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SUPPORTING INFORMATION

New Ruthenium (II) Catalysts Enable the Synthesis of 2-Amino-4H-chromenes Using Primary Alcohols via Acceptorless Dehydrogenative Coupling

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Contents

1. Experimental

Materials and Methods

Commercially available $RuCl_3.3H_2O$ was used as supplied from Loba Chemie Pvt. Ltd. The solvents were freshly distilled before use following the standard procedures.[1] The ruthenium(II) precursor complex, $[(\eta^6\text{-}p\text{-cymene})RuCl_2]_2$ was prepared by reported literature method.[2] The microanalysis of carbon, hydrogen and nitrogen were recorded by an analytical function testing Vario EL III CHNS elemental analyzer at the Sophisticated Test and Instrumentation Centre (STIC), Cochin University, Cochin. The Fourier Transform infrared spectra of complexes were recorded in KBr pellets with a Perkin-Elmer 597 spectrophotometers in the range 4000–400 cm^{-1}. The NMR spectra were recorded in $CDCl_3$ and DMSO-d_6 with a Bruker 400 MHz instrument using TMS as the internal reference. Chemical shifts are given in ppm referenced to solvents. The electronic spectra of the complexes in acetonitrile solution were recorded with a Jasco V-730 UV-Vis Varian spectrophotometer in the range 800-200 nm. Electrochemical measurements were made using a CH-Instruments CHI6000E model electrochemical analyzer scanning potentiostat using a glassy carbon-working electrode and $[(n\text{-}C_4H_9)_9N)]$ (ClO_4) (TBAP) as supporting electrolyte. All the potentials were referenced to Ag/AgCl electrode and the solutions were purged with N_2 before each set of experiments. The gas chromatograph analysis for the formation of hydrogen gas was performed on a Shimadzu GC 2014 and TCD detector, injection temperature = 30 °C, column temperature = 50 °C, detector temperature (TCD) = 60 °C, carrier gas = N_2.

2. The method for the synthesis of *p*-cymene Ru(II) complexes

Carbazolone based hydrazone derivatives (2 mmol), $[(\eta^6\text{-}p\text{-cymene})_2Ru_2Cl_2(\mu\text{-}Cl)_2]$ (1 mmol), and Et_3N (1 mmol) were dissolved in toluene solvent. The resultant mixture has been refluxed for 5 h. The formation of the complex was confirmed using thin layer chromatography. After completion, the reaction mixture was then reduced to 5 mL, and addition of excess diethylether produced brown solid. The solid was collected, washed, and dried.

3. UV-vis and CV spectra of the complexes

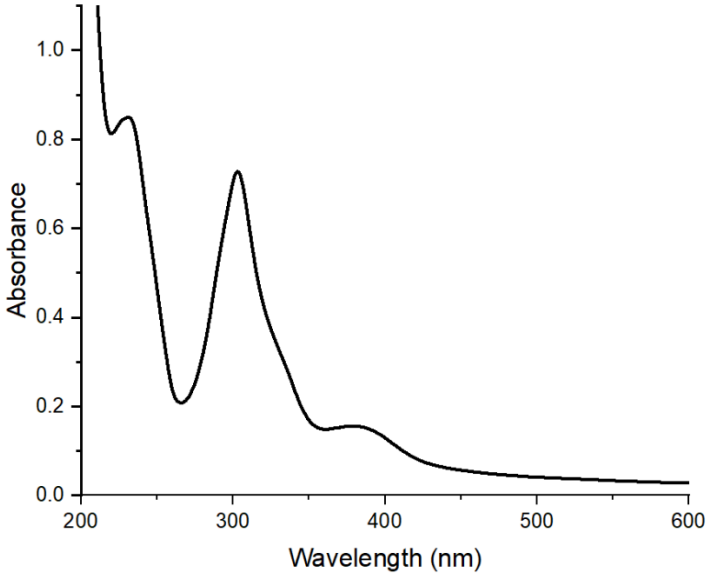


Figure 1. UV-vis spectrum of complex **1**

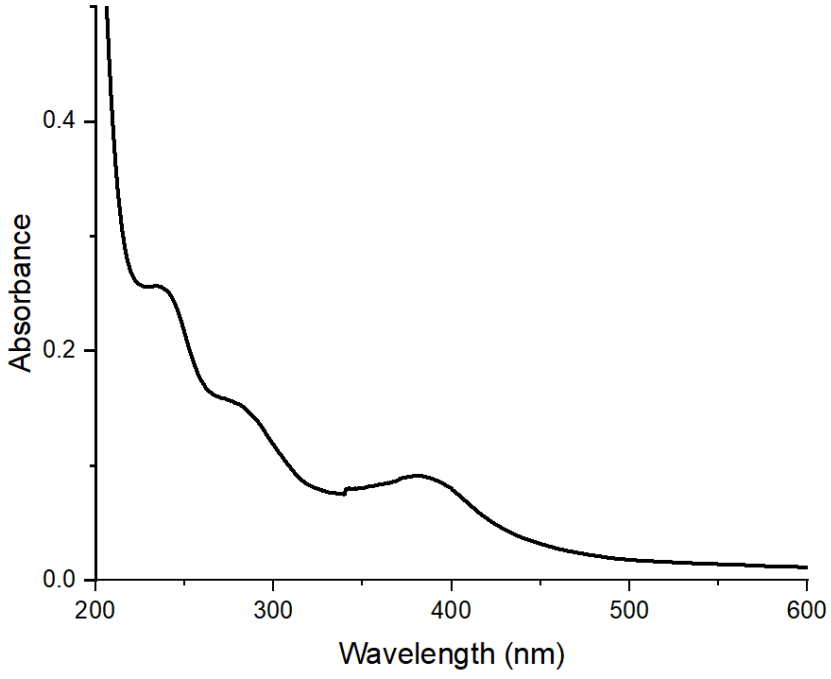


Figure 2. UV-vis spectrum of complex **2**

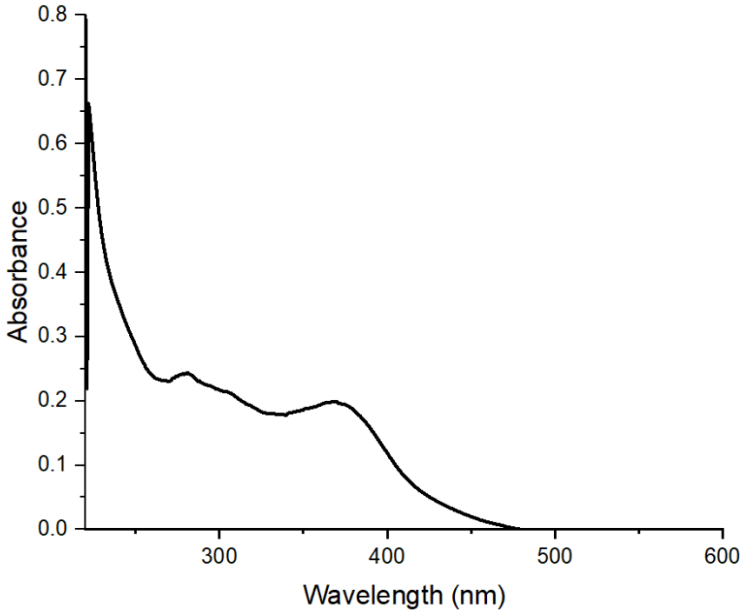


Figure 3. UV-vis spectrum of complex **3**

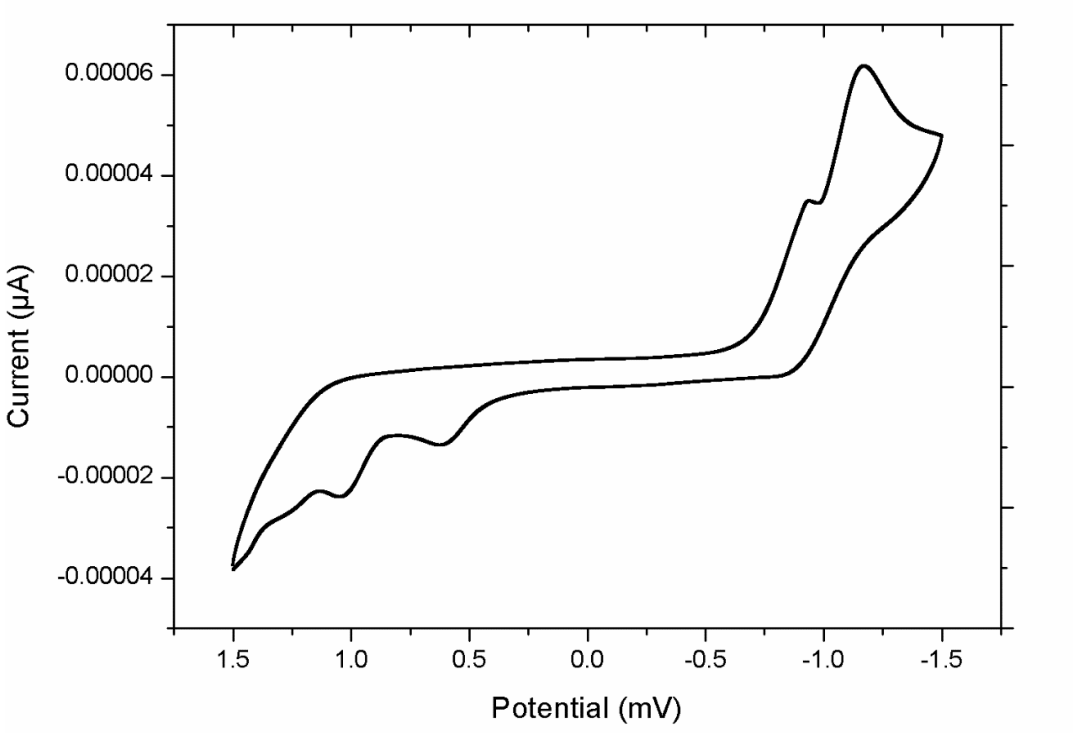


Figure 4. Cyclic voltammogram of complex **1**

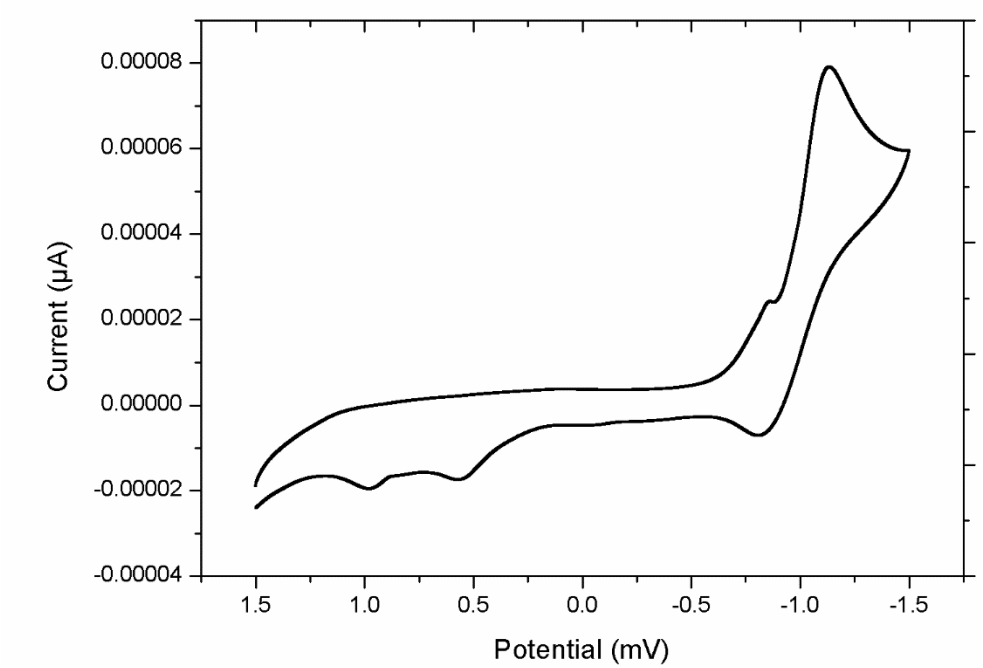


Figure 5. Cyclic voltammogram of complex **2**

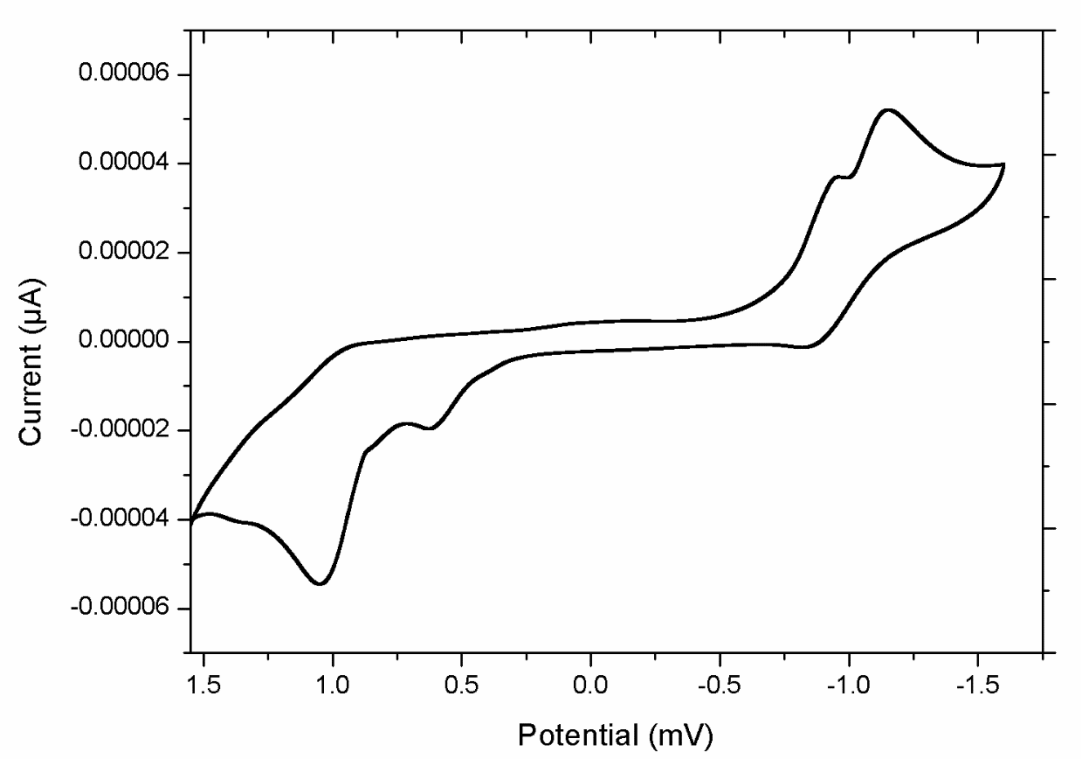


Figure 6. Cyclic voltammogram of complex **3**

4. ^{1}H and ^{13}C NMR spectra of the *p*-cymene Ru(II) complexes

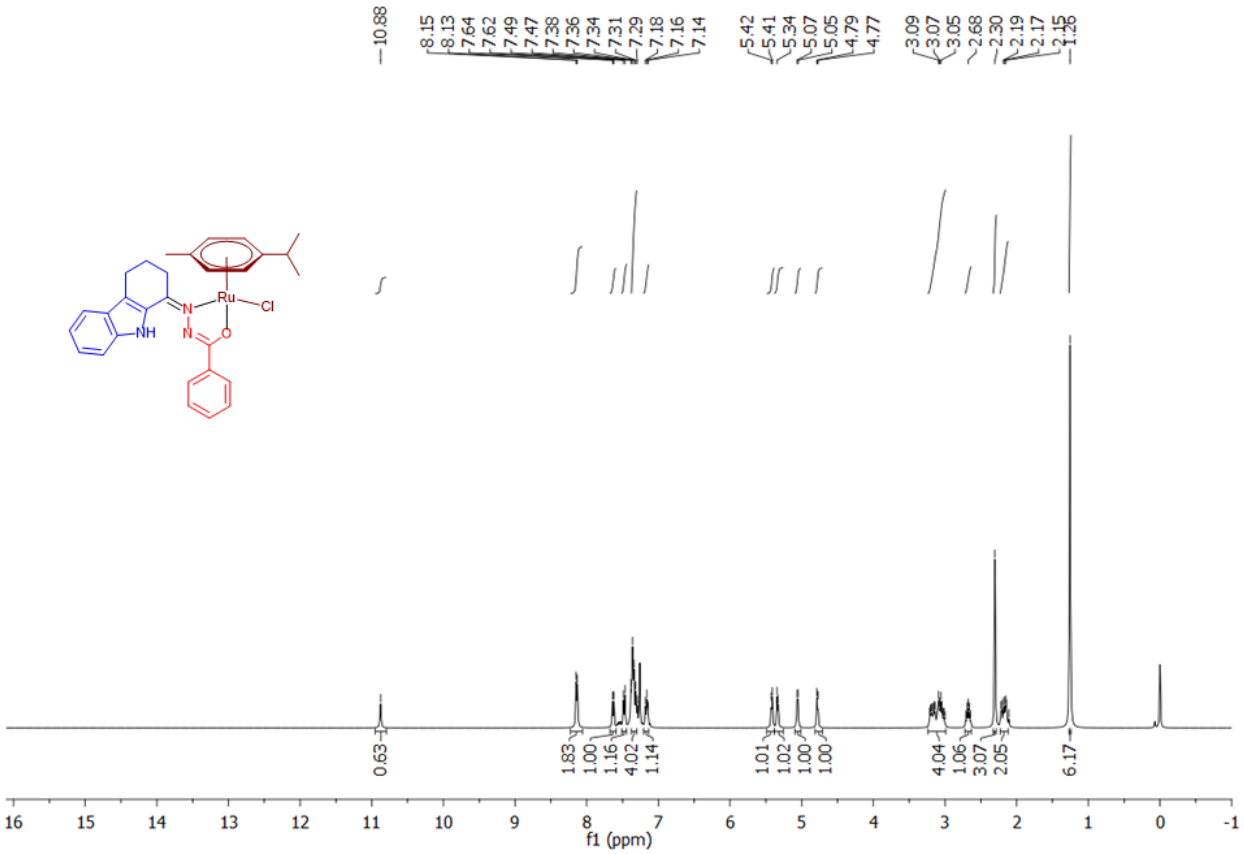


Figure 7: ^{1}H NMR spectrum for complex **1** in $CDCl_3$ (400MHz, 300K).

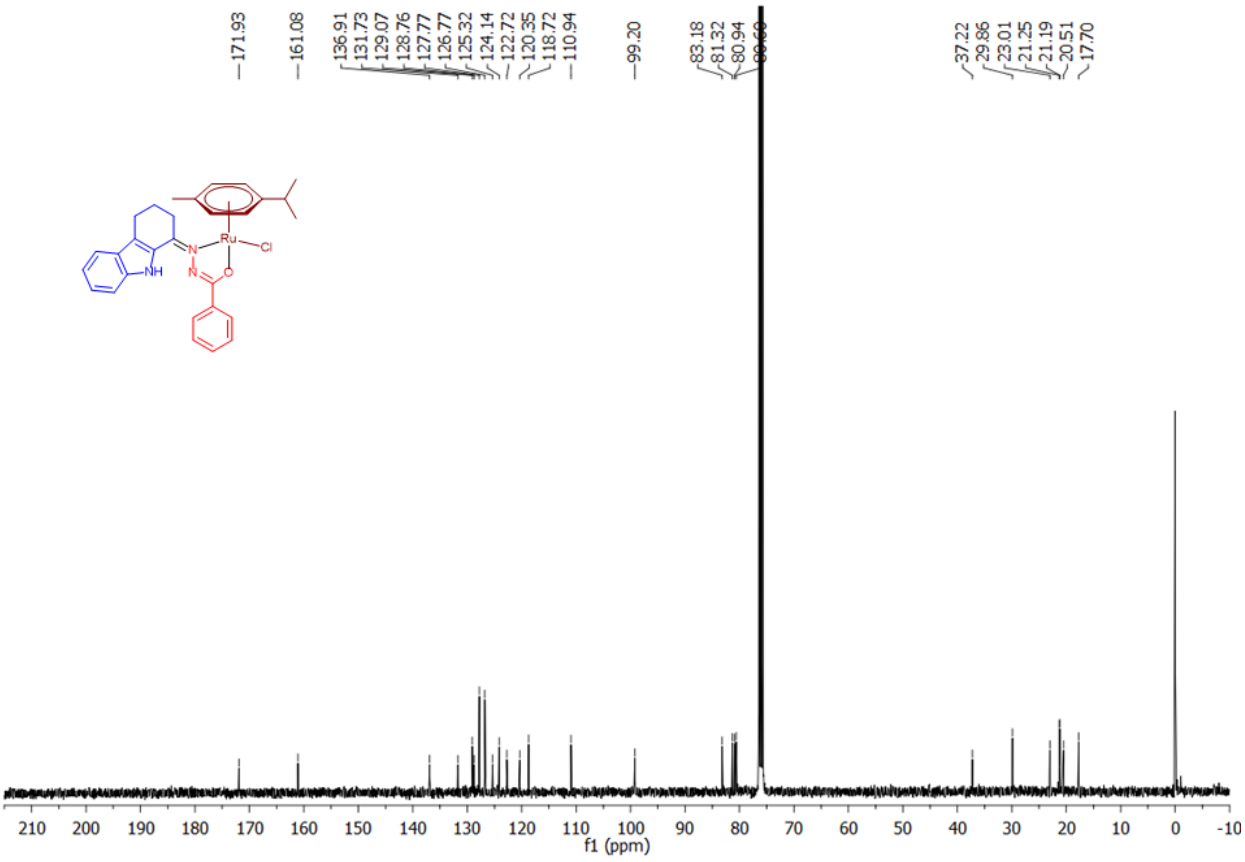


Figure 8: ^{13}C NMR spectrum for complex **1** in $CDCl_3$ (100MHz, 300K).

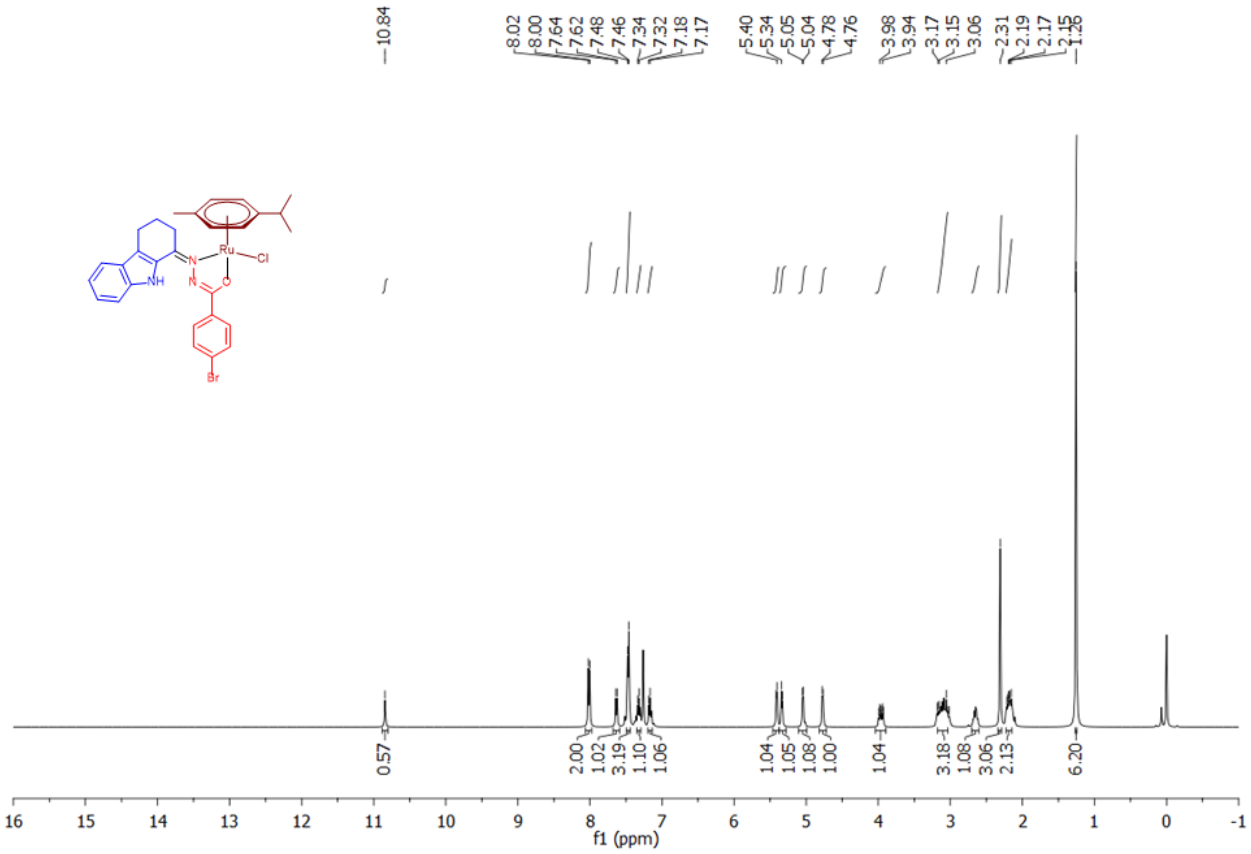


Figure 9: ^{1}H NMR spectrum for complex **2** in $CDCl_3$ (400MHz, 300K).

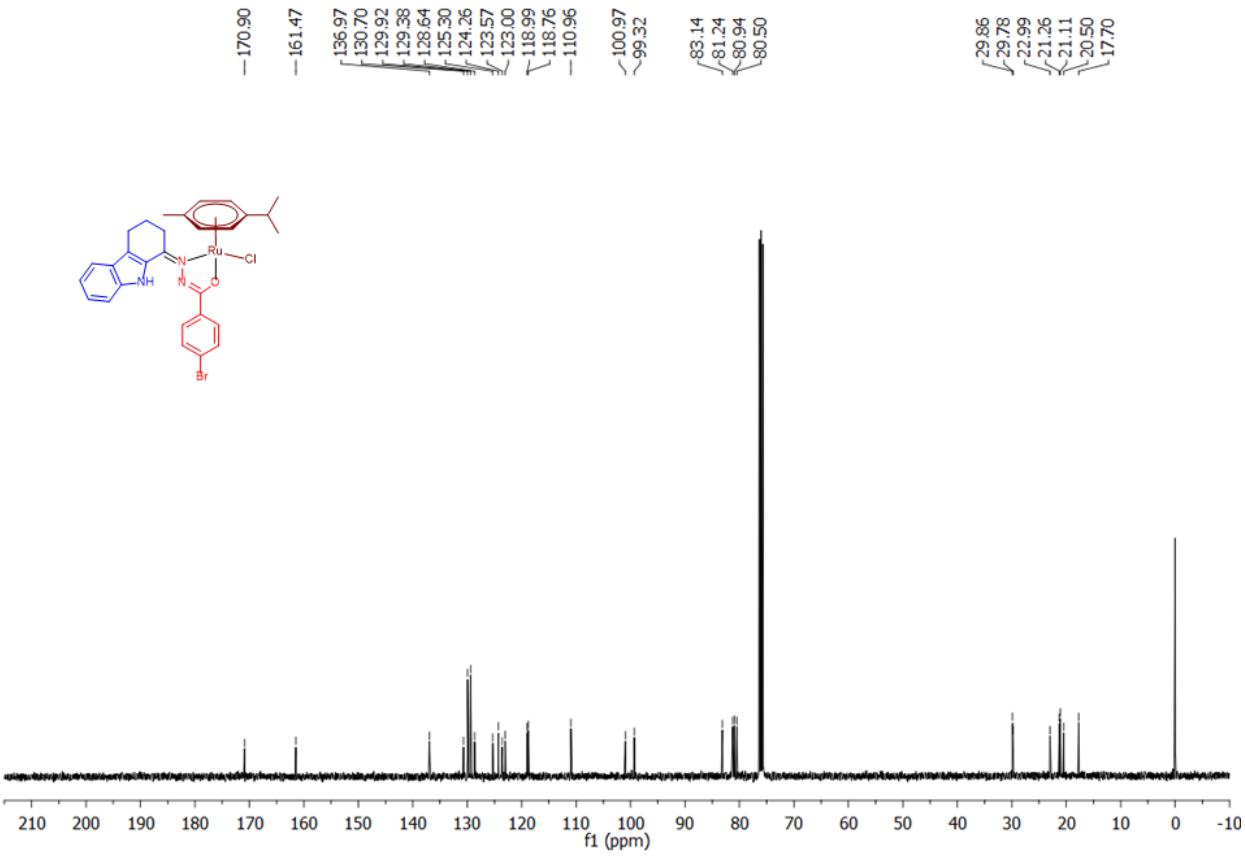


Figure 10: ^{13}C NMR spectrum for complex **2** in $CDCl_3$ (100MHz, 300K).

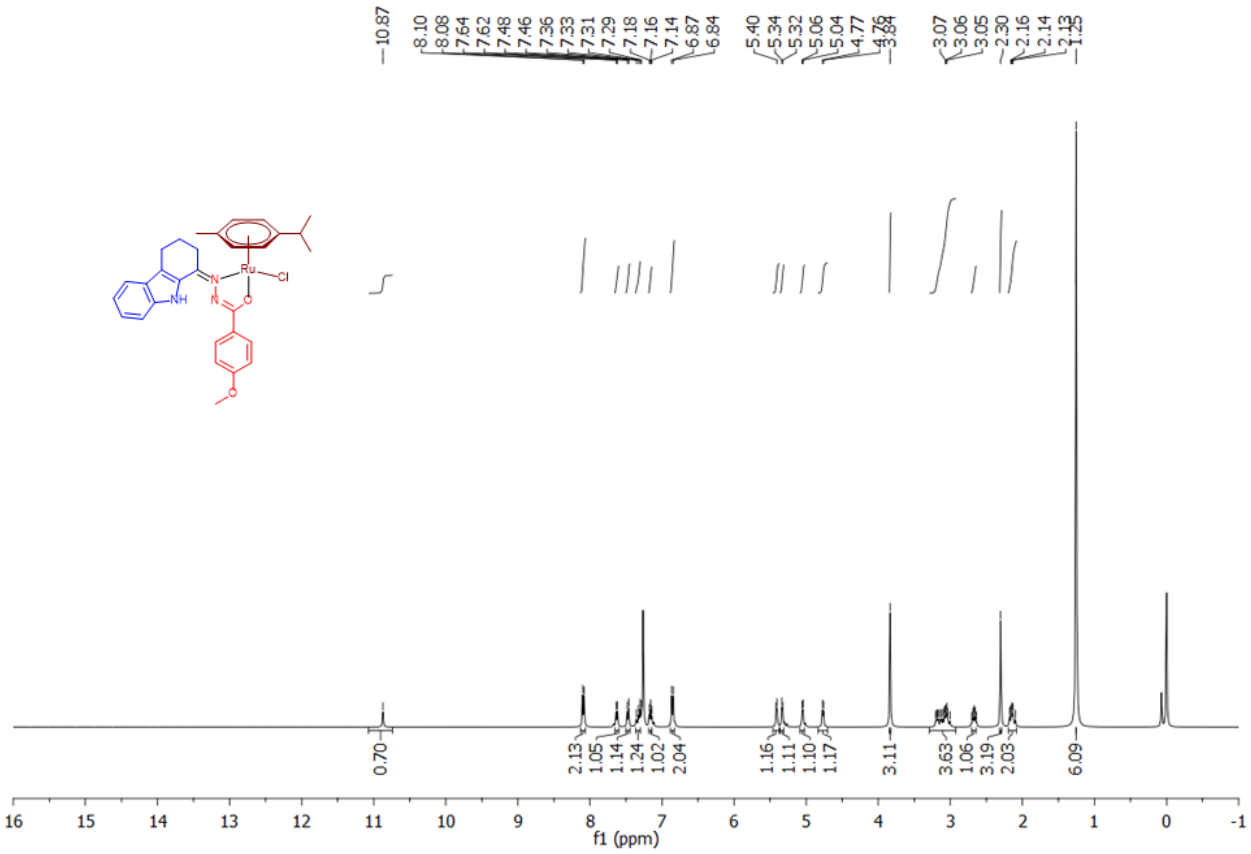


Figure 11: ^{1}H NMR spectrum for complex **3** in $CDCl_3$ (400MHz, 300K).

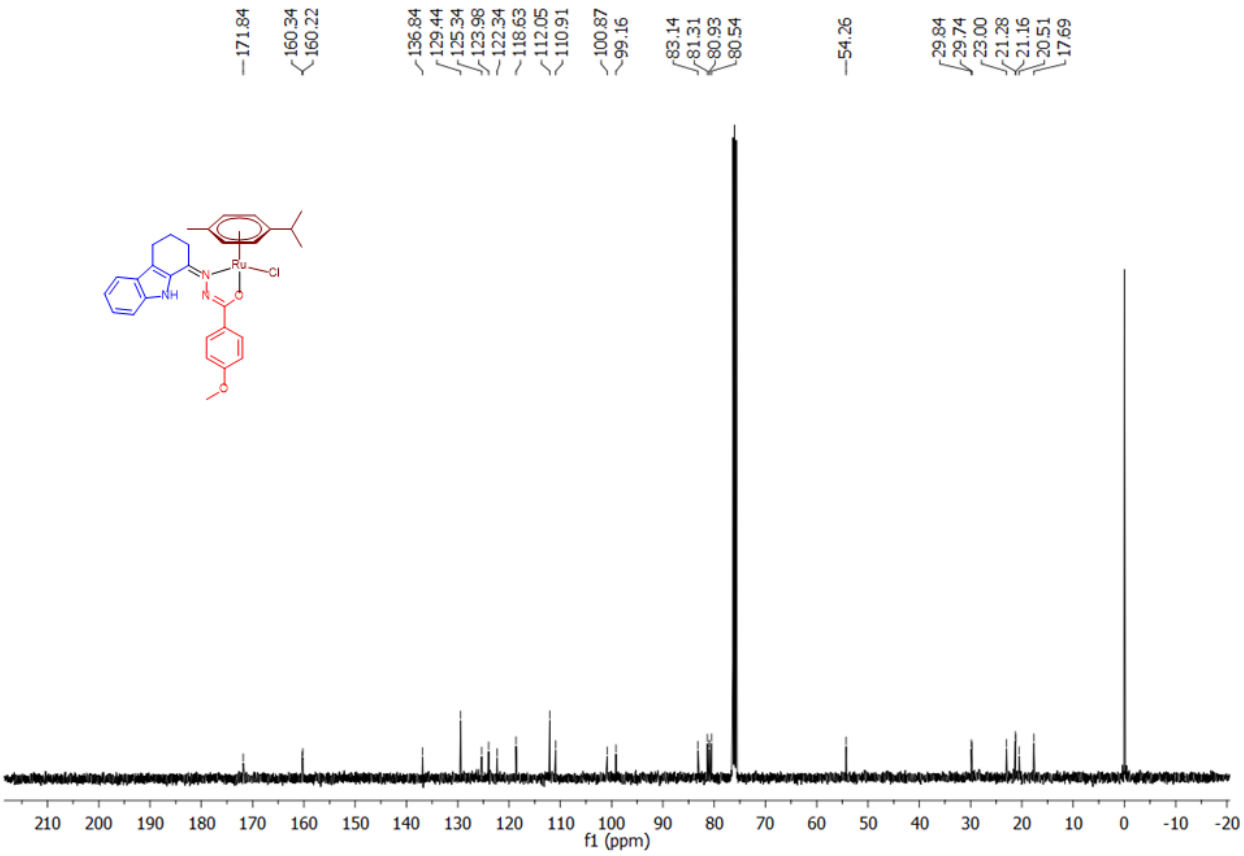


Figure 12: ^{13}C NMR spectrum for complex **3** in $CDCl_3$ (100MHz, 300K).

5. HRMS spectra of the *p*-cymene Ru(II) complexes

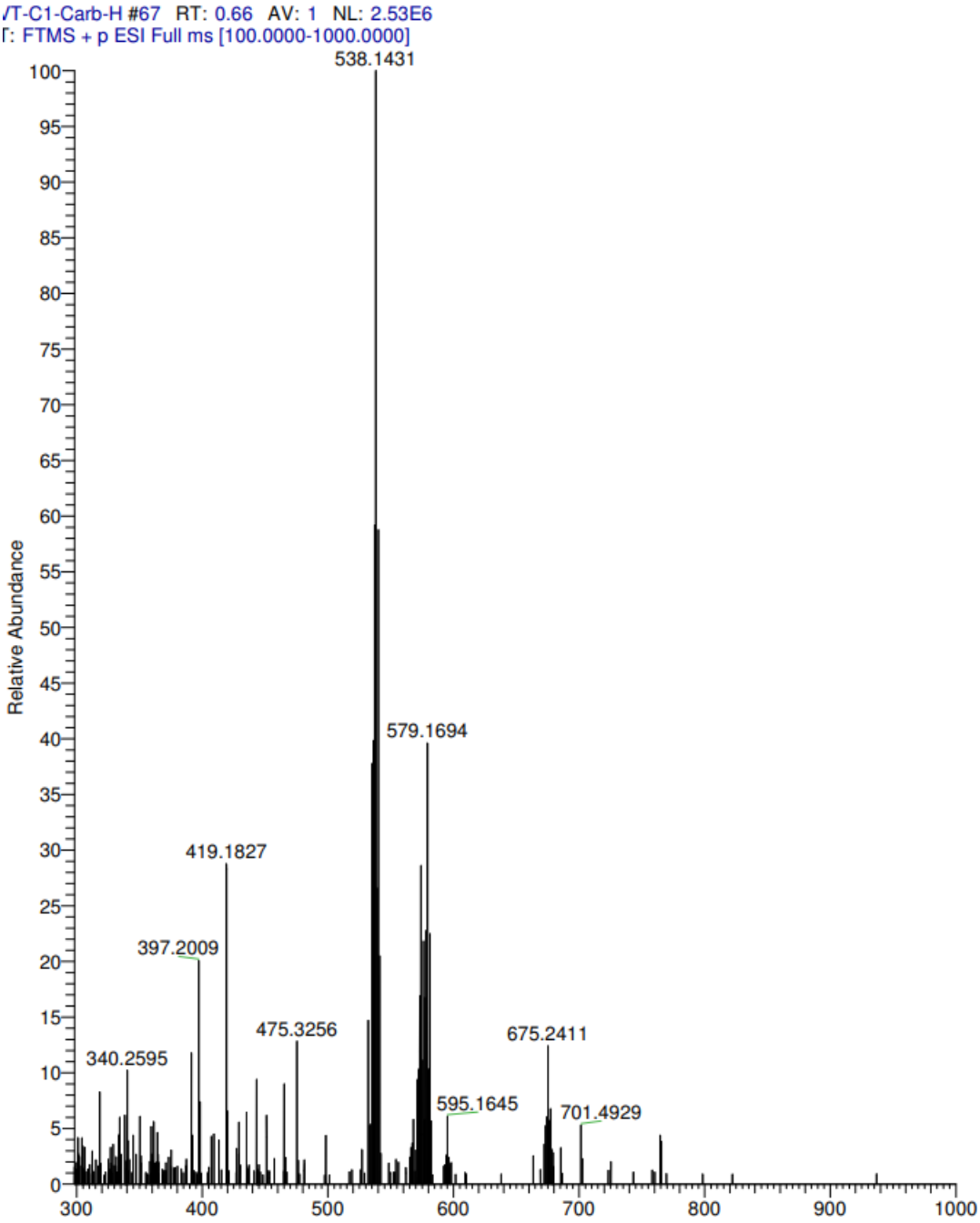


Figure 13: HRMS spectrum for complex **1**.

