Supporting Information for

Convergent Synthesis of Coumarin C3-C4 Fused Fluorogenic Quinoline Scaffolds *via* Aldehyde Activation by *in-situ* Generated Hydrazoic Acid

Ranjithkumar Ganesan and Sriraghavan Kamaraj *

Department of Chemistry, School of Advanced Sciences, Vellore Institute of Technology,

Vellore, Tamil Nadu 632014, India

Correspondence: sriraghavan.k@vit.ac.in

Table of contents

1.	Supplementary Notes	S2
2.	Supplementary Methods	S3 to S28
3.	Copies of Spectral Data	S29 to S102
4.	Gram Scale Experiment	S103
5.	Control Experiments	S104 to S106
6.	Control Experiments NMR Data	S107 to S108
7.	Single Crystal X-Ray Diffraction Analysis	S109 to S113
8.	Supplementary References	S114

1. Supplementary Notes:

1.1 General information:

All reactions were performed in an oven-dried Sigma-Aldrich pressure tube in the chemical fume hood under atmospheric conditions. An oil bath was used as the heating source for reactions requiring heat, and the reported reaction temperatures were just oil-bath temperatures. Chemicals and solvents were purchased from commercial suppliers, namely Sigma-Aldrich, Alfa Aesar, and Avra Chemicals, and all the chemicals were used without additional purification. Reactions were monitored by Thin Layer Chromatography (TLC) using 0.25 mm silica-coated aluminum foil plates (Merck DC Kiese gel 60 F254). Gravity column chromatography was carried out using silica gel (100-200 mesh) for purifications. A combination of hexane, ethyl acetate, chloroform, and ethyl alcohol were used as eluents.

The single crystal X-ray diffraction data were collected at Vellore Institute of Technology-Vellore (VIT) on a Bruker D8 Quest diffractometer using Mo-Kα/Cu-Kα radiation. Dr. P. K. Sudhadevi Antharjanam, a technical officer at IITM, and Mr. Ranjithkumar Ganesan, a research scholar at VIT Vellore, solved and refined the crystal structures using the SHELXTL software package. NMR spectra were recorded at ambient temperature on Bruker Avance-III 400 MHz (^{1}H at 400 MHz, ^{13}C at 100.6 MHz, ^{19}F at 376.6 MHz). Chemical shifts (δ) are reported in parts per million (ppm), and coupling constants (*J*) are given in Hertz (Hz). ^{1}H and ^{13}C NMR chemical shifts (δ) are referenced to the residual undertreated protons in $CDCl_3$. The following abbreviations were used in ^{1}H NMR spectra to designate the signal multiplicity: s (singlet), brs (broad singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublets), dt (doublet of triplet) and m (multiplet). Mass spectra (HRMS) were recorded on WATERS–XEVO G2-XS-QToF spectrometer. Infrared (IR) spectra were processed on an FT-IR Affinity-I Shimadzu spectrometer. The given chemical yields refer to isolated yields after purification by chromatography. Melting points were recorded on the Guna capillary melting point apparatus and were not corrected.

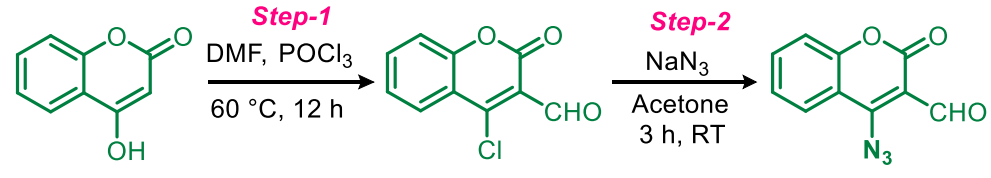
1.2 *Caution*:

Organic azides are potentially explosive materials that decompose when exposed to a small quantity of external energy, such as light, heat, or pressure. We never encountered any safety issues with these materials throughout our investigation. Sodium azide was our primary source of azide functionalization for the study. Until sodium azide is acidified to yield the volatile and highly lethal hydrazoic acid (HN_3), it is widely acknowledged that it is generally safe, primarily when employed in aqueous solutions. The excess/unreacted sodium azide from the reaction mixture was disposed of as reported.[1]

2. Supplementary Methods:

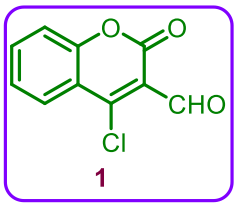
2.1 Synthesis of chromeno[4,3-*b*]quinolinone (4) from 4-azido-2-oxo-2*H*-chromene-3-carbaldehyde (2):

2.1.1 Scheme 1. Synthesis of 4-azido-2-oxo-2*H*-chromene-3-carbaldehyde (2) from 4-hydroxycoumarin (S1):



Step-1: Synthesis of 4-chloro-2-oxo-2*H*-chromene-3-carbaldehyde (1):

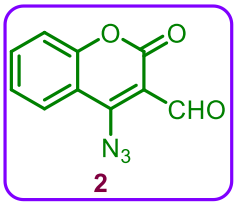
To a solution of DMF (30 mL) was added $POCl_3$ (30 mL) in one portion at 0 ºC. The resulting solution was allowed to stir for 0.5 hours. A solution of 4-hydroxycoumarin **S1** (3 g, 18.5 mmol, dissolved in 30 mL DMF) was added to the mixture at that temperature. The mixture was further heated at 60 ºC for 12 h. After the disappearance of the starting material **S1** in *tlc*, the reaction mixture was cooled to room temperature and slowly quenched with ice water. Then, the pH of the aqueous reaction mixture was adjusted to neutral with 2M aqueous $NaHCO_3$ solution. The resulting crude mixture was extracted with ethyl acetate (4 X 50 mL) and combined organic layers washed with water and dried over anhydrous Na_2SO_4. The solvents were evaporated under vacuum, and the residue was purified by column chromatography to afford 4-chloro-2-oxo-2*H*-chromene-3-carbaldehyde **1** (2.7 g, 12.9 mmol, 70%) as a yellow solid.



MP: 162-164 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 10.37 (s, 1H), 8.13 (d, *J* = 8.0 Hz, 1H), 7.74 (t, *J* = 8.4 Hz, 1H), 7.47 – 7.39 (m, 2H); **^{13}C{^{1}H} NMR** (100.6 MHz, $CDCl_3$): δ 186.9, 158.5, 153.6, 153.3, 135.8, 135.7, 127.7, 125.6, 118.4, 118.2, 117.2; **IR (neat):** 1703, 1600, 1537, 1483, 1448, 1411, 1300, 1263, 1118, 1031, 962 cm^{-1}. The spectral data of **1** is in accordance with the literature.[2]

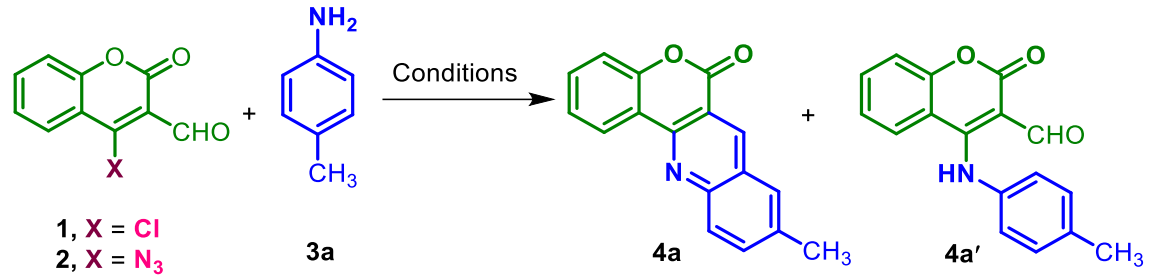
Step-2: Synthesis of 4-azido-2-oxo-2*H*-chromene-3-carbaldehyde (2):

To a solution of 4-chloro-2-oxo-2*H*-chromene-3-carbaldehyde **1** (2 g, 9.58 mmol) in acetone (25 mL) at 0 ºC was added sodium azide (1.25 g, 19.17 mmol, 2 equiv.) in small portion. After addition, the reaction was stirred at room temperature. The reaction mixture was slowly poured into the chopped ice after the disappearance of the starting material **1** in *tlc*. The spongy white solid obtained was then filtered, washed with excess water, and dried to afford 4-azido-2-oxo-2*H*-chromene-3-carbaldehyde **2** (1.90 g, 8.83 mmol, 92%).



MP: 124-126 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.33 (s, 1H), 8.13 – 8.11 (m, 1H), 7.63 – 7.59 (m, 1H), 7.40 – 7.36 (m, 2H); **^{13}C{^{1}H} NMR** (100.6 MHz, $CDCl_3$): δ 163.1, 155.6, 155.3,153.2, 133.3, 125.4, 124.6, 118.0, 110.5, 108.2; **IR (neat):** 3051, 2895, 2167, 1761, 1712, 1672, 1606, 1521, 1450, 1355, 1240, 1197, 1130, 1035, 883 cm^{-1}. The spectral data is in accordance with the literature.[2]

Table 1. Optimization of reaction condition[a] for the synthesis of C3-C4 quinoline fused coumarin 4a in the presence of aniline



entry	reactants 1 & 2	solvent	catalyst (20 mol %)	base (1 eq)	temp. (°C)	time (h)	yield, %[d] 4a	yield, %[d] 4a′
1[a]	**1**	MeOH	-	-	RT	2 min	55	19
2[a]	**1**	EtOH	-	-	RT	2 min	53	20
3[a]	**1**	CH_3CN	-	-	RT	2 min	56	18
4[a]	**1**	MeOH	$InCl_3$	-	RT	2 min	62	14
5[a]	**1**	CH_3CN	$InCl_3$	-	RT	2 min	66	13
6[a]	**1**	Toluene	*p*-TsOH	-	RT	2 min	66	17
7[a]	**1**	Toluene	*p*-TsOH	-	130	4 h	67	-
8[a]	**1**	EtOH	H_2SO_4	-	RT	2 min	69	14
9[a]	**1**	EtOH	MsOH	-	RT	4 h	65	19
10[b]	**2**	CF_3COOH	-	-	60	24 h	No reaction	
11[b]	**2**	MeOH	-	-	RT	2 min	73	-
12[b]	**2**	**CH_3CN**	**-**	**-**	**RT**	**2 min**	**97**	**-**
13[b]	**2**	CH_3CN	$InCl_3$	-	RT	2 min	98	-
14[b]	**2**	**CH_3CN**	**-**	**Et_3N**	**RT**	**5 min**	**-**	**96**
15[b]	**2**	Pyridine	-	-	RT	30 min	-	91
16[a]	**1**	CH_3CN	-	Et_3N	RT	5 min	-	91
17[c]	**4a′**	CF_3COOH	-	-	60	2	89	-

[a]Reaction conditions: The reactions were performed with 4-chloro-2-oxo-2*H*-chromene-3-carbaldehyde **1** (100 mg, 0.47 mmol), *p*-toluidine **3a** (61 mg, 0.57 mmol), catalyst (20 mol%) in appropriate solvent mentioned in the table (4 mL).

[b]Reaction conditions: The reactions were performed with 4-azido-2-oxo-2*H*-chromene-3-carbaldehyde **2** (100 mg, 0.46 mmol), *p*-toluidine **3a** (60 mg, 0.56 mmol), catalyst (20 mol%) in appropriate solvent mentioned in the table (4 mL).

[c]Reaction conditions: The reactions were performed with 4-(N-arylamino)-3-formylcoumarin **4a′** (100 mg, 0.36 mmol) in TFA (1.5 mL) at 60 °C. [d]Isolated yield.

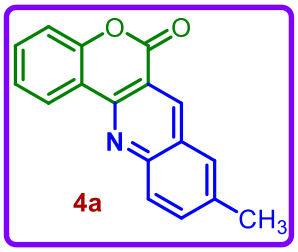
At the outset, we have explored various reaction conditions to improve the yield of CQ by using 4-chloro-3-formylcoumarin **1** with *p*-toluidine **3a** using different solvents (MeOH, EtOH, CH_3CN, and Toluene), with or without catalyst ($InCl_3$, H_2SO_4, *p*-TsOH, and MsOH) at room temperature and the results are summarized in Table-1 (entry-1 to 9). In general, it is observed that the reaction of **1** with **3a** procured the CQ **4a** and 4-(N-arylamino)-3-formylcoumarin **4a′** in a 3:1 ratio. It is worth mentioning that the reaction of **1** with **3a** in toluene using *p*-TsOH at 130 °C procured only CQ **4a** in 67% isolated yield (entry-7). Extending the reaction time to 48 hours at ambient or elevated temperature did not improve yield improvement or further conversion. Interestingly, the use of 4-azido-3-formylcoumarin **2** with **3a** in acetonitrile at RT, without any catalyst, in just two minutes, procured CQ **4a** in 97% yield (entry 12). Also, repetition of the above reaction using $InCl_3$ as catalyst procured CQ **4a** in 98% yield (entry 13).

Next, the reaction of **2** with **3a** using Et_3N as a base in acetonitrile or pyridine as a solvent afforded **4a′** in 96% and 91% yield, respectively (entries 14-15). As anticipated, the reaction of **1** with **3a** using Et_3N as a base in acetonitrile afforded **4a′** in 91% isolated yield (entry 16). From the above experiments, 4-azido-3-formylcoumarin **2** is the best pre-functionalized starting material compared with 4-chloro-3-formylcoumarin **1** for constructing the CQ scaffold. Intriguingly, the substrate **4a′** underwent an electrophilic cyclization reaction to **4a** when treated with CF_3COOH at 60 °C and failed to proceed at RT (entry 17). From the optimization results, we realized that the reaction of 4-azido-3-formylcoumarin **2** with aniline **3** without catalyst in acetonitrile as a solvent at room temperature was chosen as the ideal optimized reaction condition for further development of CQ substrates scope.

2.1.2 Synthesis of chromeno[4,3-*b*]quinolin-6-one (CQ) 4 from 4-chloro-2-oxo-2*H*-chromene-3-carbaldehyde (1):

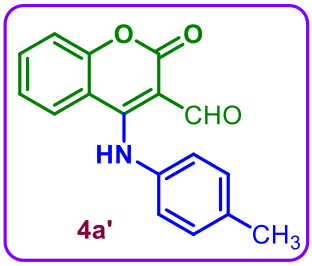
The Aldrich-Ace pressure tube (25 mL capacity) equipped with a magnetic stirrer bar was added 4-chloro-2-oxo-2*H*-chromene-3-carbaldehyde **1** (200 mg, 0.96 mmol), and *p*-toluidine **3a** (123 mg, 1.15 mmol, 1.2 equiv.) in MeOH (5mL) at room temperature. Then, the reaction mixture was allowed to stir at room temperature. After the disappearance of starting material **1** in *tlc*, the reaction mixture was quenched with ice water (30 mL) and extracted with chloroform (3 X 20 mL). The combined organic phase was washed with an aqueous solution of $NaHCO_3$ (10%, 2 X 15 mL) and water (2 X 15 mL), then dried over anhydrous $MgSO_4$, and the volatiles were removed under vacuum. The resultant crude product was purified by column chromatography on silica gel (10 -15% EtOAc in hexane) to procure the 9-methyl-6*H*-chromeno[4,3-*b*]quinolin-6-one **4a** (white solid, 138 mg, 55%) and 2-oxo-4-(*p*-tolylamino)-2*H*-chromene-3-carbaldehyde **4a′** (white solid, 51 mg, 19%).

9-methyl-6*H*-chromeno[4,3-b]quinolin-6-one (4a):



^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.07 (s, 1H), 8.73 (d, *J* = 8.0 Hz, 1H), 8.09 (d, *J* = 9.2 Hz, 1H), 7.72 (d, *J* = 2.8 Hz, 2H), 7.57 (t, *J* = 7.6 Hz, 1H), 7.41 (t, *J* = 7.6 Hz, 1H), 7.37 (d, *J* = 8.4 Hz, 1H), 2.57 (s, 3H); **^{13}C{^{1}H} NMR** (100.6 MHz, $CDCl_3$): δ 160.5, 151.5, 148.7, 147.8, 139.1, 136.6, 134.9, 131.0, 128.1, 126.9, 126.3, 124.0, 123.9, 118.7, 116.3, 114.6, 20.6; **IR (neat):** 1732, 1597, 1492, 1460, 1186, 1147, 1031, 989, 823, 750 cm^{-1}. The spectral data is in accordance with the literature.[3]

2-oxo-4-(*p*-tolylamino)-2*H*-chromene-3-carbaldehyde (4a′):



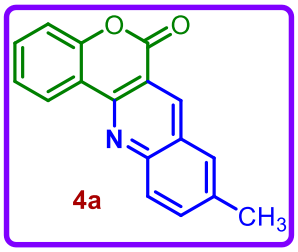
MP: 202-204 °C; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 13.17 (brs, 1H, D_2O-exchangeable), 10.26 (s, 1H), 7.51 (t, *J* = 8.0 Hz, 1H), 7.31 (d, *J* = 8.4 Hz, 1H), 7.27 (d, *J* = 8.4 Hz, 2H), 7.18 (t, *J* = 7.6 Hz, 3H), 6.70 (t, *J* = 8.0 Hz, 1H), 2.45 (s, 3H); **^{13}C{^{1}H} NMR** (100.6 MHz, $CDCl_3$): δ 192.5, 162.6, 157.8, 155.5, 138.4, 135.9, 134.4, 130.7, 128.0, 125.5, 123.1, 118.4, 113.2, 97.9, 21.2; **IR (neat):** 3174, 1647, 1596, 1458, 1310, 1215, 1116, 826, 793 cm^{-1}. The spectral data is in accordance with the literature.[4]

2.1.3 General procedure for the synthesis of chromeno[4,3-*b*]quinolin-6-one (4) from 4-azido-2-oxo-2*H*-chromene-3-carbaldehyde (2):

The Aldrich-Ace pressure tube (25 mL capacity) equipped with a magnetic stirrer bar was added 4-azido-2-oxo-2*H*-chromene-3-carbaldehyde **2** (200 mg, 0.93 mmol), and aniline **3** (1.12 mmol, 1.2 equiv.) in acetonitrile (5mL) at room temperature. Then, the reaction mixture was allowed to stir at room temperature. After the disappearance of starting material **2** in *tlc*, the reaction mixture was quenched with ice water (30 mL) (in case of precipitate formation, the resulting solid was filtered and washed with hexane) and extracted with chloroform (3 X 20 mL). The combined organic phase was washed with an aqueous solution of $NaHCO_3$ (10%, 2 X 15 mL) and water (2 X 15 mL), then dried over anhydrous $MgSO_4$, and the volatiles were removed under

vacuum. The resulting solid product was washed with cold hexane/ethanol to remove the traces of excess aniline. In the selective cases, column chromatography was used to afford the pure chromeno[4,3-*b*]quinolin-6-one (CQ) **4a-4m** with an excellent atom economy.

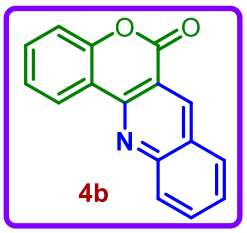
9-methyl-6*H*-chromeno[4,3-*b*]quinolin-6-one (4a):



Following the general procedure, azide **2** (200 mg, 0.93 mmol) was treated with *p*-toluidine (119 mg, 1.12 mmol) in acetonitrile (5 mL) at room temperature. Upon the disappearance of azide **2** in *tlc*, the mixture was poured into chopped ice, and the resultant solid was filtered and washed with hexane to procure pure CQ **4a** (white solid, 0.228 g, 94%). The spectral data is in accordance with the literature.[3]

6*H*-chromeno[4,3-*b*]quinolin-6-one (4b):

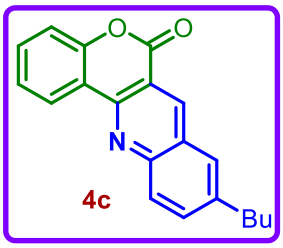
Following the above general procedure, azide **2** (200 mg, 0.93 mmol) was treated with aniline (104 mg, 1.12 mmol) in acetonitrile (5 mL) at room temperature. Upon the disappearance of azide **2** in *tlc*, the mixture was poured into chopped ice, and the resultant solid was filtered and washed with hexane to procure pure CQ **4b** (209 mg, 91%) as a white solid.



MP: 204-206 °C; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 9.20 (s, 1H), 8.77 (d, *J* = 8.0 Hz, 1H), 8.22 (d, *J* = 8.44 Hz, 1H), 8.05 (d, *J* = 8.0 Hz, 1H), 7.91 (t, *J* = 8.0 Hz, 1H), 7.65 – 7.57 (m, 2H), 7.42 (t, *J* = 7.6 Hz, 1H), 7.38 (d, J = 8.0 Hz, 1H); **^{13}C{^{1}H} NMR** ($CDCl_3$, 100.6 MHz): δ 161.4, 152.7, 151.1, 149.6, 141.1, 133.4, 132.4, 129.6, 129.4, 127.4, 127.3, 125.3, 125.0, 119.7, 117.4, 115.8; **IR (neat):** 1735, 1600, 1494, 1460, 1377, 1244, 1176, 1087, 1033, 987 cm^{-1}. The spectroscopic data are consistent with the literature report.[3]

9-butyl-6*H*-chromeno[4,3-b]quinolin-6-one (4c):

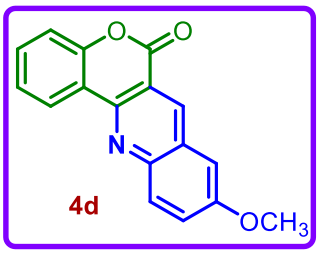
Following the general procedure, azide **2** (200 mg, 0.93 mmol) was treated with 4-butylaniline (166 mg, 1.12 mmol) in acetonitrile (5 mL) at room temperature. Upon the disappearance of azide **2** in *tlc*, the mixture was poured into chopped ice, and the resultant solid was filtered and washed with hexane to procure pure CQ **4c** (268 mg, 95%) as a white solid.



MP: 118-120 °C; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 9.11 (d, *J* = 15.2 Hz, 1H), 8.74 (t, *J* = 11.2 Hz, 1H), 8.12 (t, *J* = 11.6 Hz, 1H), 7.73-7.72 (m, 2H), 7.56 (t, *J* = 7.2 Hz, 1H), 7.44-7.35 (m, 2H), 2.82 (t, *J* = 7.6 Hz, 2H), 1.76-1.69 (m, 2H), 1.47-1.38 (m, 2H), 0.97 (t, *J* = 7.2 Hz, 3H); **^{13}C{^{1}H} NMR** ($CDCl_3$, 100.6 MHz): δ 161.5, 152.6, 150.0, 148.8, 142.5, 140.3, 135.2, 132.1, 129.3, 127.4, 127.3, 125.1, 124.9, 119.8, 117.3, 115.7, 35.6, 33.1, 22.4, 13.9; **IR (neat):** 2926, 2854, 1734, 1598, 1489, 1458, 1381, 1176, 1085, 833, 754 cm^{-1}; **HRMS** (ESI) m/z calcd. For $C_{20}H_{18}NO_2$ $[M+H]^+$: 304.1332 found: 304.1333.

9-methoxy-6*H*-chromeno[4,3-b]quinolin-6-one (4d):

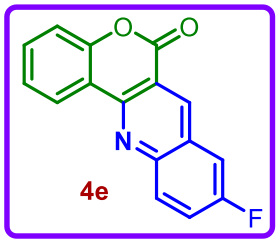
Following the general procedure, azide **2** (200 g, 0.93 mmol) was treated with *p*-anisidine (137 mg, 1.12 mmol) in acetonitrile (5 mL) at room temperature. Upon the disappearance of azide **2** in *tlc*, the mixture was poured into chopped ice, and the resultant solid was filtered and washed with hexane to procure pure CQ **4d** (white solid, 0.229 g, 89%).



^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.07 (s, 1H), 8.72 (d, *J* = 8.0 Hz, 1H), 8.12 (d, *J* = 9.2 Hz, 1H), 7.57-7.54 (m, 2H), 7.40 (dd, *J* = 10.8, 7.6 Hz, 2H), 7.20 (s, 1H), 3.98 (s, 3H); **^{13}C{^{1}H} NMR** (100.6 MHz, $CDCl_3$): δ 161.6, 158.4, 152.3, 147.7, 147.5, 138.9, 131.8, 131.0, 128.5, 127.1, 124.9, 124.8, 119.8, 117.3, 115.9, 105.6, 55.8; **IR (neat):** 1734, 1598, 1539, 1492, 1234, 1182, 1024, 835, 748 cm^{-1}. The spectral data is in accordance with the literature.[3]

9-fluoro-6*H*-chromeno[4,3-b]quinolin-6-one (4e):

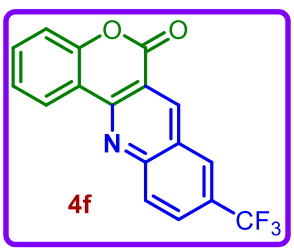
Following the general procedure, azide **2** (200 mg, 0.93 mmol) was treated with 4-F-aniline (123 mg, 1.12 mmol) in acetonitrile (5 mL) at room temperature. Upon the disappearance of azide **2** in *tlc*, the mixture was poured into chopped ice, and the resultant solid was filtered and washed with hexane to procure pure CQ **4e** (231 mg, 94%) as a white solid.



^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.17 (s, 1H), 8.75 (d, *J* = 7.6 Hz, 1H), 8.25 (t, *J* = 7.2 Hz, 1H), 7.70 (t, *J* = 8.0 Hz, 1H), 7.61 (d, *J* = 8.0, 7.6 Hz, 1H), 7.45-7.39 (m, 2H); **^{13}C{^{1}H} NMR** ($CDCl_3$, 100.6 MHz): δ 161.1, 152.6, 148.3, 140.3 (d, *J* = 6.0 Hz), 132.5, 132.2 (d, *J* = 9.1 Hz), 125.1 (d, *J* = 2.0 Hz), 124.1 (d, *J* = 27.6 Hz), 119.5, 117.5, 116.4, 112.0 (d, *J* = 22.1 Hz); **^{19}F NMR** (376.6 MHz, $CDCl_3$): δ -110.82 to -110.83 (m, F); **IR (neat):** 3057, 1735, 1602, 1494, 1462, 1355, 1224, 1192, 1112, 837, 756 cm^{-1}. The spectroscopic data are consistent with the literature report.[3]

9-(trifluoromethyl)-6*H*-chromeno[4,3-b]quinolin-6-one (4f):

Following the general procedure, azide **2** (200 mg, 0.93 mmol) was treated with 4-CF_3-aniline (180 mg, 1.12 mmol) in acetonitrile (5 mL) at room temperature. Upon the disappearance of azide **2** in *tlc*, the mixture was poured into chopped ice, and the resultant solid was filtered and washed with hexane to procure pure CQ **4f** (281 mg, 96%) as a white solid.

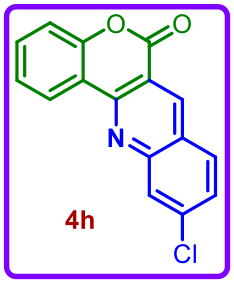


MP: 186-188 °C; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 9.25 (s, 1H), 8.72 (dd, *J* = 6.8, 1.2 Hz, 1H), 8.30 (d, *J* = 9.6 Hz, 2H), 8.04 (dd, *J* = 7.2, 1.6 Hz, 1H), 7.63-7.59 (m, 1H), 7.43 (t, *J* = 7.6 Hz, 1H), 7.36 (d, *J* = 7.6, 8.0 Hz, 1H); **^{13}C{^{1}H} NMR** ($CDCl_3$, 100.6 MHz): δ 160.6, 152.9, 151.8, 151.5, 142.0, 133.2, 130.8, 129.4, 129.0, 128.7, 128.7, 127.3, 127.3, 127.3, 127.2, 126.1, 125.5, 125.2, 124.9, 122.2, 119.1, 117.5, 116.8; **^{19}F NMR** (376.6 MHz, $CDCl_3$): δ -62.68 (s, F); **IR (neat):** 3064, 1728, 1604,

1460, 1288, 1199, 1118, 1064, 834, 754 cm^{-1}; **HRMS** (ESI) m/z calcd. For $C_{17}H_9F_3NO_2$ $[M+H]^+$: 316.0580 found: 316.0583.

10-chloro-6*H*-chromeno[4,3-b]quinolin-6-one (4h):

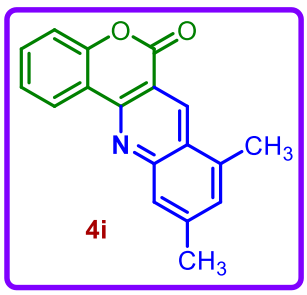
Following the general procedure, azide **2** (200 mg, 0.93 mmol) was treated with 3-Cl-aniline (142 mg, 1.12 mmol) in acetonitrile (5 mL) at room temperature. Upon the disappearance of azide **2** in *tlc*, the mixture was poured into chopped ice, and the resultant solid was filtered and washed with hexane to procure pure CQ **4h** (243 mg, 93%) as a white solid.



^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.18 (s, 1H), 8.74 (d, *J* = 7.6 Hz, 1H), 8.23 (s, 1H), 7.96 (d, *J* = 8.8 Hz, 1H), 7.60 (dd, *J* = 7.2, 6.0 Hz, 2H), 7.46-7.38 (m, 2H); **^{13}C{^{1}H} NMR** ($CDCl_3$, 100.6 MHz): δ 161.1, 152.8, 151.3, 150.6, 140.9, 140.0, 132.8, 130.5, 128.7, 128.6, 125.7, 125.4, 125.1, 119.3, 117.5, 115.9; **IR (neat):** 3066, 1734, 1604, 1498, 1462, 1172, 1114, 1066, 927, 758 cm^{-1}.The spectroscopic data are consistent with the literature report.[5]

8,10-dimethyl-6*H*-chromeno[4,3-b]quinolin-6-one (4i):

Following the general procedure, azide **2** (200 mg, 0.93 mmol) was treated with dimethyl aniline (135 mg, 1.12 mmol) in acetonitrile (5 mL) at room temperature. Upon the disappearance of azide **2** in *tlc*, the mixture was poured into chopped ice, and the resultant solid was filtered and washed with hexane to procure pure CQ **4i** (white solid, 0.248 g, 97%).

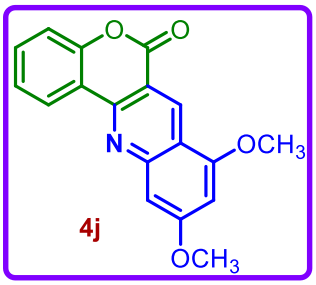


MP: 202-204 °C; **^{1}H NMR (**$CDCl_3$, 400 MHz): δ 9.17-9.15 (m, 1H), 8.69-8.67 (m, 1H), 7.75 (s, 1H), 7.57-7.54 (m, 1H), 7.41-7.33 (m, 2H), 7.19 (s, 1H), 2.68 (s, 3H), 2.53 (s, 3H); **^{13}C{^{1}H} NMR** (100.6 MHz, $CDCl_3$): δ 161.8, 152.6, 151.8, 149.1, 144.3, 137.0, 137.0, 136.3, 132.1, 130.2, 126.6, 125.1, 124.8, 119.7, 117.3, 114.2, 22.3, 18.7; **IR (neat):** 1728, 1602, 1581, 1465, 1373, 1296, 1178, 1114, 1072, 993 cm^{-1}**HRMS** (ESI) m/z calcd. For $C_{18}H_{14}NO_2$ $[M+H]^+$: 276.1019 found: 276.1019.

8,10-dimethoxy-6*H*-chromeno[4,3-b]quinolin-6-one (4j):

Following the general procedure, azide **2** (200 mg, 0.93 mmol) was treated with dimethoxy aniline (171 mg, 1.12 mmol) in acetonitrile (5 mL) at room temperature. Upon the disappearance of azide **2** in *tlc*, the mixture was poured into chopped ice, and the resultant solid was filtered and washed with hexane to procure pure CQ **4j** (white solid, 0.254 g, 89%).

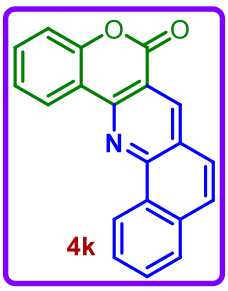
MP: 198-200 °C; **^{1}H NMR (**$CDCl_3$, 400 MHz): δ 9.85 (s, 1H), 8.75 (d, *J* = 8.0 Hz, 1H), 7.87 (t, *J* = 8.0 Hz, 1H), 7.87 (t, *J* = 8.0 Hz, 1H), 7.61 (t, *J* = 8.0 Hz, 1H), 7.53 (d, *J* = 8.4 Hz, 1H), 7.45 (s, 1H), 6.75 (d, *J* = 1.2 Hz, 1H), 4.14 (s, 3H), 4.11 (s, 3H); **^{13}C{^{1}H} NMR** (100.6 MHz, $CDCl_3$): δ 171.9, 171.7, 160.9, 160.8, 160.5, 160.4,



160.1,160.0, 159.7, 158.9, 158.8, 158.3, 153.8, 153.7, 147.0, 144.1, 144.0, 143.9, 143.8, 137.5, 137.4, 126.8, 126.7, 125.2, 125.0, 119.0, 118.8, 118.8, 118.2, 118.1, 116.2, 113.5, 113.3, 111.3, 111.1, 111.0, 110.5, 101.5, 92.4, 92.4, 57.4, 57.4; **IR (neat):** 2976, 1718, 1616, 1566, 1454, 1382, 1367, 1199, 1174, 1151, 966, 831, 759 cm^{-1}. **HRMS** (ESI) m/z calcd. For $C_{18}H_{14}NO_4$ $[M+H]^+$: 308.0918 found: 308.0918.

6*H*-benzo[h]chromeno[4,3-b]quinolin-6-one (4k):

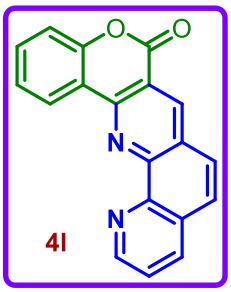
Following the general procedure, azide **2** (200 mg, 0.93 mmol) was treated with 1-napthylamine (160 mg, 1.12 mmol) in acetonitrile (5 mL) at room temperature. Upon the disappearance of azide **2** in *tlc*, the mixture was poured into chopped ice, and the resultant crude product was purified by gravity column chromatography on silica gel (10-25% EtOAc in hexane) to procure CQ **4k** (249 mg, 90%) as a white solid.



MP: 244-246 °C (decomposed); **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 9.24 (d, *J* = 7.2 Hz, 2H), 8.82 (d, *J* = 8.0 Hz, 1H), 7.96-7.28 (m, 6H), 7.45 (d, *J* = 8.0 Hz, 1H); **^{13}C{^{1}H} NMR** ($CDCl_3$, 100.6 MHz): δ 161.8, 161.2, 160.7, 159.9, 152.5, 147.5, 142.4, 135.8, 134.3, 132.0, 130.5, 128.7, 128.5, 127.4, 126.3, 125.9, 125.3, 125.1, 124.8, 118.7, 117.9, 116.6, 115.8, 115.1, 113.0, 110.2; **IR (neat):** 3061, 1734, 1597, 1504, 1396, 1259, 1178, 1101, 956, 748 cm^{-1}. The spectroscopic data are consistent with the literature report.[6]

8*H*-chromeno[4,3-b][1,10]phenanthrolin-8-one (4l):

Following the general procedure, azide **2** (200 mg, 0.93 mmol) was treated with 8-amino-quinoline (161 mg, 1.12 mmol) in acetonitrile (5 mL) at room temperature. Upon the disappearance of azide **2** in *tlc*, the mixture was poured into chopped ice, and the resultant crude product was purified by gravity column chromatography on silica gel (10-25% EtOAc in hexane) to procure CQ **4l** (269 mg, 97%) as a yellow solid.

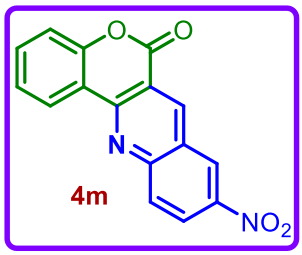


MP: 252-254 °C (decomposed); **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 9.29 (dd, *J* = 2.4, 1.6 Hz, 1H), 9.23 (s, 1H), 9.13 (dd, *J* = 6.4, 1.6 Hz, 1H), 8.30 (dd, *J* = 6.4, 1.6 Hz, 1H), 7.93 (d, *J* = 8.8 Hz, 1H), 7.85 (d, *J* = 8.8 Hz, 1H), 7.74 (dd, *J* = 4.4, 3.6 Hz, 1H), 7.64-7.60 (m, 1H), 7.50-7.46 (m, 1H), 7.42 (dd, *J* = 7.2, 0.8 Hz, 1H); **^{13}C{^{1}H} NMR** ($CDCl_3$, 100.6 MHz): δ 161.3, 152.7, 150.9, 150.3, 149.9, 145.6, 140.0, 136.5, 132.6, 130.8, 128.1, 127.7, 126.9, 126.4, 125.0, 124.5, 119.6, 117.2, 117.0; **IR (neat):** 3045, 1726, 1604, 1496, 1396, 1255, 1170, 1109, 1033, 960, 754 cm^{-1}; **HRMS** (ESI) m/z calcd. For $C_{19}H_{11}N_2O_2$ $[M+H]^+$: 299.0815 found: 299.0815.

9-nitro-6*H*-chromeno[4,3-b]quinolin-6-one (4m):

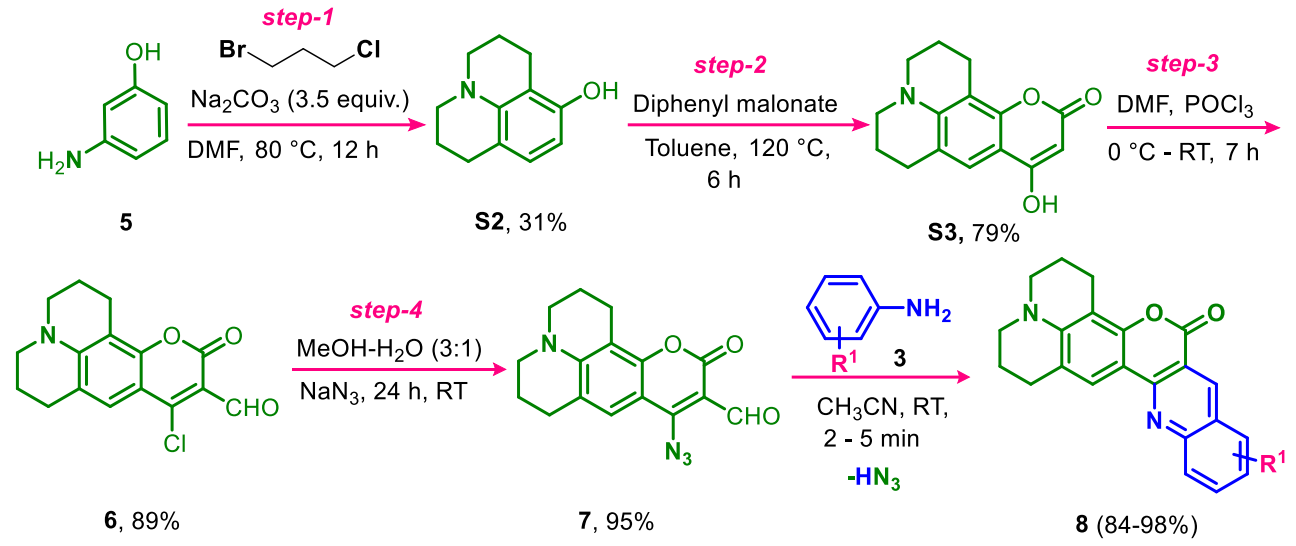
Following the general procedure, azide **2** (200 mg, 0.93 mmol) was treated with 4-NO_2-aniline (154 mg, 1.12 mmol) in acetonitri4le (5 mL) at room temperature. Upon the disappearance of azide **2** in *tlc*, the

mixture was poured into chopped ice, and the resultant crude product was purified by gravity column chromatography on silica gel (10-25% EtOAc in hexane) to procure CQ **4m** (253 mg, 93%).



MP: 256-258 °C; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 9.87 (s, 1H), 9.19 (d, *J* = 2.0 Hz, 1H), 8.93 (dd, *J* = 7.2, 2.0 Hz, 1H), 8.80 (d, *J* = 8.0 Hz, 1H), 8.67 (d, *J* = 9.2 Hz, 1H), 7.92 (t, *J* = 8.0 Hz, 1H), 7.64 (t, *J* = 7.6 Hz, 1H), 7.57 (d, *J* = 8.0 Hz, 1H); **^{13}C{^{1}H} NMR** ($CDCl_3$, 100.6 MHz): δ 161.2, 160.8, 160.4, 160.0, 158.8, 153.9, 151.0, 149.2, 146.9, 146.6, 137.7, 130.3, 126.9, 126.6, 126.5, 126.2, 126.1, 118.7, 117.7, 115.9, 113.9, 113.1, 110.2; **IR (neat):** 3064, 1720, 1604, 1560, 1527, 1485, 1336, 1197, 1089, 950, 842, 758 cm^{-1}. The spectroscopic data are consistent with the literature report.[7]

2.2 Synthesis of fluorogenic C3-C4 quinoline fused 7-julolidino-coumarins (8):



Step-1: Synthesis of 2,3,6,7-tetrahydro-1*H*,5*H*-pyrido[3,2,1-ij]quinolin-8-ol (S2):

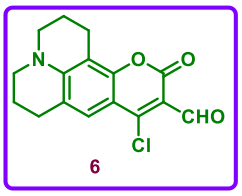
To a solution of 3-amino-phenol **5** (5.0 g, 45.8 mmol) in DMF (20 mL), was added 1-bromo-3-chloropropane (21.62 g, 137.3 mmol, 3 equiv.) and Na_2CO_3 (17.0 g, 160.2 mmol, 3.5 equiv.) at RT. Then, the reaction mixture was heated in a pre-heated oil bath at 80 ºC. After 12 h, the reaction was monitored using *tlc*. After the disappearance of the starting material **5** in *tlc*, the reaction mixture was cooled to room temperature and slowly quenched with ice water. The resulting mixture was extracted with ethyl acetate (4 X 50 mL), and the combined organic layer was washed with water and dried over anhydrous Na_2SO_4. The solvents were evaporated under vacuum, and the residue was purified by column chromatography to afford 2,3,6,7-tetrahydro-1*H*,5*H*-pyrido[3,2,1-ij]quinolin-8-ol **S2** in (2.68 g, 14.2 mmol, 31%) as a white solid.

Step-2: Synthesis of 9-hydroxy-2,3,6,7-tetrahydro-1*H*,5*H*,11*H*-pyrano[2,3-f]pyrido[3,2,1-ij]quinolin-11-one (S3):

To a solution of 2,3,6,7-tetrahydro-1*H*,5*H*-pyrido[3,2,1-ij]quinolin-8-ol **S2** (2.5 g, 13.2 mmol) in toluene (20 mL) was added Diphenyl malonate (5.1 g, 19.8 mmol, 1.5 equiv.) at room temperature. After addition, the reaction mixture was stirred at 120 ºC until the disappearance of **S2** in *tlc*. After completion, the reaction mixture was allowed to cool to room temperature; a fine solid was obtained, then it was filtered, washed with excess toluene, and dried to furnish 9-hydroxy-2,3,6,7-tetrahydro-1*H*,5*H*,11*H*-pyrano[2,3-f]pyrido[3,2,1-ij]quinolin-11-one **S3** (2.69 g, 10.5 mmol, 79%) as a grey solid.

Step-3: Synthesis of 9-chloro-11-oxo-2,3,6,7-tetrahydro-1*H*,5*H*,11*H*-pyrano[2,3-f]pyrido[3,2,1-ij]quinoline-10-carbaldehyde (6):

To a solution of DMF (10 mL) was added $POCl_3$ (10 mL) in one portion at 0 ºC. The resulting solution was stirred at the same temperature for 0.5 hours. A solution of 9-hydroxy-2,3,6,7-tetrahydro-1*H*,5*H*,11*H*-pyrano[2,3-f]pyrido[3,2,1-ij]quinolin-11-one **S3** (1.7 g, 6.6 mmol), dissolved in 10 mL DMF) was then added to the mixture at that temperature. Then, the mixture was allowed to be stirred overnight at room temperature. And the reaction was monitored by *tlc*. After the disappearance of the starting material **S3** in *tlc*, the reaction mixture was quenched with ice water (50 mL); a fine solid was obtained, then it was filtered, washed with excess water, and dried to afford 9-chloro-11-oxo-2,3,6,7-tetrahydro-1*H*,5*H*,11*H*-pyrano[2,3-f]pyrido[3,2,1-ij]quinoline-10-carbaldehyde **6** (2.23 g, 5.86 mmol, 89%) as a red solid.

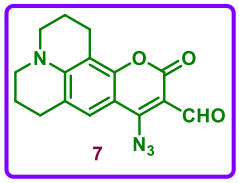


6

^{1}H NMR ($CDCl_3$, 400 MHz): δ 10.21 (s, 1H), 7.38 (s, 1H), 3.37 (dd, *J* = 11.6 Hz, 6.0 Hz, 4H), 2.83 (t, *J* = 6.4 Hz, 2H), 2.77 (t, *J* = 6.4 Hz, 2H), 2.01–1.94 (m, 4H); **^{13}C{^{1}H} NMR** (100.6 MHz, $CDCl_3$): δ 187.1, 160.2, 153.5, 151.4, 149.7, 124.9, 120.5, 109.4, 107.25, 105.6, 50.4, 50.0, 27.5, 20.9, 20.1, 19.9; **IR (neat):** 1738, 1702, 1608, 1495, 1426, 1332, 1303, 1169, 1052, 739 cm-1. The spectroscopic data are consistent with the literature report.[8]

Step-4: Synthesis of 9-azido-11-oxo-2,3,6,7-tetrahydro-1*H*,5*H*,11*H*-pyrano[2,3-f]pyrido[3,2,1-ij]quinoline-10-carbaldehyde (7):

To a solution of 9-chloro-11-oxo-2,3,6,7-tetrahydro-1*H*,5*H*,11*H*-pyrano[2,3-f]pyrido[3,2,1-ij]quinoline-10-carbaldehyde **6** (2 g, 6.58 mmol) in MeOH (15 mL), a solution of sodium azide (0.86 g, 13.16 mmol, 2 equiv.) in H_2O (5 mL) was added in one portion at room temperature. This mixture was allowed to stir until the disappearance of **6** in *tlc*; after completion, the reaction mixture was slowly poured into the beaker containing chopped ice. A fine, dense red solid was obtained, then it was filtered, washed with water, and dried to afford 9-azido-11-oxo-2,3,6,7-tetrahydro-1*H*,5*H*,11*H*-pyrano[2,3-f]pyrido[3,2,1-ij]quinoline-10-carbaldehyde **7** (1.72 g, 5.53 mmol, 84%) as a red solid. The crude product was pure enough for the next step and used without further purification.



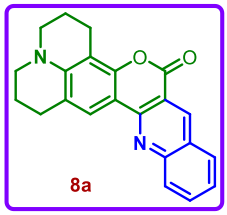
^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.15 (s, 1H), 7.46 (s, 1H), 3.27 (dd, *J* = 11.6 Hz, 6.4 Hz, 4H), 2.89 (t, *J* = 6.4 Hz, 2H), 2.80 (t, *J* = 6.4 Hz, 2H), 2.02-1.96 (m, 4H); **^{13}C{^{1}H} NMR** (100.6 MHz, $CDCl_3$): δ 162.3, 156.4, 156.0, 150.2, 145.9, 121.6, 119.4, 108.8, 107.4, 97.6, 50.2, 49.7, 27.4, 21.3, 21.0, 20.5; **IR (neat):** 3103, 2940, 2853, 2134, 1735, 1704, 1605, 1491, 1436, 1309, 1155, 1072, 1041 765 cm^{-1}; **HRMS** (ESI) m/z calcd. For $C_{16}H_{15}N_4O_3$ $[M+H]^+$: 311.1139 found: 311.1142.

2.2.1 General Procedure for the synthesis of fluorogenic C3-C4 quinoline fused 7-julolidino-coumarins CQ (8a-8j):

Following the general procedure (**1.1**), the reaction of julolidino-4-azido-3-formylcoumarin **7** (0.1 g, 0.32 mmol) and aniline **3** (0.39 mmol, 1.2 equiv.) in acetonitrile (3 mL) was stirred at room temperature. Upon the disappearance of azide **7** in *tlc*, the resultant crude product was purified by gravity column chromatography on silica gel (10-25% EtOAc in hexane) to procure CQ **8a-8j** as an orange/red solid.

2,3-phenyl-8,9,12,13-tetrahydro-5*H*,7*H*,11*H*-pyrido[3,2,1-ij]pyrido[2',3':4,5]pyrano[2,3-f]quinolin-5-one (8a):

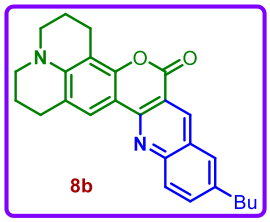
Following the general procedure, azide **7** (100 mg, 0.32 mmol) was treated with aniline (36 mg, 0.39 mmol) in acetonitrile (3 mL) at room temperature. Upon the disappearance of azide **7** in *tlc*, the mixture was poured into chopped ice, and the resultant solid was filtered and washed with hexane to procure pure CQ **8a** (110 mg, 96%) as a red solid.



MP: 196-198 °C; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 9.07 (s, 1H), 8.08 (d, *J* = 11.2 Hz, 2H), 7.89 (d, *J* = 8.0 Hz, 1H), 7.82-7.78 (m, 1H), 7.48 (t, *J* = 7.2 Hz, 1H), 2.77 (dd, *J* = 12.0, 7.6 Hz, 4H), 2.93 (t, *J* = 6.4 Hz, 2H), 2.88 (t, *J* = 6.4 Hz, 2H), 2.04-2.0 (m, 4H); **^{13}C{^{1}H} NMR** ($CDCl_3$, 100.6 MHz): δ 162.3, 151.5, 151.0, 149.7, 146.3, 140.9, 132.9, 129.4, 128.8, 126.3, 125.8, 122.2, 118.7, 114.6, 107.1, 107.0, 50.1, 49.5, 27.6, 21.7, 20.8, 20.8; **IR (neat):** 2921, 2844, 1716, 1596, 1488, 1452, 1308, 1171, 792 cm^{-1}; **HRMS** (ESI) m/z calcd. For $C_{22}H_{19}N_2O_2$ $[M+H]^+$: 343.1441 found: 343.1438.

2,3-*p*-butyl-phenyl-8,9,12,13-tetrahydro-5*H*,7*H*,11*H*-pyrido[3,2,1-ij]pyrido [2',3':4,5] pyrano[2,3-f]quinolin-5-one (8b):

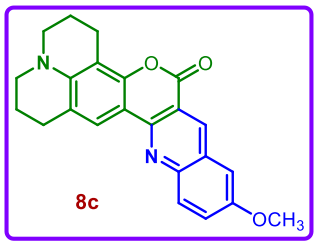
Following the general procedure, azide **7** (100 mg, 0.32 mmol) was treated with 4-butyl-aniline (58 mg, 0.39 mmol) in acetonitrile (3 mL) at room temperature. Upon the disappearance of azide **7** in *tlc*, the mixture was poured into chopped ice, and the resultant solid was filtered and washed with hexane to procure pure CQ **8b** (121 mg, 94%) as a red solid.



MP: 158-160 °C; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 8.98 (s, 1H), 8.12 (s, 1H), 8.04 (d, *J* = 8.8 Hz, 1H), 7.65 (t, *J* = 9.2 Hz, 2H), 3.28-3.24 (m, 4H), 2.93-2.86 (m, 4H), 2.78 (t, *J* = 8.0 Hz, 2H), 2.00 (t, *J* = 5.6 Hz, 4H), 1.74-1.66 (m, 2H), 1.46-1.36 (m, 2H), 0.96 (t, *J* = 7.6 Hz, 3H); **^{13}C{^{1}H} NMR** ($CDCl_3$, 100.6 MHz): δ 162.3, 150.1, 150.0, 149.6, 146.2, 140.8, 140.4, 134.9, 128.2, 127.4, 126.3, 122.2, 118.7, 114.4, 107.1, 106.8, 50.1, 49.5, 35.4, 33.2, 27.6, 22.4, 21.7, 20.8, 20.7, 13.9; **IR (neat):** 2921, 2850, 1728, 1602, 1452, 1344, 1302, 1171, 1038, 829,792 cm^{-1}; **HRMS** (ESI) m/z calcd. For $C_{26}H_{27}N_2O_2$ $[M+H]^+$: 399.2067 found: 399.2080.

2,3-*p*-anisyl-8,9,12,13-tetrahydro-5*H*,7*H*,11*H*-pyrido[3,2,1-ij]pyrido[2',3':4,5]pyrano[2,3-f]quinolin-5-one (8c):

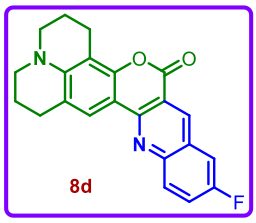
Following the general procedure, azide **7** (100 mg, 0.32 mmol) was treated with *p*-anisidine (48 mg, 0.39 mmol) in acetonitrile (3 mL) at room temperature. Upon the disappearance of azide **7** in *tlc*, the mixture was poured into chopped ice, and the resultant solid was filtered and washed with hexane to procure pure CQ **8c** (110 mg, 92%) as an orange solid.



MP: 222-224 °C; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 9.02, (s, 1H), 8.51 (s, 2H), 7.52 (dd, *J* = 9.2, 2.8 Hz, 1H), 7.15 (d, *J* = 2.4 Hz, 1H), 3.95 (s, 3H), 3.31 (dd, *J* = 11.6, 6.0 Hz, 4H), 2.91 (t, *J* = 6.4 Hz, 4H), 2.04-1.97 (m, 4H); **^{13}C{^{1}H} NMR** ($CDCl_3$, 100.6 MHz): δ 161.3, 157.6, 149.6, 146.9, 140.6, 128.3, 127.1, 126.8, 122.8, 119.2, 114.7, 107.0, 106.2, 55.8, 50.2, 49.6, 27.5, 21.5, 20.7, 20.6; **IR (neat):** 1722, 1596, 1495, 1348, 1300, 1231, 1166, 1125, 1027, 828, 788 cm^{-1}; **HRMS** (ESI) m/z calcd. For $C_{23}H_{21}N_2O_3$ $[M+H]^+$: 373.1547 found: 373.1545.

2,3-*p*-fluoro-phenyl-8,9,12,13-tetrahydro-5*H*,7*H*,11*H*-pyrido[3,2,1-ij]pyrido[2',3':4,5]pyrano[2,3-f]quinolin-5-one (8d):

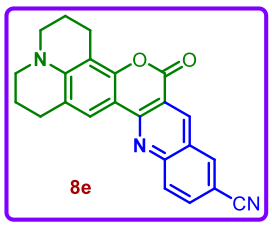
Following the general procedure, azide **7** (100 mg, 0.32 mmol) was treated with 4-fluroaniline (43 mg, 0.39 mmol) in acetonitrile (3 mL) at room temperature. Upon the disappearance of azide **7** in *tlc*, the mixture was poured into chopped ice, and the resultant solid was filtered and washed with hexane to procure pure CQ **8d** (109 mg, 94%) as a red solid.



MP: 210-212 °C; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 8.99 (s, 1H), 8.25 (d, *J* = 14.8 Hz, 2H), 7.58 (t, *J* = 7.6 Hz, 1H), 7.49 (d, *J* = 8.0 Hz, 1H), 3.29 (dd, *J* = 11.6, 6.4 Hz, 4H), 2.89 (d, *J* = 13.2, 6.4 Hz, 4H), 2.04-1.94 (m, 4H); **^{13}C{^{1}H} NMR** ($CDCl_3$, 100.6 MHz): δ 161.2, 158.7, 149.9, 147.5, 141.7, 129.3, 126.2 (d, *J* = 10.1 Hz), 124.2 (d, *J* = 25.2 Hz), 123.1, 119.4, 115.4, 112.3 (d, *J* = 22.1 Hz), 107.0, 50.2, 49.7, 27.5, 21.4, 20.6; **^{19}F NMR** (376.6 MHz, $CDCl_3$) δ -108.9 to – 109.0 (m, F); **IR (neat):** 1714, 1604, 1491, 1458, 1348, 1295, 1214, 1174, 1112, 1040, 958, 881 cm^{-1}; **HRMS** (ESI) m/z calcd. For $C_{22}H_{18}FN_2O_2$ $[M+H]^+$: 361.1347 found: 361.1349.

2,3-*p*-benzonitrile-8,9,12,13-tetrahydro-5*H*,7*H*,11*H*-pyrido[3,2,1-ij]pyrido[2',3':4,5]pyrano[2,3-f] quinolin-5-one (8e):

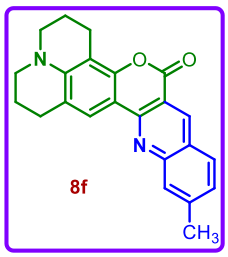
Following the general procedure, azide **7** (100 mg, 0.32 mmol) was treated with 4-aminobenzonitrile (46 mg, 0.39 mmol) in acetonitrile (3 mL) at room temperature. Upon the disappearance of azide **7** in *tlc*, the mixture was poured into chopped ice, and the resultant solid product was purified by column chromatography on silica gel (10 -15% EtOAc in hexane) to procure CQ **8e** (102 mg, 86%) as a red solid.



MP: 254-256 °C; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 9.27 (s, 1H), 8.85 (d, *J* = 2.0 Hz, 1H), 8.70 (dd, *J* = 9.2, 2.0, 1H), 8.20 (d, *J* = 9.2 Hz, 1H), 7.84 (s, 1H), 3.52 (t, *J* = 5.6 Hz, 4H), 2.90-2.81 (m, 4H), 2.08-2.02 (m, 4H); **^{13}C{^{1}H} NMR** ($CDCl_3$, 100.6 MHz): δ 160.6, 160.2, 159.8, 159.4, 157.4, 152.8, 151.6, 147.9, 146.6, 145.5, 143.3, 131.0, 126.2, 123.6, 123.1, 122.8, 120.9, 119.2, 117.5, 116.3, 110.6, 108.0, 97.7, 51.3, 50.6, 26.9, 20.5, 20.0, 19.6; **IR (neat):** 2895, 2221, 1724, 1586, 1438, 1357, 1257, 1113, 1008, 821, 759 cm^{-1}; **HRMS** (ESI) m/z calcd. For $C_{23}H_{18}N_3O_2$ $[M+H]^+$: 368.1394 found: 368.1395.

2,3-*m*-tolyl-8,9,12,13-tetrahydro-5*H*,7*H*,11*H*-pyrido[3,2,1-ij]pyrido[2',3':4,5]pyrano[2,3-f]quinolin-5-one (8f):

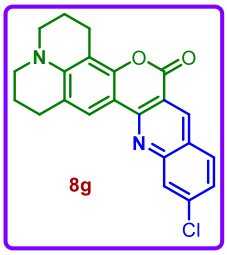
Following the general procedure, azide **7** (100 mg, 0.32 mmol) was treated with *p*-toluidine (41 mg, 0.39 mmol) in acetonitrile (3 mL) at room temperature. Upon the disappearance of azide **7** in *tlc*, the mixture was poured into chopped ice, and the resultant solid was filtered and washed with hexane to procure pure CQ **8f** (110 mg, 96%) as a red solid.



MP: 166-168 °C; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 9.0 (s, 1H), 8.07 (s, 1H), 7.85 (s, 1H), 7.77 (d, *J* = 8.4 Hz, 1H), 7.31 (dd, *J* = 8.4, 0.8 Hz, 1H), 3.26 (dd, *J* = 12.0, 7.2 Hz, 4H), 2.95-2.86 (m, 4H), 2.57 (s, 3H), 2.03-2.0 (m, 4H); **^{13}C{^{1}H} NMR** ($CDCl_3$, 100.6 MHz): δ 162.5, 151.7, 151.1, 149.7, 146.2, 143.9, 140.4, 129.0, 128.2, 127.8, 124.5, 122.1, 118.6, 113.8, 107.2, 107.1, 50.1, 49.5, 27.6, 22.3, 21.7, 20.9, 20.8; **IR (neat):** 2914, 2820, 1733, 1623, 1593, 1569, 1359, 1236, 1120, 1063, 911, 801, 779 cm^{-1}; **HRMS** (ESI) m/z calcd. For $C_{23}H_{21}N_2O_2$ $[M+H]^+$: 357.1598 found: 357.1601.

2,3-*m*-chloro-phenyl-8,9,12,13-tetrahydro-5*H*,7*H*,11*H*-pyrido[3,2,1-ij]pyrido[2',3':4,5]pyrano[2,3-f]quinolin-5-one (8g):

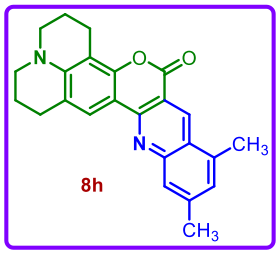
Following the general procedure, azide **2** (100 mg, 0.32 mmol) was treated with *p*-toluidine (49 mg, 0.39 mmol) in acetonitrile (3 mL) at room temperature. Upon the disappearance of azide **2** in *tlc*, the mixture was poured into chopped ice, and the resultant solid was filtered and washed with hexane to procure pure CQ **8g** (112 mg, 84%) as a red solid.



MP: 250-252; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 9.01 (s, 1H), 8.28 (s, 2H), 7.81 (d, *J* = 8.8 Hz, 1H), 7.43 (d, *J* = 8.0 Hz, 1H), 3.31 (dd, *J* = 12.0, 6.8 Hz, 4H), 2.91-2.88 (m, 4H), 2.0-1.98 (m, 4H); **^{13}C{^{1}H} NMR** ($CDCl_3$, 100.6 MHz): δ 162.0, 151.9, 151.8, 149.9, 146.6, 140.6, 139.1, 130.5, 127.7, 126.8, 124.6, 122.3, 118.8, 114.6, 107.0, 106.6, 50.1, 49.6, 27.6, 21.6, 20.8, 20.7; **IR (neat):** 3259, 2913, 1701, 1590, 1518, 1488, 1441, 1385, 1337, 1255, 1195, 1152, 1109, 1028, 842, cm^{-1}; **HRMS** (ESI) m/z calcd. For $C_{22}H_{18}ClN_2O_2$ $[M+H]^+$: 377.1052 found: 377.1044.

2,3-*m*-xylene-8,9,12,13-tetrahydro-5*H*,7*H*,11*H*-pyrido[3,2,1-ij]pyrido[2',3':4,5]pyrano[2,3-f]quinolin-5-one (8h):

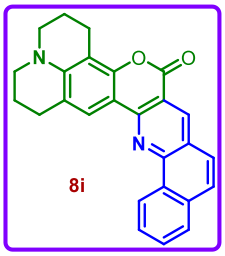
Following the general procedure, azide **7** (100 mg, 0.32 mmol) was treated with dimethylaniline (47 mg, 0.39 mmol) in acetonitrile (3 mL) at room temperature. Upon the disappearance of azide **7** in *tlc*, the mixture was poured into chopped ice, and the resultant solid was filtered and washed with hexane to procure pure CQ **8h** (117 mg, 98%) as an orange solid.



MP: 228-230 °C; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 9.15 (s, 1H), 8.06 (s, 1H), 7.70 (s, 1H), 7.13 (s, 1H), 3.26 (s, 4H), 2.94-2.88 (m, 4H), 2.69 (s, 3H), 2.51 (s, 3H), 2.01 (s, 4H); **^{13}C{^{1}H} NMR** ($CDCl_3$, 100.6 MHz): δ 162.7, 152.3, 150.6, 149.7, 146.1, 143.6, 137.0, 136.3, 128.8, 126.0, 124.2, 122.0, 118.6, 113.1, 107.2, 107.1, 50.1, 49.5, 27.6, 22.2, 21.7, 20.9, 20.8, 18.7; **IR (neat):** 3149, 2945, 1729, 1611, 1611, 1583, 1499, 1451, 1352, 1315, 1217, 1119, 1038, 868 cm^{-1}; **HRMS** (ESI) m/z calcd. For $C_{24}H_{23}N_2O_2$ $[M+H]^+$: 371.1754 found: 371.1761.

2,3-napthyl-8,9,12,13-tetrahydro-5*H*,7*H*,11*H*-pyrido[3,2,1-ij]pyrido[2',3':4,5]pyrano[2,3-f]quinolin-5-one (8i):

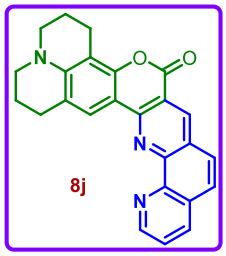
Following the general procedure, azide **7** (100 mg, 0.32 mmol) was treated with *p*-toluidine (55 mg, 0.39 mmol) in acetonitrile (3 mL) at room temperature. Upon the disappearance of azide **7** in *tlc*, the mixture was poured into chopped ice, and the resultant crude product was purified by gravity column chromatography on silica gel (10 -15% EtOAc in hexane) to procure CQ **8i** (112 mg, 89%) as a red solid.



MP: 242-244 °C; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 9.30 (d, *J* = 3.2 Hz, 1H), 8.82 (s, 1H), 8.08 (s, 1H), 7.80-7.78 (m, 1H), 7.70-7.68 (m, 2H), 7.61-7.55 (m, 2H), 3.28-3.23 (m, 4H), 2.91-2.84 (m, 4H), 2.04-1.99 (m, 4H); **^{13}C{^{1}H} NMR** ($CDCl_3$, 100.6 MHz): δ 162.3, 150.5, 150.1, 149.7, 146.0, 138.8, 135.1, 130.8, 129.6, 127.8, 126.9, 125.7, 125.6, 124.2, 122.1, 118.5, 113.8, 107.5, 107.0, 50.1, 49.5, 27.7, 21.8, 20.8, 20.7; **IR (neat):** 3046, 2918, 2848, 1710, 1600, 1429, 1306, 1260, 1162, 1016, 770 cm^{-1}; **HRMS** (ESI) m/z calcd. For $C_{26}H_{21}N_2O_2$ $[M]^+$: 392.1525 found: 392.1526.

2,3-quinoline-8,9,12,13-tetrahydro-5*H*,7*H*,11*H*-pyrido[3,2,1-ij]pyrido[2',3':4,5]pyrano[2,3-f]quinolin-5-one (8j):

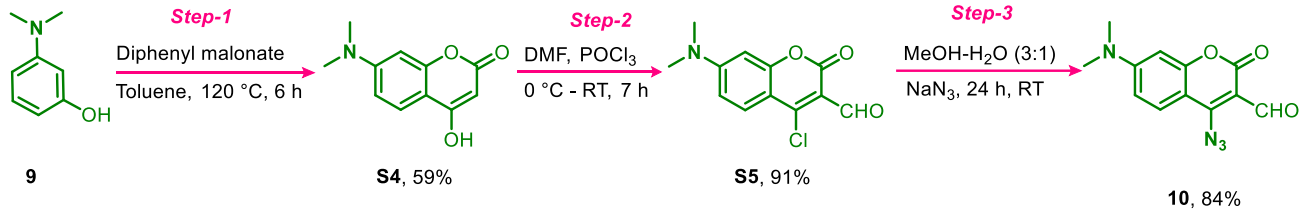
Following the general procedure, azide **7** (100 mg, 0.32 mmol) was treated with *p*-toluidine (56 mg, 0.39 mmol) in acetonitrile (3 mL) at room temperature. Upon the disappearance of azide **7** in *tlc*, the mixture was poured into chopped ice, and the resultant crude product was purified by gravity column chromatography on silica gel (10 -15% EtOAc in hexane) to procure CQ **8j** (106 mg, 84%) as a red colour solid.



MP: 186-188 °C (decomposed); **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 9.23 (dd, *J* = 4.4 Hz, 1.6 Hz, 1H), 9.09 (s, 1H), 8.45 (s, 1H), 8.24 (dd, *J* = 8.0 Hz, 1.6 Hz, 1H), 7.82 (d, *J* = 8.8 Hz, 1H), 7.71-7.66 (m, 2H), 3.31-3.27 (m, 4H), 2.98-2.92 (m, 4H), 2.06-1.98 (m, 4H); **^{13}C{^{1}H} NMR** ($CDCl_3$, 100.6 MHz): δ 162.4, 151.8, 150.5, 150.2, 149.9, 146.6, 145.6, 140.0, 136.3, 130.8, 127.2, 126.5, 125.6, 124.0, 123.4, 118.7, 115.2, 107.2, 106.8, 50.1, 49.6, 27.5, 21.7, 20.8, 20.8; **IR (neat):** 3051, 2925, 1728, 1599, 1492, 1440, 1382, 1307, 1156, 1096, 1050, 836, 789 cm^{-1}; **HRMS** (ESI) m/z calcd. For $C_{25}H_{20}N_3O_2$ $[M+H]^+$: 394.1550 found: 394.1554.

2.3 Synthesis of fluorogenic C3-C4 quinoline fused 7-dimethylamino-coumarins (12):

2.3.1 Synthesis of 4-azido-7-(dimethylamino)-2-oxo-2*H*-chromene-3-carbaldehyde (10) from 3-N, N-di-methyl-phenol (9):

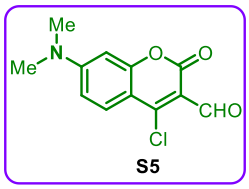


Step-1: Synthesis of 7-(dimethylamino)-4-hydroxy-2*H*-chromen-2-one (S4):

To a stirred solution of 3-N, N-di-methyl-phenol **9** (3 g, 21.86 mmol) in toluene (30 mL) was added diphenyl malonate (8.4 g, 32.8 mmol, 1.5 equiv.) at room temperature. After addition, the reaction mixture was stirred at 120 ºC until the disappearance of **9** in *tlc*. After completion, the reaction mixture was allowed to cool to room temperature; a fine solid was obtained, then it was filtered, washed with excess toluene, and dried to furnish 7-(dimethylamino)-4-hydroxy-2*H*-chromen-2-one **S4** (2.65 g, 12.9 mmol, 59%) as a grey solid.

Step-2: Synthesis of 4-chloro-7-(dimethylamino)-2-oxo-2*H*-chromene-3-carbaldehyde (S5):

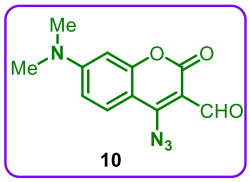
To a solution of DMF (20 mL) was added $POCl_3$ (20 mL) in one portion at 0 ºC. The resulting solution was stirred at the same temperature for 0.5 hours. A solution of 7-(dimethylamino)-4-hydroxy-2*H*-chromen-2-one **S4** (2 g, 9.75 mmol), dissolved in 20 mL) was added to the mixture at that temperature. Then, the mixture was allowed to be stirred overnight at room temperature. And the reaction was monitored by *tlc*. After the disappearance of the starting material **S4** in *tlc*, the reaction mixture was quenched with ice water (50 mL); a fine solid was obtained, then it was filtered, washed with excess water, and dried to afford 4-chloro-7-(dimethylamino)-2-oxo-2*H*-chromene-3-carbaldehyde **S5** (2.23 g, 8.86 mmol, 91%) as a red coloure solid.



MP: 92-194 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.26 (S, 1H), 7.80 (d, *J* = 9.2 Hz, 1H), 6.68 (dd, *J* = 9.6 Hz, 2.8 Hz, 1H), 6.38 (d, *J* = 2.4, 1H), 3.14 (S, 6H); **^{13}C{^{1}H} NMR** (100.6 MHz, $CDCl_3$); δ 187.0, 159.8, 156.0, 155.4, 154.2, 129.0, 111.4, 110.7, 107.9, 96.9, 40.3; **IR (neat):** 2922, 2852, 1718, 1683, 1589, 1483, 1294, 1255, 1139, 1062, 981, 894, 839,779 cm^{-1}. The spectral data is in accordance with the literature. [8]

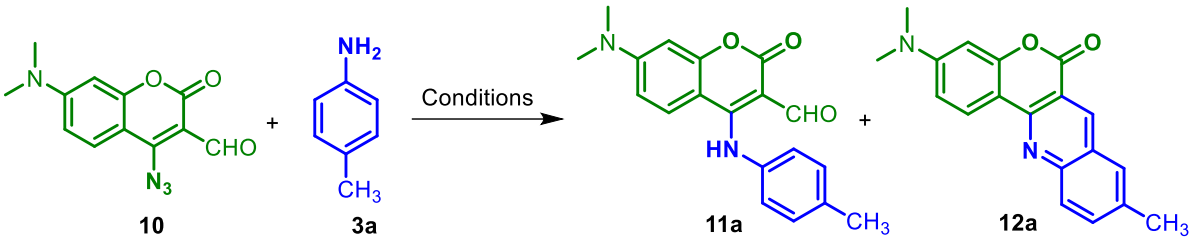
Step-3: 4-azido-7-(dimethylamino)-2-oxo-2*H*-chromene-3-carbaldehyde (10):

To a solution of 4-chloro-7-(dimethylamino)-2-oxo-2*H*-chromene-3-carbaldehyde **S5** (2 g, 7.95 mmol) in MeOH (15 mL), a solution of sodium azide (1.03 g, 15.89 mmol, 2 equiv.) in H_2O (3 mL) in one portion at room temperature. This mixture was allowed to stir until the **S5** disappeared in *tlc*. After completion, the reaction mixture was slowly poured into ice water. A fine, dense red-colored solid was obtained, then it was filtered, washed with water, and dried to afford 4-azido-7-(dimethylamino)-2-oxo-2*H*-chromene-3-carbaldehyde **10** (1.73 g, 6.70 mmol, 84%) as a red solid. The crude product was pure enough for the next step and used without further purification.



MP: 154-156 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.18 (s, 1H), 7.86 (d, *J* = 8.8 Hz, 1H), 6.66 (dd, *J* = 8.8Hz, 2.4 Hz, 1H), 6.53 (d, *J* = 2.4 Hz, 1H), 3.07 (s, 6H); **^{13}C{^{1}H} NMR** (100.6 MHz, $CDCl_3$); δ 162.3, 156.3, 155.7, 155.0, 153.7, 125.2, 109.5, 107.5, 99.0, 97.8, 40.2; **IR (neat):** 2916, 2156, 1724, 1658, 1610, 1550, 1490, 1409, 1352, 1292, 1232, 1145, 1060, 964, 896 cm^{-1}. The spectral data is in accordance with the literature.[9]

Table 2. Optimization of reaction condition[a] for the synthesis of fluorogenic C3-C4 quinoline fused 7-dimethylamino-coumarin 12a in the presence of aniline



entry	reactant	solvent	catalyst (1 eq)	temp. (°C)	time (h)	yield, %[c]	
						11a	**12a**
1[a]	**10**	CH_3CN	-	RT	0.5	76	-
2[a]	**10**	CH_3CN	$InCl_3$	100	0.5	81	-
3[a]	**10**	Toluene	-	150	6	86	-
4[a]	**10**	Toluene	*p*-TsOH	150	9	84	
5[a]	**10**	CF_3COOH	-	RT/60/100	24	No reaction	
6[a]	**10**	**CH_3CN**	**Et_3N**	**RT**	**0.5**	**92**	**-**
7[b]	**11a**	CH_3CN	$InCl_3$	RT/100	24	No reaction	
8[b]	**11a**	CH_3CN	CF_3COOH	RT/60/100	24	No reaction	
9[b]	**11a**	CF_3COOH	-	RT	48	No reaction	
10[b]	**11a**	**CF_3COOH**	**-**	**60**	**2**	**-**	**98**

[a]Reaction conditions: The reactions were performed with 4-azido-7-(dimethylamino)-2-oxo-2*H*-chromene-3-carbaldehyde **10** (100 mg, 0.38 mmol), *p*-toluidine (50 mg, 0.46 mmol), catalyst (1 equiv.), base (3 equiv.) in appropriate solvent mentioned in the table (4 mL).

[b]Reaction conditions: The reactions were performed with 7-(dimethylamino)-2-oxo-4-(*p*-tolylamino)-2*H*-chromene-3-carbaldehyde **11a** (100 mg, 0.31 mmol), in CF_3COOH (1.5 mL) at 60 °C.

[c]Isolated yield.

To our surprise, the reaction of azide **10** with *p*-toluidine **3a** in acetonitrile at RT procured significantly 7-dimethylamino-4-(*p*-toluylamino)-3-formylcoumarin **11a** in 76% isolated yield as the only product rather than the anticipated CQ **12a** (entry 1), as observed in the previous substrate azide **2** and **7**; and require further modification of previous optimized reaction condition. Further attempts using catalysts such as $InCl_3$, *p*-TsOH, and solvents such as acetonitrile, toluene, and CF_3COOH at variable temperatures furnished only **11a** in good yield 81-86% (entries 2-4). It is worth mentioning that using CF_3COOH as a solvent at RT, 60 °C and 100 °C did not furnish either **11a** and/or **12a,** and the starting material **10** was recovered as such (entry 5). Next, using one equivalent of Et_3N as a base in CH_3CN at RT exclusively furnished **11a** in an excellent yield of 92% (entry-6).

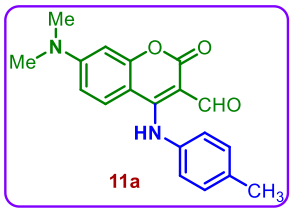
Further, we attempted the Pomeranz-Fritsch type cyclization[10] of 7-dimethylamino-4-(*p*-toluylamino)-3-formylcoumarin **11a** using indium chloride (1.0 equiv.) and CF_3COOH (1.0 equiv.) in CH_3CN at RT, 60 °C and 100 °C. In all these conditions, there was no reaction, and only starting material was recovered (entries 7 and 8). Delightfully, when we tried with CF_3COOH as a solvent (1.5 mL) at 60 °C, the reaction procured the CQ **12a** in 98% isolated yield through a simple aqueous workup. It is worth mentioning that this reaction did not take place at RT even after 48h (entries 9 and 10).

2.3.2 General Procedure for the synthesis of 7-dimethylamino-4-(N-arylamino)-3-formylcoumarin (11a-11j) from 4-azido-7-(dimethylamino)-2-oxo-2*H*-chromene-3-carbaldehyde (10):

The Aldrich-Ace pressure tube (25 mL capacity) equipped with a magnetic stirrer bar was added 4-azido-7-(dimethylamino)-2-oxo-2*H*-chromene-3-carbaldehyde **10** (100 mg, 0.39 mmol), aniline **3** (0.46 mmol, 1.2 equiv.) Et_3N (0.39 mmol, 1 equiv.) in acetonitrile (5mL) at room temperature. Then, the reaction mixture was allowed to stir at room temperature. After the disappearance of starting material **10** in *tlc*, the reaction mixture was quenched with ice water (30 mL) (in case of precipitate formation, the resulting solid was filtered and washed with hexane) and extracted with chloroform (3 X 20 mL). The combined organic phase was washed with an aqueous solution of $NaHCO_3$ (10%, 2 X 15 mL) and water (2 X 15 mL), then dried over anhydrous $MgSO_4$, and the volatiles were removed under vacuum. The resulting solid product was washed with cold hexane/ethanol to remove the traces of excess aniline, and in the selective cases, column chromatography was used to afford the pure 7-dimethylamino-4-(N-arylamino)-3-formylcoumarin **11a-11j**. The mentioned yields were calculated upon the isolation of pure products.

