Ruthenium-Catalyzed Cyclization of Anilides with Substituted Propiolates or Acrylates: an Efficient Route to 2-Quinolinones

*Rajendran Manikandan and Masilamani Jeganmohan**

Department of Chemistry, Indian Institute of Science Education and Research, Pune 411021, India

Email: mjeganmohan@iiserpune.ac.in

Supporting Information (SI)

Table of Contents

Experimental Section

General Procedure for the Synthesis of Quinolinones via Cyclization of Acetanilides with Propiolates Catalyzed by Ruthenium Complex.

A 15-mL pressure tube with septum containing [{$RuCl_2$(*p*-cymene)}$_2$] (5.0 mol %) and $AgSbF_6$ (20 mol %) was evacuated and purged with nitrogen gas three times ($AgSbF_6$ was taken inside the glove box). To the tube, were then added acetanilide **1** (100 mg), propiolate **2** (1.50 equiv), pivalic acid (10.0 equiv) and *iso*-propanol (2.5 mL) via syringes and again the reaction mixture was evacuated and purged with nitrogen gas three times. After that, the septum was taken out immediately a screw cap was used to cover the tube. Then, the reaction mixture was allowed to stir at 130 °C for 24 h. After cooling to ambient temperature, the reaction mixture was diluted with CH_2Cl_2, filtered through Celite and silica gel, and the filtrate was concentrated. The crude residue was purified through a silica gel column using dichloromethane and methanol as eluent to give pure **3**. For acetanilides **3fa-3ka and 3ad** Acetic acid solvent (3.0 mL) was used instead of pivalic acid (10.0 equiv) and *iso*-propanol (2.5 mL).

Procedure for the Synthesis of Quinolinones (5aa).

A 15-mL pressure tube with septum containing [{$RuCl_2$(*p*-cymene)}$_2$] (5.0 mol %) and $AgSbF_6$ (20 mol %) was evacuated and purged with nitrogen gas three times ($AgSbF_6$ was taken inside the glove box). To the tube, were then added acetanilide **1a** (100 mg), acrylate **4** (1.50 equiv), pivalic acid (10.0 equiv) and 1:1 mixture of $ClCH_2CH_2Cl$ (DCE) and *iso*-PrOH solvents (2.5 mL) via syringes and again the reaction mixture was evacuated and purged with nitrogen gas three times. After that, the septum was taken out immediately a screw cap was used to cover the tube. Then, the reaction mixture was allowed to stir at 130 °C for 48 h. After cooling to ambient temperature, the reaction mixture was diluted with CH_2Cl_2, filtered through Celite and silica gel, and the filtrate was concentrated. The crude residue was purified through a silica gel column using dichloromethane and methanol as eluent to give pure **5aa.**

General Procedure for the Synthesis of Quinolinones (5ba, 5ea 5fa, 5ga, 5ia and 5ka) via the cyclization of Acetanilides with Acrylates Catalyzed by Ruthenium Complex.

A 15-mL pressure tube with septum containing [{$RuCl_2$(*p*-cymene)}$_2$] (5.0 mol %) and $AgSbF_6$ (20 mol %) was evacuated and purged with nitrogen gas three times ($AgSbF_6$ was taken inside the glove box). To the tube, were then added acetanilide **1** (100 mg), acrylate **4** (1.50 equiv), $Cu(OAC)_2.H_2O$ (1.50 equiv) and 1,2 dichloroethane (3.0 mL) via syringes and again the reaction mixture was evacuated and purged with nitrogen gas three times. After that, the septum was taken out and immediately a screw cap was used to cover the tube. Then, the reaction mixture was allowed to stir at 110 °C for 12 h (for compounds **5ba** and **5ea** only 5 h). After 12 h, the reaction mixture was cooled to the room temperature. In the tube, the screw cap was removed and 0.5 mL of (30% HCl) was added to the reaction mixture and again the tube was covered with a screw cap. Then, the reaction mixture was allowed to stir at 130 °C for 10 h (for substance **5ba**, **5ea** only 5 h). After cooling to ambient temperature, the reaction mixture was diluted with CH_2Cl_2, and 0.5 mL of methanol filtered through Celite. After that, the filtrate was washed with water and the organic layer was extracted with DCM and dried over Na_2SO_4. Later, the solution was concentrated under the reduced pressure. The crude residue was purified through a silica gel column using dichloromethane and methanol as eluent to give pure **5.**

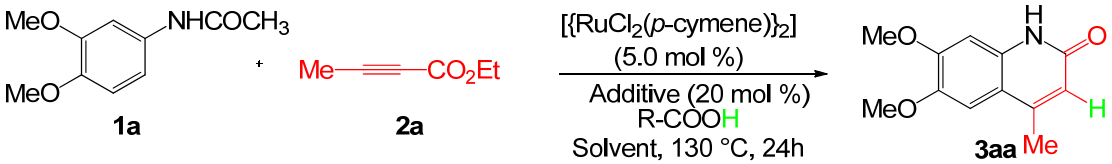
General Procedure for the Synthesis of 2-Chloro Substituted Quinolines 6a-b.

6,7-Dimethoxy-4-methylquinolin-2(1*H*)-one (**3aa)** or 6-bromo-4-propylquinolin-2(1*H*)-one **(3hc)** (100 mg) was taken in a 25-mL round bottom flask and dissolved with 3.0 mL of CH_3CN. To the flask, was then added phosphorous oxychloride ($POCl_3$) (1.2 equiv). Then, the condenser was fitted with water circulation into the round bottom flask and the reaction mixture was allowed to reflux at 90 °C for 4 h under an air atmosphere. Then, the reaction mixture was cooled to ambient temperature and ice water was poured and extracted with ethyl acetate. The organic layer was washed with brine solution and dried over Na_2SO_4. The solution was concentrated under the reduced pressure. The crude residue was purified through a silica gel column using hexanes and ethyl acetate as eluent to give pure **6**.

General Procedure for the Synthesis of 3-Bromo and 3-Chloro Substituted Quinolinones 7a-b.

6,7-Dimethoxy-4-methylquinolin-2(1*H*)-one (**3aa)** (100 mg) was taken in a 25-mL round bottom flask and dissolved with 3.0 mL of CCl_4. To the flask, were then added *N*-bromo succinimide (or) *N*-chlorosuccinimide (1.2 mmol) and AIBN (10 mol %). Then, the condenser was fitted with water circulation in the round bottom flask and the reaction mixture was allowed to reflux at 90 °C for 2 h under an air atmosphere. After cooling to ambient temperature, the reaction mixture was diluted with CH_2Cl_2. The crude residue was purified through a silica gel column using dichloromethane and methanol as eluent to give pure **7.**

Table S1. Optimization Studies for Method A.[a]

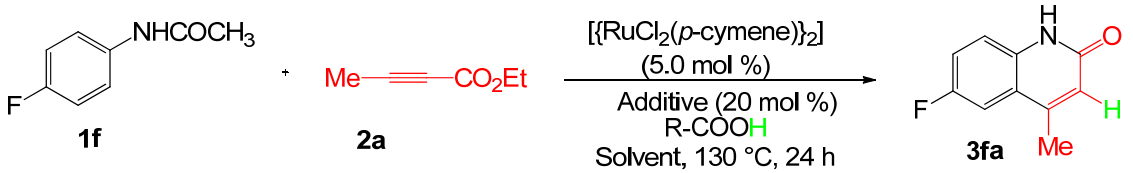


entry	solvent	co-solvent	additive	yield of **3aa** (%)[b]
1	i-propanol	No	$AgSbF_6$	NR
2	i-propanol	Acetic acid (1.0 mL)	$AgSbF_6$	62
3	i-propanol	Pivalic acid (5.0 equiv)	$AgSbF_6$	67
4	i-propanol	Mesitylenic acid (2.0 equiv)	$AgSbF_6$	15
5	i-propanol	Pivalic acid (10.0 equiv)	$AgSbF_6$	86
6	i-propanol	Pivalic acid (10.0 equiv)	AgOTf	76
7	i-propanol	Pivalic acid (10.0 equiv)	$AgBF_4$	68
8	i-propanol	Pivalic acid (10.0 equiv)	KPF_6	NR
9	Methanol	Pivalic acid (10.0 equiv)	$AgSbF_6$	61
10	DCE	Pivalic acid (10.0 equiv)	$AgSbF_6$	54
11	THF	Pivalic acid (10.0 equiv)	$AgSbF_6$	41
12	DMF	Pivalic acid (10.0 equiv)	$AgSbF_6$	NR
13	DMSO	Pivalic acid (10.0 equiv)	$AgSbF_6$	NR
14	Toluene	Pivalic acid (10.0 equiv)	$AgSbF_6$	NR
15	1,4-Dioxane	Pivalic acid (10.0 equiv)	$AgSbF_6$	37

[a]All reactions were carried out under the following conditions: **1a** (1.0 mmol), **2a** (1.50 mmol), [{$RuCl_2$(*p*-cymene)}$_2$] (5 mol %) and additive (20 mol %) in solvent (2.5 mL) at 130 °C for 24 h under N_2 atmosphere. [b]Isolated yield.

Note: The catalytic reaction was tried without ruthenium and $AgSbF_6$. No product **3aa** was observed in the reaction.

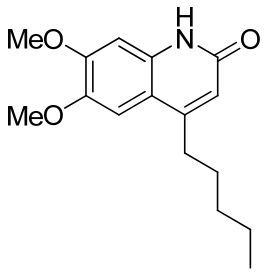
Table S2. Optimization Studies for Method B.[a]



entry	solvent	co-solvent	additive	yield of **3fa** (%)[b]
1	i-propanol	Pivalic acid (10.0 equiv)	$AgSbF_6$	41
2	i-propanol	Acetic acid (1.0 mL)	$AgSbF_6$	53
3	Acetic acid	No	$AgSbF_6$	62

[a]All reactions were carried out under the following conditions: **1f** (1.0 mmol), **2a** (1.50 mmol), [{$RuCl_2$(*p*-cymene)}$_2$] (5 mol %) and additive (20 mol %) in solvent (3.0 mL) at 130 °C for 24 h under N_2 atmosphere. [b]Isolated yield.

Crystal structure of compound **3ac.**



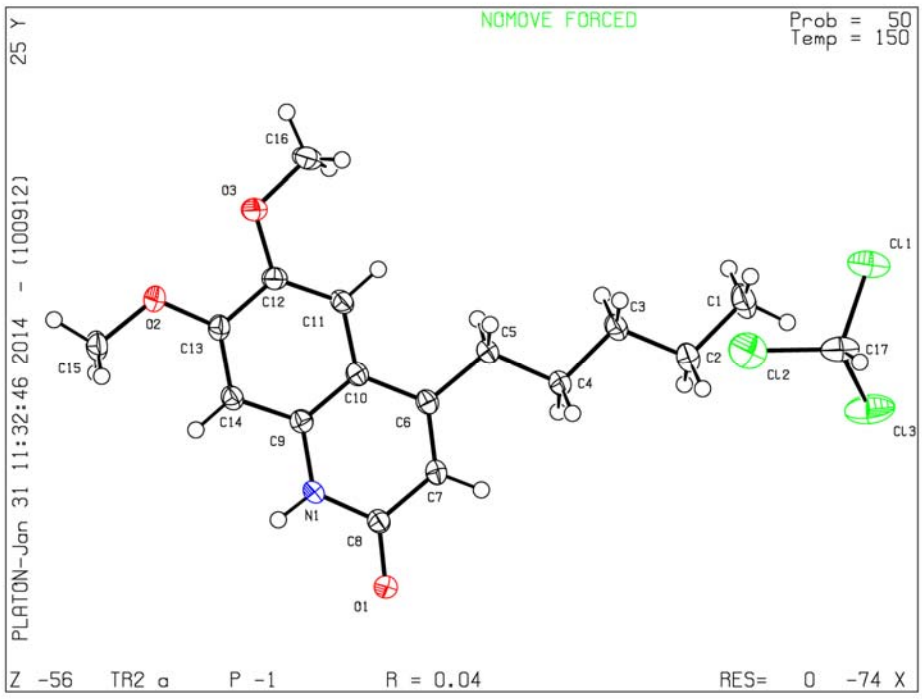


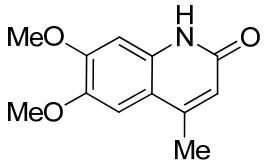
Table 1. Crystal data and structure refinement for mani 03.

Identification code	3ac
Empirical formula	$C_{16}H_{21}NO_3, CHCl_3$
Formula weight	394.71
Temperature	150 K
Wavelength	1.54178 Å
Crystal system	Triclinic
Space group	P -1

Unit cell dimensions	a = 7.1463 (3) Å	α= 99.6700(15)°.
	b = 10.1770(4) Å	β= 92.9420(16).
	c = 13.3296(5) Å	γ = 99.2950(15).
Volume	940.04 (6) $Å^3$	
Z	2	
Density (calculated)	1.395Mg/m^3	
Absorption coefficient	0.713 mm^{-1}	
F(000)	412.0	
Crystal size	0.236 x 0.101 x 0.032 mm^3	
Theta range for data collection	8.98 to 66.94°.	
Index ranges	-12<=h<=7, -6<=k<=6, -22<=l<=22	
Reflections collected	3529	
Independent reflections	1864 [R(int) = 0.0442]	
Completeness to theta = 66.94°	94.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.977 and 0.917	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	1764 / 0 / 146	
Goodness-of-fit on F^2	0.977	
Final R indices [I>2sigma(I)]	R1 = 0.0430, wR2 = 0.1621	
R indices (all data)	R1 = 0.0470, wR2 = 0.1634	
Largest diff. peak and hole	0.248 and -0.196 e.$Å^{-3}$	

Spectral Data of Compounds.

6,7-Dimethoxy-4-methylquinolin-2(1*H*)-one (3aa).



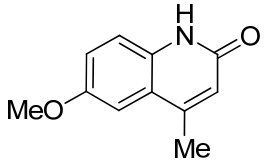
Brown colour solid; eluent (4% DCM in Methanol). The reaction scale is 100 mg, product was isolated in 96 mg, 86% yield was observed.

^{1}H NMR (DMSO-d_6, 400 MHz): δ 11.38 (s, 1 H), 7.07 (s, 1 H), 6.85 (s, 1 H), 6.22 (s, 1 H), 3.81 (s, 3 H), 3.80 (s, 3 H), 2.38 (s, 3 H).

^{13}C NMR (DMSO-d_6, 400 MHz): δ 161.6, 151.7, 147.6, 144.6, 134.2, 118.1, 112.6, 106.1, 97.9, 55.8, 55.5, 18.8.

HRMS (ESI): calc. for [($C_{12}H_{13}NO_3$)H] (M+H) 220.0973, measured 220.0978.

6-Methoxy-4-methylquinolin-2(1*H*)-one (3ba).



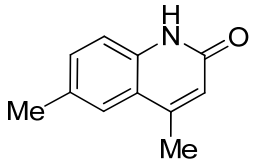
Brown colour solid; eluent (3% DCM in Methanol). The reaction scale is 100 mg, product was isolated in 92 mg, 81 % yield was observed.

^{1}H NMR (DMSO-d_6, 400 MHz): δ 11.49 (s, 1 H), 7.25 (d, J = 8.0 Hz, 1 H), 7.15 (dd, J = 8.0, 4.0 Hz, 1 H), 7.13 (s, 1 H), 6.39 (s, 1 H), 3.81 (s, 3 H), 2.41 (s, 3 H).

^{13}C NMR (DMSO-d_6, 100 MHz): δ 161.2, 154.1, 147.4, 133.0, 121.2, 120.2, 119.0, 116.6, 106.8, 55.5, 18.6.

HRMS (ESI): calc. for [($C_{11}H_{11}NO_2$)H] (M+H) 190.0868, measured 190.0872.

4,6-Dimethylquinolin-2(1*H*)-one (3ca).



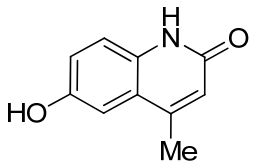
White colour solid; eluent (2% DCM in Methanol). The reaction scale is 100 mg, product was isolated in 91 mg, 79 % yield was observed.

^{1}H NMR (DMSO-d_6, 400 MHz): δ 11.52 (s, 1 H), 7.47 (s, 1 H), 7.30 (d, *J* = 8.0 Hz, 1 H), 7.20 (d, *J* = 4.0 Hz, 1 H), 6.35 (s, 1 H), 2.39 (s, 3 H), 2.35 (s, 3 H).

^{13}C NMR (DMSO-d_6, 100 MHz): δ 161.5, 147.6, 136.6, 131.4, 130.5, 124.3, 120.8, 119.5, 115.3, 20.6, 18.5.

HRMS (ESI): calc. for [($C_{11}H_{11}NO$)H] (M+H) 174.0919, measured 174.0924.

6-Hydroxy-4-methylquinolin-2(1*H*)-one (3da).



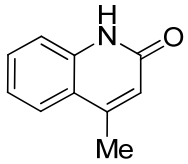
Brown colour solid; eluent (5% DCM in Methanol). The reaction scale is 100 mg, product was isolated in 88 mg, 76 % yield was observed.

^{1}H NMR (DMSO-d_6, 400 MHz): δ 11.40 (s, 1 H), 9.41 (s, 1 H), 7.16 (d, *J* = 8.0 Hz, 1 H), 7.00 (d, *J* = 8.0 Hz, 1 H), 6.99 (s, 1 H), 6.35 (s, 1 H), 2.34 (s, 3 H).

^{13}C NMR (DMSO-d_6, 100 MHz): δ 161.1, 152.1, 147.1, 131.9, 121.0, 120.5, 119.5, 116.5, 108.6, 18.5.

HRMS (ESI): calc. for [($C_{10}H_9NO_2$)H] (M+H)176.0711, measured 176.0716.

4-Methylquinolin-2(1*H*)-one (3ea).



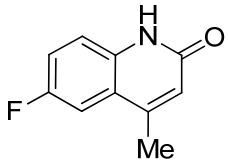
Light yellow colour solid; eluent (2% DCM in Methanol). The reaction scale is 100 mg, product was isolated in 94 mg, 80 % yield was observed.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.65 (d, *J* = 8.0 Hz, 1 H) 7.50 - 7.44 (m, 2 H), 7.21 (dd, *J* = 8.0, 4.0 Hz, 1 H), 6.58 (s, 1 H), 2.49 (s, 3 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 164.4, 149.3, 138.2, 130.4, 124.3, 122.5, 120.5, 120.4, 116.7, 19.1.

HRMS (ESI): calc. for [($C_{10}H_9NO$)H] (M+H) 160.0762, measured 160.0768.

6-Fluoro-4-methylquinolin-2(1*H*)-one (3fa).



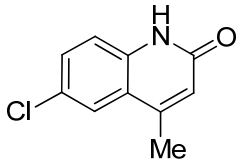
White colour solid; eluent (2% DCM in Methanol). The reaction scale is 100 mg, product was isolated in 72 mg, 62 % yield was observed.

^{1}H NMR (DMSO-d_6, 400 MHz): δ 11.67 (s, 1 H), 7.57 (dd, *J* = 8.0, 4.0 Hz, 1 H), 7.40 (td, *J* = 8.0, 4.0 Hz, 1 H) 7.33 - 7.30 (m, 1 H), 6.45 (s, 1 H), 2.39 (s, 3 H).

^{13}C NMR (DMSO-d_6, 100 MHz): δ 161.3, 158.2, 147.4, 135.3, 121.9, 120.4, 118.3 and 118.1 (F-coupling), 117.1, 110.1 and 109.9 (F-coupling), 18.5.

HRMS (ESI): calc. for [($C_{10}H_8FNO$)H] (M+H) 178.0668, measured 178.0672.

6-Chloro-4-methylquinolin-2(1*H*)-one (3ga).



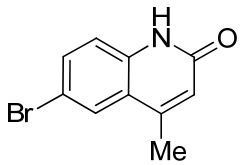
Light green colour solid; eluent (2% DCM in Methanol). The reaction scale is 100 mg, product was isolated in 73 mg, 64% yield was observed.

^{1}H NMR (DMSO-d_6, 400 MHz): δ 11.72 (s, 1 H), 7.71 (s, 1 H), 7.53 (dd, *J* = 8.0, 4.0 Hz, 1 H), 7.30 (d, *J* = 8.0 Hz, 1 H), 6.44 (s, 1 H), 2.40 (s, 3 H).

^{13}C NMR (DMSO-d_6, 100 MHz): δ 161.4, 147.2, 137.4, 130.2, 125.7, 124.0, 121.9, 120.9, 117.2, 18.4.

HRMS (ESI): calc. for [($C_{10}H_8ClNO$)H] (M+H) 194.0372, measured 194.0375.

6-Bromo-4-methylquinolin-2(1*H*)-one (3ha).



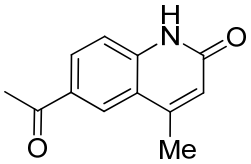
Yellow solid; eluent (2% DCM in Methanol).The reaction scale is 100 mg, product was isolated 77 mg, 69% yield.

^{1}H NMR (DMSO-d_6, 400 MHz): δ 11.73 (s, 1 H), 7.84 (s, 1 H), 7.65 (d, *J* = 8.0, Hz, 1 H), 7.25 (d, *J* = 12.0 Hz, 1 H), 6.44 (s, 1 H), 2.50 (s, 3 H).

^{13}C NMR (DMSO-d_6, 100 MHz):δ 161.4, 147.2, 137.8, 132.9, 127.0, 121.8, 121.4, 117.7, 113.6, 18.4.

HRMS (ESI): calc. for [($C_{10}H_8BrNO$)H] (M+H) 237.9867, measured 237.9868.

6-Acetyl-4-methylquinolin-2(1*H*)-one (3ia).



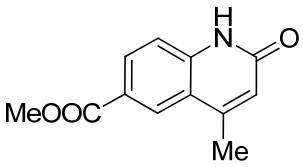
Yellow solid; eluent (2% DCM in Methanol). The reaction scale is 100 mg, product was isolated in 75 mg, 66 % yield was observed.

^{1}H NMR (DMSO-d_6, 400 MHz): δ 11.91 (s, 1 H), 8.24(s, 1 H), 8.05 (d, J = 8.0 Hz, 1 H), 7.35 (d, J = 8.0 Hz, 1 H), 6.47 (s, 1 H), 2.62 (s, 3 H), 2.49 (s, 3 H).

^{13}C NMR (DMSO-d_6, 100 MHz): δ 196.6, 161.8, 148.4, 141.9, 130.4, 129.8, 125.9, 121.6, 119.0, 115.6, 26.6, 18.4.

HRMS (ESI): calc. for [($C_{12}H_{11}NO_2$)H] (M+H) 202.0868, measured 202.0864.

Methyl 4-methyl-2-oxo-1,2-dihydroquinoline-6-carboxylate (3ja).



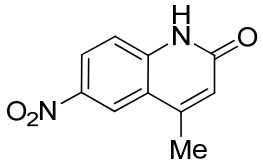
Light red colour solid; eluent (3% DCM in Methanol). The reaction scale is 100 mg, product was isolated in 79 mg, 71 % yield was observed.

^{1}H NMR (DMSO-d_6, 400 MHz): δ 11.94 (s, 1 H), 8.23 (s, 1 H), 8.03 (dd, J = 8.0, 4.0 Hz, 1 H), 7. 36 (d, J = 12.0 Hz, 1 H), 6.48 (s, 1 H), 3.86 (s, 3 H), 2.45 (s, 3 H).

^{13}C NMR (DMSO-d_6, 100 MHz): δ 165.8, 161.7, 148.0, 142.0, 130.6, 126.4, 122.7, 121.7, 119.2, 115.8, 52.1, 18.4.

HRMS (ESI): calc. for [($C_{12}H_{11}NO_3$)H] (M+H) 218.0871, measured 218.0871.

4-Methyl-6-nitroquinolin-2(1*H*)-one (3ka).



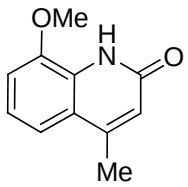
Yellow colour solid; eluent (2% DCM in Methanol). The reaction scale is 100 mg, product was isolated in 78 mg, 69 % yield was observed.

^{1}H NMR (DMSO-d_6, 400 MHz): δ 12.18 (s, 1 H), 8.49 (s, 1 H), 8.33 (d, J = 8.0 Hz, 1 H), 7.42 (d, J = 8.0 Hz, 1 H), 6.57 (s, 1 H), 2.50 (s, 3 H).

^{13}C NMR (DMSO-d_6, 100 MHz): δ 161.7, 148.1, 143.2, 141.4, 125.2, 122.6, 121.2, 119.1, 116.4, 18.3.

HRMS (ESI): calc. for [($C_{10}H_8N_2O_3$)H] (M+H) 205.0613, measured 205.0620.

8-Methoxy-4-methylquinolin-2(1*H*)-one (3la).



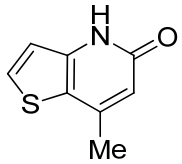
Light yellow colour solid; eluent (3% DCM in Methanol). The reaction scale is 100 mg, product was isolated in 88 mg, 77 % yield was observed.

^{1}H NMR (DMSO-d_6, 400 MHz): δ 10.59 (s, 1 H), 7.29 – 7.27 (m, 2 H), 7.15 (d, J = 8.0 Hz, 1 H), 6.42 (s, 1 H), 3.89 (s, 3 H), 2.41 (s, 3 H).

^{13}C NMR (DMSO-d_6, 100 MHz):δ 161.1, 148.1, 145.8, 128.6, 121.5, 121.4, 120.0, 116.4, 110.9, 56.0, 18.7.

HRMS (ESI): calc. for [($C_{11}H_{11}NO_2$)H] (M+H) 190.0868, measured 190.0872.

7-Methylthieno[3,2-*b*]pyridin-5(4*H*)-one (3ma).



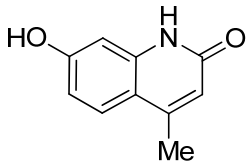
Light yellow solid; eluent (2% DCM in Methanol). The reaction scale is 100 mg, product was isolated in 93 mg, 83 % yield was observed.

^{1}H NMR (CD_3OD, 400 MHz): δ 7.20 (d, *J* = 8.0 Hz, 1 H), 7.16 (d, *J* = 8.0 Hz, 1 H), 6.32 (s, 1 H), 2.46 (s, 3 H).

^{13}C NMR (CD_3OD, 100 MHz): δ 165.6, 150.2, 147.9, 125.0, 122.0, 119.4, 115.5, 19.9.

HRMS (ESI): calc. for [(C_8H_7NOS)H] (M+H) 166.0326, measured 166.0329.

7-Hydroxy-4-methylquinolin-2(1*H*)-one (3na).



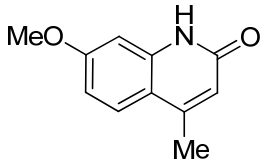
White colour solid; eluent (5% DCM in Methanol). The reaction scale is 100 mg, product was isolated in 101 mg, 88 % yield was observed.

^{1}H NMR (DMSO-d_6, 400 MHz): δ 11.38 (s, 1 H), 10.08 (s, 1 H), 7.50 (d, *J* = 8.0 Hz, 1 H), 6.70 (d, *J* = 4.0 Hz, 1 H), 6.63 - 6.65 (m, 1 H), 6.13 (s, 1 H), 2.33 (s, 3 H).

^{13}C NMR (DMSO-d_6, 100 MHz):δ 162.2, 159.5, 147.9, 140.6, 126.2, 117.0, 112.8, 111.3, 100.1, 18.6.

HRMS (ESI): calc. for [($C_{10}H_9NO_2$)H] (M+H) 176.0711, measured 176.0716.

7-Methoxy-4-methylquinolin-2(1*H*)-one (3oa).



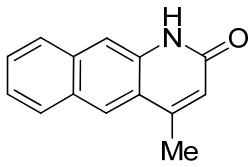
Light yellow solid; eluent (3% DCM in Methanol). The reaction scale is 100 mg, product was isolated in 98 mg, 86 % yield was observed.

^{1}H NMR (CD_3OD, 400 MHz): δ 7.69 (d, *J* = 12.0 Hz, 1 H), 6.89 (dd, *J* = 8.0, 4.0 Hz, 1 H), 6.84 (d, *J* = 4.0 Hz, 1 H), 6.33 (s, 1 H), 3.88 (s, 3 H), 2.47 (s, 3 H).

^{13}C NMR (CD_3OD, 100 MHz): δ 165.7, 163.6, 151.9, 141.4, 127.5, 117.8, 116.2, 113.4, 99.5, 56.2, 19.3.

HRMS (ESI): calc. for [($C_{11}H_{11}NO_2$)H] (M+H) 190.0868, measured 190.0872.

4-Methylbenzo[*g*]quinolin-2(1*H*)-one (3pa).



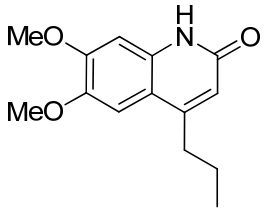
White colour solid; eluent (2% DCM in Methanol). The reaction scale is 100 mg, product was isolated in 86 mg, 76 % yield was observed.

^{1}H NMR (DMSO-d_6, 400 MHz): δ 11.61 (s, 1 H), 8.35 (s, 1 H), 8.03 (d, *J* = 8.0 Hz, 1 H), 7.87 (d, *J* = 8.0 Hz, 1 H), 7.66 (s, 1 H), 7.52 (t, *J* = 8.0 Hz, 1 H), 7.42 (t, *J* = 8.0 Hz, 1 H), 6.46 (s, 1 H), 2.50 (s, 3 H).

^{13}C NMR (DMSO-d_6, 100 MHz): δ 161.9, 147.6, 136.2, 133.7, 128.8, 128.4, 127.4, 126.5, 125.0, 124.9, 121.6, 120.7, 110.2, 18.5.

HRMS (ESI): calc. for [($C_{14}H_{11}NO$)H] (M+H) 210.0919, measured 210.0971.

6,7-dimethoxy-4-propylquinolin-2(1*H*)-one (3ab).



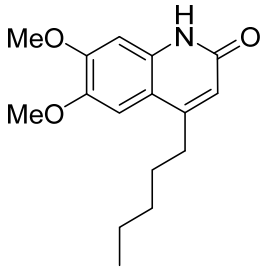
Brown solid; eluent (3% DCM in Methanol). The reaction scale is 100 mg, product was isolated in 102 mg, 81 % yield was observed.

^{1}H NMR (DMSO-d_6, 400 MHz): δ 11.31 (s, 1 H), 7.00 (s, 1 H), 6.77 (s, 1 H), 6.08 (s, 1 H), 3.71 (s, 3 H), 3.70 (s, 3 H), 2.64 (t, *J* = 8.0 Hz, 2 H), 1.57 - 1.52 (m, 2 H), 0.87 (t, *J* = 8.0 Hz, 3 H).

^{13}C NMR (DMSO-d_6, 400 MHz): δ 161.6, 151.6, 151.1, 144.6, 134.6, 117.1, 111.8, 105.8, 98.1, 55.9, 55.5, 33.4, 21.6, 13.8.

HRMS (ESI): calc. for [($C_{14}H_{17}NO_3$)H] (M+H), 248.1286 measured 248.1291.

6,7-Dimethoxy-4-pentylquinolin-2(1*H*)-one (3ac).



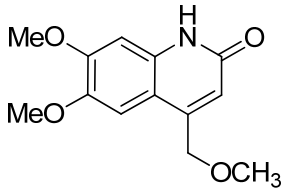
Brown colour solid; eluent (3% DCM in Methanol). The reaction scale is 100 mg, product was isolated in 111 mg, 79 % yield was observed.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.02 (s, 1 H), 6.91 (s, 1 H), 6.46 (s, 1 H), 3.98 (s, 3 H), 3.91 (s, 3 H), 2.77 (t, *J* = 8.0 Hz, 2 H), 1.71 (t, *J* = 8.0 Hz, 2 H), 1.38 - 1.37 (m, 4 H) , 0.89 (t, *J* = 8.0 Hz, 3 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 164.6, 152.8, 152.3, 145.6, 134.6, 116.6, 113.2, 104.7, 98.7, 56.3, 56.2, 32.4, 31.6, 28.3, 22.4, 13.9.

HRMS (ESI): calc. for [($C_{16}H_{21}NO_3$)H] (M+H) 276.1600 measured 276.1606.

6,7-Dimethoxy-4-(methoxymethyl)quinolin-2(1H)-one (3ad).



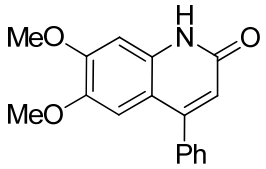
Dark yellow solid; eluent (4% DCM in Methanol). The reaction scale is 100 mg, product was isolated in 79 mg, 62 % yield was observed.

^{1}H NMR (DMSO-d_6, 400 MHz): δ 11.50 (s, 1 H), 7.05(s, 1 H), 6.87 (s, 1 H), 6.34 (s, 1 H), 4.64 (s, 2 H), 3.80 (s, 3 H), 3.79 (s, 3 H), 3.40 (s, 3 H).

^{13}C NMR (DMSO-d_6, 400 MHz): δ 161.6, 151.7, 146.9, 144.6, 134.6, 116.0, 110.3, 105.4, 97.9, 70.4, 58.1, 55.8, 55.5.

HRMS (ESI): calc. for [($C_{13}H_{15}NO_4$)H] (M+H) 250.1079, measured 250.1078.

6,7-Dimethoxy-4-phenylquinolin-2(1*H*)-one (3ae).



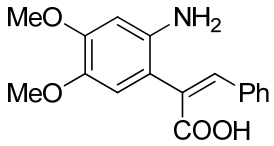
Light yellow colour solid; eluent (3% DCM in Methanol). The reaction scale is 100 mg, product was isolated in 59 mg, 41 % yield was observed.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.50 - 7.45 (m, 5 H), 7.00 (s, 1 H), 6.91 (s, 1 H), 6.57 (s, 1 H), 4.0 (s, 3 H), 3.72 (s, 3 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 164.3, 152.9, 152.6, 145.7, 137.7, 135.0, 128.7, 128.6, 117.9, 112.9, 106.9, 98.6, 56.4, 56.0.

HRMS (ESI): calc. for [($C_{17}H_{15}NO_3$)H] (M+H) 282.1130, measured 282.1139.

(Z)-2-(2-Amino-4,5-dimethoxyphenyl)-3-phenylacrylic acid (3ae').



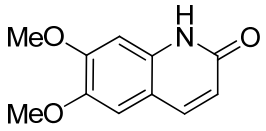
Red colour solid; eluent (2% DCM in Methanol). The reaction scale is 100 mg, product was isolated in 49 mg, 32 % yield was observed.

^{1}H NMR ($CDCl_3$ 400 MHz): δ 8.76 (s, 1 H), 7.67 (s, 1 H), 7.64 (d, *J* = 8.0 Hz, 2 H), 7.47 - 7.37 (m, 3 H), 7.18 (s, 1 H), 6.51 (s, 1 H), 3.88 (s, 3 H), 3.65 (s, 3 H), 1.64 (s, 2 H).

^{13}C NMR ($CDCl_3$ 100 MHz): δ 170.9, 151.2, 144.0, 136.7, 135.1, 134.4, 129.4, 129.2, 128.5, 112.8, 107.8, 95.3, 56.5, 56.2.

HRMS (ESI): calc. for [($C_{17}H_{17}NO_4$)Na] (M+Na) 322.1055, measured 322.1046.

6,7-Dimethoxyquinolin-2(1*H*)-one (5aa).



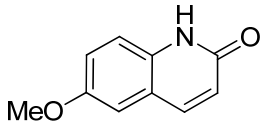
Dark brown colour solid; eluent (3% DCM in Methanol) The reaction scale is 100 mg, product was isolated in 79 mg, 76 % yield was observed.

^{1}H NMR (DMSO-d_6, 400 MHz): δ 11.54 (s, 1 H), 7.77 (d, *J* = 12.0 Hz, 1 H), 7.17(s, 1 H), 6.84 (s, 1 H), 6.31 (d, *J* = 8.0 Hz, 1 H), 3.80 (s, 3 H), 3.77 (s, 3 H).

^{13}C NMR (DMSO-d_6 100 MHz): δ 161.8, 151.8, 144.7, 139.7, 134.5, 118.7, 112.3, 108.8, 97.6, 55.7, 55.5.

HRMS (ESI): calc. for [($C_{11}H_{11}NO_3$)H] (M+H) 206.0817, measured 206.0821.

6-Methoxyquinolin-2(1*H*)-one (5ba).



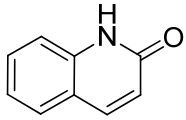
Brown colour solid; eluent (3% DCM in Methanol). The reaction scale is 100 mg, product was isolated in 68 mg, 64 % yield was observed.

^{1}H NMR (DMSO-d_6, 400 MHz): δ 11.64 (s, 1 H), 7.84 (d, *J* = 12.0 Hz, 1 H), 7.25 - 7.20 (m, 2 H), 7.14 (dd, *J* = 8.0 , 4.0 Hz, 1 H), 6.49 (d, *J* = 12.0 Hz, 1 H), 3.77 (s, 3 H).

^{13}C NMR (DMSO-d_6 100 MHz): δ 161.5, 154.1, 139.8, 133.3, 122.3, 119.7, 119.5, 116.4, 109.3, 55.4.

HRMS (ESI): calc. for [($C_{10}H_9NO_2$)H] (M+H) 176.0711, measured 176.0716.

Quinolin-2(1*H*)-one (5ea).



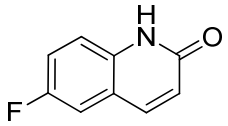
Light yellow colour solid; eluent (2% DCM in Methanol). The reaction scale is 100 mg, product was isolated in 64 mg, 60 % yield was observed.

^{1}H NMR (DMSO-d_6, 400 MHz): δ 11.75 (s, 1 H), 7.89 (d, *J* = 8.0 Hz, 1 H), 7.64 (d, *J* = 8.0 Hz, 1 H), 7.48 (t, *J* = 8.0 Hz, 1 H), 7.30 (d, *J* = 8.0 Hz, 1 H), 7.16 (t, *J* = 8.0 Hz, 1 H), 6.49 (d, *J* = 8.0 Hz, 1 H).

^{13}C NMR (DMSO-d_6 100 MHz): δ 161.9, 140.2, 138.9, 130.3, 127.9, 121.9, 121.7, 119.1, 115.1.

HRMS (ESI): calc. for [(C_9H_7NO)H] (M+H) 146.0606, measured 146.0609.

6-Fluoroquinolin-2(1*H*)-one (5fa).



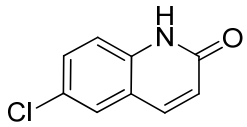
White colour solid; eluent (2% DCM in Methanol). The reaction scale is 100 mg, product was isolated in 57 mg, 54% yield was observed.

^{1}H NMR (DMSO-d_6, 400 MHz): δ 11.82 (s, 1 H), 7.78 (d, *J* = 8.0 Hz, 1 H), 7.54 (dd, *J* = 8.0, 4.0 Hz, 1 H), 7.40 (td, *J* = 8.0, 4.0 Hz, 1 H), 7.33 - 7.30 (m, 1 H), 6.56 (d, *J* = 8.0 Hz, 1 H).

(DMSO-d_6 100 MHz): δ 161.6, 155.7, 150.4, 139.4, 135.6, 123.2, 119.8, 118.5 and 118.3 (F-coupling), 112.8 and 112.5 (F-coupling).

HRMS (ESI): calc. for [(C_9H_6FNO)H] (M+H) 164.0511, measured 164.0509.

6-Chloroquinolin-2(1*H*)-one (5ga).



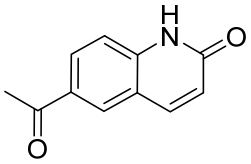
Grey colour solid; eluent (3% DCM in Methanol). The reaction scale is 100 mg, product was isolated in 59 mg, 56 % yield was observed.

^{1}H NMR (DMSO-d_6, 400 MHz): δ 11.87 (s, 1 H), 7.87 (d, *J* = 12.0 Hz, 1 H), 7.78 (d, *J* = 4.0 Hz, 1 H), 7.52 (dd, *J* = 8.0, 4.0 Hz, 1 H), 7.30 (d, *J* = 8.0 Hz, 1 H), 6.56 (d, *J* = 12.0 Hz, 1 H).

^{13}C NMR (DMSO-d_6 100 MHz): δ 161.7, 139.2, 137.6, 130.2, 126.9, 125.6, 123.2, 120.3, 117.0.

HRMS (ESI): calc. for [(C_9H_6ClNO\)H] (M+H) 180.0216, measured180.0220.

6-Acetylquinolin-2(1*H*)-one (5ia).



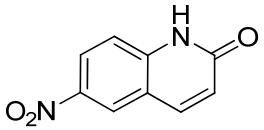
White colour solid; eluent (3% DCM in Methanol). The reaction scale is 100 mg, product was isolated in 48 mg, 46 % yield was observed.

^{1}H NMR (DMSO-d_6, 400 MHz): δ 12.06 (s, 1 H), 8.36 (d, *J* = 4.0 Hz, 1 H), 8.05 - 8.02 (m, 2 H), 7.36 (d, *J* = 12.0 Hz, 1 H), 6.58 (d, *J* = 12.0 Hz, 1 H), 2.59 (s, 3 H) .

^{13}C NMR (DMSO-d_6 100 MHz): δ 196.5, 162.2, 142.1, 140.7, 130.7, 129.7, 129.5, 122.7, 118.5, 115.4, 26.6.

HRMS (ESI): calc. for [($C_{11}H_9NO_2$)H] (M+H) 188.0711, measured 188.0713.

6-Nitroquinolin-2(1*H*)-one (5ka).



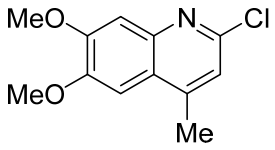
Light yellow colour solid; eluent (2% DCM in Methanol). The reaction scale is 100 mg, product was isolated in 50 mg, 48 % yield was observed.

