Iron (III)-catalyzed chelation assisted remote C-H bond oxygenation of 8-amidoquinolines.

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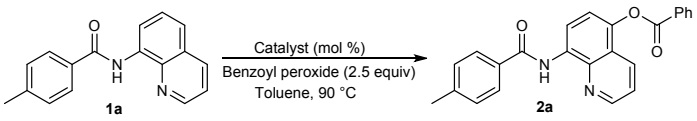
1. Optimization of Reaction Conditions:

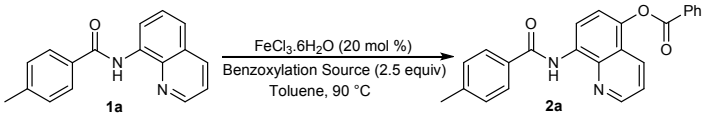
Table S1. Optimization of the catalyst[a]



Entry	Catalyst (mol %)	Yield[b]
1	$FeCl_3.6H_2O$ (10)	55
2	$FeCl_3.6H_2O$ (30)	52
3[c]	$FeCl_3.6H_2O$ (20)	61
4[d]	$FeCl_3.6H_2O$ (20)	59
5[e]	$FeCl_3.6H_2O$ (20)	54
6	$Cu(OAc)_2$ (20)	40
7	$CuBr_2$(20)	43
8	$CuCl_2$(20)	21
9	$Cu(OTf)_2$(20)	28
10	CuI (20)	46
11	Pd $(OAc)_2$ (20)	00
12	$PdCl_2$ (20)	00

[a] The reaction was performed with **1a** (1.0 mmol), Catalyst (mol %), Benzoyl peroxide (2.5 mmol, 5 × 0.5 equiv./0.5 h) in toluene (5 mL) stirred at 90 °C for 24 h in open air. [b] Isolated yields. [c]TBHP (2.0 mmol) as oxidant, [d] Under O_2 atmosphere, [e] Under N_2 atmosphere.

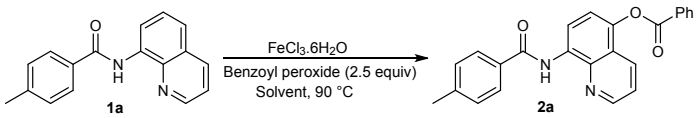
Table S2. Optimization of the Benzoxylation Source [a]



Entry	Benzoxylation Source	Yield[b]
1	Benzoyl peroxide	73
2	Benzoic acid	00
3	Benzoic anhydride	00
4	Benzoyl chloride	00
5[c]	Phenyl acetylene	00
6[c]	styrene	00
7	*m*-CPBA	00

[a] The reaction was performed with **1a** (1.0 mmol), $FeCl_3.6H_2O$ (0.2 mmol), Benzoxylation Source (2.5 mmol) in toluene (5 mL) stirred at 90 °C for 24 h in open air. [b] Isolated yields. [c] in the presence of TBHP, (*m*-CPBA = *meta*-chloro perbonzoic acid).

Table S3. Optimization of the Solvent[a]



Entry	Solvent	Yield[b]
1	ACN	53
2	DCE	42
3	DMF	00
4	DMSO	00
5	Toluene	63
6	AcOH	00
7	MeOH	00
8	H_2O	00

[a] The reaction was performed with **1a** (1.0 mmol), $FeCl_3.6H_2O$ (0.2 mmol), Benzoyl peroxide (2.5 mmol 5 × 0.5 equiv./0.5 h) in Solvent (5 mL) stirred at (entry 1, 7) and remaining solvents were at 90 °C for 24 h in open air. [b] Isolated yields.

2. Crystallographic Data of Compound 2g

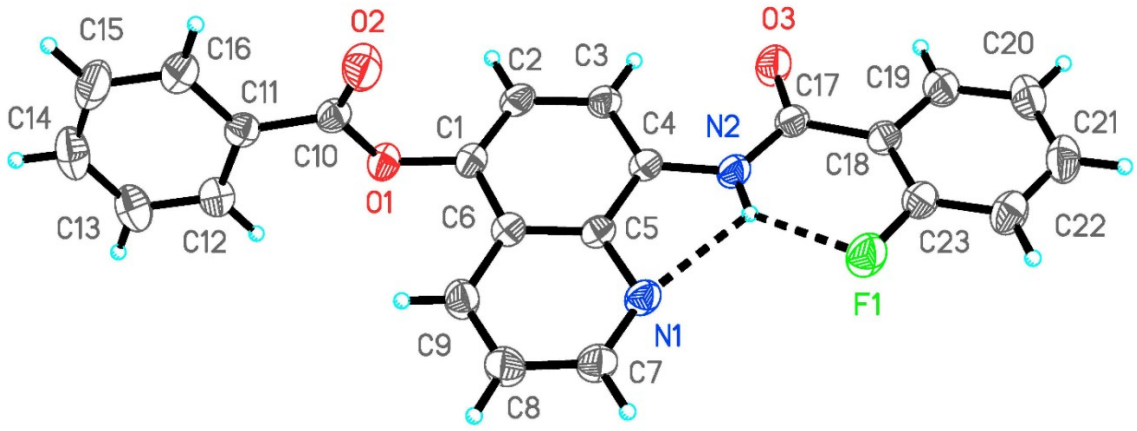


Fig.1. A view of BD71, showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are represented by circles of arbitrary radii. Intramolecular hydrogen bonds are shown as dashed lines.

X-ray data for the compound BE52 was collected at room temperature on a Bruker Smart Apex CCD diffractometer with graphite monochromated MoKα radiation (λ=0.71073Å) with ω-scan method. Data for the compound KA172 was also collected at room temperature on a Bruker D8 QUEST instrument with an IμS Mo microsource (λ = 0.7107 A) and a PHOTON-100 detector. Integration and scaling of intensity data of BD71 was accomplished using SAINT program.[1] The structure was solved by direct methods using SHELXS[2] and refinement was carried out by full-matrix least-squares technique using SHELXL.[2]

Crystal Data for 2g: $C_{23}H_{15}N_2O_3F$ (M =386.39 g/mol): triclinic, space group P-1 (no. 2), a = 8.1396(11) Å, b = 9.5365(13) Å, c = 13.2564(18) Å, α = 108.241(2)°, β = 99.899(2)°, γ = 103.051(2)°, V = 918.7(2) Å^3, Z = 2, T = 294.15 K, μ(Mo Kα) = 0.101 mm^{-1}, *Dcalc* = 1.3966 g/cm^3, 10638 reflections measured (4.68° ≤ 2Θ ≤ 50°), 3226 unique (R_{int} = 0.0249, R_{sigma} = 0.0339) which were used in all calculations. The final R_1 was 0.0593 (I>2 σ(I)) and wR_2 was 0.1375 (all data). CCDC 1559198 contains supplementary Crystallographic data for the structure. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0) 1223 336 033; email: deposit@ccdc.cam.ac.uk.

1. Bruker (2001). SAINT (Version 6.28a) & SMART (Version 5.625). Bruker AXS Inc., Madison, Wisconsin, USA.
2. Sheldrick G. M. (2015) Acta Crystallogr C71: 3-8.
3. Bruker (2016). APEX3, SAINT and SADABS. Bruker AXS, Inc., Madison, Wisconsin, USA.

3. Copies of NMR Spectral Data

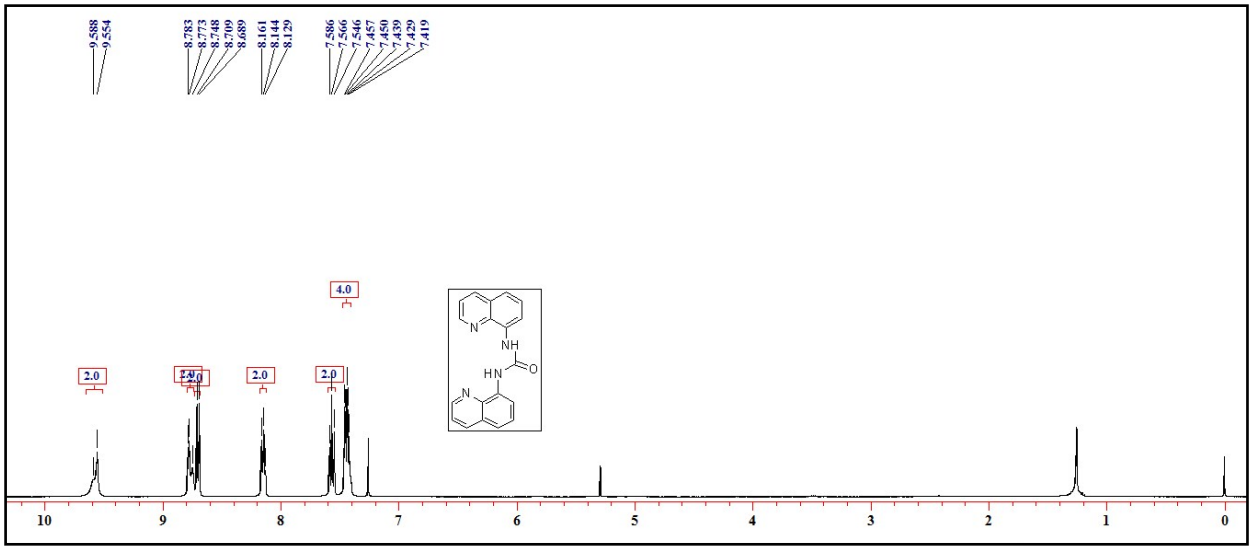


Figure S1. ^{1}H NMR spectrum of **1y** in $CDCl_3$+ CD_2Cl_2.

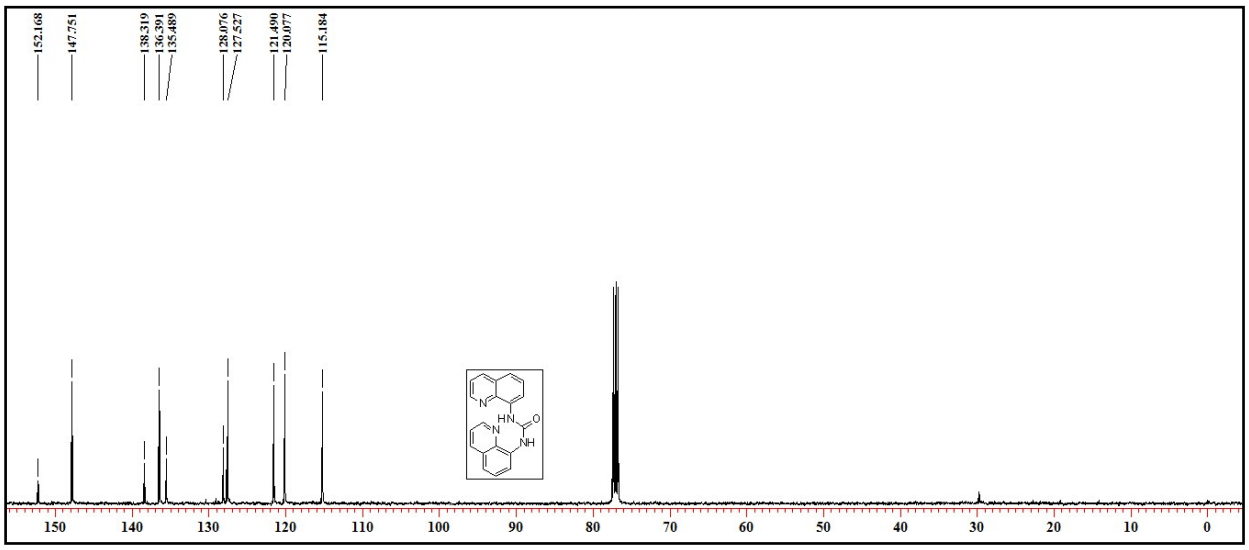


Figure S2. ^{13}C NMR spectrum of **1y** in $CDCl_3$.

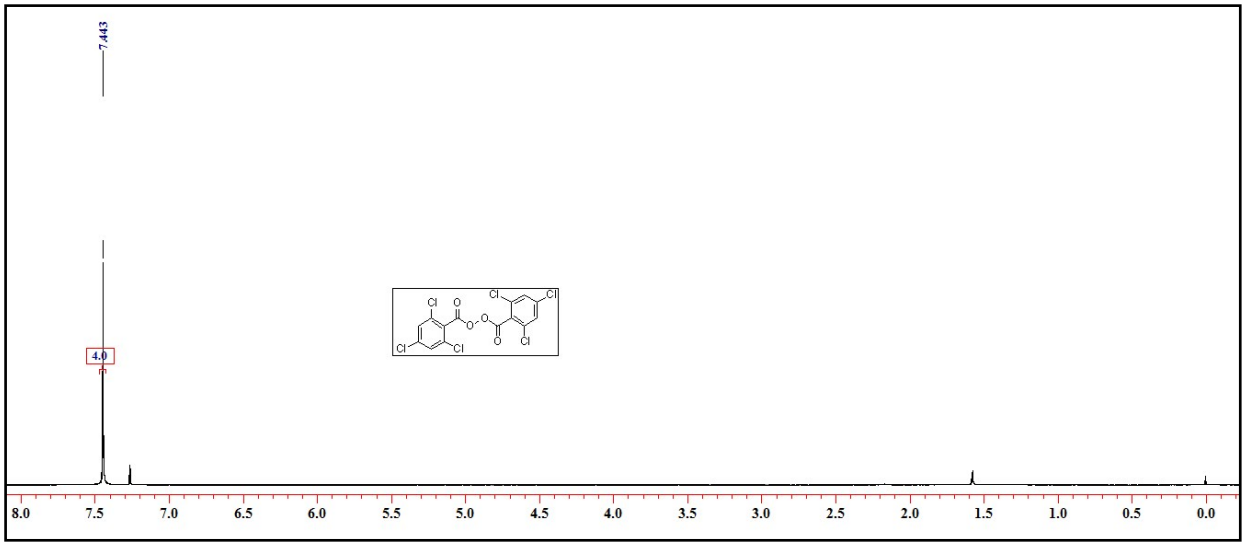


Figure S3. ^{1}H NMR spectrum of **1ae** in $CDCl_3$.

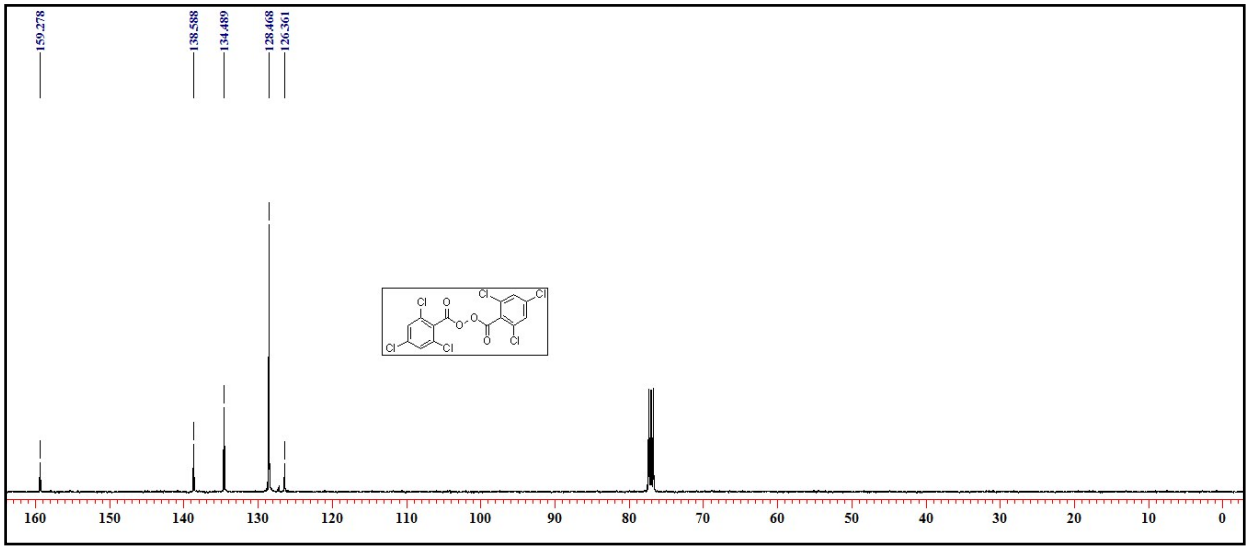


Figure S4. ^{13}C NMR spectrum of **1ae** in $CDCl_3$.

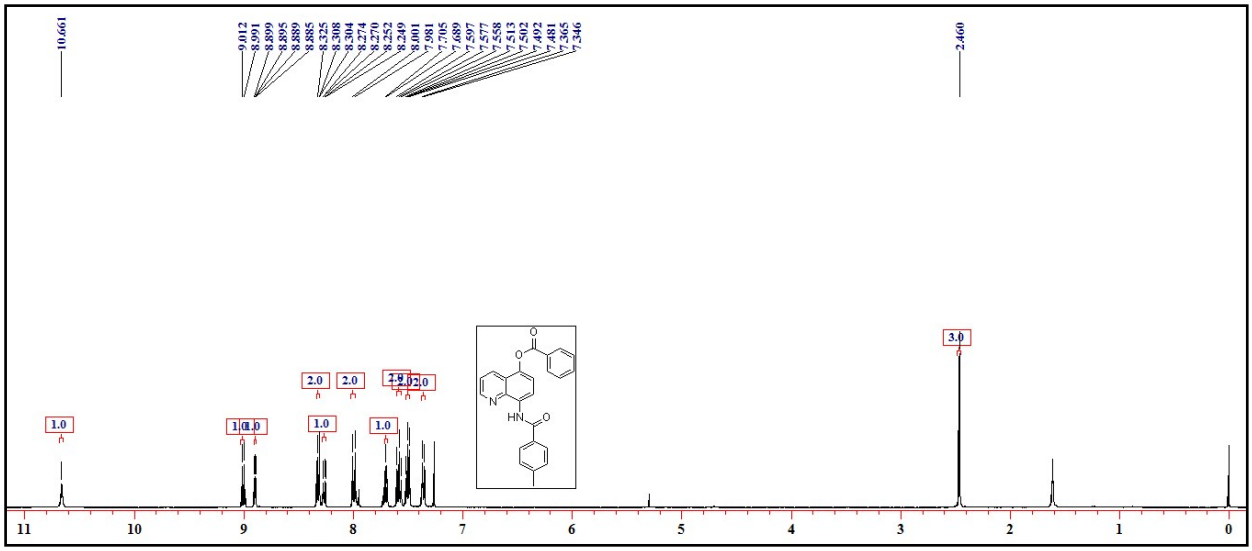


Figure S5. ^{1}H NMR spectrum of **2a** in $CDCl_3$+ CD_2Cl_2.

