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Alkynyl Triazenes Enable Divergent Syntheses of 2-Pyrones

Jin-Fay Tan,[a] Carl Thomas Bormann,[b] Kay Severin,[b] Nicolai Cramer*[a]

a. Laboratory of Asymmetric Catalysis and Synthesis, EPFL SB ISIC LCSA, BCH 430, CH-1015 Lausanne (Switzerland). E-mail: nicolai.cramer@epfl.ch
b. Laboratory of Supramolecular Chemistry, EPFL SB ISIC LCS, BCH 3307, CH-1015 Lausanne (Switzerland).

Supporting Information

Table of Content:

1. General Methods:

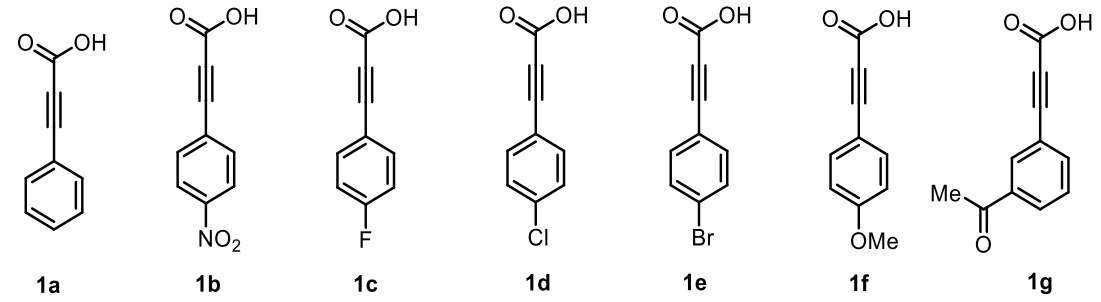
All reactions were were carried out under an atmosphere of dry nitrogen or nitrous oxide (purity: 99.999%, Messer Schweiz AG) using standard Schlenk or glovebox techniques in oven-dried glassware with magnetic stirring, unless otherwise indicated. Reagents and solvents were purchased from Aldrich, Acros, Alfa Aesar, Abcr, or TCI. Chemicals were used as obtained from the suppliers. Dry THF were obtained using a solvent purification system with an aluminum oxide column (Innovative Technologies). Falcon tubes used are 14 mL non-pyrogenic polypropylene round-bottomed tubes, (17 x 100 mm), purchased from Corning Science México S.A. De C.V.

Flash chromatography was performed with Silicycle silica gel 60 (0.040-0.063 μm grade) or basic alumina (Acros, Brockmann activity 1, 50-200 μm, 60A). Analytical thin-layer chromatography was performed with commercial glass plates coated with 0.25 mm silica gel (E. Merck, Kieselgel 60 F254). Compounds were either visualised under UV-light at 254 nm or by dipping the plates in an aqueous potassium permanganate solution followed by heating. For the purification of acid sensitive compounds, silicagel 230-400 mesh particle size (100 g) was deactivated prior to use by adding dichloromethane containing 5 vol% triethylamine (300 mL), removal of the solvent under reduced pressure, and drying of the silica at room temperature under oil pump vacuum overnight.

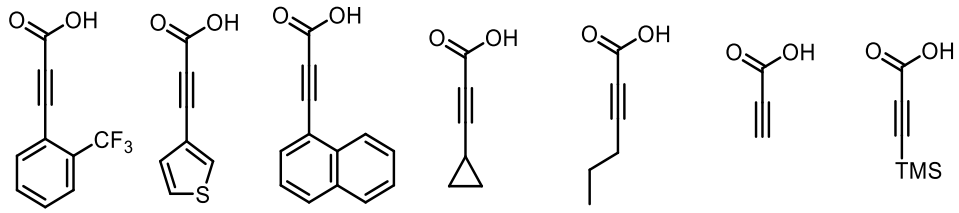
NMR spectra were recorded on a Bruker Avance 400 spectrometer with a BBFOz ATMA probe and Bruker DRX600 (600 MHz) spectrometer. Chemical shifts (δ) are reported in parts per million (ppm) relative to residual chloroform (s, 7.26 ppm). Splitting patterns are designated as s, singlet; d, doublet; t, triplet; q, quartet; sept, septet; m, multiplet; brs, broad singlet. Proton decoupled Carbon-13 nuclear magnetic resonance (^{13}C NMR) data were acquired at 101 MHz on a Bruker AV400 spectrometer. Chemical shifts are reported in ppm relative to $CDCl_3$ (77.16 ppm).

Electrospray–ionisation HRMS data were acquired on a Q–Tof Ultima mass spectrometer (Waters) or an Agilent LC-MS TOF. High resolution mass are given in *m/z*. Data from the Lock–Spray were used to calculate a correction factor for the mass scale and provide accurate mass information of the analyte. Data were processed using the MassLynx 4.1 software. IR spectra were recorded on a Perkin-Elmer FT-IR spectrometer. Absorbance frequencies are reported in reciprocal centimeters (cm-1).

2. Preparation of Propiolic Acid Substrates



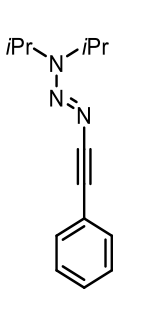
1a **1b** **1c** **1d** **1e** **1f** **1g**



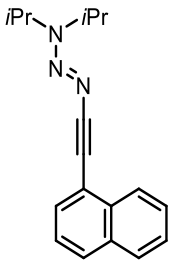
1h **1i** **1j** **1k** **1l** **1m** **1n**

1a, **1b**, **1d**, **1k**, **1l**-**1n** are commercially available. **1c**, **1f**-**1j** were prepared based on reported procedure.[1-4] All spectra were in good agreement with the reported data.

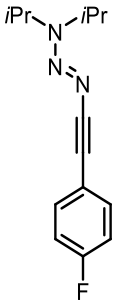
3. Preparation of 1-Alkynyl Triazenes Substrates



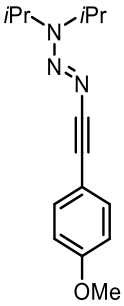
2a



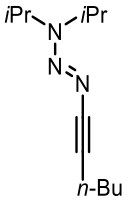
2b



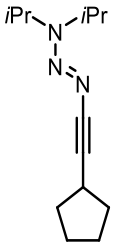
2c



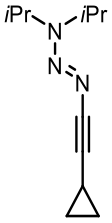
2d



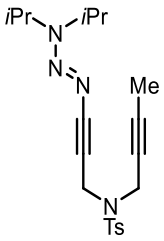
2e



2f



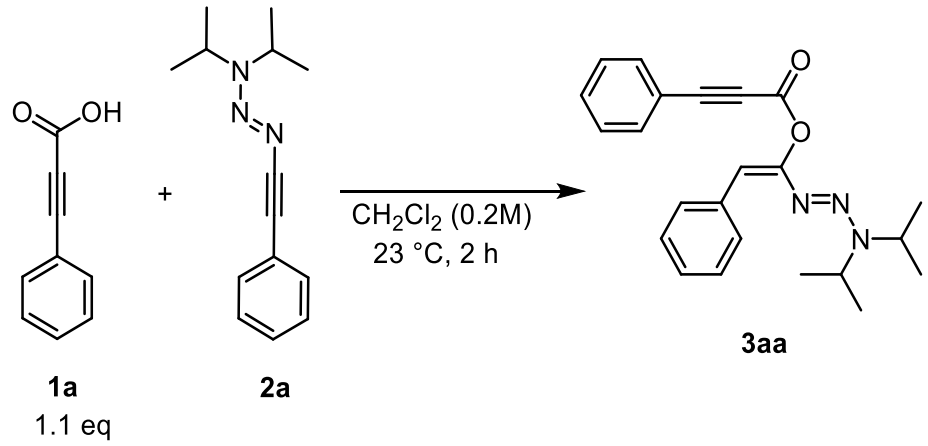
2g



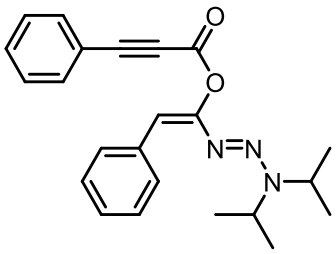
2h

Alkynyl triazenes **2a**-**2h** were previously reported and synthesized by reaction of lithium amides with N_2O and alkynyl Grignard reagents as described in the literature.[5,6] The spectra were in good agreement with the reported data.

4. Formation of 3aa, 3aa', 4aa and 4aa'

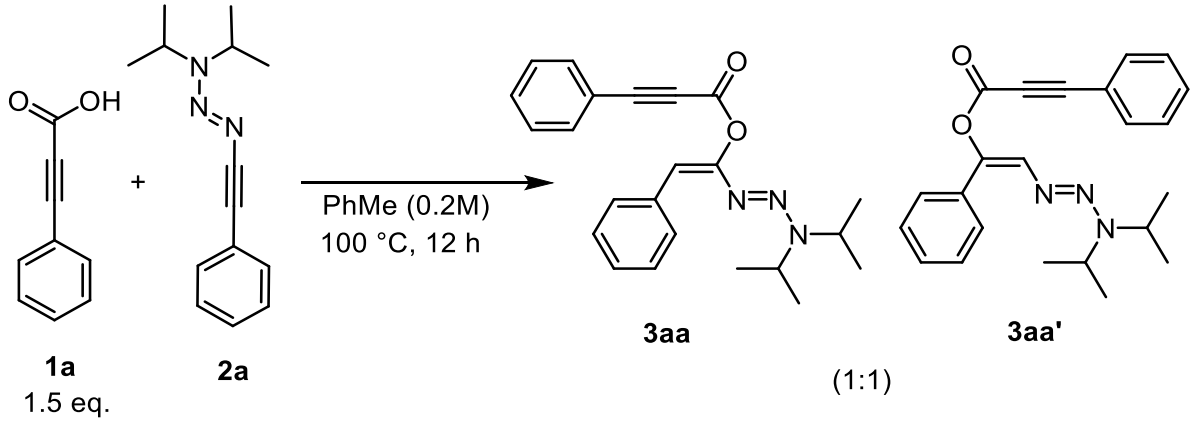


(*E*)-1-((*E*)-3,3-diisopropyltriaz-1-en-1-yl)-2-phenylvinyl 3-phenylpropiolate (**3aa**):

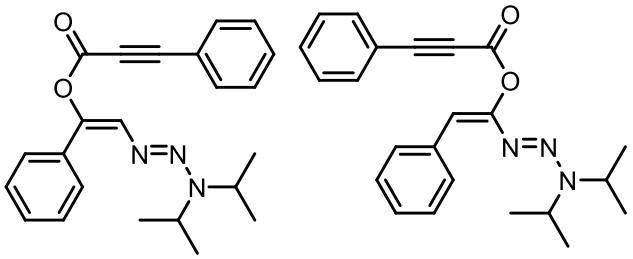


Alkynyl triazene **2a** (0.10 mmol, 22.9 mg) and phenyl propiolic acid **1a** (0.11 mmol, 16.1 mg, 1.1 equiv.) were weighed in test tube containing a magnetic stirring bar, followed by addition of CH_2Cl_2 (0.5 mL) at RT. The mixture was stirred at RT for 2 h. Volatiles were evaporated, crude was then purified by silica gel chromatography eluting with pentane/EtOAc to afford **3aa**.

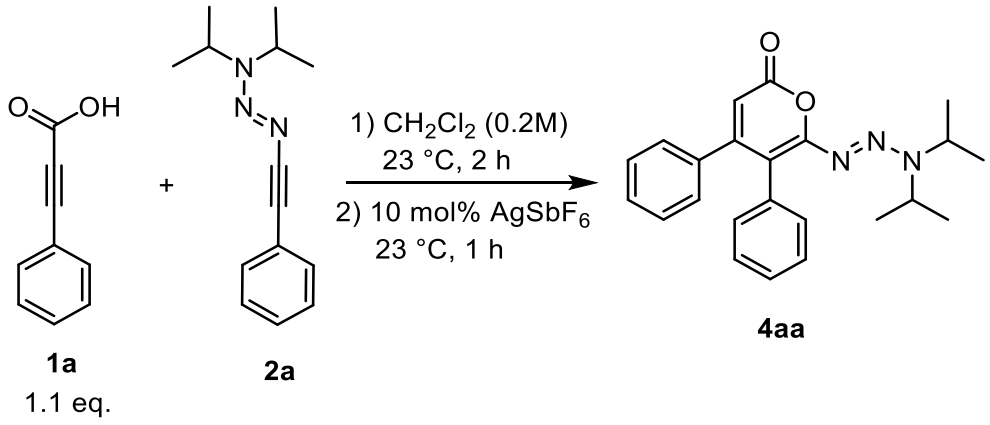
Obtained as yellow solid in 99 % yield (37.1 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) = 7.80–7.73 (m, 2H), 7.65–7.59 (m, 2H), 7.50–7.44 (m, 1H), 7.39 (dd, *J* = 8.2, 6.6 Hz, 2H), 7.32 (t, *J* = 7.7 Hz, 2H), 7.22–7.16 (m, 1H), 5.93 (s, 1H), 5.20 (hept, *J* = 6.8 Hz, 1H), 4.01 (hept, *J* = 6.6 Hz, 1H), 1.35 (d, *J* = 6.5 Hz, 6H), 1.30 (d, *J* = 6.8 Hz, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ (ppm) = 152.1, 149.2, 135.1, 133.3, 130.9, 129.7, 128.7, 128.2, 126.5, 119.8, 108.7, 87.6, 80.6, 49.7, 48.2, 23.8, 19.2; **IR (ATR):** $\tilde{\nu}$ 2975, 2220, 1726, 1445, 1148, 1120 cm^{-1}; **HRMS (ESI/QTOF)** m/z: $[M + H]^+$ Calcd for $C_{23}H_{26}N_3O_2^+$ 376.2019; Found 376.2018; **R_f:** 0.34 (1:9 EtOAc/pentane); **m.p.:** 109–112 °C.



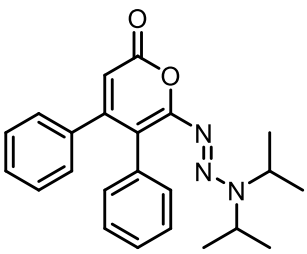
(*E*)-2-((*E*)-3,3-diisopropyltriaz-1-en-1-yl)-1-phenylvinyl 3-phenylpropiolate (**3aa'**), (*E*)-1-((*E*)-3,3-diisopropyltriaz-1-en-1-yl)-2-phenylvinyl 3-phenylpropiolate (**3aa**):



Alkynyl triazene **2a** (0.10 mmol, 22.9 mg) and phenyl propiolic acid **1a** (0.15 mmol, 21.9 mg, 1.5 equiv.) were weighed in test tube containing a magnetic stirring bar, followed by addition of PhMe (0.5 mL) at RT. After sealing the test tube with a septum, the mixture was stirred in a preheated oil bath at 100 ˚C for 12 h. Volatiles were then evaporated under reduced pressure. Crude was then purified by silica gel chromatography eluting with pentane/EtOAc to afford an inseparable mixture of **3aa'** and **3aa** at 1:1 ratio.



