ELECTRONIC SUPPLEMENTARY INFORMATION

Synthesis of Pyrano[2,3-*f*]chromen-2-ones *vs.* Pyrano[3,2-*g*]chromen-2-ones through Site Controlled Gold-Catalyzed Annulations

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Content

1. GENERAL INFORMATION

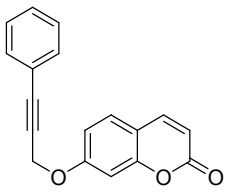
1.1. Reagents and methods

All of the commercially available reagents, catalysts, bases and solvents were used as purchased, without further purification. Reaction products have been obtained as regioisomeric mixtures by filtration on a pad of SiO_2 to eliminate the catalysts before calculating the isomeric ratio by ^1H NMR. To obtain suitable NMR spectra of each compound, the mixtures were further purified by semi-preparative HPLC under normal phase condition using a Nucleodur 100-5 column (762007.100) and eluting with *n*-hexane/AcOEt mixtures. ^1H NMR (400.13 MHz), ^{13}C NMR (100.6 MHz), and ^{19}F spectra (376.5 MHz) were recorded with a Bruker Avance 400 spectrometer. Splitting patterns are designed as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), or bs (broad singlet). IR spectra were recorded with a Jasco FT/IR-430 spectrometer. Mass spectra were determined with a Shimadzu QP2010 Gas Chromatograph Mass spectrometer (EI ion source) or with a Shimadzu QP2010-Plus Gas Chromatograph Mass spectrometer (CI ion source/ NCI ionsource, DI). HRMS were recorded with an Orbitrap Exactive Mass spectrometer with ESI source. Melting points were determined with a Büchi B-545 apparatus and are uncorrected.

2. SYNTHETIC PROCEDURES

2.1. Typical procedure for the preparation of the 7-(3-phenylprop-2-ynyloxy)-2H-chromen-2-one 1a:

A flask equipped with a magnetic stirring bar was charged with $PdCl_2(PPh_3)_2$ (49 mg, 0.07 mmol, 0.02 equiv.) and CuI (26.5 mg, 0.14 mmol, 0.04 equiv.) dissolved in diisopropylamine (7 mL) and *N,N*-dimethylformamide (5 mL). The resultant solution was stirred under nitrogen at room temperature for 10 minutes before adding iodobenzene (714 mg, 3.5 mmol, 1.0 equiv.) in diisopropylamine (3 mL) and 7-(prop-2-ynyloxy)-2*H*-chromen-2-one (841 mg, 4.2 mmol, 1.2 equiv.) and stirred for 3 hours at room temperature. After this time, the reaction mixture was diluted with Et_2O and washed with a saturated NH_4Cl solution, HCl 2N and with brine. The organic layer was dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by chromatography on SiO_2 (25-40 µm), eluting with a 80/20 (v/v) *n*-hexane/AcOEt mixture *(R_f* = 0.24) to obtain 870 mg (90% yield) of 7-(3-phenylprop-2-ynyloxy)-2H-chromen-2-one **1a**.

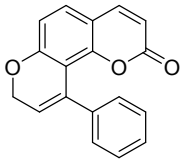


1a

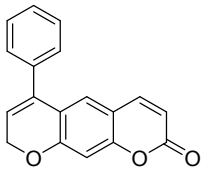
1a[1]: white solid; mp: 140-142 °C**;** IR (KBr): 2963, 2219, 1711, 1615, 1506, 1488, 1209 cm^{-1}; ^1H NMR (400.13 MHz) ($CDCl_3$): δ = 7.67 (d, *J* = 9.5 Hz, 1 H), 7.47-7.28 (m, 6 H), 7.03 (d, *J* = 2.4 Hz, 1 H), 6.98 (dd, J_1 = 8.4 Hz, J_2 = 2.4 Hz, 1 H), 6.29 (d, *J* = 9.5 Hz, 1 H), 5.00 (s, 2 H); ^{13}C NMR (100.6 MHz) ($CDCl_3$): δ = 161.1, 160.9, 155.7, 143.3, 131.9, 129.0, 128.8, 128.4, 121.8, 113.5, 113.2, 113.1, 102.2, 88.2, 82.6, 57.1; MS (EI ion source): *m/z* (%) = 276 (100, $[M^+]$), 247 (32), 199 (15), 63.00 (43); HRMS: *m/z* $[M + H]^+$ calcd for $C_{18}H_{13}O_3$: 277.0859; found: 277.0864.

2.2. Typical procedure for the preparation of 2a/3a.

A flask equipped with a magnetic stirring bar was charged with 7-(3-phenylprop-2-ynyloxy)-2*H*-chromen-2-one (82.9 mg, 0.3 mmol, 1 equiv) and CH_2Cl_2 (2 mL) before adding catalyst A or catalyst B (catalyst A: JohnPhosAu(MeCN)SbF_6 4.6 mg, 0.006 mmol, 0.02 equiv; catalyst B: Ph_3PAuCl 3.0 mg, 0.006 mmol, 0.02 equiv. and $AgSbF_6$ 2.1 mg, 0.006 mmol, 0.02 equiv.).The resulting mixture was stirred for 3 hours, then it was concentrated under reduced pressure and the residue was filtered on a pad of SiO_2 to afford 81.8 mg of **2a** + **3a** (99% overall yield) using catalyst A or 79.5 mg of **2a** +**3a** (96% overall yield) using catalyst B. **2a/3a** ratio was calculated by ^1H NMR analyses. Afterwards, the two isomers were separated by semi-preparative HPLC to obtain suitable NMR spectra of each compound.



2a



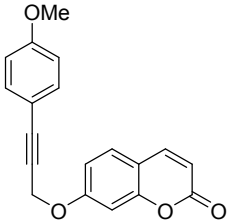
3a

Overall yield (catalyst A): 99% (81.8 mg); **2a/3a** = 60/40
Overall yield (catalyst B): 96% (79.5 mg); **2a/3a** = 95/5

2a: white solid**;** mp: 170-172 °C; IR (KBr): 3060, 2922, 1702, 1593, 1480, 1402, 1343, 1232 cm^{-1}; ^1H NMR (400.13 MHz) ($CDCl_3$): δ = 7.59 (d, *J* = 9.5 Hz, 1 H), 7.40-7.39 (m, 3 H), 7.34 (d, *J* = 8.4 Hz, 1 H), 7.28-7.26 (m, 2 H), 6.96 (d, *J* = 8.4 Hz, 1 H), 6.15 (d, *J* = 9.5 Hz, 1 H), 5.96 (t, *J* = 4.5 Hz, 1 H), 4.81 (d, *J* = 4.5 Hz, 2 H); ^{13}C NMR (100.6 MHz) ($CDCl_3$): δ = 159.6, 159.2, 150.9, 143.6, 139.2, 135.1, 128.6, 128.1, 127.7, 127.2, 121.9, 113.9, 113.5, 113.2, 112.3, 65.3; MS (EI ion source): *m/z* (%) = 276 (21 [M^+]), 207 (16), 135 (11), 73 (100); HRMS: *m/z* [M + Na]$^+$ calcd for $C_{18}H_{12}O_3Na$: 299.0679; found: 299.0680.

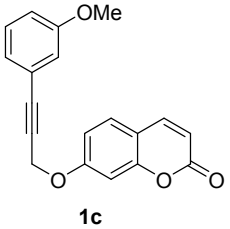
3a: white solid; mp: 163-164 °C; IR (KBr): 3076, 2818, 1734, 1620, 1487, 1401 cm^{-1}; ^1H NMR (400.13 MHz) ($CDCl_3$): δ = 7.51-7.43 (m, 4 H), 7.36-7.34 (m, 2 H), 7.06 (s, 1 H), 6.83 (s, 1 H), 6.22 (d, *J* = 9.5 Hz, 1 H), 5.83 (t, *J* = 3.8 Hz, 1 H), 5.01 (d, *J* = 3.8 Hz, 2 H); ^{13}C NMR (100.6 MHz) ($CDCl_3$): δ = 161.0, 158.3, 155.3, 143.5, 137.6, 135.6, 128.7, 128.5, 128.3, 124.6, 120.7, 120.3, 113.4, 113.0, 104.4, 66.1; MS (EI ion source): *m/z* (%) = 276 (7 [M^+]), 207 (16), 135 (11) 73 (100); HRMS: *m/z* [M + Na]$^+$ calcd for $C_{18}H_{12}O_3Na$: 299.0679; found: 299.0680

3. CHARACTERIZATION DATA OF 1b – l, 4a - e



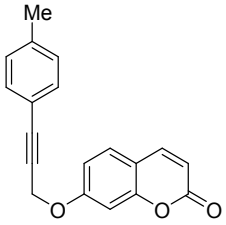
1b

1b: pale yellow solid**;** mp: 118-120 °C; IR (KBr): 3050, 2940, 2260, 1737, 1633, 1386, 1347, 1268 cm^{-1}; ^1H NMR (400.13 MHz) ($CDCl_3$): δ = 7.66 (d, *J* = 9.6 Hz, 1 H), 7.42-7.38 (m, 3 H), 7.02 (d, *J* = 2.4 Hz, 1 H), 6.97 (dd, J_1 = 8.4 Hz, J_2 = 2.4 Hz, 1 H), 6.85 (d, *J* = 8.8 Hz, 2 H), 6.29 (d, *J* = 9.6 Hz, 1 H), 4.99 (s, 2 H), 3.81 (s, 3 H); ^{13}C NMR (100.6 MHz) ($CDCl_3$): δ = 161.1, 160.9, 160.1, 155.7, 143.4, 133.5, 128.8, 114.0, 113.8, 113.5, 113.2, 113.0, 102.1, 88.2, 81.3, 57.2, 55.3; MS (EI ion source): *m/z* (%) = 306 (20, [M^+]), 207 (38), 73 (29), 44 (100); HRMS: *m/z* [M + Na]$^+$ calcd for $C_{19}H_{14}O_4Na$: 329.0784; found: 329.0787.



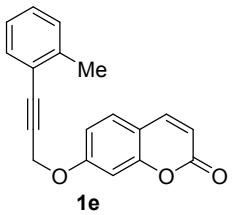
1c

1e: pale yellow solid**;** mp: 127-129 °C; IR (KBr): 3054, 2920, 2222, 1729, 1619, 1383, 1248 cm^{-1}; ^1H NMR (400.13 MHz) ($CDCl_3$): δ = 7.67 (d, *J* = 9.5 Hz, 1 H), 7.43 (d, *J* = 8.4 Hz, 1 H), 7.23 (t, *J* = 7.6 Hz, 1 H), 7.06-7.96 (m, 4 H), 6.91 (dd, J_1 = 8.4 Hz, J_2 = 2.4 Hz, 1 H), 6.30 (d, *J* = 9.5 Hz, 1 H), 4.99 (s, 2 H), 3.81 (s, 3 H); ^{13}C NMR (100.6 MHz) ($CDCl_3$): δ = 161.1, 160.8, 159.3, 155.7, 143.4, 129.5, 128.8, 124.4, 122.8, 116.7, 115.6, 113.5, 113.2, 113.1, 102.1, 88.1, 82.4, 57.1, 55.3 ; MS (EI ion source): *m/z* (%) = 306 (21, [M^+]), 207 (35), 73 (30), 44 (100); HRMS: *m/z* [M + H]$^+$ calcd for $C_{19}H_{15}O_4$: 307.0965; found: 307.0969.



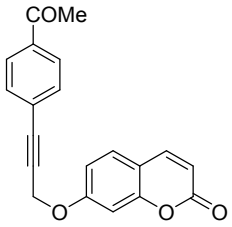
1d

1d: pale yellow solid; mp: 117-118 °C; IR (KBr): 3045, 2920, 2228, 1732, 1617, 1505, 1400, 1378, 1347, 1276 cm^{-1}; ^{1}H NMR (400.13 MHz) ($CDCl_3$): δ = 7.66 (d, *J* = 9.5 Hz, 1 H), 7.42 (d, *J* = 8.4 Hz, 1 H), 7.35 (d, *J* = 7.8 Hz, 2 H), 7.13 (d, *J* = 7.8 Hz, 2 H), 7.02 (d, *J* = 2.4 Hz, 1 H), 6.98 (dd, J_1 = 8.4 Hz, J_2 = 2.4 Hz, 1 H), 6.29 (d, *J* = 9.5 Hz, 1 H), 4.99 (s, 2 H), 2.36 (s, 3 H); ^{13}C NMR (100.6 MHz) ($CDCl_3$): δ = 161.1, 160.9, 155.7, 143.4, 139.2, 131.8, 129.1, 128.8, 118.7, 113.5, 113.2, 113.0, 102.2, 88.4, 81.9, 57.2, 21.5; MS (EI ion source): *m/z* (%) = 290 (40, $[M^+]$), 275 (24), 207 (27), 44 (100); HRMS: *m/z* $[M + Na]^+$ calcd for $C_{19}H_{14}O_3Na$: 313.0835; found: 313.0838.



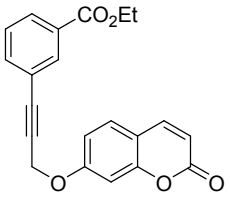
1e

1e: pale yellow solid; mp: 96-98 °C; IR (KBr): 3054, 2986, 2305, 1734, 1615, 1266 cm^{-1}; ^{1}H NMR (400.13 MHz) ($CDCl_3$): δ = 7.67 (d, *J* = 9.5, 1 H), 7.44-7.28 (m, 2 H), 7.27-7.13 (m, 3 H), 7.05 (d, *J* = 2.4 Hz, 1 H), 6,99 (dd, J_1 = 8.4 Hz, J_2 = 2.4 Hz, 1 H), 6.30 (d, *J* = 9.5 Hz, 1 H), 5.05 (s, 2 H), 2.40 (s, 3 H); ^{13}C NMR (100.6 MHz) ($CDCl_3$): δ = 161.1, 160.8, 155.7, 143.4, 140.6, 132.3, 129.5, 129.0, 128.8, 125.6, 121.6, 113.5, 113.2, 113.1, 102.3, 87.2, 86.3, 57.2, 20.7; MS (EI ion source): *m/z* (%) = 290 (100, $[M^+]$), 275 (71), 199.00 (19), 115 (37), 63 (53); HRMS: *m/z* $[M + Na]^+$ calcd for $C_{19}H_{14}O_3Na$: 313.0835; found: 313.0838.



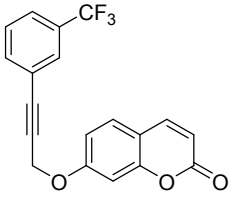
1f

1f: white solid; mp: 124-126 °C; IR (KBr): 3030, 2917, 2240, 1730, 1681, 1614, 1383, 1260 cm^{-1}; ^{1}H NMR (400.13 MHz) ($CDCl_3$): δ = 7.83 (d, *J* = 8.4 Hz, 2 H), 7.59 (d, *J* = 9.4 Hz, 1 H), 7.45 (d, *J* = 8.4 Hz, 2 H), 7.35 (d, *J* = 8.4 Hz, 1 H), 6.93 (d, *J* = 2.4 Hz, 1 H), 6.88 (dd, J_1 = 8.4 Hz, J_2 = 2.4 Hz, 1 H), 6.21 (d, *J* = 9.4 Hz, 1 H), 4.93 (s, 2 H), 2.52 (s, 3 H); ^{13}C NMR (100.6 MHz) ($CDCl_3$): δ = 197.3, 161.1, 160.7, 155.7, 143.3, 136.8, 132.0, 128.9, 128,2, 126.6, 113.7, 113.2, 113.1, 102.1, 87.2, 85.8, 56.9, 26.7; MS (EI ion source): *m/z* (%) = 318.00 (6, $[M^+]$), 281 (21), 207 (60), 73 (100); HRMS: *m/z* $[M + Na]^+$ calcd for $C_{20}H_{14}O_4Na$: 341.0784; found: 341.0775.



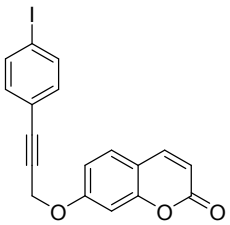
1g

1g: pale yellow solid**;** mp: 128-129 °C; IR (KBr): 3054, 2986, 2259, 1733, 1615, 1265 cm^{-1}; ^1H NMR (400.13 MHz) ($CDCl_3$): δ = 8.13 (s, 1 H), 8.03 (d, *J* = 8.0 Hz, 1 H), 7.67 (d, *J*= 9.4 Hz, 1 H), 7.60 (d, *J* = 8.0 Hz, 1 H), 7.45-7.39 (m, 2 H), 7.02 (d, *J* = 2.4 Hz, 1 H), 6.98 (dd, J_1 = 8.4 Hz, J_2 = 2.4 Hz, 1 H), 6.30 (d, *J* = 9.4 Hz, 1 H), 5.01 (s, 2 H), 4.39 (q, *J* = 7.2 Hz, 2 H), 1.41 (t, *J* = 7.2 Hz, 3 H); ^{13}C NMR (100.6 MHz) ($CDCl_3$): δ = 165.7, 161.1, 160.8, 155.7, 143.3, 135.9, 132.9, 130.9, 129.9, 128.9, 128.5, 122.2, 113.6, 113.2, 113.1, 102.1, 87.1, 83.4, 61.3, 56.9, 14.3; MS (EI ion source): *m/z* (%) = 348 (16, $[M^+]$), 275 (11), 207 (43), 73 (41), 44 (100); HRMS: *m/z* $[M + Na]^+$ calcd for $C_{21}H_{16}O_5Na$: 371.0890; found: 371.0877.



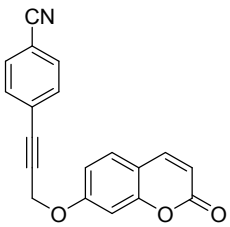
1h

1h: white solid**;** mp: 98-99 °C; IR (KBr): 3054, 2921, 2240, 1734, 1615, 1270 cm^{-1}; ^1H NMR (400.13 MHz) ($CDCl_3$): δ = 7.72-7.60 (m, 4 H), 7.49-7.43 (m, 2 H), 7.01 (d, *J* = 2.4 Hz, 1 H), 6.97 (dd, J_1 = 8.4 Hz, J_2 = 2.4 Hz, 1 H), 6.31 (d, *J* = 9.6 Hz, 1 H), 5.01 (s, 2 H); ^{13}C NMR (100.6 MHz) ($CDCl_3$): δ = 161.0, 160.7, 155.7, 143.3, 135.0, 131.0 (q, J_{CF} = 33 Hz), 128.95, 128.89, 128.6 (q, J_{CF} = 3.7 Hz), 125.6 (q, J_{CF} = 3.7 Hz), 123.6 (q, J_{CF} = 273 Hz), 122.8, 113.7, 113.2, 113.1, 102.1, 86.5, 84.2, 56.9; ^{19}F NMR (376.5 MHz) ($CDCl_3$): δ = -62.9; MS (EI ion source): *m/z* (%) = 344 (43, $[M^+]$), 207 (44), 199 (25), 44 (100); HRMS: *m/z* $[M + Na]^+$ calcd for $C_{19}H_{11}F_3O_3Na$: 367.0553; found: 367.0552.



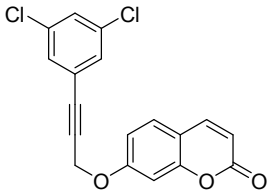
1i

1i: pale yellow solid**;** mp: 148-149 °C; IR (KBr): 3060, 2921, 2239, 1700, 1613, 1264 cm^{-1}; ^1H NMR (400.13 MHz) ($CDCl_3$): δ = 7.59-7.57 (m, 3 H), 7.34 (d, *J* = 8.8 Hz, 1 H), 7.09 (d, *J* = 8.4 Hz, 2 H), 6.91 (d, *J* = 2.4 Hz, 1 H), 6.87 (dd, J_1 = 8.8 Hz, J_2 = 2.4 Hz, 1 H), 6.21 (d, *J*= 9.6 Hz, 1 H), 4.89 (s, 2 H); ^{13}C NMR (100.6 MHz) ($CDCl_3$): δ = 161.1, 160.7, 155.7, 143.3, 137.6 (2C), 133.3, 128.9, 121.3, 113.6, 113.2, 102.1, 95.2, 87.2, 83.9, 57.0; MS (EI ion source): *m/z* (%) = 402 (27, $[M^+]$), 207 (49), 73 (44), 44 (100); HRMS: *m/z* $[M + Na]^+$ calcd for $C_{18}H_{11}IO_3Na$: 424.9645; found: 424.9648.



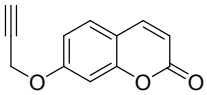
1j

1j: white solid**;** mp: 181-182 °C; IR (KBr): 3054, 2987,2304, 2230, 1734, 1616, 1265 cm^{-1}; ^1H NMR (400.13 MHz) ($CDCl_3$): δ = 7.67 (d, *J* = 9.6 Hz, 1 H), 7.62 (d, *J* = 8.4 Hz, 2 H), 7.50 (d, *J* = 8.4 Hz, 2 H), 7.44 (d, *J* = 8.4 Hz, 1 H), 6.99 (d, *J* = 2.4 Hz, 1 H), 6.96 (dd, J_1 = 8.4 Hz, J_2 = 2.4 Hz, 1 H), 6.30 (d, *J* = 9.6 Hz, 1 H), 4.93 (s, 2 H); ^{13}C NMR (100.6 MHz) ($CDCl_3$): δ = 161.0, 160.6, 155.7, 143.3, 132.4, 132.1, 128.9, 126.6, 118.2, 113.7, 113.3, 113.1, 112.4, 102.0, 86.9, 86.3, 56.8; MS (EI ion source): *m/z* (%) = 301 (13, $[M^+]$), 281 (17), 207 (55), 73 (50), 44 (100); HRMS: *m/z* $[M + Na]^+$ calcd for $C_{19}H_{11}NO_3Na$: 324.0631; found: 324.0634.



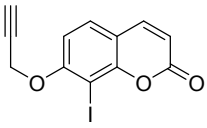
1k

1k: white solid**;** mp: 155-157 °C; IR (KBr): 3067, 2925, 2255, 1741, 1616, 1254 cm^{-1}; ^1H NMR (400.13 MHz) ($CDCl_3$): δ = 7.68 (d, *J* = 9.6 Hz, 1 H), 7.44 (d, *J* = 8.4 Hz, 1 H), 7.35-7.32 (m, 3 H), 6.98-6.94 (m, 2 H), 6.31 (d, *J*= 9.6 Hz, 1 H), 4.99 (s, 2 H); ^{13}C NMR (100.6 MHz) ($CDCl_3$): δ = 161.0, 160.6, 155.7, 143.3, 135.0, 130.0, 129.4, 128.9, 124.5, 113.7, 113.3, 113.0, 102.1, 85.3, 85.0, 56.7; MS (EI ion source): *m/z* (%) = 344 (15, $[M^+]$), 281 (21), 207 (52), 73 (50), 44 (100); HRMS: *m/z* $[(M + H)]^+$ calcd for $C_{18}H_{11}Cl_2O_3$: 345.0077; found: 345.0080; $[(M + 2) + H]^+$ calcd for $C_{18}H_{11}Cl_2O_3$: 347.0050; found: 347.0047.



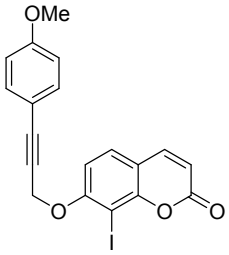
1l

1l: white solid; lit. mp**:** 118-119°C;[2] mp: 119-120 °C; IR (KBr): 3059, 2920, 2122, 1728, 1616, 1235 cm^{-1}; ^1H NMR (400.13 MHz) ($CDCl_3$): δ = 7.67 (d, *J* = 9.6 Hz, 1 H), 7.42 (d*, J* = 8.4 Hz, 1 H), 6.96-6.92 (m, 2 H), 6.30 (d, *J* = 9.6 Hz, 1 H), 4.78 (d, *J* = 2.4 Hz, 2 H), 2.60 (t, *J* = 2.4 Hz, 1 H); ^{13}C NMR (100.6 MHz) ($CDCl_3$): δ = 160.0, 160.5, 155.6, 143.3, 128.8, 113.7, 113.2, 113.1, 102.1, 76.6; 56.2; MS (EI ion source): *m/z* (%) = 200 (45, $[M^+]$), 171 (40), 144 (75), 115 (80), 77 (83), 51 (100); HRMS: *m/z* $[M + H]^+$ calcd for $C_{12}H_9O_3$: 201.0546; found: 201.0546.



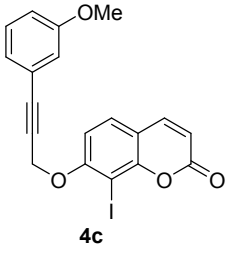
4a

4a: pale yellow solid**;** mp: 175-177 °C; IR (KBr): 3059, 2988, 2180, 1730, 1597, 1384 cm^{-1}; ^1H NMR (400.13 MHz) ($CDCl_3$): δ = 7.61 (d, *J* = 9.6 Hz, 1 H), 7.47 (d, *J* = 8.4 Hz, 1 H), 6.99 (d, *J* = 8.4 Hz, 1 H), 6.32 (d, *J* = 9.6 Hz, 1 H), 4.91 (d, *J* = 2.4 Hz, 2 H), 2.60 (t, *J* = 2.4 Hz, 1 H); ^{13}C NMR (100.6 MHz) ($CDCl_3$) δ = 160.3, 159.8, 155.1, 142.9, 128.8, 114.5, 114.3, 109.0, 77.2, 76.9, 76.8, 57.4; MS (CI ion source): *m/z* (%) = 327 (100, $[M +H]^+$), 200 (41); HRMS: *m/z* $[M + Na]^+$ calcd for $C_{12}H_7IO_3Na$: 348.9332; found: 348.9318.



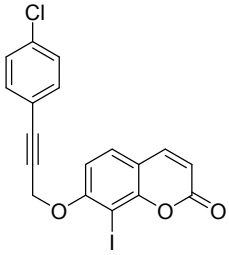
4b

4b: white solid**;** mp: 165-168 °C**;** IR (KBr): 3060, 2938, 2255, 1734, 1620, 1230 cm^{-1}; ^{1}H NMR (400.13 MHz) ($CDCl_3$): δ = 7.52 (d, *J* = 9.6 Hz, 1H), 7.38 (d, *J* = 8.8 Hz, 1H), 7.28 (d, *J* = 8.8 Hz, 2H), 7.00 (d, *J* = 8.8 Hz, 1H), 6.75 (d, *J* = 8.8 Hz, 2H), 6.21 (d, *J = 9.2* Hz, 1H), 5.02 (s, 2H), 3.73 (s, 3H); ^{13}C NMR (100.6 MHz) ($CDCl_3$): δ= 160.5, 160.18, 160.17, 155.1, 143.0, 133.4, 128.8, 114.2, 114.1, 114.0, 113.8, 109.3, 88.6, 81.2, 76.9, 58.4, 55.3 MS (CI ion source): *m/z* (%) = 433 (46, $[M+H]^+$), 306 (68), 145(100); HRMS: *m/z* $[M + Na]^+$ calcd for $C_{19}H_{13}IO_4Na$: 454.9751; found: 454.9750.



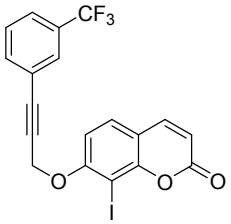
4c

4c: pale yellow solid; mp: 149-150 °C**;** IR (KBr): 3050, 2922, 2260, 1730, 1597, 1384 cm^{-1}; ^{1}H NMR (400.13 MHz) ($CDCl_3$) δ = 7.61 (d, *J*= 9.3 Hz, 1 H), 7.48 (d, *J*= 8.7 Hz, 1 H), 7.24 (t, *J*= 8.0 Hz, 1 H), 7.08 (d, *J*= 8.7 Hz, 1 H), 7.03 (d, *J*= 7.6 Hz, 1H), 6.96 (bs, 1 H), 6.91 (dd, J_1= 8.3 Hz, J_2= 2.4 Hz, 1H), 6.31 (d, *J*= 9.3 Hz, 1 H), 5.12 (s, 2 H), 3.80 (s, 3 H); ^{13}C NMR (100.6 MHz) ($CDCl_3$) δ = 160.4, 160.1, 159.3, 155.1, 143.0, 129.5, 128.9, 124.3, 122.7, 116.8, 115.5, 114.3, 114.2, 109.3, 88.4, 82.3, 76.9, 58.3, 55.3; MS (CI ion source): *m/z* (%) = 433 (28, $[M + H]^+$), 306 (46), 145(100); HRMS: *m/z* $[M + Na]^+$ calcd for $C_{19}H_{13}IO_4Na$: 454.9751; found: 454.9749.



4d

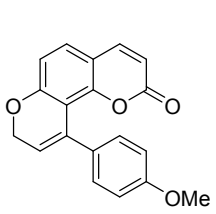
4d: pale yellow solid**;** mp: 150-152 °C**;** IR (KBr): 3060, 2955, 2255, 1730, 1616, 1244 cm^{-1}; ^{1}H NMR (400.13 MHz) ($CDCl_3$) δ = 7.52 (d, *J* = 9.5 Hz, 1 H), 7.39 (d, *J* = 8.6 Hz, 1 H), 7.28 (d, *J* = 8.7 Hz, 2 H), 7.21 (d, *J* = 8.7 Hz 2H), 6.97 (d, *J* = 8.6 Hz, 1 H), 6.23 (d, *J* = 9.5 Hz, 1 H), 5.03 (s, 2 H); ^{13}C NMR (100.6 MHz) ($CDCl_3$) δ = 160.4, 160.0, 155.1, 143.0, 135.2, 133.1, 128.8, 128.7, 120.2, 114.4, 114.2, 109.1, 87.3, 83.5, 76.9, 58.2; MS (CI ion source): *m/z* (%) = 439 (18, $[(M + 2) + H]^+$), 437 (51, $[M + H]^+$), 279 (20), 281 (6), 145(100); HRMS: *m/z* $[M + Na]^+$ calcd for $C_{18}H_{10}ClIO_3Na$: 458.9255; found: 458.9260; $[(M + 2) + Na]^+$ calcd for $C_{18}H_{10}ClIO_3Na$: 460.9227; found: 460.9230.



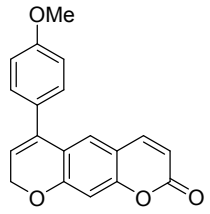
4e

4e: white solid**;** mp: 174-175 °C**;** IR (KBr): 3060, 2918, 2259, 1724, 1600, 1384 cm^{-1}; ^1H NMR (400.13 MHz) ($CDCl_3$) δ = 7,61(s, 1H), 7.54-7.51 (m, 3H), 7.41-7.36 (m, 2H), 6.97 (d, *J*= 8.6 Hz, 1H), 6.23 (d, *J*=9.48 Hz, 1H), 5.05(s, 2H); ^{13}C NMR (100.6 MHz) ($CDCl_3$) δ = 160.3, 159.9, 155.2, 142.9, 134.9, 131.1 (q, *J*= 32.9 Hz), 129.0, 128.9, 128.6 (q, *J*= 3.7 Hz), 123,5 (q, *J* = 272.6), 125.6 (q, *J* = 3.9 Hz), 122.7, 114.5, 114.3, 109.1, 86.8, 84.1, 76.9, 58.0; MS (CI ion source): *m/z* (%) = 271 (65, $[M + H]^+$), 343 (47), 183(100); HRMS: *m/z* $[M + Na]^+$ calcd for $C_{19}H_{10}F_3IO_3Na$: 492.9519; found: 492.9519.

4. CHARACTERIZATION DATA OF 2b – l, 3b – l and 5a - e



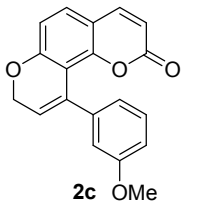
2b



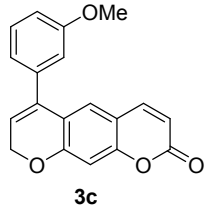
3b

Overall yield (catalyst A): 99% (91.6 mg); **2b/3b** = 15/85
Overall yield (catalyst B): 99% (91.2 mg)**; 2b/3b** = 77/23
2b: pale yellow solid; mp: 162-164 °C; IR (KBr): 3054, 1725, 1630, 1265 cm^{-1}; ^1H NMR (400.13 MHz) ($CDCl_3$): δ = 7.60 (d, *J* = 9.5 Hz, 1 H), 7.33 (d, *J* = 8.4 Hz, 1 H), 7.19 (d, *J* = 8.7 Hz, 2 H), 6.96 (d, *J* = 8.4 Hz, 1 H), 6.91 (d, *J* = 8.7 Hz, 2 H), 6.16 (d, *J* = 9.5 Hz, 1 H), 5.92 (t, *J* = 4.6 Hz, 1 H), 4.77 (d, *J* = 4.6 Hz, 2 H), 3.86 (s, 3 H); ^{13}C NMR (100.6 MHz) ($CDCl_3$): δ = 159.6, 159.4, 159.3, 151.0, 143.5, 134.7, 131.6, 128.5, 128.3, 121.0, 113.9, 113.5, 113.2 (2C), 112.5, 65.3, 55.3; MS (EI ion source): *m/z* (%) = 306 (7 $[M^+]$), 281 (13), 207 (25), 73 (100); HRMS: *m/z* $[M + Na]^+$ calcd for $C_{19}H_{14}O_4Na$: 329.0784; found: 329.0787.

3b: pale yellow solid; mp: 177-179 °C; IR (KBr): 2924, 1726, 1622, 1248, 1131 cm^{-1}; ^1H NMR (400.13 MHz) ($CDCl_3$): δ = 7.41 (d, *J* = 9.5 Hz, 1 H), 7.20-7.16 (m, 2 H), 6.99 (s, 1 H), 6.89 (d, *J* = 8.7 Hz, 2 H), 6.74 (s, 1 H), 6.13 (d, *J* = 9.5 Hz, 1 H), 5.69 (t, *J* = 3.8 Hz, 1 H), 4.89 (d, *J* = 3.8 Hz, 2 H), 3.79 (s, 3 H); ^{13}C NMR (100.6 MHz) ($CDCl_3$): δ = 161.0, 159.6, 158.4, 155.3, 143.4, 135.2, 129.9, 129.7, 124.6, 121.0, 119.6, 114.1, 113.4, 112.9, 104.4, 66.1, 55.4; MS (EI ion source): *m/z* (%) = 306 (45 $[M^+]$), 281 (12), 207 (29), 73 (100); HRMS: *m/z* $[M + Na]^+$ calcd for $C_{19}H_{14}O_4Na$: 329.0784; found: 329.0787.



2c

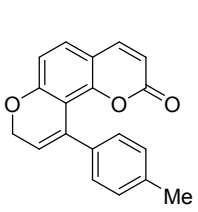


3c

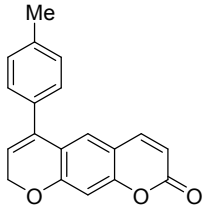
Overall yield (catalyst A): 99% (91.4 mg); **2c/3c** = 80/20
Overall yield (catalyst B): 90% (82.8 mg)**; 2c/3c** = 92/8
2c: white solid; mp: 133-135°C; IR (KBr): 2923, 1728, 1594, 1228, 1116 cm^{-1}; ^1H NMR (400.13 MHz) ($CDCl_3$): δ = 7.49 (d, *J* = 9.6 Hz, 1 H), 7.24 (d, *J* = 8.5 Hz, 1 H), 7.21 - 7.17 (m, 1 H), 6.86 (d, *J* =8.5 Hz, 1 H), 6.83 (dd, J_1 = 8.4 Hz, J_2 = 2.0

HZ, 1 H) 6.76-6.73 (m, 2 H), 6.06 (d, *J* =9.6 Hz, 1 H), 5.88 (t, *J* = 4.5 Hz, 1 H), 4.70 (d, *J* = 4.5 Hz, 2 H), 3.72 (s, 3 H); ^{13}C NMR (100.6 MHz) ($CDCl_3$): δ = 159.5, 159.3, 159.2, 150.9, 143.5, 140.6, 134.9, 129.0, 128.6, 121.9, 119.9, 113.9, 113.5, 113.4, 113.3, 112.9, 112.3, 65.3, 55.3; MS (EI ion source): *m/z* (%) = 306 (100 [M^+]), 291 (21), 275 (30), 207 (24), 63 (51); HRMS: *m/z* [M + Na]$^+$ calcd for $C_{19}H_{14}O_4Na$: 329.0784; found: 329.0787.

3c: white solid; mp: 171-172°C; IR (KBr): 2933, 1728, 1593, 1482, 1113 cm^{-1}; ^{1}H NMR (400.13 MHz) ($CDCl_3$): δ = 7.41 (d, *J* = 9.5 Hz, 1 H), 7.28 (t, *J* = 7.9 Hz, 1 H), 6.99 (s, 1 H), 6.90 (dd, J_1 = 8.0 Hz, J_2 = 2.3 HZ, 1 H), 6.84 (d, *J* = 7.6 Hz, 1 H), 6.80-6.79 (m, 1 H), 6.75 (s, 1 H), 6.13 (d, *J* = 9.5 Hz, 1 H), 5.74 (t, *J* = 3.8 Hz, 1 H), 4.91 (d, *J* = 3.8 Hz, 2 H), 3.77 (s, 3 H); ^{13}C NMR (100.6 MHz) ($CDCl_3$): δ= 160.9, 159.8, 158.2, 155.3, 143.4, 138.9, 135.5, 129.7, 124.7, 120.9, 120.6, 120.2, 114.3, 113.5, 113.4, 113.0, 104.4, 66.1, 55.3; MS (EI ion source): *m/z* (%) = 306 (100 [M^+]), 281 (24), 275 (34), 207 (59), 73 (85); HRMS: *m/z* [M + Na]$^+$ calcd for $C_{19}H_{14}O_4Na$: 329.0784; found: 329.0787.



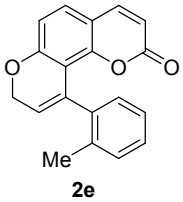
2d



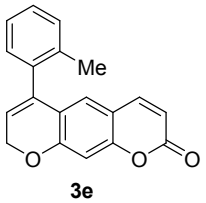
3d

Overall yield (catalyst A): 99% (86.5 mg); **2d/3d** = 43/57
Overall yield (catalyst B): 93% (80.7 mg); **2d/3d** = 86/14
2d: white solid; mp: 130-132°C; IR (KBr): 2913, 1727, 1594, 1406, 1229, 1113 cm^{-1}; mp: 130-132 °C; ^{1}H NMR (400.13 MHz) ($CDCl_3$): δ = 7.49 (d, *J* = 9.5 Hz, 1 H), 7.23 (d, *J* 8.4 = Hz, 1 H), 7.09-7.04 (m, 4 H), 6.85 (d, *J* = 8.4 Hz, 1 H), 6.05 (d, *J* = 9.5 Hz, 1 H), 5.84 (t, *J* = 4.5 Hz, 1 H), 4.68 (d, J = 4.5 Hz, 2 H), 2.31 (s, 3 H); ^{13}C NMR (100.6 MHz) ($CDCl_3$): δ = 159.6, 159.3, 150.9, 143.6, 137.3, 136.3, 135.0, 128.8, 128.5, 127.0, 121.5, 113.9, 113.5, 113.2, 112.4, 65.3, 21.3; MS (EI ion source): *m/z* (%) = 290 (100, [M^+]), 275 (58), 247 (20), 207 (9), 63 (91); HRMS: *m/z* [M + Na]$^+$ calcd for $C_{19}H_{14}O_3Na$: 313.0835; found: 313.0839.

