Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Unveiling the potency of a phenalenyl-based photocatalyst for intramolecular dehydrogenative lactonization

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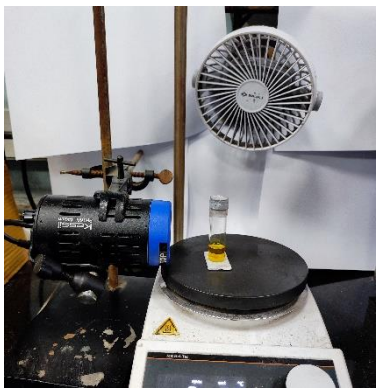
1. General Information

All the photochemical reactions were conducted in a 7 mL reaction via equipped with screw-cap purchased from Sigma-Aldrich. UV-Visible experiments were conducted on SHIMADZU-UV-2450 using HPLC grade acetonitrile (MeCN). The emission spectra were recorded on a FLS920 (Edinburgh Instruments) spectrofluorometer using HPLC grade MeCN. Cyclic voltammetry (CV) was carried out using a Metrohm Autolab PGSTAT204 potentiostat. A platinum disk working electrode (diameter: 3mm), a coiled platinum wire counter electrode and Ag/AgCl (in 3.5 M KCl) reference electrode were employed for the CV studies. Chromatographic purification of products was accomplished by column chromatography on silica gel (230-400 mesh). For thin layer chromatography (TLC) analysis throughout this work, Merck pre-coated TLC plates (silica gel 60 GF_{254}, 0.25 mm) were employed, using UV light as the visualizing agent. Organic solutions were concentrated under reduced pressure using IKA rotary evaporator. The products obtained were characterised using ^{1}H NMR and ^{13}C NMR. NMR spectra were recorded at 500 MHz for ^{1}H and 126 MHz for ^{13}C. The chemical shift (δ) for ^{1}H and ^{13}C are given in ppm relative to internal standard/residual signals of the solvents (tetramethylsilane @ 0 ppm ^{1}H NMR and $CDCl_3$ @ 77.00 ppm ^{13}C NMR). Coupling constants are given in Hertz. The following abbreviations are followed to indicate the multiplicity: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; dd.

2. Materials:

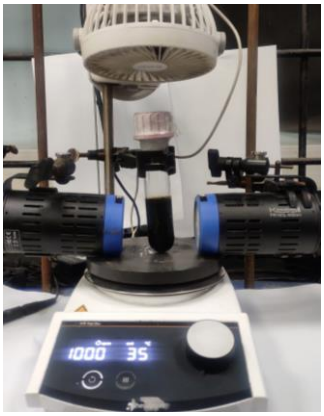
Synthesis grade solvents were used as purchased. **1a** was purchased from Sigma-Aldrich. All the other commercial grade reagents and solvents were purchased from Sigma-Aldrich at the highest commercial quality and used without further purification, unless otherwise stated. Except **1a**, all the biaryl-2-carboxylic derivatives (**1**) were synthesised from the corresponding methyl-2-iodoaroylates and arylboronic acids according to the literature procedure.[1] 3,3-diphenylacrylic acid derivatives were prepared according to the literature procedure.[2]



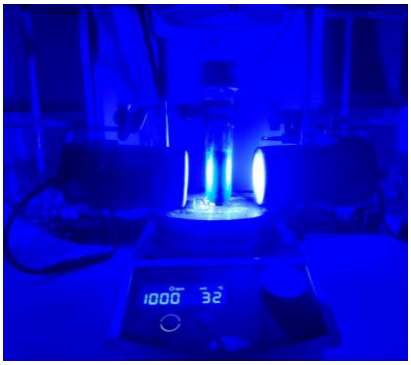
Before the Reaction

During the Reaction

Figure S1: Reaction Setup for 0.2 mmol Reaction



Before the Reaction



During the Reaction

Figure S2: Reaction Setup for 5.0 mmol Reaction

3. Reaction Setup:

The photochemical reaction setup is shown in Fig. S1. All the reactions were carried out under the blue light irradiation using a Kessil® PR160-440 nm lamp. Ambient temperature throughout the course of the reaction was maintained by a cooling fan. The reaction vial was placed 4 cm away from the Kessil light source (Fig S1 and S2).

4. Spectrum of the Light Used for the Photochemical Reaction:

The emission spectra of 440 nm Kessil light was measured by an AVASPEC-ULS2048 Ultra Low Straylight Fiber Optic Spectrometer and data was collected from 175 to 1100 nm. The light source whose spectra was to be recorded was placed in the front of the spectrometer connected via a fiber and emission was recorded using the AvaSoft software. Finally, the data obtained was plotted as shown in Fig S3.

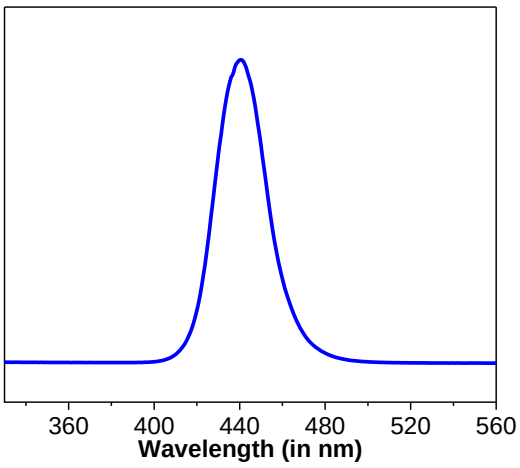


Figure S3: Emission spectra of 440 nm Kessil light source.

(*We thank Prof. Sameer Sapra, IIT Delhi for providing the access to AVASPEC-ULS2048 spectrometer and enabling us to record the emission spectra of 440 nm Kessil light*.)

5. Cyclic Voltammetry (CV) Experiments:

All the Cyclic Voltammetric (CV) experiments were carried out under Argon (Ar) atmosphere. A platinum disk electrode (3 mm diameter) and a platinum wire were used as working and counter electrodes, respectively. The reference electrode used was an Ag/AgCl (in 3.5 M KCl) electrode. The potential values were reported relative to Ag/AgCl (in 3.5M KCl), and voltammetric studies in MeCN were recorded accordingly (Figure S4). The scan rate for all the CV experiment was fixed to 0.1 V/s.

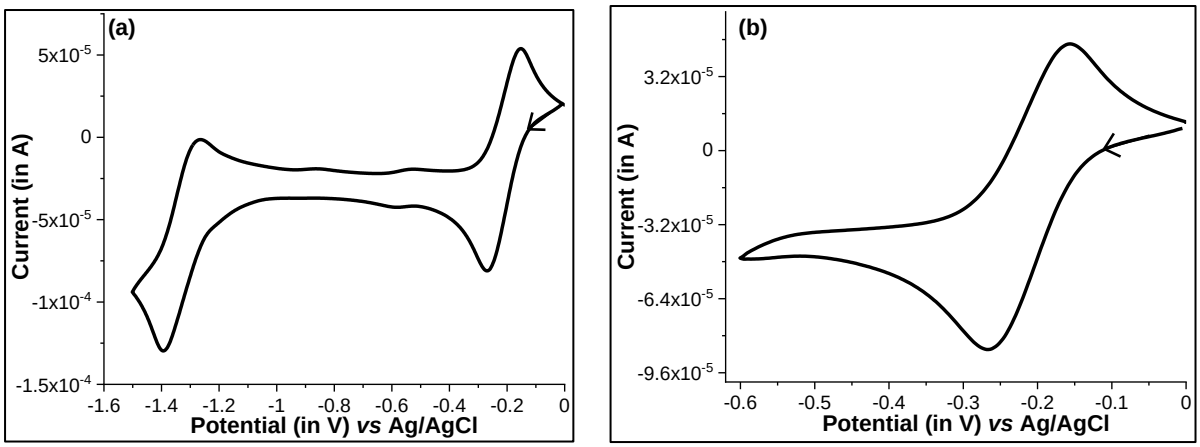


Figure S4: Cyclic voltammogram of **PC_1: (a)** For two electron reduction, **(b)** For one electron reduction.

6. Calculations of Excited State Potential ($E^*_{1/2}$) of PC_1 Using Rehm and Weller Equation[3]:

A solution of 25 μM **PC_1** in MECN was introduced into a 1 cm path length quartz cuvette equipped with a Teflon® septum and was subjected to a UV-Vis experiment using a UV-Vis spectrophotometer (UV-2450, Shimadzu, Japan). The data obtained were then normalized and plotted as shown in Fig S5.

The Rehm-Weller equation for the calculation of the excited state potential is given by equation:

$$\mathbf{E^*_{1/2} = E_{1/2} + E_{00}}$$

Where, $\mathbf{E^*_{1/2}}$ = excited-state redox potential, $\mathbf{E_{1/2}}$ = ground-state redox potential (known by experiment) and $\mathbf{E_{00}}$ = mean photon energy of the emission spectra in eV (by the exciting wavelength 440 nm and 400 nm).

For **PC_1**,

$\mathbf{E_{1/2}}$ = -0.21 V (from CV vs Ag/AgCl)

$\mathbf{E_{00}}$ = 2.82 eV (for 440 nm)

E_{00} = 3.10 eV (for 400 nm)

E_{00} = 3.00 eV (for (400+440)/2=420 nm).

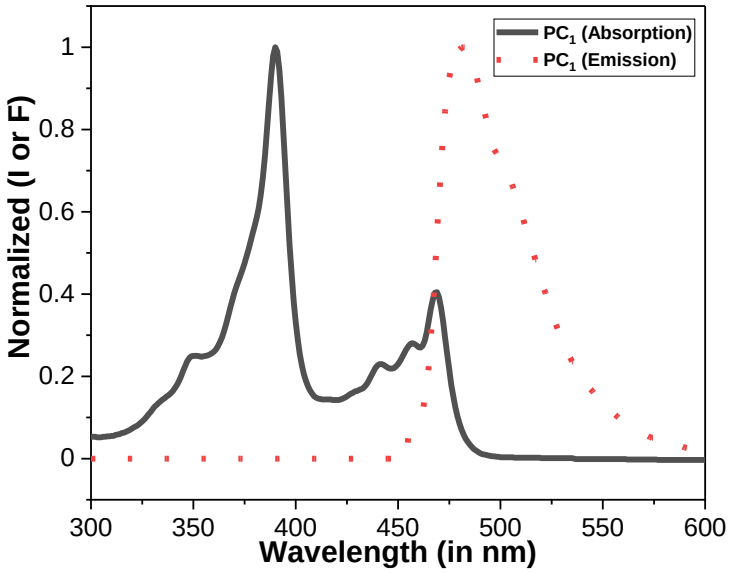


Figure S5: Normalised absorption spectra **PC_1** and emission spectra of **PC_1**.

Therefore, $E^*_{1/2}$ comes out to be **+2.61 V** (for 440 nm) and $E^*_{1/2}$ comes out to be +2.89 V (for 400 nm). $E^*_{1/2}$ comes out to be +2.79 V (for 420 nm). Note: We have considered the highest absorption wavelength (440 nm) of **PC_1** and lowest emission wavelength (400 nm) of the blue LED (440 nm) light used.

7. Photostability of PC_1:

To check the photostability of **PC_1** we have conducted the fluorescence experiment. We have noticed no decrease in the emission intensity of **PC_1** after 5 times excitation at 440 nm using Xe-900 lamp (Fig. S6). This experiment suggested no photobleaching of the photocatalyst **PC_1**.

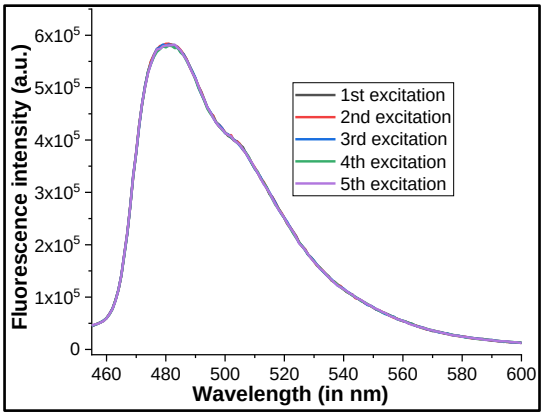


Figure S6: Photostability test of the **PC_1**.

8. Fluorescence Decay Experiments:

Excited state lifetime measurements were performed using a time-correlated single photon counting (TCSPC) spectrophotometer (Fluotime 300, PicoQuant, Germany). The instrument response function (IRF) was obtained through the use of a scattering Ludox solution. The sample of **PC_1** (3.0 μM) in dry acetonitrile was excited at 405 nm using a picosecond-pulsed diode laser. The picosecond fluorescence lifetime decays were deconvoluted using Fluofit software. The lifetime decay of the sample was collected at 483 nm (emission maxima) with a 5 nm emission slit width where the peak counts were normalized to 10000 counts. The lifetime decay was fit in two exponentials.

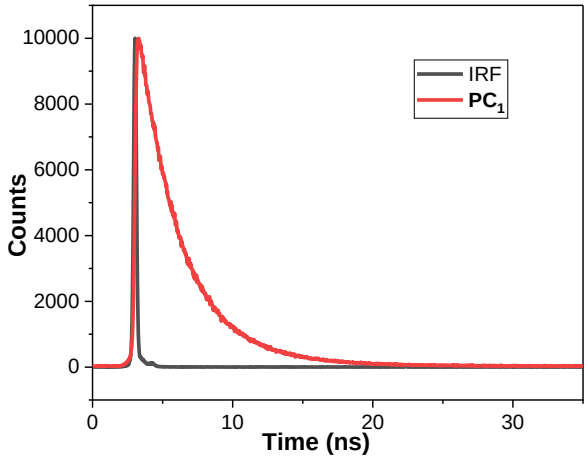
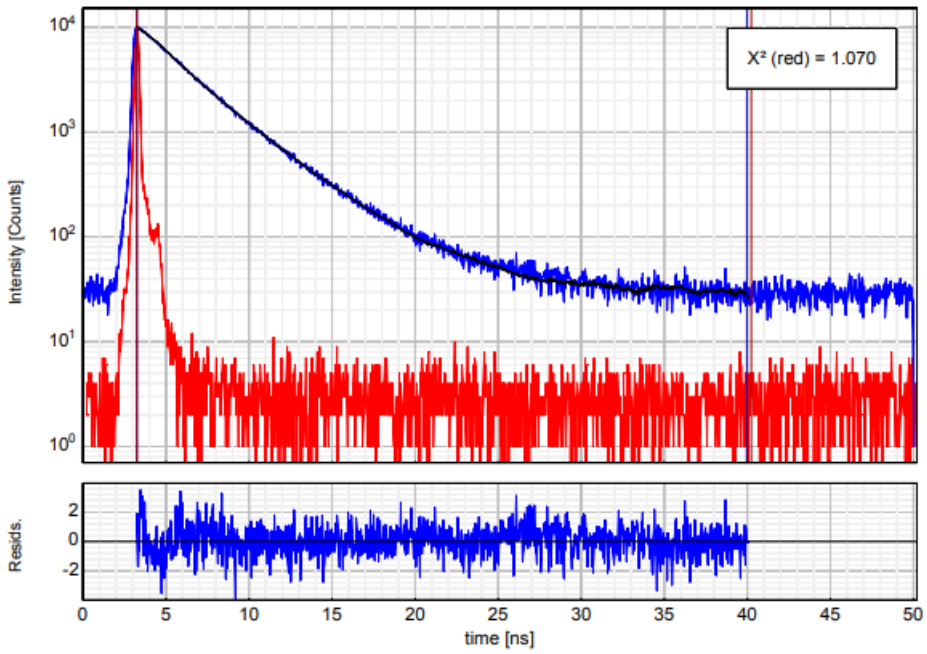


Figure S7: Fluorescence decay spectra of 3 μM solution of **PC_1** in CH_3CN.



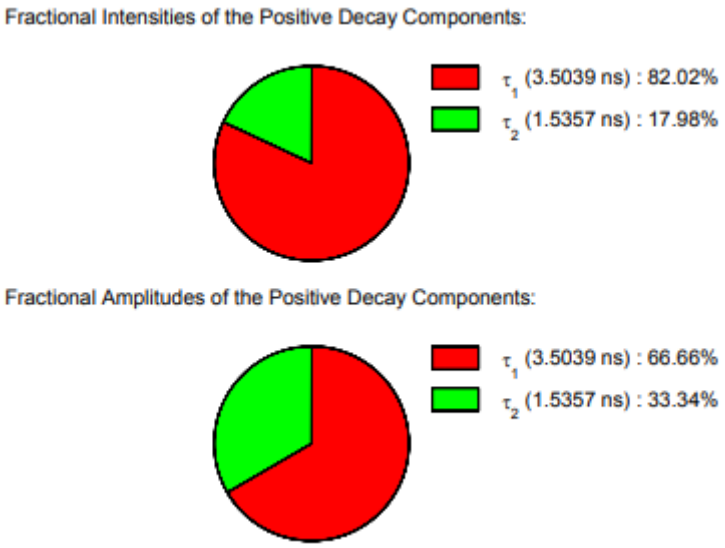


Figure S8: Lifetime dataset for 3 μM **PC$_1$** in MeCN

(*We thank Prof. Pramit Kumar Chowdhury, IIT Delhi for providing the access to spectrophotometer and enabling us to perform the fluorescence lifetime quenching experiments.)*

9. General Procedure for Photochemical Lactonization:

An oven dried 7 mL glass vial equipped with magnetic stirring bar was charged with 0.2 mmol suitable carboxylic acid **1**, **PC$_1$** (3.3 mg, 5 mol%) and $Co^{III}(dmgH)_2PyCl$ (8.1 mg, 10 mol%). Exact 2.0 mL of MeCN was added to the vial. A screw cap equipped with a PTFE septum was then fitted tightly to the reaction vial. The vial was then purged thrice with Argon (Ar) gas by using Schlenk line and then coated with parafilm to maintain inert atmosphere inside the vial. Next, the vial was placed into a magnetic stirrer and stirred for 10 minutes to ensure homogeneity. Then the reaction mixture was irradiated by a 440 nm Kessil lamp placed 4 cm away from the reaction vial (Fig S1). During the course of the reaction, room temperature was maintained by using an external cooling fan. After completion of the reaction (24 h), saturated sodium chloride solution (4.0 mL) was added to the reaction mixture and was extracted with ethyl acetate (3 × 5.0 mL), dried using anhydrous sodium sulfate (Na_2SO_4), concentrated in vacuo. The residue was finally purified using silica gel (230-400 mesh) column chromatography using ethyl acetate/hexane (1:10) as eluent. Isolated yield of the mixture of two successive batches was reported.

Note: In case of **1q** – **1y**, 2.0 equiv. of $K_2S_2O_8$ was used as a terminal oxidant instead of $Co^{III}(dmgH)_2PyCl$.

10. Procedure for Photochemical Lactonization in the 5.0 mmol Scale:

An oven-dried 50 mL sealed tube equipped with a magnetic stirring bar was charged with 1.0 mmol 6*H*-benzo[*c*]chromen-6-one **1a** (980.0 mg, 5.0 mmol), **PC$_1$** (82.5 mg, 5 mol %) and $Co^{III}(dmgH)_2PyCl$ (202.5 mg, 10 mol%). Exactly 25.0 mL of MeCN was added to the tube. A standard cap was fitted tightly to the reaction tube and properly coated with a parafilm layer. The tube was then purged thrice

with argon (Ar) gas to maintain an inert atmosphere inside the tube. Next, the tube was placed into a magnetic stirrer and stirred for 10 min to ensure homogeneity. Then, the reaction mixture was irradiated by two 440 nm Kessil lamp each placed 4 cm away from the reaction vial (Figure S2). During the course of the reaction, an ambient temperature (28-30 °C) was maintained by using an external cooling fan. After completion of the reaction (after 40 h), saturated sodium chloride solution (10.0 mL) was added to the reaction mixture and was extracted with ethyl acetate (3 × 10.0 mL), dried using anhydrous sodium sulfate, and concentrated in vacuo. The residue was finally purified using silica gel (230–400 mesh) column chromatography using ethyl acetate/hexane as eluent. Finally, 82% of the desired product **2a** was obtained.

11. UV-Visible Spectroscopic Analysis for any possible Ground State Quenching of PC_1:

To check whether any complexation or interaction between **PC_1** and **1a** was involved at the ground state, at first, the UV-Vis quenching study was conducted in MeCN. Initially, the absorbance of 40 μM **PC_1** was measured. Then, sequential addition of 10 mM, 20 mM, 30 mM, 40 mM, 50 mM, 60 mM and 70 mM **1a** to the 40 μM solution of **PC_1** in MeCN results no decrease or increase in absorbance at λ = 440 nm (Fig. S10a). This result ruled out any possibility for the ground state complexation or interaction between **PC_1** and **1a**.

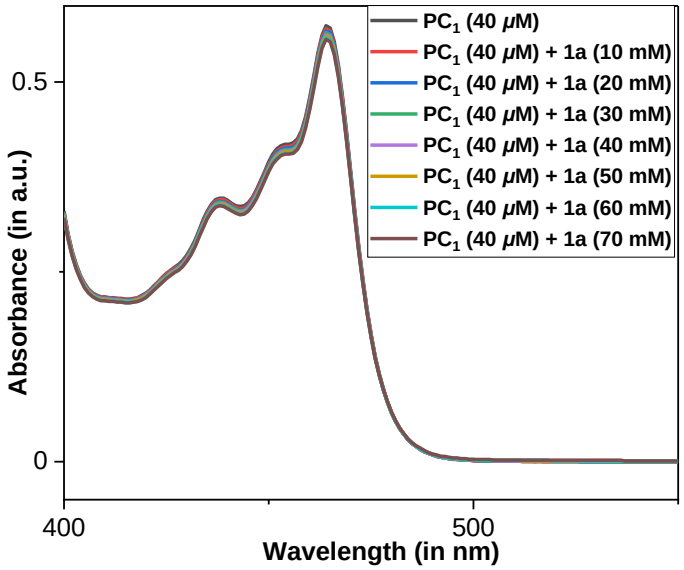


Figure S9: UV-Visible spectroscopic study for possible ground state complexation: sequential addition of **1a** to a solution of **PC_1** in MeCN.

