# Electron Donor-Acceptor Complex Enabled Photocascade Strategy for Synthesis of *trans*-Dihydrofuro[3,2-c]chromen-4-one Scaffolds *via* Radical Conjugate Addition of Pyridinium Ylide

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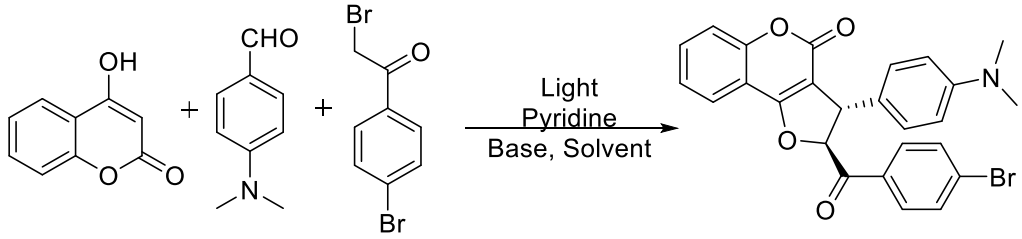
# Content

## 1. General information:

All reactions were performed using oven-dried glasswares. All the solvents and reagents used for synthesis of DHFC derivatives were purchased from commercial sources and has been used without further purification. Wipro 12W Blue LEDs (450 ± 20 nm), Green LEDs (525 ± 20 nm) and Red (650 ± 20 nm) were used as light source and the distance between the light source and the reaction vessel was kept constant at ~ 8 cm. Thin layer chromatography (TLC) was performed on Merck precoated Silica gel 60 $F_{254}$ aluminium sheets and visualized under UV light at 365 nm. Crude products were purified by column chromatography with Silica gel of mesh 100-200. Nuclear magnetic resonance (NMR) spectroscopy were performed using Bruker Avance Neo 400 spectrometer with operating frequency of 400 MHz for $^{1}H$, 100 MHz for $^{13}C$ and 376 MHz for $^{19}F$ nucleus. Deuterated chloroform ($CDCl_3$) was used for recording NMR where tetramethylsilane (TMS) was present as internal standard. The chemical shift values (δ) are reported in ppm and calibrated to the residual solvent peak for $CDCl_3$ at δ = 7.26 ppm for $^{1}H$ and δ = 77.16 ppm for $^{13}C$. $^{1}H$ NMR spectra are reported as follows: Chemical shift (multiplicity, integration, coupling constant). Following abbreviations are used to indicate multiplicities: s (singlet), d (doublet), t (triplet), q (quartet), quint (quintet), sext (sextet), sept (septet), dd (doublet of doublet), dt (doublet of triplet), m (multiplet). Exact mass (HRMS) were recorded on high resolution mass spectrometer using electrospray ionization (ESI) technique. Electron paramagnetic resonance (EPR) spectroscopy were recorded on Bruker EMXmicro spectrometer. UV-Vis experiments were performed on Agilent 8453 UV-Visible spectrophotometer.

## 2. Table S1: Complete optimization of reaction conditions[a]




**1a** **2a** **4a** **5a**

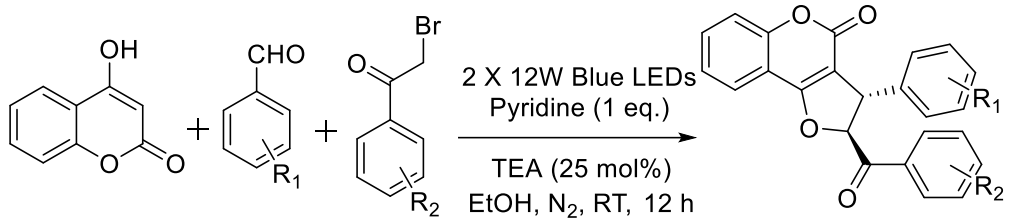
| Entry | Base (mol%) | Light source | Solvent | Yield (%)[b] |
|---|---|---|---|---|
| 1 | TEA (10) | Blue | EtOH | 48 |
| 2 | TEA (15) | Blue | EtOH | 62 |
| **3** | **TEA (25)** | **Blue** | **EtOH** | **86** |
| 4 | TEA (50) | Blue | EtOH | 71 |
| 5 | TEA (25) | Blue | MeOH | 84 |
| 6 | TEA (25) | Blue | DMSO | 79 |
| 7 | TEA (25) | Blue | ACN | 61 |
| 8 | TEA (25) | Blue | DMF | 72 |

| | | | | |
|---|---|---|---|---|
| 9 | TEA (25) | Blue | $H_2O$ | 18 |
| 10 | TEA (25) | Blue | Toluene | 23 |
| 11 | DIPEA (25) | Blue | EtOH | 76 |
| 12 | DBU (25) | Blue | EtOH | 69 |
| 13[c] | TEA (25) | Blue | EtOH | nd |
| 14 | - | Blue | EtOH | nd |
| 15 | TEA (25) | Green | EtOH | 71 |
| 16 | TEA (25) | Red | EtOH | 16 |
| 17[d] | TEA (25) | - | EtOH | 17 |
| 18[e] | TEA (25) | Blue | EtOH | 15 |
| 19[f] | TEA (25) | Blue | EtOH | 37 |

[a]Reaction conditions: (a) **1a** (1.0 mmol), **2a** (1.0 mmol), and **4a** (1.0 mmol), in different solvent with blue LEDs lamp (2x12 W) radiation at rt for 12 h under a $N_2$ atmosphere, (b) NMR yield with 1,3,5-trimethoxybenzene as internal standard, (c) reaction performed without pyridine, (d) reaction performed in absence of light, (e) reaction performed in open vessel, (f) DMAP instead of Pyrdine, nd: not detected, **TEA**: triethylamine, **DIPEA**: diisopropylethylamine, **DBU**: 1,8 Diazabicyclo(5.4.0)undec-7-ene, **ACN**: acetonitrile, nd: not detected, Blue LEDs (450 ± 20 nm), Green LEDs (525 ± 20 nm) and Red (650 ± 20 nm).

We initially, chosen 4-hydroxycoumarin (**1a**), *p*-N,N-dimethylaminobenzaldehyde (**2a**), and *p*-bromophenacyl bromide (**3a**) as model substrates to initiate the one-pot, three-component cascade radical annulation via EDA complex for synthesizing *trans*-dihydrofuro[3,2-c]chromen-4-ones. As outlined in Table S1 (entry 1), subjecting the reaction mixture to blue LED irradiation (2 x12 W) as the energy source in ethanol under a nitrogen atmosphere at room temperature for 12 hours, employing 10 mol% triethylamine (TEA) as a proton scavenger along with pyridine as a nucleophile and base, resulted in the desired *trans*-dihydrofuro[3,2-c]chromen-4-ones (**5a**) in 48% yield with excellent regio- and diastereoselectivity. We then gradually increased the TEA loading upto 50 mol% (Table S1, entries 2-4) and we got maximum yield of 86% of **5a** with 25 mol% TEA, increasing to 50 mol% caused decrease in yield of **5a**. In subsequent investigation, we attempted to improve the yield by screening the reaction media by varying the different solvents (e.g., MeOH, DMSO, ACN, DMF, toluene and water) (see Table S1, entries 5-10). However, none of the attempted conditions yielded better results than using ethanol media with 25 mol% TEA. Next we varied the base source where we use DIPEA and DBU instead of TEA in 25 mol% and we got 76 and 69% yield of **5a**, respectively (Table S1, entries 11-12), which were far lesser than the same reaction with TEA (Table S1, entry 4). The reaction did not furnish the desired product **5a** when the reaction was performed in absence of pyridine (Table S1, entry 13). The reaction also did not occur in absence of TEA (Table S1, entry 14). These results suggest that both pyridine and TEA are indispensable in the said reaction. To assess the light's role, the reaction was also attempted under green LEDs, red LEDs and in the dark, yielding only 71%, 16% and 17% of **5a**, respectively (Table S1, entries 15-17). To simplify the operation, we investigated the reaction by performing it under ambient air (open vessel) and significantly lower yield 15% of **5a** was observed (Table S1, entry 18). These control experiments underscore the essential roles of light, pyridine and TEA for the success of the reaction in an inert atmosphere.

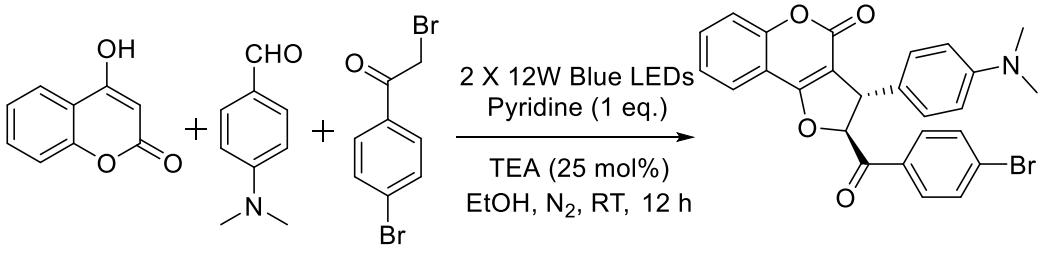
**3**. **General procedure for synthesis of *trans*-dihydrofurocoumarin derivatives (5/6)**:




**1** **2/3** **4** **5/6**

In an oven dried round bottom flask containing magnetic stir bar were taken weighed amount of 4-Hydroxycoumarin (**1a**, 1 mmol), aromatic/hetero aromatic aldehyde (**2/3**, 1 mmol), phenacyl bromide (**4**, 1 mmol), pyridine (1 mmol) and dissolved in 5 mL ethanol. The round bottom flask was capped with rubber septum and the reaction vessel was degassed using $N_2$-flow. After degassing the reaction vessel, 25 mol% triethyl amine (TEA) was added using syringe and the atmosphere of reaction vessel was kept inert with $N_2$ balloon. The reaction vessel was then placed over a magnetic stirrer and irradiated with two 12W blue LEDs, kept ~ 8 cm away from the vessel, and the reaction was kept stirring for next 12 hours at room temperature. The progress of the reaction was monitored by TLC. Upon completion, as indicated by TLC, the reaction was quenched by adding water and then extracted with ethyl acetate (3 x 20 mL). The organic portions were collected and the combined organic layer was dried over anhydrous $Na_2SO_4$, solvent was removed to get the crude mass. The so obtained crude mass was purified through column chromatography to get the pure *trans*-dihydrofurocoumarin derivatives **5**/**6**. The formation of the synthesized DHFC derivatives was confirmed by $^1H$ and $^{13}C$ NMR techniques.

**4**. **Gram scale synthesis of *trans*-dihydrofurocoumarin derivative 5a**:




**1a** **2a** **4a** **5a**

In an oven-dried round bottom flask containing magnetic stir bar were taken 4-hydroxycoumarin (**1a**, 1.620 g, 10.0 mmol), *p*-N,N-dimethylaminobenzaldehyde (**2a**, 1.490 g, 10.0 mmol), *p*-bromophenacyl bromide (**4a**, 2.779 g, 10.0 mmol), pyridine (0.791 g, 10.0 mmol) and dissolved in 20 mL ethanol. The round bottom flask was capped with a rubber septum and the reaction vessel was degassed using $N_2$ flow. To the degassed reaction vessel 25 mol% TEA was added via syringe

and the atmosphere of the reaction vessel was kept inert with $N_2$ balloon. The round bottom flask was then placed over a magnetic stirrer and irradiated with two 12W blue LEDs, kept ~ 8 cm away from the vessel, and the reaction was kept stirring for next 12 hours at room temperature. The progress of the reaction was monitored by TLC. Upon completion, as indicated by TLC, the reaction was quenched by adding water and then extracted with ethyl acetate (3 x 50 mL). The organic portions were collected and the combined organic layer was dried over anhydrous $Na_2SO_4$, solvent was removed to get the crude mass. The so obtained crude mass was purified through column chromatography to get the pure DHFC derivative **5a**. The isolated yield of the desired compound **5a** was found to be 3.92g (80%).

## 5. Mechanistic Study:

### 5.1. UV-Vis Experiment:

The UV-Vis experiments were performed on Agilent 8453 UV-Vis Spectrophotometer with a quartz cuvette of path length 1.0 cm. At first, all the reacting components, i.e., 4-Hydroxycoumarin (**1a),** *p*-N,N-dimethylaminobenzaldehyde (**2a**), *p*-bromophenacyl bromide (**4a**), pyridine and triethyl amine (TEA) were subjected to spectrophotometer individually for their individual UV-Vis spectrum at concentration of 1 x $10^{-3}$ (M) in ethanol. From their individual absorption spectrum none of the starting materials was found to absorb significantly in the visible region. Then we studied UV-Vis absorption of binary mixture of the reacting components and this time surprisingly a bathochromic shift was observed in the absorption of mixture of 4-Hydroxycoumarin (**1a)** and *p*-N,N-dimethylaminobenzaldehyde (**2a**) with appearance of a new hump at 504 nm. This bathochromic shift and the hump may be attributed to the EDA complex formed between **1a** and **2a**.

Further to study the spectral behavior of the N-(*p*-bromophenacyl) pyridinium bromide (PyB) and *in-situ* generated N-(*p*-bromophenacyl) pyridinium ylide (PyY), we subjected both of them to the UV-Vis spectrophotometer. From their absorption spectrum we found that N-(*p*-bromophenacyl) pyridinium bromide (PyB) weakly absorbs in the visible region, whereas N-(*p*-bromophenacyl)pyridinium ylide (PyY) absorbs significantly in the visible region with appearance of a hump at 430 nm. This new peak may be attributed to the electronic transition from the negatively charged C-atom to the positively charged pyridinium ring.

Finally, when the reaction mixture was subjected to the UV-Vis spectrophotometer, it shows strong absorption both at 430 nm and 504 nm, which may be attributed to the presence of both the PyY and the EDA complex in the reaction mixture. The UV-Vis spectra is shown in Figure S1.

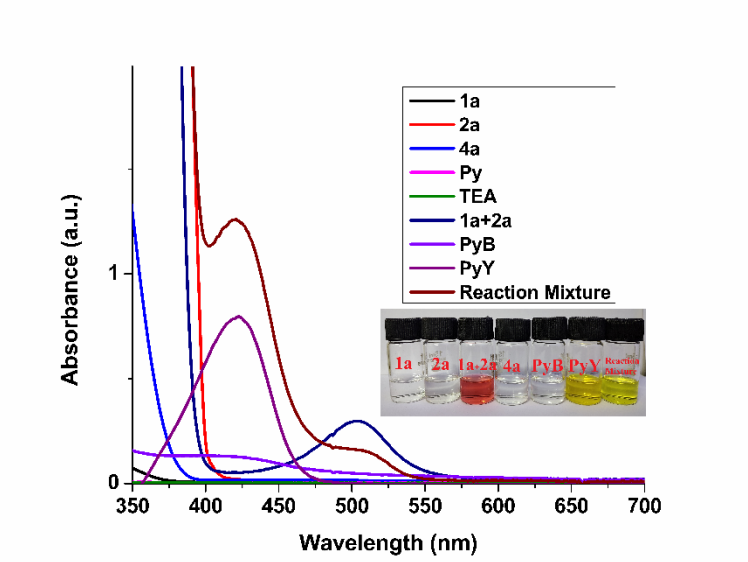



Figure S1: UV-Vis absorption spectra of individual reactants and their mixture

## 5.2. Determination of stoichiometry of the EDA complex in solution:

To determine the stoichiometry of the EDA complex formed between 4-hydroxycoumarin(**1a**) and *p*-N,N-dimethylaminobenzaldehyde (**2a**), Job's plot was constructed.[1] We choose to determine the stoichiometry spectrophotometrically and for this purpose, we measured the absorbance of ethanolic solution of **1a** and **2a** at 504 nm, having a constant concentration of 1 x $10^{-3}$ (M), but different donor/acceptor ratios. All the absorption spectra were recorded in 1 cm path quartz cuvette using Agilent 8453 UV-Visible spectrophotometer at room temperature. The difference in absorbance values are plotted against mole fraction of **2a**. The maximum difference in absorbance was detected at 50% mole fraction of **2a**, suggesting 1:1 complexation of **1a** and **2a**. Hence, the stoichiometry of the EDA complex formed between **1a** and **2a** is 1:1. The Job's plot is shown in Figure S2.


Figure S2: Job's plot

### 5.3. Determination of Association constant ($K_{EDA}$) of the EDA complex:

The association constant ($K_{EDA}$) formed between 4-hydroxycoumarin(**1a**) and *p*-N,N-dimethylaminobenzaldehyde (**2a**) was determined spectrophotometrically in ethanol employing Benesi-Hildebrand methodology.[2] For this purpose we measured the absorbance of solution **2a** with constant concentration of 0.02 M at 504 nm, but increased donor/acceptor ratio, adding an excess of **1a**. All the absorption spectra were recorded in 1 cm path quartz cuvette using Agilent 8453 UV-Visible spectrophotometer at room temperature. According to the methodology a straight line is obtained by plotting reciprocal of differential absorbance against the reciprocal of concentration of **1a**. The association constant ($K_{EDA}$) is obtained by dividing the intercept by slope and found to be $K_{EDA}$ = 18.0 $M^{-1}$. The plot for association constant is shown in Figure S3.

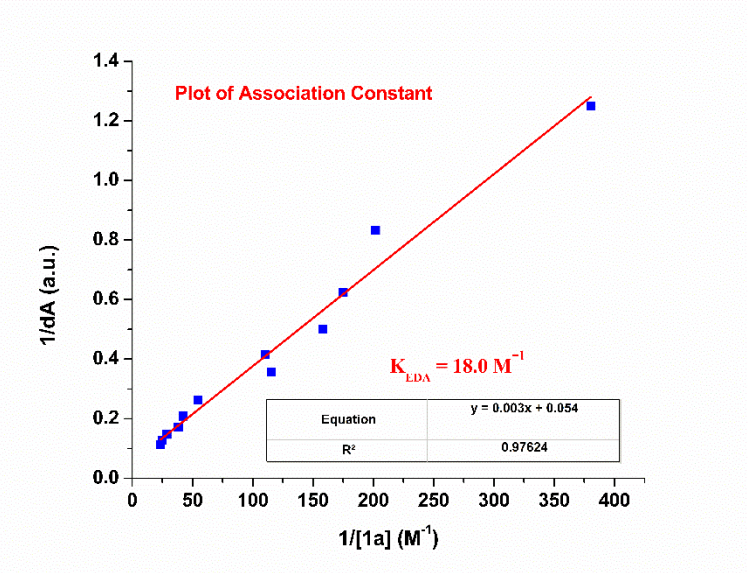



Figure S3: Plot for $K_{EDA}$ of the EDA complex between **1a** and **2a**.

### 5.4. Determination of molar extinction coefficient of EDA complex:

The molar extinction coefficient ($\varepsilon_{EDA}$) of EDA complex formed between 4-hydroxycoumarin (**1a**) and *p*-N,N-dimethylaminobenzaldehyde (**2a**) was calculated spectrophotometrically by measuring the absorbance of different concentrations (0.01 M to 0.0008 M) of 1:1 mixture of **1a** and **2a** in ethanol. The absorbance at 504 nm was plotted against the concentration, with the gradient of the slope equal to the molar extinction coefficient ($\varepsilon_{EDA}$), according to the following equation

$$\varepsilon_{EDA} = A/(c \times l)$$

where, 'A' is the absorbance, 'c' is the concentration of solution and 'l' is the path length of the cuvette (here 1 cm). The $\varepsilon_{EDA}$ of the EDA complex between **1a** and **2a** is found to be 158.8 L. $mol^{-1}$. $cm^{-1}$. The plot for molar extinction coefficient is shown in Figure S4.

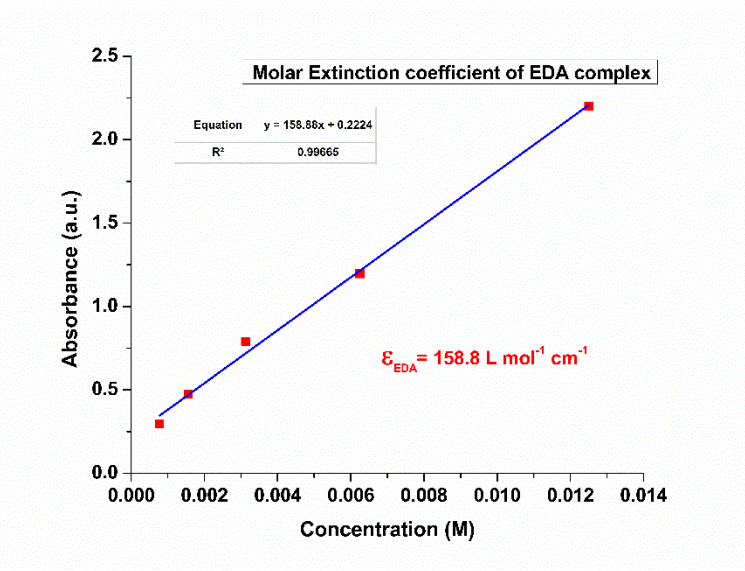
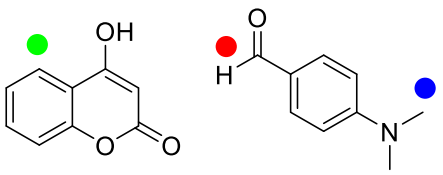



Figure S4: Plot for molar extinction coefficient

### 5.5. NMR titration of EDA complex:

The $^1$H NMR spectra of 4-hydroxycoumarin (**1a**) and *p*-N,N-dimethylaminobenzaldehyde (**2a**) were recorded individually in $CDCl_3$ at room temperature. Then $^1$H NMR titration was carried out for mixture of **1a** and **2a** in $CDCl_3$. For this purpose, at first in an NMR tube **2a** (0.04 mmol) was dissolved in 500 µL $CDCl_3$ and then **1a** (0.04 mmol) was added in portions gradually maintaining molar ratio of **2a**: **1a** at 100:20, 10:40, 100:60, 100:80 and 100:100, etc. The final volume of $CDCl_3$ was 600 µL. $^1$H NMR was recorded after each interval of addition of **1a**. From the $^1$H NMR we found that the aldehyde peak of **2a** showed up field shifting with gradual addition of **1a**. Also the peak of $NMe_2$ group showed slight up field shifting. On the other hand, downfield shifting of the aromatic protons of **1a** was observed. This indicates the possible formation of EDA complex between **1a** and **2a**, where **1a** acts as donor and **2a** as acceptor. The shifting of peaks are shown below.




**1a** **2a**

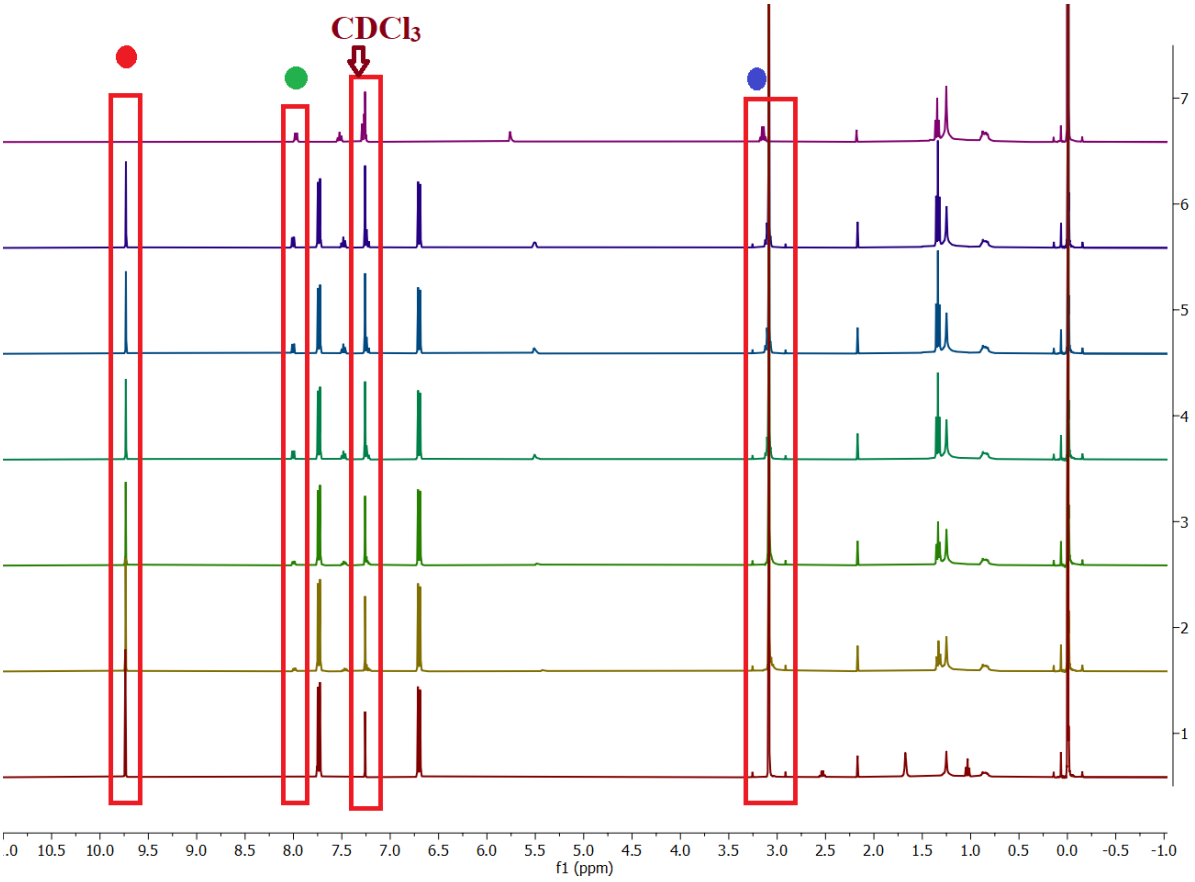



Figure S5: $^{1}$H NMR titration between **1a** and **2a**

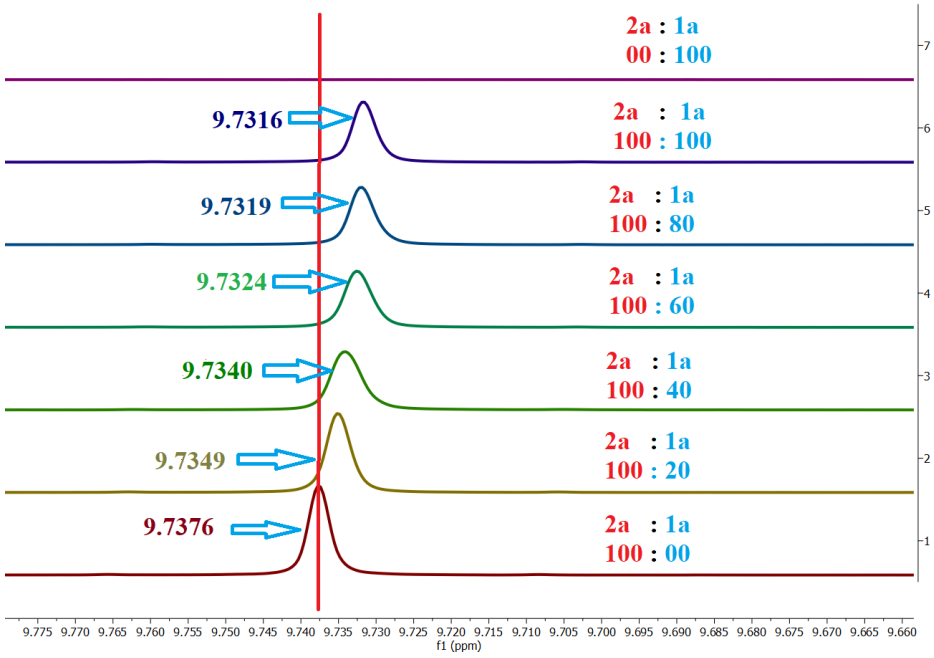



Figure S6: $^{1}$H NMR spectrum with aldehyde peak up field shifting in **2a**

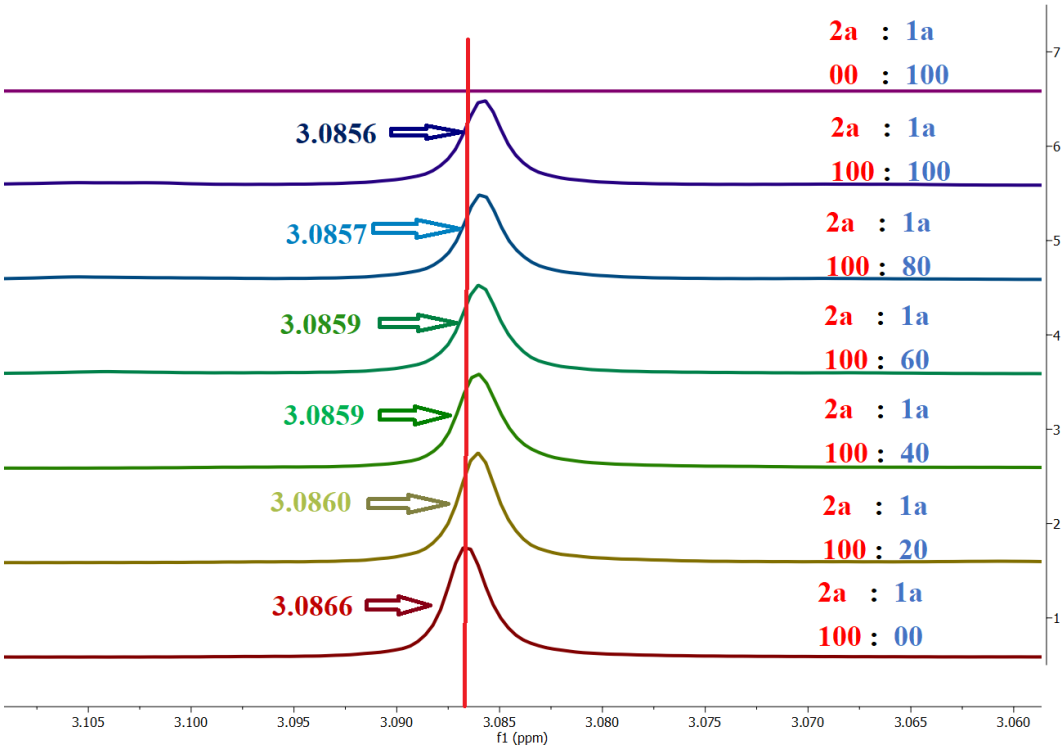



Figure S7: $^{1}$H NMR titration showing $NMe_2$ peak up field shifting in **2a**

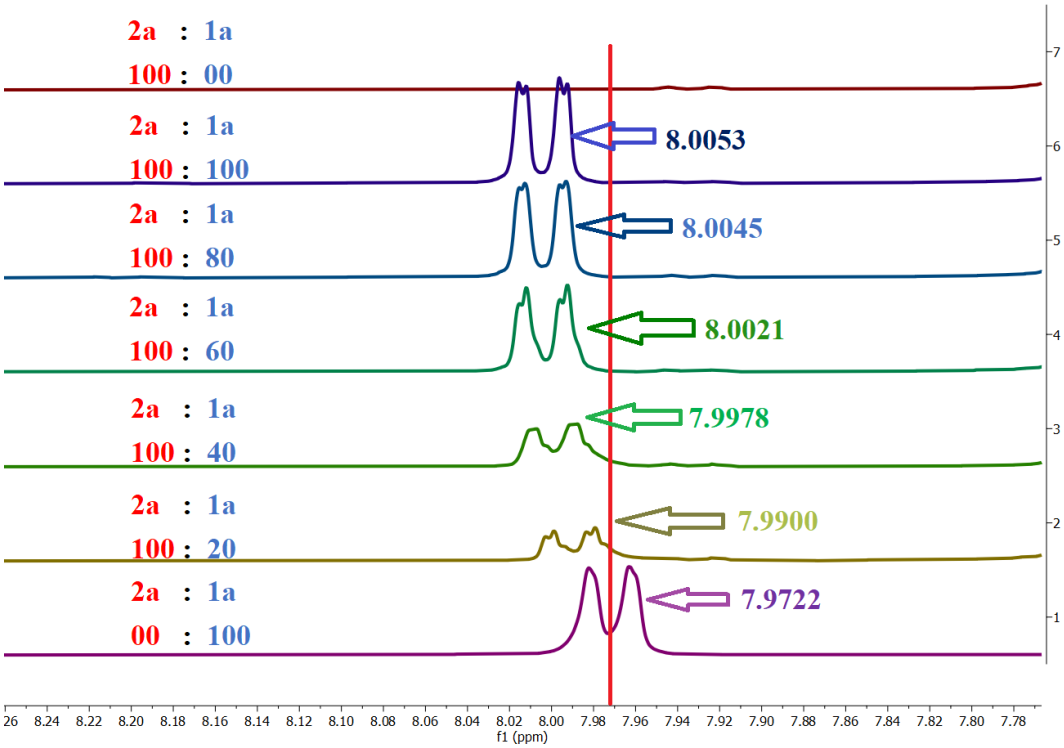



Figure S8: $^{1}$H NMR titration showing aromatic peak down field shifting in **1a**

## 5.6. Cyclic voltammetric analysis:

The cyclic voltammetric (CV) measurements were carried out on a PGLyte electrochemical work station by a standard three electrode system (working electrode: Glassy carbon electrode; counter electrode: Pt; reference electrode: Ag wire) using tetrabutylammonium perchlorate (0.02 M) as the electrolyte in ethanol at scan rate of 50 mV/s at room temperature. Ferrocene was used as the internal standard. Ag wire being pseudo-reference electrode, we measure the CV of Ferrocene and potential of all the analytes were normalized with respect to ferrocene. The concentration of all the analyte was kept constant at 0.01 M throughout the whole experiment. The cyclic voltammograms so obtained are shown in Figure S9. From the cyclic voltammograms we can observe that **1a** shows irreversible oxidation, whereas **2a**, PyB and PyY showed irreversible reduction. The oxidation potential of **1a** is $(E_{ox})^{1a}$ = +1.22 V vs $Fc^{+/0}$. The reduction potential of **2a**, PyB and PyY are $(E_{red})^{2a}$ = -1.46 V vs $Fc^{+/0}$; $(E_{red})^{PyB}$ = -1.49 V vs $Fc^{+/0}$; and $(E_{red})^{PyY}$ = -1.32 V vs $Fc^{+/0}$, respectively.

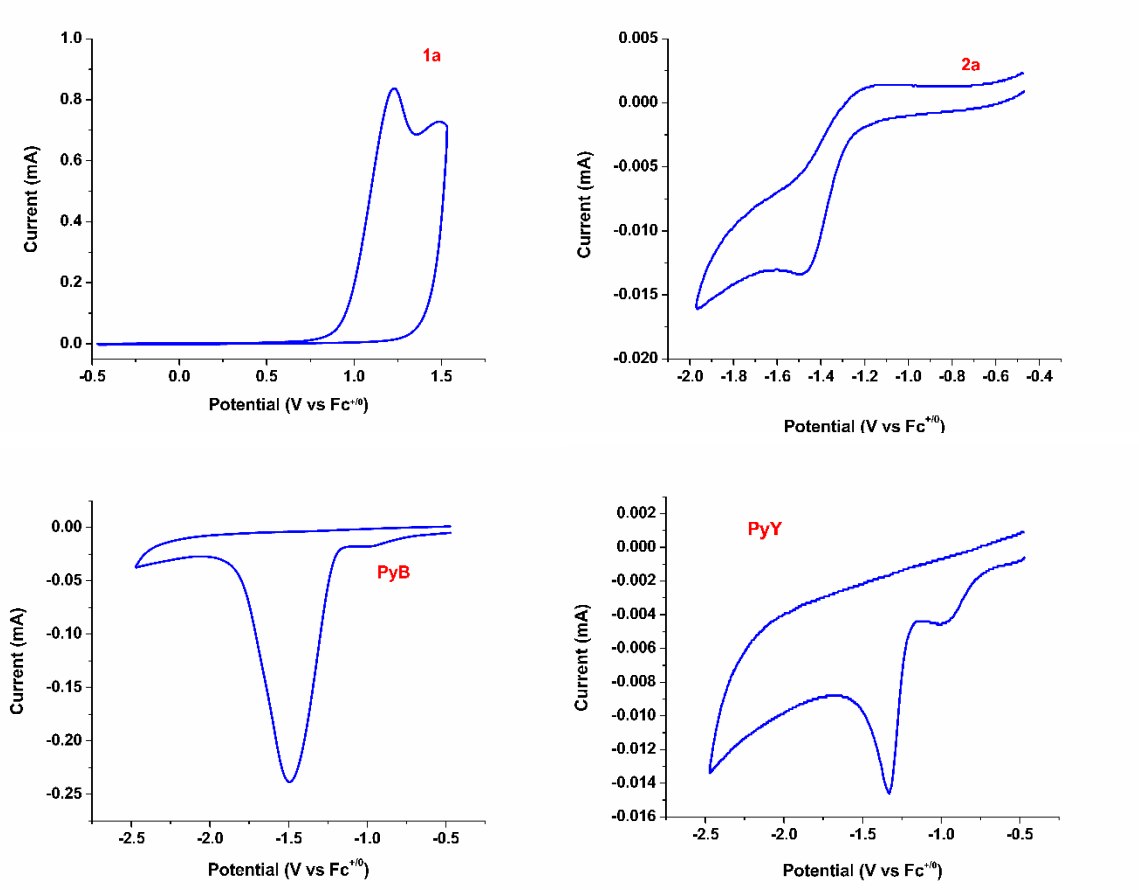


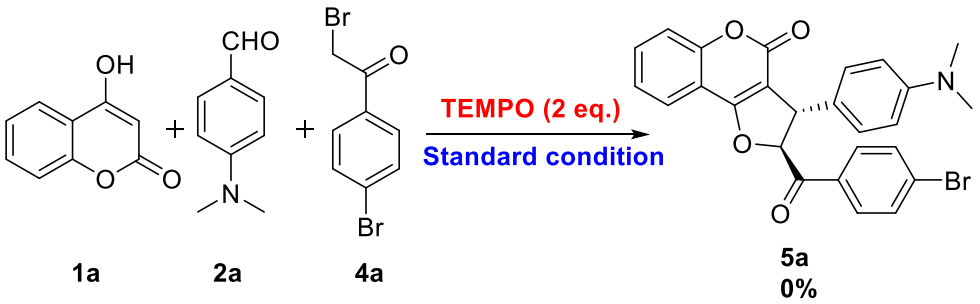

Figure S9: Cyclic voltammograms of **1a**, **2a**, **PyB** and **PyY**

The cyclic voltammograms suggest the formation of EDA complex between **1a** and **2a** followed by electron transfer from **1a** to **2a** on photo-irradiation. On the other hand lower reduction potential of PyY compared to PyB accounts for the facile SET occurring in PyY on photo-irradiation.

## 5.7. Radical quenching experiment:

### 5.7.1. Radical quenching experiment with TEMPO:

In an oven-dried round bottom flask containing magnetic stir bar were taken 4-hydroxycoumarin (**1a**, 162.0 mg, 1.0 mmol), *p*-N,N-dimethylaminobenzaldehyde (**2a**, 149.0 mg, 1.0 mmol), *p*-bromophenacyl bromide (**4a**, 277.9 mg, 1.0 mmol), pyridine (79.1 g, 1.0 mmol) and dissolved in 5 mL ethanol. To this TEMPO (312.5 mg, 2 mmol) was added as radical quencher. The round bottom flask was capped with a rubber septum and the reaction vessel was degassed using $N_2$ flow. To the degassed reaction vessel 25 mol% TEA was added via syringe and the atmosphere of the reaction vessel was kept inert with $N_2$ balloon. The round bottom flask was then placed over a magnetic stirrer and irradiated with two 12W blue LEDs, kept ~ 8 cm away from the vessel, and the reaction was kept stirring for next 12 hours at room temperature. The progress of the reaction was monitored by TLC. Upon completion of the stipulated time, the reaction was quenched by adding water and then extracted with ethyl acetate (3 x 20 mL). The organic portions were collected and the combined organic layer was dried over anhydrous $Na_2SO_4$, solvent was removed to get the crude product. The so obtained crude was subjected to HRMS analysis.

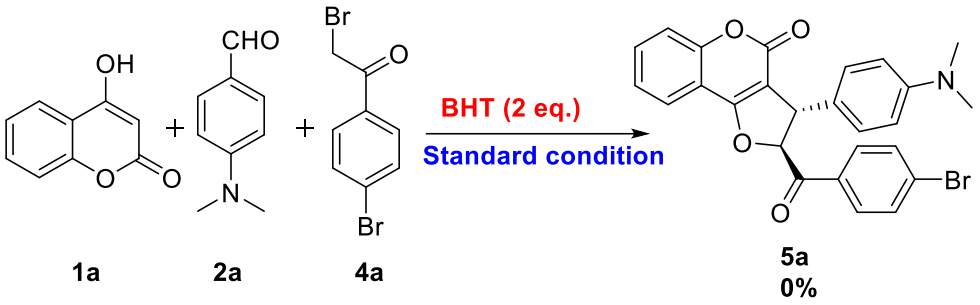



From the HRMS analysis as expected we did not get peak corresponding to the product **5a**, but we were unable to detect any TEMPO-adduct.

### 5.7.2. Radical quenching experiment with BHT:

In an oven-dried round bottom flask containing magnetic stir bar were taken 4-hydroxycoumarin (**1a**, 162.0 mg, 1.0 mmol), *p*-N,N-dimethylaminobenzaldehyde (**2a**, 149.0 mg, 1.0 mmol), *p*-bromophenacyl bromide (**4a**, 277.9 mg, 1.0 mmol), pyridine (79.1 g, 1.0 mmol) and dissolved in 5 mL ethanol. To this BHT (440.7 mg, 2 mmol) was added as radical quencher. The round bottom flask was capped with a rubber septum and the reaction vessel was degassed using $N_2$ flow. To the degassed reaction vessel 25 mol% TEA was added via syringe and the atmosphere of the reaction vessel was kept inert with $N_2$ balloon. The round bottom flask was then placed over a magnetic stirrer and irradiated with two 12W blue LEDs, kept ~ 8 cm away from the vessel, and the reaction was kept stirring for next 12 hours at room temperature. The progress of the reaction was monitored by TLC. Upon completion of the stipulated time, the reaction was quenched by adding water and then extracted with ethyl acetate (3 x 20 mL). The organic portions were collected and

the combined organic layer was dried over anhydrous $Na_2SO_4$, solvent was removed to get the crude mass. The so obtained crude was subjected to HRMS analysis.




From the HRMS analysis as expected we did not get peak corresponding to the product **5a**, but we were unable to detect any BHT-adduct.

## 5.8. EPR Experiment:

In an oven-dried round bottom flask containing magnetic stir bar were taken 4-hydroxycoumarin (**1a**, 8.1 mg, 0.05 mmol), *p*-N,N-dimethylaminobenzaldehyde (**2a**, 7.4 mg, 0.05 mmol), N-(4-bromophenacyl)pyridinium bromide (PyB, 17.8 mg, 0.05 mmol) and dissolved in 1 mL DMSO. The round bottom flask was capped with a rubber septum and the reaction vessel was degassed using $N_2$ flow. To the degassed reaction vessel 44 µL TEA was added and the atmosphere of the reaction vessel was kept inert with $N_2$ balloon. The round bottom flask was then placed over a magnetic stirrer and irradiated with two 12W blue LEDs, kept ~ 8 cm away from the vessel, and the reaction was kept stirring at room temperature. After 1 hour 200 µL aliquot was withdrawn from reaction vessel and added to EPR tube containing 5 µL DMPO. The EPR spectra was then recorded. The EPR spectra is shown in Figure S10.

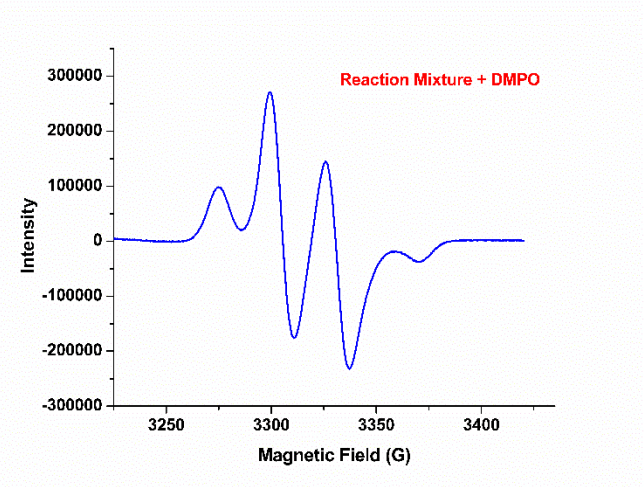



Figure S10: EPR spectra of reaction mixture with DMPO

The appearance of EPR signal at magnetic field 3274-3370 G indicates the reaction follows radical pathway.

To check whether PyY is radical in nature and has triplet state or not, we subjected *in situ* generated PyY, generated from PyB by treatment with TEA, in EPR spectrometer with prior photoillumination. In brief, In an oven-dried round bottom flask containing magnetic stir bar were taken N-(4-bromophenacyl)pyridinium bromide (PyB, 17.8 mg, 0.05 mmol) and dissolved in 1 mL DMSO. The round bottom flask was capped with a rubber septum and the reaction vessel was degassed using $N_2$ flow. To the degassed reaction vessel 44 µL TEA was added and the atmosphere of the reaction vessel was kept inert with $N_2$ balloon. The round bottom flask was then placed over a magnetic stirrer and irradiated with two 12W blue LEDs, kept ~ 8 cm away from the vessel, and the reaction was kept stirring at room temperature. After 1 hour 200 µL aliquot was withdrawn from reaction vessel and added to EPR tube containing 5 µL DMPO. The EPR spectra was then recorded. The EPR spectra is shown in Figure S11.

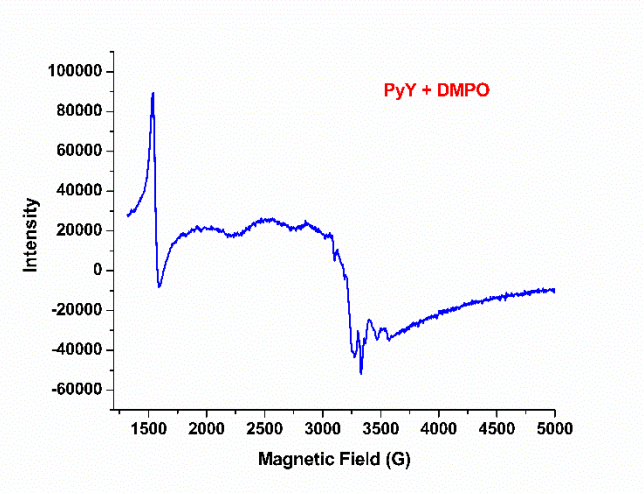



Figure S11: EPR spectra of PyY with DMPO

This time appearance of EPR signal at 3251-3367 G indicates the radical nature of the PyY. Also the signal at 1557 G indicates the triplet diradical nature of the PyY.

## 5.9. $^1$H NMR titration of PyY :

The triplet diradical in nature of pyridinium ylide (PyY) is further verified when we subjected *in situ* generated PyY (from PyB by treatment with TEA) in $^1$H NMR titration. For this purpose initially we measured the $^1$H NMR of 0.08 M solution of PyB in DMSO-*d6*. To this equimolar amount of TEA (0.08 M) was added portion wise gradually under degassed condition and maintaining PyB : TEA ratio of 100:20; 100:40; 100:60; 100:80; and 100:100. After each addition of TEA the solution was degassed with $N_2$ and irradiated with two 12 W blue LEDs for 5 minutes and then $^1$H NMR was recorded. From the NMR titration we found that with gradual addition of TEA to PyB, the sharp peaks of PyB started broadening and it gets broadened up to the ratio of PyB : TEA of 100:100. This observation strongly supports for the formation of triplet diradical in

PyY on photo-irradiation via intramolecular SET from negatively charged α-carbon to the pyridinium ring.

Surprisingly when trifluoroacetic acid (TFA) was added in two portions to the final solution the so broadened peaks gets back to their sharp forms. This observation accounts for the protonation of the negatively charged α-carbon followed by disruption in SET leading to the triplet diradical formation. The stacked images of the $^1$H NMR studies is shown in Figure S12.

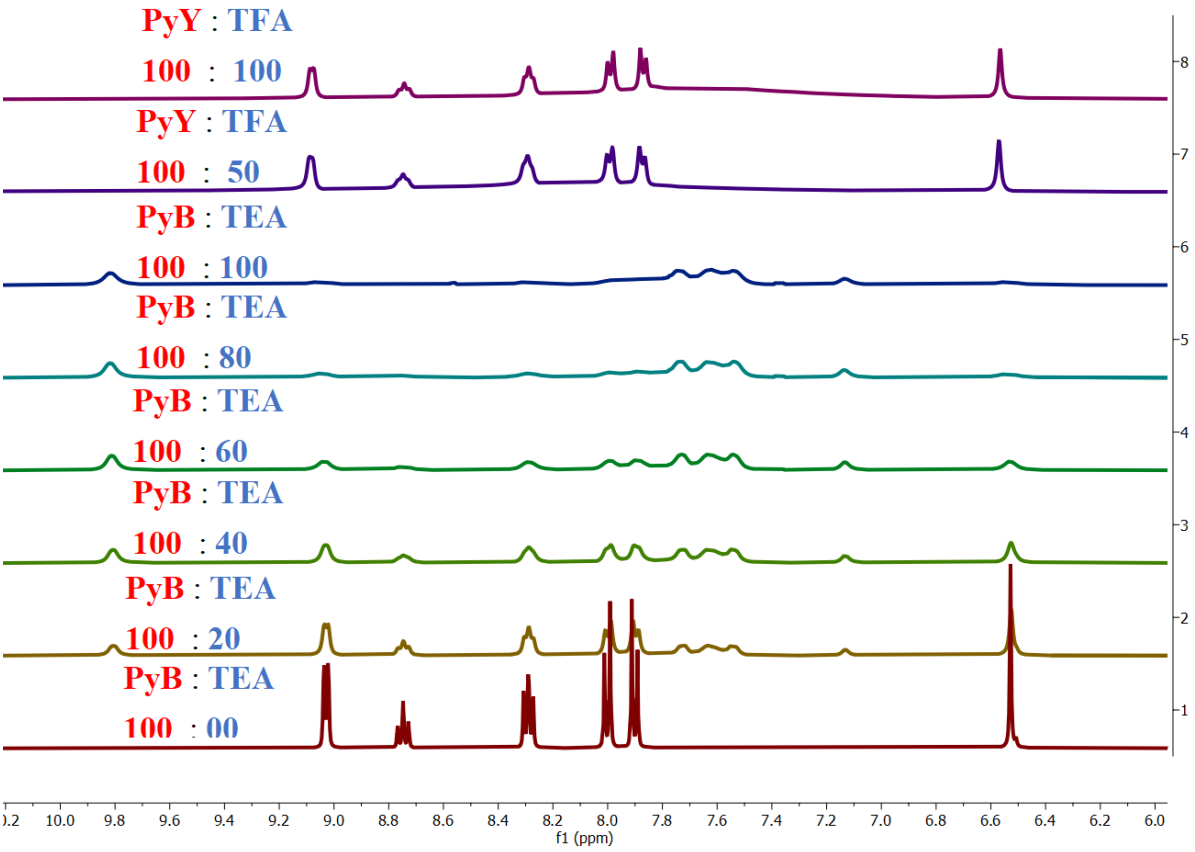



Figure S12: $^1$H NMR titration PyY after photoirradiation.

### 5.10. Light On-Off experiment:

In an oven dried round bottom flask containing magnetic stir bar were taken weighed amount of 4-Hydroxycoumarin (**1a**, 162.0 mg, 1 mmol), *p*-N,N-dimethylaminobenzaldehyde (**2a**, 149.0 mg, 1.0 mmol), *p*-bromophenacyl bromide (**4a**, 277.9 mg, 1.0 mmol), pyridine (79.1 mg, 1.0 mmol) and dissolved in 5 mL ethanol. To this 1,3,5-trimethoxybenzene (168.2 mg, 1 mmol) was added as internal standard. The round bottom flask was capped with rubber septum and the reaction vessel was degassed using $N_2$-flow. After degassing the reaction vessel, 25 mol% trimethylamine (TEA) was added using syringe and the atmosphere of reaction vessel was kept inert with $N_2$ balloon. The reaction vessel was then placed over a magnetic stirrer and irradiated with two 12W blue LEDs, kept ~ 8 cm away from the vessel, at room temperature. The light source was altered (i.e., on and off) after every 1 hour interval and aliquot was taken in each interval. The aliquots were worked

up using water and extracted with ethyl acetate, dried over $Na_2SO_4$ and evaporated to get the crude mass, which was subjected to $^1H$ NMR analysis. The yield of the desired product **5a** in each interval was plotted against time and the plot is shown in Figure S13.

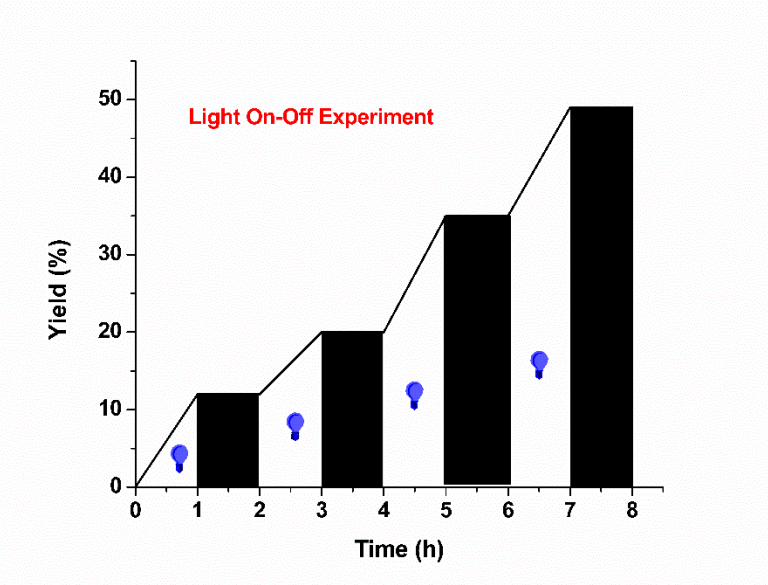


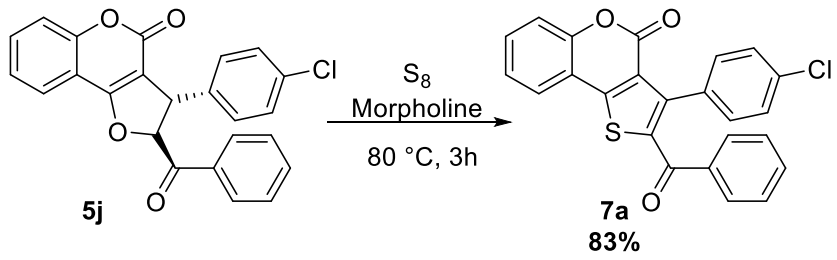

Figure S13: Light on-off experiment

From the light on-off plot we found that the yield of the product **5a** remain same when the light was off whereas it increases when it was on. Therefore, it is confirmed that continuous irradiation of light is necessary for the progress of the reaction.

## 6. Synthetic application of *trans*-dihydrofurocoumarin derivative 5j:

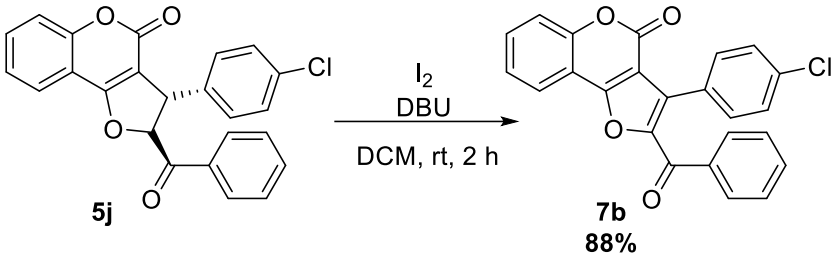
### 6.1. Synthesis of thiophenocoumarin (7a):

In an oven-dried round bottom flask containing magnetic stir bar were taken **5j** (100.5 mg, 0.25 mmol), sulfur powder (8.0 mg, 0.25 mmol), and morpholine (6.5 mg, 0.075 mmol). The mixture was heated to 80 °C and stirred for 3h. After completion of the reaction as indicated from TLC, the reaction was quenched by adding water and extracted with ethyl acetate (3 x 10 mL). The combined organic portions were collected, dried over $Na_2SO_4$ and evaporated under reduced pressure to get the crude mass. The crude mass was then purified by column chromatography to get the desired product **7a** in 83% yield (86.3 mg).



### 6.2. **Aromatization 5j to furocoumarin (7b)**:

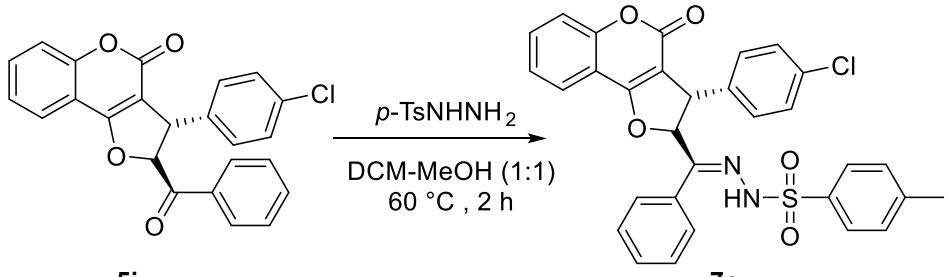
In an oven-dried round bottom flask containing magnetic stir bar were taken **5j** (100.5 mg, 0.25 mmol), molecular iodine (63.4 mg, 0.25 mmol), DBU (76.1 mg, 0.5 mmol) and dissolved in 1 ml DCM. The mixture was stirred for 2 hours at room temperature. The progress of the reaction was monitored by TLC. After completion of the reaction as indicated by TLC, the reaction was quenched with water and extracted with ethyl acetate (3 x 10 mL). The combined organic portions were collected, dried over $Na_2SO_4$ and evaporated under reduced pressure to get the crude mass. The crude mass was then purified by column chromatography to get the desired aromatized product **7b** in 88% yield (88.0 mg).