3d: off-white solid; mp: 139-141°C; IR (KBr): 2924, 1727, 1623, 1591, 1149, 1131 cm^{-1}; mp: 139-141 °C; ^{1}H NMR (400.13 MHz) ($CDCl_3$): δ = 7.40 (d, *J* = 9.5 Hz, 1 H), 7.19-7.14 (m, 4 H), 6.99 (s, 1 H), 6.74 (s, 1 H), 6.12 (d, *J* = 9.5 Hz, 1 H), 5.71 (t, *J* = 3.8 Hz, 1 H), 4.90 (d, *J* = 3.8 Hz, 2 H), 2.35 (s, 3 H); ^{13}C NMR (100.6 MHz) ($CDCl_3$): δ = 160.9, 158.3, 155.3, 143.5, 138.1, 135.5, 134.6, 129.4, 128.4, 124.6, 120.9, 119.9, 113.3, 112.9, 104.4, 66.1, 29.7, 21.3; MS (EI ion source): *m/z* (%) = 290 (37, [M^+]), 275 (21), 207 (52), 73 (100); HRMS: *m/z* [M + Na]$^+$ calcd for $C_{19}H_{14}O_3Na$: 313.0835; found: 313.0838.



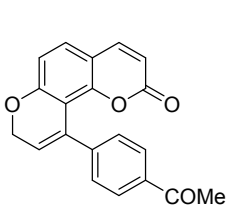
2e



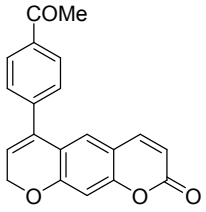
3e

Overall yield (catalyst A): 99 % (86.2 mg); **2e/3e** = 85/15
Overall yield (catalyst B): 26% (22.8 mg); **2e/3e** = 84/16
2e: pale yellow solid; mp: 136-138 °C IR (KBr): 2920, 1730, 1595, 1230, 1118 cm^{-1}; ^{1}H NMR (400.13 MHz) ($CDCl_3$): δ = 7.43 (d, *J* = 9.5 Hz, 1 H), 7.42-7.10 (m, 5 H), 6.82 (d, *J* = 8.4 Hz, 1 H), 5.99 (d, *J* = 9.5 Hz, 1 H), 5.72 (t, *J* = 4.2 Hz, 1 H), 4.85-4.72 (m, 2 H), 1.99 (s, 3 H); ^{13}C NMR (100.6 MHz) ($CDCl_3$): δ = 159.4, 158.2, 150.9, 143.4, 139.5, 135.4, 134.4, 129.6, 128.5, 128.4, 127.7, 125.7, 122.2, 113.51, 113.48, 113.2, 112.4, 65.4, 19.9; MS (EI ion source): *m/z* (%) = 290 (36 [M^+]), 281 (43), 207 (100), 73 (28); HRMS: *m/z* [M + Na]$^+$ calcd for $C_{19}H_{14}O_3Na$: 313.0835; found: 313.0837.

3e: pale yellow solid; mp: 157-158 °C IR (KBr): 2922, 1728, 1621, 1401, 1150, 1135 cm^{-1}; ^1H NMR (400.13 MHz) ($CDCl_3$): δ = 7.34 (d, *J* = 9.5 Hz, 1 H), 7.28-7.18 (m, 3 H), 7.10-7.08 (m, 1 H), 6.72 (s, 1 H), 6.53 (s, 1 H), 6.09 (d, *J* = Hz, 1 H), 5.62 (t, *J* = 3.7 Hz, 1 H), 4.98 (t, *J* = 3.7 Hz, 2 H), 2.09 (s, 3 H); ^{13}C NMR (100.6 MHz) ($CDCl_3$): δ = 161.0, 157.7, 155.4, 143.4, 136.9, 136.4, 135.0, 130.3, 129.6, 128.3, 126.2, 124.2, 120.7, 120.6, 113.3, 113.1, 104.2, 66.3, 19.7; MS (EI ion source): *m/z* (%) = 290 (5 [M^+]), 281(15), 207 (100), 77 (14); HRMS: *m/z* [M + Na]$^+$ calcd for $C_{19}H_{14}O_3Na$: 313.0835; found: 313.0837.



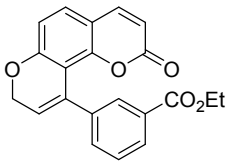
2f



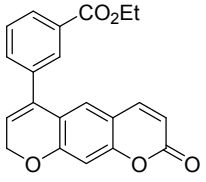
3f

Overall yield (catalyst A): 92% (87.6 mg)**; 2f/3f** = 85/15
Overall yield (catalyst B): 94% (90.0 mg)**; 2f/3f** = 85/15
2f: white solid; mp: 185-186°C; IR (KBr): 2919, 1713, 1671, 1603, 1272 cm^{-1}; ^1H NMR (400.13 MHz) ($CDCl_3$): δ = 7.86 (d, *J* = 8.3 Hz, 2 H), 7.51 (d, *J* = 9.5 Hz, 1 H), 7.28-7.25 (m, 3 H), 6.88 (d, *J* = 8.4 Hz, 1 H), 6.05 (d, *J* = 9.5 Hz, 1 H), 5.92 (t, *J* = 4.5 Hz, 1 H), 4.72 (d, *J* = 4.5 Hz, 2 H), 2.54 (s, 3 H); ^{13}C NMR (100.6 MHz) ($CDCl_3$): δ = 197.7, 159.3, 159.1, 150.7, 144.1, 143.5, 136.2, 134.2, 128.9, 128.3, 127.3, 123.3, 113.9, 113.6, 113.3, 111.7, 65.2, 26.7; MS (EI ion source): *m/z* (%) = 318 (17 [M^+]), 281 (24), 207 (62), 73 (100); HRMS: *m/z* [M + Na]$^+$ calcd for $C_{20}H_{14}O_4Na$: 341.0784; found: 341.0774.

3f: white solid; mp: 236-238°C; IR (KBr): 2922, 1714, 1672, 1595, 1118; ^1H NMR (400.13 MHz) ($CDCl_3$): 7.96 (d, *J* = 8.3 Hz, 2 H), 7.41-7.36 (m, 3 H), 6.91 (s, 1 H), 6.78 (s, 1 H), 6.15 (d, *J* = 9.4 Hz, 1 H), 5.80 (t, *J* = 3.9 Hz, 1 H), 4.90 (d, *J* = 3.9 Hz, 2 H), 2.59 (s, 3 H); δ = ^{13}C NMR (100.6 MHz) ($CDCl_3$): δ = 197.5, 160.8, 158.1, 155.5, 143.2, 142.3, 136.9, 135.0, 128.8, 128.7, 124.4, 121.2, 120.1, 113.7, 113.1, 104.7, 66.0, 26.7; MS (EI ion source): *m/z* (%) =318 (4, [M^+]), 281 (39), 207 (100), 73 (39); HRMS: *m/z* [M + Na]$^+$ calcd for $C_{20}H_{14}O_4Na$: 341.0784; found: 341.0777.



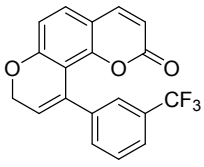
2g



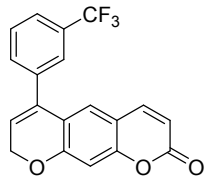
3g

Overall yield (catalyst A): **99%** (104.3 mg)**; 2g/3g** = 80/20
Overall yield (catalyst A): **95%** (99.2 mg)**; 2g/3g** = 88/12
2g: off-white solid; mp: 142-144 °C; IR (KBr): 2923, 1728, 1621, 1149, 1126 cm^{-1}; ^1H NMR (400.13 MHz) ($CDCl_3$): δ = 8.07-8.05 (m, 1 H), 7.98 (s, 1 H), 7.59 (d, *J* = 9.5 Hz, 1 H), 7.45 - 7.43 (m, 2 H), 7.35 (d, *J* = 8.5 Hz, 1 H), 6.96 (d, *J* = 8.5 Hz, 1 H), 6.14 (d, *J* = 9.5 Hz, 1 H), 6.00 (t, *J* = 4.5 Hz, 1 H), 4.82 (d, *J* = 4.5 Hz, 2 H), 4.38 (q, *J* = 7.2 Hz, 2 H), 1.40 (t, *J* = 7.2 Hz, 3 H); ^{13}C NMR (100.6 MHz) ($CDCl_3$): δ = 166.6, 159.4, 159.1, 150.8, 143.5, 139.5, 134.3, 131.7, 130.4, 128.9, 128.8, 128.3, 128.0, 122.7, 113.9, 113.6, 113.2, 111.8, 65.2, 60.9, 14.3; MS (EI ion source): *m/z* (%) = 348 (19 [M^+]), 281 (22), 207 (57), 199 (11), 73 (100); HRMS: *m/z* [M + Na]$^+$ calcd for $C_{21}H_{16}O_5Na$: 371.0890; found: 371.0878.

3g: off-white solid; mp: 179-180 °C; IR (KBr): 2978, 1726, 1623, 1400, 1265 m^{-1}; ^1H NMR (400.13 MHz) ($CDCl_3$): δ = 8.04-8.01 (m, 1 H), 7.95 (s, 1 H), 7.45-7.44 (m, 2 H), 7.40 (d, *J* = 9.5 Hz, 1 H), 6.88 (s, 1 H), 6.77 (s, 1 H), 6.14 (d, *J* = 9.5 Hz, 1 H), 5.78 (t, *J* = 3.8 Hz, 1 H), 4.93 (d, *J* = 3.8 Hz, 2 H), 4.33 (q, *J* = 7.1 Hz, 2 H), 1.33 (t, *J* = 7.1 Hz, 3 H); ^{13}C NMR (100.6 MHz) ($CDCl_3$): δ = 166.2, 160.8, 158.1, 155.5, 143.3, 137.9, 135.0, 132.8, 131.2, 129.6, 129.4, 128.8, 124.4, 121.0, 120.4, 113.5, 113.1, 104.6, 66.0, 61.3, 14.4; MS (EI ion source): *m/z* (%) = 348 (72, [M^+]), 281 (24), 207 (54), 199 (44), 73 (100); HRMS: *m/z* [M + Na]$^+$ calcd for $C_{21}H_{16}O_5Na$: 371.0890; found: 371.0880.



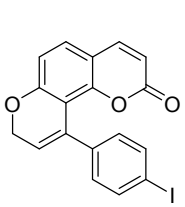
2h



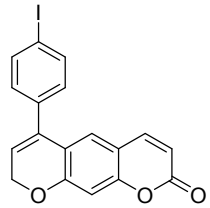
3h

Overall yield (catalyst A): 99% (102.9 mg)**; 2h/3h** = 77/23
Overall yield (catalyst B): 93% (96.3 mg)**; 2h/3h** = 94/6
2h: white solid; mp: 139-140 °C; IR (KBr): 2921, 1733, 1594, 1324, 1116 cm^{-1}; ^{1}H NMR (400.13 MHz) ($CDCl_3$): δ = 7.55 (bd, *J*= 7.5 Hz, 1 H), 7.50 (d, *J*= 9.5 Hz, 1 H), 7.43-7.35 (m, 3 H), 7.27 (d, *J* = 8.4 Hz, 1 H), 6.88 (d, *J* = 8.4 Hz, 1 H), 6.87 (d, *J* = 9.5 Hz, 1 H), 5.91 (t, *J* = 4.4 Hz, 1 H), 4.74 (d, *J* = 4.4 Hz, 2 H); ^{13}C NMR (100.6 MHz) ($CDCl_3$): δ = 159.1, 159.0, 150.7, 143.5, 139.9, 133.9, 130.6, 130.4 (q, J_{CF}= 32 Hz), 129.0, 128.5, 124.5 (q, J_{CF}= 3.7 Hz), 124.2 (q, J_{CF} = 273 Hz), 124.1 (q, J_{CF} = 3.7 Hz), 123.1, 113.9, 113.6, 113.3, 111.5, 65.2; ^{19}F NMR (376.5 MHz) ($CDCl_3$): δ = -62.5; MS (EI ion source): *m/z* (%) = 344 (11 [M^+]), 281 (18), 207 (52), 73 (100); HRMS: *m/z* [M + Na]$^+$ calcd for $C_{19}H_{11}F_3O_3Na$: 367.0553; found: 367.0552.

3h: white solid; mp: 139-141 °C; IR (KBr): 2920, 1728, 1623, 1325, 1151, 1131 cm^{-1}; ^{1}H NMR (400.13 MHz) ($CDCl_3$): δ = 7.61 (bd, *J*= 7.6 Hz, 1 H), 7.54-7.44 (m, 3 H); 7.41 (d, *J* = 9.5 Hz, 1 H), 6.87 (s, 1 H), 6.77 (s, 1 H), 6.15 (d, *J* = 9.5 Hz, 1 H), 5.79 (t, *J* = 3.8 Hz, 1 H), 4.93 (d, *J* = 3.8 Hz, 2 H); ^{13}C NMR (100.6 MHz) ($CDCl_3$): δ = 160.7, 158.1, 155.5, 143.2, 138.4, 134.7, 131.8, 131.3 (q, J_{CF} = 32 Hz), 129.2, 125.3, (q, J_{CF} = 3.3 Hz), 125.1 (q, J_{CF} = 3.3 Hz), 124.2, 123.9 (q, J_{CF} = 273 Hz), 121.4, 120.1, 113.7, 113.1, 104.7, 65.9; ^{19}F NMR (376.5 MHz) ($CDCl_3$): δ = -62.6; MS (EI ion source): *m/z* (%) = 344 (58, [M^+]), 199 (88), 69 (100); HRMS: *m/z* [M + Na]$^+$ calcd for $C_{19}H_{11}F_3O_3Na$: 367.0553; found: 367.0552.



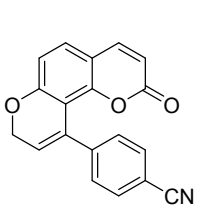
2i



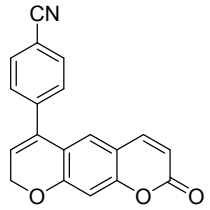
3i

Overall yield (catalyst A): 67% (81.0 mg); **2i/3i** = 65/35
Overall yield (catalyst B): 99% (120.2 mg); **2i/3i** = 90/10
2i: white solid; mp: 222-224 °C; IR (KBr): 2921, 1712, 1597, 1385, 1035 cm^{-1}; ^{1}H NMR (400.13 MHz) ($CDCl_3$): δ = 7.60 (d, *J* = 8.4 Hz, 2 H), 7.51 (d, *J* = 9.5 Hz, 1 H), 7.26 (d, *J* = 8.4 Hz, 1 H), 6.90 (d, *J* = 8.4 Hz, 2 H), 6.87 (d, *J* = 8.4 Hz, 1 H), 6.08 (d, *J*= 9.5 Hz, 1 H), 5.86 (t, *J* = 4.5 Hz, 1 H), 4.70 (d, *J* = 4.5 Hz, 2 H); ^{13}C NMR (100.6 MHz) ($CDCl_3$): δ = 159.4, 159.2, 150.8, 143.5, 138.8, 137.2, 134.2, 129.0, 128.8, 122.4, 113.9, 113.6, 113.3, 111.8, 93.2, 65.2; MS (EI ion source): *m/z* (%) = 402 (10 [M^+]), 281 (40), 207 (100), 73 (36); HRMS: *m/z* [M + Na]$^+$ calcd for $C_{18}H_{11}IO_3Na$: 424.9645; found: 424.9648.

3i: white solid; mp: 188-190 °C; IR (KBr): 2923, 1724, 1622, 1398, 1150, 1131 cm^{-1}; ^{1}H NMR (400.13 MHz) ($CDCl_3$): δ = 7.70 (d, *J* = 8.3 Hz, 2 H), 7.41 (d, *J*= 9.5 Hz, 1 H), 7.01 (d, *J* = 8.3 Hz, 2 H), 6.92 (s, 1 H), 6.75 (s, 1 H), 6.15 (d, *J* = 9.5 Hz, 1 H), 5.74 (t, *J* = 3.8 Hz, 1 H), 4.90 (d, *J* = 3.8 Hz, 2 H); ^{13}C NMR (100.6 MHz) ($CDCl_3$): δ = 160.8, 158.1, 155.4, 143.3, 137.9, 137.1, 134.9, 130.4, 124.4, 120.6, 120.2, 113.6, 113.0, 104.6, 93.9, 65.9; MS (EI ion source): *m/z* (%) = 402 (15, [M^+]), 281 (21), 207 (47), 73 (100); HRMS: *m/z* [M + Na]$^+$ calcd for $C_{18}H_{11}IO_3Na$: 424.9645; found: 424.9649.



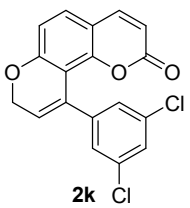
2j



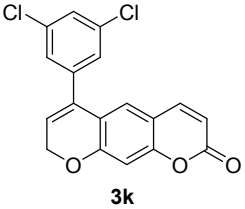
2j'

Overall yield (catalyst A): 92% (83.3 mg)**; 2j/3j** = 85/15
Overall yield (catalyst B): 15% (13.7 mg)**; 2j/3j** = 85/15
2j: off-white solid; mp: 220-221 °C; IR (KBr): 3051, 2918, 2224, 1720, 1595, 1507, 1482 cm^{-1}; ^1H NMR (400.13 MHz) ($CDCl_3$): δ = 7.56 (d, *J* = 8.2 Hz, 2 H), 7.51 (d, *J* = 9.5 Hz, 1 H), 7.28-7.26 (m, 3 H), 6.87 (d, *J* = 8.5 Hz, 1 H), 6.06 (d, *J* = 9.5 Hz, 1 H), 5.90 (t, *J* = 4.4 Hz, 1 H), 4.73 (d, *J* = 4.4 Hz, 2 H); ^{13}C NMR (100.6 MHz) ($CDCl_3$): δ = 159.2, 159.0, 150.6, 144.0, 143.5, 133.7, 132.0, 129.1, 127.9, 123.8, 119.0, 113.9, 113.7, 113.4, 111.4, 111.2, 65.1; MS (EI ion source): *m/z* (%) = 301 (59 [M^+]), 281 (20), 207 (44), 199 (27), 73 (100); HRMS: *m/z* [M + Na]$^+$ calcd for $C_{19}H_{11}NO_3Na$: 324.0631; found: 324.0634.

3j: pale yellow solid; mp: 219-221 °C; IR (KBr): 2922, 2227, 1747, 1621, 1398 cm^{-1}; ^1H NMR (400.13 MHz) ($CDCl_3$): δ = 7.67 (d, *J* = 8.3 Hz, 2 H), 7.42-7.38 (m, 3 H), 6.86 (s, 1 H), 6.78 (s, 1 H), 6.16 (d, *J* = 9.5 Hz, 1 H), 5.81 (t, *J* = 3.8 Hz, 1 H), 4.93 (d, *J* = 3.8 Hz, 2 H); ^{13}C NMR (100.6 MHz) ($CDCl_3$): δ = 160.6, 158.1, 155.6, 143.1, 142.3, 134.6, 132.6, 129.3, 124.2, 121.9, 119.7, 118.5, 113.9, 113.1, 112.3, 104.8, 65.9; MS (EI ion source): *m/z* (%) = 301 (12 [M^+]), 281 (21), 207 (55), 73 (100); HRMS: *m/z* [M + H]$^+$ calcd for $C_{19}H_{12}NO_3$: 302.0812; found: 302.0816.



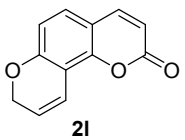
2k



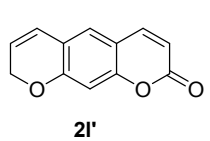
3k

Overall yield (catalyst A): 97% (99.7 mg); **2k/3k** = 86/14
Overall yield (catalyst B): **99%** (102.0 mg)**; 2k/3k** = 86/14
2k:white solid; mp: 191-193 °C; IR (KBr): 2923, 1722, 1615, 1596, 1122 cm^{-1}; ^1H NMR (400.13 MHz) ($CDCl_3$): δ = 7.52 (d, *J* = 9.5 Hz, 1 H), 7.29-7.27 (m, 2 H), 7.07-7.06 (m, 2 H), 6.87 (d, *J* = 8.4 Hz, 1 H), 6.10 (d, *J*= 9.5 Hz, 1 H), 5.89 (t, *J* = 4.4 Hz, 1 H), 4.72 (d, *J* = 4.4 Hz, 2 H); ^{13}C NMR (100.6 MHz) ($CDCl_3$): δ = 159.2, 159.0, 150.6, 143.5, 142.1, 134.5, 133.0, 129.1, 127.8, 125.8, 123.5, 114.0, 113.7, 113.4, 111.2, 65.1; MS (EI ion source): *m/z* (%) = 346 (38, [M+2]$^+$), 344 (59, [M^+]), 309 (53), 281 (33), 207 (44), 199 (46), 73 (100); HRMS: *m/z* [M + H]$^+$ calcd for $C_{18}H_{11}Cl_2O_3$: 345.0080; found: 345.0079; [(M + 2)+H]$^+$ calcd for $C_{18}H_{11}Cl_2O_3$: 347.0050; found: 347.0049.

3k: pale yellow solid; mp: 187-189 °C; IR (KBr): 3055, 2924, 1729, 1623, 1265 cm^{-1}; ^1H NMR (400.13 MHz) ($CDCl_3$): δ = 7.46 (d, *J* = 9.5 Hz, 1 H), 7.34 (bs, 1 H), 7.16-7.56 (m, 2 H), 6.89 (s, 1 H), 6.76 (s, 1 H), 6.17 (d, *J* = 9.5 Hz, 1 H), 5.77 (t, *J* = 3.7 Hz, 1 H), 4.90 (d, *J* = 3.7 Hz, 2 H); ^{13}C NMR (100.6 MHz) ($CDCl_3$): δ = 160.7, 157.9, 155.6, 143.3, 104.5, 135.4, 133.7, 128.4, 127.0, 124.2, 121.7, 119.7, 113.8, 113.2, 104.7, 65.9; MS (EI ion source): *m/z* (%) = 346 (50, [M+2]$^+$), 344 (71, [M^+]) 281 (28), 207 (52), 199 (92), 73 (100); HRMS: *m/z* [M + H]$^+$ calcd for $C_{18}H_{11}Cl_2O_3$: 345.0080; found: 345.0086; [(M + 2)+H]$^+$ calcd for $C_{18}H_{11}Cl_2O_3$: 347.0050; found: 347.0057.



2l



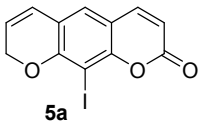
2l'

Overall yield (catalyst A): 99% (59.6 mg)**; 2l/3l** = 63/37

Overall yield (catalyst A): 65% (39.0 mg)**; 2l/3l** = 65/35

2l: white solid; mp: 170-173 °C IR (KBr): 2919, 1714, 1643, 1601, 1242, 1121 cm^{-1}; ^1H NMR (400.13 MHz) ($CDCl_3$): δ = 7.51 (d, *J* = 9.5 Hz, 1 H), 7.12 (d, *J* = 8.5 Hz, 1 H), 6.87 (d, *J* = 10.2 Hz, 1 H), 6.62 (d, *J* = 8.5 Hz, 1 H), 6.15 (d, *J* = 9.5 Hz, 1 H), 5.90 (dt, J_1= 10.2 Hz, J_2= 3.4 Hz, 1H), 4.85 (bs, 2 H); ^{13}C NMR (100.6 MHz) ($CDCl_3$): δ = 160.9, 157.2, 149.9, 143.8, 127.9, 121.9, 117.4, 113.04, 112.96, 112.94, 110.3, 66.1; MS (EI ion source): *m/z* (%) = 200 (56 [M^+]), 281 (31), 207 (82), 171 (59), 115 (48), 77 (100); HRMS: *m/z* [M + H]$^+$ calcd for $C_{12}H_9O_3$: 201.0546; found: 201.0546.

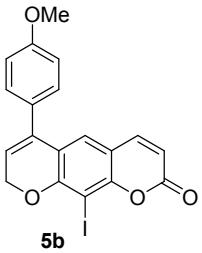
3l: white solid; mp: 179-181 °C; IR (KBr): 2922, 1715, 1627, 1401, 1271, 1145 cm^{-1}; ^1H NMR (400.13 MHz) ($CDCl_3$): δ = 7.48 (d, *J* = 9.5 Hz, 1 H), 6.91 (s, 1 H), 6.59 (s, 1 H), 6.33 (d, *J* = 10.0 Hz, 1 H), 6.13 (d, J = 9.5 Hz, 1 H), 5.73 (dt, J_1 = 10.0 Hz, J_2 = 3.3 Hz, 1 H), 4.86-4.83 (m, 2 H); ^{13}C NMR (100.6 MHz) ($CDCl_3$): δ = 161.0, 157.6, 155.4, 143.3, 125.0, 122.9, 122.3, 119.2, 113.3, 113.1, 103.9, 66.2; MS (EI ion source): *m/z* (%) =200 (100, [M^+]), 171 (71), 115 (59); HRMS: *m/z* [M + Na]$^+$ calcd for $C_{12}H_8O_3Na$: 223.0366; found: 223.0366.



5a

Yield: 90% (87.6 mg);

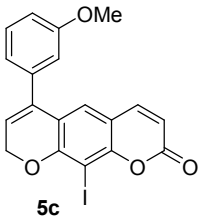
5a: pale yellow solid; mp: 161-163 °C; IR (KBr): 2916, 1724, 1609, 1272, 1144 cm^{-1}; ^1H NMR (400.13 MHz) ($CDCl_3$) δ = 7.43 (d, *J* = 9.4 Hz, 1 H), 6.92 (s, 1 H), 6.31 (dt, J_1 = 9.8 Hz, J_2 = 1.8 Hz, 1 H), 6.17 (d, *J* = 9.4 Hz, 1 H), 5.75 (dt, J_1 = 9.8 Hz, J_2 = 3.2 Hz, 1 H), 5.01 (dd, J_1 = 3.2 Hz, J_2 = 1.8 Hz, 2 H); ^{13}C NMR (100.6 MHz) ($CDCl_3$): δ = 160.4, 157.3, 154.8, 143.0, 125.1, 122.7, 122.4, 119.1, 113.9, 113.7, 74.5, 67.4; MS (NCI ion source): *m/z* (%) = 326(100 [M^-]); HRMS: *m/z* [M + Na]$^+$ calcd for $C_{12}H7IO_3Na$: 348.9332; found: 348.9327.



5b

Yield: 98% (127.2 mg);

5b: white solid; mp: 178-179 °C IR (KBr): 3060, 2925, 1732, 1598, 1270, 1116 cm^{-1}; ^1H NMR (400.13 MHz) ($CDCl_3$): δ = 7.36 (d, *J* = 9.5 Hz, 1 H), 7.19-7.16 (m, 2 H), 6.98 (s, 1 H), 6.91-6.88 (m, 2 H), 6.15 (d, *J* = 9.5 Hz, 1 H), 5.72 (t, *J* = 3.8 Hz, 1 H), 5.03 (d, *J* = 3.8 Hz, 2 H), 3.79 (s, 3 H); ^{13}C NMR (100.6 MHz) ($CDCl_3$): δ = 160.4, 159.7, 158.0, 154.6, 143.3, 135.1, 129.7, 129.4, 129.2, 124.8, 121.1, 119.7, 114.2, 113.9, 113.5, 67.1, 55.4; MS (NCI ion source): *m/z* (%) = 432 (100 [M^-]); HRMS: *m/z* [M + Na]$^+$ calcd for $C_{19}H_{13}IO_4Na$: 454.9751; found: 454.9748.

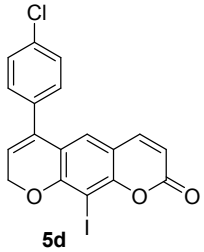


5c

Yield: 99% (128.9 mg);

5c: pale yellow solid; mp: 202-204 °C; IR (KBr): 3054, 2918, 1729, 1608, 1384, 1238 cm^{-1}; ^1H NMR (400.13 MHz) ($CDCl_3$): δ = 7.35 (d, *J* = 9.4 Hz, 1 H) 7.28 (t, *J* = 8.0 Hz, 1 H), 6.9 (s, 1 H) 6.88 (dd, J_1 = 8.0 Hz, J_2 = 1.9 Hz, 1 H) 6.82 (d, *J* =

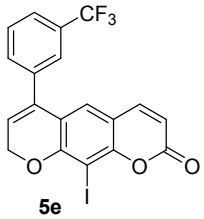
7.4 Hz, 1 H), 6.78 (s, 1 H), 6.14 (d, *J* = 9.4 Hz, 1 H), 5.76 (t, *J* = 3.4 Hz, 1 H) 5.04 (d, *J* = 3.6 Hz, 2 H), 3.76 (s, 3 H); ^{13}C NMR (100.6 MHz) ($CDCl_3$): δ = 160.4, 159.8, 157.8, 154.7, 143.3, 138.5, 135.4, 129.8, 124.8 120.9, 120.6, 120.4, 114.4, 113.9, 113.7, 113.6, 74.9, 67.0, 55.4; MS (NCI ion source): *m/z* (%) = 432 (100 [M^-]); HRMS: *m/z* [M + Na]$^+$ calcd for $C_{19}H_{13}IO_4Na$: 454.9751; found: 454.9752.



5d

Yield: 96% (125.5 mg)**;**

5d: pale yellow solid; mp: 213-215 °C; IR (KBr): 3030, 2923, 1727, 1610, 1233, 1134 cm^{-1}; ^{1}H NMR (400.13 MHz) ($CDCl_3$): δ = 7.36-7.34 (m, 3 H), 7.20-7.18 (m, 2 H), 6.90 (s, 1 H), 6.17 (d, *J* = 9.4 Hz, 1 H), 5.76 (t, *J* = 3.8 Hz, 1 H), 5.04 (d, *J* = 3.8 Hz, 2 H); ^{13}C NMR (100.6 MHz) ($CDCl_3$): δ = 160.2, 157.8, 154.8, 143.1, 135.6, 134.6, 134.4, 129.9, 129.1, 124.5, 120.8, 120.4, 114.1, 113.6, 75.1, 66.9; MS (NCI ion source): *m/z* (%) = 436 (100 [M^-]); HRMS: *m/z* [M + Na]$^+$ calcd for $C_{18}H_{10}ClIO_3Na$: 458.9255; found: 458.9258; [(M + 2) + Na]$^+$ calcd for $C_{18}H_{10}ClIO_3Na$: 460.9227; found: 460.9228.



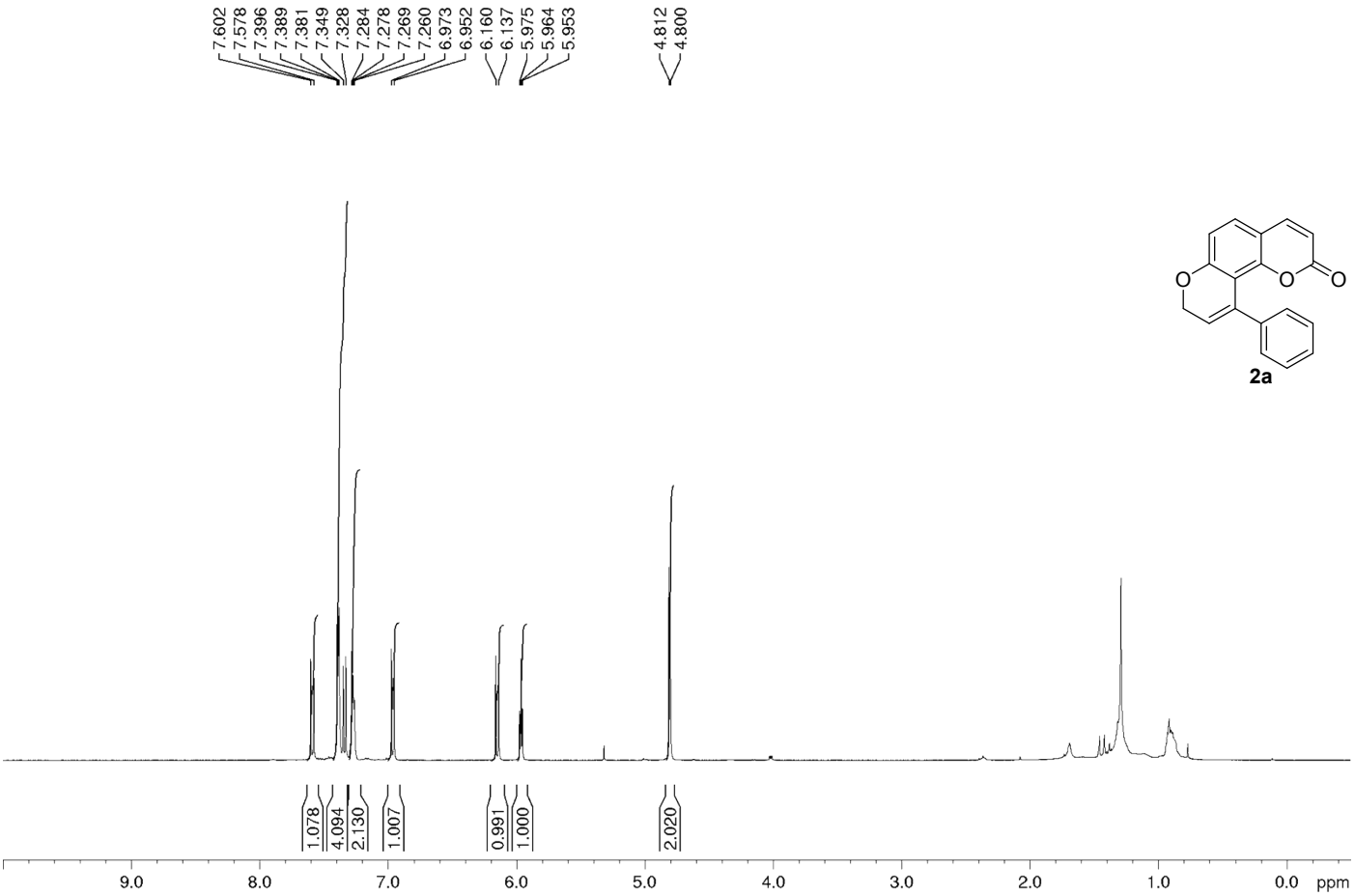
5e

Yield: 98% (138.4 mg)**;**

5e: white solid; mp: 202-204 °C; IR (KBr): 2921, 1730, 1611, 1327, 1134 cm^{-1}; ^{1}H NMR (400.13 MHz) ($CDCl_3$): δ =7.62 (d, *J* = 7.9 Hz, 1 H) 7.53 (s, 1 H), 7.50 (d, *J* = 7.7 Hz,1 H) 7.44 (d, *J* = 7.9 Hz, 1 H) 7.35 (d, *J* = 9.5 Hz, 1 H) 6.85 (s, 1 H) 6.17 (d, *J* = 9.5 Hz, 1 H) 5.82 (t, *J* = 3.8 Hz, 1 H) 5.07 (d, *J* = 3.8 Hz, 2 H); ^{13}C NMR (100.6 MHz) ($CDCl_3$): δ = 160.2, 157.7, 154.9, 143.1, 138.0, 134.6, 131.9, 131.4 (q, J_{CF} = 32.5 Hz), 129.3, 125.4 (q, J_{CF} = 3.7 Hz), 125.3 (q, J_{CF} = 3.7 Hz), 124.4, 122.5, 121.6, 120.1, 114.2, 113.7, 75.3, 66.9; MS (NCI ion source): *m/z* (%) = 470 (100 [M^-]); HRMS: *m/z* [M + Na]$^+$ calcd for $C_{19}H_{10}F_3IO_3Na$: 492.9519; found: 492.9520.