7-(dimethylamino)-2-oxo-4-(*p*-tolylamino)chromane-3-carbaldehyde (11a):

Following the general procedure, azide **10** (100 mg, 0.39 mmol) was treated with *p*-toluidine (50 mg, 0.46 mmol) in acetonitrile (3 mL) at room temperature. Upon the disappearance of azide **10** in *tlc*, the mixture was poured into chopped ice, and the resultant solid was filtered and washed with EtOH to procure pure CQ **11a** (115 mg, 92%) as a yellow solid.

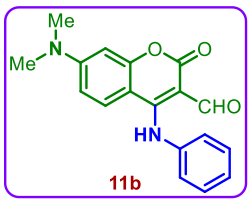


11a

MP: 228-230 °C; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 12.89 (brs, 1H, D_2O-exchangeable), 10.14 (s, 1H), 7.22 (d, J = 8.0 Hz, 2H), 7.14 (d, J = 8.0 Hz, 2H), 6.93 (d, J = 9.2 Hz, 1H), 6.41 (d, J = 2.4 Hz, 1H), 6.23 (dd, J = 9.2, 2.4 Hz, 1H), 3.02 (s, 6H), 2.41 (s, 3H); **^{13}C{^{1}H} NMR** ($CDCl_3$, 100.6 MHz): δ 191.5, 163.7, 157.9, 157.7, 153.9, 137.7, 136.6, 130.5, 129.1, 125.7, 108.2, 101.2, 98.5, 96.1, 40.0, 21.2; **IR (neat):** 2890, 1696, 1590, 1438, 1337, 1261, 1118, 1012, 798, 759 cm^{-1}; **HRMS** (ESI) m/z calcd. For $C_{19}H_{19}N_2O_3$ $[M+H]^+$: 323.1390 found: 323.1393.

7-(dimethylamino)-2-oxo-4-(phenylamino)chromane-3-carbaldehyde (11b):

Following the general procedure, azide **10** (100 mg, 0.39 mmol) was treated with aniline (43 mg, 0.46 mmol) in acetonitrile (3 mL) at room temperature. Upon the disappearance of azide **10** in *tlc*, the mixture was poured into chopped ice, and the resultant solid was filtered and washed with EtOH to procure pure CQ **11b** (98 mg, 82%) as a yellow solid.



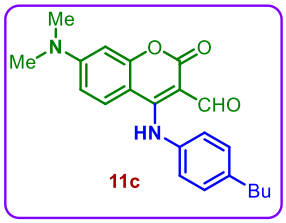
11b

MP: 204-206 °C; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 12.93 (brs, 1H, D_2O-exchangeable), 10.15 (s, 1H), 7.45-7.42 (m, 2H), 7.38-7.34 (m, 1H), 7.28-7.26 (m, 2H), 6.88 (d, J = 9.6 Hz, 1H), 6.38 (d, J = 2.8 Hz, 1H), 6.18 (dd, J = 9.6, 2.8 Hz, 1H), 3.02 (s, 6H); **^{13}C{^{1}H} NMR** ($CDCl_3$, 100.6 MHz): δ 191.6, 163.7, 157.8, 157.8, 154.1, 139.4, 129.9, 129.0,

127.6, 125.8, 108.0, 100.8, 98.2, 96.2, 39.9; **IR (neat):** 1694, 1608, 1580, 1462, 1434, 1340, 1231, 1112, 1011, 861 cm^{-1}; **HRMS** (ESI) m/z calcd. For $C_{18}H_{17}N_2O_3$ $[M+H]^+$: 309.1234 found: 309.1238.

4-((4-butylphenyl)amino)-7-(dimethylamino)-2-oxochromane-3-carbaldehyde (11c):

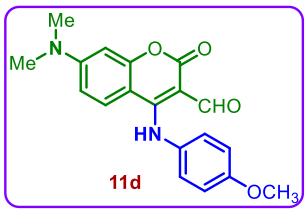
Following the general procedure, azide **10** (100 mg, 0.39 mmol) was treated with 4-butyl-aniline (69 mg, 0.46 mmol) in acetonitrile (3 mL) at room temperature. Upon the disappearance of azide **10** in *tlc*, the mixture was poured into chopped ice, and the resultant solid was filtered and washed with EtOH to procure pure CQ **11c** (121 mg, 86%) as a yellow solid.



MP: 168-170 °C; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 12.88 (brs, 1H, D_2O-exchangeable), 10.12 (s, 1H), 7.22 (d, J = 8.0 Hz, 2H), 7.15 (d, J = 7.6 Hz, 2H), 6.89 (d, J = 9.2 Hz, 1H), 6.36 (s, 1H), 6.16 (d, J = 9.6 Hz, 1H), 3.01 (s, 6H), 2.66 (t, J = 7.6 Hz, 2H), 1.71-1.59 (m, 3H), 1.42-1.33 (m, 2H), 0.95 (t, J = 7.6 Hz, 3H); **^{13}C{^{1}H} NMR** ($CDCl_3$, 100.6 MHz): δ 191.5, 163.8, 157.9, 157.7, 154.0, 142.7, 136.8, 129.8, 129.0, 125.7, 107.9, 100.9, 98.2, 96.0, 39.9, 35.2, 33.5, 22.3, 13.9; **IR (neat):** 2928, 2856, 1704, 1608, 1470, 1434, 1350, 1278, 1230, 1112, 1008, 817 cm^{-1}; **HRMS** (ESI) m/z calcd. For $C_{22}H_{25}N_2O_3$ $[M+H]^+$: 365.1860 found: 365.1862.

7-(dimethylamino)-4-((4-methoxyphenyl)amino)-2-oxochromane-3-carbaldehyde (11d):

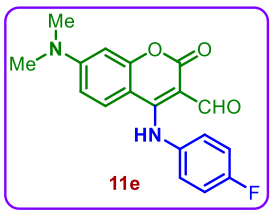
Following the general procedure, azide **10** (100 mg, 0.39 mmol) was treated with *p*-anisidine (57 mg, 0.46 mmol) in acetonitrile (3 mL) at room temperature. Upon the disappearance of azide **10** in *tlc*, the mixture was poured into chopped ice, and the resultant solid was filtered and washed with EtOH to procure pure CQ **11d** (115 mg, 88%) as a yellow solid.



MP: 186-188 °C; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 12.8 (brs, 1H, D_2O-exchangeable), 10.12 (s, 1H), 7.17 (d, J = 8.8 Hz, 2H), 6.93 (d, J = 8.8 Hz, 2H), 6.88 (d, J = 9.2 Hz, 1H), 6.36 (d, J = 2.4 Hz, 1H), 6.18 (dd, J = 9.2, 2.4 Hz, 1H); **^{13}C{^{1}H} NMR** ($CDCl_3$, 100.6 MHz): δ 191.5, 163.7, 159.0, 158.1, 157.7, 153.9, 131.9, 129.0, 127.2, 115.1, 108.1, 101.1, 98.4, 95.9, 55.6, 39.9; **IR (neat):** 1706, 1592, 1511, 1496, 1438, 1352, 1279, 1235, 1169, 1112, 1032, 1007, 909, 816 cm^{-1}; **HRMS** (ESI) m/z calcd. For $C_{19}H_{19}N_2O_4$ $[M+H]^+$: 339.1340 found: 339.1345.

7-(dimethylamino)-4-((4-fluorophenyl)amino)-2-oxochromane-3-carbaldehyde (11e):

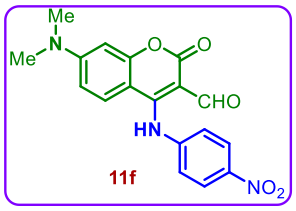
Following the general procedure, azide **10** (100 mg, 0.39 mmol) was treated with 4-F-Aniline (52 mg, 0.46 mmol) in acetonitrile (3 mL) at room temperature. Upon the disappearance of azide **10** in *tlc*, the mixture was poured into chopped ice, and the resultant solid was filtered and washed with EtOH to procure pure CQ **11e** (103 mg, 82%) as a yellow solid.



MP: 222-224 °C; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 12.88 (brs, 1H, D_2O-exchangeable), 10.14 (s, 1H), 7.28-7.25 (m, 2H), 7.14 (t, *J* = 8.8 Hz, 2H), 6.86 (d, *J* = 9.6 Hz, 1H), 6.40 (d, *J* = 2.0 Hz, 1H), 6.22 (dd, *J* = 9.6, 2.4 Hz, 1H), 3.04 (s, 6H); **^{13}C{^{1}H} NMR** ($CDCl_3$, 100.6 MHz): δ 191.6, 163.6, 162.6 (d, *J* = 248.5 Hz), 157.9 (d, *J* = 26.2 Hz), 154.1, 135.4 (d, *J* = 3.0 Hz), 128.8, 127.7, (d, *J* = 9.1 Hz), 116.9, (d, *J* = 22.1 Hz), 108.2, 100.6, 98.3, 96.2, 39.9; **^{19}F NMR** (376.6 MHz, $CDCl_3$): δ -113.2 to -113.3 (m, F); **IR (neat):** 2863, 1705, 1595, 1439, 1379, 1351, 1265, 1214, 1115, 1012, 862, 846 cm^{-1}; **HRMS** (ESI) m/z calcd. For $C_{18}H_{16}FN_2O_3$ $[M+H]^+$: 327.1140 found: 327.1142.

7-(dimethylamino)-4-((4-nitrophenyl)amino)-2-oxochromane-3-carbaldehyde (11f):

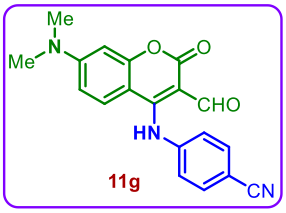
Following the general procedure, azide **10** (100 mg, 0.39 mmol) was treated with 4-NO_2-aniline (64 mg, 0.46 mmol) in acetonitrile (3 mL) at room temperature. Upon the disappearance of azide **10** in *tlc*, the mixture was poured into chopped ice, and the resultant solid was filtered and washed with EtOH to procure pure CQ **11f** (111 mg, 81%) as a yellow solid.



MP: 248-250 °C; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 12.55 (brs, 1H, D_2O-exchangeable), 10.02 (s, 1H), 8.32 (d, *J* = 8.8 Hz, 2H), 7.46 (d, *J* = 8.8 Hz, 2H), 6.99 (d, *J* = 9.6 Hz, 1H), 6.46 (d, *J* = 2.4 Hz, 1H), 6.37 (dd, *J* = 9.6, 2.4 Hz, 1H), 3.13 (s, 6H); **^{13}C{^{1}H} NMR** ($CDCl_3$, 100.6 MHz): δ 192.0, 165.7, 159.8, 159.4, 159.0, 158.6, 158.0, 157.5, 155.2, 146.2, 145.0, 128.9, 125.5, 125.4, 118.9, 116.0, 113.2, 110.4, 109.7, 99.9, 98.5, 97.0, 40.2; **IR (neat):** 2862, 1710, 1614, 1506, 1440, 1338, 1260, 1171, 1116, 1014, 882, 768 cm^{-1}; **HRMS** (ESI) m/z calcd. For $C_{18}H_{16}N_3O_5$ $[M+H]^+$: 354.1085 found: 354.1086.

4-((7-(dimethylamino)-3-formyl-2-oxochroman-4-yl)amino)benzonitrile (11g):

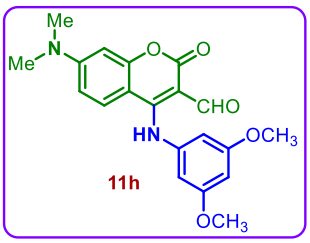
Following the general procedure, azide **10** (100 mg, 0.39 mmol) was treated with 4-aminobenzonitrile (55 mg, 0.46 mmol) in acetonitrile (3 mL) at room temperature. Upon the disappearance of azide **10** in *tlc*, the mixture was poured into chopped ice, and the resultant solid was filtered and washed with EtOH to procure pure CQ **11g** (107 mg, 83%) as a yellow solid.



MP: 224-226 °C; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 12.79 (brs, 1H, D_2O-exchangeable), 10.11 (s, 1H), 7.68 (d, *J* = 8.4 Hz, 2H), 7.34 (d, *J* = 8.4 Hz, 2H), 6.93 (d, *J* = 9.6 Hz, 1H), 6.40 (d, *J* = 2.8 Hz, 1H), 6.28 (dd, *J* = 9.6, 2.8 Hz, 1H), 3.06 (s, 6H); **^{13}C{^{1}H} NMR** ($CDCl_3$, 100.6 MHz): δ 192.0, 163.1, 157.9, 157.3, 154.5, 144.1, 133.6, 128.7, 125.3, 118.2, 110.1, 108.4, 100.2, 98.2, 97.6, 40.0; **IR (neat):** 2926, 2226, 1716, 1590, 1428, 1356, 1242, 1112, 1002, 913, 865 cm^{-1}; **HRMS** (ESI) m/z calcd. For $C_{19}H_{16}N_3O_3$ $[M+H]^+$: 334.1186 found: 334.1187.

4-((3,5-dimethoxyphenyl)amino)-7-(dimethylamino)-2-oxochromane-3-carbaldehyde (11h):

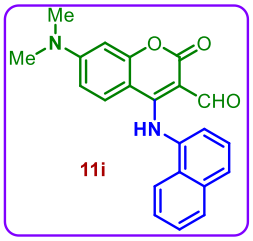
Following the general procedure, azide **10** (100 mg, 0.39 mmol) was treated with dimethoxy aniline (71 mg, 0.46 mmol) in acetonitrile (3 mL) at room temperature. Upon the disappearance of azide **10** in *tlc*, the mixture was poured into chopped ice, and the resultant solid was filtered and washed with EtOH to procure pure CQ **11h** (112 mg, 84%) as a red solid.



MP: 258-260 °C; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 12.84 (brs, 1H, D_2O-exchangeable), 10.12 (s, 1H), 7.05 (d, J = 9.2 Hz, 1H), 6.44-6.42 (m, 1H), 6.41 (d, J = 2.0 Hz, 1H), 6.37 (d, J = 2.4 Hz, 1H), 6.24 (dd, J = 9.6, 2.8 Hz, 1H), 3.77 (s, 1H), 3.03 (s, 1H); **^{13}C{^{1}H} NMR** ($CDCl_3$, 100.6 MHz): δ 191.5, 163.7, 161.6, 157.7, 154.1, 140.9, 129.2, 108.2, 104.0, 100.8, 100.0, 98.1, 96.1, 55.6, 39.9; **IR (neat):** 2865, 1704, 1584, 1458, 1434, 1356, 1266, 1212, 1147, 1065, 1014, 768 cm^{-1}; **HRMS** (ESI) m/z calcd. For $C_{20}H_{21}N_2O_5$ $[M+H]^+$: 369.1445 found: 369.1446.

7-(dimethylamino)-4-(naphthalen-1-ylamino)-2-oxochromane-3-carbaldehyde (11i):

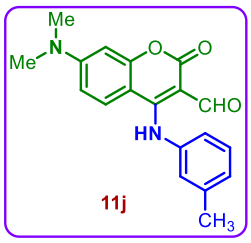
Following the general procedure, azide **10** (100 mg, 0.39 mmol) was treated with α-naphthylamine (67 mg, 0.46 mmol) in acetonitrile (3mL) at room temperature. Upon the disappearance of azide **10** in *tlc*, the mixture was poured into chopped ice, and the resultant solid was filtered and washed with EtOH to procure pure CQ **11i** (122 mg, 81%) as a yellow solid.



MP: 236-238 °C; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 13.26 (brs, 1H, D_2O-exchangeable), 10.24 (s, 1H), 8.02 (d, J = 7.2 Hz, 1H), 7.96-7.91 (m, 2H), 7.58-7.42 (m, 4H), 6.59 (d, J = 8.8 Hz, 1H), 6.37 (s, 1H), 5.96 (d, J = 8.8 Hz, 1H), 2.96 (s, 6H); **^{13}C{^{1}H} NMR** ($CDCl_3$, 100.6 MHz): δ 191.8, 163.8, 159.0, 157.7, 154.0, 135.6, 134.4, 129.5, 128.6, 128.5, 128.4, 127.6, 127.2, 125.7, 124.0, 122.7, 108.3, 100.9, 98.2, 96.1, 39.8; **IR (neat):** 1718, 1592, 1491, 1405, 1365, 1267, 1121, 1015, 906, 812, 780 cm^{-1}; **HRMS** (ESI) m/z calcd. For $C_{22}H_{19}N_2O_3$ $[M+H]^+$: 359.1390 found: 359.1396.

7-(dimethylamino)-2-oxo-4-(m-tolylamino)chromane-3-carbaldehyde (11j):

Following the general procedure, azide **10** (100 mg, 0.39 mmol) was treated with *m*-toluidine (50 mg, 0.46 mmol) in acetonitrile (3 mL) at room temperature. Upon the disappearance of azide **10** in *tlc*, the mixture was poured into chopped ice, and the resultant solid was filtered and washed with EtOH to procure pure CQ **11j** (111 mg, 89%) as a yellow solid.



MP: 186-188 °C; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 12.88 (brs, 1H, D_2O-exchangeable), 10.13 (s, 1H), 7.29 (t, J = 8.0 Hz, 1H), 7.16 (d, J = 7.6 Hz, 1H), 7.08 (s, 1H), 7.05 (d, J = 8.0 Hz, 1H), 6.92 (d, J = 9.2 Hz, 1H), 6.39 (d, J = 2.8 Hz, 1H), 6.21 (dd, J = 9.2, 2.4 Hz, 1H), 3.02 (s, 6H), 2.36 (s, 3H); **^{13}C{^{1}H} NMR** ($CDCl_3$, 100.6 MHz): δ 191.5, 163.7, 157.8, 157.7, 153.9, 140.1, 139.2, 129.6, 129.1, 128.4, 126.3, 122.9, 108.2, 101.1, 98.4,

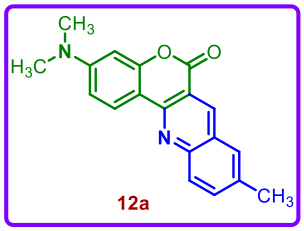
96.1, 40.0, 21.3; **IR (neat):** 2892, 2813, 1701, 1593, 1461, 1437, 1384, 1338, 1268, 1114, 1017,847,802 cm^{-1}; **HRMS** (ESI) m/z calcd. For $C_{19}H_{19}N_2O_3$ \[M+H]$^+$: 323.1390 found: 323.1397.

2.3.3 General Procedure for the Synthesis of 7-dimethylamino-C3-C4 fused chromeno[4,3-*b*]quinolin-6-one (12a-12j):

The Aldrich-Ace pressure tube (25 mL capacity), equipped with a magnetic stirrer bar, was added 7-dimethylamino-4-(N-arylamino)-3-formylcoumarin **11a-11j** (100 mg) and CF_3COOH (Trifluoroacetic acid) (1.5 mL) and the reaction tube was sealed with screw cap. Next, the reaction mixture was allowed to stir at 60 °C. Upon the disappearance of the starting material in *tlc*, the reaction mixture was quenched with ice water (20 mL) (in case of precipitate formation, the resulting solid was filtered and washed with hexane) and extracted with chloroform (3 X 20 mL). The combined organic phase was washed with an aqueous solution of $NaHCO_3$ (10%, 2 X 15 mL) and water (2 X 15 mL), then dried over anhydrous $MgSO_4$, and the volatiles were removed under vacuum. The resulting solid product was washed with cold hexane/ethanol, and in the selective cases, column chromatography was used to obtain pure chromeno-quinolin-6-one (CQ) **12a-12j**. The mentioned yields were calculated upon the isolation of pure products.

3-(dimethylamino)-9-methyl-6*H*-chromeno[4,3-b]quinolin-6-one (12a):

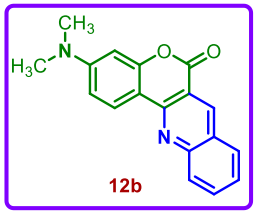
Following the general procedure, 7-(dimethylamino)-2-oxo-4-(*p*-tolylamino)-2*H*-chromene-3-carbaldehyde **11a** (100 mg, 0.30 mmol) was treated with CF_3COOH (1.5 mL) at 60 °C. Upon the disappearance of **11a** in *tlc*, the mixture was poured into chopped ice, and the resultant solid was filtered and washed with hexane to procure pure CQ **12a** (92 mg, 98%) as an orange solid.



MP: 252-254 °C; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 8.45 (d, *J* = 6.8 Hz, 1H), 8.23 (d, *J* = 6.8 Hz, 1H), 7.94 (d, *J* = 6.0 Hz, 1H), 7.87 (s, 1H), 6.85 (d, *J* = 5.6 Hz, 1H), 6.52 (s, 1H), 3.2 (s, 6H), 2.6 (s, 3H); **^{13}C{^{1}H} NMR** ($CDCl_3$, 100.6 MHz): δ 160.7, 160.4, 159.9, 159.5, 158.4, 156.6, 156.0, 148.4, 145.8, 140.9, 140.1, 138.8, 129.5, 126.8, 125.1, 119.6, 116.3, 115.0, 113.5, 111.8, 98.5, 98.4, 40.4, 21.4; **IR (neat):** 2918, 1727, 1594, 1434, 1378, 1246, 1128, 1016, 918, 800 cm^{-1}; **HRMS** (ESI) m/z calcd. For $C_{19}H_{17}N_2O_2$ [M+H]$^+$: 305.1285 found: 305.1281.

3-(dimethylamino)-6*H*-chromeno[4,3-b]quinolin-6-one (12b):

Following the general procedure, 7-(dimethylamino)-2-oxo-4-(phenylamino)-2*H*-chromene-3-carbaldehyde **11b** (100 mg, 0.32 mmol) was treated with CF_3COOH (1.5 mL) at 60 °C. Upon the disappearance of **11b** in *tlc*, the mixture was poured into chopped ice, and the resultant solid was filtered and washed with hexane to procure pure CQ **12b** (88 mg, 93%) as an orange solid.

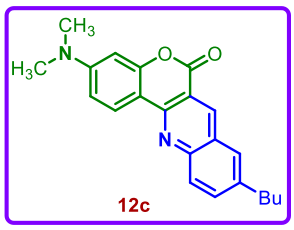


MP: 218-220 °C; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 9.08 (s, 1H), 8.50 (d, *J* = 8.8 Hz, 1H), 8.11 (d, *J* = 8.4 Hz, 1H), 7.91 (d, *J* = 8.0 Hz, 1H), 7.84-7.80 (m, 1H), 7.51 (t, *J* = 7.2 Hz, 1H), 6.73 (dd, *J* = 9.2, 2.8 Hz, 1H), 6.52 (d, *J* = 2.4 Hz, 1H); **^{13}C{^{1}H} NMR** ($CDCl_3$, 100.6 MHz): δ 162.2, 154.4, 153.4, 154.4, 150.6, 140.9, 133.0, 129.4, 129.0, 126.4,

126.1, 126.1, 114.8, 109.5, 108.0, 98.5, 40.2; **IR (neat):** 2897, 1725, 1596, 1488, 1362, 1236, 1123, 1008, 913, 817 cm^{-1}; **HRMS** (ESI) m/z calcd. For $C_{18}H_{15}N_2O_2$ $[M+H]^+$: 291.1128 found: 291.1128.

9-butyl-3-(dimethylamino)-6*H*-chromeno[4,3-b]quinolin-6-one (12c):

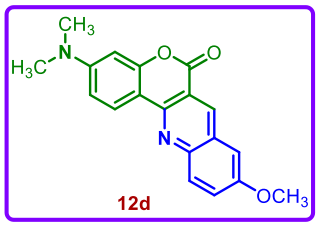
Following the general procedure, 4-((4-butylphenyl)amino)-7-(dimethylamino)-2-oxo-2*H*-chromene-3-carbaldehyde **11c** (100 mg, 0.28 mmol) was treated with CF_3COOH (1.5 mL) at 60 °C. Upon the disappearance of **11c** in *tlc*, the mixture was poured into chopped ice, and the resultant solid was filtered and washed with hexane to procure pure CQ **12c** (90 mg, 95%) as an orange solid.



MP: 166-168 °C; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 8.99 (s, 1H), 8.48 (d, *J* = 9.2 Hz, 1H), 8.15 (d, *J* = 8.4 Hz, 1H), 7.69-7.65 (m, 2H), 6.72 (m, 1H), 6.52 (d, *J* = 2.4 Hz, 1H), 3.07 (s, 6H), 2.79 (t, *J* = 8.0 Hz, 2H), 1.74-1.67 (m, 3H), 1.46-1.37 (m, 2H), 0.96 (t, *J* = 7.6 Hz, 3H); **^{13}C{^{1}H} NMR** ($CDCl_3$, 100.6 MHz): δ 162.3, 154.2, 153.2, 150.3, 149.9, 141.0, 140.2, 134.8, 128.7, 127.4, 126.5, 125.9, 114.7, 109.4, 108.2, 98.6, 40.2, 35.5, 33.2, 22.4, 13.9; **IR (neat):** 2923, 1727, 1618, 1597, 1484, 1462, 1439, 1370, 1241, 1013, 822 cm^{-1}; **HRMS** (ESI) m/z calcd. For $C_{22}H_{23}N_2O_2$ $[M+H]^+$: 347.1754 found: 347.1751.

3-(dimethylamino)-9-methoxy-6*H*-chromeno[4,3-b]quinolin-6-one (12d):

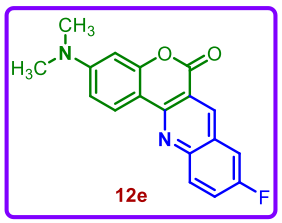
Following the general procedure, 7-(dimethylamino)-4-((4-methoxyphenyl)amino)-2-oxo-2*H*-chromene-3-carbaldehyde **11d** (100 mg, 0.30 mmol) was treated with CF_3COOH (1.5 mL) at 60 °C. Upon the disappearance of **11d** in *tlc*, the mixture was poured into chopped ice, and the resultant solid was filtered and washed with hexane to procure pure CQ **12d** (86 mg, 91%) as an orange solid.



MP: 212-214 °C; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 8.94 (s, 1H), 8.47 (d, *J* = 8.4 Hz, 1H), 8.04 (d, *J* = 9.6 Hz, 1H), 7.47 (dd, *J* = 9.2, 2.8 Hz, 1H), 7.12 (d, *J* = 2.8 Hz, 1H), 6.72 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.51 (d, *J* = 2.4 Hz, 1H), 3.94 (s, 1H); **^{13}C{^{1}H} NMR** ($CDCl_3$, 100.6 MHz): δ 162.2, 157.5, 154.0, 153.1, 148.5, 147.5, 139.1, 130.1, 127.3, 127.2, 126.6, 125.7, 114.9, 109.5, 107.9, 105.9, 98.6, 55.7, 40.2; **IR (neat):** 1726, 1625, 1596, 1486, 1357, 1223, 1125, 1007, 816, 775 cm^{-1}; **HRMS** (ESI) m/z calcd. For $C_{19}H_{17}N_2O_3$ $[M+H]^+$: 321.1234 found: 321.1242.

3-(dimethylamino)-9-fluoro-6*H*-chromeno[4,3-b]quinolin-6-one (12e):

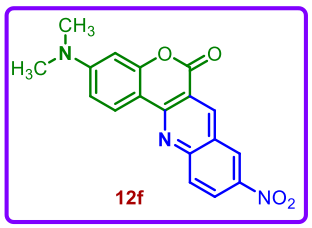
Following the general procedure, 7-(dimethylamino)-4-((4-fluorophenyl)amino)-2-oxo-2H-chromene-3-carbaldehyde **11e** (100 mg, 0.30 mmol) was treated with CF_3COOH (1.5 mL) at 60 °C. Upon the disappearance of **11e** in *tlc*, the mixture was poured into chopped ice, and the resultant solid was filtered and washed with hexane to procure pure CQ **12e** (86 mg, 91%) as an orange solid.



MP: 250-252 °C; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 9.38 (s, 1H), 8.47-8.41 (m, 2H), 7.87 (t, *J* = 7.2 Hz, 1H), 7.76 (dd, *J* = 7.2, 2.4 Hz, 1H), 6.89 (d, *J* = 7.6 Hz, 1H), 6.55 (d, *J* = 2.0 Hz, 1H), 3.24 (s, 6H); **^{13}C{^{1}H} NMR** ($CDCl_3$, 100.6 MHz): δ 160.7, 160.3, 159.9, 159.8, 157.6, 156.7, 156.2, 147.8 (d, *J* = 5.0 Hz), 146.3, 137.6, 128.0 (d, *J* = 25.15 Hz), 127.6, 125.8 (d, *J* = 11.1 Hz), 123.5 (d, *J* = 9.05 Hz), 116.6, 116.4, 114.2 (d, *J* = 23.1 Hz), 113.7, 111.9, 98.6, 40.5; **^{19}F NMR** (376.6 MHz, $CDCl_3$): δ; -75.94 (s, F); **IR (neat):** 2914, 1730, 1603, 1572, 1492, 1376, 1358, 1213, 1067, 848 cm^{-1}; **HRMS** (ESI) m/z calcd. For $C_{18}H_{14}FN_2O_2$ $[M+H]^+$: 309.1034 found: 309.1028.

3-(dimethylamino)-9-nitro-6*H*-chromeno[4,3-b]quinolin-6-one (12f):

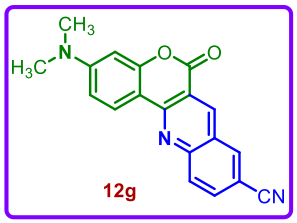
Following the general procedure, 7-(dimethylamino)-4-((4-nitrophenyl)amino)-2-oxo-2*H*-chromene-3-carbaldehyde **11f** (100 mg, 0.28 mmol) was treated with TFA (1.5 mL) at 60 °C. Upon the disappearance of **11f** in *tlc*, the mixture was poured into chopped ice, and the resultant solid product was purified by gravity column chromatography on silica gel (15-20% EtOAc in hexane) to procure CQ **12f** (78 mg, 82%) as an orange solid.



MP: 268-270 °C (decomposed); **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 9.45 (s, 1H), 8.95 (d, *J* = 2.4 Hz, 1H), 8.79 (dd, *J* = 8.8, 1.6 Hz, 1H), 8.47-8.41 (m, 2H), 6.96-6.94 (m, 1H), 6.58 (d, *J* = 2.0 Hz, 1H), 3.30 (s, 6H); **^{13}C{^{1}H} NMR** ($CDCl_3$, 100.6 MHz): δ 160.7, 160.3, 159.9, 159.5, 157.8, 157.2, 157.0, 149.1, 147.9, 146.1, 131.4, 128.3, 126.4, 123.7, 121.9, 118.9, 117.6, 116.1, 113.2, 113.0, 110.4, 99.1, 98.9, 40.9; **IR (neat):** 3086, 2913, 1731, 1602, 1572, 1545, 1485, 1333, 1233, 1144, 1088, 1012, 910, 834 cm^{-1}; **HRMS** (ESI) m/z calcd. For $C_{18}H_{14}N_3O_4$ $[M+H]^+$: 336.0979 found: 336.0970.

3-(dimethylamino)-6-oxo-6*H*-chromeno[4,3-b]quinoline-9-carbonitrile (12g):

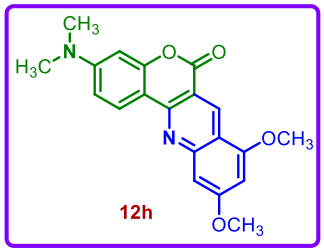
Following the general procedure, 4-((7-(dimethylamino)-3-formyl-2-oxo-2*H*-chromen-4-yl)amino)benzonitrile **11g** (100 mg, 0.30 mmol) was treated with CF_3COOH (1.5 mL) at 60 °C. Upon the disappearance of **11g** in *tlc*, the mixture was poured into chopped ice, and the resultant solid product was purified by gravity column chromatography on silica gel (15-20% EtOAc in hexane) to procure CQ **12g** (78 mg, 83%) as an orange solid.



MP: 274-276 °C (decomposed); **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 9.36 (s, 1H), 8.42 (d, *J* = 1.6 Hz, 1H), 8.36 (t, *J* = 10.8 Hz, 2H), 8.20 (dd, *J* = 8.8, 1.6 Hz, 1H), 6.94 (dd, *J* = 9.2, 2.4 Hz, 1H), 6.59 (d, *J* = 2.4 Hz, 1H), 3.30 (s, 6H); **^{13}C{^{1}H} NMR** ($CDCl_3$, 100.6 MHz): δ 160.8, 160.4, 160.0, 159.6, 157.7, 157.4, 156.8, 148.1, 147.6, 142.0, 138.7, 135.6, 127.8, 123.8, 121.3, 118.9, 117.2, 116.0, 113.2, 112.7, 112.0, 110.4, 99.0, 98.6, 40.8; **IR (neat):** 2918, 2228, 1727, 1601, 1441, 1371, 1232, 1128, 1009, 912, 780 cm^{-1}; **HRMS** (ESI) m/z calcd. For $C_{19}H_{14}N_3O_2$ $[M+H]^+$: 316.1081 found: 316.1099.

3-(dimethylamino)-8,10-dimethoxy-6*H*-chromeno[4,3-b]quinolin-6-one (12h):

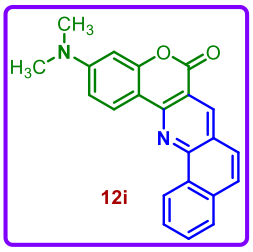
Following the general procedure, 4-(3,5-dimethoxyphenyl)amino)-7-(dimethylamino)-2-oxo-2*H*-chromene-3-carbaldehyde **11h** (100 mg, 0.28 mmol) was treated with CF_3COOH (1.5 mL) at 60 °C. Upon the disappearance of **11h** in *tlc*, the mixture was poured into chopped ice, and the resultant solid was filtered and washed with hexane to procure pure CQ **12h** (90 mg, 96%) as an orange solid.



MP: 264-266 °C; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 9.47 (s, 1H), 8.56 (d, *J* = 9.6 Hz, 1H), 7.40 (s, 1H), 6.81 (dd, *J* = 9.2, 2.0 Hz, 1H), 6.56 (s, 1H), 6.47 (d, *J* = 2.0 Hz, 1H), 4.54 (d, *J* = 10.0 Hz, 6H), 3.19 (s, 1H); **^{13}C{^{1}H} NMR** ($CDCl_3$, 100.6 MHz): δ 170.1, 160.7, 160.3, 158.5, 158.5, 156.1, 156.1, 147.0, 144.1, 142.4, 127.2, 117.1, 114.7, 114.2, 111.2, 110.1, 99.7, 98.9, 98.1, 92.4, 57.0, 56.7, 40.3; **IR (neat):** 2916, 1722, 1620, 1596, 1572, 1458, 1386, 1213, 1123, 1020, 918, 817 cm^{-1}; **HRMS** (ESI) m/z calcd. For $C_{20}H_{19}N_2O_4$ $[M+H]^+$: 351.1340 found: 351.1337.

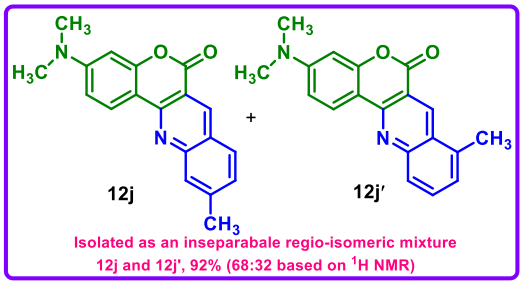
3-(dimethylamino)-6*H*-benzo[h]chromeno[4,3-b]quinolin-6-one (12i):

Following the general procedure, 7-(dimethylamino)-4-(naphthalen-1-ylamino)-2-oxo-2*H*-chromene-3-carbaldehyde **11i** (100 mg, 0.28 mmol) was treated with CF_3COOH (1.5 mL) at 60 °C. Upon the disappearance of **11i** in *tlc*, the mixture was poured into chopped ice, and the resultant solid was filtered and washed with hexane to procure pure CQ **12i** (84 mg, 89%) as an orange solid.



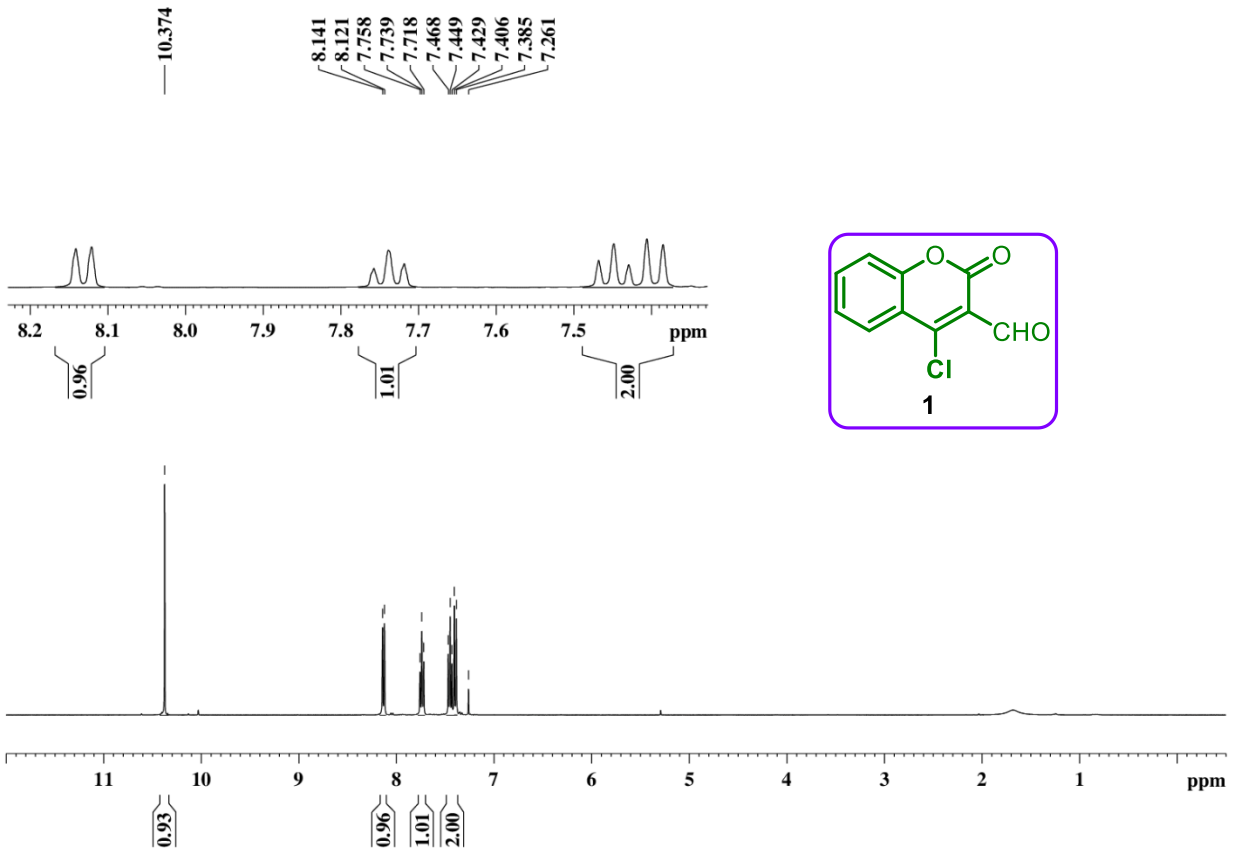
MP: 202-204 °C; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 9.35 (s, 1H), 8.87 (s, 1H), 8.56 (d, *J* = 8.4 Hz, 1H), 7.81 (s, 1H), 7.72-7.61 (m, 4H), 6.71 (d, *J* = 8.0 Hz, 1H), 6.47 (s, 1H), 3.06 (s, 6H); **^{13}C{^{1}H} NMR** ($CDCl_3$, 100.6 MHz): δ 162.2, 154.3, 153.1, 150.4, 149.8, 138.9, 135.1, 130.8, 129.7, 127.8, 127.3, 127.1, 125.8, 125.7, 125.6, 124.5, 114.2, 109.3, 108.4, 98.4, 40.2; **IR (neat):** 2913, 1726, 1618, 1597, 1571, 1497, 1374, 1250,1133, 935, 800 cm^{-1}; **HRMS** (ESI) m/z calcd. For $C_{22}H_{17}N_2O_2$ $[M+H]^+$: 341.1285 found: 341.1276.

3-(dimethylamino)-10-methyl-6*H*-chromeno[4,3-b]quinolin-6-one and 3-(dimethylamino)-8-methyl-6*H*-chromeno[4,3-*b*]quinolin-6-one (inseparable regio-isomeric mixture of 12j and 12j′):

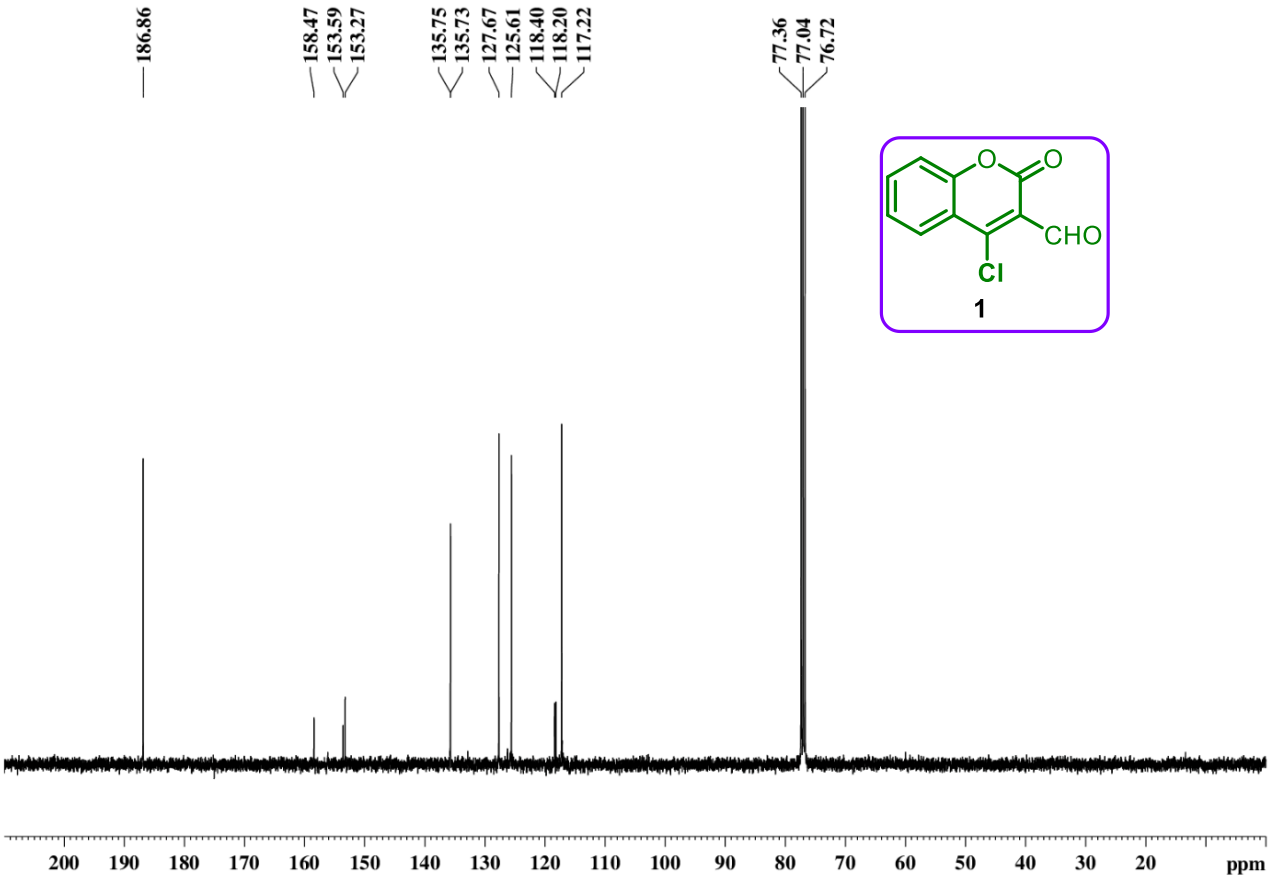


Following the general procedure, 7-(dimethylamino)-2-oxo-4-(*m*-tolylamino)-2*H*-chromene-3-carbaldehyde **11j** (100 mg, 0.30 mmol) was treated with CF_3COOH (1.5 mL) at 60 °C. Upon the disappearance of **11j** in *tlc*, the mixture was poured into chopped ice, and the resultant solid was filtered and washed with hexane to procure an inseparable regio-isomeric mixture of chromeno[4,3-*b*]quinoline **12j** and **12j′** (68:32 based on ^{1}H NMR) (86 mg, 92%) as an orange solid.

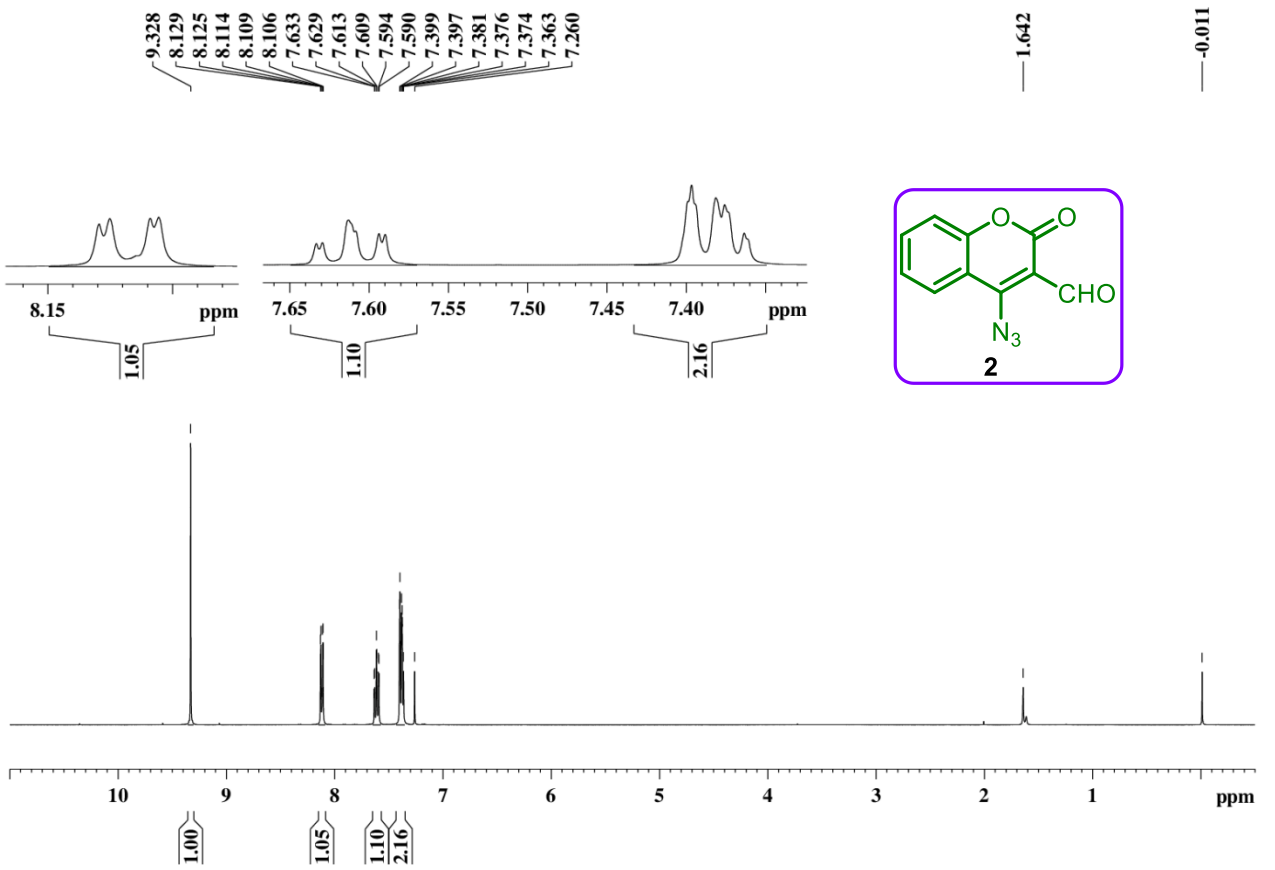
3. Copies of Spectral Data:



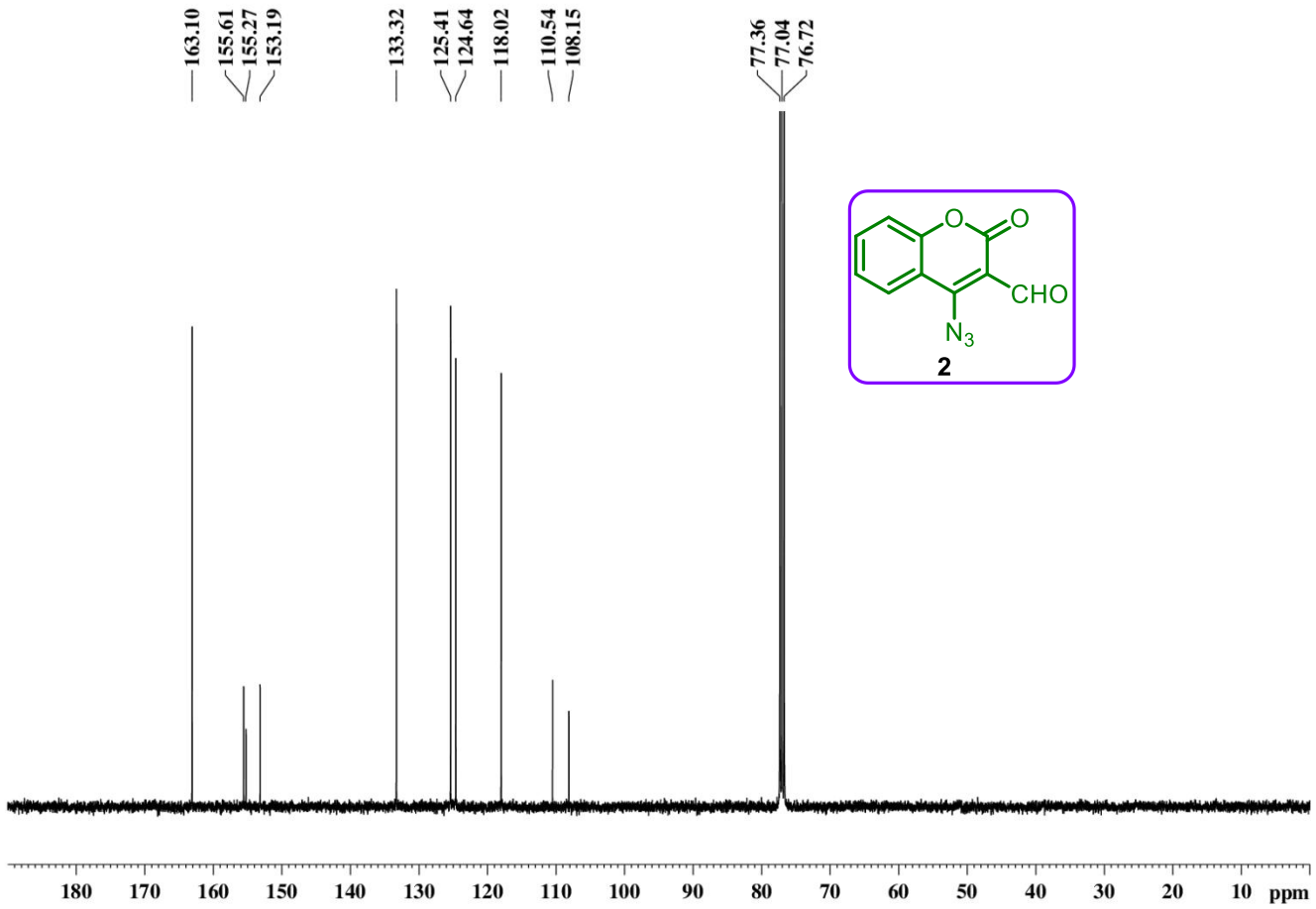
^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **1**



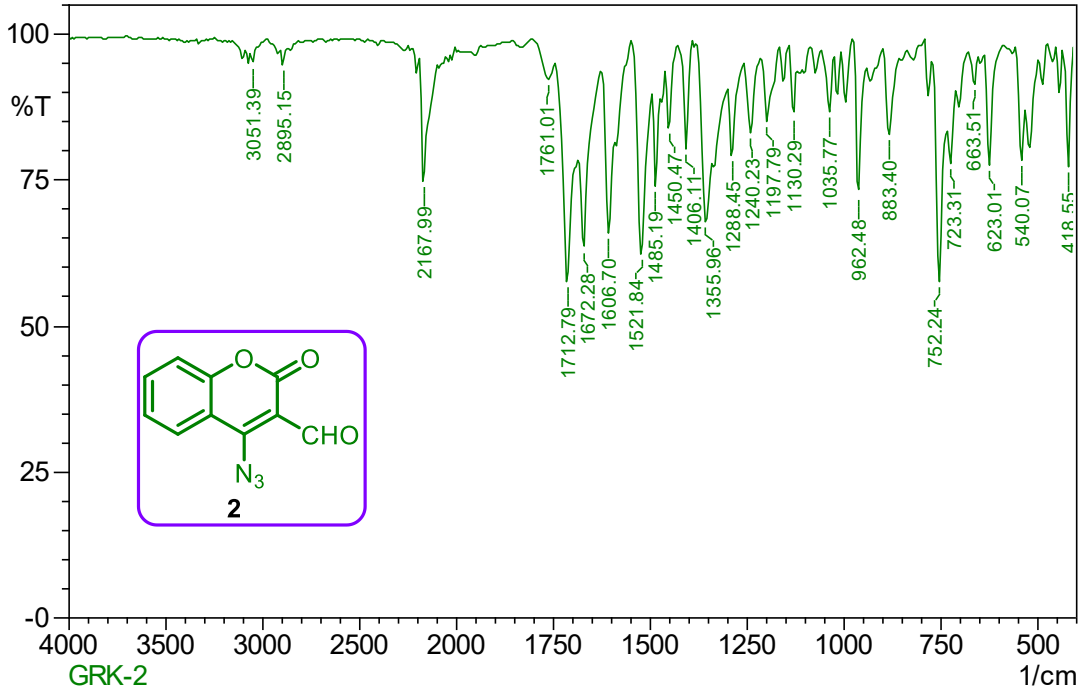
^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$) spectra of compound **1**



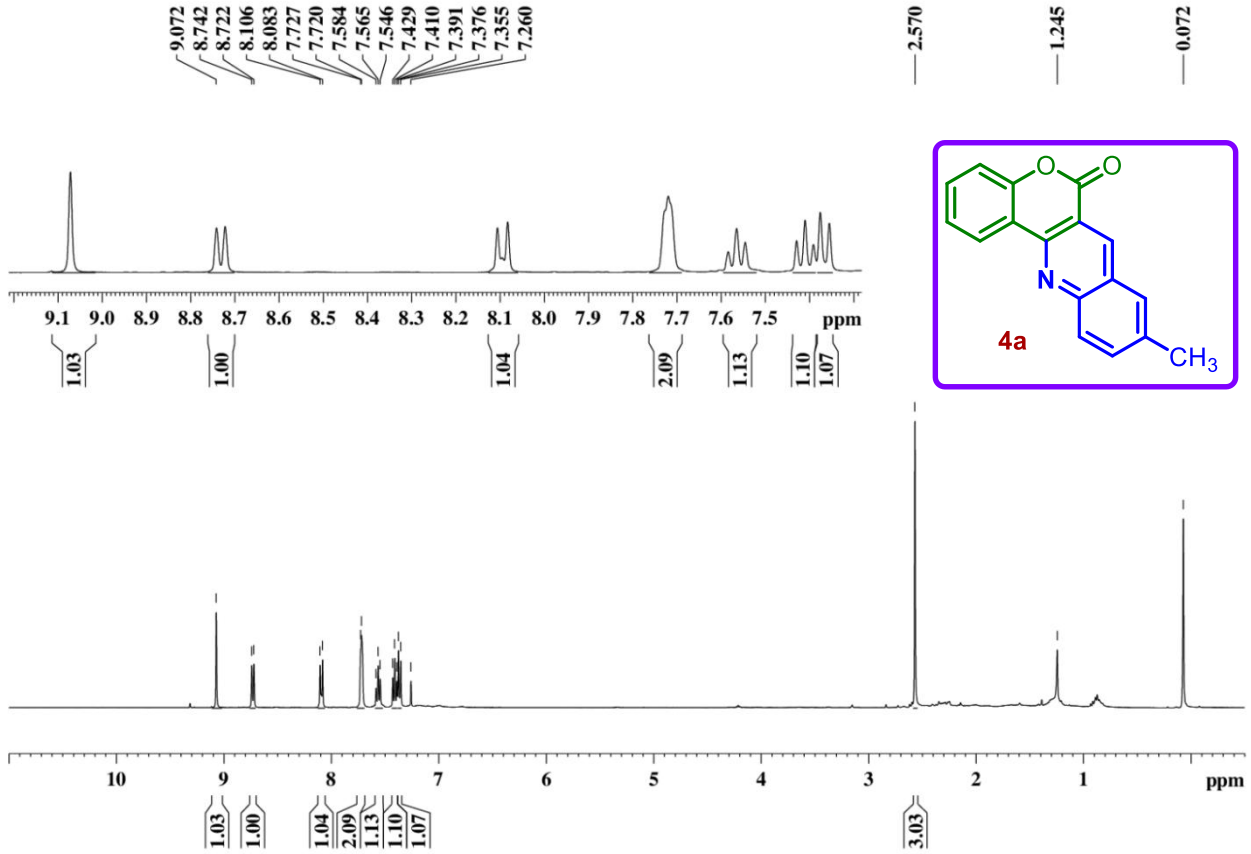
^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **2**



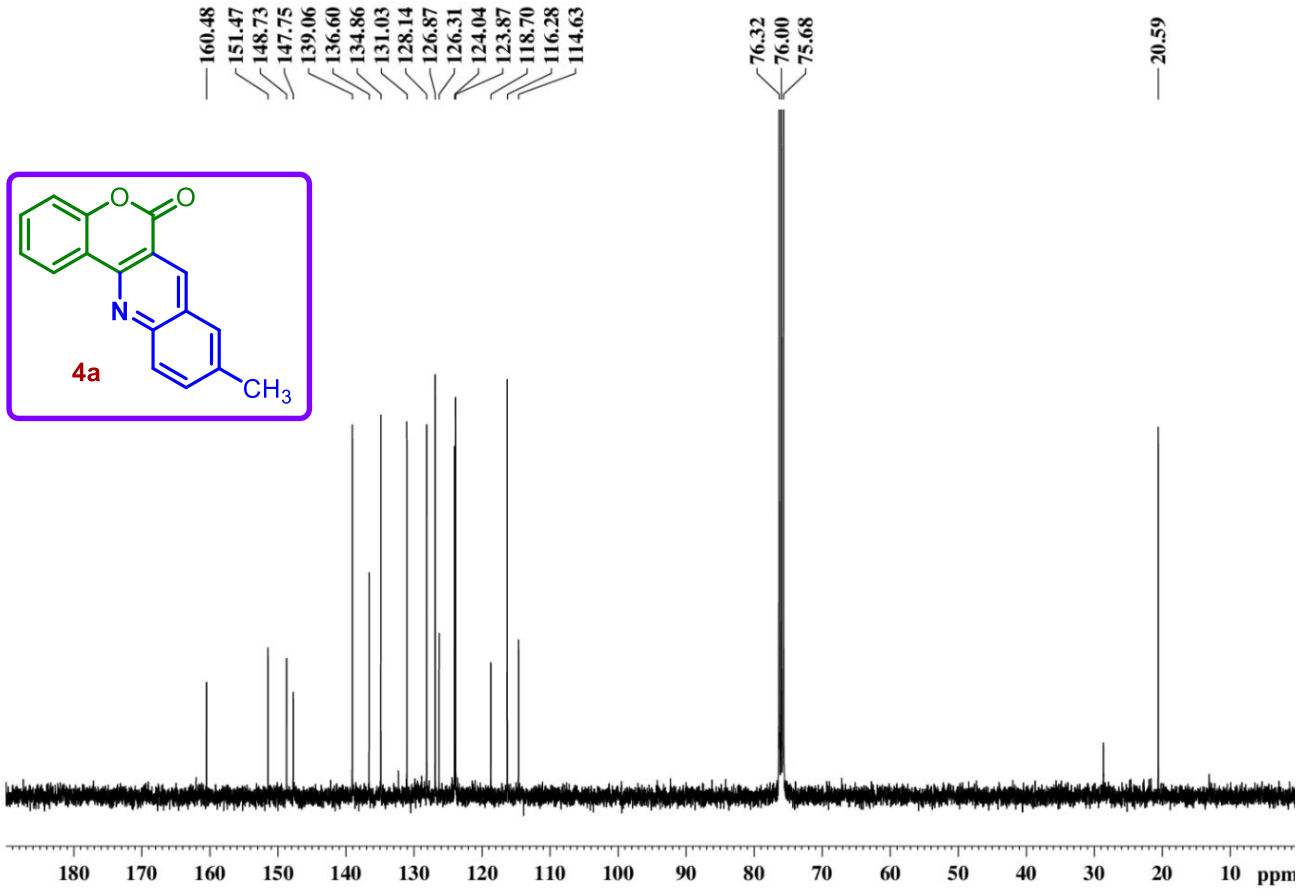
^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$) spectra of compound **2**



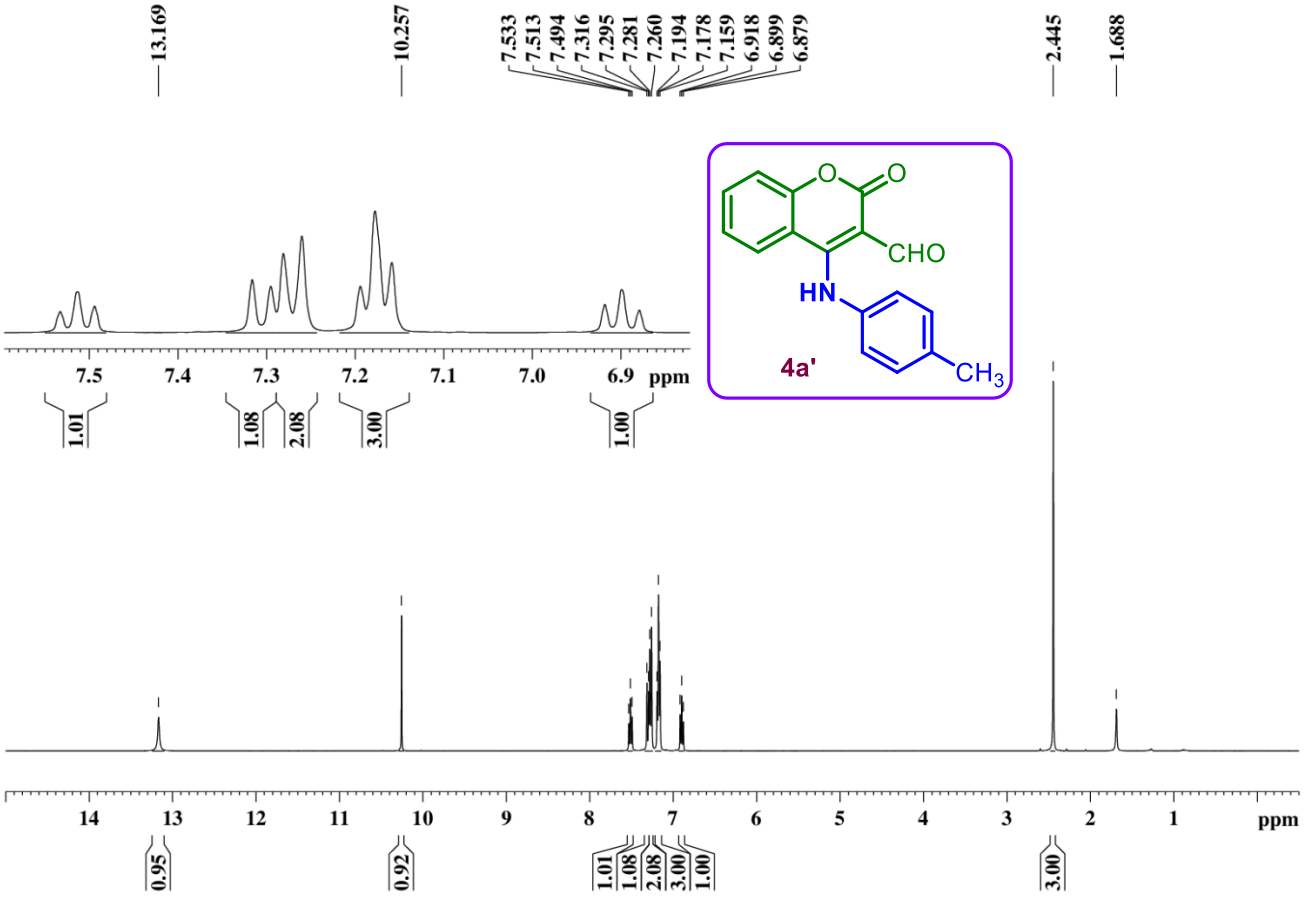
FT-IR spectra of compound **2**



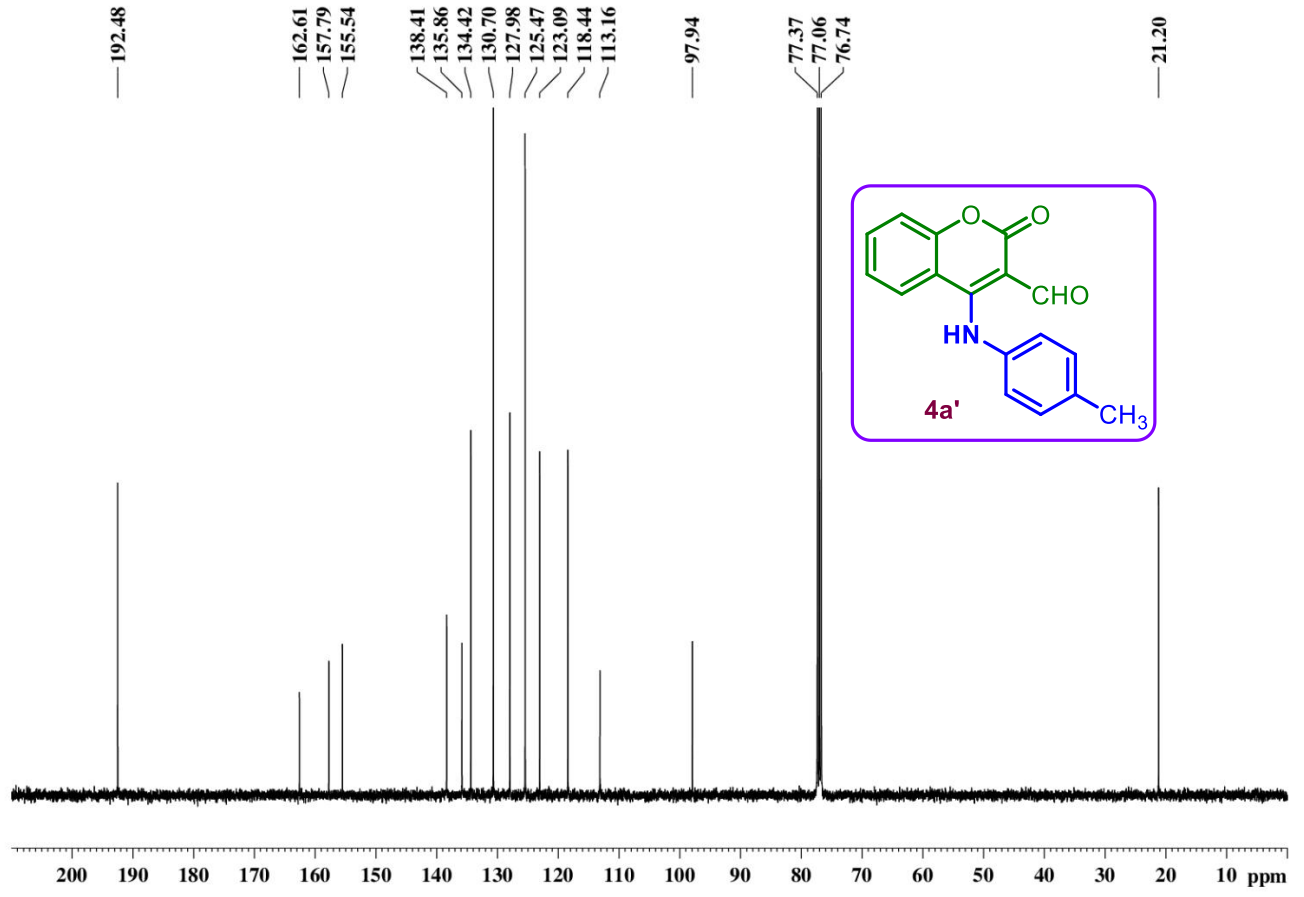
^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **4a**



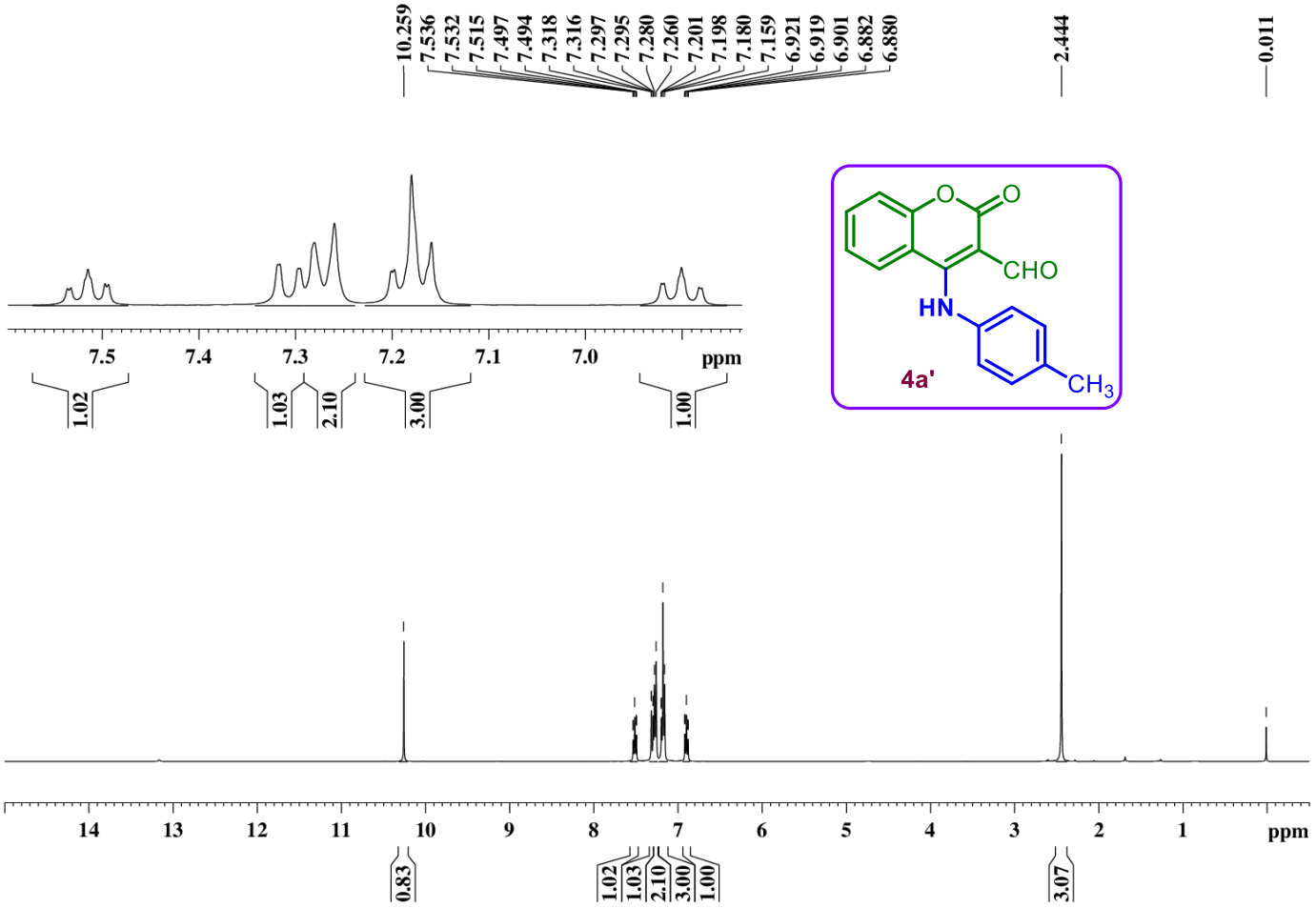
^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$) spectra of compound **4a**



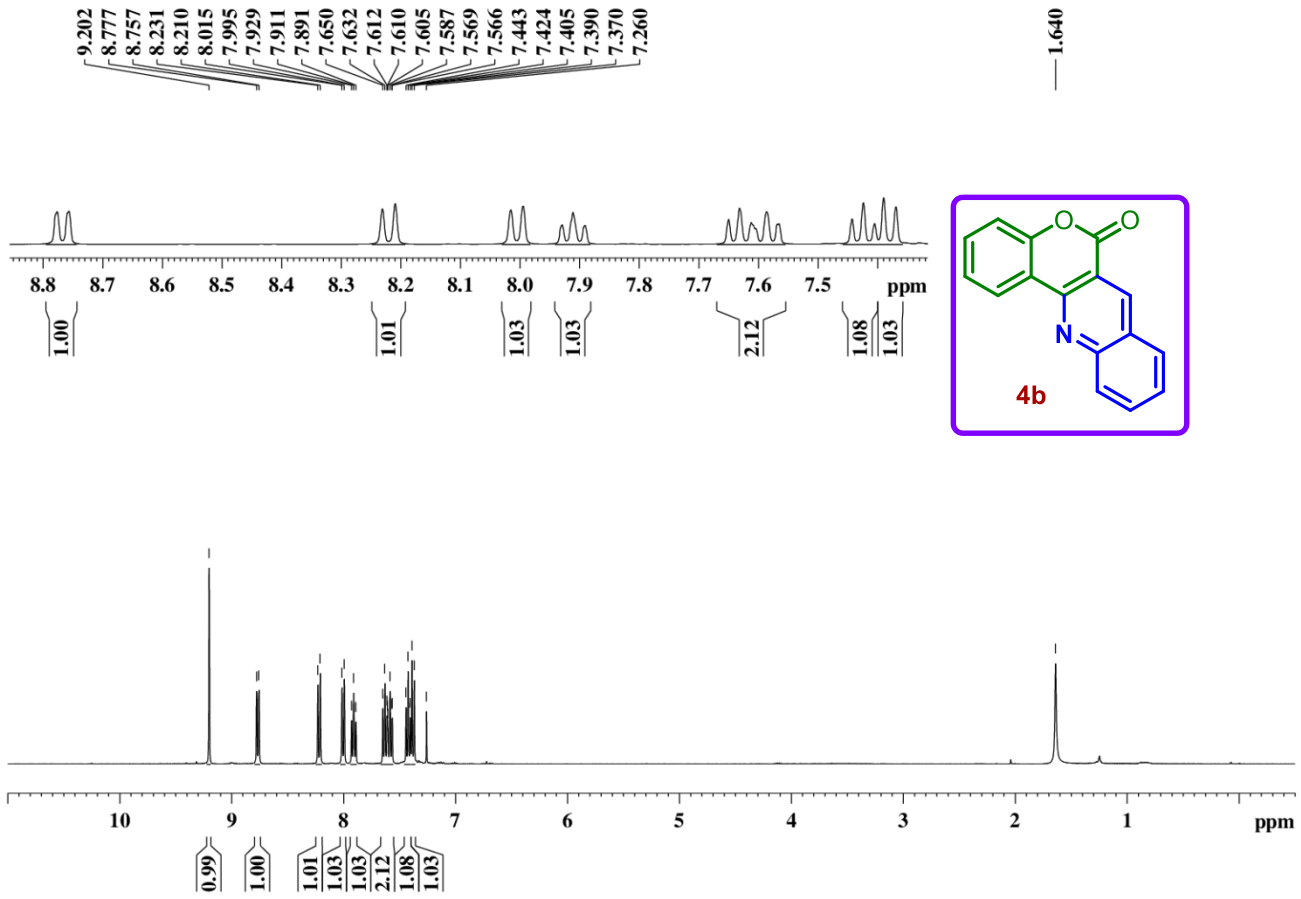
^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **4a′**



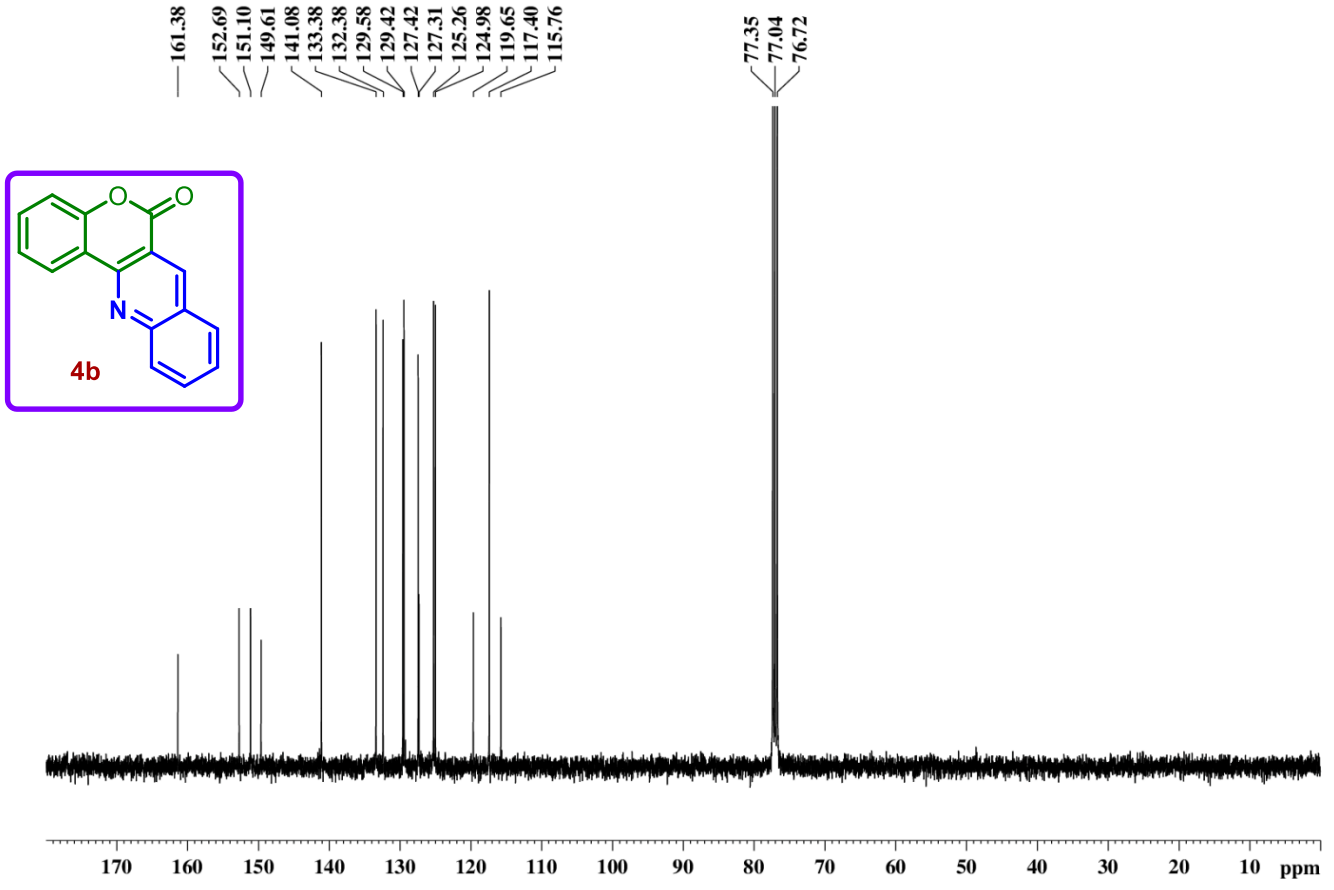
^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$) spectra of compound **4a′**