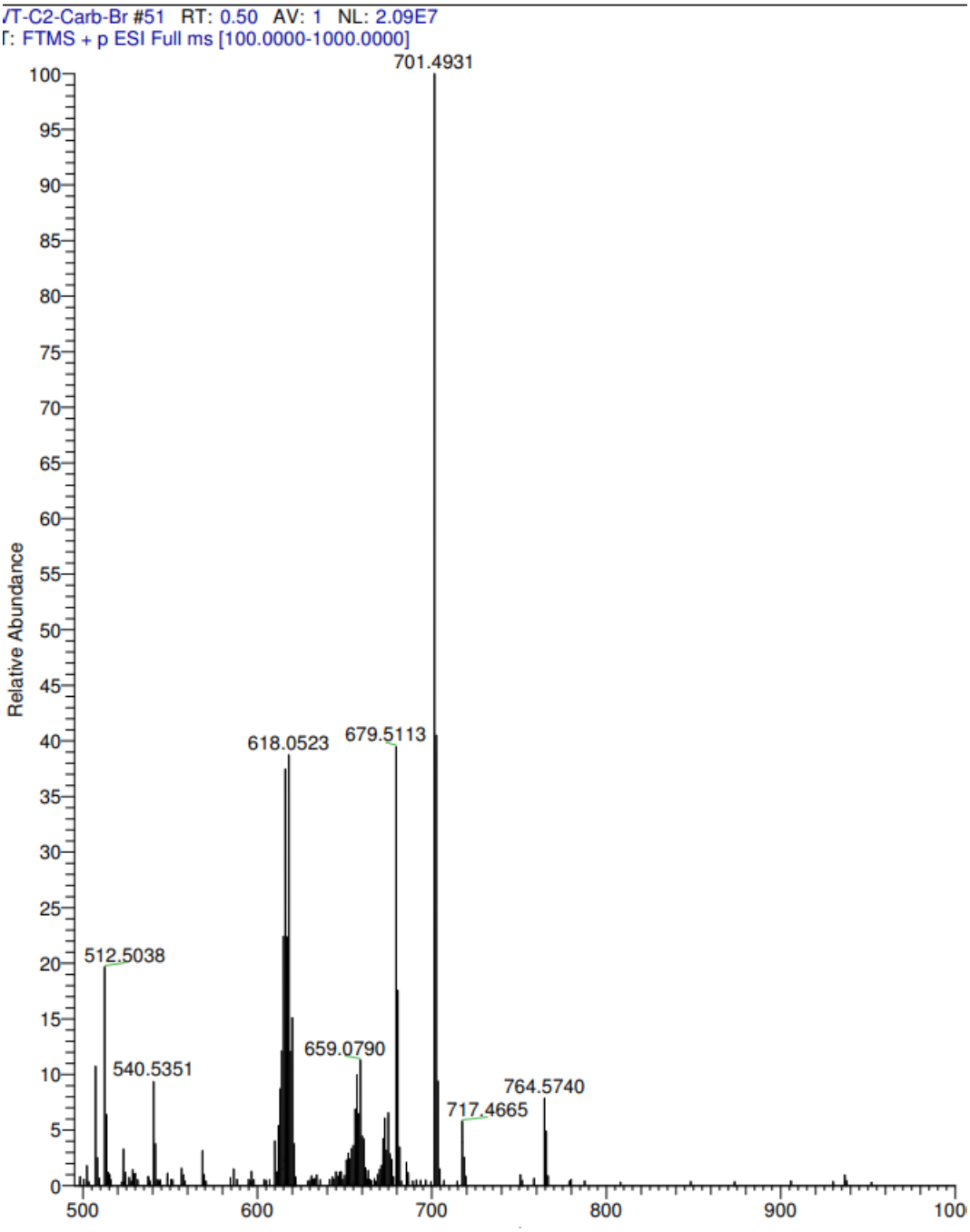


Figure 14: HRMS spectrum for complex **2**.

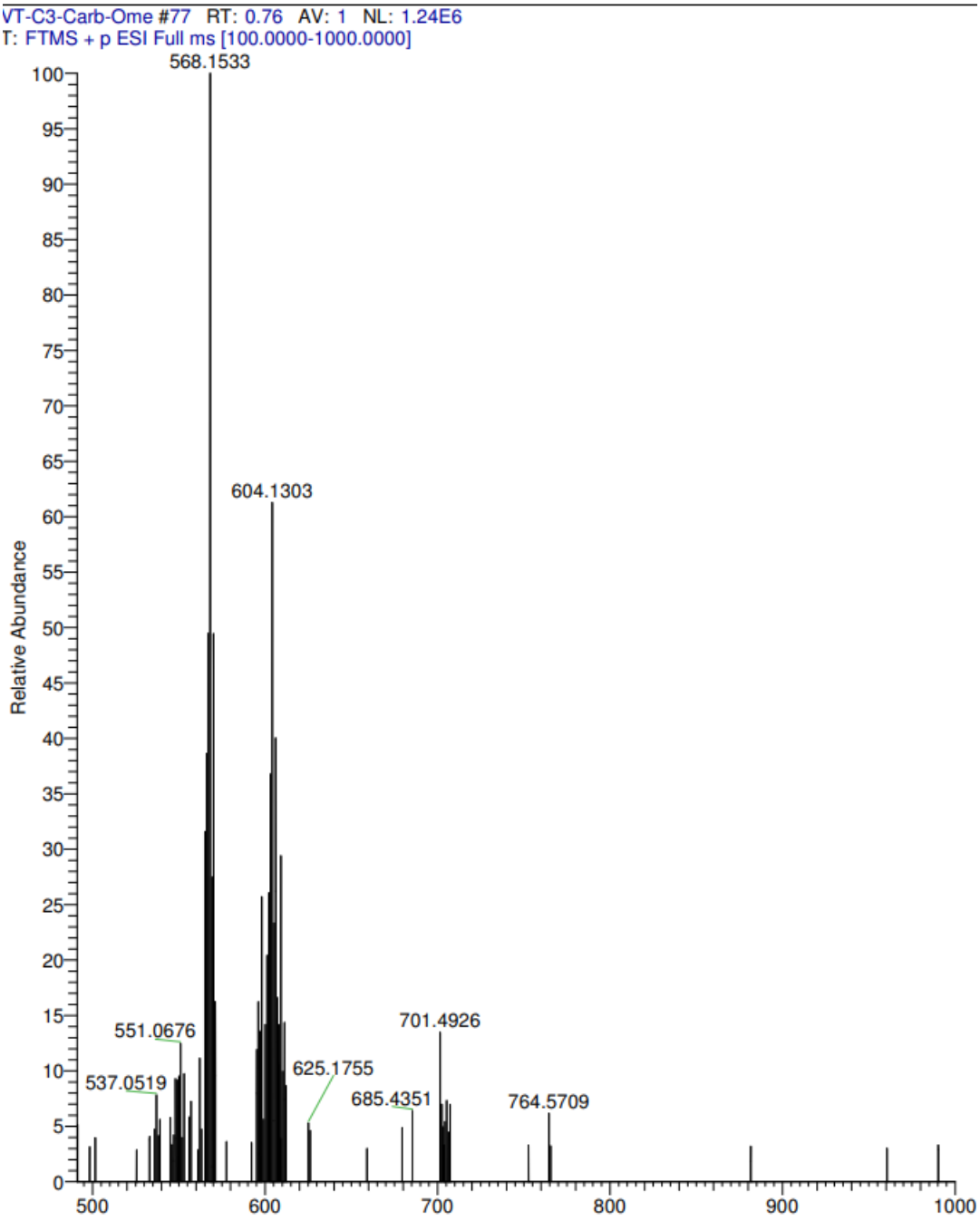


Figure 15: HRMS spectrum for complex **3**.

6. X-ray crystallography

Single crystals of complex were grown by slow evaporation of a dichloromethane – methanol solution at room temperature. The data collection was carried out using a Bruker AXS Kappa APEX II single crystal X-ray diffractometer using monochromated Mo–Kα radiation (kI = 0.71073 A°). Data was collected at 296 K. The absorption corrections were performed by the multi-scan method using SADABS software.[3] Corrections were made for Lorentz and polarization effects. The structures were solved by direct methods (SHELXS 97) and refined by full-matrix least squares on F2 using SHELXL 97.[4] All non-hydrogen atoms were refined anisotropically and the hydrogen atoms in these structures were located from the difference Fourier map and constrained to the ideal positions in the refinement procedure. The unit cell parameters were determined by the method of difference vectors using reflections scanned from three different zones of the reciprocal lattice. The intensity data were measured using ω and φ scan with a frame width of 0.5°. Frame integration and data reduction were performed using the Bruker SAINT-Plus (Version 7.06a) software.[5]

7. Table 1. Crystal data and structure refinement for complex 2.

CCDC	2025903
Empirical formula	$C_{29}H_{29}BrClN_3ORu$
Formula weight	651.98
Temperature/K	295(2)
Crystal system	Triclinic
Space group	P1
a/Å, b/Å, c/Å	8.0310(4), 16.1519(7), 20.7720(8)
α/°, β/°, γ/°	90, 90, 90
Volume/Å3	2694.47(19)
Z	4
ρcalcmg/mm3	1.607
m/mm-1	2.191
F(000)	1312
Crystal size/mm3	0.42 × 0.13 × 0.07
Theta range for data collection	3.446 to 29.330°
Index ranges	$-8 \leq h \leq 10$, $-15 \leq k \leq 22$, $-25 \leq l \leq 28$
Reflections collected	16543
Independent reflections	6452[R(int) = 0.0353]
Data/restraints/parameters	6452/0/332
Goodness-of-fit on F2	1.025
Final R indexes [I>2σ (I)]	R1 = 0.0412, wR2 = 0.0859
Final R indexes [all data]	R1 = 0.0624, wR2 = 0.0928
Largest diff. peak/hole / e Å-3	0.353/-0.726

8. Table 2. Selected bond lengths (Å) and angles (°) for the complex 2

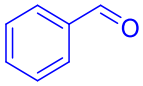
Bond lengths (Å)	
Ru1-Cl1	2.409 (16)
Ru1-O1	2.051 (4)
Ru1-N1	2.107 (4)
Ru1-C20	2.193 (5)
Ru1-C21	2.166 (5)
Ru1-C22	2.195 (6)
Ru1-C23	2.227 (6)
Ru1-C24	2.191 (6)
Ru1-C25	2.158 (6)
Br1-C17	1.893 (6)
O1-C13	1.292 (6)
N1-N2	1.409 (6)
N1-C1	1.304 (6)
N2-C13	1.296 (7)
N3-C11	1.377 (7)
C1-C2	1.514 (7)
C1-C12	1.446 (7)
C5-C12	1.379 (7)

Bond angles **(°)**	
O(1)-Ru(1)-Cl(1)	86.51 (12)
O(1)-Ru(1)-N(1)	76.37 (15)
Cl(1)-Ru(1)-C(21)	152.89 (15)
N(2)- C(13)-O(1)	126.3 (5)
N(1)-Ru(1)-Cl(1)	85.12 (12)
N(1)-N(2)-C(13)	110.5 (4)
C(11)-N(3)-C(12)	108.6 (5)
C(16)-C(17)-Br(1)	119.0 (5)
C(12)-C(1)-N(1)	123.9 (5)
C(11)-N(3)-C(12)	108.6 (5)
C(20)-Ru(1)-Cl(1)	161.71 (15)
C(21)-Ru(1)-Cl(1)	152.89 (15)
C(22)-Ru(1)-Cl(1)	116.13 (17)
C(23)-Ru(1)-Cl(1)	93.12 (18)
C(24)-Ru(1)-Cl(1)	96.30 (19)
C(25)-Ru(1)-Cl(1)	123.62 (19)
C(26)-C(20)-Ru(1)	126.0 (4)
C(29)-C(23)-Ru(1)	129.7 (5)
C(13)-O(1)-Ru(1)	111.7 (3)

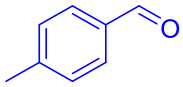
9. Typical procedure for the *p*-cymene Ru(II) catalyzed synthesis of 2-amino-4H-chromenes.

Aromatic alcohols (1 mmol), malononitrile (**2**) (66 mg), resorcinol (**3**) (110 mg), KOH (23 mg), and catalyst **3** (6 mg, 1 mol %) have been dissolved with 5 mL of toluene solvent. Then the mixture was refluxed for 18 h at 100 ºC in nitrogen atmosphere. The reaction mixture has been quenched with water and extracted using EtOAc. The organic fractions were separated and dried over anhydrous Na_2SO_4 and the solvent was removed under vacuum. The products have been isolated by column chromatography with petroleum ether/EtOAc (80:20).

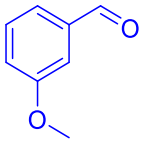
10. Spectral data of the catalytic products



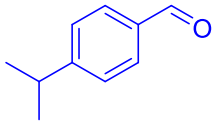
Benzaldehyde (**1a'**)[6]. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) δ 9.96 (s, 1H), 7.83 (d, *J* = 7.6 Hz, 1H), 7.58-7.41 (m, 4H), 2.91-2.83 (s, 1H), 1.19 (s, 6H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ (ppm) 192.63, 136.36, 134.55, 129.79, 129.03.



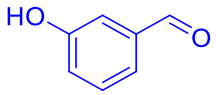
4-methylbenzaldehyde (**1b'**)[7]. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) δ 9.93 (s, 1H), 7.75 (d, *J* = 7.9 Hz, 2H), 7.29 (d, *J* = 7.7 Hz, 2H), 2.40 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ (ppm) 192.06, 145.57, 134.16, 130.13, 129.84, 129.71, 129.13, 21.82.



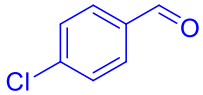
3-methoxybenzaldehyde (**1c'**)[8]. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) δ 9.93 (s, 1H), 7.41 (d, *J* = 7.3 Hz, 2H), 7.35 (s, 1H), 7.15 (d, *J* = 2.2 Hz, 1H), 3.80 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ (ppm) 192.02, 160.07, 137.77, 129.97, 123.27, 121.24, 112.15, 55.25.



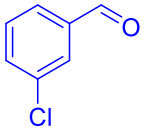
4-isopropylbenzaldehyde (**1d'**)[9]. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) δ 9.88 (s, 1H), 7.72 (d, *J* = 7.5 Hz, 2H), 7.29 (d, *J* = 7.4 Hz, 1H), 2.91-2.83 (s, 1H), 1.19 (s, 6H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ (ppm) 191.84, 156.06, 134.52, 130.27, 129.93, 127.07, 34.37, 23.53.



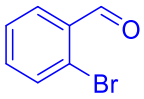
3-hydroxybenzaldehyde (**1e'**)[10]. ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) δ 9.96 (s, 1H), 9.90 (s, 1H), 7.42 – 7.34 (m, 2H), 7.26 (s, 1H), 7.10 (d, *J* = 7.8 Hz, 1H). ^{13}C {^{1}H} NMR (100 MHz, DMSO-d_6): δ (ppm) 192.99, 157.94, 137.61, 130.22, 121.76, 121.04, 114.62.



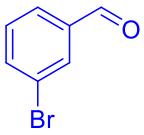
4-chlorobenzaldehyde (**1f'**)[11]. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) δ 9.97 (s, 1H), 7.86 – 7.80 (m, 2H), 7.54 – 7.47 (m, 2H).^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ (ppm) 190.83, 140.79, 134.70, 130.88, 129.44, 129.39.



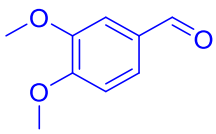
3-chlorobenzaldehyde (**1g'**)[12]. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) δ 9.94 (s, 1H), 7.86 – 7.79 (m, 3H), 7.64 -7.57 (m, 1H), 2.91-2.83 (s, 1H), 1.19 (s, 6H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ (ppm) 191.68, 166.01, 133.29, 132.81, 128.81, 127.73.



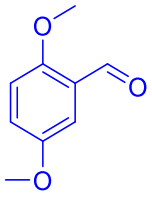
2-bromobenzaldehyde (**1h'**)[13]. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) δ 10.37 (s, 1H), 7.93 – 7.91(m, 1H), 7.65 (d, *J* = 7.5 Hz, 1H), 7.47-7.43 (m, 2H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ (ppm) 191.91, 135.37, 133.92, 133.53, 129.89, 127.94, 127.15.



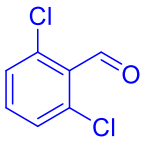
3-bromobenzaldehyde (**1i'**)[14]. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) δ 9.95 (s, 1H), 8.01 (d, *J* = 5.9 Hz, 1H), 7.81-7.75 (m, 2H), 7.43 – 7.27 (m, 1H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ (ppm) 190.81, 137.98, 137.33, 132.37, 130.66, 128.42, 123.38.



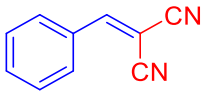
3,4-dimethoxybenzaldehyde (**1j'**)[12]. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) δ 9.85 (s, 1H), 7.46 (d, *J* = 8.1 Hz, 1H), 7.40 (s, 1H), 6.98 (d, *J* = 8.1 Hz, 1H), 3.96 (s, 3H), 3.93 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ (ppm) 190.77, 154.40, 149.53, 130.06, 126.72, 110.38, 108.89, 56.08, 55.89.



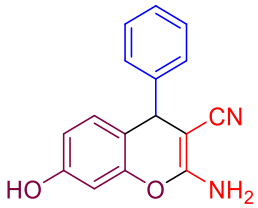
2,5-dimethoxybenzaldehyde (**1k'**)[15]. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) δ 10.43 (s, 1H), 7.32 (d, *J* = 3.1 Hz, 1H), 7.13 (dd, *J* = 9.0, 3.2 Hz, 1H), 6.94 (d, *J* = 9.1 Hz, 1H), 3.89 (s, 3H), 3.79 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ (ppm) 189.54, 156.70, 153.59, 124.91, 123.42, 113.34, 110.44, 56.17, 55.81.



2,6-dichlorobenzaldehyde (**1l'**)[16]. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) δ 10.48 (s, 1H), 7.39 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ (ppm) 188.79, 136.82, 133.67, 130.34, 129.79.

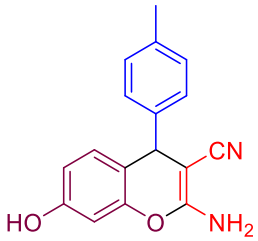


2-benzylidenemalononitrile (**2a'**)[17]. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.91 (d, *J* = 7.6 Hz, 2H), 7.79 (s, 1H), 7.64 (t, *J* = 7.4 Hz, 1H), 7.55 (t, *J* = 7.6 Hz, 2H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ (ppm) 160.05, 134.70, 130.96, 130.79, 129.68, 113.77, 112.61, 82.86.

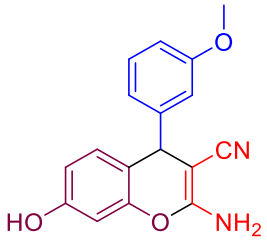


2-amino-7-hydroxy-4-phenyl-4H-chromene-3-carbonitrile **(4a)**[18]**.** ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 9.72 (s, 1H), 7.30 (t, *J* = 7.4 Hz, 2H), 7.23 – 7.14 (m, 3H), 6.88 (s, 2H), 6.81 (d, *J* = 8.5 Hz, 1H), 6.49 (dd, *J* = 8.4, 1.3 Hz, 1H), 6.42 (d, *J* = 2.2 Hz, 1H), 4.62 (s, 1H). ^{13}C {^{1}H} NMR

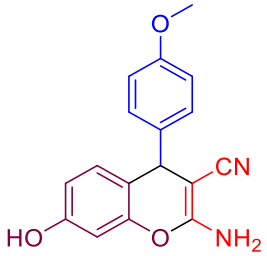
(100 MHz, DMSO-d_6): δ (ppm) 160.22, 157.04, 148.82, 146.34, 129.88, 128.55, 127.34, 126.60, 120.65, 113.71, 112.34, 102.14, 56.22



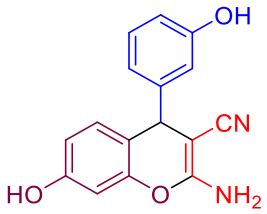
2-amino-7-hydroxy-4-(p-tolyl)-4H-chromene-3-carbonitrile **(4b)**[18]**.** ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 9.74 (s, 1H), 7.11 (d, *J* = 7.9 Hz, 2H), 7.05 (d, *J* = 7.9 Hz, 2H), 6.84 (s, 2H), 6.78 (d, *J* = 8.4 Hz, 1H), 6.48 (dd, *J* = 8.4, 2.1 Hz, 1H), 6.42 (d, *J* = 2.1 Hz, 1H), 4.57 (s, 1H), 2.25 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, DMSO-d_6): δ (ppm) 160.12, 156.96, 148.75, 143.39, 135.68, 129.87, 129.09, 127.26, 120.67, 113.85, 112.30, 102.10, 56.36, 20.54.



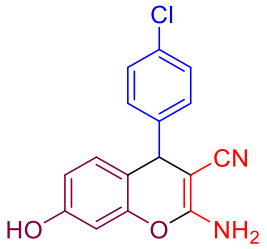
2-amino-7-hydroxy-4-(3-methoxyphenyl)-4H-chromene-3-carbonitrile **(4c)**[19]**.** ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 9.76 (s, 1H), 7.22 (t, *J* = 8.0 Hz, 1H), 6.89 (s, 2H), 6.85 (d, *J* = 8.5 Hz, 1H), 6.76 (m, 3H), 6.51 (dd, *J* = 8.3, 1.7 Hz, 1H), 6.45 (s, 1H), 4.61 (s, 1H), 3.71 (s, 3H).^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ (ppm) 160.30, 159.31, 157.06, 148.79, 147.93, 129.85, 129.71, 120.67, 119.56, 113.60, 113.46, 112.35, 111.43, 102.17, 56.11, 54.90.



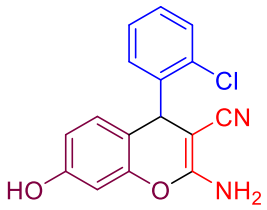
2-amino-7-hydroxy-4-(4-methoxyphenyl)-4H-chromene-3-carbonitrile **(4d)**[20]**.** ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 9.71 (s, 1H), 6.94-6.82 (m, 5H), 6.75 (d, *J* = 6.8 Hz, 1H), 6.56 (s, 1H), 6.49 (d, *J* = 8.3 Hz, 1H), 6.44 (s, 1H), 4.95 (s, 1H), 3.71 (s, 3H).^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ (ppm) 160.94, 156.91, 153.26, 150.57, 149.09, 135.27, 129.21, 120.76, 115.06, 113.76, 112.75, 112.18, 111.47, 102.10, 56.19, 55.13.



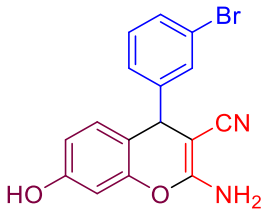
2-amino-7-hydroxy-4-(3-hydroxyphenyl)-4H-chromene-3-carbonitrile **(4e)**[21]**.** ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 9.53 (s, 1H), 7.09 (t, *J* = 7.8 Hz, 1H), 6.85 – 6.81 (m, 3H), 6.64-6.58 (m, 2H), 6.54 (s, 1H), 6.50 (dd, *J* = 8.4, 2.0 Hz, 1H), 6.42 (d, *J* = 1.9 Hz, 1H), 4.51 (s, 1H).^{13}C {^{1}H} NMR (100 MHz, DMSO-d_6): δ (ppm) 160.20, 157.48, 156.99, 148.79, 147.82, 129.83, 129.44, 120.70, 118.05, 114.06, 113.78, 113.69, 112.31, 102.12, 56.31.



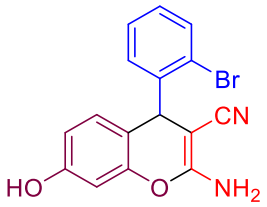
2-amino-4-(4-chlorophenyl)-7-hydroxy-4H-chromene-3-carbonitrile **(4f)**[20]**.** ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 9.75 (s, 1H), 7.37 (d, *J* = 8.4 Hz, 2H), 7.19 (d, *J* = 8.4 Hz, 2H), 6.93 (s, 2H), 6.79 (d, *J* = 8.5 Hz, 1H), 6.49 (dd, *J* = 8.4, 2.1 Hz, 1H), 6.42 (s, 1H), 4.67 (s, 1H).^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ (ppm) 160.21, 157.18, 148.78, 145.30, 131.20, 129.87, 129.25, 128.54, 120.49, 113.16, 112.45, 102.19, 55.79.



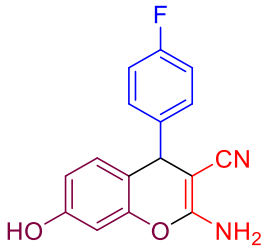
2-amino-4-(2-chlorophenyl)-7-hydroxy-4H-chromene-3-carbonitrile **(4g)**[19]**.** ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 9.82 (s, 1H), 7.41 (d, *J* = 7.6 Hz, 1H), 7.29 – 7.18 (m, 3H), 6.95 (s, 2H), 6.75 (d, *J* = 8.5 Hz, 1H), 6.50 (dd, *J* = 8.4, 2.2 Hz, 1H), 6.45 (d, *J* = 2.1 Hz, 1H), 5.15 (s, 1H).^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ (ppm) 160.49, 157.28, 148.97, 142.77, 131.80, 130.74, 129.70, 129.22, 128.53, 127.77, 120.32, 112.49, 112.44, 102.24, 54.84.



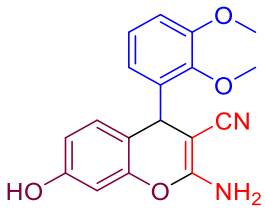
2-amino-4-(3-bromophenyl)-7-hydroxy-4H-chromene-3-carbonitrile **(4h)**[18]**.** ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 9.77 (s, 1H), 7.41 (d, *J* = 7.7 Hz, 1H), 7.35 (s, 1H), 7.28 (t, *J* = 7.8 Hz, 1H), 7.18 (d, *J* = 7.6 Hz, 1H), 6.96 (s, 2H), 6.82 (d, *J* = 8.4 Hz, 1H), 6.51 (d, *J* = 8.4 Hz, 1H), 6.42 (d, *J* = 1.4 Hz, 1H), 4.68 (s, 1H). ^{13}C {^{1}H}NMR (100 MHz, $CDCl_3$): δ (ppm) 160.32, 157.25, 149.08, 148.77, 130.89, 129.93, 129.57, 126.55, 121.81, 120.45, 112.94, 102.23, 56.00.



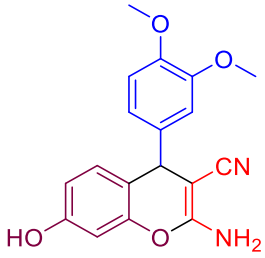
2-amino-4-(2-bromophenyl)-7-hydroxy-4H-chromene-3-carbonitrile **(4i)**[18]**.** ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 9.78 (s, 1H), 7.58 (d, *J* = 6.8 Hz, 1H), 7.32 (s, 1H), 7.15 (d, *J* = 6.5 Hz, 2H), 6.95 (s, 2H), 6.75 (d, *J* = 7.4 Hz, 1H), 6.49 (d, *J* = 7.6 Hz, 1H), 6.44 (s, 1H), 5.16 (s, 1H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ (ppm) 160.38, 157.33, 148.85, 144.56, 132.82, 130.96, 129.13, 128.79, 128.43, 122.28, 120.22, 112.54, 102.27, 55.10.



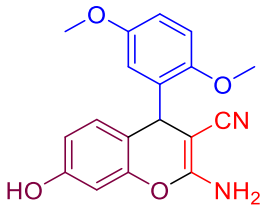
2-amino-4-(4-fluorophenyl)-7-hydroxy-4H-chromene-3-carbonitrile **(4j)**[18]**.** ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 9.75 (s, 1H), 7.22-7.19 (m, 2H), 7.13 (t, *J* = 8.8 Hz, 2H), 6.89 (s, 2H), 6.79 (d, *J* = 8 Hz, 1H), 6.50 (dd, *J* = 8.4, 2.2 Hz, 1H), 6.43 (d, *J* = 2.2 Hz, 1H), 4.66 (s, 1H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ (ppm) 162.13, 160.17, 159.72, 157.10, 148.77, 142.53, 142.50, 129.86, 129.24, 129.16, 120.55, 115.36, 115.15, 113.50, 112.42, 102.18, 56.15.



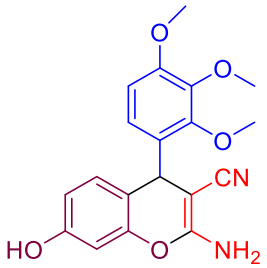
2-amino-4-(2,3-dimethoxyphenyl)-7-hydroxy-4H-chromene-3-carbonitrile **(4k)**[22]**.** ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 9.72 (s, 1H), 6.98 (t, *J* = 7.9 Hz, 1H), 6.89 (d, *J* = 7.5 Hz, 1H), 6.81 (s, 2H), 6.74 (d, *J* = 8.4 Hz, 1H), 6.64 (d, *J* = 7.5 Hz, 1H), 6.46 (dd, *J* = 8.4, 2.2 Hz, 1H), 6.41 (d, *J* = 2.1 Hz, 1H), 4.86 (s, 1H), 3.78 (s, 3H), 3.62 (s, 3H).^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ (ppm) 160.37, 156.87, 152.38, 148.95, 145.96, 139.22, 129.48, 124.04, 120.84, 120.74, 113.68, 112.12, 111.17, 102.10, 60.18, 55.63, 55.48.



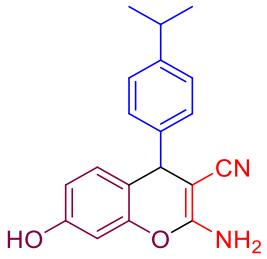
2-amino-4-(3,4-dimethoxyphenyl)-7-hydroxy-4H-chromene-3-carbonitrile **(4l)**[19]**.** ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 9.68 (s, 1H), 6.83-6.89 (m, 5H), 6.67 (d, *J* = 7.9 Hz, 1H), 6.49 (d, *J* = 8.3 Hz, 1H), 6.40 (s, 1H), 4.57 (s, 1H), 3.71 (s, 6H). ^{13}C {^{1}H} NMR (100 MHz, DMSO-d_6): δ (ppm) 160.13, 156.92, 148.65, 147.52, 138.84, 129.86, 120.72, 119.35, 113.91, 112.25, 111.92, 111.20, 102.06, 56.34, 55.45, 55.41.



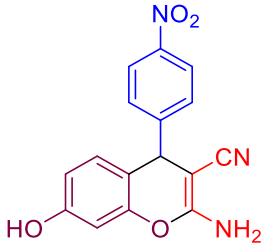
2-amino-4-(2,5-dimethoxyphenyl)-7-hydroxy-4H-chromene-3-carbonitrile **(4m)**[20]**.** ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 9.66 (s, 1H), 7.53 (d, *J* = 2.5 Hz, 3H), 7.30-7.27 (m, 2H), 7.16 (d, *J* = 9.2 Hz, 2H), 6.50 (dd, *J* = 29.8, 5.5 Hz, 1H), 6.39 (s, 1H), 4.91 (s, 1H), 3.85 (s, 3H), 3.75 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ (ppm) 155.27, 153.20, 152.65, 122.77, 119.92, 114.35, 113.63, 112.31, 81.36, 56.35, 55.54.



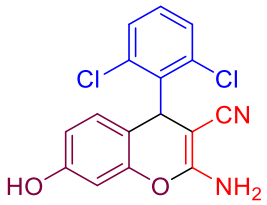
2-amino-7-hydroxy-4-(2,3,4-trimethoxyphenyl)-4H-chromene-3-carbonitrile **(4n)**[22]**.** ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 9.67 (s, 1H), 6.77-6.73 (m, 5H), 6.46 (dd, *J* = 8.4, 2.2 Hz, 1H), 6.40 (d, *J* = 2.1 Hz, 1H), 4.75 (s, 1H), 3.75 (s, 3H), 3.74 (s, 3H), 3.64 (s, 3H).^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ (ppm) 160.26, 156.78, 152.26, 150.90, 148.97, 141.64, 131.54, 129.44, 123.34, 120.89, 113.93, 112.05, 107.82, 102.03, 60.68, 60.18, 55.84, 55.68.



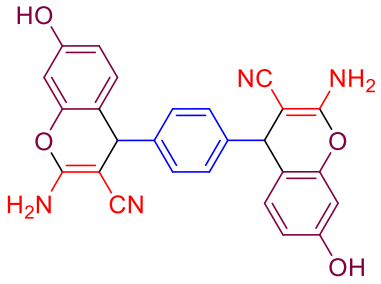
2-amino-7-hydroxy-4-(4-isopropylphenyl)-4H-chromene-3-carbonitrile **(4o)**[23]**.** ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 9.69 (s, 1H), 7.17 (d, *J* = 8.1 Hz, 2H), 7.07 (d, *J* = 8.1 Hz, 2H), 6.85 (s, 2H), 6.81 (d, *J* = 8.5 Hz, 1H), 6.48 (dd, *J* = 8.4, 2.3 Hz, 1H), 6.40 (d, *J* = 2.2 Hz, 1H), 4.57 (s, 1H), 2.88 – 2.78 (sept, 1H), 1.18 (s, 3H), 1.16 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, DMSO-d_6): δ (ppm) 160.21, 156.97, 148.81, 146.56, 143.82, 129.86, 127.16, 126.45, 120.74, 113.92, 112.31, 102.10, 56.31, 32.98, 23.84.



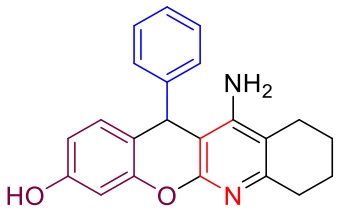
2-amino-7-hydroxy-4-(4-nitrophenyl)-4H-chromene-3-carbonitrile **(4p)**[19]**.** ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 9.86 (s, 1H), 8.21 (d, *J* = 8.6 Hz, 2H), 7.47 (d, *J* = 8.6 Hz, 2H), 7.07 (s, 2H), 6.83 (d, *J* = 8.4 Hz, 1H), 6.53 (dd, *J* = 8.4, 2.2 Hz, 1H), 6.48 (d, *J* = 2.1 Hz, 1H), 4.88 (s, 1H). ^{13}C {^{1}H} NMR (100 MHz, DMSO-d_6): δ (ppm) 160.39, 157.47, 153.71, 148.85, 146.26, 129.92, 128.66, 123.96, 120.31, 112.61, 112.29, 102.38, 55.09.



2-amino-4-(2,6-dichlorophenyl)-7-hydroxy-4H-chromene-3-carbonitrile **(4q)**[21]**.** ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 9.81 (s, 1H), 7.53 (d, *J* = 7.7 Hz, 1H), 7.30-7.37 (m, 2H), 6.95 (s, 2H), 6.59 (d, *J* = 8.4 Hz, 1H), 6.47 (dd, *J* = 8.4, 1.9 Hz, 1H), 6.40 (s, 1H), 5.70 (s, 1H).^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ (ppm) 160.73, 157.45, 149.57, 137.86, 135.28, 134.68, 130.68, 129.55, 128.37, 120.01, 112.24, 110.05, 102.01, 52.12.



4,4'-(1,4-phenylene)bis(2-amino-7-hydroxy-4H-chromene-3-carbonitrile **(4r)**[24]**.** ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 9.97 (s, 1H), 7.10 (s, 4H), 6.84 (d, *J* = 11.7 Hz, 6H), 6.50 (d, *J* = 8.1 Hz, 2H), 6.43 (s, 2H), 4.58 (s, 2H). ^{13}C {^{1}H} NMR (100 MHz, DMSO-d_6): δ (ppm) 160.28, 157.09, 148.86, 144.65, 129.85, 127.43, 120.71, 113.62, 112.42, 102.18, 56.23, 56.02.