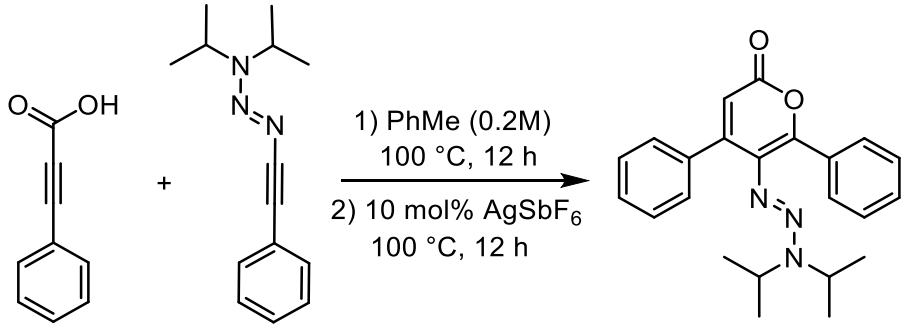
(*E*)-6-(3,3-diisopropyltriaz-1-en-1-yl)-4,5-diphenyl-2*H*-pyran-2-one (**4aa**):



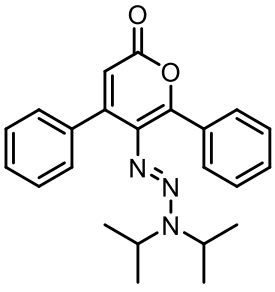
Alkynyl triazene **2a** (0.10 mmol, 22.9 mg) and phenyl propiolic acid **1a** (0.11 mmol, 16.1 mg, 1.1 equiv.) were weighed in test tube containing a magnetic stirring bar, followed by addition of CH_2Cl_2 (0.5 mL) at RT. The test tube was sealed with a septum.

The mixture was stirred at RT for 2 h. $AgSbF_6$ (10 mol%, 0.01 mmol, 3.4 mg) was then added at RT. After sealing the test tube with a septum, the mixture was stirred at RT for 1 h. After completion of the reaction, volatiles were evaporated. Crude was analyzed by ^{1}H NMR to determine regiomeric ratio to be >20:1. Crude was then purified by silica gel chromatography eluting with pentane/EtOAc to afford the 6-triazenyl-2-pyrone product **4aa** with inseparable regioisomer **4aa'** (>1:20).

Obtained as yellow wax in 98 % yield (36.8 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) = 7.25–7.21 (m, 1H), 7.20–7.10 (m, 5H), 7.10–7.06 (m, 2H), 7.04–6.99 (m, 2H), 6.14 (s, 1H), 4.54 (hept, *J* = 6.8 Hz, 1H), 4.13 (hept, *J* = 6.7 Hz, 1H), 1.37 (d, *J* = 6.7 Hz, 6H), 1.08 (d, *J* = 6.8 Hz, 6H), minor regioisomer **4aa'** = 6.22 (s, 1H), 1.41 (d, *J* = 6.6 Hz, 7H), 1.30 (d, *J* = 6.8 Hz, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ (ppm) = 162.0, 160.4, 159.0, 137.9, 134.8, 131.9, 128.7, 128.6, 128.0, 127.3, 126.5, 110.6, 108.8, 52.9, 49.4, 23.1, 19.0; **IR (ATR):** $\tilde{\nu}$ 2975, 2926, 1721, 1487, 1471, 1443, 1412, 1352, 1254, 1211, 1159, 1129, 700 cm^{-1}; **HRMS (ESI/QTOF)** m/z: [M + Na]$^+$ Calcd for $C_{23}H_{25}N_3NaO_2^+$ 398.1839; Found 398.1839; **R_f:** 0.24 (1:4 EtOAc/pentane).



1a 1.5 eq. **2a** **4aa'**



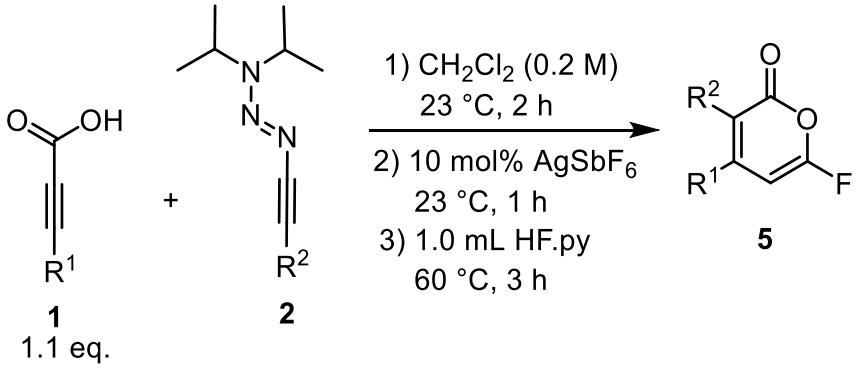
(*E*)-5-(3,3-diisopropyltriaz-1-en-1-yl)-4,6-diphenyl-2*H*-pyran-2-one (**4aa'**):

Alkynyl triazene **2a** (0.10 mmol, 22.9 mg) and phenyl propiolic acid **1a** (0.10 mmol, 21.9 mg, 1.5 equiv.) were weighed in test tube containing a magnetic stirring bar, followed by addition of PhMe (0.5 mL) at RT. The test tube was sealed with a septum. The mixture was stirred in a preheated oil bath at 100 ˚C for 12 h. The mixture was allowed to cool to RT, followed by addition of $AgSbF_6$ (10 mol%, 0.01 mmol, 3.4 mg). After sealing the test tube with a septum, the mixture was stirred in a preheated oil bath at 100 ˚C for 12 h. After completion of the reaction, volatiles were

evaporated. Crude was analyzed by NMR to determine regiomeric ratio to be 5.8:1. Crude was then purified by silica gel chromatography eluting with pentane/EtOAc to afford the 5-triazenyl-2-pyrone product **4aa'**.

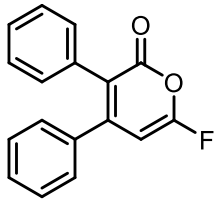
Obtained as yellow wax in 72 % yield (27.1 mg). **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) = 7.25–7.12 (m, 10H), 6.22 (s, 1H), 5.27 (hept, *J* = 6.8 Hz, 1H), 4.13 (hept, *J* = 6.6 Hz, 1H), 1.41 (d, *J* = 6.6 Hz, 6H), 1.30 (d, *J* = 6.8 Hz, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ (ppm) = 162.9, 162.5, 155.3, 138.9, 134.82, 131.3, 128.9, 128.4, 128.3, 127.9, 127.2, 118.6, 95.2, 51.3, 48.5, 23.7, 19.3; **IR (ATR):** $\tilde{\nu}$ 2957, 2922, 1706, 1394, 1375, 1361, 1335, 1261, 1217, 1156, 1130, 1097, 792, 767, 698 cm^{-1}; **HRMS (ESI/QTOF)** m/z: $[M + H]^+$ Calcd for $C_{23}H_{26}N_3O_2^+$ 376.2020; Found 376.2021; **R_f:** 0.20 (1:4 EtOAc/pentane).

5. General Procedure A for the One-Pot Synthesis of 6-Fluoro-α-Pyrones 5:



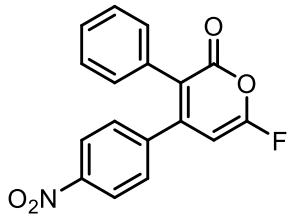
General Procedure A: Alkynyl triazene **2** (0.10 mmol, 1.0 equiv.) and propiolic acid **1** (0.11 mmol, 1.1 equiv.) were weighed in test tube containing a magnetic stirring bar, followed by addition of CH_2Cl_2 (0.5 mL) at RT. The test tube was sealed with a septum, and the mixture was stirred at RT for 2 h. $AgSbF_6$ (10 mol%, 3.4 mg) was then added at RT. After sealing the test tube with a septum, the mixture was stirred at RT for 1 h (for **5ha**, **5ka**, **5la** and **5ma**, mixture was stirred at 60 ˚C for 12 h after adding $AgSbF_6$) Using a glass pipette, the crude was then transferred to a Falcon tube (rinsing was done with additional 0.5 mL CH_2Cl_2). 1.0 mL HF.py was added via a syringe, and the mixture was allowed to stir under air at 60 ˚C for 3 h (for **5da**, **5ea**, **5fa**, **5ja**, **5ad**, **5ae** and **5af**, mixture was stirred at RT for 48 h after adding HF.py). After completion of reaction, the mixture was allowed to cool to RT, and 2.0 mL EtOAc was added, followed by 6.0 mL H_2O. Calcium gluconate (c.a. 200 mg) was added to the biphasic layer, followed by rigourous stirring. The organic phase was removed using a glass pipette, and the aqueous phase was washed using the same method with EtOAc (2.0 mL x 2). The organic phases were combined, dried over Na_2SO_4, filtered and concentrated under reduced pressure. If necessary, a known amount of internal standard (dimethyl sulfone) was added and crude was analyzed by NMR to determine regiomeric ratio. Crude was then purified by silica gel chromatography eluting with pentane/EtOAc to afford the 6-fluoro-2-pyrone product **5**.

6-Fluoro-3,4-diphenyl-2*H*-pyran-2-one (**5aa**):



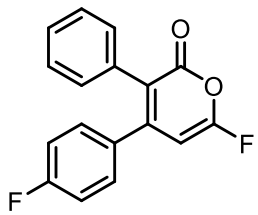
Obtained as yellow solid in 88 % yield (23.3 mg), **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) = 7.28 (s, 1H), 7.26–7.20 (m, 5H), 7.15–7.07 (m, 4H), 5.88 (s, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ (ppm) = 159.8 (d, $J_{C\text{-}F}$ = 6.0 Hz), 158.9 (d, $J_{C\text{-}F}$ = 281.4 Hz), 156.0 (d, $J_{C\text{-}F}$ = 8.7 Hz), 137.1 (d, $J_{C\text{-}F}$ = 4.2 Hz), 133.2, 131.0, 129.4, 128.7, 128.6, 128.3, 128.0, 120.2 (d, $J_{C\text{-}F}$ = 7.6 Hz), 86.3 (d, $J_{C\text{-}F}$ = 21.3 Hz); **^{19}F NMR** (376 MHz, $CDCl_3$) δ (ppm) = -72.3; **IR (ATR):** $\tilde{\nu}$ 1742, 1659, 1537, 1357, 1205, 1064, 860, 804, 768, 751, 697, 573 cm^{-1}; **HRMS (ESI/QTOF)** m/z: $[M + H]^+$ Calcd for $C_{17}H_{12}FO_2^+$ 267.0815; Found 267.0813; **R_f:** 0.67 (1:9 EtOAc/pentane); **m.p.:** 135–137 °C.

6-Fluoro-4-(4-nitrophenyl)-3-phenyl-2*H*-pyran-2-one (**5ba**):



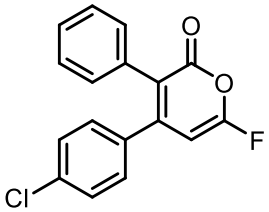
Obtained as yellow solid in 90 % yield (27.9 mg), **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) = 8.14–8.07 (m, 2H), 7.31–7.24 (m, 5H), 7.11–7.05 (m, 2H), 5.86 (s, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ (ppm) = 159.2 (d, $J_{C\text{-}F}$ = 282.8 Hz), 159.0 (d, $J_{C\text{-}F}$ = 5.8 Hz), 153.2 (d, $J_{C\text{-}F}$ = 8.7 Hz), 148.0, 143.5 (d, $J_{C\text{-}F}$ = 3.6 Hz), 132.2, 130.8, 129.8, 128.8, 128.7, 123.9, 121.6 (d, $J_{C\text{-}F}$ = 8.0 Hz), 85.5 (d, $J_{C\text{-}F}$ = 22.2 Hz); **^{19}F NMR** (376 MHz, $CDCl_3$) δ (ppm) = -70.5; **IR (ATR):** $\tilde{\nu}$ 2956, 2923, 2853, 1750, 1661, 1542, 1521, 1460, 1347, 1259, 1064, 1015, 842, 798, 701 cm^{-1}; **HRMS (ESI/QTOF)** m/z: $[M + H]^+$ Calcd for $C_{17}H_{11}FNO_4^+$ 312.0667; Found 312.0673; **R_f:** 0.44 (1:4 EtOAc/pentane); **m.p.:** 138–140 °C.

6-Fluoro-4-(4-fluorophenyl)-3-phenyl-2*H*-pyran-2-one (**5ca**):



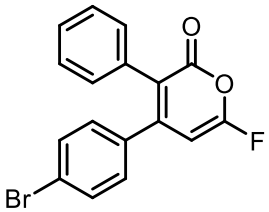
Obtained as pale yellow solid in 82 % yield (23.2 mg), **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) = 7.30–7.24 (m, 3H), 7.16–7.07 (m, 4H), 6.98–6.91 (m, 2H), 5.88 (s, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ (ppm) = 163.1 (d, J = 250.9 Hz), 159.6 (d, J = 5.6 Hz), 158.9 (d, J = 281.3 Hz), 154.8 (d, J = 8.7 Hz), 133.0, 133.0 (t, J = 3.5 Hz), 130.9, 130.8 (d, J = 8.6 Hz), 128.5, 128.2, 120.3 (d, J = 7.6 Hz), 115.8 (d, J = 21.9 Hz), 86.1 (d, J = 21.4 Hz); **^{19}F NMR** (376 MHz, $CDCl_3$) δ (ppm) = -71.8, -113.2.; **IR (ATR):** $\tilde{\nu}$ 1746, 1660, 1602, 1537, 1509, 1361, 1234, 1160, 1065, 869, 699, 574 cm^{-1}; **HRMS (ESI/QTOF)** m/z: $[M + H]^+$ Calcd for $C_{17}H_{11}F_2O_2^+$ 285.0722; Found 285.0726; **R_f:** 0.59 (1:9 EtOAc/pentane); **m.p.:** 145–148 °C.

