

**- Electronic Supplementary Information -**

**Ruthenium(II)-catalyzed C–H activation/lactonization of aromatic acids with diazonaphthoquinones: regioselective synthesis of polycyclic coumarin frameworks**

**Chandan Kumar Giri, Sudeshna Mondal and Mahiuddin Baidya\***

Department of Chemistry, Indian Institute of Technology Madras, Chennai-600036, India  
mbaidya@iitm.ac.in

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### General information:

Benzoic acids, 2-Chloro-1,3-dimethylimidazolium chloride, 1-Naphthol, 2-Naphthols, organic solvents, and inorganic bases were purchased from Avra chemicals and Bld pharma and Spectrochem chemicals.  $[\text{Ru}(p\text{-cymene})\text{Cl}_2]_2$  was recieved from Alfa Aesar company. All the compounds were utilized without further purification. Commercial-grade solvent was directly used for the reaction without drying.  $\text{CH}_3\text{CN}$ , DCE, and toluene were dried over calcium hydride. Dry dioxane and THF was prepared by distilling over sodium ketyl.

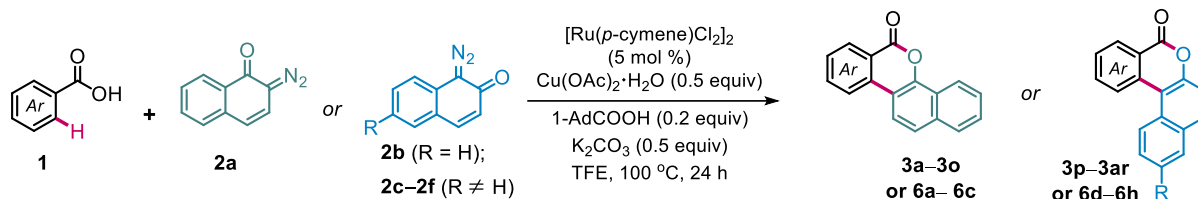
All reactions were monitored by thin layer chromatography (TLC) on Merck 60 F 254 precoated silica plates and visualized using a UV lamp (366 or 254 nm) or by use of potassium permanganate, 5 g  $\text{K}_2\text{CO}_3$ /100 mL water. Products were isolated by column chromatography (Merck silica gel 100–200  $\mu\text{m}$ ).

$^{13}\text{C}$  and  $^1\text{H}$  NMR spectra were recorded on a Bruker 400 MHz or Bruker 500 MHz spectrometers. Chemical shift values ( $\delta$ ) are reported in ppm and calibrated to the residual solvent peak-  $\text{CDCl}_3$   $\delta = 7.26$  ppm for  $^1\text{H}$ ,  $\delta = 77.16$  for  $^{13}\text{C}$ ;  $\text{DMSO-d}_6$   $\delta = 2.51$  ppm for  $^1\text{H}$ ,  $\delta = 39.50$  ppm for  $^{13}\text{C}$ ; or calibrated to tetramethylsilane ( $\delta = 0.00$ ). All NMR spectra were recorded at ambient temperature (290 K) unless otherwise noted.  $^1\text{H}$  NMR spectra are reported as follows: chemical shift (multiplicity, coupling constant, integration). The following abbreviations are used to indicate multiplicities: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; dd, doublet of doublet; dt, doublet of triplet; dq, doublet of quartet; td, triplet of doublet; tt, triplet of triplet; dq, doublet of quartet; br, broad. All Diazonaphthoquinones (**2**) are known in literature and were prepared following the previous report. (*Org. Lett.* 2022, **24**, 7888–7893). The  $\text{Cu}(\text{1-AdCOO})_2$  complex was prepared following the similar procedure reported previously (*Synlett*, 2020, **31**, 359–362).

Mass spectra were recorded by electron spray ionization (ESI) method on a Q-TOF Micro with lock spray source.

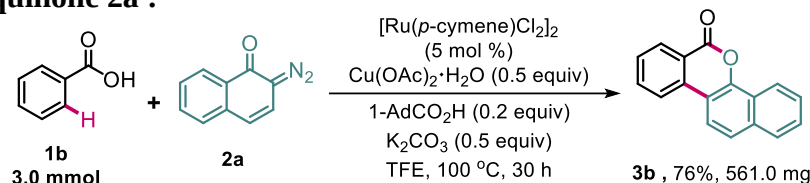
Compounds **3b**, **3p-q**, **3t-w**, **3y** and **3an** were reported in literature (*Org. Lett.*, 2017, **19**, 4002–4005; *Adv. Synth. Catal.*, 2019, **361**, 5223–5238).

**Typical Ru(II)-catalyzed (3+3) annulation of aromatic acids (1/5) and diazonaphthoquinones (2):**



**Procedure:** To an oven-dried screw cap reaction tube (10 × 1.5 cm), corresponding aromatic acids **1/5** (0.25 mmol, 1.0 equiv), diazonaphthoquinones **2** (1.5 equiv),  $[\text{Ru}(p\text{-cymene})\text{Cl}_2]_2$  (5.0 mol %),  $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$  (0.5 equiv),  $\text{K}_2\text{CO}_3$  (0.5 equiv) and 1-AdCOOH (0.2 equiv) were taken. Next 1.0 mL TFE solvent was added and the reaction tube was capped. The reaction mixture was then stirred at 100 °C for 24 h. After completion of the reaction (monitored by TLC), it was allowed to cool to room temperature. The volatiles were first evaporated, and then the residue was dissolved in ethyl acetate and transferred into a separating funnel. It was then washed with saturated sodium bicarbonate solution and dried over anhydrous  $\text{Na}_2\text{SO}_4$ . After evaporation under reduced pressure, the resulting residue was purified by column chromatography on silica gel, using hexane and ethyl acetate as eluent, to obtain pure product **3/6**.

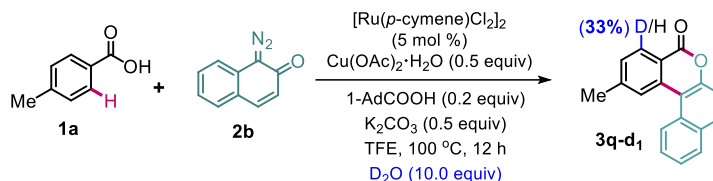
**Scaled up Ru(II)-catalyzed (3+3) annulation of aromatic acid **1b** and diazonaphthoquinone **2a** :**



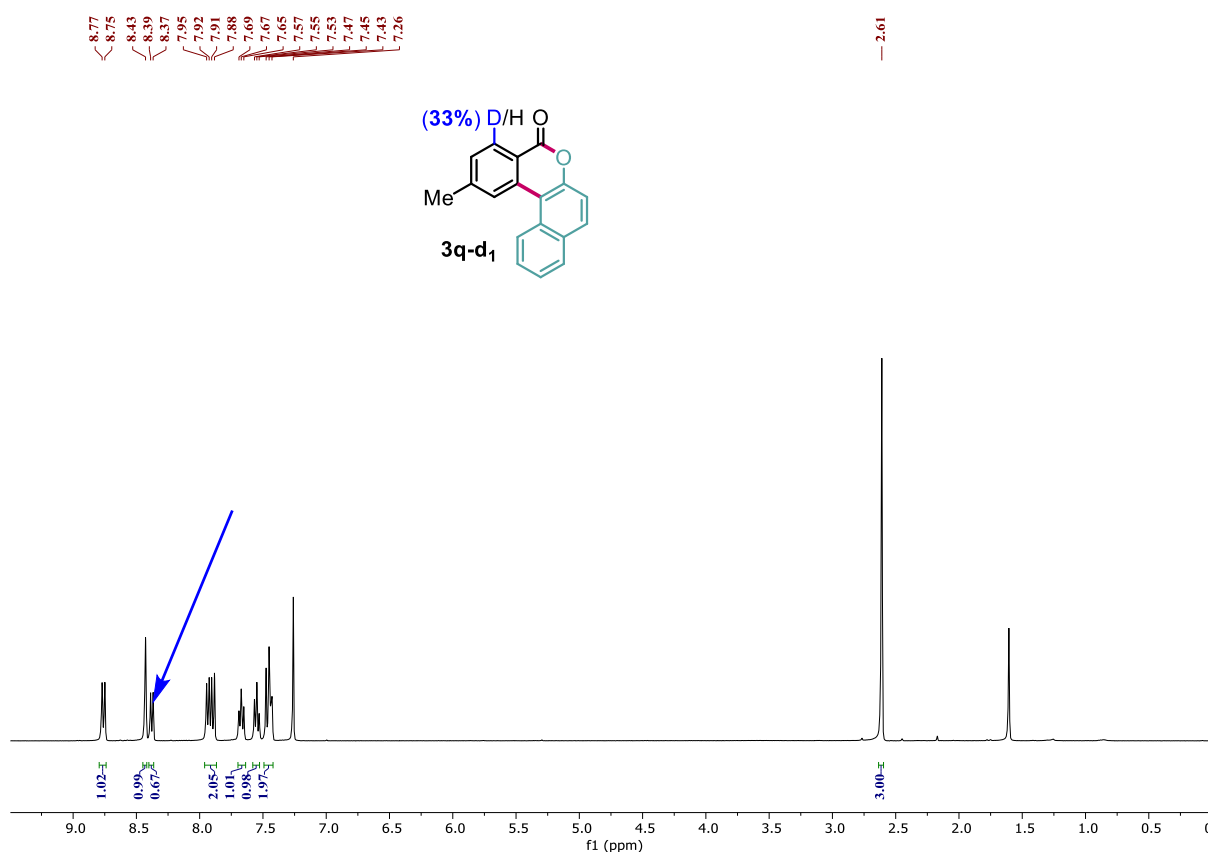
**Procedure:** To an oven-dried 25 mL round bottom flask, aromatic acid **1b** (3.0 mmol, 1.0 equiv), diazonaphthoquinone **2a** (1.5 equiv),  $[\text{Ru}(p\text{-cymene})\text{Cl}_2]_2$  (5.0 mol %),  $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$  (0.5 equiv),  $\text{K}_2\text{CO}_3$  (0.5 equiv) and 1-AdCOOH (0.2 equiv) were taken. Next 10.0 mL TFE solvent was added and the reaction tube was capped. The reaction mixture was then stirred at 100 °C for 30 h. After completion of the reaction (monitored by TLC), it was allowed to cool to room temperature. The volatiles were first evaporated, and then the residue was dissolved in ethyl acetate and transferred into a separating funnel. It was then washed with saturated sodium bicarbonate solution and dried over anhydrous  $\text{Na}_2\text{SO}_4$ . After evaporation under reduced pressure, the resulting residue was purified by column chromatography on silica gel, with a gradient eluent of Hexane/EtOAc = (95/5) to get the pure product **3b** (561.0 mg, 76%).

## Mechanistic studies:

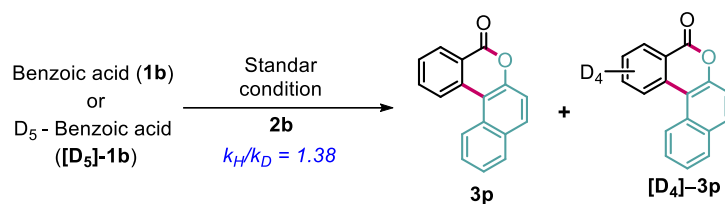
### (a) (H/D exchange study):



**Procedure:** To an oven-dried screw cap reaction tube (10 × 1.5 cm), aromatic acid **1a** (0.25 mmol, 1.0 equiv), diazonaphthoquinone **2b** (1.5 equiv),  $[\text{Ru}(p\text{-cymene})\text{Cl}_2]_2$  (5.0 mol %),  $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$  (0.5 equiv),  $\text{K}_2\text{CO}_3$  (0.5 equiv) and 1-AdCOOH (0.2 equiv) were taken. Next 1.0 mL TFE solvent was added into the reaction mixture followed by addition of  $\text{D}_2\text{O}$  (10.0 equiv). The reaction mixture was then stirred at 100 °C for 12 h. After that, volatiles were first evaporated, and the residue was dissolved in ethyl acetate and transferred into a separating funnel. It was then washed with saturated sodium bicarbonate solution and dried over anhydrous  $\text{Na}_2\text{SO}_4$ . After evaporation under reduced pressure, the resulting residue was purified by column chromatography on silica gel with a gradient eluent of Hexane/EtOAc = (95/5) to get the pure product. The H/D-scrambling was observed through  $^1\text{H}$  NMR spectroscopy.

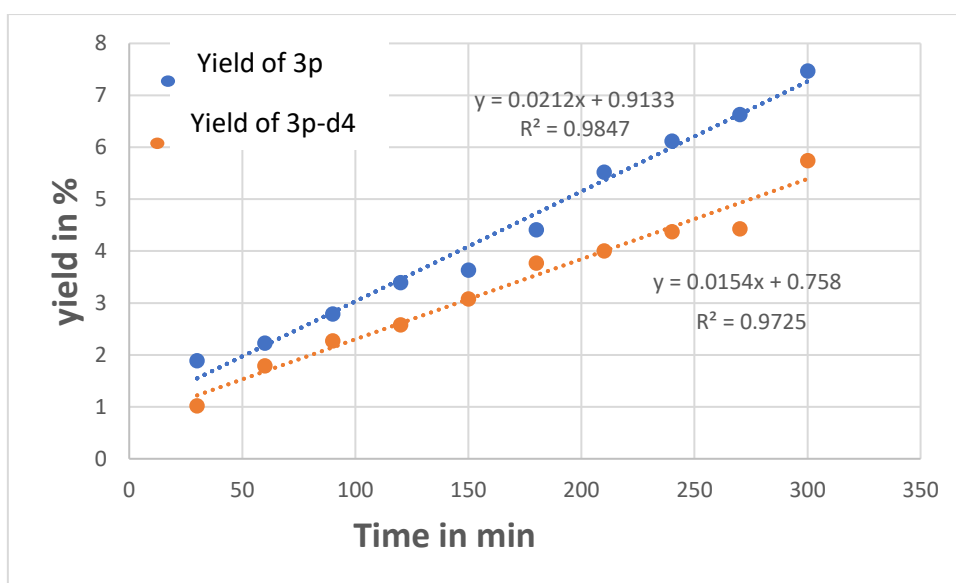


## (b) Intermolecular KIE through parallel experiments

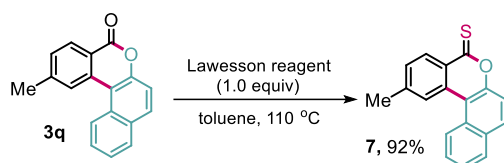


Two independent annulation reactions with **1b** and **[D]<sub>5</sub>-1b** under the standard reaction conditions were performed. In an oven-dried screw cap reaction tube, benzoic acid **1b** (0.4 mmol) or **[D]<sub>5</sub>-1b** (0.4 mmol), diazonaphthoquinone **2b** (1.5 equiv), [Ru(*p*-cymene)Cl<sub>2</sub>]<sub>2</sub> (5.0 mol %), Cu(OAc)<sub>2</sub>·H<sub>2</sub>O (0.5 equiv), K<sub>2</sub>CO<sub>3</sub> (0.5 equiv) and 1-AdCOOH (0.2 equiv) were taken. Next, 2.0 mL TFE solvent was added into the reaction mixture and stirred at 100 °C. After the reaction times indicated below, aliquots of 0.1 mL were taken out from the reaction mixture and concentrated under reduced pressure. Yields of products were determined by <sup>1</sup>H NMR spectroscopy using dibromomethane as an internal standard.

| t (min)                       | 30   | 60   | 90   | 120  | 150  | 180  | 210  | 240  | 270  | 300  |
|-------------------------------|------|------|------|------|------|------|------|------|------|------|
| <b>3p</b> (%)                 | 1.89 | 2.23 | 2.79 | 3.39 | 3.63 | 4.41 | 5.52 | 6.12 | 6.63 | 7.47 |
| <b>[D<sub>4</sub>]-3p</b> (%) | 1.02 | 1.79 | 2.27 | 2.58 | 3.08 | 3.77 | 4.00 | 4.37 | 4.43 | 5.74 |

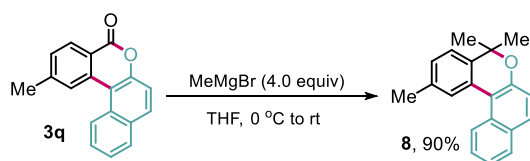


### Synthesis of compound 7:



To an oven-dried screw cap reaction tube (10 × 1.5 cm), compound **3q** (0.25 mmol) in toluene (1.0 mL) was taken. Then Lawesson reagent (1.0 equiv) was added and the mixture was stirred for 3 h at 110 °C. The solvent was removed under reduced pressure. In order to get pure compound **7**, the residue was purified by silica gel column chromatography with a gradient eluent of hexane/EtOAc = (95/05).

### Synthesis of compound 8:

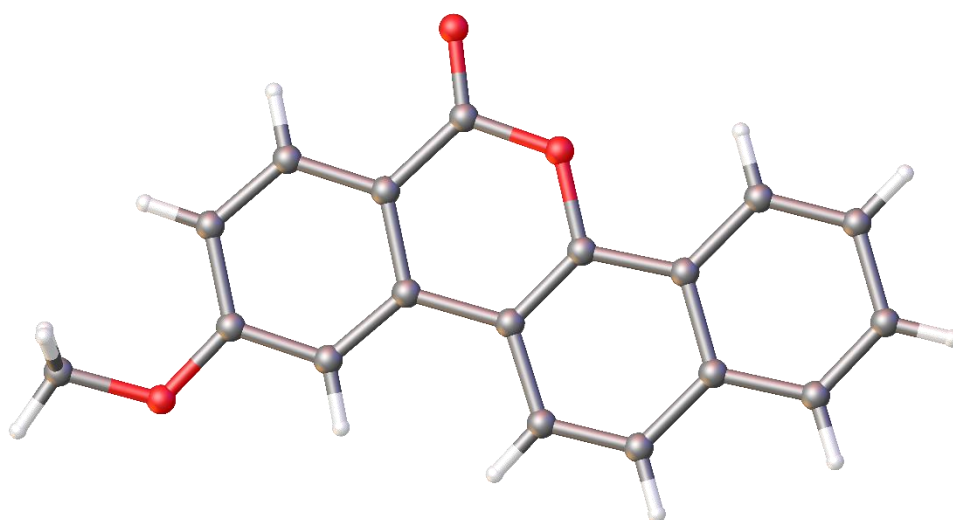


To an oven-dried screw cap reaction tube (10 × 1.5 cm), compound **3q** (0.25 mmol) was taken in THF (1.0 mL) at 0 °C under nitrogen. Then, MeMgBr (3 M in Et<sub>2</sub>O, 4.0 equiv) was added dropwise. The reaction was allowed to stir at 0 °C for 1 h followed by 2 h at room temperature. Then, 2 M HCl was added and after 20 minutes, the product was extracted with EtOAc (3 × 5 mL). The combined organic layers were dried (Na<sub>2</sub>SO<sub>4</sub>), concentrated under reduced pressure, and purified by silica gel column chromatography with a gradient eluent of hexane/EtOAc = (85/15) to get pure product **8**.

### X-ray crystal data of compound **3e**:

**Crystallization:** Crystals of compound **3e** were obtained through a slow evaporation technique at room temperature from a solution in CHCl<sub>3</sub>:DCM solvent combination.

Crystal structure of compound **3e** (CCDC number: **2284012**, Ellipsoid Probability 50%):



|                             |                                                                                                                        |
|-----------------------------|------------------------------------------------------------------------------------------------------------------------|
| Identification code         | <b>3e</b>                                                                                                              |
| Empirical formula           | C <sub>18</sub> H <sub>12</sub> O <sub>3</sub>                                                                         |
| Formula weight              | 276.28                                                                                                                 |
| Temperature                 | 298(2) K                                                                                                               |
| Wavelength                  | 0.71073 Å                                                                                                              |
| Crystal system, space group | Monoclinic, P 2 <sub>1</sub> /c                                                                                        |
| Unit cell dimensions        | a = 7.4483(3) Å    alpha = 90 deg.<br>b = 12.3287(4) Å    beta = 93.347(2) deg.<br>c = 13.9849(6) Å    gamma = 90 deg. |
| Volume                      | 1282.01(9) Å <sup>3</sup>                                                                                              |
| Z, Calculated density       | 4, 1.431 Mg/m <sup>3</sup>                                                                                             |

|                                   |                                             |
|-----------------------------------|---------------------------------------------|
| Absorption coefficient            | 0.097 mm <sup>-1</sup>                      |
| F(000)                            | 576                                         |
| Crystal size                      | 0.223 x 0.186 x 0.090 mm                    |
| Theta range for data collection   | 2.739 to 25.363 deg.                        |
| Limiting indices                  | -8<=h<=8, -14<=k<=14, -16<=l<=16            |
| Reflections collected / unique    | 22014 / 2342 [R(int) = 0.0437]              |
| Completeness to theta = 25.242    | 99.7 %                                      |
| Absorption correction             | Semi-empirical from equivalents             |
| Max. and min. transmission        | 0.7452 and 0.6950                           |
| Refinement method                 | Full-matrix least-squares on F <sup>2</sup> |
| Data / restraints / parameters    | 2342 / 0 / 191                              |
| Goodness-of-fit on F <sup>2</sup> | 1.056                                       |
| Final R indices [I>2sigma(I)]     | R1 = 0.0425, wR2 = 0.1034                   |
| R indices (all data)              | R1 = 0.0574, wR2 = 0.1142                   |
| Extinction coefficient            | n/a                                         |
| Largest diff. peak and hole       | 0.154 and -0.164 e.A <sup>-3</sup>          |

### X-ray crystal data of compound **3al**:

**Crystallization:** Crystals of compound **3al** were obtained through a slow evaporation technique at room temperature from a solution in CHCl<sub>3</sub>:DCM solvent combination.

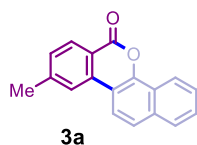
Crystal structure of compound **3al** (CCDC number: **2284013**, Ellipsoid Probability 50%):



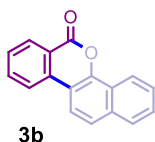
|                             |                                                                                                                                     |
|-----------------------------|-------------------------------------------------------------------------------------------------------------------------------------|
| Identification code         | <b>3al</b>                                                                                                                          |
| Empirical formula           | C <sub>18</sub> H <sub>10</sub> O <sub>4</sub>                                                                                      |
| Formula weight              | 290.26                                                                                                                              |
| Temperature                 | 298(2) K                                                                                                                            |
| Wavelength                  | 0.71073 Å                                                                                                                           |
| Crystal system, space group | Triclinic, P -1                                                                                                                     |
| Unit cell dimensions        | a = 8.6565(5) Å    alpha = 79.041(2) deg.<br>b = 9.0691(5) Å    beta = 70.617(2) deg.<br>c = 10.0037(5) Å    gamma = 62.258(2) deg. |
| Volume                      | 655.09(6) Å <sup>3</sup>                                                                                                            |
| Z, Calculated density       | 2, 1.472 Mg/m <sup>3</sup>                                                                                                          |

|                                   |                                             |
|-----------------------------------|---------------------------------------------|
| Absorption coefficient            | 0.105 mm <sup>-1</sup>                      |
| F(000)                            | 300                                         |
| Crystal size                      | 0.264 x 0.211 x 0.090 mm                    |
| Theta range for data collection   | 2.998 to 25.681 deg.                        |
| Limiting indices                  | -10 ≤ h ≤ 10, -11 ≤ k ≤ 11, -12 ≤ l ≤ 12    |
| Reflections collected / unique    | 21364 / 2479 [R(int) = 0.0464]              |
| Completeness to theta = 25.242    | 99.6 %                                      |
| Absorption correction             | Semi-empirical from equivalents             |
| Max. and min. transmission        | 0.7453 and 0.7051                           |
| Refinement method                 | Full-matrix least-squares on F <sup>2</sup> |
| Data / restraints / parameters    | 2479 / 0 / 199                              |
| Goodness-of-fit on F <sup>2</sup> | 1.052                                       |
| Final R indices [I > 2σ(I)]       | R1 = 0.0406, wR2 = 0.0924                   |
| R indices (all data)              | R1 = 0.0560, wR2 = 0.1018                   |
| Extinction coefficient            | n/a                                         |
| Largest diff. peak and hole       | 0.160 and -0.187 e.Å <sup>-3</sup>          |

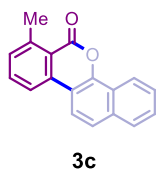
## NMR spectroscopic data of synthesized compounds:



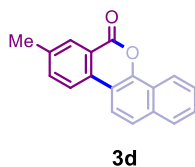
**9-methyl-6H-dibenzo[c,h]chromen-6-one (3a):** Eluent:(Hexane/EtOAc=95/5): white solid; yield = 59.0 mg (91%); Melting point: 181–183 °C;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.49 (d,  $J$  = 7.9 Hz, 1H), 8.23 (d,  $J$  = 8.0 Hz, 1H), 7.91 (d,  $J$  = 8.8 Hz, 1H), 7.82 (s, 1H), 7.79 (d,  $J$  = 7.3 Hz, 1H), 7.65 (d,  $J$  = 8.7 Hz, 1H), 7.59 – 7.52 (m, 2H), 7.30 (d,  $J$  = 8.0 Hz, 1H), 2.51 (s, 3H) ppm.  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  161.3, 147.3, 146.0, 135.3, 134.2, 130.5, 129.9, 127.8, 127.7, 127.0, 124.4, 123.9, 122.3, 122.1, 119.2, 118.7, 113.0, 22.4 ppm. **HRMS**(ESI)  $m/z$ :  $[\text{M}+\text{H}]^+$  Calcd. For  $\text{C}_{18}\text{H}_{13}\text{O}_2$  261.0910 Found 261.0914.



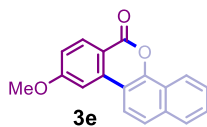
**6H-dibenzo[c,h]chromen-6-one (3b):** Eluent:(Hexane/EtOAc=96/4): white solid; yield = 50.0 mg (81%);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.50 (d,  $J$  = 7.6 Hz, 1H), 8.40 (d,  $J$  = 7.7 Hz, 1H), 8.09 (d,  $J$  = 7.9 Hz, 1H), 7.95 (d,  $J$  = 8.6 Hz, 1H), 7.81 (d,  $J$  = 6.5 Hz, 2H), 7.68 (d,  $J$  = 8.6 Hz, 1H), 7.60 – 7.53 (m, 3H) ppm.  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  161.3, 147.2, 135.4, 135.0, 134.3, 130.6, 128.6, 127.9, 127.7, 127.1, 124.5, 123.9, 122.3, 122.1, 121.2, 119.2, 113.0 ppm. **HRMS**(ESI)  $m/z$ :  $[\text{M}+\text{H}]^+$  Calcd. For  $\text{C}_{17}\text{H}_{11}\text{O}_2$  247.0754 Found 247.0756.



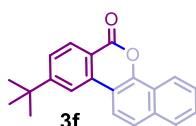
**7-methyl-6H-dibenzo[c,h]chromen-6-one (3c):** Eluent:(Hexane/EtOAc=95/5): white solid; yield = 42.0 mg (65%); Melting point: 178–180 °C;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.54 (d,  $J$  = 7.9 Hz, 1H), 8.01 (t,  $J$  = 9.5 Hz, 2H), 7.84 (d,  $J$  = 7.6 Hz, 1H), 7.70 – 7.65 (m, 2H), 7.63 – 7.56 (m, 2H), 7.37 (d,  $J$  = 7.4 Hz, 1H), 2.90 (s, 3H) ppm.  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  160.6, 147.3, 144.6, 136.8, 134.3, 134.2, 131.9, 127.9, 127.7, 127.1, 124.2, 123.7, 122.5, 120.2, 119.7(2×C), 113.3, 24.0 ppm. **HRMS** (ESI)  $m/z$ :  $[\text{M}+\text{H}]^+$  Calcd. For  $\text{C}_{18}\text{H}_{13}\text{O}_2$  261.0910 Found 261.0909.



**8-methyl-6H-dibenzo[c,h]chromen-6-one(3d):** Eluent:(Hexane/EtOAc=95/5): white solid; yield = 47.0 mg (72%); Melting point: 181–183 °C;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.50 (d,  $J$  = 7.8 Hz, 1H), 8.18 (s, 1H), 7.99 – 7.93 (m, 2H), 7.81 (d,  $J$  = 7.6 Hz, 1H), 7.68 (d,  $J$  = 8.6 Hz, 1H), 7.60 – 7.53 (m, 3H), 2.46 (s, 3H) ppm.  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  161.5, 146.8, 139.0, 136.2, 134.0, 132.8, 130.4, 127.71, 127.67, 127.1, 124.5, 123.9, 122.2, 122.0, 121.0, 119.2, 113.2, 21.4 ppm. **HRMS** (ESI)  $m/z$ :  $[\text{M}+\text{H}]^+$  Calcd. For  $\text{C}_{18}\text{H}_{13}\text{O}_2$  261.0910 Found 261.0914.

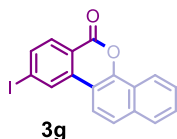


**9-methoxy-6H-dibenzo[c,h]chromen-6-one(3e):** Eluent:(Hexane/EtOAc=90/10): white solid; yield = 57.0 mg (83%); Melting point: 153–155 °C;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.56 (d,  $J$  = 7.8 Hz, 1H), 8.36 (d,  $J$  = 8.8 Hz, 1H), 7.95 (d,  $J$  = 8.8 Hz, 1H), 7.85 (d,  $J$  = 7.1 Hz, 1H), 7.72 (d,  $J$  = 8.7 Hz, 1H), 7.63 – 7.57 (m, 2H), 7.50 (s, 1H), 7.10 (d,  $J$  = 8.7 Hz, 1H), 4.00 (s, 3H) ppm.  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  165.1, 161.2, 147.8, 137.7, 134.4, 133.1, 128.0, 127.7, 127.2, 124.4, 124.0, 122.6, 119.3, 116.1, 114.4, 113.0, 105.4, 55.9 ppm. **HRMS** (ESI)  $m/z$ :  $[\text{M}+\text{H}]^+$  Calcd. For  $\text{C}_{18}\text{H}_{13}\text{O}_3$  277.0859 Found 277.0863.

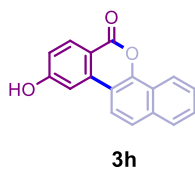


**9-(tert-butyl)-6H-dibenzo[c,h]chromen-6-one(3f):**

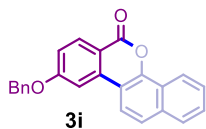
Eluent:(Hexane/EtOAc=92/8): white solid; yield = 66.0 mg (87%); Melting point: 160–162 °C;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.58 (d,  $J$  = 8.0 Hz, 1H), 8.38 (d,  $J$  = 8.3 Hz, 1H), 8.17 (s, 1H), 8.09 (d,  $J$  = 8.7 Hz, 1H), 7.86 (d,  $J$  = 7.6 Hz, 1H), 7.75 (d,  $J$  = 8.7 Hz, 1H), 7.67 – 7.57 (m, 3H), 1.47 (s, 9H) ppm.  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  161.4, 159.0, 147.5, 135.2, 134.3, 130.6, 127.9, 127.7, 127.1, 126.7, 124.4, 124.1, 122.5, 119.3, 118.8, 118.4, 113.5, 35.9, 31.2 ppm. **HRMS** (ESI)  $m/z$ :  $[\text{M}+\text{H}]^+$  Calcd. For  $\text{C}_{21}\text{H}_{19}\text{O}_2$  303.1380 Found 303.1385.



**9-iodo-6H-dibenzo[c,h]chromen-6-one(3g):** Eluent:(Hexane/EtOAc=93/7): white solid; yield = 58.0 mg (62%); Melting point: 172–174 °C;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.55 – 8.52 (m, 2H), 8.11 (d,  $J$  = 8.3 Hz, 1H), 7.95 (d,  $J$  = 8.7 Hz, 1H), 7.91 (d,  $J$  = 8.3 Hz, 1H), 7.86 (d,  $J$  = 7.5 Hz, 1H), 7.75 (d,  $J$  = 8.8 Hz, 1H), 7.66 – 7.59 (m, 2H) ppm.  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  161.0, 147.8, 137.9, 136.8, 134.6, 131.9, 131.5, 128.4, 127.8, 127.4, 124.9, 123.9, 122.5, 120.4, 119.0, 111.8, 103.9 ppm. **HRMS** (ESI)  $m/z$ :  $[\text{M}+\text{H}]^+$  Calcd. For  $\text{C}_{17}\text{H}_{10}\text{IO}_2$  372.9720 Found 372.9723.

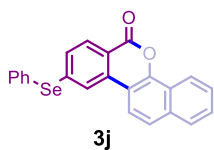


**9-hydroxy-6H-dibenzo[c,h]chromen-6-one(3h):** Eluent:(Hexane/EtOAc=85/15): white solid; yield = 44.0 mg (67%); Melting point: 173–175 °C;  $^1\text{H NMR}$  (400 MHz,  $\text{DMSO}-d_6$ )  $\delta$  8.39 (d,  $J$  = 8.1 Hz, 1H), 8.21 (t,  $J$  = 9.2 Hz, 2H), 8.05 (d,  $J$  = 7.3 Hz, 1H), 7.90 (d,  $J$  = 8.8 Hz, 1H), 7.71 – 7.67 (m, 3H), 7.14 (d,  $J$  = 8.6 Hz, 1H) ppm.  $^{13}\text{C NMR}$  (101 MHz,  $\text{DMSO}-d_6$ )  $\delta$  164.0, 160.0, 146.7, 137.2, 133.9, 132.6, 127.9(2×C), 127.3, 124.3, 123.0, 121.4, 120.1, 117.8, 112.9, 112.0, 107.7 ppm. **HRMS** (ESI)  $m/z$ :  $[\text{M}+\text{H}]^+$  Calcd. For  $\text{C}_{17}\text{H}_{11}\text{O}_3$  263.0703 Found 263.0709.



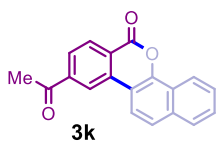
### 9-(benzyloxy)-6H-dibenzo[c,h]chromen-6-one(3i):

Eluent:(Hexane/EtOAc=90/10): white solid; yield = 65.0 mg (74%); Melting point: 176–178 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.52 (d, *J* = 8.3 Hz, 1H), 8.33 (d, *J* = 8.8 Hz, 1H), 7.87 (d, *J* = 8.7 Hz, 1H), 7.81 (d, *J* = 7.1 Hz, 1H), 7.68 (d, *J* = 8.7 Hz, 1H), 7.60 – 7.55 (m, 3H), 7.50 (d, *J* = 7.4 Hz, 2H), 7.45 (t, *J* = 7.3 Hz, 2H), 7.40 (d, *J* = 7.3 Hz, 1H), 7.13 (d, *J* = 8.8 Hz, 1H), 5.23 (s, 2H) ppm. <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 164.1, 161.0, 147.7, 137.6, 135.9, 134.4, 133.0, 129.0, 128.6, 128.0, 127.72, 127.69, 127.1, 124.4, 123.9, 122.5, 119.2, 116.6, 114.5, 113.3, 106.5, 70.6 ppm. HRMS (ESI) *m/z*: [M+H]<sup>+</sup> Calcd. For C<sub>24</sub>H<sub>17</sub>O<sub>3</sub> 353.1172 Found 353.1169.



### 9-(phenylselanyl)-6H-dibenzo[c,h]chromen-6-one(3j):

Eluent:(Hexane/EtOAc=90/10): white solid; yield = 60.0 mg (60%); Melting point: 185–187 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.52 (d, *J* = 7.9 Hz, 1H), 8.21 (d, *J* = 8.3 Hz, 1H), 8.00 (s, 1H), 7.82 (d, *J* = 7.3 Hz, 1H), 7.74 (d, *J* = 8.8 Hz, 1H), 7.71 – 7.65 (m, 3H), 7.62 – 7.55 (m, 2H), 7.50 – 7.42 (m, 3H), 7.40 (d, *J* = 7.8 Hz, 1H) ppm. <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 161.1, 147.7, 143.9, 135.9, 135.8, 134.4, 131.0, 130.2, 129.9, 129.4, 128.1, 127.73, 127.69, 127.2, 124.6, 123.9, 122.6, 122.5, 119.0, 118.9, 112.5 ppm. HRMS (ESI) *m/z*: [M+H]<sup>+</sup> Calcd. For C<sub>23</sub>H<sub>15</sub>O<sub>2</sub>Se 403.0232 Found 403.0218.

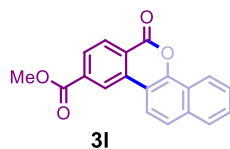


### 9-acetyl-6H-dibenzo[c,h]chromen-6-one (3k):

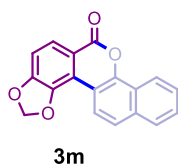
Eluent:(Hexane/EtOAc=92/8): white solid; yield = 52.0 mg (72%); Melting point: 156–158 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.69 (s, 1H), 8.54 – 8.50 (m, 2H), 8.09 (d, *J* = 8.8 Hz, 1H), 8.06 (d, *J* = 8.2 Hz, 1H), 7.87 (d, *J* = 8.1 Hz, 1H), 7.77 (d, *J* = 8.8 Hz, 1H), 7.65 – 7.62 (m, 2H), 2.76 (s, 3H) ppm. <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 197.3, 160.5, 147.6, 141.8, 135.8, 134.6, 131.4, 128.4, 127.9, 127.7, 127.5, 125.0, 124.1, 123.8, 122.4, 122.1, 119.2, 112.7, 27.2 ppm. HRMS (ESI) *m/z*: [M+H]<sup>+</sup> Calcd. For C<sub>19</sub>H<sub>13</sub>O<sub>3</sub> 289.0859 Found 289.0862.

### methyl 6-oxo-6H-dibenzo[c,h]chromene-9-carboxylate(3l):

Eluent:(Hexane/EtOAc=90/10): white solid; yield = 60.0 mg (79%); Melting point: 197–200 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.85 (s, 1H), 8.57 (d, *J* = 7.6 Hz, 1H), 8.52 (d, *J* = 8.2 Hz, 1H), 8.19 (d, *J* = 8.2 Hz, 1H), 8.14 (d, *J* = 8.7 Hz, 1H), 7.89 (d,

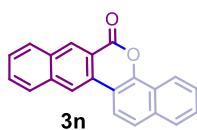


$J = 7.6$  Hz, 1H), 7.80 (d,  $J = 8.7$  Hz, 1H), 7.67 – 7.61 (m, 2H), 4.04 (s, 3H) ppm.  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  166.0, 160.7, 147.7, 135.9, 135.7, 134.6, 131.1, 128.9, 128.4, 127.9, 127.5, 125.0, 124.2, 123.9 (2 $\times$ C), 122.5, 119.3, 112.7, 53.0 ppm. HRMS (ESI)  $m/z$ :  $[\text{M}+\text{H}]^+$  Calcd. For  $\text{C}_{19}\text{H}_{13}\text{O}_4$  305.0808 Found 305.0812.

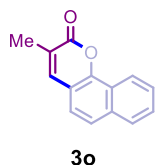


**13H-[1,3]dioxolo[4',5':3,4]benzo[1,2-c]benzo[h]chromen-13-one(3m):**

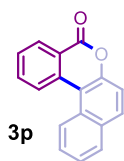
Eluent:(Hexane/EtOAc=83/17): white solid; yield = 64.0 mg (88%); Melting point: 180–184 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.55 (d,  $J = 8.2$  Hz, 1H), 8.34 (d,  $J = 8.8$  Hz, 1H), 8.08 (d,  $J = 8.3$  Hz, 1H), 7.84 (d,  $J = 7.1$  Hz, 1H), 7.67 (d,  $J = 8.8$  Hz, 1H), 7.63 – 7.57 (m, 2H), 7.03 (d,  $J = 8.4$  Hz, 1H), 6.27 (s, 2H) ppm.  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  160.7, 153.2, 147.0, 143.1, 134.1, 127.9, 127.7, 127.03, 126.95, 124.2, 123.5, 122.9, 122.4, 119.4, 115.6, 111.5, 109.6, 102.8 ppm. HRMS (ESI)  $m/z$ :  $[\text{M}+\text{H}]^+$  Calcd. For  $\text{C}_{18}\text{H}_{11}\text{O}_4$  291.0652 Found 291.0642.



**6H-benzo[h]naphtho[2,3-c]chromen-6-one (3n):** Eluent:(Hexane/EtOAc=92/8): white solid; yield = 63.0 mg (85%); Melting point: 162–164 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.96 (s, 1H), 8.49 (d,  $J = 8.0$  Hz, 1H), 8.46 (s, 1H), 8.11 (d,  $J = 8.7$  Hz, 1H), 7.96 (d,  $J = 8.2$  Hz, 2H), 7.81 (d,  $J = 7.6$  Hz, 1H), 7.72 (d,  $J = 8.7$  Hz, 1H), 7.64 (t,  $J = 7.5$  Hz, 1H), 7.59 – 7.52 (m, 3H) ppm.  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  161.6, 146.5, 136.4, 134.3, 132.9, 132.4, 130.3, 129.7, 129.6, 128.2, 127.73, 127.70, 127.2, 127.1, 124.6, 124.1, 122.3, 121.0, 119.5, 119.2, 113.3 ppm. HRMS (ESI)  $m/z$ :  $[\text{M}+\text{H}]^+$  Calcd. For  $\text{C}_{21}\text{H}_{13}\text{O}_2$  297.0910 Found 297.0909.