11-amino-12-phenyl-7,9,10,12-tetrahydro-8H-chromeno[2,3-b]quinolin-3-ol **(5)**[25]. ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 7.21 (d, *J* = 9.5 Hz, 4H), 7.10 (s, 1H), 6.98 (d, *J* = 7.6 Hz, 1H), 6.47 – 6.43 (m, 2H), 5.50 (s, 2H), 5.20 (s, 1H), 2.30 – 2.17 (m, 2H), 1.84 (s, 2H), 1.69 (s, 4H). ^{13}C {^{1}H} NMR (100 MHz, DMSO-d_6): δ (ppm) 156.85, 155.33, 152.22, 151.31, 145.95, 129.44, 128.43, 127.03, 126.24, 115.88, 111.96, 111.11, 102.60, 98.58, 31.92, 22.87, 22.28, 22.08.

11. NMR spectra for aldehyde intermediates

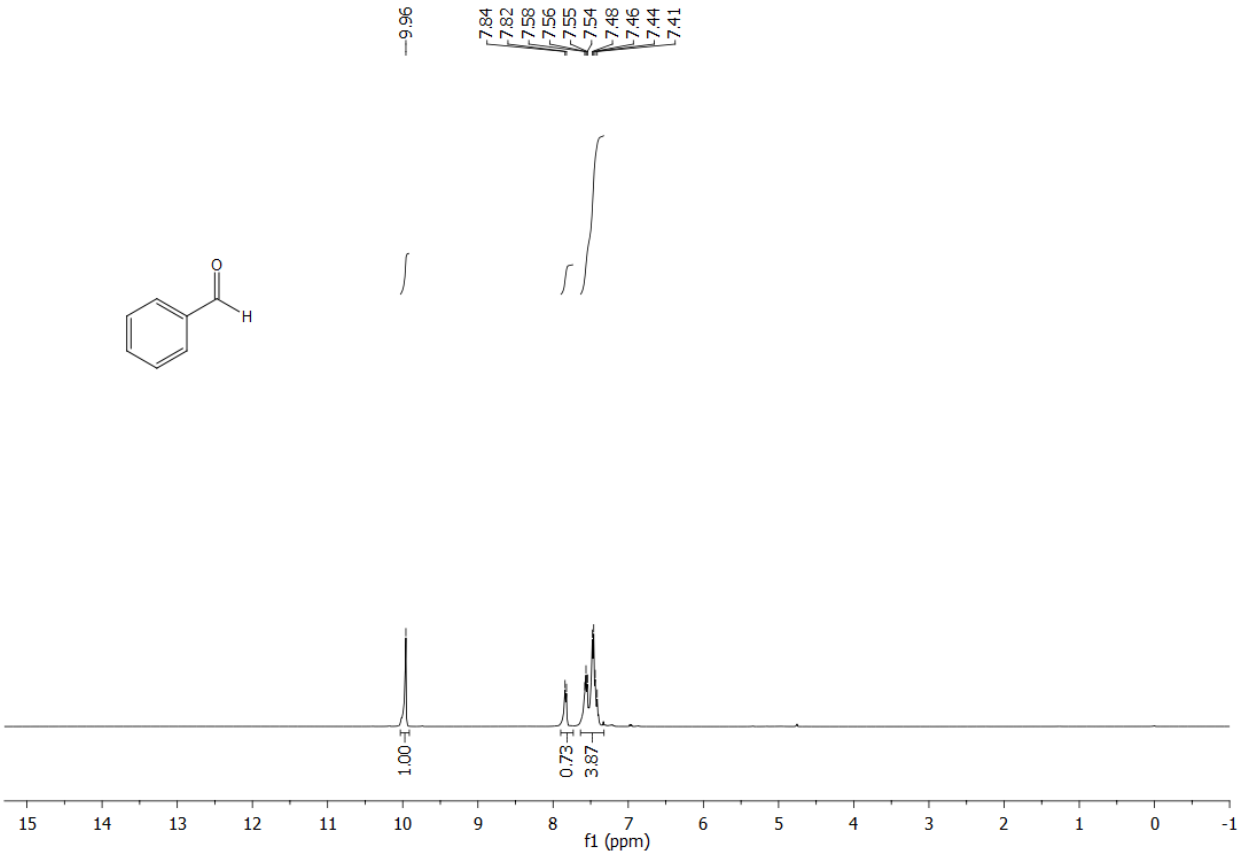


Figure 16: ^{1}H NMR spectrum for (**1a'**) in $CDCl_3$ (400MHz, 300K).

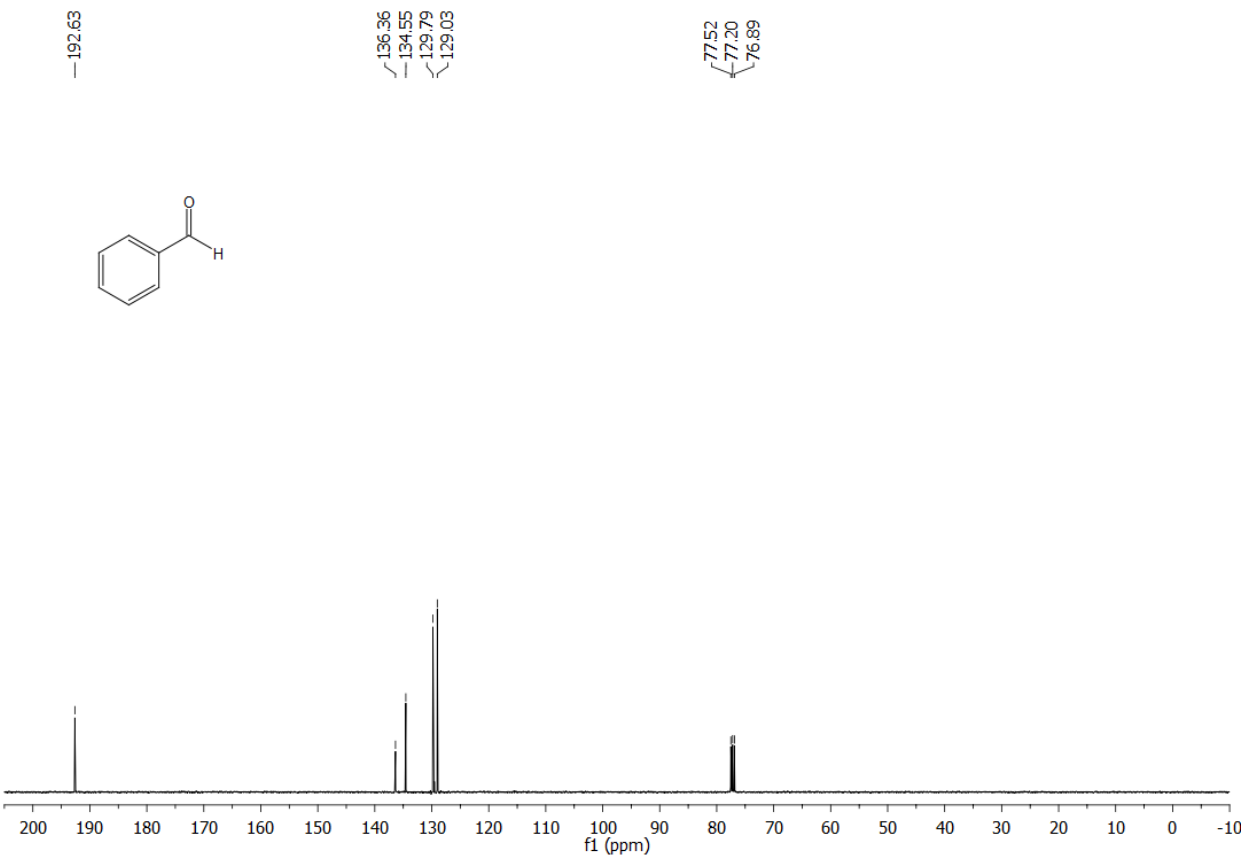


Figure 17: ^{13}C NMR spectrum for (**1a'**) in in $CDCl_3$ (100MHz, 300K).

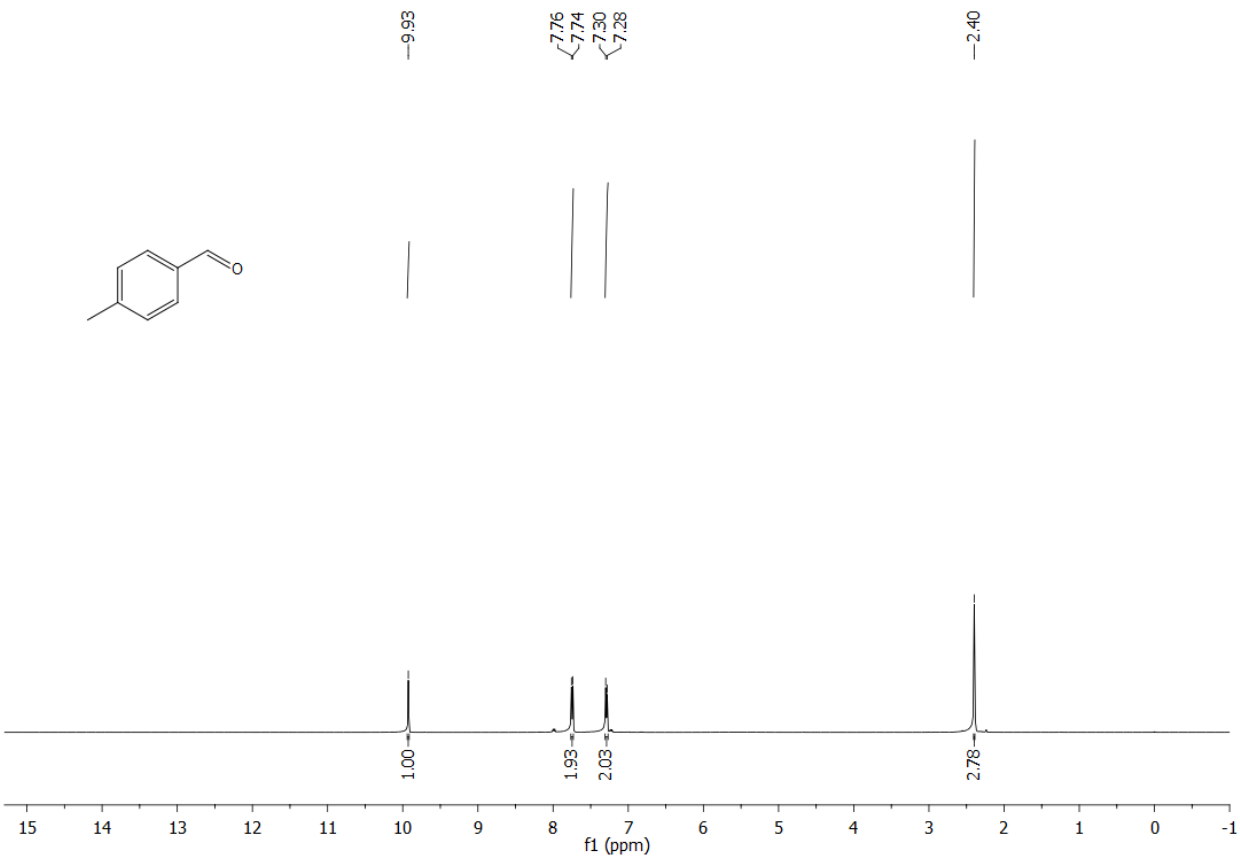


Figure 18: ^{1}H NMR spectrum for (**1b'**) in $CDCl_3$ (400MHz, 300K).

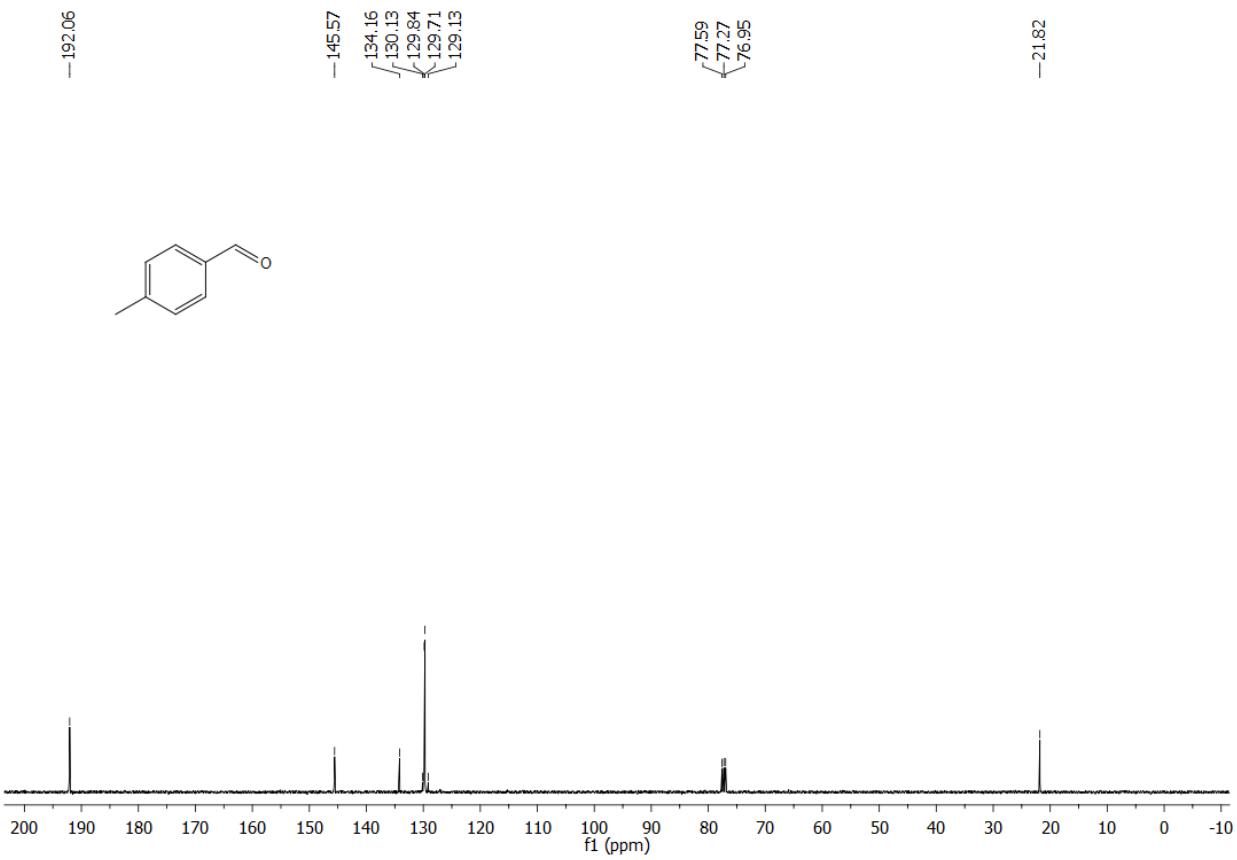


Figure 19: ^{13}C NMR spectrum for (**1b'**) in in $CDCl_3$ (100MHz, 300K).

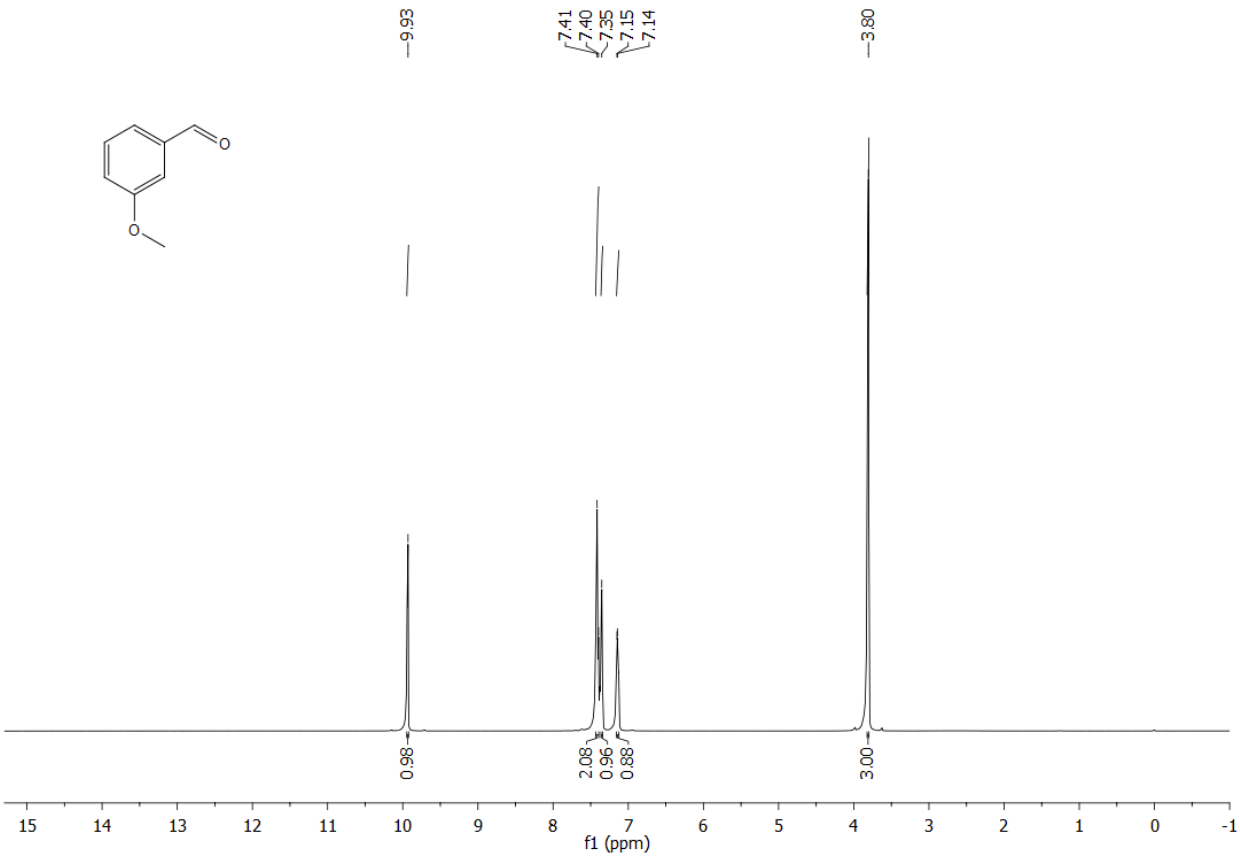


Figure 20: ^{1}H NMR spectrum for (**1c'**) in $CDCl_3$ (400MHz, 300K).

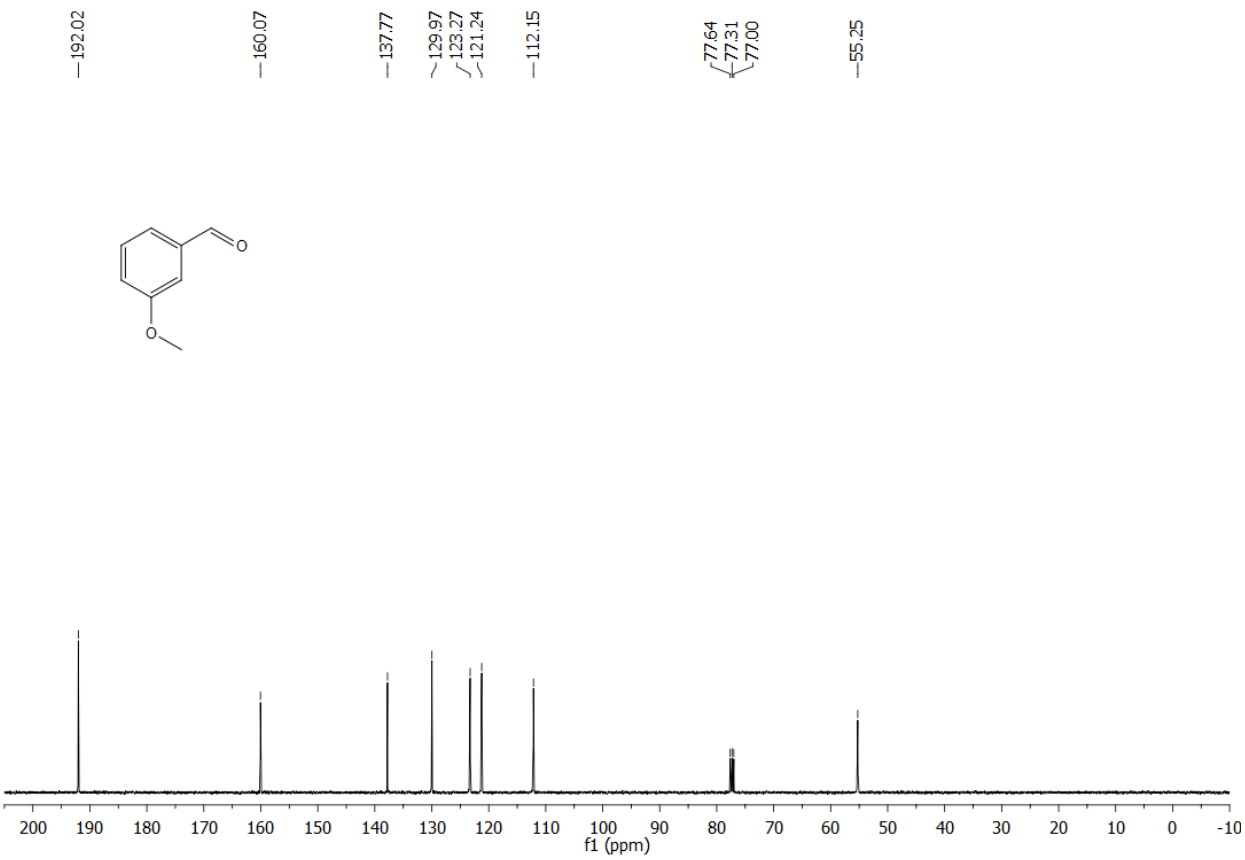


Figure 21: ^{13}C NMR spectrum for (**1c'**) in in $CDCl_3$ (100MHz, 300K).

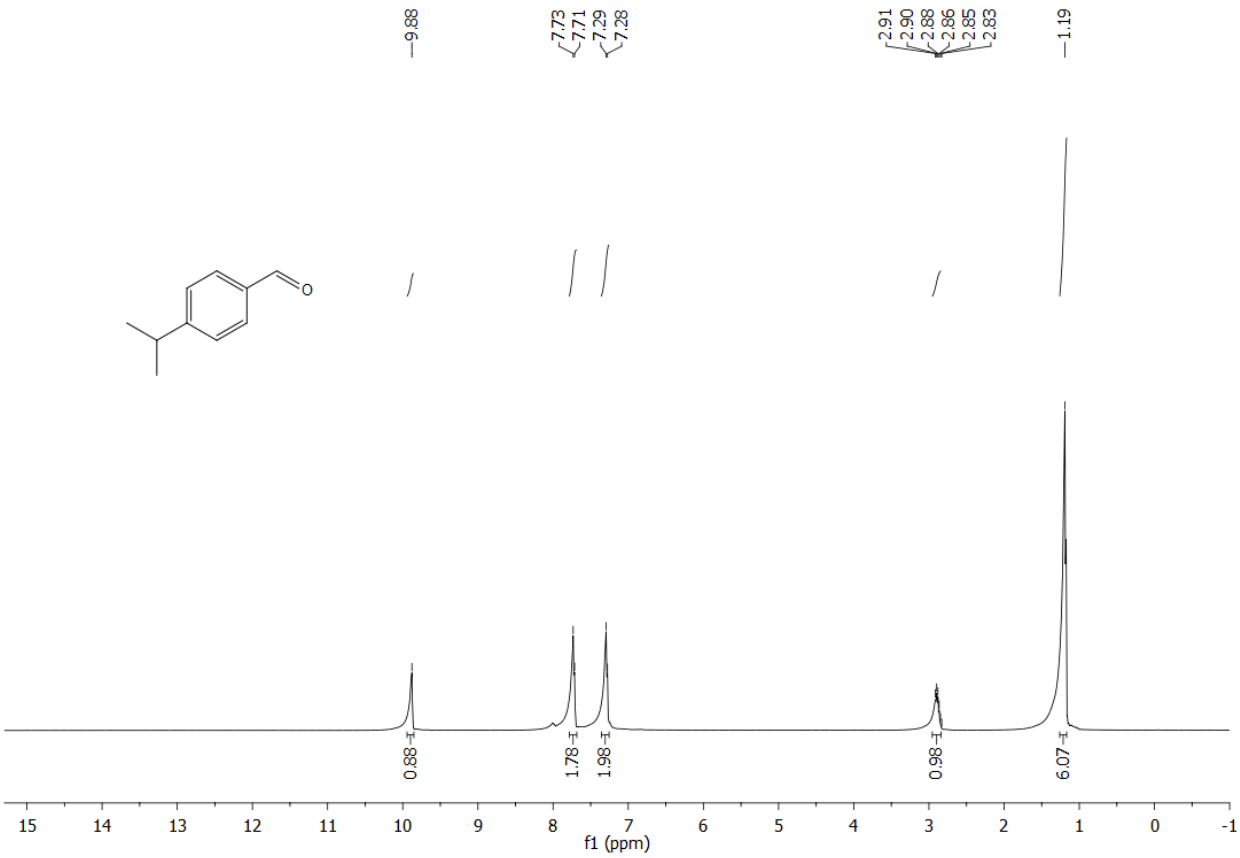


Figure 22: ^{1}H NMR spectrum for (**1d'**) in $CDCl_3$ (400MHz, 300K).

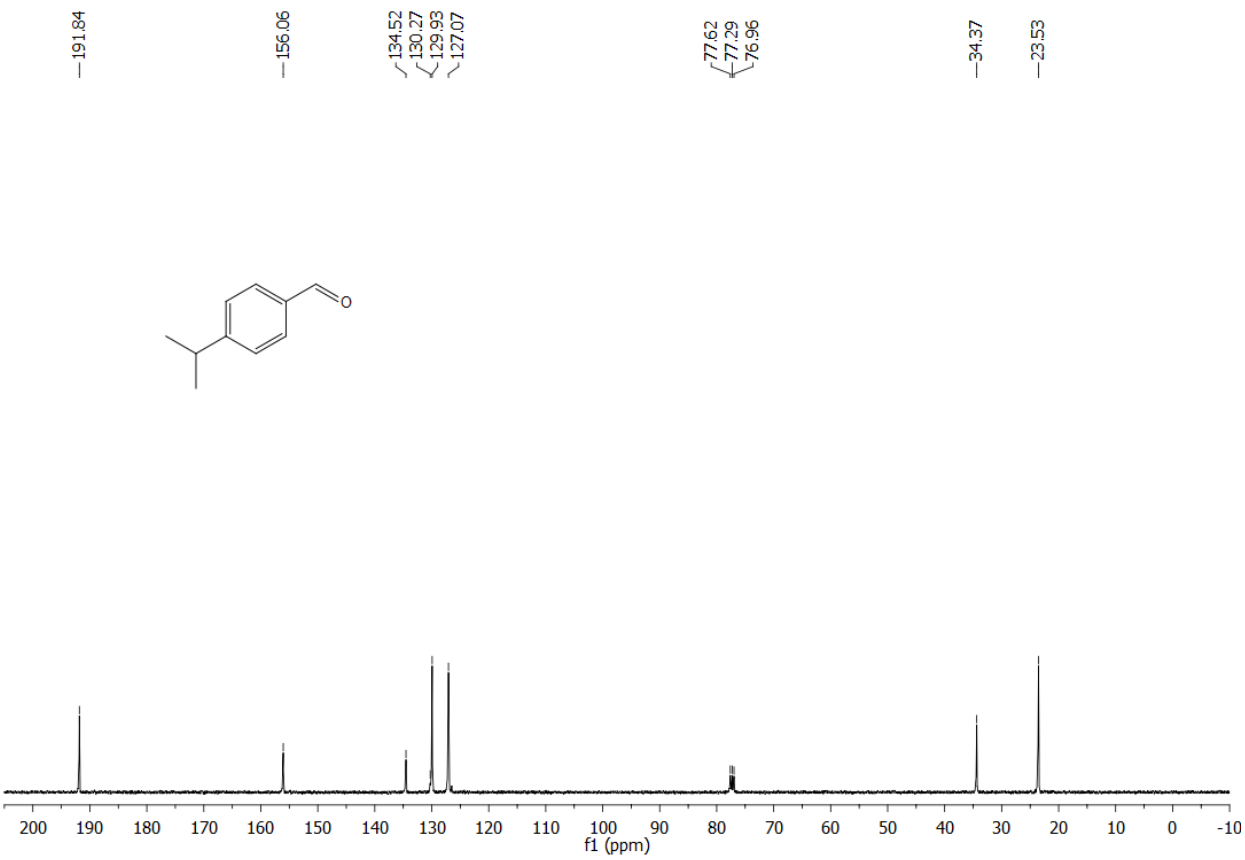


Figure 23: ^{13}C NMR spectrum for **(1d')** in in $CDCl_3$ (100MHz, 300K).

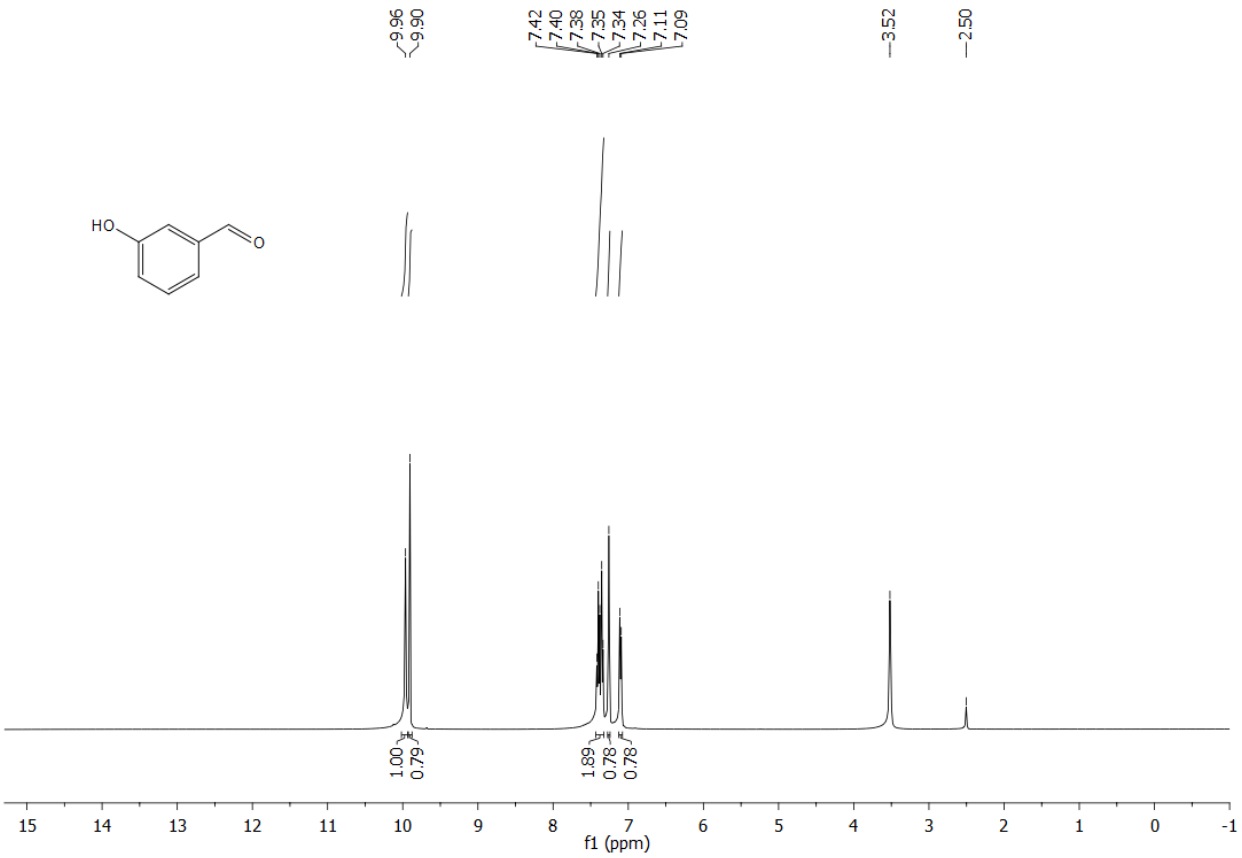


Figure 24: ^{1}H NMR spectrum for (**1e'**) in DMSO-d_6 (400MHz, 300K).

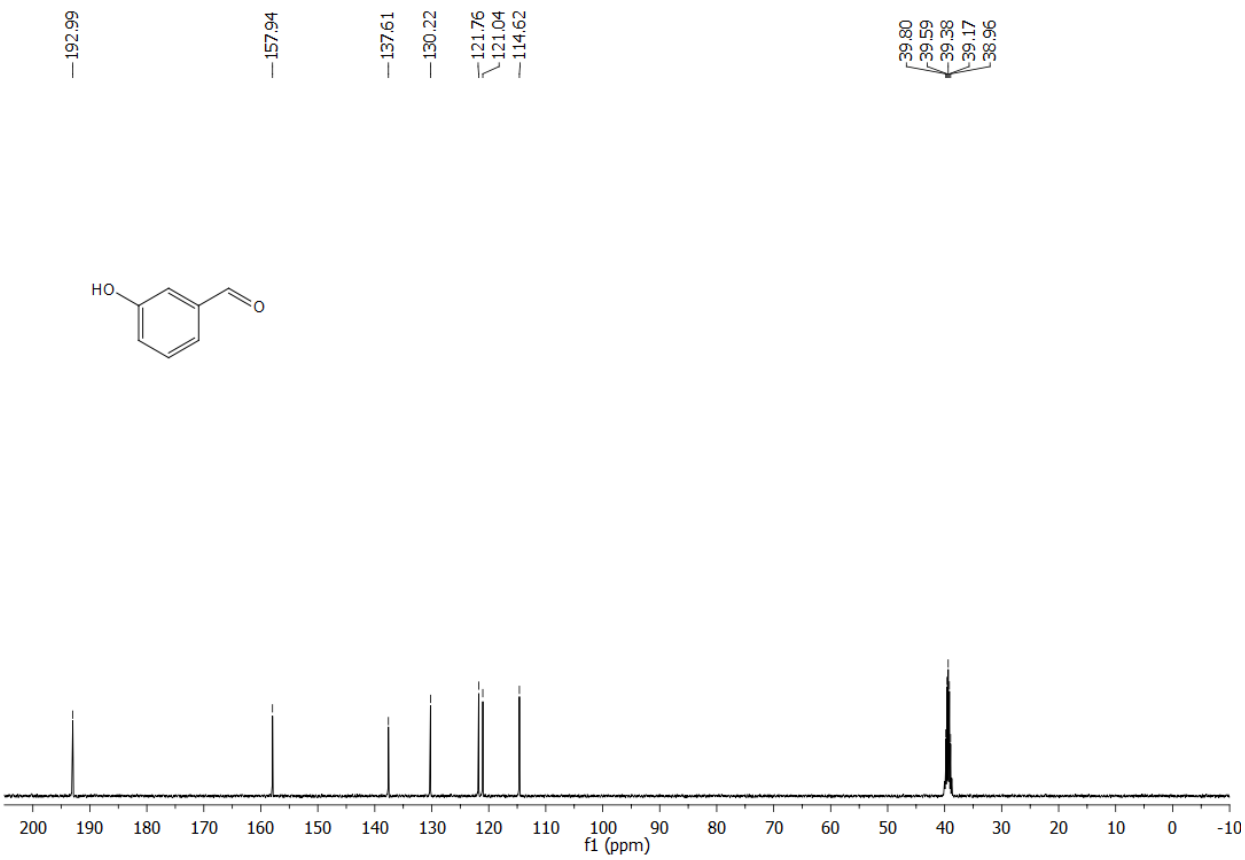


Figure 25: ^{13}C NMR spectrum for (**1e'**) in DMSO-d_6 (100MHz, 300K).

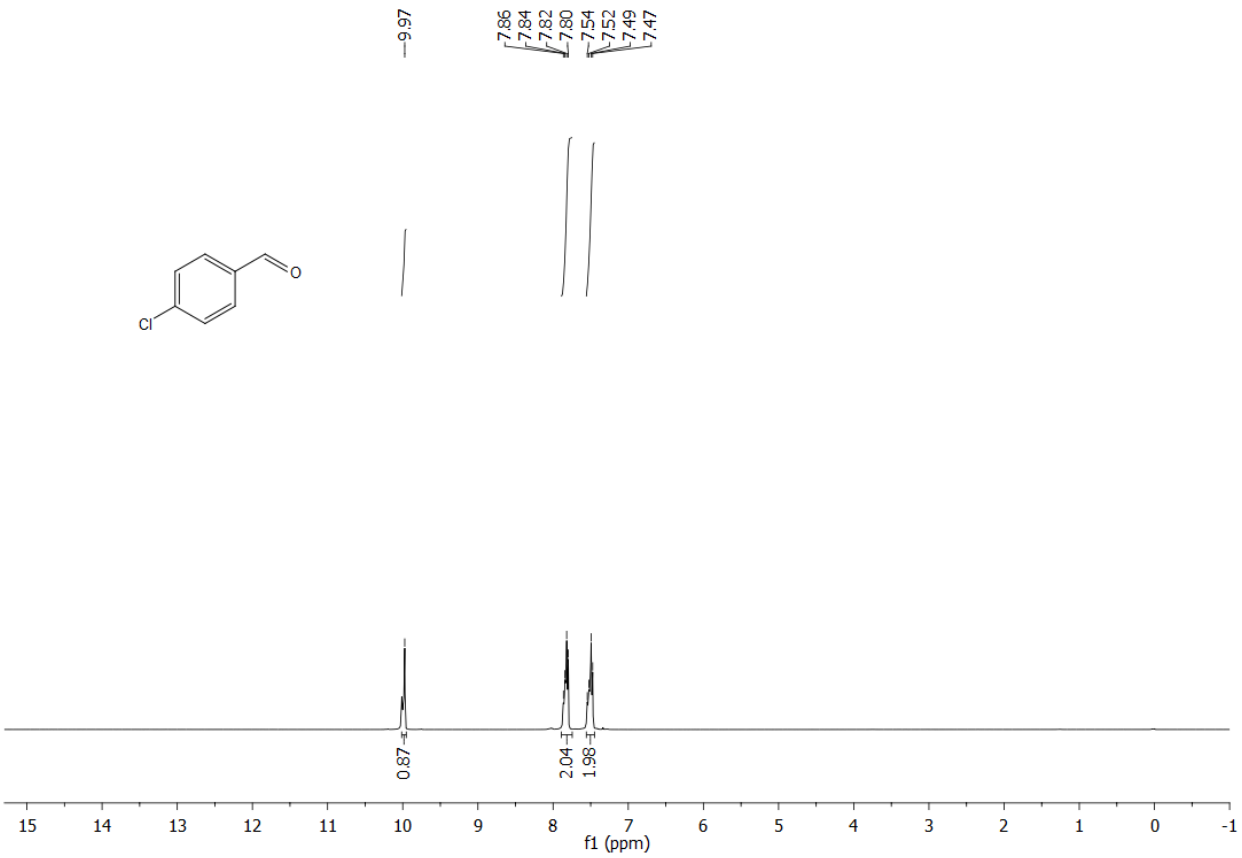


Figure 26: ^{1}H NMR spectrum for (**1f'**) in $CDCl_3$ (400MHz, 300K).

