Supporting Information for

Novel Electron Donor-Acceptor Complexes (EDA) Promoted Arylation of 2-Oxo-2*H*-Chromene-3-Carbonitrile under Visible Light Irradiation

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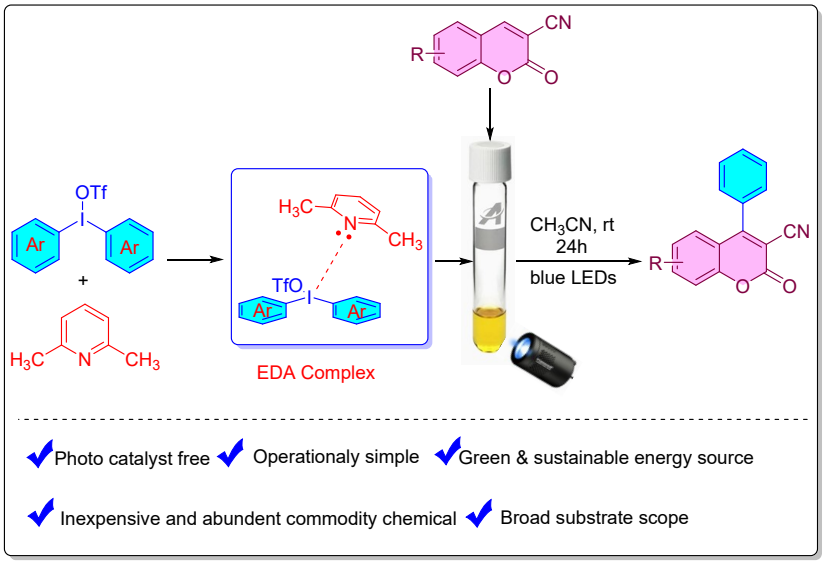
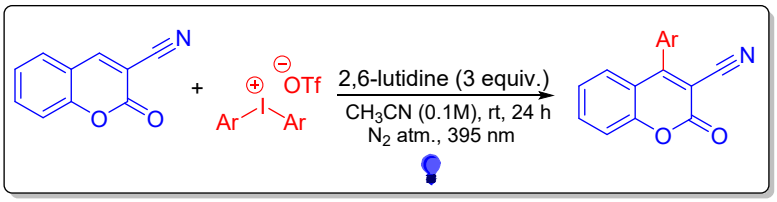


1. General Information

All the reactions were performed in an oven-dried glass apparatus under inert atmosphere (nitrogen) in freshly distilled anhydrous solvents. Commercially available reagents were used as such without further purification. All reactions were monitored by thin-layer chromatography and TLC plates were visualized by exposure to UV light at 254 nm, and by exposure to iodine vapors or using *p*-anisaldehyde stain. Crude products were purified by column chromatography on silica gel 100-200 mesh using hexanes and ethyl acetate as eluent. ^{1}H NMR was recorded in $CDCl_3$ and MeOH-d_4 on 500 MHz, 400 MHz and 300 MHz, ^{13}C NMR was recorded on 126 MHz, 101 MHz and 75 MHz and ^{19}F NMR was recorded on 376MHz. Chemical shifts were reported in δ (ppm) relative to TMS as an internal standard and *J* values were given in Hz (hertz). Multiplicity is indicated as, s (singlet); d (doublet); t (triplet); m (multiplet); dd (doublet of doublet), etc. δ **7.26** and δ **1.56** are corresponding to $CDCl_3$ and moisture respectively in ^{1}H NMR, δ **77.16** is related to $CDCl_3$ in ^{13}C NMR. Mass spectra and HRMS were recorded on mass spectrometer by Electrospray ionization (ESI) and Atmospheric pressure chemical ionization (APCI) techniques.

2. Experimental procedure for the light driven synthesis of 4-aryl-2-oxo-2*H*-chromene-3-carbonitrile:



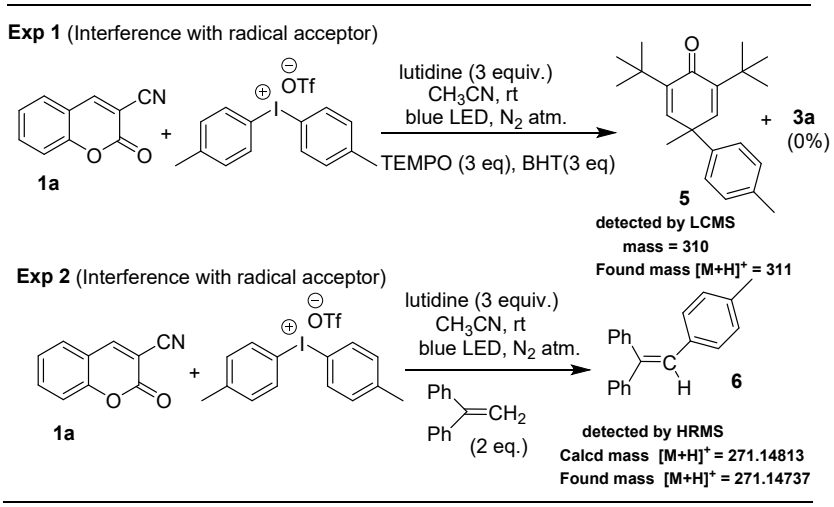
In oven dry 10 mL reaction vial, diaryliodonium triflate **2** (1.5 equiv), and 2,6-lutidine (3 equiv) were dissolved in dry acetonitrile (0.1 M) under N_2 atmosphere. The resulting light-yellow colour EDA complex was allowed to stir for 5 min and then 2-oxo-2*H*-chromene-3-carbonitrile **1** (1.0 equiv) was added to the mixture and purged with N_2 for several times. The mixture was kept into **Penn *PhD* photo reactor m2** (blue LEDs, **395** nm) and then stirred at room temperature under N_2 atmosphere for 24h. Upon completion, the reaction was quenched by addition of dil. HCl, and then the compound was extracted with ethyl acetate and the crude product was purified by column chromatography to afford the pure product.

Reaction set ctor m2:

): 1020,

Radical trapping experiment with TEMPO, BHT and 1,1-diphenylethylene:

To gain the insight into the reaction mechanism, we performed a few control experiments. The reaction failed to furnish the desired product when radical scavenger, TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy) (3.0 equiv) and 2,6-di-tert-butyl-4- methylphenol (BHT). The corresponding radical quenching adduct **5** was detected. In another experiment, a highly reactive 1,1-diphenylethylene was added to trap the radical. In this experiment, the respective radical trapping adduct **6** was observed. (**Scheme 1)**. These results indicate that the reaction proceeds through a radical process.

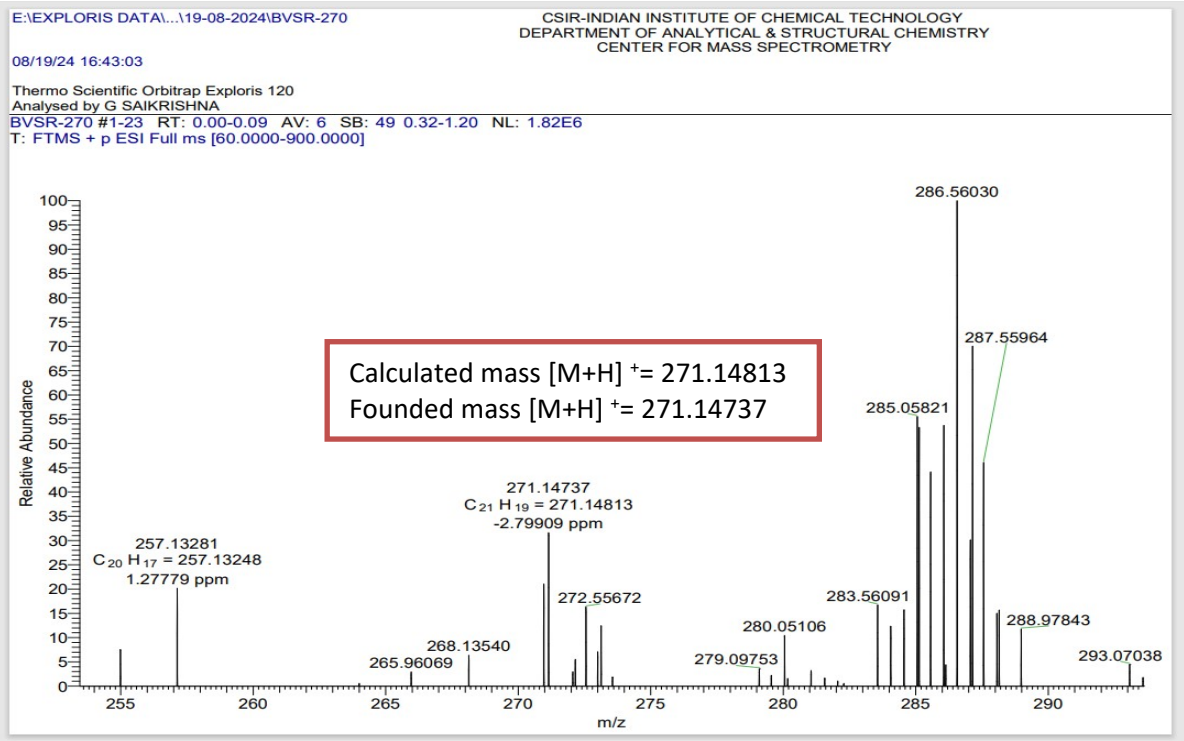


Scheme 1. Control experiments

Experimental procedure for radical quenching study:

2-oxo-2*H*-chromene-3-carbonitrile (1 equiv.), diaryliodonium triflate **2** (1.5 equiv), lutidine (3 equiv.) and radical acceptor (2-3 equiv.) were placed in a 15 mL oven dried vial under N_2 atmosphere. Then CH_3CN (0.1 M) was added to it and purged with N_2 for several times. The reaction mixture was kept into **Penn *PhD* photo reactor m2** (blue LED 395 nm) and stirred at room temperature under N_2 atmosphere for 24h. After the reaction time, no desired product was formed and the starting material was recovered.

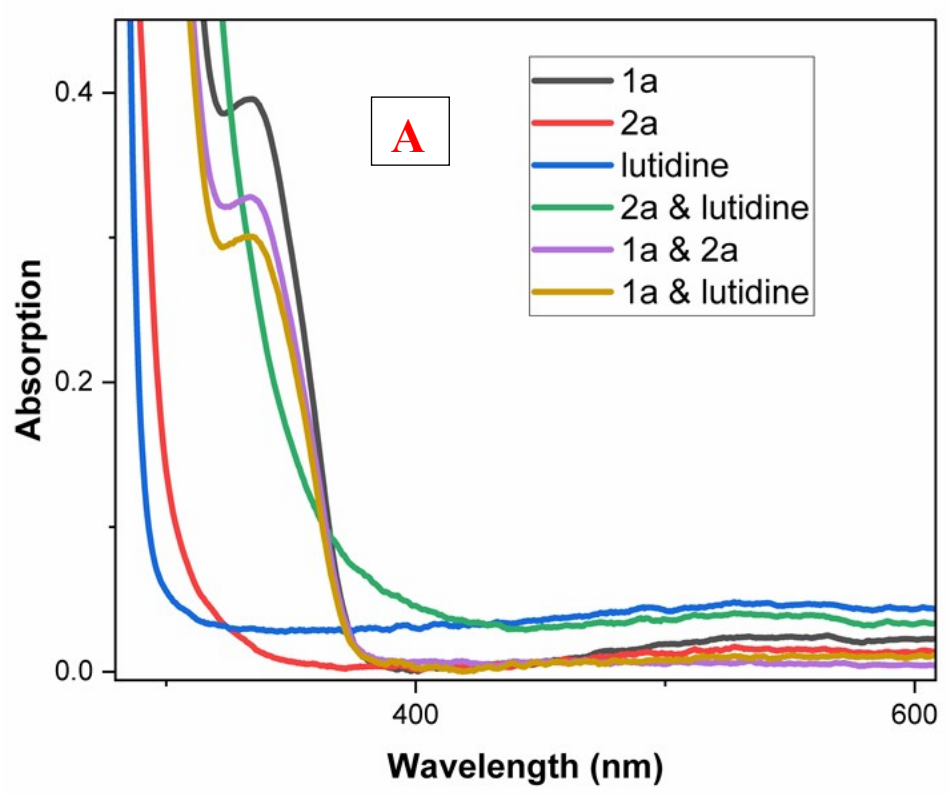
HRMS of compound 6:

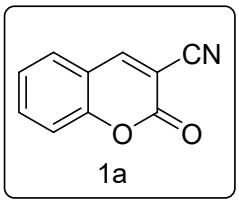


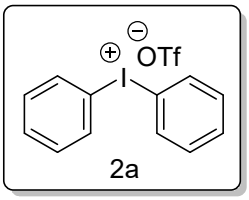
3. Photophysical study:

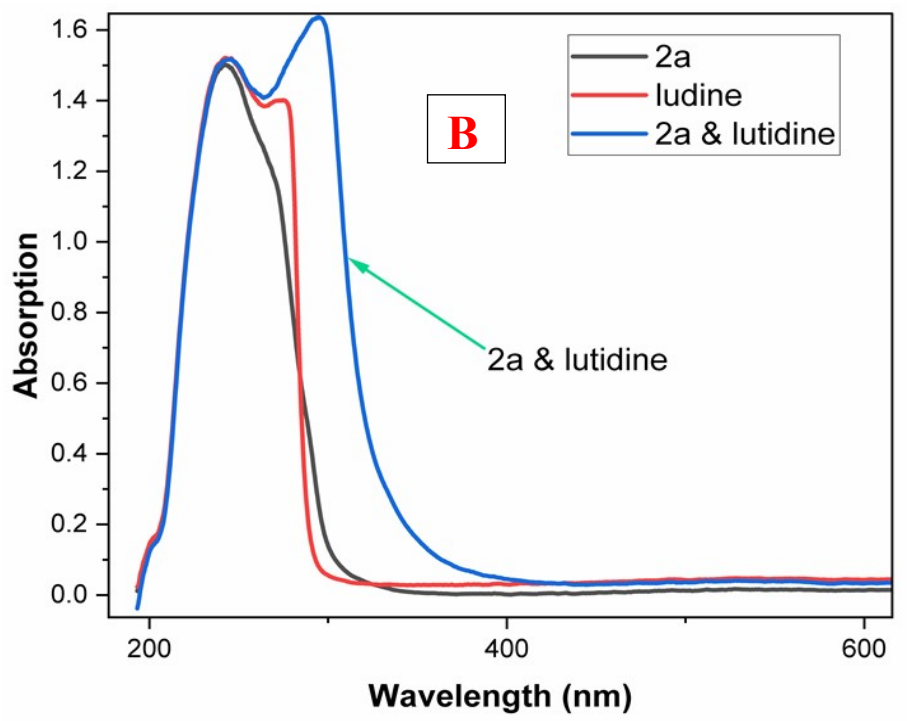
UV-Vis Analysis:

UV-Vis analysis was carried out on an Agilent Cary 60 UV-Vis spectrophotometer using a Hellma quartz cuvette with a 10 mm path length. Both the cuvette and vials storing solutions were oven-dried prior to use. Analyses were run in MeCN solvent and the data was collected as a .csv file and processed using Origin software. Absorption spectra of individual and combined reaction components in CH_3CN reveals that the EDA complex was formed between diphenyliodonium triflate **2a (0.15M)** and 2,6-lutidine **(0.3M)**. While diphenyliodonium triflate **2a (0.15M)** and 2,6-lutidine **(0.3M)** have individually shown an absorption band in the near UV region but a mixture of these compounds exhibits a significant bathochromic shift in the absorption band in visible region. Whereas no such red-shift was perceived when **1a** was mixed either with diphenyliodonium triflate **2a** or with 2,6-lutidine. It reveals that there is no involvement of **1a** in the formation of EDA.









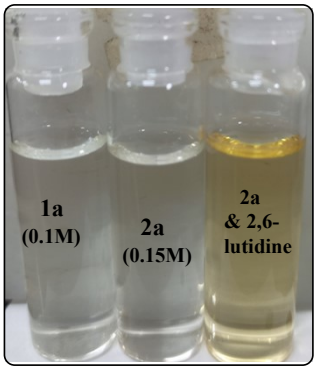


Figure S1. (A) UV-Visible spectra of the compound **1a (0.1M)**, **2a (0.15M)**, 2,6-lutidine **(0.3M)** and mixture of component **2a**: lutidine, **1a**:**2a**, and **1a**: lutidine in acetonitrile solvent. **(B)** UV-Visible spectra of the compound **2a**, 2,6-lutidine and **2a**:2,6-lutidine mixture in acetonitrile solvent.

Cyclic voltammetry experiments:

Cyclic voltammetry measurements were carried out with **IKA Electrasyn 2.0.** The solution of interest was sparged with nitrogen for 10 min before data collection. The experiment was performed in a three-electrode cell with acetonitrile (6 mL) as the solvent, ***n*-Bu_4NPF_6 (0.1 M)** as the supporting electrolyte, and the concentration of the tested compound was **2.0 mM** under inert atmosphere using three electrode system at a sweeps rate of 100 mV/s in which glassy carbon is used as working electrode, Ag/Ag^+ as a reference, platinum electrode as a counter electrode. The potential range investigated for redox was -3.0 to +3.0 V vs Ag/Ag^+. CV plotting convention is IUPAC. The oxidation peak potential of **1a** and 2,6-lutidine are approximately +2671 and +1950 mV whereas **2a** exhibits no oxidation peak potential in the experimental region.

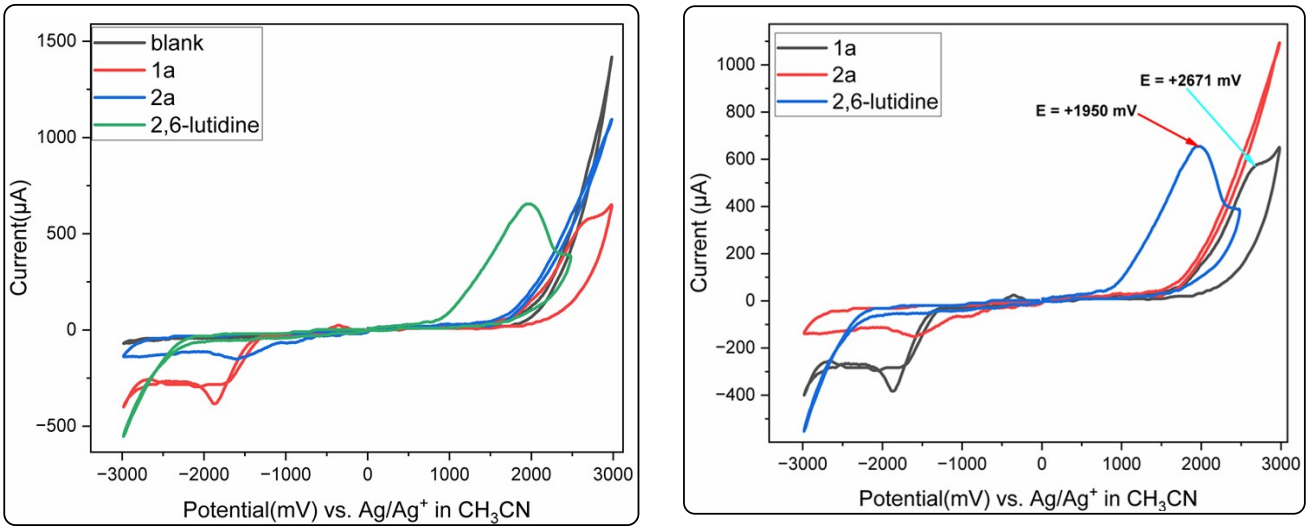
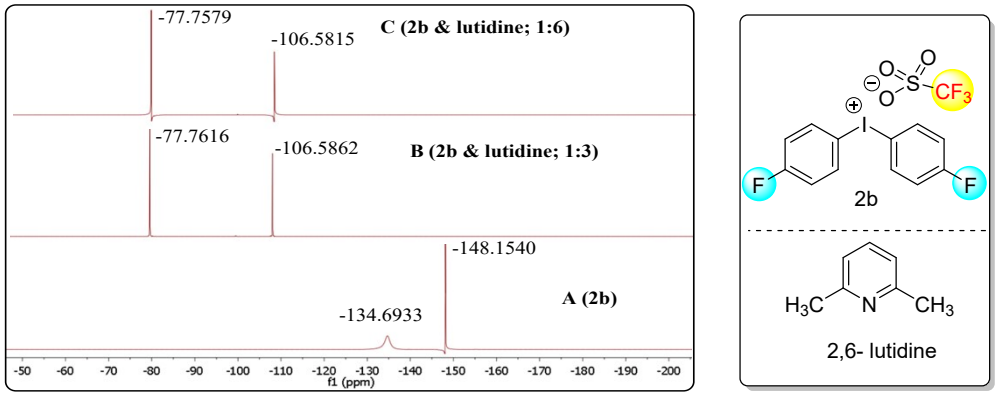


Figure S2. Cyclic Voltammogram of compound **1a**, **2a** and 2,6-lutidine in acetonitrile solvent.

^{19}F NMR experiment:

Change in a chemical shift (δ) of the F in iodonium salt **2b** was determined by NMR **^{19}F** (376 MHz). The measurements were carried out at a constant amount of iodonium salt **2b** (20 mg) and an increasing the amount of lutidine in 5 mm NMR tube in DMSO at rt. ^{19}F NMR (376 MHz, DMSO) δ -134.6933, -148.1540. ^{19}F NMR (376 MHz, DMSO) δ -77.7616, -106.5862. ^{19}F NMR (376 MHz, DMSO) δ -77.7579, -106.5815.



Job's method:

A Jobs method was conducted to evaluate the ration of diaryliodonium triflate salt and 2, 6-lutidine in EDA Complex in acetonitrile. The stoichiometry of EDA Complex was determined using Jobs method with varying the ration of diphenyliodonium salt and lutidine in acetonitrile solvent (0.1M). The absorbance was plotted against mole fraction of 2,6 lutidine and the maximum absorbance was observed at 0.7 mole fraction of lutidine indicating ~1:2 stoichiometry of the EDA complex.

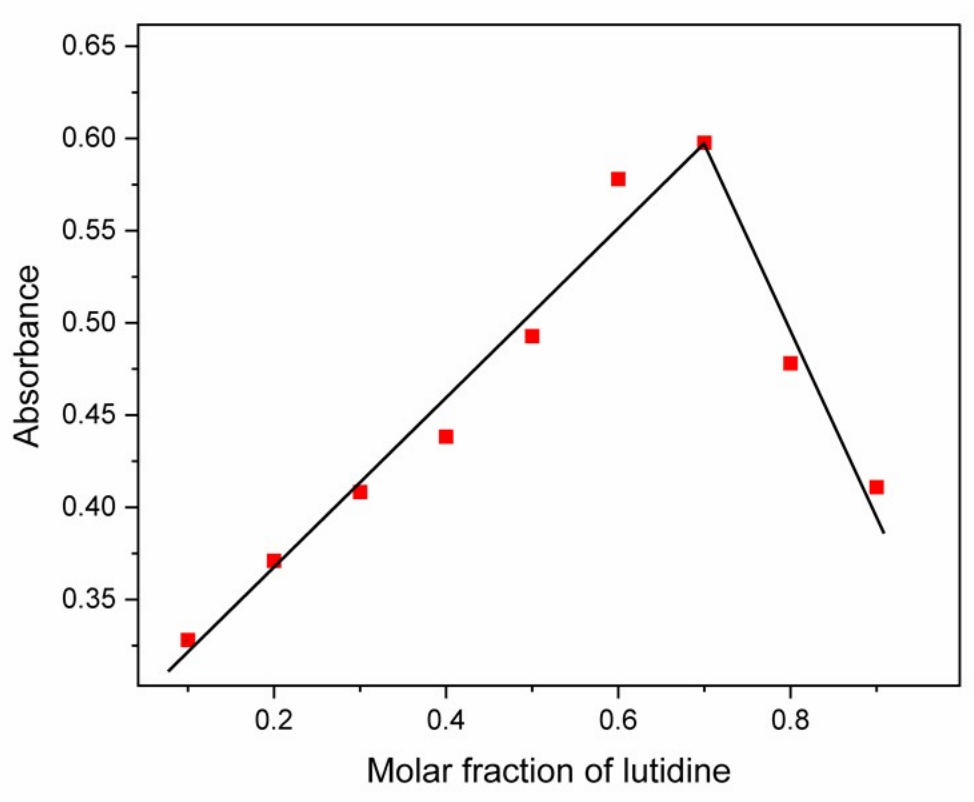
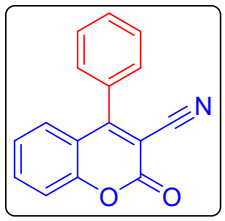


Figure S3. Job's plot of EDA Complex between 2,6-lutidine and DAIR (2a).

