Electronic Supplementary Material (ESI) for Chemical Communications.

-Electronic Supplementary Information-

Enaminone-directed ruthenium(II)-catalyzed C–H activation and annulation of arenes with diazonaphthoquinones for polycyclic benzocoumarins

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General Information:

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 K_2CO_3/100 mL water. Products were isolated by column chromatography (Merck silica gel 100-200 μm).

^{13}C and ^{1}H NMR spectra were recorded on a Bruker 400 MHz or Bruker 500 MHz spectrometers. Chemical shift values (δ) are reported in ppm and calibrated to the residual solvent peak- $CDCl_3$ δ = 7.26 ppm for ^{1}H, δ = 77.16 for ^{13}C; DMSO-d_6 δ = 2.51 ppm for ^{1}H, δ = 39.5 ppm for ^{13}C; or calibrated to tetramethyl silane (δ = 0.00). All NMR spectra were recorded at ambient temperature (290 K) unless otherwise noted. ^{1}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.

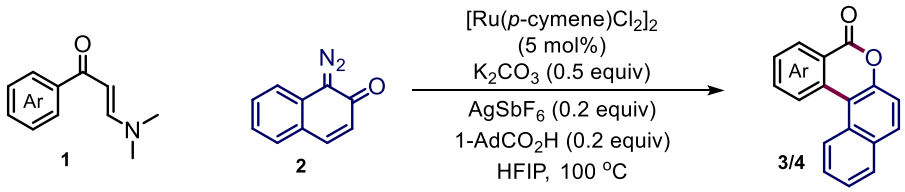
Mass spectra were recorded by electron spray ionization (ESI) method on a Q-TOF Micro with lock spray source. The crystal data were collected and integrated using a Bruker Axs kappa apex 2 CCD diffractometer, with graphite monochromated Mo-Kα radiation.

$[Ru(p\text{-cymene})Cl_2]_2$ was purchased from Alfa Aesar company. Ketones, naphthol, hexafluoroisopropanol (HFIP), organic solvents, and inorganic bases were purchased from Avra chemicals, Spectrochem, and TCI chemicals, and all the compounds were utilized without further purification. All enaminones compounds were synthesized according to previous literature report *(Angew. Chem. Int. Ed.* 2016, **55**, 9384*)*. Diazonaphthoquinones were prepared following previous literature report (*Org. Lett.* 2023, **25**, 2873).

For the complete list of reference 3:

3. (a) L. Ackermann and J. Pospech, *Org. Lett.*, 2011, **13**, 4153; (b) L. Ackermann and S. Fenner, *Org. Lett.*, 2011, **13**, 6548; (c) L. Ackermann, A. V. Lygin and N. Hofmann, *Angew. Chem. Int. Ed.*, 2011, **50**, 6379; (d) B. Li, J. Ma, N. Wang, H. Feng, S. Xu and B. Wang, *Org. Lett.*, 2012, **14**, 736; (e) H. Tan, H. Li, J. Wang and L. Wang, *Chem. Eur. J.*, 2015, **21**, 1904; (f) J. Wu, W. Xu, Z. X. Yu and J. Wang, *J. Am. Chem. Soc.*, 2015, **137**, 9489; (g) A. Bechtoldt, C. Tirler, K. Raghuvanshi, S. Warratz, C. Kornhaaß and L. Ackermann, *Angew. Chem. Int. Ed.*, 2016, **55**, 264; (h) A. Bechtoldt, M. E. Baumert, L. Vaccaro and L. Ackermann, *Green Chem.*, 2018, 20, 398; (i) A. Mandal, G. Mehta, S. Dana and M. Baidya, *Org. Lett.*, 2019, **21**, 5879; (j) Q. Lu, S. Mondal, S. Cembellín, S. Greßies and F. Glorius, *Chem. Sci.*, 2019, **10**, 6560; (k) D. Chowdhury, S. Dana, A. Mandal and M. Baidya, *Chem. Commun.*, 2019, **55**, 11908; (l) S. Dana, P. Dey, S. A. Patil and M. Baidya, *Chem Asian J.*, 2020, **15**, 564; (m) S. Kumar, A. M. Nair, C. M. R. Volla, *Org. Lett.*, 2020, **22**, 2141; (n) D. Chowdhury, S. Dana, S. Maity and M. Baidya, *Org. Lett.*, 2020, **22**, 6760; (o) S. Dana, C. K. Giri and M. Baidya, *Chem. Commun.*, 2020, **56**, 13048; (p) C. K. Giri, S. Dana and M. Baidya, *Chem. Commun.*, 2021, **57**, 10536; (q) C. K. Giri, S. Dana and M. Baidya, *Chem Asian J.*, 2022, **17**, *e202200861*; (r) N. Aravindan, V. Vinayagam and M. Jeganmohan, *Org. Lett.*, 2022, **24**, 5260.

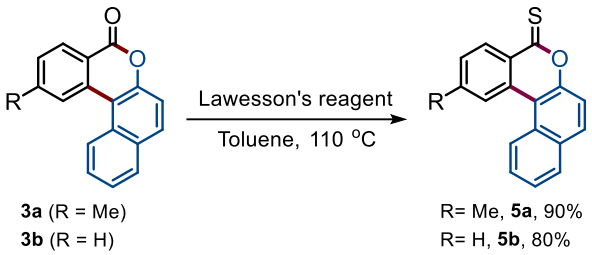
Typical Ruthenium(II)-Catalyzed Annulation Between Enaminone (1) and Diazonaphthoquinone (2):



To an oven dried pressure tube (10 × 1.5 cm), corresponding enaminone **1** (0.2 mmol, 1.0 equiv), diazonaphthoquinone **2** (1.5 equiv), [Ru(*p*-cymene)Cl_2]$_2$ (5.0 mol %), K_2CO_3 (0.5 equiv) and 1-AdCOOH (0.2 equiv) were taken. Silver hexafluoroantimonate (20 mol %) was weighed in a glass vial inside the glove-box and then added to the reaction tube under the flow of nitrogen. Next, hexafluoroisopropanol (1.0 mL) 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 Na_2SO_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 polycyclic benzocoumarin **3**/**4.**

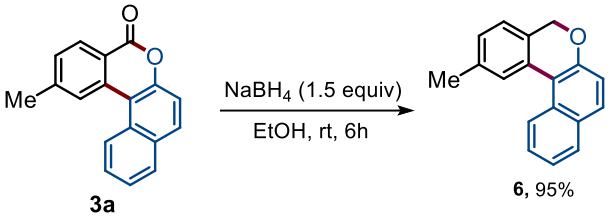
Post-synthetic manipulations

Synthesis of compounds 5a and 5b:



To an oven-dried screw cap reaction tube (10 × 1.5 cm), corresponding coumarin (**3a** or **3b**, 0.2 mmol) in toluene (1.0 mL) was taken. Then, Lawesson's reagent (1.0 equiv) was added and the mixture was stirred for 3 h at 110 °C. The solvent was removed under reduced pressure and the residue was purified by silica gel column chromatography with a gradient eluent of hexane/EtOAc = (95/05) to get pure compound (**5a** or **5b**).

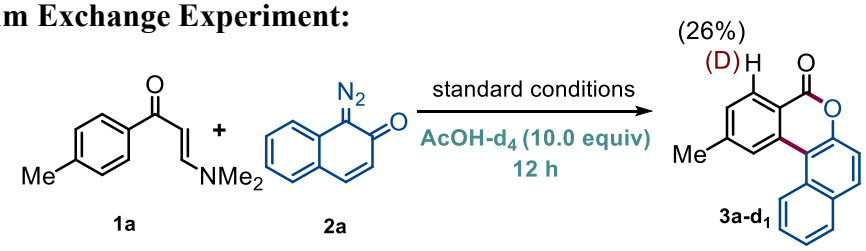
Synthesis of compound 6:



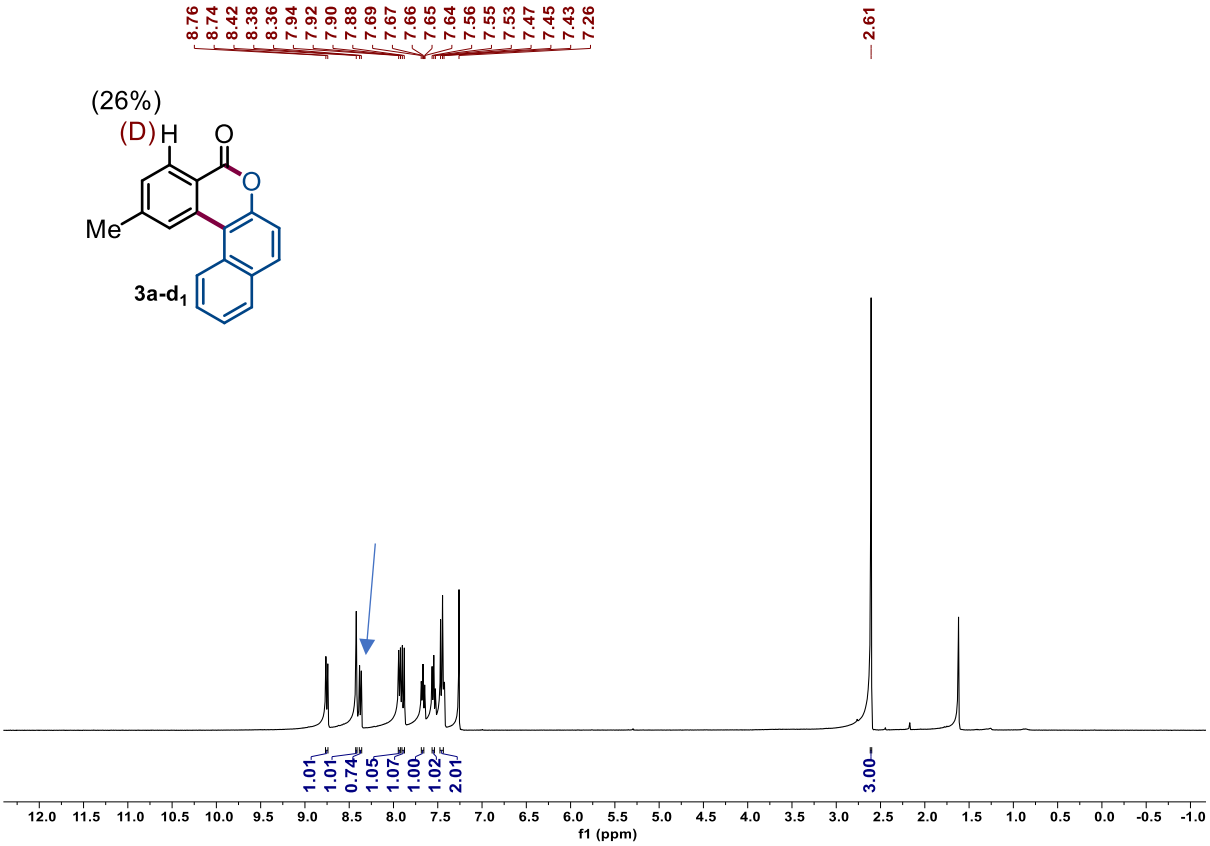
To an oven-dried screw cap reaction tube (10 × 1.5 cm), compound **3a** (0.2 mmol) in EtOH (1.0 mL) was taken. Then $NaBH_4$ (1.5 equiv) was added and the mixture was stirred for 6 h at rt. The solvent was removed under reduced pressure and the residue was purified by silica gel column chromatography with a gradient eluent of hexane/EtOAc = (95/25) to get pure compound **6**.

Mechanistic Studies:

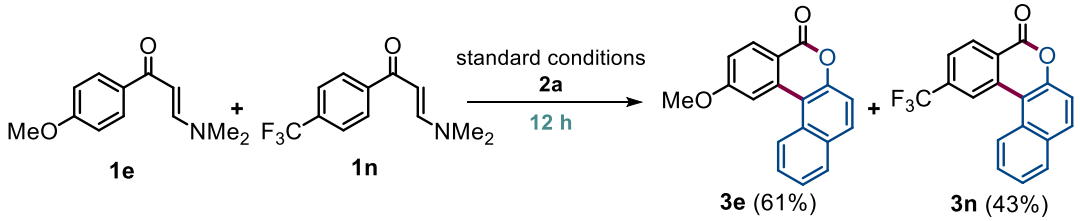
(i) Deuterium Exchange Experiment:



To an oven-dried pressure tube (10 × 1.5 cm), enaminone **1a** (0.2 mmol, 1.0 equiv), diazonaphthoquinone **2a** (1.5 equiv), $[Ru(p\text{-cymene})Cl_2]_2$ (5.0 mol %), K_2CO_3 (0.5 equiv), 1-AdCOOH (0.2 equiv) and AcOH-d_4 (10 equiv) were taken. Silver hexafluoroantimonate (20 mol %) was weighed in a glass vial inside the glove-box and then added to the tube under the flow of nitrogen. Then hexafluoroisopropanol (1.0 mL) was added and the reaction tube was capped. The reaction mixture was 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 Na_2SO_4. After evaporation under reduced pressure, the resulting residue was purified by column chromatography on silica gel with a gradient eluent of Hexane/EtOAc = (10/90) to get the pure product. The H/D-scrambling was observed through ^1H NMR spectroscopy.



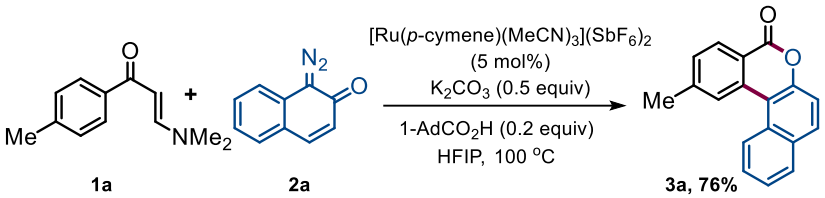
(ii) Competition Experiment:



To an oven-dried pressure tube (10 × 1.5 cm), enaminones **1e** and **1n** (0.2 mmol, 1:1 mixture), diazonaphthoquinone (**2a**, 1.5 equiv), [Ru(*p*-cymene)Cl_2]$_2$ (5.0 mol %), K_2CO_3 (0.5 equiv), 1-AdCOOH (0.2 equiv) were taken. Silver hexafluoroantimonate (20 mol %) was weighed in a glass vial inside the glove box and then added to the reaction tube under the flow of nitrogen. Next, hexafluoroisopropanol (1 mL) was added and the reaction tube was capped. The reaction mixture was then stirred at 100 ^oC for 12 h. Afterwards, 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 Na_2SO_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 yield pure polycyclic benzocoumarins **3e** and **3n**. The ratio of yield of **3e** and **3n** was 1.4:1.

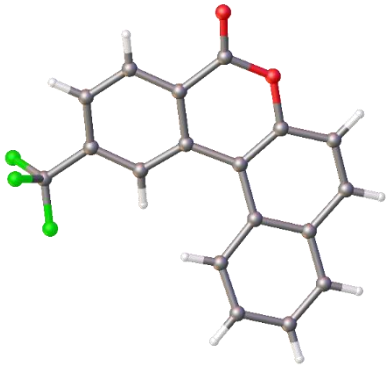
(iii) Reaction with the Cationic Complex:



To an oven-dried pressure tube (10 × 1.5 cm), enaminone **1a** (0.2 mmol, 1.0 equiv), diazonaphthoquinone **2a** (1.5 equiv), {[Ru(*p*-cymene)(MeCN)$_3$](SbF$_6$)$_2$} (5.0 mol %), K_2CO_3 (0.5 equiv), 1-AdCOOH (0.2 equiv) were taken. Next, hexafluoroisopropanol (1.0 mL) was added and the reaction tube was capped. The reaction mixture was then stirred at 100 ^oC for 24 h. After that, 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 Na_2SO_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 yield pure polycyclic benzocoumarin **3a** (40 mg, 76%).

Crystallographic Experimental Section: Crystals of compound **3n** were obtained through a slow evaporation technique at room temperature from hexane/DCM solvent mixture.

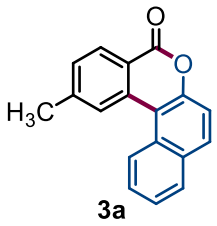
X-ray crystal data of compound 3n: (CCDC 2284004, Ellipsoid Probability 50%)



Identification code	**3n**
Empirical formula	C18 H9 F3 O2
Formula weight	314.25

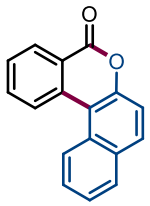
Temperature	298(2) K
Wavelength	0.71073 A
Crystal system, space group	Triclinic, P -1
Unit cell dimensions	a = 10.9295(9) A alpha = 103.951(3) deg. b = 11.7939(9) A beta = 106.880(3) deg. c = 17.2156(13) A gamma = 91.212(3) deg.
Volume	2050.9(3) A^3
Z, Calculated density	6, 1.527 Mg/m^3
Absorption coefficient	0.126 mm^-1
F(000)	960
Crystal size	0.207 x 0.119 x 0.049 mm
Theta range for data collection	2.453 to 25.000 deg.
Limiting indices	-12<=h<=12, -14<=k<=14, -20<=l<=20
Reflections collected / unique	73634 / 7202 [R(int) = 0.2233]
Completeness to theta = 25.000	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7452 and 0.6607
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	7202 / 204 / 678
Goodness-of-fit on F^2	1.119
Final R indices [I>2sigma(I)]	R1 = 0.1169, wR2 = 0.2837
R indices (all data)	R1 = 0.2058, wR2 = 0.3493
Extinction coefficient	n/a
Largest diff. peak and hole	0.322 and -0.479 e.A^-3

NMR Spectroscopic Data of Synthesized Compounds



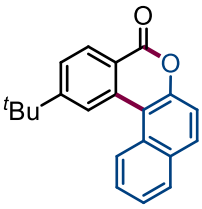
3a

2-Methyl-5H-dibenzo[c,f]chromen-5-one (3a): White solid; Eluent: 5–10% EtOAc in Hexane; yield = 94% (49 mg); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.70 (d, *J* = 8.7 Hz, 1H), 8.37 – 8.33 (m, 2H), 7.90 (d, *J* = 9.4 Hz, 1H), 7.85 (d, *J* = 8.9 Hz, 1H), 7.64 (dd, *J* = 9.3, 6.2 Hz, 1H), 7.54 – 7.51 (m, 1H), 7.43 – 7.39 (m, 2H), 2.58 (s, 3H) ppm; **^{13}C NMR** (126 MHz, $CDCl_3$) δ 161.4, 150.5, 145.4, 135.5, 131.7, 131.4, 130.8, 129.7, 129.5, 129.4, 127.7, 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.



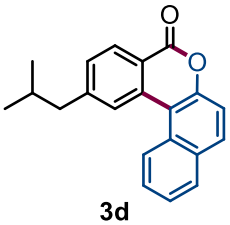
3b

5H-Dibenzo[c,f]chromen-5-one (3b): White solid; Eluent: 5–10% EtOAc in Hexane; yield = 84% (42 mg); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.76 (d, *J* = 8.6 Hz, 1H), 8.64 (d, *J* = 8.3 Hz, 1H), 8.50 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.95 – 7.87 (m, 3H), 7.68 – 7.61 (m, 2H), 7.57 – 7.53 (m, 1H), 7.48 (d, *J* = 10.2 Hz, 1H) ppm; **^{13}C NMR** (126 MHz, $CDCl_3$) δ 161.4, 150.5, 135.6, 134.4, 131.8, 131.7, 130.9, 129.7, 129.5, 128.3, 127.9, 126.5, 125.5, 125.2, 122.6, 117.7, 112.7 ppm; **HRMS** (ESI) m/z: [M+H]+ Calcd. For $C_{17}H_{11}O_2^+$ 247.0754 Found 247.0765.



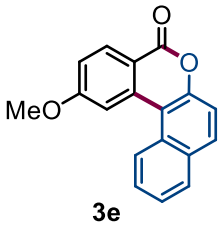
3c

2-(Tert-butyl)-5H-dibenzo[c,f]chromen-5-one (3c): White solid; Eluent: 5–10% EtOAc in Hexane; yield = 86% (52 mg); Melting point: 160–162 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.75 (d, *J* = 8.7 Hz, 1H), 8.66 (s, 1H), 8.43 (d, *J* = 8.3 Hz, 1H), 7.94 (dd, *J* = 18.4, 8.5 Hz, 2H), 7.70 (d, *J* = 6.2 Hz, 2H), 7.58 – 7.54 (m, 1H), 7.51 – 7.48 (m, 1H), 1.48 (s, 9H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 161.5, 158.3, 150.5, 135.4, 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



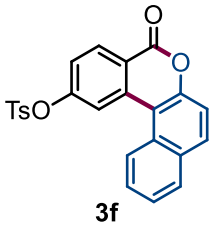
3d

2-Isobutyl-5H-dibenzo[c,f]chromen-5-one (3d): White solid; Eluent: 5–10% EtOAc in Hexane; yield = 82% (50 mg); Melting point: 158–160 ^{o}C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.75 (d, *J* = 8.7 Hz, 1H), 8.42 – 8.40 (m, 2H), 7.94 (d, *J* = 8.1 Hz, 1H), 7.90 (d, *J* = 8.8 Hz, 1H), 7.70 – 7.65 (m, 1H), 7.57 – 7.53 (m, 1H), 7.48 (d, *J* = 9.5 Hz, 1H), 7.43 (d, *J* = 8.0, 2.8 Hz, 1H), 2.73 (d, *J* = 7.3 Hz, 2H), 2.07 – 2.01 (m, 1H), 1.01 (d, *J* = 6.6 Hz, 6H) ppm; **^{13}C NMR** (126 MHz, $CDCl_3$) δ 161.5, 150.6, 149.1, 135.5, 131.8, 131.5, 130.7, 129.8, 129.54, 129.48, 127.8, 127.0, 125.4, 125.1, 120.4, 117.8, 112.9, 46.2, 30.4, 22.5 ppm; **HRMS** (ESI) m/z: [M+H]+ Calcd. For $C_{21}H_{19}O_2^+$ 303.1380 Found 303.1383.



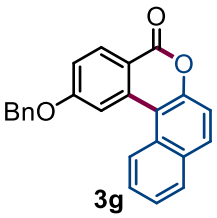
3e

2-Methoxy-5H-dibenzo[c,f]chromen-5-one (3e): White solid; Eluent: 5–10% EtOAc in Hexane; yield = 88% (49 mg); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.76 (d, *J* = 9.4 Hz, 1H), 8.43 (d, *J* = 8.8 Hz, 1H), 8.07 (d, 1H), 7.94 – 7.89 (m, 2H), 7.67 – 7.64 (m, 1H), 7.56 – 7.52 (m, 1H), 7.45 (d, *J* = 8.9 Hz, 1H), 7.15 (dd, *J* = 8.8, 2.4 Hz, 1H), 4.01 (s, 3H) ppm; **^{13}C NMR** (126 MHz, $CDCl_3$) δ 164.6, 161.2, 150.9, 137.5, 133.2, 131.8, 131.7, 129.8, 129.5, 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.



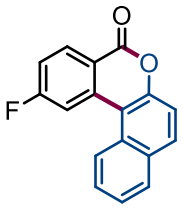
3f

5-Oxo-5H-dibenzo[c,f]chromen-2-yl 4-methylbenzenesulfonate (3f): White solid; Eluent: 5–10% EtOAc in Hexane; yield = 87% (72 mg); Melting point: 180–182 ^{o}C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.42 (d, *J* = 8.6 Hz, 1H), 8.31 – 8.26 (m, 2H), 7.93 (d, *J* = 8.3 Hz, 2H), 7.81 (d, *J* = 7.8 Hz, 2H), 7.61 – 7.54 (m, 2H), 7.45 (d, *J* = 8.9 Hz, 1H), 7.38 (d, *J* = 7.8 Hz, 2H), 7.22 – 7.19 (m, 1H), 2.46 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 160.5, 154.1, 150.9, 146.2, 137.2, 133.0, 132.6, 132.0, 131.7, 130.3, 129.6, 129.4, 128.8, 128.4, 125.8, 124.3, 122.4, 120.9, 120.4, 117.6, 111.7, 22.0 ppm; **HRMS** (ESI) m/z: [M+H]+ Calcd. For $C_{24}H_{17}O_5S^+$ 417.0791 Found 417.0794.



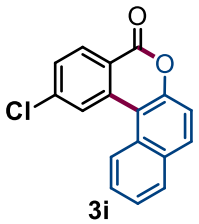
3g

2-(Benzyloxy)-5H-dibenzo[c,f]chromen-5-one (3g): White solid; Eluent: 5–10% EtOAc in Hexane; yield = 85% (60 mg); Melting point: 168–170 ^{o}C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.42 (dd, *J* = 11.3, 8.6 Hz, 2H), 8.04 (s, 1H), 7.88 (dd, *J* = 16.5, 8.3 Hz, 2H), 7.55 – 7.45 (m, 4H), 7.48 – 7.44 (m, 2H), 7.43 – 7.38 (m, 2H), 7.23 (dd, *J* = 8.9, 2.3 Hz, 1H), 5.28 (s, 2H) ppm; **^{13}C NMR** (126 MHz, $CDCl_3$) δ 163.5, 161.1, 150.9, 137.5, 136.0, 133.1, 131.8, 131.7, 129.7, 129.4, 129.0, 128.6, 127.9, 127.5, 125.3, 124.7, 117.8, 116.1, 115.7, 112.5, 111.7, 70.6 ppm; **HRMS** (ESI) m/z: [M+H]+ Calcd. For $C_{24}H_{17}O_3^+$ 353.1172 Found 353.1167.



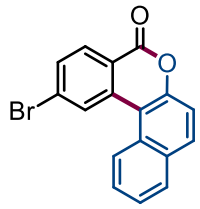
3h

2-Fluoro-5H-dibenzo[c,f]chromen-5-one (3h): White solid; Eluent: 5–10% EtOAc in Hexane; yield = 78% (41 mg); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.67 (d, *J* = 8.7 Hz, 1H), 8.54 – 8.50 (m, 1H), 8.30 (dd, *J* = 11.0, 4.6 Hz, 1H), 7.95 – 7.93 (m, 2H), 7.72 – 7.68 (m, 1H), 7.59 – 7.55 (m, 1H), 7.48 – 7.45 (m, 1H), 7.35 – 7.30 (m, 1H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.7 (d, *J* = 255.1 Hz), 160.6, 151.0, 138.1 (d, *J* = 10.4 Hz), 134.0 (d, *J* = 10.4 Hz), 132.5, 131.7, 129.6, 129.5, 128.4, 125.7, 124.5, 118.8 (d, *J* = 2.1 Hz), 117.7, 116.3 (d, *J* = 22.9 Hz), 113.0 (d, *J* = 25.0 Hz), 111.9 (d, *J* = 2.5 Hz) ppm; **^{19}F NMR** (471 MHz, $CDCl_3$) δ -101.3 ppm; **HRMS** (ESI) m/z: [M+H]+ Calcd. For $C_{17}H_{10}O_2F^+$ 265.0659 Found 265.0649.



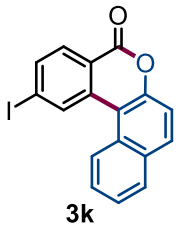
3i

2-Chloro-5H-dibenzo[c,f]chromen-5-one (3i): White solid; Eluent: 5–10% EtOAc in Hexane; yield = 82 % (46 mg); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.64 (d, *J* = 8.7 Hz, 1H), 8.58 (s, 1H), 8.40 (d, *J* = 8.5 Hz, 1H), 7.92 (dd, *J* = 8.6, 4.8 Hz, 2H), 7.71 – 7.68 (m, 1H), 7.57 – 7.55 (m, 2H), 7.44 (d, *J* = 8.9 Hz, 1H) ppm; **^{13}C NMR** (126 MHz, $CDCl_3$) δ 160.6, 151.0, 141.5, 136.9, 132.5, 132.4, 131.7, 129.6, 129.5, 128.7, 128.4, 126.3, 125.8, 124.6, 120.8, 117.7, 111.6 ppm; **HRMS** (ESI) m/z: [M+H]+ Calcd. For $C_{17}H_{10}O_2Cl^+$ 281.0364 Found 281.0367.



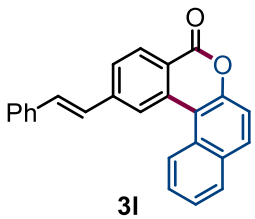
3j

2-Bromo-5H-dibenzo[c,f]chromen-5-one (3j): White solid; Eluent: 5-10% EtOAc in Hexane; yield = 84% (54 mg); Melting point: 200–202 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.67 (s, 1H), 8.56 (d, *J* = 8.7 Hz, 1H), 8.27 (d, *J* = 8.4 Hz, 1H), 7.90 – 7.87 (m, 2H), 7.70 – 7.64 (m, 2H), 7.55 – 7.51 (m, 1H), 7.40 (d, *J* = 9.0 Hz, 1H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 160.7, 150.8, 136.8, 132.4, 132.2, 131.6, 131.5, 130.1, 129.5, 129.2, 129.1, 128.4, 125.7, 124.5, 120.9, 117.5, 111.3 ppm; **HRMS** (ESI) m/z: [M+H]+ Calcd. For $C_{17}H_{10}O_2Br^+$ 324.9859 Found 324.9866.



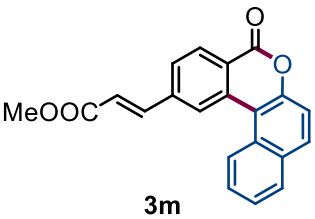
3k

2-Iodo-5H-dibenzo[c,f]chromen-5-one (3k): White solid; Eluent: 5-10% EtOAc in Hexane; yield = 80% (59 mg); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.97 (s, 1H), 8.62 (d, *J* = 8.6 Hz, 1H), 8.14 (d, *J* = 8.3 Hz, 1H), 7.96 – 7.90 (m, 3H), 7.74 – 7.68 (m, 1H), 7.58 – 7.54 (m, 1H), 7.44 (d, *J* = 8.9 Hz, 1H) ppm; **^{13}C NMR** (126 MHz, $CDCl_3$) δ 161.0, 150.8, 137.3, 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; .**HRMS** (ESI) m/z: [M+H]+ Calcd. For $C_{17}H_{10}O_2I^+$ 372.9720 Found 372.9732.



3l

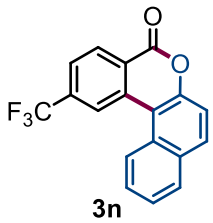
(E)-2-Styryl-5H-dibenzo[c,f]chromen-5-one (3l): White solid; Eluent: 5-10% EtOAc in Hexane; yield = 77% (54 mg); Melting point: 213–214 ºC; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.77 (d, *J* = 8.6 Hz, 1H), 8.61 (s, 1H), 8.43 (dd, *J* = 8.2, 1.4 Hz, 1H), 7.94 (d, *J* = 8.1 Hz, 1H), 7.90 (d, *J* = 8.8 Hz, 1H), 7.77 (d, *J* = 8.3 Hz, 1H), 7.71 – 7.68 (m, 1H), 7.60 – 7.55 (m, 3H), 7.47 – 7.40 (m, 3H), 7.33 (dd, *J* = 15.4, 7.6 Hz, 2H), 7.23 (s, 1H) ppm; **^{13}C NMR**(126 MHz, $CDCl_3$) δ 161.2, 150.7, 143.5, 136.5, 136.1, 133.0, 131.8, 131.7, 131.2, 129.7, 129.5, 129.0, 128.9, 128.0, 127.5, 127.2, 125.6, 125.5, 125.1, 124.9, 121.1, 117.8, 112.7 ppm; **HRMS** (ESI) m/z: [M+H]+ Calcd. For $C_{25}H_{17}O_2^+$ 349.1223 Found 349.1228.



3m

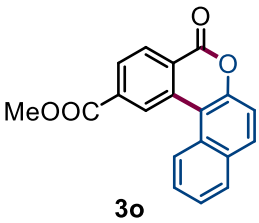
Methyl (E)-3-(5-oxo-5H-dibenzo[c,f]chromen-2-yl)acrylate (3m): White solid; Eluent: 5-10% EtOAc in Hexane; yield = 79 % (52 mg); Melting point: 210–212 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.69 – 8.66 (m, 2H), 8.47 (d, *J* = 8.2 Hz, 1H), 7.95 – 7.91 (m, 2H), 7.84 (d, *J* = 16.0 Hz, 1H), 7.76 (dd, *J* =

8.2, 1.4 Hz, 1H), 7.70 (dd, *J* = 10.2, 6.9 Hz, 1H), 7.59 – 7.55 (m, 1H), 7.45 (d, *J* = 8.9 Hz, 1H), 6.65 (d, *J* = 16.0 Hz, 1H), 3.87 (s, 3H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.9, 160.8, 150.7, 143.3, 140.1, 136.1, 132.2, 131.8, 131.4, 129.6, 129.5, 128.3, 126.8, 126.4, 125.7, 124.8, 123.1, 121.7, 117.6, 112.2, 52.2 ppm; **HRMS** (ESI) m/z: [M+H]+ Calcd. For $C_{21}H_{15}O_4^+$ 331.0965 Found 331.0971.



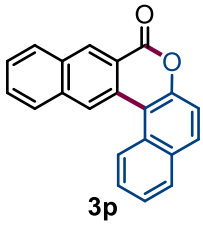
3n

2-(Trifluoromethyl)-5H-dibenzo[c,f]chromen-5-one (3n): White solid; Eluent: 5-10% EtOAc in Hexane; yield = 76% (48 mg); Melting point: 170–174 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.87 (s, 1H), 8.64 – 8.58 (m, 2H), 7.96 – 7.94 (m, 2H), 7.85 – 7.83 (m, 1H), 7.72 (dd, *J* = 10.6, 4.1 Hz, 1H), 7.60 – 7.57 (m, 1H), 7.47 (dd, *J* = 9.1, 3.8 Hz, 1H) ppm; **^{13}C NMR** (126 MHz, $CDCl_3$) δ 160.2, 150.9, 136.0, 135.9 (q, *J* = 32.7 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* = 4.0 Hz), 117.5, 111.7 ppm; **^{19}F NMR** (471 MHz, $CDCl_3$) δ -63.2 ppm; **HRMS** (ESI) m/z: [M+H]+ Calcd. For $C_{18}H_{10}O_2F_3^+$ 315.0627 Found 315.0628.



3o

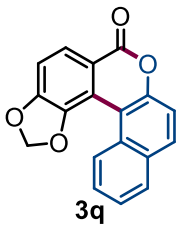
Methyl 5-oxo-5H-dibenzo[c,f]chromene-2-carboxylate (3o): White solid; Eluent: 5-10% EtOAc in Hexane; yield = 81% (49 mg); Melting point: 200–202 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.31 (s, 1H), 8.75 (d, *J* = 8.6 Hz, 1H), 8.54 (d, *J* = 8.2 Hz, 1H), 8.21 (d, *J* = 9.6 Hz, 1H), 7.94 (dd, *J* = 8.6, 4.2 Hz, 2H), 7.74 – 7.70 (m, 1H), 7.57 (dd, *J* = 9.2, 6.9 Hz, 1H), 7.47 (d, *J* = 8.8 Hz, 1H), 4.04 (s, 3H) ppm; **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.2, 160.7, 150.7, 135.6, 135.4, 132.4 (2×C), 131.8, 131.1, 129.6, 128.5 (2×C), 128.0, 125.8, 125.4, 124.9, 117.6, 112.2, 53.0 ppm; **HRMS** (ESI) m/z: [M+H]+ Calcd. For $C_{19}H_{13}O_4^+$ 305.0808 Found 305.0812.



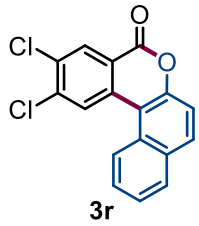
3p

8H-Benzo[f]naphtho[2,3-c]chromen-8-one (3p): White solid; Eluent: 5-10% EtOAc in Hexane; yield = 85% (50 mg); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.03 (s, 1H), 8.97 (s, 1H), 8.88 (d, *J* = 8.7 Hz, 1H), 8.05 – 8.01 (m, 2H), 7.94 – 7.92 (m, 1H), 7.88 (d, *J* = 8.9 Hz, 1H), 7.71 – 7.67 (m, 2H), 7.63 – 7.59 (m, 1H), 7.57 – 7.54 (m, 1H), 7.45 (d, *J* = 8.9 Hz, 1H) ppm; **^{13}C NMR**

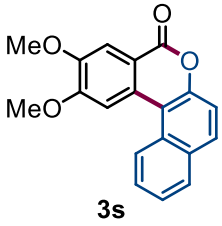
(126 MHz, $CDCl_3$) δ 161.7, 149.8, 136.1, 132.7, 131.9, 131.3, 130.1, 129.9, 129.6, 129.5, 129.4, 128.5, 128.0, 127.4, 125.9, 125.4 (2×C), 125.1, 120.6, 117.8, 112.8 ppm; **HRMS** (ESI) m/z: [M+H]+ Calcd. For $C_{21}H_{13}O_2^+$ 297.0910 Found 297.0921.


3q

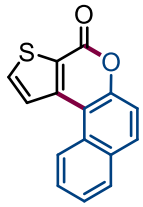
6H-[1,3]Dioxolo[4',5':3,4]benzo[1,2-c]benzo[f]chromen-6-one (3q): White solid; Eluent: 5-10% EtOAc in Hexane; yield = 91 % (53 mg); Melting point: 170–172 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.22 (d, *J* = 8.4 Hz, 1H), 8.16 (d, *J* = 8.3 Hz, 1H), 7.94 (d, *J* = 8.8 Hz, 1H), 7.88 (d, *J* = 7.9 Hz, 1H), 7.59 – 7.50 (m, 2H), 7.43 (d, *J* = 8.8 Hz, 1H), 7.13 (d, *J* = 8.3 Hz, 1H), 6.20 (s, 2H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 161.1, 153.3, 150.4, 142.4, 132.2, 131.4, 128.9, 128.3, 127.63, 127.56, 126.0, 125.5, 118.3, 117.30, 117.27, 110.5, 109.5, 101.8 ppm; **HRMS** (ESI) m/z: [M+H]+ Calcd. For $C_{18}H_{11}O_4^+$ 291.0652 Found 291.0642.


3r

2,3-Dichloro-5H-dibenzo[c,f]chromen-5-one (3r): White solid; Eluent: 5-10% EtOAc in Hexane; yield = 78 % (49 mg); Melting point: 210–214 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.76 (s, 1H), 8.64 (d, *J* = 8.6 Hz, 1H), 8.55 (s, 1H), 7.97 (d, *J* = 10.7 Hz, 2H), 7.76 – 7.72 (m, 1H), 7.62 – 7.58 (m, 1H), 7.48 (dd, *J* = 8.9, 2.0 Hz, 1H) ppm; **^{13}C NMR** (126 MHz, $CDCl_3$) δ 159.7, 151.1, 139.8, 134.9, 132.84, 132.79, 132.3, 131.9, 129.8, 129.4, 128.7, 128.3, 126.0, 124.4, 122.0, 117.7, 111.1 ppm; **HRMS** (ESI) m/z: [M+H]+ Calcd. For $C_{17}H_9Cl_2O_2^+$ 314.9974 Found 331.9968.

