Electronic Supplementary Material (ESI) for Green Chemistry


*Supporting information*

# A facile eco-friendly three-component protocol for the regio- and stereoselective synthesis of novel functionalized *trans*-dihydrofuro[3,2-*c*]-quinolin-4(2*H*)-ones

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## Details of Spectra

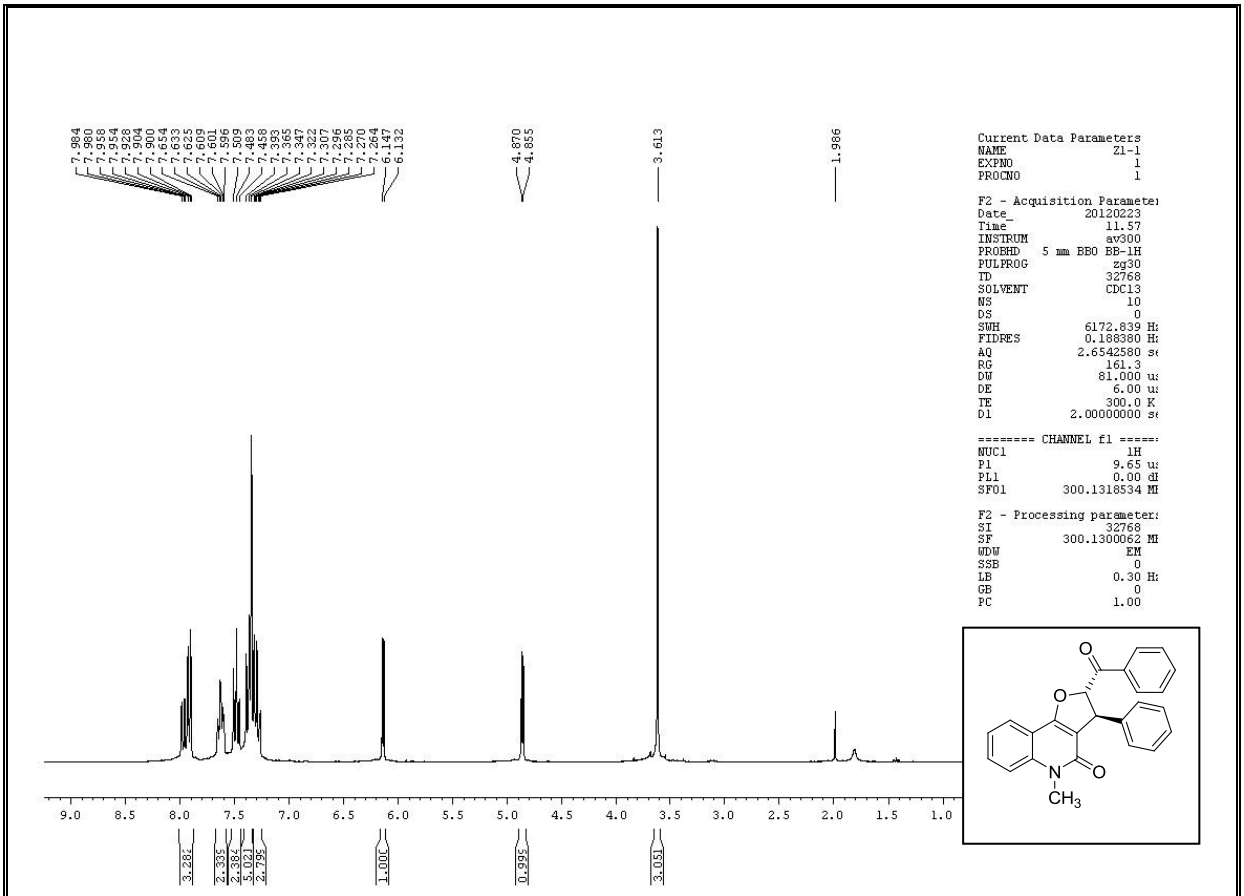


**Figure 1.** $^{1}$H NMR spectrum of **4a**

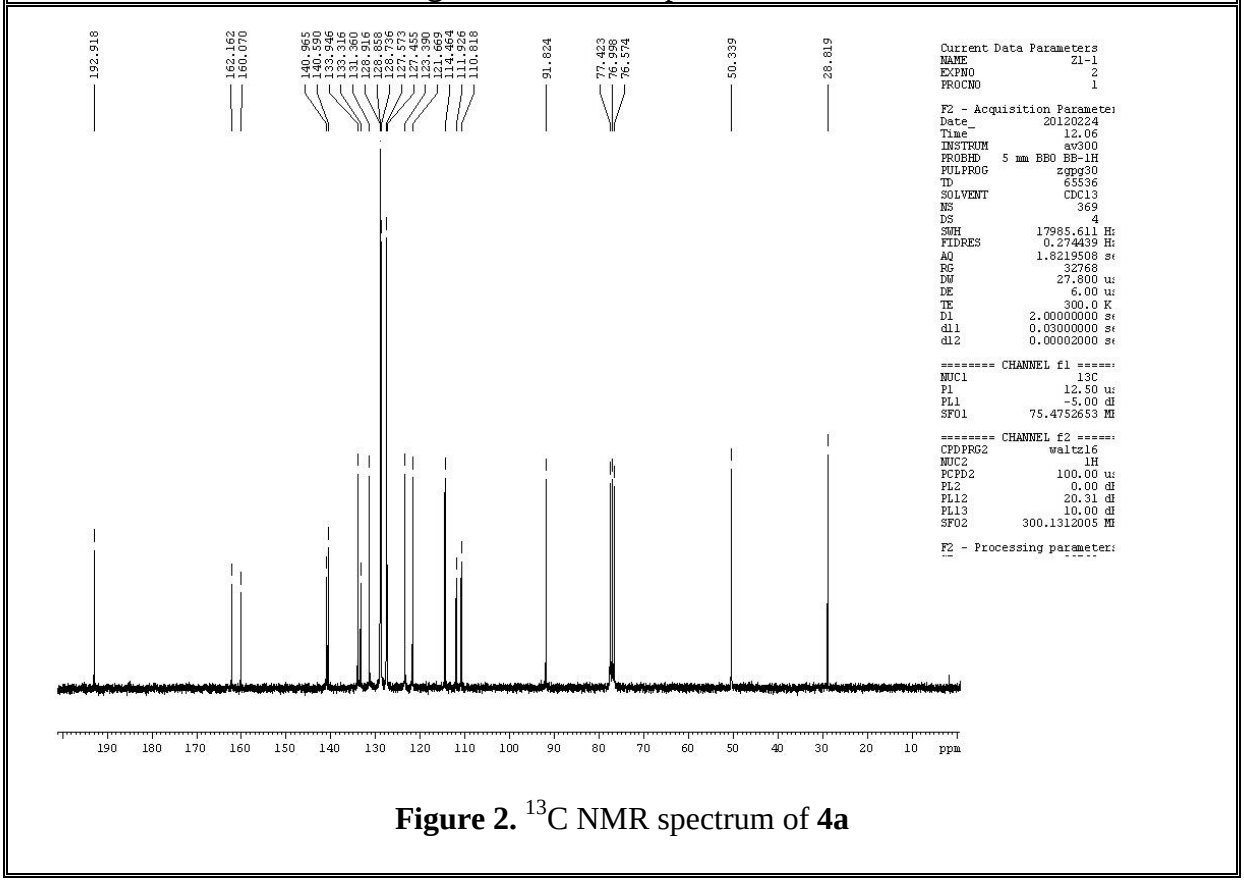


**Figure 2.** $^{13}$C NMR spectrum of **4a**

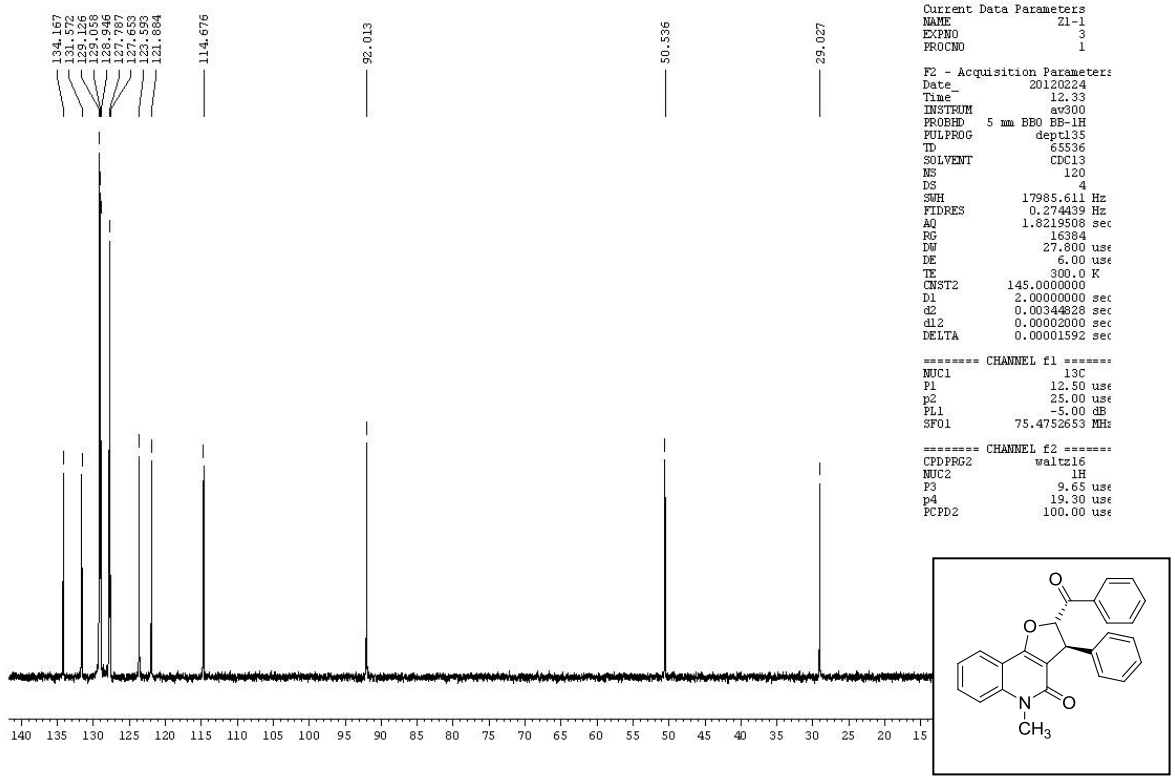


**Figure 3.** DEPT 135 spectrum of **4a**

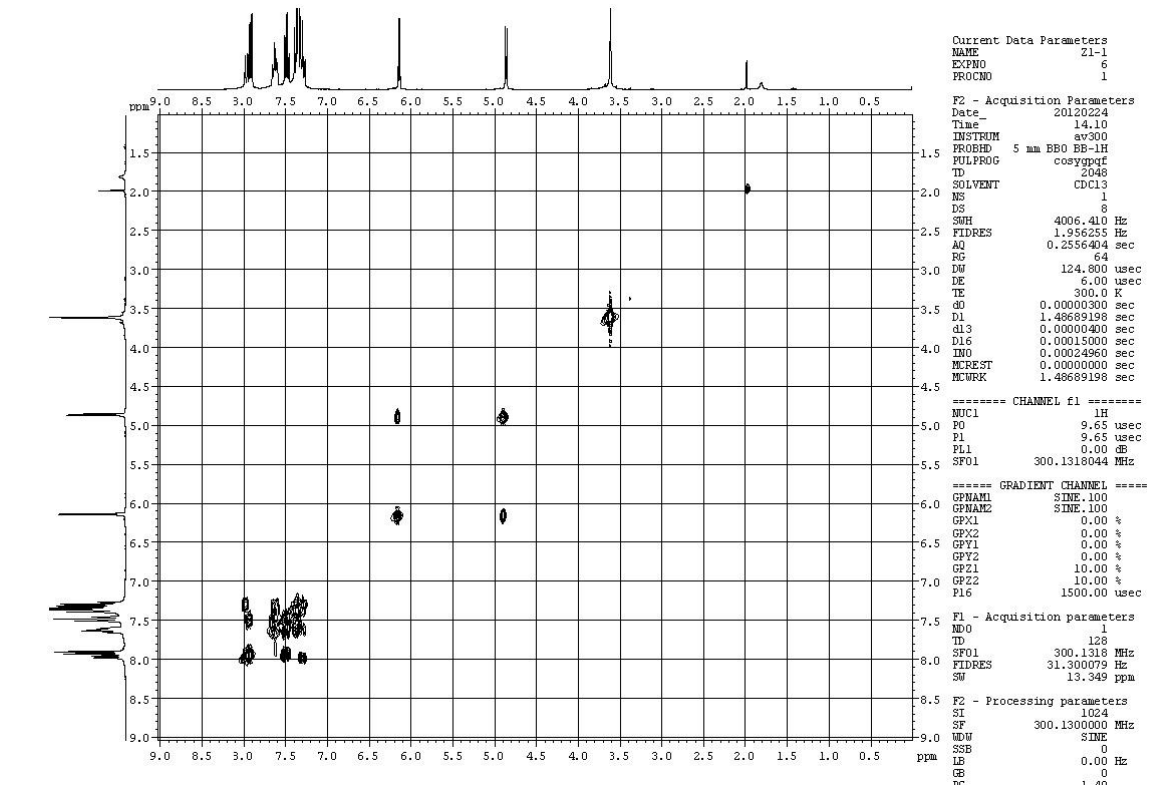


**Figure 4.** H-H COSY spectrum of **4a**

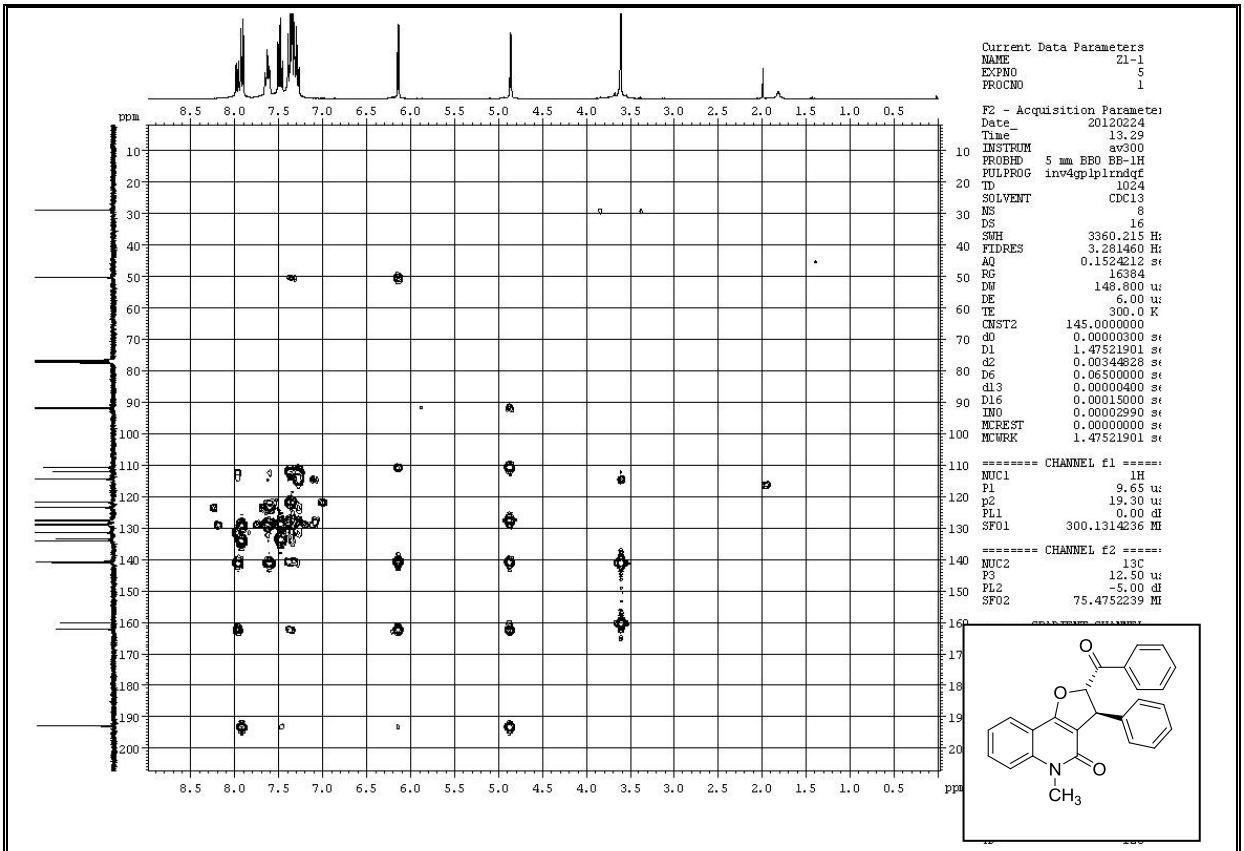


**Figure 5.** HMBC spectrum of **4a**

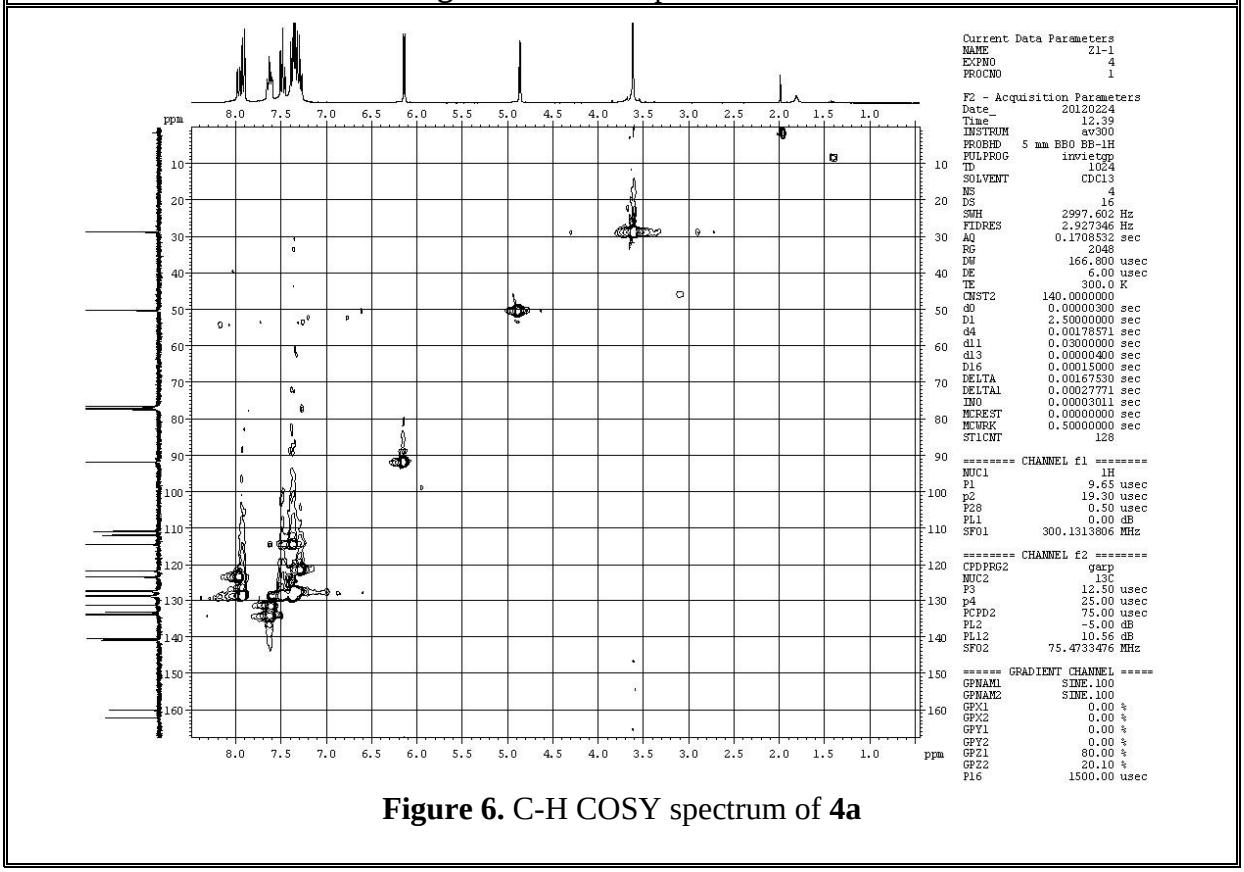


**Figure 6.** C-H COSY spectrum of **4a**

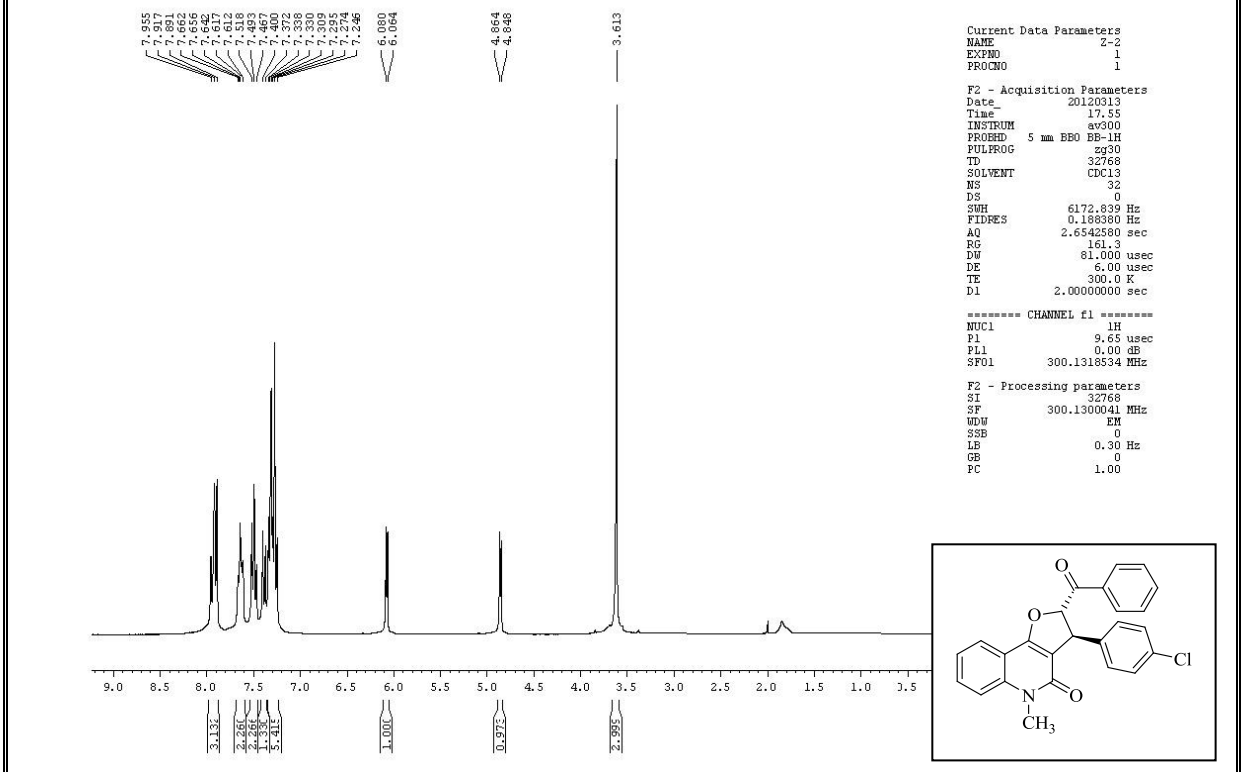