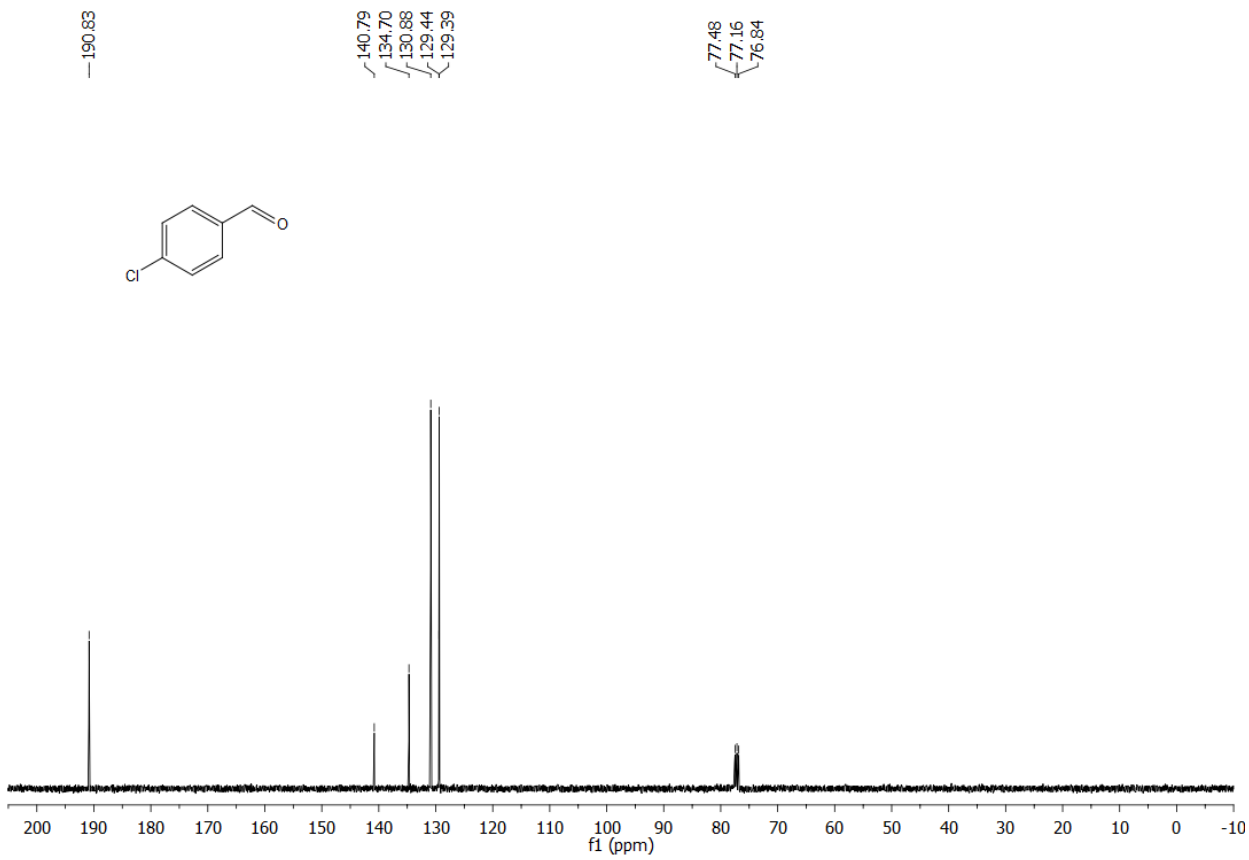


Figure 27: ^{13}C NMR spectrum for (**1f'**) in in $CDCl_3$ (100MHz, 300K).

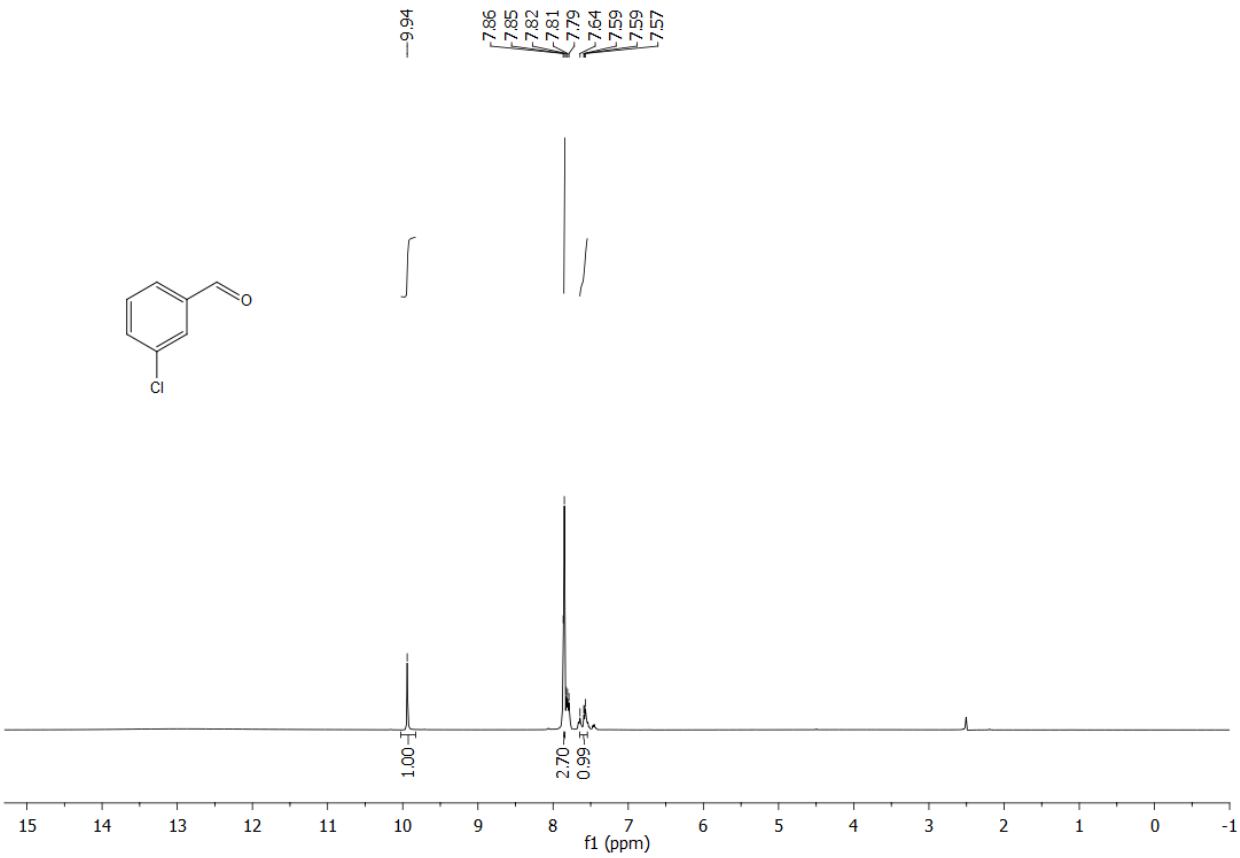


Figure 28: ^{1}H NMR spectrum for (**1g'**) in $CDCl_3$ (400MHz, 300K).

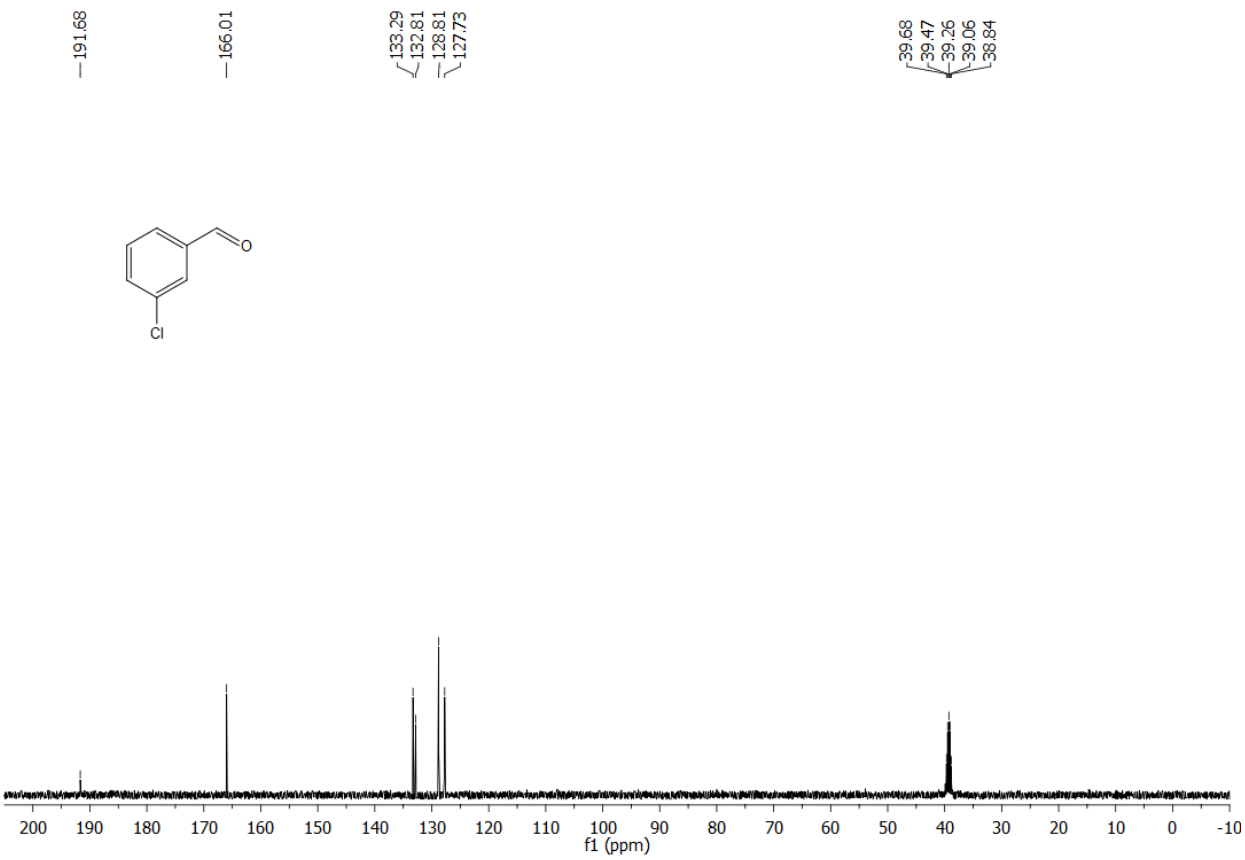


Figure 29: ^{13}C NMR spectrum for (**1g'**) in $CDCl_3$ (100MHz, 300K).

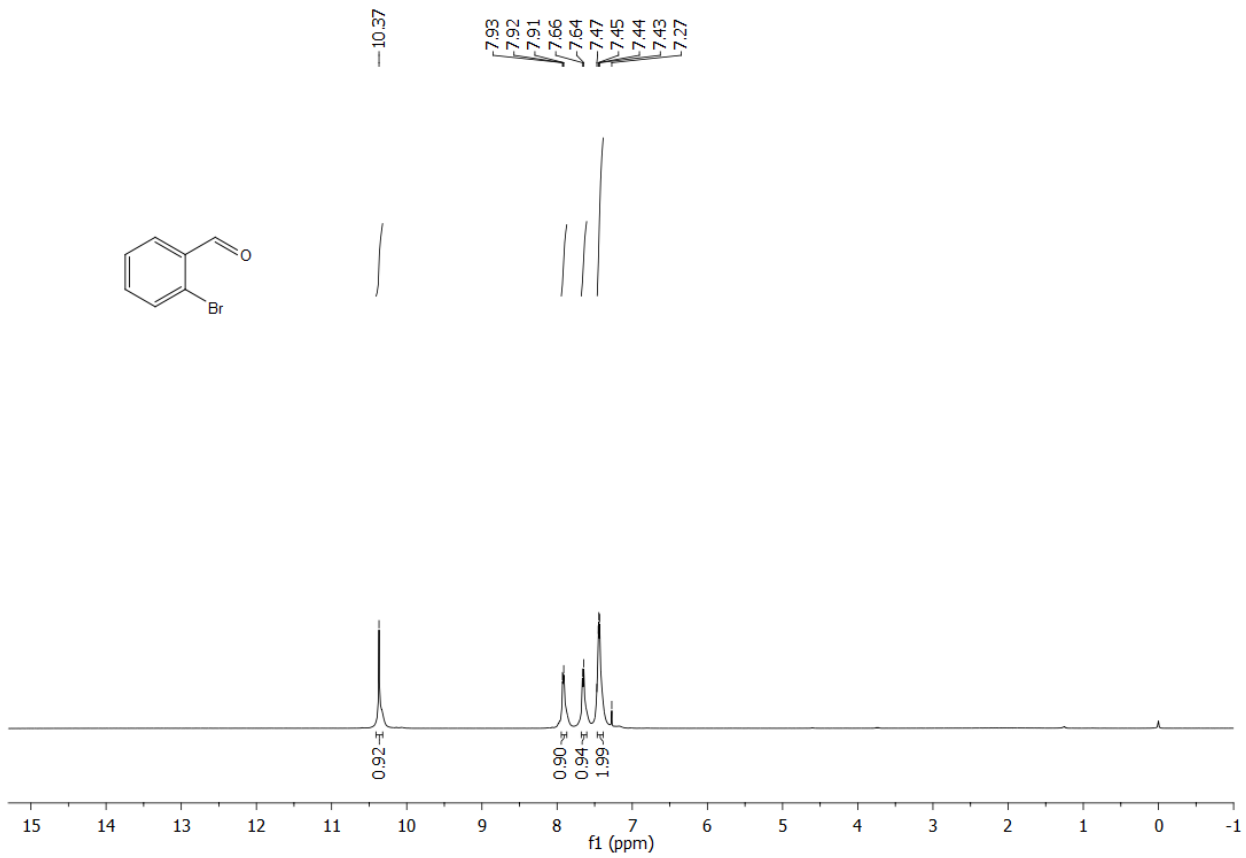


Figure 30: ^{1}H NMR spectrum for (**1h'**) in $CDCl_3$ (400MHz, 300K).

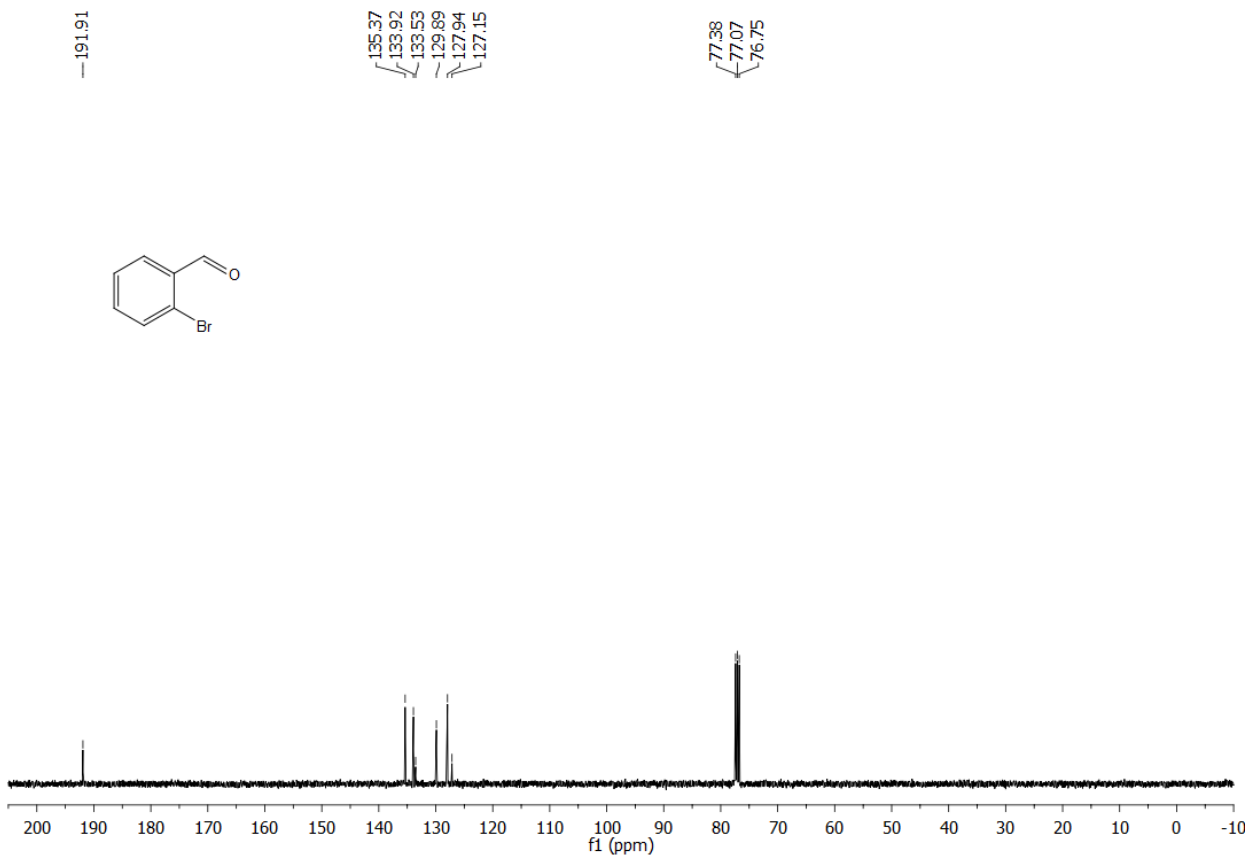


Figure 31: ^{13}C NMR spectrum for (**1h'**) in $CDCl_3$ (100MHz, 300K).

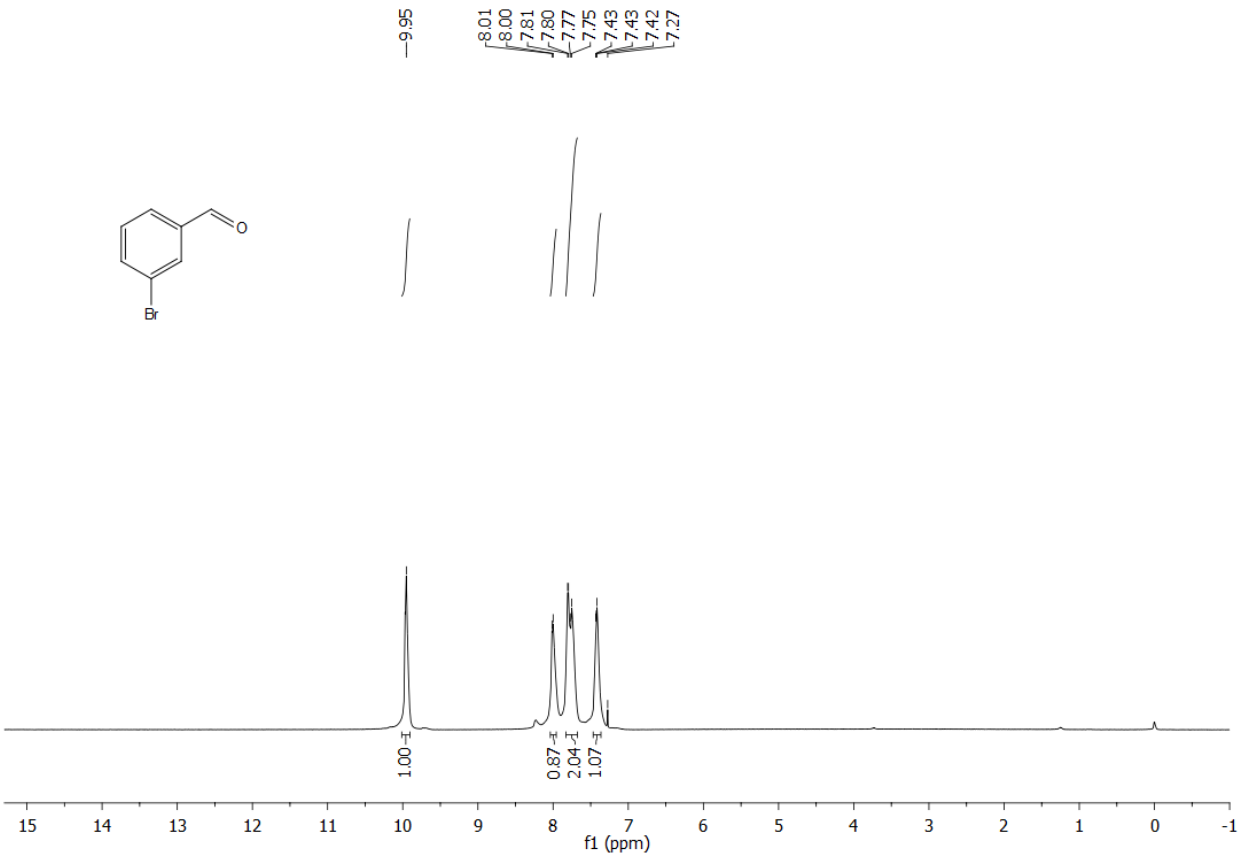


Figure 32: ^{1}H NMR spectrum for (**1i'**) in $CDCl_3$ (400MHz, 300K).

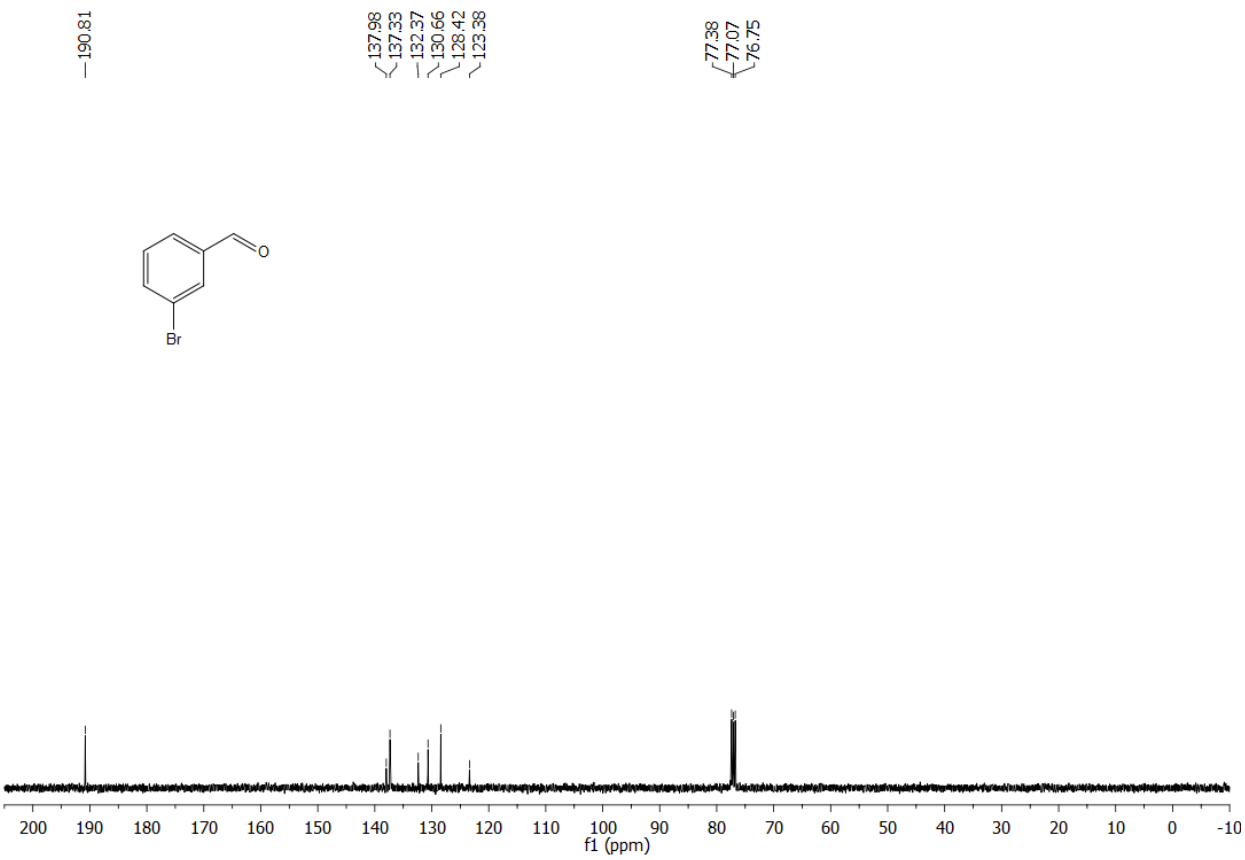


Figure 33: ^{13}C NMR spectrum for (**1i'**) in $CDCl_3$ (100MHz, 300K).

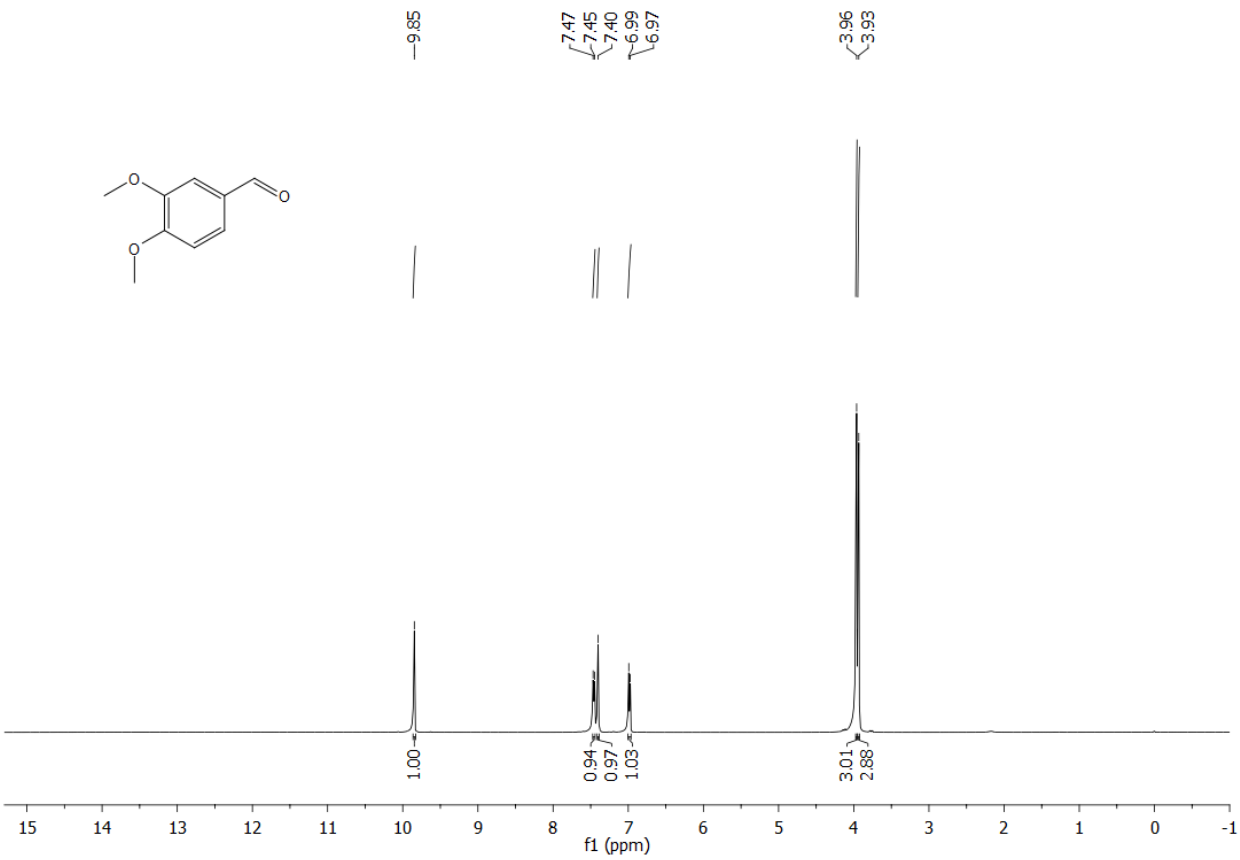


Figure 34: ^{1}H NMR spectrum for (**1j'**) in $CDCl_3$ (400MHz, 300K).

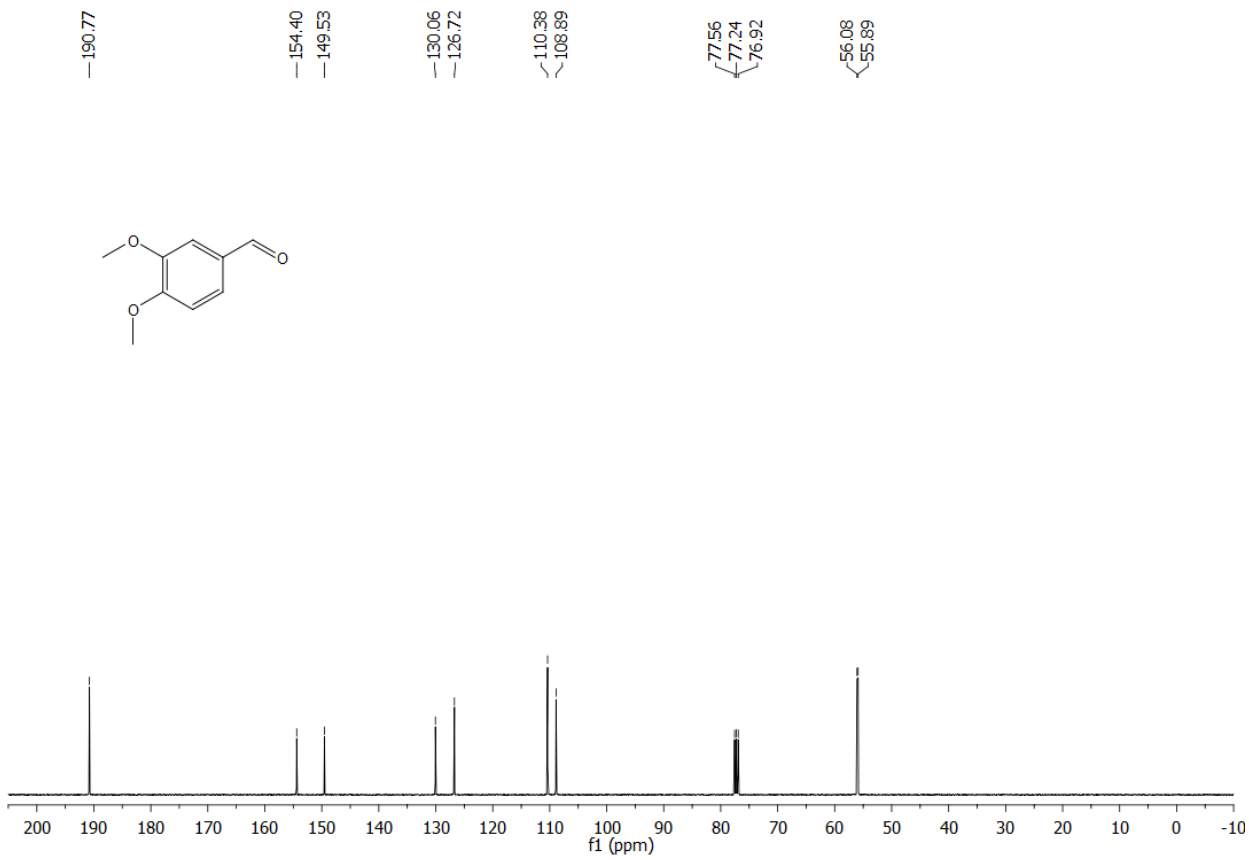


Figure 35: ^{13}C NMR spectrum for **(1j')** in $CDCl_3$ (100MHz, 300K).

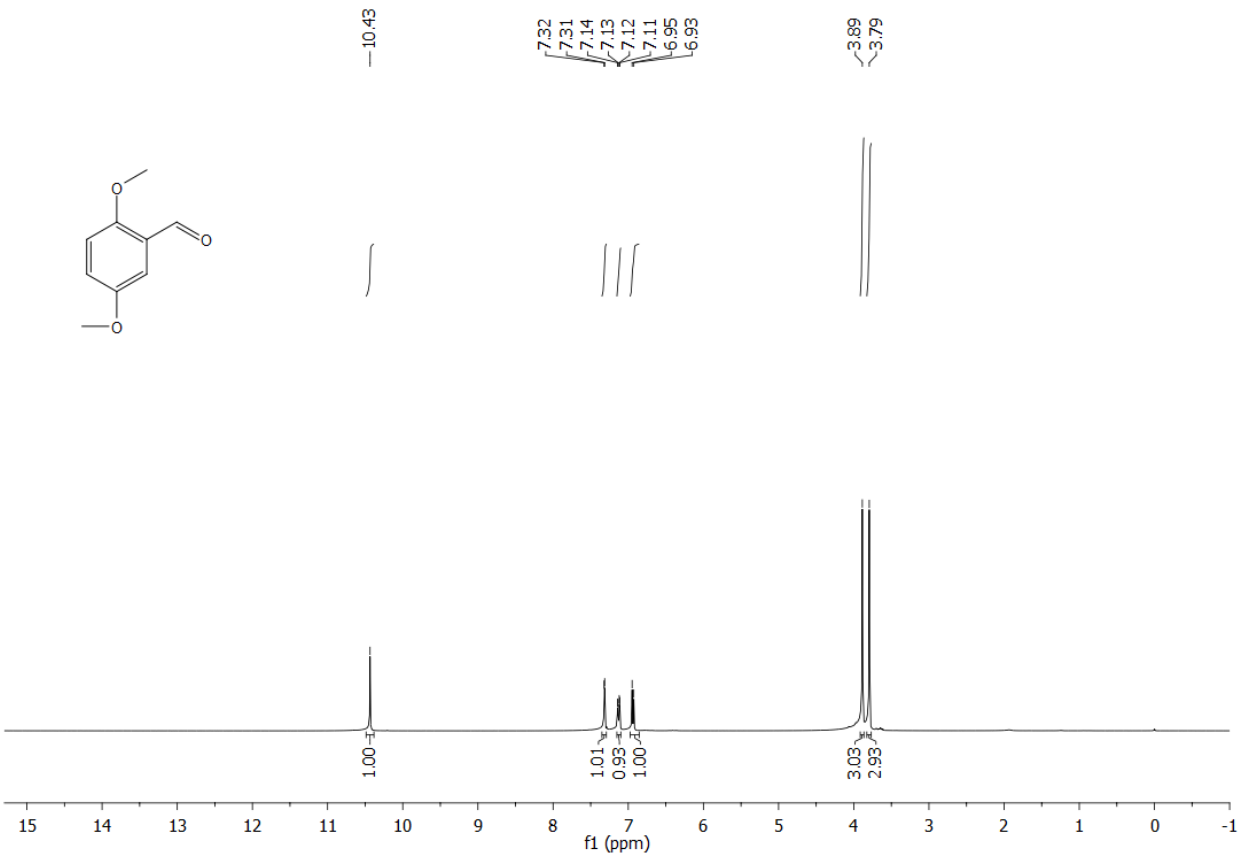


Figure 36: ^{1}H NMR spectrum for (**1k'**) in $CDCl_3$ (400MHz, 300K).