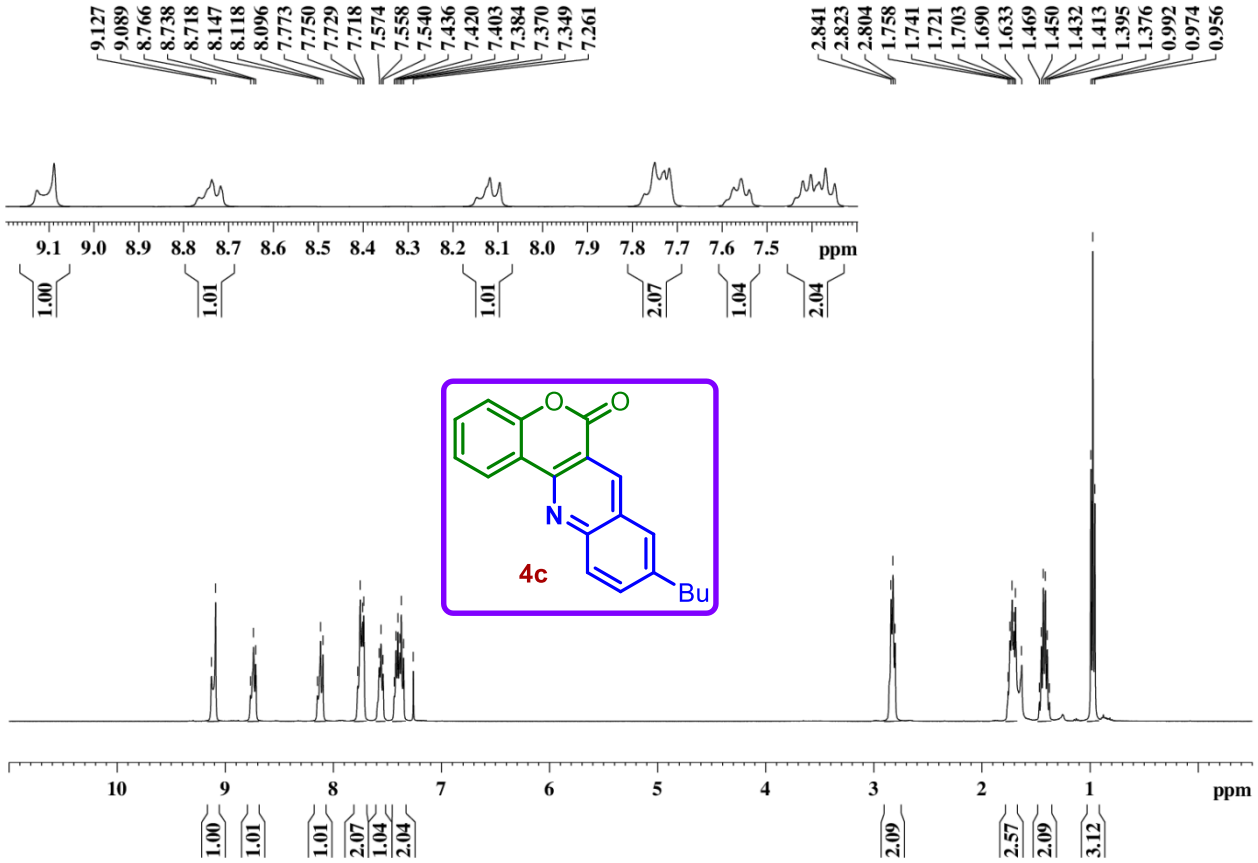
^{1}H NMR (400 MHz, $CDCl_3$ + D_2O) spectra of compound **4a′** (Deuterium exchange)



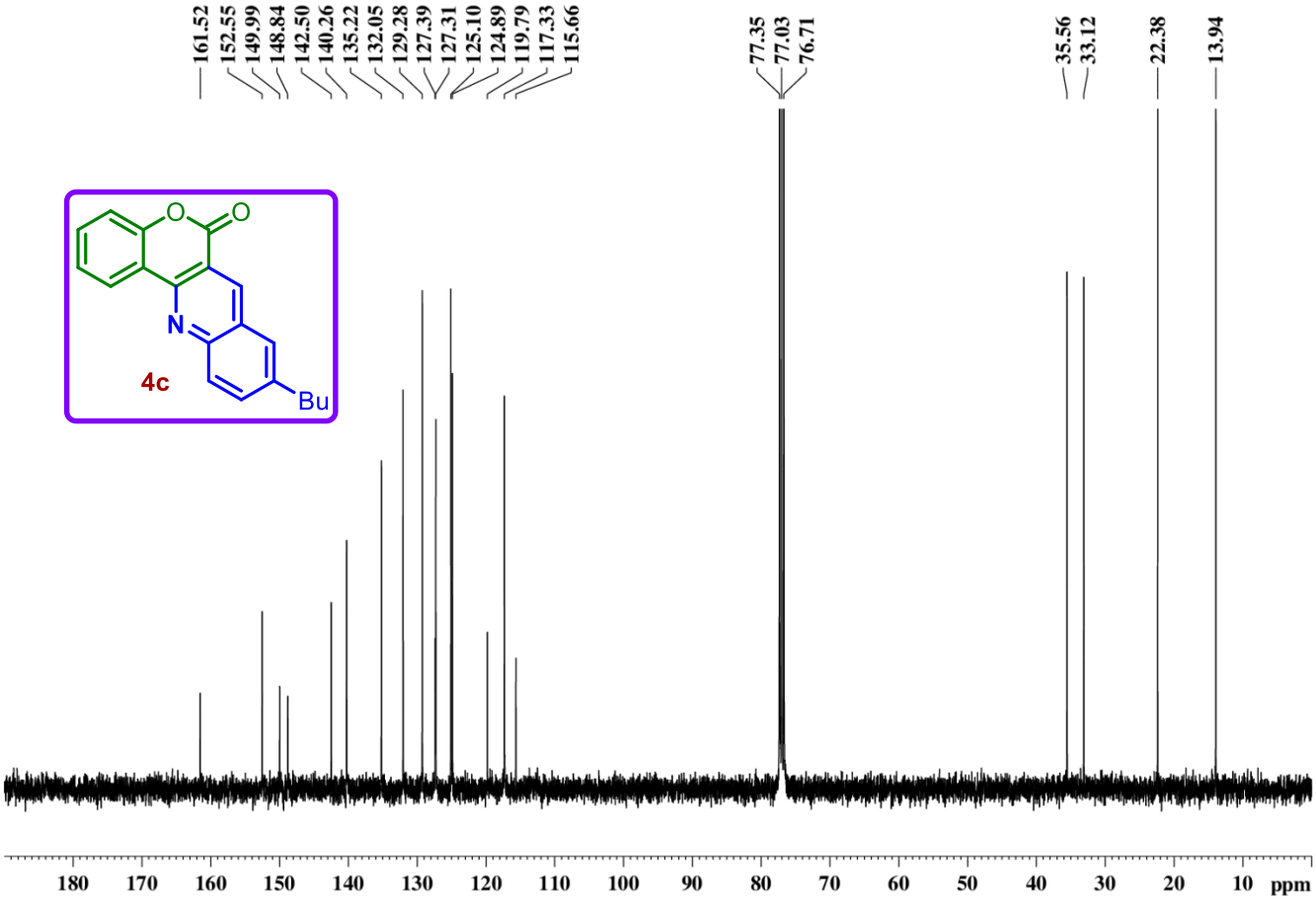
^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **4b**



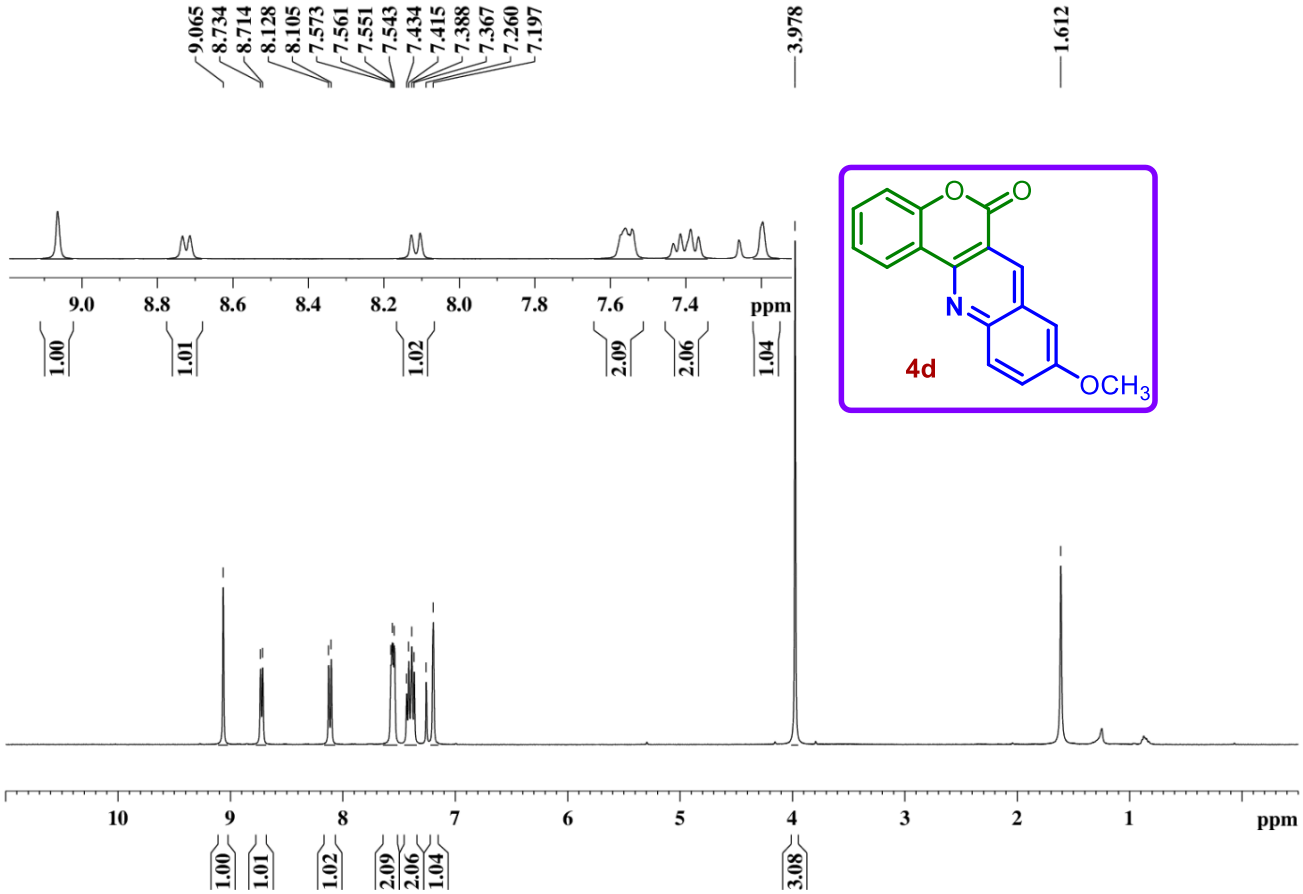
^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$) spectra of compound **4b**



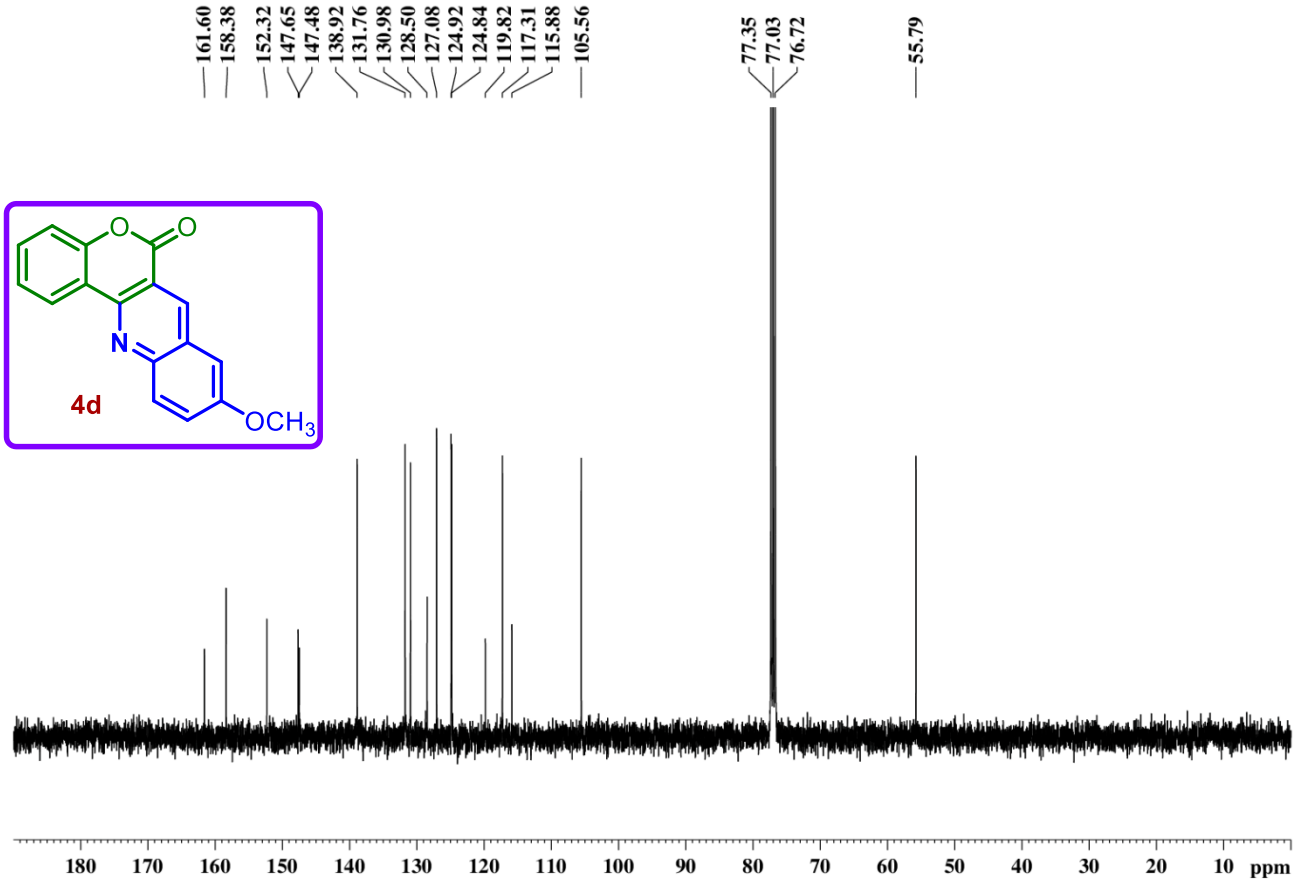
^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **4c**



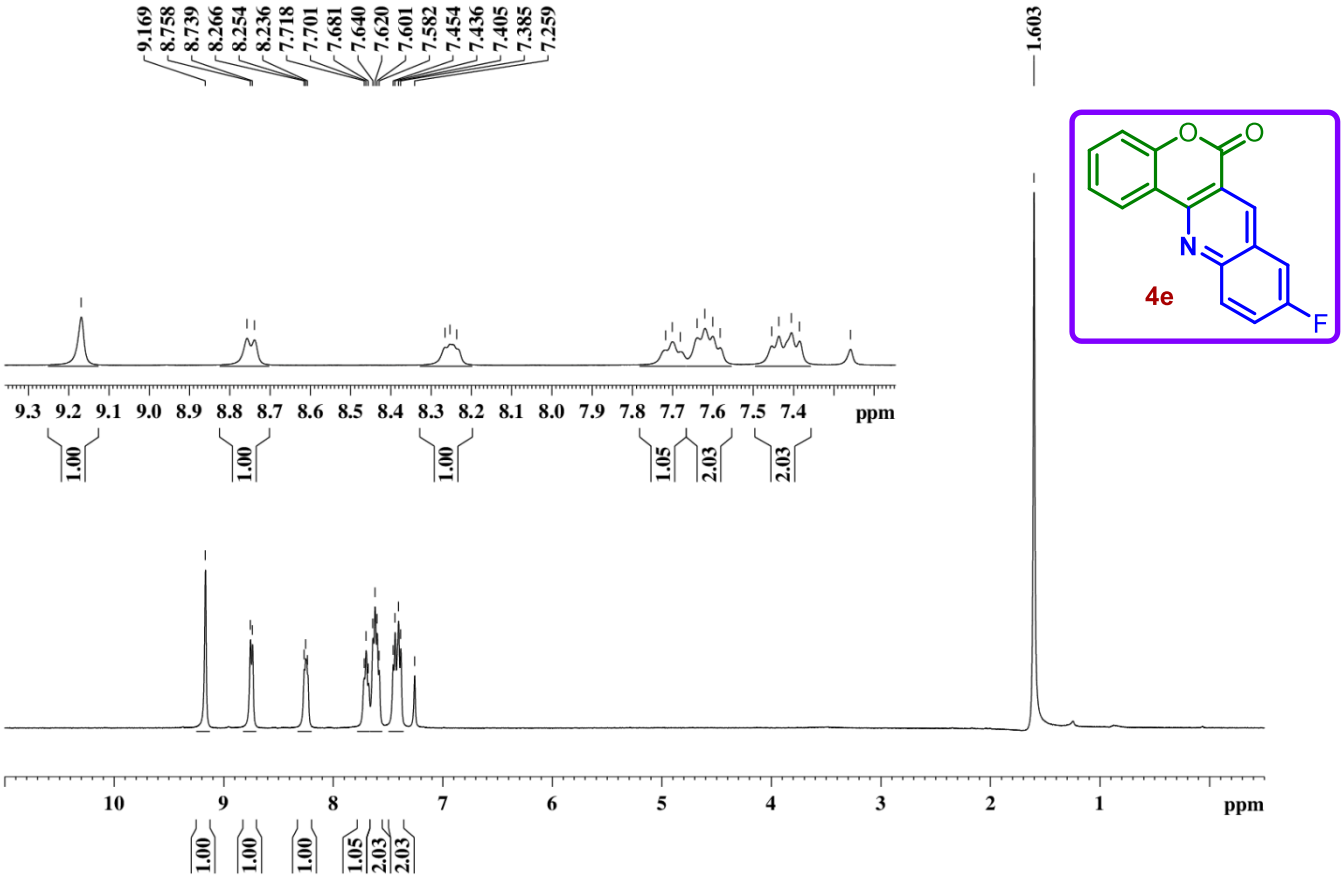
^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$) spectra of compound **4c**



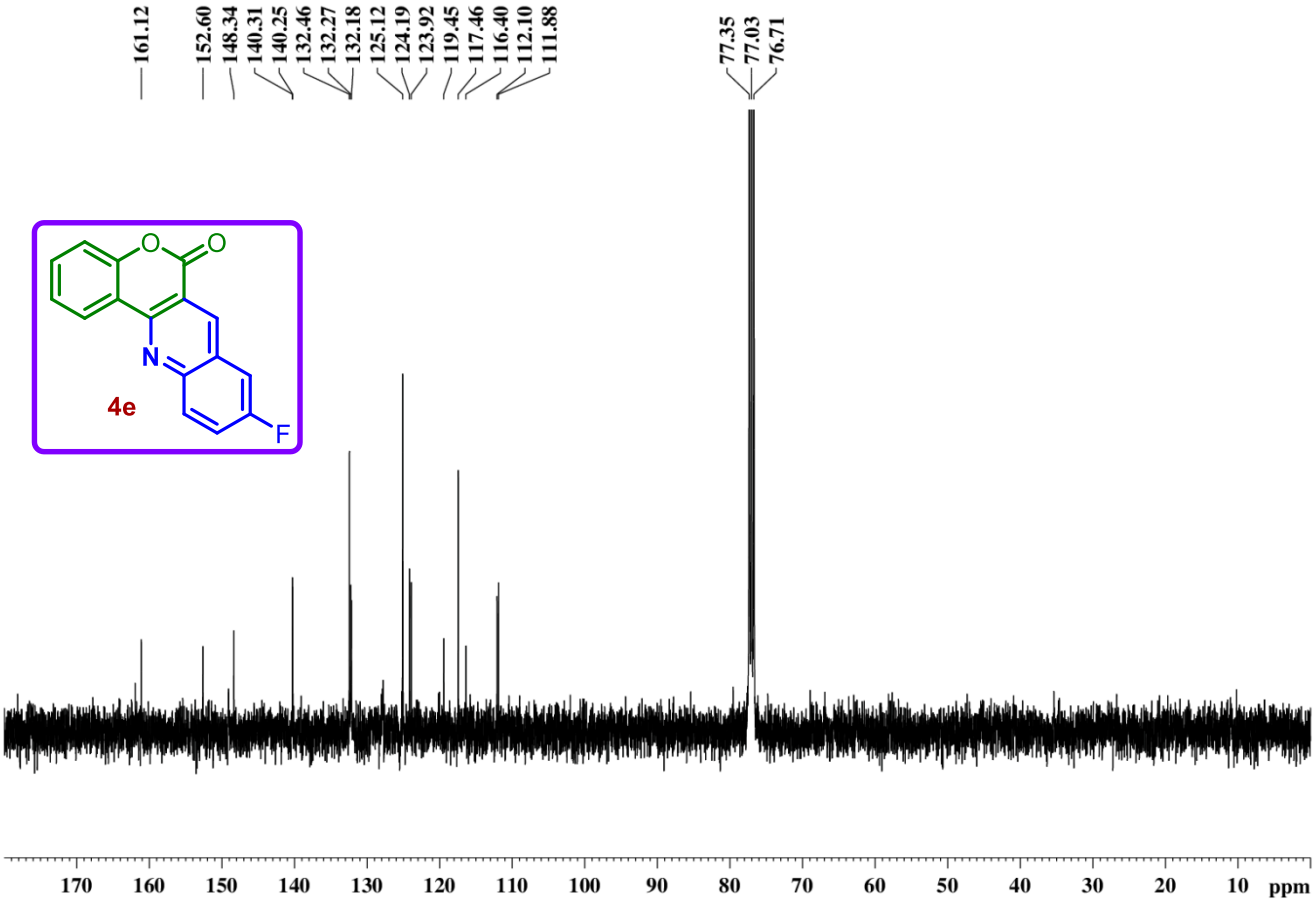
^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **4d**



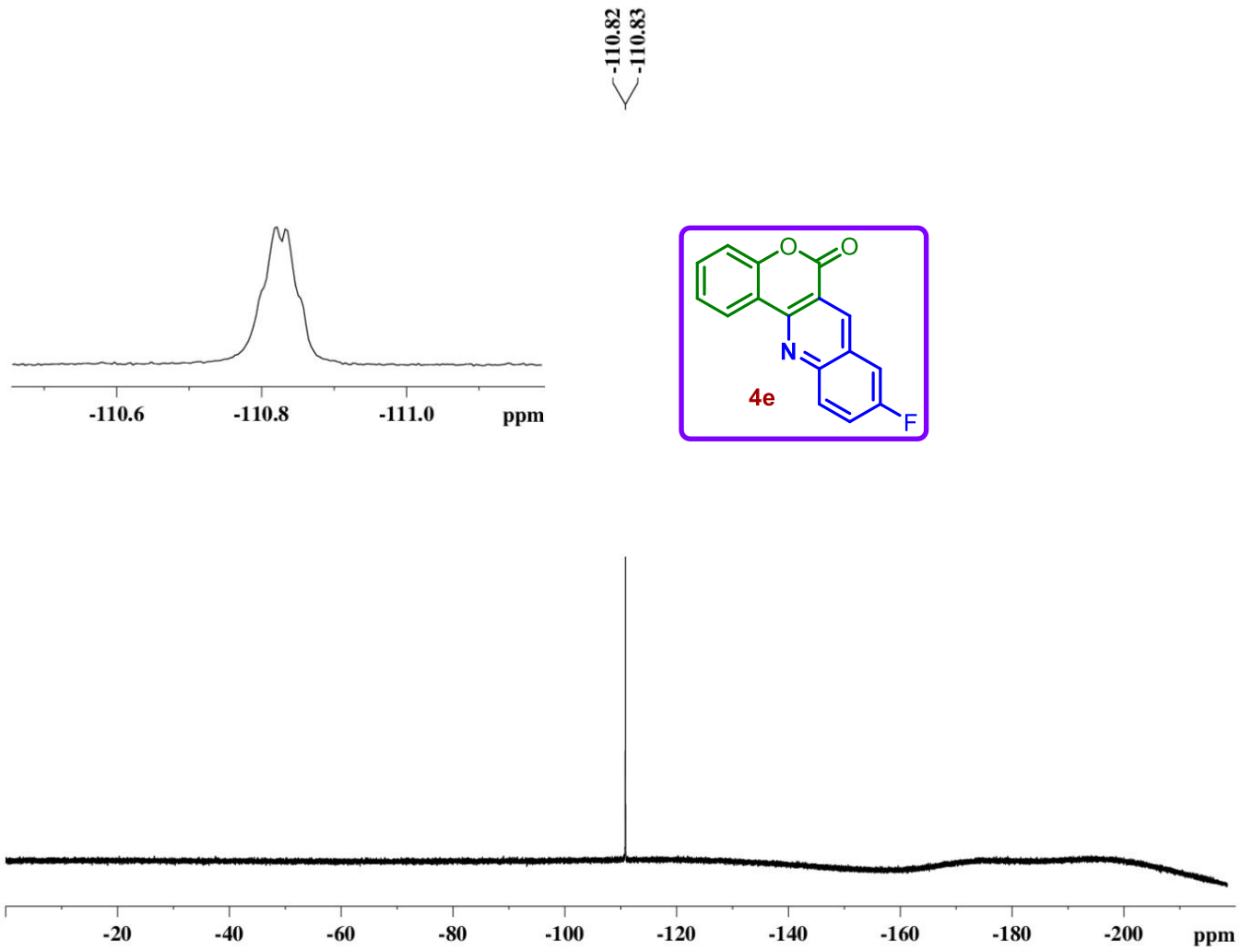
^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$) spectra of compound **4d**



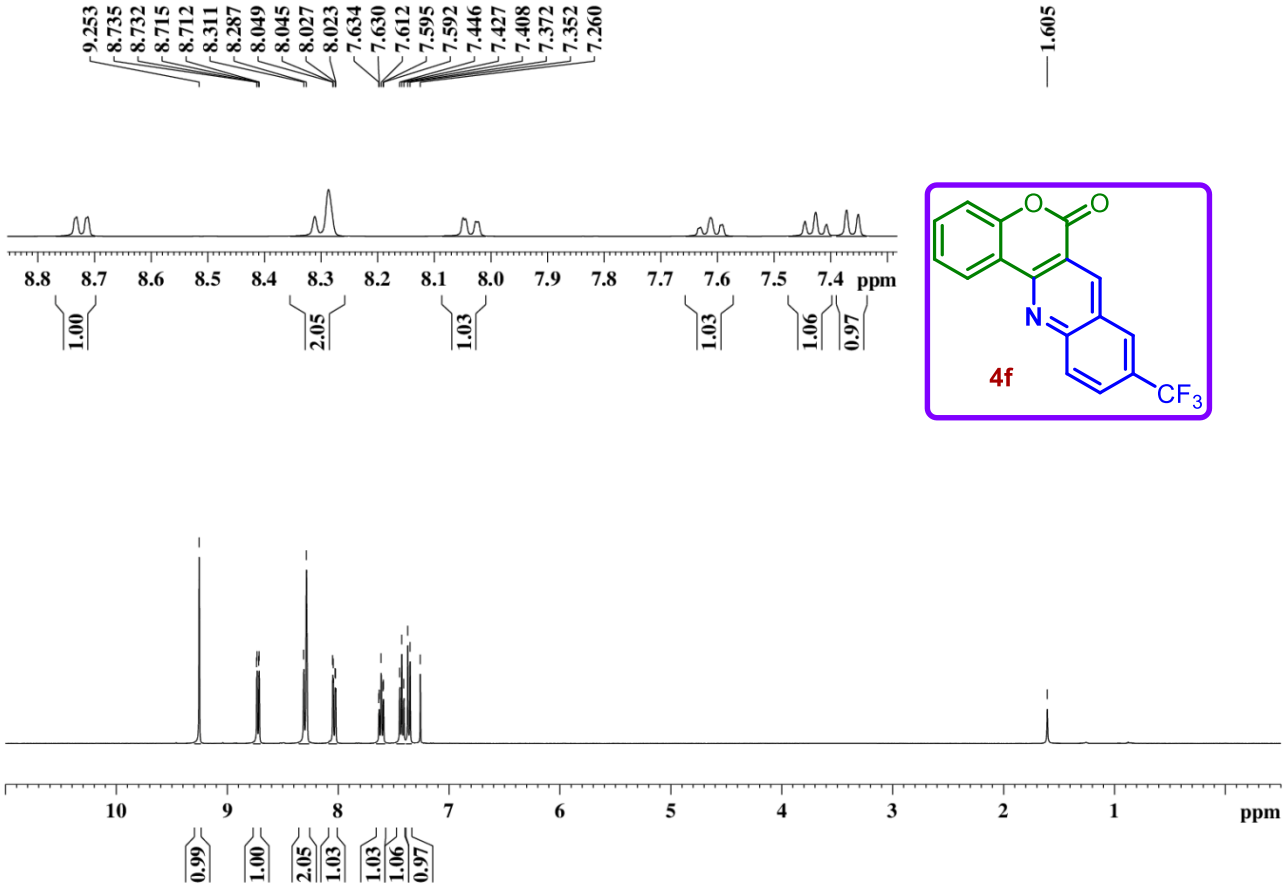
^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **4e**



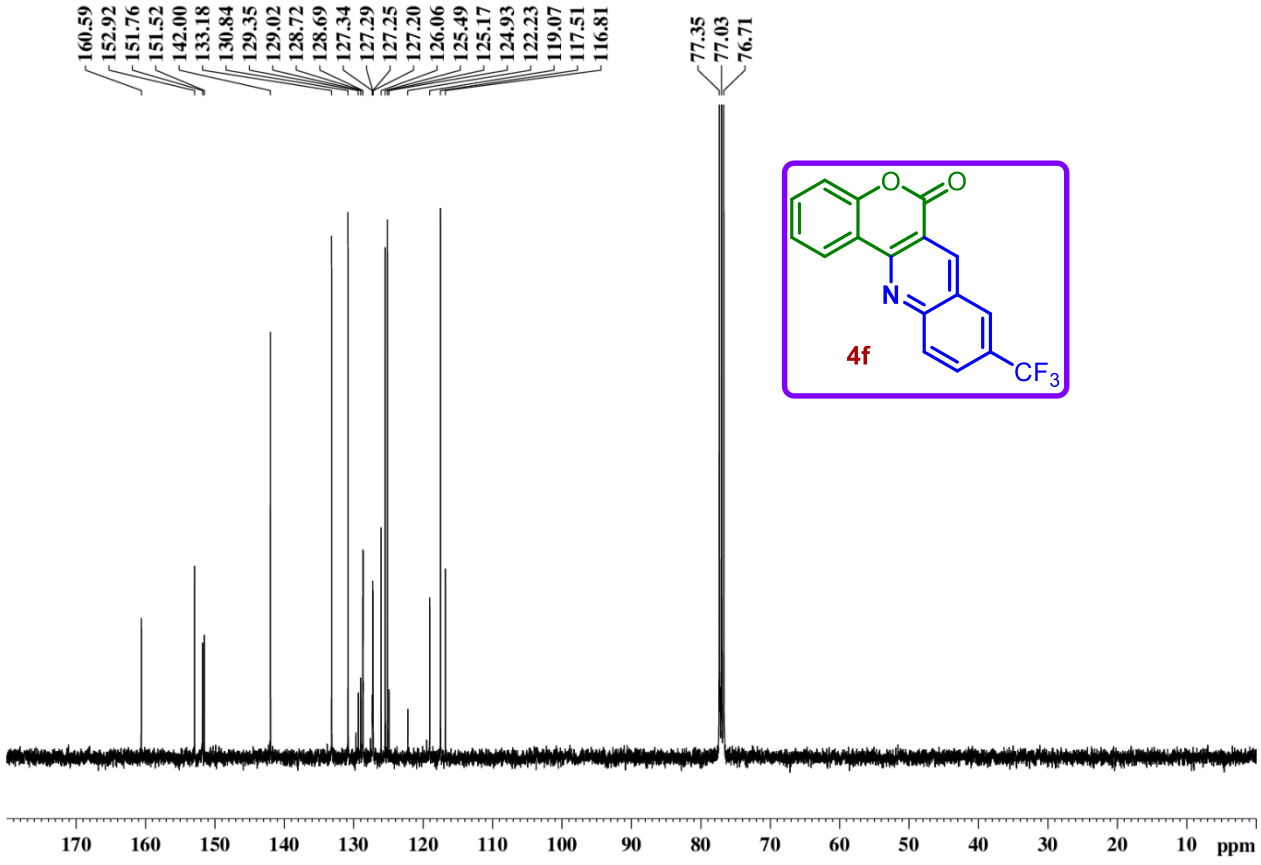
^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$) spectra of compound **4e**



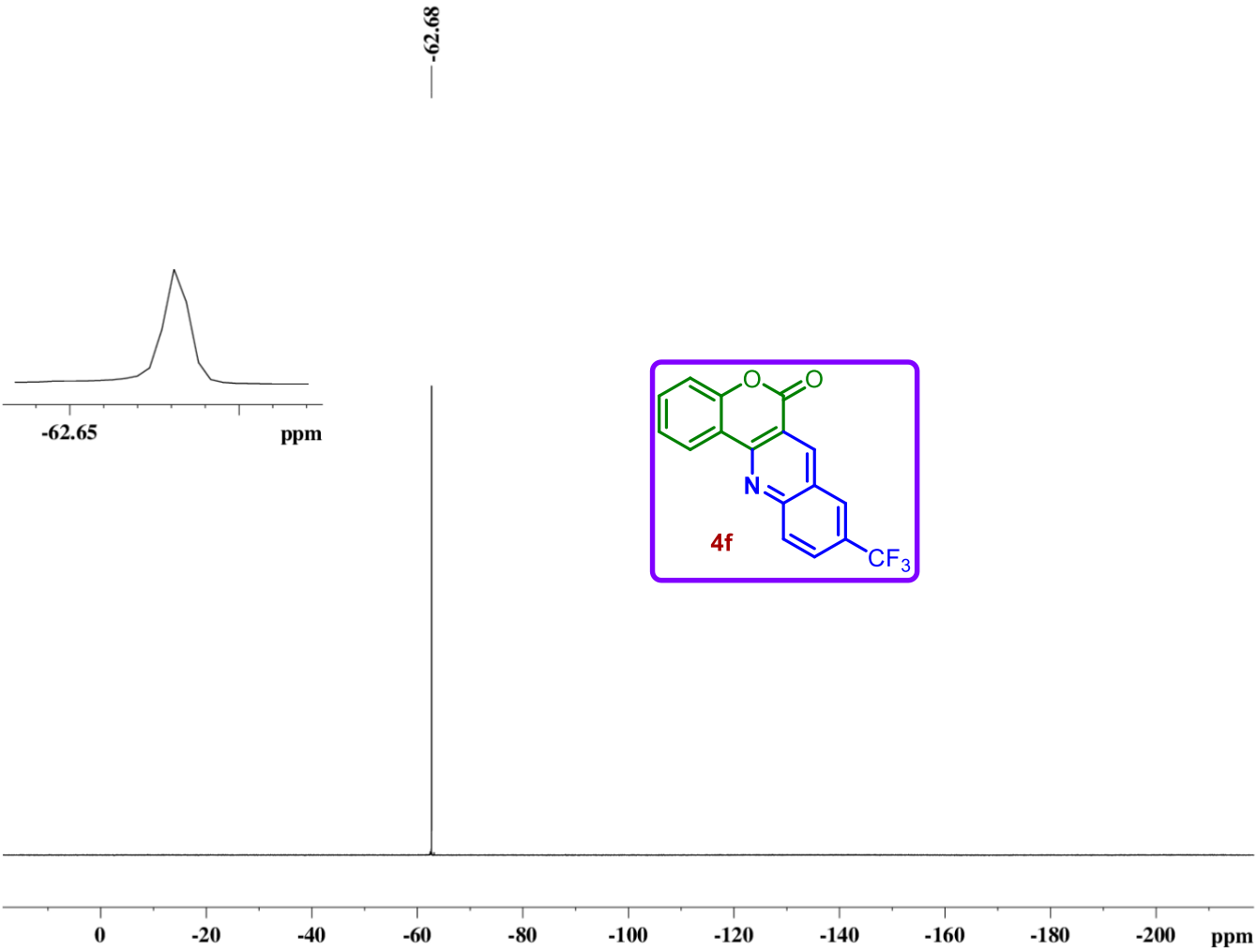
^{19}F NMR (376.6 MHz, $CDCl_3$) spectra of compound **4e**



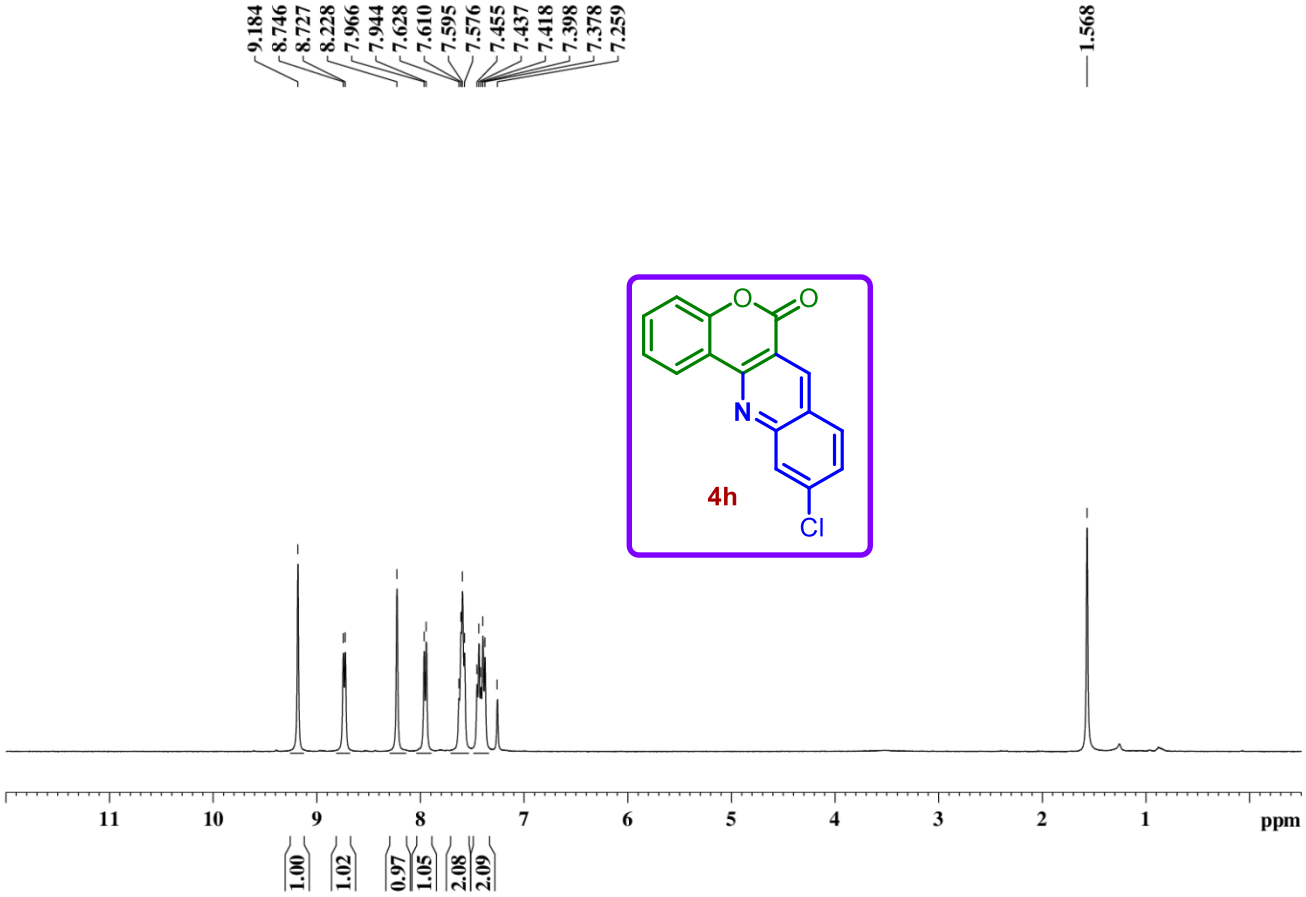
^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **4f**



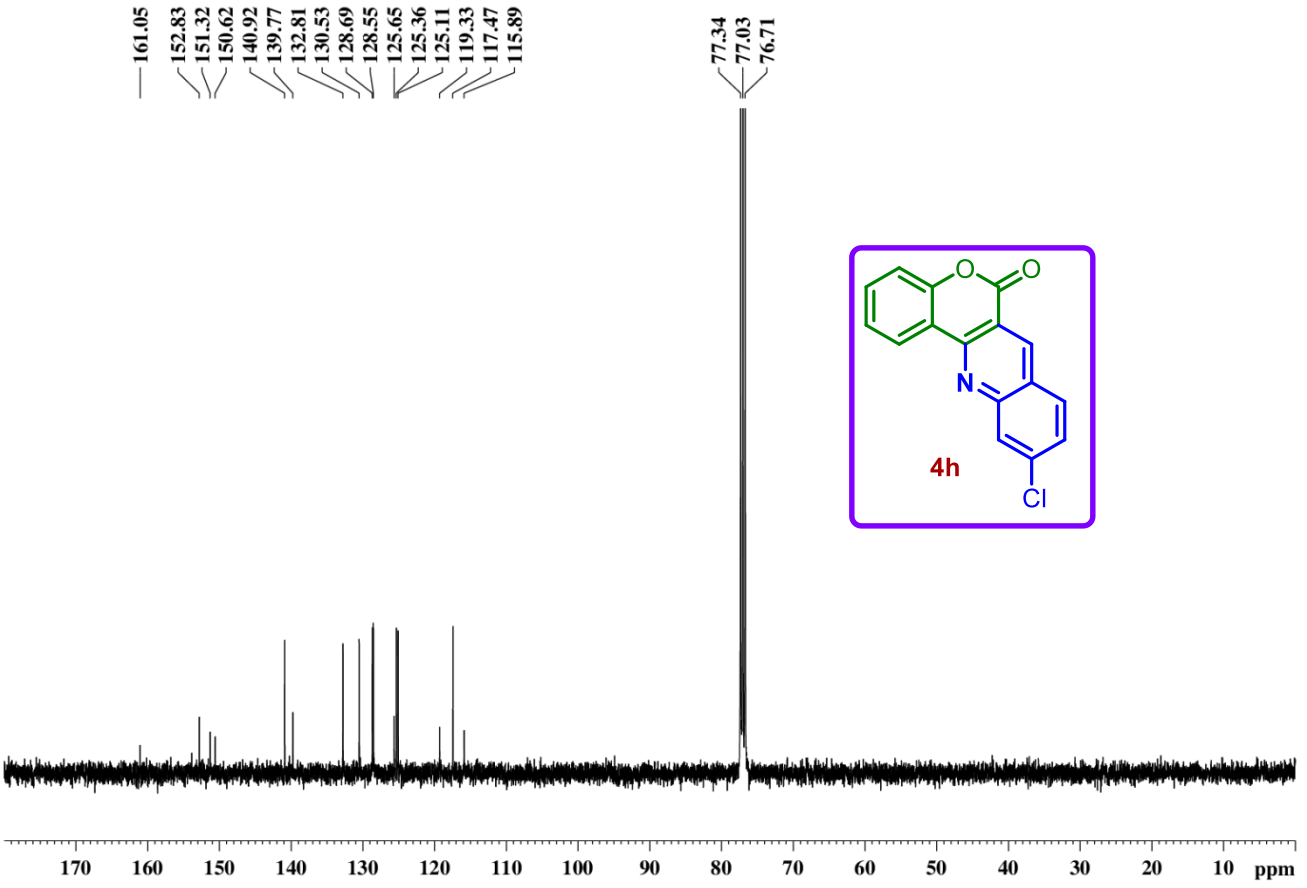
^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$) spectra of compound **4f**



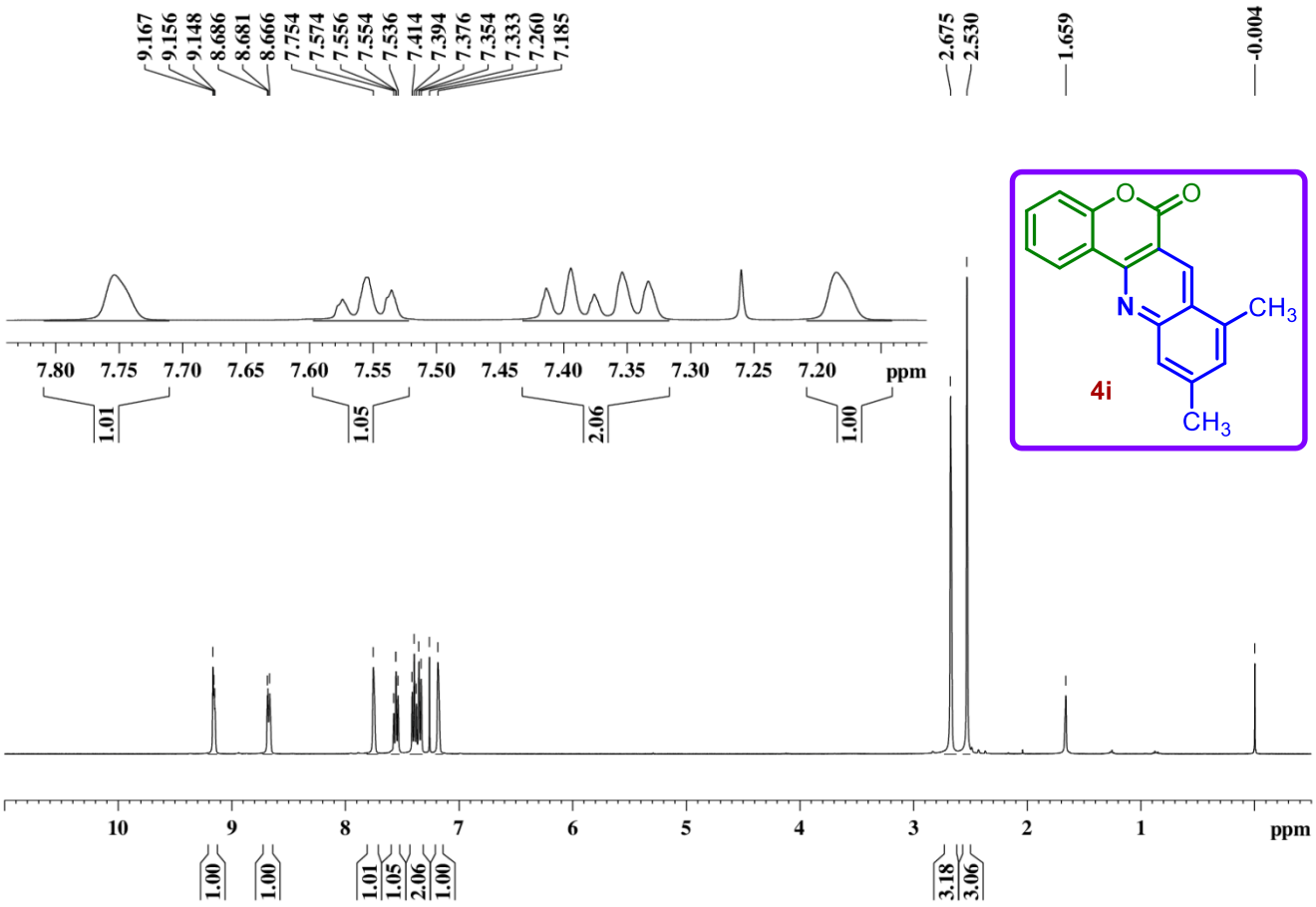
^{19}F NMR (376.6 MHz, $CDCl_3$) spectra of compound **4f**



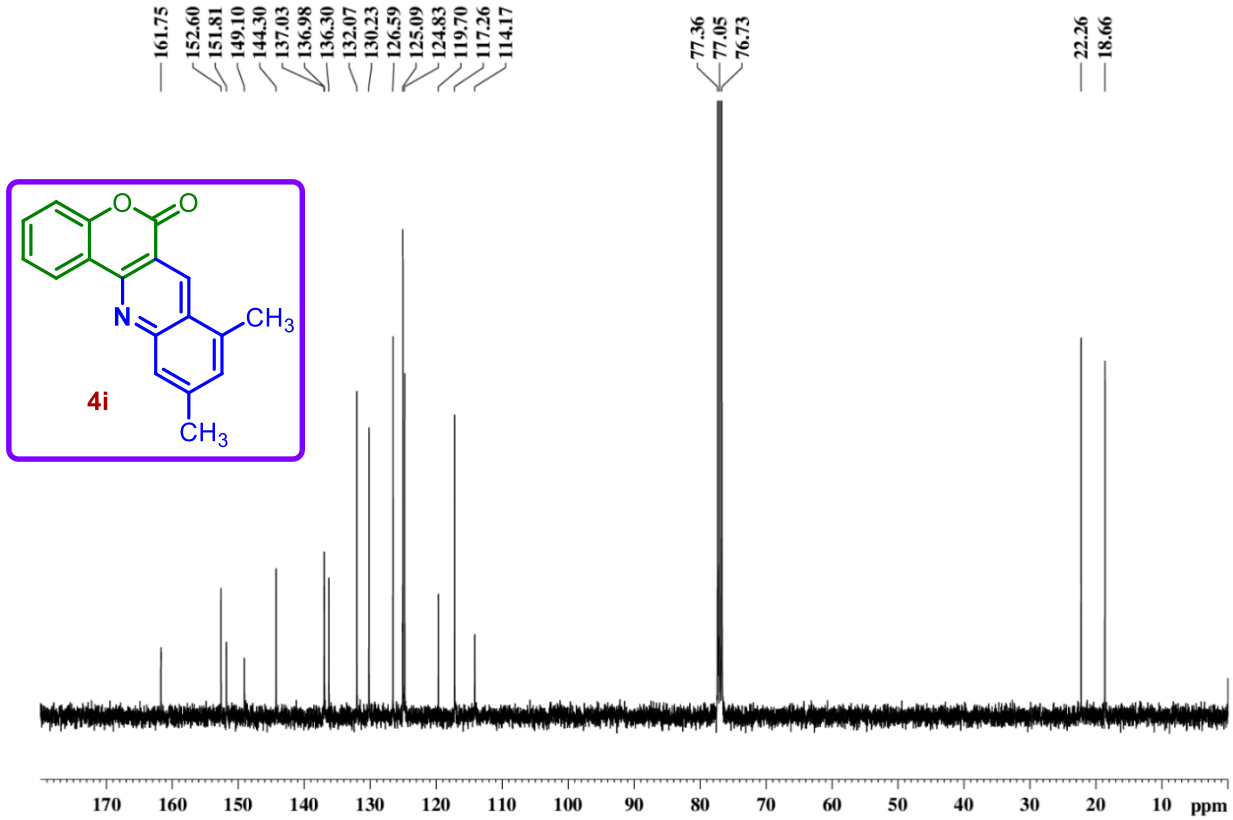
^{1}HNMR (400 MHz, $CDCl_3$) spectra of compound **4h**



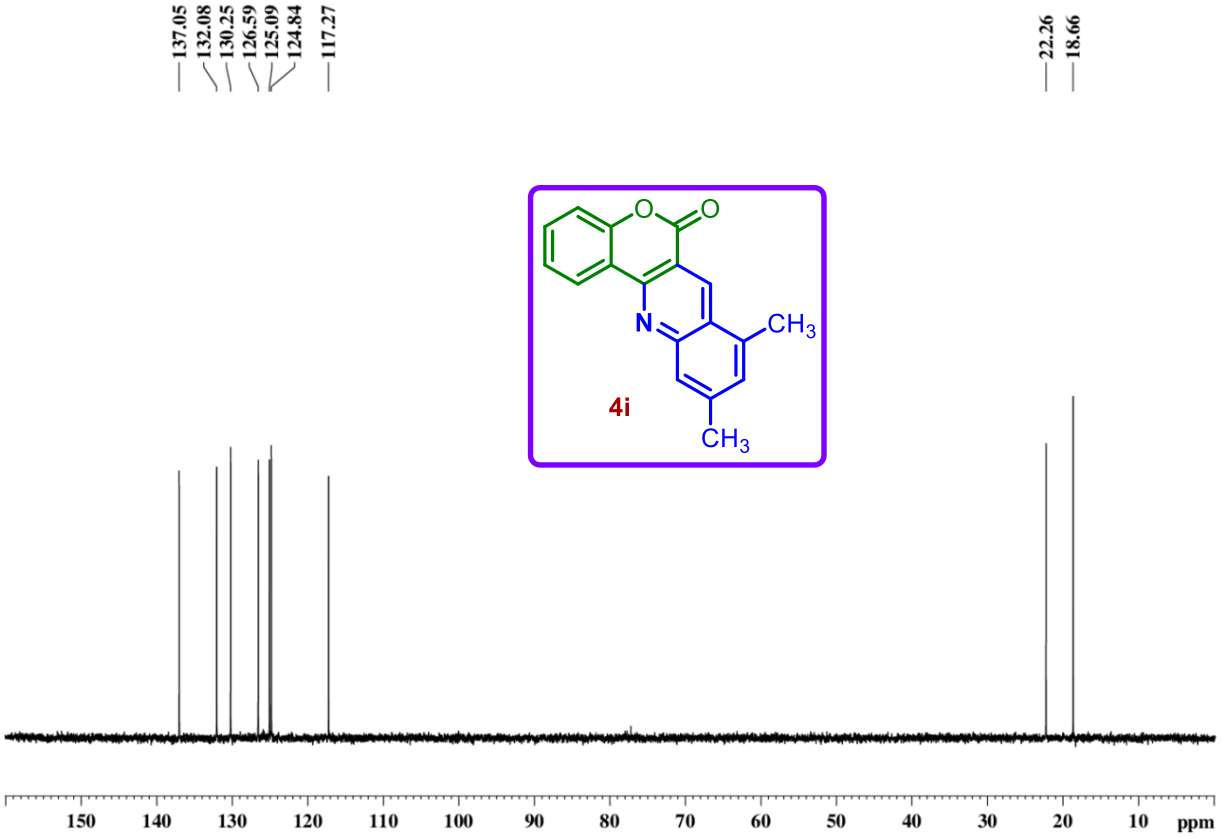
^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$) spectra of compound **4h**



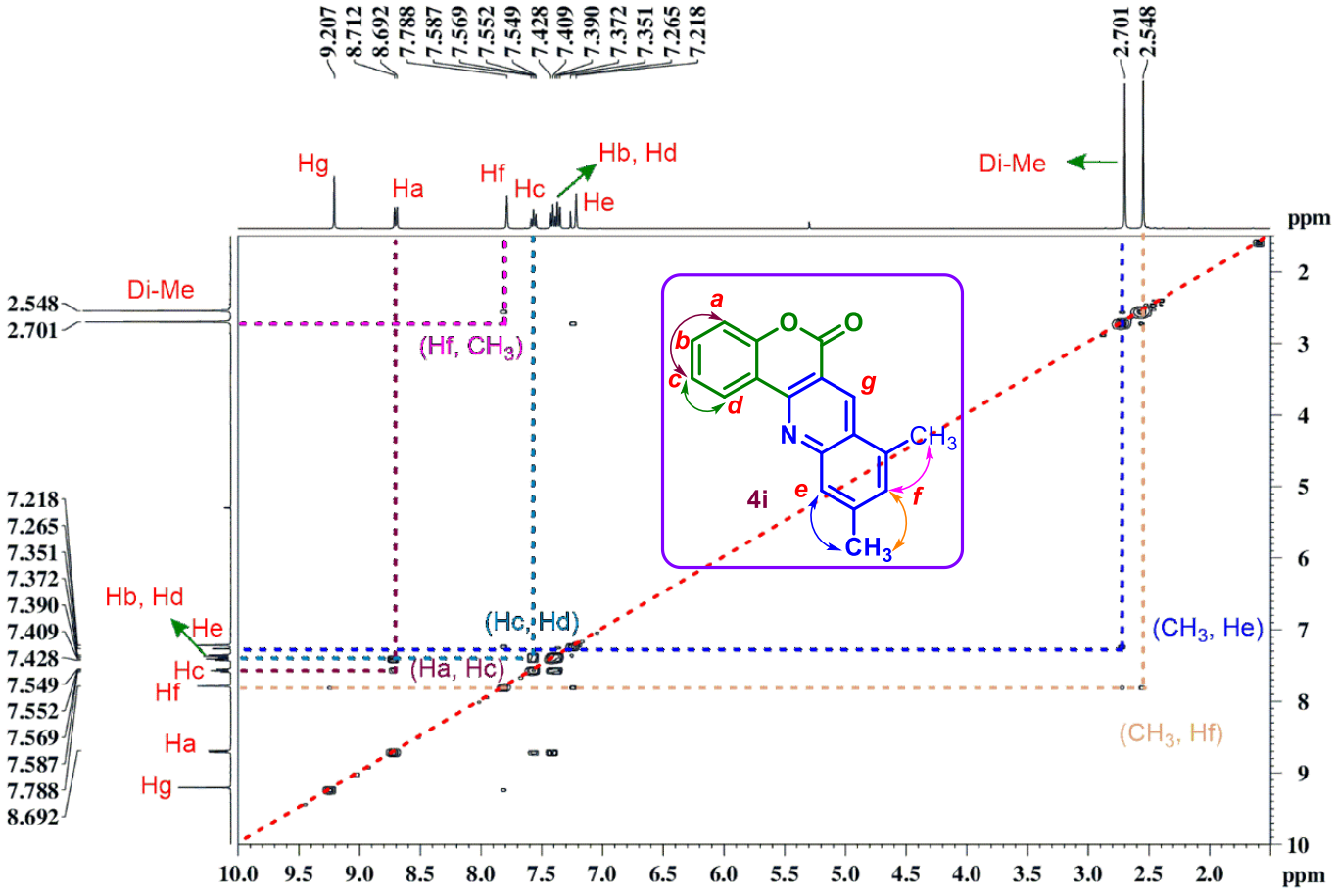
^{1}HNMR (400 MHz, $CDCl_3$) spectra of compound **4i**



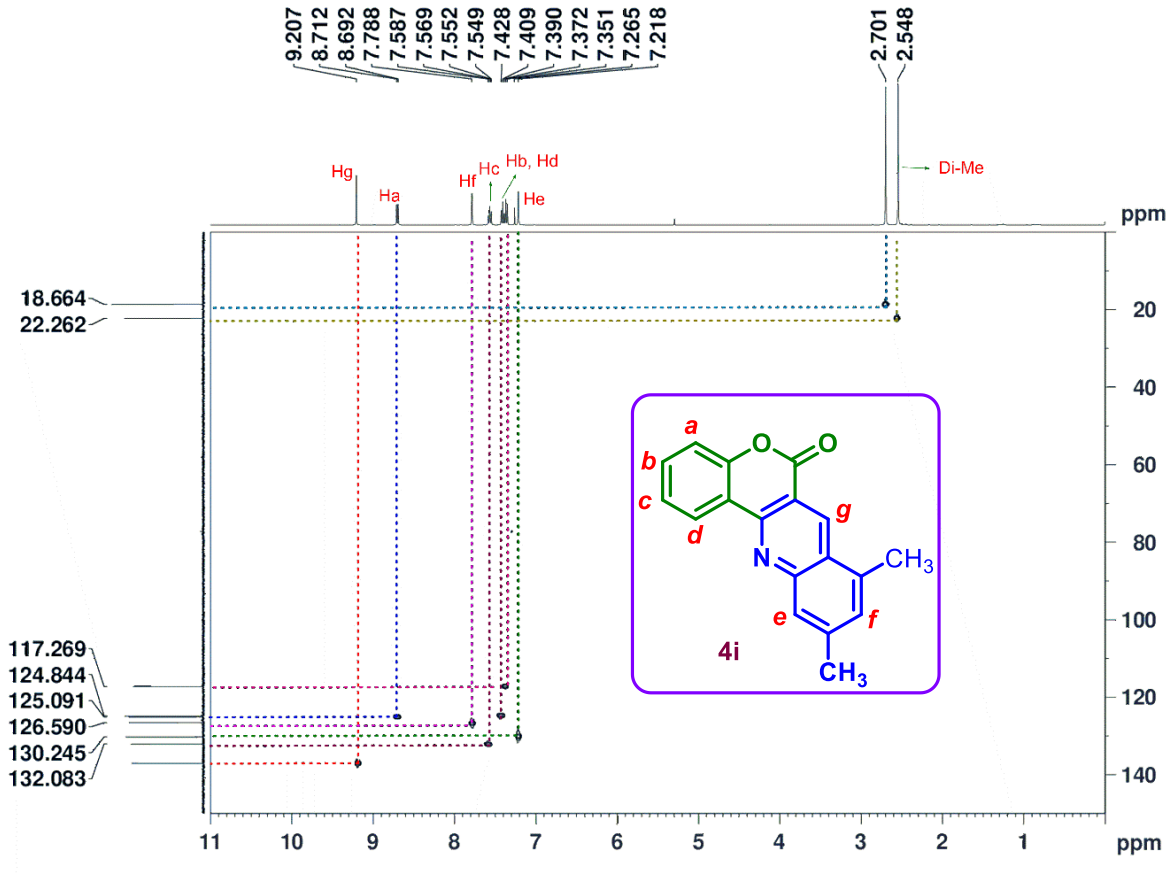
^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$) spectra of compound **4i**



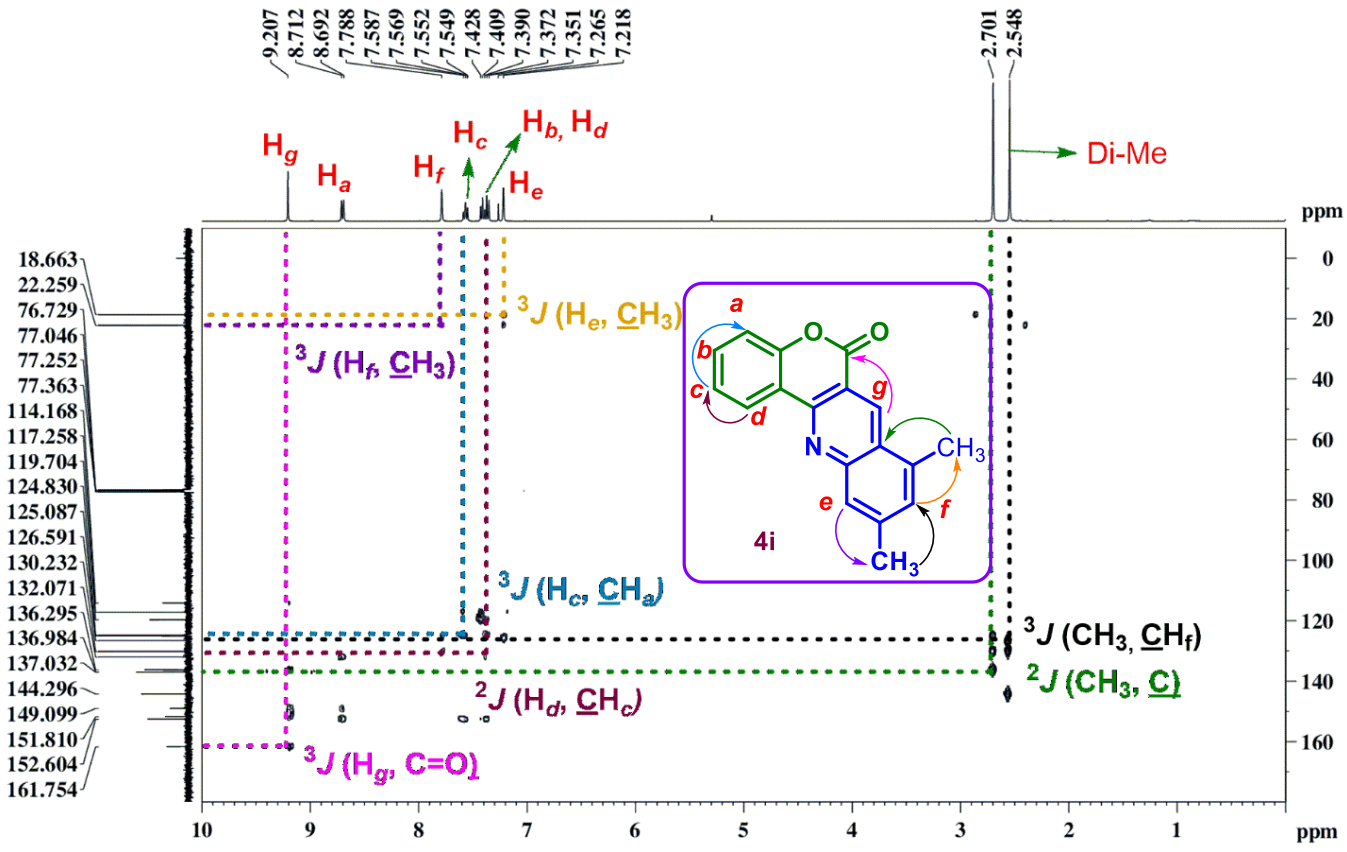
DEPT-135 NMR (100.6 MHz, $CDCl_3$) spectra of compound **4i**



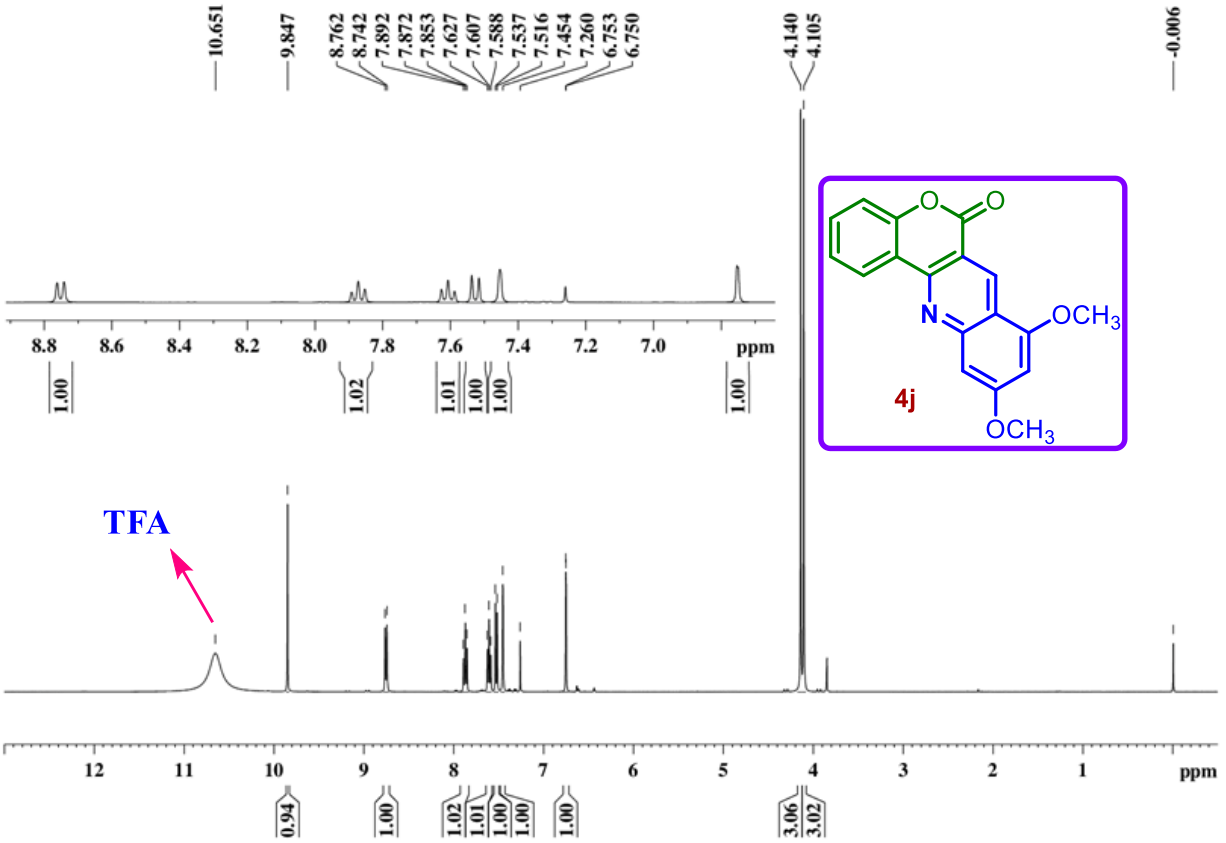
^{1}H-^{1}H COSY NMR spectra of compound **4i**



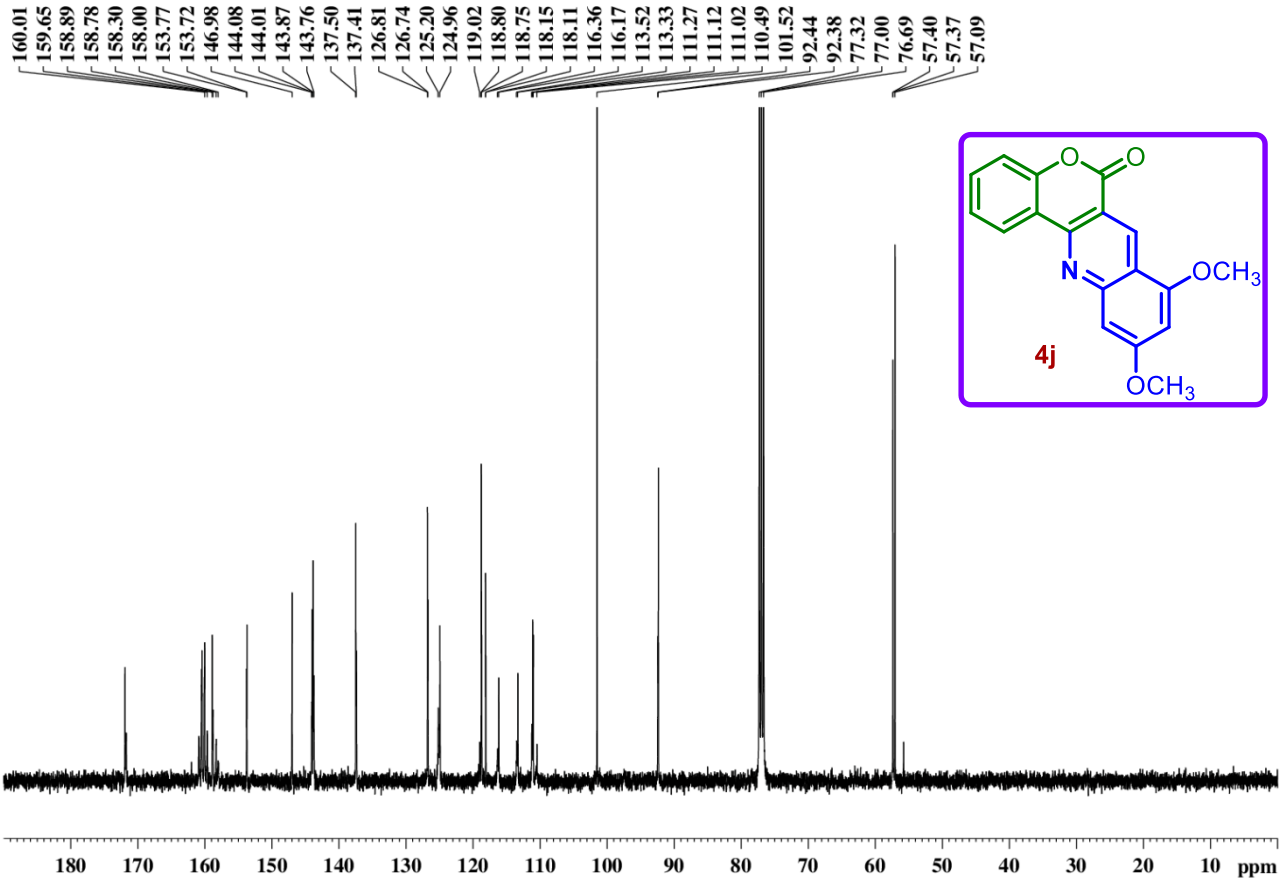
^{1}H-^{13}C (DEPT-135) HSQC NMR spectra of compound **4i**



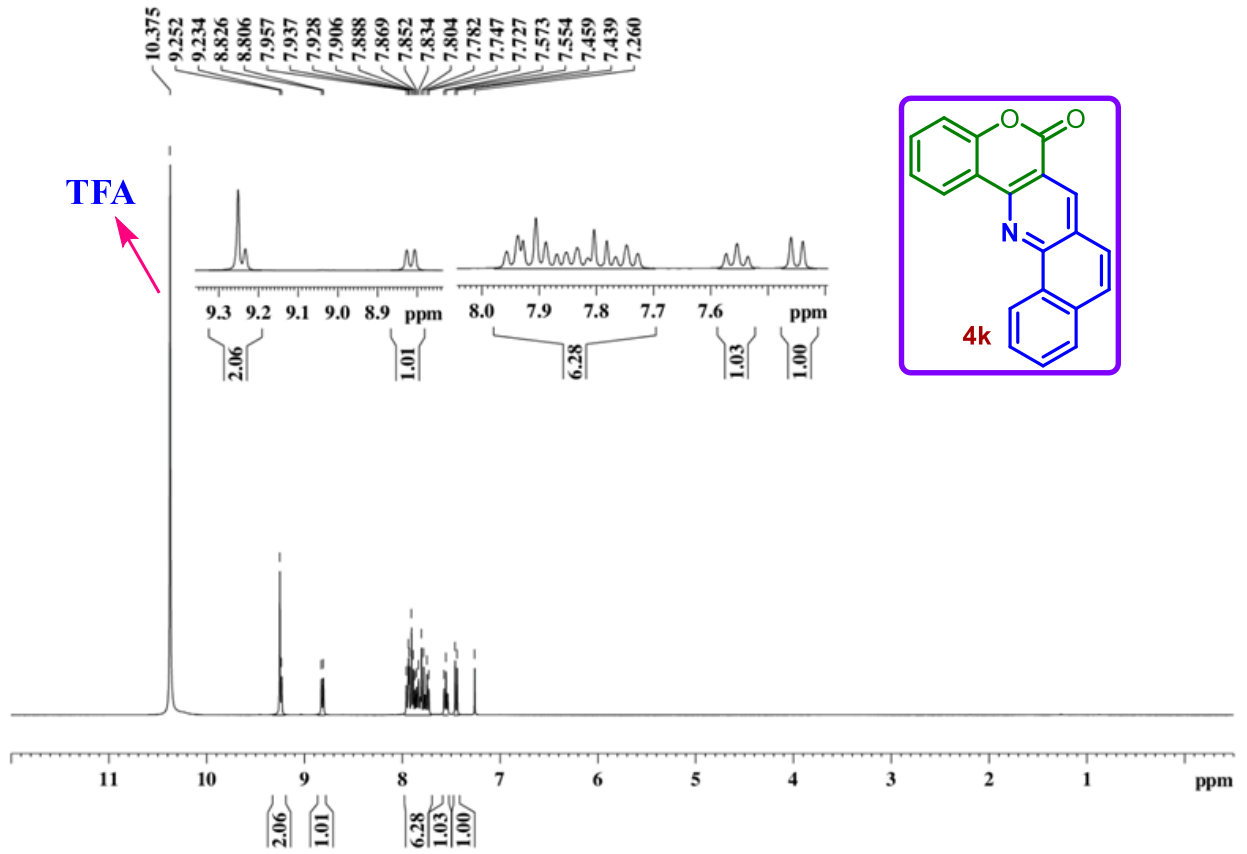
^{1}H-^{13}C HMBC NMR spectra of compound **4i**



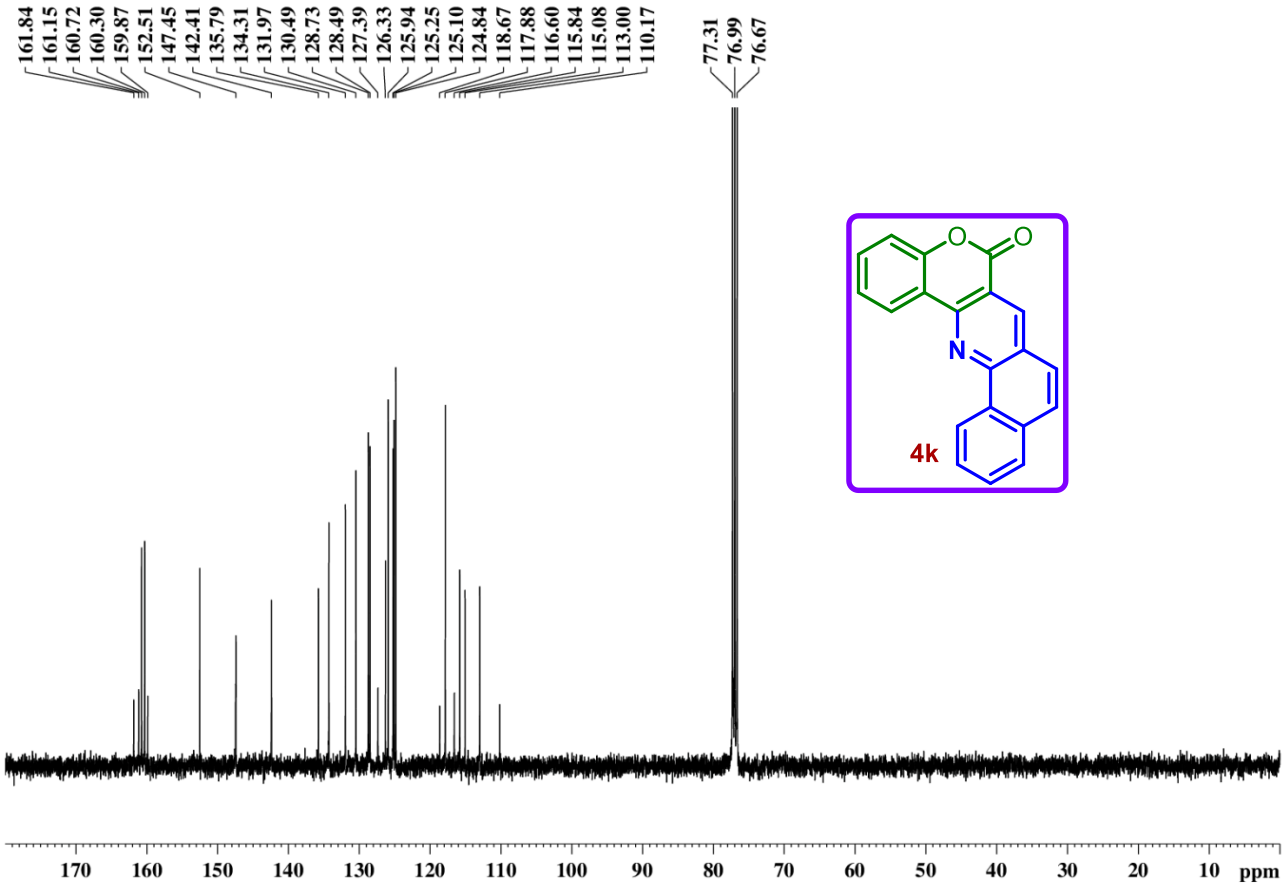
^{1}H NMR (400 MHz, $CDCl_3$+TFA) spectra of compound **4j**