**Figure 7**. $^{1}$H NMR spectrum of **4b**

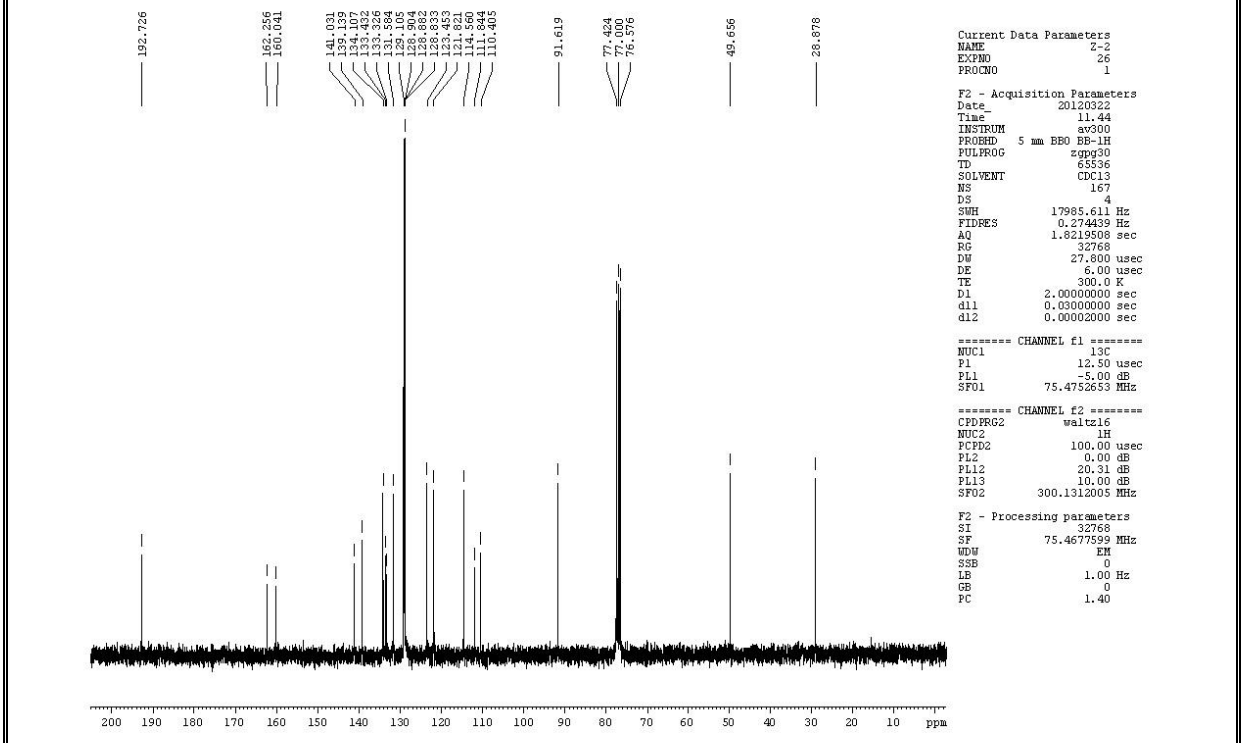


**Figure 8**. $^{13}$C NMR spectrum of **4b**

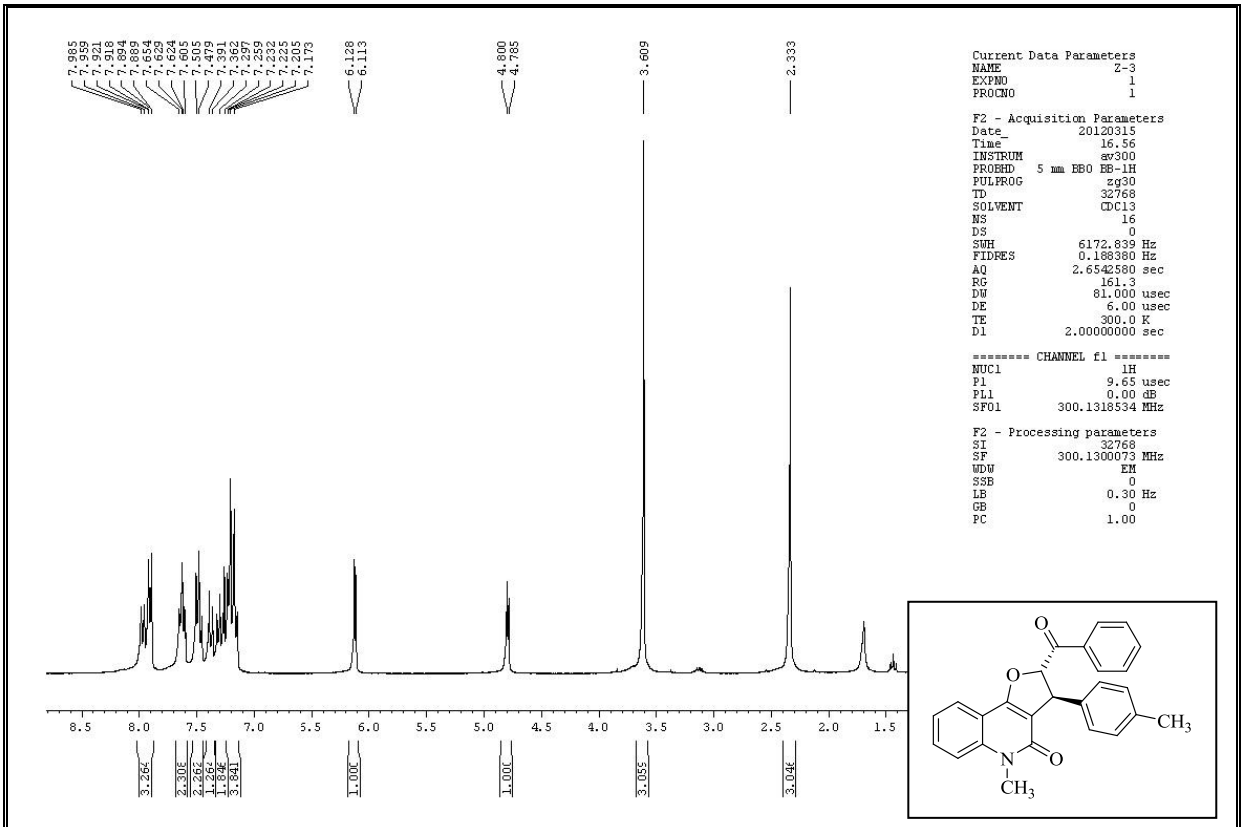


**Figure 9**. $^{1}$H NMR spectrum of **4c**

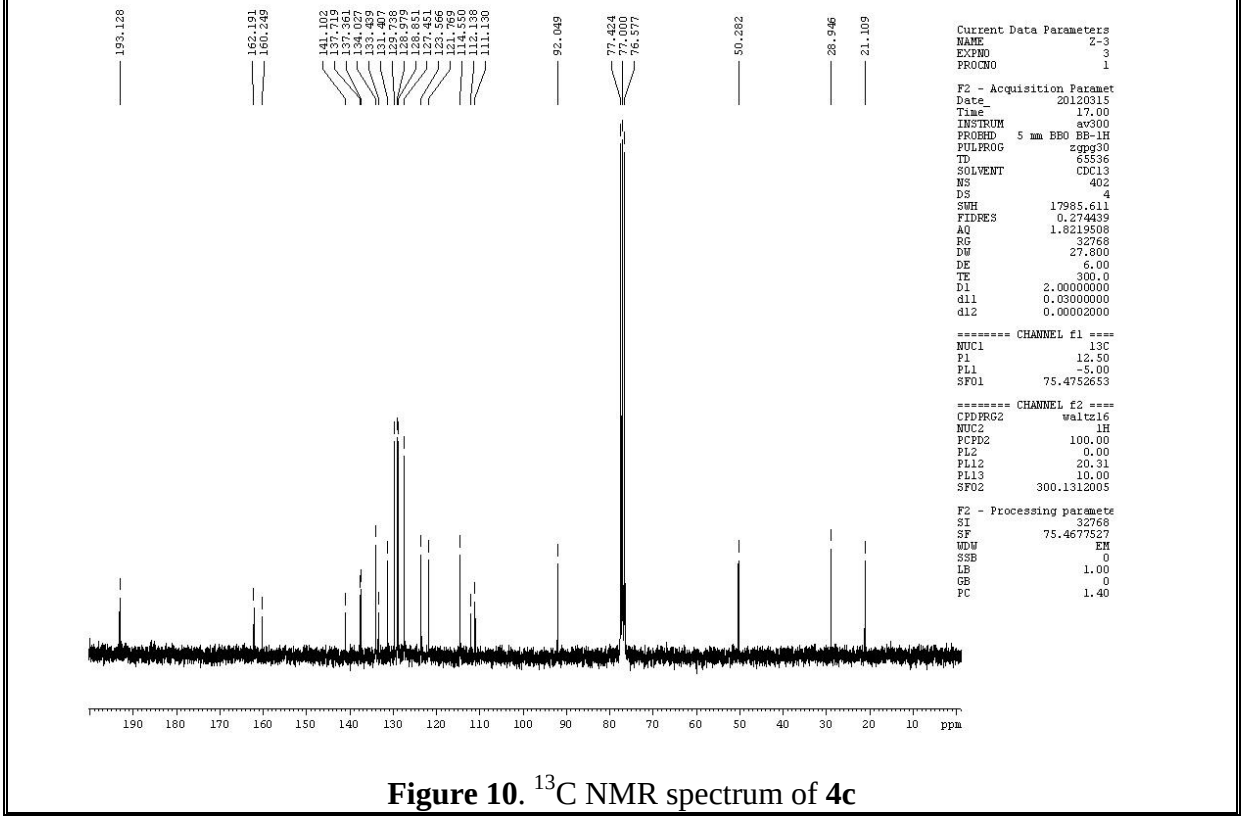


**Figure 10**. $^{13}$C NMR spectrum of **4c**

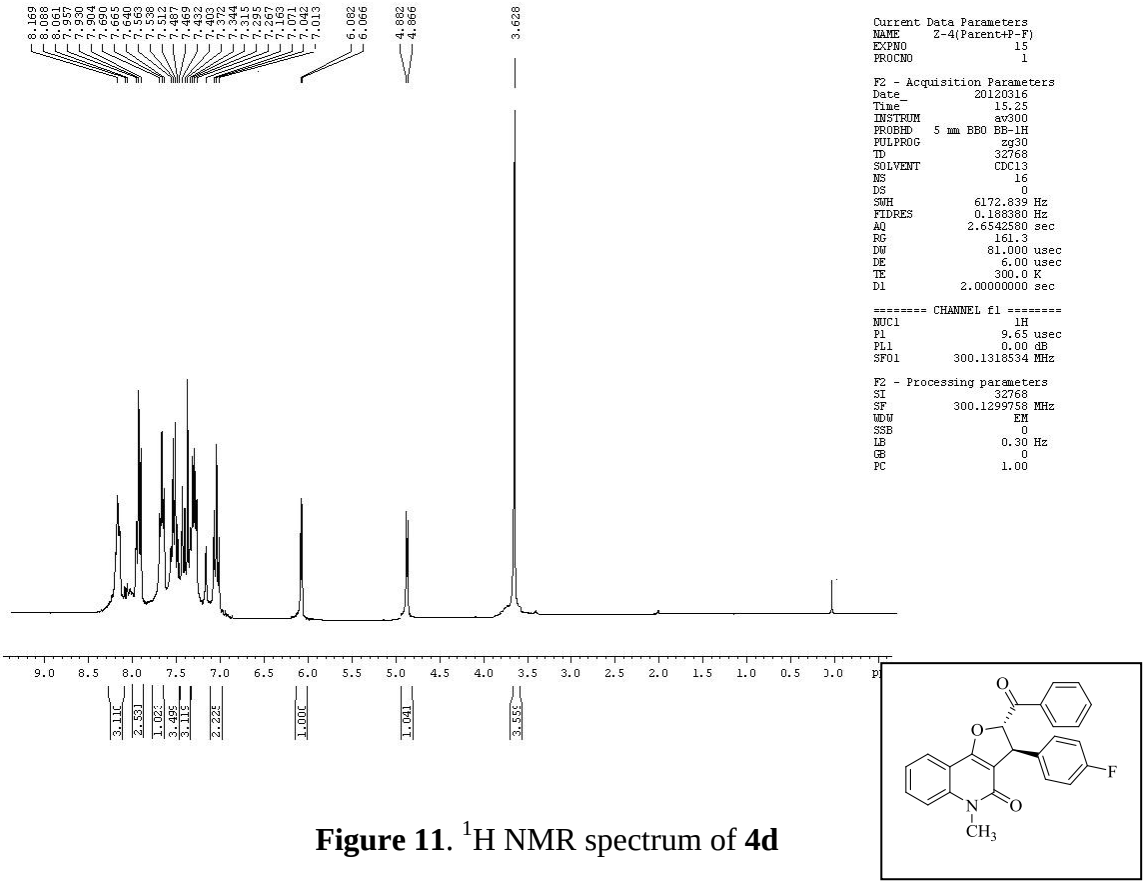


**Figure 11**. $^{1}$H NMR spectrum of **4d**

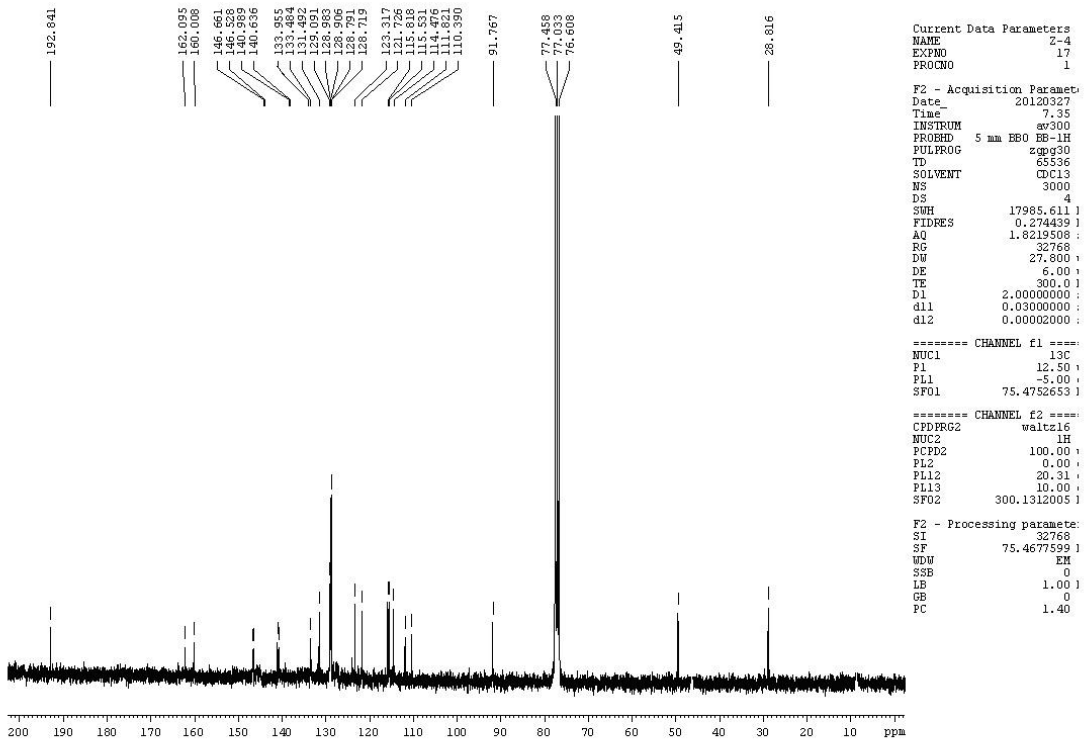


**Figure 12**. $^{13}$C NMR spectrum of **4d**

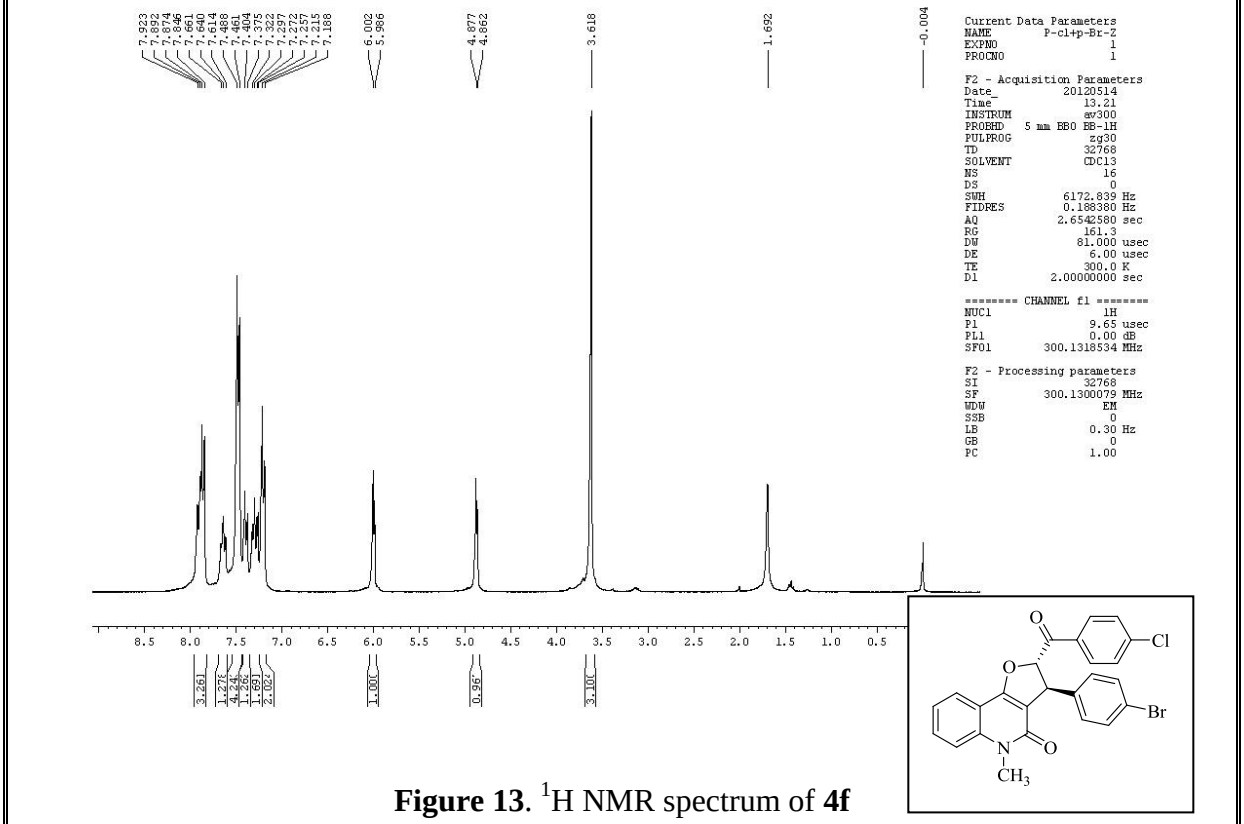


**Figure 13**. $^{1}$H NMR spectrum of **4f**

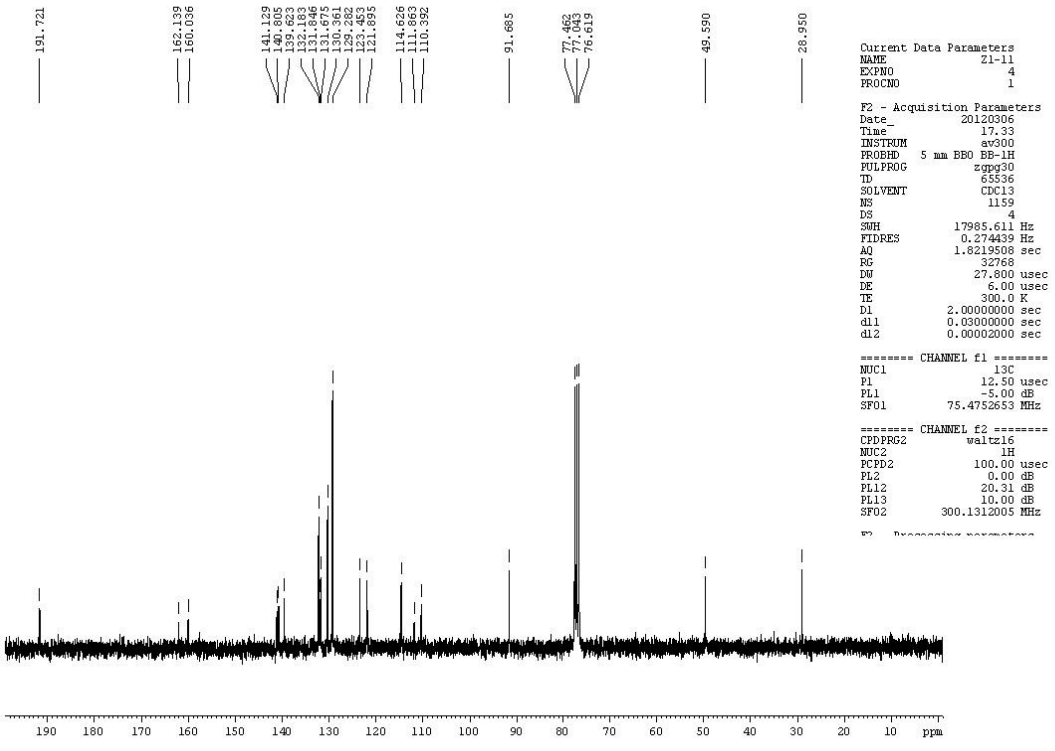


**Figure 14**. $^{13}$C NMR spectrum of **4f**

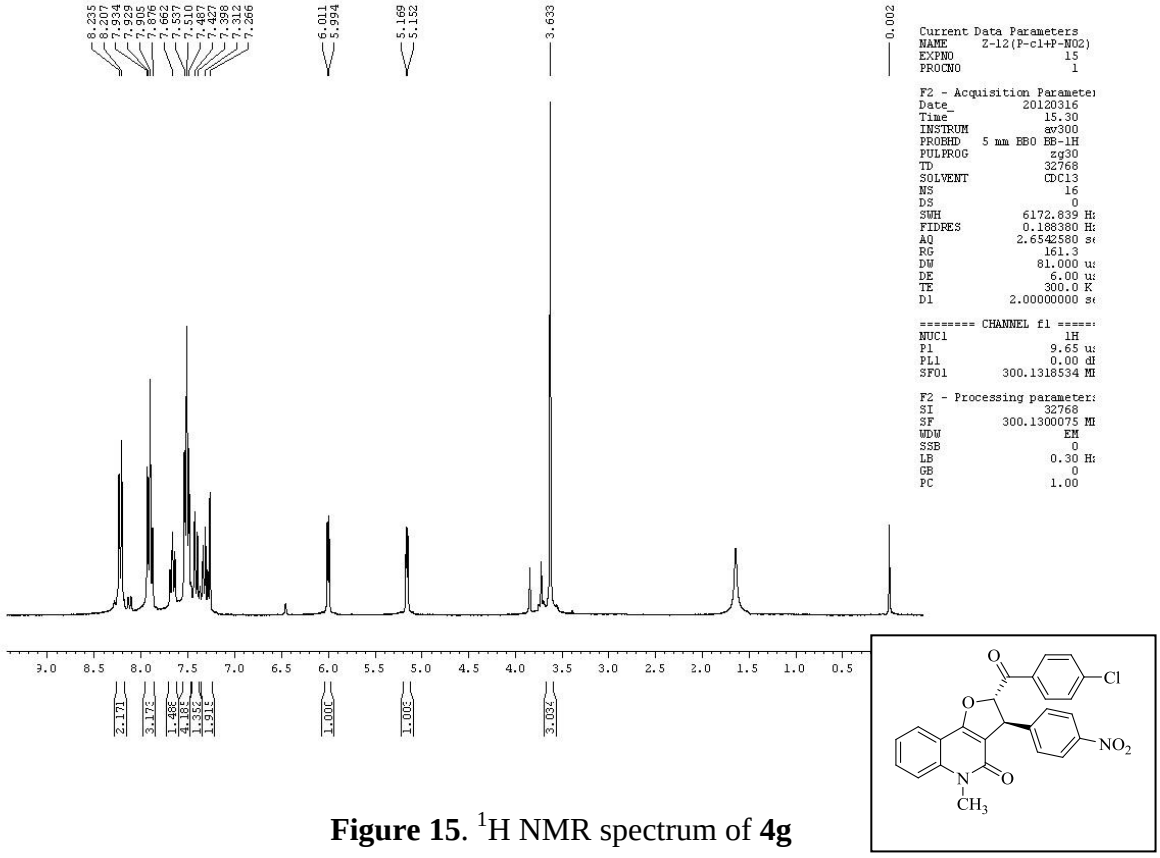


**Figure 15**. $^{1}$H NMR spectrum of **4g**

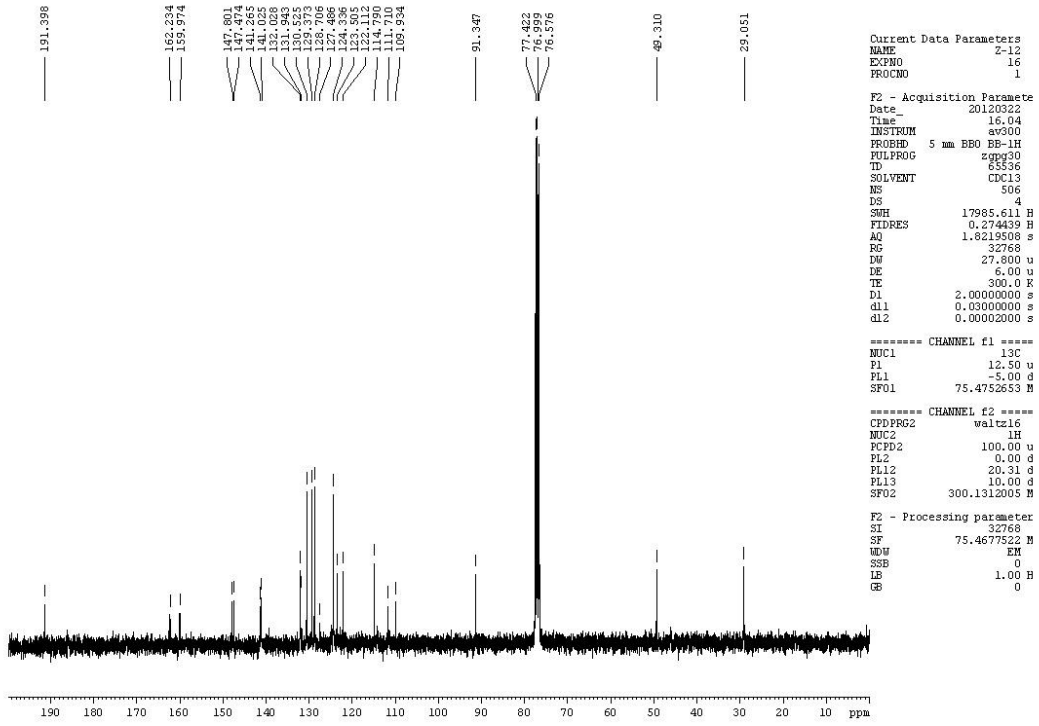


**Figure 16**. $^{13}$C NMR spectrum of **4g**

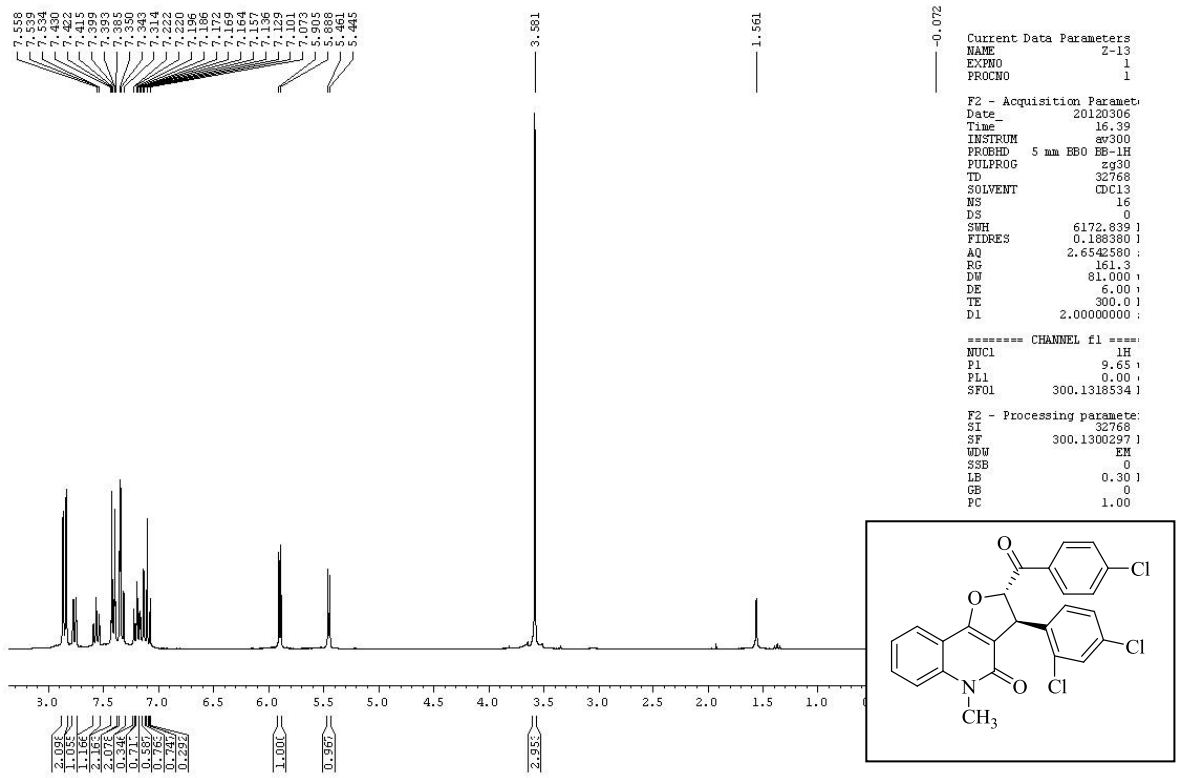


**Figure 17**. $^{1}$H NMR spectrum of **4h**

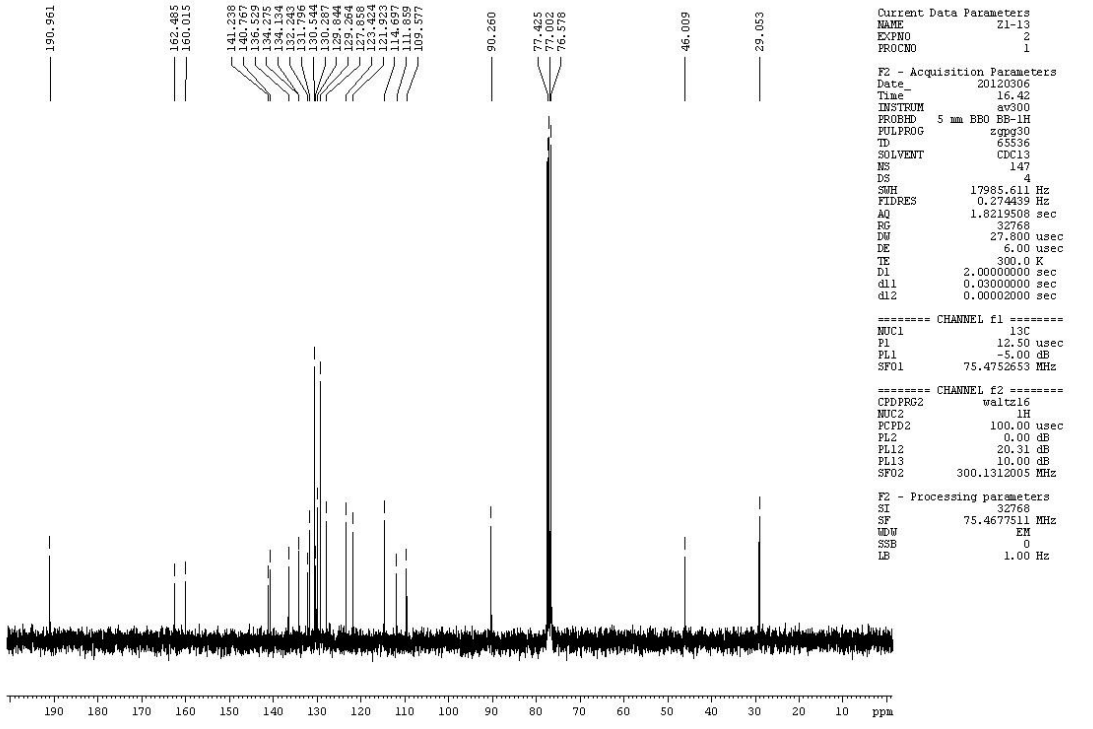