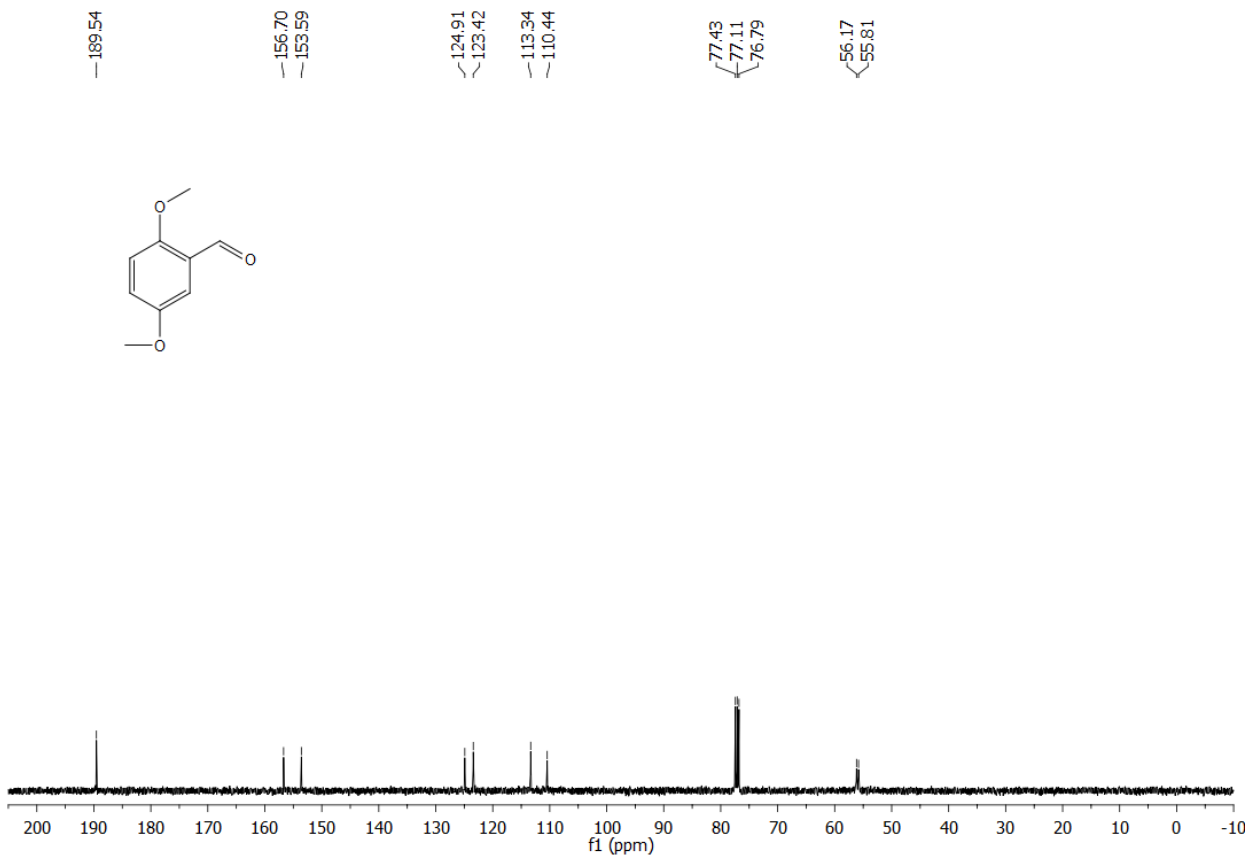


Figure 37: ^{13}C NMR spectrum for (**1k'**) in $CDCl_3$ (100MHz, 300K).

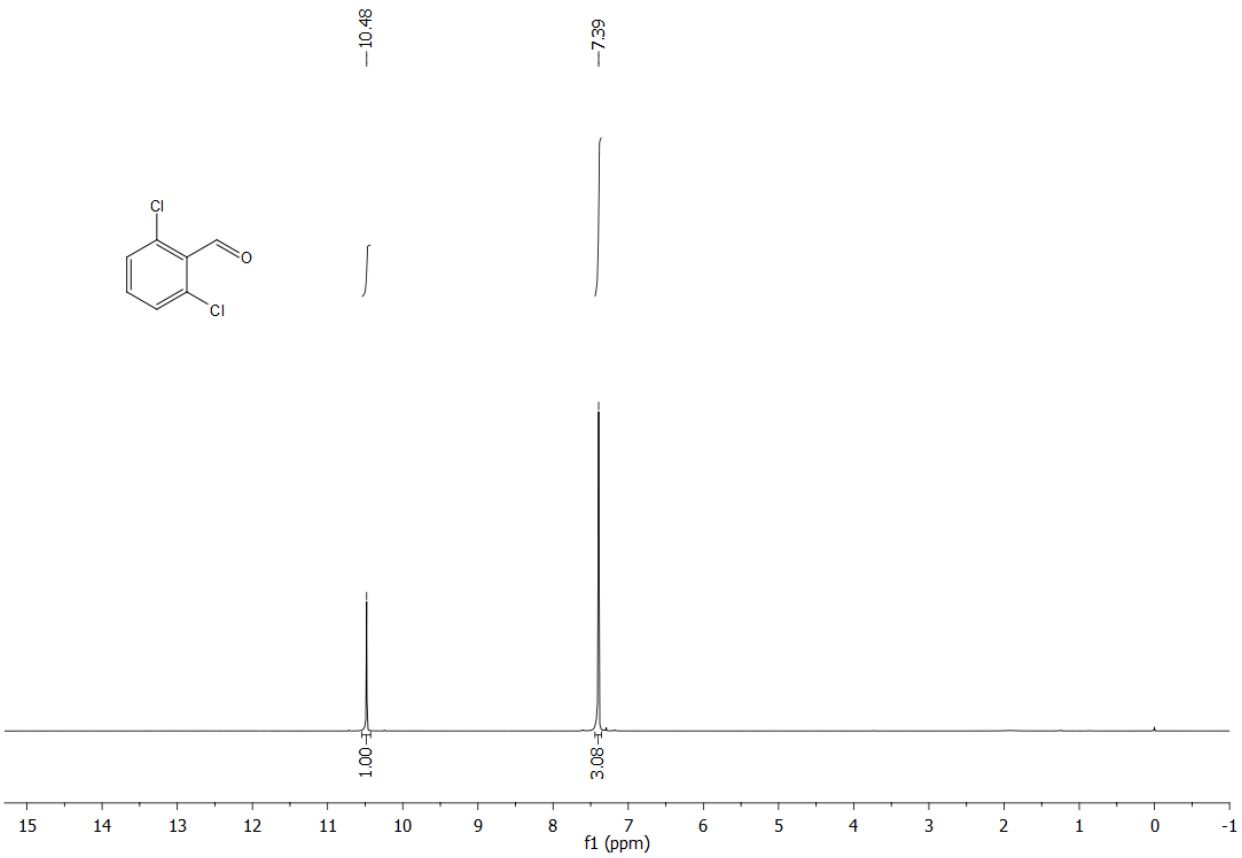


Figure 38: ^{1}H NMR spectrum for (**1l'**) in $CDCl_3$ (400MHz, 300K).

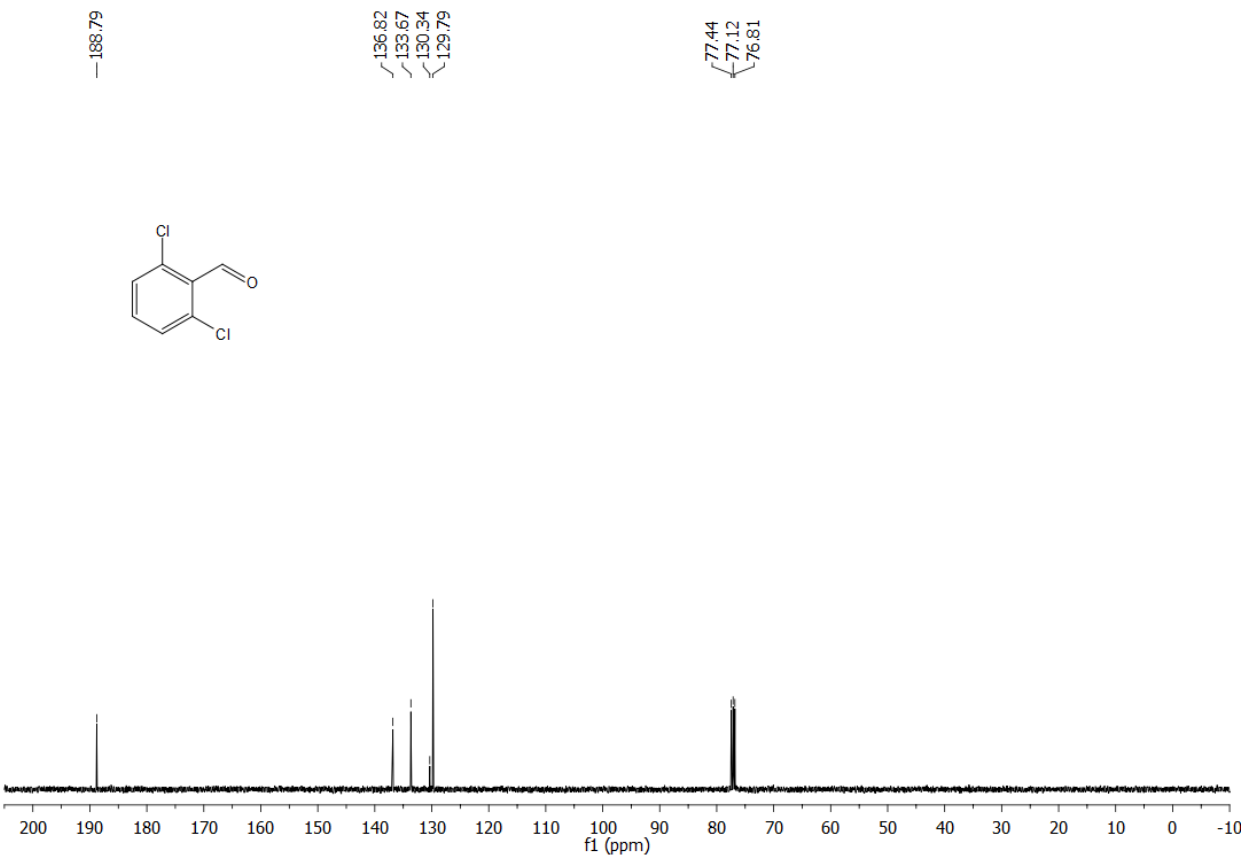


Figure 39: ^{13}C NMR spectrum for (**1l'**) in $CDCl_3$ (100MHz, 300K).

12. NMR spectra for benzylidinemalonitrile intermediate

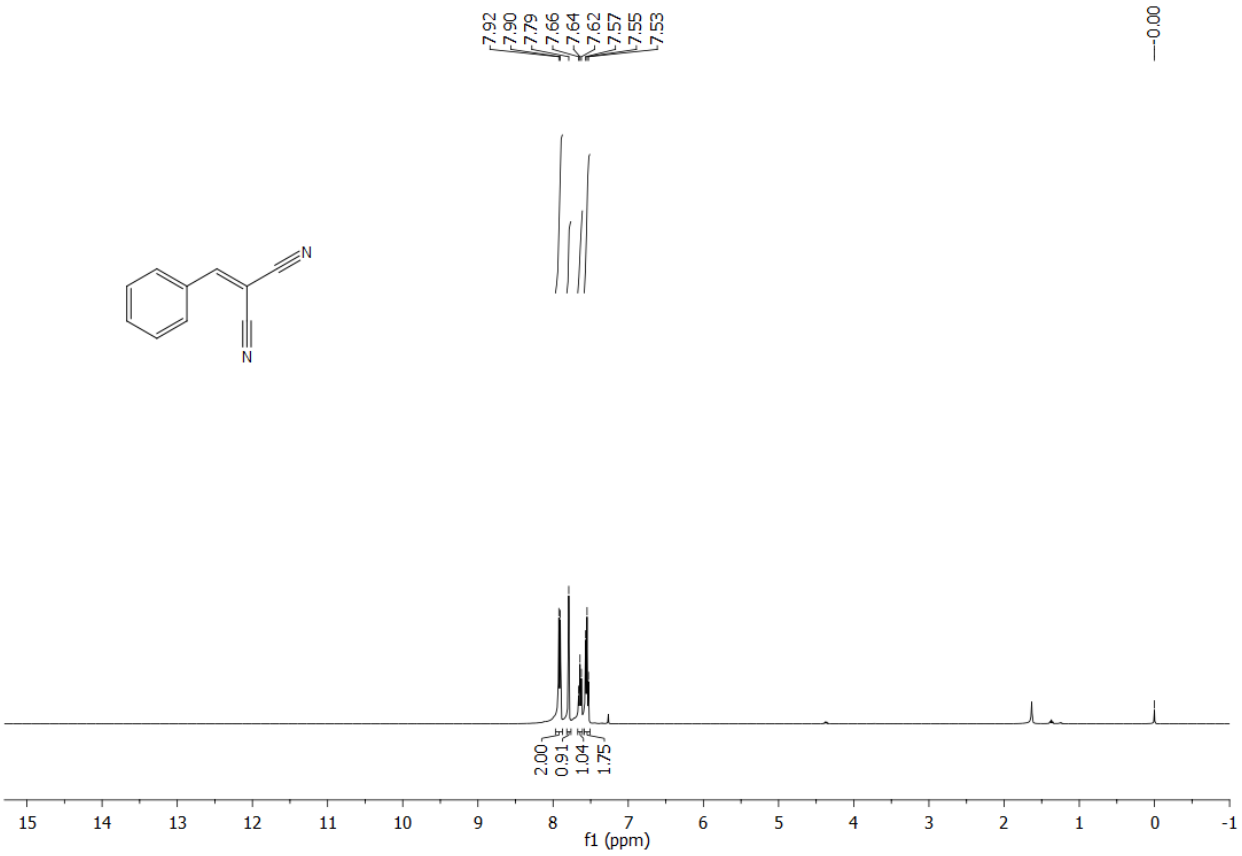


Figure 40: ^{1}H NMR spectrum for (**2a'**) in $CDCl_3$ (400MHz, 300K).

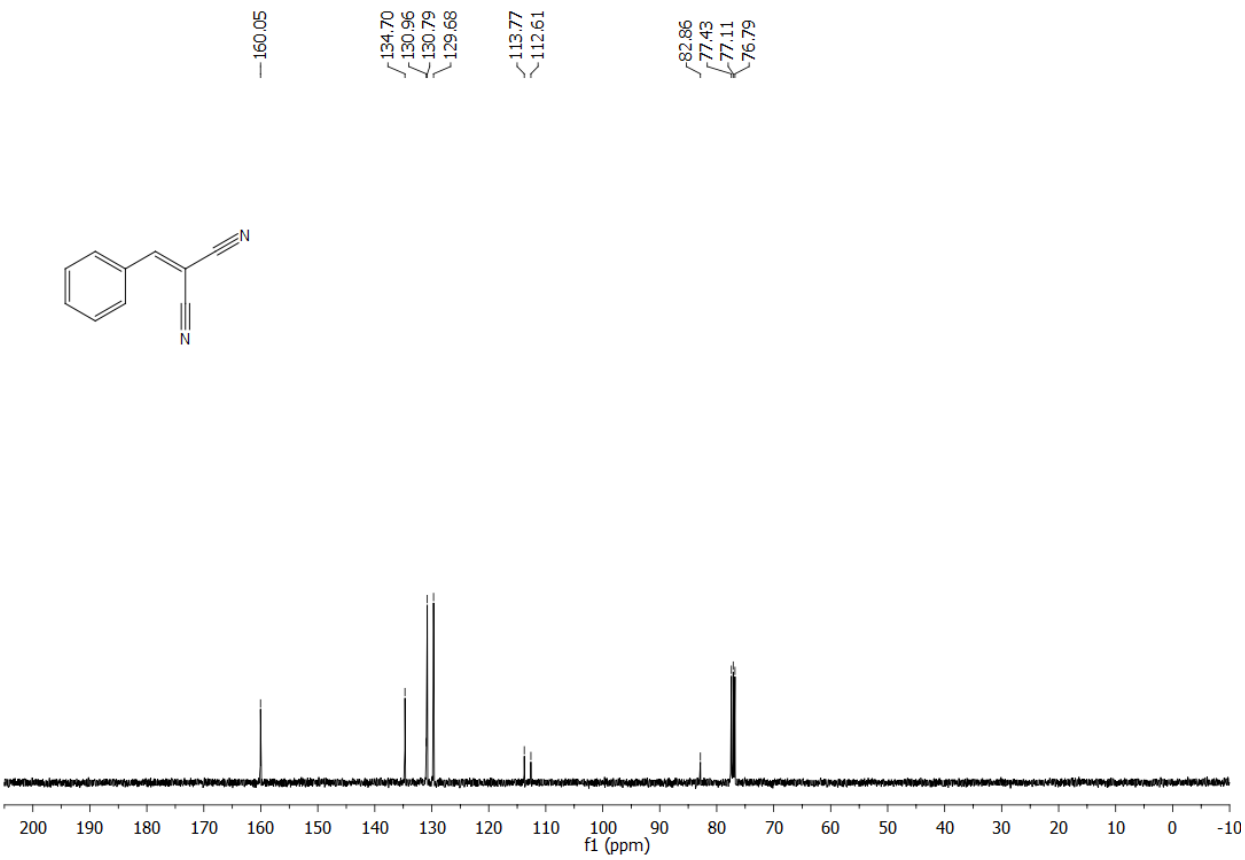


Figure 41: ^{13}C NMR spectrum for (**2a'**) in $CDCl_3$ (100MHz, 300K).

13. NMR spectra for chromene products

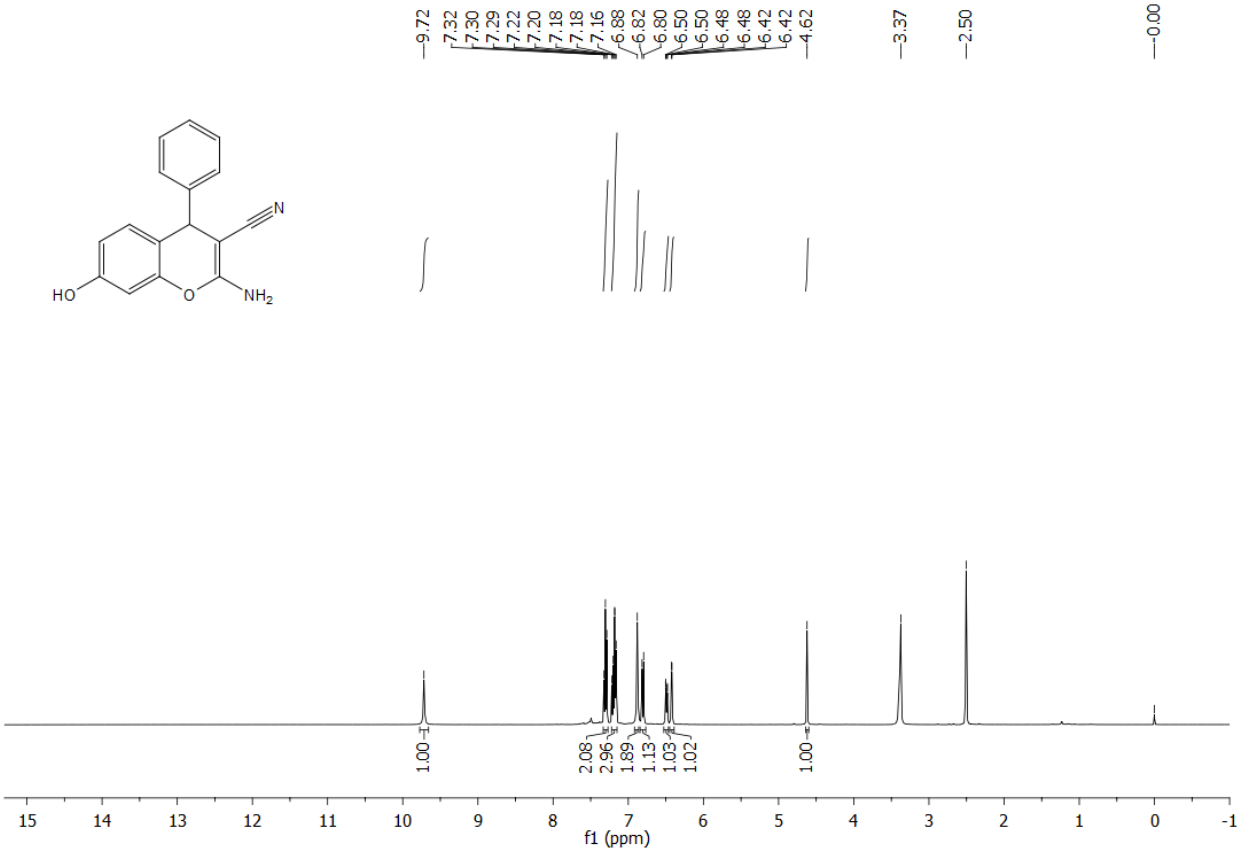


Figure 42: ^{1}H NMR spectrum for (**4a**) in DMSO-d_6 (400MHz, 300K).

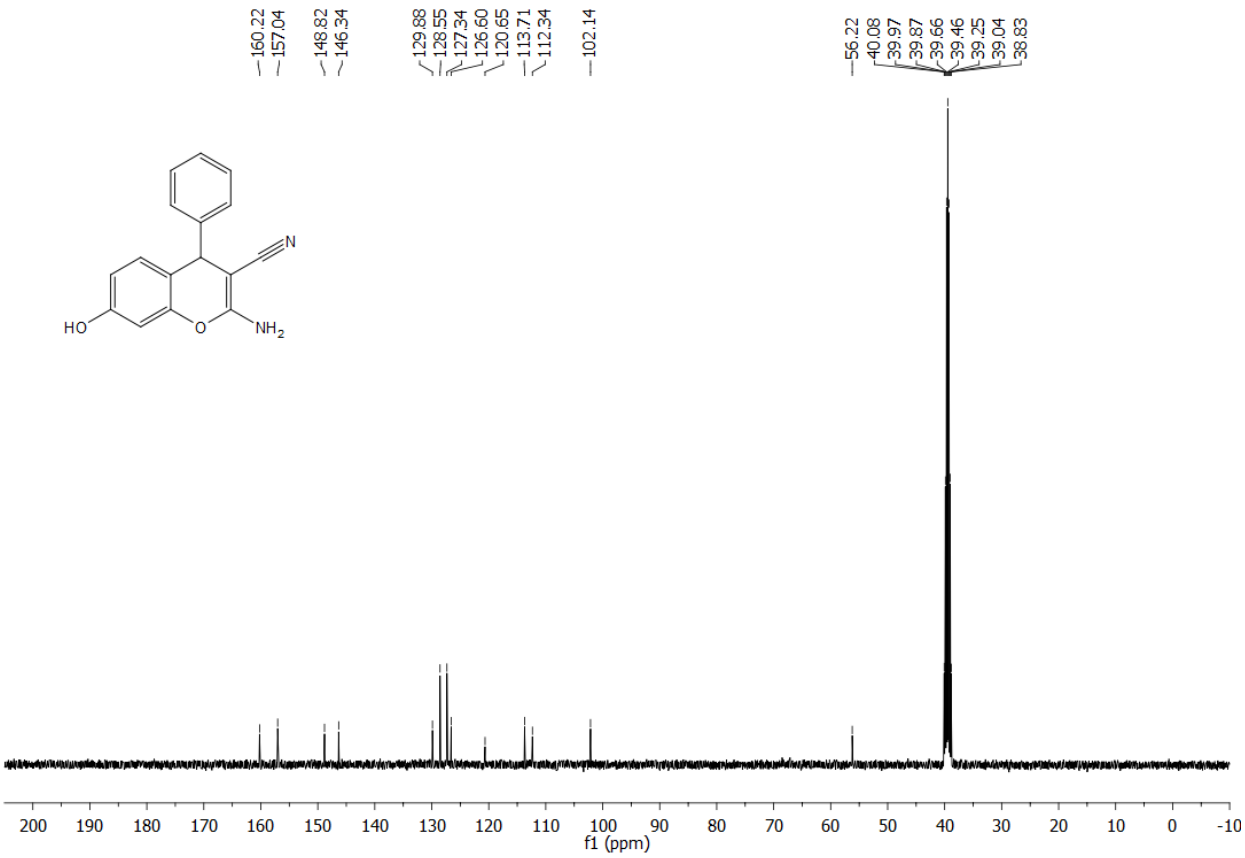


Figure 43: ^{13}C NMR spectrum (**4a**) in DMSO-d_6 (100MHz, 300K).

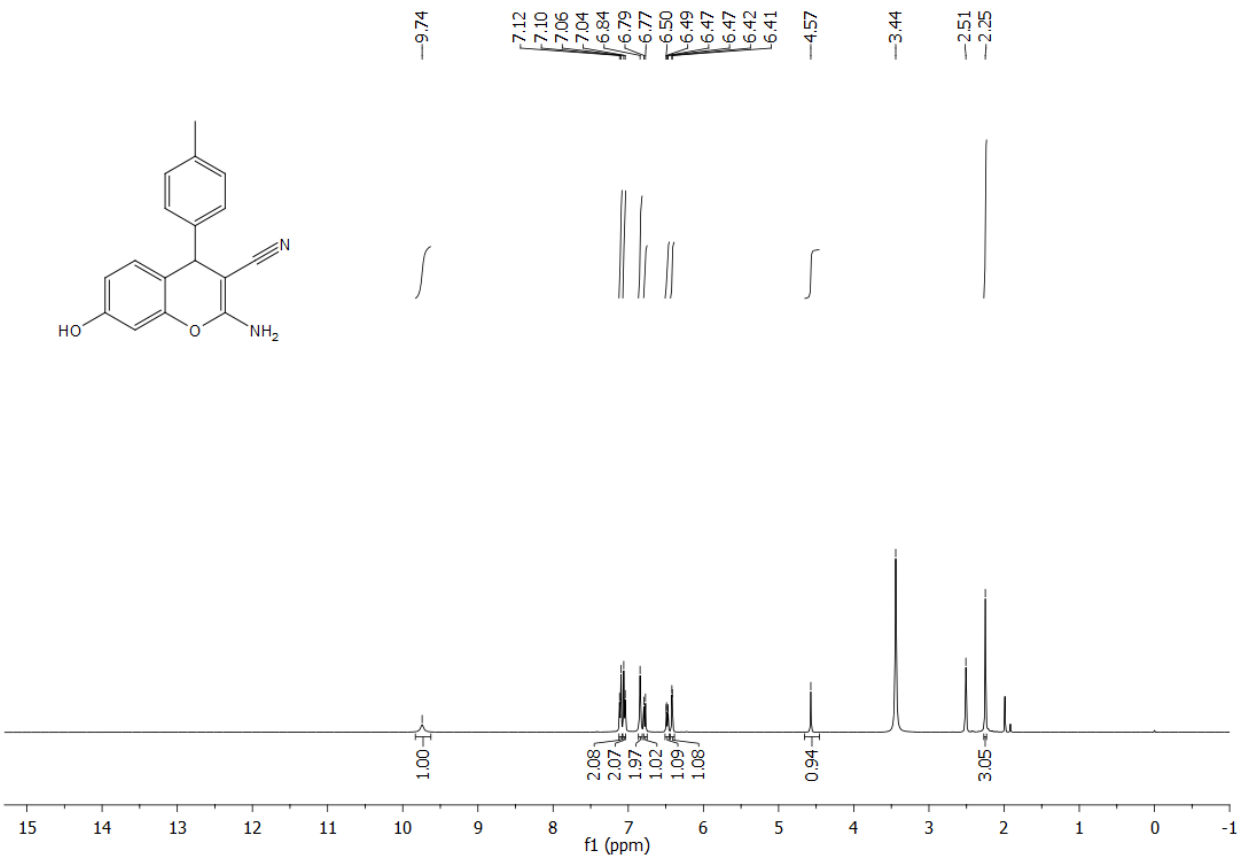


Figure 44: ^{1}H NMR spectrum for (**4b**) in DMSO-d_6 (400MHz, 300K).

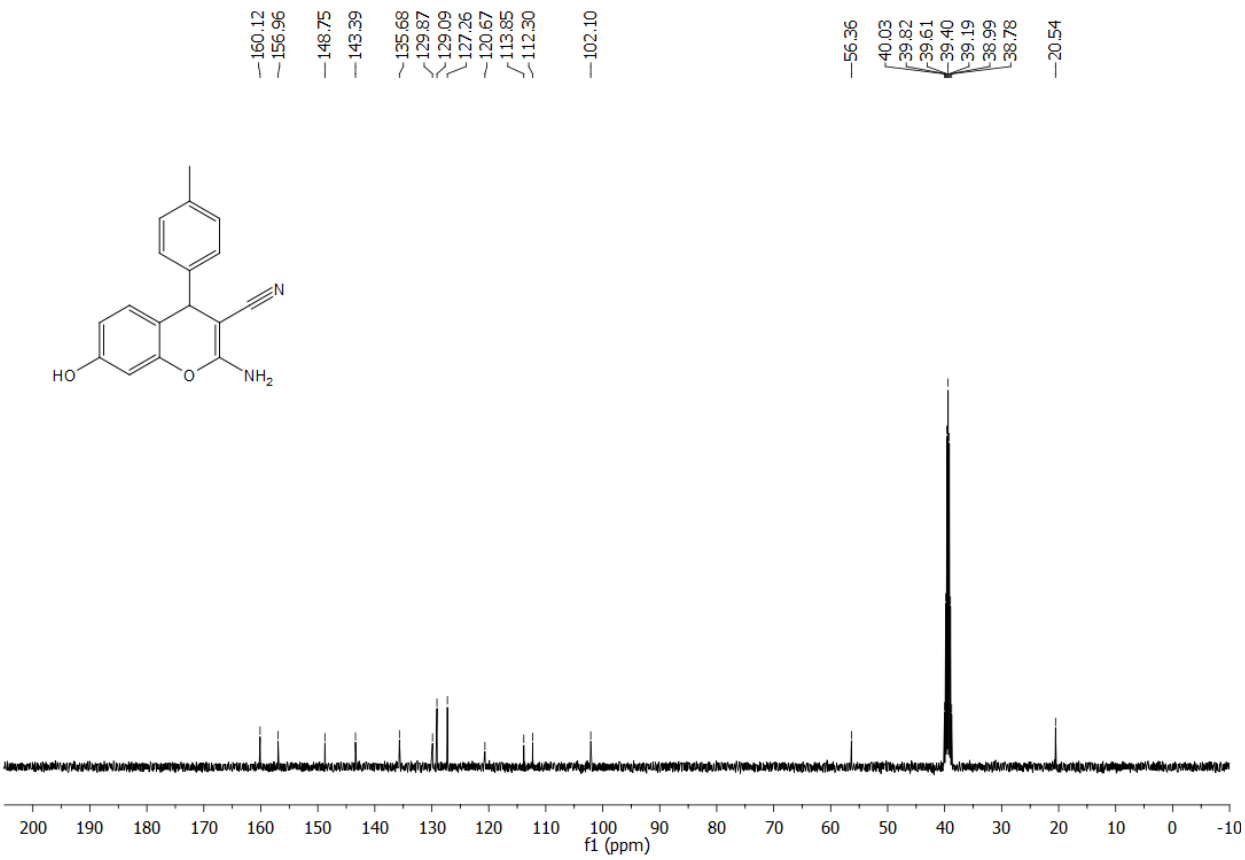


Figure 45: ^{13}C NMR spectrum (**4b**) in DMSO-d_6 (100MHz, 300K).

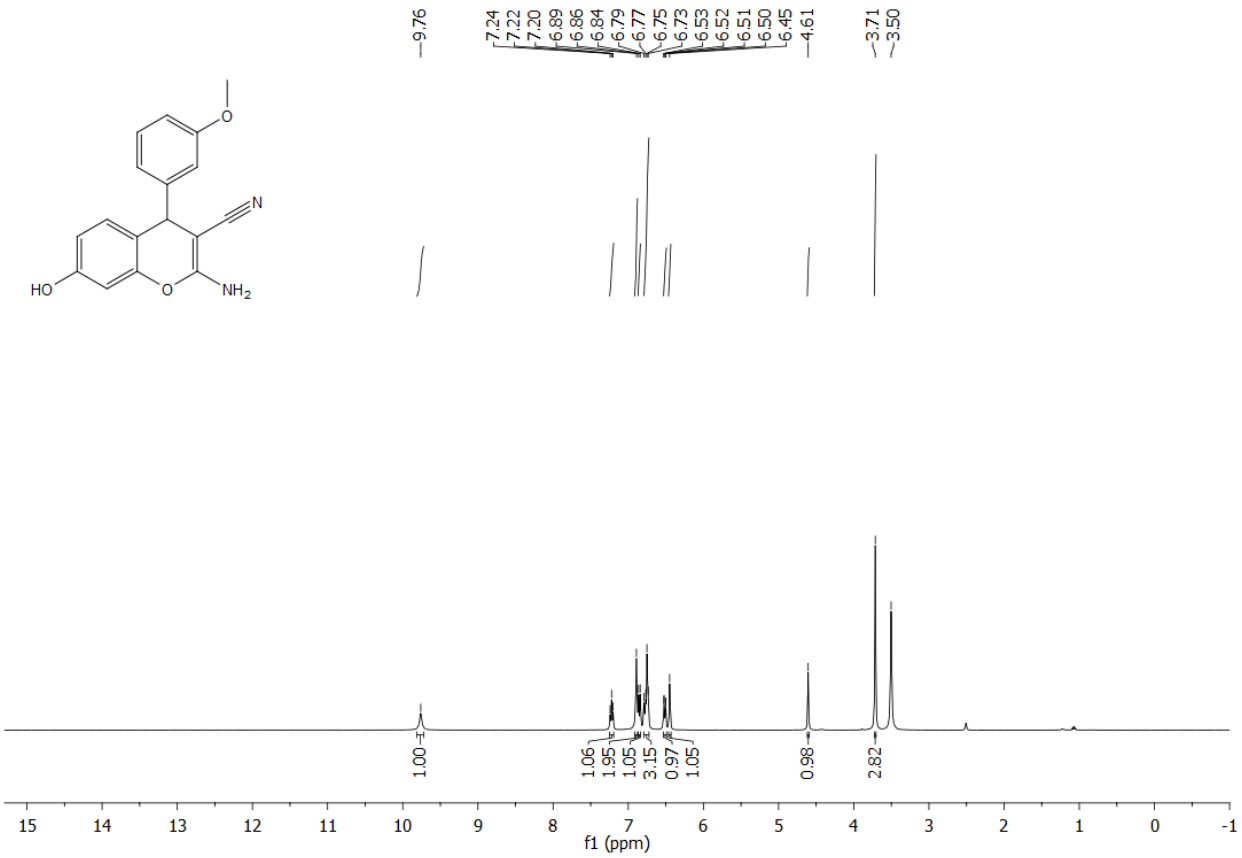


Figure 46: ^{1}H NMR spectrum for (**4c**) in DMSO-d_6 (400MHz, 300K).

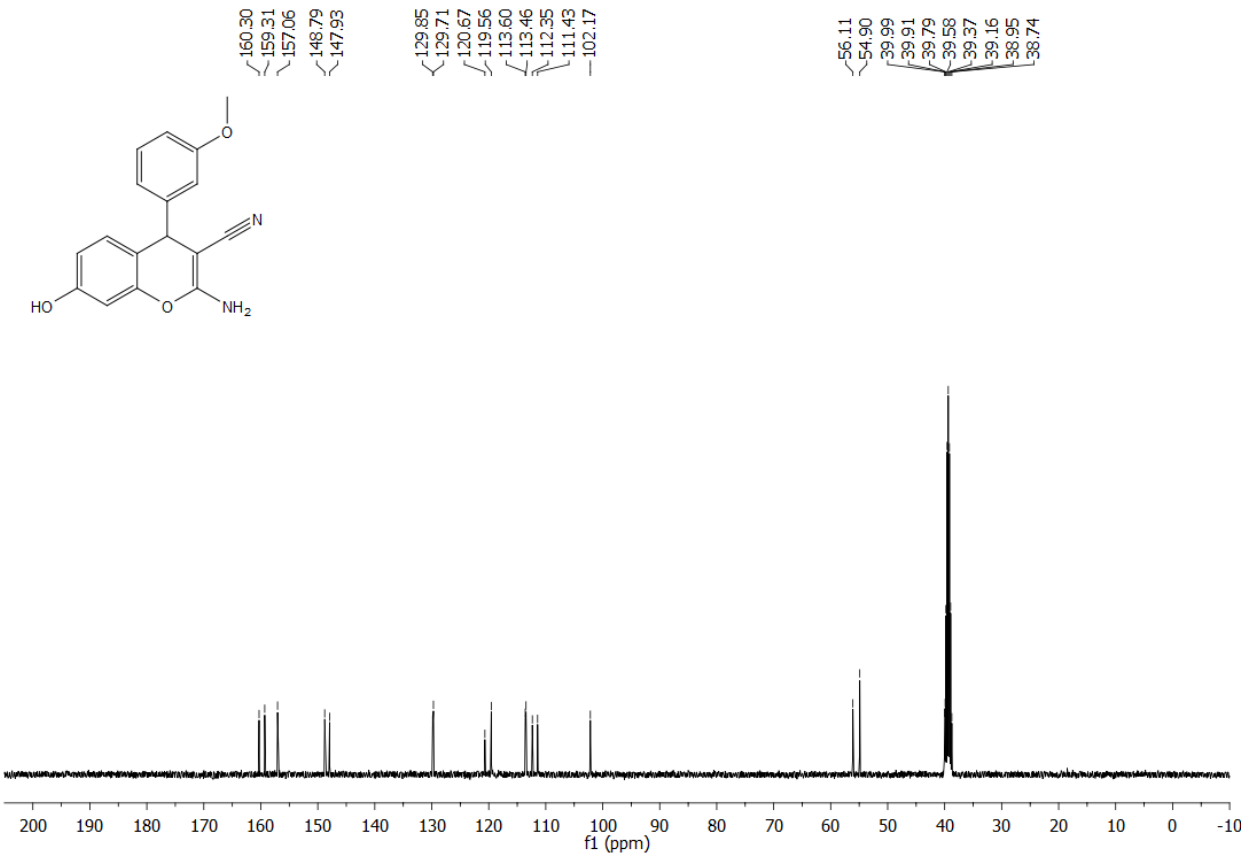


Figure 47: ^{13}C NMR spectrum (**4c**) in DMSO-d_6 (100MHz, 300K).