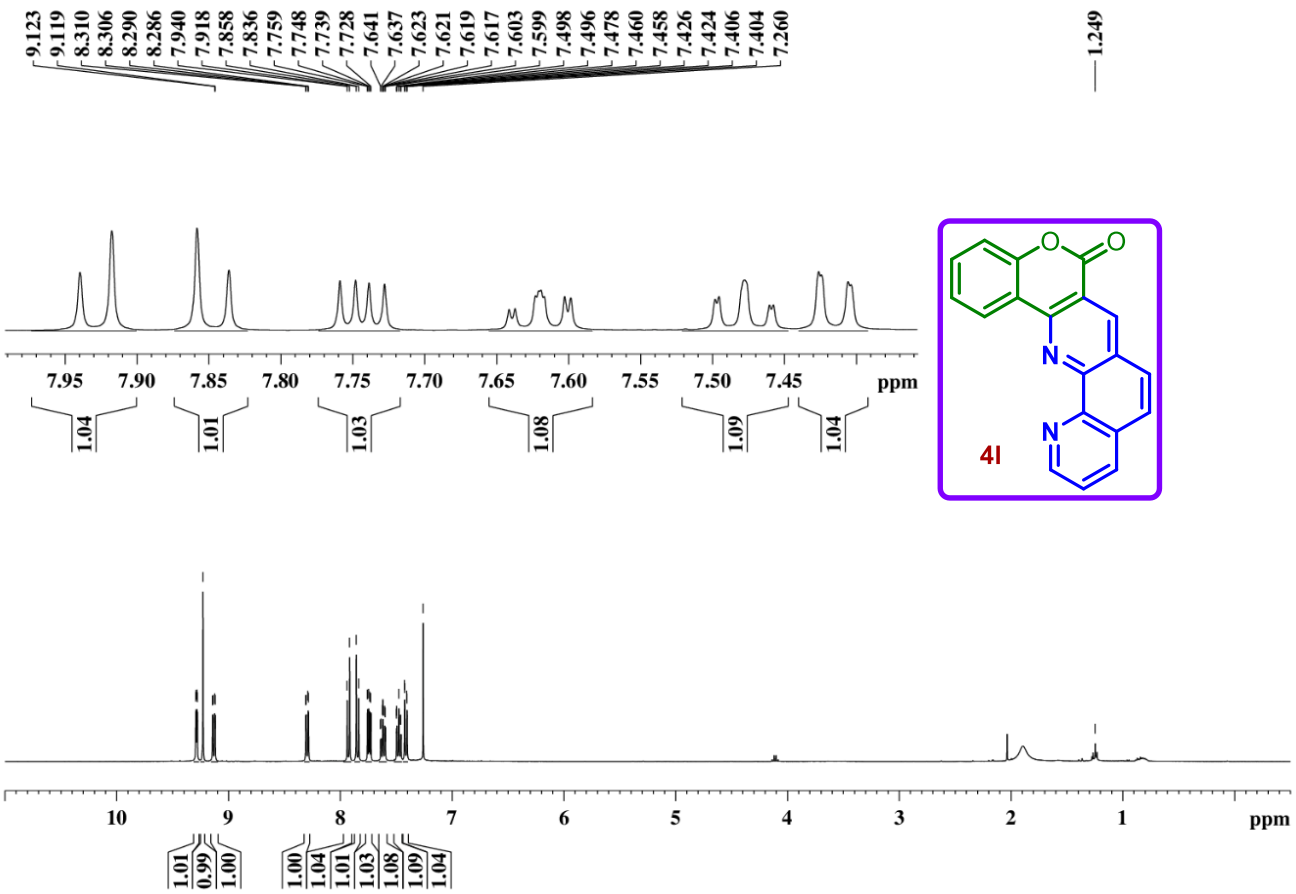
^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$+TFA) spectra of compound **4j**



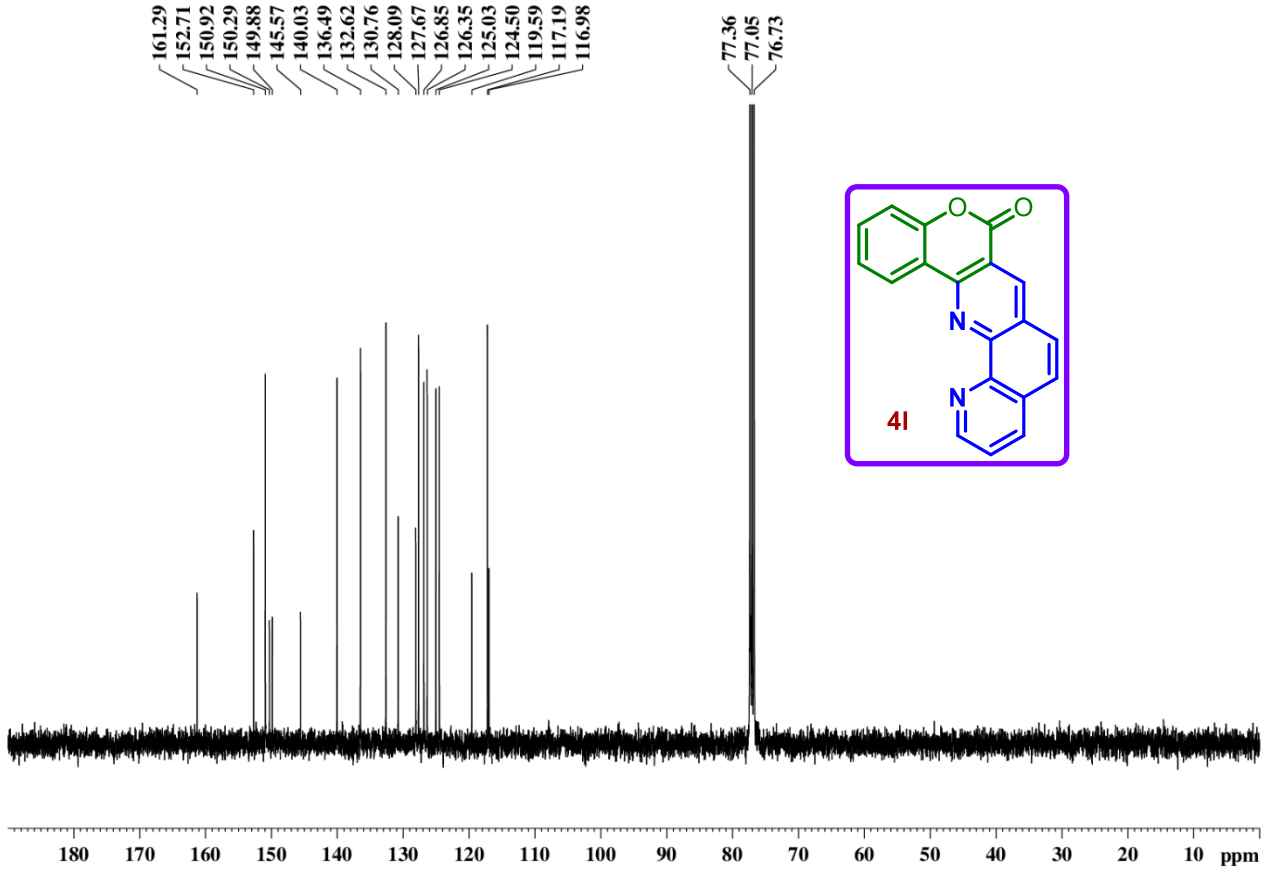
^{1}H NMR (400 MHz, $CDCl_3$+TFA) spectra of compound **4k**



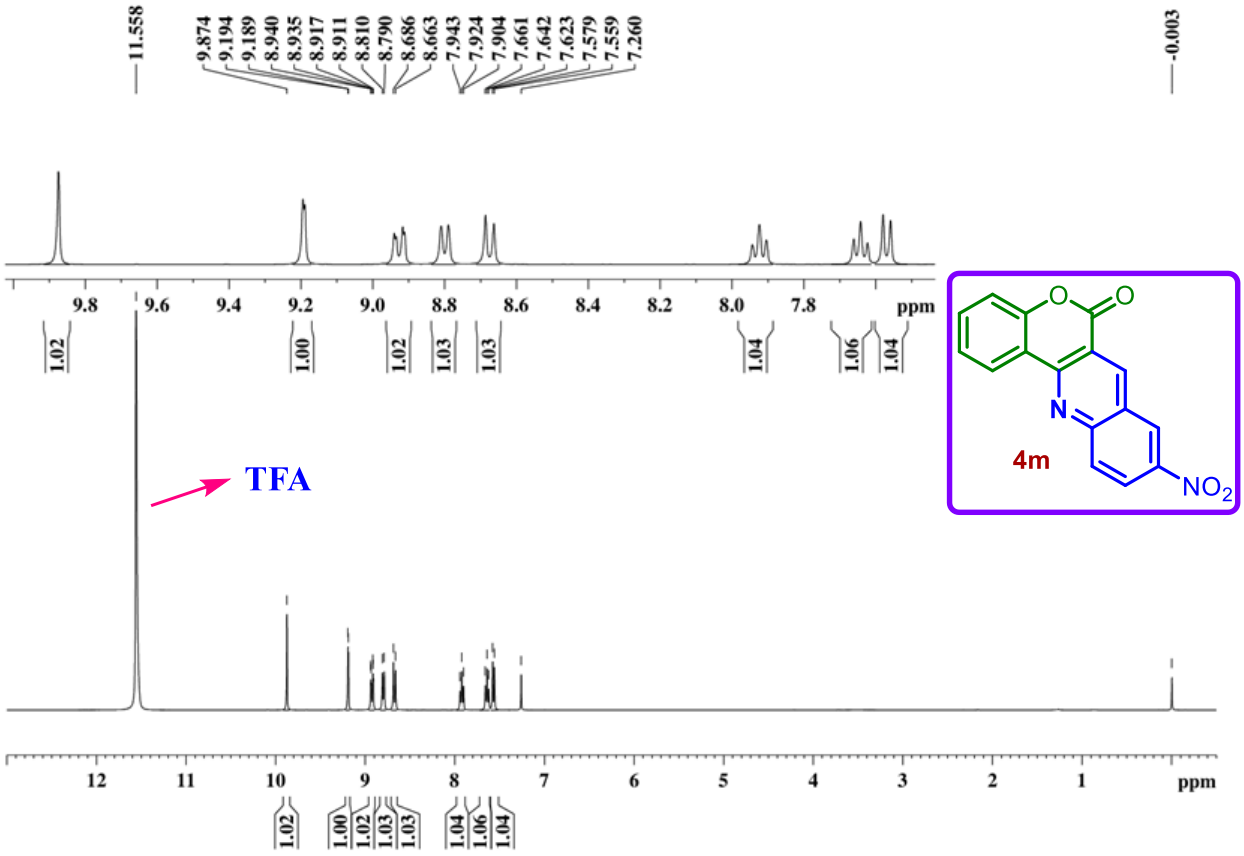
^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$+TFA) spectra of compound **4k**



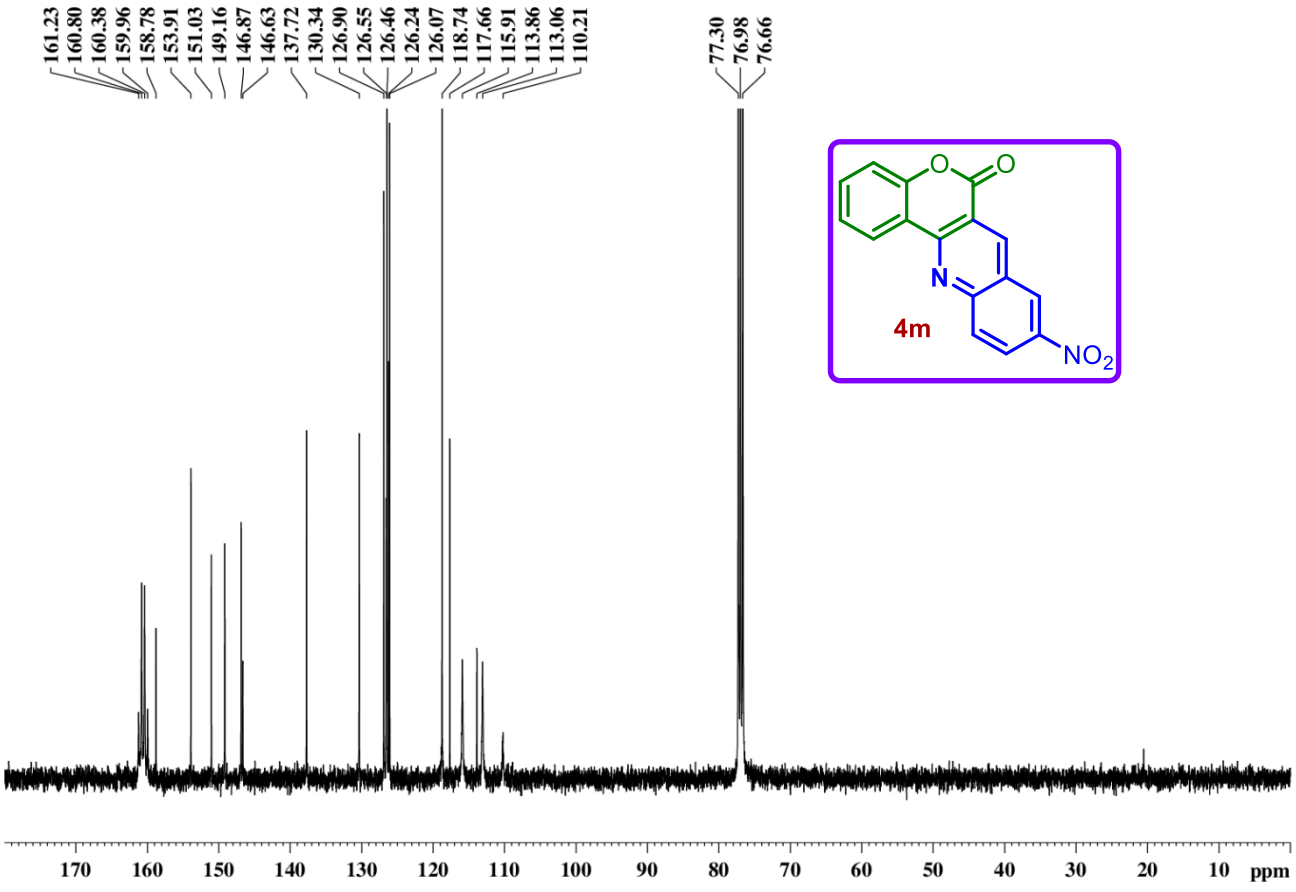
^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **4l**



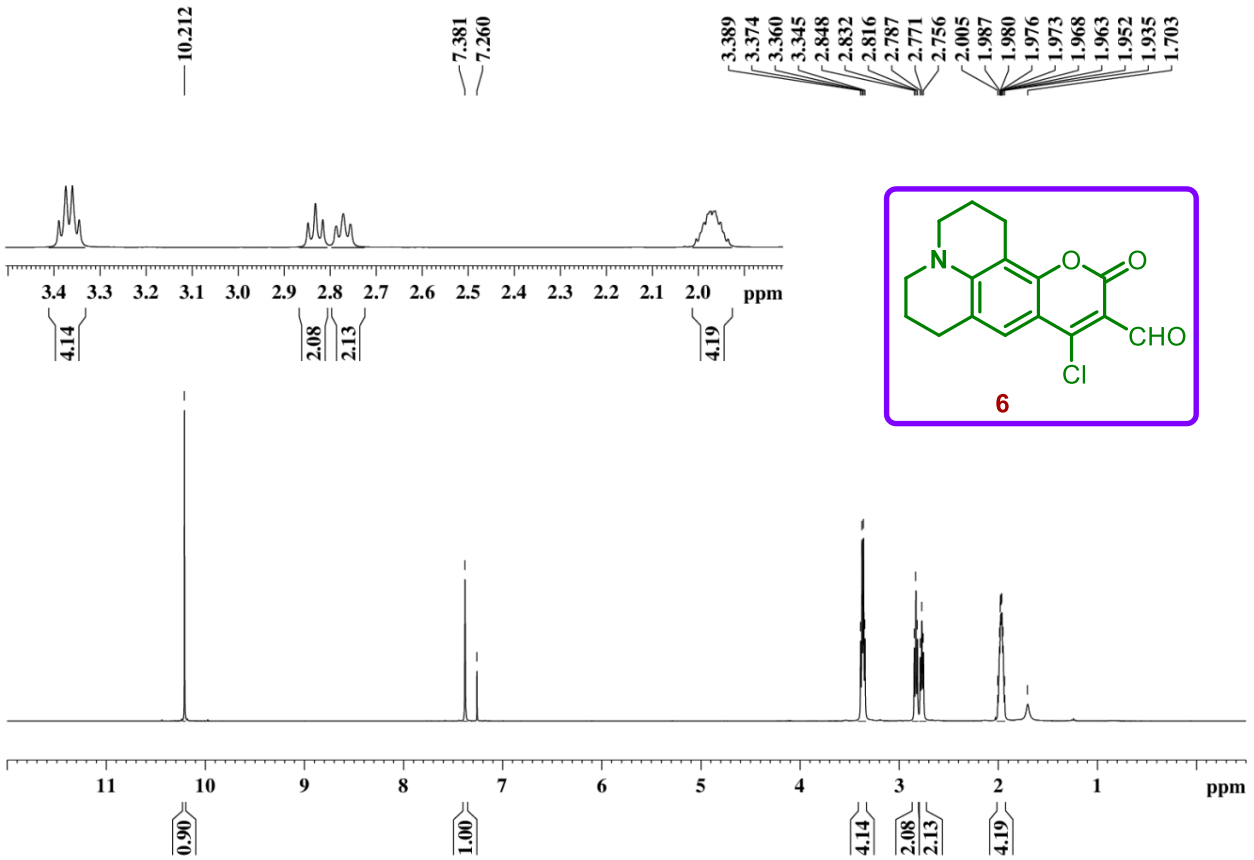
^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$) spectra of compound **4l**



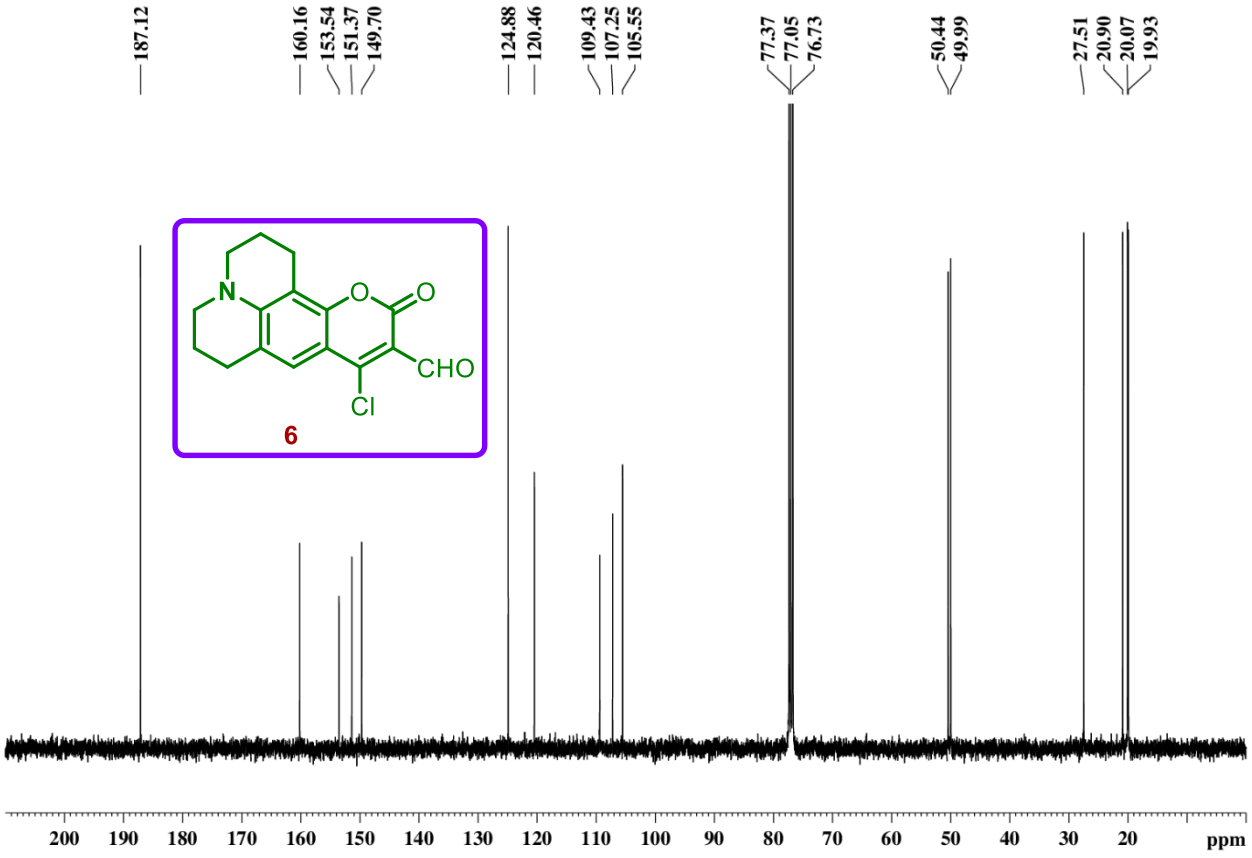
^{1}H NMR (400 MHz, $CDCl_3$+TFA) spectra of compound **4m**



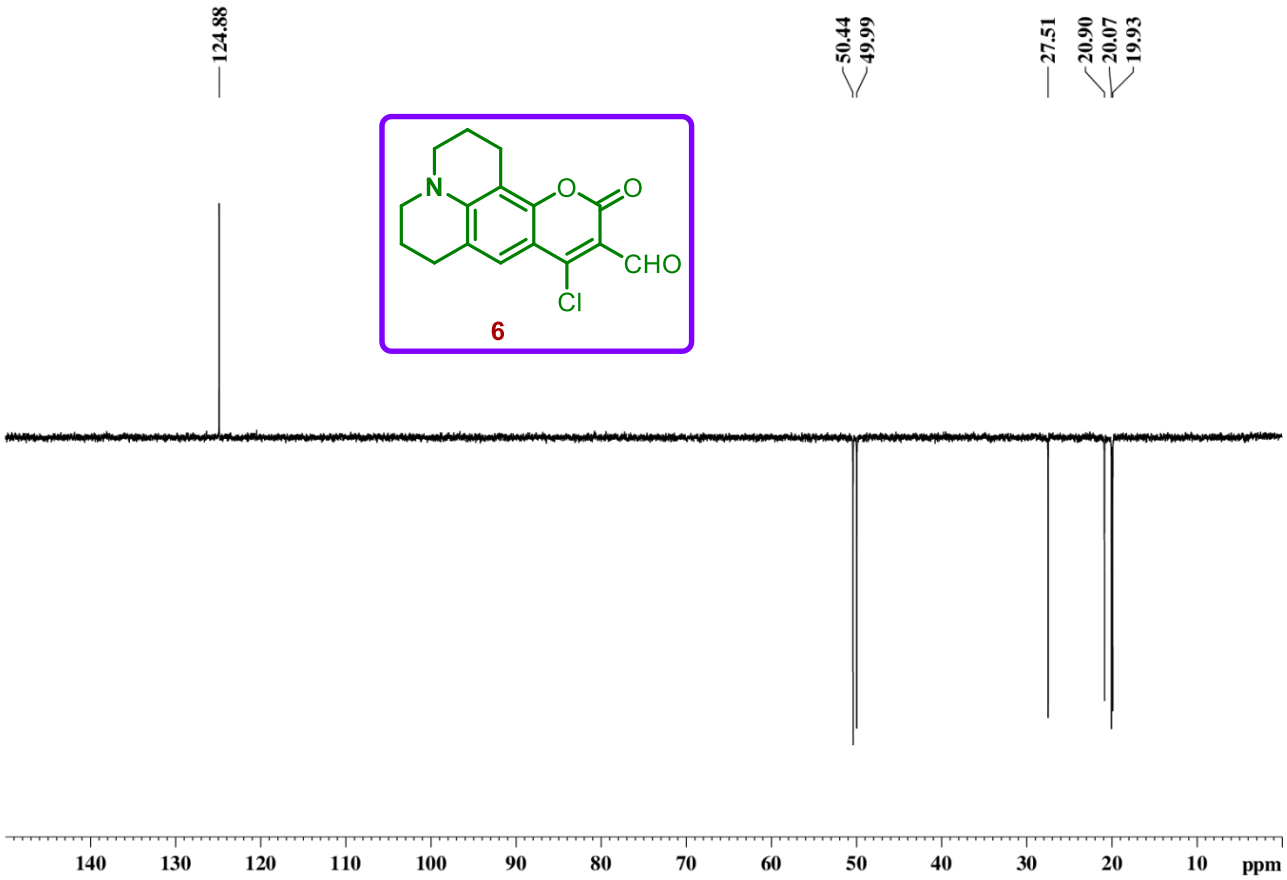
^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$+TFA) spectra of compound **4m**



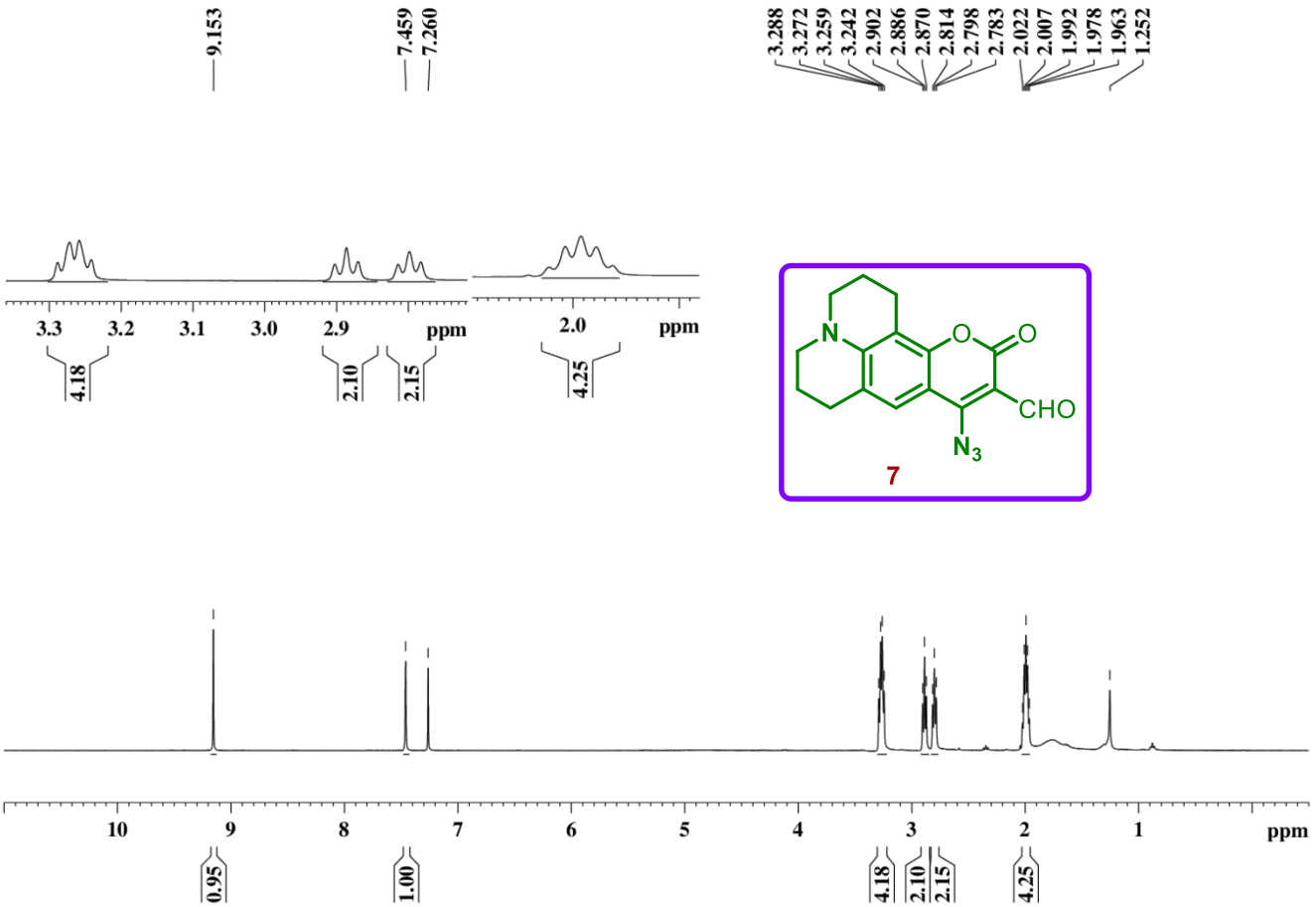
^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **6**



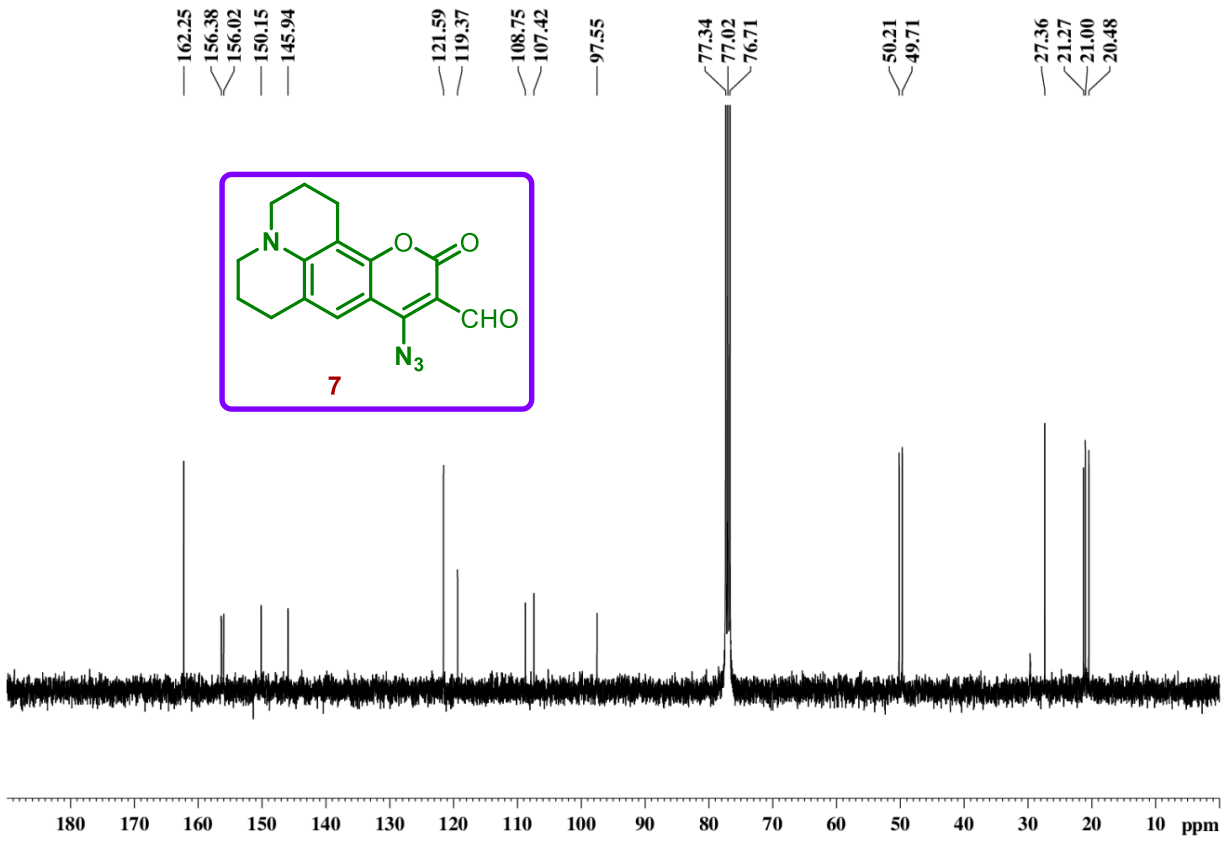
^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$) spectra of compound **6**



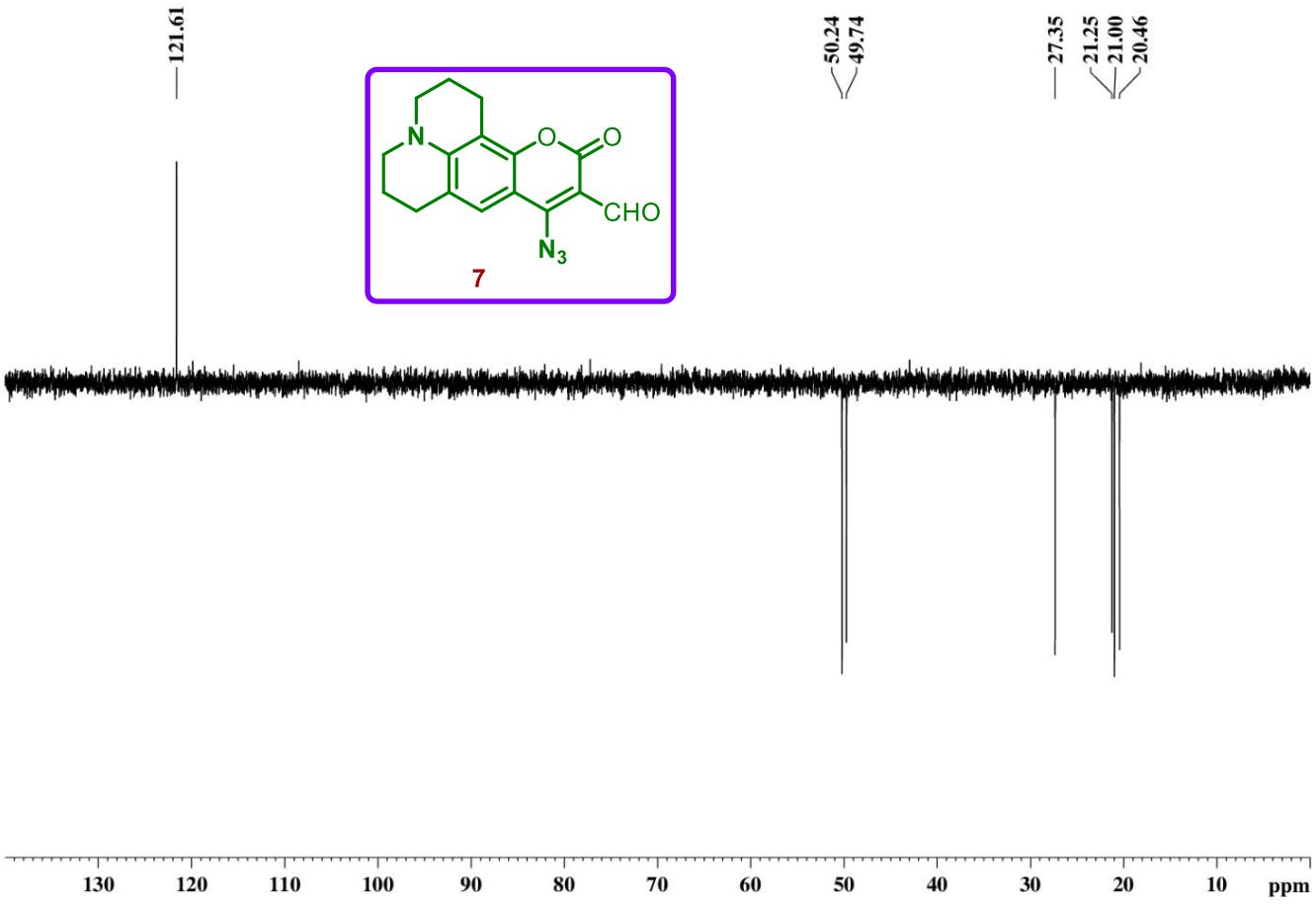
DEPT-135 NMR (100.6 MHz, $CDCl_3$) spectra of compound **6**



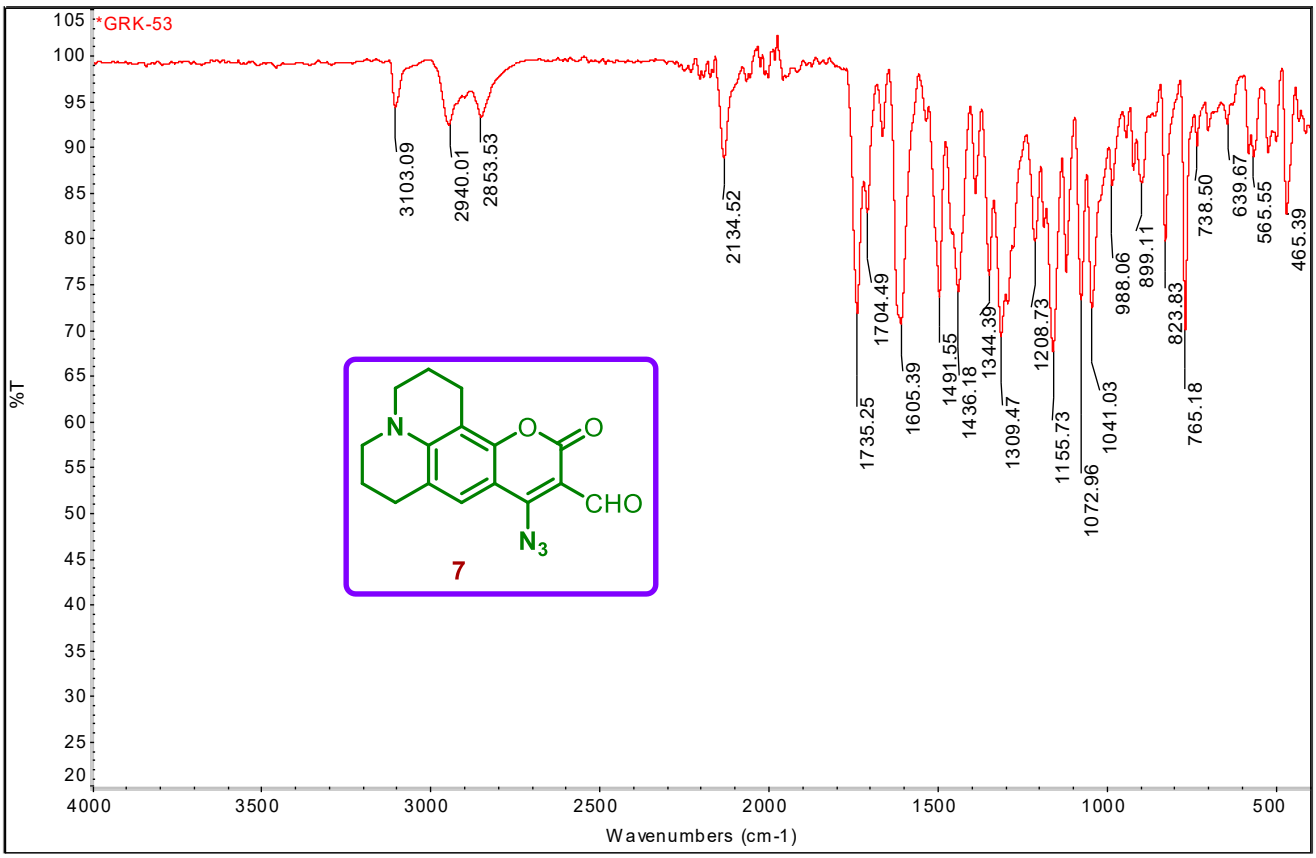
^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **7**



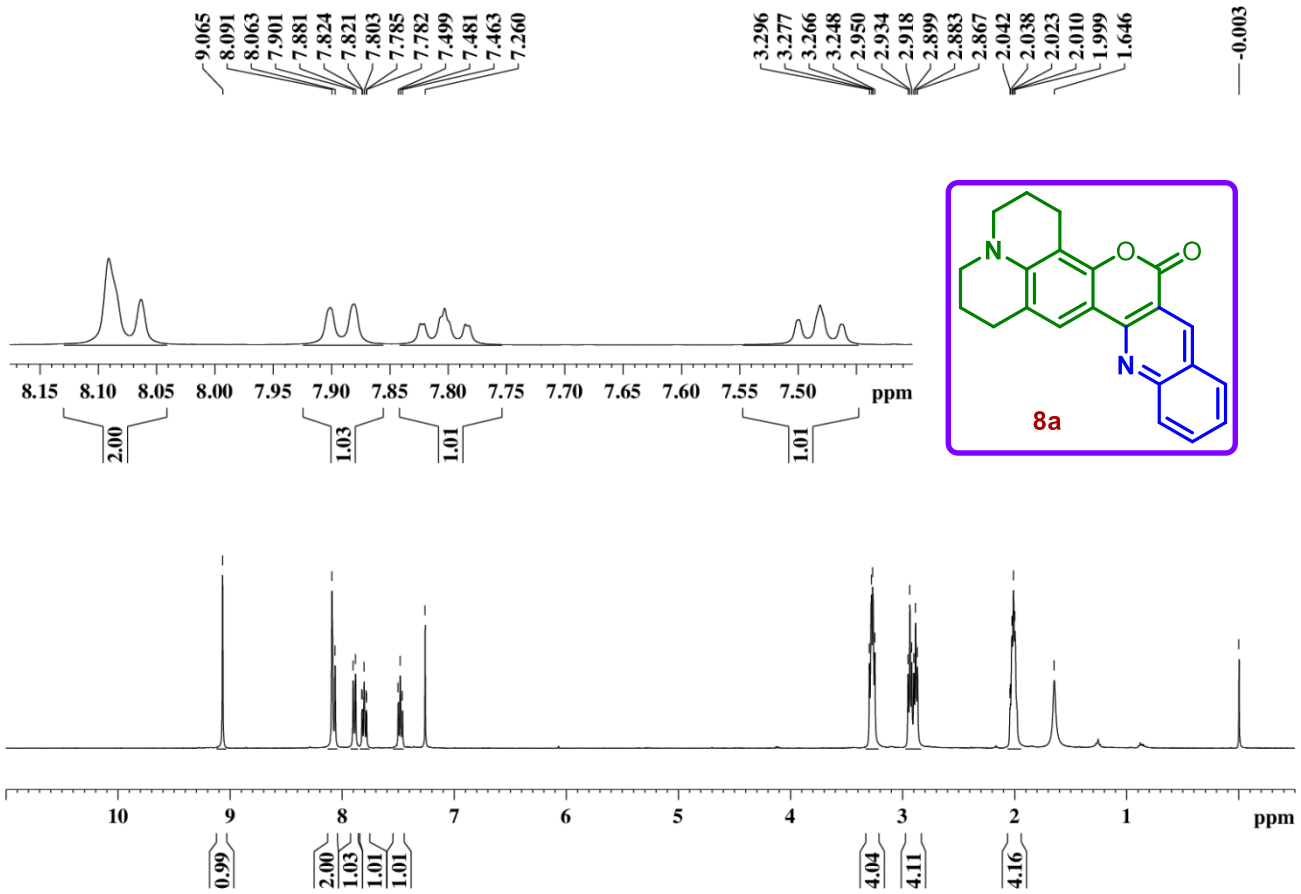
^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$) spectra of compound **7**



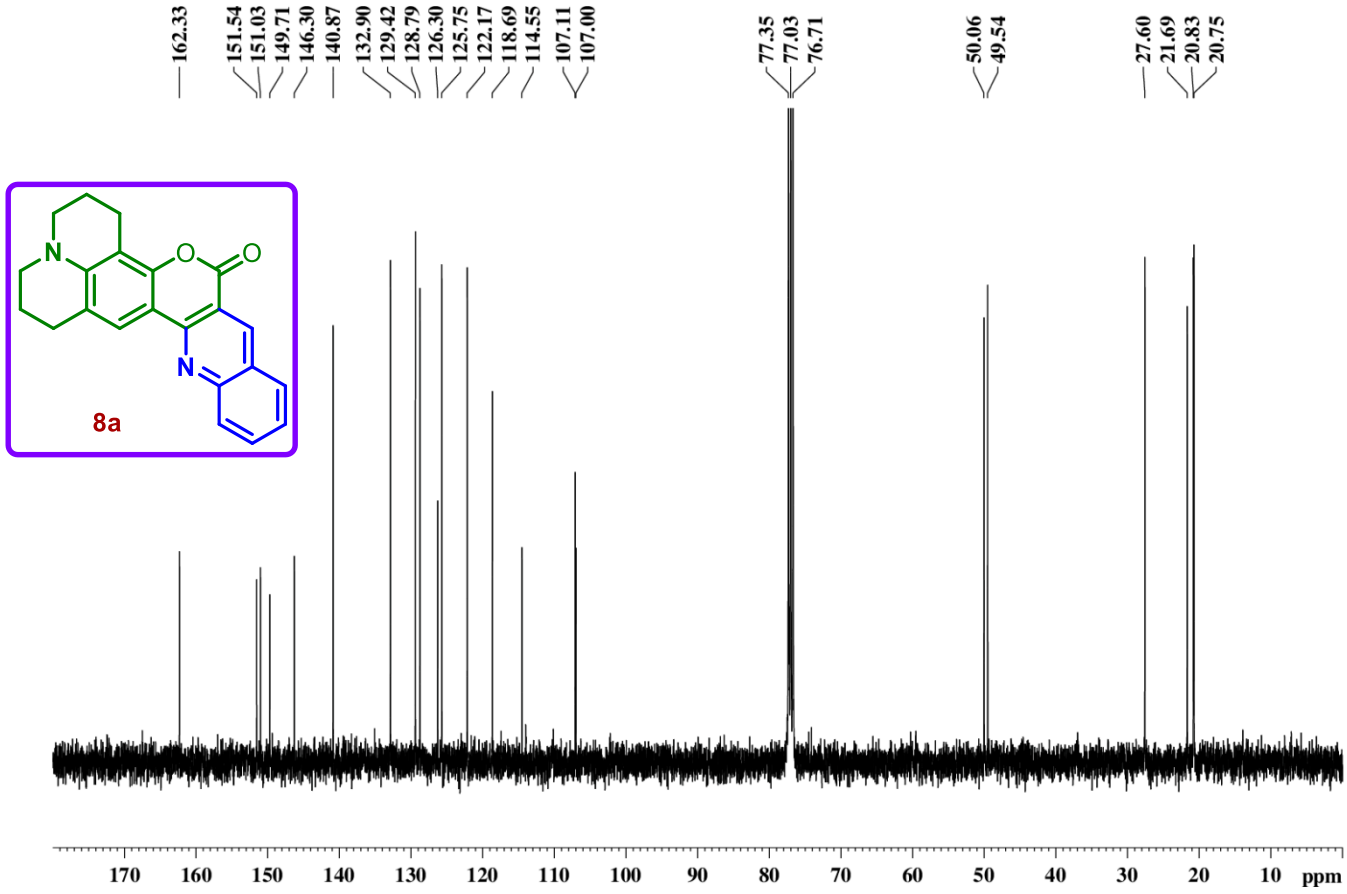
DEPT-135 NMR (100.6 MHz, $CDCl_3$) spectra of compound **7**



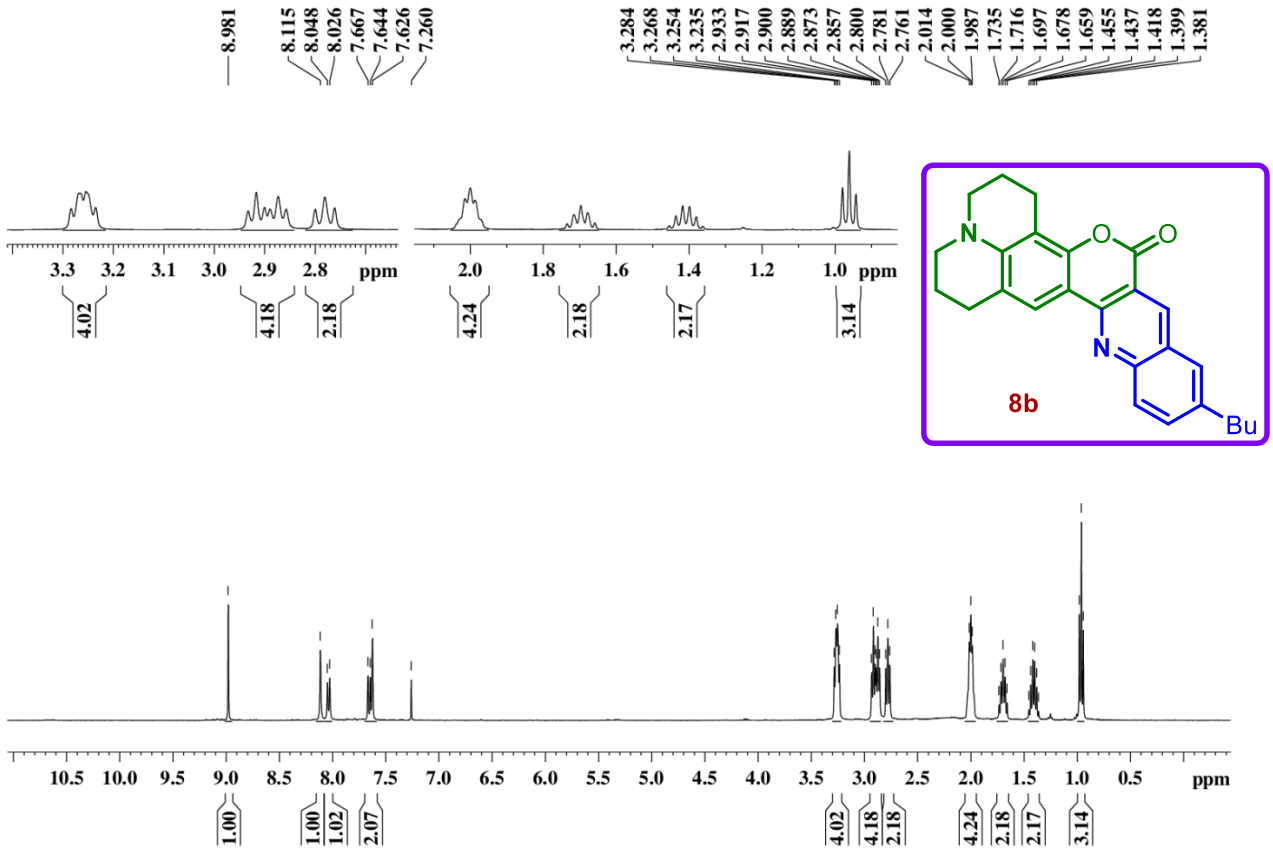
FT-IR spectra of compound **7**



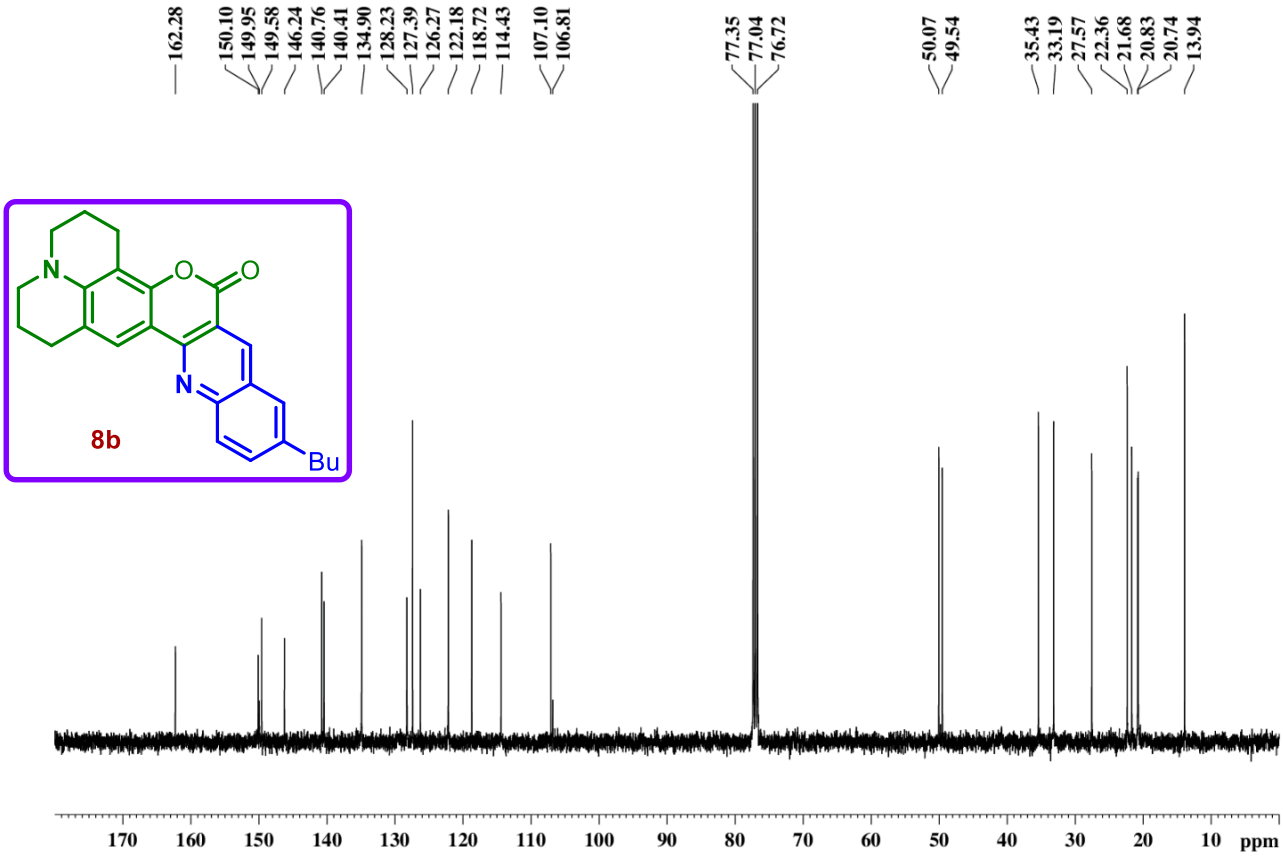
^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **8a**



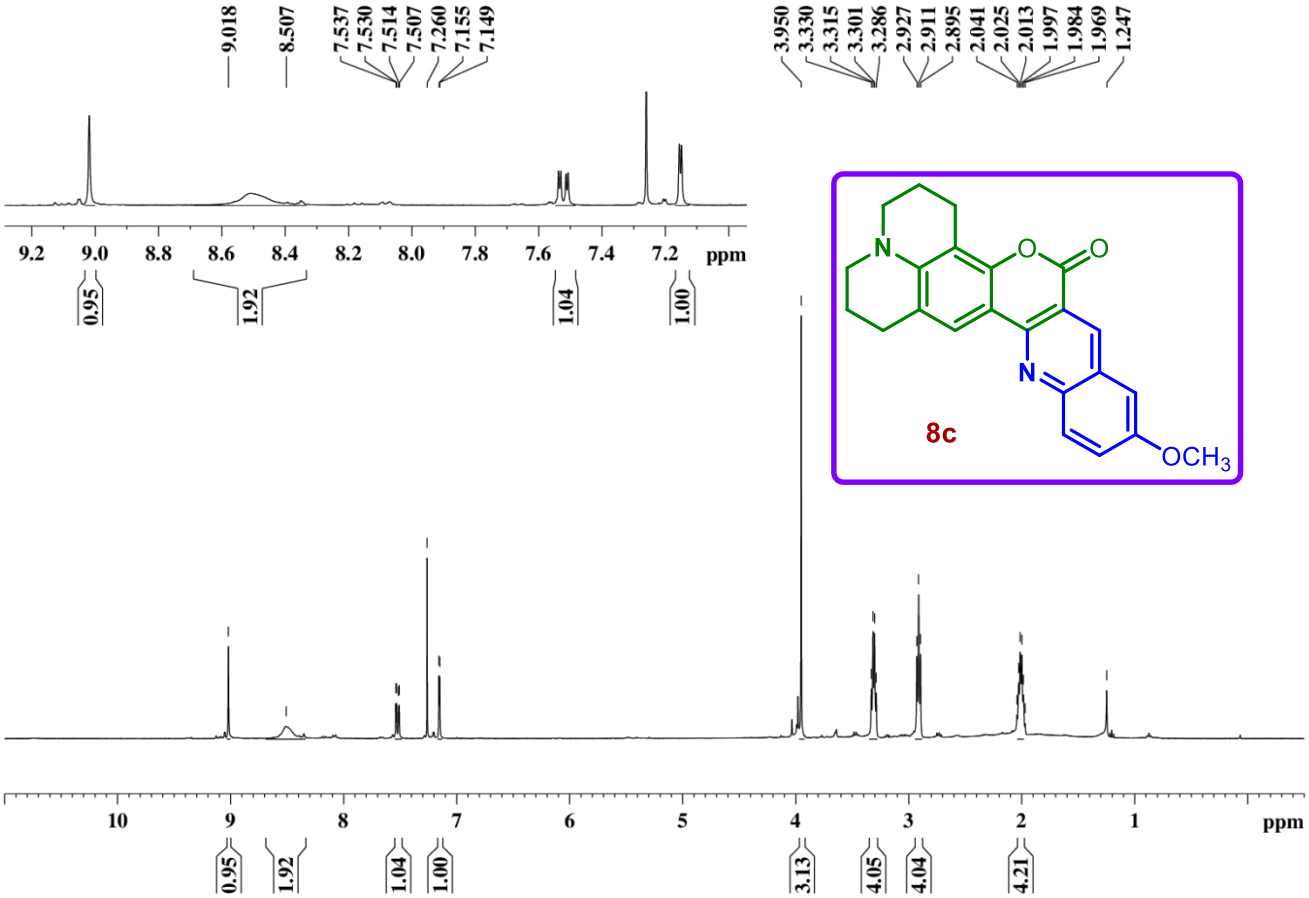
^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$) spectra of compound **8a**



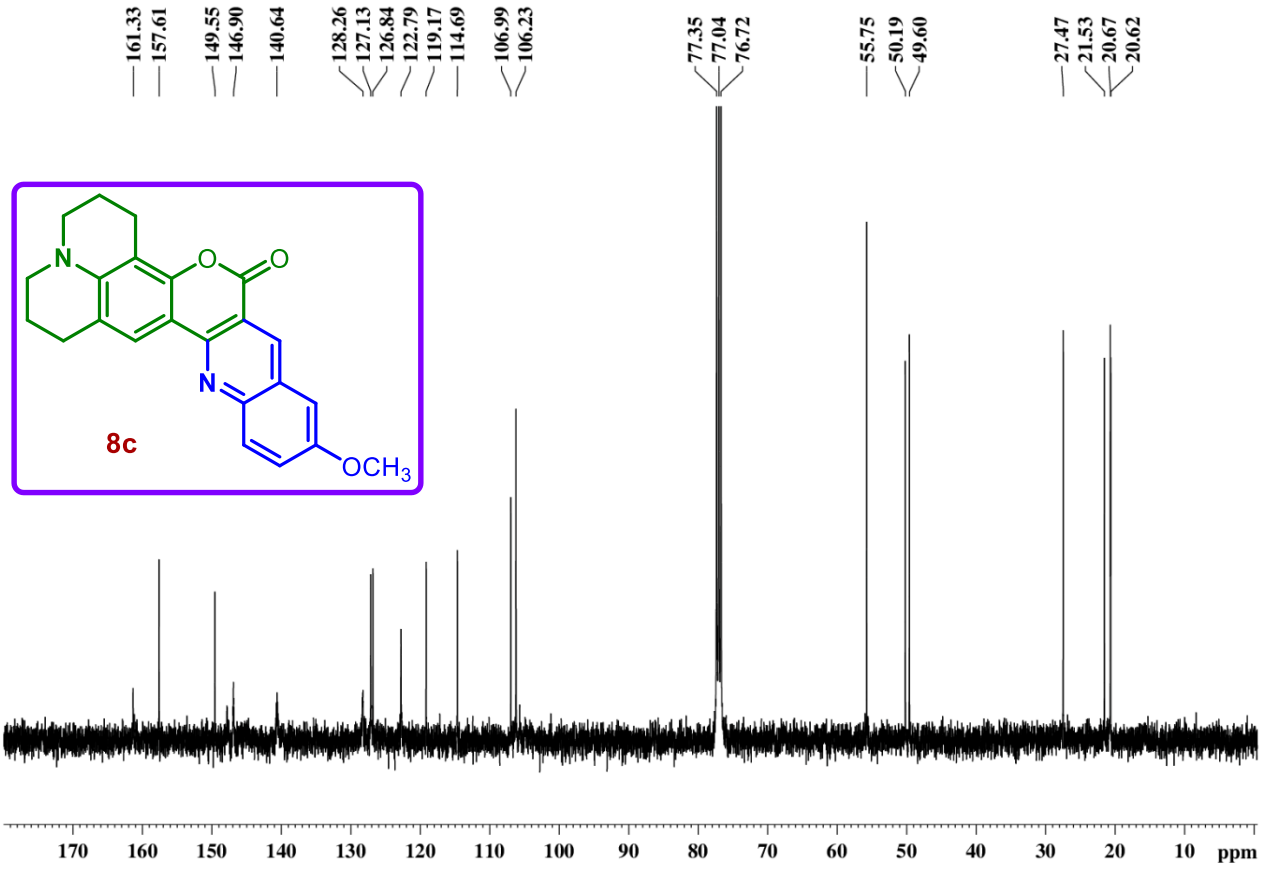
^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **8b**



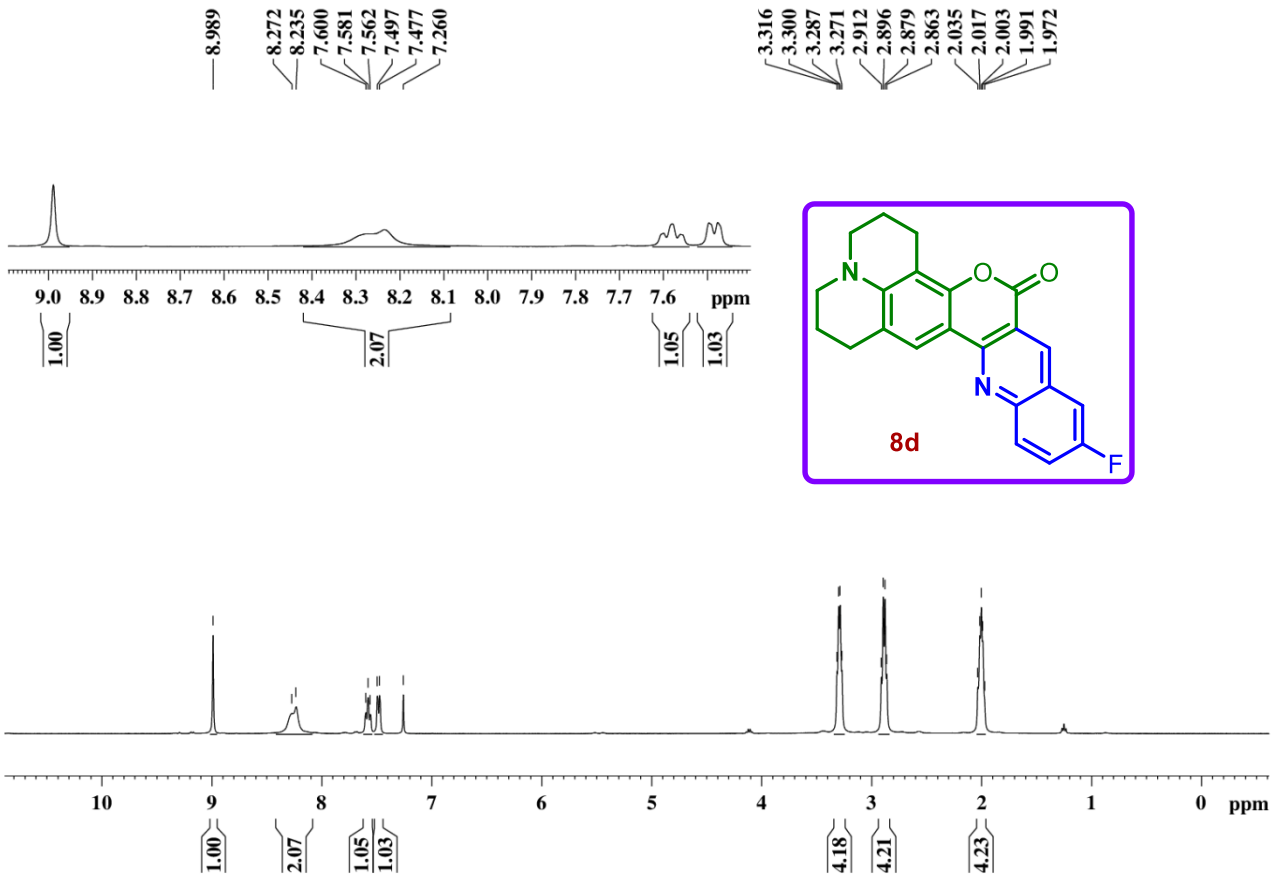
^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$) spectra of compound **8b**



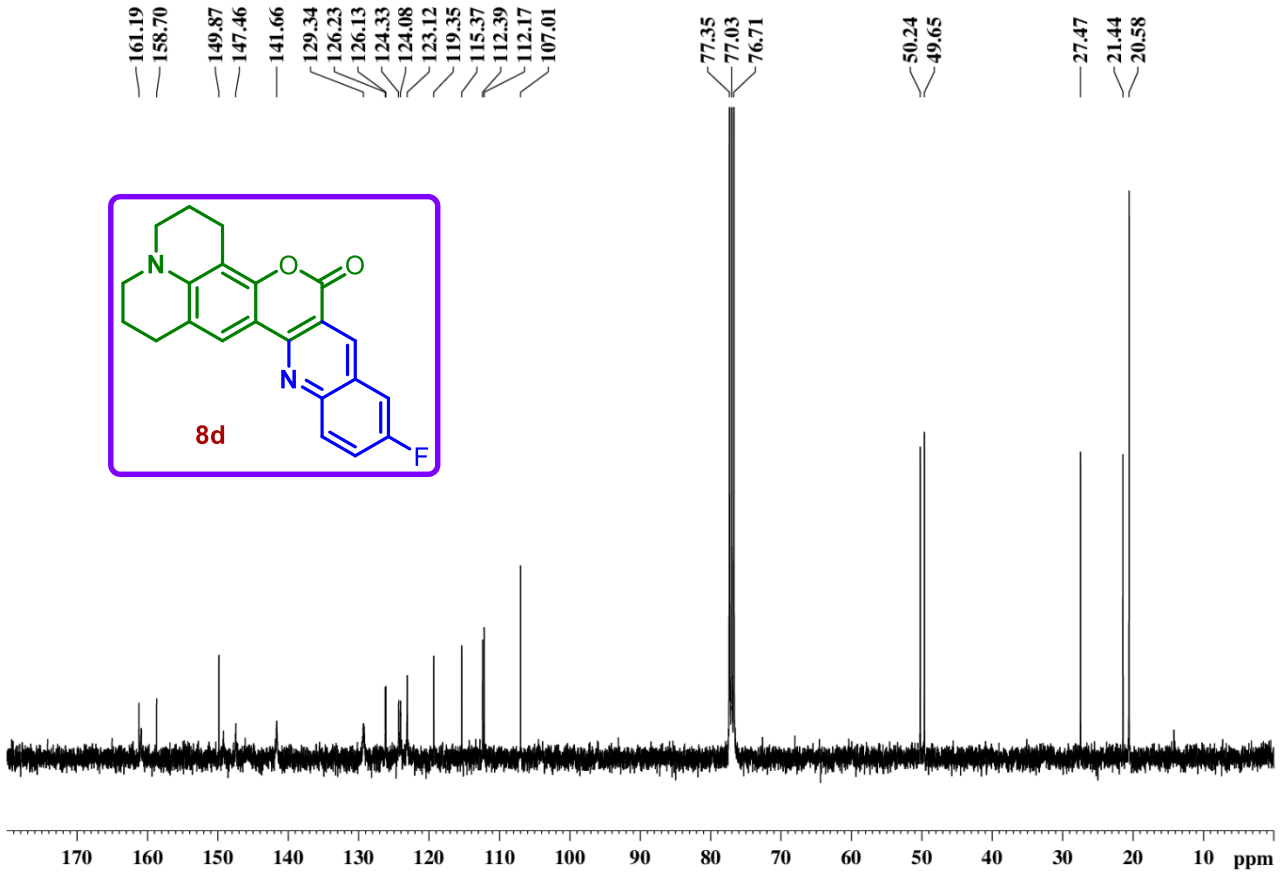
^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **8c**



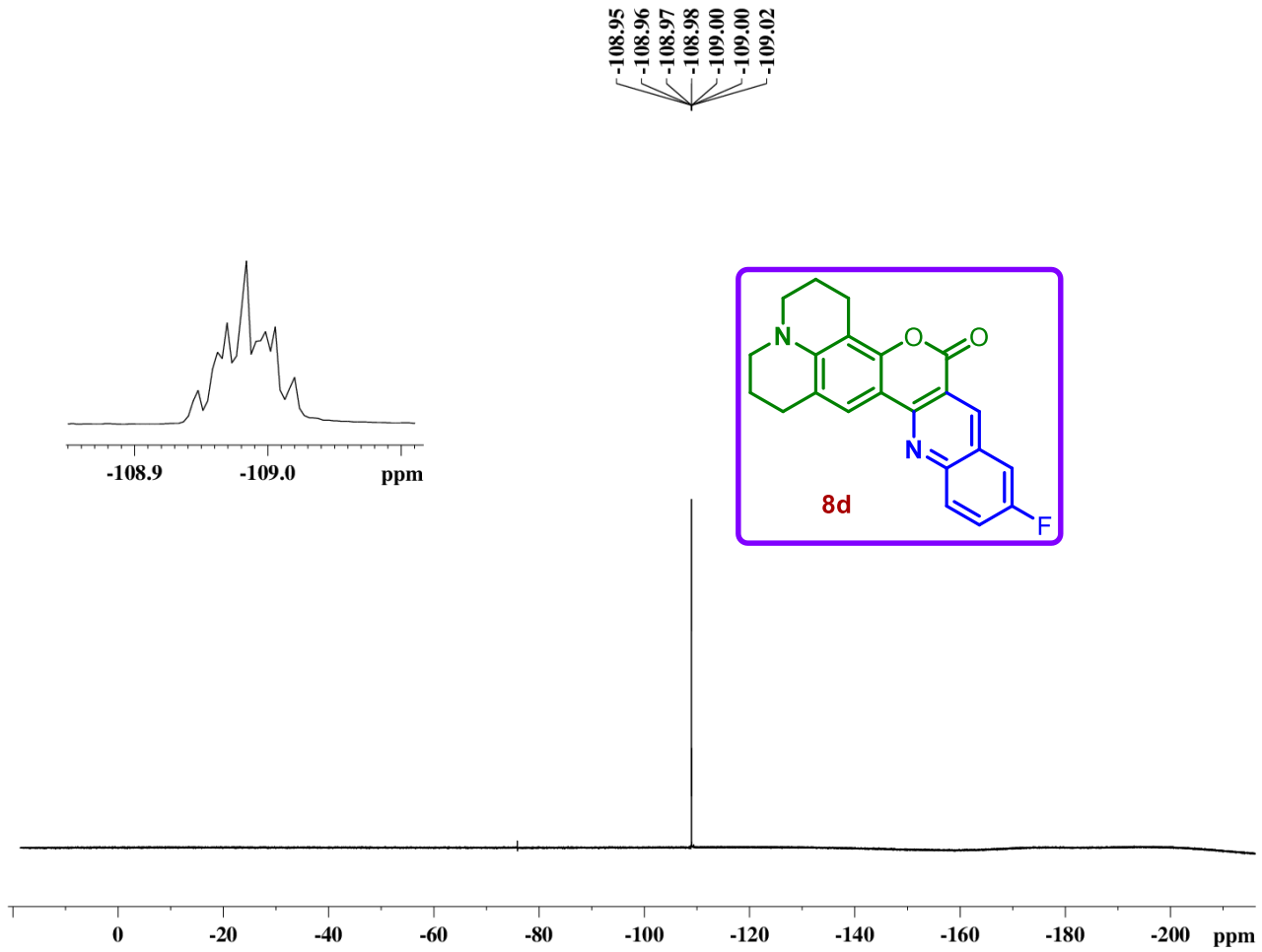
^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$) spectra of compound **8c**



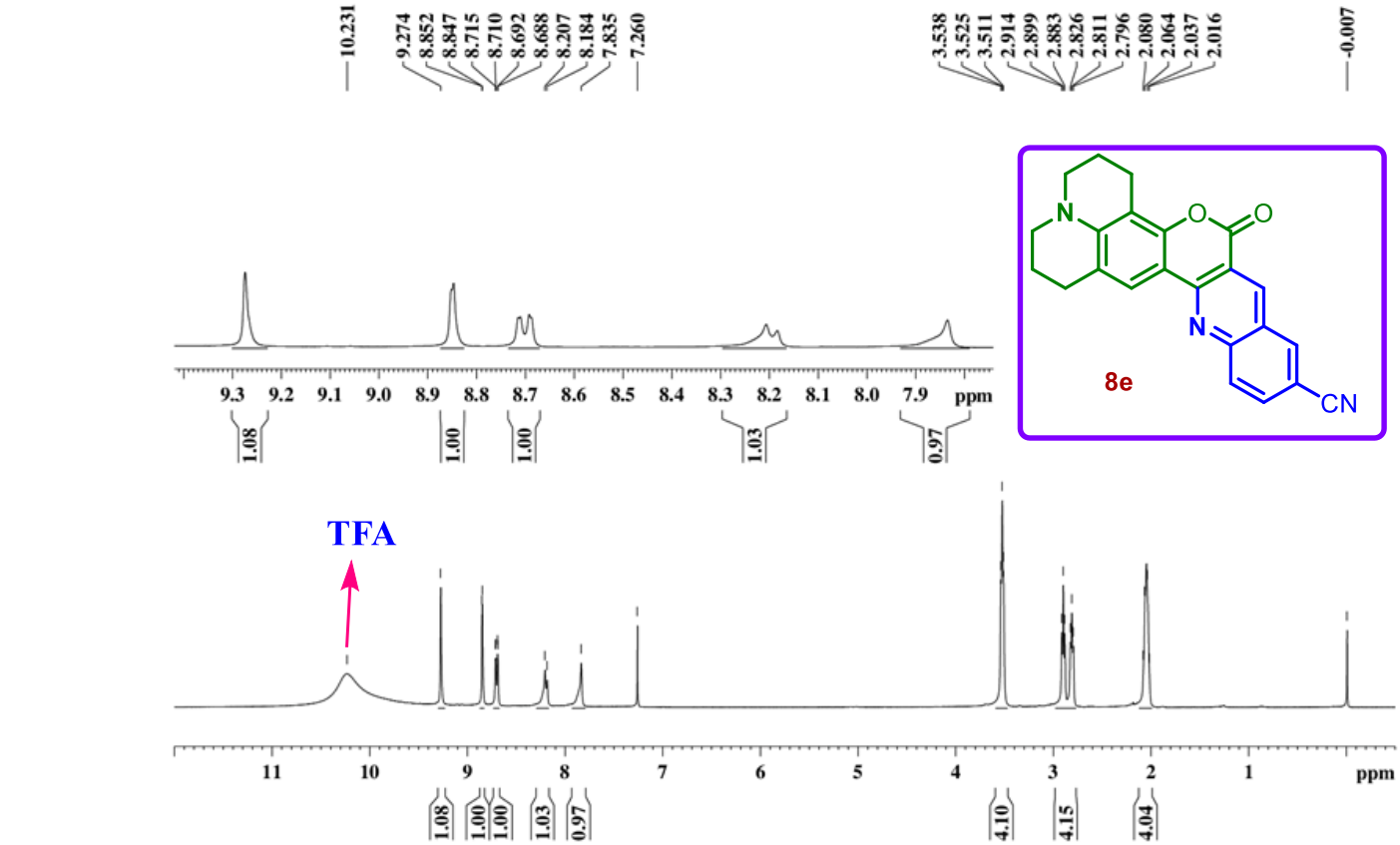
^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **8d**



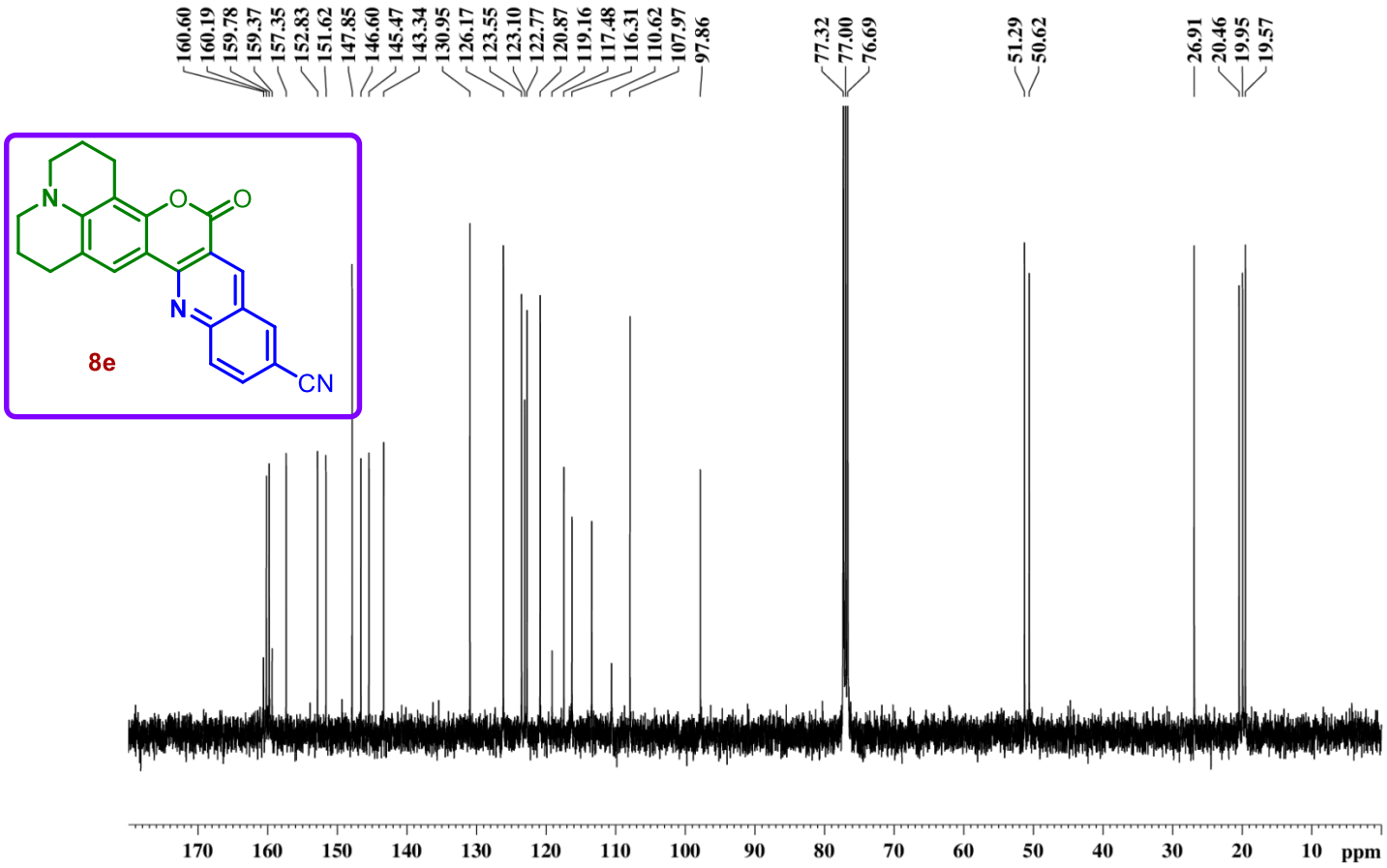
^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$) spectra of compound **8d**