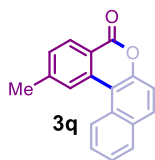


**3-methyl-2H-benzo[h]chromen-2-one (3o):** Eluent:(Hexane/EtOAc=93/7): white solid; yield = 47.0 mg (90%); Melting point: 148–152 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.51 (d,  $J = 7.6$  Hz, 1H), 7.85 (d,  $J = 7.7$  Hz, 1H), 7.65 – 7.59 (m, 4H), 7.39 (d,  $J = 8.5$  Hz, 1H), 2.26 (s, 3H) ppm.  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  162.5, 150.1, 140.2, 134.3, 128.2, 127.9, 127.1, 125.5, 124.4, 123.4, 123.1, 122.1, 115.0, 17.3 ppm. HRMS (ESI)  $m/z$ :  $[\text{M}+\text{H}]^+$  Calcd. For  $\text{C}_{14}\text{H}_{11}\text{O}_2$  211.0754 Found 211.0760.

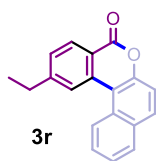


**5H-dibenzo[c,f]chromen-5-one (3p):** Eluent:(Hexane/EtOAc=96/4): white solid; yield = 51.0 mg (83%);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.69 (d,  $J = 8.3$  Hz, 1H), 8.57 (d,  $J = 7.9$  Hz, 1H), 8.46 (d,  $J = 7.4$  Hz, 1H), 7.91 – 7.83 (m, 3H), 7.64 – 7.58 (m, 2H), 7.52 (t,  $J = 6.9$  Hz, 1H), 7.42 (d,  $J = 8.7$  Hz, 1H) ppm.  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  161.4, 150.3, 135.4, 134.4, 131.7, 131.6, 130.7, 129.5, 129.4, 128.3,

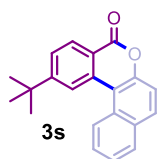
127.8, 126.4, 125.5, 125.0, 122.3, 117.6, 112.6 ppm. **HRMS** (ESI)  $m/z$ :  $[M+H]^+$  Calcd. For  $C_{17}H_{11}O_2$  247.0754 Found 247.0765.



**2-methyl-5H-dibenzo[c,f]chromen-5-one (3q):** Eluent:(Hexane/EtOAc=95/5): white solid; yield = 61.0 mg (93%);  **$^1H$  NMR** (400 MHz,  $CDCl_3$ )  $\delta$  8.73 (d,  $J$  = 8.6 Hz, 1H), 8.39 (s, 1H), 8.36 (d,  $J$  = 7.7 Hz, 1H), 7.92 (d,  $J$  = 8.1 Hz, 1H), 7.87 (d,  $J$  = 8.8 Hz, 1H), 7.63 (t,  $J$  = 7.7 Hz, 1H), 7.53 (t,  $J$  = 7.4 Hz, 1H), 7.43 (t,  $J$  = 7.7 Hz, 2H), 2.59 (s, 3H) ppm.  **$^{13}C$  NMR** (101 MHz,  $CDCl_3$ )  $\delta$  161.5, 150.5, 145.5, 135.5, 131.7, 131.5, 130.8, 129.7, 129.5, 129.4, 127.8, 126.7, 125.4, 125.1, 120.0, 117.7, 112.6, 22.6 ppm. **HRMS** (ESI)  $m/z$ :  $[M+H]^+$  Calcd. For  $C_{18}H_{13}O_2$  261.0910 Found 261.0919.

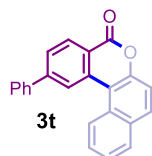


**2-ethyl-5H-dibenzo[c,f]chromen-5-one (3r):** Eluent:(Hexane/EtOAc=95/5): Sticky liquid; yield = 59.0 mg (86%);  **$^1H$  NMR** (500 MHz,  $CDCl_3$ )  $\delta$  8.75 (d,  $J$  = 8.6 Hz, 1H), 8.44 (s, 1H), 8.40 (d,  $J$  = 8.1 Hz, 1H), 7.93 (d,  $J$  = 8.1 Hz, 1H), 7.89 (d,  $J$  = 8.8 Hz, 1H), 7.67 (t,  $J$  = 8.3 Hz, 1H), 7.55 (t,  $J$  = 7.9 Hz, 1H), 7.46 (d,  $J$  = 8.9 Hz, 2H), 2.90 (q,  $J$  = 7.6 Hz, 2H), 1.38 (t,  $J$  = 7.6 Hz, 3H) ppm.  **$^{13}C$  NMR** (126 MHz,  $CDCl_3$ )  $\delta$  161.5, 151.6, 150.5, 135.7, 131.8, 131.5, 131.0, 129.8, 129.5, 128.4, 127.8, 125.7, 125.4, 125.2, 120.3, 117.8, 112.8, 29.8, 15.4 ppm. **HRMS** (ESI)  $m/z$ :  $[M+H]^+$  Calcd. For  $C_{19}H_{15}O_2$  275.1067 Found 275.1069.



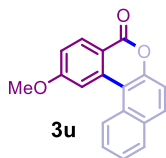
**2-(tert-butyl)-5H-dibenzo[c,f]chromen-5-one(3s):**

Eluent:(Hexane/EtOAc=95/5): white solid; yield = 69.0 mg (91%); Melting point: 162–164 °C;  **$^1H$  NMR** (400 MHz,  $CDCl_3$ )  $\delta$  8.74 (d,  $J$  = 8.6 Hz, 1H), 8.65 (s, 1H), 8.42 (d,  $J$  = 8.3 Hz, 1H), 7.95 (d,  $J$  = 8.1 Hz, 1H), 7.90 (d,  $J$  = 8.9 Hz, 1H), 7.70 – 7.67 (m, 2H), 7.55 (t,  $J$  = 7.5 Hz, 1H), 7.48 (d,  $J$  = 8.9 Hz, 1H), 1.48 (s, 9H) ppm.  **$^{13}C$  NMR** (101 MHz,  $CDCl_3$ )  $\delta$  161.5, 158.3, 150.5, 135.3, 131.8, 131.4, 130.6, 129.7, 129.5, 127.8, 126.1, 125.4, 125.1, 123.4, 120.0, 117.8, 113.2, 35.9, 31.3 ppm. **HRMS** (ESI)  $m/z$ :  $[M+H]^+$  Calcd. For  $C_{21}H_{19}O_2$  303.1380 Found 303.1364.

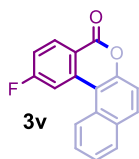


**phenyl-5H-dibenzo[c,f]chromen-5-one (3t):** Eluent:(Hexane/EtOAc=93/7): white solid; yield = 64.0 mg (79%);  **$^1H$  NMR** (500 MHz,  $CDCl_3$ )  $\delta$  8.81 (d,  $J$  = 7.9 Hz, 2H), 8.54 (d,  $J$  = 8.2 Hz, 1H), 7.95 (d,  $J$  = 8.1 Hz, 1H), 7.93 (d,  $J$  = 8.9 Hz, 1H), 7.83 (d,  $J$  = 9.2 Hz, 1H), 7.72 (d,  $J$  = 7.3 Hz, 2H), 7.68 (t,  $J$  = 7.8 Hz, 1H), 7.57 – 7.54 (m, 3H), 7.50 – 7.47 (m, 2H) ppm.  **$^{13}C$  NMR** (126 MHz,  $CDCl_3$ )  $\delta$  161.4, 150.7, 147.4, 140.0, 136.0, 131.83, 131.77, 131.4, 129.7, 129.6, 129.4, 128.9, 128.1, 127.7,

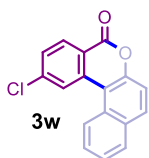
127.3, 125.5, 125.09, 125.06, 121.2, 117.8, 112.8 ppm HRMS (ESI)  $m/z$ :  $[M+Na]^+$  Calcd. For  $C_{23}H_{14}O_2Na$  345.0886 Found 345.0891.



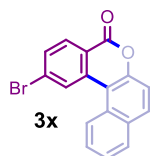
**2-methoxy-5H-dibenzo[c,f]chromen-5-one (3u):** Eluent:(Hexane/EtOAc=88/12): white solid; yield = 61.0 mg (89%);  $^1H$  NMR (500 MHz,  $CDCl_3$ )  $\delta$  8.76 (d,  $J$  = 8.6 Hz, 1H), 8.43 (d,  $J$  = 8.8 Hz, 1H), 8.07 (s, 1H), 7.93 (d,  $J$  = 8.1 Hz, 1H), 7.90 (d,  $J$  = 8.9 Hz, 1H), 7.65 (t,  $J$  = 7.7 Hz, 1H), 7.54 (t,  $J$  = 7.5 Hz, 1H), 7.45 (d,  $J$  = 8.9 Hz, 1H), 7.15 (d,  $J$  = 8.1 Hz, 1H), 4.01 (s, 3H) ppm.  $^{13}C$  NMR (126 MHz,  $CDCl_3$ )  $\delta$  164.6, 161.2, 151.0, 137.5, 133.2, 131.8, 131.7, 129.8, 129.6, 127.9, 125.4, 124.8, 117.9, 115.6, 114.8, 112.6, 111.2, 55.9 ppm. HRMS (ESI)  $m/z$ :  $[M+H]^+$  Calcd. For  $C_{18}H_{13}O_3$  277.0859 Found 277.0855.



**2-fluoro-5H-dibenzo[c,f]chromen-5-one (3v):** Eluent:(Hexane/EtOAc=94/6): white solid; yield = 50.0 mg (76%);  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  8.68 (d,  $J$  = 8.6 Hz, 1H), 8.54 – 8.50 (m, 1H), 8.31 (d,  $J$  = 10.9 Hz, 1H), 7.95 (d,  $J$  = 8.9 Hz, 2H), 7.70 (t,  $J$  = 7.8 Hz, 1H), 7.57 (t,  $J$  = 7.5 Hz, 1H), 7.47 (d,  $J$  = 8.9 Hz, 1H), 7.32 (t,  $J$  = 8.2 Hz, 1H) ppm.  $^{13}C$  NMR (101 MHz,  $CDCl_3$ )  $\delta$  166.7 (d,  $J$  = 254.9 Hz), 160.6, 151.0, 138.2 (d,  $J$  = 10.1 Hz), 134.1 (d,  $J$  = 10.4 Hz), 132.6, 131.7, 129.7, 129.5, 128.4, 125.8, 124.5, 118.9, 117.7, 116.3 (d,  $J$  = 22.9 Hz), 113.0 (d,  $J$  = 25.0 Hz), 111.9 ppm.  $^{19}F$  NMR (471 MHz,  $CDCl_3$ )  $\delta$  -101.33 ppm; HRMS (ESI)  $m/z$ :  $[M+H]^+$  Calcd. For  $C_{17}H_{10}FO_2$  265.0659 Found 265.0649.



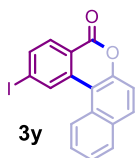
**2-chloro-5H-dibenzo[c,f]chromen-5-one (3w):** Eluent:(Hexane/EtOAc=95/5): white solid; yield = 60.0 mg (85%);  $^1H$  NMR (500 MHz,  $CDCl_3$ )  $\delta$  8.62 (d,  $J$  = 8.6 Hz, 1H), 8.56 (s, 1H), 8.39 (d,  $J$  = 8.4 Hz, 1H), 7.92 – 7.89 (m, 2H), 7.70 – 7.66 (m, 1H), 7.56 – 7.53 (m, 2H), 7.43 (d,  $J$  = 8.9 Hz, 1H) ppm.  $^{13}C$  NMR (126 MHz,  $CDCl_3$ )  $\delta$  160.6, 151.0, 141.4, 136.9, 132.5, 132.4, 131.7, 129.6, 129.4, 128.6, 128.4, 126.2, 125.8, 124.6, 120.7, 117.6, 111.6 ppm. HRMS (ESI)  $m/z$ :  $[M+H]^+$  Calcd. For  $C_{17}H_{10}ClO_2$  281.0364 Found 281.0367.



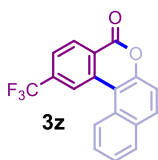
**2-bromo-5H-dibenzo[c,f]chromen-5-one (3x):** Eluent:(Hexane/EtOAc=95/5): white solid; yield = 62.0 mg (77%); Melting point: 205–207 °C  $^1H$  NMR (500 MHz,  $CDCl_3$ )  $\delta$  8.75 (s, 1H), 8.64 (d,  $J$  = 8.6 Hz, 1H), 8.31 (d,  $J$  = 8.4 Hz, 1H), 7.94 – 7.91 (m, 2H), 7.73 – 7.68 (m, 2H), 7.56 (t,  $J$  = 7.5 Hz, 1H), 7.44 (d,  $J$  = 8.9 Hz, 1H) ppm.  $^{13}C$  NMR (126 MHz,  $CDCl_3$ )  $\delta$  160.8, 151.0, 137.0, 132.5, 132.3, 131.7,

131.6, 130.2, 129.6, 129.4, 129.3, 128.5, 125.8, 124.6, 121.1, 117.6, 111.5 ppm.

**HRMS** (ESI)  $m/z$ :  $[M+H]^+$  Calcd. For  $C_{17}H_{10}BrO_2$  324.9859 Found 324.9866.

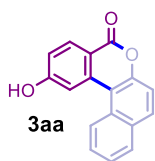


**2-iodo-5H-dibenzo[c,f]chromen-5-one (3y)**: Eluent:(Hexane/EtOAc=95/5): white solid; yield = 60.0 mg (65%);  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  8.94 (s, 1H), 8.60 (d,  $J$  = 8.7 Hz, 1H), 8.12 (d,  $J$  = 8.4 Hz, 1H), 7.91 (t,  $J$  = 7.5 Hz, 3H), 7.69 (t,  $J$  = 7.7 Hz, 1H), 7.55 (t,  $J$  = 7.5 Hz, 1H), 7.43 (d,  $J$  = 8.8 Hz, 1H) ppm.  $^{13}C$  NMR (101 MHz,  $CDCl_3$ )  $\delta$  161.0, 150.8, 137.4, 136.7, 135.3, 132.4, 131.9, 131.7, 129.6, 129.3, 128.4, 125.7, 124.5, 121.5, 117.6, 111.2, 103.0 ppm.



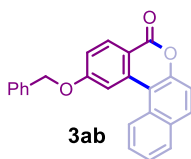
**2-(trifluoromethyl)-5H-dibenzo[c,f]chromen-5-one(3z):**

Eluent:(Hexane/EtOAc=97/3): white solid; yield = 58.0 mg (74%); Melting point: 167–169 °C;  $^1H$  NMR (500 MHz,  $CDCl_3$ )  $\delta$  8.87 (s, 1H), 8.62 (d,  $J$  = 8.7 Hz, 1H), 8.59 (d,  $J$  = 8.2 Hz, 1H), 7.95 (d,  $J$  = 8.6 Hz, 2H), 7.83 (d,  $J$  = 8.2 Hz, 1H), 7.71 (t,  $J$  = 7.2 Hz, 1H), 7.58 (t,  $J$  = 7.5 Hz, 1H), 7.46 (d,  $J$  = 8.9 Hz, 1H) ppm.  $^{13}C$  NMR (126 MHz,  $CDCl_3$ )  $\delta$  160.2, 150.9, 136.01, 135.95 (q,  $J$  = 32.6 Hz), 132.8, 131.8, 131.7, 129.7, 129.4, 128.7, 125.9, 124.9, 124.5 (q,  $J$  = 3.5 Hz), 124.4, 123.6 (q,  $J$  = 273.4 Hz), 123.5 (q,  $J$  = 3.8 Hz), 117.6, 111.7 ppm.  $^{19}F$  NMR (471 MHz,  $CDCl_3$ )  $\delta$  -63.2 ppm. **HRMS** (ESI)  $m/z$ :  $[M+H]^+$  Calcd. For  $C_{18}H_{10}F_3O_2$  315.0627 Found 315.0628.



**2-hydroxy-5H-dibenzo[c,f]chromen-5-one(3aa):**

Eluent:(Hexane/EtOAc=85/15): white solid; yield = 52.0 mg (79%); Melting point: 181–183 °C ;  $^1H$  NMR (400 MHz,  $DMSO-d_6$ )  $\delta$  11.05 (brs, 1H), 8.77 (d,  $J$  = 8.6 Hz, 1H), 8.23 (d,  $J$  = 8.6 Hz, 1H), 8.12 – 8.07 (m, 3H), 7.76 (t,  $J$  = 7.3 Hz, 1H), 7.62 (t,  $J$  = 7.3 Hz, 1H), 7.54 (d,  $J$  = 8.8 Hz, 1H), 7.14 (d,  $J$  = 7.6 Hz, 1H) ppm.  $^{13}C$  NMR (101 MHz,  $DMSO-d_6$ )  $\delta$  163.5, 160.2, 150.4, 136.8, 132.9, 132.0, 131.3, 129.6, 129.1, 128.2, 125.5, 124.7, 117.5, 117.3, 113.2, 111.8, 111.7 ppm. **HRMS** (ESI)  $m/z$ :  $[M+H]^+$  Calcd. For  $C_{17}H_{11}O_3$  263.0703 Found 263.0688.



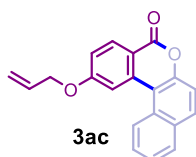
**2-(benzyloxy)-5H-dibenzo[c,f]chromen-5-one(3ab):**

Eluent:(Hexane/EtOAc=90/10): white solid; yield = 64.0 mg (73%); Melting point: 166–168 °C;  $^1H$  NMR (500 MHz,  $CDCl_3$ )  $\delta$  8.44 – 8.40 (m, 2H), 8.03 (d,  $J$  = 2.2 Hz, 1H), 7.90 – 7.85 (m, 2H), 7.55 – 7.50 (m, 4H), 7.48 – 7.45 (m, 2H), 7.43 – 7.40 (m, 2H), 7.23 (dd,  $J$  = 8.8, 2.2 Hz, 1H), 5.28 (s, 2H) ppm.  $^{13}C$  NMR (126 MHz,  $CDCl_3$ )  $\delta$  163.5, 161.1, 150.9, 137.5, 136.1, 133.1, 131.8, 131.7, 129.7, 129.4,

129.0, 128.6, 127.9, 127.5, 125.3, 124.7, 117.8, 116.2, 115.7, 112.5, 111.7, 70.6 ppm. HRMS (ESI) m/z: [M+H]<sup>+</sup> Calcd. For C<sub>24</sub>H<sub>17</sub>O<sub>3</sub> 353.1172 Found 353.1167.

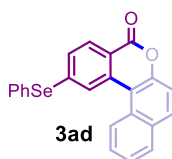
**2-(allyloxy)-5H-dibenzo[c,f]chromen-5-one(3ac):**

Eluent:(Hexane/EtOAc=88/12): white solid; yield = 57.0 mg (76%); Melting point: 172–174 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.73 (d, *J* = 8.6 Hz, 1H), 8.42 (d, *J* = 8.8 Hz, 1H), 8.07 (s, 1H), 7.93 (d, *J* = 8.1 Hz, 1H), 7.89 (d, *J* = 8.9 Hz, 1H), 7.65 (t, *J* = 7.7 Hz, 1H), 7.54 (t, *J* = 7.5 Hz, 1H), 7.45 (d, *J* = 8.9 Hz, 1H), 7.16 (dd, *J* = 8.8, 2.3 Hz, 1H), 6.17 – 6.09 (m, 1H), 5.52 (d, *J* = 17.3 Hz, 1H), 5.42 (d, *J* = 10.5 Hz, 1H), 4.75 (d, *J* = 5.3 Hz, 2H) ppm. <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 163.6, 161.2, 150.9, 137.5, 133.1, 132.6, 131.8, 131.7, 129.8, 129.5, 127.9, 125.4, 124.9, 118.8, 117.74, 115.66, 115.7, 112.6, 111.7, 69.5 ppm. HRMS (ESI) m/z: [M+H]<sup>+</sup> Calcd. For C<sub>20</sub>H<sub>15</sub>O<sub>3</sub> 303.1016 Found 303.1019.



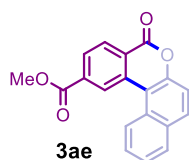
**2-(phenylselanyl)-5H-dibenzo[c,f]chromen-5-one(3ad):**

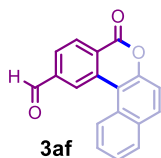
Eluent:(Hexane/EtOAc=88/12): white solid; yield = 68.0 mg (68%); Melting point: 192–194 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.29 – 8.27 (m, 2H), 8.07 (d, *J* = 8.6 Hz, 1H), 7.86 – 7.83 (m, 2H), 7.77 – 7.76 (m, 2H), 7.56 – 7.54 (m, 2H), 7.50 – 7.44 (m, 3H), 7.40 (d, *J* = 8.9 Hz, 1H), 7.35 – 7.32 (m, 1H) ppm. <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 161.2, 150.9, 144.0, 136.6, 135.9, 131.9, 131.6, 130.9, 130.3, 129.51, 129.45, 129.4, 128.9, 127.83, 127.77, 126.6, 125.4, 124.6, 120.0, 117.7, 112.0 ppm. HRMS (ESI) m/z: [M+H]<sup>+</sup> Calcd. For C<sub>23</sub>H<sub>15</sub>O<sub>2</sub>Se 403.0232 Found 403.0237.



**Methyl5-oxo-5H-dibenzo[c,f]chromene-2-carboxylate(ae):**

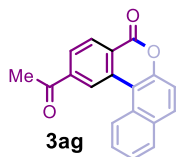
Eluent:(Hexane/EtOAc=90/10): white solid; yield = 61.0 mg (80%); Melting point: 206–208 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 9.24 (s, 1H), 8.69 (d, *J* = 8.6 Hz, 1H), 8.49 (d, *J* = 8.2 Hz, 1H), 8.17 (d, *J* = 8.2 Hz, 1H), 7.92 – 7.89 (m, 2H), 7.68 (t, *J* = 7.7 Hz, 1H), 7.54 (t, *J* = 7.5 Hz, 1H), 7.43 (d, *J* = 8.9 Hz, 1H), 4.03 (s, 3H) ppm. <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 166.1, 160.6, 150.6, 135.5, 135.2, 132.3, 131.7, 131.0, 129.5, 129.4, 128.4(2×C), 127.9, 125.7, 125.3, 124.8, 117.5, 112.1, 53.0 ppm. HRMS (ESI) m/z: [M+H]<sup>+</sup> Calcd. For C<sub>19</sub>H<sub>13</sub>O<sub>4</sub> 305.0808 Found 305.0812.



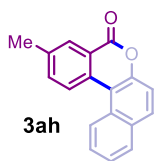


**5-oxo-5H-dibenzo[c,f]chromene-2-carbaldehyde(3af):**

Eluent:(Hexane/EtOAc=90/10): white solid; yield = 47.0 mg (69%); Melting point: 187–189 °C;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  10.27 (s, 1H), 9.10 (s, 1H), 8.73 (d,  $J$  = 8.7 Hz, 1H), 8.63 (d,  $J$  = 8.0 Hz, 1H), 8.07 (d,  $J$  = 7.9 Hz, 1H), 7.96 (d,  $J$  = 8.5 Hz, 2H), 7.73 (t,  $J$  = 7.6 Hz, 1H), 7.59 (t,  $J$  = 7.4 Hz, 1H), 7.48 (d,  $J$  = 8.9 Hz, 1H) ppm.  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  191.5, 160.6, 150.7, 140.1, 136.2, 132.7, 131.81, 131.78, 129.7, 129.4, 128.6, 128.1, 128.0, 126.3, 125.9, 124.7, 117.5, 112.0 ppm. **HRMS** (ESI)  $m/z$ :  $[\text{M}+\text{H}]^+$  Calcd. For  $\text{C}_{18}\text{H}_{11}\text{O}_3$  275.0703 Found 275.0713.



**2-acetyl-5H-dibenzo[c,f]chromen-5-one (3ag):** Eluent:(Hexane/EtOAc=94/6): white solid; yield = 60.0 mg (83%); Melting point: 164–166 °C;  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  9.20 (s, 1H), 8.73 (d,  $J$  = 8.6 Hz, 1H), 8.56 (d,  $J$  = 8.1 Hz, 1H), 8.10 (d,  $J$  = 8.1 Hz, 1H), 7.96 – 7.93 (m, 2H), 7.72 (t,  $J$  = 7.7 Hz, 1H), 7.58 (t,  $J$  = 7.5 Hz, 1H), 7.47 (d,  $J$  = 8.9 Hz, 1H), 2.76 (s, 3H) ppm.  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  197.3, 160.6, 150.7, 141.4, 135.9, 132.4, 131.8, 131.4, 129.63, 129.55, 128.5, 127.3, 126.4, 125.8, 125.3, 124.8, 117.6, 112.3, 27.2 ppm. **HRMS** (ESI)  $m/z$ :  $[\text{M}+\text{H}]^+$  Calcd. For  $\text{C}_{19}\text{H}_{13}\text{O}_3$  289.0859 Found 289.0869.

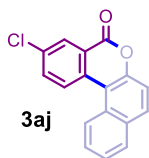


**3-methyl-5H-dibenzo[c,f]chromen-5-one (3ah):** Eluent:(Hexane/EtOAc=94/6): white solid; yield = 49.0 mg (75%); Melting point: 175–177 °C;  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.73 (d,  $J$  = 8.6 Hz, 1H), 8.52 (d,  $J$  = 8.4 Hz, 1H), 8.29 (s, 1H), 7.92 (d,  $J$  = 8.0 Hz, 1H), 7.87 (d,  $J$  = 8.8 Hz, 1H), 7.69 – 7.63 (m, 2H), 7.53 (t,  $J$  = 7.5 Hz, 1H), 7.46 (d,  $J$  = 8.8 Hz, 1H), 2.53 (s, 3H) ppm.  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  161.6, 150.1, 138.7, 135.6, 133.0, 131.8, 131.1, 130.7, 129.7, 129.4, 127.7, 126.5, 125.4, 125.2, 122.4, 117.7, 112.8, 21.3 ppm. **HRMS** (ESI)  $m/z$ :  $[\text{M}+\text{Na}]^+$  Calcd. For  $\text{C}_{18}\text{H}_{12}\text{O}_2\text{Na}$  283.0730 Found 283.0735.

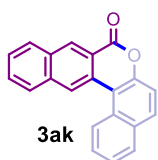


**3-methoxy-5H-dibenzo[c,f]chromen-5-one(3ai):** Eluent:(Hexane/EtOAc=88/12): white solid; yield = 43.0 mg (62%); Melting point: 187–189 °C;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.72 (d,  $J$  = 8.4 Hz, 1H), 8.58 (d,  $J$  = 8.9 Hz, 1H), 7.94 – 7.92 (m, 2H), 7.87 (d,  $J$  = 8.1 Hz, 1H), 7.66 – 7.63 (m, 1H), 7.54 (t,  $J$  = 8.1 Hz, 1H), 7.46 (t,  $J$  = 8.1 Hz, 2H), 3.98 (s, 3H) ppm.  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  161.5, 159.4, 149.3, 131.8, 130.5, 129.4 (2×C), 129.0, 128.2, 127.7, 125.4, 125.2, 123.8, 123.6,

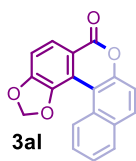
117.6, 112.8, 111.7, 56.0 ppm. **HRMS** (ESI)  $m/z$ :  $[M+H]^+$  Calcd. For  $C_{18}H_{13}O_3$  277.0859 Found 277.0862.



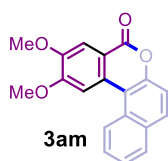
**3-chloro-5H-dibenzo[c,f]chromen-5-one (3aj):** Eluent:(Hexane/EtOAc=92/8): white solid; yield = 44.0 mg (63%); Melting point: 167–169 °C;  **$^1H$  NMR** (400 MHz,  $CDCl_3$ )  $\delta$  8.56 (d,  $J$  = 8.4 Hz, 1H), 8.49 (d,  $J$  = 8.7 Hz, 1H), 8.35 (s, 1H), 7.84 (t,  $J$  = 7.8 Hz, 2H), 7.72 (d,  $J$  = 8.8 Hz, 1H), 7.57 (d,  $J$  = 7.3 Hz, 1H), 7.47 (t,  $J$  = 7.0 Hz, 1H), 7.37 (d,  $J$  = 8.9 Hz, 1H) ppm.  **$^{13}C$  NMR** (101 MHz,  $CDCl_3$ )  $\delta$  160.3, 150.4, 134.7, 134.3, 134.0, 132.1, 131.8, 130.3, 129.6, 129.4, 128.2, 128.0, 125.8, 124.8, 123.8, 117.6, 112.0 ppm. **HRMS** (ESI)  $m/z$ :  $[M+H]^+$  Calcd. For  $C_{17}H_{10}ClO_2$  281.0364 Found 281.0363.



**8H-benzo[f]naphtho[2,3-c]chromen-8-one (3ak):** Eluent:(Hexane/EtOAc=92/8): white solid; yield = 58.0 mg (78%); Melting point: 150–152 °C;  **$^1H$  NMR** (500 MHz,  $CDCl_3$ )  $\delta$  9.03 (s, 1H), 8.98 (s, 1H), 8.89 (d,  $J$  = 8.6 Hz, 1H), 8.03 (t,  $J$  = 8.3 Hz, 2H), 7.93 (d,  $J$  = 8.0 Hz, 1H), 7.88 (d,  $J$  = 8.8 Hz, 1H), 7.69 (t,  $J$  = 7.8 Hz, 2H), 7.61 (t,  $J$  = 7.5 Hz, 1H), 7.55 (t,  $J$  = 7.5 Hz, 1H), 7.45 (d,  $J$  = 8.8 Hz, 1H) ppm.  **$^{13}C$  NMR** (126 MHz,  $CDCl_3$ )  $\delta$  161.7, 149.8, 136.2, 132.8, 132.0, 131.9, 131.3, 130.1, 130.0, 129.6, 129.49, 129.46, 128.5, 128.0, 127.5, 126.0, 125.5, 125.1, 120.6, 117.9, 112.9 ppm. **HRMS** (ESI)  $m/z$ :  $[M+H]^+$  Calcd. For  $C_{21}H_{13}O_2$  297.0910 Found 297.0921.

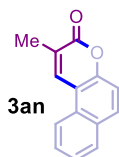


**6H-[1,3]dioxolo[4',5':3,4]benzo[1,2-c]benzo[f]chromen-6-one (3al):** Eluent:(Hexane/EtOAc=83/17): white solid; yield = 62.0 mg (86%); Melting point: 174–176 °C  **$^1H$  NMR** (500 MHz,  $CDCl_3$ )  $\delta$  8.20 (d,  $J$  = 8.6 Hz, 1H), 8.14 (d,  $J$  = 8.3 Hz, 1H), 7.92 (d,  $J$  = 8.8 Hz, 1H), 7.87 (d,  $J$  = 8.0 Hz, 1H), 7.57–7.50 (m, 2H), 7.42 (d,  $J$  = 8.8 Hz, 1H), 7.11 (d,  $J$  = 9.3 Hz, 1H), 6.19 (s, 2H) ppm.  **$^{13}C$  NMR** (126 MHz,  $CDCl_3$ )  $\delta$  161.0, 153.3, 150.4, 142.4, 132.1, 131.4, 128.9, 128.3, 127.6, 127.5, 125.9, 125.4, 118.3, 117.34, 117.25, 110.5, 109.5, 101.7 ppm. **HRMS** (ESI)  $m/z$ :  $[M+H]^+$  Calcd. For  $C_{18}H_{11}O_4$  291.0652 Found 291.0642.

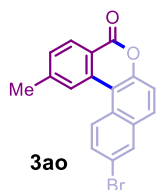


**2,3-dimethoxy-5H-dibenzo[c,f]chromen-5-one (3am):** Eluent:(Hexane/EtOAc=80/20): white solid; yield = 63.0 mg (83%); Melting point: 216–218 °C;  **$^1H$  NMR** (500 MHz,  $CDCl_3$ )  $\delta$  8.73 (d,  $J$  = 8.6 Hz, 1H), 8.04 (s, 1H), 7.94 (d,  $J$  = 8.1 Hz, 1H), 7.85 (d,  $J$  = 12.2 Hz, 2H), 7.67–7.64 (m, 1H), 7.54 (t,  $J$  =

7.5 Hz, 1H), 7.45 (d,  $J$  = 8.9 Hz, 1H), 4.09 (s, 3H), 4.03 (s, 3H) ppm.  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  161.2, 154.6, 150.1, 149.6, 131.8, 130.74, 130.72, 129.6, 129.5, 127.7, 125.3, 124.6, 117.8, 115.9, 112.7, 111.0, 108.2, 56.5, 56.4 ppm. HRMS (ESI)  $m/z$ :  $[\text{M}+\text{Na}]^+$  Calcd. For  $\text{C}_{19}\text{H}_{14}\text{O}_4\text{Na}$  329.0784 Found 329.0790.

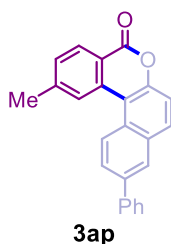


**2-methyl-3H-benzo[f]chromen-3-one (3an):** Eluent: (Hexane/EtOAc=93/7): white solid; yield = 43.0 mg (81%);  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.26 (s, 1H), 8.20 (d,  $J$  = 8.4 Hz, 1H), 7.89 (d,  $J$  = 4.2 Hz, 1H), 7.88 (d,  $J$  = 3.1 Hz, 1H), 7.65 (t,  $J$  = 7.7 Hz, 1H), 7.54 (t,  $J$  = 7.5 Hz, 1H), 7.42 (d,  $J$  = 9.0 Hz, 1H), 2.32 (s, 3H) ppm.  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  162.4, 152.7, 135.2, 131.7, 130.5, 129.1, 128.9, 128.0, 125.9, 125.2, 121.6, 116.9, 113.6, 17.7 ppm. HRMS (ESI)  $m/z$ :  $[\text{M}+\text{H}]^+$  Calcd. For  $\text{C}_{14}\text{H}_{11}\text{O}_2$  211.0754 Found 211.0750.



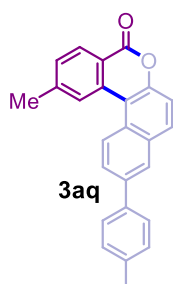
**10-bromo-2-methyl-5H-dibenzo[c,f]chromen-5-one(3ao):**

Eluent: (Hexane/EtOAc=93/7): white solid; yield = 61.0 mg (72%);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.57 (d,  $J$  = 9.1 Hz, 1H), 8.35 (d,  $J$  = 8.0 Hz, 1H), 8.27 (s, 1H), 8.05 (s, 1H), 7.77 (d,  $J$  = 8.9 Hz, 1H), 7.70 (d,  $J$  = 9.1 Hz, 1H), 7.45 (d,  $J$  = 8.9 Hz, 2H), 2.60 (s, 3H) ppm.  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  161.2, 150.5, 145.7, 135.0, 132.9, 131.3, 131.0, 130.9, 130.3, 129.9, 128.2, 126.9, 126.5, 120.1, 119.2, 119.0, 113.0, 22.7 ppm. HRMS (ESI)  $m/z$ :  $[\text{M}+\text{H}]^+$  Calcd. For  $\text{C}_{18}\text{H}_{12}\text{BrO}_2$  339.0015 Found 339.0016.



**2-methyl-10-phenyl-5H-dibenzo[c,f]chromen-5-one(3ap):**

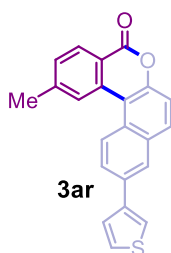
Eluent: (Hexane/EtOAc=94/6): white solid; yield = 72.0 mg (86%); Melting point: 192–194 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.69 (d,  $J$  = 8.9 Hz, 1H), 8.33 (s, 1H), 8.28 (d,  $J$  = 8.0 Hz, 1H), 8.00 (s, 1H), 7.82 (dd,  $J$  = 9.0, 5.2 Hz, 2H), 7.65 (d,  $J$  = 7.6 Hz, 2H), 7.44 – 7.40 (m, 2H), 7.38 – 7.32 (m, 3H), 2.52 (s, 3H) ppm.  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  161.4, 150.5, 145.6, 140.2, 138.0, 135.5, 132.1, 131.7, 130.9, 129.6, 129.1, 128.8, 127.8, 127.3, 127.2, 127.0, 126.7, 125.7, 120.0, 118.2, 112.7, 22.7 ppm. HRMS (ESI)  $m/z$ :  $[\text{M}+\text{H}]^+$  Calcd. For  $\text{C}_{24}\text{H}_{17}\text{O}_2$  337.1223 Found 337.0311.



**2-methyl-10-(p-tolyl)-5H-dibenzo[c,f]chromen-5-one(3aq):**

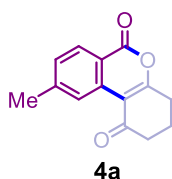
Eluent: (Hexane/EtOAc=93/7): white solid; yield = 80.0 mg (91%); Melting point: 202–204 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.77 (d,  $J$  = 8.9 Hz, 1H), 8.42 (s, 1H), 8.37 (d,  $J$  = 8.1 Hz, 1H), 8.08 (d,  $J$  = 2.1 Hz, 1H), 7.90 (dd,  $J$  = 9.1, 5.4 Hz, 2H),

7.65 (d,  $J = 7.7$  Hz, 2H), 7.44 (t,  $J = 8.5$  Hz, 2H), 7.32 (d,  $J = 7.7$  Hz, 2H), 2.61 (s, 3H), 2.44 (s, 3H) ppm.  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  161.5, 150.5, 145.5, 137.9, 137.7, 137.2, 135.5, 132.1, 131.7, 130.9, 129.9, 129.6, 128.6, 127.15, 127.11, 126.68, 126.65, 125.7, 120.0, 118.1, 112.7, 22.7, 21.3 ppm. HRMS (ESI)  $m/z$ :  $[\text{M}+\text{H}]^+$  Calcd. For  $\text{C}_{25}\text{H}_{19}\text{O}_2$  351.1380 Found 351.0441.



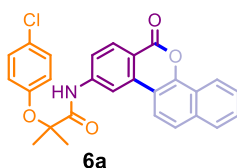
**2-methyl-10-(thiophen-3-yl)-5H-dibenzo[c,f]chromen-5-one(3ar):**

Eluent:(Hexane/EtOAc=90/10): white solid; yield = 74.0 mg (87%); Melting point: 210–212 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.76 (d,  $J = 9.0$  Hz, 1H), 8.42 (s, 1H), 8.38 (d,  $J = 8.1$  Hz, 1H), 8.10 (d,  $J = 2.0$  Hz, 1H), 7.90 (dd,  $J = 9.1, 4.5$  Hz, 2H), 7.62 (d,  $J = 3.1$  Hz, 1H), 7.55 (d,  $J = 5.0$  Hz, 1H), 7.48 – 7.43 (m, 3H), 2.62 (s, 3H) ppm.  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  161.5, 150.5, 145.6, 141.4, 135.5, 132.8, 132.1, 131.6, 130.9, 129.6, 128.7, 126.8, 126.7 (2 $\times$ C), 126.3, 126.1, 125.8, 121.1, 120.1, 118.3, 112.8, 22.7 ppm. HRMS (ESI)  $m/z$ :  $[\text{M}+\text{H}]^+$  Calcd. For  $\text{C}_{22}\text{H}_{15}\text{O}_2\text{S}$  343.0787 Found 343.9893.



**9-methyl-3,4-dihydro-1H-benzo[c]chromene-1,6(2H)-dione(4a):**

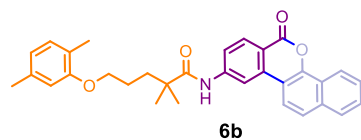
Eluent:(Hexane/EtOAc=88/12): white solid; yield = 37.0 mg (65%);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.83 (s, 1H), 8.14 (d,  $J = 8.1$  Hz, 1H), 7.32 (d,  $J = 8.2$  Hz, 1H), 2.91 (t,  $J = 6.3$  Hz, 2H), 2.65 – 2.62 (m, 2H), 2.49 (s, 3H), 2.16 (q,  $J = 6.5$  Hz, 2H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  197.2, 169.7, 160.6, 147.1, 134.1, 129.8, 129.7, 126.2, 117.5, 111.7, 39.1, 29.1, 22.6, 20.1 ppm.



**2-(4-chlorophenoxy)-2-methyl-N-(6-oxo-6H-dibenzo[c,h]chromen-9-yl)propanamide (6a):**

Eluent:(Hexane/EtOAc=80/20): white solid; yield = 88.0 mg (77%); Melting point: 186–188 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  9.04 (s, 1H), 8.78 (s, 1H), 8.50 (d,  $J = 6.9$  Hz, 1H), 8.36 (d,  $J = 8.4$  Hz, 1H), 8.02 (d,  $J = 8.6$  Hz, 1H), 7.82 (d,  $J = 6.8$  Hz, 1H), 7.69 (d,  $J = 8.5$  Hz, 1H), 7.57 (d,  $J = 6.4$  Hz, 3H), 7.27 (d,  $J = 7.3$  Hz, 2H), 6.96 (d,  $J = 8.3$  Hz, 2H), 1.62 (s, 6H) ppm.  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  173.6, 160.9, 152.1, 147.7, 143.6, 137.1, 134.5, 132.0, 129.8, 129.7, 128.1, 127.7, 127.1, 124.5, 123.9, 123.7, 122.4, 119.9, 119.5, 117.0, 113.0, 111.6, 82.7, 24.9 ppm. HRMS (ESI)  $m/z$ :  $[\text{M}+\text{H}]^+$  Calcd. For  $\text{C}_{27}\text{H}_{21}\text{ClNO}_4$  458.1154 Found 458.1153.