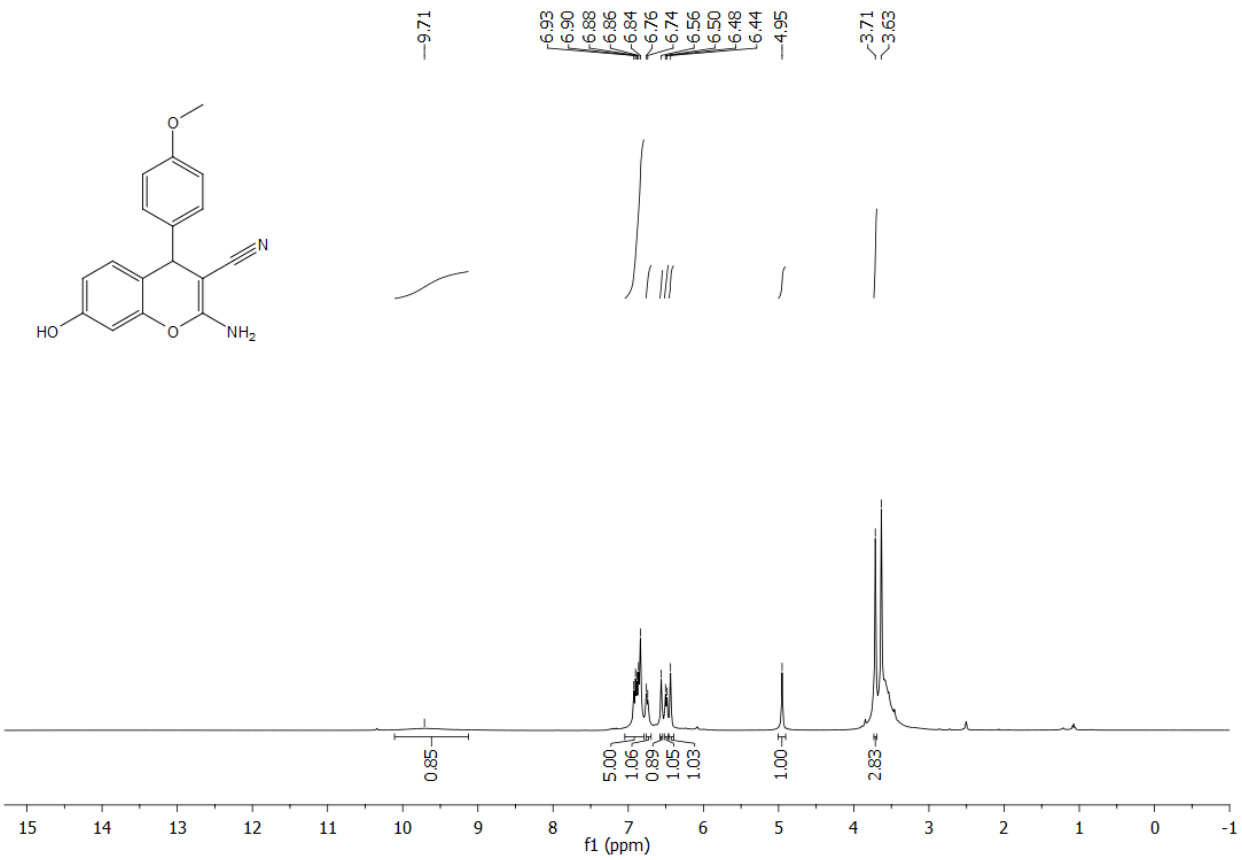


Figure 48: ^{1}H NMR spectrum for (**4d**) in DMSO-d_6 (400MHz, 300K).

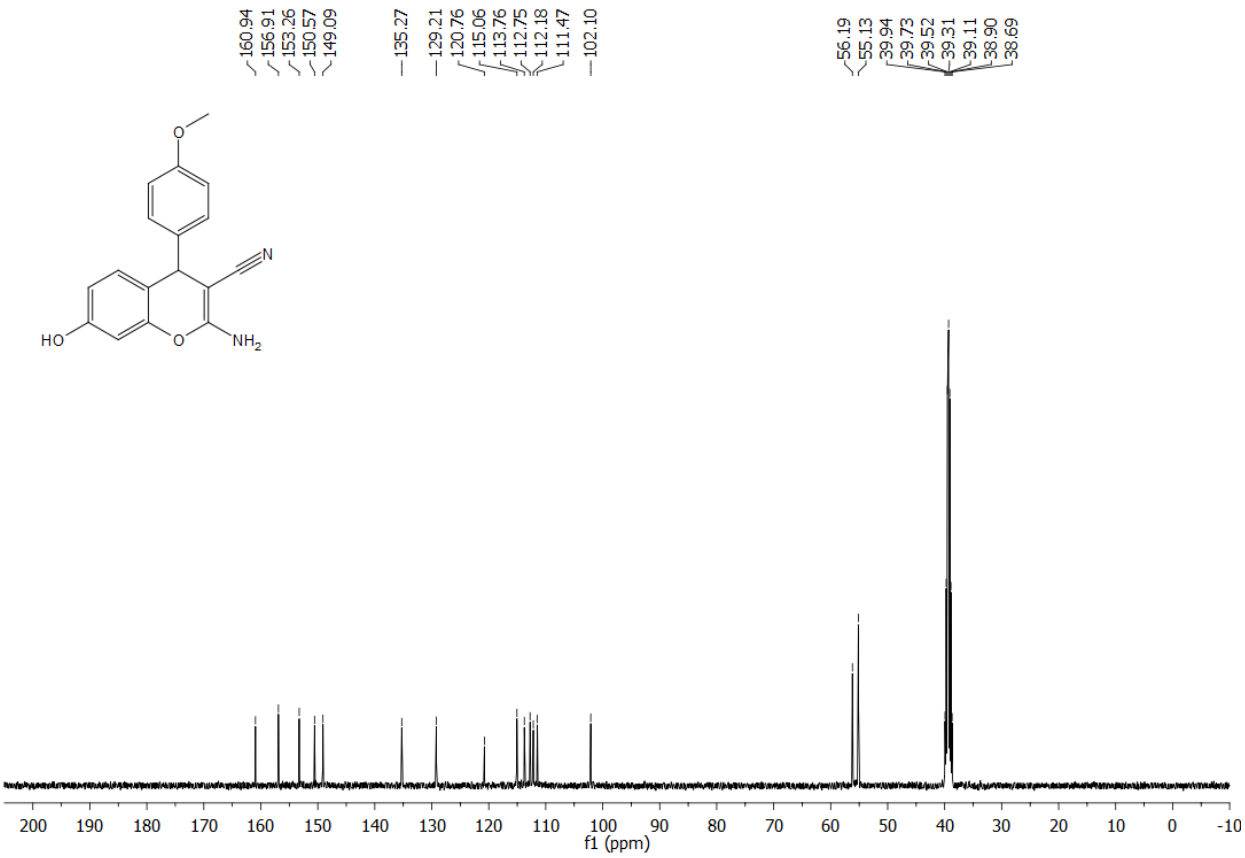


Figure 49: ^{13}C NMR spectrum (**4d**) in DMSO-d_6 (100MHz, 300K).

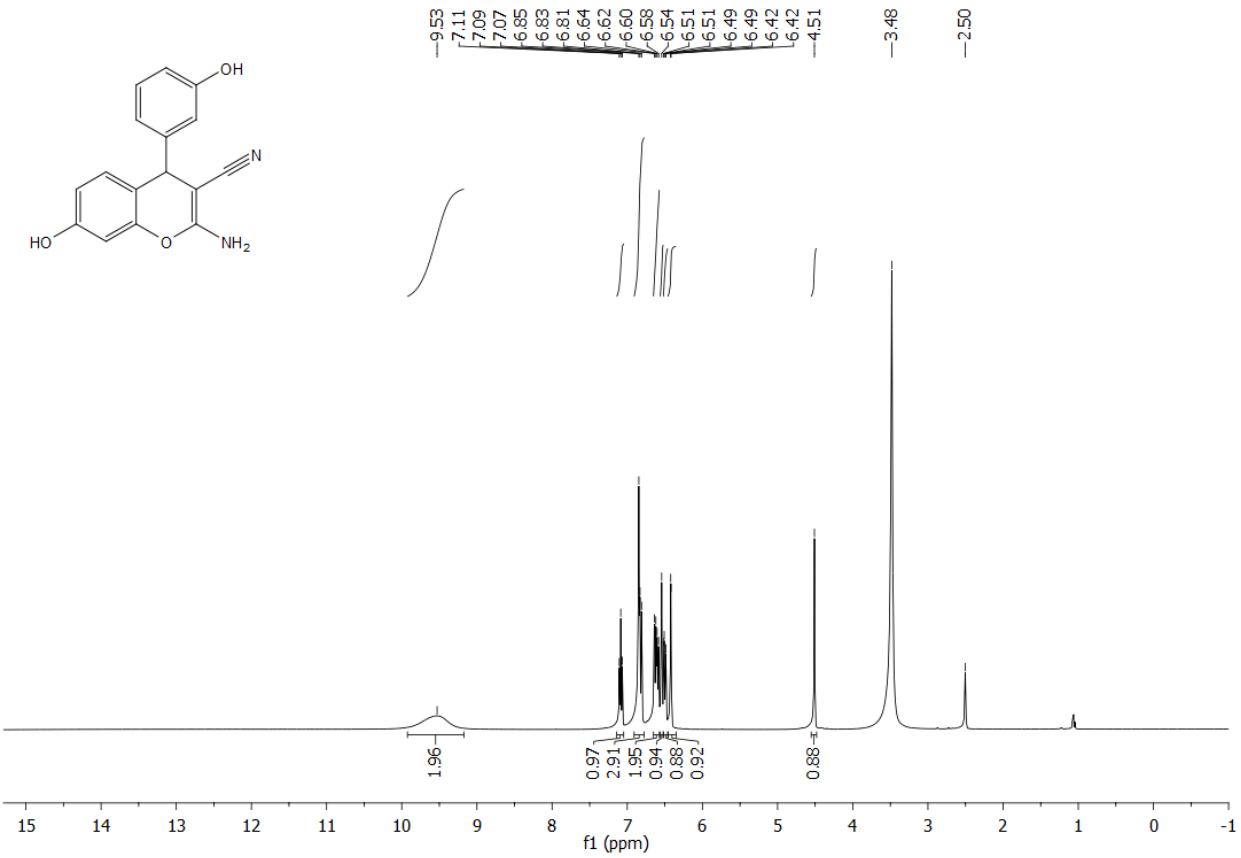


Figure 50: ^{1}H NMR spectrum for (**4e**) in DMSO-d_6 (400MHz, 300K).

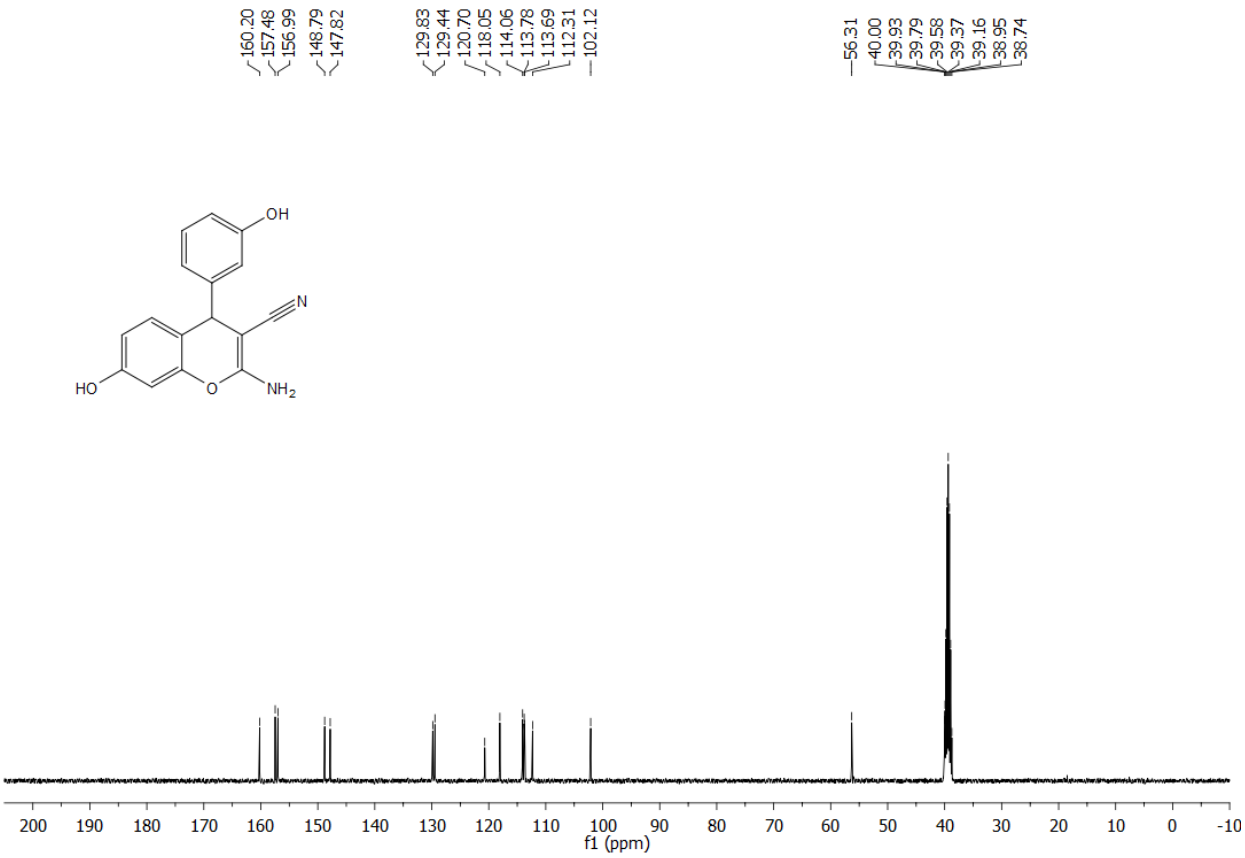


Figure 51: ^{13}C NMR spectrum (**4e**) in DMSO-d_6 (100MHz, 300K).

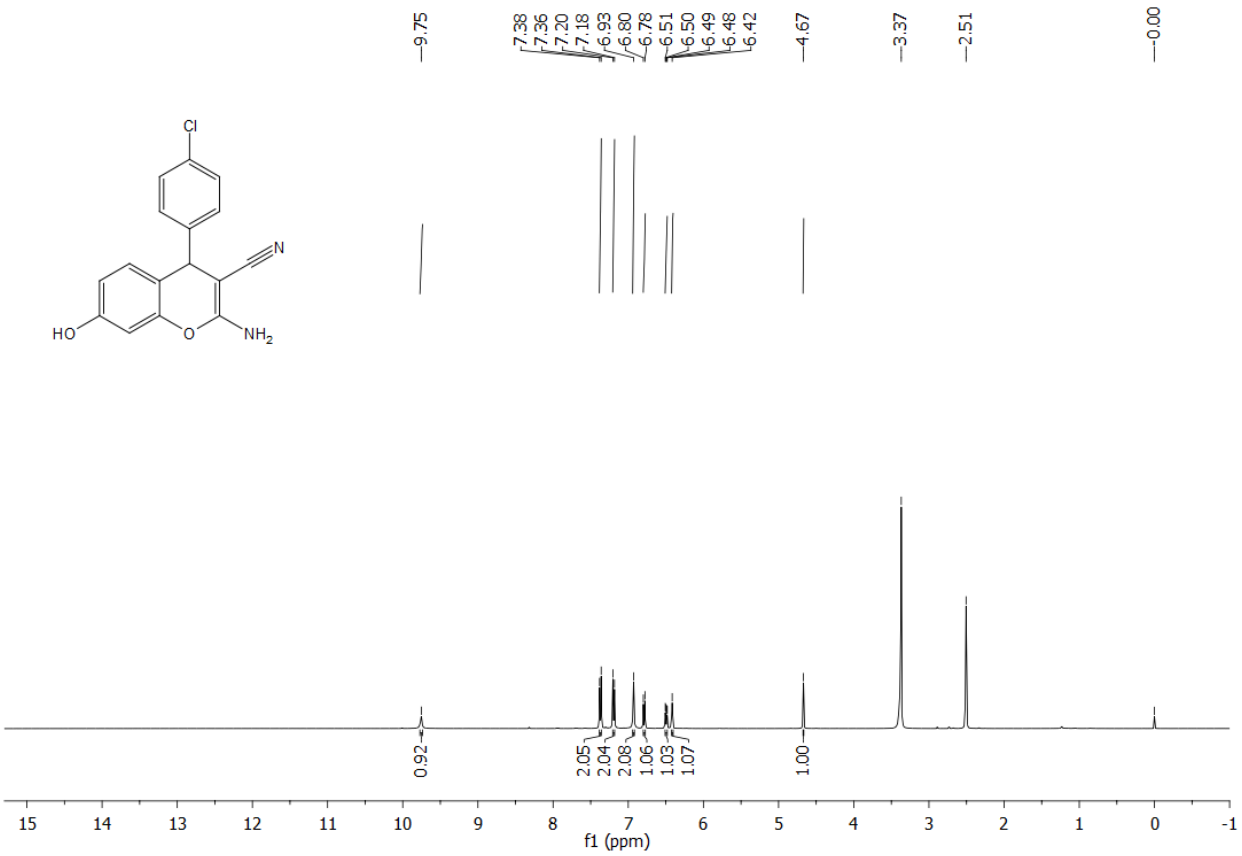


Figure 52: ^{1}H NMR spectrum for (**4f**) in DMSO-d_6 (400MHz, 300K).

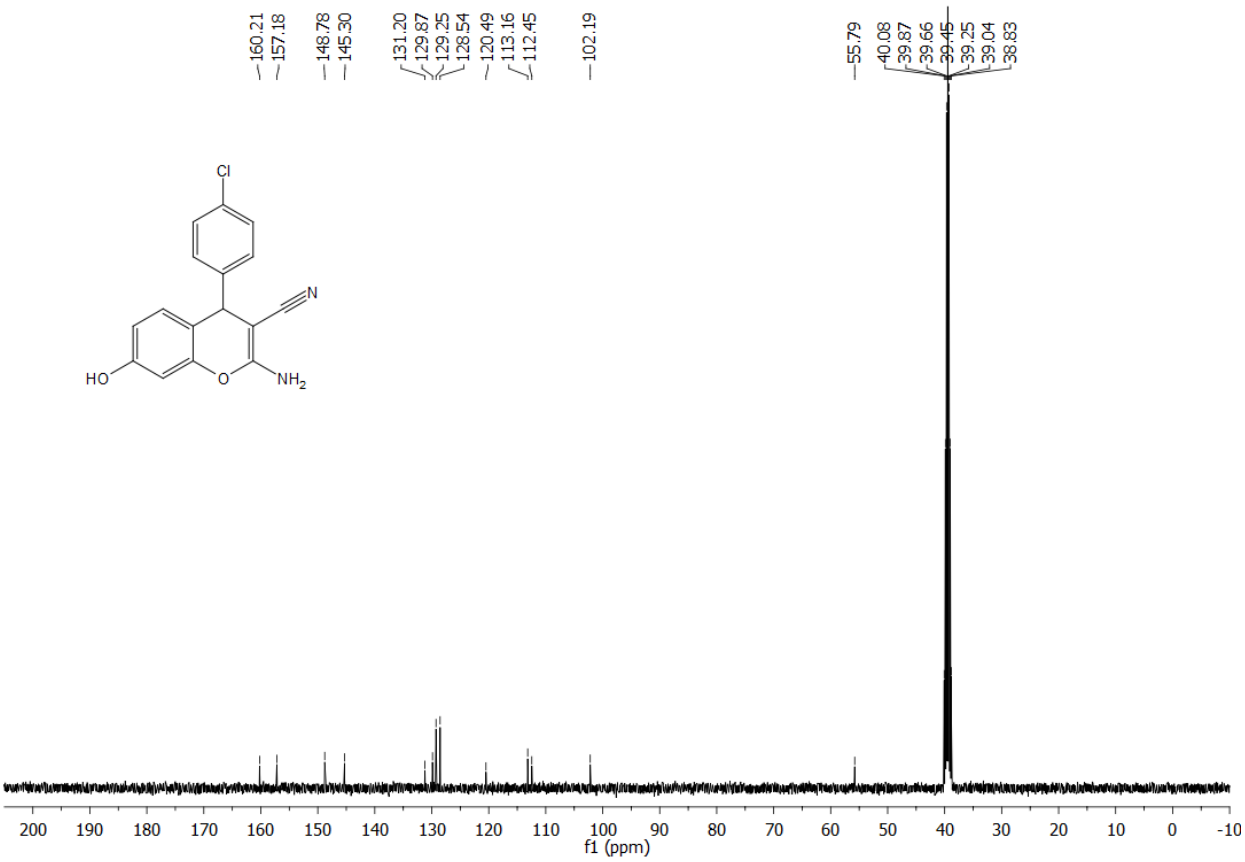


Figure 53: ^{13}C NMR spectrum (**4f**) in DMSO-d_6 (100MHz, 300K).

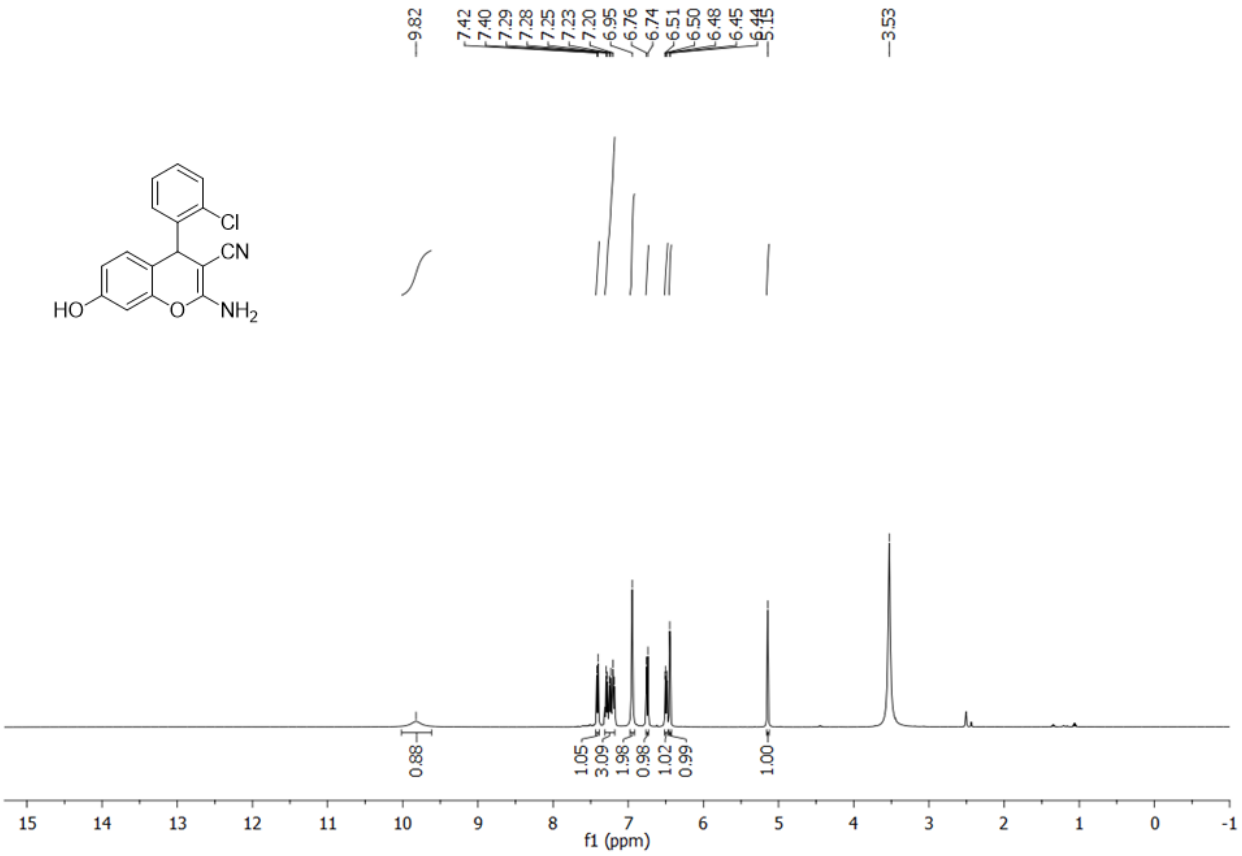


Figure 54: ^{1}H NMR spectrum for (**4g**) in DMSO-d_6 (400MHz, 300K).

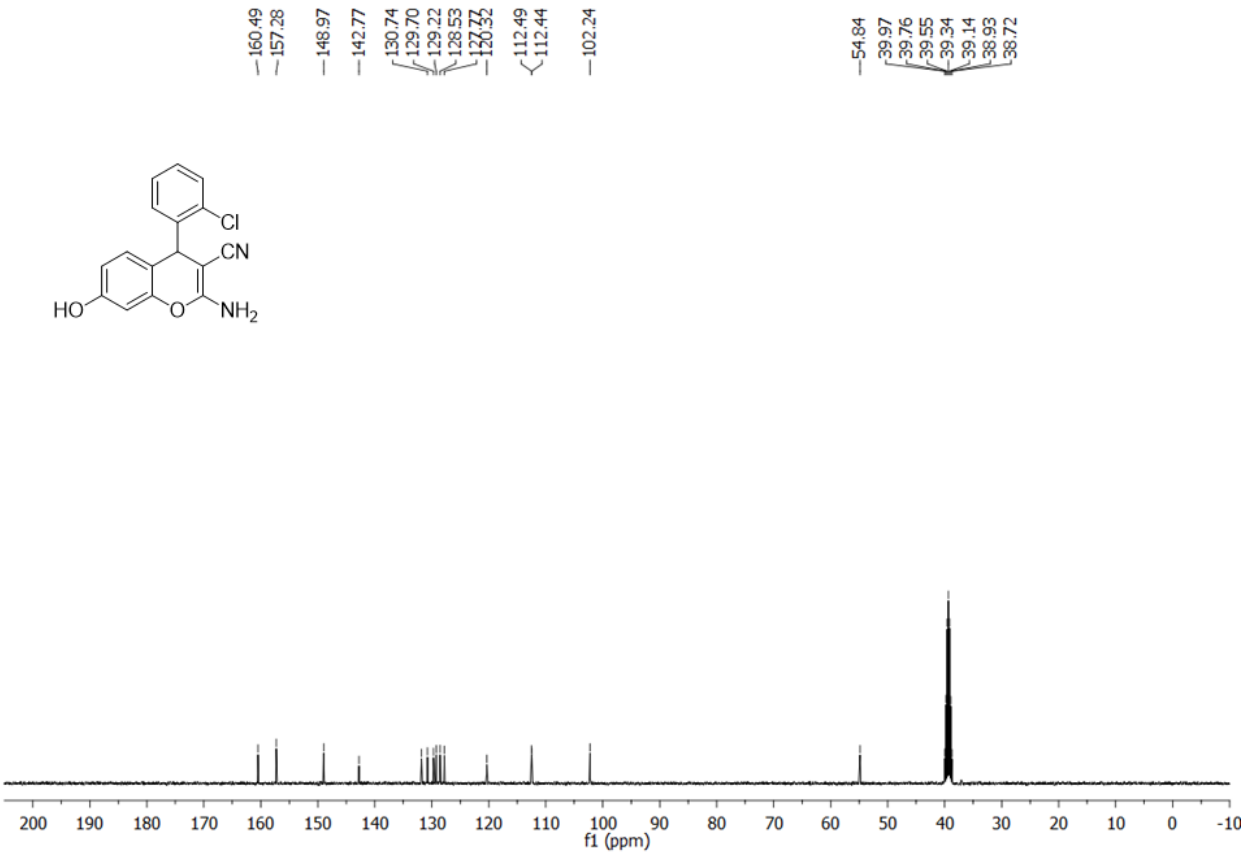


Figure 55: ^{13}C NMR spectrum (**4g**) in DMSO-d_6 (100MHz, 300K).

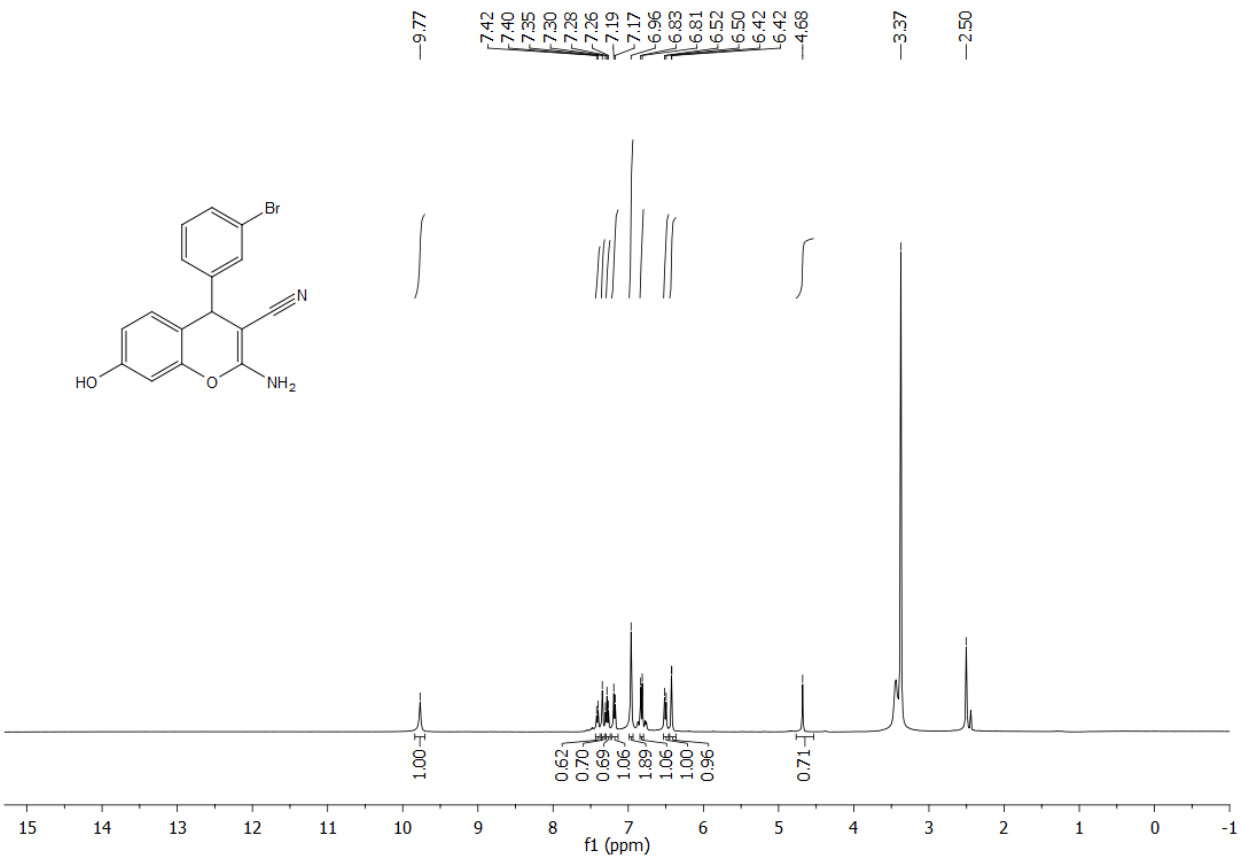


Figure 56: ^{1}H NMR spectrum for (**4h**) in DMSO-d_6 (400MHz, 300K).

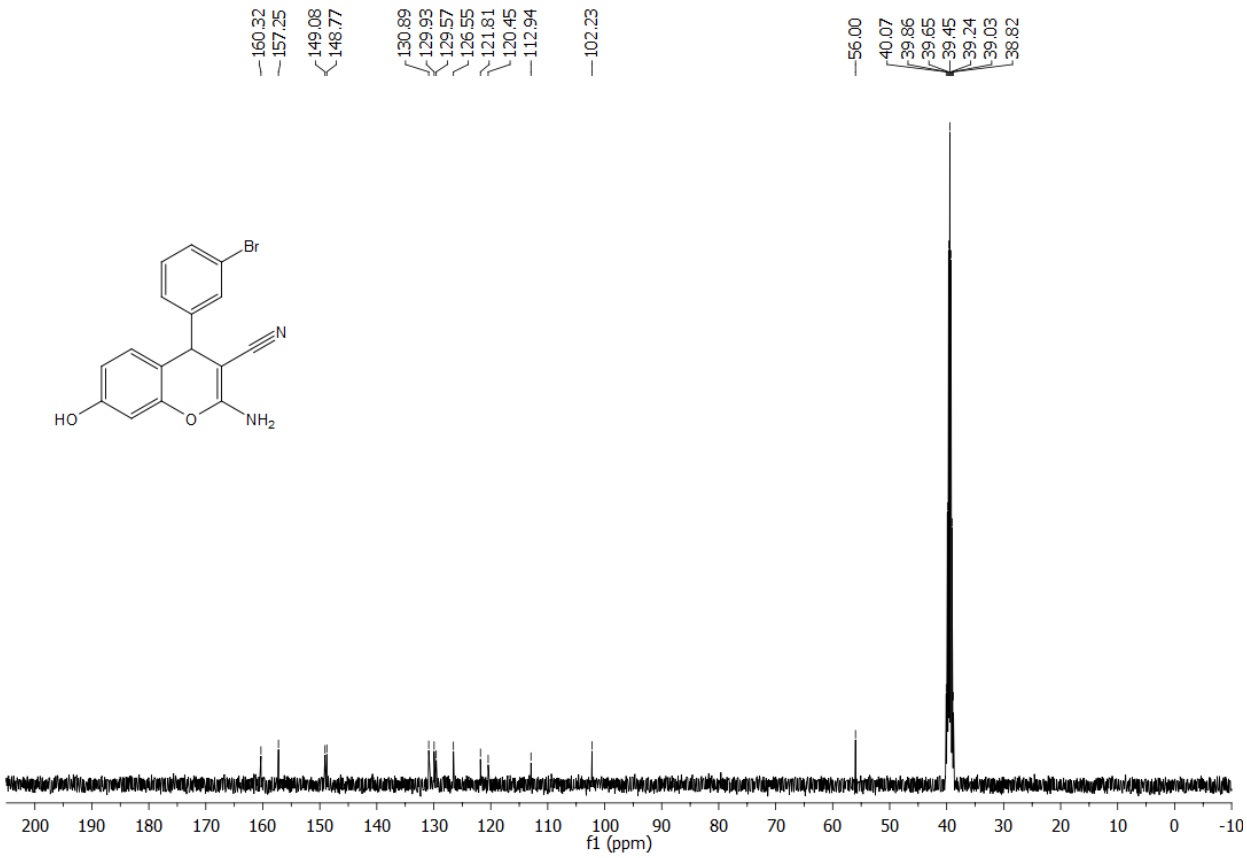


Figure 57: ^{13}C NMR spectrum (**4h**) in DMSO-d_6 (100MHz, 300K).

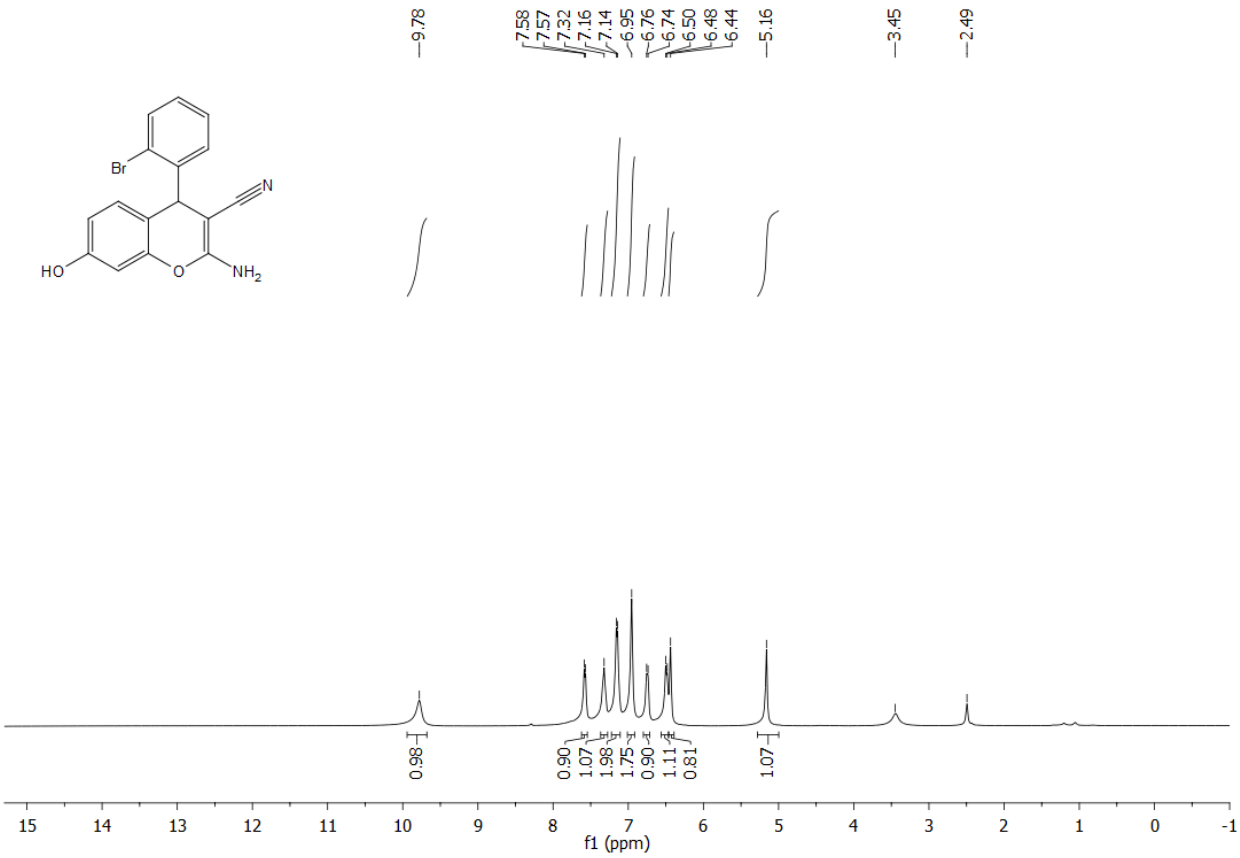


Figure 58: ^{1}H NMR spectrum for (**4i**) in DMSO-d_6 (400MHz, 300K).