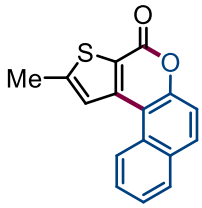

3s

2,3-Dimethoxy-5H-dibenzo[c,f]chromen-5-one (3s): White solid; Eluent: 5-10% EtOAc in Hexane; yield = 80 % (53 mg); Melting point: 220–222 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.73 (d, *J* = 8.6 Hz, 1H), 8.04 (s, 1H), 7.94 (d, *J* = 7.9 Hz, 1H), 7.86 (d, *J* = 10.5 Hz, 2H), 7.67 – 7.64 (m, 1H), 7.56 – 7.52 (m, 1H), 7.46 (d, *J* = 8.8 Hz, 1H), 4.09 (s, 3H), 4.03 (s, 3H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 161.3, 154.5, 150.0, 149.5, 131.8, 130.8, 130.7, 129.6, 129.4, 127.7, 125.3, 124.6, 117.8, 115.9, 112.7, 110.9, 108.1, 56.5, 56.4 ppm; **HRMS** (ESI) m/z: [M+Na]+ Calcd. For $C_{19}H_{14}O_4Na^+$ 329.0784 Found 329.0790.



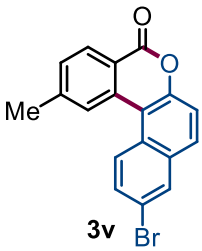
3t

4H-benzo[f]thieno[2,3-c]chromen-4-one (3t): White solid; Eluent: 5-10% EtOAc in Hexane; yield = 79 % (40 mg); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.61 (d, *J* = 8.6 Hz, 1H), 8.22 (d, *J* = 6.4 Hz, 1H), 8.01 (d, *J* = 6.4 Hz, 1H), 7.90 – 7.86 (m, 2H), 7.68 – 7.65 (m, 1H), 7.56 – 7.53 (m, 1H), 7.49 (d, *J* = 9.2 Hz, 1H) ppm; **^{13}C NMR** (126 MHz, $CDCl_3$) δ 157.3, 152.2, 144.0, 136.7, 131.4, 131.2, 129.5, 129.2, 128.1, 126.1, 125.9, 125.7, 124.1, 117.9, 112.1 ppm; **HRMS** (ESI) m/z: [M+H]+ Calcd. For $C_{15}H_9SO_2^+$ 253.0318 Found 253.0319.



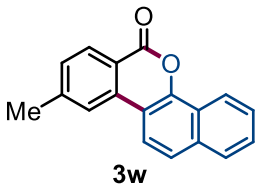
3u

2-Methyl-4H-benzo[f]thieno[2,3-c]chromen-4-one (3u): White solid; Eluent: 5-10% EtOAc in Hexane; yield = 71 % (38 mg); Melting point: 184–188 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.64 (d, *J* = 8.6 Hz, 1H), 7.93 – 7.88 (m, 3H), 7.69 (t, *J* = 7.3 Hz, 1H), 7.56 (t, *J* = 7.5 Hz, 1H), 7.52 (d, *J* = 8.9 Hz, 1H), 2.75 (s, 3H) ppm; **^{13}C NMR** (126 MHz, $CDCl_3$) δ 152.7, 152.4, 144.7, 131.3 (2×C), 131.2, 129.5, 129.3, 128.0, 125.6, 124.7, 124.3 (2×C), 118.1, 112.1, 16.9 ppm; **HRMS** (ESI) m/z: [M+H]+ Calcd. For $C_{16}H_{11}SO_2^+$ 267.0474 Found 267.0474.



3v

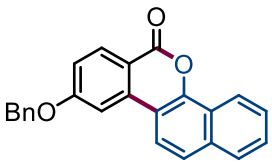
10-Bromo-2-methyl-5H-dibenzo[c,f]chromen-5-one (3v): White solid; Eluent: 5-10% EtOAc in Hexane; yield = 92 % (62 mg); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.48 (d, *J* = 9.1 Hz, 1H), 8.30 (d, *J* = 8.0 Hz, 1H), 8.18 (s, 1H), 7.99 (s, 1H), 7.71 (d, *J* = 8.9 Hz, 1H), 7.64 (d, *J* = 11.3 Hz, 1H), 7.42 – 7.37 (m, 2H), 2.57 (s, 3H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 161.0, 150.4, 145.6, 134.8, 132.8, 131.2, 130.9, 130.8, 130.2, 129.8, 128.1, 126.7, 126.4, 119.9, 119.1, 118.8, 112.8, 22.6 ppm; **HRMS** (ESI) m/z: [M+H]+ Calcd. For $C_{18}H_{12}O_2Br^+$ 339.0015 Found 339.0016.



3w

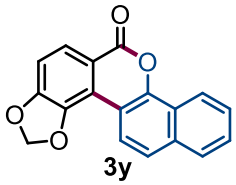
9-Methyl-6H-dibenzo[c,h]chromen-6-one (3w): White solid; Eluent: 5-10% EtOAc in Hexane; yield = 70 % (36 mg); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.56 (d, *J* = 8.1 Hz, 1H), 8.32 (d, *J* = 8.1 Hz, 1H), 8.02 (d, *J* = 8.8 Hz, 1H),

7.94 (s, 1H), 7.85 (d, *J* = 7.7 Hz, 1H), 7.73 (d, *J* = 8.7 Hz, 1H), 7.64 – 7.57 (m, 2H), 7.38 (d, *J* = 8.2 Hz, 1H), 2.57 (s, 3H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 161.5, 147.5, 146.2, 135.5, 134.3, 130.7, 130.0, 127.9, 127.7, 127.1, 124.5, 124.0, 122.5, 122.3, 119.3, 118.8, 113.2, 22.5 ppm; **HRMS** (ESI) m/z: [M+H]+ Calcd. For $C_{18}H_{13}O_2^+$ 261.0910 Found 261.0914.



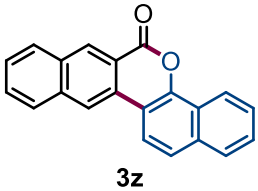
3x

9-(Benzyloxy)-6H-dibenzo[c,h]chromen-6-one (3x): White solid; Eluent: 5-10% EtOAc in Hexane; yield = 75 % (53 mg); Melting point: 176–180 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.52 (d, *J* = 9.2 Hz, 1H), 8.33 (d, *J* = 8.8 Hz, 1H), 7.87 (d, *J* = 8.8 Hz, 1H), 7.81 (d, *J* = 8.4 Hz, 1H), 7.68 (d, *J* = 8.8 Hz, 1H), 7.59 – 7.54 (m, 3H), 7.50 (d, *J* = 7.5 Hz, 2H), 7.47 – 7.43 (m, 2H), 7.40 (d, *J* = 7.1 Hz, 1H), 7.13 (dd, *J* = 8.7, 2.3 Hz, 1H), 5.23 (s, 2H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) 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, 113.0, 106.5, 70.6 ppm; **HRMS** (ESI) m/z: [M+H]+ Calcd. For $C_{24}H_{17}O_3^+$ 353.1172 Found 353.1178.



3y

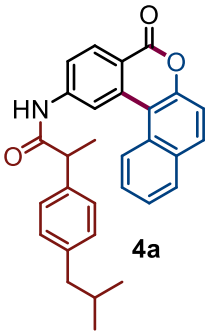
13H-[1,3]dioxolo[4',5':3,4]benzo[1,2-c]benzo[h]chromen-13-one (3y): White solid; Eluent: 5-10% EtOAc in Hexane; yield = 73 % (42 mg); Melting point: 180–184 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.54 (d, *J* = 7.1 Hz, 1H), 8.33 (dd, *J* = 9.0, 5.0 Hz, 1H), 8.08 (dd, *J* = 9.2, 2.7 Hz, 1H), 7.85 – 7.83 (m, 1H), 7.66 (dd, *J* = 8.8, 3.6 Hz, 1H), 7.61 – 7.58 (m, 2H), 7.03 (dd, *J* = 8.3, 3.6 Hz, 1H), 6.26 (s, 2H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 160.7, 153.1, 147.0, 143.1, 134.1, 127.9, 127.7, 127.0, 126.9, 124.2, 123.5, 122.9, 122.4, 119.4, 115.5, 111.5, 109.6, 102.8 ppm; **HRMS** (ESI) m/z: [M+H]+ Calcd. For $C_{18}H_{11}O_4^+$ 291.0652 Found 291.0639.



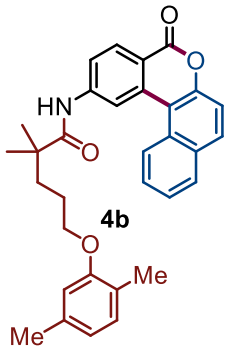
3z

6H-Benzo[h]naphtho[2,3-c]chromen-6-one (3z): White solid; Eluent: 5-10% EtOAc in Hexane; yield = 78 % (46 mg); Melting point: 160–164 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.90 (s, 1H), 8.45 – 8.40 (m, 2H), 8.06 (d, *J* = 8.8 Hz, 1H), 7.92 (d, *J* = 8.4 Hz, 2H), 7.78 (d, *J* = 7.7 Hz, 1H), 7.68 (d, *J* = 8.8 Hz, 1H), 7.63 – 7.59 (m, 1H), 7.56 – 7.48 (m, 3H) ppm; **^{13}C NMR** (101

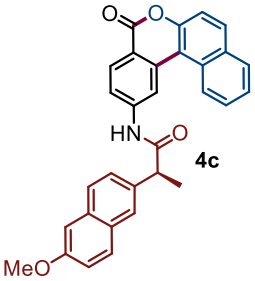
MHz, $CDCl_3$) δ 161.5, 146.4, 136.3, 134.2, 132.8, 132.3, 130.2, 129.63, 129.58, 128.2, 127.68, 127.66, 127.13, 127.06, 124.6, 124.0, 122.2, 121.0, 119.4, 119.2, 113.2 ppm; **HRMS** (ESI) m/z: [M+H]+ Calcd. For $C_{21}H_{13}O_2^+$ 297.0910 Found 297.0909.



2-(4-Isobutylphenyl)-N-(5-oxo-5H-dibenzo[c,f]chromen-2-yl)propanamide (4a): Yellow liquid; Eluent: 10-20% EtOAc in Hexane; yield = 78 % (70 mg); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.04 (d, *J* = 2.0 Hz, 1H), 8.70 (d, *J* = 8.6 Hz, 1H), 8.23 (d, *J* = 8.6 Hz, 1H), 8.18 (s, 1H), 7.78 (d, *J* = 8.6 Hz, 2H), 7.48 – 7.44 (m, 1H), 7.41 – 7.37 (m, 2H), 7.34 (d, *J* = 8.1 Hz, 2H), 7.31 (d, *J* = 8.8 Hz, 1H), 7.15 (d, *J* = 8.1 Hz, 2H), 3.91 – 3.86 (m, 1H), 2.43 (d, *J* = 7.2 Hz, 2H), 1.87 – 1.77 (m, 1H), 1.66 (d, *J* = 7.1 Hz, 3H), 0.87 (d, *J* = 6.7 Hz, 6H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.7, 161.2, 150.5, 143.8, 141.4, 137.8, 136.5, 131.8, 131.7, 131.5, 130.0, 129.4, 129.2, 128.0, 127.5, 125.4, 124.8, 119.1, 117.4, 117.3, 116.0, 112.3, 48.1, 45.1, 30.2, 22.5, 18.8 ppm; **HRMS** (ESI) m/z: [M+H]+ Calcd. For $C_{30}H_{28}NO_3^+$ 450.2064 Found 450.2067.

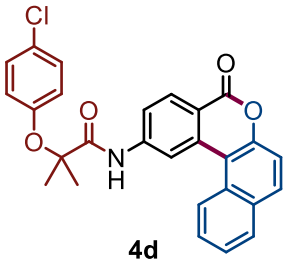


5-(2,5-Dimethylphenoxy)-2,2-dimethyl-N-(5-oxo-5H-dibenzo[c,f]chromen-2-yl)pentanamide (4b): Colourless liquid; Eluent: 10-20% EtOAc in Hexane; yield = 81 % (80 mg); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.16 (s, 1H), 8.86 (d, *J* = 8.6 Hz, 1H), 8.35 (d, *J* = 8.3 Hz, 1H), 7.98 (s, 1H), 7.88 – 7.84 (m, 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}C NMR** (101 MHz, $CDCl_3$) δ 176.6, 161.2, 156.8, 150.6, 143.7, 136.7, 136.6, 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, 112.2, 67.8, 43.4, 37.6, 25.7, 25.2, 21.4, 15.9 ppm; **HRMS** (ESI) m/z: [M+H]+ Calcd. For $C_{32}H_{32}NO_{4+}$ 494.2326 Found 494.2322.



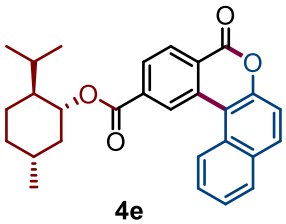
4c

(R)-2-(6-Methoxynaphthalen-2-yl)-N-(5-oxo-5H-dibenzo[c,f]chromen-2-yl)propenamide (4c): White solid; Eluent: 10-20% EtOAc in Hexane; yield = 85 % (80 mg); Melting point: 184–190 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.11 (s, 1H), 8.73 (d, *J* = 8.6 Hz, 1H), 8.63 (s, 1H), 8.23 (d, *J* = 8.6 Hz, 1H), 7.79 – 7.74 (m, 3H), 7.64 (d, *J* = 8.5 Hz, 1H), 7.59 (d, *J* = 9.0 Hz, 1H), 7.49 – 7.44 (m, 3H), 7.40 – 7.36 (m, 1H), 7.29 (d, *J* = 4.1 Hz, 1H), 7.05 (d, *J* = 8.9 Hz, 1H), 6.99 (s, 1H), 4.05 – 4.01 (m, 1H), 3.83 (s, 3H), 1.74 – 1.71 (m, 3H)ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.7, 161.3, 157.8, 150.4, 143.9, 136.5, 135.6, 133.9, 131.8, 131.6, 131.5, 129.4, 129.2 (2×C), 129.0, 127.9, 127.8, 126.3, 126.0, 125.4, 124.8, 119.3, 119.2, 117.2, 117.1, 116.1, 112.3, 105.6, 55.3, 48.2, 18.9 ppm. **HRMS** (ESI) m/z: [M+H]+ Calcd. For $C_{31}H_{24}NO_4^+$ 474.1700 Found 474.1705.



4d

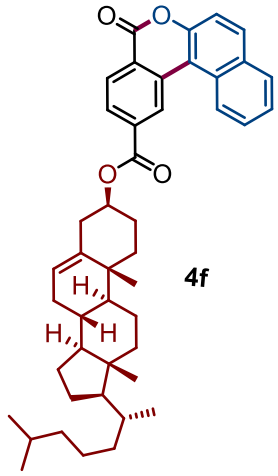
2-(4-Chlorophenoxy)-2-methyl-N-(5-oxo-5H-dibenzo[c,f]chromen-2-yl)propanamide (4d): Sticky liquid; Eluent: 10-20% EtOAc in Hexane; yield = 83 % (76 mg); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.22 (s, 1H), 9.09 (s, 1H), 8.86 (d, *J* = 8.7 Hz, 1H), 8.37 (d, *J* = 8.6 Hz, 1H), 7.88 – 7.83 (m, 2H), 7.72 – 7.68 (m, 1H), 7.58 (d, *J* = 8.6 Hz, 1H), 7.52 – 7.48 (m, 1H), 7.37 (d, *J* = 8.8 Hz, 1H), 7.24 (d, *J* = 8.4 Hz, 2H), 6.94 (d, *J* = 8.3 Hz, 2H), 1.62 (s, 6H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.5, 161.0, 152.2, 150.7, 143.0, 136.7, 131.94, 131.92, 131.6, 129.60, 129.58, 129.56, 129.3, 128.2, 125.5, 125.0, 123.5, 119.4, 117.9, 117.5, 116.4, 112.4, 82.6, 25.0 ppm; **HRMS** (ESI) m/z: [M+H]+ Calcd. For $C_{27}H_{21}NO_4Cl^+$ 458.1154 Found 458.1153.



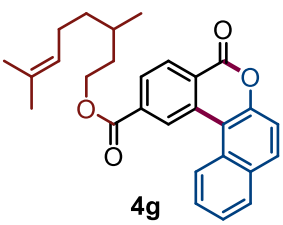
4e

(1R,2S,5R)-2-isopropyl-5-methylcyclohexyl 5-oxo-5H- dibenzo [c,f] chromene-2-carboxylate (4e): Sticky liquid; Eluent: 10-20% EtOAc in Hexane; yield = 77 % (66 mg); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.31 (s, 1H), 8.74 (d, *J* = 8.7 Hz, 1H), 8.53 (d, *J* = 8.2 Hz, 1H), 8.21 (d, *J* = 8.2 Hz, 1H), 7.92 (dd, *J* = 8.6, 4.8 Hz, 2H), 7.70 – 7.66 (m, 1H), 7.58 – 7.54 (m, 1H), 7.45 (d, *J* = 8.9 Hz, 1H), 5.05 – 4.98 (m, 1H), 2.22 (d, *J* = 16.2 Hz, 1H), 2.09 – 2.02 (m, 1H), 1.77 (d, *J* = 5.3 Hz, 2H), 1.67 – 1.58 (m, 2H), 1.23 – 1.12 (m, 2H), 0.99 (d, *J* = 7.1 Hz, 3H), 0.96 (d, *J* = 6.5 Hz, 3H), 0.87 (d, *J* = 6.9 Hz, 3H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.1, 160.7, 150.6, 136.0, 135.4,

132.2, 131.7, 131.0, 129.51, 129.47, 128.4, 128.3, 127.9, 125.7, 125.1, 124.8, 117.5, 112.2, 76.3, 47.4, 41.0, 34.3, 31.6, 26.9, 23.8, 22.1, 20.9, 16.8 ppm; **HRMS** (ESI) m/z: [M+Na]+ Calcd. For $C_{28}H_{28}O_4Na^+$ 451.1880 Found 451.1921.

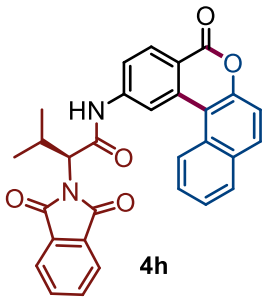


(3S,8S,9S,10R,13R,14S,17R)-10,13-Dimethyl-17-((R)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl 5-oxo-5H-dibenzo[c,f]chromene-2-carboxylate (4f): White solid; Eluent: 5-10% EtOAc in Hexane; yield = 80 % (105 mg); Melting point: 200–222 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.32 (s, 1H), 8.76 (d, *J* = 8.7 Hz, 1H), 8.52 (d, *J* = 8.1 Hz, 1H), 8.20 (d, *J* = 8.3 Hz, 1H), 7.94 (d, *J* = 8.1 Hz, 2H), 7.73 – 7.69 (m, 1H), 7.59 – 7.55 (m, 1H), 7.47 (d, *J* = 8.8 Hz, 1H), 5.46 (s, 1H), 4.95 – 4.93 (m, 1H), 2.54 (d, *J* = 7.6 Hz, 2H), 2.09 – 1.94 (m, 4H), 1.85 – 1.79 (m, 2H), 1.65 – 1.49 (m, 7H), 1.39 – 1.25 (m, 6H), 1.11 (d, *J* = 18.6 Hz, 7H), 1.02 (d, *J* = 10.5 Hz, 3H), 0.92 (d, *J* = 6.4 Hz, 3H), 0.87 (d, *J* = 6.6 Hz, 6H), 0.69 (s, 3H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.0, 160.8, 150.6, 139.5, 136.0, 135.5, 132.3, 131.8, 130.9, 129.5 (2×C), 128.4, 128.0, 125.8 (2×C), 125.2, 124.9, 123.3, 117.5, 112.2, 75.9, 56.8, 56.3, 50.2, 42.4, 39.8, 39.6, 38.3, 37.1, 36.8, 36.3, 35.9, 32.1, 32.0, 28.4, 28.2, 28.0, 24.4, 24.0, 23.0, 22.7, 21.2, 19.5, 18.9, 12.0 ppm; ; **HRMS** (ESI) m/z: [M+H]+ Calcd. For $C_{45}H_{55}O_4^+$ 659.4095 Found 659.4062.



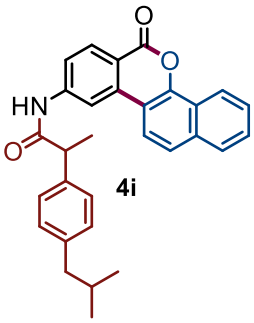
3,7-Dimethyloct-6-en-1-yl 5-oxo-5H-dibenzo[c,f]chromene-2 carboxylate (4g): Orange liquid; Eluent: 5-10% EtOAc in Hexane; yield = 68 % (76 mg); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.30 (s, 1H), 8.73 (d, *J* = 8.6 Hz, 1H), 8.52 (d, *J* = 8.1 Hz, 1H), 8.19 (d, *J* = 8.2 Hz, 1H), 7.93 (dd, *J* = 10.8, 3.1 Hz, 2H), 7.71 – 7.66 (m, 1H), 7.58 – 7.54 (m, 1H), 7.47 (d, 1H), 5.10 (t, *J* = 7.2 Hz, 1H), 4.50 – 4.45 (m, 2H), 2.04 (t, *J* = 13.3 Hz, 2H), 1.93 – 1.85 (m, 1H), 1.75 – 1.68 (m, 2H), 1.65 (s, 3H), 1.60 (s, 3H), 1.49 – 1.40 (m, 1H), 1.33 – 1.25 (m, 1H), 1.03 (d, *J* = 6.4 Hz, 3H) ppm **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.6, 160.7, 150.6, 135.6, 135.5, 132.3, 131.7, 131.6, 131.0, 129.53, 129.47, 128.39, 128.35, 127.9, 125.7, 125.2, 124.8, 124.5, 117.5,

112.2, 64.6, 37.1, 35.5, 29.8, 25.8, 25.5, 19.7, 17.8 ppm; **HRMS** (ESI) m/z: [M+H]+ Calcd. For $C_{28}H_{29}O_4^+$ 429.2060 Found 429.2066.



4h

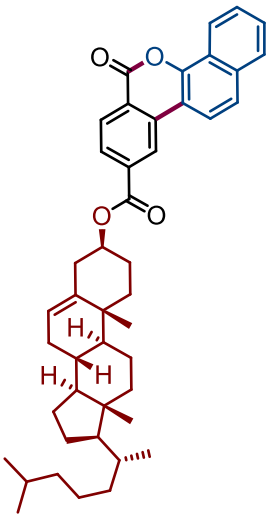
2-(1,3-dioxoisoindolin-2-yl)-3-methyl-N-(5-oxo-5H-dibenzo[c,f]chromen-2-yl)butanamide (4h): White solid; Eluent: 10-20% EtOAc in Hexane; yield = 79 % (77 mg); Melting point: 270–274 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.81 (s, 1H), 9.27 (s, 1H), 8.86 (d, *J* = 8.7 Hz, 1H), 8.38 (d, *J* = 8.2 Hz, 1H), 7.90 – 7.86 (m, 4H), 7.76 – 7.74 (m, 2H), 7.71 – 7.67 (m, 1H), 7.49 (d, *J* = 7.9 Hz, 2H), 7.41 (d, *J* = 8.7 Hz, 1H), 4.65 (d, *J* = 11.3 Hz, 1H), 3.02 – 2.94 (m, 1H), 1.20 (d, *J* = 6.4 Hz, 3H), 0.94 (d, *J* = 6.4 Hz, 3H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.0, 167.8, 161.1, 150.7, 143.4, 136.8, 134.9, 132.0, 131.9, 131.6, 131.2, 129.6, 129.3, 128.3, 125.5, 125.0, 124.1, 119.5, 117.9, 117.5, 116.5, 112.5, 64.8, 28.1, 19.8, 19.6 ppm; **HRMS** (ESI) m/z: [M+H]+ Calcd. For $C_{30}H_{23}N_2O_5^+$ 491.1601 Found 491.1603.



4i

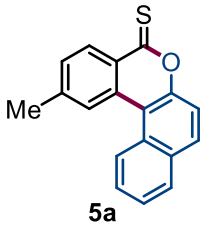
2-(4-isobutylphenyl)-N-(6-oxo-6H-dibenzo[c,h]chromen-9-yl)propanamide (4i): Sticky liquid; Eluent: 10-20% EtOAc in Hexane; yield = 75 % (67 mg); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.75 (d, *J* = 1.9 Hz, 1H), 8.52 – 8.50 (m, 1H), 8.29 (d, *J* = 8.6 Hz, 1H), 8.00 (d, *J* = 8.8 Hz, 1H), 7.84 – 7.82 (m, 1H), 7.69 (d, *J* = 8.8 Hz, 1H), 7.64 (s, 1H), 7.58 – 7.56 (m, 2H), 7.31 (d, *J* = 7.9 Hz, 2H), 7.26 (s, 1H), 7.18 (d, *J* = 7.8 Hz, 2H), 3.81 (q, *J* = 7.0 Hz, 1H), 2.48 (d, *J* = 7.1 Hz, 2H), 1.90 – 1.83 (m, 1H), 1.65 (d, *J* = 7.1 Hz, 3H), 0.91 (d, *J* = 6.6 Hz, 6H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.5, 161.1, 147.7, 144.2, 141.6, 137.6, 137.1, 134.5, 131.8, 130.2, 128.0, 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: [M+H]+ Calcd. For $C_{30}H_{28}NO_3$ 450.2064 Found 450.2052.

(3S,8S,9S,10R,13R,14S,17R)-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl 6-oxo-6H-dibenzo[c,h]chromene-9-carboxylate (4j): White solid; Eluent: 10-20% EtOAc in Hexane; yield = 66



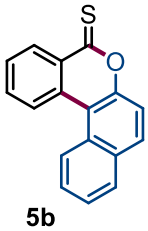
4j

% (87 mg); Melting point: 244–246 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.86 (s, 1H), 8.59 (d, *J* = 9.1 Hz, 1H), 8.53 (d, *J* = 8.2 Hz, 1H), 8.20 (d, *J* = 8.3 Hz, 1H), 8.16 (d, *J* = 8.8 Hz, 1H), 7.90 (d, *J* = 8.4 Hz, 1H), 7.82 (d, *J* = 8.7 Hz, 1H), 7.68 – 7.61 (m, 2H), 5.46 (d, *J* = 5.1 Hz, 1H), 5.01 – 4.94 (m, 1H), 2.57 – 2.54 (m, 2H), 2.09 – 1.94 (m, 4H), 1.85 (d, *J* = 24.4 Hz, 2H), 1.58 (s, 5H), 1.55 – 1.46 (m, 4H), 1.36 (d, *J* = 14.5 Hz, 3H), 1.26 (t, *J* = 13.4 Hz, 3H), 1.12 (d, *J* = 5.2 Hz, 4H), 1.03 (d, *J* = 16.2 Hz, 4H), 0.93 (d, *J* = 6.5 Hz, 3H), 0.87 (d, *J* = 8.3 Hz, 6H), 0.70 (s, 3H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.0, 160.8, 147.7, 139.5, 136.7, 135.6, 134.6, 131.0, 128.9, 128.3, 127.9, 127.4, 125.0, 124.1, 123.9, 123.8, 123.3, 122.5, 119.4, 112.8, 76.0, 56.8, 56.3, 50.2, 42.5, 39.9, 39.7, 38.3, 37.2, 36.8, 36.3, 36.0, 32.1, 32.0, 28.4, 28.2, 28.0, 24.5, 24.0, 23.0, 22.7, 21.2, 19.6, 18.9, 12.0 ppm; **HRMS** (ESI) m/z: [M+H]+ Calcd. For $C_{45}H_{55}O_4^+$ 659.4095 Found 659.4064.



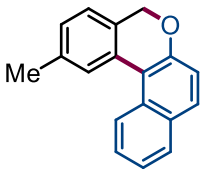
5a

2-Methyl-5H-dibenzo[c,f]chromene-5-thione (5a): Sticky yellow solid; Eluent: 2–5% EtOAc in Hexane; yield = 90 % (50 mg); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.79 (d, *J* = 8.5 Hz, 1H), 8.68 (d, *J* = 8.5 Hz, 1H), 8.31 (s, 1H), 7.92 – 7.86 (m, 2H), 7.64 (d, *J* = 7.5 Hz, 1H), 7.54 (d, *J* = 7.5 Hz, 2H), 7.37 (d, *J* = 8.3 Hz, 1H), 2.55 (s, 3H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 198.4, 151.2, 145.0, 133.3, 131.0, 130.6, 129.1, 128.8, 128.4, 128.34, 128.31, 126.9, 125.2, 124.8, 124.5, 116.2, 112.9, 21.6 ppm; **HRMS** (ESI) m/z: [M+H]+ Calcd. For $C_{18}H_{13}OS^+$ 277.0682 Found 277.0595.



5b

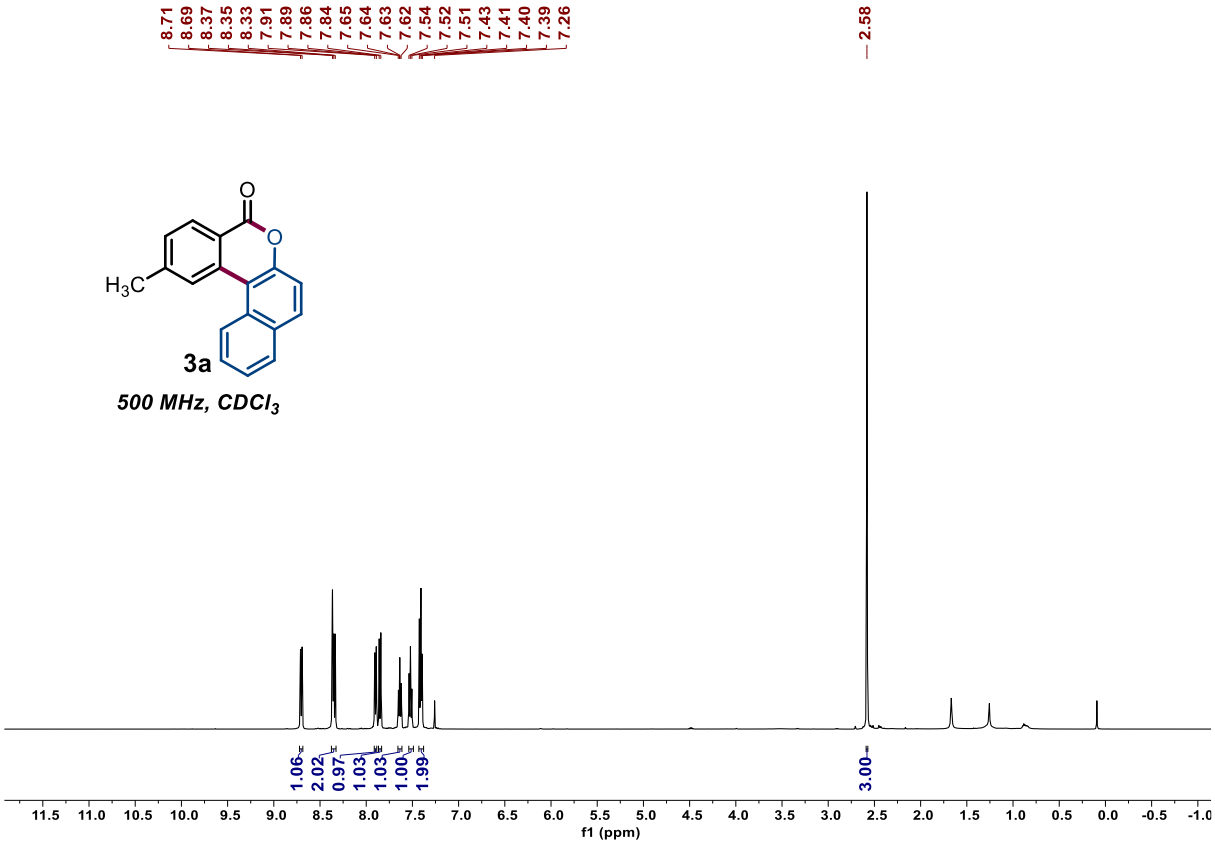
5H-Dibenzo[c,f]chromene-5-thione (5b): Sticky yellow solid; Eluent: 2–5% EtOAc in Hexane; yield = 88 % (46 mg); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.94 (d, *J* = 9.6 Hz, 1H), 8.73 (d, *J* = 8.6 Hz, 1H), 8.59 (d, *J* = 8.2 Hz, 1H), 7.96 – 7.92 (m, 2H), 7.90 – 7.86 (m, 1H), 7.69 – 7.65 (m, 1H), 7.62 – 7.56 (m, 3H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 199.7, 152.2, 134.6, 134.2, 132.1, 131.9, 131.4, 129.9, 129.5, 129.3, 128.8, 128.1, 126.4, 126.0, 125.5, 117.2, 114.0 ppm; **HRMS** (ESI) m/z: [M+H]+ Calcd. For $C_{17}H_{11}OS^+$ 263.0525 Found 263.0530.

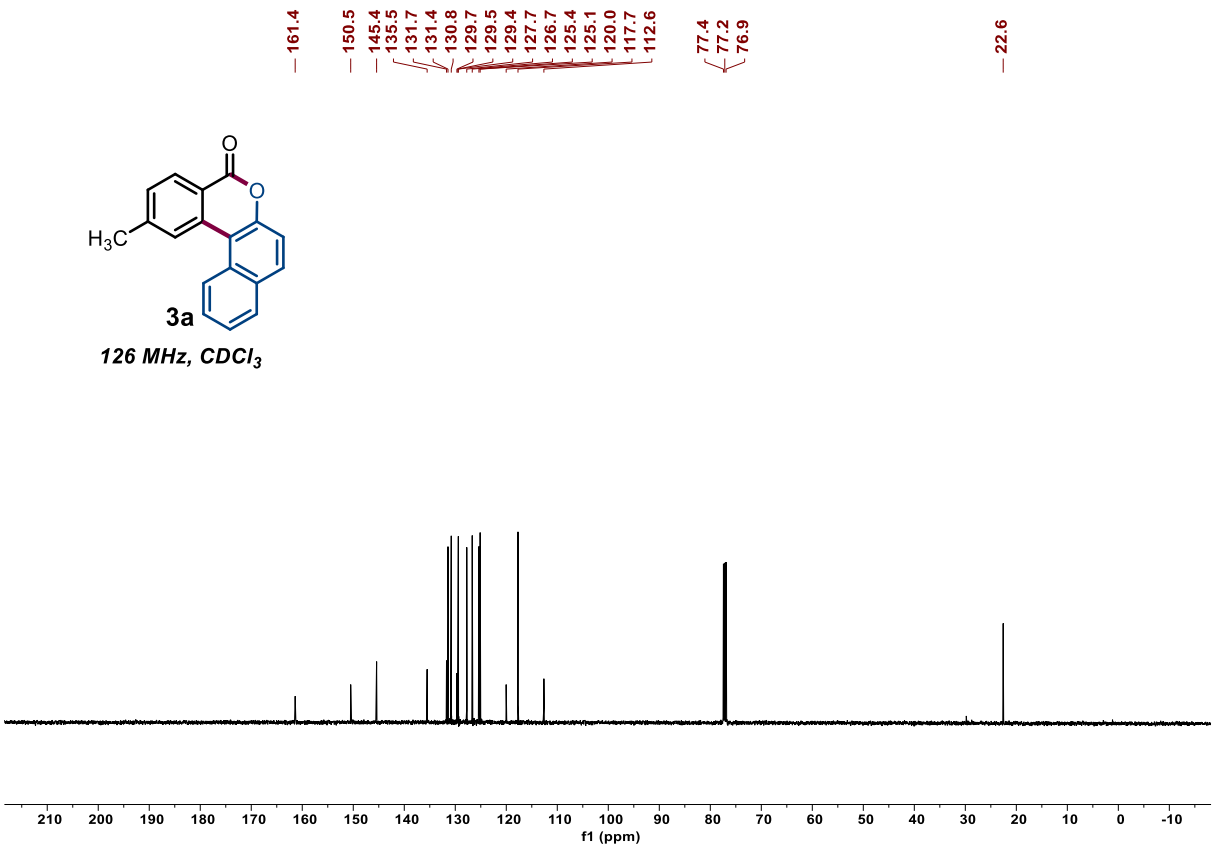


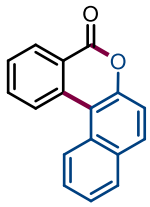
6

2-Methyl-5H-dibenzo[c,f]chromene (6): Sticky liquid; Eluent: 20–25% EtOAc in Hexane; yield = 95 % (47 mg); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.97 (t, *J* = 8.8 Hz, 2H), 7.68 (d, *J* = 7.8 Hz, 1H), 7.50 – 7.45 (m, 3H), 7.42 – 7.38 (m, 1H), 7.34 – 7.32 (m, 1H), 7.26 (s, 1H), 4.48 – 4.40 (m, 2H), 2.56 (s, 3H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 150.7, 138.7, 137.7, 133.7, 133.4, 132.6, 129.9, 129.7, 129.6, 129.1, 128.2, 126.7, 124.6, 123.6, 120.1, 118.2, 63.5, 21.2 ppm; **HRMS** (ESI) m/z: [M+H]+ Calcd. For $C_{18}H_{14}OK^{+}$ 285.0676 Found 285.0792.