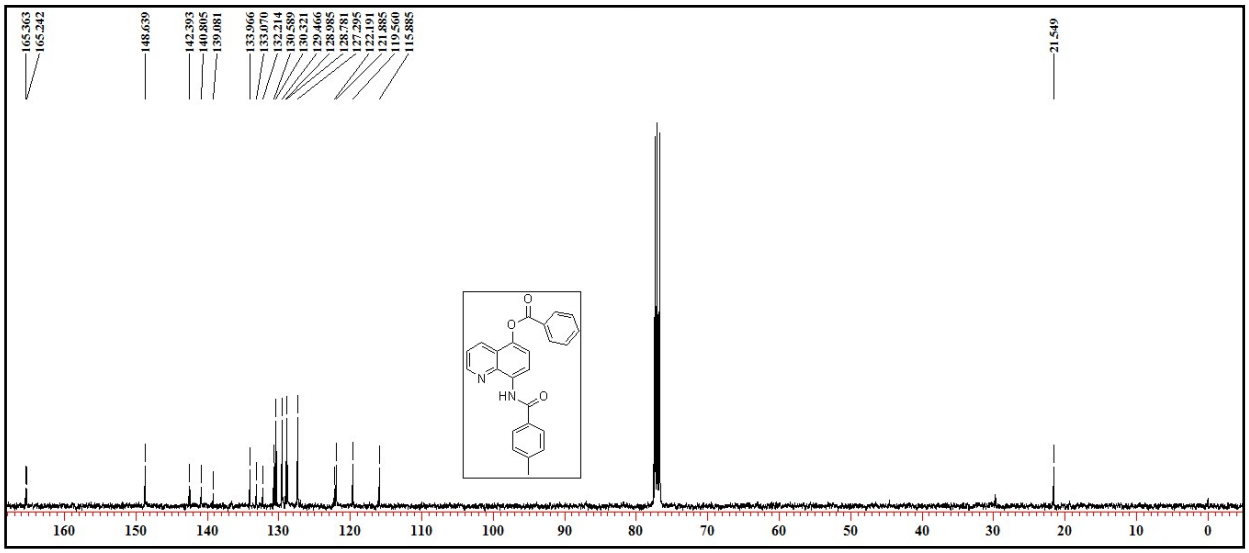


Figure S6. ^{13}C NMR spectrum of **2a** in $CDCl_3$.

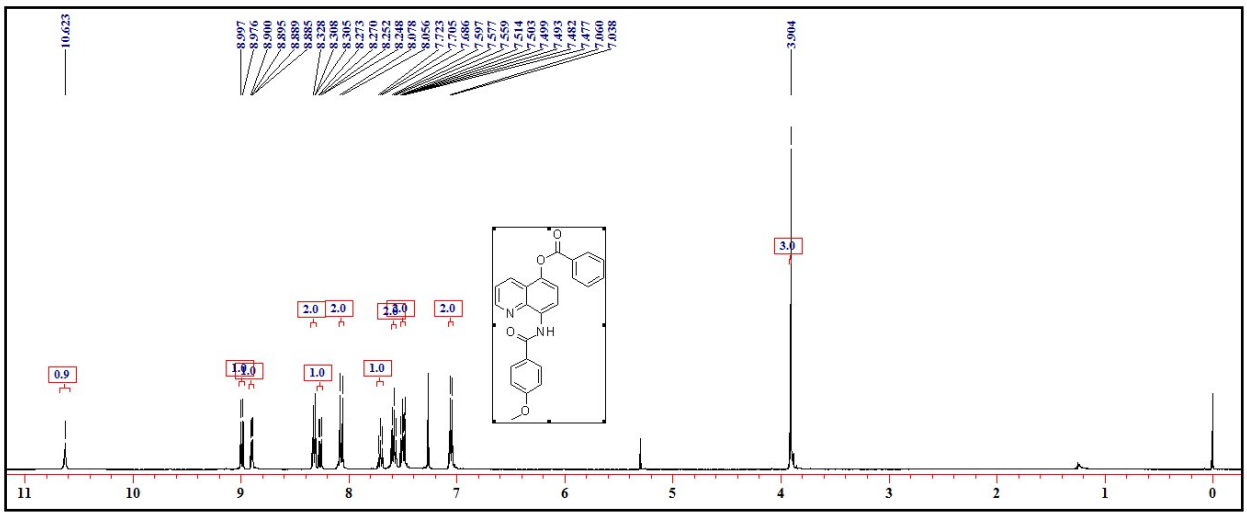


Figure S7. ^{1}H NMR spectrum of **2b** in $CDCl_3$+ CD_2Cl_2.

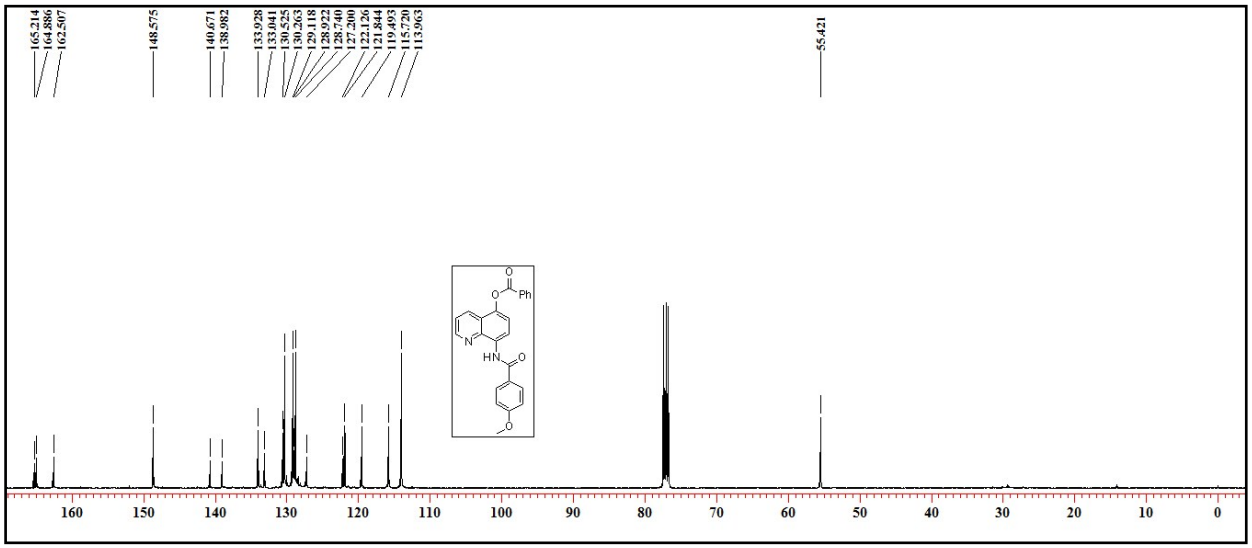


Figure S8. ^{13}C NMR spectrum of **2b** in $CDCl_3$.

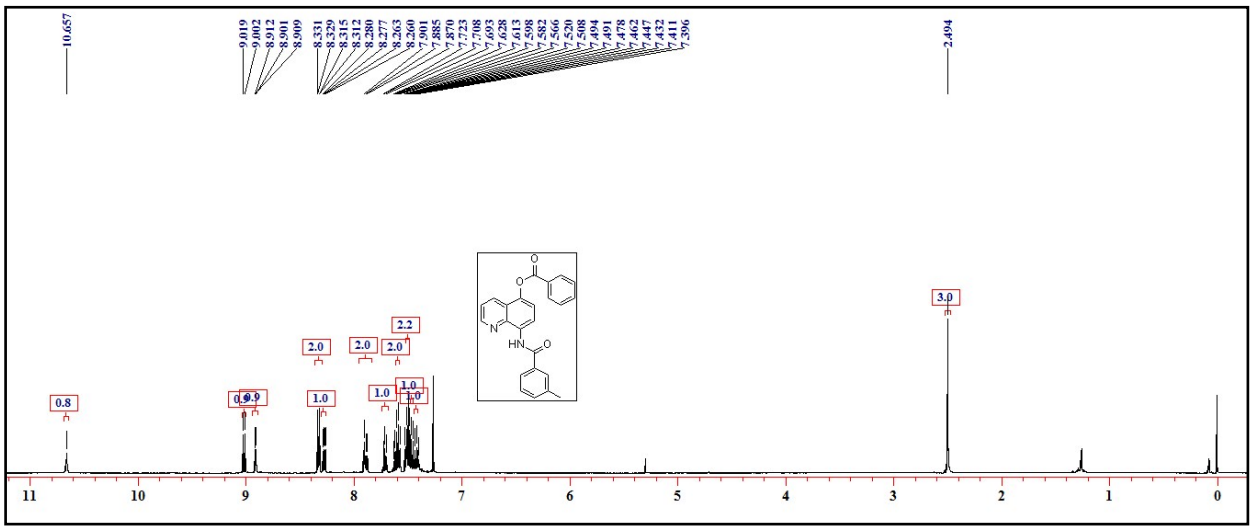


Figure S9. ^{1}H NMR spectrum of **2c** in $CDCl_3$+CD_2Cl_2.

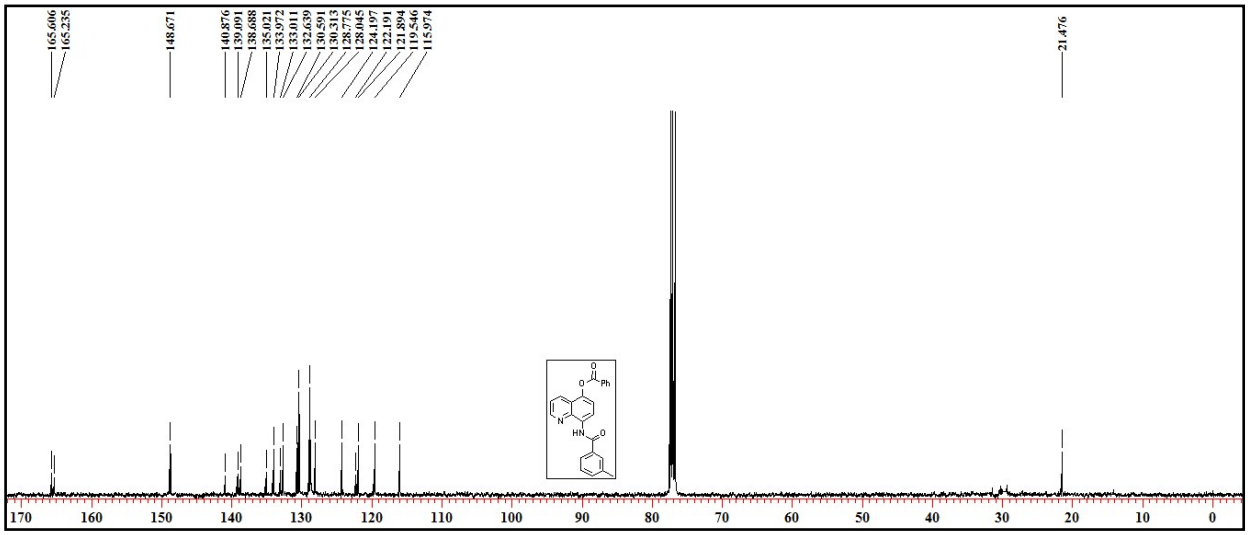


Figure S10. ^{13}C NMR spectrum of **2c** in $CDCl_3$.

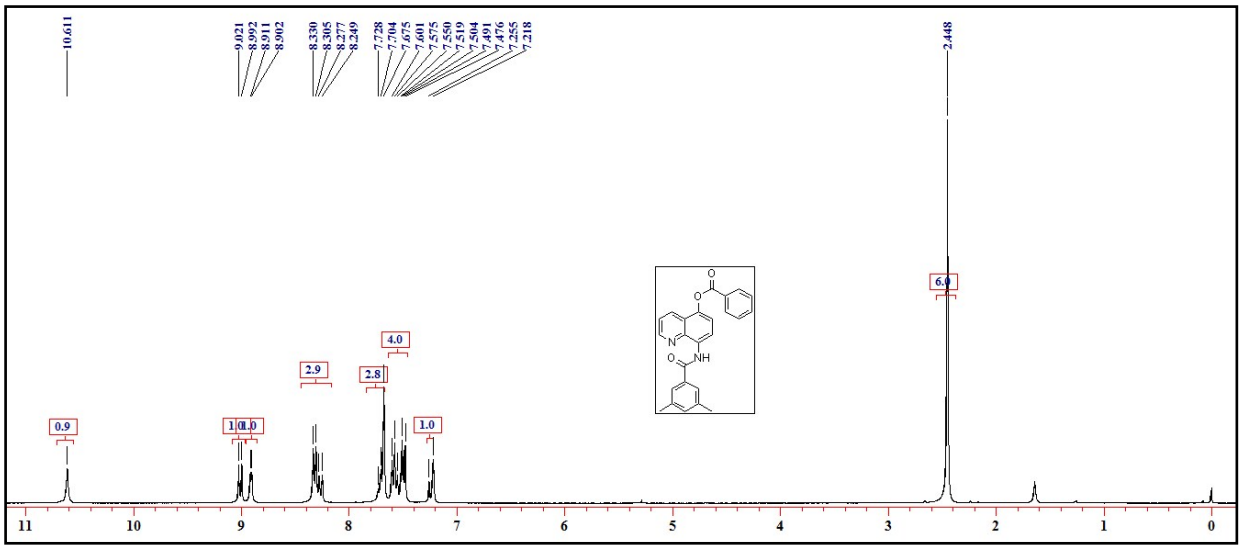


Figure S11. ^{1}H NMR spectrum of **2d** in $CDCl_3$.

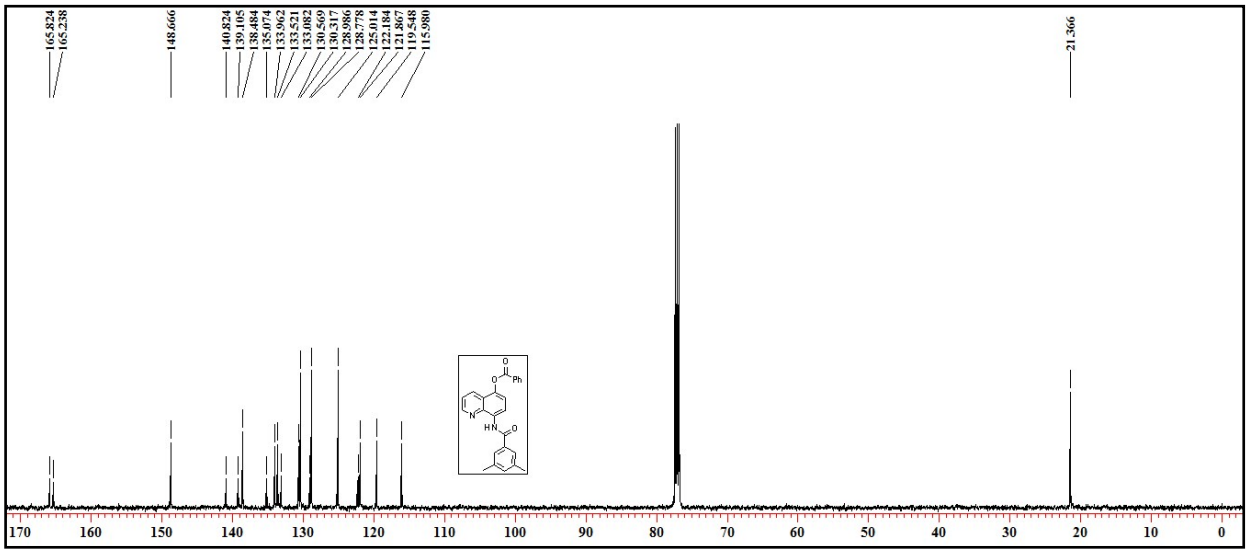


Figure S12. ^{13}C NMR spectrum of **2d** in $CDCl_3$.

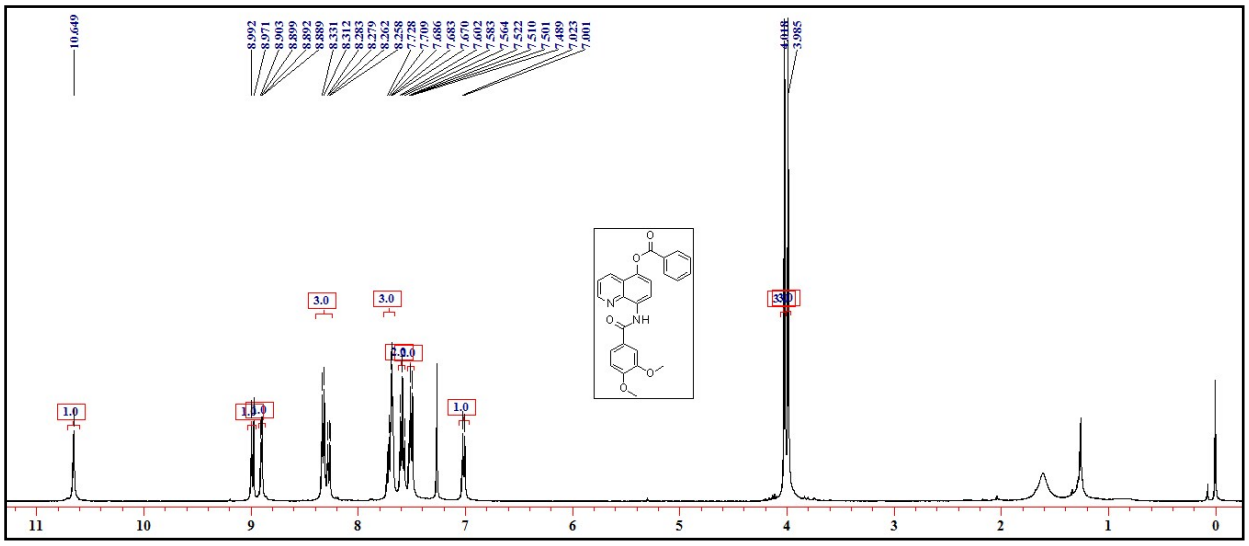


Figure S13. ^{1}H NMR spectrum of **2e** in $CDCl_3$.

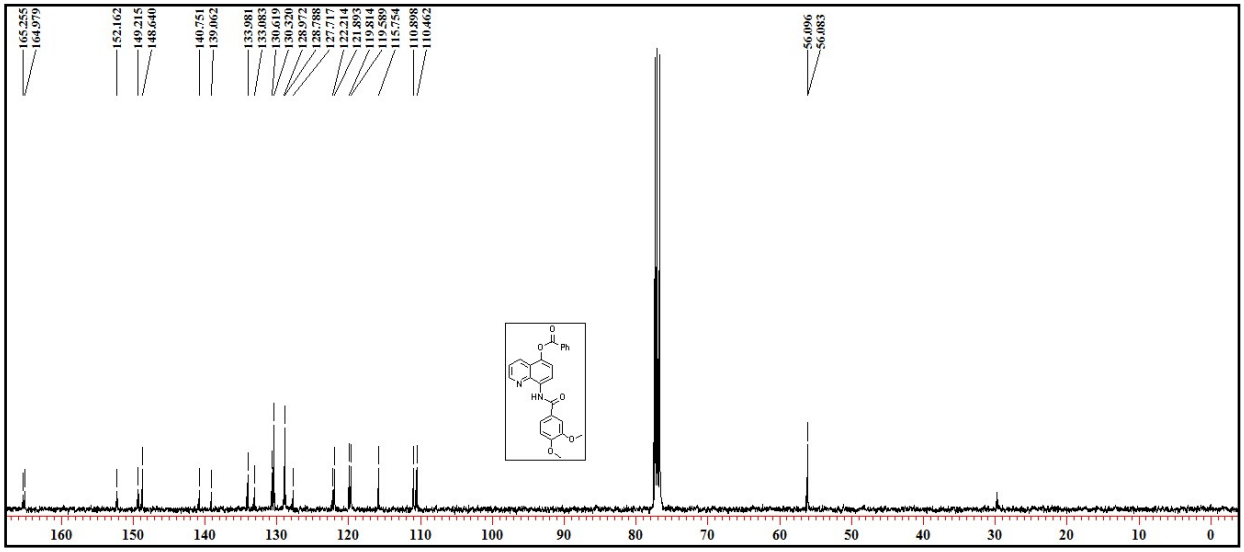


Figure S14. ^{13}C NMR spectrum of **2e** in $CDCl_3$.