^{1}H NMR (DMSO-d_6, 400 MHz): δ 12.31 (s, 1 H), 8.70 (s, 1 H), 8.33 (dd, *J* = 8.0, 4.0 Hz, 1 H), 8.13 (d, *J* = 8.0 Hz, 1 H), 7.43 (d, *J* = 12.0 Hz, 1 H), 6.68 (d, *J* = 12.0 Hz, 1 H).

^{13}C NMR (DMSO-d_6 100 MHz): δ 162.0, 143.3, 141.5, 140.2, 125.1, 124.4, 123.9, 118.6, 116.1.

HRMS (ESI): calc. for [($C_9H_6N_2O_3$)H] (M+H) 191.0456, measured 191.0457.

2-chloro-6,7-dimethoxy-4-methylquinoline (6a).



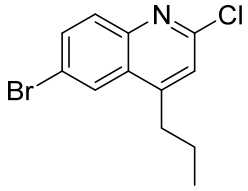
White colour solid; eluent (7% petether in ethylacetate) The reaction scale is 100 mg, product was isolated in 85 mg, 79 % yield was observed.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.30 (s, 1 H), 7.07 (s, 1 H), 7.04 (s, 1 H), 3.98 (s, 3 H), 3.97 (s, 3 H) 2.57 (s, 3 H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 152.6, 149.6 148.2, 145.7, 144.6, 122.0, 120.6, 107.9, 101.6, 56.1, 55.1, 18.8.

HRMS (ESI): calc. for [($C_{12}H_{12}ClNO_2$)H] (M+H) 238.0635, measured 238.0626.

6-bromo-2-chloro-4-propylquinoline (6b).



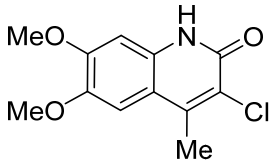
White colour solid; eluent ((3% petether in ethylacetate) The reaction scale is 100 mg, product was isolated in 75 mg, 71 % yield was observed.

^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.10 (d, *J* = 4.0 Hz, 1 H), 7.85 (d, *J* = 4.0 Hz, 1 H), 7.75 dd, (*J* = 8.0, 4.0 Hz, 1 H) 7.22 (s, 1 H), 2.94 (t, *J* = 8.0 Hz, 2 H), 1.75 (sex, *J* = 8.0 Hz, 2 H), 1.04 (t, *J* = 8.0 Hz, 3 H) .

^{13}C NMR ($CDCl_3$, 100 MHz): δ 151.0, 146.6 133.5, 130.9, 127.5, 126.2, 122.3, 120.7, 33.8, 22.8, 14.0.

HRMS (ESI): calc. for [($C_{12}H_{11}BrCl$)H] (M+H) 283.9841, measured 283.9842.

3-Chloro-6,7-dimethoxy-4-methylquinolin-2(1H)-one (7a).



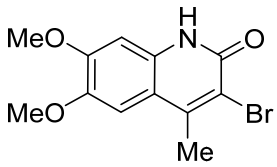
White colour solid; eluent (2% DCM in Methanol) reaction scale is 100 mg, product was isolated in 90 mg, 78 % yield was observed.

^{1}H NMR (DMSO-d_6, 400 MHz): δ 11.94 (s, 1 H), 7.09 (s, 1 H), 6.82 (s, 1 H), 3.82 (s, 3 H), 3.80 (s, 3 H) 2.52 (s, 3 H).

^{13}C NMR (DMSO-d_6 100 MHz): δ 156.9, 151.7 145.1, 143.6, 132.2, 122.2, 112.2, 106.1, 97.7, 55.8, 55.6, 16.4.

HRMS (ESI): calc. for [($C_{12}H_{13}ClNO_3$)H] (M+H) 254.0584, measured 254.0577.

3-Bromo-6,7-dimethoxy-4-methylquinolin-2(1*H*)-one (7b).



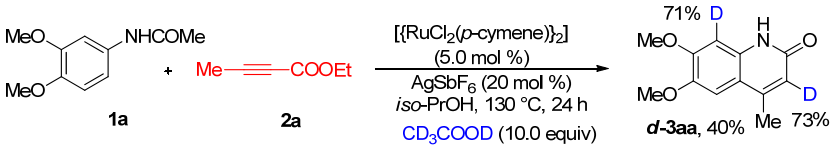
White colour solid; eluent (2% DCM in Methanol). The reaction scale is 100 mg, product was isolated in 112 mg, 83 % yield was observed.

^{1}H NMR (DMSO-d_6, 400 MHz): δ 11.96 (s, 1 H), 7.18 (s, 1 H), 6.87 (s, 1 H), 3.83 (s, 3 H), 3.81 (s, 3 H), 2.61(s, 3 H).

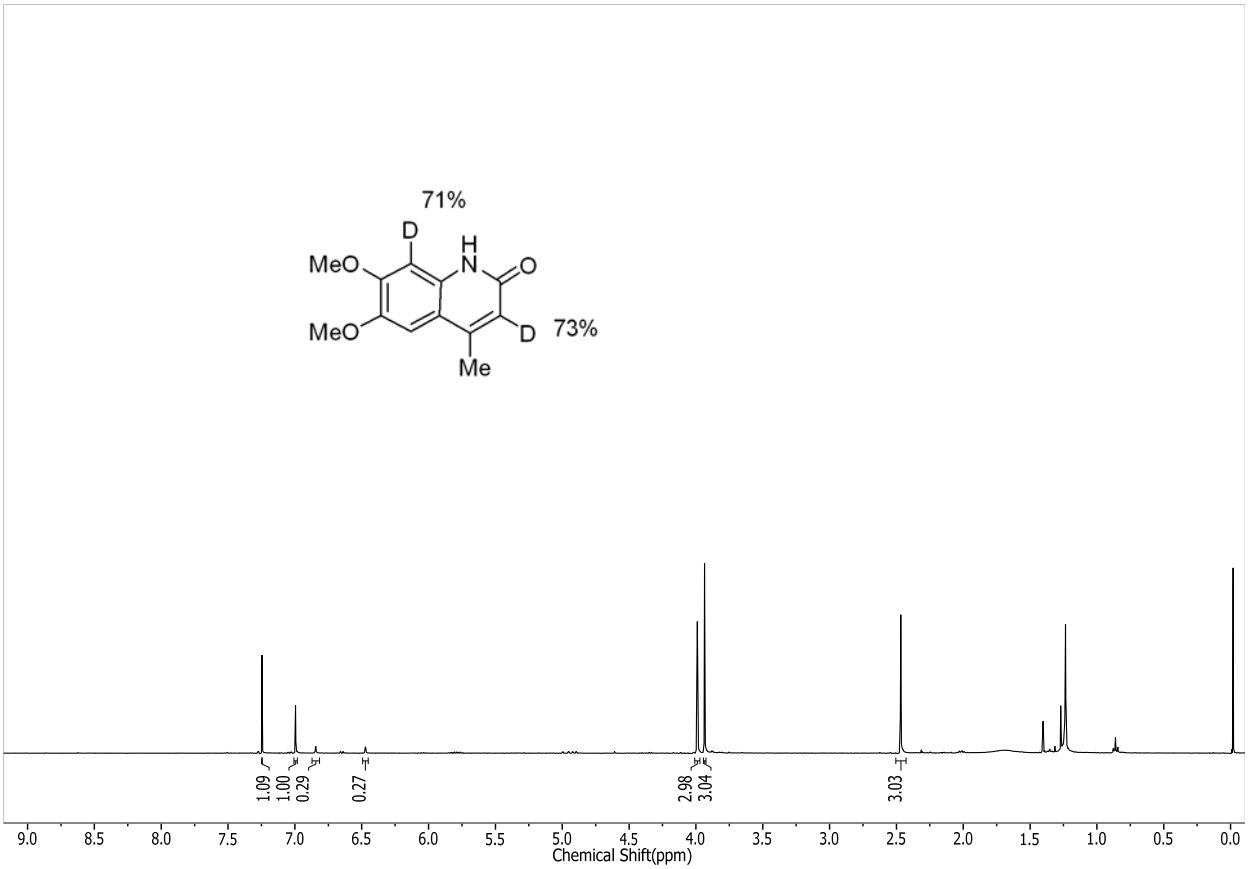
^{13}C NMR (DMSO-d_6 100 MHz): δ 157.2, 151.9, 146.4, 145.0, 132.7, 116.1, 112.3, 106.4, 97.7, 55.9, 55.6, 19.9.

HRMS (ESI): calc. for [($C_{12}H_{12}BrNO_3$)H] (M+H), 298.0079 measured 298.0071.

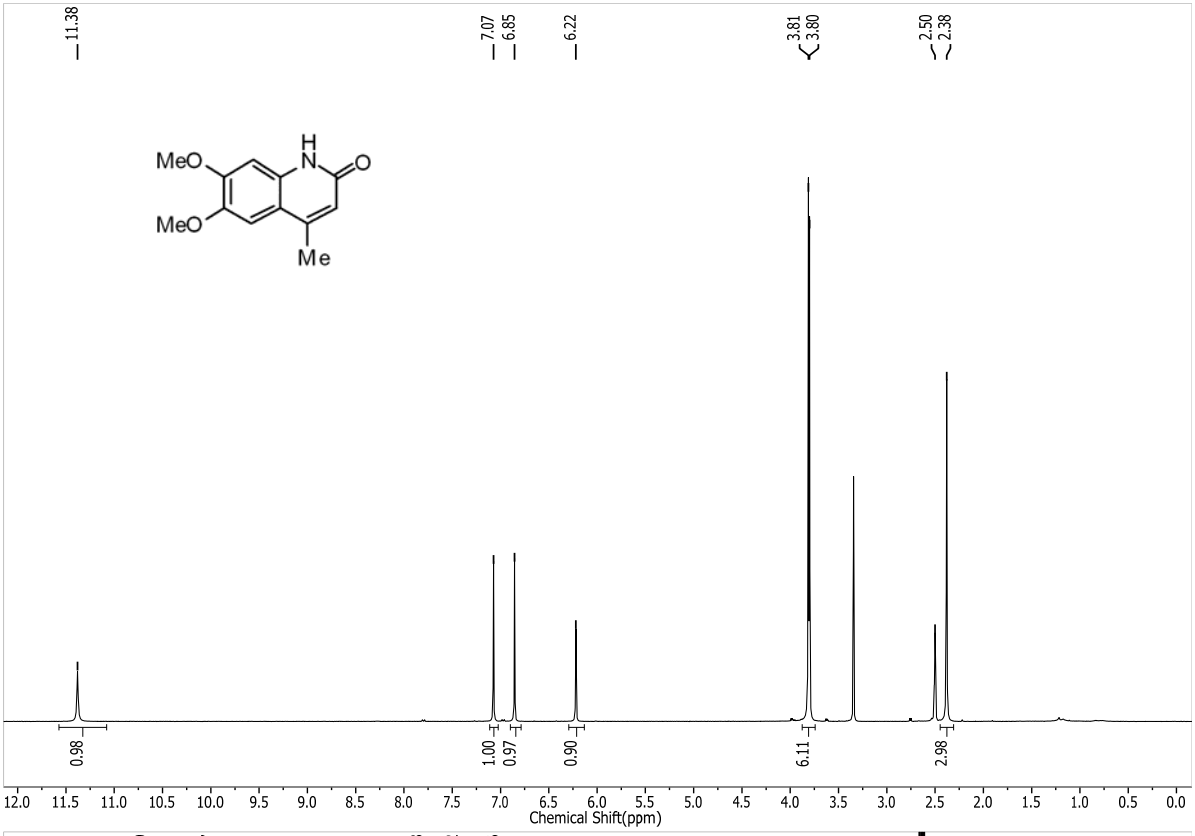
Mechanistic Evidence (Deuterium Studies).

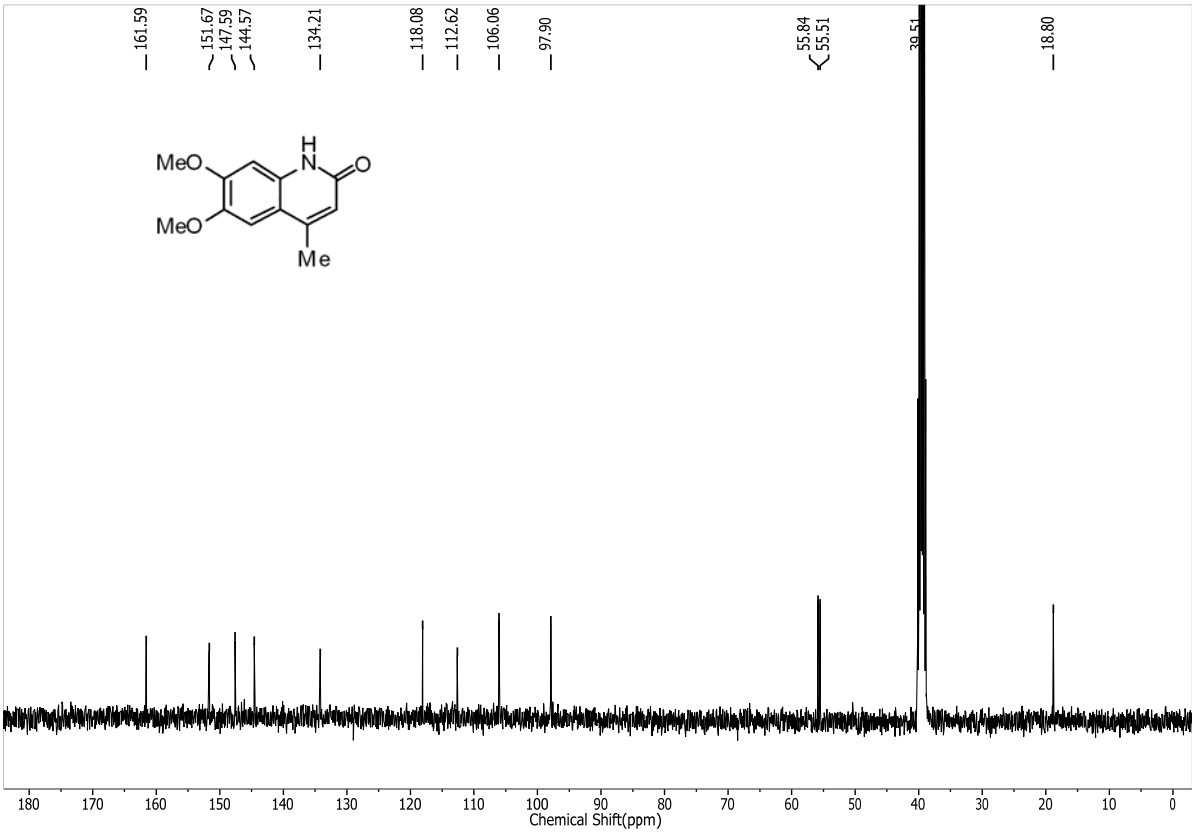


^{1}H NMR Spectrum of Compound ***d*-3aa**. ($CDCl_3$ Solvent was used).

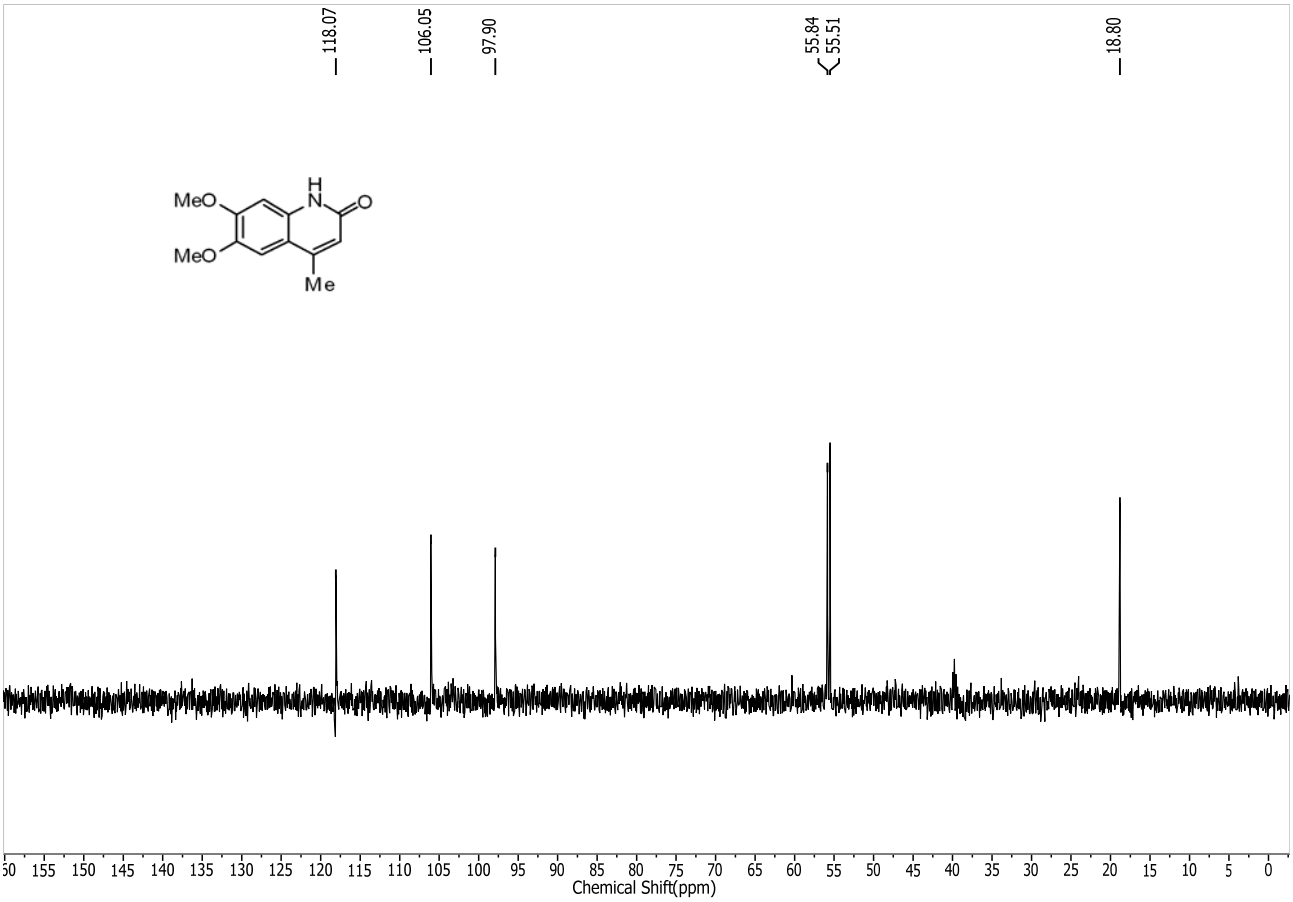


^{1}H and^{13}CNMR Spectra of Compound **3aa** (DMSO-d_6 solvent was used).

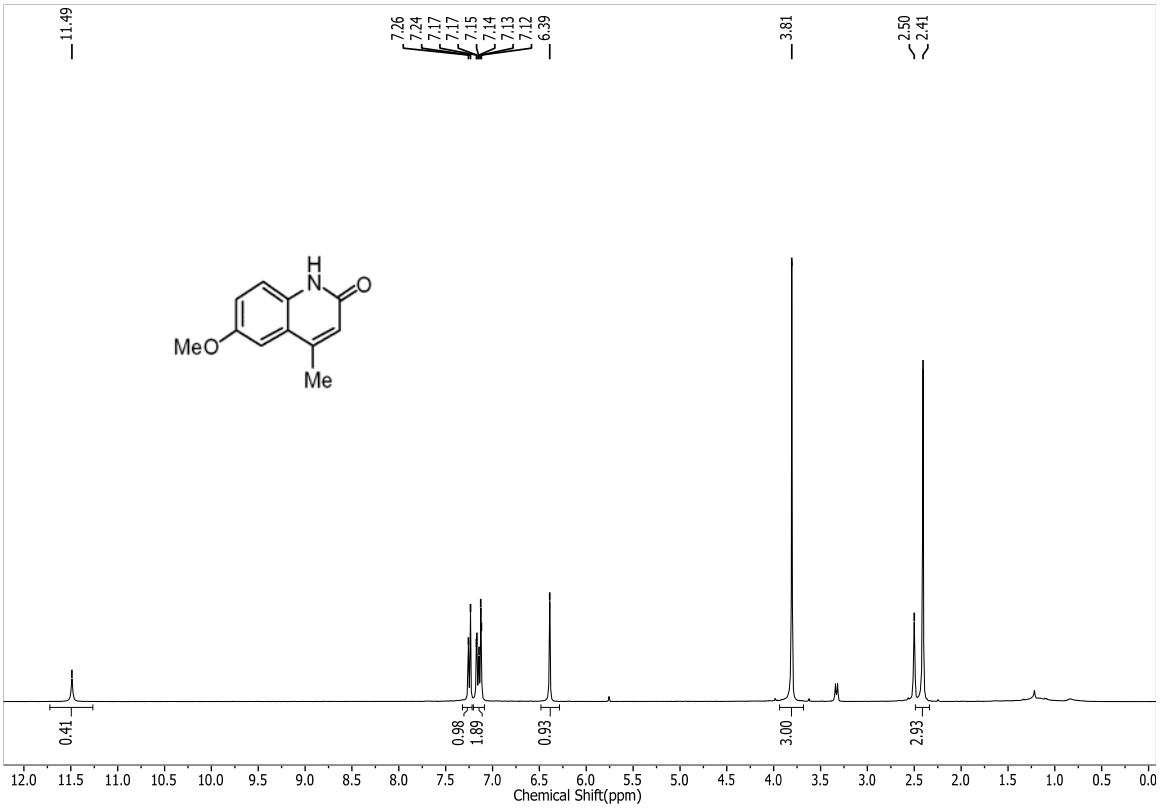


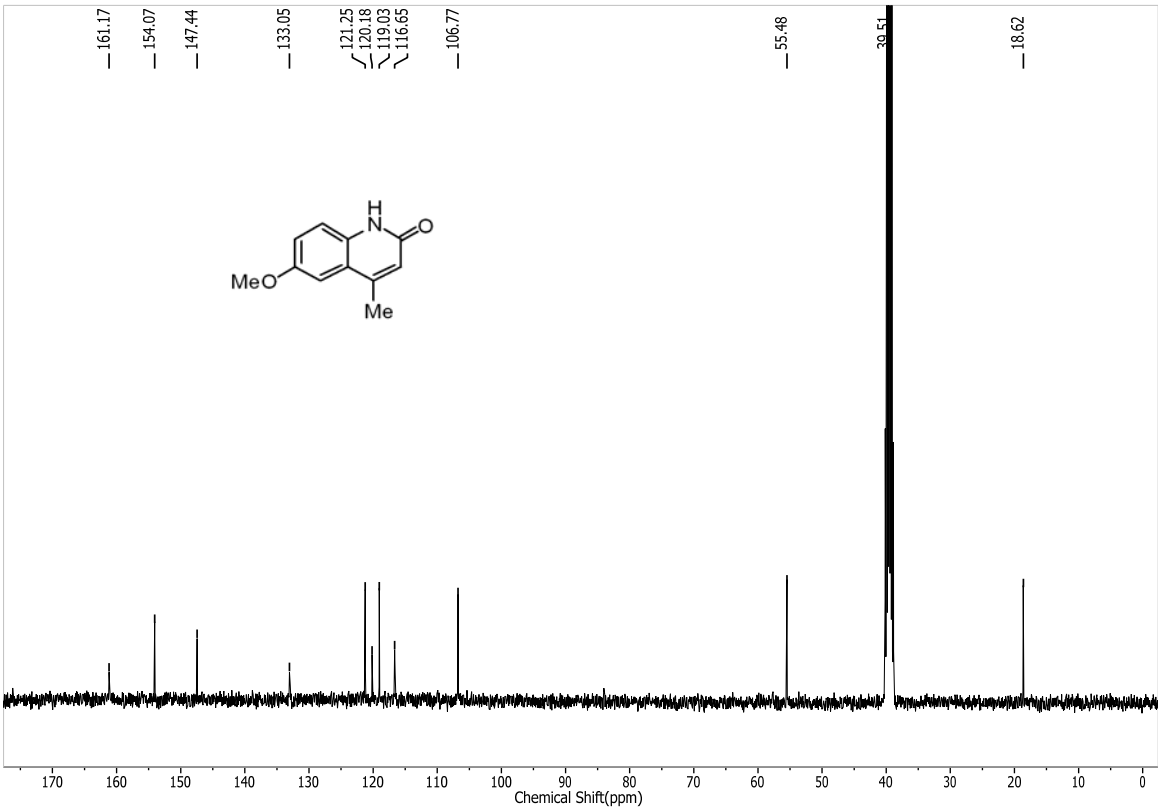


DEPT (135) NMR Spectrum of Compound **3aa** (DMSO-d_6 solvent was used).

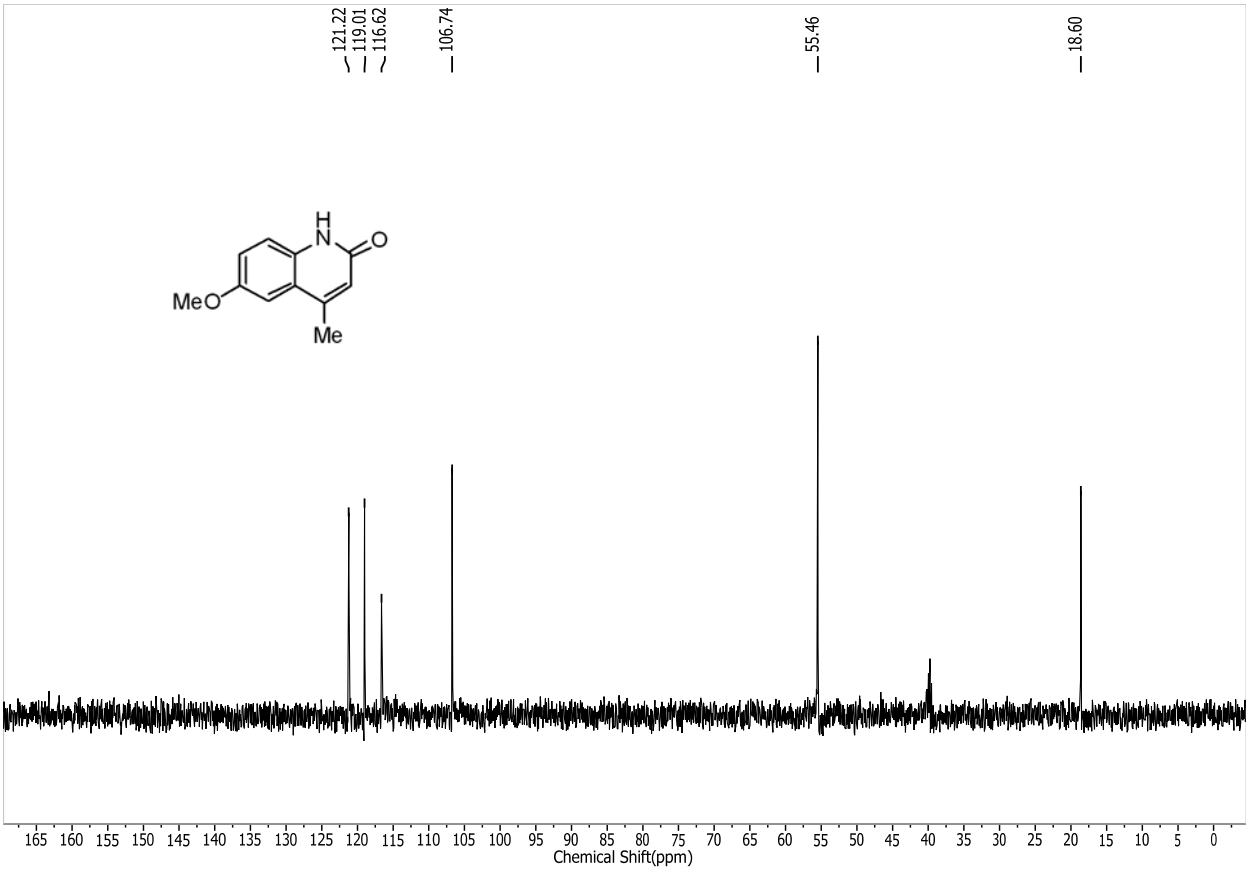


^{1}H and ^{13}C NMR Spectra of Compound **3ba** (DMSO-d_6 solvent was used).

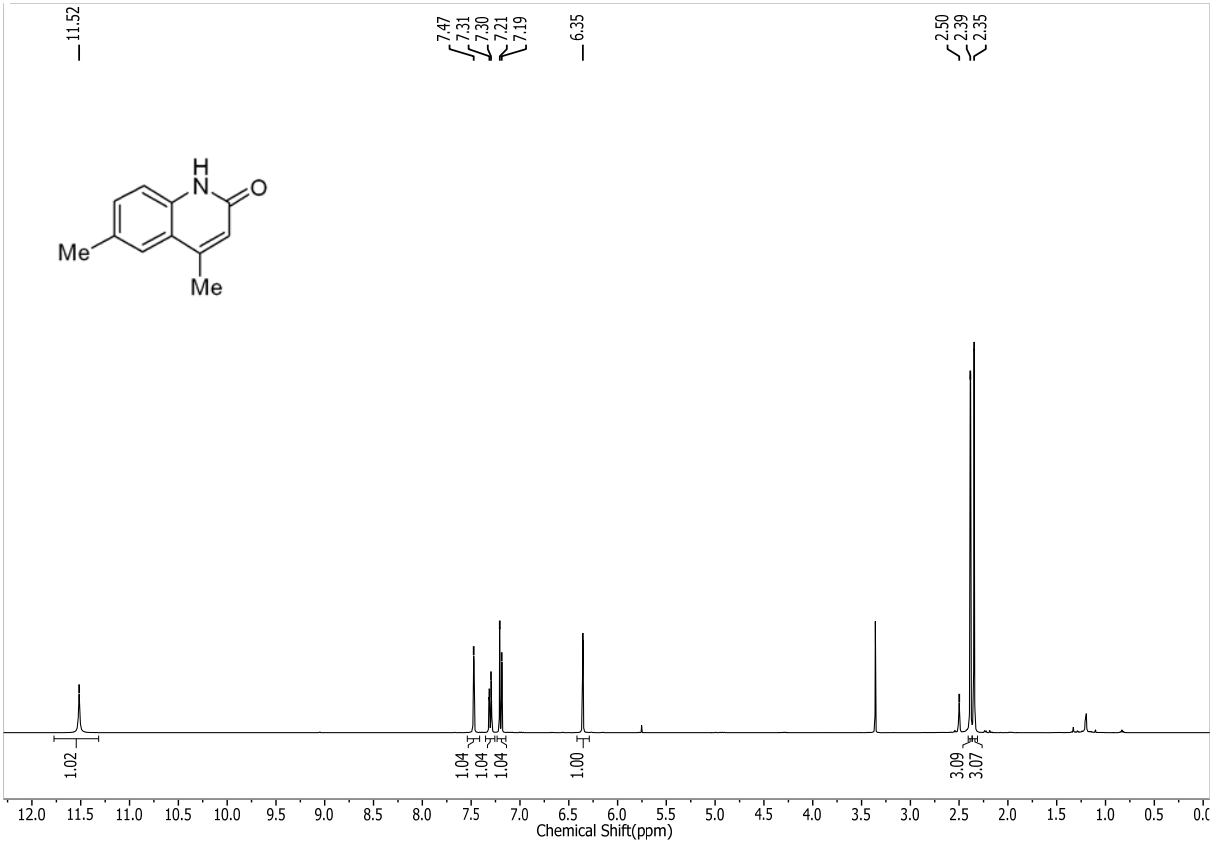


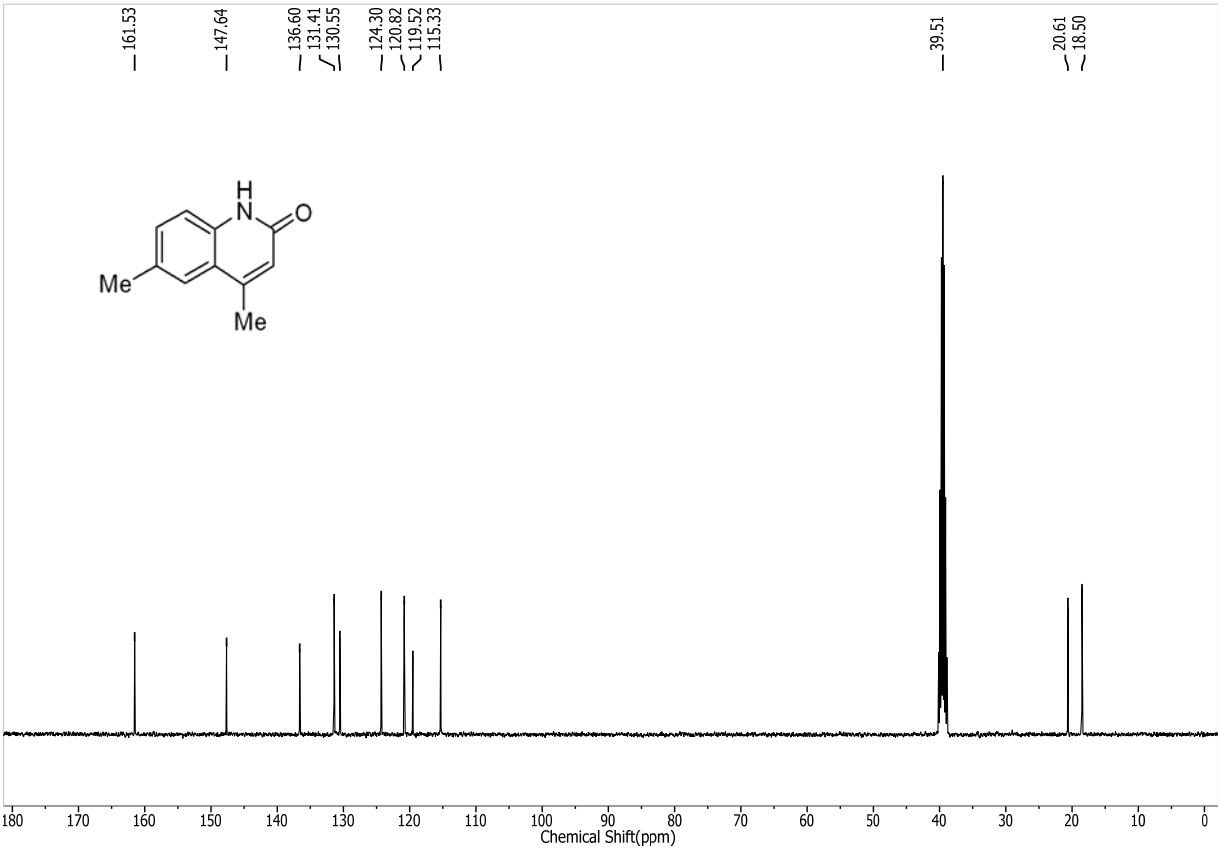


DEPT (135) NMR Spectrum of Compound **3ba** (DMSO-d_6 solvent was used).

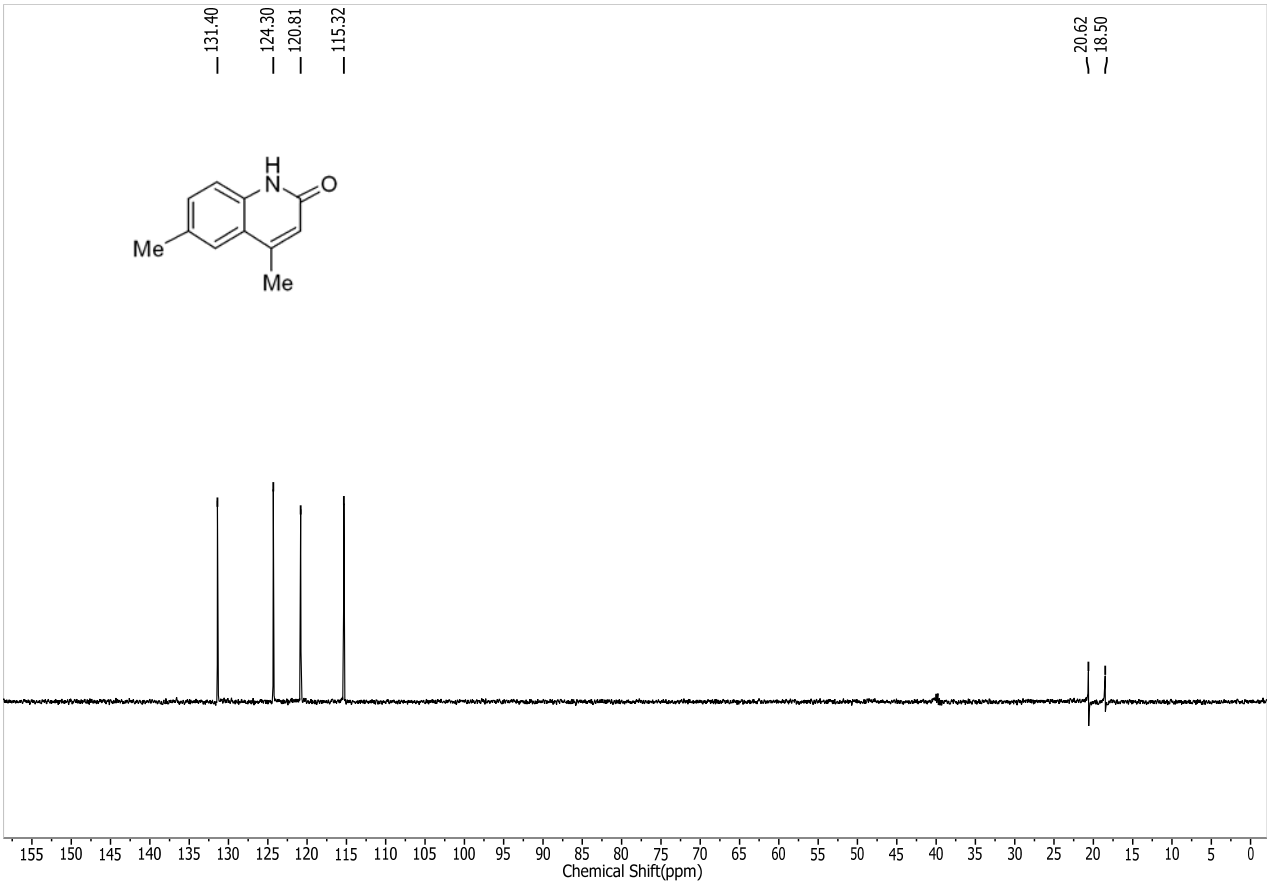


^{1}H and ^{13}C NMR Spectra of Compound **3ca** (DMSO-d_6 solvent was used).

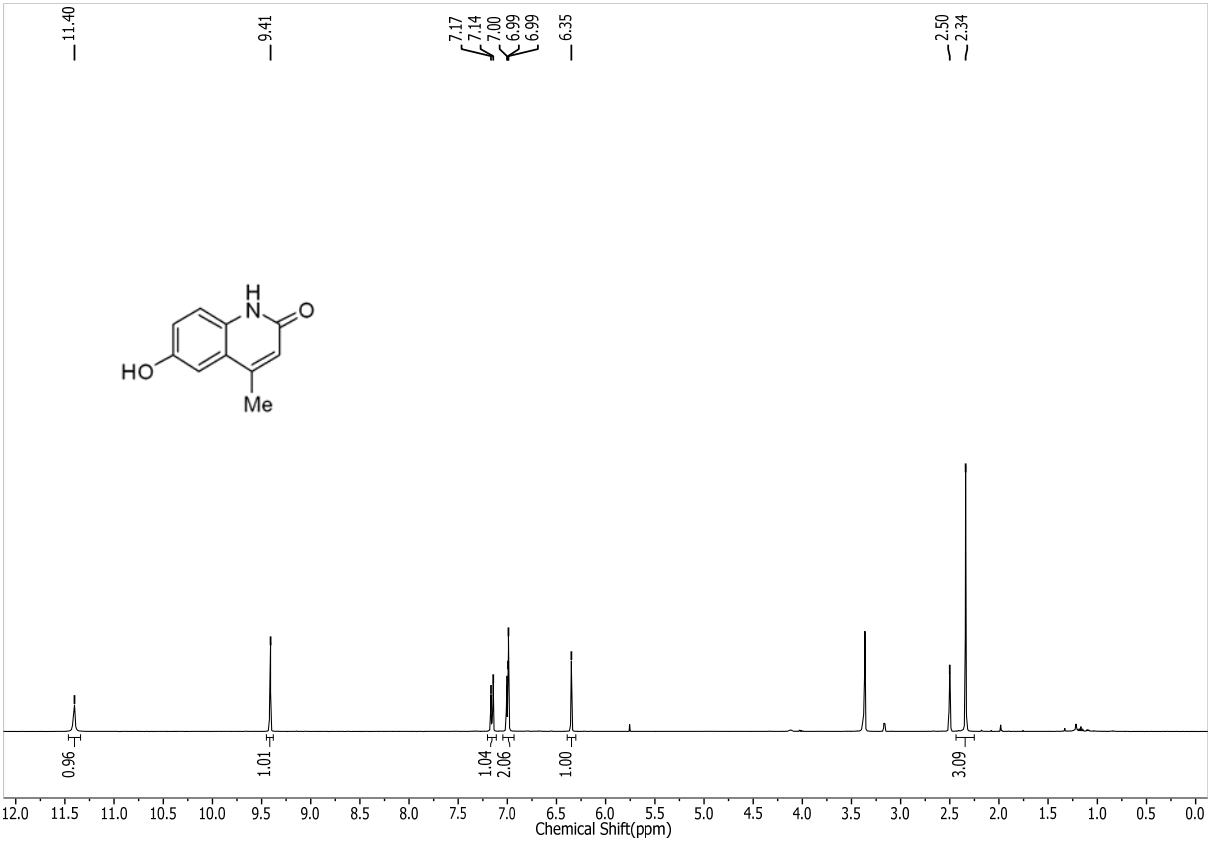


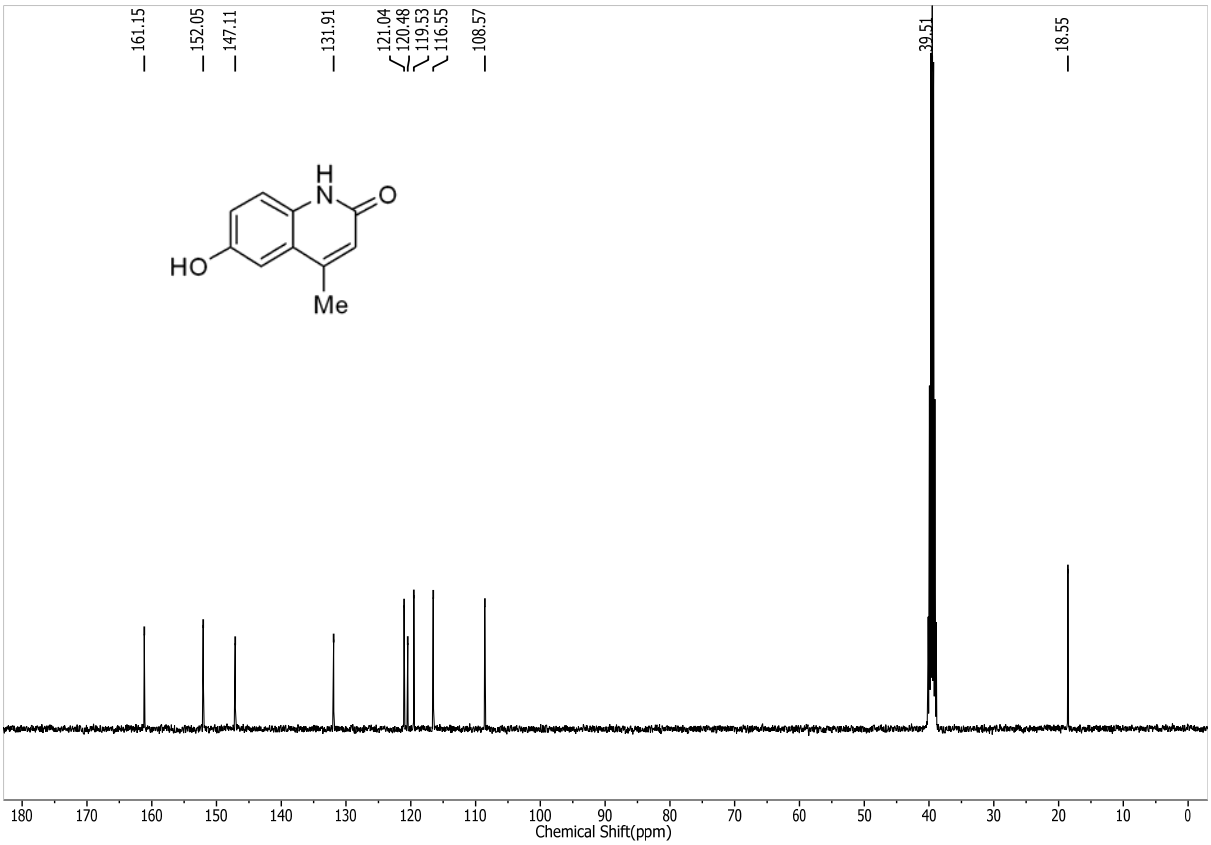


DEPT (135) NMR Spectrum of Compound **3ca** (DMSO-d_6 solvent was used).