12. Fluorescence Quenching Analysis:

To visualize the involvement of light for the lactonization, the excited state quenching study of **PC_1** i.e., fluorescence quenching experiment was performed. The components under consideration must satisfy the linear correlation obtained from Stern-Volmer[4] plot for successful quenching:

$$F_0/F = 1 + K_{SV}\,[Q]$$

Where, F_0 = Fluorescence intensity in absence of quencher, F = Fluorescence intensity in presence of quencher, K_{SV} = Stern Volmer constant, [Q] = concentration of quencher.

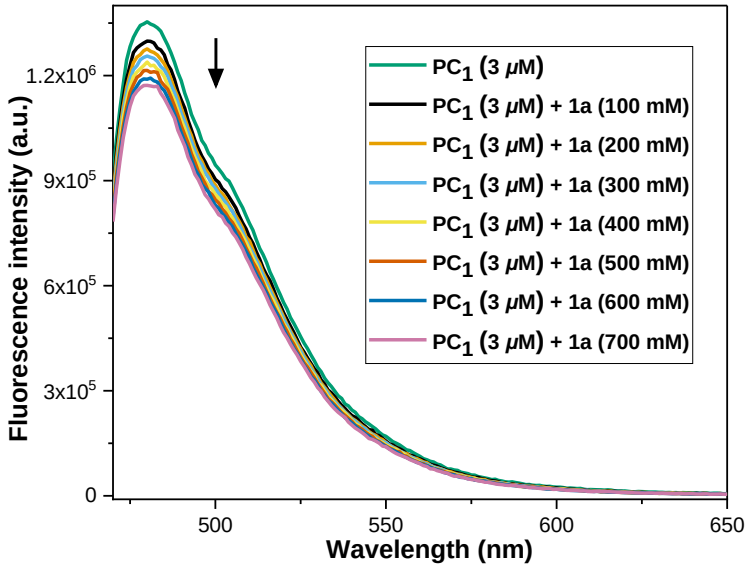


Figure S10: Fluorescence quenching study: sequential addition of **1a** to a solution of **PC_1** in MeCN.

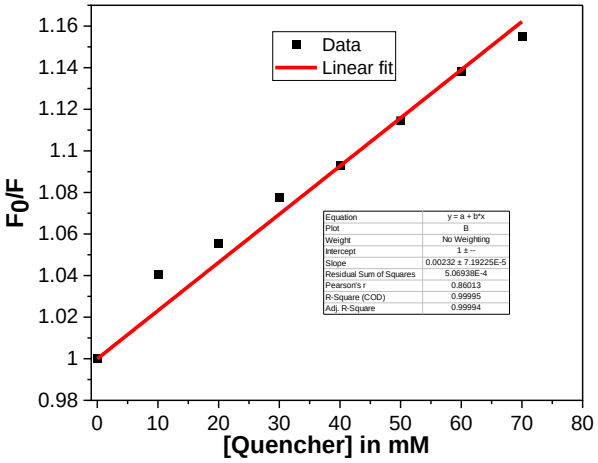


Figure S11: Stern-Volmer plot of F_0/F vs [Quencher] in MeCN.

Initially, the fluorescence emission intensity of a solution containing 3.0 μM **PC_1** (in MeCN) in 1 cm path length quartz cuvette equipped with a Teflon® septum was recorded by exciting at 440 nm and data was collected from 470 nm to 650 nm. Then to the solution of 3.0 μM **PC_1** sequential addition of

100 mM, 200 mM, 300 mM, 400 mM, 500 mM, 600 mM and 700 mM **1a** results in a sharp decrease in the fluorescence intensity (fluorescence quenching) after each addition (Fig. S10).

From the data obtained, a plot of F_0/F vs [Quencher] was drawn (Fig. S11).

13. Electron Paramagnetic Resonance (EPR) Analysis:

Continuous wave (CW) EPR spectra was obtained using a Bruker A300-9.5/12/S/W instrument with X-band of 8.75-9.65 GHz. The spectral data was collected at 77 K with the following spectrometer settings: microwave power = 0.48 mW, center field = 3350 G, sweep width = 100 G, sweep time = 30 s, modulation frequency = 9.6 GHz, modulation amplitude = 10 G, time constant = 0.01 ms.

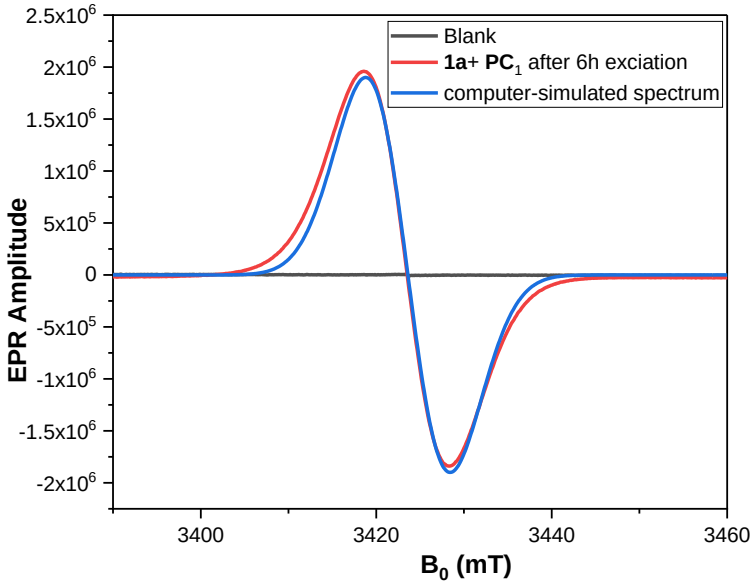


Figure S12: EPR spectral analysis.

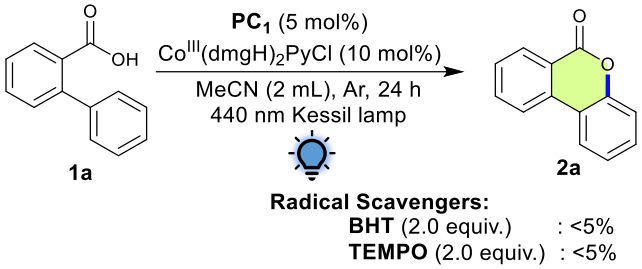
For all the EPR measurements, the corresponding sample solution was transferred into the EPR tube and then placed in liquid Nitrogen to freeze the sample solution prior to recording the spectra. Then, the sample tube was inserted in the EPR cavity which was kept frozen with continuous supply of liquid nitrogen for the recording of the spectra.

For experiment in which the sample was irradiated, the sample tube was kept at 4 cm distance from the 440 nm Kessil lamp. Initially, an oven dried 7 mL glass vial equipped with magnetic stirring bar was charged with 0.2 mmol **1a** and **PC_1** (3.3 mg, 5 mol%). Exact 2.0 mL of MeCN was added to the vial. A screw cap equipped with a PTFE septum was then fitted tightly to the reaction vial. The vial was then purged thrice with Argon (Ar) gas by using Schlenk line and then coated with parafilm to maintain inert atmosphere inside the vial. Next, the vial was placed into a magnetic stirrer and stirred for 10 minutes to ensure homogeneity. Then, from the reaction mixture, 500 μL solution was transferred into the EPR tube and EPR spectra was recorded (Fig. 12, black line) after freezing the solution by using liquid nitrogen (liq. N_2). Then the tube containing reaction mixture was left 5 minutes to attain room

temperature and irradiated for 6 h. Instantly after irradiation, the EPR spectra was recorded in a similar fashion (Fig. 12, blue line). The blue line corresponds to computer-stimulated spectrum (stimulated parameters: Hydrogen hyperfine coupling constant = 2 G and g_{iso} = 2.00688).

(We thank Prof. Sayantan Paria, IIT Delhi for helping to simulate the EPR Spectrum.)

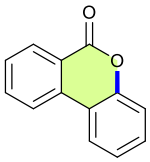
14. Radical Inhibition Experiments:



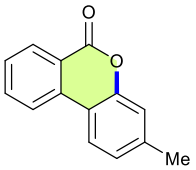
An oven dried 7 mL glass vial equipped with magnetic stirring bar was charged with 0.2 mmol suitable carboxylic acid **1**, **PC$_1$** (3.3 mg, 5 mol%), TEMPO (2.0 eq.) or BHT (2.0 eq.) and $Co^{III}(dmgH)_2PyCl$ (8.1 mg, 10 mol%). Exact 2.0 mL of MeCN was added to the vial. A screw cap equipped with a PTFE septum was then fitted tightly to the reaction vial. The vial was then purged thrice with Argon (Ar) gas by using Schlenk line and then coated with parafilm to maintain inert atmosphere inside the vial. Next, the vial was placed into a magnetic stirrer and stirred for 10 minutes to ensure homogeneity. Then the reaction mixture was irradiated by a 440 nm Kessil lamp placed 4 cm away from the reaction vial (Fig S1). During the course of the reaction, room temperature was maintained by using an external cooling fan. After completion of the reaction (24 h), the reaction mixtures were individually subjected to GC for observing desired product formation. Negligible amount of the desired product was formed in both the cases.

15. Spectral Data:

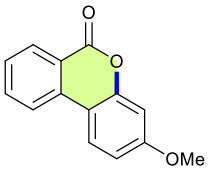
6*H*-benzo[*c*]chromen-6-one (2a)[5] was synthesised by following General Procedure. After appropriate work up process, the reaction mixture was purified by column chromatography eluted with 10% EtOAc in *n*-hexane to provide **2a** as white solid (75 mg, 96% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.38 (d, *J* = 7.8 Hz, 1H), 8.10 – 8.08 (m, 1H), 8.04 – 8.02 (m, 1H), 7.82 – 7.79 (m, 1H), 7.56 (t, *J* = 7.5 Hz, 1H), 7.48 – 7.45 (m, 1H), 7.35 – 7.31 (m, 2H), ppm. **^{13}C {^{1}H} NMR** (126 MHz, $CDCl_3$) δ 161.1, 151.2, 134.8, 134.7, 130.5, 130.4, 128.8, 124.5, 122.7, 121.6, 121.2, 117.9, 117.7 ppm.



3-methyl-6*H*-benzo[*c*]chromen-6-one (2b)[5] was synthesised by following General Procedure. After appropriate work up process, the reaction mixture was purified by column chromatography eluted with 10% EtOAc in *n*-hexane to provide **2b** as white solid (71 mg, 85% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.31 (dd, *J* = 7.9, 0.8 Hz, 1H), 7.99 (d, *J* = 8.1 Hz, 1H), 7.83 (d, *J* = 8.5 Hz, 1H), 7.76 – 7.73 (m, 1H), 7.51 – 7.48 (m, 1H), 7.09 – 7.08 (m, 2H), 2.40 (s, 3H) ppm. **^{13}C {^{1}H} NMR** (126 MHz, $CDCl_3$) 161.2, 151.1, 141.1, 134.8, 134.6, 130.3, 128.2, 125.5, 122.4, 121.3, 120.7, 117.7, 115.2, 21.3 ppm.

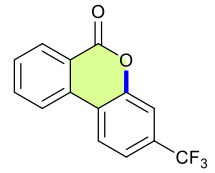


3-methoxy-6*H*-benzo[*c*]chromen-6-one (2c)[5] was synthesised by following General Procedure. After appropriate work up process, the reaction mixture was purified by column chromatography eluted with 10% EtOAc in *n*-hexane to provide **2c** as white solid (75 mg, 83% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.33 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.97 (d, *J* = 8.0 Hz, 1H), 7.91 (d, *J* = 8.8 Hz, 1H), 7.80 – 7.73 (m, 1H), 7.51 – 7.45 (m, 1H), 6.89 (dd, *J* = 8.8, 2.5 Hz, 1H), 6.84 (d, *J* = 2.5 Hz, 1H), 3.87 (s, 3H) ppm. **^{13}C {^{1}H} NMR** (126 MHz, $CDCl_3$) δ 161.4, 161.4, 152.5, 135.1, 134.8, 130.5, 127.6, 123.7, 121.0, 119.9, 112.3, 111.1, 101.6, 55.6 ppm.

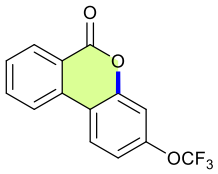


3-(tert-butyl)-6*H*-benzo[*c*]chromen-6-one (2d)[6] was synthesised by following General Procedure. After appropriate work up process, the reaction mixture was purified by column chromatography eluted with 10% EtOAc in *n*-hexane to provide **2d** as white solid (82 mg, 82% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.38 (d, *J* = 7.9 Hz, 1H), 8.07 (d, *J* = 8.1 Hz, 1H), 7.97 – 7.96 (m, 1H), 7.79 (t, *J* = 7.6 Hz, 1H), 7.54 (t, *J* = 7.6 Hz, 1H), 7.38 – 7.37 (m, 2H), 1.37 (s, 9H) ppm. **^{13}C {^{1}H} NMR** (126 MHz, $CDCl_3$) δ 161.4, 154.6, 151.1, 134.8, 134.7, 130.5, 128.3, 122.3, 121.9, 121.4, 120.9, 115.3, 114.5, 35.0, 31.0 ppm.

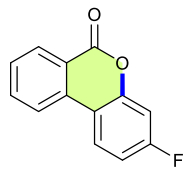
3-(trifluoromethyl)-6*H*-benzo[*c*]chromen-6-one (2e)[5] was synthesised by following General Procedure. After appropriate work up process, the reaction mixture was purified by column chromatography eluted with 10% EtOAc in *n*-hexane to provide **2e** as white solid (90 mg, 85% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.41 (dd, *J* = 7.9, 0.9 Hz, 1H), 8.16 (t, *J* = 8.8 Hz, 2H), 7.90 – 7.87 (m, 1H), 7.68 – 7.65 (m, 1H), 7.60 – 7.57 (m, 2H) ppm. **^{13}C {^{1}H} NMR** (126 MHz, $CDCl_3$) δ 160.2, 150.9, 135.2, 133.3, 132.2 (q, $J_{C–F}$ = 37.8 Hz), 130.8, 130.1, 123.6, 123.2 (q, $J_{C–F}$ = 277.0 Hz), 122.2, 121.6, 121.0 (q, $J_{C–F}$ = 3.78 Hz), 115.2 (q, $J_{C–F}$ = 3.78 Hz) ppm.



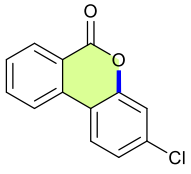
3-(trifluoromethoxy)-6*H*-benzo[*c*]chromen-6-one (2f)[7] was synthesised by following General Procedure. After appropriate work up process, the reaction mixture was purified by column chromatography eluted with 10% EtOAc in *n*-hexane to provide **2f** as white solid (100 mg, 89% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.35 (dd, *J* = 7.9, 0.9 Hz, 1H), 8.05 – 8.03 (m, 2H), 7.83 (td, *J* = 7.8, 1.3 Hz, 1H), 7.60 – 7.57 (m, 1H), 7.20 – 7.18 (m, 2H) ppm. **^{13}C {^{1}H} NMR** (126 MHz, $CDCl_3$) δ 160.4, 151.7, 150.1 (q, $J_{C–F}$ = 2.5 Hz), 135.1, 133.7, 130.6, 129.2, 124.1, 121.7, 120.7, 120.3 (q, $J_{C–F}$ = 264.6 Hz), 116.9, 116.6, 110.0 ppm.



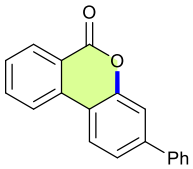
3-fluoro-6*H*-benzo[*c*]chromen-6-one (2g)[5] was synthesised by following General Procedure. After appropriate work up process, the reaction mixture was purified by column chromatography eluted with 10% EtOAc in *n*-hexane to provide **2g** as white solid (77 mg, 90% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.35 (d, *J* = 7.9 Hz, 1H), 8.03 – 8.00 (m, 2H), 7.82 (t, *J* = 7.7 Hz, 1H), 7.56 (t, *J* = 7.6 Hz, 1H), 7.08 – 7.05 (m, 2H) ppm. **^{13}C {^{1}H} NMR** (126 MHz, $CDCl_3$) δ 163.3 (d, $J_{C–F}$ = 252.0 Hz), 160.7, 152.0 (d, $J_{C–F}$ = 12.6 Hz), 135.0, 134.1, 130.6, 128.7, 124.3 (d, $J_{C–F}$ = 10.0 Hz), 121.4, 120.4, 114.5 (d, $J_{C–F}$ = 3.78 Hz), 112.4 (C–F, 2$J_{C–F}$ = 25.2 Hz), 105.0 (d, $J_{C–F}$ = 25.2 Hz) ppm.



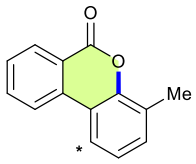
3-chloro-6*H*-benzo[*c*]chromen-6-one (2h)[5] was synthesised by following General Procedure. After appropriate work up process, the reaction mixture was purified by column chromatography eluted with 10% EtOAc in *n*-hexane to provide **2h** as white solid (77 mg, 84% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.35 (d, *J* = 7.9 Hz, 1H), 8.03 (d, *J* = 8.1 Hz, 1H), 7.94 (d, *J* = 8.5 Hz, 1H), 7.82 (t, *J* = 7.6 Hz, 1H), 7.58 (t, *J* = 7.6 Hz, 1H), 7.32 – 7.27 (m, 2H) ppm. **^{13}C {^{1}H} NMR** (126 MHz, $CDCl_3$) δ 160.5, 151.4, 135.8, 135.0, 133.9, 130.6, 129.1, 124.9, 123.7, 121.6, 120.8, 117.8, 116.6 ppm.



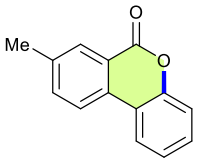
3-phenyl-6*H*-benzo[*c*]chromen-6-one (2i)[8] was synthesised by following General Procedure. After appropriate work up process, the reaction mixture was purified by column chromatography eluted with 10% EtOAc in *n*-hexane to provide **2i** as white solid (84 mg, 77% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.39 (dd, *J* = 7.9, 0.9 Hz, 1H), 8.12 – 8.07 (m, 2H), 7.83 – 7.80 (m, 1H), 7.65 – 7.63 (m, 2H), 7.58 – 7.56 (m, 3H), 7.49 – 7.46 (m, 2H), 7.42 – 7.39 (m, 1H) ppm. **^{13}C {^{1}H} NMR** (126 MHz, $CDCl_3$) δ 161.2, 151.6, 143.5, 139.2, 134.8, 134.6, 130.6, 129.0, 128.8, 128.2, 127.0, 123.3, 123.1, 121.6, 121.1, 116.9, 115.8 ppm.



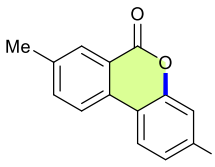
2-methyl-6*H*-benzo[*c*]chromen-6-one and 4-methyl-6*H*-benzo[*c*]chromen-6-one (2j)[9] was synthesised by following General Procedure. After appropriate work up process, the crude reaction mixture was purified by column chromatography eluted with 10% EtOAc in *n*-hexane to provide 2j (mixture of isomers) as white solid (62 mg, 74% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.37 – 8.33 (m, 1.42H), 8.04 (t, *J* = 7.8 Hz, 1.49H), 7.84 (d, *J* = 7.8 Hz, 0.48H), 7.79 – 7.76 (m, 2.55H), 7.53 (t, *J* = 7.6 Hz, 1.49H), 7.30 – 7.17 (m, 3.29H), 2.46 (s, 1.25H), 2.43 (s, 3H) ppm. **^{13}C {^{1}H} NMR** (126 MHz, $CDCl_3$) δ 161.3, 161.1, 149.4, 149.1, 134.6, 134.6, 134.0, 131.7, 131.2, 130.4, 130.3, 128.6, 128.5, 126.8, 123.9, 122.6, 121.7, 121.5, 121.0, 120.9, 120.2, 117.5, 117.4, 117.3, 21.0, 15.9 ppm.



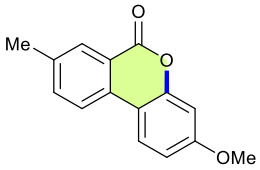
8-methyl-6*H*-benzo[*c*]chromen-6-one (2k)[5] was synthesised by following General Procedure. After appropriate work up process, the reaction mixture was purified by column chromatography eluted with 10% EtOAc in *n*-hexane to provide **2k** as white solid (75 mg, 89% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.17 (s, 1H), 7.98 (dd, *J* = 9.7, 8.5 Hz, 2H), 7.61 (d, *J* = 8.1 Hz, 1H), 7.45 – 7.42 (m, 1H), 7.34 – 7.29 (m, 2H), 2.48 (s, 3H) ppm. **^{13}C {^{1}H} NMR** (126 MHz, $CDCl_3$) δ 161.3, 150.9, 139.2, 136.0, 132.1, 130.3, 129.8, 124.4, 122.5, 121.6, 121.0, 118.1, 117.6, 21.2 ppm.



3,8-dimethyl-6*H*-benzo[*c*]chromen-6-one (2l)[9] was synthesised by following General Procedure. After appropriate work up process, the reaction mixture was purified by column chromatography eluted with 10% EtOAc in *n*-hexane to provide **2l** as white solid (72 mg, 80% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.08 (s, 1H), 7.85 (d, *J* = 8.2 Hz, 1H), 7.79 (d, *J* = 8.5 Hz, 1H), 7.53 (dd, *J* = 8.2, 1.2 Hz, 1H), 7.06 – 7.05 (m, 2H), 2.43 (s, 3H), 2.39 (s, 3H) ppm. **^{13}C {^{1}H} NMR** (126 MHz, $CDCl_3$) δ 161.4, 150.8, 140.5, 138.4, 135.8, 132.2, 130.0, 125.4, 122.1, 121.2, 120.5, 117.5, 115.4, 21.3, 21.1 ppm.