**5j** **7b** **88%**

### 6.3. **Synthesis of tosyl hydrazone of 5j (7c)**:

In an oven-dried round bottom flask containing magnetic stir bar were taken **5j** (100.5 mg, 0.25 mmol), tosyl hydrazide (46.5 mg, 0.25 mmol) and dissolved in 1 mL DCM-MeOH (1:1). The mixture was then stirred for 2 hours at 60 °C. The progress of the reaction was monitored by TLC. After completion of the reaction as indicated by TLC, the solvent of the reaction was evaporated and water was added to it. The organic portions were extracted with ethyl acetate (3 x 10 mL). The combined organic portions were collected, dried over $Na_2SO_4$ and evaporated under reduced pressure to get the crude mass. The crude mass was then purified by column chromatography to get the desired product **7C** in 80% yield (113.8 mg).

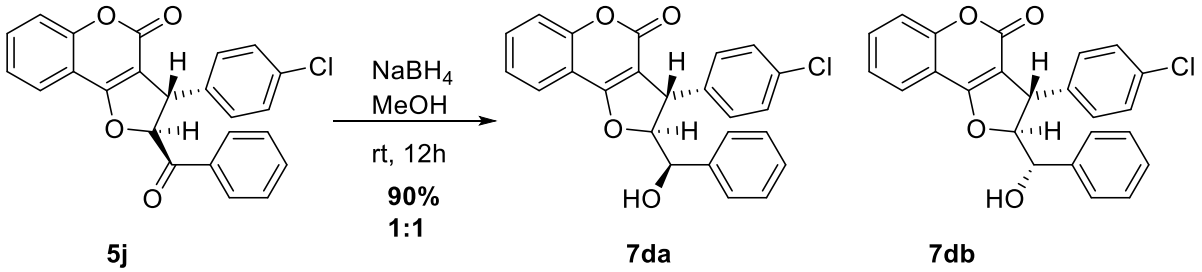



**5j** **7c** **80%**

### 6.4. **Reduction of carbonyl group of 5j (7d)**:

In an oven-dried round bottom flask containing magnetic stir bar were taken **5j** (100.5 mg, 0.25 mmol), sodium borohydride (41.1 mg, 1.08 mmol) and dissolved in MeOH. The mixture was stirred for 12 hours at room temperature. The progress of the reaction was monitored by TLC. After completion of the reaction as indicated by TLC, the reaction was quenched with water and extracted with ethyl acetate (3 x 10 mL). The combined organic portions were collected, dried over

$Na_2SO_4$ and evaporated under reduced pressure to get the crude mass. The crude mass was then subjected to $^1H$ NMR analysis. Also, the crude mass was then purified by column chromatography to get the desired product **7d** in 90% yield (90.4 mg) as a mixture of two diastereomeric alcohol **7da** (45.2 mg) and **7db** (45.2 mg).




## 7. Theoretical studies:

All the geometries were optimized using the DFT approach using the B3LYP functional[3] and 6-311G(d) basis set[4]. Before choosing this basis set for all calculations, some geometrical parameters from scXRD data of compound **5a** were compared with data from DFT calculations using B3LYP functionals and five different basis sets: 6-31G (d), 6-31+G (d), 6-31+G (d,p), 6-311G(d), 6-311+G(d,p) as shown in Table S2. The table clearly shows that the 6-311G(d) basis set has the lowest average deviation from the experimental data. Hence, this basis set was used for all subsequent theoretical calculations.

Table S2: Comparison of bond length data obtained from XRD analysis with theoretical calculations.

| Bond length (Å) | experiment | 6-31gd | 6-31+g(d) | 6-31+g(d,p) | 6-311g(d) | 6-311+g(d,p) |
|---|---|---|---|---|---|---|
| C1-C2 | 1.45310 | 1.45054 | 1.45101 | 1.4513 | 1.45081 | 1.45049 |
| C2-C3 | 1.57206 | 1.58043 | 1.58237 | 1.58263 | 1.57764 | 1.57915 |
| C3-C4 | 1.51167 | 1.51352 | 1.51429 | 1.51397 | 1.51286 | 1.51382 |
| C4-C5 | 1.34678 | 1.35657 | 1.35841 | 1.35843 | 1.35368 | 1.35485 |
| C5-C1 | 1.35486 | 1.34912 | 1.34860 | 1.34845 | 1.34638 | 1.34577 |
| Average deviation | -- | 0.00566 | 0.00658 | 0.00655 | 0.00489 | 0.00580 |

**Results and discussion:**

The molecular orbitals of the EDA complex between **1a** and **2a** were investigated thoroughly to understand whether the electron transfer is taking place from compound **1a** to **2a** or from compound **2a** to **1a**. From the molecular orbitals it was observed that the HOMO of the EDA complex is mainly due to the contribution from **1a**, while in case of the HOMO-1, it is mainly due to the contribution from **2a**. Similarly, in orbital LUMO, and LUMO+1, the contributions are

mainly from **2a** and **1a** respectively. Now to check the electron transfer possibility from **1a** to **2a** the energy difference between HOMO to LUMO is checked, and for electron transfer possibility from **2a** to **1a** the energy difference between HOMO-1 to LUMO+1 is checked. From the calculations it was observed that the energy difference between the HOMO and LUMO of GS-EDA complex is 0.14 a.u., while the energy difference between HOMO-1 and LUMO+1 of GS-EDA complex is 0.19 a.u. (Figure S14**)**. Since the HOMO-LUMO energy gap is lowest in the first case, the possibility of electron transfer is more from compound **1a** to **2a**.

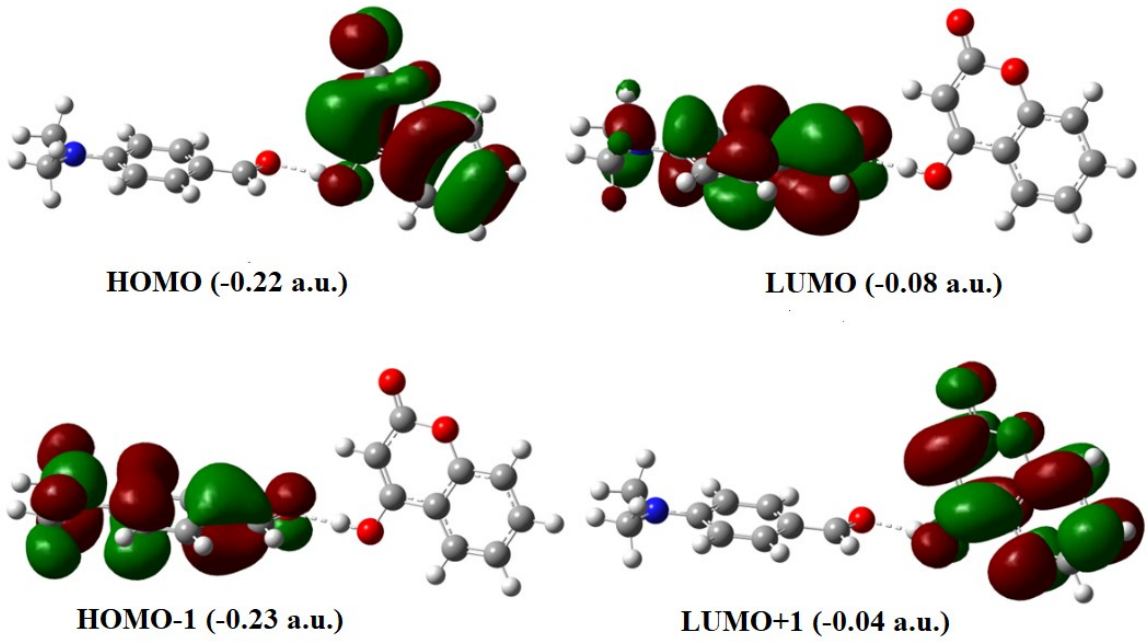



Figure S14: Molecular orbitals of EDA complex

Given that the reaction has the potential to generate both **IV** (Z form) and **IV'** (E form), the B3LYP/6-311G(d) method was utilized to theoretically optimize both molecules in order to assess their thermodynamic stability. It was determined through theoretical calculations that **IV** is 0.35 kcal/mol more stable than **IV'**. As a result, the likelihood of forming **IV** is greater than that of **IV'**. Additionally, the identical method was employed to optimize the potential intermediates $^{3}$**VIII**, $^{3}$**VIII'**, $^{3}$**VIII''**, $^{3}$**VIII'''**; $^{3}$**IX**, $^{3}$**IX'**, $^{3}$**IX''**, $^{3}$**IX'''**, and products **5a**, **5a'**, **5a''**, and **5a'''**. Based on the data presented in Table S3, it can be concluded that $^{3}$**VIII**, $^{3}$**IX**, and **5a** possesses the highest thermodynamic stability among all the compounds. Consequently, this result suggests that $^{3}$**VIII**, $^{3}$**IX**, and **5a** have the greatest potential for formation among all the compounds. Given that the energy difference between **5a** and **5a'** is negligible i.e. 0.11 kcal/mol, the energy difference between these two geometries was recalculated using the MP2 method, which employs a higher level of theory, and the result is 0.21 kcal/mol. Since, the probability of formation of **5a** is the highest, the mechanism of formation of **5a** from the compounds $^{3}$**VII** and $^{1}$**IV** is investigated theoretically with the help of potential energy surface calculated with B3LYP/6-311G(d) method. First, 1,4-radical conjugate addition (1,4-RCA) of pyridinium ylide radical $^{3}$**VII** (PyYR) to the Michael acceptor $^{1}$**IV** results the diradical intermediate $^{3}$**VIII** *via* $^{3}$**TS1** of energy barrier 12.0 kcal/mol. Then hemolytic cleavage of pyridine occurred to produce intermediate $^{3}$**IX** *via* $^{3}$**TS2** of energy barrier 11.77 kcal/mol. Concurrent intersystem crossing (ISC) in $^{3}$**IX** results tricyclic intermediate $^{1}$**IX**, which then rearranged to the desired

product **5a** *via* **$^{1}$TS3** with energy barrier of 40.45 kcal/mol, resulting a net gain in stability by 8.09 kcal/mol. Overall the formation of **5a** from **$^{3}$VII** and **$^{1}$IV** is kinetically as well as thermodynamically favorable which is in line with the experimental observations.

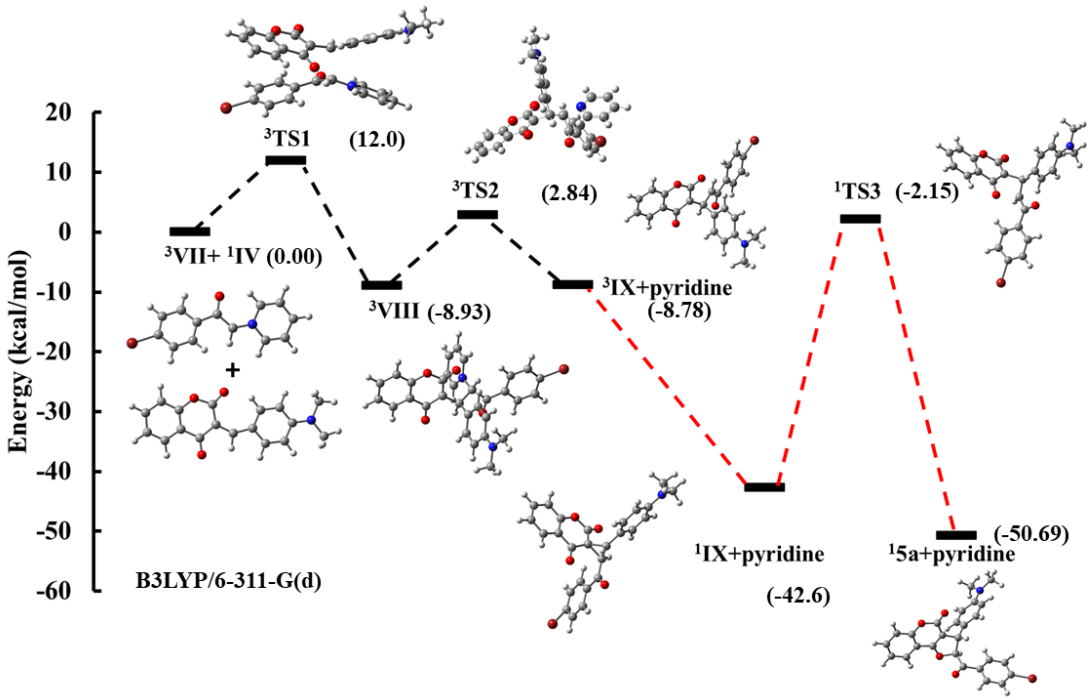


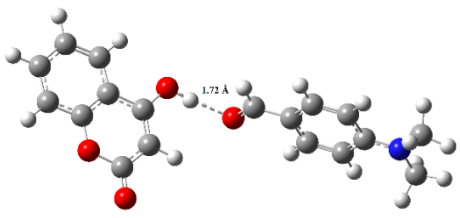

Figure S15: Potential energy surface of the reaction mechanism at B3LYP/6-311G(d) level of theory.

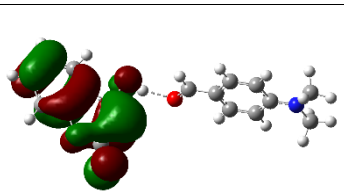
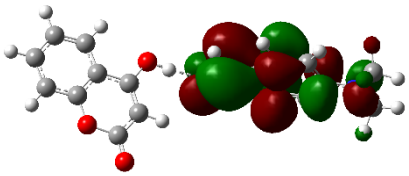
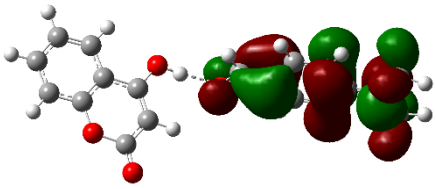
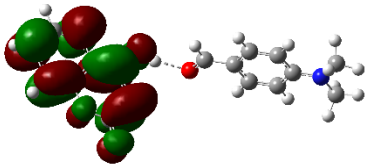
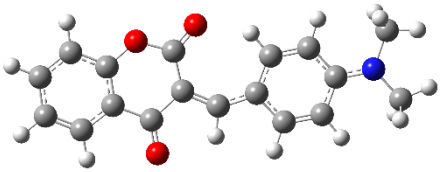
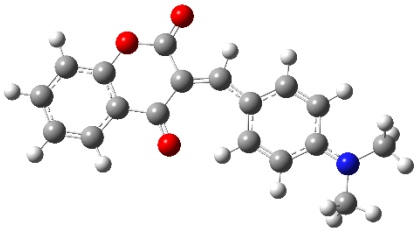
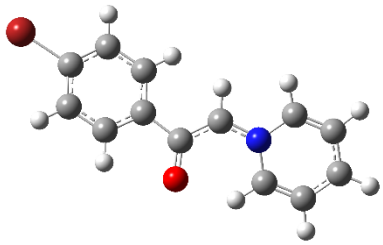
Table S3: Comparison of energies between **5a**, **5a'**, **5a''**, and **5a'''**

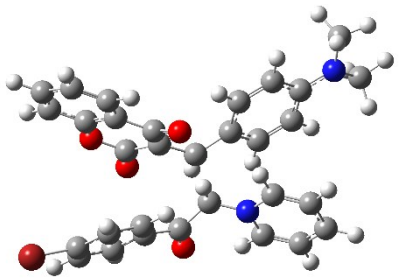
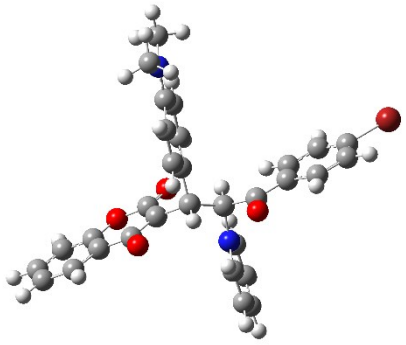
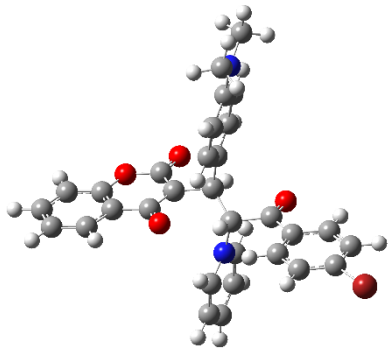
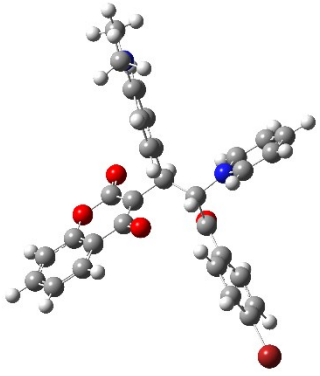
| Geometries | Relative Energy (kcal/mol) | Geometries | Relative Energy (kcal/mol) | Geometries | Relative Energy (kcal/mol) |
|---|---|---|---|---|---|
| **$^{3}$VIII** | **0.00** | **$^{3}$IX** | **0.00** | **5a** | **0.00** |
| **$^{3}$VIII'** | **0.09** | **$^{3}$IX'** | **0.10** | **5a'** | **0.11 (0.21)[a]** |
| **$^{3}$VIII''** | **1.16** | **$^{3}$IX''** | **4.90** | **5a''** | **2.98** |
| **$^{3}$VIII'''** | **14.0** | **$^{3}$IX'''** | **5.81** | **5a'''** | **3.07** |

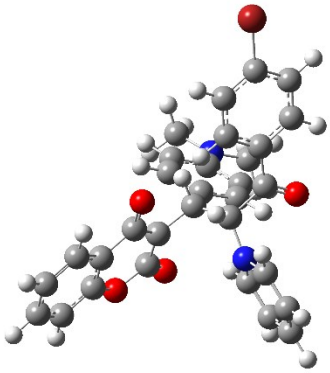
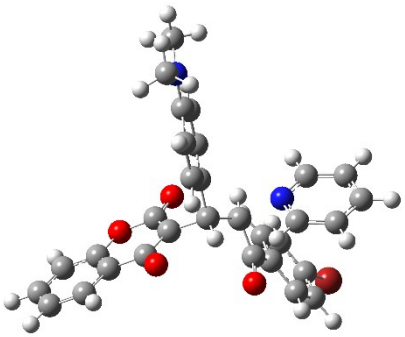
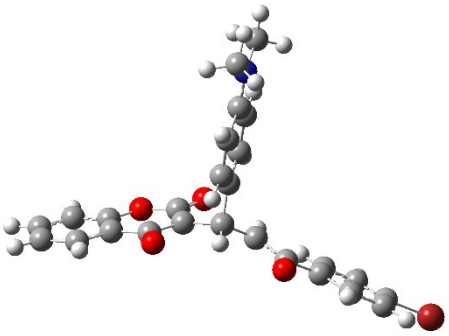
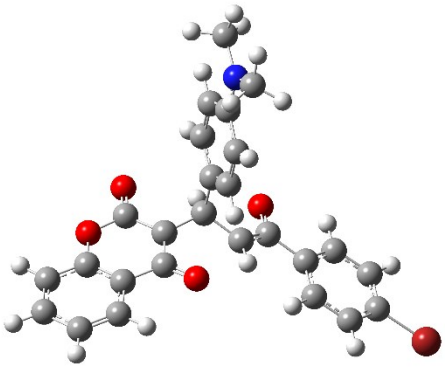
[a]using MP2 method

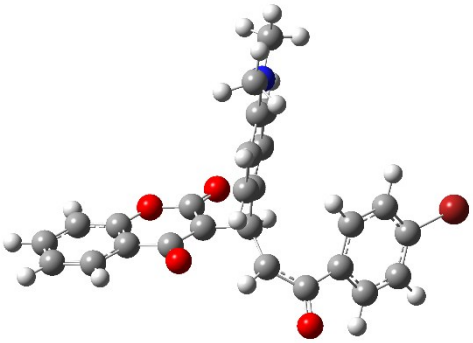
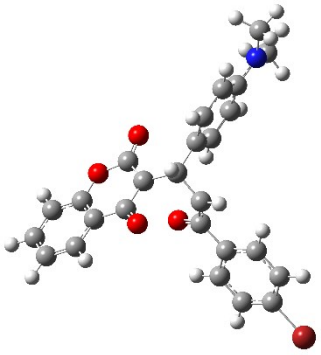
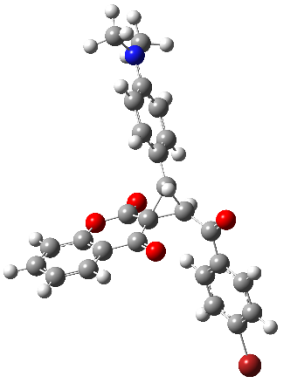
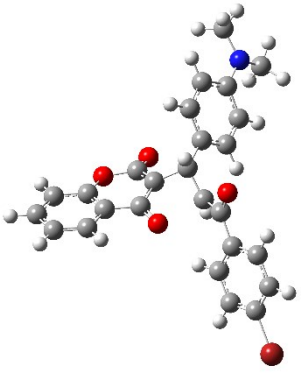
Table S4: **Optimised geometries**

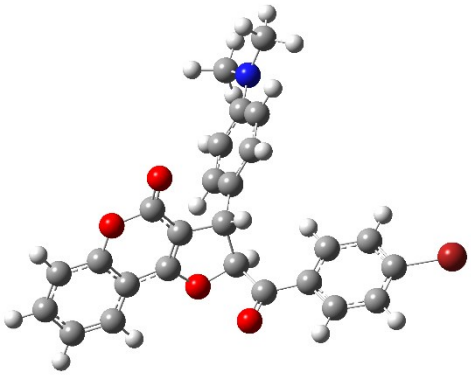
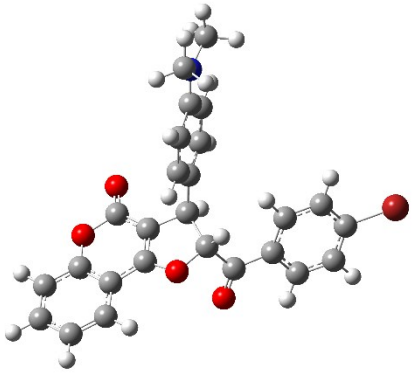
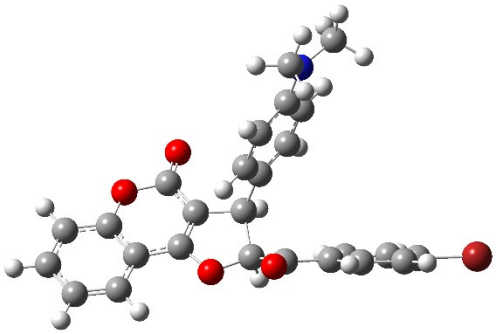
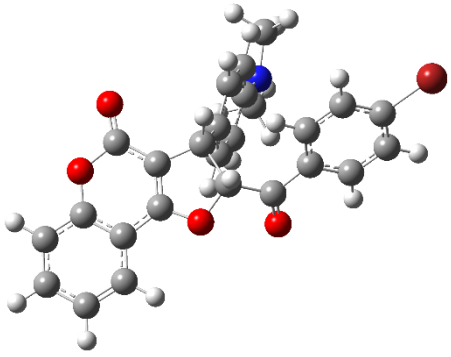
| Entry | Structure | Optimised geometry |
|---|---|---|
| **1** | **GS-EDA Complex** |  |

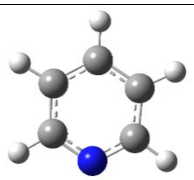
| | | |
|---|---|---|
| **2** | **HOMO** |  |
| **3** | **LUMO** |  |
| **4** | **HOMO-1** |  |
| **5** | **LUMO+1** |  |
| **6** | **$^{1}$IV (Z-form)** |  |
| **7** | **$^{1}$IV' (E-form)** |  |
| **8** | **$^{3}$VII** |  |

| | | |
|---|---|---|
| **9** | **$^{3}$TS1** |  |
| **10** | **$^{3}$VIII** |  |
| **11** | **$^{3}$VIII'** |  |
| **12** | **$^{3}$VIII"** |  |

| | | |
|---|---|---|
| **13** | **$^{3}$VIII'"** |  |
| **14** | **$^{3}$TS2** |  |
| **15** | **$^{3}$IX** |  |
| **16** | **$^{3}$IX'** |  |

| | | |
|---|---|---|
| **17** | **$^{3}$IX”** |  |
| **18** | **$^{3}$IX”’** |  |
| **19** | **$^{1}$IX** |  |
| **20** | **$^{1}$TS3** |  |

| | | |
|---|---|---|
| **21** | **5a** |  |
| **22** | **5a'** |  |
| **23** | **5a"** |  |
| **24** | **5a"'** |  |

| 25 | Pyridine |  |
|---|---|---|

## Coordinates of intermediates and transition states

### GS-EDA Complex

0 1

| | | | |
|---|---|---|---|
| C | 2.843228 | 0.147366 | 0.464998 |
| C | 4.207867 | 0.524225 | 0.146917 |
| C | 4.702701 | 1.829793 | 0.28834 |
| H | 4.0345 | 2.598542 | 0.656761 |
| O | 3.065352 | -3.33294 | -0.36787 |
| C | 5.062623 | -0.4829 | -0.32733 |
| C | 6.388482 | -0.19216 | -0.65456 |
| H | 7.021464 | -0.99349 | -1.01757 |
| O | 4.647574 | -1.76643 | -0.48905 |
| C | 6.017997 | 2.12009 | -0.03601 |
| H | 6.395447 | 3.130669 | 0.076372 |
| C | 6.859034 | 1.104662 | -0.50812 |
| H | 7.889803 | 1.329293 | -0.76273 |
| C | 3.331053 | -2.17364 | -0.18795 |
| O | 2.0583 | 1.132547 | 0.908902 |
| H | 1.141354 | 0.81422 | 1.093459 |
| C | 2.445679 | -1.1463 | 0.302725 |
| H | 1.438152 | -1.46336 | 0.539654 |
| C | -4.71669 | -0.37193 | 0.998768 |
| C | -5.43333 | 0.089088 | -0.14094 |
| C | -4.70174 | 0.779095 | -1.14271 |
| C | -3.34442 | 0.988554 | -1.00427 |
| C | -2.64352 | 0.530073 | 0.122453 |
| C | -3.3627 | -0.15506 | 1.119234 |
| C | -1.2191 | 0.758138 | 0.242927 |
| C | -7.49192 | 0.344431 | -1.44375 |
| C | -7.51286 | -0.82937 | 0.777675 |
| O | -0.52297 | 0.388329 | 1.186099 |
| N | -6.77856 | -0.12606 | -0.26506 |
| H | -0.74989 | 1.310493 | -0.59432 |
| H | -2.82696 | -0.514 | 1.991062 |
| H | -5.23163 | -0.90449 | 1.786778 |
| H | -2.80915 | 1.518974 | -1.78729 |
| H | -7.45619 | -0.30504 | 1.737616 |
| H | -8.56128 | -0.89479 | 0.495261 |
| H | -7.13945 | -1.84902 | 0.92068 |
| H | -5.201 | 1.148617 | -2.02794 |
| H | -7.09951 | -0.10681 | -2.36148 |
| H | -8.54165 | 0.071855 | -1.36066 |
| H | -7.43451 | 1.433731 | -1.54531 |

Number of imaginary frequencies = 0

### IV (Z-form)

0 1

| | | | |
|---|---|---|---|
| C | 6.172329 | -0.60746 | 0.000199 |
| C | 5.045223 | -1.41741 | 0.000131 |
| C | 3.782535 | -0.82368 | 0.000036 |
| C | 3.639712 | 0.562898 | 0.000015 |
| C | 4.790578 | 1.364039 | 0.000081 |
| C | 6.049949 | 0.787939 | 0.000168 |
| H | 7.156305 | -1.06526 | 0.00027 |
| H | 5.11654 | -2.49882 | 0.00015 |
| H | 4.654544 | 2.439308 | 0.000062 |
| H | 6.936936 | 1.412019 | 0.00022 |
| O | 2.708239 | -1.67063 | -7E-06 |
| C | 1.38824 | -1.23687 | -0.00011 |
| O | 0.56411 | -2.1171 | -0.00021 |
| C | 2.292299 | 1.164961 | -7.5E-05 |
| O | 2.143423 | 2.380631 | -0.00012 |
| C | 1.142507 | 0.209944 | -0.0001 |
| C | -0.0967 | 0.816879 | -0.00013 |
| H | 0.035952 | 1.897973 | -0.00013 |
| C | -3.413 | -1.04102 | -8.1E-05 |
| C | -4.32321 | 0.048298 | -3.1E-05 |
| C | -3.76715 | 1.353904 | -6.2E-05 |
| C | -2.40299 | 1.533513 | -0.00011 |
| C | -1.48314 | 0.452278 | -0.00013 |

| | | | |
|---|---|---|---|
| C | -2.04909 | -0.84727 | -0.00012 |
| C | -6.58644 | 0.985514 | 0.000288 |
| C | -6.22263 | -1.50054 | 0.000148 |
| N | -5.67608 | -0.15053 | 0.000039 |
| H | -1.39204 | -1.70243 | -0.00016 |
| H | -3.7832 | -2.05769 | -9.2E-05 |
| H | -2.01504 | 2.547555 | -0.00012 |
| H | -5.91302 | -2.06313 | 0.887269 |
| H | -7.30918 | -1.44718 | 0.000251 |
| H | -5.91319 | -2.06319 | -0.88699 |
| H | -4.40762 | 2.225647 | -6.2E-05 |
| H | -6.45148 | 1.61332 | -0.88712 |
| H | -7.61227 | 0.623563 | 0.000506 |
| H | -6.45106 | 1.613257 | 0.887675 |

Number of imaginary frequencies = 0

**IV' (E-form)**

0 1

| | | | |
|---|---|---|---|
| C | -5.91906 | -1.06098 | 0.000284 |
| C | -5.37117 | 0.214111 | 0.000243 |
| C | -3.98359 | 0.357716 | 0.00009 |
| C | -3.14272 | -0.7545 | -1.8E-05 |
| C | -3.71702 | -2.03406 | 0.000017 |
| C | -5.0929 | -2.19181 | 0.000169 |
| H | -6.99809 | -1.17686 | 0.000405 |
| H | -5.9898 | 1.103946 | 0.000327 |
| H | -3.04606 | -2.88504 | -7.5E-05 |
| H | -5.52909 | -3.18476 | 0.000197 |
| O | -3.50276 | 1.637905 | 0.000047 |
| C | -2.15015 | 1.931281 | -6.9E-05 |
| O | -1.86484 | 3.100757 | -0.0001 |
| C | -1.67118 | -0.58799 | -0.00016 |
| O | -0.94652 | -1.57938 | -0.00032 |
| C | -1.17896 | 0.799947 | -0.00013 |
| C | 0.135648 | 1.229113 | -0.00016 |
| H | 0.176457 | 2.315857 | -0.00017 |
| C | 3.844616 | 1.203773 | -8.4E-05 |
| C | 4.195905 | -0.17141 | -0.00002 |
| C | 3.131329 | -1.11042 | -0.00009 |
| C | 1.812482 | -0.71282 | -0.00016 |
| C | 1.450349 | 0.657577 | -0.00016 |
| C | 2.523446 | 1.587641 | -0.00015 |
| C | 5.838301 | -1.99045 | -0.00018 |
| C | 6.574937 | 0.411647 | 0.000679 |
| N | 5.502861 | -0.57316 | 0.000088 |
| H | 2.293939 | 2.648922 | -0.0002 |
| H | 4.610301 | 1.968057 | -0.00016 |
| H | 1.028227 | -1.45381 | -0.00019 |
| H | 6.536181 | 1.052714 | 0.888021 |
| H | 7.534034 | -0.1015 | 0.001372 |
| H | 6.537359 | 1.052596 | -0.88681 |
| H | 3.343906 | -2.17135 | -4.7E-05 |
| H | 5.44643 | -2.4992 | -0.88726 |
| H | 6.920348 | -2.10249 | -0.00067 |
| H | 5.447152 | -2.49945 | 0.887096 |

Number of imaginary frequencies = 0

**$^3$VII**

0 3

| | | | |
|---|---|---|---|
| C | -3.04073 | -0.0239 | 0.011971 |
| C | -2.55409 | 1.240734 | -0.3121 |
| C | -2.17326 | -1.06085 | 0.341344 |
| C | -1.18323 | 1.45952 | -0.31268 |
| C | -0.28019 | 0.430361 | -0.00489 |
| C | -0.8017 | -0.82806 | 0.3328 |
| H | -2.56173 | -2.03506 | 0.612405 |
| H | -0.14675 | -1.64025 | 0.629881 |
| H | -3.23805 | 2.043535 | -0.55972 |
| H | -0.78413 | 2.438192 | -0.55028 |
| C | 1.176935 | 0.765479 | -0.02477 |
| O | 1.542637 | 1.96231 | -0.00449 |
| C | 2.100391 | -0.32769 | -0.13299 |
| N | 3.472655 | -0.27708 | -0.09616 |
| H | 1.714583 | -1.32114 | -0.31595 |
| C | 4.207355 | 0.884941 | 0.266243 |
| C | 5.558185 | 0.834315 | 0.369541 |
| C | 6.287644 | -0.36153 | 0.11704 |
| C | 4.197393 | -1.47085 | -0.37084 |
| C | 5.550225 | -1.50843 | -0.26558 |
| H | 3.596197 | -2.31713 | -0.67101 |
| H | 3.603653 | 1.764209 | 0.417642 |
| H | 6.077091 | 1.744364 | 0.648455 |
| H | 7.365307 | -0.39126 | 0.204343 |
| H | 6.055098 | -2.44211 | -0.48718 |
| Br | -4.93145 | -0.33733 | 0.019712 |

Number of imaginary frequencies = 0

**$^3$TS1**

0 3

| | | | |
|---|---|---|---|
| C | 4.451564 | -1.33231 | -0.29819 |
| C | 4.087605 | -1.68922 | 0.999204 |
| C | 3.497453 | -1.17754 | -1.29871 |
| C | 2.747326 | -1.89941 | 1.288956 |
| C | 1.762177 | -1.73868 | 0.30323 |
| C | 2.154622 | -1.37645 | -0.99179 |
| H | 3.794431 | -0.90257 | -2.30305 |
| H | 1.425147 | -1.25412 | -1.78293 |
| H | 4.840569 | -1.79942 | 1.769701 |
| H | 2.439053 | -2.18104 | 2.288183 |
| C | 0.348576 | -2.03959 | 0.697267 |
| O | 0.125914 | -2.71773 | 1.689132 |
| C | -0.75423 | -1.45937 | -0.12991 |
| N | -1.88429 | -2.2184 | -0.41511 |
| H | -0.46723 | -0.84465 | -0.97043 |
| C | -2.38697 | -3.23463 | 0.425079 |
| C | -3.47975 | -3.96091 | 0.053569 |
| C | -4.16303 | -3.71091 | -1.15592 |
| C | -2.59409 | -1.92742 | -1.59809 |
| C | -3.68389 | -2.65397 | -1.96449 |
| H | -2.21406 | -1.09242 | -2.16793 |
| H | -1.83872 | -3.38844 | 1.338128 |
| H | -3.81798 | -4.74011 | 0.727714 |
| H | -5.02852 | -4.29226 | -1.44512 |
| H | -4.18251 | -2.39232 | -2.89086 |
| H | -3.44986 | -0.80021 | 2.056294 |
| H | -5.76353 | -0.34535 | 1.538242 |
| C | -3.67319 | -0.07899 | 1.275998 |
| C | -4.99895 | 0.178971 | 0.980315 |
| C | -1.24697 | 0.228505 | 1.045274 |
| H | -1.23793 | -0.26524 | 2.012019 |
| C | -2.60745 | 0.569268 | 0.620306 |
| C | -5.35017 | 1.116375 | -0.01776 |
| C | -2.96291 | 1.512913 | -0.36281 |
| C | -4.28487 | 1.784074 | -0.6677 |
| H | -2.19309 | 2.034758 | -0.91237 |
| H | -4.48994 | 2.530629 | -1.4239 |
| C | 3.70811 | 4.250062 | -0.20435 |
| C | 3.315022 | 3.550901 | 0.928563 |
| C | 2.223966 | 2.686114 | 0.849406 |
| C | 1.523446 | 2.51514 | -0.34744 |
| C | 1.943535 | 3.224273 | -1.48344 |
| C | 3.023317 | 4.088361 | -1.416 |
| H | 4.556387 | 4.924253 | -0.14641 |
| H | 3.834953 | 3.653707 | 1.873862 |
| C | 0.373439 | 1.597836 | -0.40048 |
| H | 1.393142 | 3.072364 | -2.40473 |
| H | 3.339475 | 4.637374 | -2.29635 |
| C | -0.05582 | 1.032643 | 0.866415 |
| C | 0.803956 | 1.151016 | 2.051396 |
| O | 0.633274 | 0.567634 | 3.095711 |
| O | 1.894355 | 2.003971 | 1.987389 |
| O | -0.17073 | 1.311042 | -1.48242 |
| N | -6.66787 | 1.368807 | -0.3446 |
| C | -7.7336 | 0.774978 | 0.443769 |
| H | -8.69499 | 1.048576 | 0.012042 |
| H | -7.6695 | -0.31704 | 0.436217 |
| H | -7.72201 | 1.108852 | 1.49056 |
| C | -6.99442 | 2.465238 | -1.24021 |
| H | -6.52644 | 2.331478 | -2.22019 |
| H | -8.07181 | 2.493286 | -1.39445 |
| H | -6.68068 | 3.440928 | -0.84478 |
| Br | 6.29901 | -1.04905 | -0.70997 |

Imaginary frequency value = -302.00

**$^3$VIII**

0 3

| | | | |
|---|---|---|---|
| Br | 7.179025 | -0.42196 | -0.76574 |
| O | -3.61512 | -0.14998 | 2.001628 |
| O | -3.67727 | -1.03045 | -2.00137 |
| O | -1.50724 | -0.67582 | -2.19312 |
| O | 1.083273 | -0.34343 | 2.398237 |
| C | -1.3325 | 2.372922 | 1.460366 |
| H | -1.6932 | 1.97658 | 2.402729 |
| N | -0.59102 | 5.652219 | -0.06654 |
| C | 3.734451 | -0.26526 | 1.574686 |
| H | 3.479188 | -0.10245 | 2.614853 |
| C | -4.87391 | -0.78312 | 0.092554 |
| C | -1.20466 | 3.739324 | 1.30717 |
| H | -1.46045 | 4.37986 | 2.140676 |
| C | -6.10125 | -0.85124 | 0.767126 |
| H | -6.1069 | -0.62449 | 1.827069 |
| C | -0.99499 | 1.478671 | 0.430219 |

| | | | |
|---|---|---|---|
| C | 5.056934 | -0.23889 | 1.162041 |
| H | 5.852359 | -0.05322 | 1.873884 |
| C | 2.68694 | -0.50363 | 0.66461 |
| C | -2.4175 | -0.40031 | -0.01679 |
| C | -4.83811 | -1.07333 | -1.27271 |
| C | 3.019919 | -0.72293 | -0.68292 |
| H | 2.252937 | -0.91584 | -1.42251 |
| C | 0.123045 | -0.82944 | 0.273674 |
| H | 0.357142 | -0.64997 | -0.76837 |
| C | -0.73797 | 4.296108 | 0.089009 |
| C | 5.353239 | -0.45844 | -0.18364 |
| C | -0.43854 | 3.394901 | -0.96298 |
| H | -0.10101 | 3.764293 | -1.9221 |
| C | -0.57661 | 2.029878 | -0.79388 |
| H | -0.36646 | 1.378187 | -1.63328 |
| C | 4.343784 | -0.7033 | -1.10944 |
| H | 4.585812 | -0.87718 | -2.15094 |
| C | -5.99619 | -1.42349 | -1.966 |
| H | -5.92854 | -1.64193 | -3.02533 |
| C | -1.13119 | -0.02188 | 0.662586 |
| H | -1.29244 | -0.15552 | 1.730542 |
| C | -0.14816 | 6.201474 | -1.33873 |
| H | 0.829978 | 5.803577 | -1.62704 |
| H | -0.05506 | 7.281838 | -1.25088 |
| H | -0.85639 | 5.986826 | -2.14769 |
| C | -7.25849 | -1.19856 | 0.090237 |
| H | -8.20489 | -1.25025 | 0.617275 |
| C | -7.20129 | -1.48439 | -1.27982 |
| H | -8.1049 | -1.75775 | -1.81486 |
| C | -0.96491 | 6.560384 | 1.006876 |
| H | -2.03202 | 6.492189 | 1.24803 |
| H | -0.75342 | 7.583013 | 0.701869 |
| H | -0.39484 | 6.358929 | 1.919514 |
| C | -2.46101 | -0.69139 | -1.43929 |
| C | -3.63057 | -0.41444 | 0.797479 |
| C | 1.303671 | -0.4954 | 1.197754 |
| C | -0.42737 | -2.85815 | 1.62203 |
| C | -0.43138 | -4.21641 | 1.782342 |
| C | -0.12084 | -5.07835 | 0.710932 |
| C | 0.167287 | -4.4861 | -0.53482 |
| C | 0.170407 | -3.12626 | -0.6817 |
| N | -0.0989 | -2.28632 | 0.393861 |
| H | -0.12334 | -6.15341 | 0.835157 |
| H | -0.63421 | -2.16811 | 2.424541 |
| H | -0.69128 | -4.61352 | 2.757256 |
| H | 0.37185 | -5.0961 | -1.40776 |
| H | 0.330991 | -2.63444 | -1.62994 |

Number of imaginary frequencies = 0

**$^{3}$VIII'**

0 3

| | | | |
|---|---|---|---|
| O | 1.752206 | -0.77381 | -1.7911 |
| C | 2.495325 | -0.33234 | 0.412037 |
| C | 2.681133 | -0.73602 | -0.97037 |
| C | 1.287189 | 2.52572 | 1.624432 |
| H | 1.565602 | 2.198529 | 2.619629 |
| N | 0.667958 | 5.685056 | -0.18272 |
| C | 4.054335 | -1.11998 | -1.34849 |
| C | 1.167165 | 3.877029 | 1.367483 |
| H | 1.345331 | 4.575406 | 2.174383 |
| C | 4.352921 | -1.56214 | -2.64608 |
| H | 3.539231 | -1.61518 | -3.36004 |
| C | 1.042708 | 1.560425 | 0.63286 |
| O | 3.552645 | 0.11389 | 2.487376 |
| C | 5.086281 | -1.0408 | -0.40937 |
| C | 0.80485 | 4.344523 | 0.078087 |
| C | 0.600806 | 3.370711 | -0.93156 |
| H | 0.346998 | 3.671051 | -1.93942 |
| C | 0.730086 | 2.022214 | -0.65824 |
| H | 0.600792 | 1.310378 | -1.46464 |
| C | 6.393419 | -1.39335 | -0.74552 |
| H | 7.166722 | -1.31916 | 0.010058 |
| O | 4.878019 | -0.61606 | 0.874306 |
| C | 0.314157 | 6.141727 | -1.51786 |
| H | 1.081082 | 5.881618 | -2.25679 |
| H | 0.207048 | 7.224277 | -1.51066 |
| H | -0.63756 | 5.713253 | -1.84793 |
| C | 5.646286 | -1.91552 | -2.99069 |
| H | 5.870114 | -2.2578 | -3.99511 |
| C | 6.66647 | -1.82964 | -2.03417 |
| H | 7.681924 | -2.10647 | -2.29825 |
| C | 0.942477 | 6.667732 | 0.854796 |
| H | 0.284634 | 6.533593 | 1.719757 |
| H | 0.77184 | 7.666137 | 0.457996 |
| H | 1.980217 | 6.614376 | 1.202638 |
| C | 3.624782 | -0.24745 | 1.335358 |
| C | -1.31266 | -0.36171 | 1.321755 |
| C | -2.64227 | -0.43036 | 0.669866 |

| | | | |
|---|---|---|---|
| C | -3.76926 | -0.13248 | 1.459502 |
| C | -2.85086 | -0.76332 | -0.67932 |
| C | -5.04948 | -0.15774 | 0.92952 |
| H | -3.60977 | 0.118383 | 2.501252 |
| C | -4.1309 | -0.79658 | -1.22244 |
| H | -2.0196 | -1.00477 | -1.32966 |
| C | -5.22145 | -0.49065 | -0.41445 |
| H | -5.90695 | 0.074823 | 1.549648 |
| H | -4.27685 | -1.05822 | -2.26341 |
| Br | -6.98638 | -0.52482 | -1.16168 |
| O | -1.20171 | -0.10679 | 2.519966 |
| C | -0.05407 | -0.75958 | 0.536646 |
| H | -0.1894 | -0.65814 | -0.53246 |
| C | 1.162277 | 0.080374 | 0.975993 |
| H | 1.228827 | 0.01733 | 2.059866 |
| C | -0.01368 | -3.11905 | -0.24721 |
| C | -0.0254 | -4.46463 | -0.002 |
| C | 0.142313 | -4.96346 | 1.305271 |
| C | 0.348403 | -4.02408 | 2.336029 |
| C | 0.360101 | -2.68107 | 2.077297 |
| N | 0.152119 | -2.20175 | 0.784989 |
| H | 0.132541 | -6.02666 | 1.506975 |
| H | -0.08025 | -2.69746 | -1.23947 |
| H | -0.14646 | -5.13782 | -0.84355 |
| H | 0.511954 | -4.34755 | 3.357935 |
| H | 0.48473 | -1.93353 | 2.844687 |

Number of imaginary frequencies = 0

**$^{3}$VIII''**

0 3

| | | | |
|---|---|---|---|
| O | 0.103354 | -1.37009 | -1.35089 |
| C | 1.116175 | -1.38537 | 0.788773 |
| C | 0.515582 | -2.0147 | -0.37474 |
| C | 3.751736 | 0.624925 | 0.984043 |
| H | 3.697998 | 0.547328 | 2.064174 |
| N | 6.276565 | 1.331463 | -1.61692 |
| C | 0.404862 | -3.48416 | -0.32428 |
| C | 4.962805 | 0.926157 | 0.390961 |
| H | 5.822383 | 1.095416 | 1.025824 |
| C | -0.21138 | -4.20118 | -1.361 |
| H | -0.60452 | -3.63817 | -2.19939 |
| C | 2.58723 | 0.419679 | 0.22571 |
| O | 2.254412 | -1.73681 | 2.839592 |
| C | 0.919011 | -4.18684 | 0.768971 |
| C | 5.080214 | 1.020355 | -1.01867 |
| C | 3.914285 | 0.767862 | -1.78414 |
| H | 3.95172 | 0.797528 | -2.86503 |
| C | 2.711711 | 0.465361 | -1.17389 |
| H | 1.851765 | 0.242723 | -1.79422 |
| C | 0.827175 | -5.57697 | 0.837757 |
| H | 1.237338 | -6.08691 | 1.70149 |
| O | 1.539557 | -3.56203 | 1.815847 |
| C | 6.37777 | 1.396647 | -3.06633 |
| H | 6.176011 | 0.427043 | -3.53687 |
| H | 7.384698 | 1.701886 | -3.34288 |
| H | 5.679743 | 2.12985 | -3.4831 |
| C | -0.30968 | -5.58064 | -1.30244 |
| H | -0.78977 | -6.12885 | -2.10556 |
| C | 0.212426 | -6.26638 | -0.19775 |
| H | 0.136785 | -7.3476 | -0.14574 |
| C | 7.473959 | 1.51719 | -0.81175 |
| H | 7.356271 | 2.340714 | -0.09958 |
| H | 8.311272 | 1.757879 | -1.46328 |
| H | 7.732376 | 0.613016 | -0.24885 |
| C | 1.67638 | -2.18549 | 1.877986 |
| C | -1.19165 | 0.651125 | 1.305587 |
| C | -2.53147 | 0.64834 | 0.663137 |
| C | -3.65448 | 0.803069 | 1.494946 |
| C | -2.73996 | 0.462645 | -0.71272 |
| C | -4.94012 | 0.798551 | 0.975449 |
| H | -3.49148 | 0.9298 | 2.5586 |
| C | -4.02572 | 0.446287 | -1.24433 |
| H | -1.90715 | 0.275479 | -1.3789 |
| C | -5.11502 | 0.62288 | -0.39704 |
| H | -5.79762 | 0.929993 | 1.624427 |
| H | -4.17682 | 0.289623 | -2.3054 |
| Br | -6.88707 | 0.612143 | -1.1281 |
| O | -1.06979 | 0.578087 | 2.525109 |
| C | 0.061225 | 0.940166 | 0.460958 |
| H | -0.1176 | 0.7546 | -0.58974 |
| C | 1.273283 | 0.106464 | 0.930641 |
| H | 1.408953 | 0.293671 | 1.994133 |
| C | 0.597081 | 2.961761 | 1.832672 |
| C | 0.652329 | 4.32064 | 1.979023 |
| C | 0.432098 | 5.185143 | 0.887685 |
| C | 0.155583 | 4.589948 | -0.3624 |
| C | 0.099796 | 3.231929 | -0.495 |
| N | 0.308843 | 2.38764 | 0.592898 |

| | | | |
|---|---|---|---|
| H | 0.476382 | 6.260309 | 1.001915 |
| H | 0.723782 | 2.27461 | 2.653558 |
| H | 0.876559 | 4.71691 | 2.963358 |
| H | -0.00834 | 5.198567 | -1.24495 |
| H | -0.10091 | 2.740269 | -1.43656 |

Number of imaginary frequencies = 0

**$^{3}$VIII'''**

0 3

| | | | |
|---|---|---|---|
| O | 0.575948 | -2.46596 | -1.21128 |
| C | 0.64558 | 0.074375 | -0.07265 |
| C | 1.892791 | -0.62816 | -0.54705 |
| C | 1.703559 | -1.96386 | -1.0944 |
| C | 0.786787 | 1.992114 | -1.65124 |
| H | 0.870629 | 1.244666 | -2.43499 |
| N | 0.751245 | 5.667361 | -1.34792 |
| C | 2.921708 | -2.69277 | -1.47962 |
| C | 0.823266 | 3.324656 | -2.00455 |
| H | 0.927788 | 3.584058 | -3.04964 |
| C | 2.864288 | -3.99943 | -1.9878 |
| H | 1.88876 | -4.46185 | -2.08381 |
| C | 0.64748 | 1.569867 | -0.31572 |
| O | 3.477484 | 1.076407 | -0.04002 |
| C | 4.165875 | -2.07153 | -1.34431 |
| C | 0.707358 | 4.335489 | -1.01792 |
| C | 0.52722 | 3.911885 | 0.321556 |
| H | 0.407935 | 4.638669 | 1.113977 |
| C | 0.50209 | 2.570032 | 0.656659 |
| H | 0.348488 | 2.307161 | 1.694139 |
| C | 5.340092 | -2.73111 | -1.7093 |
| H | 6.287709 | -2.21895 | -1.59079 |
| O | 4.299999 | -0.80184 | -0.85854 |
| H | -0.10587 | -0.3101 | -0.7761 |
| C | 0.601921 | 6.68596 | -0.31947 |
| H | -0.36406 | 6.606494 | 0.190603 |
| H | 0.658334 | 7.670592 | -0.77833 |
| H | 1.393467 | 6.618518 | 0.434598 |
| C | 4.023237 | -4.66331 | -2.35077 |
| H | 3.975027 | -5.67355 | -2.74199 |
| C | 5.262081 | -4.02325 | -2.20899 |
| H | 6.173679 | -4.5401 | -2.49079 |
| C | 0.955715 | 6.074726 | -2.72905 |
| H | 1.898361 | 5.685378 | -3.12822 |
| H | 0.992123 | 7.160579 | -2.78256 |
| H | 0.141904 | 5.73233 | -3.37826 |
| C | 3.215652 | -0.03029 | -0.451 |
| C | -1.24893 | 0.094703 | 1.691852 |
| C | -2.49142 | -0.3493 | 0.991715 |
| C | -3.69073 | 0.294371 | 1.341752 |
| C | -2.53016 | -1.34807 | 0.004343 |
| C | -4.8904 | -0.03755 | 0.730841 |
| H | -3.6576 | 1.059641 | 2.107987 |
| C | -3.72921 | -1.68952 | -0.61465 |
| H | -1.63527 | -1.87566 | -0.30586 |
| C | -4.89901 | -1.03181 | -0.24694 |
| H | -5.80883 | 0.464797 | 1.009594 |
| H | -3.74865 | -2.46193 | -1.3736 |
| Br | -6.55053 | -1.50115 | -1.09673 |
| O | -1.30018 | 0.888156 | 2.6159 |
| C | 0.10897 | -0.52844 | 1.273871 |
| H | -0.09389 | -1.56932 | 1.015972 |
| C | 1.990934 | 0.366119 | 2.701883 |
| C | 2.648454 | 0.365021 | 3.899564 |
| C | 2.370014 | -0.5951 | 4.896783 |
| C | 1.389179 | -1.56539 | 4.589813 |
| C | 0.74399 | -1.55809 | 3.389287 |
| N | 1.035089 | -0.60766 | 2.39975 |
| H | 2.880403 | -0.58806 | 5.85073 |
| H | 2.230882 | 1.064457 | 1.918171 |
| H | 3.406115 | 1.125088 | 4.057283 |
| H | 1.131698 | -2.34157 | 5.302686 |
| H | -0.01133 | -2.28706 | 3.126255 |

Number of imaginary frequencies = 0

**$^{3}$TS2**

0 3

| | | | |
|---|---|---|---|
| C | 5.309588 | 0.139211 | 0.476869 |
| C | 5.101257 | 0.115006 | -0.90044 |
| C | 4.240127 | 0.121134 | 1.366398 |
| C | 3.800815 | 0.060535 | -1.38453 |
| C | 2.700851 | 0.014191 | -0.51443 |
| C | 2.942275 | 0.058124 | 0.866853 |
| H | 4.414204 | 0.168153 | 2.434625 |
| H | 2.116577 | 0.09466 | 1.568408 |

| | | | |
|---|---|---|---|
| H | 5.943045 | 0.139982 | -1.58228 |
| H | 3.609249 | 0.055046 | -2.45107 |
| C | 1.334579 | -0.0353 | -1.11576 |
| O | 1.163679 | 0.256454 | -2.31328 |
| C | 0.228496 | -0.57993 | -0.33263 |
| N | 0.16842 | -2.38651 | -0.89831 |
| C | 0.861163 | -3.26191 | -0.12891 |
| C | 1.529213 | -4.3483 | -0.65865 |
| C | 1.50045 | -4.5628 | -2.04017 |
| C | 0.124823 | -2.60245 | -2.23691 |
| C | 0.778482 | -3.66818 | -2.83087 |
| H | -0.4383 | -1.88629 | -2.81958 |
| H | 0.858778 | -3.06043 | 0.936657 |
| H | 2.056758 | -5.02475 | 0.004654 |
| H | 2.023223 | -5.40224 | -2.48383 |
| H | 0.708859 | -3.79815 | -3.9051 |
| H | -1.53942 | -1.02684 | 1.935907 |
| H | -3.40264 | -2.28787 | 2.823733 |
| C | -2.36193 | -1.27334 | 1.275552 |
| C | -3.43355 | -1.98271 | 1.786066 |
| C | -1.16018 | -0.07878 | -0.66452 |
| C | -2.32864 | -0.85256 | -0.06424 |
| C | -1.42458 | 1.348646 | -0.24837 |
| C | -4.55731 | -2.29221 | 0.980267 |
| C | -3.46134 | -1.1177 | -0.85101 |
| C | -4.54256 | -1.82343 | -0.3567 |
| H | -3.48855 | -0.75316 | -1.8719 |
| H | -5.38156 | -2.01217 | -1.01337 |
| Br | 7.101971 | 0.215835 | 1.160068 |
| N | -5.62258 | -3.00553 | 1.477693 |
| C | -6.80484 | -3.22218 | 0.659028 |
| H | -7.5264 | -3.81303 | 1.219506 |
| H | -7.28687 | -2.27945 | 0.37353 |
| H | -6.56331 | -3.77184 | -0.25654 |
| C | -5.64049 | -3.42021 | 2.871067 |
| H | -6.53642 | -4.00833 | 3.059314 |
| H | -4.77534 | -4.04601 | 3.111784 |
| H | -5.64491 | -2.56518 | 3.558276 |
| C | -2.37086 | 3.595311 | -0.73521 |
| C | -1.88762 | 4.011197 | 0.507119 |
| C | -3.2057 | 5.832838 | -1.12874 |
| H | -3.71652 | 6.548158 | -1.76396 |
| C | -2.71474 | 6.229494 | 0.121685 |
| H | -2.84607 | 7.253504 | 0.455841 |
| C | -2.0564 | 5.324779 | 0.943235 |
| H | -1.66748 | 5.609914 | 1.91373 |
| O | -1.23234 | 3.162024 | 1.362156 |
| C | -0.98845 | 1.837937 | 1.05039 |
| O | -0.41414 | 1.181403 | 1.894993 |
| C | -3.03364 | 4.52468 | -1.5495 |
| H | -3.39913 | 4.181984 | -2.51066 |
| C | -2.18085 | 2.196726 | -1.16652 |
| O | -2.62324 | 1.774205 | -2.23625 |
| H | -1.26348 | -0.07802 | -1.74949 |
| H | 0.4137 | -0.76718 | 0.714179 |