**Figure 18**. $^{13}$C NMR spectrum of **4h**

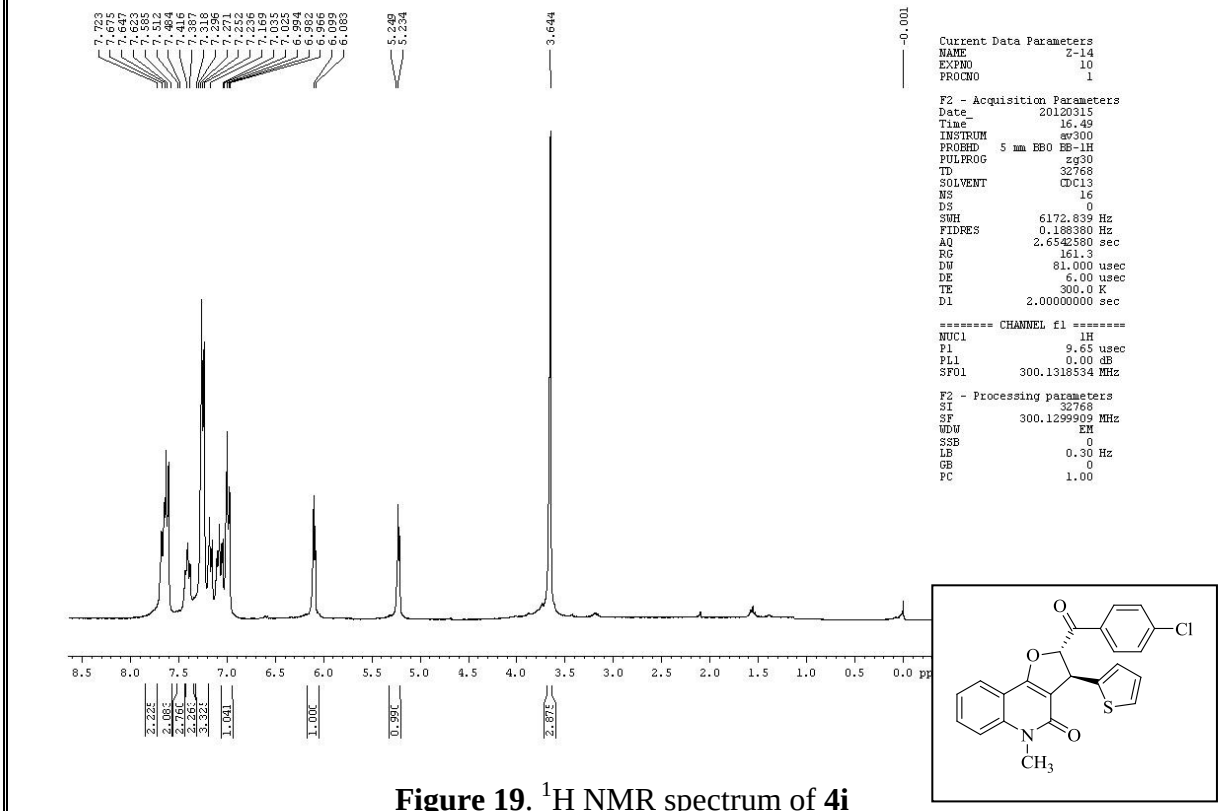


**Figure 19**. $^{1}$H NMR spectrum of **4i**

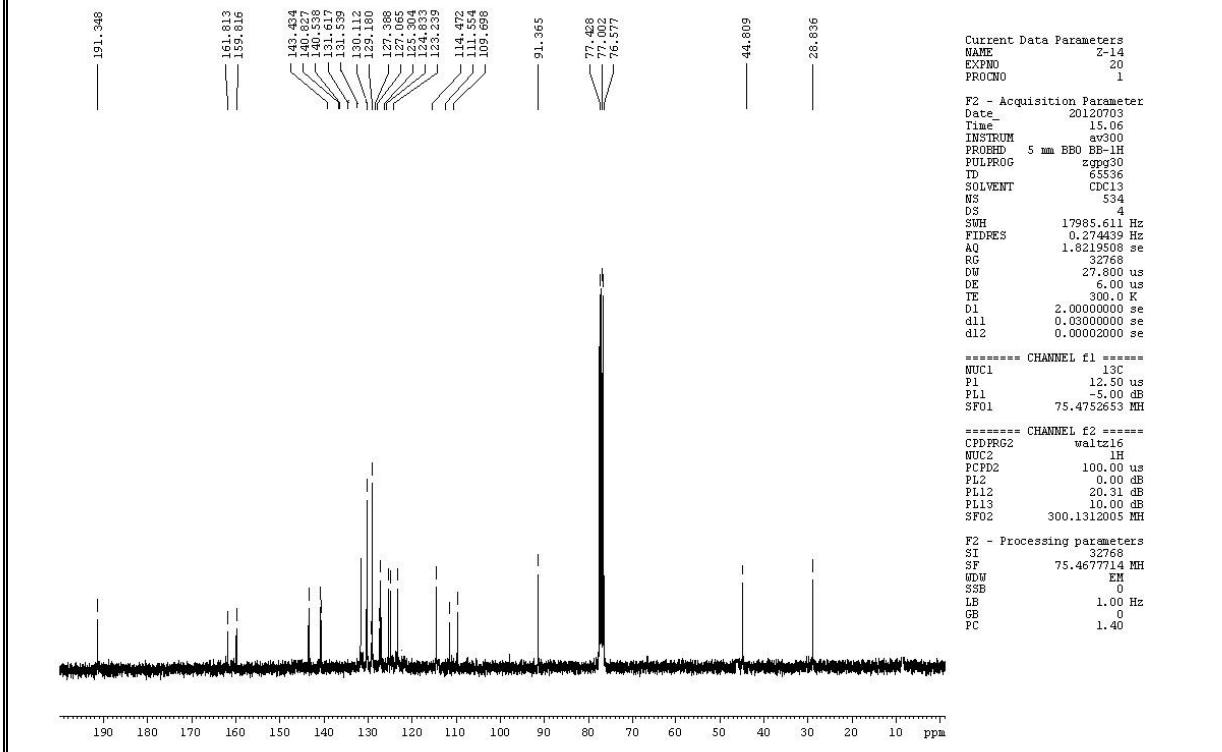


**Figure 20**. $^{13}$C NMR spectrum of **4i**

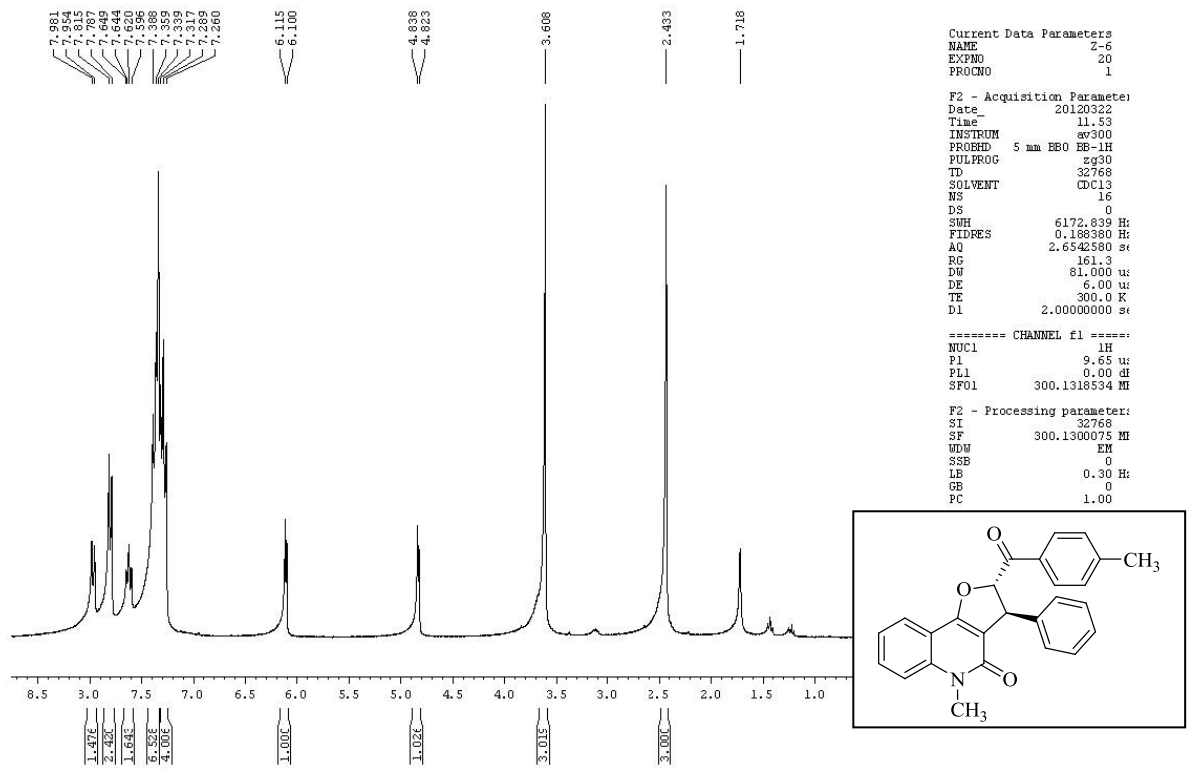


**Figure 21**. $^{1}$H NMR spectrum of **4j**

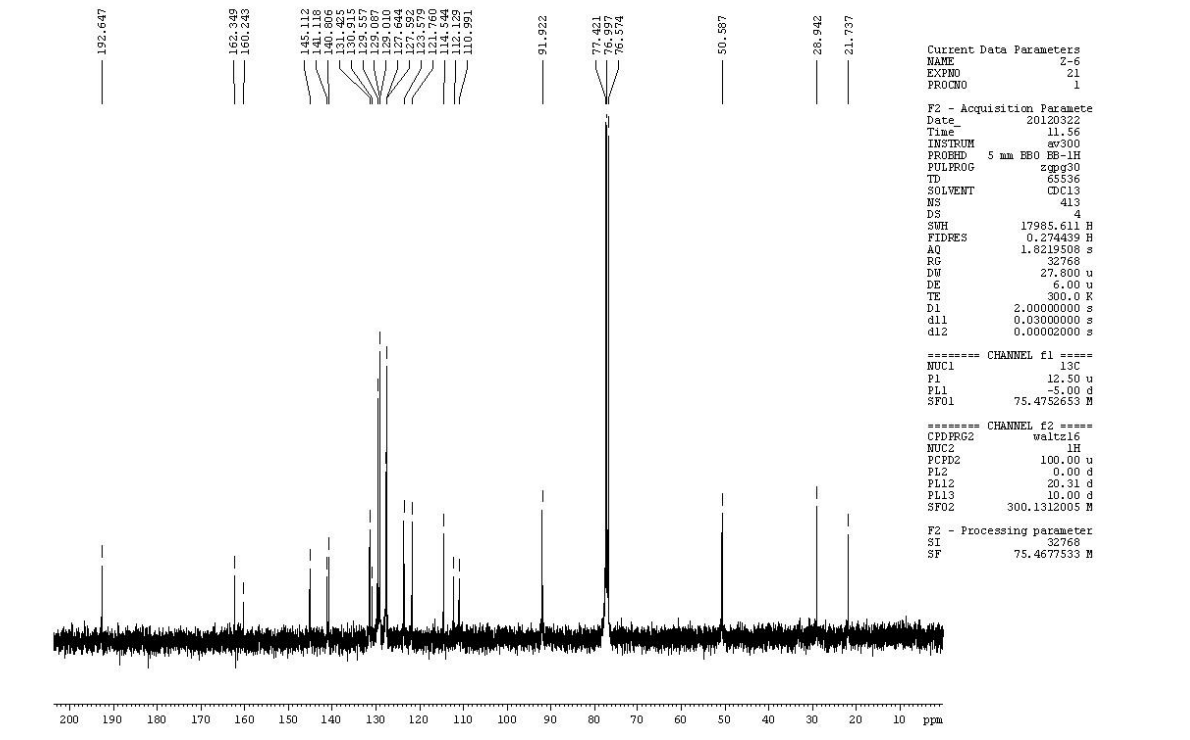


**Figure 22**. $^{13}$C NMR spectrum of **4j**

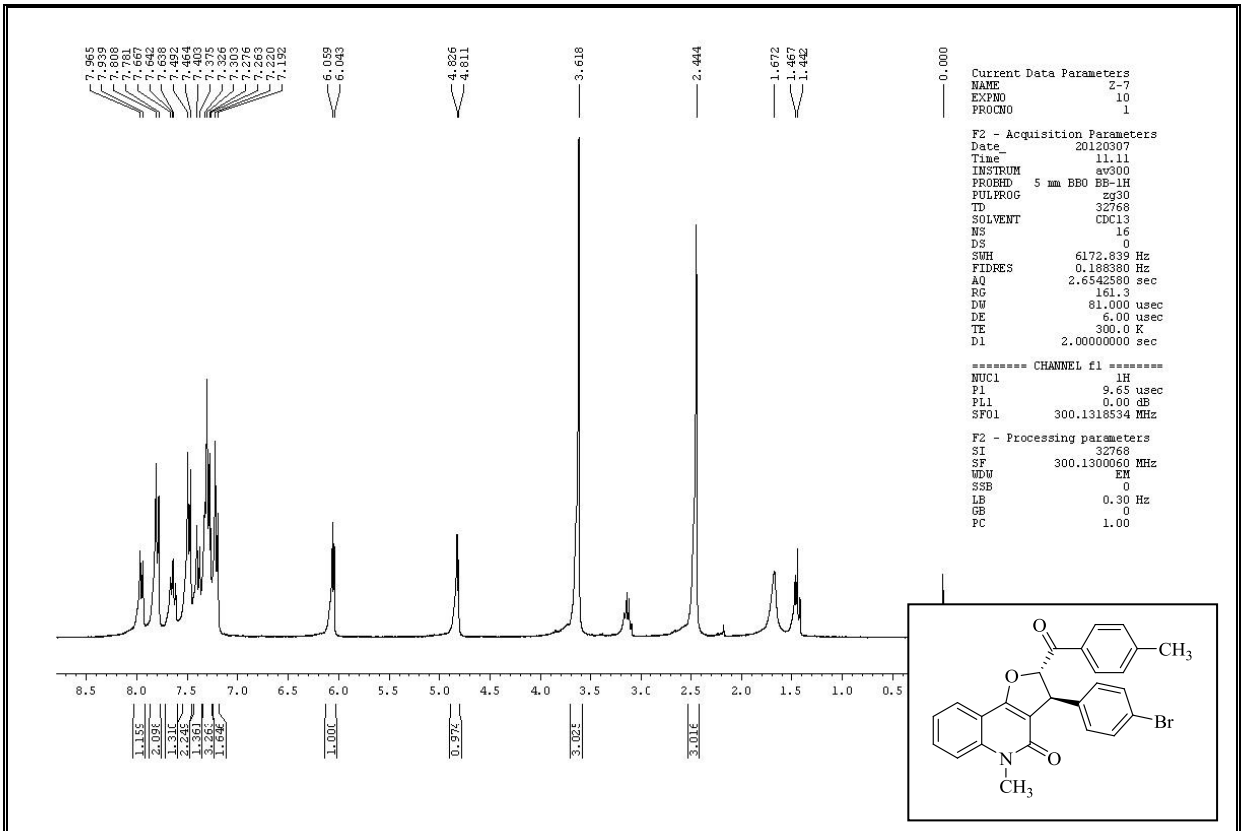


**Figure 23**. $^{1}$H NMR spectrum of **4k**

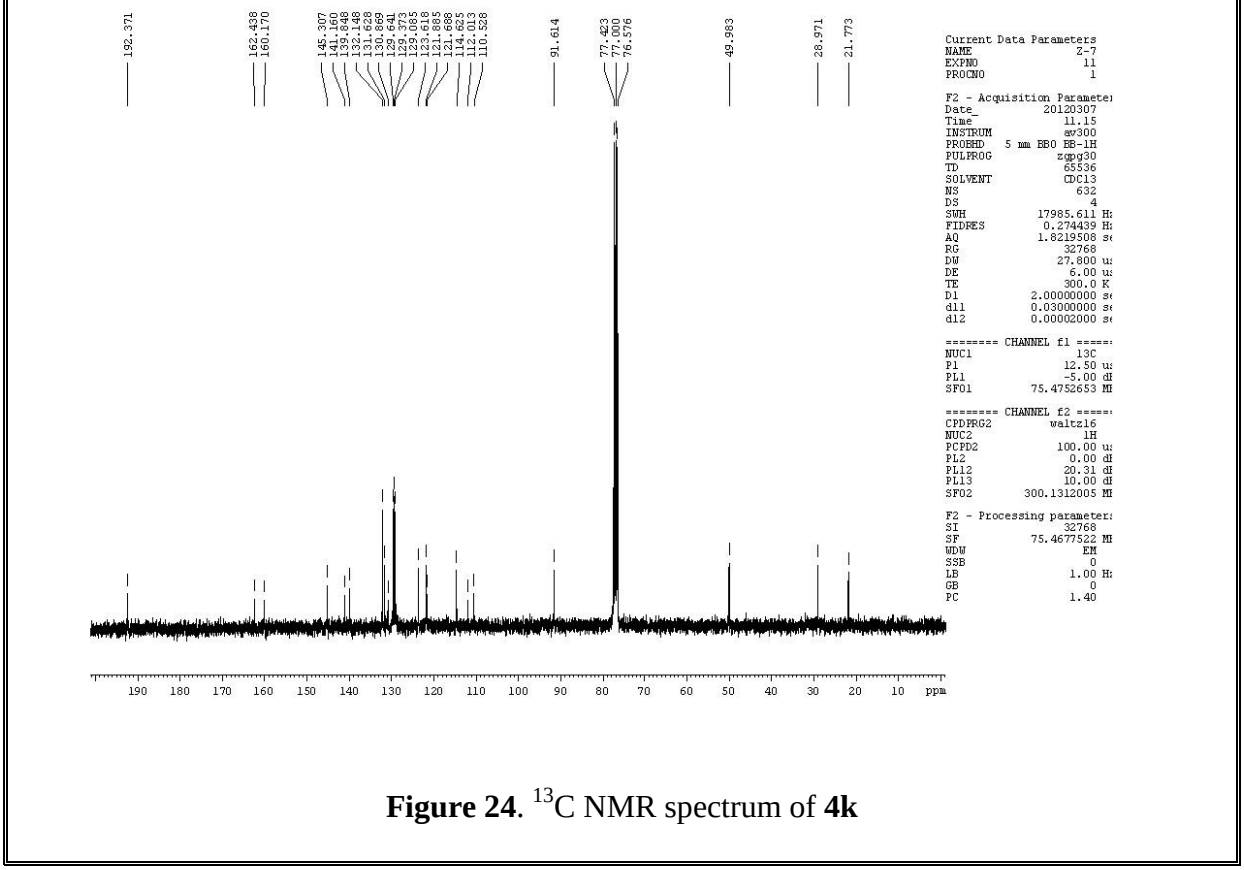


**Figure 24**. $^{13}$C NMR spectrum of **4k**

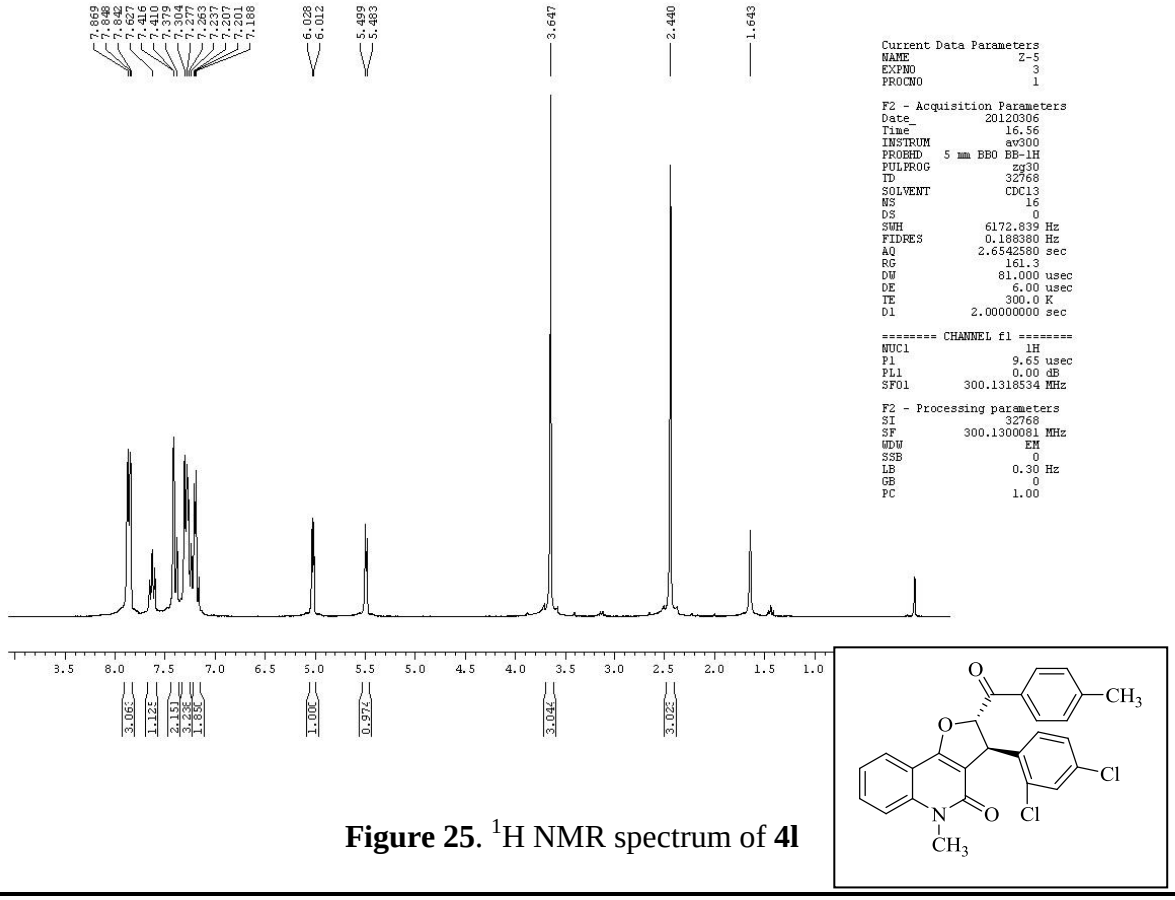


**Figure 25**. $^{1}$H NMR spectrum of **4l**

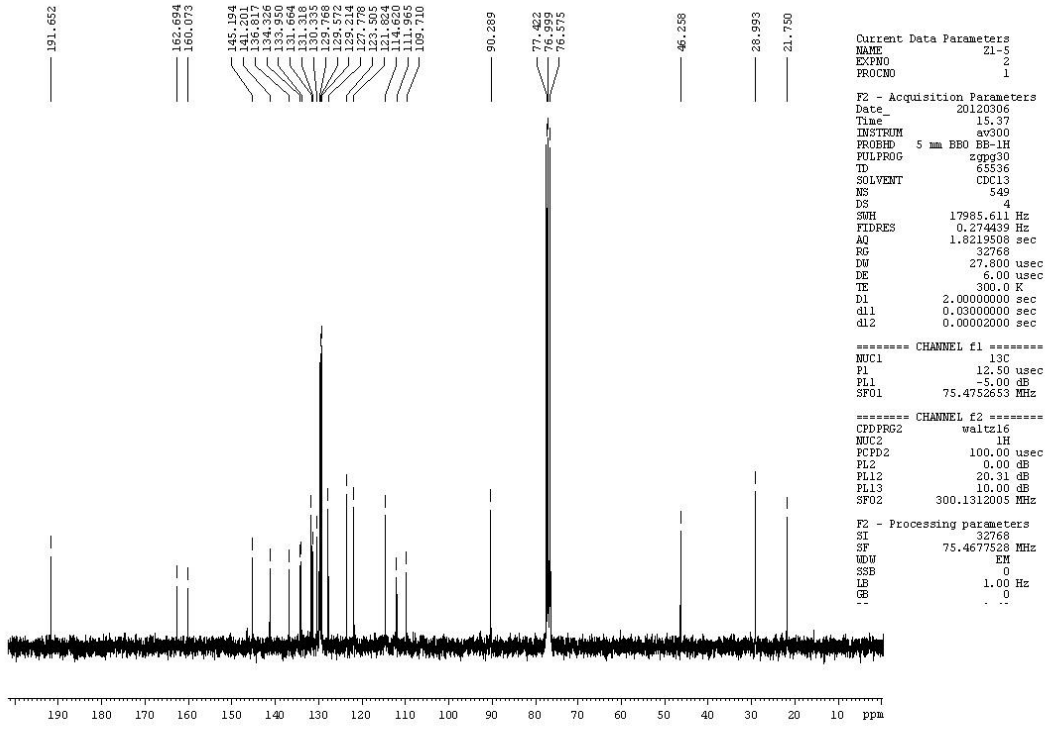


**Figure 26**. $^{13}$C NMR spectrum of **4l**

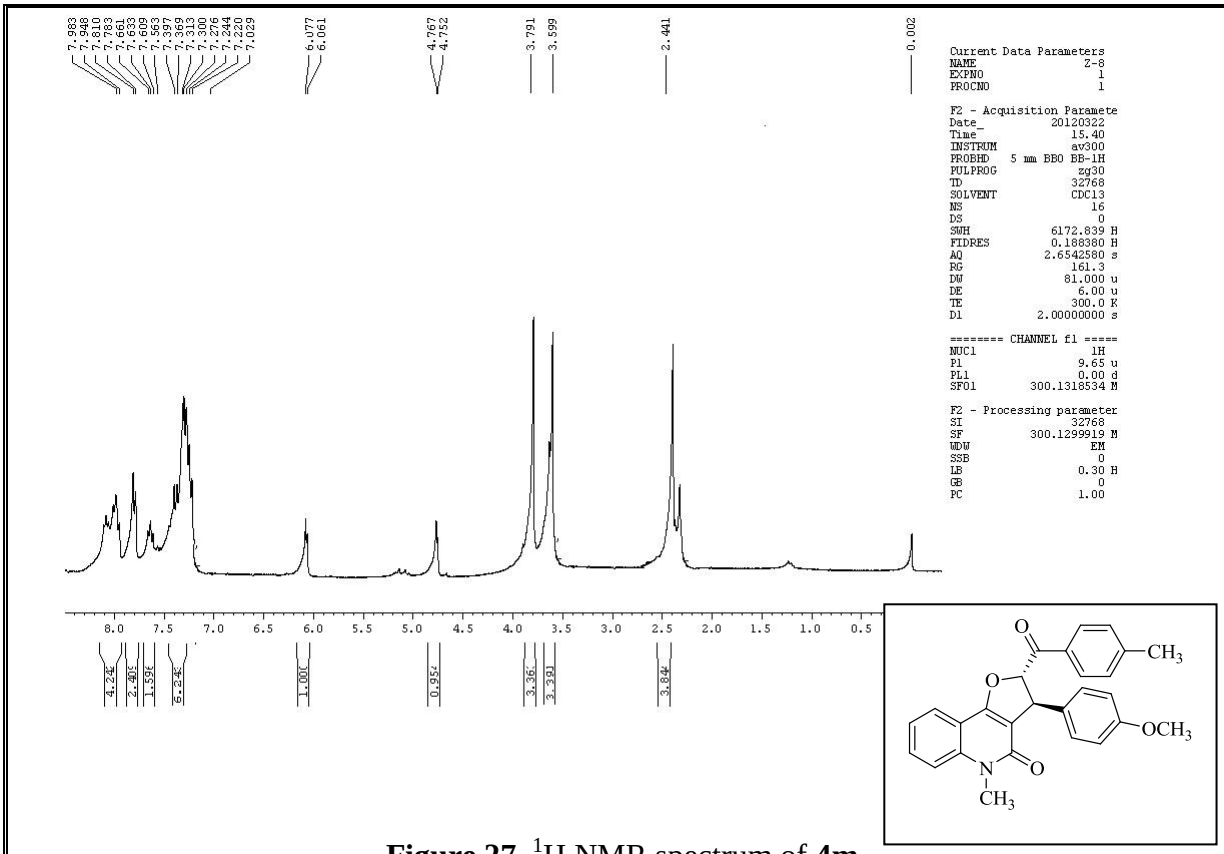


**Figure 27**. $^{1}$H NMR spectrum of **4m**

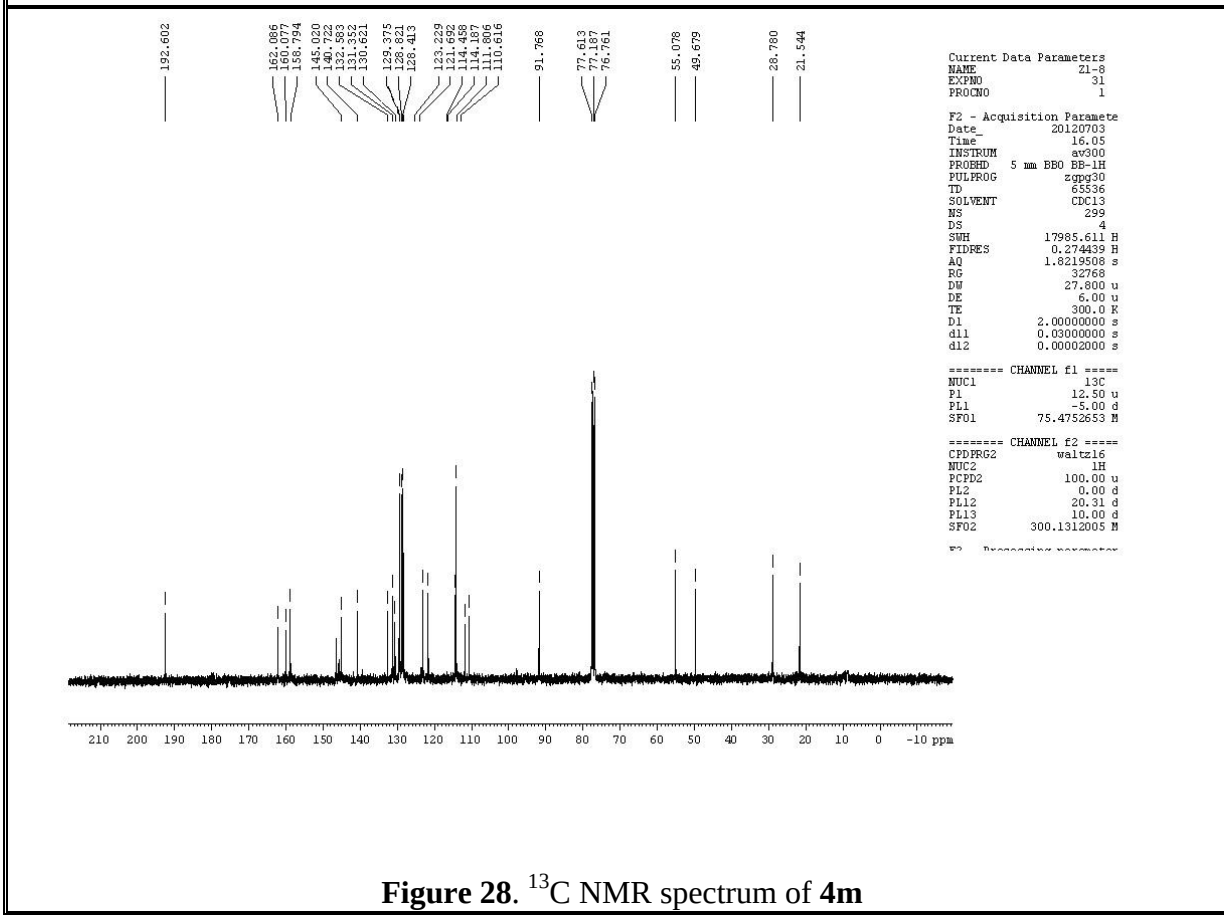