4-(4-Chlorophenyl)-6-fluoro-3-phenyl-2*H*-pyran-2-one (**5da**):



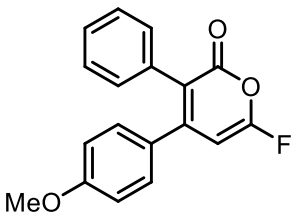
Obtained as light yellow solid in 78 % yield (23.5 mg), **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) = 7.27 (d, *J* = 2.5 Hz, 1H), 7.26–7.24 (m, 2H), 7.24–7.20 (m, 2H), 7.14–7.09 (m, 2H), 7.06–7.01 (m, 2H), 5.84 (s, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ (ppm) = 159.5 (d, $J_{C\text{-}F}$ = 5.7 Hz), 159.0 (d, $J_{C\text{-}F}$ = 281.5 Hz), 154.5 (d, $J_{C\text{-}F}$ = 8.8 Hz), 135.7, 135.5 (d, $J_{C\text{-}F}$ = 3.7 Hz), 132.9, 130.9, 130.1, 128.9, 128.5, 128.3, 120.5 (d, $J_{C\text{-}F}$ = 7.9 Hz), 85.9 (d, *J* = 21.6 Hz); **^{19}F NMR** (376 MHz, $CDCl_3$) δ (ppm) = -71.75; **IR (ATR):** $\tilde{\nu}$ 1734, 1664, 1536, 1354, 1095, 1065, 848, 806, 783, 703 cm^{-1}; **HRMS (ESI/QTOF)** m/z: $[M + H]^+$ Calcd for $C_{17}H_{11}ClFO_2^+$ 301.0426; Found 301.0429; **R_f:** 0.70 (1:4 EtOAc/pentane); **m.p.:** 129–132 °C.

4-(4-Bromophenyl)-6-fluoro-3-phenyl-2*H*-pyran-2-one (**5ea**):



Obtained as light yellow solid in 71 % yield (24.6 mg), **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) = 7.41–7.36 (m, 2H), 7.27 (dt, *J* = 4.4, 1.6 Hz, 3H), 7.15–7.10 (m, 2H), 7.00–6.95 (m, 2H), 5.85 (s, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ (ppm) = 159.5 (d, $J_{C\text{-}F}$ = 5.8 Hz), 159.0 (d, $J_{C\text{-}F}$ = 281.5 Hz), 154.6 (d, $J_{C\text{-}F}$ = 8.4 Hz), 135.9 (d, $J_{C\text{-}F}$ = 3.5 Hz), 132.9, 131.9, 130.9, 130.3, 128.5, 128.3, 123.9, 120.5 (d, $J_{C\text{-}F}$ = 7.5 Hz), 85.8 (d, $J_{C\text{-}F}$ = 21.5 Hz); **^{19}F NMR** (376 MHz, $CDCl_3$) δ (ppm) = -71.7; **IR (ATR):** $\tilde{\nu}$ 1733, 1661, 1586, 1536, 1353, 1260, 1203, 1064, 1012, 863, 847, 804, 783, 755, 704, 573, 498 cm^{-1}; **HRMS (ESI/QTOF)** m/z: $[M + H]^+$ Calcd for $C_{17}H_{11}BrFO_2^+$ 344.9921; Found 344.9925; **R_f:** 0.64 (1:9 EtOAc/pentane); **m.p.:** 141–144 °C.

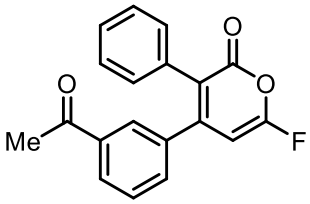
6-Fluoro-4-(4-methoxyphenyl)-3-phenyl-2*H*-pyran-2-one (**5fa**):



Obtained as pale yellow solid in 61 % yield (18.2 mg), **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) = 7.29–7.23 (m, 3H), 7.17–7.12 (m, 2H), 7.07–7.01 (m, 2H), 5.88 (s, 1H), 3.77 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ (ppm) = 160.5, 160.0 (d, $J_{C\text{-}F}$ = 6.3 Hz), 158.9 (d, $J_{C\text{-}F}$ = 280.1 Hz), 155.5 (d, $J_{C\text{-}F}$ = 8.8 Hz), 133.7, 131.0, 130.5, 129.1 (d, $J_{C\text{-}F}$ = 3.6 Hz), 128.4, 127.9, 119.2 (d, $J_{C\text{-}F}$ = 7.4 Hz), 114.0, 86.1 (d, $J_{C\text{-}F}$ = 21.1 Hz), 55.4; **^{19}F NMR** (376 MHz, $CDCl_3$) δ (ppm) = -72.8; **IR (ATR):** $\tilde{\nu}$ 1743, 1660, 1537, 1355, 1206, 1153, 1042, 779, 762, 699, 586 cm^{-1}; **HRMS (ESI/QTOF)** m/z: $[M + H]^+$ Calcd for

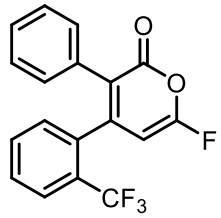
$C_{18}H_{14}FO_3^+$ 297.0921; Found 297.0923; **R_f:** 0.25 (1:9 EtOAc/pentane); **m.p.:** 127–128 °C.

4-(3-Acetylphenyl)-6-fluoro-3-phenyl-2*H*-pyran-2-one (**5ga**):



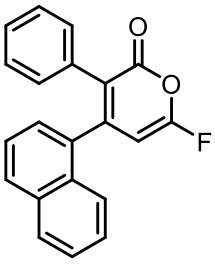
Obtained as pale yellow solid in 83 % yield (25.7 mg), **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) = 7.89 (dt, *J* = 7.6, 1.5 Hz, 1H), 7.71 (td, *J* = 1.8, 0.6 Hz, 1H), 7.38 (td, *J* = 7.7, 0.6 Hz, 1H), 7.32 (dt, *J* = 7.8, 1.5 Hz, 1H), 7.29–7.25 (m, 3H), 7.18–7.12 (m, 2H), 5.95 (s, 1H), 2.42 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ (ppm) = 197.3, 159.5 (d, J_{C-F} = 5.6 Hz), 159.1 (d, J_{C-F} = 281.7 Hz), 154.7 (d, J_{C-F} = 8.6 Hz), 137.4 (d, J_{C-F} = 3.6 Hz), 137.2, 133.1, 132.9, 130.9, 129.1, 129.0, 129.0, 128.5, 128.3, 120.8 (d, J_{C-F} = 7.6 Hz), 85.9 (d, J_{C-F} = 21.6 Hz), 26.6; **^{19}F NMR** (376 MHz, $CDCl_3$) δ (ppm) = -71.4; **IR (ATR):** $\tilde{\nu}$ 1742, 1686, 1661, 1539, 1360, 1265, 1199, 1067, 787, 701 cm^{-1}; **HRMS (ESI/QTOF)** m/z: [M + H]$^+$ Calcd for $C_{19}H_{14}FO_3^+$ 309.0921; Found 309.0928; **R_f:** 0.40 (1:4 EtOAc/pentane); **m.p.:** 122–125 °C.

6-Fluoro-3-phenyl-4-(2-(trifluoromethyl)phenyl)-2*H*-pyran-2-one (**5ha**):



Obtained as light brown film in 73 % yield (24.4 mg), **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) = 7.67 (dd, *J* = 7.5, 1.7 Hz, 1H), 7.42–7.32 (m, 2H), 7.17 (dd, *J* = 5.3, 1.9 Hz, 3H), 7.10 (dt, *J* = 6.7, 2.3 Hz, 2H), 7.00 (dd, *J* = 7.2, 1.6 Hz, 1H), 5.79 (s, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ (ppm) = 159.2 (d, J_{C-F} = 5.3 Hz), 158.2 (d, J_{C-F} = 281.8 Hz), 154.9 (d, J_{C-F} = 8.9 Hz), 135.4, 132.5, 131.8, 130.6, 130.3, 129.2, 128.2, 128.2, 128.1–127.7 (q, J_{C-F} = 30.7 Hz), 126.9 (q, J_{C-F} = 5.0 Hz), 123.9 (q, J_{C-F} = 274.0 Hz), 122.1 (d, J_{C-F} = 7.9 Hz), 86.6 (d, J_{C-F} = 21.6 Hz); **^{19}F NMR** (376 MHz, $CDCl_3$) δ (ppm) = -57.8, -72.9; **IR (ATR):** $\tilde{\nu}$ 1752, 1663, 1543, 1560, 1315, 1173, 1128, 1070, 1054, 1036, 769, 699, 574 cm^{-1}; **HRMS (ESI/QTOF)** m/z: [M + H]$^+$ Calcd for $C_{18}H_{11}F_4O_2^+$ 335.0690; Found 335.0689; **R_f:** 0.56 (1:4 EtOAc/pentane).

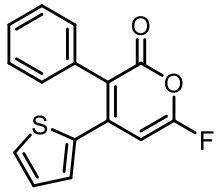
6-Fluoro-4-(naphthalen-1-yl)-3-phenyl-2*H*-pyran-2-one (**5ia**):



Obtained as pale yellow solid in 55 % yield (17.4 mg), **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) = 7.87–7.82 (m, 1H), 7.81–7.75 (m, 2H), 7.55–7.48 (m, 2H), 7.29 (dd, *J* = 8.3, 7.1 Hz, 1H), 7.11–7.01 (m, 6H), 5.86 (s, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ (ppm) = 159.6 (d, J_{C-F} = 5.6 Hz), 158.5 (d, J_{C-F} = 282.2 Hz), 156.1 (d, J_{C-F} = 8.8 Hz), 134.9 (d, J_{C-F}

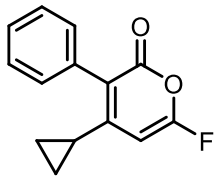
= 3.3 Hz), 133.6, 133.0, 130.1, 129.4, 128.9, 128.0, 127.1, 126.7, 126.5, 125.1, 124.9, 122.4 (d, J_{C-F} = 7.7 Hz), 87.5 (d, J_{C-F} = 20.7 Hz); **^{19}F NMR** (376 MHz, $CDCl_3$) δ (ppm) = -73.0; **IR (ATR):** $\tilde{\nu}$ 1742, 1658, 1539, 1385, 1356, 1177, 879, 802, 699, 543 cm^{-1}; **HRMS (ESI/QTOF)** m/z: $[M + H]^+$ Calcd for $C_{21}H_{14}FO_2^+$ 317.0972; Found 317.0970; **R_f:** 0.25 (1:9 EtOAc/pentane); **m.p.:** 151–155 °C.

6-Fluoro-3-phenyl-4-(thiophen-2-yl)-2*H*-pyran-2-one (**5ja**):



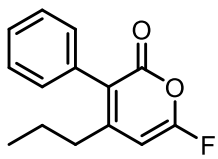
Obtained as yellow wax in 39 % yield (10.6 mg), **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) = 7.46–7.42 (m, 3H), 7.39 (d, *J* = 5.1 Hz, 1H), 7.29–7.23 (m, 2H), 7.07 (d, *J* = 3.8 Hz, 1H), 6.95 (t, *J* = 4.4 Hz, 1H), 6.10 (s, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ (ppm) = 159.9 (d, J_{C-F} = 5.2 Hz), 159.0 (d, J_{C-F} = 277.8 Hz), 147.2 (d, J_{C-F} = 9.6 Hz), 138.2 (d, J_{C-F} = 4.5 Hz), 133.7, 131.5, 131.2, 130.8, 129.4, 129.1, 127.5, 118.0 (d, J_{C-F} = 7.0 Hz), 84.1 (d, J_{C-F} = 23.0 Hz); **^{19}F NMR** (376 MHz, $CDCl_3$) δ (ppm) = -73.7; **IR (ATR):** $\tilde{\nu}$ 1728, 1664, 1543, 1422, 1393, 1364, 777, 724, 701 cm^{-1}; **HRMS (ESI/QTOF)** m/z: $[M + H]^+$ Calcd for $C_{15}H_{10}FO_2S^+$ 273.0380; Found 273.0390; **R_f:** 0.54 (1:4 EtOAc/pentane).

4-Cyclopropyl-6-fluoro-3-phenyl-2*H*-pyran-2-one (**5ka**):



Obtained as pale yellow oil in 73 % yield (16.7 mg), **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) = 7.48–7.41 (m, 2H), 7.37 (m, 3H), 5.12 (s, 1H), 1.84 (m, 1H), 1.07–0.99 (m, 2H), 0.88–0.84 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ (ppm) = 161.3 (d, J_{C-F} = 8.7 Hz), 159.9 (d, J_{C-F} = 277.6 Hz), 159.0 (d, J_{C-F} = 6.5 Hz), 133.5, 130.7, 128.7, 128.3, 119.7 (d, J_{C-F} = 6.6 Hz), 78.9 (d, J_{C-F} = 22.4 Hz), 14.4 (d, J_{C-F} = 3.7 Hz), 10.4; **^{19}F NMR** (376 MHz, $CDCl_3$) δ (ppm) = -72.5; **IR (ATR):** $\tilde{\nu}$ 2949, 2869, 1743, 1664, 1538, 1446, 1355, 1203, 1141, 1046, 805, 702 cm^{-1}; **HRMS (ESI/QTOF)** m/z: $[M + H]^+$ Calcd for $C_{14}H_{12}FO_2^+$ 231.0816; Found 231.0815; **R_f:** 0.45 (1:9 EtOAc/pentane).

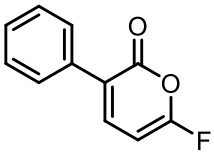
6-Fluoro-3-phenyl-4-propyl-2*H*-pyran-2-one (**5la**):



Obtained as pale yellow oil in 55 % yield (12.7 mg), **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) = 7.46–7.35 (m, 3H), 7.24–7.20 (m, 2H), 5.70 (s, 1H), 2.40–2.24 (m, 2H), 1.59–1.45 (m, 2H), 0.85 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ (ppm) = 159.7 (d, J_{C-F} = 6.1 Hz), 159.3 (d, J_{C-F} = 8.0 Hz), 159.1 (d, J_{C-F} = 280.3 Hz), 133.4, 130.1, 128.7, 128.4, 121.1 (d, J_{C-F} = 6.9 Hz), 84.7 (d, J_{C-F} = 20.4 Hz), 35.6 (d, J_{C-F} = 3.1 Hz), 22.3, 13.9; **^{19}F NMR** (376 MHz, $CDCl_3$) δ (ppm) = -73.3; **IR (ATR):** $\tilde{\nu}$ 2965, 2932, 2874, 1739, 1665, 1551, 1537, 1184, 701, 564

cm^{-1}; **HRMS (ESI/QTOF)** m/z: [M + H]$^+$ Calcd for $C_{14}H_{14}FO_2^+$ 233.0972; Found 233.0972; **R_f:** 0.30 (1:9 EtOAc/pentane).