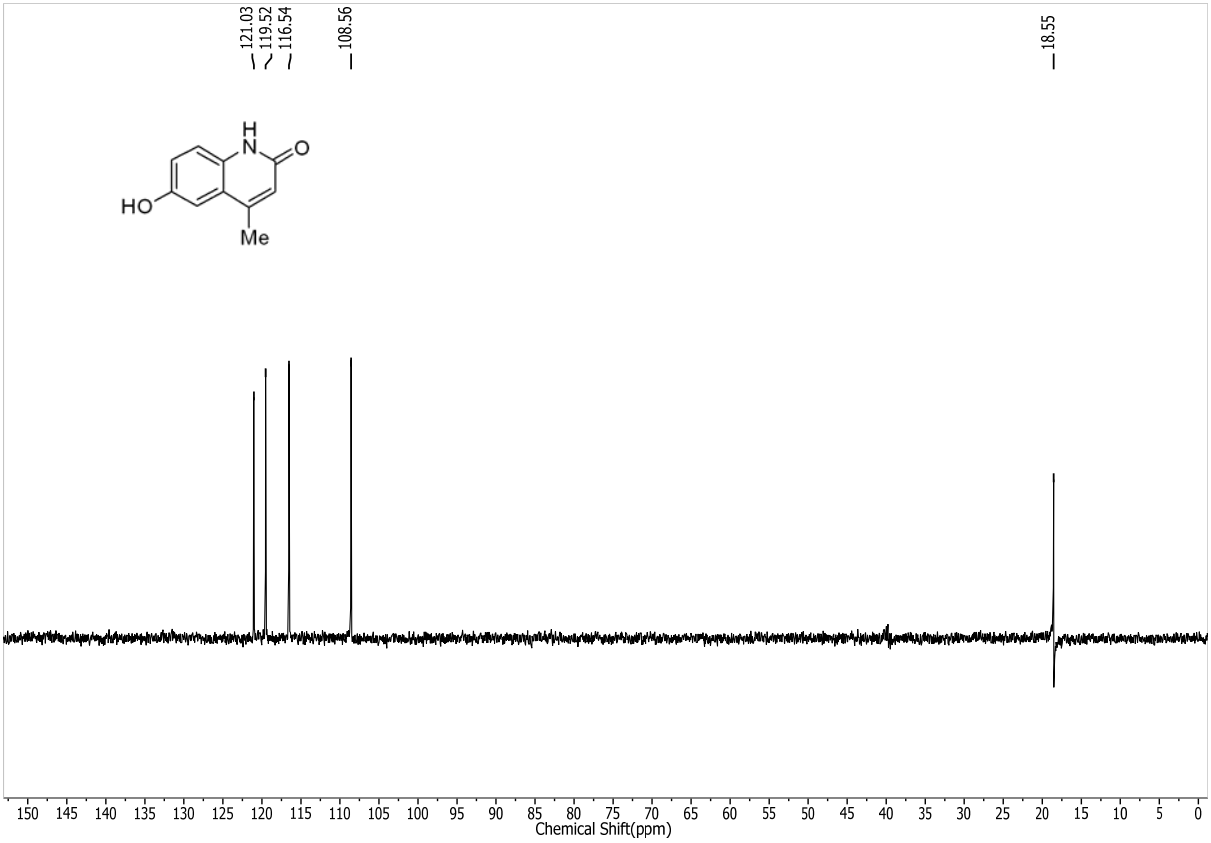


^{1}H and ^{13}C NMR Spectra of Compound **3da** (DMSO-d_6 solvent was used).

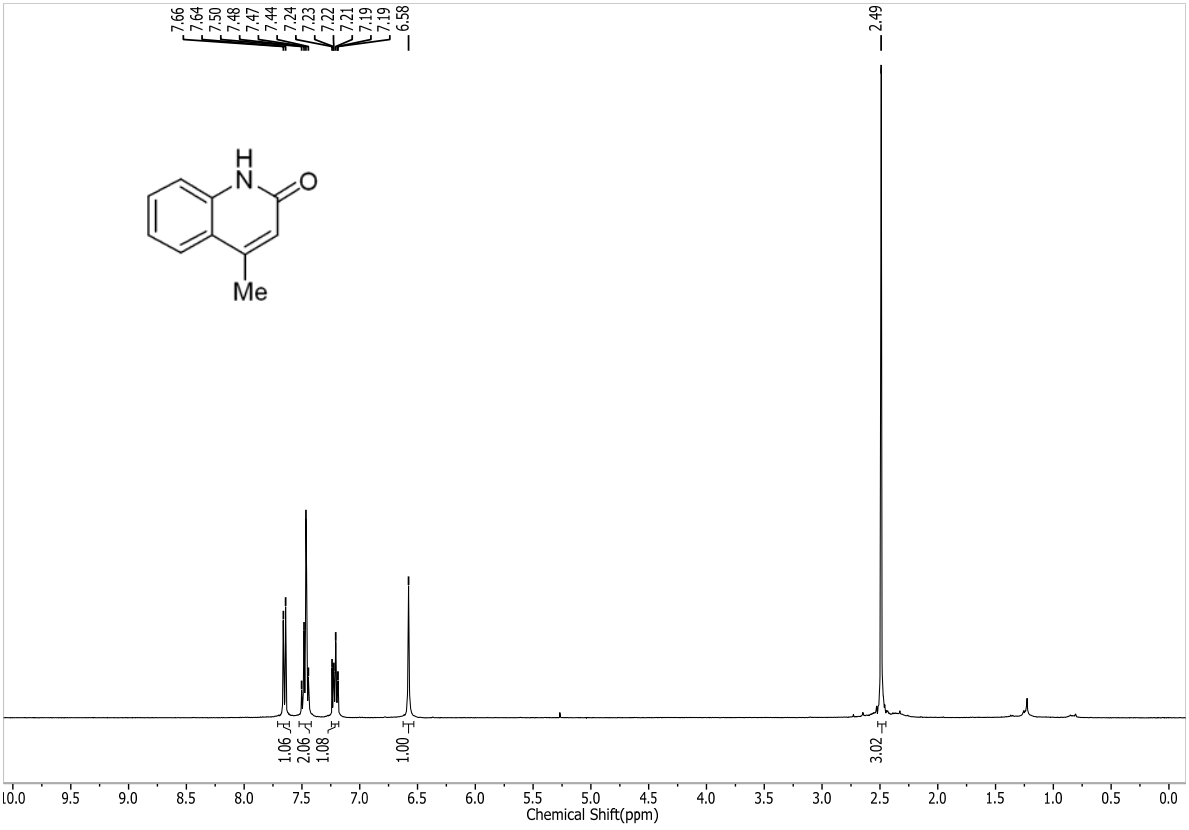


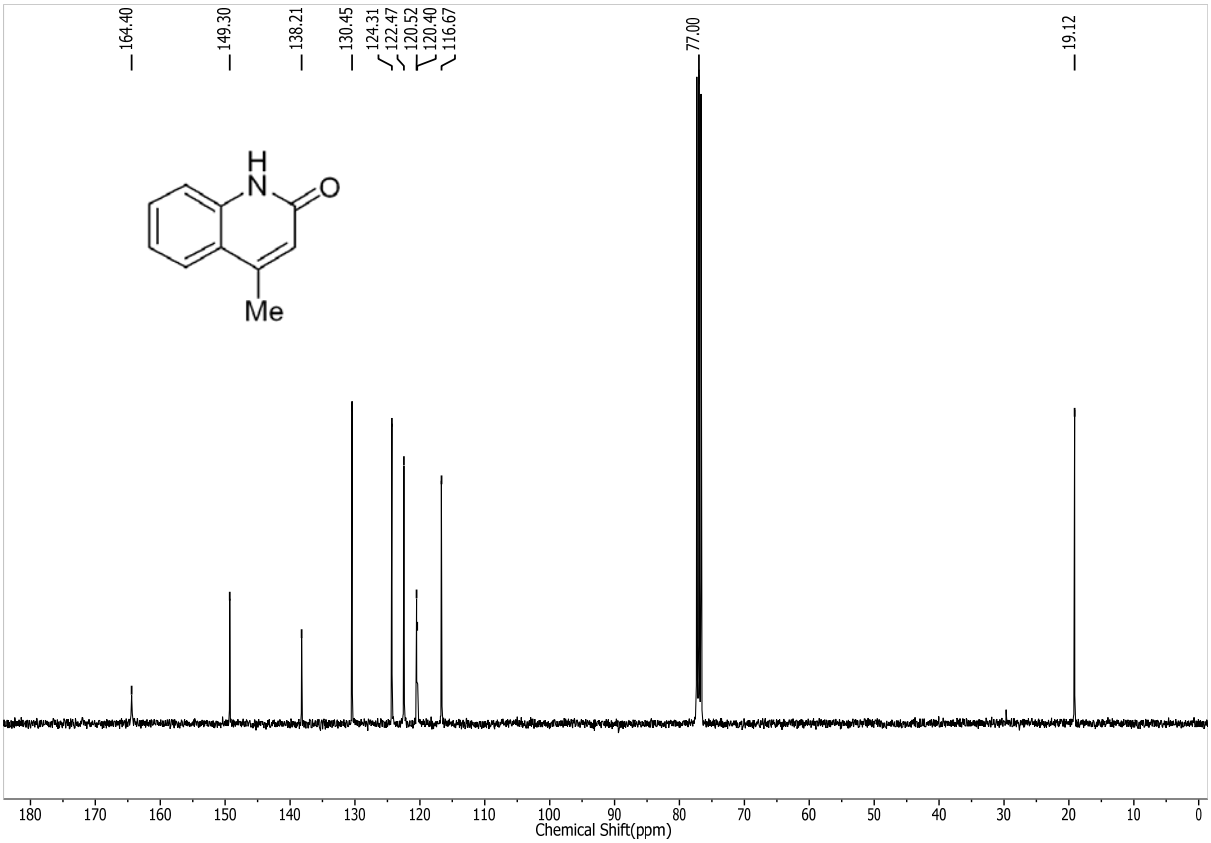


DEPT (135) NMR Spectrum of Compound **3da** (DMSO-d_6 solvent was used).

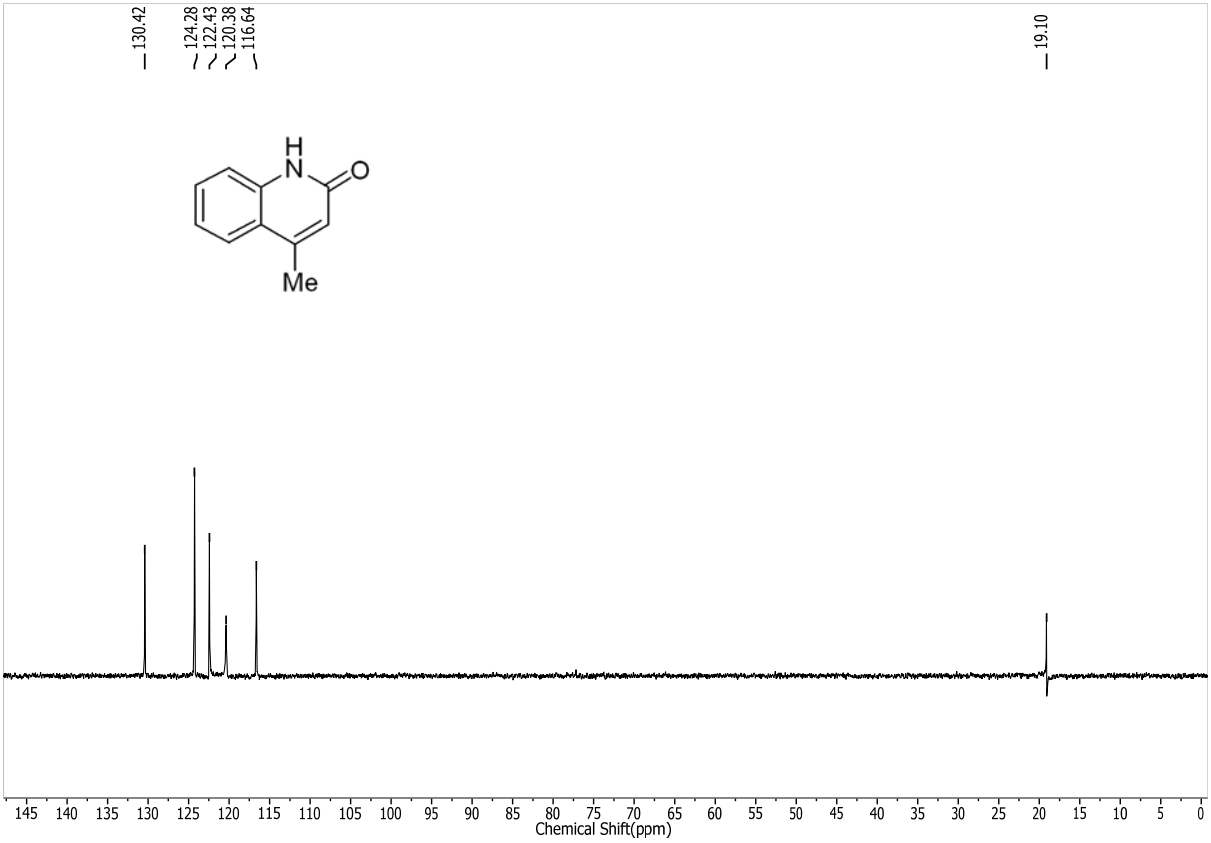


^{1}H and ^{13}C NMR Spectra of Compound **3ea** ($CDCl_3$ Solvent was used).

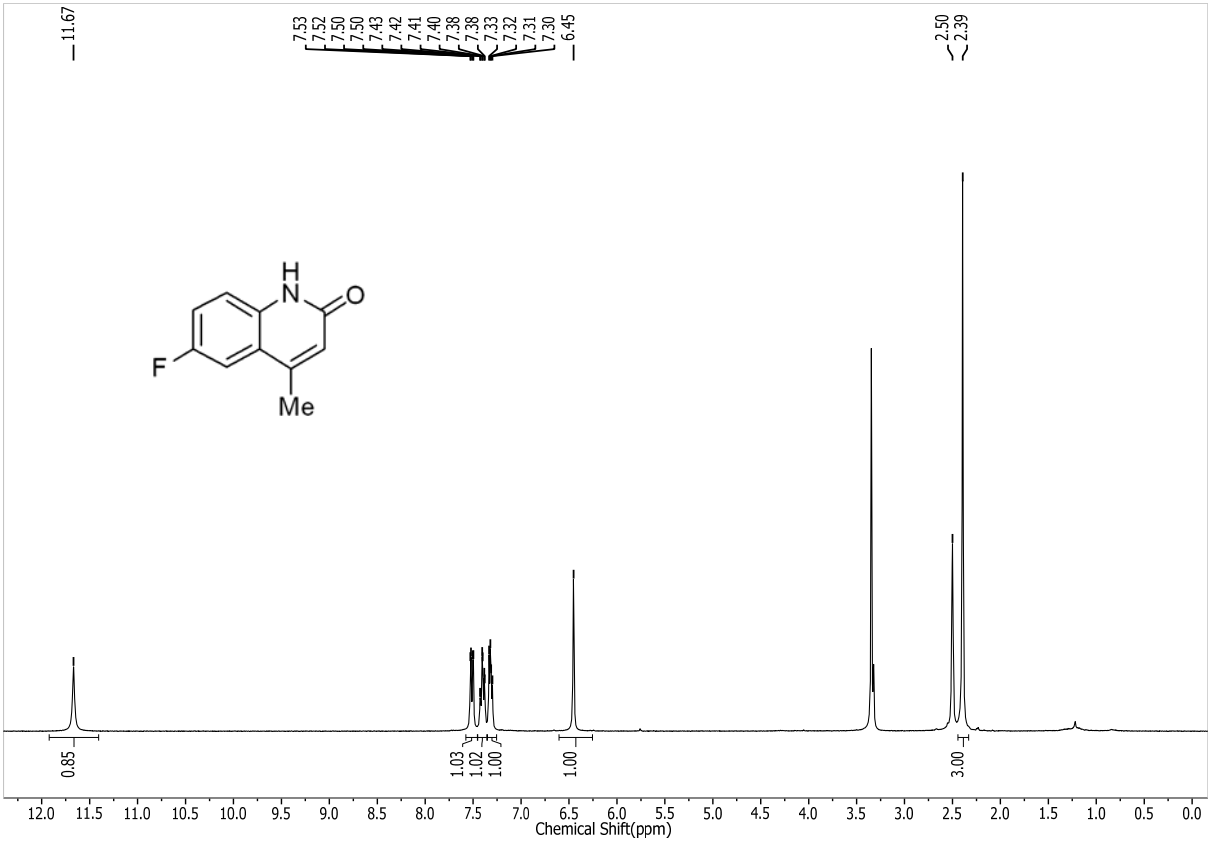


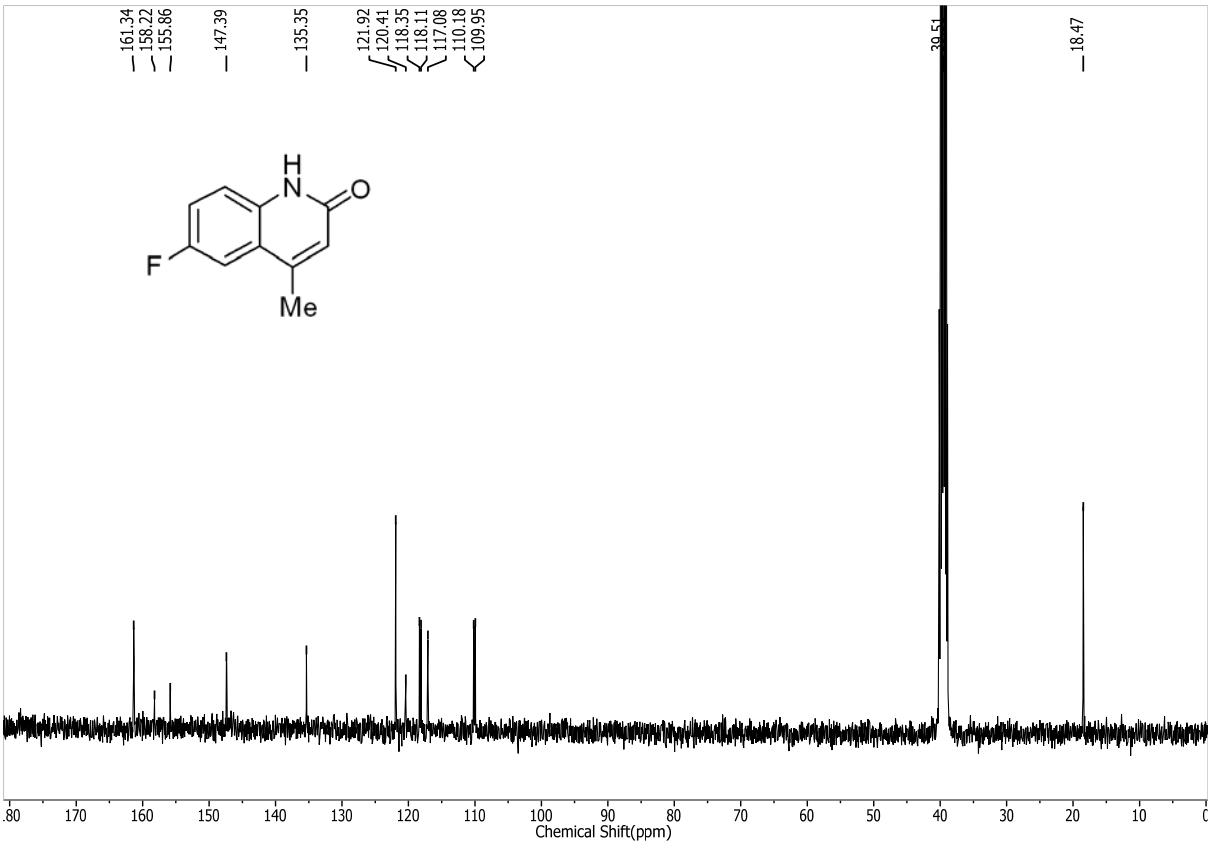


DEPT (135) NMR Spectrum of Compound **3ea** ($CDCl_3$ Solvent was used).

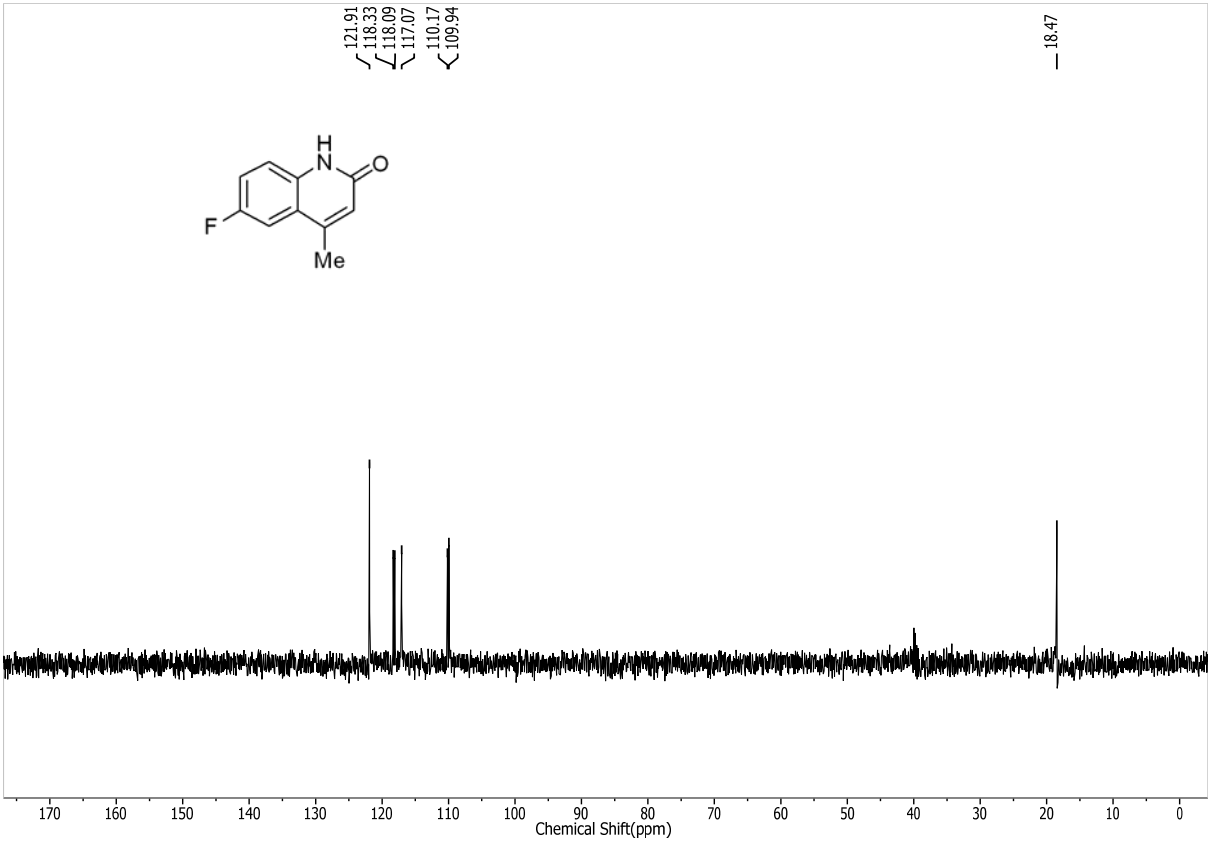


^{1}H and ^{13}C NMR Spectra of Compound **3fa** (DMSO-d_6 solvent was used).

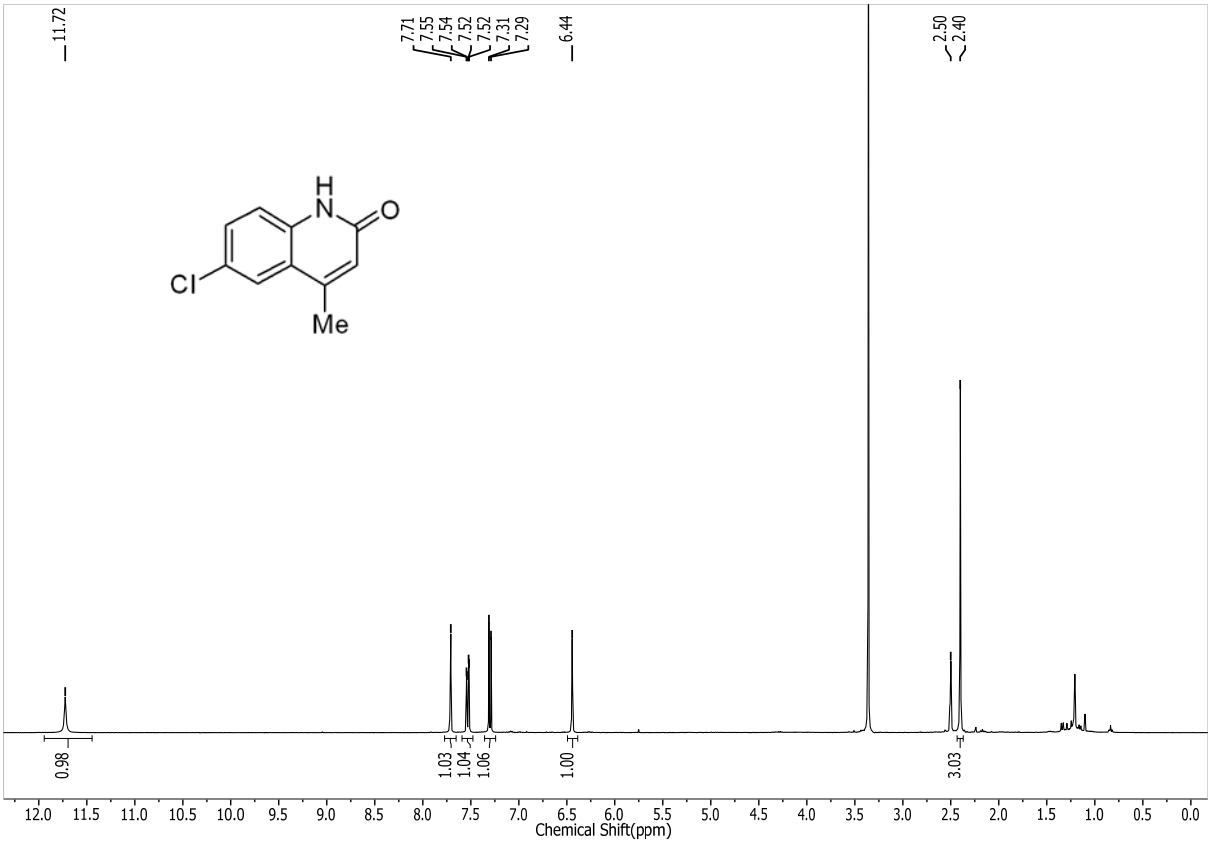


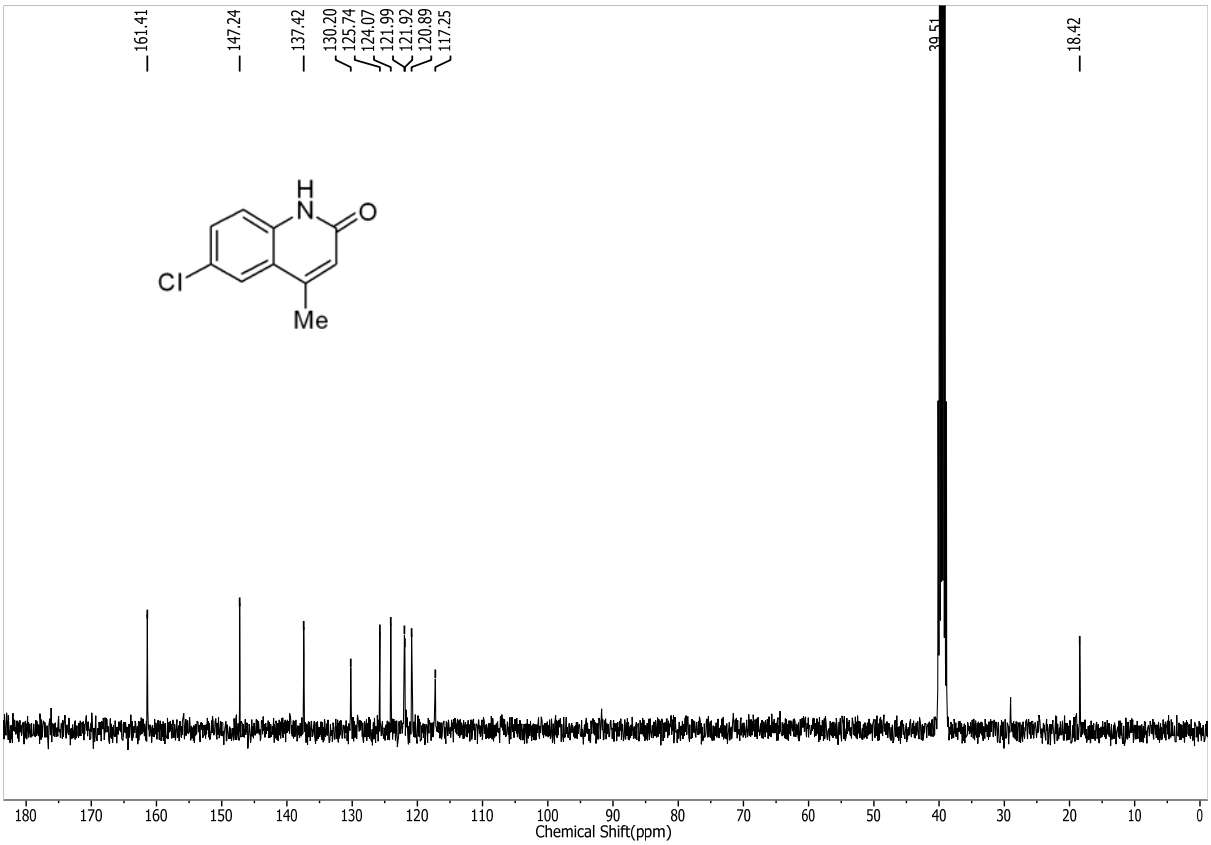


DEPT (135) NMR Spectrum of Compound **3fa** (DMSO-d_6 solvent was used).

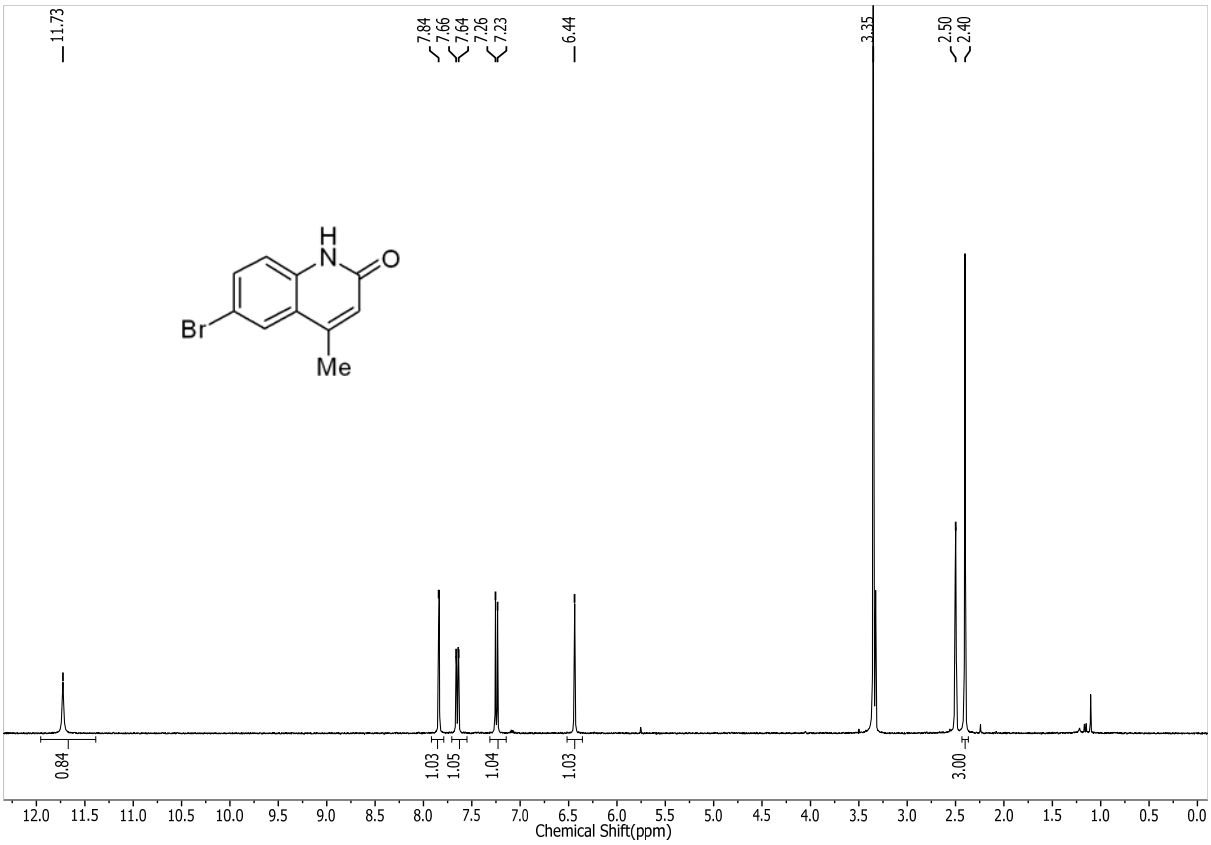


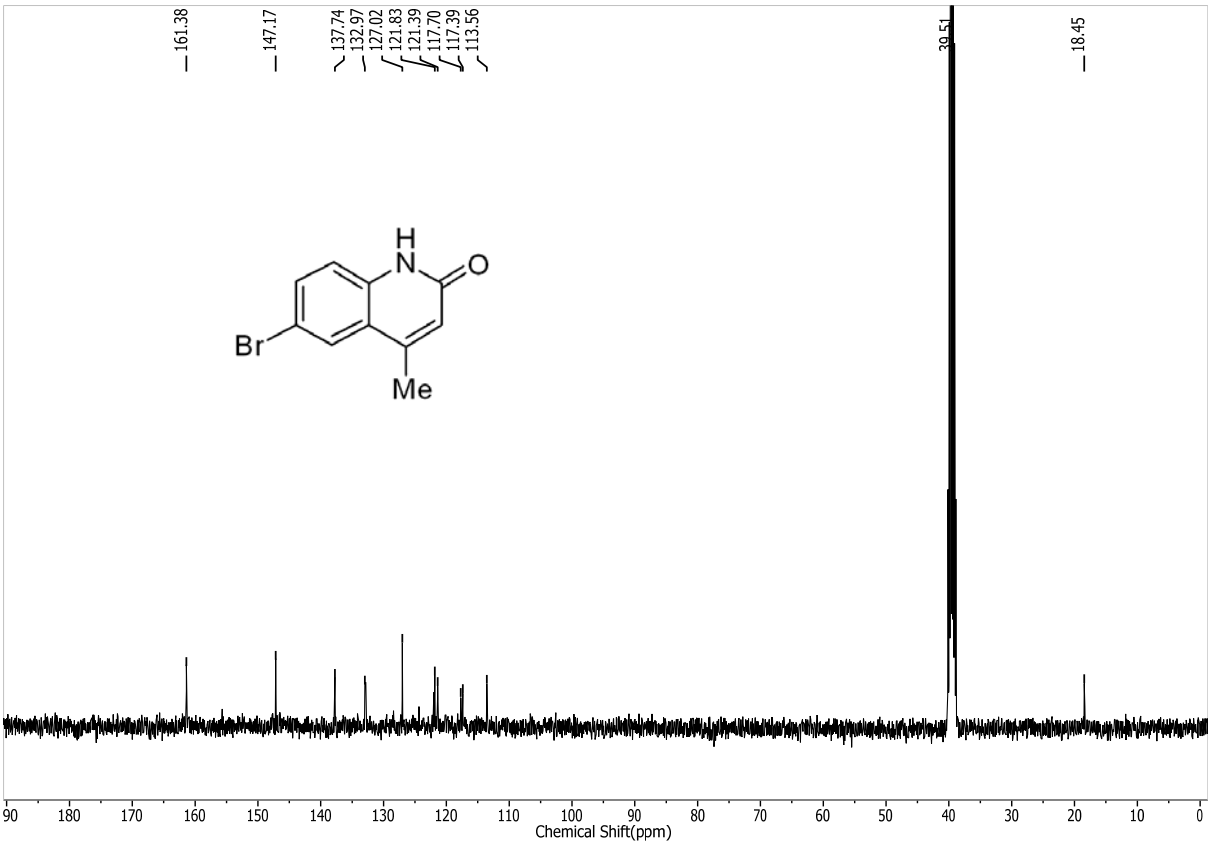
^{1}H and ^{13}C NMR Spectra of Compound **3ga** (DMSO-d_6 solvent was used).