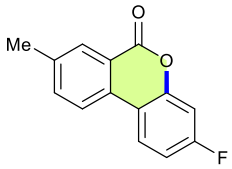


3-methoxy-8-methyl-6*H*-benzo[*c*]chromen-6-one (2m)[10] was synthesised by following General Procedure. After appropriate work up process, the reaction mixture was purified by column chromatography eluted with 10% EtOAc in *n*-hexane to provide **2m** as white solid (78 mg, 81% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.07 (s, 1H), 7.80 (t, *J* = 9.0 Hz, 2H), 7.53 (d, *J* = 8.1 Hz, 1H), 6.84 (dd, *J* =

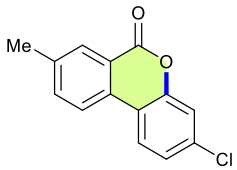


8.8, 2.4 Hz, 1H), 6.77 (d, *J* = 2.4 Hz, 1H), 3.84 (s, 3H), 2.43 (s, 3H) ppm. **^{13}C {^{1}H} NMR** (126 MHz, $CDCl_3$) δ 161.5, 161.0, 152.1, 137.7, 135.9, 132.4, 130.0, 123.4, 120.9, 119.6, 112.1, 111.1, 101.4, 55.5, 21.1 ppm.

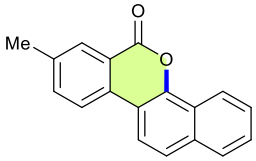
3-fluoro-8-methyl-6*H*-benzo[*c*]chromen-6-one (2n)[10] was synthesised by following General Procedure. After appropriate work up process, the reaction mixture was purified by column chromatography eluted with 10% EtOAc in *n*-hexane to provide **2n** as white solid (82 mg, 90% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.08 (s, 1H), 7.92 (t, *J* = 6.1 Hz, 1H), 7.85 (d, *J* = 6.2 Hz, 1H), 7.58 (d, *J* = 8.0 Hz, 1H), 7.01 (dd, *J* = 16.6, 8.6 Hz, 2H), 2.45 (s, 3H) ppm. **^{13}C {^{1}H} NMR** (126 MHz, $CDCl_3$) δ 163.0 (d, $J_{C–F}$ = 250.7 Hz), 160.8, 151.7, 151.1 (d, $J_{C–F}$ = 10.0 Hz), 139.0, 136.1, 131.5, 130.2, 124.0, 123.9 (d, $J_{C–F}$ = 10.0 Hz), 121.35, 120.1, 114.6, 112.2 (d, $J_{C–F}$ = 10.0 Hz), 104.8 (d, $J_{C–F}$ = 10.0 Hz), 21.1 ppm.



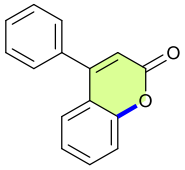
3-chloro-8-methyl-6*H*-benzo[*c*]chromen-6-one (2o)[11] was synthesised by following General Procedure. After appropriate work up process, the reaction mixture was purified by column chromatography eluted with 10% EtOAc in *n*-hexane to provide **2o** as white solid (86 mg, 88% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.09 (s, 1H), 7.86 (dd, *J* = 8.2, 5.0 Hz, 2H), 7.59 (d, *J* = 8.1 Hz, 1H), 7.27 – 7.23 (m, 2H), 2.46 (s, 3H) ppm. **^{13}C {^{1}H} NMR** (126 MHz, $CDCl_3$) δ 160.5, 151.0, 139.5, 136.1, 135.2, 131.2, 130.3, 124.8, 123.4, 121.5, 120.5, 117.6, 116.7, 21.2 ppm.



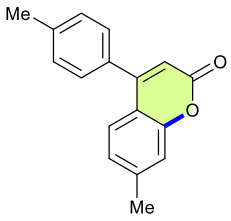
8-methyl-6*H*-dibenzo[c,h]chromen-6-one (2p)[10] was synthesised by following General Procedure. After appropriate work up process, the reaction mixture was purified by column chromatography eluted with 10% EtOAc in *n*-hexane to provide **2p** as white solid (77 mg, 74% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.44 (d, *J* = 8.1 Hz, 1H), 8.11 (s, 1H), 7.87 (dd, *J* = 18.1, 8.5 Hz, 2H), 7.76 (d, *J* = 8.0 Hz, 1H), 7.61 (d, *J* = 8.7 Hz, 1H), 7.56 – 7.50 (m, 3H), 2.41 (s, 3H) ppm. **^{13}C {^{1}H} NMR** (126 MHz, $CDCl_3$) δ 161.2, 146.5, 138.7, 135.9, 133.8, 132.6, 130.1, 127.5, 127.4, 126.8, 124.2, 123.65, 122.0, 121.8, 120.7, 118.9, 112.9, 21.2 ppm.



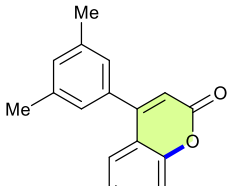
4-phenyl-2*H*-chromen-2-one (2q)[12] was synthesised by following General Procedure. After appropriate work up process, the reaction mixture was purified by column chromatography eluted with 10% EtOAc in *n*-hexane to provide **2q** as white solid (80 mg, 90% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.57 – 7.52 (m, 4H), 7.50 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.47 – 7.45 (m, 2H), 7.42 (dd, *J* = 8.3, 0.9 Hz, 1H), 7.25 – 7.22 (m, 1H), 6.39 (s, 1H) ppm. **^{13}C {^{1}H} NMR** (126 MHz, $CDCl_3$) δ 160.7, 155.7, 154.2, 135.2, 131.9, 129.7, 128.9, 128.4, 127.0, 124.1, 119.0, 117.3, 115.2 ppm.



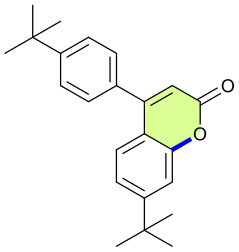
7-methyl-4-(p-tolyl)-2*H*-chromen-2-one (2r)[13] was synthesised by following General Procedure. After appropriate work up process, the reaction mixture was purified by column chromatography eluted with 10% EtOAc in *n*-hexane to provide **2r** as white solid (86 mg, 86% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.39 (d, *J* = 8.1 Hz, 1H), 7.36 – 7.29 (m, 4H), 7.20 (s, 1H), 7.03 (d, *J* = 8.1 Hz, 1H), 6.28 (d, *J* = 1.1 Hz, 1H), 2.44 (s, 6H) ppm. **^{13}C {^{1}H} NMR** (126 MHz, $CDCl_3$) δ 161.1, 155.7, 154.3, 143.0, 139.7, 132.5, 129.5, 128.3, 126.7, 125.2, 117.4, 116.6, 113.7, 21.5, 21.3 ppm.



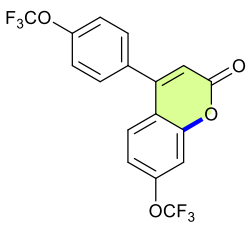
4-(3,5-dimethylphenyl)-6,8-dimethyl-2*H*-chromen-2-one (2s) was synthesised by following General Procedure. After appropriate work up process, the reaction mixture was purified by column chromatography eluted with 10% EtOAc in *n*-hexane to provide **2s** as white solid (92 mg, 83% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.21 (s, 1H), 7.14 (s, 1H), 7.09 (s, 1H), 7.02 (s, 2H), 6.29 (s, 1H), 2.46 (s, 3H), 2.40 (s, 6H), 2.29 (s, 3H) ppm. **^{13}C {^{1}H} NMR** (126 MHz, $CDCl_3$) δ 161.1, 156.3, 150.5, 138.3, 135.6, 134.2, 133.0, 130.9, 126.1, 126.0, 124.5, 118.5, 114.5, 21.2, 20.8, 15.6 ppm. mp. 157–159 °C. HRMS (ESI-TOF): m/z [M + H]+ calcd for $C_{19}H_{19}O_2$ 279.1380, found 279.1377.



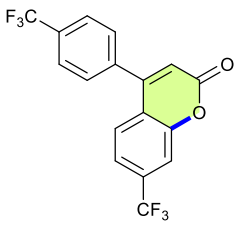
7-(tert-butyl)-4-(4-(tert-butyl)phenyl)-2*H*-chromen-2-one (2t) was synthesised by following General Procedure. After appropriate work up process, the reaction mixture was purified by column chromatography eluted with 10% EtOAc in *n*-hexane to provide **2t** as white solid (111 mg, 83% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.4 Hz, 2H), 7.49 (d, *J* = 8.4 Hz, 1H), 7.42 – 7.38 (m, 3H), 7.27 (dd, *J* = 8.6, 1.7 Hz, 1H), 6.32 (s, 1H), 1.39 (s, 9H), 1.36 (s, 9H) ppm. **^{13}C {^{1}H} NMR** (126 MHz, $CDCl_3$) δ 161.3, 156.3, 155.5, 154.2, 152.9, 132.4, 128.2, 126.6, 125.7, 121.6, 116.5, 114.1, 113.9, 35.1, 34.8, 31.2, 31.0 ppm. mp. 163–165 °C. HRMS (ESI-TOF): m/z [M + H]+ calcd for $C_{23}H_{27}O_2$ 335.2006, found 335.1992.



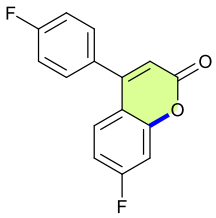
7-(trifluoromethoxy)-4-(4-(trifluoromethoxy)phenyl)-2*H*-chromen-2-one (2u) was synthesised by following General Procedure. After appropriate work up process, the reaction mixture was purified by column chromatography eluted with 10% EtOAc in *n*-hexane to provide **2u** as white solid (137 mg, 88% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.48 (t, *J* = 9.0 Hz, 3H), 7.40 (d, *J* = 8.3 Hz, 2H), 7.29 (s, 1H), 7.11 (d, *J* = 8.8 Hz, 1H), 6.38 (s, 1H) ppm. **^{13}C {^{1}H} NMR** (126 MHz, $CDCl_3$) δ 159.8, 154.9, 153.4, 151.5, 150.4, 133.2, 130.0, 128.1, 121.4, 121.3, 119.4, 119.2, 117.2, 116.5, 115.5, 109.5 ppm. mp. 177–179 °C. HRMS (ESI-TOF): m/z [M + H]+ calcd for $C_{17}H_9F_6O_4$ 391.0400, found 391.0392.



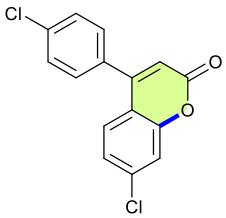
7-(trifluoromethyl)-4-(4-(trifluoromethyl)phenyl)-2*H*-chromen-2-one (2v) was synthesised by following General Procedure. After appropriate work up process, the reaction mixture was purified by column chromatography eluted with 10% EtOAc in *n*-hexane to provide **2v** as white solid (122 mg, 85% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.1 Hz, 2H), 7.68 (s, 1H), 7.59 (d, *J* = 8.0 Hz, 2H), 7.50 (dt, *J* = 8.4, 4.8 Hz, 2H), 6.50 (s, 1H) ppm. **^{13}C {^{1}H} NMR** (126 MHz, $CDCl_3$) δ 159.1, 153.9, 153.1, 137.9, 134.4, 134.1, 133.9, 133.6, 132.4, 132.1, 131.9, 128.8, 127.4, 126.2, 126.2, 126.2, 126.2, 124.7, 124.1, 122.5, 121.9, 121.1, 120.9, 120.9, 120.9, 120.9, 117.8, 114.9, 114.9 ppm. mp. 192–194 °C. HRMS (ESI-TOF): m/z [M + H]+ calcd for $C_{17}H_9F_6O_2$ 359.0501, found 359.0507.



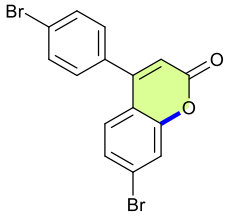
7-fluoro-4-(4-fluorophenyl)-2*H*-chromen-2-one (2w)[12] was synthesised by following General Procedure. After appropriate work up process, the reaction mixture was purified by column chromatography eluted with 10% EtOAc in *n*-hexane to provide **2w** as white solid (95 mg, 92% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.84 – 7.78 (m, 1H), 7.17 (t, *J* = 8.6 Hz, 1H) ppm. **^{13}C {^{1}H} NMR** (126 MHz, $CDCl_3$) δ 165.6, 164.6, 163.5, 162.6, 160.1, 155.4, 154.2, 131.0, 130.3, 130.3, 128.5, 128.4, 116.3, 116.1, 114.1, 112.4, 112.2, 105.0, 104.8 ppm.



7-chloro-4-(4-chlorophenyl)-2*H*-chromen-2-one (2x)[13] was synthesised by following General Procedure. After appropriate work up process, the reaction mixture was purified by column chromatography eluted with 10% EtOAc in *n*-hexane to provide **2x** as white solid (109 mg, 94% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.52 (d, *J* = 8.3 Hz, 2H), 7.42 – 7.34 (m, 4H), 7.21 (dd, *J* = 8.6, 1.8 Hz, 1H), 6.34 (s, 1H) ppm. **^{13}C {^{1}H} NMR** (126 MHz, $CDCl_3$) δ 159.7, 154.4, 153.8, 138.1, 136.2, 133.1, 129.7, 129.3, 127.6, 124.8, 117.6, 117.3, 115.2 ppm.



7-bromo-4-(4-bromophenyl)-2*H*-chromen-2-one (2y)[13] was synthesised by following General Procedure. After appropriate work up process, the reaction mixture was purified by column chromatography eluted with 10% EtOAc in *n*-hexane to provide **2y** as white solid (134 mg, 88% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.3 Hz, 2H), 7.57 (d, *J* = 1.5 Hz, 1H), 7.37 (dd, *J* = 8.5, 1.6 Hz, 1H), 7.31 (dd, *J* = 10.4, 8.6 Hz, 3H), 6.36 (s, 1H) ppm. **^{13}C {^{1}H} NMR** (126 MHz, $CDCl_3$) δ 159.6, 154.3, 153.9, 133.5, 132.3, 139.9, 127.7, 127.7, 126.1, 124.4, 120.6, 117.6, 115.3 ppm.



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17. ^{1}H and ^{13}C NMR Spectra:

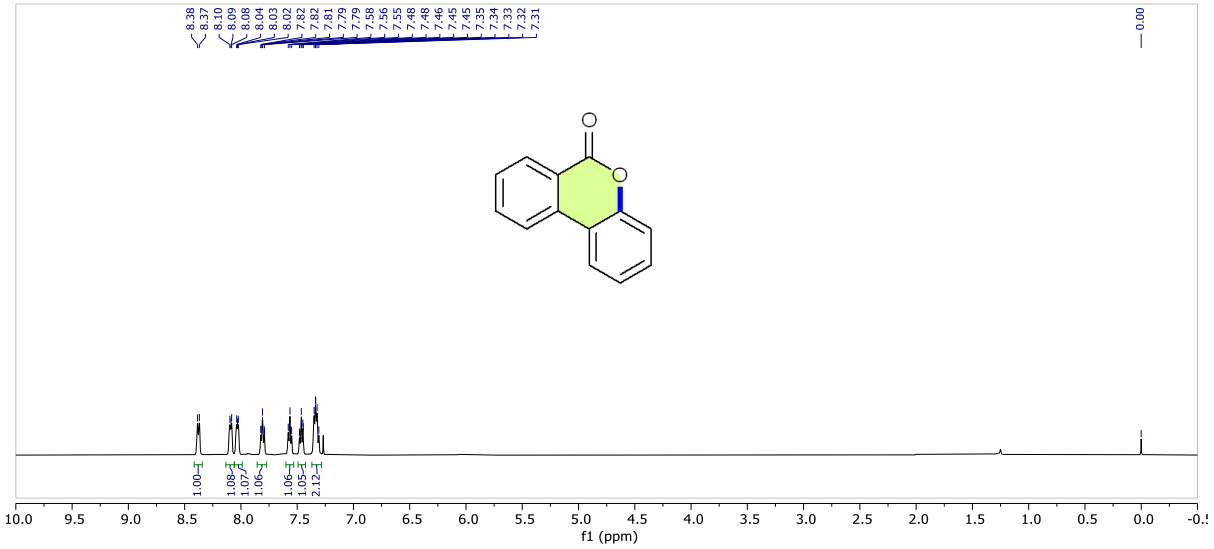

Figure S13: ^{1}H NMR (500 MHz, $CDCl_3$) of compound **2a**

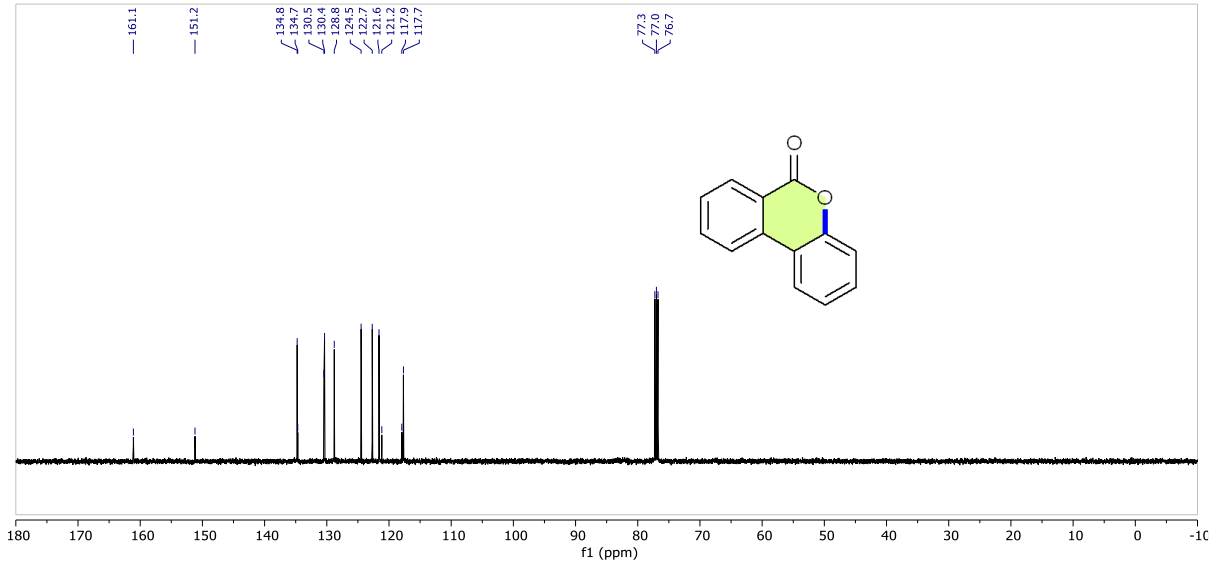

Figure S14: ^{13}C NMR (126 MHz, $CDCl_3$) of compound **2a**

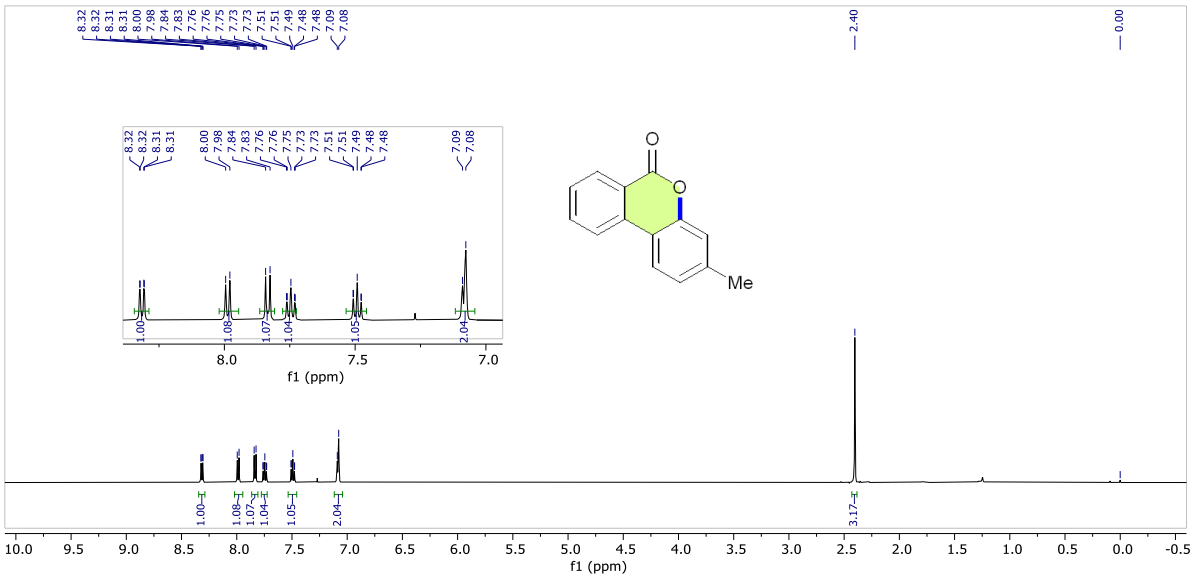

Figure S15: ^{1}H NMR (500 MHz, $CDCl_3$) of compound **2b**

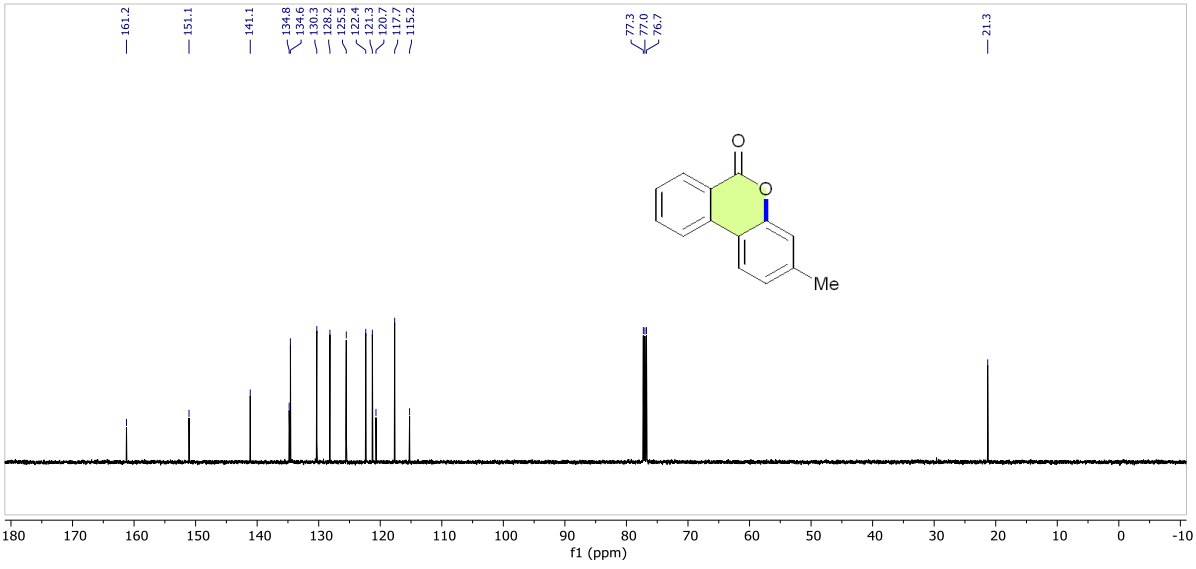

Figure S16: ^{13}C NMR (126 MHz, $CDCl_3$) of compound **2b**

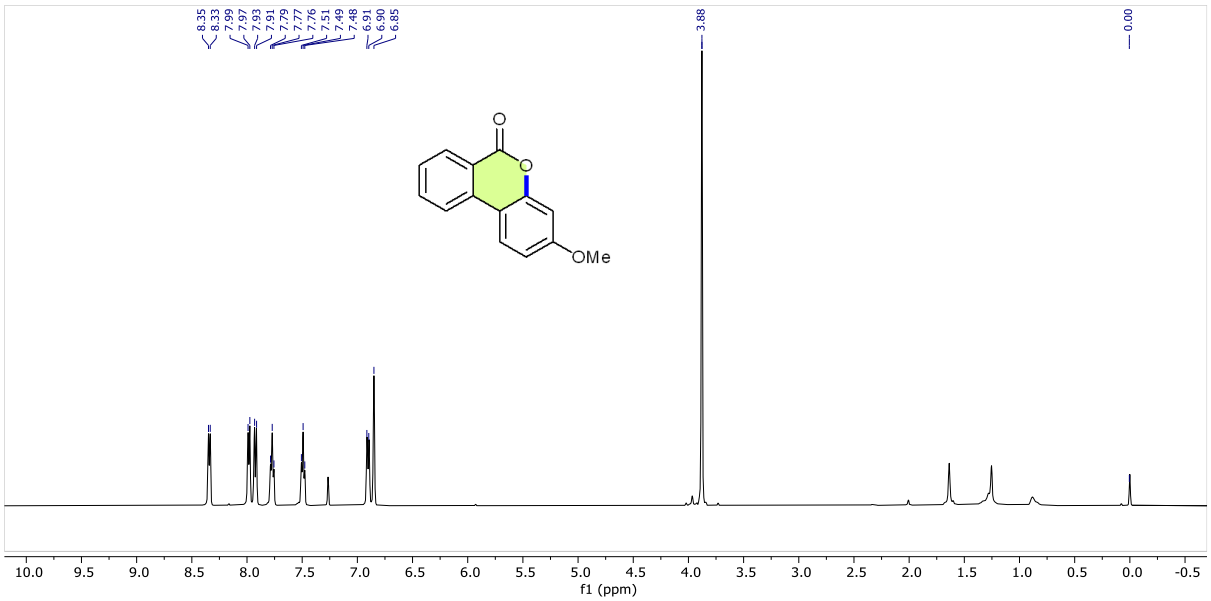

Figure S17: ^{1}H NMR (500 MHz, $CDCl_3$) of compound **2c**

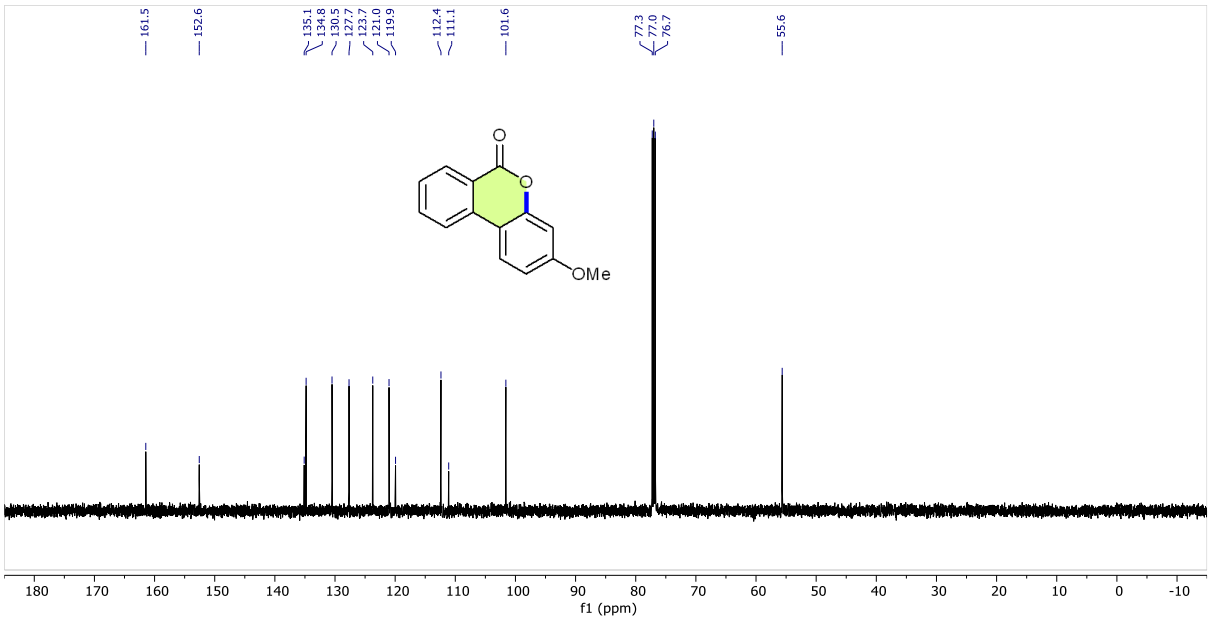

Figure S18: ^{13}C NMR (126 MHz, $CDCl_3$) of compound **2c**

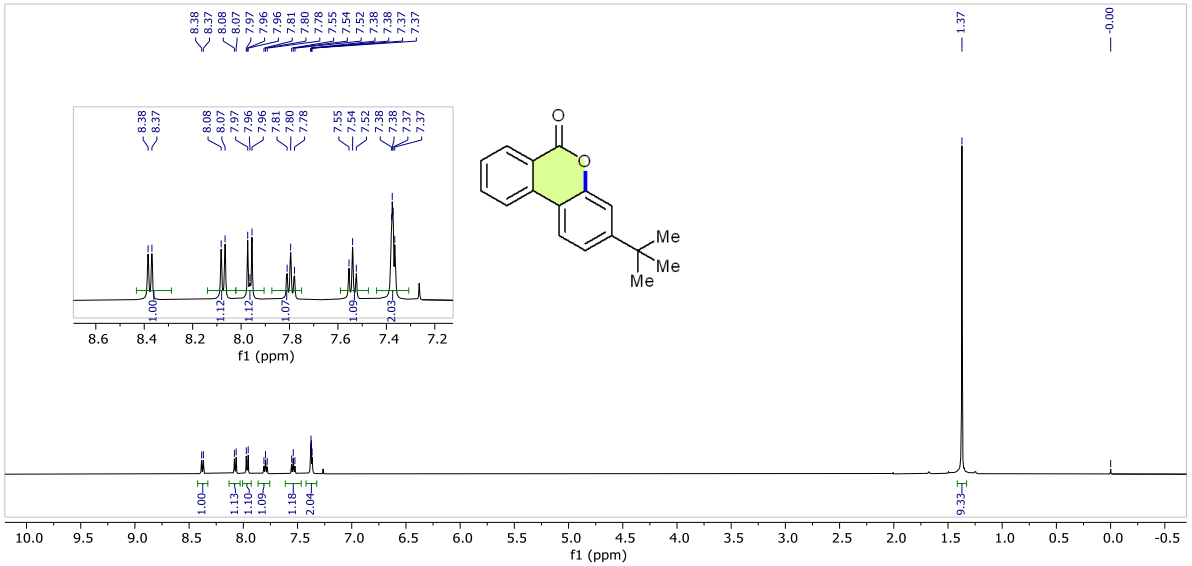

Figure S19: ^{1}H NMR (500 MHz, $CDCl_3$) of compound **2d**

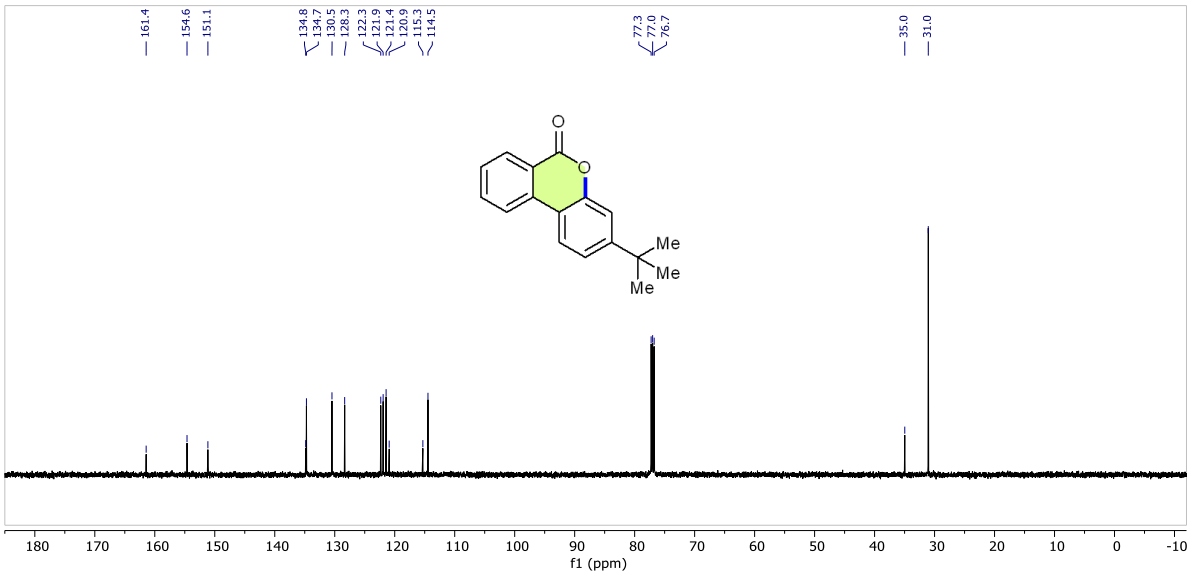

Figure S20: ^{13}C NMR (126 MHz, $CDCl_3$) of compound **2d**

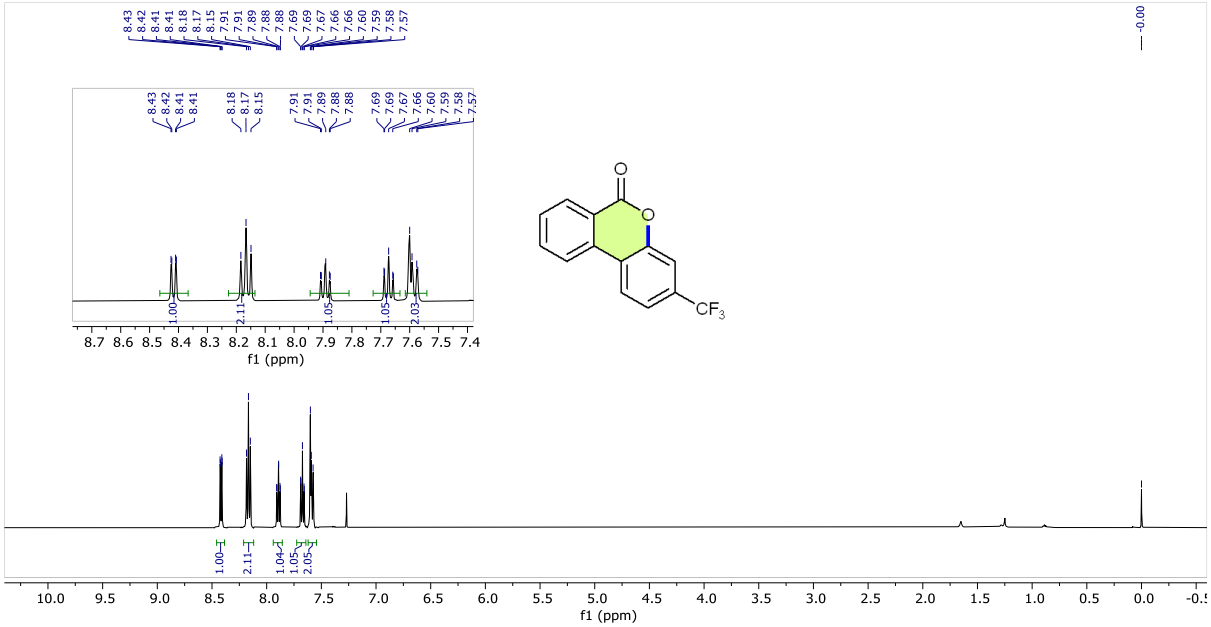

Figure S21: ^{1}H NMR (500 MHz, $CDCl_3$) of compound **2e**

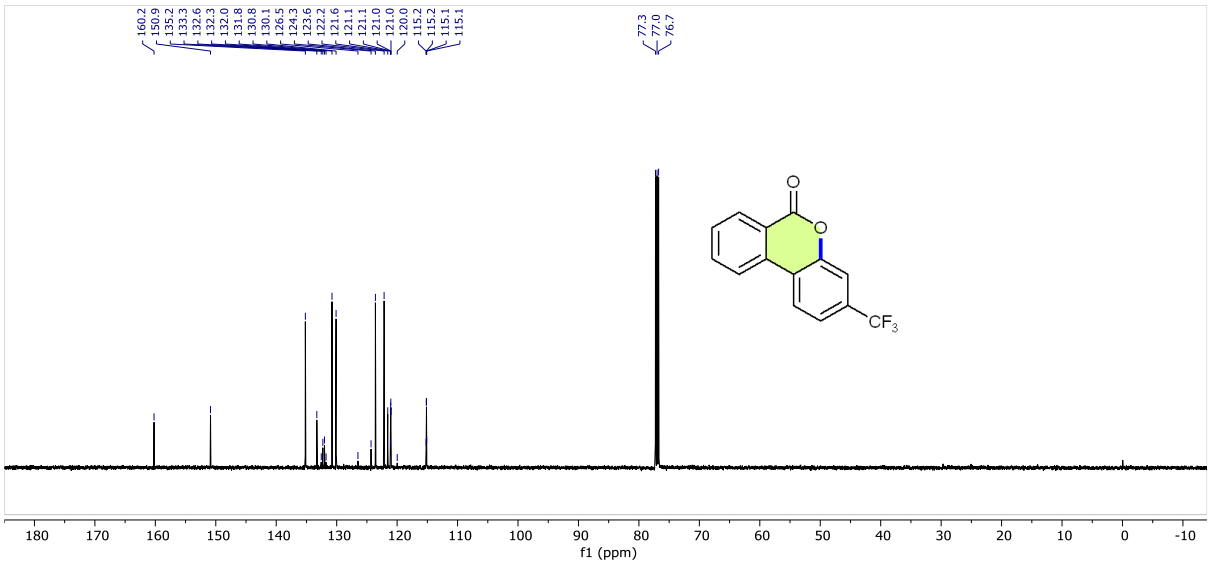

Figure S22: ^{13}C NMR (126 MHz, $CDCl_3$) of compound **2e**