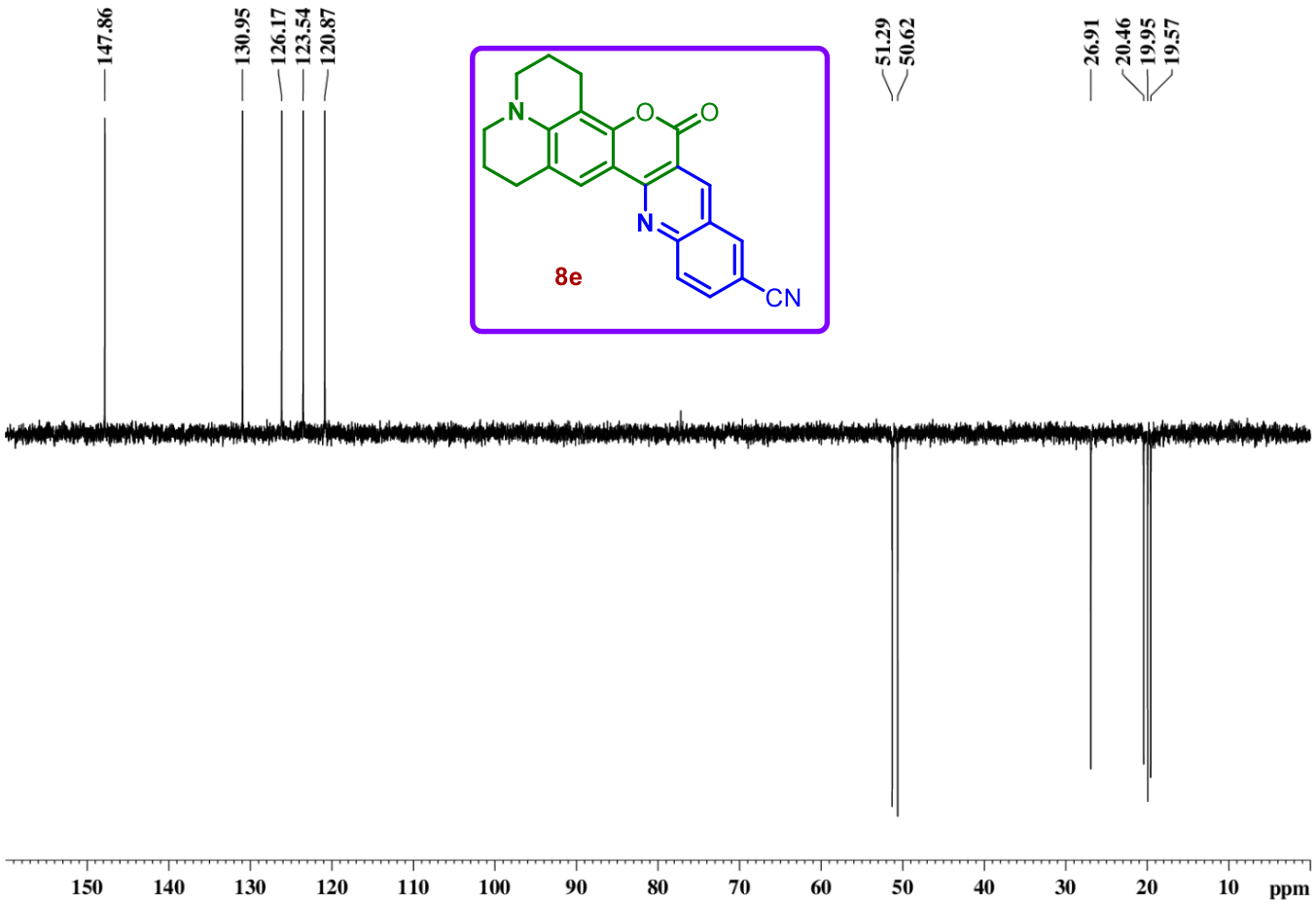
^{19}F NMR (400 MHz, $CDCl_3$) spectra of compound **8d**



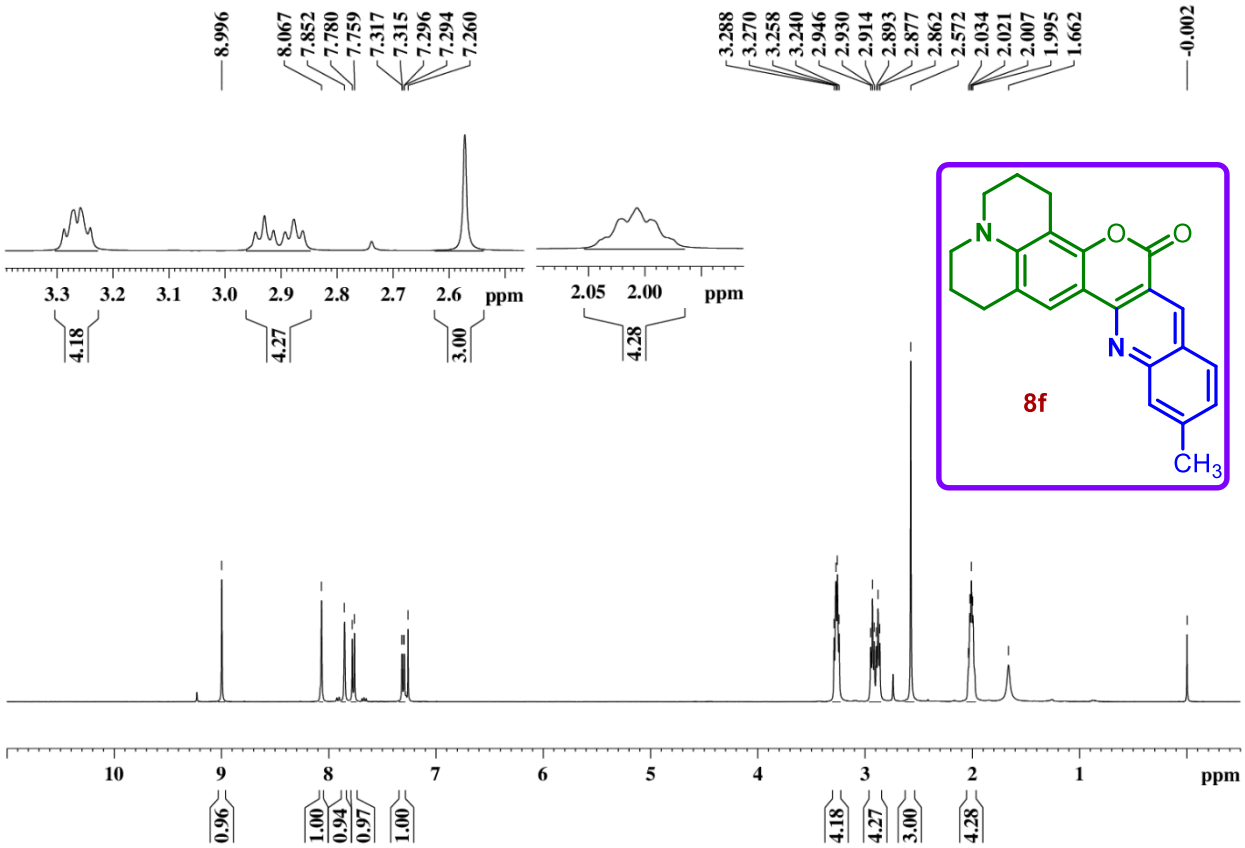
^{1}H NMR (400 MHz, $CDCl_3$+TFA) spectra of compound **8e**



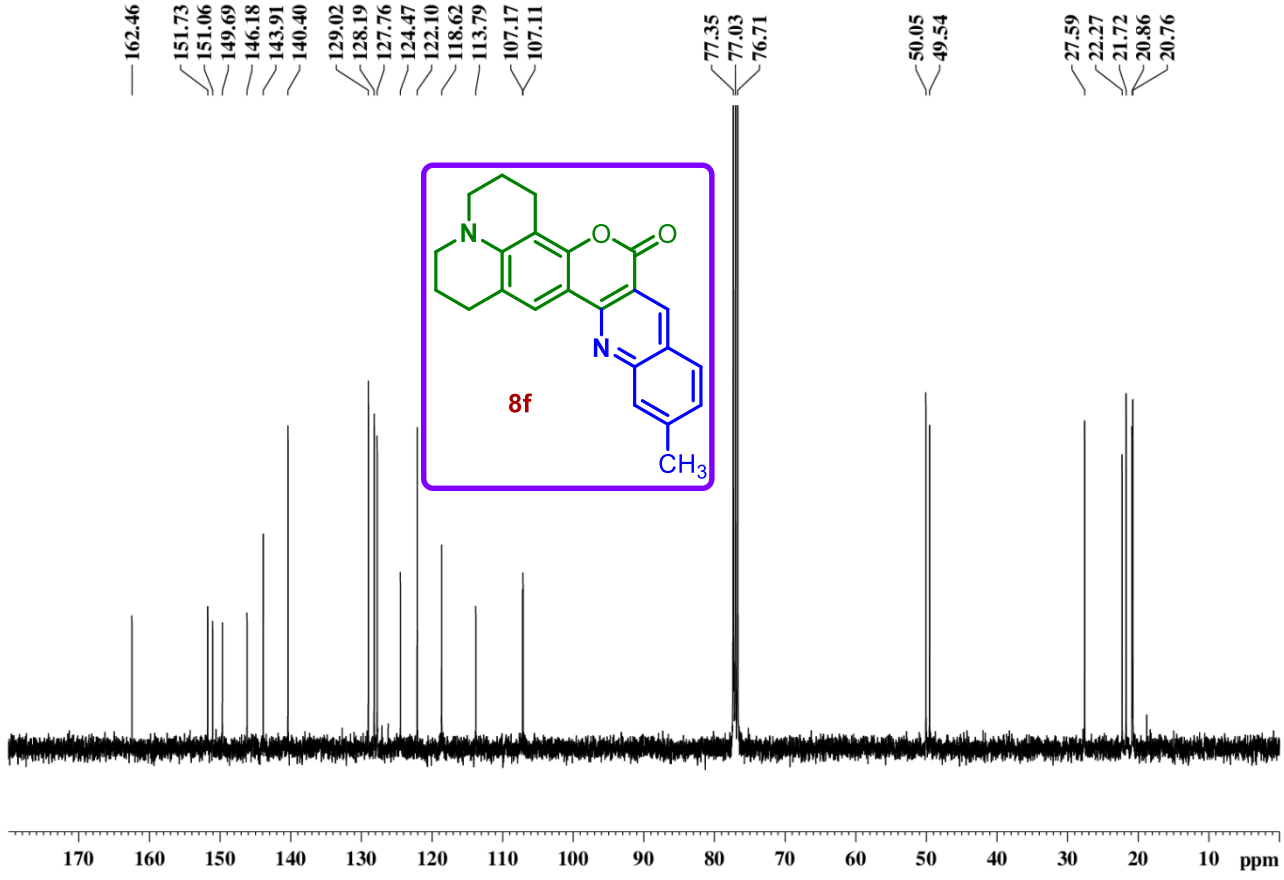
^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$+TFA) spectra of compound **8e**



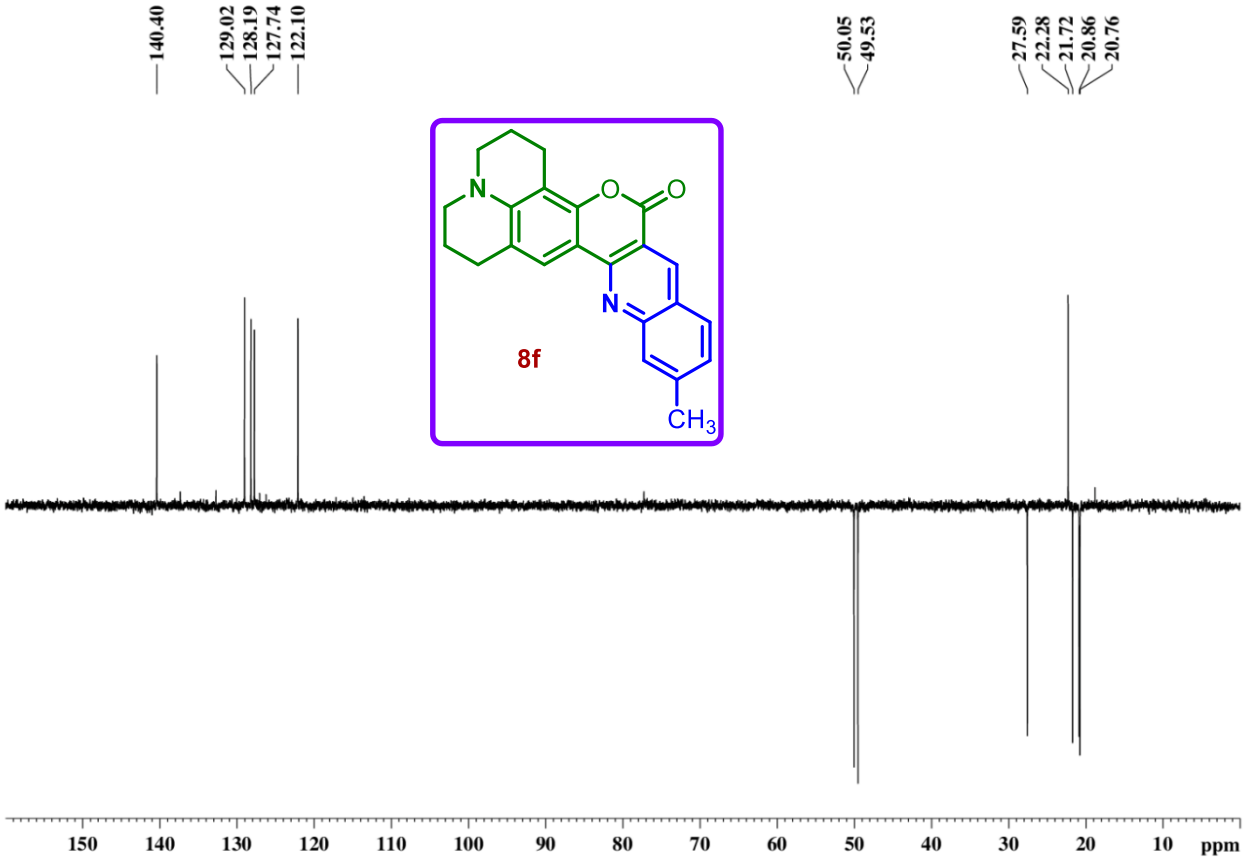
DEPT-135 NMR (100.6 MHz, $CDCl_3$) spectra of compound **8e**



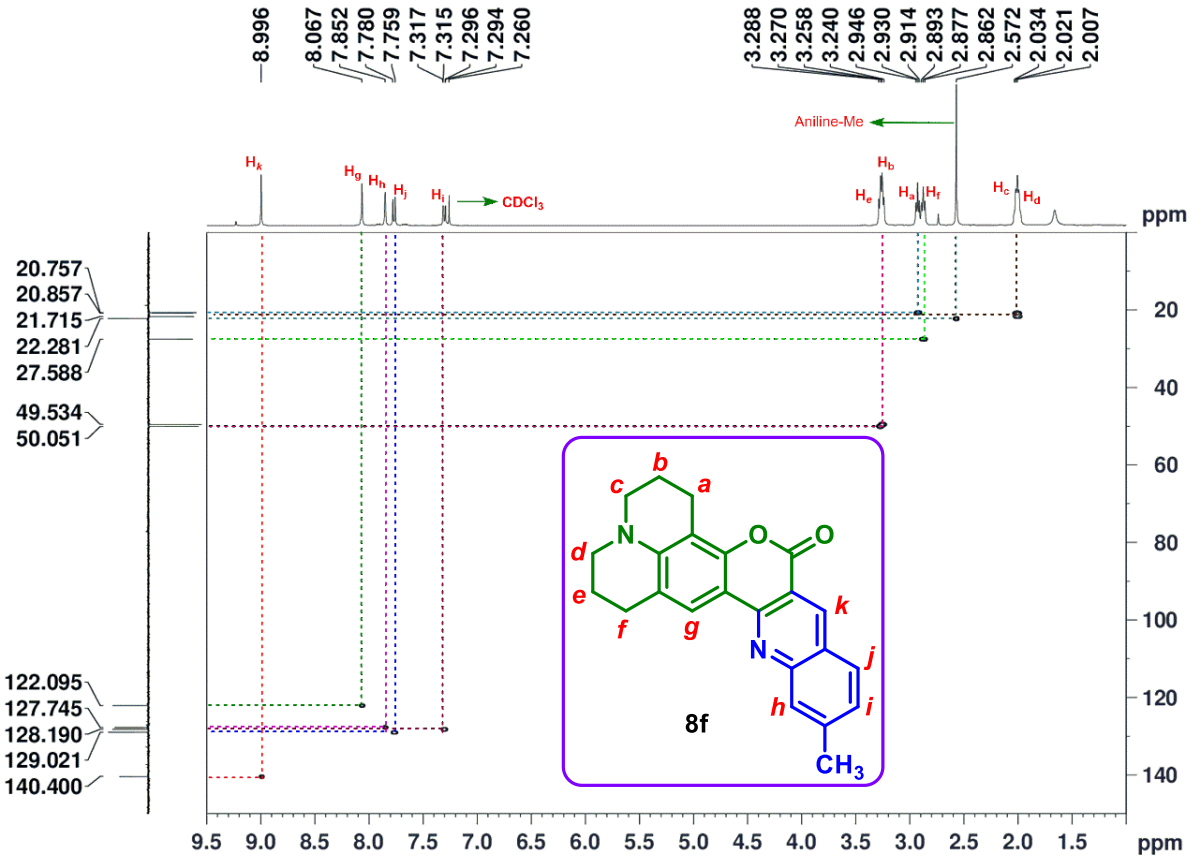
^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **8f**



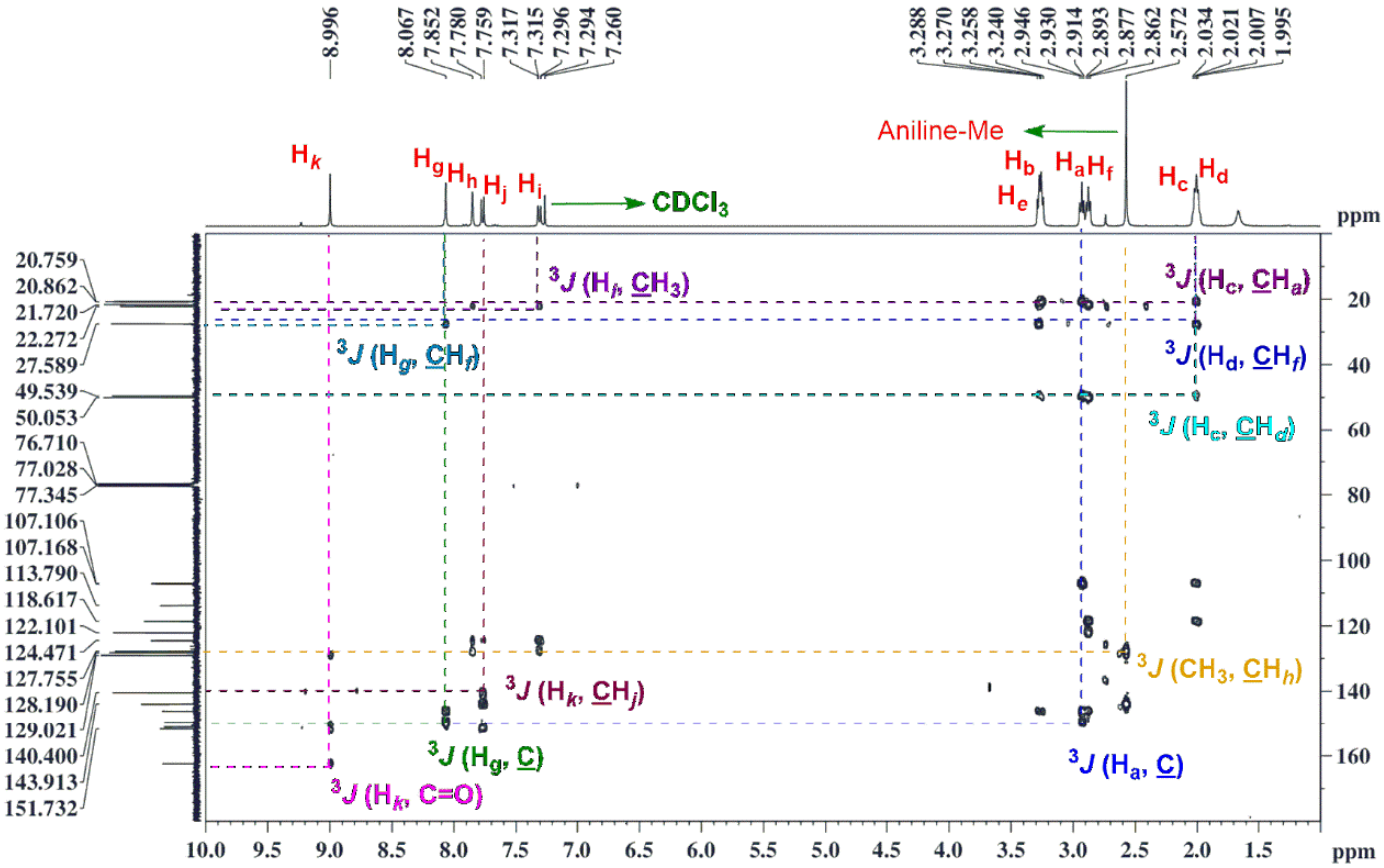
^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$) spectra of compound **8f**



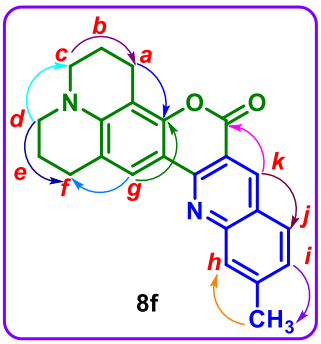
DEPT-135 NMR (100.6 MHz, $CDCl_3$) spectra of compound **8f**

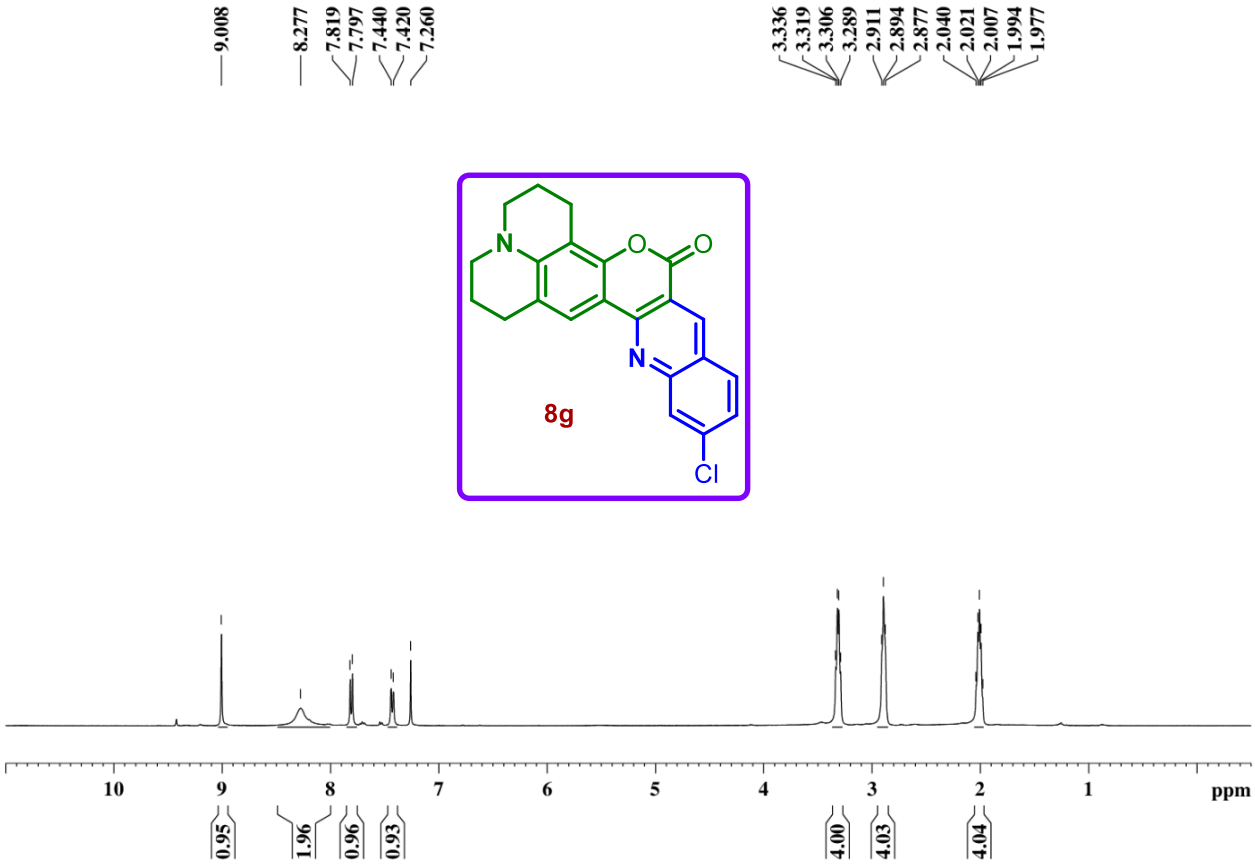


^{1}H-^{13}C (DEPT-135) HSQC NMR spectra of compound **8f**

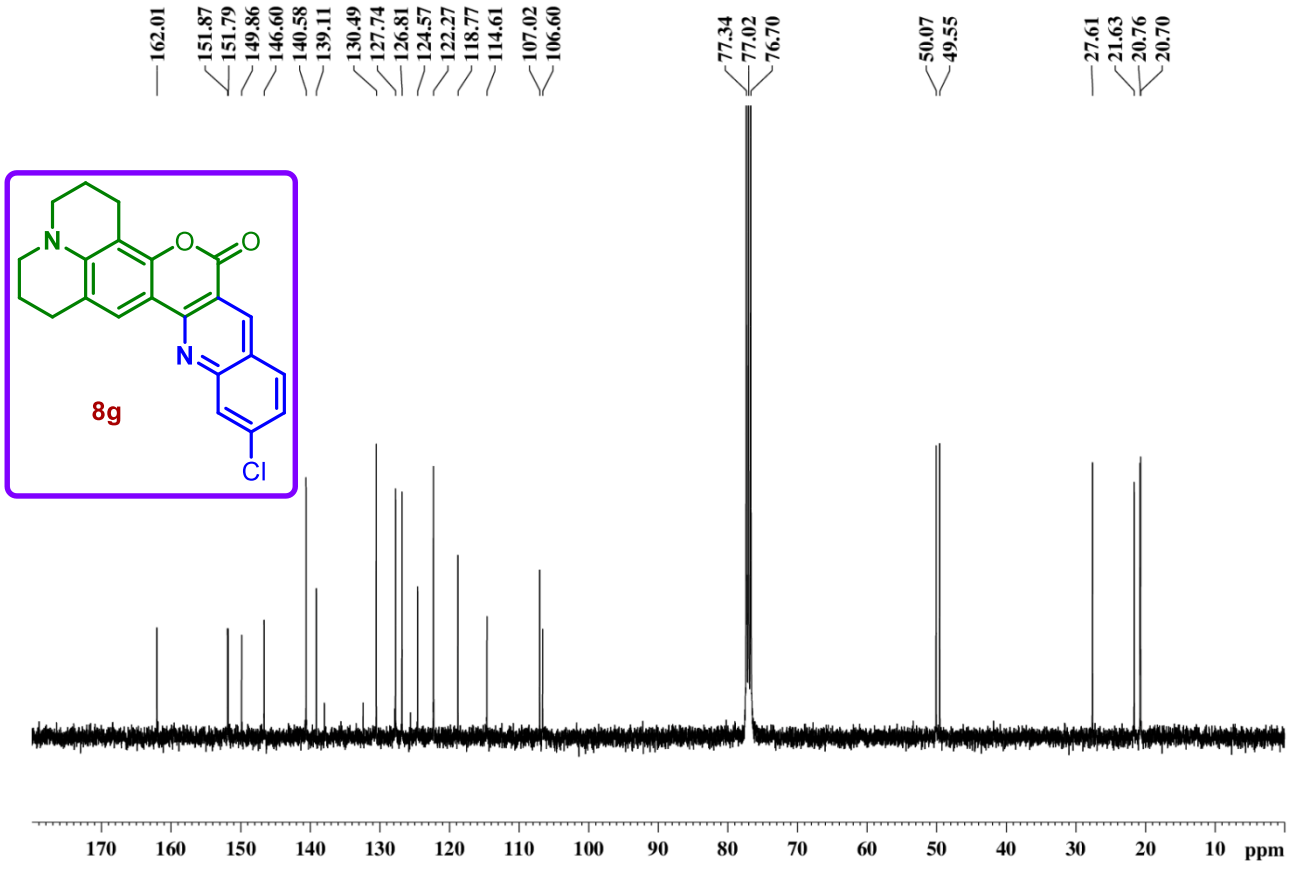


^{1}H-^{13}C HMBC NMR spectra of compound **8f**

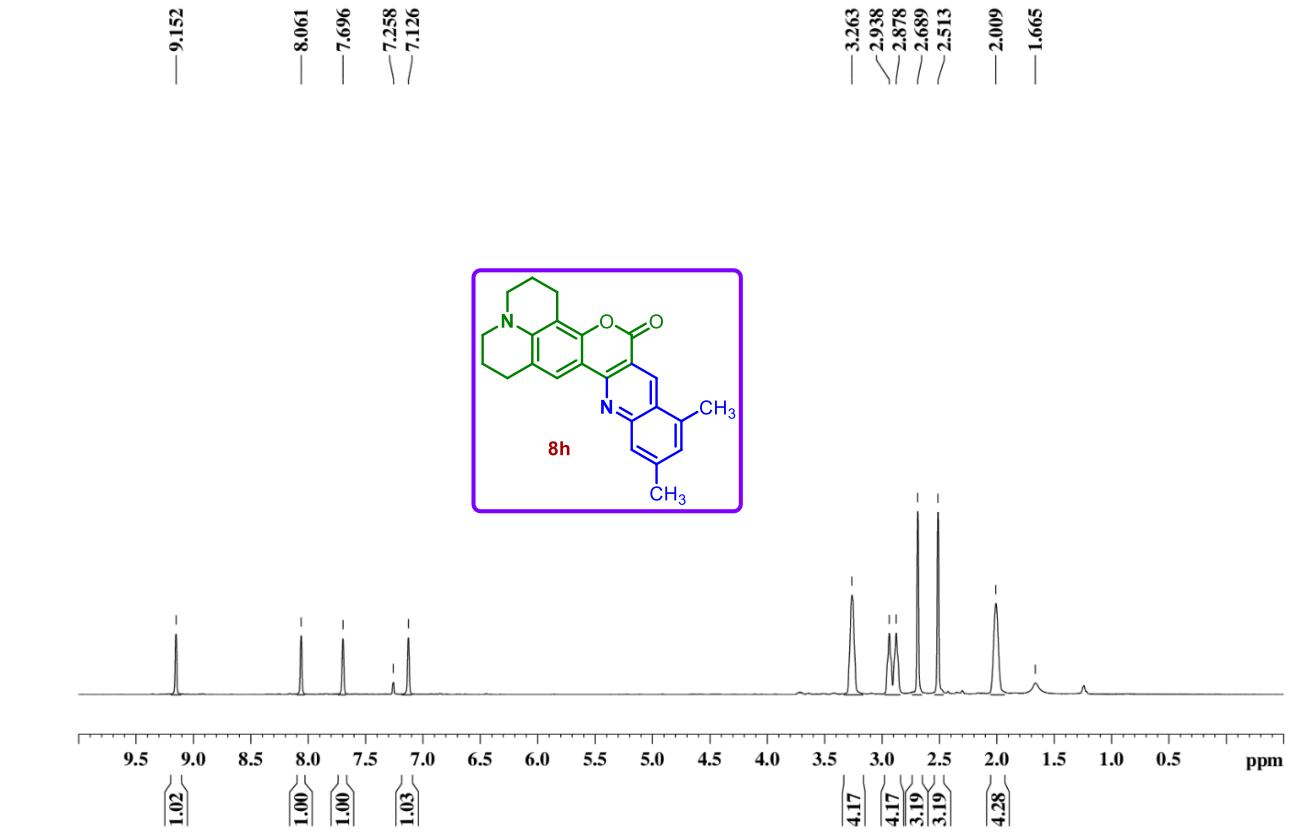




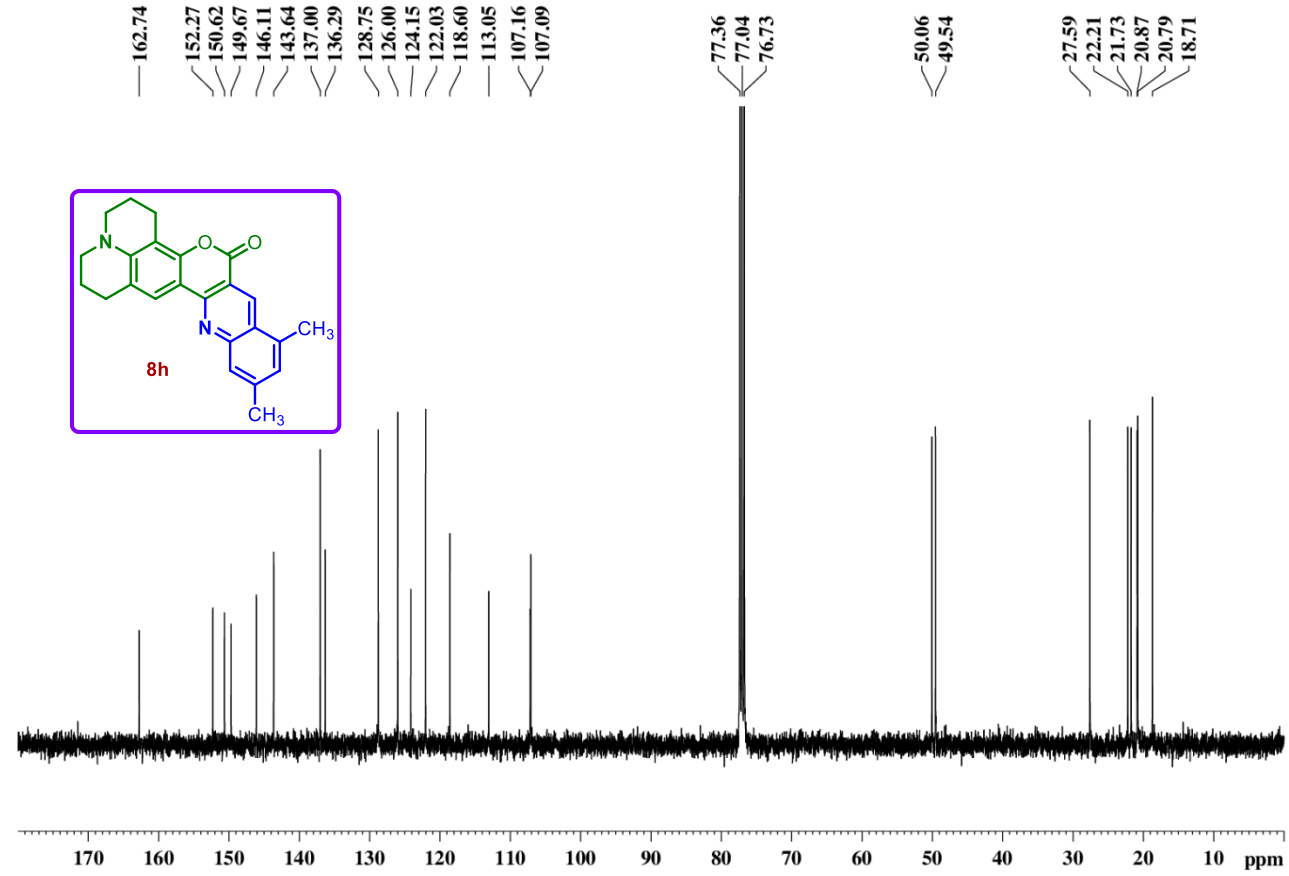
^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **8g**



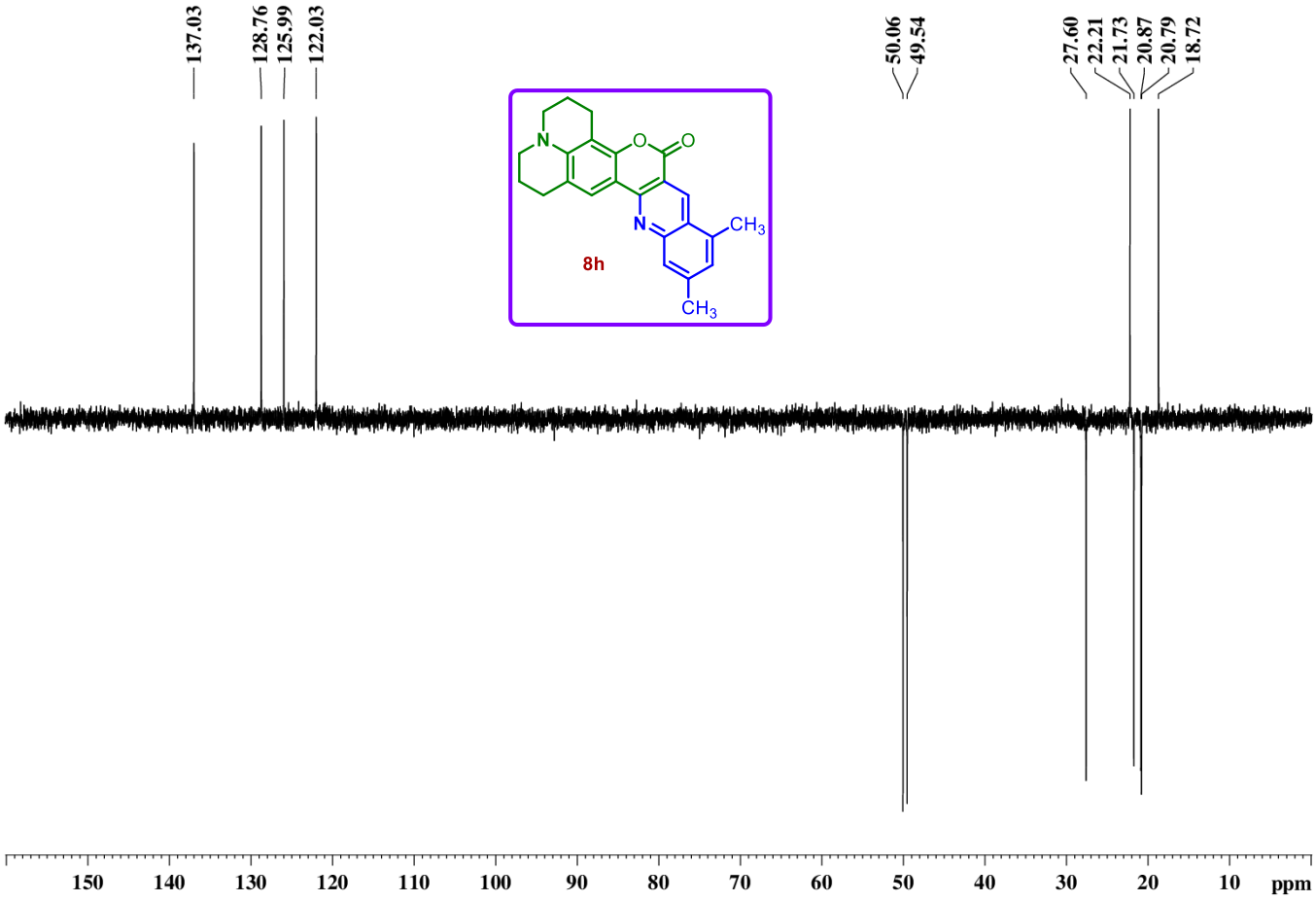
^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$) spectra of compound **8g**



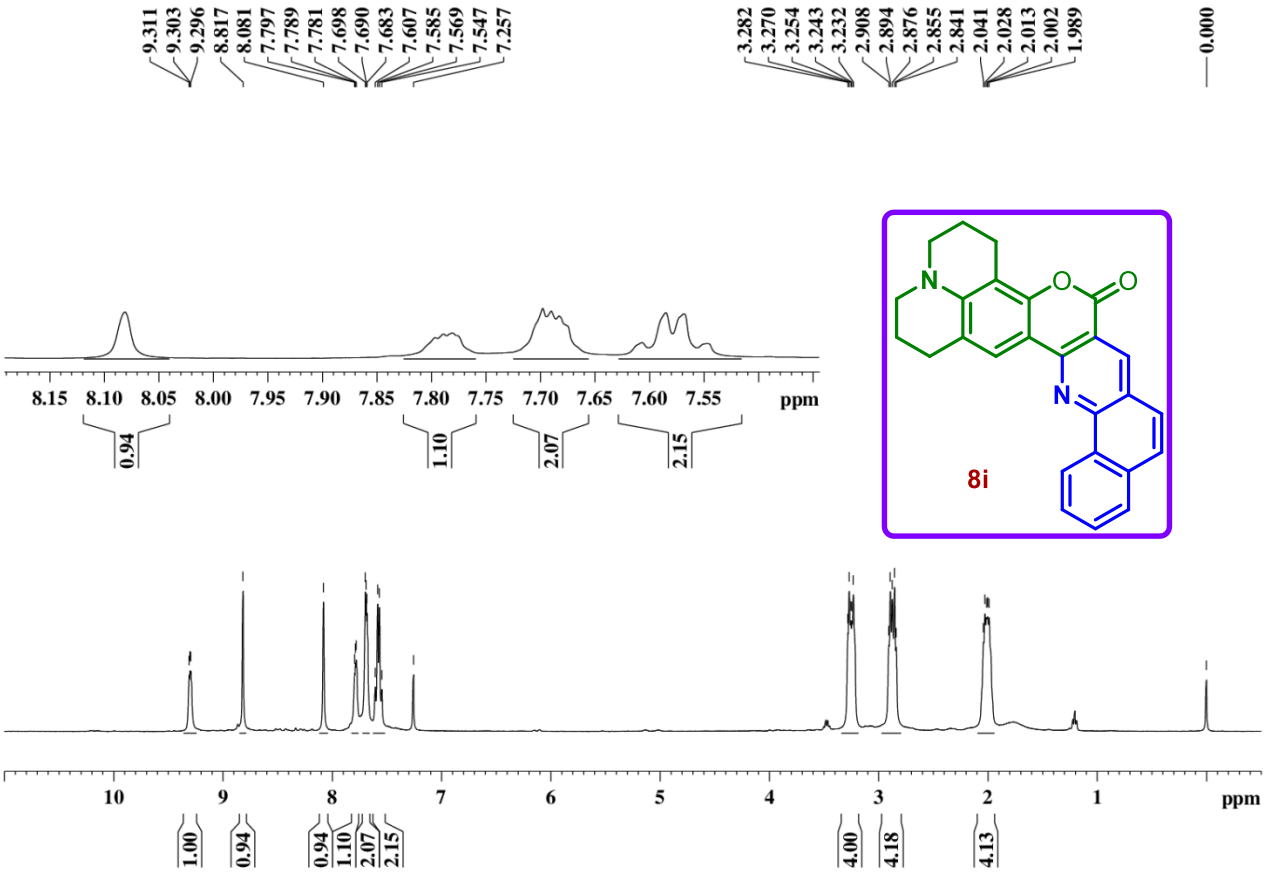
^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **8h**



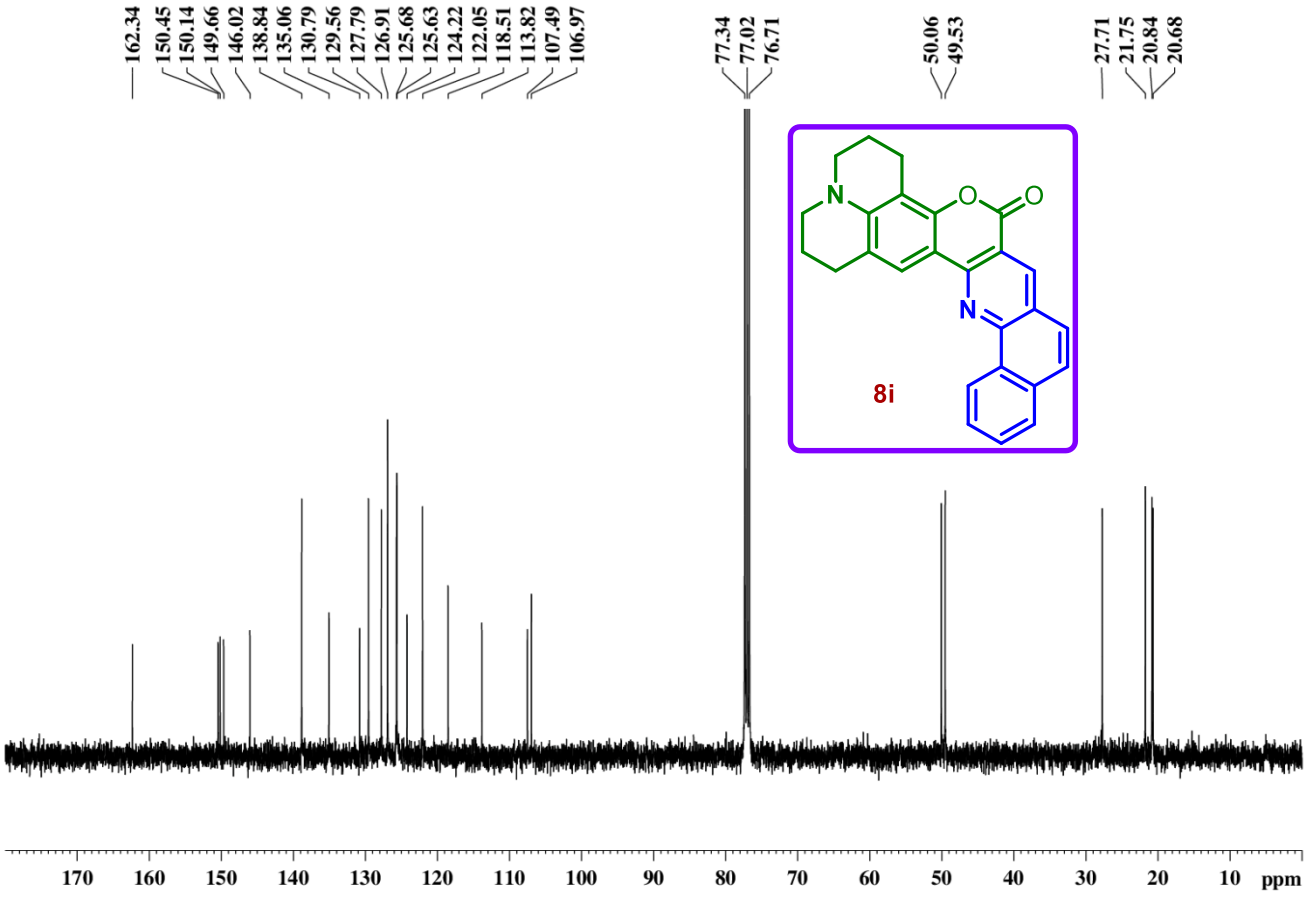
^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$) spectra of compound **8h**



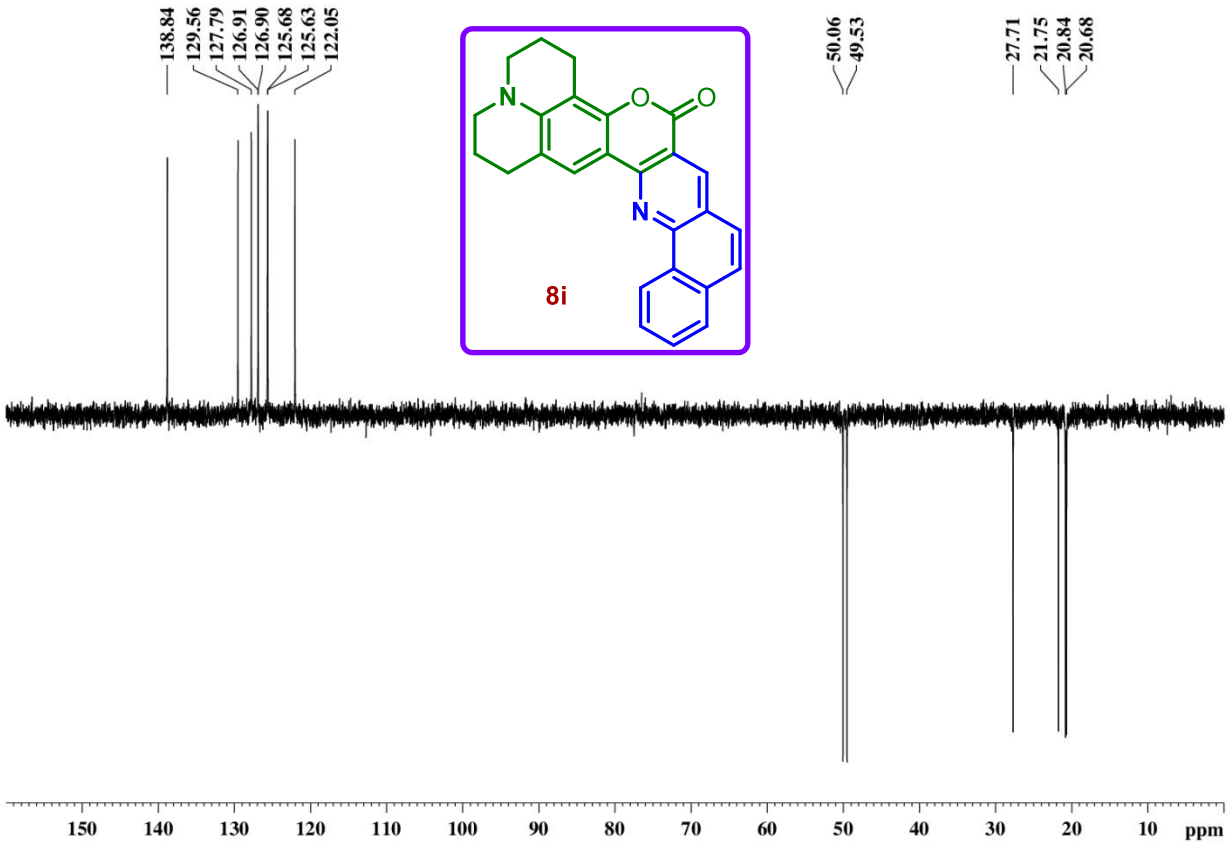
DEPT-135 NMR (100.6 MHz, $CDCl_3$) spectra of compound **8h**



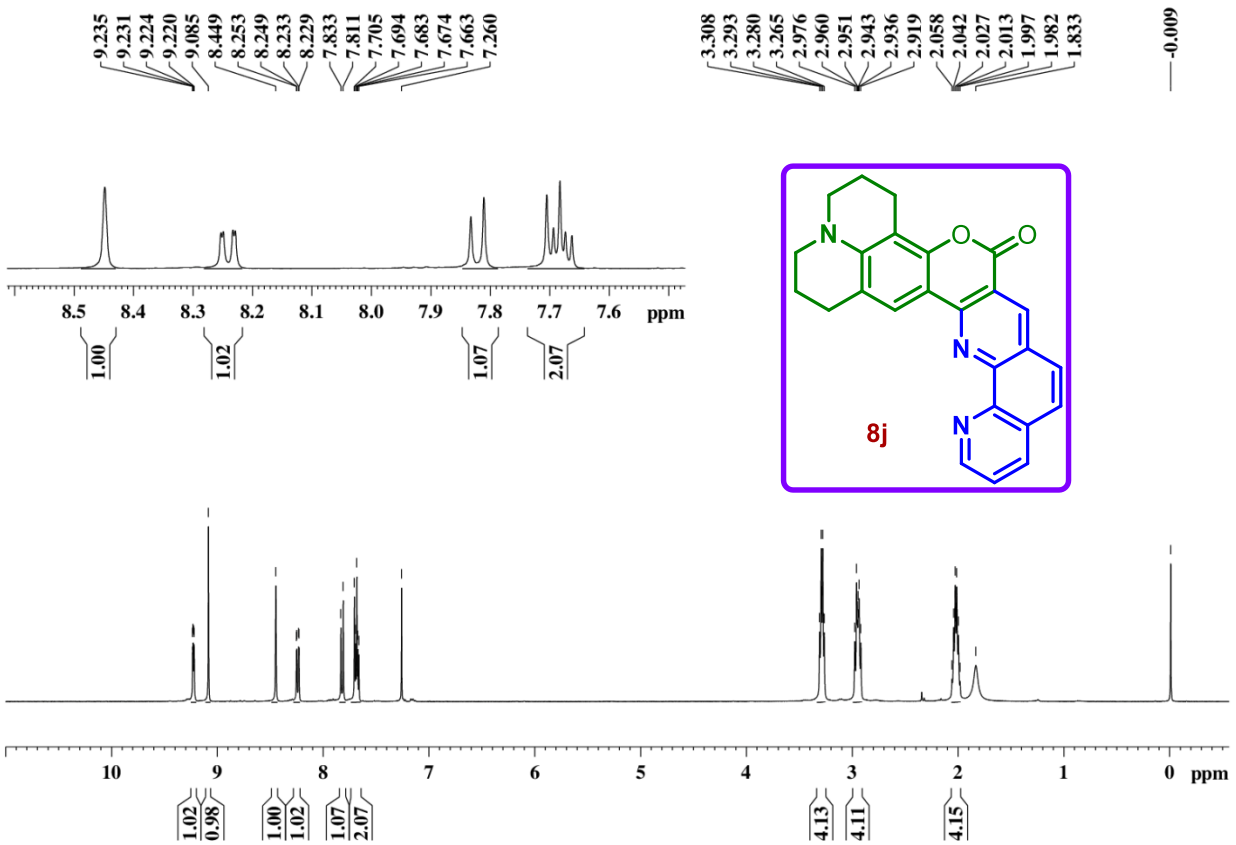
^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **8i**



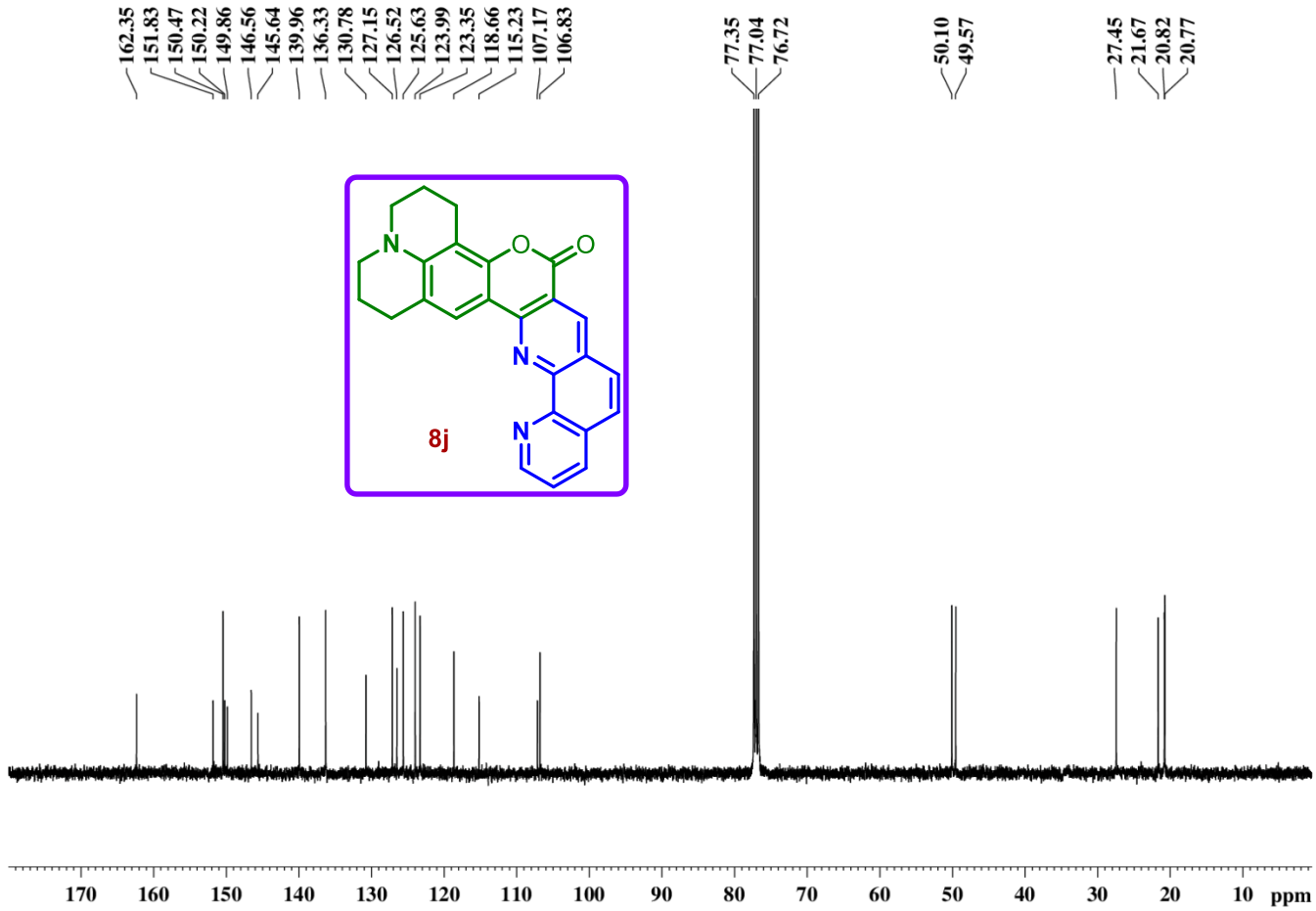
^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$) spectra of compound **8i**



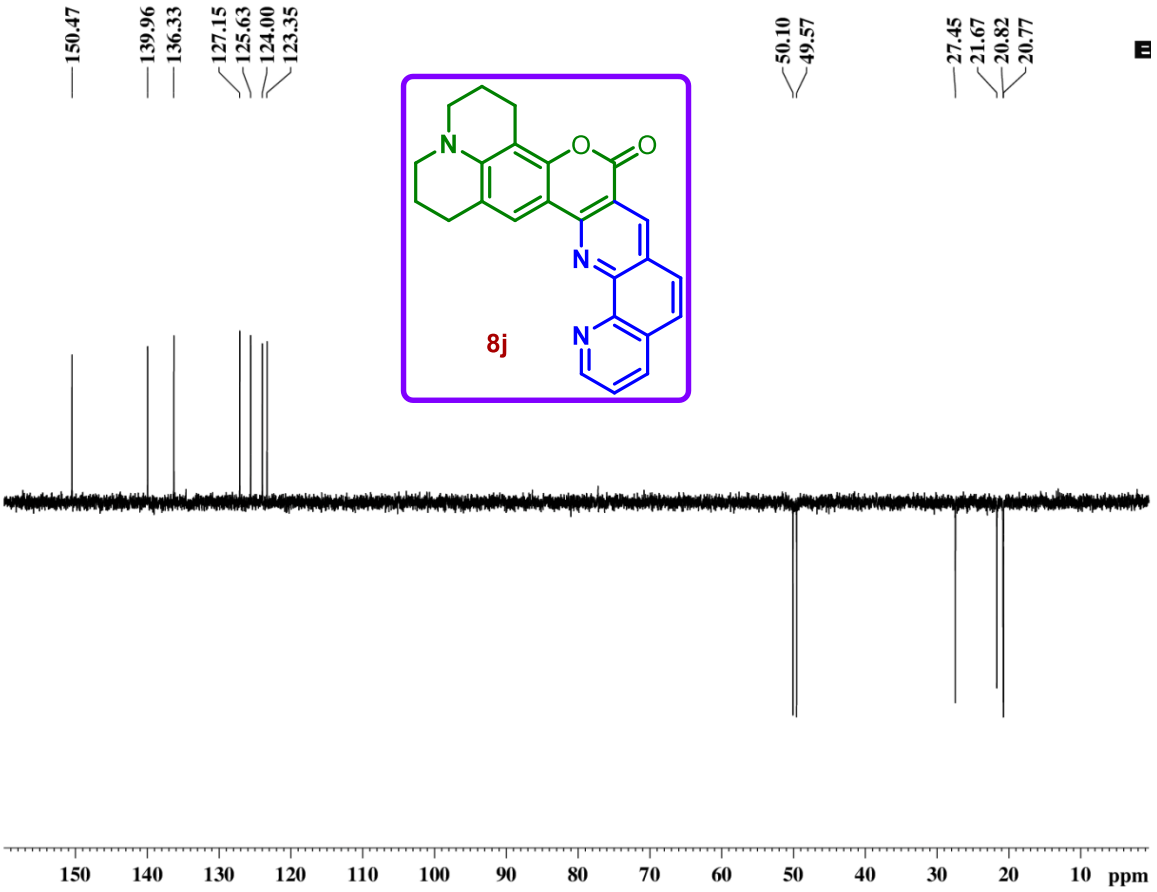
DEPT-135 NMR (100.6 MHz, $CDCl_3$) spectra of compound **8i**



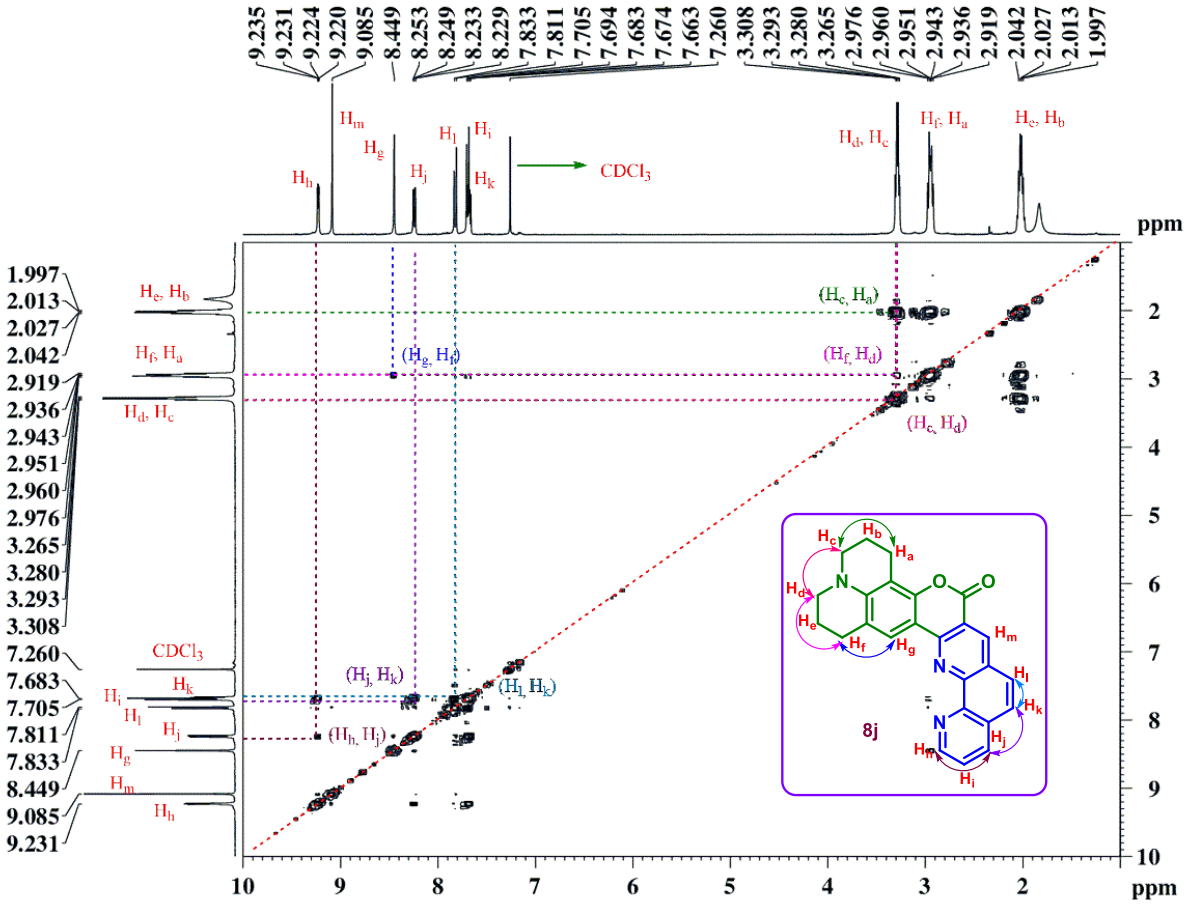
^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **8j**



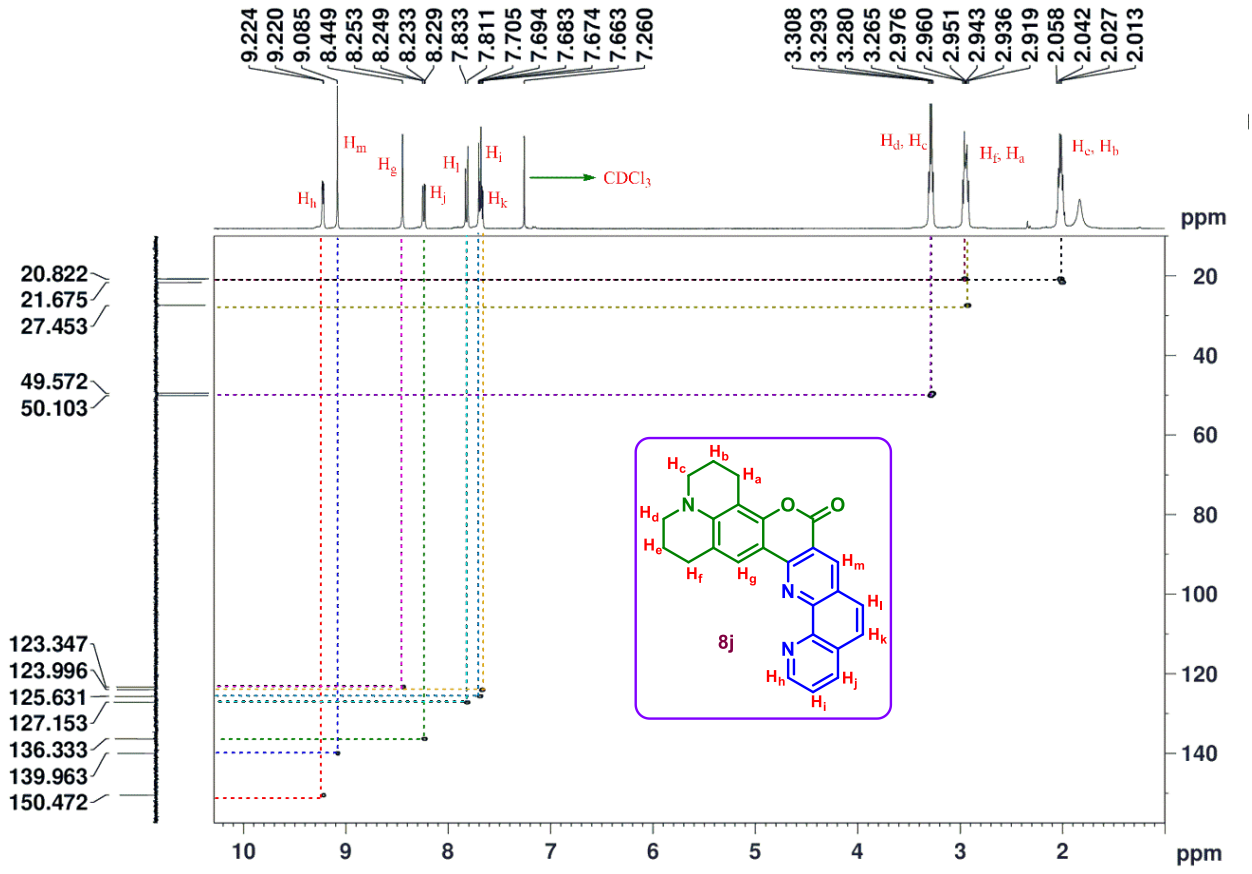
^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$) spectra of compound **8j**



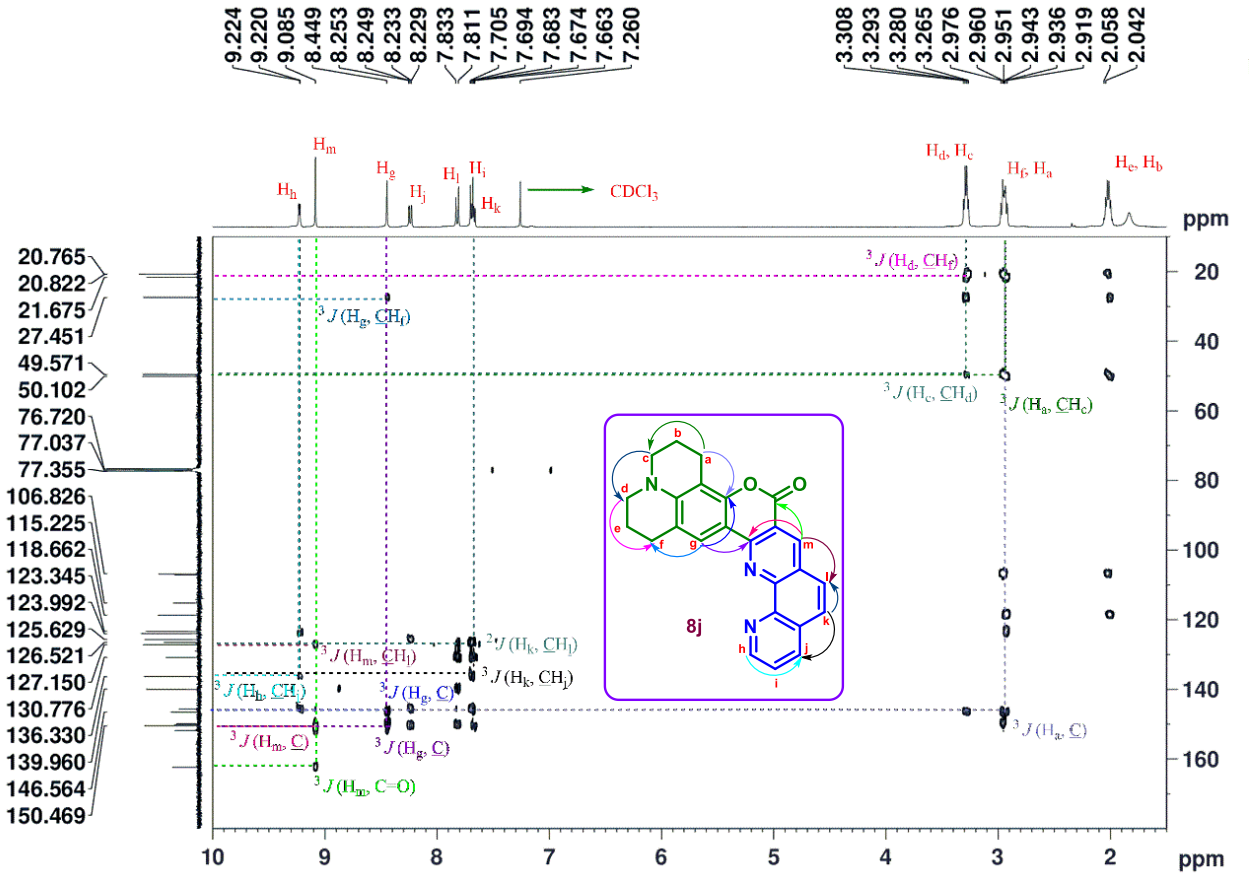
DEPT-135 NMR (100.6 MHz, $CDCl_3$) spectra of compound **8j**



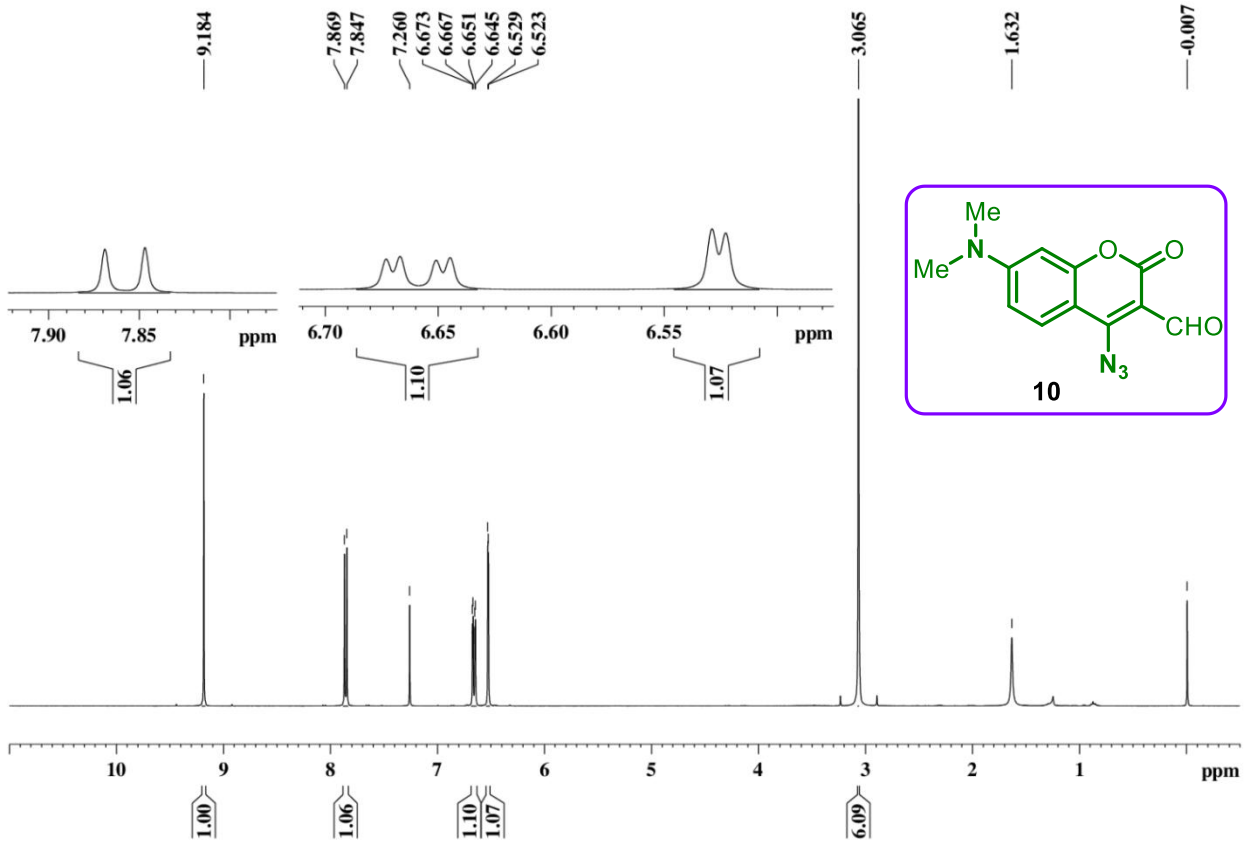
^{1}H-^{1}H COSY NMR spectra of compound **8j**



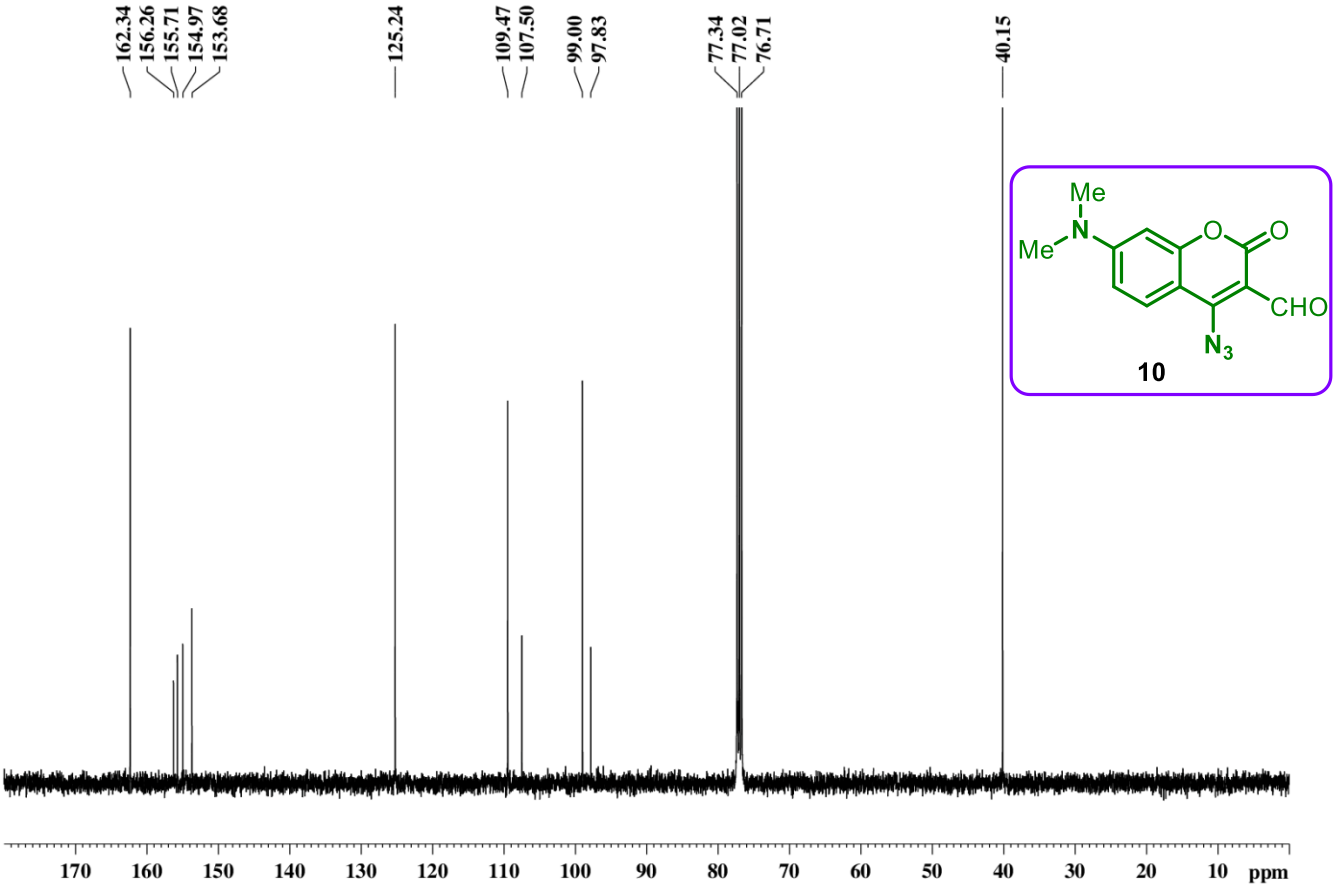
^{1}H-^{13}C (DEPT-135) HSQC NMR spectra of compound **8j**