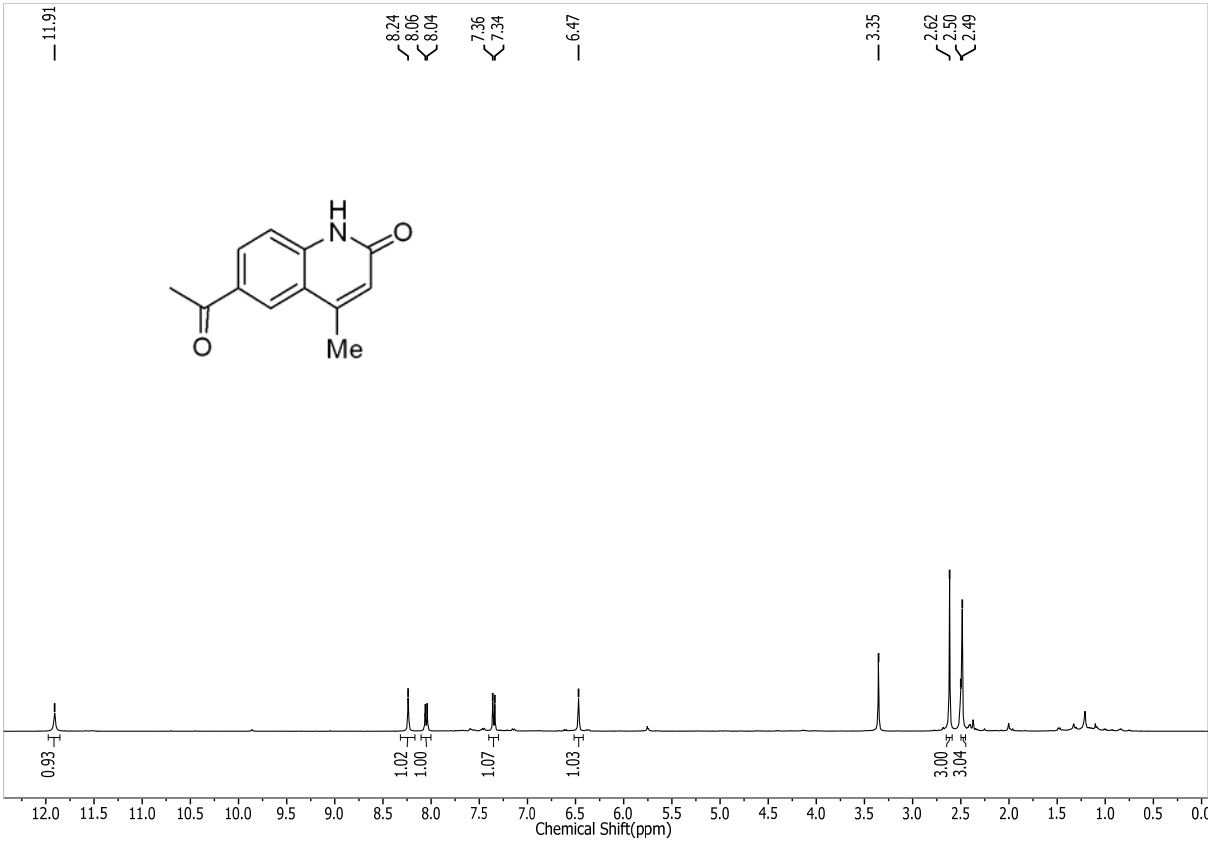


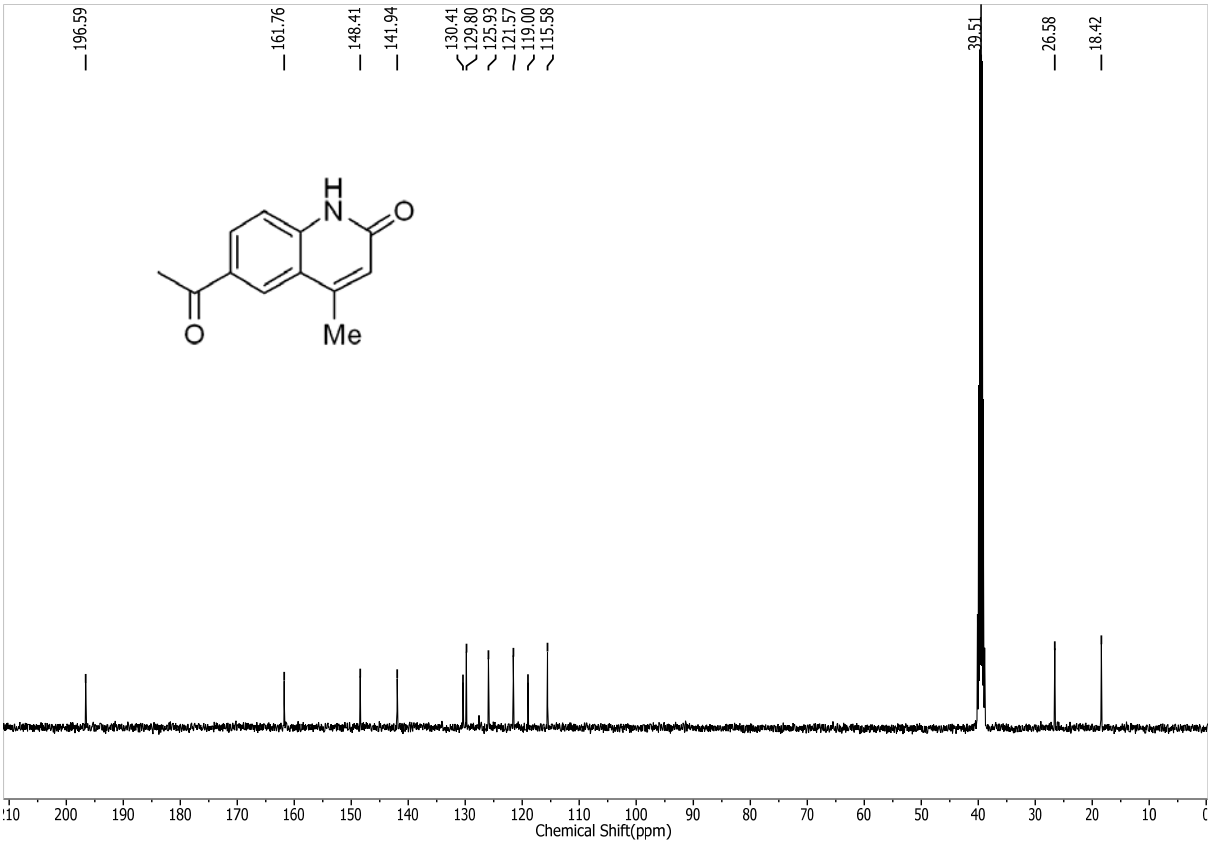
^{1}H and ^{13}C NMR Spectra of Compound **3ha** (DMSO-d_6 solvent was used).



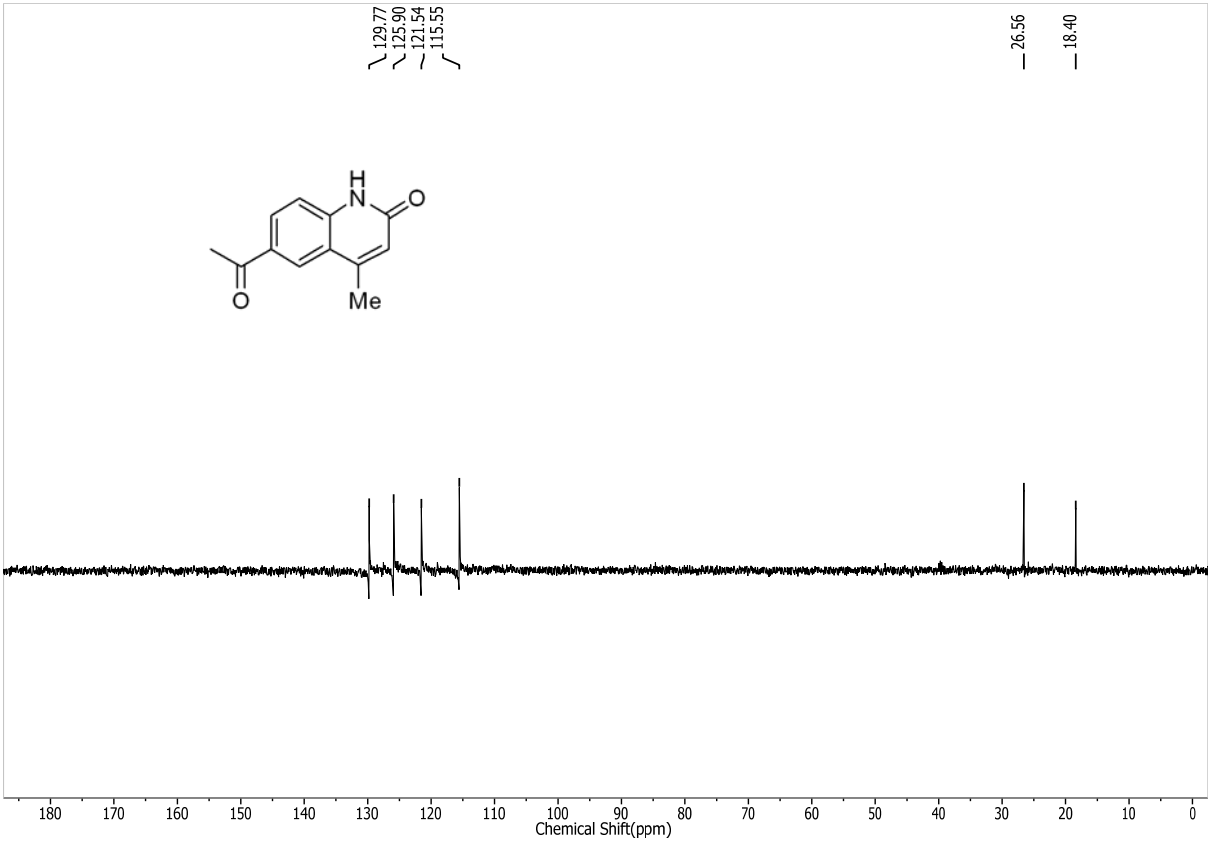


^{1}H and ^{13}C NMR Spectra of Compound **3ia** (DMSO-d_6 solvent was used).

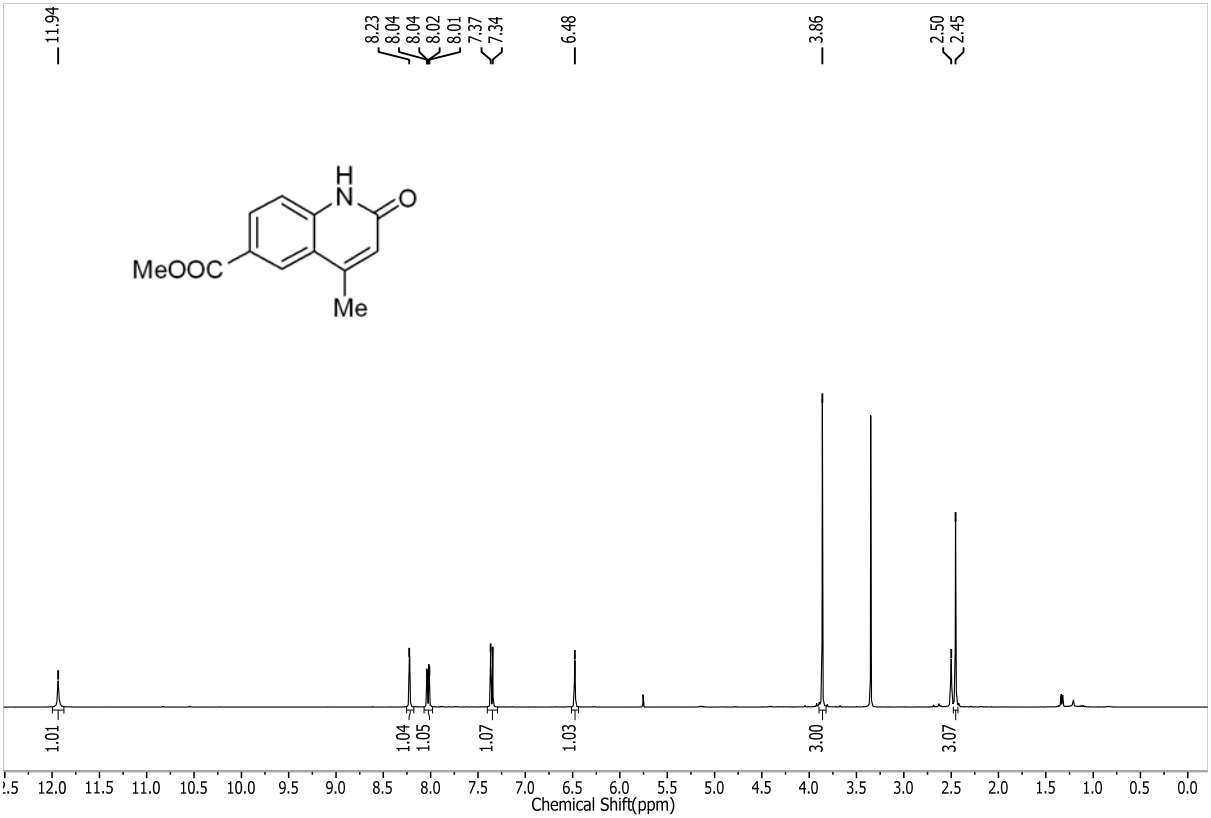


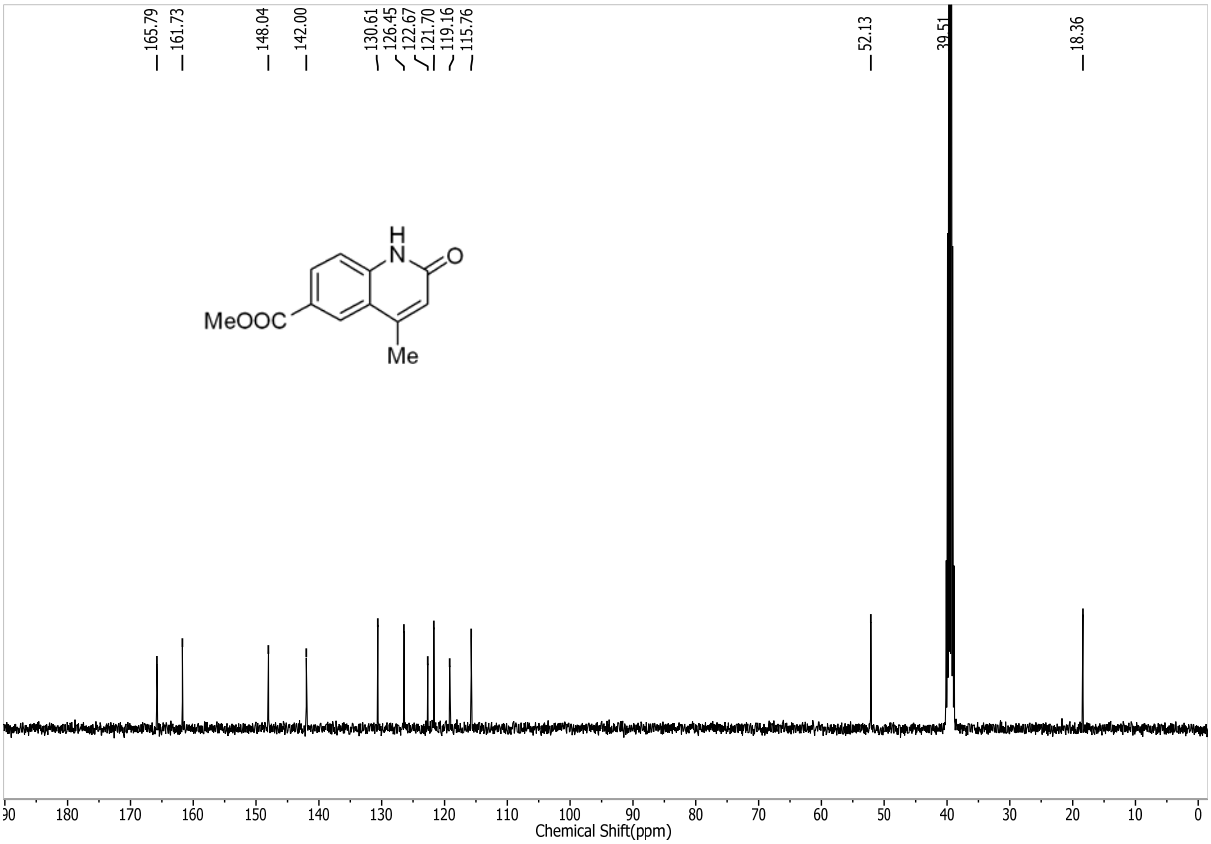


DEPT (135) NMR Spectrum of Compound **3ia** (DMSO-d_6 solvent was used).

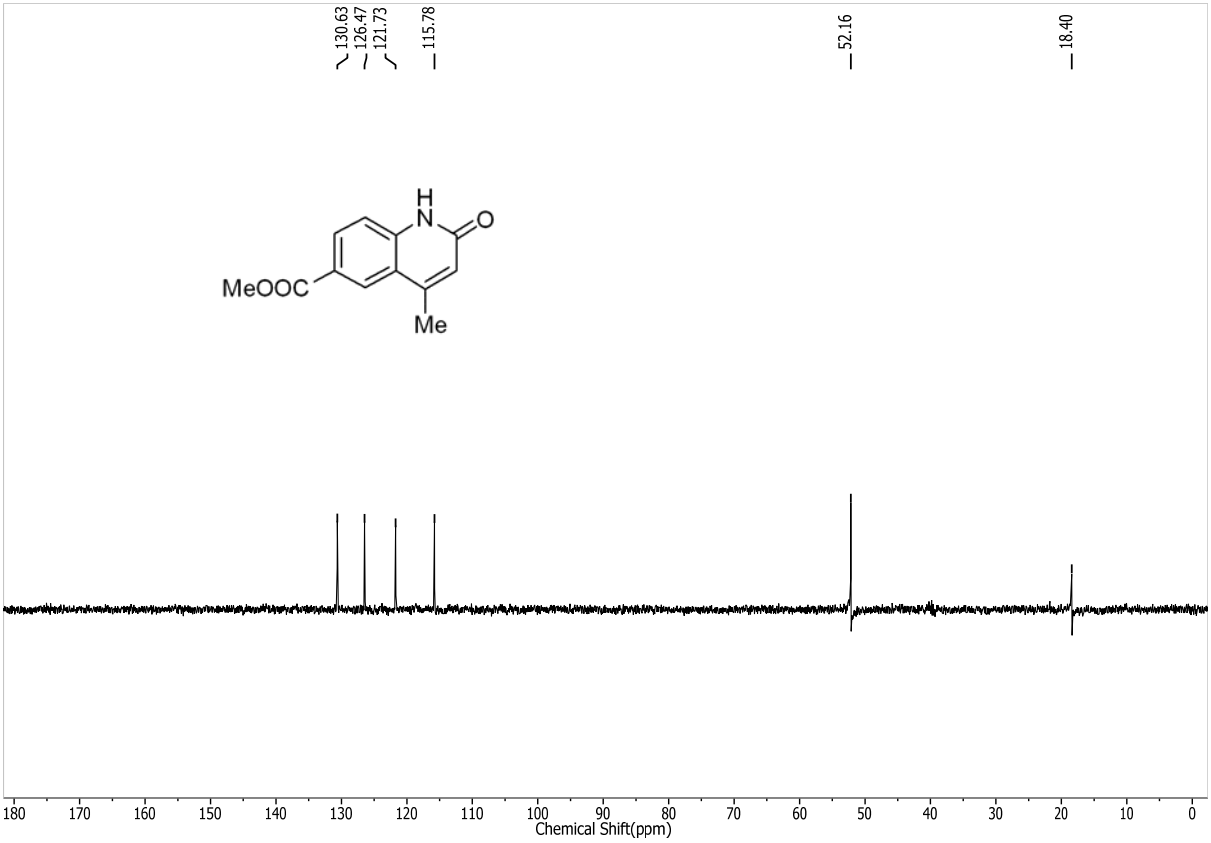


^{1}H and ^{13}C NMR Spectra of Compound **3ja** (DMSO-d_6 solvent was used).

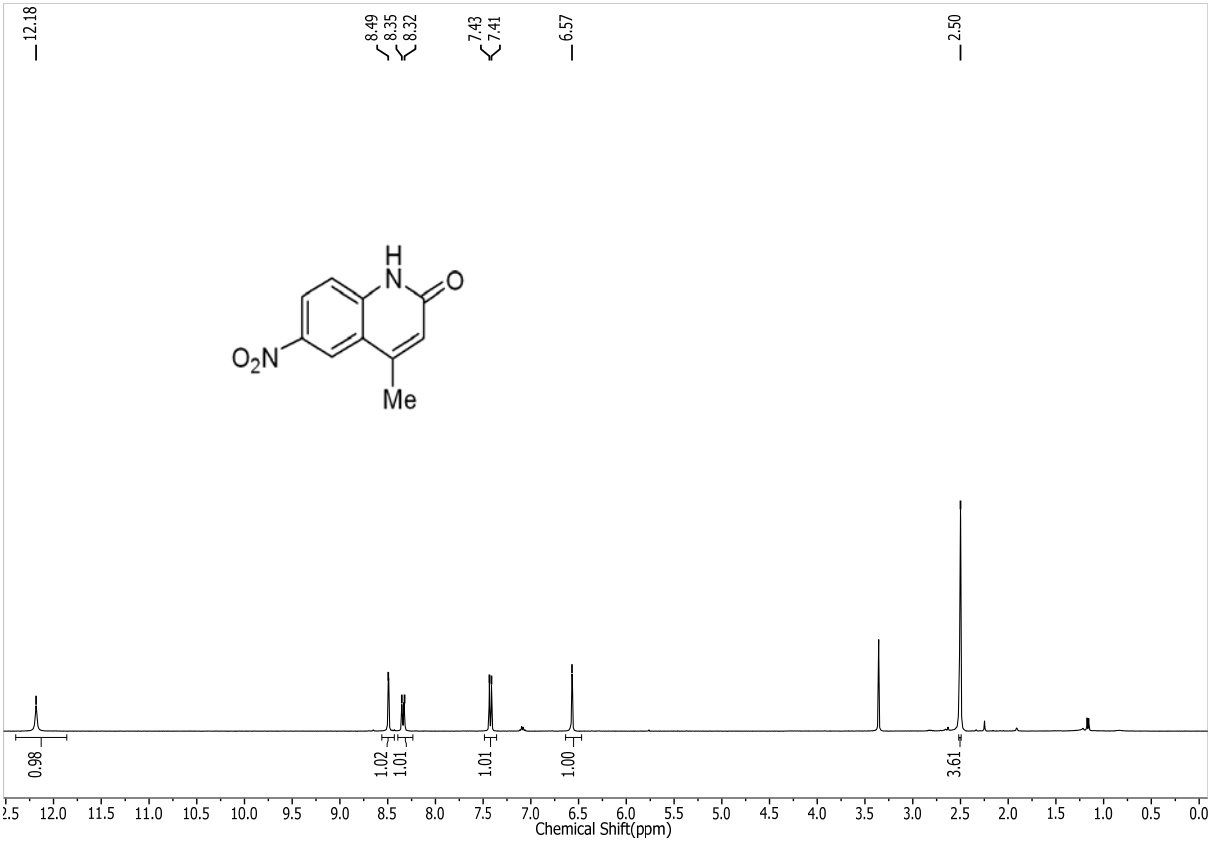


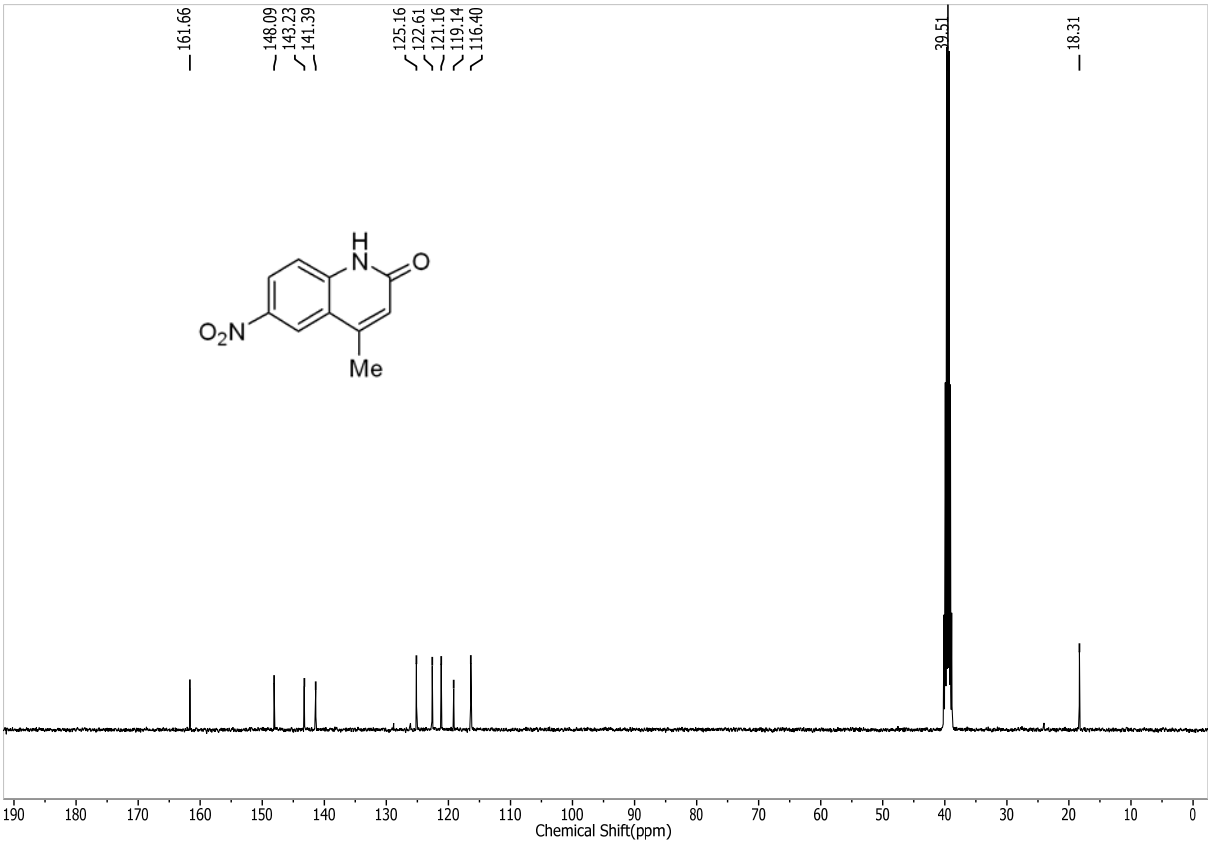


DEPT (135) NMR Spectrum of Compound **3ja** (DMSO-d_6 solvent was used).

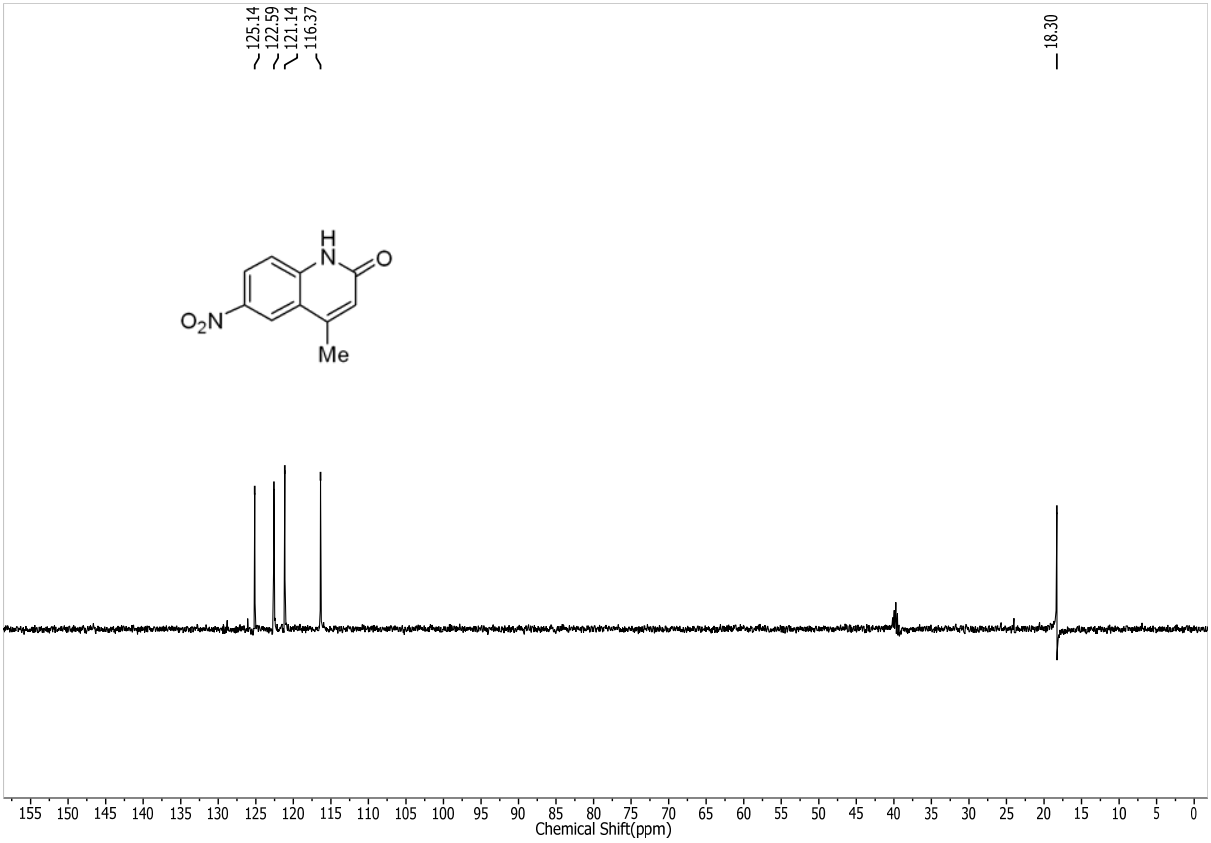


^{1}H and ^{13}C NMR Spectra of Compound **3ka** (DMSO-d_6 solvent was used).

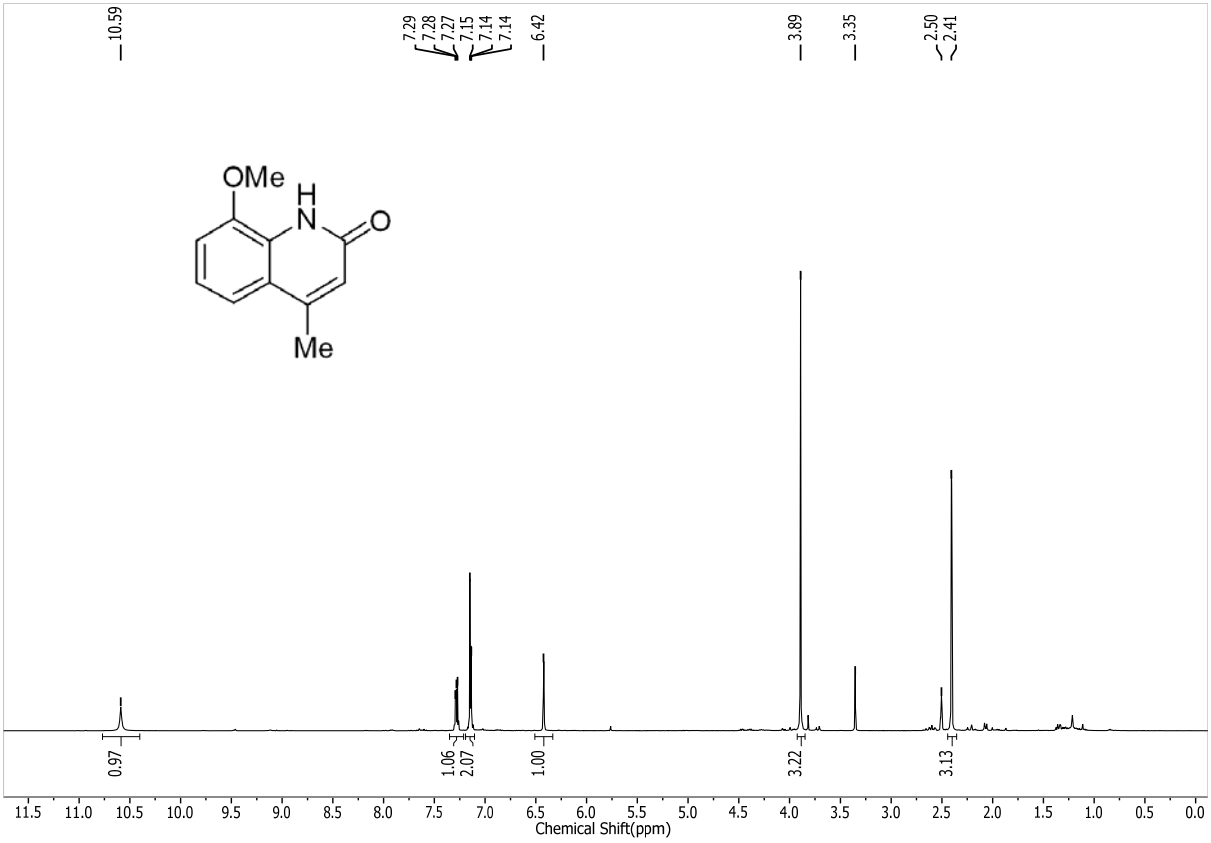


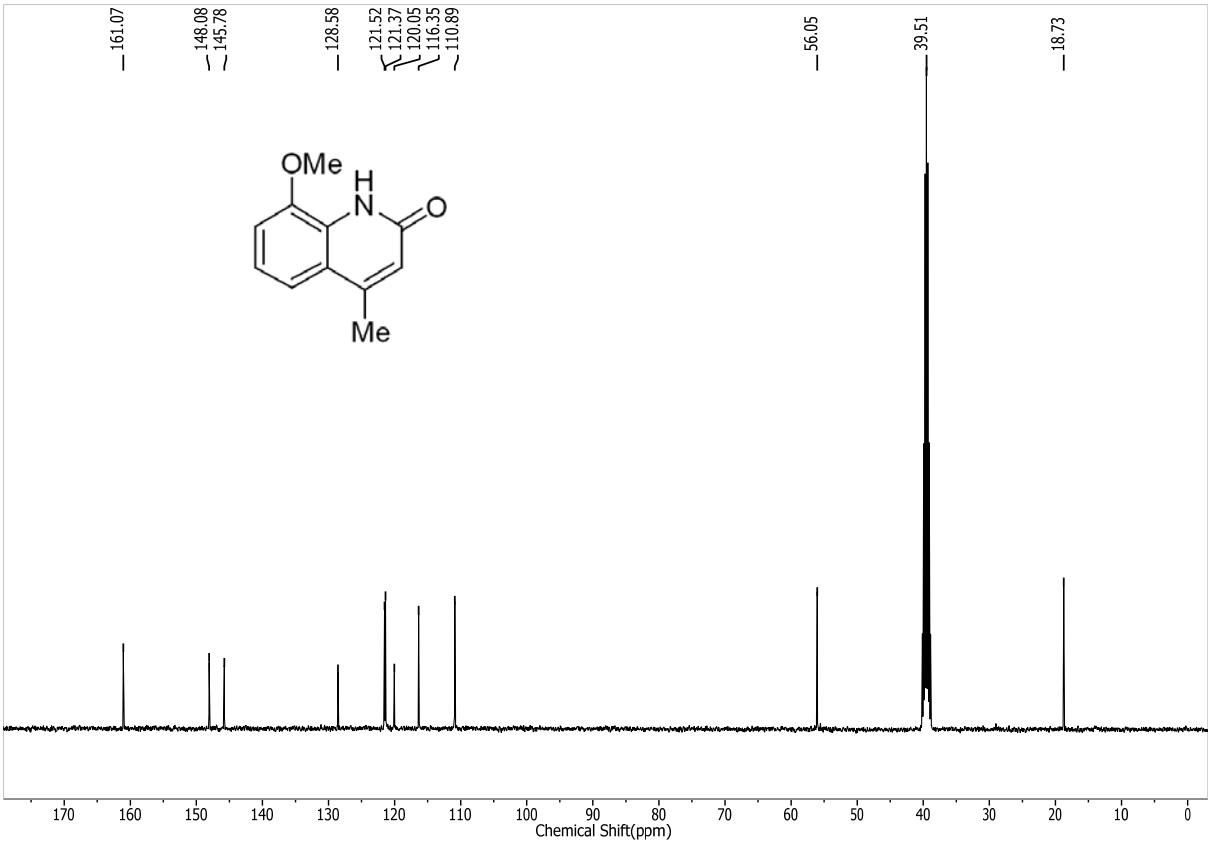


DEPT (135) NMR Spectrum of Compound **3ka** (DMSO-d_6 solvent was used).

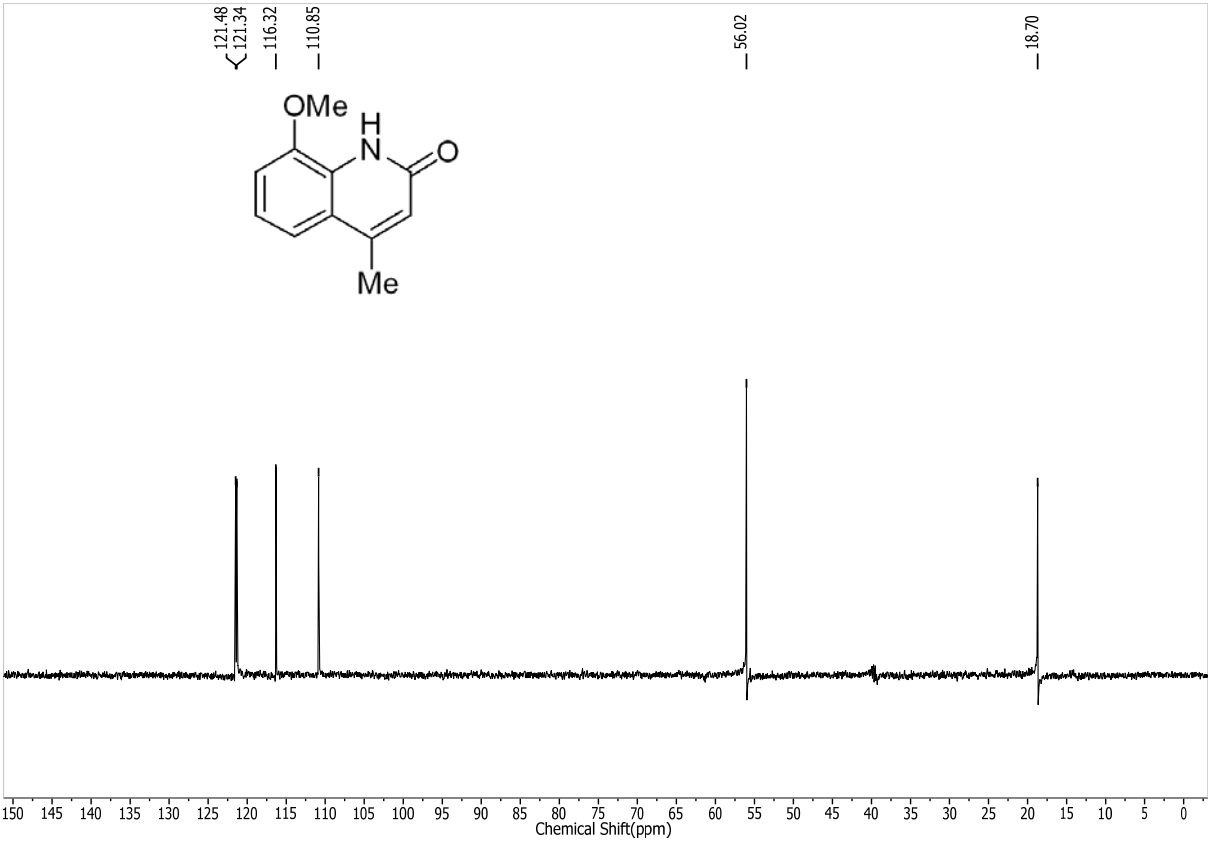


^{1}H and ^{13}C NMR Spectra of Compound **3la** (DMSO-d_6 solvent was used).