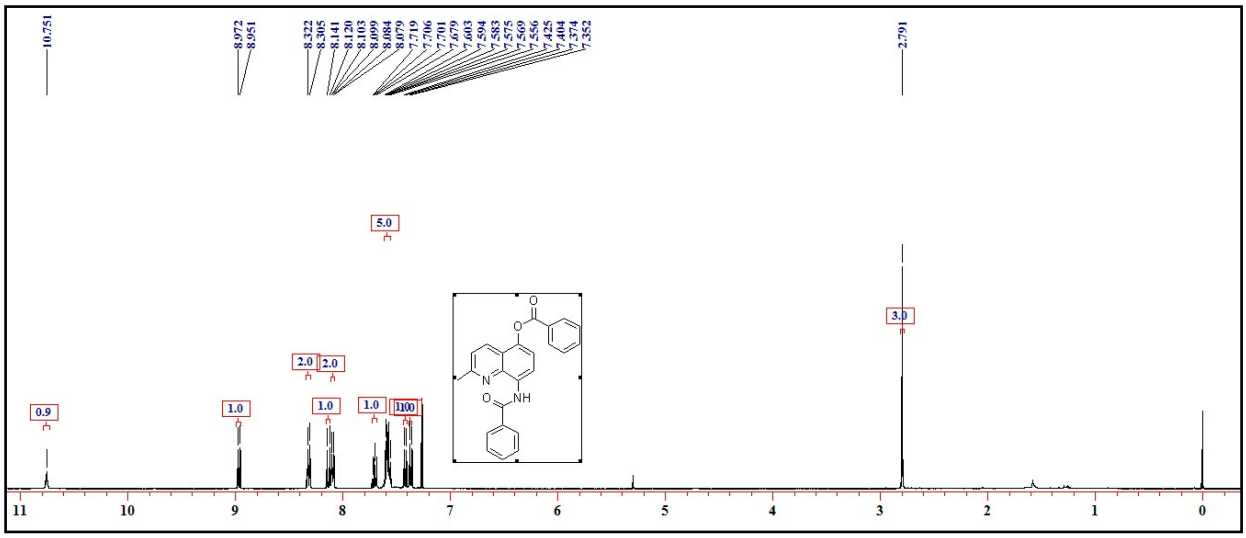


Figure S15. ^{1}H NMR spectrum of **2f** in $CDCl_3$+ CD_2Cl_2.

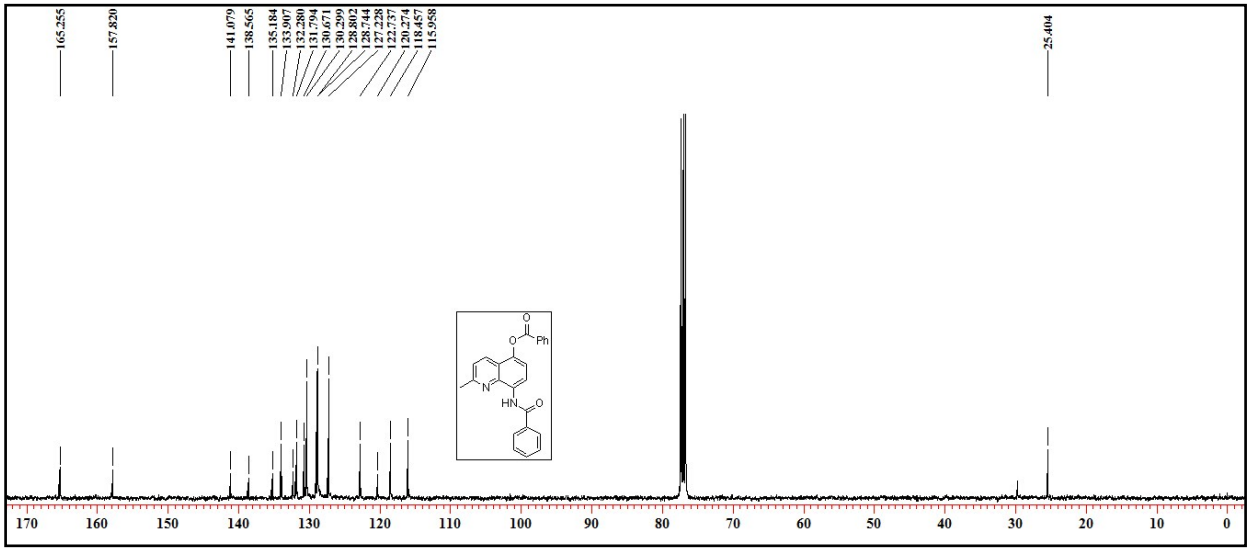


Figure S16. ^{13}C NMR spectrum of **2f** in $CDCl_3$.

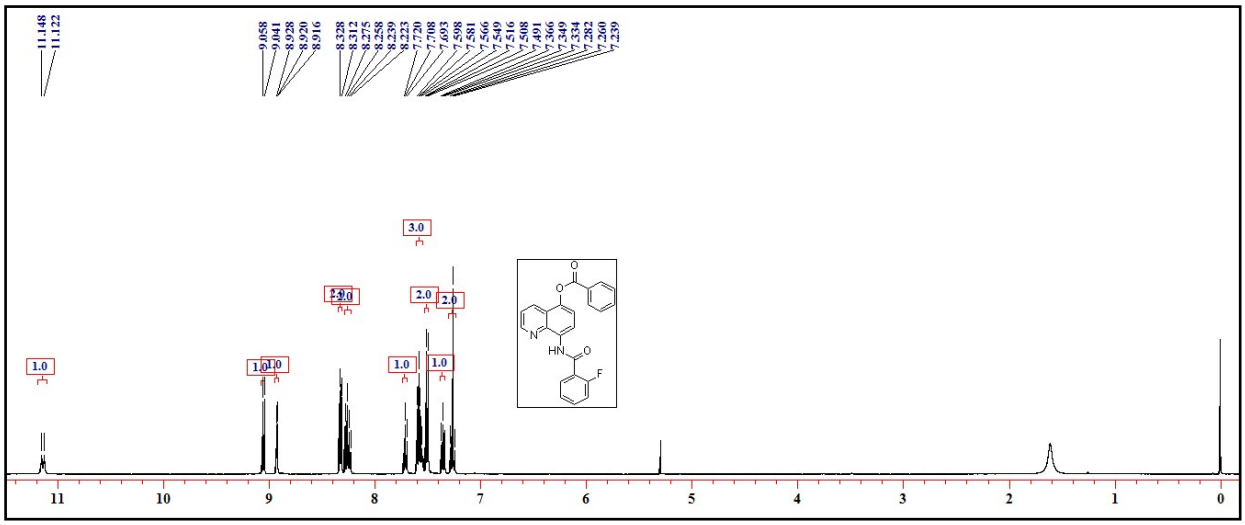


Figure S17. ^{1}H NMR spectrum of **2g** in $CDCl_3$+ CD_2Cl_2.

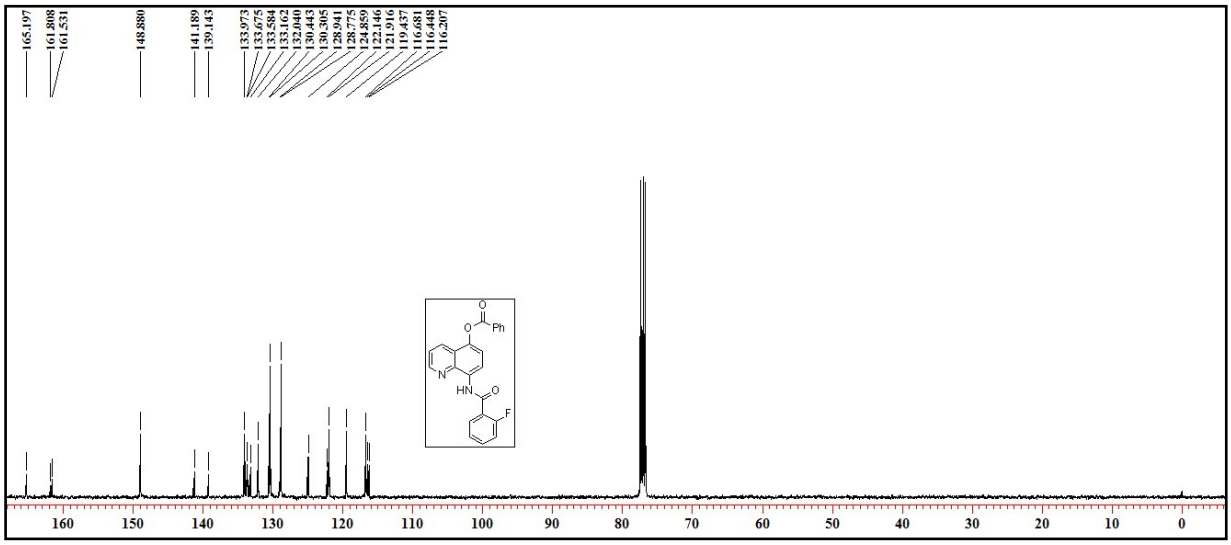


Figure S18. ^{13}C NMR spectrum of **2g** in $CDCl_3$.

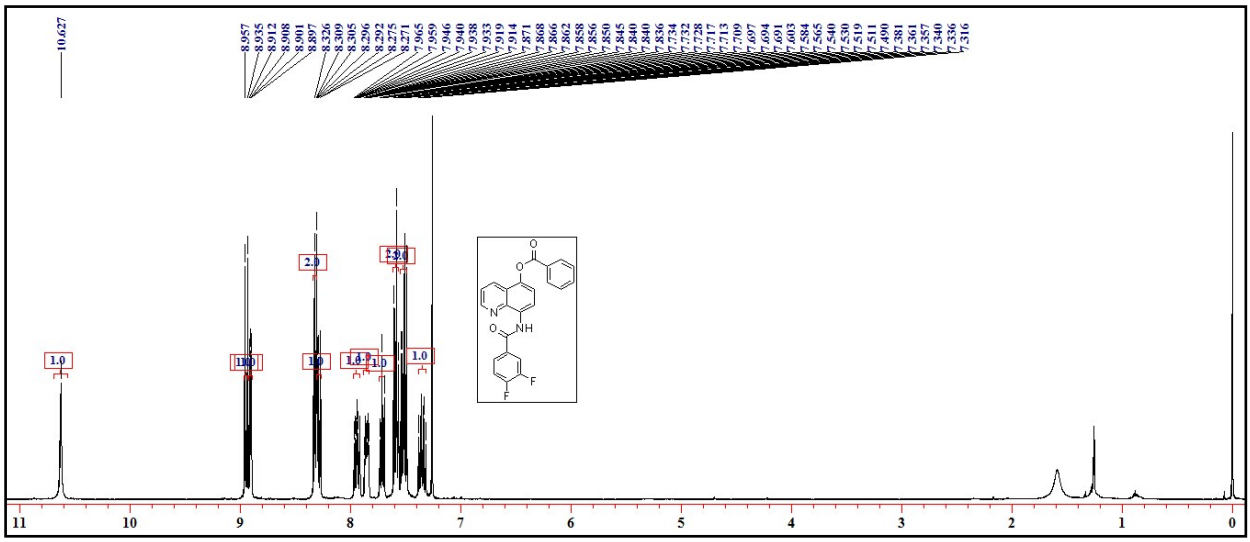


Figure S19. ^{1}H NMR spectrum of **2h** in $CDCl_3$.

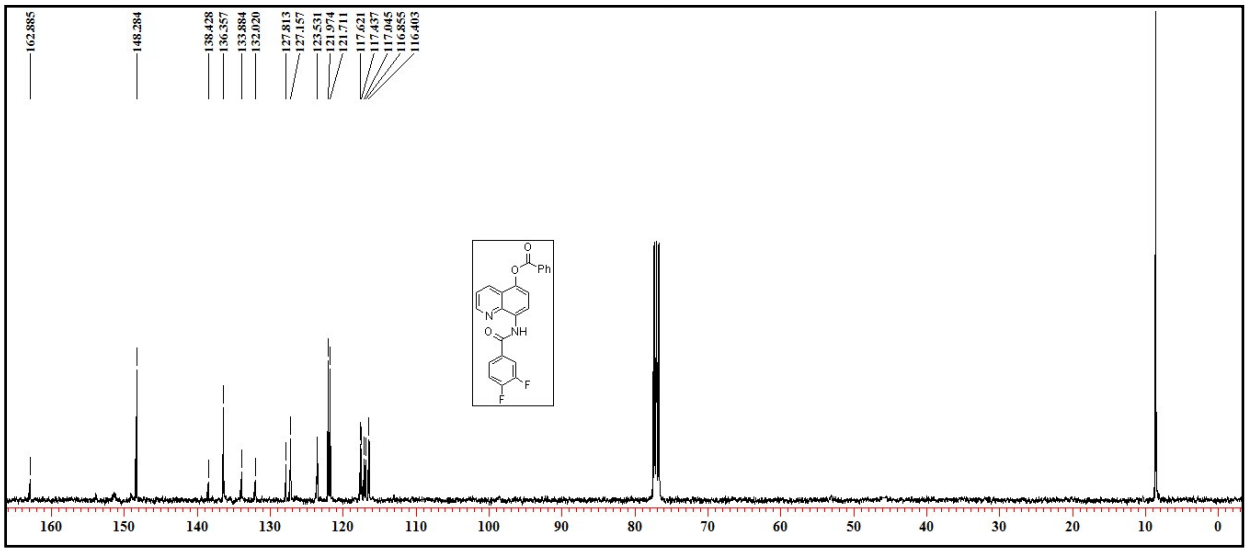


Figure S20. ^{13}C NMR spectrum of **2h** in $CDCl_3$.

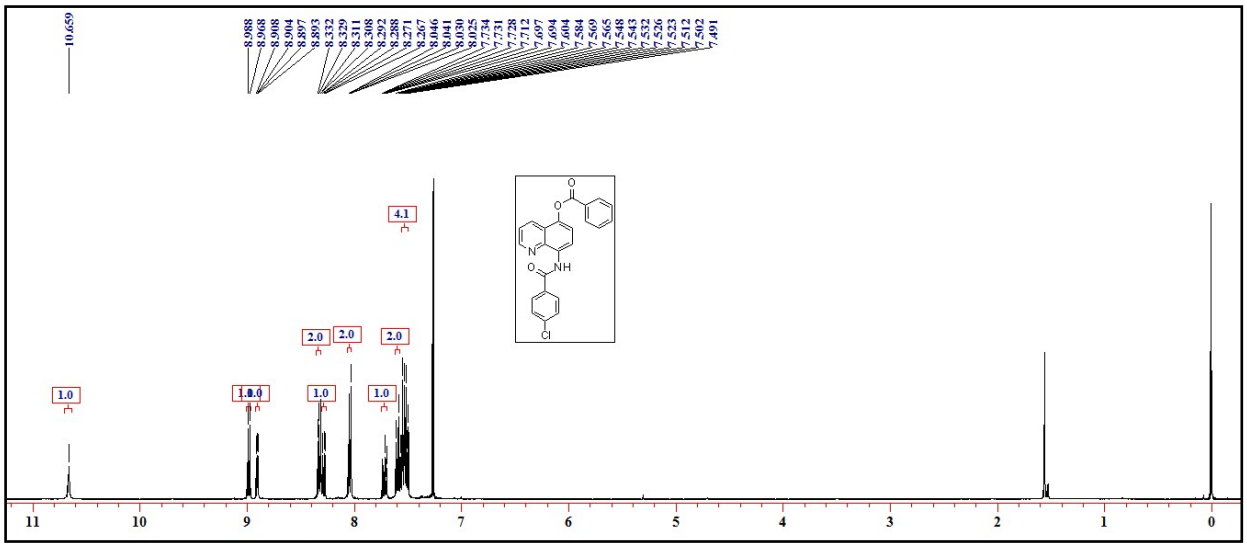


Figure S21. ^{1}H NMR spectrum of **2i** in $CDCl_3$.

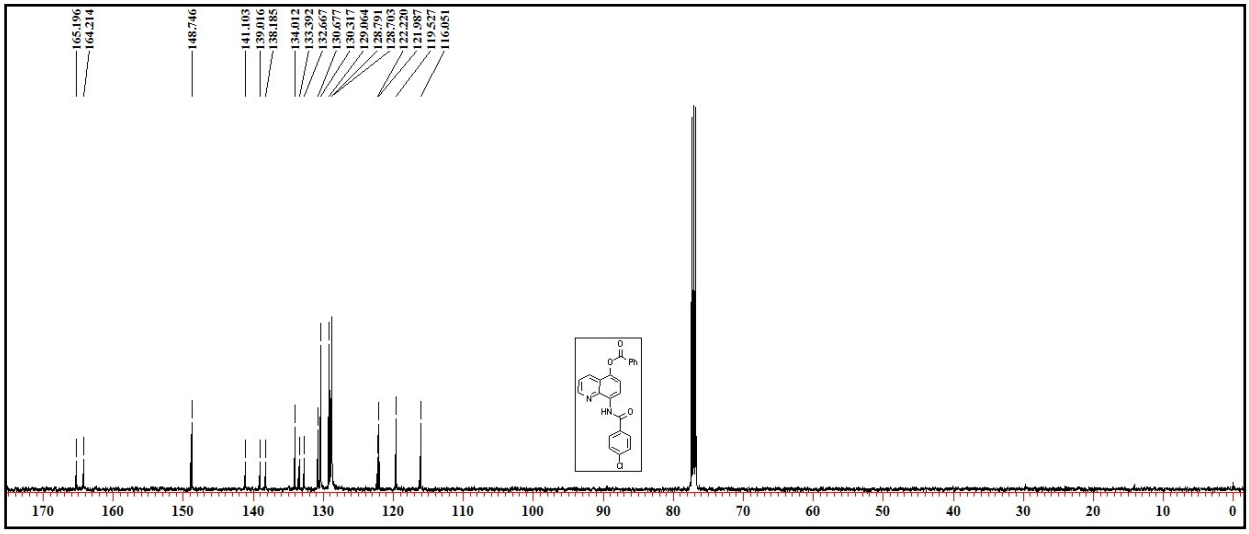


Figure S22. ^{13}C NMR spectrum of **2i** in $CDCl_3$.

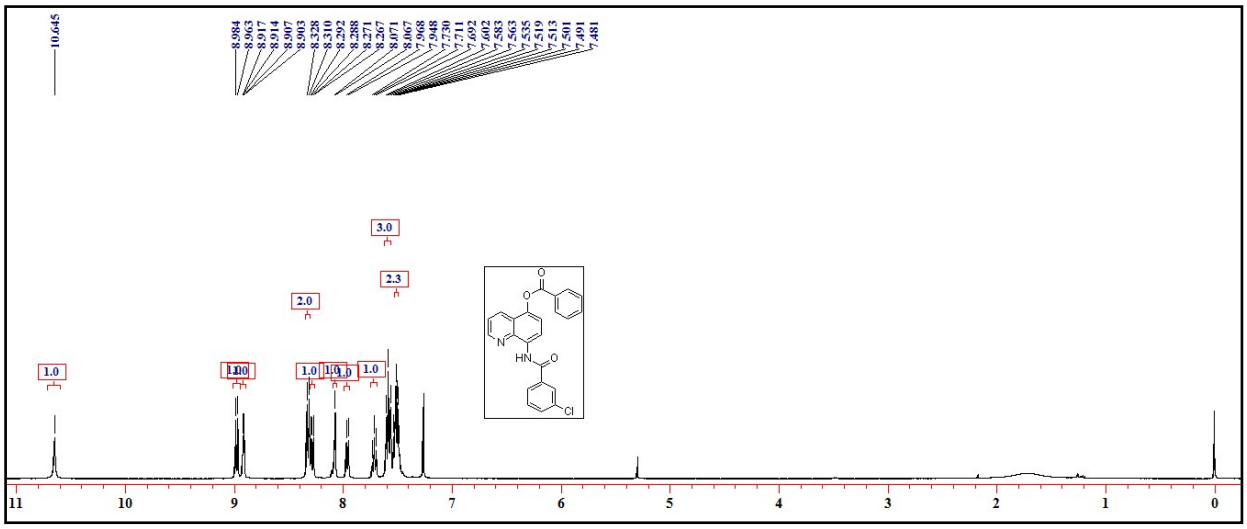


Figure S23. ^{1}H NMR spectrum of **2j** in $CDCl_3$+ CD_2Cl_2.