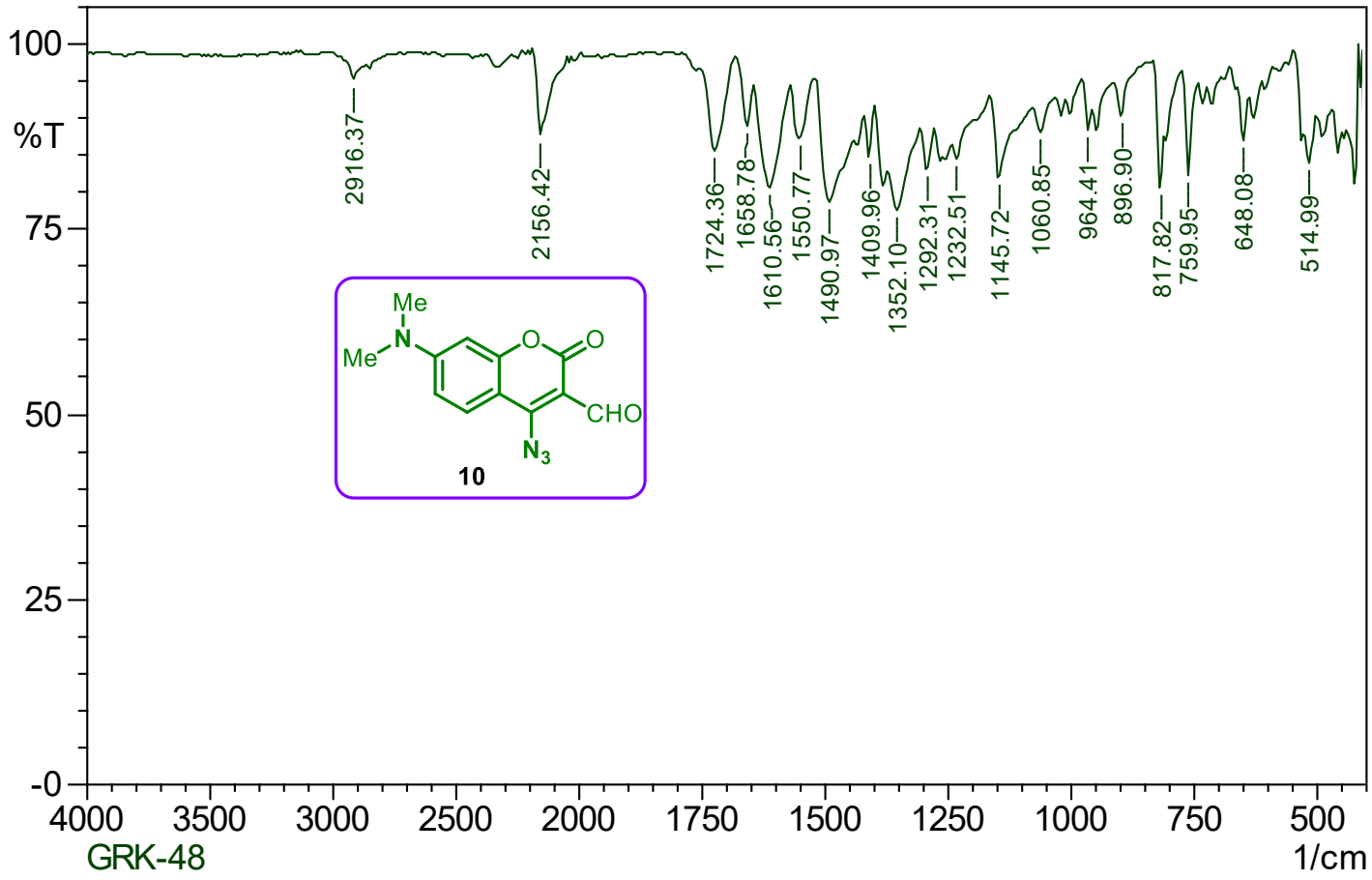
^{1}H-^{13}C HMBC NMR spectra of compound **8j**



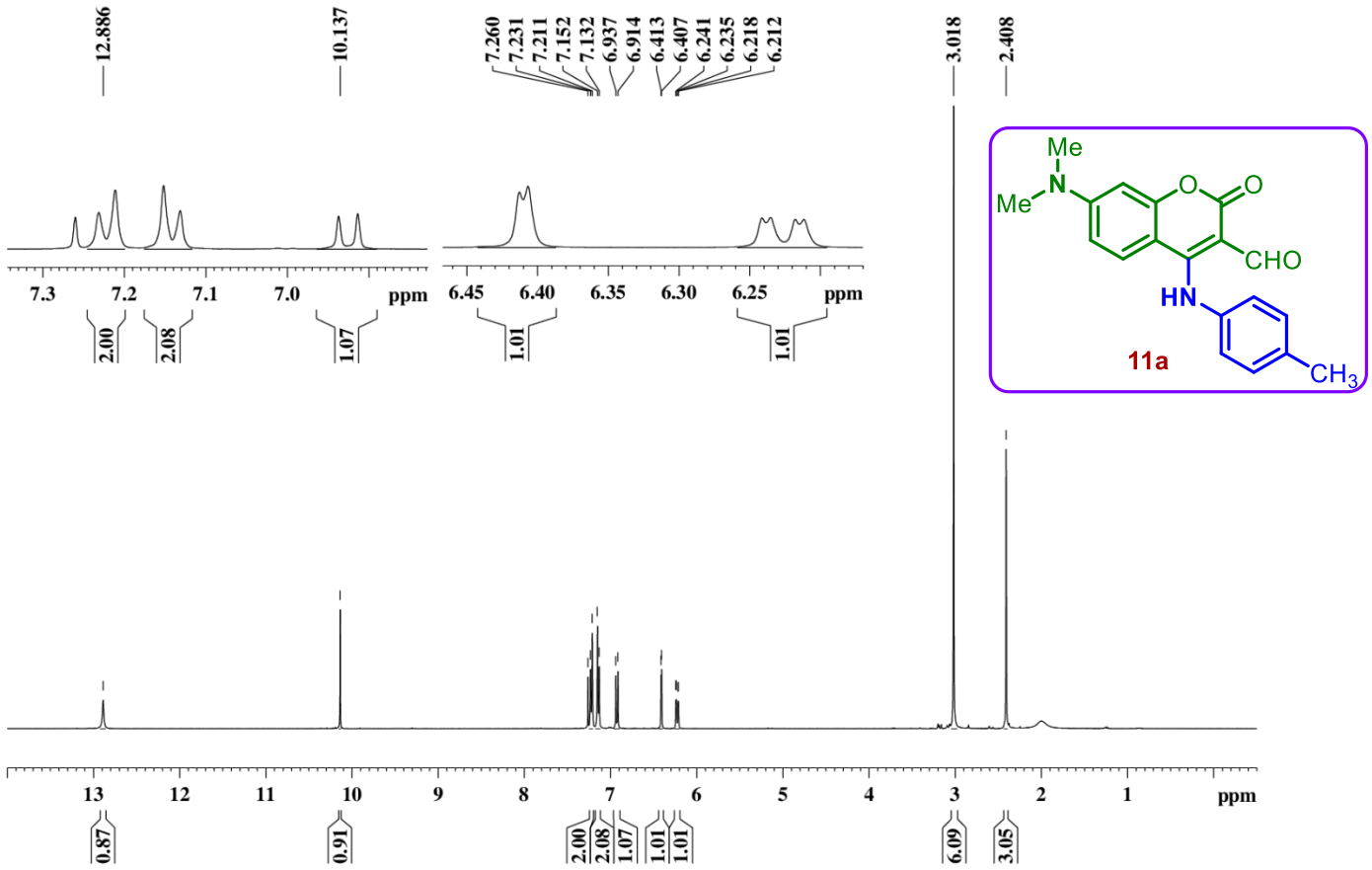
^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **10**



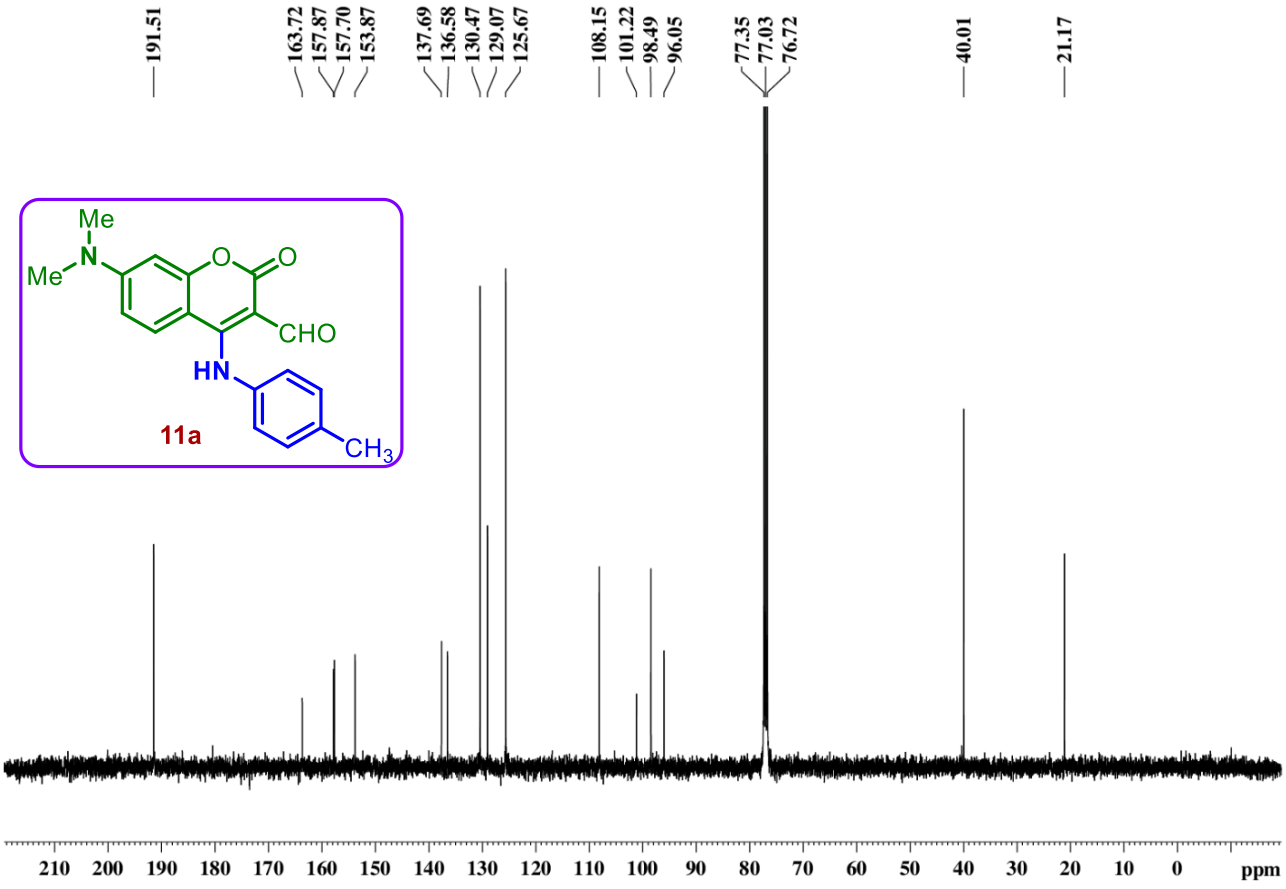
^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$) spectra of compound **10**



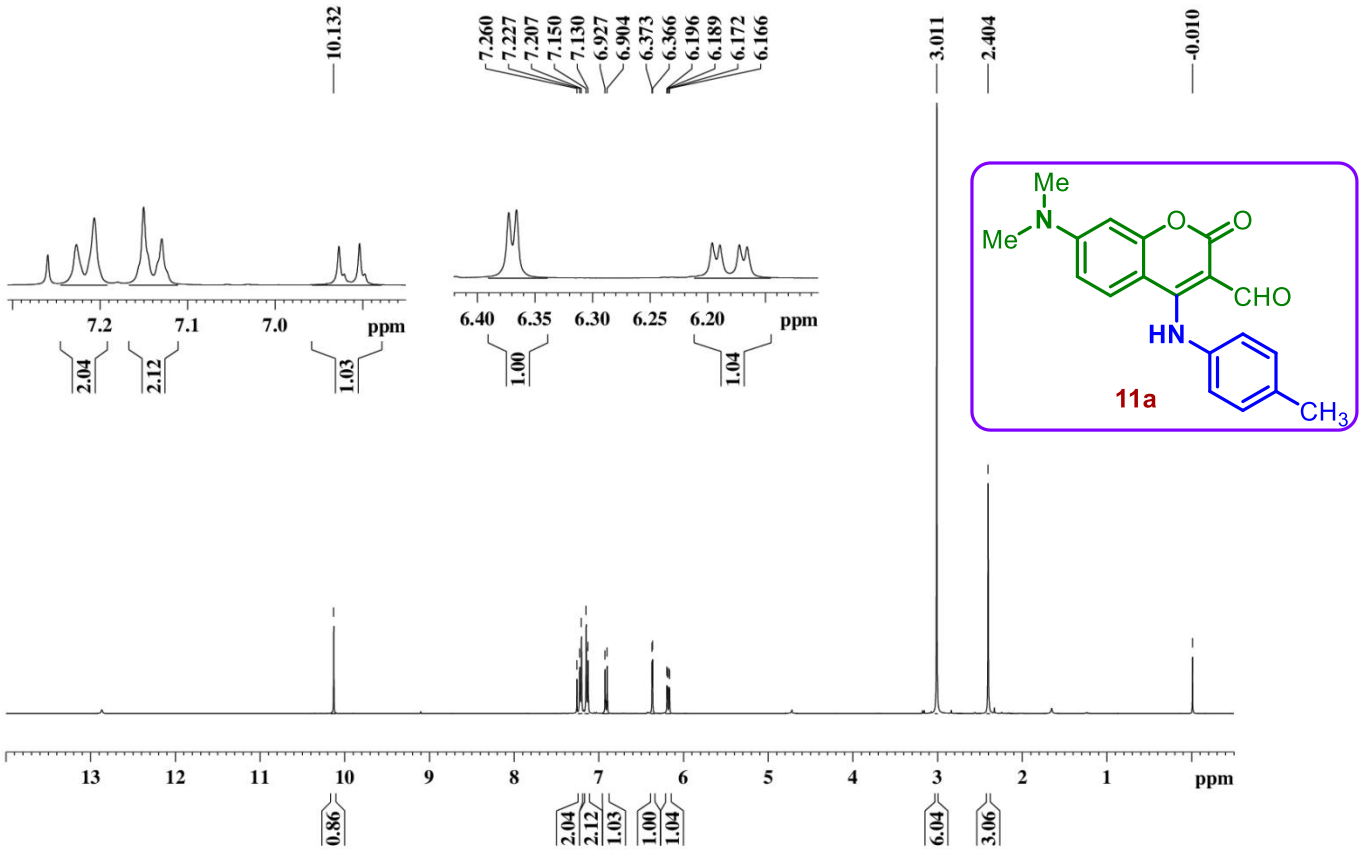
FT-IR spectra of compound **10**



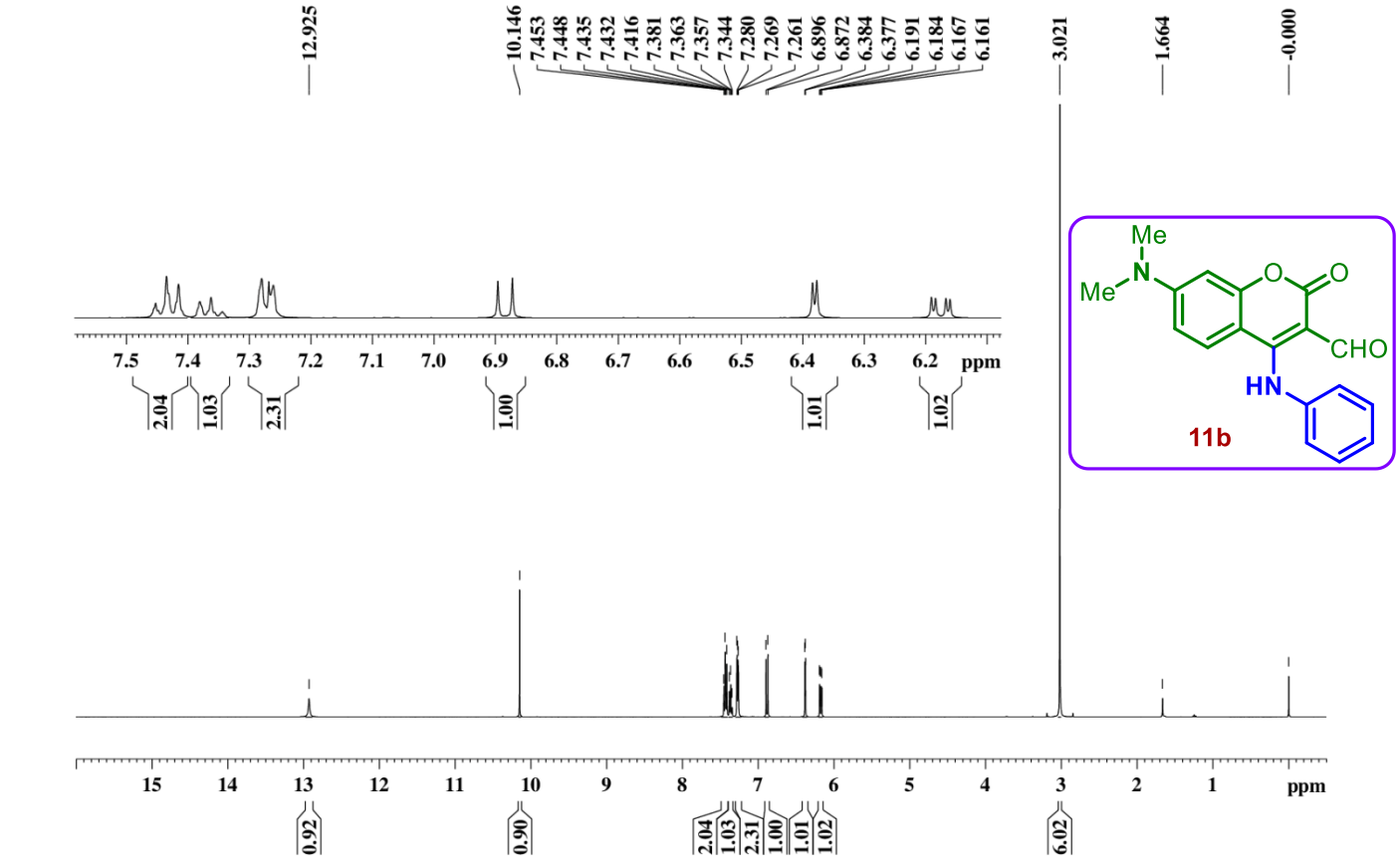
^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **11a**



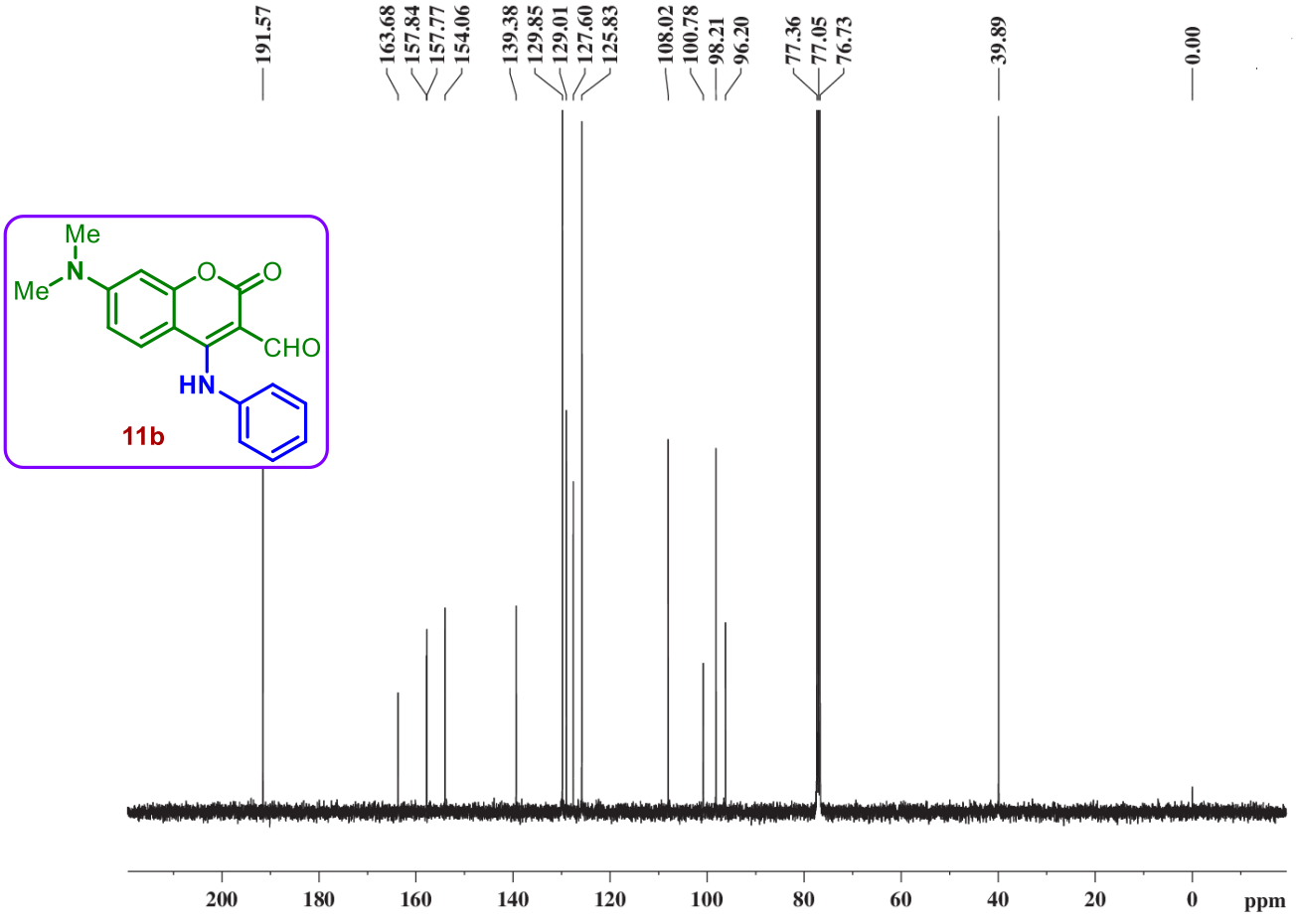
^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$) spectra of compound **11a**



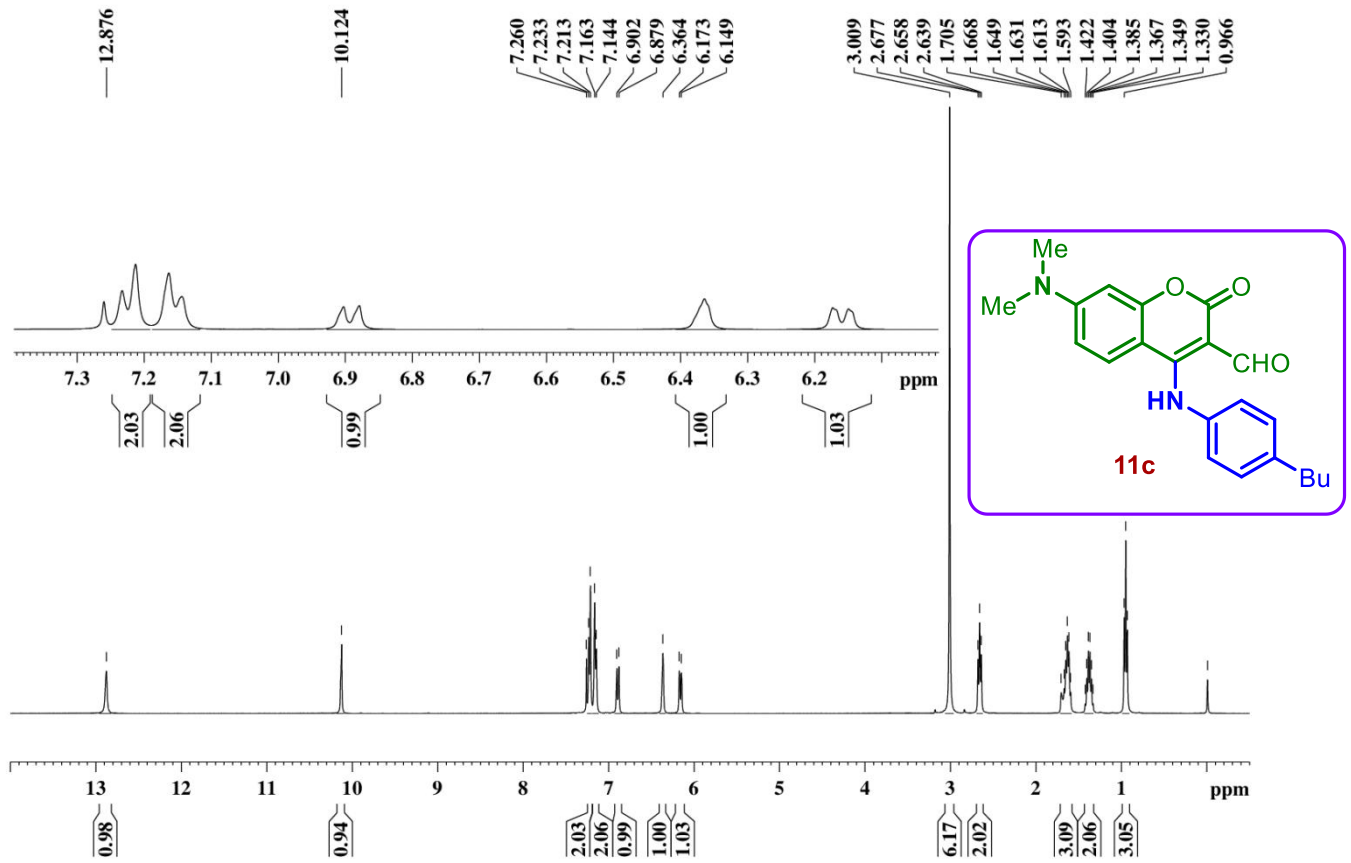
^{1}H NMR (400 MHz, $CDCl_3$ + D_2O) spectra of compound **11a** (Deuterium exchange)



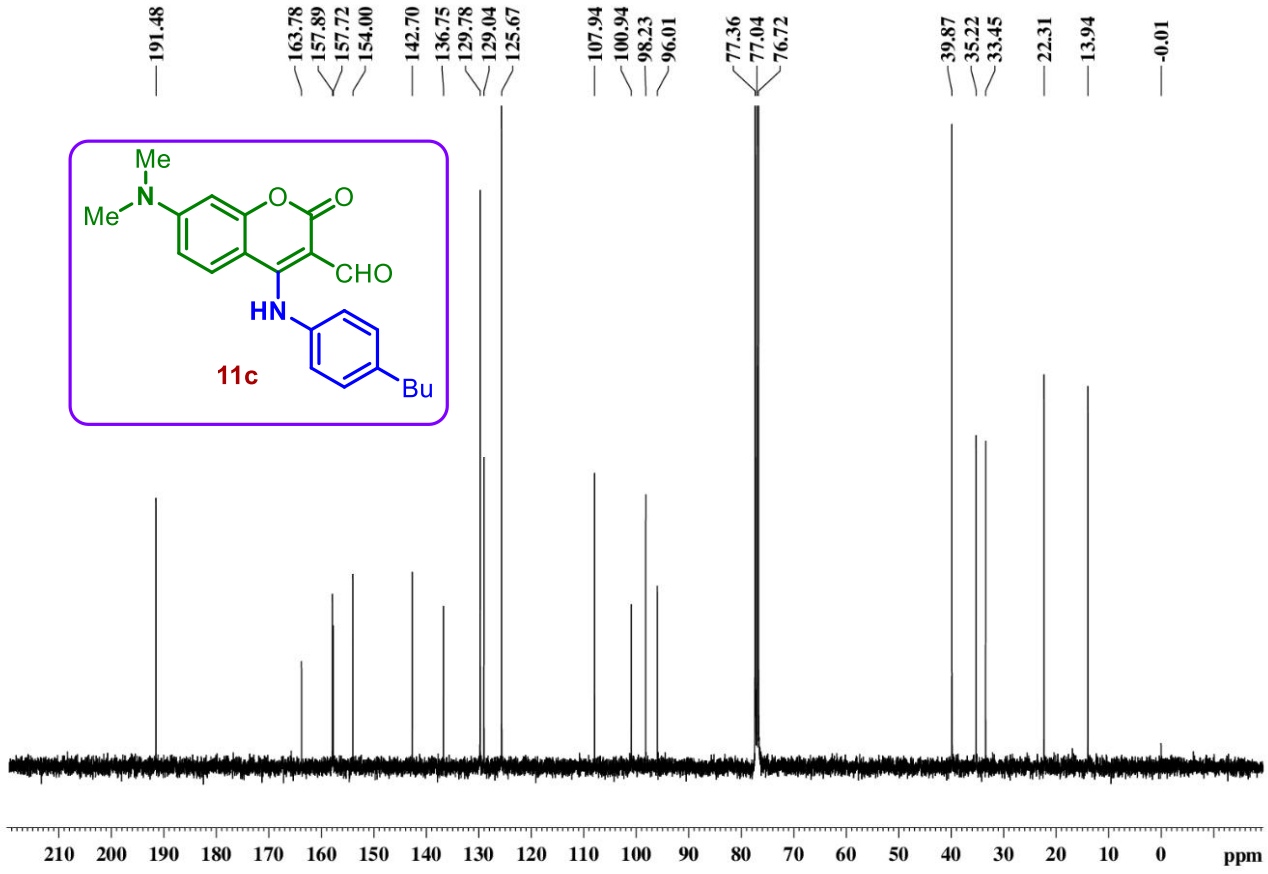
^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **11b**



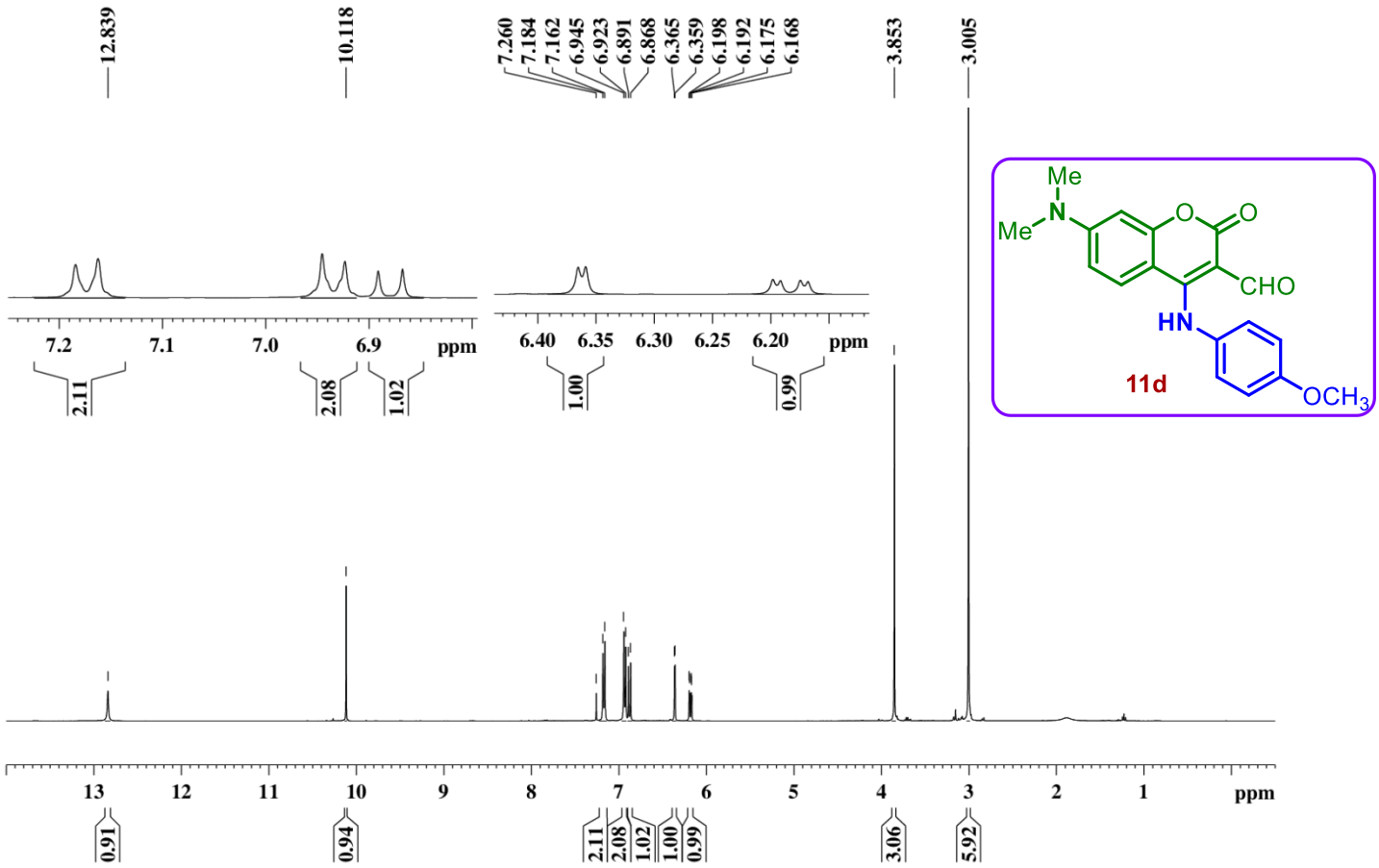
^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$) spectra of compound **11b**



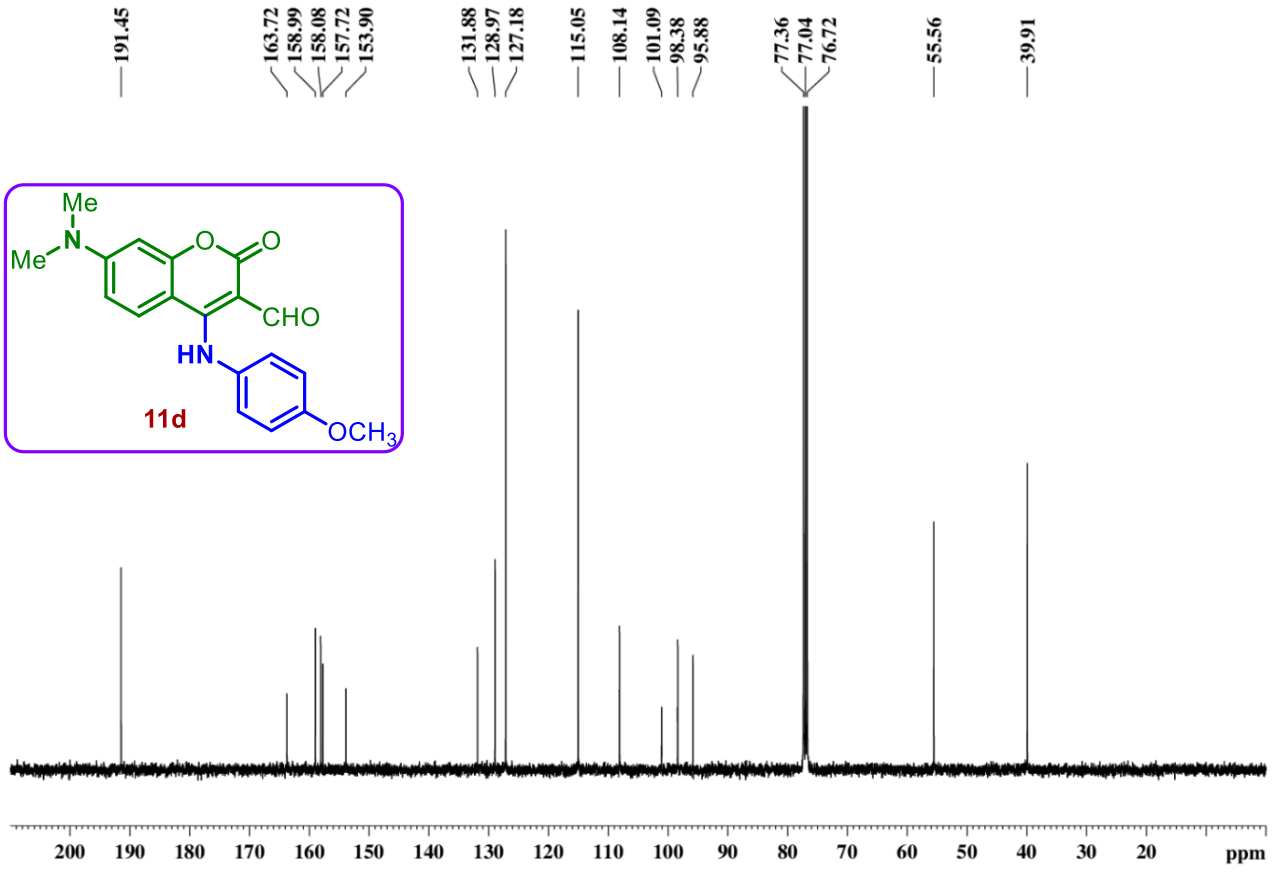
^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **11c**



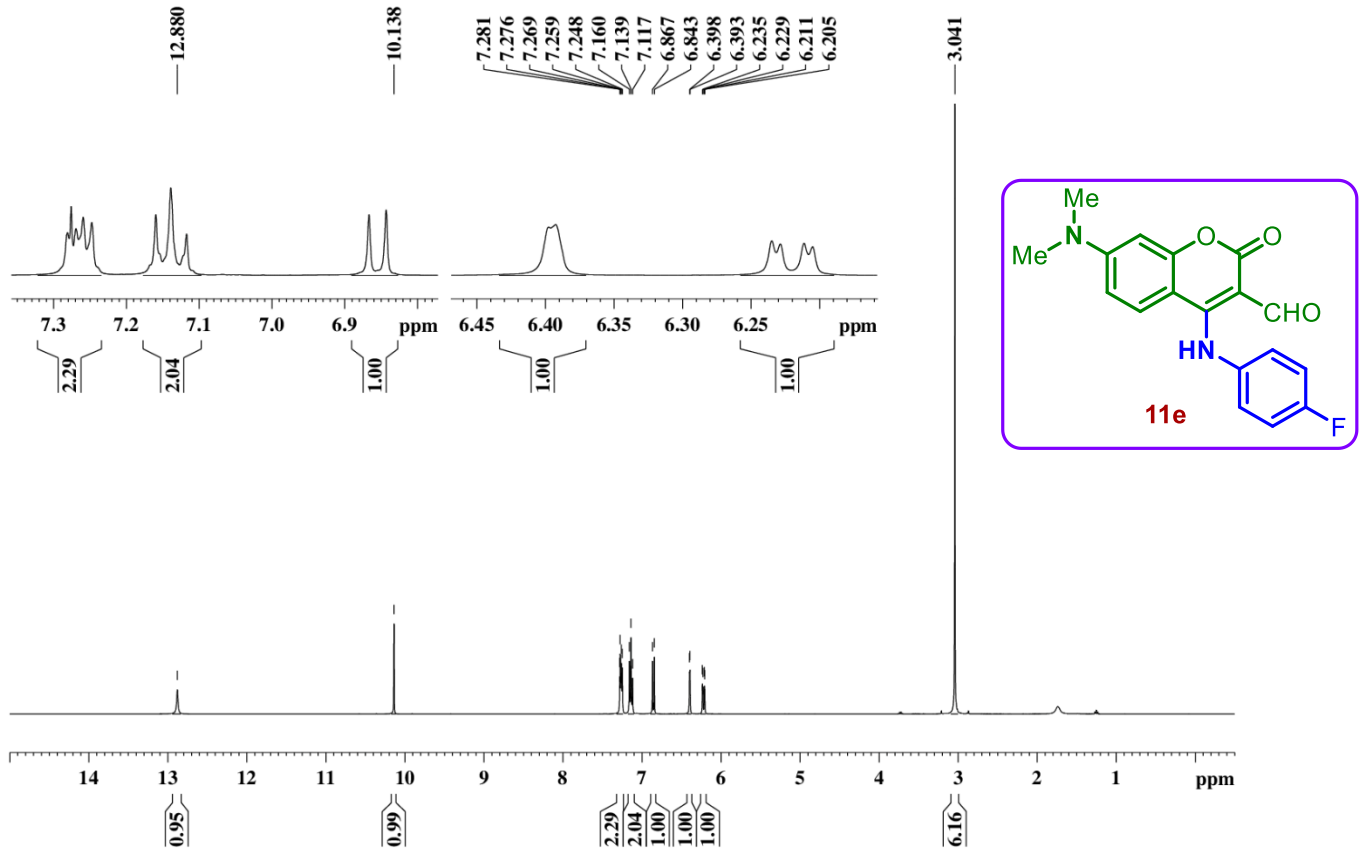
^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$) spectra of compound **11c**



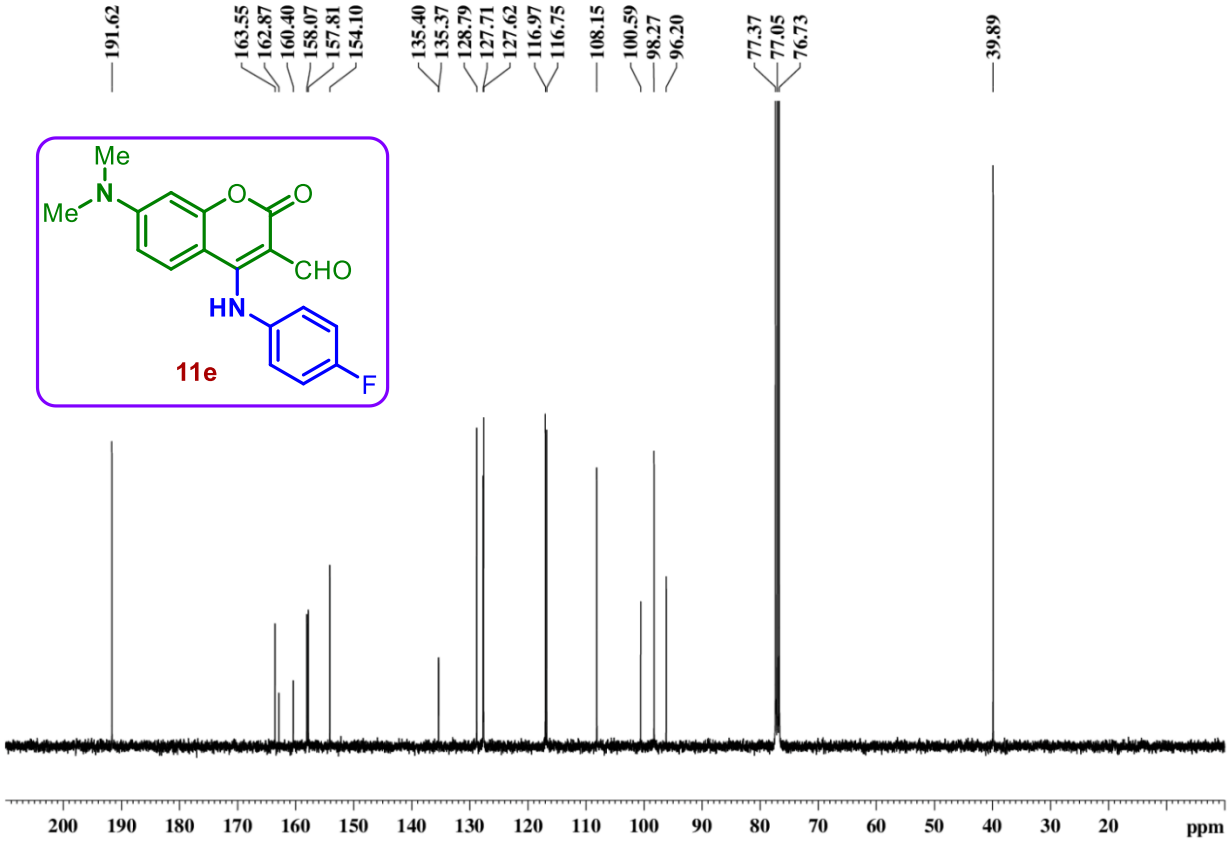
^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **11d**



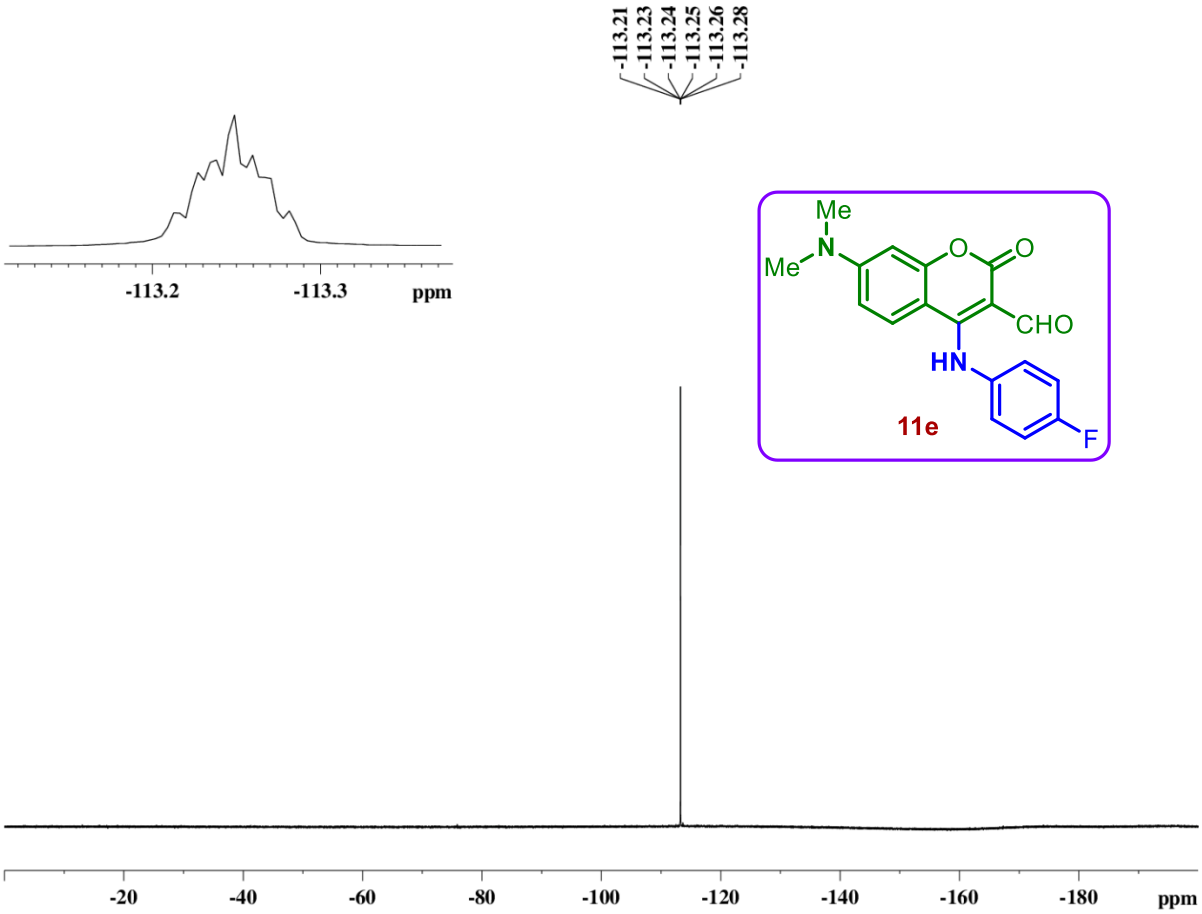
^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$) spectra of compound **11d**



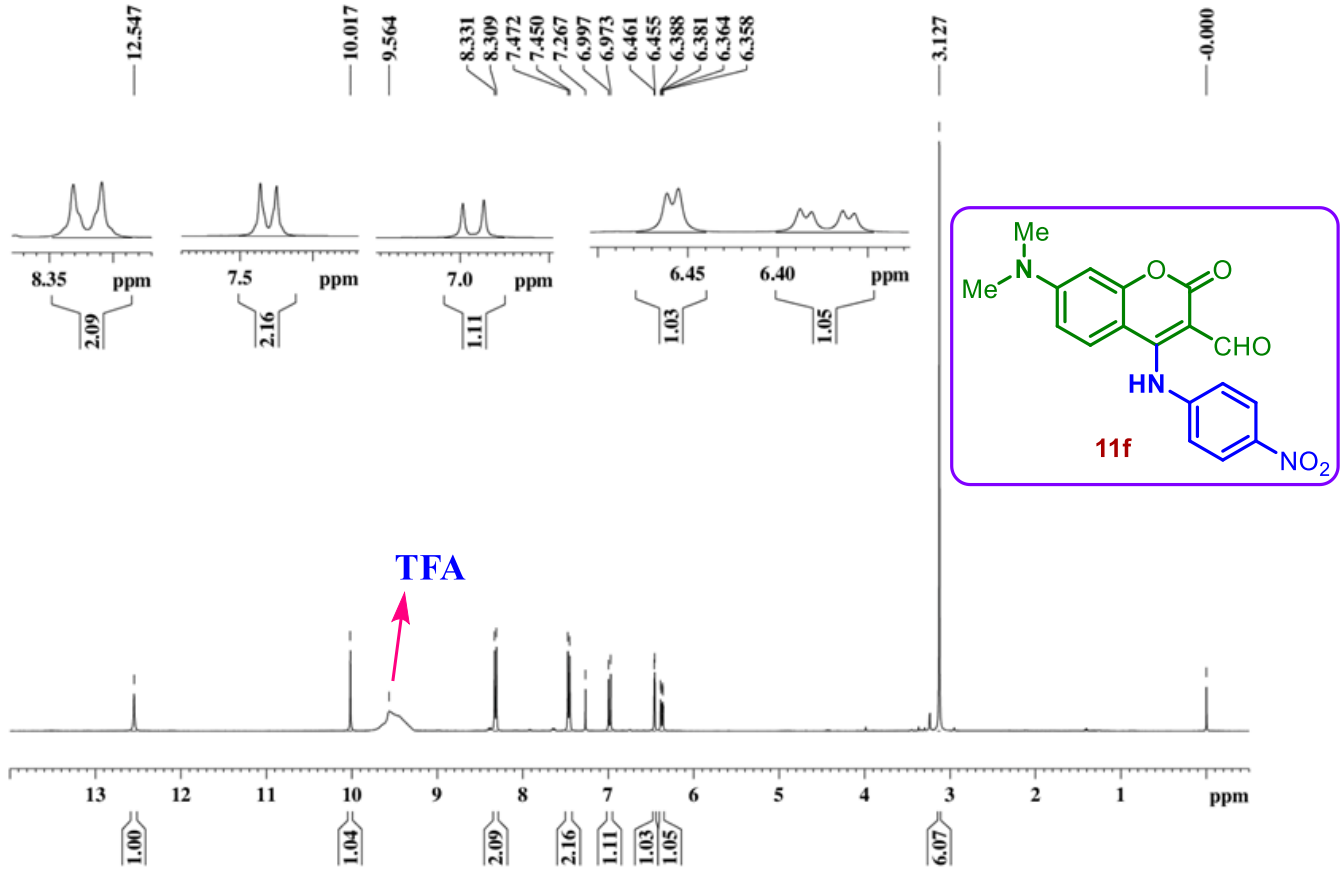
^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **11e**



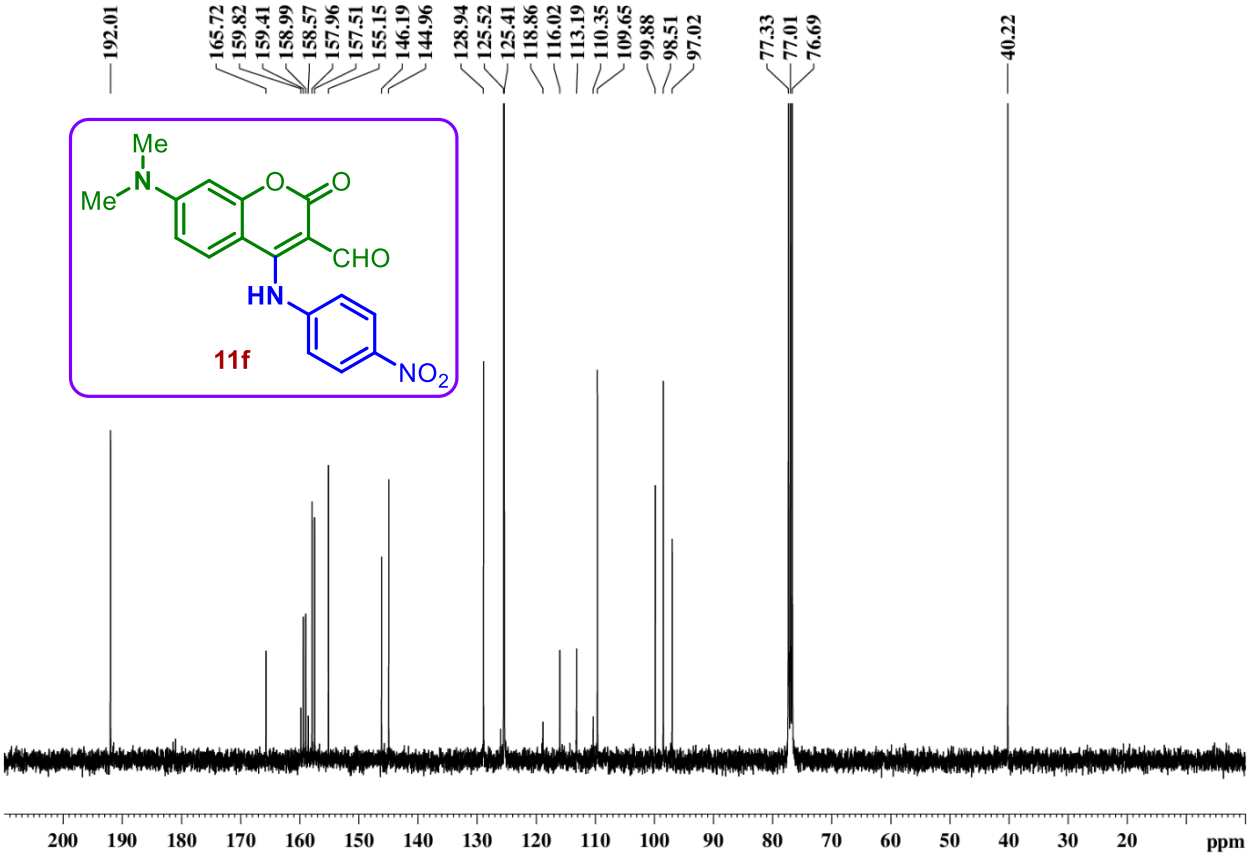
^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$) Compound **11e**



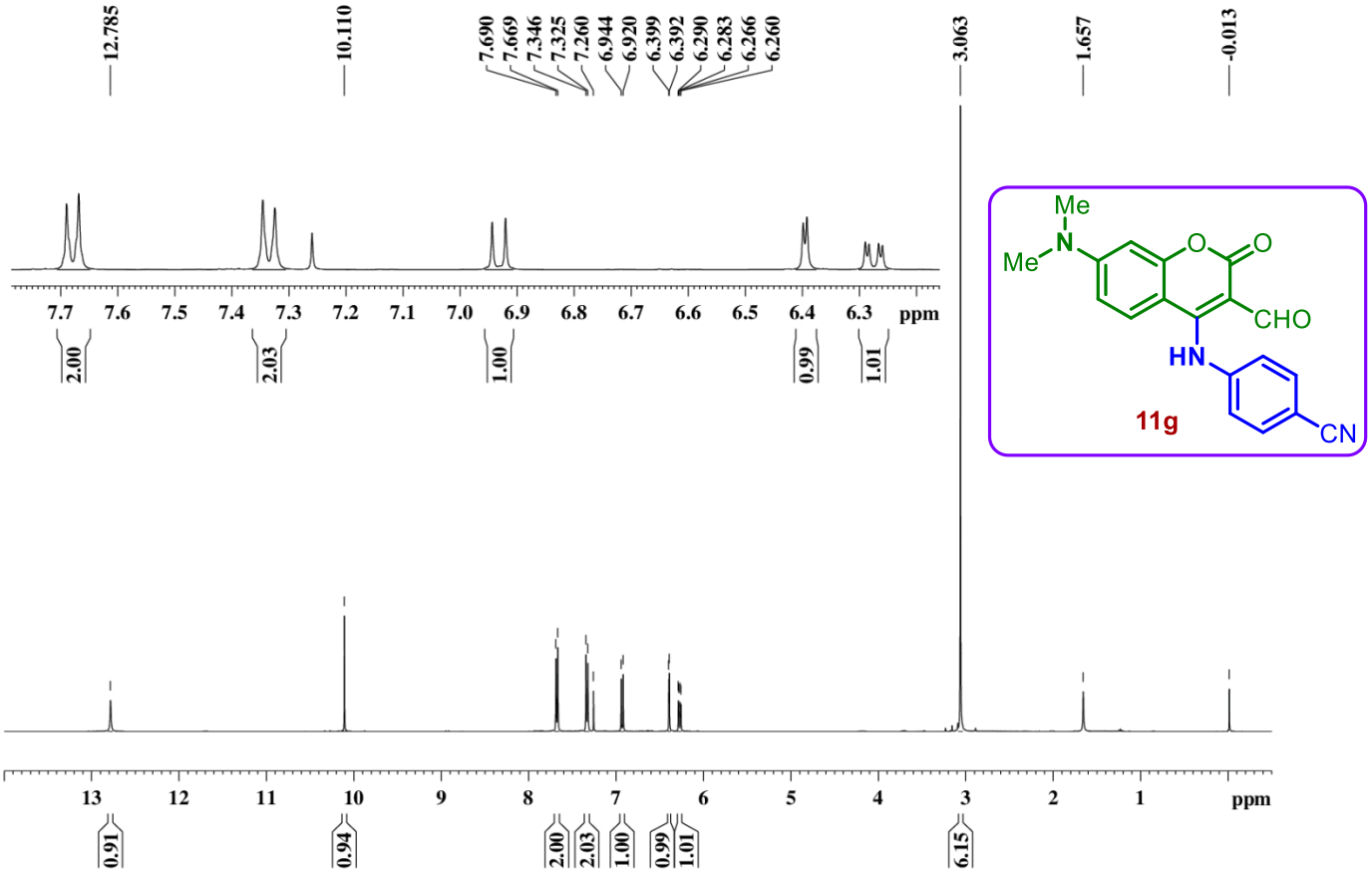
^{19}F NMR (376.6 MHz, $CDCl_3$) spectra of compound **11e**



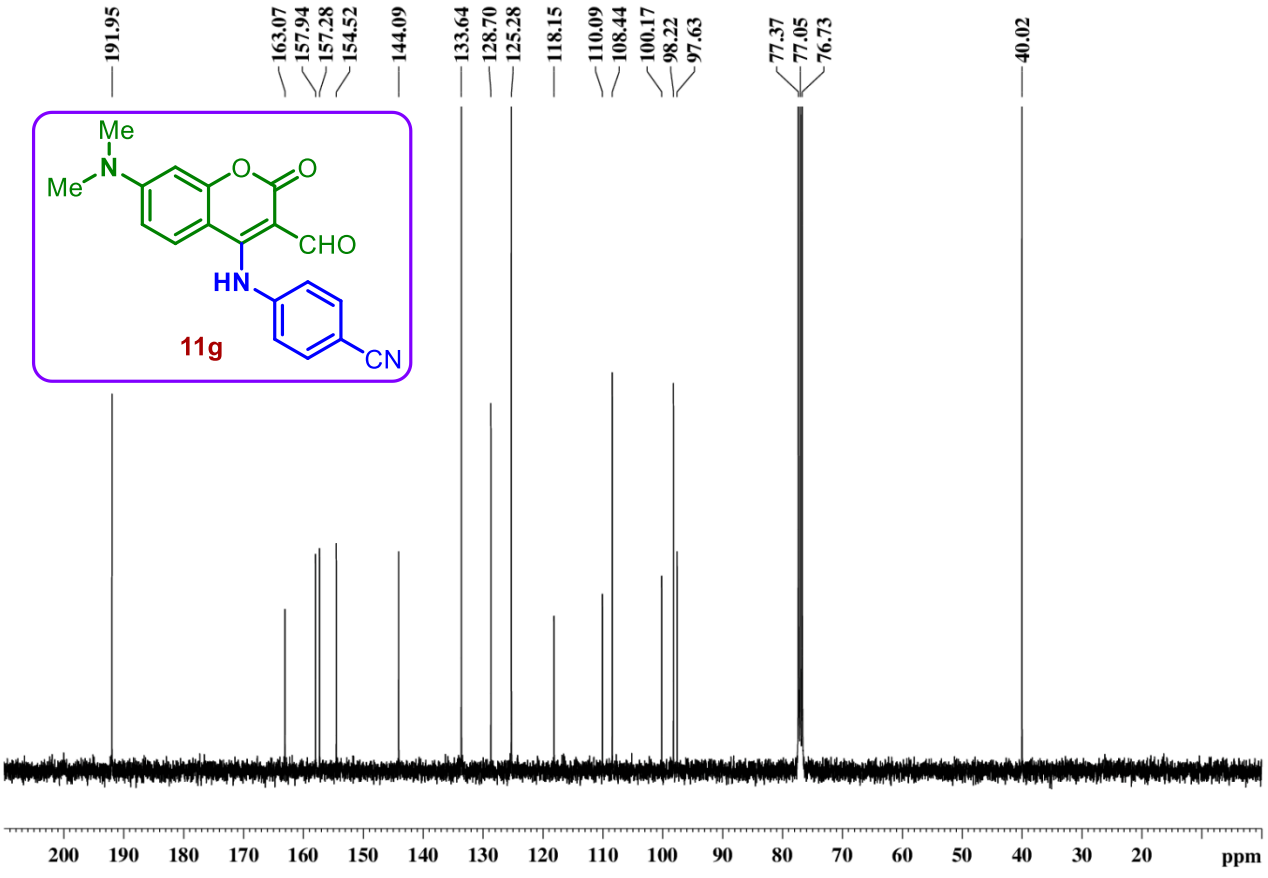
^{1}H NMR (400 MHz, $CDCl_3$+TFA) spectra of compound **11f**



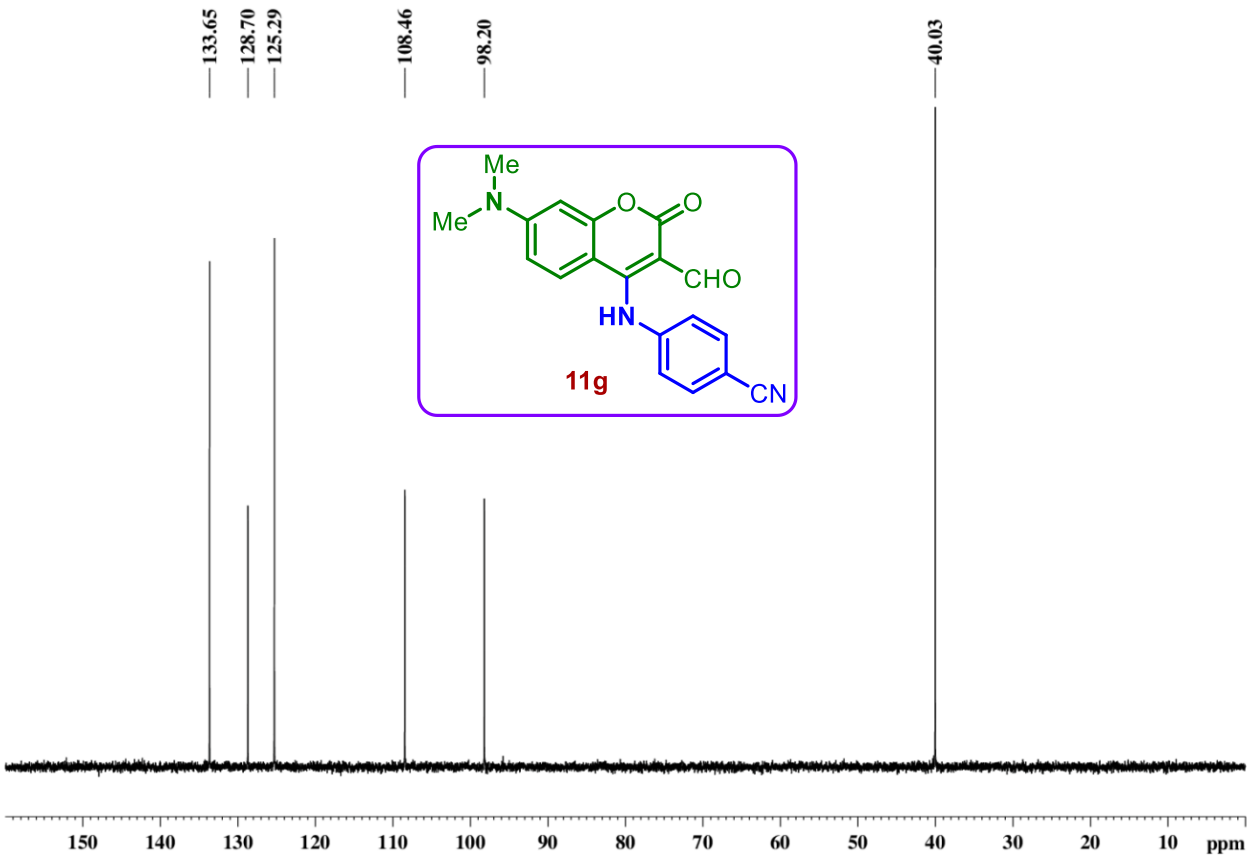
^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$+TFA) spectra of compound **11f**



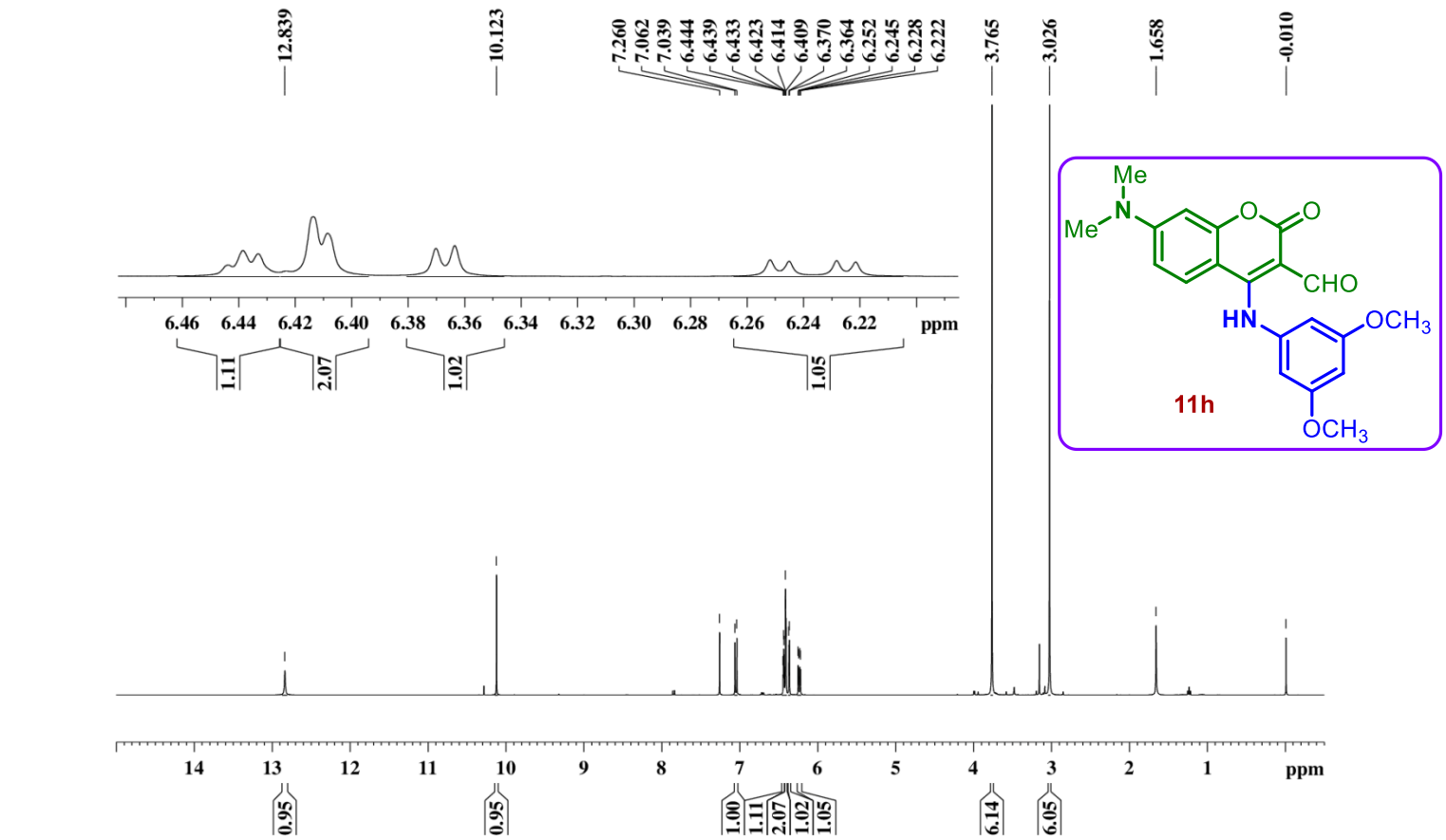
^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **11g**



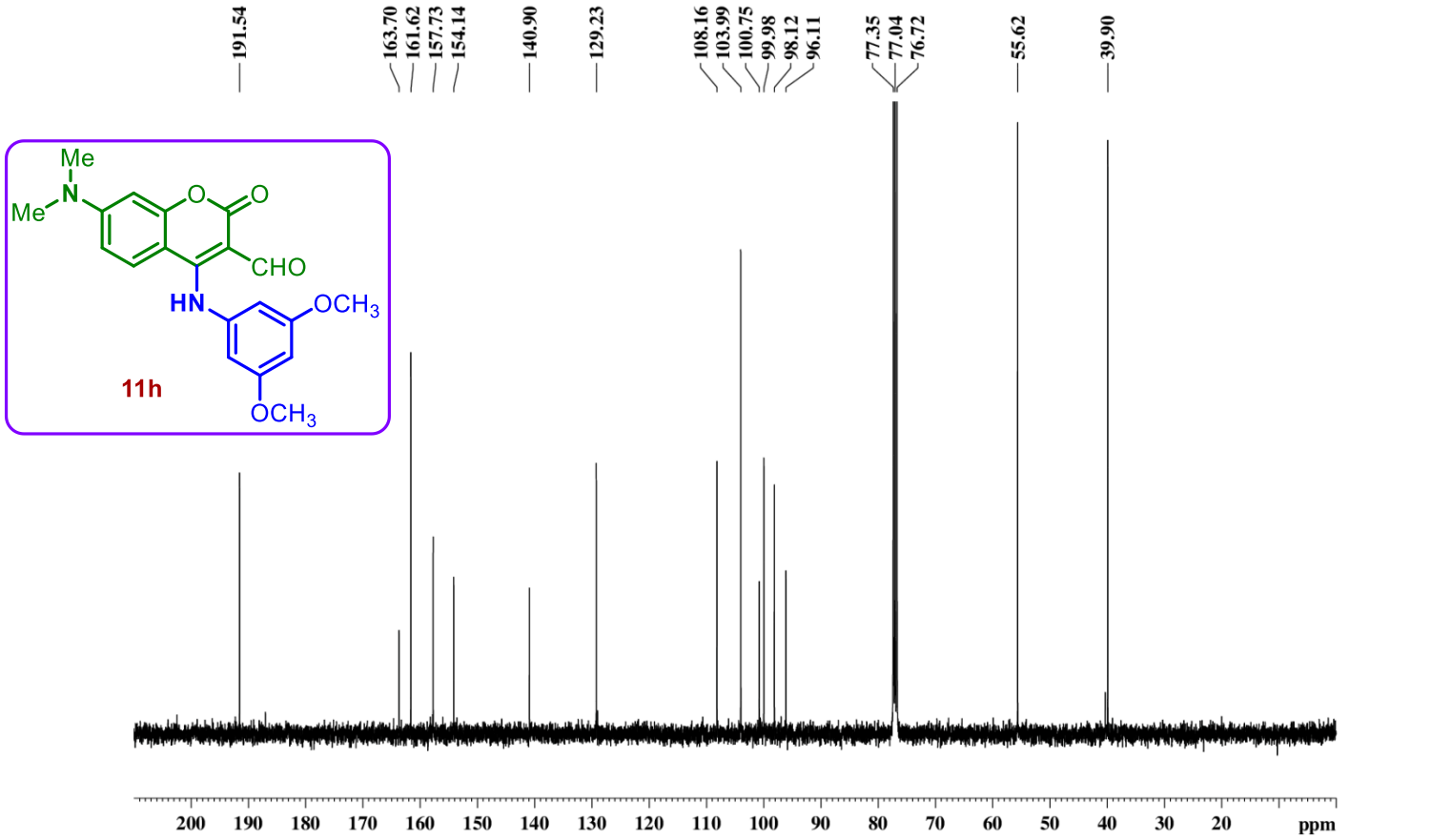
^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$) spectra of compound **11g**



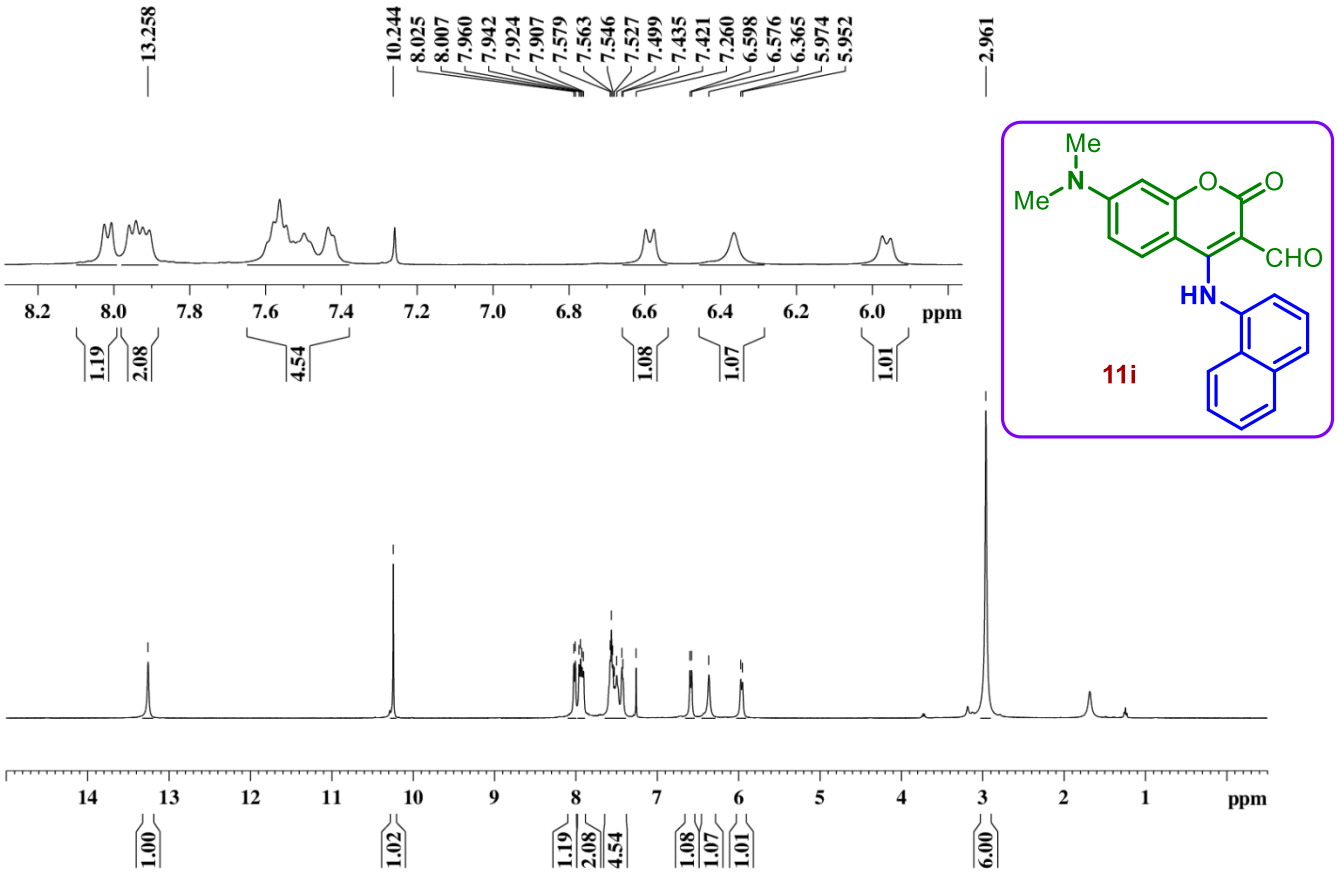
DEPT-135 NMR (100.6 MHz, $CDCl_3$) spectra of compound **11g**