NMR Spectra of Synthesized Compounds

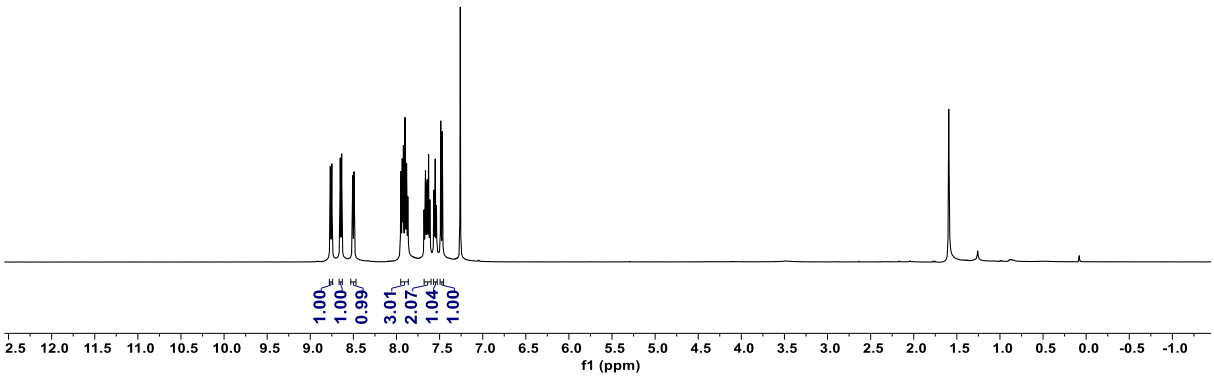

8.71
8.69
8.37
8.35
8.33
7.91
7.89
7.86
7.84
7.65
7.64
7.63
7.62
7.54
7.52
7.51
7.43
7.41
7.40
7.39
7.26
2.58
O
O
H3C
3a
500 MHz, CDCl3
1.06
2.02
0.97
1.03
1.03
1.00
1.99
3.00
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

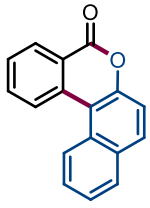

161.4
150.5
145.4
135.5
131.7
131.4
130.8
129.7
129.5
129.4
127.7
126.7
125.4
125.1
120.0
117.7
112.6
77.4
77.2
76.9
22.6
O
O
H3C
3a
126 MHz, CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



3b

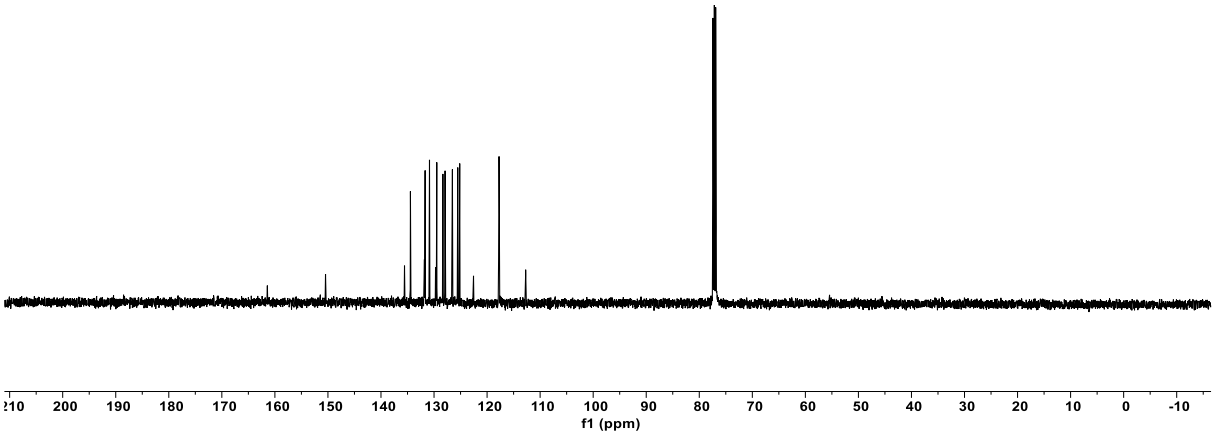
500 MHz, $CDCl_3$

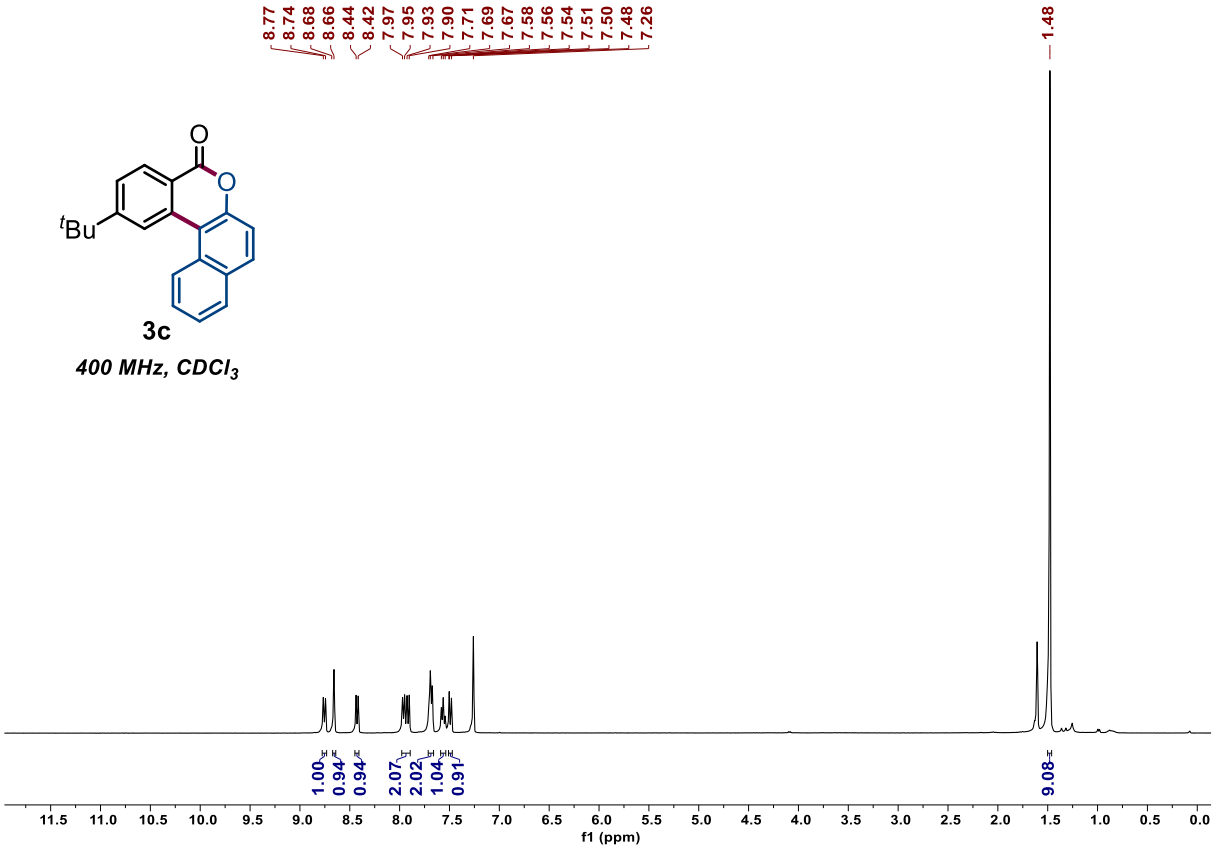




3b

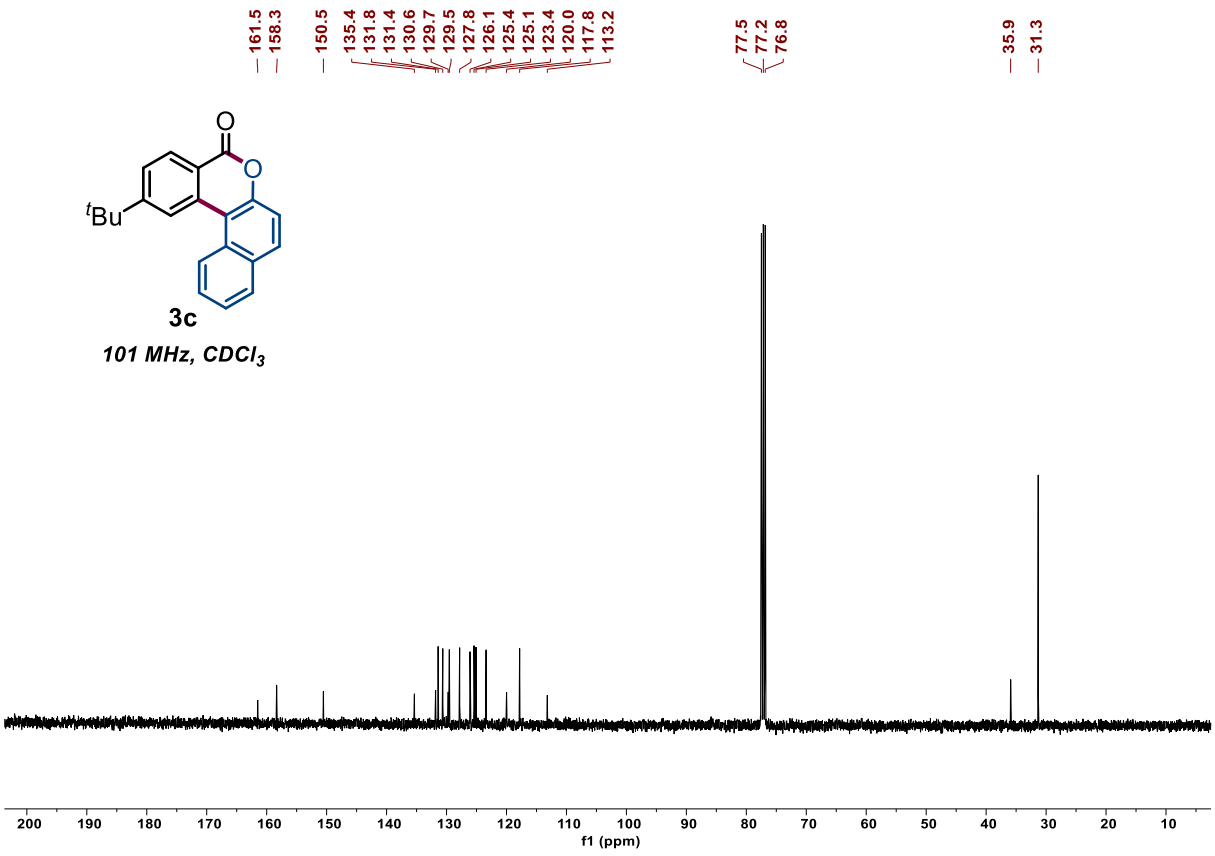
126 MHz, $CDCl_3$





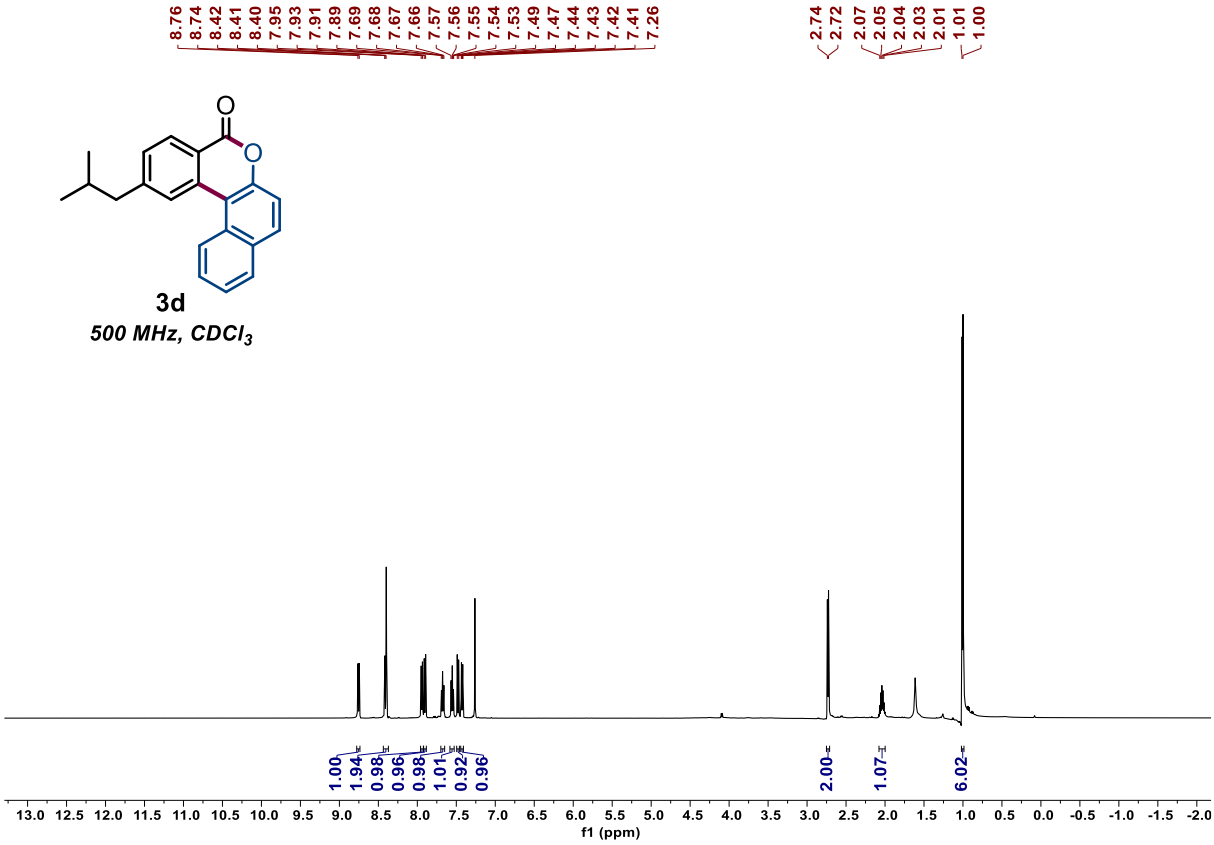
3c

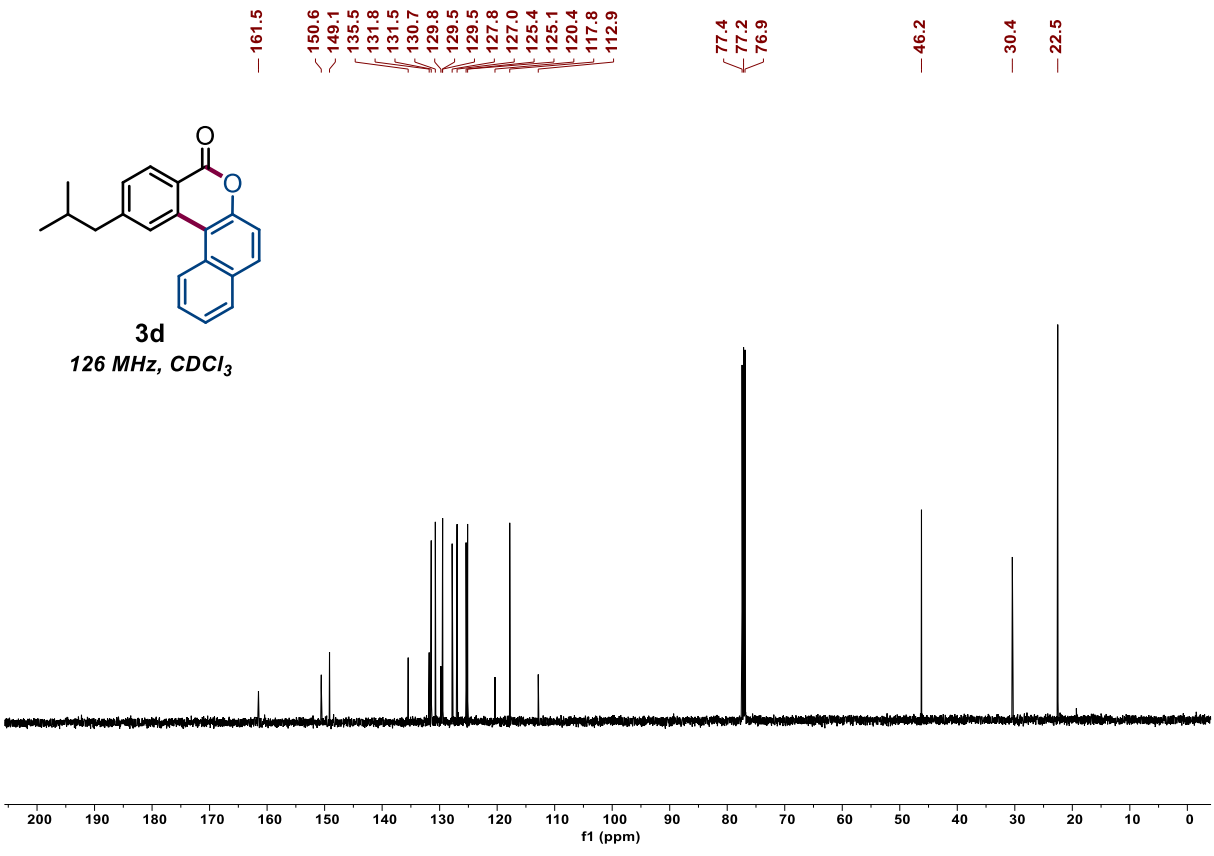
400 MHz, $CDCl_3$

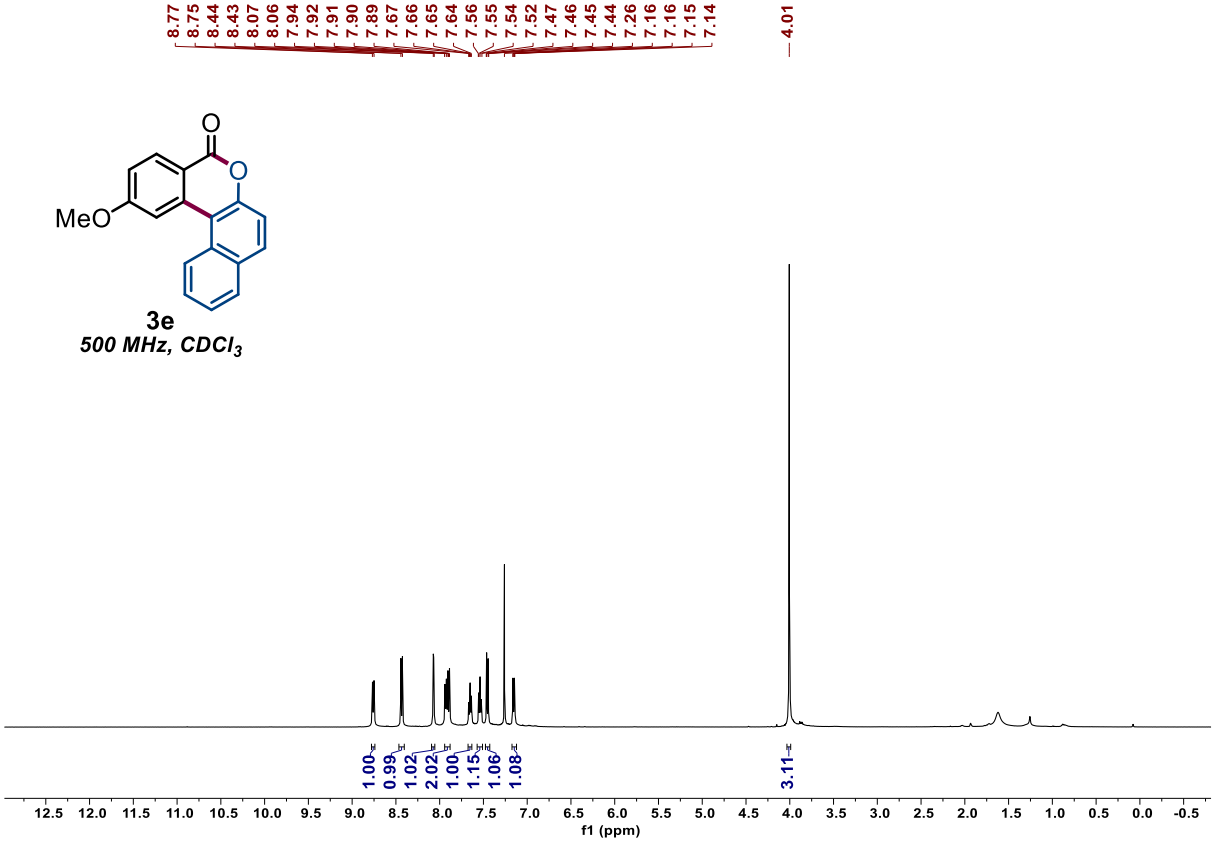


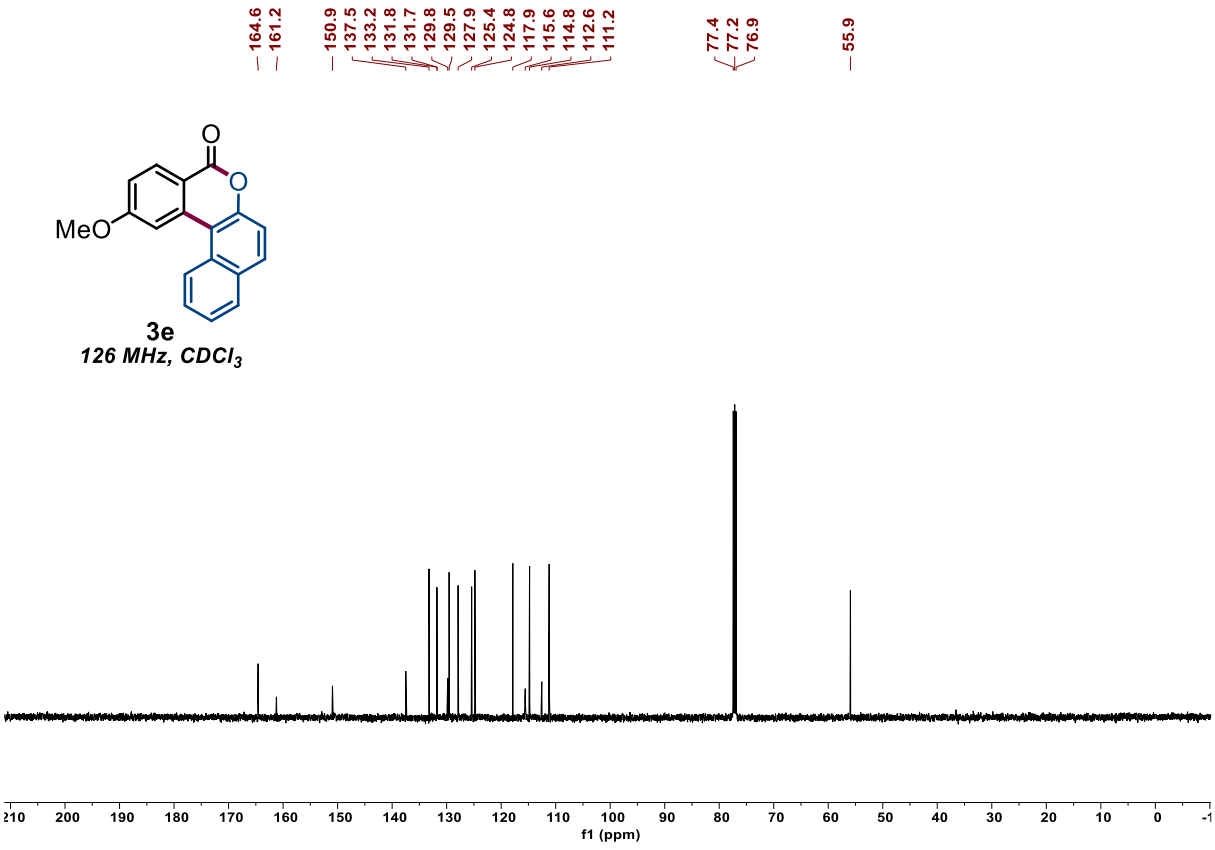
3c

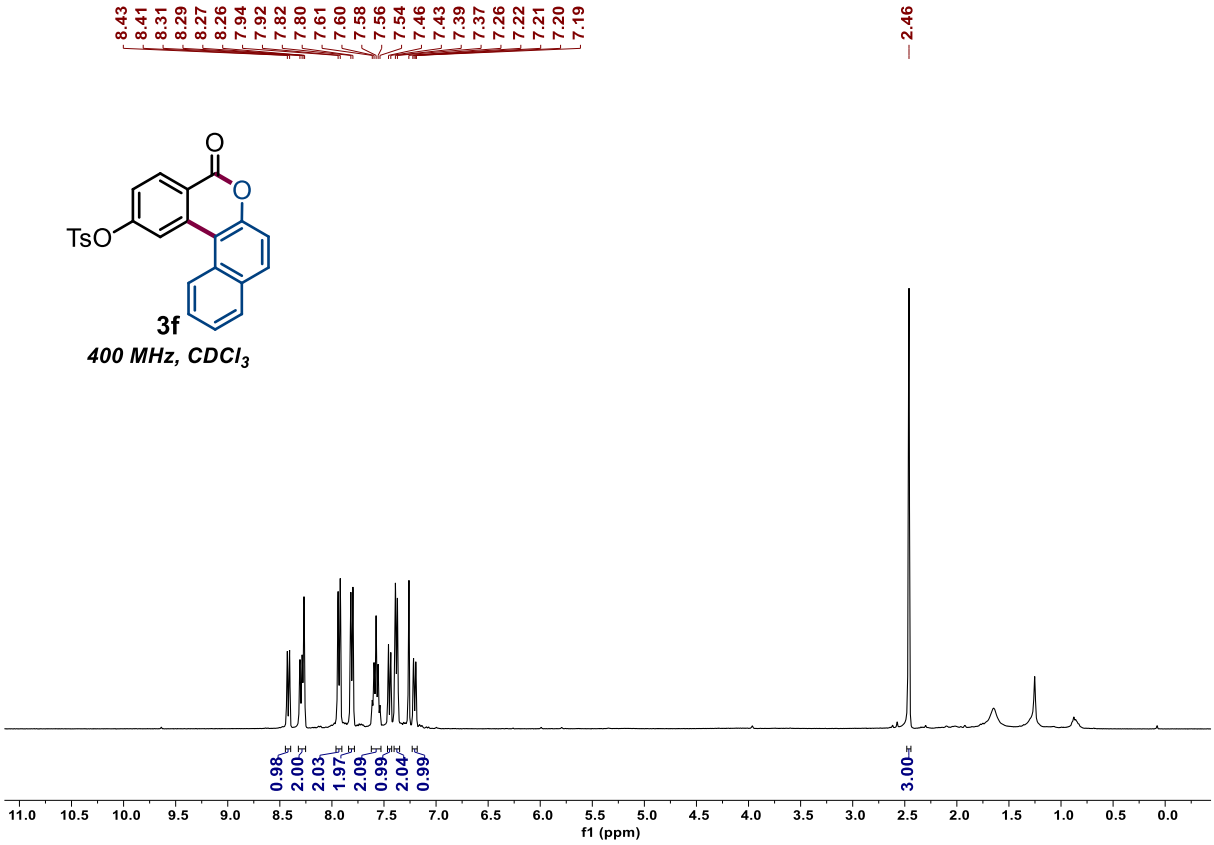
101 MHz, $CDCl_3$

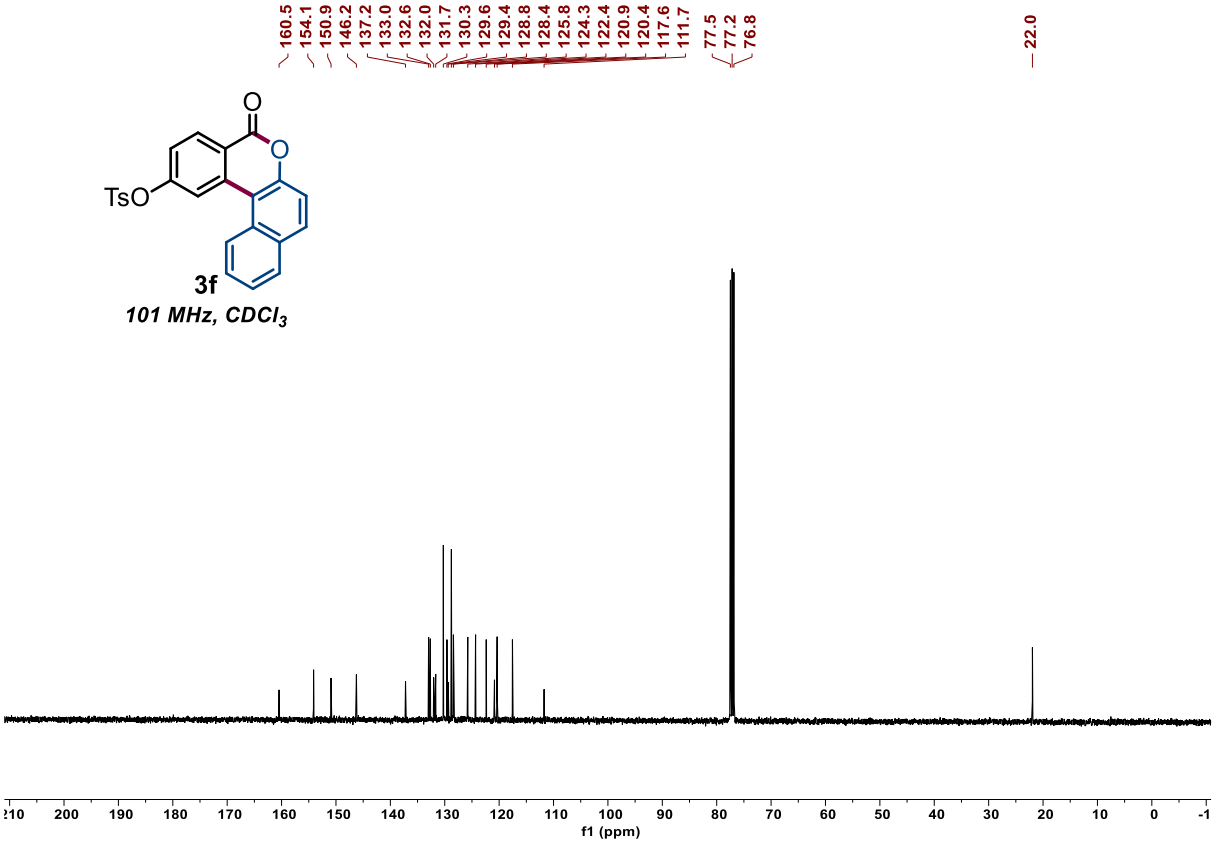

8.76
8.74
8.42
8.41
8.40
7.95
7.93
7.91
7.89
7.69
7.68
7.67
7.66
7.57
7.56
7.55
7.54
7.53
7.49
7.47
7.44
7.43
7.42
7.41
7.26
2.74
2.72
2.07
2.05
2.04
2.03
2.01
1.01
1.00
3d
500 MHz, CDCl3
1.00
1.94
0.98
0.96
0.98
1.01
0.92
0.96
2.00
1.07
6.02
13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5 -2.0
f1 (ppm)

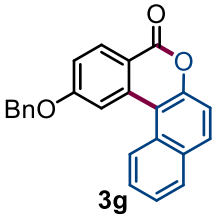

161.5
150.6
149.1
135.5
131.8
131.5
130.7
129.8
129.5
129.5
127.8
127.0
125.4
125.1
120.4
117.8
112.9
77.4
77.2
76.9
46.2
30.4
22.5
3d
126 MHz, CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


8.77
8.75
8.44
8.43
8.07
8.06
7.94
7.92
7.91
7.90
7.89
7.67
7.66
7.65
7.64
7.56
7.55
7.54
7.52
7.47
7.46
7.45
7.44
7.26
7.16
7.16
7.15
7.14
4.01
MeO
O
O
3e
500 MHz, CDCl3
1.00
0.99
1.02
2.02
1.00
1.15
1.06
1.08
3.11
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


164.6
161.2
150.9
137.5
133.2
131.8
131.7
129.8
129.5
127.9
125.4
124.8
117.9
115.6
114.8
112.6
111.2
77.4
77.2
76.9
55.9
MeO
O
O
3e
126 MHz, CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

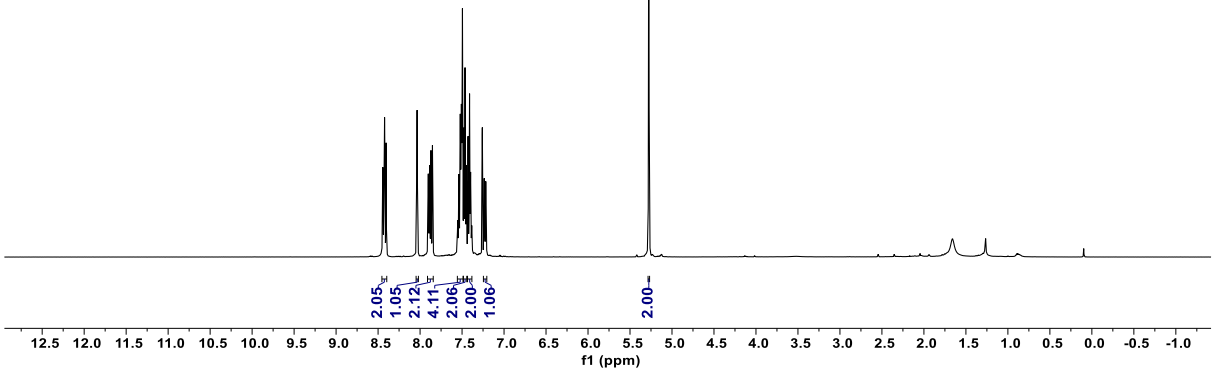

8.43
8.41
8.31
8.29
8.27
8.26
7.94
7.92
7.82
7.80
7.61
7.60
7.58
7.56
7.54
7.46
7.43
7.39
7.37
7.26
7.22
7.21
7.20
7.19
2.46
TsO
3f
400 MHz, CDCl3
0.98
2.00
2.03
1.97
2.09
0.99
2.04
0.99
3.00
f1 (ppm)

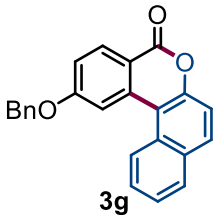

160.5
154.1
150.9
146.2
137.2
133.0
132.6
132.0
131.7
130.3
129.6
129.4
128.8
128.4
125.8
124.3
122.4
120.9
120.4
117.6
111.7
77.5
77.2
76.8
22.0
TsO
3f
101 MHz, CDCl3
f1 (ppm)