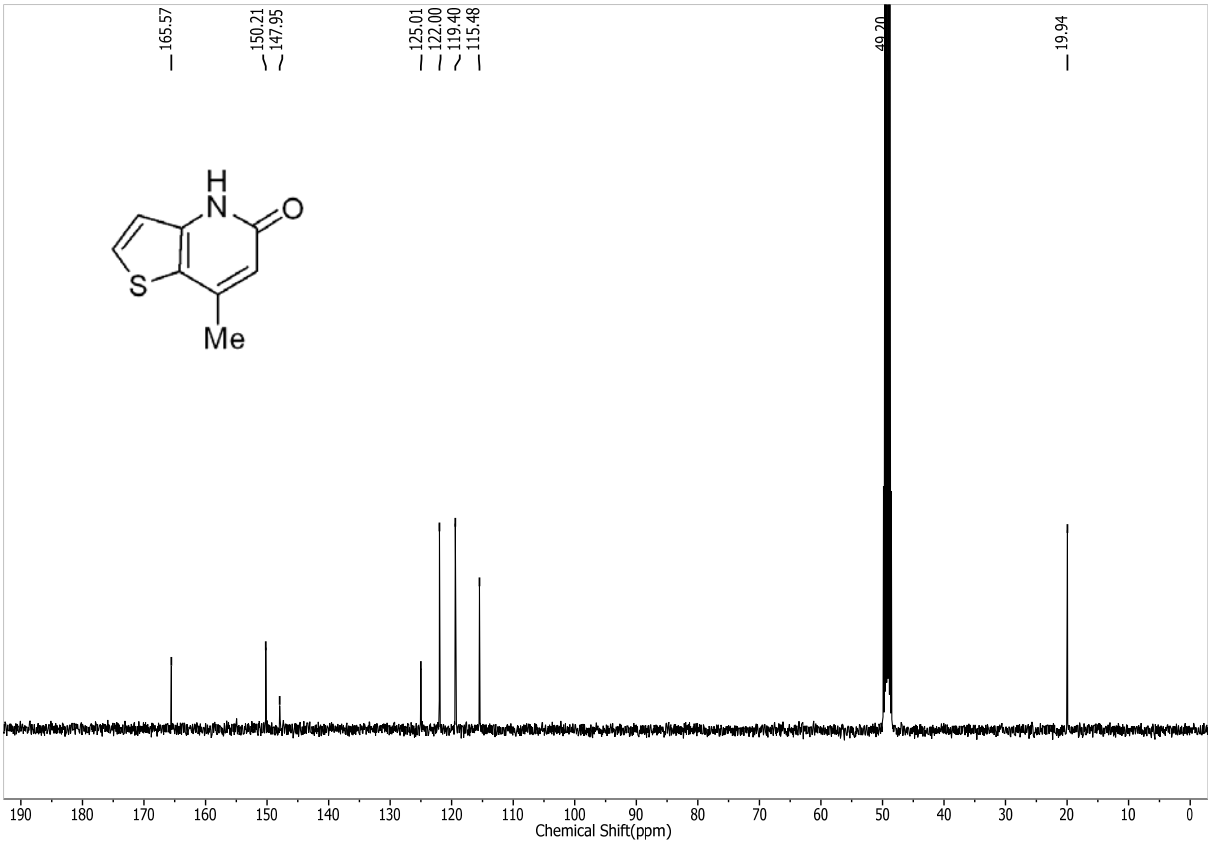




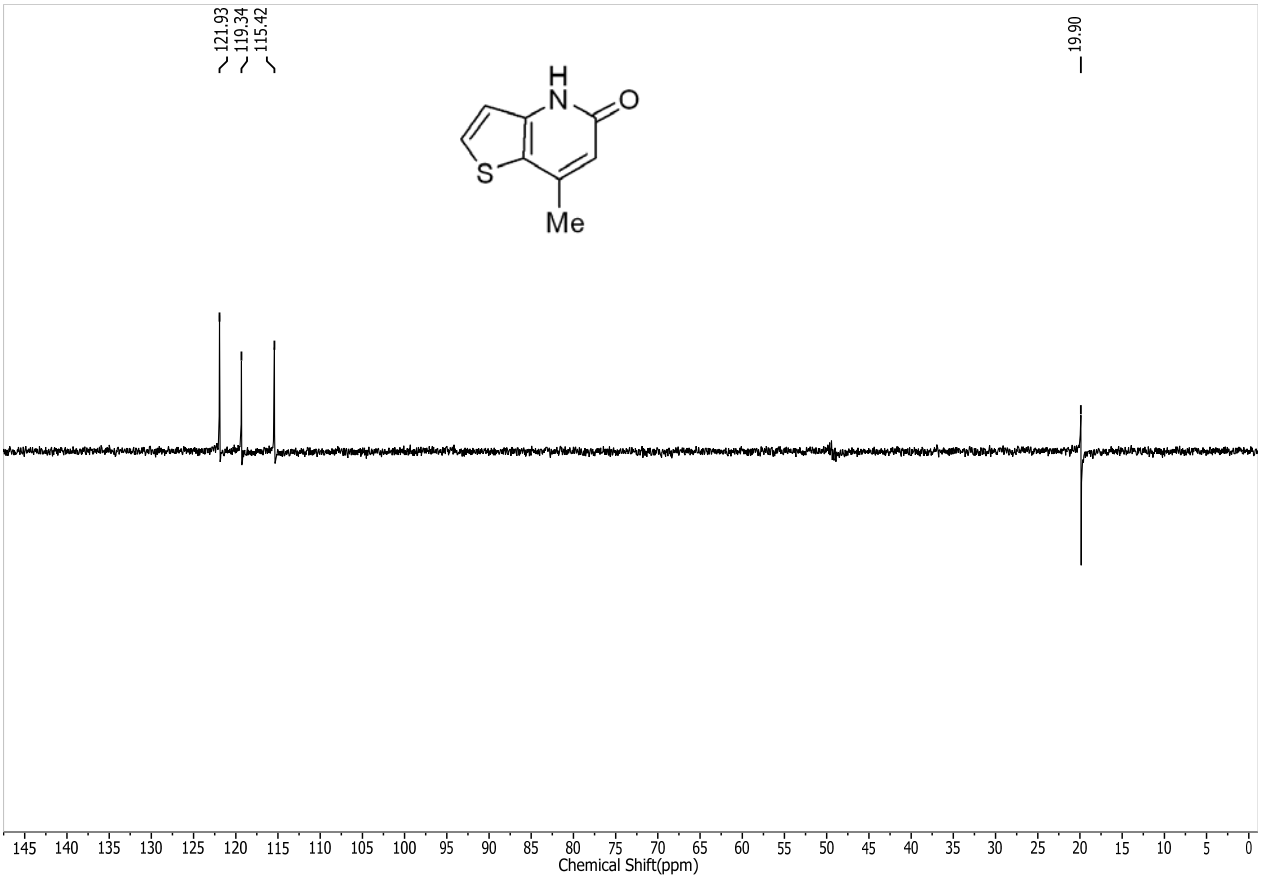
DEPT (135) NMR Spectrum of Compound **3la** (DMSO-d_6 solvent was used).



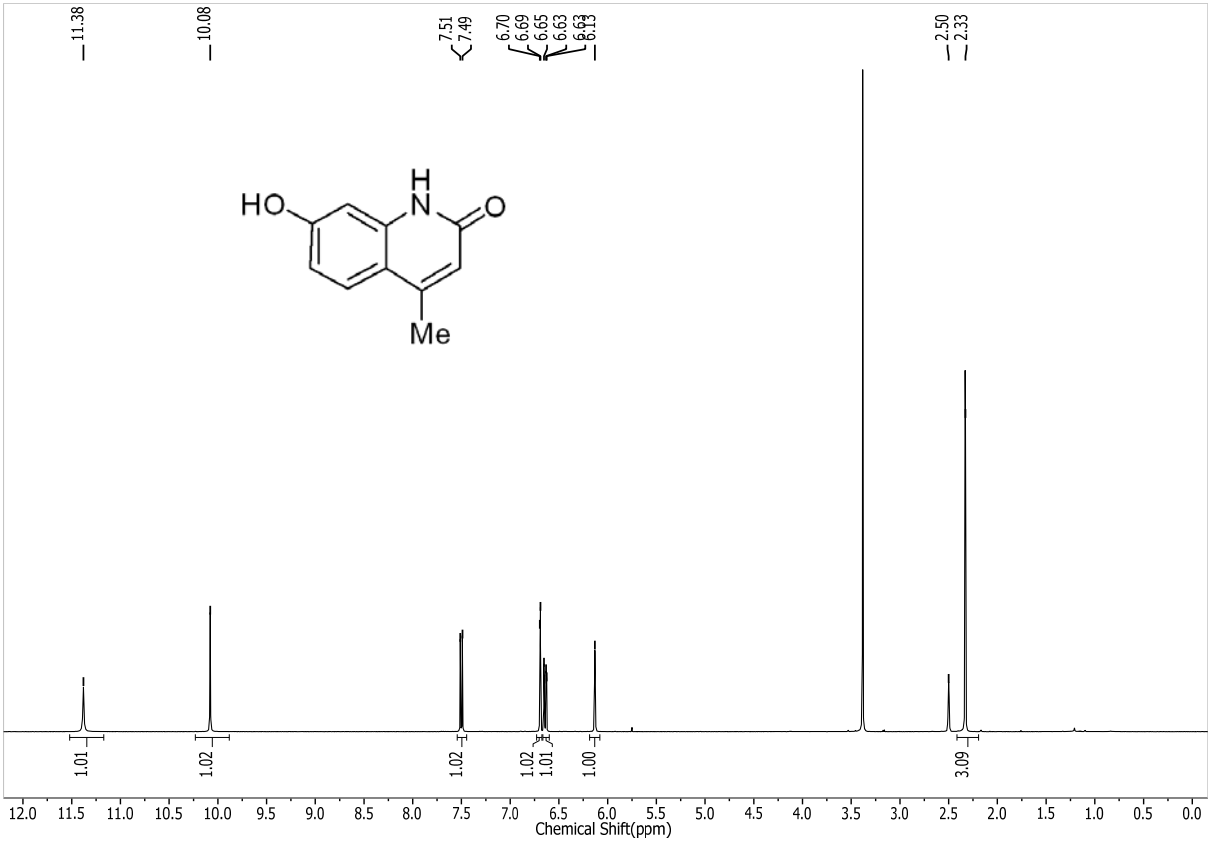
^{1}H and ^{13}C NMR Spectra of Compound **3ma** (CD_3OD solvent was used).

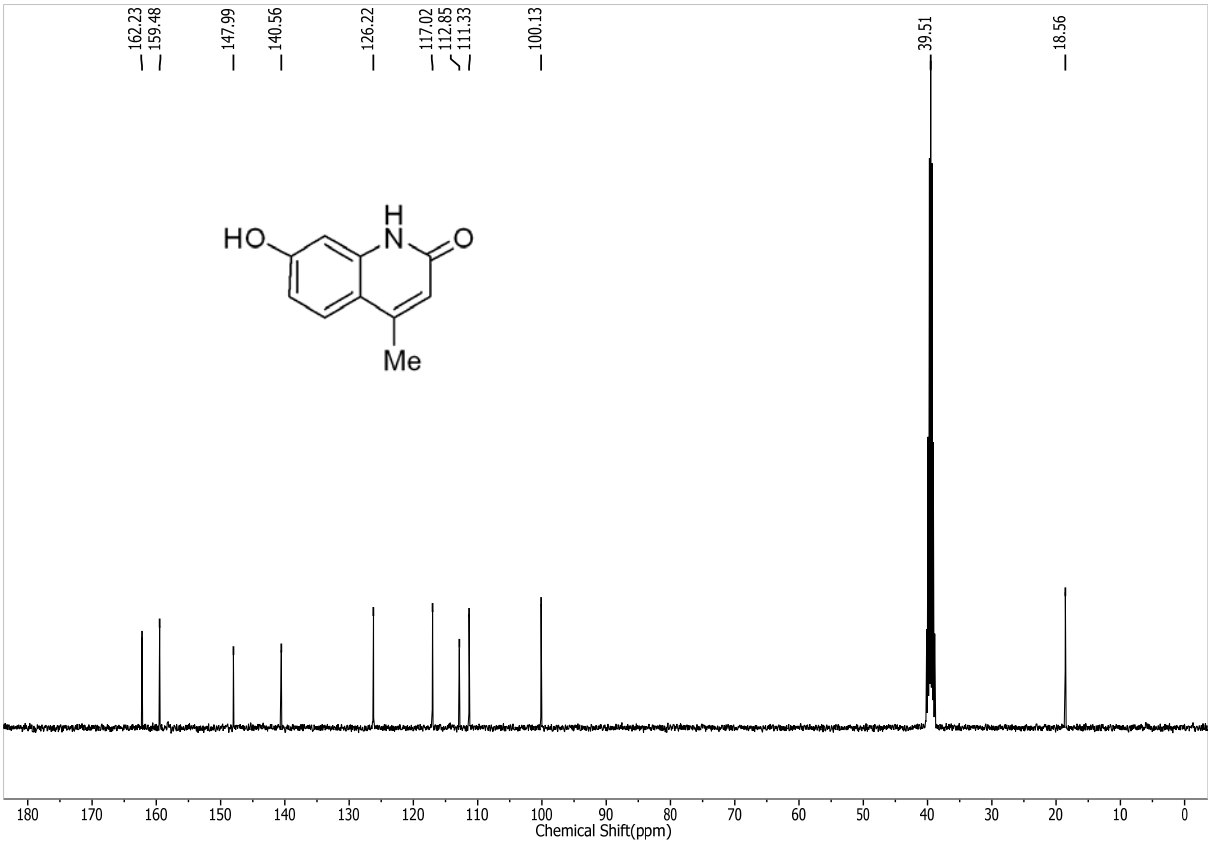


DEPT (135) NMR Spectrum of Compound **3ma** (CD_3OD solvent was used).

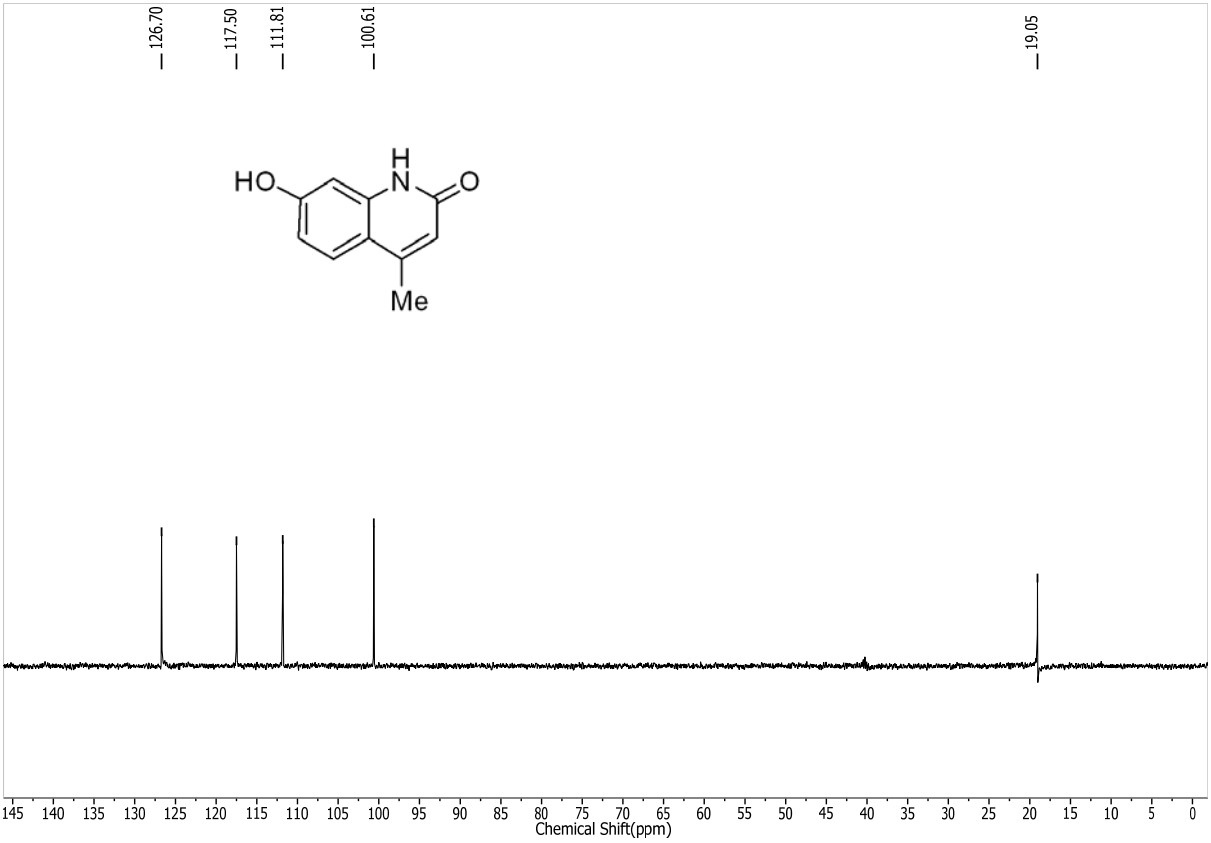


^{1}H and ^{13}C NMR Spectra of Compound **3na** (DMSO-d_6 solvent was used).

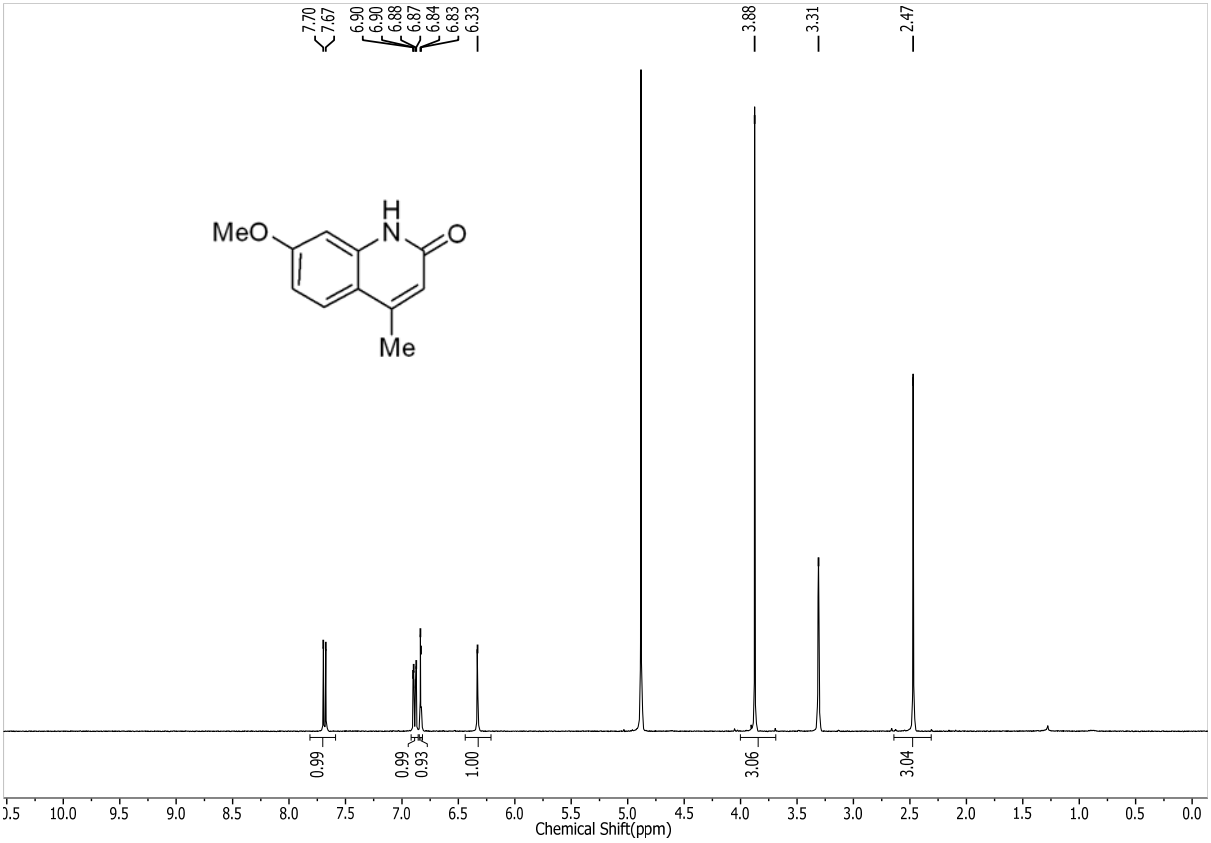


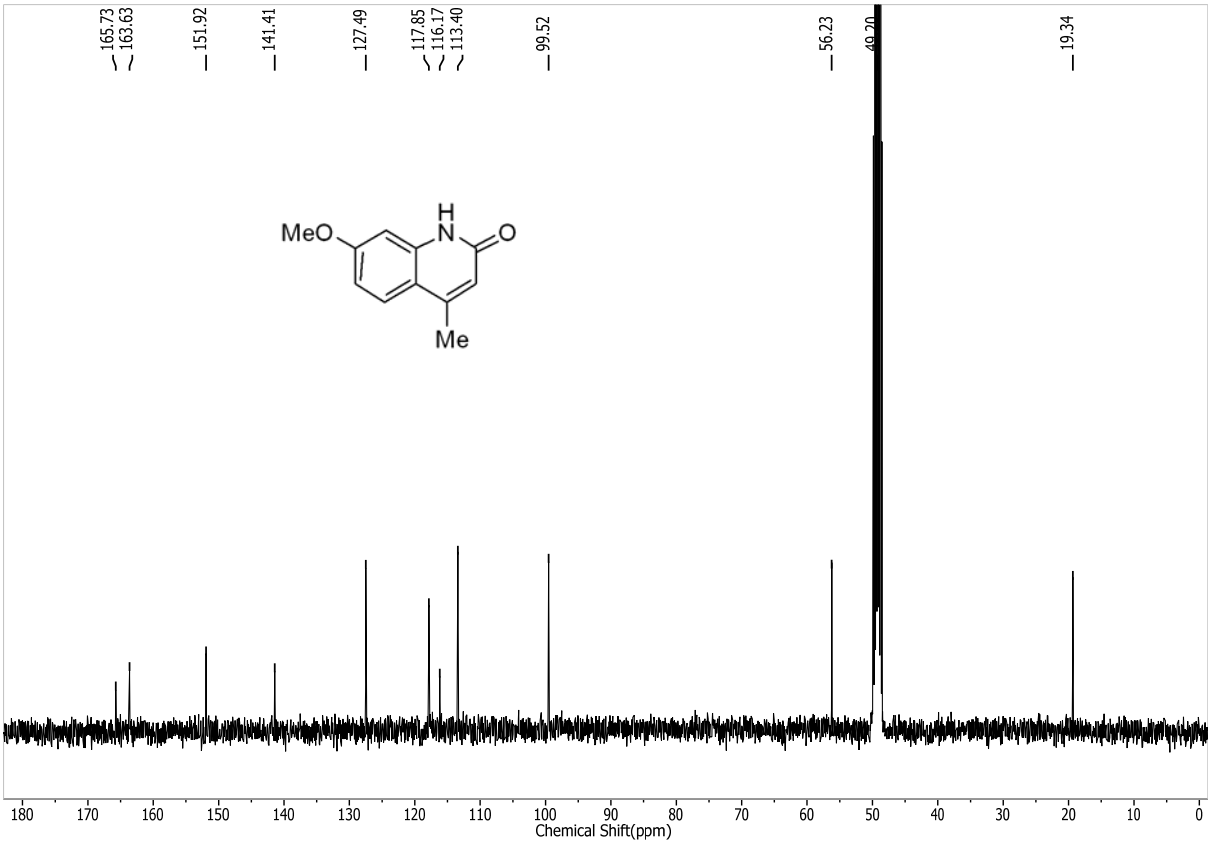


DEPT (135) NMR Spectrum of Compound **3na** (DMSO-d_6 solvent was used).

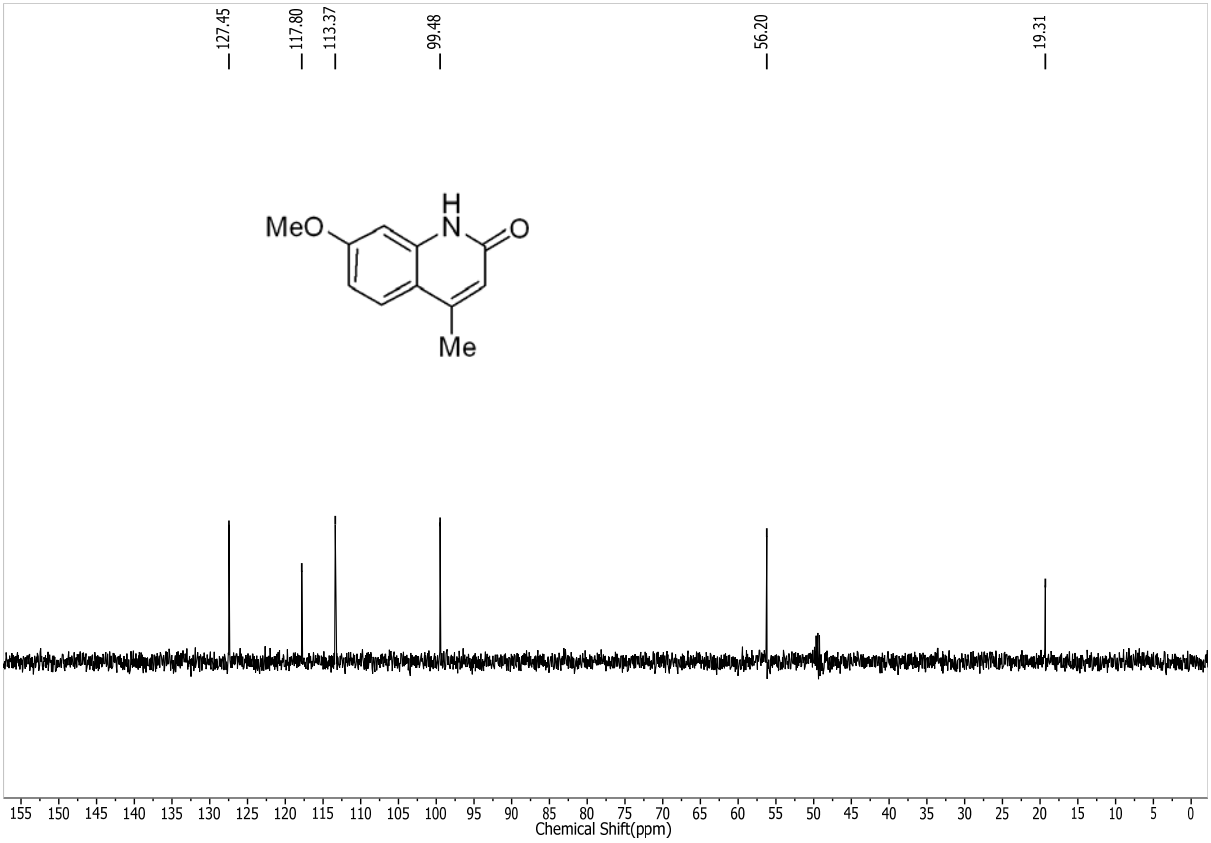


^{1}H and ^{13}C NMR Spectra of Compound **3oa** (CD_3OD solvent was used).

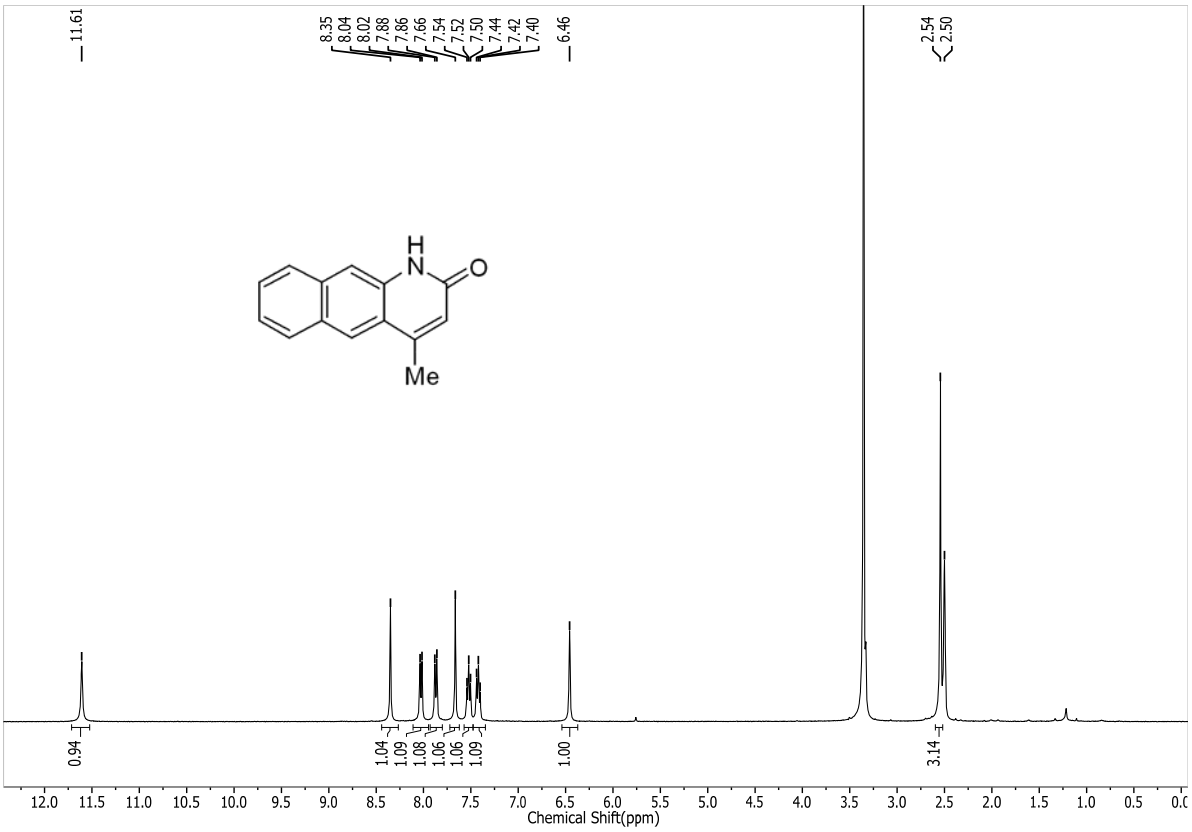


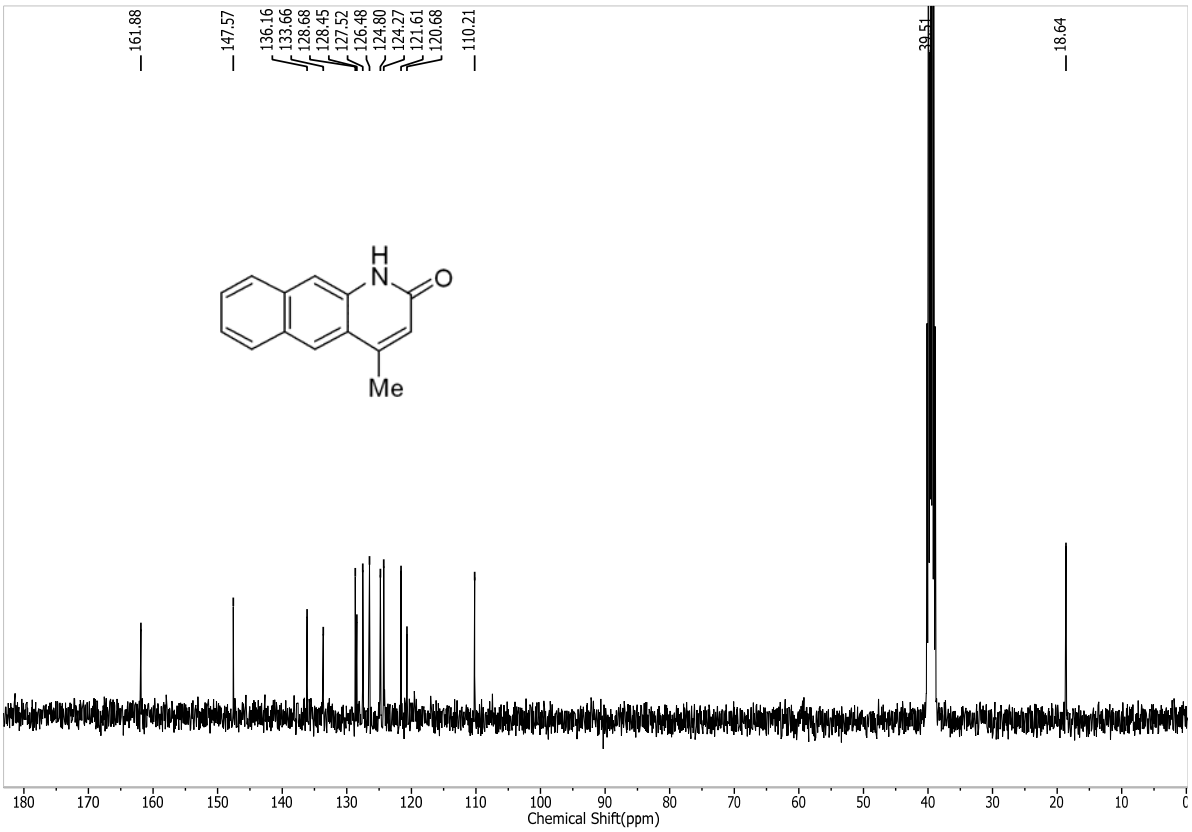


DEPT (135) NMR Spectrum of Compound **3oa** (CD_3OD solvent was used).

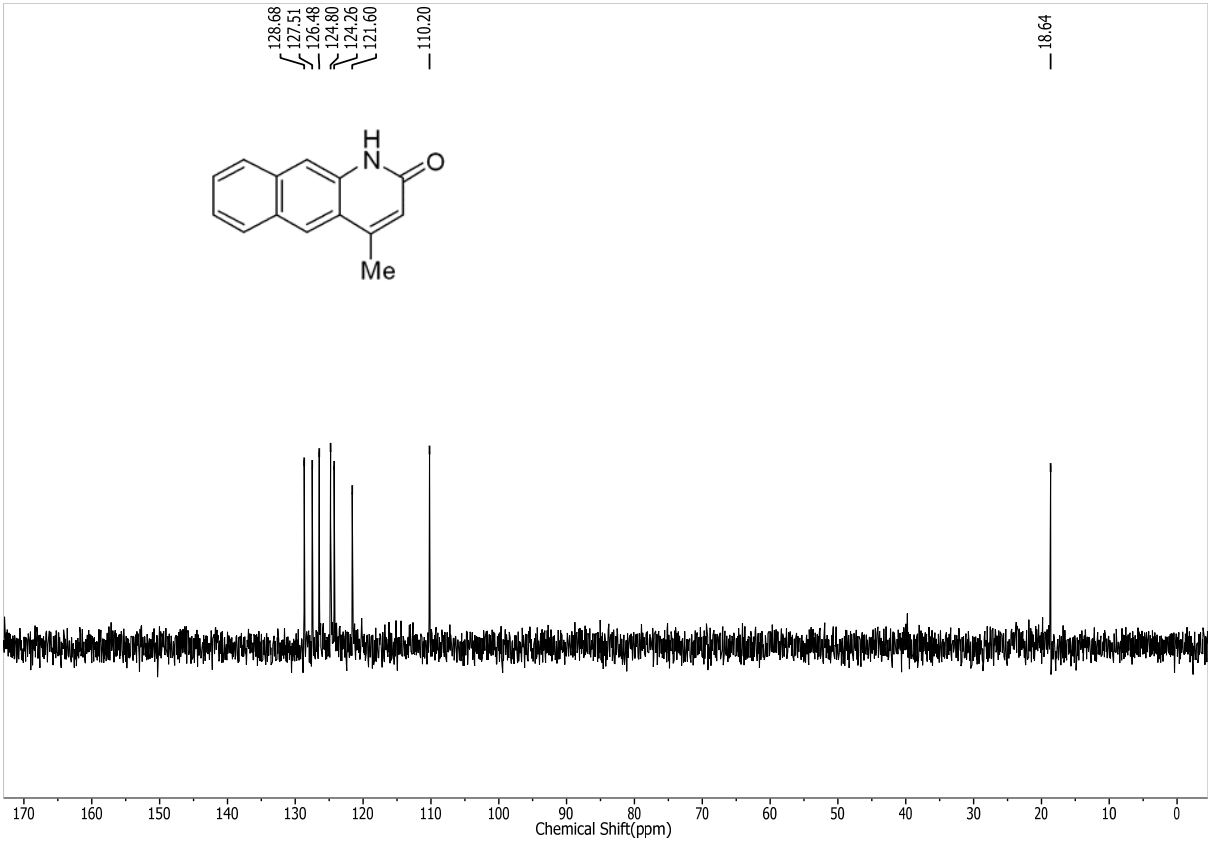


^{1}H and ^{13}C NMR Spectra of Compound **3pa** (DMSO-d_6 solvent was used).

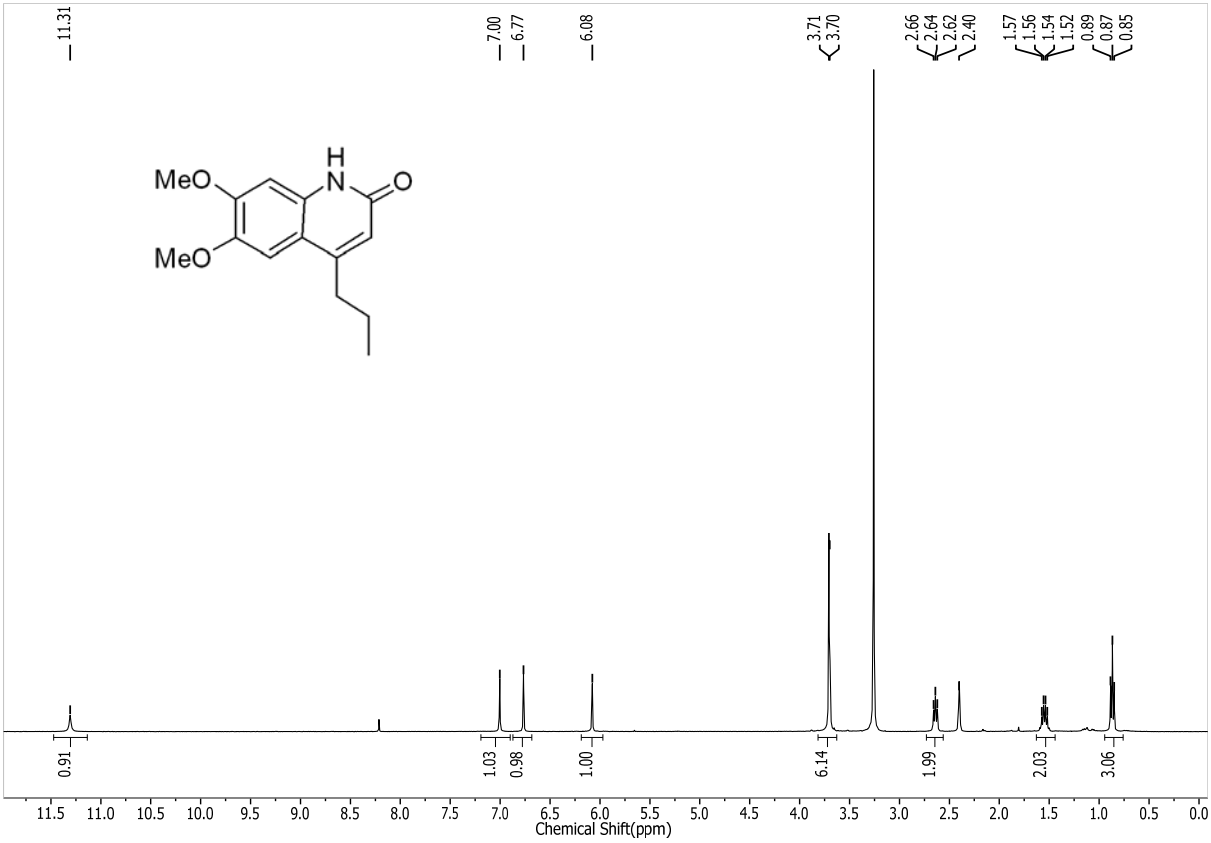


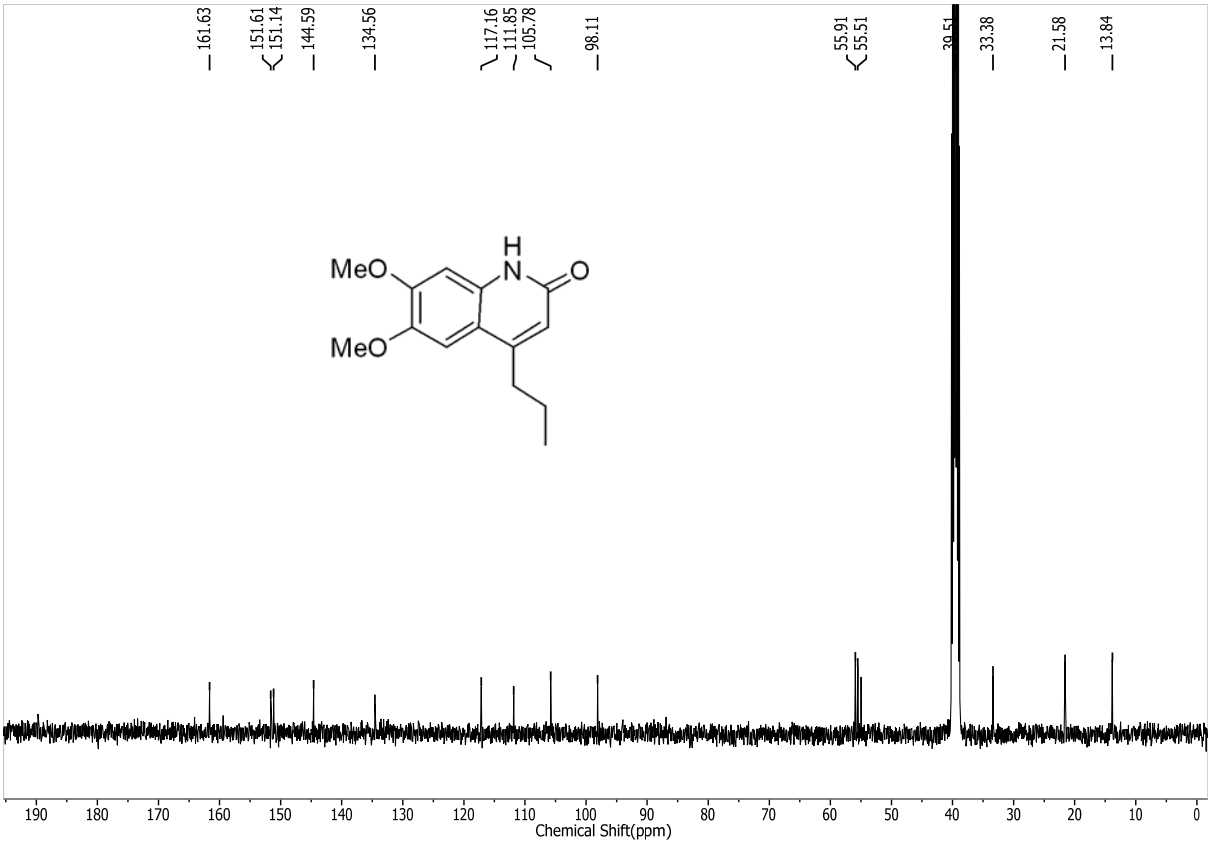


DEPT (135) NMR Spectrum of Compound **3pa** (DMSO-d_6 solvent was used).