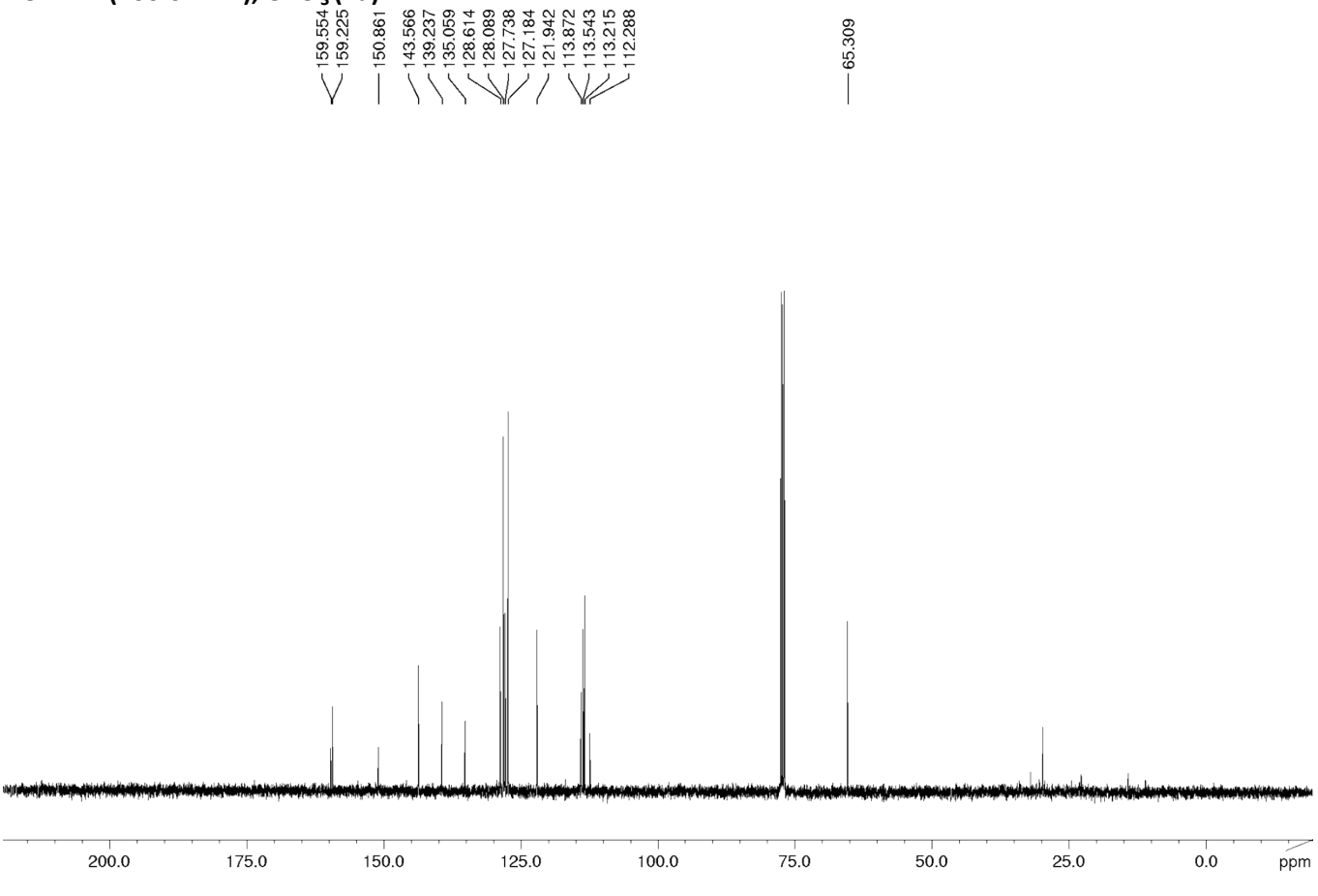
^{1}H, ^{13}C ^{19}F NMR SPECTRA OF COMPOUNDS 2a - l, 3a - l, 5a - e

^{1}H NMR (400.13 MHz), $CDCl_3$ (2a)

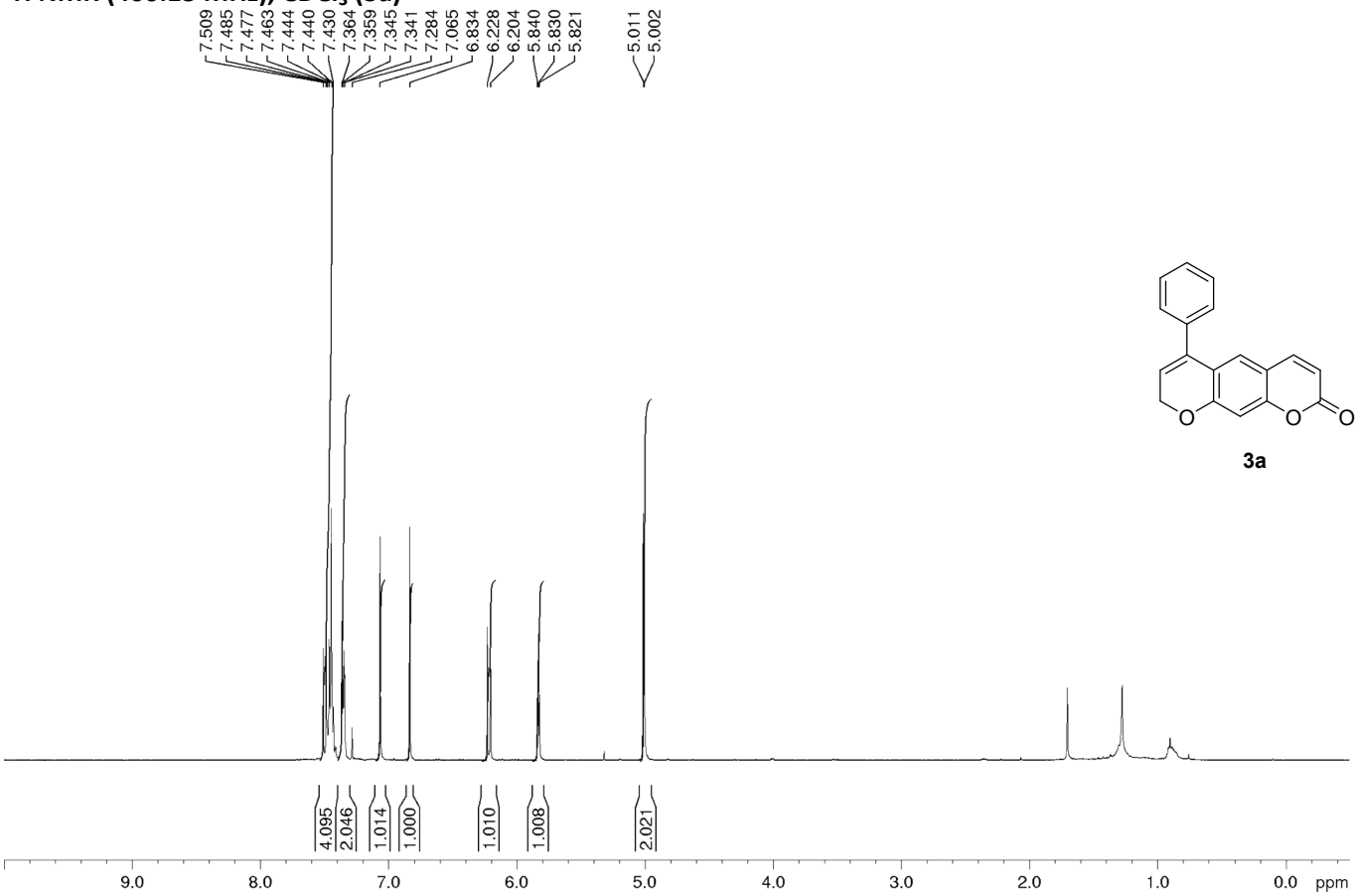


2a

^{13}C NMR (100.6 MHz), $CDCl_3$ (2a)

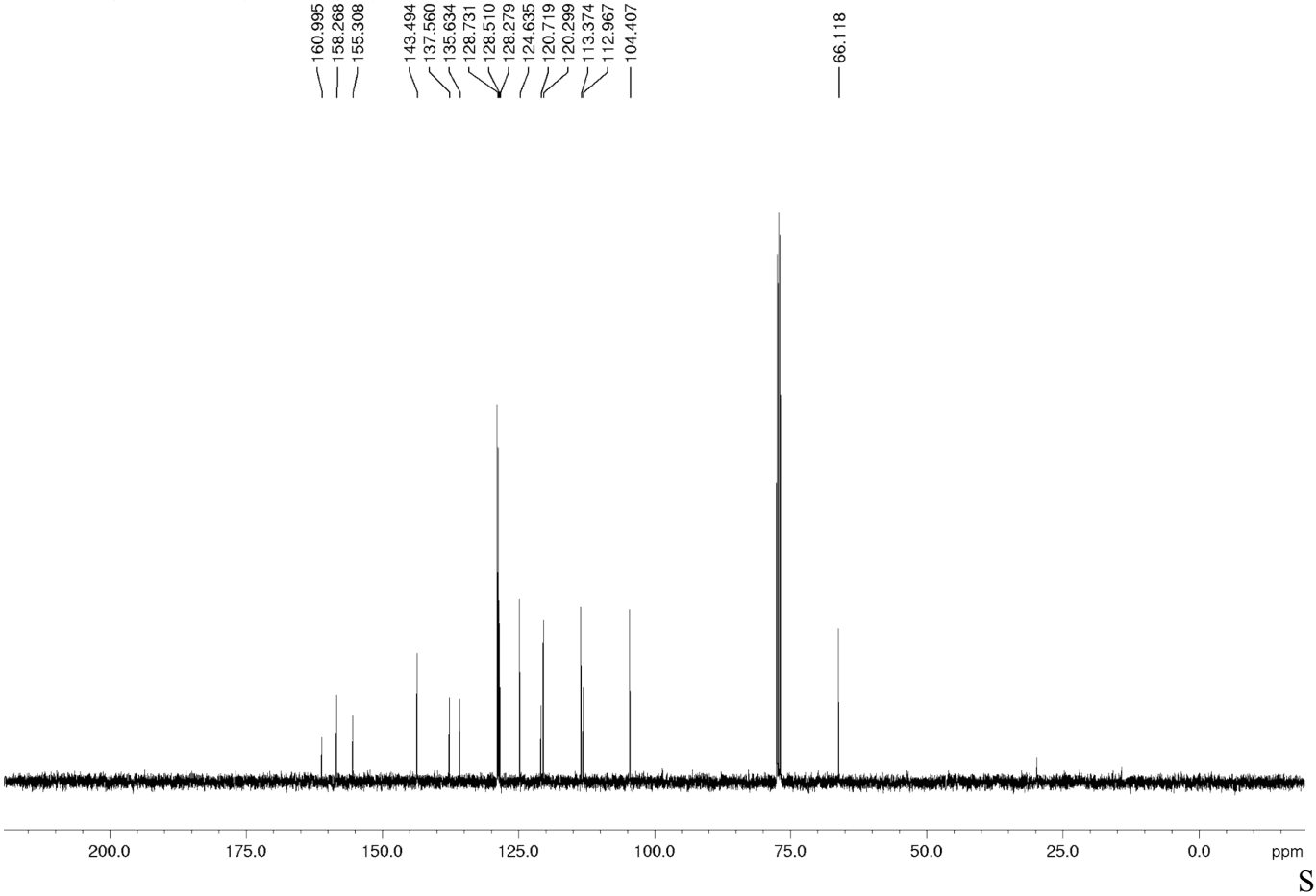


^{1}H NMR (400.13 MHz), $CDCl_3$ (3a)

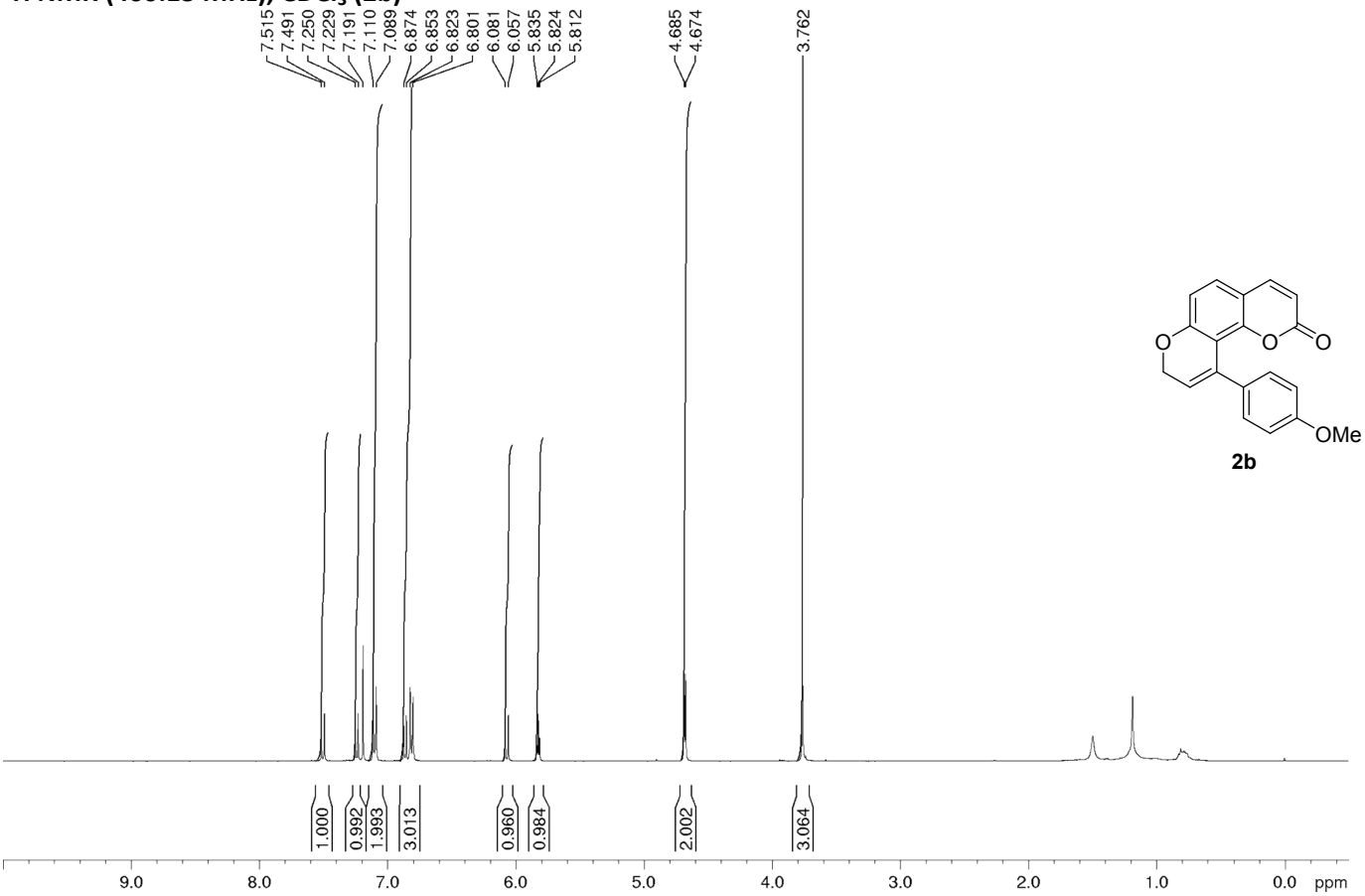


3a

^{13}C NMR (100.6 MHz), $CDCl_3$ (3a)

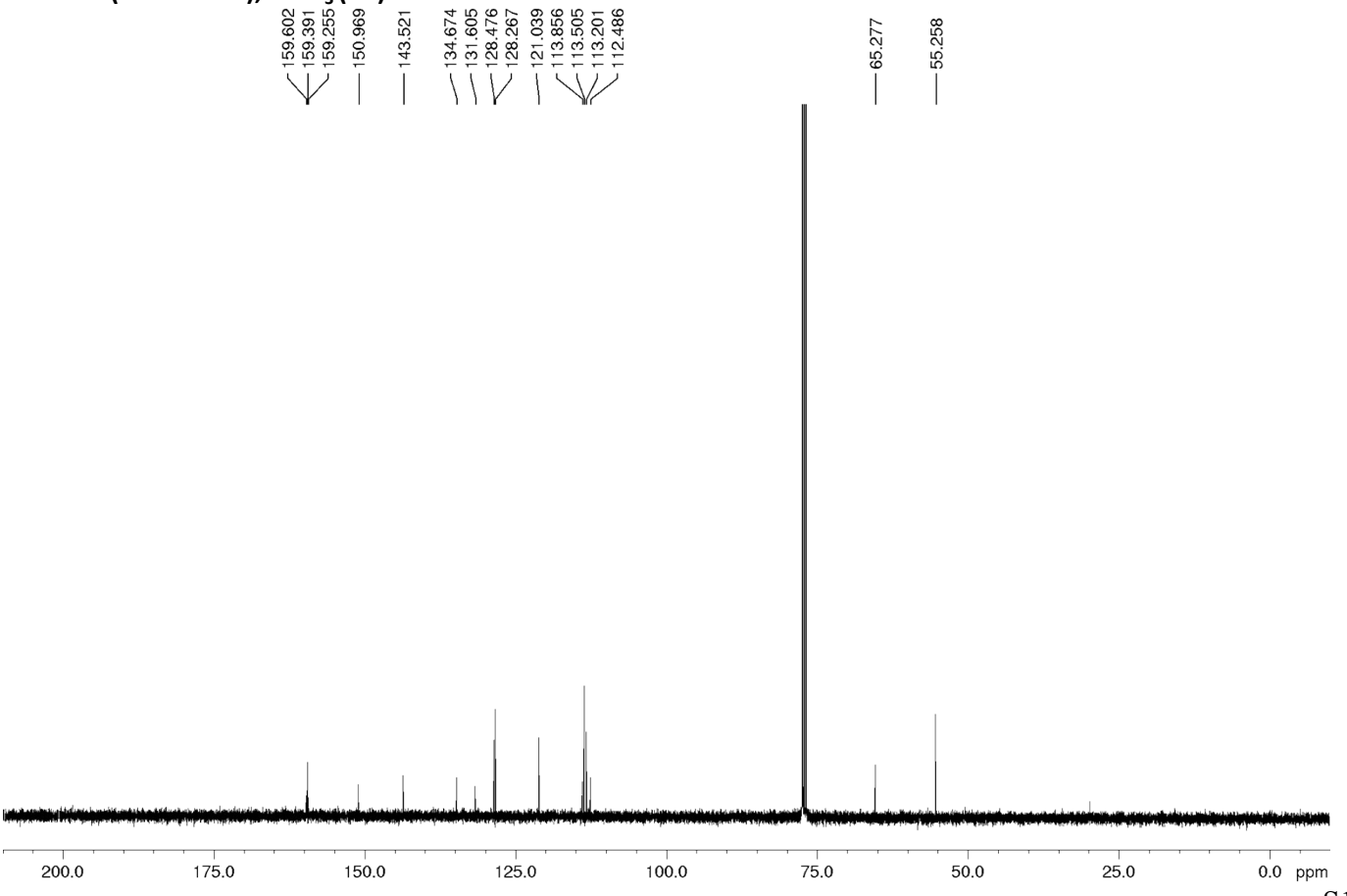


^{1}H NMR (400.13 MHz), $CDCl_3$ (2b)

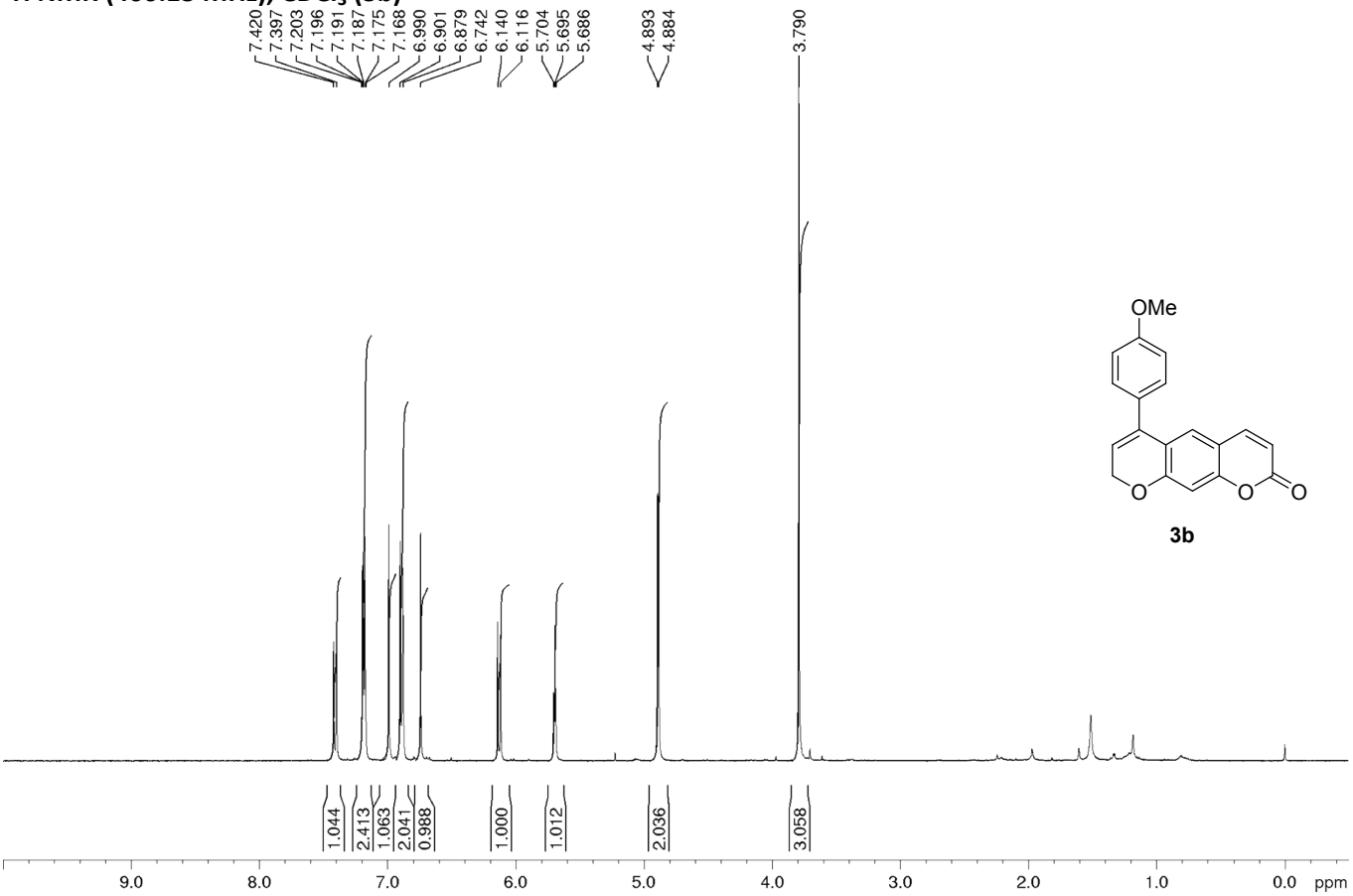


2b

^{13}C NMR (100.6 MHz), $CDCl_3$ (2b)

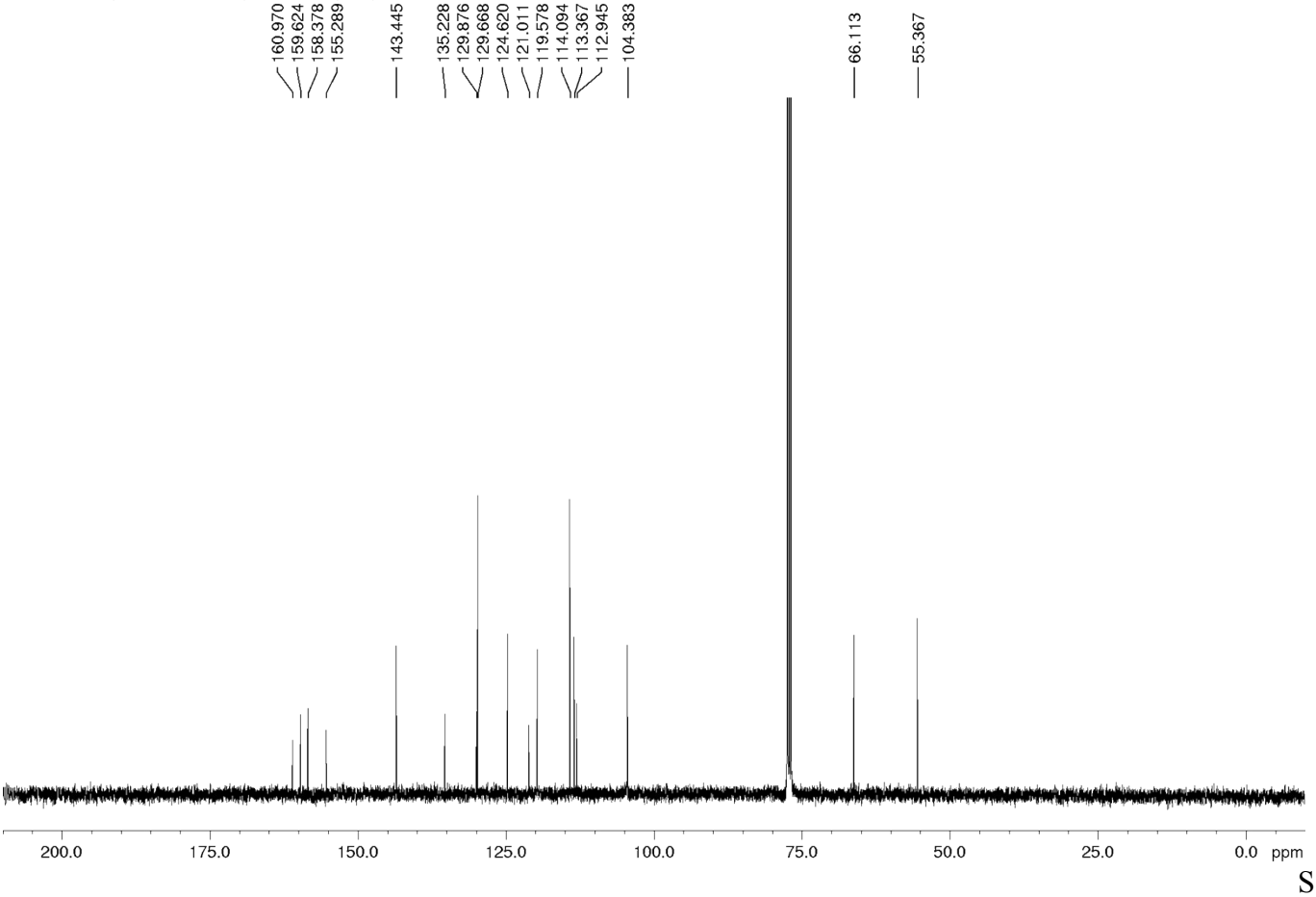


^{1}H NMR (400.13 MHz), $CDCl_3$ (3b)

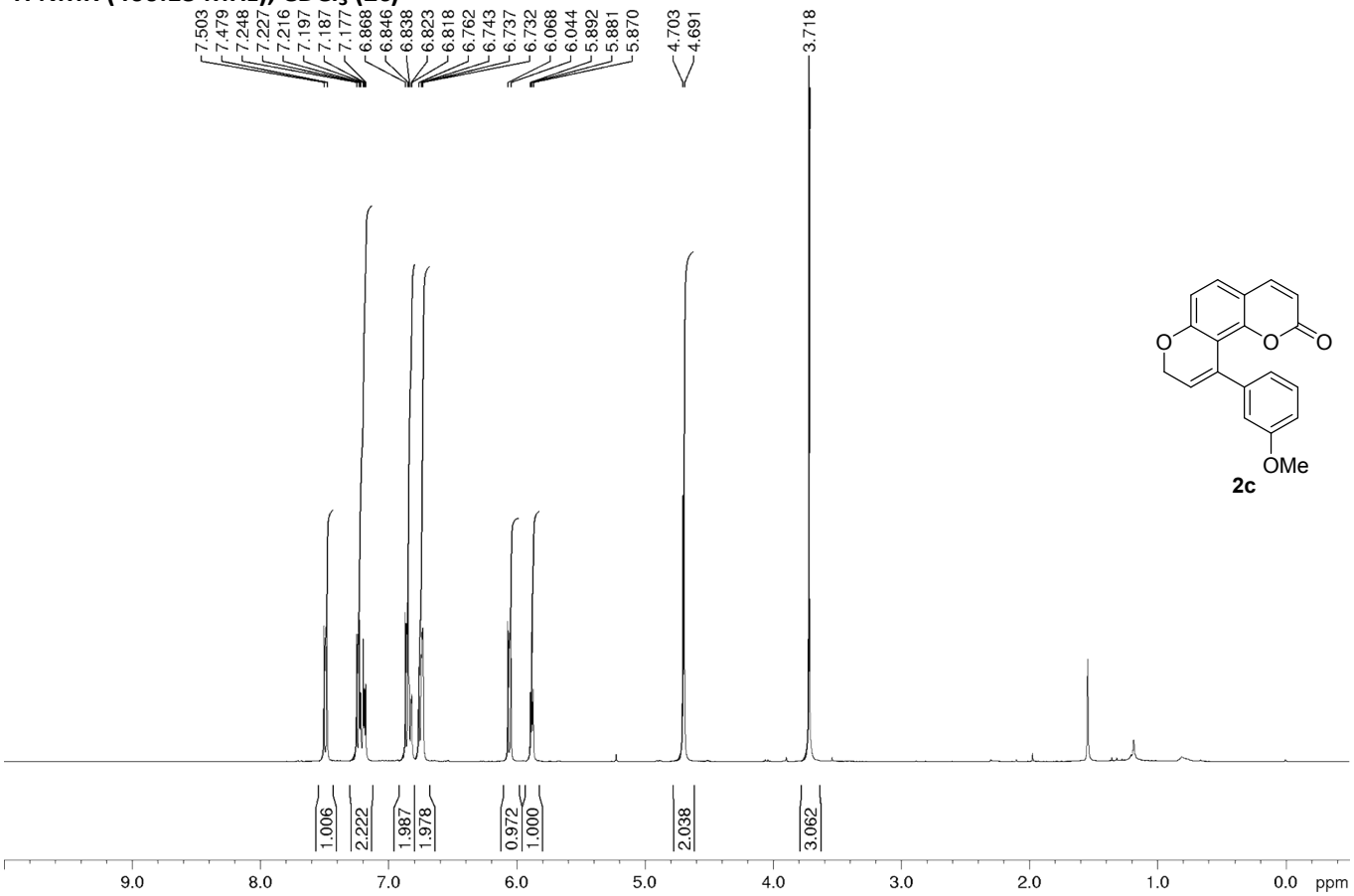


3b

^{13}C NMR (100.6 MHz), $CDCl_3$ (3b)

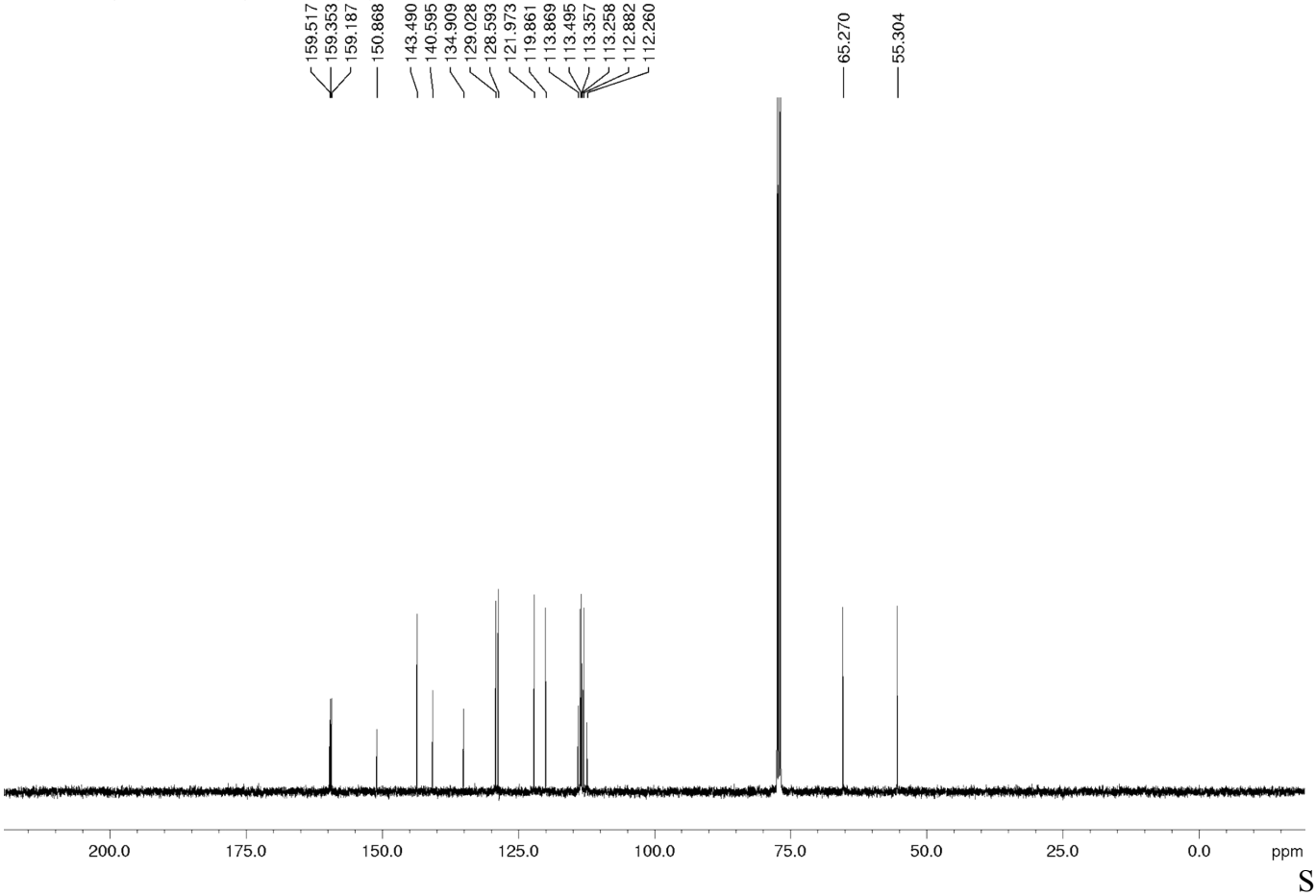


^{1}H NMR (400.13 MHz), $CDCl_3$ (2c)

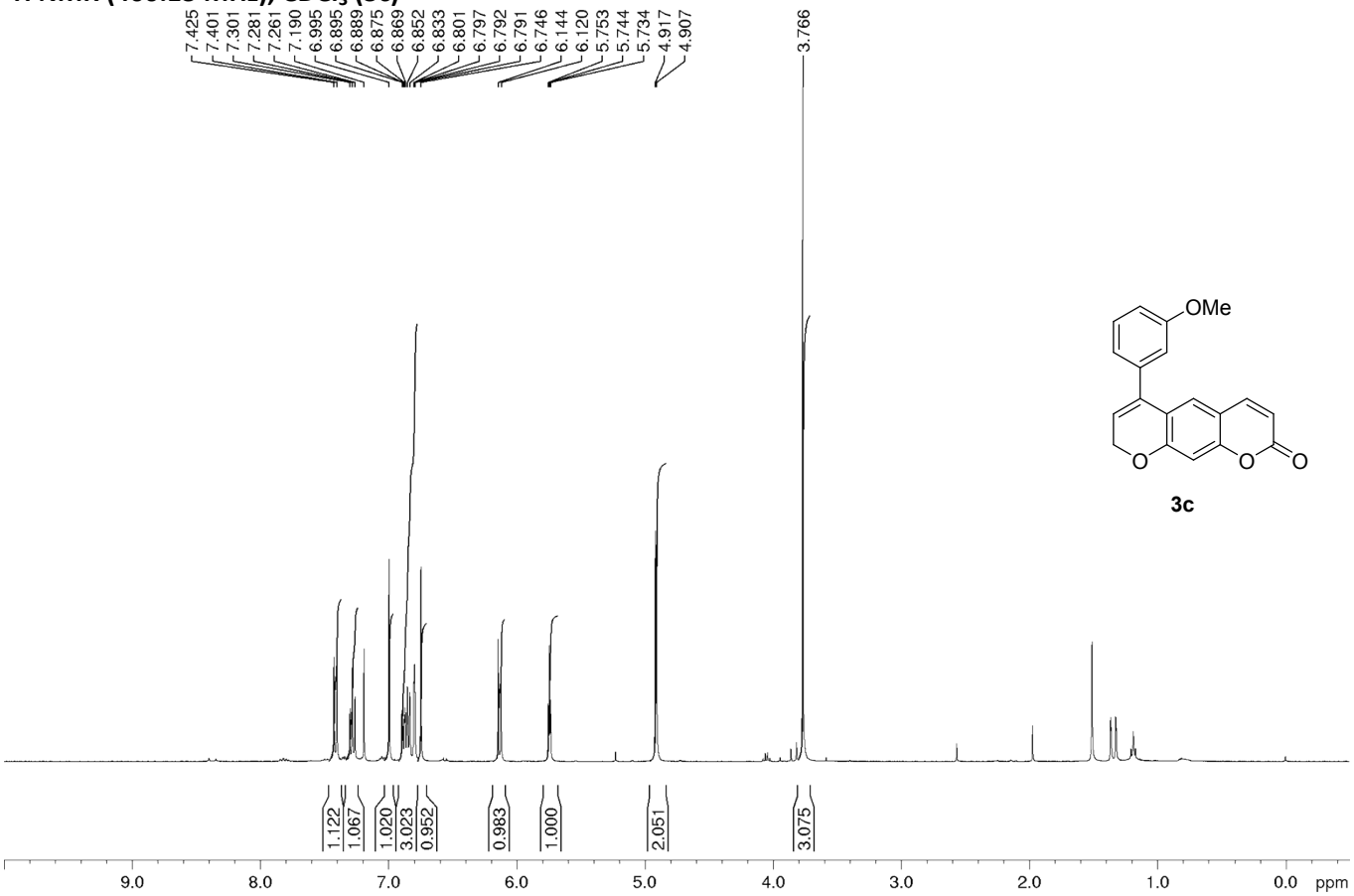


2c

^{13}C NMR (100.6 MHz), $CDCl_3$ (2c)

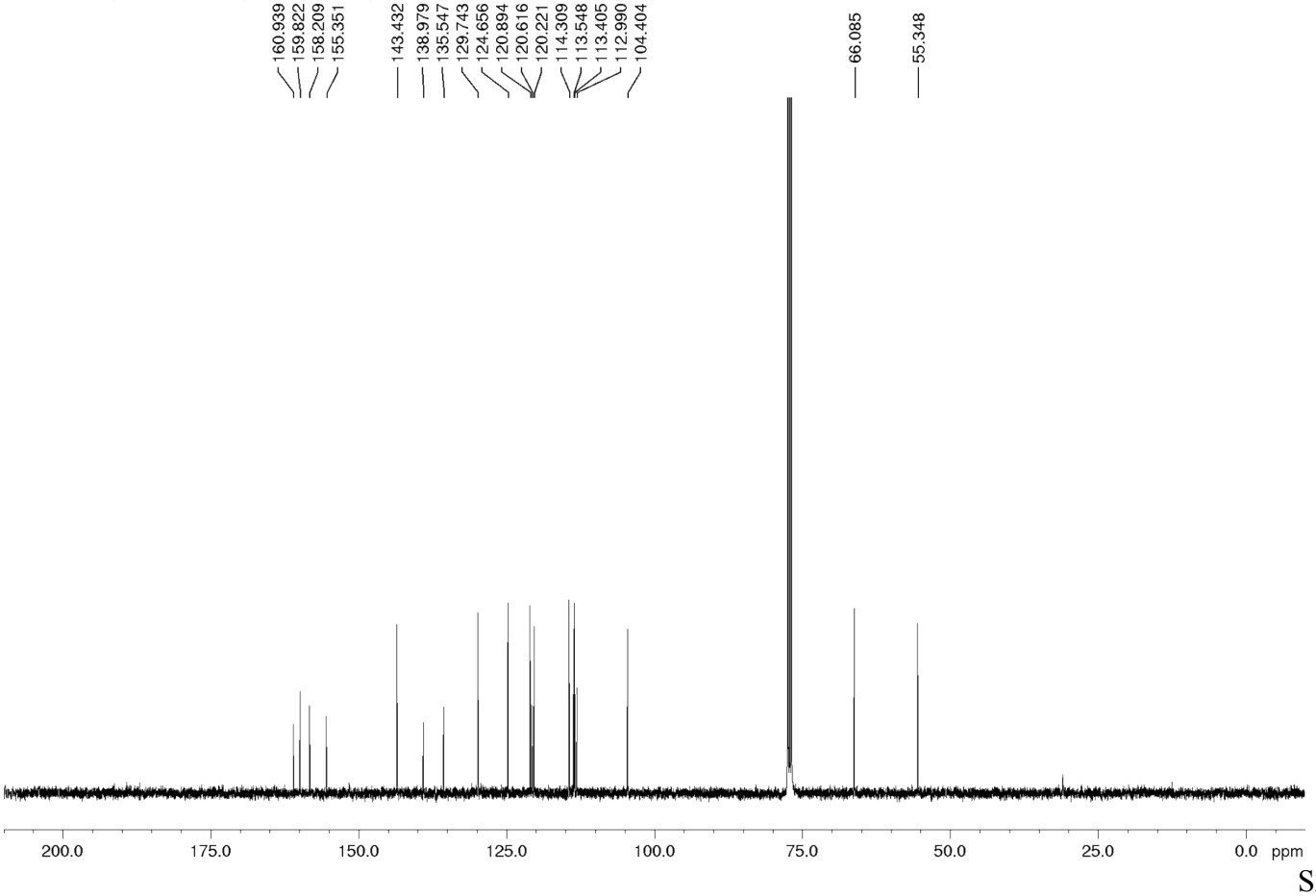


^{1}H NMR (400.13 MHz), $CDCl_3$ (3c)