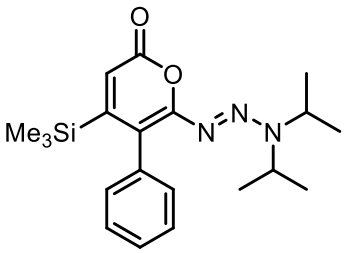
6-Fluoro-3-phenyl-2*H*-pyran-2-one (**5ma**):



Obtained as brown film in 62 % yield (11.7 mg), **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) = 7.63–7.55 (m, 3H), 7.46–7.34 (m, 3H), 5.81 (dd, *J* = 7.4, 1.7 Hz, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ (ppm) = 159.8 (d, J_{C-F} = 283.9 Hz), 158.4 (d, J_{C-F} = 6.6 Hz), 143.4 (d, J_{C-F} = 8.6 Hz), 134.0, 128.8, 128.7, 128.1, 123.2 (d, J_{C-F} = 7.6 Hz), 83.4 (d, J_{C-F} = 21.4 Hz); **^{19}F NMR** (376 MHz, $CDCl_3$) δ (ppm) = -70.3; **IR (ATR):** $\tilde{\nu}$ 1770, 1652, 1578, 1550, 1356, 1315, 1245, 1095, 1051, 772, 753, 734, 699, 562 cm^{-1}; **HRMS (ESI/QTOF)** m/z: [M + H]$^+$ Calcd for $C_{11}H_8FO_2^+$ 191.0503; Found 191.0503; **R_f:** 0.26 (1:9 EtOAc/pentane).

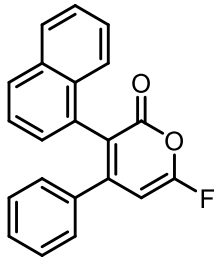
(*E*)-6-(3,3-diisopropyltriaz-1-en-1-yl)-5-phenyl-4-(trimethylsilyl)-2*H*-pyran-2-one (**4na**):

Alkynyl triazene **1a** (0.10 mmol, 1.0 equiv.) and propiolic acid **2n** (0.11 mmol, 1.1 equiv.) were weighed in test tube containing a magnetic stirring bar, followed by addition of CH_2Cl_2 (0.5 mL) at RT. The test tube was sealed with a septum, and the mixture was stirred at RT for 2 h. $AgSbF_6$ (10 mol%, 3.4 mg) was then added at RT. After sealing the test tube with a septum, the mixture was stirred at RT for 1 h. Volatiles were evaporated under reduced pressure, and crude was then purified by silica gel chromatography eluting with pentane/EtOAc to afford **4na**.



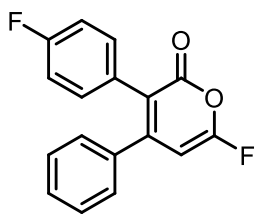
Obtained as bright yellow film in 89 % yield (32.9 mg), **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) = 7.73 (dd, *J* = 8.6, 1.2 Hz, 2H), 7.30 (dd, *J* = 8.4, 7.0 Hz, 2H), 7.2 –7.14 (m, 1H), 5.87 (s, 1H), 5.17 (p, *J* = 6.8 Hz, 1H), 4.01 (p, *J* = 6.6 Hz, 1H), 1.34 (d, *J* = 6.6 Hz, 6H), 1.29 (d, *J* = 6.8 Hz, 6H), 0.26 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ (ppm) = 151.1, 149.1, 135.1, 129.7, 128.2, 126.5, 108.7, 95.6, 94.6, 49.7, 48.2, 23.7, 19.2, -0.73; **IR (ATR):** $\tilde{\nu}$ 2975, 2930, 1729, 1446, 1367, 1263, 1191, 1157, 1122, 1101, 848, 759, 693 cm^{-1}; **HRMS (ESI/QTOF)** m/z: [M + Na]$^+$ Calcd for $C_{20}H_{29}N_3NaO_2Si^+$ 394.1921; Found 394.1927; **R_f:** 0.23 (1:9 EtOAc/pentane).

6-Fluoro-3-(naphthalen-1-yl)-4-phenyl-2*H*-pyran-2-one (**5ab**):



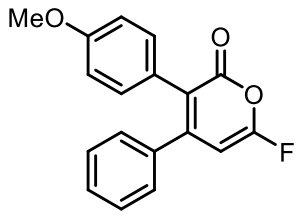
Obtained as yellow solid in 79 % yield (25.1 mg), **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) = δ 7.87–7.82 (m, 1H), 7.78 (d, *J* = 8.2 Hz, 1H), 7.73–7.70 (m, 1H), 7.49–7.44 (m, 2H), 7.32 (dd, *J* = 8.3, 7.1 Hz, 1H), 7.18–7.12 (m, 2H), 7.10–7.05 (m, 2H), 7.04 – 7.01 (m, 2H), 6.01 (s, 1H).; **^{13}C NMR** (101 MHz, $CDCl_3$) δ (ppm) = 159.6 (d, J_{C-F} = 281.2 Hz), 159.4 (d, J_{C-F} = 5.9 Hz), 157.8 (d, J_{C-F} = 8.8 Hz), 136.9 (d, J_{C-F} = 3.6 Hz), 133.7, 132.4, 131.2, 129.5, 129.2, 129.1, 128.8, 128.4, 127.9, 126.7, 126.1, 125.5, 125.0, 119.0 (d, J_{C-F} = 7.5 Hz), 86.0 (d, J_{C-F} = 21.4 Hz); **^{19}F NMR** (376 MHz, $CDCl_3$) δ (ppm) = -71.8; **IR (ATR):** $\tilde{\nu}$ 1742, 1658, 1539, 1383, 1356, 1229, 1177, 879, 802, 779, 752, 699, 543 cm^{-1}; **HRMS (ESI/QTOF)** m/z: $[M + Na]^+$ Calcd for $C_{21}H_{13}FNaO_2^+$ 339.0792; Found 339.0792; **R_f:** 0.38 (1:9 EtOAc/pentane); **m.p.:** 149–152 °C.

6-Fluoro-3-(4-fluorophenyl)-4-phenyl-2H-pyran-2-one (**5ac**):



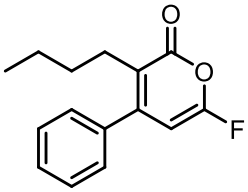
Obtained as colourless solid in 75 % yield (21.3 mg), **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) = 7.33–7.22 (m, 3H), 7.14–7.05 (m, 4H), 6.96–6.88 (m, 2H), 5.88 (s, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ (ppm) = 162.4 (d, J_{C-F} = 248.2 Hz), 159.7 (d, J_{C-F} = 5.7 Hz), 158.9 (d, J_{C-F} = 281.5 Hz), 156.3 (d, J_{C-F} = 8.8 Hz), 136.9 (d, J_{C-F} = 3.4 Hz), 132.8 (d, J_{C-F} = 8.2 Hz), 129.5, 129.1 (d, J_{C-F} = 3.5 Hz), 128.7, 128.6, 119.2 (d, J_{C-F} = 7.6 Hz), 115.4 (d, J_{C-F} = 21.6 Hz), 86.3 (d, J_{C-F} = 21.3 Hz); **^{19}F NMR** (376 MHz, $CDCl_3$) δ (ppm) = -72.0, -113.4; **IR (ATR):** $\tilde{\nu}$ 1742, 1660, 1540, 1395, 1358, 1225, 1206, 1159, 1063, 866, 834, 765, 700, 525 cm^{-1}; **HRMS (ESI/QTOF)** m/z: $[M + H]^+$ Calcd for $C_{17}H_{11}F_2O_2^+$ 285.0722; Found 285.0731; **R_f:** 0.26 (1:9 EtOAc/pentane); **m.p.:** 147–150 °C.

6-Fluoro-3-(4-methoxyphenyl)-4-phenyl-2*H*-pyran-2-one (**5ad**):



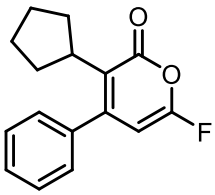
Obtained as bright yellow film in 55 % yield (16.0 mg), **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) = 7.31–7.22 (m, 3H), 7.14–7.09 (m, 2H), 7.07–7.02 (m, 2H), 6.76 (d, *J* = 8.7 Hz, 2H), 5.86 (s, 1H), 3.77 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ (ppm) = 160.1 (d, J_{C-F} = 5.7 Hz), 159.2, 158.7 (d, J_{C-F} = 280.7 Hz), 155.4 (d, J_{C-F} = 8.6 Hz), 137.3 (d, J_{C-F} = 3.5 Hz), 132.2, 129.3, 128.7, 128.6, 125.3, 119.9 (d, J_{C-F} = 7.5 Hz), 113.8, 86.3 (d, J_{C-F} = 21.3 Hz), 55.3; **^{19}F NMR** (376 MHz, $CDCl_3$) δ (ppm) = -73.0; **IR (ATR):** $\tilde{\nu}$ 1743, 1660, 1537, 1395, 1355, 1206, 1153, 1042, 921, 800, 779, 762, 699, 586 cm^{-1}; **HRMS (ESI/QTOF)** m/z: $[M + H]^+$ Calcd for $C_{18}H_{14}FO_3^+$ 297.0921; Found 297.0932; **R_f:** 0.33 (1:9 EtOAc/pentane).

3-Butyl-6-fluoro-4-phenyl-2*H*-pyran-2-one (**5ae**):



Obtained as pale yellow oil in 43 % yield (10.5 mg), **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) = 7.50–7.41 (m, 3H), 7.28–7.21 (m, 2H), 5.63 (s, 1H), 2.43–2.34 (m, 2H), 1.47 (tt, *J* = 8.0, 6.4 Hz, 2H), 1.23 (m, 2H), 0.80 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ (ppm) = 160.4 (d, J_{C-F} = 6.2 Hz), 157.9 (d, J_{C-F} = 279.3 Hz), 155.2 (d, J_{C-F} = 8.2 Hz), 137.6 (d, J_{C-F} = 3.6 Hz), 129.2, 128.9, 127.5, 121.1 (d, J_{C-F} = 7.4 Hz), 85.9 (d, J_{C-F} = 20.4 Hz), 30.8, 27.5, 22.7, 13.8; **^{19}F NMR** (376 MHz, $CDCl_3$) δ (ppm) = -75.5; **IR (ATR):** $\tilde{\nu}$ 2959, 2930, 1745, 1664, 1546, 1394, 1149, 1042, 767, 702 cm^{-1}; **HRMS (ESI/QTOF)** m/z: $[M + H]^+$ Calcd for $C_{15}H_{16}FO_2^+$ 247.1129; Found 247.1130; **R_f:** 0.43 (1:9 EtOAc/pentane).

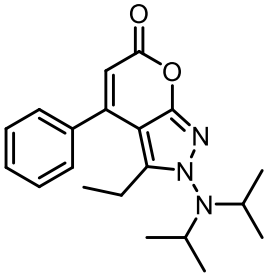
3-Cyclopentyl-6-fluoro-4-phenyl-2*H*-pyran-2-one (**5af**):



Obtained as pale yellow solid in 57 % yield (14.7 mg), **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) = 7.50–7.42 (m, 3H), 7.25 (m, 2H), 5.60 (s, 1H), 2.90 (m, 1H), 2.05–1.94 (m, 2H), 1.84 (qt, *J* = 7.9, 4.7 Hz, 2H), 1.65–1.57 (m, 2H), 1.49 (dtt, *J* = 7.0, 4.7, 2.9 Hz, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ (ppm) = 158.3 (d, J_{C-F} = 6.6 Hz), 158.0 (d, J_{C-F} = 279.9 Hz), 155.6 (d, J_{C-F} = 8.0 Hz), 138.3 (d, J_{C-F} = 3.6 Hz), 129.1, 128.9, 127.5, 123.2 (d, J_{C-F} = 7.2 Hz), 85.9 (d, J_{C-F} = 20.2 Hz), 39.3, 30.5, 26.9; **^{19}F NMR** (376 MHz, $CDCl_3$) δ (ppm) = -75.4; **IR (ATR):** $\tilde{\nu}$ 2949, 2869, 1743, 1664, 1538, 1446, 1395, 1355, 1203, 1141, 1046, 857, 805, 766, 702 cm^{-1}; **HRMS (ESI/QTOF)** m/z **HRMS (ESI/QTOF)** m/z: $[M + H]^+$ Calcd for $C_{16}H_{16}FO_2^+$ 259.1129; Found 259.1127; **R_f:** 0.45 (1:9 EtOAc/pentane); **m.p.:** 115–118 °C.

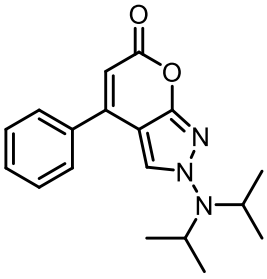
6. Formation of 6ag and 6ah:

6ag and **6ah** were synthesized according to General Procedure **A**, using alkynyl triazenes **2g** and **2h** respectively. Side product **7** was isolated along with **6ah**.



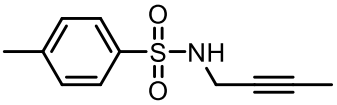
2-(Diisopropylamino)-3-ethyl-4-phenylpyrano[2,3-c]pyrazol-6(2*H*)-one (**6ag**):

Obtained as pale yellow solid in 76 % yield (25.8 mg), **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) = 7.49 (dd, *J* = 5.0, 2.0 Hz, 3H), 7.44–7.40 (m, 2H), 5.96 (s, 1H), 3.67 (hept, *J* = 6.4 Hz, 2H), 2.71 (q, *J* = 7.5 Hz, 2H), 1.03 (d, *J* = 6.5 Hz, 6H), 0.98 (d, *J* = 6.4 Hz, 6H), 0.48 (t, *J* = 7.6 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ (ppm) = 161.7, 156.9, 153.6, 144.9, 136.7, 129.8, 128.9, 127.3, 109.5, 97.4, 51.9, 20.7, 18.7, 12.9; **IR (ATR):** $\tilde{\nu}$ 2973, 2930, 1732, 1589, 1573, 1469, 1177, 1144, 849, 775, 705 cm^{-1}; **HRMS (ESI/QTOF)** m/z: $[M + H]^+$ Calcd for $C_{20}H_{26}N_3O_2^+$ 340.2020; Found 340.2024; **R_f:** 0.44 (1:4 EtOAc/pentane).



2-(Diisopropylamino)-4-phenylpyrano[2,3-c]pyrazol-6(2*H*)-one (**6ah**):

Obtained as red solid in 27 % yield (8.3 mg), **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) = 7.65–7.61 (m, 2H), 7.58 (s, 1H), 7.55–7.50 (m, 3H), 6.23 (s, 1H), 3.67 (hept, *J* = 6.4 Hz, 2H), 1.03 (d, *J* = 6.4 Hz, 12H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ (ppm) = 161.8, 157.1, 150.7, 135.4, 131.0, 129.4, 127.5, 108.5, 98.9, 51.6, 19.7; **IR (ATR):** $\tilde{\nu}$ 2959, 2924, 2853, 1730, 1595, 1574, 1463, 1446, 1383, 1260, 1186, 1166, 1093, 1019, 984, 850, 799, 772, 745, 698, 551 cm^{-1}; **HRMS (ESI/QTOF)** m/z: $[M + H]^+$ Calcd for $C_{18}H_{22}N_3O_2^+$ 312.1707; Found 312.1706; **R_f:** 0.57 (1:4 EtOAc/pentane).