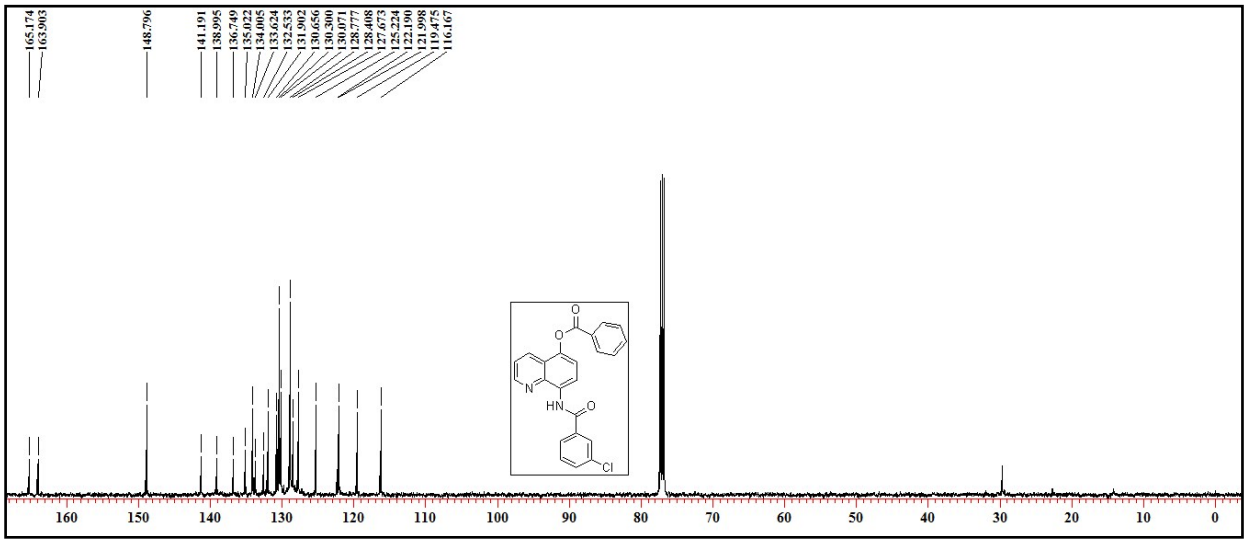


Figure S24. ^{13}C NMR spectrum of **2j** in $CDCl_3$.

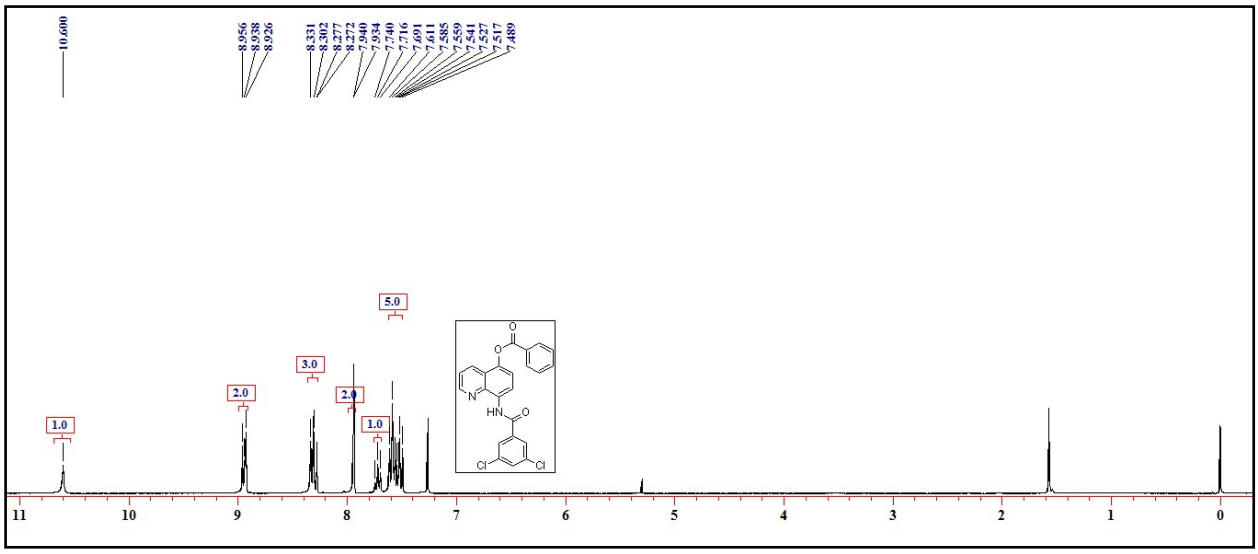


Figure S25. ^{1}H NMR spectrum of **2k** in $CDCl_3$+ CD_2Cl_2.

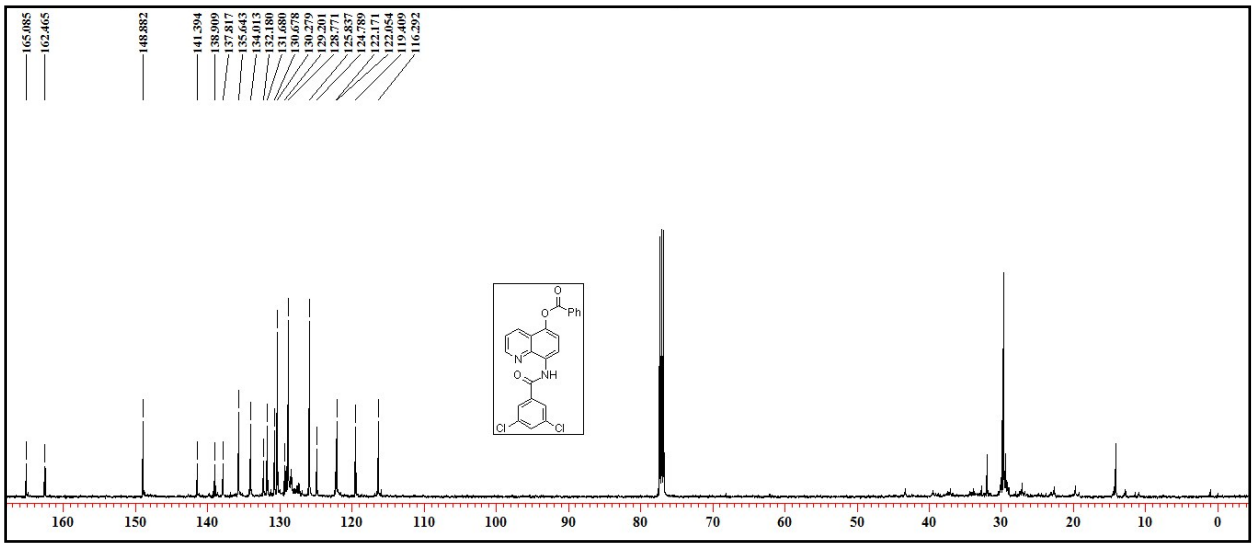


Figure S26. ^{13}C NMR spectrum of **2k** in $CDCl_3$.

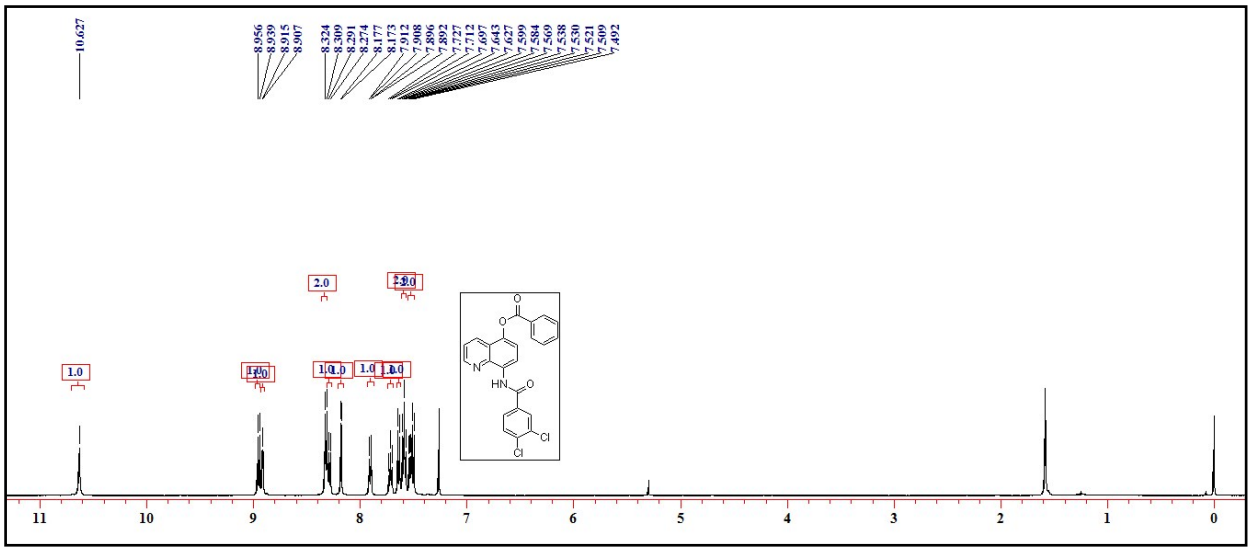


Figure S27. ^{1}H NMR spectrum of **2l** in $CDCl_3$+CD_2Cl_2.

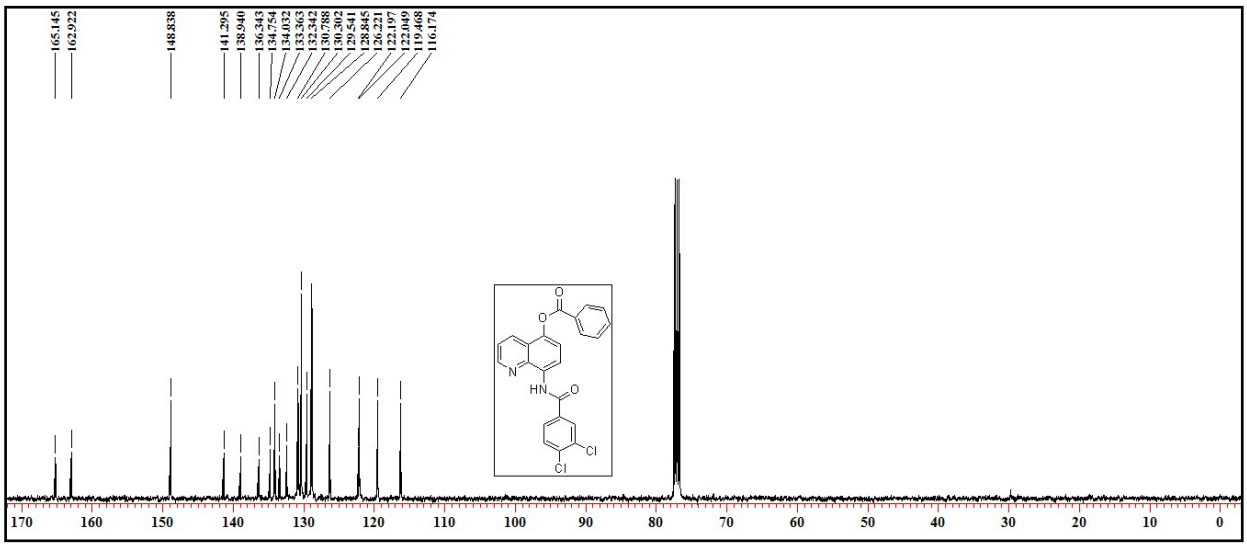


Figure S28. ^{13}C NMR spectrum of **2l** in $CDCl_3$.

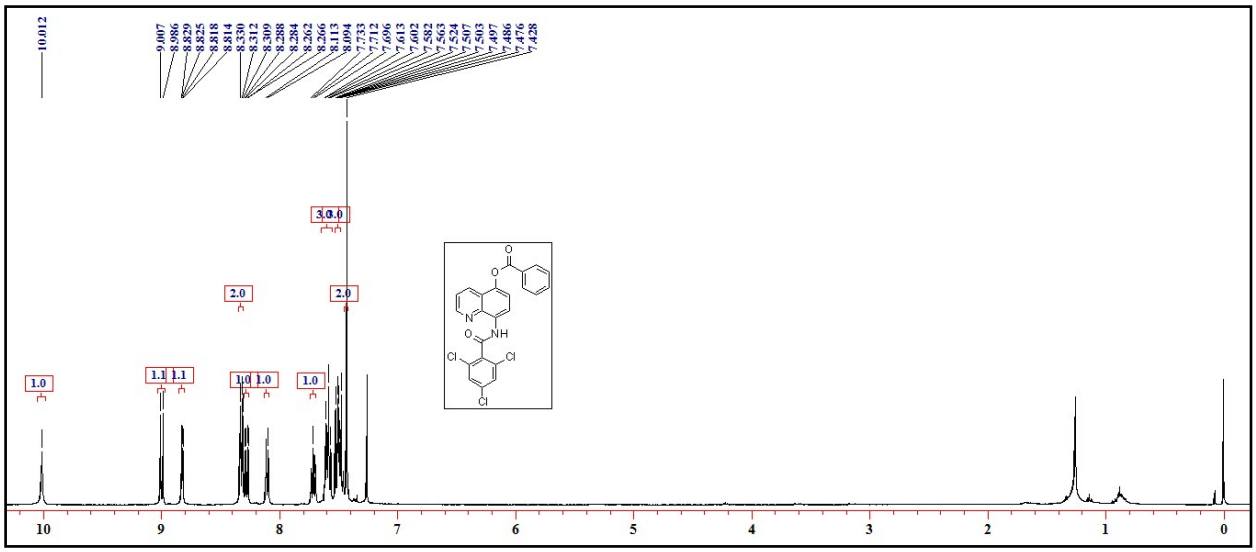


Figure S29. ^{1}H NMR spectrum of **2m** in $CDCl_3$.

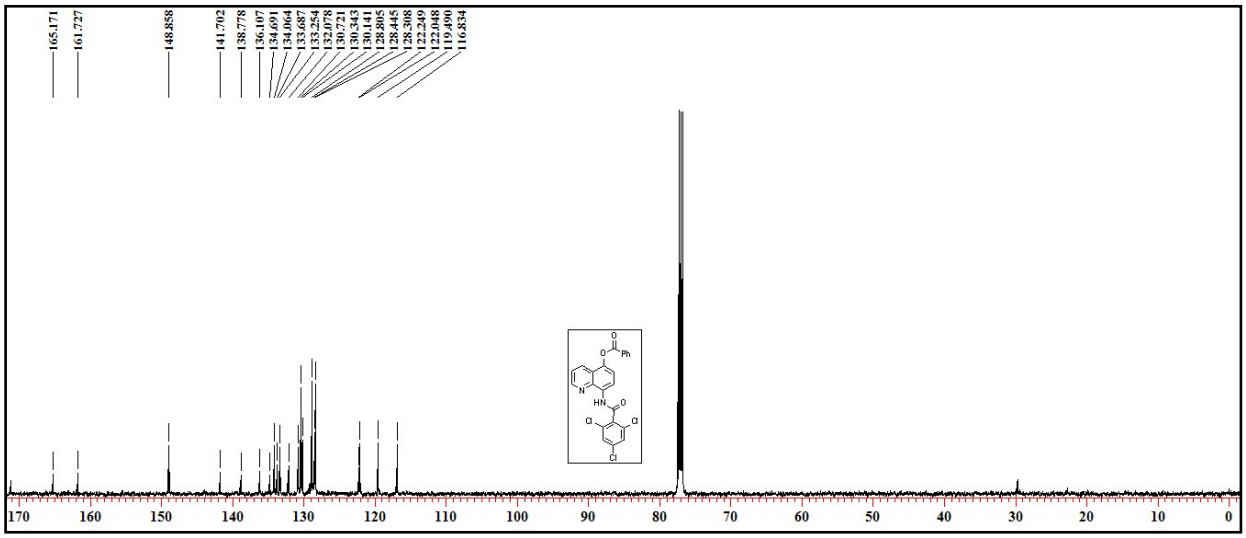


Figure S30. ^{13}C NMR spectrum of **2m** in $CDCl_3$.

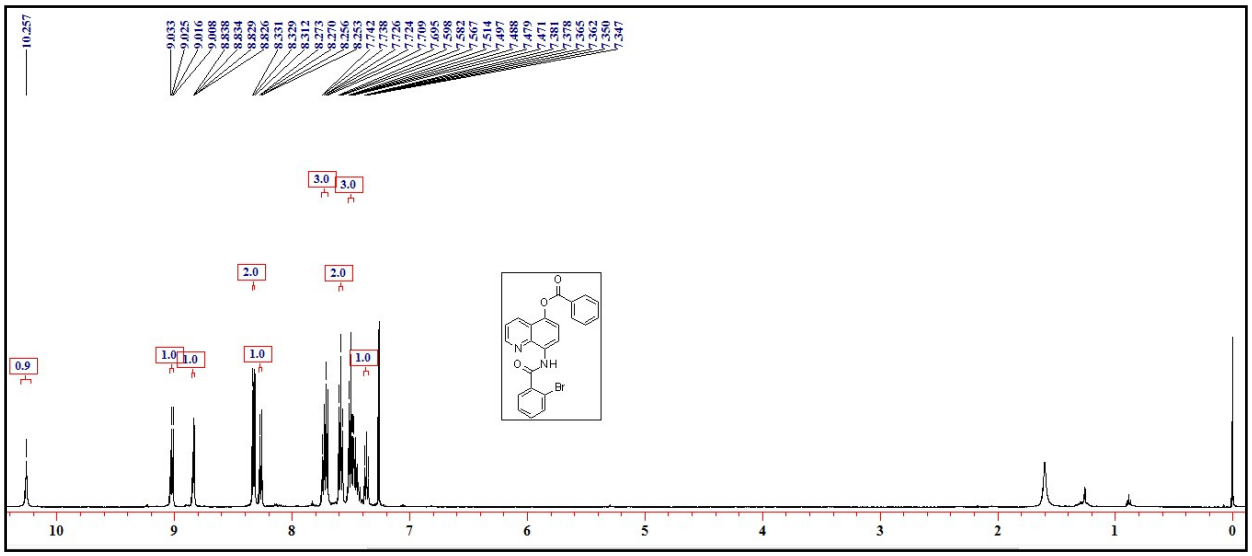


Figure S31. ^{1}H NMR spectrum of **2n** in $CDCl_3$.

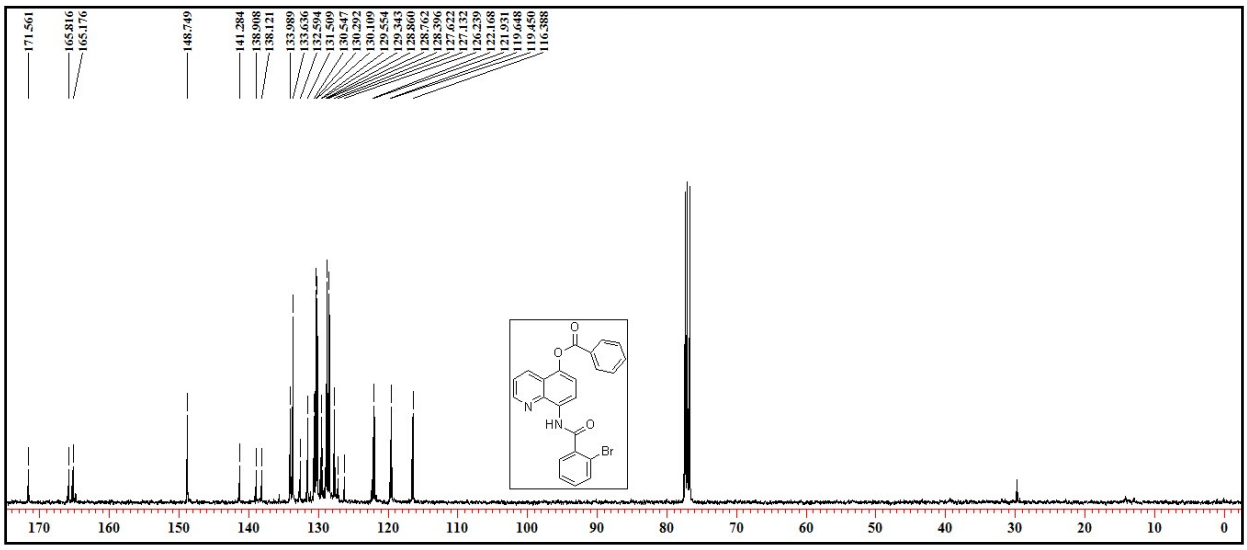


Figure S32. ^{13}C NMR spectrum of **2n** in $CDCl_3$.