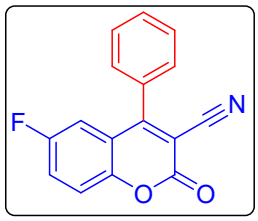
3. Characterization of compounds

2-Oxo-4-phenyl-2*H*-chromene-3-carbonitrile (3a):



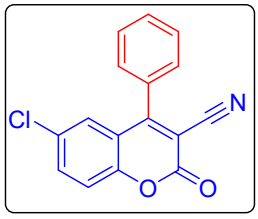
The general procedure was followed using **1a** (0.35 mmol, 1 equiv.), diaryliodonium triflate **2** (1.5 equiv,) and 2,6-lutidine (3 equiv.). Purification by column chromatography on silica gel (petroleum ether:EtOAc = 91:9) yielded **3a** (58.9 mg, 68%) as a white solid. mp = 216-218 °C; **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.71-7.67 (m, 1H), 7.64 – 7.59 (m, 3H), 7.49-7.44 (m, 3H), 7.38 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.30 (td, *J* = 7.8, 1.0 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 164.1, 157.0, 154.1, 135.2, 131.8, 131.2, 129.2, 129.1, 128.5, 125.4, 118.2, 117.7, 113.5, 101.8. HRMS (ESI Orbitrap) calcd for $C_{16}H_{10}O_2N$ $[M+H]^+$: 248.07061, found: 248.07039.

6-Fluoro-2-oxo-4-phenyl-2*H*-chromene-3-carbonitrile (3b):



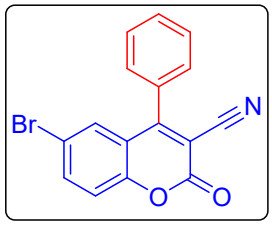
The general procedure was followed using **1b** (0.31 mmol, 1equiv.), diaryliodonium triflate 2 (1.5 equiv,) and 2,6-lutidine (3 equiv.) and purification by column chromatography on silica gel (petroleum ether:EtOAc = 92:8) yielded 3b as a white solid (56.9 mg, 70%); mp = 175-180 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.71 – 7.56 (m, 3H), 7.54 – 7.36 (m, 4H), 7.07 (dd, *J* = 8.5, 2.6 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 163.2, 159.0 (d, *J* = 246.6 Hz), 156.6, 150.2, 131.5, 131.3, 129.4, 128.4, 122.7 (d, *J* = 24.7 Hz), 119.4 (d, *J* = 8.2 Hz), 119.0 (d, *J* = 8.1 Hz), 114.3 (d, *J* = 25.5 Hz), 113.2, 102.9. **^{19}F NMR (377 MHz, $CDCl_3$)** δ -114.53. HRMS (ESI Orbitrap) calcd for $C_{16}H_9O_2NF$ $[M+H]^+$: 266.06118, found: 266.06067.

6-Chloro-2-oxo-4-phenyl-2*H*-chromene-3-carbonitrile (3c):



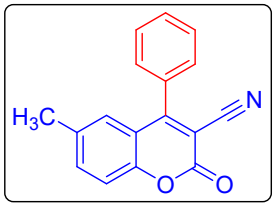
The general procedure was followed using **1c** (0.28 mmol, 1equiv.), diaryliodonium triflate 2 (1.5 equiv,) and 2,6-lutidine (3 equiv.). Purification by column chromatography on silica gel (petroleum ether:EtOAc = 92:8) yielded 3c as a white solid (58.7 mg, 73%); mp = 158-162 °C; **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.21 (s, 1H), 7.70 – 7.62 (m, 3H), 7.60 (d, *J* = 2.4 Hz, 1H), 7.49-7.46 (m, 1H), 7.44 – 7.33 (m, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 155.8, 152.9, 150.5, 135.4, 131.5, 131.2, 129.5, 128.4, 128.3, 119.2, 118.9, 118.0, 113.1, 104.7. HRMS (ESI Orbitrap) calcd for $C_{16}H_9O_2NCl$ $[M+H]^+$: 282.03163, found: 282.03121.

6-Bromo-2-oxo-4-phenyl-2*H*-chromene-3-carbonitrile (3d):



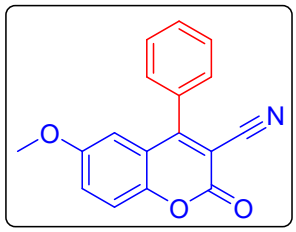
The general procedure was followed using **1d** (0.24 mmol, 1equiv.), diaryliodonium triflate 2 (1.5 equiv,) and 2,6-lutidine (3 equiv.). Purification by column chromatography on silica gel (petroleum ether:EtOAc = 92:8) yielded 3d as a white solid (61.6 mg, 78%); mp = 180-183 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.21 (s, 1H), 7.85 – 7.79 (m, 2H), 7.77 (d, *J* = 2.2 Hz, 1H), 7.70 – 7.65 (m, 1H), 7.53 – 7.47 (m, 1H), 7.41 – 7.28 (m, 2H). **^{13}C NMR (176 MHz, $CDCl_3$)** δ 155.7, 153.4, 150.4, 138.2, 131.3, 131.1, 129.5, 128.4, 119.2, 118.5, 118.4, 113.1, 104.7. HRMS (ESI Orbitrap) calcd for $C_{16}H_9O_2NBr$ $[M+H]^+$: 325.98112, found: 325.98087.

6-Methyl-2-oxo-4-phenyl-2*H*-chromene-3-carbonitrile (3e):



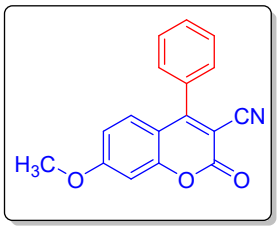
The general procedure was followed using **1e** (0.33 mmol, 1equiv.), diaryliodonium triflate 2 (1.5 equiv,) and 2,6-lutidine (3 equiv.). Purification by column chromatography on silica gel (petroleum ether:EtOAc = 92:8) yielded 3e as a white solid (62.9 mg, 72%); mp = 164-169 °C; **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.66 – 7.60 (m, 3H), 7.54 – 7.43 (m, 3H), 7.38 – 7.30 (m, 1H), 7.13 (d, *J* = 1.0 Hz, 1H), 2.34 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 164.1, 157.2, 152.3, 136.3, 135.3, 131.9, 131.1, 129.2, 128.6, 128.5, 128.5, 117.9, 117.4, 113.6, 20.9. HRMS (ESI Orbitrap) calcd for $C_{17}H_{12}O_2N$ $[M+H]^+$: 262.08626, found: 262.08612.

6-Methoxy-2-oxo-4-phenyl-2*H*-chromene-3-carbonitrile (3f):



The general procedure was followed using **1f** (0.30 mmol, 1equiv.), diaryliodonium triflate 2(1.5 equiv,) and 2,6-lutidine (3 equiv.). Purification by column chromatography on silica gel (petroleum ether:EtOAc = 92:8) yielded 3f as a white solid (54.7 mg, 66%); mp = 156-159 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.65 – 7.60 (m, 3H), 7.55 – 7.46 (m, 2H), 7.39 (t, *J* = 8.2 Hz, 1H), 7.28 (d, *J* = 3.0 Hz, 1H), 6.77 (d, *J* = 2.9 Hz, 1H), 3.72 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)**: δ 163.8, 157.2, 156.6, 148.6, 131.9, 131.2, 130.6, 129.3, 128.8, 128.4, 122.7, 118.7, 118.6, 111.1, 55.9. HRMS (ESI Orbitrap) calcd for $C_{17}H_{12}O_3N$ $[M+H]^+$: 278.08117, found: 278.08070.

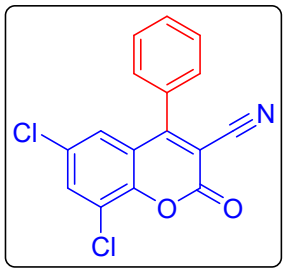
7-methoxy-2-oxo-4-phenyl-2H-chromene-3-carbonitrile (3h):



The general procedure was followed using **1h** (0.31 mmol, 1equiv.), diaryliodonium triflate 2 (1.5 equiv,) and 2,6-lutidine (3 equiv.). Purification by column chromatography on silica gel (petroleum ether:EtOAc = 92:8) yielded 3h as a white solid (47.7 mg, 56%); mp = 180-185 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.62-7.58 (m, 3H), 7.44-7.49 (m, 2H), 7.28 (d, *J* = 9.1 Hz, 1H), 6.91 (d, *J* = 2.4 Hz, 1H), 6.85

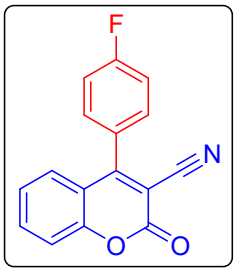
(dd, J = 9.0, 2.5 Hz, 1H), 3.93 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 165.6, 164.0, 157.7, 156.4, 132.2, 131.0, 130.3, 129.1, 128.5, 114.0, 111.8, 101.2, 97.8, 56.2. HRMS (ESI Orbitrap) calcd for $C_{17}H_{12}O_3N$ $[M+H]^+$: 278.08117, found: 278.08092.

6, 8-Dichloro-2-oxo-4-phenyl-2*H*-chromene-3-carbonitrile (3i):



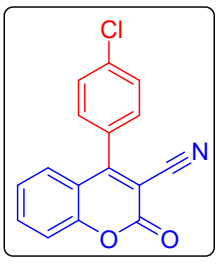
The general procedure was followed using **1i** (0.25 mmol, 1equiv.), diaryliodonium triflate 2(1.5 equiv.) and 2,6-lutidine (3 equiv.). Purification by column chromatography on silica gel (petroleum ether:EtOAc = 92:8) yielded 3i as a white solid (38.7 mg, 49%); mp = 208-214 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.75 (d, J = 2.4 Hz, 1H), 7.70 – 7.62 (m, 3H), 7.55 – 7.49 (m, 1H), 7.48-7.44 (m, 1H), 7.24 (d, J = 2.4 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 162.7, 155.2, 148.4, 134.9, 131.7, 130.9, 130.7, 129.6, 128.9, 128.6, 128.3, 126.7, 123.9, 120.2, 112.7. HRMS (ESI Orbitrap) calculated for $C_{16}H_8Cl_2NO_2$ $[M+H]^+$: 315.99267, found: 315.99227.

4-(4-Fluorophenyl)-2-oxo-2H-chromene-3-carbonitrile (3j):



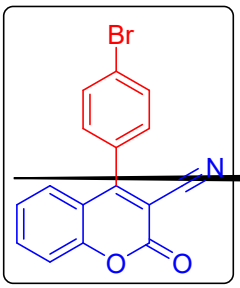
The general procedure was followed using **1j** (0.35 mmol, 1equiv.), diaryliodonium triflate 2(1.5 equiv,) and 2,6-lutidine (3 equiv.). Purification by column chromatography on silica gel (petroleum ether:EtOAc = 92:8) yielded 3j as a white solid (53.9 mg, 58%); mp = 160-164 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.73 (t, J = 6.8 Hz, 1H), 7.68 – 7.56 (m, 1H), 7.55 – 7.46 (m, 2H), 7.44 – 7.29 (m, 4H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 165.5, 163.1, 155.5 (d, J = 273.5 Hz), 151.8, 135.4, 130.9 (d, J = 8.7 Hz), 129.3, 128.8, 127.7 (d, J = 3.3 Hz), 125.7, 125.5, 118.1, 117.8, 116.7 (d, J = 22.3 Hz), 113.5. **^{19}F NMR (377 MHz, $CDCl_3$)** δ -107.73. HRMS (ESI Orbitrap) calculated for $C_{16}H_9O_2NF$ $[M+H]^+$: 266.06118, found: 266.06064.

4-(4-Chlorophenyl)-2-oxo-2H-chromene-3-carbonitrile (3k):



The general procedure was followed using **1k** (0.35 mmol, 1equiv.), diaryliodonium triflate 2(1.5 equiv,) and 2,6-lutidine (3 equiv.). Purification by column chromatography on silica gel (petroleum ether:EtOAc = 92:8) yielded 3k as a white solid (64.1 mg, 65%); mp = 170-174 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 – 7.70 (m, 1H), 7.69 – 7.56 (m, 3H), 7.53 – 7.39 (m, 3H), 7.39 – 7.30 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.9, 156.7, 154.1, 135.5, 130.0, 129.7, 129.6, 128.7, 128.6, 125.7, 125.5, 117.8, 113.3. HRMS (ESI Orbitrap) calculated for $C_{16}H_9O_2NCl$ $[M+H]^+$: 282.03163, found: 282.03111.

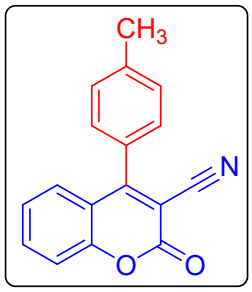
4-(4-Bromophenyl)-2-oxo-2H-chromene-3-carbonitrile (3l):



The general procedure was followed using **1l** (0.35 mmol, 1equiv.), diaryliodonium triflate 2 (1.5 equiv,) and 2,6-lutidine (3 equiv.). Purification by column chromatography on silica gel (petroleum

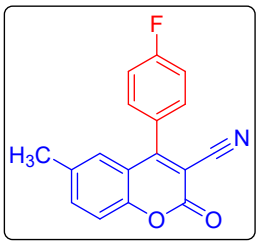
ether:EtOAc = 92:8) yielded 3l as a white solid (78.4 mg, 69%); mp = 215-218 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.77 (d, *J* = 8.4 Hz, 1H), 7.73 (ddd, *J* = 8.6, 6.8, 2.1 Hz, 1H), 7.68 – 7.56 (m, 1H), 7.54 – 7.30 (m, 5H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 162.9, 156.7, 154.1, 135.5, 132.6, 130.5, 130.1, 128.7, 126.0, 125.5, 117.8, 113.3, 101.9. HRMS (ESI Orbitrap) calculated for $C_{16}H_9O_2NBr$ $[M+H]^+$: 325.98112, found: 325.98080.

2-Oxo-4-(p-tolyl)-2*H*-chromene-3-carbonitrile (3m):



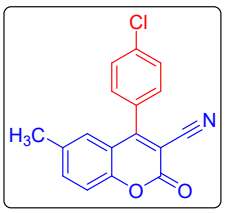
The general procedure was followed using **1m** (0.35 mmol, 1equiv.), diaryliodonium triflate 2(1.5 equiv,) and 2,6-lutidine (3 equiv.). Purification by column chromatography on silica gel (petroleum ether:EtOAc = 92:8) yielded 3m as a white solid (57.7 mg, 63%); mp = 218-220 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.70 (ddd, *J* = 8.6, 7.3, 1.6 Hz, 1H), 7.47 – 7.37 (m, 6H), 7.34 – 7.27 (m, 1H), 2.49 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 164.3, 157.1, 154.1, 141.8, 135.1, 129.9, 129.1, 128.8, 128.6, 125.2, 118.3, 117.7, 113.7, 21.6. HRMS (ESI Orbitrap) calculated for $C_{17}H_{12}O_2N$ $[M+H]^+$: 262.08626, found: 262.08580.

4-(4-Fluorophenyl)-6-methyl-2-oxo-2*H*-chromene-3-carbonitrile (3o):



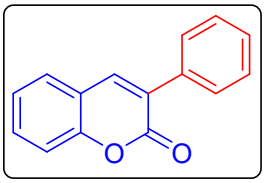
The general procedure was followed using **1o** (0.32 mmol, 1equiv.), diaryliodonium triflate 2(1.5 equiv,) and 2,6-lutidine (3 equiv.). Purification by column chromatography on silica gel (petroleum ether:EtOAc = 92:8) yielded 3o as a white solid (55.2 mg, 61%); mp = 185-190 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.55 – 7.47 (m, 3H), 7.38 – 7.30 (m, 3H), 7.10 (s, 1H), 2.36 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 164.2 (d, J = 253.0 Hz), 163.0, 157.0, 152.3, 136.5, 135.5, 130.8 (d, *J* = 8.8 Hz), 128.2, 127.8 (d, *J* = 3.1 Hz), 117.8, 117.5, 116.7 (d, *J* = 22.2 Hz), 113.6, 20.9. **^{19}F NMR (377 MHz, $CDCl_3$)** δ -107.95. HRMS (ESI Orbitrap) calculated for $C_{17}H_{11}O_2NF$ $[M+H]^+$: 280.07684, found: 280. 07657.

4-(4-Chlorophenyl)-6-methyl-2-oxo-2*H*-chromene-3-carbonitrile (3p):



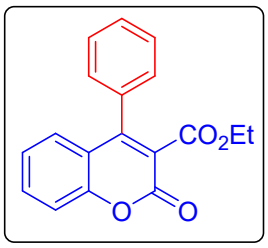
The general procedure was followed using **1p** (0.32 mmol, 1equiv.), diaryliodonium triflate 2 (1.5 equiv,) and 2,6-lutidine (3 equiv.). Purification by column chromatography on silica gel (petroleum ether:EtOAc = 92:8) yielded 3p as a white solid (65.0 mg, 68%); mp = 207-212 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.65 – 7.56 (m, 2H), 7.56 – 7.49 (m, 1H), 7.47 – 7.39 (m, 2H), 7.36 (d, *J* = 8.5 Hz, 1H), 7.08 (d, *J* = 0.9 Hz, 1H), 2.35 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 162.8, 156.9, 152.3, 137.6, 136.6, 135.5, 130.9, 130.2, 129.9, 129.7, 129.5, 128.2, 117.6, 113.5, 20.9. HRMS (ESI Orbitrap) calculated for $C_{17}H_{11}O_2NCl$ $[M+H]^+$:296.04729, found: 296.04687.

3-Phenyl-2*H*-chromen-2-one (4a):



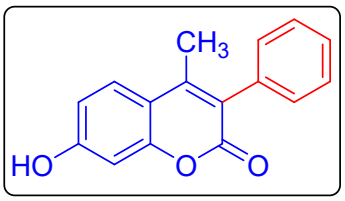
The general procedure was followed using **coumarine** (0.41 mmol, 1equiv.), diaryliodonium triflate 2 (1.5 equiv,) and 2,6-lutidine (3 equiv.). Purification by column chromatography on silica gel (petroleum ether:EtOAc = 93:7) yielded **4a** as a white solid (51 mg, 56%); mp = 137-139 °C; **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.82 (s, 1H), 7.71 (dd, *J* = 8.1, 1.4 Hz, 2H), 7.57 – 7.51 (m, 2H), 7.49 – 7.36 (m, 4H), 7.31 (td, *J* = 7.5, 1.0 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 160.6, 153.6, 139.9, 134.7, 131., 128.9, 128.6, 128.5, 127.9, 124.5, 119.7, 116.5. HRMS (ESI Orbitrap) calculated for $C_{15}H_{11}O_2$ $[M+H]^+$: 223.07536, found: 223.07513. NMR data matched with reported data.[1]

ethyl 2-oxo-4-phenyl-2H-chromene-3-carboxylate (4b):



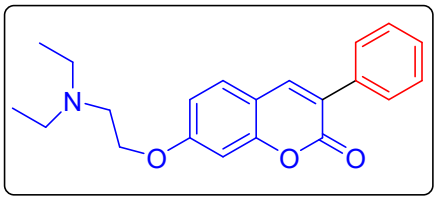
The general procedure was followed using ethyl 2-oxo-2H-chromene-3-carboxylate (0.27 mmol, 1equiv.), diaryliodonium triflate 2 (1.5 equiv,) and 2,6-lutidine (3 equiv.). Purification by column chromatography on silica gel (petroleum ether:EtOAc = 92:8) yielded **4b** as a white solid (53 mg, 66%); mp = 110-114 °C, **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.59 (ddd, J = 8.6, 7.0, 1.9 Hz, 1H), 7.52 – 7.48 (m, 3H), 7.42 (d, *J* = 8.2 Hz, 1H), 7.39 – 7.35 (m, 2H), 7.27 – 7.20 (m, 2H), 4.08 (q, J = 7.1 Hz, 2H), 0.97 (t, J = 7.1 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 164.0, 157.9, 153.6, 153.1, 133.0, 132.9, 129.6, 128.6, 128.3, 128.1, 124.6, 124.5,124.0, 119.2, 117.2, 61.8, 13.7. NMR data matched with reported data.[2]

7-Hydroxy-4-methyl-3-phenyl-2*H*-chromen-2-one (4c):



The general procedure was followed using 4-methyl-7-hydroxy coumarin (0.34 mmol, 1equiv.), diaryliodonium triflate 2 (1.5 equiv,) and 2,6-lutidine (3 equiv.). Purification by column chromatography on silica gel (petroleum ether:EtOAc = 85:15) yielded **4c** as a white solid (32 mg, 38%); mp = 230-232 °C; **^{1}H NMR (400 MHz, MeOH-d_4)** δ 7.69 (d, *J* = 8.8 Hz, 1H), 7.50 – 7.43 (m, 2H), 7.43 – 7.37 (m, 1H), 7.32 – 7.27 (m, 2H), 6.87 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.77 (d, *J* = 2.4 Hz, 1H), 2.28 (s, 3H). **^{13}C NMR (101 MHz, MeOH-d_4)** δ 162.2, 161.2, 154.2, 149.5, 134.9, 130.0, 128.0, 127.5, 126.6, 122.8, 113.0, 113.0, 101.9, 15.4. data matched with reported data.[1]

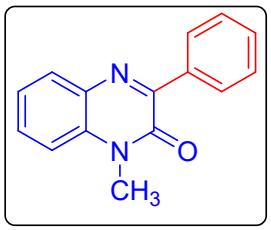
7-(2-(diethylamino)ethoxy)-3-phenyl-2H-chromen-2-one (4d):



The general procedure was followed using 7-(2-(diethylamino)ethoxy)-2H-chromen-2-one (0.22 mmol, 1equiv.), diaryliodonium triflate 2 (1.5 equiv,) and 2,6-lutidine (3 mol%,). The crude product was purified by column chromatography on silica gel. (DCM : MeOH = 95:5). White semi solid (42 mg, 54%); **^{1}H NMR (400**

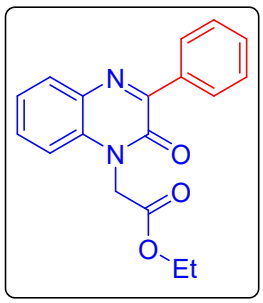
MHz, $CDCl_3$) δ 7.76 (s, 1H), 7.69-7.61 (m, 2H), 7.48-7.34 (m, 4H), 6.91 (dd, *J* = 8.7, 2.0 Hz, 1H), 6.87 – 6.81 (m, 1H), 4.62-4.56 (m, 2H), 3.50-3.44 (m, 2H), 3.25 (q, *J* = 13.6, 6.4 Hz, 4H), 1.49 – 1.37 (m, 6H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 160.6, 160.1, 155.0, 139.7, 134.8, 131.9, 129.3, 128.7, 128.5, 128.4, 125.6, 114.3, 112.2, 101.9, 63.6, 50.6, 47.3, 8.8. HRMS (ESI Orbitrap) calculated for $C_{21}H_{24}NO_3$ $[M+H]^+$:338.17507, found: 338.17464.

