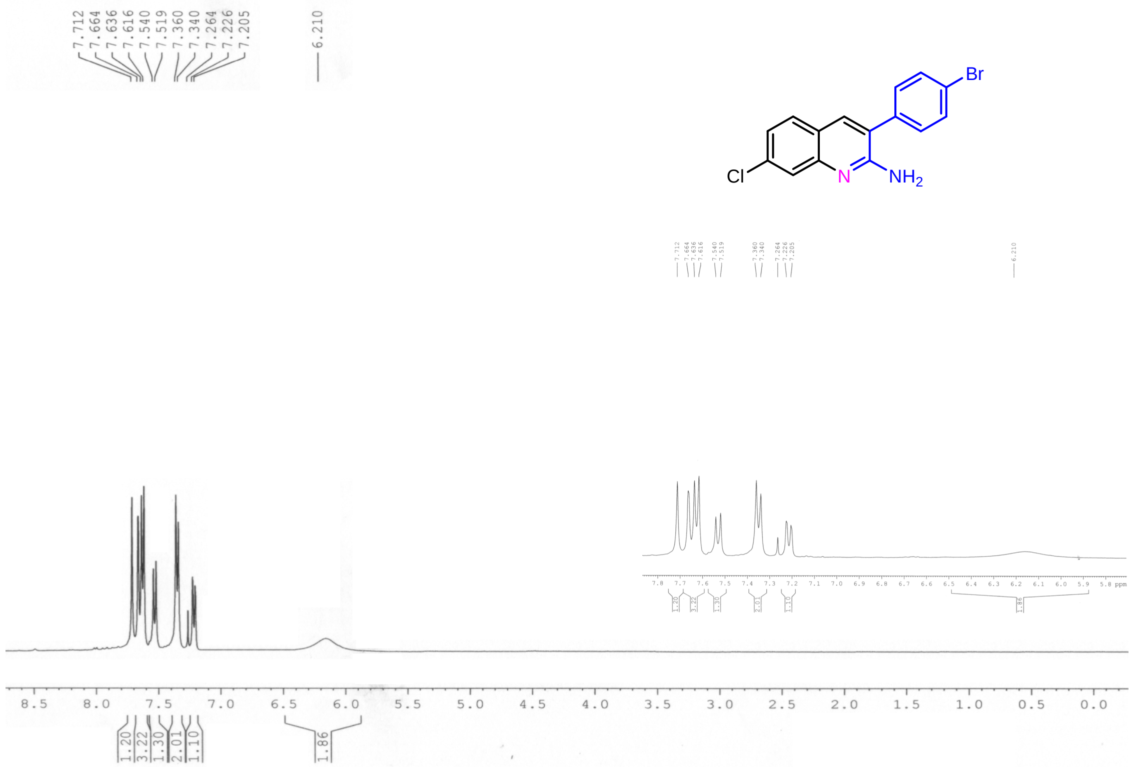


Figure S57. ^{1}H and ^{13}C NMR spectra of compound **9ea** in $CDCl_3$.