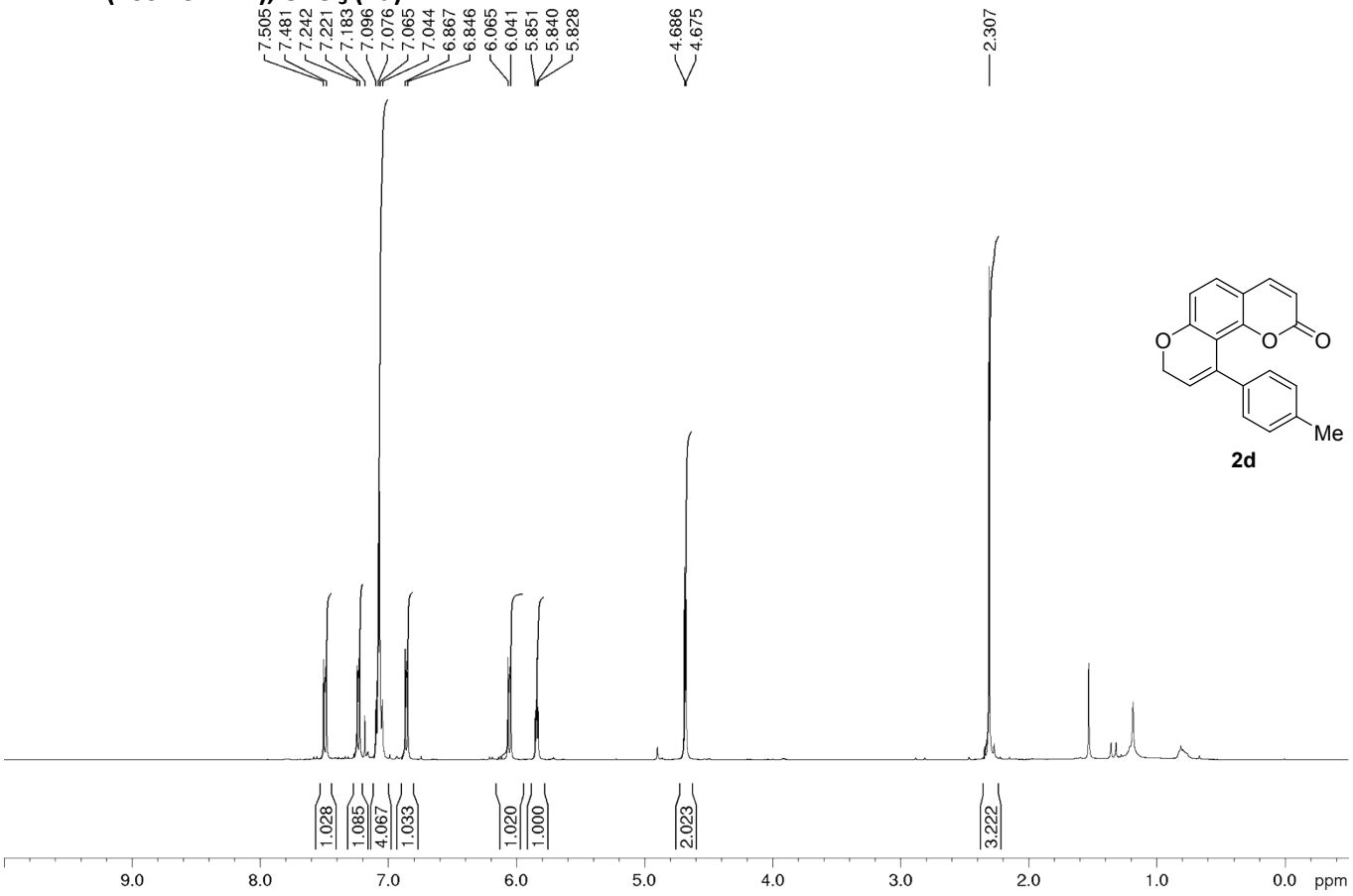


3c

^{13}C NMR (100.6 MHz), $CDCl_3$ (3c)

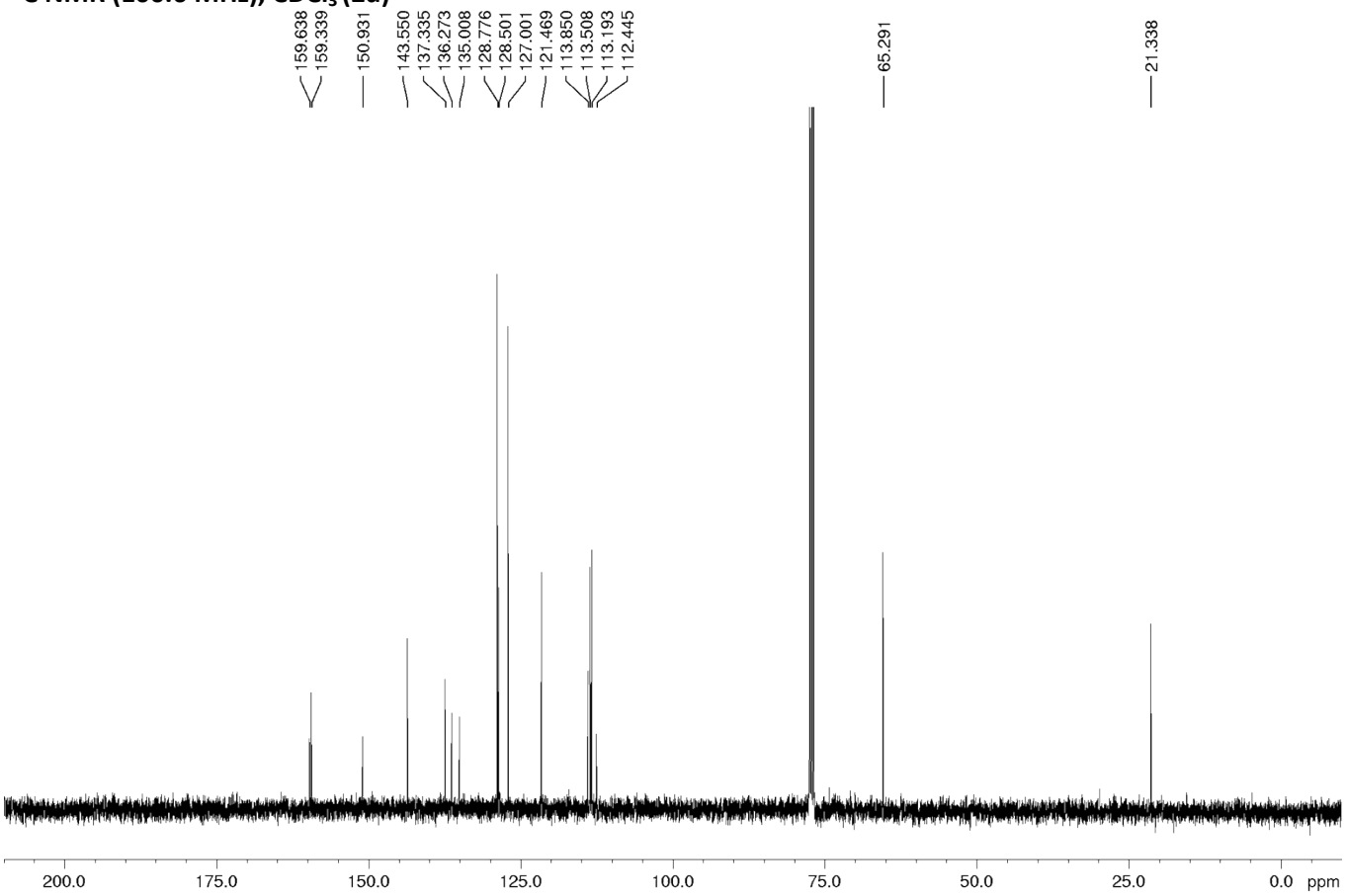


^{1}H NMR (400.13 MHz), $CDCl_3$ (2d)

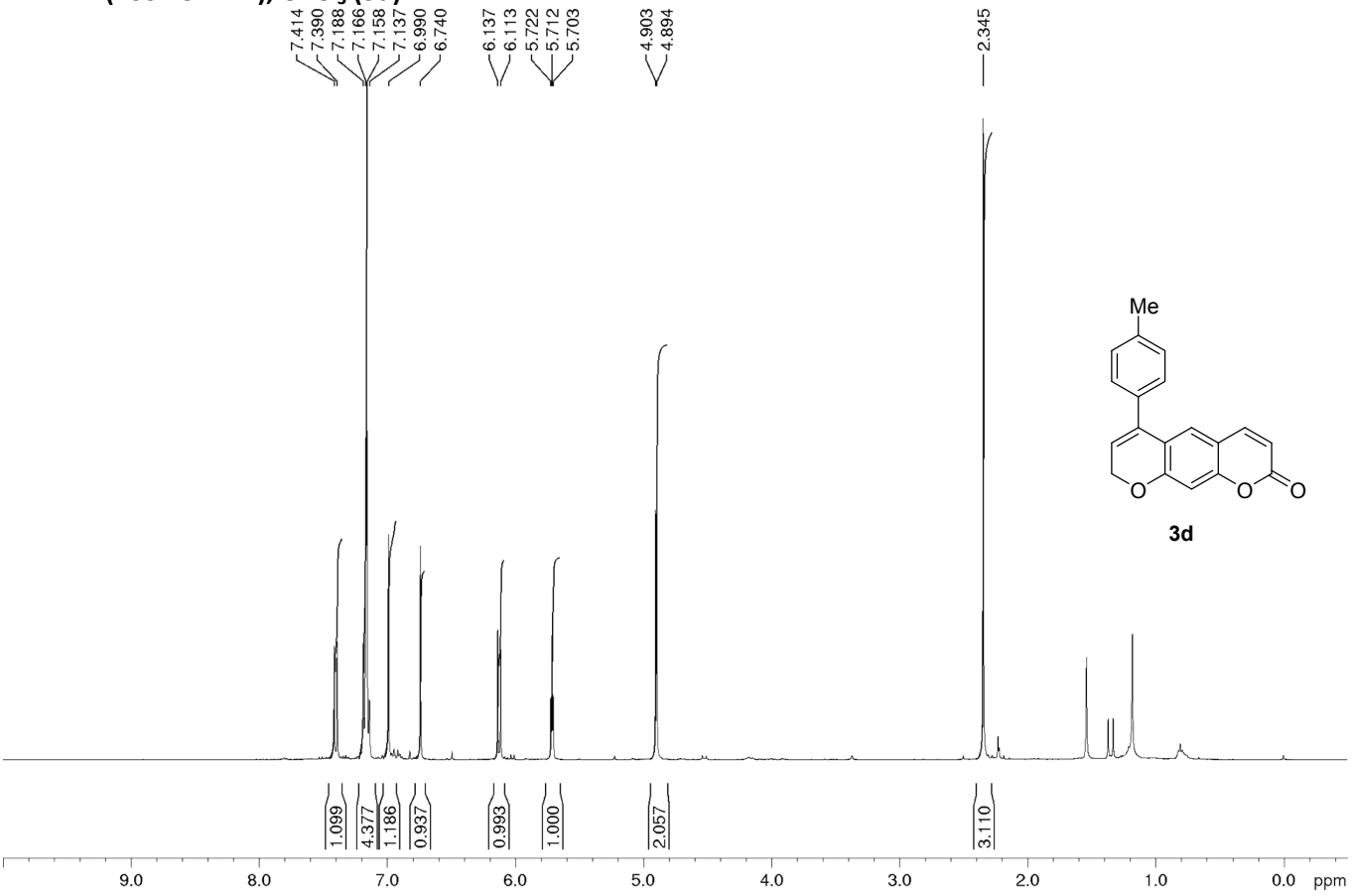


2d

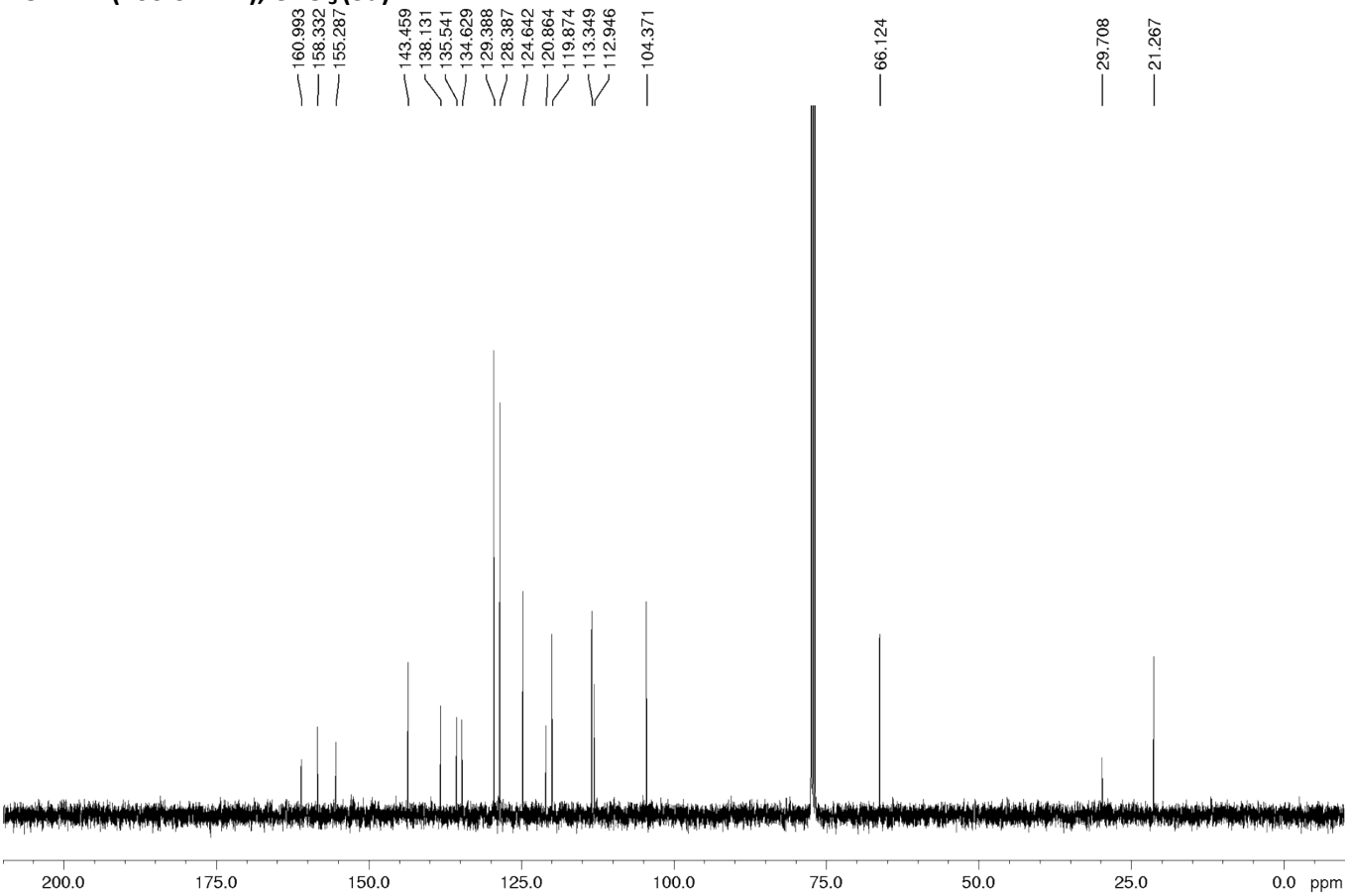
^{13}C NMR (100.6 MHz), $CDCl_3$ (2d)



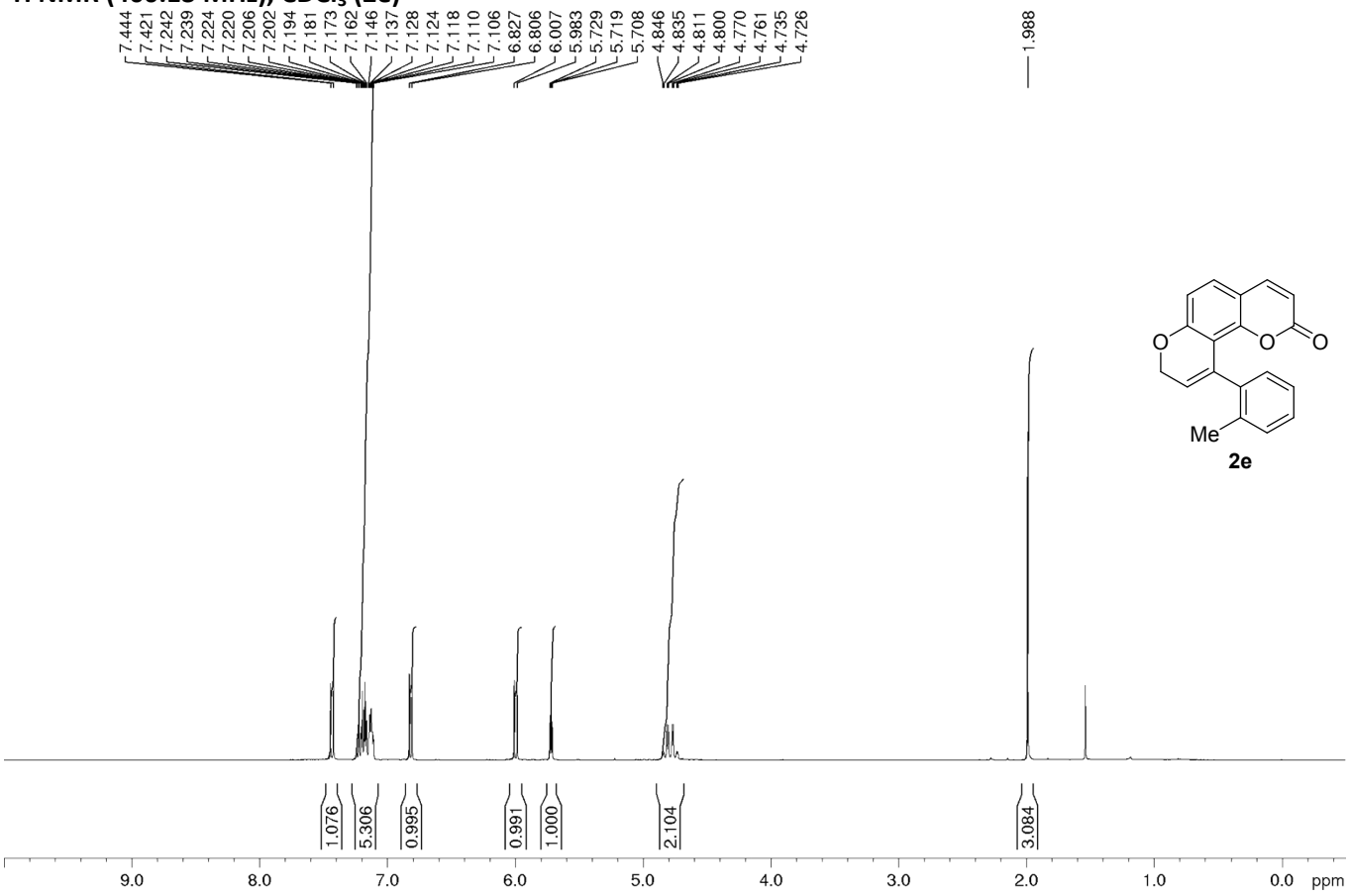
^{1}H NMR (400.13 MHz), $CDCl_3$ (3d)



^{13}C NMR (100.6 MHz), $CDCl_3$ (3d)

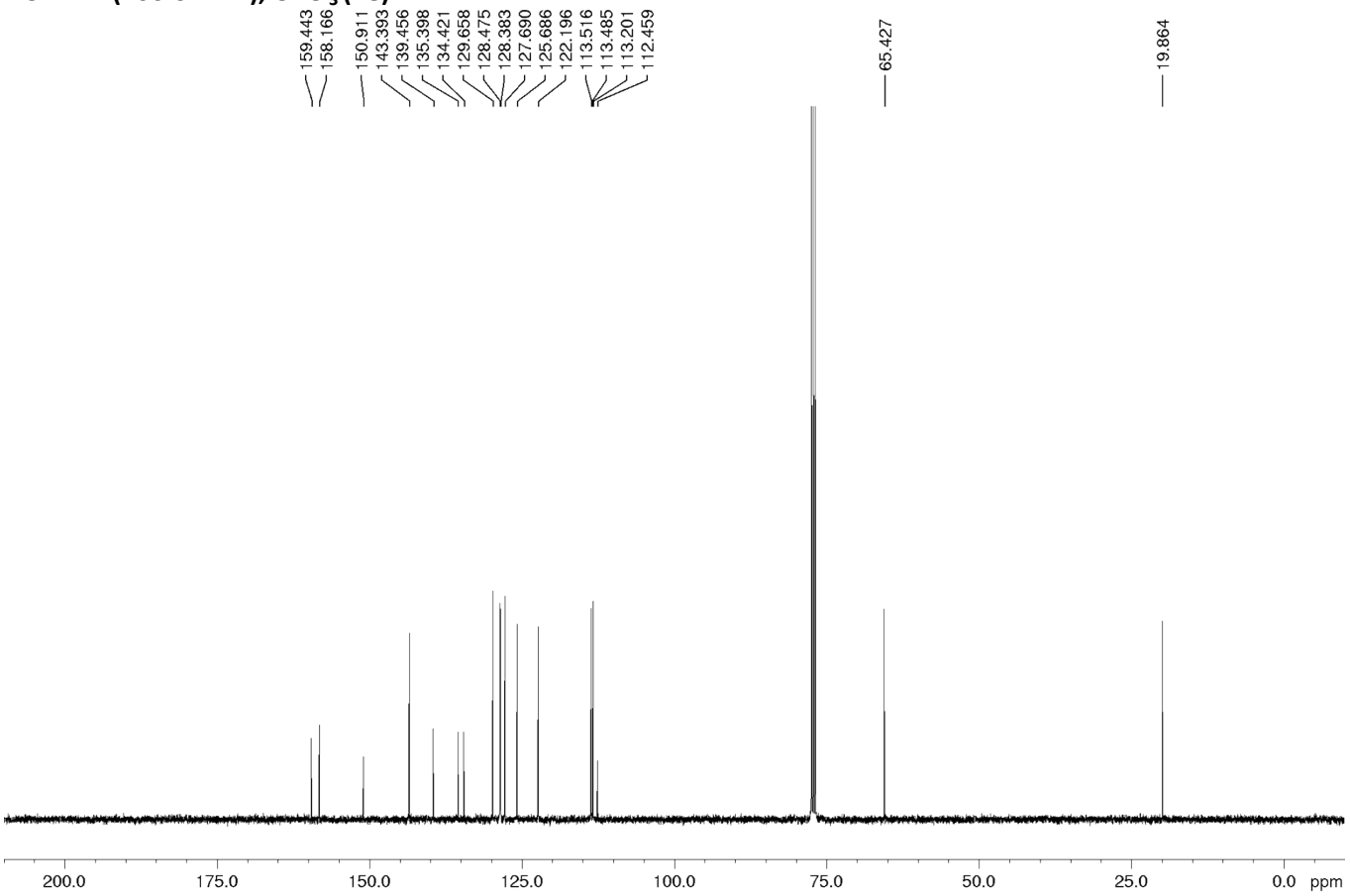


^{1}H NMR (400.13 MHz), $CDCl_3$ (2e)

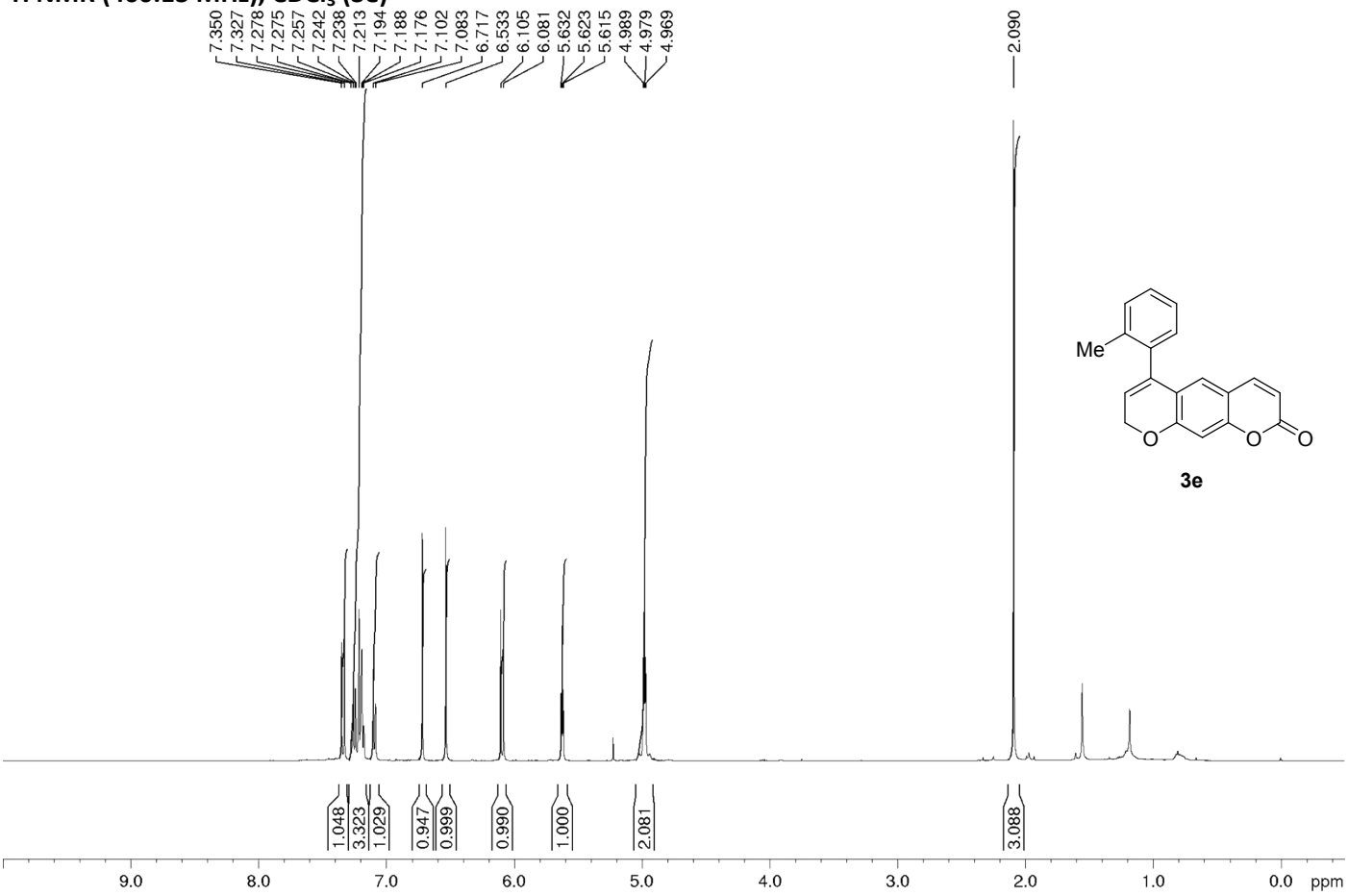


2e

^{13}C NMR (100.6 MHz), $CDCl_3$ (2e)

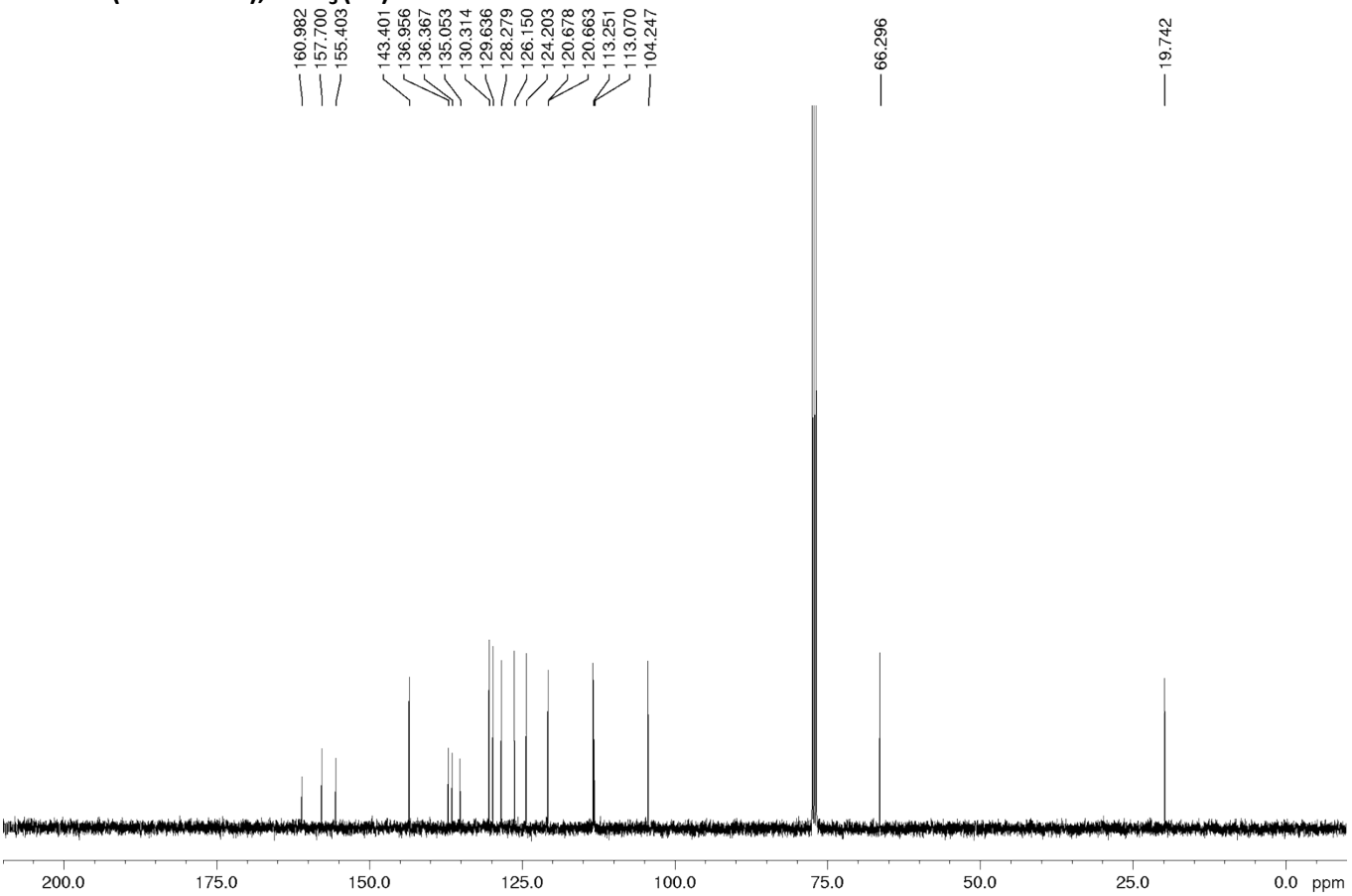


^{1}H NMR (400.13 MHz), $CDCl_3$ (3e)

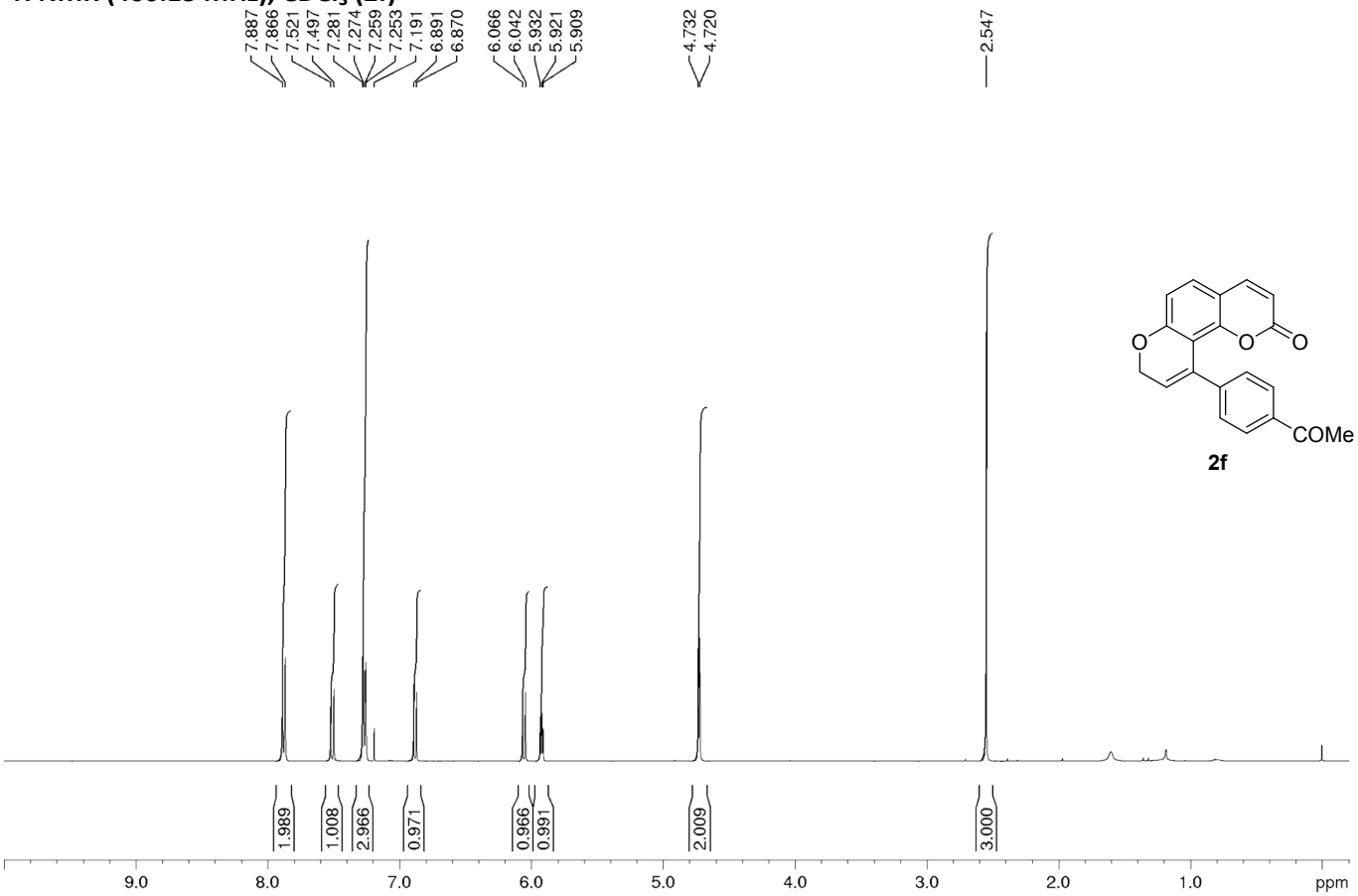


3e

^{13}C NMR (100.6 MHz), $CDCl_3$ (3e)

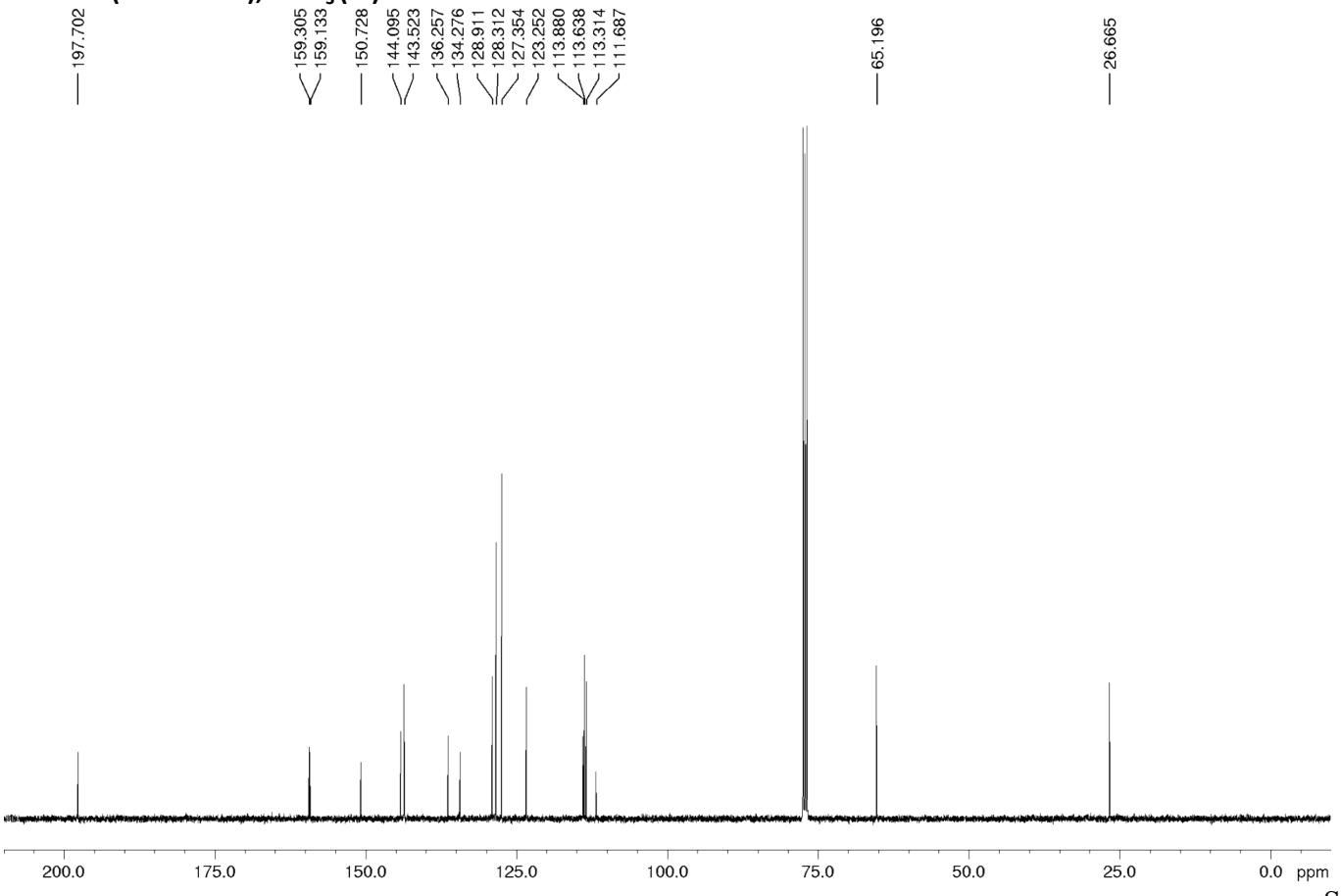


^{1}H NMR (400.13 MHz), $CDCl_3$ (2f)