3g

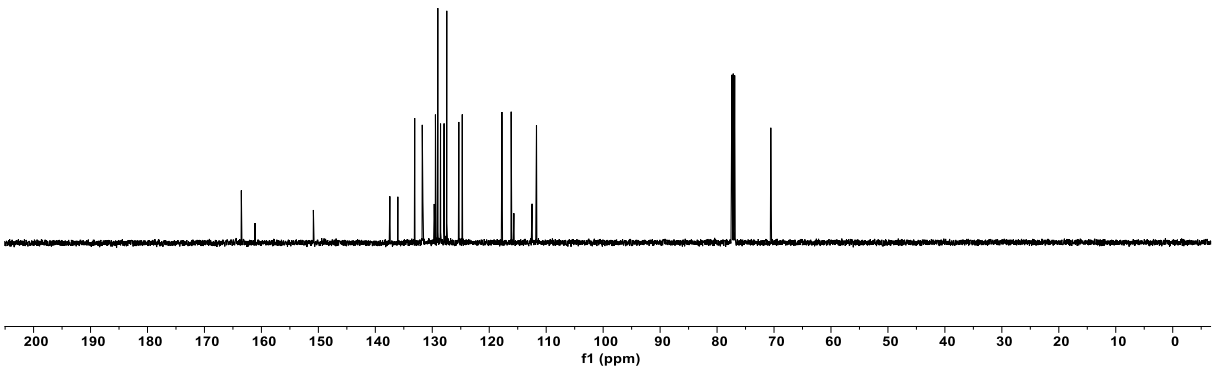
500 MHz, $CDCl_3$

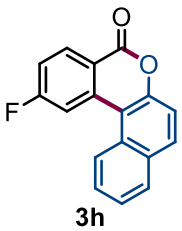




3g

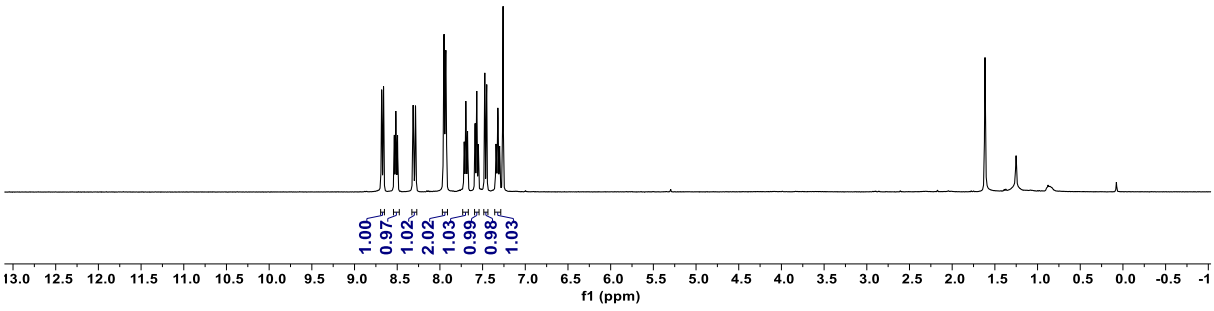
126 MHz, $CDCl_3$

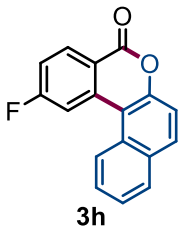




3h

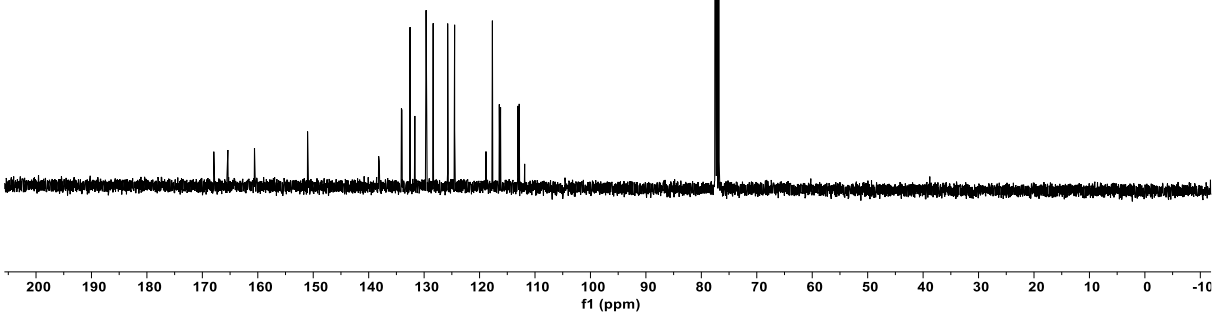
400 MHz, $CDCl_3$

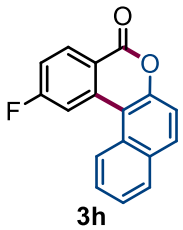




3h

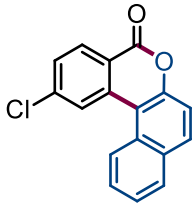
101 MHz, $CDCl_3$





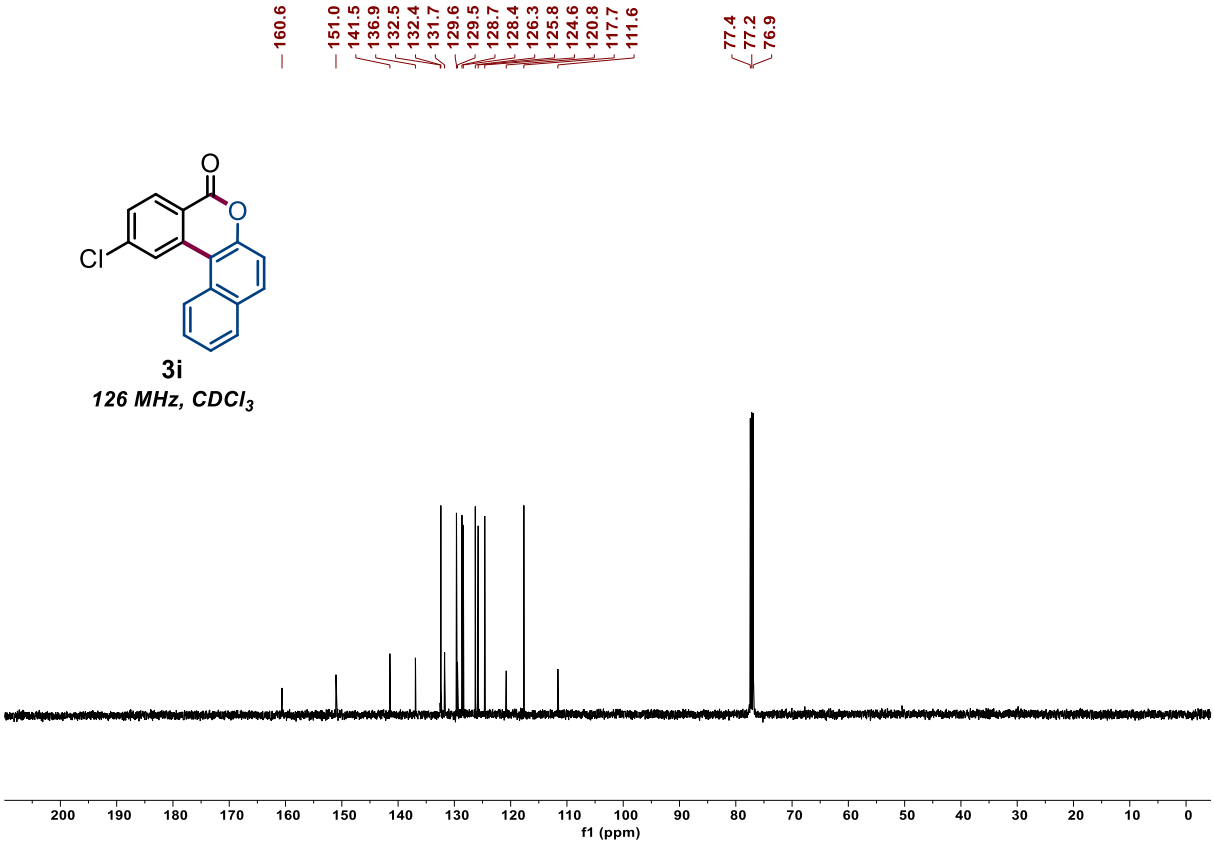
3h

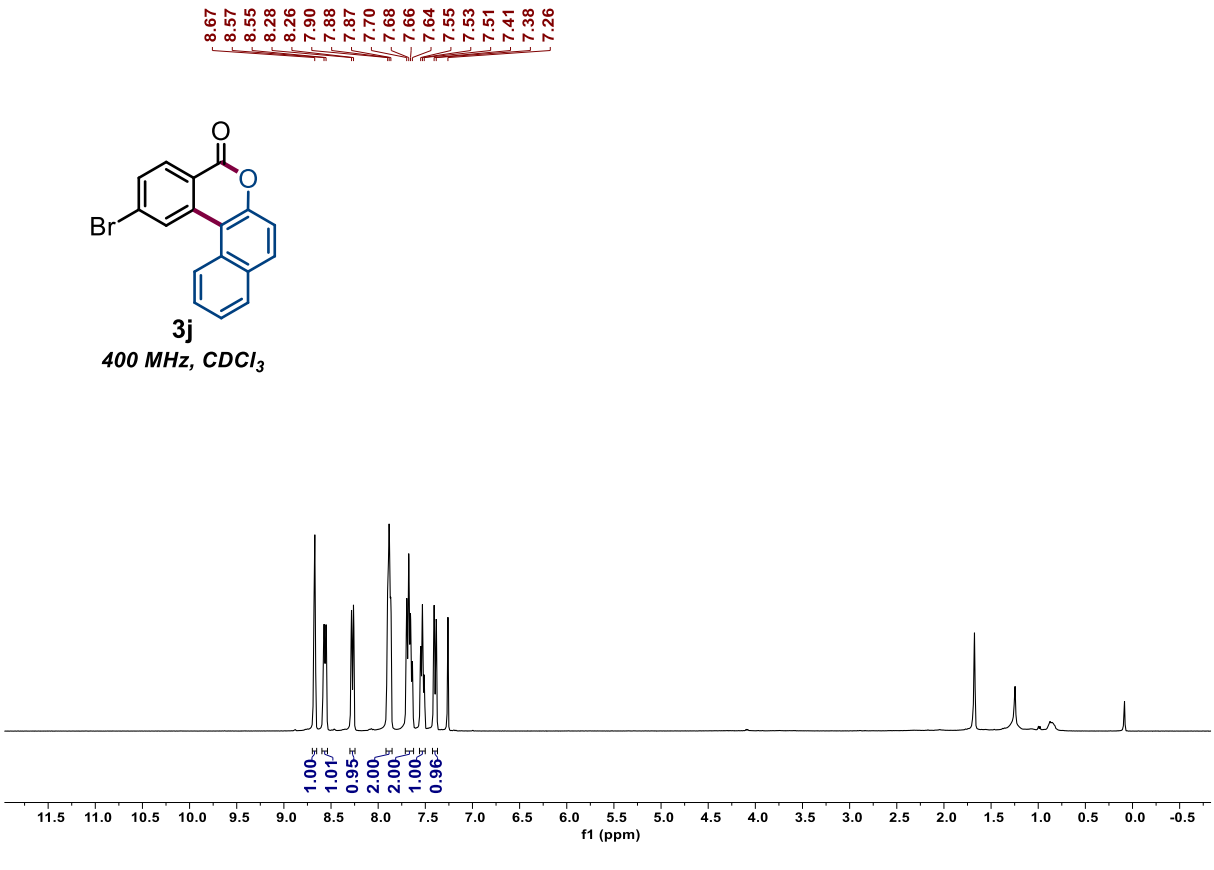
471 MHz, $CDCl_3$

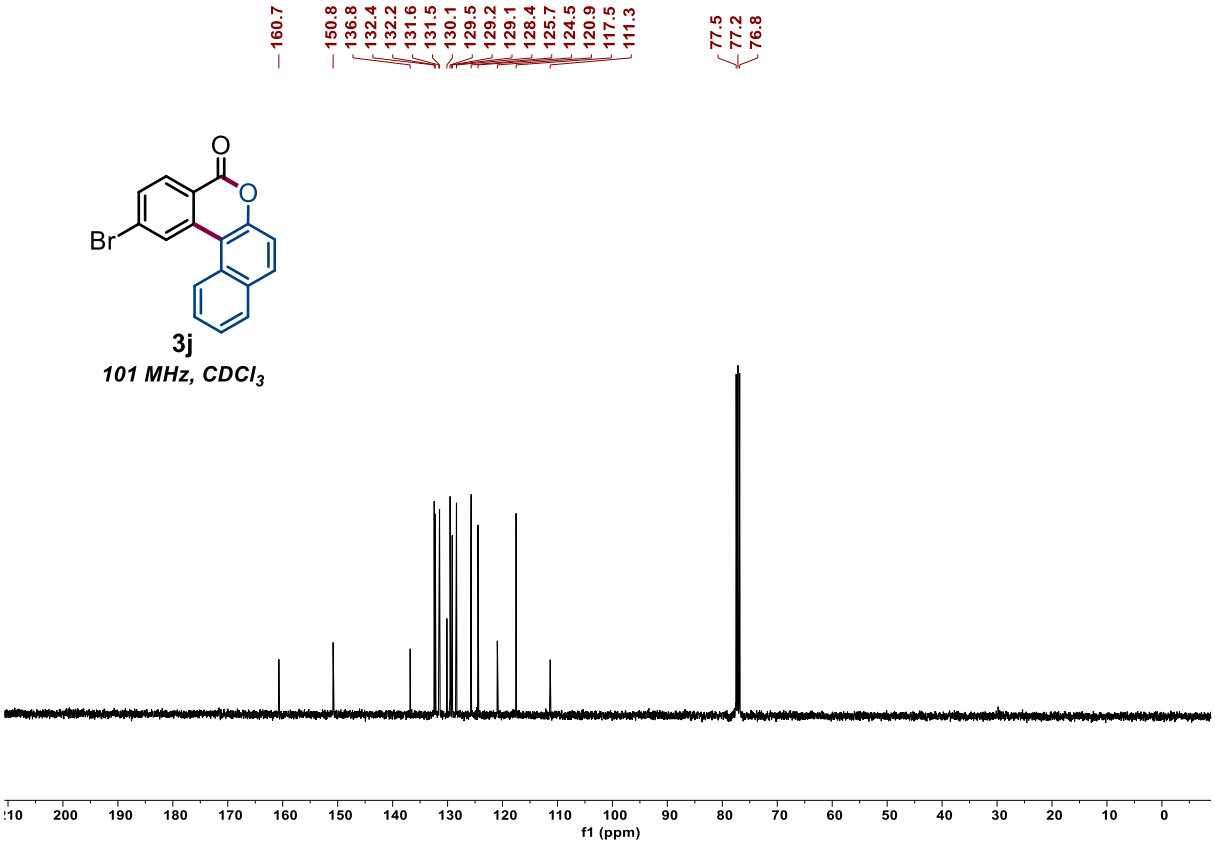


3i

500 MHz, $CDCl_3$

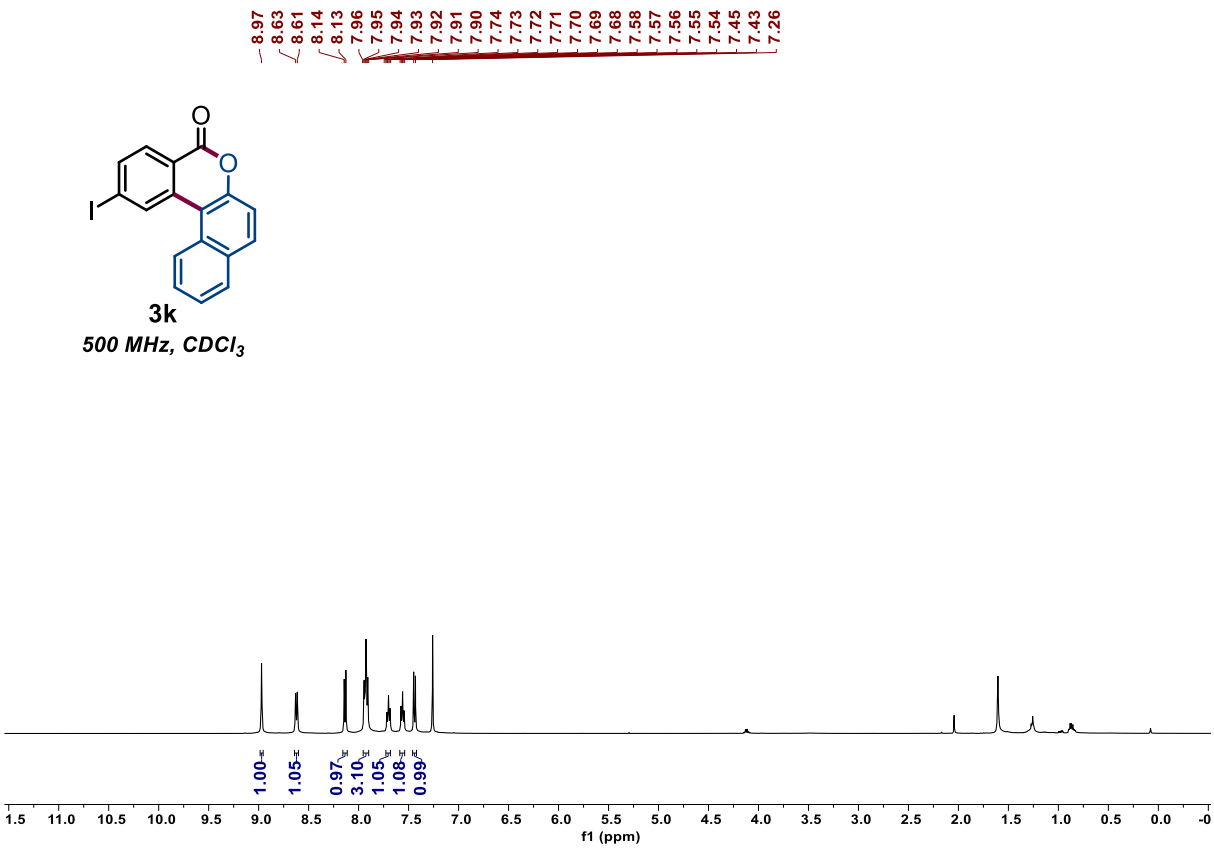

160.6
151.0
141.5
136.9
132.5
132.4
131.7
129.6
129.5
128.7
128.4
126.3
125.8
124.6
120.8
117.7
111.6
77.4
77.2
76.9
O
O
Cl
3i
126 MHz, CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


8.67
8.57
8.55
8.28
8.26
7.90
7.88
7.87
7.70
7.68
7.66
7.64
7.55
7.53
7.51
7.41
7.38
7.26
O
O
Br
3j
400 MHz, CDCl3
1.00
1.01
0.95
2.00
2.00
1.00
0.96
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)



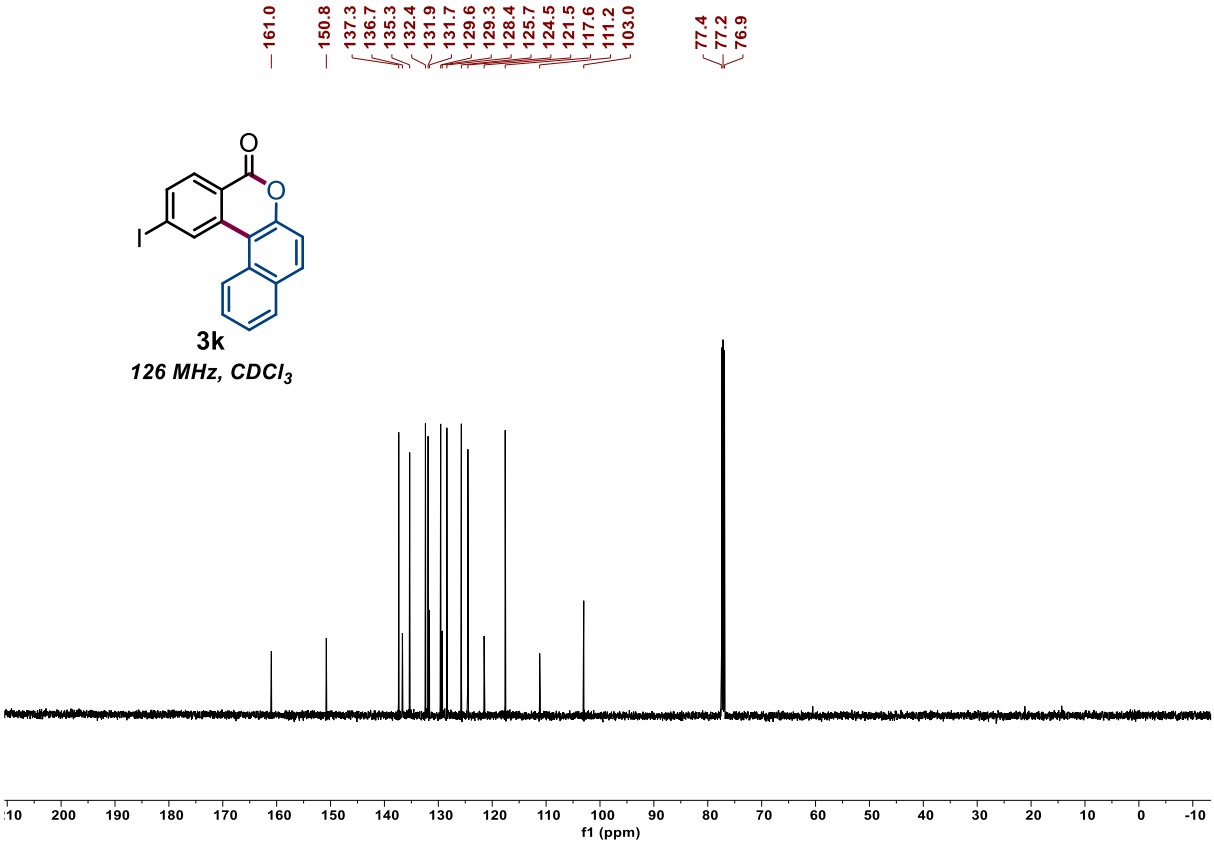
3j

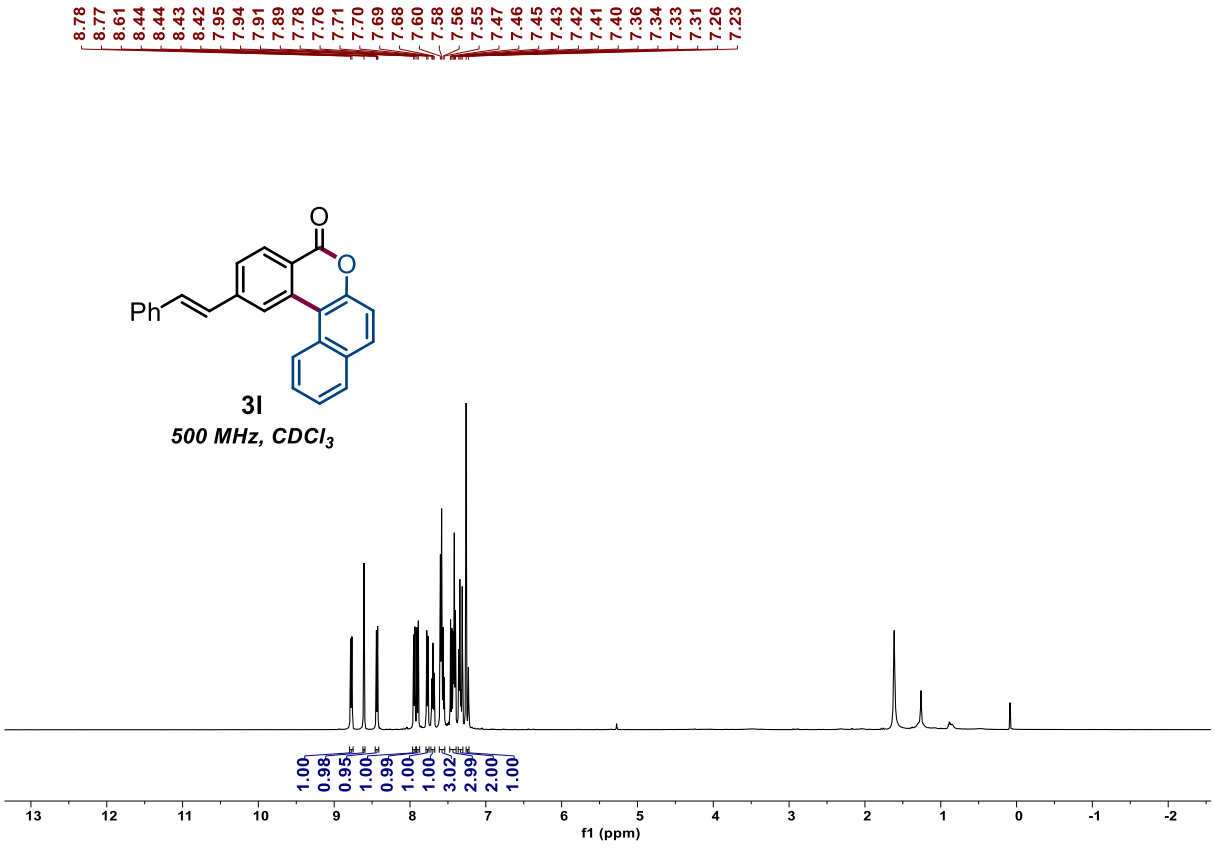
101 MHz, $CDCl_3$

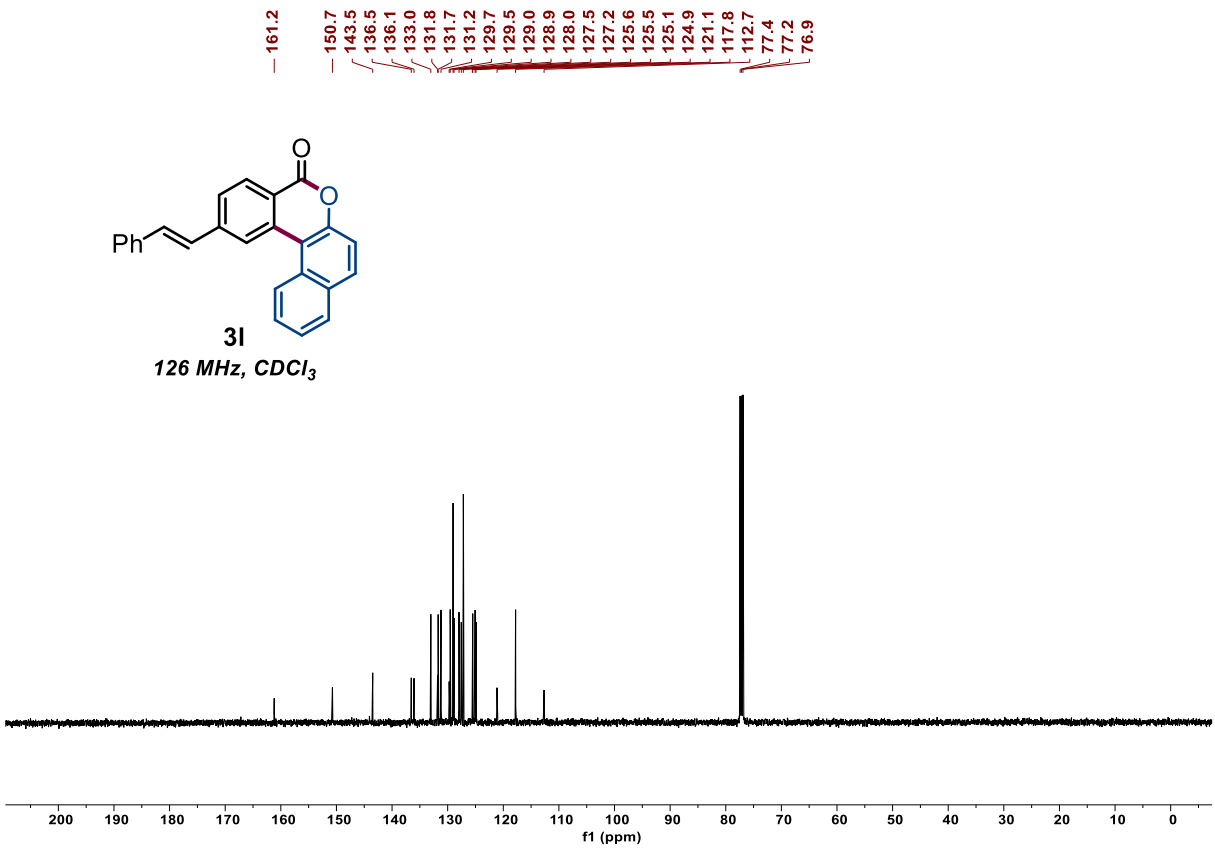


3k

500 MHz, $CDCl_3$

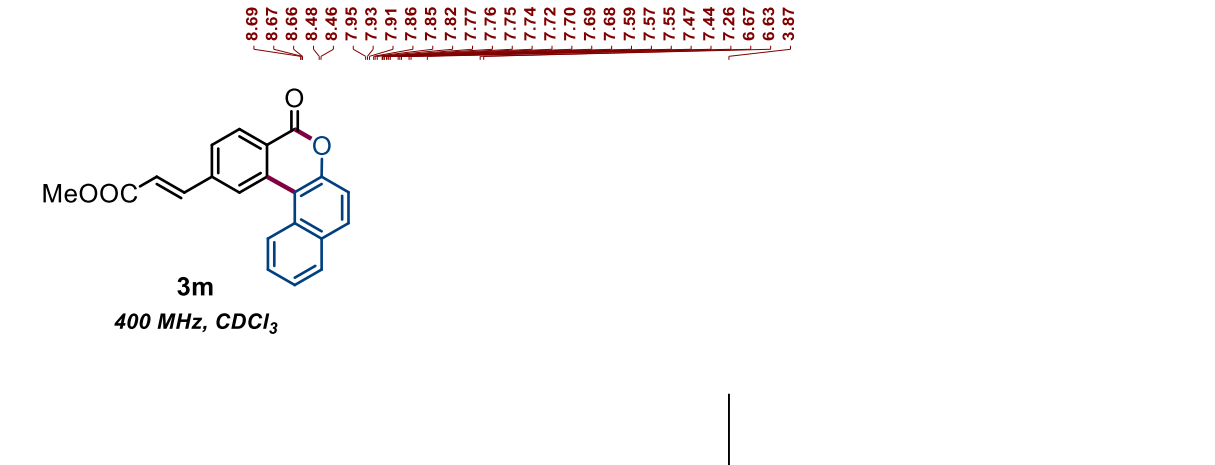

161.0
150.8
137.3
136.7
135.3
132.4
131.9
131.7
129.6
129.3
128.4
125.7
124.5
121.5
117.6
111.2
103.0
77.4
77.2
76.9
O
O
I
3k
126 MHz, CDCl3
f1 (ppm)


8.78
8.77
8.61
8.44
8.44
8.43
8.42
7.95
7.94
7.91
7.89
7.78
7.76
7.71
7.70
7.69
7.68
7.60
7.58
7.56
7.55
7.47
7.46
7.45
7.43
7.42
7.41
7.40
7.36
7.34
7.33
7.31
7.26
7.23
O
O
Ph
3l
500 MHz, CDCl3
1.00
0.98
0.95
1.00
0.99
1.00
1.00
3.02
2.99
2.00
1.00
f1 (ppm)



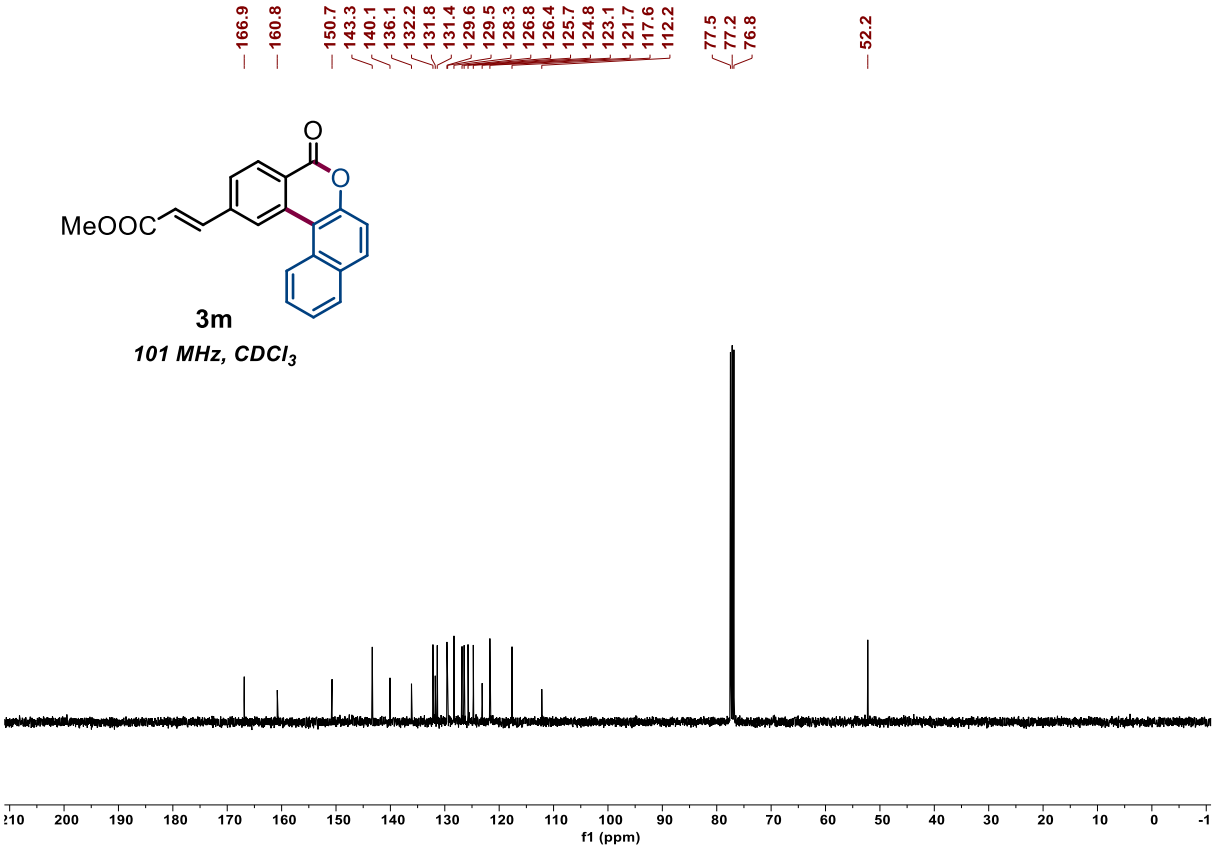
3l

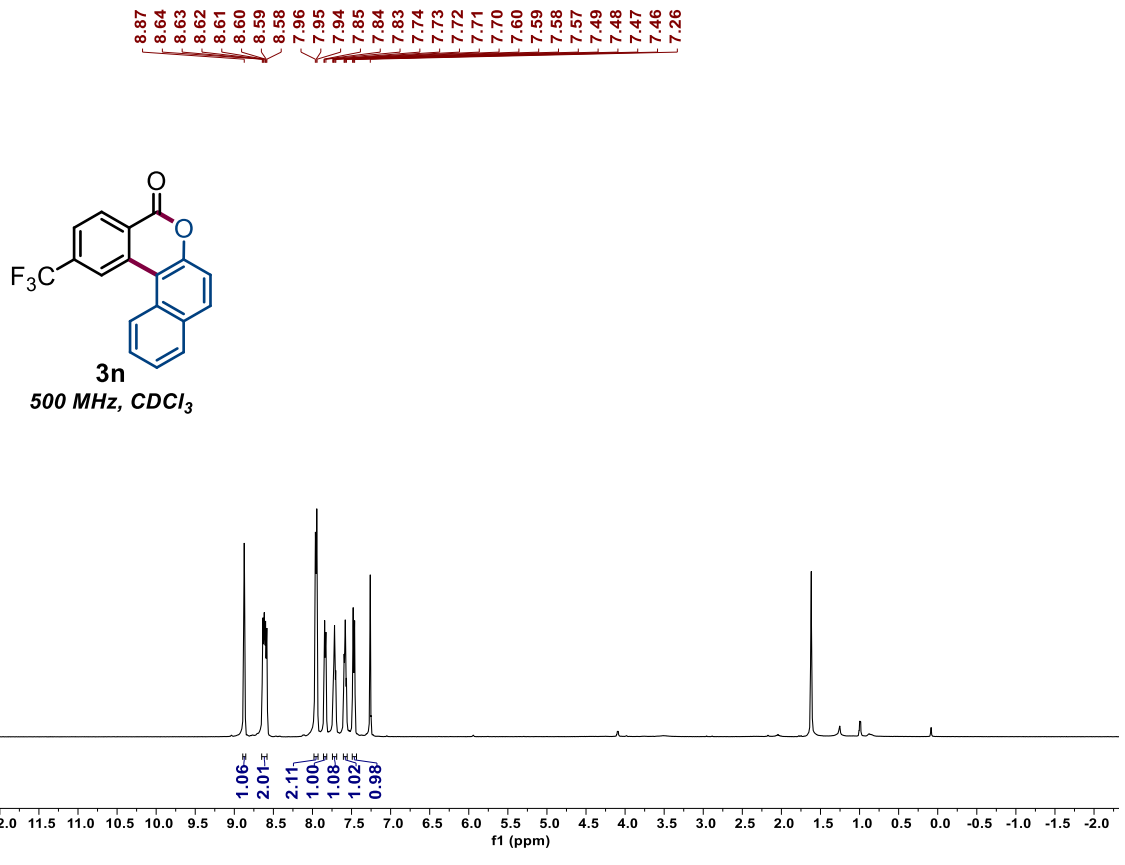
126 MHz, $CDCl_3$

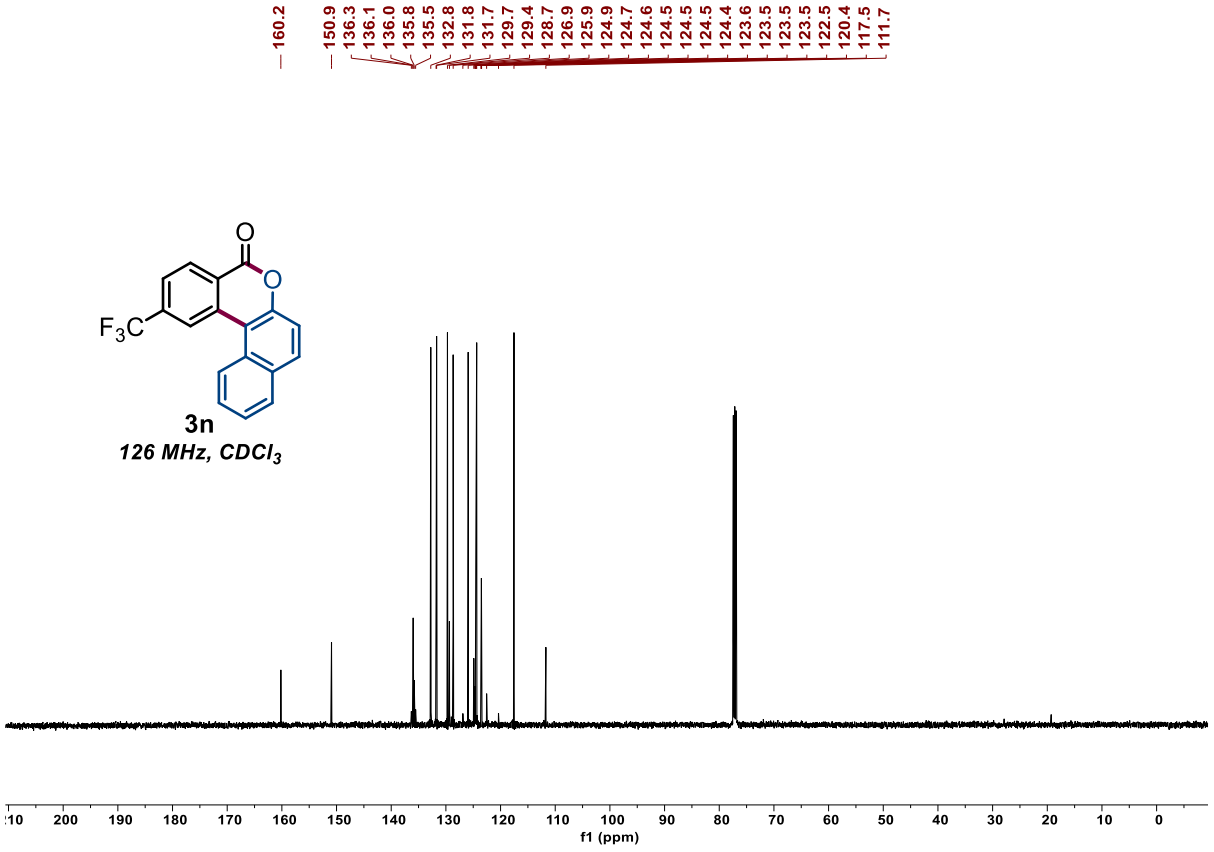


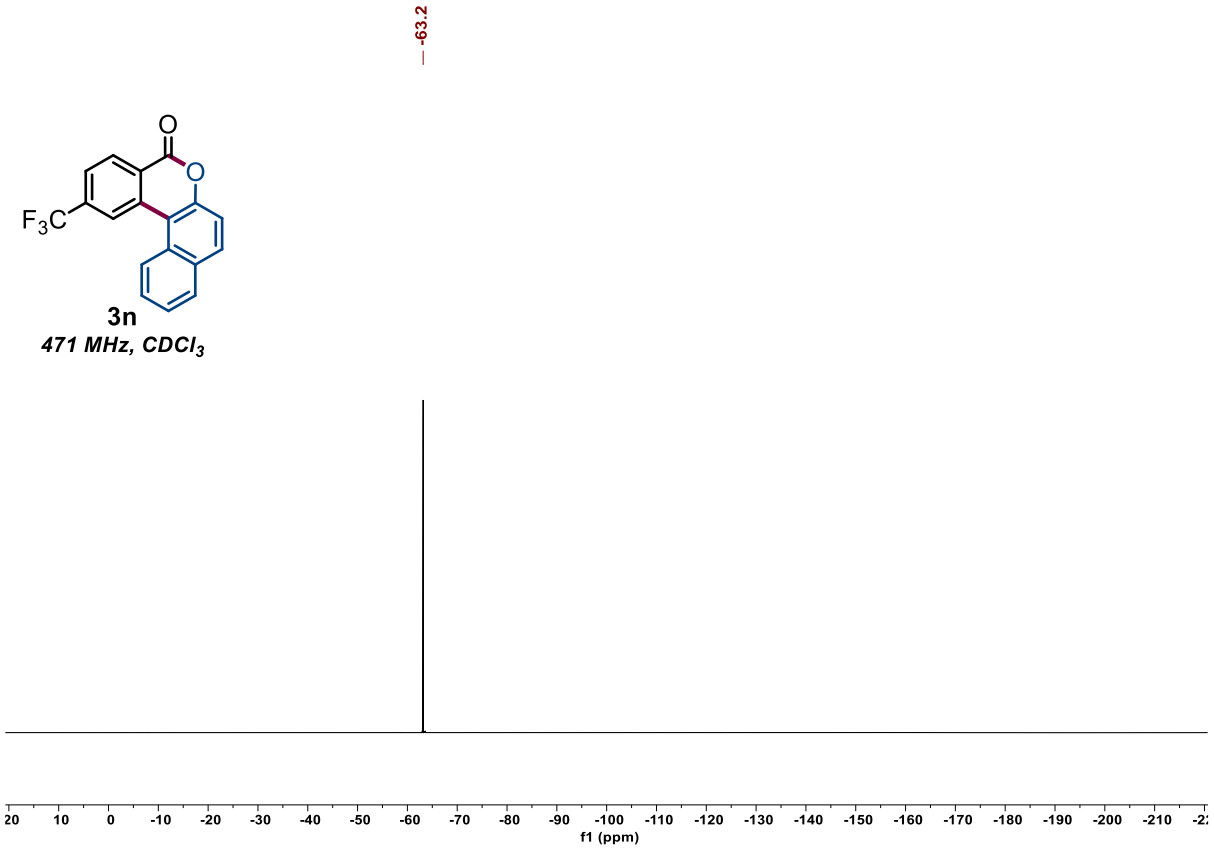
3m

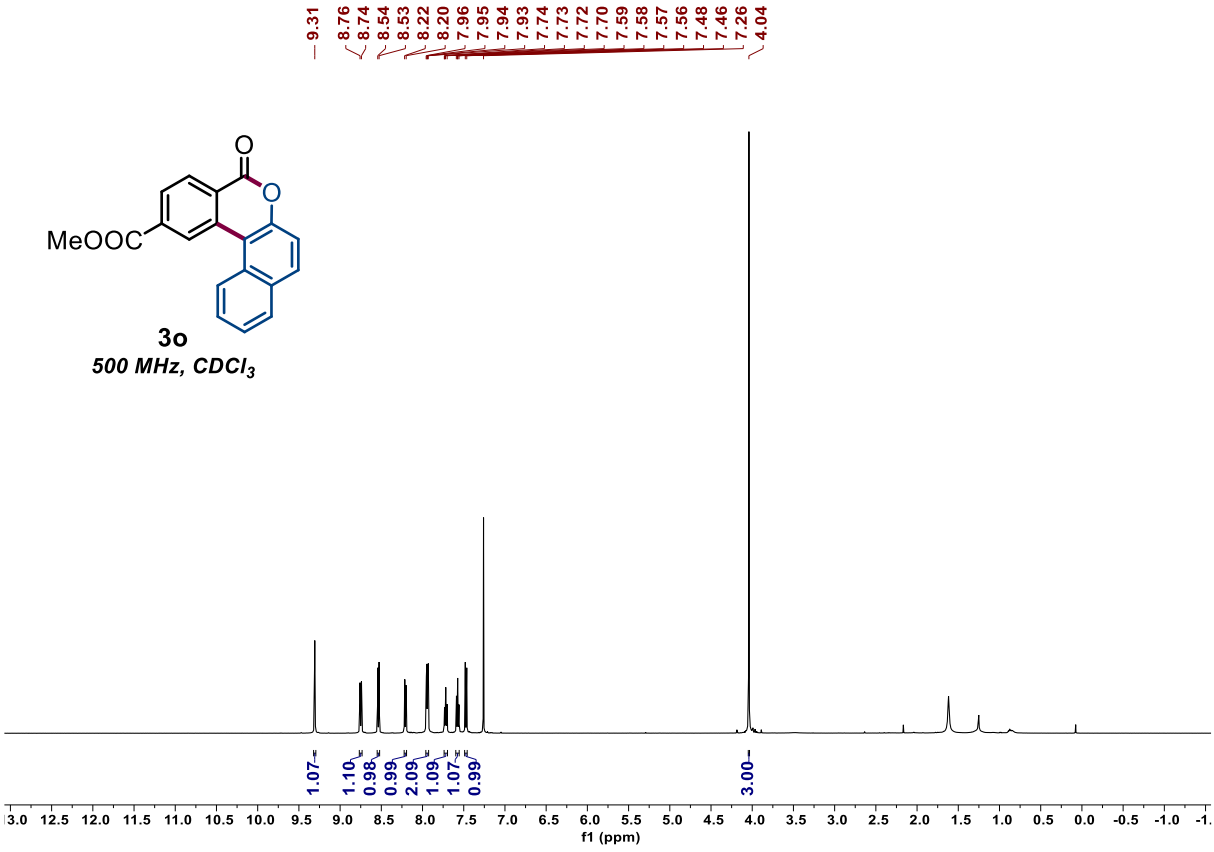
400 MHz, $CDCl_3$


166.9
160.8
150.7
143.3
140.1
136.1
132.2
131.8
131.4
129.6
129.5
128.3
126.8
126.4
125.7
124.8
123.1
121.7
117.6
112.2
77.5
77.2
76.8
52.2
MeOOC
O
O
3m
101 MHz, CDCl3
f1 (ppm)