N-(but-2-yn-1-yl)-4-methylbenzenesulfonamide (**7**):

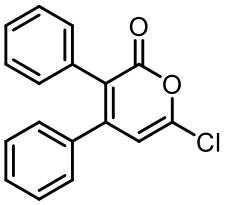
Obtained as colourless solid in 88 % yield (19.7 mg), **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) = 7.77 (d, *J* = 8.4 Hz, 2H), 7.36–7.26 (m, 2H), 4.64 (t, *J* = 6.0 Hz, 1H), 3.76 (dq, *J* = 6.0, 2.4 Hz, 2H), 2.42 (s, 3H), 1.59 (t, *J* = 2.4 Hz, 3H). The spectra obtained fit with reported literature.[7]

7. Product Diversifications:

General Procedure **B**: (0.10 mmol, 22.9 mg) and phenyl propiolic acid **1a** (0.11 mmol, 16.1 mg, 1.1 equiv.) were weighed in a microwave tube containing a magnetic stirring bar, followed by addition of CH_2Cl_2 (0.5 mL) at RT. The microwave tube was sealed, and the mixture was stirred at RT for 2 h. $AgSbF_6$ (10 mol%, 3.4 mg) was then added at RT. After sealing the microwave tube, the mixture was stirred at RT for 1 h.

6-Chloro-3,4-diphenyl-2*H*-pyran-2-one (**8**):

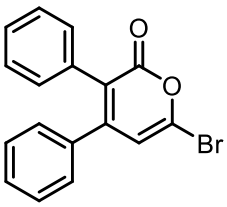
Following General Procedure **B**, without purification, 2 eq. TMSCl and 1.5 eq. TfOH were added to the crude at RT. After sealing the tube, mixture was stirred at 50 ˚C for 3 h. Volatiles were evaporated under reduced pressure, and crude was then purified by silica gel chromatography eluting with pentane/EtOAc to afford **8**.



Obtained as pale yellow solid in 83 % yield (23.6 mg), **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) = 7.26–7.19 (m, 6H), 7.15–7.10 (m, 2H), 7.09–7.05 (m, 2H), 6.42 (s, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ (ppm) = 161.8, 153.5, 147.4, 136.7, 133.1, 130.8, 129.3, 128.7, 128.6, 128.3, 128.2, 122.5, 108.0; **IR (ATR):** $\tilde{\nu}$ 1725, 1616, 1576, 1527, 1445, 1310, 1100, 1037, 980, 877, 766, 749, 697 cm^{-1}; **HRMS (ESI/QTOF)** m/z: $[M + Na]^+$ Calcd for $C_{17}H_{11}ClNaO_2^+$ 305.0340; Found 305.0343; **R_f:** 0.41 (1:9 EtOAc/pentane).

6-Bromo-3,4-diphenyl-2*H*-pyran-2-one (**9**):

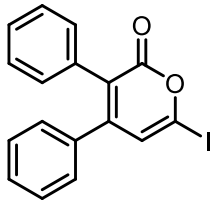
Following General Procedure **B**, without purification, 2 eq. TMSBr and 1.5 eq. TfOH were added to the crude at RT. After sealing the tube, mixture was stirred at 50 ˚C for 3 h. Volatiles were evaporated under reduced pressure, and crude was then purified by silica gel chromatography eluting with pentane/EtOAc to afford **9**.



Obtained as pale yellow oil in 80 % yield (26.2 mg), **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) = 7.32–7.27 (m, 2H), 7.27–7.24 (m, 4H), 7.18–7.15 (m, 2H), 7.13–7.10 (m, 2H), 6.62 (s, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ (ppm) = 161.9, 153.3, 136.6, 136.5, 133.1, 130.8, 129.3, 128.8, 128.6, 128.3, 128.2, 122.6, 112.7; **IR (ATR):** $\tilde{\nu}$ 1726, 1619, 1601, 1529, 1445, 1320, 1108, 1040, 987, 889, 830, 767, 750, 697, 636, 564; **HRMS (ESI/QTOF)** m/z: $[M + H]^+$ Calcd for $C_{17}H_{12}BrO_2^+$ 327.0015; Found 327.0017; **R_f:** 0.23 (1:9 EtOAc/pentane).

6-Iodo-3,4-diphenyl-2*H*-pyran-2-one (**10**):

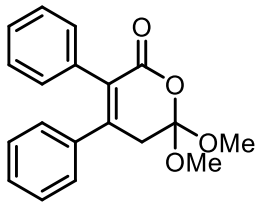
Following General Procedure **B**, without purification, 2 eq. TMSI and 1.5 eq. TfOH were added to the crude at RT. After sealing the tube, mixture was stirred at 50 ˚C for 3 h. Volatiles were evaporated under reduced pressure, and crude was then purified by silica gel chromatography eluting with pentane/EtOAc to afford **10**.



Obtained as yellow solid in 71 % yield (26.6 mg), **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) = 7.26–7.20 (m, 6H), 7.15–7.11 (m, 2H), 7.10–7.06 (m, 2H), 6.85 (s, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ (ppm) = 162.2, 152.6, 136.3, 133.1, 130.8, 129.2, 128.7, 128.6, 128.2, 128.2, 123.2, 121.4, 108.4; **IR (ATR):** $\tilde{\nu}$ 1719, 1608, 1598, 1574, 1522, 1445, 1309, 1095, 1034, 974, 766, 698; **HRMS (nanochip-ESI/LTQ-Orbitrap)** m/z: $[M + Na]^+$ Calcd for $C_{17}H_{11}INaO_2^+$ 396.9696; Found 396.9701; **R_f:** 0.43 (1:9 EtOAc/pentane).

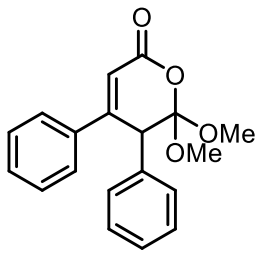
6,6-Dimethoxy-3,4-diphenyl-5,6-dihydro-2*H*-pyran-2-one (**11**):

Following General Procedure **B**, without purification, 5 eq. MeOH and 1.5 eq. TMSOTf were added to the crude at RT. After sealing the tube, mixture was stirred at 50 ˚C for 3 h. Volatiles were evaporated under reduced pressure, and crude was then purified by silica gel chromatography eluting with pentane/EtOAc to afford **11** and **11'**.



Obtained as yellow solid in 70 % yield (21.7 mg), **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) = 7.16–7.09 (m, 6H), 7.06–7.00 (m, 4H), 3.89 (s, 2H), 3.75 (s, 3H), 3.69 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ (ppm) = 171.0, 168.9, 143.9, 141.1, 137.1, 134.6, 130.3, 128.8, 128.1, 127.9, 127.5, 127.2, 52.3, 52.2, 41.8; **IR (ATR):** $\tilde{\nu}$ 2923, 2852, 1738, 1712, 1434, 1255, 1202, 1166, 699; **HRMS** (nanochip-ESI/LTQ-Orbitrap) m/z: $[M + Na]^+$ Calcd for $C_{19}H_{18}NaO_4^+$ 333.1097; Found 333.1101; **R_f:** 0.65 (1:9 EtOAc/pentane).

6,6-Dimethoxy-3,4-diphenyl-5,6-dihydro-2*H*-pyran-2-one (**11'**):

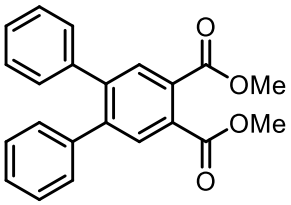


Obtained as yellow solid in 16 % yield (5.1 mg), **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) = 7.26–7.14 (m, 10H), 6.42 (s, 1H), 6.19 (s, 1H), 3.77 (s, 3H), 3.69 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ (ppm) = 172.1, 166.6, 156.3, 140.0, 136.3, 129.6, 128.7, 128.3, 128.1,

128.1, 127.3, 121.0, 52.6, 52.4, 51.7. **IR (ATR):** $\tilde{\nu}$ 2950, 2924, 1736, 1713, 1626, 1433, 1349, 1267, 1239, 1195, 1169, 1011, 881, 767, 698; **HRMS** (nanochip-ESI/LTQ-Orbitrap) m/z: $[M + Na]^+$ Calcd for $C_{19}H_{18}NaO_4^+$ 333.1097; Found 333.1101; **R_f:** 0.55 (1:9 EtOAc/pentane).

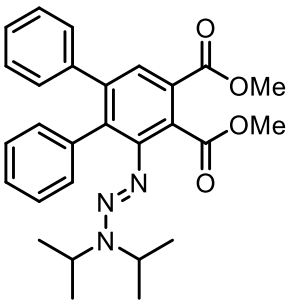
Dimethyl [1,1':2',1''-terphenyl]-4',5'-dicarboxylate (**12**):

Following General Procedure **B**, solvent was concentrated under reduced pressure, followd by addition of 1.5 eq. methyl acetylene dicarboxylate and 0.5 mL *p*-xylene. After sealing the tube, mixture was stirred at 140 ˚C for 1 d. Volatiles were evaporated under reduced pressure, and crude was then purified by silica gel chromatography eluting with pentane/EtOAc to afford **12** and **13**.



Obtained as yellow oil in 79 % yield (27.4 mg), **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) = 7.80 (s, 2H), 7.25–7.22 (m, 6H), 7.15–7.12 (m, 4H), 3.94 (s, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ (ppm) = 168.0, 143.6, 139.7, 131.4, 130.9, 129.8, 128.3, 127.6, 52.9; **IR (ATR):** $\tilde{\nu}$ 2953, 1731, 1435, 1317, 1248, 1169, 1135, 1077, 1028, 702; **HRMS (nanochip-ESI/LTQ-Orbitrap)** m/z: $[M + Na]^+$ Calcd for $C_{22}H_{18}NaO_4^+$ 369.1097; Found 369.1101; **R_f:**

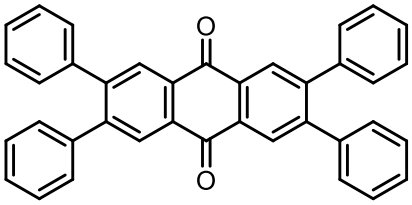
Dimethyl (*E*)-3'-(3,3-diisopropyltriaz-1-en-1-yl)-[1,1':2',1''-terphenyl]-4',5'-dicarboxylate (**13**):



Obtained as light yellow solid in 6 % yield (2.8 mg), **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) = 7.82 (s, 1H), 7.17–7.13 (m, 3H), 7.12–7.01 (m, 5H), 6.98–6.94 (m, 2H), 4.65 (m, 1H), 3.90 (s, 3H), 3.87 (s, 3H), 3.80 (m, 1H), 1.10 (d, *J* = 6.6 Hz, 6H), 0.99 (d, *J* = 6.8 Hz, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ (ppm) = 169.1, 166.4, 149.1, 143.4, 140.6, 139.1, 137.9, 131.4, 129.84, 128.0, 127.8, 127.7, 127.3, 127.0, 126.9, 126.2, 52.6, 52.5, 50.1, 46.8, 23.2, 19.0; **IR (ATR):** $\tilde{\nu}$ 2972, 2950, 1727, 1428, 1382, 1366, 1327, 1293, 1243, 1195, 1155, 1125, 1099, 1066, 1010, 766, 754, 700; **HRMS (nanochip-ESI/LTQ-Orbitrap)** m/z: $[M + H]^+$ Calcd for $C_{28}H_{32}N_3O_4^+$ 474.2387; Found 474.2391; **R_f:** 0.38 (1:4 EtOAc/pentane).

2,3,6,7-Tetraphenylanthraquinone (**14**):

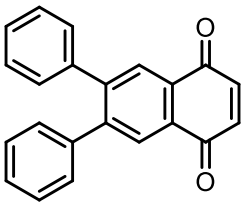
Following General Procedure **B**, solvent was concentrated under reduced pressure, followd by addition of 2.5 eq. *p*-quinone and 0.5 mL *p*-xylene. After sealing the tube, mixture was stirred at 140 ˚C for 3 d. Volatiles were evaporated under reduced pressure, and crude was then purified by silica gel chromatography eluting with pentane/EtOAc to afford **14**.



Obtained as yellow solid in 69 % yield (35.6 mg), **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) = 8.41 (s, 4H), 7.31–7.27 (m, 12H), 7.26–7.21 (m, 8H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ (ppm) = 183.0, 146.6, 139.8, 132.6, 129.8, 128.5, 127.9. The spectra obtained fit with reported literature.[8]

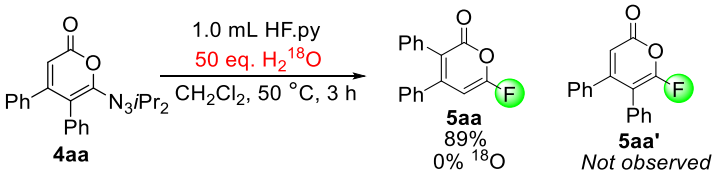
6,7-Diphenylnaphthoquinone (**15**):

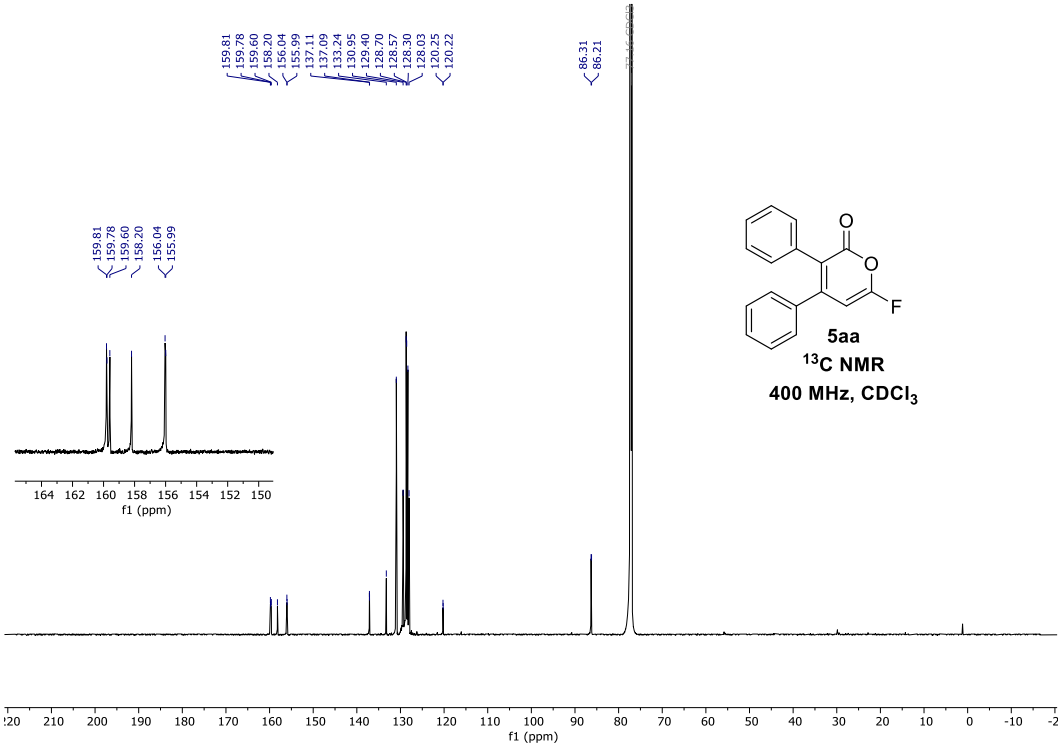
Following General Procedure **B**, solvent was concentrated under reduced pressure, followd by addition of 6 eq. *p*-quinone and 0.5 mL *p*-xylene. After sealing the tube, mixture was stirred at 140 ˚C for 3 d. Volatiles were evaporated under reduced pressure, and crude was then purified by silica gel chromatography eluting with pentane/EtOAc to afford **15**.