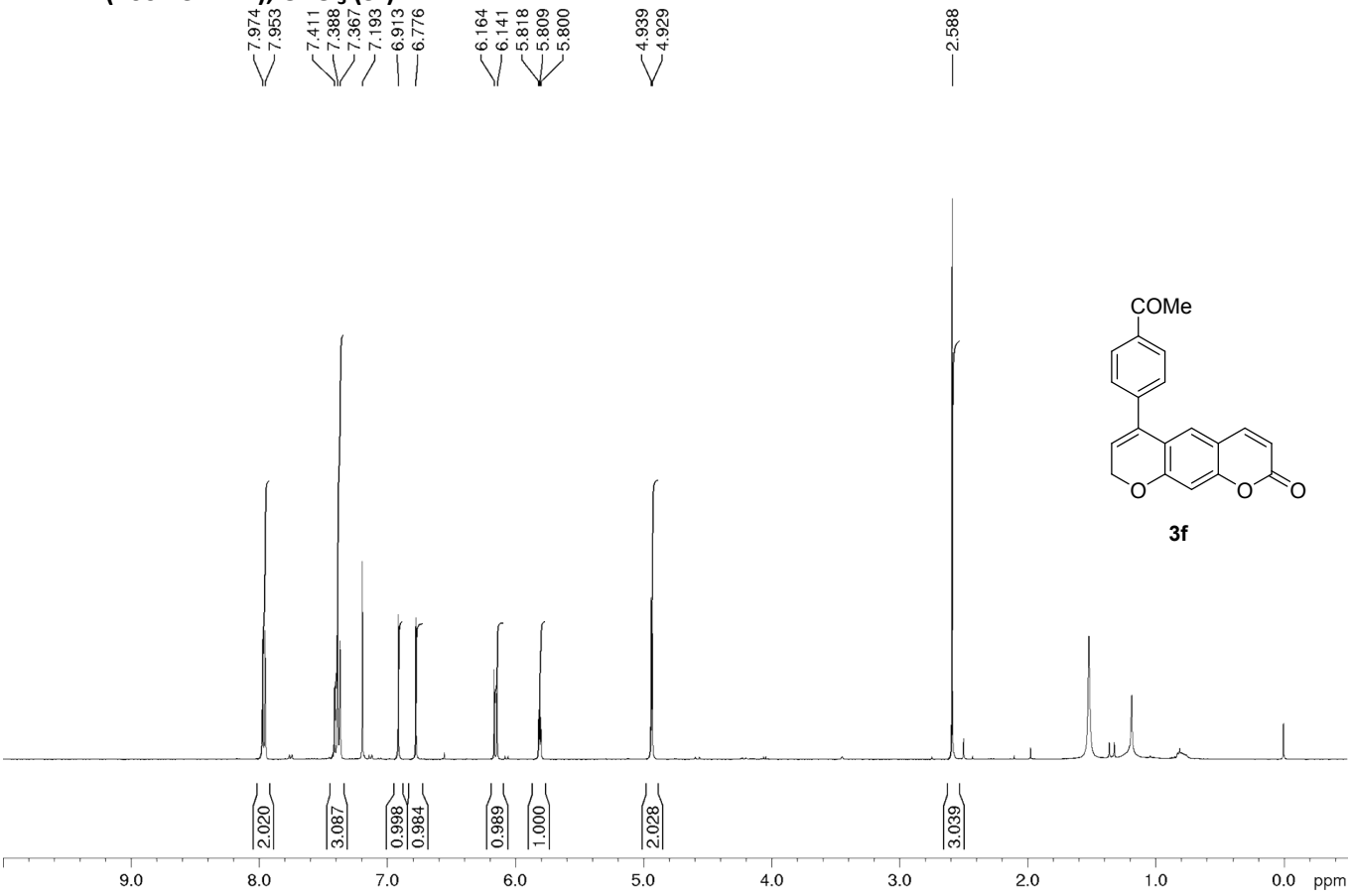


2f

^{13}C NMR (100.6 MHz), $CDCl_3$ (2f)

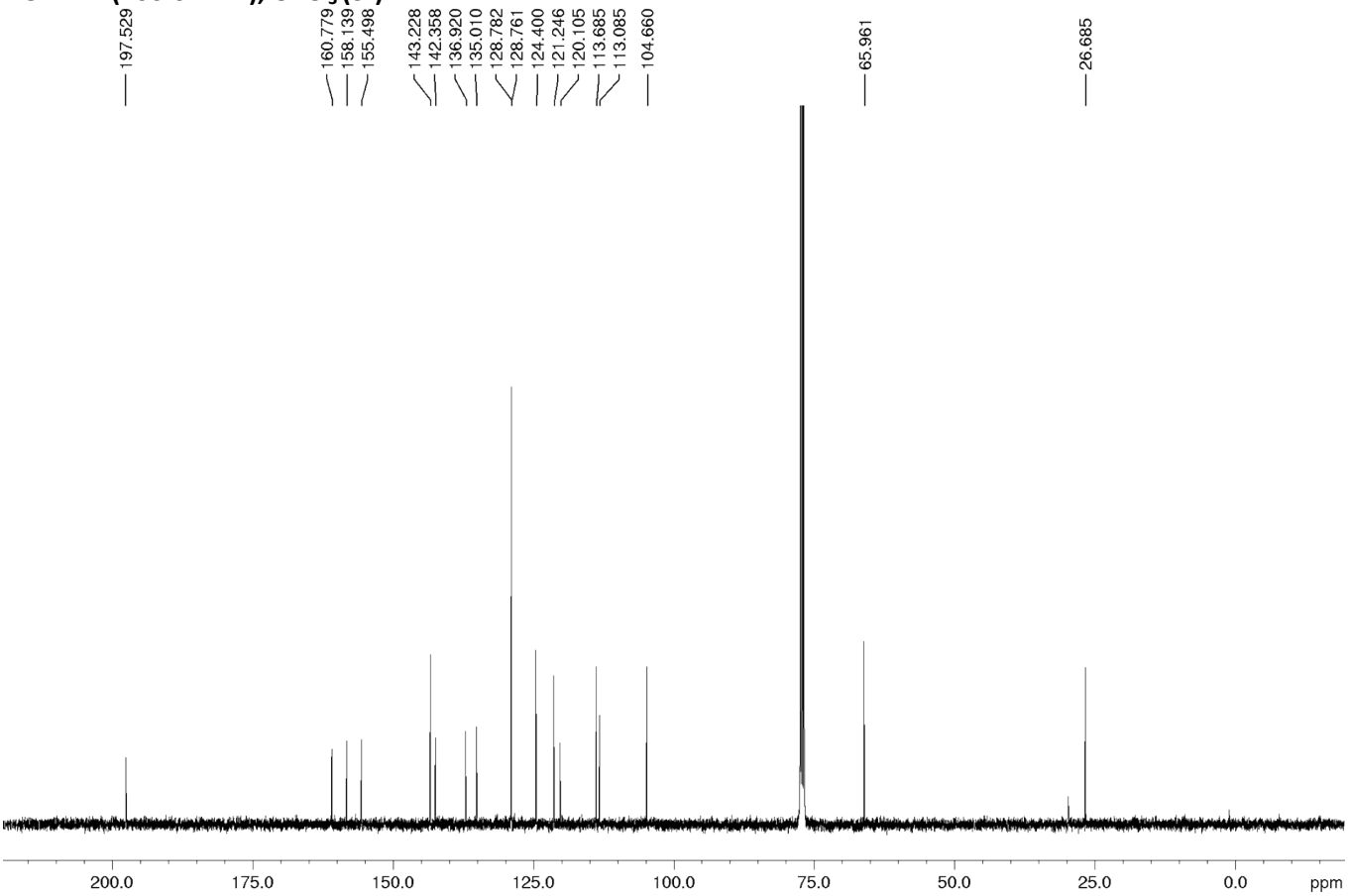


^{1}H NMR (400.13 MHz), $CDCl_3$ (3f)

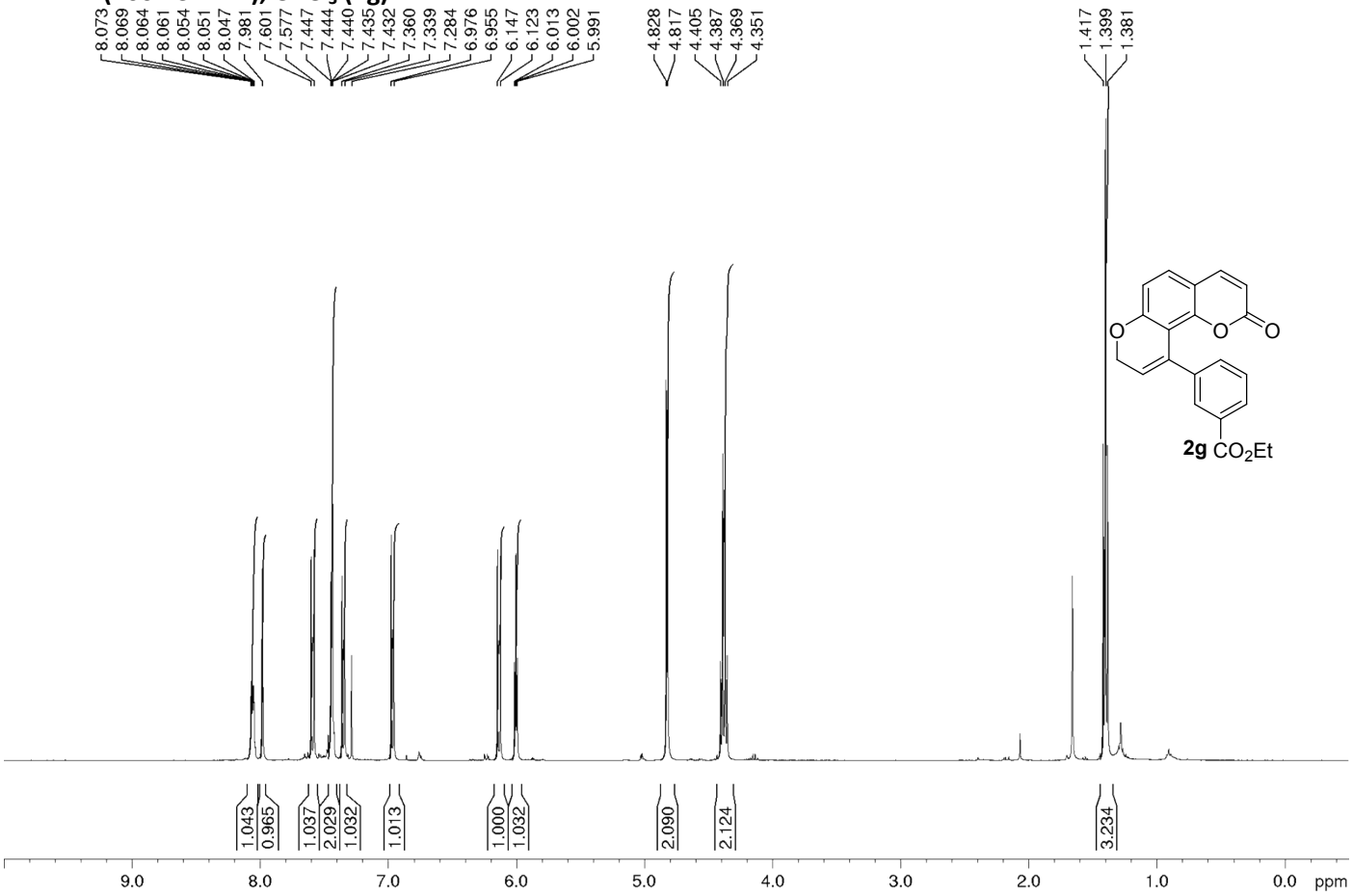


3f

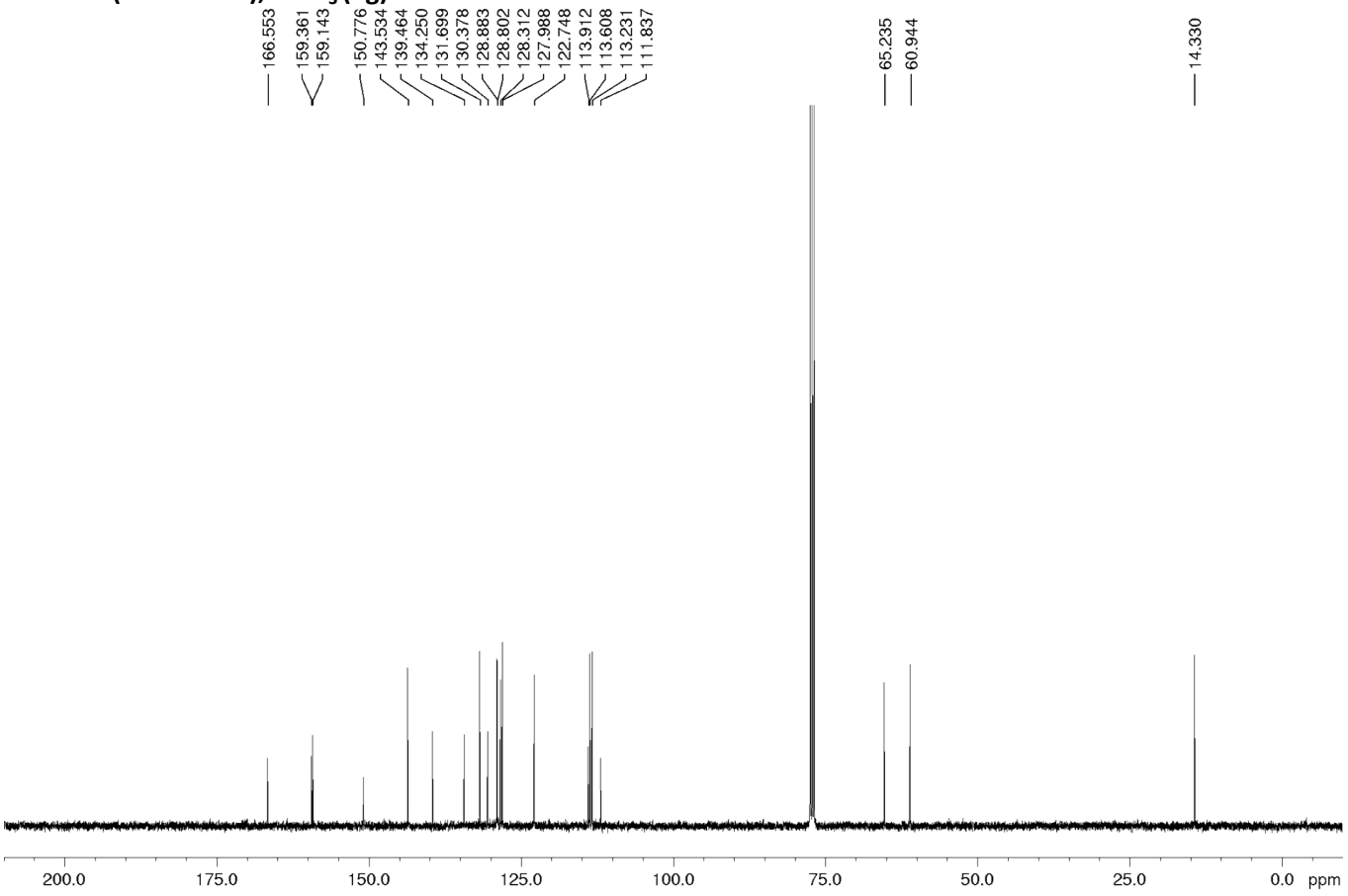
^{13}C NMR (100.6 MHz), $CDCl_3$ (3f)



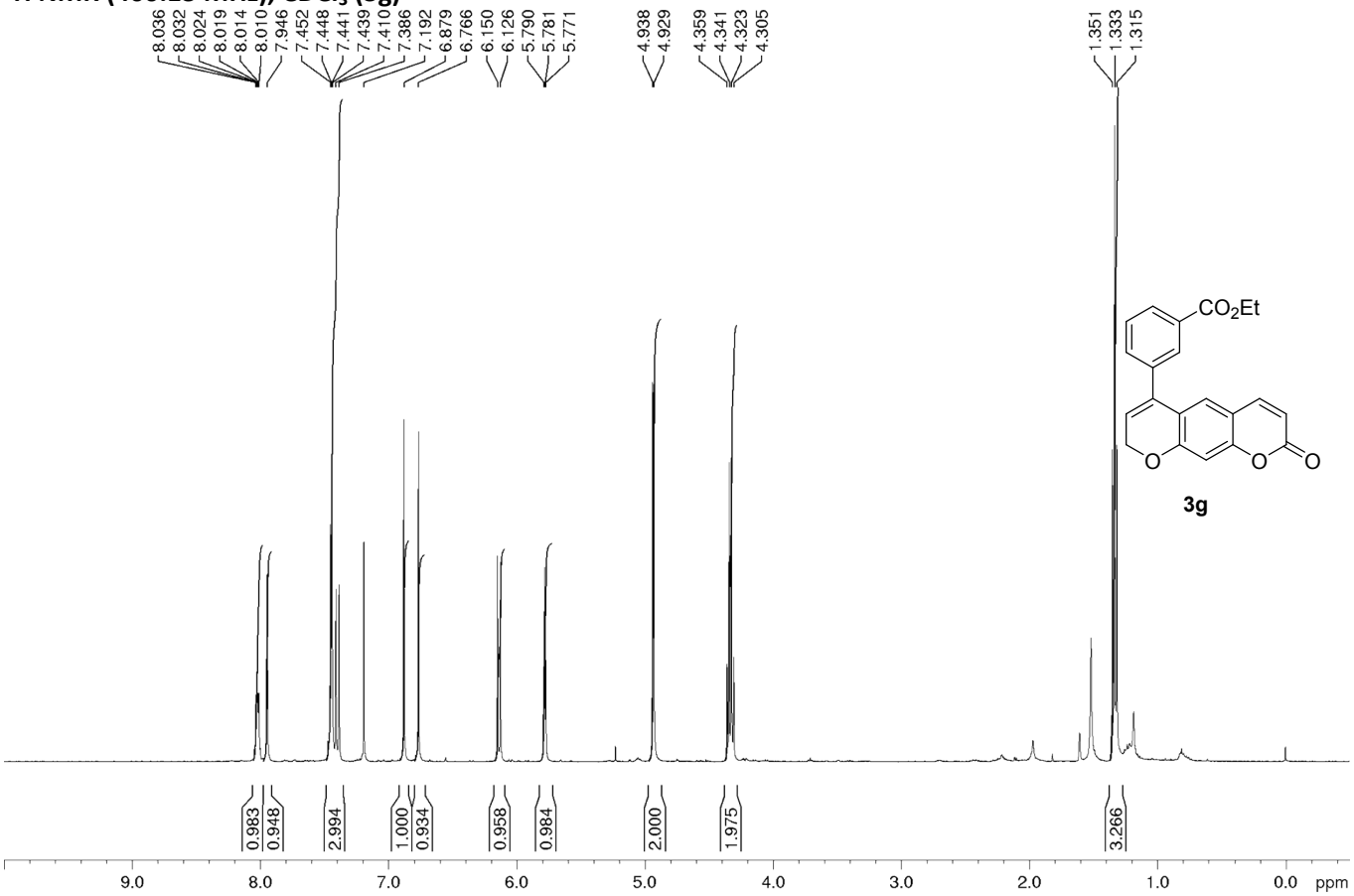
^{1}H NMR (400.13 MHz), $CDCl_3$ (2g)



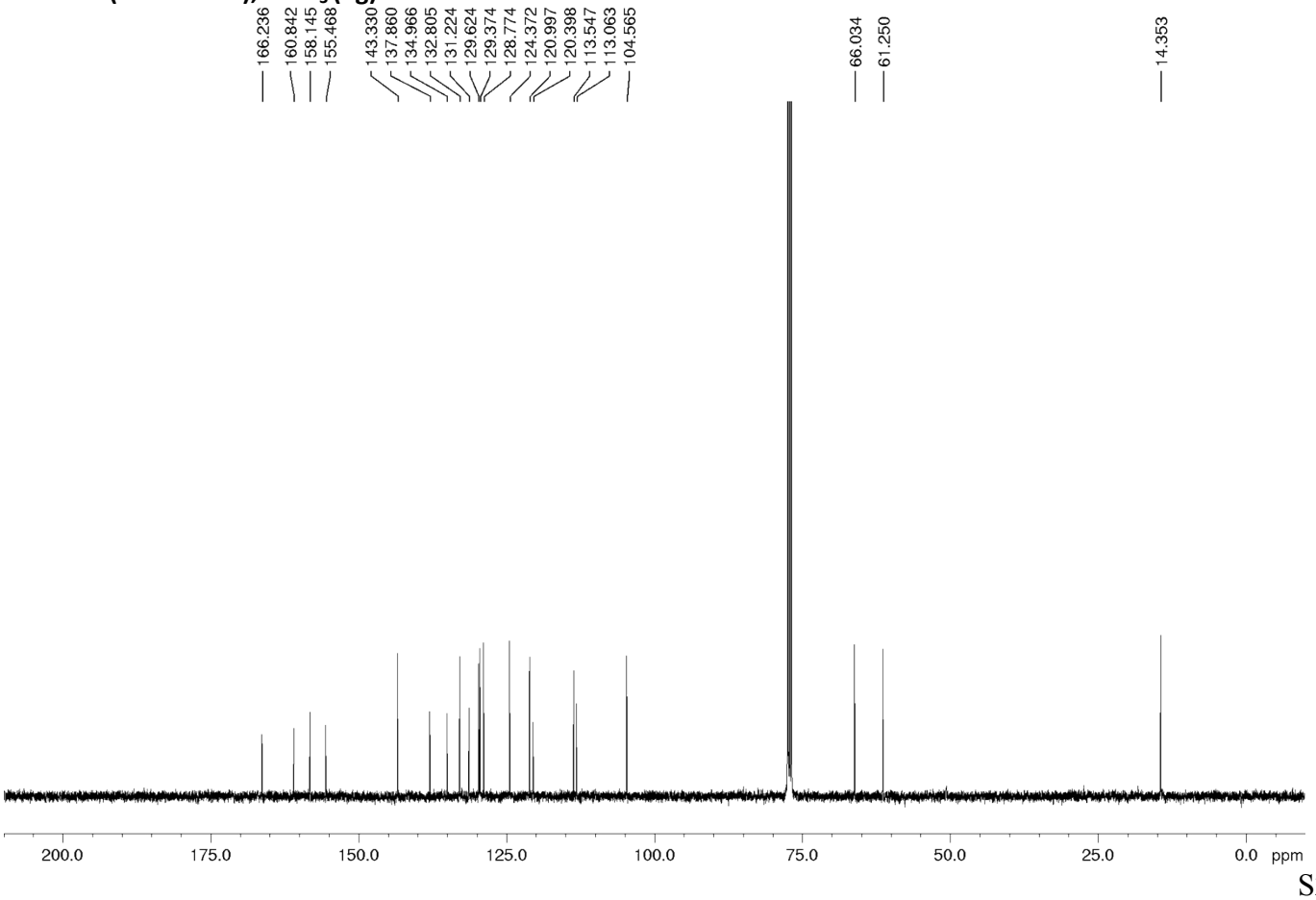
^{13}C NMR (100.6 MHz), $CDCl_3$ (2g)



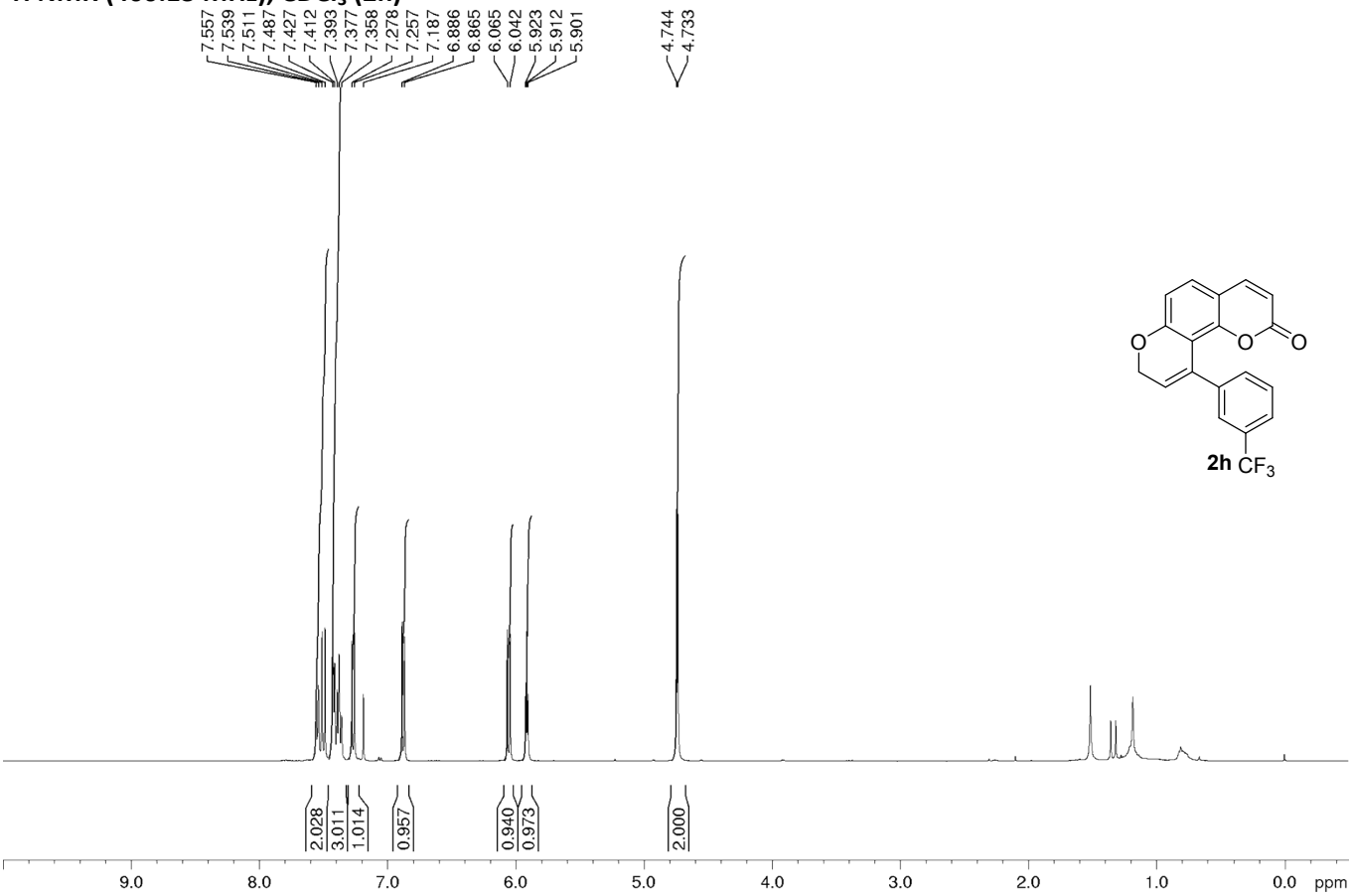
^{1}H NMR (400.13 MHz), $CDCl_3$ (3g)



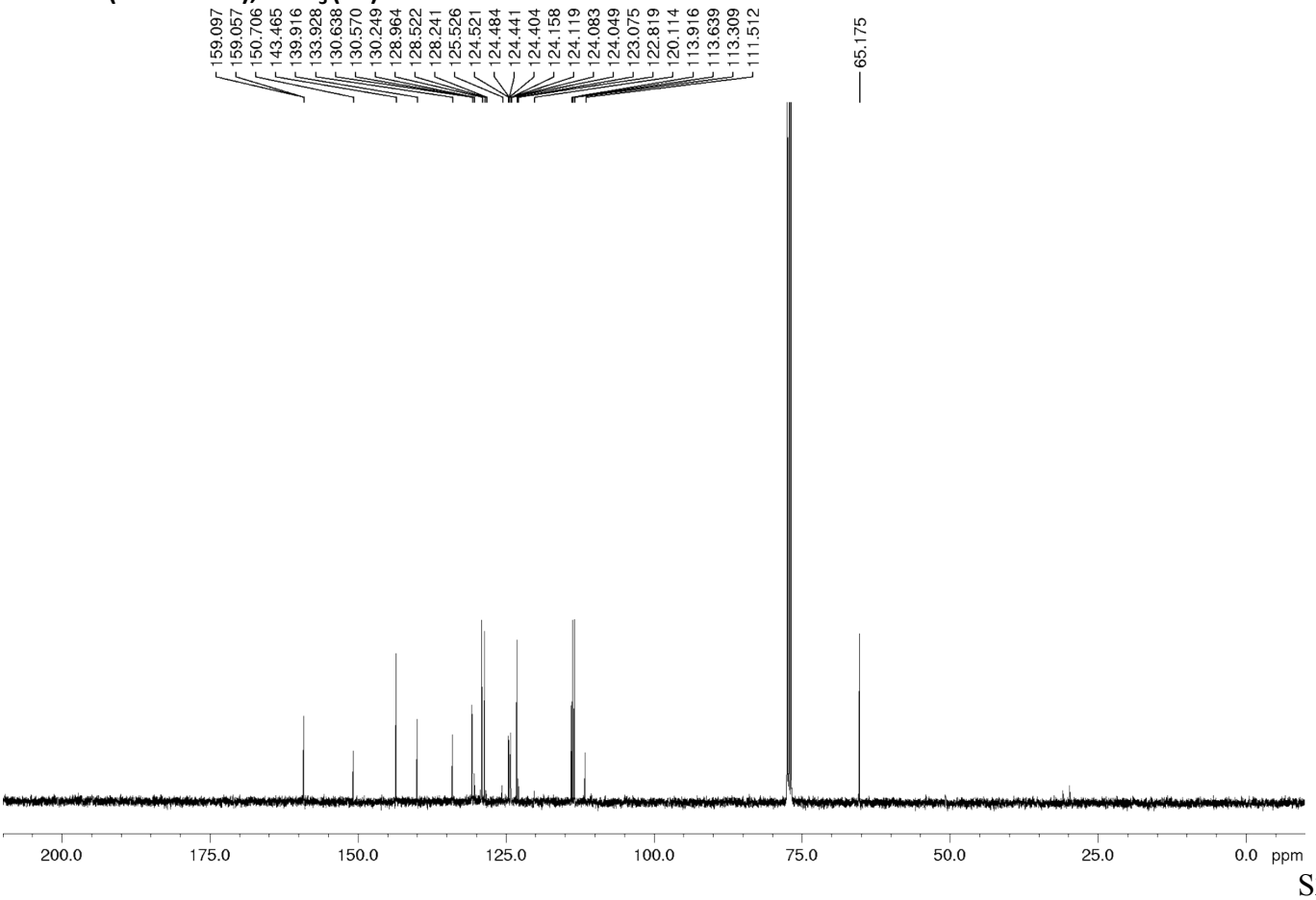
^{13}C NMR (100.6 MHz), $CDCl_3$ (3g)



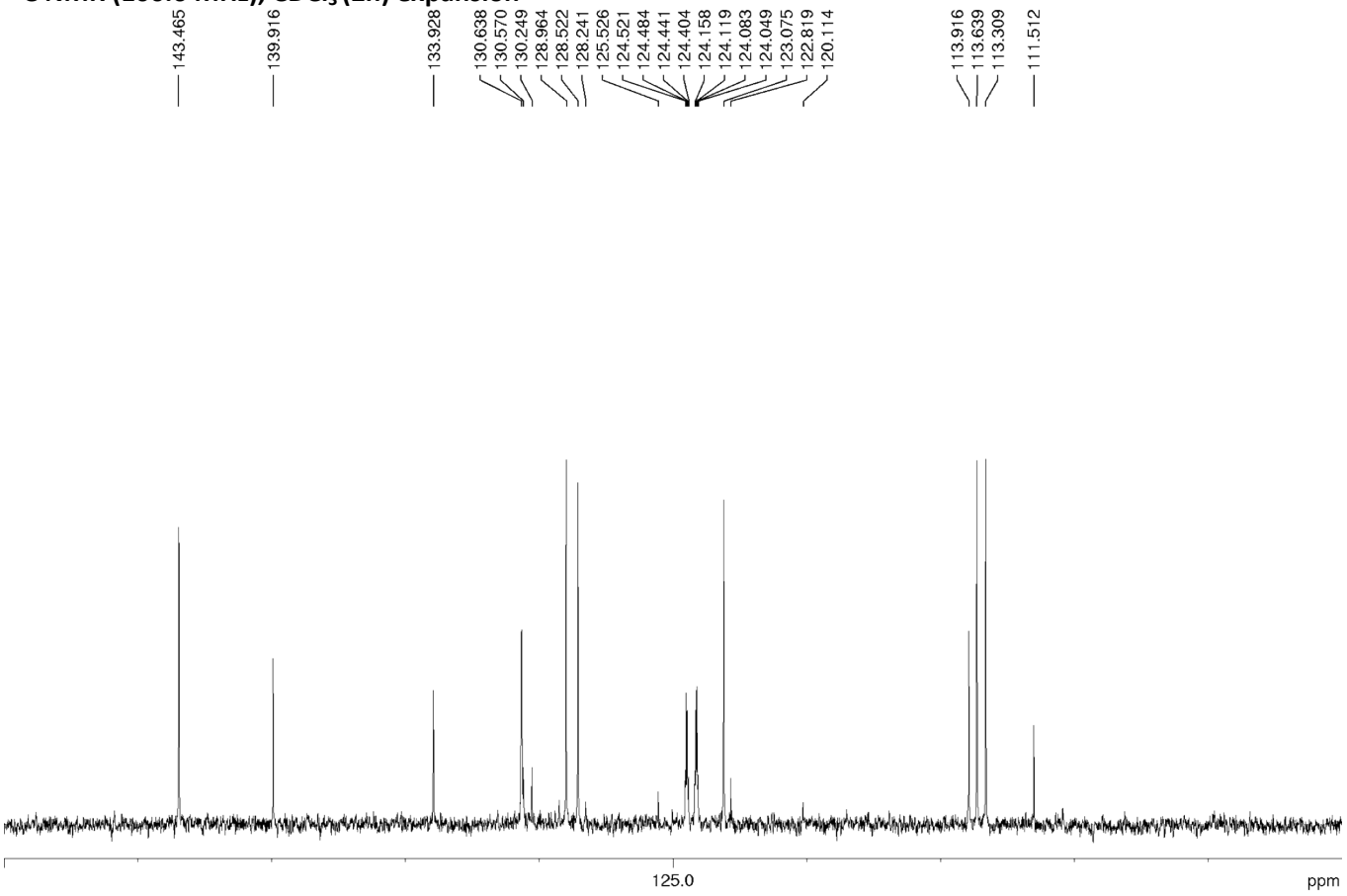
^{1}H NMR (400.13 MHz), $CDCl_3$ (2h)



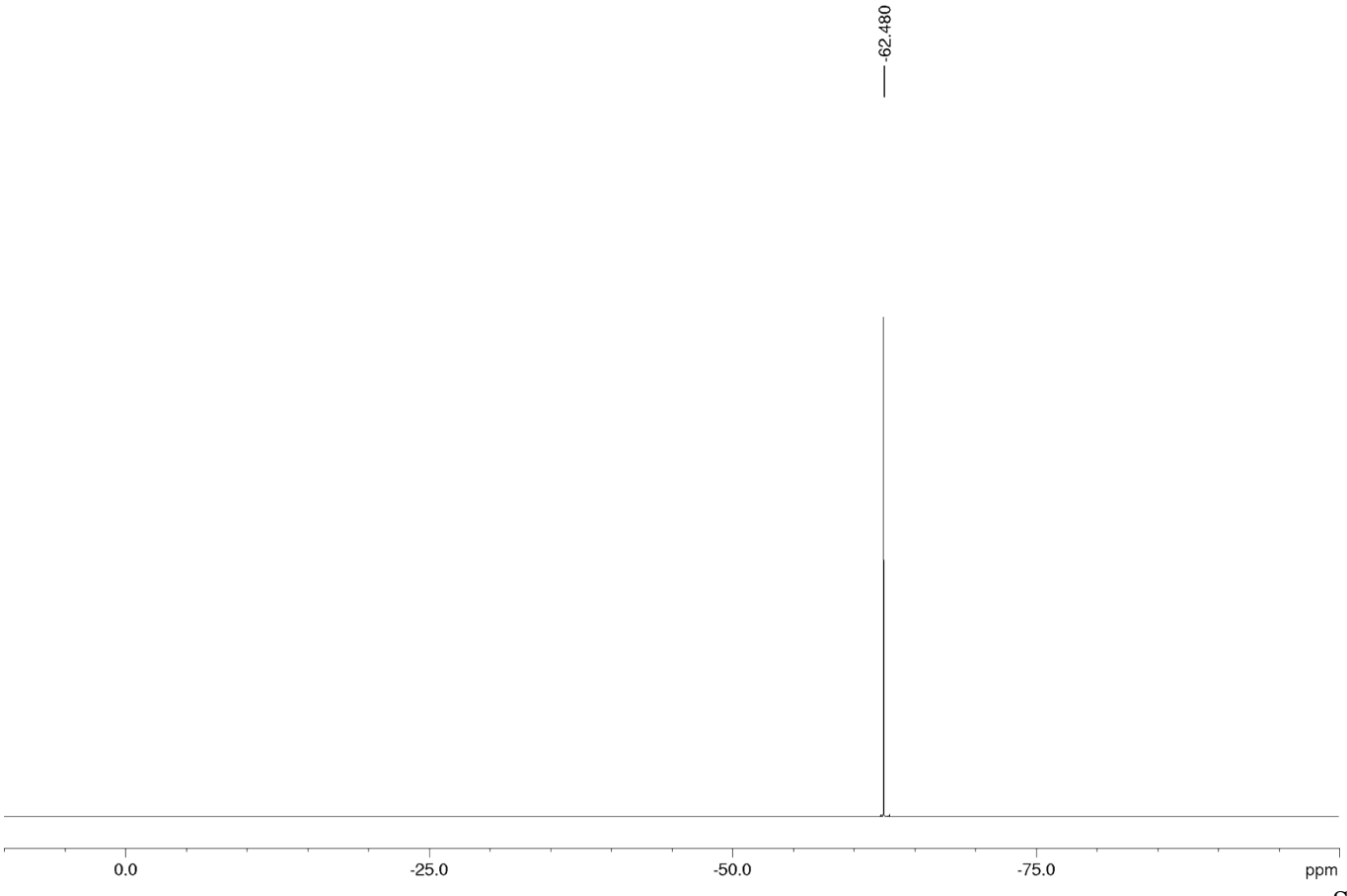
^{13}C NMR (100.6 MHz), $CDCl_3$ (2h)



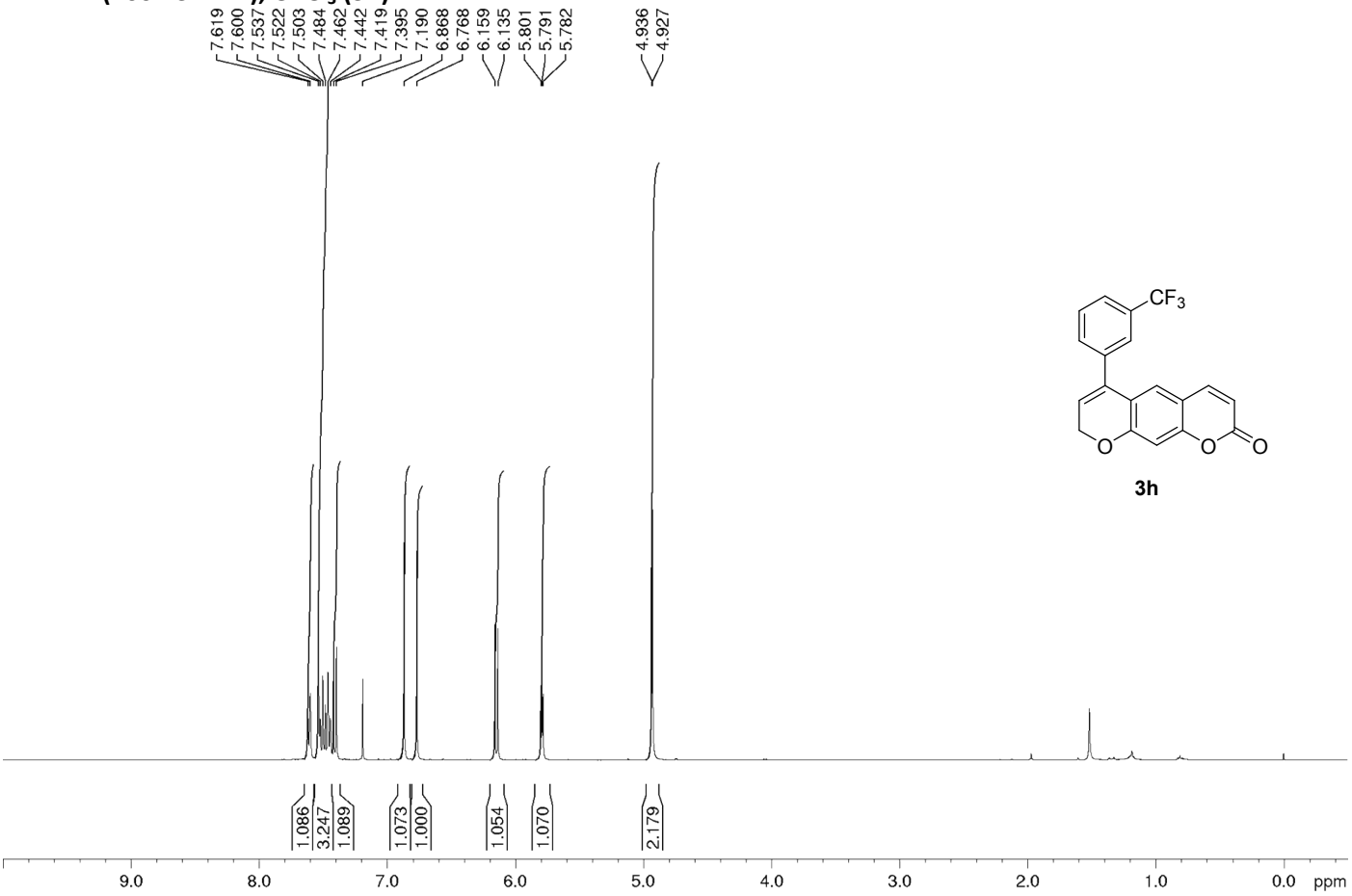
^{13}C NMR (100.6 MHz), $CDCl_3$ (2h) expansion