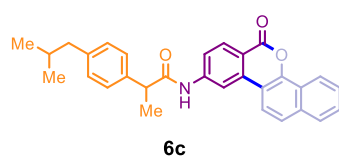
**5-(2,5-dimethylphenoxy)-2,2-dimethyl-N-(6-oxo-6H-dibenzo[c,h]chromen-9-yl)pentanamide (6b):** Eluent:(Hexane/EtOAc=78/22): sticky liquid; yield = 112.0



mg (91%);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  9.16 (s, 1H), 8.86 (d,  $J = 8.6$  Hz, 1H), 8.35 (d,  $J = 8.3$  Hz, 1H), 7.98 (s, 1H), 7.88 – 7.84 (m, 2H), 7.71 – 7.67 (m, 1H), 7.52 – 7.48 (m, 2H), 7.39 (d,  $J = 8.6$  Hz, 1H), 6.93 (d,  $J = 6.9$  Hz, 1H), 6.61 – 6.57 (m, 2H), 3.95 (s, 2H), 2.23 (s, 3H), 2.14 (s, 3H), 1.90 – 1.86 (m, 4H), 1.43 (s, 6H) ppm;  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  176.6, 161.2, 156.8, 150.6, 143.7, 136.69, 136.65, 131.9, 131.8, 131.6, 130.4, 129.6, 129.3, 128.2, 125.5, 125.0, 123.5, 121.0, 119.5, 117.6, 117.5, 116.6, 112.5, 112.3, 67.8, 43.5, 37.6, 25.7, 25.3, 21.4, 16.0 ppm. **HRMS** (ESI)  $m/z$ :  $[\text{M}+\text{H}]^+$  Calcd. For  $\text{C}_{32}\text{H}_{32}\text{NO}_4$  494.2326 Found 494.2322.

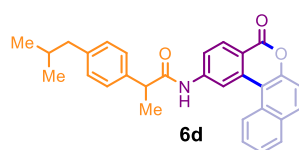
### 2-(4-isobutylphenyl)-N-(6-oxo-6H-dibenzo[c,h]chromen-9-yl)propenamide

**(6c):** Eluent:(Hexane/EtOAc=82/18): sticky liquid; yield = 97.0 mg (86%);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.75 (s, 1H), 8.52 – 8.49 (m, 1H), 8.29 (d,  $J = 8.6$  Hz, 1H), 8.00 (d,  $J = 8.8$  Hz, 1H), 7.84 – 7.82 (m, 1H), 7.69 (d,  $J = 8.8$  Hz, 1H), 7.65 (s, 1H), 7.58 – 7.56 (m, 2H), 7.31 (d,  $J = 7.8$  Hz, 2H), 7.25 (s, 1H), 7.18 (d,  $J = 7.8$  Hz, 2H), 3.82 (q,  $J = 7.0$  Hz, 2H), 2.48 (d,  $J = 7.1$  Hz, 2H), 1.90 – 1.83 (m, 1H) 1.65 (d,  $J = 7.0$  Hz, 3H), 0.91 (d,  $J = 6.6$  Hz, 6H) ppm.  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  173.5, 161.1, 147.7, 144.3, 141.7, 137.6, 137.1, 134.5, 131.8, 130.2, 128.1, 127.8, 127.6, 127.1, 124.5, 123.9, 122.4, 119.6, 119.5, 116.6, 113.1, 111.4, 48.2, 45.1, 30.3, 22.5, 18.6 ppm. **HRMS** (ESI)  $m/z$ :  $[\text{M}+\text{H}]^+$  Calcd. For  $\text{C}_{30}\text{H}_{28}\text{NO}_3$  450.2064 Found 450.2067.



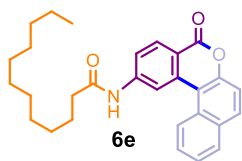
### 2-(4-isobutylphenyl)-N-(6-oxo-6H-dibenzo[c,h]chromen-9-yl)propenamide(6d):

**(6d):** Eluent:(Hexane/EtOAc=82/18): sticky liquid; yield = 95.0 mg (85%);  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  9.03 (s, 1H), 8.68 – 8.66 (m, 1H), 8.33 (brs, 1H), 8.22 (d,  $J = 8.6$  Hz, 1H), 7.76 (d,  $J = 8.2$  Hz, 2H), 7.43 – 7.37 (m, 2H), 7.35 (d,  $J = 8.0$  Hz, 3H), 7.30 – 7.28 (m, 1H), 7.14 (d,  $J = 7.9$  Hz, 2H), 3.90 (q,  $J = 6.9$  Hz, 1H), 2.42 (d,  $J = 7.1$  Hz, 2H), 1.84 – 1.79 (m, 1H), 1.67 (d,  $J = 7.1$  Hz, 3H), 0.87 (d,  $J = 6.6$  Hz, 6H) ppm.  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  173.7, 161.2, 150.5, 143.9, 141.4, 137.9, 136.5, 131.8, 131.7, 131.5, 130.0, 129.4, 129.2, 128.0, 127.5(2×C), 125.4, 124.8, 119.1, 117.3, 116.0, 112.3, 48.0, 45.1, 30.2, 22.4, 18.8 ppm. **HRMS**(ESI)  $m/z$ :  $[\text{M}+\text{H}]^+$  Calcd. For  $\text{C}_{30}\text{H}_{28}\text{NO}_3$  450.2064 Found 450.2069.

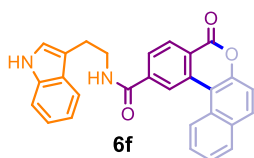


### N-(5-oxo-5H-dibenzo[c,f]chromen-2-yl)dodecanamide(6e):

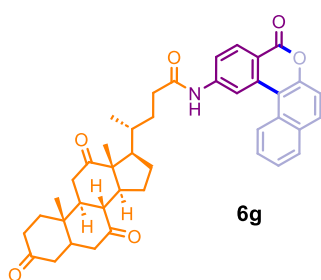
Eluent:(Hexane/EtOAc=75/25): grey solid; yield = 100.0 mg (90%); Melting point: 157–159 °C;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  9.09 (s, 1H), 8.75 (d,  $J = 8.6$  Hz, 1H),



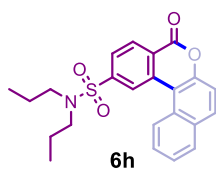
8.56 (s, 1H), 8.28 (d,  $J = 8.5$  Hz, 1H), 7.79 (d,  $J = 8.5$  Hz, 2H), 7.57 (t,  $J = 9.5$  Hz, 2H), 7.40 (t,  $J = 7.4$  Hz, 1H), 7.32 (d,  $J = 8.8$  Hz, 1H), 2.52 (t,  $J = 7.5$  Hz, 2H), 1.83 – 1.76 (m, 2H), 1.43 – 1.36 (m, 2H), 1.29–1.21 (m, 14H), 0.84 (t,  $J = 6.5$  Hz, 3H) ppm.  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  172.8, 161.3, 150.5, 144.0, 136.6, 131.9, 131.8, 131.5, 129.4, 129.3, 127.9, 125.4, 124.9, 119.2, 117.4, 117.1, 116.1, 112.4, 38.2, 32.0, 29.74, 29.71, 29.6, 29.52, 29.48, 29.4, 25.7, 22.8, 14.2 ppm. HRMS (ESI)  $m/z$ :  $[\text{M}+\text{H}]^+$  Calcd. For  $\text{C}_{29}\text{H}_{34}\text{NO}_3$  444.2533 Found 444.2536.



**N-(2-(1H-indol-3-yl)ethyl)-5-oxo-5H-dibenzo[c,f]chromene-2-carboxamide (6f):** Eluent:(Hexane/EtOAc=70/30): white solid; yield = 95.0 mg (88%); Melting point: 192–194 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO}-d_6$ )  $\delta$  10.86 (s, 1H), 9.07 (s, 2H), 8.79 (d,  $J = 8.6$  Hz, 1H), 8.43 (d,  $J = 8.2$  Hz, 1H), 8.16 (d,  $J = 8.9$  Hz, 1H), 8.12 (d,  $J = 8.0$  Hz, 2H), 7.78 (t,  $J = 7.6$  Hz, 1H), 7.67 – 7.58 (m, 3H), 7.36 (d,  $J = 8.0$  Hz, 1H), 7.25 (s, 1H), 7.07 (t,  $J = 7.5$  Hz, 1H), 6.98 (t,  $J = 7.4$  Hz, 1H), 3.64 (t,  $J = 9.8$  Hz, 2H), 3.04 (t,  $J = 7.2$  Hz, 2H) ppm.  $^{13}\text{C}$  NMR (101 MHz,  $\text{DMSO}-d_6$ )  $\delta$  165.3, 159.9, 150.1, 140.2, 136.3, 134.6, 132.2, 131.3, 130.2, 129.4, 128.8, 128.5, 127.3, 126.8, 125.7, 125.4, 124.8, 123.4, 122.8, 121.0, 118.3(2×C), 117.3, 111.8, 111.7, 111.4, 40.6, 25.0 ppm. HRMS (ESI)  $m/z$ :  $[\text{M}+\text{H}]^+$  Calcd. For  $\text{C}_{28}\text{H}_{21}\text{N}_2\text{O}_3$  433.1547 Found 433.1531.

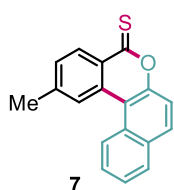


**(4R)-4-((8R,9S,10S,13R,14S,17R)-10,13-dimethyl-3,7,12-trioxohexadecahydro-1H-cyclopenta[a]phenanthren-17-yl)-N-(5-oxo-5H-dibenzo[c,f]chromen-2-yl)pentanamide (6g):** Eluent:(Hexane/EtOAc=45/55): white solid; yield = 118.0 mg (73%); Melting point: 223 – 225 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO}-d_6$ )  $\delta$  10.57 (s, 1H), 9.10 – 9.09 (m, 1H), 8.85 (d,  $J = 8.7$  Hz, 1H), 8.29 (d,  $J = 8.7$  Hz, 1H), 8.11 (t,  $J = 8.6$  Hz, 2H), 7.90 (dd,  $J = 8.7, 1.7$  Hz, 1H), 7.76 (t,  $J = 7.7$  Hz, 1H), 7.63 (t,  $J = 7.4$  Hz, 1H), 7.55 (d,  $J = 8.9$  Hz, 1H), 3.06 – 2.95 (m, 2H), 2.82 (t,  $J = 12.7$  Hz, 1H), 2.46 – 2.16 (m, 7H), 1.99 – 1.90 (m, 6H), 1.85 – 1.67 (m, 4H), 1.46 – 1.26 (m, 7H), 1.01 (s, 3H), 0.86 (d,  $J = 6.4$  Hz, 3H) ppm.  $^{13}\text{C}$  NMR (101 MHz,  $\text{DMSO}-d_6$ )  $\delta$  211.9, 209.53, 209.47, 172.8, 159.8, 150.2, 145.1, 135.5, 132.0, 131.4, 131.2, 129.4, 128.9, 128.1, 125.4, 124.6, 119.0, 117.4, 115.9, 115.0, 111.7, 56.2, 51.2, 47.9, 46.0, 45.3, 44.5, 44.0, 42.5, 38.3, 36.1, 35.6, 35.1, 34.5, 33.9, 30.6, 27.3, 24.6, 21.1, 18.9, 11.4 ppm. HRMS (ESI)  $m/z$ :  $[\text{M}+\text{Na}]^+$  Calcd. For  $\text{C}_{41}\text{H}_{43}\text{NO}_6\text{Na}$  668.2983 Found 668.2988.



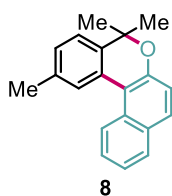
**5-oxo-N,N-dipropyl-5H-dibenzo[c,f]chromene-2-sulfonamide(6h):**

Eluent:(Hexane/EtOAc=70/30): white solid; yield = 70.0 mg (68%); Melting point: 178–180 °C;  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  9.08 (s, 1H), 8.68 (d,  $J$  = 8.6 Hz, 1H), 8.59 (d,  $J$  = 8.2 Hz, 1H), 7.98 – 7.95 (m, 3H), 7.72 (t,  $J$  = 7.7 Hz, 1H), 7.58 (t,  $J$  = 7.5 Hz, 1H), 7.48 (d,  $J$  = 8.9 Hz, 1H), 3.21 – 3.18 (m, 4H), 1.68 – 1.57 (m, 4H), 0.89 (t,  $J$  = 7.4 Hz, 6H) ppm.  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  160.2, 151.0, 146.1, 136.2, 132.9, 131.9, 131.8, 129.7, 129.4, 128.8, 126.0, 125.7, 125.2, 124.8, 124.4, 117.5, 111.8, 50.3, 22.2, 11.3 ppm. **HRMS** (ESI)  $m/z$ :  $[\text{M}+\text{H}]^+$  Calcd. For  $\text{C}_{23}\text{H}_{24}\text{NO}_4\text{S}$  410.1421 Found 410.1417.



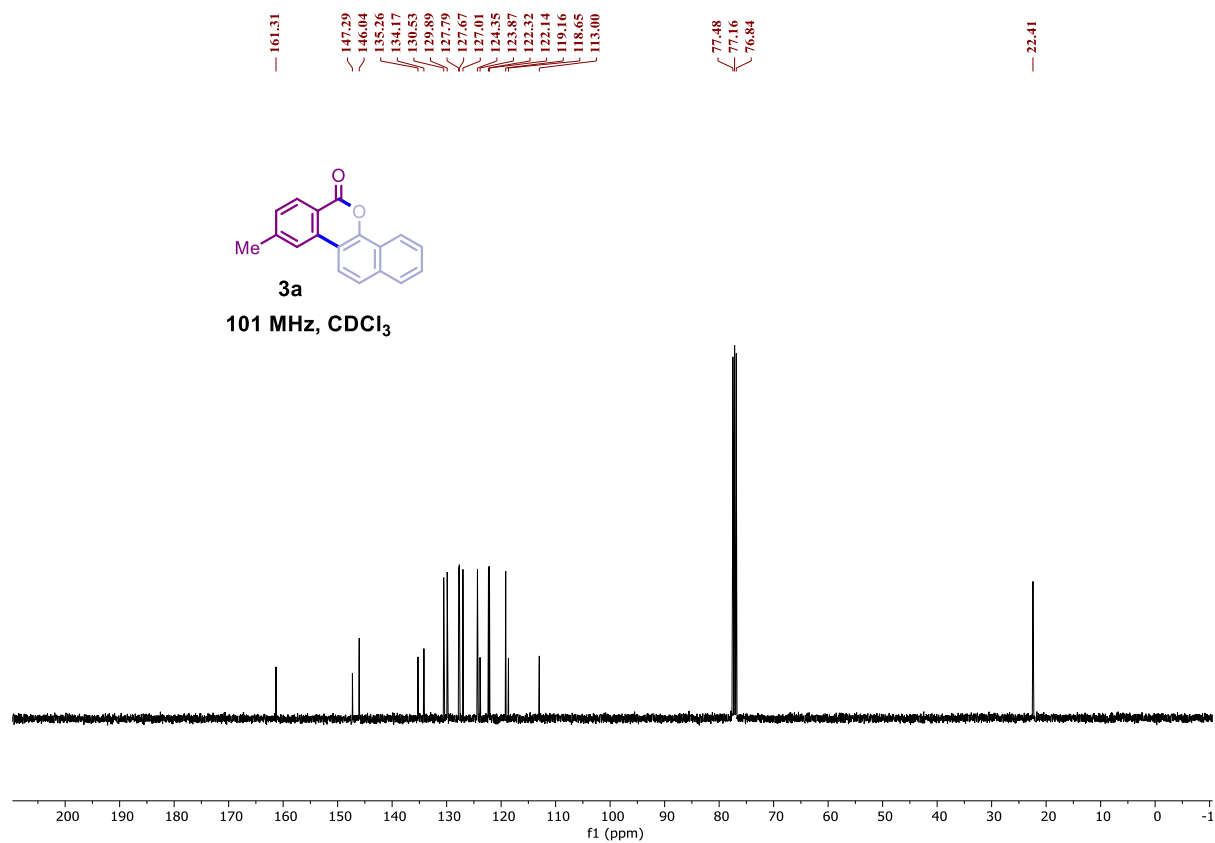
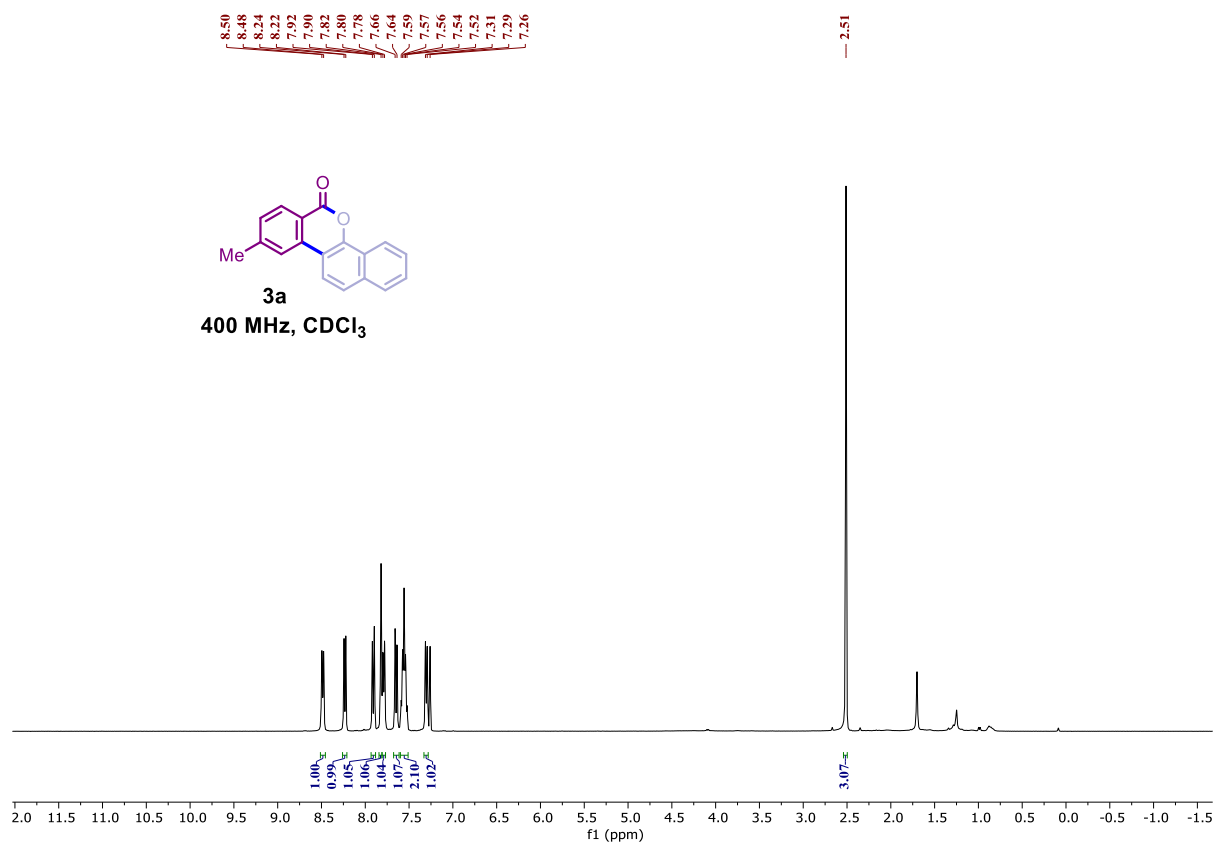
**2-methyl-5H-dibenzo[c,f]chromene-5-thione(7):**

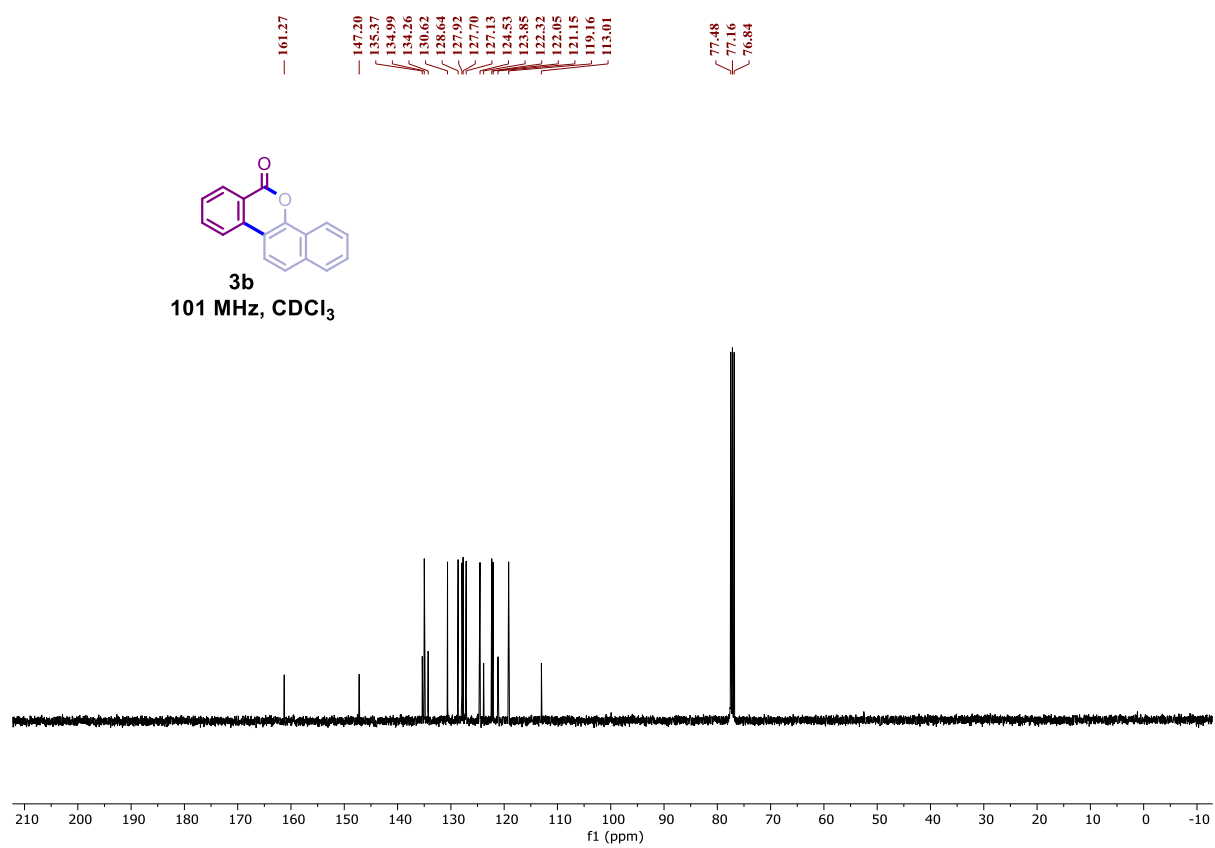
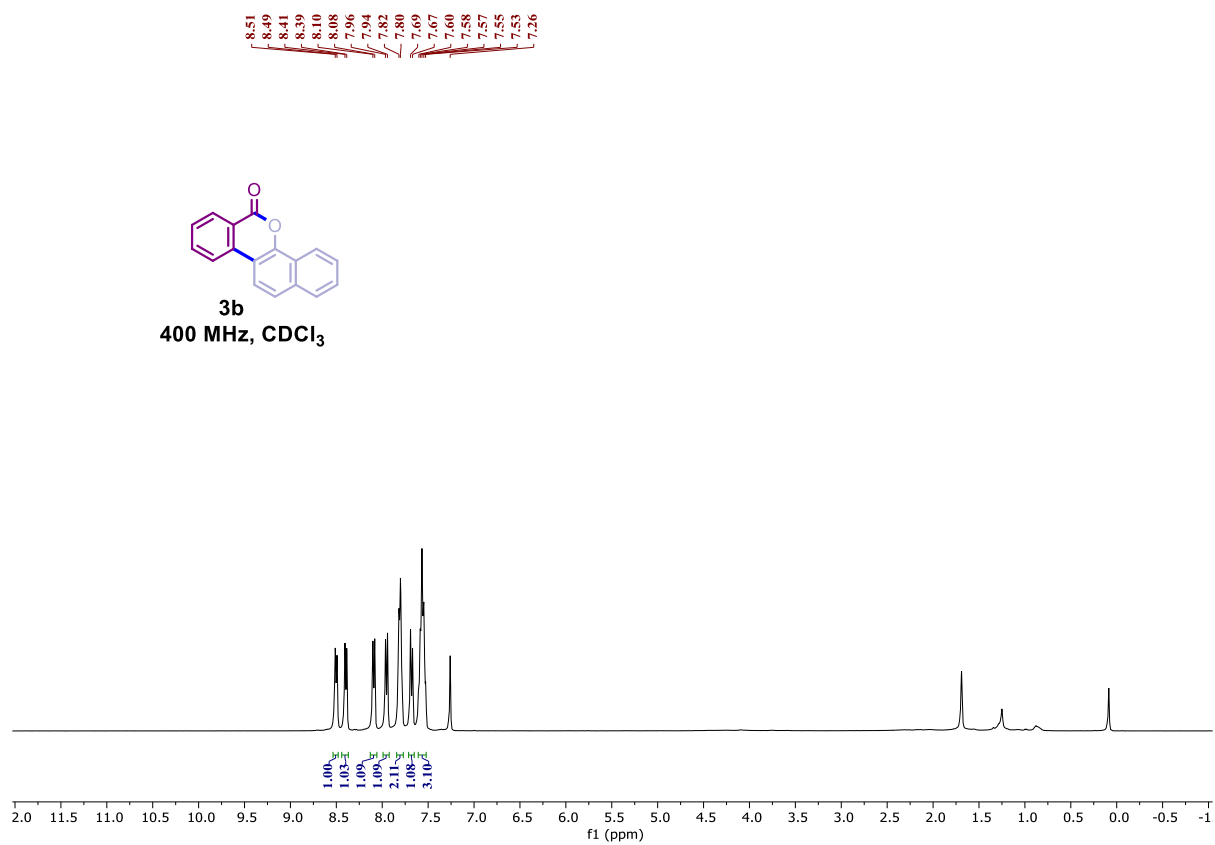
Eluent:(Hexane/EtOAc=95/05): yellow solid; yield = 64.0 mg (92%); Melting point: 180–182 °C;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.77 (d,  $J$  = 8.3 Hz, 1H), 8.66 (d,  $J$  = 8.5 Hz, 1H), 8.28 (s, 1H), 7.90 – 7.85 (m, 2H), 7.64 (t,  $J$  = 7.5 Hz, 1H), 7.53 (t,  $J$  = 8.8 Hz, 2H), 7.35 (d,  $J$  = 8.2 Hz, 1H), 2.54 (s, 3H) ppm.  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  199.4, 152.2, 146.0, 134.2, 131.9, 131.6, 130.1, 129.8, 129.4, 129.26, 129.25, 127.9, 126.2, 125.8, 125.5, 117.1, 113.8, 22.6 ppm. **HRMS** (ESI)  $m/z$ :  $[\text{M}+\text{H}]^+$  Calcd. For  $\text{C}_{18}\text{H}_{13}\text{OS}$  277.0682 Found 277.0595.

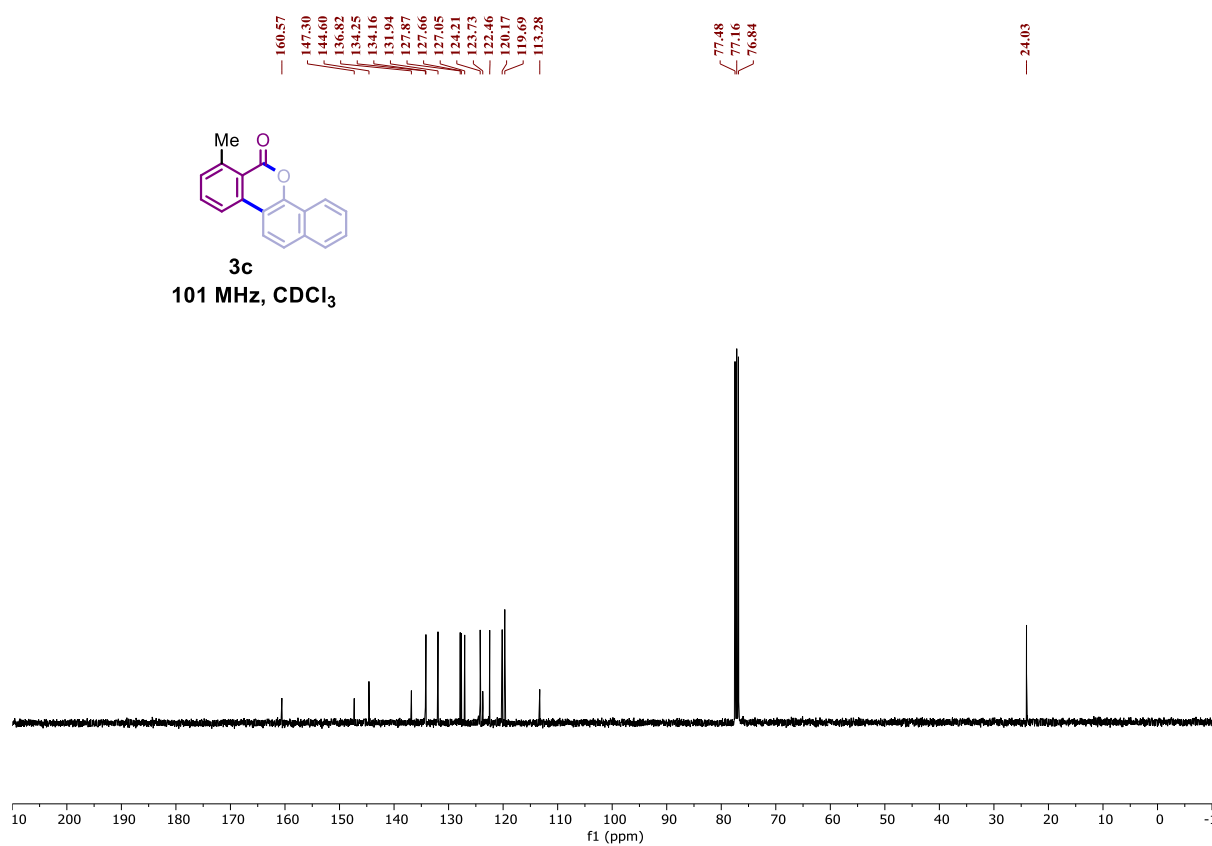
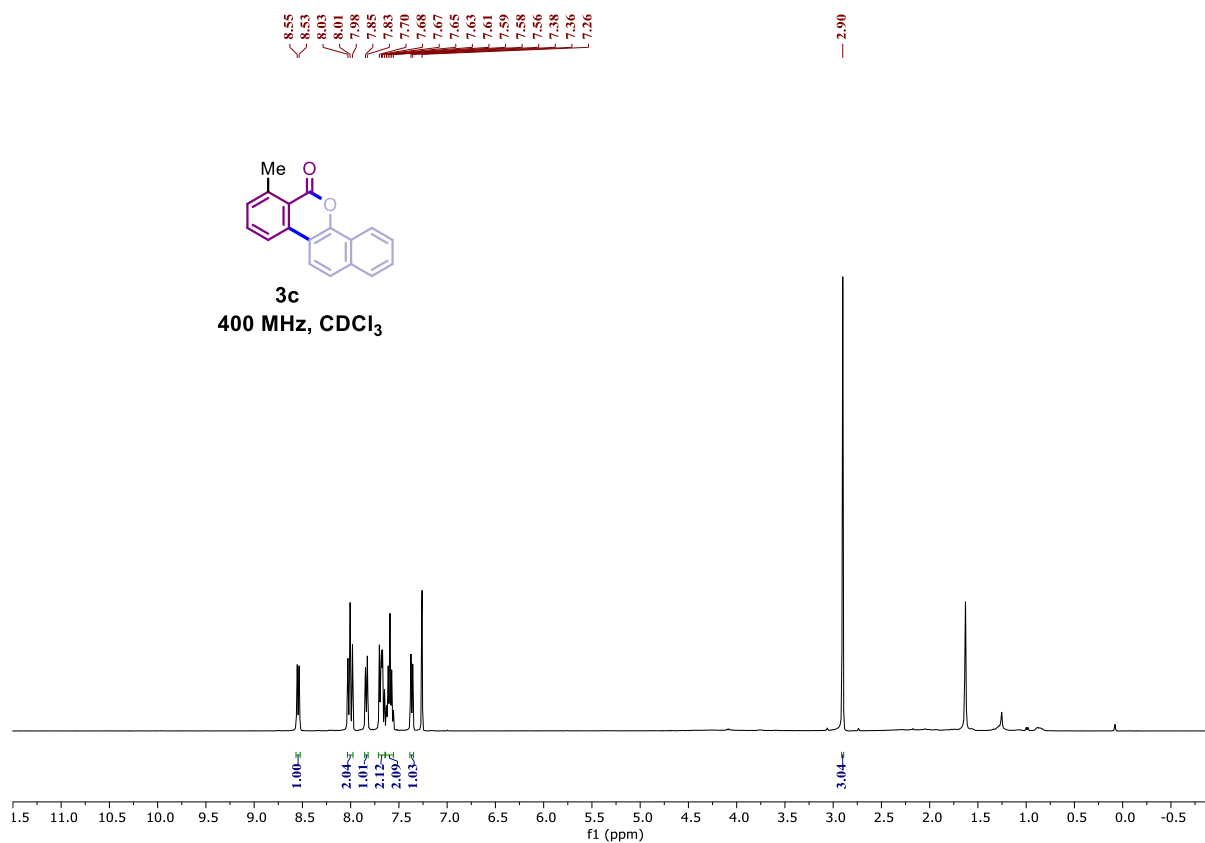


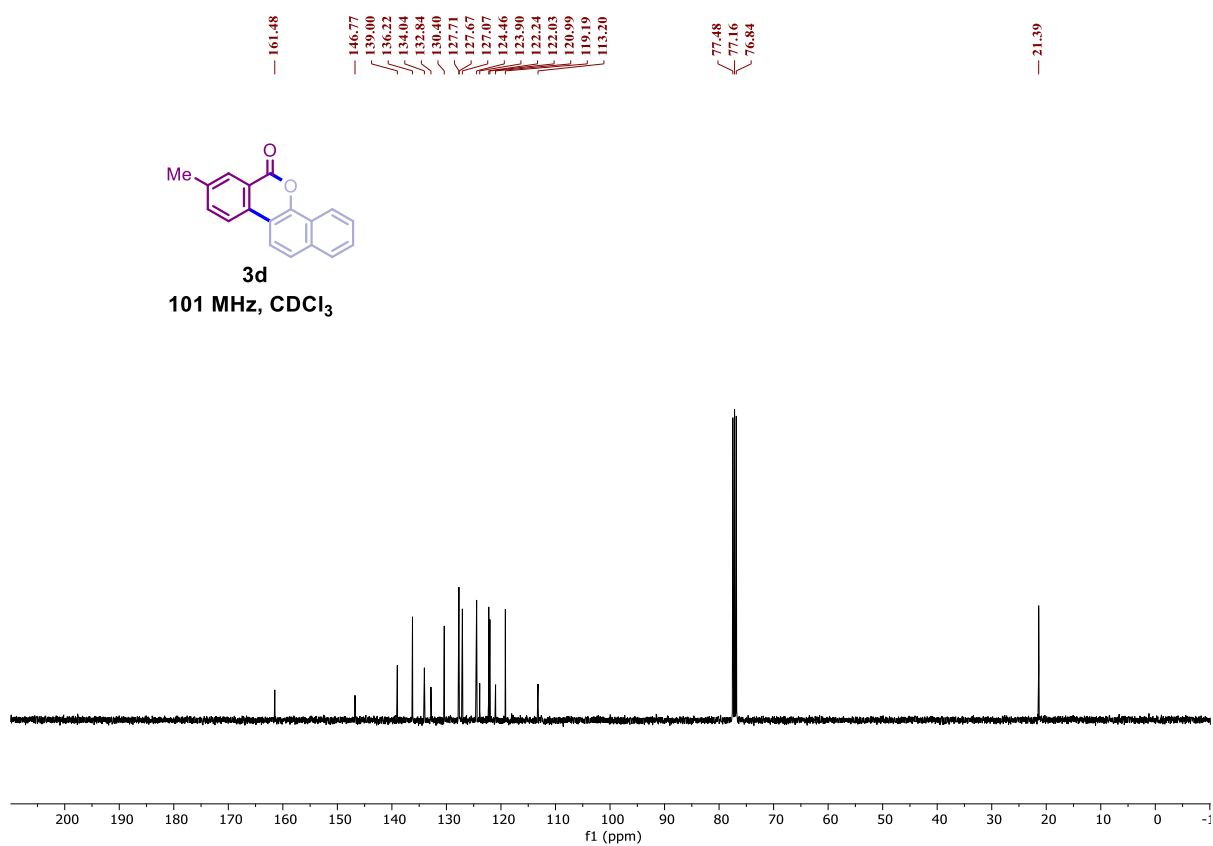
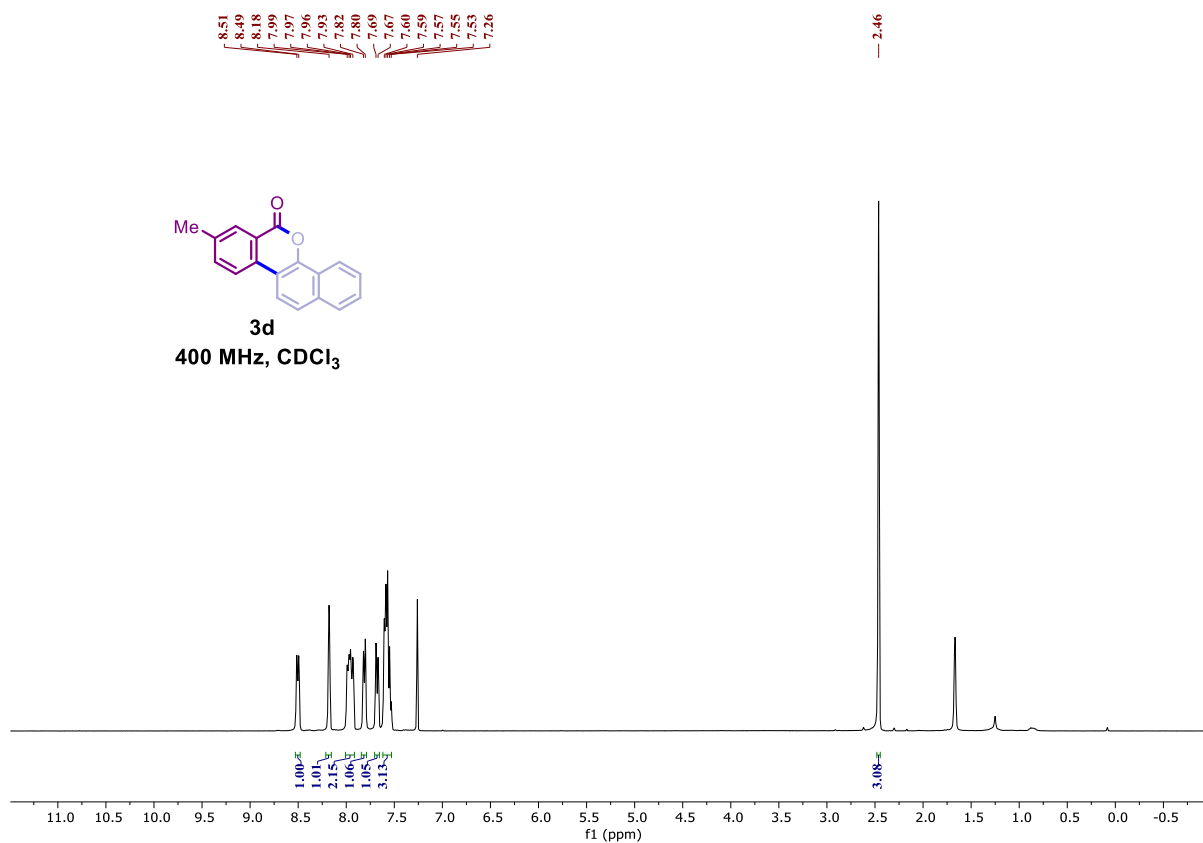
**2,5,5-trimethyl-5H-dibenzo[c,f]chromene (8):** Eluent:(Hexane/EtOAc=85/15): sticky liquid; yield = 62.0 mg (90%);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.72 – 7.69 (m, 2H), 7.54 (d,  $J$  = 8.2 Hz, 1H), 7.24 – 7.21 (m, 2H), 7.19 – 7.16 (m, 1H), 7.14 (d,  $J$  = 8.9 Hz, 1H), 7.05 – 7.03 (m, 1H), 6.82 (s, 1H), 2.24 (s, 3H), 1.40 (s, 3H), 1.19 (s, 3H) ppm.  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  150.4, 145.2, 137.7, 134.7, 134.2, 131.9, 129.54, 129.49, 129.1, 128.0, 126.8, 126.4, 125.7, 123.7, 123.4, 118.4, 73.7, 31.7, 31.1, 20.8 ppm. **HRMS** (ESI)  $m/z$ :  $[\text{M}]^+$  Calcd. For  $\text{C}_{20}\text{H}_{18}\text{O}$  274.1358 Found 274.1245.