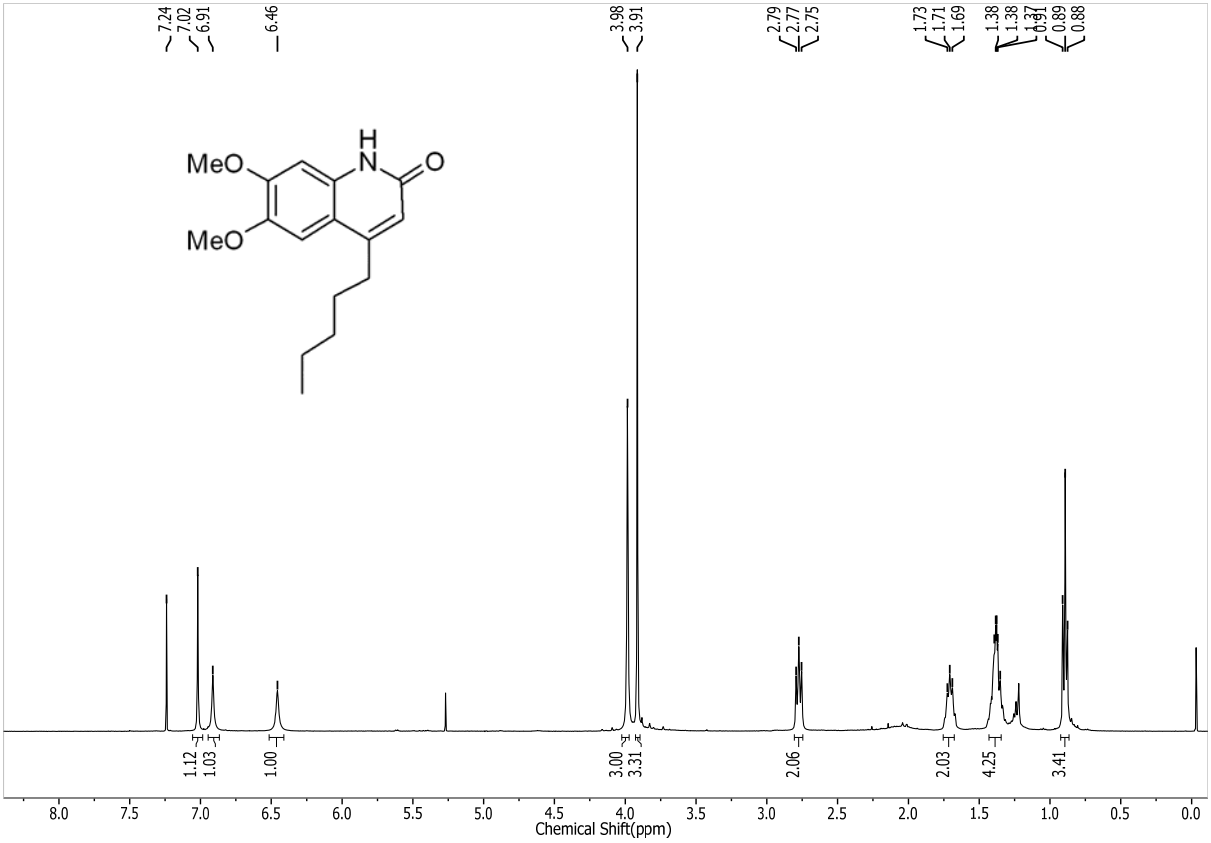


^{1}H and ^{13}C NMR Spectra of Compound **3ab** (DMSO-d_6 solvent was used).

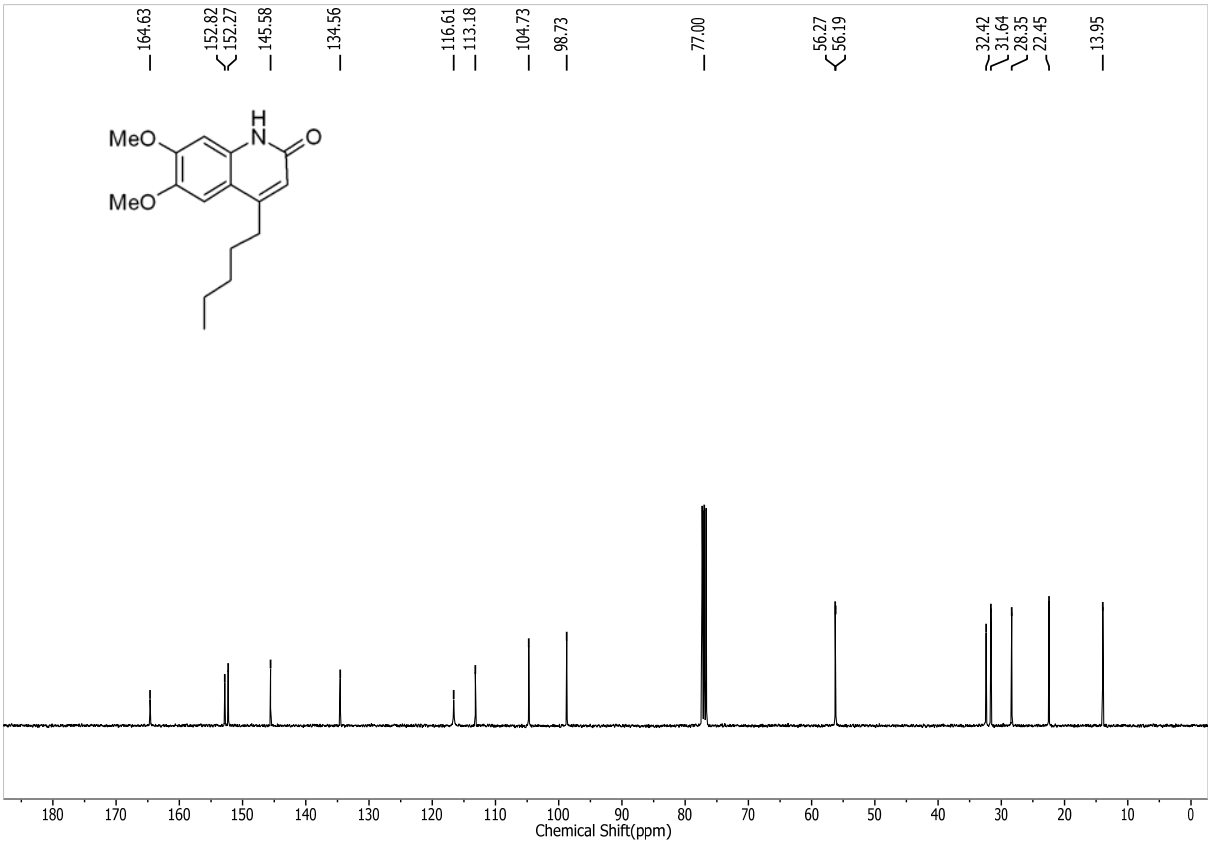




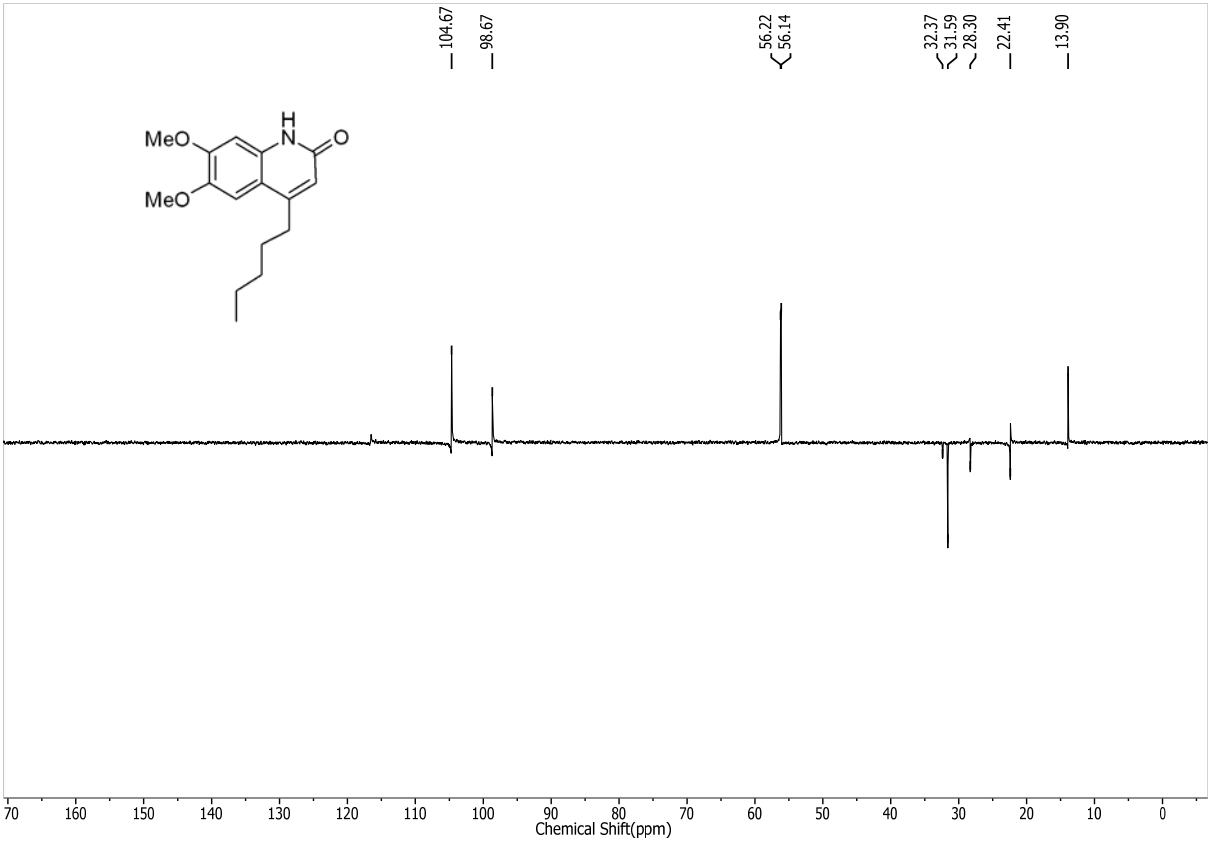
^{1}H and ^{13}C NMR Spectra of Compound **3ac** ($CDCl_3$ solvent was used).



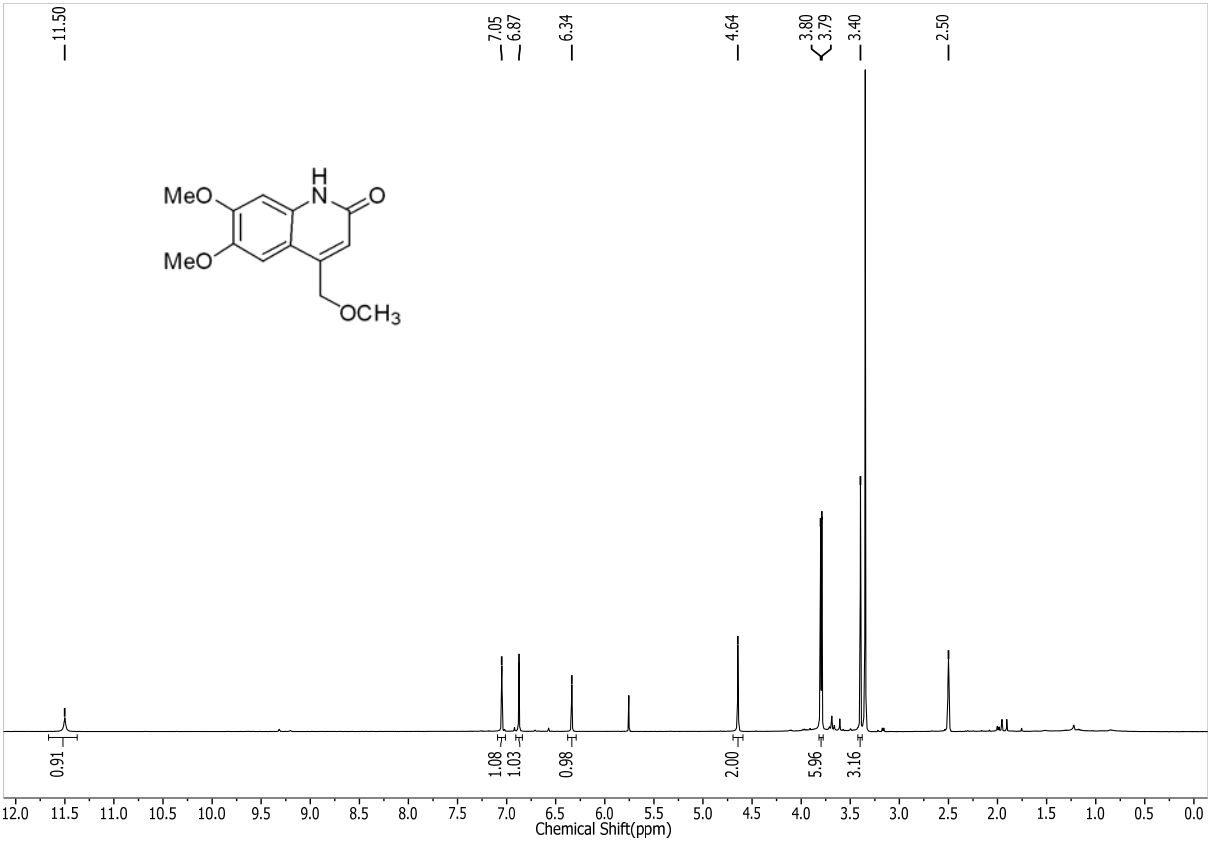
.

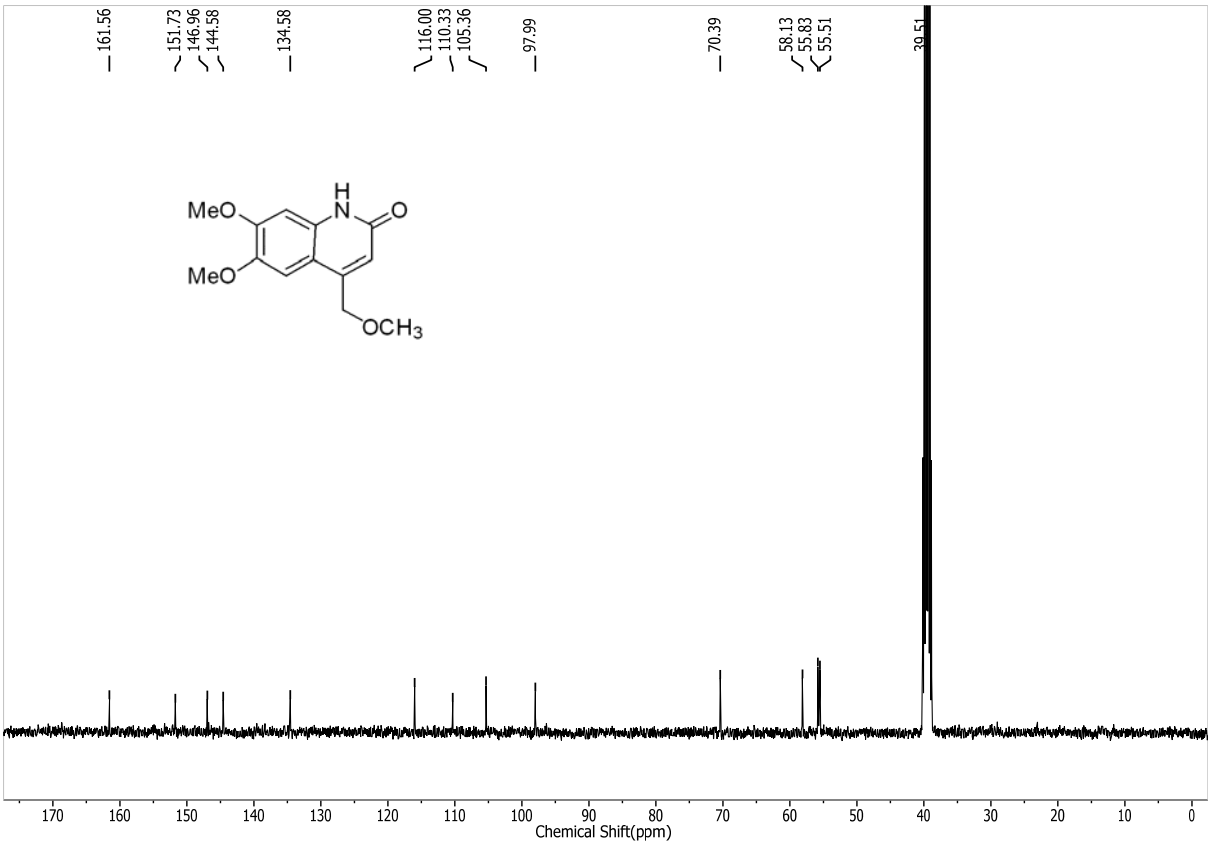


DEPT (135) NMR Spectrum of Compound **3ac** ($CDCl_3$ solvent was used).

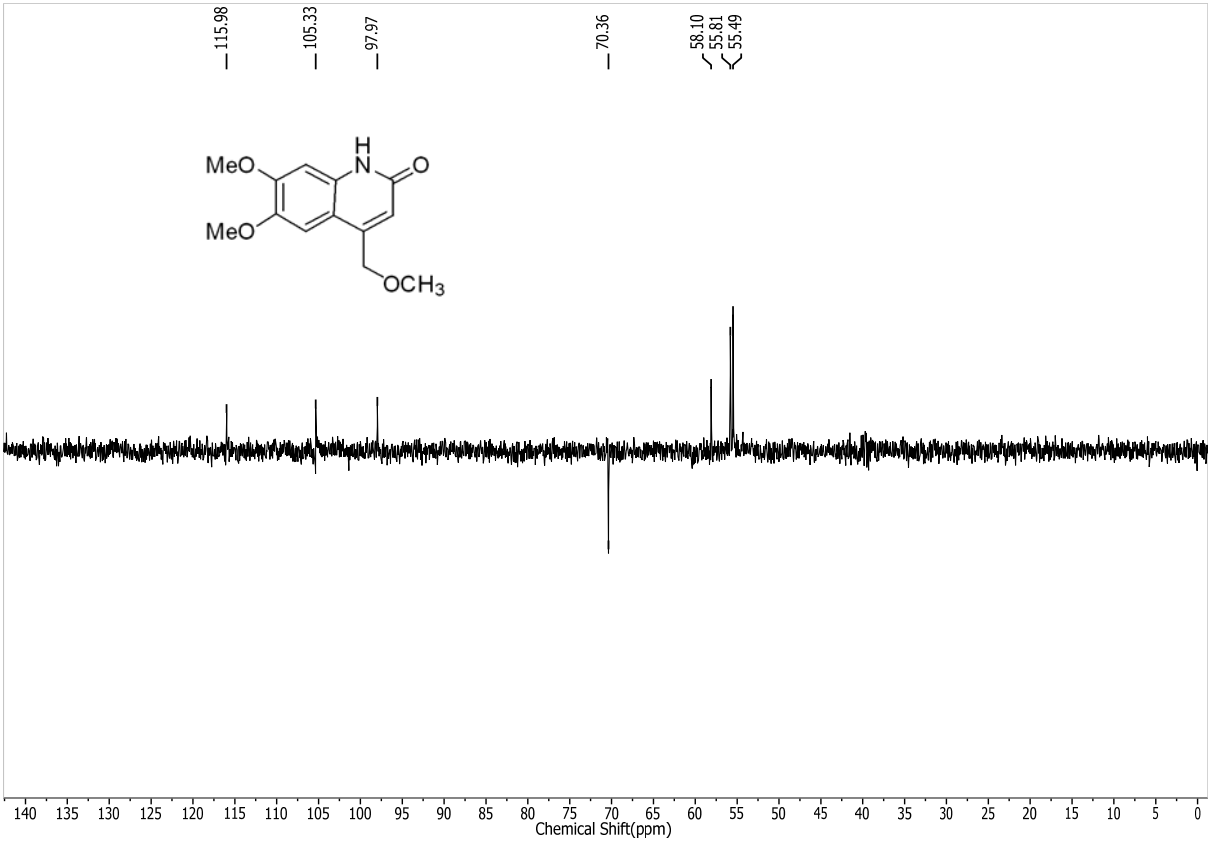


^{1}H and ^{13}C NMR Spectra of Compound **3ad** (DMSO-d_6 solvent was used).

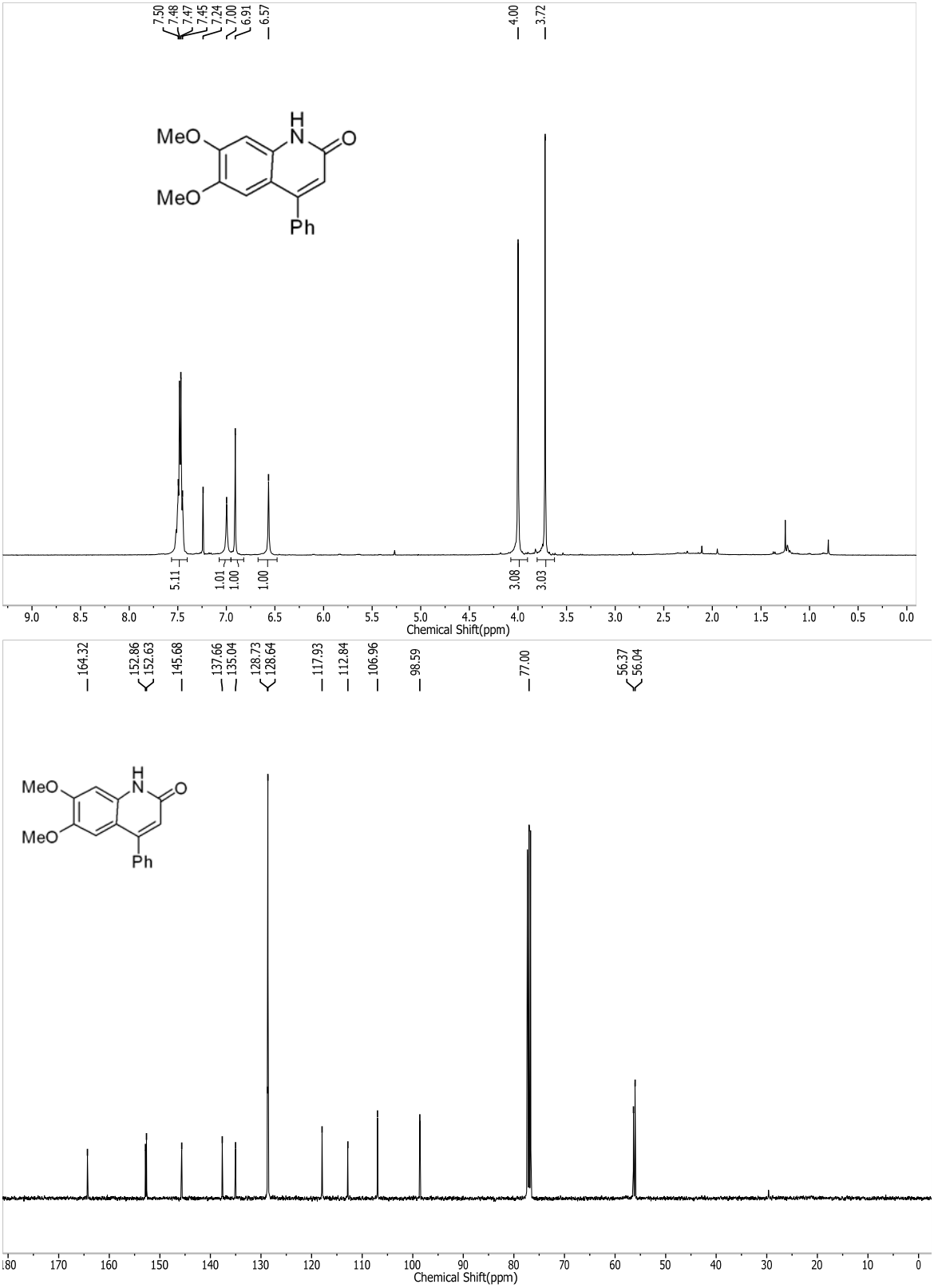




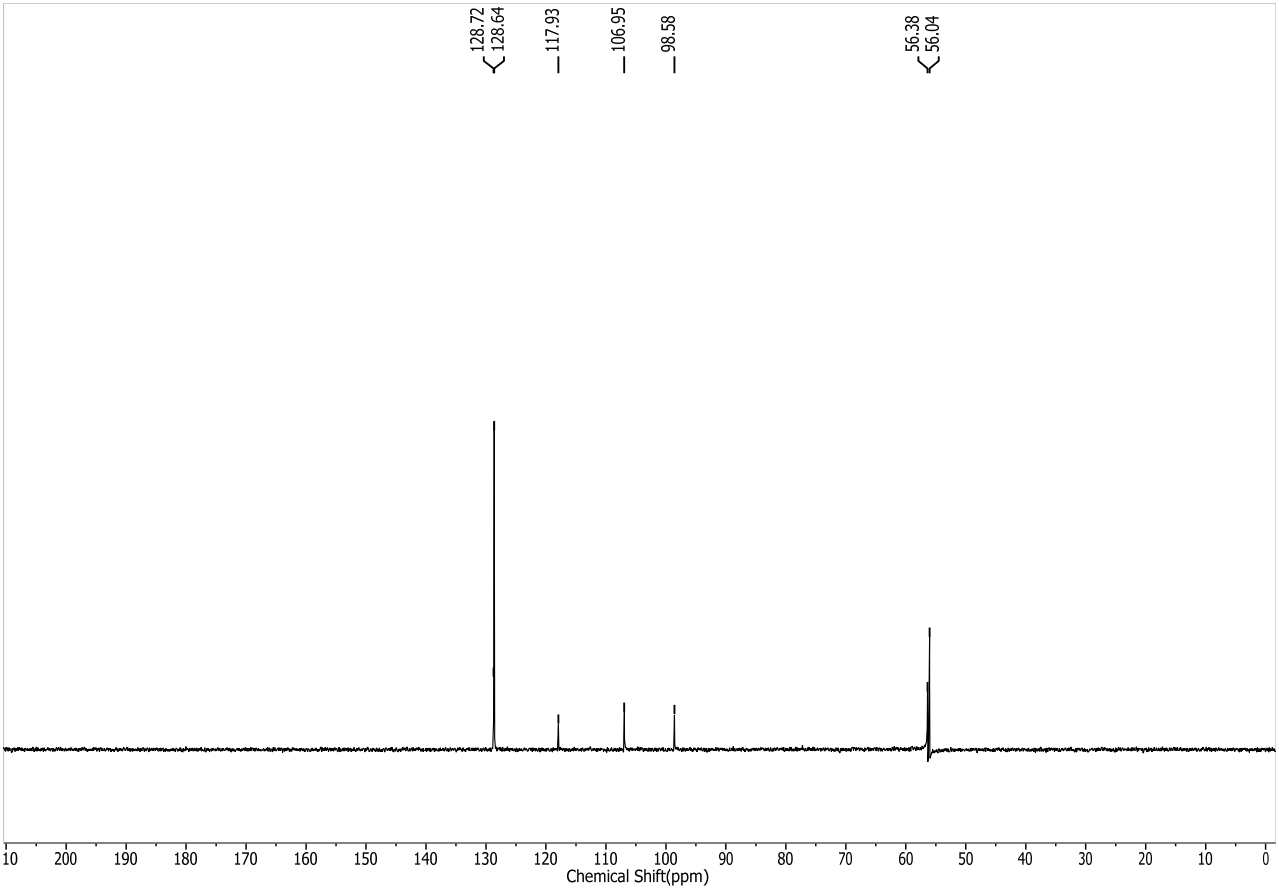
DEPT NMR Spectra of Compound **3ad** (DMSO-d_6 solvent was used).



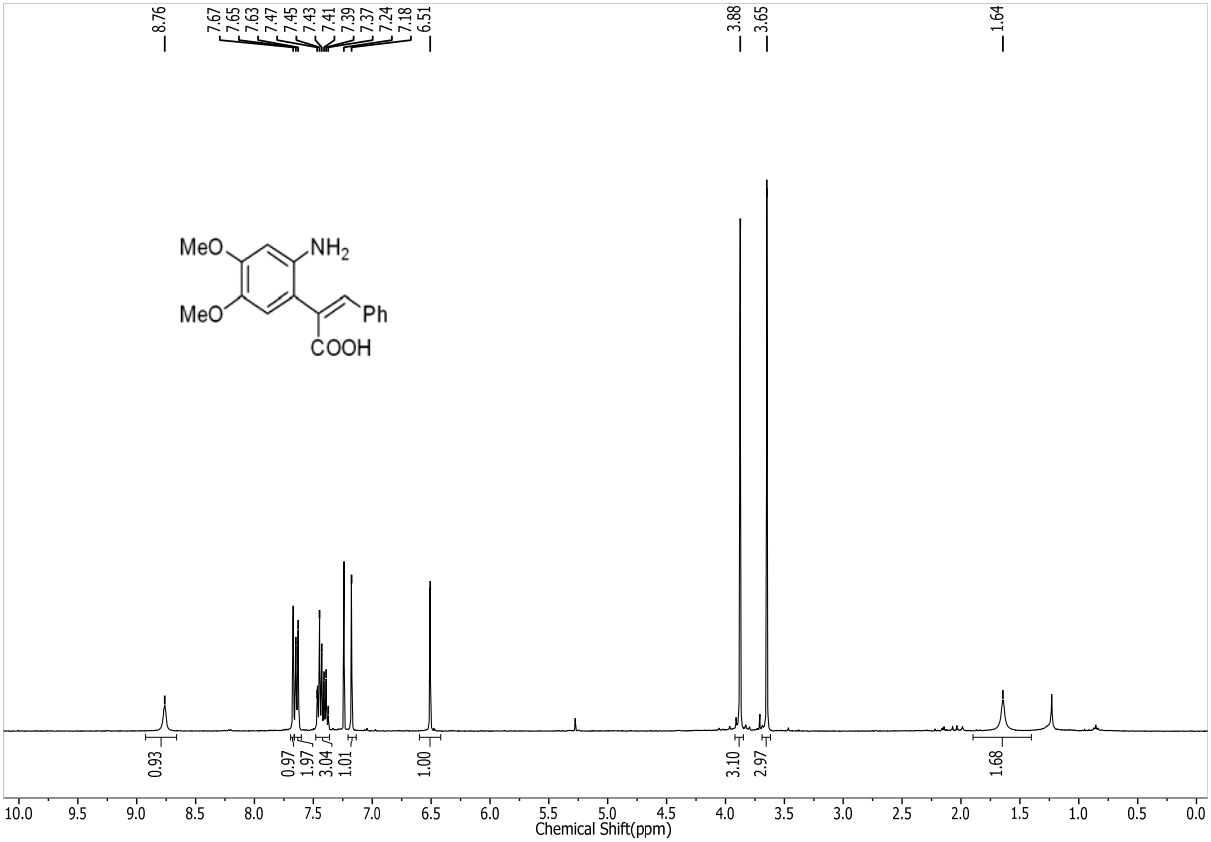
^{1}H and ^{13}C NMR Spectra of Compound **3ae** ($CDCl_3$ solvent was used).

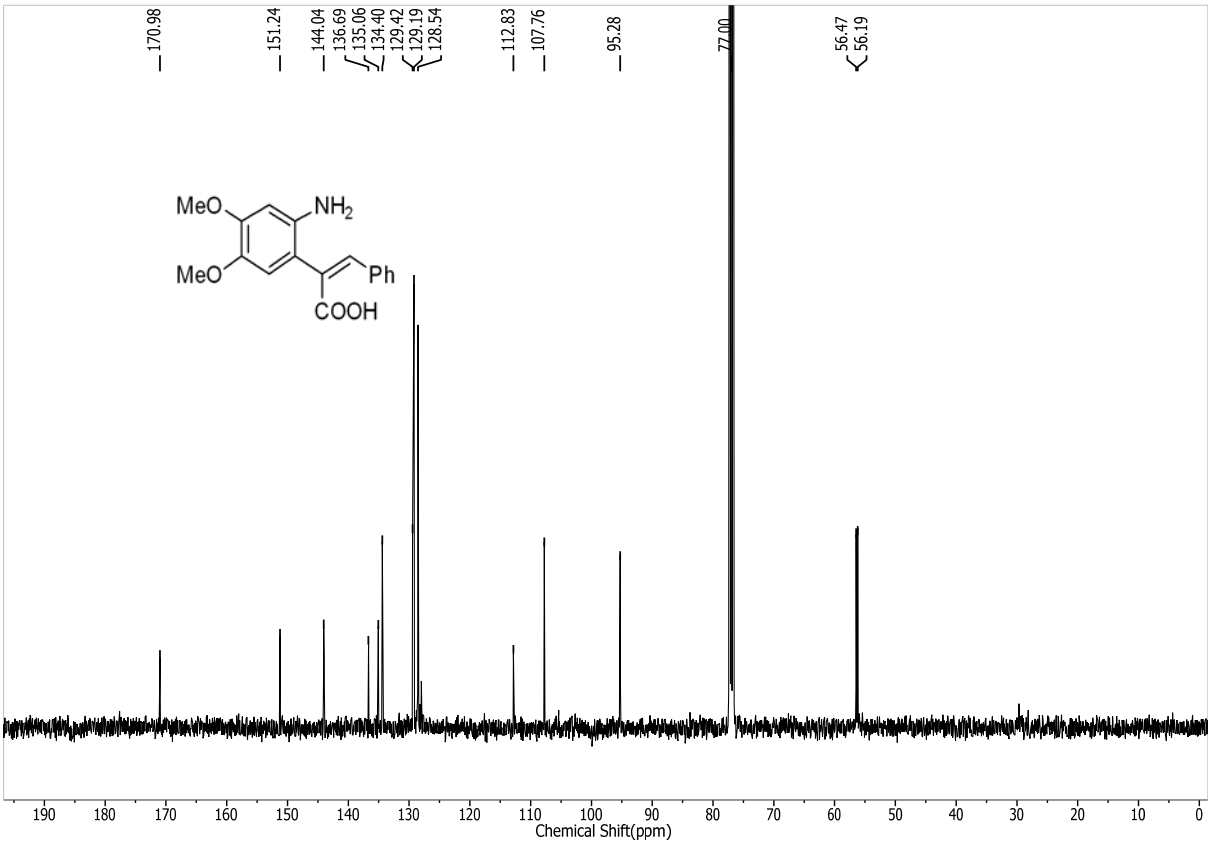


DEPT (135) NMR Spectrum of Compound **3ae** ($CDCl_3$ solvent was used).

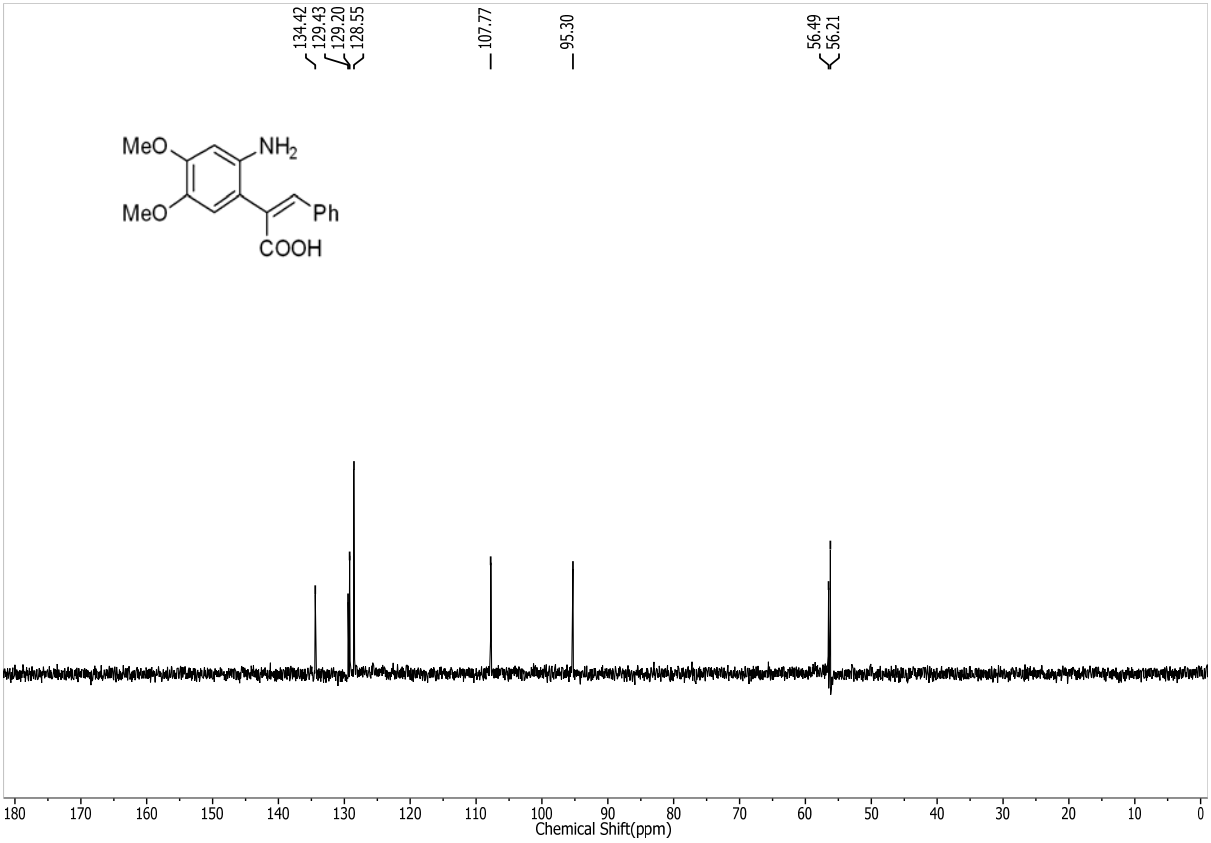


^{1}H and ^{13}C NMR Spectra of Compound **3ae'** ($CDCl_3$ solvent was used).

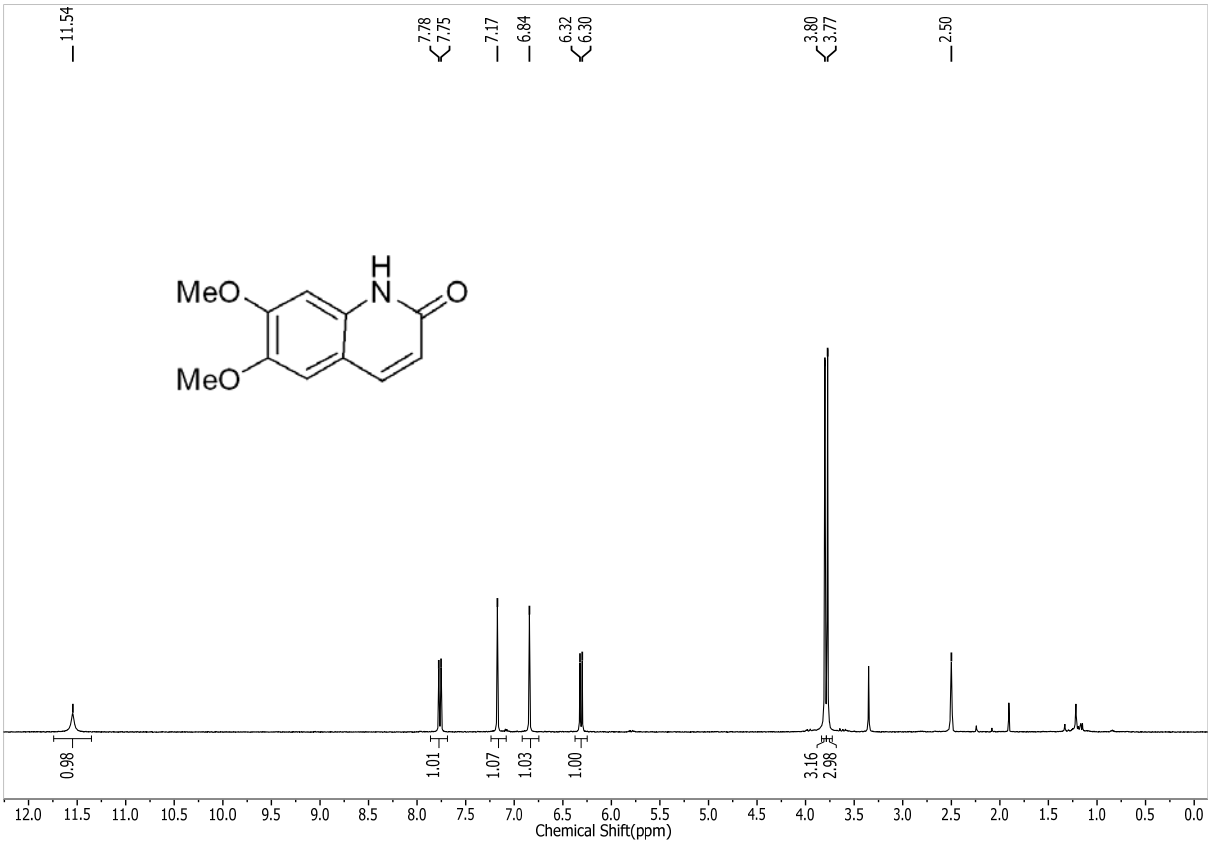


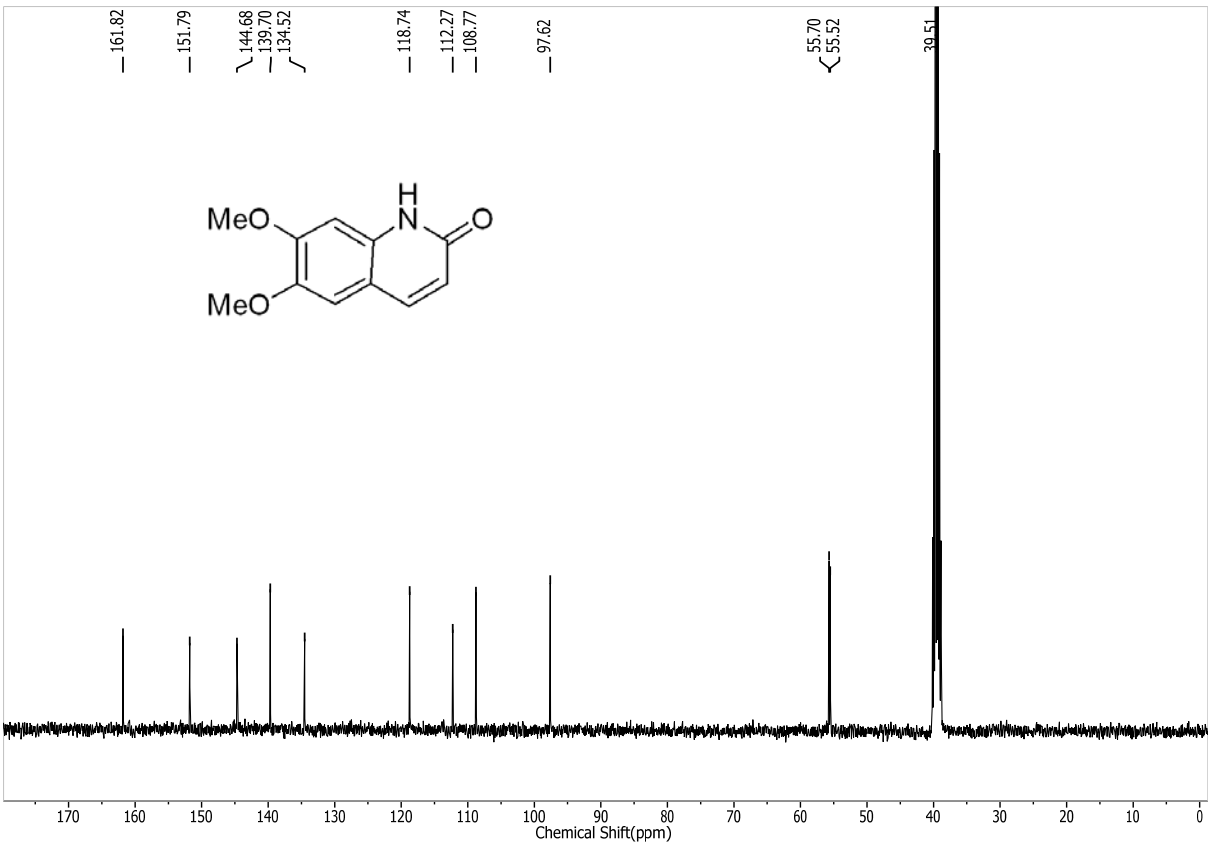


DEPT (135) NMR Spectrum of Compound **3ae'** ($CDCl_3$ solvent was used).