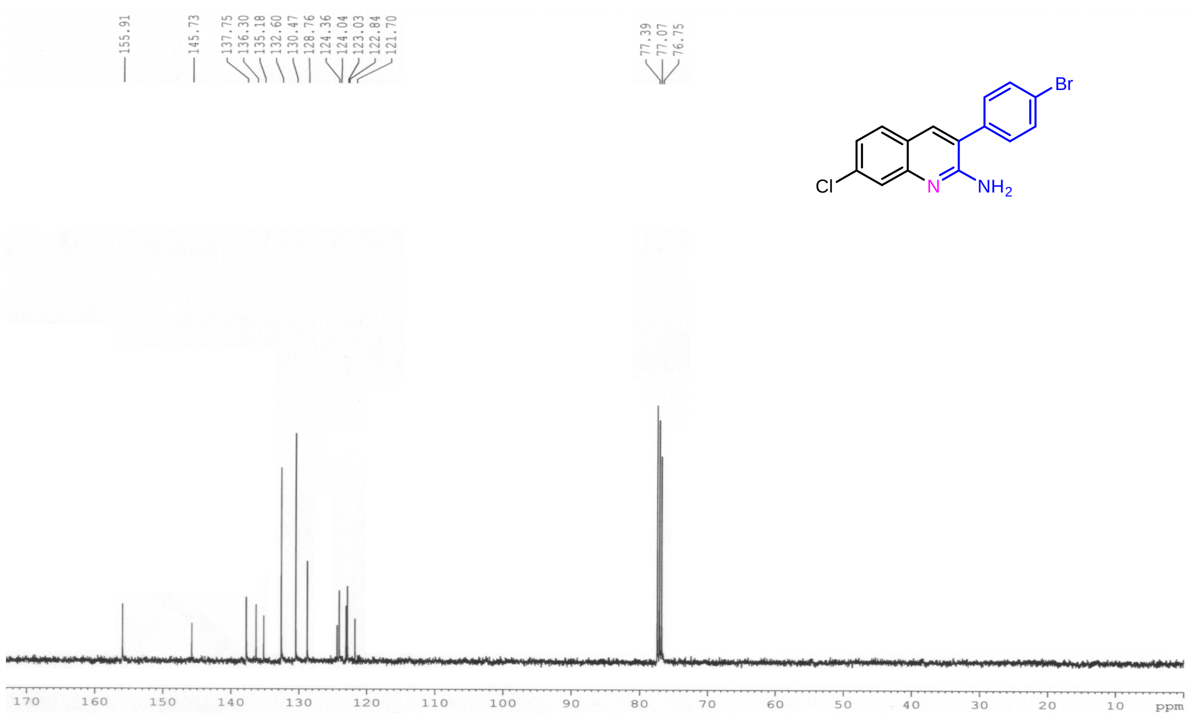
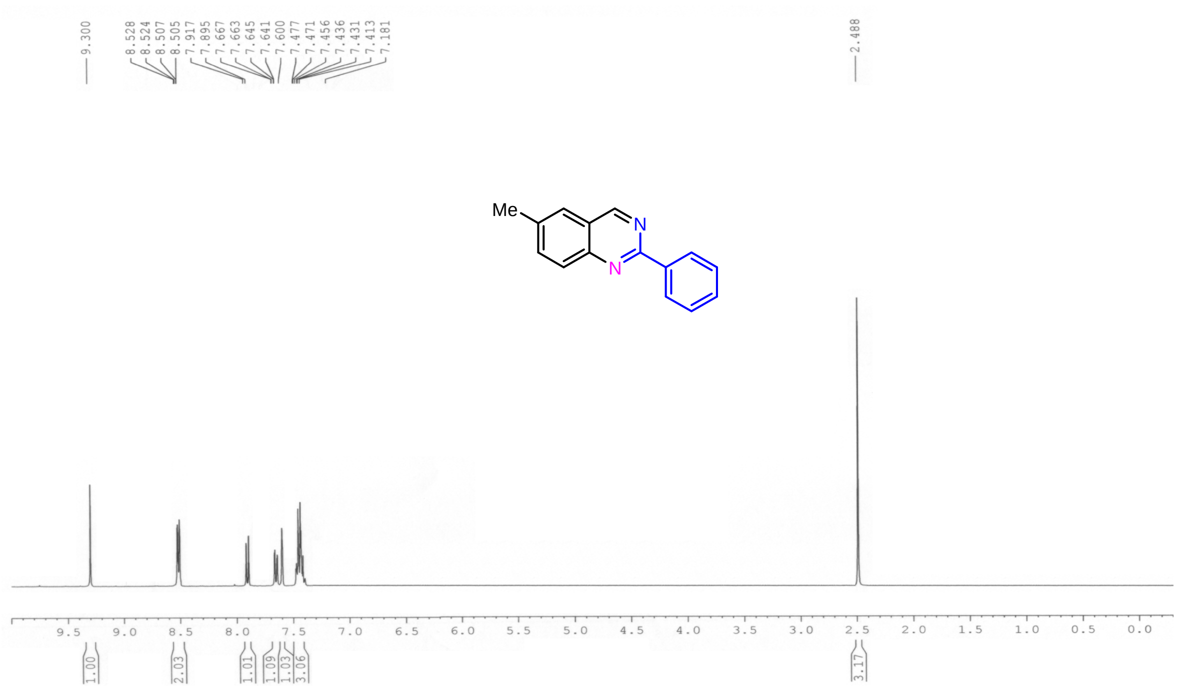


Figure S58. ^{1}H and ^{13}C NMR spectra of compound **9fa** in $CDCl_3$.



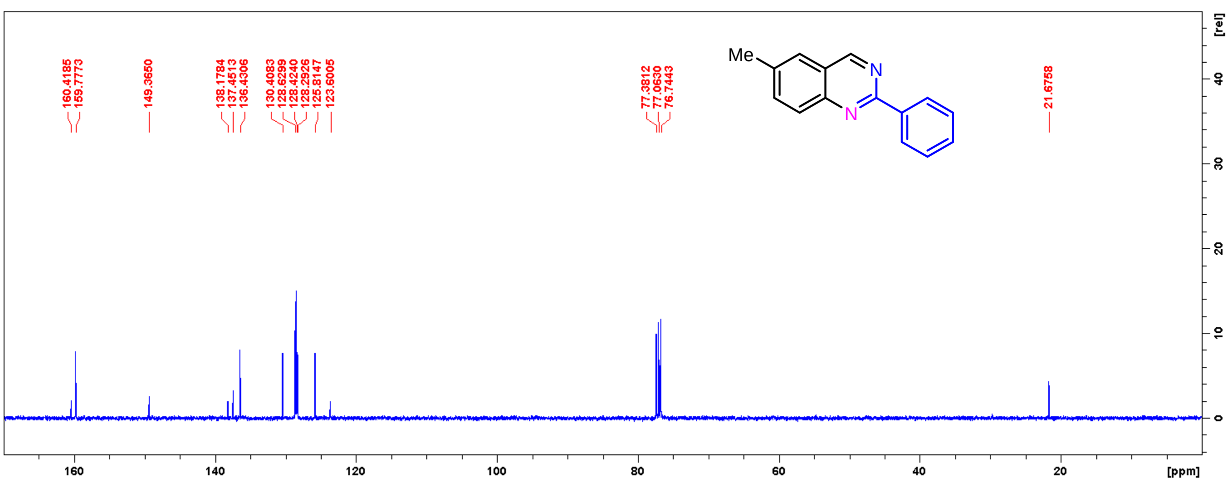


Figure S59. ^{1}H and ^{13}C NMR spectra of compound **10ba** in $CDCl_3$.