Imaginary frequency value = -434.25

**$^{3}$IX**

0 3

| | | | |
|---|---|---|---|
| Br | 7.570159 | -0.54156 | -0.46652 |
| O | -3.05884 | -1.15985 | 2.194781 |
| O | -2.85645 | -2.47283 | -1.68428 |
| O | -1.07058 | -1.23809 | -2.08842 |
| O | 1.348684 | 0.249462 | 2.320963 |
| C | -2.13358 | 1.937904 | 1.31809 |
| H | -2.24405 | 1.512253 | 2.308658 |
| N | -3.0252 | 5.032252 | -0.49153 |
| C | 4.023587 | 0.170276 | 1.601458 |
| H | 3.723882 | 0.543648 | 2.573326 |
| C | -3.97252 | -2.50715 | 0.468153 |
| C | -2.64325 | 3.195557 | 1.058373 |
| H | -3.13068 | 3.73114 | 1.862202 |
| C | -5.02679 | -3.00879 | 1.244808 |
| H | -5.09596 | -2.67774 | 2.274612 |
| C | -1.47066 | 1.198818 | 0.326322 |
| C | 5.367714 | 0.080596 | 1.264956 |
| H | 6.133225 | 0.387747 | 1.967079 |
| C | 3.021988 | -0.21892 | 0.702643 |
| C | -1.92253 | -1.14163 | 0.125599 |
| C | -3.85875 | -2.91879 | -0.86128 |
| C | 3.404807 | -0.71278 | -0.55078 |
| H | 2.66497 | -1.03824 | -1.27237 |
| C | 0.520384 | -0.34752 | 0.226064 |
| H | 0.714932 | -0.59968 | -0.80527 |
| C | -2.52815 | 3.779269 | -0.22921 |
| C | 5.718777 | -0.41224 | 0.010178 |

| | | | |
|---|---|---|---|
| C | -1.88843 | 3.01257 | -1.23518 |
| H | -1.78893 | 3.400496 | -2.24021 |
| C | -1.38488 | 1.754711 | -0.96115 |
| H | -0.92161 | 1.188384 | -1.76016 |
| C | 4.748276 | -0.8135 | -0.9017 |
| H | 5.033654 | -1.20055 | -1.87222 |
| C | -4.77263 | -3.81172 | -1.41991 |
| H | -4.65206 | -4.10779 | -2.4554 |
| C | -0.89343 | -0.18801 | 0.670426 |
| H | -0.91476 | -0.26777 | 1.756754 |
| C | -2.93735 | 5.591183 | -1.83159 |
| H | -1.89826 | 5.660554 | -2.16923 |
| H | -3.35393 | 6.596156 | -1.82966 |
| H | -3.49507 | 4.994203 | -2.56282 |
| C | -5.94039 | -3.89668 | 0.701957 |
| H | -6.7533 | -4.28234 | 1.307358 |
| C | -5.8093 | -4.29626 | -0.63419 |
| H | -6.52213 | -4.99225 | -1.06426 |
| C | -3.73687 | 5.771167 | 0.540191 |
| H | -4.63891 | 5.244743 | 0.872931 |
| H | -4.03902 | 6.73859 | 0.144979 |
| H | -3.10353 | 5.950257 | 1.415088 |
| C | -1.88872 | -1.58106 | -1.25899 |
| C | -2.99074 | -1.55995 | 1.031462 |
| C | 1.593414 | -0.09084 | 1.15548 |

Number of imaginary frequencies = 0

**$^3$IX'**

0 3

| | | | |
|---|---|---|---|
| O | 1.221496 | -1.57022 | -1.49735 |
| C | 1.957221 | -1.08808 | 0.6988 |
| C | 2.002027 | -1.80419 | -0.56458 |
| C | 2.206095 | 2.176654 | 1.338869 |
| H | 2.213024 | 1.956476 | 2.400108 |
| N | 3.363086 | 4.834115 | -0.95146 |
| C | 3.037553 | -2.84989 | -0.67191 |
| C | 2.782602 | 3.348138 | 0.886118 |
| H | 3.217285 | 4.023411 | 1.611061 |
| C | 3.14709 | -3.64569 | -1.82204 |
| H | 2.442866 | -3.46843 | -2.62664 |
| C | 1.605254 | 1.268502 | 0.454055 |
| O | 3.004802 | -0.7385 | 2.797479 |
| C | 3.933986 | -3.05705 | 0.379859 |
| C | 2.801348 | 3.666887 | -0.49577 |
| C | 2.224892 | 2.727237 | -1.38705 |
| H | 2.229118 | 2.90904 | -2.45355 |
| C | 1.65341 | 1.558829 | -0.91988 |
| H | 1.243277 | 0.850658 | -1.6301 |
| C | 4.925009 | -4.03529 | 0.297756 |
| H | 5.602347 | -4.16637 | 1.133449 |
| O | 3.89466 | -2.32024 | 1.53252 |
| C | 3.404581 | 5.120326 | -2.37689 |
| H | 3.998801 | 4.380816 | -2.9264 |
| H | 3.854928 | 6.097997 | -2.53453 |
| H | 2.399559 | 5.14089 | -2.8107 |
| C | 4.125337 | -4.621 | -1.9137 |
| H | 4.203713 | -5.23441 | -2.80455 |
| C | 5.014859 | -4.81263 | -0.84832 |
| H | 5.783371 | -5.57585 | -0.91439 |
| C | 4.000375 | 5.755374 | -0.02295 |
| H | 3.294968 | 6.11638 | 0.732704 |
| H | 4.370856 | 6.618764 | -0.5714 |
| H | 4.849101 | 5.293722 | 0.494608 |
| C | 2.948728 | -1.3306 | 1.745475 |
| C | -1.56319 | 0.200221 | 1.299443 |
| C | -2.96127 | 0.031486 | 0.771504 |
| C | -4.00779 | 0.594363 | 1.513218 |
| C | -3.27358 | -0.66462 | -0.40292 |
| C | -5.32766 | 0.480642 | 1.096966 |
| H | -3.76312 | 1.122653 | 2.426924 |
| C | -4.59215 | -0.79246 | -0.83077 |
| H | -2.49719 | -1.13153 | -0.99732 |
| C | -5.60823 | -0.21396 | -0.07757 |
| H | -6.12833 | 0.923753 | 1.676588 |
| H | -4.82366 | -1.33712 | -1.73788 |
| Br | -7.42509 | -0.37869 | -0.66377 |
| O | -1.38686 | 0.702171 | 2.418253 |
| C | -0.44019 | -0.20327 | 0.489503 |
| H | -0.5717 | -0.5898 | -0.50912 |
| C | 0.946791 | -0.01166 | 1.003163 |
| H | 0.88603 | 0.109187 | 2.083644 |

Number of imaginary frequencies = 0

**$^3$IX''**

| | | | |
|---|---|---|---|
| 0 | 3 | | |
| O | -0.94169 | -1.25167 | -2.27285 |
| C | -1.87502 | -1.36866 | -1.51024 |
| C | -1.84668 | -0.99925 | -0.09744 |
| C | -0.53105 | -0.45527 | 0.411924 |
| C | -0.73091 | 1.068123 | 0.302453 |
| C | -0.37948 | 1.728901 | -0.88641 |
| C | -0.52729 | 3.096829 | -1.02355 |
| C | -1.05939 | 3.881364 | 0.030316 |
| N | -1.20405 | 5.241049 | -0.09238 |
| C | -0.8533 | 5.906476 | -1.33765 |
| C | -1.80092 | 6.016623 | 0.984338 |
| C | -1.4455 | 3.201646 | 1.213857 |
| C | -1.29302 | 1.833396 | 1.336492 |
| C | -0.11799 | -0.93716 | 1.768868 |
| C | 1.1829 | -1.41865 | 2.166434 |
| C | 2.419576 | -1.21404 | 1.338069 |
| C | 3.408803 | -2.2042 | 1.378314 |
| C | 4.596886 | -2.05917 | 0.673366 |
| C | 4.809286 | -0.89406 | -0.06033 |
| Br | 6.449699 | -0.67808 | -1.0288 |
| C | 3.857275 | 0.118427 | -0.09544 |
| C | 2.662603 | -0.05039 | 0.601376 |
| O | 1.265331 | -2.0702 | 3.218053 |
| C | -3.04059 | -1.08581 | 0.732403 |
| O | -3.07001 | -0.70174 | 1.905529 |
| C | -4.22334 | -1.68489 | 0.082361 |
| C | -5.41614 | -1.88356 | 0.793188 |
| C | -6.52011 | -2.44427 | 0.173677 |
| C | -6.44496 | -2.81443 | -1.1753 |
| C | -5.27468 | -2.62537 | -1.89726 |
| C | -4.16896 | -2.06192 | -1.26165 |
| O | -3.04234 | -1.89748 | -2.02528 |
| H | 0.229571 | -0.73168 | -0.31737 |
| H | 0.014106 | 1.15229 | -1.71655 |
| H | -0.23117 | 3.557773 | -1.95649 |
| H | 0.201278 | 5.755041 | -1.59017 |
| H | -1.46045 | 5.550362 | -2.17804 |
| H | -1.01931 | 6.97642 | -1.23239 |
| H | -2.83593 | 5.714686 | 1.18254 |
| H | -1.23175 | 5.916 | 1.914073 |
| H | -1.80449 | 7.069168 | 0.709324 |
| H | -1.87259 | 3.748092 | 2.04418 |
| H | -1.62403 | 1.344824 | 2.243983 |
| H | -0.88223 | -1.05582 | 2.525717 |
| H | 3.235027 | -3.0899 | 1.978208 |
| H | 5.350924 | -2.83637 | 0.698302 |
| H | 4.043295 | 1.028007 | -0.65337 |
| H | 1.935524 | 0.753511 | 0.588759 |
| H | -5.43762 | -1.58511 | 1.834922 |
| H | -7.43872 | -2.59773 | 0.729172 |
| H | -7.30691 | -3.25512 | -1.66542 |
| H | -5.19415 | -2.90452 | -2.94126 |

Number of imaginary frequencies = 0

**$^{3}$IX'''**

| | | | |
|---|---|---|---|
| 0 | 3 | | |
| O | 0.583535 | -2.46273 | -2.17142 |
| C | 1.559012 | -0.09857 | -1.16335 |
| C | 1.844373 | -1.41608 | -0.48573 |
| C | 1.235661 | -2.58415 | -1.13303 |
| C | 3.071726 | 1.884084 | -1.5908 |
| H | 3.282643 | 1.466162 | -2.57156 |
| N | 3.9913 | 4.887612 | 0.371061 |
| C | 1.433929 | -3.8786 | -0.46636 |
| C | 3.663212 | 3.090552 | -1.24349 |
| H | 4.319404 | 3.568623 | -1.95875 |
| C | 0.843669 | -5.05259 | -0.95736 |
| H | 0.244553 | -4.97934 | -1.85772 |
| C | 2.242584 | 1.188038 | -0.70835 |
| O | 3.419143 | -0.71613 | 1.155251 |
| C | 2.209714 | -3.94177 | 0.693314 |
| C | 3.424967 | 3.678088 | 0.019025 |
| C | 2.573912 | 2.975725 | 0.904629 |
| H | 2.367869 | 3.36729 | 1.891841 |
| C | 1.996399 | 1.772389 | 0.541925 |
| H | 1.36438 | 1.261907 | 1.259141 |
| C | 2.398016 | -5.15042 | 1.36412 |
| H | 3.006835 | -5.16358 | 2.26048 |
| O | 2.835875 | -2.84478 | 1.21642 |
| H | 1.830758 | -0.25419 | -2.21528 |
| C | 3.864519 | 5.3751 | 1.734076 |
| H | 2.81619 | 5.536634 | 2.004313 |
| H | 4.375315 | 6.332491 | 1.821396 |
| H | 4.302422 | 4.686528 | 2.468947 |
| C | 1.024638 | -6.25716 | -0.29996 |
| H | 0.565408 | -7.16262 | -0.68101 |
| C | 1.803474 | -6.30041 | 0.864266 |

| | | | |
|---|---|---|---|
| H | 1.947371 | -7.24188 | 1.384387 |
| C | 4.96696 | 5.510423 | -0.50586 |
| H | 5.864435 | 4.892372 | -0.64652 |
| H | 5.276215 | 6.463276 | -0.07968 |
| H | 4.540026 | 5.71654 | -1.49231 |
| C | 2.741712 | -1.57717 | 0.65485 |
| C | -0.75918 | -0.19768 | -0.09515 |
| C | -2.20266 | 0.19507 | -0.06606 |
| C | -3.05771 | -0.5048 | 0.795471 |
| C | -2.73117 | 1.23936 | -0.83523 |
| C | -4.40732 | -0.18849 | 0.877963 |
| H | -2.64399 | -1.30288 | 1.399975 |
| C | -4.0794 | 1.573213 | -0.75655 |
| H | -2.0939 | 1.821916 | -1.49009 |
| C | -4.90769 | 0.851335 | 0.097418 |
| H | -5.06256 | -0.74098 | 1.540229 |
| H | -4.47895 | 2.386182 | -1.3502 |
| Br | -6.76608 | 1.299689 | 0.204613 |
| O | -0.30156 | -0.91902 | 0.816464 |
| C | 0.087161 | 0.212269 | -1.17016 |
| H | -0.28972 | 0.797911 | -1.99791 |

Number of imaginary frequencies = 0

**$^{1}$IX**

0 1

| | | | |
|---|---|---|---|
| C | -4.98674 | -1.20972 | -0.15071 |
| C | -4.73523 | -1.57217 | 1.171911 |
| C | -3.9518 | -0.88049 | -1.02007 |
| C | -3.42304 | -1.60458 | 1.622217 |
| C | -2.36178 | -1.27317 | 0.770413 |
| C | -2.64107 | -0.91176 | -0.55219 |
| H | -4.16329 | -0.60378 | -2.04551 |
| H | -1.84018 | -0.65578 | -1.23647 |
| H | -5.55332 | -1.82403 | 1.83562 |
| H | -3.19658 | -1.88427 | 2.644303 |
| C | -0.97158 | -1.33709 | 1.315781 |
| O | -0.74039 | -1.77701 | 2.420321 |
| C | 0.172096 | -0.92509 | 0.396138 |
| H | 2.290636 | -2.15742 | -1.08293 |
| H | 4.554592 | -2.7693 | -1.63376 |
| C | 3.092998 | -1.73995 | -0.48768 |
| C | 4.39515 | -2.09018 | -0.80682 |
| C | 1.442604 | -0.46915 | 0.973176 |
| C | 2.805281 | -0.86197 | 0.565657 |
| C | 0.489123 | 0.536194 | 0.094662 |
| C | 5.493453 | -1.57908 | -0.07856 |
| C | 3.895063 | -0.351 | 1.286267 |
| C | 5.20228 | -0.68835 | 0.981025 |
| H | 3.712744 | 0.329834 | 2.113256 |
| H | 5.999321 | -0.2604 | 1.574425 |
| Br | -6.79348 | -1.16539 | -0.78377 |
| N | 6.790433 | -1.94045 | -0.38012 |
| C | 7.899516 | -1.29443 | 0.299326 |
| H | 7.856729 | -1.45857 | 1.380953 |
| H | 8.835913 | -1.71934 | -0.05797 |
| H | 7.928484 | -0.21086 | 0.121496 |
| C | 7.061298 | -2.75661 | -1.55074 |
| H | 6.550914 | -3.72308 | -1.48983 |
| H | 6.752715 | -2.26827 | -2.48482 |
| H | 8.130031 | -2.95488 | -1.61066 |
| C | 0.781853 | 3.1861 | -0.79886 |
| C | -0.10945 | 1.619729 | 0.918631 |
| O | -0.71282 | 1.38789 | 1.953561 |
| C | 0.938373 | 0.827159 | -1.28739 |
| O | 1.146772 | -0.00059 | -2.13287 |
| C | 0.137602 | 2.988206 | 0.425159 |
| C | 1.049607 | 4.469917 | -1.26991 |
| H | 1.54779 | 4.585399 | -2.22526 |
| C | 0.010389 | 5.387364 | 0.718856 |
| H | -0.28894 | 6.248934 | 1.305188 |
| C | 0.664562 | 5.56407 | -0.50643 |
| H | 0.872228 | 6.564927 | -0.87042 |
| C | -0.25052 | 4.106561 | 1.176657 |
| H | -0.75299 | 3.929712 | 2.120734 |
| O | 1.158051 | 2.147394 | -1.61788 |
| H | 1.350361 | -0.16867 | 2.01228 |
| H | 0.238345 | -1.5329 | -0.50195 |

Number of imaginary frequencies = 0

**$^{1}$TS3**

0 1

| | | | |
|---|---|---|---|
| C | -5.10119 | -1.30708 | -0.12342 |
| C | -4.67768 | -1.92623 | 1.051757 |
| C | -4.24056 | -0.5085 | -0.87146 |
| C | -3.36887 | -1.74149 | 1.47547 |
| C | -2.47763 | -0.95877 | 0.730623 |

| | | | |
|---|---|---|---|
| C | -2.92818 | -0.34172 | -0.44179 |
| H | -4.59044 | -0.0193 | -1.77201 |
| H | -2.27119 | 0.309868 | -1.00481 |
| H | -5.3618 | -2.53996 | 1.624692 |
| H | -3.01748 | -2.20225 | 2.391257 |
| C | -1.08542 | -0.8007 | 1.238594 |
| O | -0.77446 | -1.09935 | 2.379017 |
| C | -0.00222 | -0.41801 | 0.284104 |
| H | 1.511277 | -2.26491 | -0.97918 |
| H | 3.414721 | -3.69394 | -1.36636 |
| C | 2.431357 | -2.04968 | -0.4451 |
| C | 3.525751 | -2.873 | -0.67059 |
| C | 1.327564 | -0.04896 | 0.729742 |
| C | 2.49993 | -0.97292 | 0.435746 |
| C | 1.336752 | 1.316833 | -0.00033 |
| C | 4.753374 | -2.65485 | -0.00995 |
| C | 3.709181 | -0.75027 | 1.093708 |
| C | 4.81392 | -1.56062 | 0.880481 |
| H | 3.800016 | 0.083817 | 1.784172 |
| H | 5.728041 | -1.33377 | 1.412779 |
| Br | -6.90326 | -1.55447 | -0.71639 |
| N | 5.843449 | -3.48759 | -0.21263 |
| C | 7.138347 | -3.10879 | 0.325058 |
| H | 7.101631 | -3.01852 | 1.414463 |
| H | 7.864368 | -3.8859 | 0.090084 |
| H | 7.509903 | -2.15762 | -0.08282 |
| C | 5.813046 | -4.44506 | -1.30441 |
| H | 4.999764 | -5.16564 | -1.17673 |
| H | 5.693075 | -3.96748 | -2.28739 |
| H | 6.744859 | -5.0087 | -1.31226 |
| C | 1.665648 | 4.009865 | -0.54222 |
| C | 0.272133 | 2.19467 | 0.355793 |
| O | -0.81506 | 1.766599 | 0.80062 |
| C | 2.350027 | 1.70919 | -0.95506 |
| O | 3.078495 | 1.00874 | -1.6041 |
| C | 0.540321 | 3.628245 | 0.201365 |
| C | 1.950586 | 5.361568 | -0.74698 |
| H | 2.821087 | 5.628562 | -1.33454 |
| C | -0.01434 | 5.955062 | 0.546357 |
| H | -0.66135 | 6.717021 | 0.966531 |
| C | 1.115847 | 6.32334 | -0.19622 |
| H | 1.34205 | 7.373404 | -0.35034 |
| C | -0.3045 | 4.614415 | 0.732458 |
| H | -1.17805 | 4.294802 | 1.288593 |
| O | 2.495101 | 3.103739 | -1.12758 |
| H | 1.28814 | 0.123457 | 1.808438 |
| H | -0.16035 | -0.57041 | -0.77853 |

Imaginary frequency value = -230.85

**5a**

0 1

| | | | |
|---|---|---|---|
| Br | 6.565507 | -1.16827 | 0.156137 |
| O | -1.70888 | -1.51165 | -1.28293 |
| O | -4.38659 | -0.65666 | 1.682718 |
| O | -2.80973 | 0.535663 | 2.739456 |
| O | 0.018135 | -3.22064 | -0.20281 |
| C | 0.080512 | 2.249909 | 1.075876 |
| H | 0.502152 | 1.805896 | 1.972911 |
| N | -0.1281 | 5.60289 | -0.49971 |
| C | 2.780329 | -2.89743 | 0.053524 |
| H | 2.340329 | -3.87582 | 0.206912 |
| C | -3.96786 | -1.80643 | -0.41387 |
| C | 0.237019 | 3.614768 | 0.870253 |
| H | 0.780602 | 4.186829 | 1.610299 |
| C | -4.45742 | -2.63428 | -1.43529 |
| H | -3.793 | -2.915 | -2.24422 |
| C | -0.62275 | 1.4456 | 0.17806 |
| C | 4.148813 | -2.71084 | 0.183237 |
| H | 4.797095 | -3.54016 | 0.43819 |
| C | 1.934959 | -1.8303 | -0.28054 |
| C | -2.22526 | -0.47643 | 0.671789 |
| C | -4.80949 | -1.44316 | 0.655918 |
| C | 2.492834 | -0.56029 | -0.47664 |
| H | 1.871766 | 0.294049 | -0.72015 |
| C | -0.45586 | -0.95854 | -0.80455 |
| H | -0.03871 | -0.38602 | -1.63162 |
| C | -0.30676 | 4.247646 | -0.26791 |
| C | 4.67962 | -1.43721 | -0.01918 |
| C | -1.03591 | 3.433798 | -1.16461 |
| H | -1.50217 | 3.863373 | -2.0414 |
| C | -1.18376 | 2.072812 | -0.93915 |
| H | -1.76539 | 1.493227 | -1.65149 |
| C | 3.863798 | -0.35829 | -0.34481 |
| H | 4.288653 | 0.626633 | -0.49311 |
| C | -6.12834 | -1.89789 | 0.693798 |
| H | -6.75706 | -1.60591 | 1.526648 |
| C | -0.79645 | -0.04054 | 0.43247 |
| H | -0.16943 | -0.31568 | 1.28614 |

| | | | |
|---|---|---|---|
| C | -0.88611 | 6.252179 | -1.55508 |
| H | -0.67098 | 5.803062 | -2.52877 |
| H | -0.5944 | 7.299911 | -1.61228 |
| H | -1.97273 | 6.207463 | -1.3923 |
| C | -5.76672 | -3.08277 | -1.39366 |
| H | -6.14755 | -3.72333 | -2.18127 |
| C | -6.59794 | -2.71081 | -0.32834 |
| H | -7.62333 | -3.06414 | -0.29626 |
| C | 0.42027 | 6.438149 | 0.55509 |
| H | -0.2007 | 6.443147 | 1.462291 |
| H | 0.502583 | 7.462254 | 0.194002 |
| H | 1.425715 | 6.111004 | 0.835174 |
| C | -3.0757 | -0.12857 | 1.77458 |
| C | -2.63975 | -1.27536 | -0.33932 |
| C | 0.472423 | -2.11827 | -0.41467 |

Number of imaginary frequencies = 0

**5a'**

0 1

| | | | |
|---|---|---|---|
| O | 1.742954 | -1.46701 | -1.29139 |
| C | 2.243052 | -0.45174 | 0.677957 |
| C | 2.669536 | -1.23139 | -0.34309 |
| C | -0.08156 | 2.247598 | 1.112336 |
| H | -0.50128 | 1.789841 | 2.003344 |
| N | 0.160805 | 5.629075 | -0.39142 |
| C | 4.004701 | -1.74351 | -0.42292 |
| C | -0.25022 | 3.61313 | 0.921395 |
| H | -0.80688 | 4.171504 | 1.662288 |
| C | 4.506813 | -2.55061 | -1.4548 |
| H | 3.847321 | -2.82942 | -2.26841 |
| C | 0.622137 | 1.457614 | 0.202005 |
| O | 2.810757 | 0.539107 | 2.760509 |
| C | 4.840051 | -1.38328 | 0.652839 |
| C | 0.297662 | 4.264413 | -0.20477 |
| C | 1.001618 | 3.459835 | -1.12989 |
| H | 1.438104 | 3.898108 | -2.01769 |
| C | 1.161433 | 2.098072 | -0.9185 |
| H | 1.728119 | 1.526914 | -1.64946 |
| C | 6.165038 | -1.82016 | 0.686209 |
| H | 6.788735 | -1.53074 | 1.523719 |
| O | 4.405156 | -0.61688 | 1.689727 |
| C | 0.573645 | 6.22893 | -1.6472 |
| H | 1.641937 | 6.076453 | -1.82962 |
| H | 0.402415 | 7.303368 | -1.60485 |
| H | 0.021909 | 5.830188 | -2.51053 |
| C | 5.822161 | -2.98144 | -1.41758 |
| H | 6.212713 | -3.60586 | -2.21335 |
| C | 6.646989 | -2.61253 | -0.34626 |
| H | 7.677158 | -2.952 | -0.31768 |
| C | -0.70002 | 6.392297 | 0.493929 |
| H | -1.75012 | 6.069276 | 0.450005 |
| H | -0.65837 | 7.444241 | 0.215916 |
| H | -0.36704 | 6.316318 | 1.533427 |
| C | 3.087109 | -0.10782 | 1.786877 |
| C | -0.42879 | -2.11603 | -0.42987 |
| C | -1.89506 | -1.85036 | -0.28994 |
| C | -2.72537 | -2.93387 | 0.028715 |
| C | -2.47044 | -0.58524 | -0.46618 |
| C | -4.09617 | -2.76804 | 0.162558 |
| H | -2.27188 | -3.90835 | 0.166891 |
| C | -3.84384 | -0.40407 | -0.32987 |
| H | -1.86127 | 0.281079 | -0.69722 |
| C | -4.6445 | -1.49882 | -0.01983 |
| H | -4.73278 | -3.60995 | 0.405409 |
| H | -4.28239 | 0.577039 | -0.46271 |
| Br | -6.53364 | -1.25782 | 0.161527 |
| O | 0.041015 | -3.21472 | -0.23354 |
| C | 0.48212 | -0.93822 | -0.80631 |
| H | 0.055655 | -0.36297 | -1.62673 |
| C | 0.809643 | -0.02951 | 0.440692 |
| H | 0.184156 | -0.32041 | 1.290215 |

Number of imaginary frequencies = 0

**5a''**

0 1

| | | | |
|---|---|---|---|
| O | -2.00463 | -1.81351 | 0.722527 |
| C | -2.52319 | -0.41368 | -0.99099 |
| C | -2.97254 | -1.21596 | 0.003099 |
| C | 0.365518 | 1.750673 | -1.34815 |
| H | 0.674295 | 1.324791 | -2.29891 |
| N | 0.883746 | 4.892181 | 0.552933 |
| C | -4.36568 | -1.40584 | 0.278945 |
| C | 0.834081 | 3.011284 | -1.00295 |
| H | 1.499522 | 3.519485 | -1.68819 |
| C | -4.89007 | -2.20045 | 1.309688 |
| H | -4.20514 | -2.72567 | 1.965369 |

| | | | |
|---|---|---|---|
| C | -0.49463 | 1.029683 | -0.51887 |
| O | -3.13722 | 0.987211 | -2.80925 |
| C | -5.23786 | -0.7115 | -0.58236 |
| C | 0.447272 | 3.623059 | 0.208593 |
| C | -0.41577 | 2.886284 | 1.05063 |
| H | -0.73557 | 3.293607 | 2.000548 |
| C | -0.87783 | 1.630961 | 0.684714 |
| H | -1.54019 | 1.107951 | 1.366789 |
| C | -6.61902 | -0.81491 | -0.41057 |
| H | -7.27067 | -0.27251 | -1.08536 |
| O | -4.78749 | 0.069154 | -1.60166 |
| C | 0.631179 | 5.39796 | 1.890227 |
| H | -0.44161 | 5.451812 | 2.097842 |
| H | 1.027604 | 6.408989 | 1.972013 |
| H | 1.097693 | 4.783557 | 2.673728 |
| C | -6.26109 | -2.29766 | 1.477897 |
| H | -6.66918 | -2.90861 | 2.275306 |
| C | -7.12059 | -1.60385 | 0.615315 |
| H | -8.19468 | -1.68126 | 0.748013 |
| C | 1.909817 | 5.537249 | -0.24601 |
| H | 2.857247 | 4.97897 | -0.25638 |
| H | 2.106364 | 6.530075 | 0.156201 |
| H | 1.582305 | 5.664991 | -1.28204 |
| C | -3.41357 | 0.28151 | -1.87827 |
| C | 0.343368 | -1.33971 | 1.103081 |
| C | 1.771217 | -1.42854 | 0.664638 |
| C | 2.760636 | -1.19312 | 1.628441 |
| C | 2.164916 | -1.74141 | -0.64184 |
| C | 4.107338 | -1.26625 | 1.303735 |
| H | 2.449295 | -0.95073 | 2.637507 |
| C | 3.511749 | -1.82016 | -0.983 |
| H | 1.430515 | -1.9277 | -1.4167 |
| C | 4.471758 | -1.58137 | -0.00452 |
| H | 4.866223 | -1.08108 | 2.053929 |
| H | 3.809102 | -2.06355 | -1.99553 |
| Br | 6.325907 | -1.68632 | -0.46307 |
| O | 0.048594 | -1.12922 | 2.258109 |
| C | -1.01211 | -0.33503 | -0.94044 |
| H | -0.57537 | -0.57668 | -1.91276 |
| C | -0.74625 | -1.54103 | 0.046757 |
| H | -0.52676 | -2.43911 | -0.53901 |

Number of imaginary frequencies = 0

**5a'''**

0 1

| | | | |
|---|---|---|---|
| O | 1.982687 | -1.84881 | 0.702224 |
| C | 0.994863 | -0.34261 | -0.93899 |
| C | 2.505515 | -0.42568 | -0.99068 |
| C | 2.952213 | -1.24449 | -0.00885 |
| C | -0.38672 | 1.74669 | -1.31451 |
| H | -0.69418 | 1.335208 | -2.27204 |
| N | -0.9608 | 4.832185 | 0.663075 |
| C | 4.344759 | -1.44434 | 0.263062 |
| C | -0.8543 | 3.002675 | -0.95156 |
| H | -1.51199 | 3.524291 | -1.63412 |
| C | 4.866338 | -2.25624 | 1.281687 |
| H | 4.179537 | -2.7878 | 1.930261 |
| C | 0.479638 | 1.017231 | -0.49927 |
| O | 3.124449 | 1.000476 | -2.7876 |
| C | 5.219305 | -0.74147 | -0.58879 |
| C | -0.47505 | 3.593235 | 0.272656 |
| C | 0.418132 | 2.860786 | 1.086302 |
| H | 0.763894 | 3.267648 | 2.027238 |
| C | 0.878683 | 1.60994 | 0.703249 |
| H | 1.560328 | 1.087549 | 1.366595 |
| C | 6.60013 | -0.85385 | -0.42 |
| H | 7.253706 | -0.30479 | -1.0875 |
| O | 4.771506 | 0.056375 | -1.5959 |
| H | 0.557133 | -0.57072 | -1.91416 |
| C | -0.3716 | 5.49917 | 1.810966 |
| H | -0.48347 | 4.897886 | 2.717574 |
| H | -0.89078 | 6.44111 | 1.982661 |
| H | 0.697987 | 5.716881 | 1.677447 |
| C | 6.237041 | -2.36219 | 1.447144 |
| H | 6.643056 | -2.98655 | 2.235173 |
| C | 7.098946 | -1.65997 | 0.593814 |
| H | 8.172789 | -1.74438 | 0.724266 |
| C | -1.69045 | 5.64464 | -0.29429 |
| H | -1.08916 | 5.911922 | -1.17534 |
| H | -2.0117 | 6.566088 | 0.189503 |
| H | -2.59068 | 5.130261 | -0.64257 |
| C | 3.398266 | 0.279032 | -1.86795 |
| C | -0.36071 | -1.36311 | 1.095518 |
| C | -1.79036 | -1.43528 | 0.660254 |
| C | -2.77513 | -1.19692 | 1.628078 |
| C | -2.19015 | -1.73471 | -0.64753 |
| C | -4.12321 | -1.25386 | 1.305945 |

| | | | |
|---|---|---|---|
| H | -2.45907 | -0.96451 | 2.638009 |
| C | -3.53845 | -1.79743 | -0.98608 |
| H | -1.45946 | -1.92298 | -1.42545 |
| C | -4.49375 | -1.55585 | -0.00368 |
| H | -4.87843 | -1.06584 | 2.059102 |
| H | -3.84058 | -2.03054 | -1.99961 |
| Br | -6.34986 | -1.63856 | -0.45885 |
| O | -0.06048 | -1.16808 | 2.251819 |
| C | 0.724235 | -1.55989 | 0.033419 |
| H | 0.497201 | -2.44924 | -0.56258 |

Number of imaginary frequencies = 0

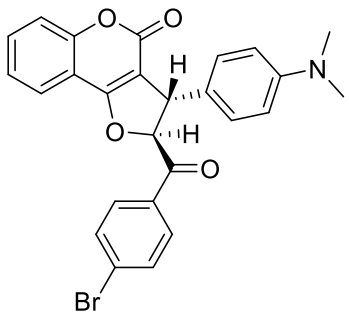
**Pyridine**

| 0 | 1 | | |
|---|---|---|---|
| C | -1.14086 | -0.72048 | -0.00022 |
| C | -1.19633 | 0.671875 | -0.00012 |
| C | 0.000246 | 1.38274 | 0.000097 |
| C | 1.196567 | 0.671467 | 0.000214 |
| C | 1.140609 | -0.72087 | 0.000123 |
| N | -0.00025 | -1.41727 | -9.5E-05 |
| H | 0.000409 | 2.46812 | 0.000169 |
| H | -2.05594 | -1.30804 | -0.00037 |
| H | -2.1541 | 1.180965 | -0.00024 |
| H | 2.154532 | 1.180186 | 0.000351 |
| H | 2.055469 | -1.30876 | 0.000184 |

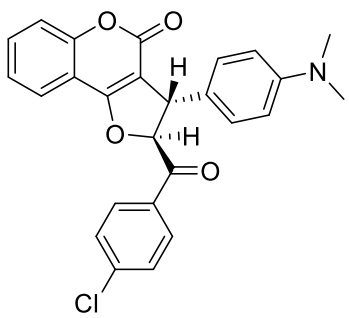
Number of imaginary frequencies = 0

## 8. Spectroscopic data of synthesized compounds:

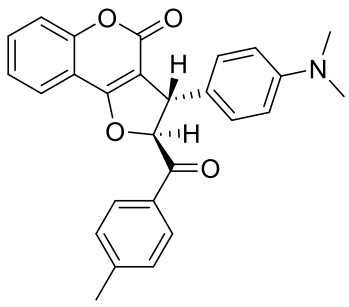
**(2S,3S)-2-(4-bromobenzoyl)-3-(4-(dimethylamino)phenyl)-2,3-dihydro-4H-furo[3,2-c]chromen-4-one (5a)** $R_f$ = 0.4 (EtOAc/petroleum ether 30:70); eluent: (EtOAc/petroleum ether 20:80); light orange solid; yield: 85% (416 mg); **$^1$H NMR (400 MHz, $CDCl_3$)**: δ 7.84 (dd, 1H, *J* = 7.6 and 1.6 Hz, Ar-H), 7.76 (d, 2H, *J* = 8.4 Hz, Ar-H), 7.64 (d, 2H, *J* = 8.8 Hz, Ar-H), 7.61-7.58 (m, 1H, Ar-H), 7.40-7.33 (m, 2H, Ar-H), 7.15 (d, 2H, *J* = 8.4 Hz, Ar-H), 6.72 (d, 2H, *J* = 8.8 Hz, Ar-H), 6.09 (d, 1H, *J* = 4.8 Hz, $C_2$-H), 4.64 (d, 1H, *J* = 5.2 Hz, $C_3$-H), 2.96 (s, 6H, -$NMe_2$) ppm. **$^{13}$C {$^1$H} NMR (100 MHz, $CDCl_3$)**: δ 191.7, 165.9, 159.5, 155.5, 150.5, 132.9, 132.5, 132.0, 130.6, 129.9, 128.4, 126.8, 124.2, 123.3, 117.2, 113.1, 112.4, 105.8, 92.9, 49.2, 40.6 ppm. **HRMS (ESI)** m/z: $[M+H]^+$ calculated for $C_{26}H_{21}BrNO_4$ 490.0654, found 490.0668; $[M+H+2]^+$ calculated for $C_{26}H_{21}BrNO_4$ 492.0633, found 492.0662.



**(2S,3S)-2-(4-chlorobenzoyl)-3-(4-(dimethylamino)phenyl)-2,3-dihydro-4H-furo[3,2-c]chromen-4-one (5b)** $R_f$ = 0.3 (EtOAc/petroleum ether 15:85); eluent: (EtOAc/petroleum ether 20:80); brown solid; yield: 84% (374 mg); **$^1$H NMR (400 MHz, $CDCl_3$)**: δ 7.86- 7.83 (m, 3H, Ar-H), 7.62-7.58 (m, 1H, Ar-H), 7.47 (dd, 2H, *J* = 6.8 and 2.0 Hz, Ar-H), 7.40-7.33 (m, 2H, Ar-H), 7.15 (dd, 2H, *J* = 6.8 and 2.0 Hz, Ar-H), 6.72 (dd, 2H, *J* = 6.8 and 2.0 Hz, Ar-H), 6.09 (d, 1H, *J* = 4.8 Hz, $C_2$-H), 4.64 (d, 1H, *J* = 4.8 Hz, $C_3$-H), 2.96 (s, 6H, -$NMe_2$) ppm. **$^{13}$C {$^1$H} NMR (100 MHz, $CDCl_3$)**: δ 191.5, 165.9, 159.4, 155.5, 150.5, 141.1, 132.8, 131.6, 130.6, 129.5, 128.8, 128.4, 126.9, 124.2, 123.2, 117.1, 113.2, 105.8, 92.9, 49.1, 40.6 ppm. **HRMS (ESI)** m/z: $[M+H]^+$ calculated for $C_{26}H_{21}ClNO_4$ 446.1159, found 446.1162.

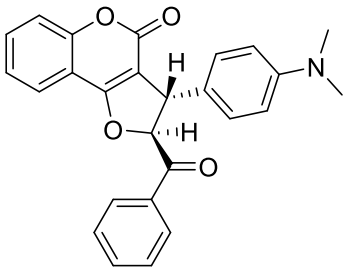


**(2S,3S)-3-(4-(dimethylamino)phenyl)-2-(4-methylbenzoyl)-2,3-dihydro-4H-furo[3,2-c]chromen-4-one** (**5c**) $R_f$ = 0.4 (EtOAc/petroleum ether 20:80); eluent: (EtOAc/petroleum ether 20:80); yellow solid; yield: 90% (382 mg); **$^1$H NMR (400 MHz, $CDCl_3$)**: δ 7.86 (dd, 1H, *J* = 8.0 and 1.6 Hz, Ar-H), 7.80 (dd, 2H, *J* = 6.4 and 1.6 Hz, Ar-H), 7.62-7.57 (m, 1H, Ar-H), 7.40-7.32 (m, 2H, Ar-H), 7.28 (d, 2H, *J* = 8.0 Hz, Ar-H), 7.16 (dd, 2H, *J* = 6.8 and 1.6 Hz, Ar-H), 6.72 (dd, 2H, *J* = 6.8 and 2.0 Hz, Ar-H), 6.13 (d, 1H, *J* = 5.2 Hz, $C_2$-H), 4.63 (d, 1H, *J* = 4.8 Hz, $C_3$-H), 2.96 (s, 6H, -$NMe_2$), 2.44 (s, 3H, -Me) ppm. **$^{13}$C {$^1$H} NMR (100 MHz, $CDCl_3$)**: δ 192.1, 166.2, 159.6, 155.4, 150.4, 145.5, 132.7, 130.7, 129.8, 129.2, 128.3,



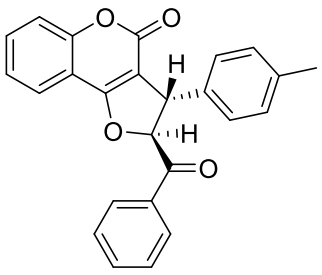
127.2, 124.1, 123.3, 117.1, 113.1, 112.5, 105.9, 92.9, 49.3, 40.6, 21.9 ppm. **HRMS (ESI)** m/z: $[M+H]^+$ calculated for $C_{27}H_{24}NO_4$ 426.1705, found 426.1712.

**(2S,3S)-2-benzoyl-3-(4-(dimethylamino)phenyl)-2,3-dihydro-4H-furo[3,2-c]chromen-4-one**

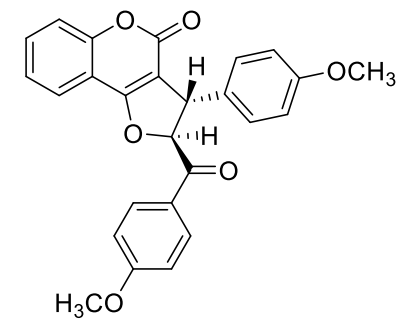


(**5d**) $R_f$ = 0.4 (EtOAc/petroleum ether 10:90); eluent: (EtOAc/petroleum ether 15:85); yellow solid; yield: 88% (362 mg); **$^1$H NMR (400 MHz, $CDCl_3$)**: δ 7.91 (dd, 2H, *J* = 6.4 and 1.6 Hz, Ar-H), 7.86 (dd, 1H, *J* = 7.6 and 1.6 Hz, Ar-H), 7.66-7.57 (m, 2H, Ar-H), 7.51-7.47 (m, 2H, Ar-H), 7.40-7.32 (m, 2H, Ar-H), 7.15 (dd, 2H, *J* = 6.8 and 2.0 Hz, Ar-H), 6.72 (dd, 2H, *J* = 6.4 and 2.0 Hz, Ar-H), 6.16 (d, 1H, *J* = 4.8 Hz, $C_2$-H), 4.65 (d, 1H, *J* = 4.8 Hz, $C_3$-H), 2.95 (s, 6H, -$NMe_2$) ppm. **$^{13}$C {$^1$H} NMR (100 MHz, $CDCl_3$)**: δ 192.6, 166.2, 159.6, 155.5, 150.5, 134.4, 133.3, 132.8, 129.2, 129.1, 128.4, 127.1, 124.2, 123.3, 117.1, 113.1, 112.5, 105.9, 93.1, 49.2, 40.6 ppm. **HRMS (ESI)** m/z: $[M+H]^+$ calculated for $C_{26}H_{22}NO_4$ 412.1549, found 412.1540.

**(2S,3S)-2-benzoyl-3-(p-tolyl)-2,3-dihydro-4H-furo[3,2-c]chromen-4-one** (**5e**) $R_f$ = 0.6 (EtOAc/petroleum ether 20:80); eluent: (EtOAc/petroleum ether 15:85); white solid; yield: 81% (309 mg); **$^1$H NMR (400 MHz, $CDCl_3$)**: δ 7.90 (dd, 2H, *J* = 8.4 and 1.2 Hz, Ar-H), 7.85 (dd, 1H, *J* = 8.0 and 1.6 Hz, Ar-H), 7.68-7.59 (m, 2H, Ar-H), 7.52-7.48 (m, 2H, Ar-H), 7.41-7.33 (m, 2H, Ar-H), 7.19-7.18 (m, 4H, Ar-H), 6.16 (d, 1H, *J* = 5.2 Hz, $C_2$-H), 4.74 (d, 1H, *J* = 4.8 Hz, $C_3$-H), 2.36 (s, 3H, -Me) ppm. **$^{13}$C {$^1$H} NMR (100 MHz, $CDCl_3$)**: δ 192.3, 166.4, 159.4, 155.6, 138.01, 136.7, 134.5, 133.4, 132.9, 130.1, 129.2, 129.1, 127.6, 124.2, 123.3, 117.1, 112.4, 105.6, 92.9, 49.3, 21.3 ppm. **HRMS (ESI)** m/z: $[M+Na]^+$ calculated for $C_{25}H_{18}O_4Na$ 405.1103, found 405.1106.



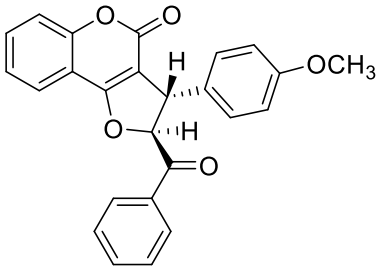
**(2S,3S)-2-(4-methoxybenzoyl)-3-(4-methoxyphenyl)-2,3-dihydro-4H-furo[3,2-c]chromen-4-one** (**5f**) $R_f$ = 0.4 (EtOAc/petroleum ether 20:80); eluent: (EtOAc/petroleum ether 20:80); brown solid; yield: 83% (355 mg); **$^1$H NMR (400 MHz, $CDCl_3$)**: δ 7.84-7.79 (m, 3H, Ar-H), 7.57-7.53 (m, 1H, Ar-H), 7.35-7.27 (m, 2H, Ar-H), 7.21-7.16 (m, 2H, Ar-H), 6.91 (d, 2H, *J* = 8.8 Hz, Ar-H), 6.86 (d, 2H, *J* = 8.8 Hz, Ar-H), 6.05 (d, 1H, *J* = 5.2 Hz, $C_2$-H), 4.67 (d, 1H, *J* = 5.2 Hz, $C_3$-H), 3.85 (s, 3H, -OMe), 3.76 (s, 3H, OMe) ppm.



**$^{13}$C {$^1$H} NMR (100 MHz, $CDCl_3$)**: δ 190.8, 166.4, 164.6, 159.5, 155.5, 132.9, 131.9, 131.6, 128.8, 126.3, 124.2, 123.3, 117.2, 114.8, 114.4, 112.4, 105.7, 92.8, 55.7, 55.5, 49.2 ppm.

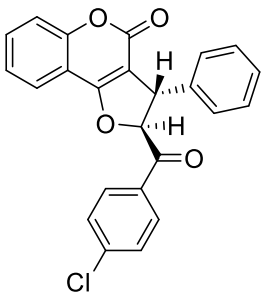
**HRMS (ESI)** m/z: $[M+H]^+$ calculated for $C_{26}H_{21}O_6$ 429.1338, found 429.1335.

**(2S,3S)-2-benzoyl-3-(4-methoxyphenyl)-2,3-dihydro-4H-furo[3,2-c]chromen-4-one (5g)**



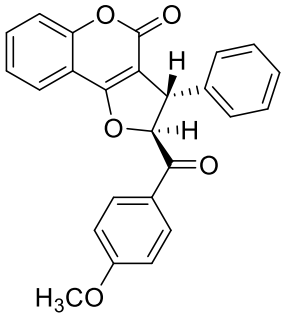
$R_f$ = 0.5 (EtOAc/petroleum ether 20:80); eluent: (EtOAc/petroleum ether 12:88); white solid; yield: 88% (350 mg); **$^1$H NMR (400 MHz, $CDCl_3$)**: δ 7.90 (dd, 2H, *J* = 8.4 and 1.2 Hz, Ar-H), 7.85 (dd, 1H, *J* = 8.0 and 1.6 Hz, Ar-H), 7.68-7.64 (m ,1H, Ar-H), 7.63-7.59 (m ,1H, Ar-H), 7.52-7.48 (m, 2H, Ar-H), 7.41-7.37 (m, 1H, Ar-H), 7.35-7.31 (m, 1H, Ar-H), 7.22 (d, 2H, *J* = 8.4 Hz, Ar-H), 6.91 (d , 2H, *J* = 8.8 Hz, Ar-H), 6.15 (d, 1H, *J* = 4.8 Hz, $C_2$-H), 4.73 (d, 1H, *J* = 5.2 Hz, $C_3$-H), 3.81 (s, 3H, -OMe) ppm. **$^{13}$C {$^1$H} NMR (100 MHz, $CDCl_3$)**: δ 192.3, 166.3, 159.5, 159.4, 155.5, 134.5, 133.3, 132.9, 131.7, 129.2, 129.1, 128.8, 124.2, 123.3, 117.1, 114.8, 112.3, 105.6, 92.9, 55.4, 48.9 ppm. **HRMS (ESI)** m/z: $[M+Na]^+$ calculated for $C_{25}H_{18}O_5Na$ 421.1052, found 421.1058.

**(2S,3S)-2-(4-chlorobenzoyl)-3-phenyl-2,3-dihydro-4H-furo[3,2-c]chromen-4-one (5h)**



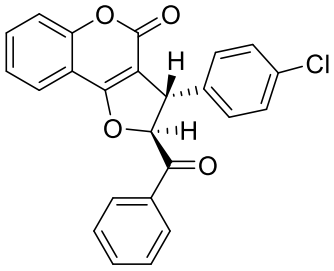
$R_f$ = 0.7 (EtOAc/petroleum ether 20:80); eluent: (EtOAc/petroleum ether 10:90); light yellow solid; yield: 82% (330 mg); **$^1$H NMR (400 MHz, $CDCl_3$)**: δ 7.86 (d, 2H, *J* = 8.8 Hz, Ar-H), 7.82 (dd, 1H, *J* = 8.0 and 1.6 Hz, Ar-H), 7.64-7.60 (m, 1H, Ar-H), 7.48 (d, 2H, *J* = 8.8 Hz, Ar-H), 7.40 (dd, 2H, *J* = 8.4 and 1.6 Hz, Ar-H), 7.38-7.37 (m, 1H, Ar-H), 7.36-7.29 (m, 4H, Ar-H), 6.11 (d, 1H, *J* = 5.2 Hz, $C_2$-H), 4.82 (d, 1H, *J* = 4.8 Hz, $C_3$-H) ppm. **$^{13}$C {$^1$H} NMR (100 MHz, $CDCl_3$)**: δ 191.2, 166.3, 159.3, 155.5, 141.2, 139.5, 133.1, 131.7, 130.6, 129.5, 129.5, 128.4, 127.7, 124.3, 123.3, 117.2, 112.2, 105.4, 92.7, 49.3 ppm. **HRMS (ESI)** m/z: $[M+H]^+$ calculated for $C_{24}H_{16}ClO_4$ 403.0737, found 403.0754.

**(2S,3S)-2-(4-methoxybenzoyl)-3-phenyl-2,3-dihydro-4H-furo[3,2-c]chromen-4-one (5i)**



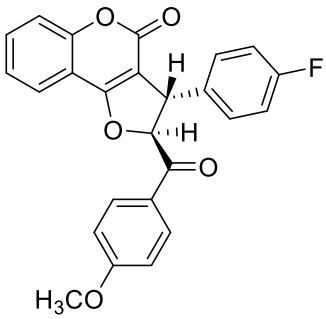
$R_f$ = 0.5 (EtOAc/petroleum ether 30:70); eluent: (EtOAc/petroleum ether 20:80); white solid; yield: 82% (326 mg); **$^1$H NMR (400 MHz, $CDCl_3$)**: δ 7.88 (dd, 2H, *J* = 6.8 and 2.0 Hz, ), 7.85 (dd, 1H, *J* = 8.0 and 1.6 Hz, ), 7.63-7.58 (m, 1H, ), 7.39 (dd, 2H, *J* = 8.2 and 1.6 Hz, ), 7.37-7.36 (m, 1H, ), 7.34-7.30 (m, 4H, ), 6.96 (dd, 2H, *J* = 6.8 and 2.0 Hz, ), 6.14 (d, 1H, *J* = 5.2 Hz, $C_2$-H), 4.80 (d, 1H, *J* = 4.8 Hz, $C_3$-H), 3.89 (s, 3H, -OMe) ppm. **$^{13}$C {$^1$H} NMR (100 MHz, $CDCl_3$)**: δ 190.7, 166.6, 164.6, 159.5, 155.5, 139.8, 132.9, 131.6, 129.4, 128.2, 127.7, 126.2, 124.2, 123.3, 117.2, 114.4, 112.4, 105.5, 92.6, 55.7, 49.7 ppm.

**(2S,3S)-2-benzoyl-3-(4-chlorophenyl)-2,3-dihydro-4H-furo[3,2-c]chromen-4-one** (**5j**)



$R_f$ = 0.4 (EtOAc/petroleum ether 20:80); eluent: (EtOAc/petroleum ether 15:85); white solid; yield: 87% (350 mg); **$^1$H NMR (400 MHz, CDCl$_3$)**: δ 7.76 (dd, 2H, *J* = 8.4 and 1.6 Hz, Ar-H), 7.69 (dd, 1H, *J* = 7.6 and 1.6 Hz, Ar-H), 7.55-7.51 (m, 1H, Ar-H), 7.50-7.46 (m, 1H, Ar-H), 7.39-7.36 (m, 2H, Ar-H), 7.27 (dd, 1H, *J* = 8.4 and 1.2 Hz, Ar-H), 7.23-7.19 (m, 3H, Ar-H), 7.12-7.10 (m, 2H, Ar-H) 5.98 (d, 1H, *J* = 5.2 Hz, $C_2$-H), 4.68 (d, 1H, *J* = 5.2 Hz, $C_3$-H) ppm. **$^{13}$C {$^1$H} NMR (100 MHz, CDCl$_3$)**: δ 191.9, 166.6, 159.3, 155.5, 138.1, 134.7, 134.2, 133.3, 133.2, 129.6, 129.2, 129.1, 124.4, 123.3, 117.2, 112.1, 105.0, 92.5, 48.7 ppm. **HRMS (ESI)** m/z: $[M+H]^+$ calculated for $C_{24}H_{16}ClO_4$ 403.0737, found 403.0732, $[M+H+2]^+$ calculated for $C_{24}H_{16}ClO_4$ 405.0708, found 405.0678.

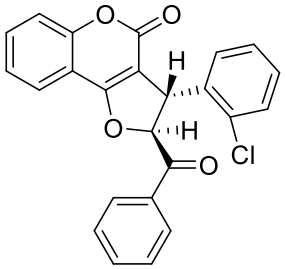
**(2S,3S)-3-(4-fluorophenyl)-2-(4-methoxybenzoyl)-2,3-dihydro-4H-furo[3,2-c]chromen-4-one** (**5k**)



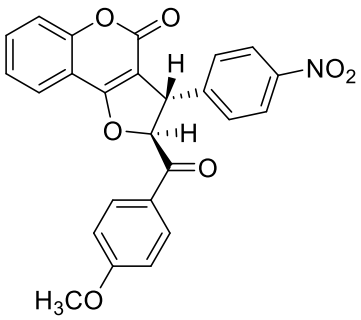
$R_f$ = 0.4 (EtOAc/petroleum ether 20:80); eluent: (EtOAc/petroleum ether 20:80); white solid; yield: 80% (333 mg); **$^1$H NMR (400 MHz, CDCl$_3$)**: δ 7.83 (d, 2H, *J* = 8.8 Hz, Ar-H), 7.78 (dd, 1H, *J* = 7.6 and 1.6 Hz, Ar-H), 7.58-7.54 (m, 1H, Ar-H), 7.34 (dd, 1H, *J* = 1.2 and 0.8 Hz, Ar-H), 7.31-7.27 (m, 1H, Ar-H), 7.25-7.21 (m, 2H, Ar-H), 7.04-7.00 (m, 2H, Ar-H), 6.92 (d, 2H, *J* = 8.8 Hz, Ar-H), 6.02 (d, 1H, *J* = 5.2 Hz, $C_2$-H), 4.77 (d, 1H, *J* = 5.2 Hz, $C_3$-H), 3.85 (s, 3H, -OMe) ppm. **$^{13}$C {$^1$H} NMR (100 MHz, CDCl$_3$)**: δ 190.5, 165.6 (d, $^1J_{C\text{-}F}$ = 180.0 Hz), 159.4, 155.6, 135.6 (d, $^4J_{C\text{-}F}$ = 3.0 Hz), 133.1, 131.6, 129.4 (d, $^3J_{C\text{-}F}$ = 8.0 Hz), 126.2, 124.3, 123.3, 117.2, 116.3 (d, $^2J_{C\text{-}F}$ = 22 Hz), 114.5, 112.3, 105.3, 92.6, 55.8, 48.9 ppm. **$^{19}$F NMR (376 MHz, CDCl$_3$)**: δ -114.02 ppm. **HRMS (ESI)** m/z: $[M+Na]^+$ calculated for $C_{25}H_{17}FO_5Na$ 439.0958, found 439.0954.