1-methyl-3-phenylquinoxalin-2(1H)-one (4f):



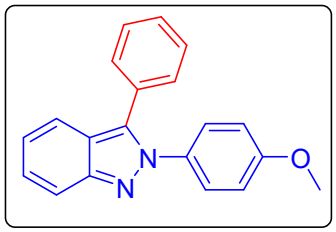
The general procedure was followed using 1-methyl quinoxalin-2(1H)-one (0.38 mmol, 1equiv.), diaryliodonium triflate 2 (1.5 equiv,) and 2,6-lutidine (3 equiv.). Purification by column chromatography on silica gel (petroleum ether:EtOAc = 98:8) yielded **4f** as a yellow solid (69 mg, 78%); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.35 – 8.26 (m, 2H), 7.95 (d, *J* = 7.7 Hz, 1H), 7.56 (dd, *J* = 7.8, 4.1 Hz, 1H), 7.52 – 7.45 (m, 3H), 7.36 (dd, *J* = 8.4, 1.0 Hz, 2H), 3.77 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 154.8, 154.2, 136.1, 133.4, 133.1, 130.5, 130.4, 130.4, 129.6, 128.1, 123.8, 113.6, 29.3. NMR data matched with reported data.[3]

ethyl 2-(2-oxo-3-phenylquinoxalin-1(2H)-yl)acetate (4g):



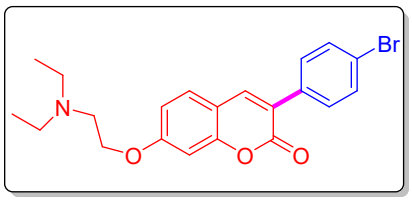
The general procedure was followed using ethyl 2-(2-oxoquinoxalin-1(2H)-yl) acetate (0.26 mmol, 1equiv.), diaryliodonium triflate 2 (1.5 equiv,) and 2,6-lutidine (3 equiv.). Purification by column chromatography on silica gel (petroleum ether:EtOAc = 93:7) yielded **4g** as a yellow solid (60 mg, 75%); **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.33-8.27 (m, 2H), 7.98 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.53 (td, *J* = 8.0, 1.1 Hz, 1H), 7.49-7.44 (m, 3H), 7.39 (td, *J* = 7.6, 1.0 Hz, 1H), 7.11 (d, *J* = 8.3 Hz, 1H), 5.10 (s, 2H), 4.27 (q, *J* = 7.1 Hz, 2H), 1.29 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 167.2, 154.3, 154.0, 135.8, 133.2, 132.6, 130.8, 130.5, 129.9, 129.6, 128.1, 124.1, 113.1, 62.1, 43.8, 14.2. NMR data matched with reported data.[3]

2-(4-methoxyphenyl)-3-phenyl-2H-indazole (4h):



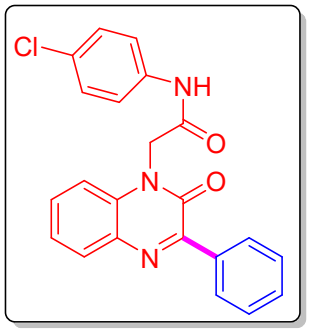
The general procedure was followed using 2-(4-methoxyphenyl) -2H-indazole (0.27 mmol, 1equiv.), diaryliodonium triflate 2 (1.5 equiv,) and 2,6-lutidine (3 equiv.). Purification by column chromatography on silica gel (petroleum ether:EtOAc = 90:10) yielded **4h** as a white solid (35 mg, 44%); **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.79 (d, *J* = 8.4 Hz, 1H), 7.71 (d, *J* = 8.4 Hz, 1H), 7.43 – 7.32 (m, 8H), 7.16 – 7.11 (m, 1H), 6.89 (d, *J* = 8.7 Hz, 2H), 3.83 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 159.4, 148.8, 135.3, 133.4, 130.0, 129.7, 128.8, 128.2, 127.2, 126.9, 122.4, 121.6, 120.5, 117.7, 114.2, 55.5. NMR data matched with reported data.[4]

3-(4-bromophenyl)-7-(2-(diethylamino)ethoxy)-2H-chromen-2-one (4i) :



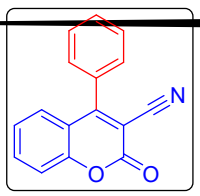
The general procedure was followed using 7-(2-(diethylamino)ethoxy)-2H-chromen-2-one (0.22 mmol, 1equiv.), diaryliodonium triflate 2 (1.5 equiv,) and 2,6-lutidine (3 mol%,). The crude product was purified by column chromatography on silica gel. (DCM**:**MeOH = 95:5). White solid (59 mg, 62%); m.p.199-201 ºC; **^{1}H NMR (400 MHz, CDCl$_3$)**: δ 7.77 (s, 1H), 7.61-7.55 (m, 4H), 7.49 (d, *J* = 8.3 Hz, 1H), 6.93 (d, *J* = 8.1 Hz, 1H), 6.87 (s, 1H), 4.74-4.62 (m, 2H), 3.54-3.47 (m, 2H), 3.28 (q, *J* = 6.7 Hz, 4H), 1.49 (t, *J* = 5.9 Hz, 6H). **^{13}C NMR (101 MHz, CDCl$_3$)**: δ 162.1, 162.0, 156.9, 141.6, 135.5, 133.5, 131.9, 131.3, 126.5, 124.8, 116.2, 114.0, 104.0, 65.3, 52.6, 49.2, 10.5. NMR data matched with the data reported in the literature.[5]

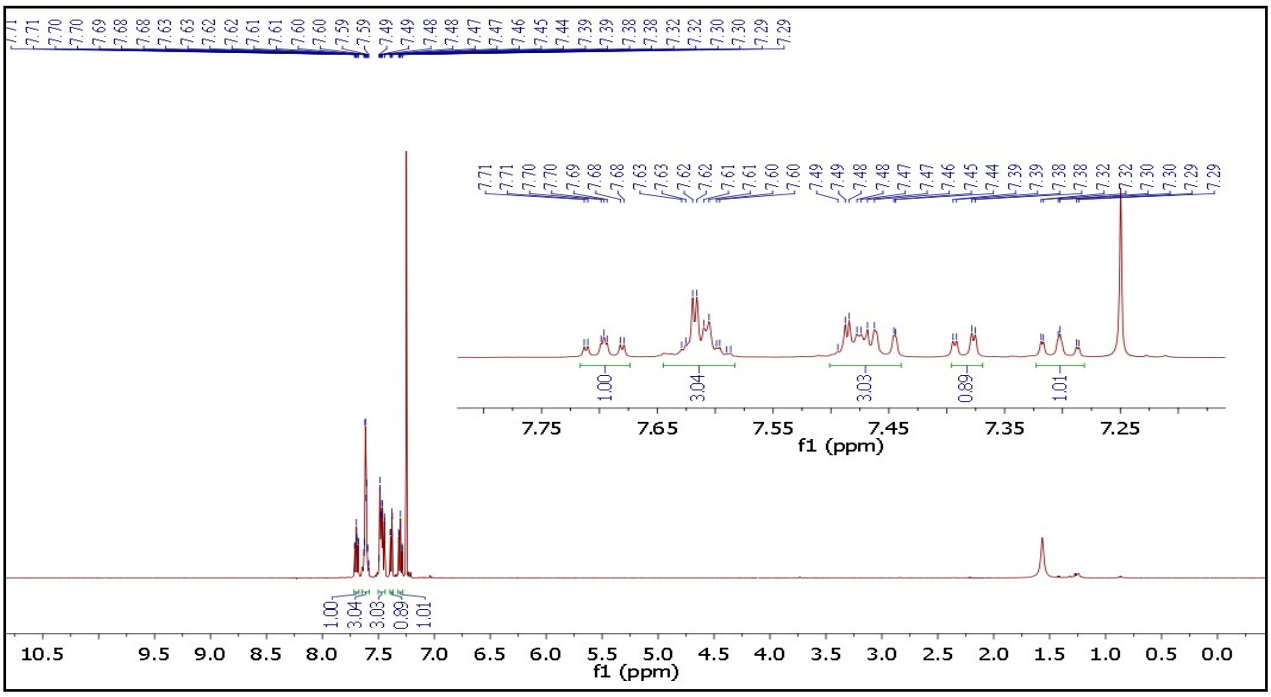
N-(4-chlorophenyl)-2-(2-oxo-3-phenylquinoxalin-1(2H)-yl) acetamide (4j):



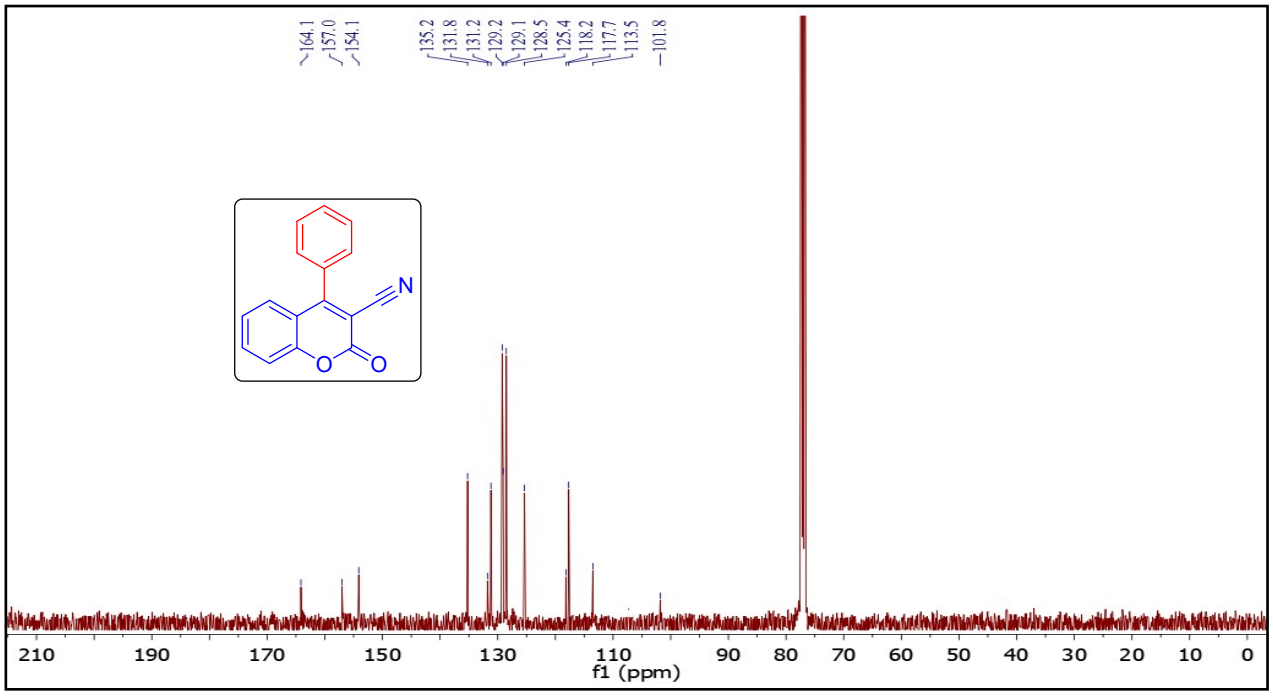
The general procedure was followed using N-(4-chlorophenyl)-2-(2-oxo-quinoxalin-1(2H)-yl)acetamide (0.19 mmol, 1equiv.), diaryliodonium triflate 2 (1.5 equiv,) and 2,6-lutidine (3 equiv.). Purification by column chromatography on silica gel (petroleum ether:EtOAc = 75:25) yielded **4** as a yellow solid (43 mg, 58%); **^{1}H NMR (400 MHz, DMSO)** δ 10.60 (s, 1H), 8.24 (d, *J* = 6.2Hz, 2H), 7.91 (d, *J* = 6.3 Hz, 1H), 7.68 – 7.23 (m, 10H), 5.17 (s, 2H). **^{13}C NMR (101 MHz, DMSO-d$_6$)** δ 165.5, 154.4, 153.4, 138.0, 136.1, 133.6, 132.8, 131.2, 130.8, 130.3, 129.8, 129.3, 128.4, 127.7, 124.3, 121.3, 115.2, 46.1. NMR data is consistent with the data reported in the literature.[3]

Copies of NMR spectra of products**: ^{1}H NMR (500 MHz, CDCl$_3$) spectrum of 3a:**

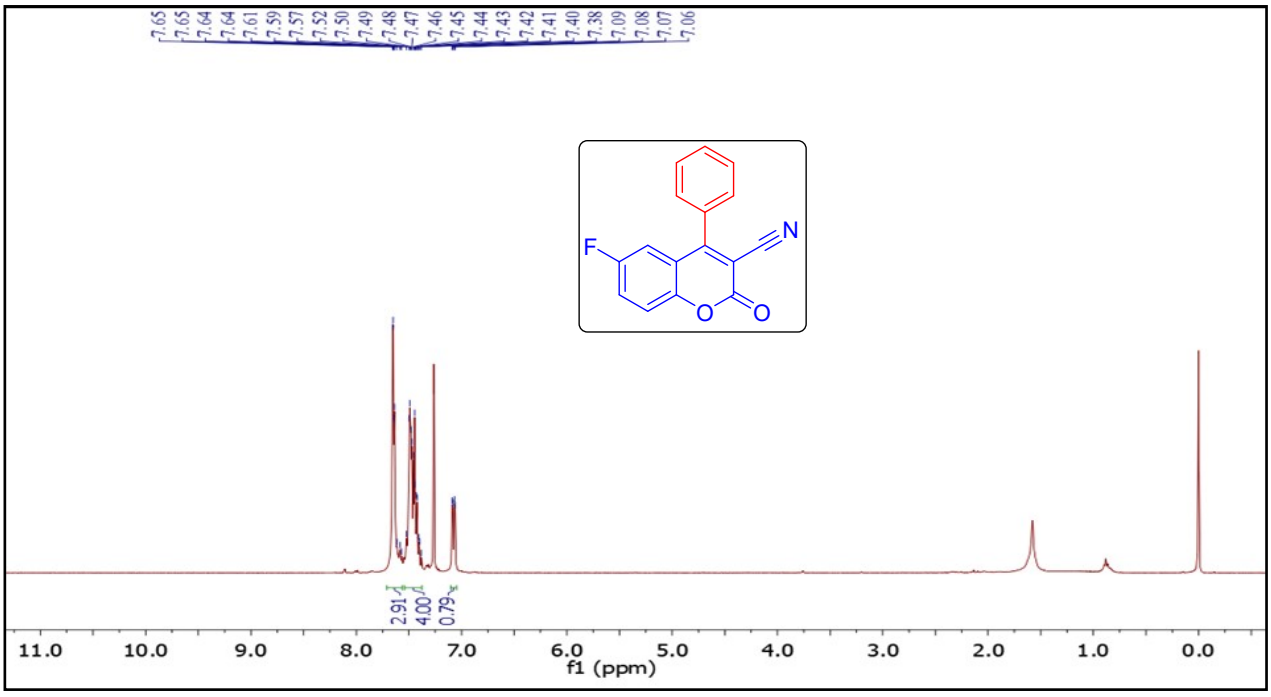




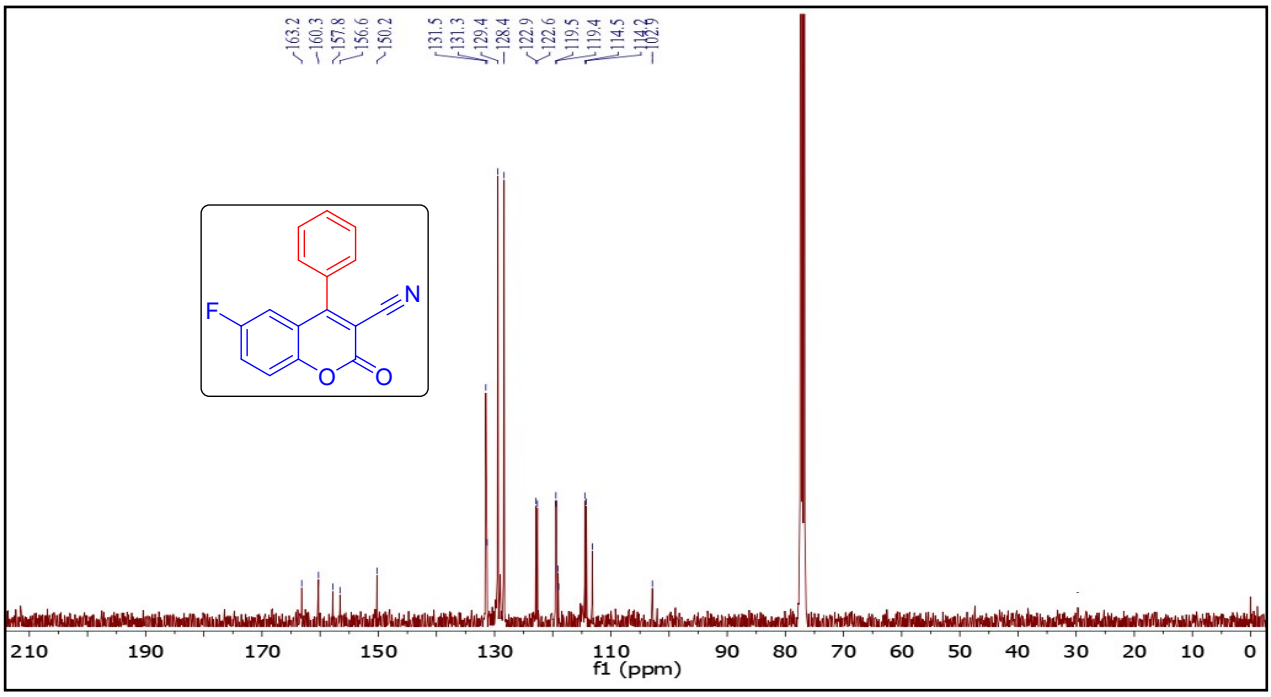
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of 3a:



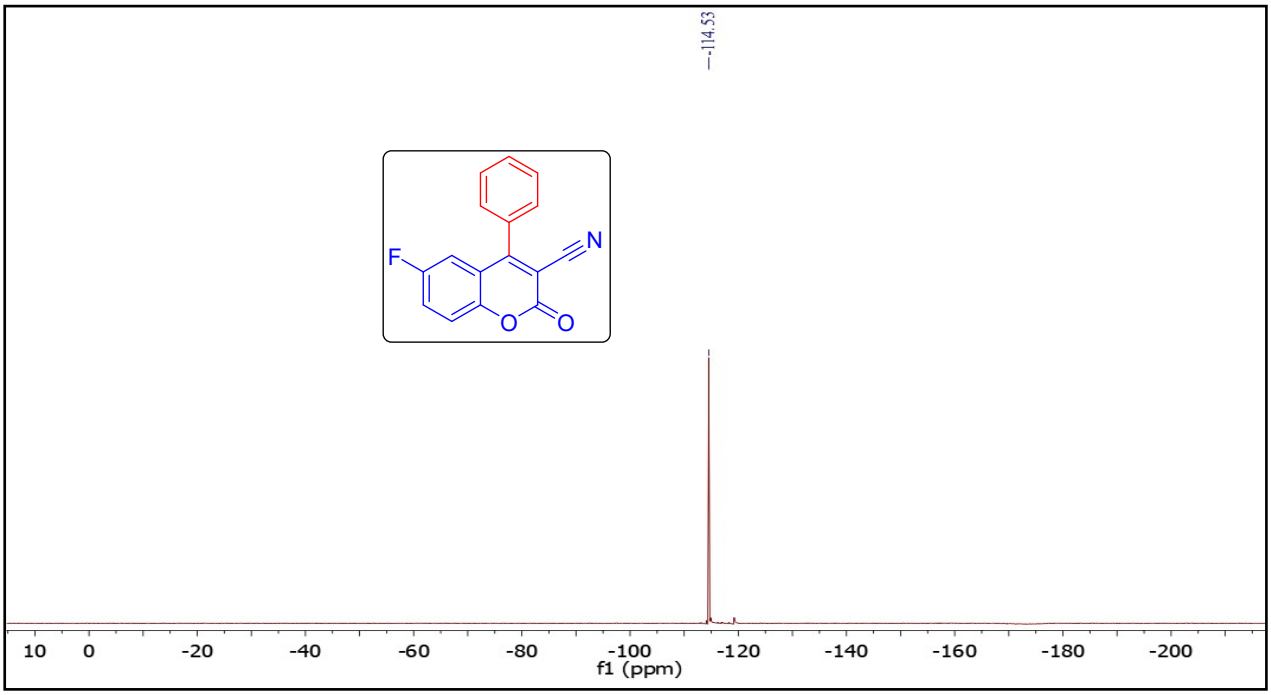
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 3b:



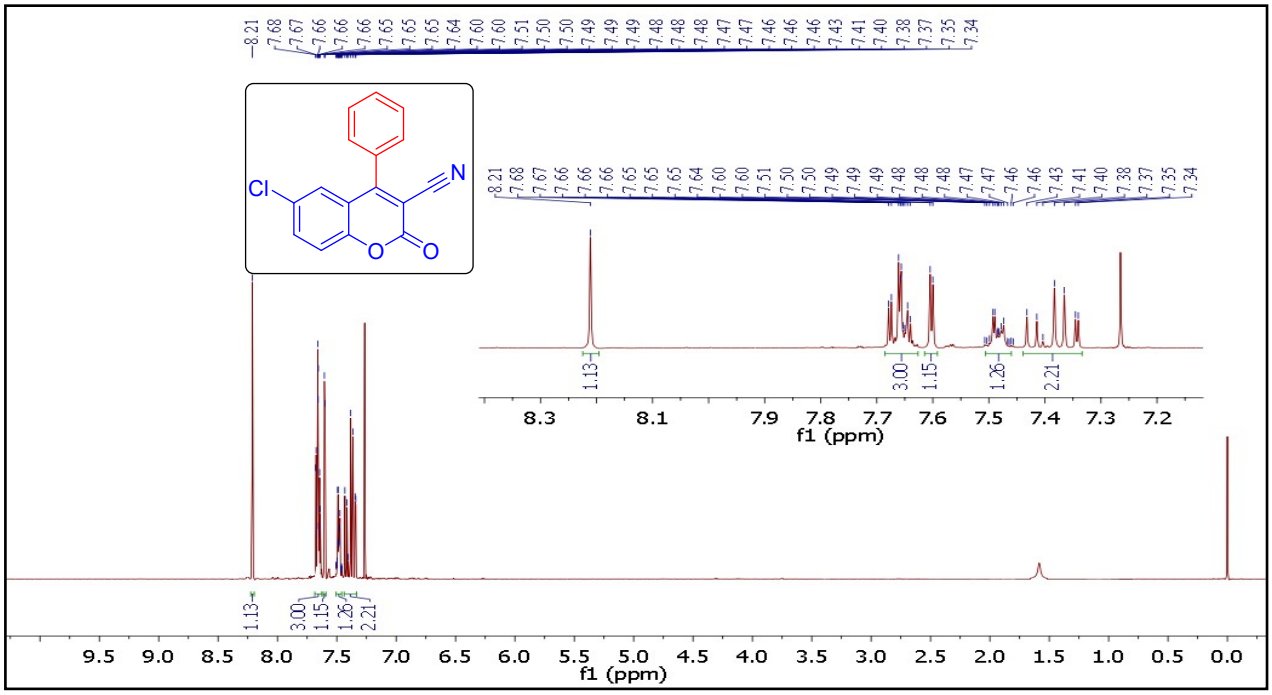
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound 3b:



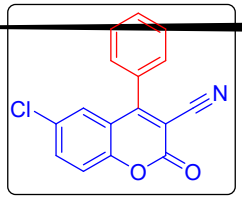
^{19}F NMR (377 MHz, $CDCl_3$) spectrum of compound 3b:

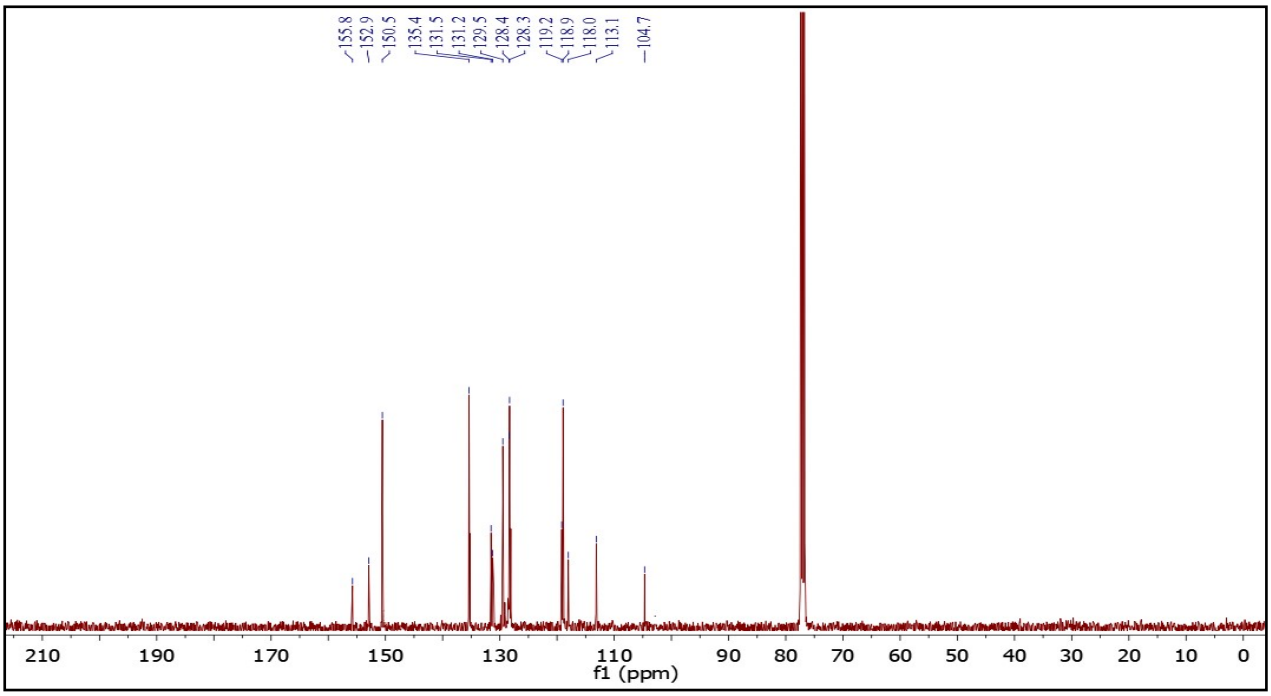


^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound 3c:

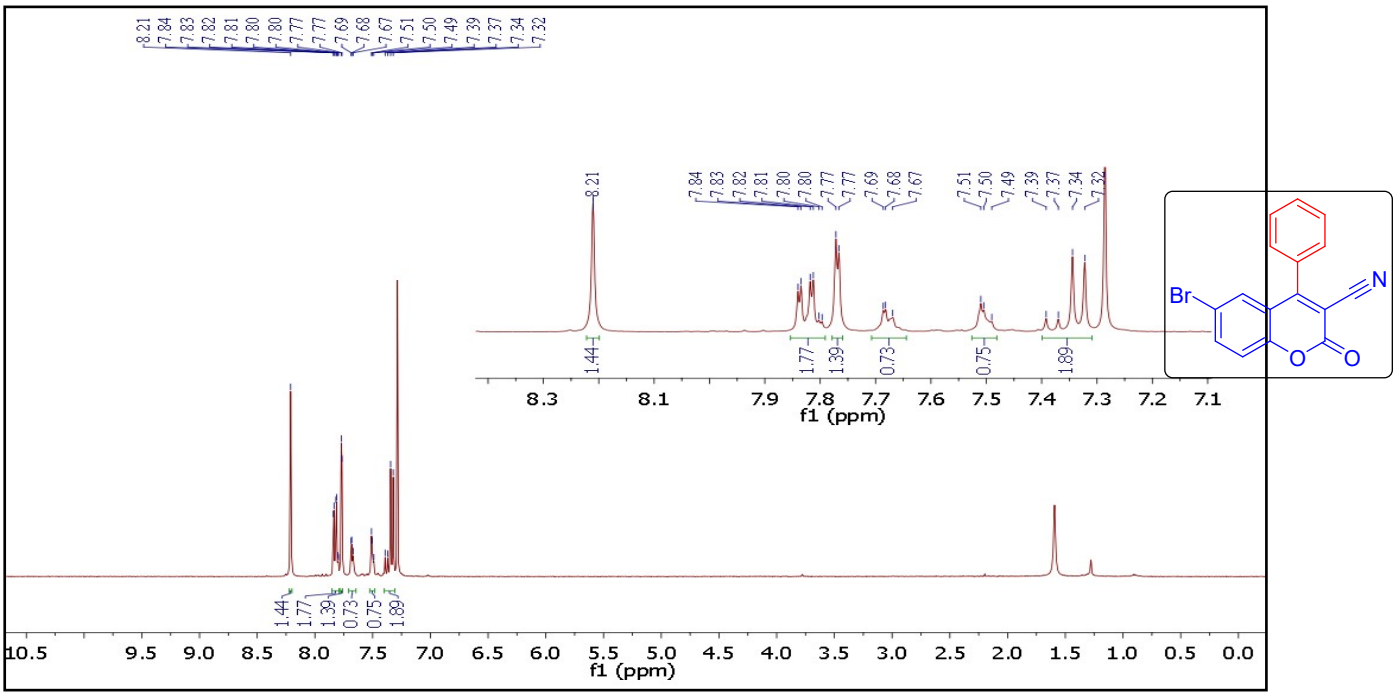


^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound 3c:

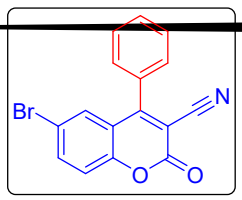


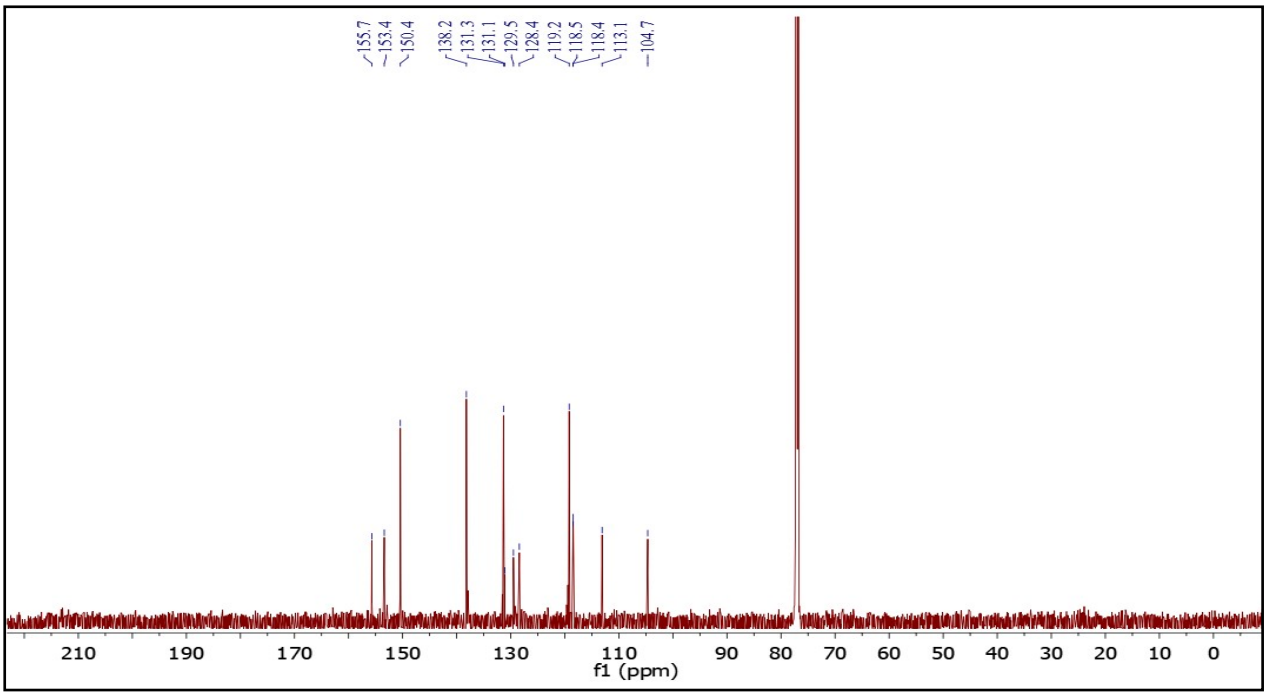


^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 3d:

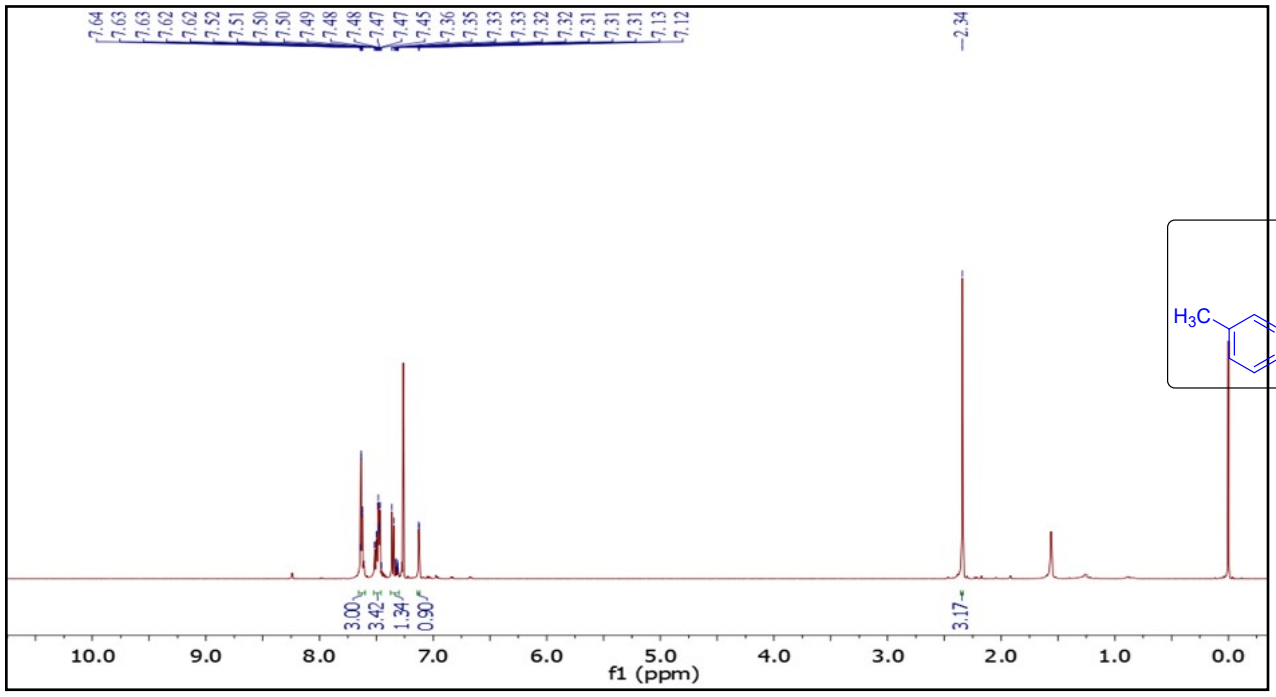


^{13}C NMR (176 MHz, $CDCl_3$) spectrum of compound 3d:

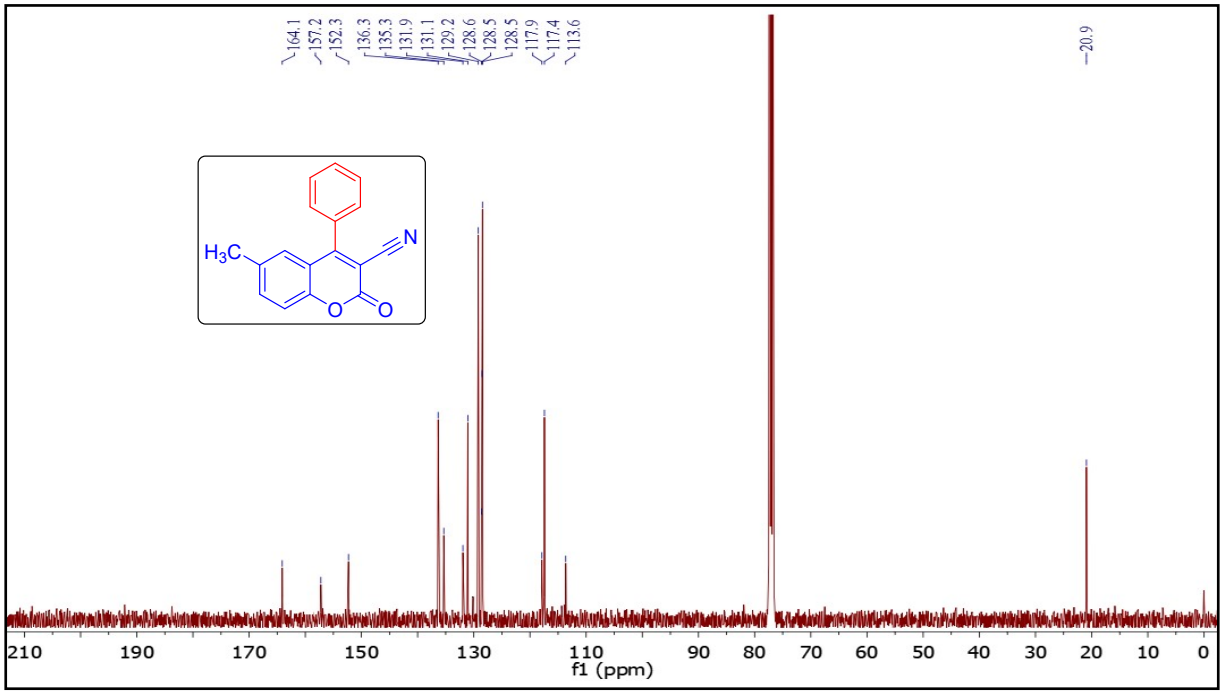




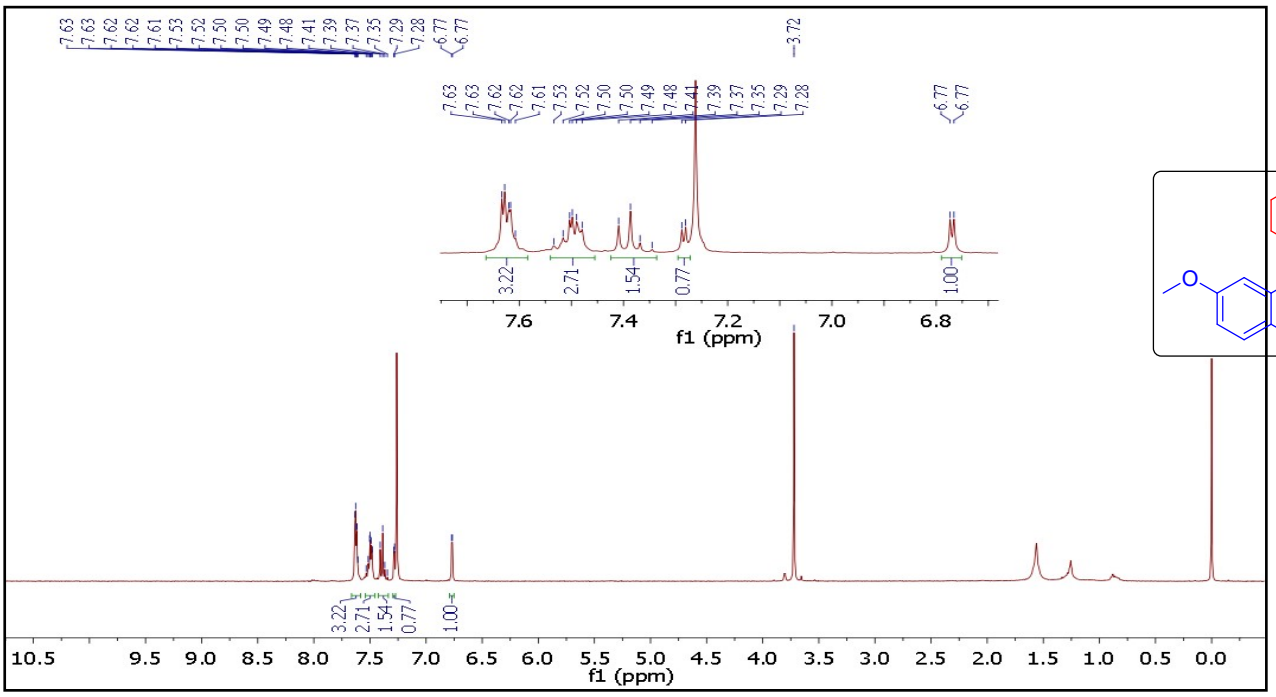
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound 3e:



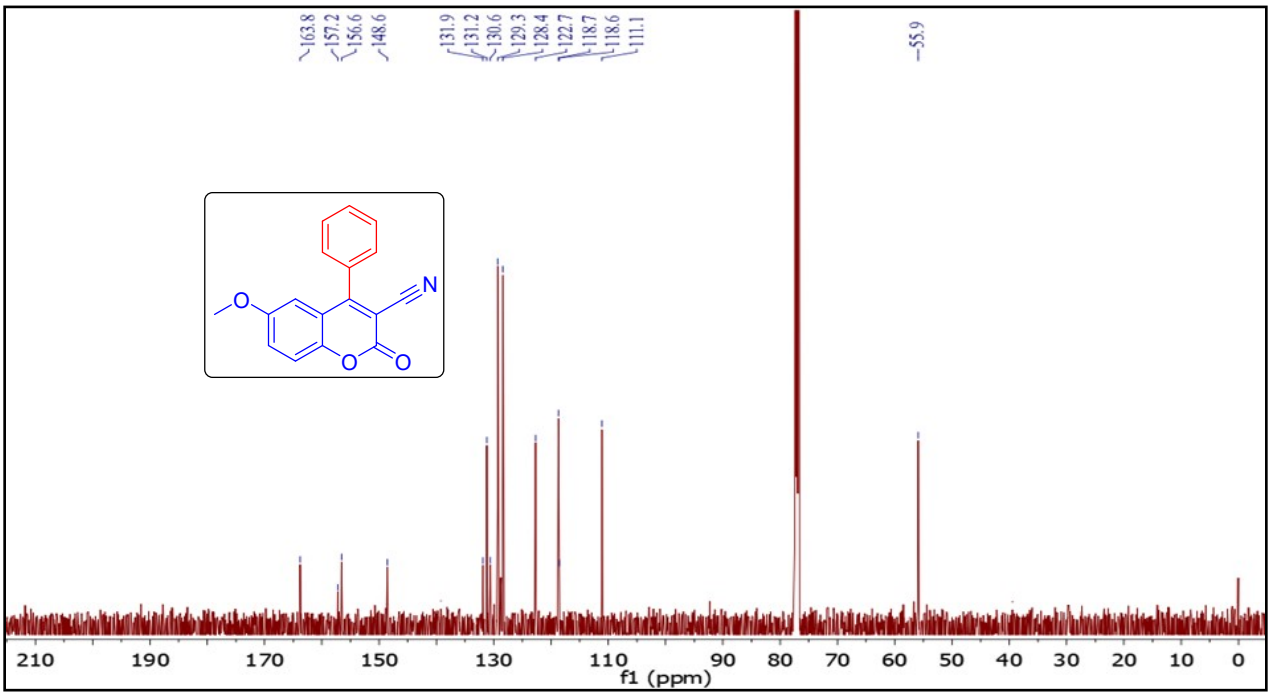
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound 3e:



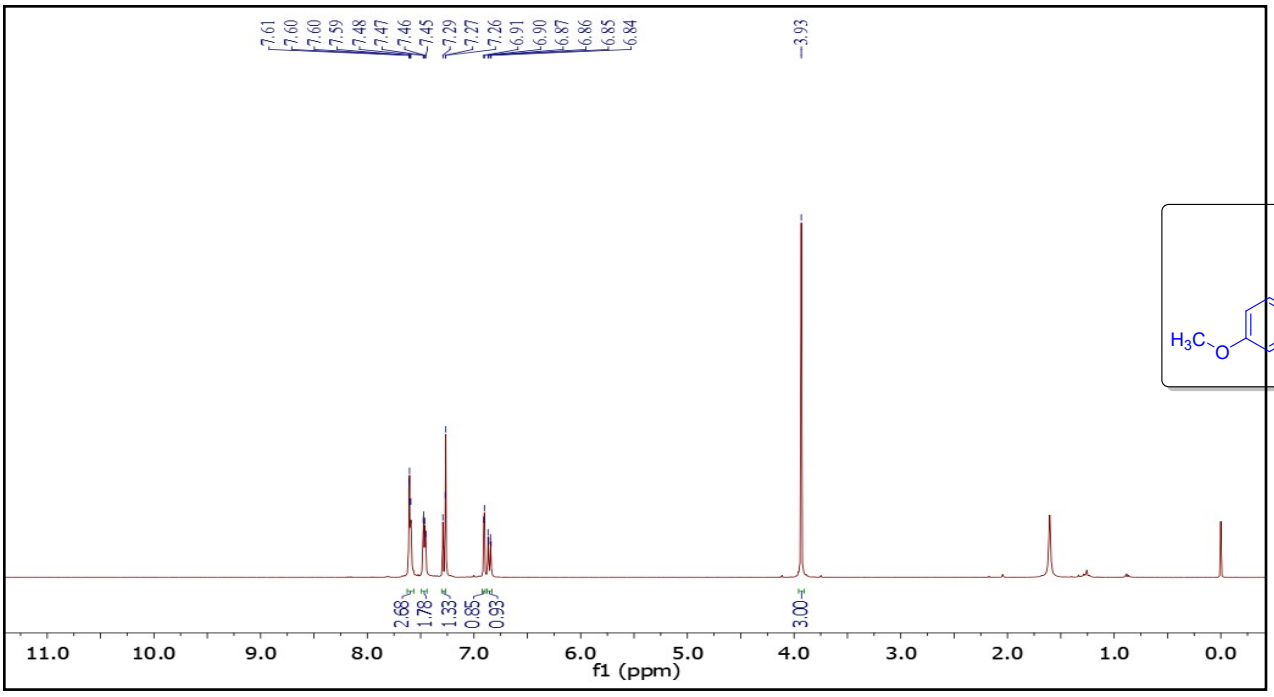
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 3f:



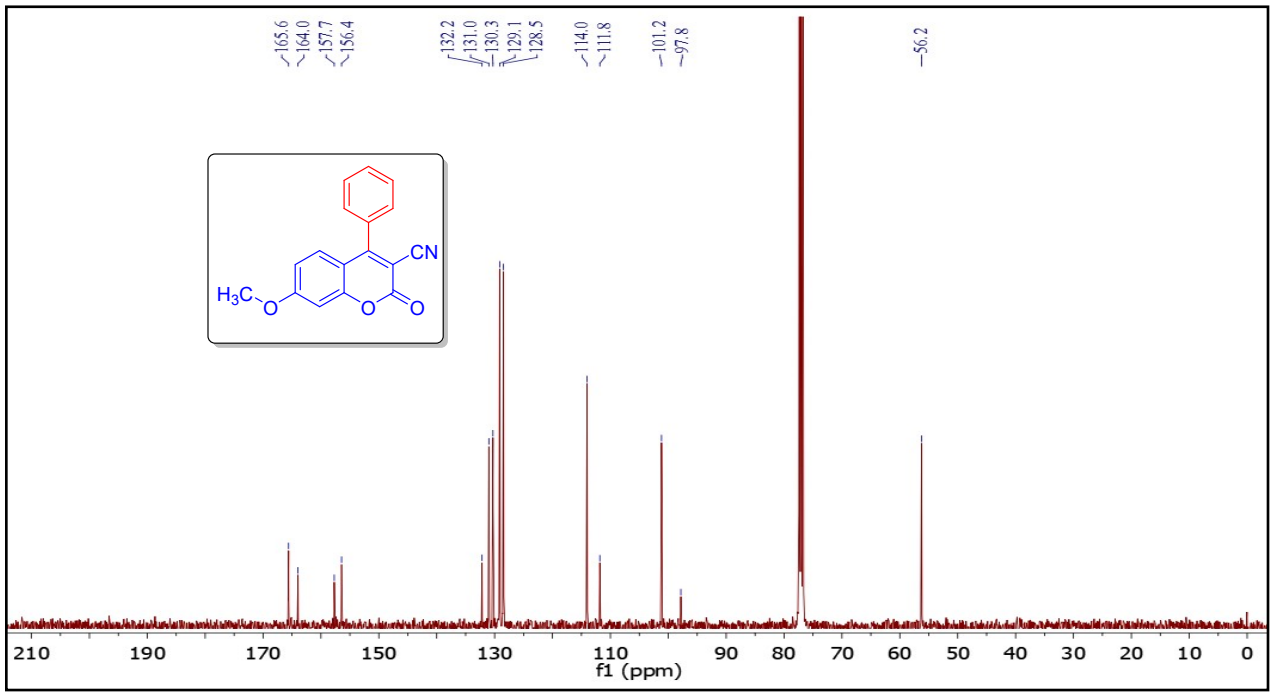
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound 3f:



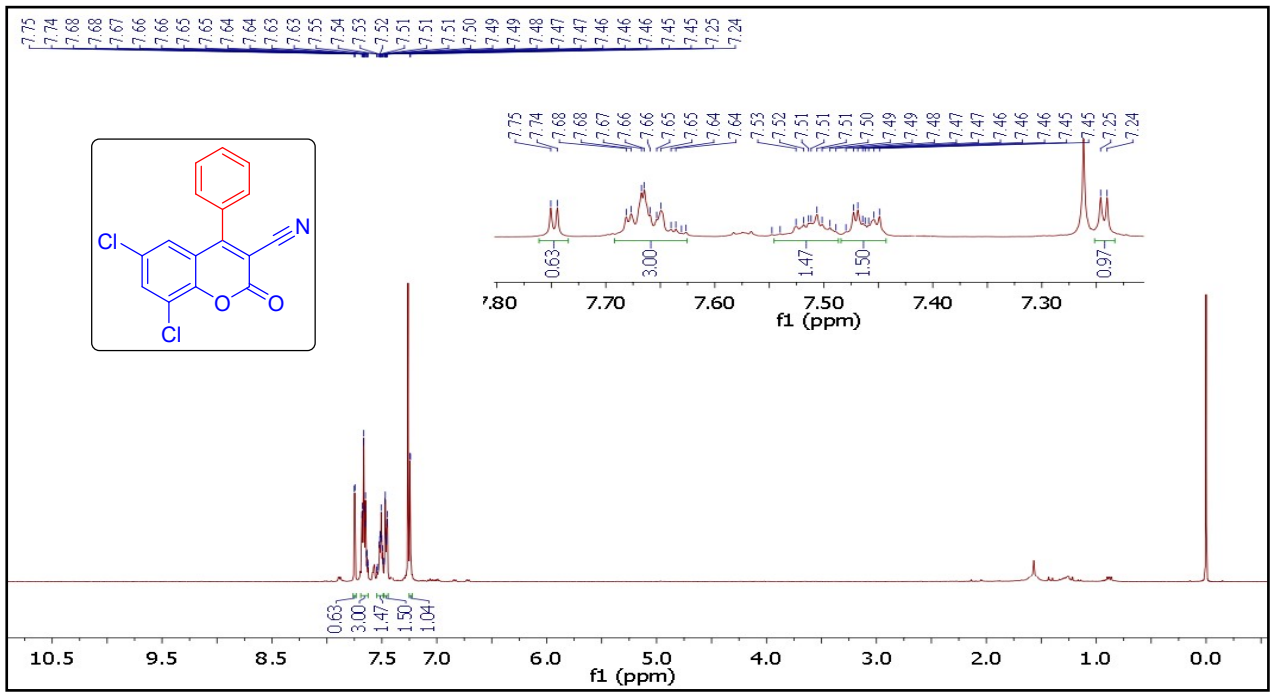
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 3h:



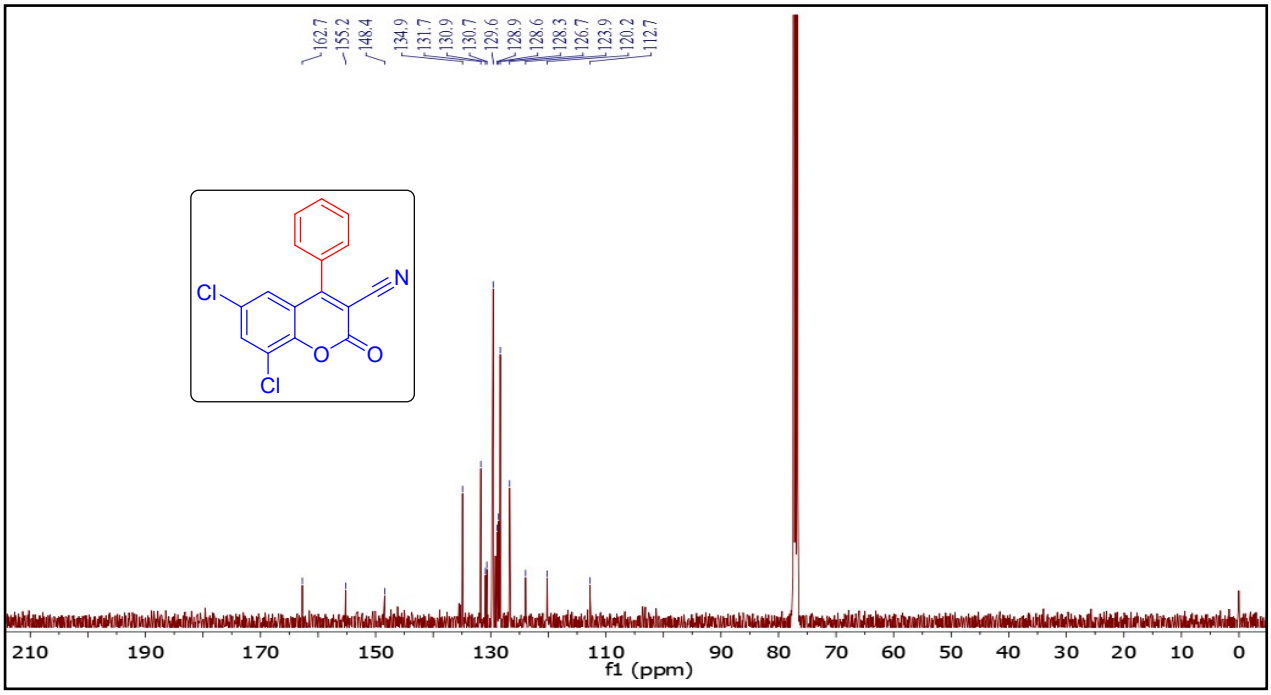
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound 3h:



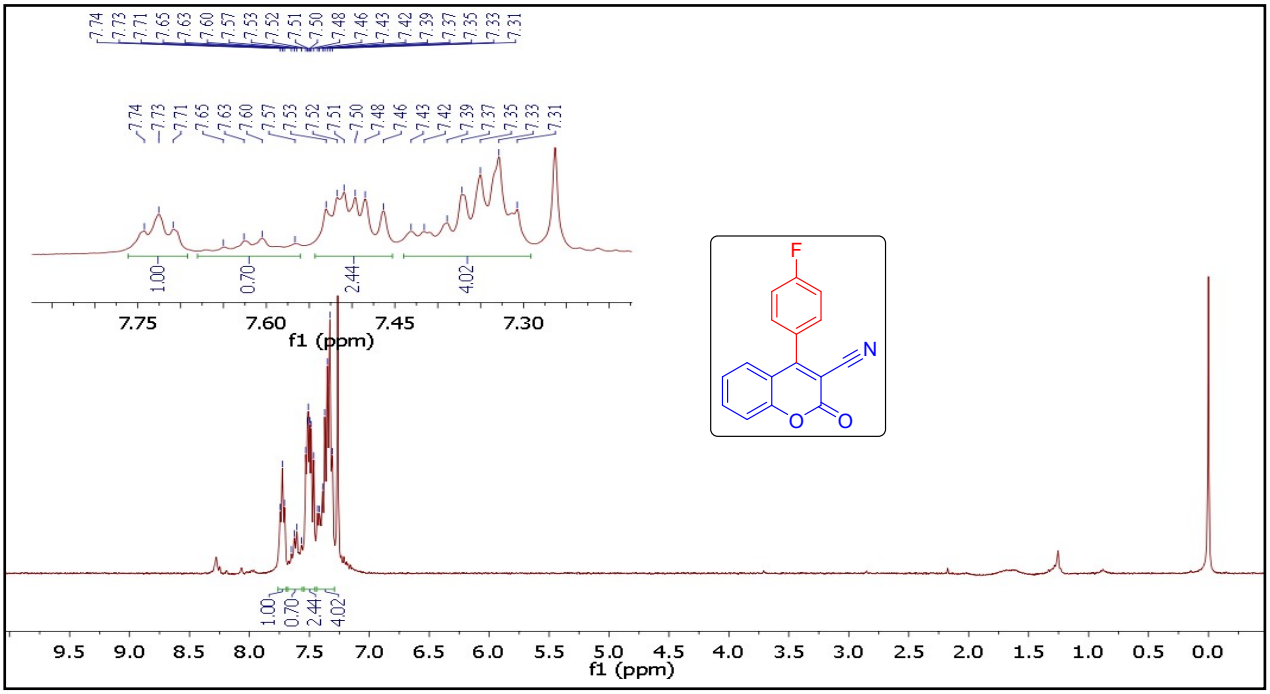
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 3i:



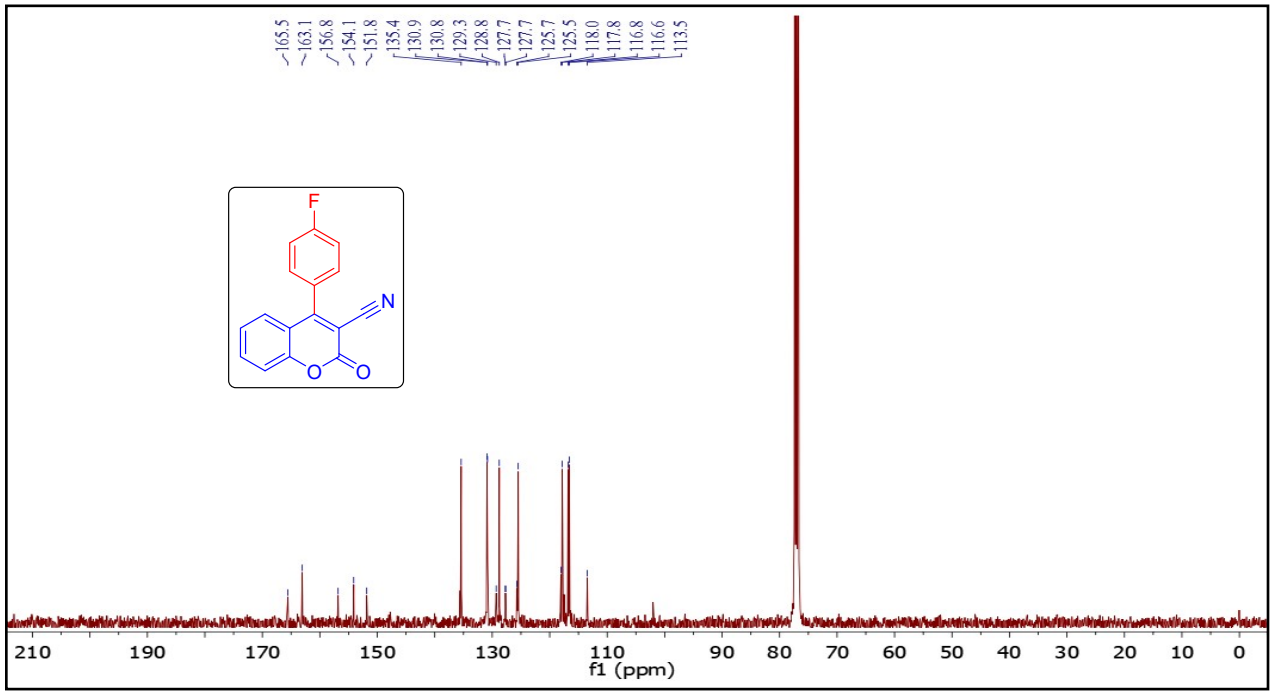
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound 3i:



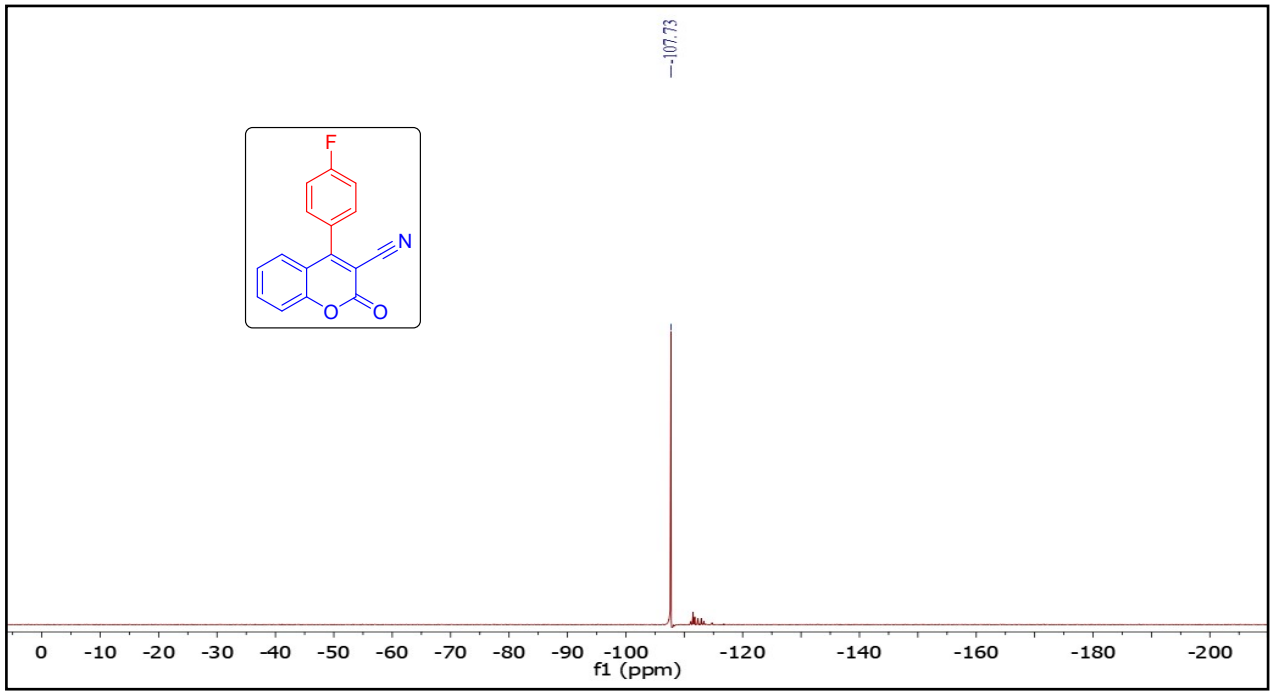
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 3j:



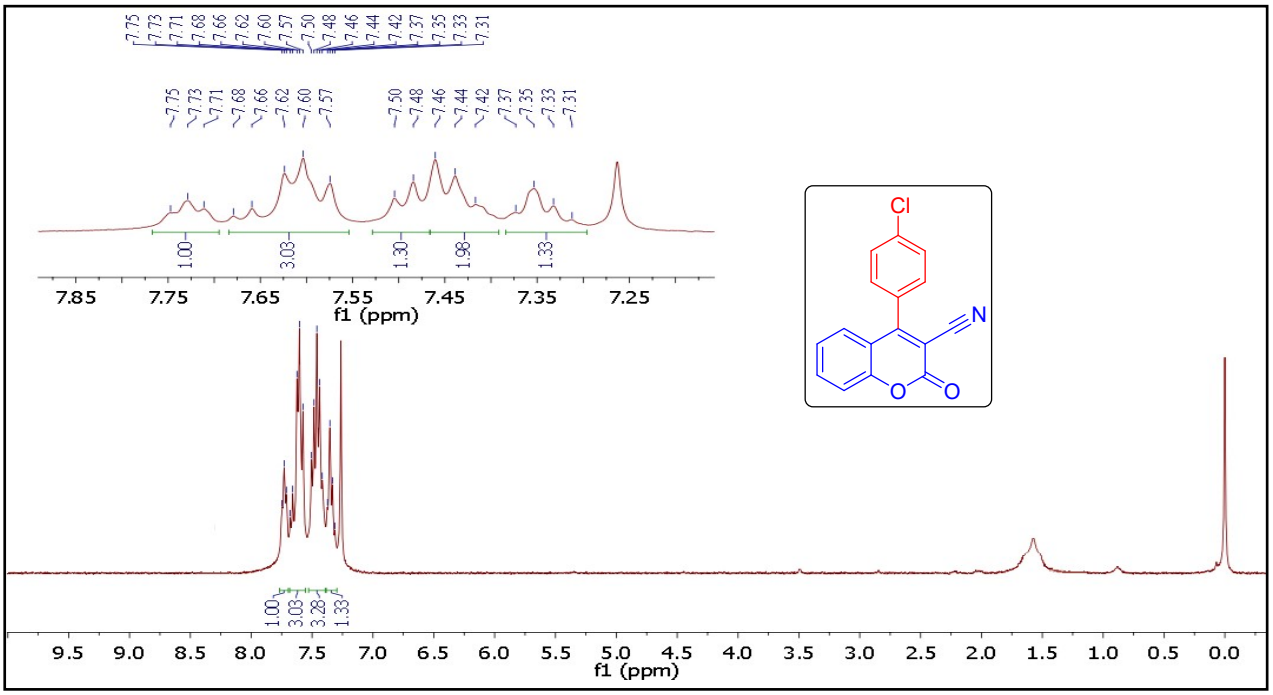
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound 3j:



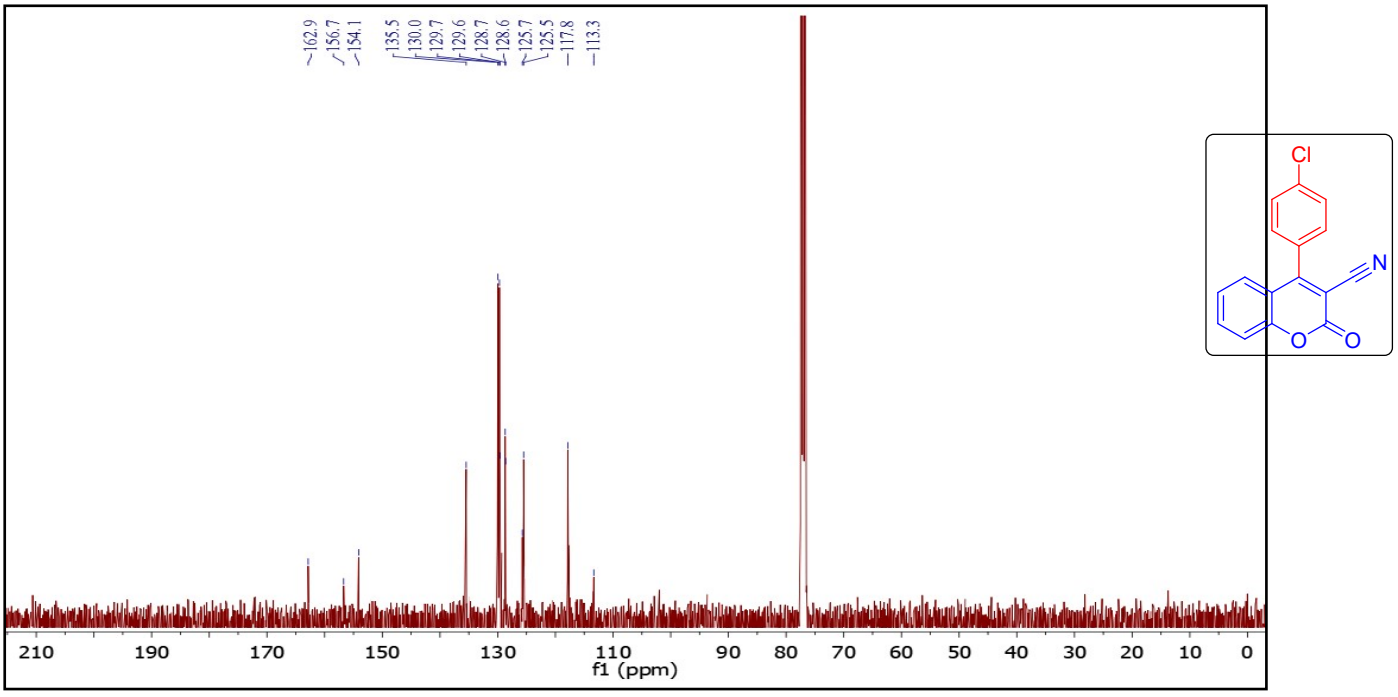
^{19}F NMR (377MHz, $CDCl_3$) spectrum of compound 3j:



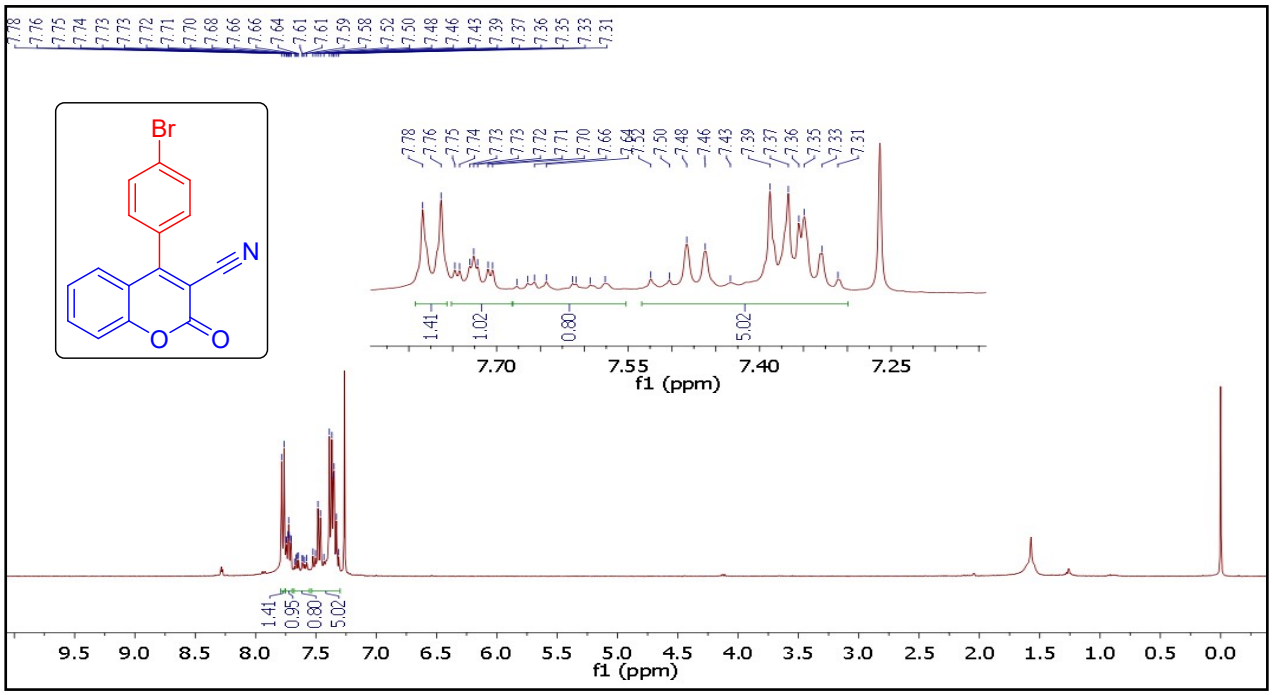
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 3k:



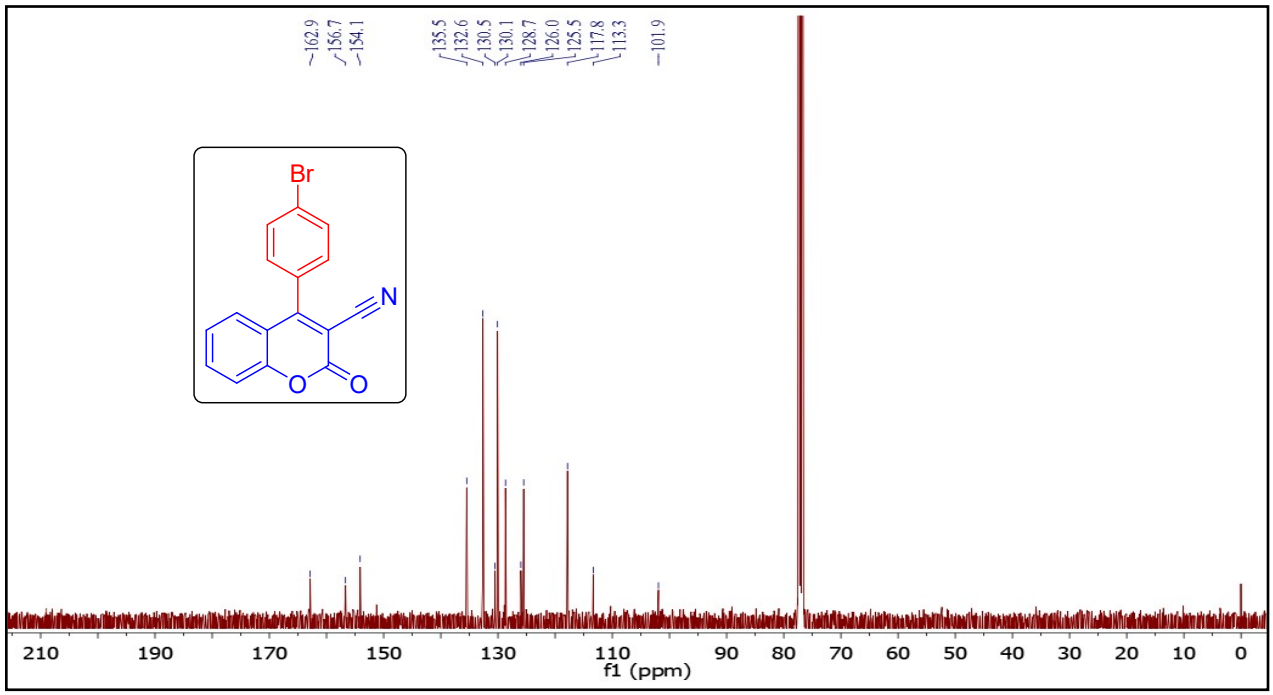
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound 3k:



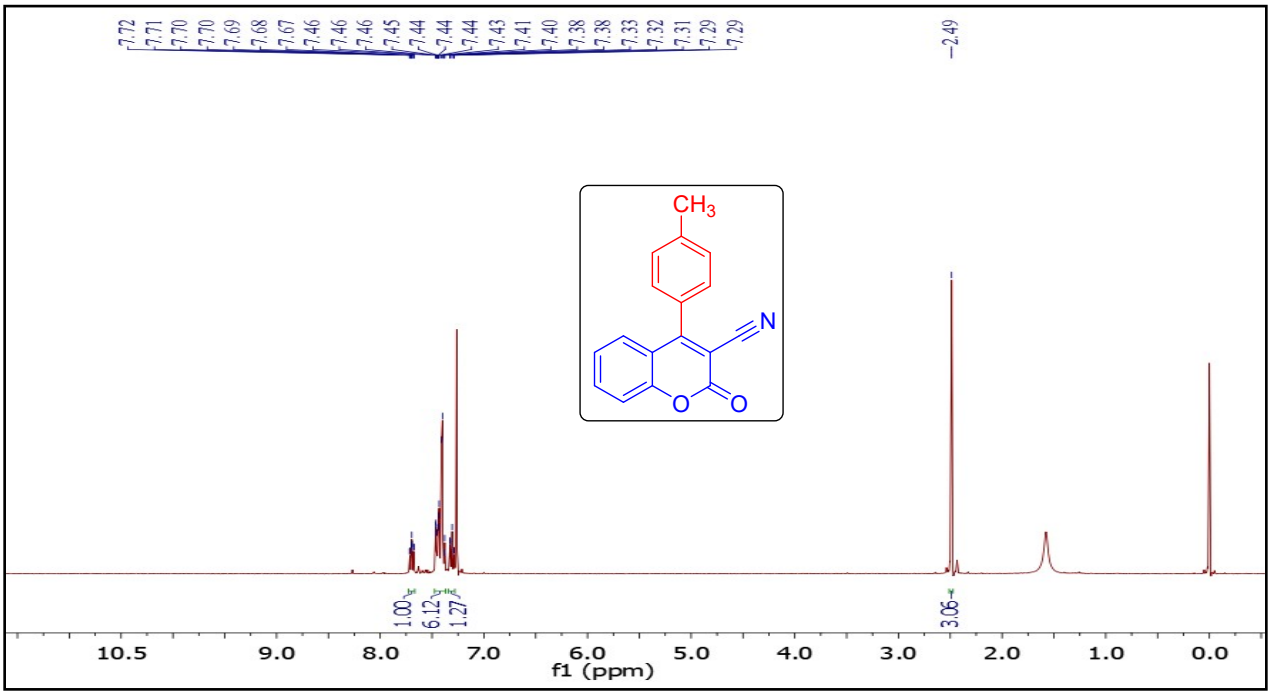
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 3l:



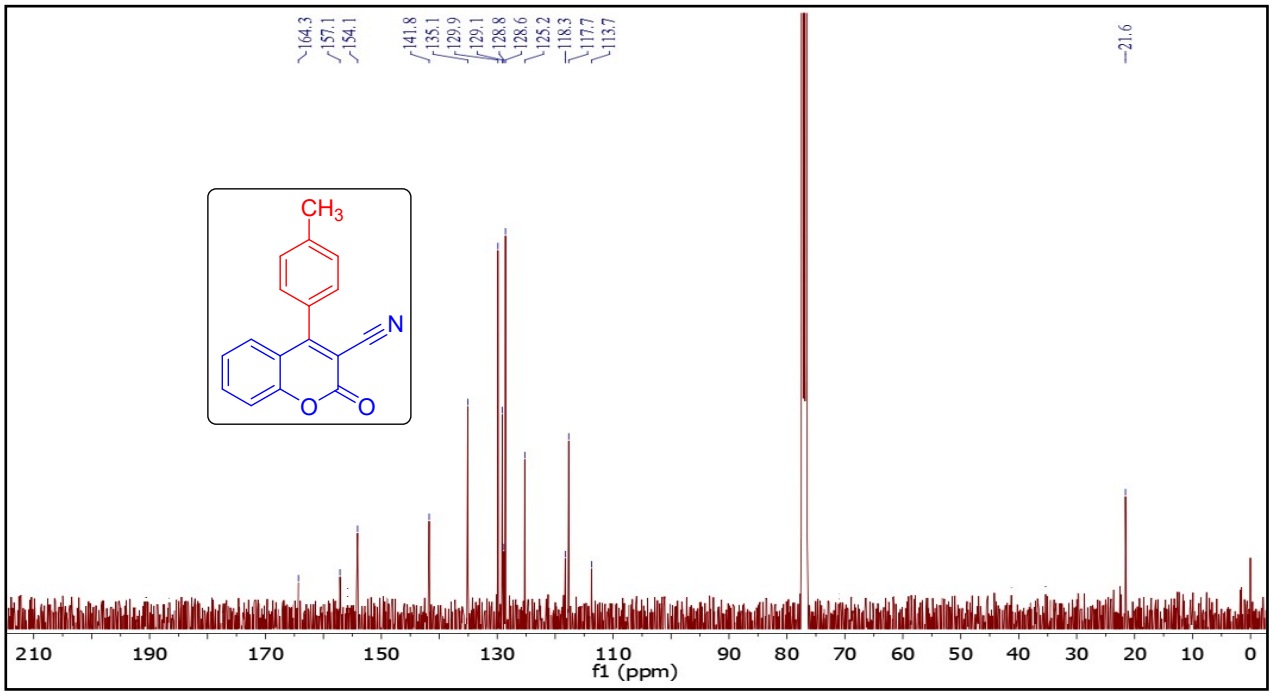
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound 3l:



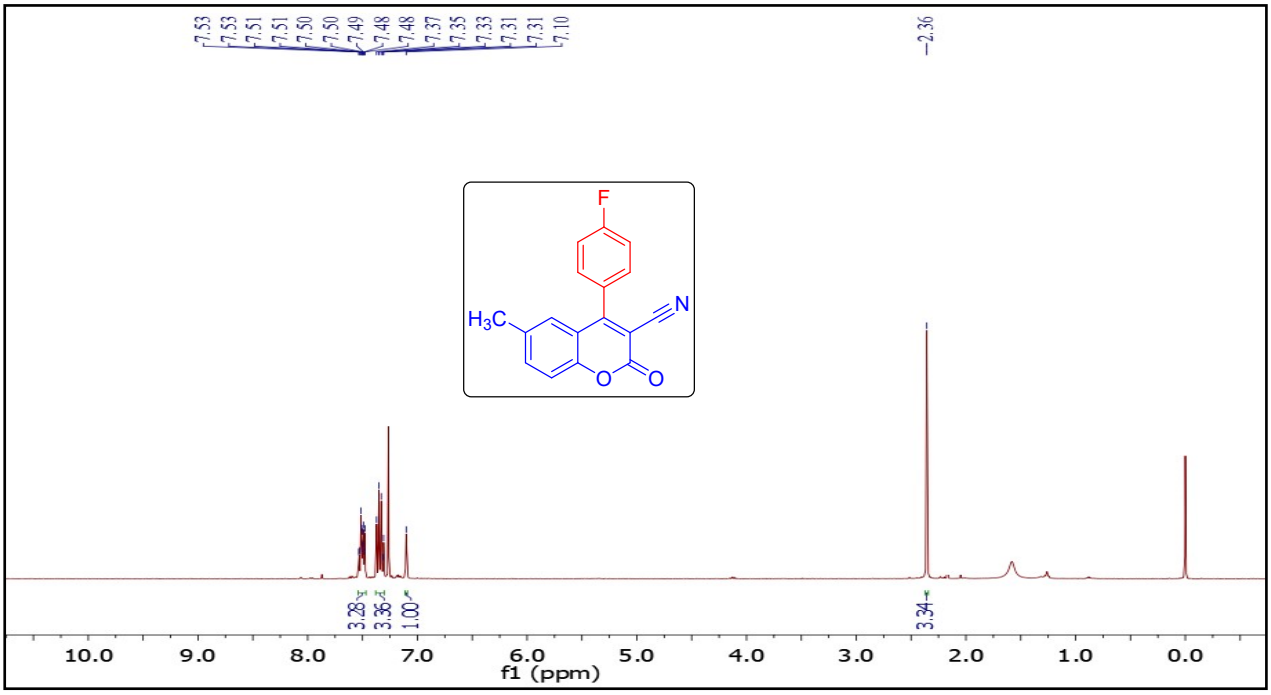
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 3m:



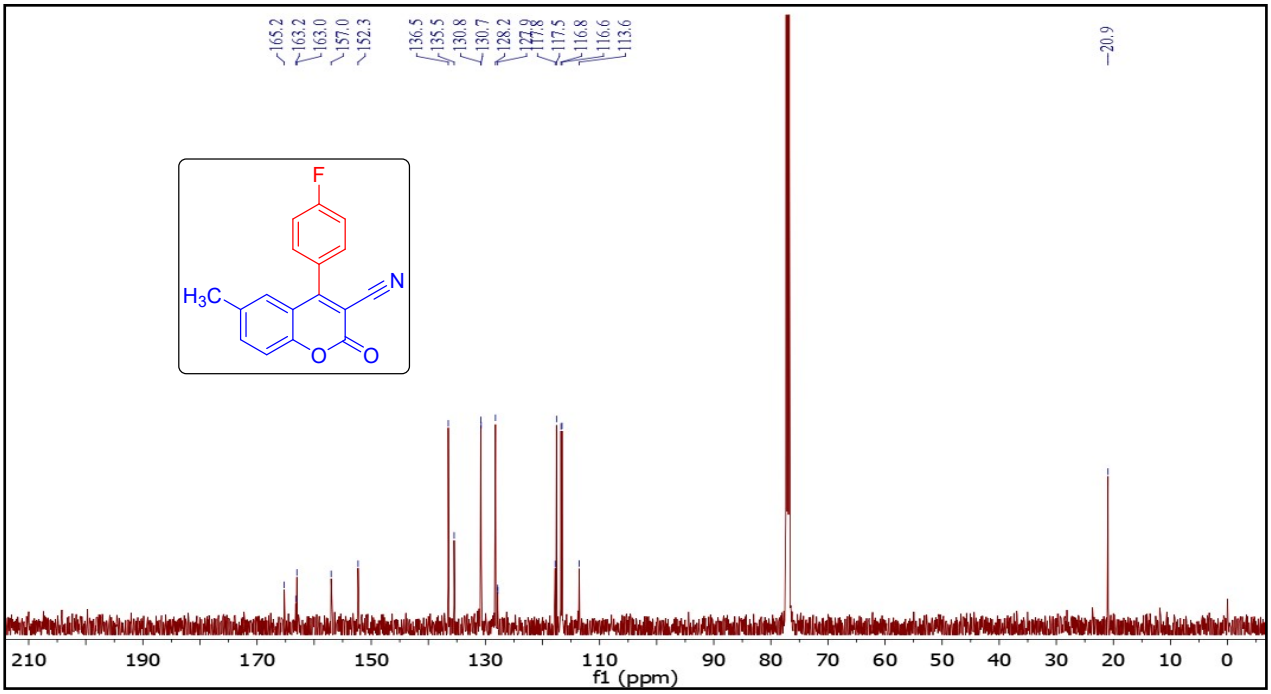
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound 3m:



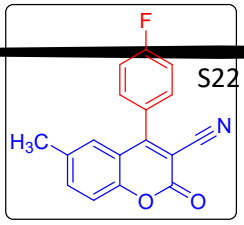
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 3o:

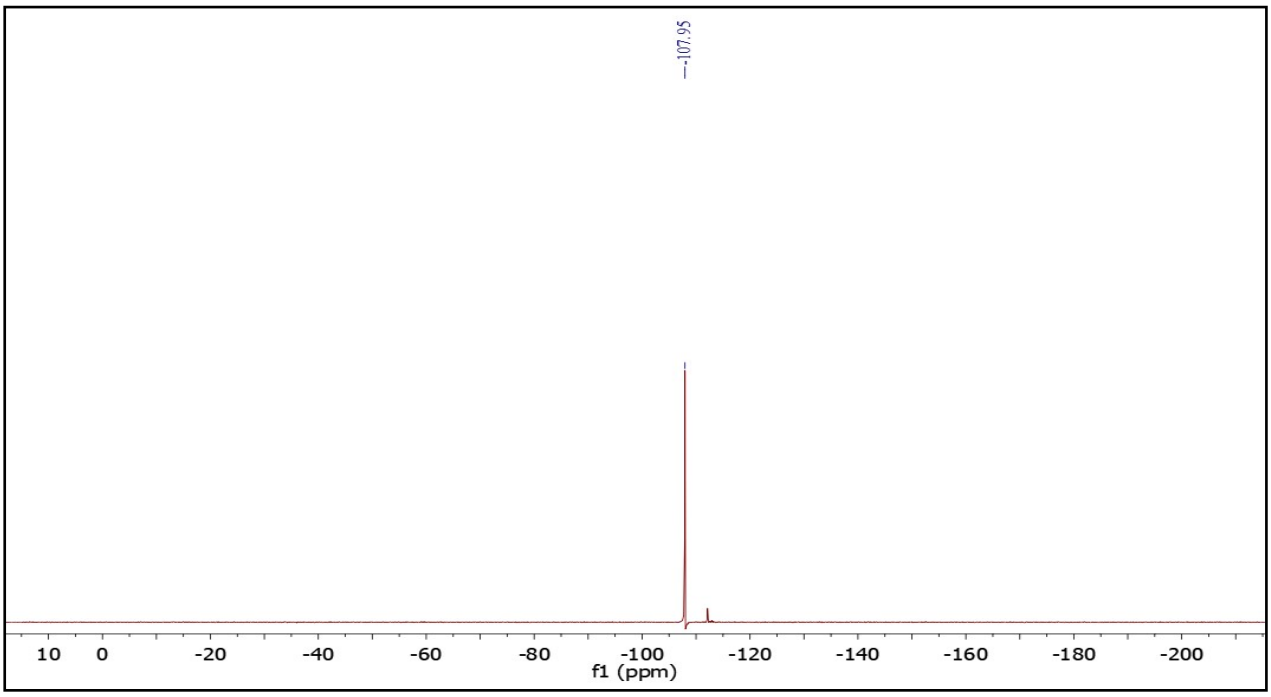


^{13}C NMR (126 MHz, $CDCl_3$) spectrum of compound 3o:

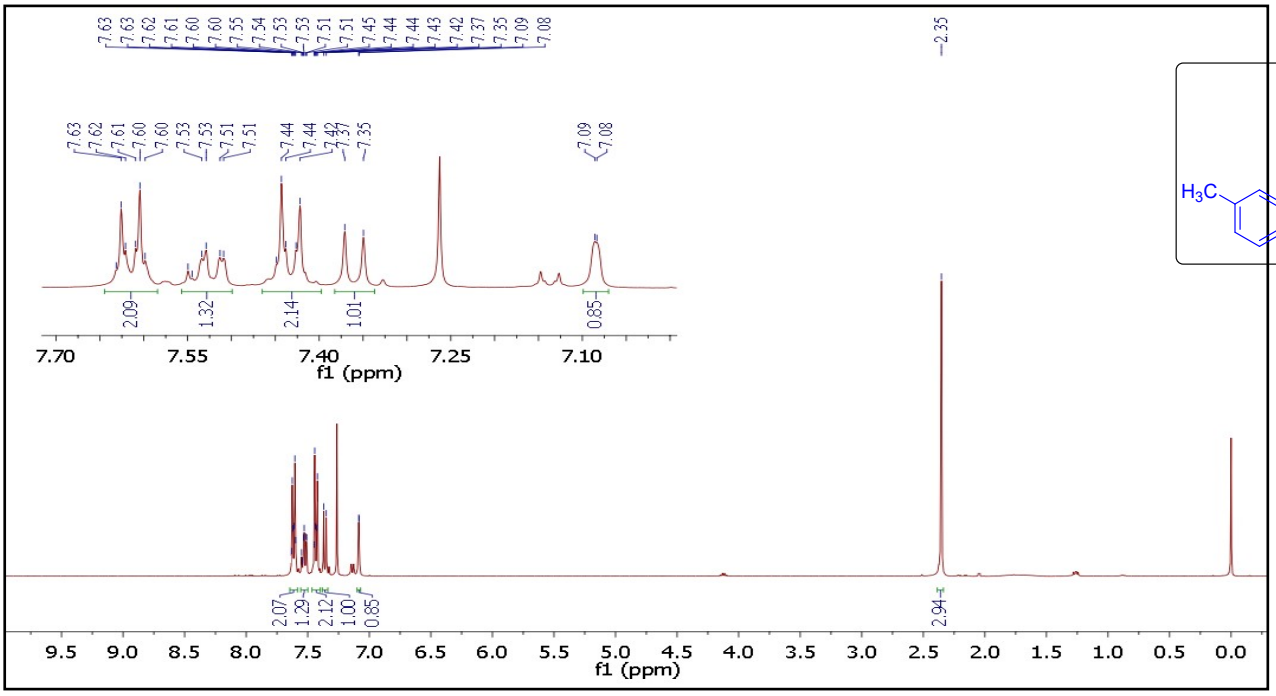


^{19}F NMR (377MHz, $CDCl_3$) spectrum of compound 3o:

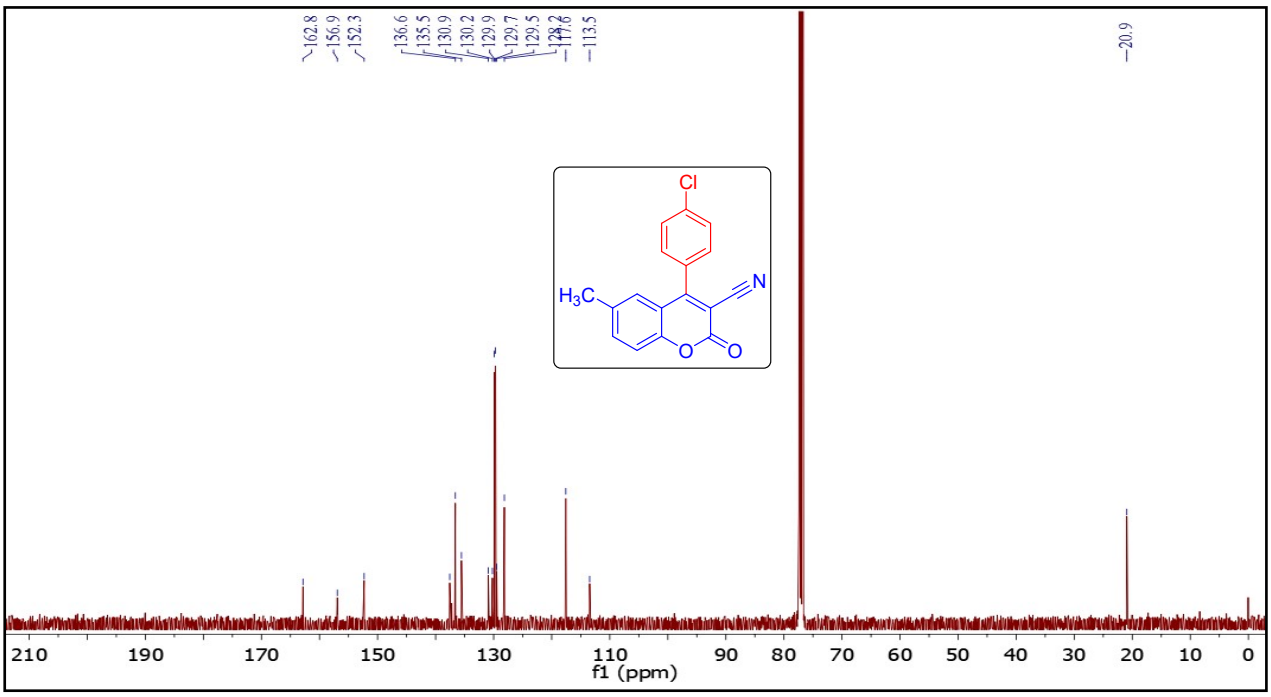




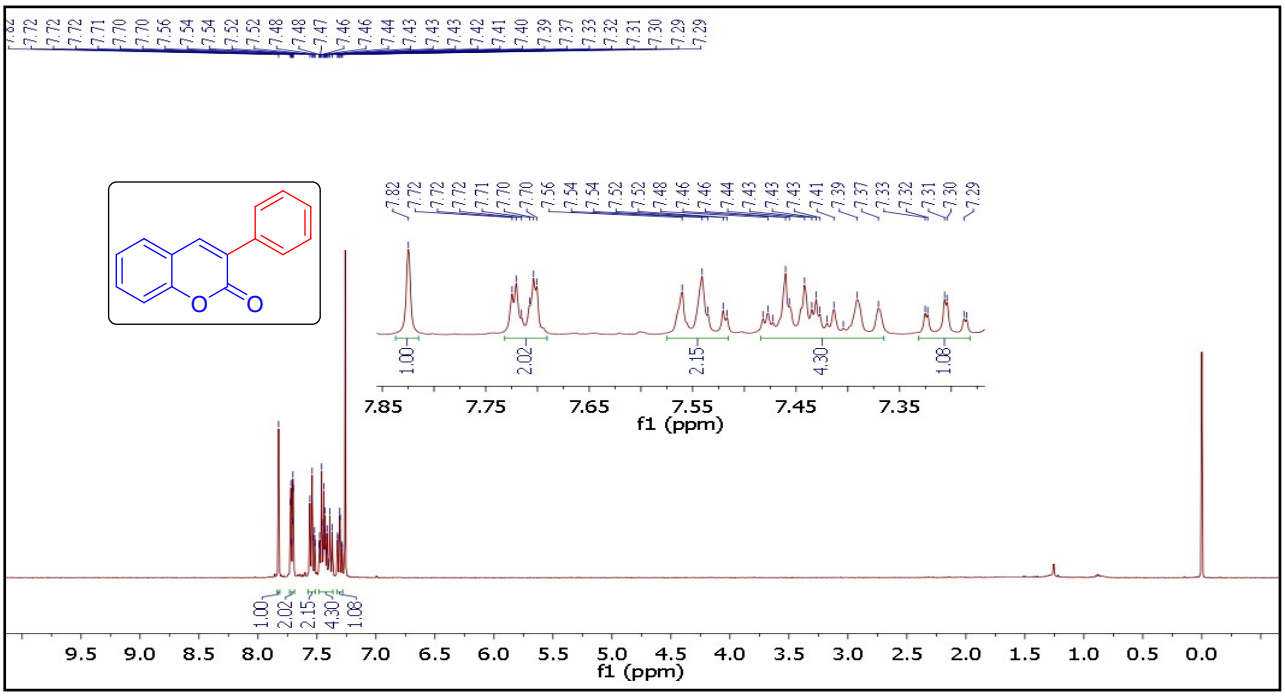
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 3p:



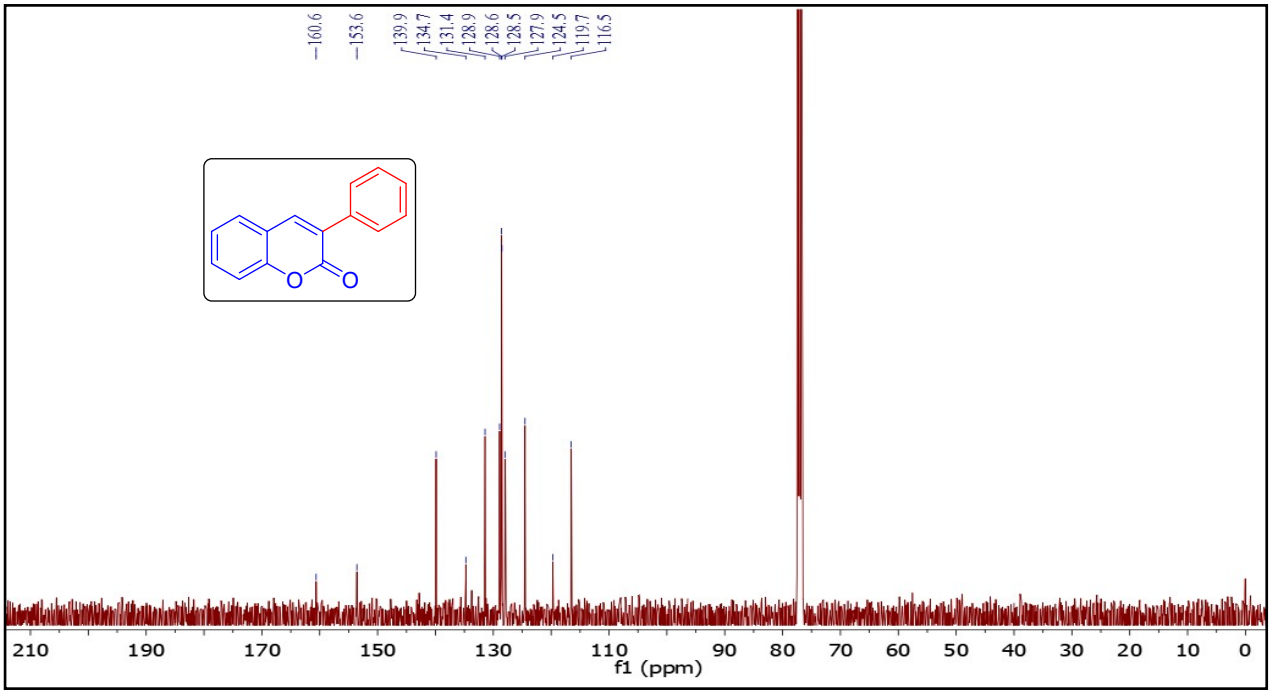
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound 3p:



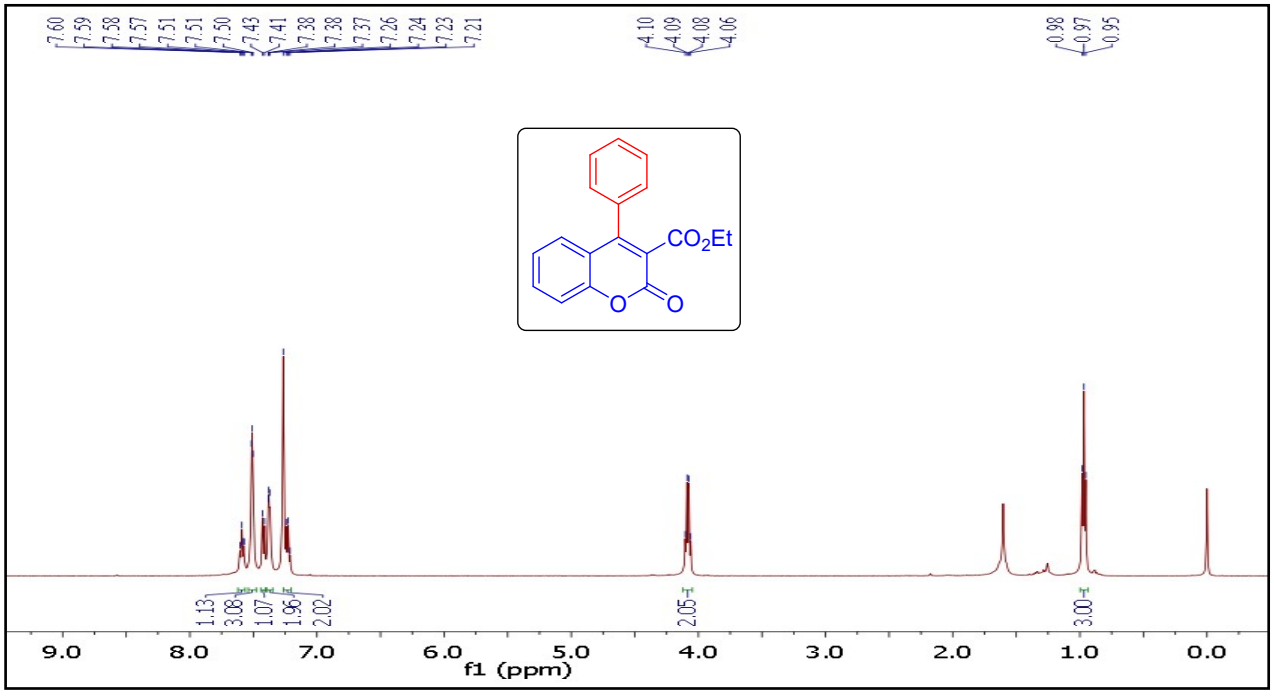
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 4a:



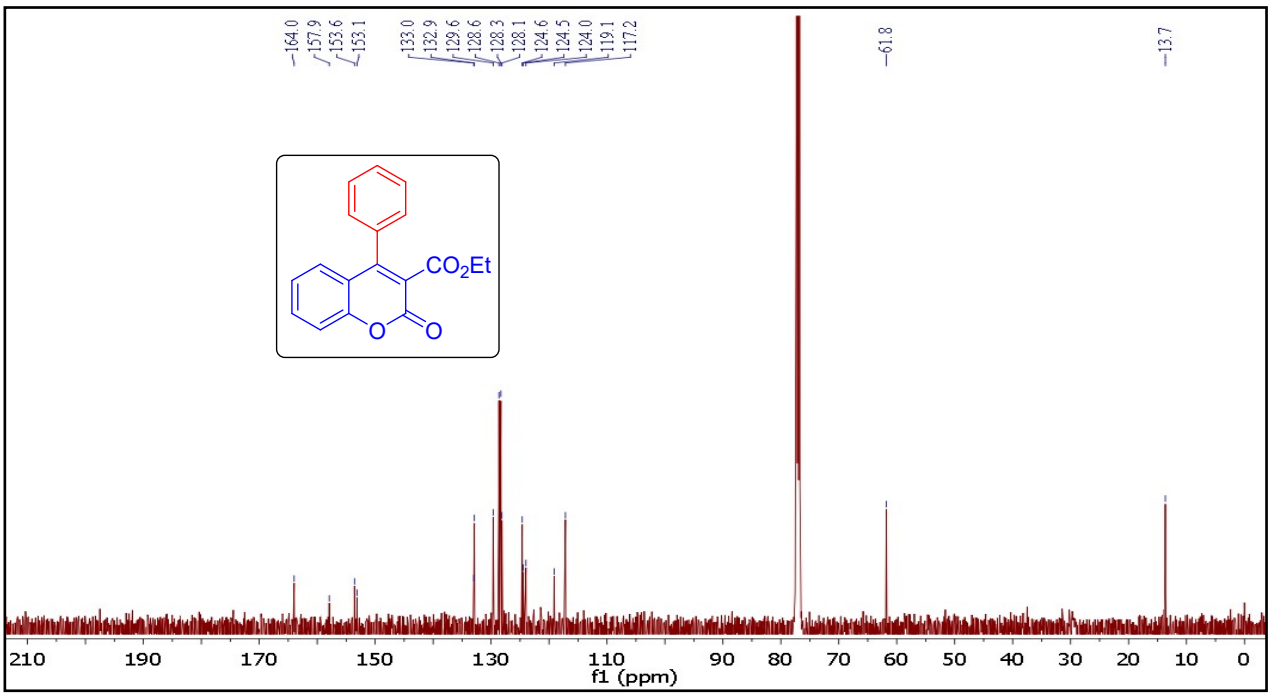
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound 4a:



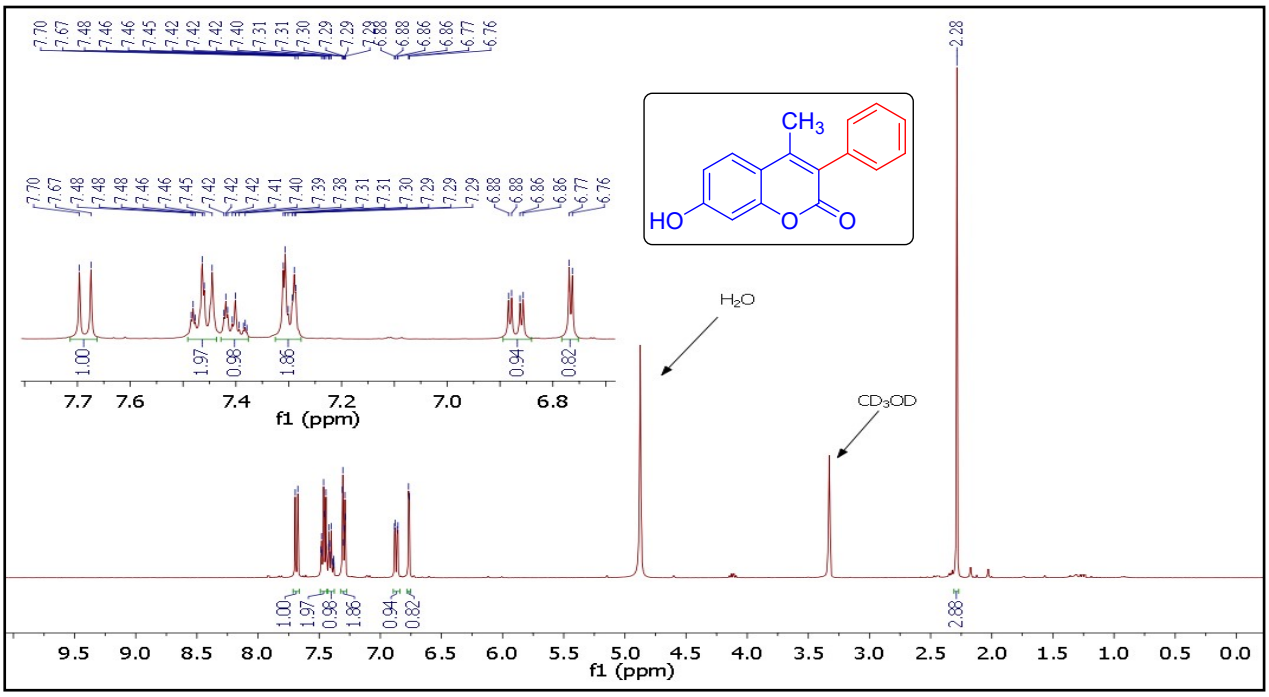
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound 4b:



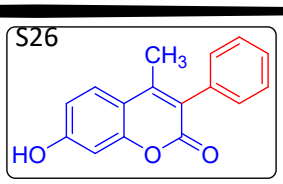
^{13}C NMR (126 MHz, $CDCl_3$) spectrum of compound 4b:

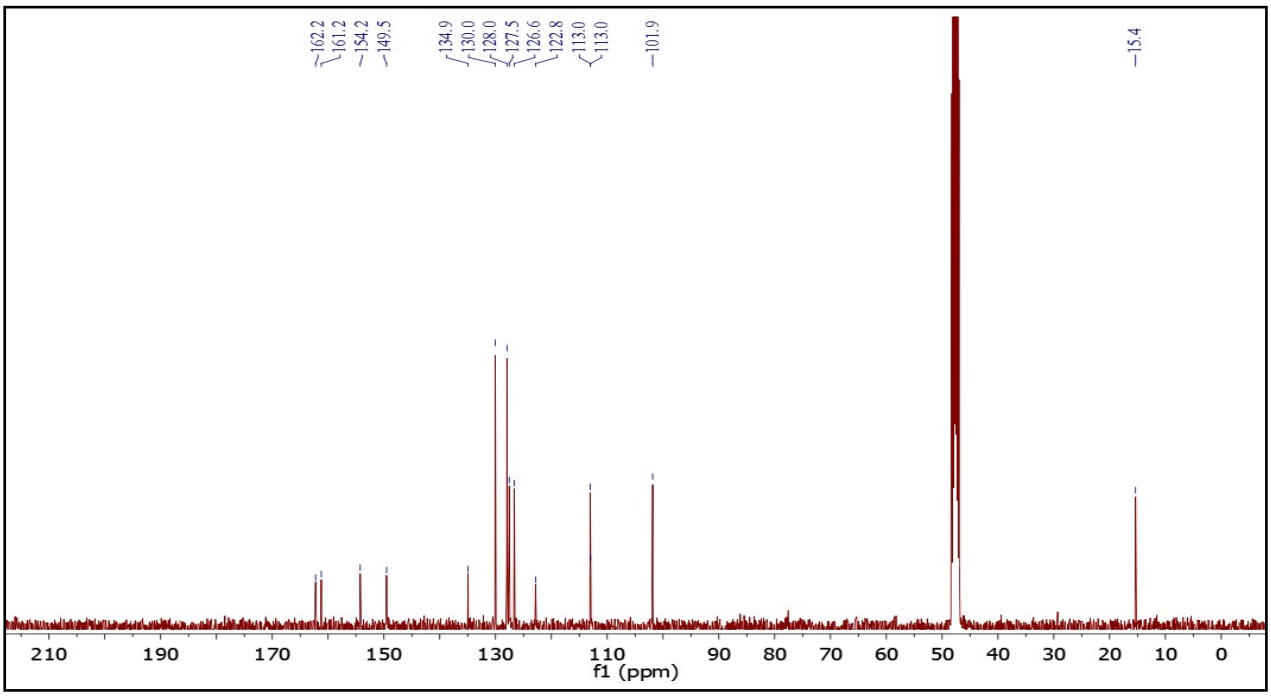


^{1}H NMR (400 MHz, MeOH-d_4) spectrum of compound 4c:

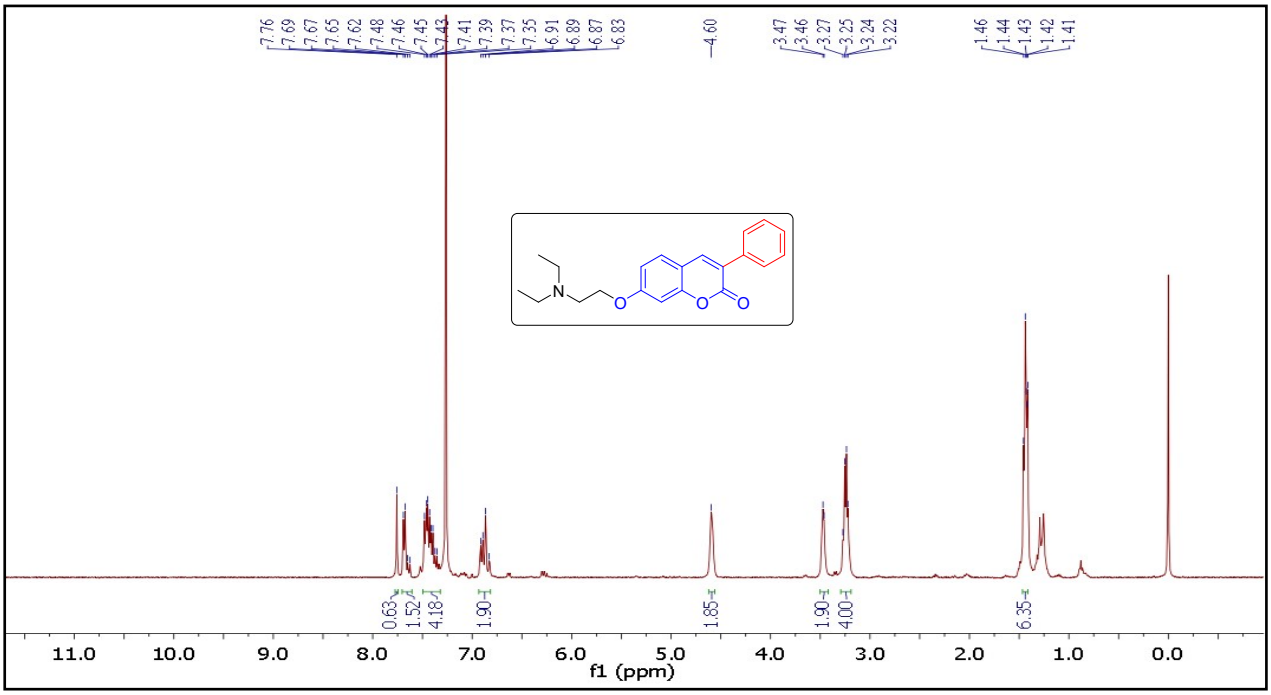


^{13}C NMR (101 MHz, MeOH-d_4) spectrum of compound 4c:

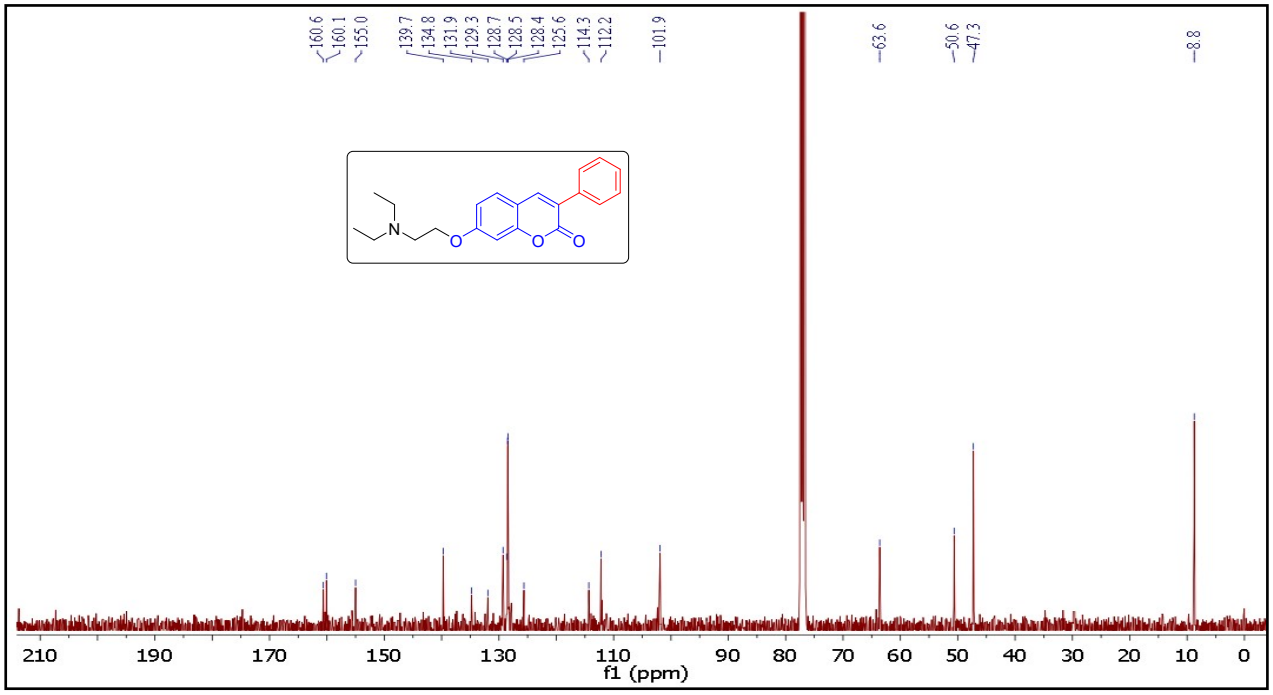




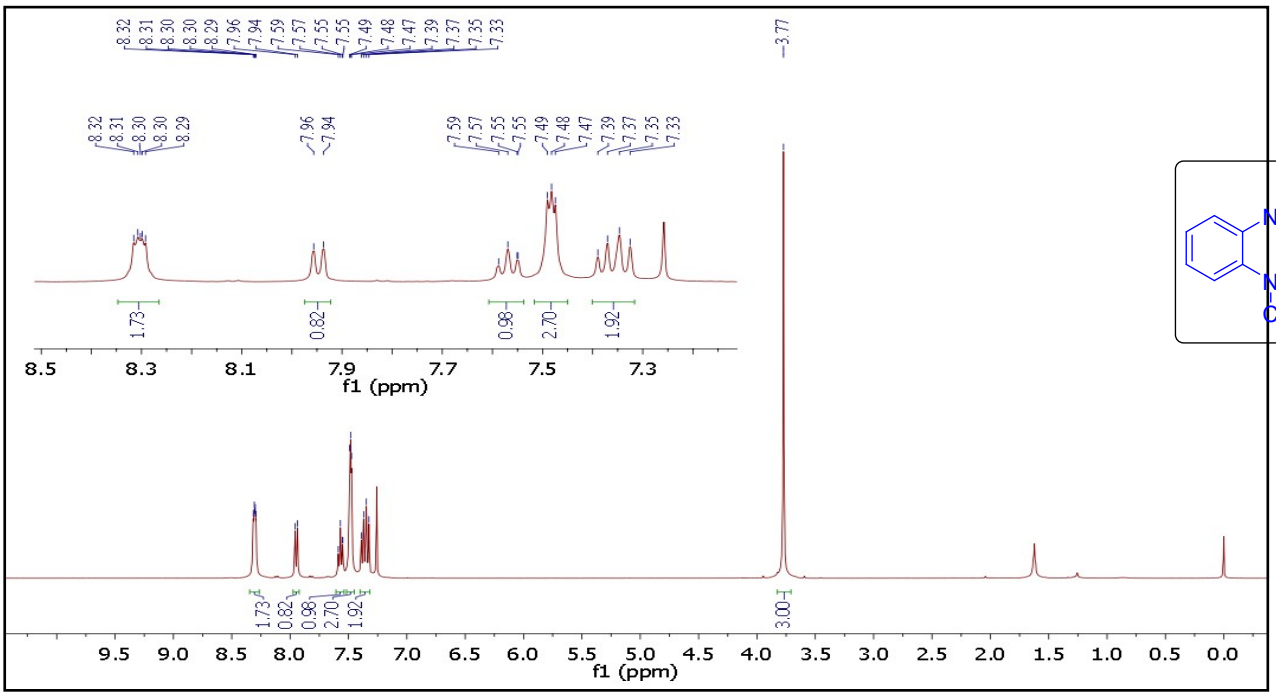
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 4d:



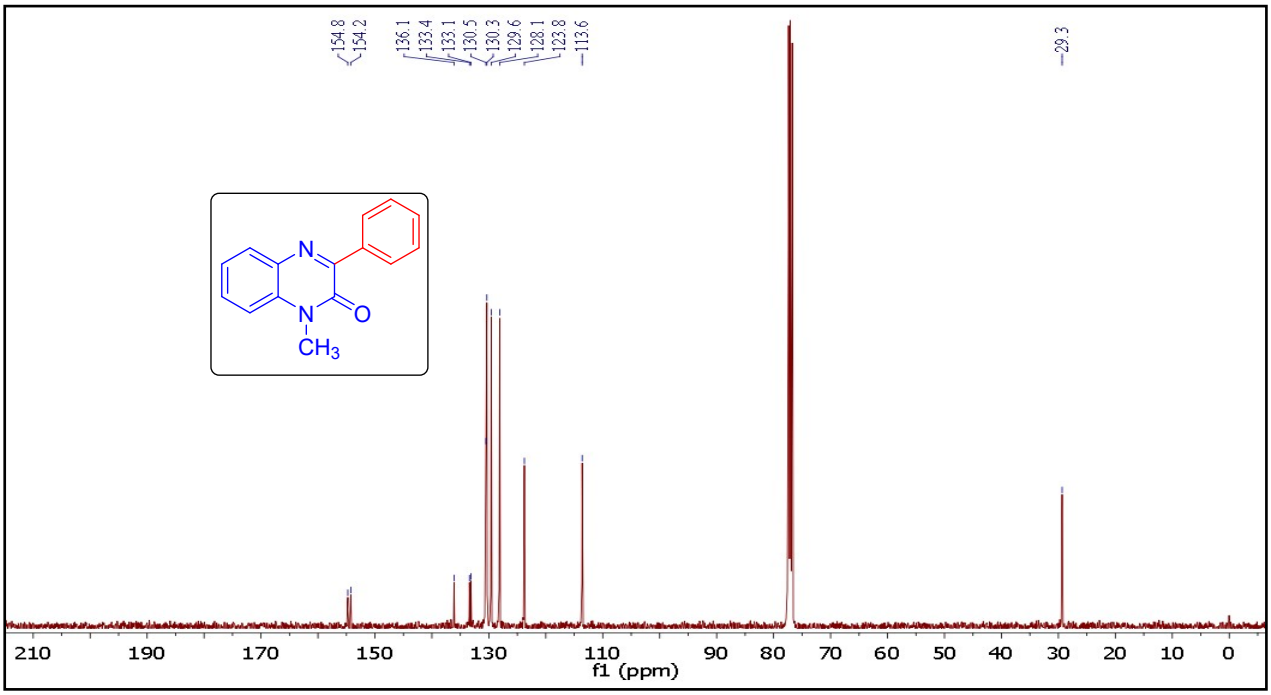
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound 4d:



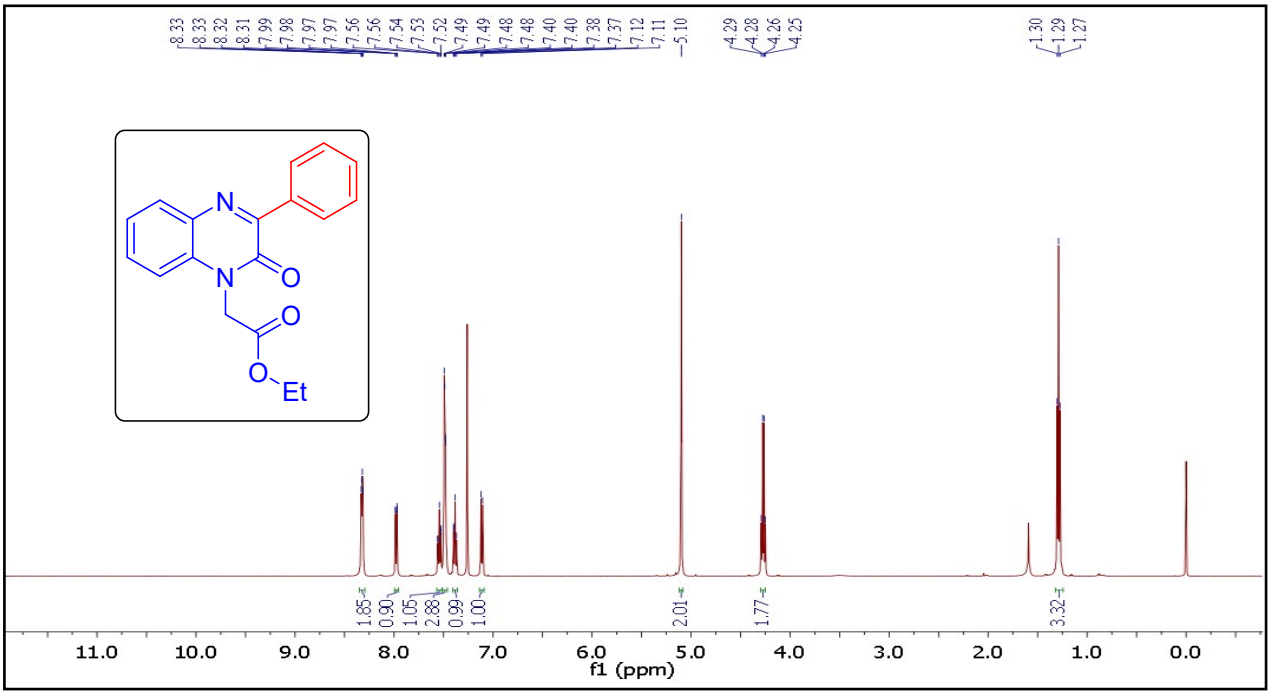
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 4f:



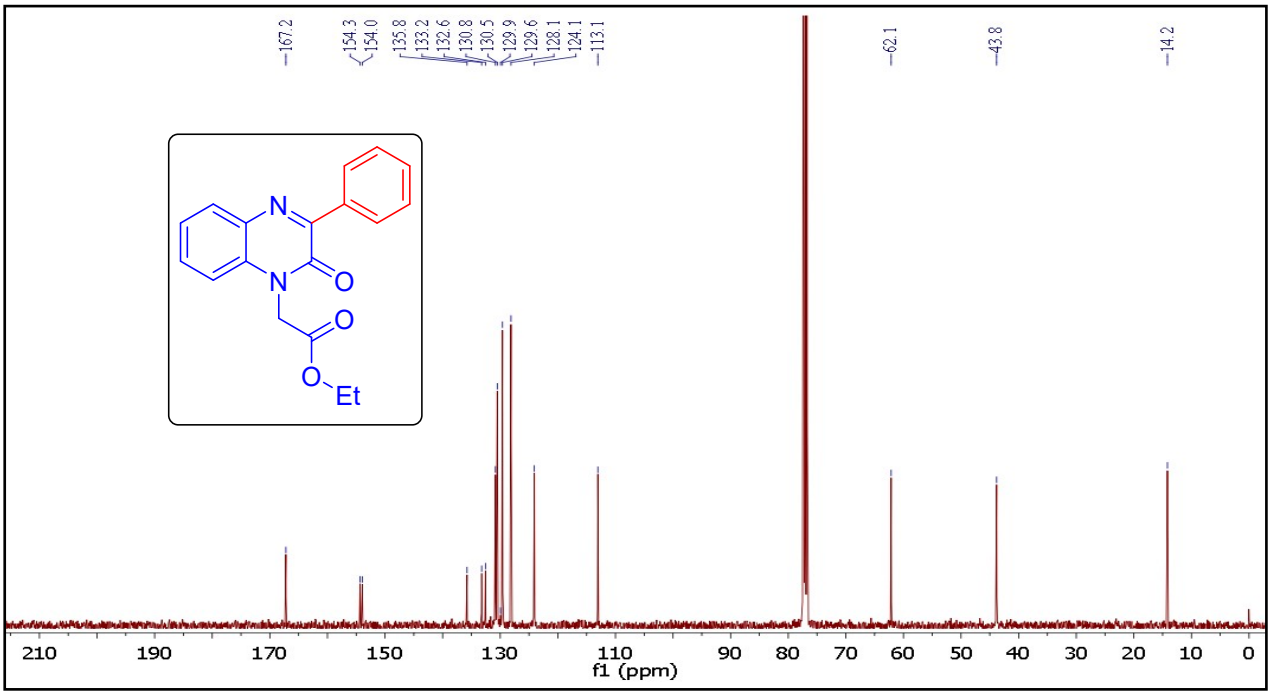
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound 4f:



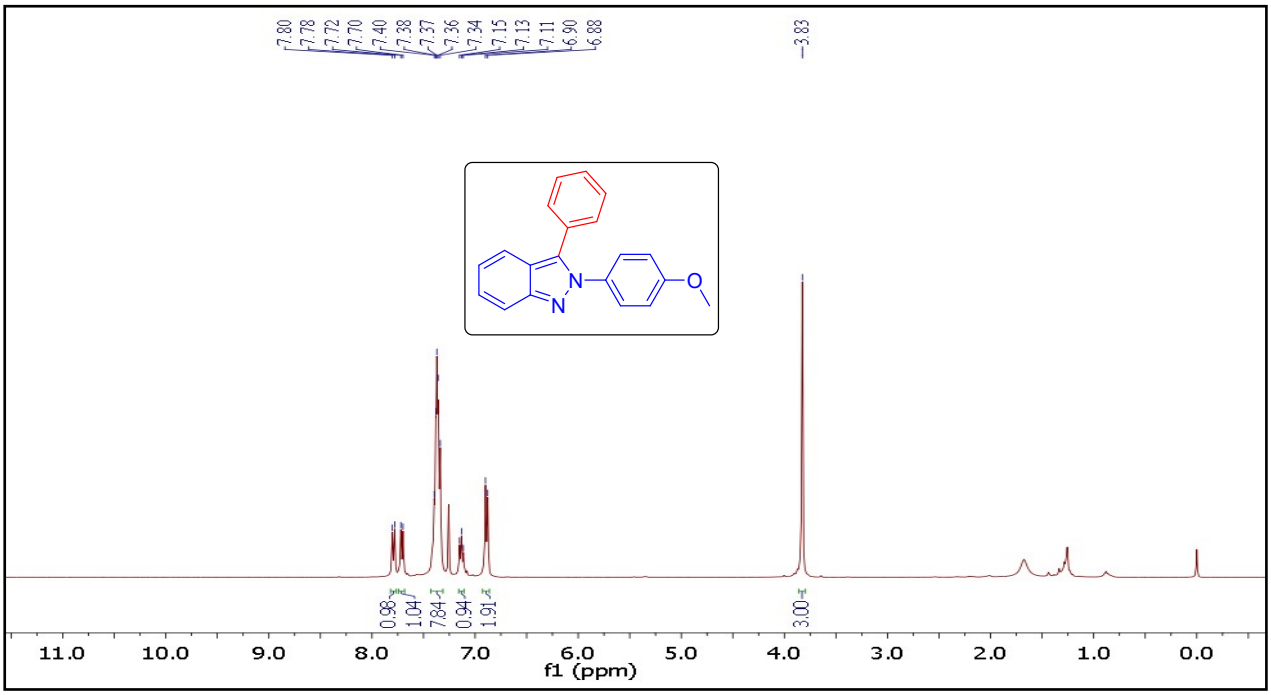
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound 4g:



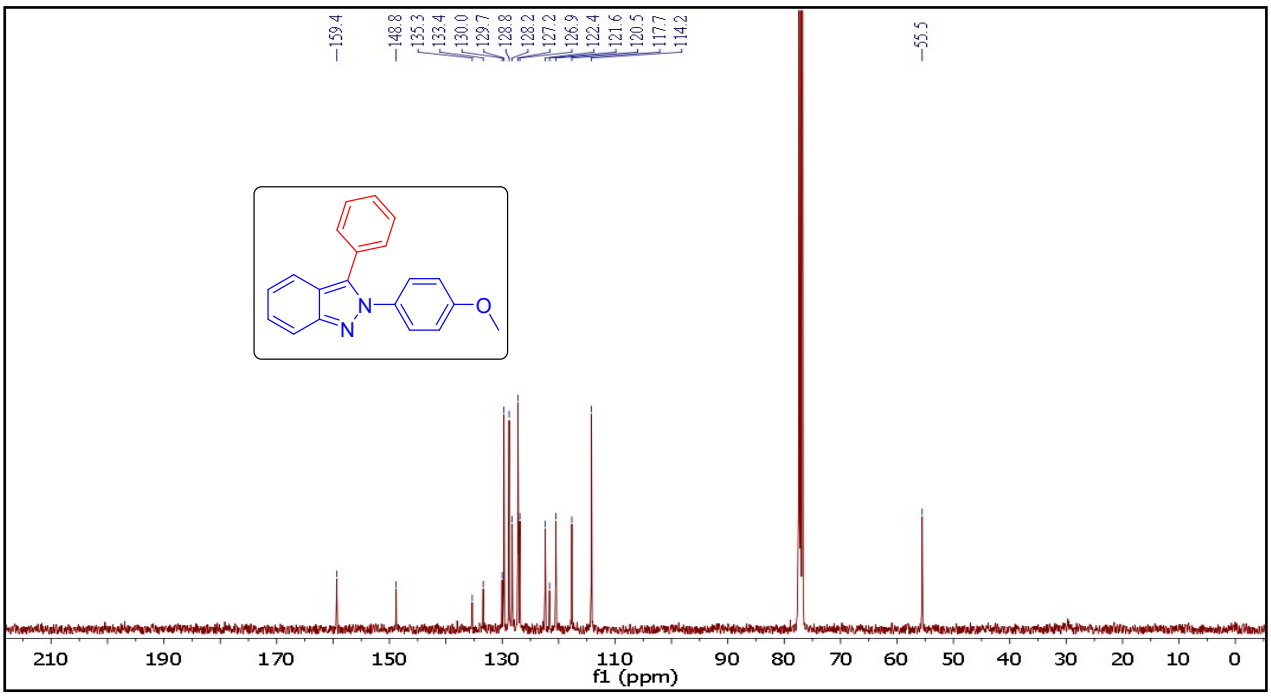
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound 4g:



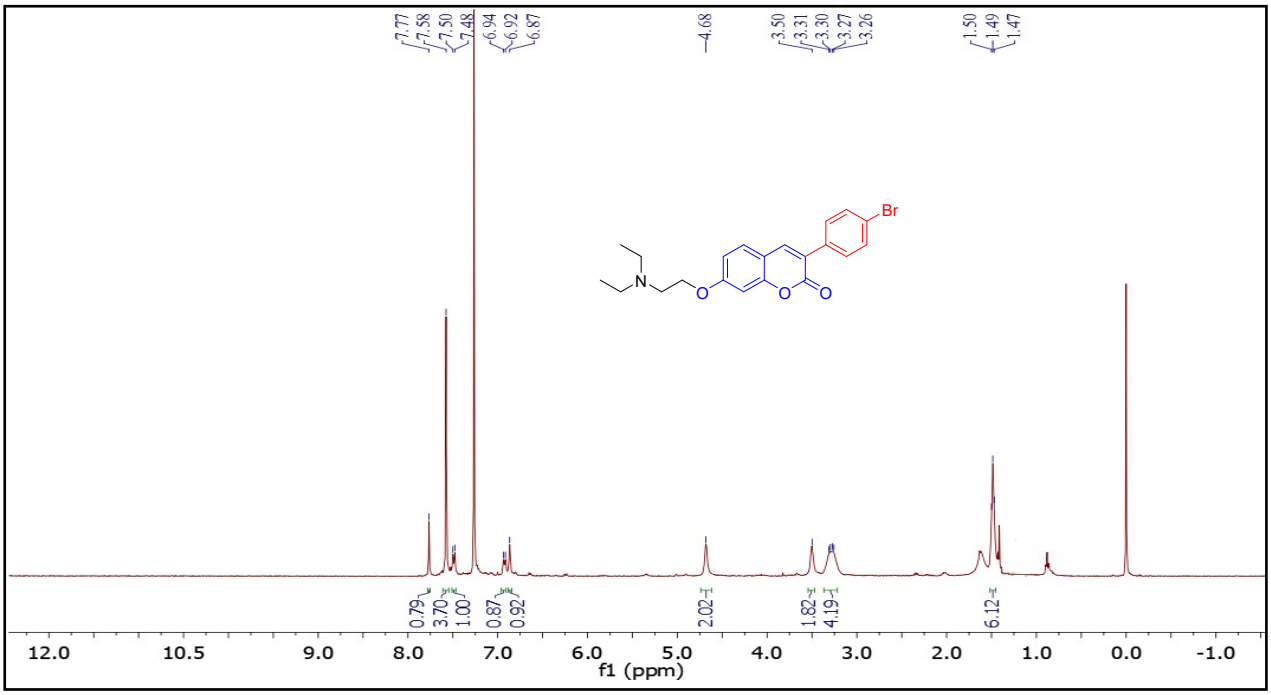
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 4h:



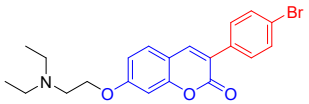
^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound 4h:

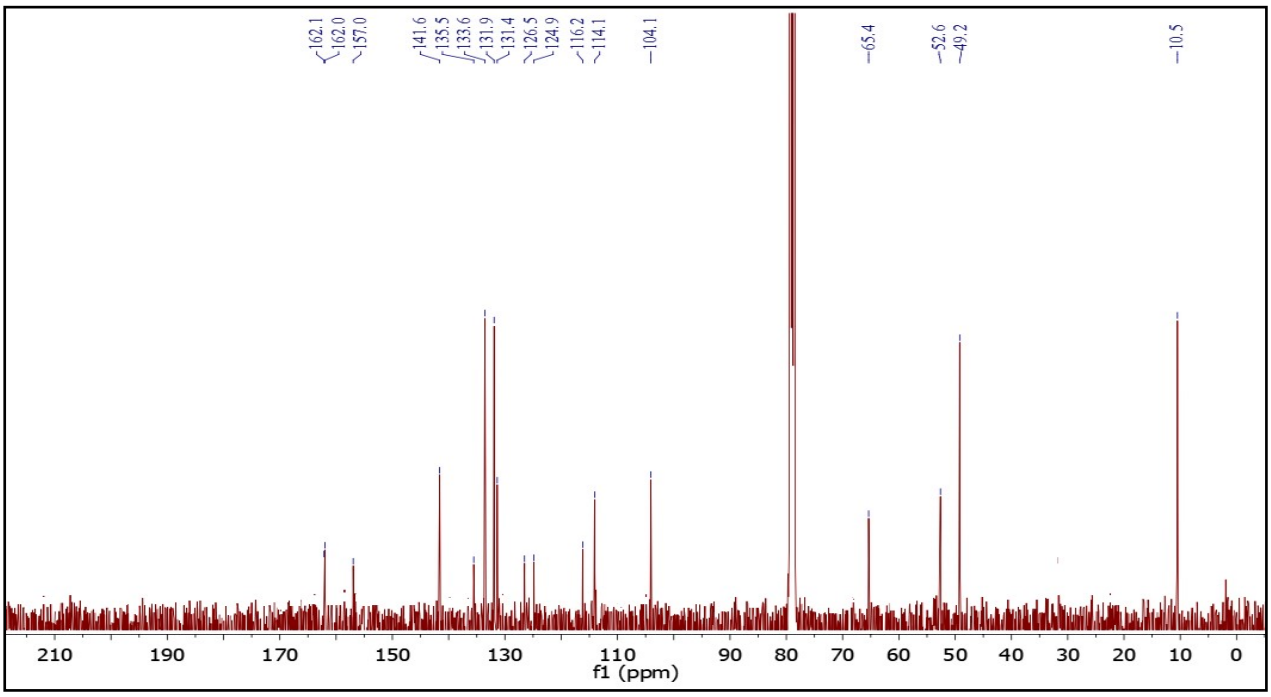


^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 4i:

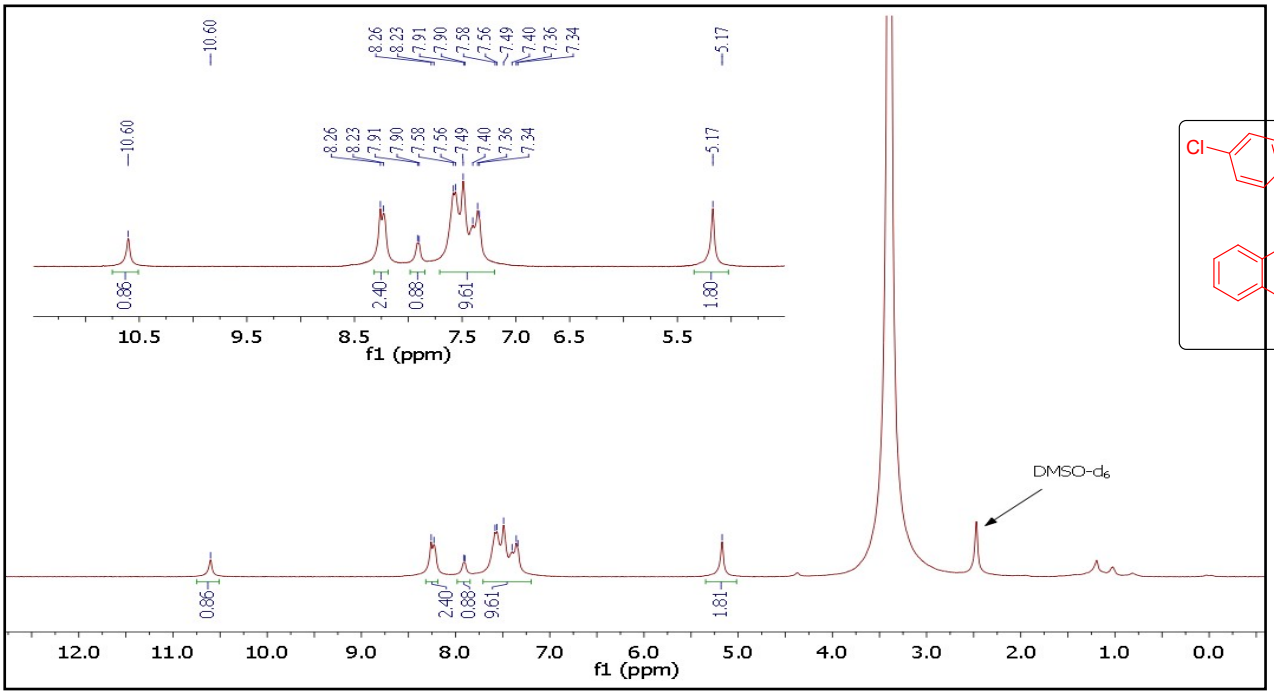


^{13}C NMR (101 MHz, $CDCl_3$) spectrum of compound 4i:

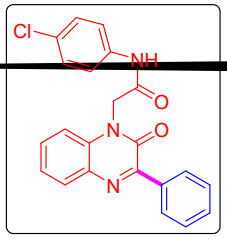


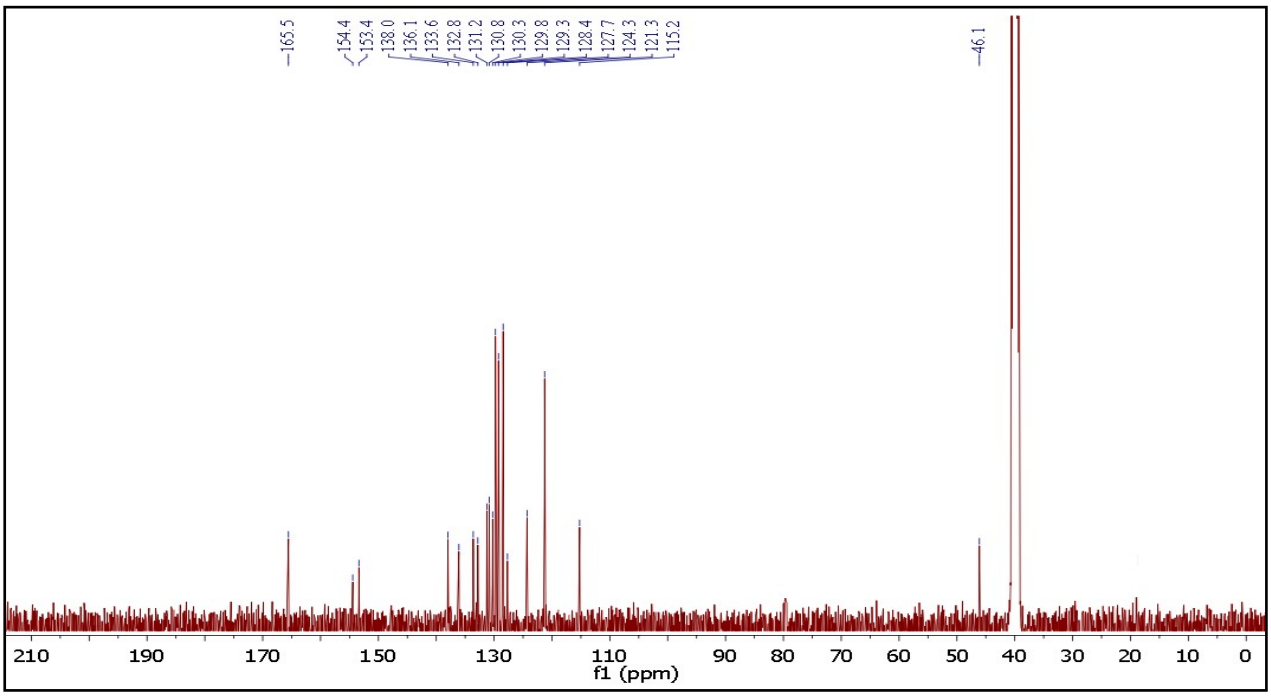


^{1}H NMR (400 MHz, DMSO-d$_6$) spectrum of compound 4j:



^{13}C NMR (101 MHz, DMSO-d$_6$) spectrum of compound 4j:





5. X ray Crystallography:

X-ray data for the compound was collected at room temperature on a Bruker D8 QUEST instrument with an IμS Mo microsource (λ = 0.7107 Å) and a PHOTON-III detector. The raw data frames were reduced and corrected for absorption effects using the Bruker Apex 3 software suite programs [1]. The structure was solved using intrinsic phasing method [2] and further refined with the SHELXL [2] program and expanded using Fourier techniques. Anisotropic displacement parameters were included for all non-hydrogen atoms. All C bound H atoms were positioned geometrically and treated as riding on their parent C atoms [C-H = 0.93-0.97 Å, and Uiso(H) = 1.5Ueq(C) for methyl H or 1.2Ueq(C) for other H atoms].

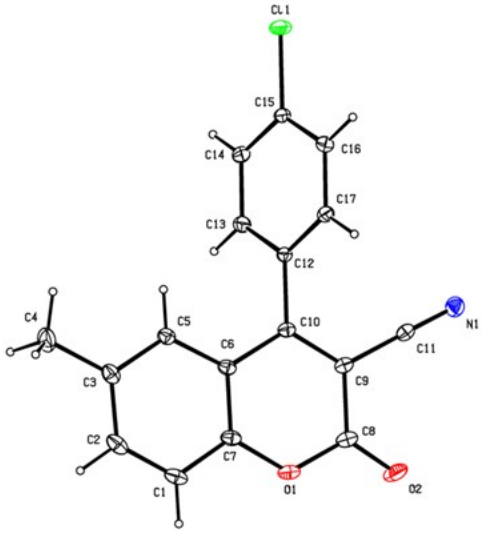


Figure S4. ORTEP diagram of **3p**

Crystal structure determination of [3p**]**

Crystal Data for $C_{17}H_{10}NO_2Cl$ (M =295.71 g/mol): monoclinic, space group $P2_1/n$ (no. 14), a = 10.719(2) Å, b = 6.7143(18) Å, c = 19.670(5) Å, β = 99.990(10)°, V = 1394.2(6) Å^3, Z = 4, T = 294.15 K, μ(MoKα) = 0.277 mm^{-1}, $Dcalc$ = 1.409 g/cm^3, 13735 reflections measured (4.206° ≤ 2Θ ≤ 56.814°), 3451 unique (R_{int} = 0.0395, R_{sigma} = 0.0419) which were used in all calculations. The final R_1 was 0.0446 (I > 2σ(I)) and wR_2 was 0.1421 (all data). **CCDC 2379731** deposition number contains the supplementary crystallographic data for this paper which can be obtained free of charge at https://www.ccdc.cam.ac.uk/structures/

1. Bruker (2016). APEX3, SAINT and SADABS. Bruker AXS, Inc., Madison, Wisconsin, USA.
2. Sheldrick G. M. (2015).ActaCrystallogr C71: 3-8.

Figure caption: ORTEP diagram of **3p** compound with the atom-numbering. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radius.

6. Reference:

1. (a) M. Golshani, M. Khoobi, N. Jalalimanesh, F. Jafarpour, A. Ariafard, *Chem. Commun.*, 2017, **53**, 10676-10679; (b) A. Moazzam, F. Jafarpour, *New J. Chem.*, 2020, **44,** 16692-16696.

2. S. Banik, A. Saikiran, P. Permula, K. S. Srivishnu, B. Sridhar, B. V. S. Reddy, *Chem. Asian J.,* **2024**, e202400042.

3. R. K. Samanta, P. Meher, S. Murarka, *J. Org. Chem.,* 2022, **87**, 10947– 10957.

4. R. Prasanna, S. Banik, C. Ajay, B. Sridhar, D. K. Mohapatra, B. V. Subba Reddy, *Org. Biomol. Chem.*, 2024, **22**, 6129-6134.

5. P. K. Dwivedi, A. Pathak, P. Malairajan, D. Chaturvedi, *Asian J. Chem.*, 2020, **32**, 2397–2402.