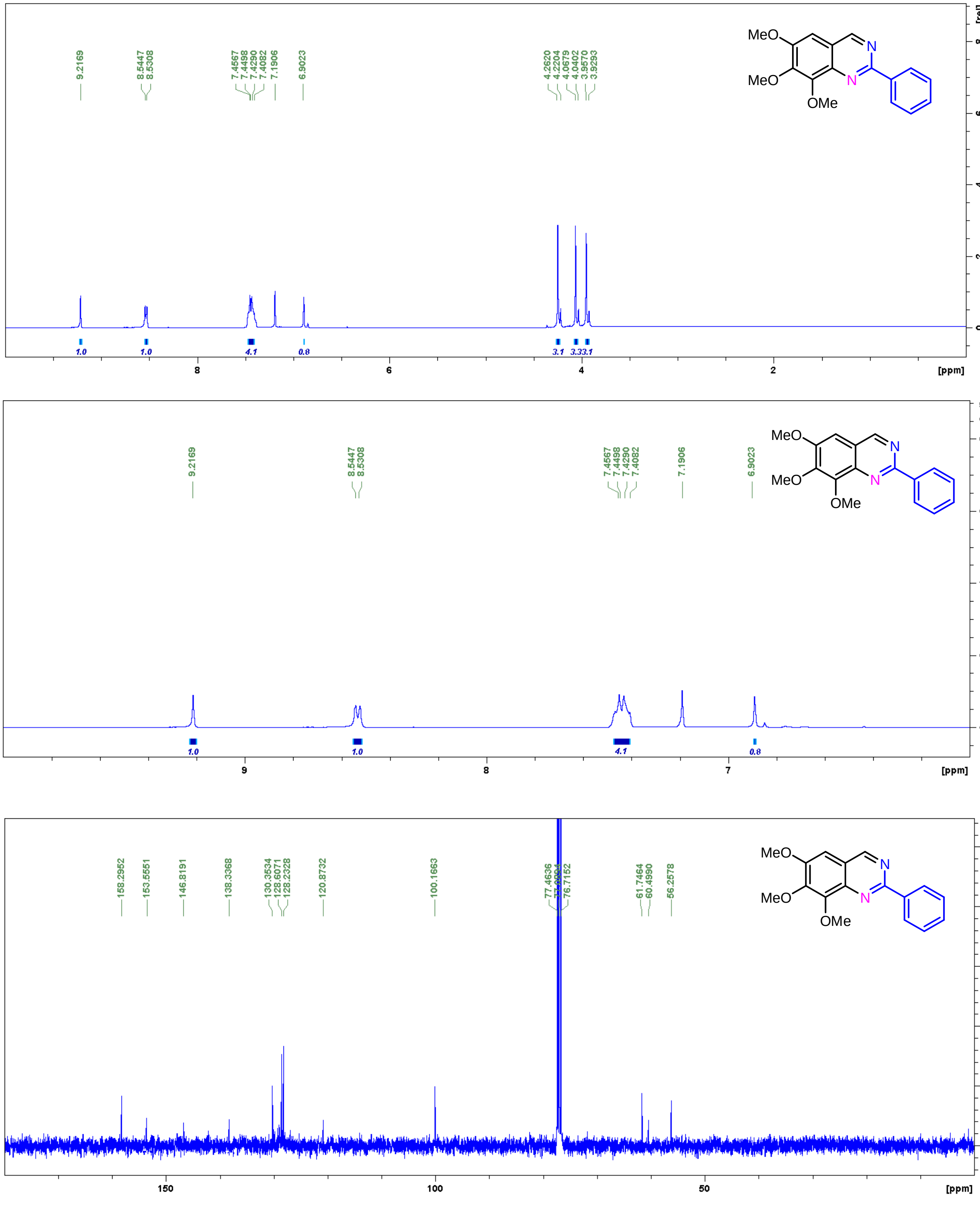
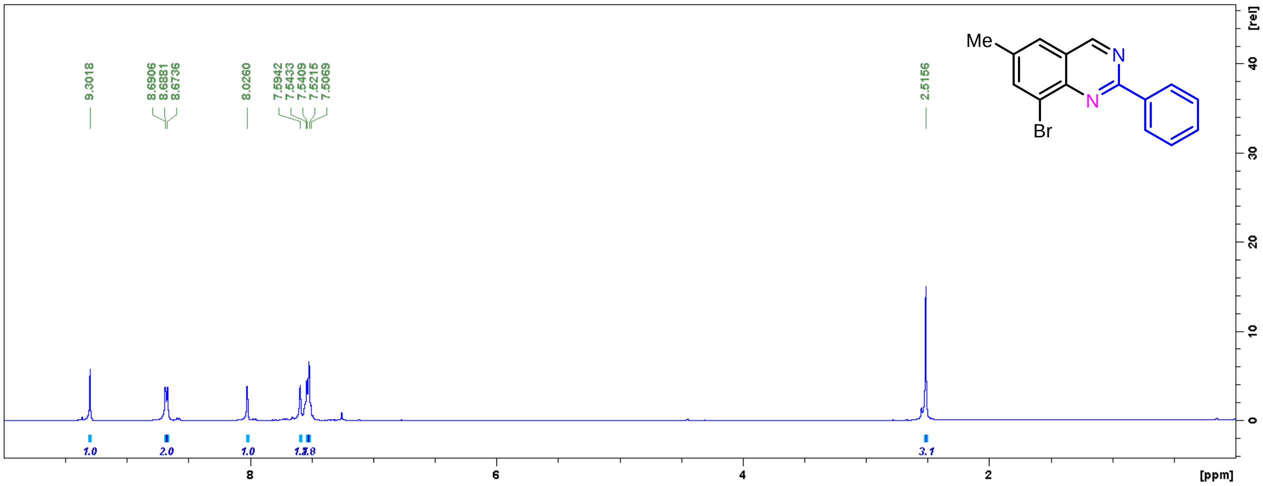