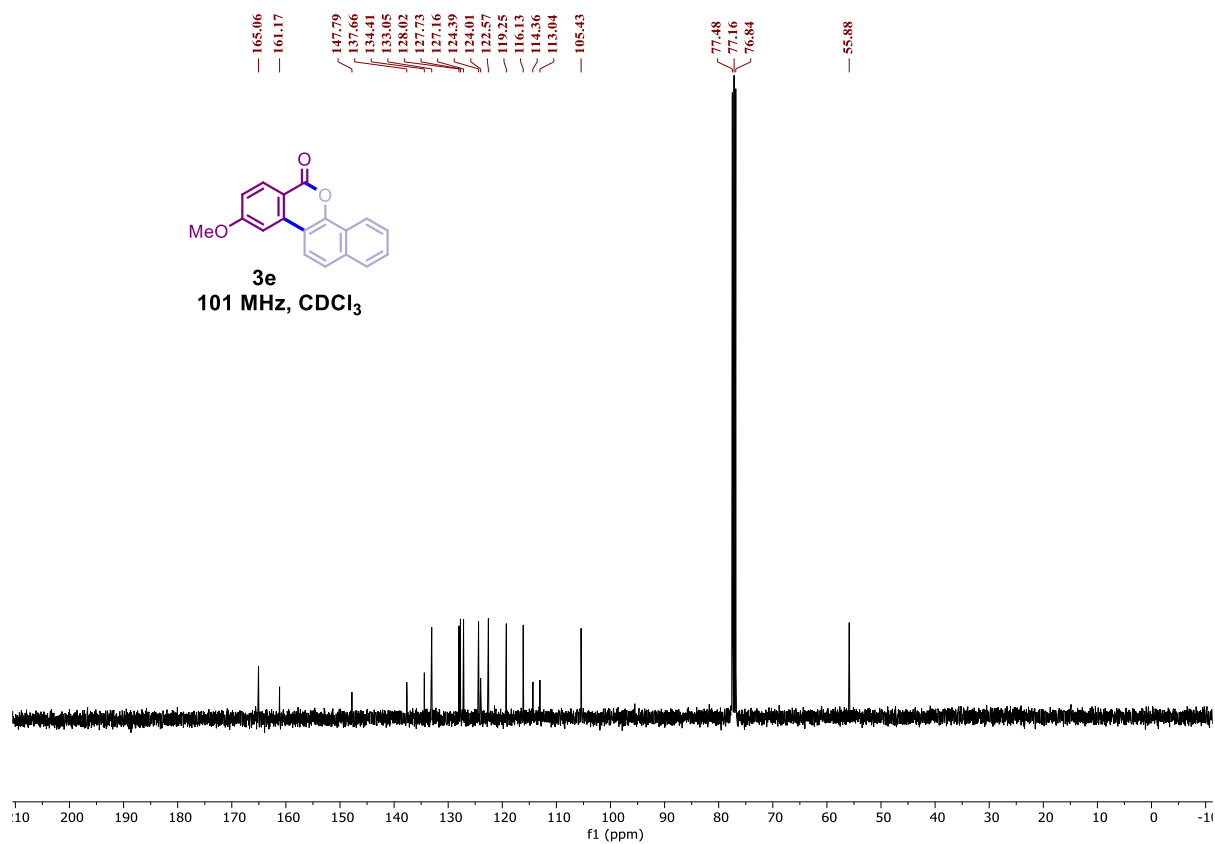
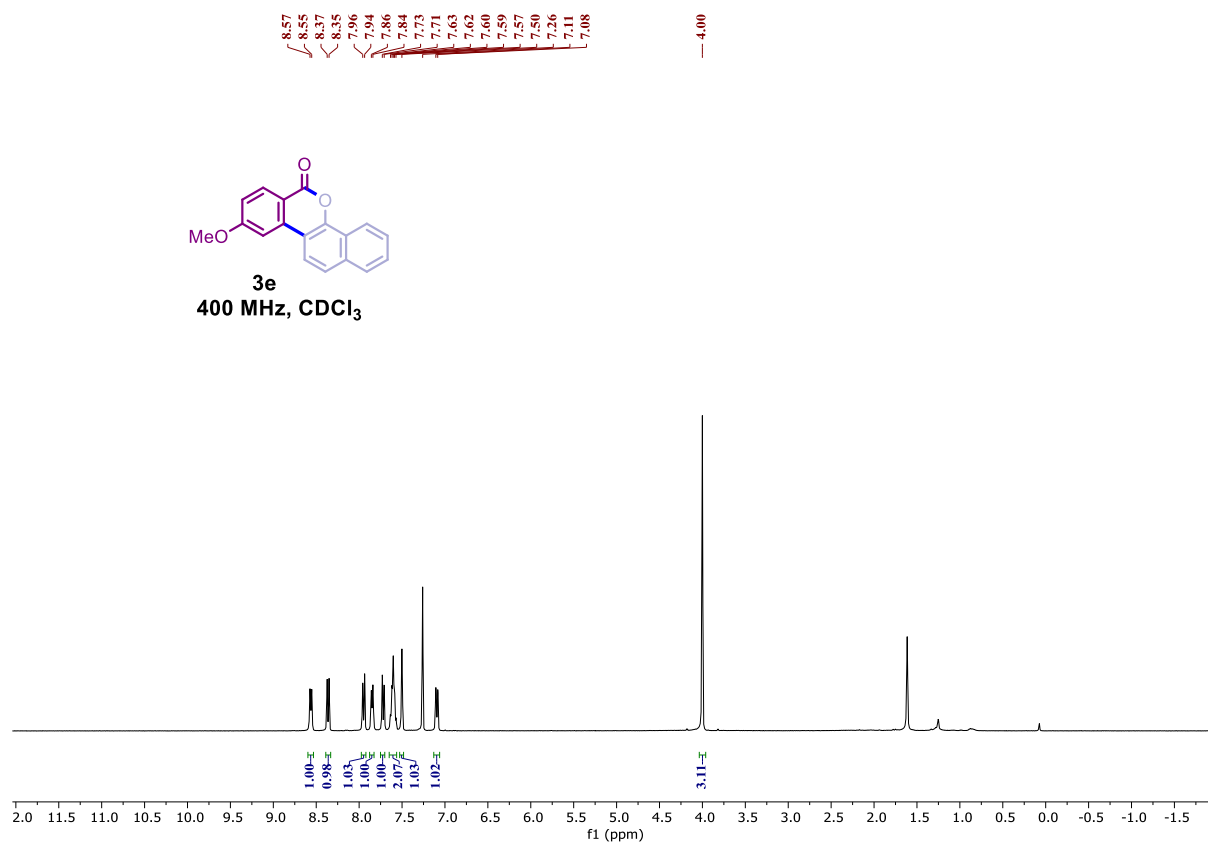
## NMR Spectra of Synthesized Compounds:

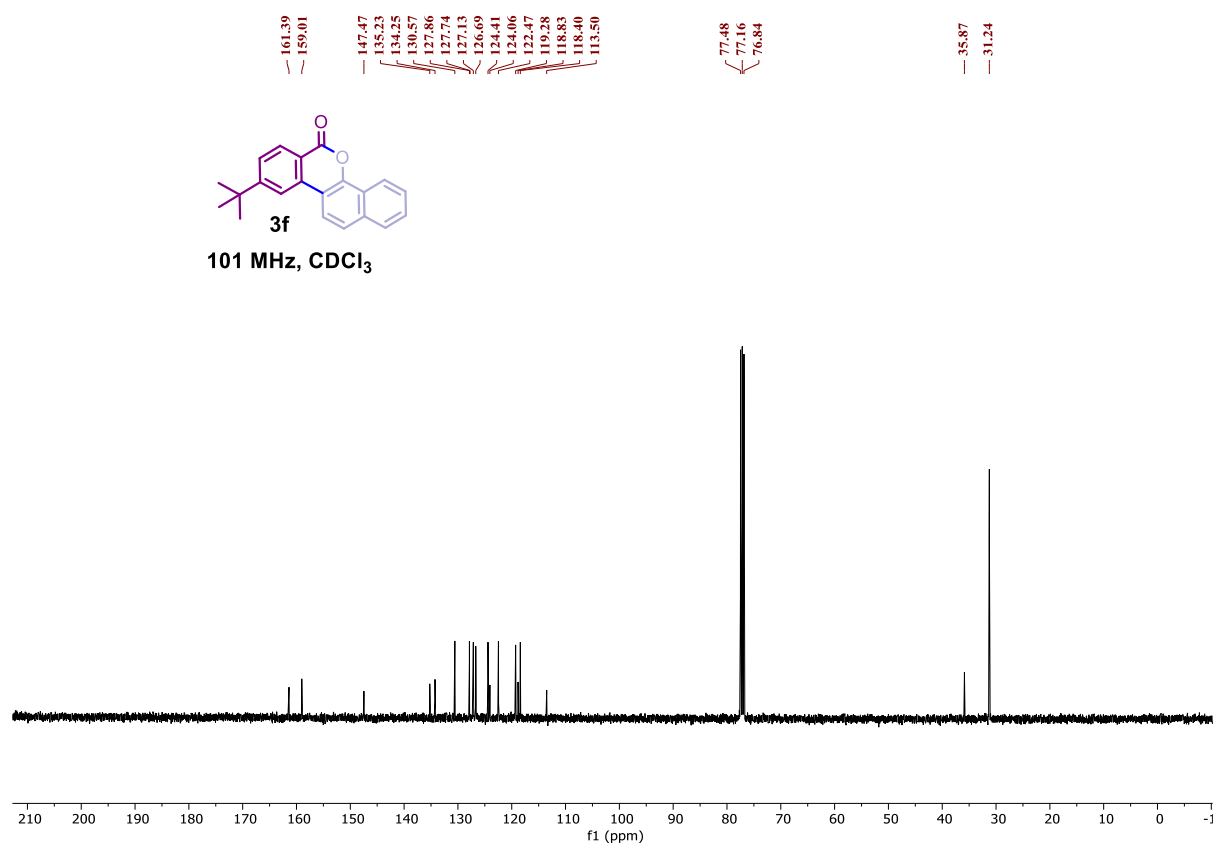
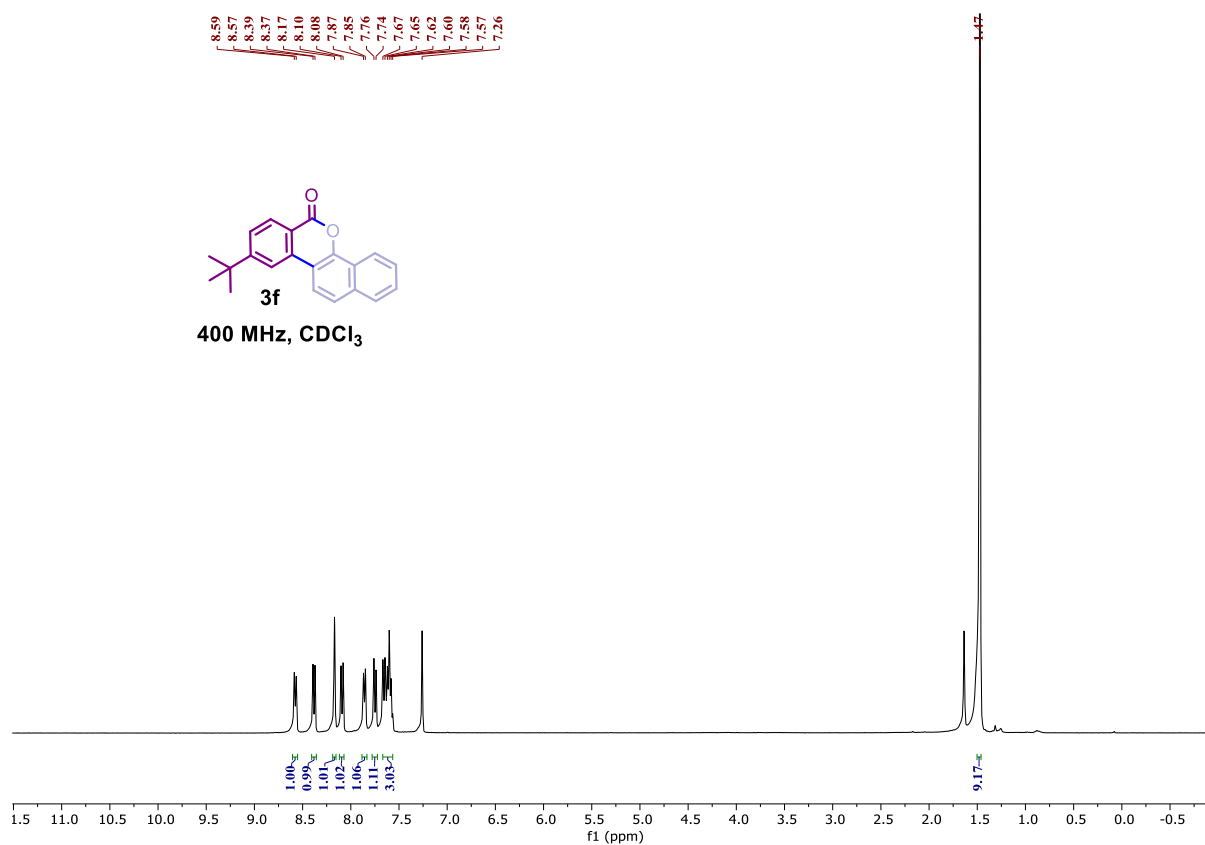


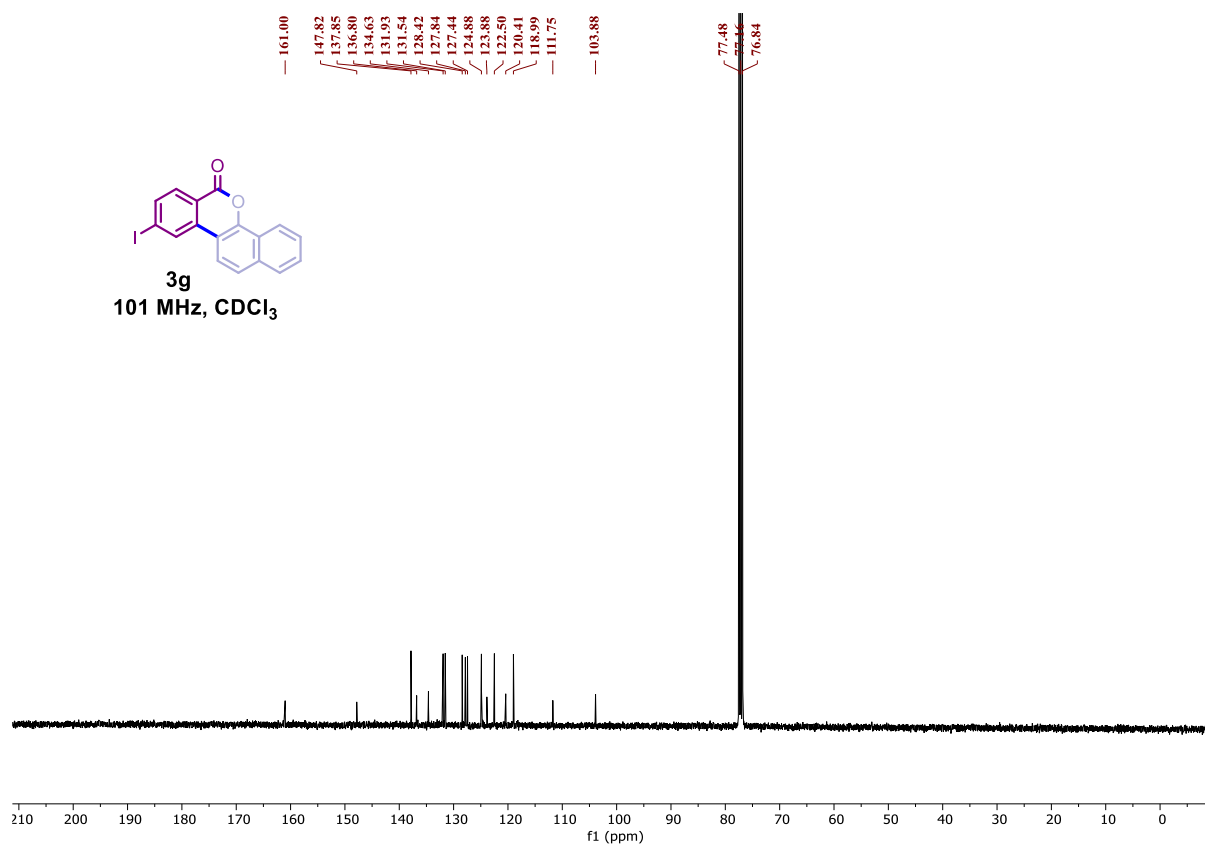
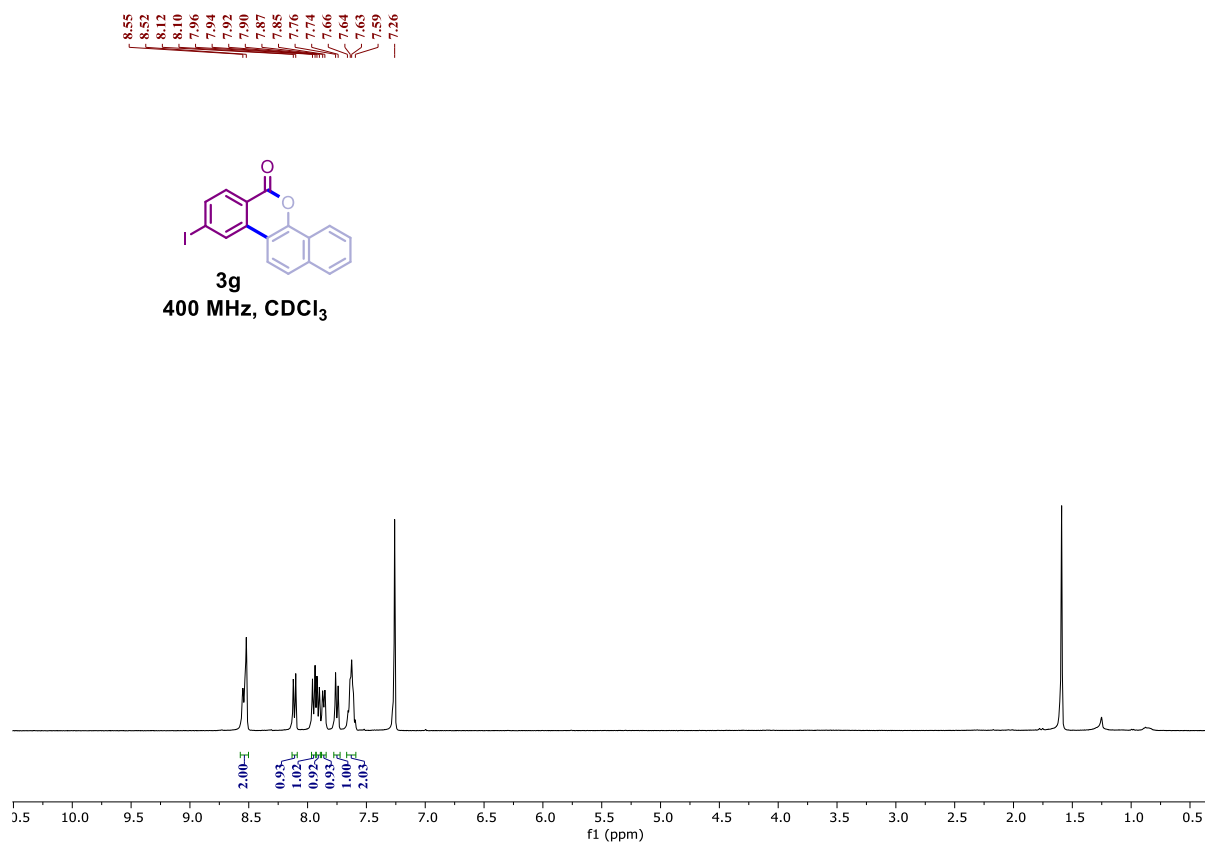


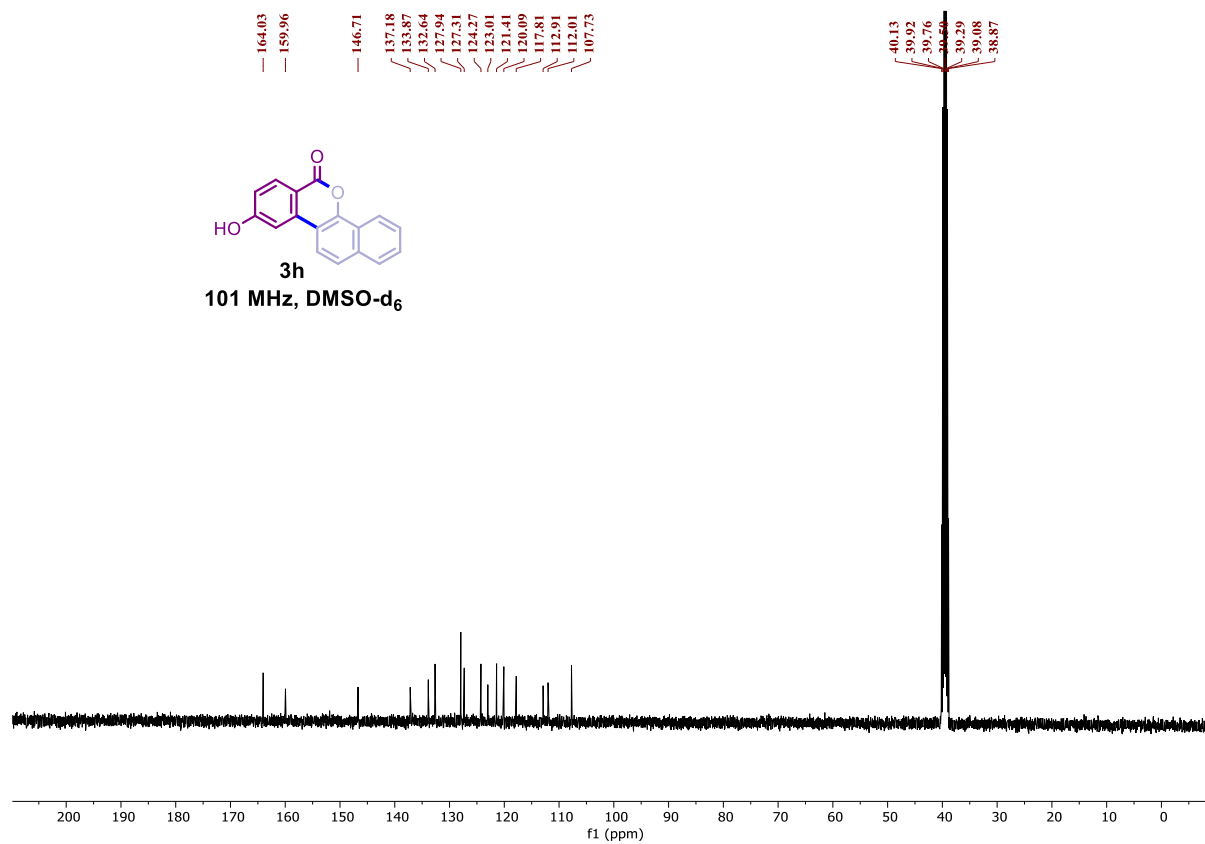
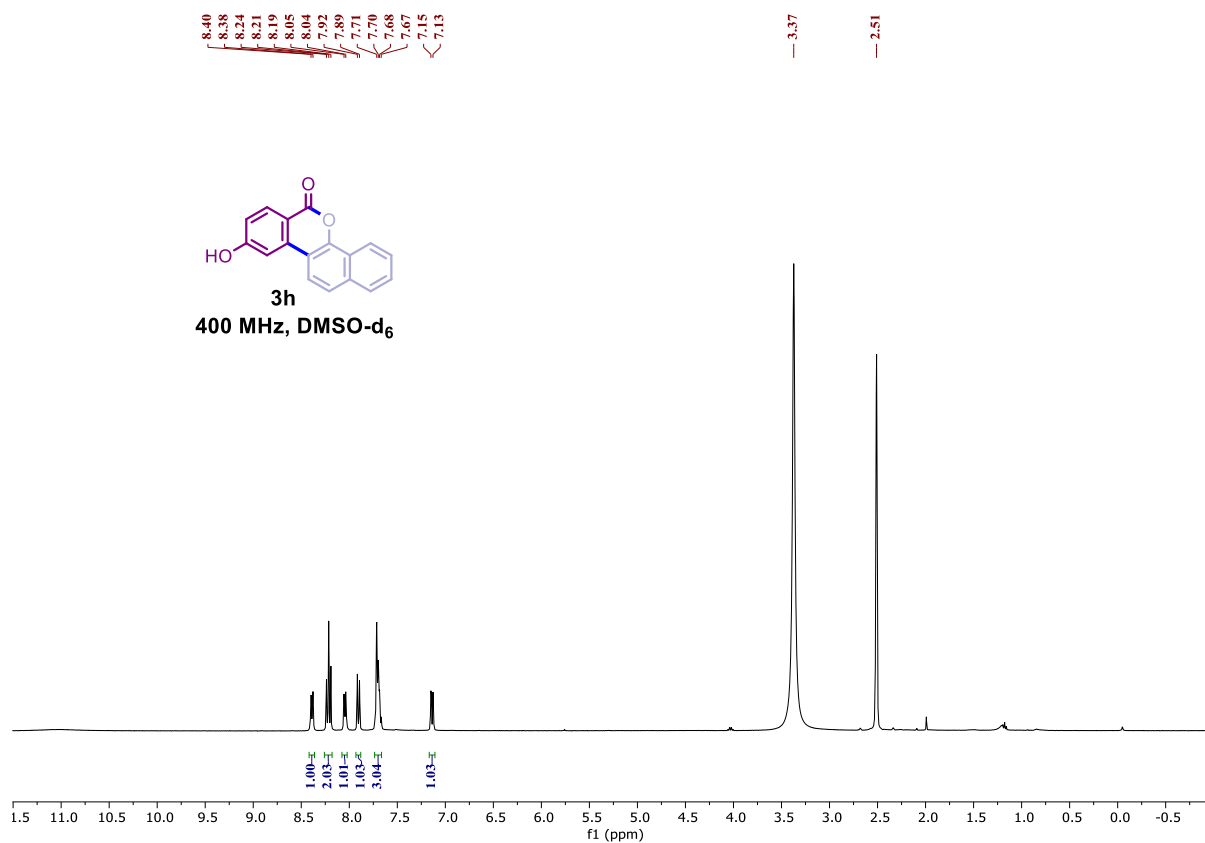


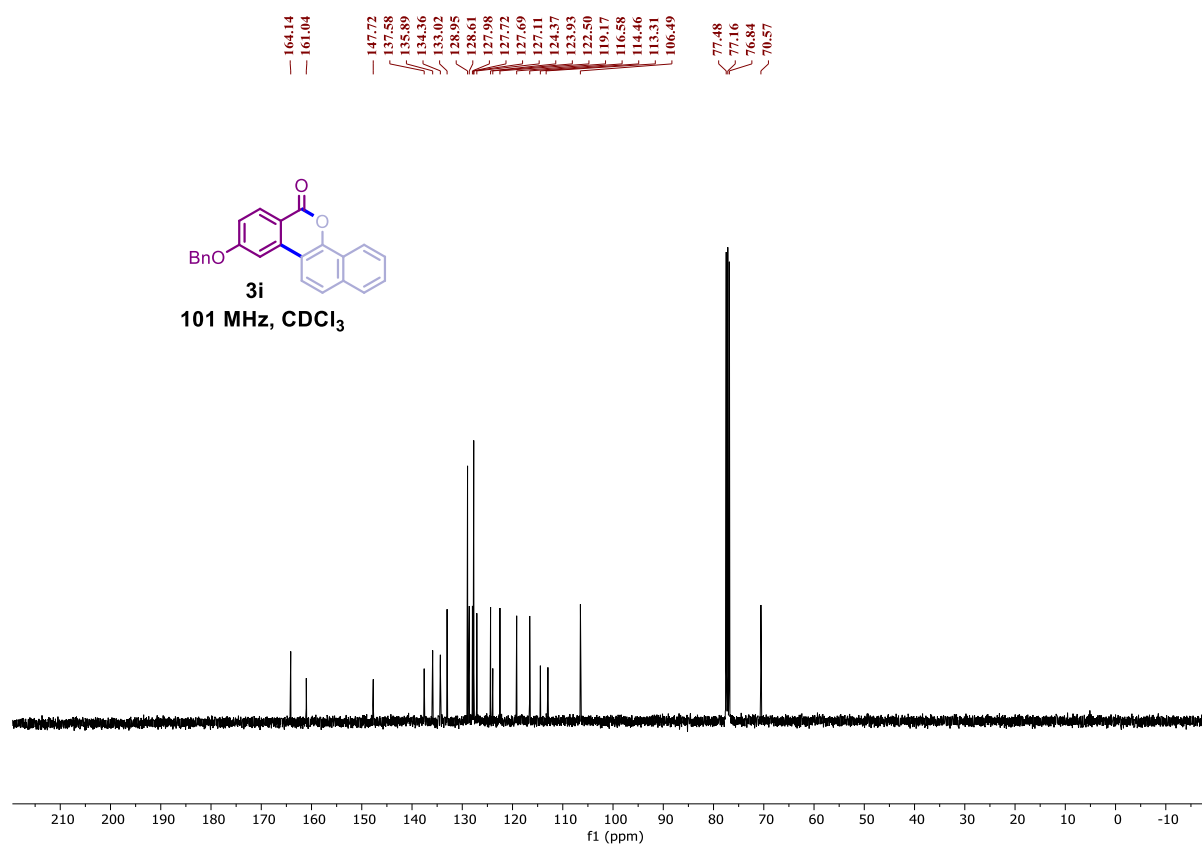
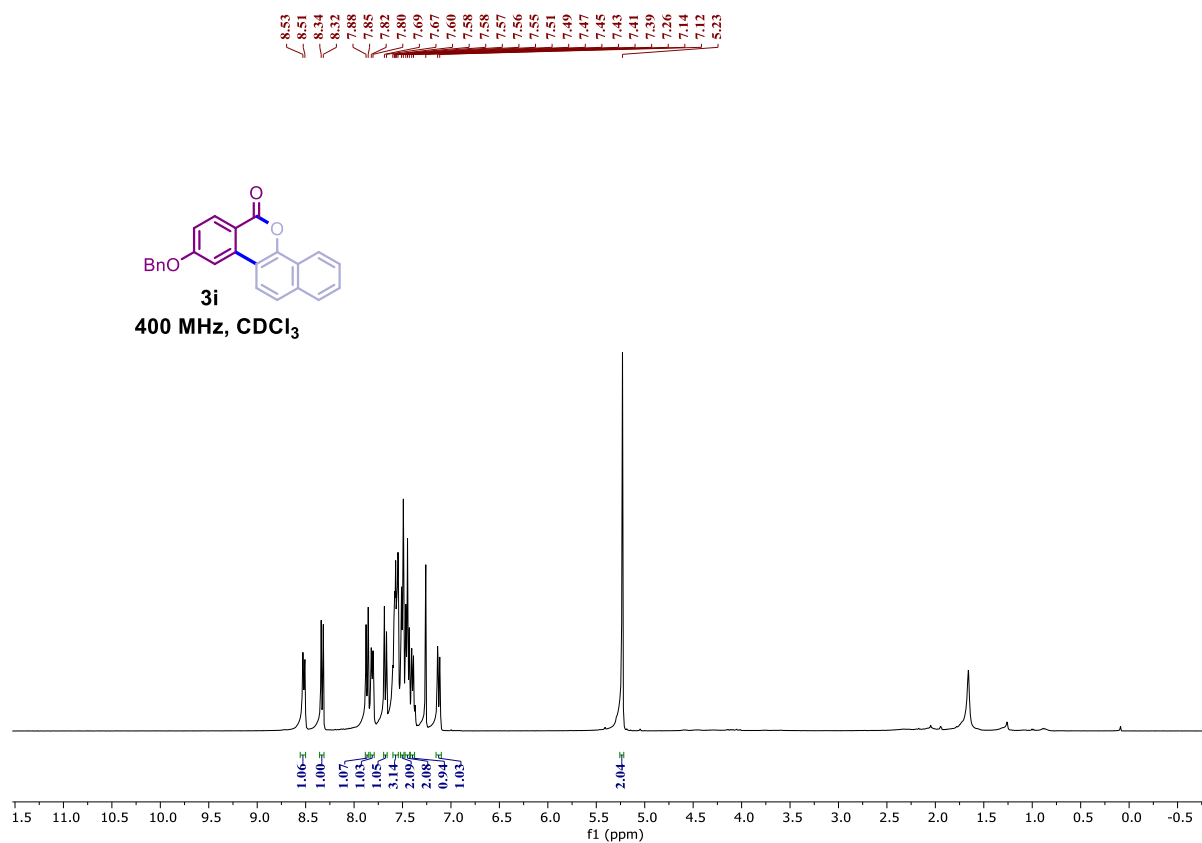


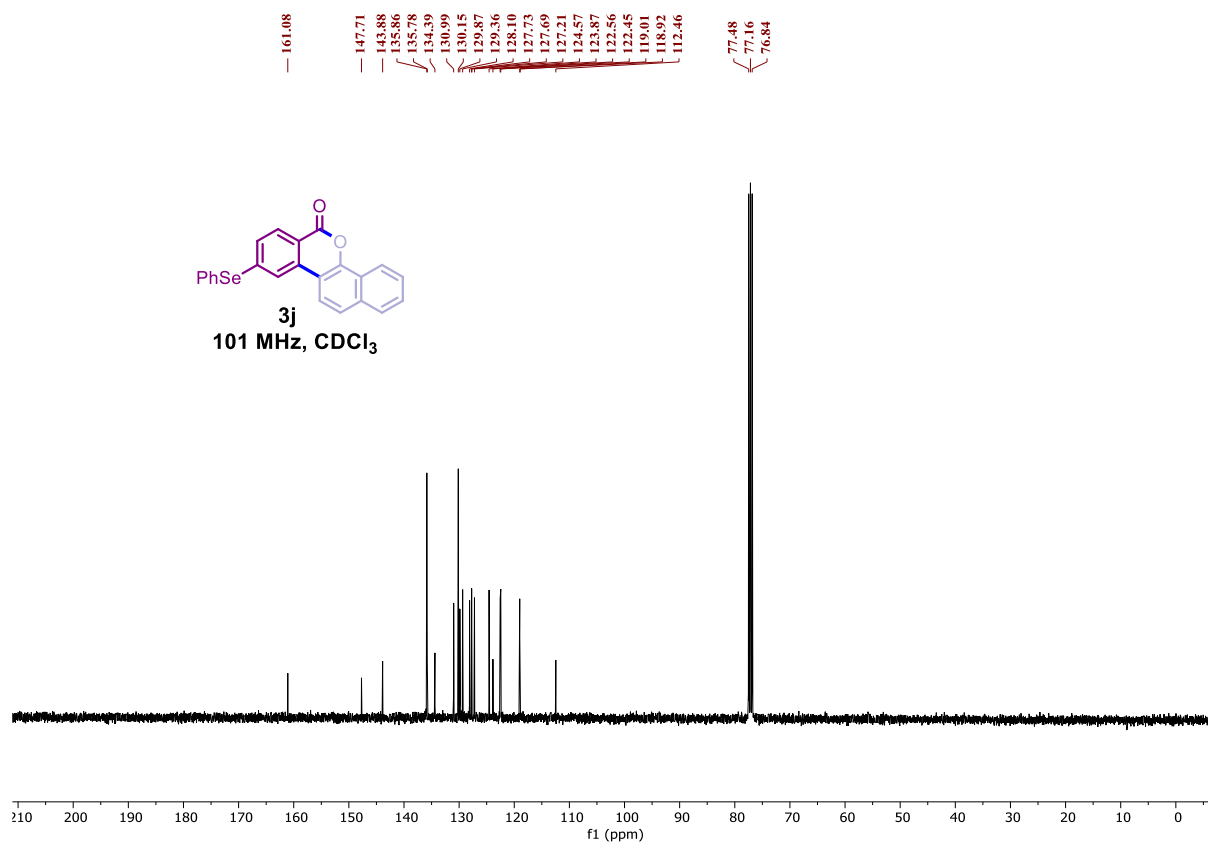
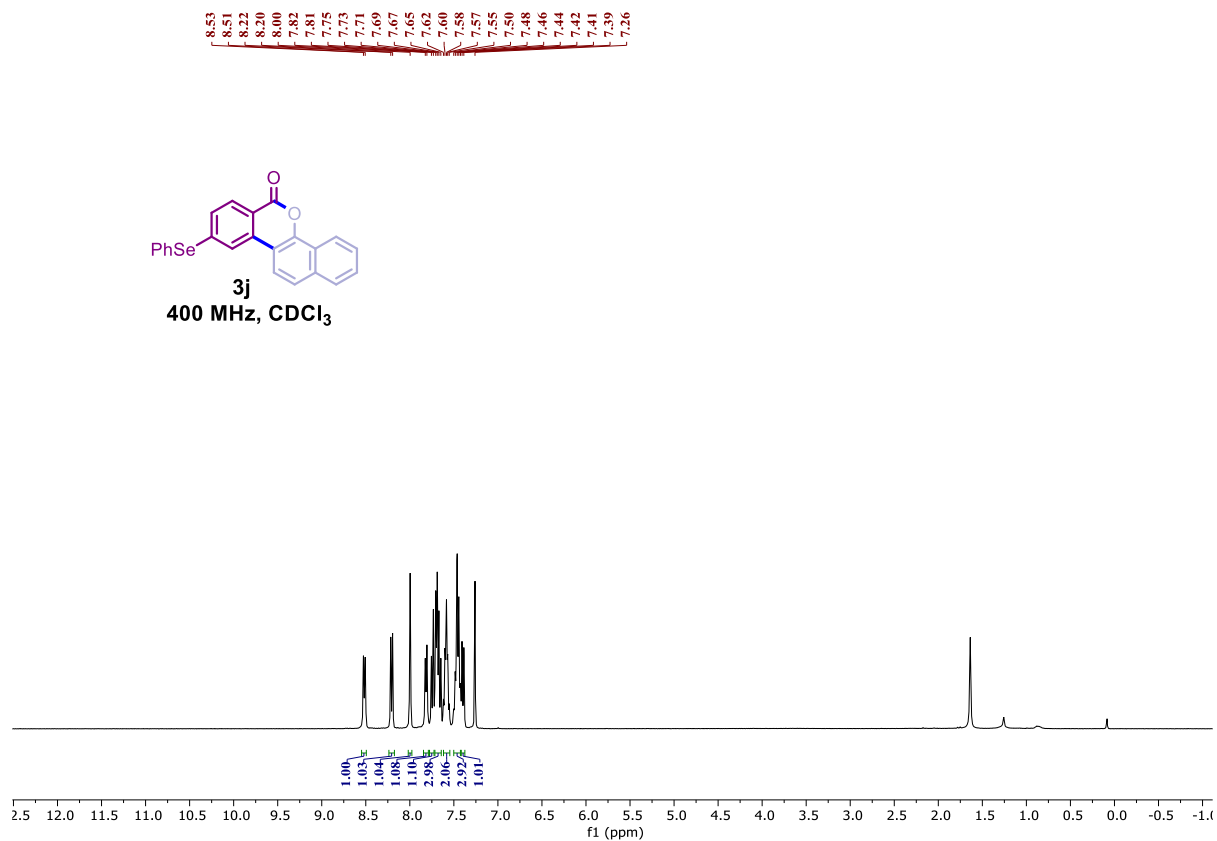