**(2S,3R)-2-benzoyl-3-(2-chlorophenyl)-2,3-dihydro-4H-furo[3,2-c]chromen-4-one** (**5l**)

$R_f$ = 0.4 (EtOAc/petroleum ether 20:80); eluent: (EtOAc/petroleum ether 15:85); light yellow solid; yield: 65% (261 mg); **$^1$H NMR (400 MHz, CDCl$_3$)**: δ 7.91 (dd, 2H, *J* = 8.0 and 1.6 Hz, Ar-H), 7.70 (dd, 1H, *J* = 8.8 and 1.6 Hz, Ar-H), 7.61-7.57 (m, 1H, Ar-H), 7.57-7.52 (m, 1H, Ar-H), 7.46-7.42 (m, 2H, Ar-H), 7.36-7.33 (m, 2H, Ar-H), 7.28-7.23 (m, 1H, Ar-H), 7.21-7.19 (m, 3H, Ar-H), 6.09 (d, 1H, *J* = 5.2 Hz, $C_2$-H), 5.42 (d, 1H, *J* = 5.2 Hz, $C_3$-H) ppm. **$^{13}$C {$^1$H} NMR (100 MHz, CDCl$_3$)**: δ 191.5, 166.8, 159.3, 155.5, 136.9, 134.5, 133.7, 133.7, 133.1, 130.4, 129.5, 129.4, 129.3, 129.1, 127.7, 124.2, 123.2, 117.2, 112.2, 104.3, 91.1, 45.8 ppm. **HRMS (ESI)** m/z: $[M+Na]^+$ calculated for $C_{24}H_{15}ClO_4Na$ 425.0557, found 425.0542.

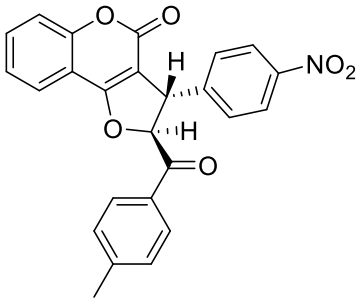


**(2S,3S)-2-(4-methoxybenzoyl)-3-(4-nitrophenyl)-2,3-dihydro-4H-furo[3,2-c]chromen-4-one**



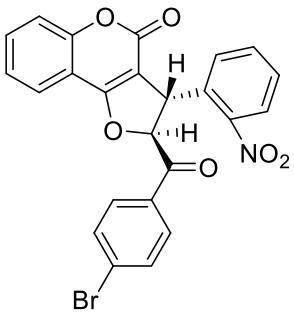
(**5m**) $R_f$ = 0.4 (EtOAc/petroleum ether 20:80); eluent: (EtOAc/petroleum ether 20:80); white solid; yield: 69% (306 mg); **$^1$H NMR (400 MHz, CDCl$_3$)**: δ 8.23 (dd,2H, *J* = 6.8 and 2.0 Hz, Ar-H), 7.91 (dd, 2H, *J* = 6.8 and 2.0 Hz, Ar-H), 7.81 (dd, 1H, *J* = 7.60 and 2.0 Hz, Ar-H), 7.65-7.61 (m, 1H, Ar-H), 7.50 (dd, 2H, *J* = 6.8 and 2.0 Hz, Ar-H), 7.41-7.33 (m, 2H, Ar-H), 6.98 (dd, 2H, *J* = 6.8 and 2.0 Hz, Ar-H), 6.08 (d, 1H, *J* = 5.6 Hz, $C_2$-H), 5.08 (d, 1H, *J* = 5.6 Hz, $C_3$-H), 3.90 (s, 3H, -OMe) ppm. **$^{13}$C {$^1$H} NMR (100 MHz, CDCl$_3$)**: δ 189.9, 166.8, 164.9, 159.2, 155.6, 147.8, 146.9, 133.5, 131.7, 128.9, 126.2, 124.6, 124.56, 123.3, 117.3, 114.5, 112.0, 104.4, 91.9, 55.8, 48.6 ppm. **HRMS (ESI)** m/z: $[M+H]^+$ calculated for $C_{25}H_{18}NO_7$ 444.1083, found 444.1080.

**(2S,3S)-2-(4-methylbenzoyl)-3-(4-nitrophenyl)-2,3-dihydro-4H-furo[3,2-c]chromen-4-one**



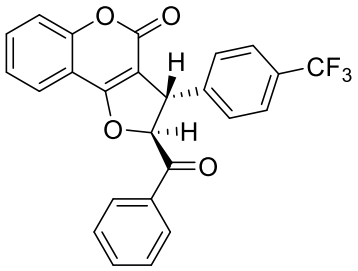
(**5n**) $R_f$ = 0.4 (EtOAc/petroleum ether 20:80); eluent: (EtOAc/petroleum ether 15:85); yellow solid; yield: 65% (278 mg); **$^1$H NMR (400 MHz, CDCl$_3$)**: δ 8.24 (d, 2H, *J* = 8.8 Hz, Ar-H), 7.84-7.81 (m, 3H, Ar-H), 7.66-7.62 (m, 1H, Ar-H), 7.50 (d, 2H, *J* = 8.8 Hz, Ar-H), 7.42-7.36 (m, 2H, Ar-H), 7.34-7.31 (m, 2H, Ar-H), 6.12 (d, 1H, *J* = 5.6 Hz, $C_2$-H), 5.04 (d, 1H, *J* = 5.2 Hz, $C_3$-H), 2.46 (s, 3H, -Me) ppm. **$^{13}$C {$^1$H} NMR (100 MHz, CDCl$_3$)**: δ 191.1, 166.9, 159.2, 155.6, 147.9, 146.9, 146.2, 133.5, 130.8, 130.0, 129.4, 128.9, 124.6, 124.5, 123.4, 117.3, 112.0, 104.5, 92.1, 48.7, 21.9 ppm. **HRMS (ESI)** m/z: $[M+H]^+$ calculated for $C_{25}H_{18}NO_6$ 428.1134, found 428.1141.

**(2S,3S)-2-(4-bromobenzoyl)-3-(2-nitrophenyl)-2,3-dihydro-4H-furo[3,2-c]chromen-4-one**



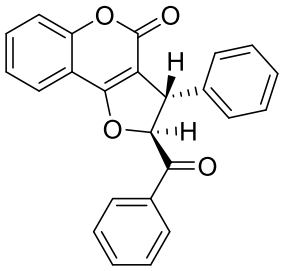
(**5o**) $R_f$ = 0.5 (EtOAc/petroleum ether 50:50); eluent: (EtOAc/petroleum ether 20:80); brown solid; yield: 60% (295 mg); **$^1$H NMR (400 MHz, CDCl$_3$)**: δ 8.00 (dd, 1H, *J* = 8.0 and 1.2 Hz, Ar-H), 7.94 (dd, 2H, *J* = 6.8 and 2.0 Hz, Ar-H), 7.68-7.66 (m, 3H, Ar-H), 7.63-7.60 (m, 2H, Ar-H), 7.51-7.47 (m, 1H, Ar-H), 7.42 (d, 1H, *J* = 8.4 Hz, Ar-H), 7.38 (dd, 1H, *J* = 7.6 and 1.6 Hz, Ar-H), 7.33-7.29 (m, 1H, Ar-H), 6.15 (d, 1H, *J* = 4.4 Hz, $C_2$-H), 5.67 (d, 1H, *J* = 4.4 Hz, $C_3$-H) ppm. **$^{13}$C {$^1$H} NMR (100 MHz, CDCl$_3$)**: δ 190.0, 167.1, 159.3, 155.6, 148.8, 134.2, 134.0, 133.5, 133.2, 132.5, 130.9, 129.9, 129.2, 125.6, 124.4, 123.1, 117.3, 112.0, 103.4, 90.0, 43.9 ppm. **HRMS (ESI)** m/z: $[M+H]^+$ calculated for $C_{24}H_{15}BrNO_6$ 492.0083, found 492.0087; $[M+H+2]^+$ calculated for $C_{24}H_{15}BrNO_6$ 494.0062, found 494.0084.

**(2S,3S)-2-benzoyl-3-(4-(trifluoromethyl)phenyl)-2,3-dihydro-4H-furo[3,2-c]chromen-4-one**



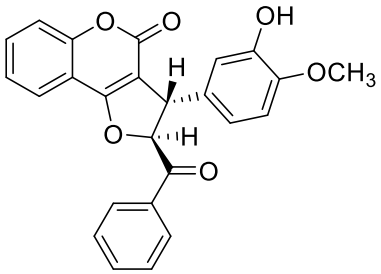
(**5p**) $R_f$ = 0.5 (EtOAc/petroleum ether 20:80); eluent: (EtOAc/petroleum ether 10:90); white solid; yield: 84% (366 mg); **$^1$H NMR (400 MHz, CDCl$_3$)**: δ 7.92 (dd, 2H, *J* = 8.4 and 1.2 Hz, Ar-H), 7.84 (dd, 1H, *J* = 7.6 and 1.6 Hz, Ar-H), 7.70-7.61 (m, 4H, Ar-H), 7.55-7.51 (m, 2H, Ar-H), 7.45-7.34 (m, 4H, Ar-H), 6.14 (d, 1H, *J* = 5.2 Hz, $C_2$-H), 4.95 (d, 1H, *J* = 5.2 Hz, $C_3$-H) ppm. **$^{13}$C {$^1$H} NMR (100 MHz, CDCl$_3$)**: δ 191.8, 166.7, 159.3, 155.6, 143.6, 134.8, 133.4, 133.3, 130.6 (q, $^2J_{C\text{-}F}$ = 32.0 Hz), 129.3, 128.2, 126.4 (q, $^3J_{C\text{-}F}$ = 3.0 Hz), 124.1 (q, $^1J_{C\text{-}F}$ = 270.0 Hz), 123.4, 122.7, 117.3, 112.1, 104.8, 92.4, 48.9 ppm. **$^{19}$F NMR (376 MHz, CDCl$_3$)**: δ - 62.57 ppm. **HRMS (ESI)** m/z: $[M+H]^+$ calculated for $C_{25}H_{16}F_3O_4$ 437.1001, found 437.0998.

**(2S,3S)-2-benzoyl-3-phenyl-2,3-dihydro-4H-furo[3,2-c]chromen-4-one** (**5q**)



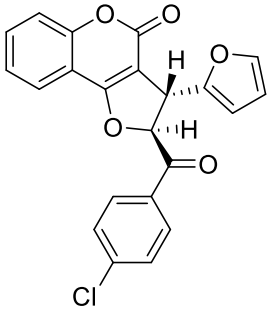
$R_f$ = 0.6 (EtOAc/petroleum ether 20:80); eluent: (EtOAc/petroleum ether 10:90); light yellow solid; yield: 80% (295 mg); **$^1$H NMR (400 MHz, CDCl$_3$)**: δ 7.91 (dd, 2H, *J* = 8.4 and 1.2 Hz, Ar-H), 7.85 (dd, 1H, *J* = 8.0 and 1.6 Hz, Ar-H), 7.68-7.64 (m , 1H, Ar-H), 7.64-7.59 (m, 1H, Ar-H), 7.52-7.48 (m, 2H, Ar-H), 7.41-7.29 (m, 7H, Ar-H), 6.19 (d, 1H, *J* = 4.8 Hz, $C_2$-H), 4.80 (d, 1H, *J* = 4.8 Hz, $C_3$-H) ppm. **$^{13}$C {$^1$H} NMR (100 MHz, CDCl$_3$)**: δ 192.2, 166.5, 159.4, 155.6, 139.7, 134.6, 133.3, 133.0, 129.4, 129.2, 129.2, 128.3, 127.7, 124.3, 123.3, 117.2, 112.3, 105.5, 92.8, 49.5 ppm. **HRMS (ESI)** m/z: $[M+H]^+$ calculated for $C_{24}H_{17}O_4$ 369.1127, found 369.1117.

**(2S,3S)-2-benzoyl-3-(3-hydroxy-4-methoxyphenyl)-2,3-dihydro-4H-furo[3,2-c]chromen-4-one** (**5r**)



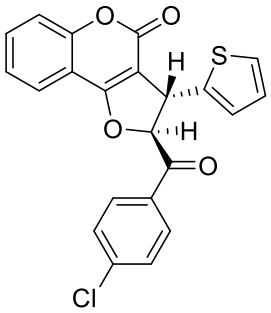
$R_f$ = 0.5 (EtOAc/petroleum ether 40:60); eluent: (EtOAc/petroleum ether 25:75); brown solid; yield: 78% (323 mg); **$^1$H NMR (400 MHz, CDCl$_3$)**: δ 7.86 (dd, 2H, *J* = 8.4 and 1.2 Hz, Ar-H), 7.79 (dd, 1H, *J* = 7.6 and 1.6 Hz, Ar-H), 7.62-7.58 (m, 1H, Ar-H), 7.58-7.53 (m, 1H, Ar-H), 7.47-7.43 (m, 2H, Ar-H), 7.35-7.28 (m, 2H, Ar-H), 6.80-6.73 (m, 3H, Ar-H), 6.09 (d, 1H, *J* = 4.8 Hz, $C_2$-H), 5.63 (br s, 1H, Ar-OH), 4.63 (d, 1H, *J* = 4.4 Hz, $C_3$-H), 3.84 (s, 3H, -OMe) ppm. **$^{13}$C {$^1$H} NMR (100 MHz, CDCl$_3$)**: δ 192.3, 166.4, 159.5, 155.5, 146.6, 146.5, 134.5, 133.3, 132.9, 132.9, 129.2, 129.1, 124.3, 123.3, 119.7, 117.2, 113.3, 112.4, 111.1, 105.5, 92.8, 56.1, 49.2 ppm. **HRMS (ESI)** m/z: $[M+Na]^+$ calculated for $C_{25}H_{18}O_6Na$ 437.1001, found 437.1000.

**(2S,3S)-2-(4-chlorobenzoyl)-3-(furan-2-yl)-2,3-dihydro-4H-furo[3,2-c]chromen-4-one** (**6a**)



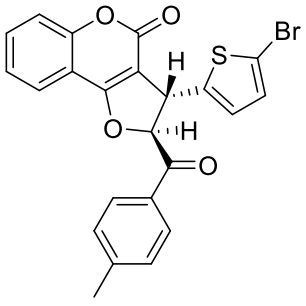
$R_f$ = 0.4 (EtOAc/petroleum ether 20:80); eluent: (EtOAc/petroleum ether 15:85); brown solid; yield: 81% (318 mg); **$^1$H NMR (400 MHz, CDCl$_3$)**: δ 7.97 (dd, 2H, *J* = 6.8 and 20. Hz, Ar-H), 7.77 (dd, 1H, *J* = 8.0 and 1.6 Hz, Ar-H), 7.63-7.58 (m, 1H, Ar-H), 7.51 (dd, 2H, *J* = 6.4 and 2.0 Hz, Ar-H), 7.42-7.38 (m, 2H, Ar-H), 7.34-7.30 (m, 1H, Ar-H), 6.39-6.33 (m, 2H, Ar-H), 6.27 (d, 1H, *J* = 5.2 Hz, $C_2$-H), 5.03 (d, 1H, *J* = 4.8 Hz, $C_3$-H) ppm. **$^{13}$C {$^1$H} NMR (100 MHz, CDCl$_3$)**: δ 190.7, 166.8, 159.3, 155.5, 150.8, 142.9, 141.3, 133.3, 131.6, 130.7, 129.6, 124.3, 123.2, 117.2, 112.1, 111.1, 108.5, 102.4, 89.1, 42.6 ppm. **HRMS (ESI)** m/z: $[M+H]^+$ calculated for $C_{22}H_{14}ClO_5$ 393.0530, found 393.0543; $[M+H+2]^+$ calculated for $C_{22}H_{14}ClO_5$ 395.0500, found 395.0491.

**(2S,3S)-2-(4-chlorobenzoyl)-3-(thiophen-2-yl)-2,3-dihydro-4H-furo[3,2-c]chromen-4-one**

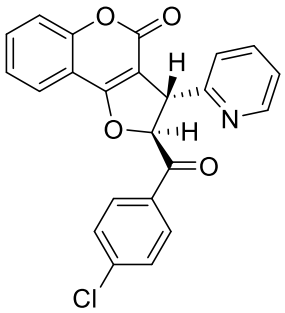


(**6b**) $R_f$ = 0.6 (EtOAc/petroleum ether 30:70); eluent: (EtOAc/petroleum ether 15:85); brown solid; yield: 77% (314 mg); **$^1$H NMR (400 MHz, CDCl$_3$)**: δ 7.99 (dd, 2H, *J* = 6.8 and 2.0 Hz, Ar-H), 7.85 (dd, 1H, *J* = 8.0 Hz and 1.6 Hz, Ar-H), 7.70-7.65 (m, 1H, Ar-H), 7.57 (dd, 2H, *J* = 6.8 and 2.0 Hz, Ar-H), 7.46 (d, 1H, *J* = 8.4 Hz, Ar-H), 7.41-7.37 (m, 1H, Ar-H), 7.32 (dd, 1H, *J* = 5.2 and 1.2 Hz, Ar-H), 7.10-7.05 (m, 2H, Ar-H), 6.19 (d , 1H, *J* = 4.8 Hz, $C_2$-H), 5.24 (d, 1H, *J* = 5.2 Hz, $C_3$-H) ppm. **$^{13}$C {$^1$H} NMR (100 MHz, CDCl$_3$)**: δ 190.7, 166.2, 159.2, 155.5, 142.6, 141.4, 133.3, 131.6, 130.7, 129.6, 127.7, 126.2, 125.7, 124.4, 123.3, 117.2, 112.1, 104.8, 92.4, 44.3 ppm.

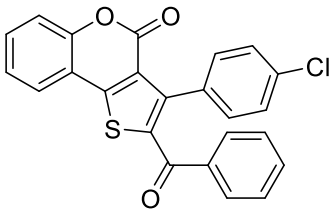
**(2S,3S)-3-(5-bromothiophen-2-yl)-2-(4-methylbenzoyl)-2,3-dihydro-4H-furo[3,2-c]chromen-4-one** (**6c**) $R_f$ = 0.6 (EtOAc/petroleum ether 20:80); eluent: (EtOAc/petroleum ether 15:85); light yellow solid; yield: 85% (397 mg); **$^1$H NMR (400 MHz, CDCl$_3$)**: δ 7.88 (dd, 2H, *J* = 6.4 and 2.0 Hz, Ar-H), 7.81 (dd, 1H, *J* = 7.6 and 1.6 Hz, Ar-H), 7.65-7.60 (m ,1H, Ar-H), 7.41 (dd, 1H, *J* = 8.4 and 1.2 Hz, Ar-H), 7.36-7.32 (m, 3H, Ar-H), 6.96 (dd, 1H, *J* = 3.6 and 1.6 Hz, Ar-H), 6.80 (d, 1 H, *J* = 3.6 Hz, Ar-H), 6.15 (d, 1H, *J* = 4.8 Hz, $C_2$-H), 5.09 (d, 1H, *J* = 4.8 Hz, $C_3$-H), 2.47 (s, 3H, -Me) ppm. **$^{13}$C {$^1$H} NMR (100 MHz, CDCl$_3$)**: δ 191.1, 166.7, 159.2, 155.6, 146.1, 144.4, 133.4, 130.7, 130.4, 130.0, 129.4, 126.5, 124.4, 123.4, 117.3, 111.3, 112.1, 104.2, 92.0, 44.8, 22.8 ppm. **HRMS (ESI)** m/z: $[M+H]^+$ calculated for $C_{23}H_{16}BrO_4S$ 466.9953, found 466.9945; $[M+H+2]^+$ calculated for $C_{23}H_{16}BrO_4S$ 468.9932, found 468.9922.



**(2S,3R)-2-(4-chlorobenzoyl)-3-(pyridin-2-yl)-2,3-dihydro-4H-furo[3,2-c]chromen-4-one** (**6d**)



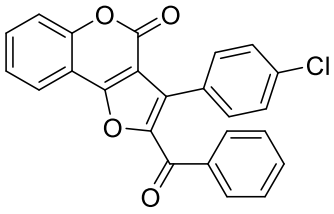
$R_f$ = 0.4 (EtOAc/petroleum ether 20:80); eluent: (EtOAc/petroleum ether 20:80); white solid; yield: 70% (282 mg); **$^1$H NMR (400 MHz, $CDCl_3$)**: δ 8.65-8.63 (m, 1H, Ar-H), 7.99 (dd, 2H, *J* = 6.8 and 2.0 Hz, Ar-H), 7.80 (dd, 1H, *J* = 8.0 and 1.6 Hz, Ar-H), 7.72-7.70 (m, 1H, Ar-H), 7.62-7.56 (m, 2H, Ar-H), 7.46 (dd, 2H, *J* = 6.8 and 2.0 Hz, Ar-H), 7.33-7.29 (m, 2H, Ar-H), 7.28-7.24 (m, 1H, Ar-H), 7.00 (d, 1H, *J* = 4.8 Hz, $C_2$-H), 5.06 (d, 1H, *J* = 4.8 Hz, $C_3$-H) ppm. **$^{13}$C {$^1$H} NMR (100 MHz, $CDCl_3$)**: δ 191.9, 166.6, 159.9, 157.0, 155.5, 149.9, 141.0, 137.3, 133.1, 132.0, 130.7, 129.5, 124.4, 124.2, 123.5, 123.2, 117.1, 112.4, 104.5, 89.9, 50.2 ppm. **HRMS (ESI)** m/z: $[M+H]^+$ calculated for $C_{23}H_{15}ClNO_4$ 404.0690, found 404.0698; $[M+H+2]^+$ calculated for $C_{23}H_{15}ClNO_4$ 406.0660, found 406.0655.



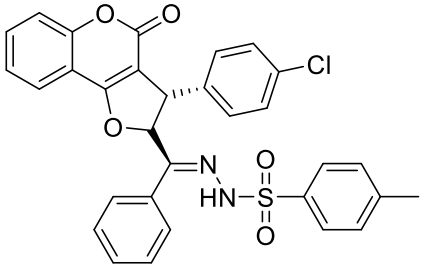
**2-benzoyl-3-(4-chlorophenyl)-4H-thieno[3,2-c]chromen-4-one** (**7a**) $R_f$ = 0.4 (EtOAc/petroleum ether 10:90); eluent: (EtOAc/petroleum ether 5:85); white solid; yield: 83% (86.3mg); **$^1$H NMR (400 MHz, $CDCl_3$)**: δ 7.84 (dd, 1H, *J* = 8.0 and 2.0 Hz, Ar-H), 7.60-7.56 (m, 1H, Ar-H), 7.51 (dd, 2H, *J* = 8.8 and 1.6 Hz, Ar-H), 7.44 (dd, 1H, *J* = 8.4 and 1.2 Hz, Ar-H), 7.42-7.35 (m, 2H, Ar-H), 7.23-7.16 (m, 4H, Ar-H), 7.13-7.10 (m, 2H, Ar-H) ppm. **$^{13}$C {$^1$H} NMR (100 MHz, $CDCl_3$)**: δ 189.8, 156.1, 152.1, 151.7, 144.9, 139.0, 136.8, 134.8, 132.9, 132.1, 131.9, 131.5, 129.5, 128.2, 127.8, 125.0, 123.9, 122.9, 117.6, 116.5 ppm. **HRMS (ESI)** m/z: $[M+H]^+$ calculated for $C_{24}H_{14}ClSO_3$ 417.0352, found 417.0382.

**2-benzoyl-3-(4-chlorophenyl)-4H-furo[3,2-c]chromen-4-one** (**7b**)

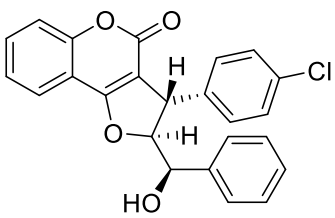
$R_f$ = 0.6 (EtOAc/petroleum ether 20:80); eluent: (EtOAc/petroleum ether 7:93); white solid; yield: 88% (88.0 mg); **$^1$H NMR (400 MHz, $CDCl_3$)**: δ 8.01 (dd, 1H, *J* = 8.0 and 2.0 Hz, Ar-H), 7.77 (dd, 2H, *J* = 8.4 and 2.0 Hz, Ar-H), 7.65-7.61 (m, 1H, Ar-H), 7.54-7.47 (m, 2H, Ar-H), 7.43-7.37 (m, 4H, Ar-H), 7.36-7.34 (m, 1H, Ar-H), 7.28 (dd, 1H, *J* = 6.4 and 1.6 Hz, Ar-H), 7.25 (d, 1H, *J* = 1.2 Hz, Ar-H) ppm. **$^{13}$C {$^1$H} NMR (100 MHz, $CDCl_3$)**: δ 183.8, 158.8, 156.9, 153.8, 148.1, 136.5, 135.4, 133.3, 132.8, 132.1, 132.0, 129.7, 128.5, 128.2, 126.7, 125.1, 122.1, 117.6, 112.0, 110.2 ppm. **HRMS (ESI)** m/z: $[M+H]^+$ calculated for $C_{24}H_{14}ClO_4$ 401.0581, found 401.0578.



**N'-((E)-((2R,3S)-3-(4-chlorophenyl)-4-oxo-2,3-dihydro-4H-furo[3,2-c]chromen-2-yl)(phenyl)methylene)-4-methylbenzenesulfonohydrazide** (**7c**) $R_f$ = 0.6 (EtOAc/petroleum ether 30:70); eluent: (EtOAc/petroleum ether 18:82); white solid; yield: 80% (113 mg); **$^1$H NMR (400 MHz, CDCl$_3$)**: δ 7.74-7.70 (m, 3H, Ar-H), 7.60-7.55 (m, 2H, Ar-H), 7.45-7.44 (m, 3H, Ar-H), 7.35 (d, 1H, *J* = 8.8 Hz, Ar-H), 7.29 (d, 1H, *J* = 7.6 Hz, Ar-H), 7.23-7.22 (m, 3H, Ar-H), 7.16-7.14 (m, 2H, Ar-H), 7.01 (d, 2H, *J* = 8.0 Hz, Ar-H), 5.48 (d, 1H, *J* = 6.0 Hz, $C_2$-H), 4.83 (d, 1H, *J* = 6.0 Hz, $C_3$-H), 2.39 (s, 3H, Ar-Me) ppm. **$^{13}$C {$^1$H} NMR (100 MHz, CDCl$_3$)**: δ 166.0, 159.4, 155.4, 150.5, 144.8, 138.1, 134.9, 133.8, 133.1, 131.1, 130.2, 129.9, 129.3, 128.9, 128.9, 128.1, 127.7, 124.3, 122.9, 117.2, 112.1, 104.9, 94.9, 48.1, 21.8 ppm.

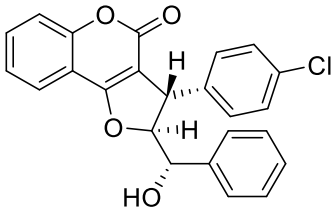


**(2S,3S)-3-(4-chlorophenyl)-2-((R)-hydroxy(phenyl)methyl)-2,3-dihydro-4H-furo[3,2-c]chromen-4-one** (**7da**) $R_f$ = 0.5 (EtOAc/petroleum ether 30:70); eluent: (EtOAc/petroleum ether 20:80); white solid; yield: 45% (45 mg); **$^1$H NMR (400 MHz, CDCl$_3$)**: δ 7.74 (dd, 1H, *J* = 8.0 and 2.0 Hz, Ar-H), 7.63-7.59 (m, 1H, Ar-H), 7.44-7.38 (m, 5H, Ar-H), 7.37-7.32 (m, 2H, Ar-H), 7.12 (dd, 2H, *J* = 6.4 and 2.0 Hz, Ar-H), 6.72 (dd, 2H, J = 6.4 and 2.0 Hz, Ar-H), 5.26 (t, 1H, J = 7.2 and 3.6 Hz, >CHOH), 5.01 (dd, 1H, *J* = 5.6 and 4.0 Hz, $C_2$-H), 4.71 (d, 1H, *J* = 5.6 Hz, $C_3$-H), 2.32 (s, 1H, -OH) ppm. **$^{13}$C {$^1$H} NMR (100 MHz, CDCl$_3$)**: δ 166.9, 159.9, 155.4, 139.5, 137.9, 133.1, 132.9, 129.0, 128.9, 128.7, 128.7, 126.4, 124.2, 123.0, 117.3, 112.4, 105.4, 97.7, 73.9, 45.4 ppm.



**HRMS (ESI)** m/z: $[M+H]^+$ calculated for $C_{24}H_{18}ClO_4$ 405.0894, found 405.0898.

**(2S,3S)-3-(4-chlorophenyl)-2-((S)-hydroxy(phenyl)methyl)-2,3-dihydro-4H-furo[3,2-c]chromen-4-one** (**7db**) $R_f$ = 0.4 (EtOAc/petroleum ether 30:70); eluent: (EtOAc/petroleum ether 25:75); white solid; yield: 45% (45 mg); **$^1$H NMR (400 MHz, CDCl$_3$)**: δ 7.82 (dd, 1H, *J* = 8.0 and 2.0 Hz, Ar-H), 7.65-7.61 (m, 1H, Ar-H), 7.42-7.41 (m, 6H, Ar-H), 7.38-7.34 (m, 1H, Ar-H), 6.66 (dd, 2H, *J* = 6.4 and 2.0 Hz, Ar-H), 7.14 (dd, 2H, *J* = 6.8 and 2.0 Hz, Ar-H), 5.00 (dd, 1H, *J* = 7.6 and 5.6 Hz, $C_2$-H), 4.89 (dd, 1H, *J* = 7.2 and 2.0 Hz, >CHOH), 4.36 (d, 1H, *J* = 5.6 Hz, $C_3$-H), 2.64 (s, 1H, -OH) ppm. **$^{13}$C {$^1$H} NMR (100 MHz, CDCl$_3$)**: δ 166.6, 159.7, 155.5, 138.7, 137.6, 133.4, 133.1, 129.4, 129.1, 129.1, 128.6, 127.8, 124.3, 123.1, 117.3, 112.4, 105.2, 98.2, 76.2, 47.3 ppm.



**HRMS (ESI)** m/z: $[M+H]^+$ calculated for $C_{24}H_{18}ClO_4$ 405.0894, found 405.0894.

**References**:

1. P. Job, *Annales de Chimie*. 1928, **9**, 113.

2. A. H. Benesi, H. J. Hildebrand, *J. Am. Chem. Soc.* 1949, **71**, 2703.

3. (a) A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648; (b) C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1988, **37**, 785.

4. (a) A. D. McLean, G. S. Chandler, *J. Chem. Phys.*, 1980, **72**, 5639; (b) K. Raghavachari, J. S. Binkley, R. Seeger, J. A. Pople, *J. Chem. Phys*., 1980, **72**, 650.

## 9. Crystallographic Data:

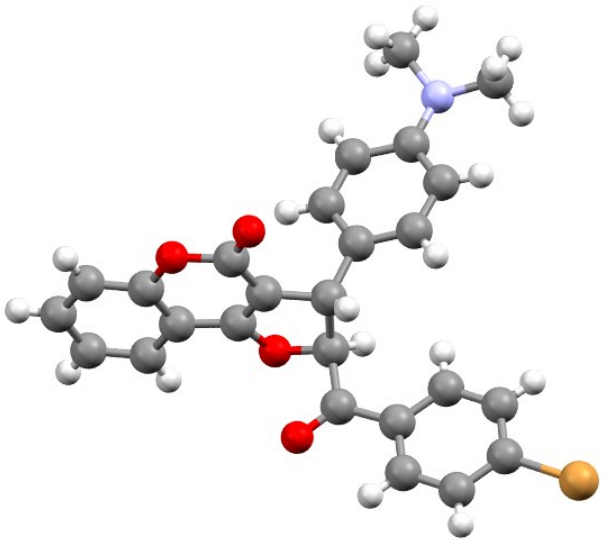


Figure S16: Crystal structure of **5a** (CCDC# 2366844)

**Table S5 Crystal data and structure refinement for 5a**

| | |
|---|---|
| Identification code | KSK_KC_65_auto (1) |
| Empirical formula | $C_{26}H_{20}BrNO_4$ |
| Formula weight | 490.34 |
| Temperature/K | 100.00(10) |
| Crystal system | triclinic |
| Space group | P-1 |
| a/Å | 5.03990(8) |
| b/Å | 14.26675(16) |
| c/Å | 15.1370(2) |
| α/° | 82.4456(10) |
| β/° | 83.3581(12) |
| γ/° | 85.9012(11) |
| Volume/Å$^3$ | 1069.96(3) |
| Z | 2 |
| $\rho_{calc}$g/cm$^3$ | 1.522 |
| μ/mm$^{-1}$ | 2.905 |
| F(000) | 500.0 |
| Crystal size/mm$^3$ | 0.002 × 0.001 × 0.001 |
| Radiation | Cu Kα (λ = 1.54184) |
| 2Θ range for data collection/° | 5.924 to 136.364 |

| | |
|---|---|
| Index ranges | $-6 \le h \le 6$, $-15 \le k \le 17$, $-17 \le l \le 18$ |
| Reflections collected | 16451 |
| Independent reflections | 3872 [$R_{int}$ = 0.0579, $R_{sigma}$ = 0.0327] |
| Data/restraints/parameters | 3872/0/292 |
| Goodness-of-fit on $F^2$ | 1.049 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0394, $wR_2$ = 0.1069 |
| Final R indexes [all data] | $R_1$ = 0.0404, $wR_2$ = 0.1079 |
| Largest diff. peak/hole / e $Å^{-3}$ | 0.58/-0.83 |

**Table S6 Bond Lengths for 5a**

| Atom | Atom | Length/Å | Atom | Atom | Length/Å |
|---|---|---|---|---|---|
| Br32 | C29 | 1.894(2) | C6 | C7 | 1.385(3) |
| O3 | C2 | 1.453(2) | C14 | C15 | 1.394(3) |
| O3 | C4 | 1.355(2) | C14 | C1 | 1.514(3) |
| O11 | C10 | 1.374(2) | C28 | C29 | 1.393(3) |
| O11 | C12 | 1.400(2) | C26 | C31 | 1.401(3) |
| O25 | C12 | 1.210(2) | C26 | C23 | 1.494(3) |
| O24 | C23 | 1.213(3) | C13 | C1 | 1.512(3) |
| C19 | C18 | 1.385(3) | C13 | C12 | 1.432(3) |
| C19 | C14 | 1.394(3) | C13 | C4 | 1.347(3) |
| N20 | C17 | 1.390(3) | C10 | C9 | 1.389(3) |
| N20 | C22 | 1.451(3) | C31 | C30 | 1.383(3) |
| N20 | C21 | 1.451(3) | C2 | C1 | 1.572(3) |
| C27 | C28 | 1.380(3) | C2 | C23 | 1.526(3) |
| C27 | C26 | 1.400(3) | C17 | C16 | 1.402(3) |
| C5 | C6 | 1.406(3) | C29 | C30 | 1.386(3) |
| C5 | C10 | 1.400(3) | C16 | C15 | 1.384(3) |
| C5 | C4 | 1.430(3) | C9 | C8 | 1.386(3) |
| C18 | C17 | 1.404(3) | C7 | C8 | 1.395(3) |

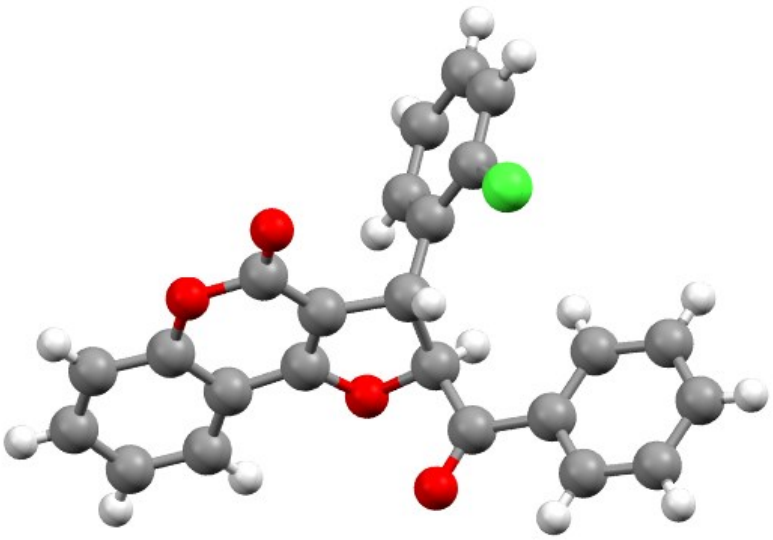


Figure S17: Crystal structure of **5l** (CCDC# 2366843)

**Table S7 Crystal data and structure refinement for 5l**

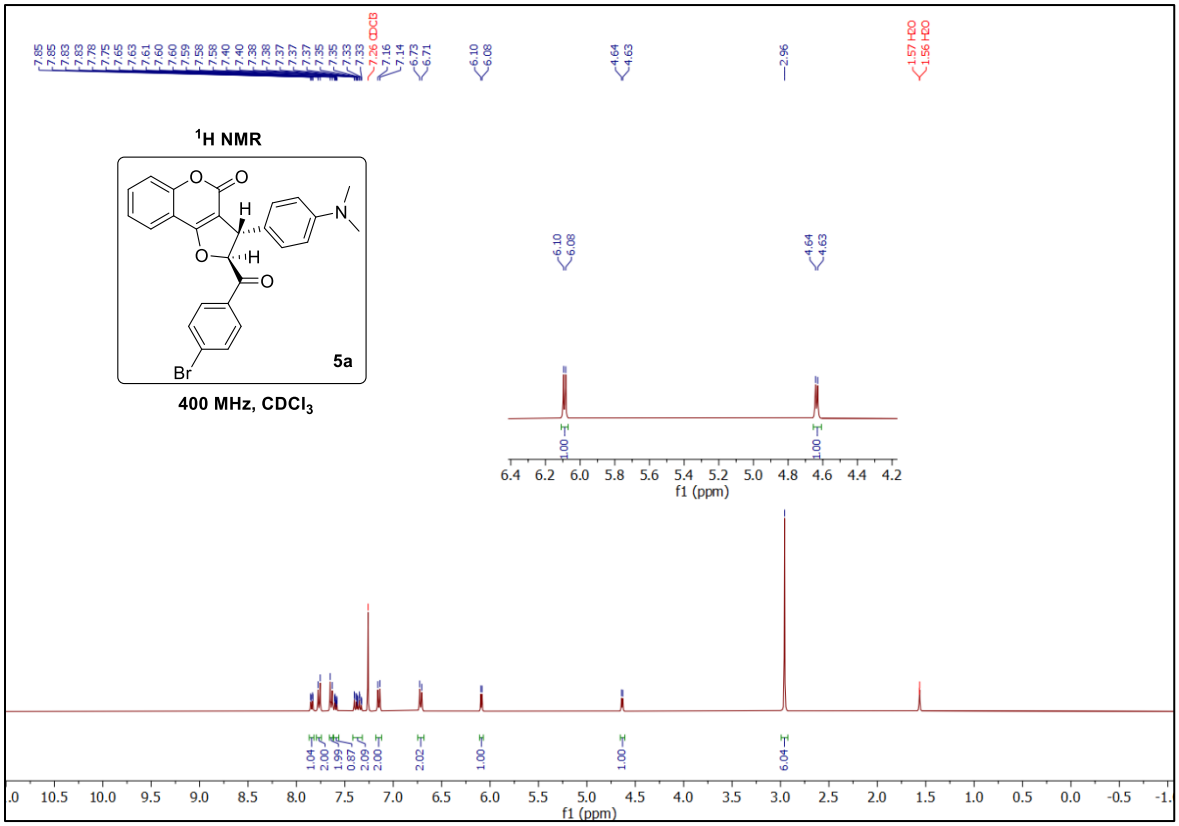
| | |
|---|---|
| Identification code | KSK_SD_2017_auto |
| Empirical formula | $C_{24}H_{15}ClO_4$ |
| Formula weight | 402.81 |
| Temperature/K | 100.00(10) |
| Crystal system | monoclinic |
| Space group | $P2_1/n$ |
| a/Å | 11.9410(4) |
| b/Å | 8.3910(3) |
| c/Å | 19.4783(7) |
| α/° | 90 |
| β/° | 107.214(4) |
| γ/° | 90 |
| Volume/Å$^3$ | 1864.24(12) |
| Z | 4 |
| $\rho_{calc}$g/cm$^3$ | 1.435 |
| μ/mm$^{-1}$ | 0.235 |
| F(000) | 832.0 |
| Crystal size/mm$^3$ | 0.002 × 0.001 × 0.001 |
| Radiation | Mo Kα (λ = 0.71073) |
| 2Θ range for data collection/° | 4.378 to 54.182 |
| Index ranges | $-14 \leq h \leq 14$, $-9 \leq k \leq 10$, $-24 \leq l \leq 24$ |
| Reflections collected | 23819 |
| Independent reflections | 3939 [$R_{int}$ = 0.0939, $R_{sigma}$ = 0.0465] |
| Data/restraints/parameters | 3939/0/262 |
| Goodness-of-fit on F$^2$ | 1.061 |

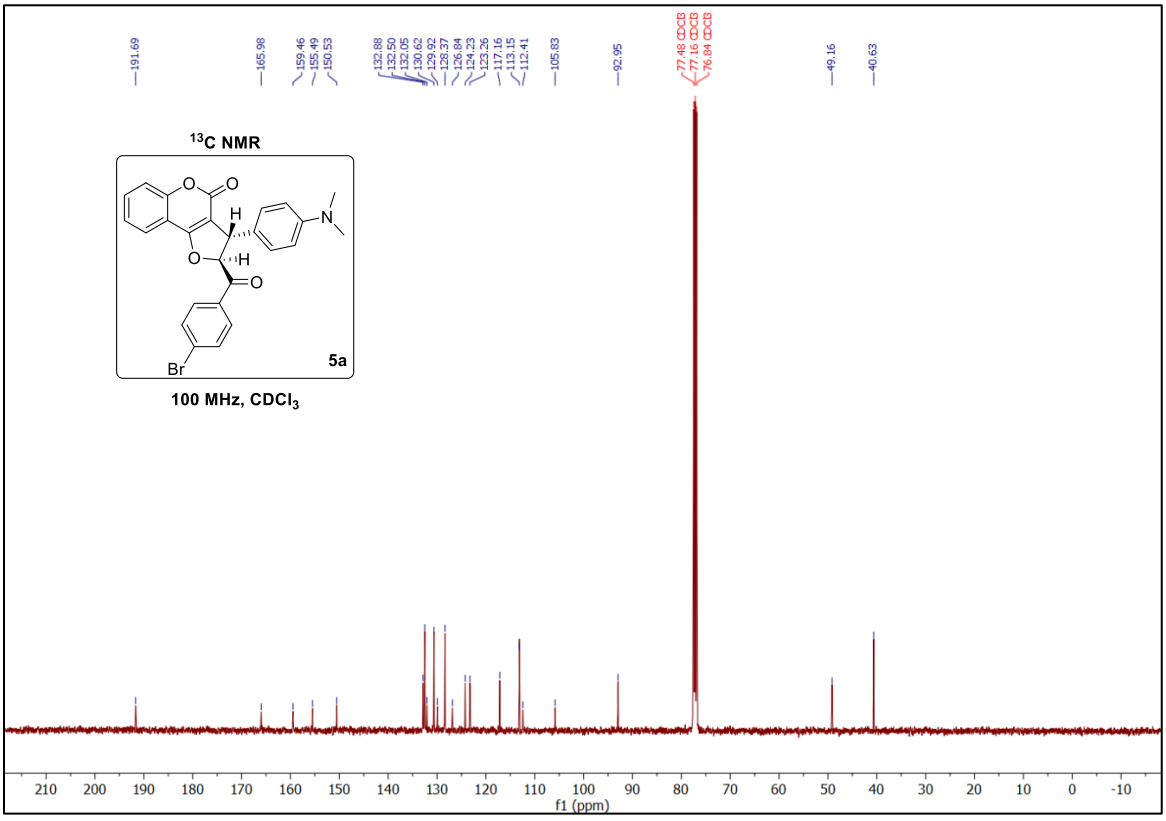
Final R indexes [I>=2σ (I)] $R_1 = 0.0437$, $wR_2 = 0.1116$
Final R indexes [all data] $R_1 = 0.0518$, $wR_2 = 0.1189$
Largest diff. peak/hole / e $Å^{-3}$ 0.27/-0.36

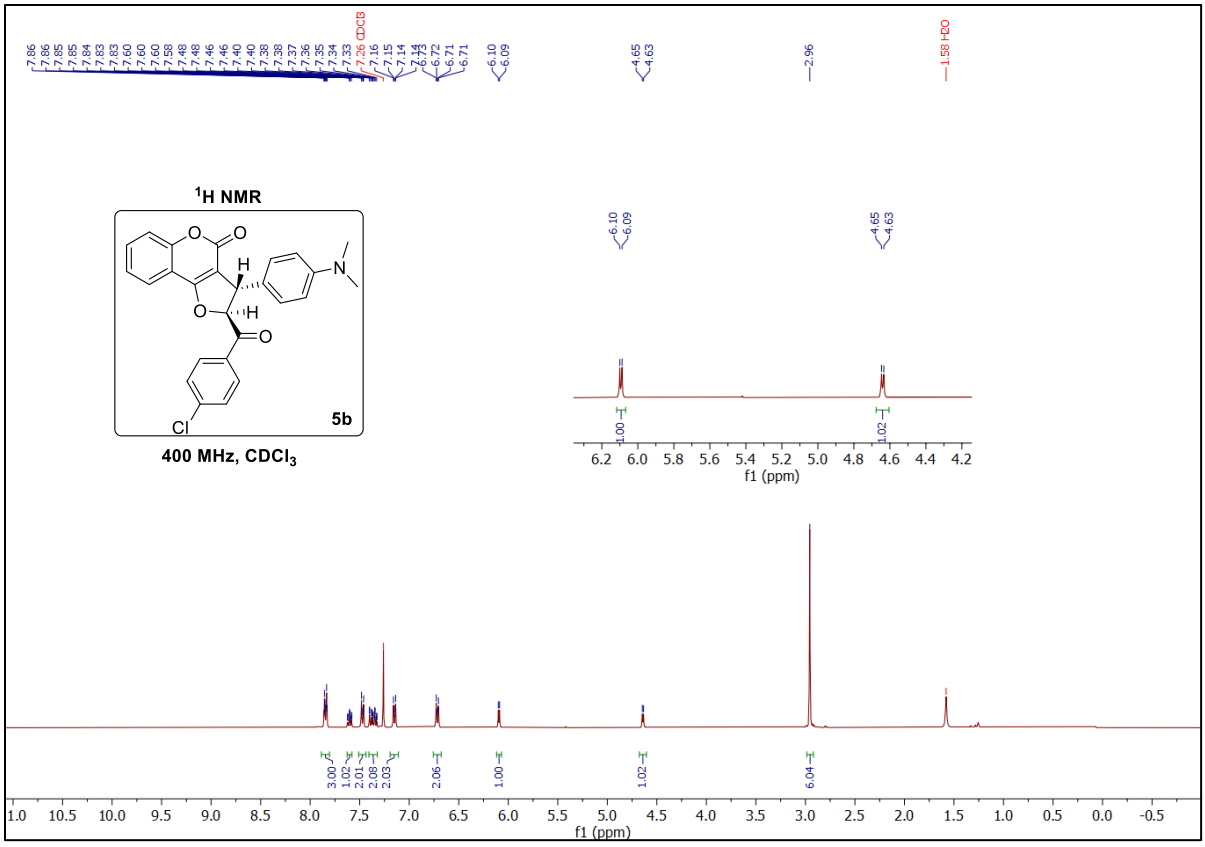
**Table S8 Bond Lengths for 5l**

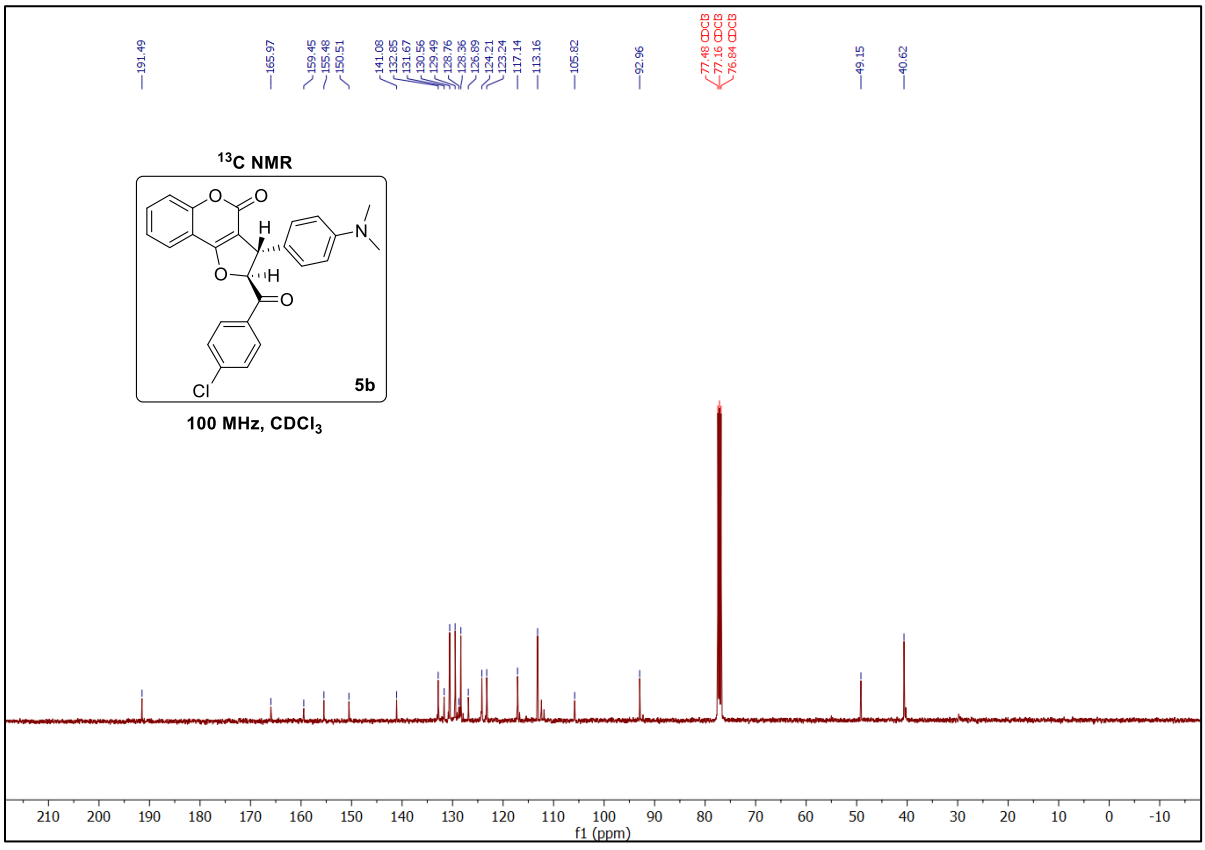
| Atom | Atom | Length/Å | Atom | Atom | Length/Å |
|---|---|---|---|---|---|
| Cl01 | C00G | 1.7492(17) | C00A | C00G | 1.390(2) |
| O002 | C006 | 1.3532(19) | C00A | C00M | 1.379(3) |
| O002 | C00C | 1.4565(18) | C00B | C00C | 1.522(2) |
| O003 | C00E | 1.4026(19) | C00C | C00H | 1.569(2) |
| O003 | C00I | 1.374(2) | C00D | C00I | 1.401(2) |
| O004 | C00E | 1.204(2) | C00D | C00L | 1.401(2) |
| O005 | C00B | 1.2135(19) | C00F | C00J | 1.382(2) |
| C006 | C008 | 1.343(2) | C00I | C00P | 1.393(2) |
| C006 | C00D | 1.428(2) | C00J | C00M | 1.387(2) |
| C007 | C00F | 1.401(2) | C00K | C00O | 1.388(2) |
| C007 | C00G | 1.395(2) | C00L | C00S | 1.380(2) |
| C007 | C00H | 1.512(2) | C00N | C00R | 1.382(2) |
| C008 | C00E | 1.431(2) | C00O | C00Q | 1.384(3) |
| C008 | C00H | 1.512(2) | C00P | C00T | 1.383(3) |
| C009 | C00B | 1.491(2) | C00Q | C00R | 1.381(3) |
| C009 | C00K | 1.394(2) | C00S | C00T | 1.390(3) |
| C009 | C00N | 1.391(2) | | | |

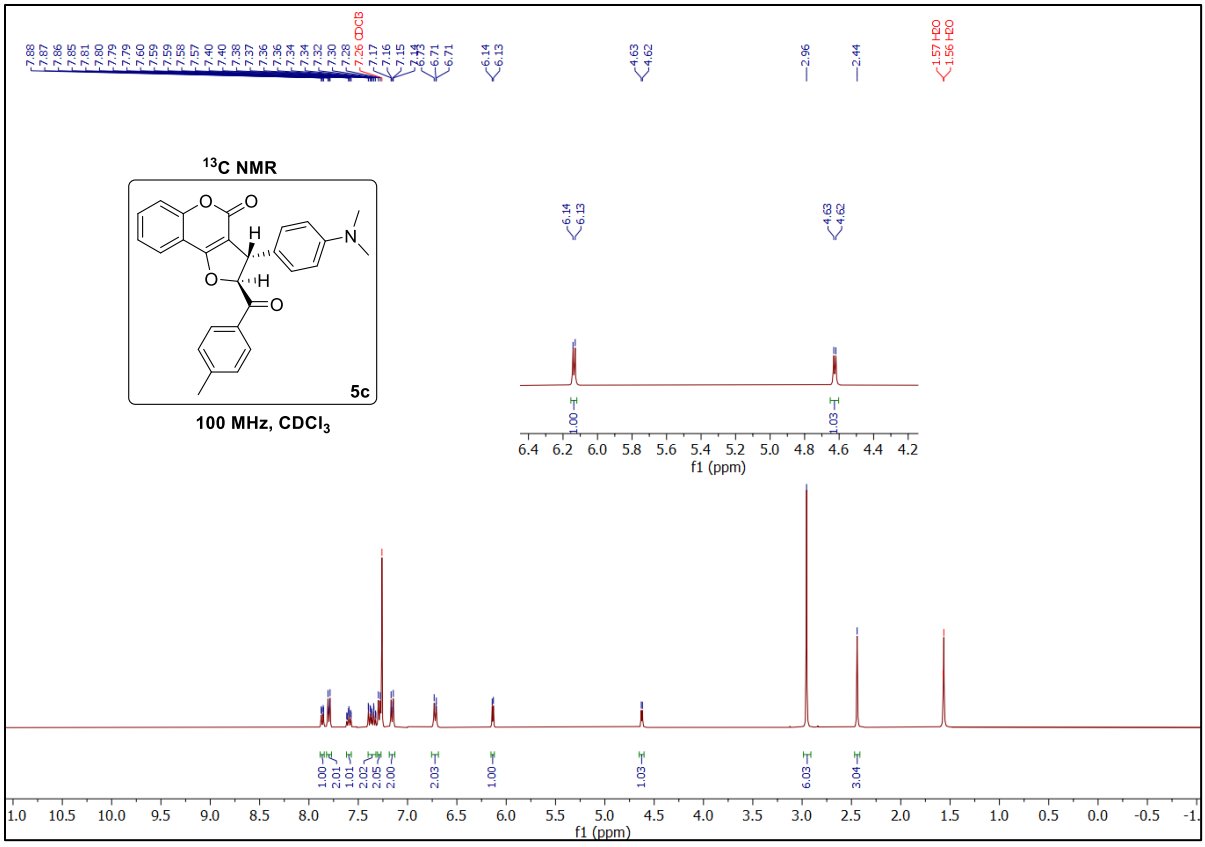
## 10. Copies of $^{1}H$ and $^{13}C$ NMR spectra of synthesized compounds:

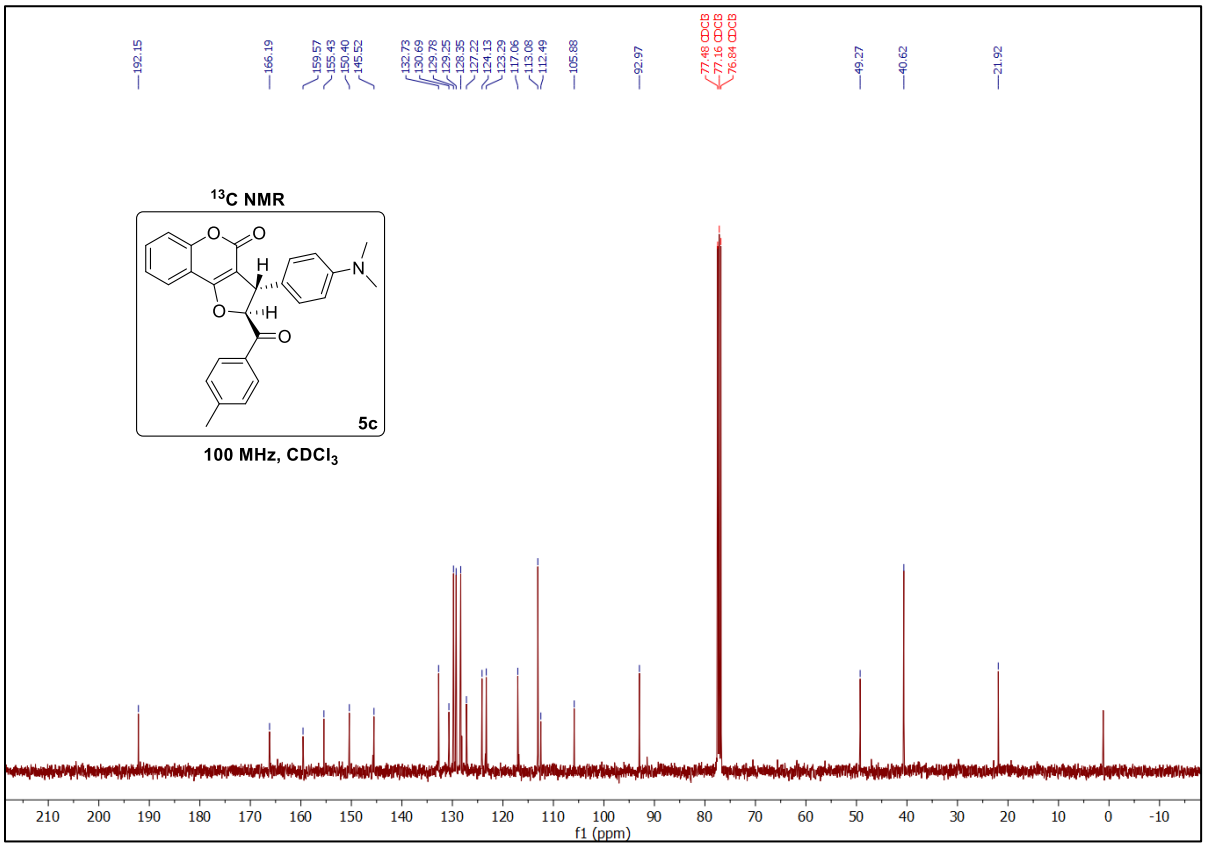


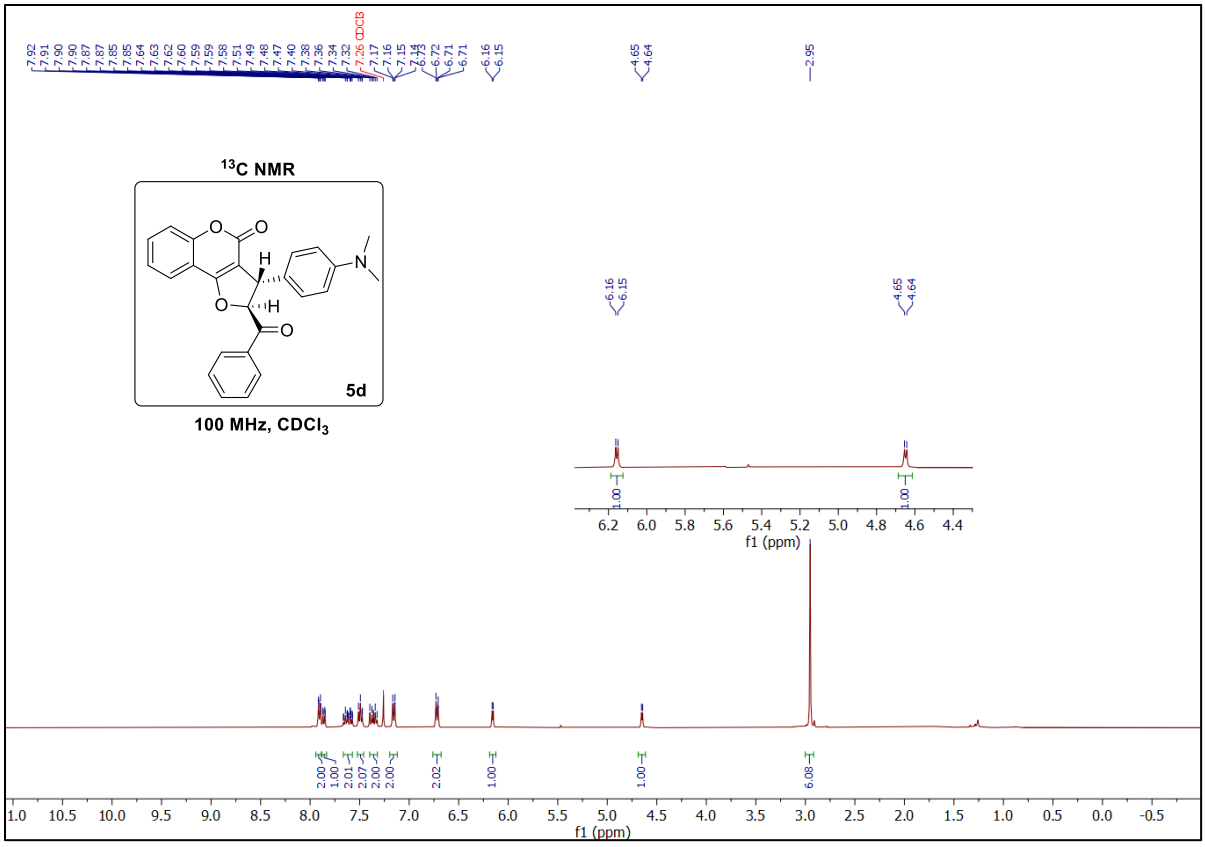



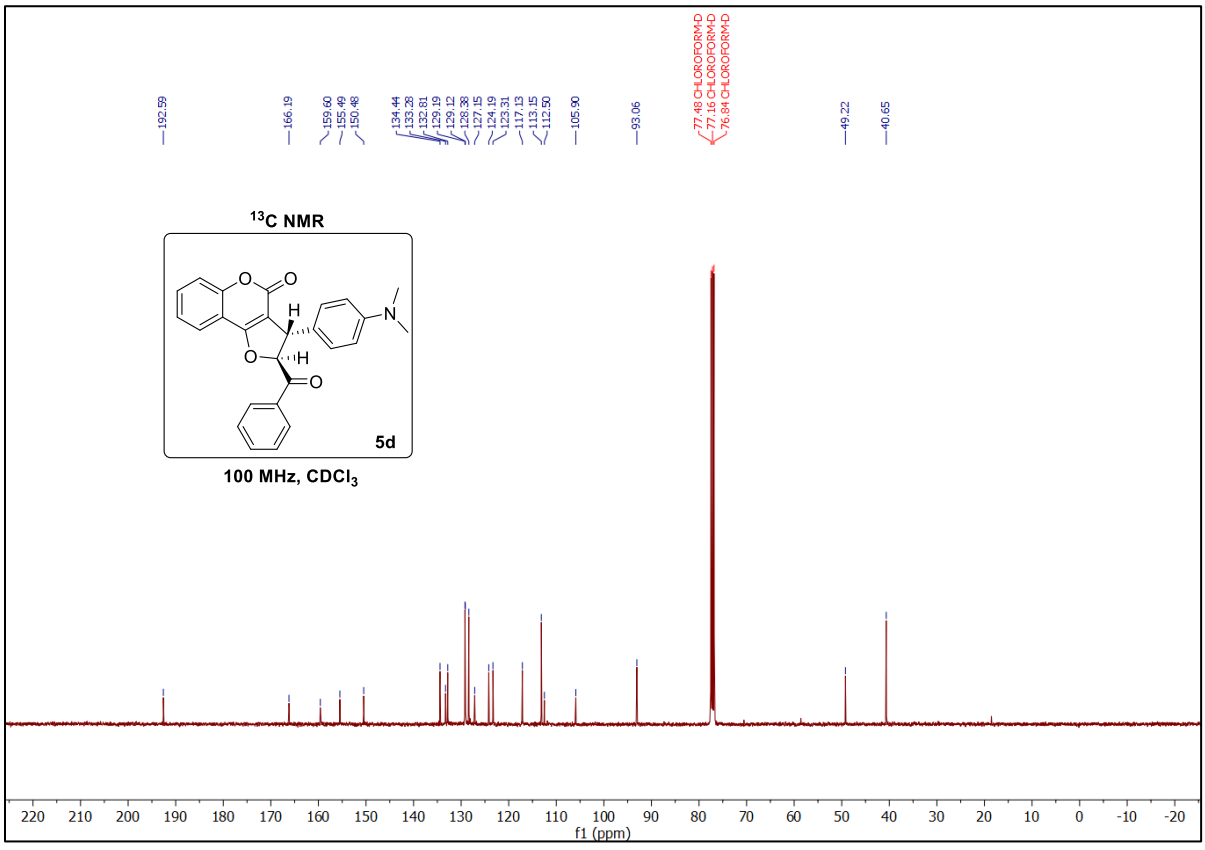

$^{1}$H NMR
5b
400 MHz, $CDCl_3$
f1 (ppm)

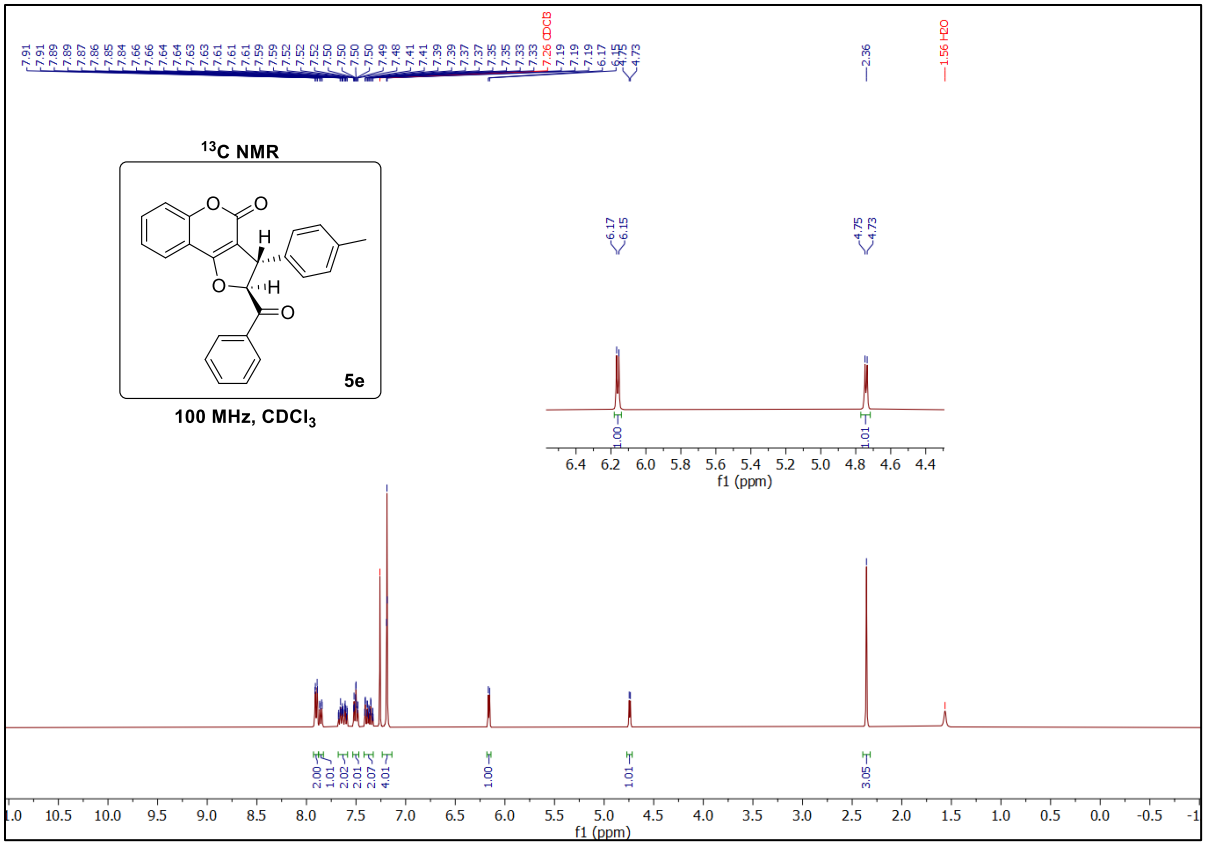

$^{13}$C NMR
5b
100 MHz, $CDCl_3$
f1 (ppm)

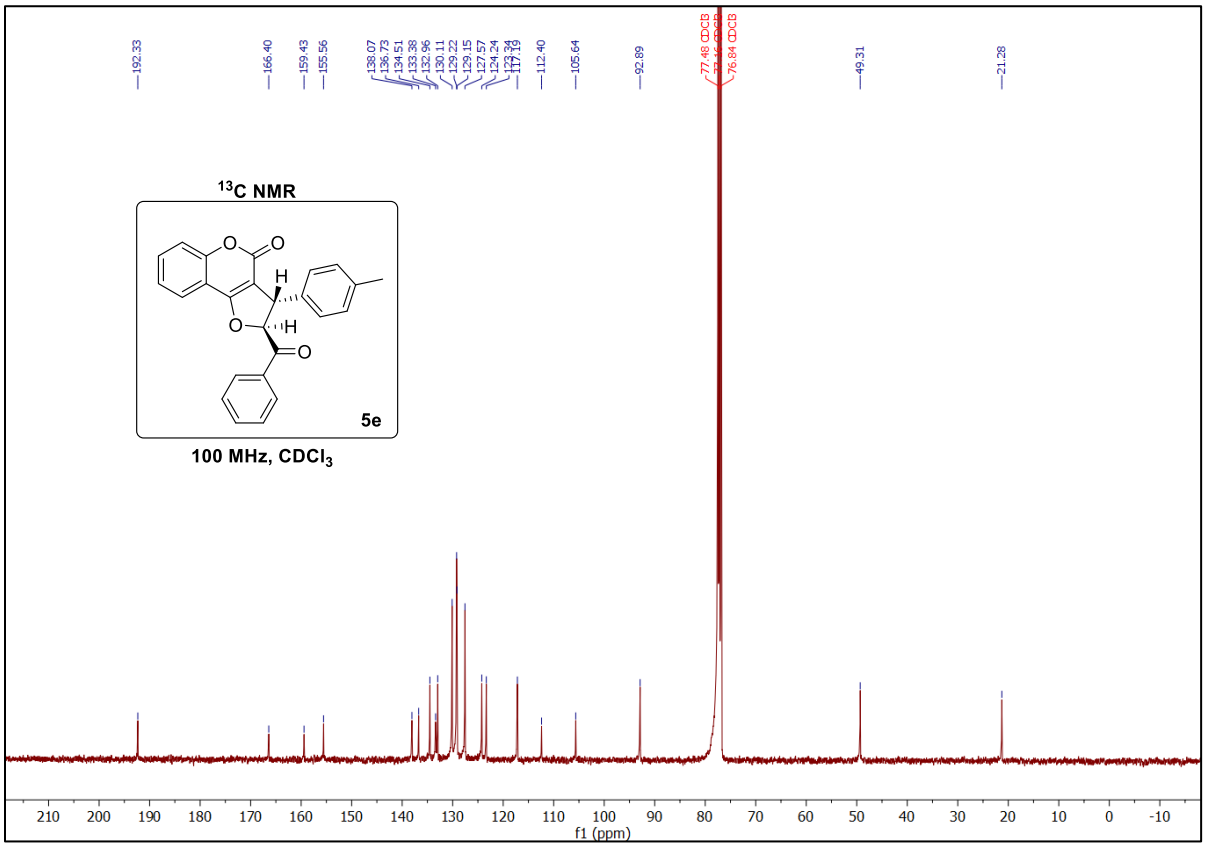

$^{13}$C NMR
5c
100 MHz, $CDCl_3$
f1 (ppm)

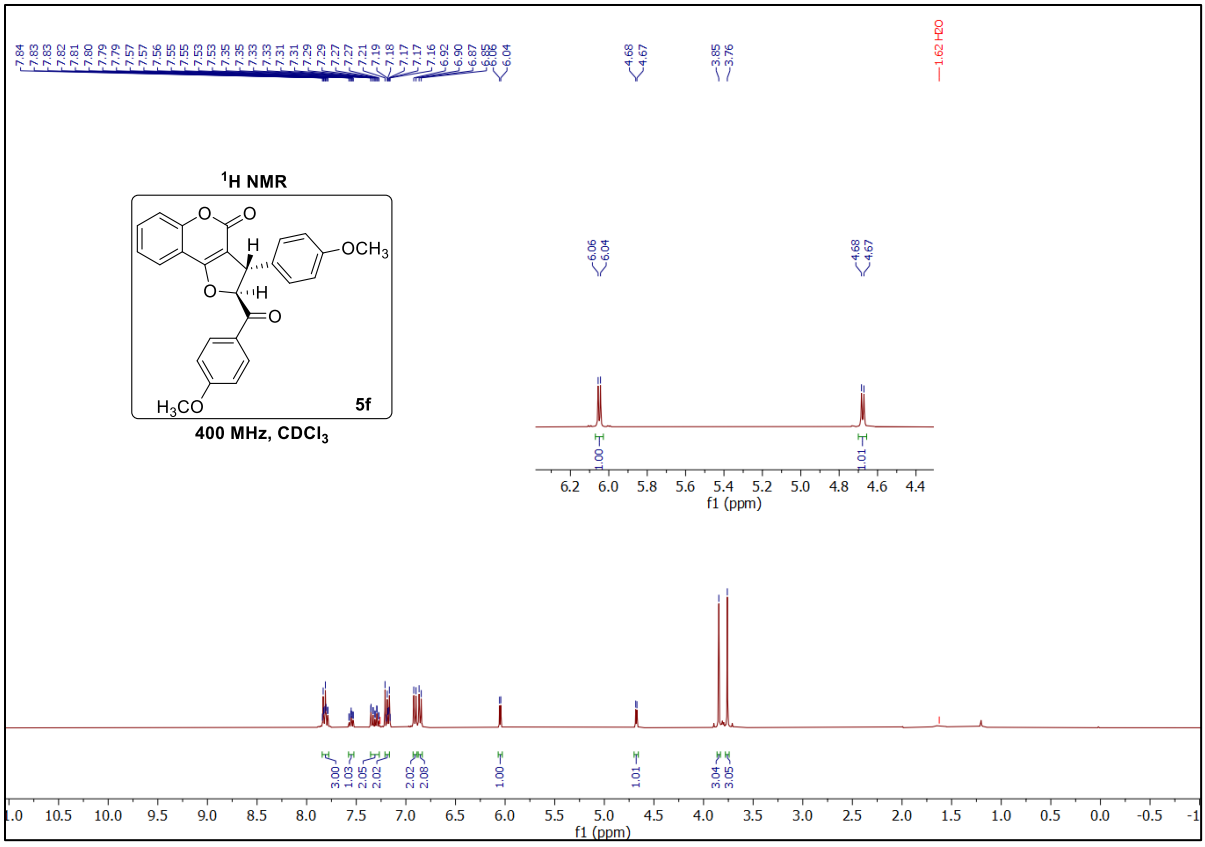

$^{13}$C NMR
5c
100 MHz, $CDCl_3$
f1 (ppm)

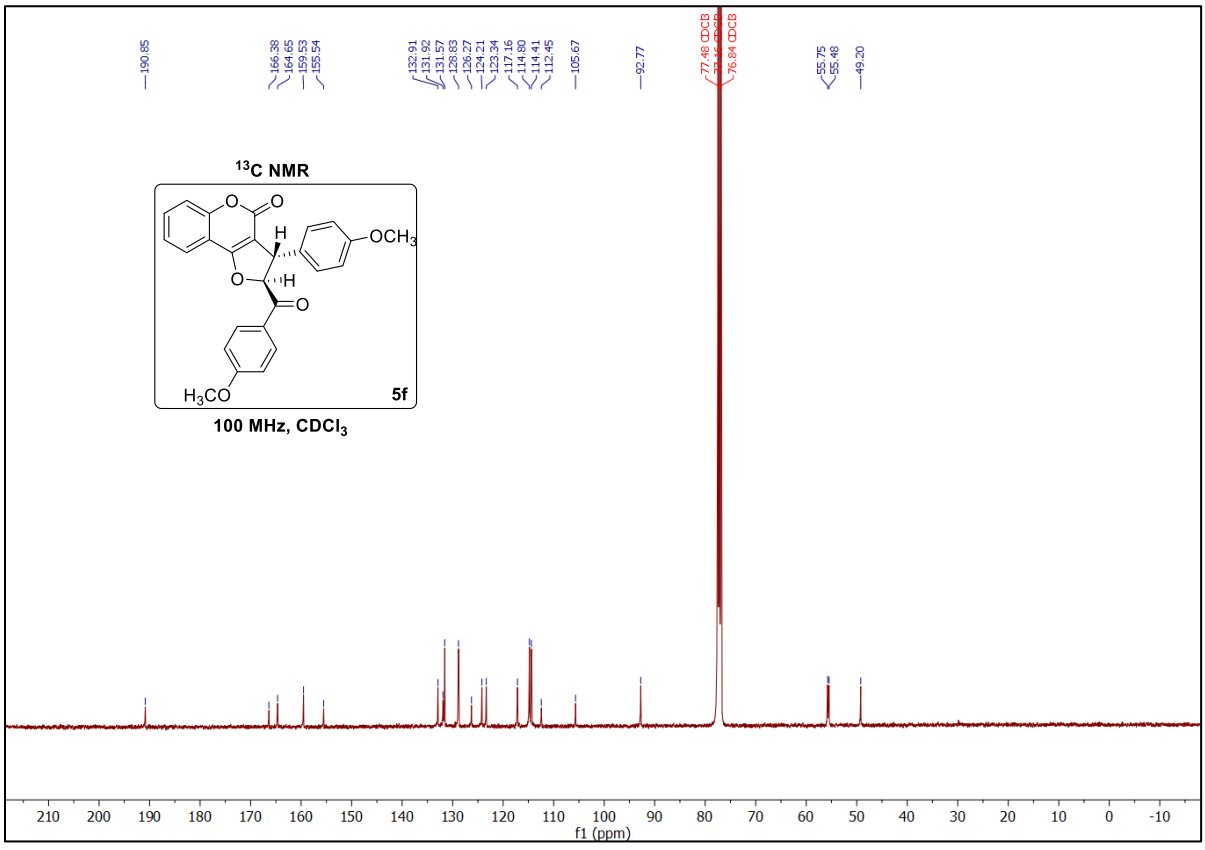

$^{13}$C NMR
5d
100 MHz, $CDCl_3$
f1 (ppm)

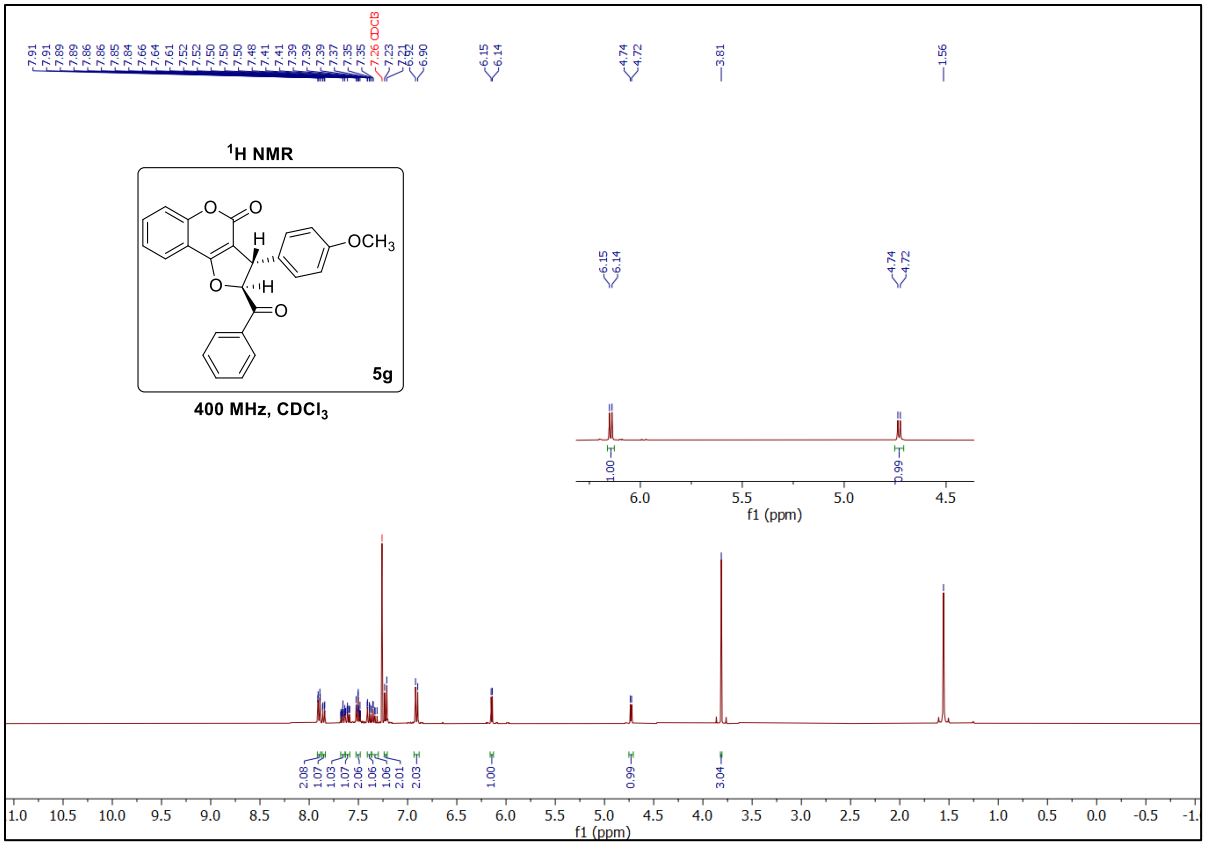

$^{13}$C NMR
5d
100 MHz, $CDCl_3$
f1 (ppm)

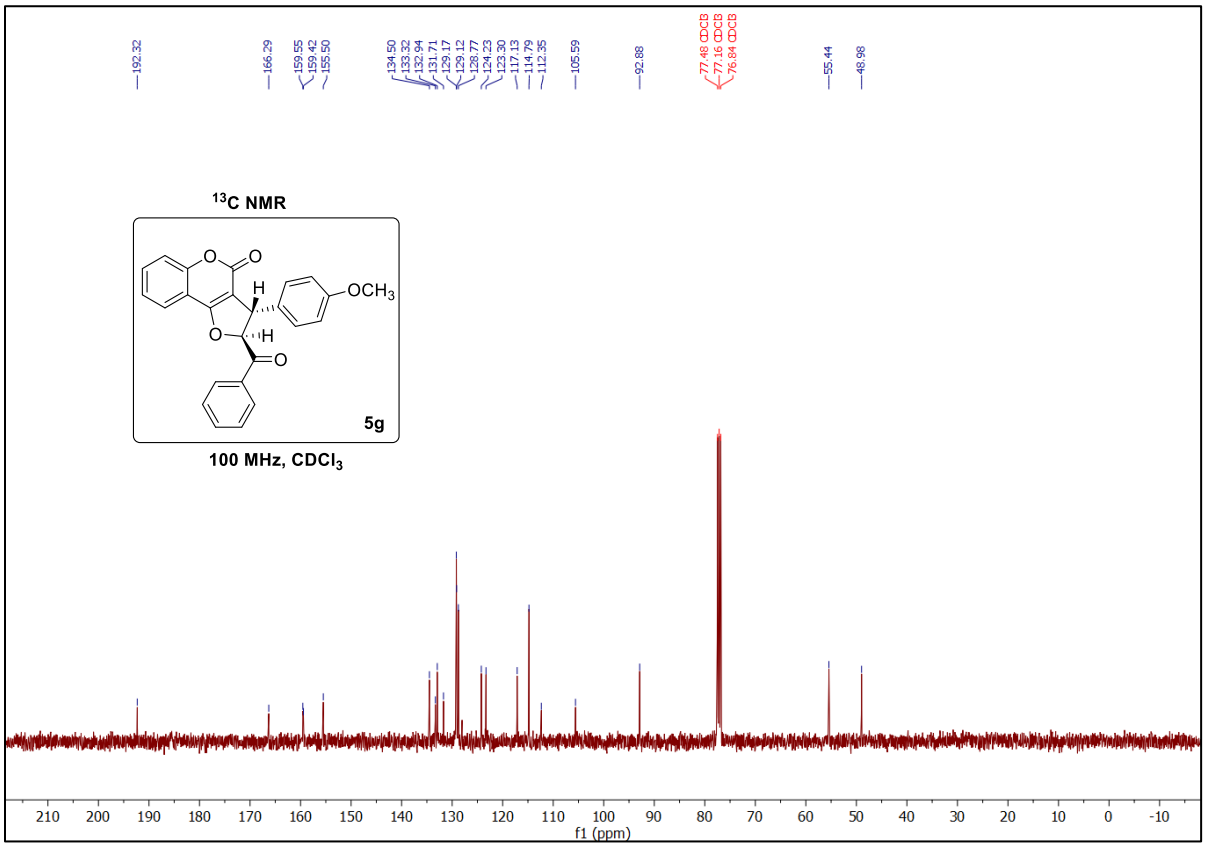

$^{13}$C NMR
5e
100 MHz, $CDCl_3$
f1 (ppm)

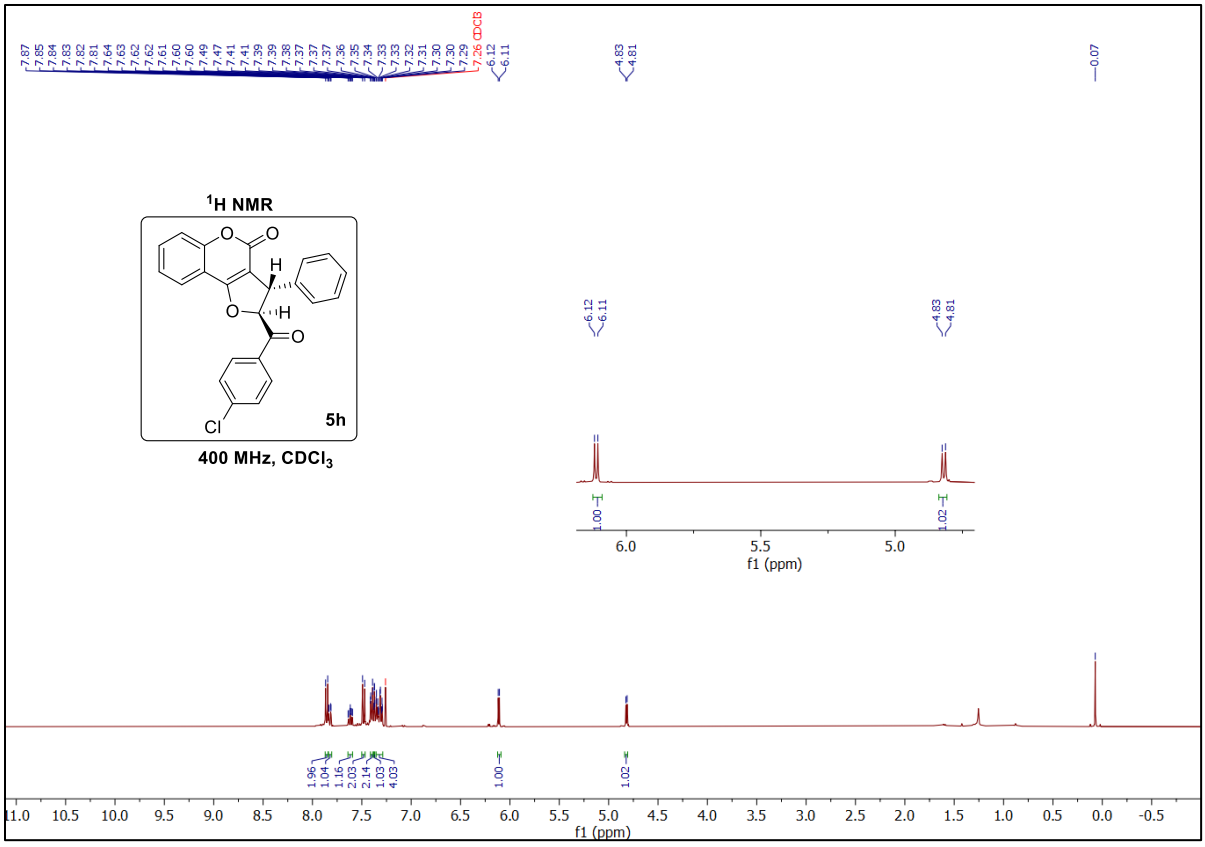

$^{13}$C NMR
5e
100 MHz, $CDCl_3$
f1 (ppm)

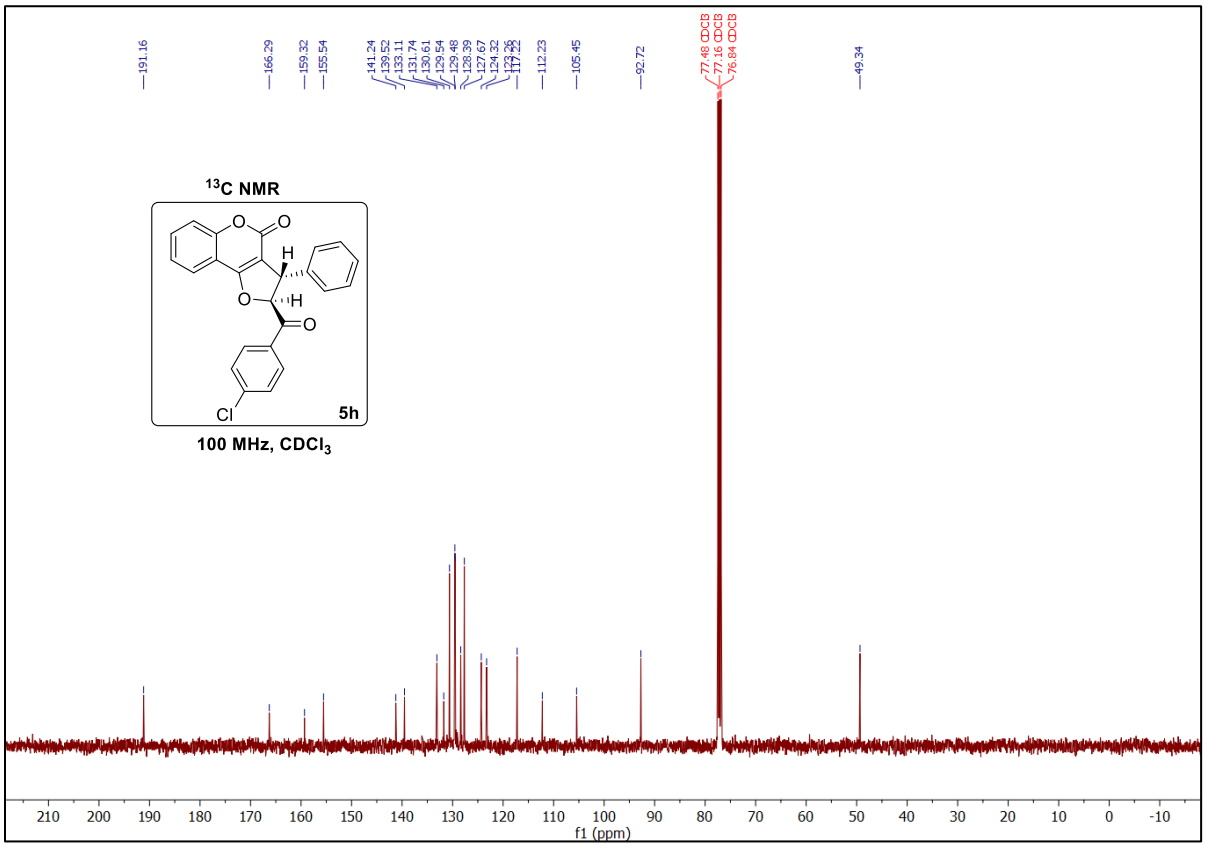

1H NMR
5f
400 MHz, CDCl3
f1 (ppm)


13C NMR
5f
100 MHz, CDCl3
f1 (ppm)


$^1$H NMR
5g
400 MHz, $CDCl_3$
f1 (ppm)


$^{13}$C NMR
5g
100 MHz, $CDCl_3$
f1 (ppm)


$^1$H NMR
5h
400 MHz, $CDCl_3$
f1 (ppm)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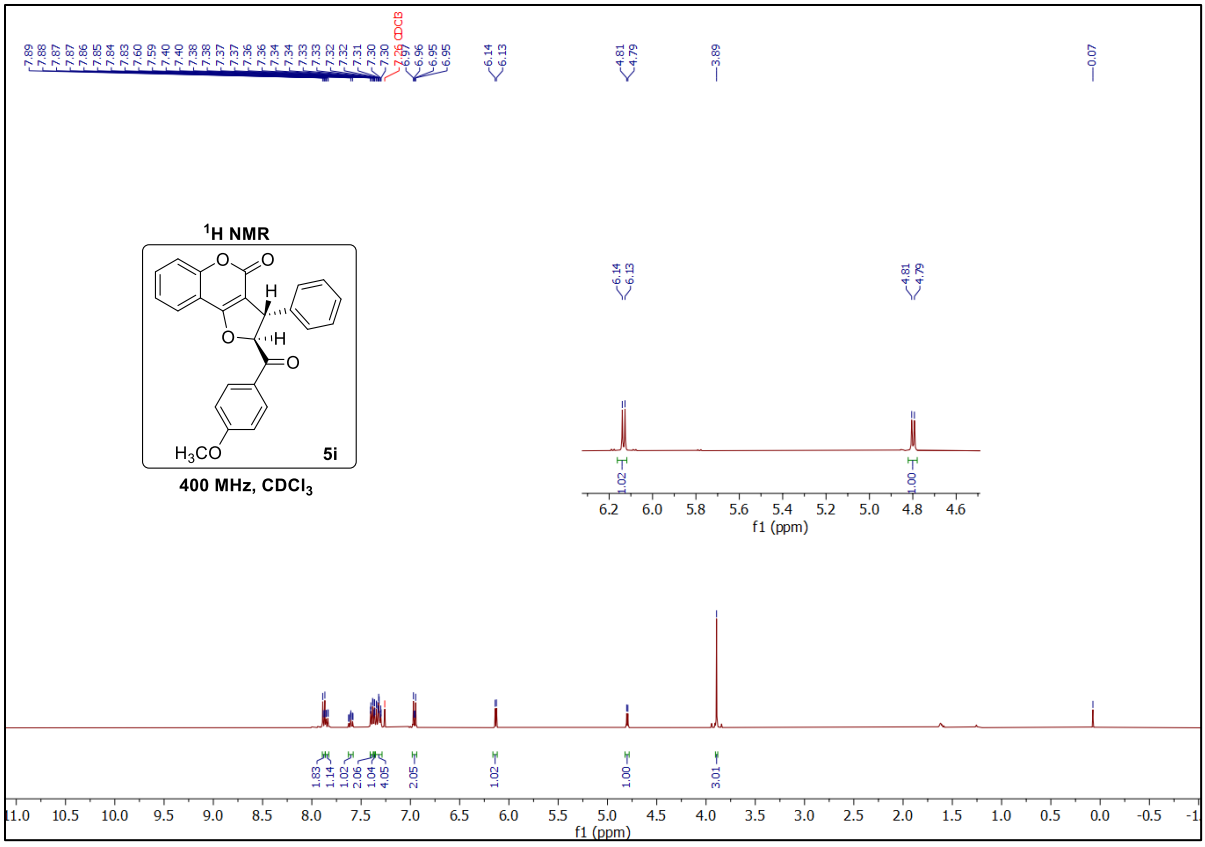
5h
100 MHz, $CDCl_3$
f1 (ppm)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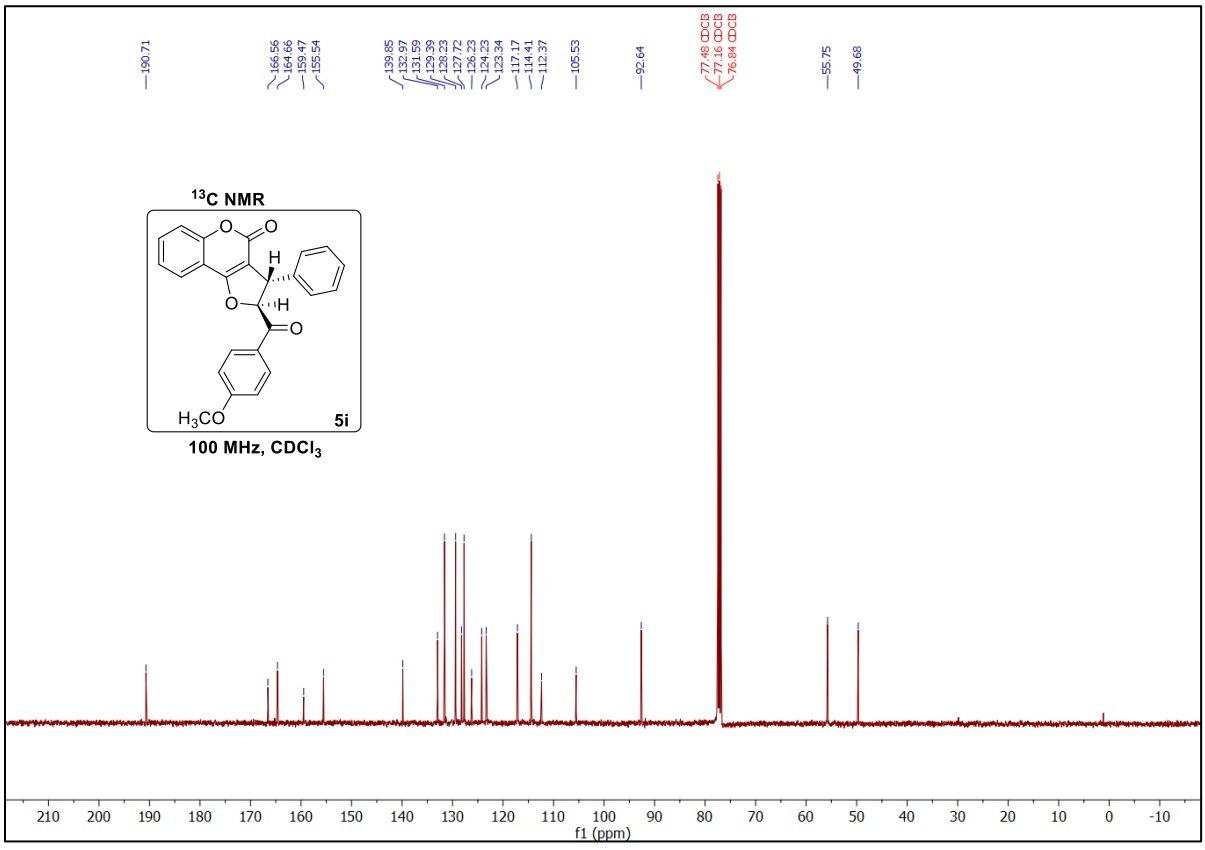
5i
400 MHz, $CDCl_3$
f1 (ppm)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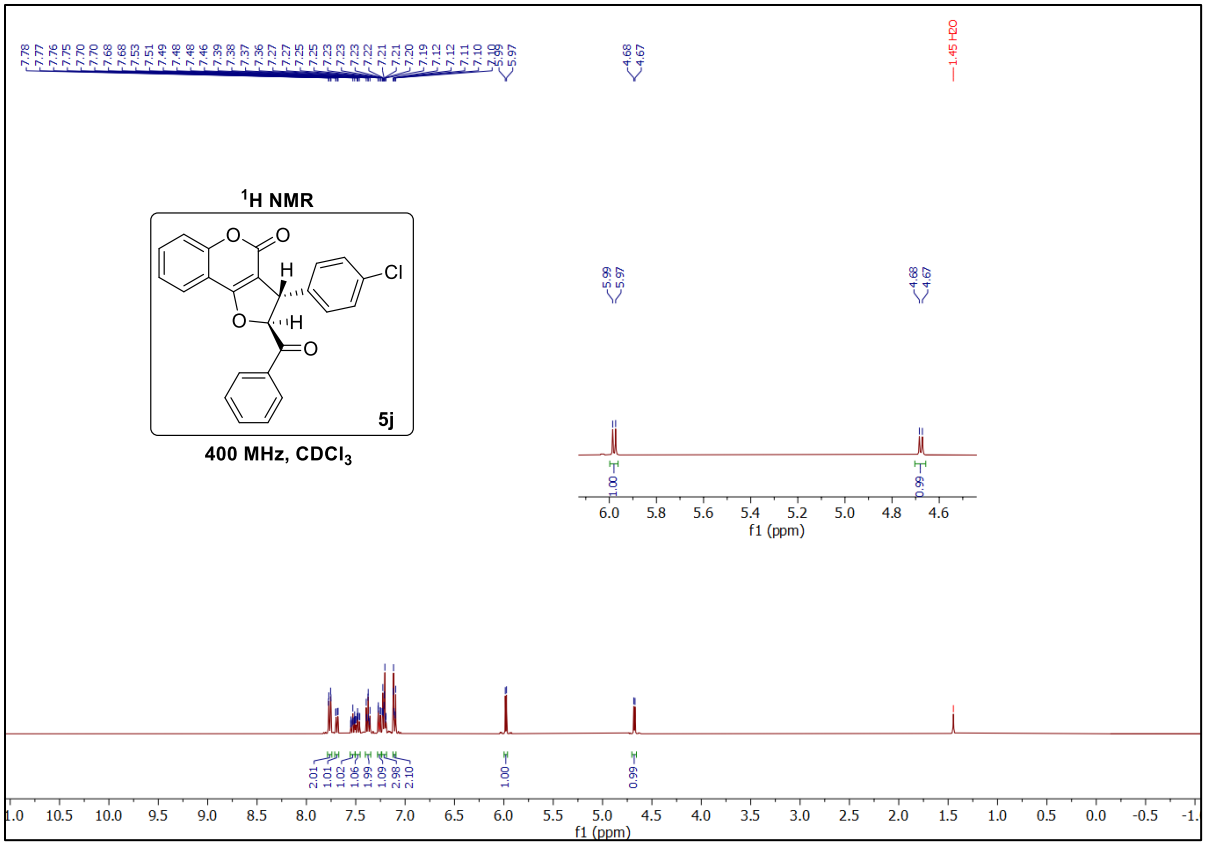
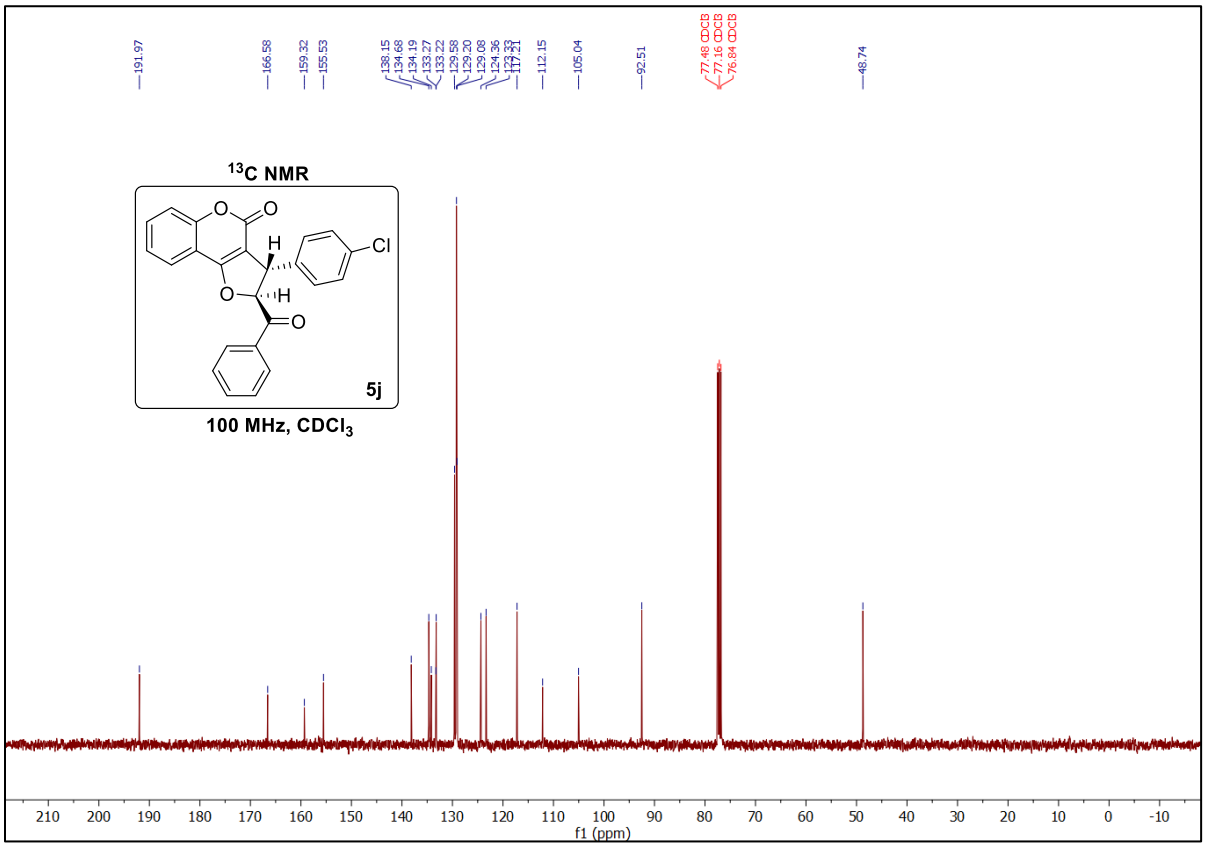
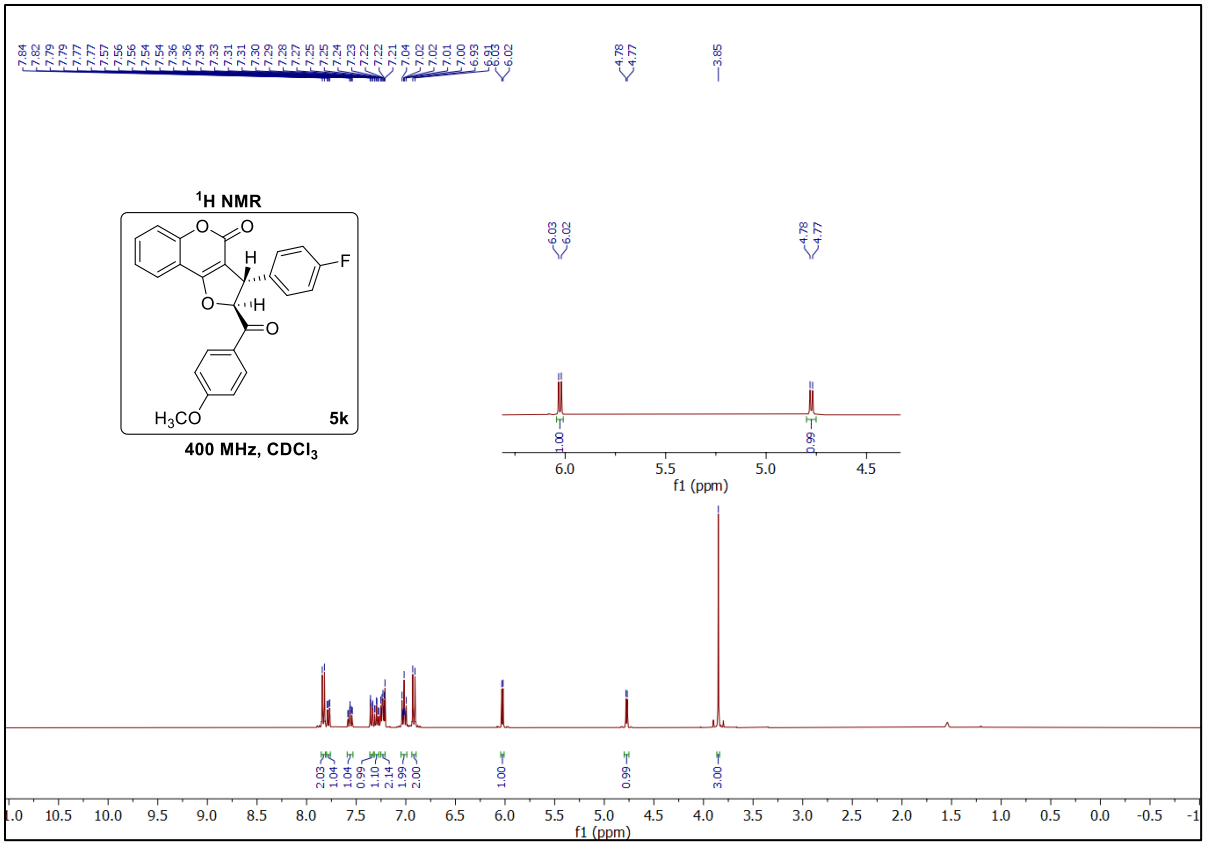
5i
100 MHz, $CDCl_3$
f1 (ppm)


1H NMR
5j
400 MHz, CDCl3
f1 (ppm)