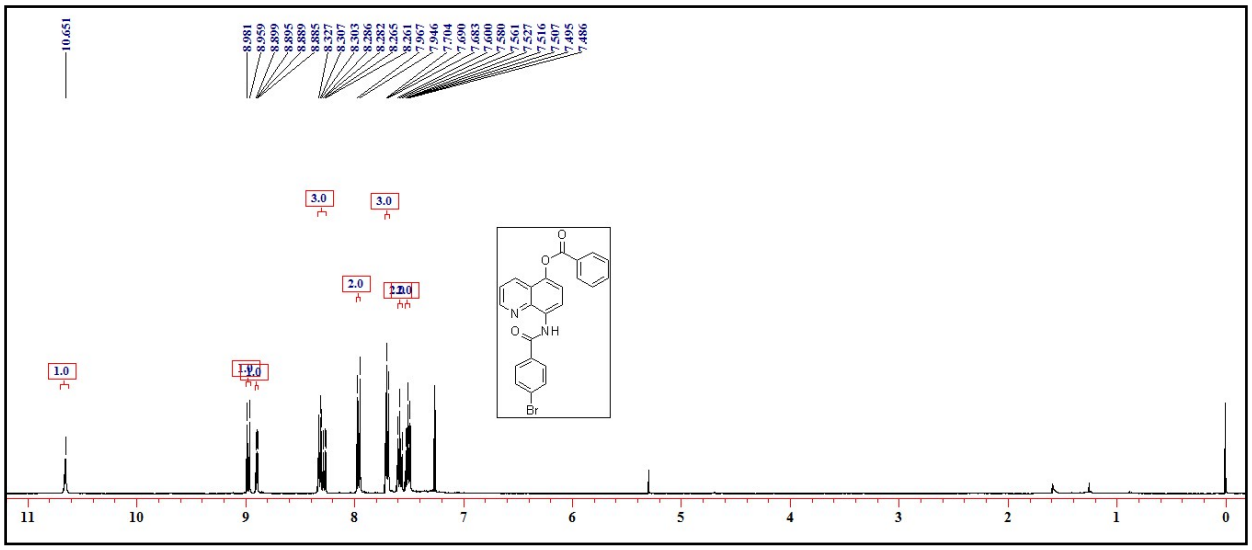


Figure S33. ^{1}H NMR spectrum of **2o** in $CDCl_3$+ CD_2Cl_2.

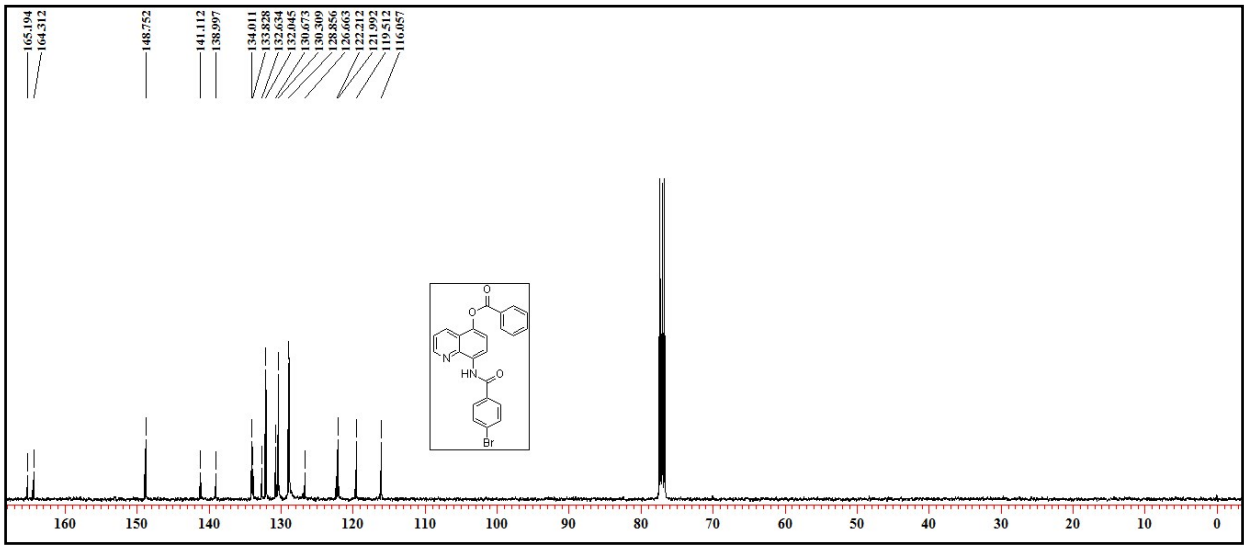


Figure S34. ^{13}C NMR spectrum of **2o** in $CDCl_3$.

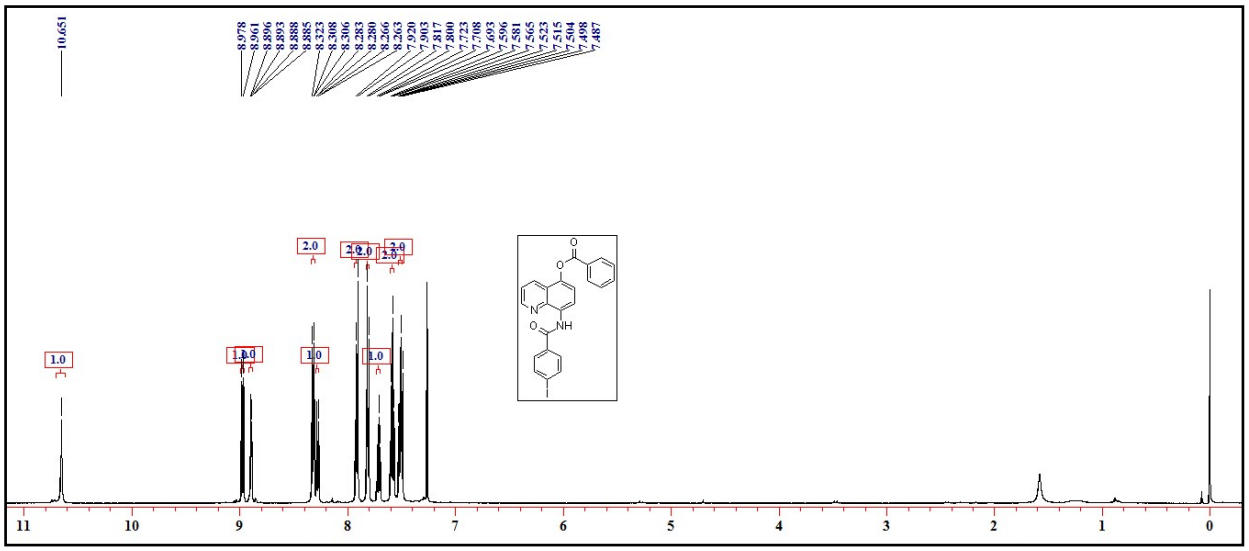


Figure S35. ^{1}H NMR spectrum of **2p** in $CDCl_3$.

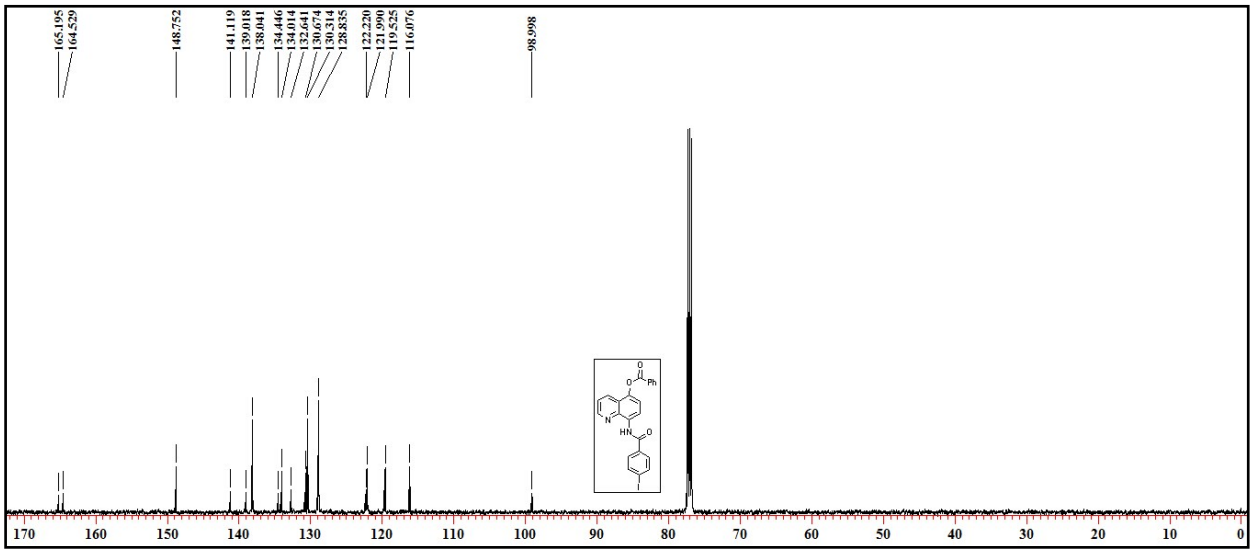


Figure S36. ^{13}C NMR spectrum of **2p** in $CDCl_3$.

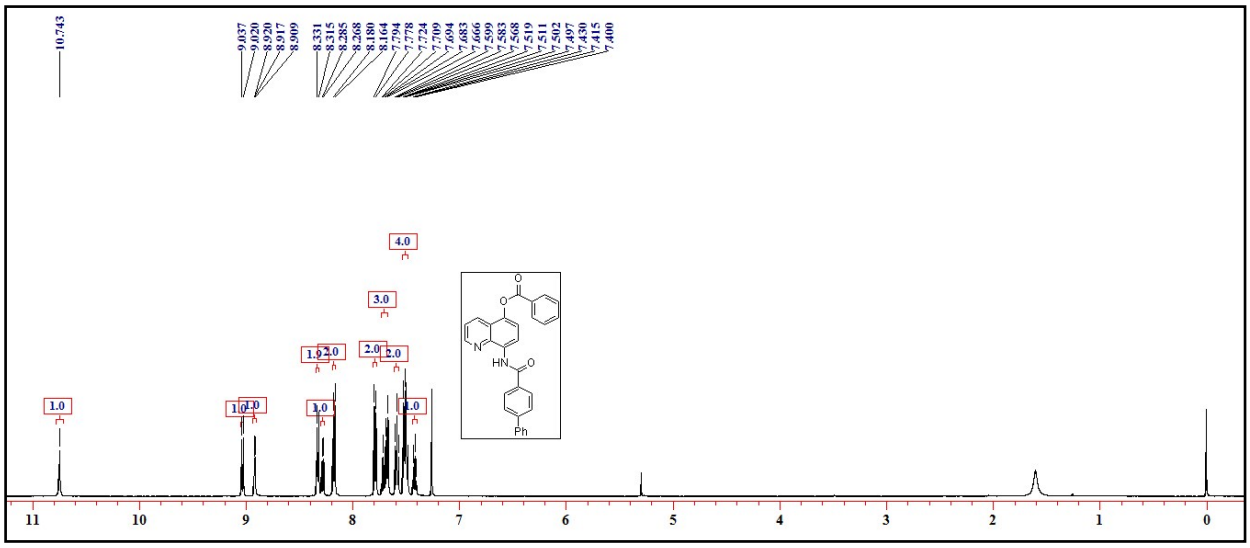


Figure S37. ^{1}H NMR spectrum of **2q** in $CDCl_3$+ CD_2Cl_2.

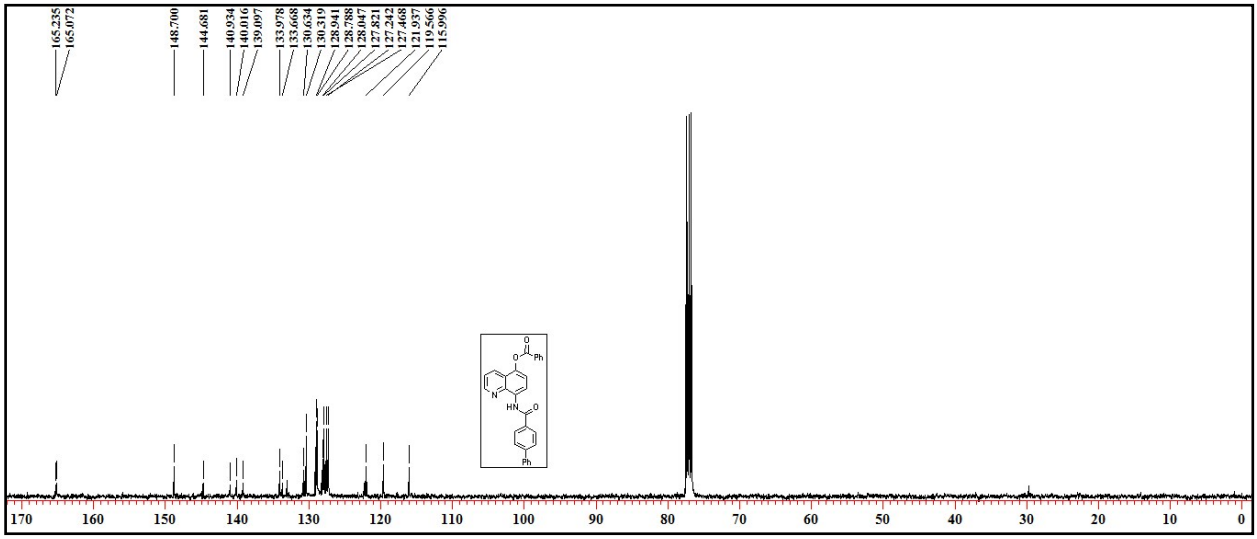


Figure S38. ^{13}C NMR spectrum of **2q** in $CDCl_3$.

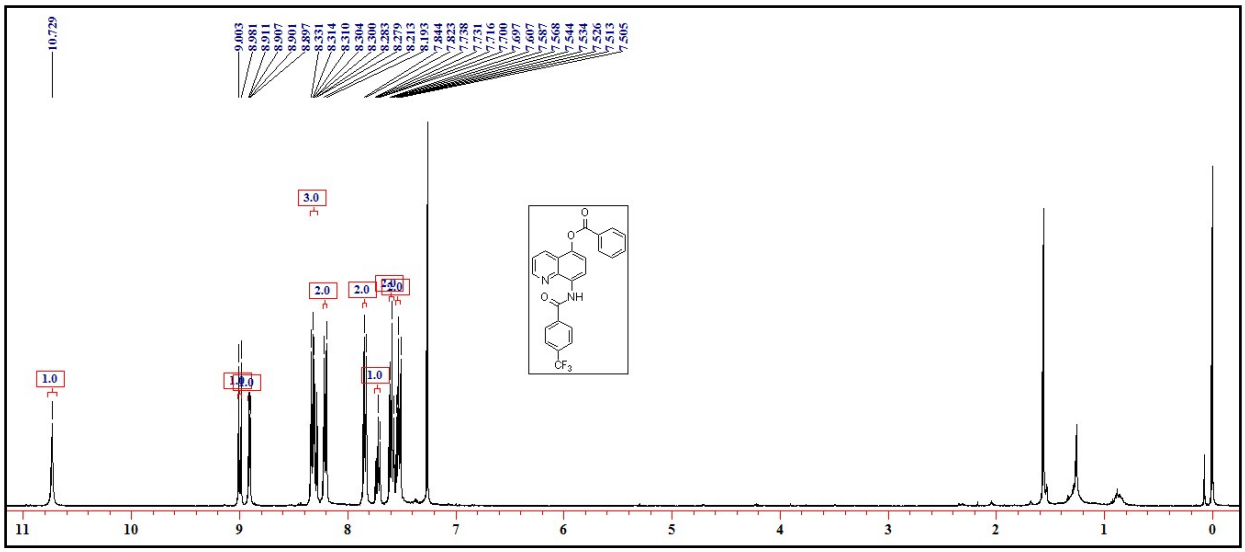


Figure S39. ^{1}H NMR spectrum of **2r** in $CDCl_3$.

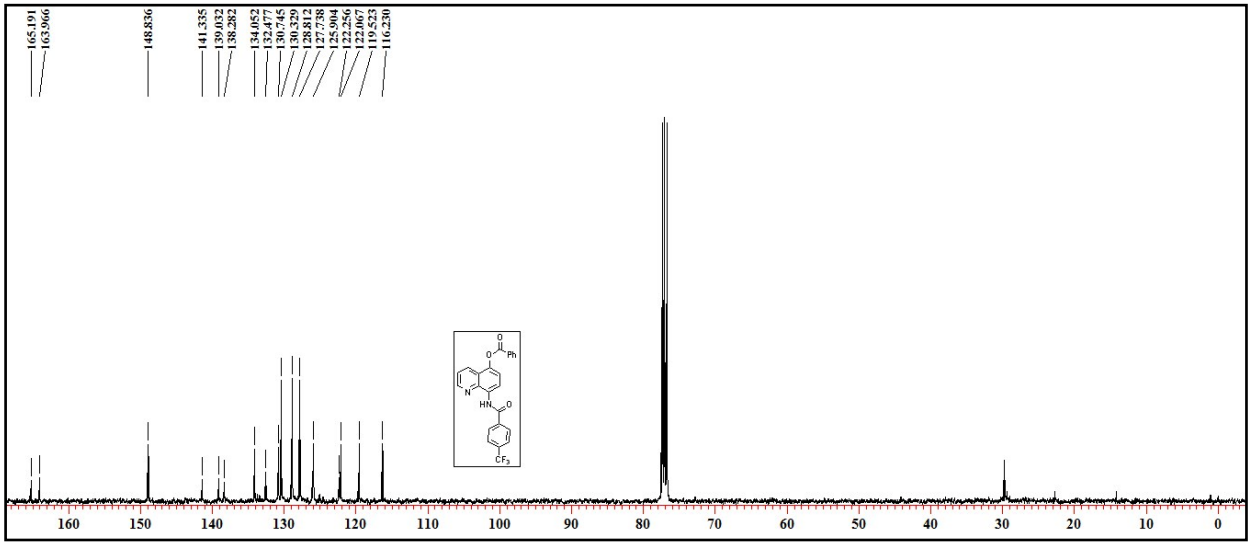


Figure S40. ^{13}C NMR spectrum of **2r** in $CDCl_3$.