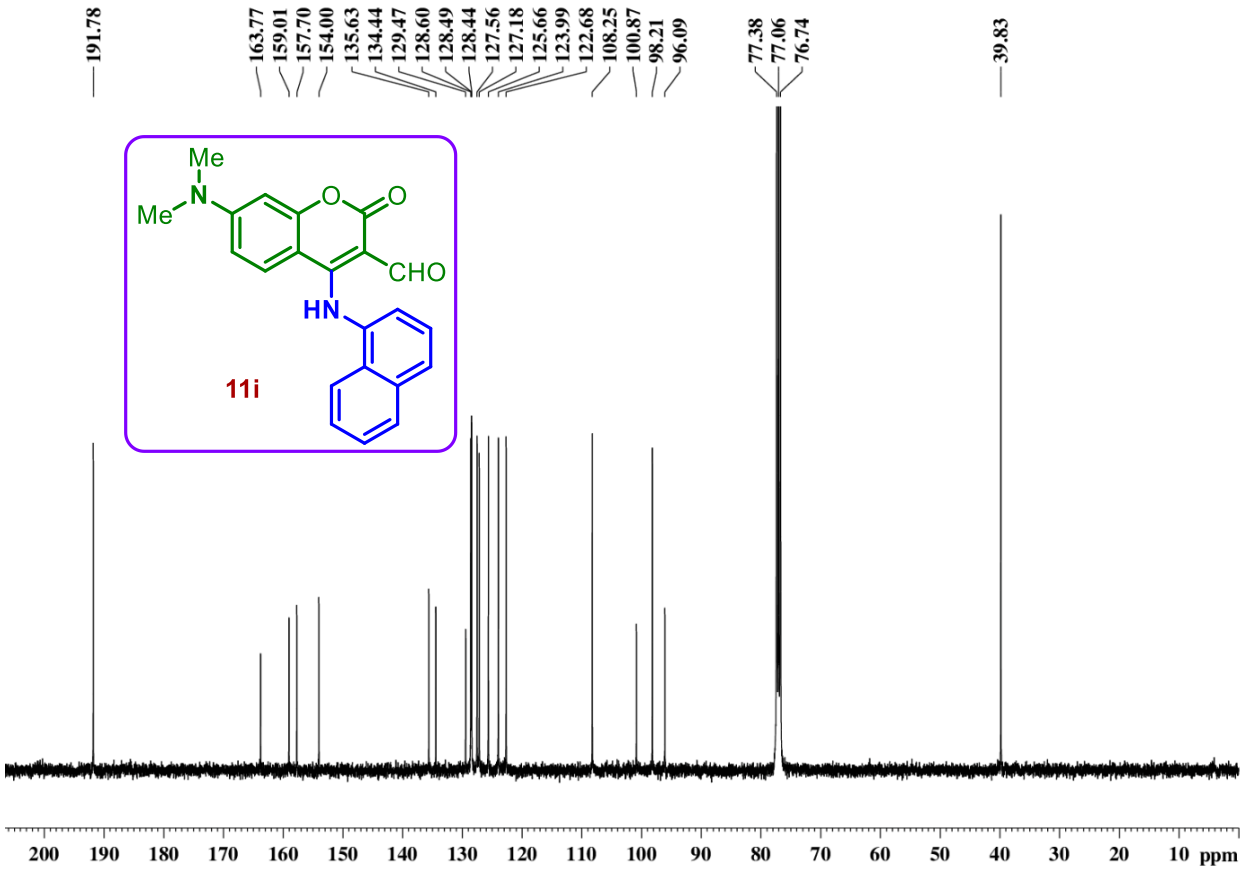
^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **11h**



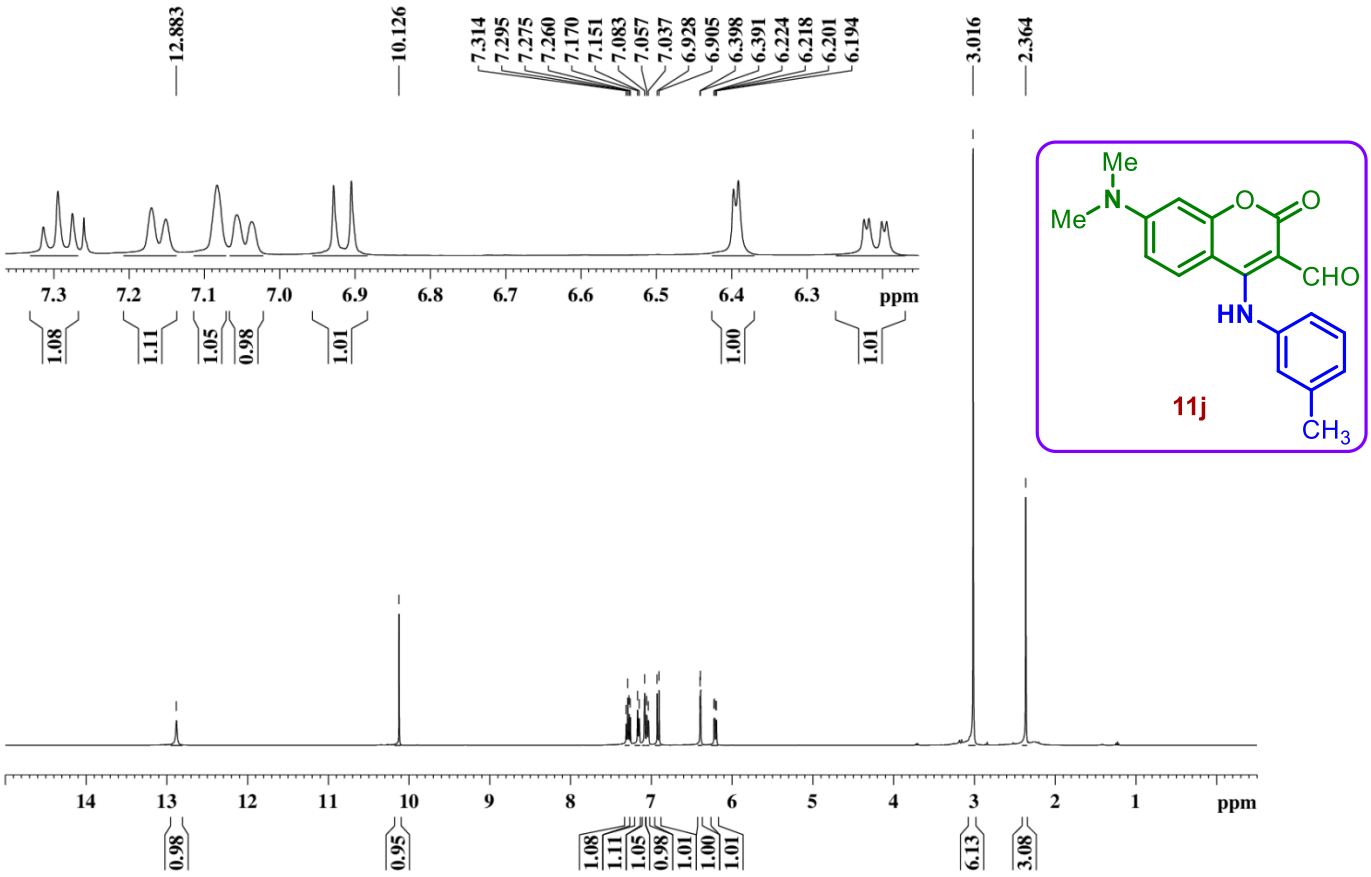
^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$) spectra of compound **11h**



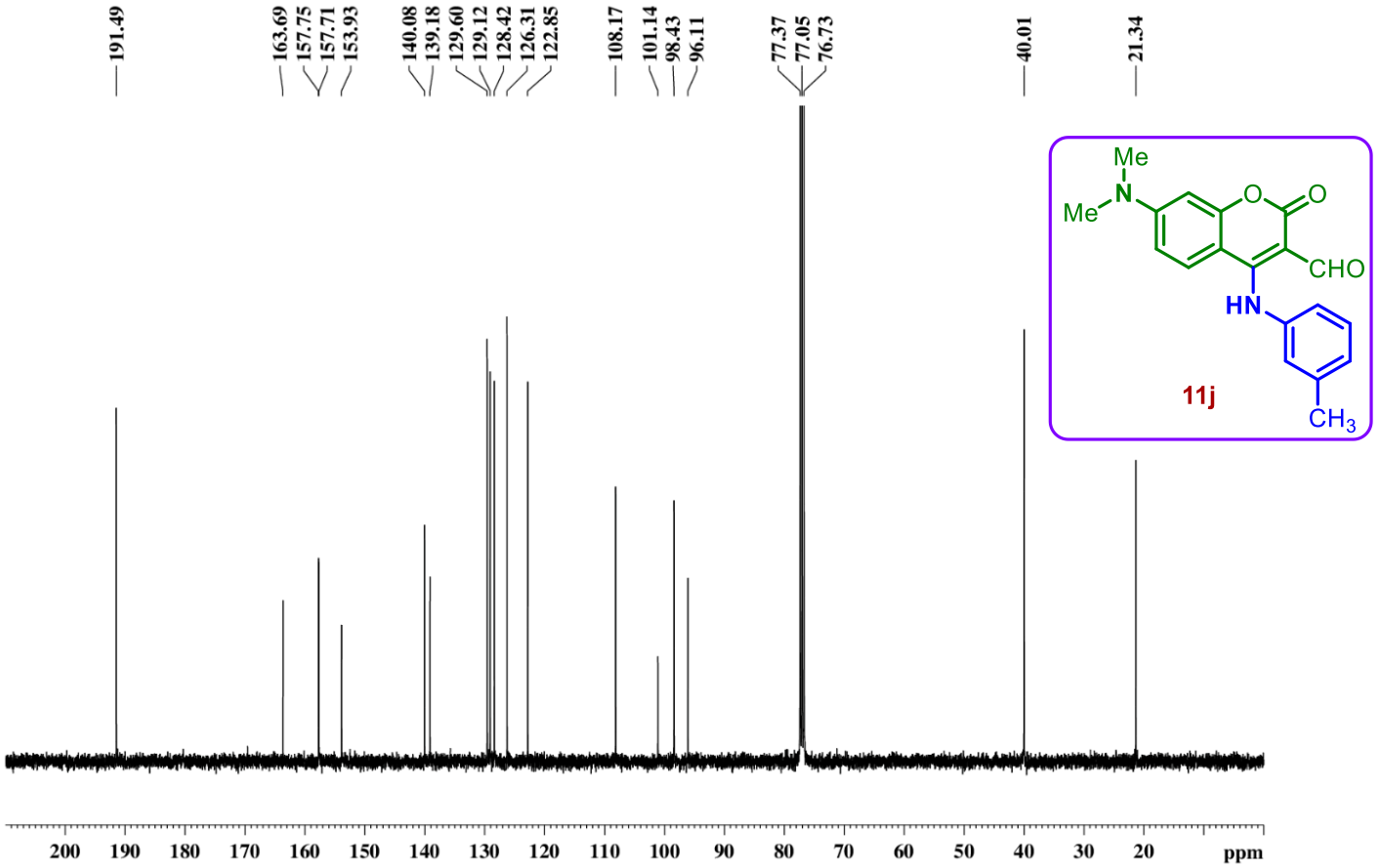
^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **11i**



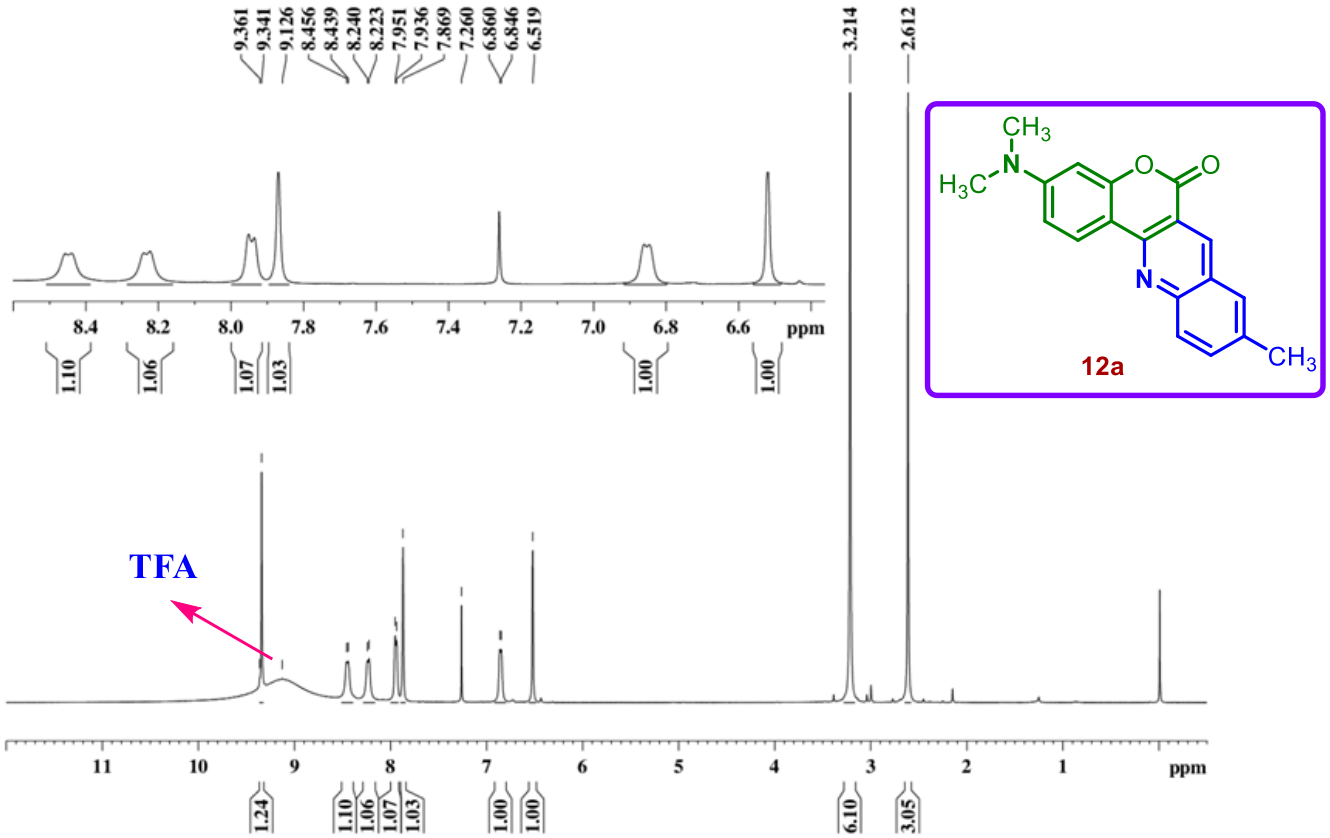
^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$) spectra of compound **11i**



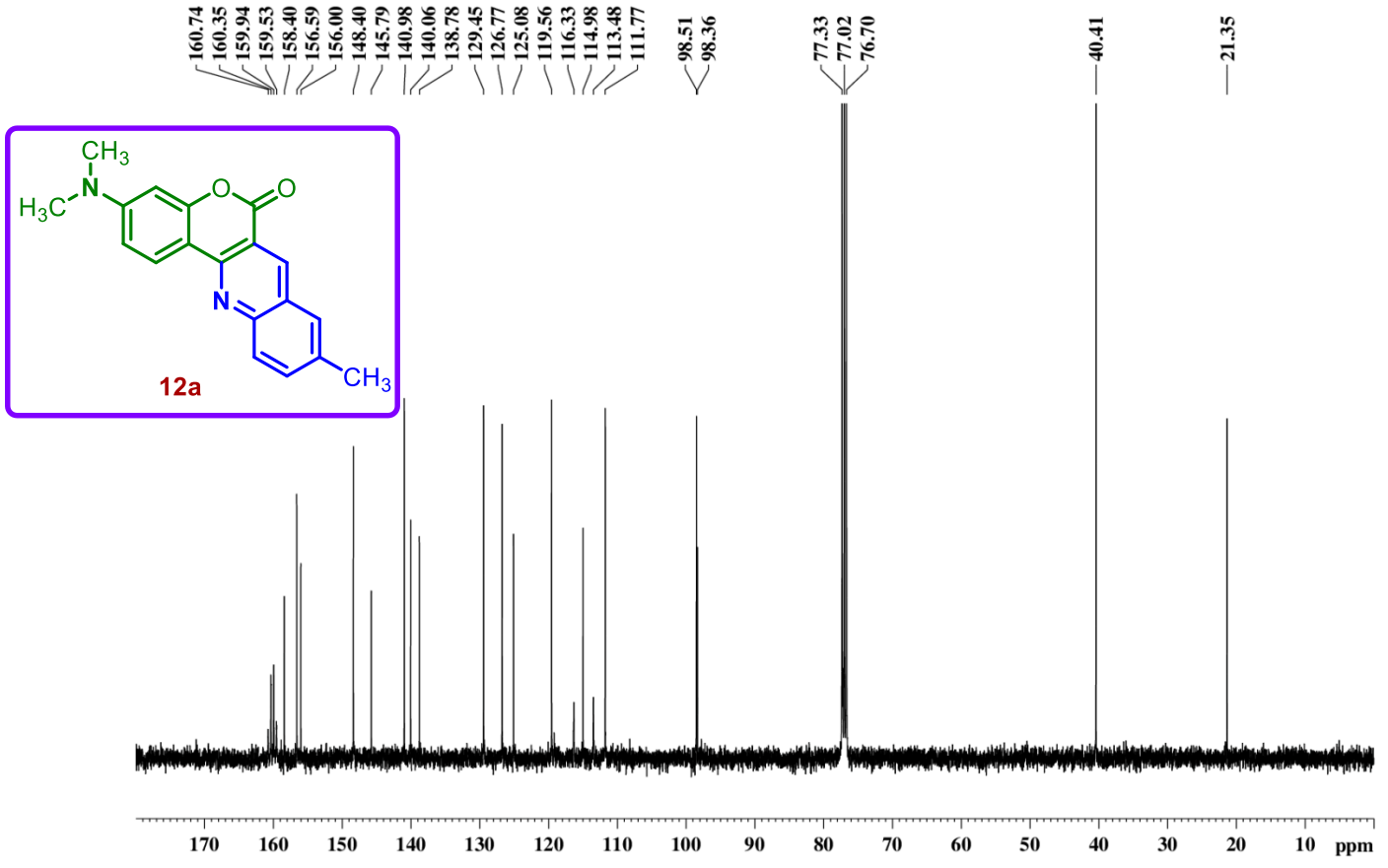
^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **11j**



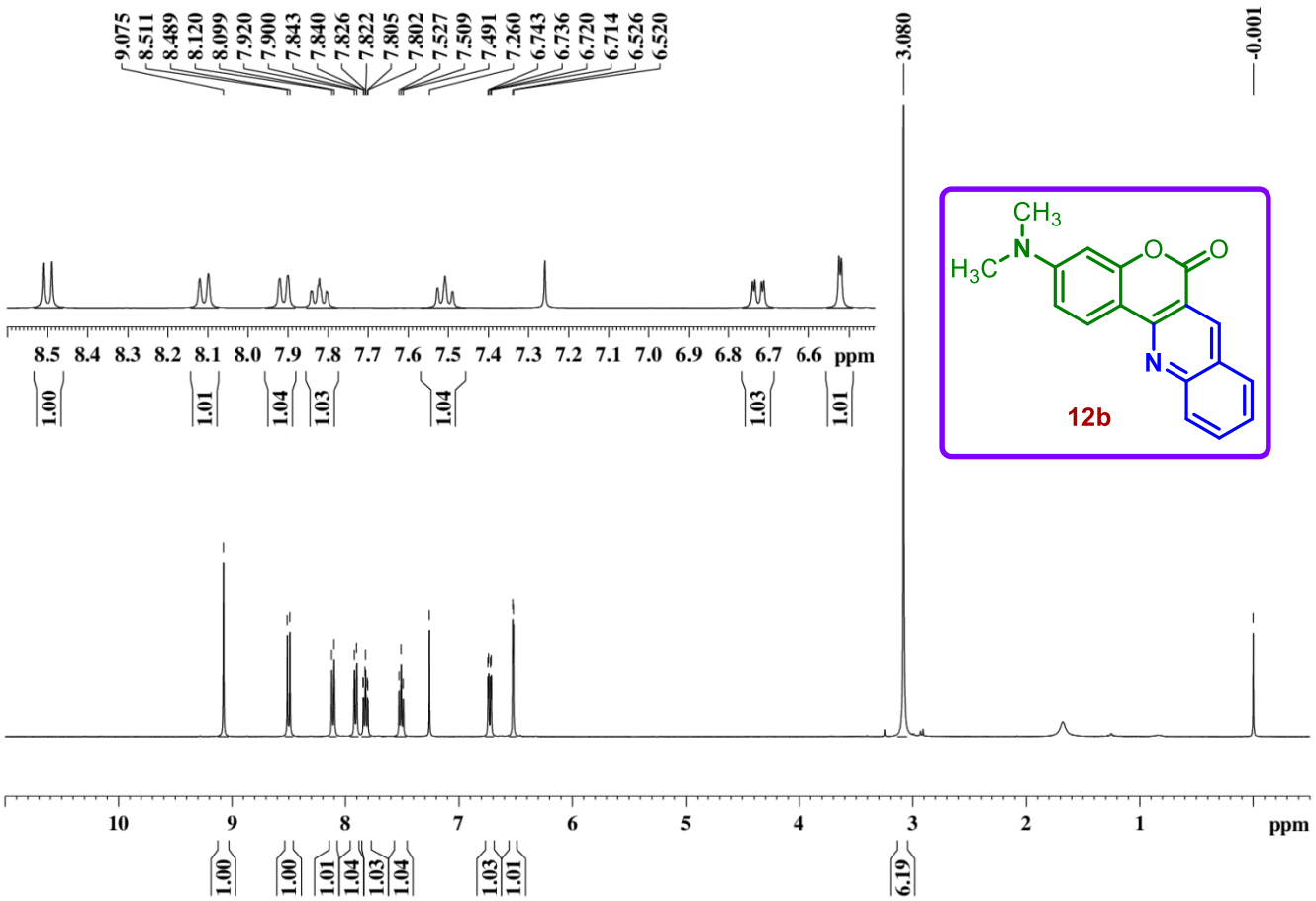
^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$) spectra of compound **11j**



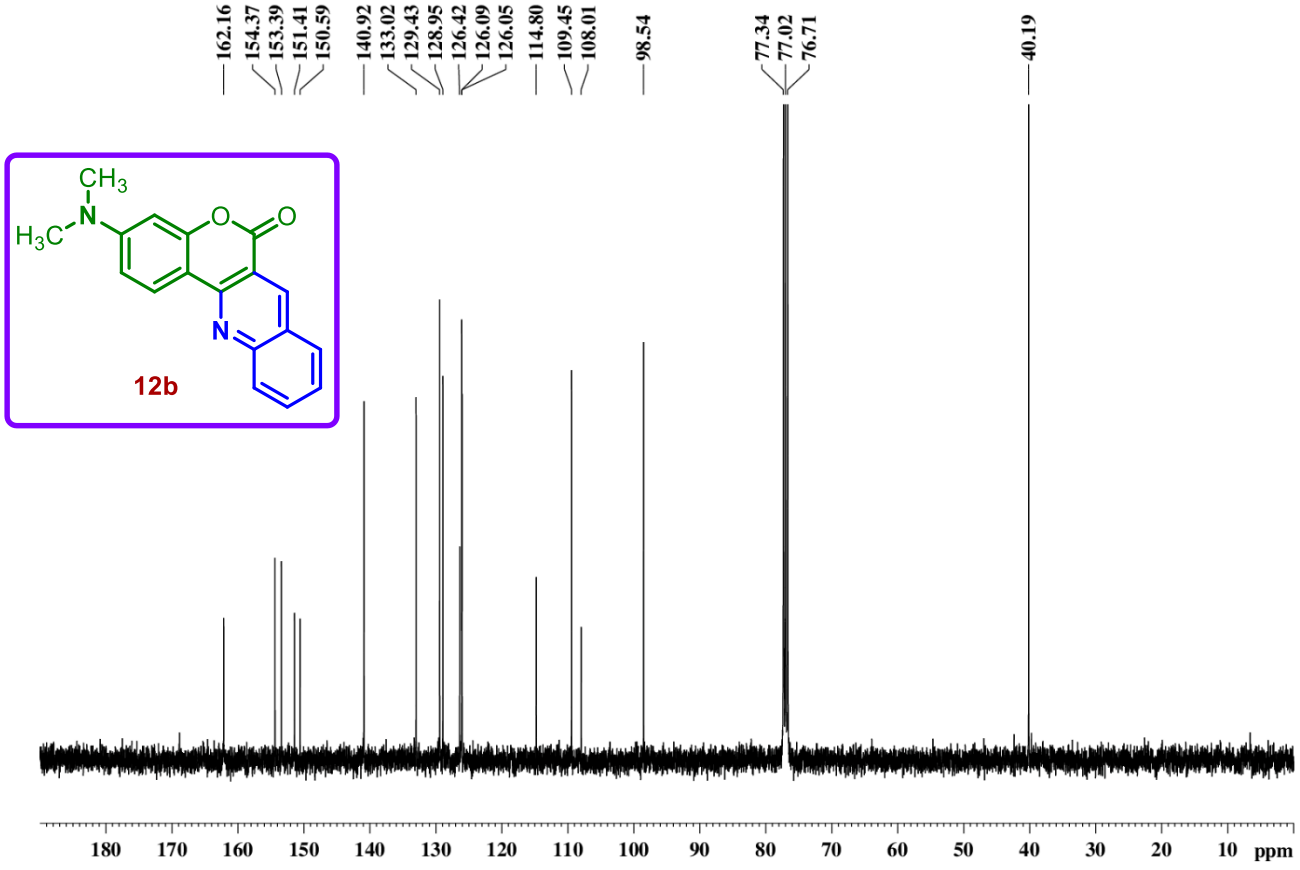
^{1}H NMR (400 MHz, $CDCl_3$+TFA) spectra of compound **12a**



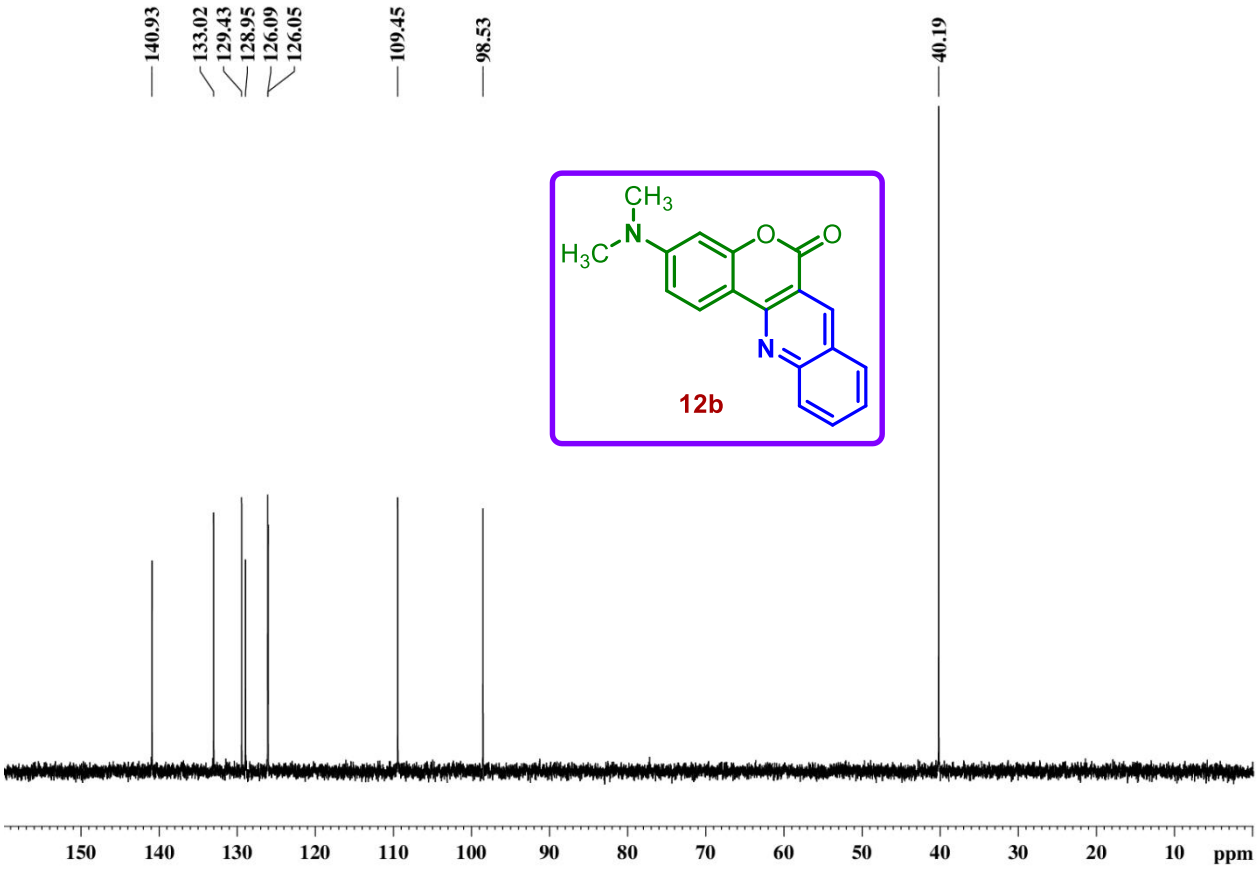
^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$+TFA) spectra of compound **12a**



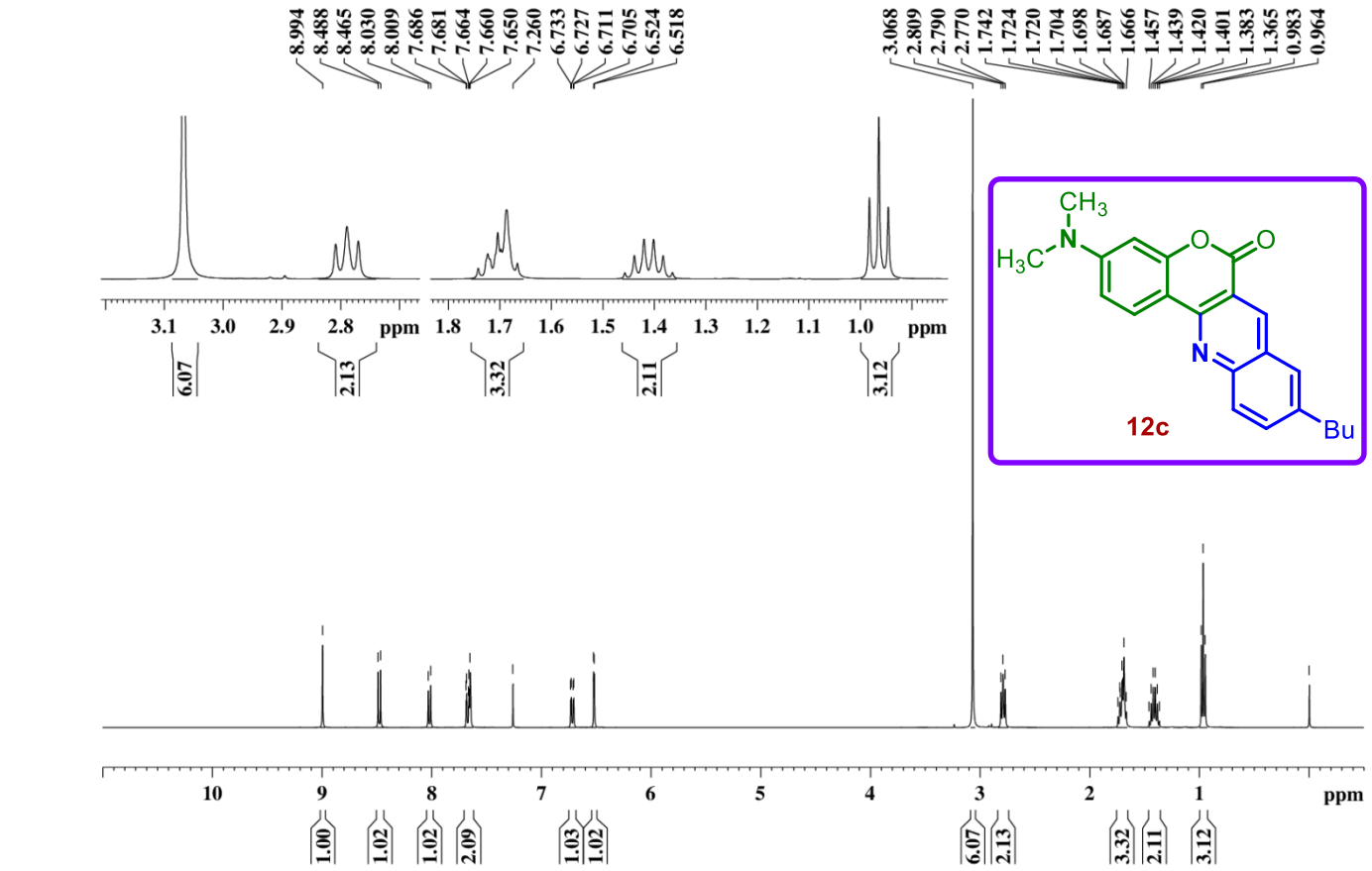
^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **12b**



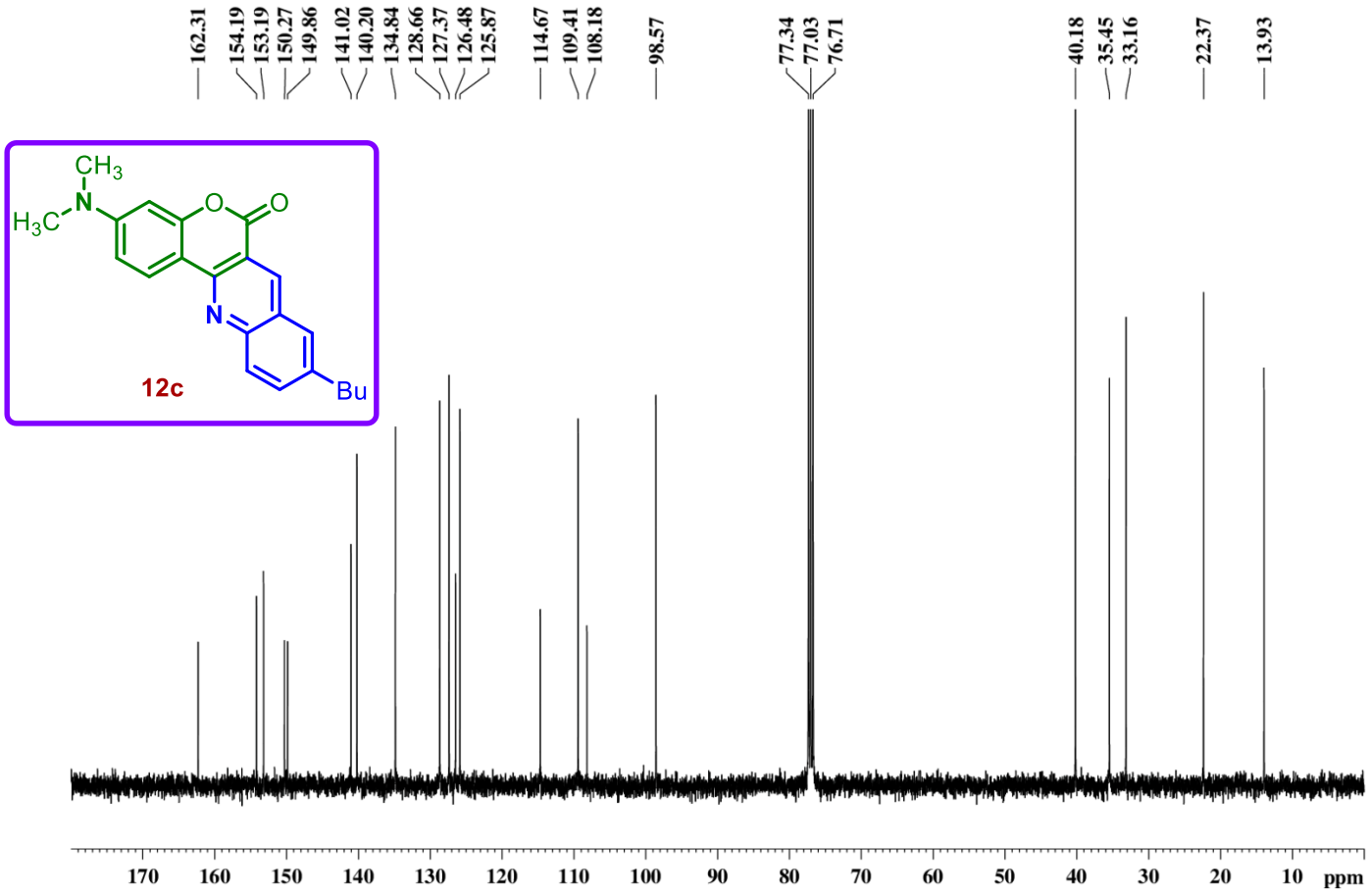
^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$) spectra of compound **12b**



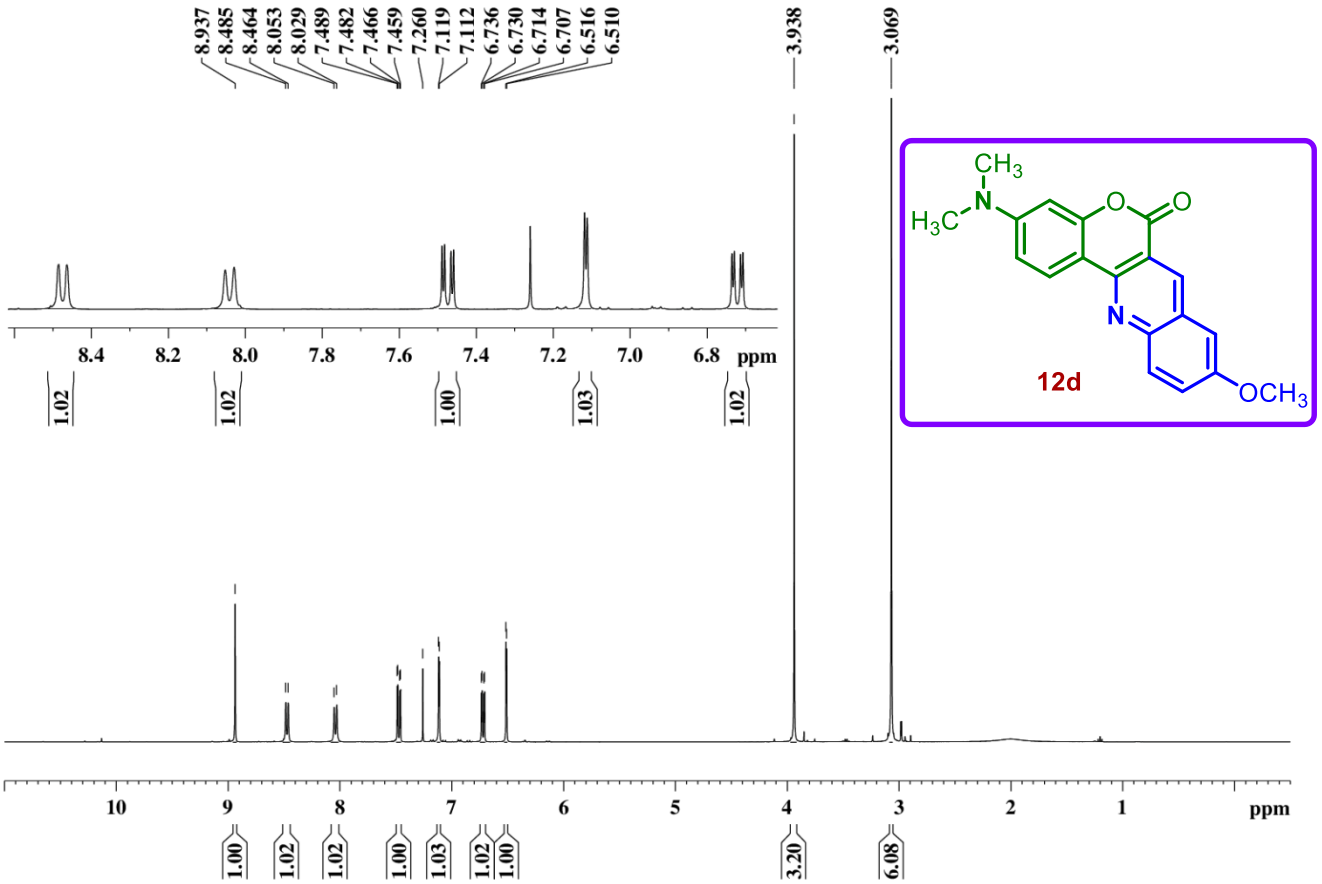
DEPT-135 NMR (100.6 MHz, $CDCl_3$) spectra of compound **12b**



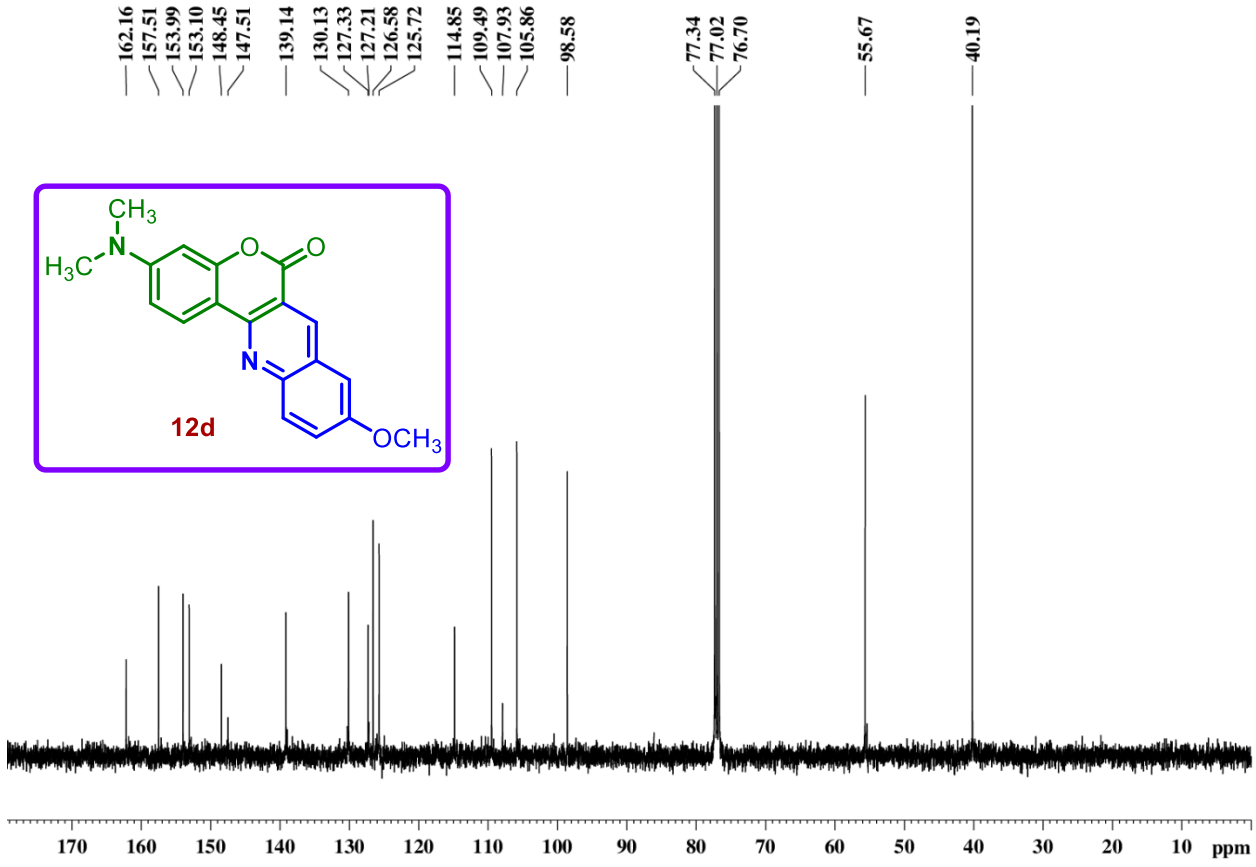
^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **12c**



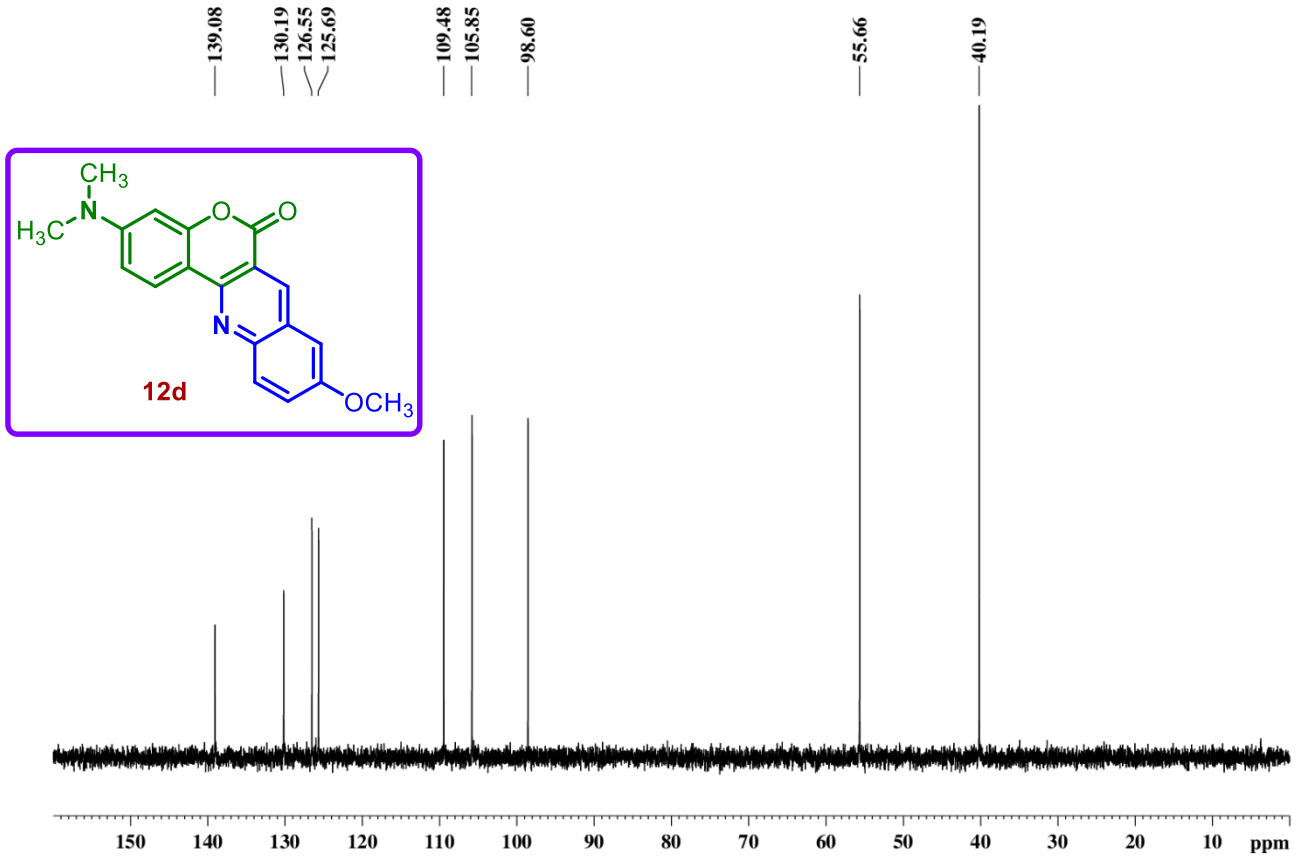
^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$) spectra of compound **12c**



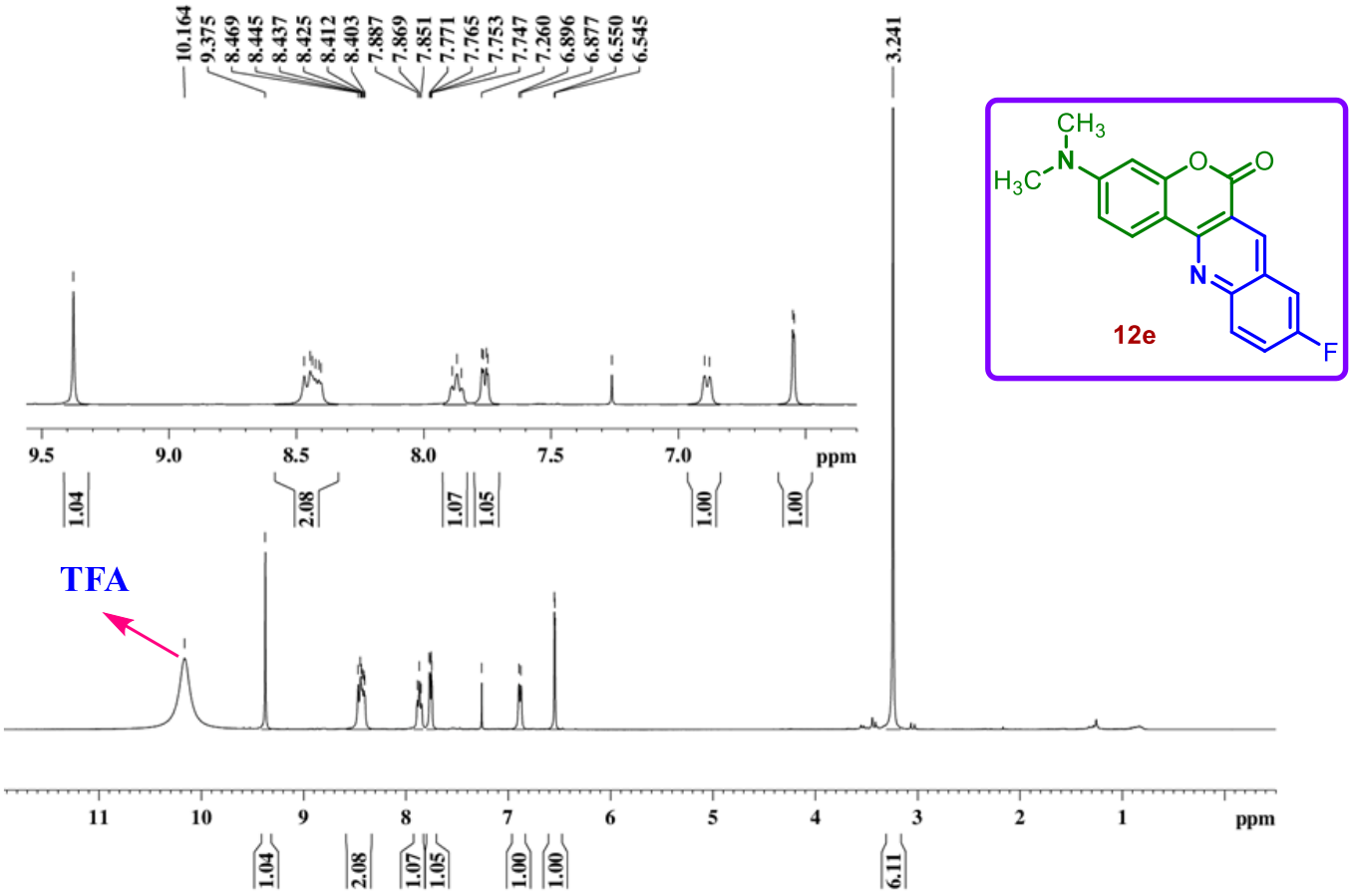
^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **12d**



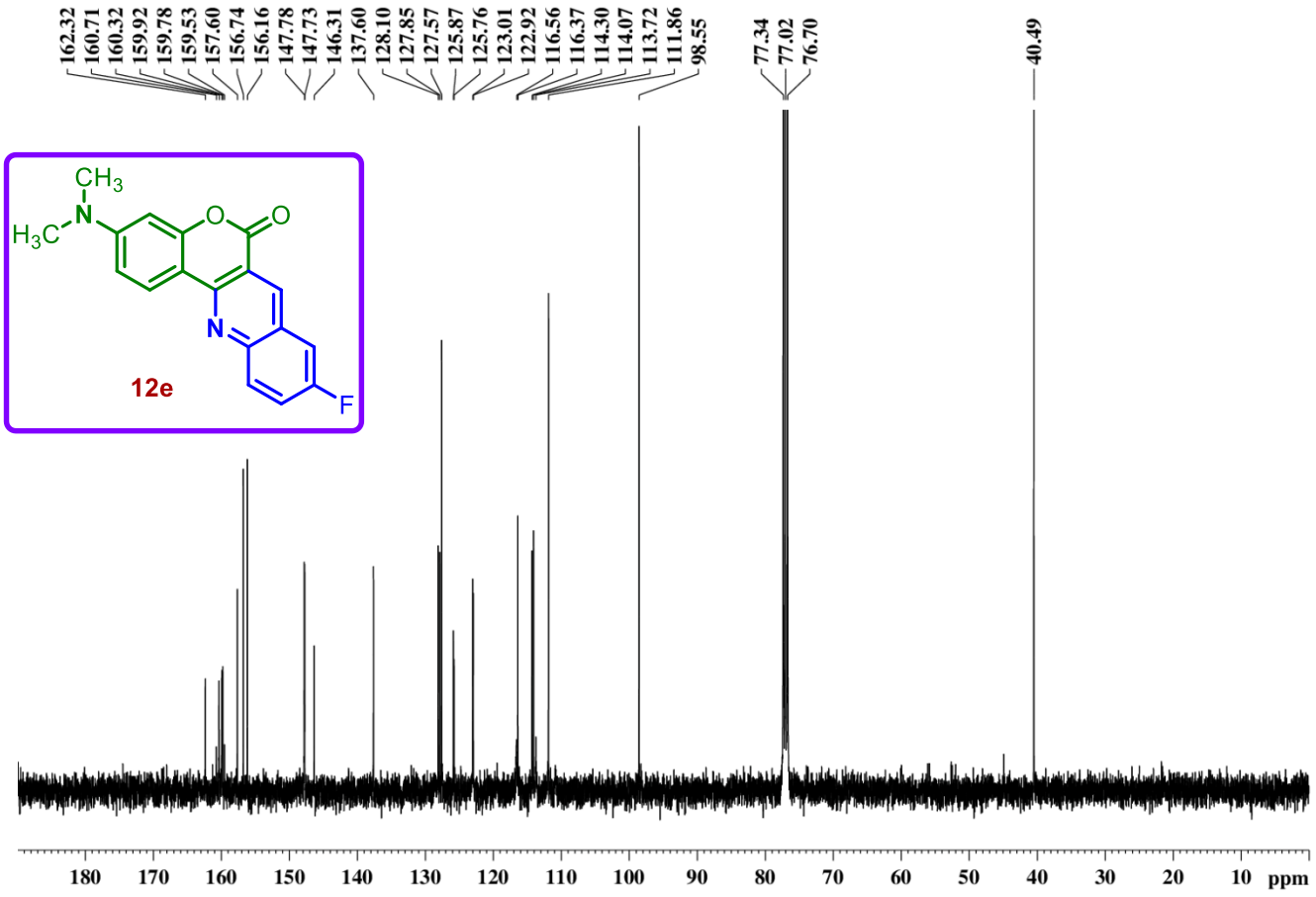
^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$) spectra of compound **12d**



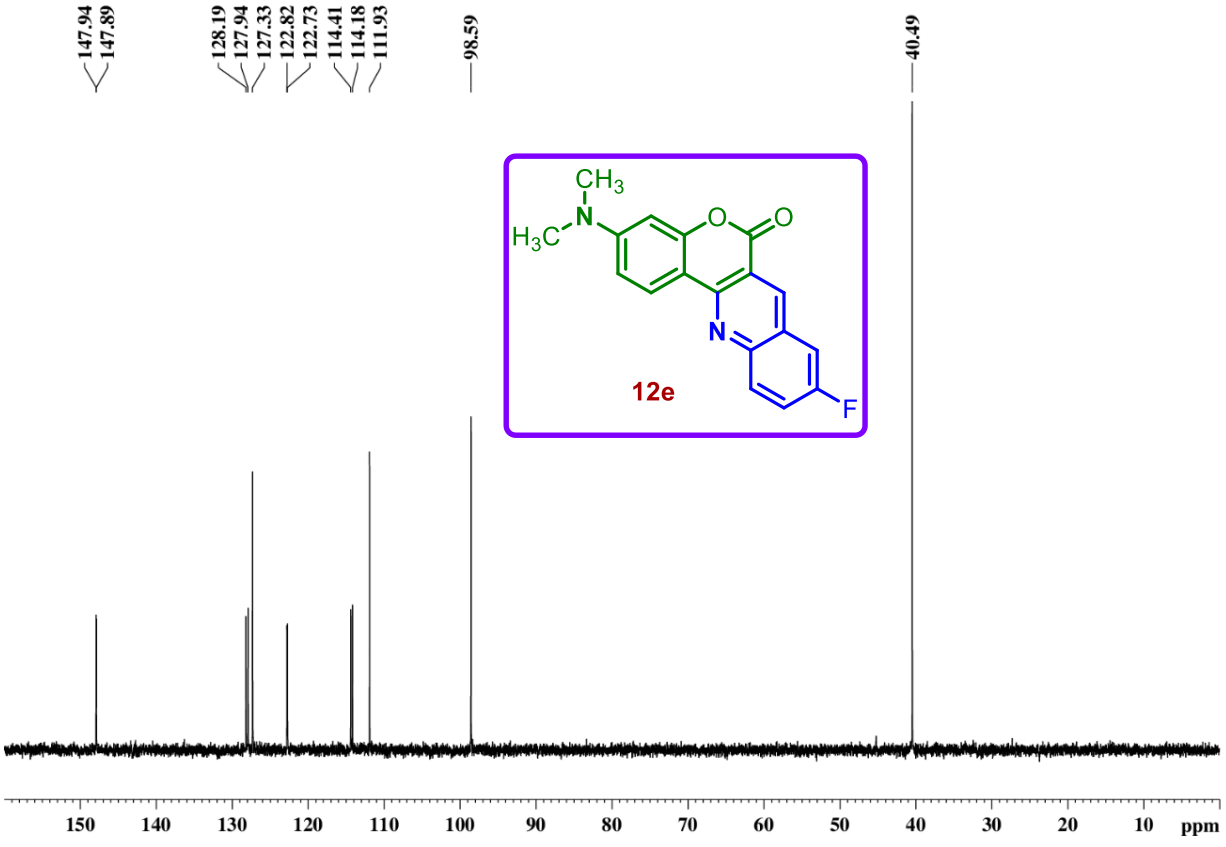
DEPT-135 NMR (100.6 MHz, $CDCl_3$) spectra of compound **12d**



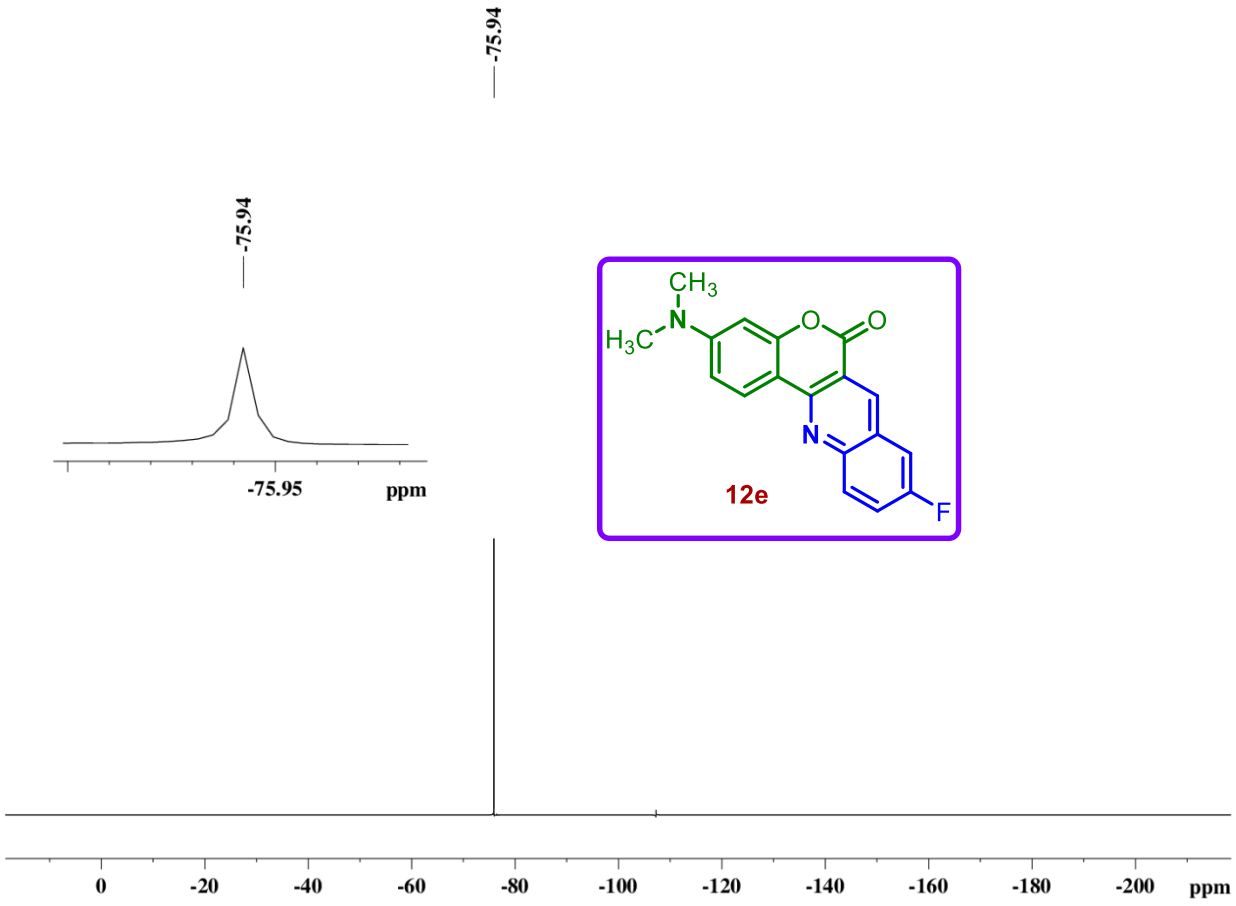
^{1}H NMR (400 MHz, $CDCl_3$+ TFA) spectra of compound **12e**



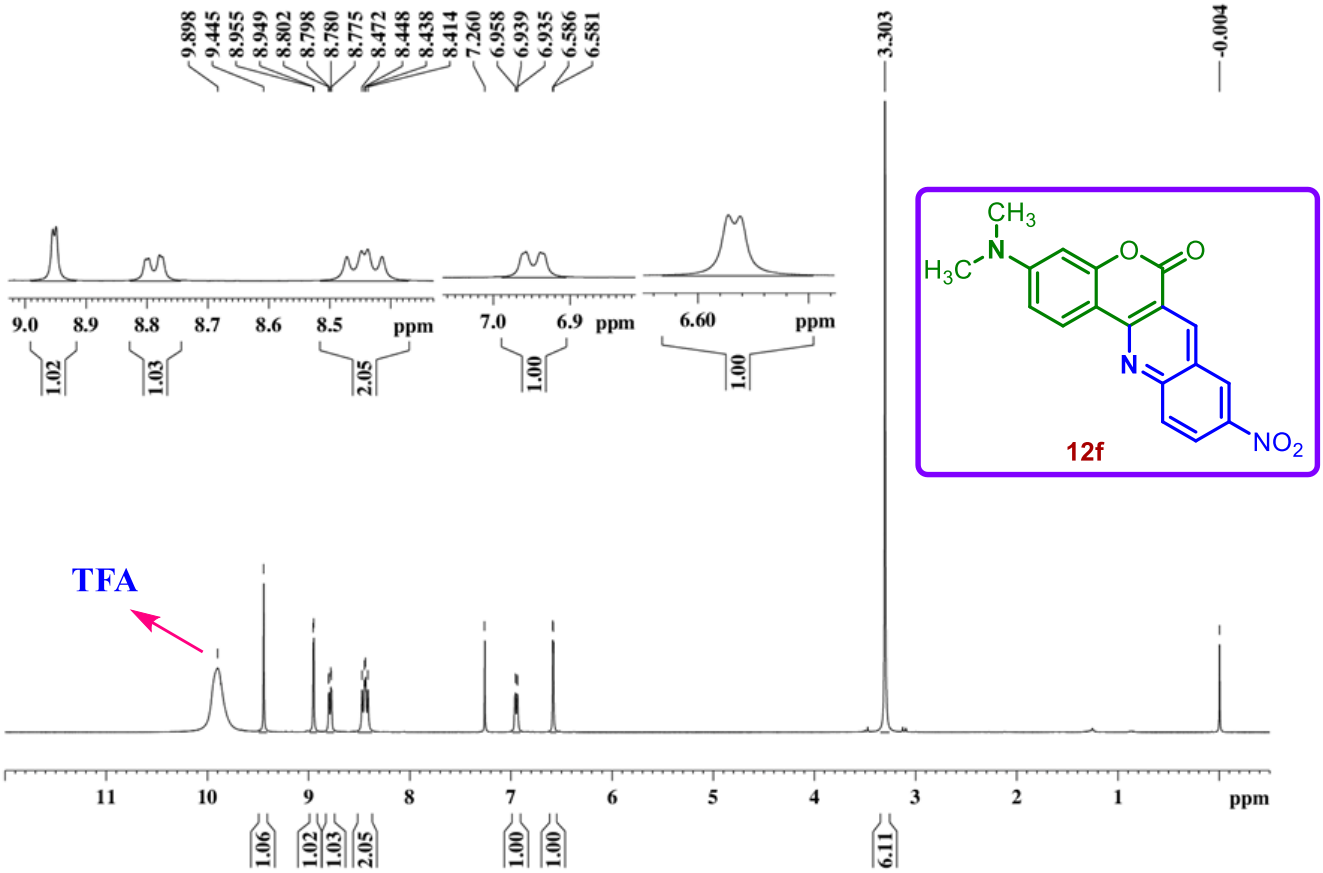
^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$+ TFA) spectra of compound **12e**



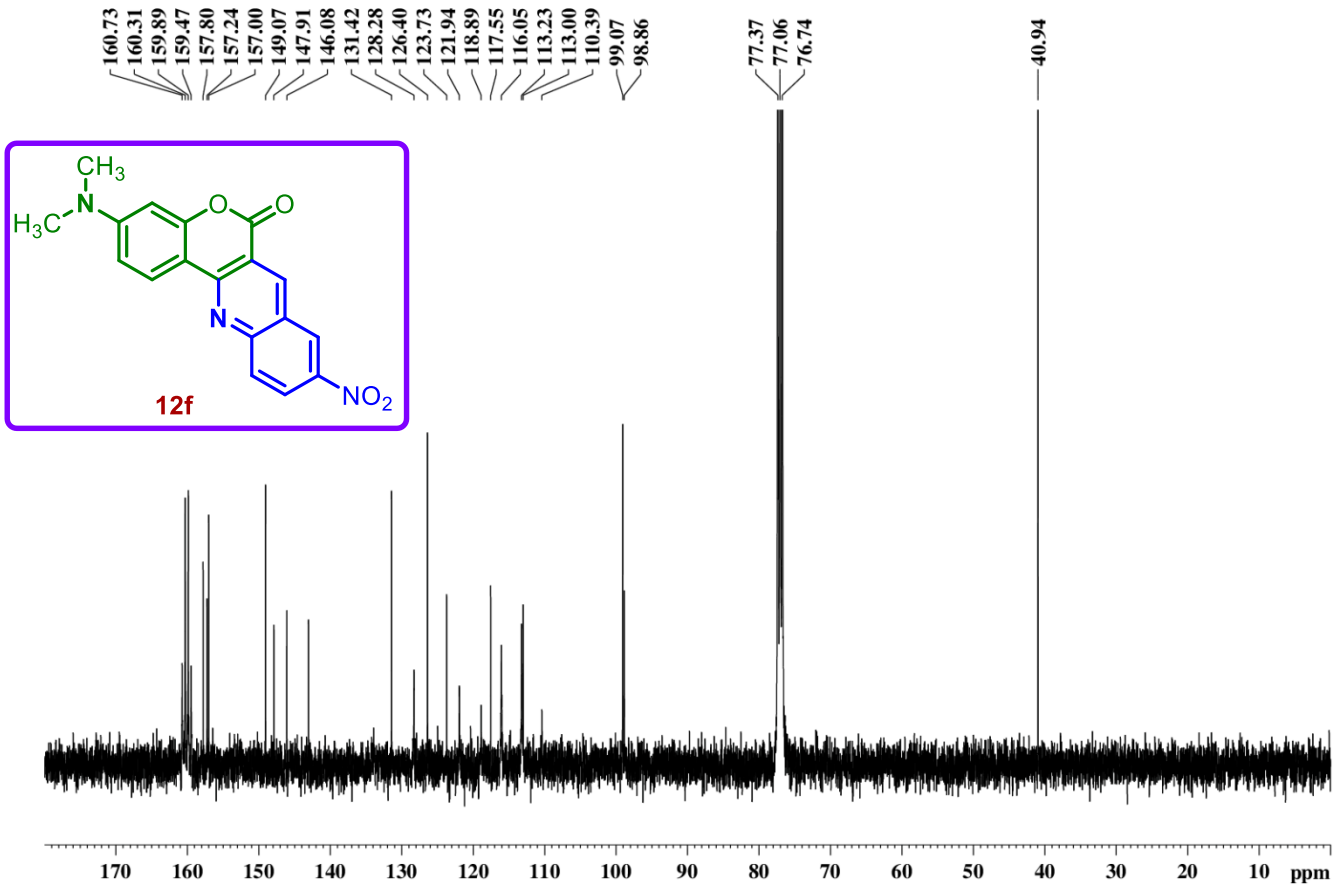
DEPT-135 NMR (100.6 MHz, $CDCl_3$) spectra of compound **12e**



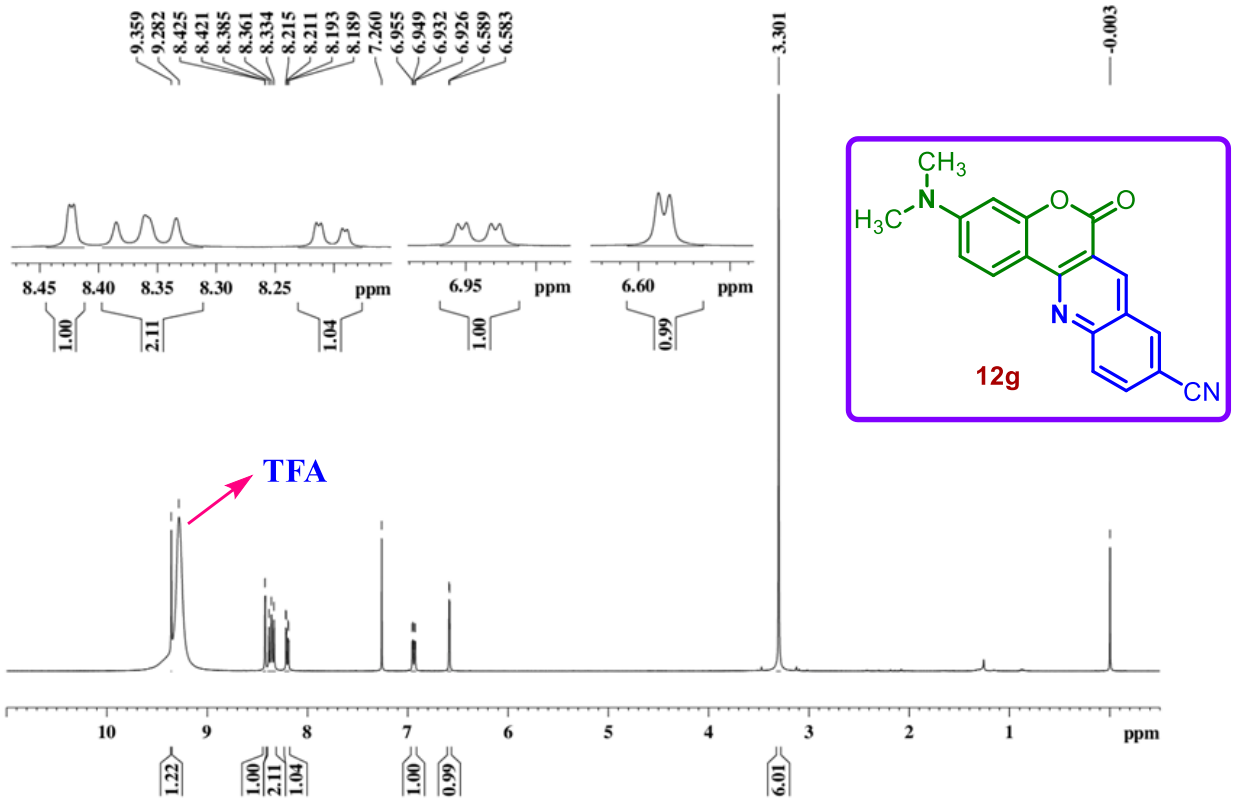
^{19}F NMR (100.6 MHz, $CDCl_3$) spectra of compound **12e**



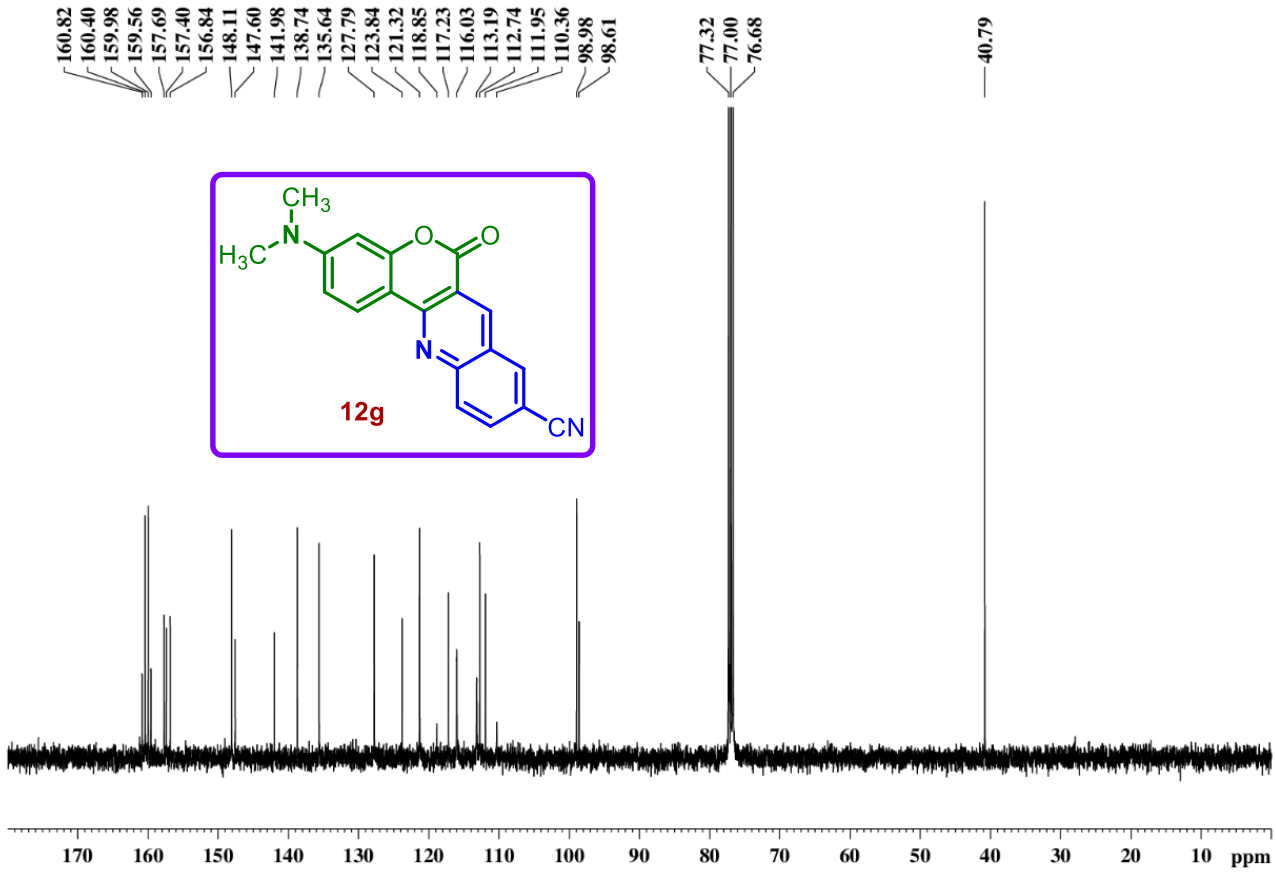
^{1}H NMR (400 MHz, $CDCl_3$+TFA) spectra of compound **12f**



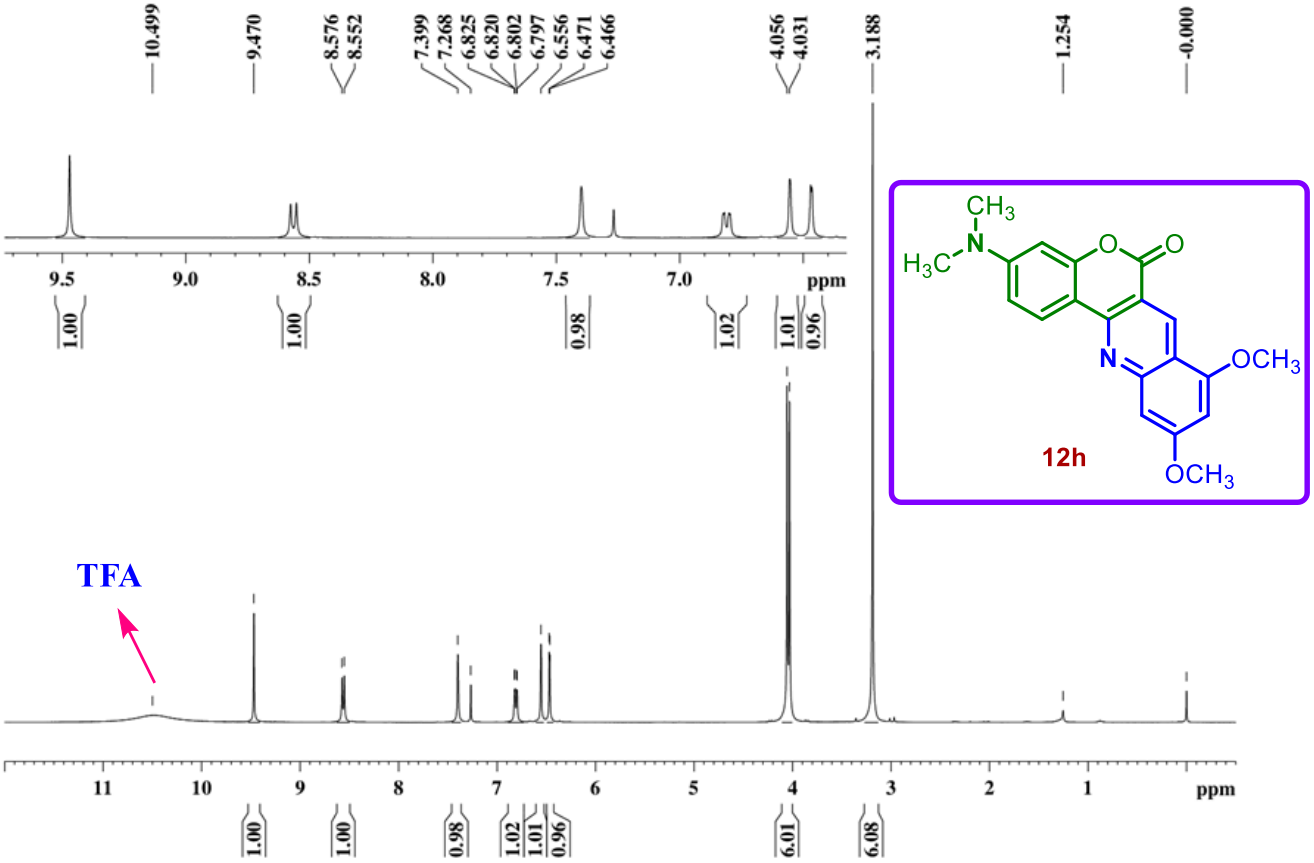
^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$+TFA) spectra of compound **12f**