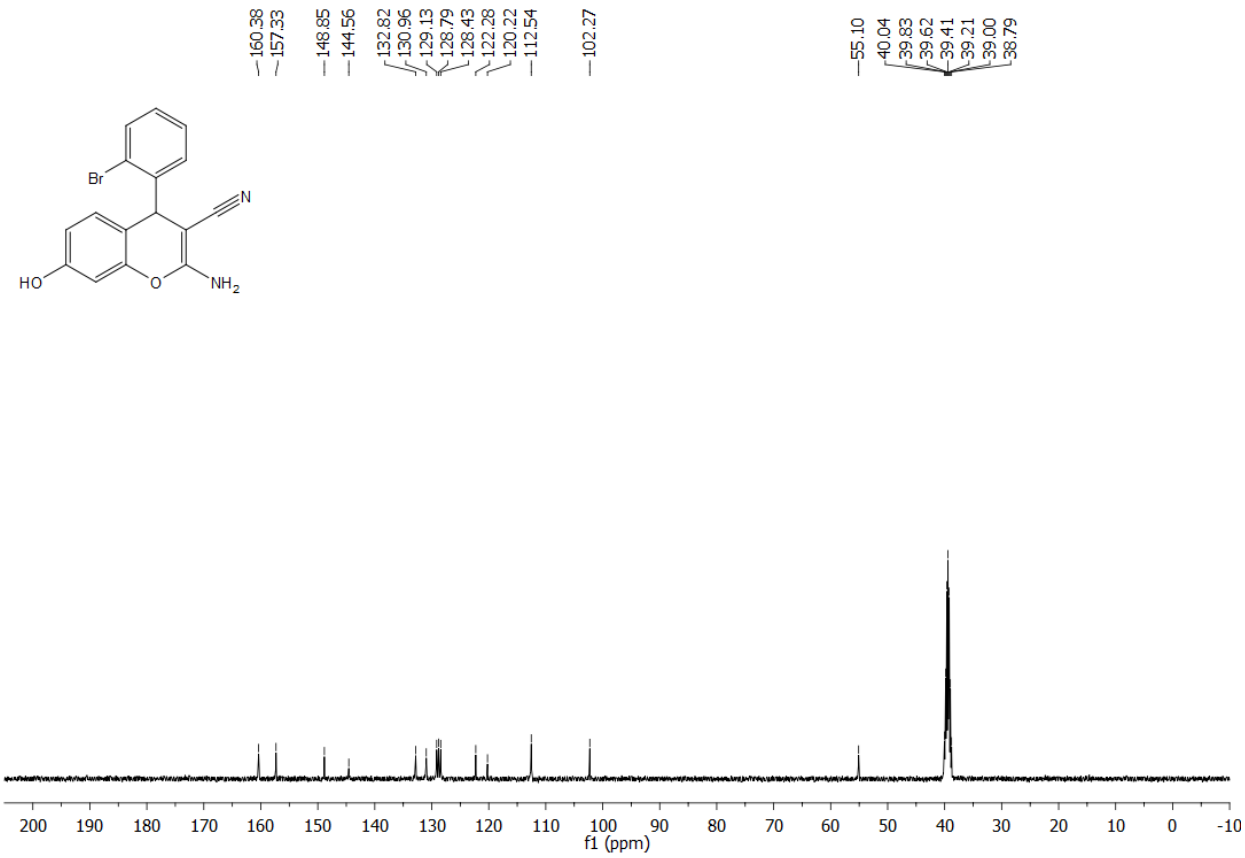


Figure 59: ^{13}C NMR spectrum (**4i**) in DMSO-d_6 (100MHz, 300K).

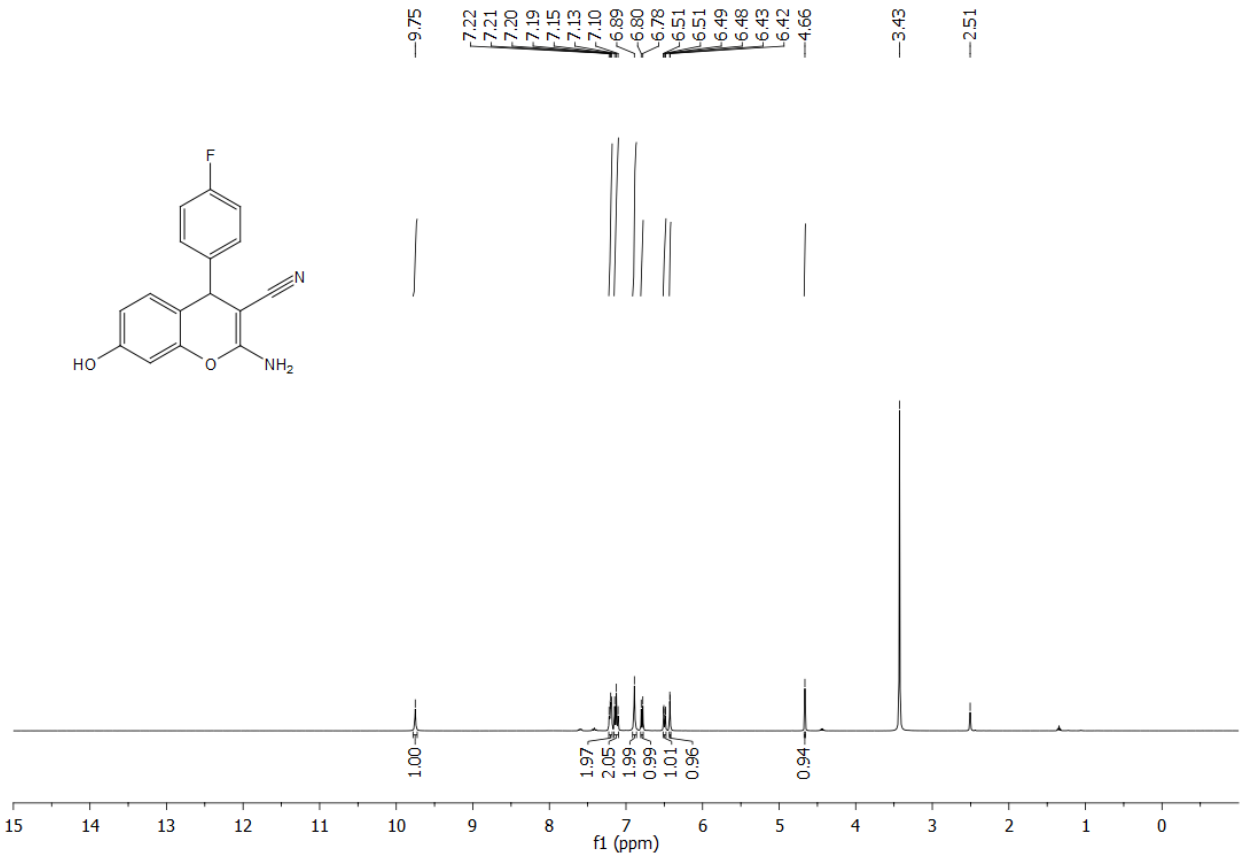


Figure 60: ^{1}H NMR spectrum for (**4j**) in DMSO-d_6 (400MHz, 300K).

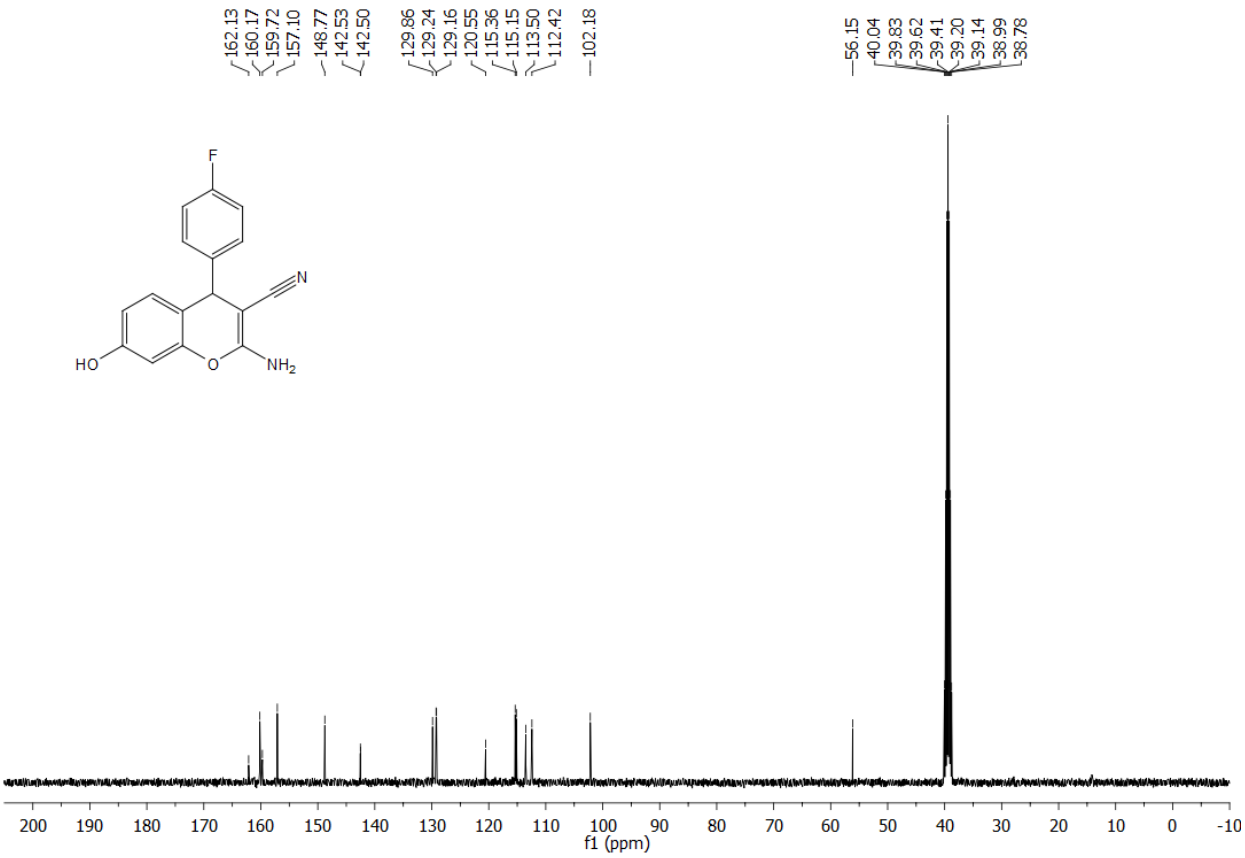


Figure 61: ^{13}C NMR spectrum (**4j**) in DMSO-d_6 (100MHz, 300K).

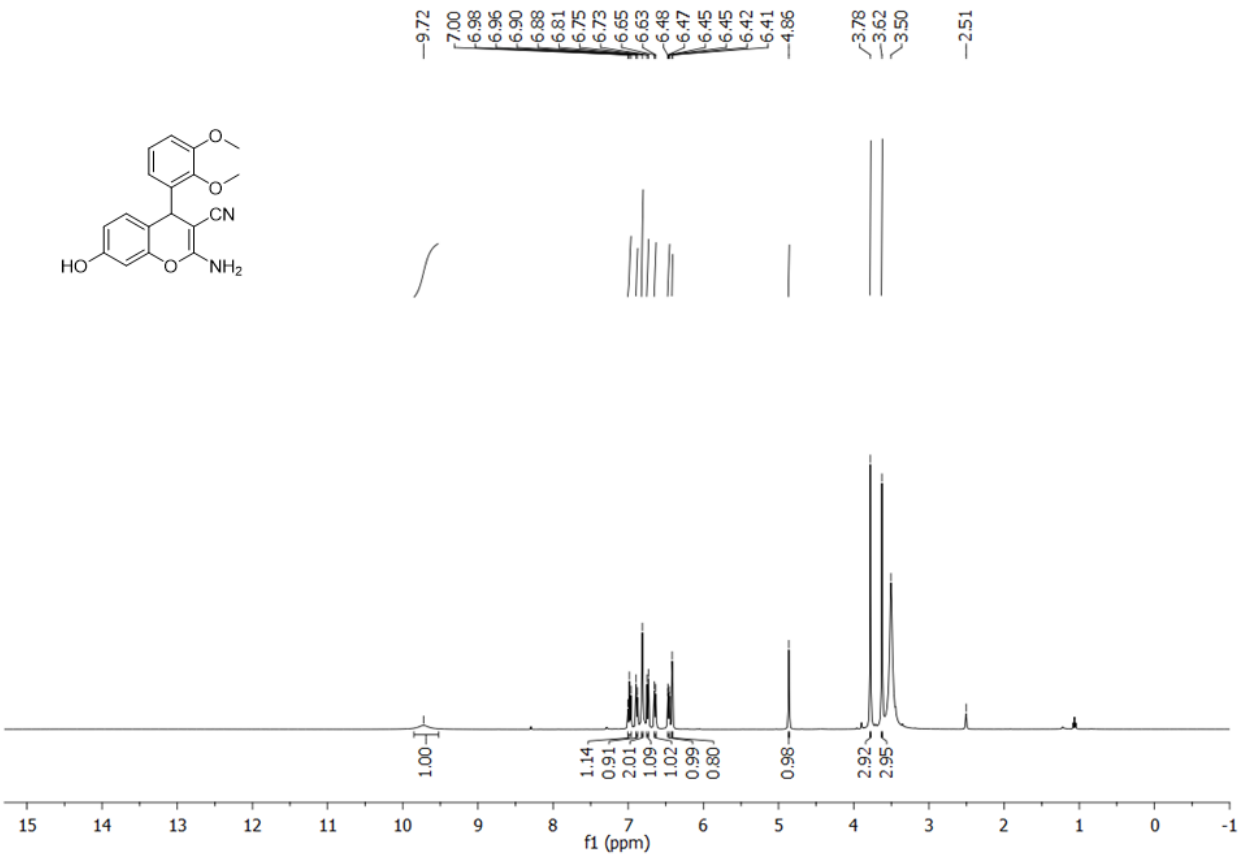


Figure 62: ^{1}H NMR spectrum for (**4k**) in DMSO-d_6 (400MHz, 300K).

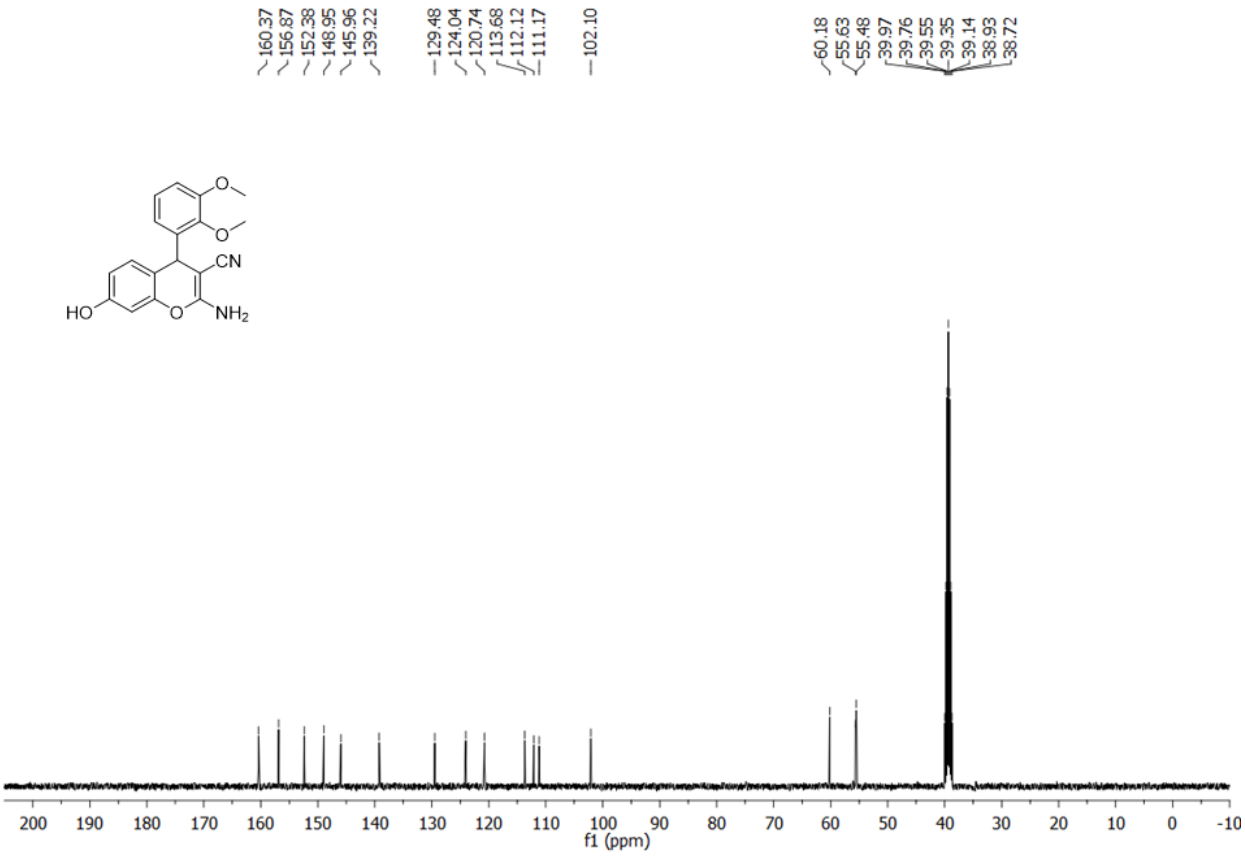


Figure 63: ^{13}C NMR spectrum (**4k**) in DMSO-d_6 (100MHz, 300K).

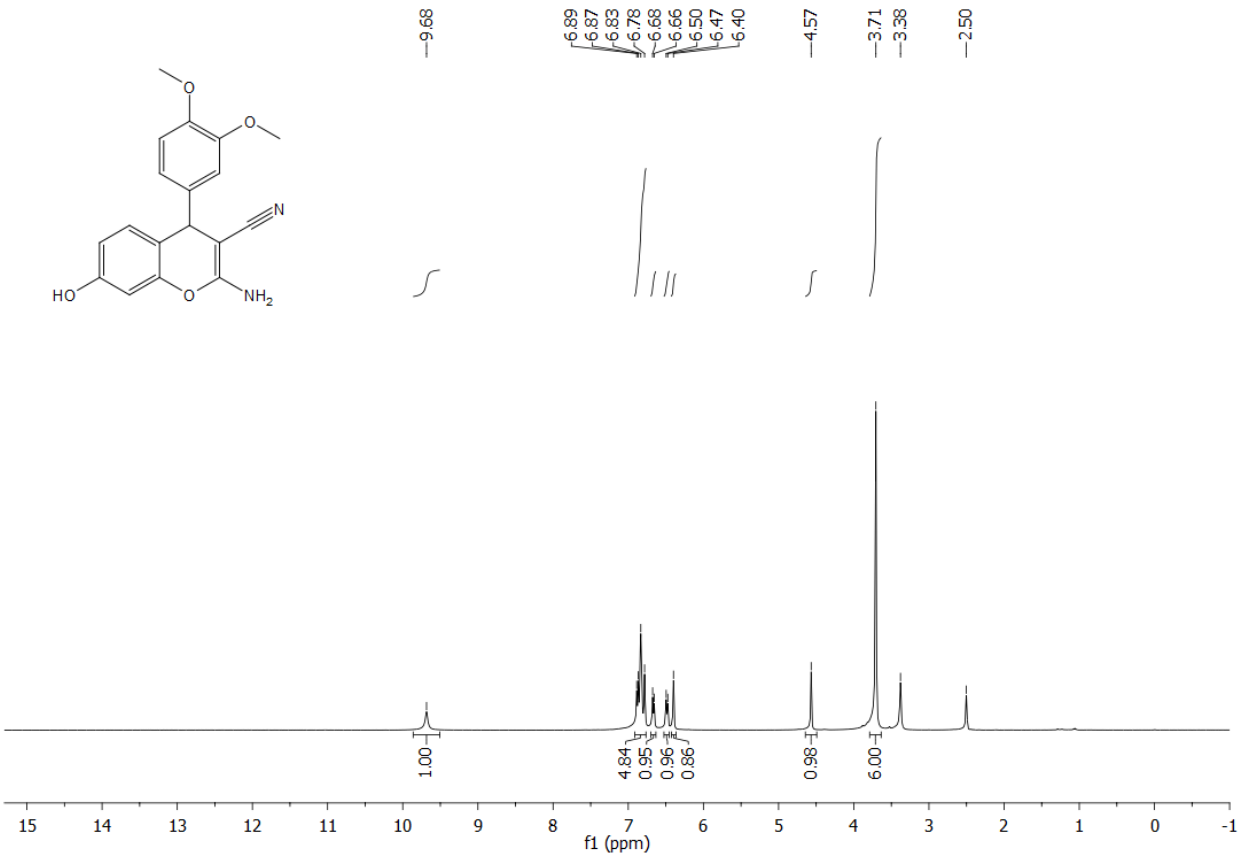


Figure 64: ^{1}H NMR spectrum for (**4l**) in DMSO-d_6 (400MHz, 300K).

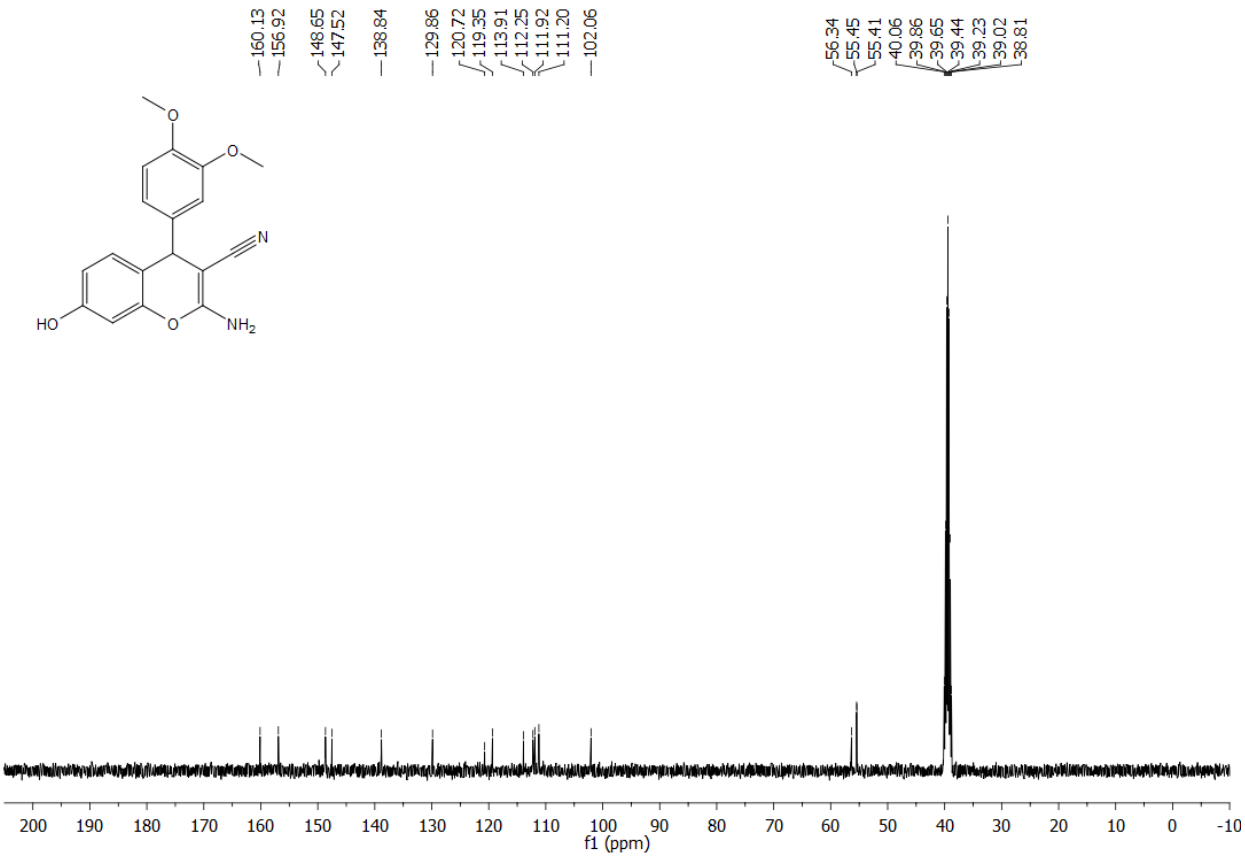


Figure 65: ^{13}C NMR spectrum (**4l**) in DMSO-d_6 (100MHz, 300K).

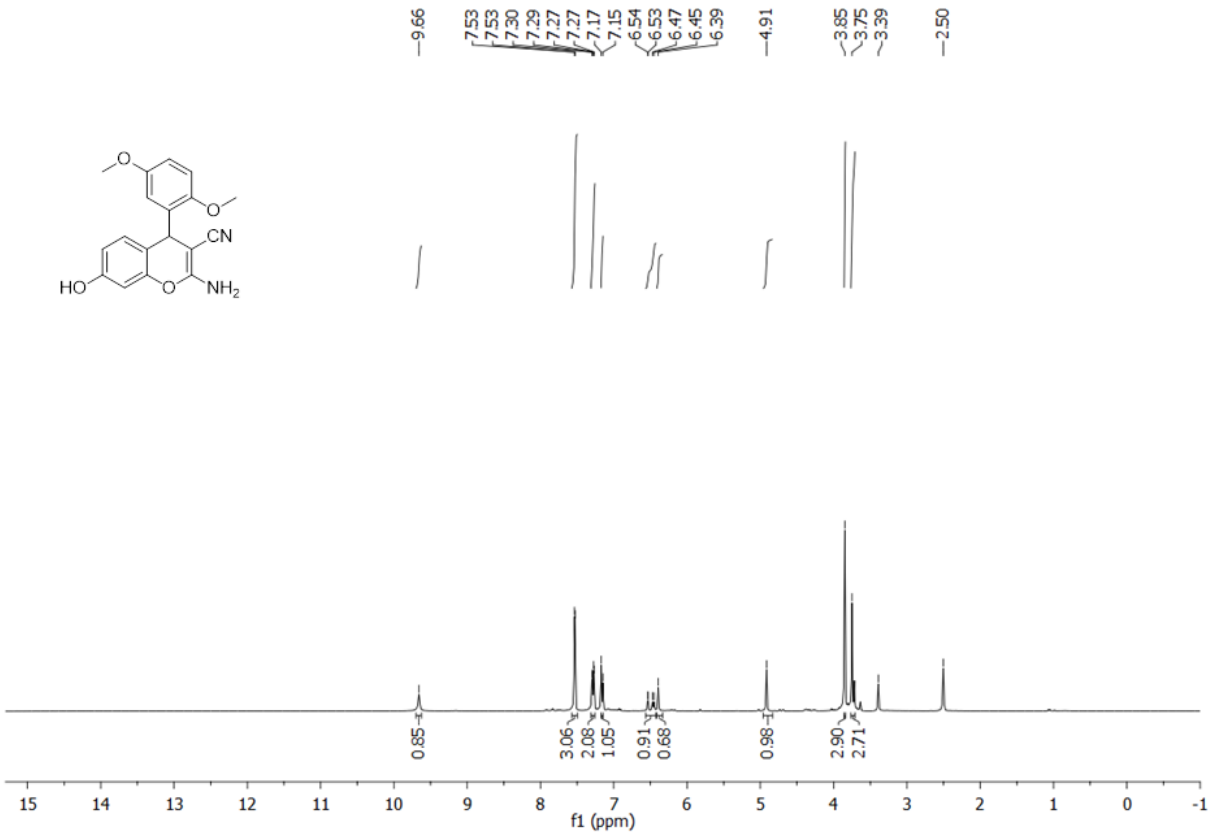


Figure 66: ^{1}H NMR spectrum for (**4m**) in DMSO-d_6 (400MHz, 300K).

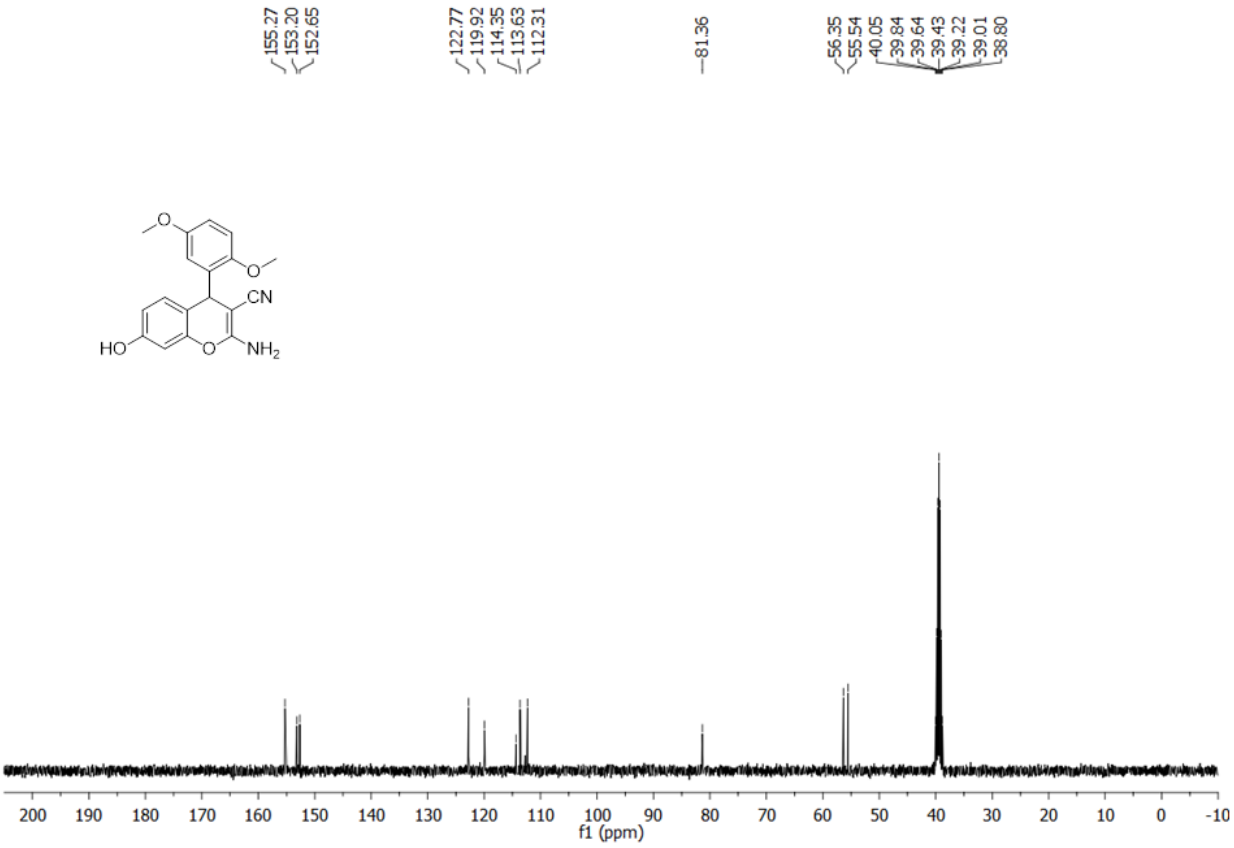


Figure 67: ^{13}C NMR spectrum (**4m**) in DMSO-d_6 (100MHz, 300K).

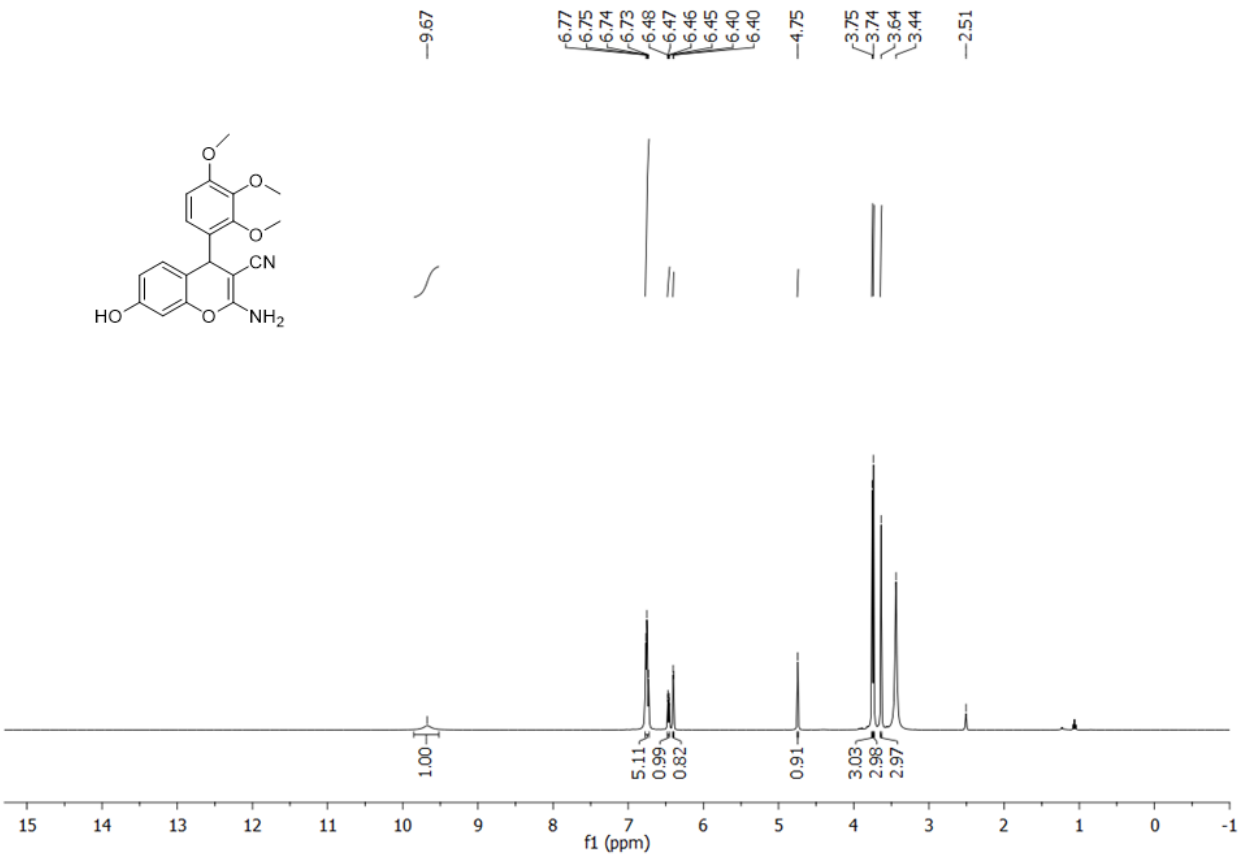


Figure 68: ^{1}H NMR spectrum for (**4n**) in DMSO-d_6 (400MHz, 300K).

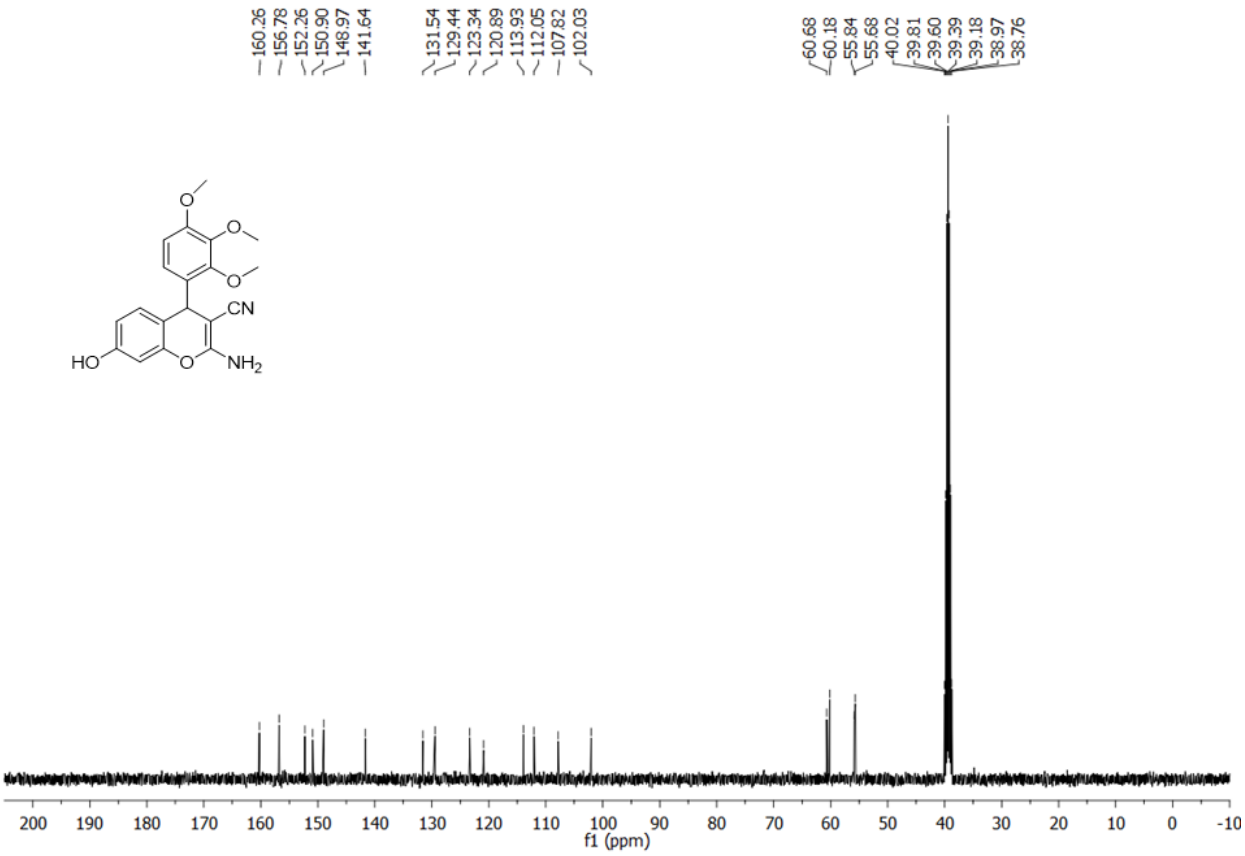


Figure 69: ^{13}C NMR spectrum (**4n**) in DMSO-d_6 (100MHz, 300K).