13C NMR
5j
100 MHz, CDCl3
f1 (ppm)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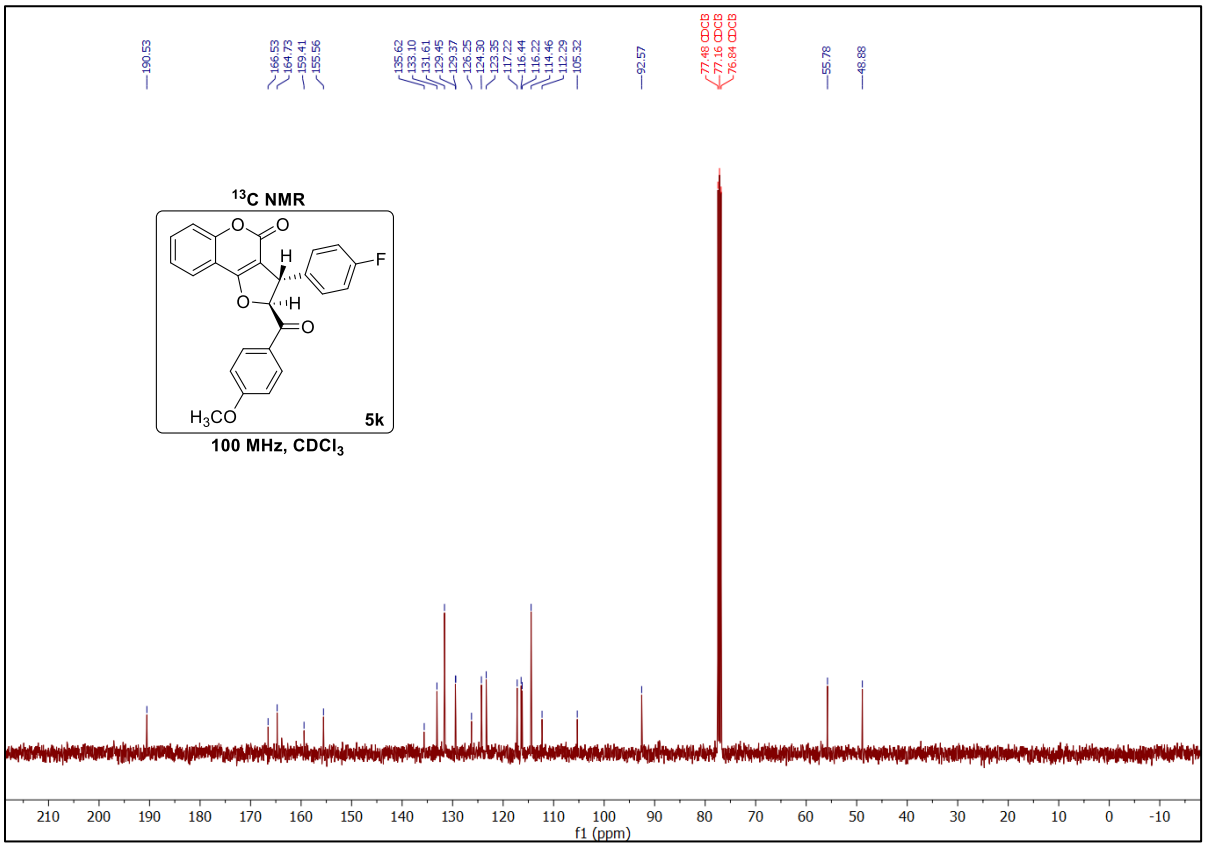
5k
400 MHz, $CDCl_3$
f1 (ppm)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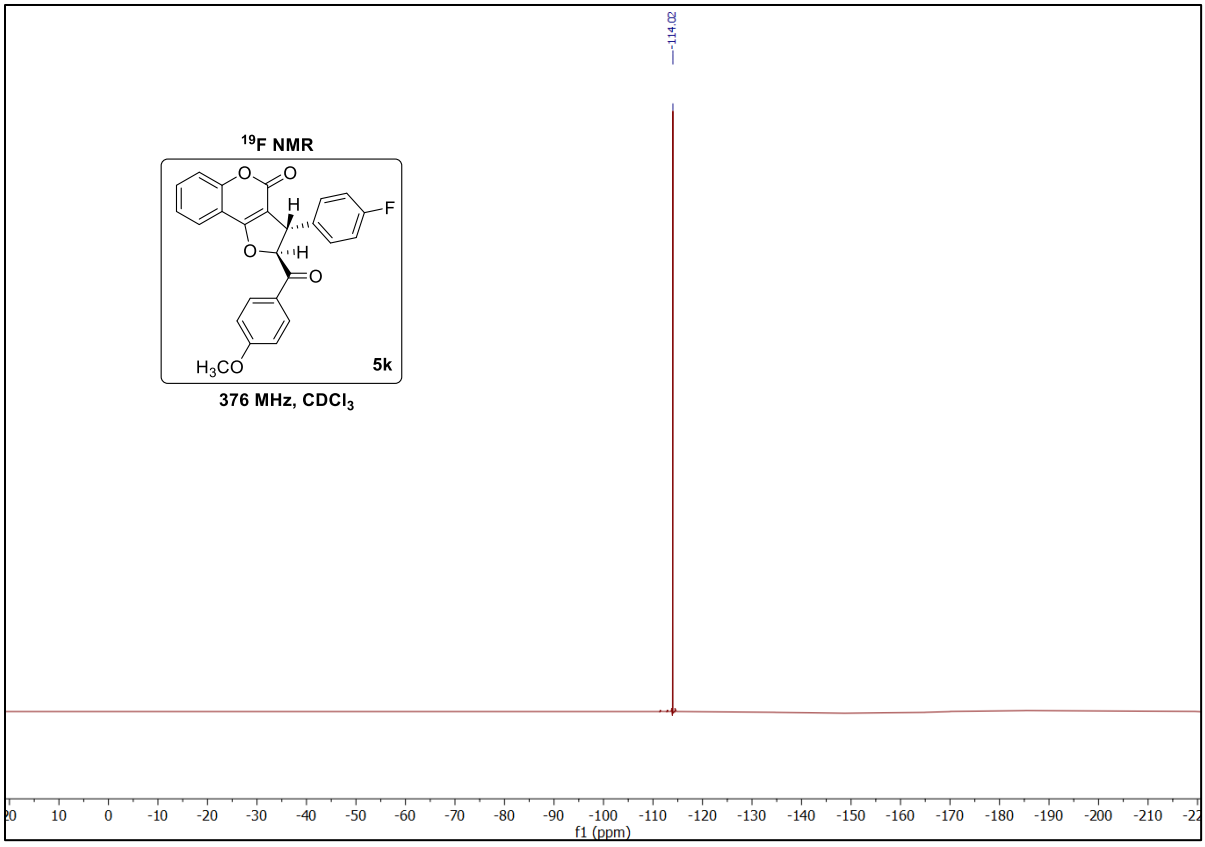
5k
100 MHz, $CDCl_3$
f1 (ppm)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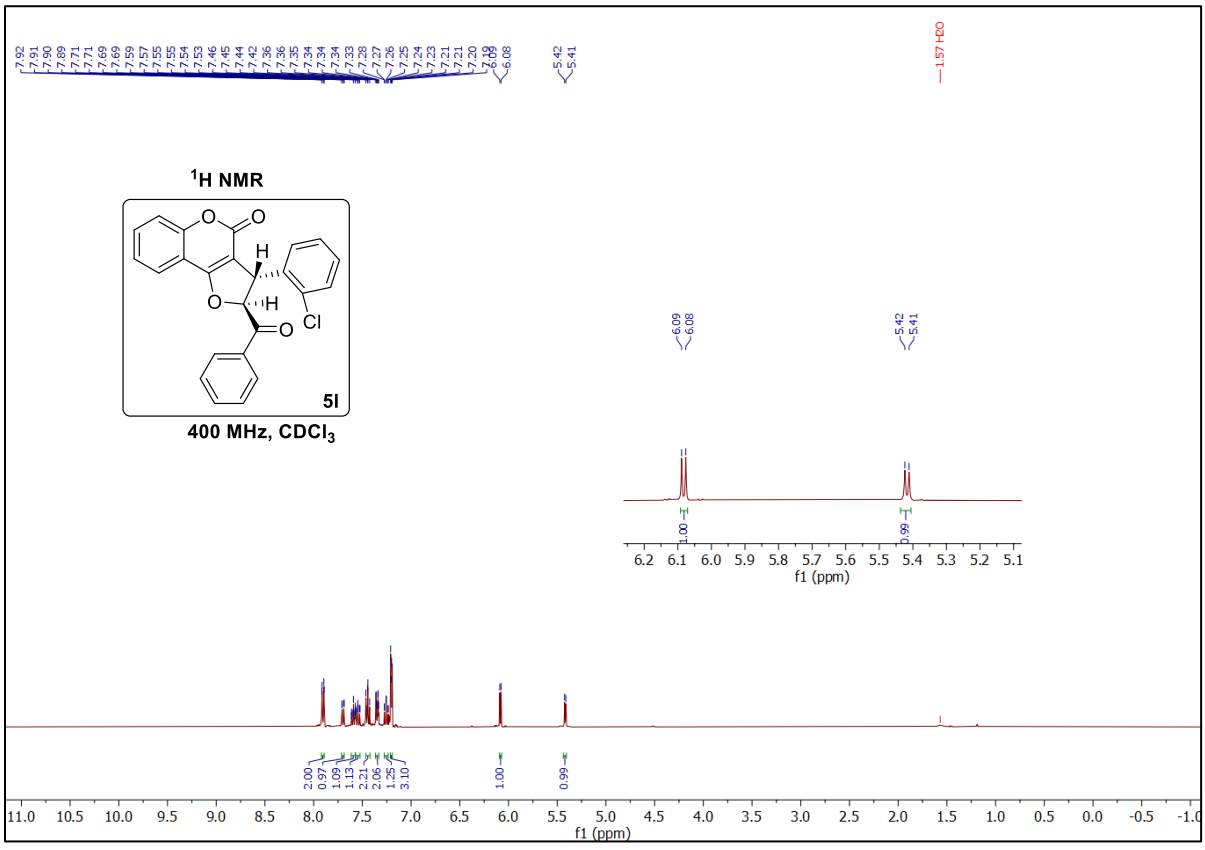
5k
376 MHz, CDCl3
-114.02
f1 (ppm)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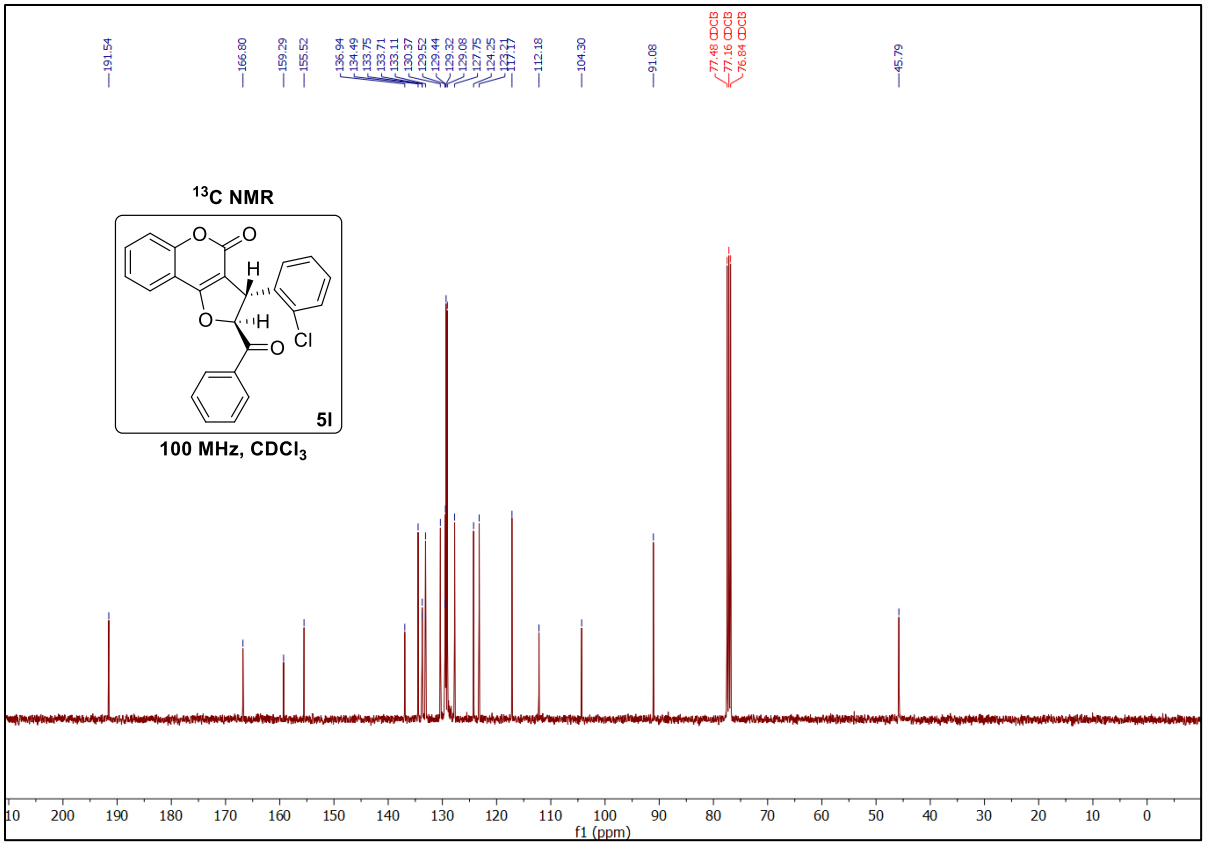
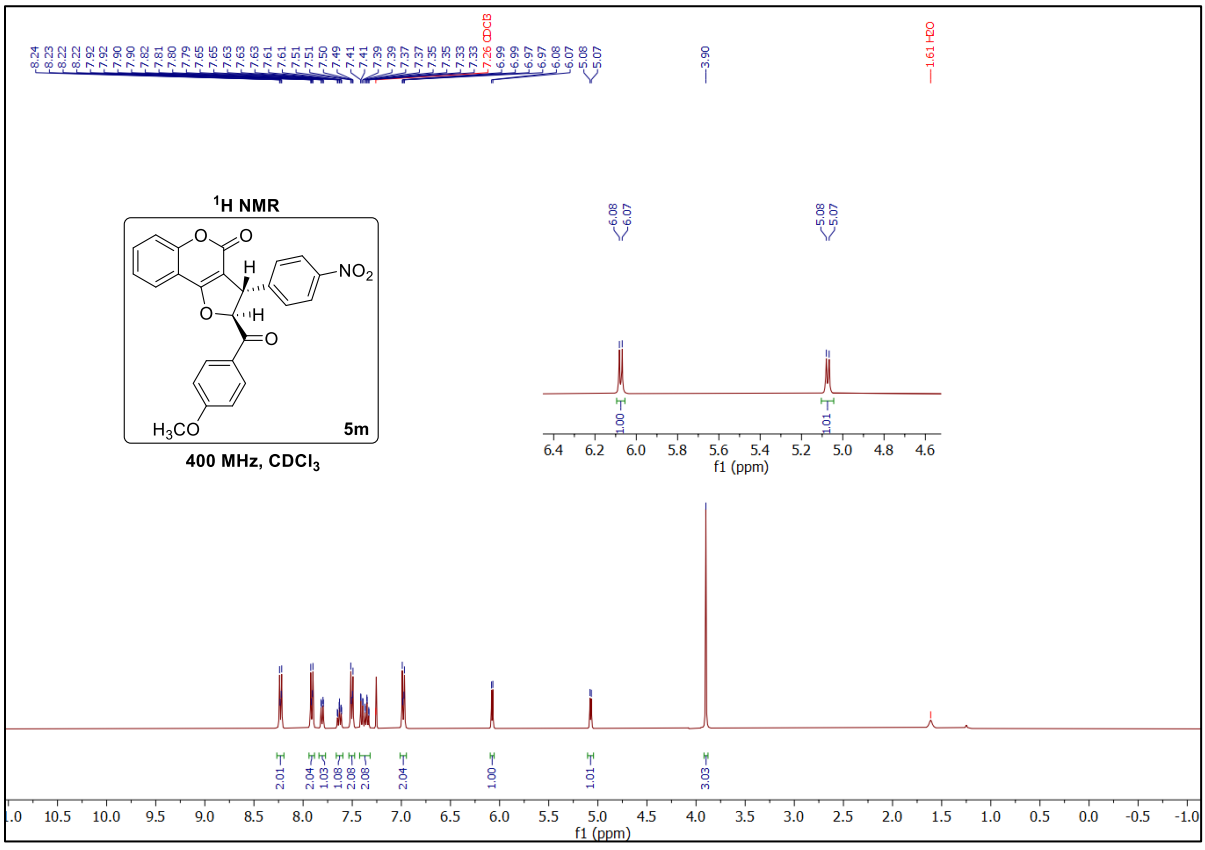
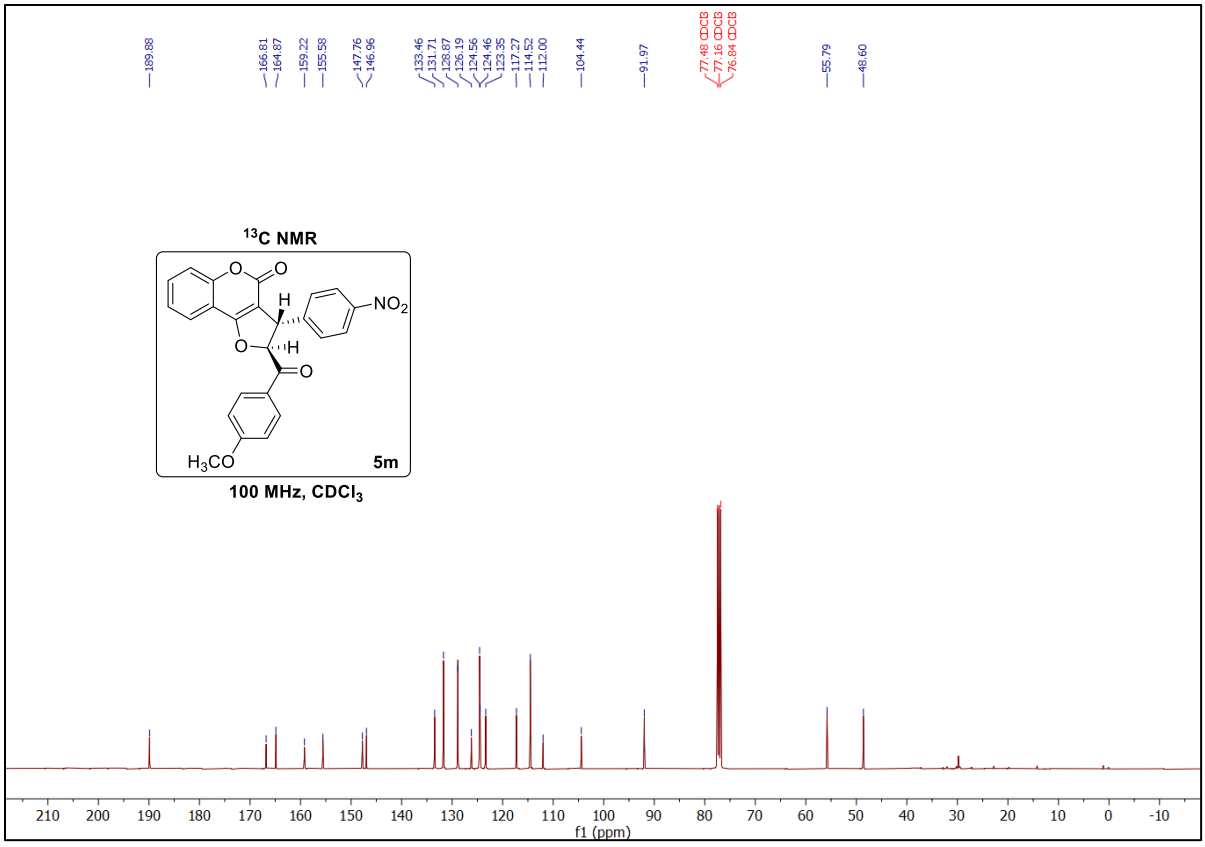
5l
400 MHz, CDCl3
1.57 H2O
6.09
6.08
5.42
5.41
f1 (ppm)


$^{13}$C NMR
5l
100 MHz, CDCl$_3$
f1 (ppm)


$^{1}$H NMR
5m
400 MHz, CDCl$_3$
f1 (ppm)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155.58
147.76
146.96
133.46
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128.87
126.19
124.56
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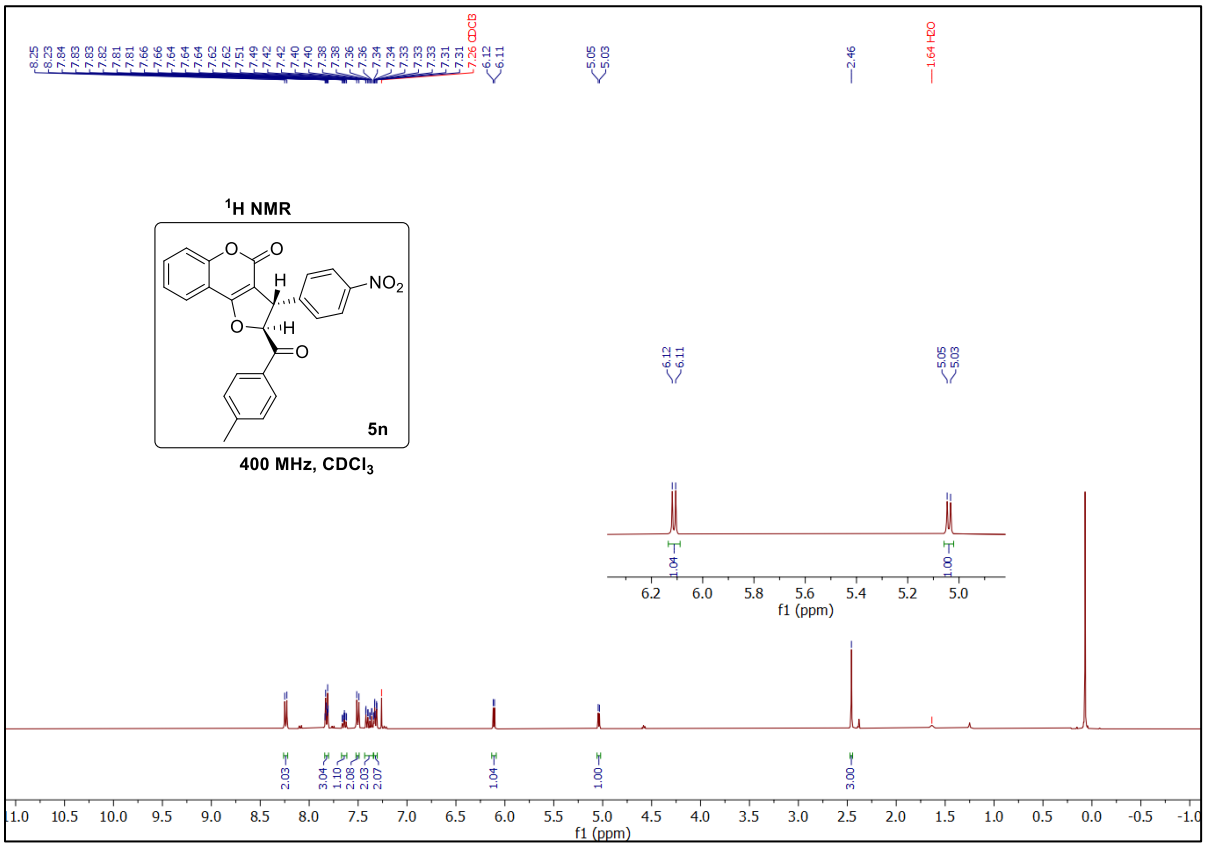
123.35
117.27
114.52
112.00
104.44
91.97
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
55.79
48.60
13C NMR
NO2
H3CO
5m
100 MHz, CDCl3
f1 (ppm)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8.23
7.84
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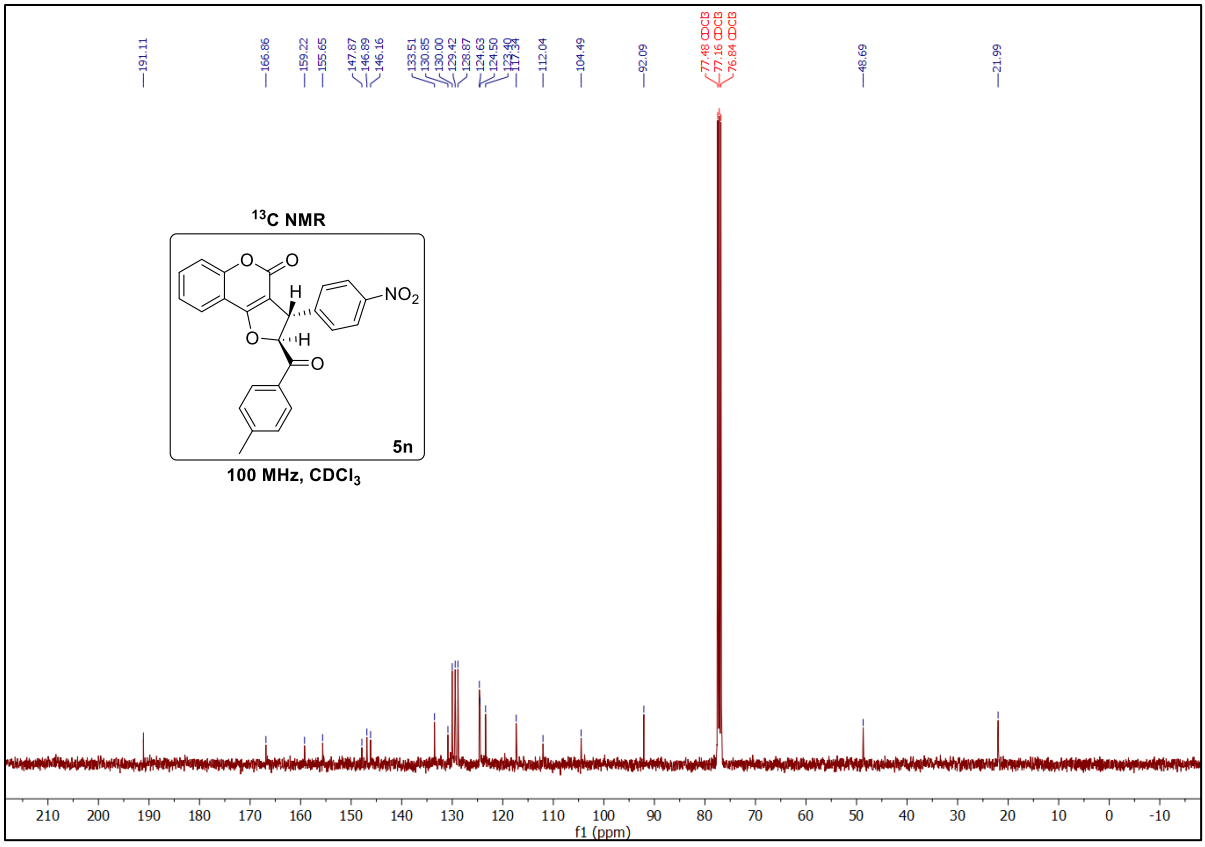
7.83
7.82
7.81
7.81
7.66
7.66
7.64
7.64
7.64
7.62
7.62
7.51
7.49
7.42
7.42
7.40
7.40
7.38
7.38
7.36
7.36
7.34
7.34
7.33
7.33
7.31
7.31
7.26 CDCl3
6.12
6.11
5.05
5.03
2.46
1.64 H2O
1H NMR
NO2
5n
400 MHz, CDCl3
6.12
6.11
5.05
5.03
1.04
1.00
f1 (ppm)
2.03
3.04
1.10
2.08
2.03
2.07
1.04
1.00
3.00
f1 (ppm)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166.86
159.22
155.65
147.87
146.89
146.16
133.51
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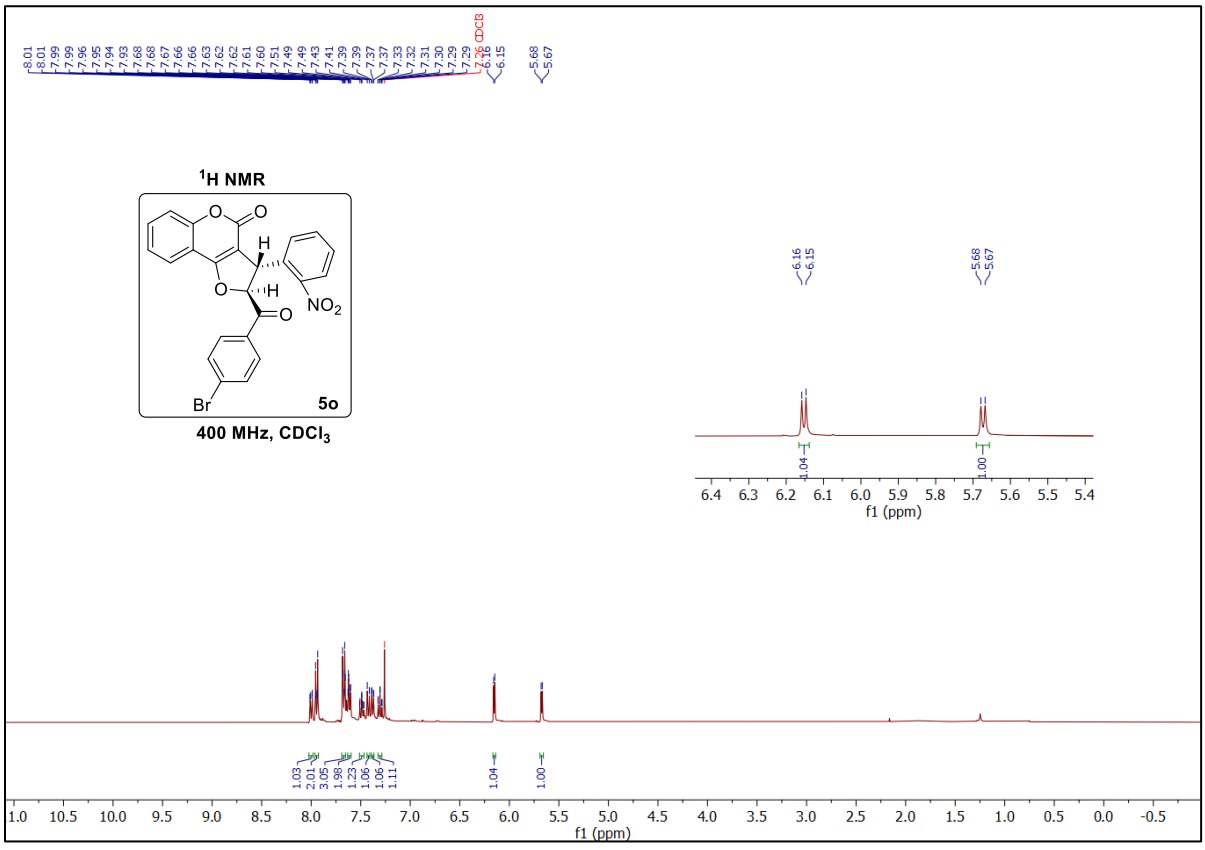
130.00
129.42
128.87
124.63
124.50
112.04
104.49
92.09
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
48.69
21.99
13C NMR
5n
100 MHz, CDCl3
f1 (ppm)


8.01
7.99
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7.95
7.94
7.93
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7.67
7.66
7.63
7.62
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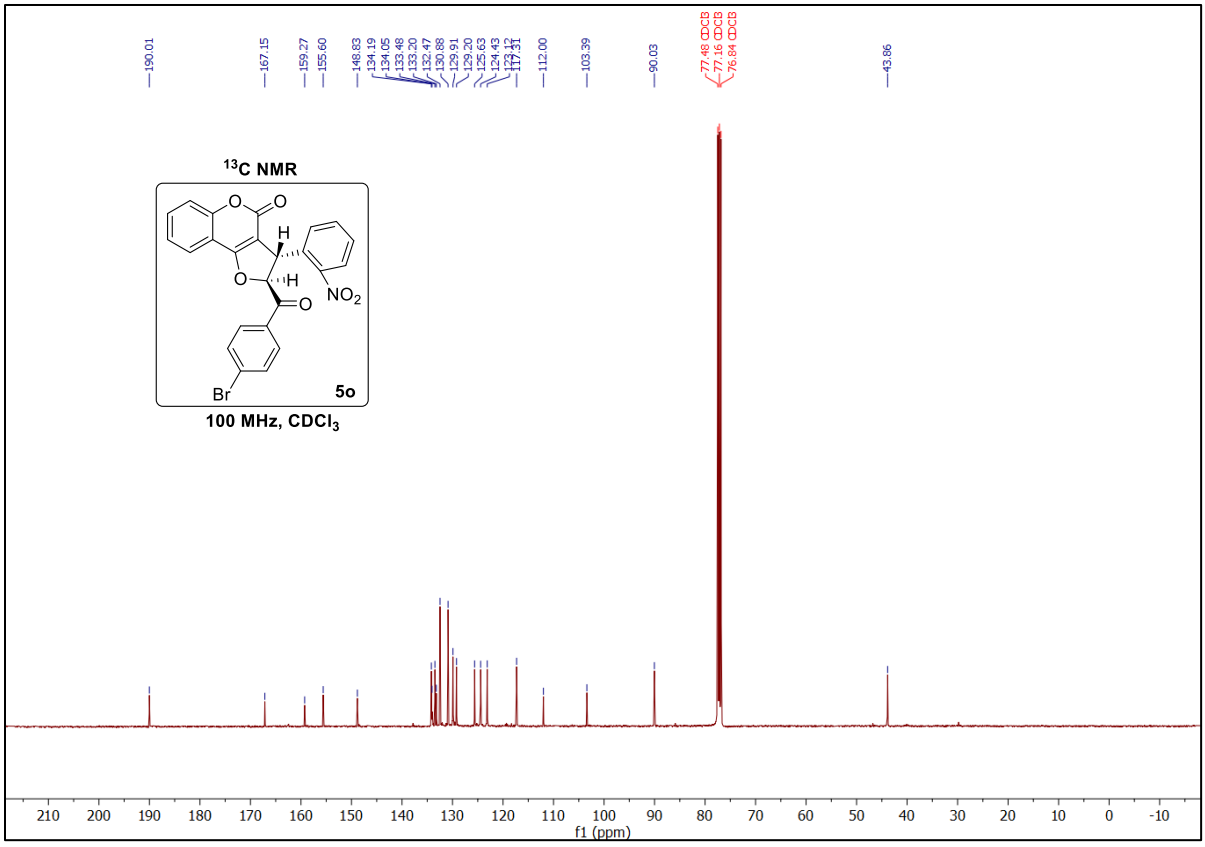
7.60
7.51
7.49
7.43
7.41
7.39
7.37
7.33
7.32
7.31
7.30
7.29
7.26 CDCl3
6.16
6.15
5.68
5.67
1H NMR
5o
400 MHz, CDCl3
1.04
1.00
f1 (ppm)
1.03
2.01
3.05
1.98
1.23
1.06
1.06
1.11
1.04
1.00
f1 (ppm)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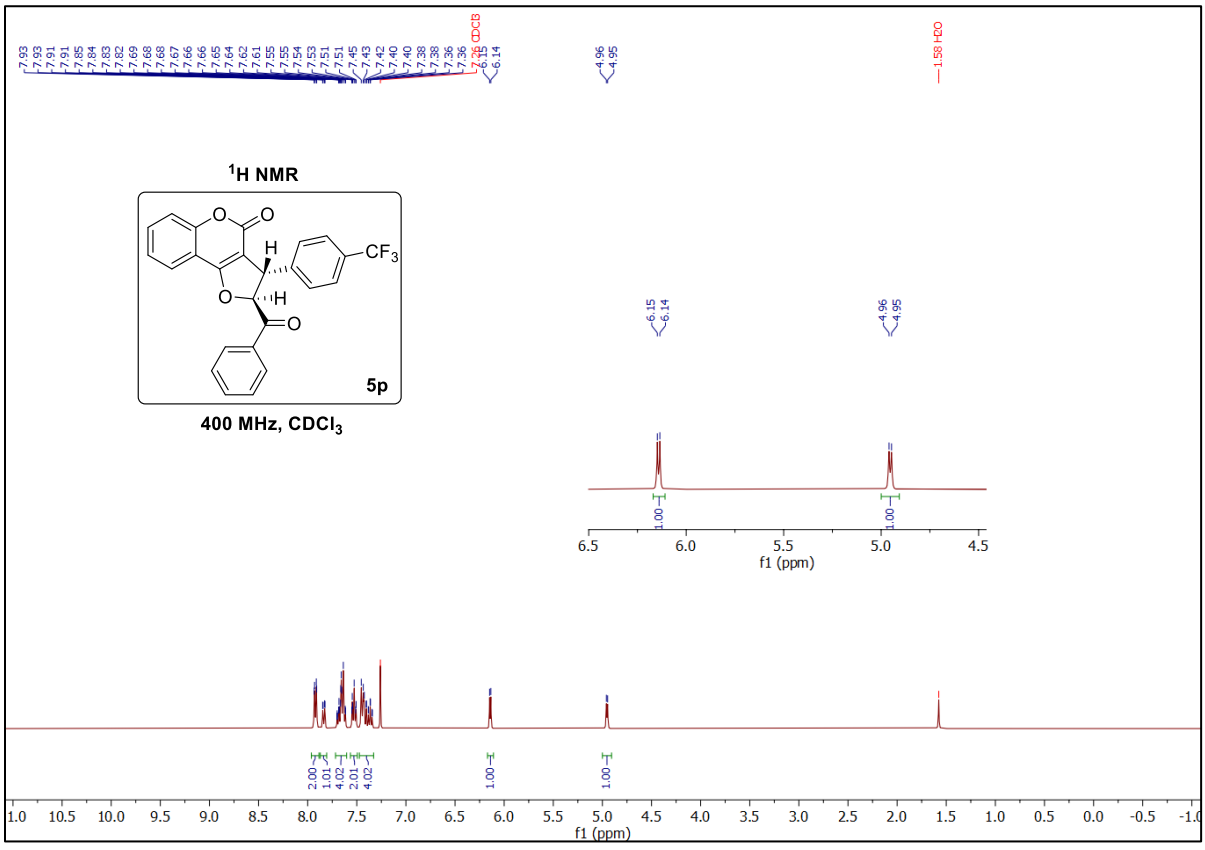
5o
100 MHz, CDCl$_3$
f1 (ppm)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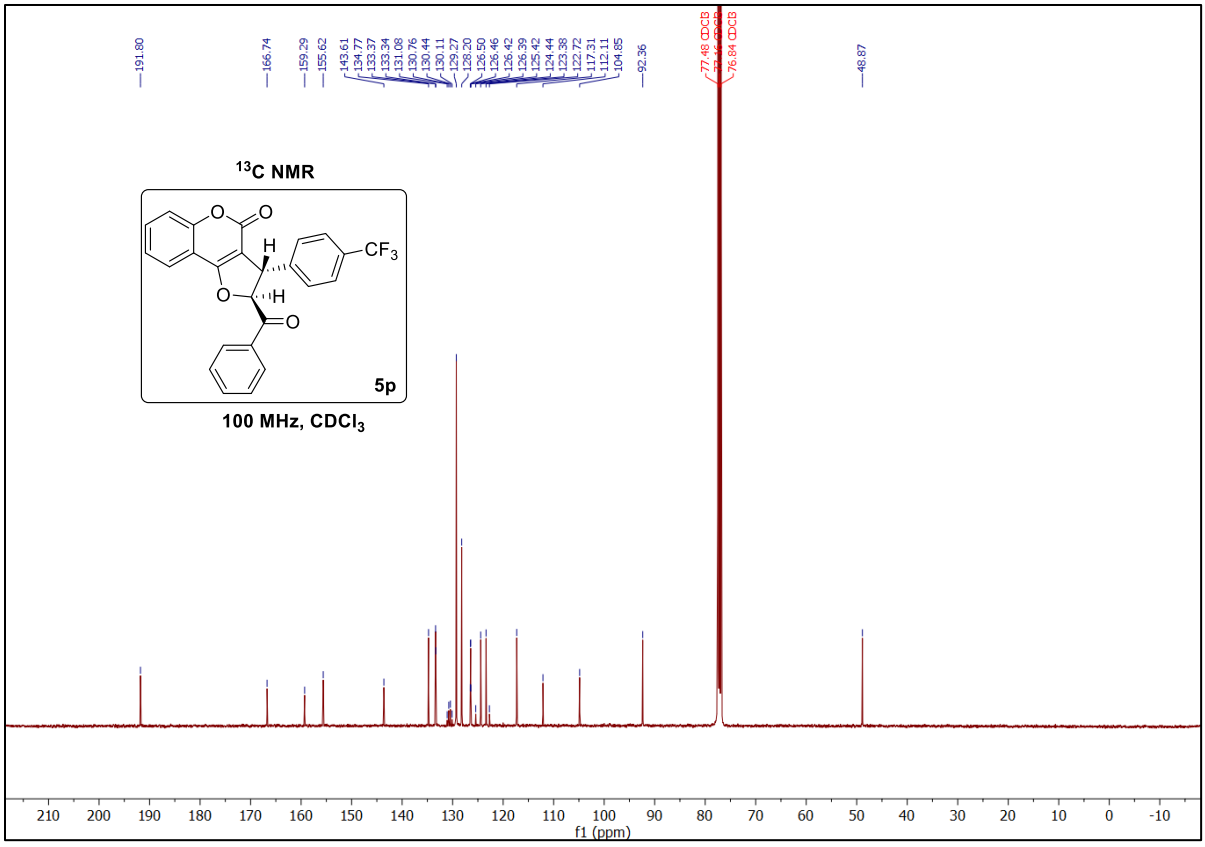
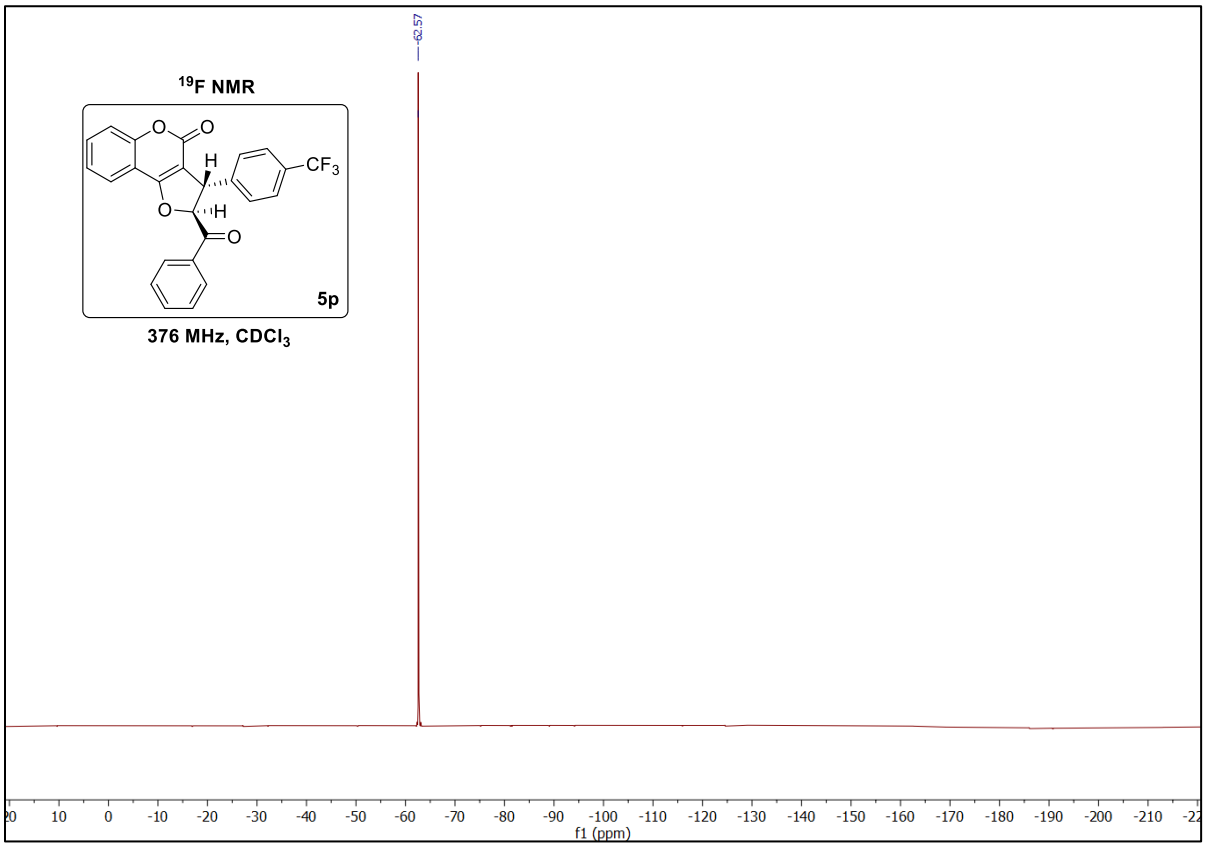
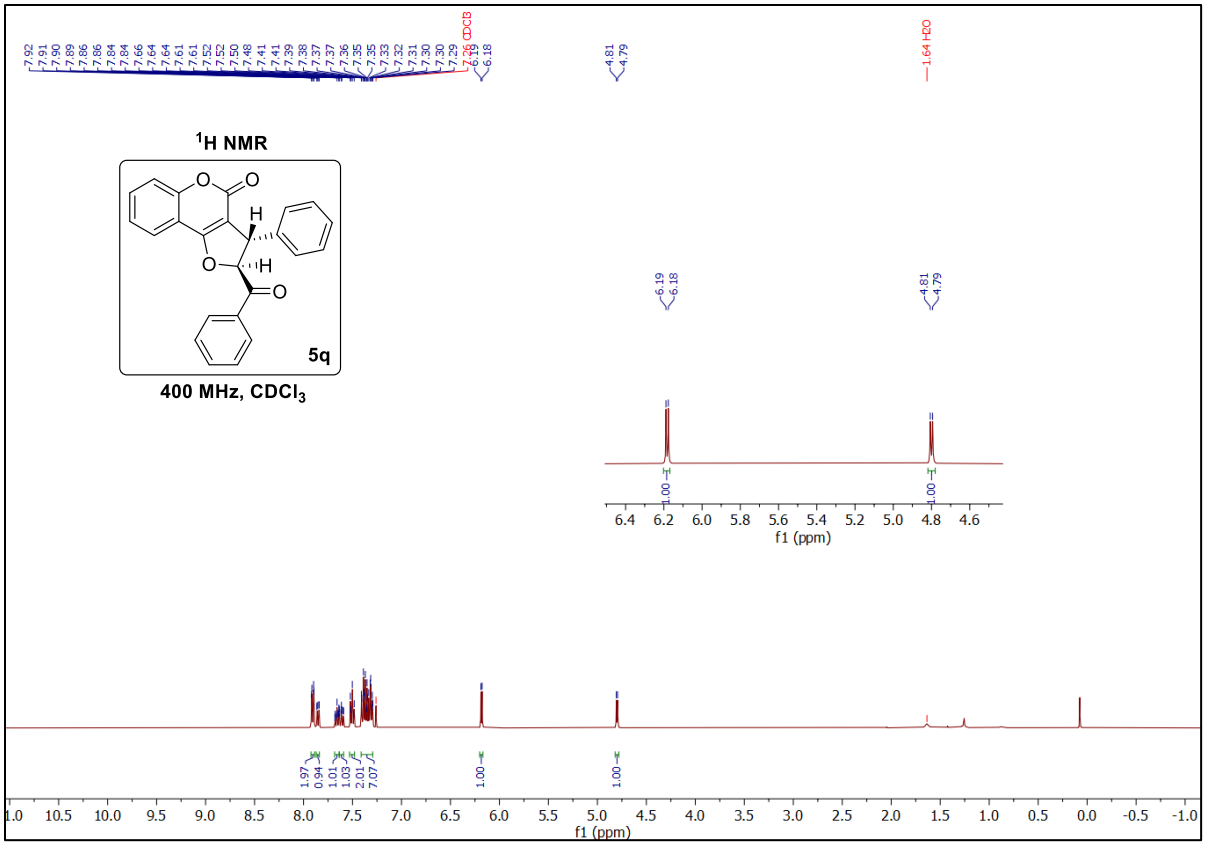
5p
400 MHz, CDCl$_3$
f1 (ppm)


$^{13}$C NMR
5p
100 MHz, $CDCl_3$
f1 (ppm)