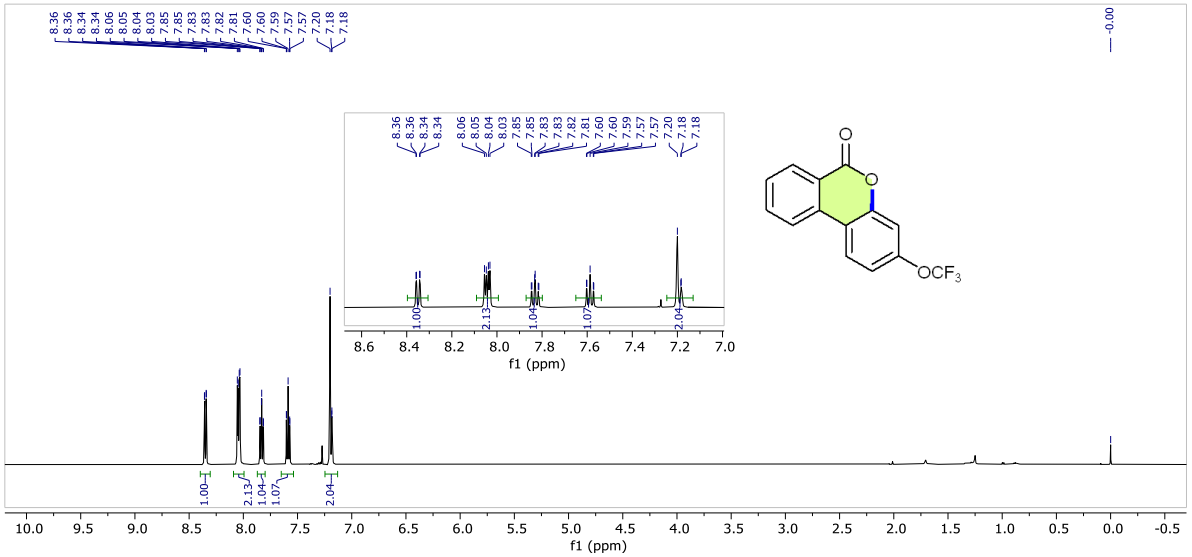

Figure S23: ^{1}H NMR (500 MHz, $CDCl_3$) of compound **2f**

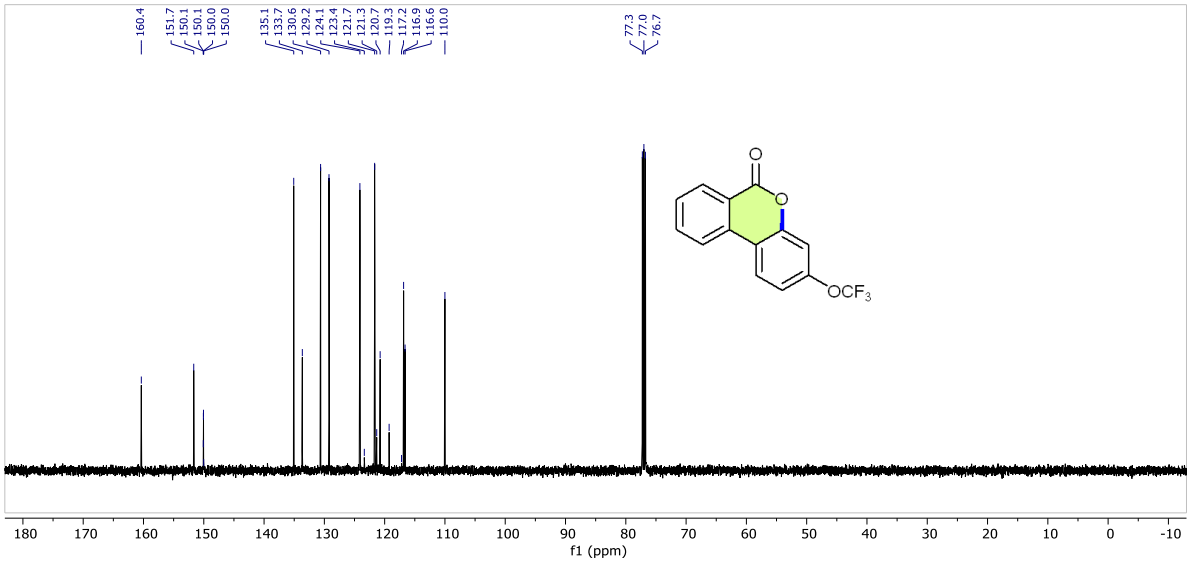

Figure S24: ^{13}C NMR (126 MHz, $CDCl_3$) of compound **2f**

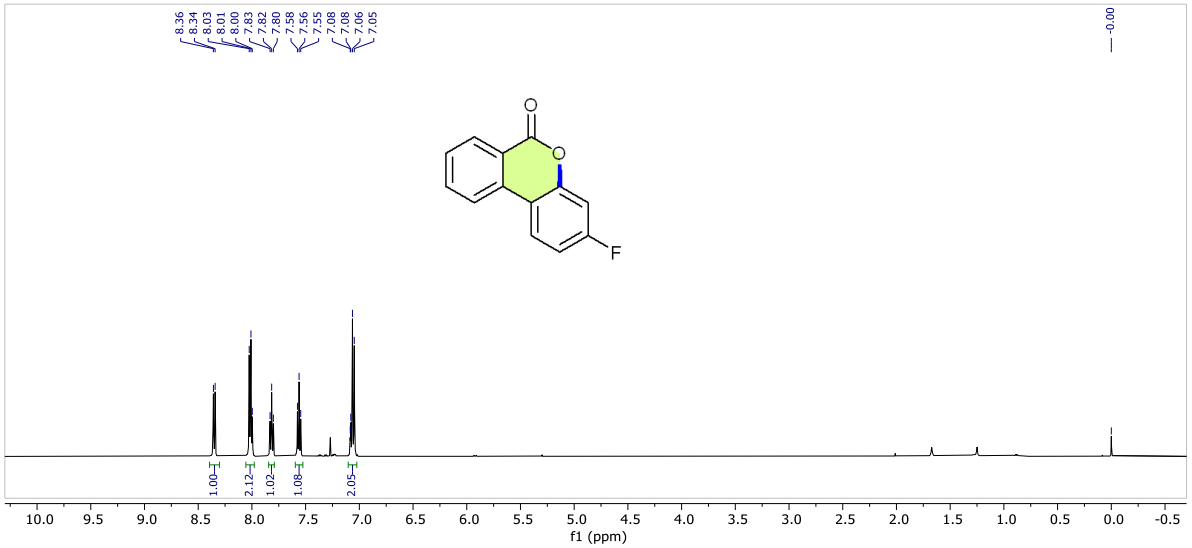

Figure S25: ^{1}H NMR (500 MHz, $CDCl_3$) of compound **2g**

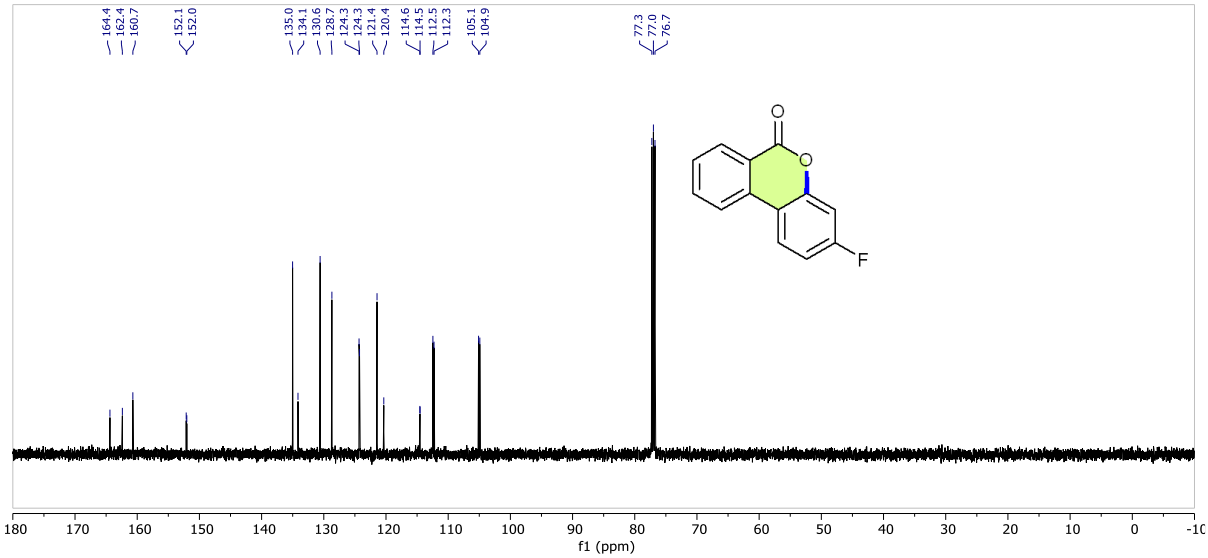

Figure S26: ^{13}C NMR (126 MHz, $CDCl_3$) of compound **2g**

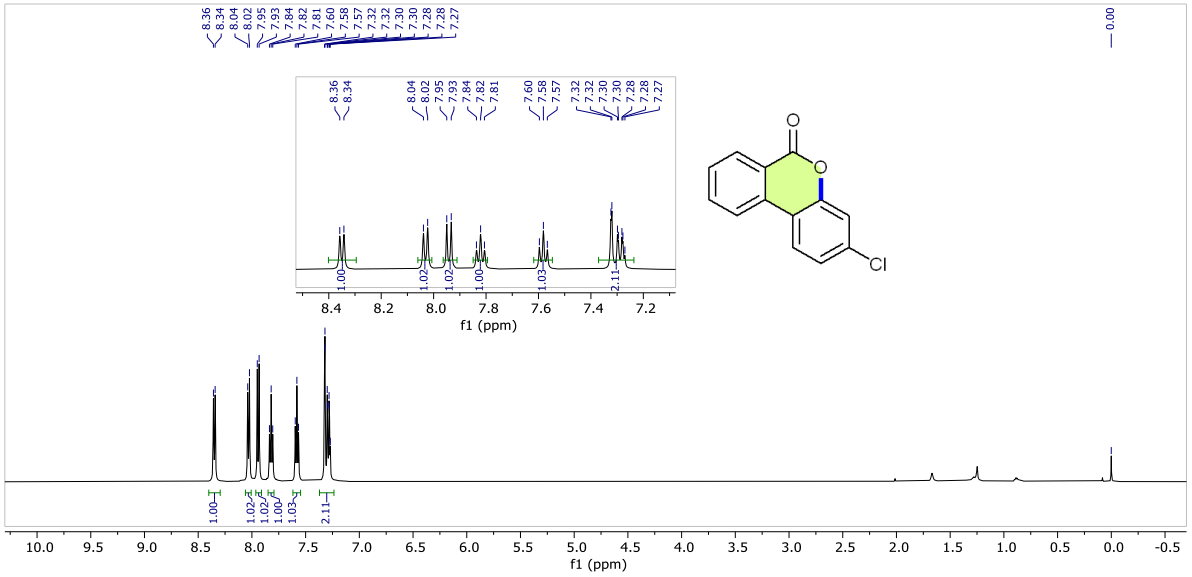

Figure S27: ^{1}H NMR (500 MHz, $CDCl_3$) of compound **2h**

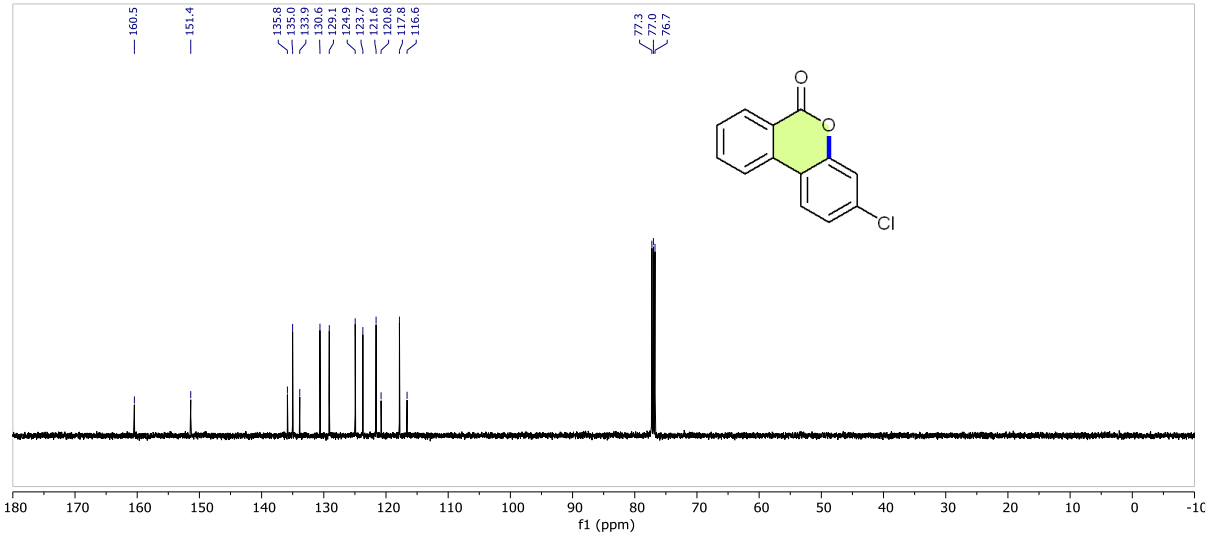

Figure S28: ^{13}C NMR (126 MHz, $CDCl_3$) of compound **2h**

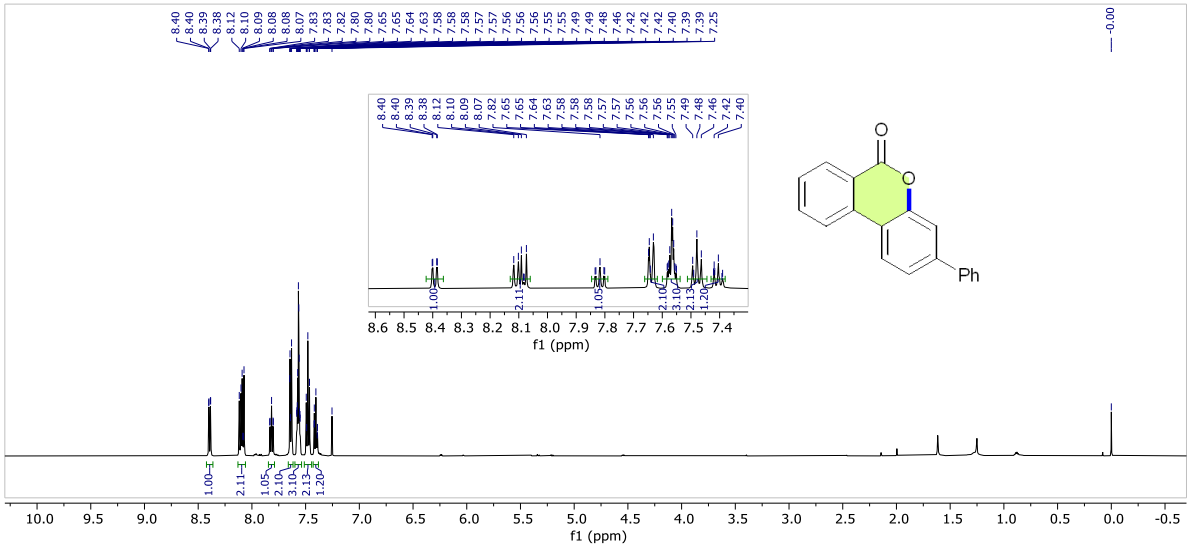

Figure S29: ^{1}H NMR (500 MHz, $CDCl_3$) of compound **2i**

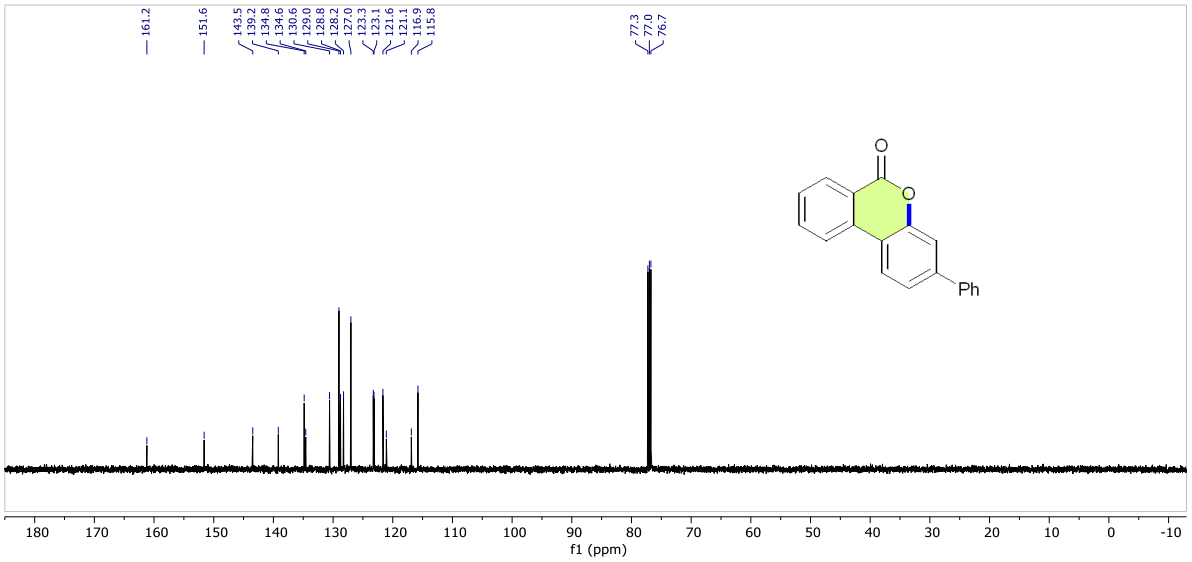

Figure S30: ^{13}C NMR (126 MHz, $CDCl_3$) of compound **2i**

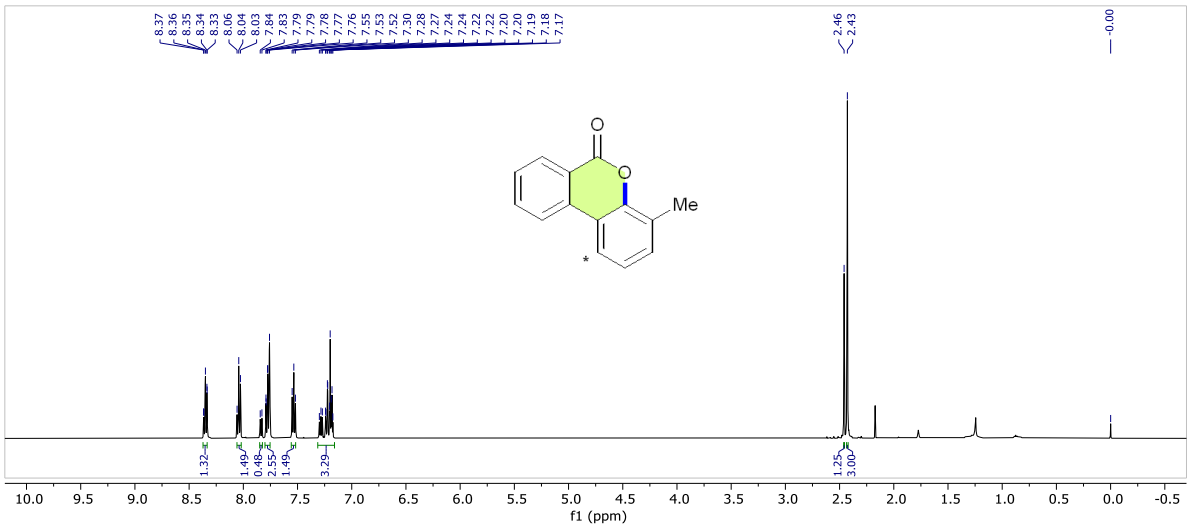

Figure S31: ^{1}H NMR (500 MHz, $CDCl_3$) of compound **2j**

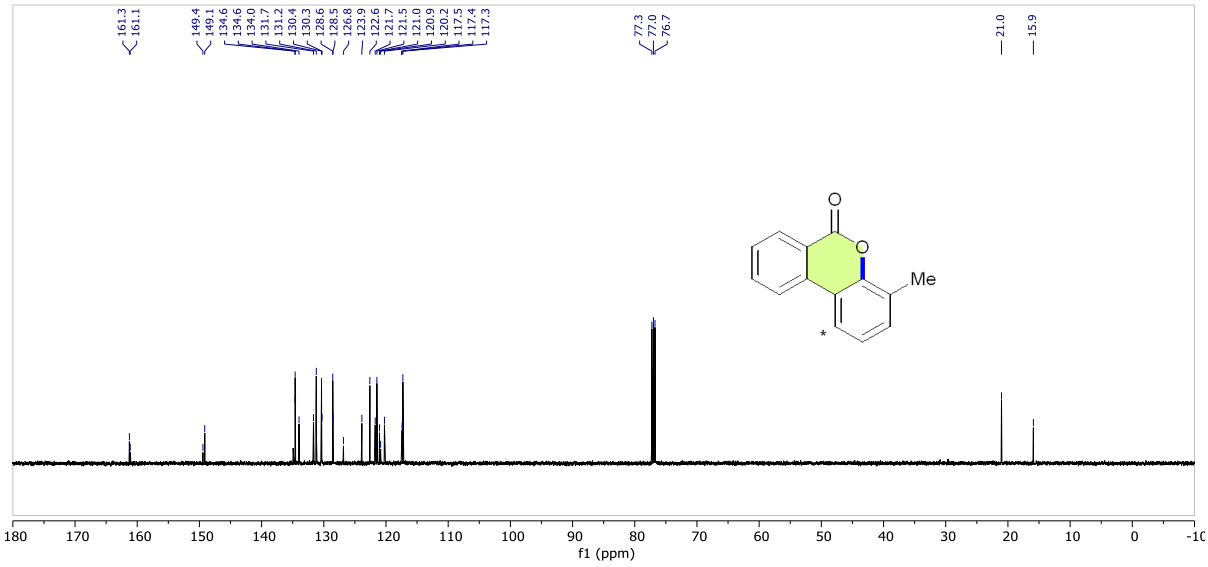

Figure S32: ^{13}C NMR (126 MHz, $CDCl_3$) of compound **2j**