8.87
8.64
8.63
8.62
8.61
8.60
8.59
8.58
7.96
7.95
7.94
7.85
7.84
7.83
7.74
7.73
7.72
7.71
7.70
7.60
7.59
7.58
7.57
7.49
7.48
7.47
7.46
7.26
F3C
O
O
3n
500 MHz, CDCl3
1.06
2.01
2.11
1.00
1.08
1.02
0.98
f1 (ppm)

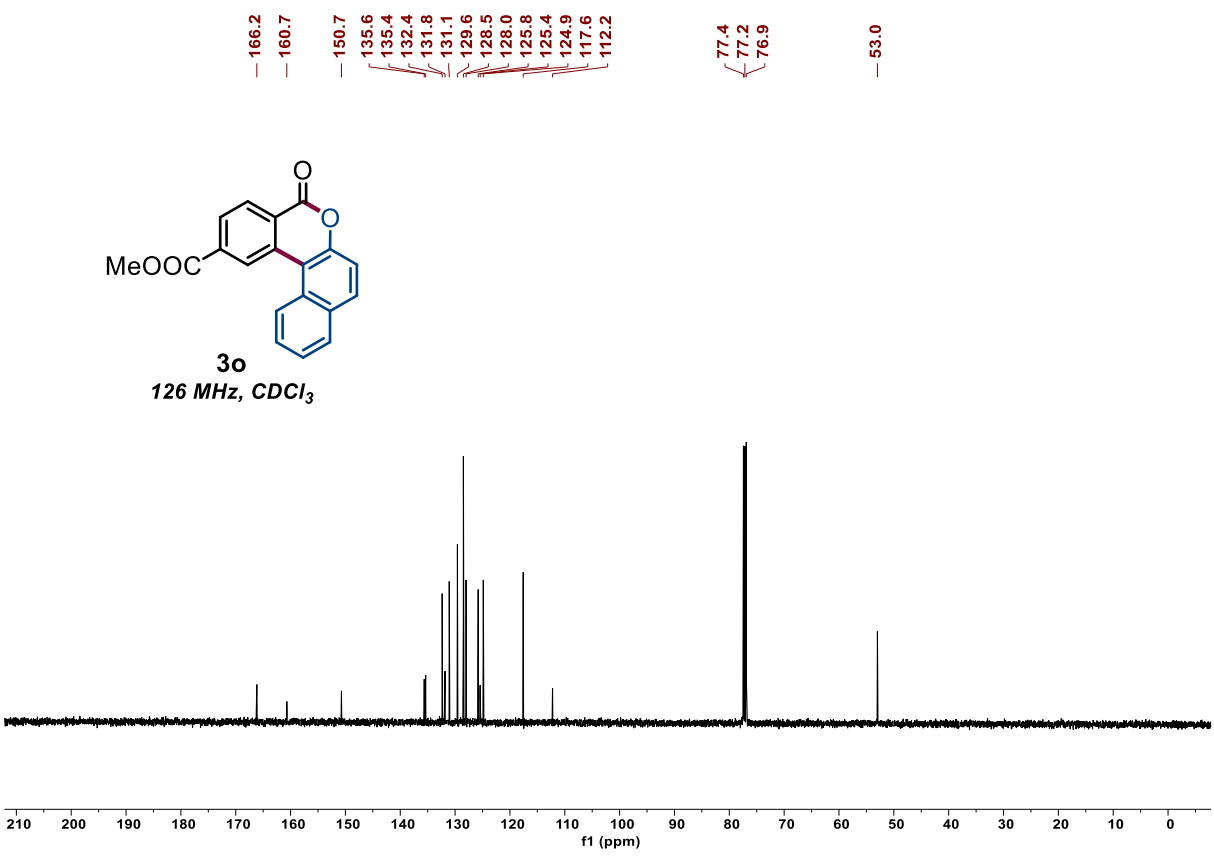

160.2
150.9
136.3
136.1
136.0
135.8
135.5
132.8
131.8
131.7
129.7
129.4
128.7
126.9
125.9
124.9
124.7
124.6
124.5
124.5
124.5
124.4
123.6
123.5
123.5
123.5
122.5
120.4
117.5
111.7
O
O
F3C
3n
126 MHz, CDCl3
f1 (ppm)


-63.2
O
O
F3C
3n
471 MHz, CDCl3
f1 (ppm)



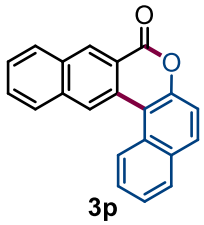
3o

500 MHz, $CDCl_3$



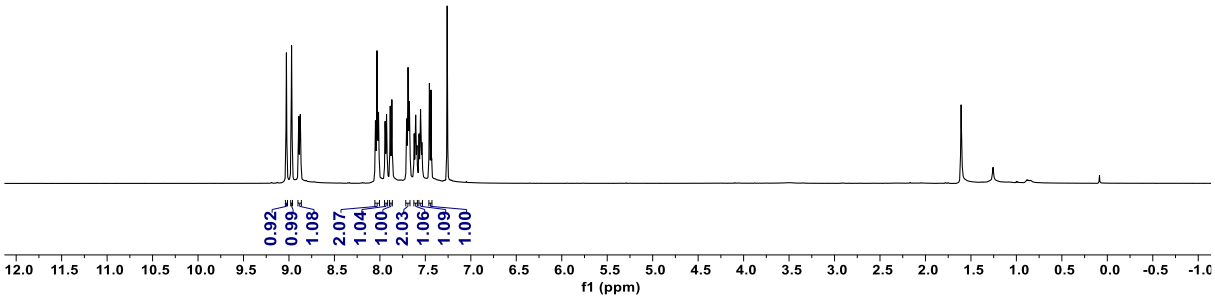
3o

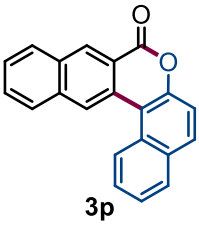
126 MHz, $CDCl_3$



3p

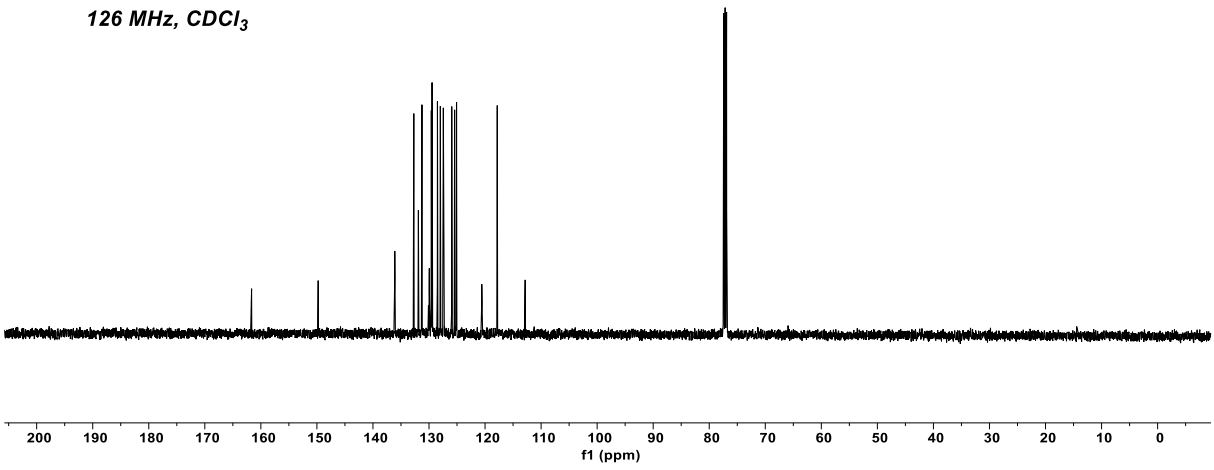
500 MHz, $CDCl_3$

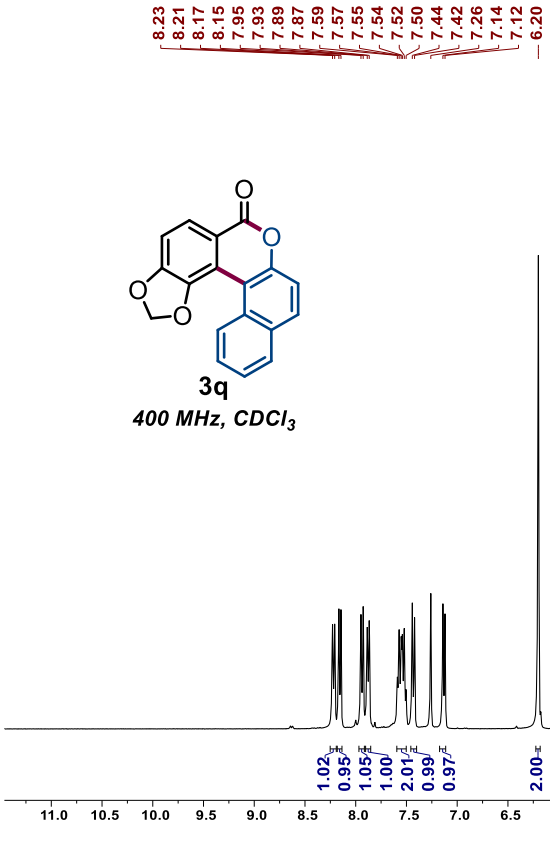


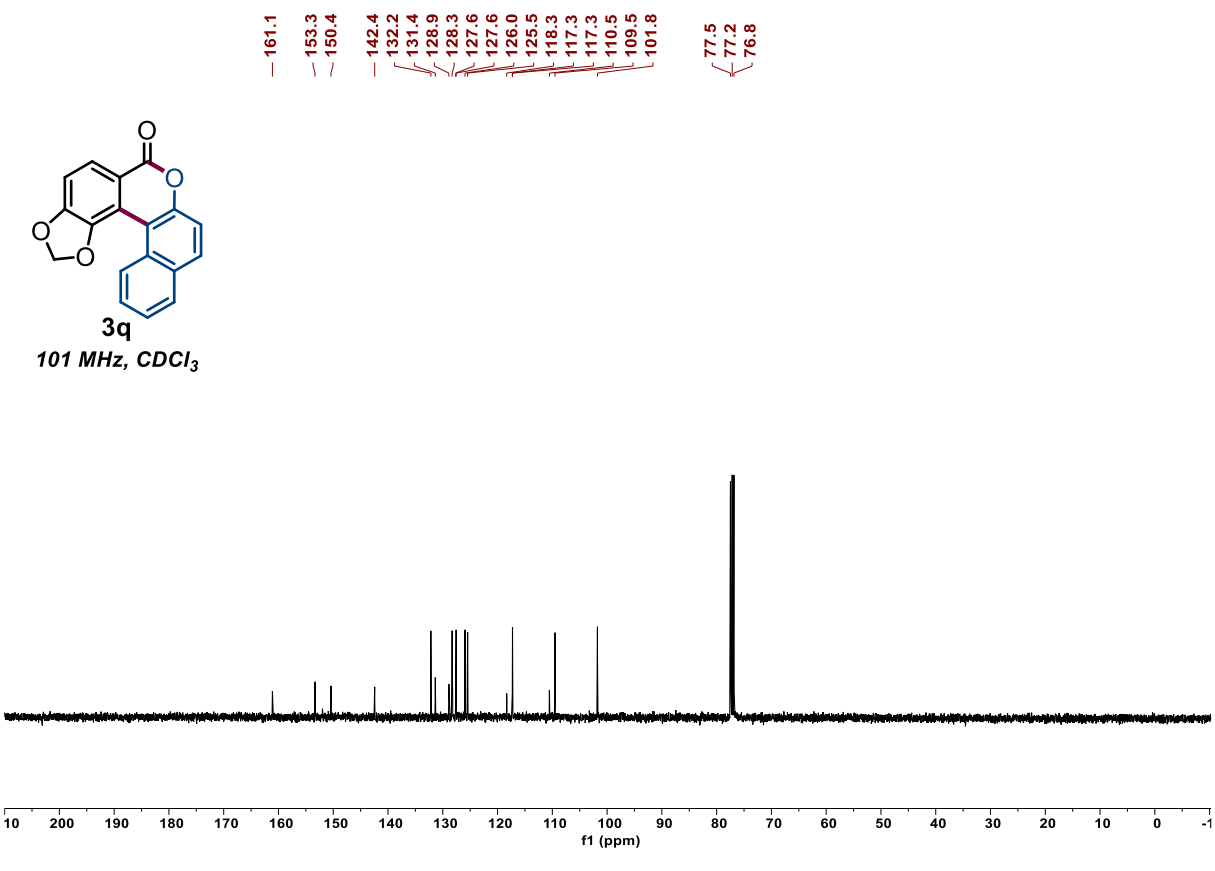


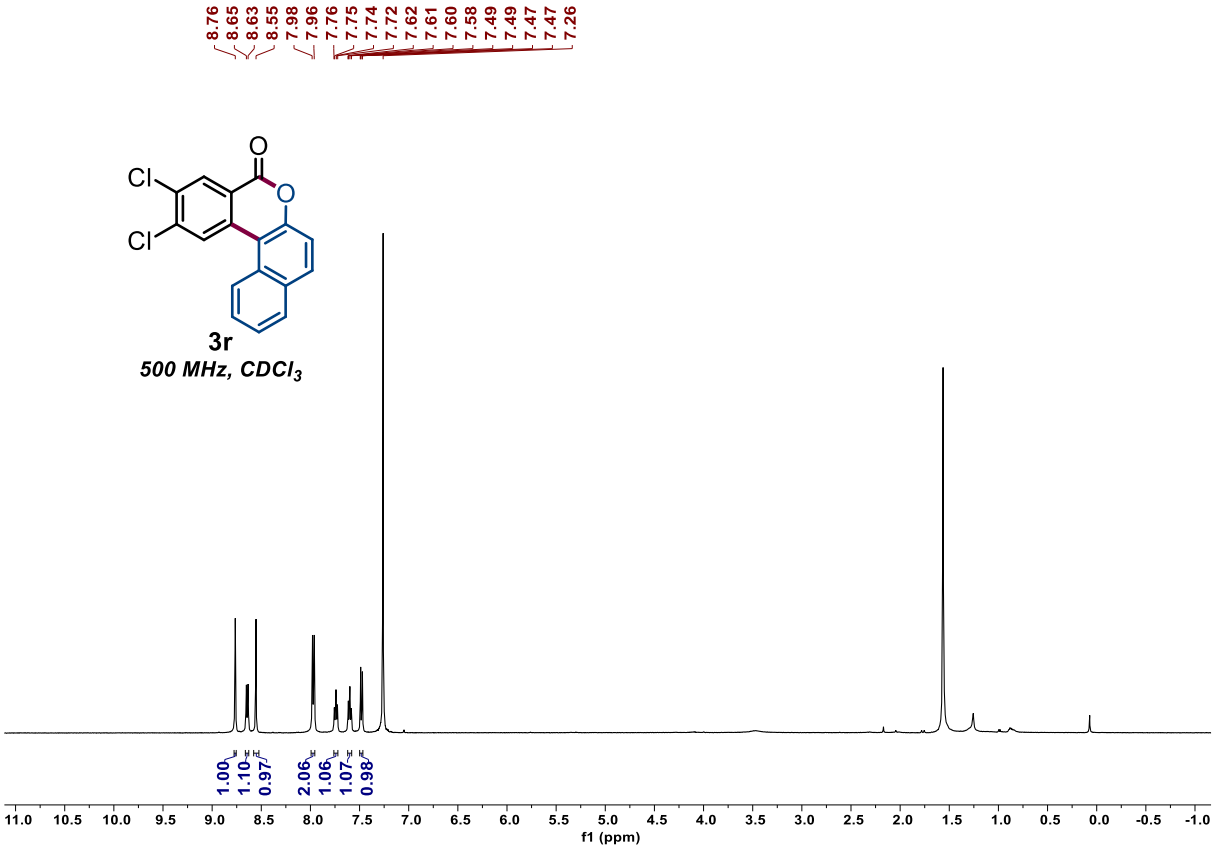
3p

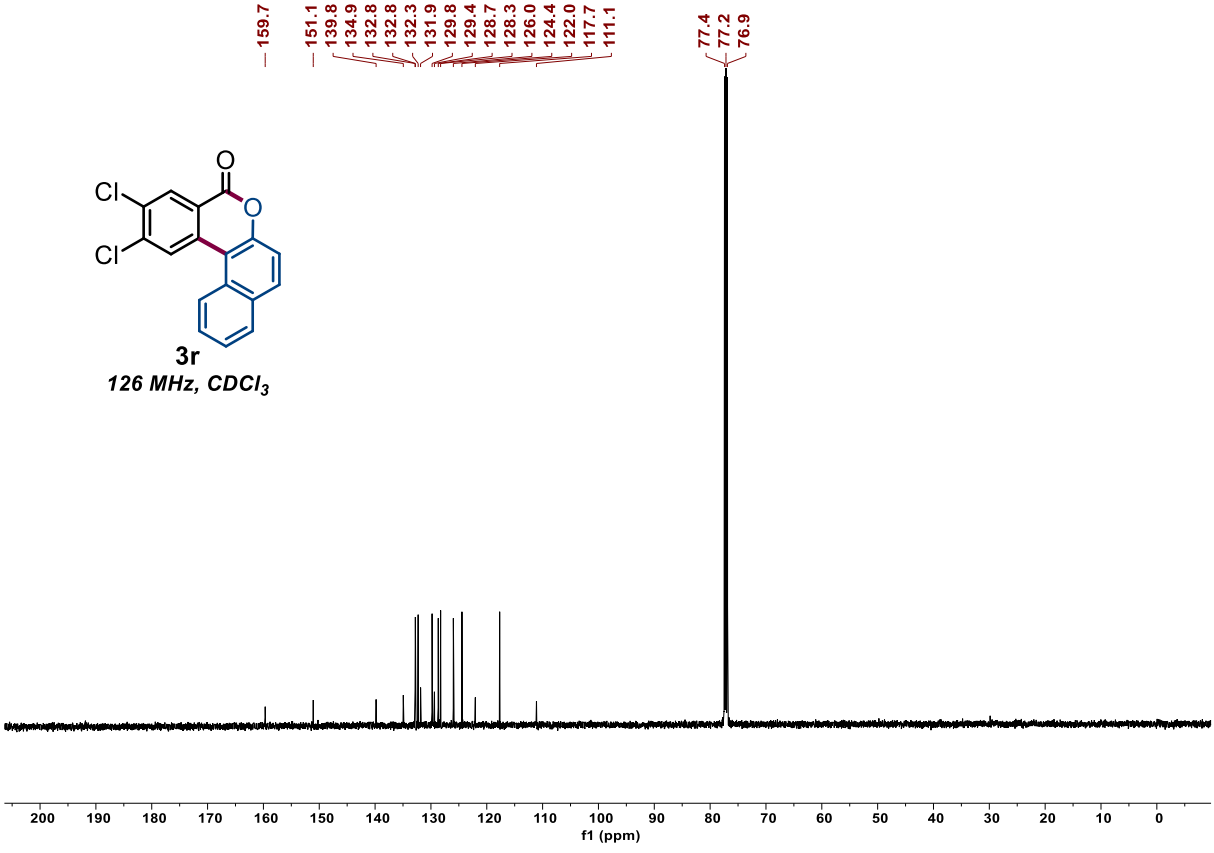
126 MHz, $CDCl_3$

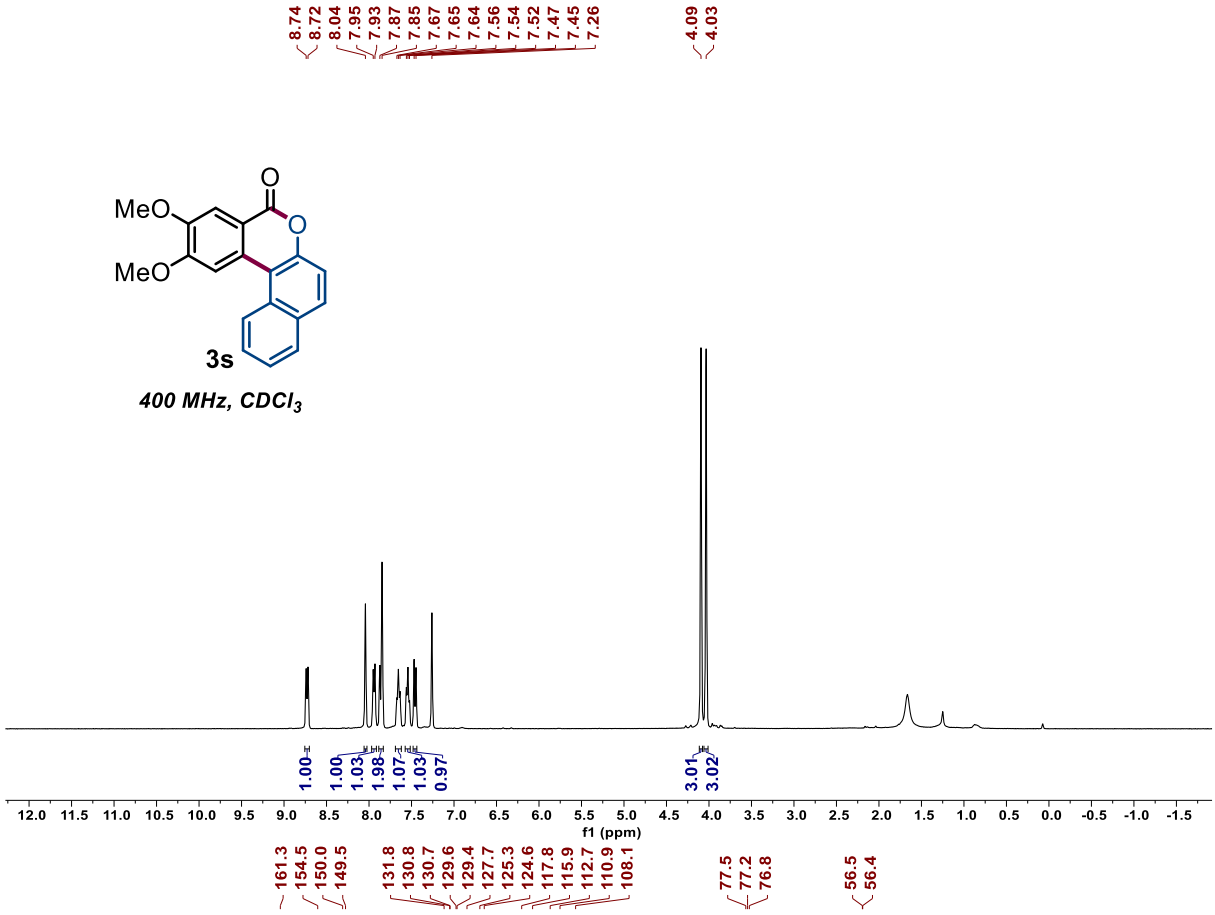


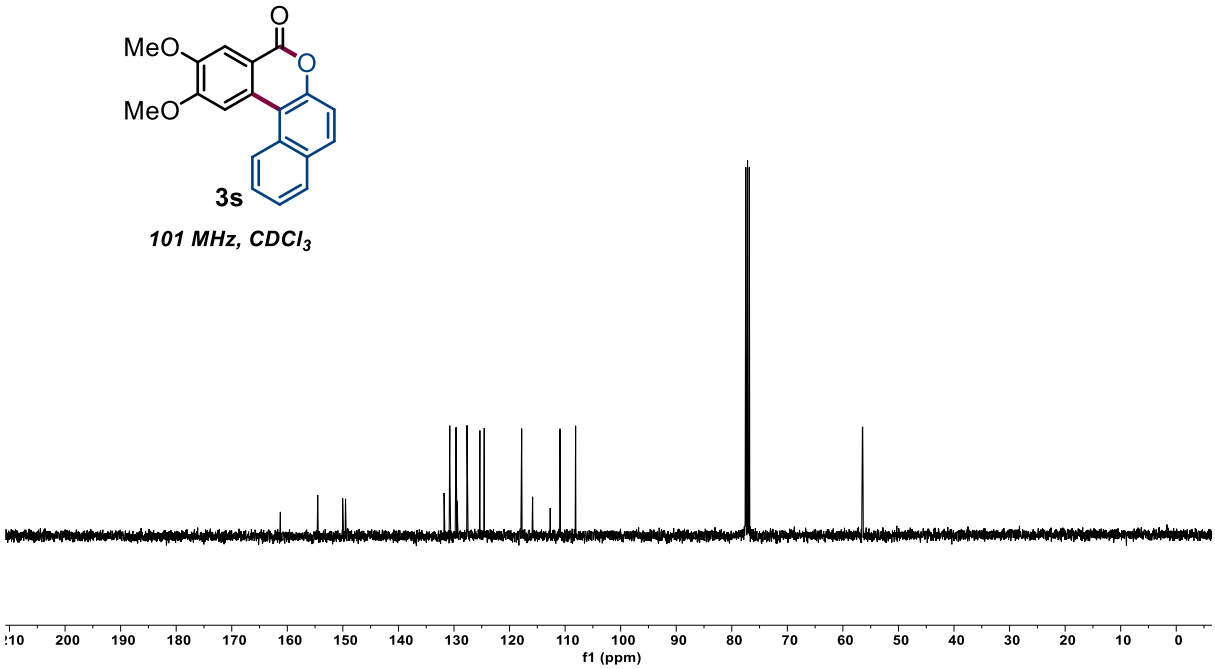

8.23
8.21
8.17
8.15
7.95
7.93
7.89
7.87
7.59
7.57
7.55
7.54
7.52
7.50
7.44
7.42
7.26
7.14
7.12
6.20
3q
400 MHz, CDCl3
1.02
0.95
1.05
1.00
2.01
0.99
0.97
2.00
f1 (ppm)

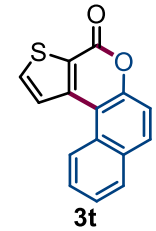

161.1
153.3
150.4
142.4
132.2
131.4
128.9
128.3
127.6
127.6
126.0
125.5
118.3
117.3
117.3
110.5
109.5
101.8
77.5
77.2
76.8
3q
101 MHz, CDCl3
f1 (ppm)


8.76
8.65
8.63
8.55
7.98
7.96
7.76
7.75
7.74
7.72
7.62
7.61
7.60
7.58
7.49
7.47
7.47
7.26
Cl
Cl
O
O
3r
500 MHz, CDCl3
1.00
1.10
0.97
2.06
1.06
1.07
0.98
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


159.7
151.1
139.8
134.9
132.8
132.8
132.3
131.9
129.8
129.4
128.7
128.3
126.0
124.4
122.0
117.7
111.1
77.4
77.2
76.9
Cl
Cl
O
O
3r
126 MHz, CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

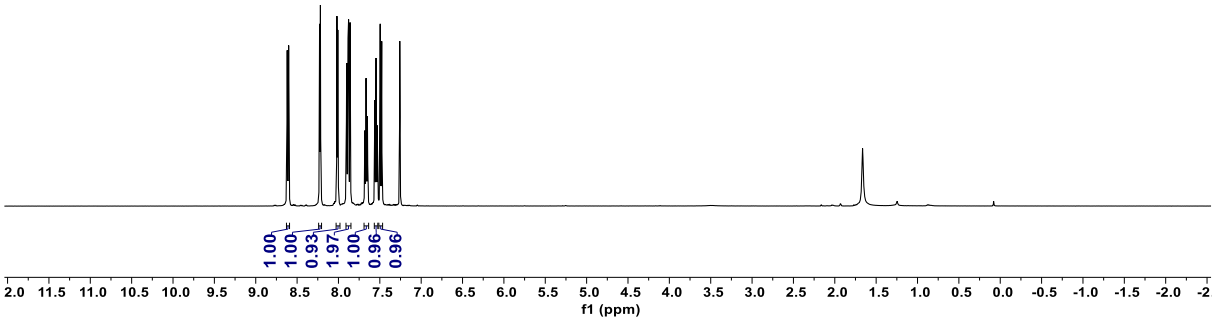

8.74
8.72
8.04
7.95
7.93
7.87
7.85
7.67
7.65
7.64
7.56
7.54
7.52
7.47
7.45
7.26
4.09
4.03
MeO
MeO
O
O
3s
400 MHz, CDCl3
1.00
1.00
1.03
1.98
1.07
1.03
0.97
3.01
3.02
f1 (ppm)

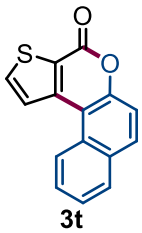

161.3
154.5
150.0
149.5
131.8
130.8
130.7
129.6
129.4
127.7
125.3
124.6
117.8
115.9
112.7
110.9
108.1
77.5
77.2
76.8
56.5
56.4
MeO
MeO
O
O
3s
101 MHz, CDCl3
f1 (ppm)