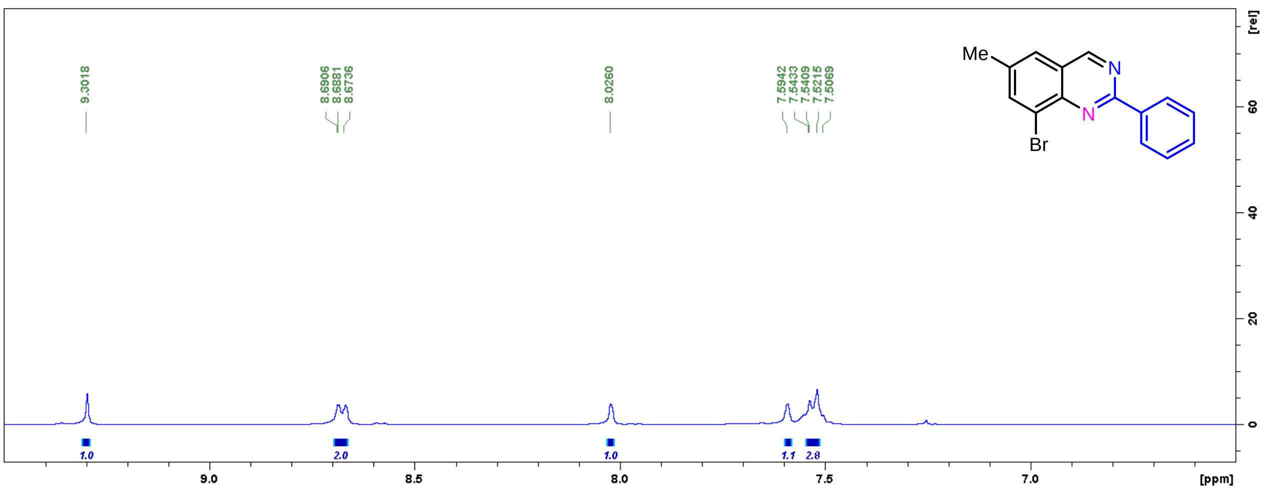