$^{19}$F NMR
5p
376 MHz, $CDCl_3$
f1 (ppm)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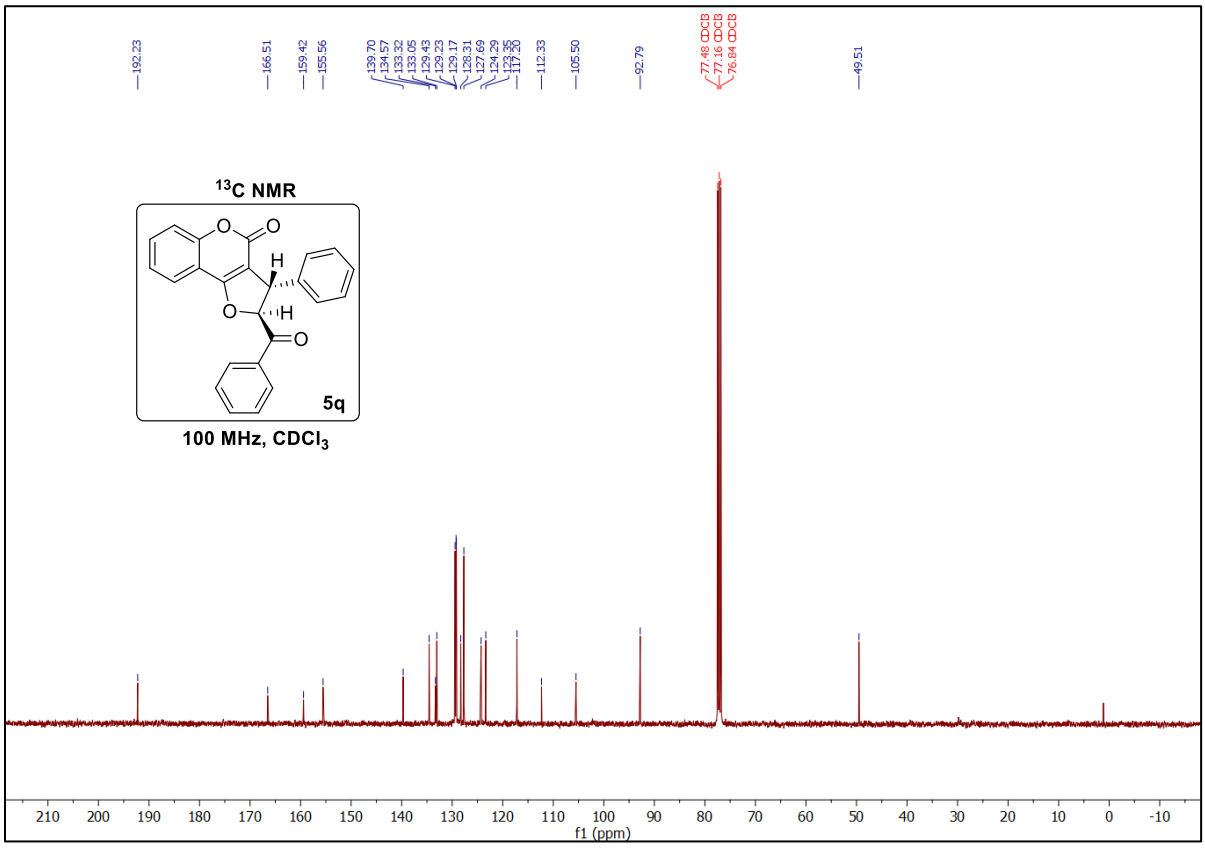
5q
400 MHz, $CDCl_3$
f1 (ppm)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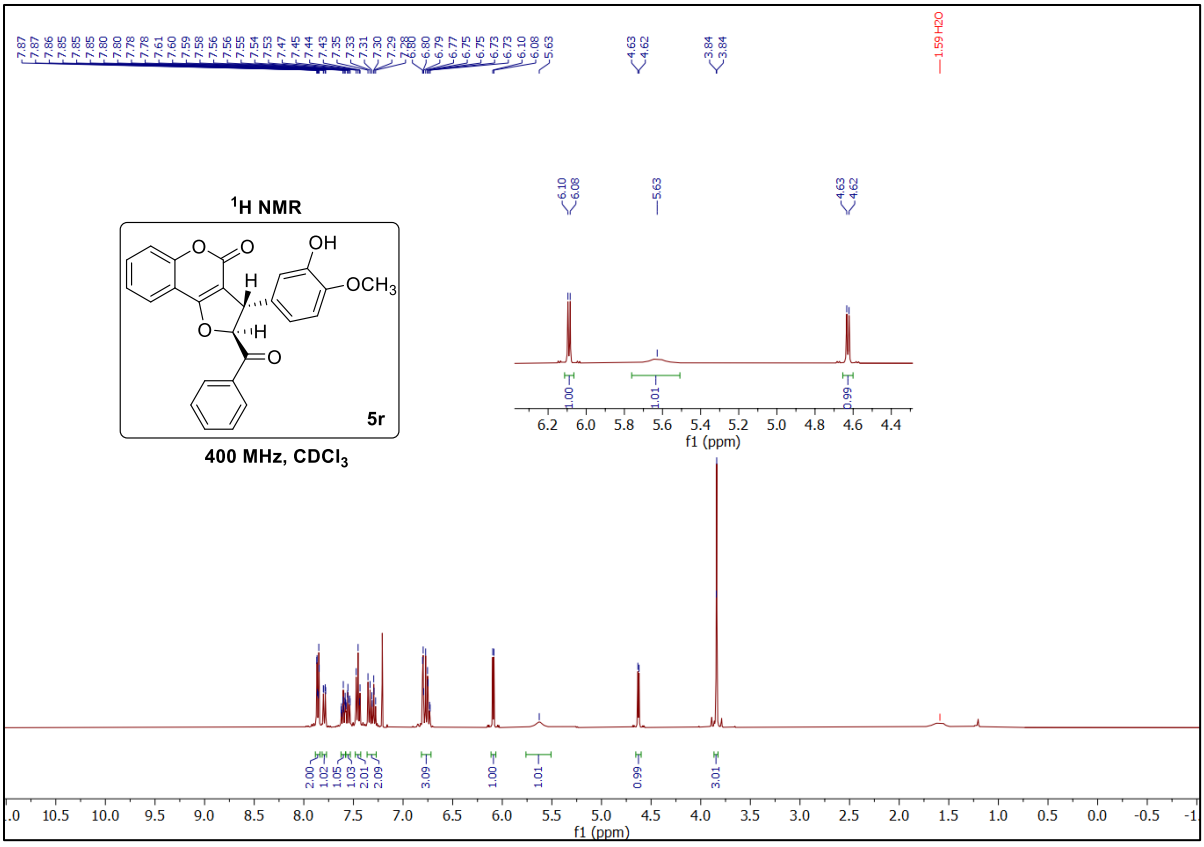
5q
100 MHz, $CDCl_3$
f1 (ppm)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5r
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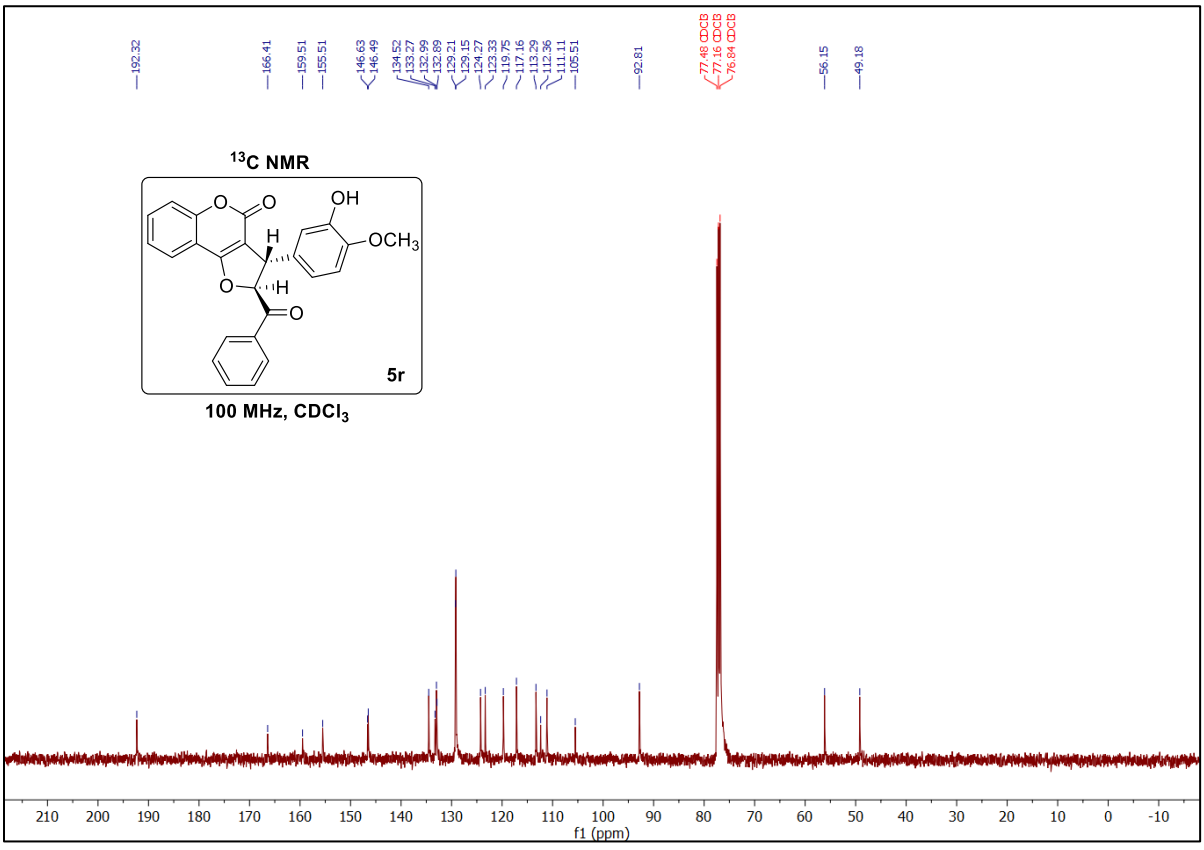
f1 (ppm)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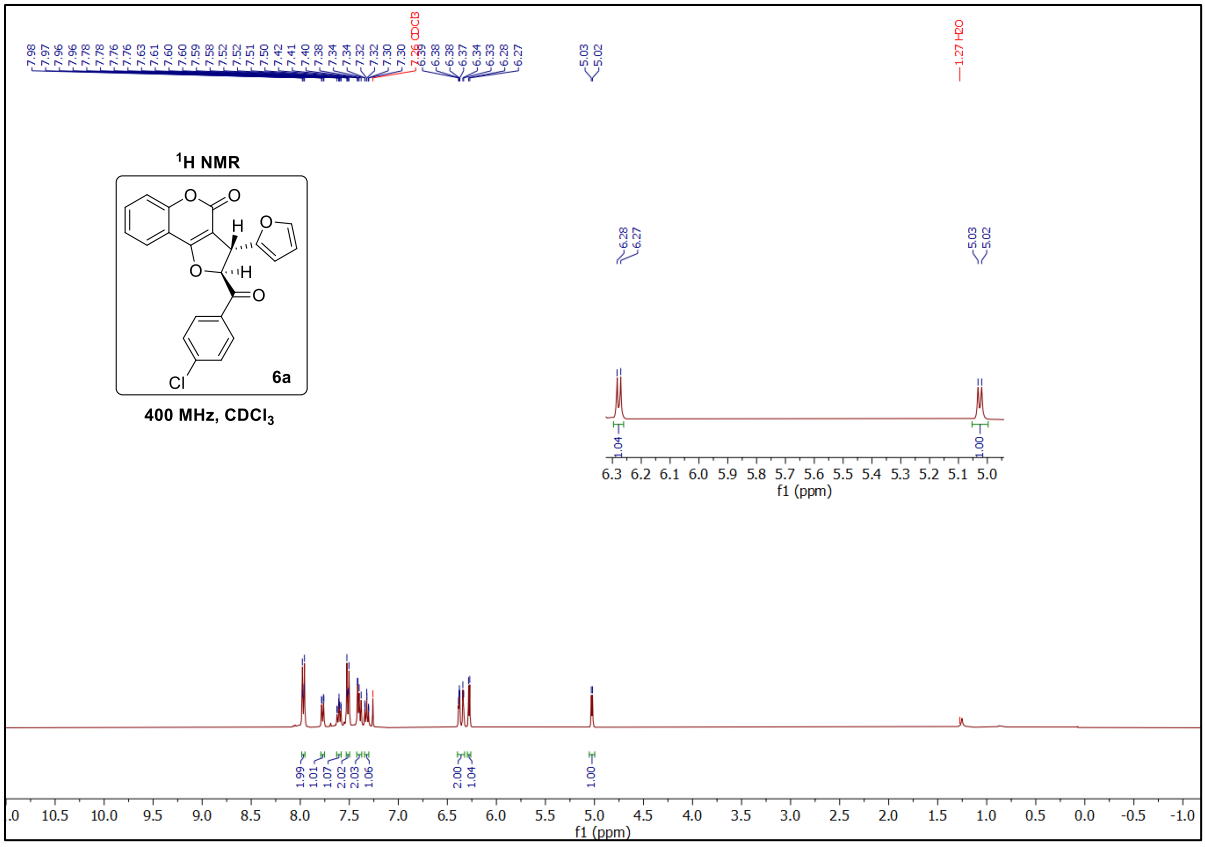
5r
100 MHz, CDCl3
f1 (ppm)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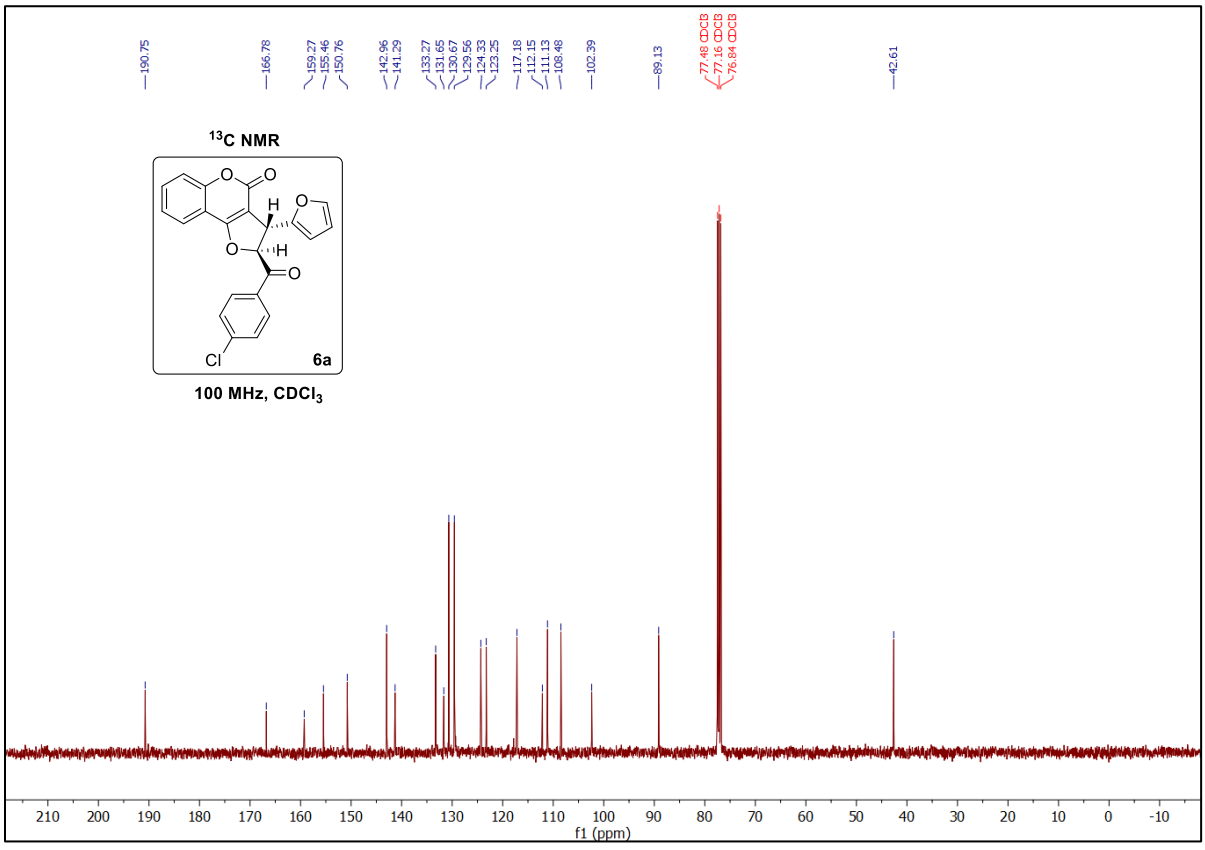
6a
400 MHz, $CDCl_3$
f1 (ppm)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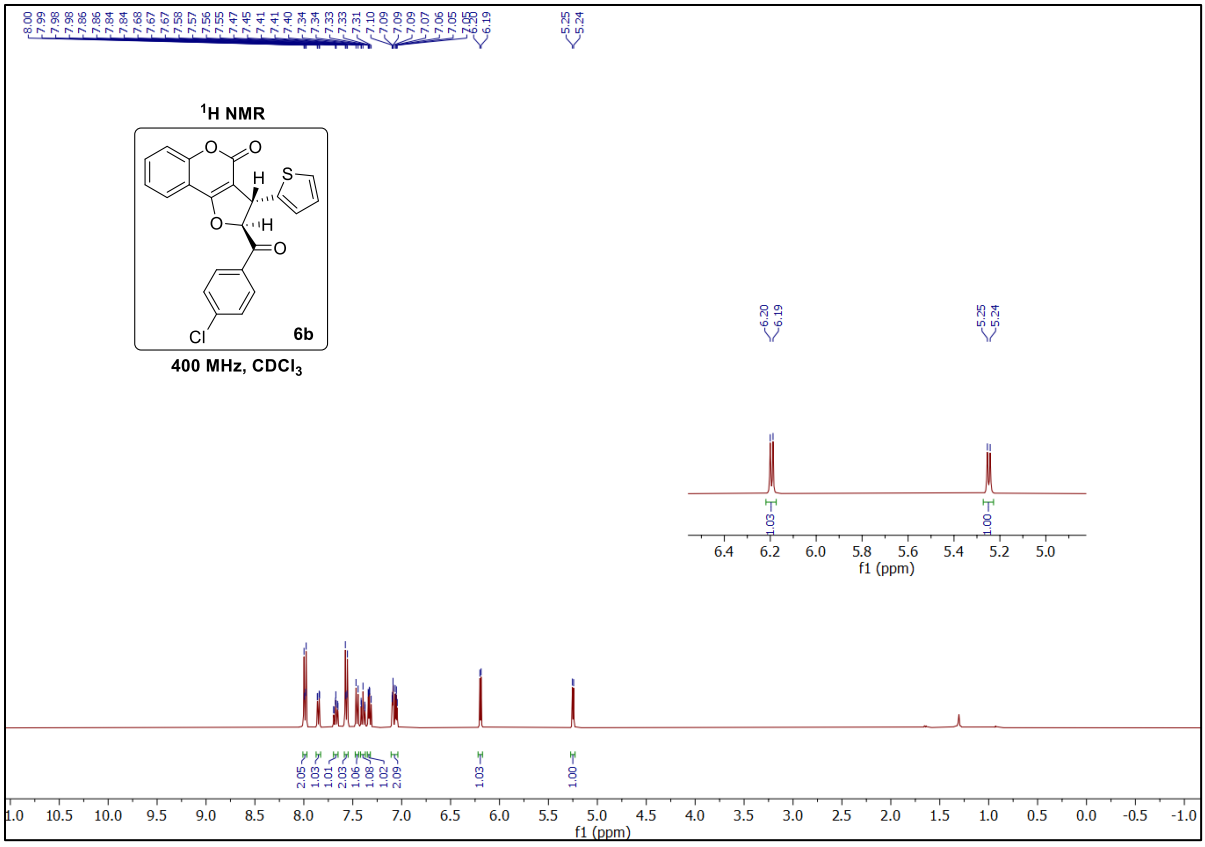
6a
100 MHz, $CDCl_3$
f1 (ppm)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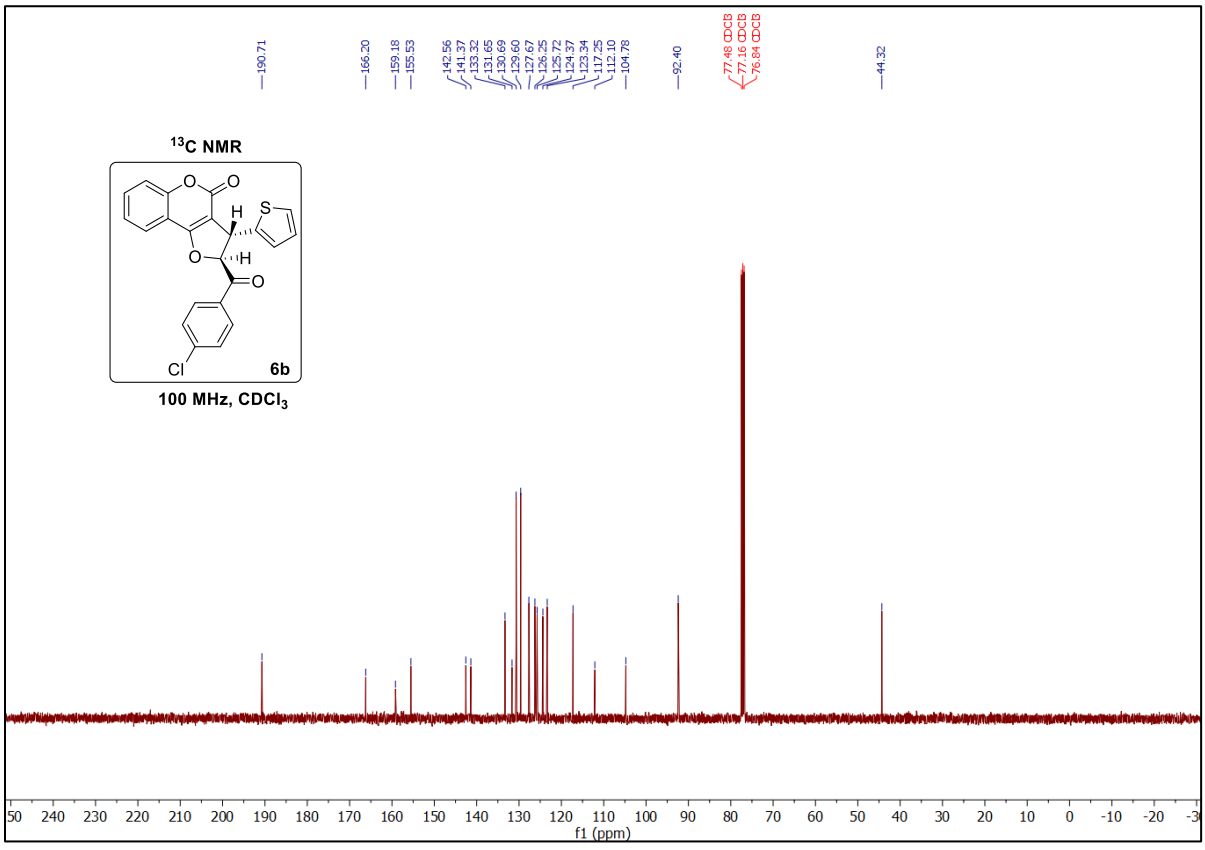
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6b
100 MHz, $CDCl_3$
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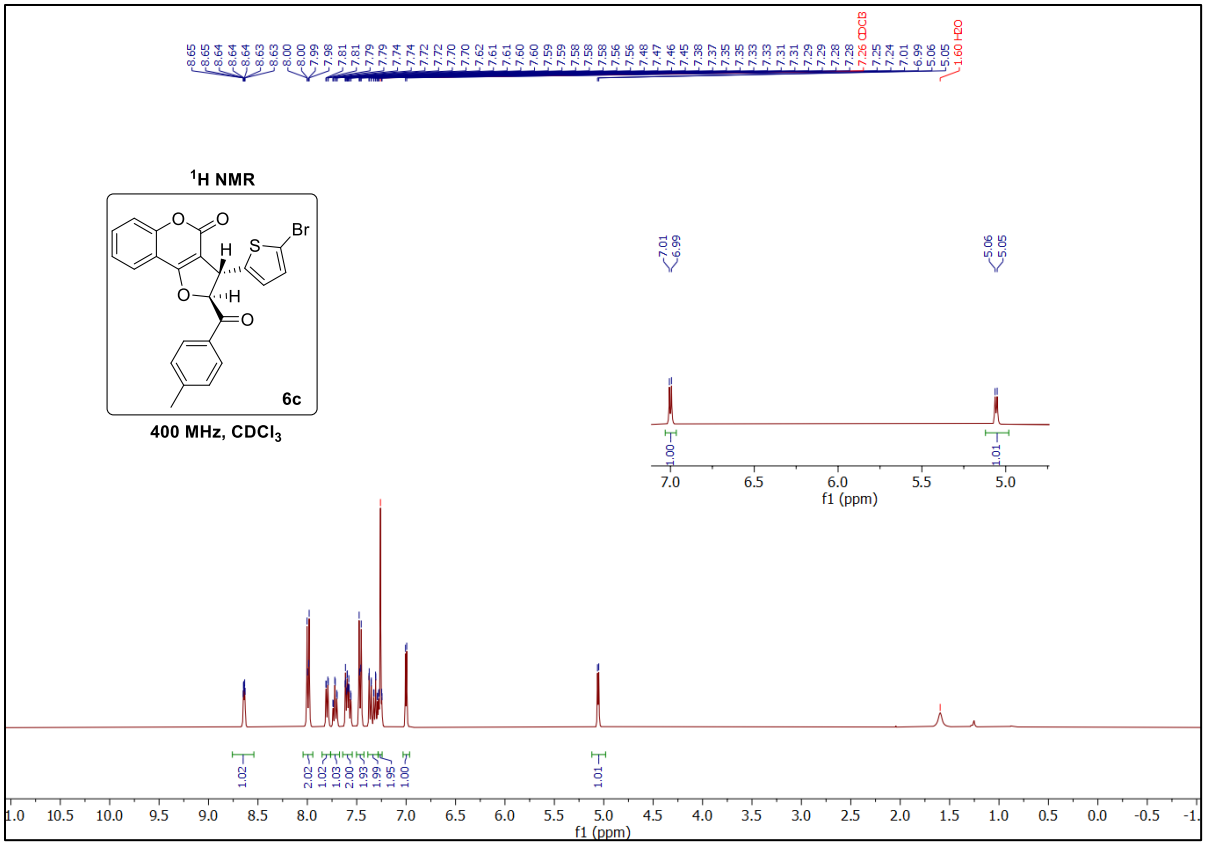
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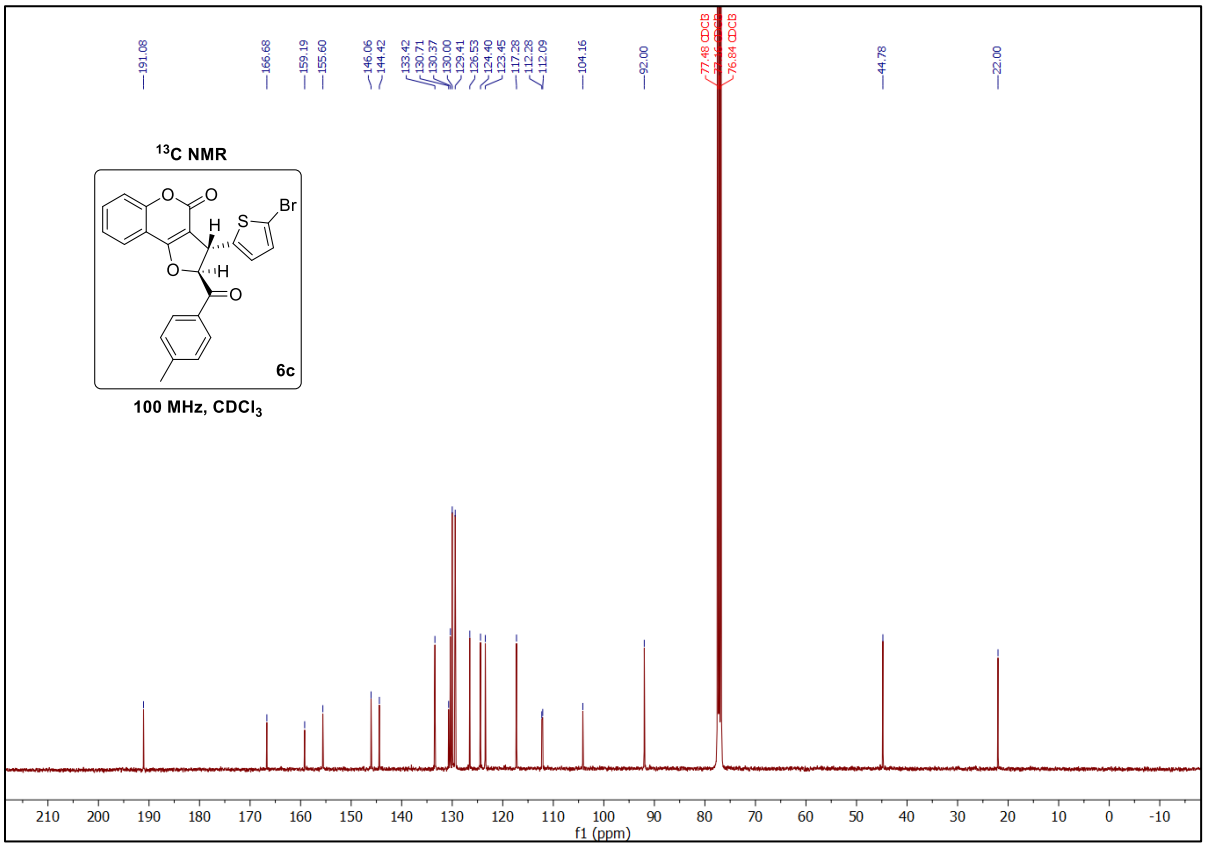
6c
400 MHz, $CDCl_3$
f1 (ppm)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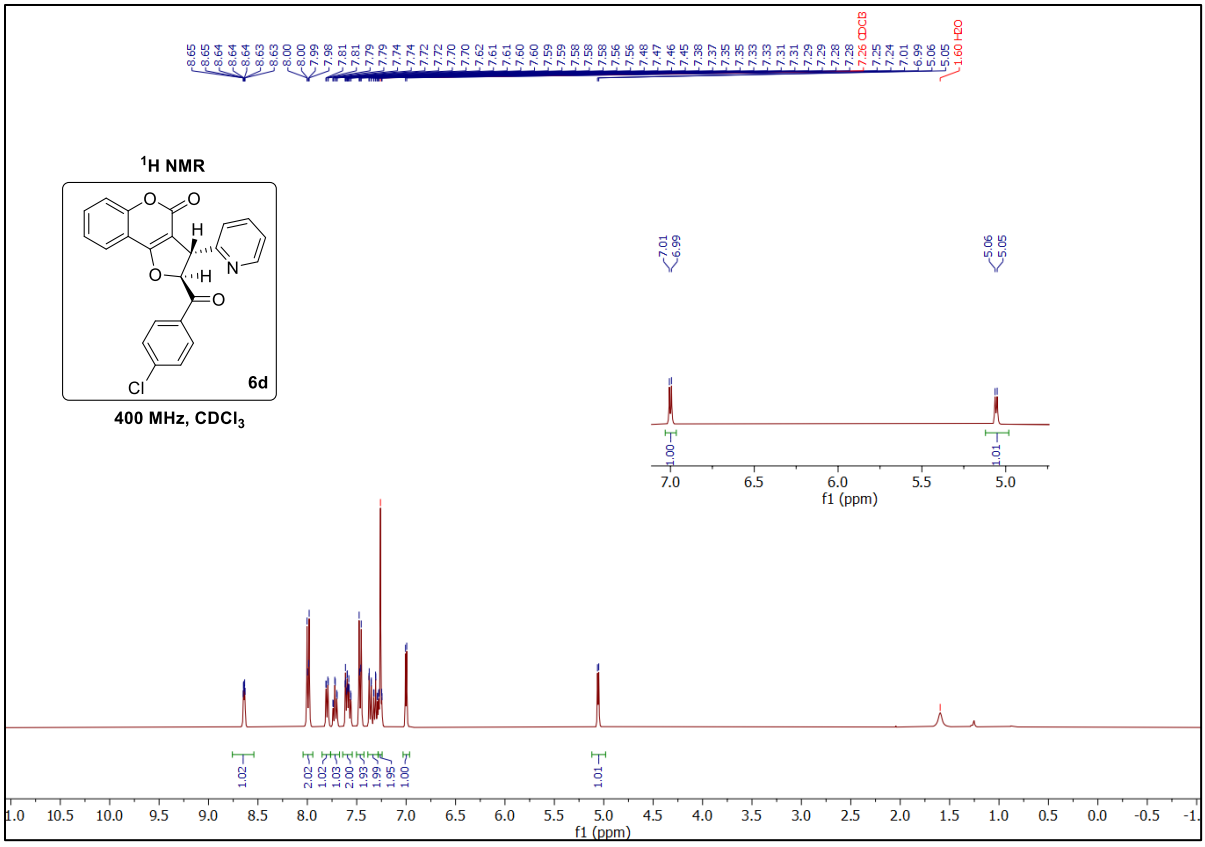
6c
100 MHz, $CDCl_3$
f1 (ppm)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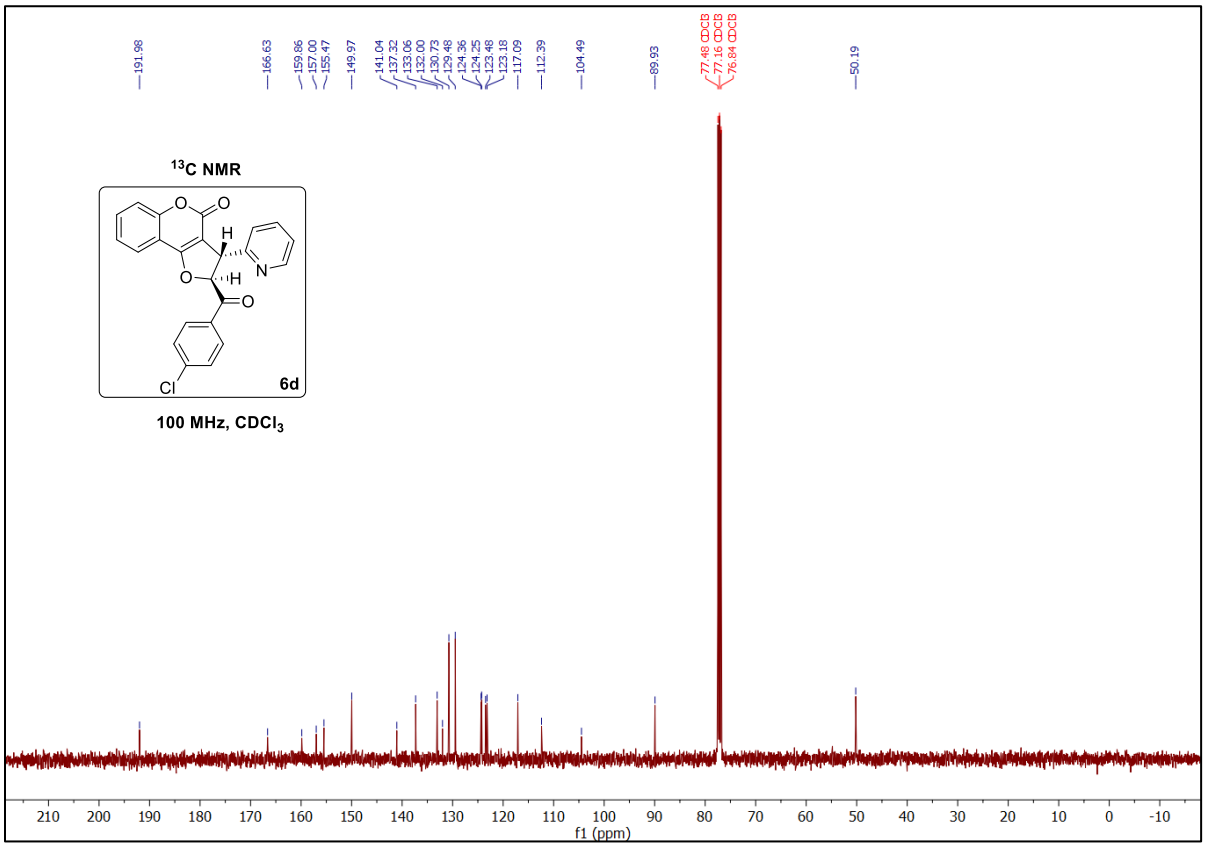
6d
400 MHz, $CDCl_3$
f1 (ppm)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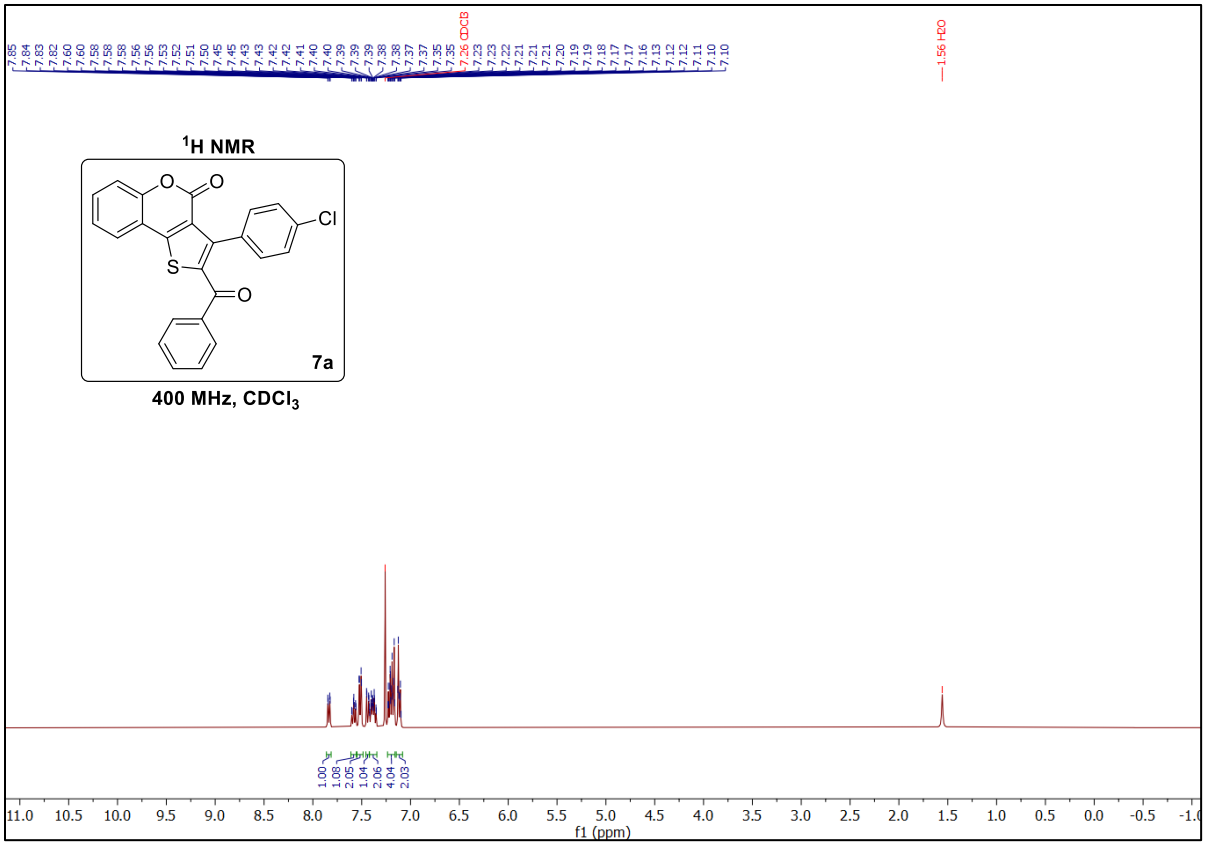
6d
100 MHz, $CDCl_3$
f1 (ppm)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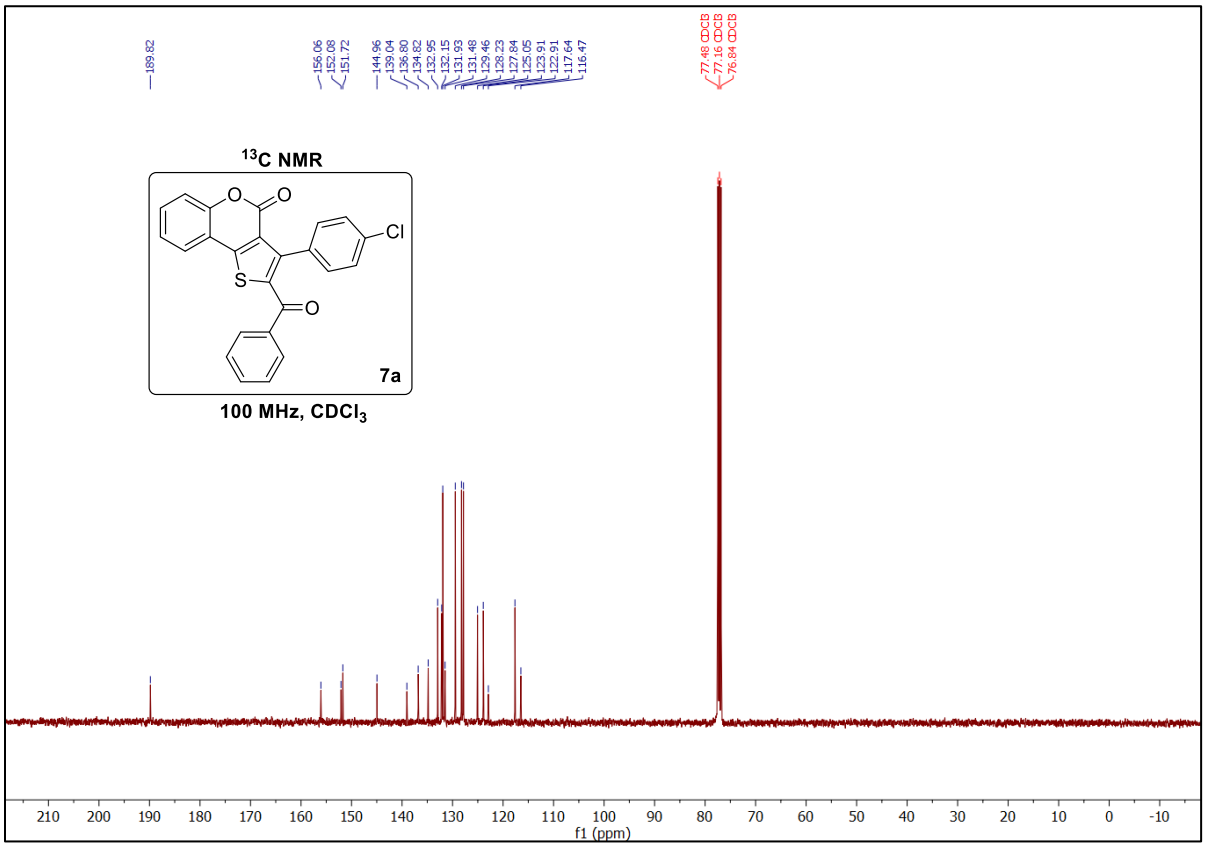
7a
400 MHz, $CDCl_3$
f1 (ppm)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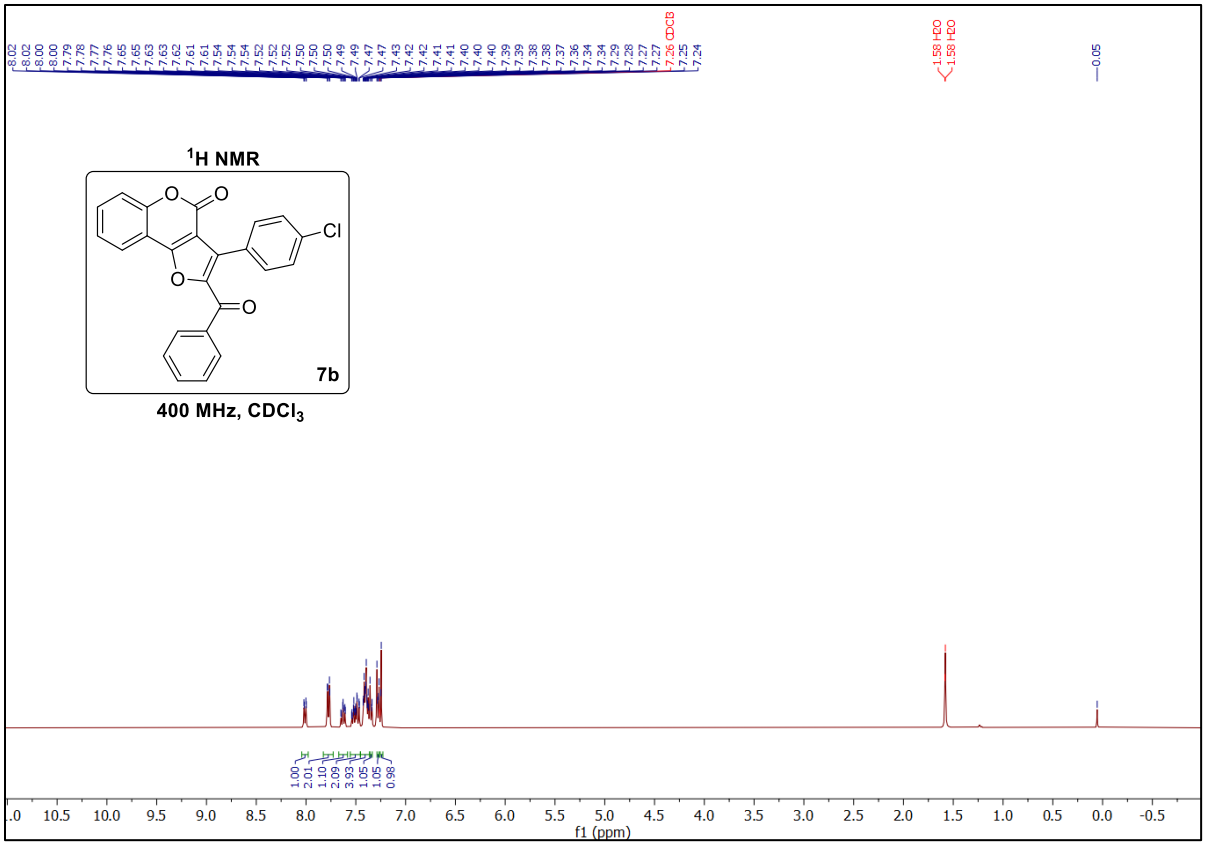
7a
100 MHz, $CDCl_3$
f1 (ppm)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7b
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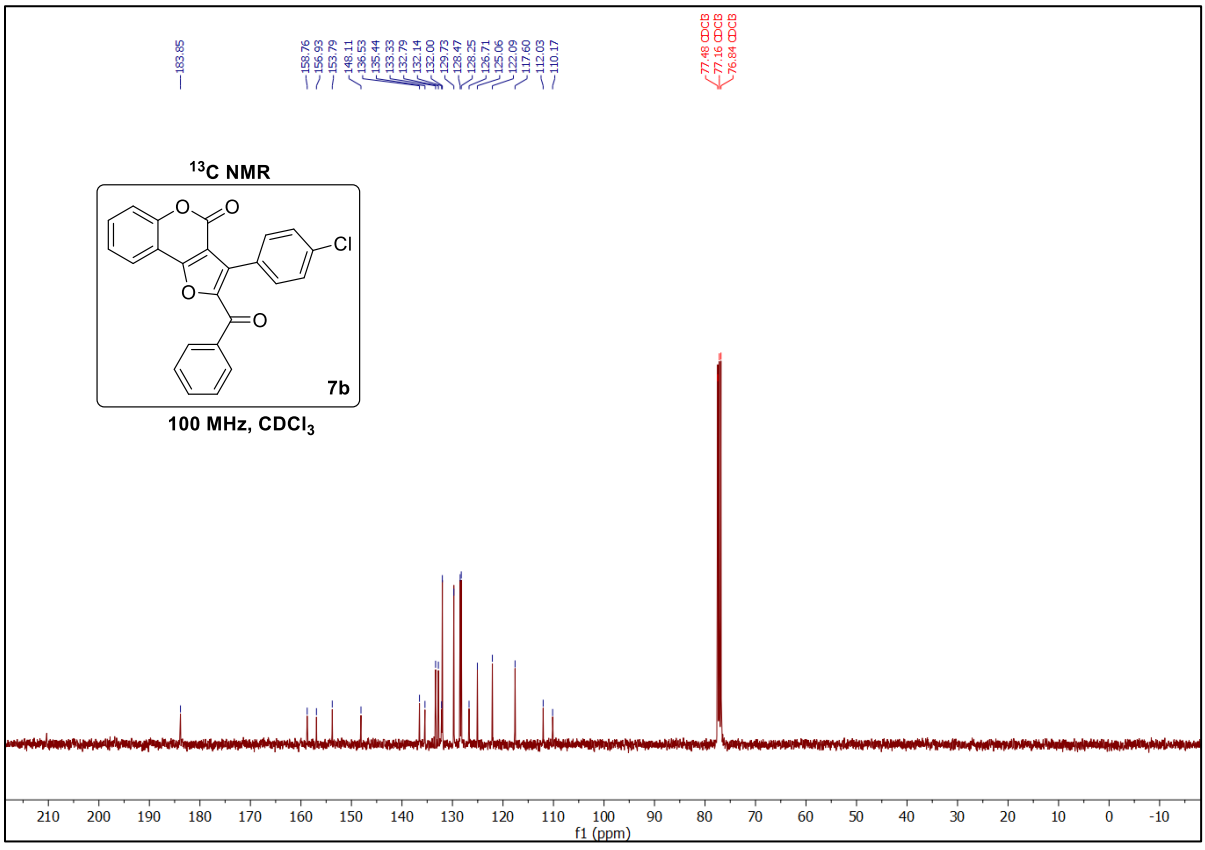
f1 (ppm)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7b
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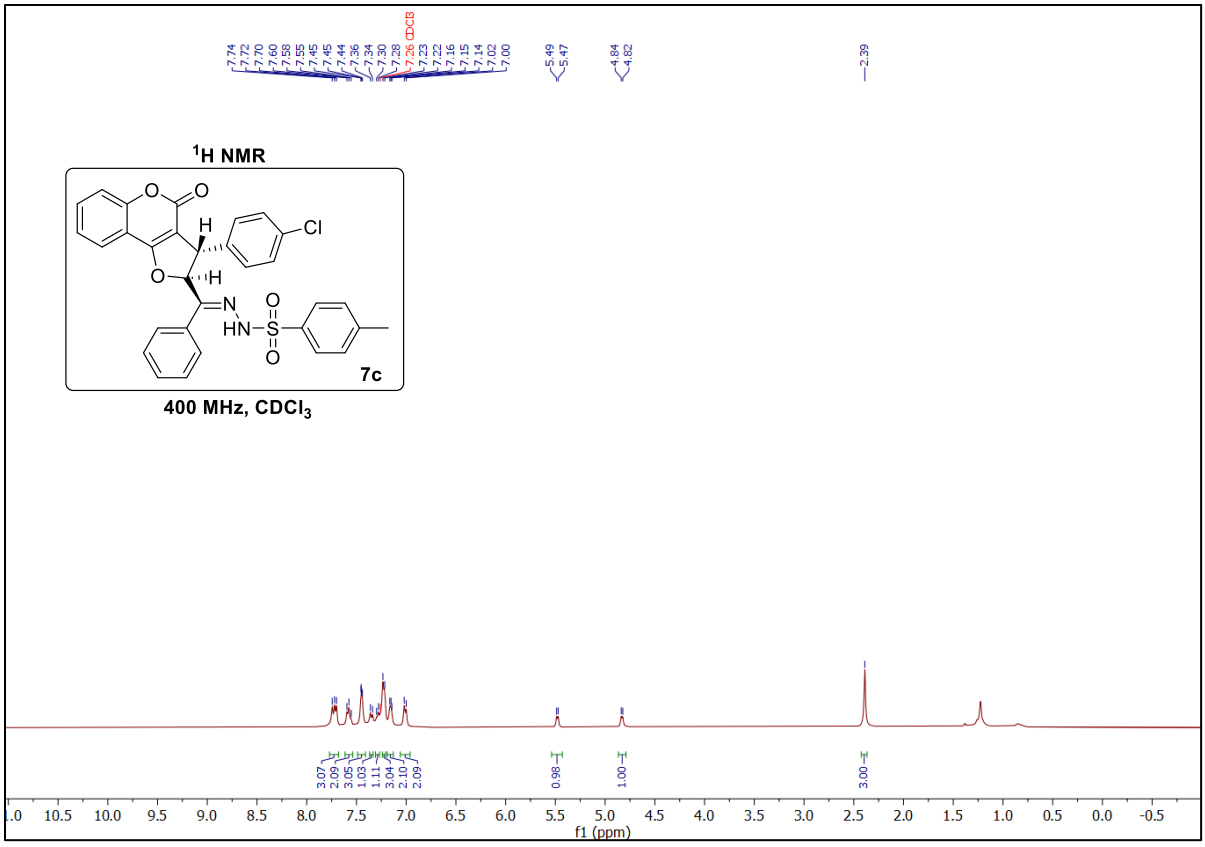
f1 (ppm)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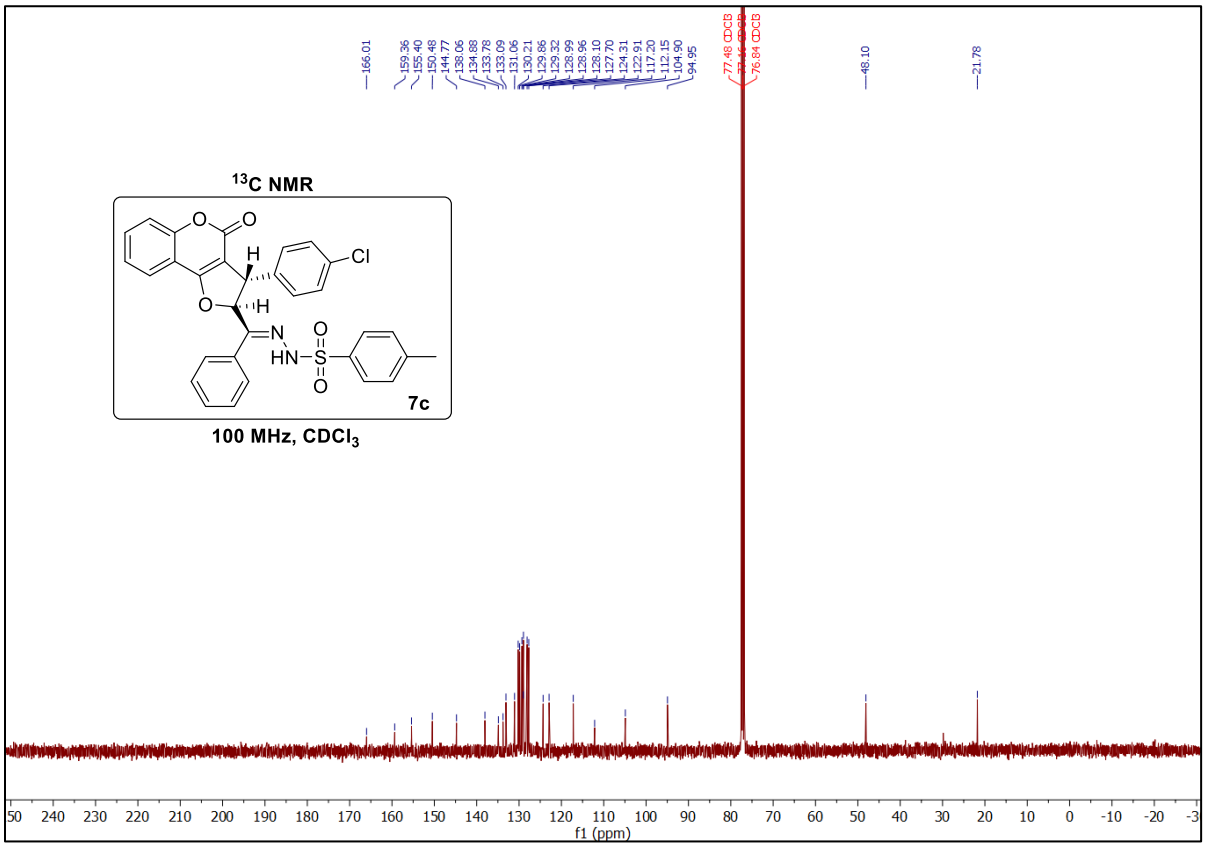
7c
400 MHz, $CDCl_3$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7c
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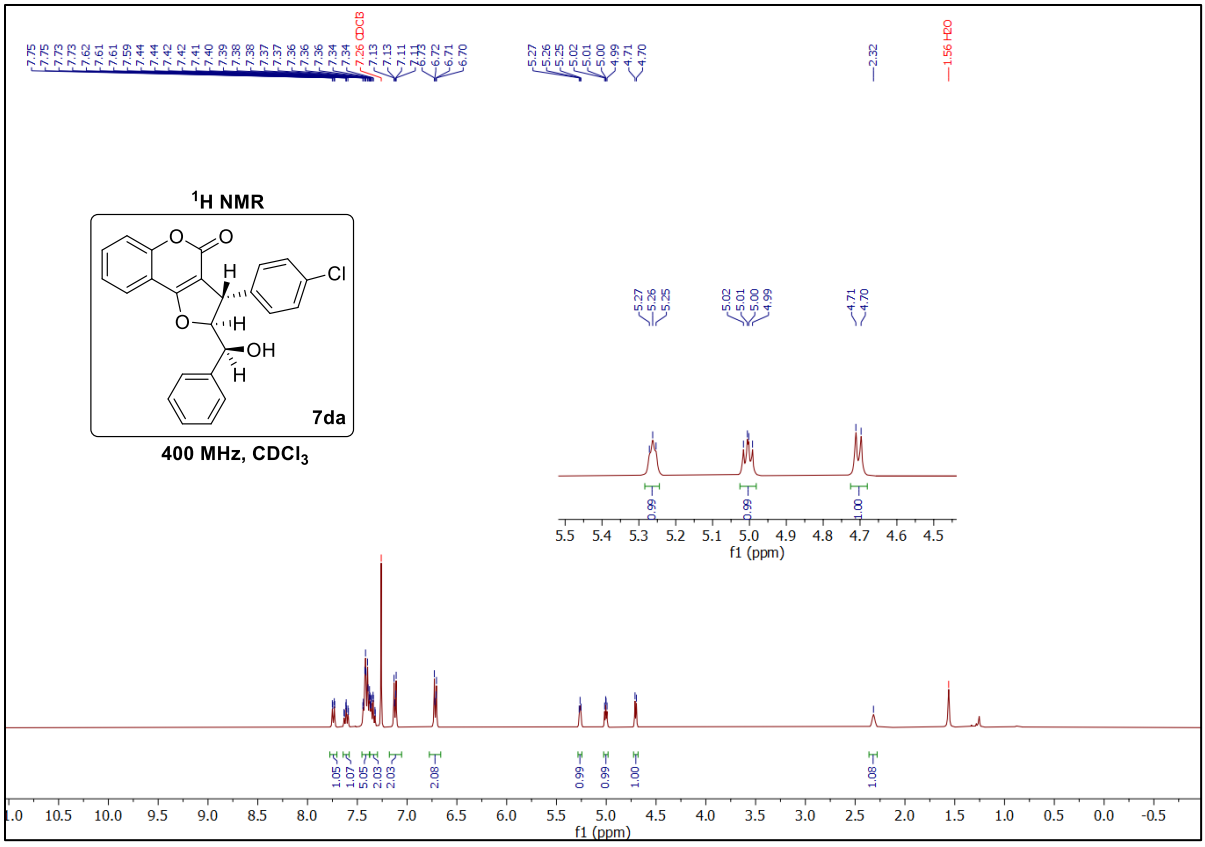
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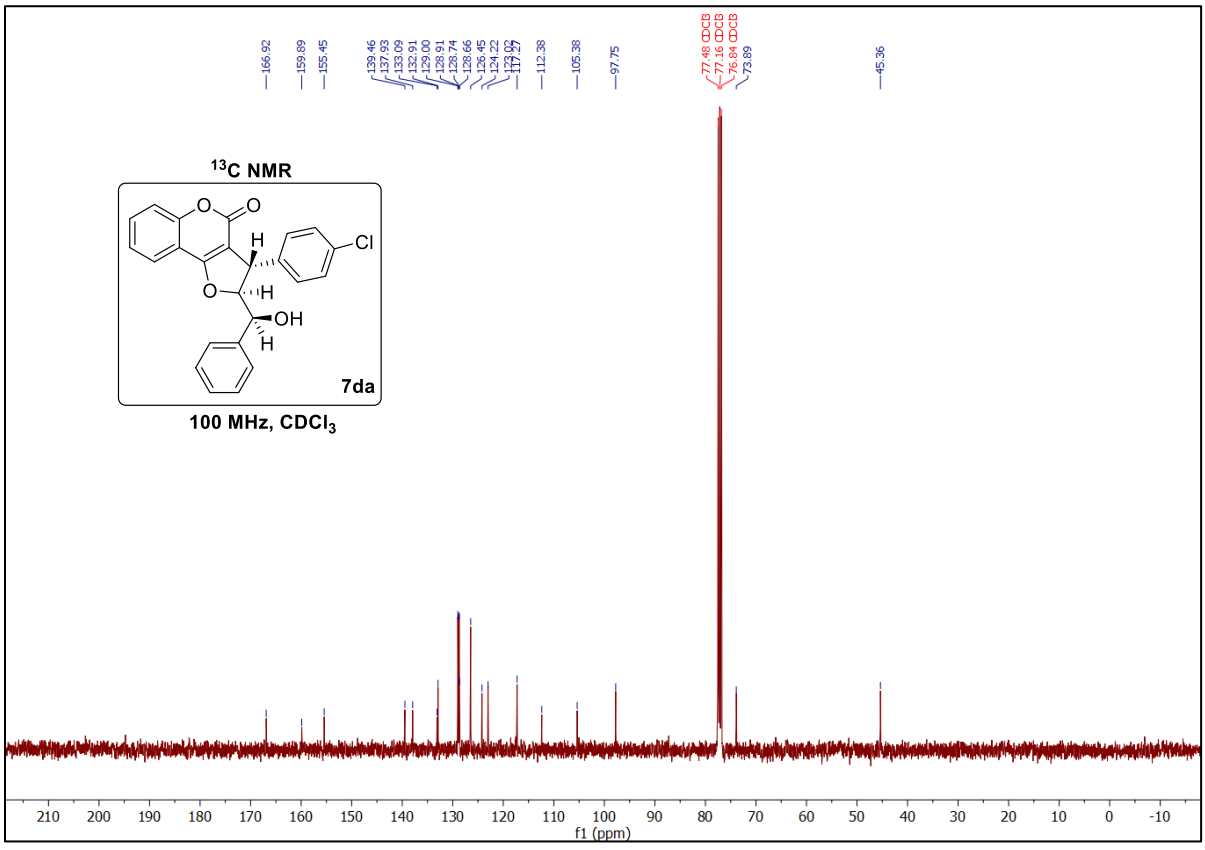
f1 (ppm)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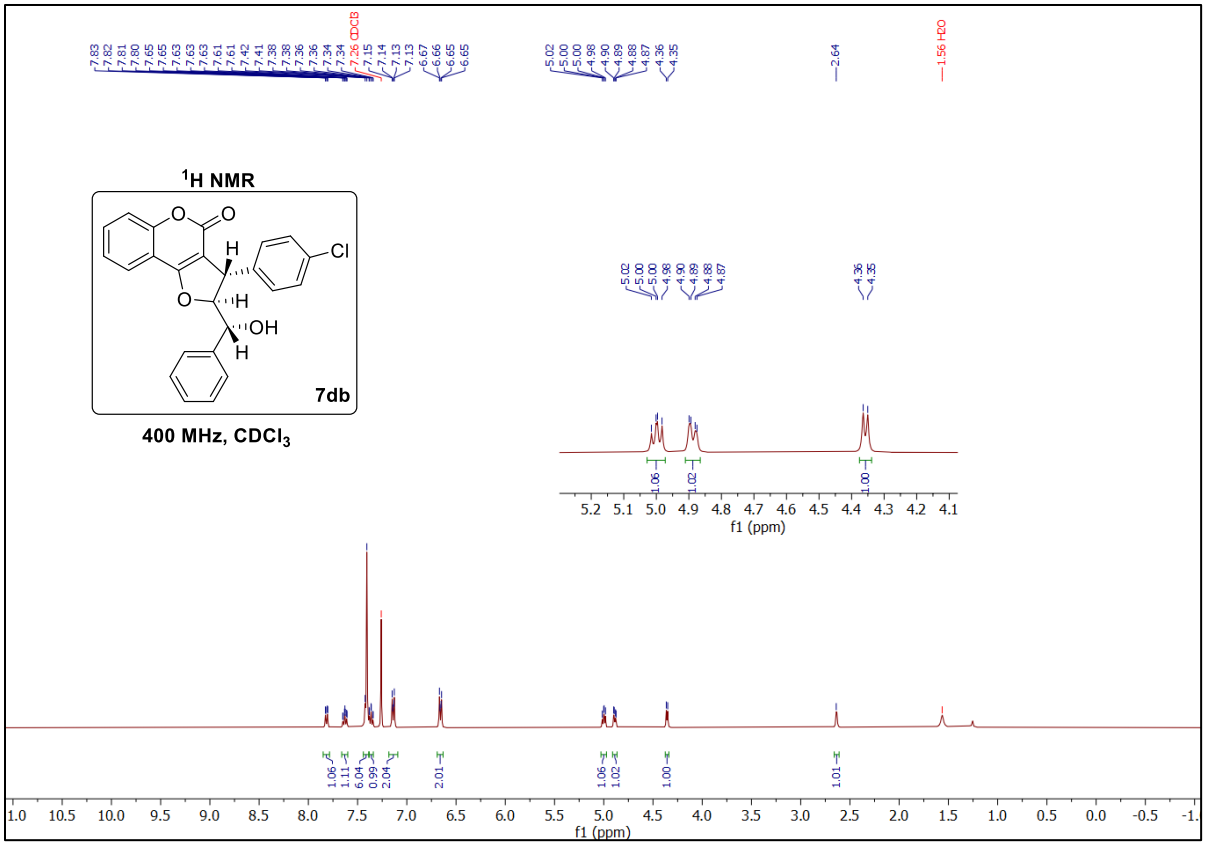
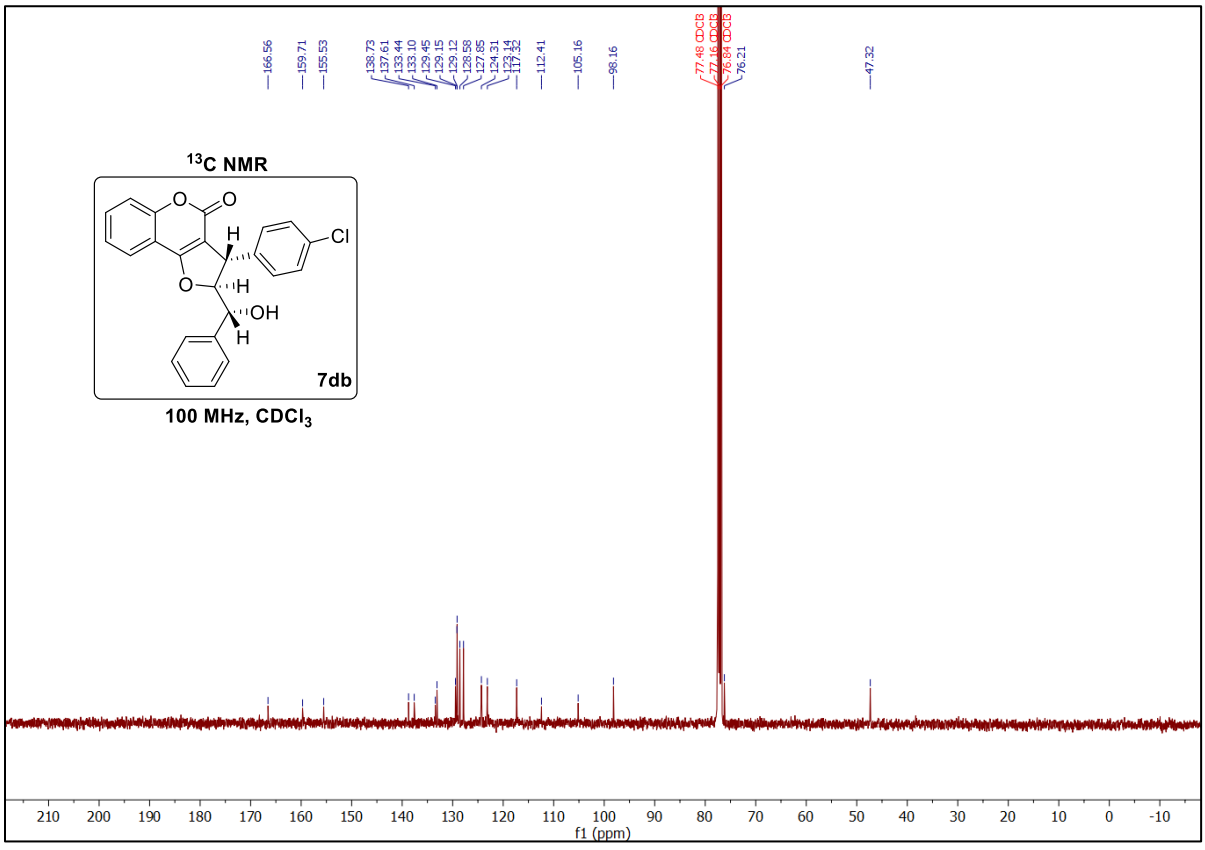
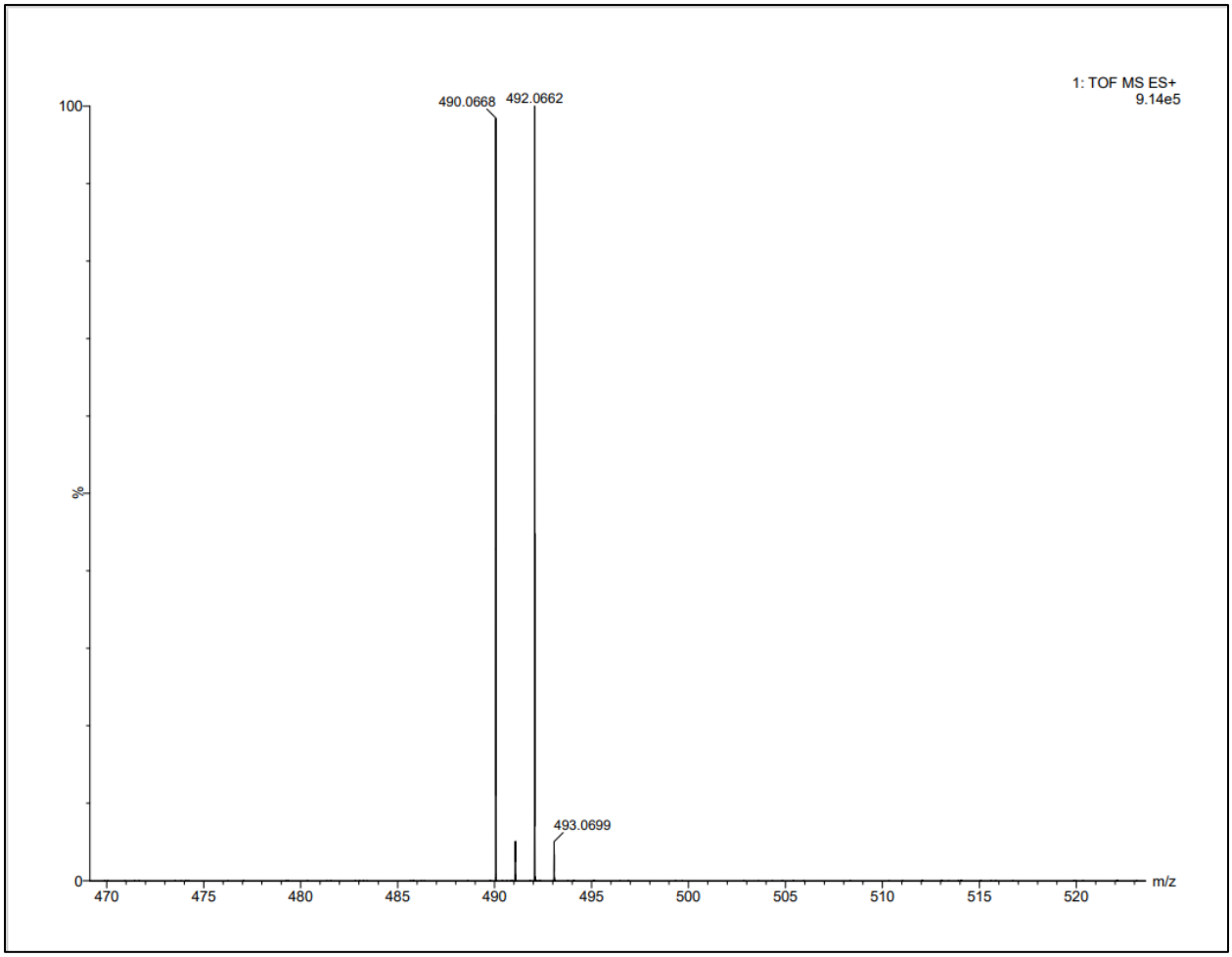
7da
100 MHz, $CDCl_3$
f1 (ppm)