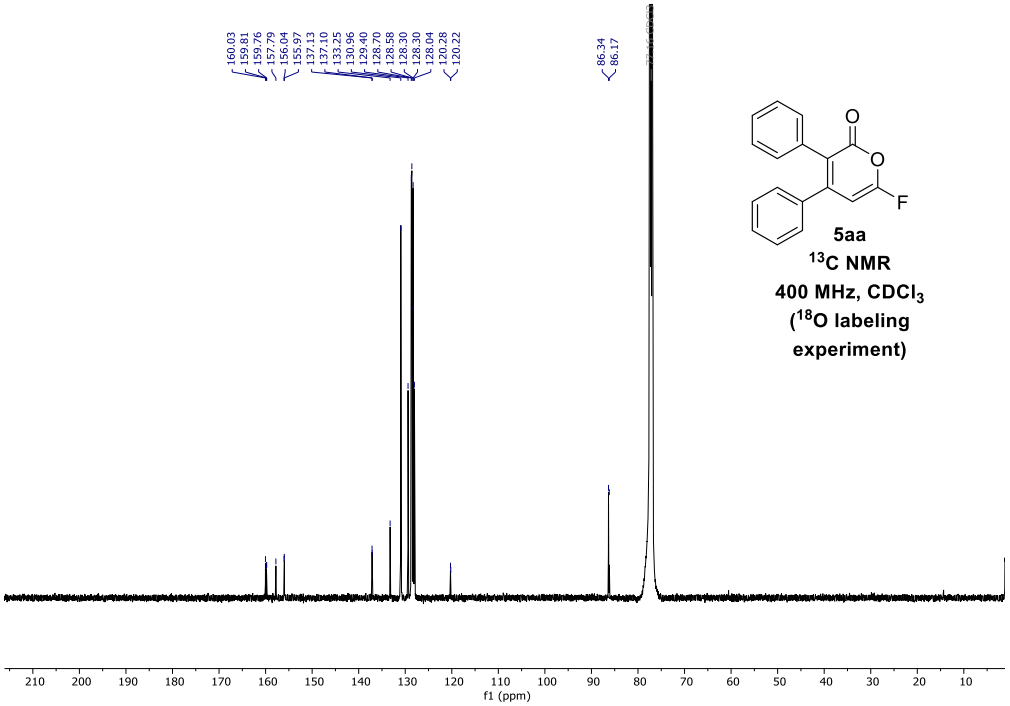
Obtained as yellow solid in 60 % yield (18.5 mg), **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm) = 8.15 (s, 2H), 7.28 (m, 6H), 7.18 (m, 4H), 7.02 (s, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ (ppm) = 185.1, 146.4, 139.6, 139.0, 130.8, 129.7, 129.0, 128.4, 127.9. The spectra obtained fit with reported literature.[8]

8. ^{18}O Labeling Experiments:

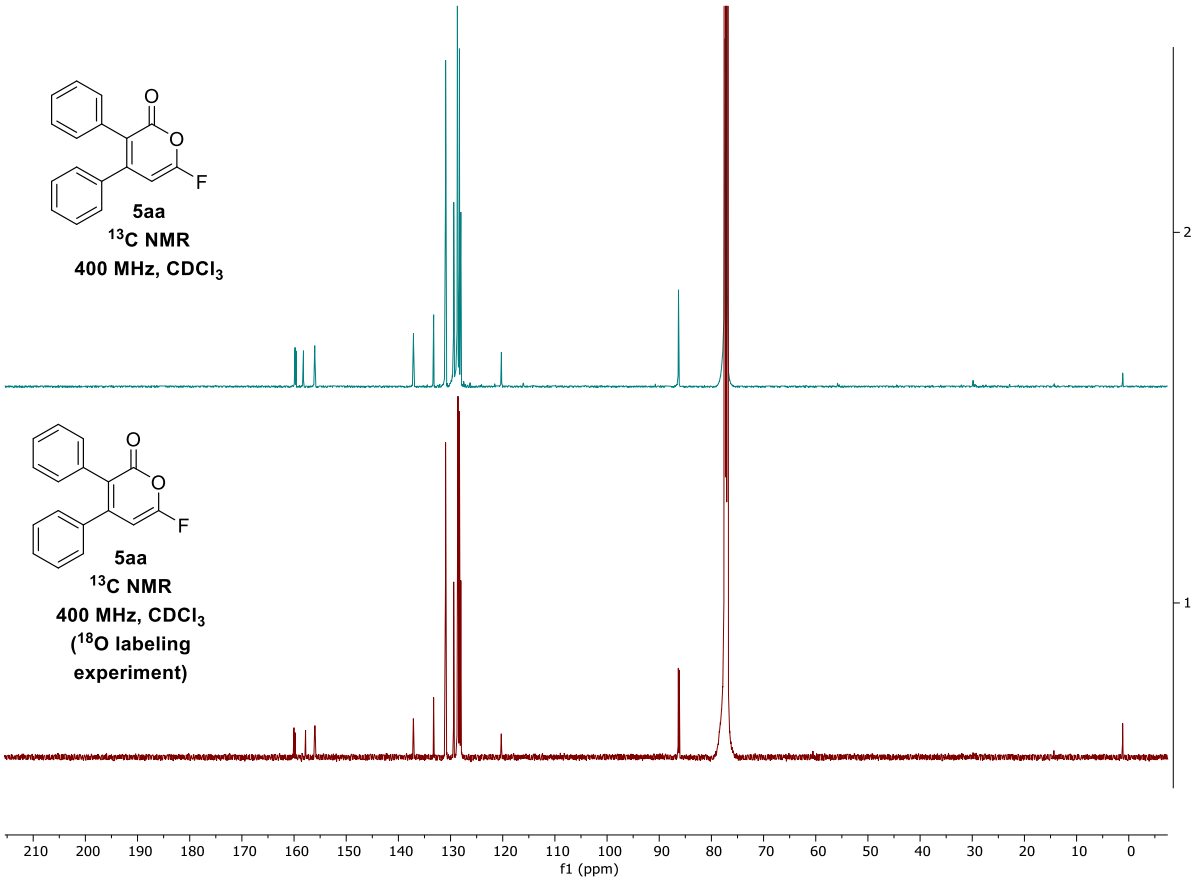


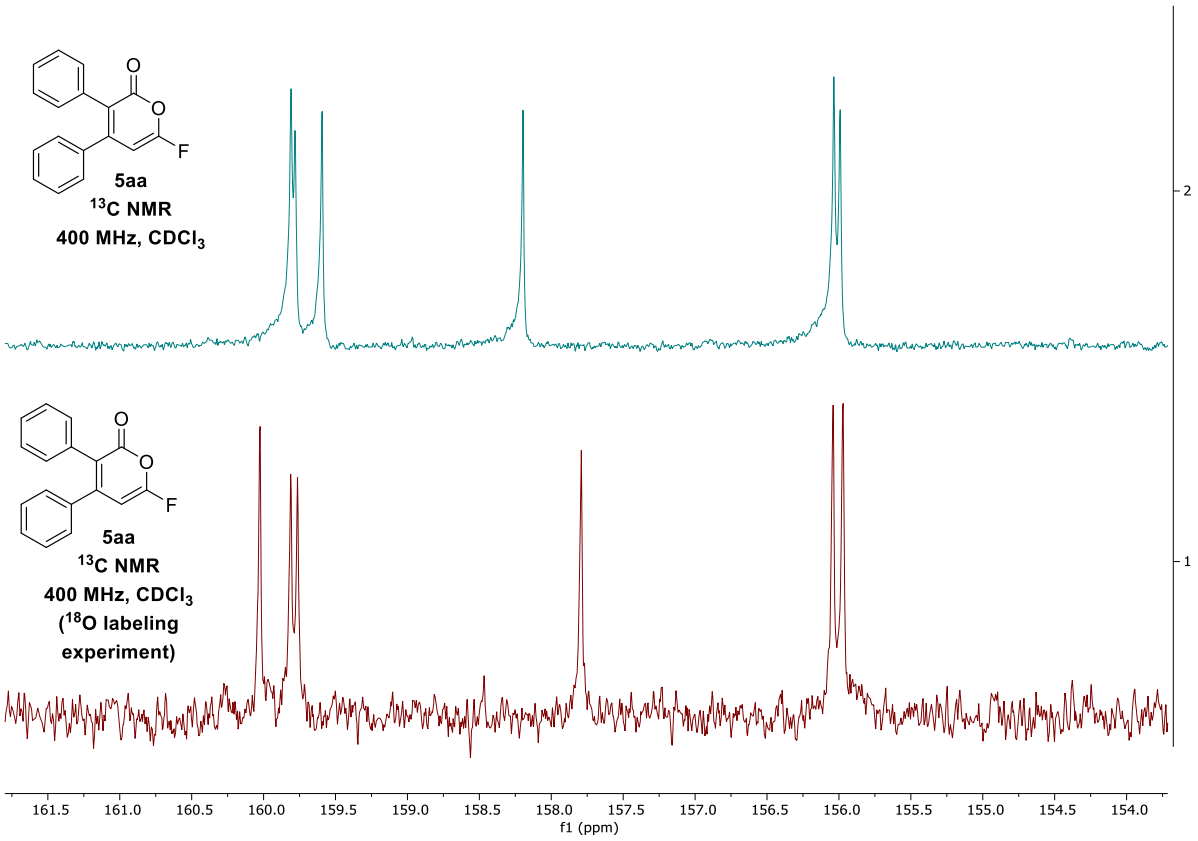


Original **5aa**: **^{13}C NMR** (101 MHz, $CDCl_3$) 159.80 (d, *J* = 5.9 Hz), 158.90 (d, *J* = 281.5 Hz), 156.01 (d, *J* = 8.7 Hz), 137.10 (d, *J* = 4.3 Hz), 133.24, 130.95, 129.40, 128.70, 128.58, 128.30, 128.03, 120.23 (d, *J* = 7.6 Hz), 86.26 (d, *J* = 21.2 Hz). **HRMS (ESI/QTOF)** m/z: $[M + H]^+$ Calcd for $C_{17}H_{12}FO_2^+$ 267.0815; Found 267.0813.



Isolated **5aa** from ^{18}O labelling experiment: **^{13}C NMR** (101 MHz, $CDCl_3$) 159.79 (d, *J* = 6.1 Hz), 158.91 (d, *J* = 281.3 Hz), 156.01 (d, *J* = 8.7 Hz), 137.12 (d, *J* = 3.3 Hz), 133.25, 130.96, 129.40, 128.70, 128.58, 128.30, 128.04, 120.25 (d, *J* = 7.7 Hz), 86.25 (d, *J* = 21.1 Hz). **HRMS (ESI/QTOF)** m/z: $[M + H]^+$ Calcd for $C_{17}H_{12}FO_2^+$ 267.0815; Found 267.0859.


5aa
^{13}C NMR
400 MHz, CDCl$_3$
5aa
^{13}C NMR
400 MHz, CDCl$_3$
(^{18}O labeling
experiment)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

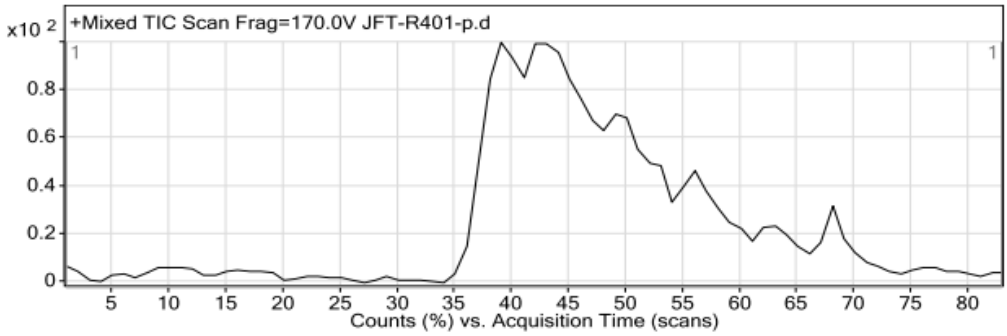

5aa
^{13}C NMR
400 MHz, CDCl$_3$
5aa
^{13}C NMR
400 MHz, CDCl$_3$
(^{18}O labeling
experiment)
161.5 161.0 160.5 160.0 159.5 159.0 158.5 158.0 157.5 157.0 156.5 156.0 155.5 155.0 154.5 154.0
f1 (ppm)

Qualitative Analysis Report

Data Filename	JFT-R401-p.d	**Sample Name**	JFT-R401-p
Sample Type	Sample	**Position**	Vial 61
Instrument Name	Instrument 1	**User Name**	
Acq Method	Bypass_ACN.m	**Acquired Time**	4/7/2021 11:27:00 AM
IRM Calibration Status	Success	**DA Method**	Default.m
Comment			