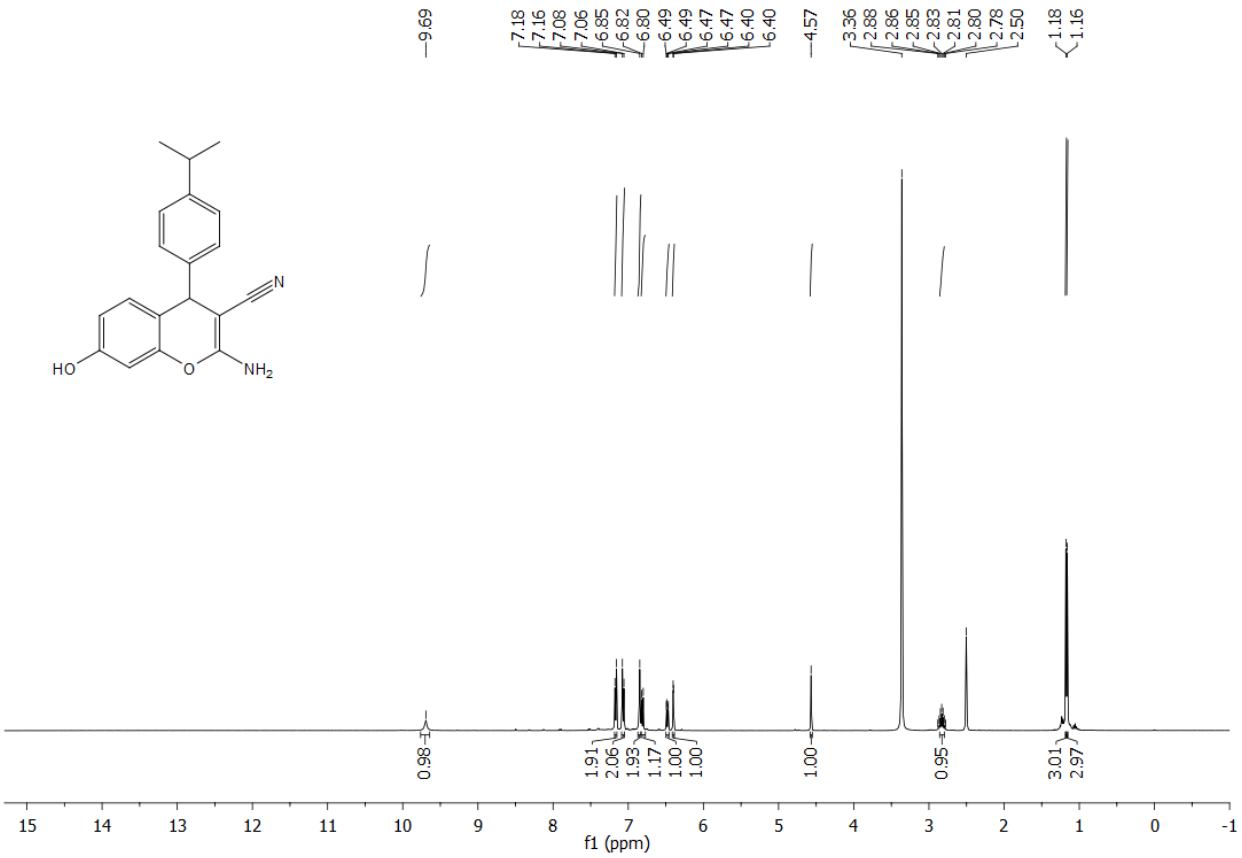


Figure 70: ^{1}H NMR spectrum for (**4o**) in DMSO-d_6 (400MHz, 300K).

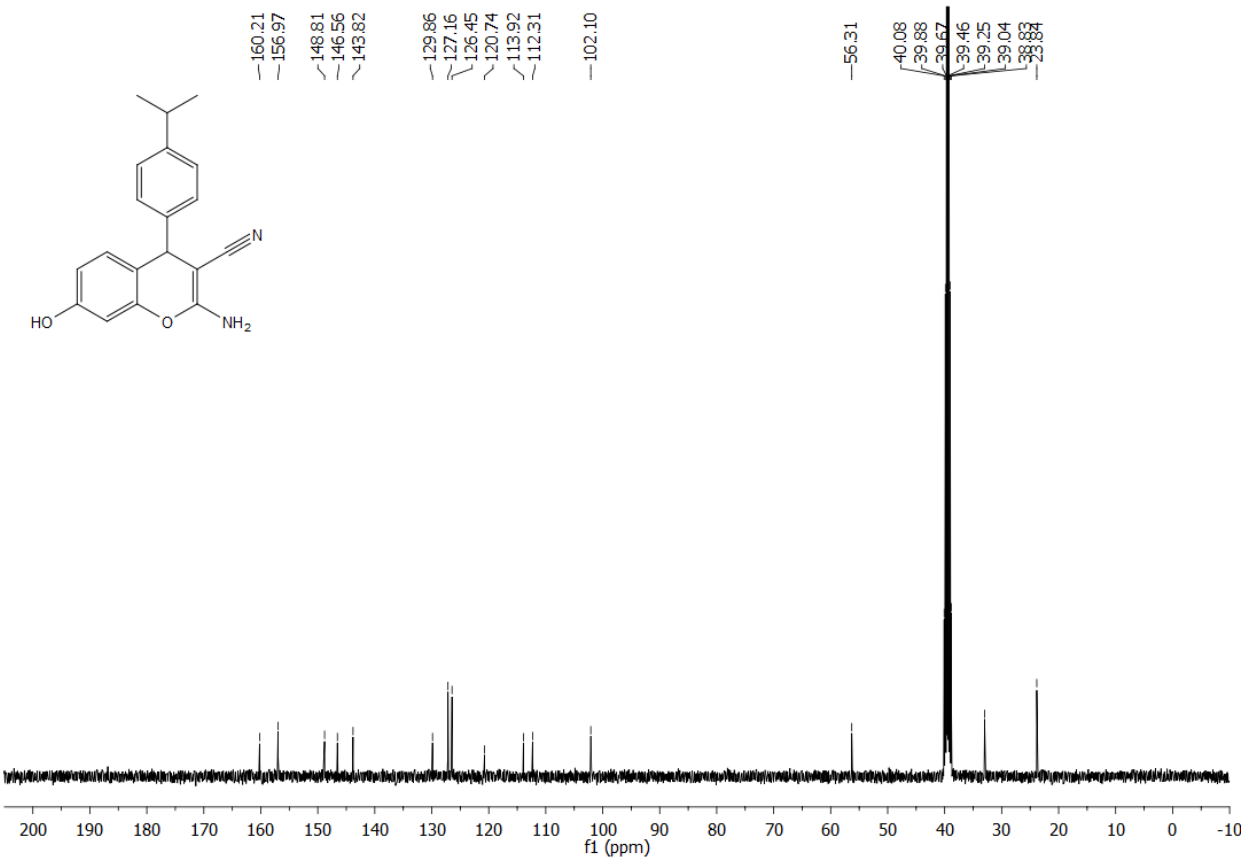


Figure 71: ^{13}C NMR spectrum (**4o**) in DMSO-d_6 (100MHz, 300K).

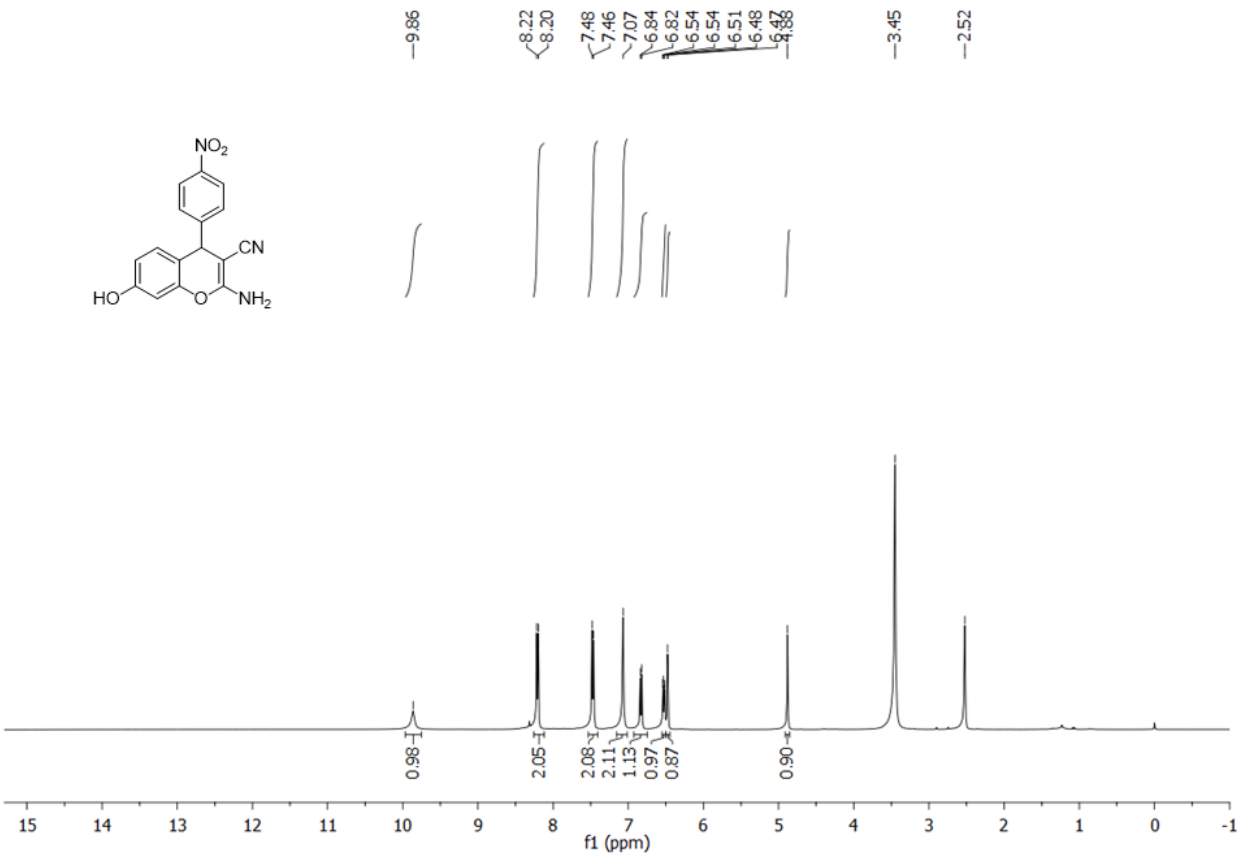


Figure 72: ^{1}H NMR spectrum for (**4p**) in DMSO-d_6 (400MHz, 300K).

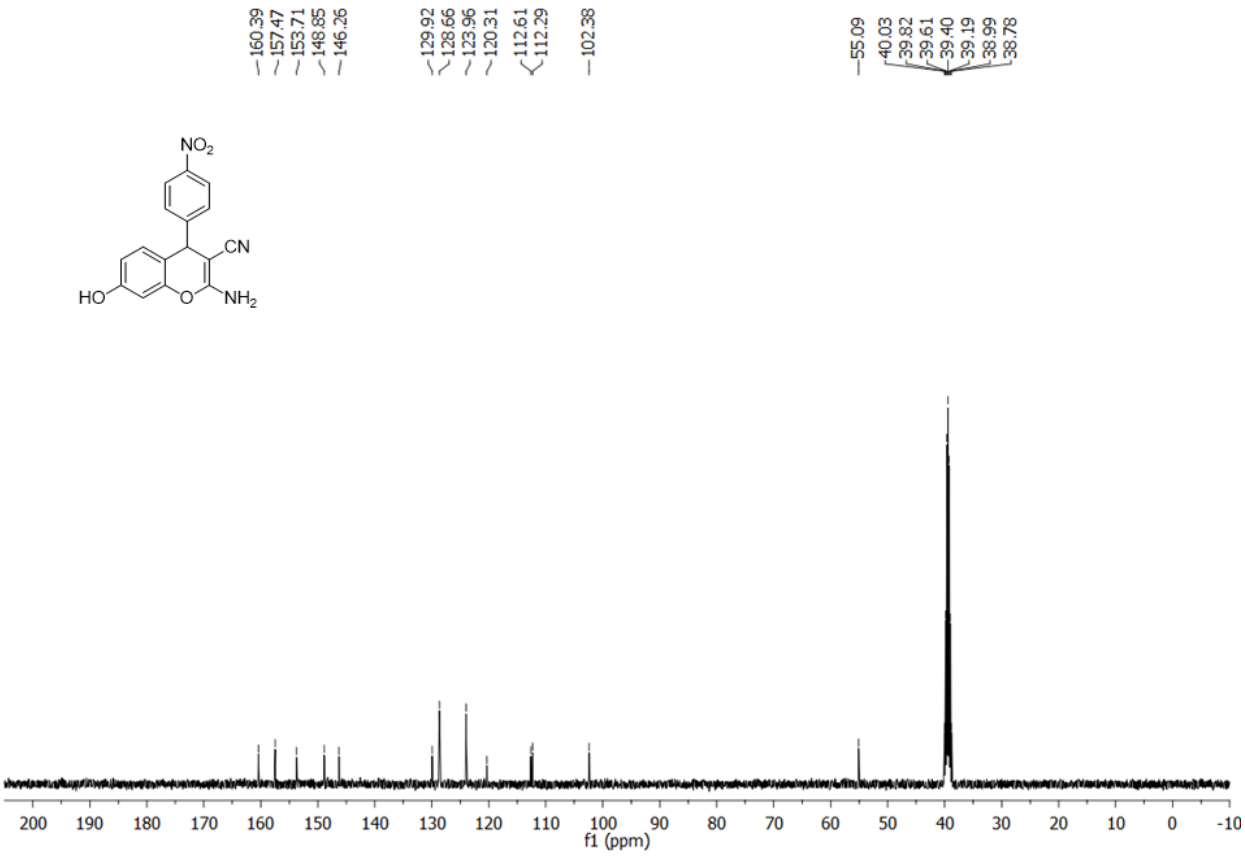


Figure 73: ^{13}C NMR spectrum (**4p**) in DMSO-d_6 (100MHz, 300K).

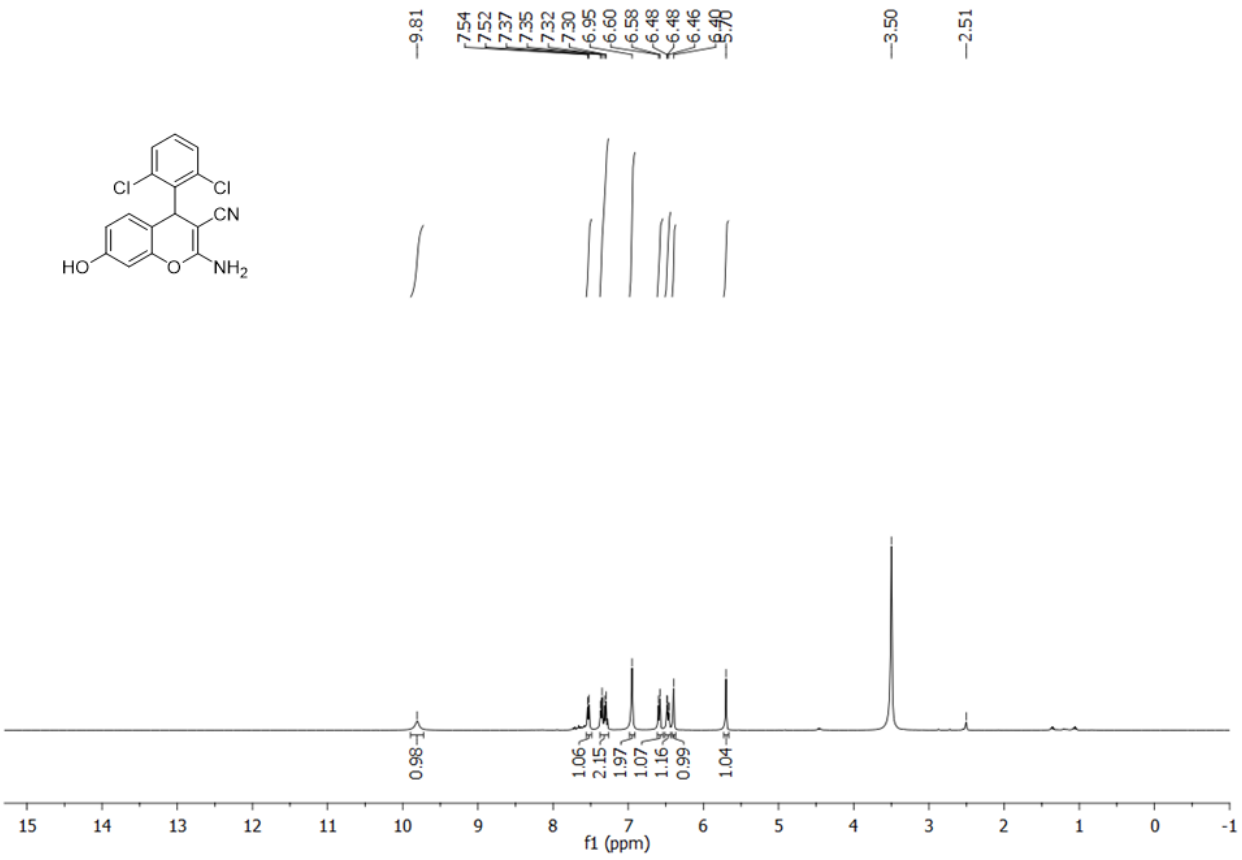


Figure 74: ^{1}H NMR spectrum for (**4q**) in DMSO-d_6 (400MHz, 300K).

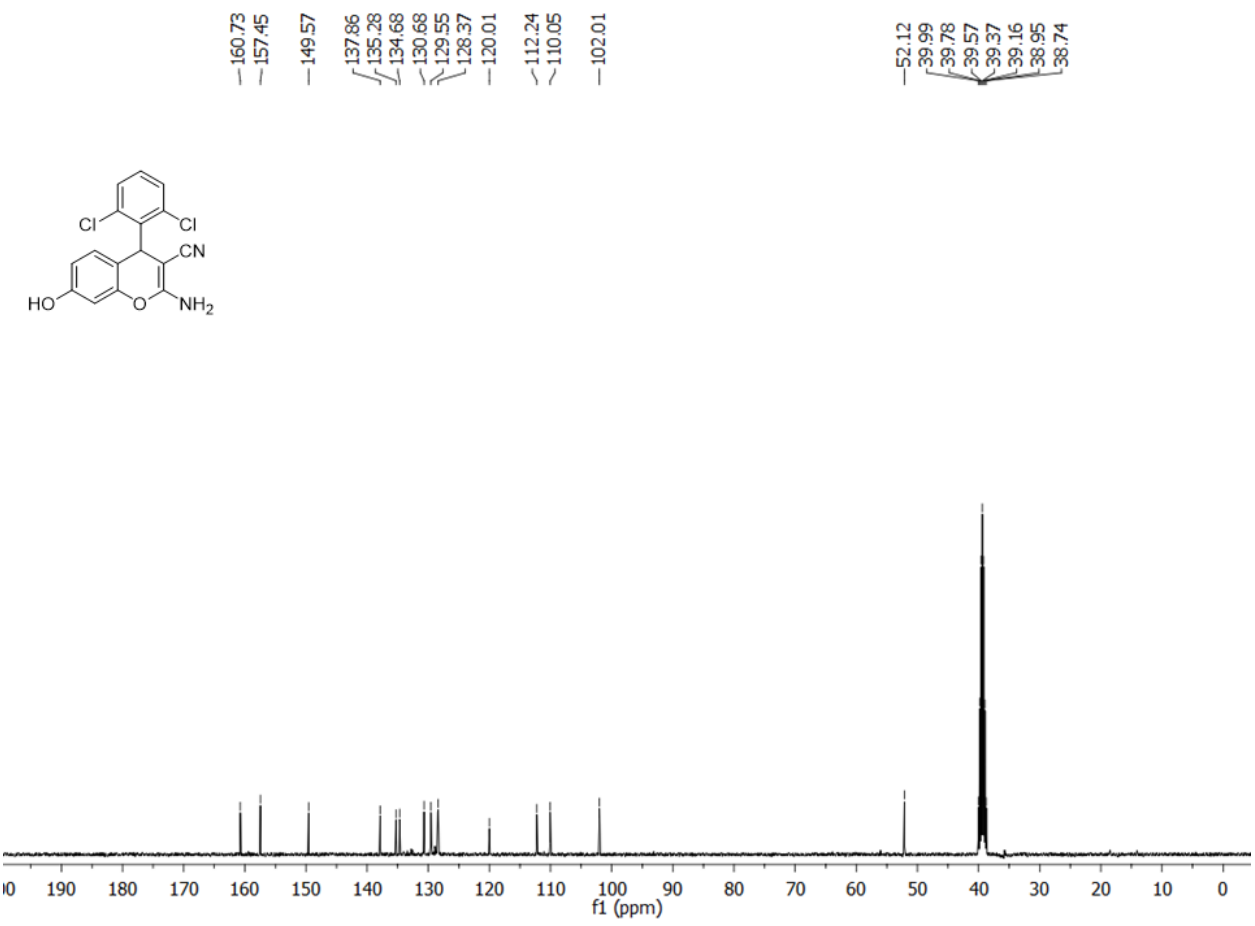


Figure 75: ^{13}C NMR spectrum (**4q**) in DMSO-d_6 (100MHz, 300K).

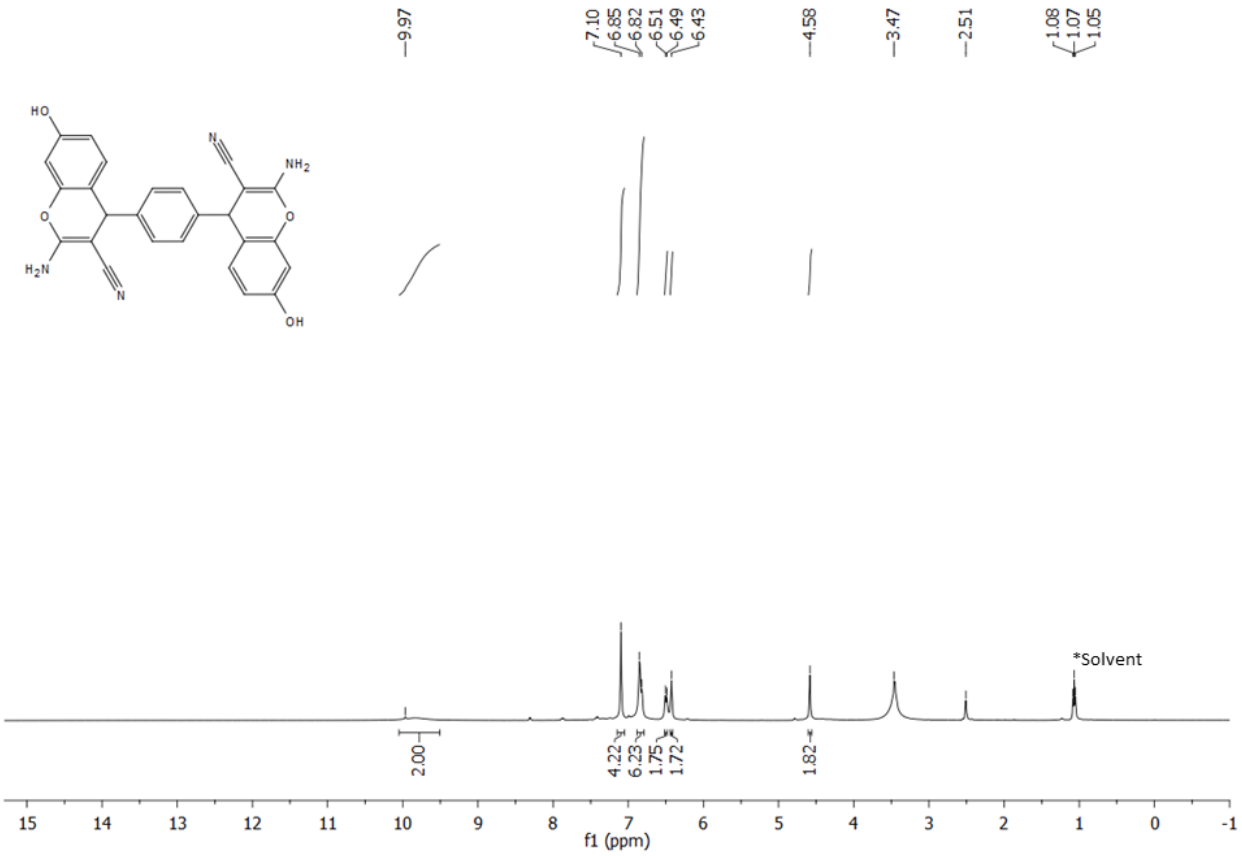


Figure 76: ^{1}H NMR spectrum for (**4r**) in DMSO-d_6 (400MHz, 300K).

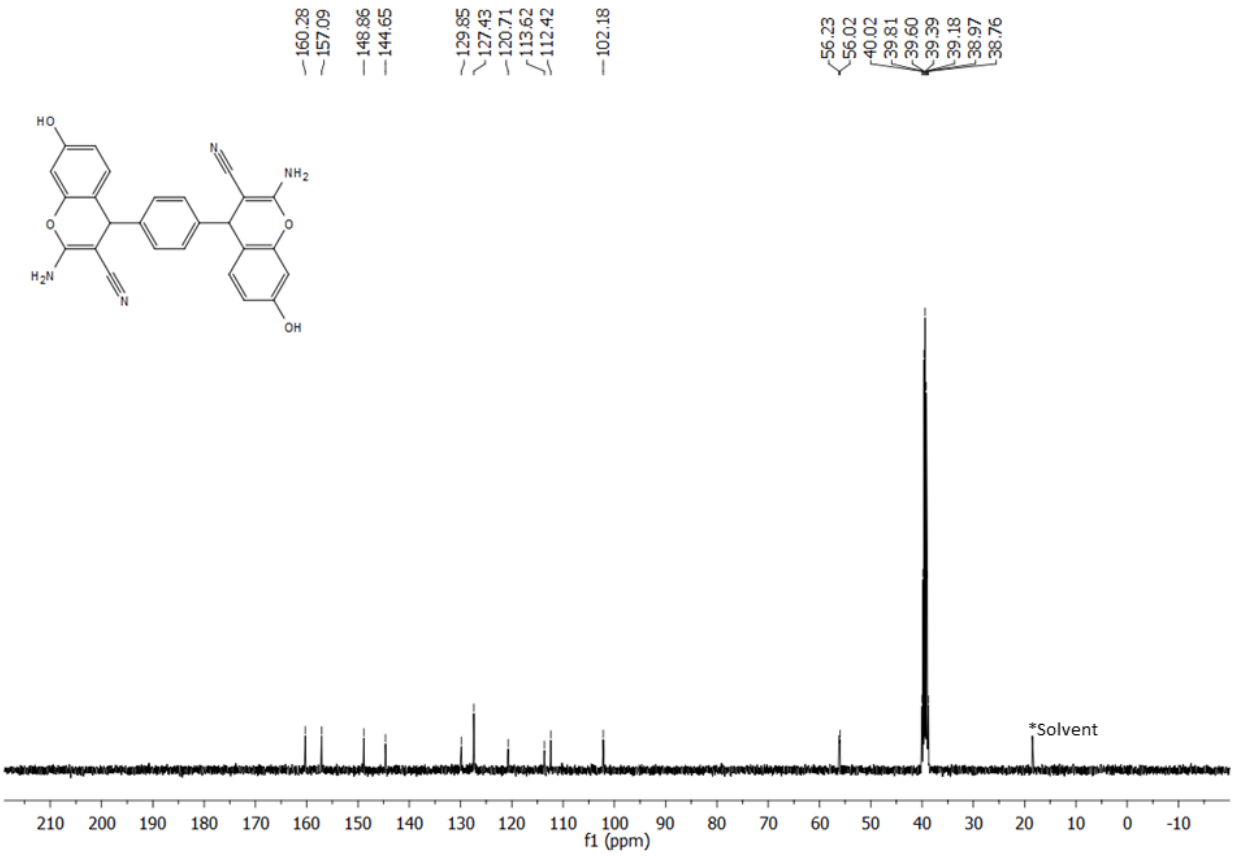


Figure 77: ^{13}C NMR spectrum (**4r**) in DMSO-d_6 (100MHz, 300K).

14. NMR spectra for tacrine analogue (5)

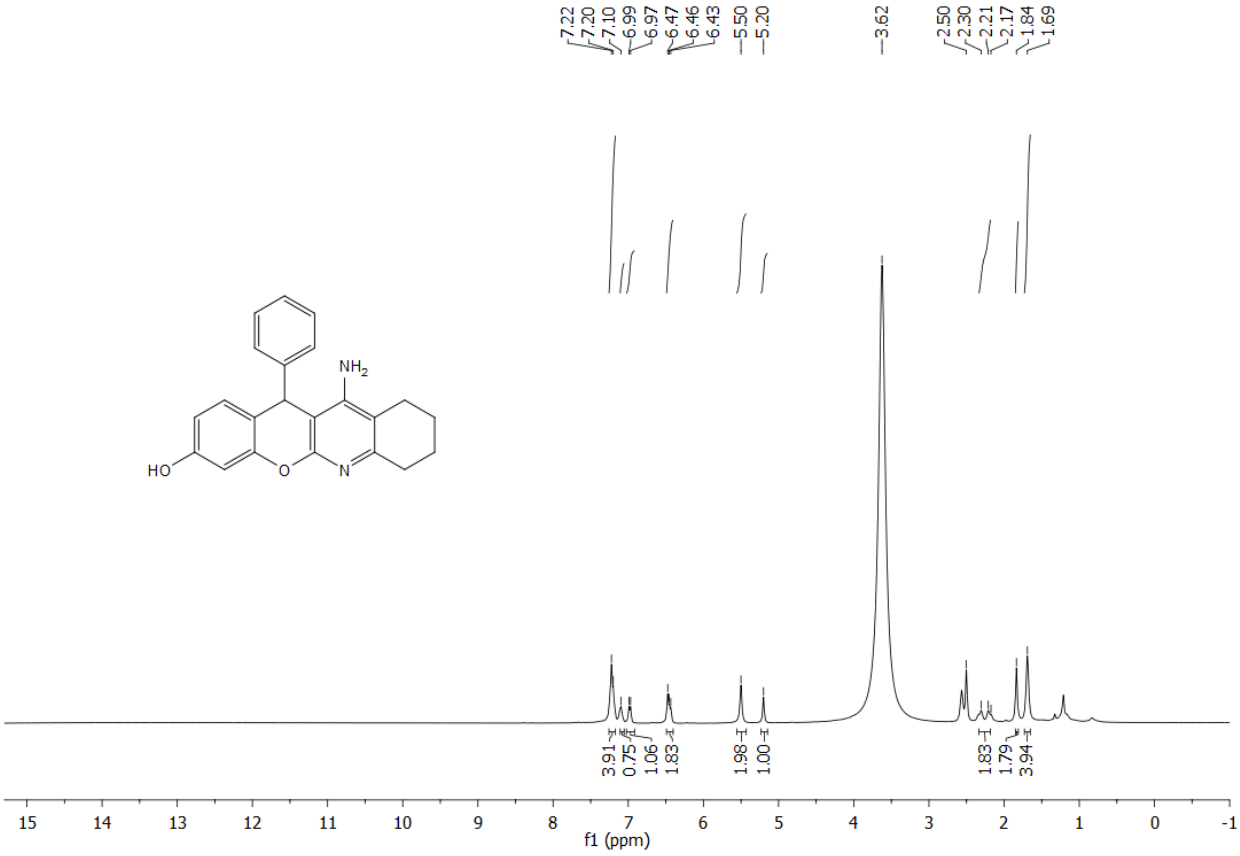


Figure 78: ^{1}H NMR spectrum for (**5**) in DMSO-d_6 (400MHz, 300K).

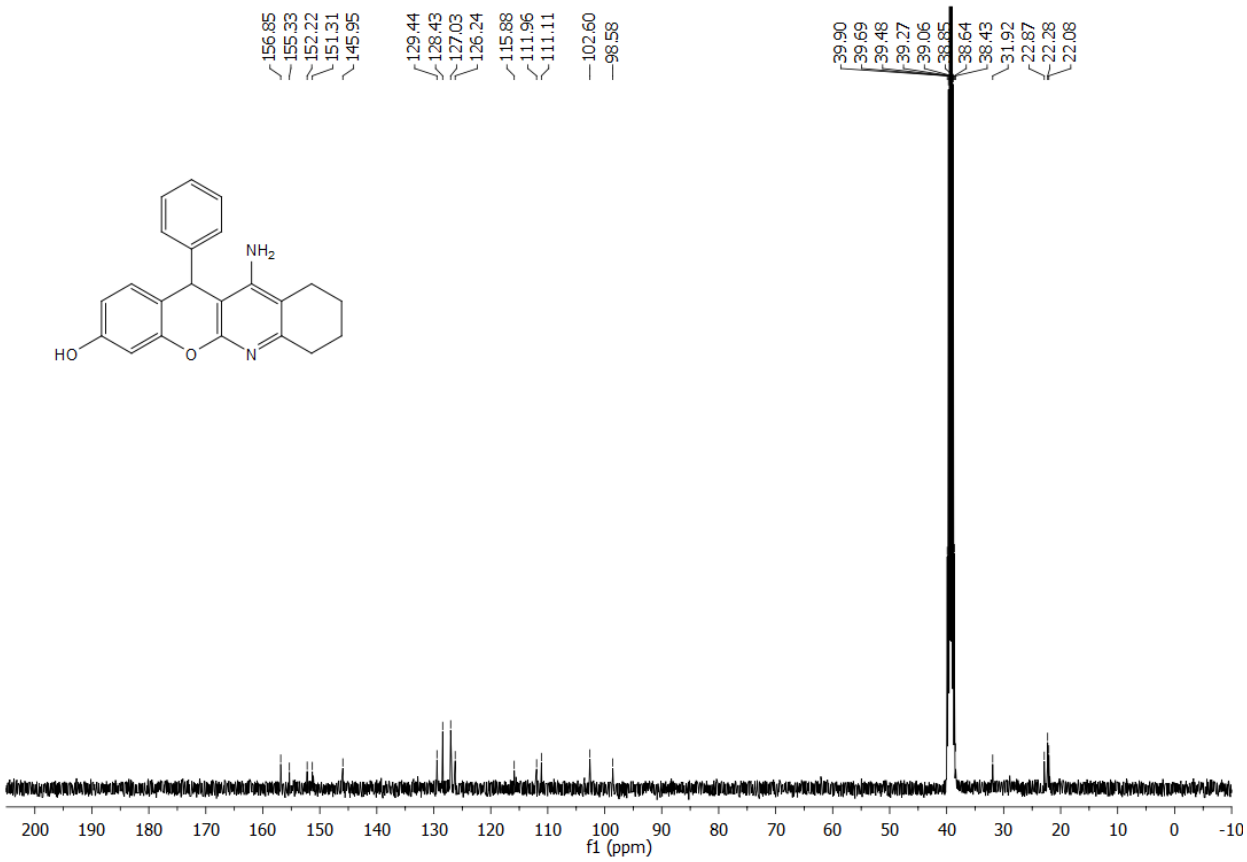


Figure 79: ^{13}C NMR spectrum for (**5**) in DMSO-d_6 (100MHz, 300K).

15. Experiment for confirmation of hydrogen gas using Gas chromatography

Benzyl alcohol 1a (1 mmol), malononitrile 2 (1 mmol), resorcinol 3 (1 mmol), Ru (II) catalyst 3(1 mol%, 6 mg), KOH (0.5 mmol), 2 mL of toluene were transferred in a dried 10 mL Schlenk flask under N_2 atmosphere, and the reaction mixture was heated at 100 °C for 5 h. The reaction mixture was then analysed using GC (TCD detector), confirming the liberation of hydrogen gas.

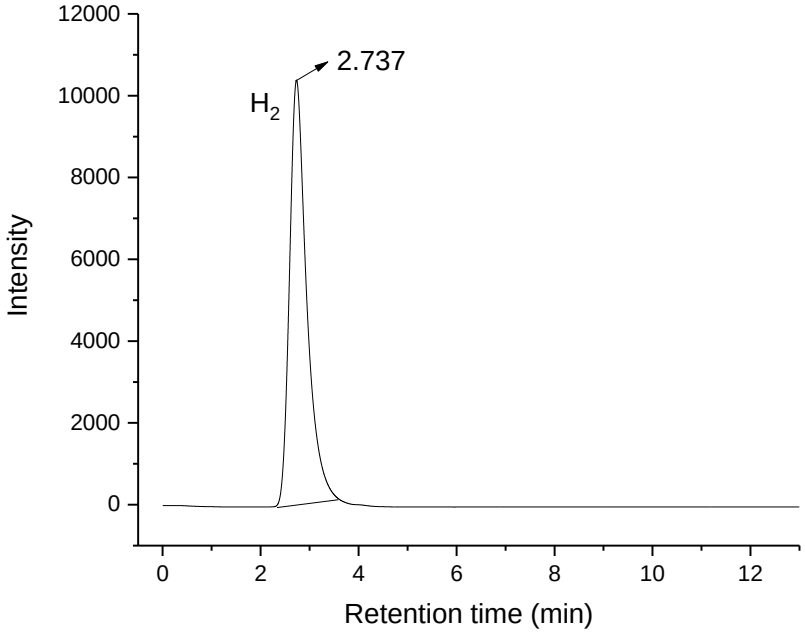


Figure 80: Chromatogram of H_2

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