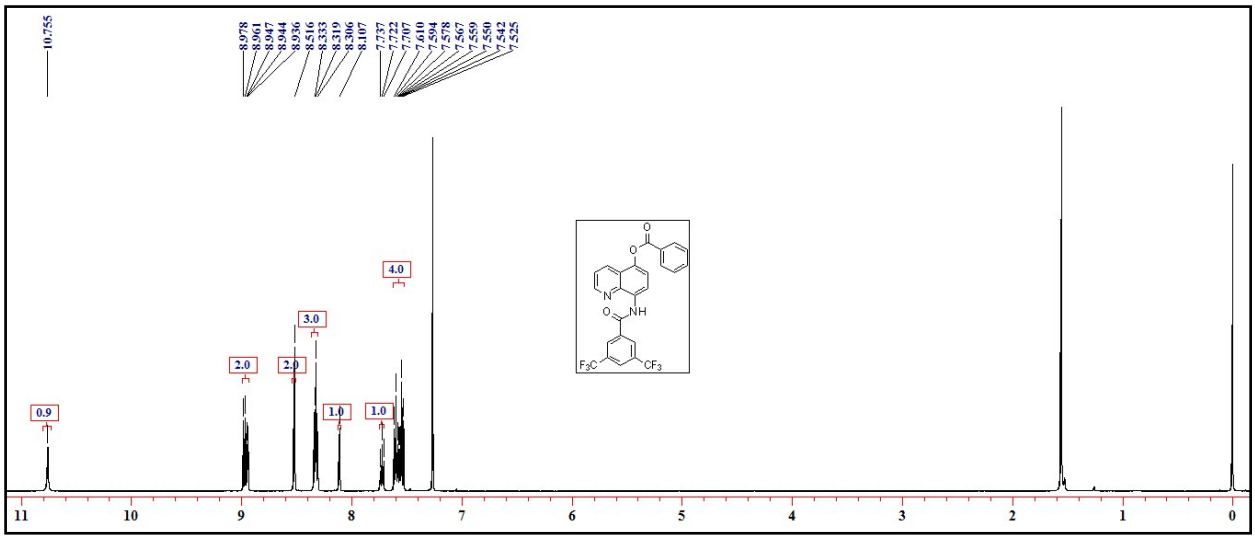


Figure S41. ^{1}H NMR spectrum of **2s** in $CDCl_3$.

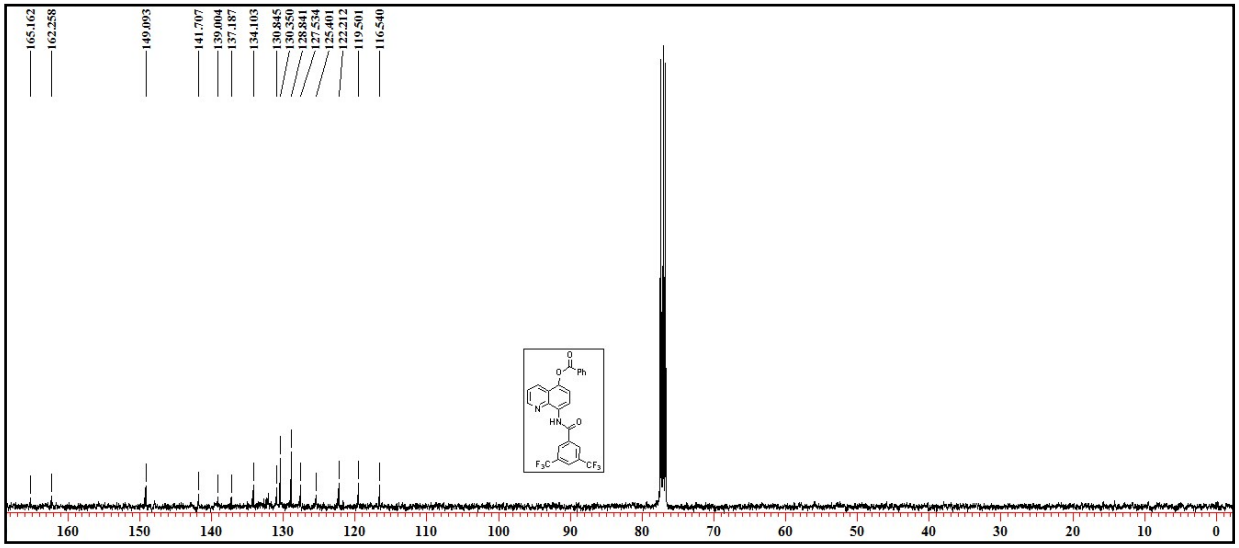


Figure S42. ^{13}C NMR spectrum of **2s** in $CDCl_3$.

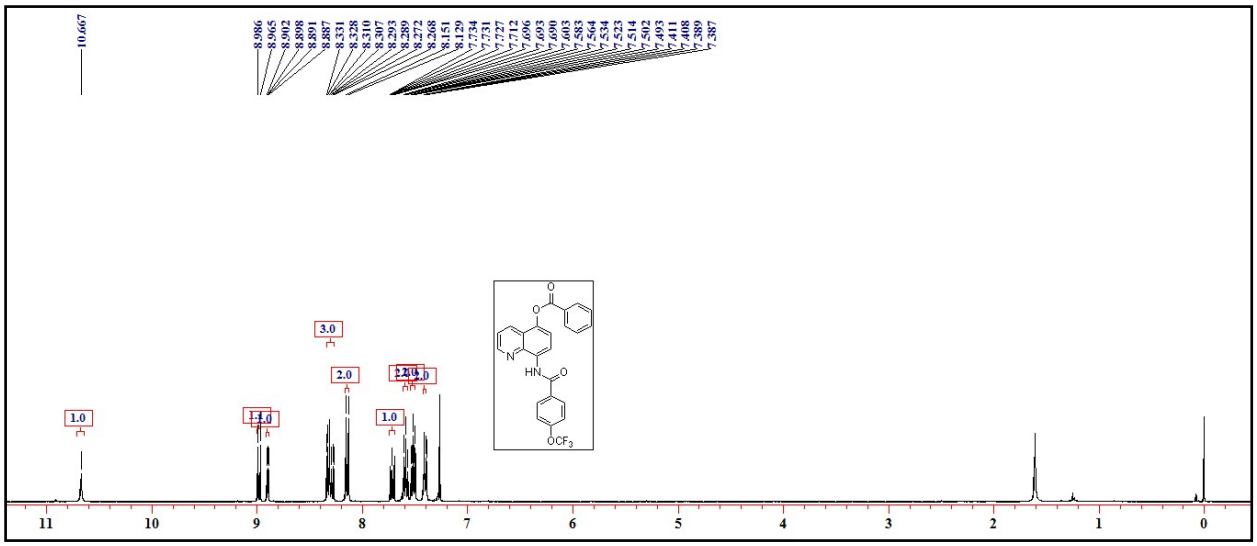


Figure S43. ^{1}H NMR spectrum of **2t** in $CDCl_3$.

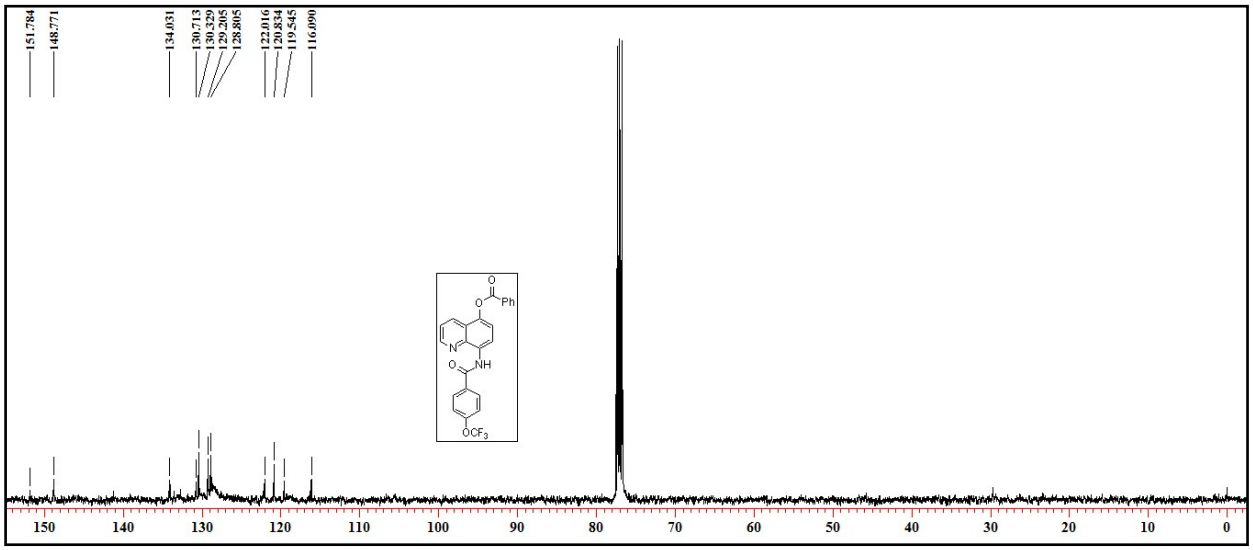


Figure S44. ^{13}C NMR spectrum of **2t** in $CDCl_3$.

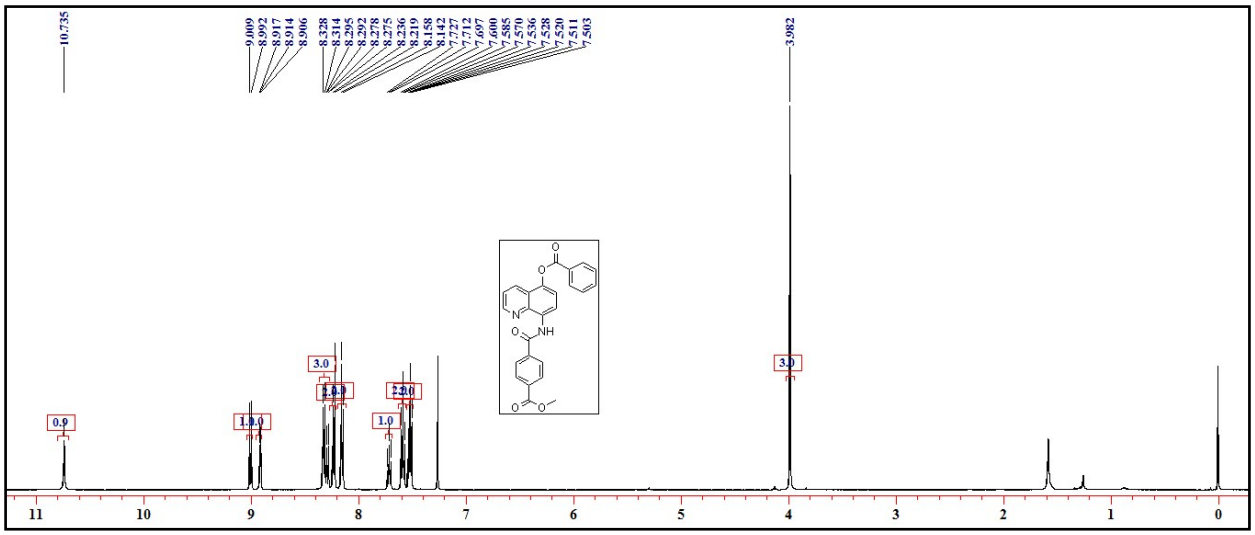


Figure S45. ^{1}H NMR spectrum of **2u** in $CDCl_3$.

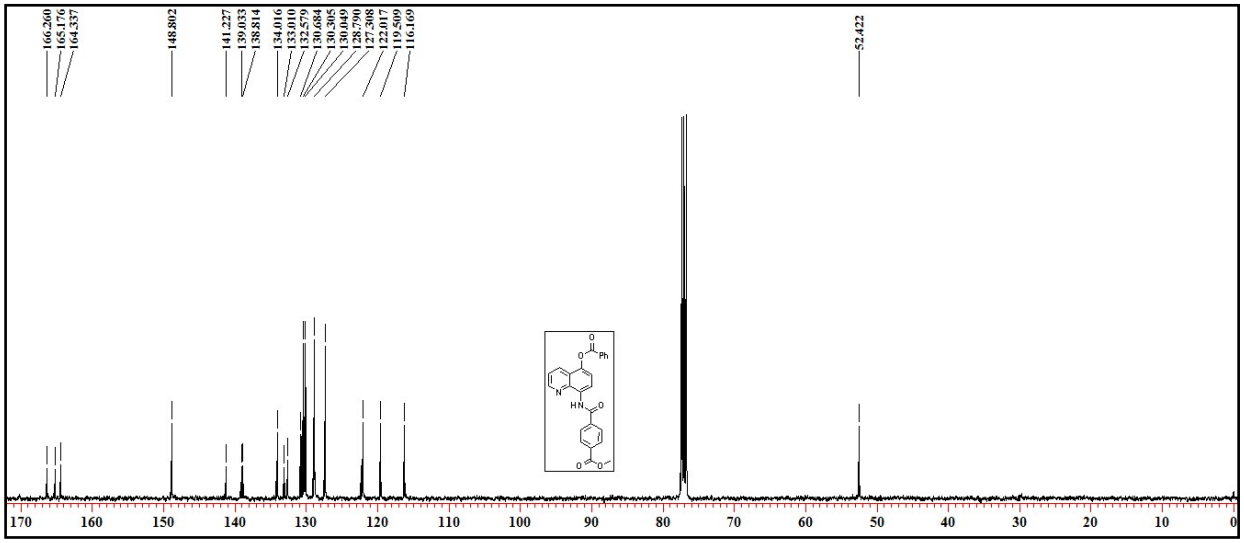


Figure S46. ^{13}C NMR spectrum of **2u** in $CDCl_3$.

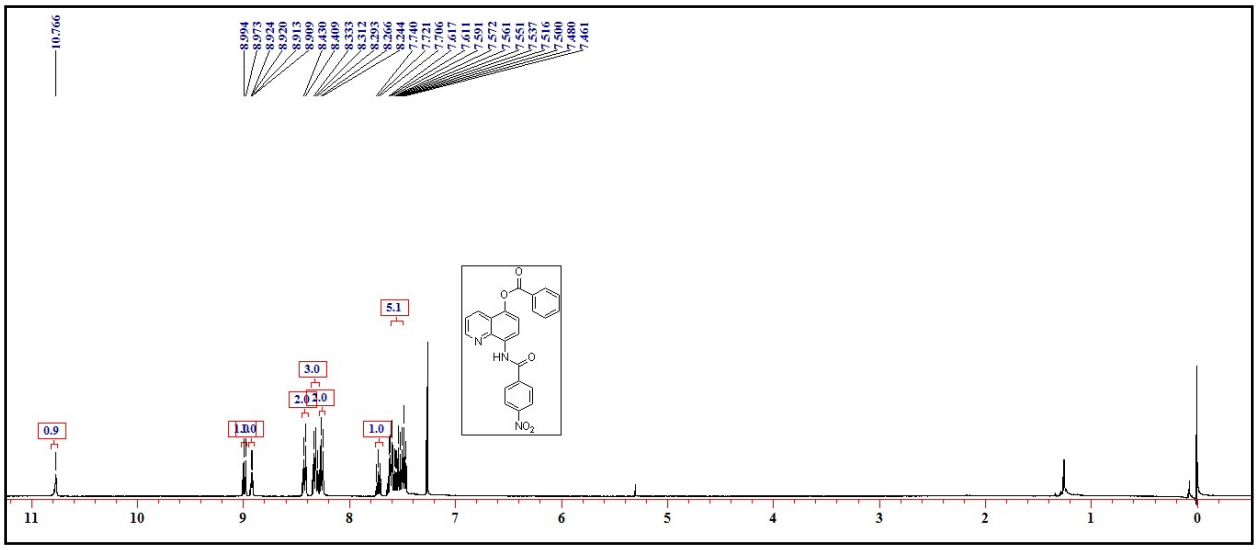


Figure S47. ^{1}H NMR spectrum of **2v** in $CDCl_3$.

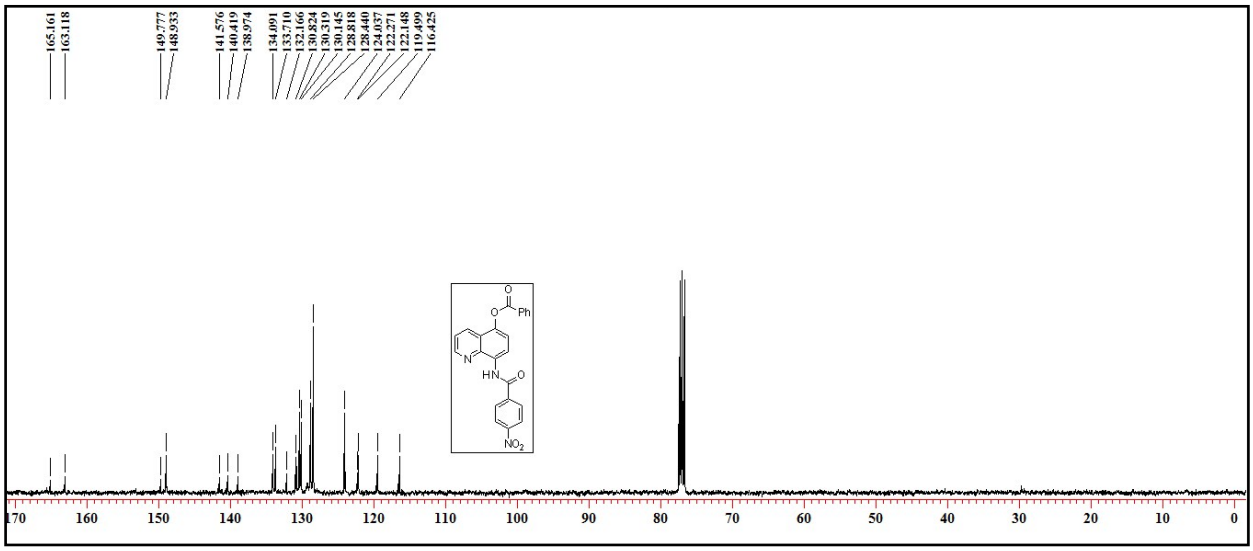


Figure S48. ^{13}C NMR spectrum of **2v** in $CDCl_3$.

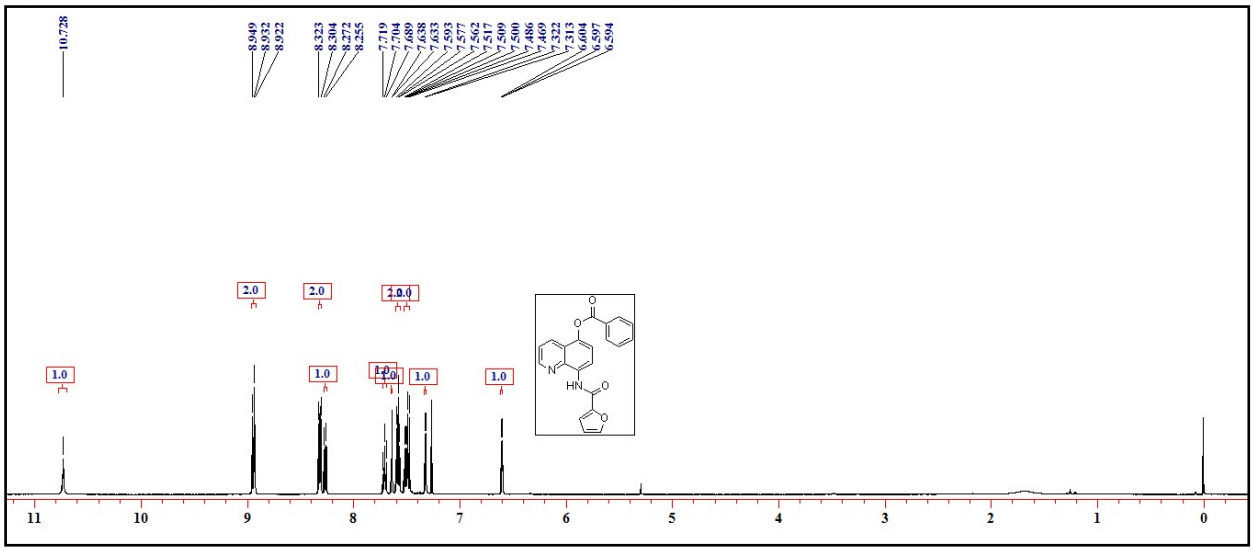


Figure S49. ^{1}H NMR spectrum of **2w** in $CDCl_3$+ CD_2Cl_2.