Figure S60. ^1H and ^{13}C NMR spectra of compound **10ca** in $CDCl_3$.





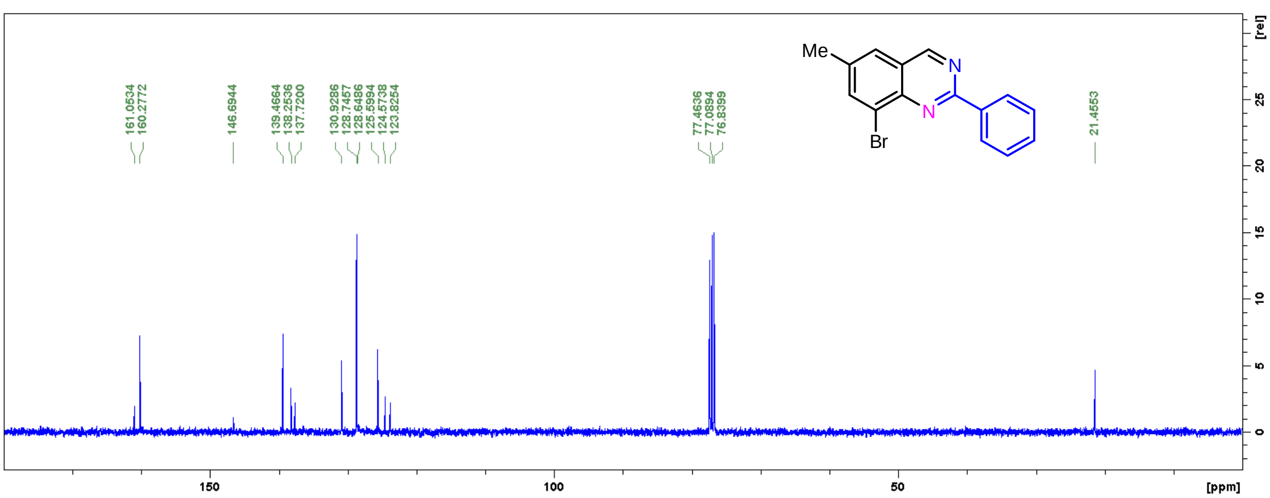
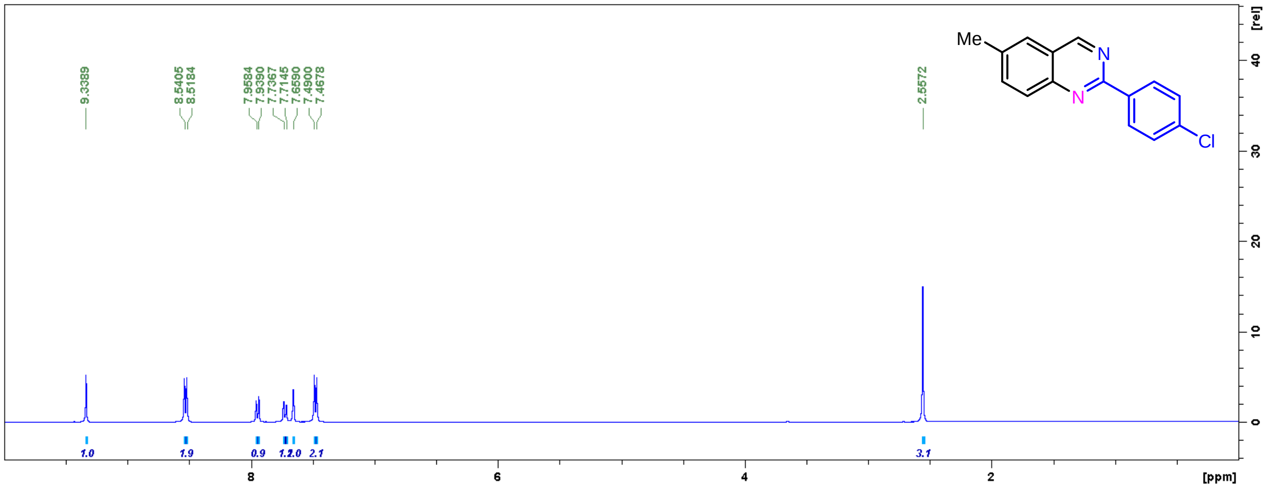
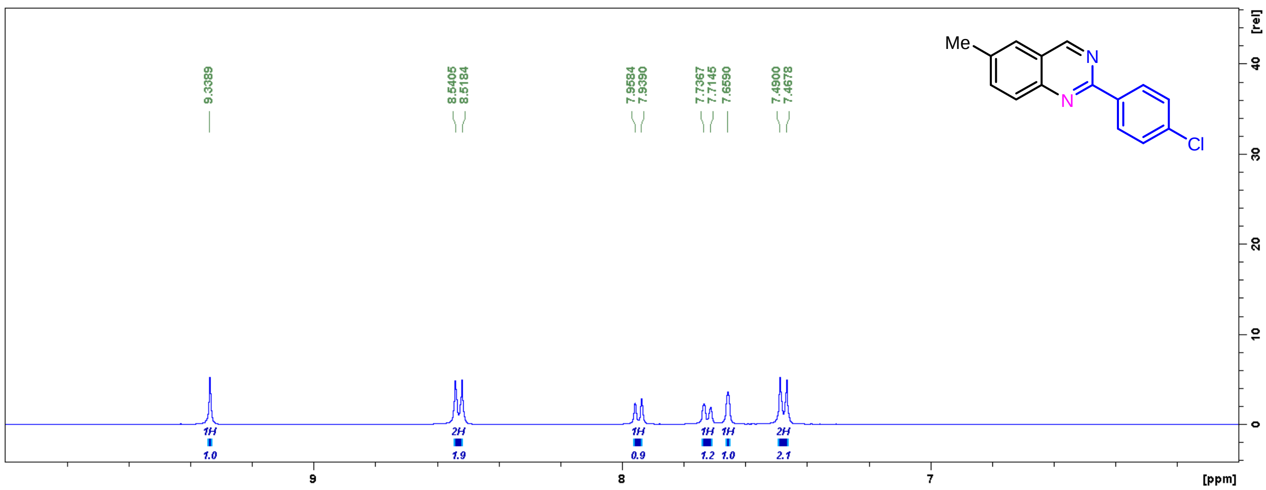


Figure S61. ^{1}H and ^{13}C NMR spectra of compound **10da** in $CDCl_3$.