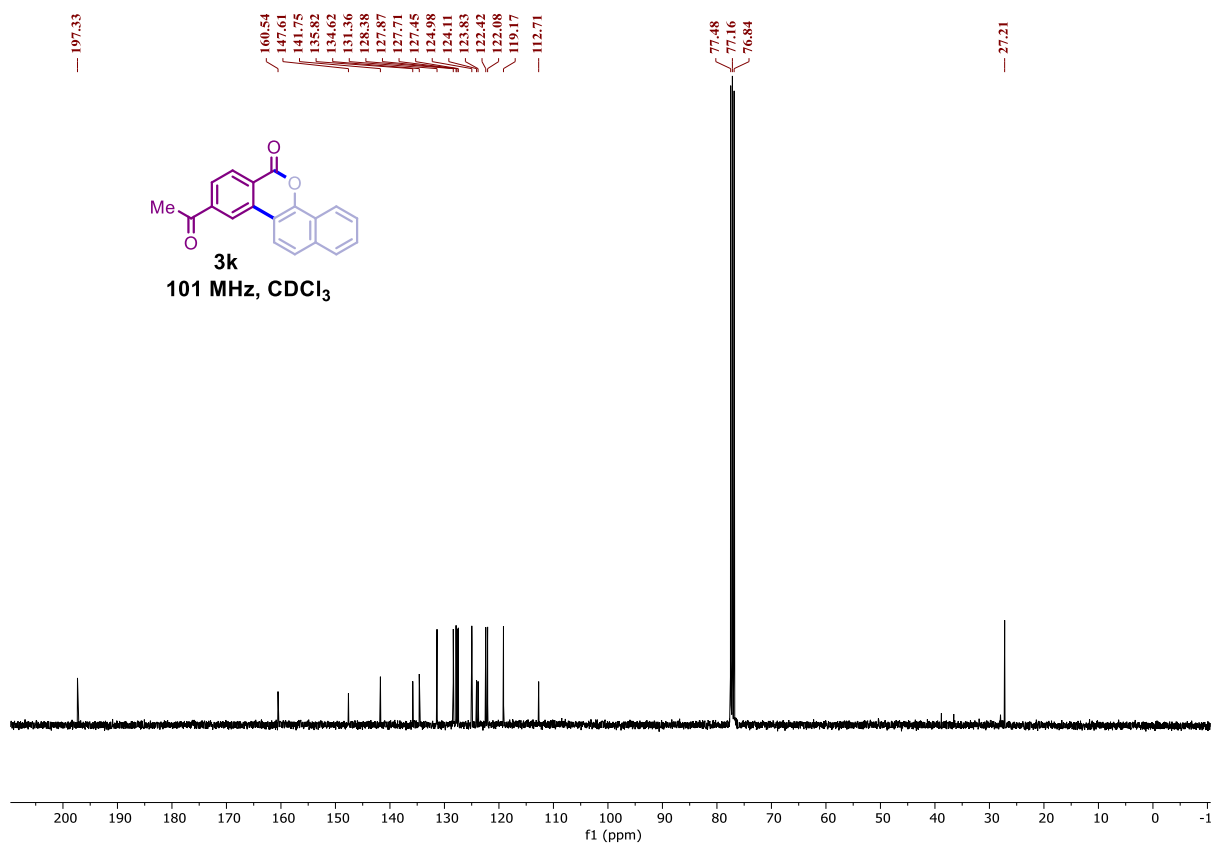
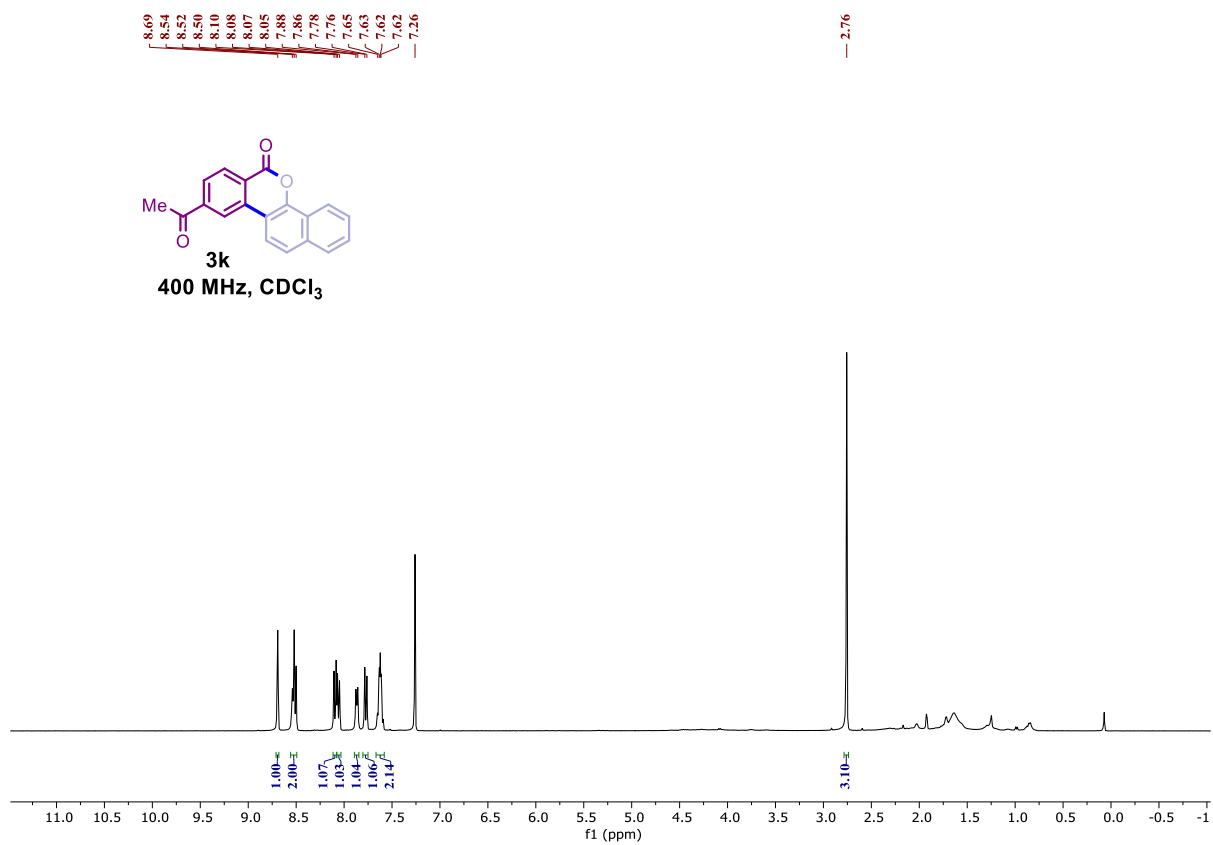


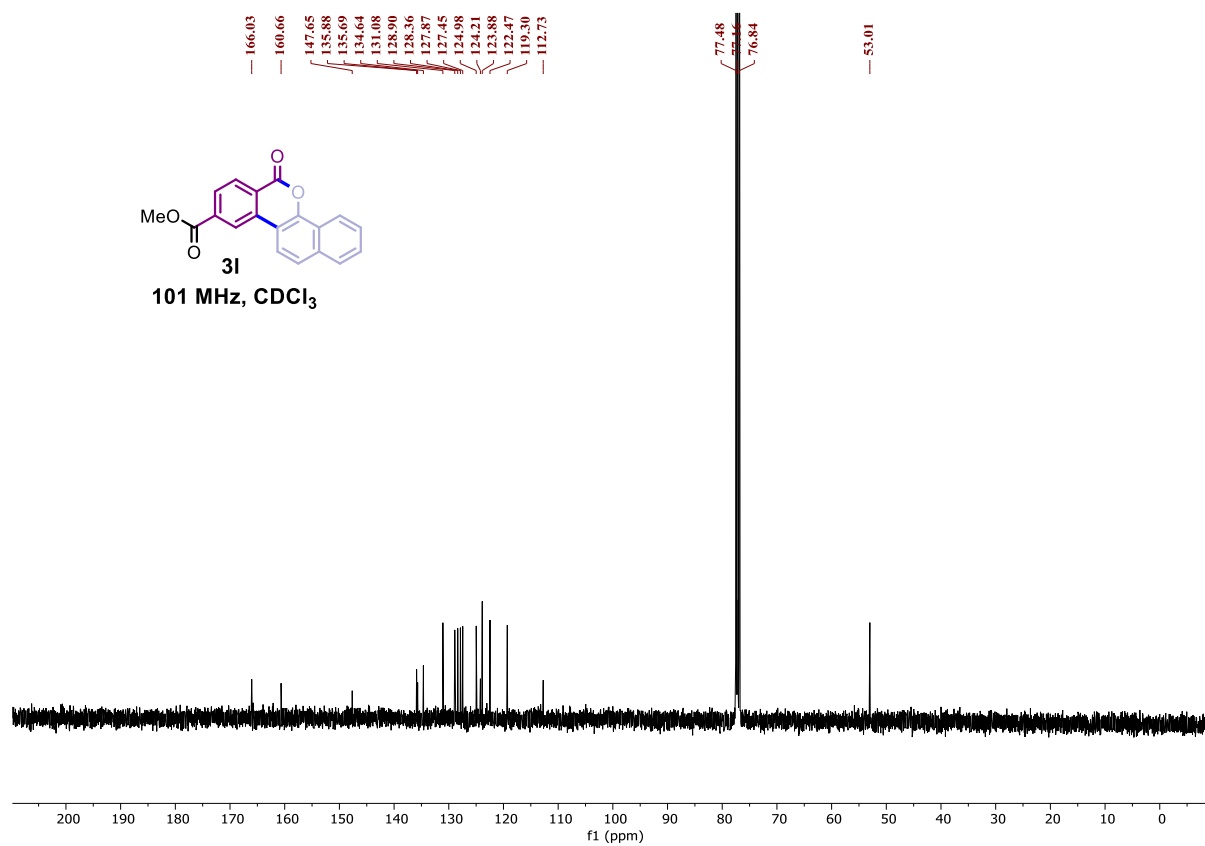
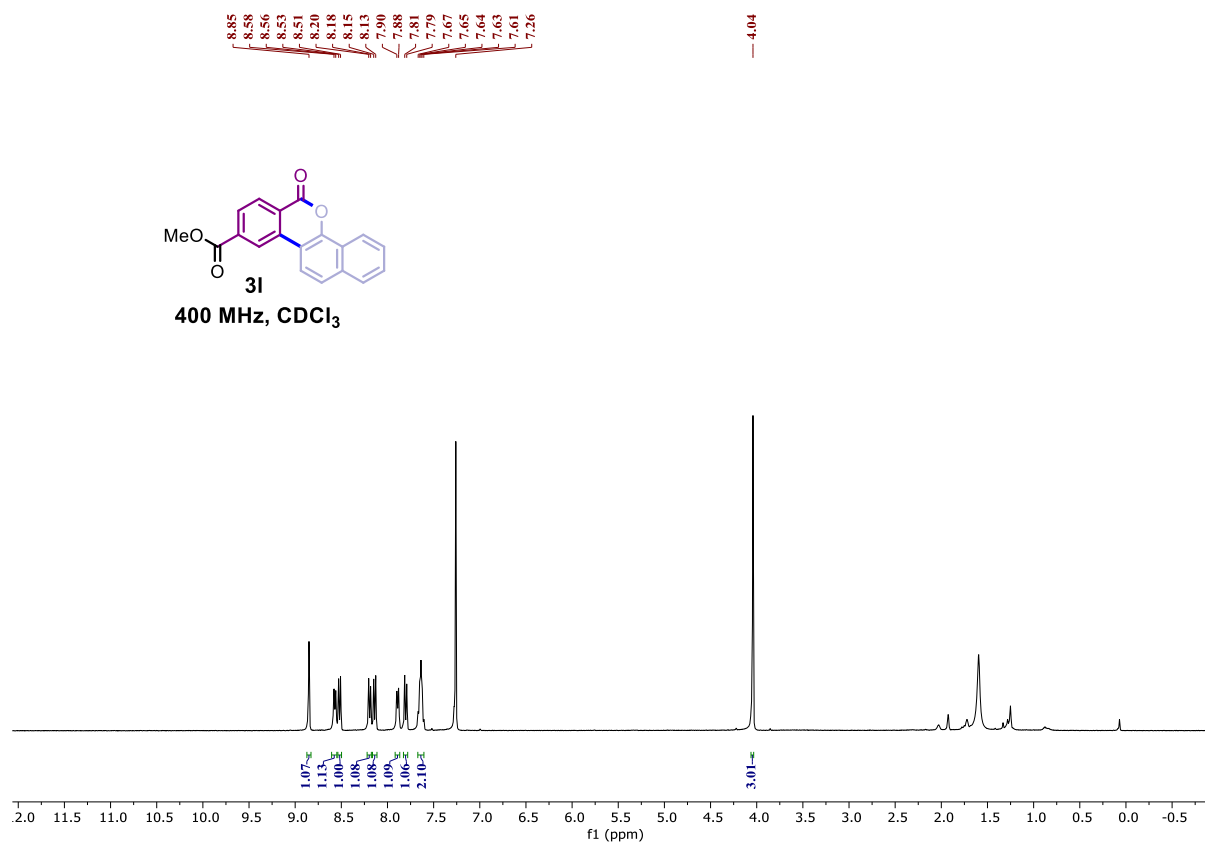


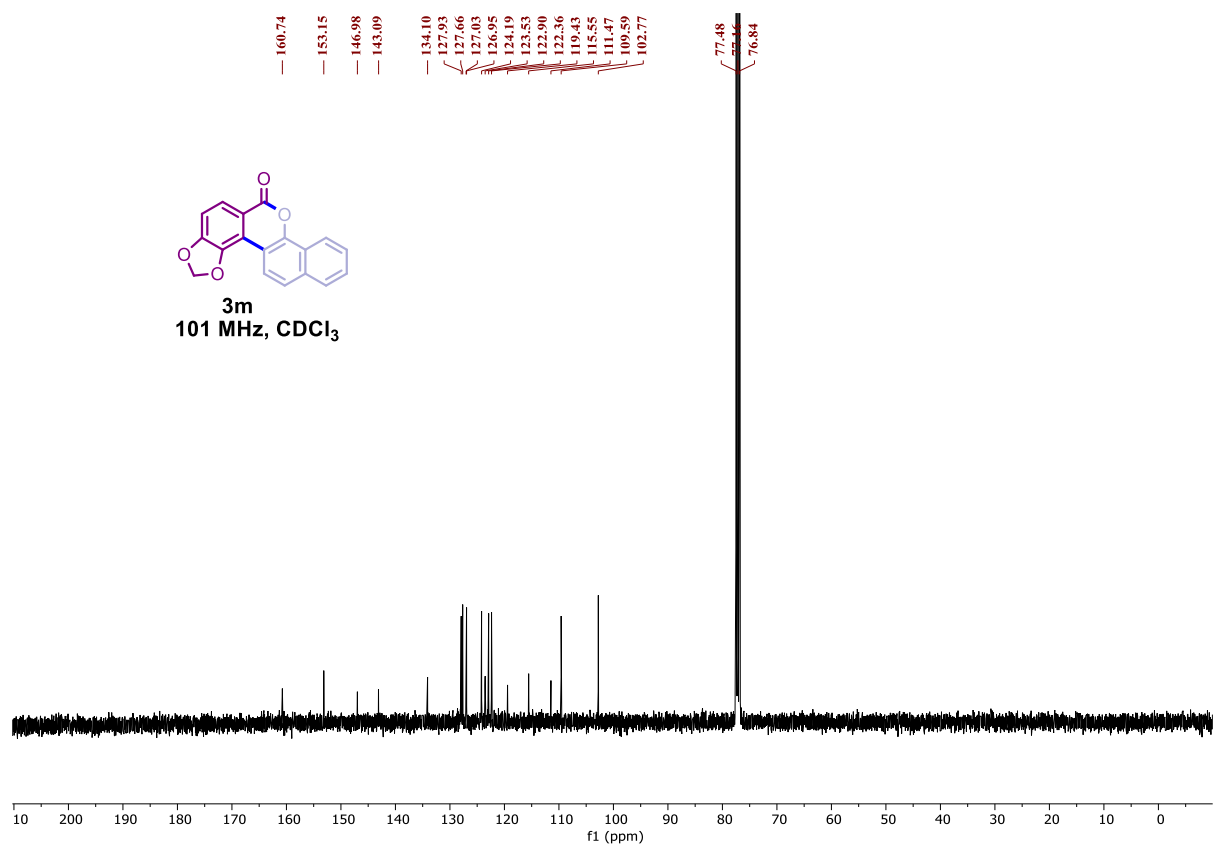
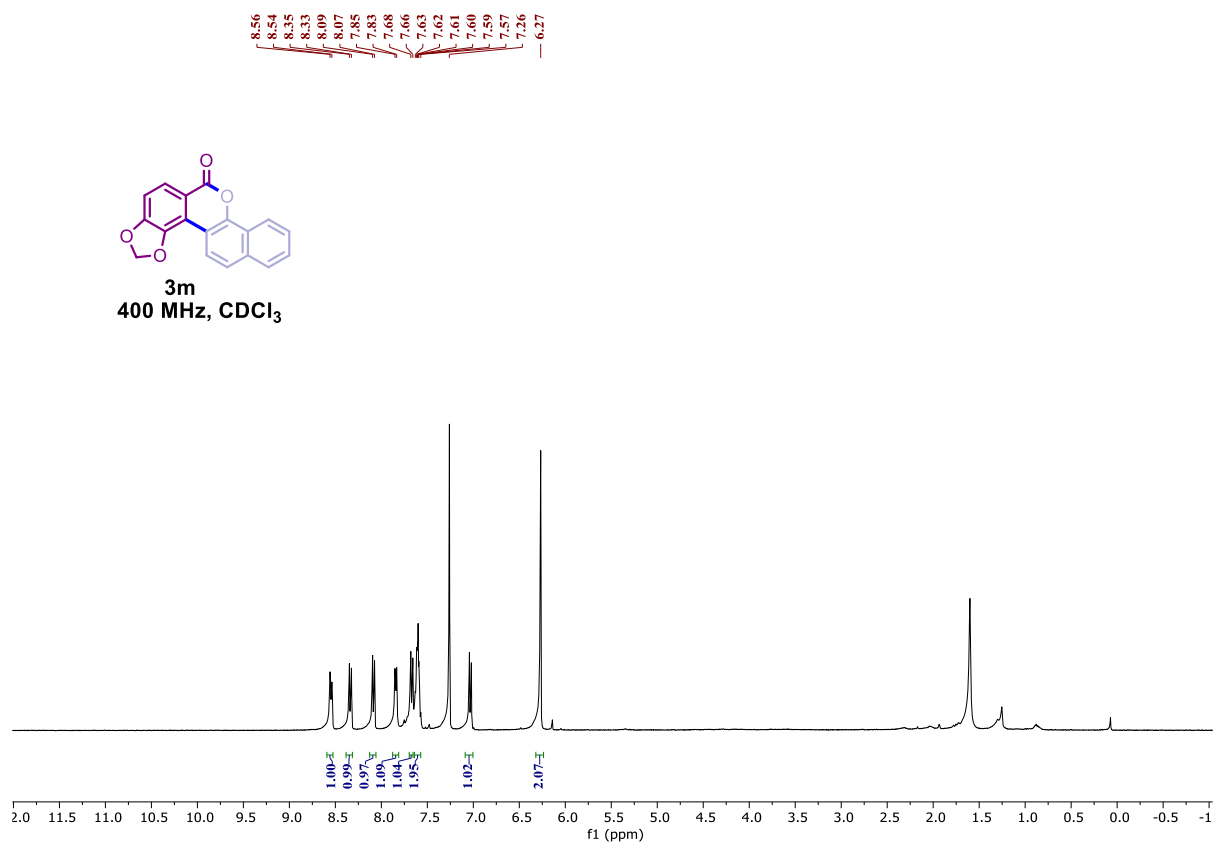


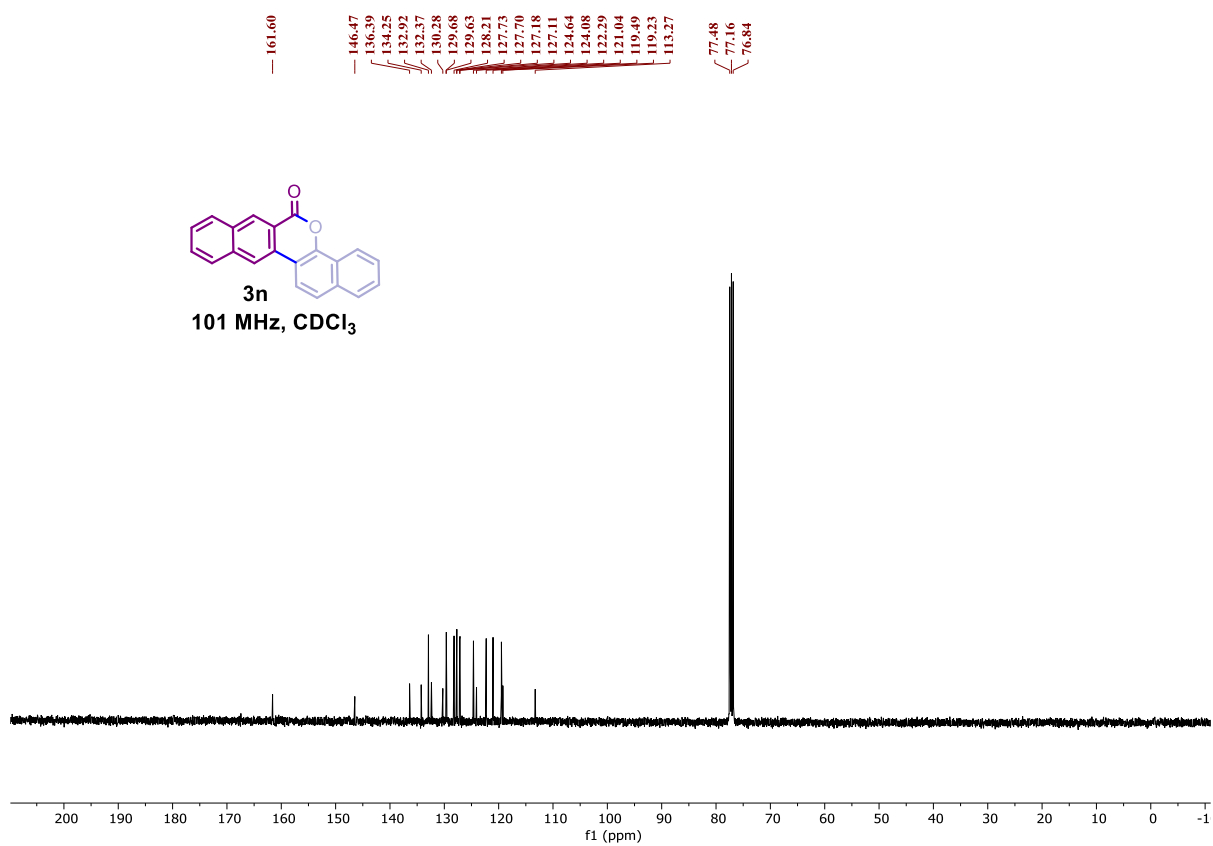
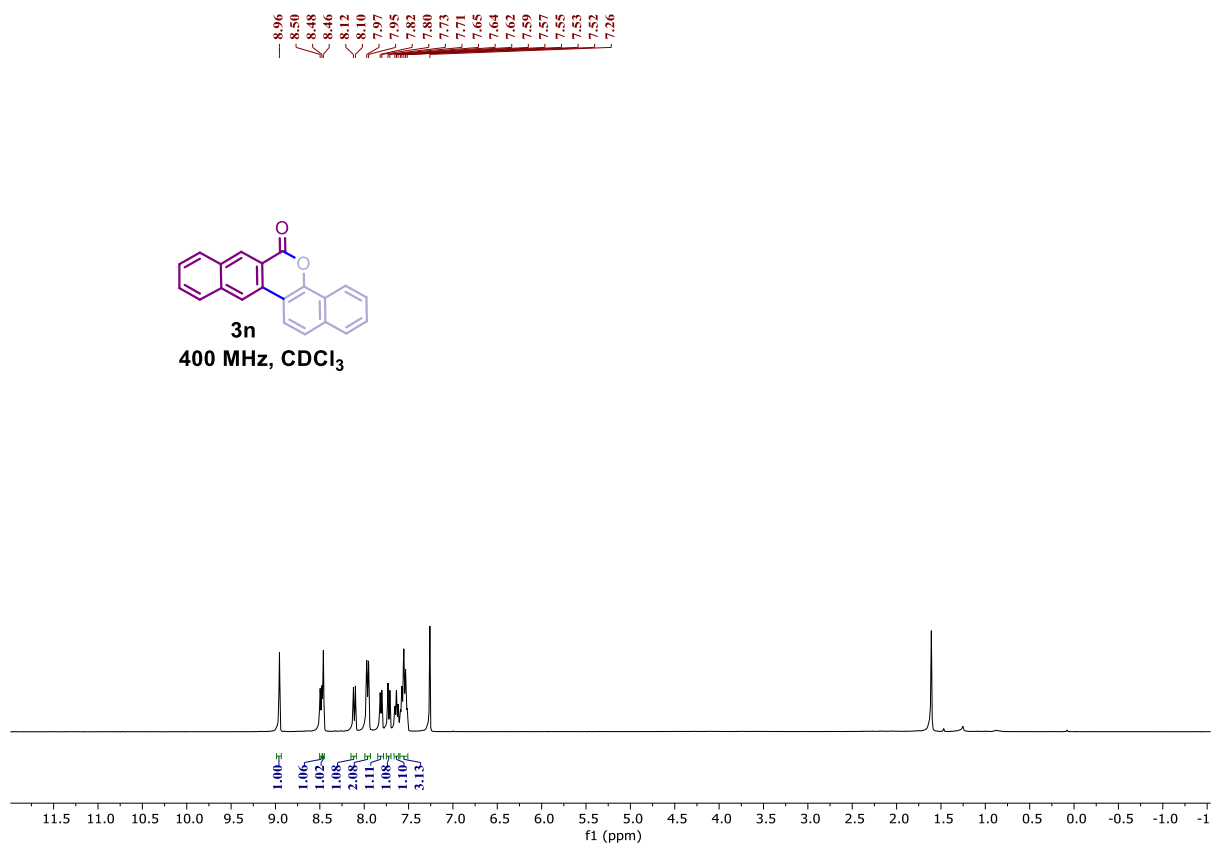


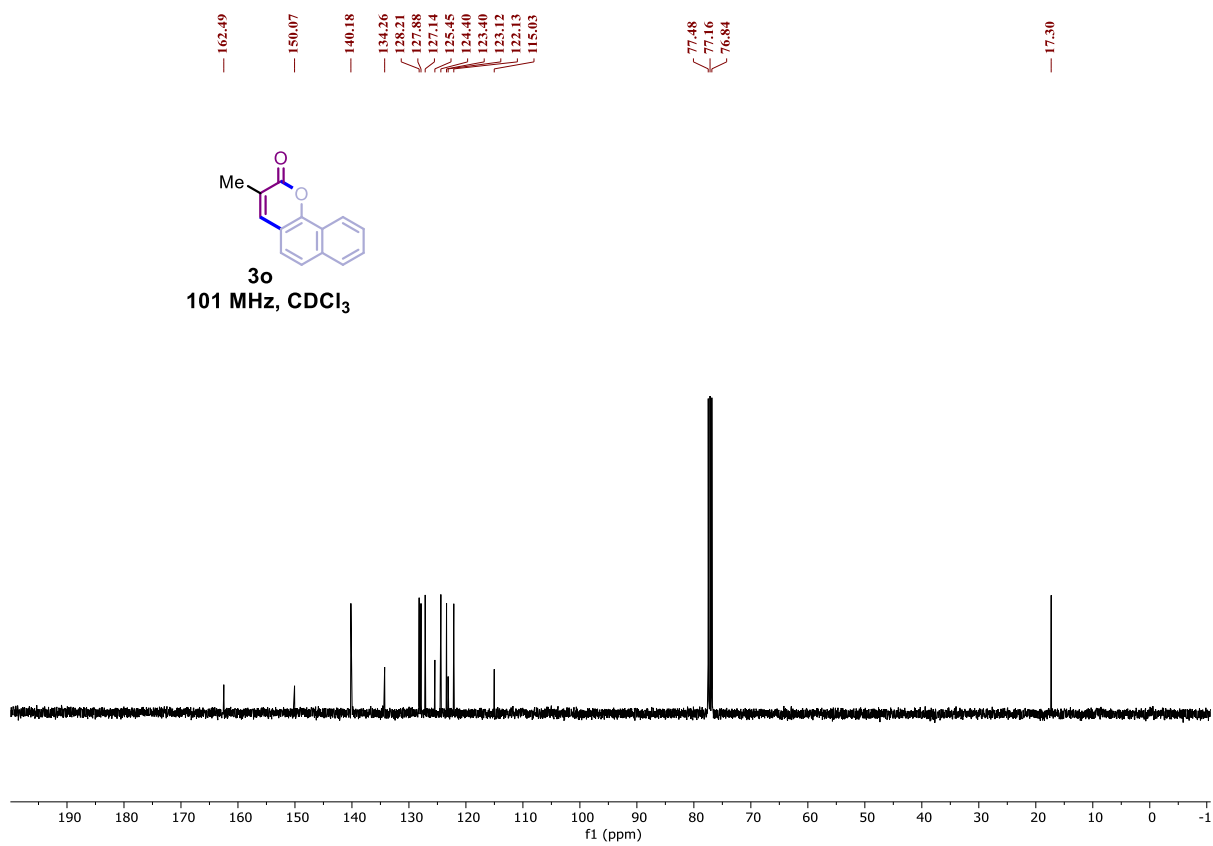
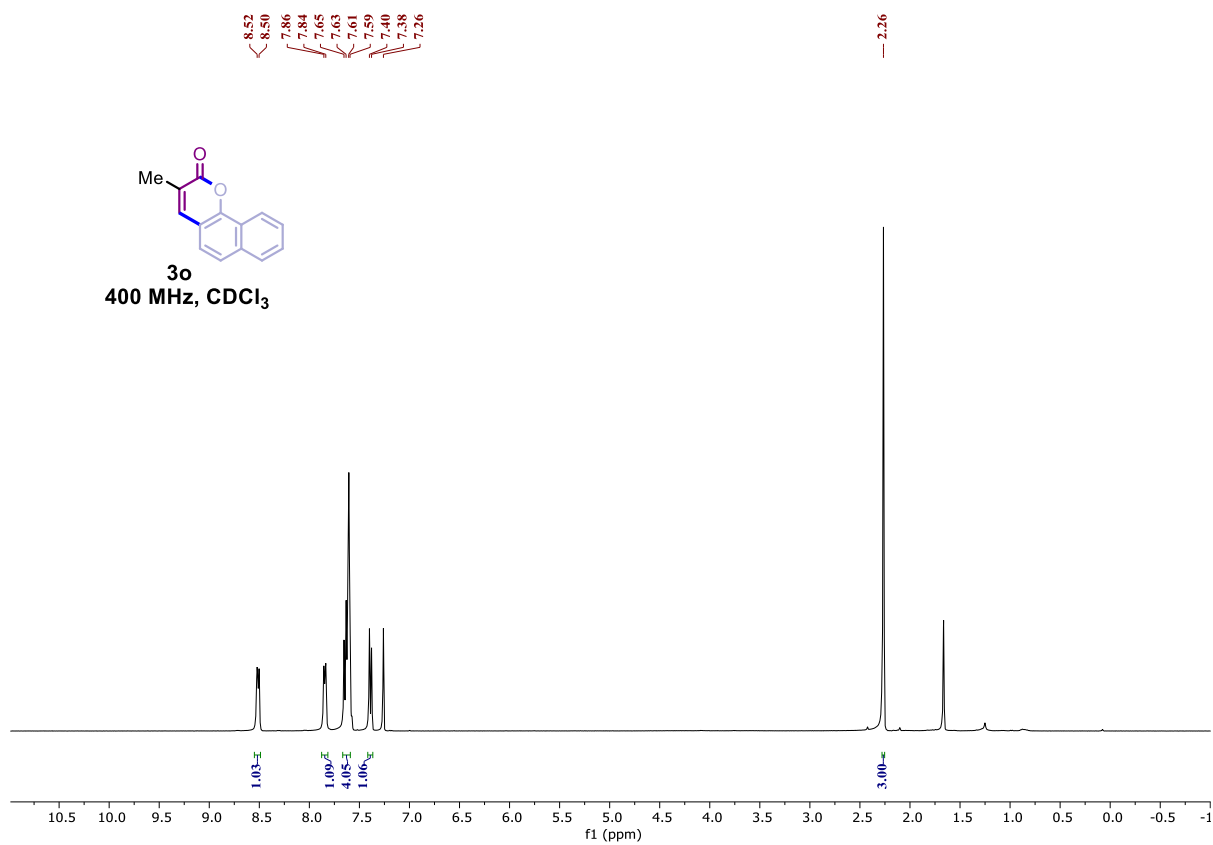


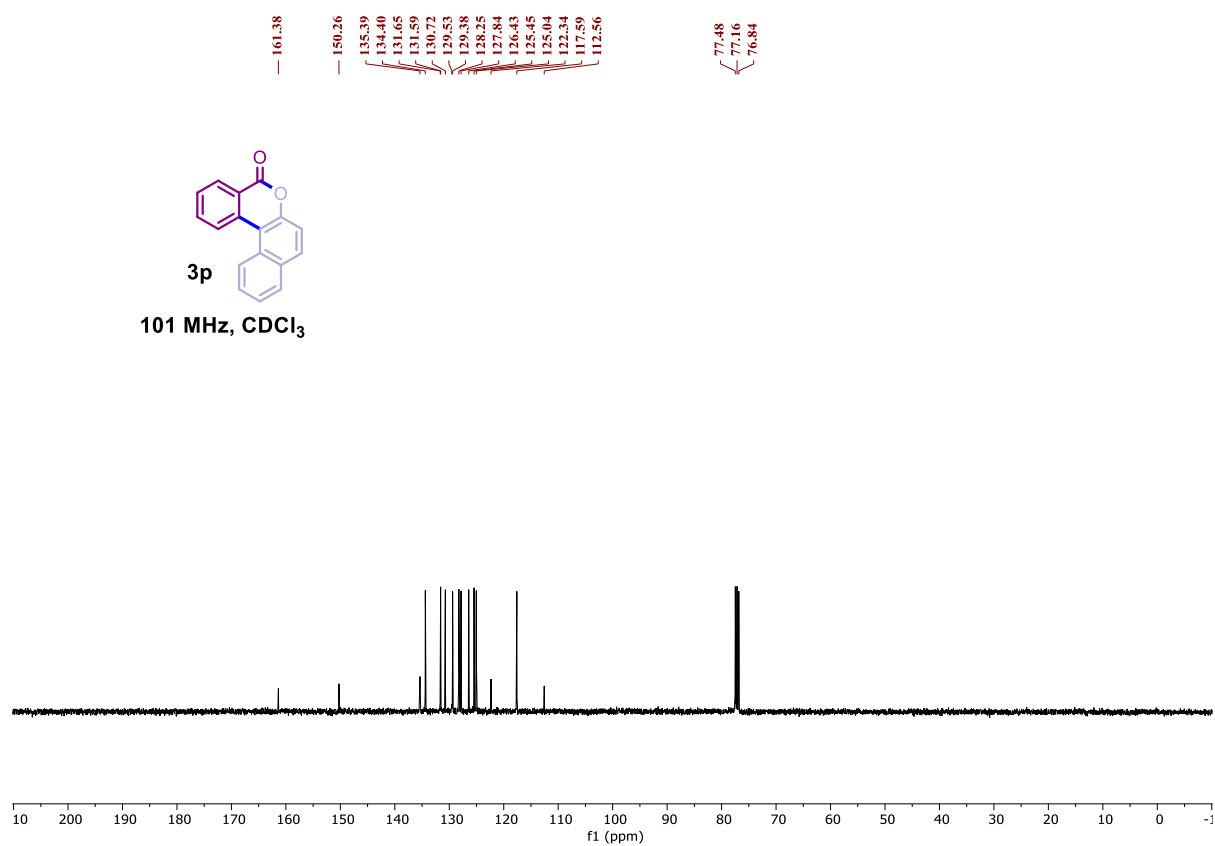
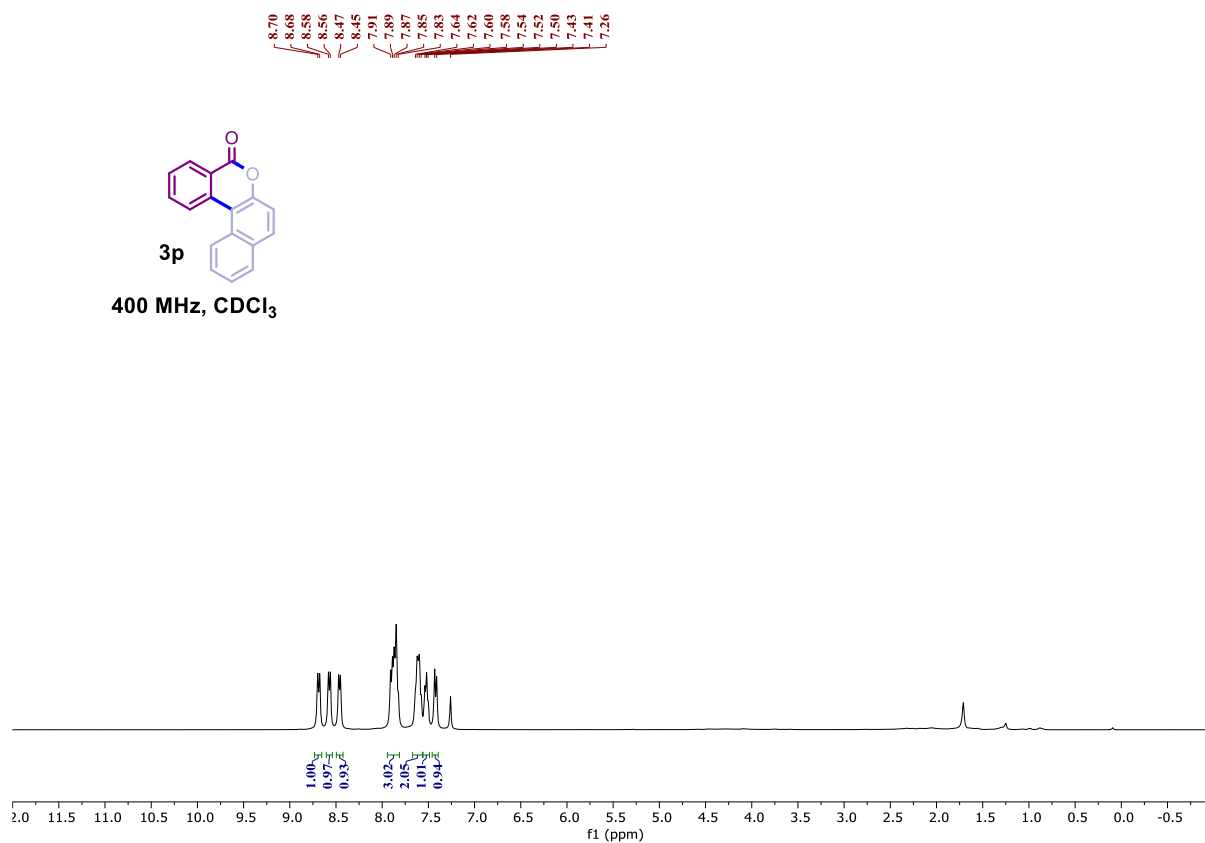