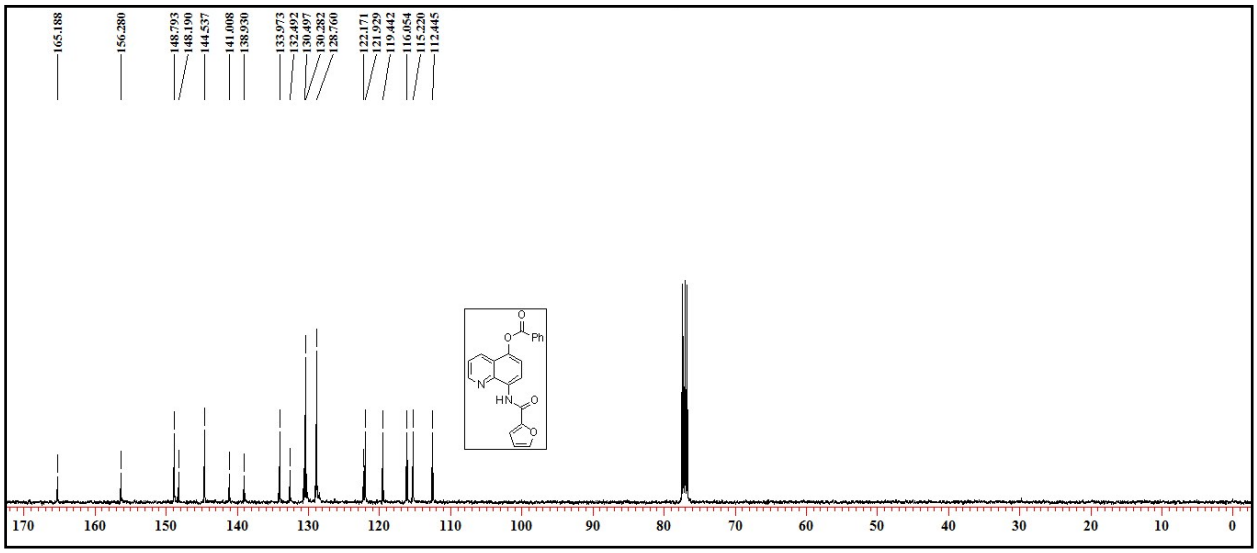


Figure S50. ^{13}C NMR spectrum of **2w** in $CDCl_3$.

Figure S51. ^{1}H NMR spectrum of **2x** in $CDCl_3$.

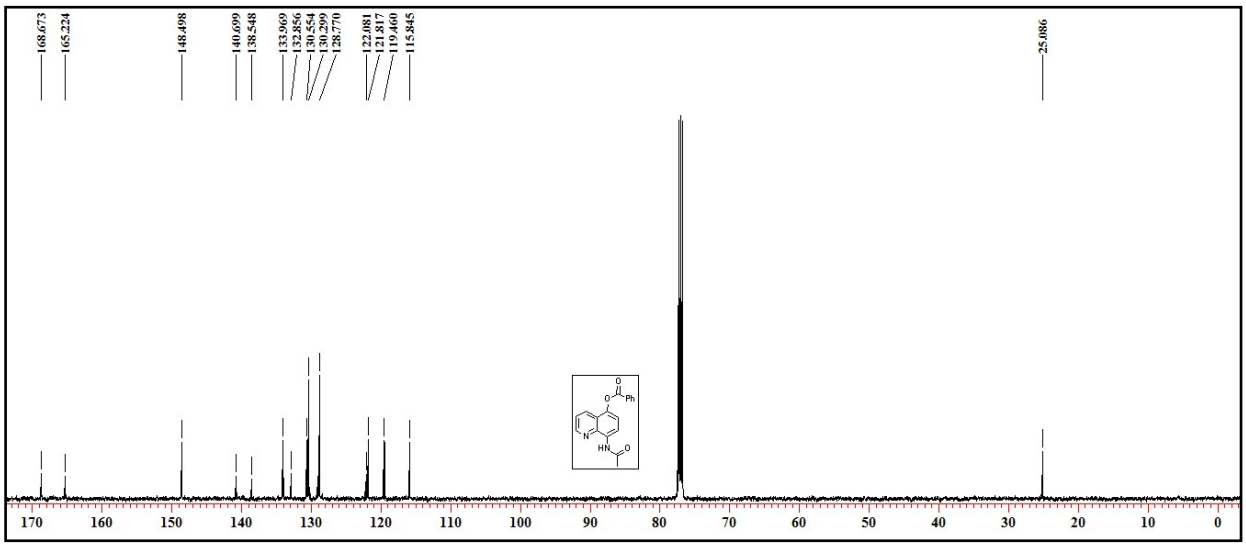


Figure S52. ^{13}C NMR spectrum of **2x** in $CDCl_3$.

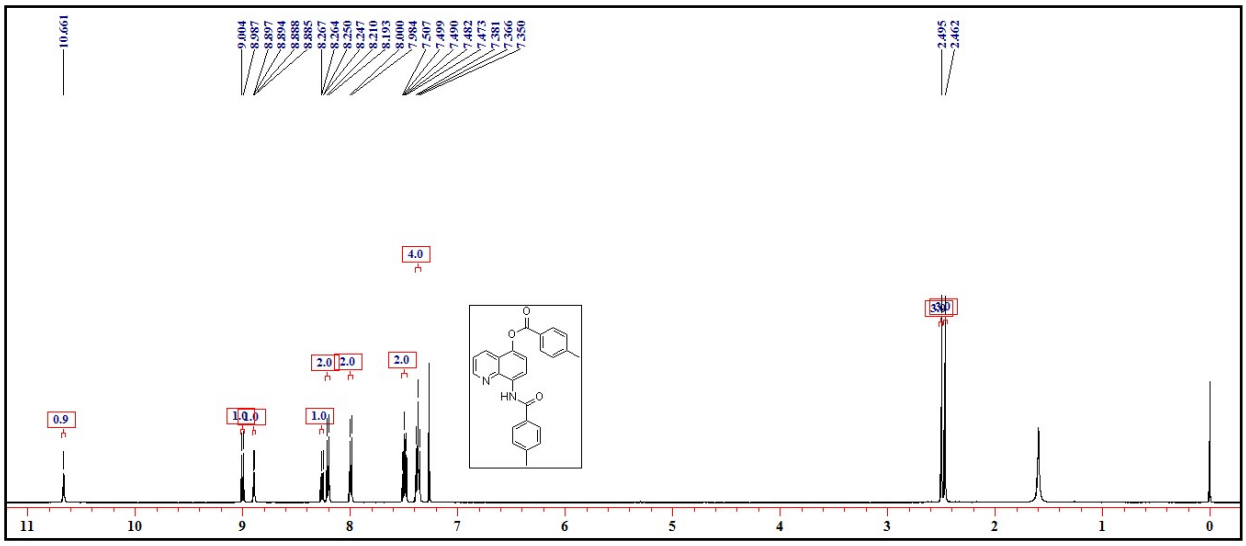


Figure S55. ^{1}H NMR spectrum of **3a** in $CDCl_3$.

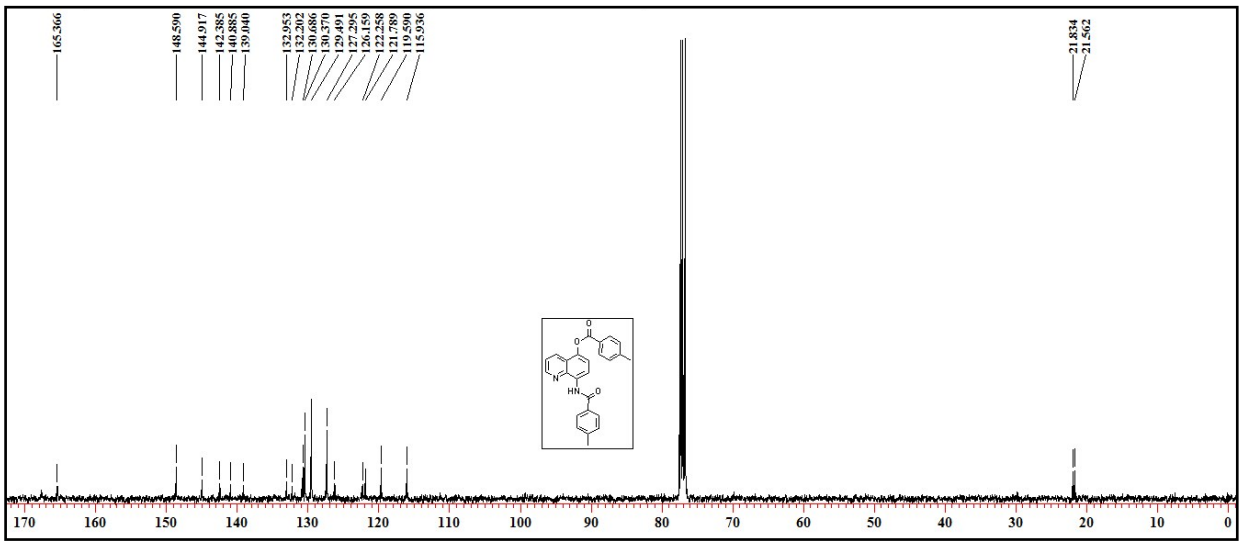


Figure S56. ^{13}C NMR spectrum of **3a** in $CDCl_3$.

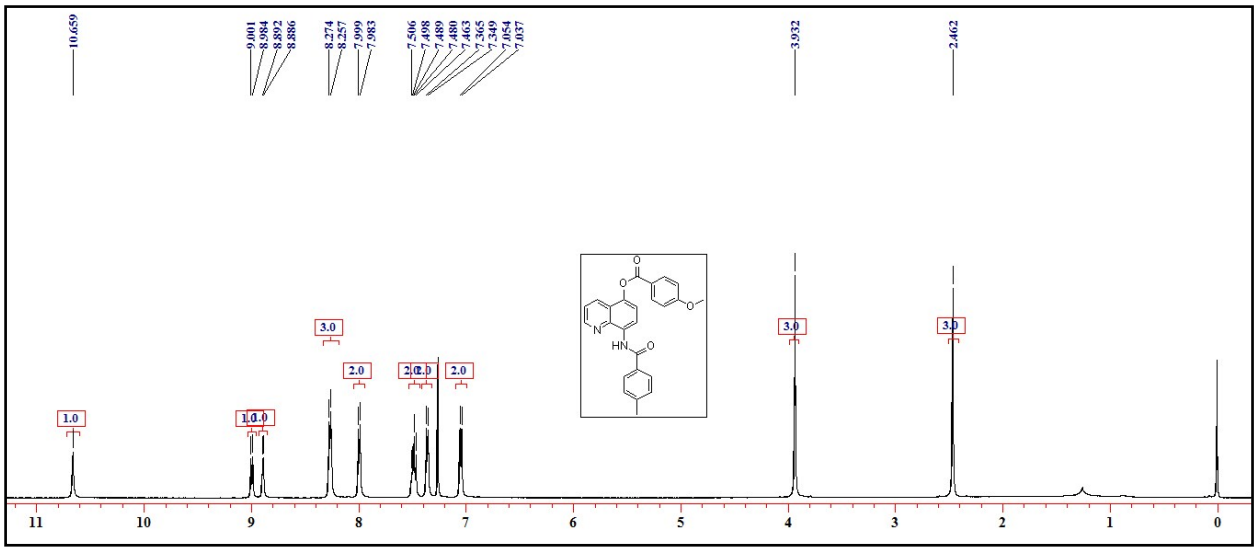


Figure S57. ^{1}H NMR spectrum of **3b** in $CDCl_3$.

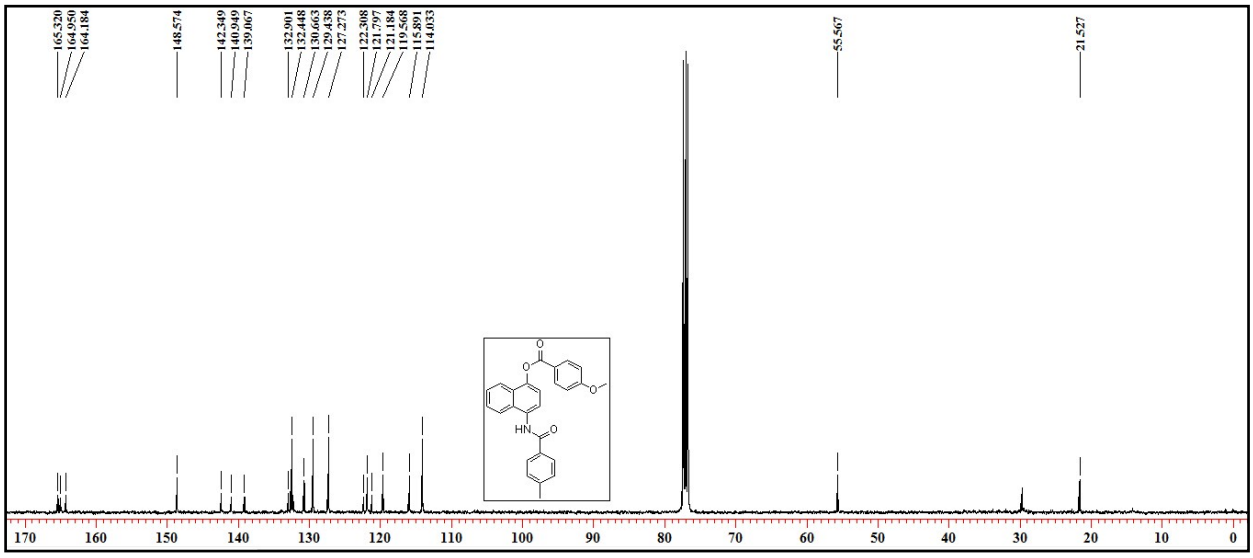


Figure S58. ^{13}C NMR spectrum of **3b** in $CDCl_3$.

Figure S59. ^{1}H NMR spectrum of **3c** in $CDCl_3$.

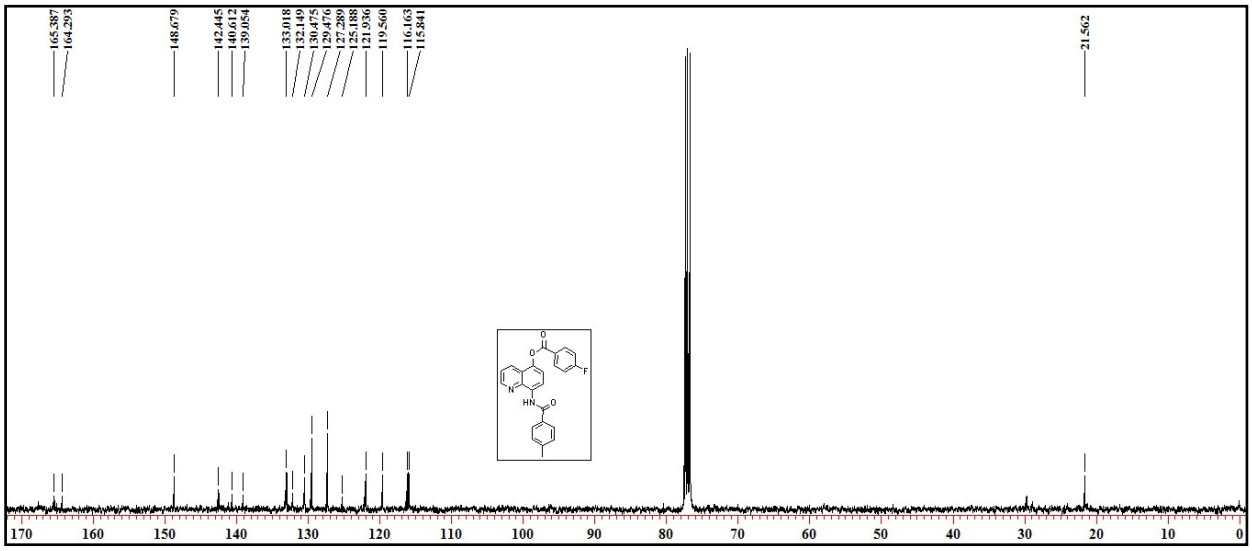


Figure S60. ^{13}C NMR spectrum of **3c** in $CDCl_3$

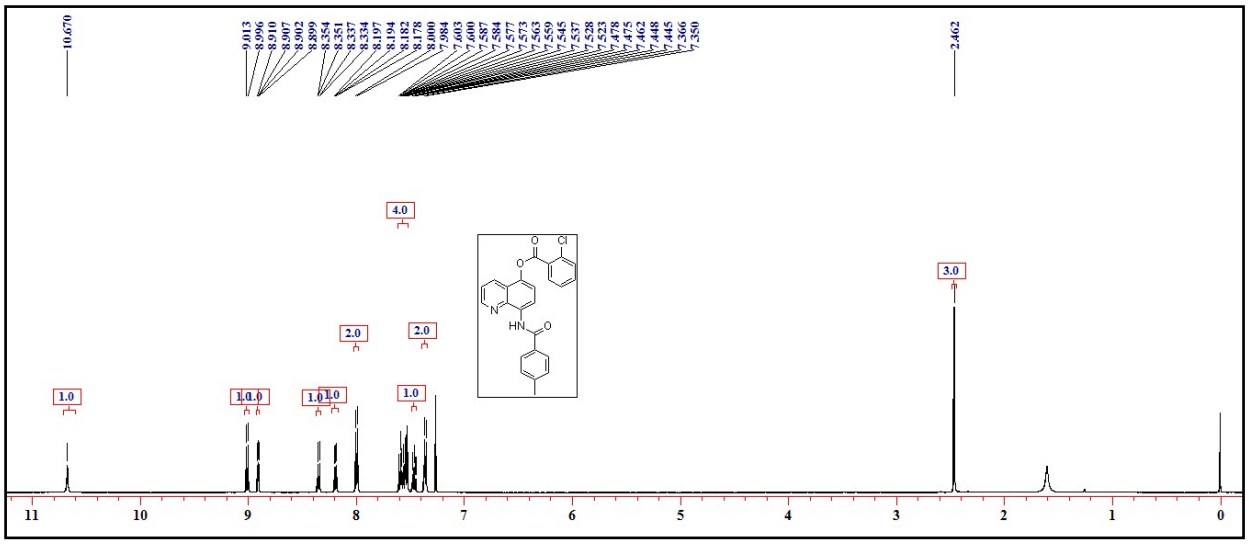


Figure S61. ^{1}H NMR spectrum of **3d** in $CDCl_3$.