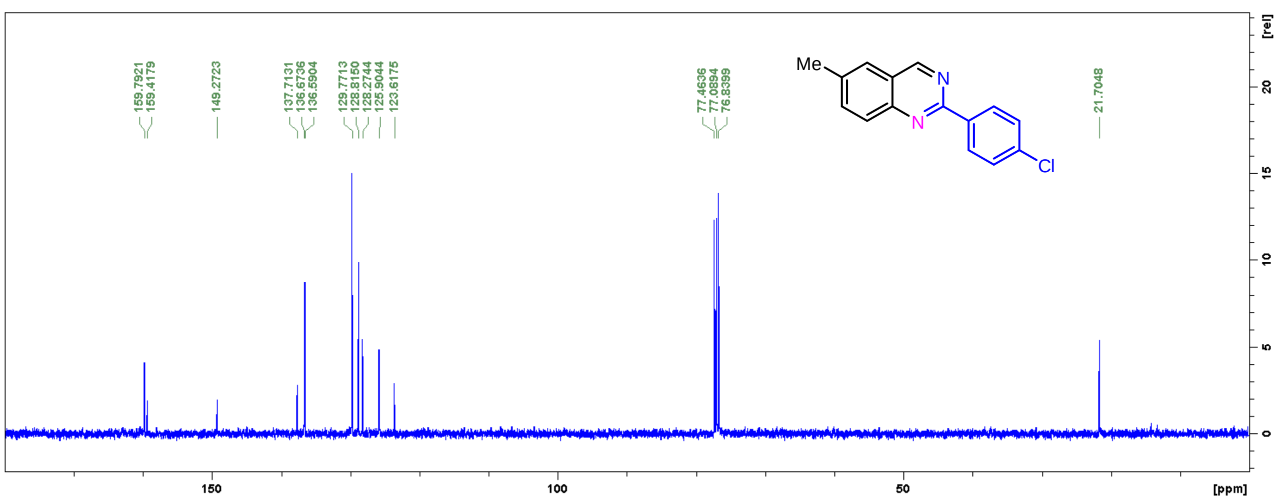
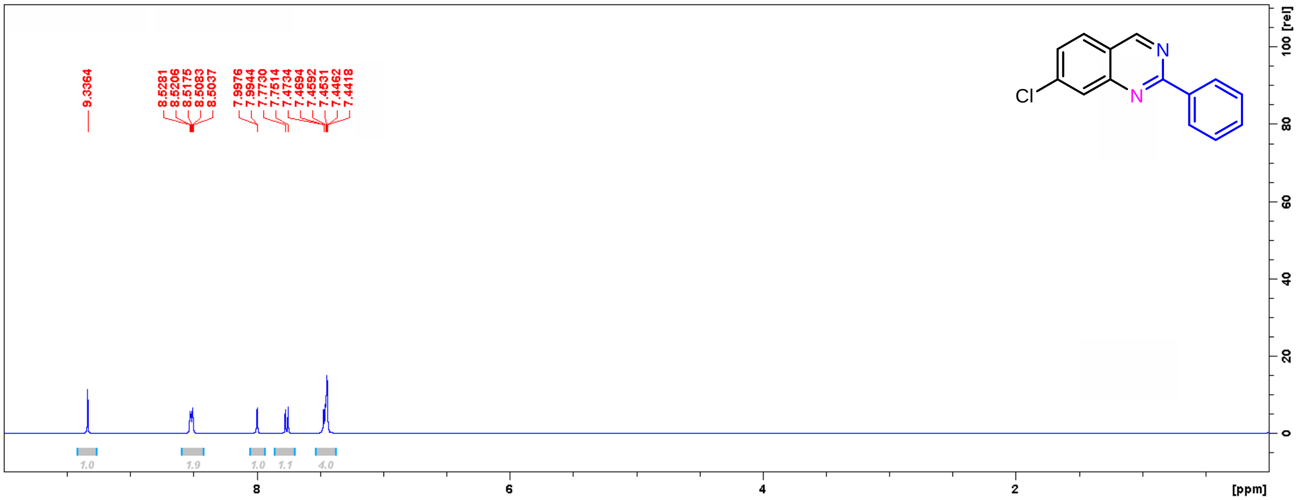
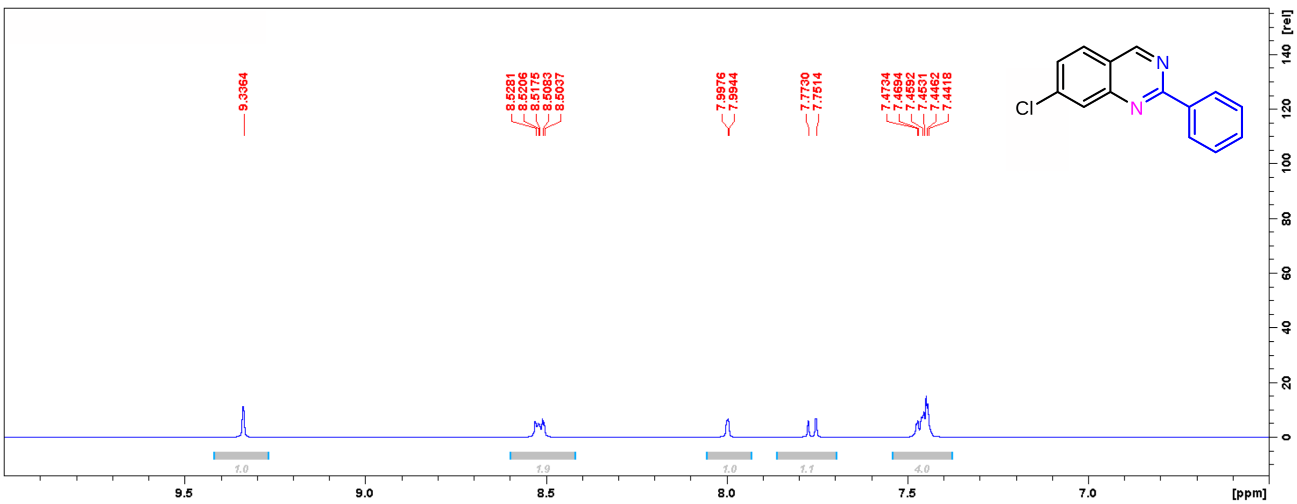


Figure S62. ^{1}H and ^{13}C NMR spectra of compound **10ea** in $CDCl_3$.