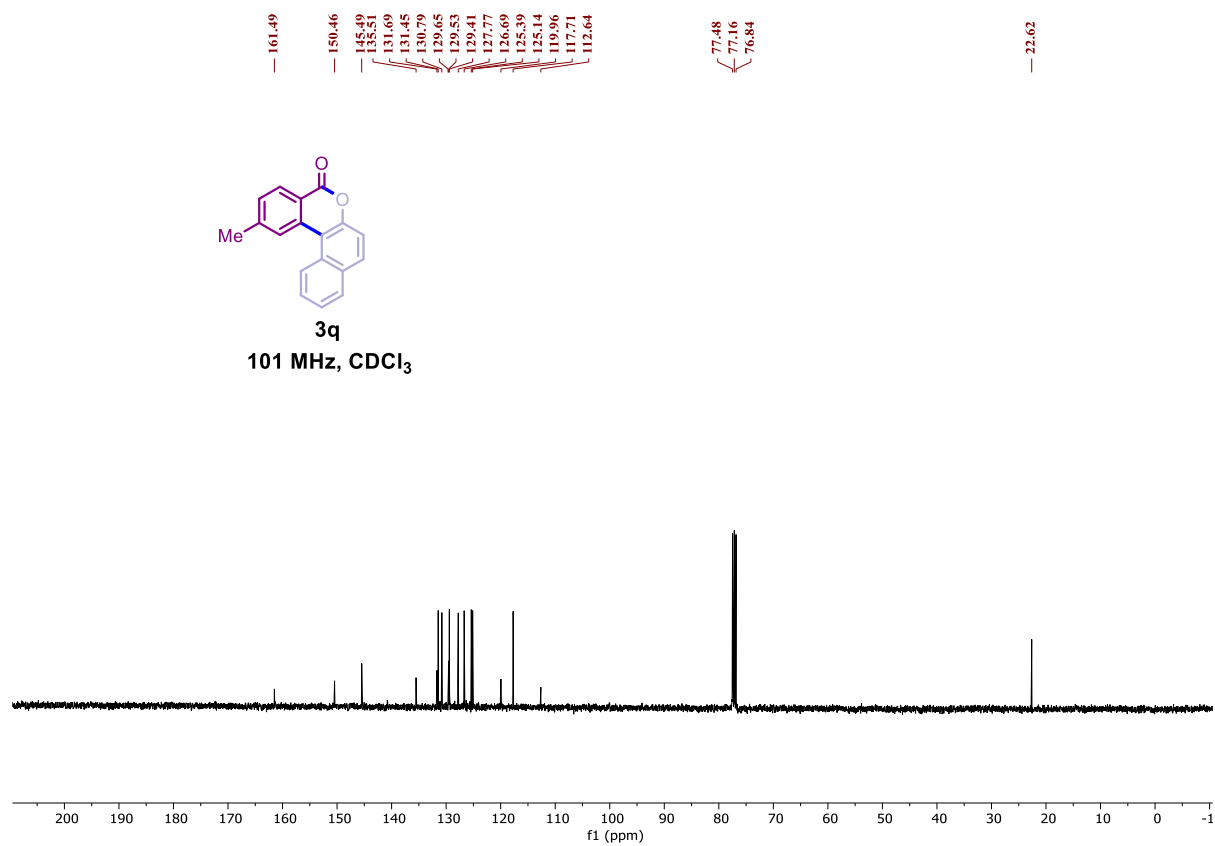
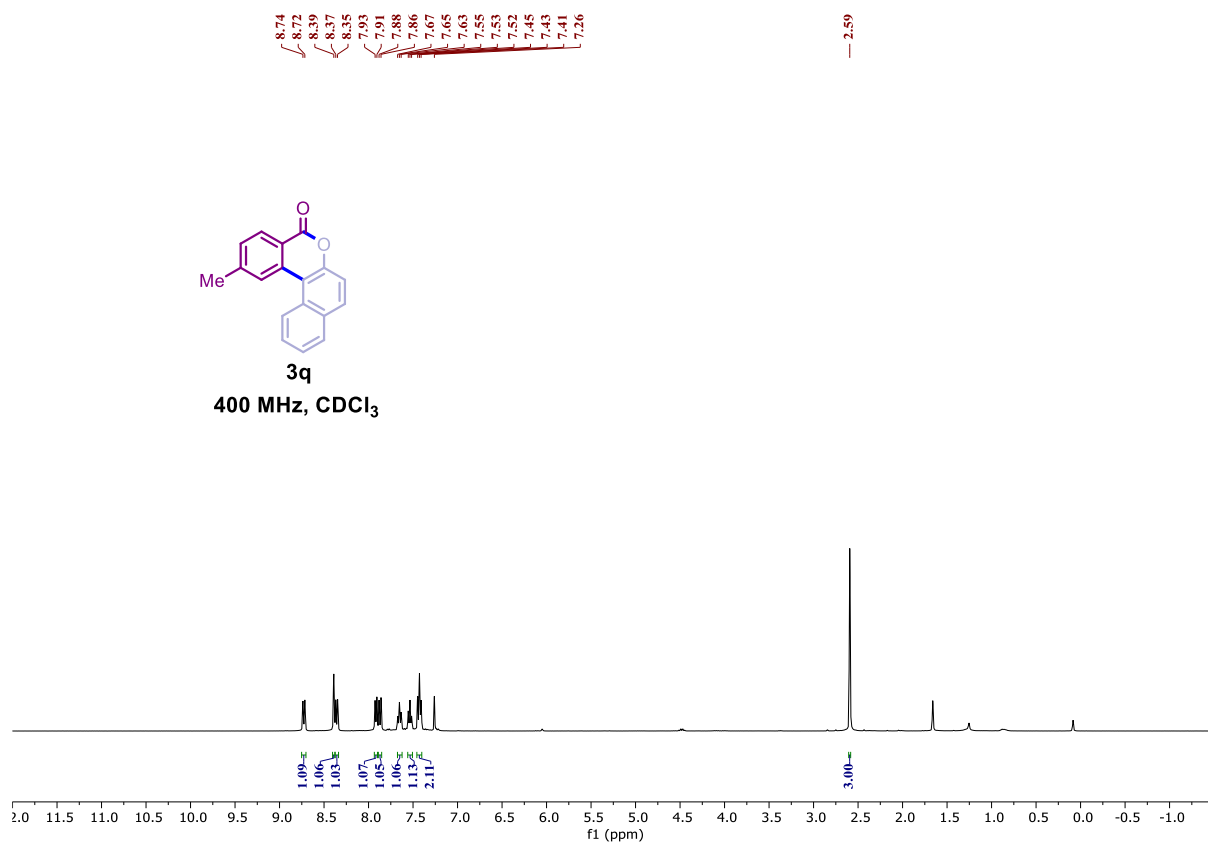




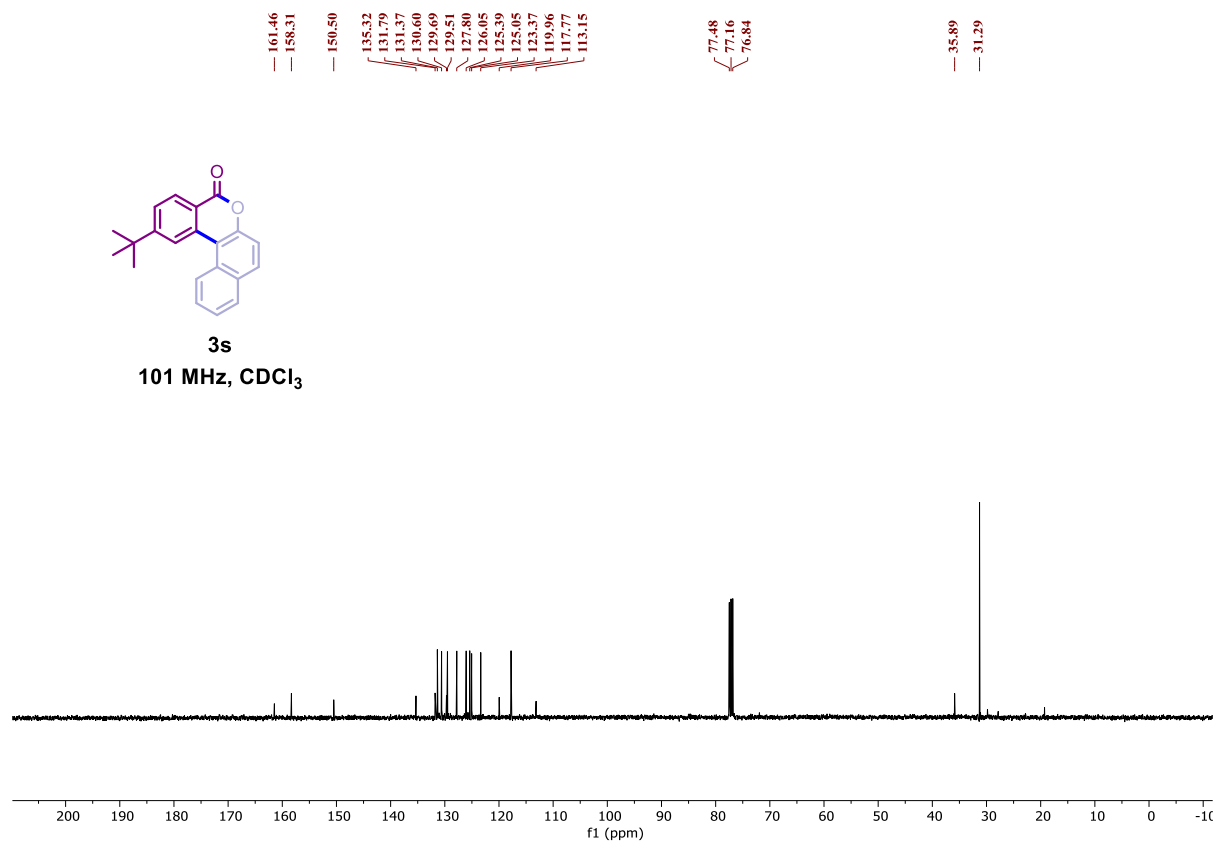
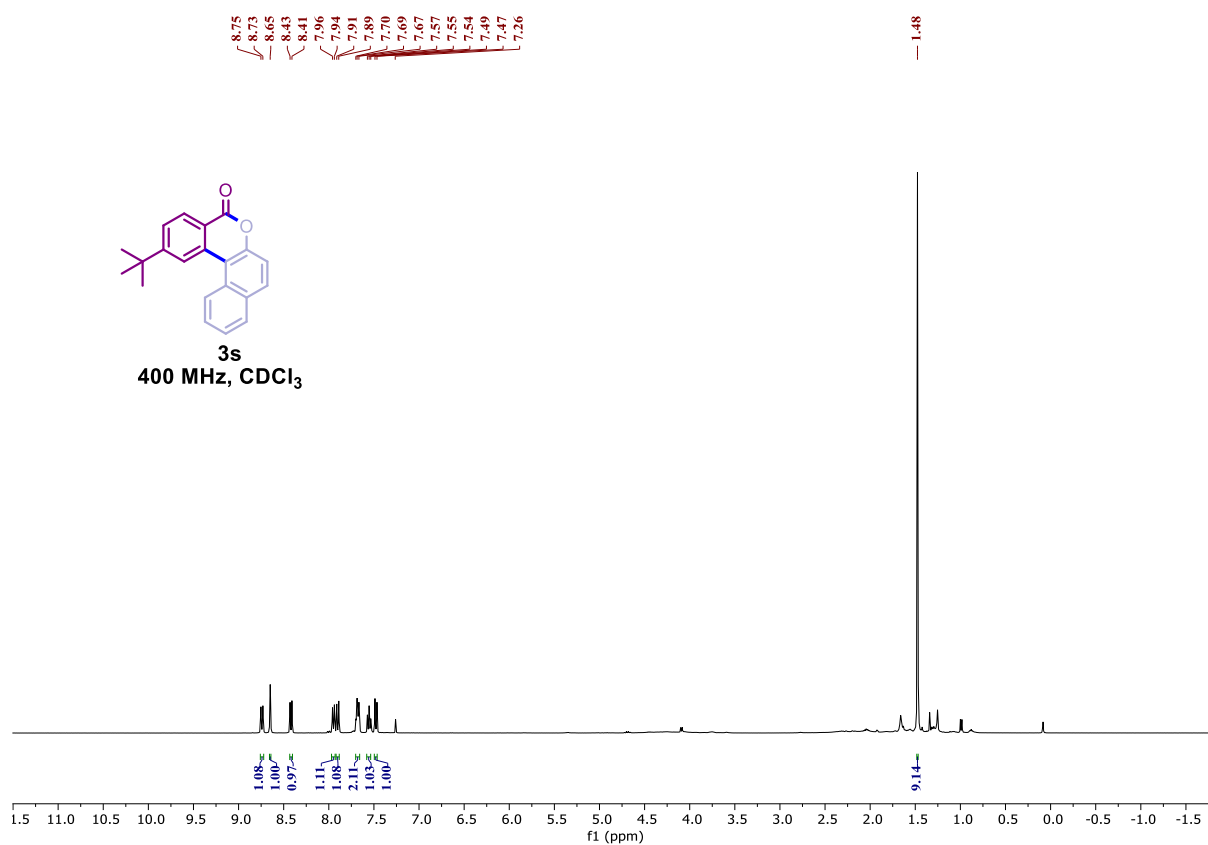


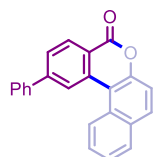




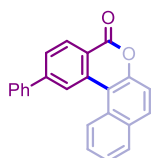
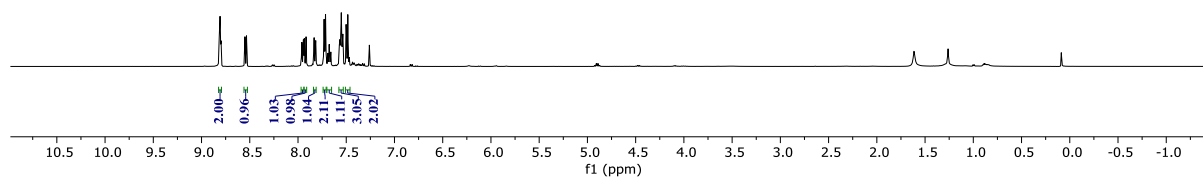




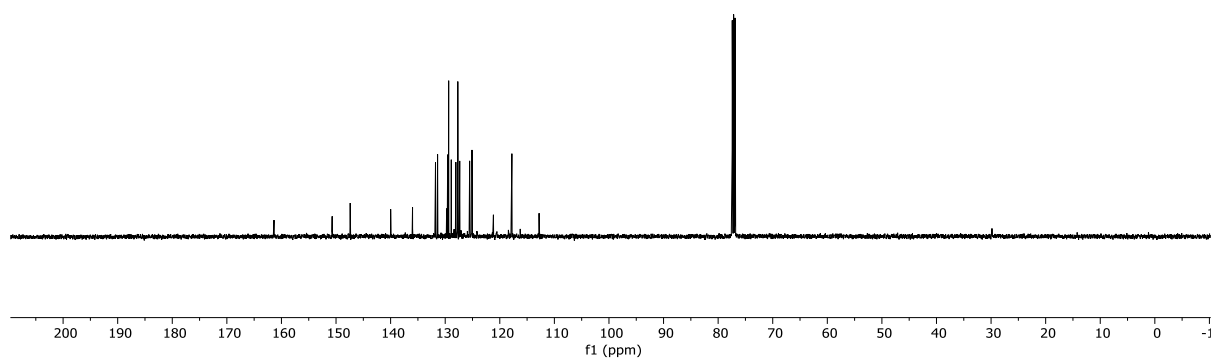


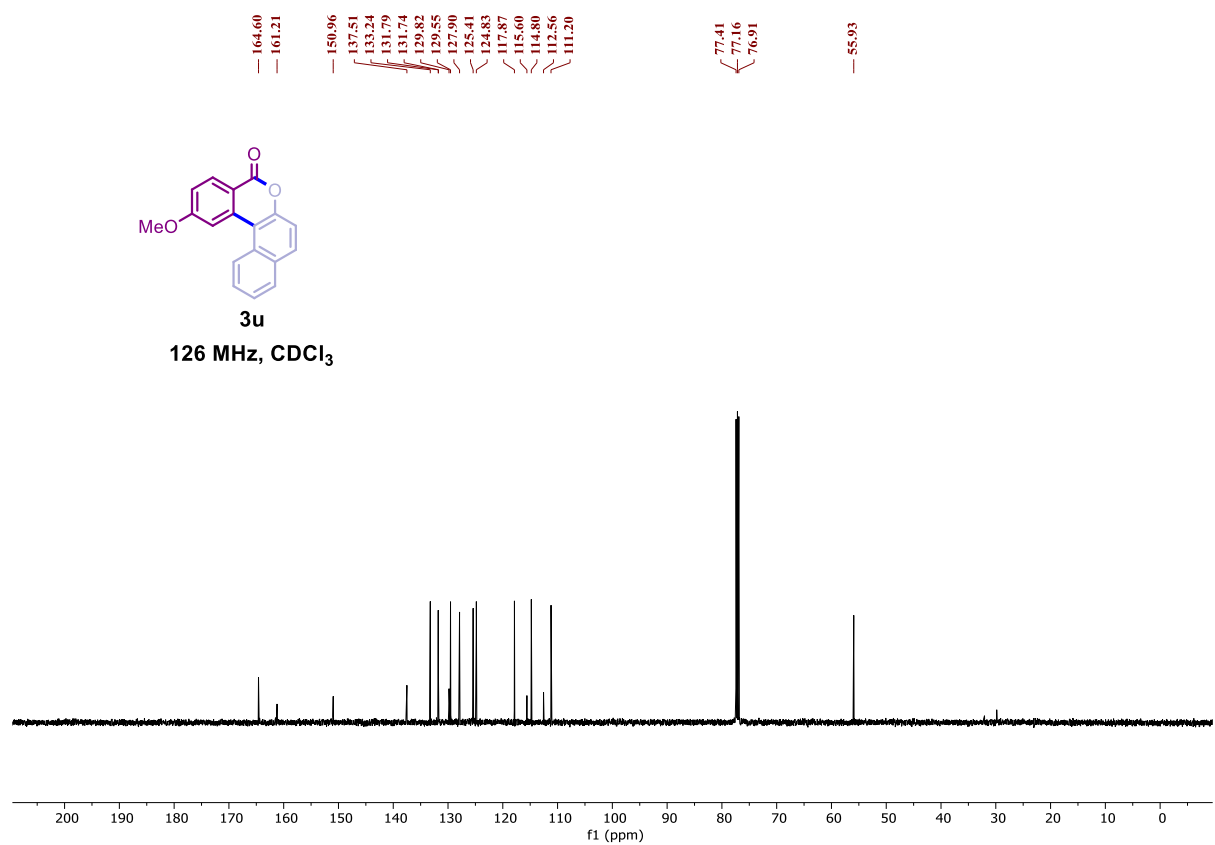
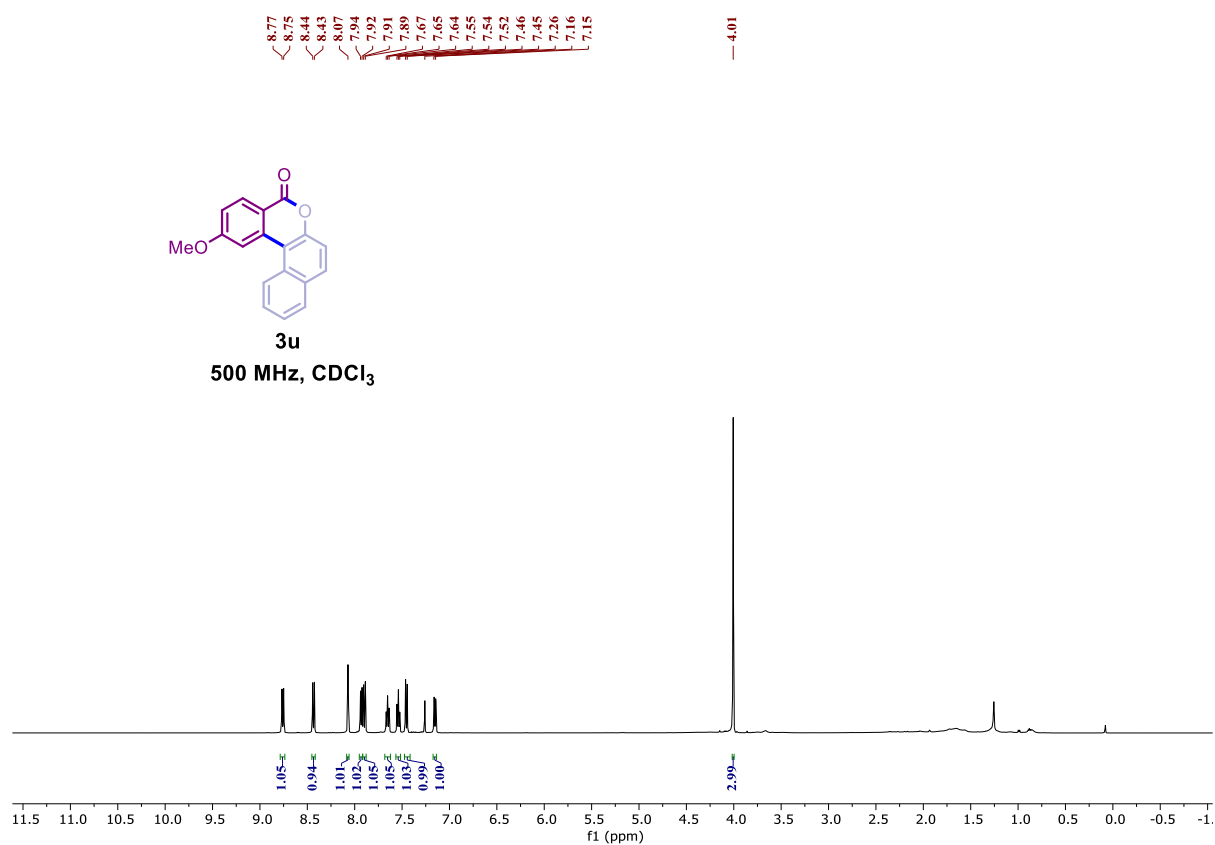


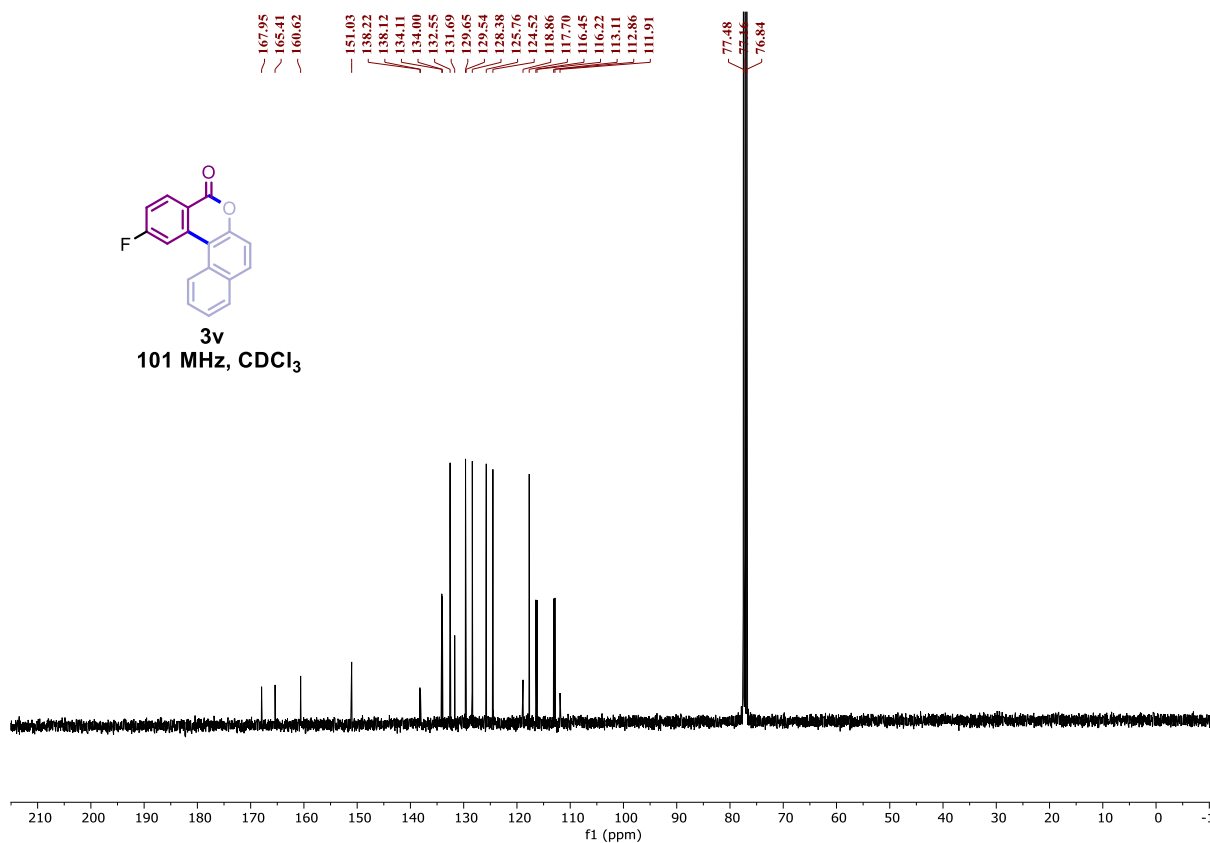
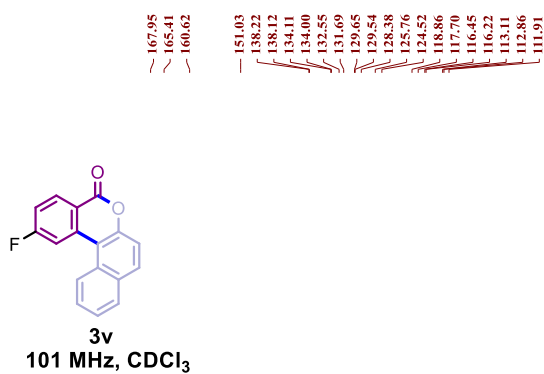
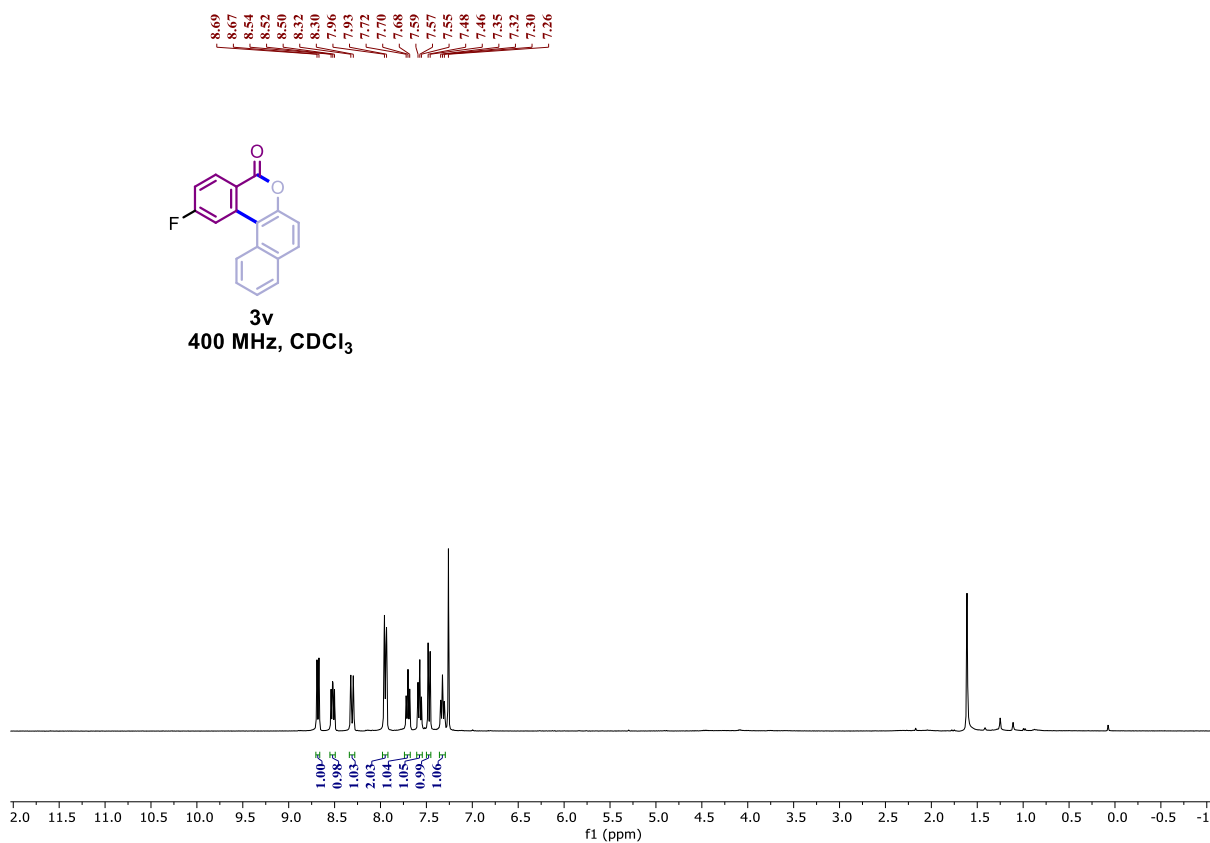
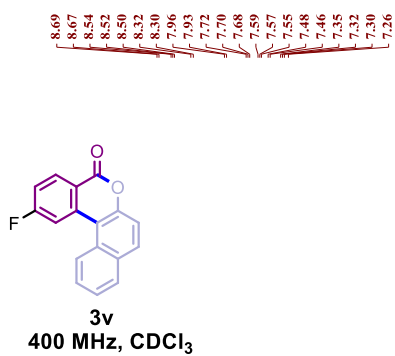
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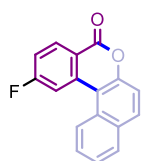


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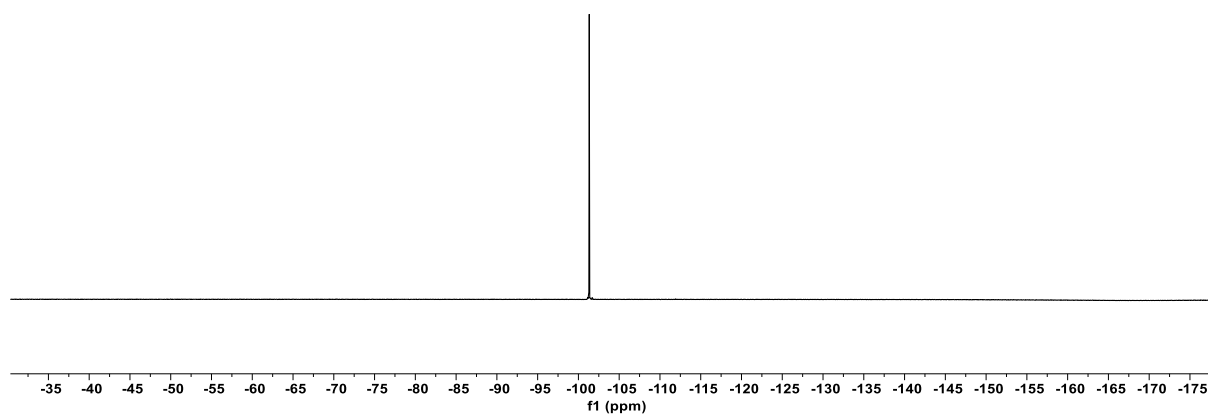


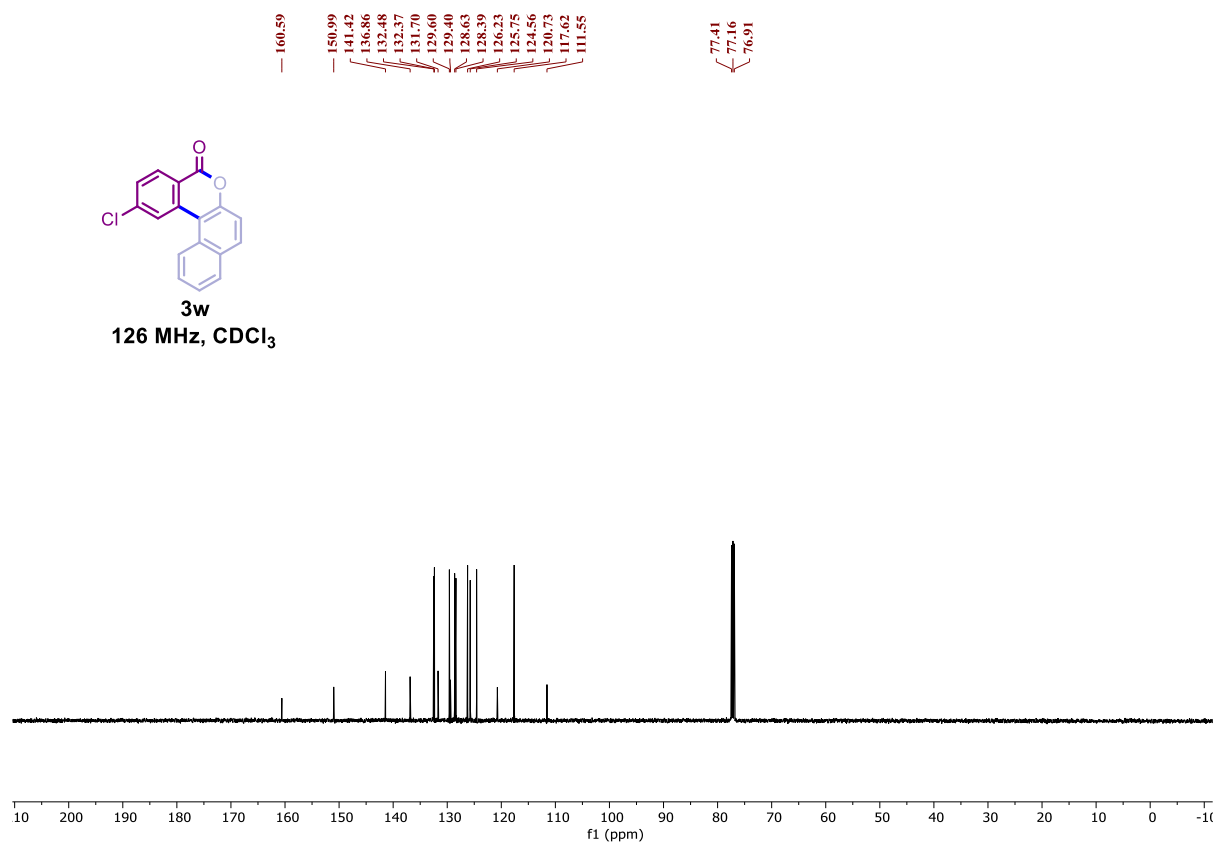
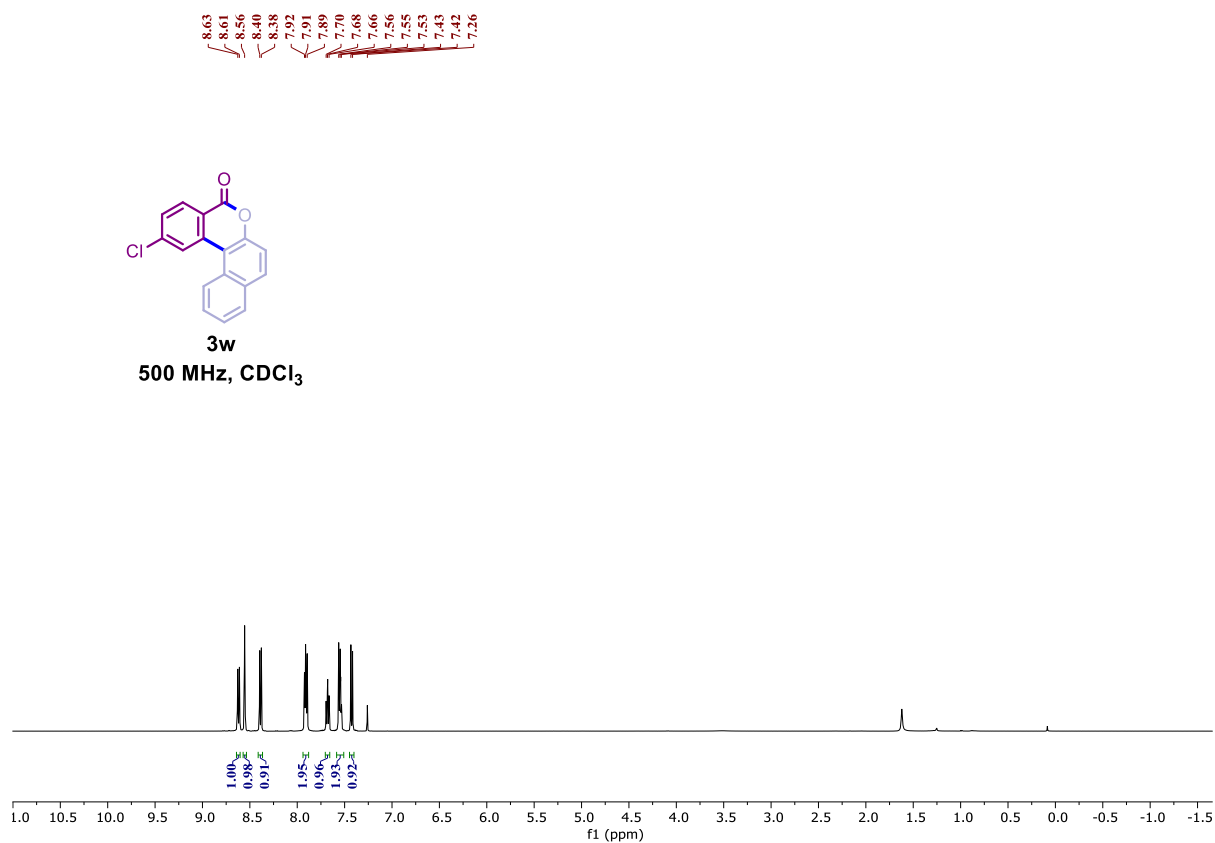


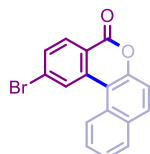


**3v**  
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— -101.33

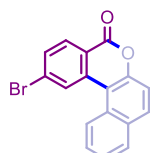
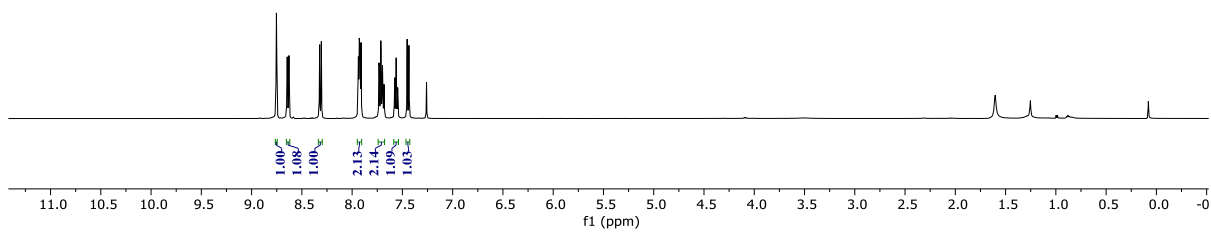






**3x**  
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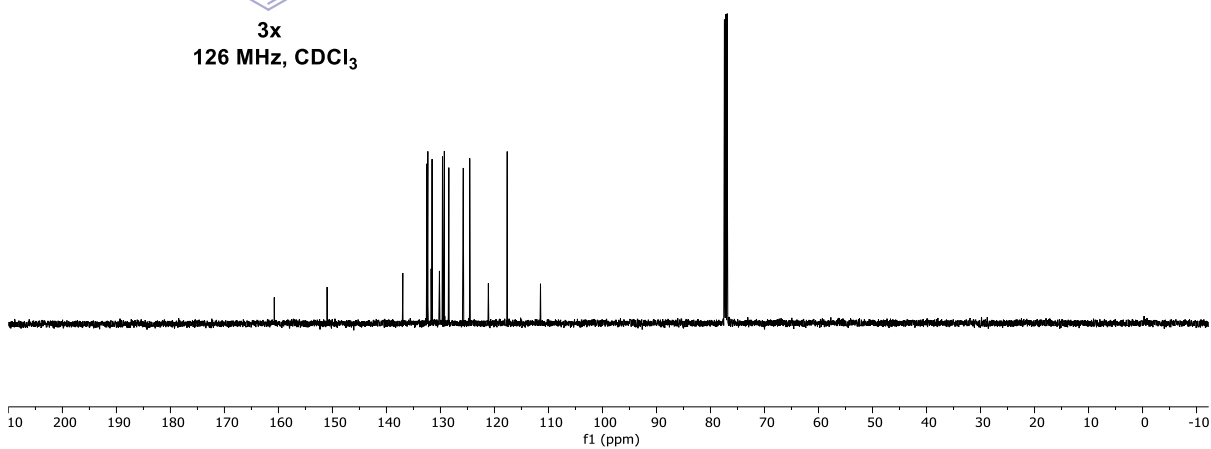
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8.65  
8.63  
8.32  
8.31  
7.94  
7.93  
7.92  
7.91  
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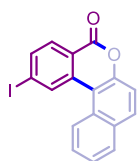


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126 MHz, CDCl<sub>3</sub>

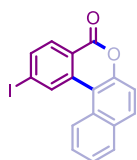
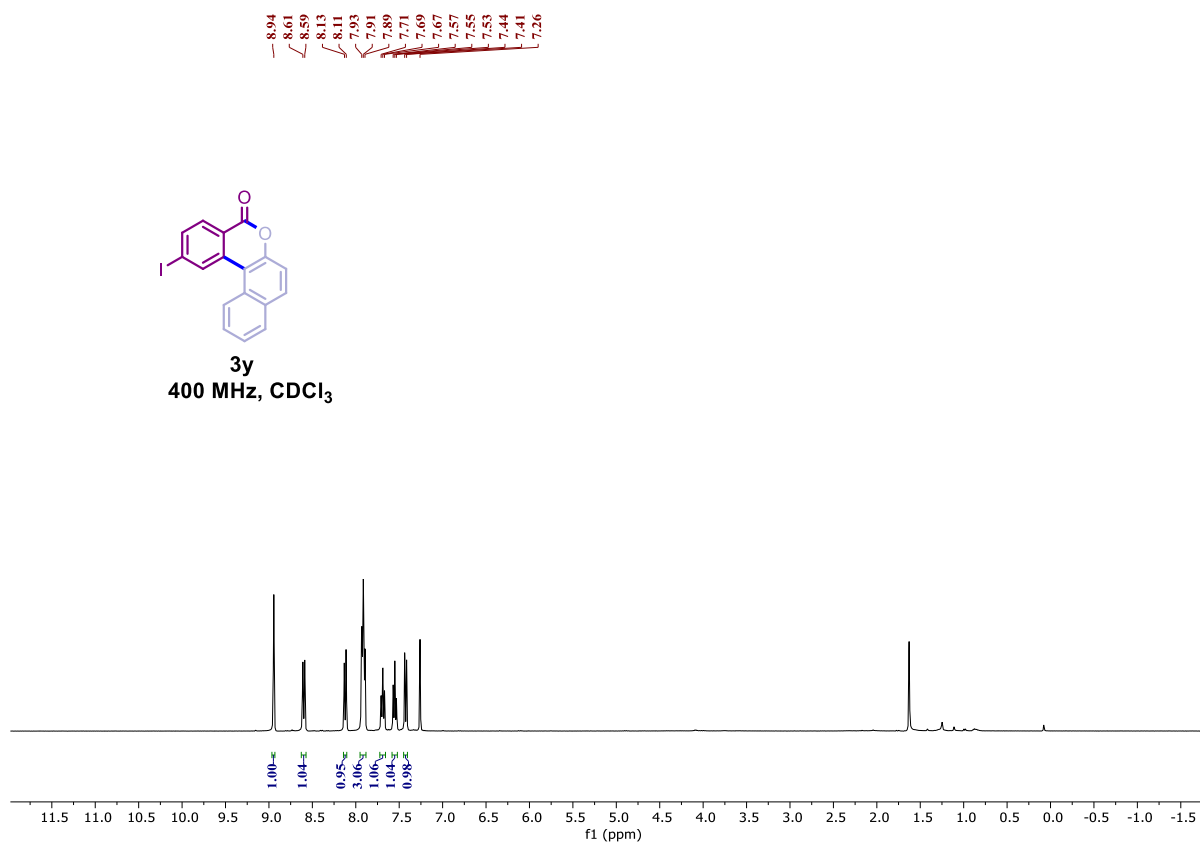
160.77  
150.99  
136.97  
132.51  
132.54  
131.73  
131.55  
130.19  
129.62  
129.40  
128.45  
125.78  
124.58  
121.13  
117.64  
111.48