^{19}F NMR (376.5 MHz MHz), $CDCl_3$ (2h)

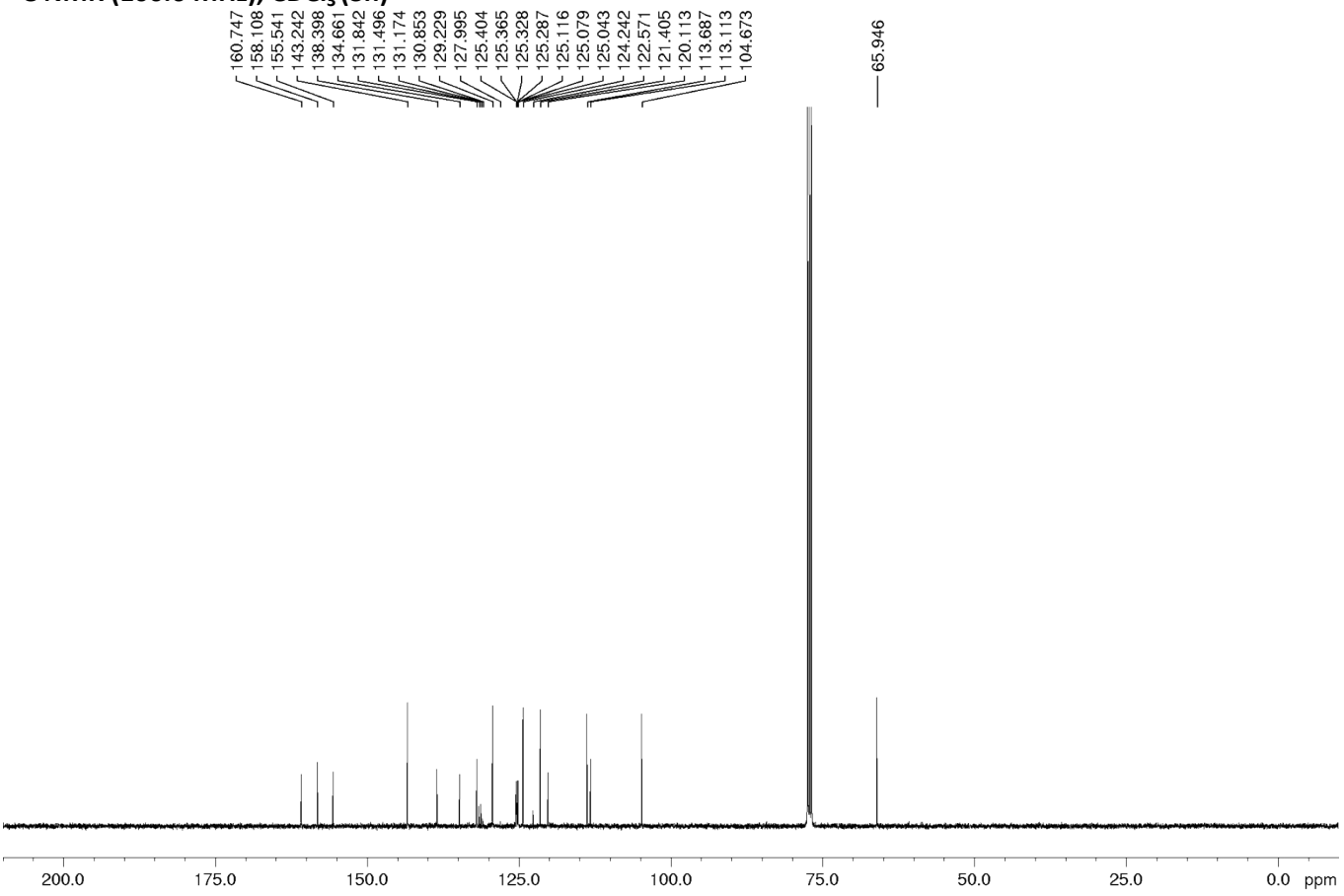


^{1}H NMR (400.13 MHz), $CDCl_3$ (3h)

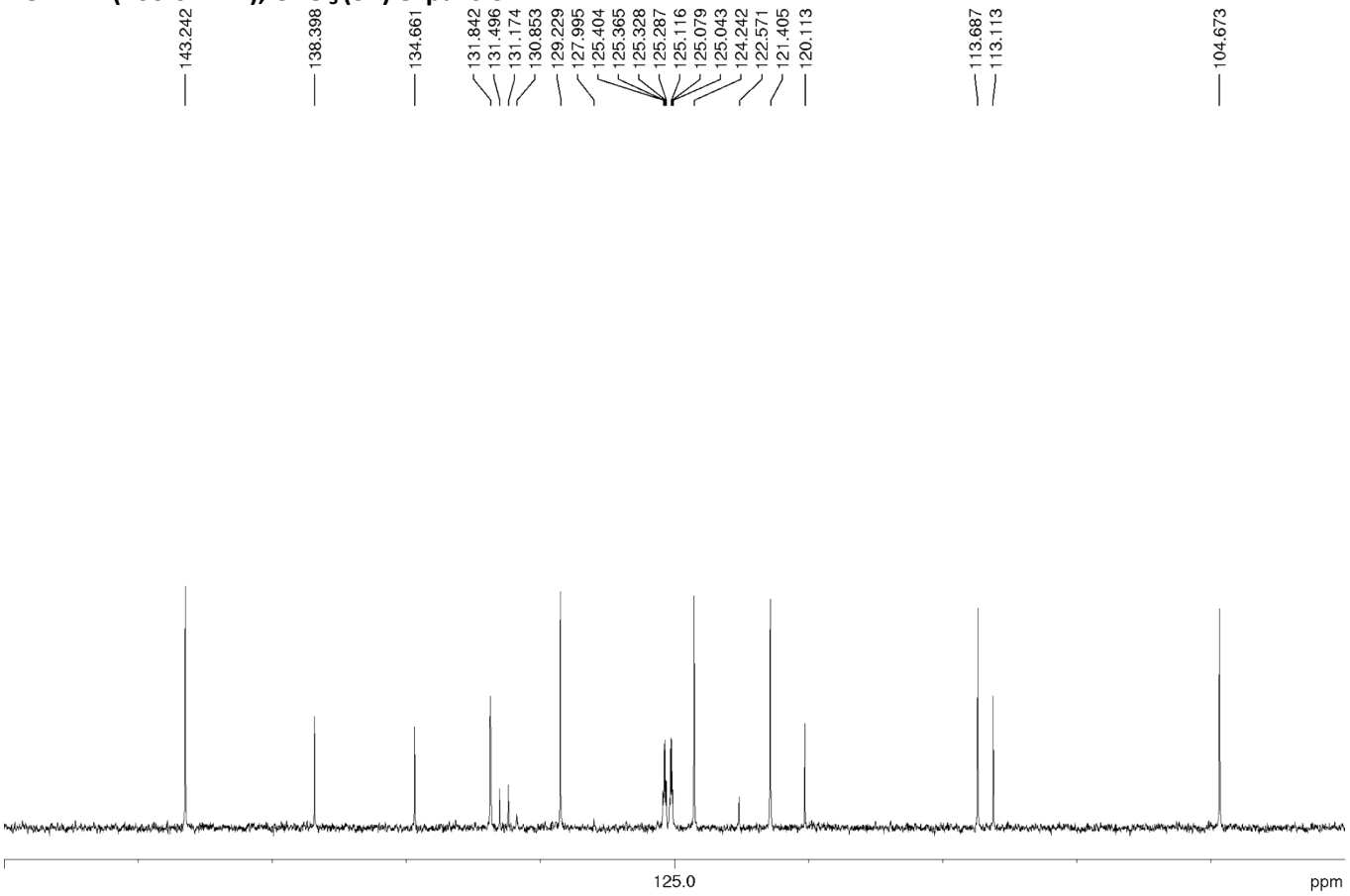


3h

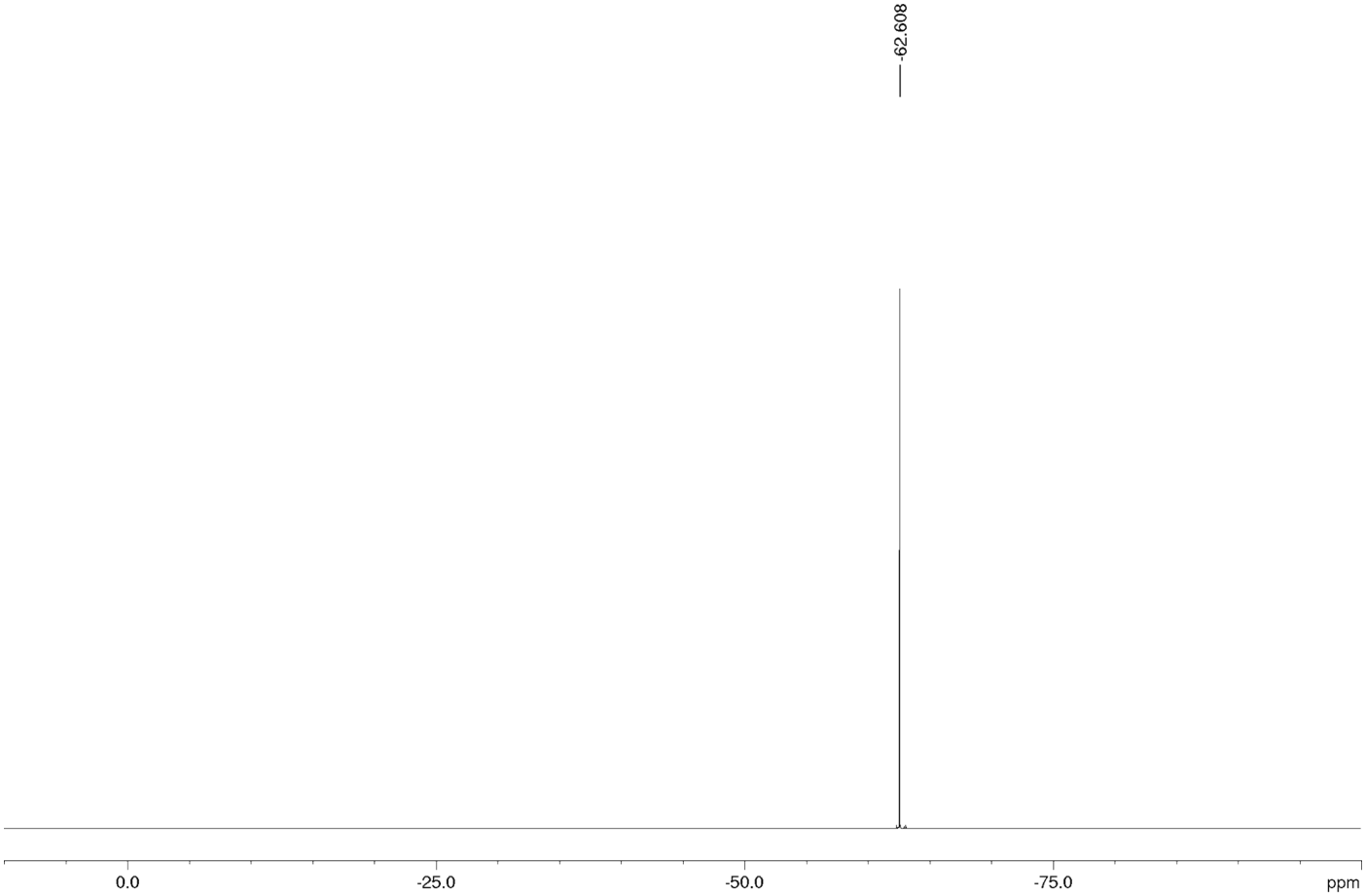
^{13}C NMR (100.6 MHz), $CDCl_3$ (3h)



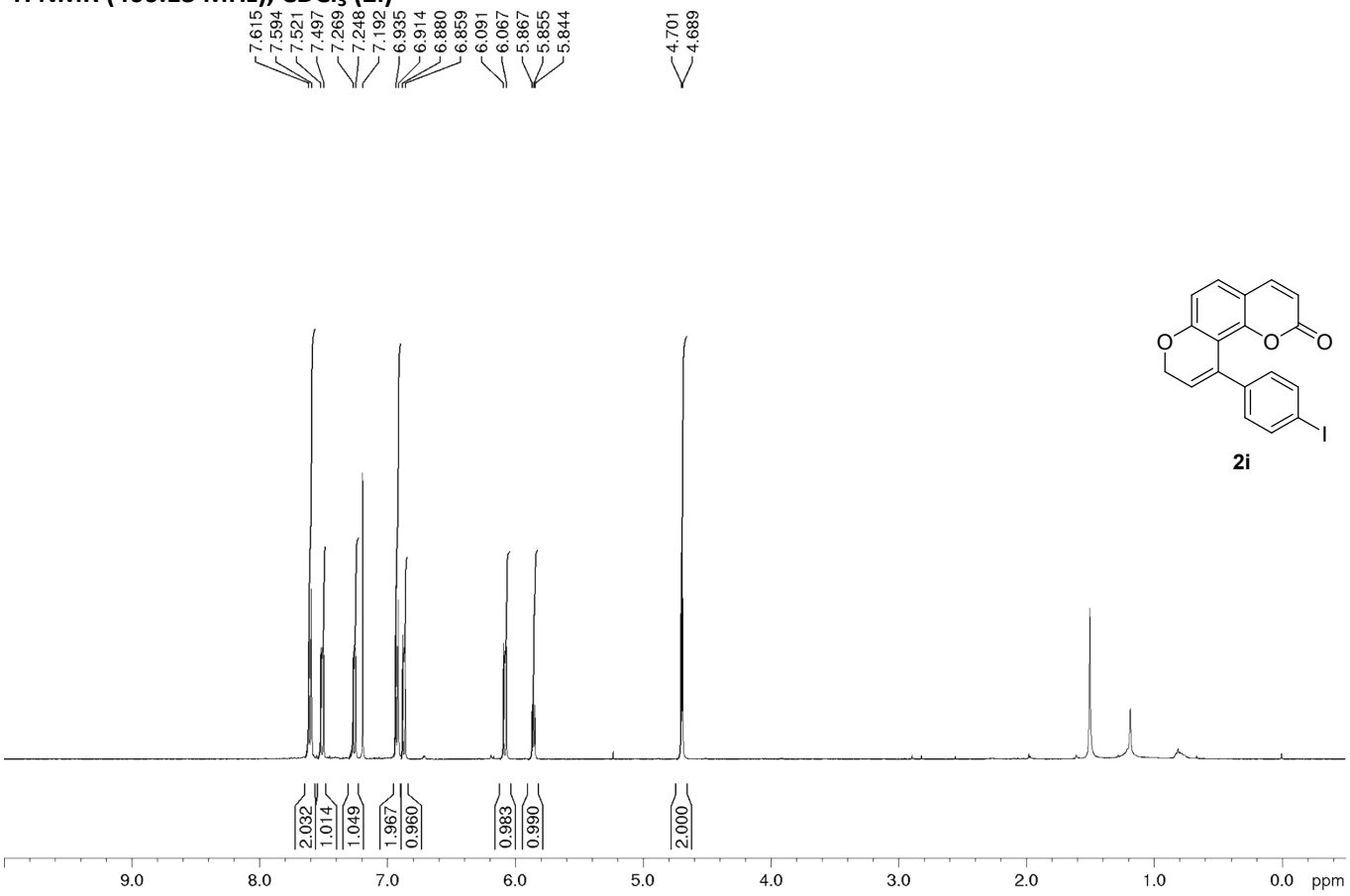
^{13}C NMR (100.6 MHz), $CDCl_3$ (3h) expansion



^{19}F NMR (376.5 MHz MHz), $CDCl_3$ (3h)

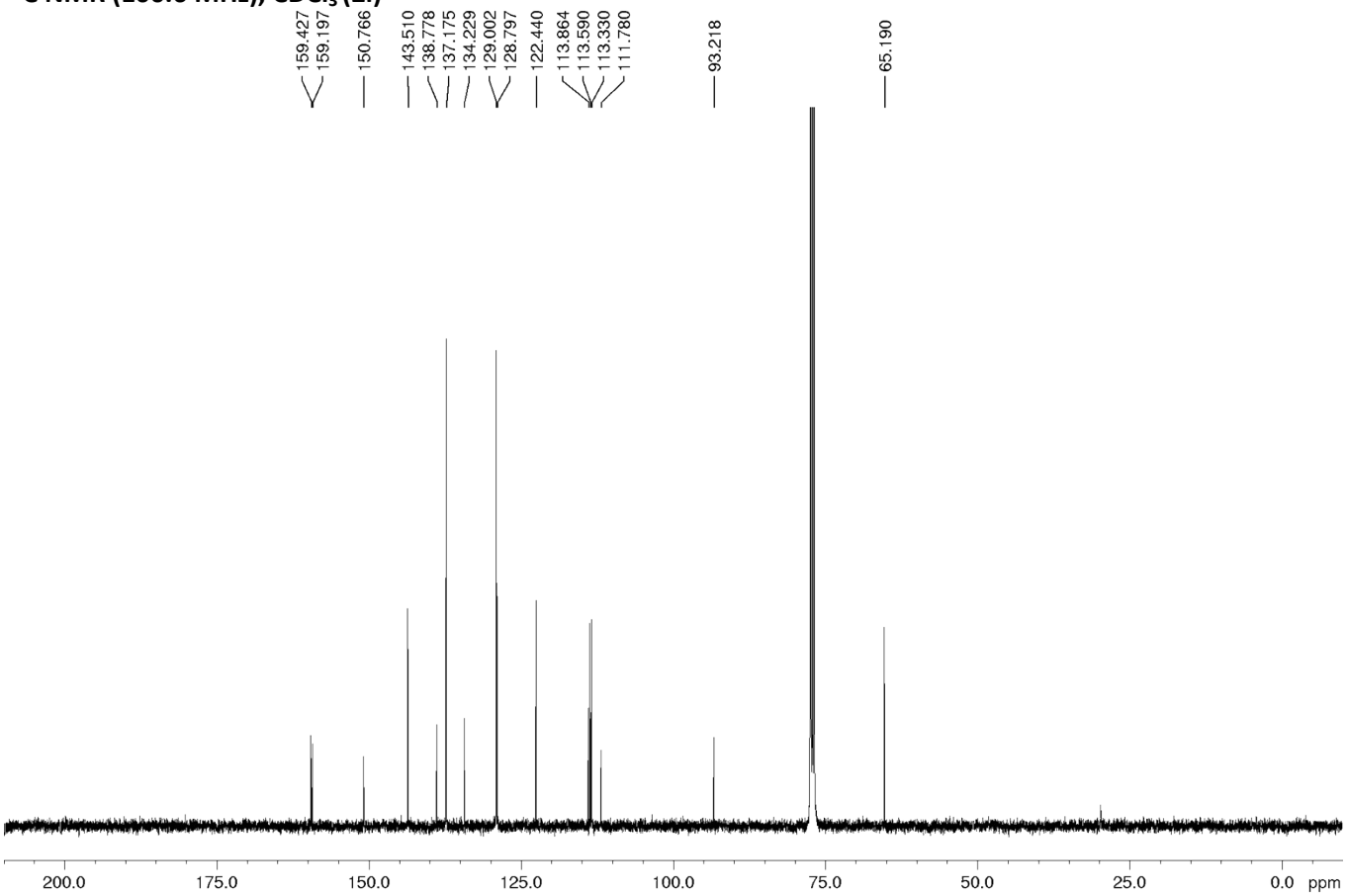


^{1}H NMR (400.13 MHz), $CDCl_3$ (2i)

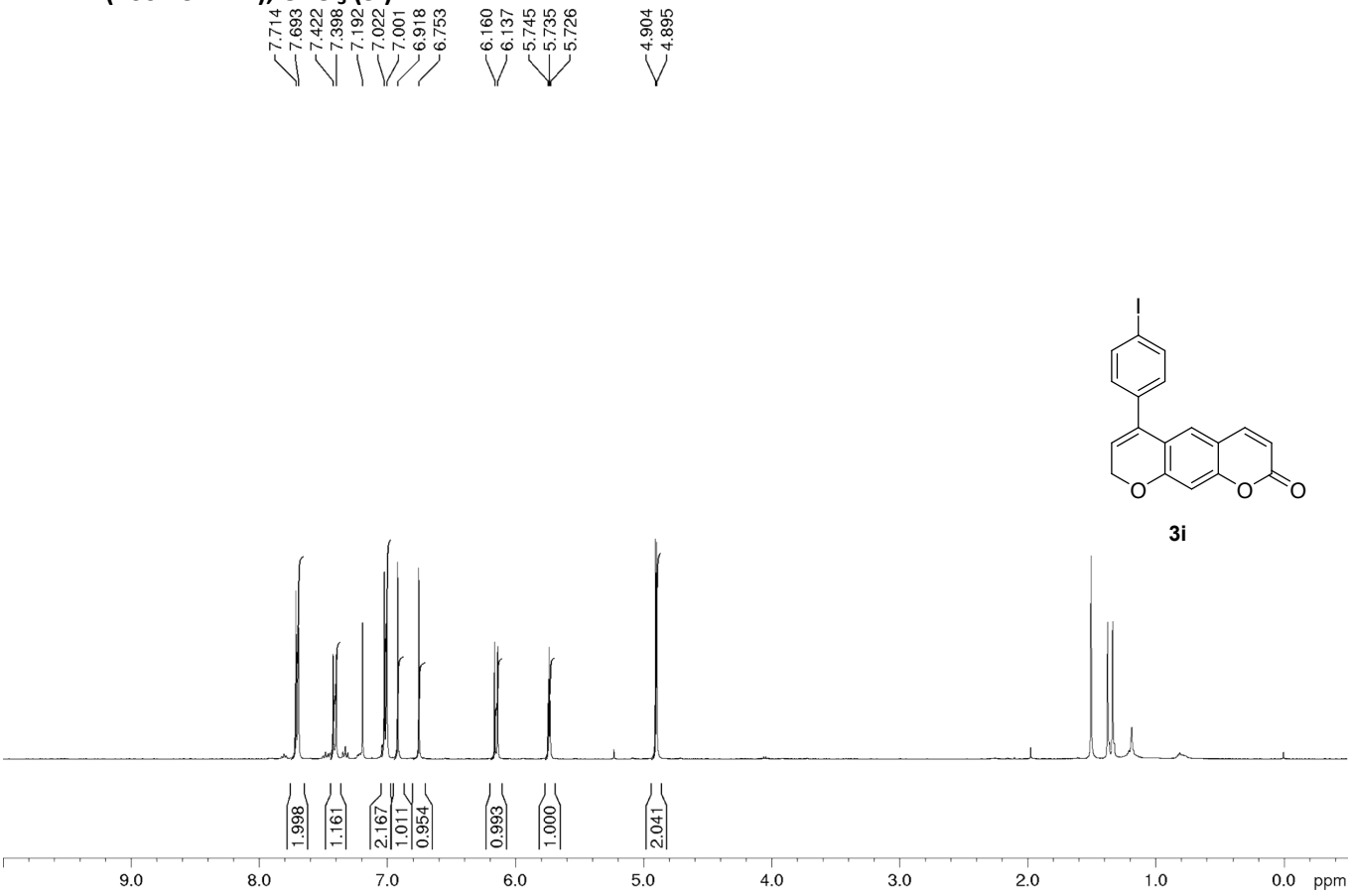


2i

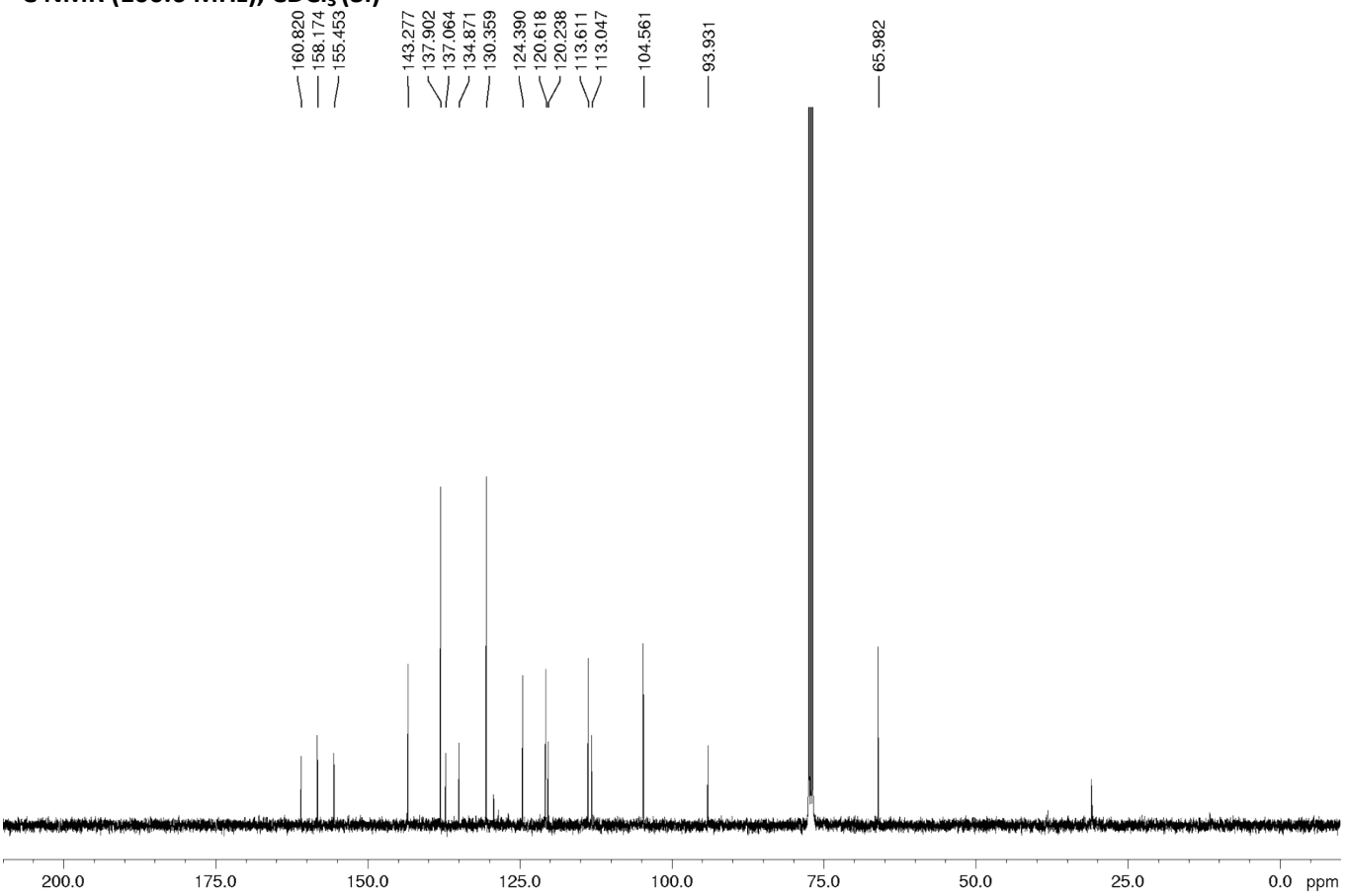
^{13}C NMR (100.6 MHz), $CDCl_3$ (2i)



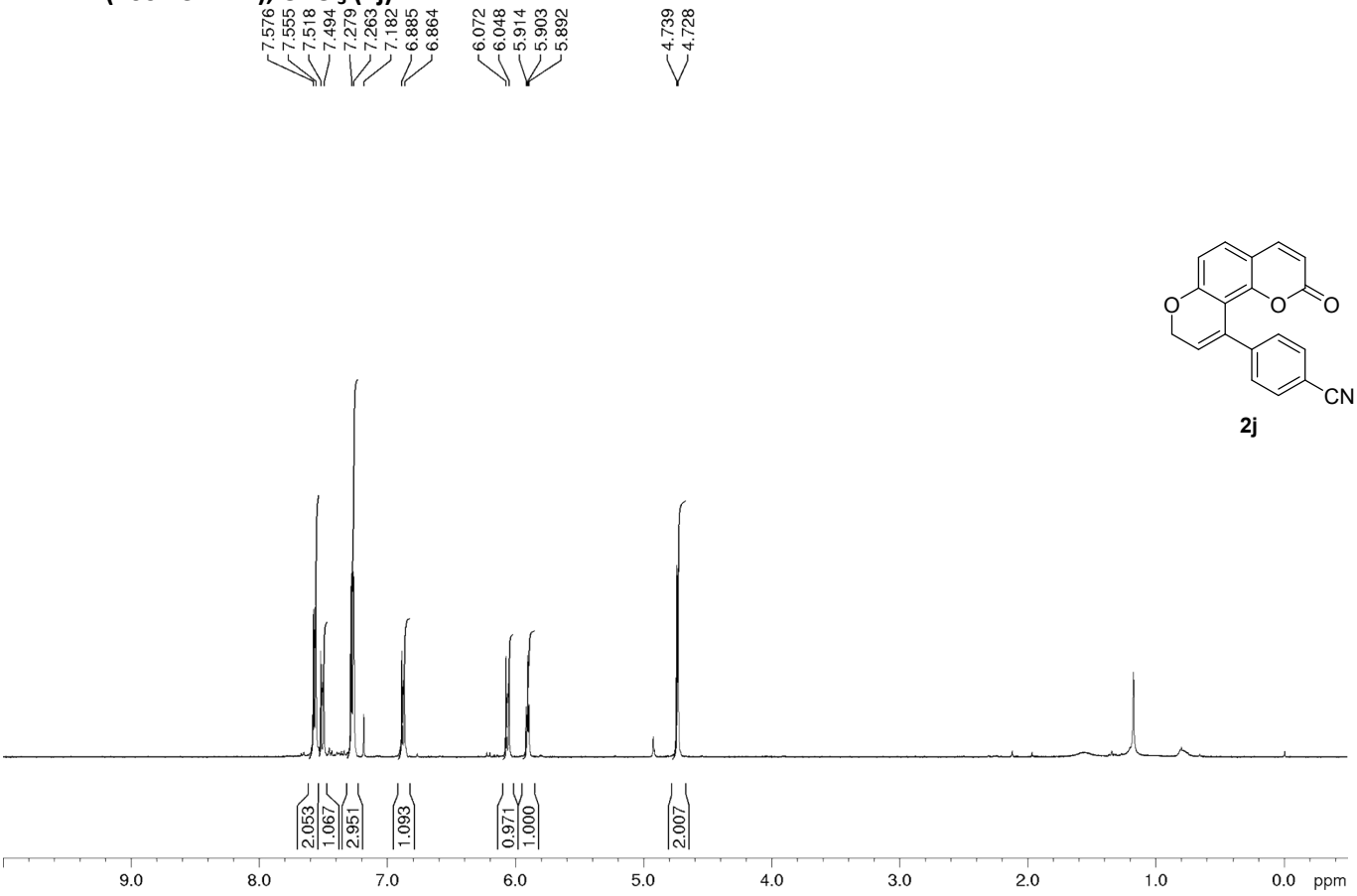
^{1}H NMR (400.13 MHz), $CDCl_3$ (3i)



^{13}C NMR (100.6 MHz), $CDCl_3$ (3i)

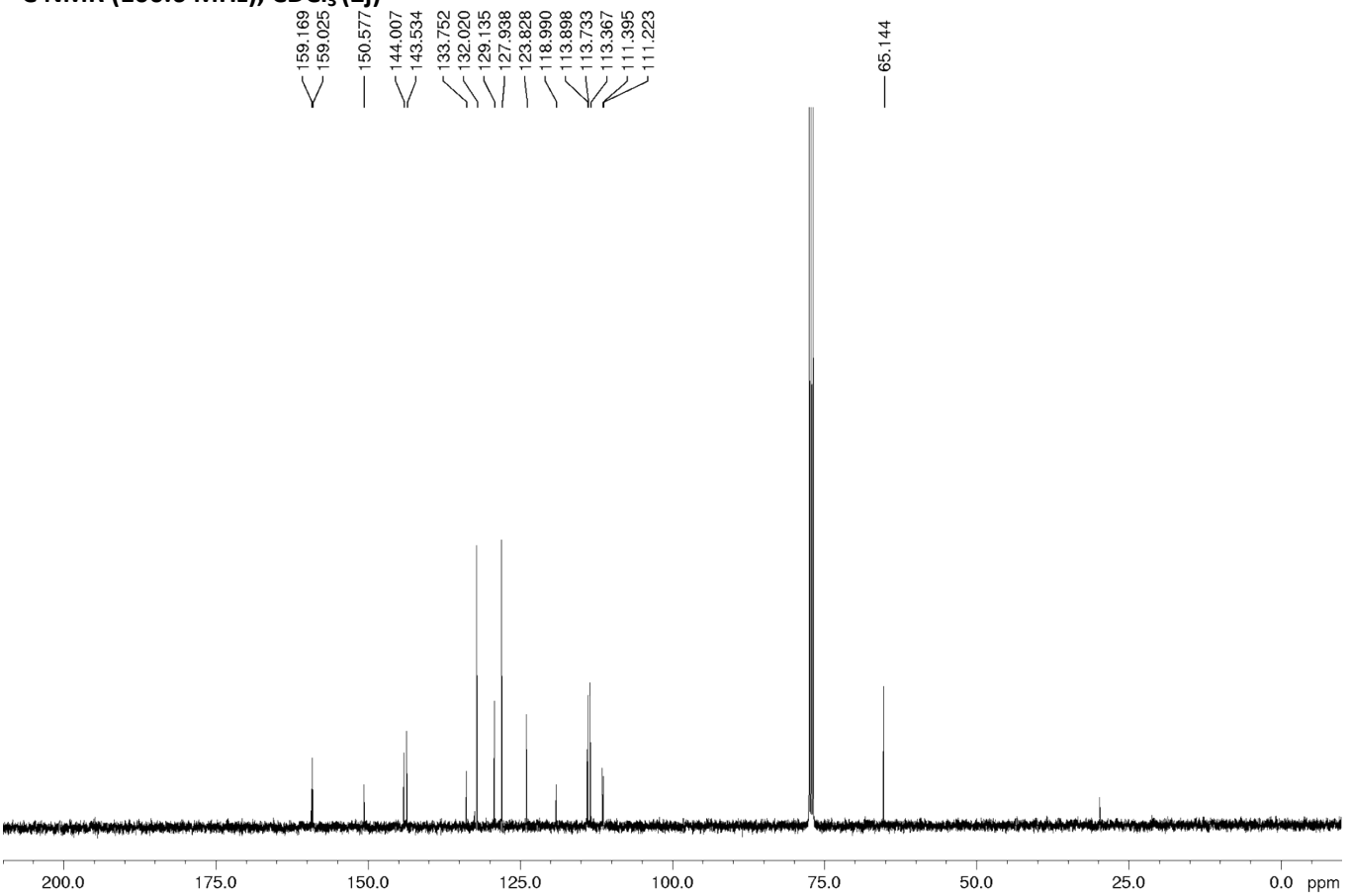


^{1}H NMR (400.13 MHz), $CDCl_3$ (2j)

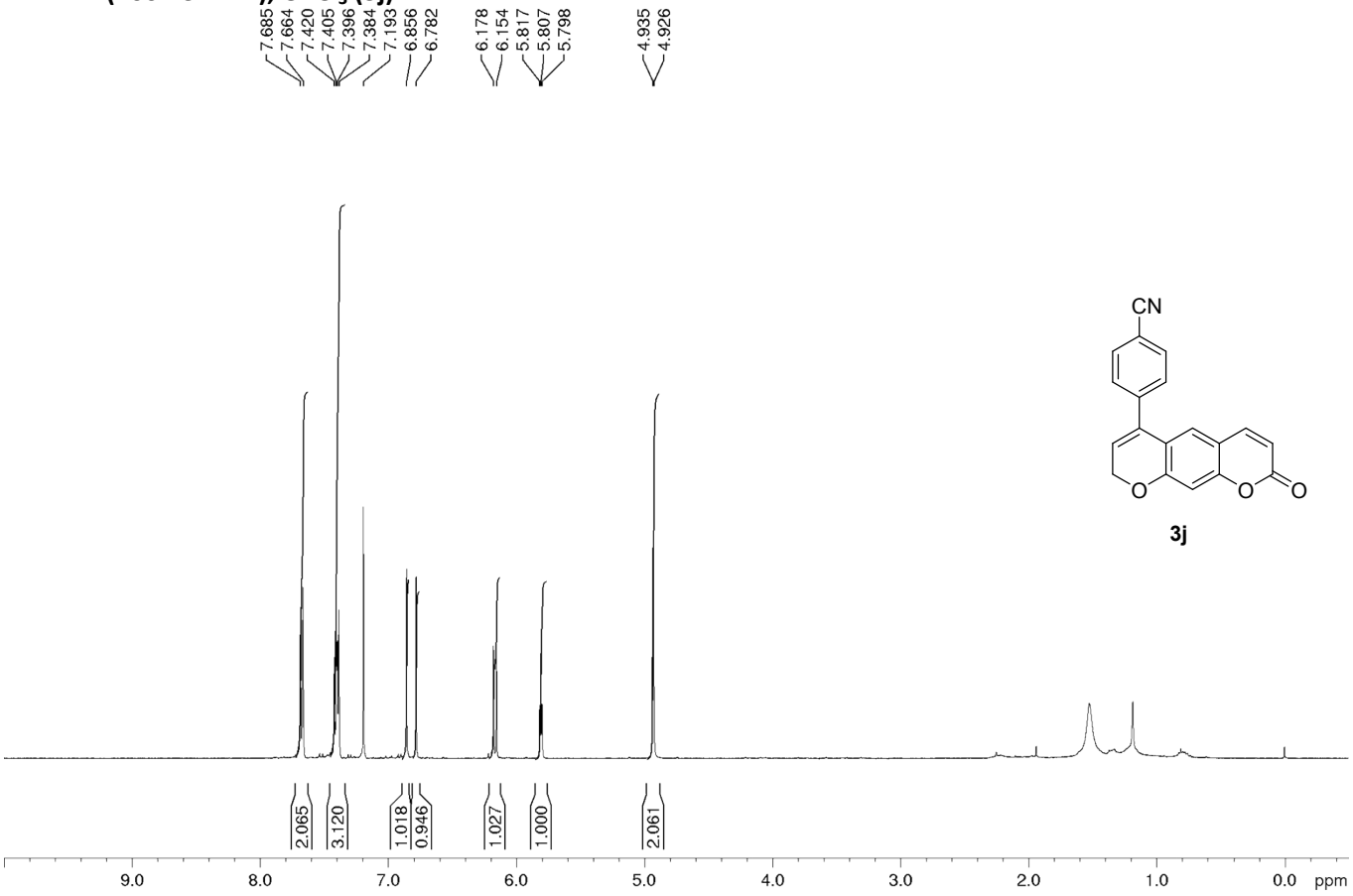


2j

^{13}C NMR (100.6 MHz), $CDCl_3$ (2j)