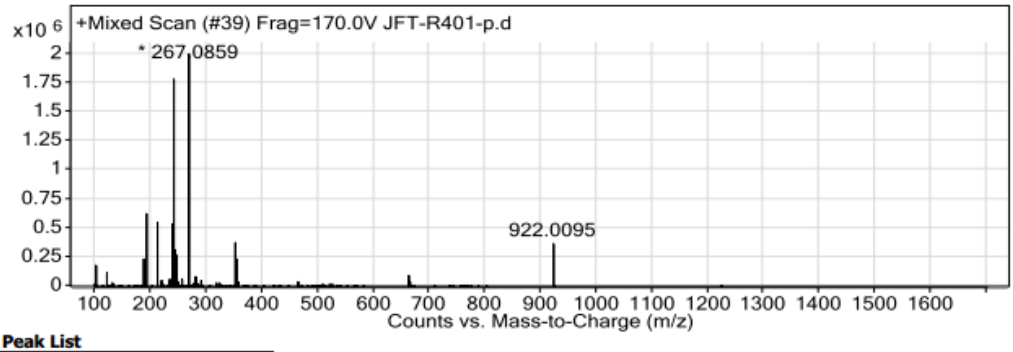
User Chromatograms

Fragmentor Voltage 170 **Collision Energy** 0 **Ionization Mode** Mixed



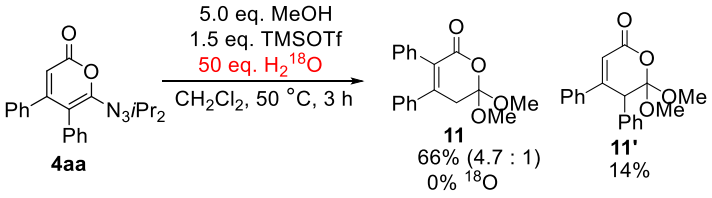
User Spectra

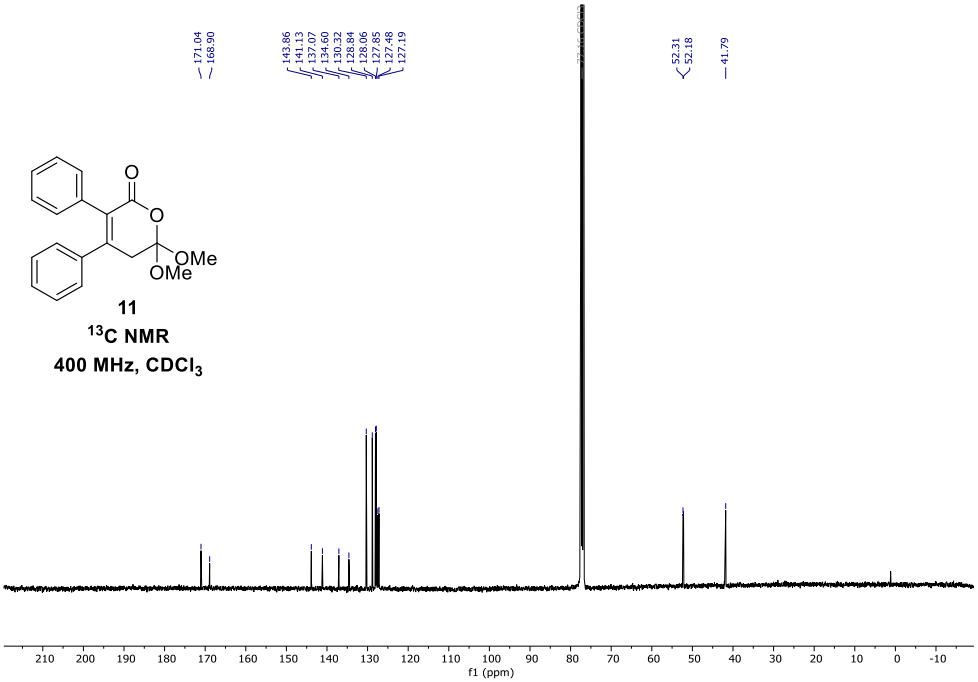
Fragmentor Voltage 170 **Collision Energy** 0 **Ionization Mode** Mixed



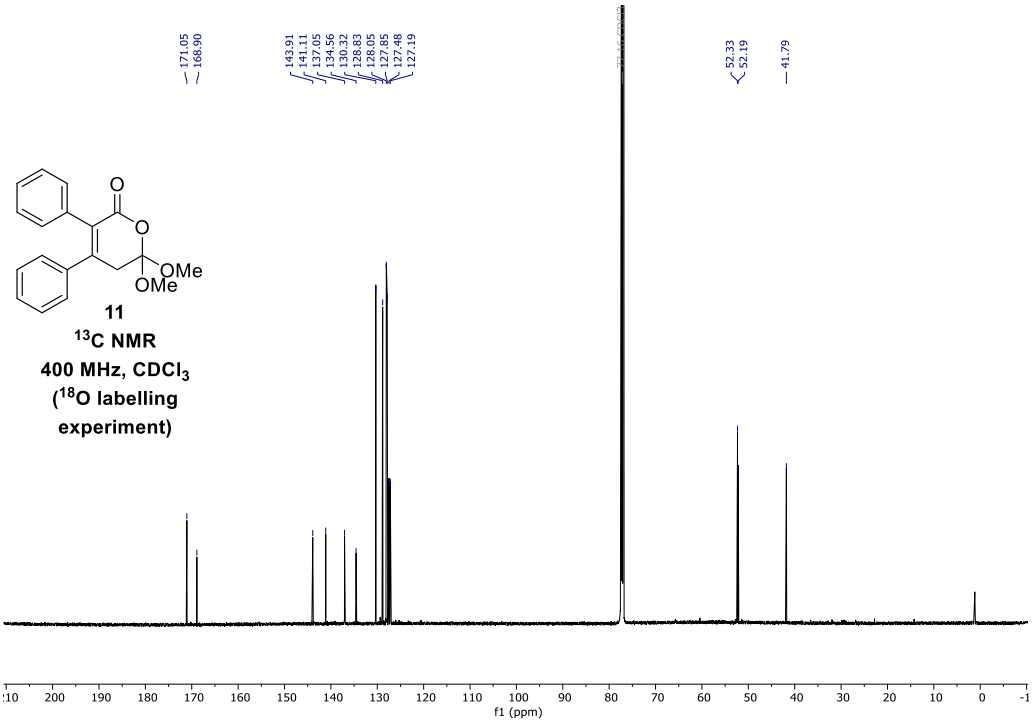
Peak List

m/z	z	Abund
191.0857		629242
211.092		565806
239.0869		535041
242.2851	1	1790877
243.2874	1	325701
267.0859	1	1994830
267.2259		271721
268.0857	1	811754
352.2165		389903
922.0095		365921

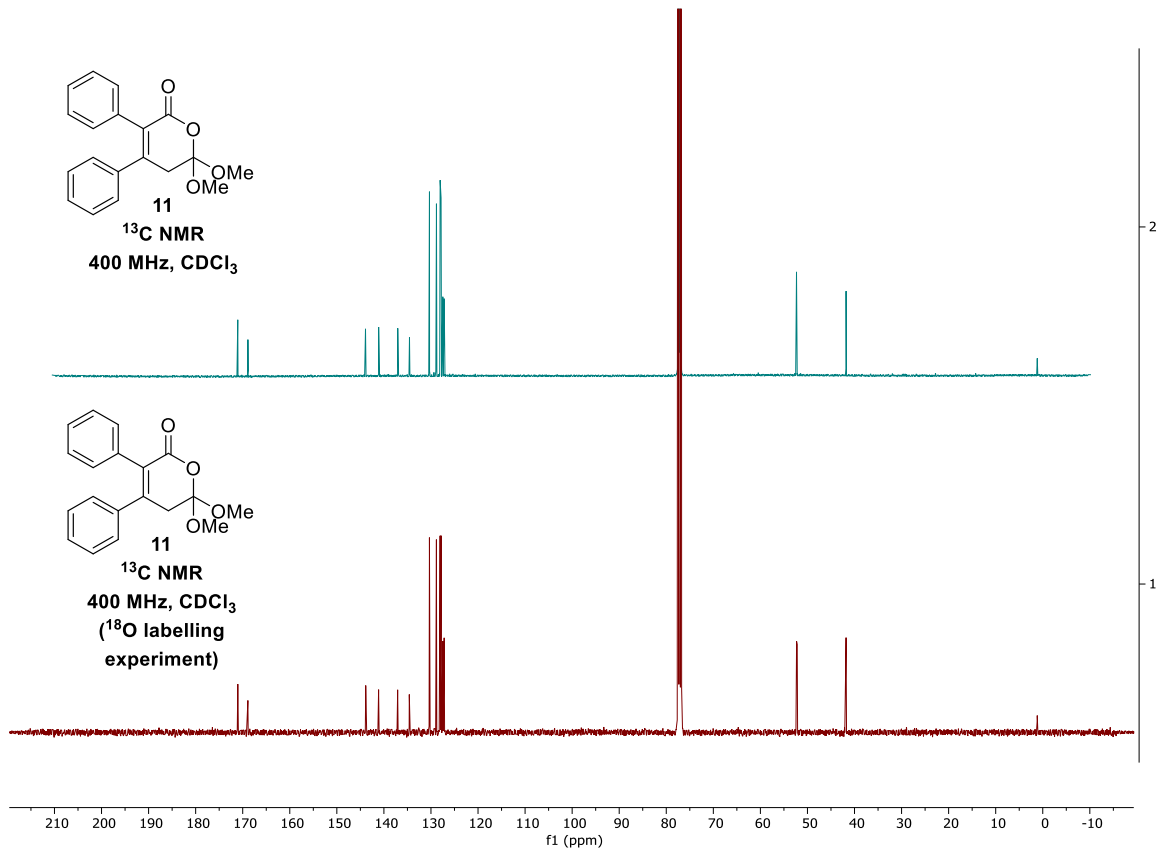


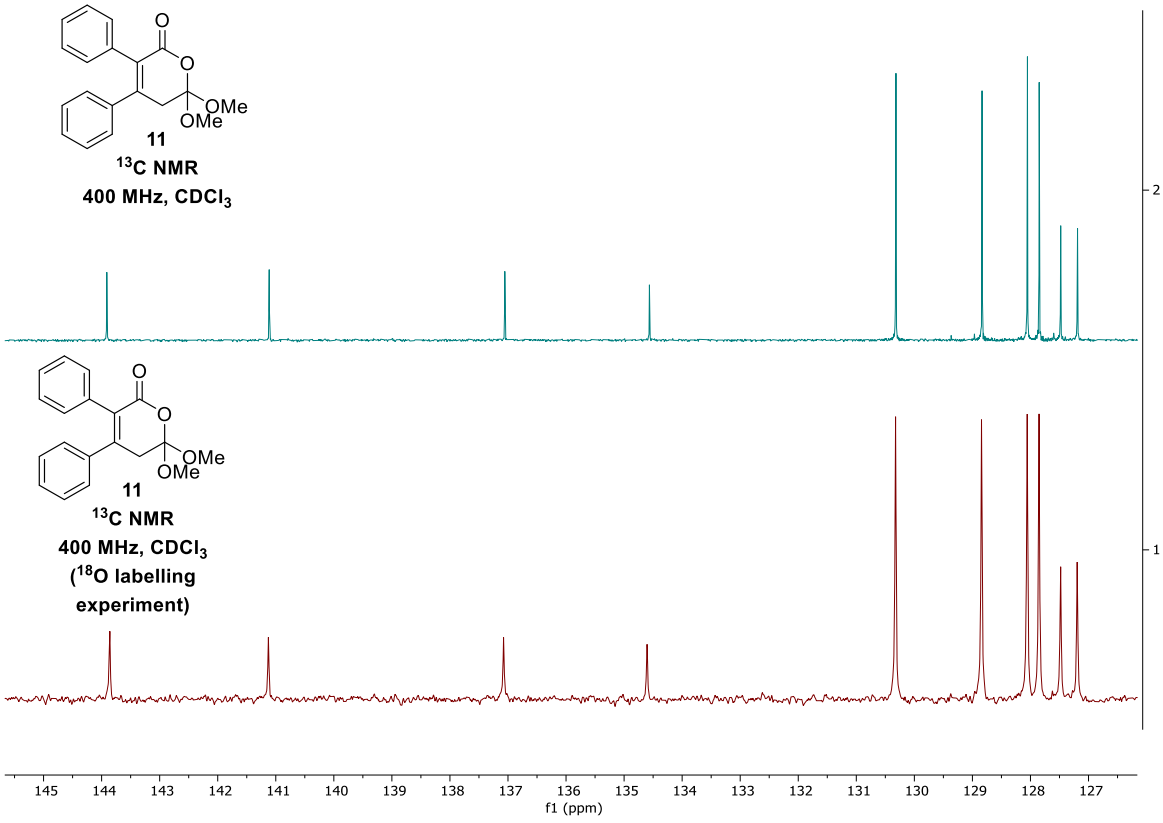


Original **11**: **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.04, 168.90, 143.86, 141.13, 137.07, 134.60, 130.32, 128.84, 128.06, 127.85, 127.48, 127.19, 52.31, 52.18, 41.79. **HRMS** (nanochip-ESI/LTQ-Orbitrap) m/z: $[M + Na]^+$ Calcd for $C_{19}H_{18}NaO_4^+$ 333.1097; Found 333.1101

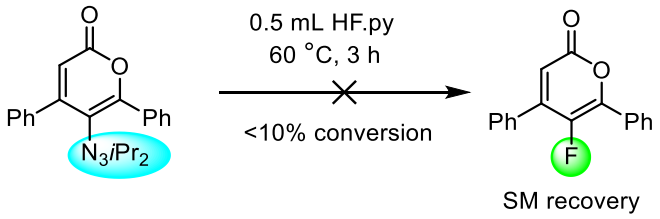


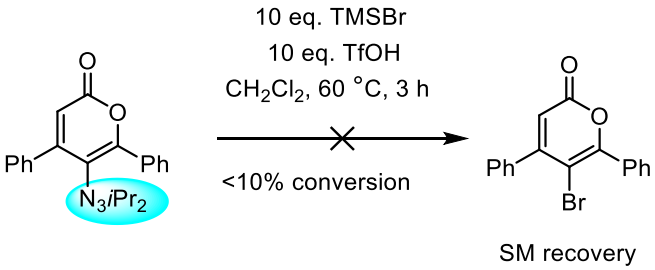
Isolated **11** from ^{18}O labelling experiment: **^{13}C NMR** (151 MHz, $CDCl_3$) δ 171.05, 168.90, 143.91, 141.11, 137.05, 134.56, 130.32, 128.83, 128.05, 127.85, 127.48, 127.19, 52.33, 52.19, 41.79. **HRMS** (nanochip-ESI/LTQ-Orbitrap) m/z: $[M + Na]^+$ Calcd for $C_{19}H_{18}NaO_4^+$ 333.1097; Found 333.1100

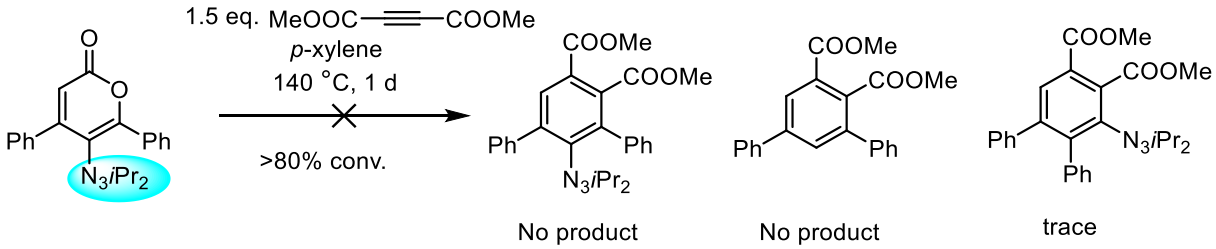

11
^{13}C NMR
400 MHz, $CDCl_3$
11
^{13}C NMR
400 MHz, $CDCl_3$
(^{18}O labelling
experiment)
f1 (ppm)


11
^{13}C NMR
400 MHz, $CDCl_3$
11
^{13}C NMR
400 MHz, $CDCl_3$
(^{18}O labelling
experiment)
f1 (ppm)

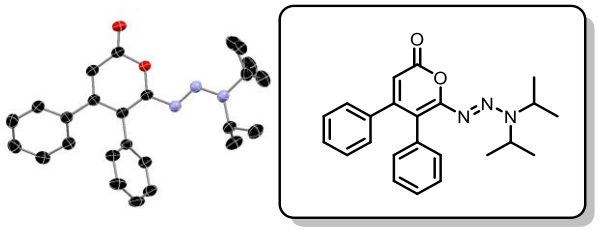
9. Derivatization attempts for 4aa':







10. X-ray Structures:



Crystal data and structure refinement for **4aa**.