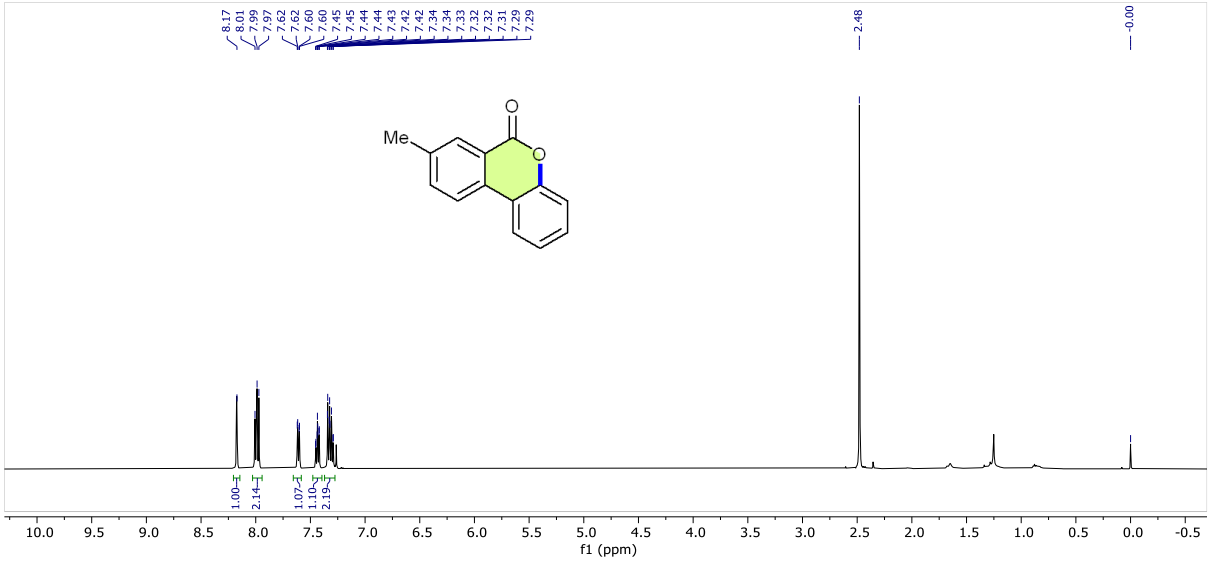

Figure S33: ^{1}H NMR (500 MHz, $CDCl_3$) of compound **2k**

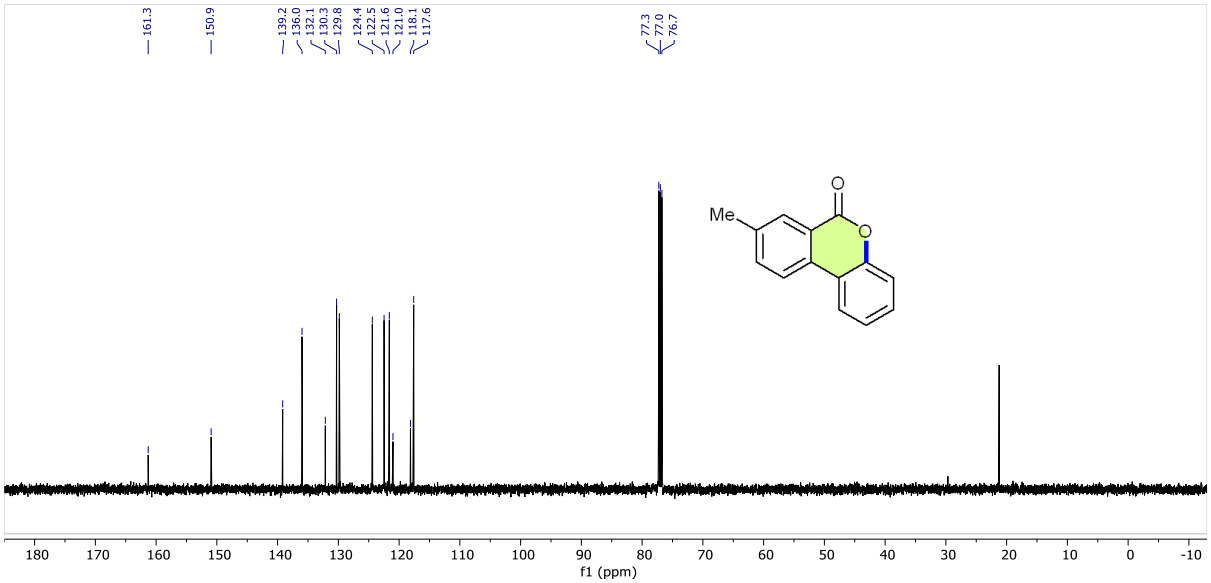

Figure 34: ^{13}C NMR (126 MHz, $CDCl_3$) of compound **2k**

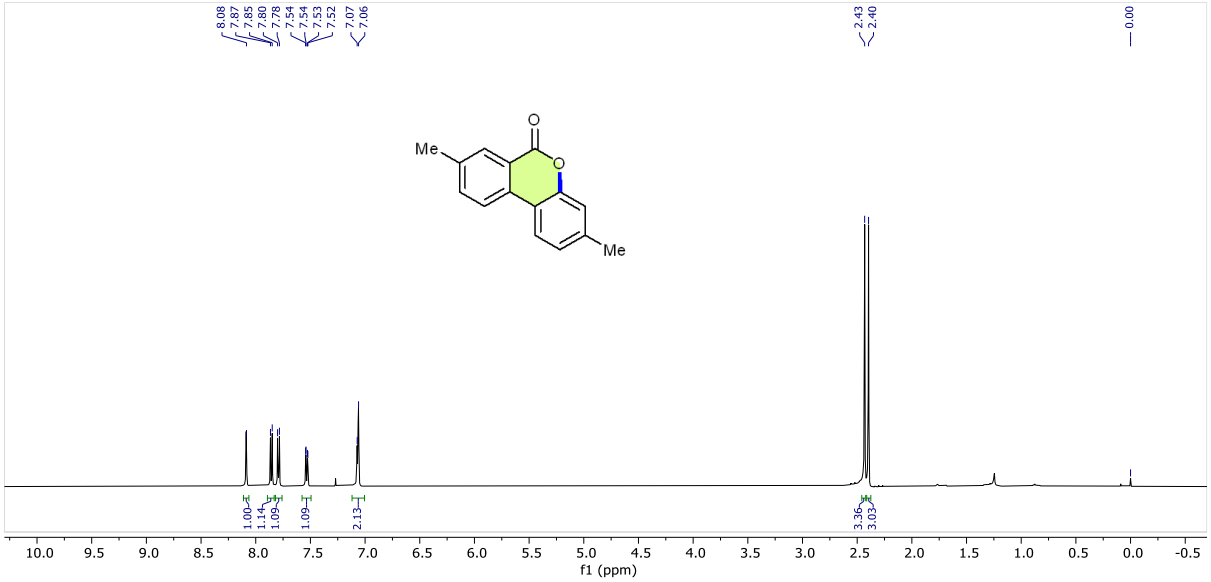

Figure S35: ^{1}H NMR (500 MHz, $CDCl_3$) of compound **2l**

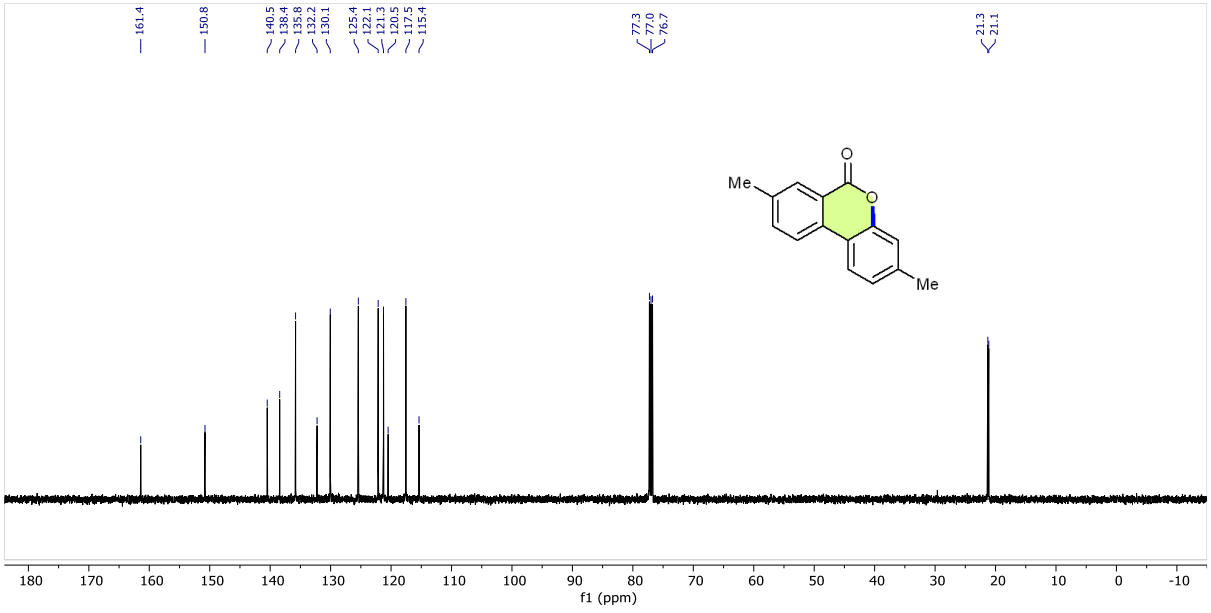

Figure S36: ^{13}C NMR (126 MHz, $CDCl_3$) of compound **2l**

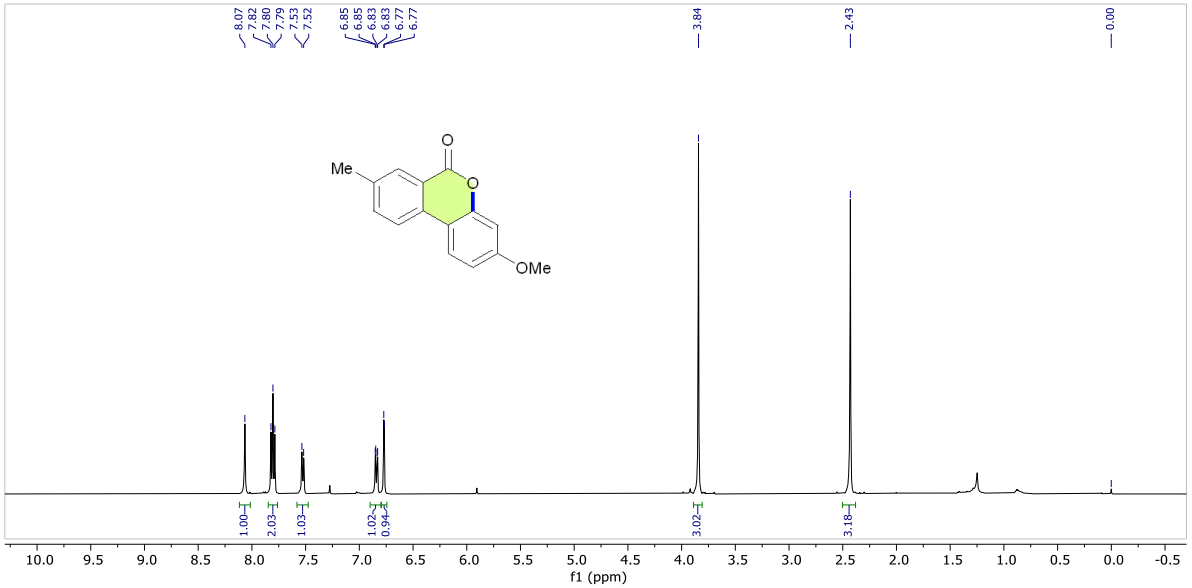

Figure S37: ^{1}H NMR (500 MHz, $CDCl_3$) of compound **2m**

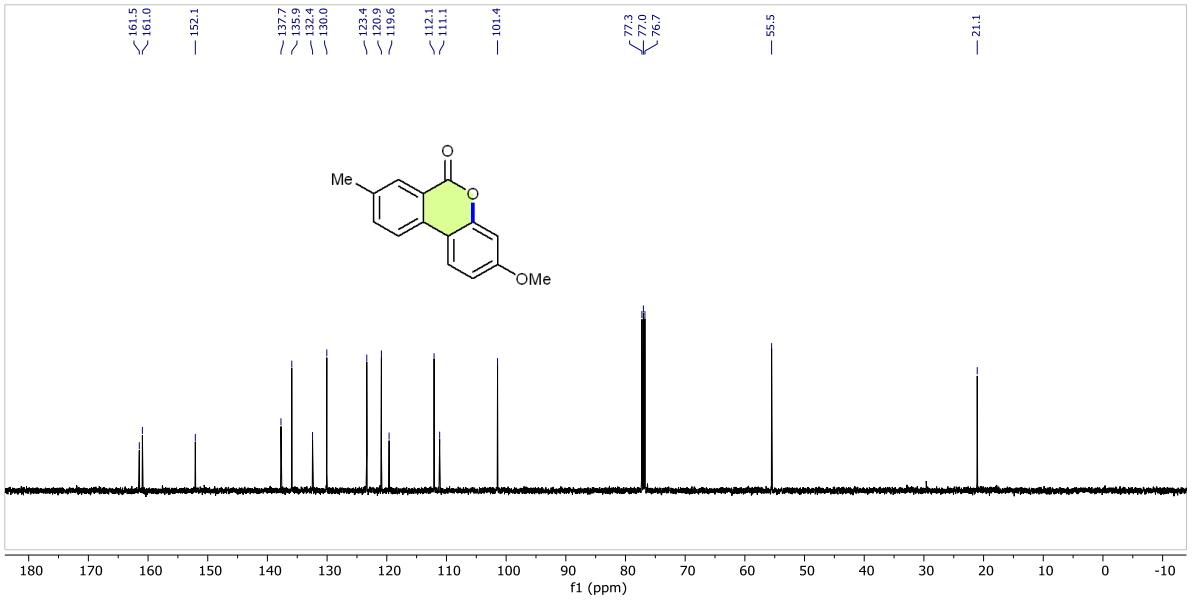

Figure S38: ^{13}C NMR (126 MHz, $CDCl_3$) of compound **2m**

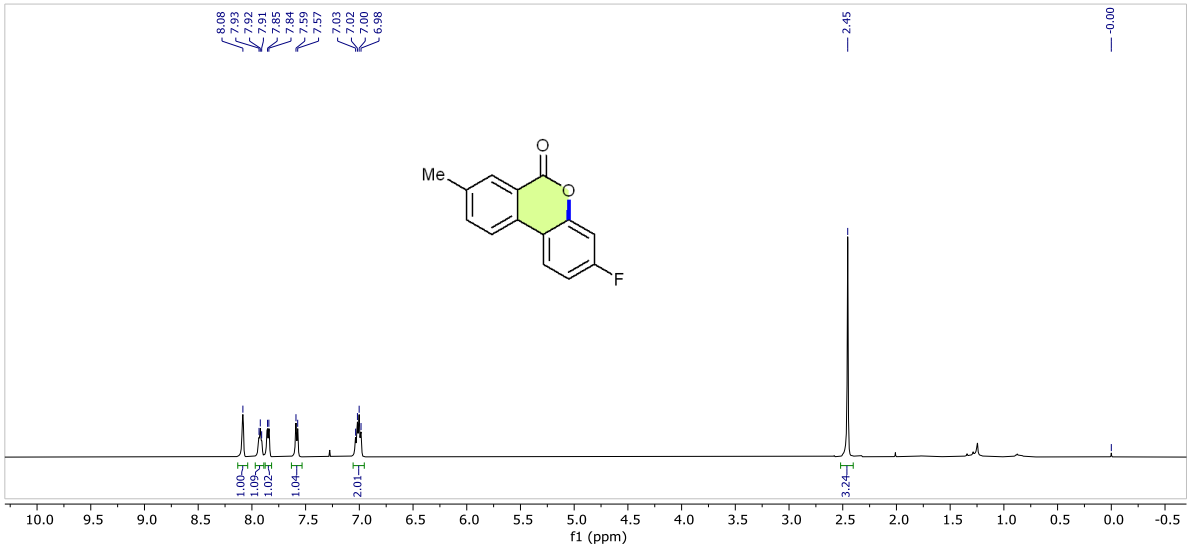

Figure S39: ^{1}H NMR (500 MHz, $CDCl_3$) of compound **2n**

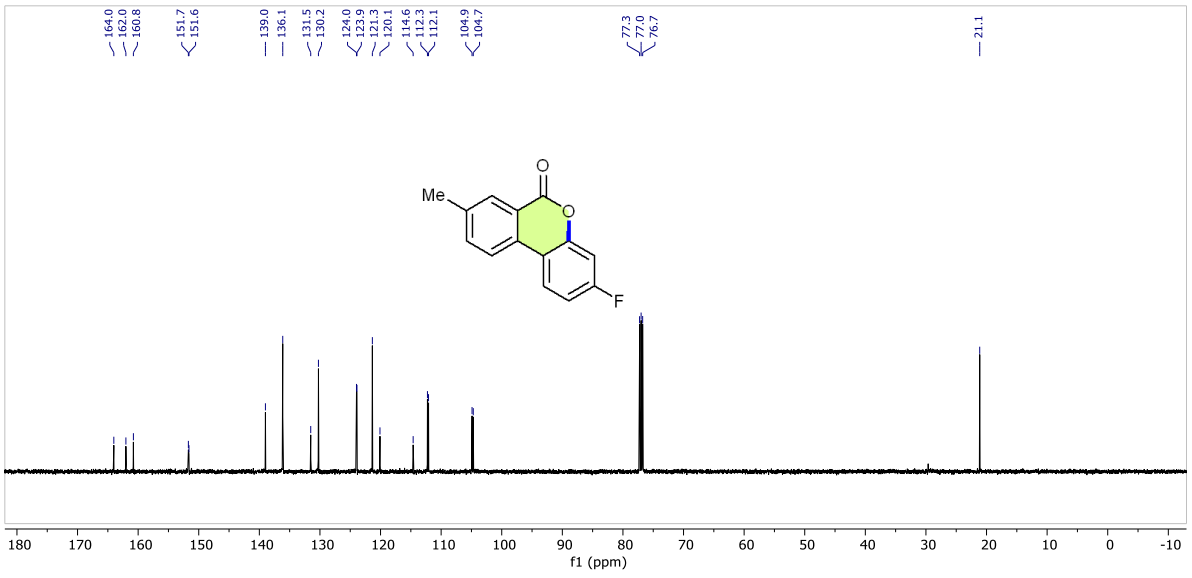

Figure S40: ^{13}C NMR (126 MHz, $CDCl_3$) of compound **2n**

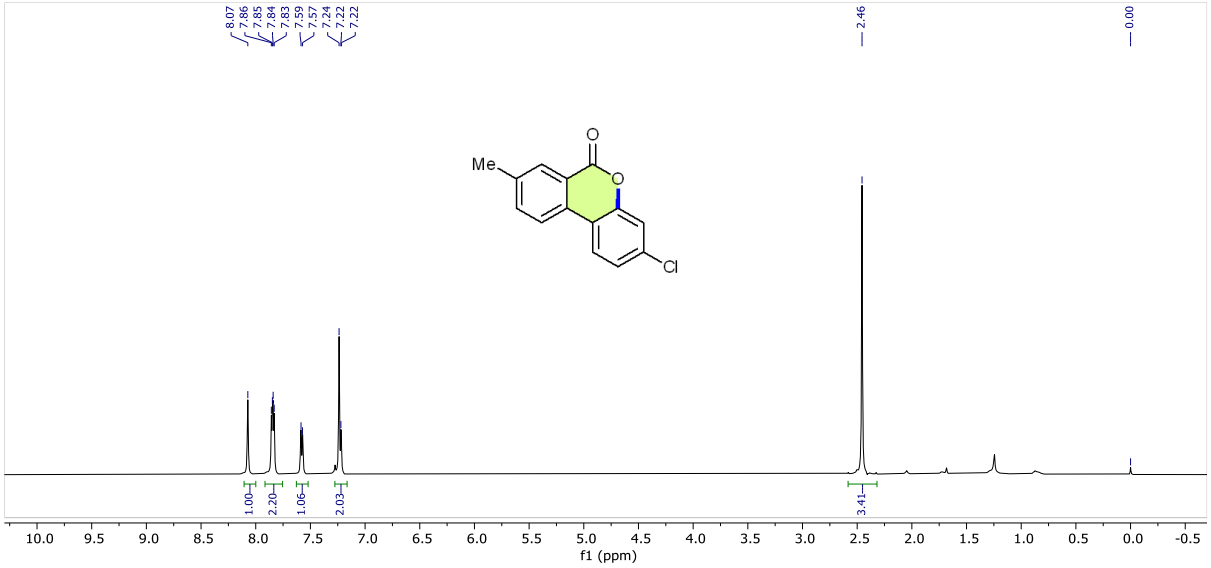

Figure S41: ^{1}H NMR (500 MHz, $CDCl_3$) of compound **2o**

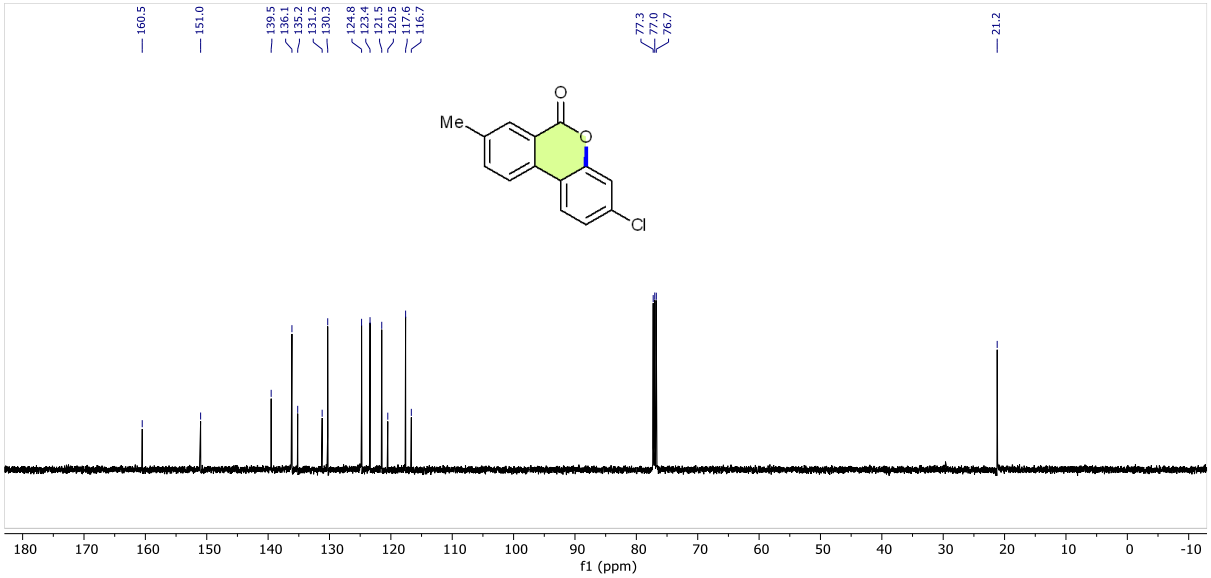

Figure S42: ^{13}C NMR (126 MHz, $CDCl_3$) of compound **2o**