3t

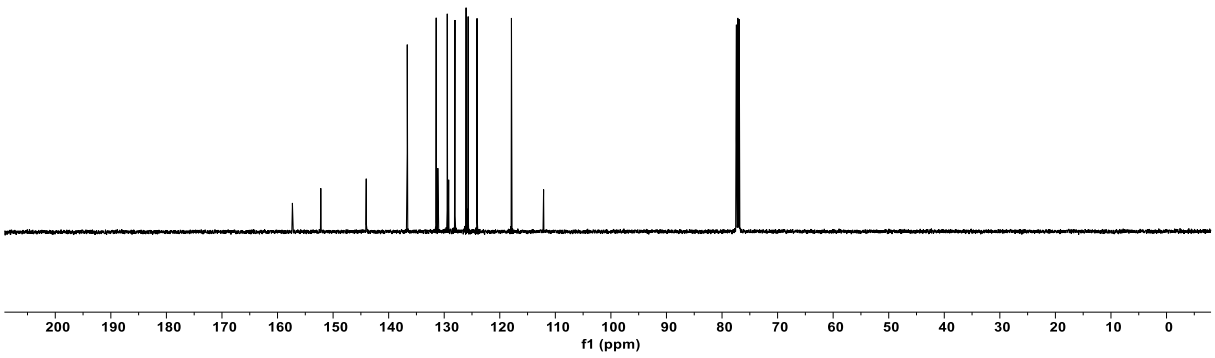
500 MHz, $CDCl_3$

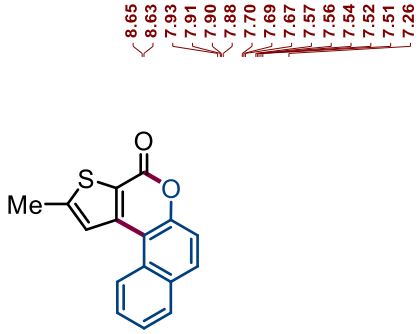




3t

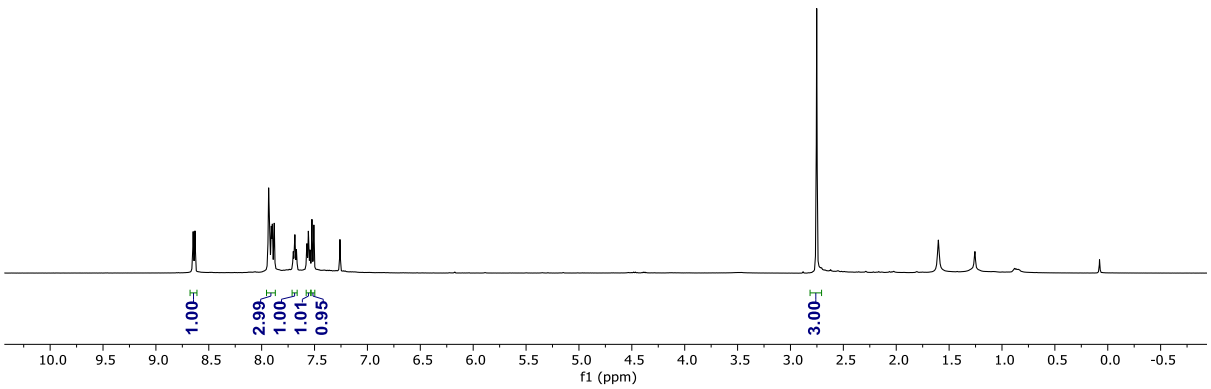
126 MHz, $CDCl_3$

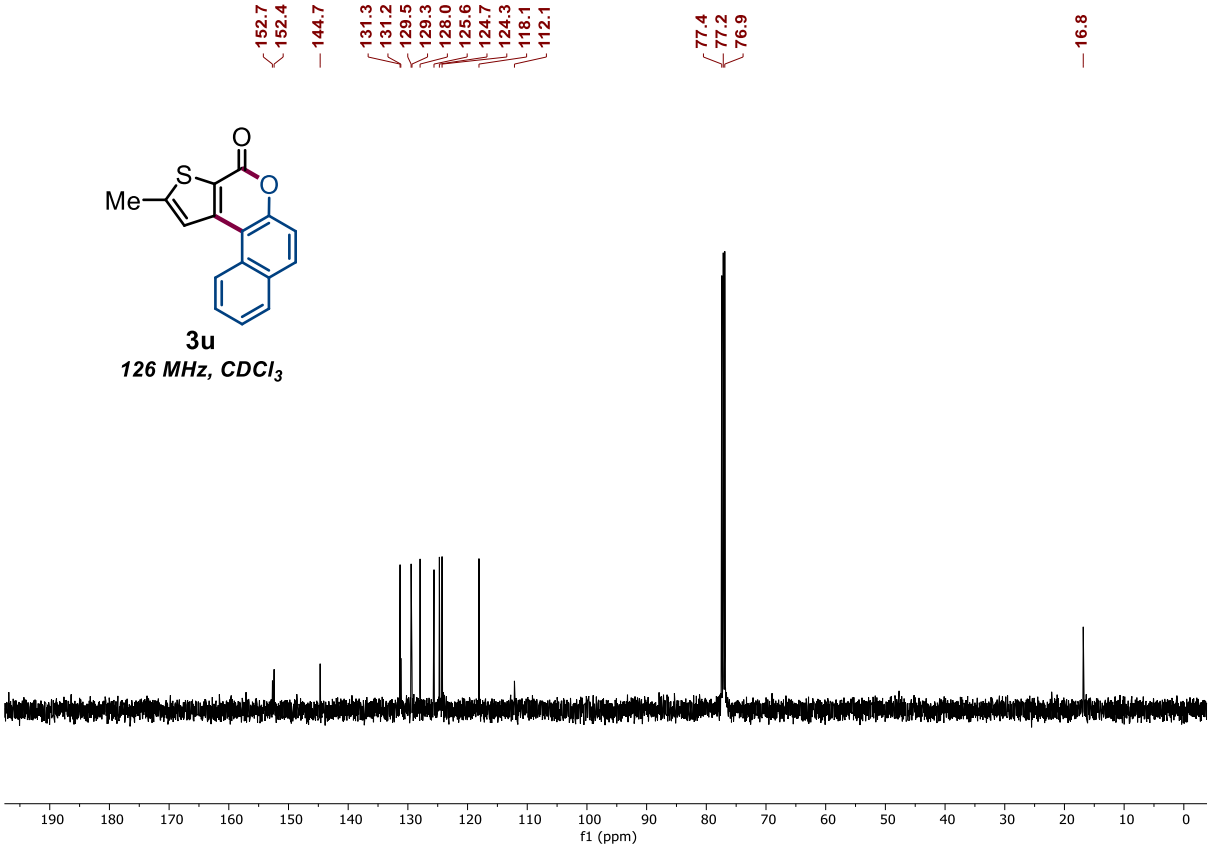




3u

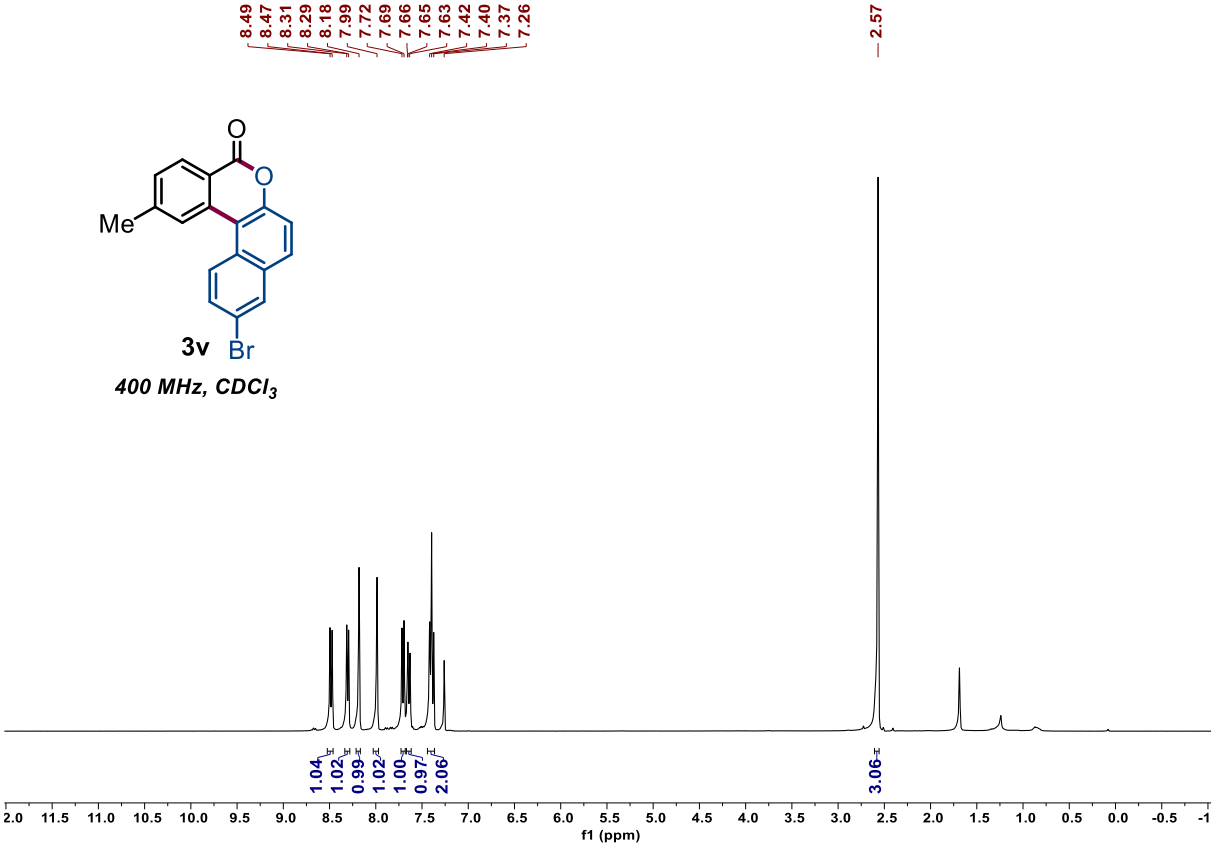
500 MHz, $CDCl_3$

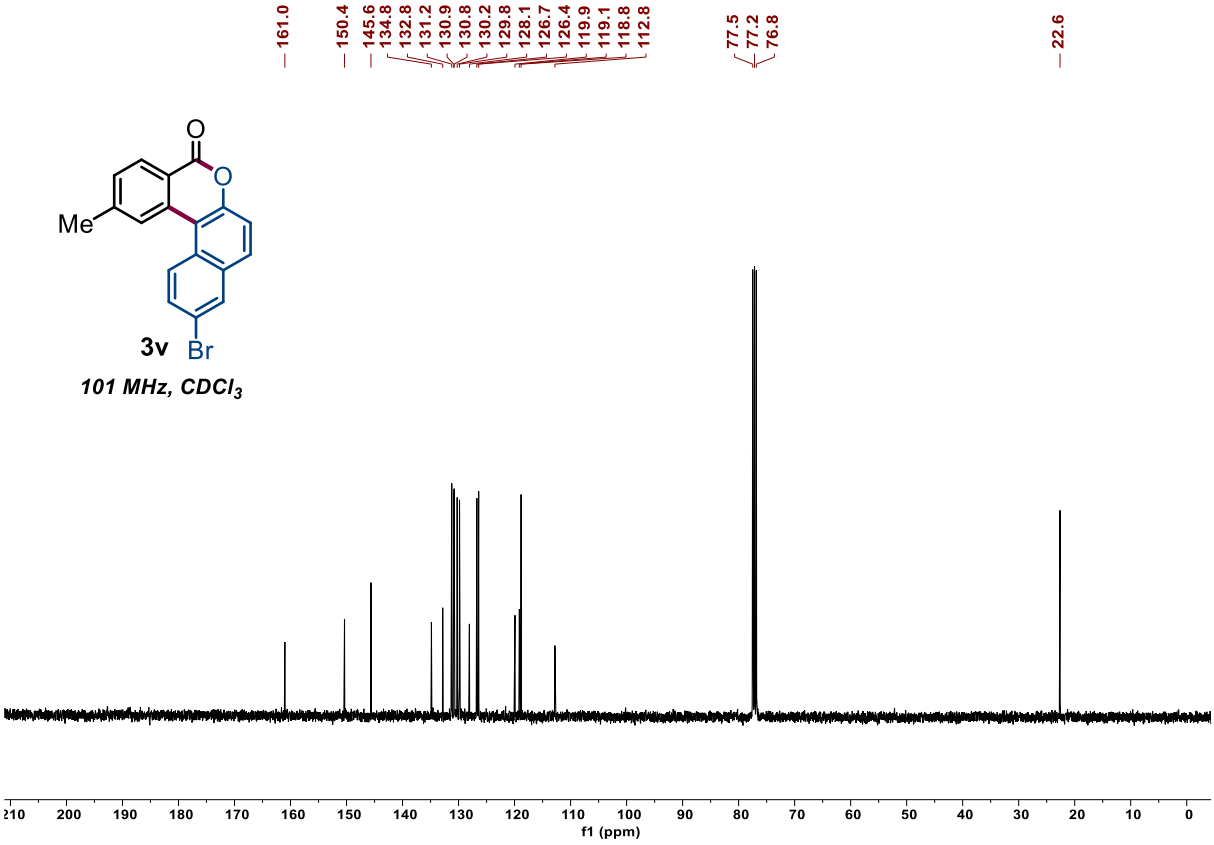


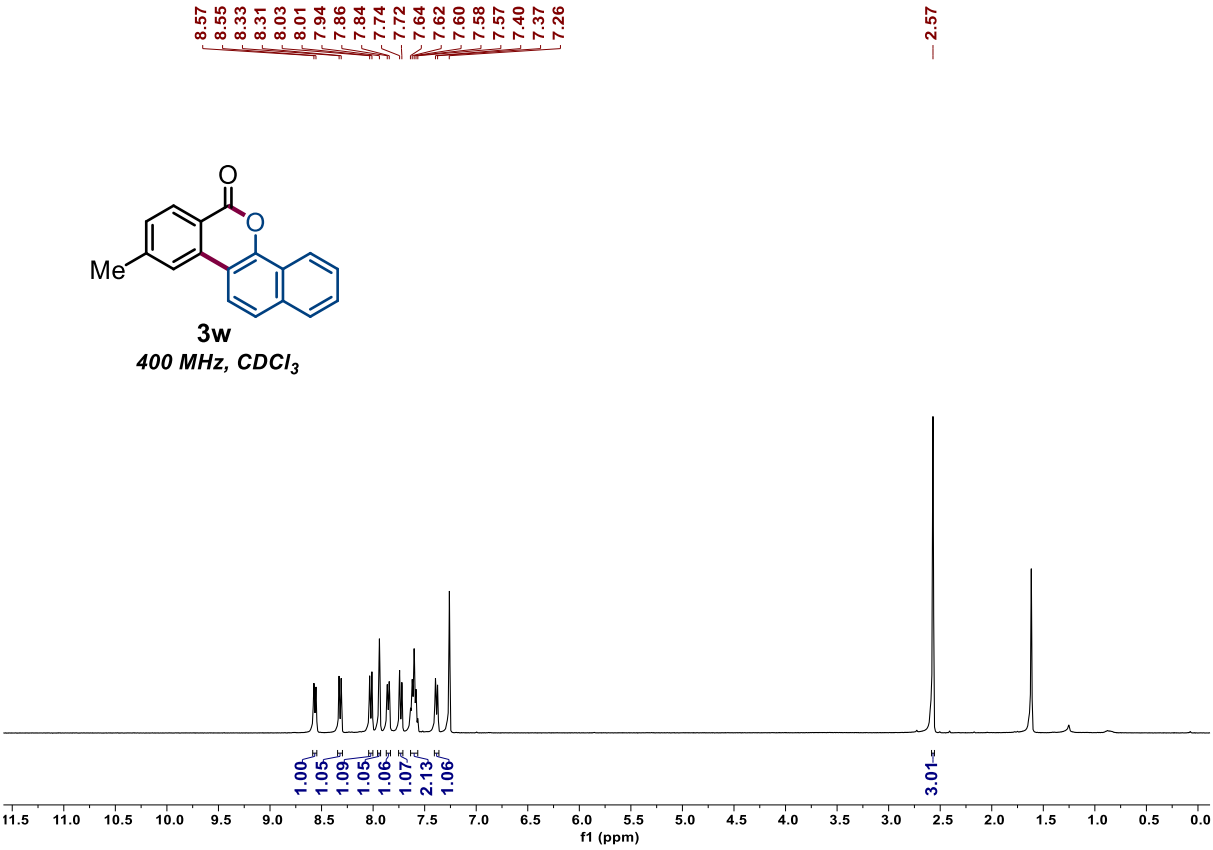


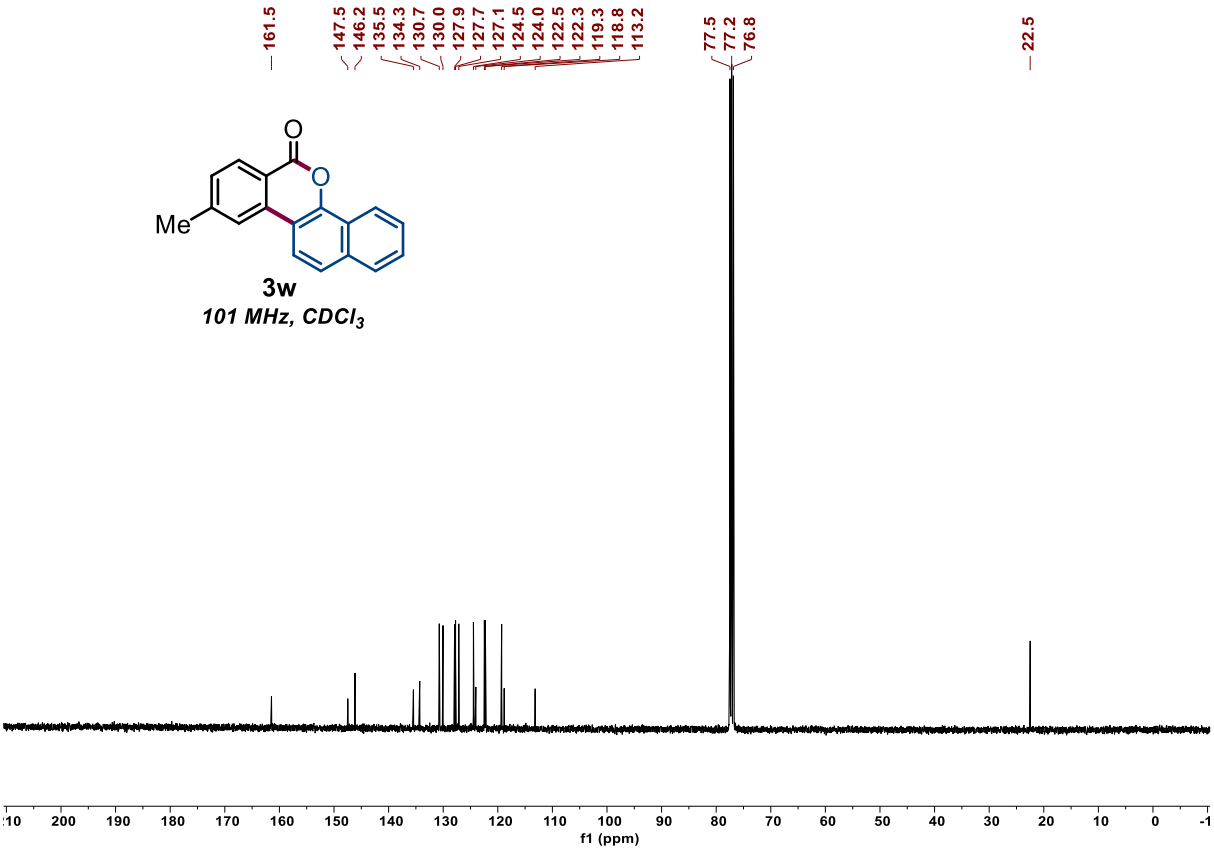
3u

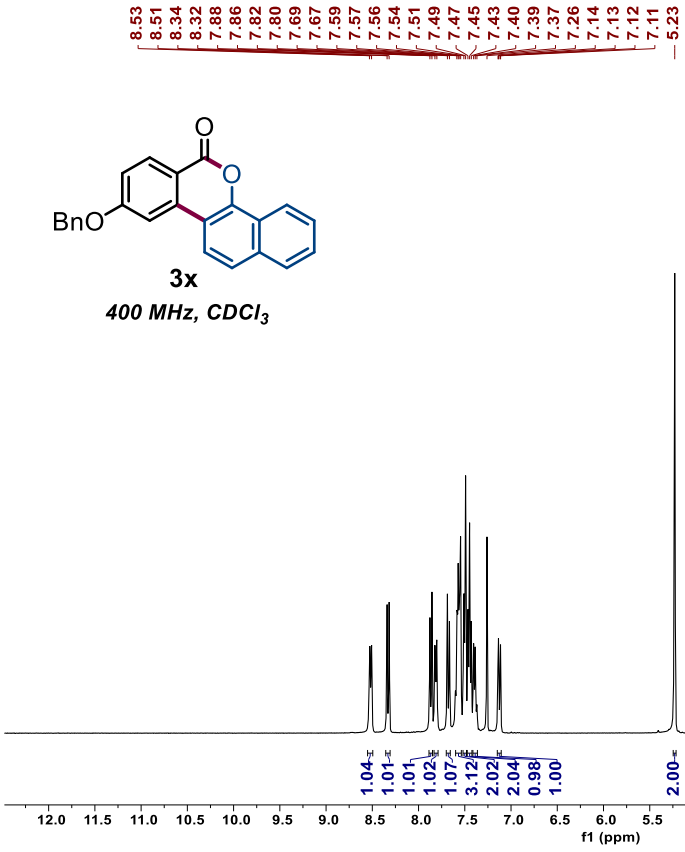
126 MHz, $CDCl_3$

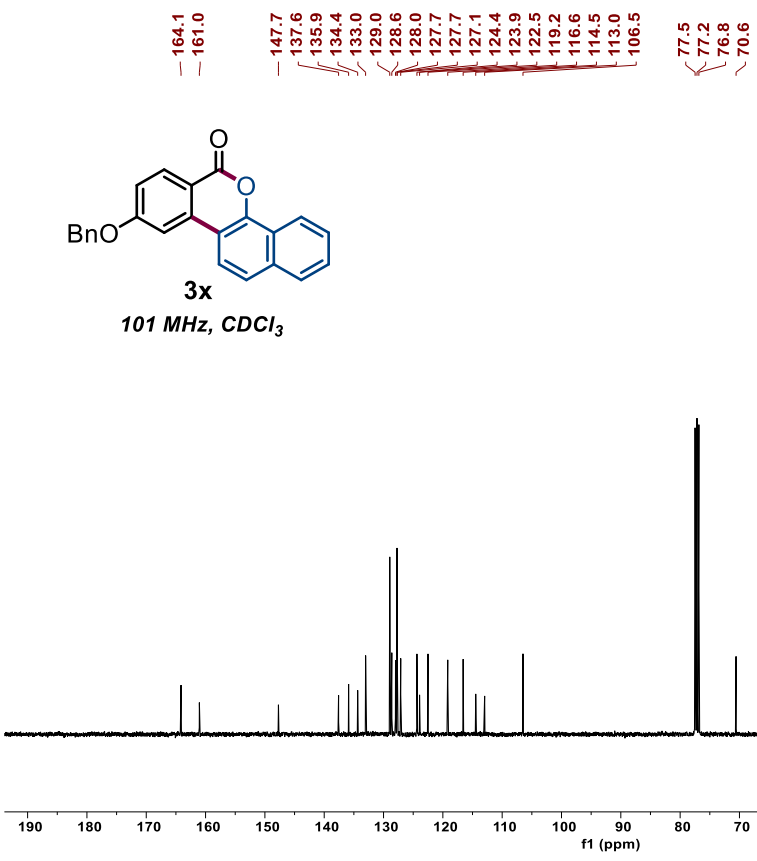

8.49
8.47
8.31
8.29
8.18
7.99
7.72
7.69
7.66
7.65
7.63
7.42
7.40
7.37
7.26
2.57
O
O
Me
3v Br
400 MHz, CDCl3
1.04
1.02
0.99
1.02
1.00
0.97
2.06
3.06
f1 (ppm)

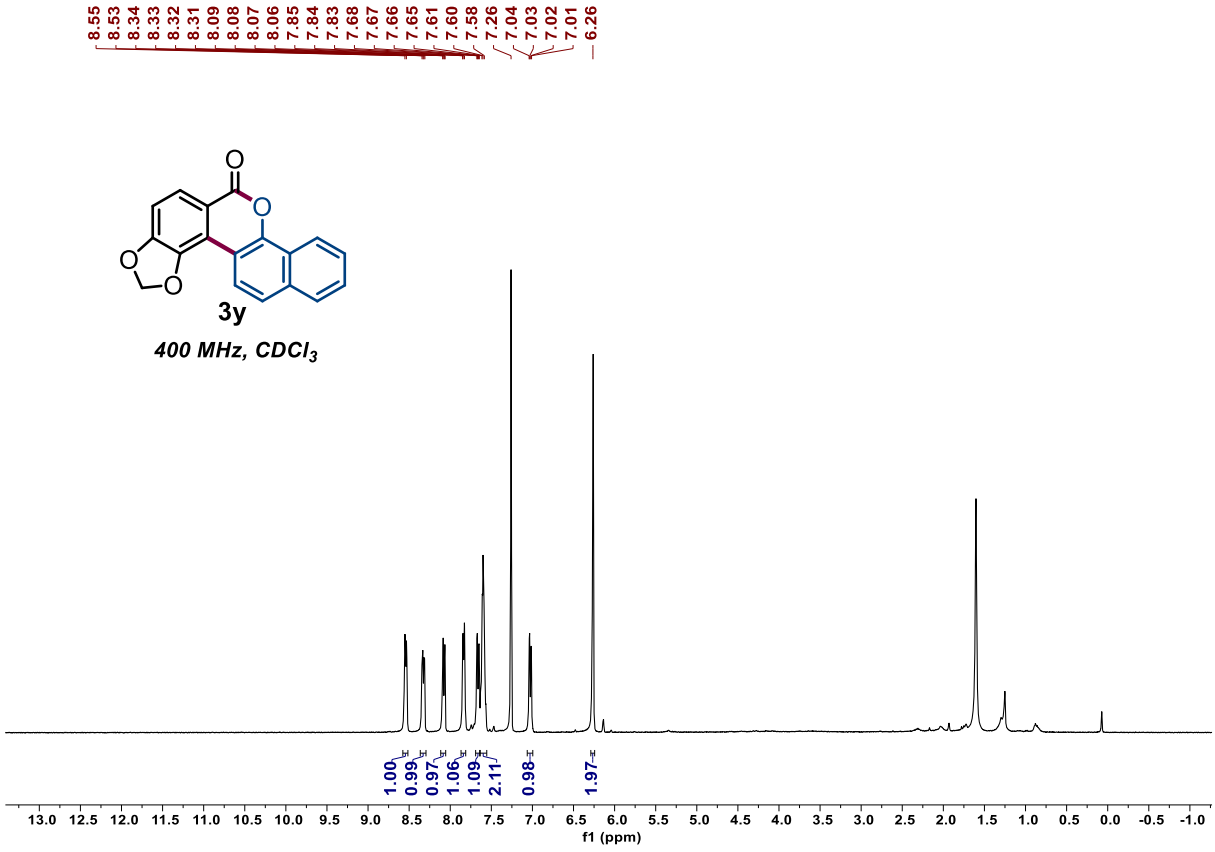

161.0
150.4
145.6
134.8
132.8
131.2
130.9
130.8
130.2
129.8
128.1
126.7
126.4
119.9
119.1
118.8
112.8
77.5
77.2
76.8
22.6
O
O
Me
3v Br
101 MHz, CDCl3
f1 (ppm)

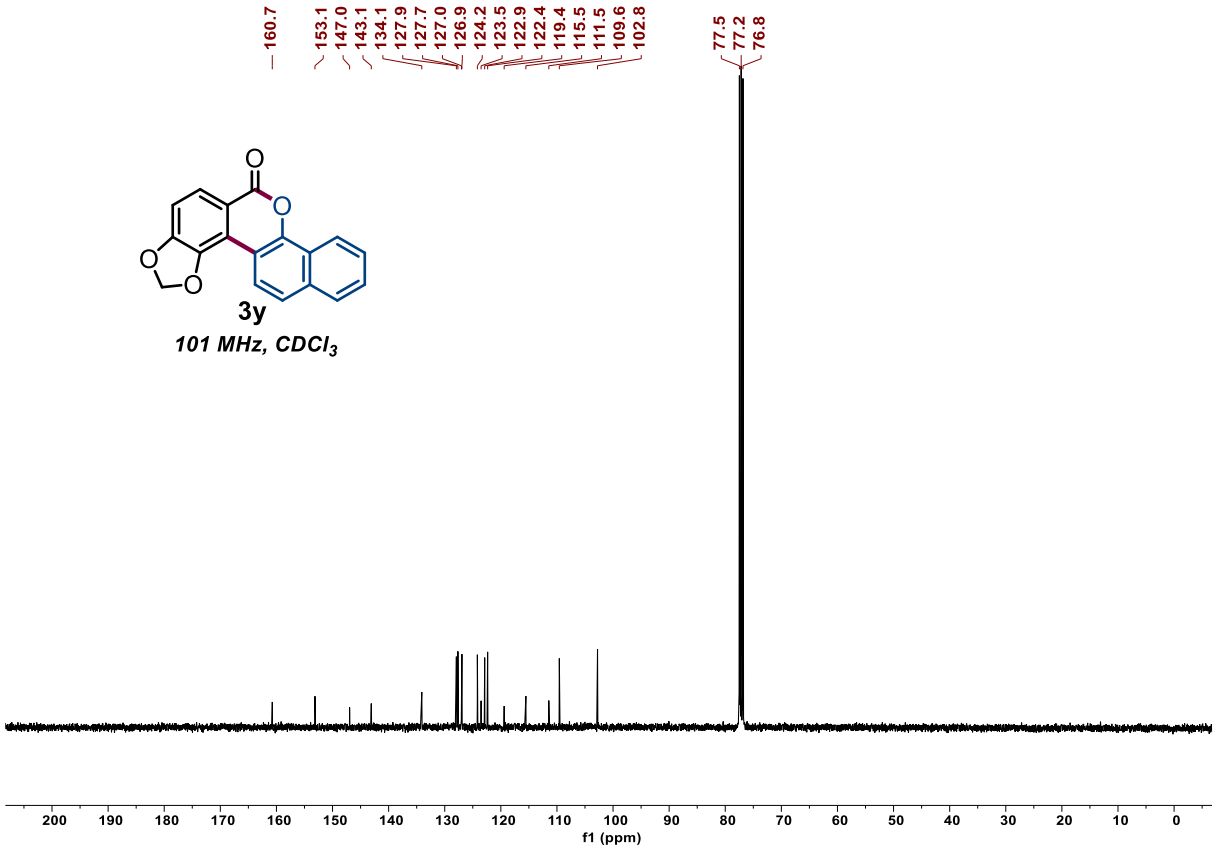

8.57
8.55
8.33
8.31
8.03
8.01
7.94
7.86
7.84
7.74
7.72
7.64
7.62
7.60
7.58
7.57
7.40
7.37
7.26
2.57
O
O
Me
3w
400 MHz, CDCl3
1.00
1.05
1.09
1.05
1.06
1.07
2.13
1.06
3.01
f1 (ppm)

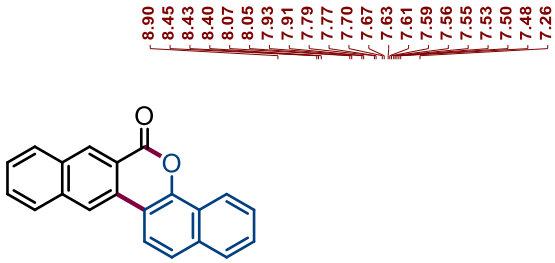

161.5
147.5
146.2
135.5
134.3
130.7
130.0
127.9
127.7
127.1
124.5
124.0
122.5
122.3
119.3
118.8
113.2
77.5
77.2
76.8
22.5
O
O
Me
3w
101 MHz, CDCl3
f1 (ppm)


8.53
8.51
8.34
8.32
7.88
7.86
7.82
7.80
7.69
7.67
7.59
7.57
7.56
7.54
7.51
7.49
7.47
7.45
7.43
7.40
7.39
7.37
7.26
7.14
7.13
7.12
7.11
5.23
O
O
BnO
3x
400 MHz, CDCl3
1.04
1.01
1.01
1.02
1.07
3.12
2.02
2.04
0.98
1.00
2.00
f1 (ppm)


164.1
161.0
147.7
137.6
135.9
134.4
133.0
129.0
128.6
128.0
127.7
127.7
127.1
124.4
123.9
122.5
119.2
116.6
114.5
113.0
106.5
77.5
77.2
76.8
70.6
O
O
BnO
3x
101 MHz, CDCl3
f1 (ppm)

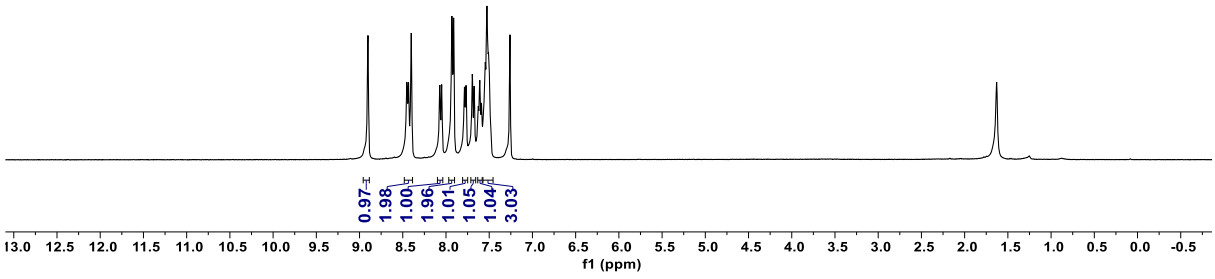

8.55
8.53
8.34
8.33
8.32
8.31
8.09
8.08
8.07
8.06
7.85
7.84
7.83
7.68
7.67
7.66
7.65
7.61
7.60
7.58
7.26
7.04
7.03
7.02
7.01
6.26
3y
400 MHz, CDCl3
1.00
0.99
0.97
1.06
1.09
2.11
0.98
1.97
f1 (ppm)


160.7
153.1
147.0
143.1
134.1
127.9
127.7
127.0
126.9
124.2
123.5
122.9
122.4
119.4
115.5
111.5
109.6
102.8
77.5
77.2
76.8
3y
101 MHz, CDCl3
f1 (ppm)