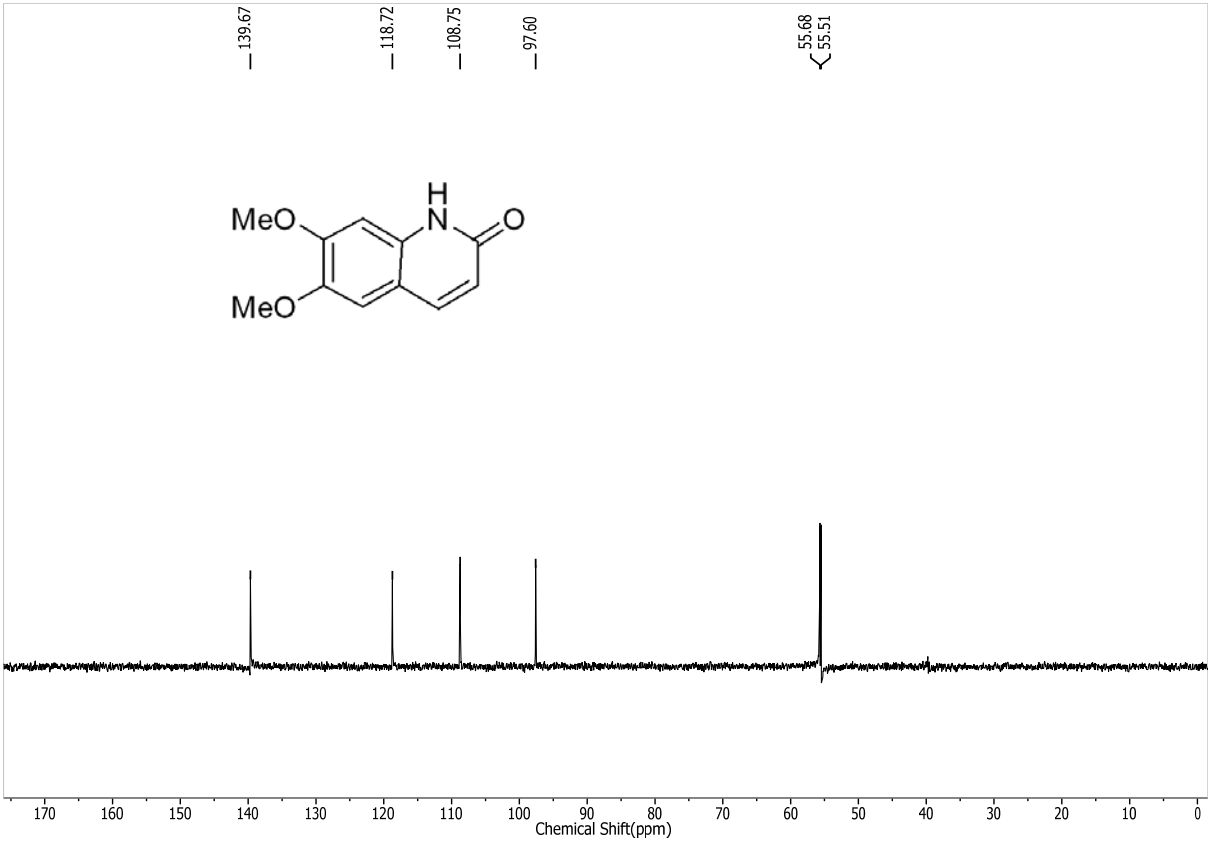


^{1}H and ^{13}C NMR Spectra of Compound **5aa** (DMSO-d_6 solvent was used).

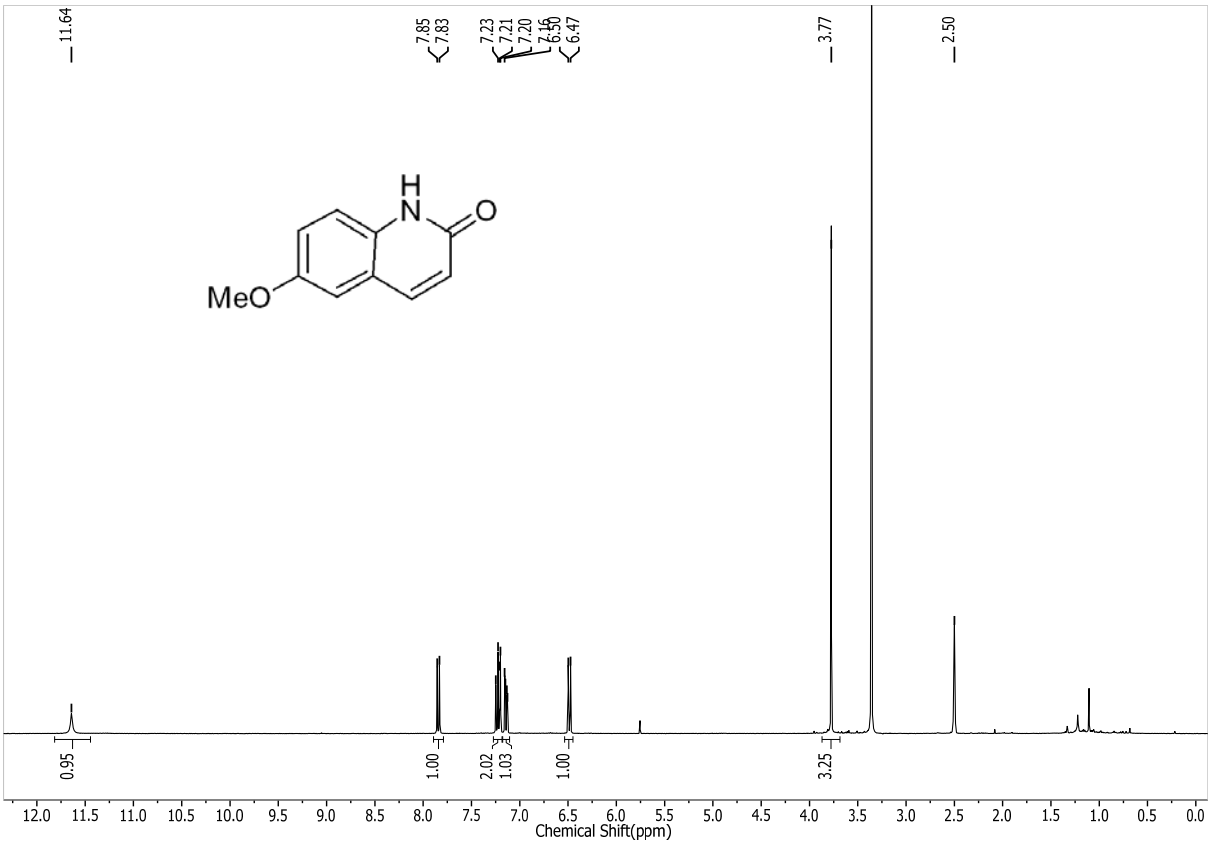


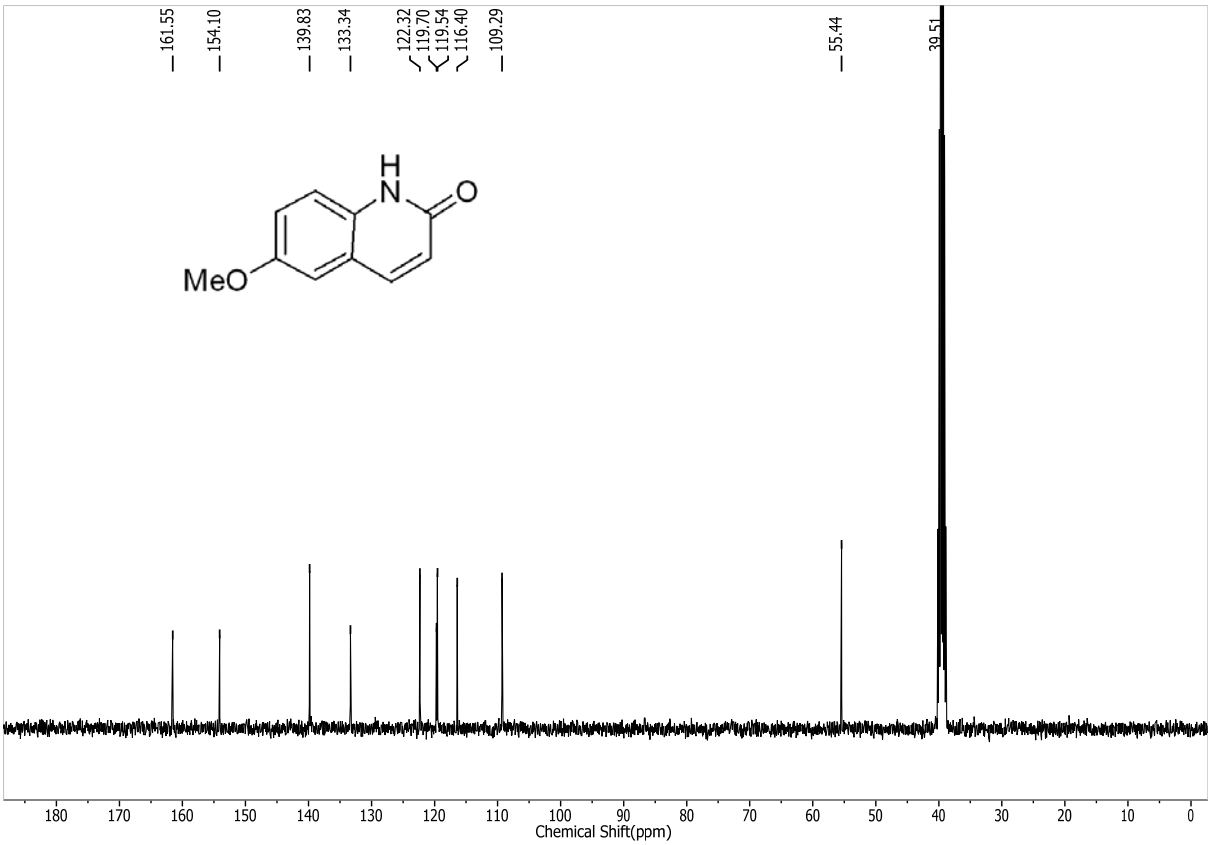


DEPT (135) NMR Spectrum of Compound **5aa** (DMSO-d_6 solvent was used).

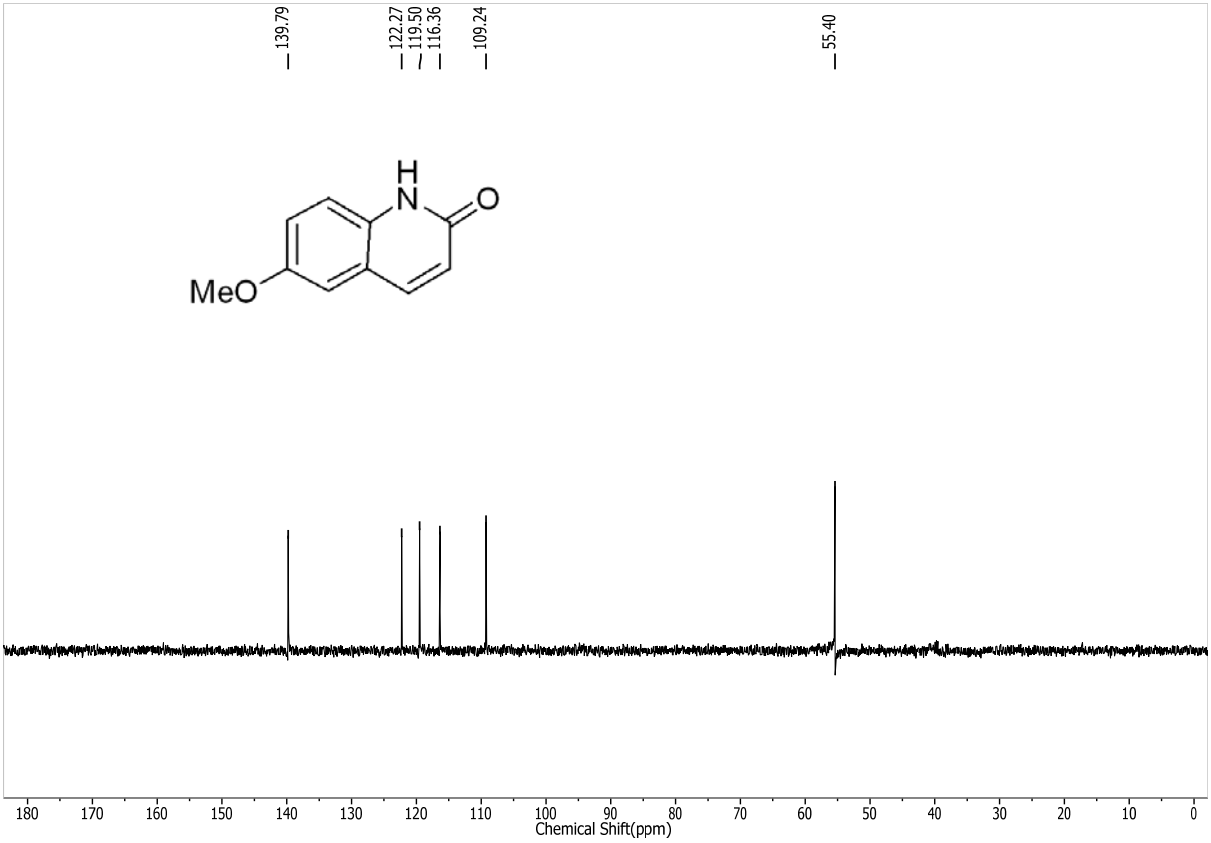


^{1}H and ^{13}C NMR Spectra of Compound 5**ba** (DMSO-d_6 solvent was used).

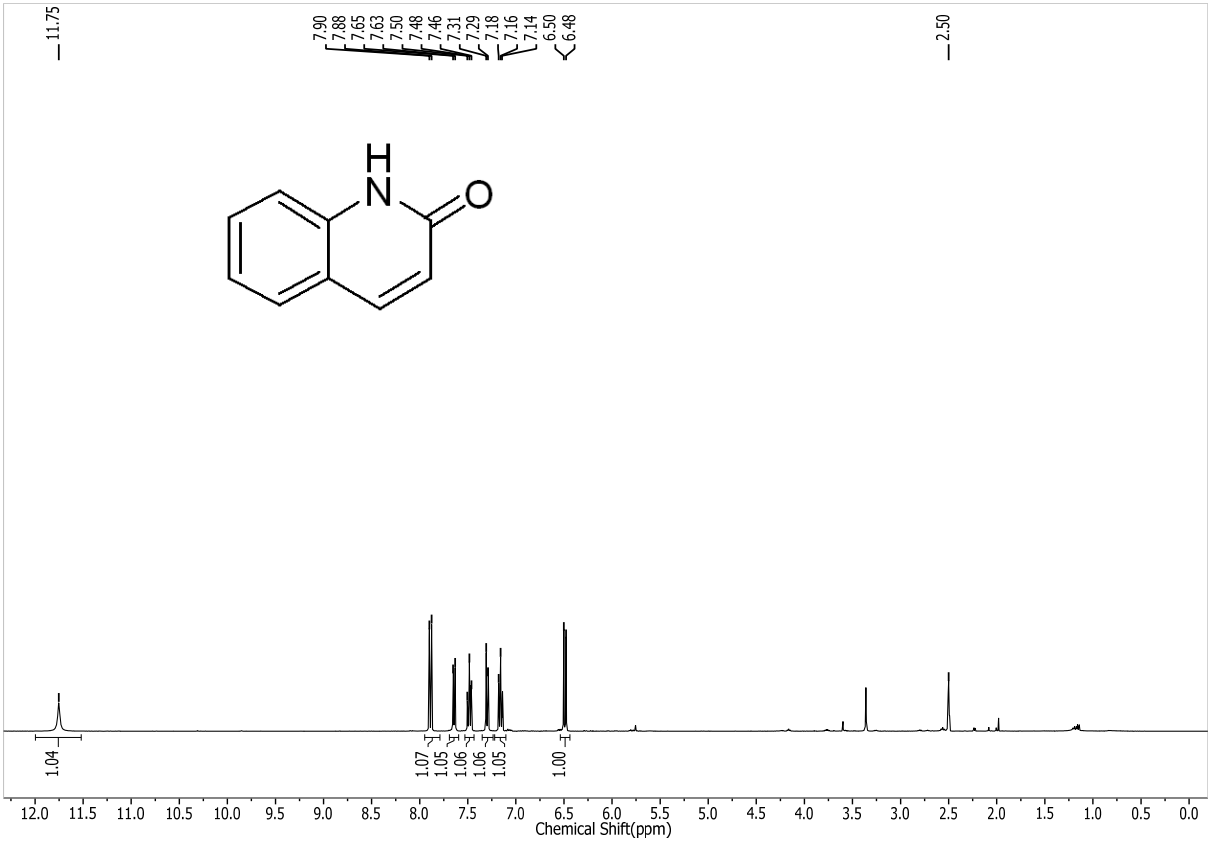


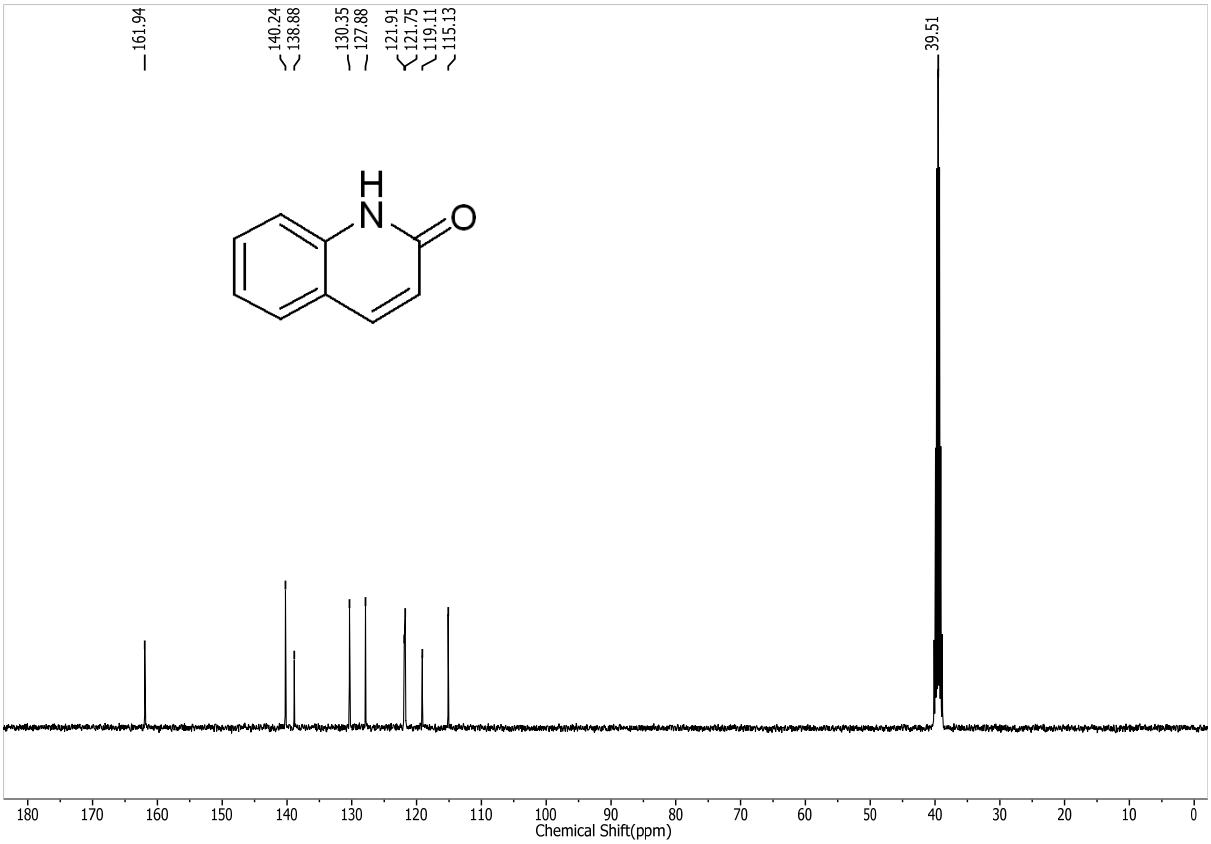


DEPT (135) NMR Spectrum of Compound **5ba** (DMSO-d_6 solvent was used).

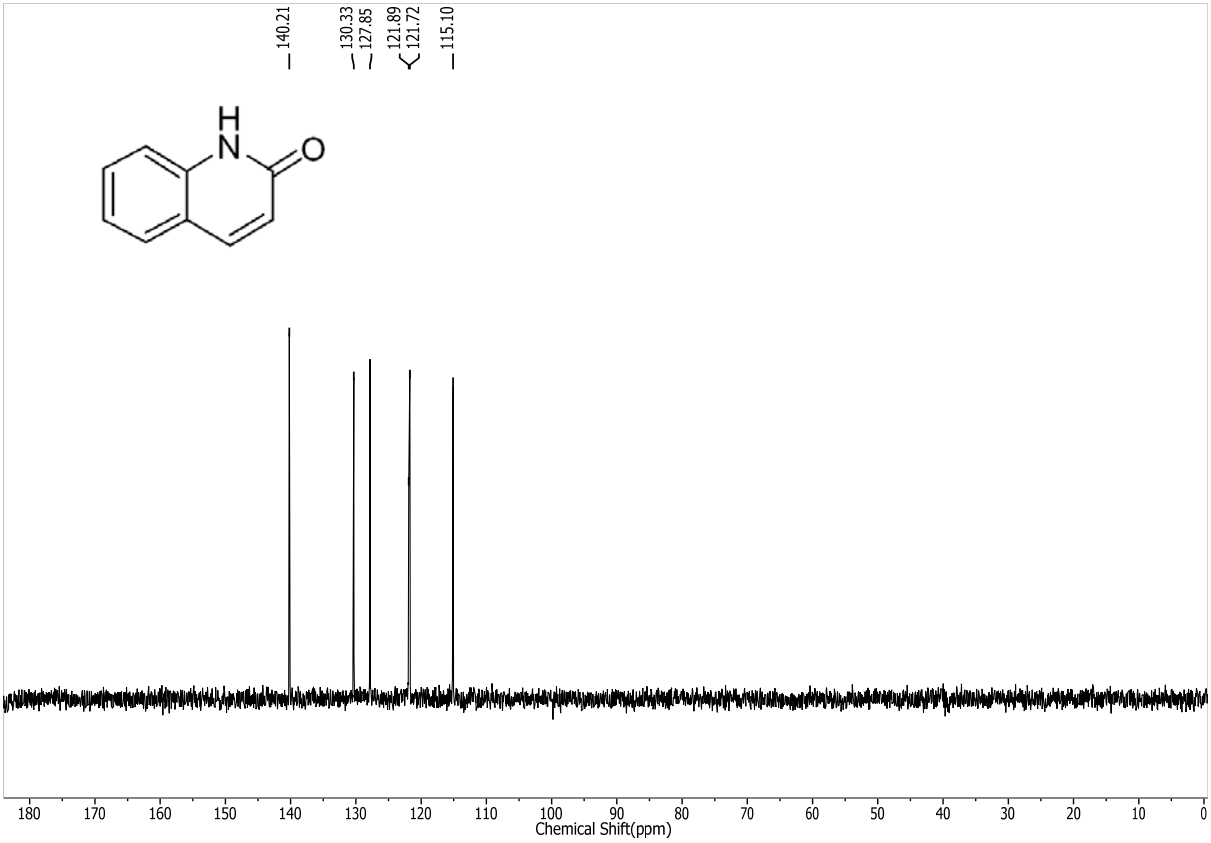


^{1}H and ^{13}C NMR Spectra of Compound **5ea** (DMSO-d_6 solvent was used).

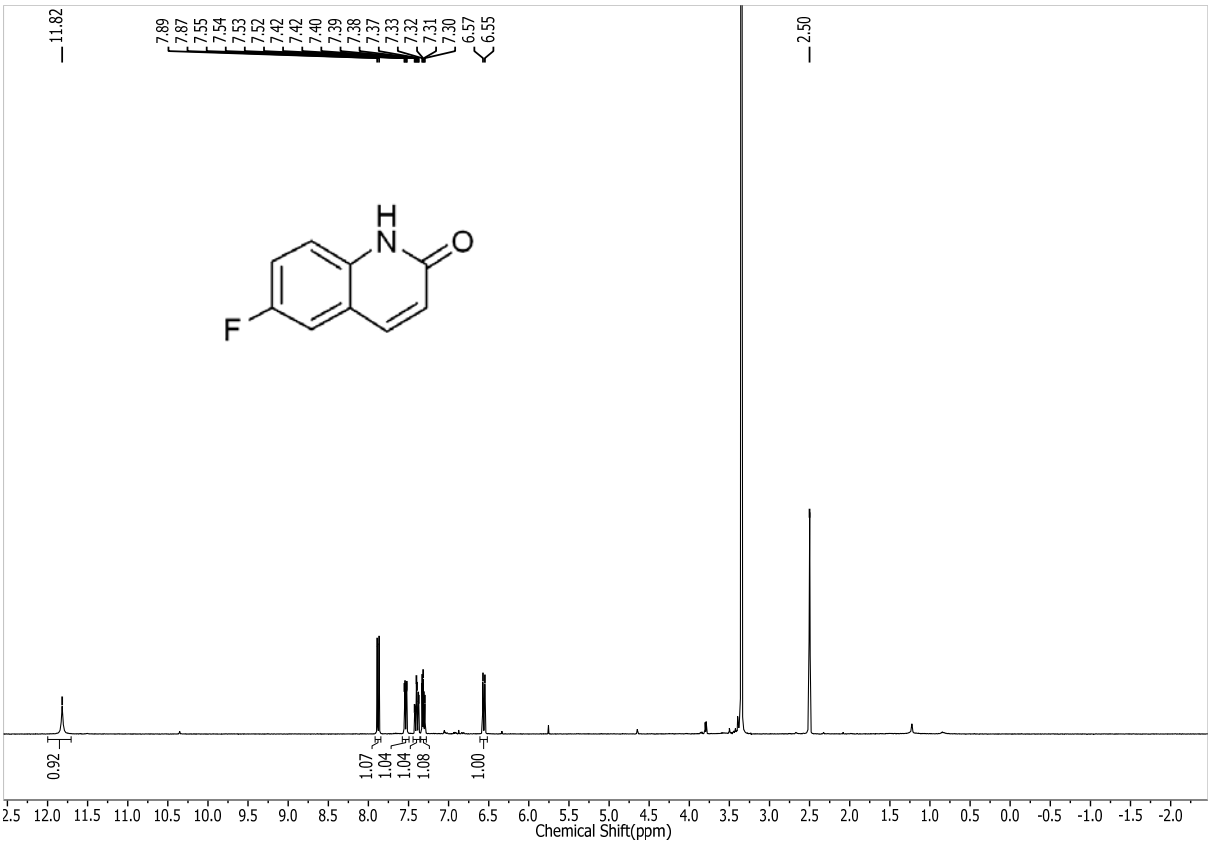


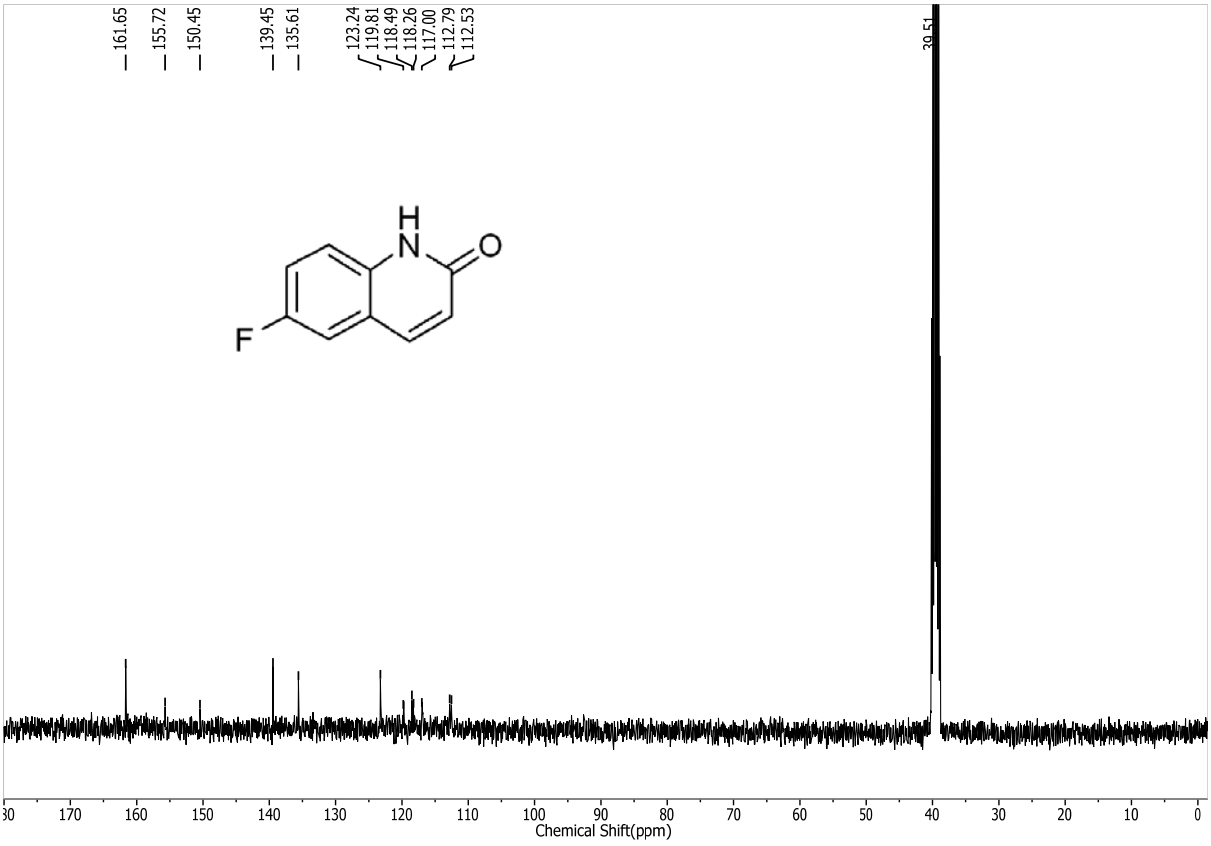


DEPT (135) NMR Spectrum of Compound **5ea** (DMSO-d_6 solvent was used).

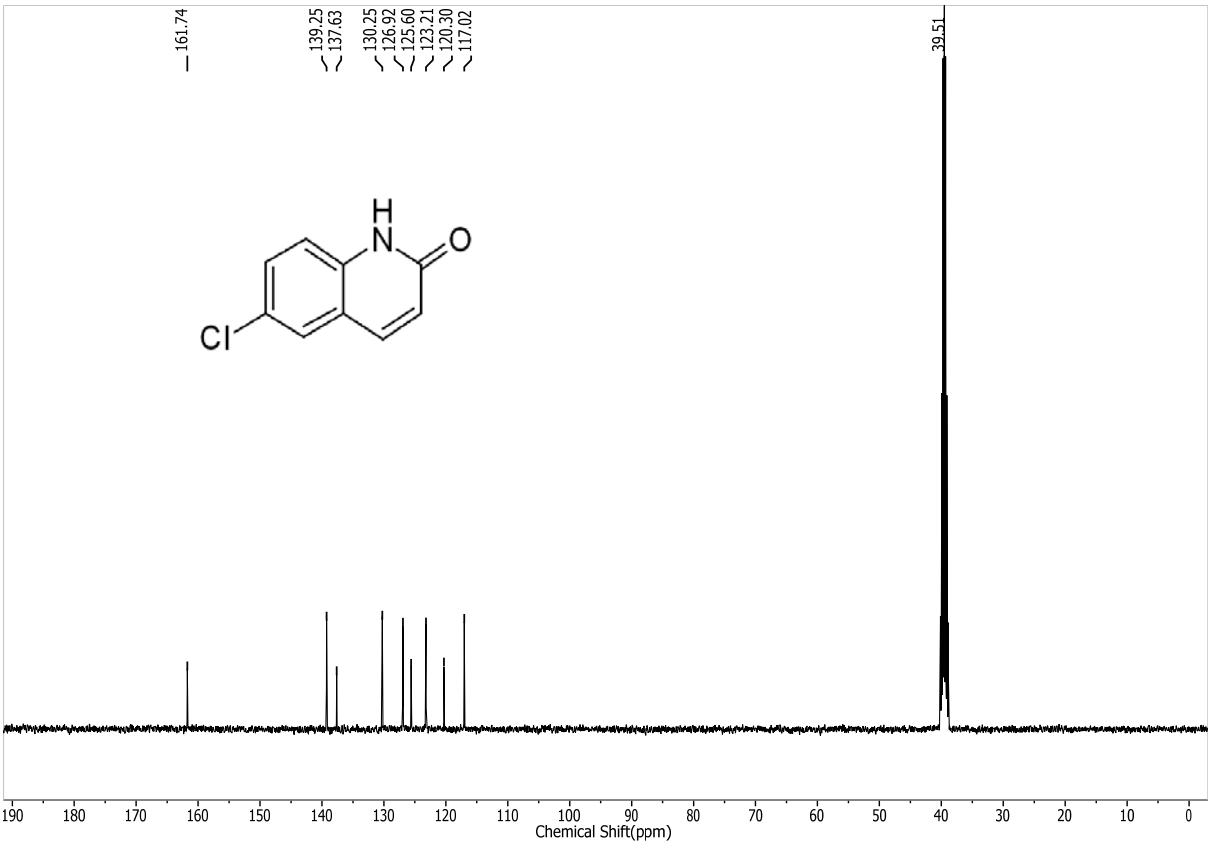


^{1}H and ^{13}C NMR Spectra of Compound **5fa** (DMSO-d_6 solvent was used).

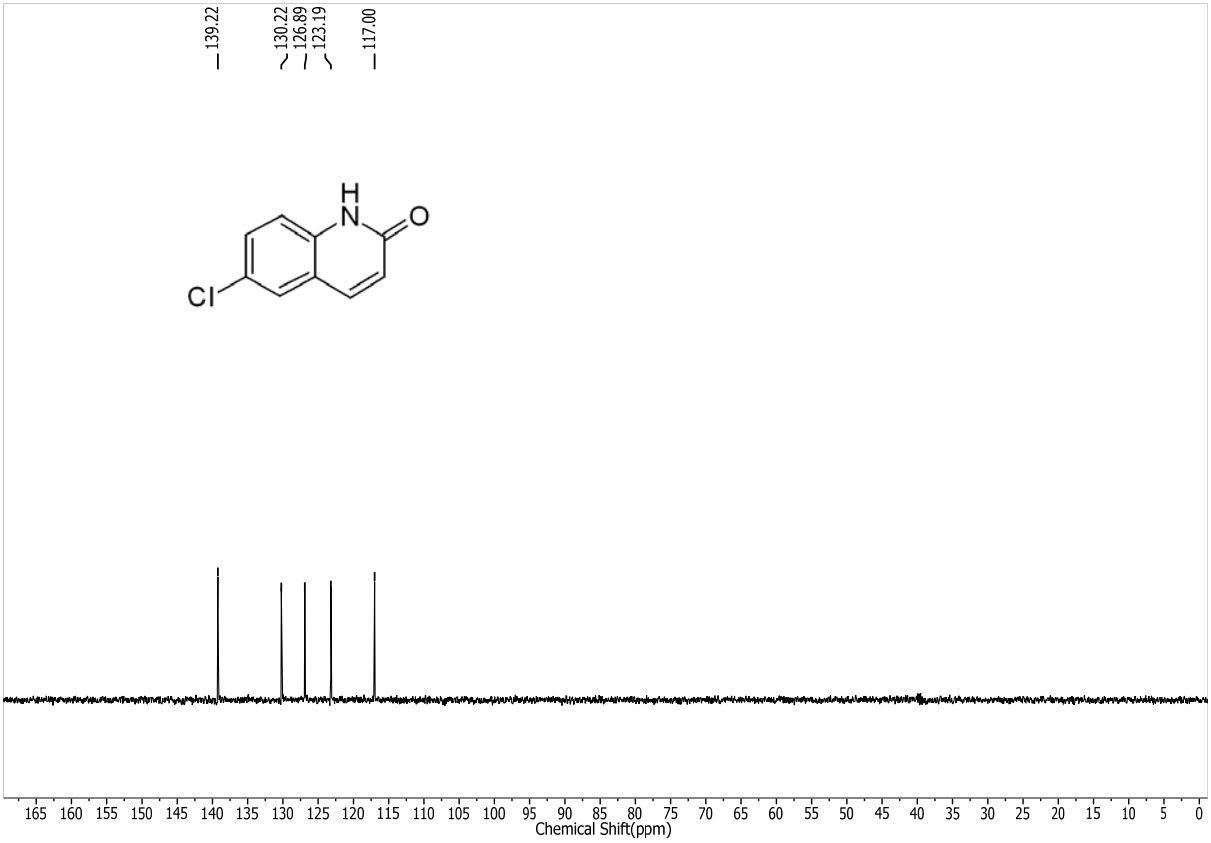




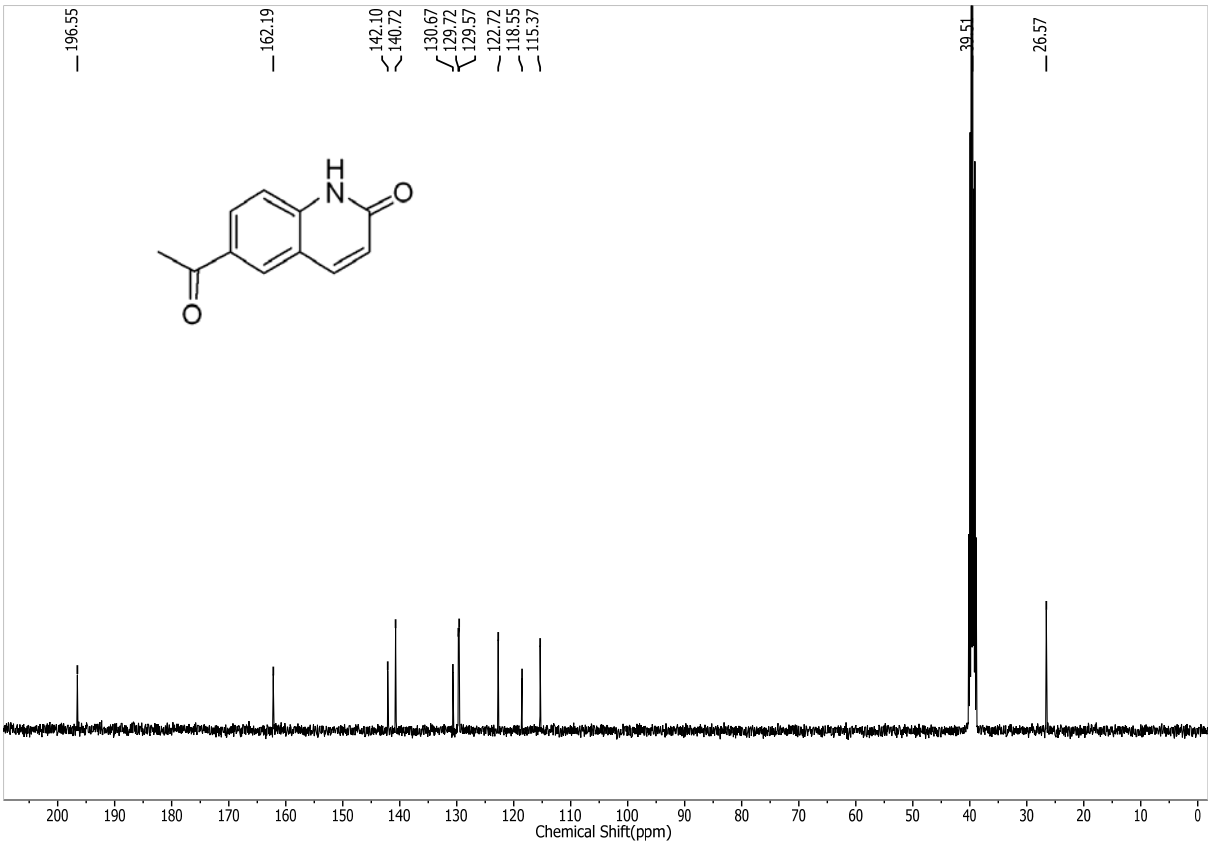
^{1}H and ^{13}C NMR Spectra of Compound **5ga** (DMSO-d_6 solvent was used).