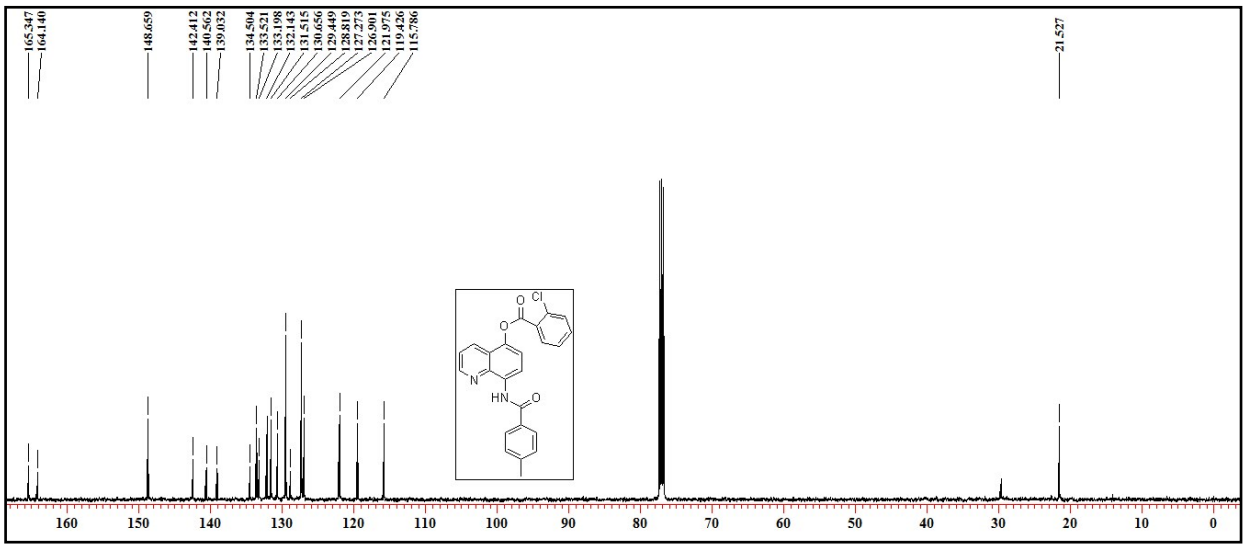


Figure S62. ^{13}C NMR spectrum of **3d** in $CDCl_3$.

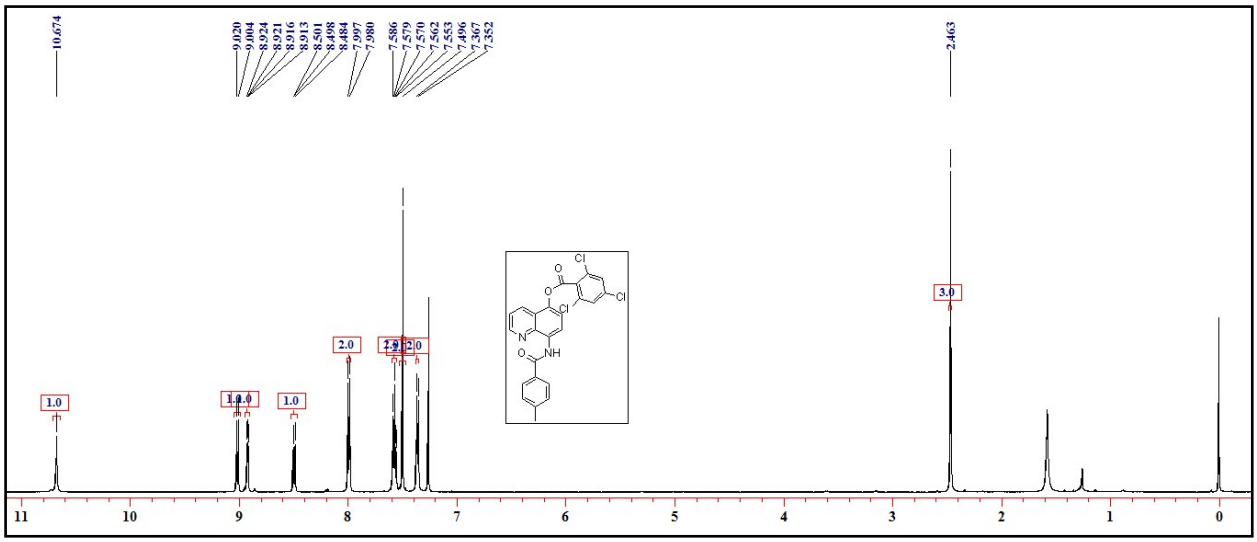


Figure S63. ^{1}H NMR spectrum of **3e** in $CDCl_3$.

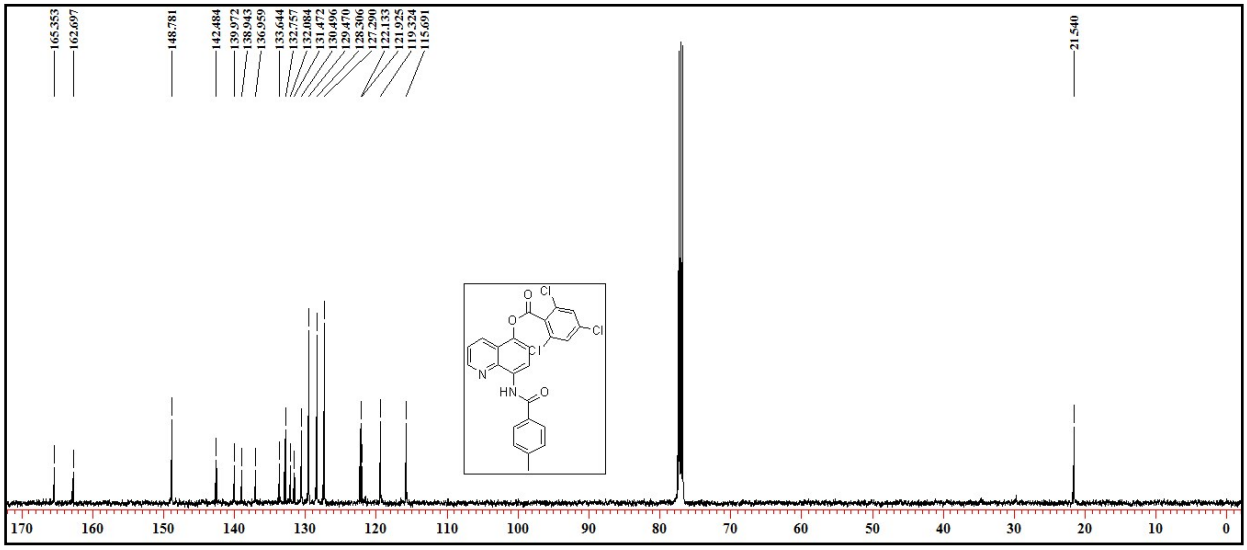


Figure S64. ^{13}C NMR spectrum of **3e** in $CDCl_3$.

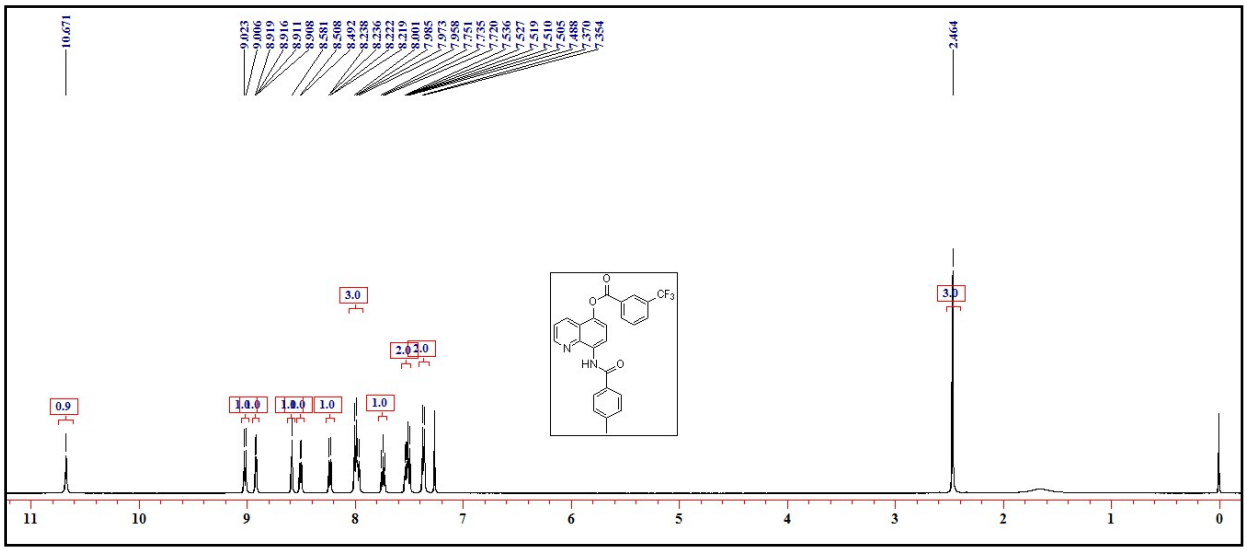


Figure S65. ^{1}H NMR spectrum of **3f** in $CDCl_3$.

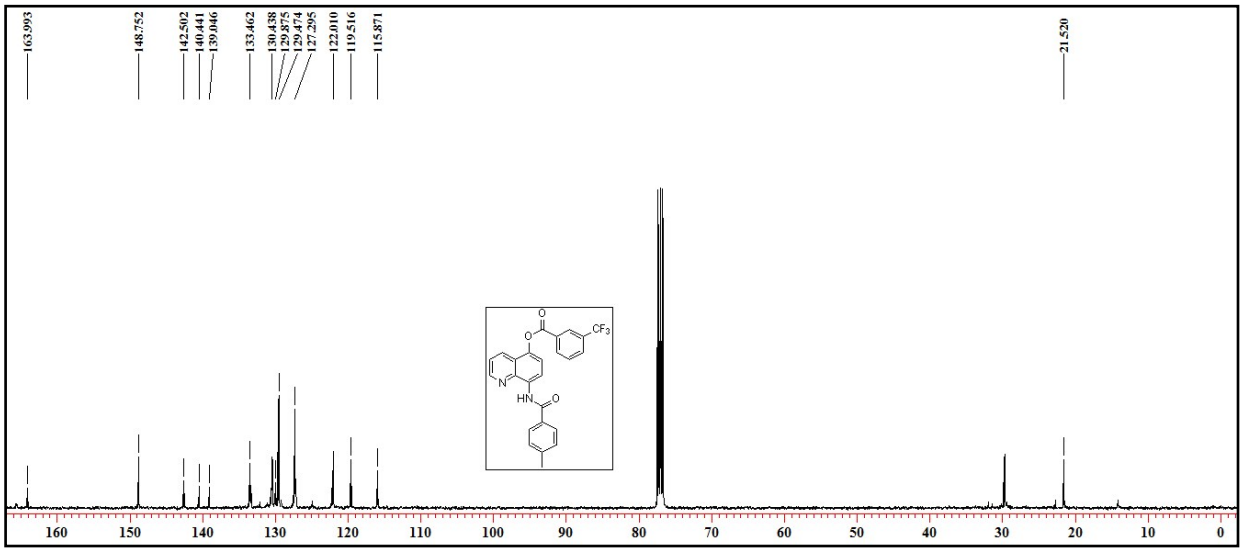


Figure S66. ^{13}C NMR spectrum of **3f** in $CDCl_3$.

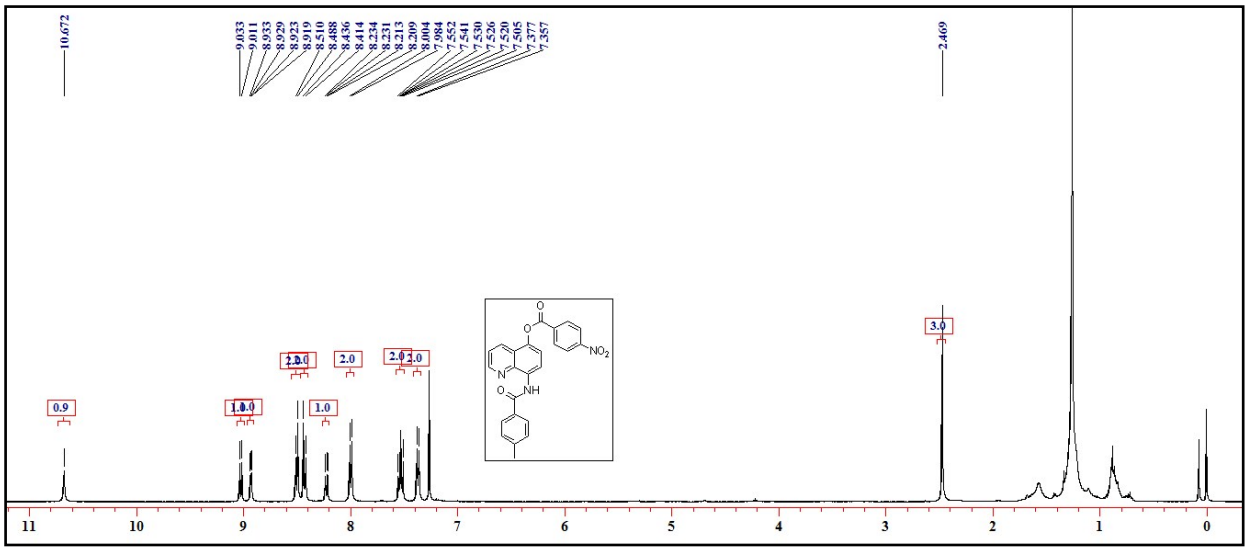


Figure S67. ^{1}H NMR spectrum of **3g** in $CDCl_3$.

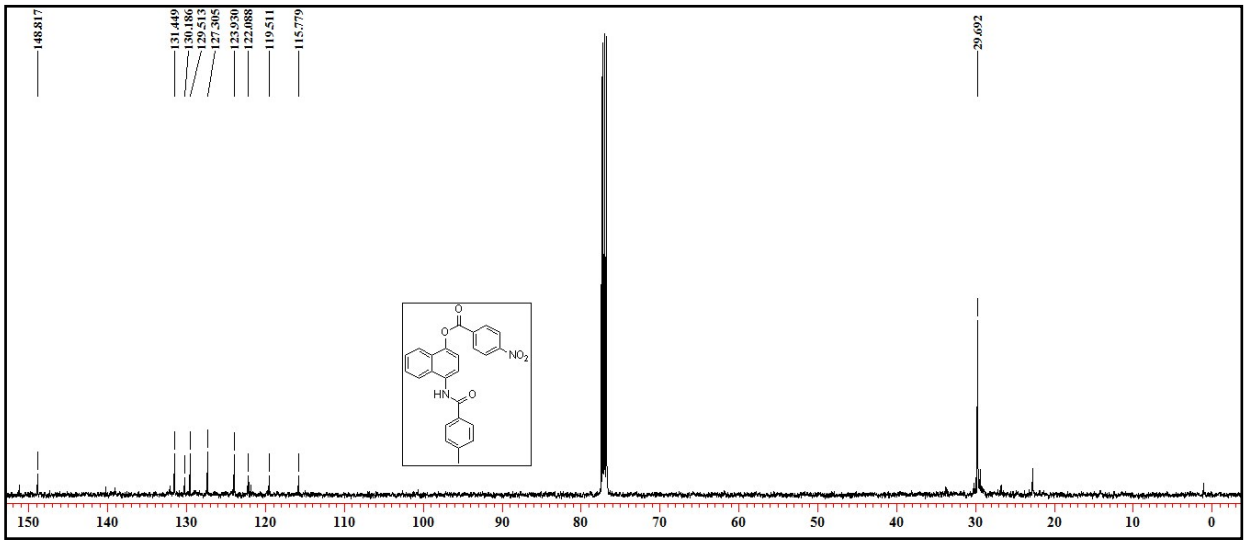


Figure S68. ^{13}C NMR spectrum of **3g** in $CDCl_3$.

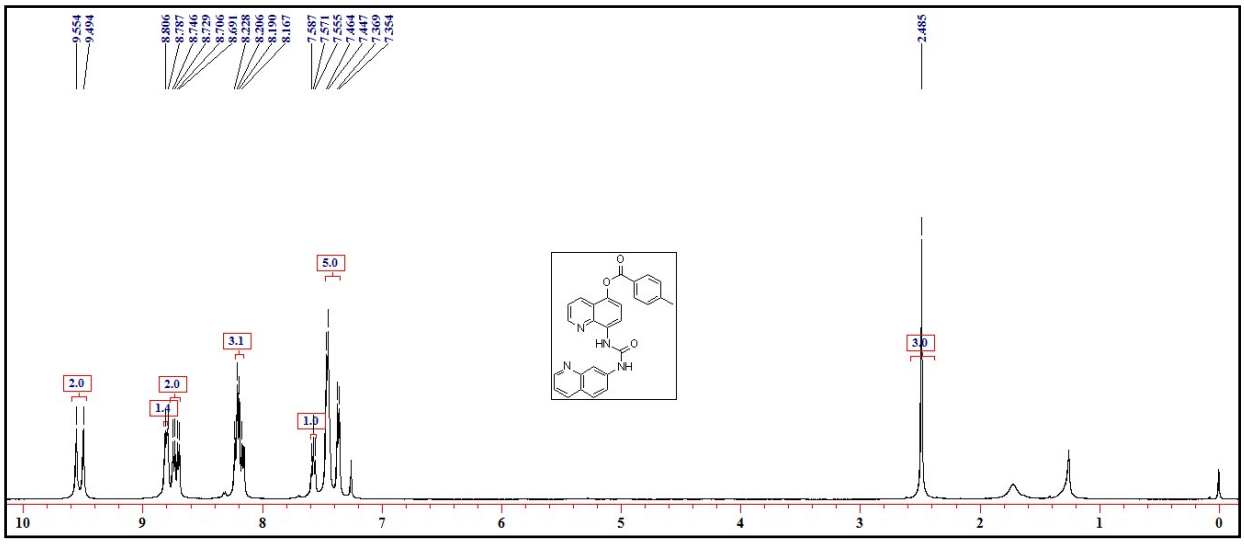


Figure S53. ^{1}H NMR spectrum of **3h** in $CDCl_3$.

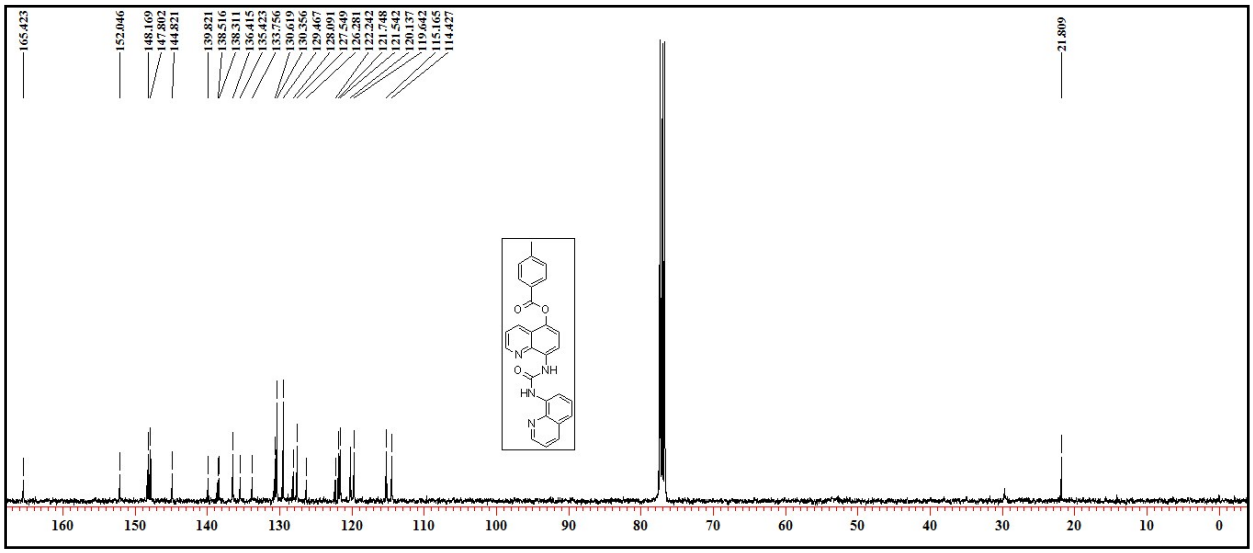


Figure S54. ^{1}H NMR spectrum of **3h** in $CDCl_3$.