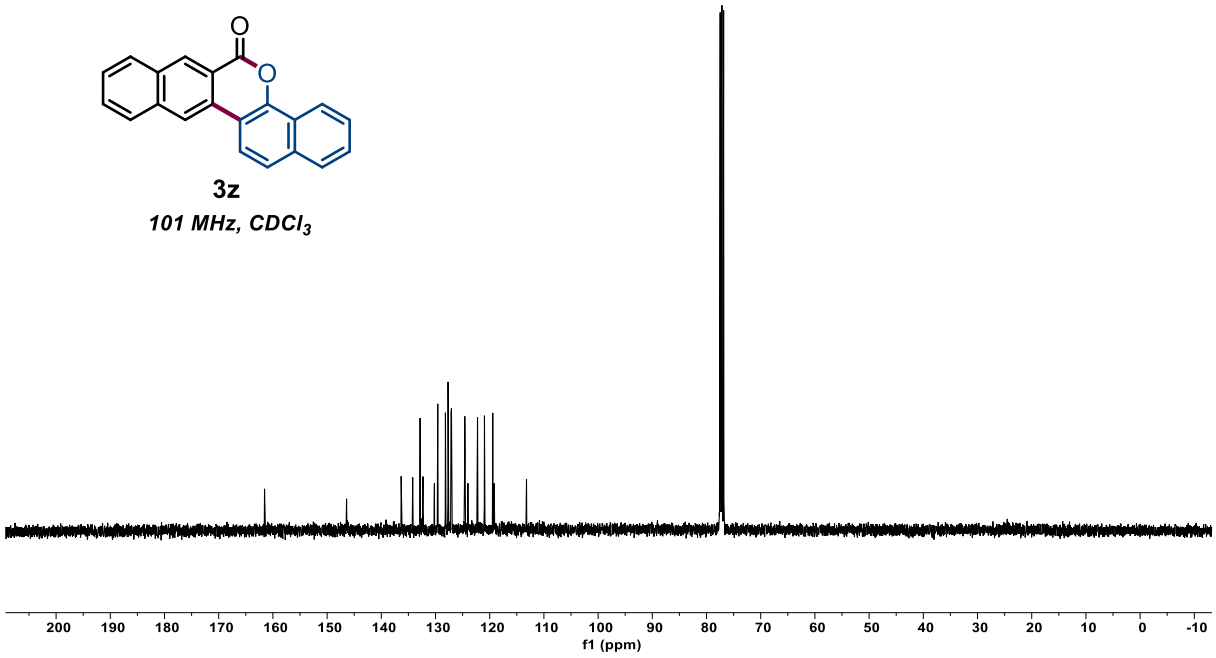
3z

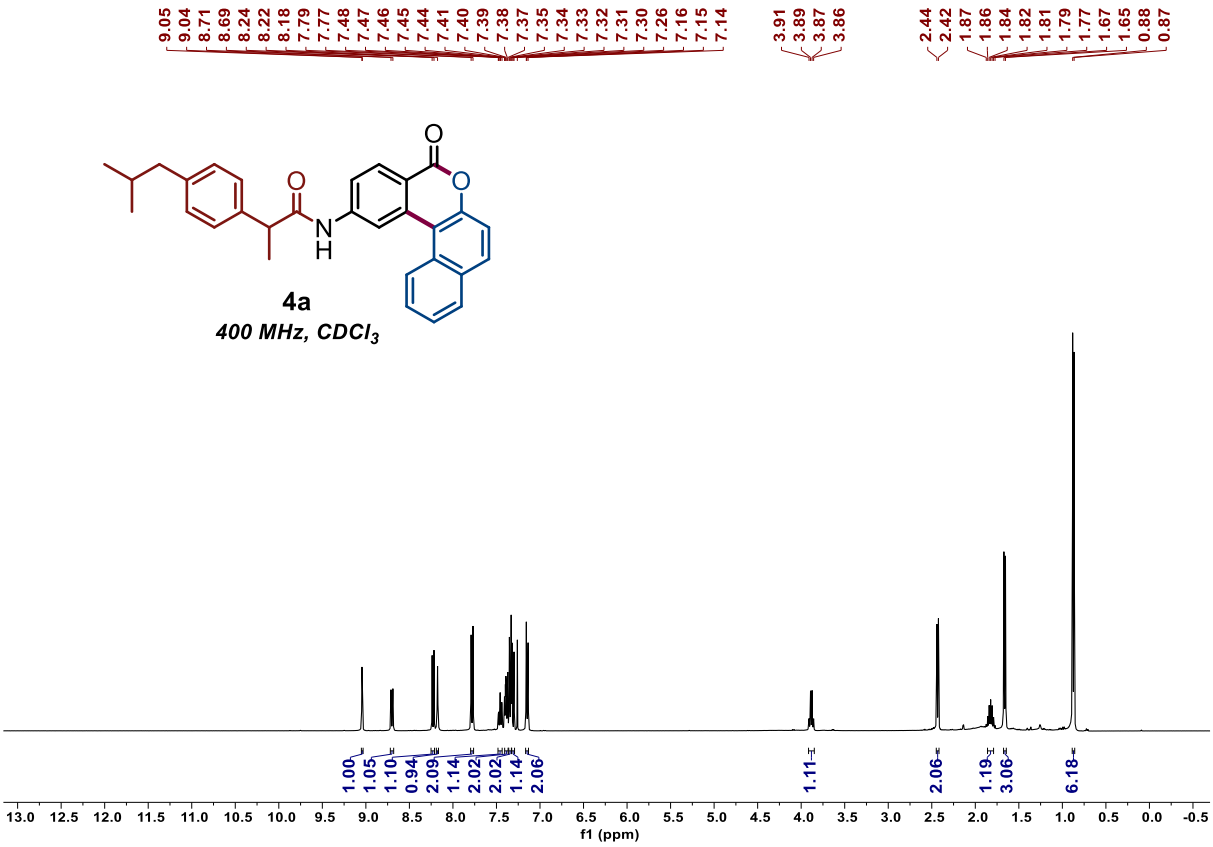
400 MHz, $CDCl_3$

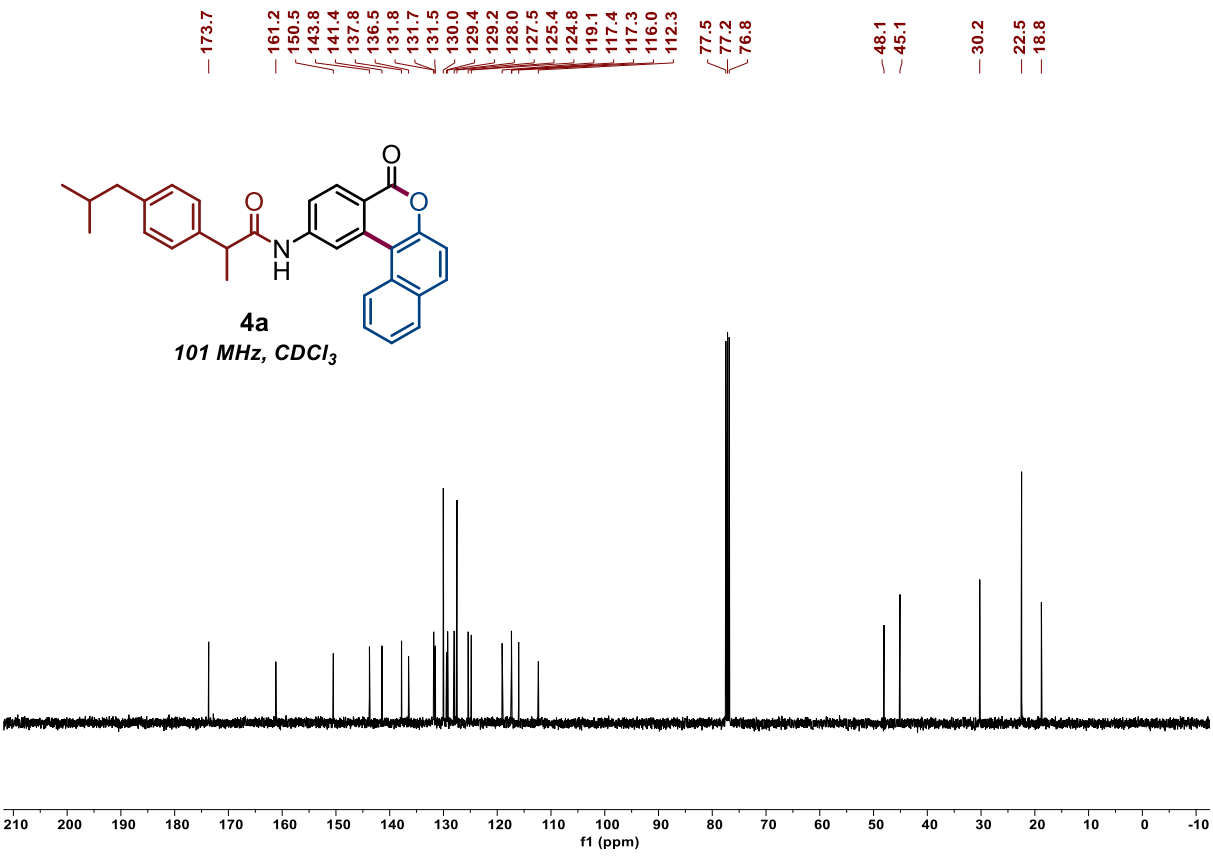


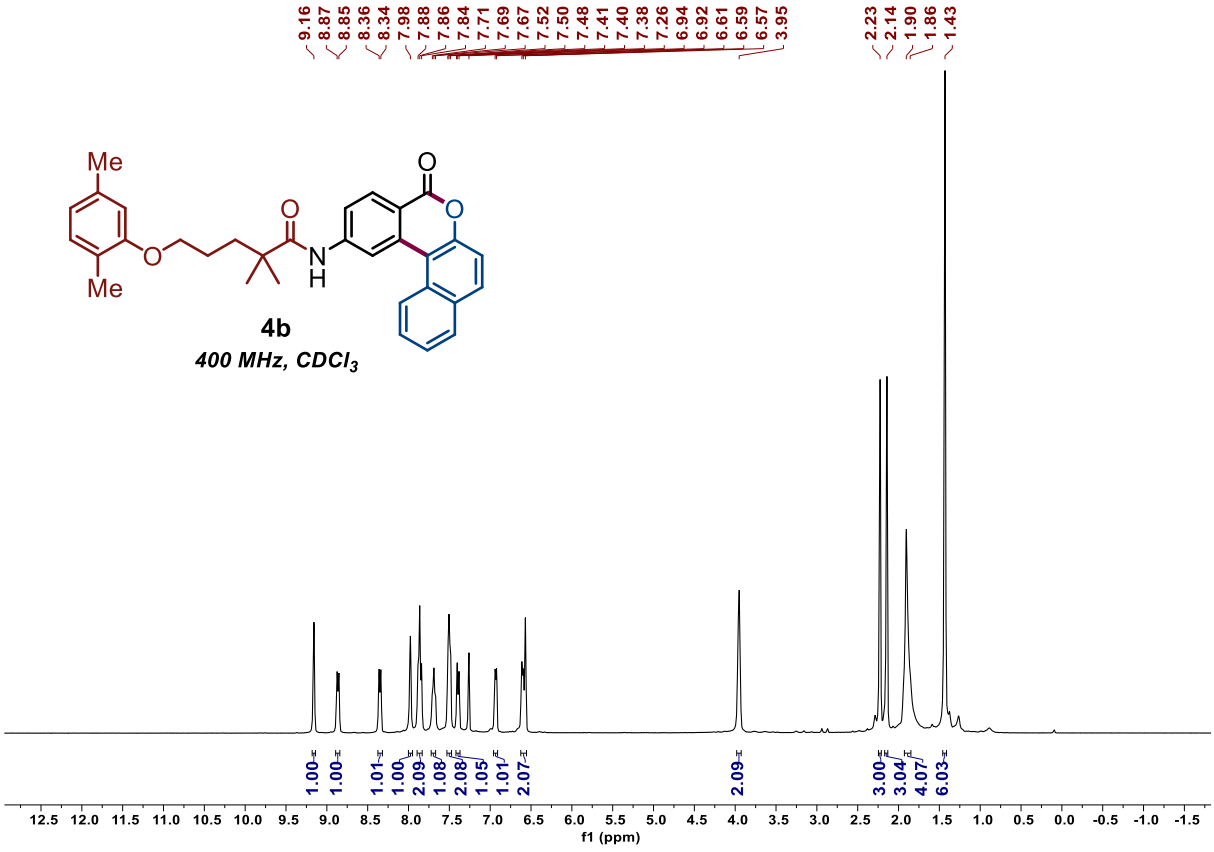
3z

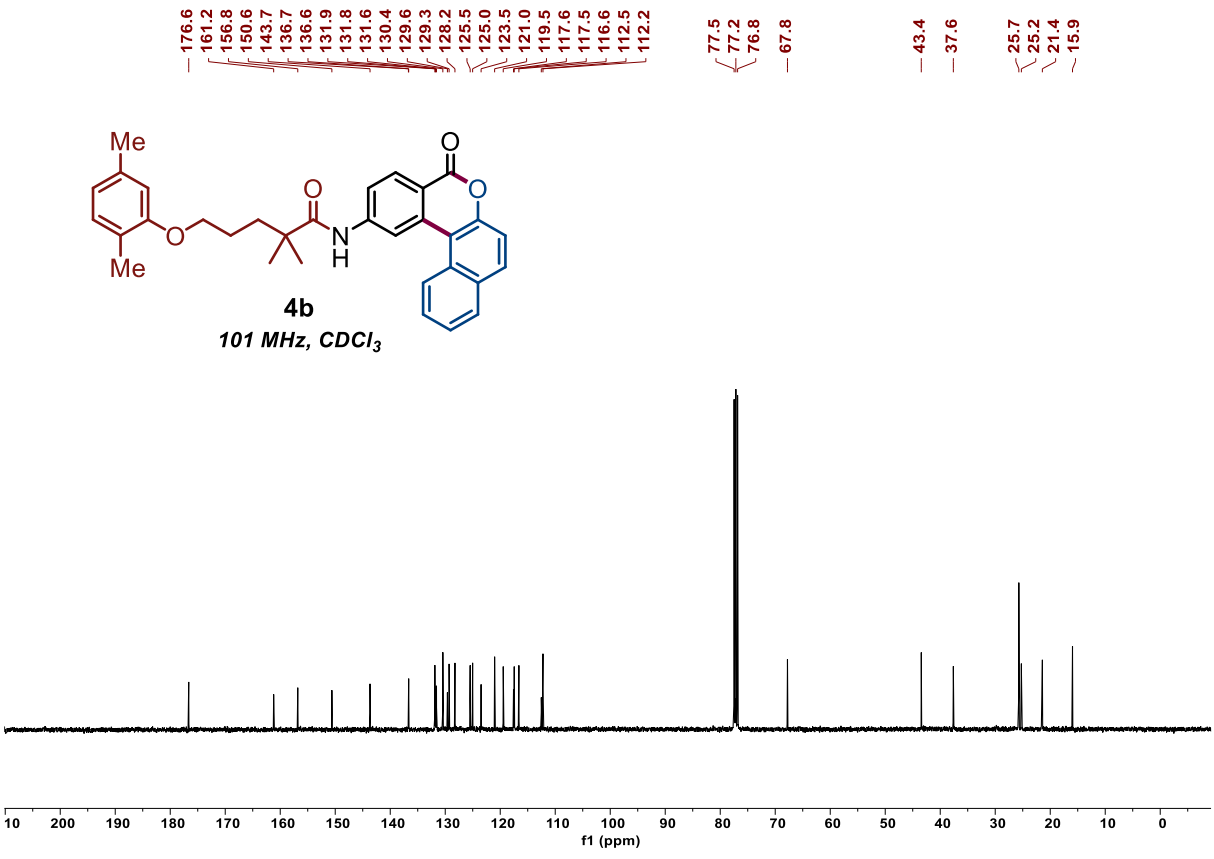
101 MHz, $CDCl_3$

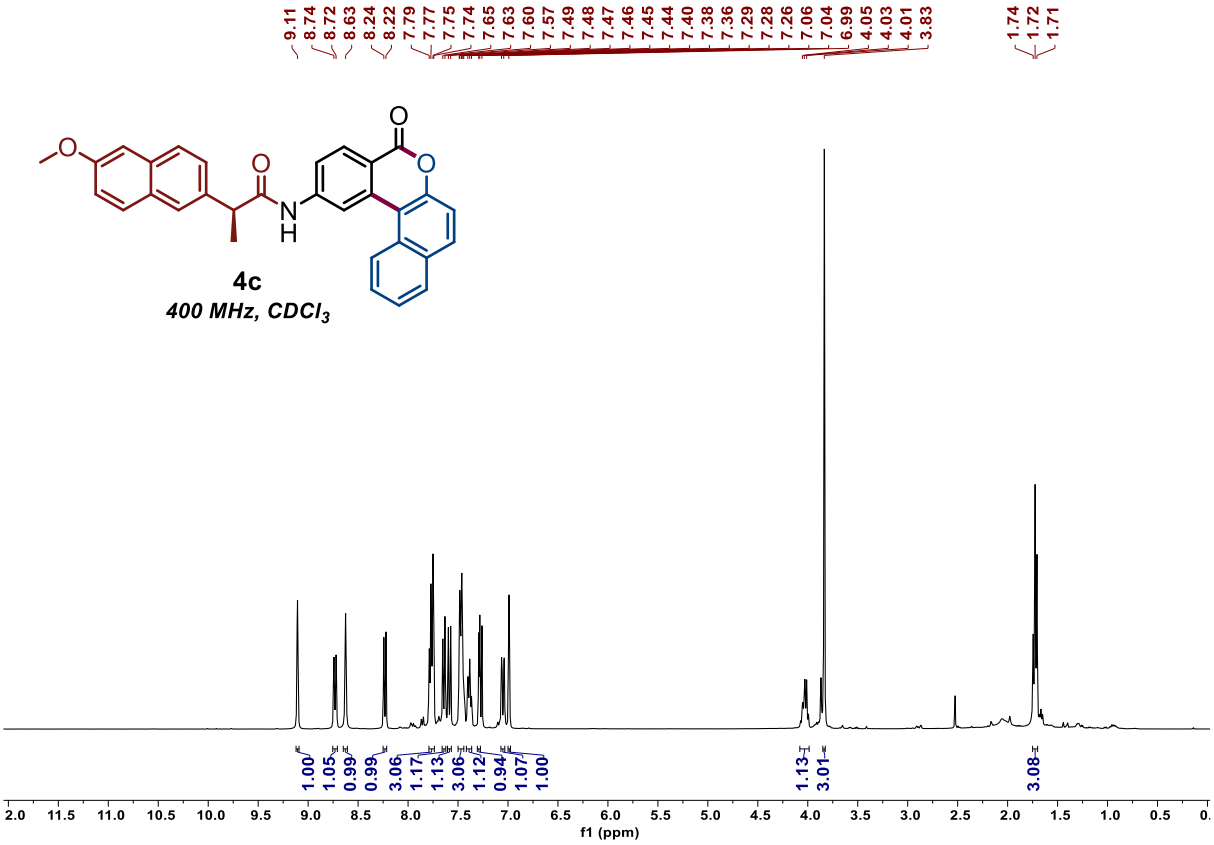


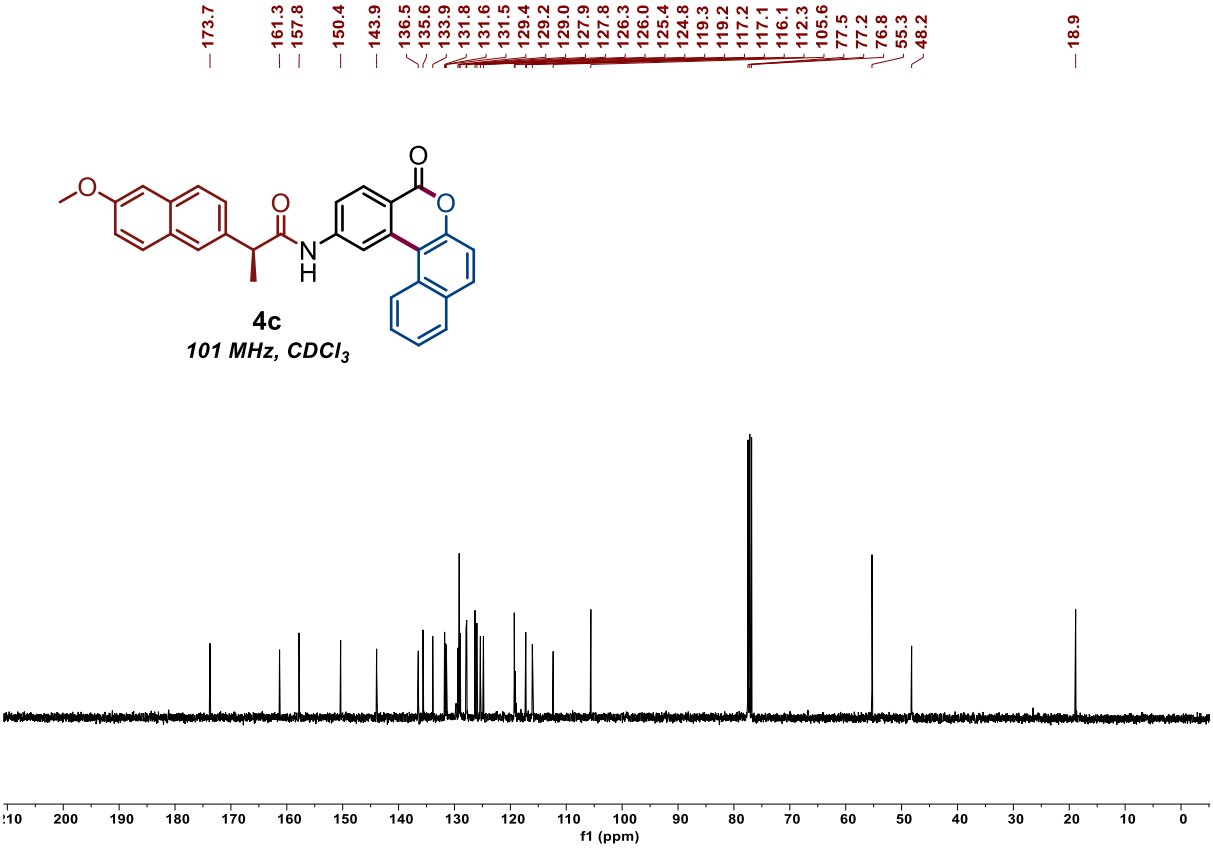

9.05 9.04 8.71 8.69 8.24 8.22 8.18 7.79 7.77 7.48 7.47 7.46 7.45 7.44 7.41 7.40 7.39 7.38 7.37 7.35 7.34 7.33 7.32 7.31 7.30 7.26 7.16 7.15 7.14
3.91 3.89 3.87 3.86
2.44 2.42 1.87 1.86 1.84 1.82 1.81 1.79 1.77 1.67 1.65 0.88 0.87
4a
400 MHz, CDCl3
1.00 1.05 1.10 0.94 2.09 1.14 2.02 2.02 1.14 2.06 1.11 2.06 1.19 3.06 6.18
f1 (ppm)

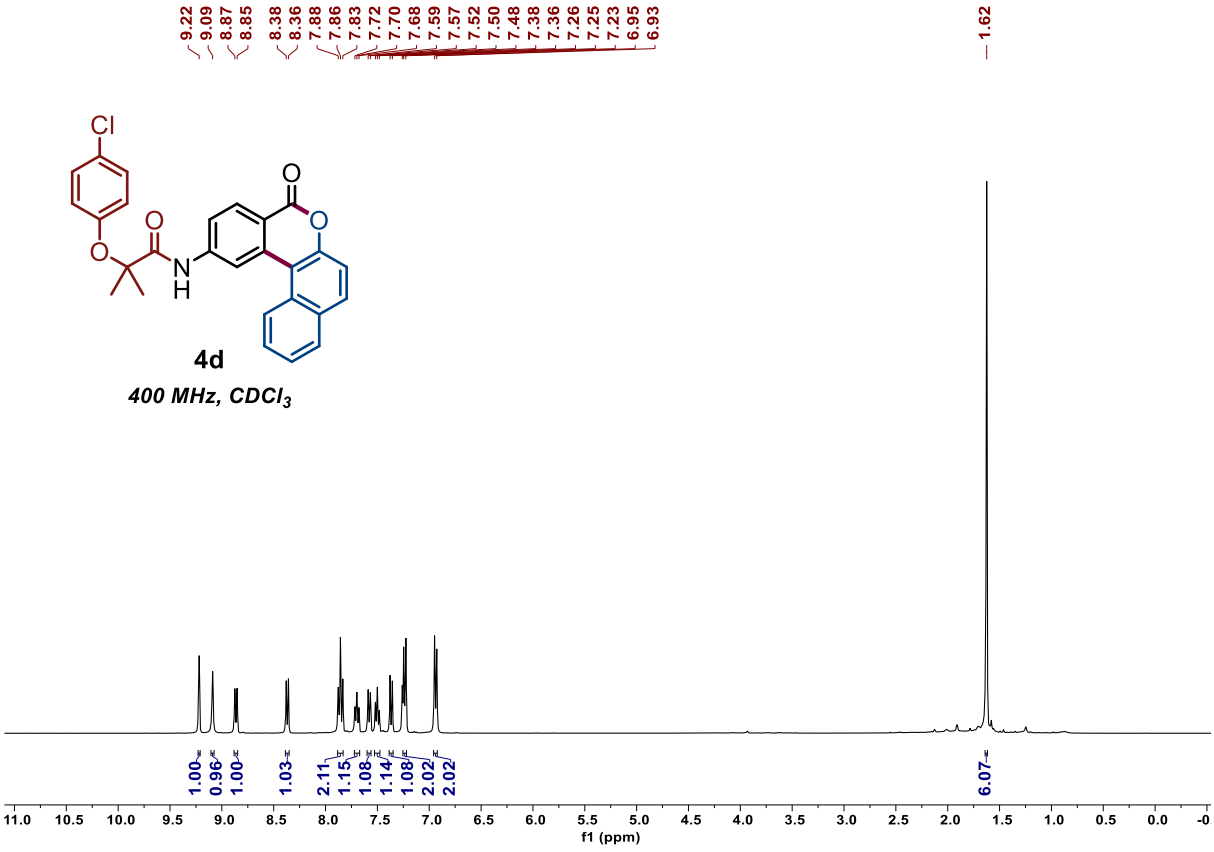

173.7 161.2 150.5 143.8 141.4 137.8 136.5 131.8 131.7 131.5 130.0 129.4 129.2 128.0 127.5 125.4 124.8 119.1 117.4 117.3 116.0 112.3
77.5 77.2 76.8
48.1 45.1 30.2 22.5 18.8
4a
101 MHz, CDCl3
f1 (ppm)


9.16
8.87
8.85
8.36
8.34
7.98
7.88
7.86
7.84
7.71
7.69
7.67
7.52
7.50
7.48
7.41
7.40
7.38
7.26
6.94
6.92
6.61
6.59
6.57
3.95
2.23
2.14
1.90
1.86
1.43
Me
Me
O
O
N
H
O
O
4b
400 MHz, CDCl3
1.00
1.00
1.01
1.00
2.09
1.08
2.08
1.05
1.01
2.07
2.09
3.00
3.04
4.07
6.03
f1 (ppm)


176.6
161.2
156.8
150.6
143.7
136.7
136.6
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
112.2
77.5
77.2
76.8
67.8
43.4
37.6
25.7
25.2
21.4
15.9
Me
Me
O
O
N
H
O
O
4b
101 MHz, CDCl3
f1 (ppm)

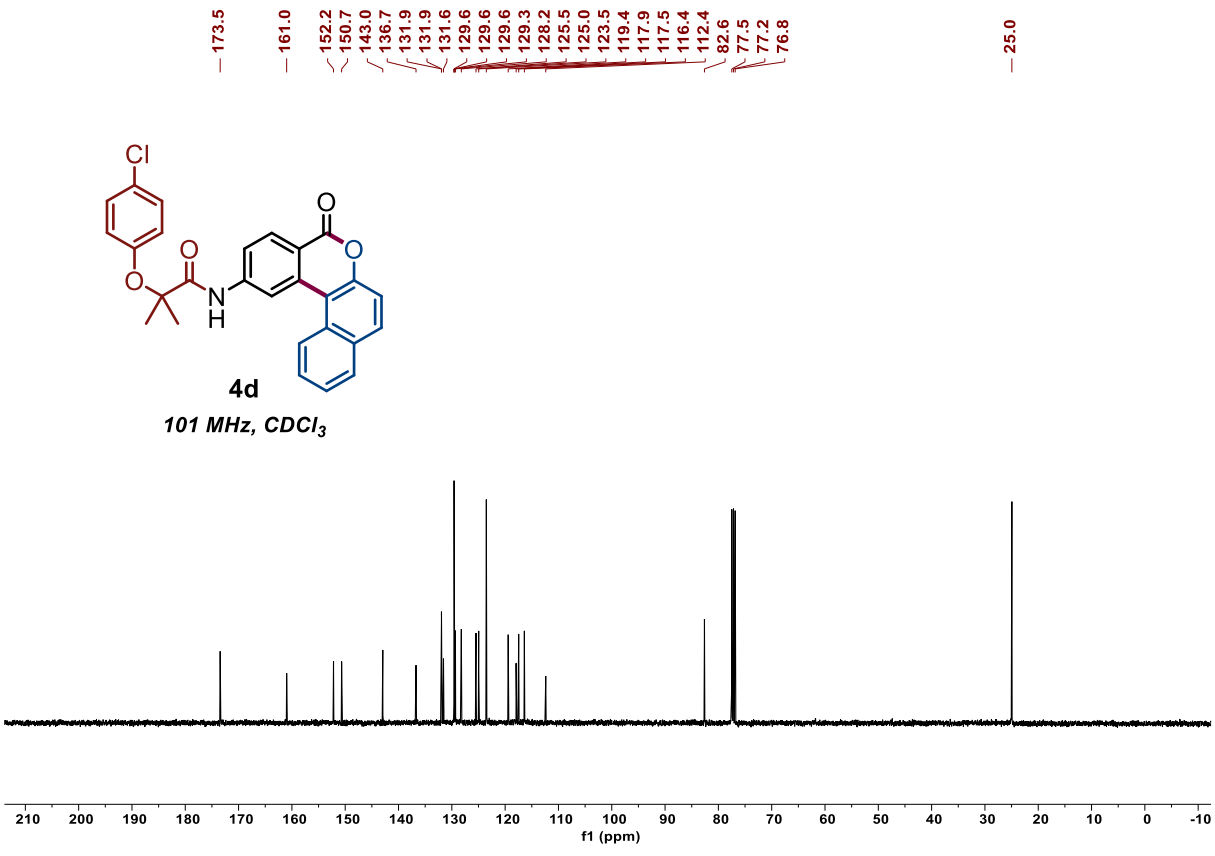

9.11
8.74
8.72
8.63
8.24
8.22
7.79
7.77
7.75
7.74
7.65
7.63
7.60
7.57
7.49
7.48
7.47
7.46
7.45
7.44
7.40
7.38
7.36
7.29
7.28
7.26
7.06
7.04
6.99
4.05
4.03
4.01
3.83
1.74
1.72
1.71
4c
400 MHz, CDCl3
1.00
1.05
0.99
0.99
3.06
1.17
1.13
3.06
1.12
0.94
1.07
1.00
1.13
3.01
3.08
f1 (ppm)


173.7
161.3
157.8
150.4
143.9
136.5
135.6
133.9
131.8
131.6
131.5
129.4
129.2
129.0
127.9
127.8
126.3
126.0
125.4
124.8
119.3
119.2
117.2
117.1
116.1
112.3
105.6
77.5
77.2
76.8
55.3
48.2
18.9
4c
101 MHz, CDCl3
f1 (ppm)



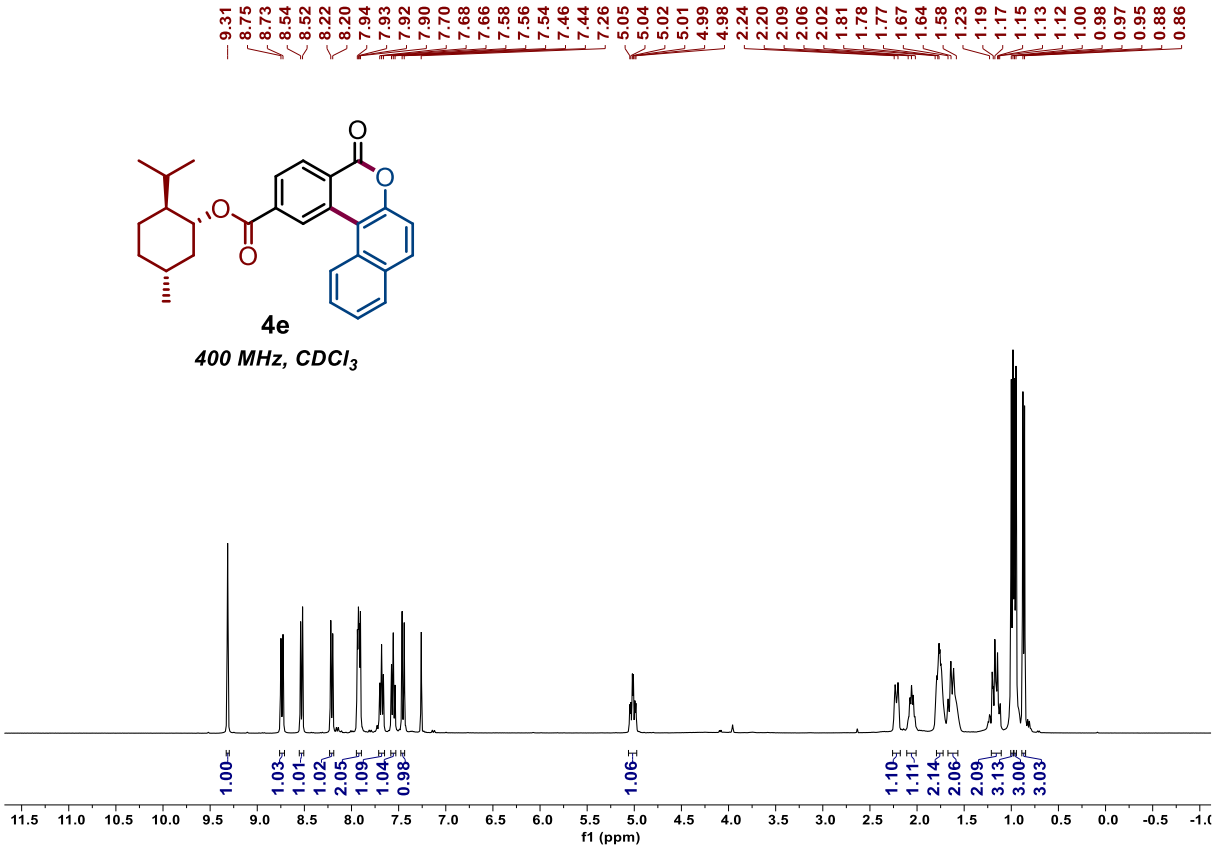
4d

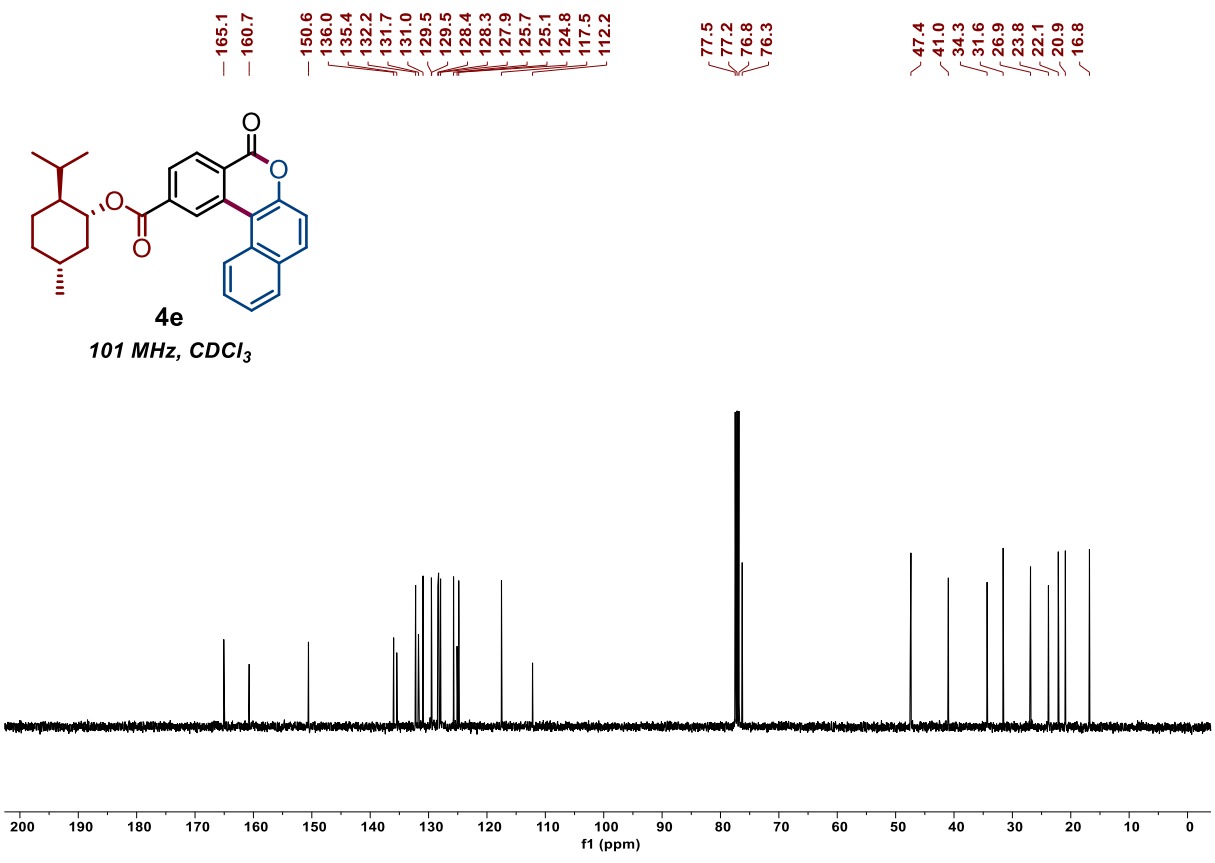
400 MHz, $CDCl_3$

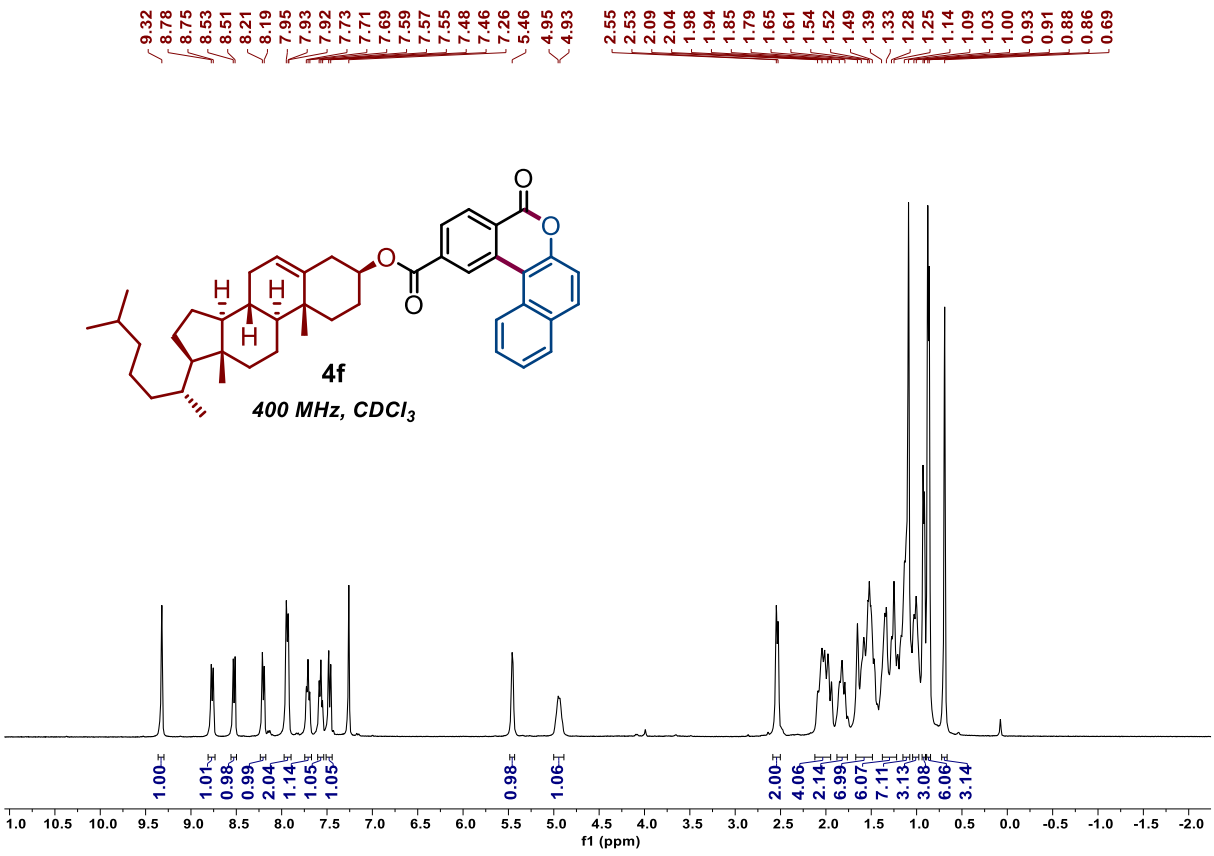


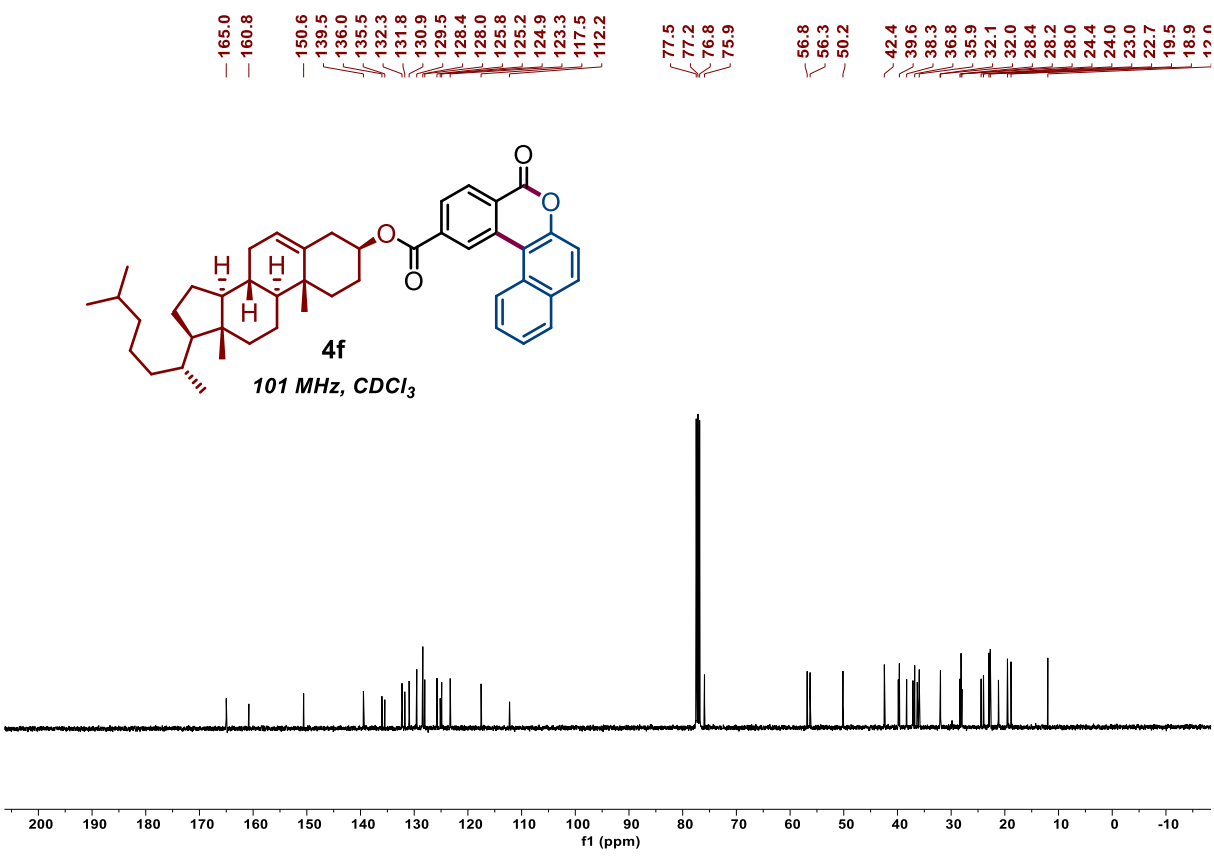
4d

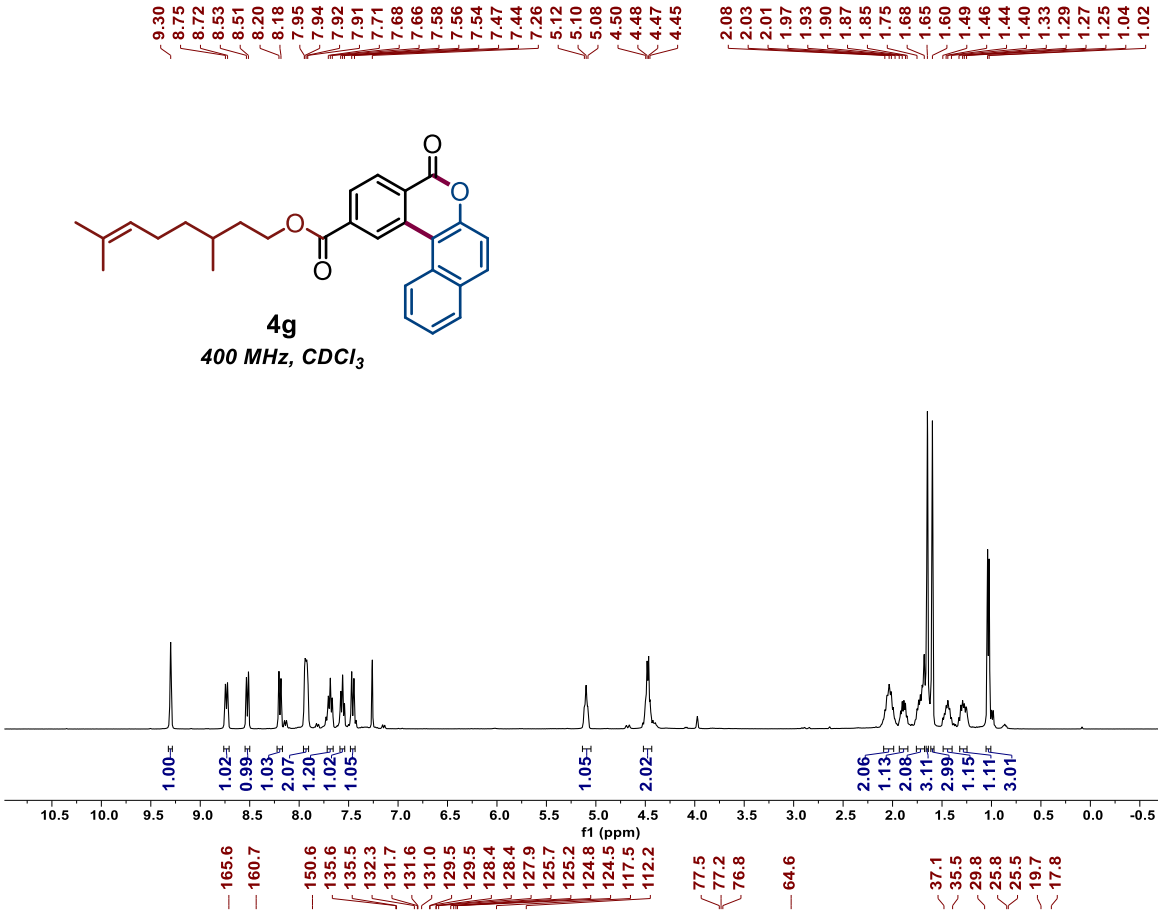
101 MHz, $CDCl_3$

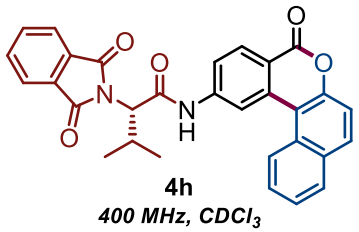

9.31
8.75
8.73
8.54
8.52
8.22
8.20
7.94
7.93
7.92
7.90
7.70
7.68
7.66
7.58
7.56
7.54
7.46
7.44
7.26
5.05
5.04
5.02
5.01
4.99
4.98
2.24
2.20
2.09
2.06
2.02
1.81
1.78
1.77
1.67
1.64
1.58
1.23
1.19
1.17
1.15
1.13
1.12
1.00
0.98
0.97
0.95
0.88
0.86
4e
400 MHz, CDCl3
1.00
1.03
1.01
1.02
2.05
1.09
1.04
0.98
1.06
1.10
1.11
2.14
2.06
2.09
3.13
3.00
3.03
f1 (ppm)


165.1
160.7
150.6
136.0
135.4
132.2
131.7
131.0
129.5
129.5
128.4
128.3
127.9
125.7
125.1
124.8
117.5
112.2
77.5
77.2
76.8
76.3
47.4
41.0
34.3
31.6
26.9
23.8
22.1
20.9
16.8
4e
101 MHz, CDCl3
f1 (ppm)


9.32
8.78
8.75
8.53
8.51
8.21
8.19
7.95
7.93
7.92
7.73
7.71
7.69
7.59
7.57
7.55
7.48
7.46
7.26
5.46
4.95
4.93
2.55
2.53
2.09
2.04
1.98
1.94
1.85
1.79
1.65
1.61
1.54
1.52
1.49
1.39
1.33
1.28
1.25
1.14
1.09
1.03
1.00
0.93
0.91
0.88
0.86
0.69
4f
400 MHz, CDCl3
1.00
1.01
0.98
0.99
2.04
1.14
1.05
1.05
0.98
1.06
2.00
4.06
2.14
6.99
6.07
7.11
3.13
3.08
6.06
3.14
f1 (ppm)

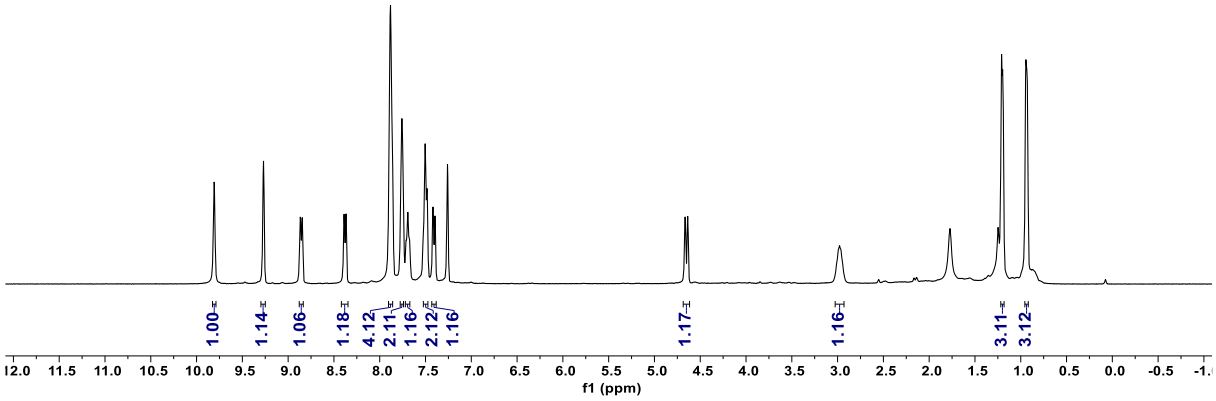

165.0
160.8
150.6
139.5
136.0
135.5
132.3
131.8
130.9
129.5
128.4
128.0
125.8
125.2
124.9
123.3
117.5
112.2
77.5
77.2
76.8
75.9
56.8
56.3
50.2
42.4
39.6
38.3
36.8
35.9
32.1
32.0
28.4
28.2
28.0
24.4
24.0
23.0
22.7
19.5
18.9
4f
101 MHz, CDCl3
f1 (ppm)