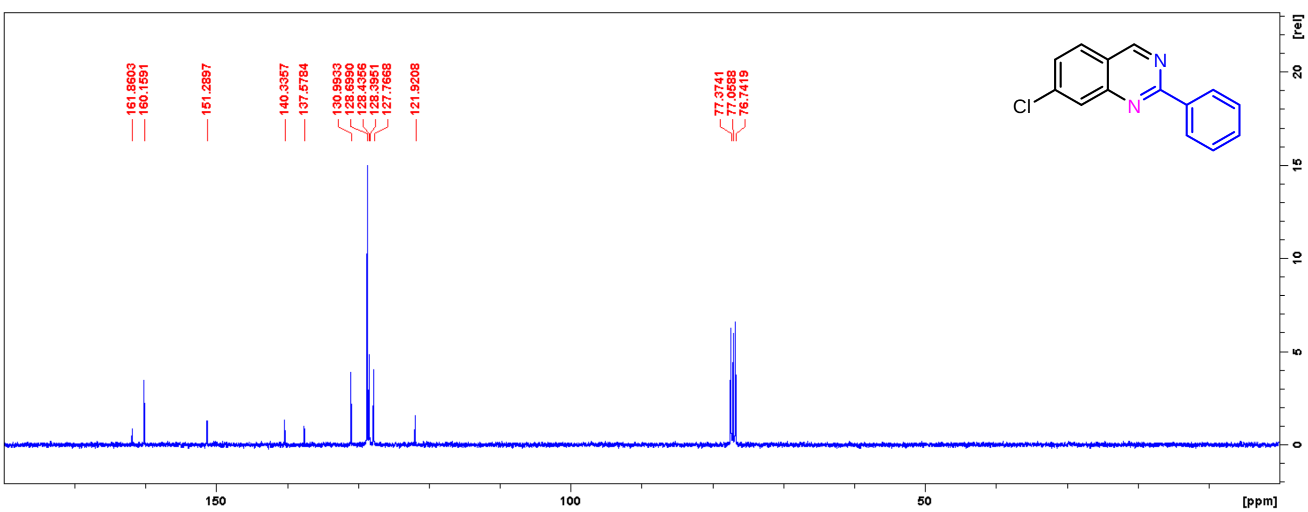


Figure S63. ^{1}H and ^{13}C NMR spectra of compound **10fa** in $CDCl_3$.

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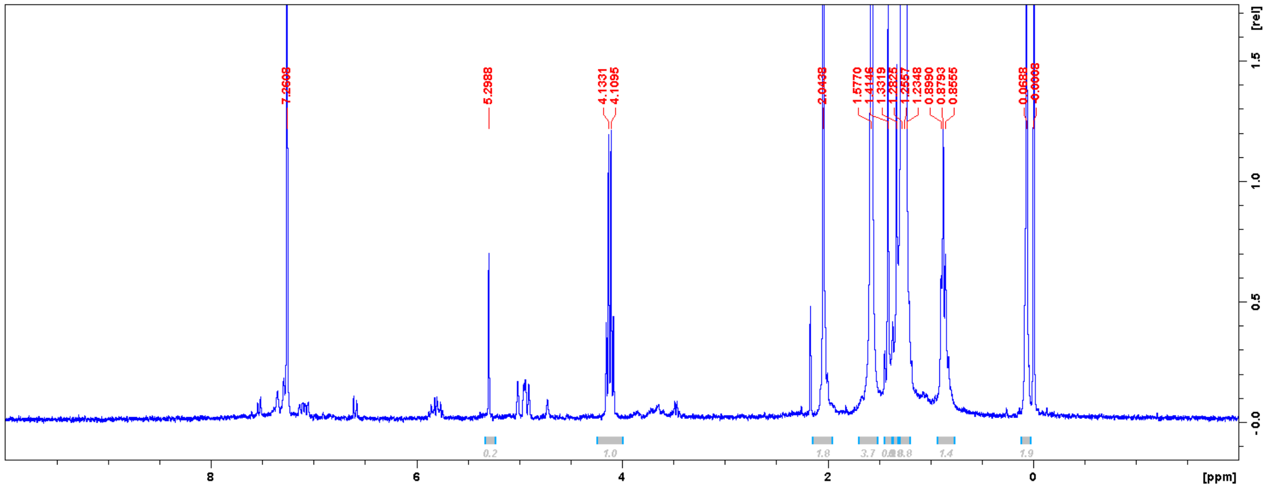

Figure S64. ^{1}H NMR spectrum of reaction mixture of obtained after the dehydrogenation of cyclobutanol, catalyzed by **3** in $CDCl_3$.