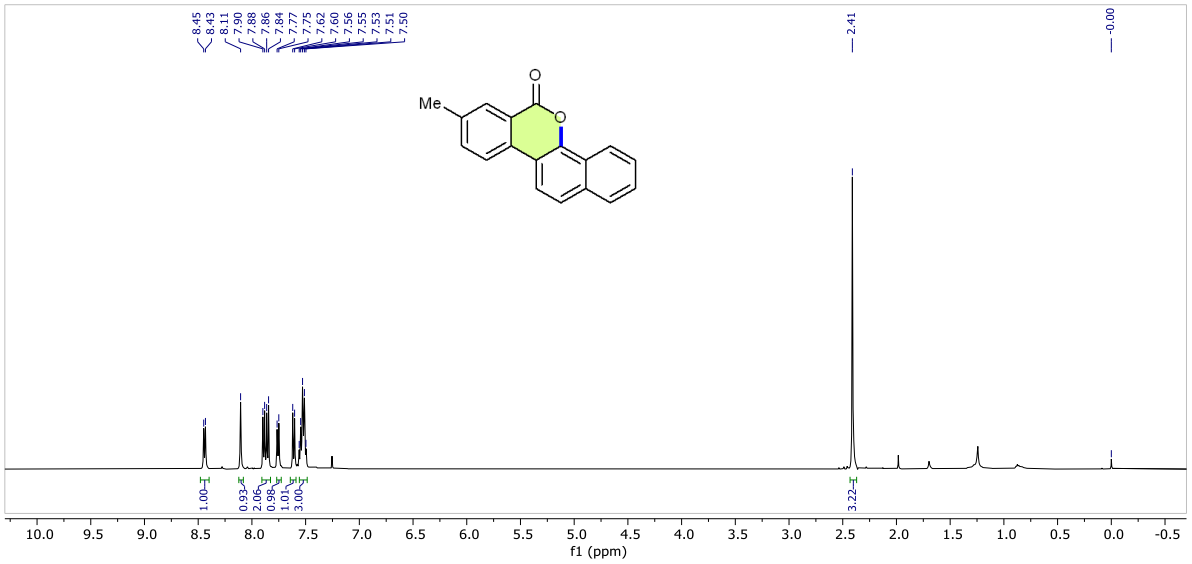

Figure S43: ^{1}H NMR (500 MHz, $CDCl_3$) of compound **2p**

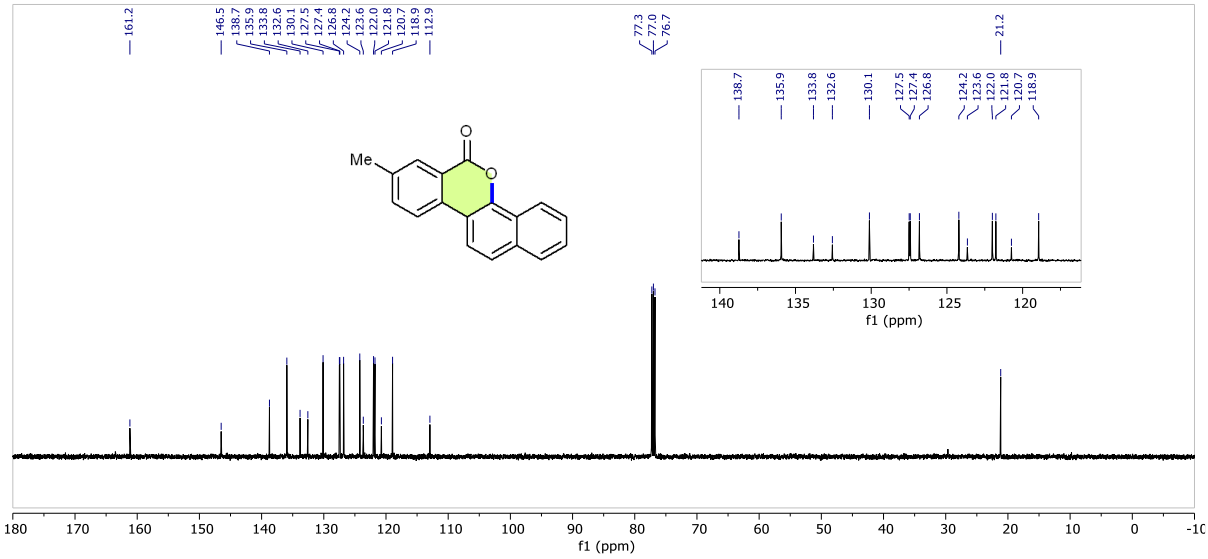

Figure S44: ^{13}C NMR (126 MHz, $CDCl_3$) of compound **2p**

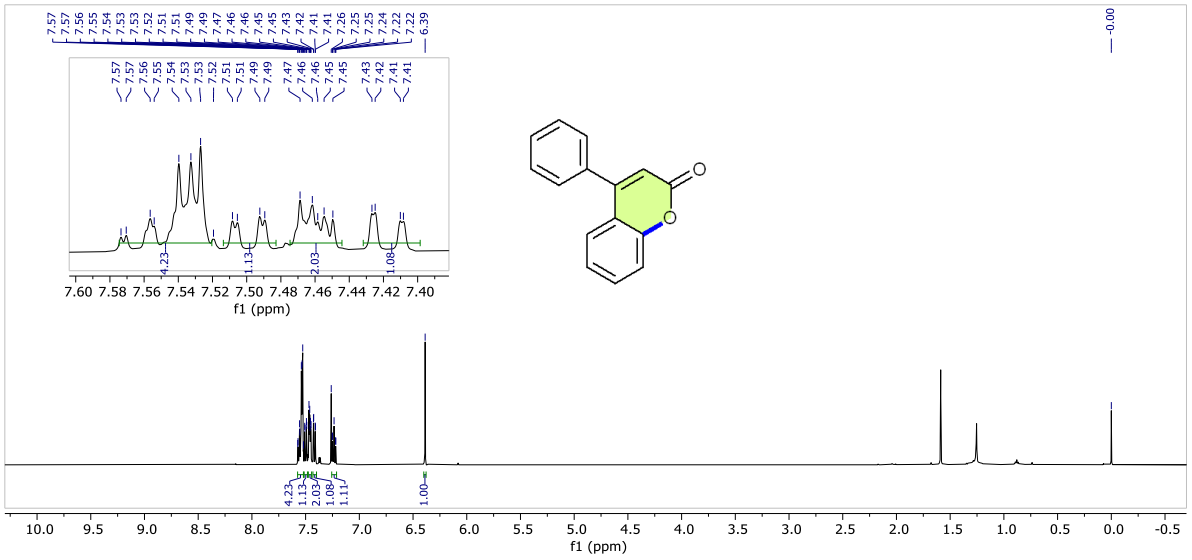

Figure S45: ^{1}H NMR (500 MHz, $CDCl_3$) of compound **2q**

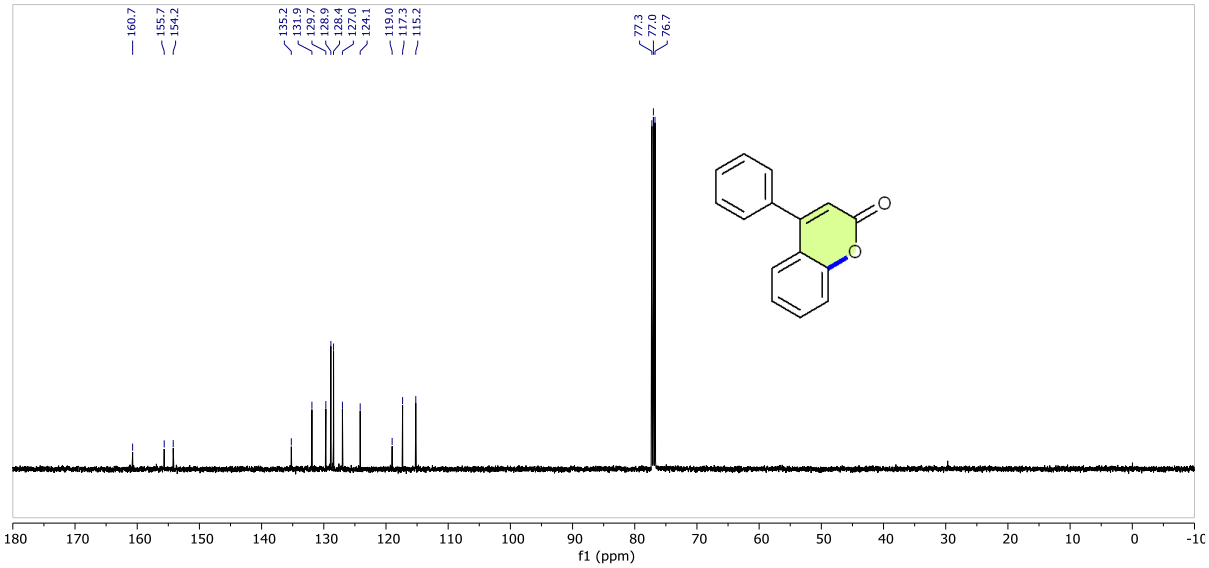

Figure S46: ^{13}C NMR (126 MHz, $CDCl_3$) of compound **2q**

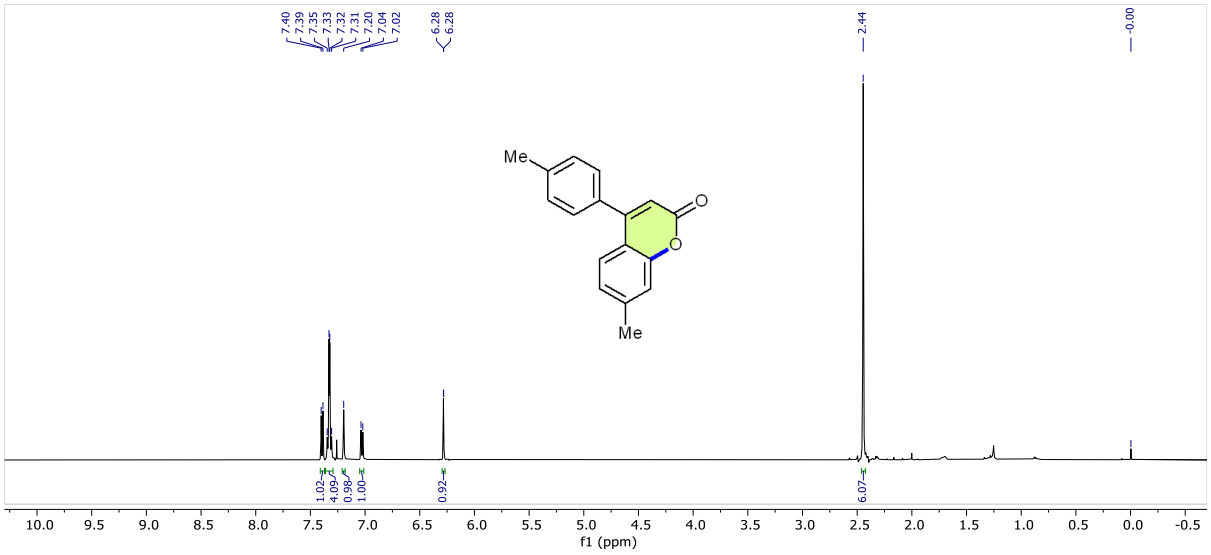

Figure S47: ^{1}H NMR (500 MHz, $CDCl_3$) of compound **2r**

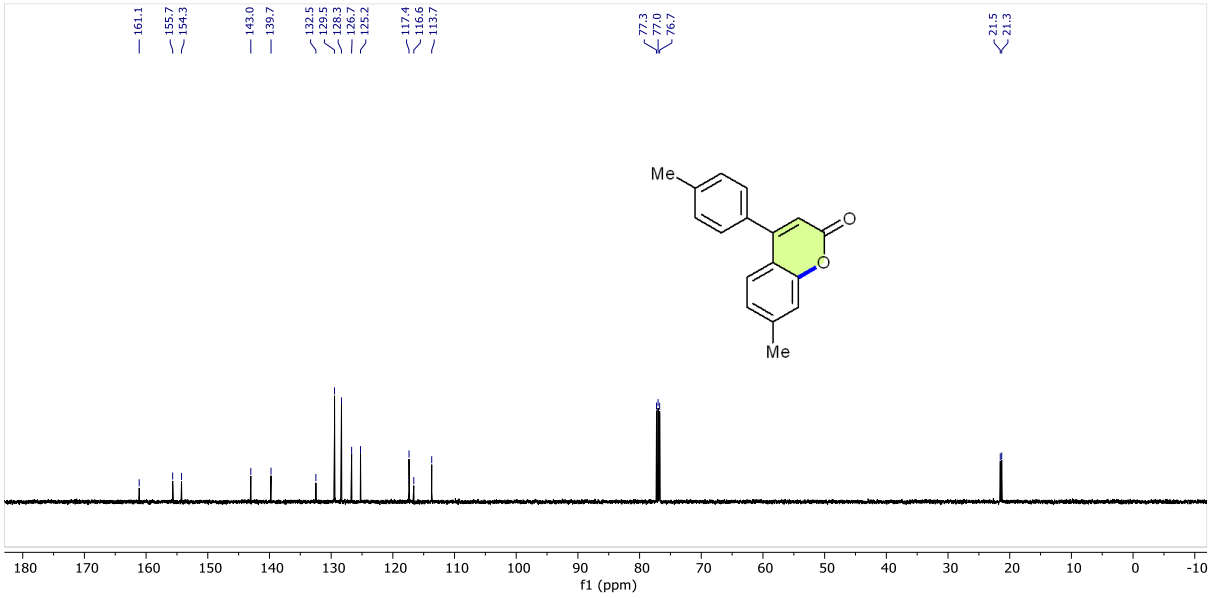

Figure S48: ^{13}C NMR (126 MHz, $CDCl_3$) of compound **2r**

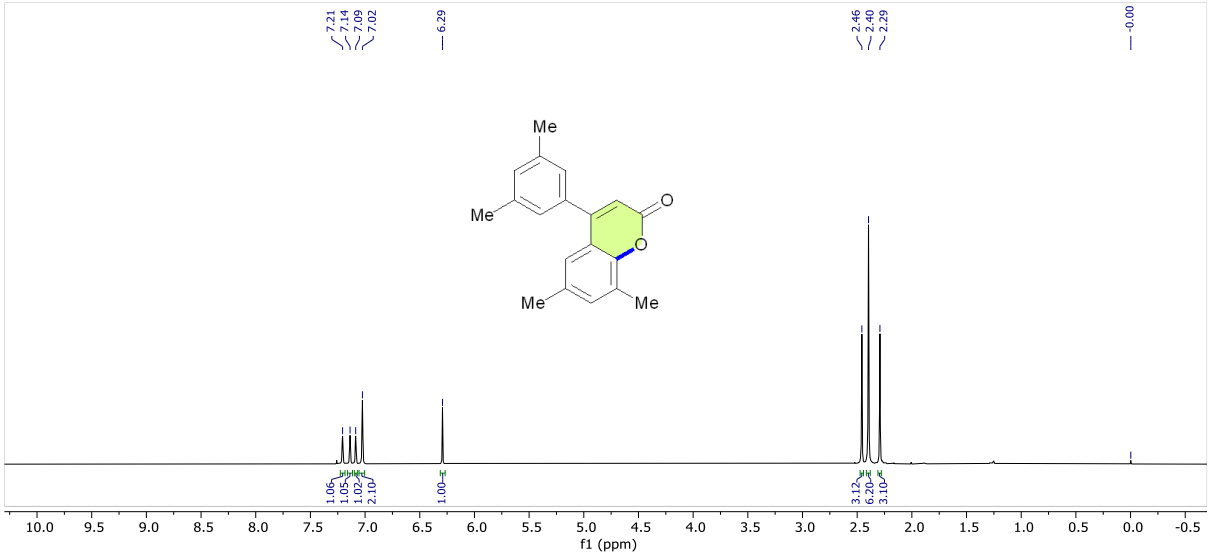

Figure S49: ^{1}H NMR (500 MHz, $CDCl_3$) of compound **2s**

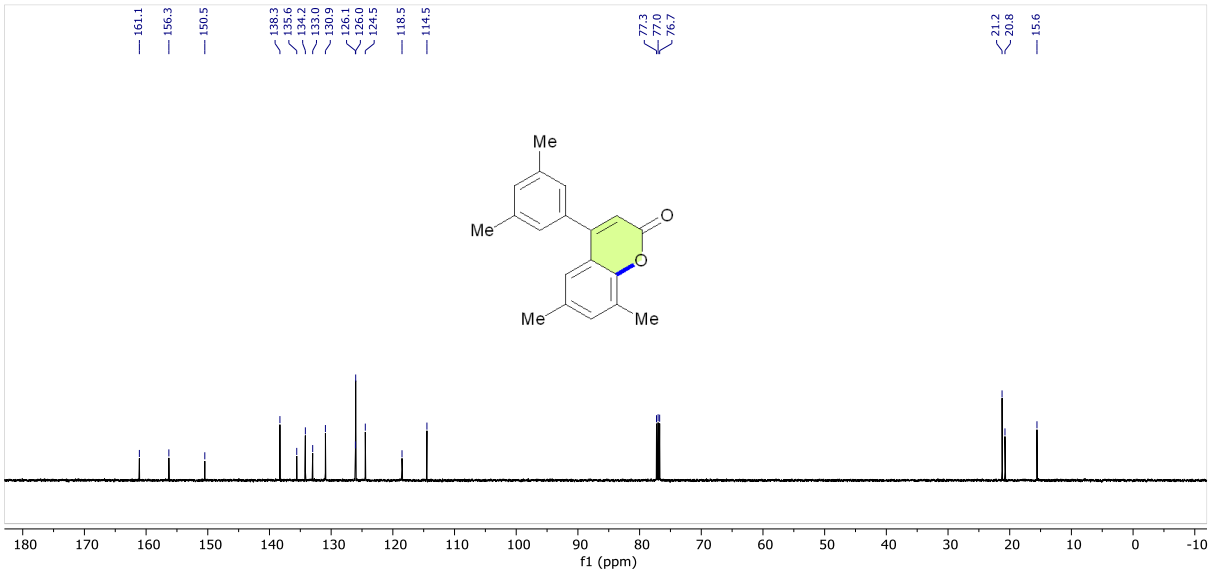

Figure S50: ^{13}C NMR (126 MHz, $CDCl_3$) of compound **2s**

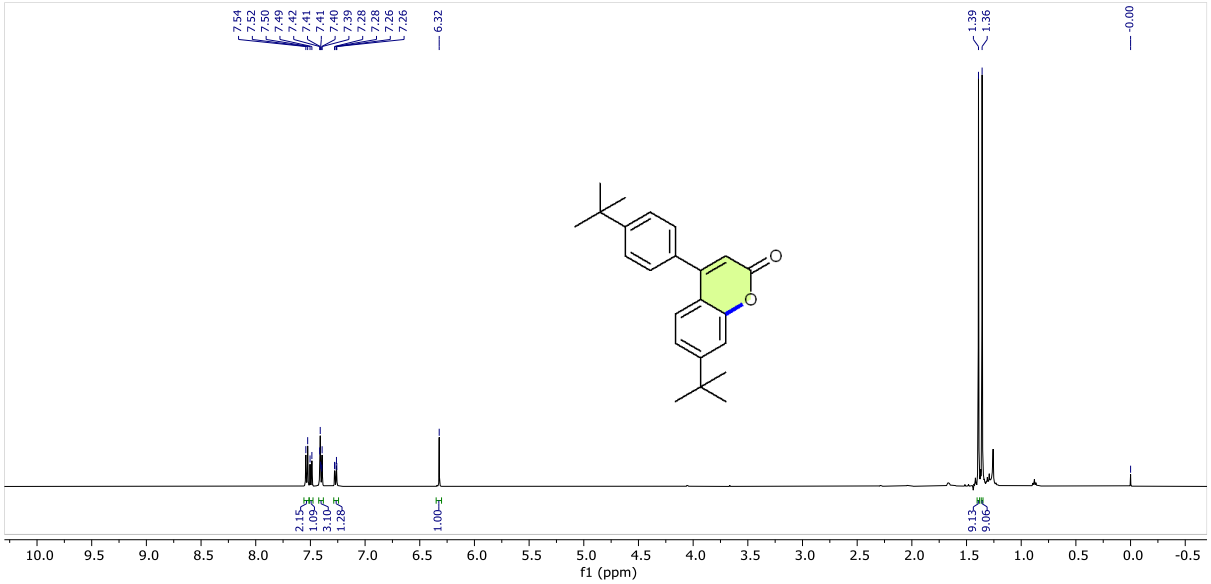

Figure S51: ^{1}H NMR (500 MHz, $CDCl_3$) of compound **2t**

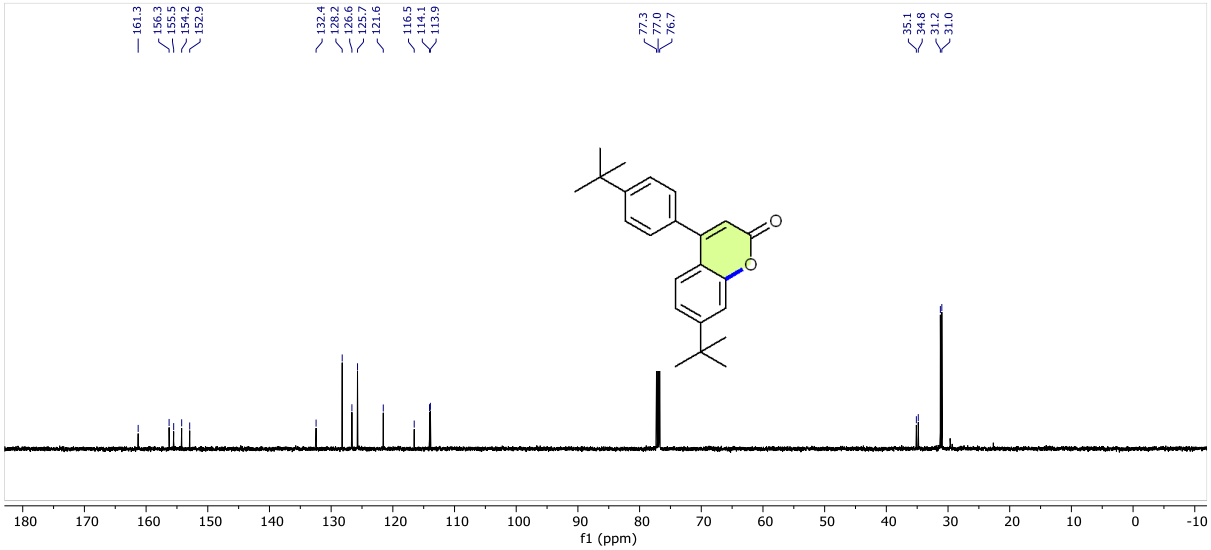

Figure S52: ^{13}C NMR (126 MHz, $CDCl_3$) of compound **2t**