77.41  
77.16  
76.91

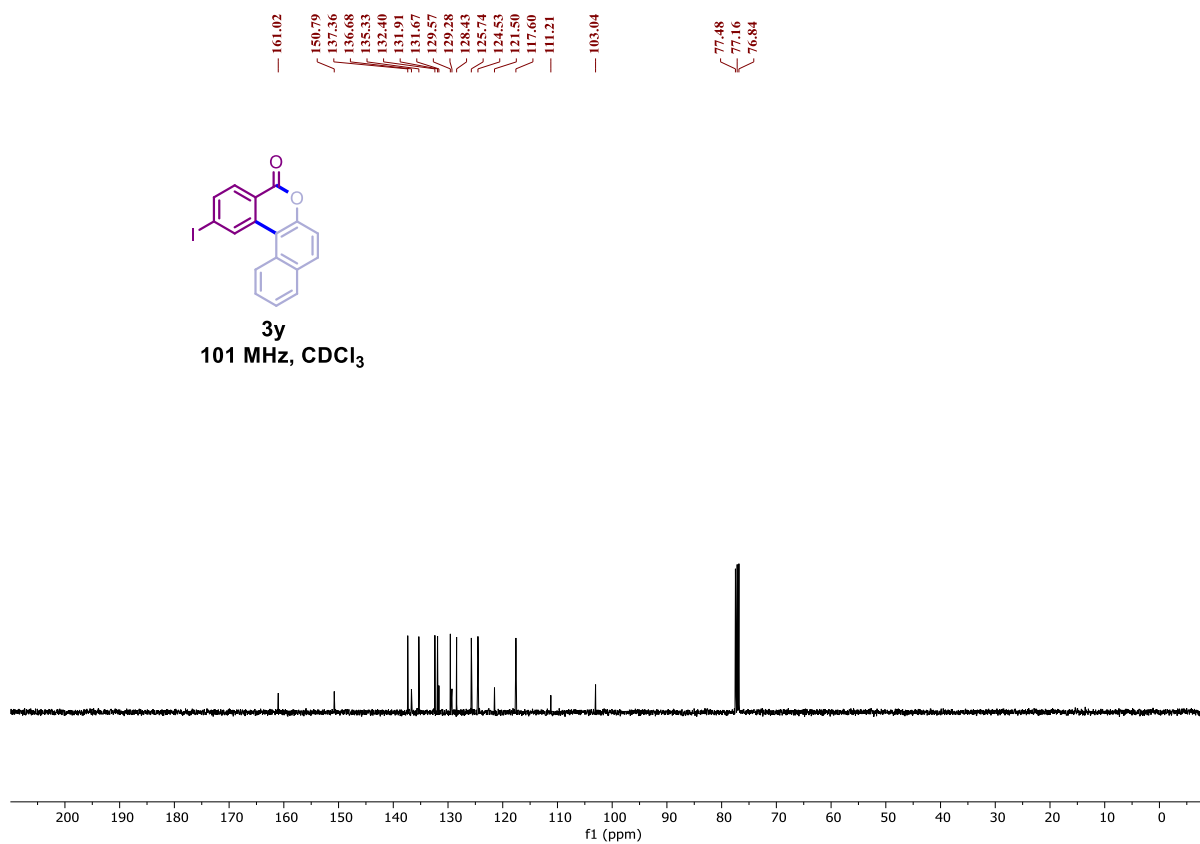


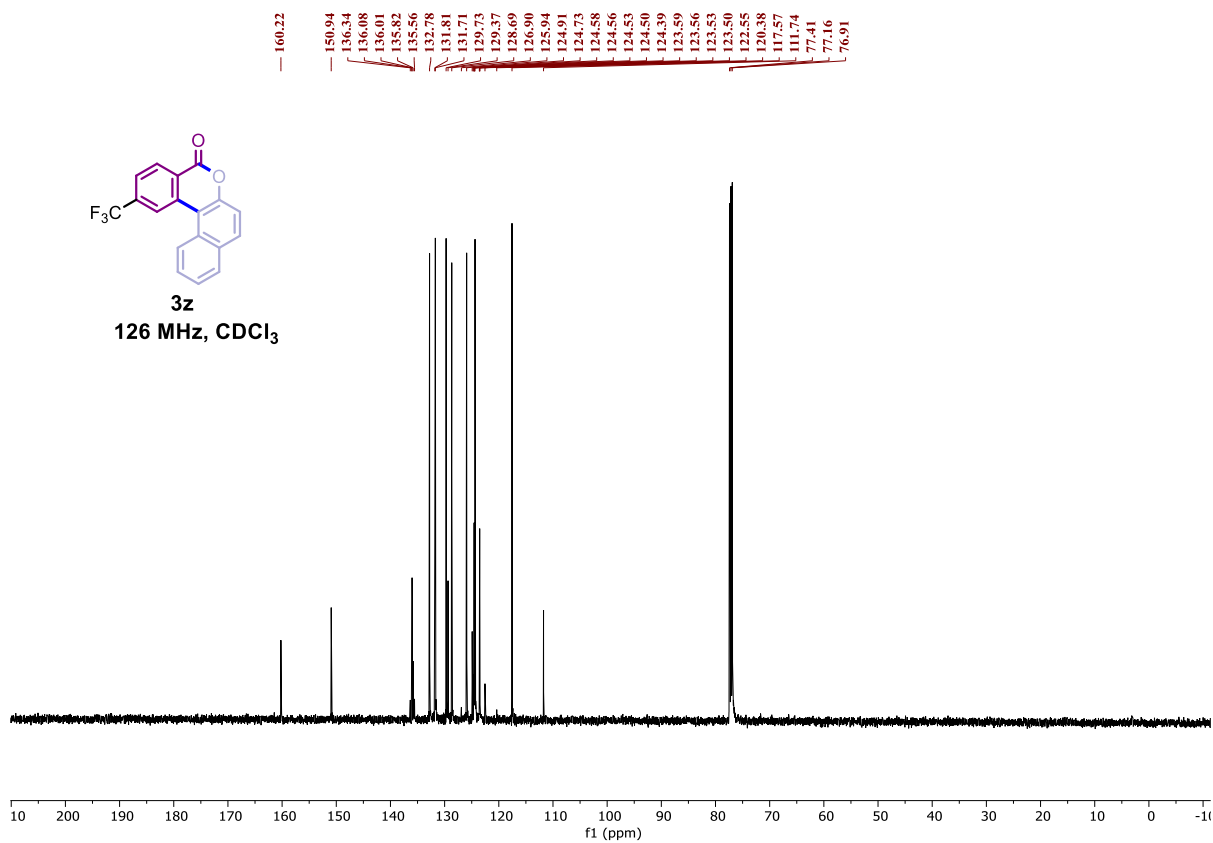
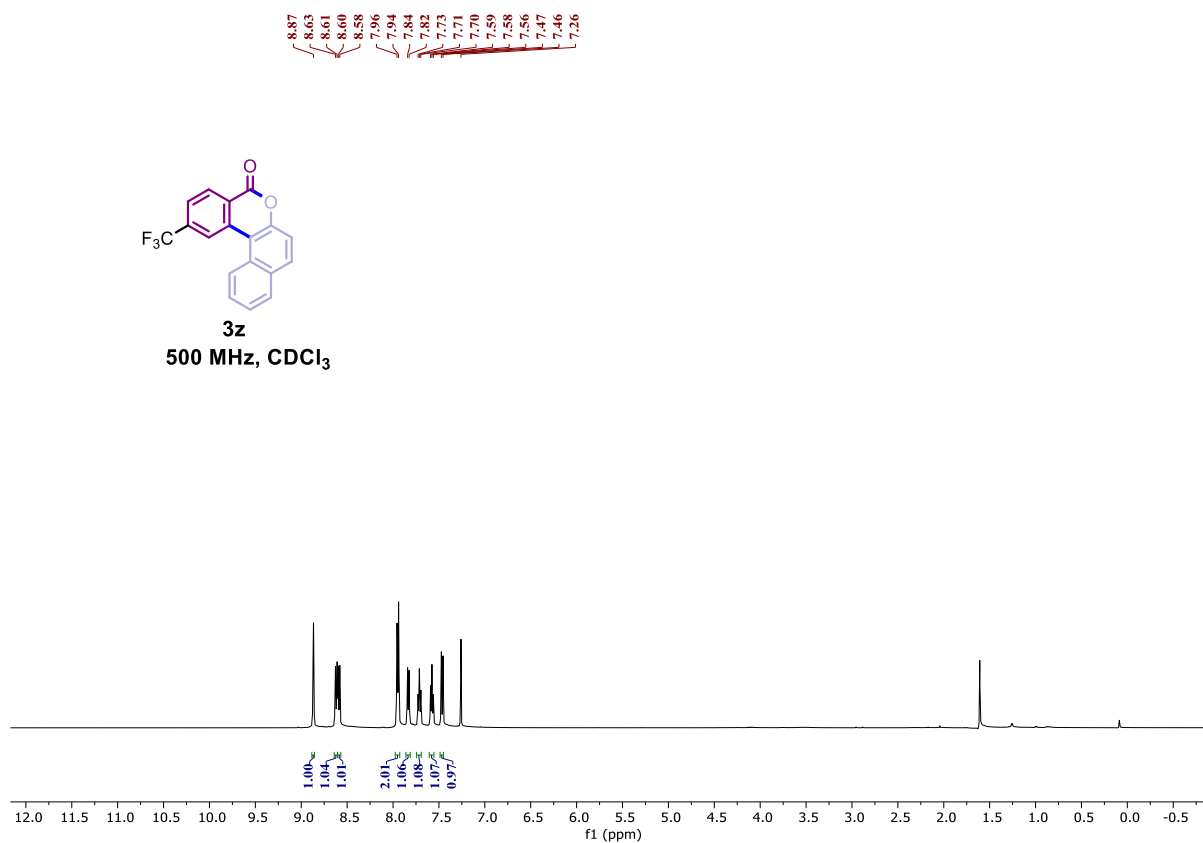


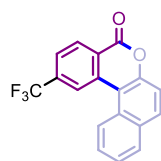
**3y**  
400 MHz, CDCl<sub>3</sub>



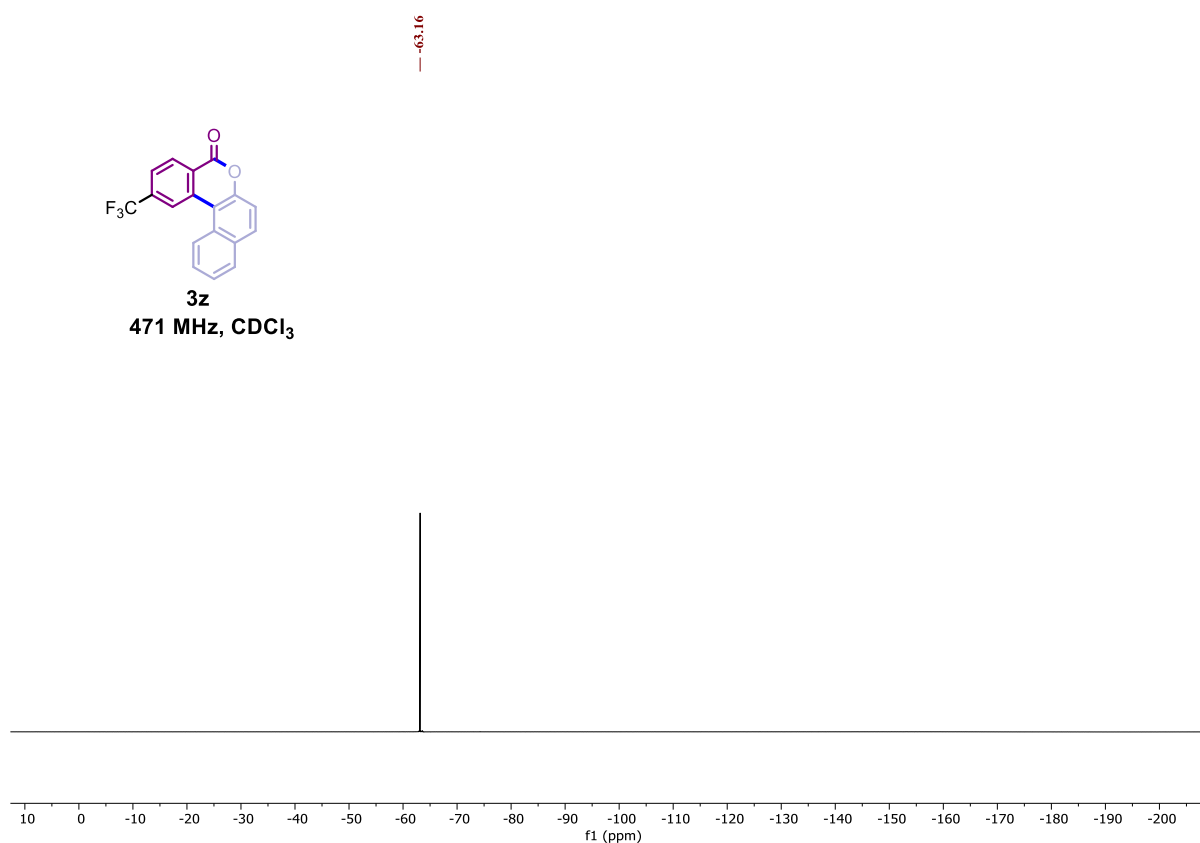
**3y**  
101 MHz, CDCl<sub>3</sub>

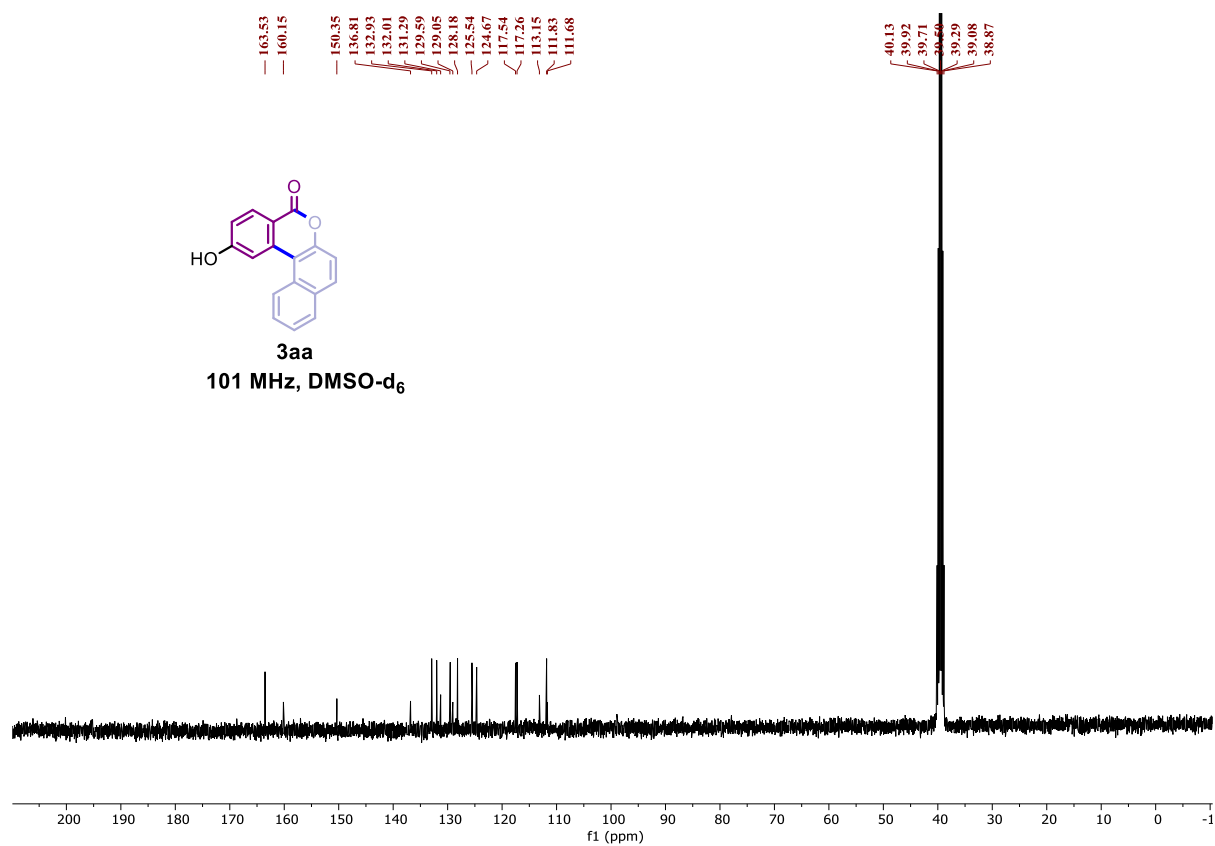
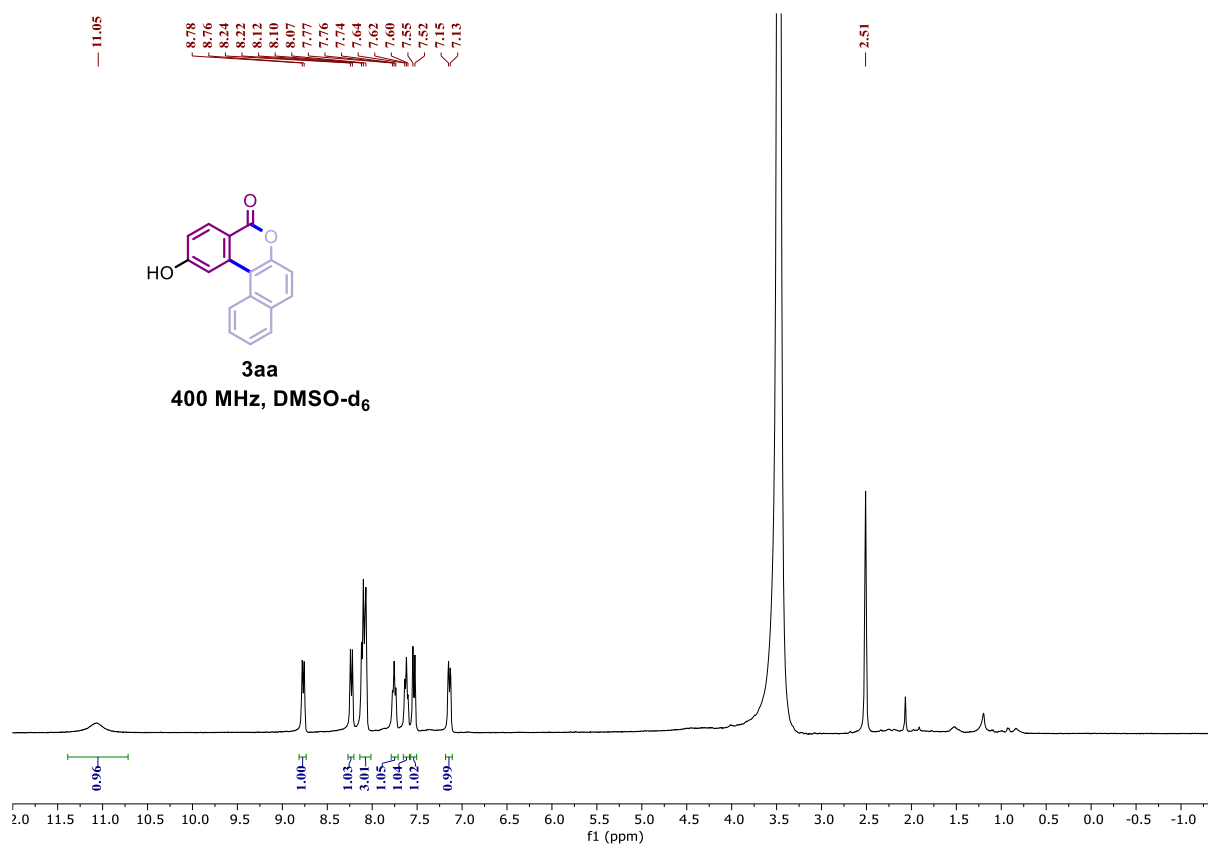


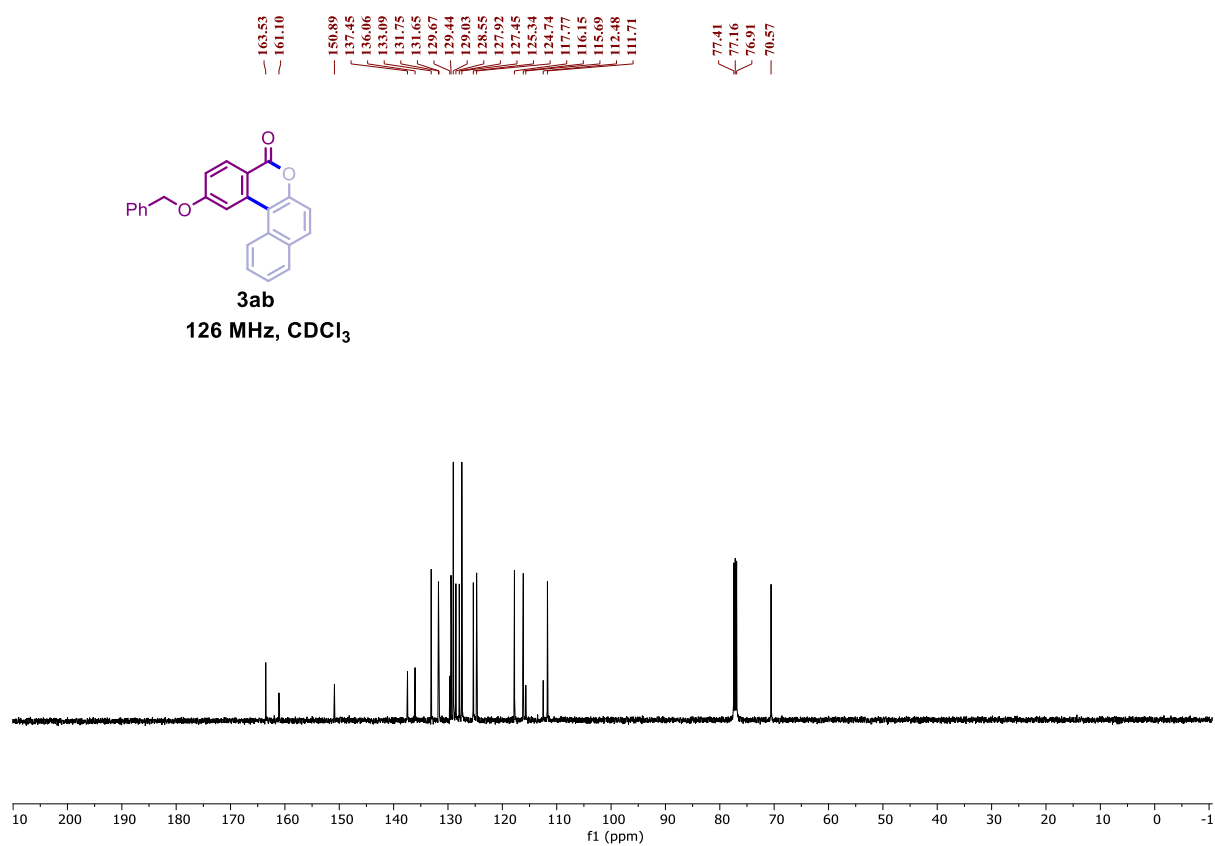
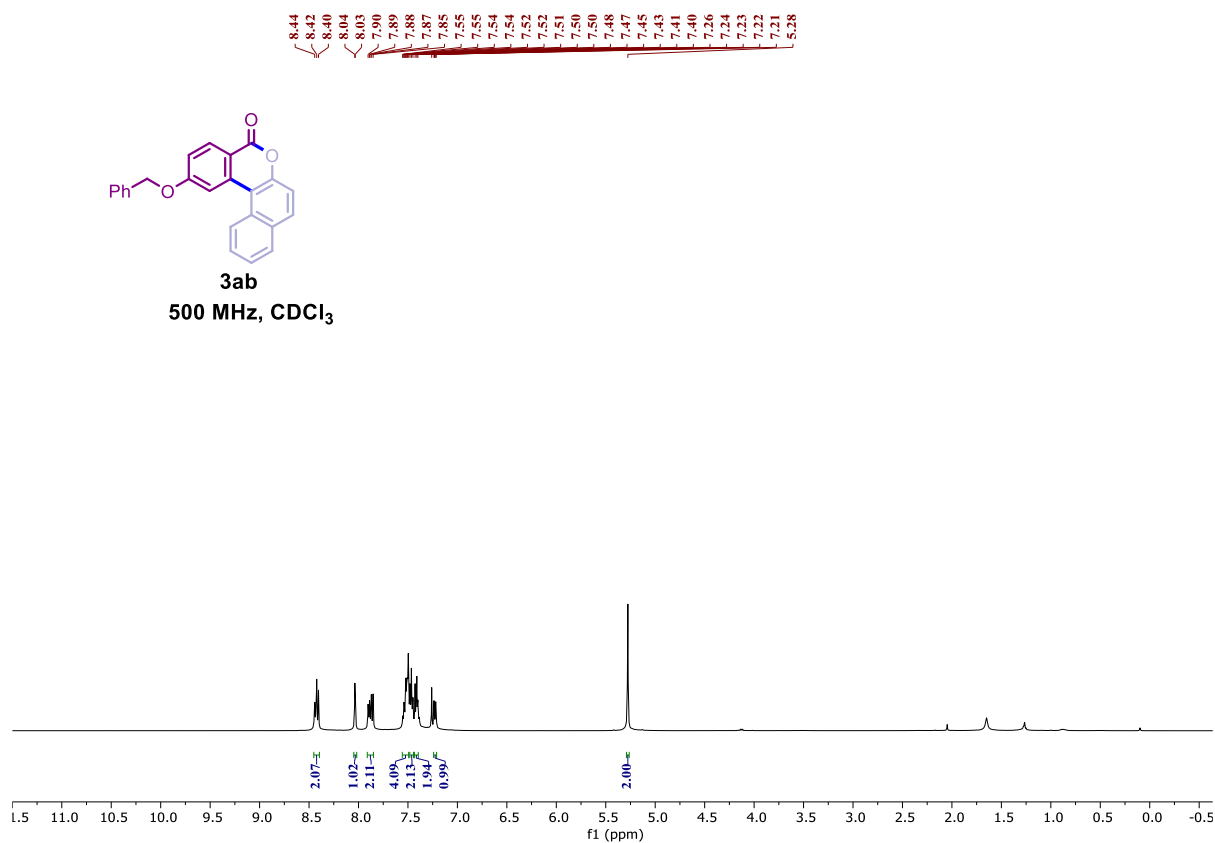


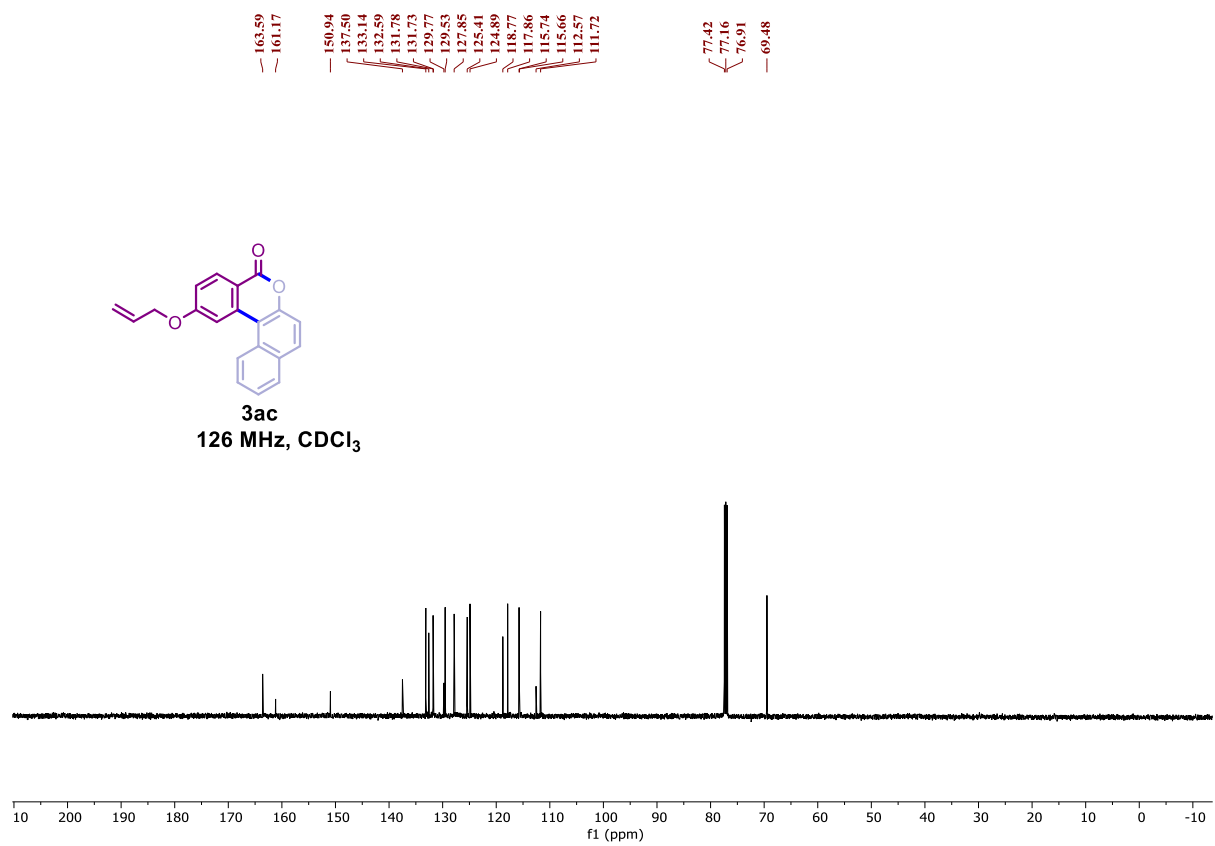
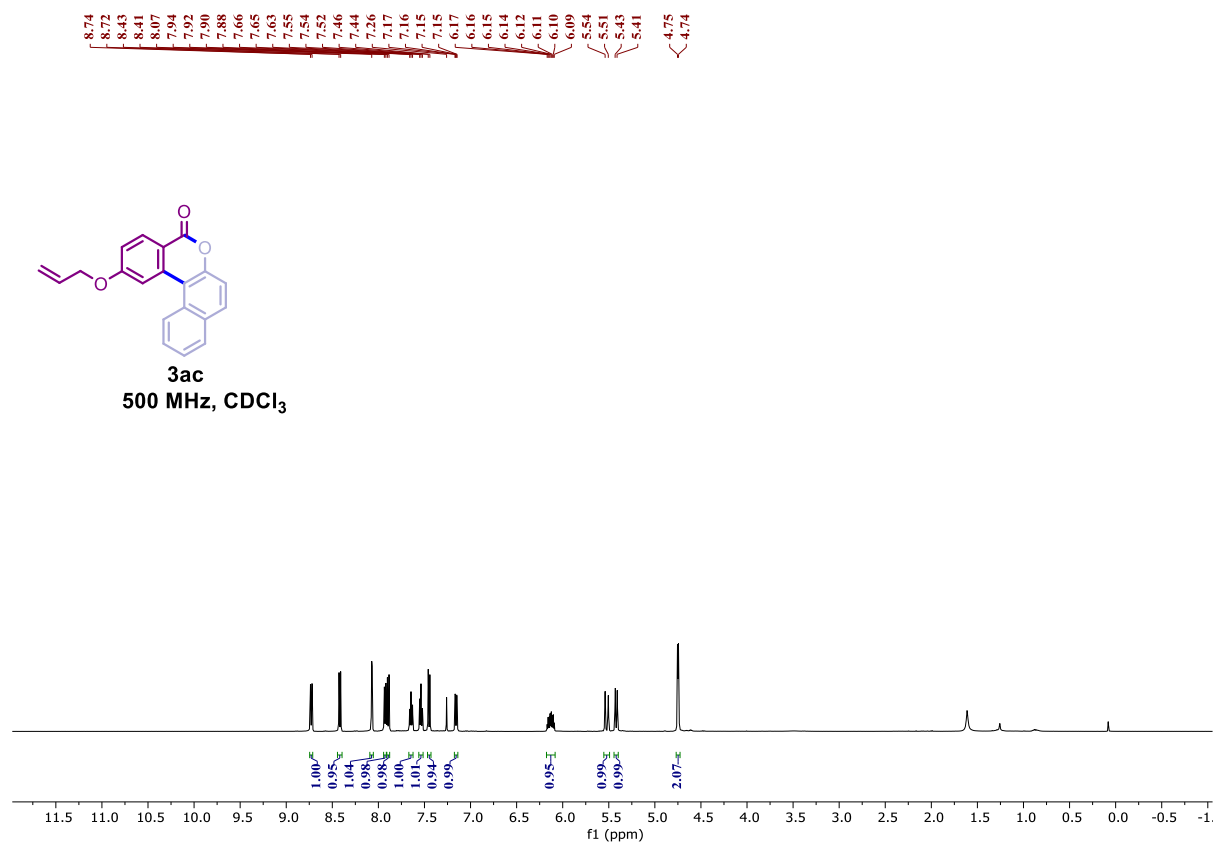


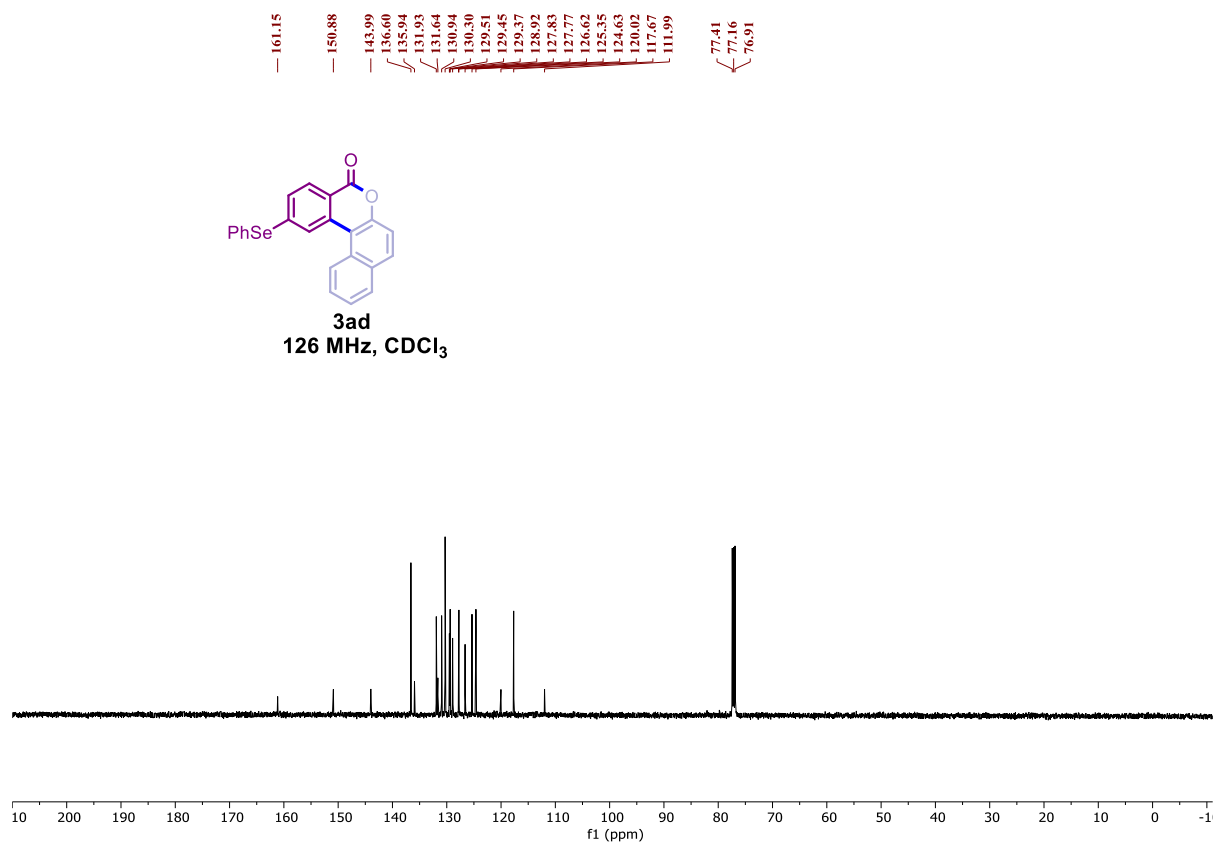
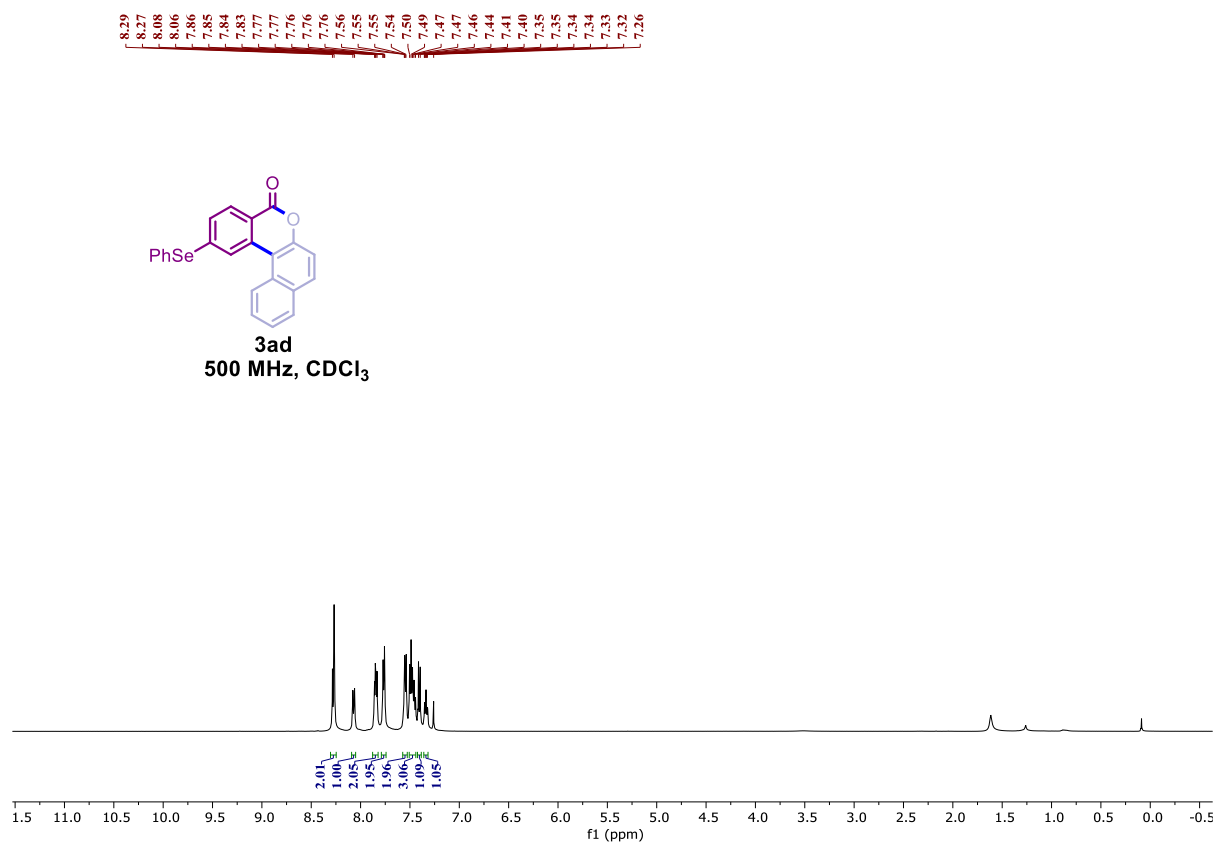
**3z**  
471 MHz, CDCl<sub>3</sub>