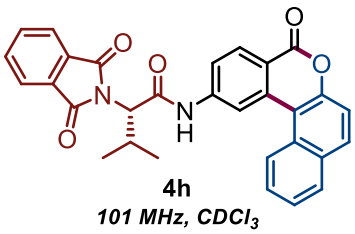

9.30
8.75
8.72
8.53
8.51
8.20
8.18
7.95
7.94
7.92
7.91
7.71
7.68
7.66
7.58
7.56
7.54
7.47
7.44
7.26
5.12
5.10
5.08
4.50
4.48
4.47
4.45
2.08
2.03
2.01
1.97
1.93
1.90
1.87
1.85
1.75
1.68
1.65
1.60
1.49
1.46
1.44
1.40
1.33
1.29
1.27
1.25
1.04
1.02
4g
400 MHz, CDCl3
1.00
1.02
0.99
1.03
2.07
1.20
1.02
1.05
1.05
2.02
2.06
1.13
2.08
3.11
2.99
1.15
1.11
3.01
f1 (ppm)
165.6
160.7
150.6
135.6
135.5
132.3
131.7
131.6
131.0
129.5
129.5
128.4
128.4
127.9
125.7
125.2
124.8
124.5
117.5
112.2
77.5
77.2
76.8
64.6
37.1
35.5
29.8
25.8
25.5
19.7
17.8
4g
101 MHz, CDCl3
f1 (ppm)



4h

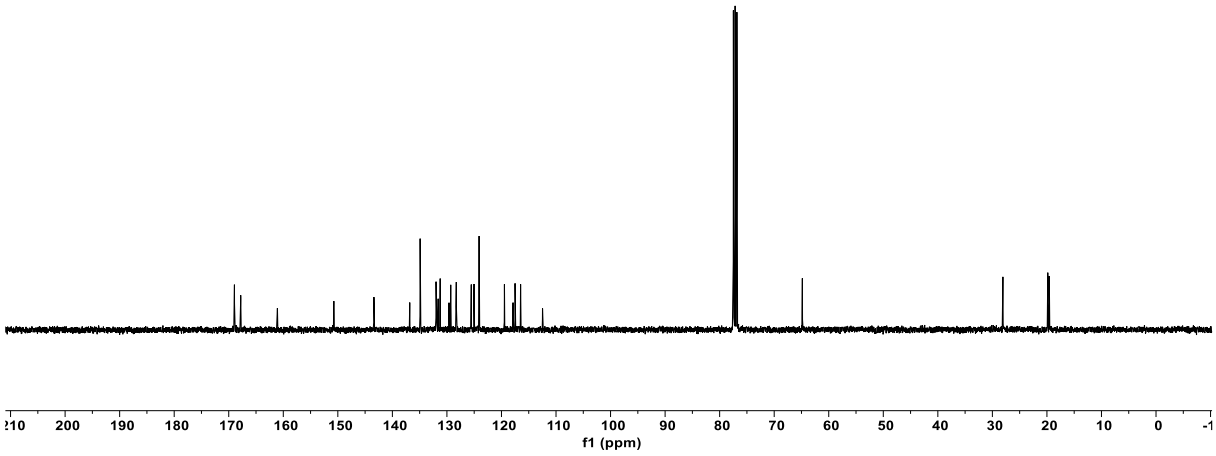
400 MHz, $CDCl_3$

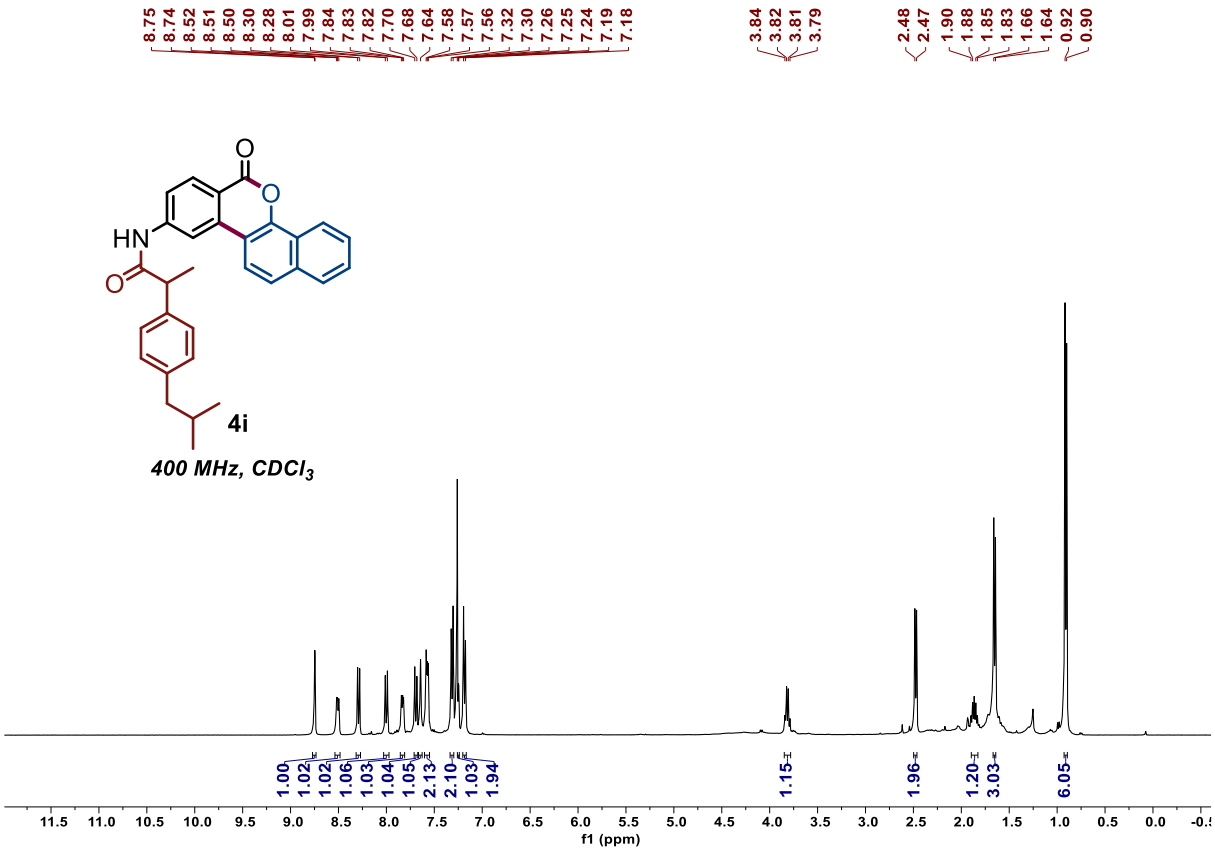


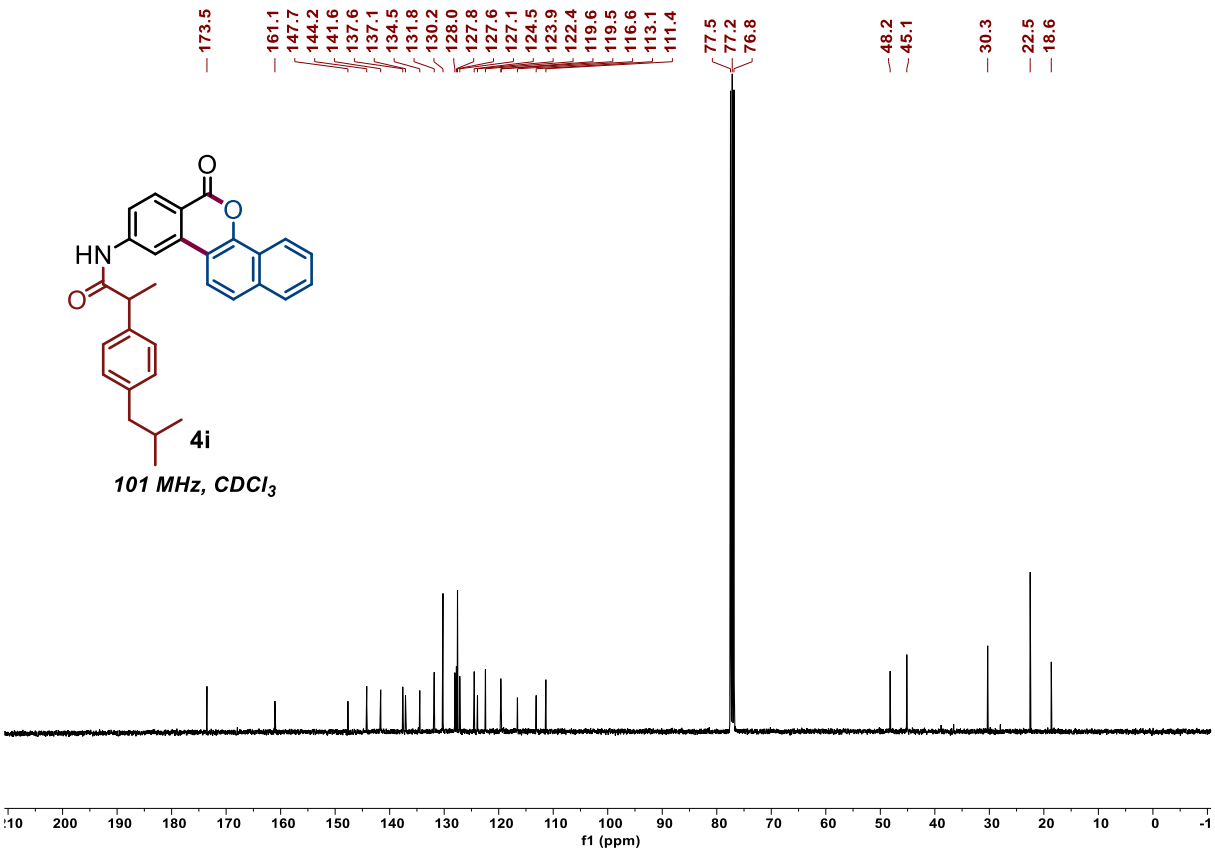


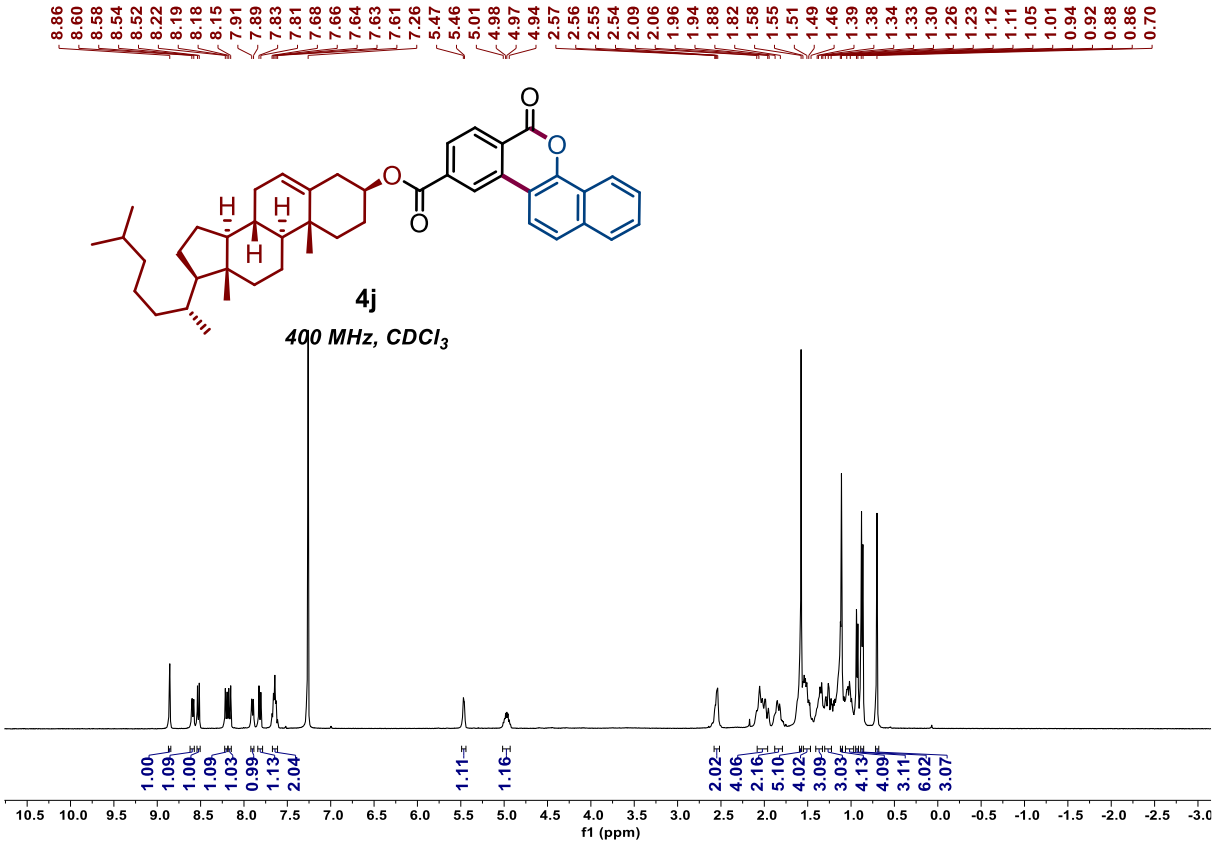
4h

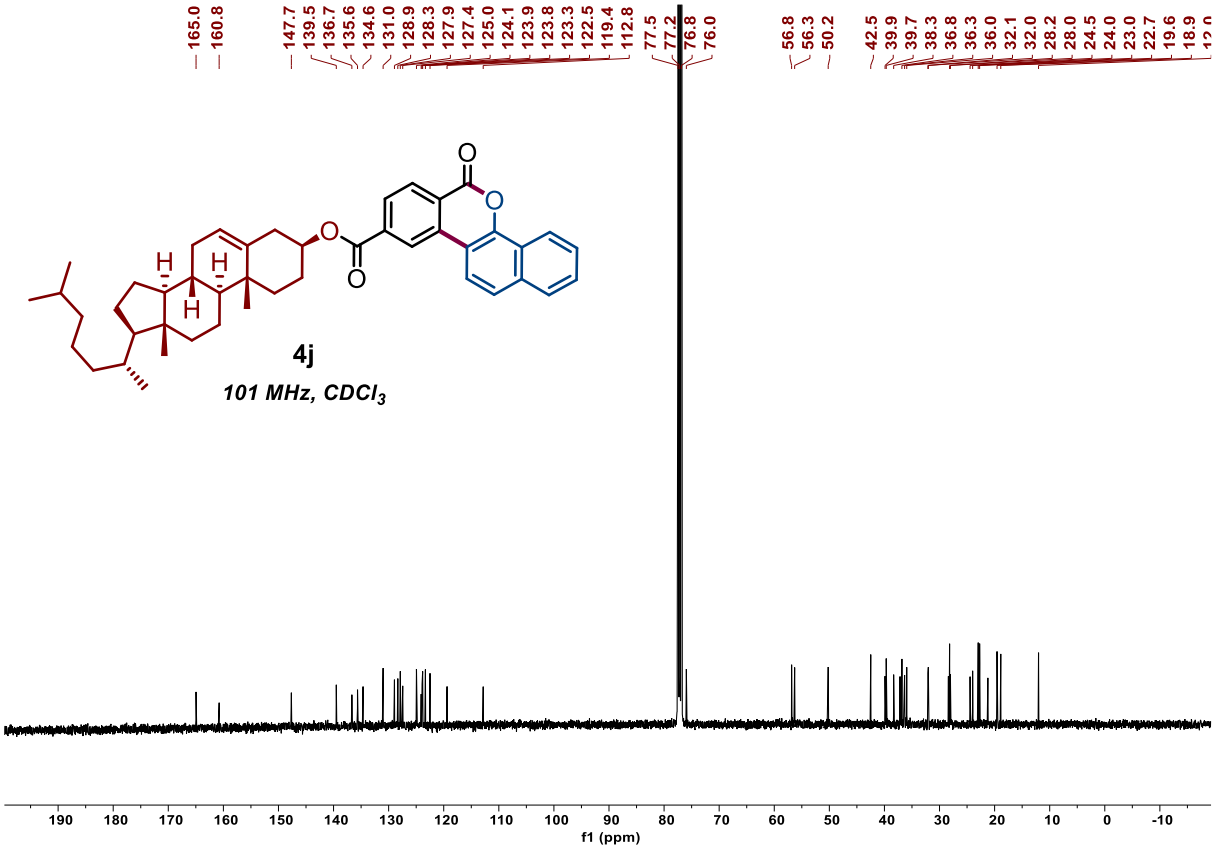
101 MHz, $CDCl_3$

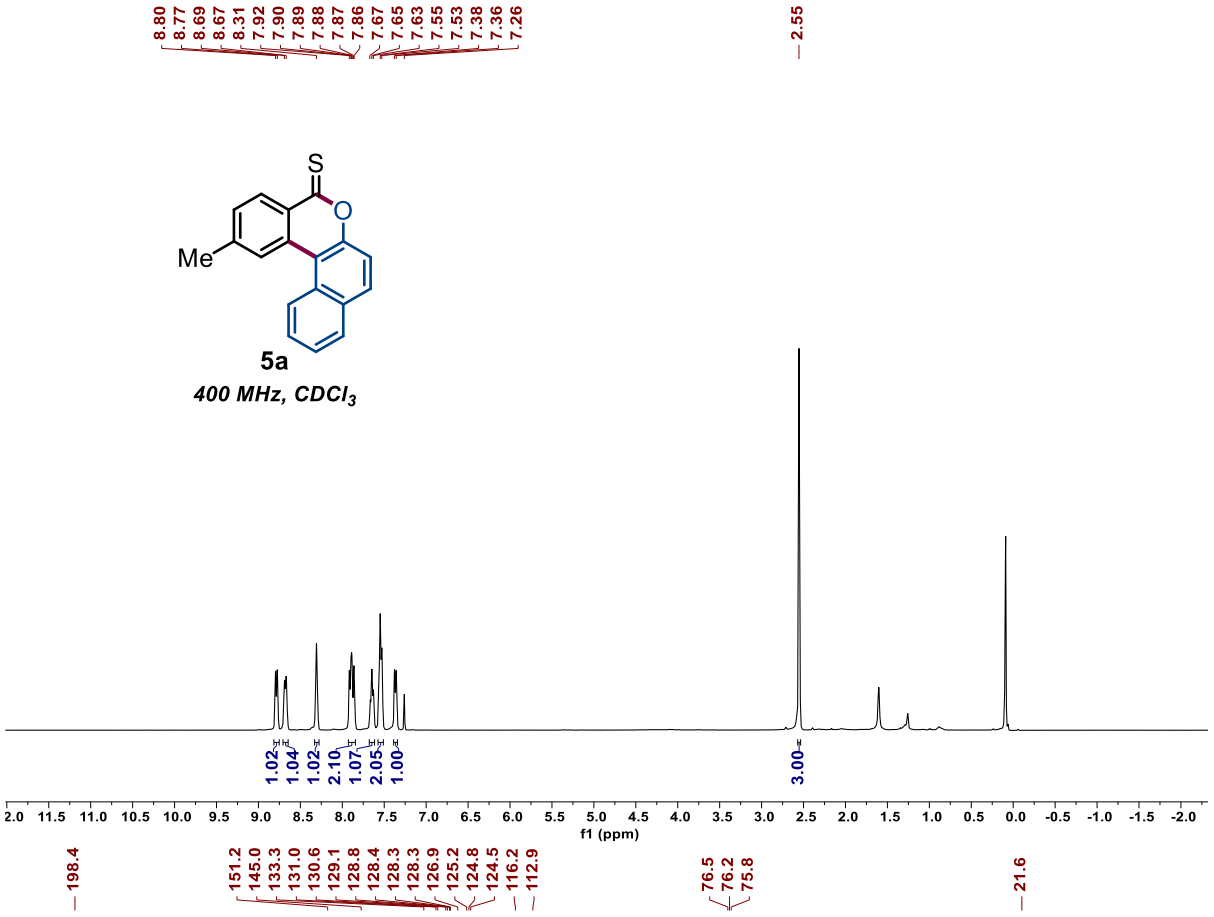



8.75
8.74
8.52
8.51
8.50
8.30
8.28
8.01
7.99
7.84
7.83
7.82
7.70
7.68
7.64
7.58
7.57
7.56
7.32
7.30
7.26
7.25
7.24
7.19
7.18
3.84
3.82
3.81
3.79
2.48
2.47
1.90
1.88
1.85
1.83
1.66
1.64
0.92
0.90
HN
O
O
4i
400 MHz, CDCl3
1.00
1.02
1.02
1.06
1.03
1.04
1.05
2.13
2.10
1.03
1.94
1.15
1.96
1.20
3.03
6.05
f1 (ppm)


173.5
161.1
147.7
144.2
141.6
137.6
137.1
134.5
131.8
130.2
128.0
127.8
127.6
127.1
124.5
123.9
122.4
119.6
119.5
116.6
113.1
111.4
77.5
77.2
76.8
48.2
45.1
30.3
22.5
18.6
HN
O
O
4i
101 MHz, CDCl3
f1 (ppm)

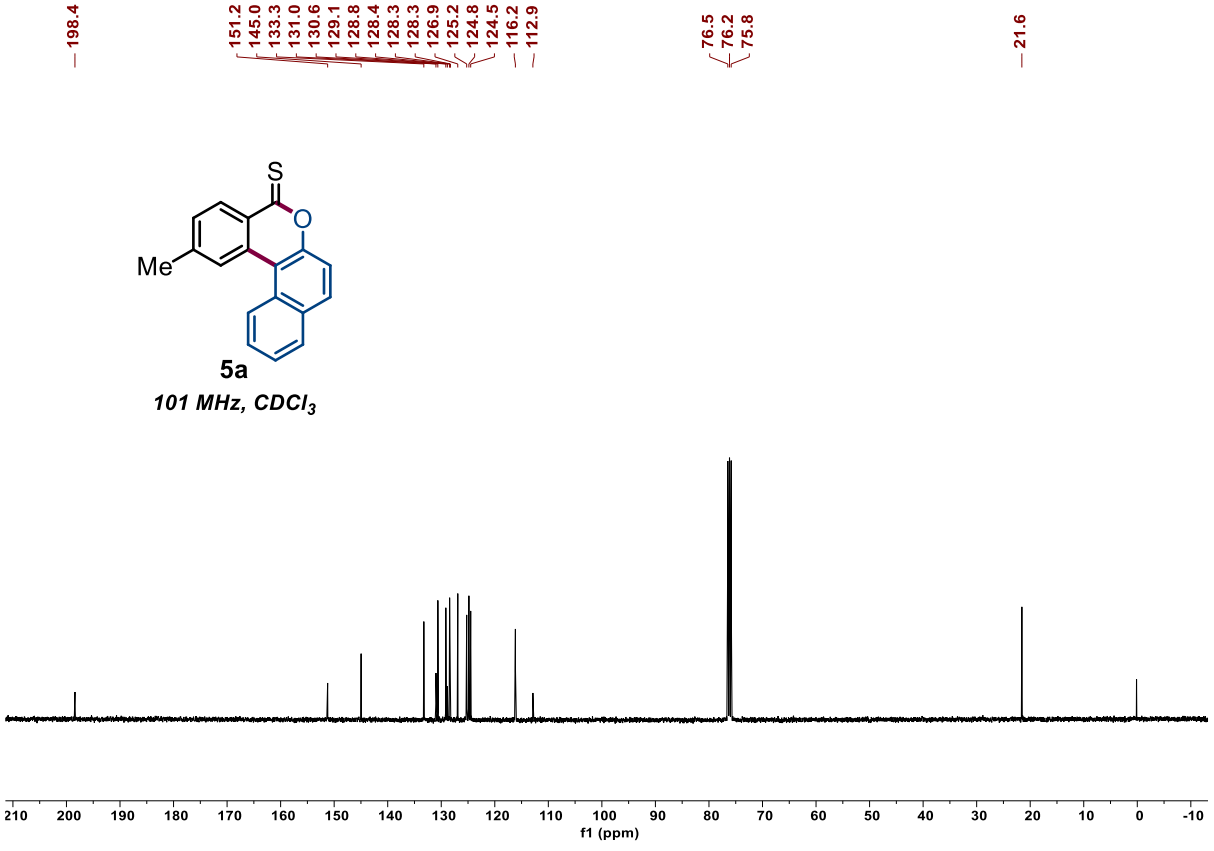

8.86 8.60 8.58 8.54 8.52 8.22 8.19 8.18 8.15 7.91 7.89 7.83 7.81 7.68 7.66 7.64 7.63 7.61 7.26 5.47 5.46 5.01 4.98 4.97 4.94 2.57 2.56 2.55 2.54 2.09 2.06 1.96 1.94 1.88 1.82 1.58 1.55 1.51 1.49 1.46 1.39 1.38 1.34 1.33 1.30 1.26 1.23 1.12 1.11 1.05 1.01 0.94 0.92 0.88 0.86 0.70
4j
400 MHz, CDCl3
1.00 1.09 1.00 1.09 1.03 0.99 1.13 2.04 1.11 1.16 2.02 4.06 2.16 5.10 4.02 3.09 3.03 4.13 4.09 3.11 6.02 3.07
f1 (ppm)


165.0 160.8 147.7 139.5 136.7 135.6 134.6 131.0 128.9 128.3 127.9 127.4 125.0 124.1 123.9 123.8 123.3 122.5 119.4 112.8 77.5 77.2 76.8 76.0 56.8 56.3 50.2 42.5 39.9 39.7 38.3 36.8 36.3 36.0 32.1 32.0 28.2 28.0 24.5 24.0 23.0 22.7 19.6 18.9
4j
101 MHz, CDCl3
f1 (ppm)



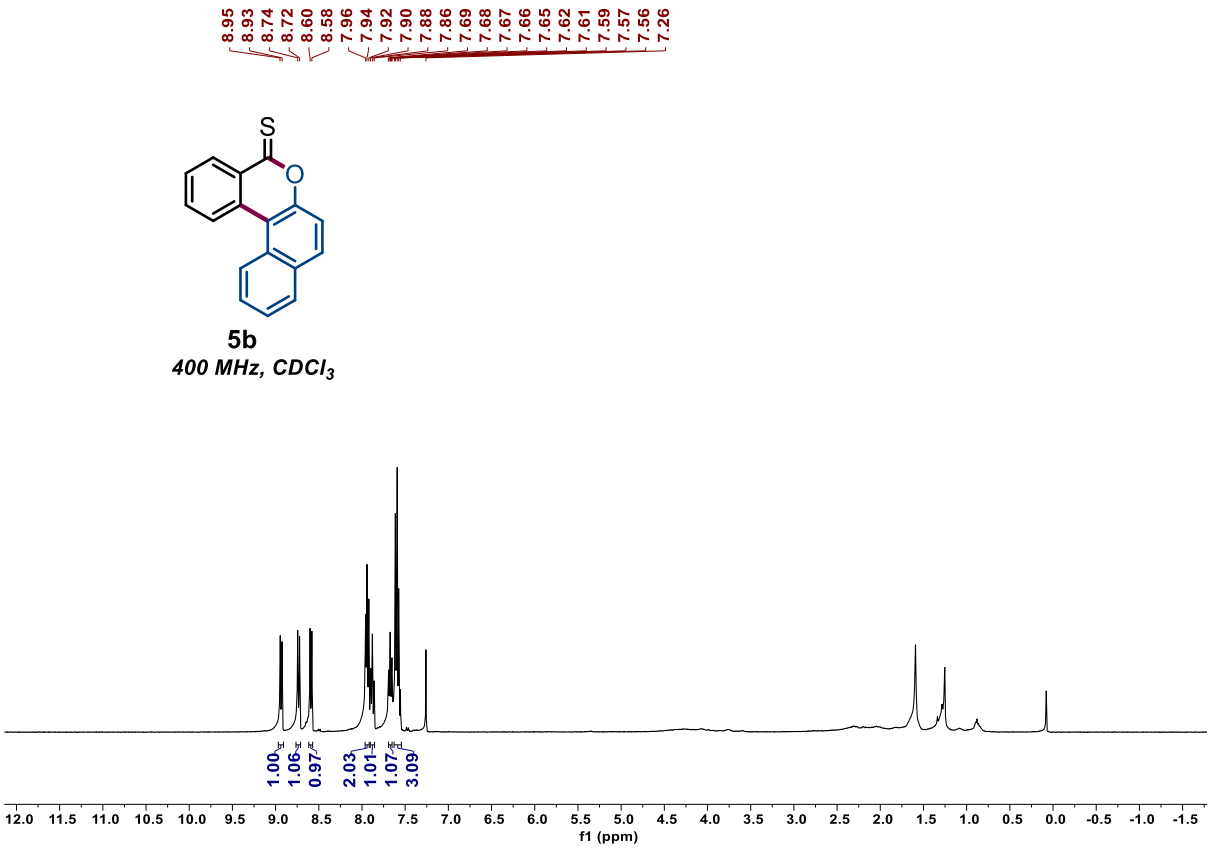
5a

400 MHz, $CDCl_3$



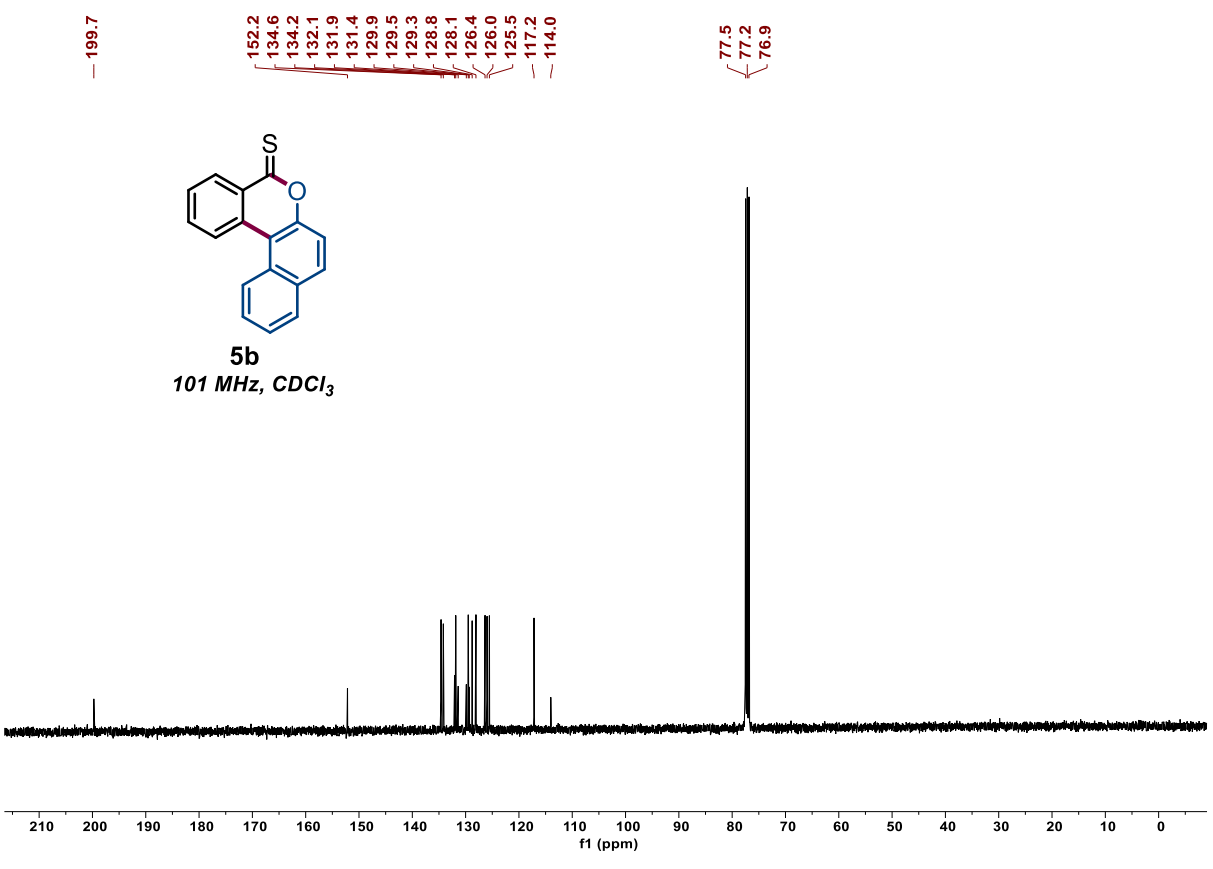
5a

101 MHz, $CDCl_3$



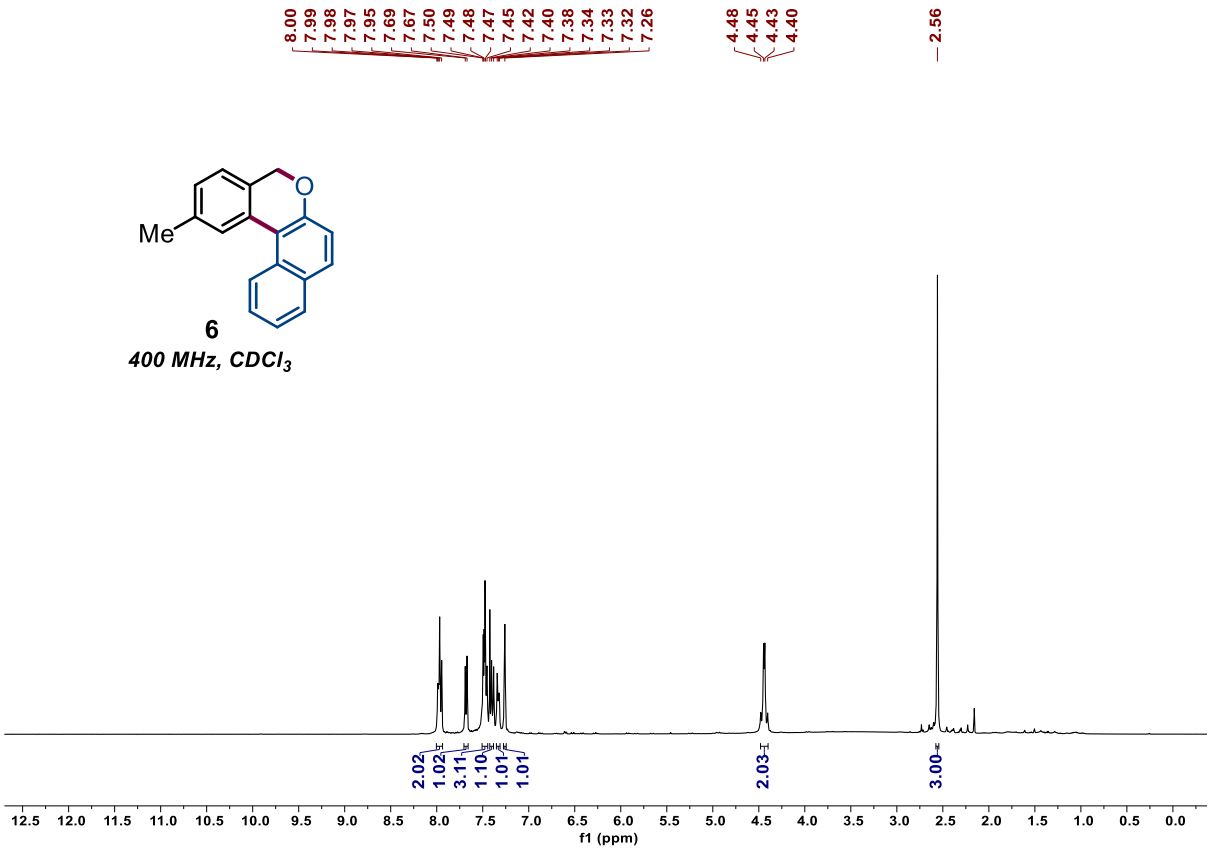
5b

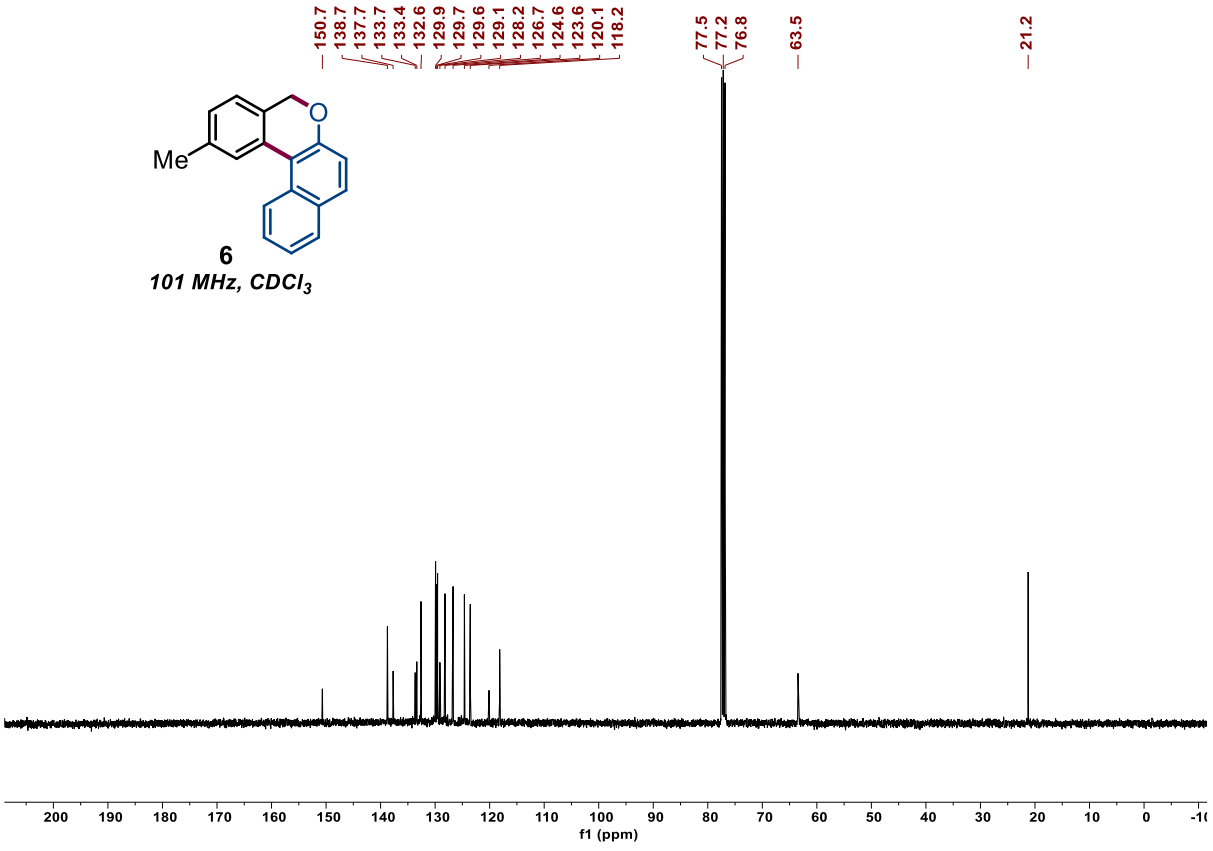
400 MHz, $CDCl_3$



5b

101 MHz, $CDCl_3$


8.00
7.99
7.98
7.97
7.95
7.69
7.67
7.50
7.49
7.48
7.47
7.45
7.42
7.40
7.38
7.34
7.33
7.32
7.26
4.48
4.45
4.43
4.40
2.56
Me
O
6
400 MHz, CDCl3
2.02
1.02
3.11
1.10
1.01
1.01
2.03
3.00
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


150.7
138.7
137.7
133.7
133.4
132.6
129.9
129.7
129.6
129.1
128.2
126.7
124.6
123.6
120.1
118.2
77.5
77.2
76.8
63.5
21.2
Me
O
6
101 MHz, CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)