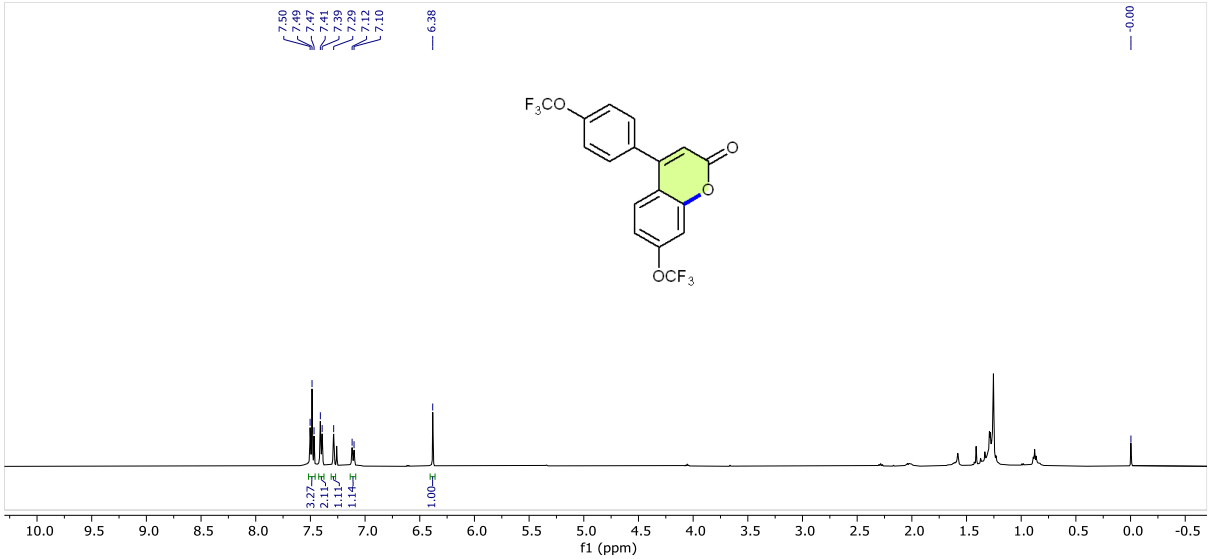

Figure S53: ^{1}H NMR (500 MHz, $CDCl_3$) of compound **2u**

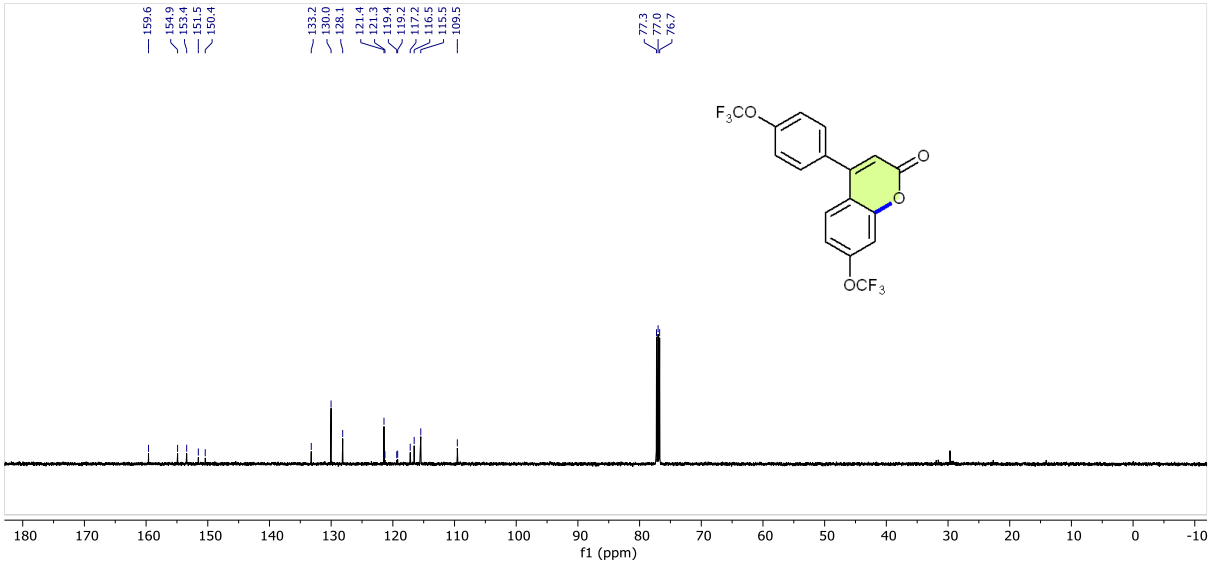

Figure S54: ^{13}C NMR (126 MHz, $CDCl_3$) of compound **2u**

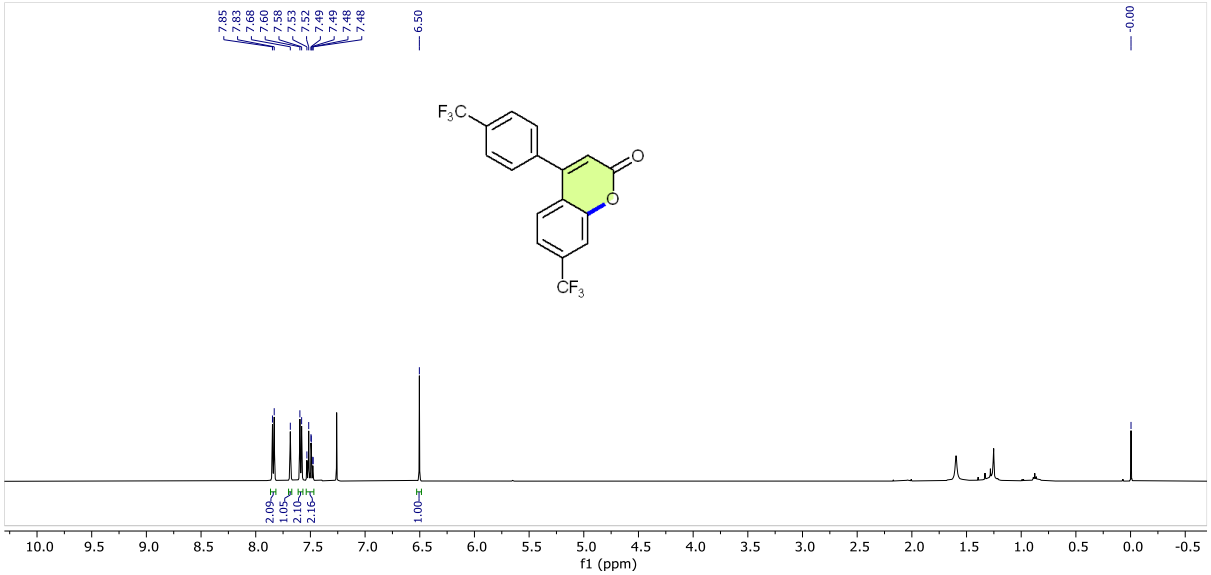

Figure S55: ^{1}H NMR (500 MHz, $CDCl_3$) of compound **2v**

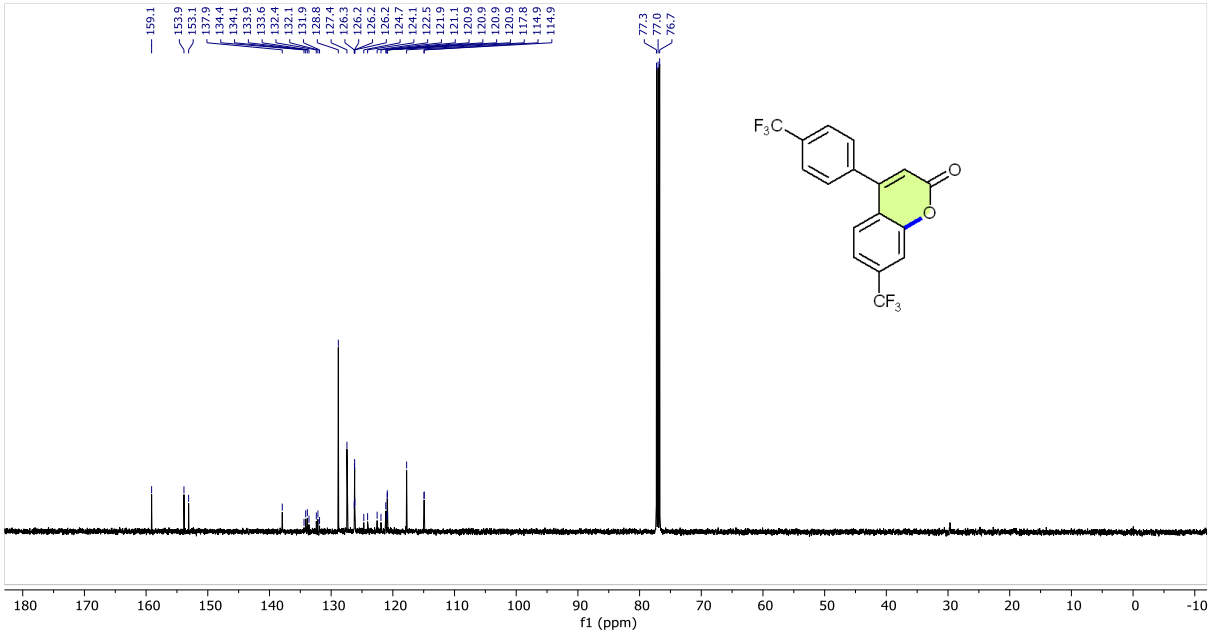

Figure S56: ^{13}C NMR (126 MHz, $CDCl_3$) of compound **2v**

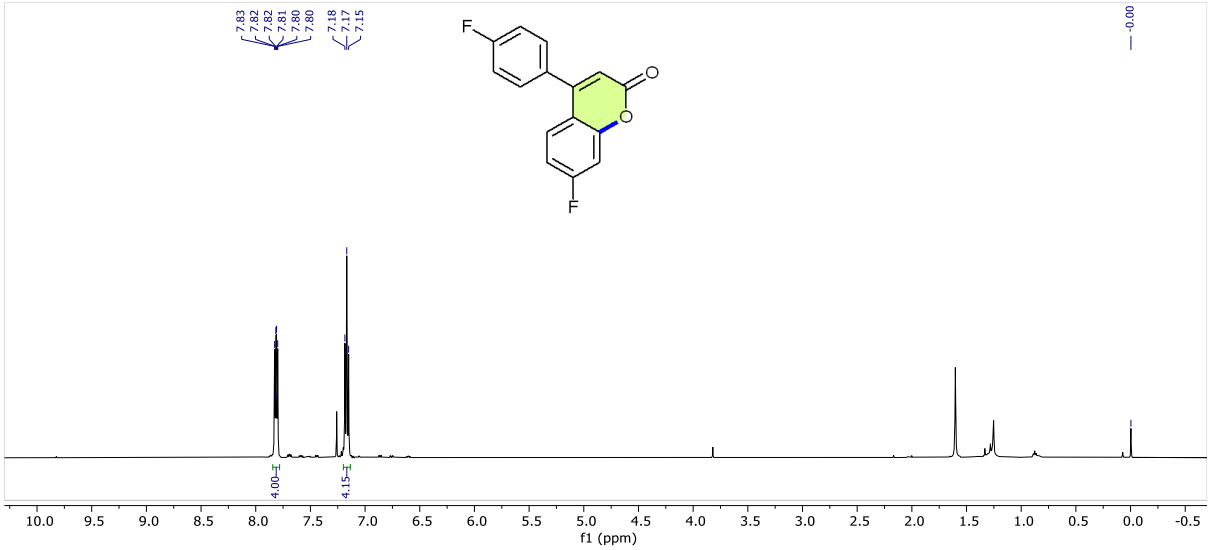

Figure S57: ^{1}H NMR (500 MHz, $CDCl_3$) of compound **2w**

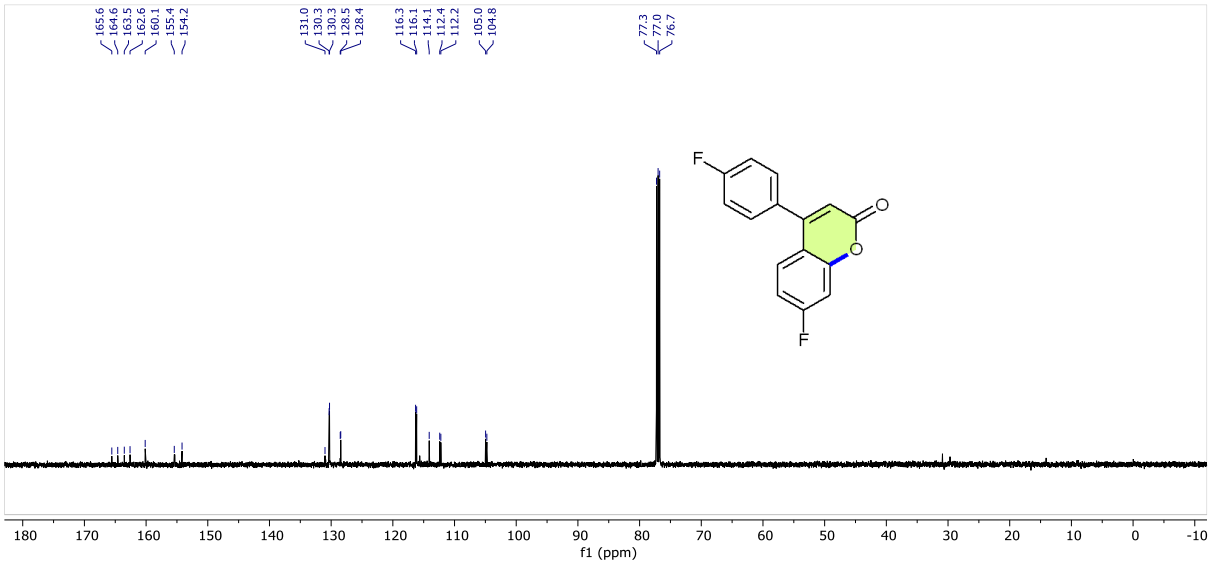

Figure S58: ^{13}C NMR (126 MHz, $CDCl_3$) of compound **2w**

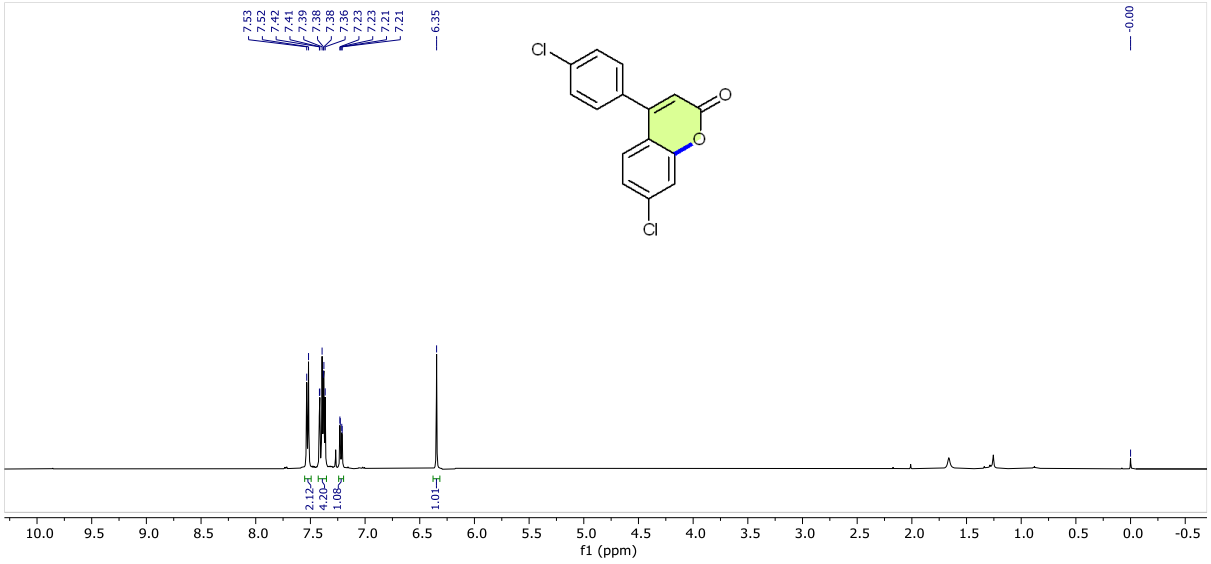

Figure S59: ^{1}H NMR (500 MHz, $CDCl_3$) of compound **2x**

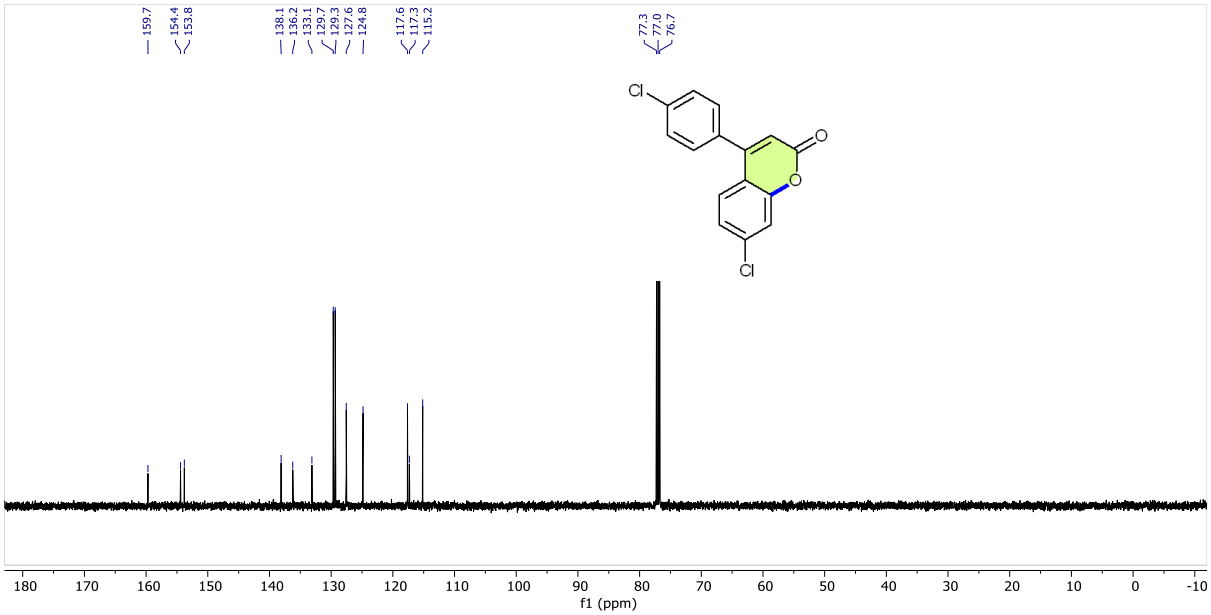

Figure S60: ^{13}C NMR (126 MHz, $CDCl_3$) of compound **2x**

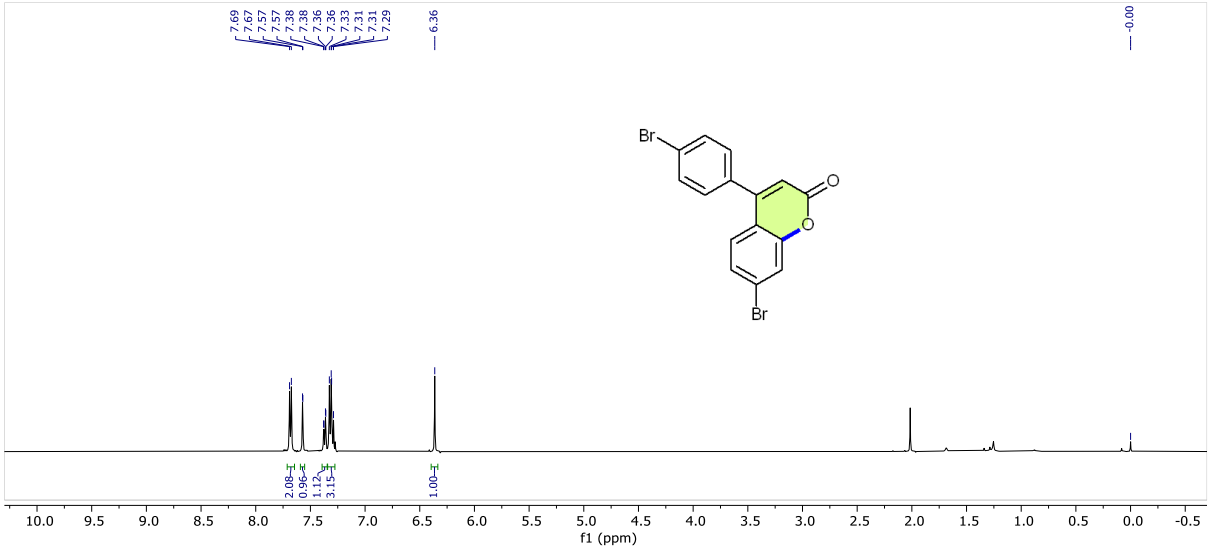

Figure S61: ^{1}H NMR (500 MHz, $CDCl_3$) of compound **2y**

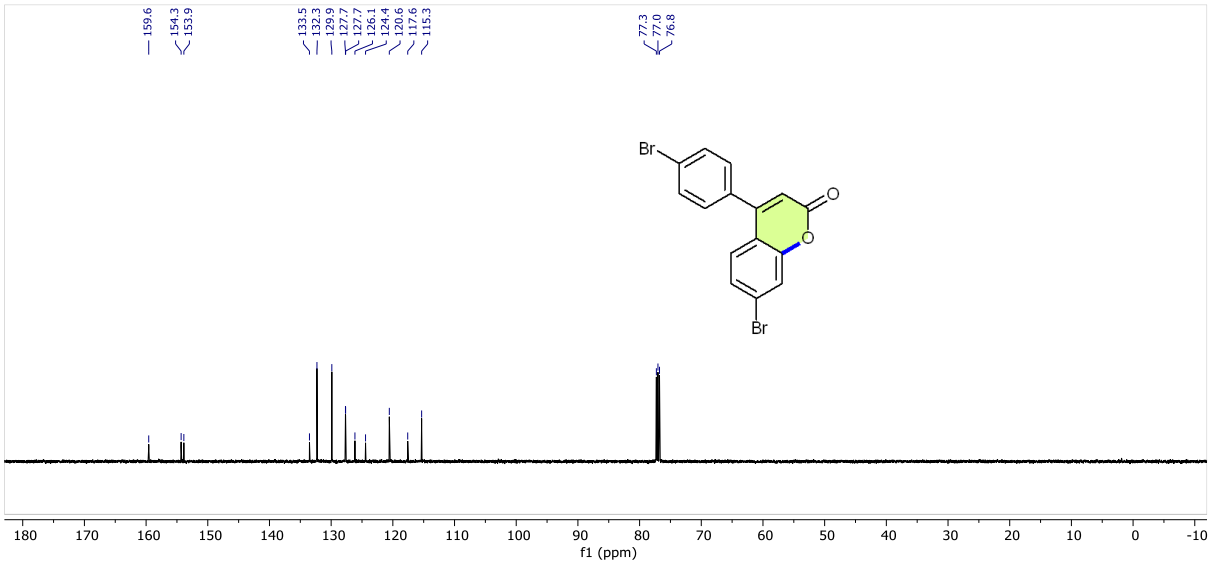

Figure S62: ^{13}C NMR (126 MHz, $CDCl_3$) of compound **2y**