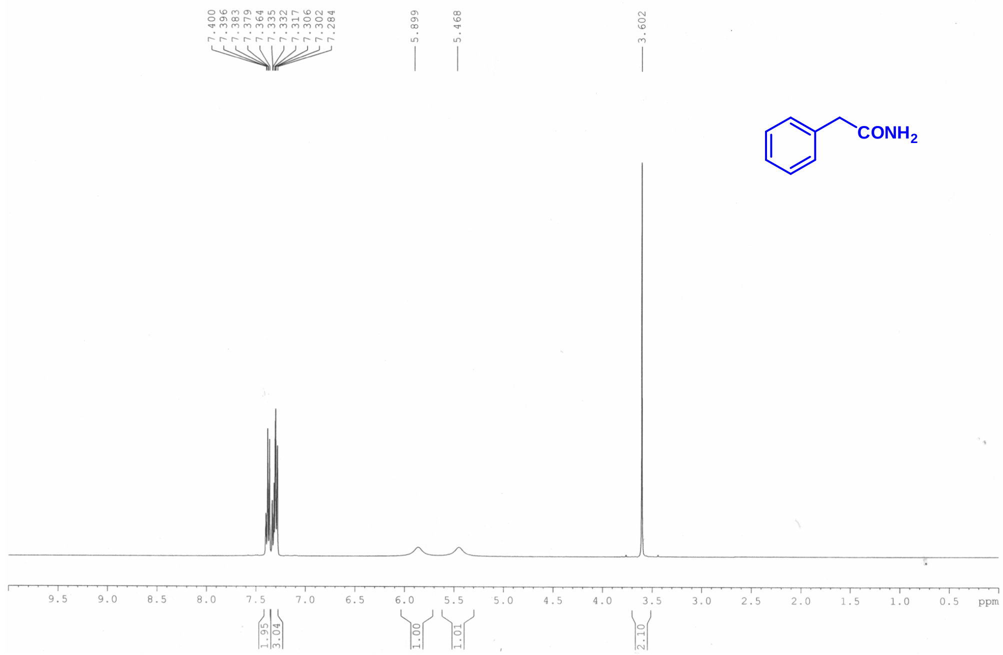

Figure S65. ^{1}H NMR spectrum of **6a'** in $CDCl_3$.

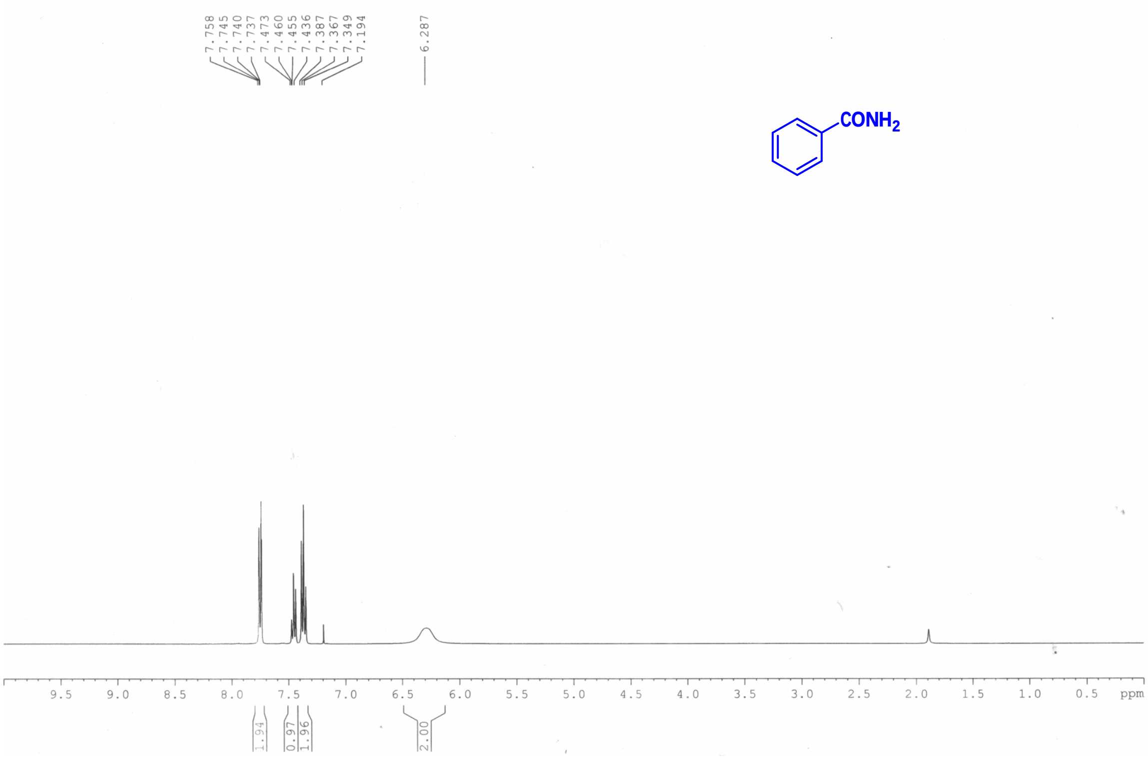

Figure S66. ^{1}H NMR spectrum of **7a'** in $CDCl_3$.

References.

(1) Sinha, S.; Das, S.; Sikari, R.; Parua, S.; Brandaõ, P.; Demeshko, S.; Meyer, F.; Paul, N. D. Redox Noninnocent Azo-Aromatic Pincers and Their Iron Complexes. Isolation, Characterization, and Catalytic Alcohol Oxidation. *Inorg. Chem.* **2017**, *56*, 14084–14100.