**Figure 28**. $^{13}$C NMR spectrum of **4m**

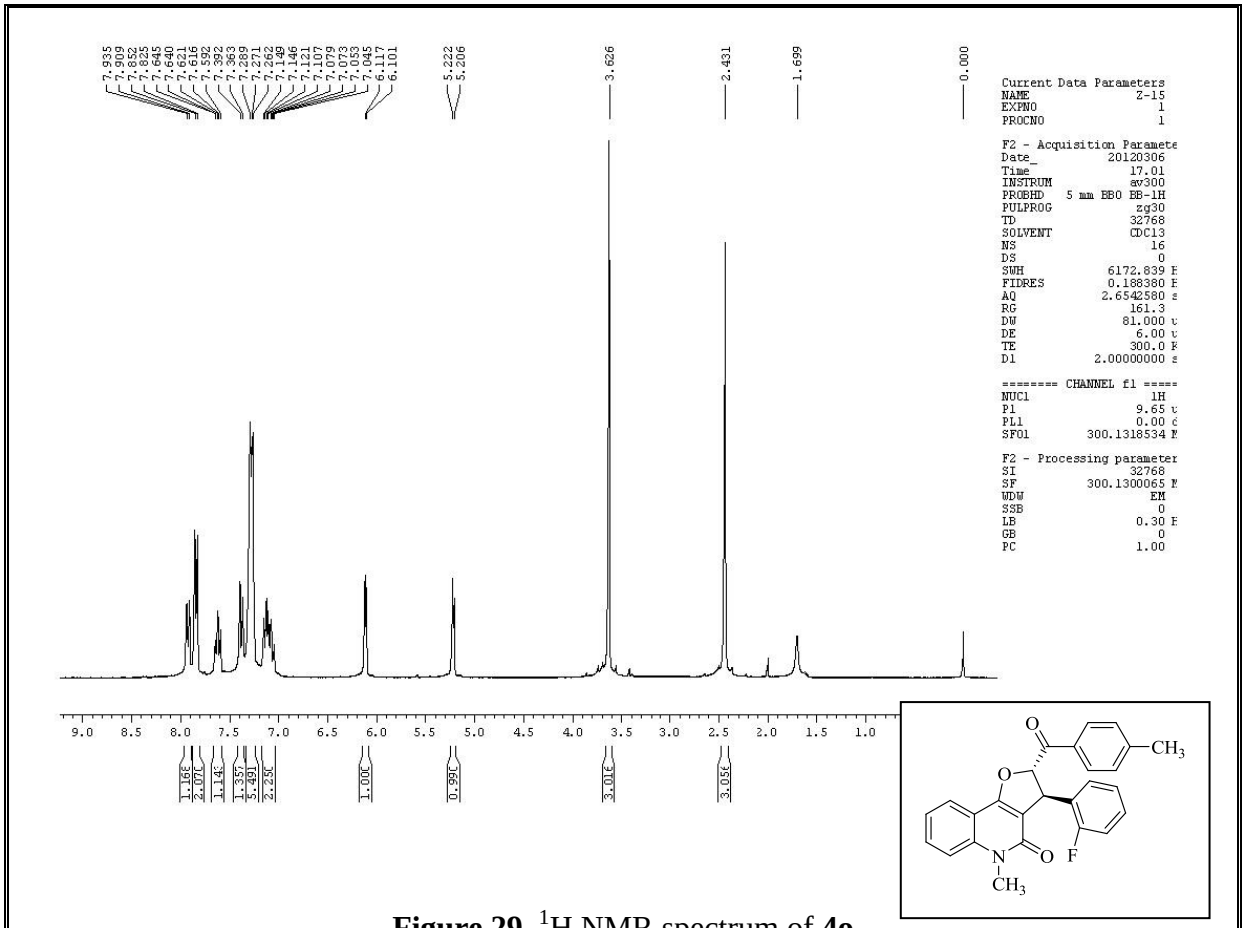


**Figure 29**. $^{1}$H NMR spectrum of **4o**

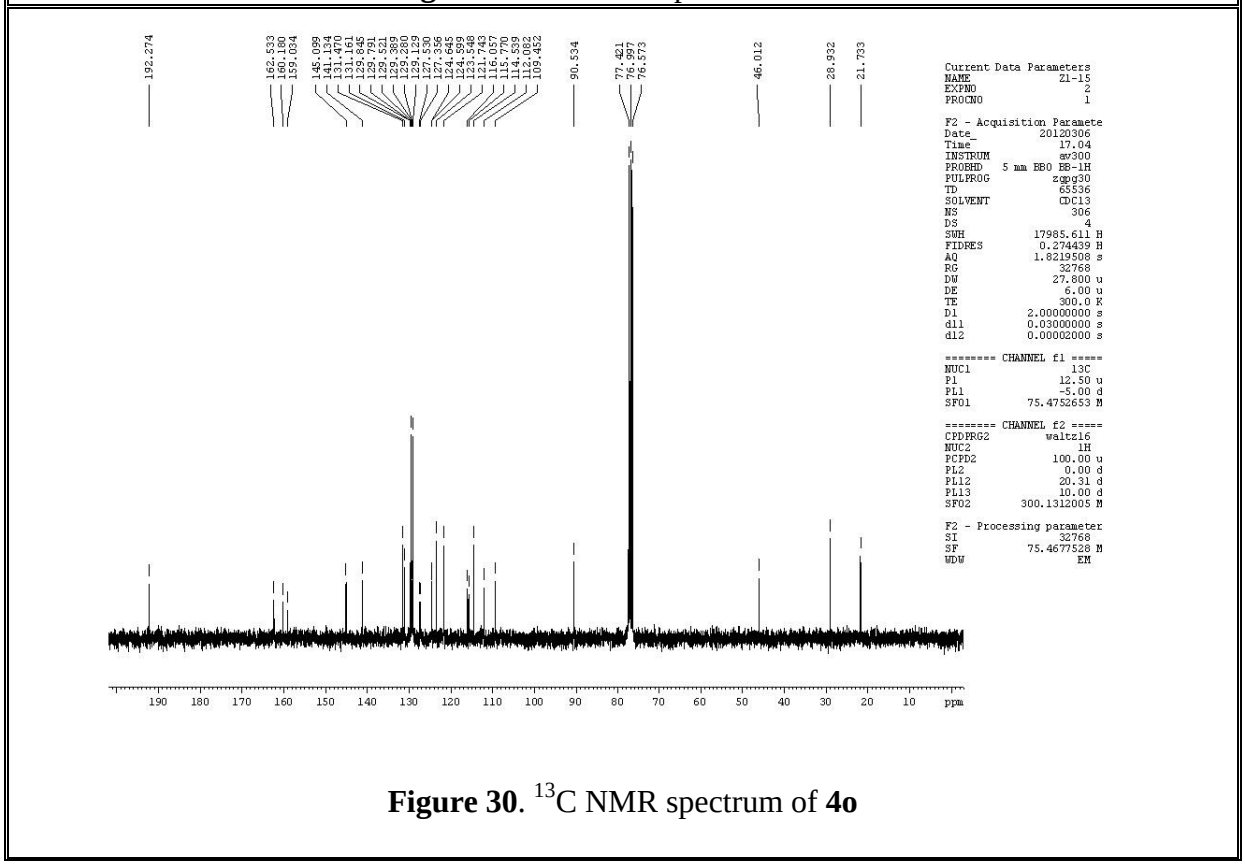


**Figure 30**. $^{13}$C NMR spectrum of **4o**

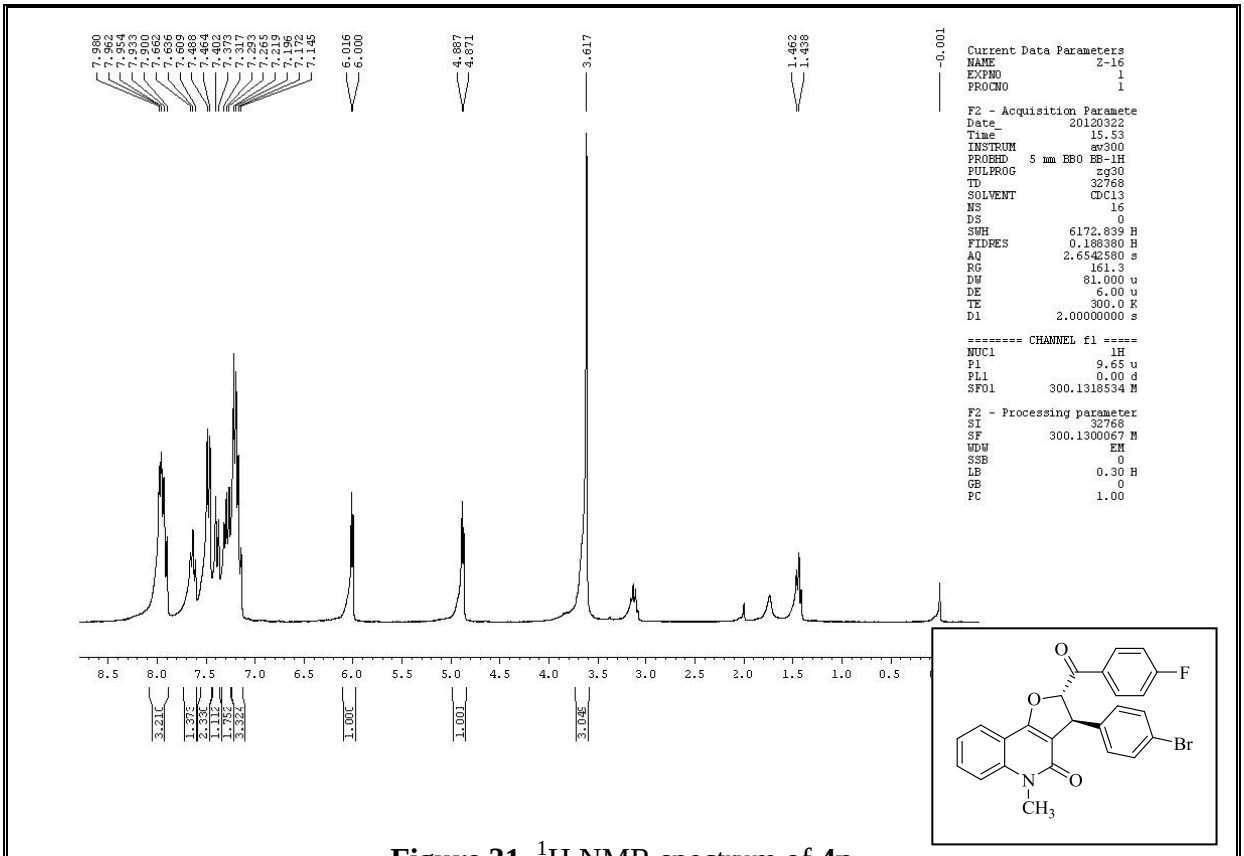


**Figure 31**. $^{1}$H NMR spectrum of **4p**

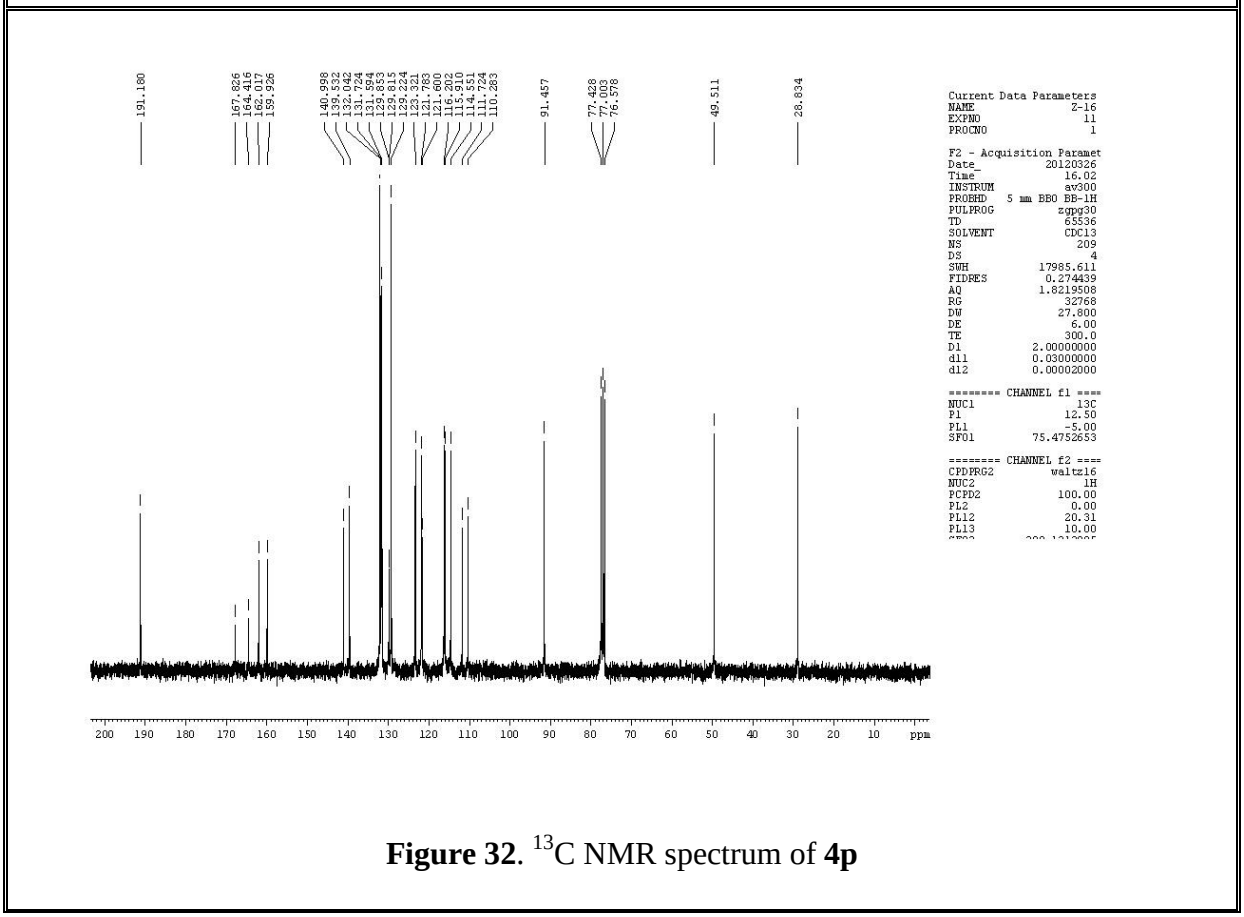


**Figure 32**. $^{13}$C NMR spectrum of **4p**

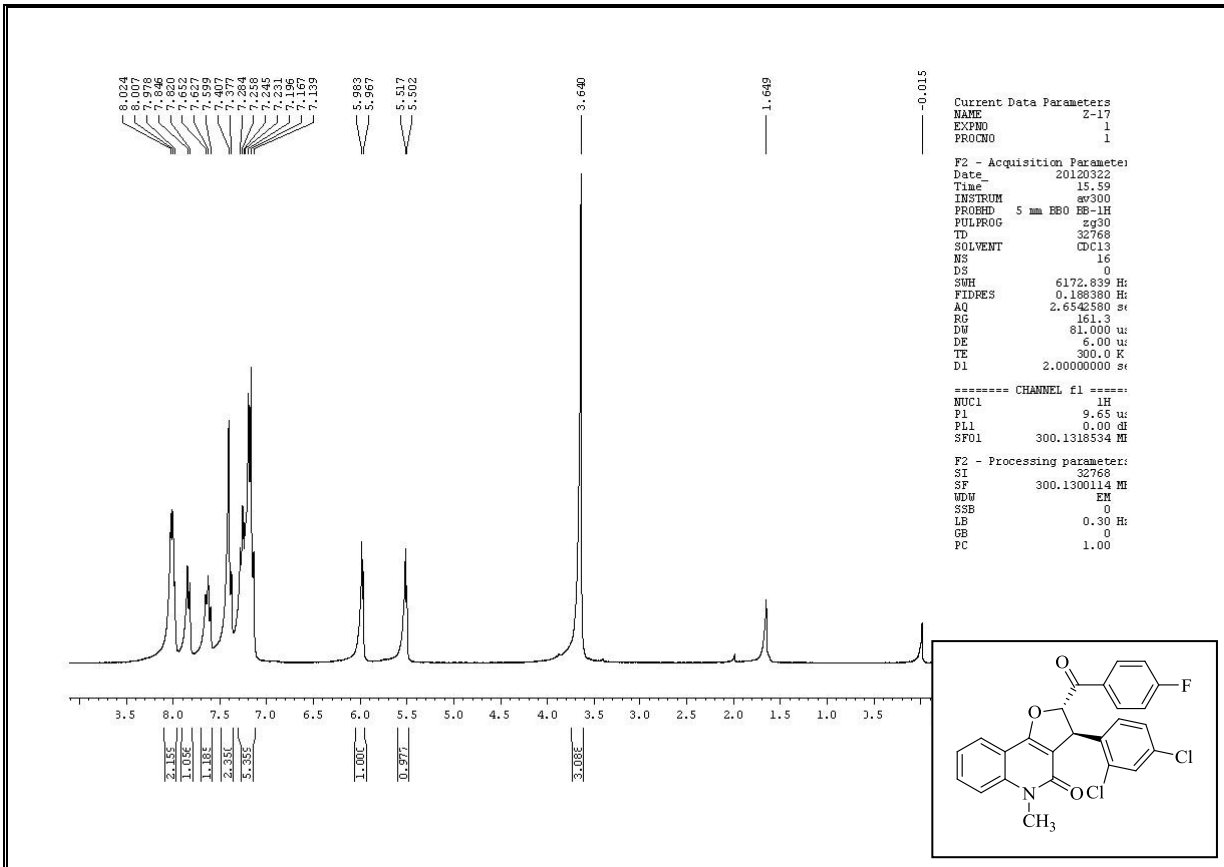


**Figure 33**. $^{1}$H NMR spectrum of **4q**

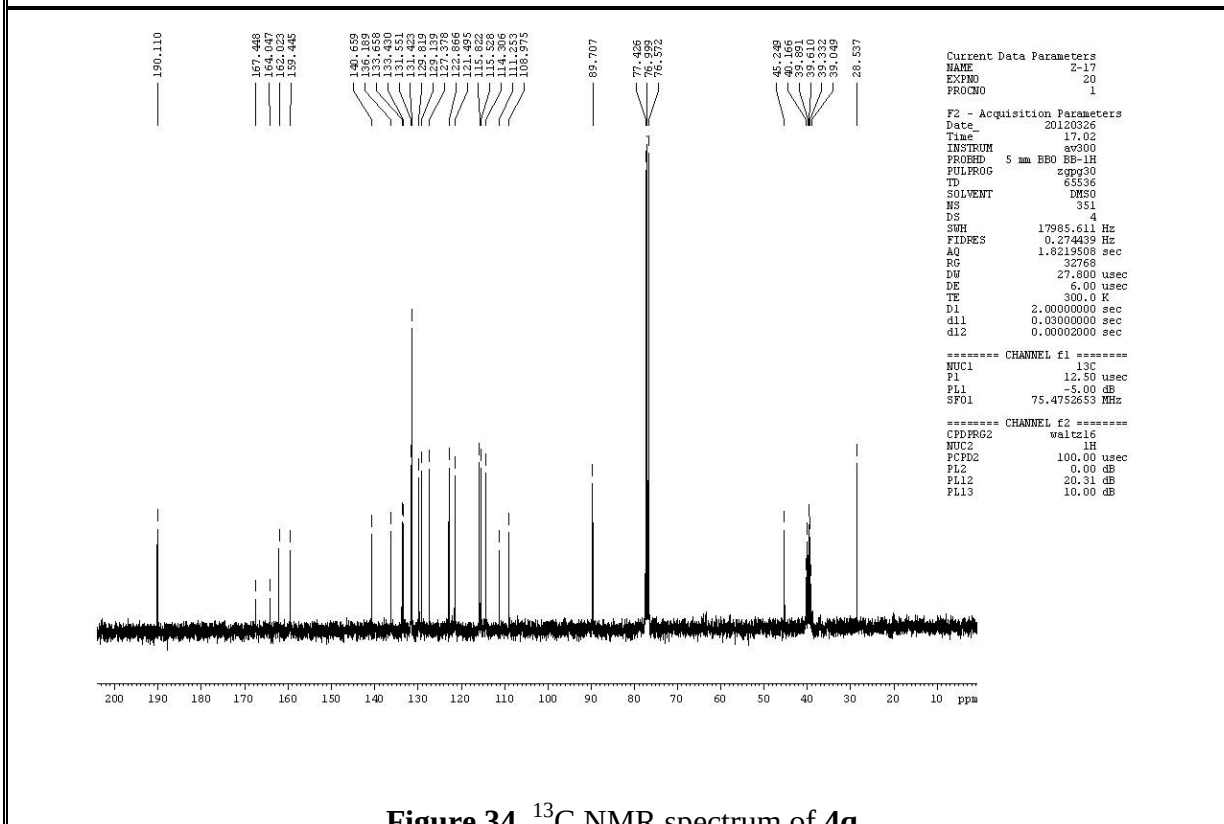


**Figure 34**. $^{13}$C NMR spectrum of **4q**

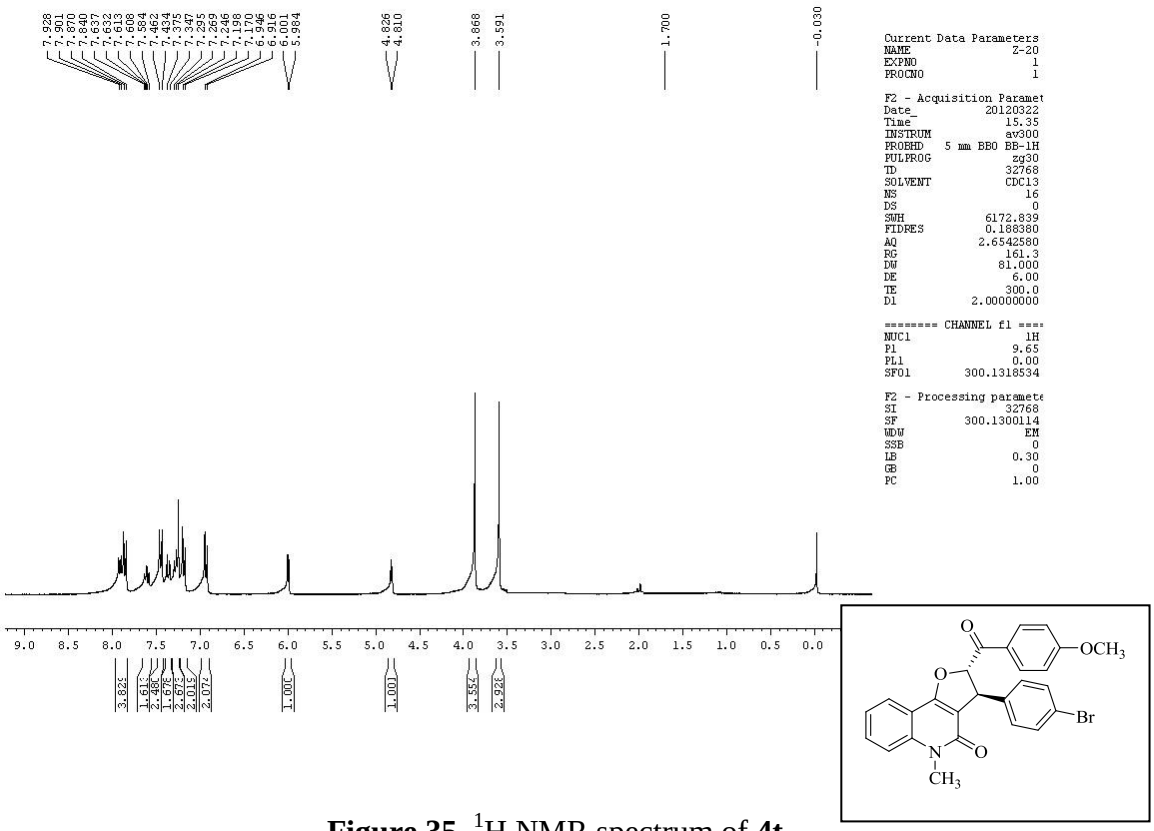


**Figure 35**. $^{1}$H NMR spectrum of **4t**

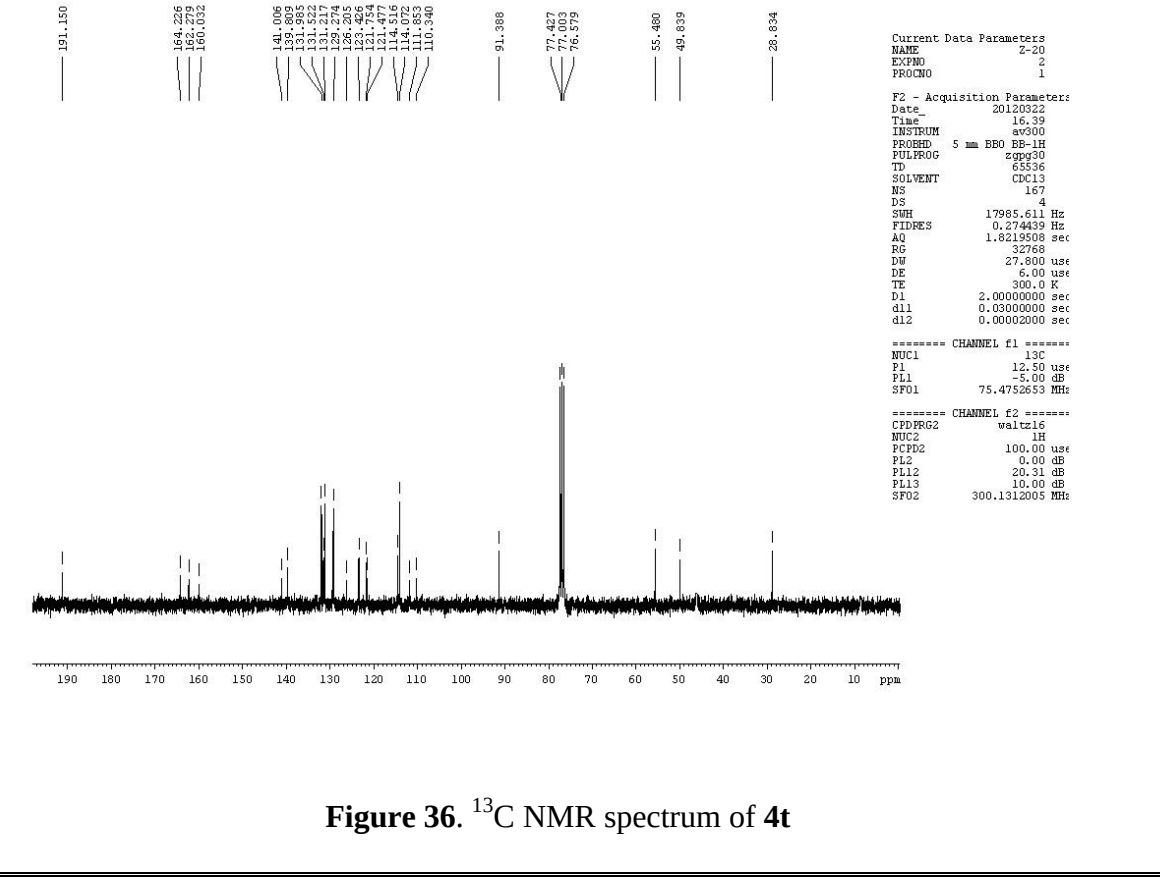


**Figure 36**. $^{13}$C NMR spectrum of **4t**

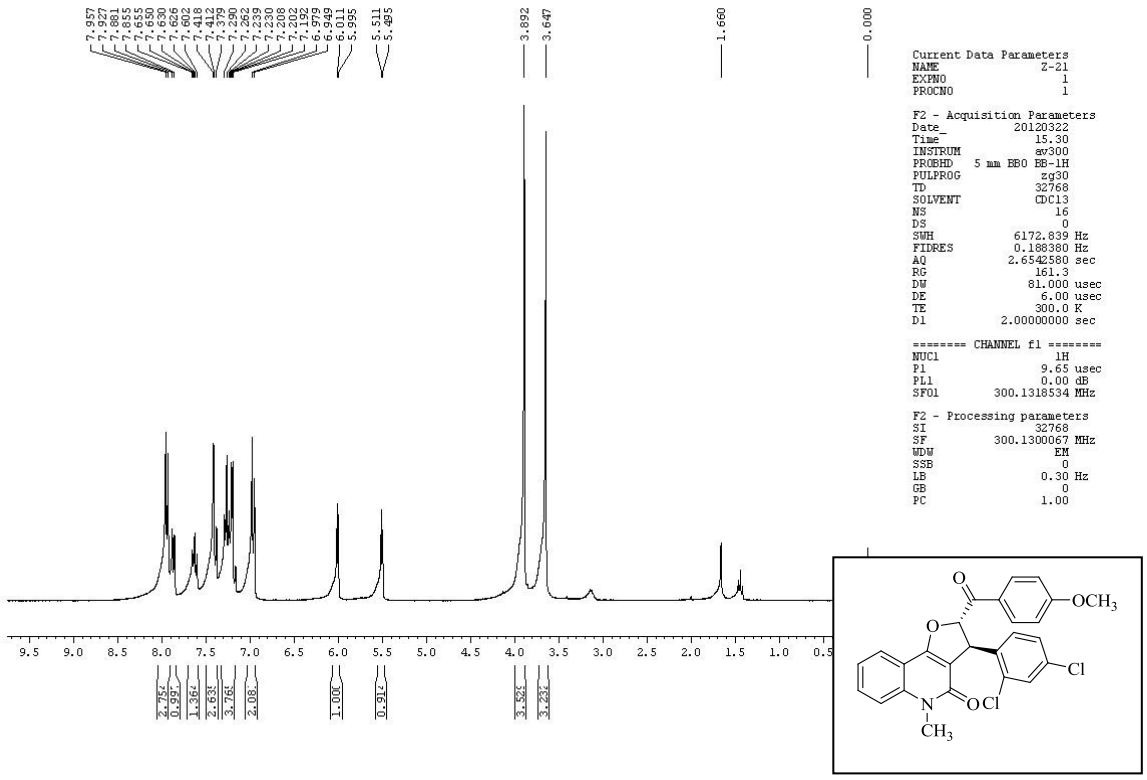


**Figure 37**. $^{1}$H NMR spectrum of **4u**

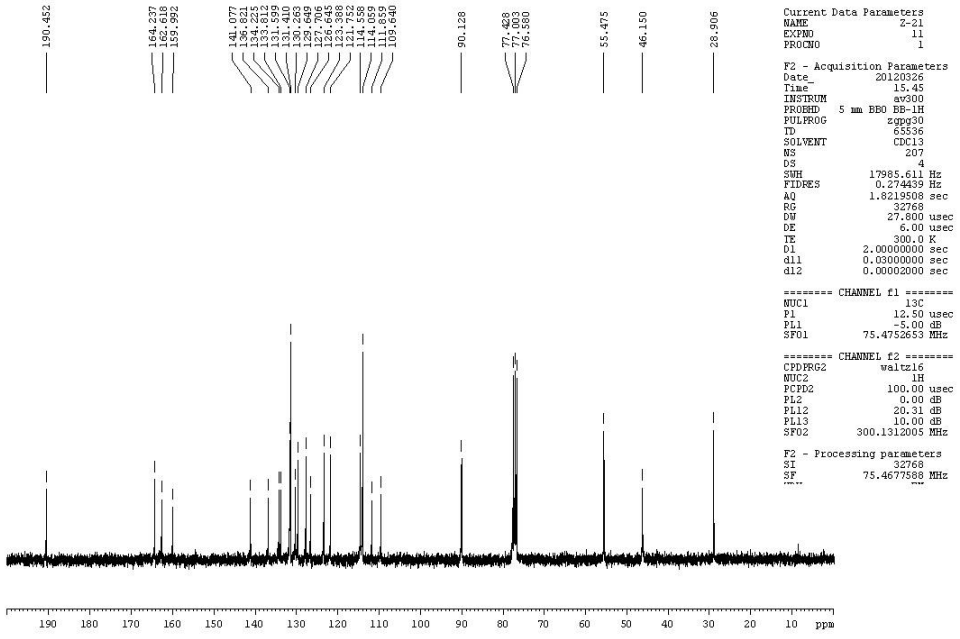