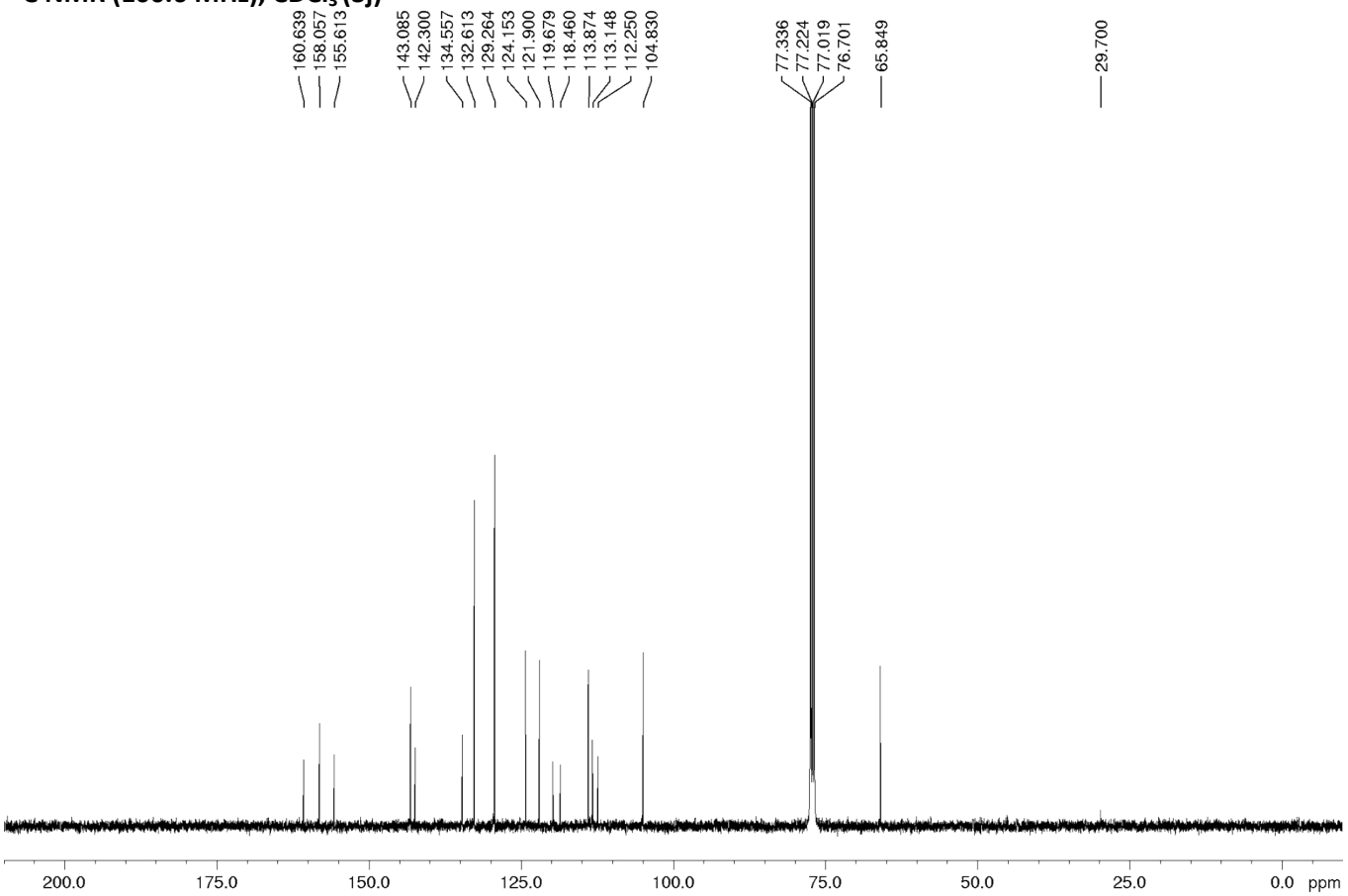


^{1}H NMR (400.13 MHz), $CDCl_3$ (3j)

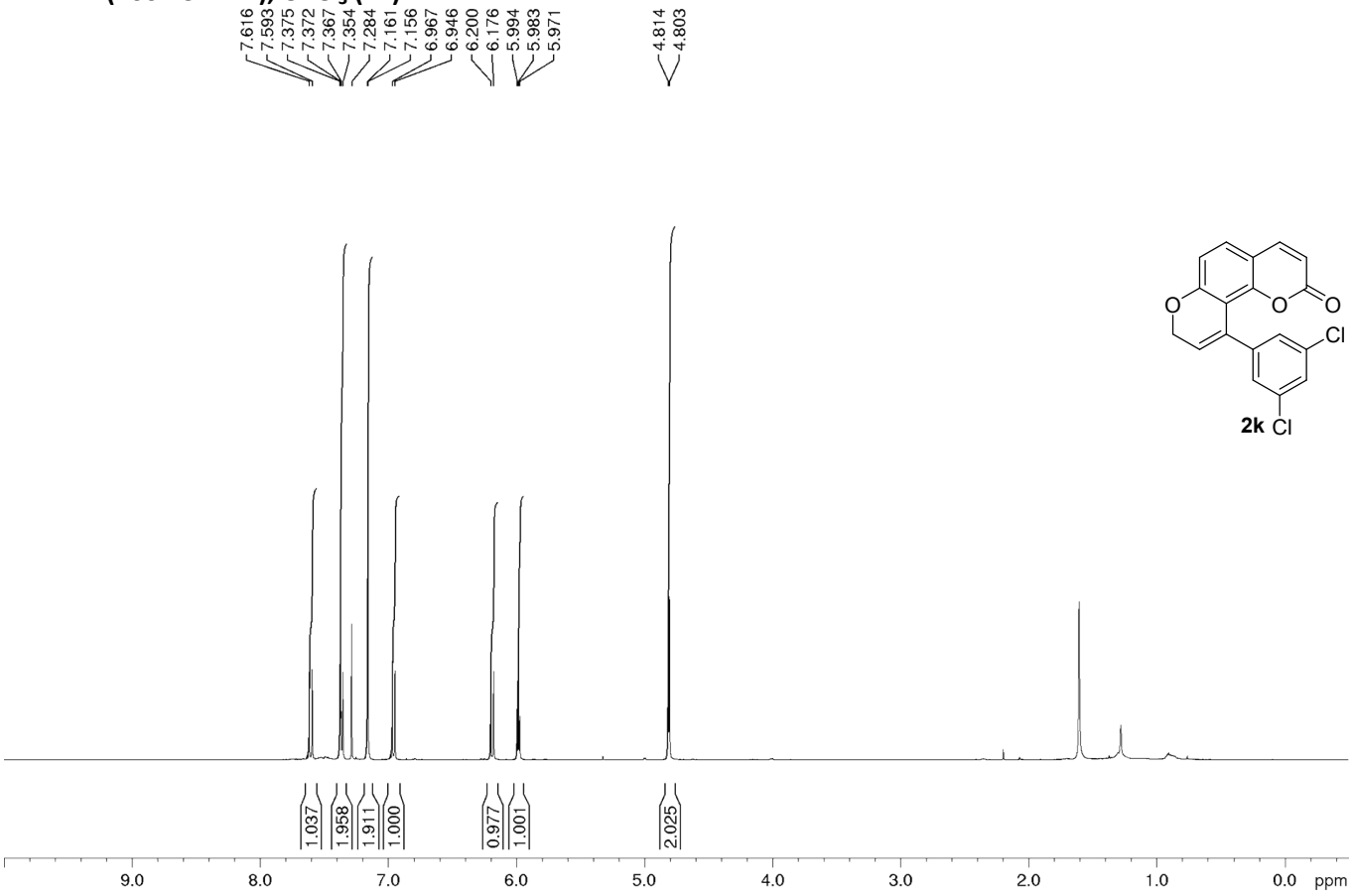


3j

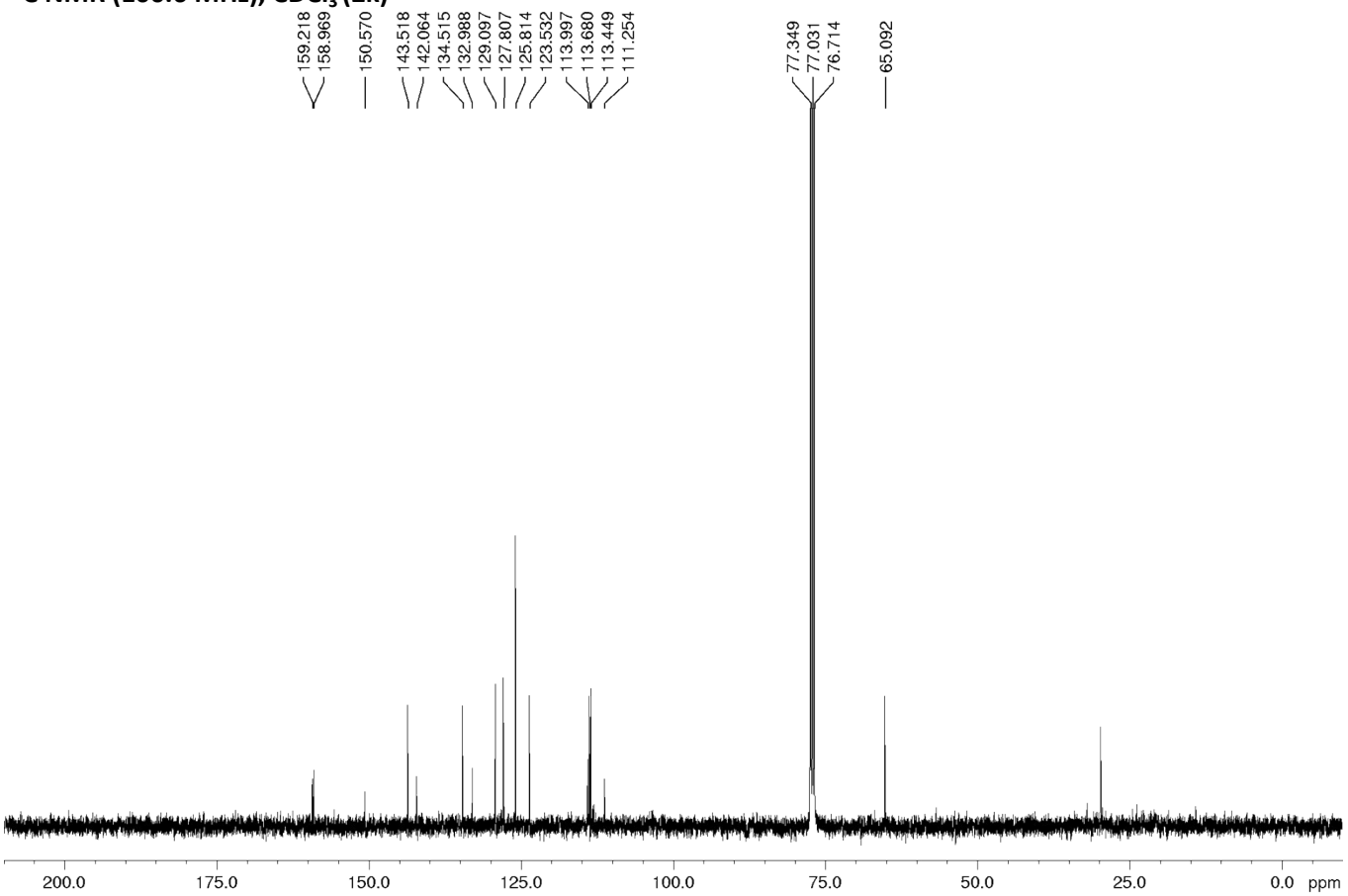
^{13}C NMR (100.6 MHz), $CDCl_3$ (3j)



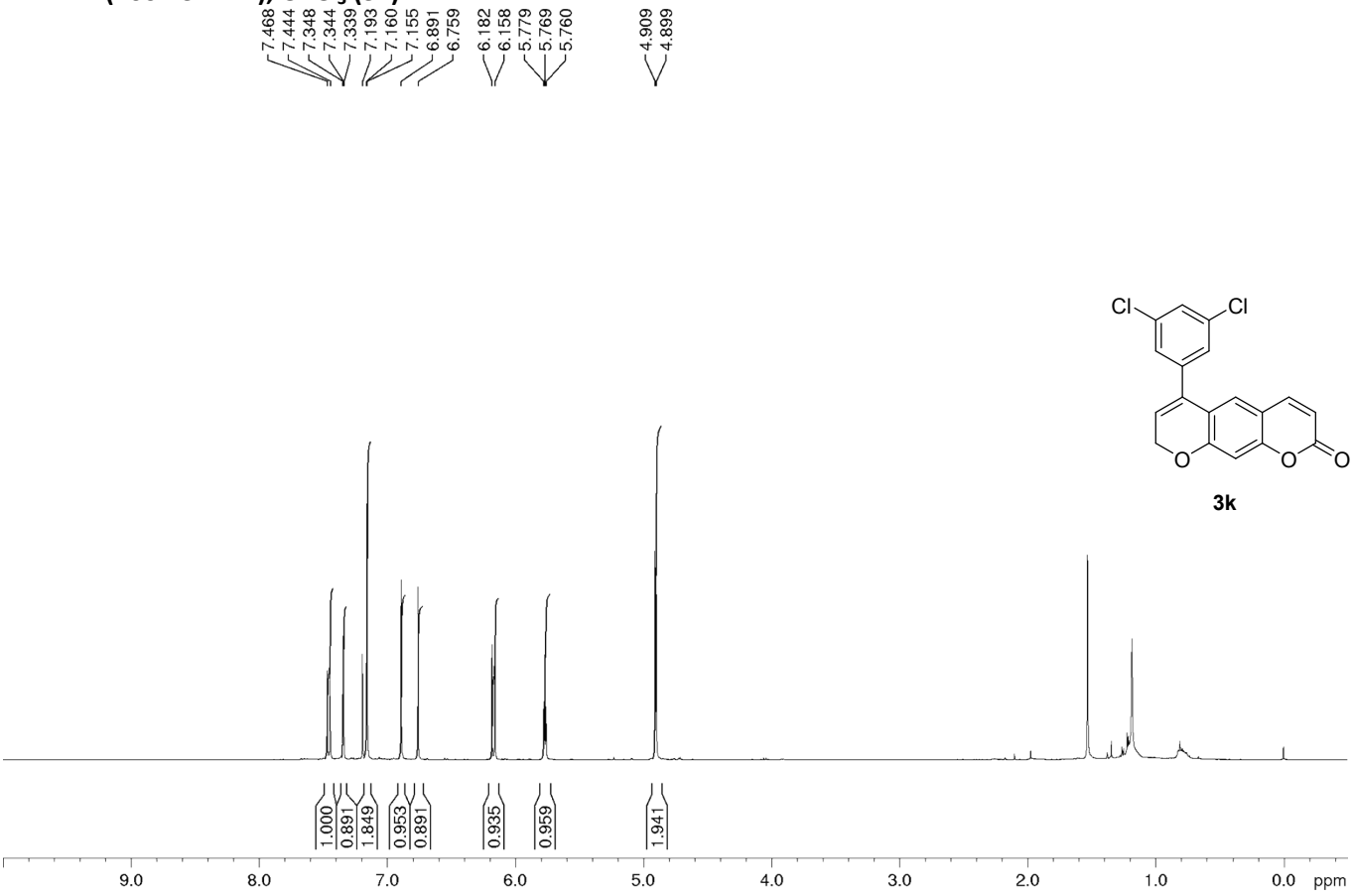
^{1}H NMR (400.13 MHz), $CDCl_3$ (2k)



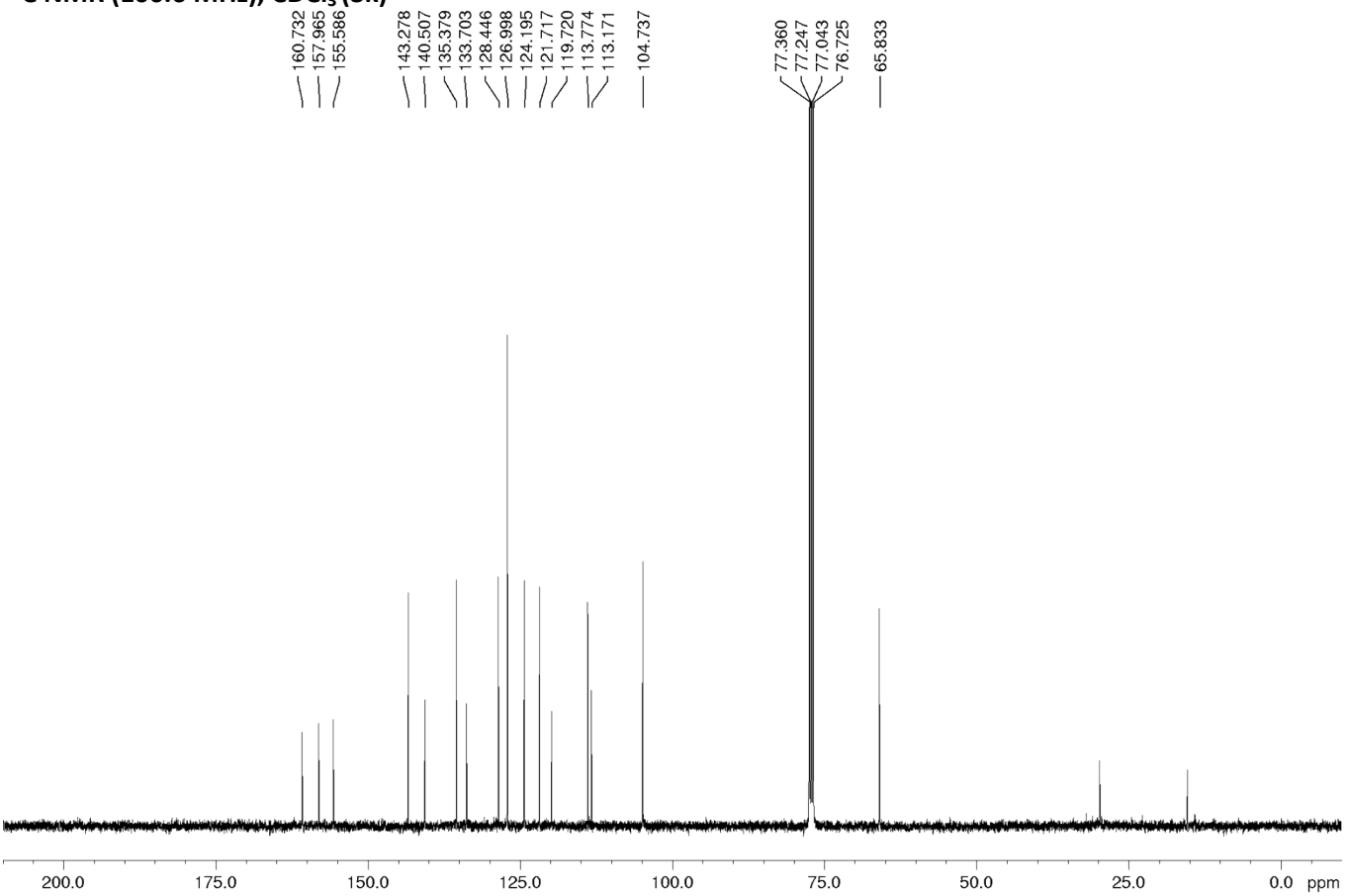
^{13}C NMR (100.6 MHz), $CDCl_3$ (2k)



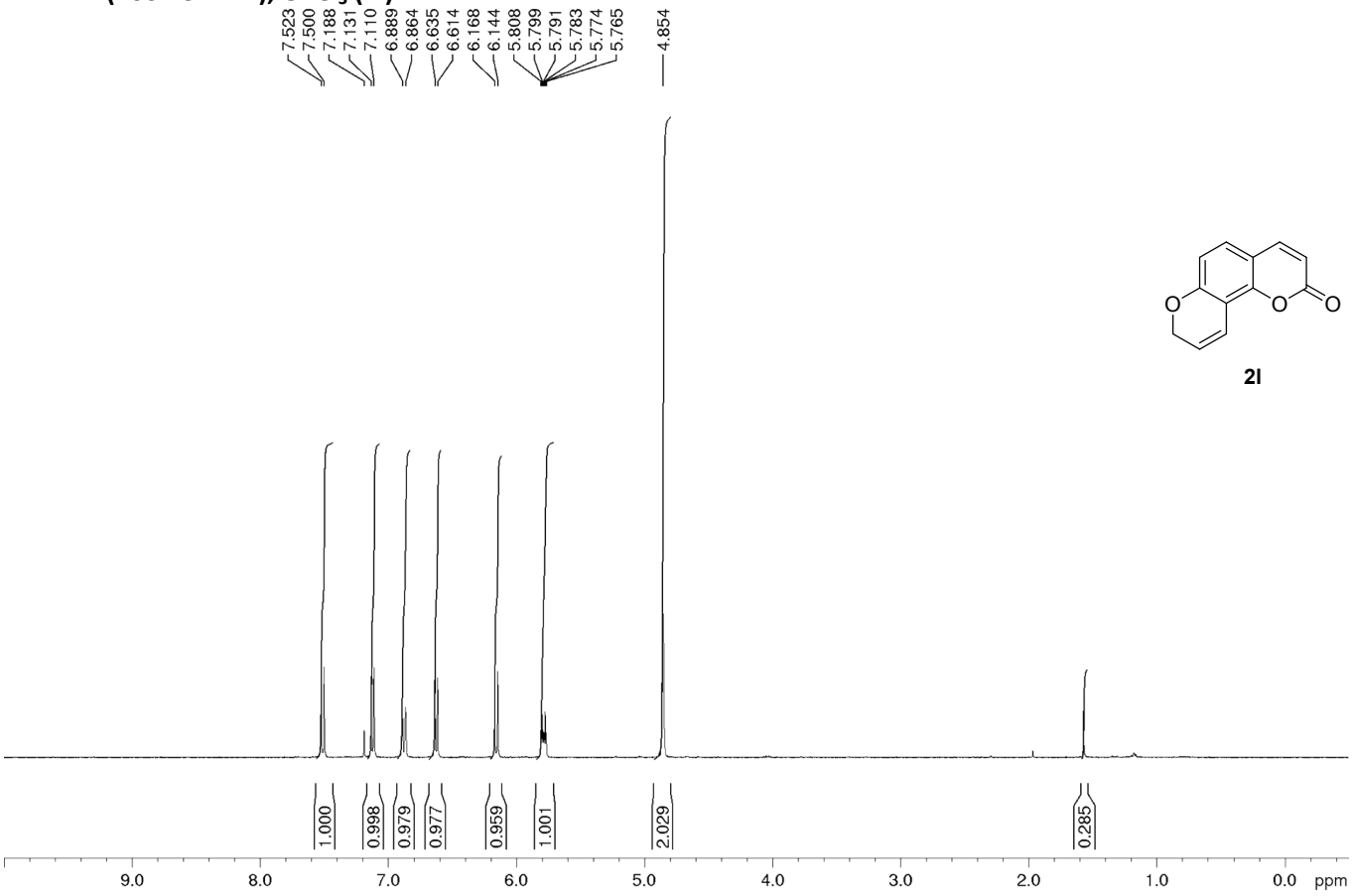
^{1}H NMR (400.13 MHz), $CDCl_3$ (3k)



^{13}C NMR (100.6 MHz), $CDCl_3$ (3k)

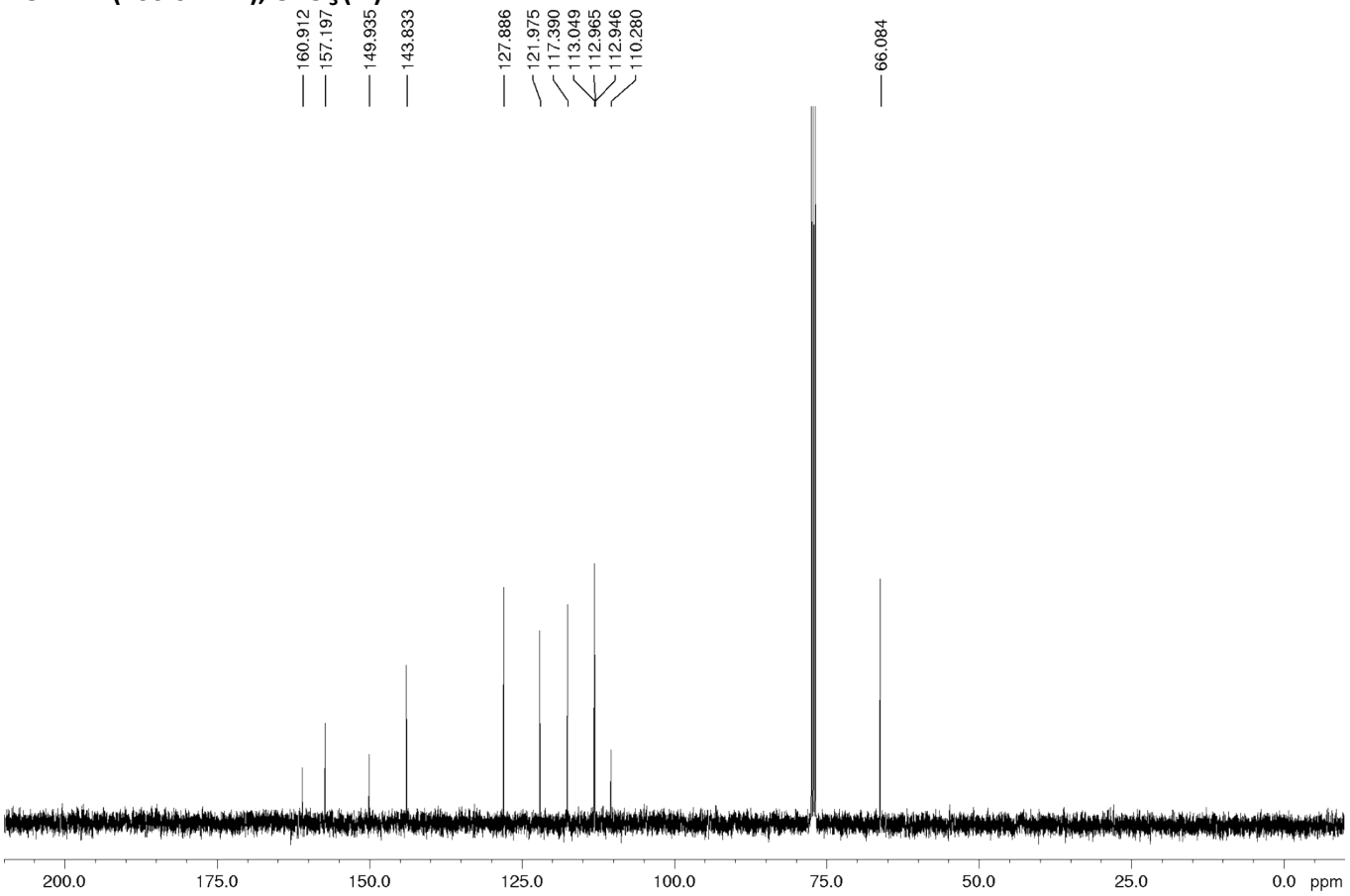


^{1}H NMR (400.13 MHz), $CDCl_3$ (2l)

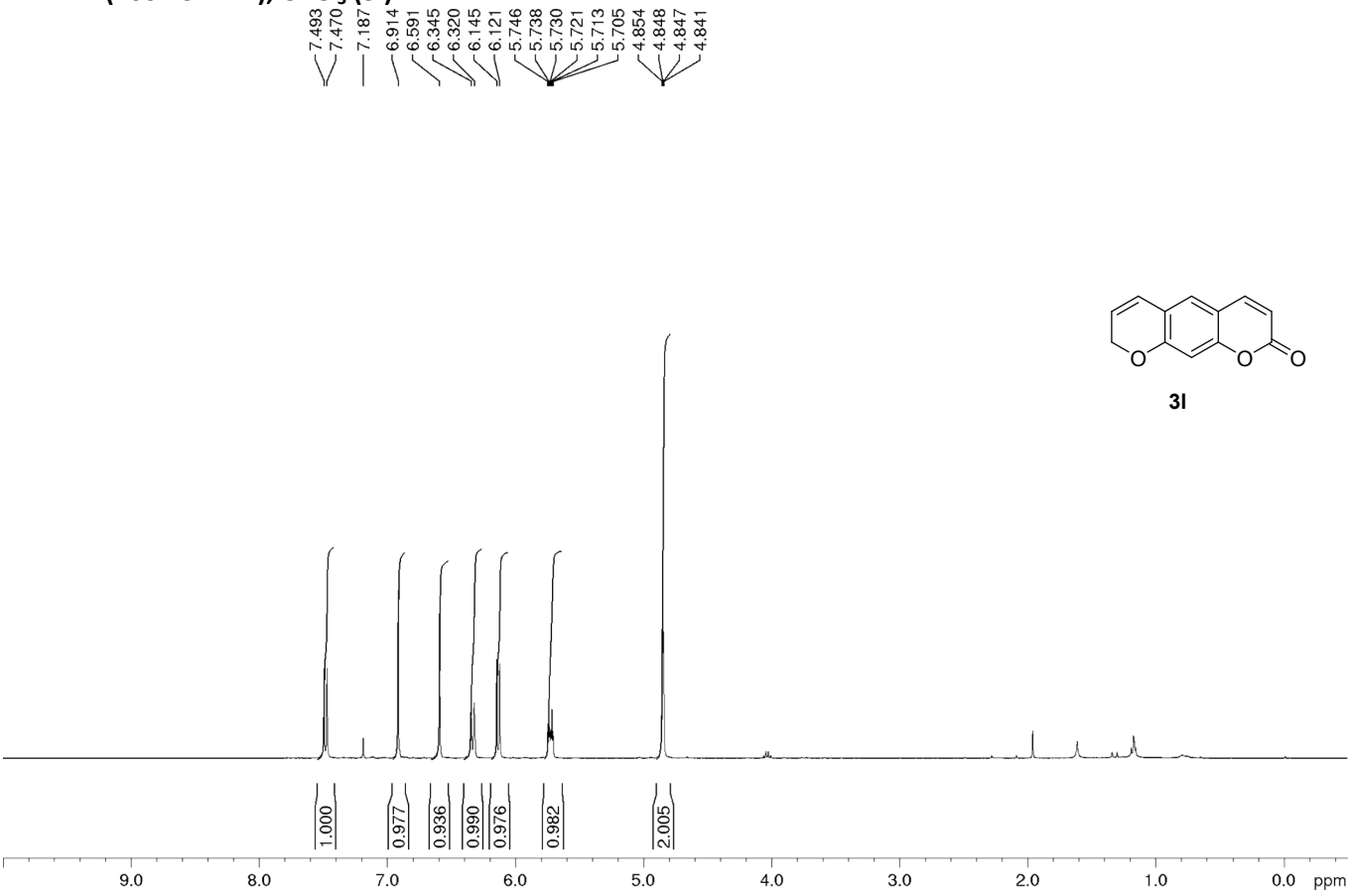


2l

^{13}C NMR (100.6 MHz), $CDCl_3$ (2l)

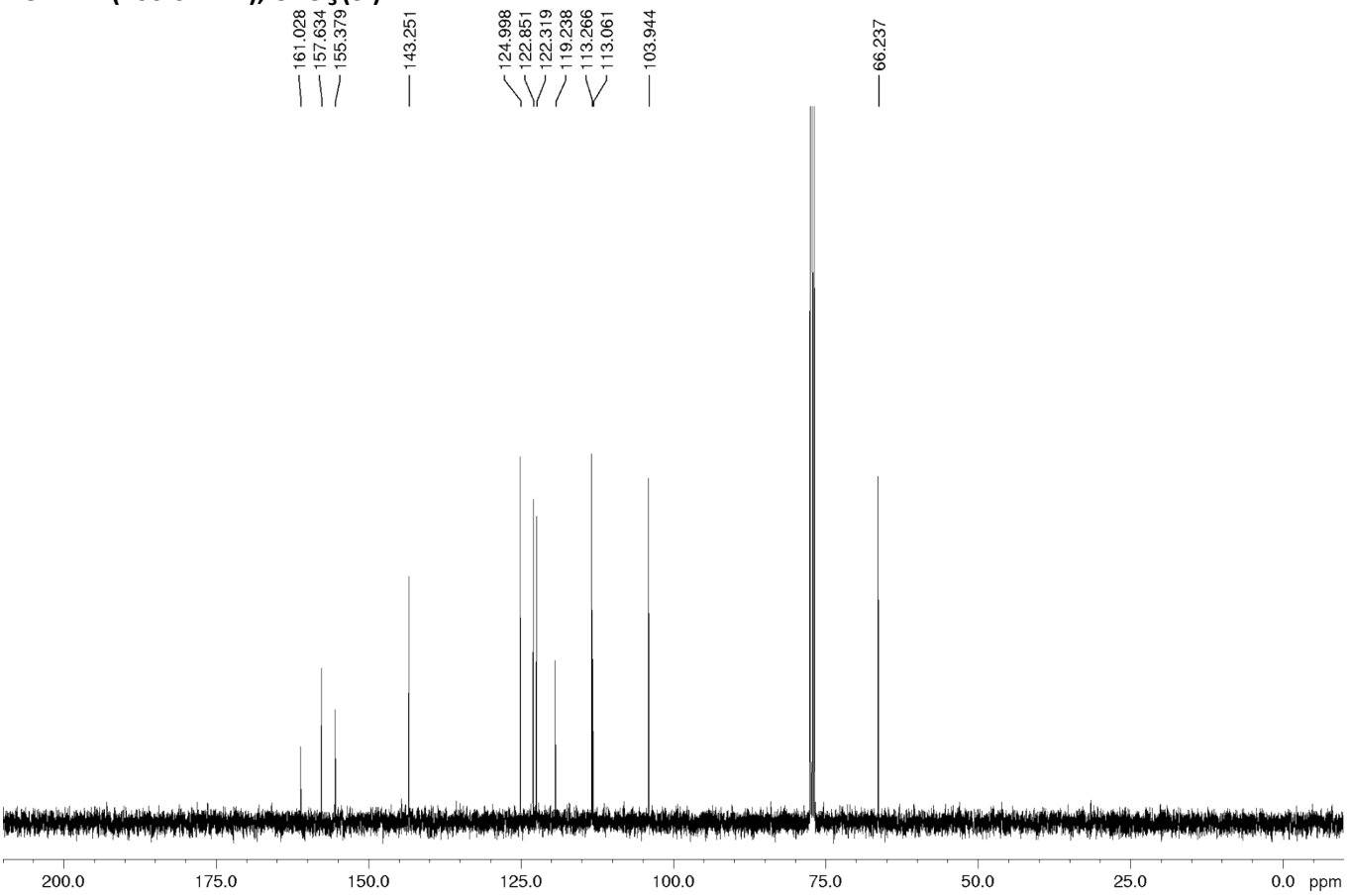


^{1}H NMR (400.13 MHz), $CDCl_3$ (3l)

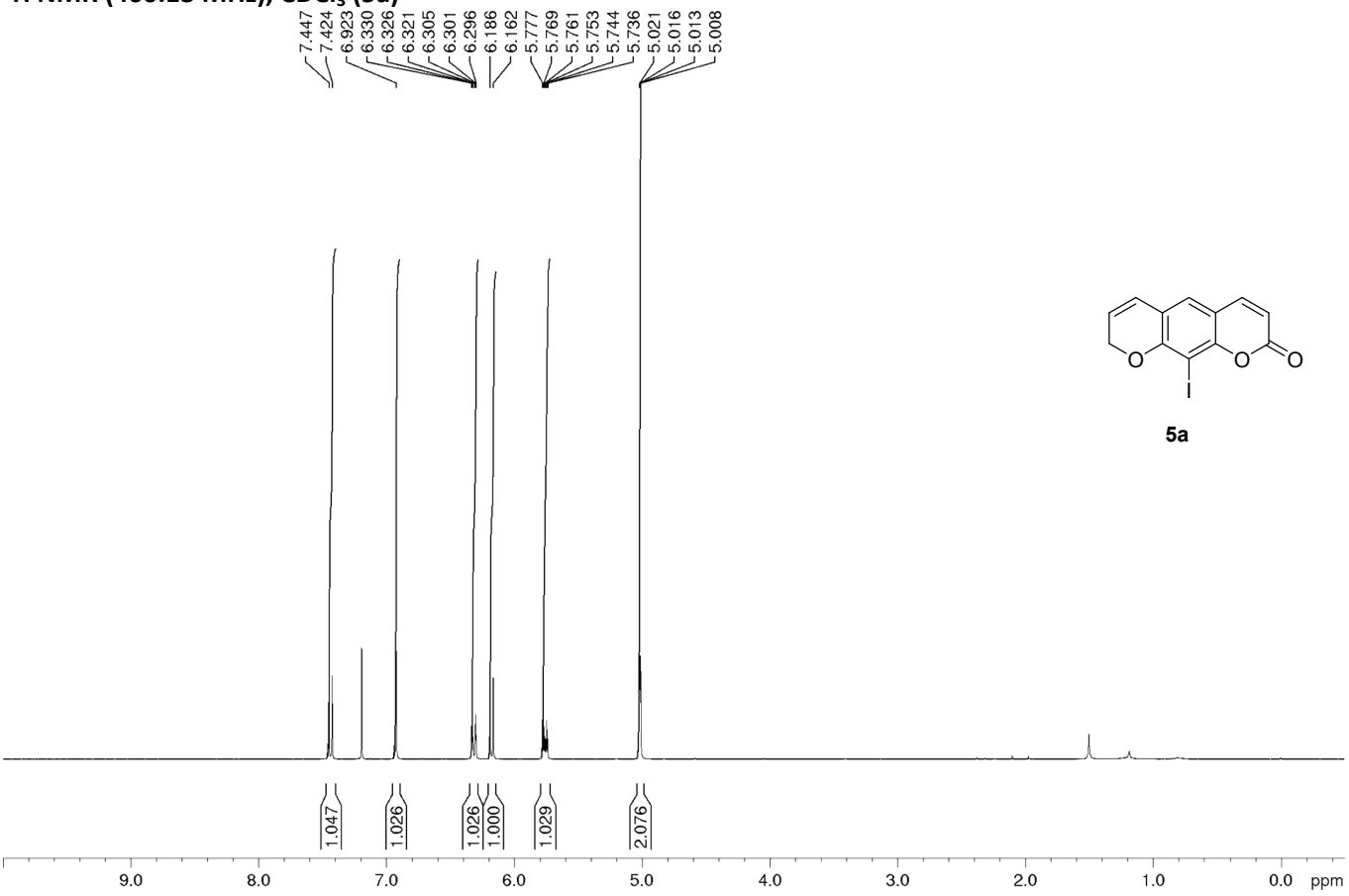


3l

^{13}C NMR (100.6 MHz), $CDCl_3$ (3l)