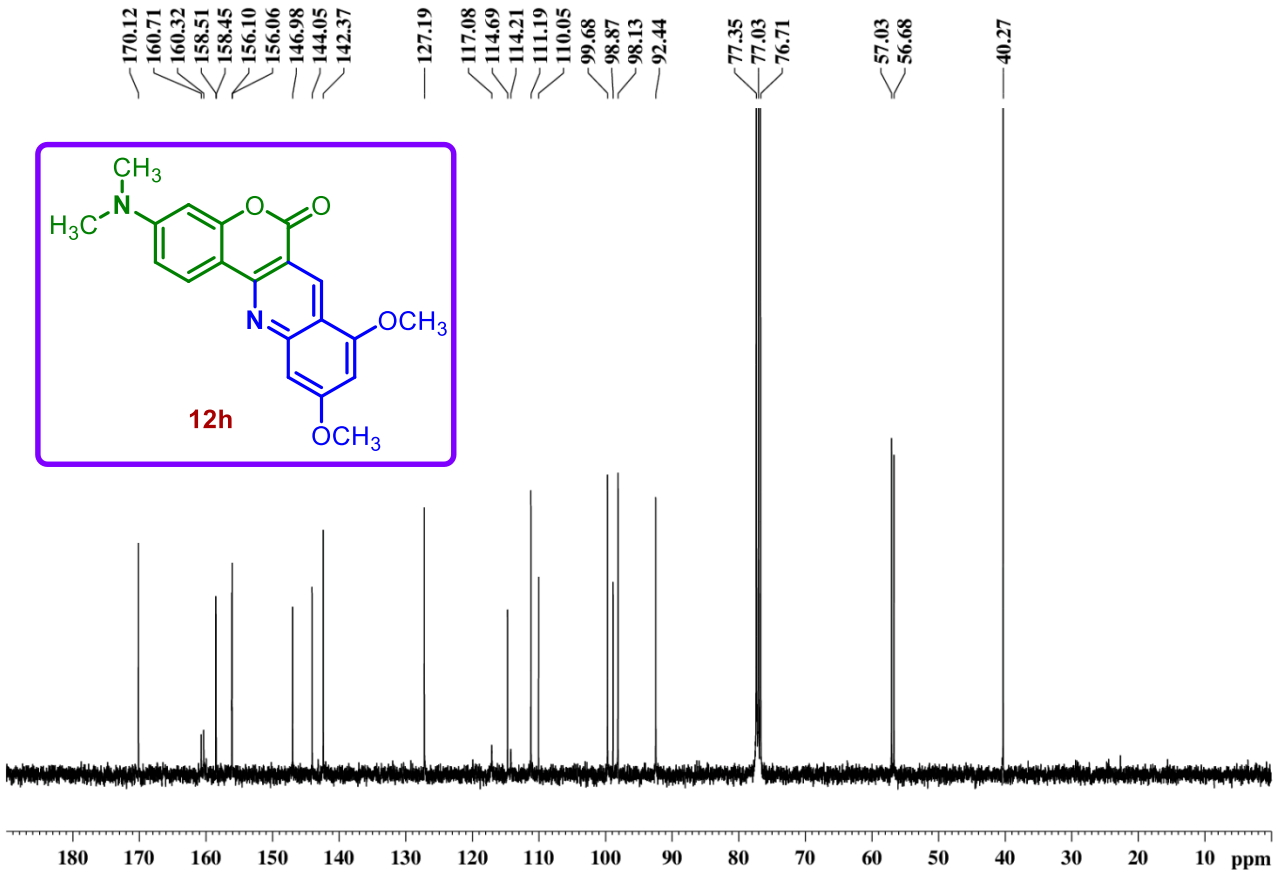
^{1}H NMR (400 MHz, $CDCl_3$+TFA) spectra of compound **12g**



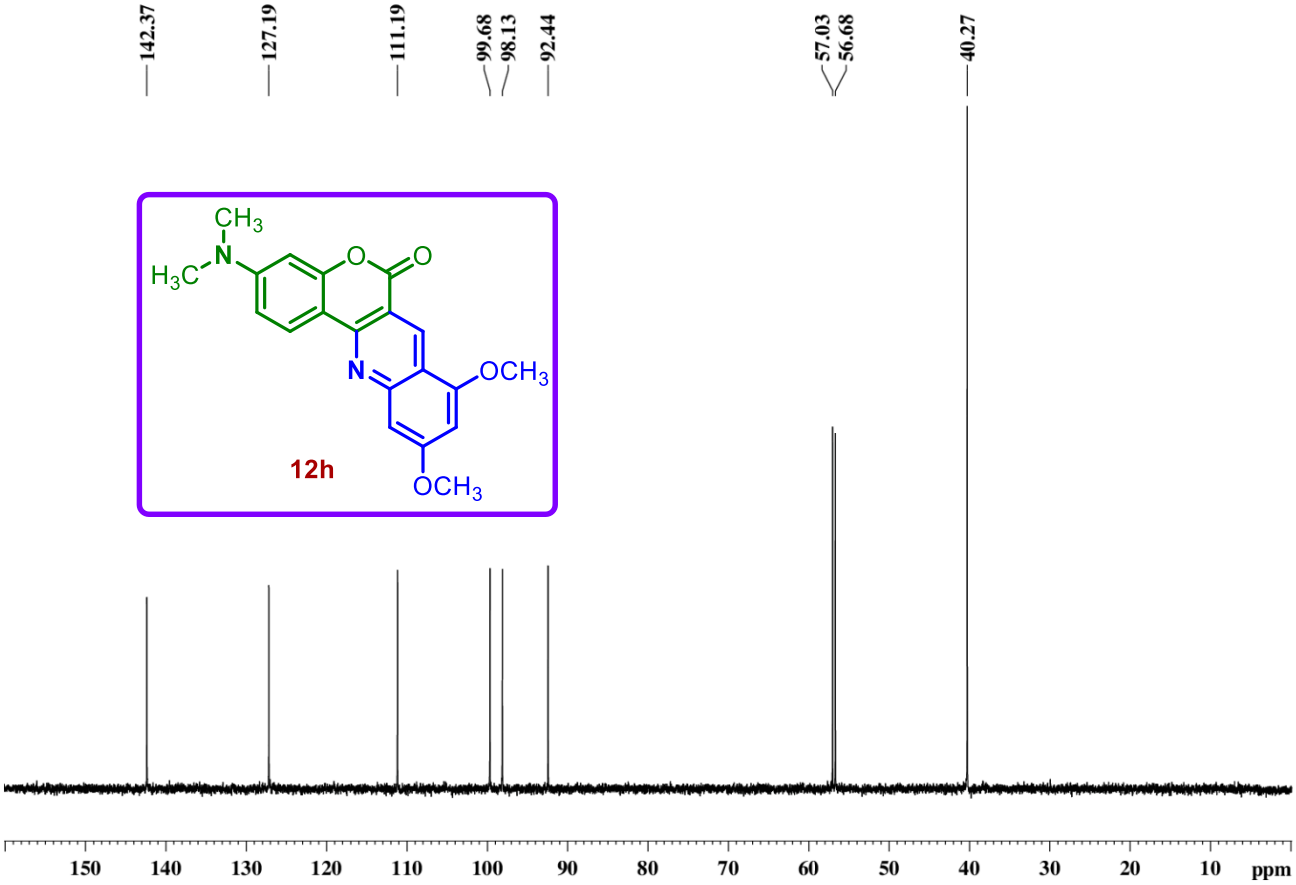
^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$+TFA) spectra of compound **12g**



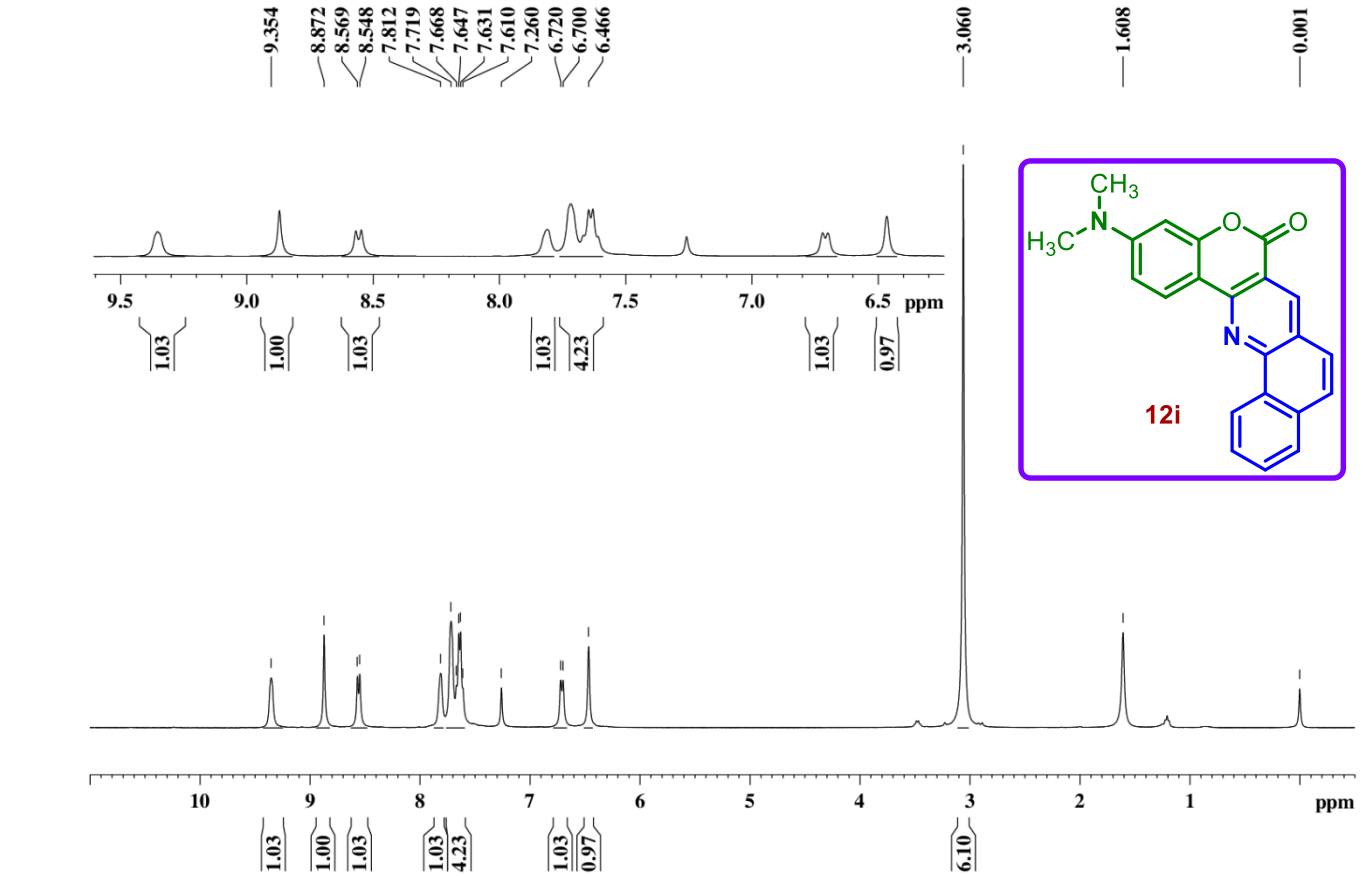
^{1}H NMR (400 MHz, $CDCl_3$+TFA) spectra of compound **12h**



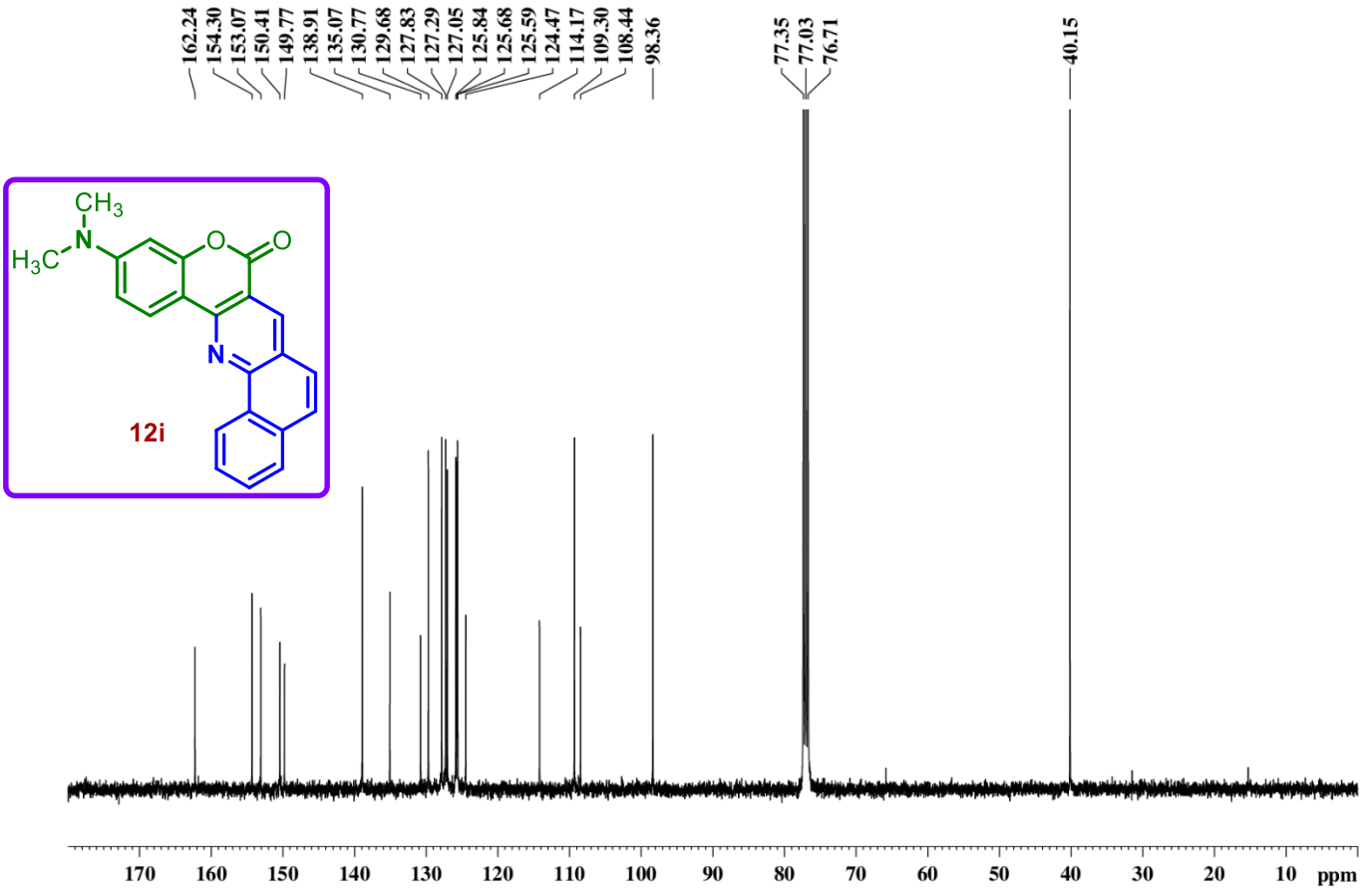
^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$+ TFA) spectra of compound **12h**



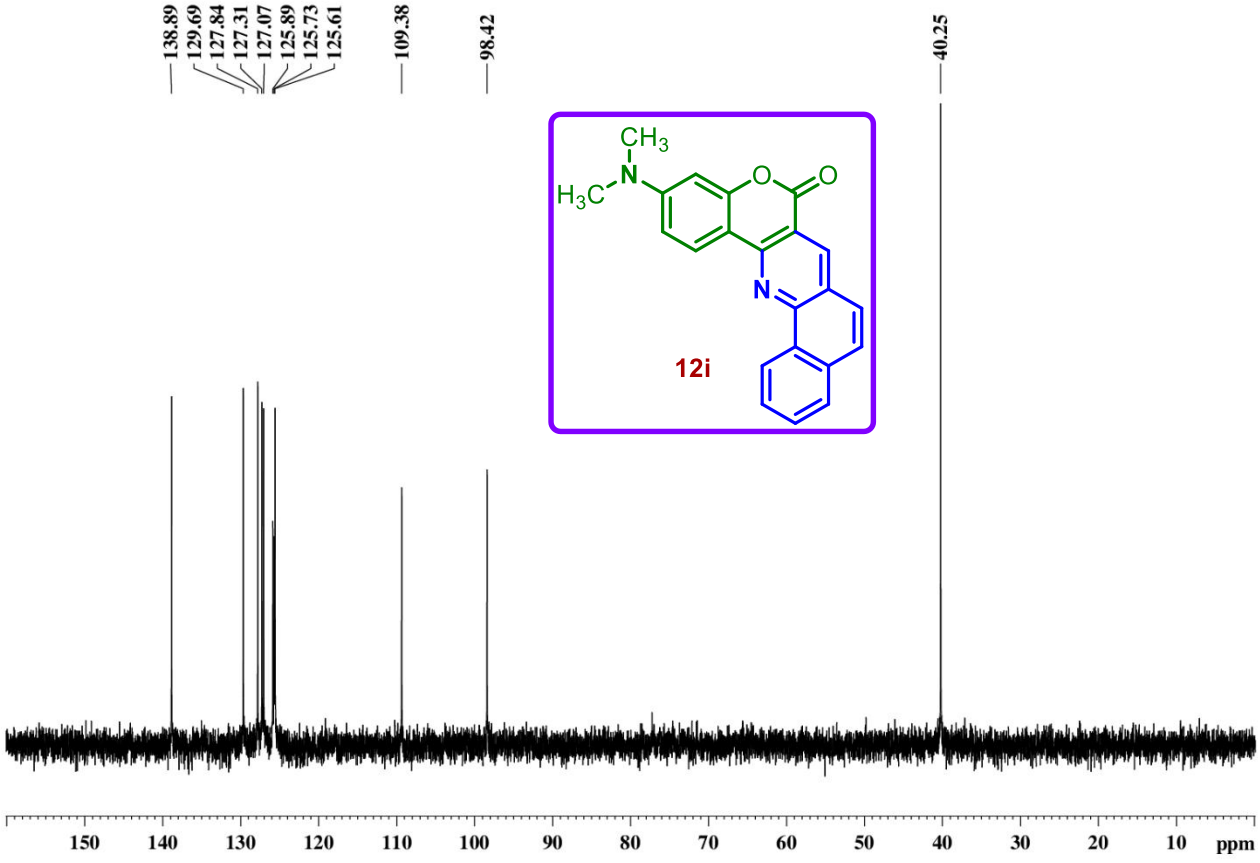
DEPT-135 NMR (100.6 MHz, $CDCl_3$) spectra of compound **12h**



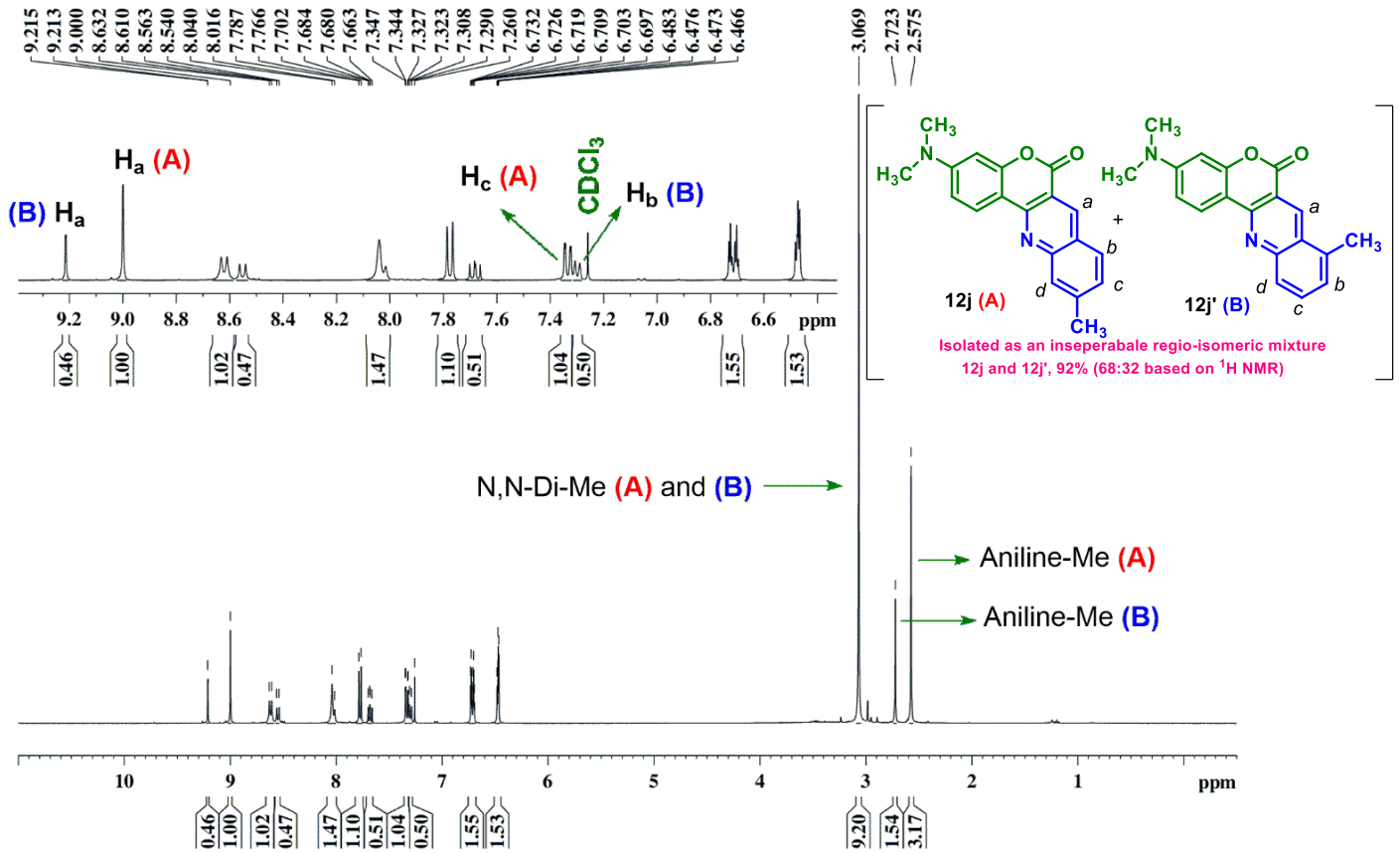
^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **12i**



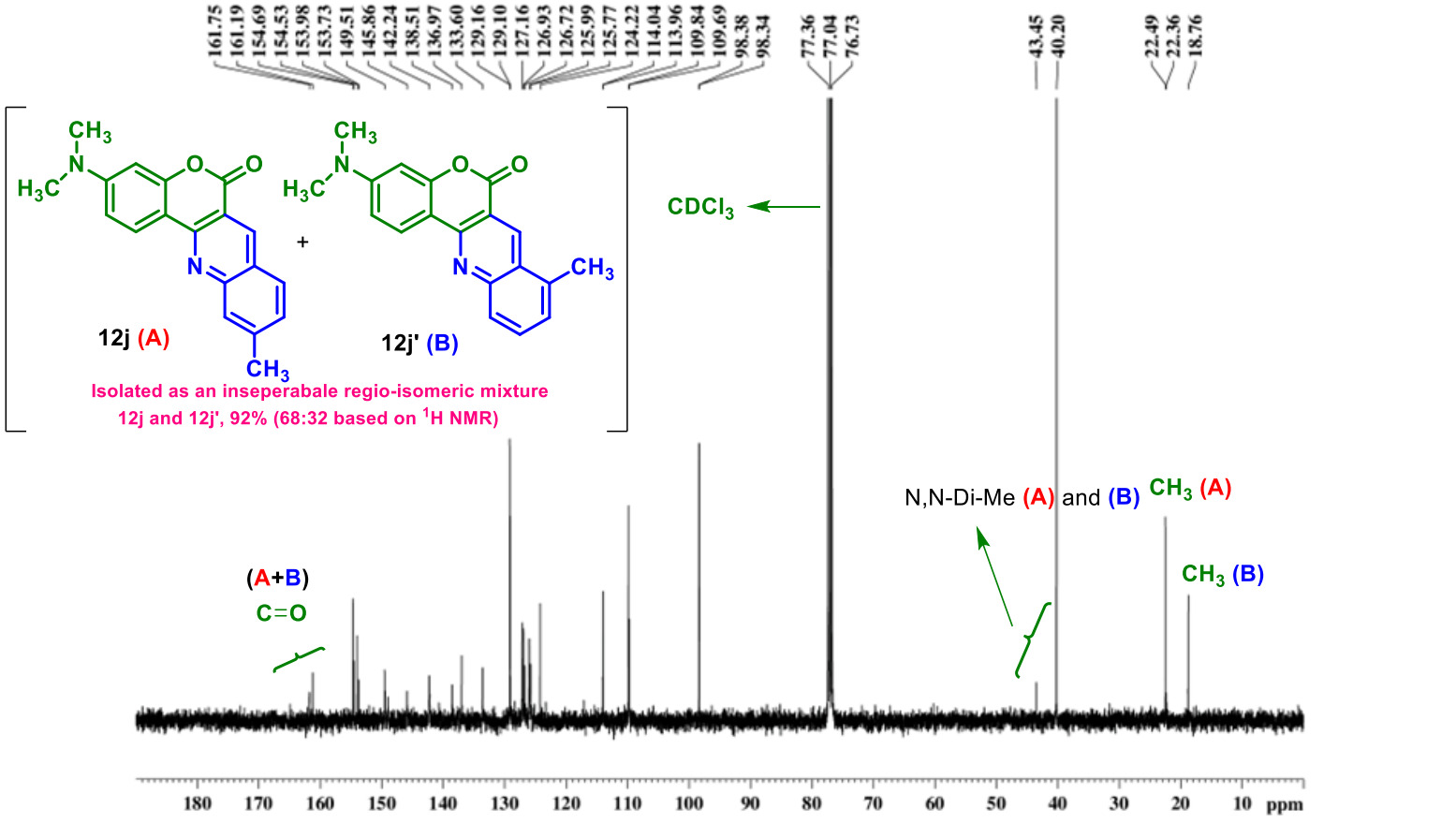
^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$) spectra of compound **12i**



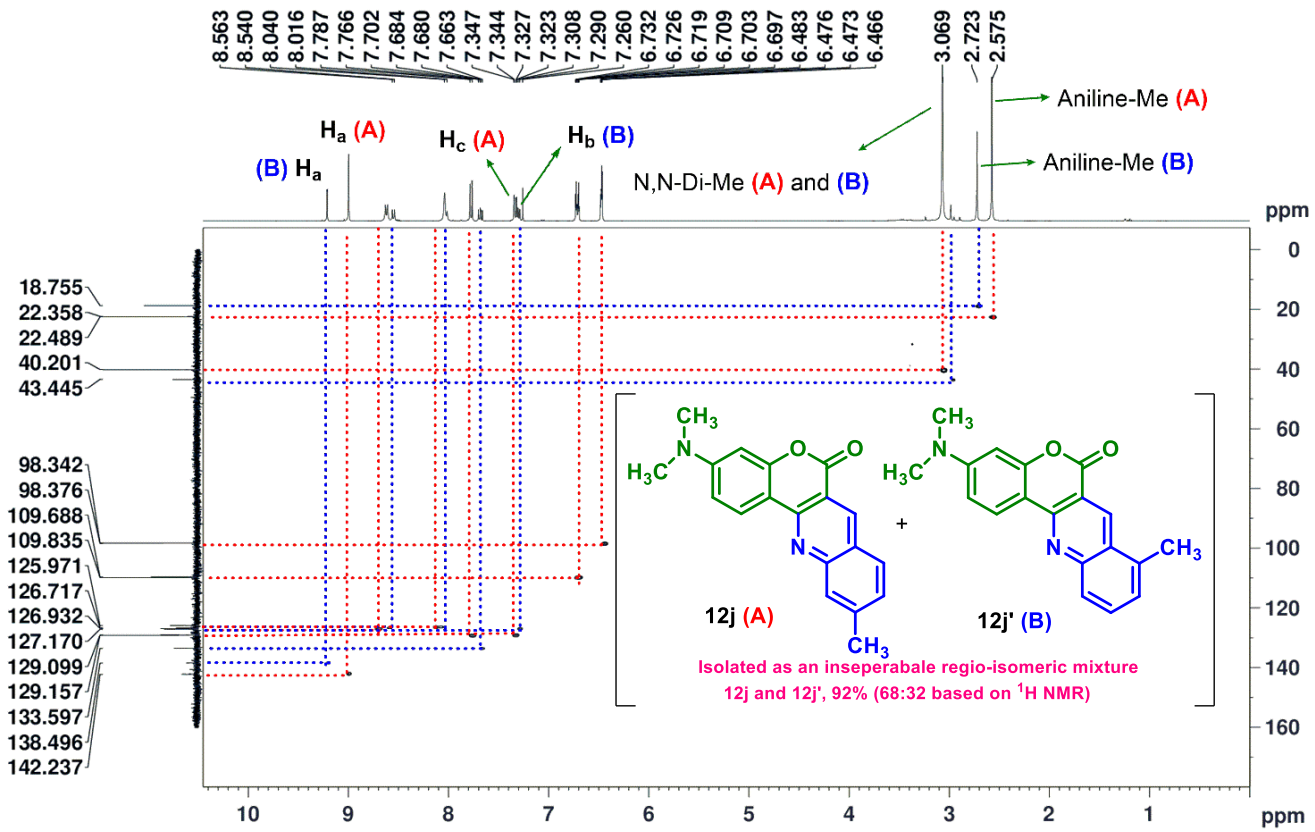
DEPT-135 NMR (100.6 MHz, $CDCl_3$) spectra of compound **12i**



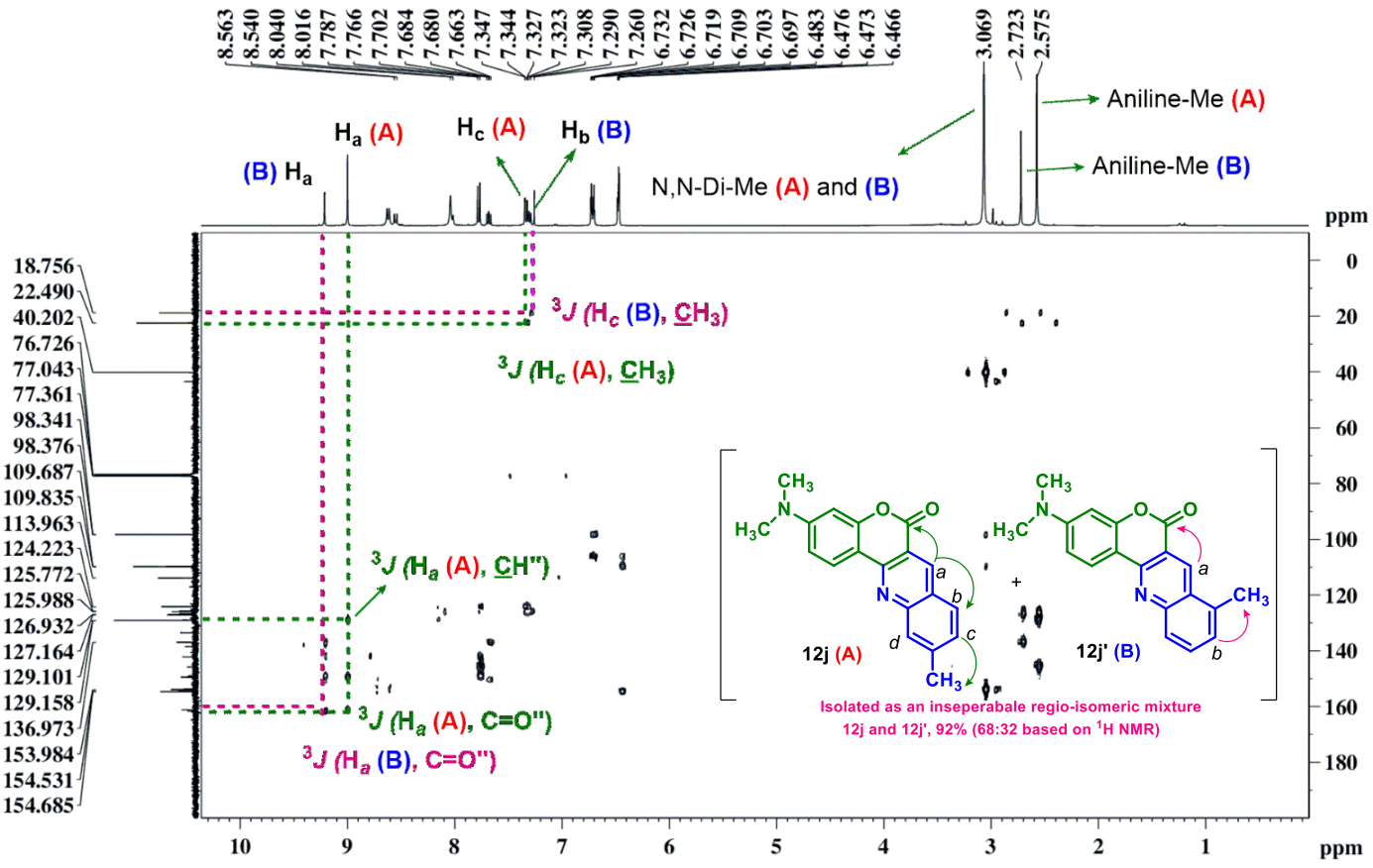
^{1}H NMR (400 MHz, $CDCl_3$) spectra of regio-isomeric mixture **12j (A)** and **12j′ (B)**



^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$+ TFA) spectra of regio-isomeric mixture **12j (A)** and **12j′ (B)**

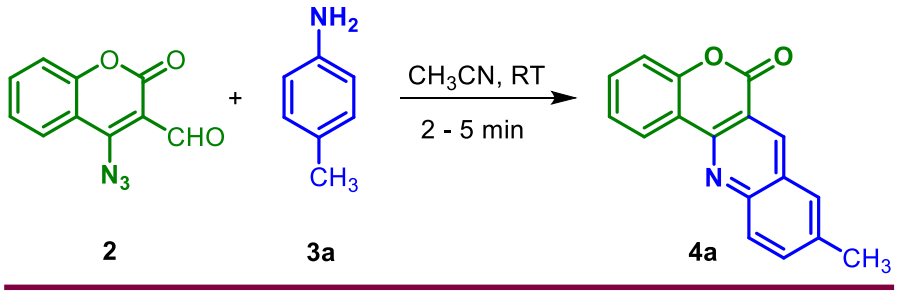


^{1}H-DEPT-135 HSQC-NMR spectra of a regio-isomeric mixture of **12j** and **12j′**



^{1}H-^{13}C HMBC NMR spectra of a regio-isomeric mixture of **12j** and **12j′**

4. Gram-Scale Synthesis of C3-C4 quinoline fused coumarin (4a) from 4-azido-2-oxo-2*H*-chromene-3-carbaldehyde (2):



To a solution of 4-azido-2-oxo-2*H*-chromene-3-carbaldehyde **2** (1 g, 4.65 mmol) in CH_3CN was added *p*-toluidine **3a** (0. 498 g, 5.58 mmol, 1.2 equiv.) at room temperature. After addition, the reaction mixture was stirred for 5 min. Then, the reaction was monitored using *tlc*. Upon completion, it was slowly poured into chopped ice. The solid obtained was filtered, washed with excess water and hexane, and dried to furnish pure 6*H*-chromeno[4,3-*b*]quinolin-6-one **5b** (1.17 g, 4.48 mmol, 97%) as a white solid.

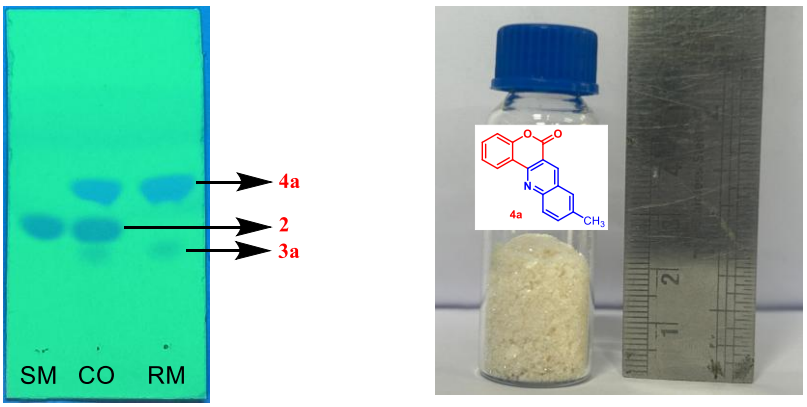
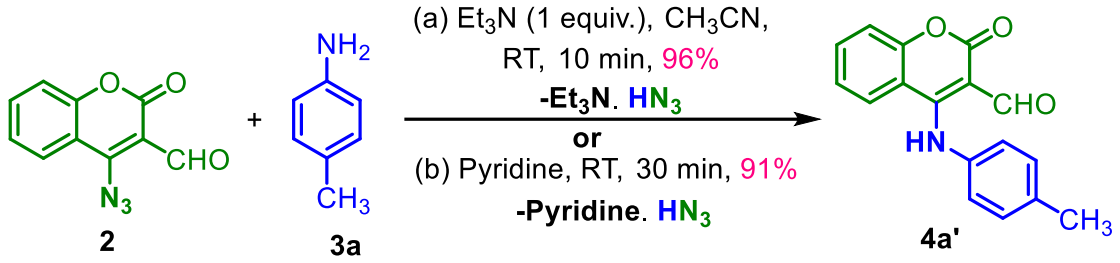


Figure S1. The images of *tlc* vision of crude reaction mixture (left) and isolated compound (right)

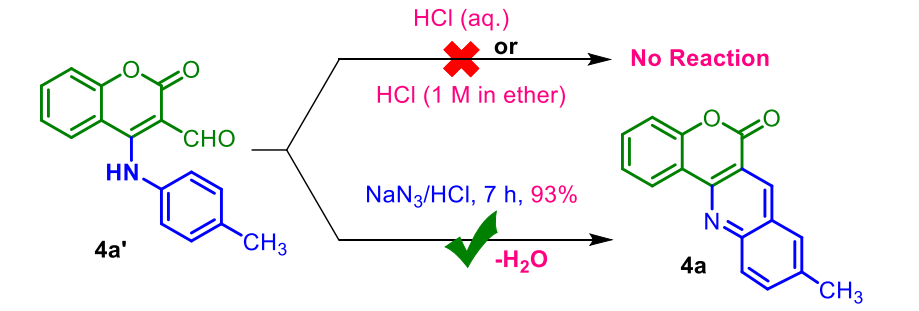
5. Control Experiment Discussion:

A. Entrapment of *"in-situ"* generated HN_3 by triethylamine and pyridine:[11]

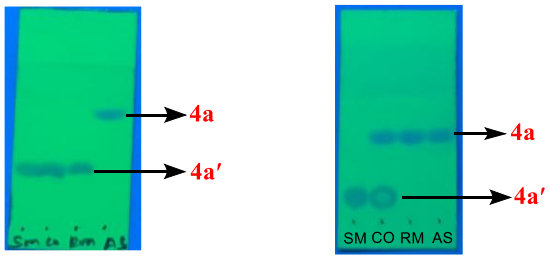


To a solution of 4-azido-2-oxo-2*H*-chromene-3-carbaldehyde **2** (100 mg, 0.46 mmol) in CH_3CN was added Et_3N (47 mg, 0.46 mmol, 1 equiv.) followed by the addition of *p*-toluidine **3a** (60 mg, 0.56 mmol, 1.2 equiv.) at room temperature. Then, the reaction was monitored using *tlc*. Upon completion, it was slowly poured into chopped ice. The solid obtained was filtered, washed with excess water and hexane, and dried to furnish pure 2-oxo-4-(*p*-tolylamino)-2*H*-chromene-3-carbaldehyde **4a′** (125 mg, 0.45 mmol, 96%) as a white solid. Similarly, repetition of the reaction in pyridine as a solvent/base furnish pure 2-oxo-4-(*p*-tolylamino)-2*H*-chromene-3-carbaldehyde **4a′** (118 mg, 0.42 mmol, 91%) as a white solid.

B. Comparison of aldehyde activation by HCl and HN_3:



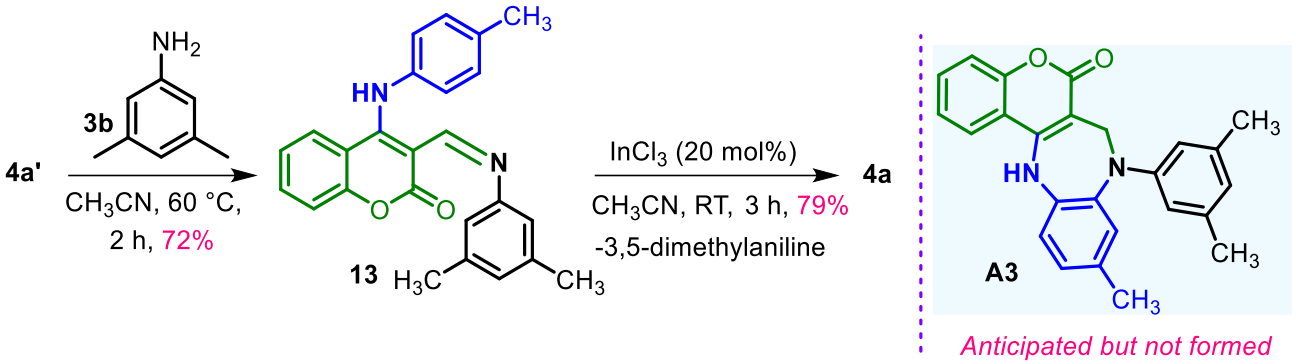
The Aldrich-Ace pressure tube (25 mL capacity) equipped with a magnetic stirrer bar was added 2-oxo-4-(*p*-tolylamino)-2*H*-chromene-3-carbaldehyde **4a′** (0.05 g, 0.18 mmol) in aqueous HCl at room temperature. Then, the reaction was monitored for up to 48 hours. Further, we observed no progress in this transformation when using aqueous HCl as a solvent at RT; only the starting material **4a′** was recovered. Similarly, on the other hand, the reaction of 4-(N-arylamino)-3-formylcoumarin **4a′** was carried using aqueous HCl as a solvent in the presence of sodium azide (10 equiv.) at RT furnished the CQ **4a** in (44 mg, 0.17 mmol, 93% as a white solid) isolated yield and this observation corroborates that the activation of aldehyde group by an '*in-situ*' generated hydrazoic acid[12] is very efficient rather than HCl for this transformation.



TLC vision under ultraviolet (254 nm)

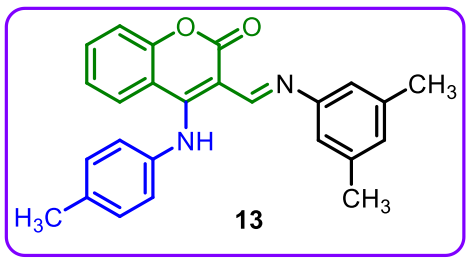
Figure S1. The images of *tlc* vision of crude reaction mixture of aqueous HCl (left) and crude reaction mixture of NaN_3 (10 equiv) and aqueous HCl (right).

C. Attempted synthesis of coumarin C3-C4 fused 1,5-benzodiazepine scaffold:



(*E*)-3-(((3,5-dimethylphenyl)imino)methyl)-4-(*p*-tolylamino)-2*H*-chromen-2-one (13):

To a solution of 2-oxo-4-(*p*-tolylamino)-2*H*-chromene-3-carbaldehyde **4a′** (0.2 g, 0.72 mmol) in CH_3CN was added dimethylaniline (104 mg, 0.86 mmol, 1.2 equiv.) at room temperature. After addition, the reaction mixture was heated at 60 °C in a pre-heated oil bath with continuous stirring until the disappearance of starting material **4a′** in *tlc*; upon completion, the solid product was filtered through German filter paper then washed with EtOH and Hexane and dried to furnish pure imine derivative **13** (0.197 g, 0.51 mmol, 72%) as a yellow solid.

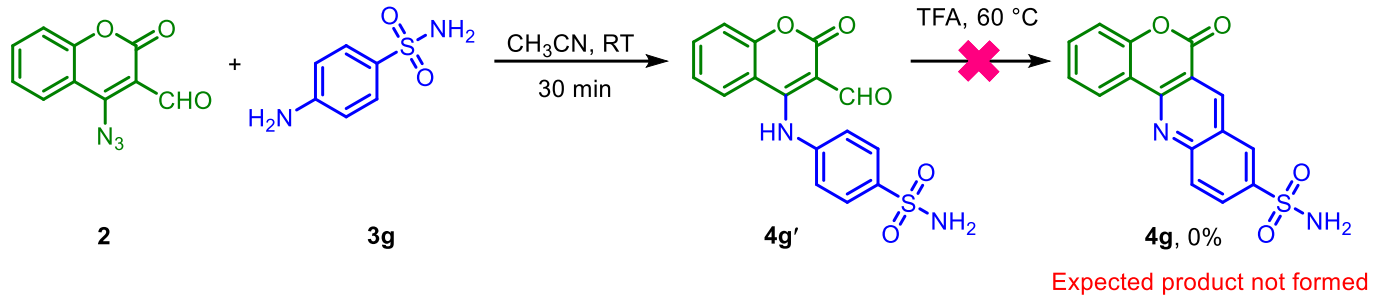


MP: 172-174 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 14.45 (brs, 1H, D_2O-exchangeable), 9.15 (s, 1H), 7.43 (t, J = 8.0 Hz, 1H), 7.31-7.28 (m, 2H), 7.22 (d, J = 8.0 Hz, 2H), 7.12 (t, J = 8.0 Hz, 2H), 6.91–6.86 (m, 4H), 2.41 (s, 3H), 2.32 (s, 6H); **^{13}C{^{1}H} NMR** ($CDCl_3$, 100.6 MHz): δ 163.1, 158.0, 154.6, 154.3, 148.6, 139.0, 138.5, 136.5, 132.6, 130.4, 127.9, 127.4, 124.4, 122.7, 118.7, 118.1, 114.4, 96.1, 21.3, 21.1; **IR (neat):** 2914, 1703, 1601, 1559, 1462, 1293, 1180, 1042, 987, 854; **HRMS** (ESI) m/z calcd. For $C_{25}H_{23}N_2O_2$ $[M+H]^+$: 383.1754 found: 383.1756.

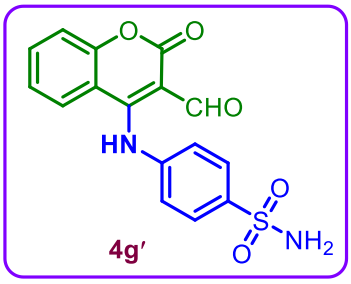
9-methyl-6*H*-chromeno[4,3-b]quinolin-6-one (4a):

To a solution of (*E*)-3-(((3,5-dimethylphenyl)imino)methyl)-4-(*p*-tolylamino)-2*H*-chromen-2-one (50 mg, 0.13 mmol) in CH_3CN was added $InCl_3$ (6 mg, 0.02 mmol, 0.2 equiv.) at room temperature. After addition, the reaction mixture was stirred at room temperature until the starting material disappeared in *tlc;* upon completion, it was slowly poured into chopped ice. Then, the mixture was extracted with $CHCl_3$ (3× 10 mL), washed with water filtered, and purified through column chromatography. To obtain 6*H*-chromeno[4,3-*b*]quinolin-6-one **4a** (27 mg, 0.10 mmol, 79%) as a white solid with the elimination of 3,5-dimethylaniline[13].

D. Reaction of 4-azido-2-oxo-2*H*-chromene-3-carbaldehyde (2) with 4-aminobenzenesulfonamide (3g):

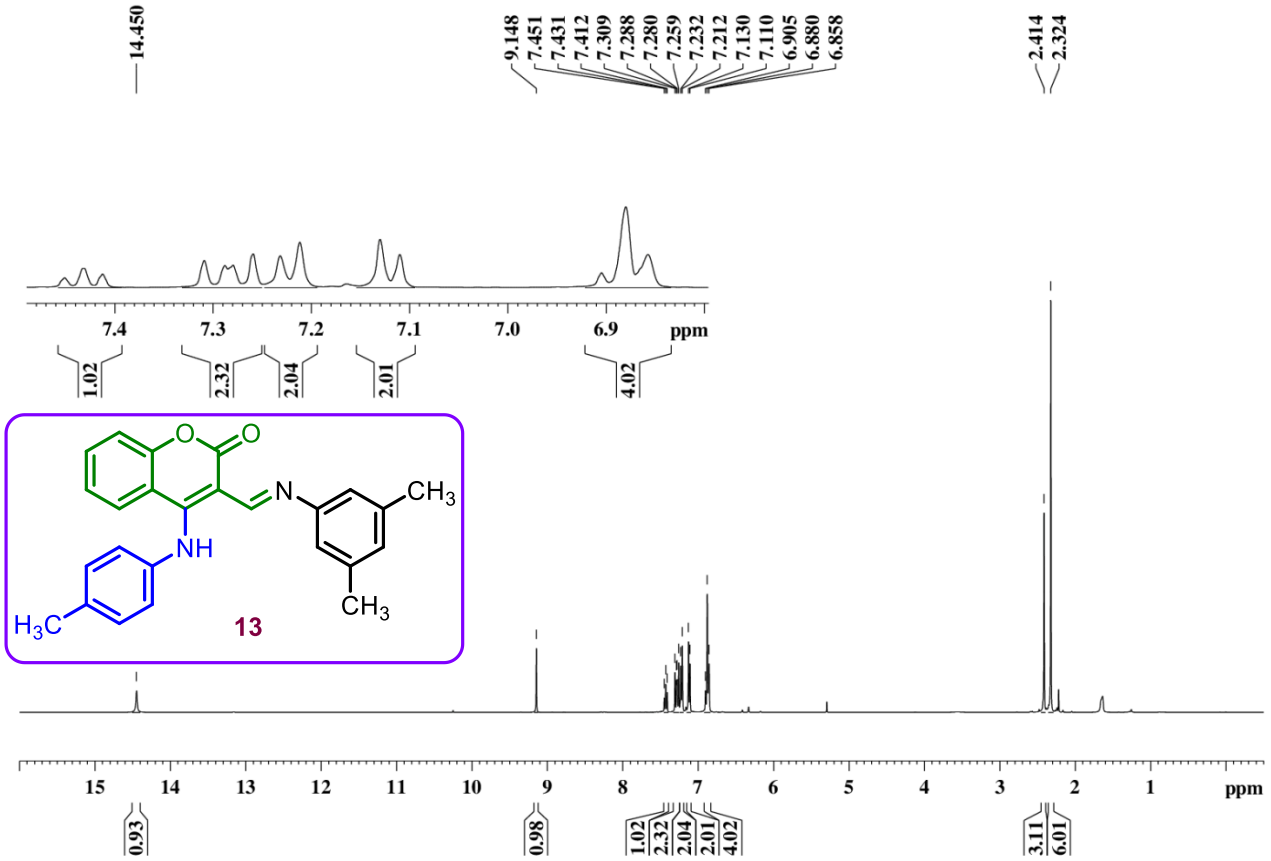


The reaction of azide **2** (100 mg, 0.46 mmol) with 4-aminobenzenesulfonamide **3g** (96 mg, 0.56 mmol, 1.2 equiv.) in acetonitrile at RT procured significantly 4-((3-formyl-2-oxo-2*H*-chromen-4-yl)amino)benzenesulfonamide **4g′** (0.141 g, 0.41 mmol) in 88% isolated yield as the only product rather than the anticipated CQ **4g**. Further, we attempted the Pomeranz-Fritsch type cyclization[10] of 4-((3-formyl-2-oxo-2*H*-chromen-4-yl)amino)benzene sulfonamide **4g′** using CF_3COOH at 60 °C did not furnish CQ **4g** even after 48h; and the starting material **4g′** was recovered as such due to the poor nucleophilicity of aniline nitrogen in 4-aminobenzenesulfonamide.

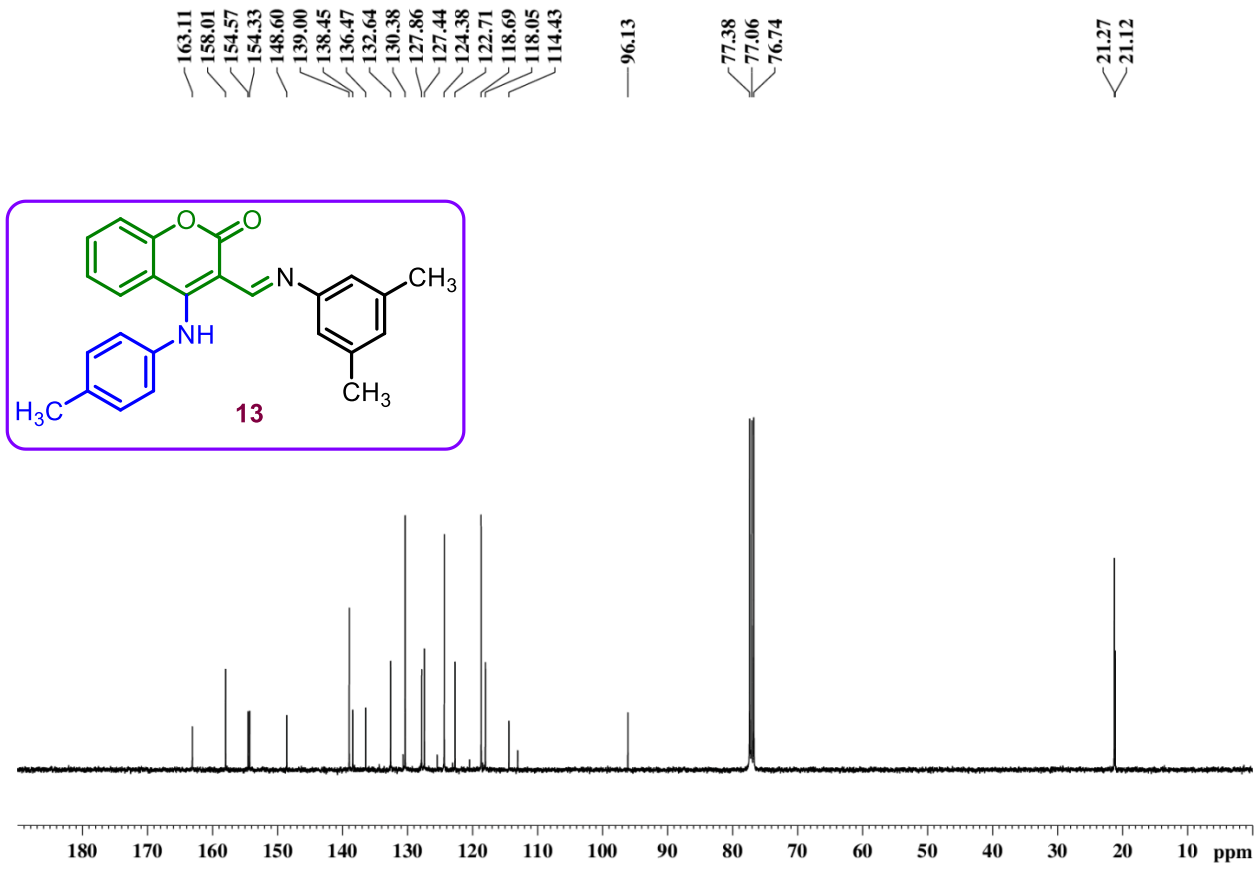


MP: 262-264 °C; **^{1}H NMR** (400 MHz, DMSO-d_6): δ 12.4 (brs, 1H, D_2O-exchangeable), 10.0 (s, 1H), 7.83-7.80 (m, 2H), 7.65-7.61 (m, 1H), 7.55 (d, J = 8.8 Hz, 2H), 7.42 (brs, 2H, D_2O-exchangeable), 7.40-7.38 (m, 1H), 7.22 (dd, J = 8.0 Hz, 1.2 Hz, 1H), 7.07-7.03 (m, 1H); **^{13}C{^{1}H} NMR** (DMSO-d_6, 100.6 MHz,): δ 191.5, 161.9, 157.1, 155.3, 142.9, 142.5, 135.5, 127.7, 127.6, 125.5, 124.0, 118.6, 113.6, 99.9; **IR (neat):** 3331, 3243, 2868, 1703, 1620, 1562, 1494, 1449, 1374, 1294, 1162, 1093, 1014, 991; **HRMS** (ESI) m/z calcd. For $C_{16}H_{13}N_2O_5S$ $[M+H]^+$: 345.0540 found: 345.0546.

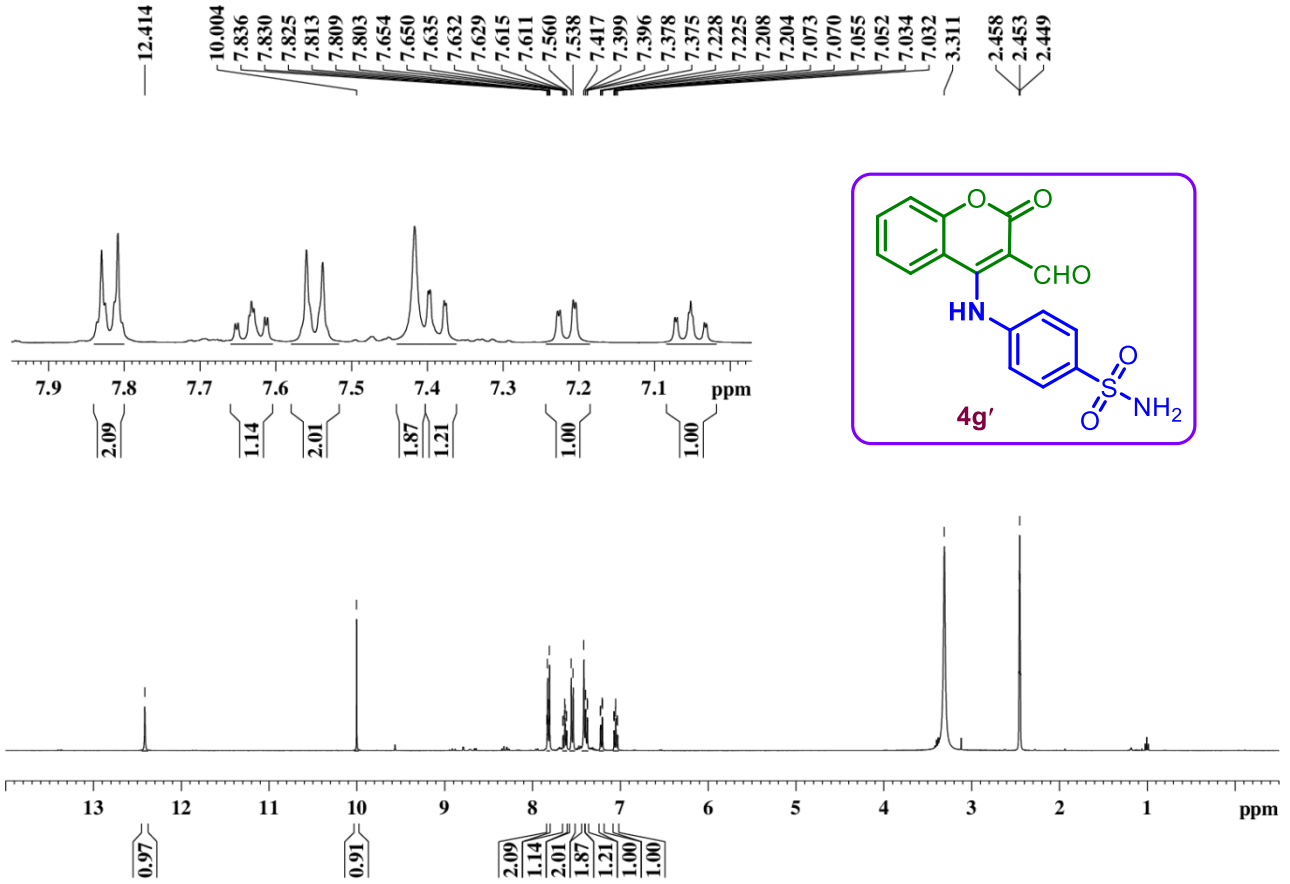
6. Control experiment NMR Spectra:



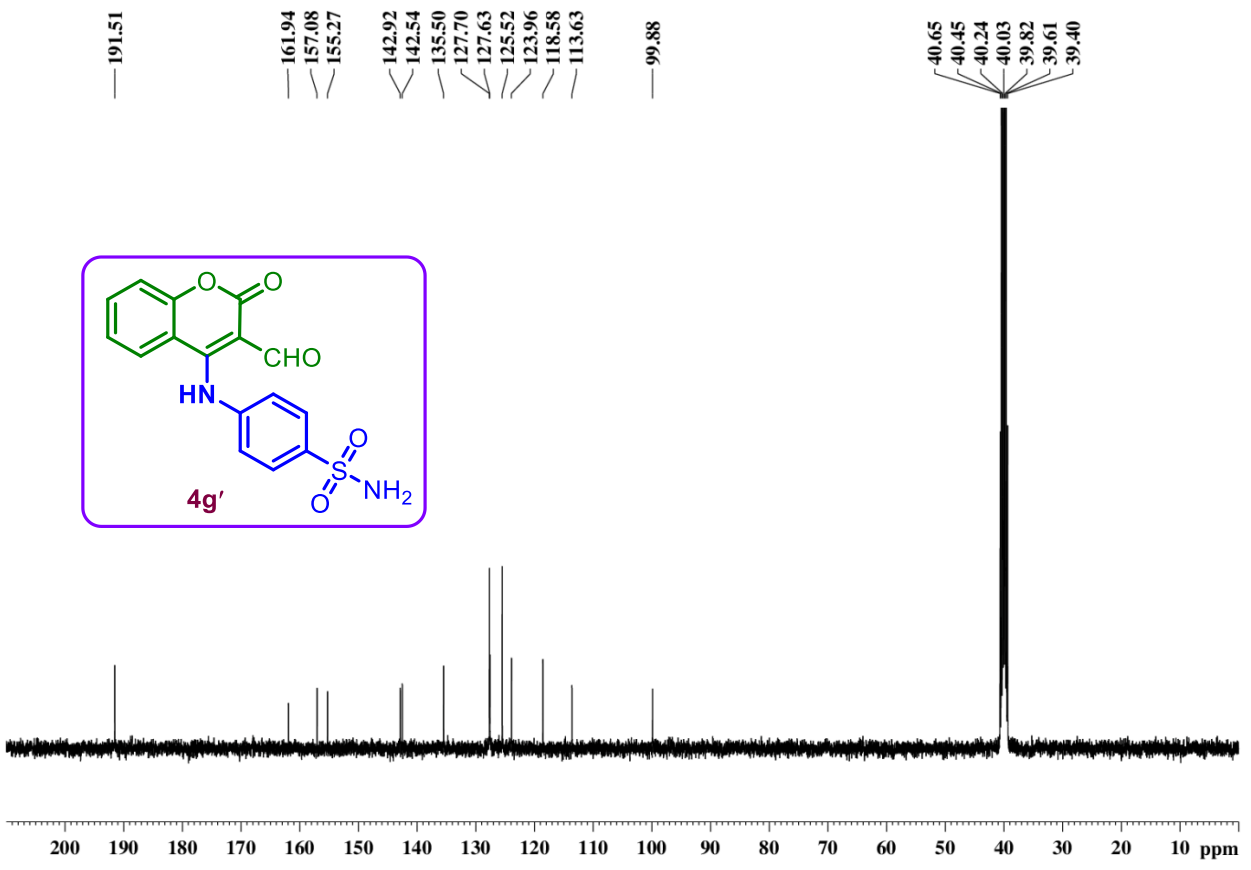
^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound **13**



^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$) spectra of compound **13**



^{1}H NMR (400 MHz, DMSO-d_6) spectra of compound **4g′**

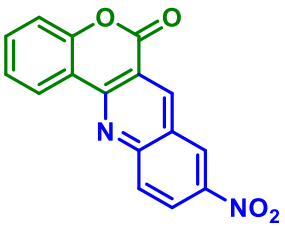


^{13}C{^{1}H} NMR (100.6 MHz, DMSO-d_6) spectra of compound **4g′**

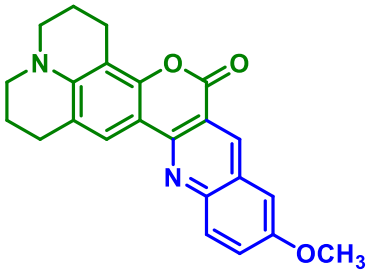
7. Single Crystal X-ray Diffraction Analysis:

List of compounds analyzed by XRD with CCDC

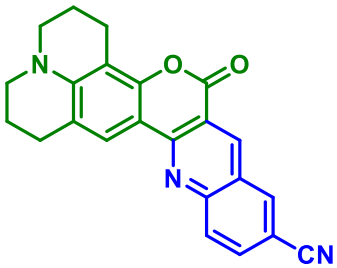
The crystallographic data of the following compound can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.



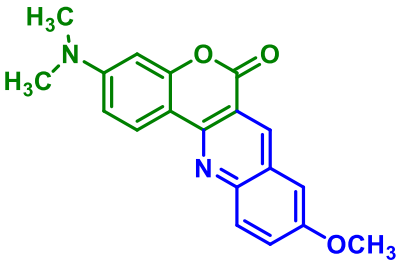
4m, **CCDC: 2208633**



8c, **CCDC: 2295078**



8e, **CCDC: 2295085**

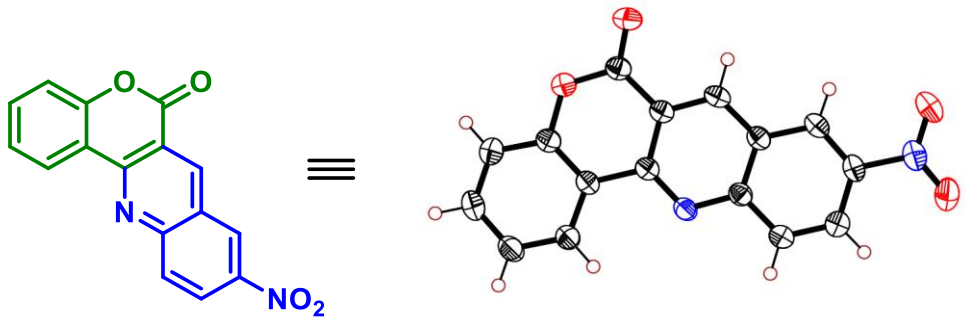


12d, **CCDC: 2201656**

X-Ray Crystallographic Data

1. Crystal data and structure refinement for compound 4m, CCDC: 2208633

Single crystals of **4m** were obtained by recrystallization from dichloroethane/ethyl acetate, furnished colorless crystals. The molecular structure and X-ray diffraction data/refinement of **4m** are given below.



4m

CCDC: 2208633

Datablock: GRK_1_070922_0m_a

Bond precision: C-C = 0.0021 A Wavelength=0.71073

Cell: a=9.822(3) b=5.4227(16) c=23.386(6)
alpha=90 beta=99.596(10) gamma=90
Temperature: 300 K

	Calculated	Reported
Volume	1228.2(6)	1228.2(6)
Space group	P 21/n	P 21/n
Hall group	-P 2yn	-P 2yn
Moiety formula	C16 H8 N2 O4	C16 H8 N2 O4
Sum formula	C16 H8 N2 O4	C16 H8 N2 O4
Mr	292.24	292.24
Dx,g cm-3	1.581	1.580
Z	4	4
Mu (mm-1)	0.117	0.117
F000	600.0	600.0
F000'	600.32	
h,k,lmax	12,6,29	12,6,29
Nref	2493	2474
Tmin,Tmax	0.971,0.988	0.659,0.745
Tmin'	0.962	

Correction method= # Reported T Limits: Tmin=0.659 Tmax=0.745
AbsCorr = MULTI-SCAN

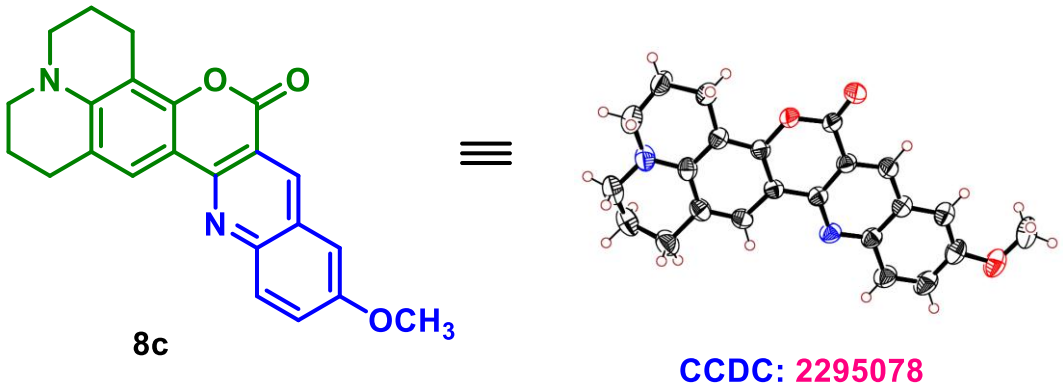
Data completeness= 0.992 Theta(max)= 26.316

R(reflections)= 0.0422(1807) wR2(reflections)= 0.1138(2474)

S = 1.018 Npar= 199

2. Crystal data and structure refinement for compound 8c, CCDC: 2295078

Single crystals of **8c** were obtained by recrystallization from dichloroethane/ethyl acetate, furnished orange crystals. The molecular structure and X-ray diffraction data/refinement of **8c** are given below.



Datablock: shelx

Bond precision: C-C = 0.0050 A Wavelength=0.71073

Cell: a=19.0707(13) b=9.5161(7) c=20.4834(14)
alpha=90 beta=90 gamma=90
Temperature: 300 K

	Calculated	Reported
Volume	3717.3(5)	3717.3(5)
Space group	P c a 21	P c a 21
Hall group	P 2c -2ac	P 2c -2ac
Moiety formula	C23 H20 N2 O3 [+ solvent]	?
Sum formula	C23 H20 N2 O3 [+ solvent]	C23 H20 N2 O3
Mr	372.41	372.41
Dx,g cm-3	1.331	1.331
Z	8	8
Mu (mm-1)	0.089	0.089
F000	1568.0	1568.0
F000'	1568.70	
h,k,lmax	25,12,27	25,12,27
Nref	9225[4742]	8759
Tmin,Tmax	0.979,0.988	0.628,0.746
Tmin'	0.979	

Correction method= # Reported T Limits: Tmin=0.628 Tmax=0.746
AbsCorr = MULTI-SCAN

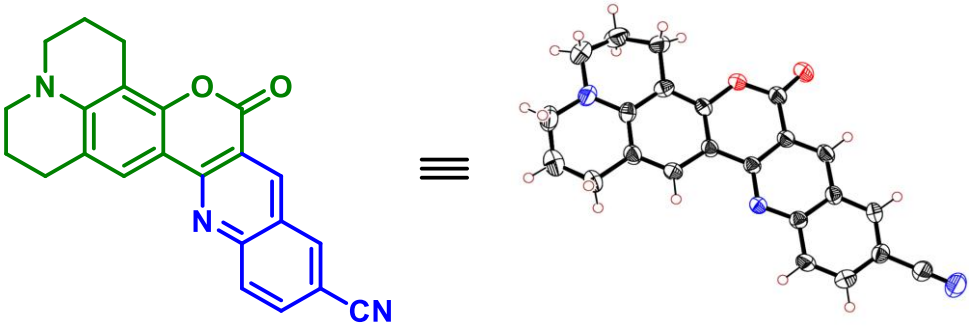
Data completeness= 1.85/0.95 Theta(max)= 28.277

R(reflections)= 0.0475(5327) wR2(reflections)= 0.1274(8759)

S = 1.020 Npar= 507

3. Crystal data and structure refinement for compound 8e, CCDC: 2295085

Single crystals of **8e** were obtained by recrystallization from $CDCl_3$, furnished red-colored crystals. The molecular structure and X-ray diffraction data/refinement of **8e** are given below.



8e ≡ **CCDC: 2295085**

Datablock: shelx

Bond precision: C-C = 0.0056 A Wavelength=0.71073

Cell: a=8.815(2) b=9.048(3) c=14.657(3)
alpha=77.286(10) beta=85.08(2) gamma=75.836(16)

Temperature: 300 K

	Calculated	Reported
Volume	1105.1(5)	1105.1(5)
Space group	P -1	P -1
Hall group	-P 1	-P 1
Moiety formula	C23 H17 N3 O2, C H Cl3	?
Sum formula	C24 H18 Cl3 N3 O2	C24 H18 Cl3 N3 O2
Mr	486.76	486.76
Dx,g cm-3	1.463	1.463
Z	2	2
Mu (mm-1)	0.442	0.443
F000	500.0	500.0
F000'	501.06	
h,k,lmax	11,12,19	11,12,19
Nref	5476	5451
Tmin,Tmax	0.876,0.960	0.644,0.746
Tmin'	0.876	

Correction method= # Reported T Limits: Tmin=0.644 Tmax=0.746 AbsCorr = MULTI-SCAN

Data completeness= 0.995 Theta(max)= 28.276

R(reflections)= 0.1006(3129) wR2(reflections)= 0.2250(5451)

S = 1.061 Npar= 289

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

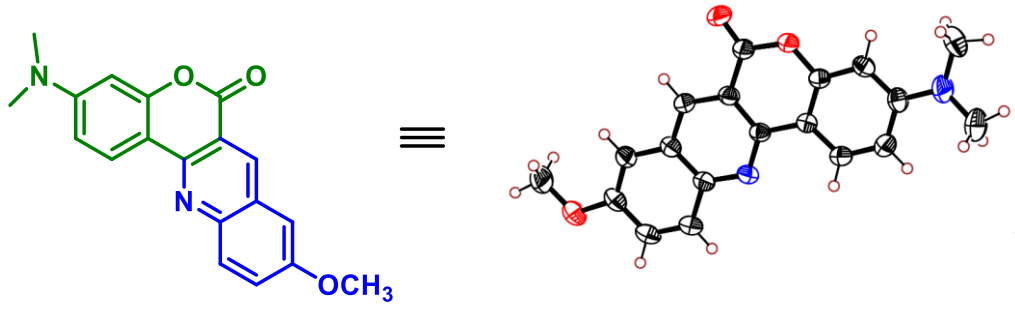
Alert level C

PLAT241_ALERT_2_C High 'MainMol' Ueq as Compared to Neighbors of C2 Check
PLAT244_ALERT_4_C Low 'Solvent' Ueq as Compared to Neighbors of C24 Check
PLAT340_ALERT_3_C Low Bond Precision on C-C Bonds ..... 0.00562 Ang.
PLAT790_ALERT_4_C Centre of Gravity not Within Unit Cell: Resd. # 1 Note

https://checkcif.iucr.org/cgi-bin/checkcif_hkl.pl

4. Crystal data and structure refinement for compound 12d, CCDC: 2201656

Single crystals of **12d** were obtained by recrystallization from $CDCl_3$, furnished red-colored crystals. The molecular structure and X-ray diffraction data/refinement of **12d** are given below.



12d

CCDC: 2201656

Datablock: GRK_6_190722_0m_a

Bond precision: C-C = 0.0020 A Wavelength=0.71073

Cell: a=7.7786(6) b=14.2417(11) c=14.3928(11)
alpha=85.179(2) beta=87.476(3) gamma=79.599(2)
Temperature: 300 K

	Calculated	Reported
Volume	1562.0(2)	1562.0(2)
Space group	P -1	P -1
Hall group	-P 1	-P 1
Moiety formula	C19 H16 N2 O3	C19 H16 N2 O3
Sum formula	C19 H16 N2 O3	C19 H16 N2 O3
Mr	320.34	320.34
Dx,g cm-3	1.362	1.362
Z	4	4
Mu (mm-1)	0.094	0.094
F000	672.0	672.0
F000'	672.31	
h,k,lmax	10,18,19	10,18,19
Nref	7767	7715
Tmin,Tmax	0.979,0.985	0.690,0.746
Tmin'	0.972	

Correction method= # Reported T Limits: Tmin=0.690 Tmax=0.746
AbsCorr = MULTI-SCAN

Data completeness= 0.993 Theta(max)= 28.287

R(reflections)= 0.0532(5408) wR2(reflections)= 0.1456(7715)

S = 1.042 Npar= 439

8. References:

1 Armour, M.-A. Hazardous Laboratory Chemicals Disposal Guide, Boca Raton, Florida, U.S.A, 3rd edn., 2003.

2 A. Sabatié, D. Végh, A. Loupy and L. Floch, *Arkivoc.*, 2001, **(vi)**, 122–128.

3 N. Mulakayala, D. Rambabu, M. R. Raja, M. C. Chaitanya, C. S. Kumar, A. M. Kalle, G. Rama Krishna, C. Malla Reddy, M. V. Basaveswara Rao and M. Pal, *Bioorganic Med. Chem*., 2012, **20**, 759–768.

4 C. Bandyopadhyay, K. Ranabir Sur, R. Patra and A. Sen, *Tetrahedron*., 2000, **56**, 3583–3587.

5 P. Patra, *Org. Prep. Proced. Int.*, 2021, **53**, 184–189.

6 Y. Weng, H. Zhou, C. Sun, Y. Xie and W. Su, *J. Org. Chem.*, 2017, **82**, 9047–9053.

7 J. V. Prasad, J. S. Reddy, N. R. Kumar, K. A. Solomon and G. Gopikrishna, *J. Chem. Sci.*, 2011, **123**, 673–679.

8 P. Zhang, W. Liu, G. Niu, H. Xiao, M. Wang, J. Ge, J. Wu, H. Zhang, Y. Li and P. Wang, *J. Org. Chem.*, 2017, **82,** 3456−3462.

9 T. Steinführer, A. Hantschmann, M. Pietsch and M. Weißenfels, *Liebigs Ann. der Chemie.,* 1992, 23–28.

10 (a) X. Ji, Z. Huang and J. P. Lumb, *J. Org. Chem*., 2020, **85**, 1062–1072; (b) Ó. Vázquez-Vera, J. S. Sánchez-Badillo, A. Islas-Jácome, M. A. Rentería-Gómez, S. G. Pharande, C. J. Cortes-García, M. A. Rincón-Guevara, I. A. Ibarra, R. Gámez-Montaño and E. González-Zamora, *Org. Biomol. Chem*., 2017, **15**, 2363–2369; (c) H. Jiang, Y. Cheng, R. Wang, Y. Zhang and S. Yu, *Chem. Commun*., 2014, **50**, 6164–6167.

11 A. Krishnan and S. Kamaraj, *J. Org. Chem.*, 2023, **88**, 16315–16329.

12 D. Jankovič, M. Virant and M. Gazvoda, *J. Org. Chem.*, 2022, **87**, 4018–4028.

13 T. Vivekanand, A. Kumar, J. C. Menéndez and S. Kumar, *Chemistry Select*., 2021, **6**, 10436–10439.

*****