**Figure 38**. $^{13}$C NMR spectrum of **4u**

**Method for removal of TEA and pyridine from aqueous solution after the solid product has been taken off.**

After removal of the solid product from the reaction mixture, the aqueous filtrate (10 mL) from a single experiment could have a maximum of 0.25 mmol of TEA and 1 mmol of pyridine, which is equivalent to 2.53 g of TEA and 7.9 g pyridine in 1L aqueous solution (vide experimental procedure for the synthesis of *trans*-dihydrofuro [3,2-c]-quinolin-4(2H)-ones). Hence, to develop a method for the removal of triethylamine and pyridine from this solution, an aqueous stock solution (1 L) containing 7.9 g of pyridine and 2.53 g of TEA was prepared, which has a pH value of 10.5. This solution was passed through 10 mL of Indion 790 ion exchange resin packed in wet form in a glass column of diameter 0.5". The above pyridine-TEA stock solution was passed through this column of indion at a flow rate of 4 bed volume (one bed volume = 10 mL) per hour (*viz.* 40 mL per hour) and the pH of the elute was measured after collection of every 10 mL of elute from the column. It was found that the pH gradually increased from 5 to 7 when 0 to 13 bed volumes of amine solution was passed through the column. v*iz.* the pH reached 7 after 130 mL of amine solution passed through the column. Thereafter, the pH reaches alkaline region suggesting leaching of amine.

Table 1 : pH measurements of column elute after passing the stock solution with ETA and pyridine of volume V through ion exchange resin column

| Volume of solution, V | pH | Volume of solution, V | pH | Volume of solution, V | pH |
|---|---|---|---|---|---|
| 0 | 5 | 70 | 5 | 140 | 7.1 |
| 10 | 5.4 | 80 | 5 | 150 | 7.2 |
| 20 | 4.9 | 90 | 5.4 | 160 | 7.3 |
| 30 | 4.5 | 100 | 5.6 | 170 | 9.1 |
| 40 | 4.2 | 110 | 6 | 180 | 9.4 |
| 50 | 4.3 | 120 | 6.6 | 190 | 9.4 |
| 60 | 4.7 | 130 | 7 | 200 | 9.5 |