$^{1}$H NMR
7db
400 MHz, $CDCl_3$
f1 (ppm)

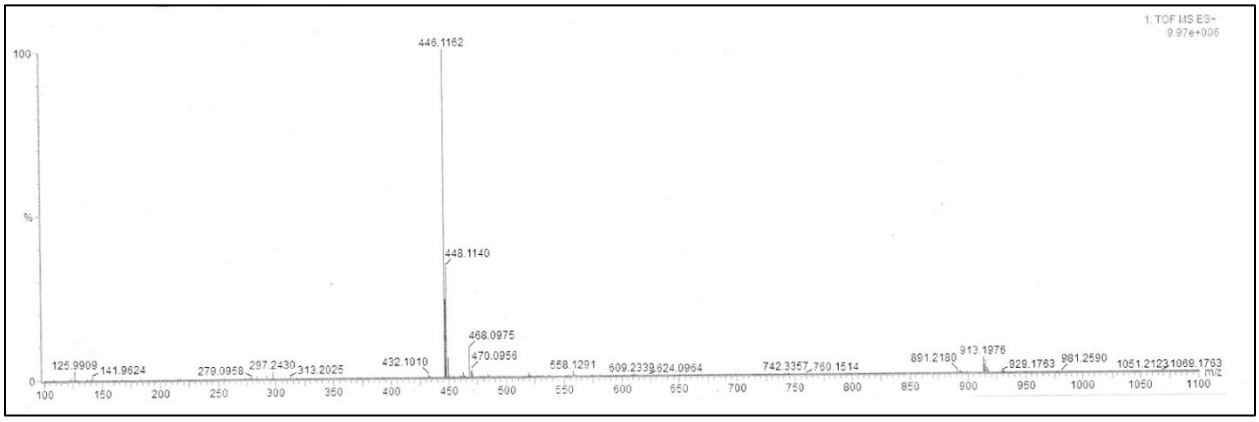

$^{13}$C NMR
7db
100 MHz, $CDCl_3$
f1 (ppm)

## 11. HRMS spectra of synthesized compounds:

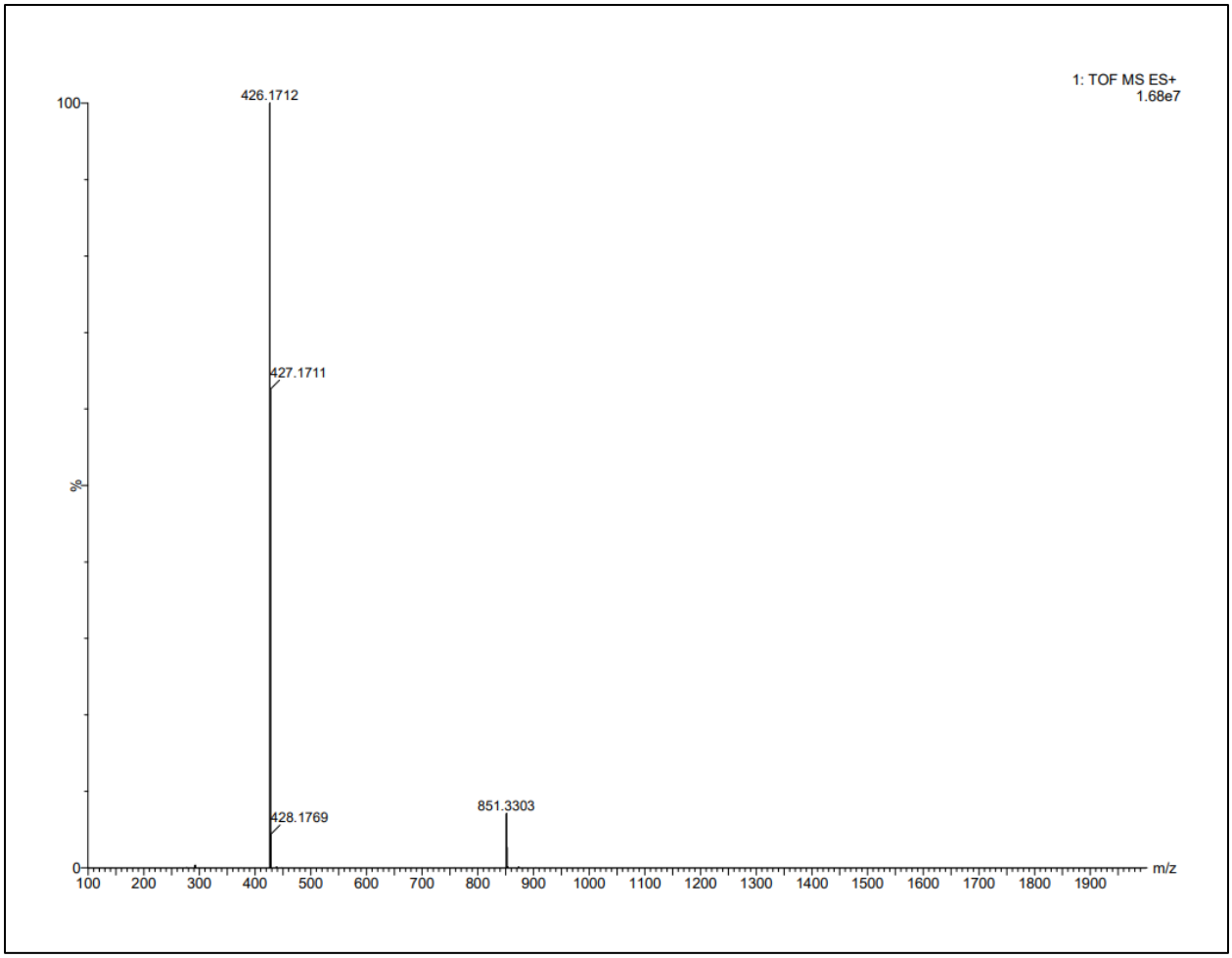
### HRMS spectra of 5a



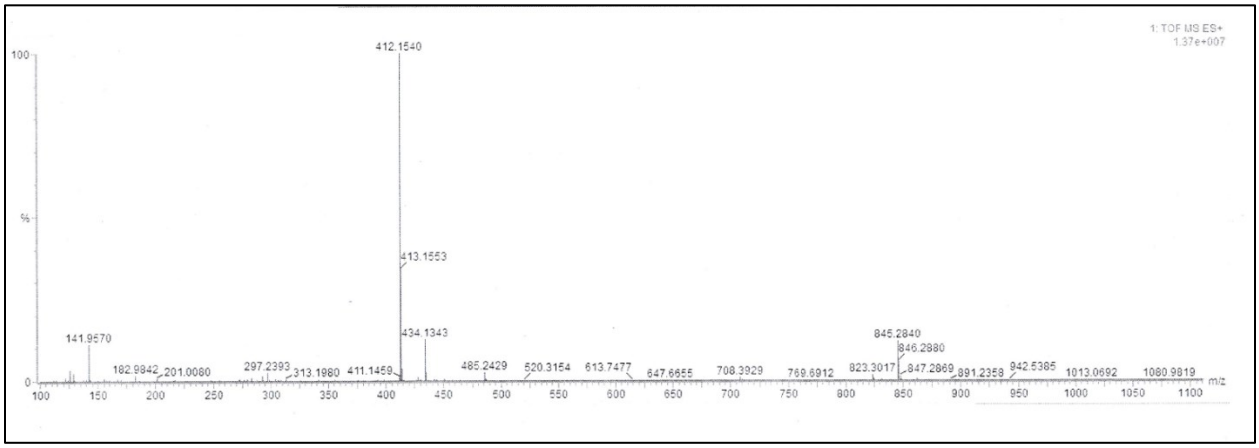

### HRMS spectra of 5b



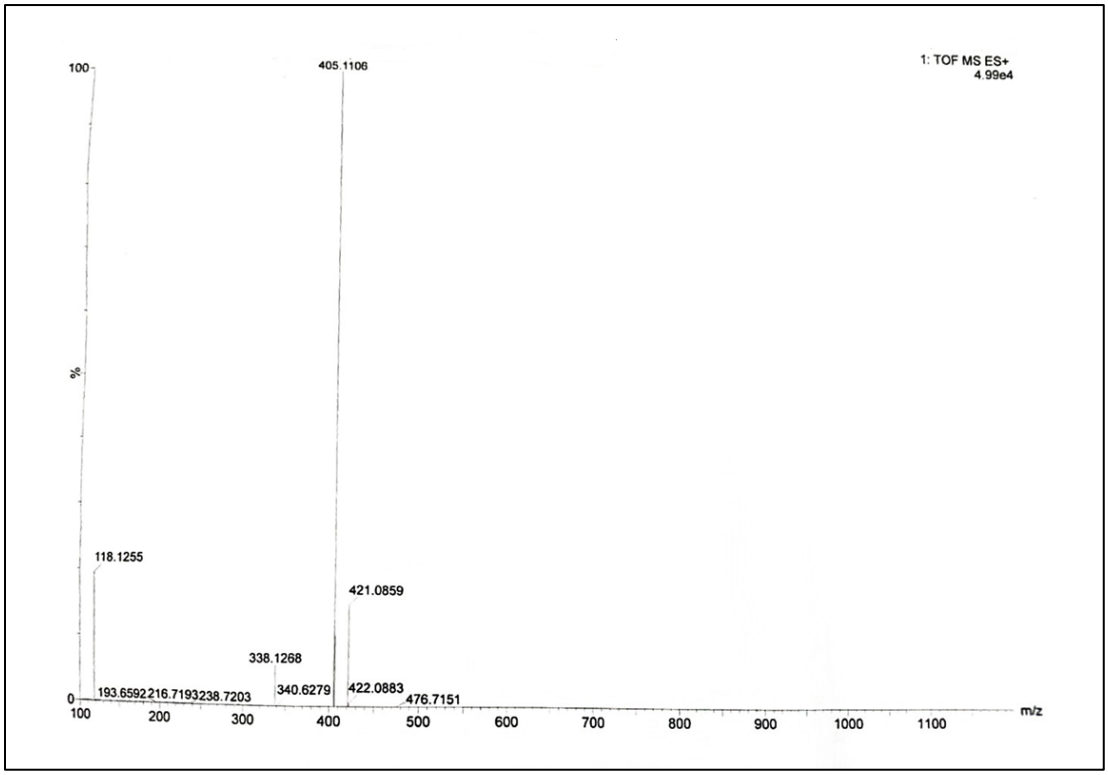
## HRMS spectra of 5c



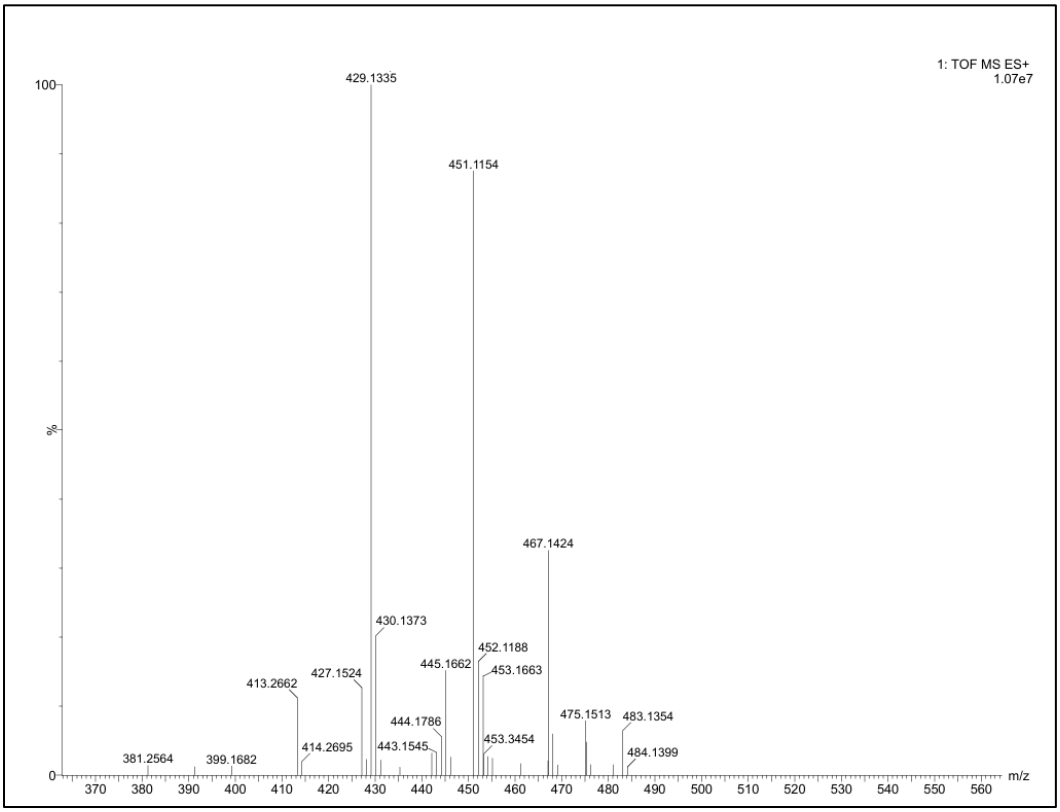

## HRMS spectra of 5d



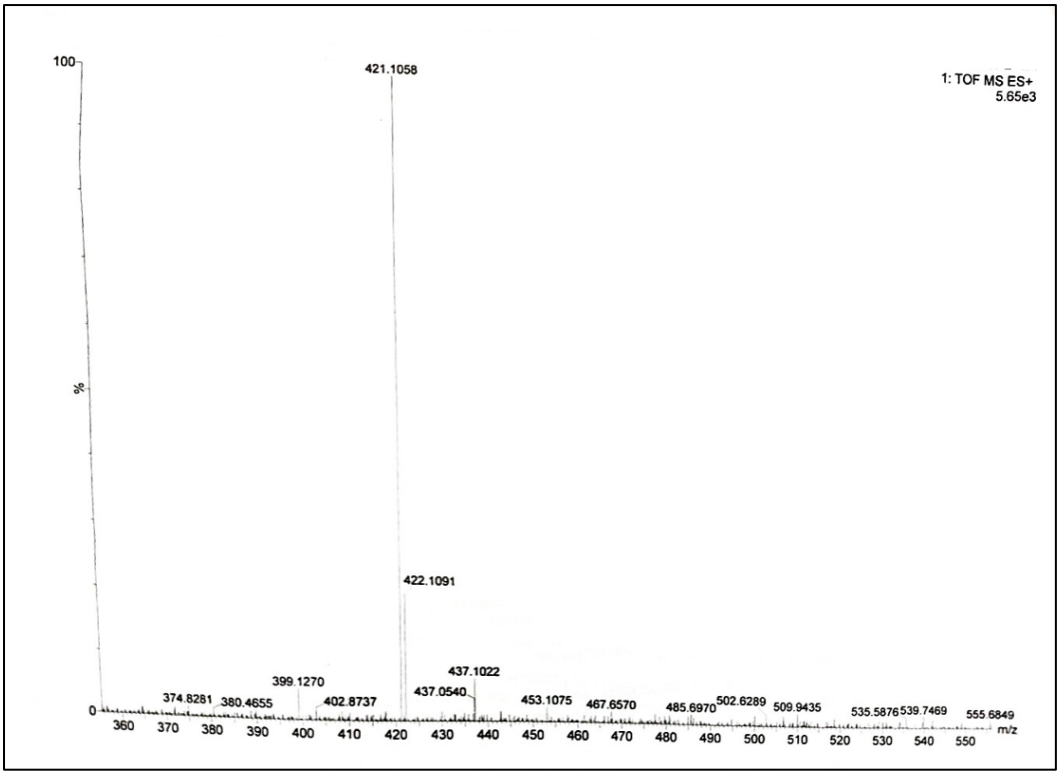
## HRMS spectra of 5e



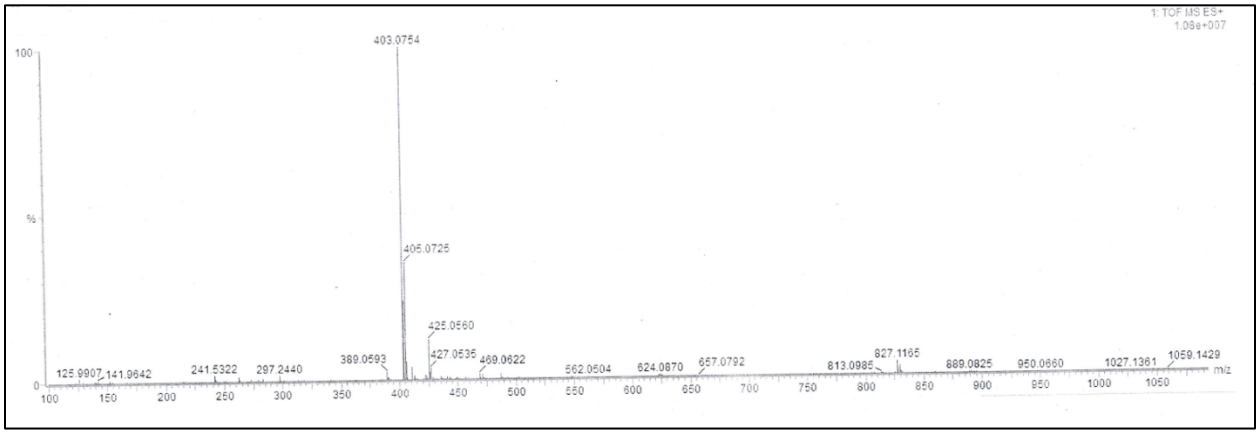

## HRMS spectra of 5f



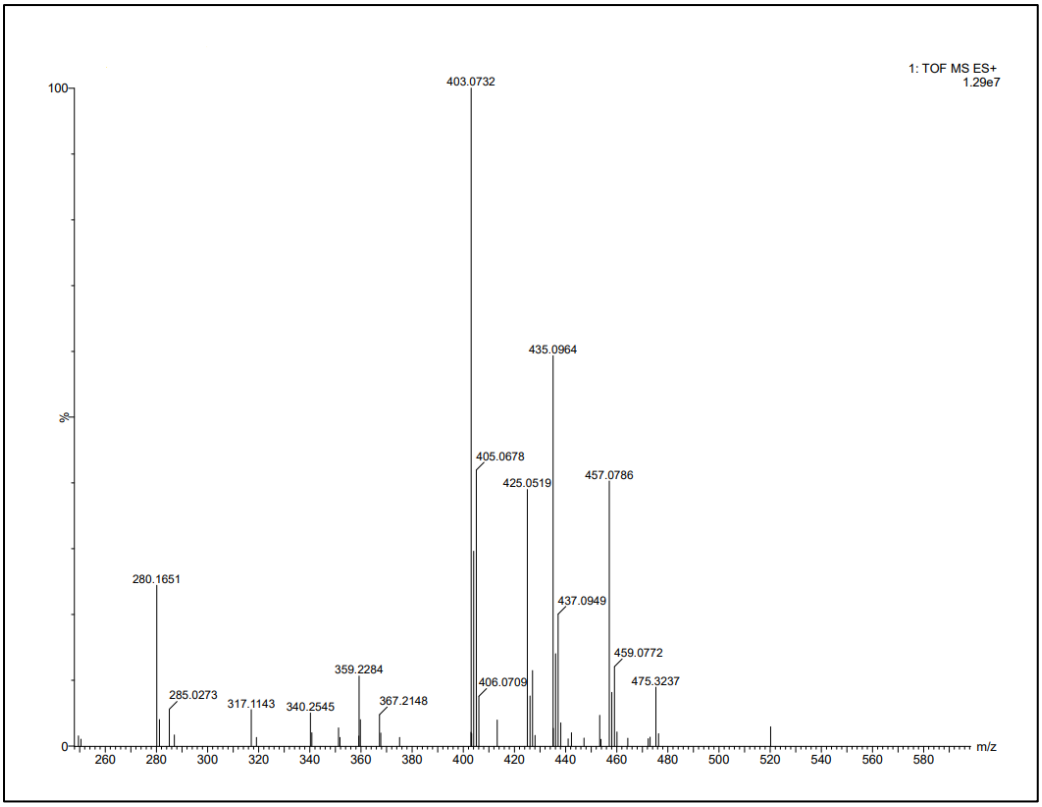
## HRMS spectra of 5g



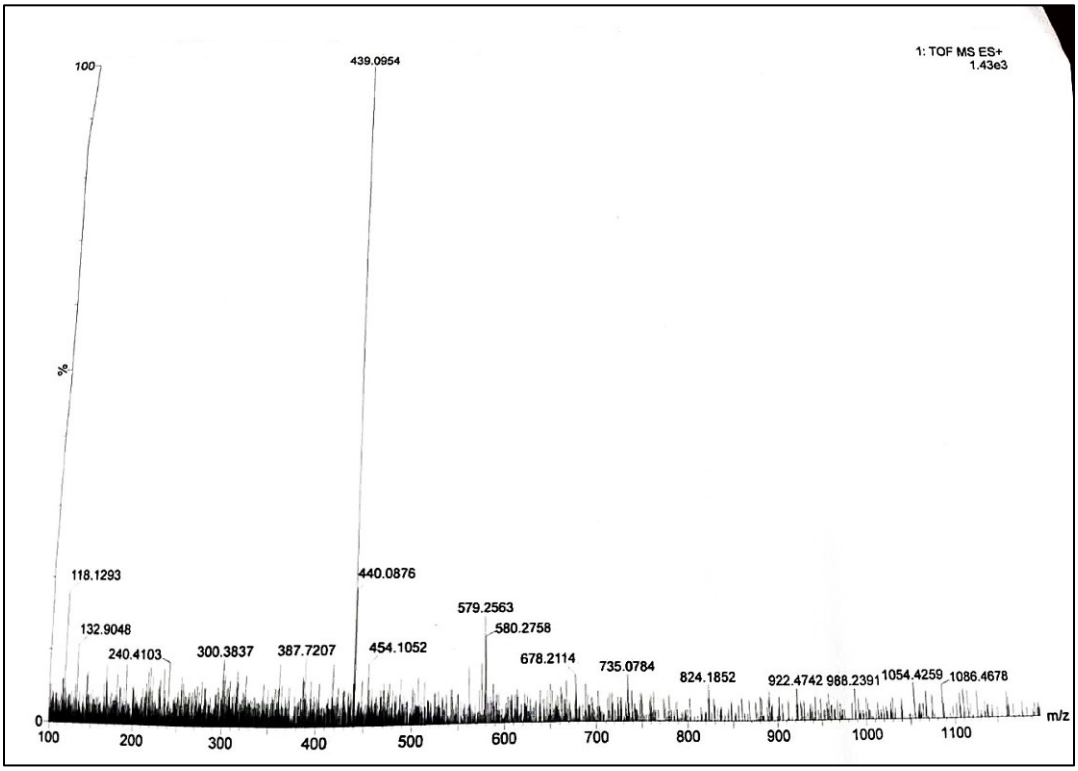

## HRMS spectra of 5h



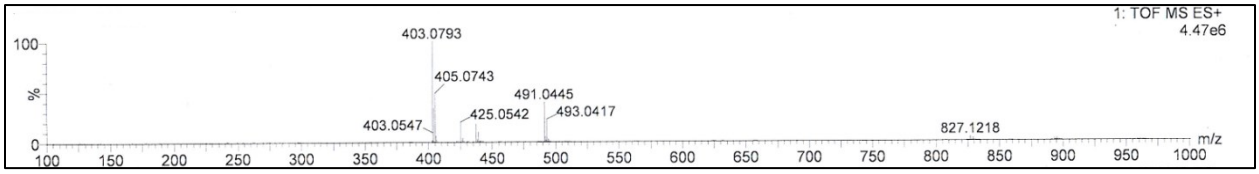
## HRMS spectra of 5j



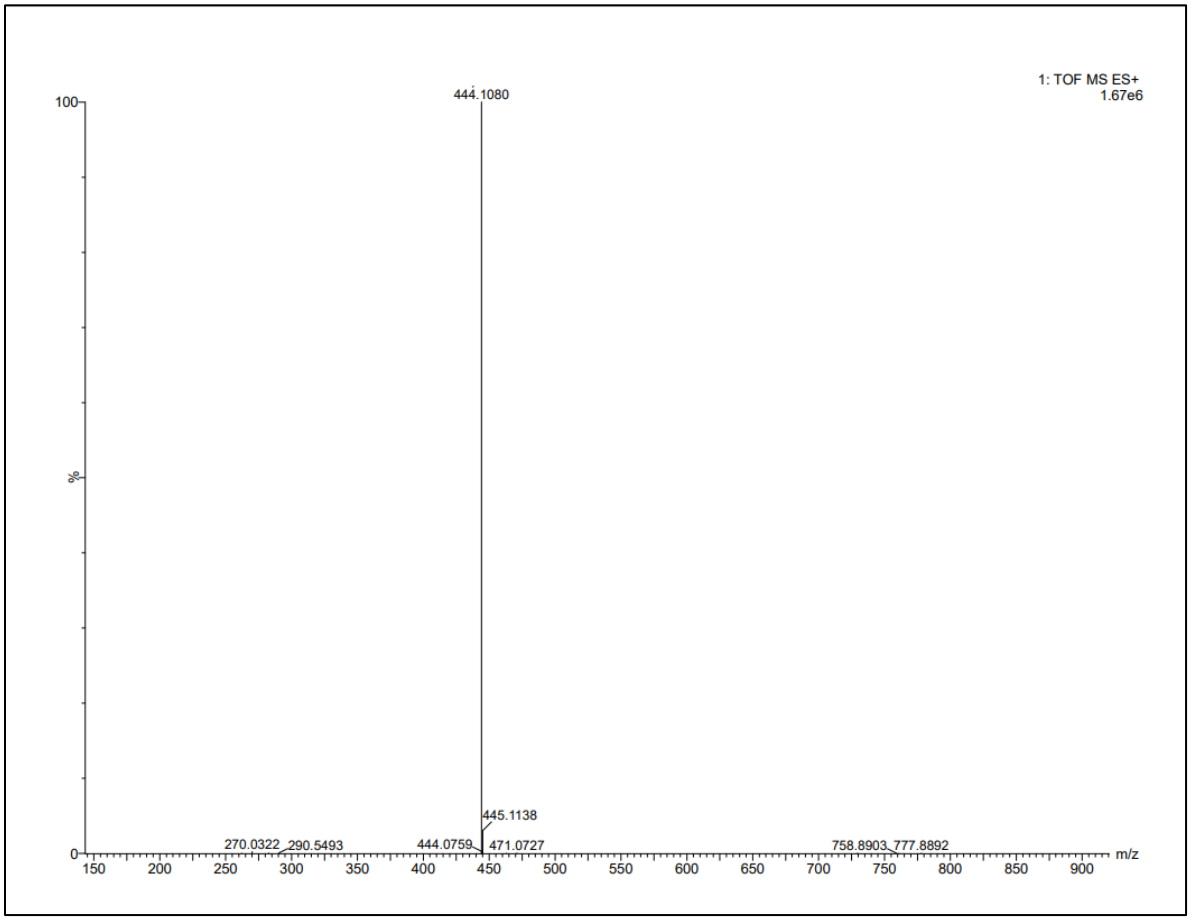

## HRMS spectra of 5k



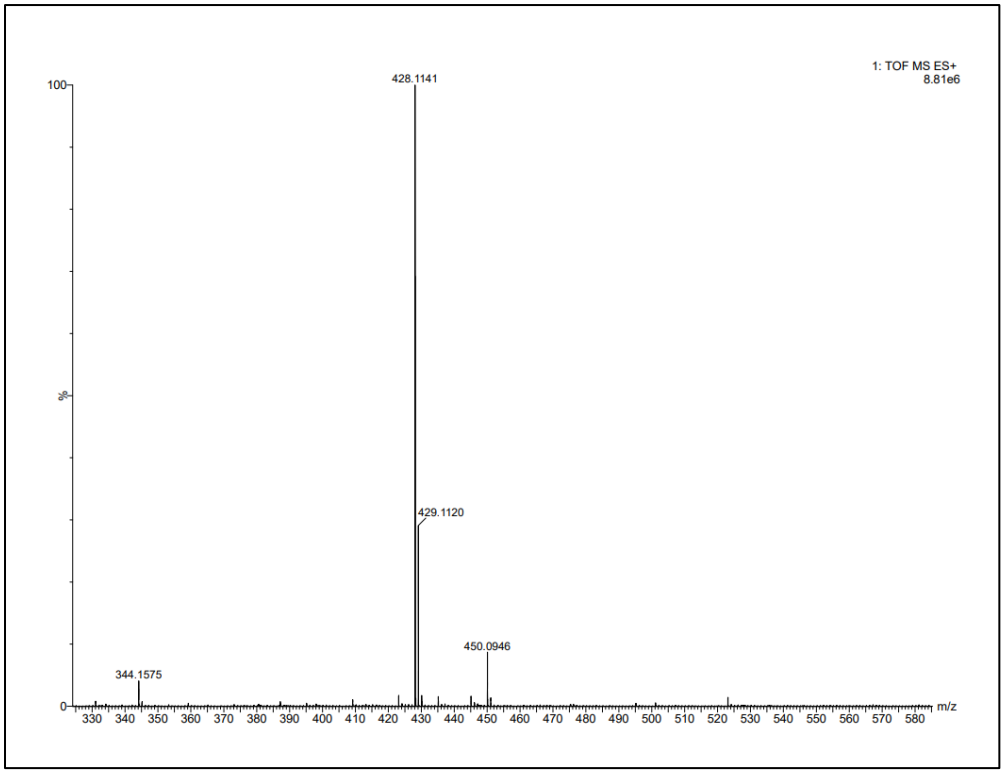
## HRMS spectra of 5l



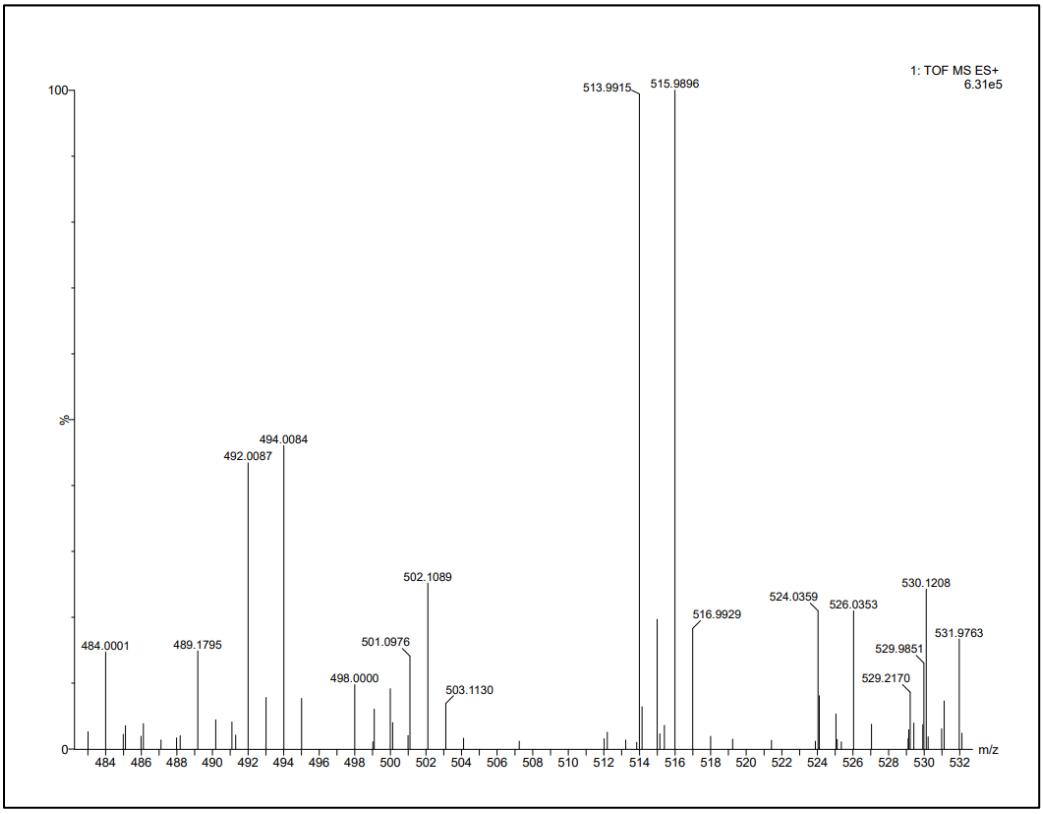

## HRMS spectra of 5m



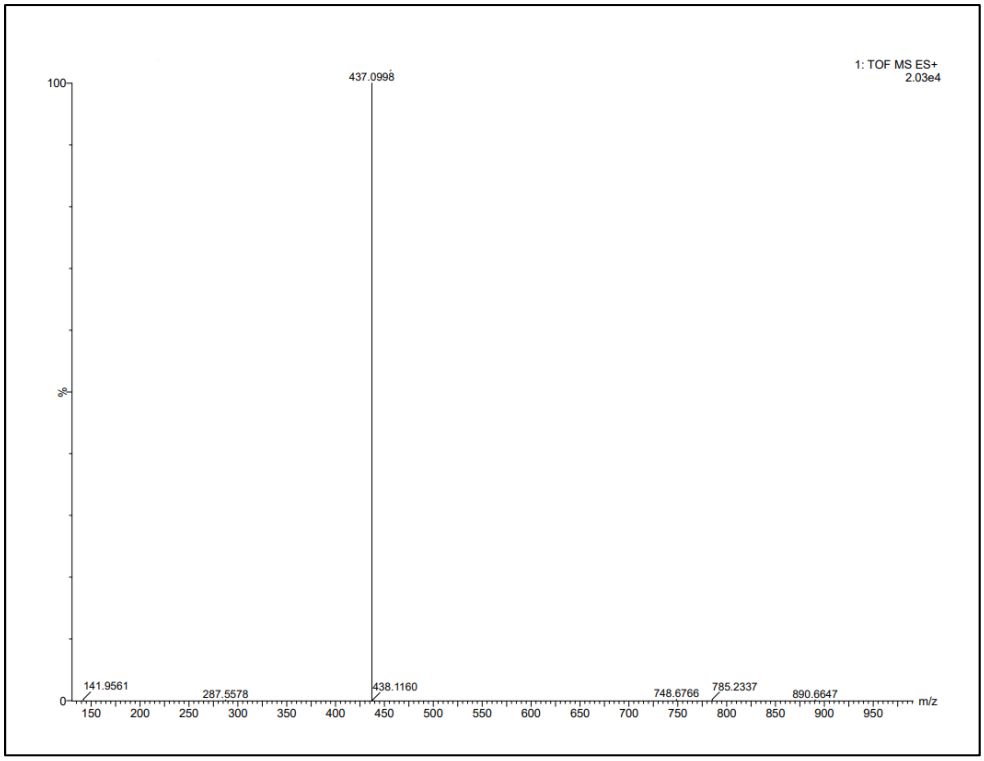
## HRMS spectra of 5n



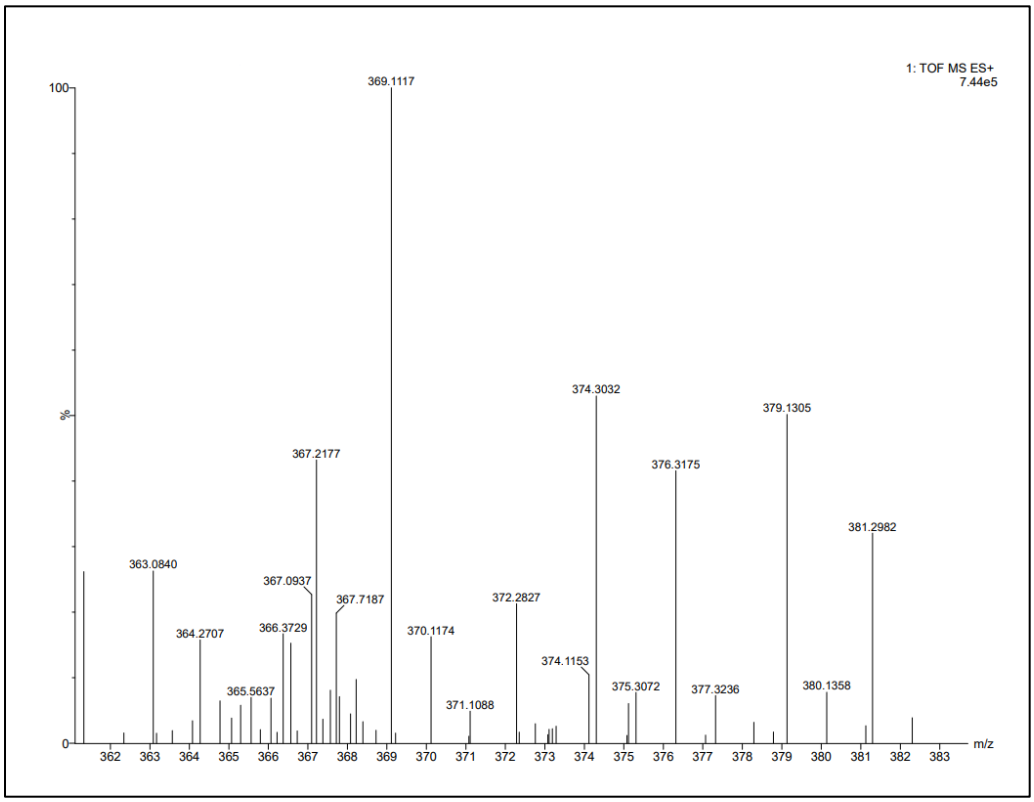

## HRMS spectra of 5o



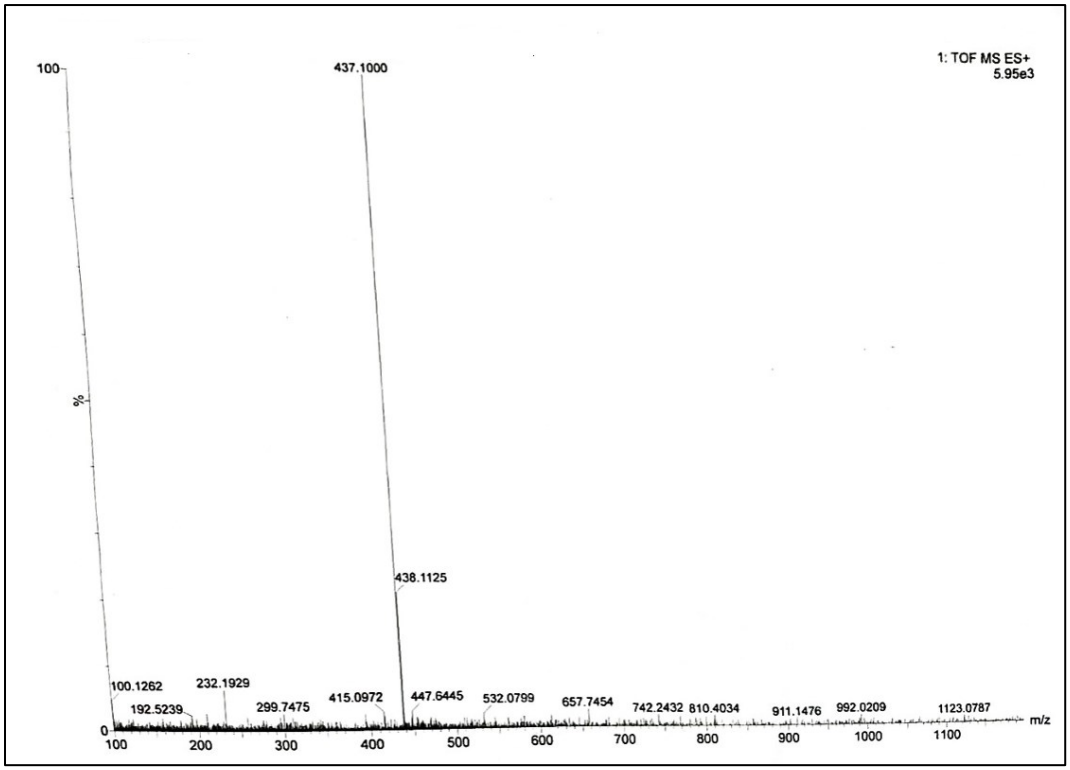
## HRMS spectra of 5p



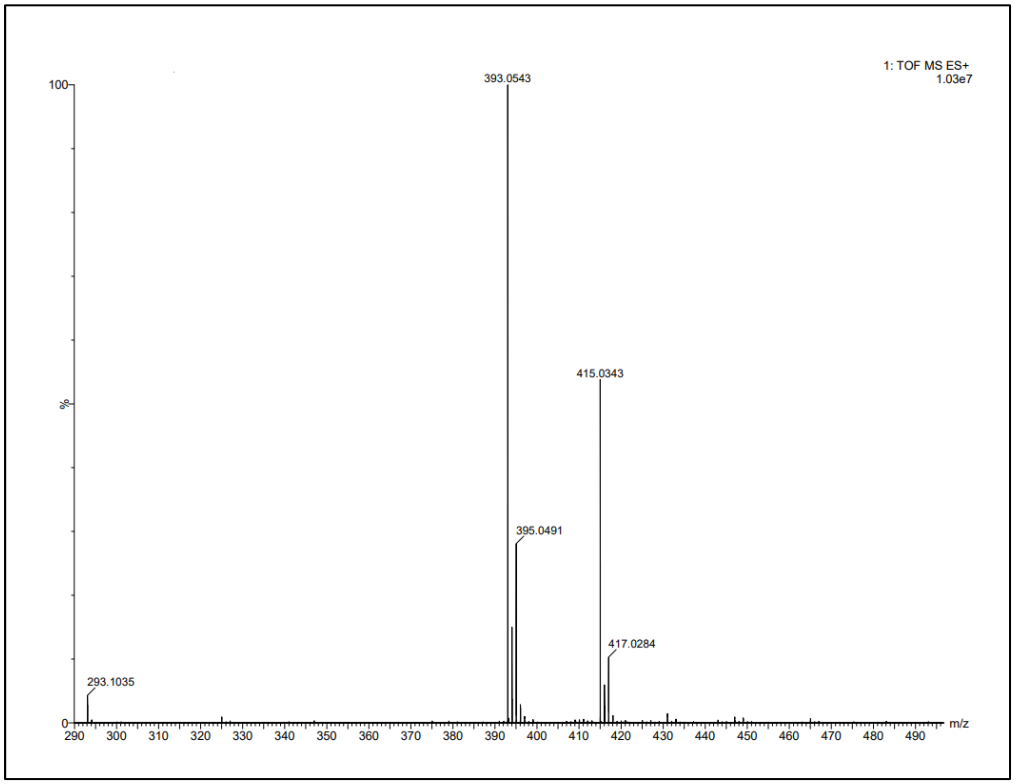

## HRMS spectra of 5q



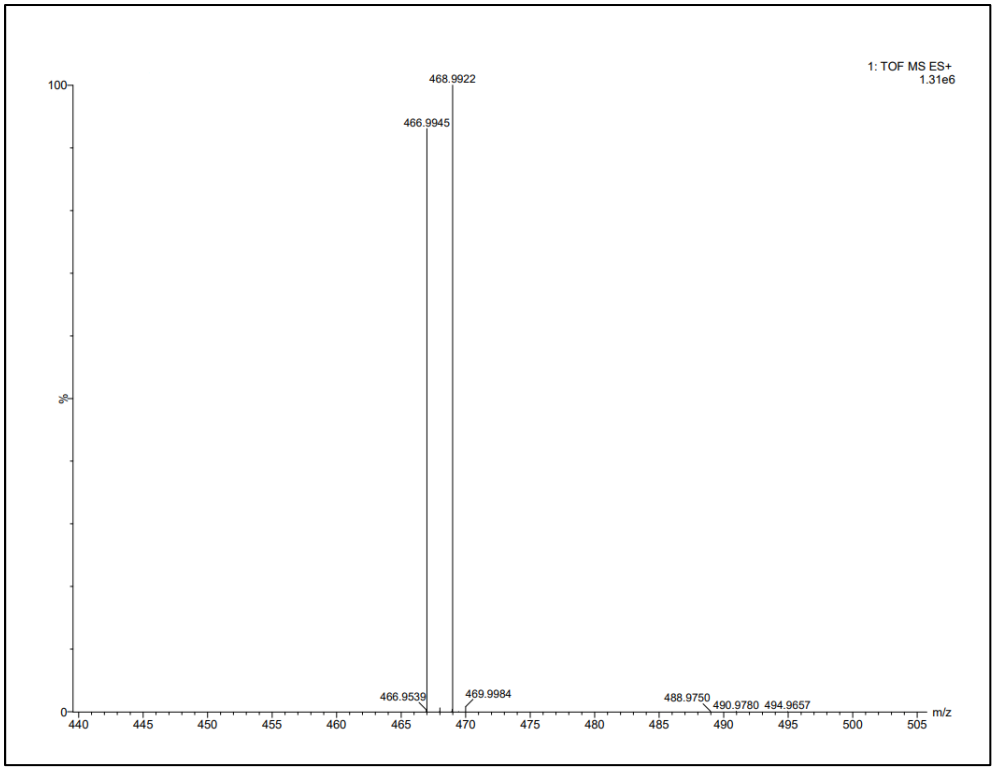
## HRMS spectra of 5r



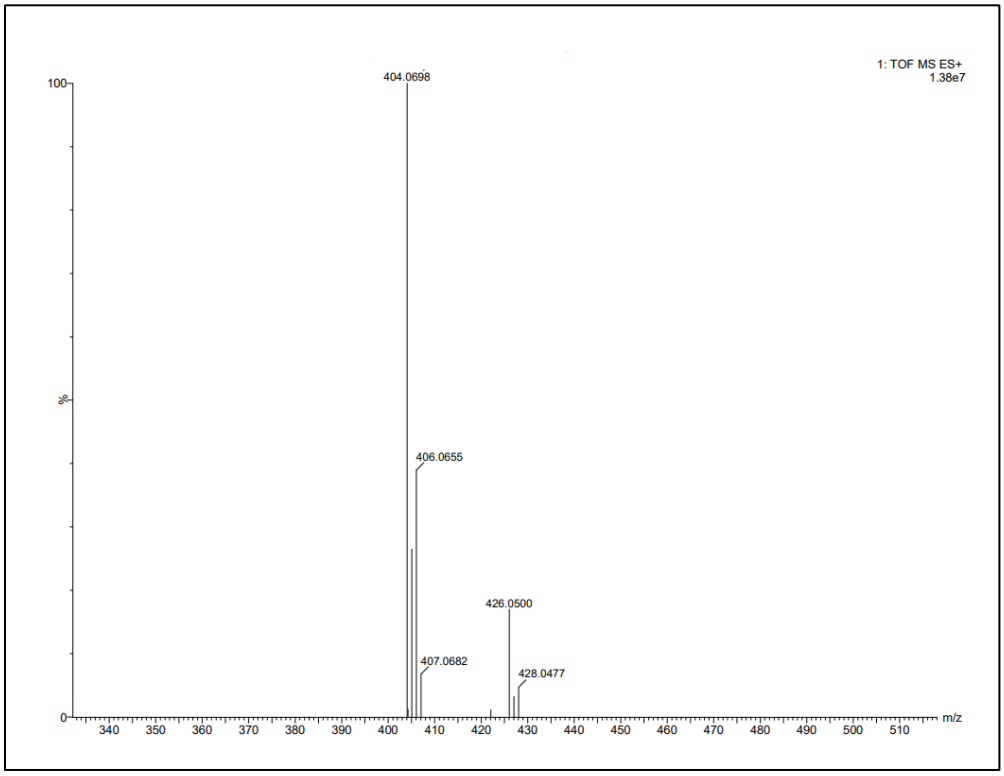

## HRMS spectra of 6a



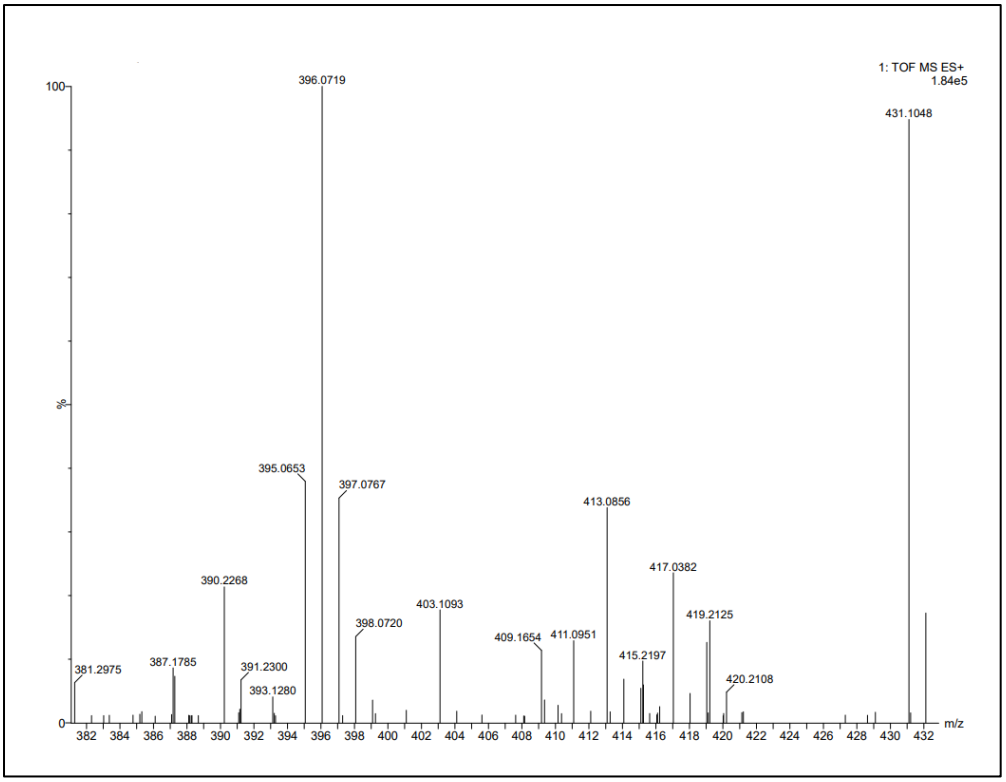
## HRMS spectra of 6c



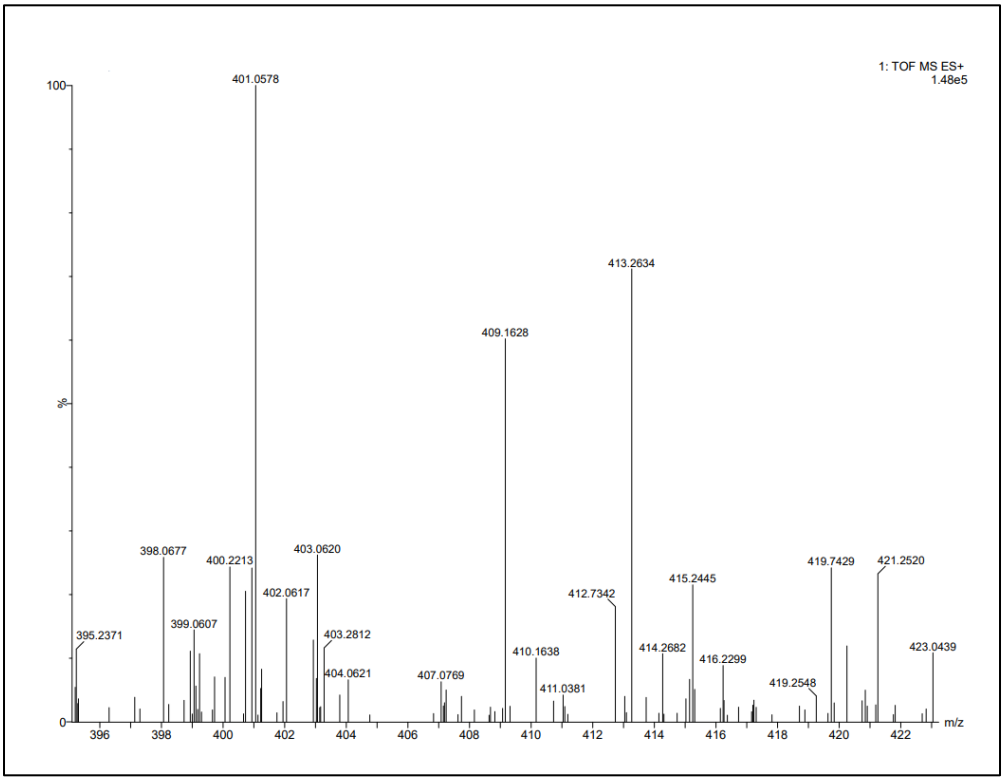

## HRMS spectra of 6d



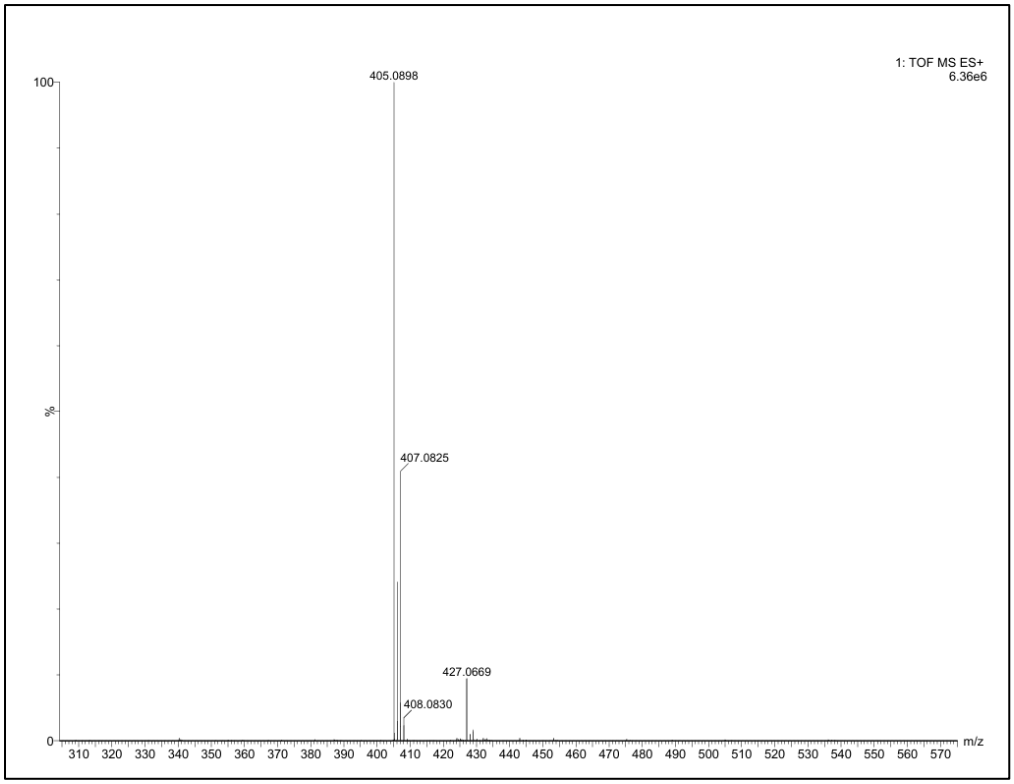
## HRMS spectra of 7a




## HRMS spectra of 7b



## HRMS spectra of 7da




## HRMS spectra of 7db