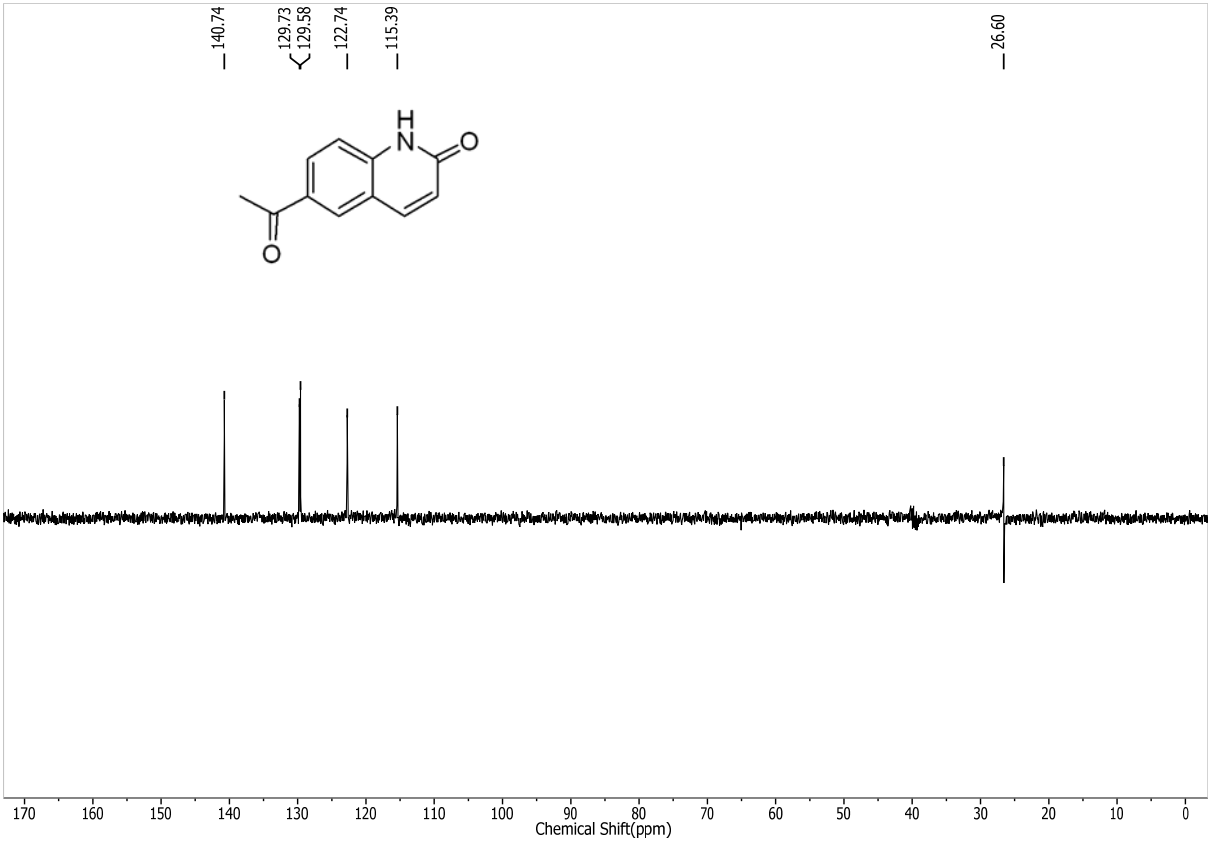
DEPT (135) NMR Spectrum of Compound **5ga** (DMSO-d_6 solvent was used).



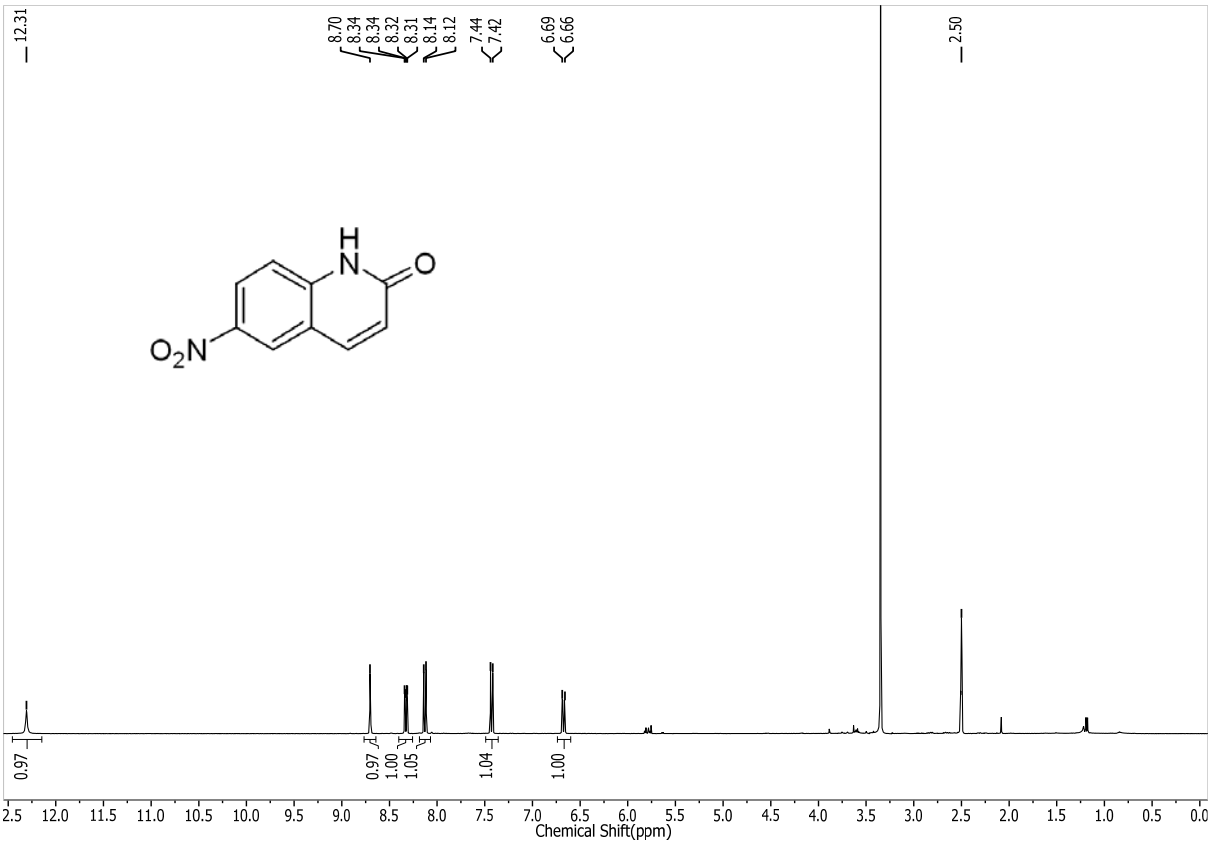
^{1}H and ^{13}C NMR Spectra of Compound **5ia** (DMSO-d_6 solvent was used).

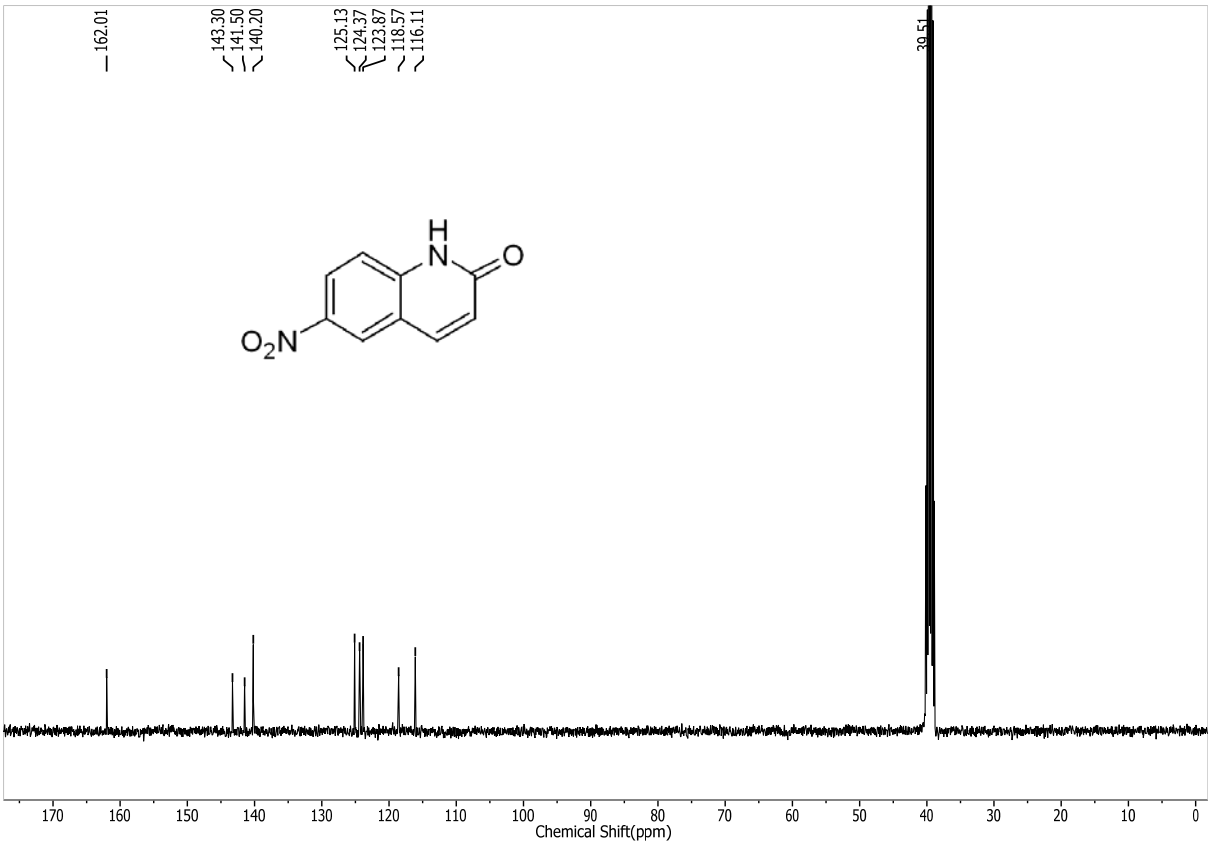


DEPT (135) NMR Spectrum of Compound **5ia** (DMSO-d_6 solvent was used).

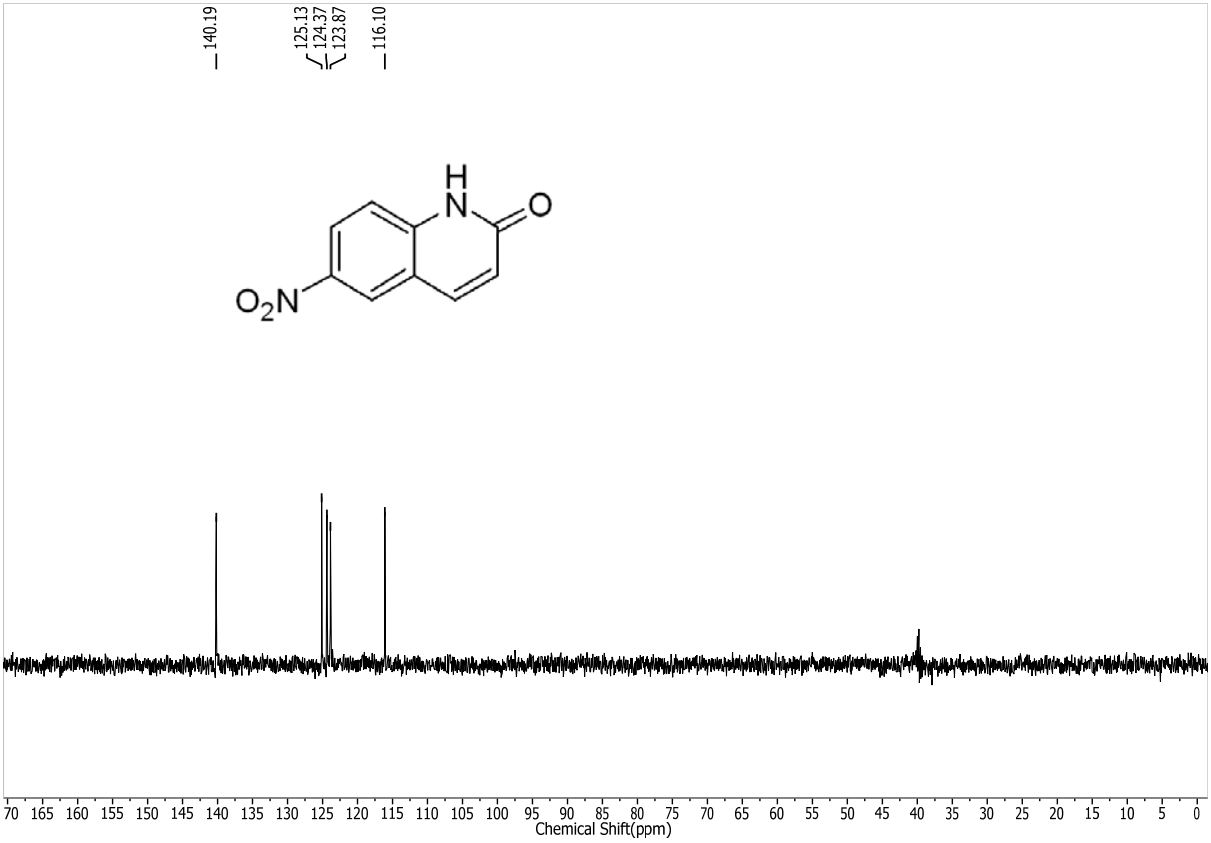


^{1}H and ^{13}C NMR Spectra of Compound **5ka** (DMSO-d_6 solvent was used).

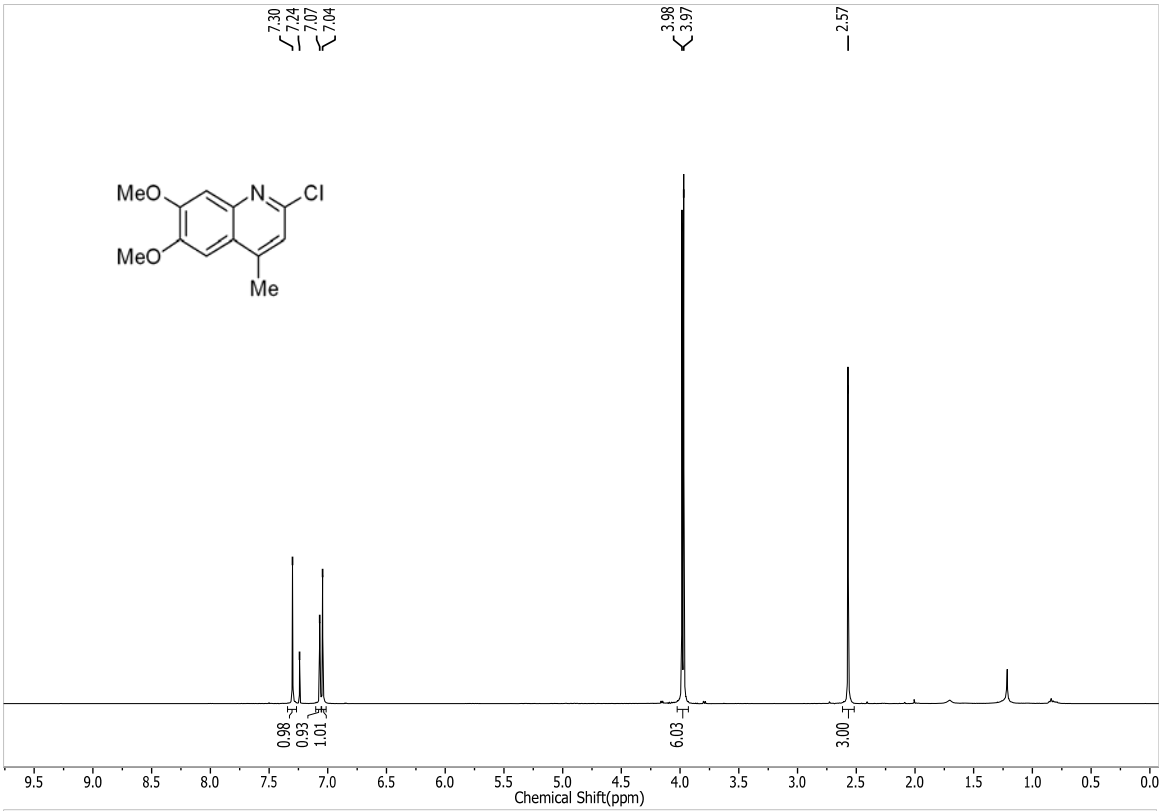


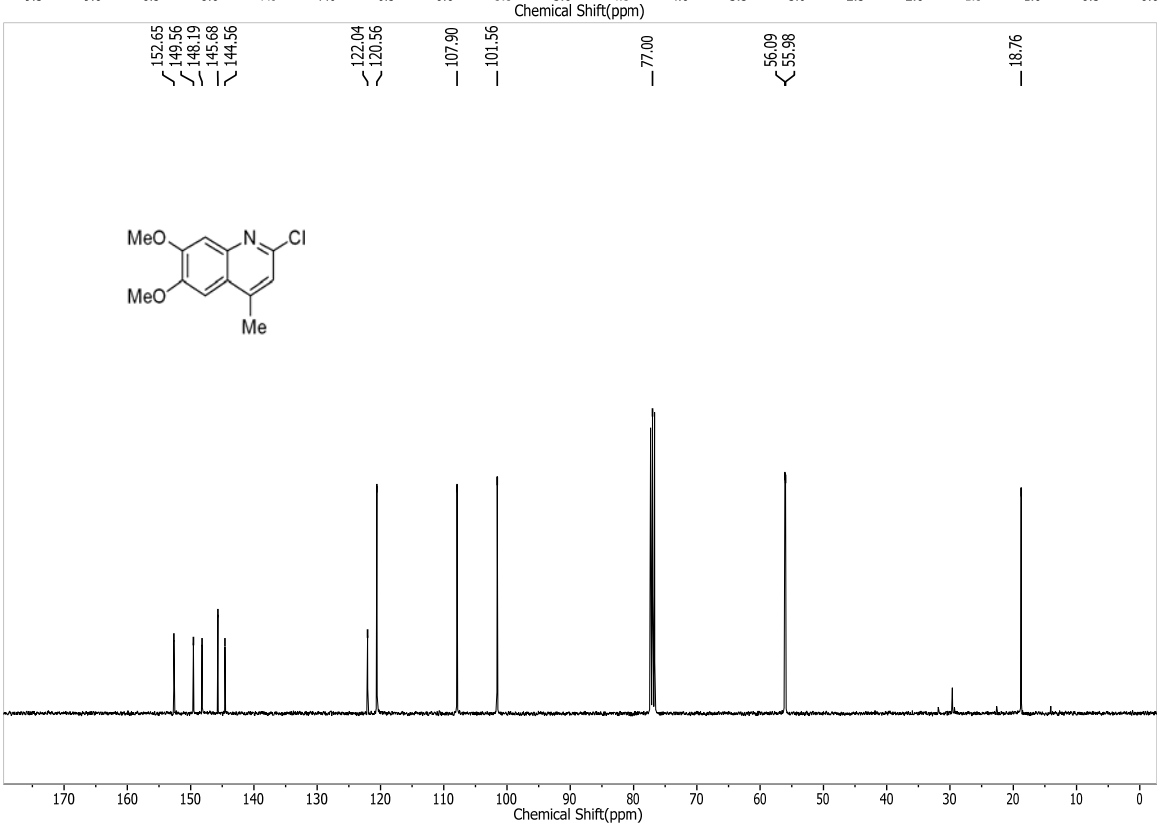


DEPT (135) NMR Spectrum of Compound **5ka** (DMSO-d_6 solvent was used).

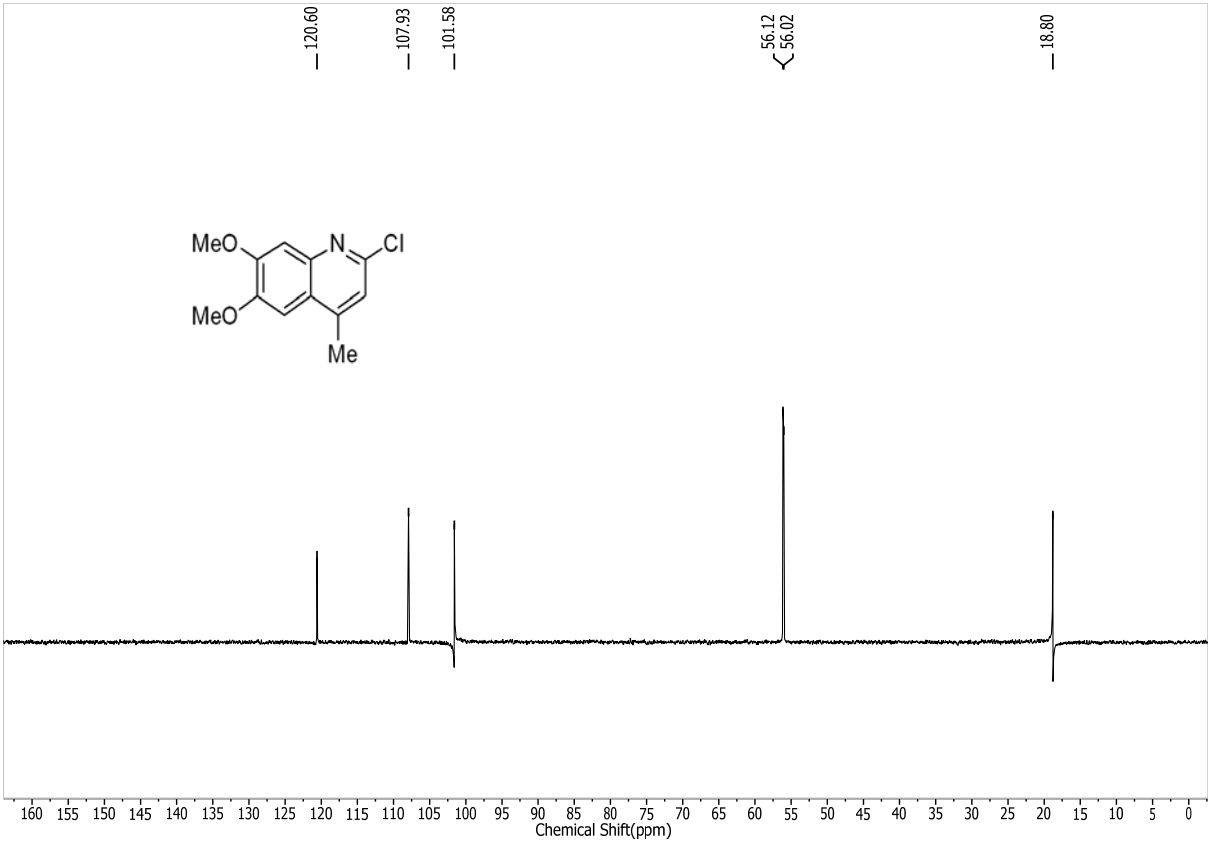


^{1}H and ^{13}C NMR Spectra of Compound **6a** ($CDCl_3$ solvent was used).

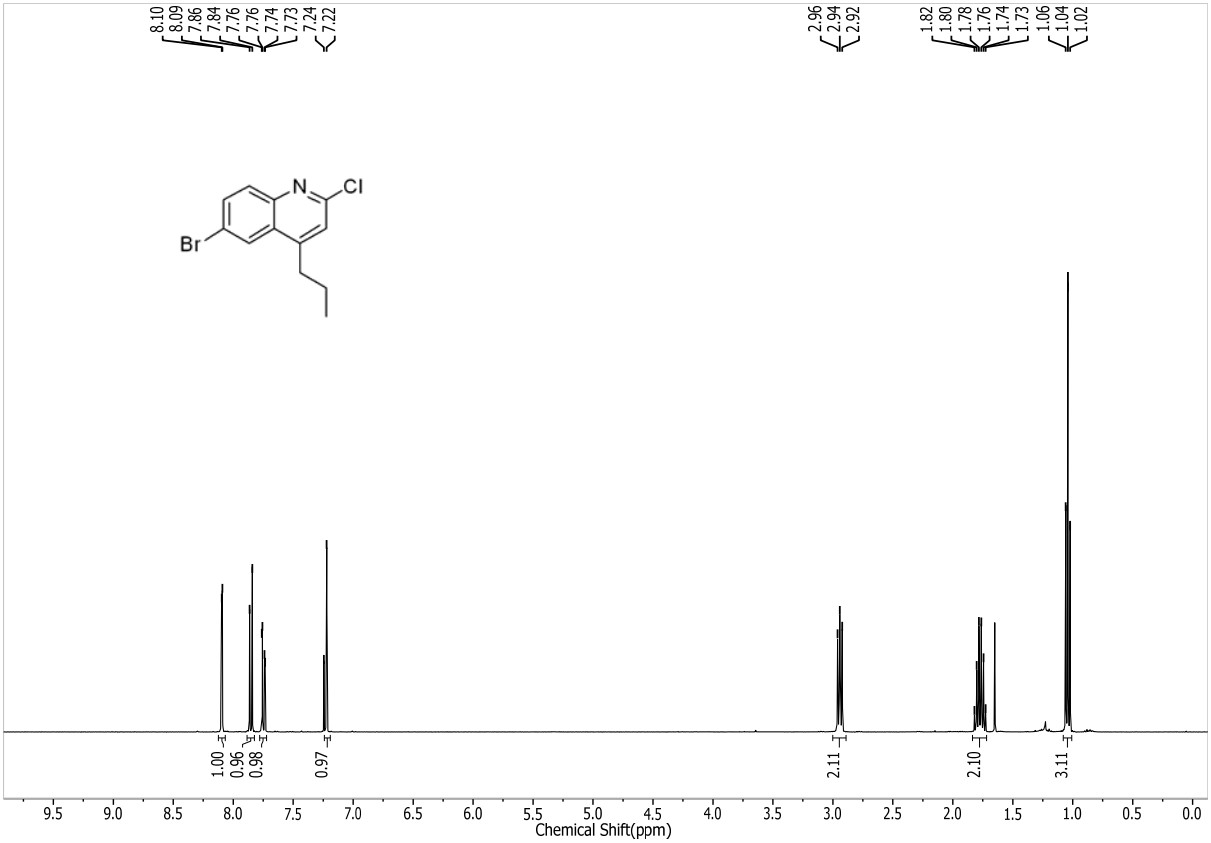


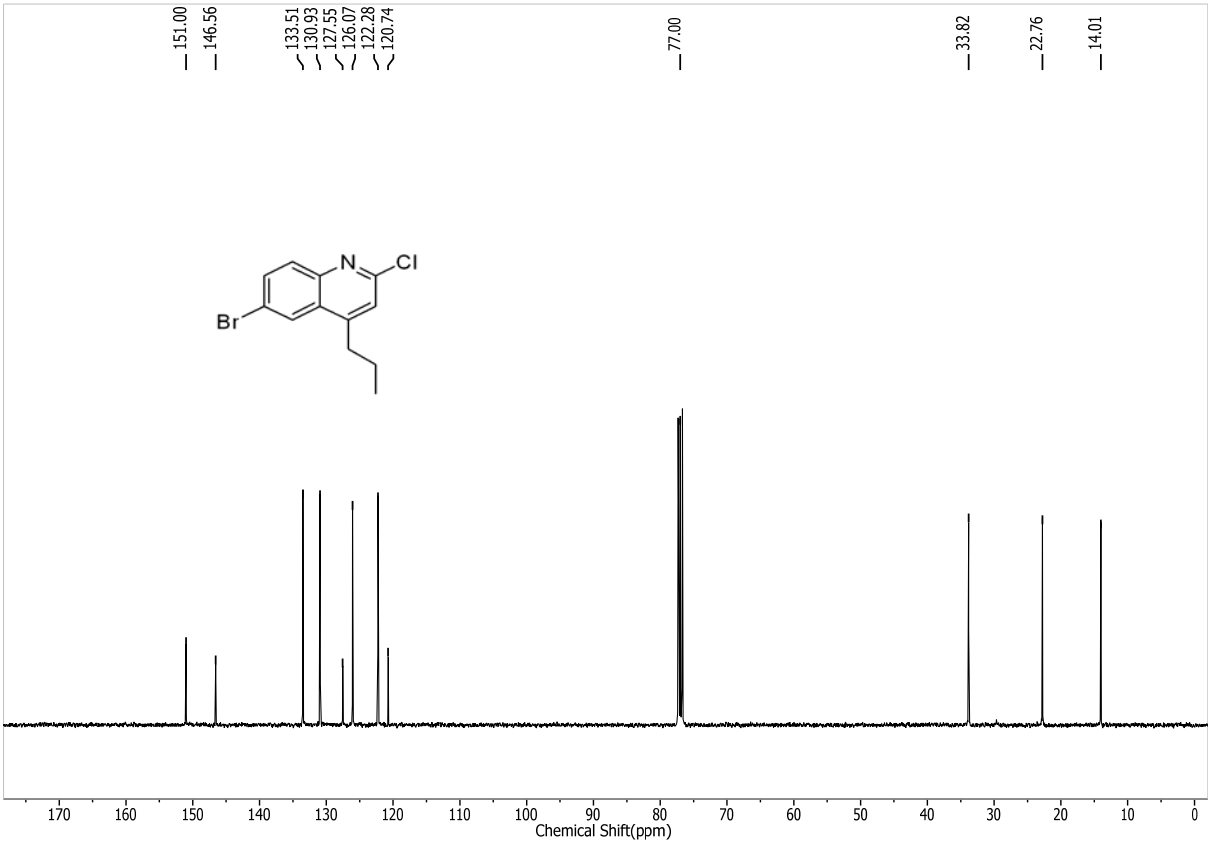


DEPT (135) NMR Spectrum of Compound **6a** ($CDCl_3$ solvent was used).

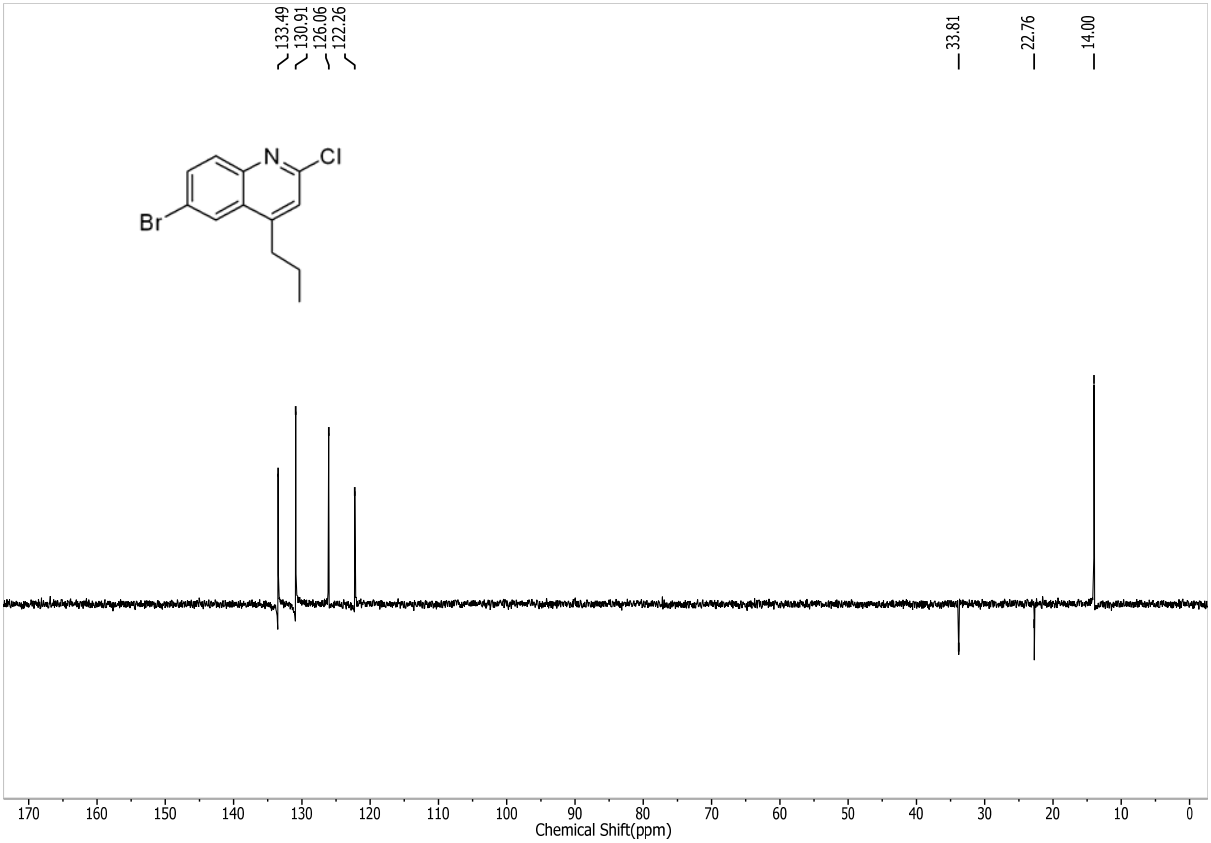


^{1}H and ^{13}C NMR Spectra of Compound **6b** ($CDCl_3$ solvent was used).

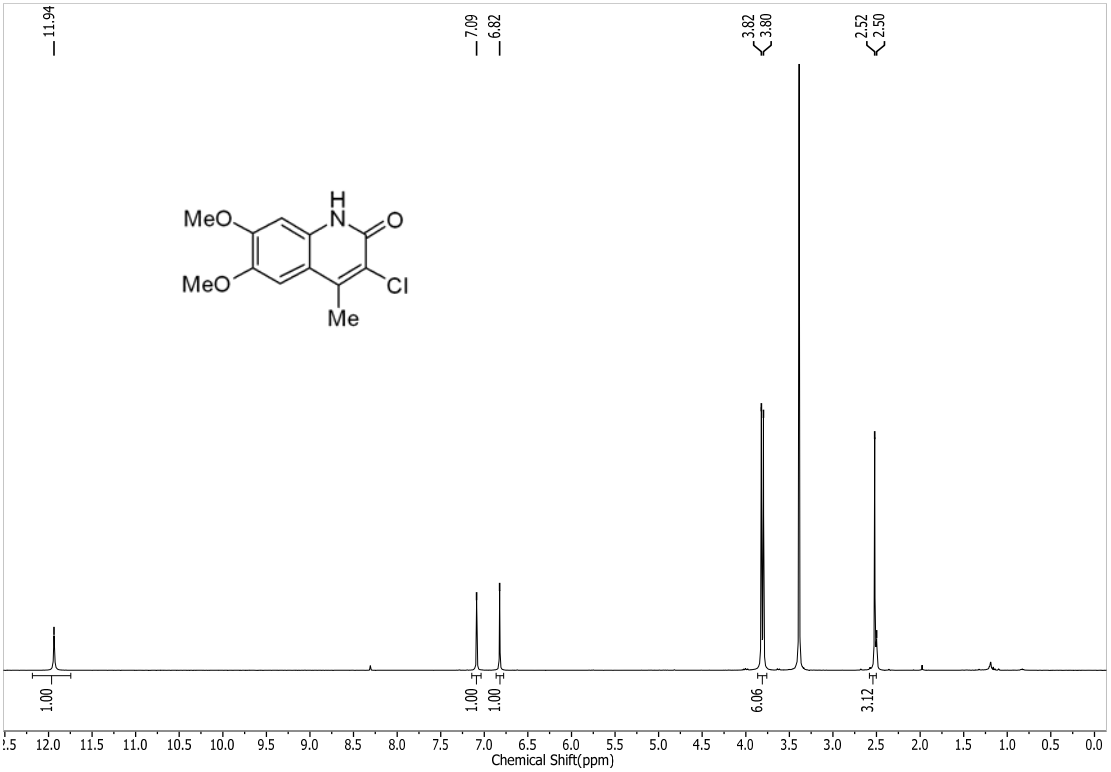


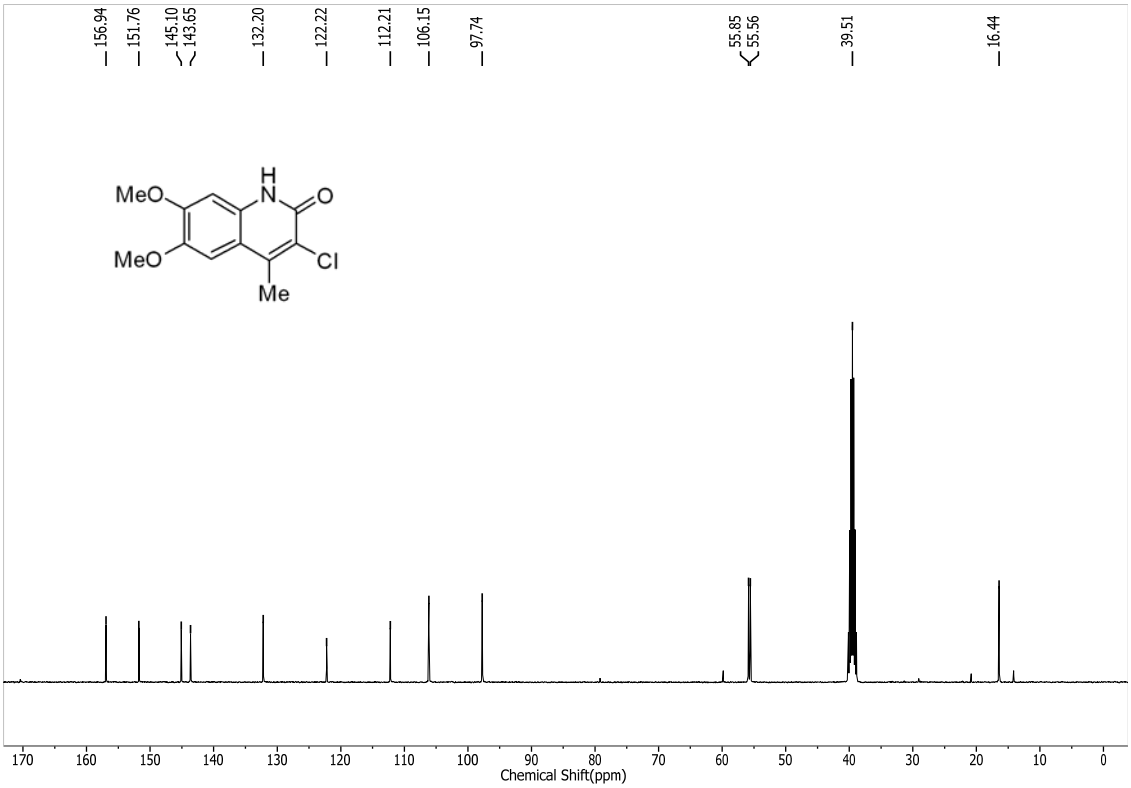


DEPT (135) NMR Spectrum of Compound **6b** ($CDCl_3$ solvent was used).

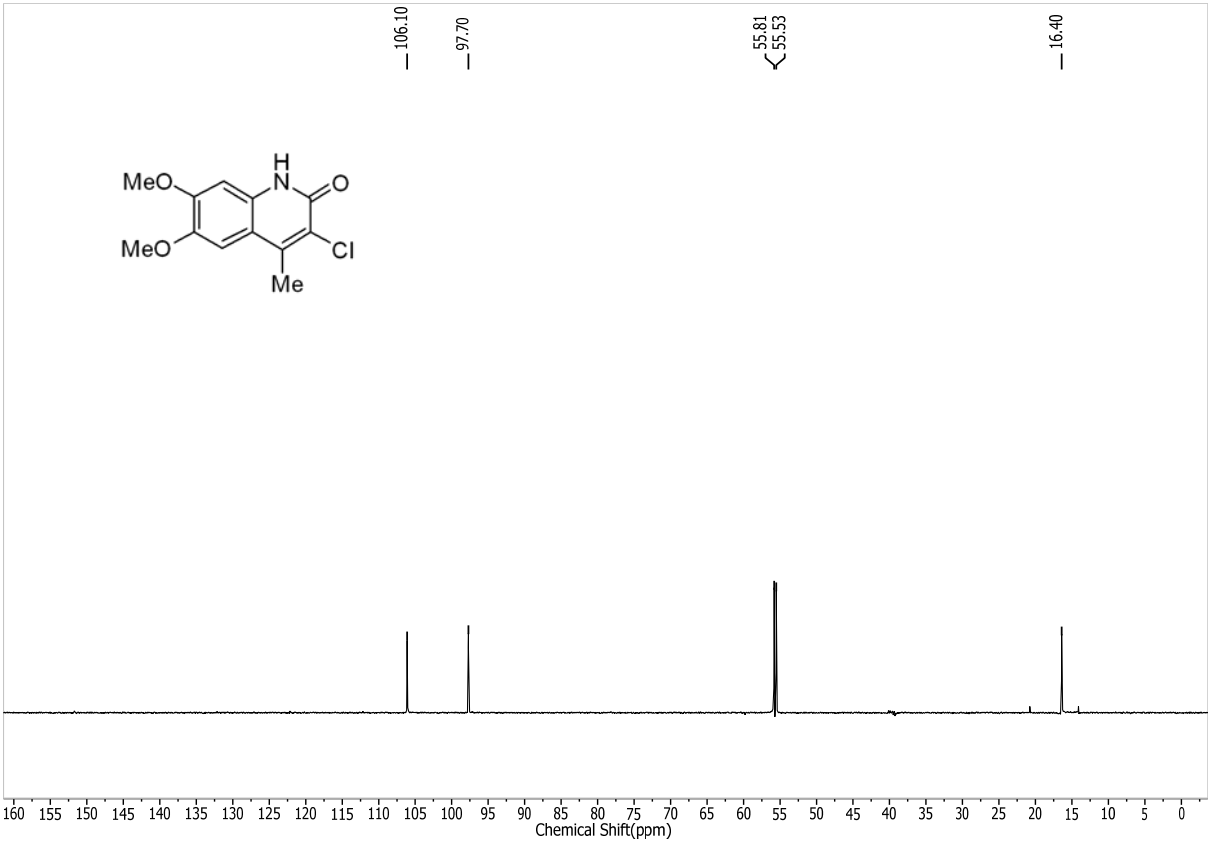


^{1}H and ^{13}C NMR Spectra of Compound **7a** (DMSO-d_6 solvent was used).





DEPT (135) NMR Spectrum of Compound **7a** (DMSO-d_6 solvent was used).



^{1}H and ^{13}C NMR Spectra of Compound **7b** (DMSO-d_6 solvent was used).