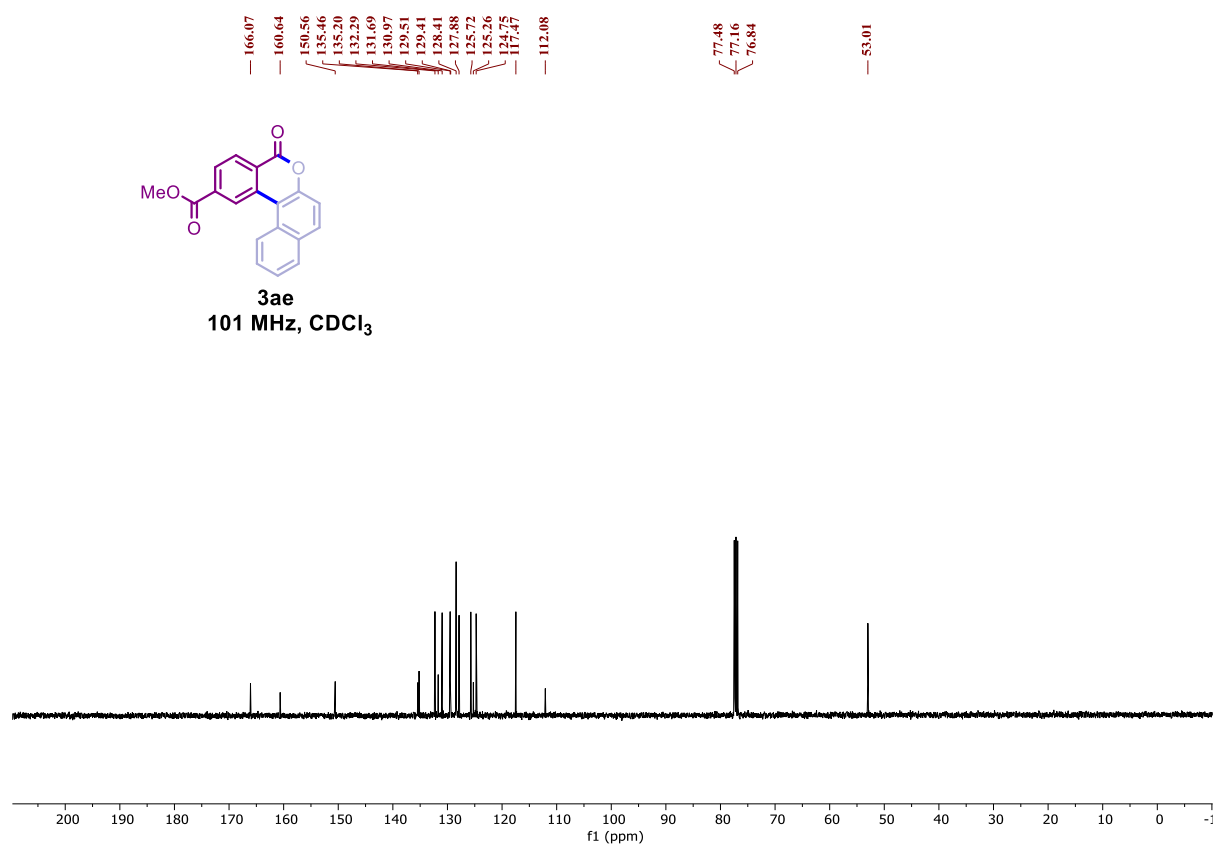
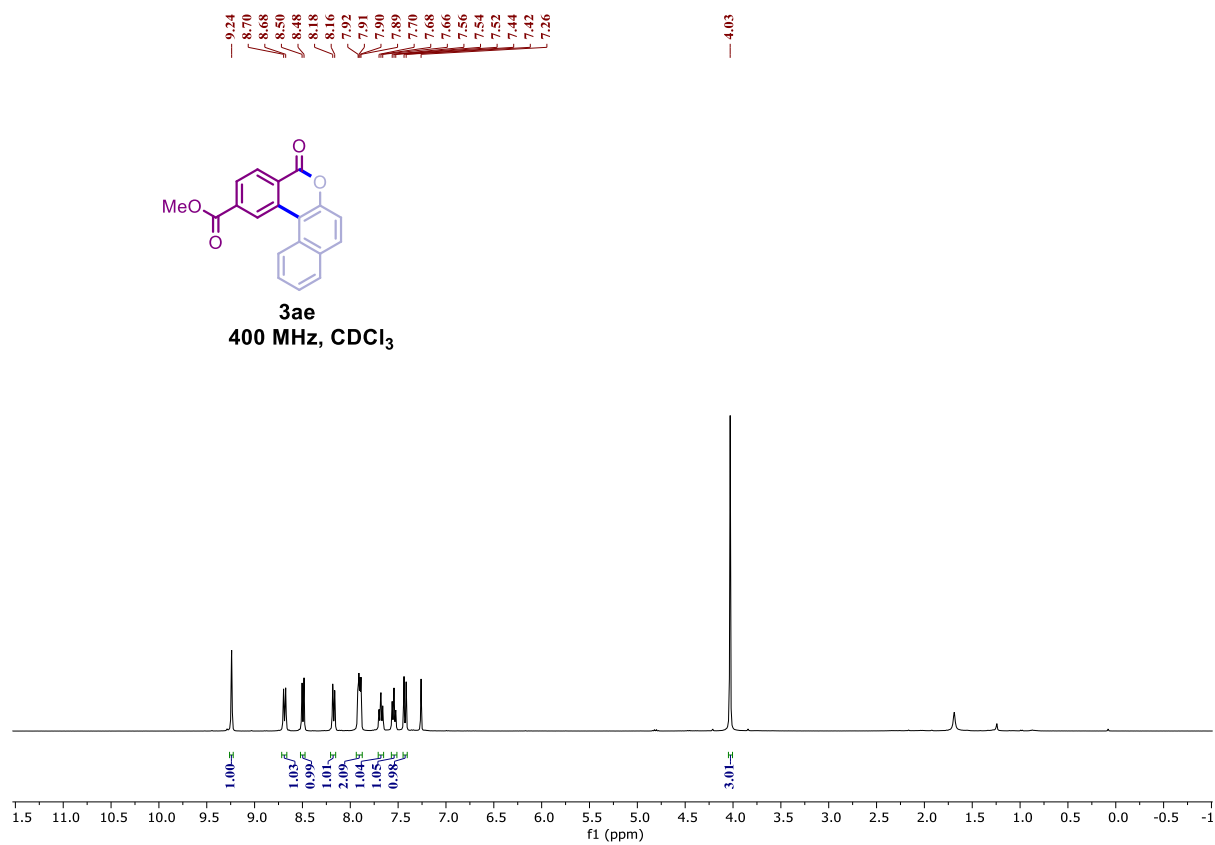


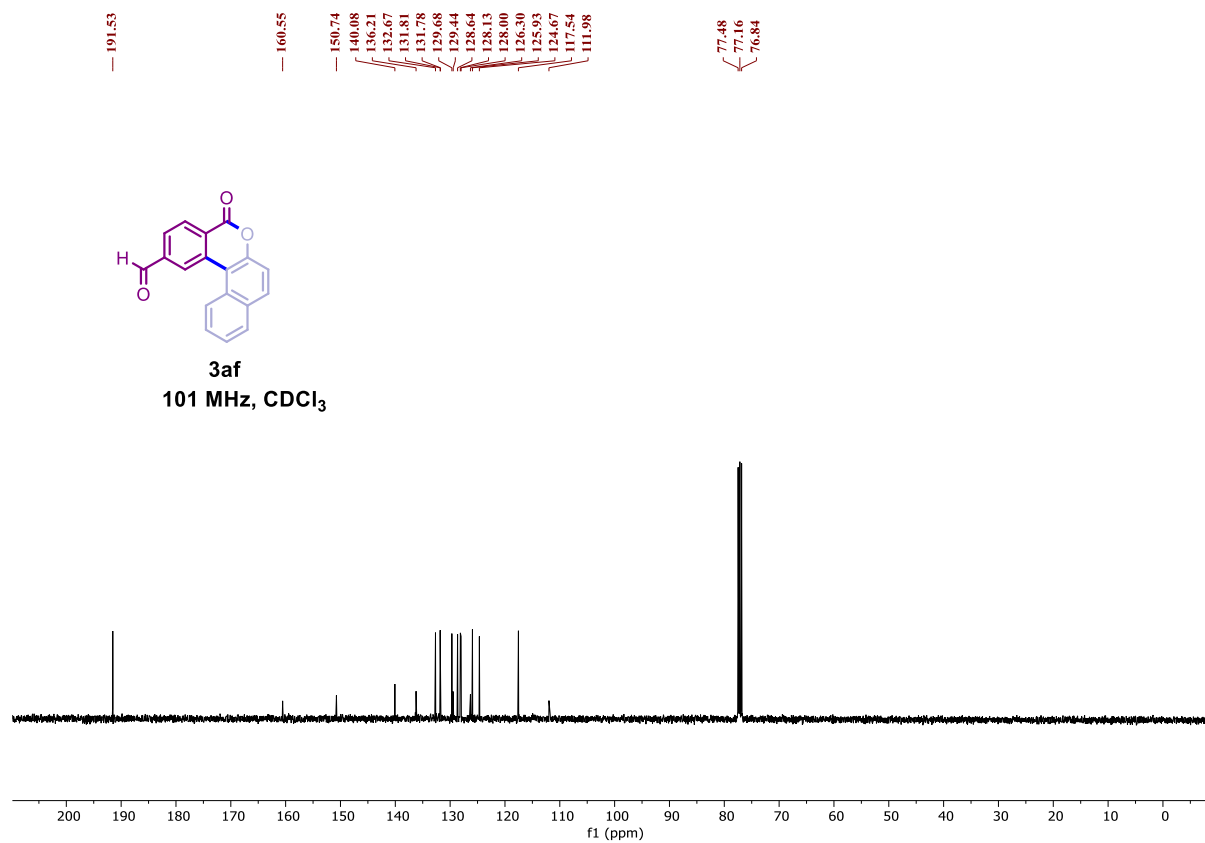
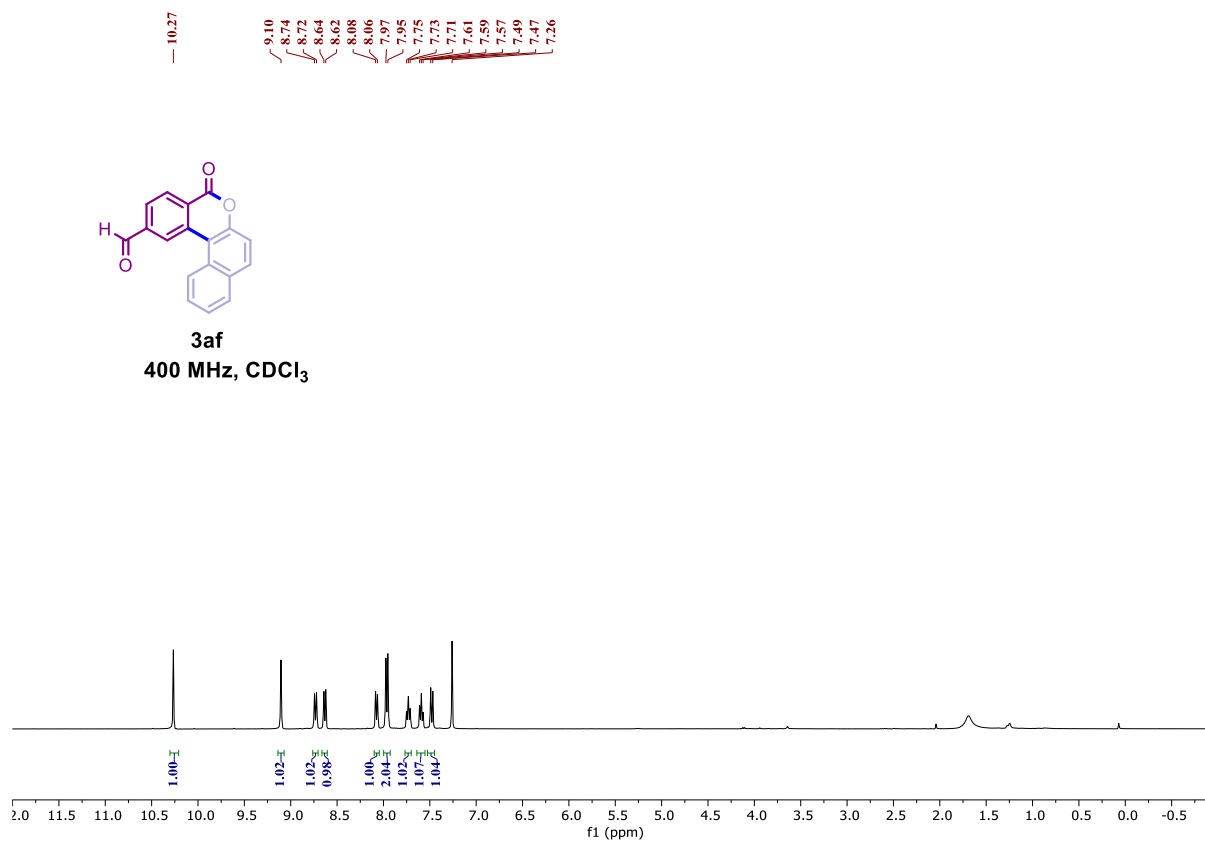


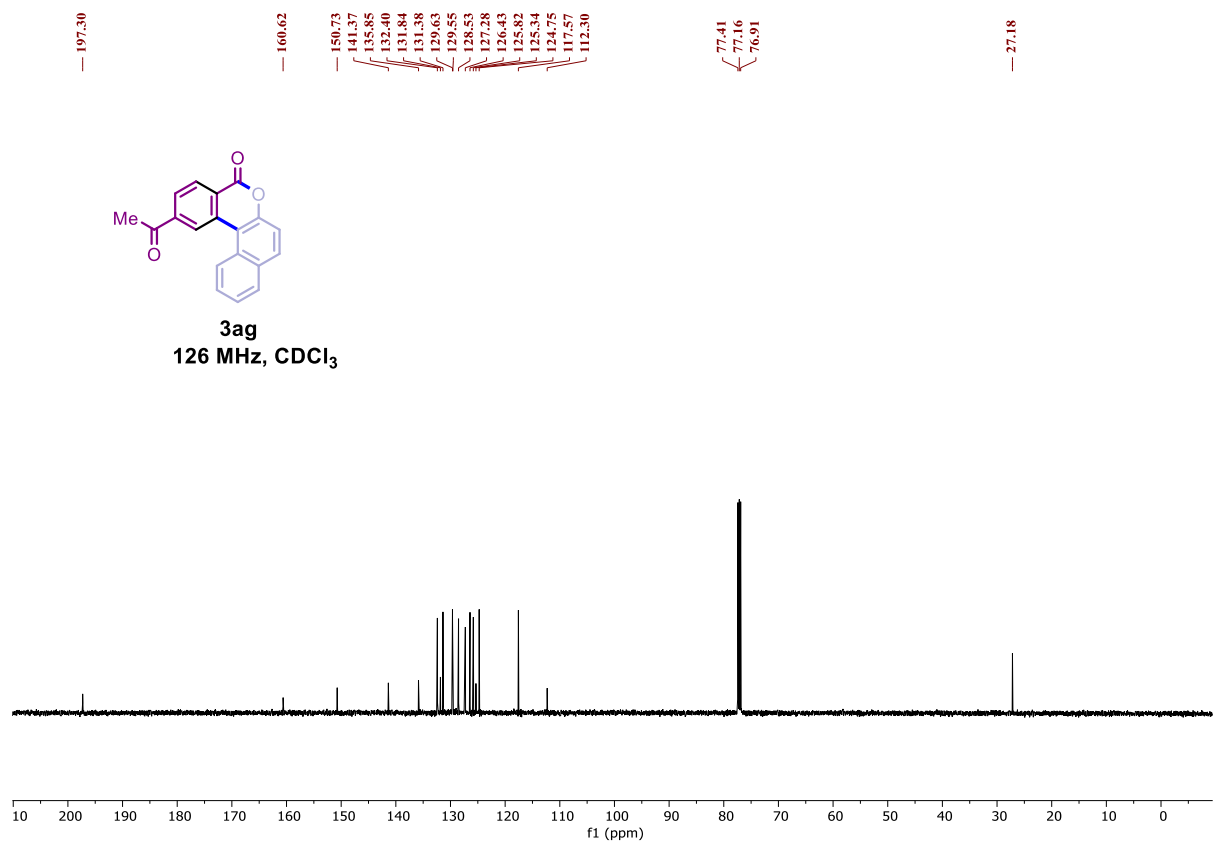
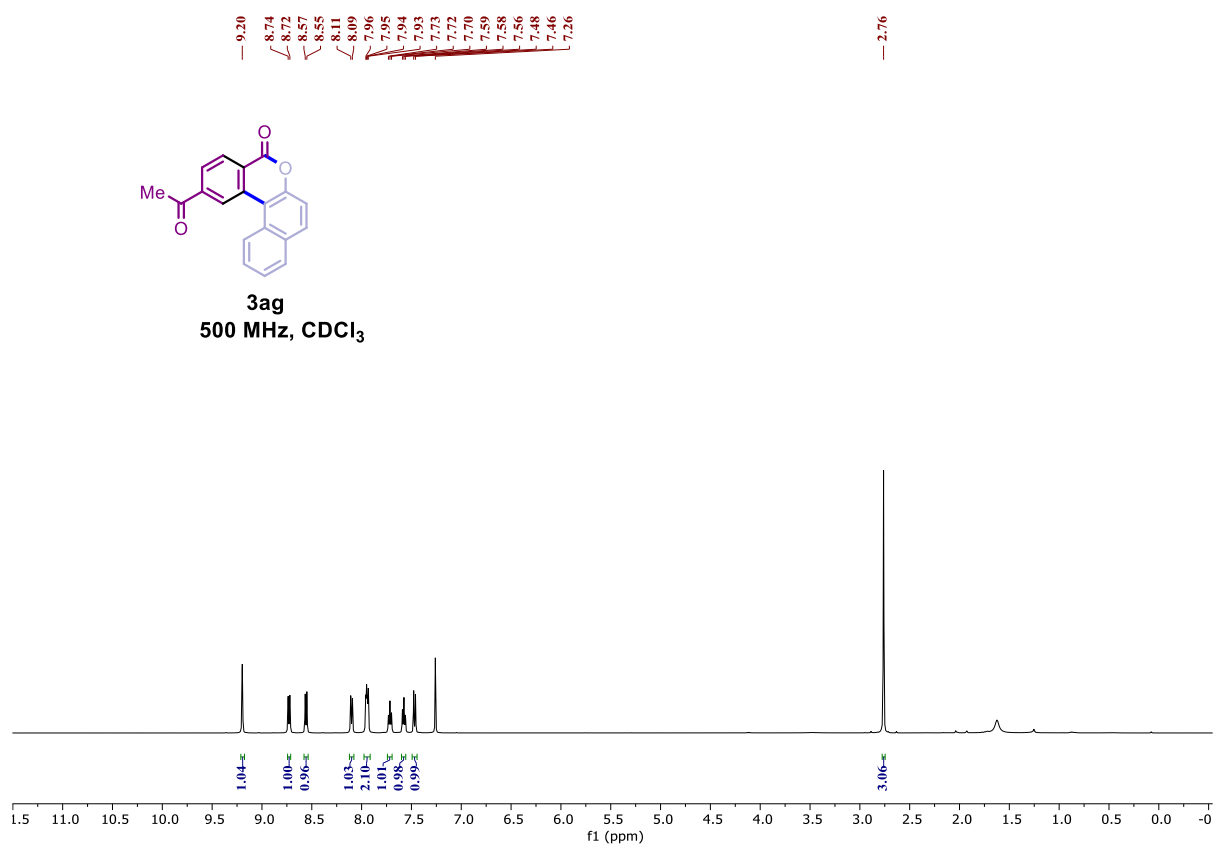


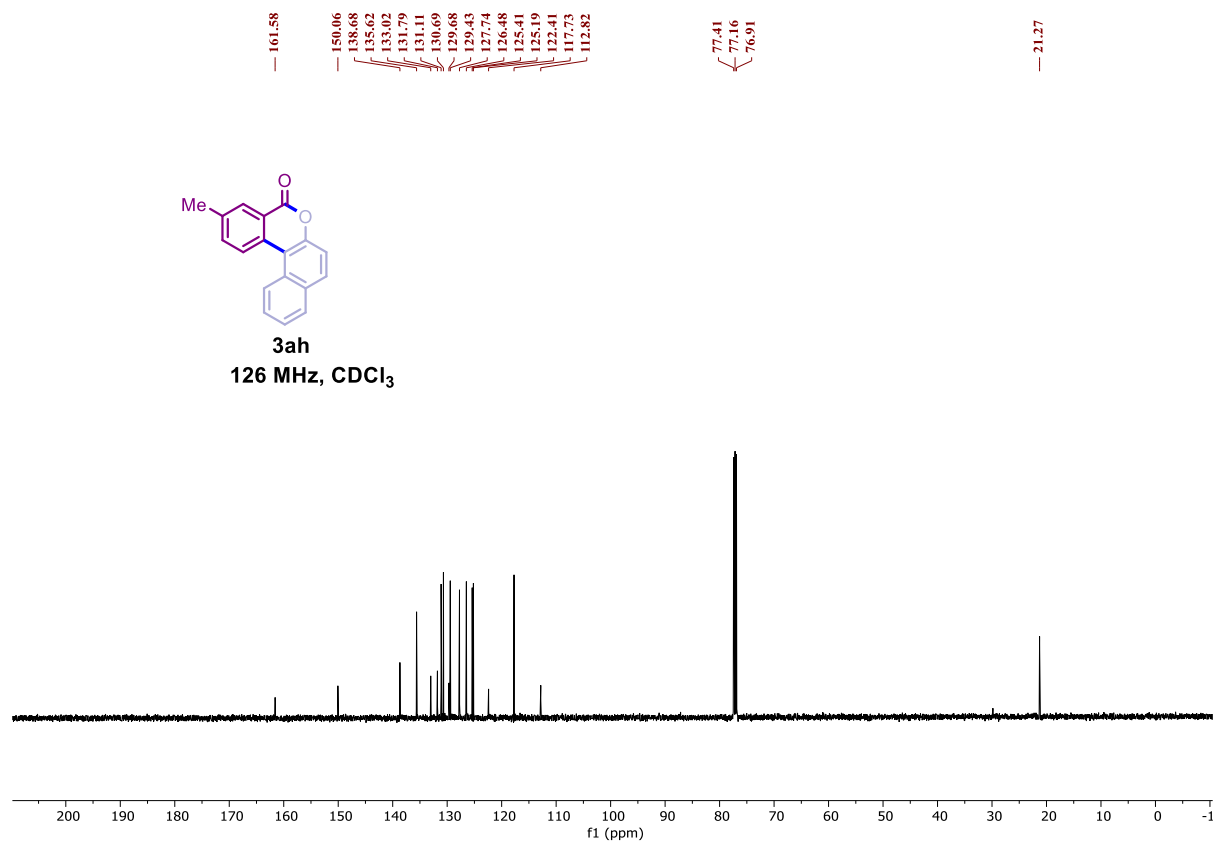
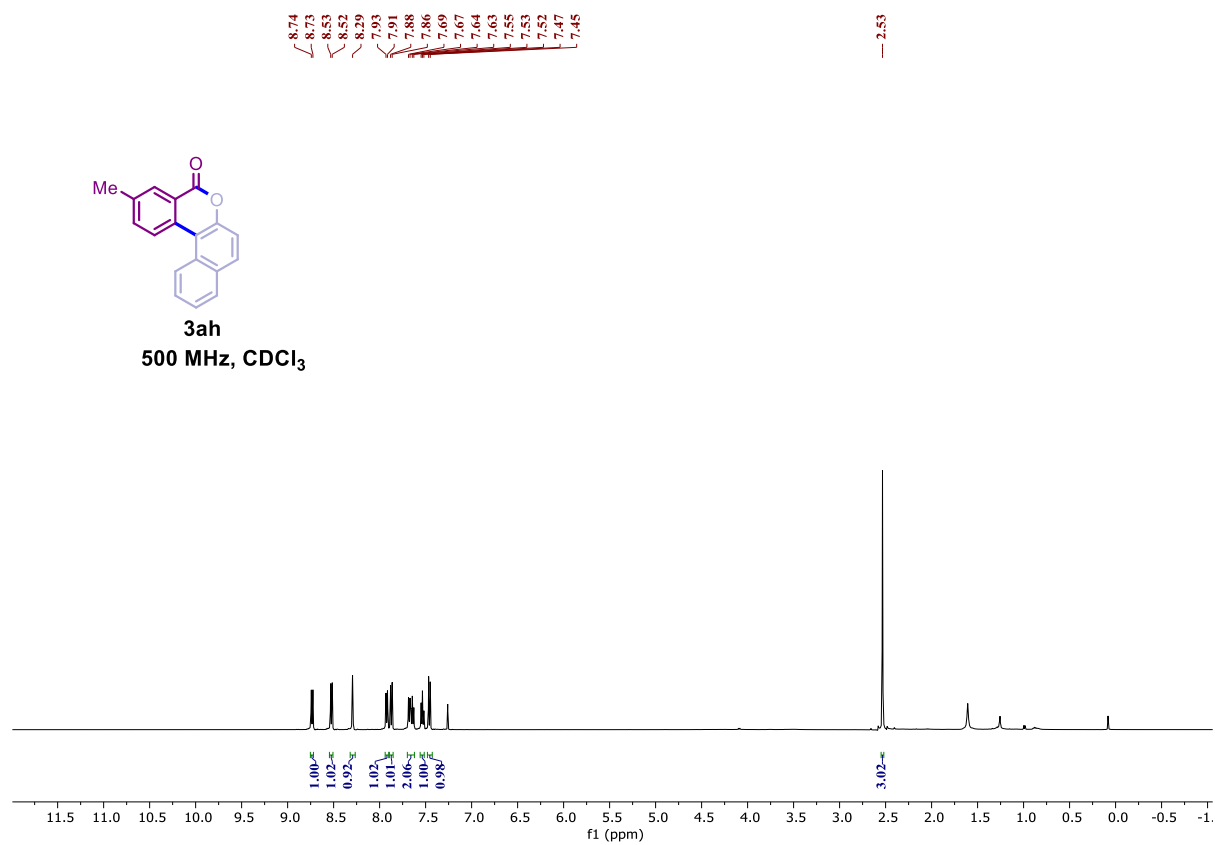


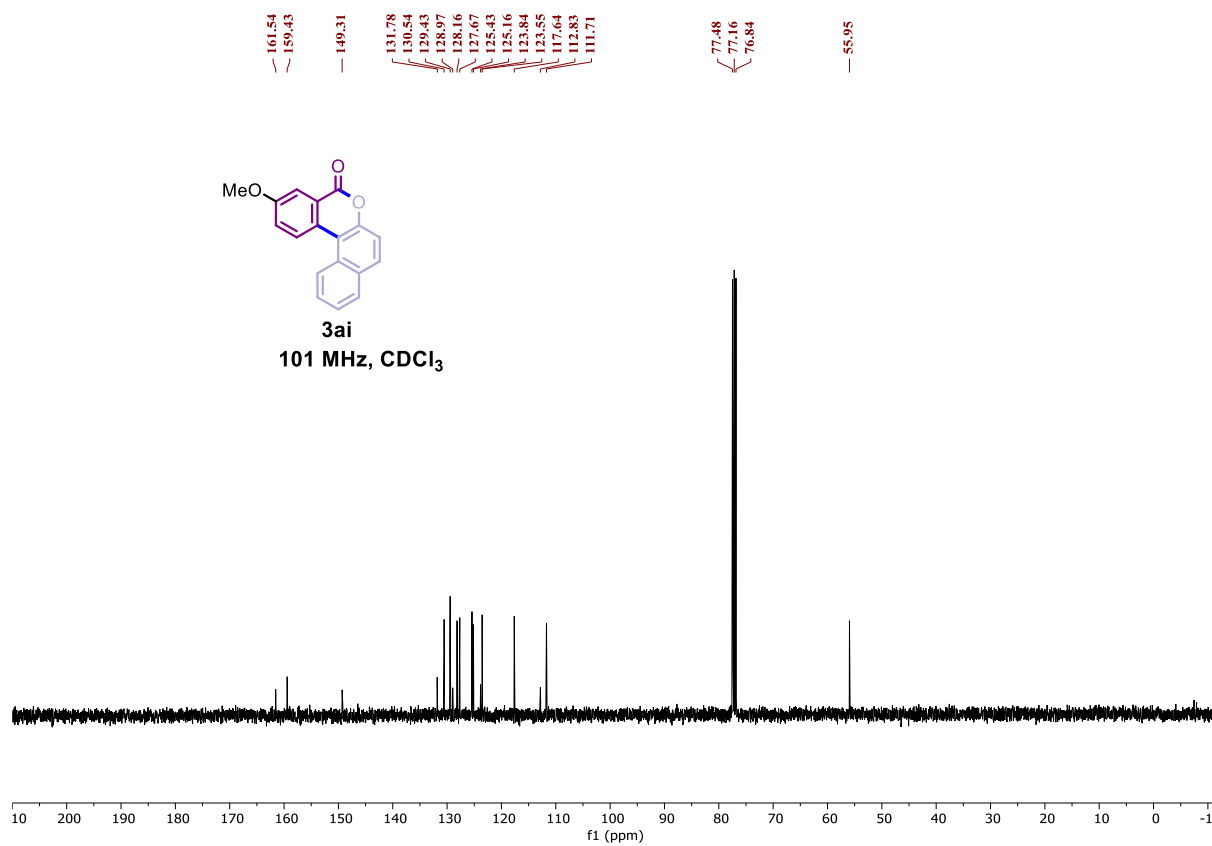
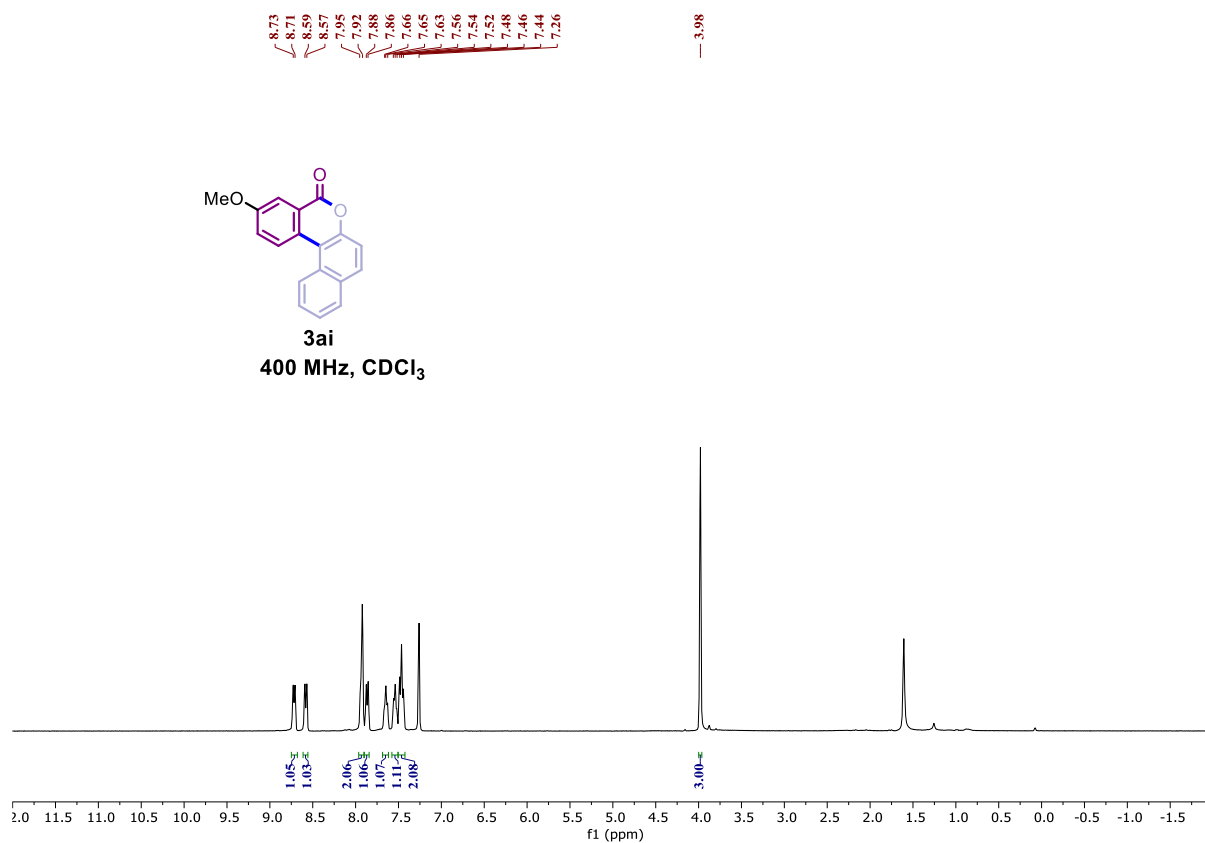


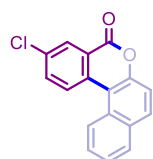




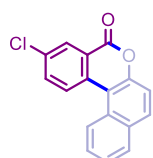
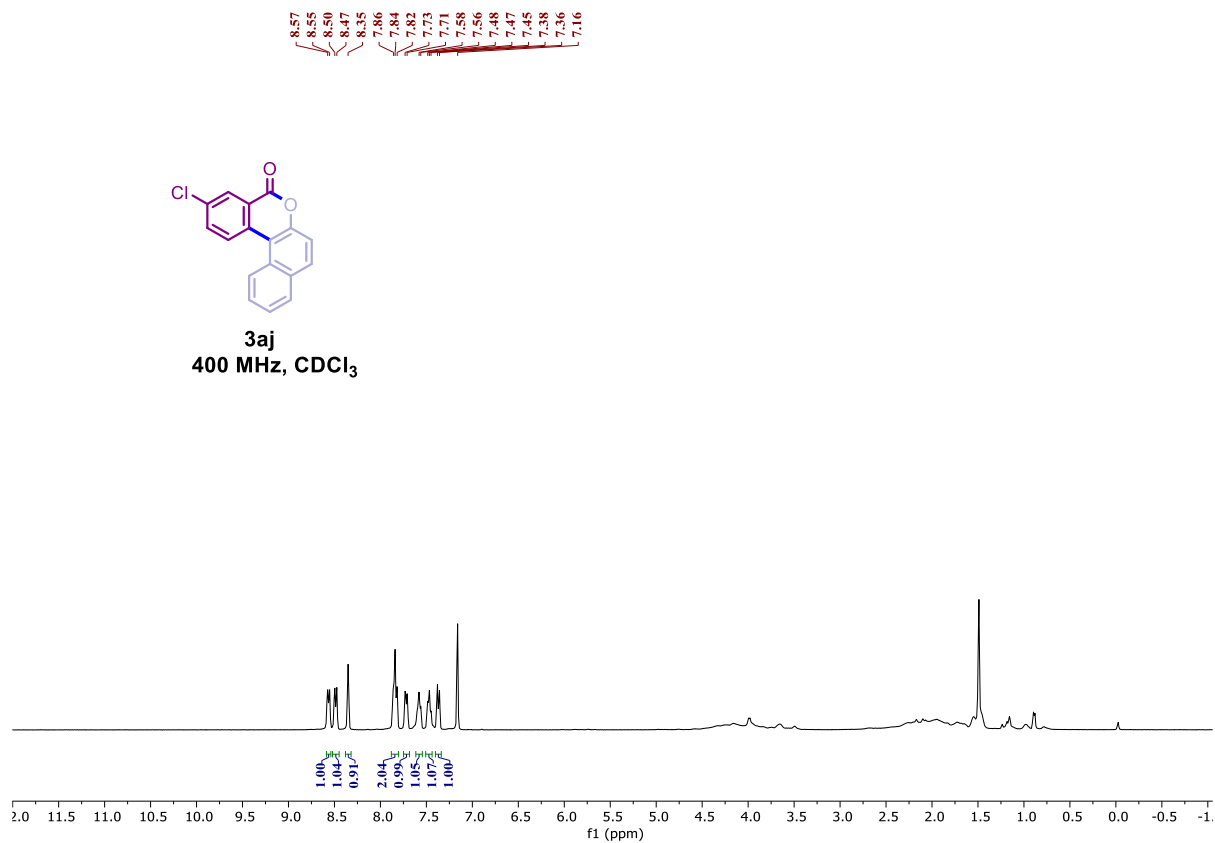




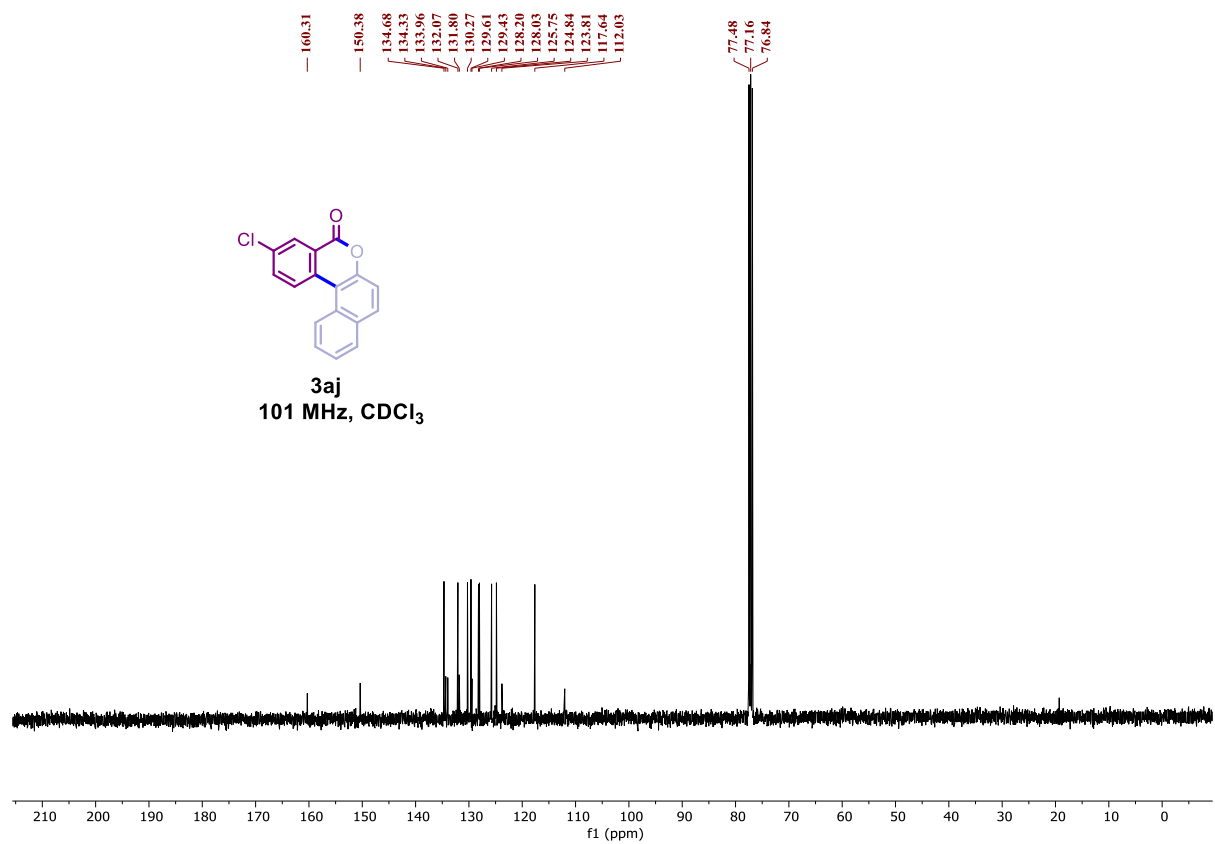




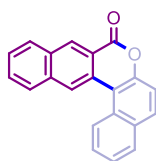
**3aj**  
400 MHz, CDCl<sub>3</sub>



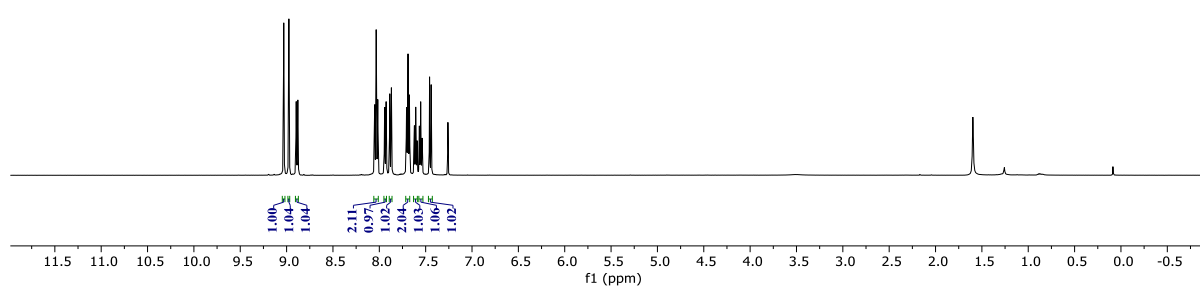
**3aj**  
101 MHz, CDCl<sub>3</sub>



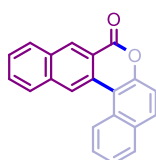
9.03  
8.98  
8.90  
8.88  
8.05  
8.02  
7.94  
7.93  
7.89  
7.87  
7.71  
7.69  
7.68  
7.62  
7.61  
7.59  
7.57  
7.55  
7.54  
7.46  
7.44  
7.26



**3ak**  
500 MHz, CDCl<sub>3</sub>



161.72  
149.80  
136.15  
132.77  
131.95  
131.92  
131.30  
130.13  
129.98  
129.63  
129.49  
129.46  
128.52  
128.01  
127.48  
126.00  
125.46  
125.12  
120.63  
117.87  
112.89  
77.41  
77.16  
76.91



**3ak**  
126 MHz, CDCl<sub>3</sub>