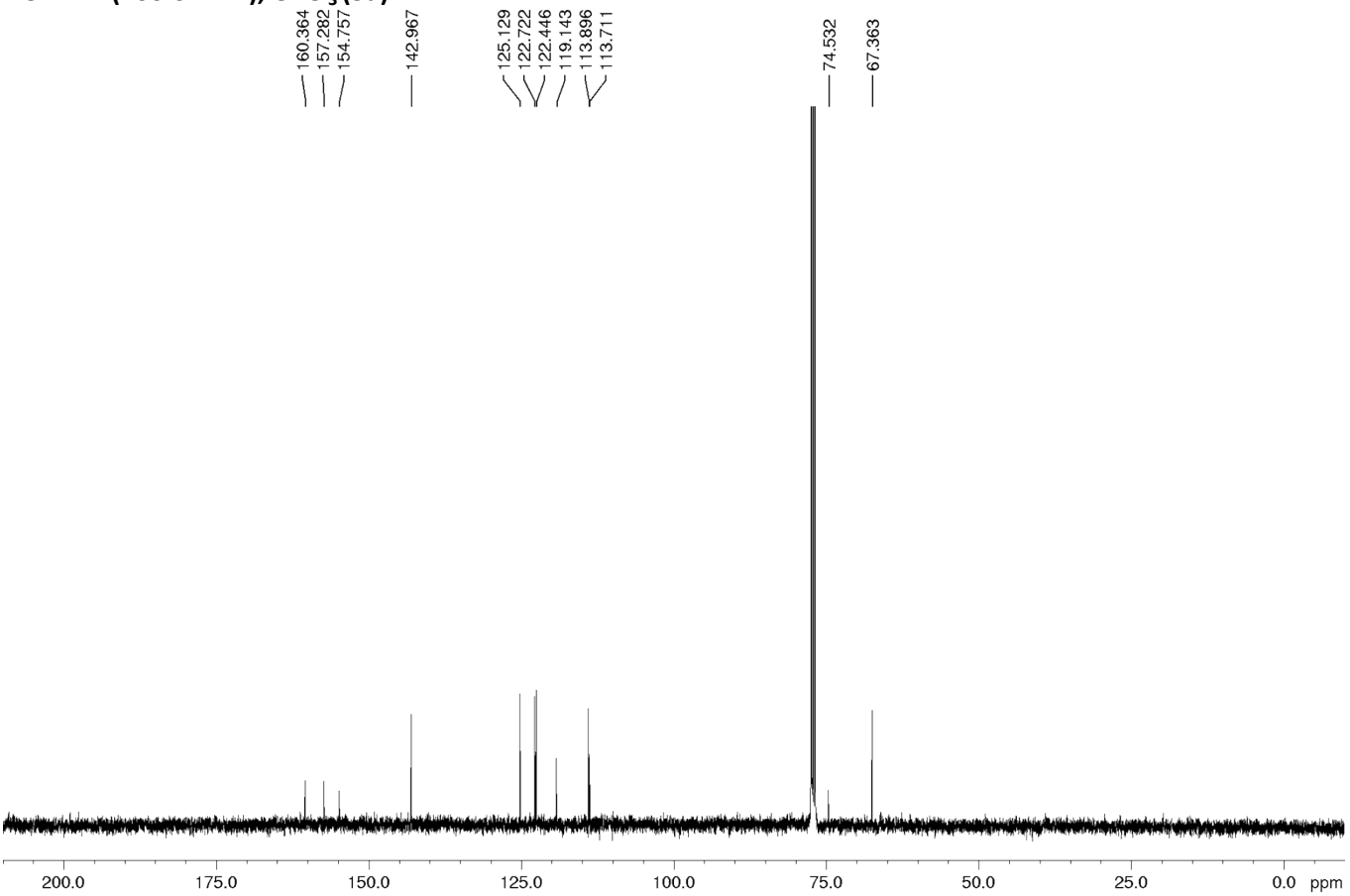


^{1}H NMR (400.13 MHz), $CDCl_3$ (5a)

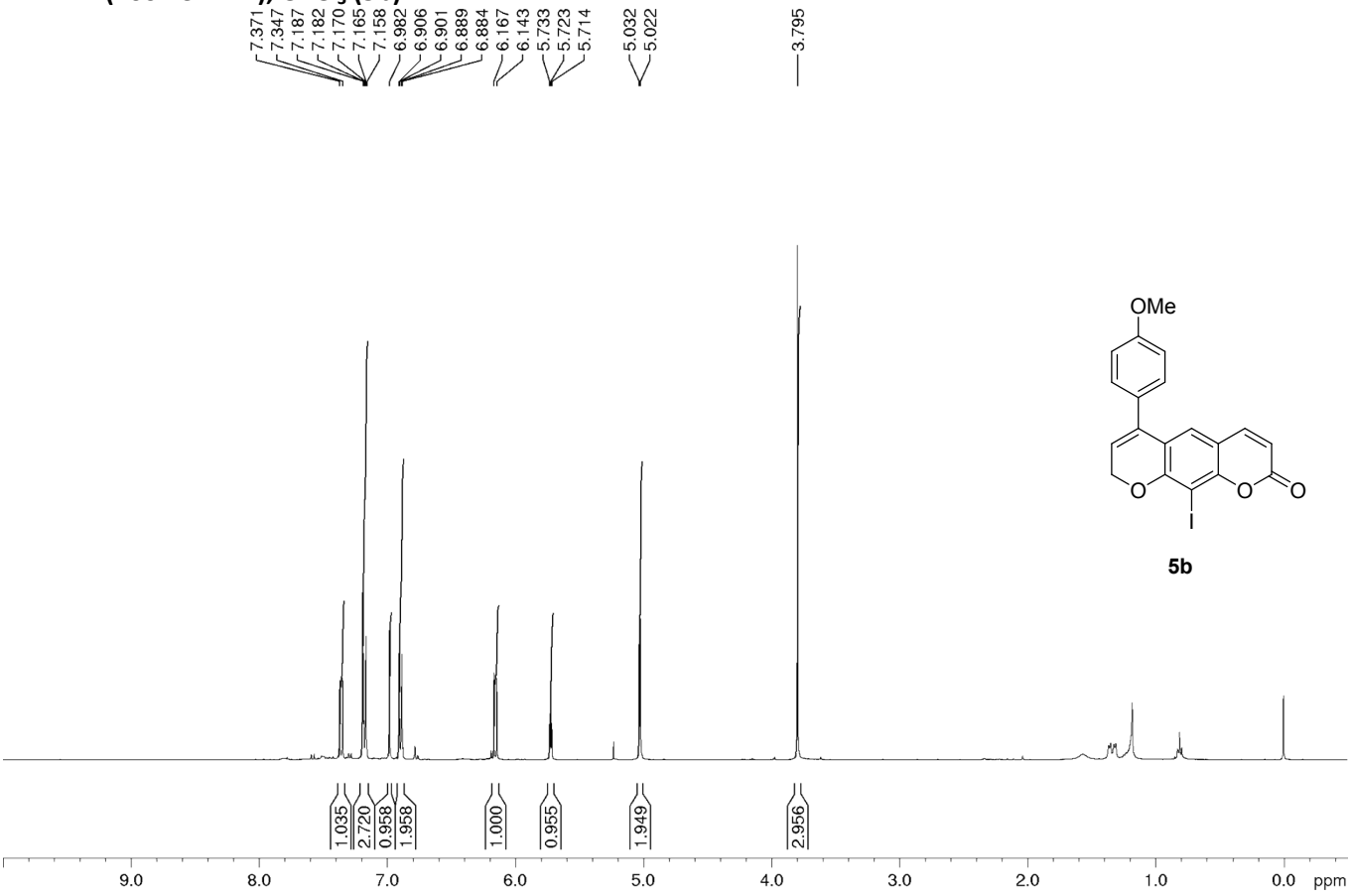


5a

^{13}C NMR (100.6 MHz), $CDCl_3$ (5a)

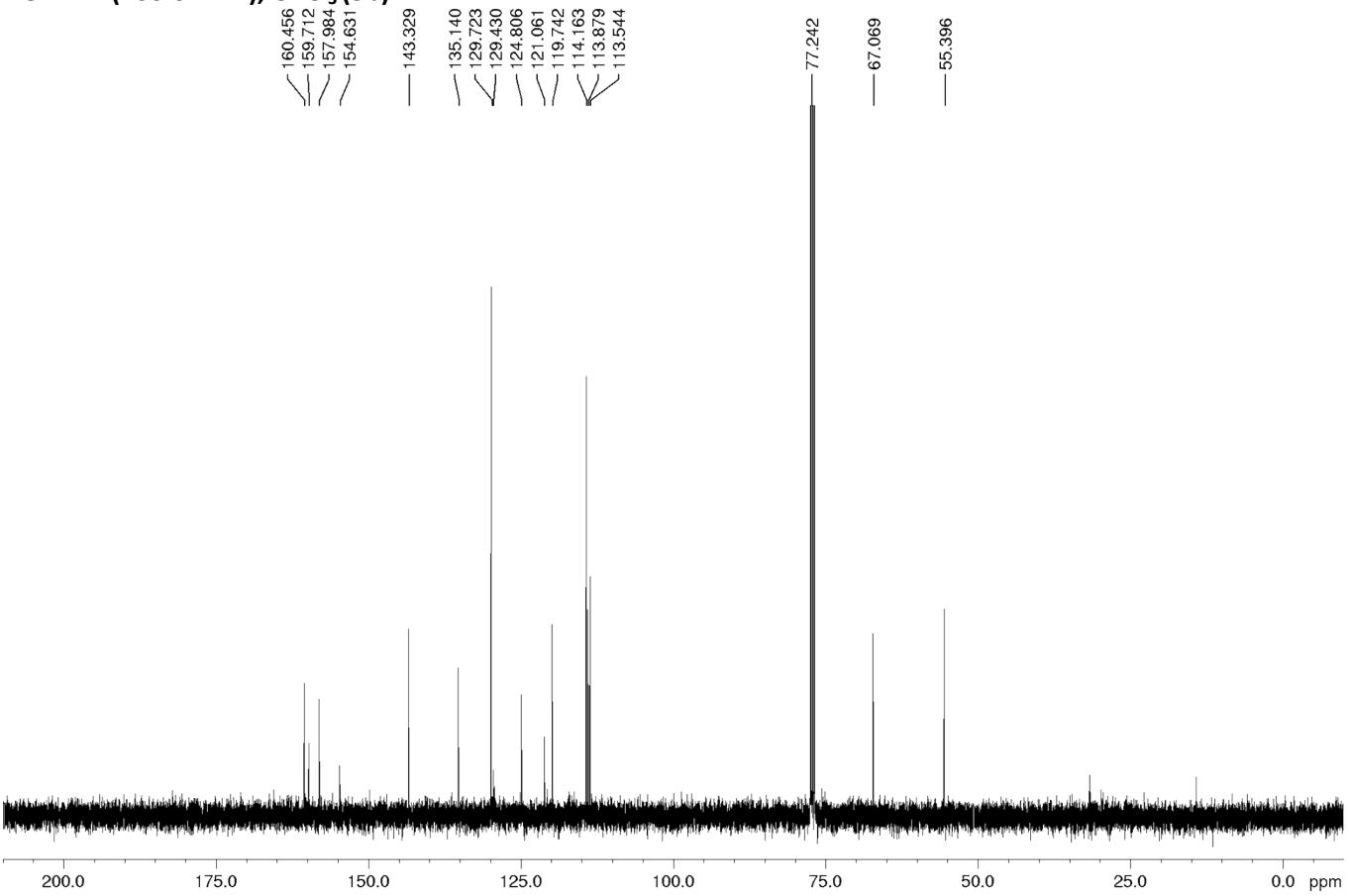


^{1}H NMR (400.13 MHz), $CDCl_3$ (5b)

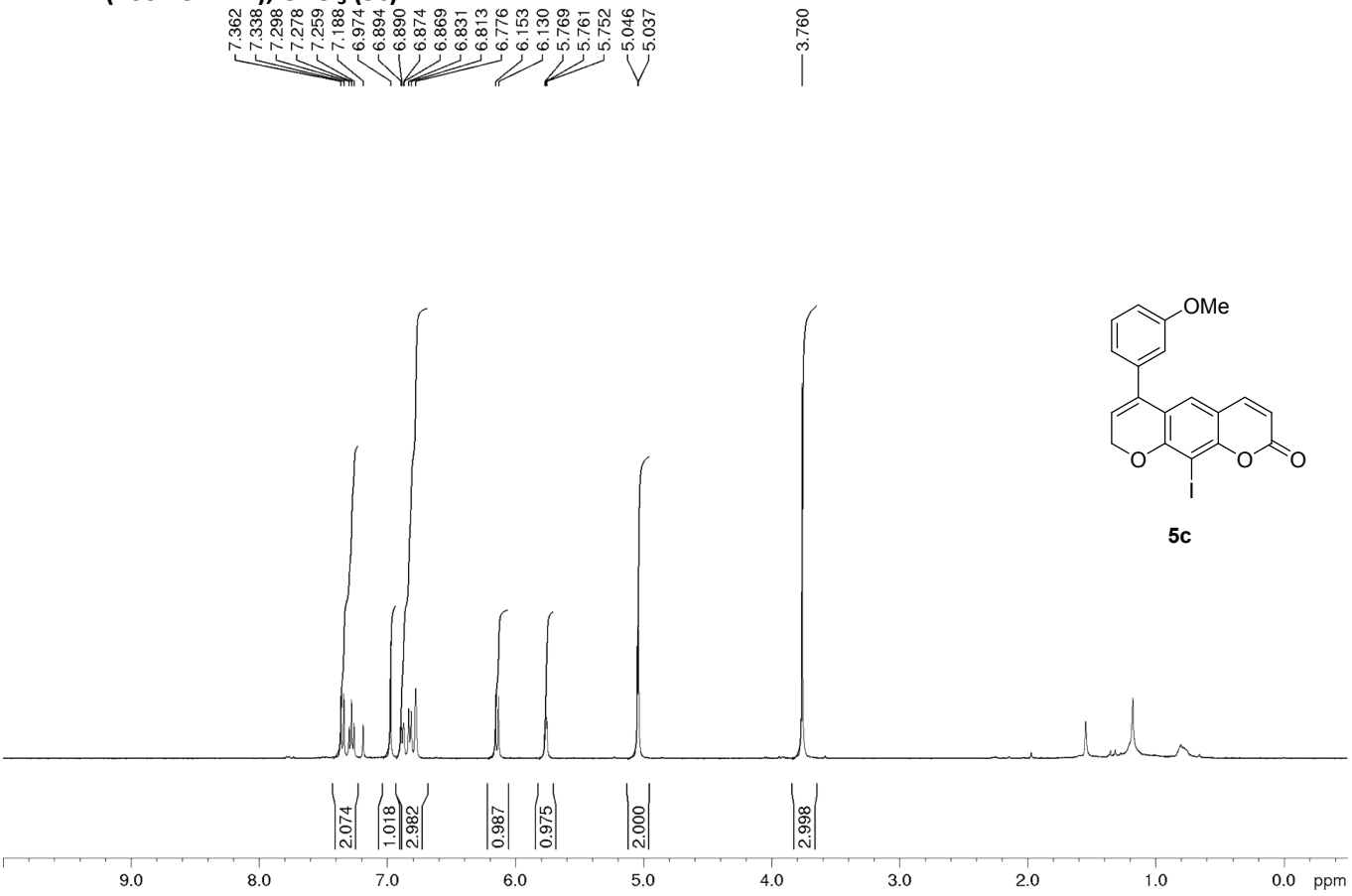


5b

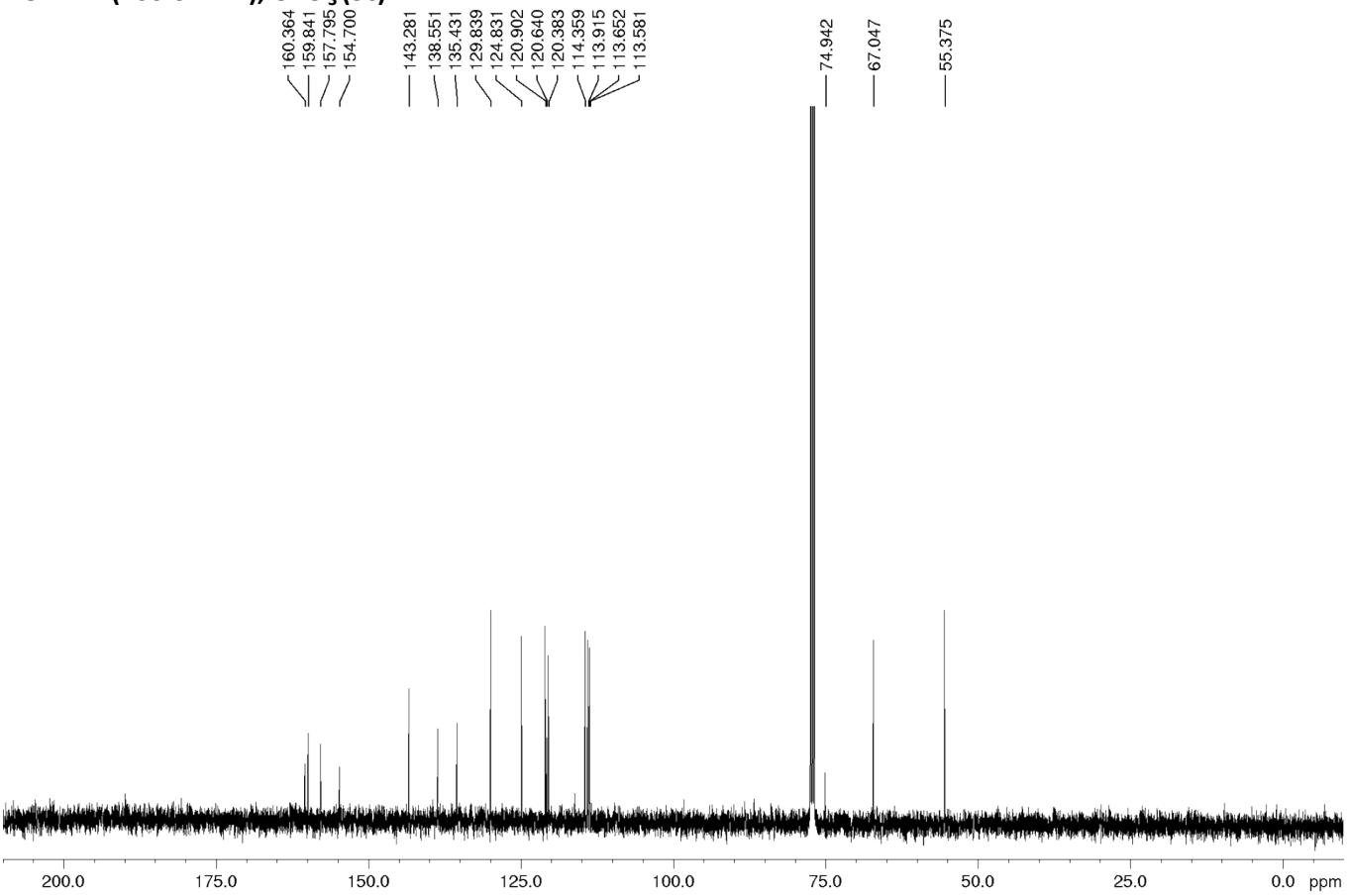
^{13}C NMR (100.6 MHz), $CDCl_3$ (5b)



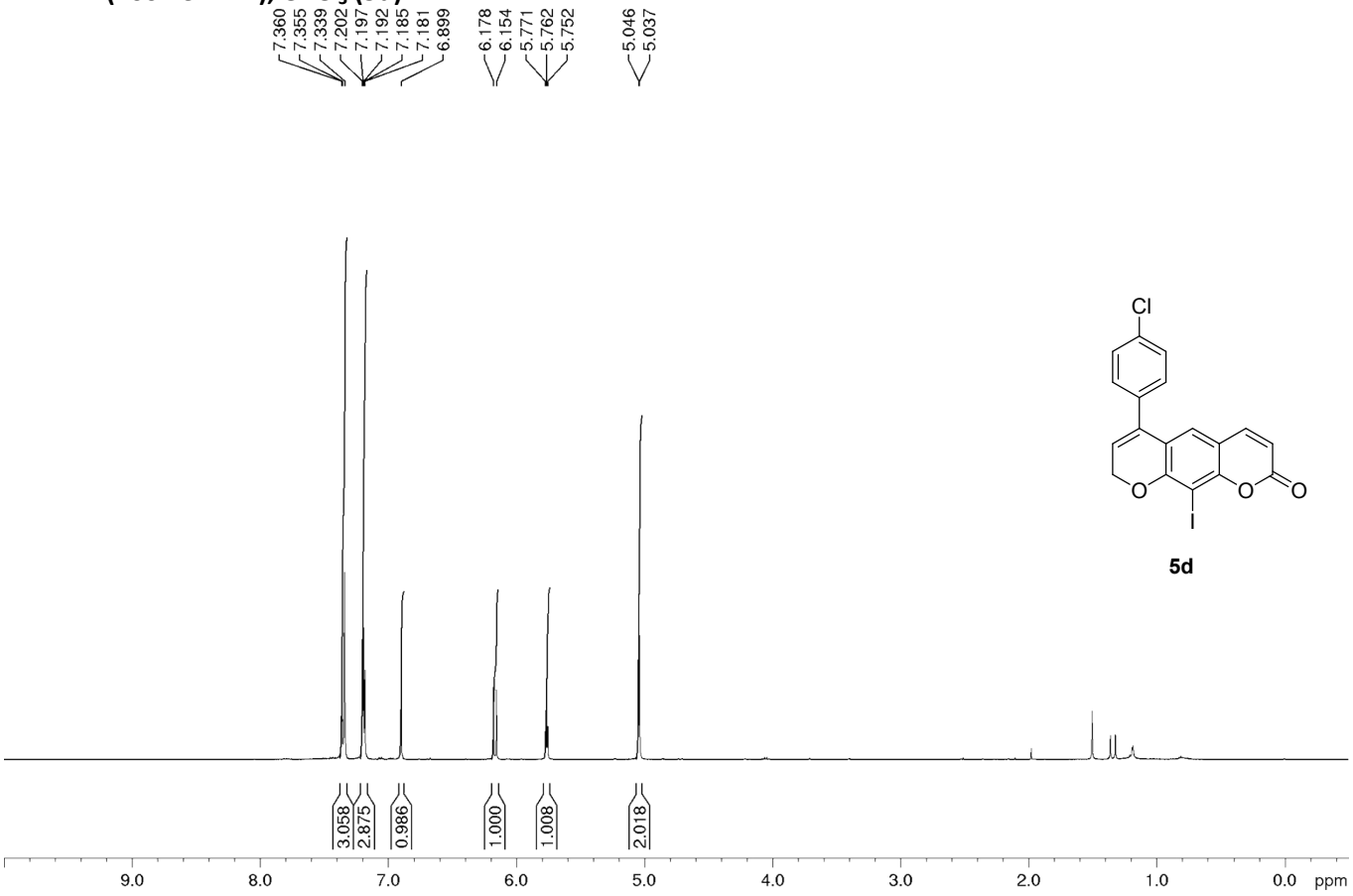
^{1}H NMR (400.13 MHz), $CDCl_3$ (5c)



^{13}C NMR (100.6 MHz), $CDCl_3$ (5c)

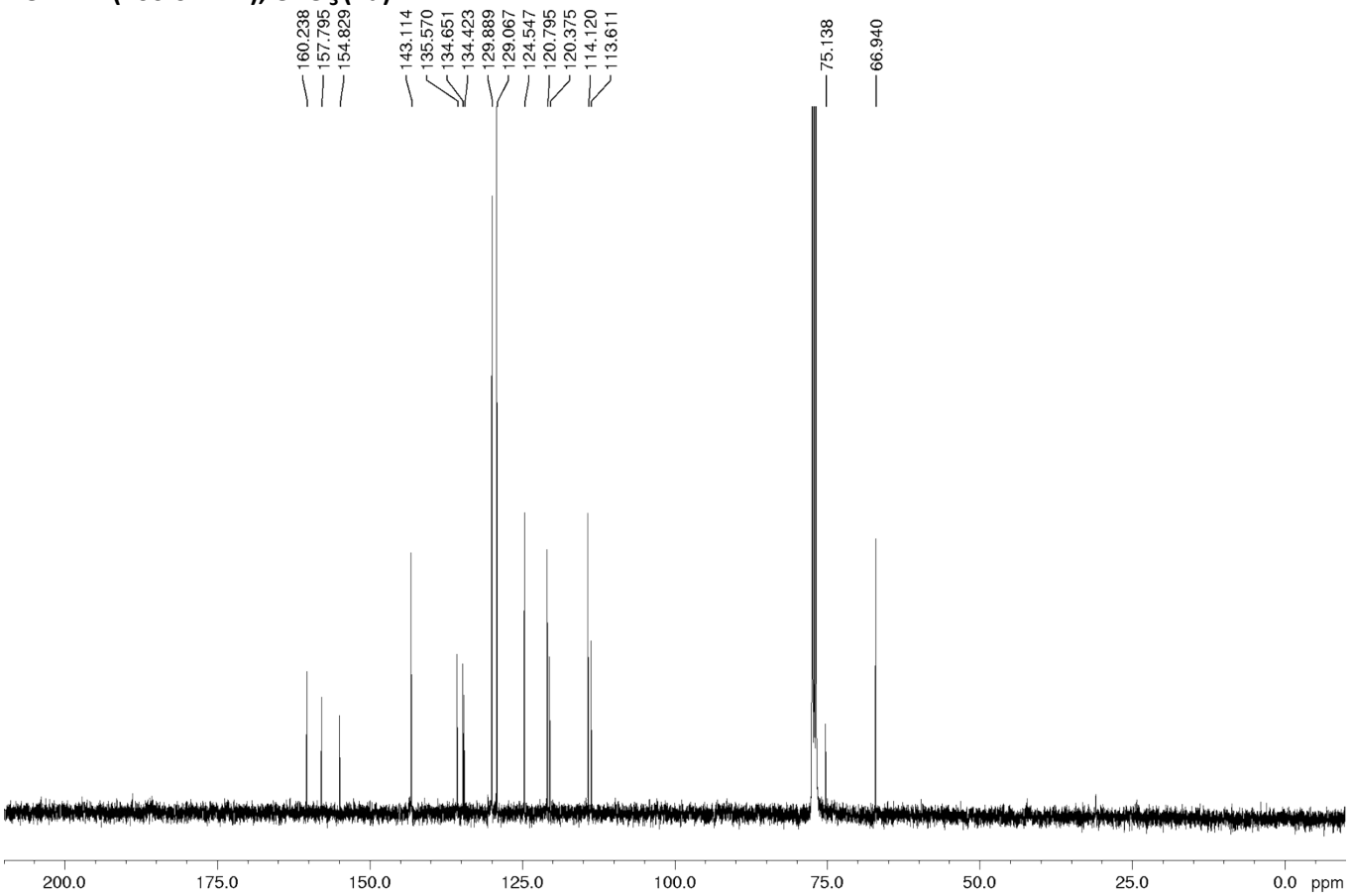


^{1}H NMR (400.13 MHz), $CDCl_3$ (5d)

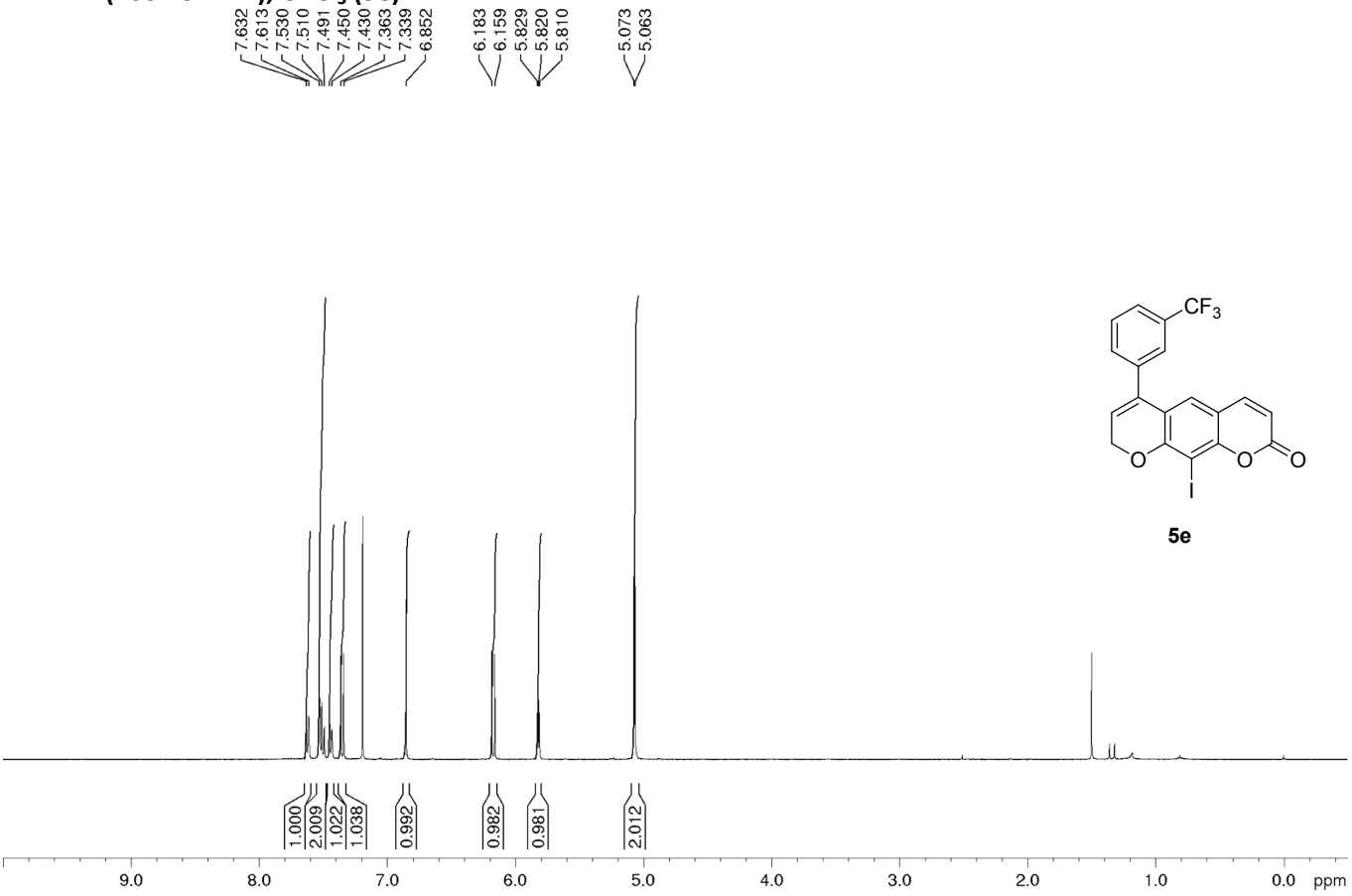


5d

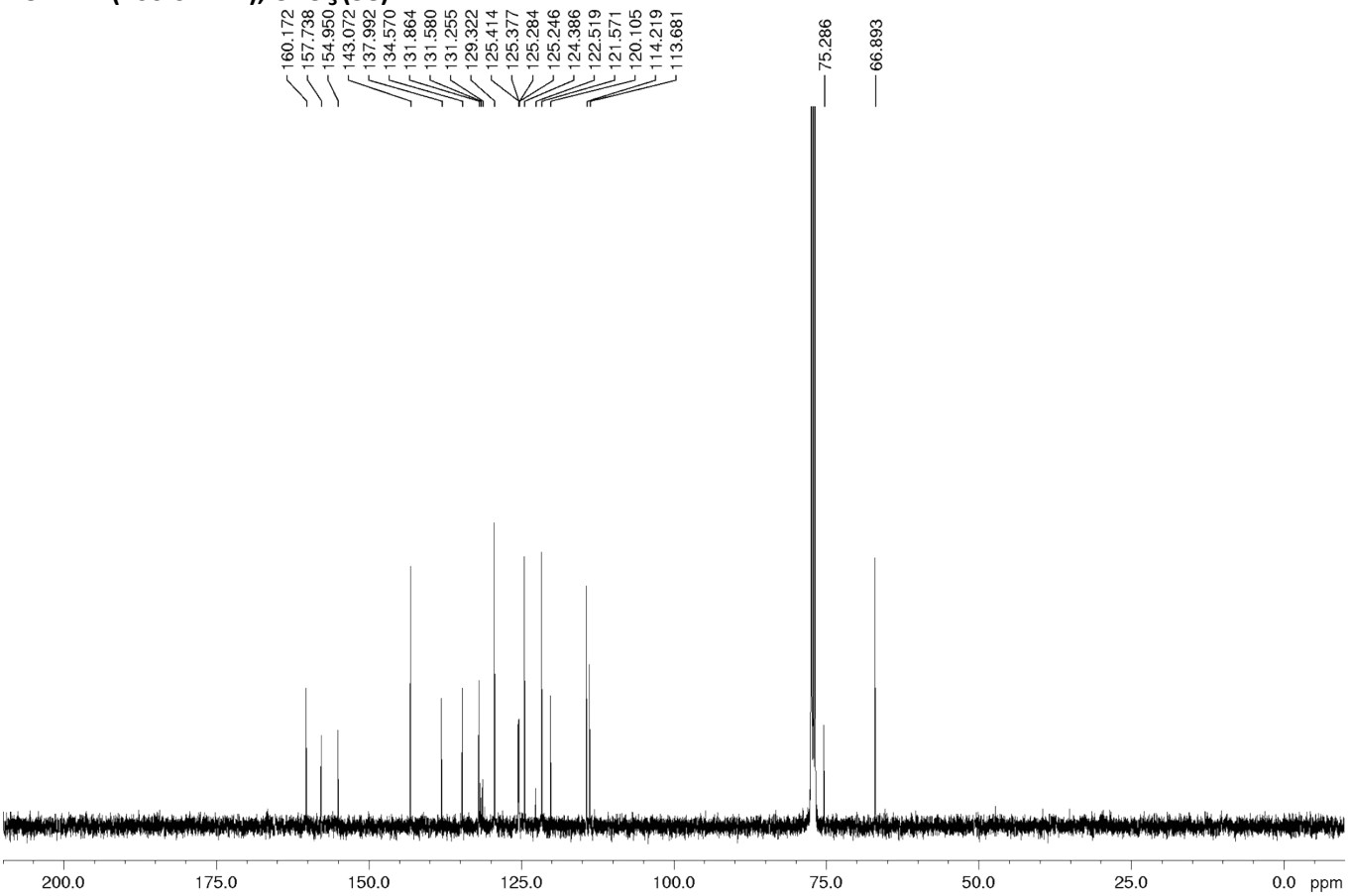
^{13}C NMR (100.6 MHz), $CDCl_3$ (7d)



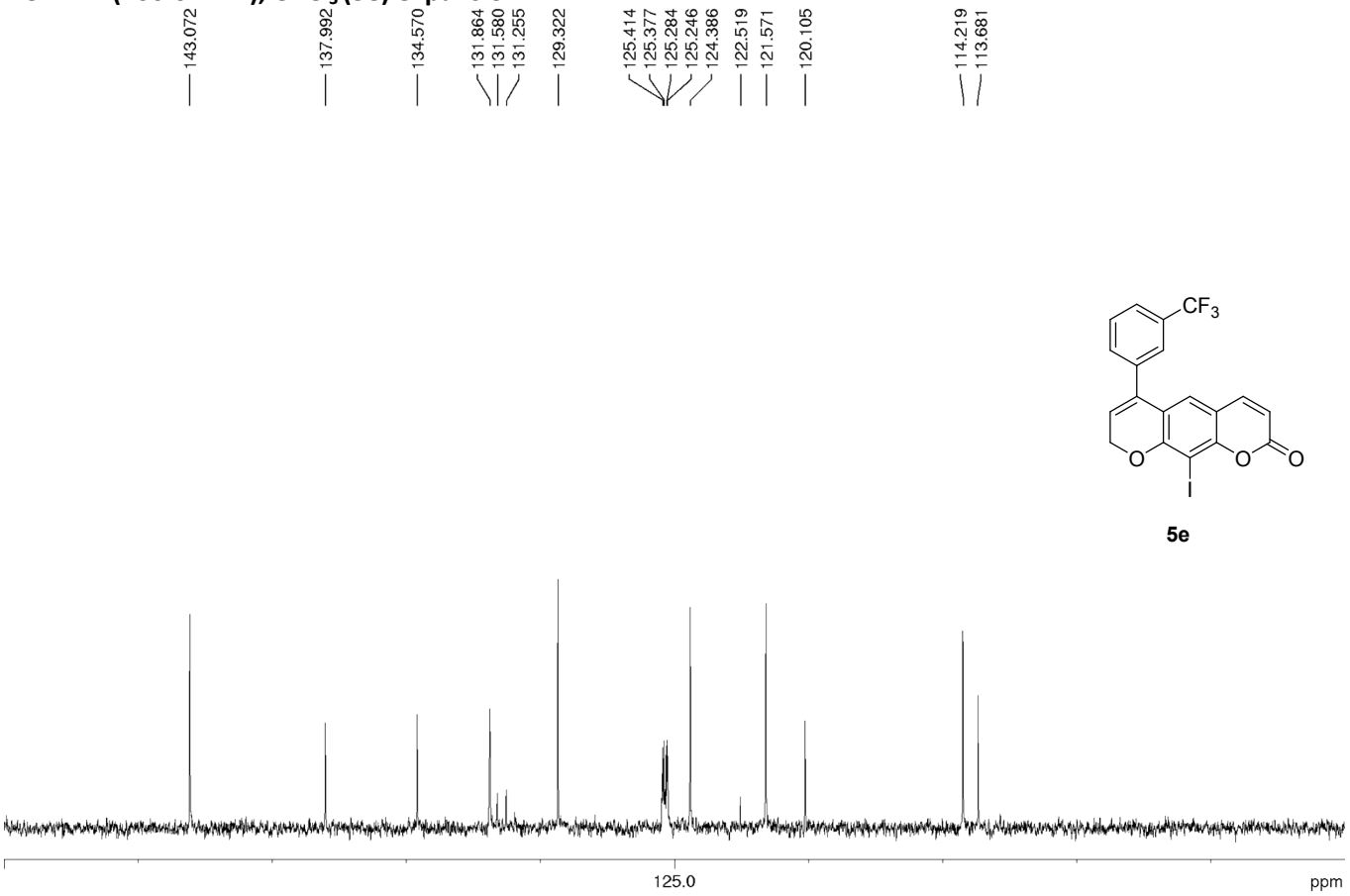
^{1}H NMR (400.13 MHz), $CDCl_3$ (5e)



^{13}C NMR (100.6 MHz), $CDCl_3$ (5e)



^{13}C NMR (100.6 MHz), $CDCl_3$ (5e) expansion



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[1] D. Wang, C. Deraedt, L. Salmon, C. Labrugre, L. Etienne, J. Ruiz, D. Astruc, *Chem. Eur. J.,*2015, **21**, 1508.
[2] A. Nocentini et al., *Bioorg. Med. Chem.*, 2015, **23**, 6955.