**Calculation for finding the maximum volume of the triethylamine-pyridine stock solution that could be passed through 10 mL of resin column for removing fully the TEA and pyridine.**

Mol.Wt of Pyridine = 79

Mol.Wt of TEA = 101

Exchange Capacity of Indion 790 = 1.9 eq/L;

Weight of pyridine that could be Exchanged by 1L of resin = 150.1 g

Weight of triethylamine that could be Exchanged by 1L of resin = 191.9 g

Amount of Pyridine (in 1 litre of Py-TEA stock solution) = 7.9 g per litre.

Resin qty reqd.to exchange the pyridine In1 litre of stock solution =52.6 mL

Amount of triethylamine (in 1 litre of Py-TEA stock solution)= 2.53 g/L.

Resin qty reqd.to exchange the triethylamine in 1 L of stock solution =13.18 mL

Qty of resin required to treat one litre of py-TEA solution = 65.82 mL

Volume of the above aqueous solution containing triethylamine and pyridine which can be treated by 10 mL of resin = (1000 x 10)/65.82 = 151.9 mL solution

*viz.* Theoretically 151.9 mL of Py-TEA solution could be treated by 10 ml resin. In our experiment, it is found that till 130 mL of aqueous solution (0.1 M pyridine and 0.25 M triethylamine) is passed through the column, the resin is able to remove fully pyridine and TEA. This conclusion is also evident from the following.

Pyridine and TEA emits amine type smell in alkaline condition even at very low concentrations (ppm). Therefore, sodium hydroxide was added to the elute and it was tested for its smell. Upto 130 mL, the smell was absent. Above 130 mL the smell started appearing slowly. It indicates that the amine leakage starts from the column after 150 mL of the solution was passed to it.

From the above, it is found that by using appropriate amount of the above polymer bound acid resin, it is possible to remove pyridine and triethylamine completely from aqueous solution, that remains after the removal of the solid product.