Formula	$C_{23}H_{25}N_3O_2$
$D_{calc.}$/ g cm^{-3}	1.214
m /mm^{-1}	0.625
Formula Weight	375.46
Colour	clear intense yellow
Shape	prism
Size/mm^3	0.40×0.28×0.25
T/K	140.00(10)
Crystal System	monoclinic
Space Group	$P2_1/c$
a/Å	11.4016(3)
b/Å	9.5092(2)
c/Å	19.0932(4)
a /°	90
b /°	96.950(2)
g /°	90
V/Å^3	2054.86(9)
Z	4
Z'	1
Wavelength/Å	1.54184
Radiation type	Cu K_a
Q_{min}/°	3.906
Q_{max}/°	76.556
Measured Refl's.	11847
Indep't Refl's	4260
Refl's I≥2 σ(I)	3775
R_{int}	0.0226
Parameters	348
Restraints	67
Largest Peak	0.272
Deepest Hole	-0.339
GooF	1.043
wR_2 (all data)	0.1321
wR_2	0.1244
R_1 (all data)	0.0498
R_1	0.0452

Reflection Statistics

Total reflections (after filtering)	12230	Unique reflections	4260
Completeness	0.989	Mean I/σ	25.25
hkl_{max} collected	(14, 11, 24)	hkl_{min} collected	(-13, -6, -24)
hkl_{max} used	(14, 11, 24)	hkl_{min} used	(-14, 0, 0)
Lim d_{max} collected	100.0	Lim d_{min} collected	0.77
d_{max} used	11.32	d_{min} used	0.79
Friedel pairs	666	Friedel pairs merged	1
Inconsistent equivalents	9	R_{int}	0.0226
R_{sigma}	0.0193	Intensity transformed	0
Omitted reflections	0	Omitted by user (OMIT hkl)	0
Multiplicity	(4826, 2307, 678, 126, 48, 2)	Maximum multiplicity	9
Removed systematic absences	383	Filtered off (Shel/OMIT)	0

Table 1: Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for **4aa**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij}.

Atom	x	y	z	U_{eq}
O1	3137.0(7)	1298.0(9)	5119.3(4)	32.1(2)
O2	3040.9(8)	510.7(10)	4025.8(5)	41.9(2)
N1	3103.5(8)	2089.5(10)	6271.5(5)	30.7(2)
N2	2042.2(8)	1606.4(10)	6156.8(5)	30.5(2)
N3	1442.1(9)	1676.5(11)	6700.7(5)	32.7(2)
C1	3706.0(10)	1978.9(11)	5688.2(5)	29.0(2)
C2	3635.1(10)	1134.6(12)	4495.6(6)	32.9(2)
C3	4766.6(11)	1767.3(12)	4477.3(6)	34.0(3)
C4	5347.6(10)	2458.3(11)	5047.7(6)	29.9(2)
C5	4810.1(10)	2543.5(11)	5691.9(6)	28.8(2)
C6	6470.6(10)	3189.5(12)	4952.6(6)	31.1(2)
C7	7256.2(11)	2580.4(14)	4532.1(7)	38.2(3)
C8	8231.7(12)	3328.3(16)	4365.2(7)	44.1(3)
C9	8451.4(11)	4672.1(15)	4624.0(7)	41.5(3)
C10	7697.8(11)	5269.5(13)	5058.7(7)	38.2(3)
C11	6712.1(10)	4534.8(12)	5221.9(6)	34.4(3)
C12	5401.3(10)	3147.2(12)	6367.2(6)	29.9(2)
C13	4936.8(11)	4321.9(13)	6675.5(7)	37.8(3)
C14	5459.8(13)	4810.0(15)	7328.3(7)	44.7(3)
C15	6435.4(13)	4130.0(15)	7672.0(7)	45.1(3)
C16	6906.9(13)	2972.7(15)	7365.6(7)	44.6(3)
C17	6391.2(11)	2484.8(12)	6711.0(6)	36.1(3)
C18	1925.7(12)	2358.7(13)	7370.7(6)	36.3(3)
C19	1701.6(16)	3940.2(15)	7330.2(8)	49.3(3)
C20	1468.9(16)	1667.0(17)	8002.9(7)	48.8(3)
C21	195.5(11)	1238.7(14)	6533.1(7)	38.6(3)
C22	-612(14)	2519(16)	6437(16)	60(5)
C23	-482.6(15)	2265(3)	6026.6(15)	59.1(7)
C24	10(17)	300(30)	5876(13)	67(6)
C25	133.5(16)	-251(2)	6247.4(12)	50.5(5)

Table 2: Anisotropic Displacement Parameters (×10^4) for **4aa**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2} \times U_{11} + ... + 2hka^* \times b^* \times U_{12}]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O1	34.6(4)	34.9(4)	26.7(4)	-4.6(3)	2.9(3)	-3.1(3)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O2	43.5(5)	48.4(5)	33.0(4)	-12.9(4)	1.1(3)	-4.2(4)
N1	34.0(5)	32.1(5)	26.2(4)	0.5(3)	4.6(3)	-0.7(4)
N2	34.3(5)	30.9(5)	26.7(4)	2.4(3)	5.3(3)	0.5(4)
N3	36.0(5)	36.4(5)	26.5(5)	1.4(4)	7.0(4)	0.0(4)
C1	34.9(5)	28.4(5)	23.5(5)	-0.9(4)	1.9(4)	0.8(4)
C2	38.6(6)	32.9(6)	26.8(5)	-4.8(4)	1.8(4)	2.3(4)
C3	39.2(6)	36.7(6)	26.5(5)	-3.5(4)	5.4(4)	0.3(5)
C4	35.0(5)	28.5(5)	26.3(5)	0.1(4)	3.6(4)	2.4(4)
C5	34.0(5)	27.6(5)	24.6(5)	-0.5(4)	2.4(4)	1.3(4)
C6	35.3(5)	33.8(5)	24.3(5)	1.9(4)	3.2(4)	0.5(4)
C7	41.1(6)	41.0(7)	33.4(6)	-4.0(5)	8.2(5)	-1.6(5)
C8	41.9(6)	54.8(8)	37.5(6)	-0.2(6)	12.7(5)	-1.0(6)
C9	39.4(6)	48.6(7)	36.6(6)	10.6(5)	4.2(5)	-6.6(5)
C10	44.7(6)	33.4(6)	35.1(6)	6.2(5)	0.0(5)	-3.8(5)
C11	39.9(6)	32.7(6)	30.6(5)	3.6(4)	3.9(4)	1.5(4)
C12	35.5(5)	30.4(5)	24.2(5)	-1.5(4)	5.0(4)	-5.3(4)
C13	41.4(6)	37.0(6)	35.4(6)	-7.1(5)	6.4(5)	-1.1(5)
C14	54.5(7)	43.4(7)	37.8(6)	-14.5(5)	11.8(5)	-8.2(6)
C15	60.3(8)	46.5(7)	27.6(6)	-6.8(5)	1.0(5)	-16.5(6)
C16	52.7(7)	42.6(7)	35.1(6)	0.5(5)	-9.2(5)	-5.6(6)
C17	42.2(6)	32.4(6)	32.2(6)	-2.3(4)	-1.2(5)	-2.3(5)
C18	46.2(7)	37.6(6)	25.7(5)	0.1(4)	6.3(4)	1.0(5)
C19	76.0(10)	38.4(7)	34.2(6)	-2.2(5)	9.4(6)	2.2(6)
C20	69.5(9)	48.8(8)	29.8(6)	3.4(5)	12.9(6)	-1.3(7)
C21	35.7(6)	45.6(7)	35.8(6)	4.8(5)	9.3(4)	-2.0(5)
C22	31(7)	77(9)	73(14)	-3(8)	3(8)	4(6)
C23	37.0(8)	74.6(13)	64.5(14)	25.6(11)	1.8(8)	3.2(8)
C24	47(9)	71(11)	81(11)	-19(9)	6(9)	-14(8)
C25	46.1(8)	54.3(10)	52.6(11)	-7.2(8)	12.2(7)	-13.8(7)

Table 3: Bond Lengths in Å for **4aa**.

Atom	Atom	Length/Å
O1	C1	1.3599(13)
O1	C2	1.3888(13)
O2	C2	1.2118(15)
N1	N2	1.2880(14)
N1	C1	1.3814(14)
N2	N3	1.3127(13)
N3	C18	1.4801(15)
N3	C21	1.4784(15)
C1	C5	1.3678(16)
C2	C3	1.4277(17)
C3	C4	1.3719(16)
C4	C5	1.4413(15)
C4	C6	1.4873(16)
C5	C12	1.4953(14)
C6	C7	1.3987(16)
C6	C11	1.3937(17)
C7	C8	1.3894(18)

Atom	Atom	Length/Å
C8	C9	1.382(2)
C9	C10	1.3865(19)
C10	C11	1.3903(17)
C12	C13	1.3965(16)
C12	C17	1.3864(17)
C13	C14	1.3945(18)
C14	C15	1.382(2)
C15	C16	1.385(2)
C16	C17	1.3947(17)
C18	C19	1.5258(18)
C18	C20	1.5209(17)
C21	C22	1.524(12)
C21	C23	1.518(2)
C21	C24	1.534(13)
C21	C25	1.517(2)

Table 4: Bond Angles in ° for **4aa**.

Atom	Atom	Atom	Angle/°
C1	O1	C2	122.22(9)
N2	N1	C1	112.60(9)
N1	N2	N3	114.60(9)
N2	N3	C18	122.06(10)
N2	N3	C21	113.20(9)

Atom	Atom	Atom	Angle/°
C21	N3	C18	123.94(9)
O1	C1	N1	116.39(9)
O1	C1	C5	122.74(10)
C5	C1	N1	120.88(10)
O1	C2	C3	115.99(9)

Atom	Atom	Atom	Angle/°
O2	C2	O1	116.08(10)
O2	C2	C3	127.89(11)
C4	C3	C2	122.23(10)
C3	C4	C5	119.34(10)
C3	C4	C6	117.85(10)
C5	C4	C6	122.62(10)
C1	C5	C4	117.36(10)
C1	C5	C12	118.27(10)
C4	C5	C12	124.30(10)
C7	C6	C4	119.80(10)
C11	C6	C4	121.24(10)
C11	C6	C7	118.70(11)
C8	C7	C6	120.38(12)
C9	C8	C7	120.44(12)
C8	C9	C10	119.62(12)
C9	C10	C11	120.30(12)
C10	C11	C6	120.50(11)
C13	C12	C5	121.07(10)
C17	C12	C5	119.35(10)
C17	C12	C13	119.49(11)
C14	C13	C12	120.00(12)
C15	C14	C13	120.09(12)
C14	C15	C16	120.16(12)
C15	C16	C17	119.98(13)
C12	C17	C16	120.27(12)
N3	C18	C19	110.22(10)
N3	C18	C20	111.65(11)
C20	C18	C19	113.28(11)
N3	C21	C22	110.6(7)
N3	C21	C23	111.04(11)
N3	C21	C24	112.0(7)
N3	C21	C25	110.04(11)
C22	C21	C24	110.3(11)
C25	C21	C23	111.94(15)

Table 5: Torsion Angles in ° for **4aa**.

Atom	Atom	Atom	Atom	Angle/°
O1	C1	C5	C4	3.10(16)
O1	C1	C5	C12	-174.21(9)
O1	C2	C3	C4	1.99(17)
O2	C2	C3	C4	179.46(12)
N1	N2	N3	C18	4.49(15)
N1	N2	N3	C21	174.59(9)
N1	C1	C5	C4	-176.26(9)
N1	C1	C5	C12	6.44(15)
N2	N1	C1	O1	-4.89(14)
N2	N1	C1	C5	174.50(10)
N2	N3	C18	C19	84.71(14)
N2	N3	C18	C20	-148.48(11)
N2	N3	C21	C22	-101.6(12)
N2	N3	C21	C23	-66.75(18)
N2	N3	C21	C24	21.9(14)
N2	N3	C21	C25	57.75(15)
C1	O1	C2	O2	-179.87(10)
C1	O1	C2	C3	-2.09(15)
C1	N1	N2	N3	179.25(9)
C1	C5	C12	C13	-64.56(14)
C1	C5	C12	C17	112.03(12)
C2	O1	C1	N1	178.90(9)
C2	O1	C1	C5	-0.48(16)
C2	C3	C4	C5	0.58(17)
C2	C3	C4	C6	-174.61(11)
C3	C4	C5	C1	-3.09(16)
C3	C4	C5	C12	174.04(10)
C3	C4	C6	C7	-37.96(16)
C3	C4	C6	C11	136.13(11)
C4	C5	C12	C13	118.34(13)
C4	C5	C12	C17	-65.07(15)
C4	C6	C7	C8	171.75(11)
C4	C6	C11	C10	-172.40(10)
C5	C4	C6	C7	147.03(11)
C5	C4	C6	C11	-38.88(16)
C5	C12	C13	C14	175.81(11)

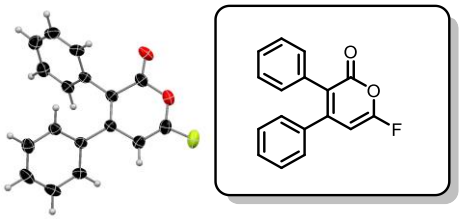
Atom	Atom	Atom	Atom	Angle/°
C5	C12	C17	C16	-175.52(11)
C6	C4	C5	C1	171.86(10)
C6	C4	C5	C12	-11.02(17)
C6	C7	C8	C9	1.3(2)
C7	C6	C11	C10	1.75(17)
C7	C8	C9	C10	0.6(2)
C8	C9	C10	C11	-1.38(19)
C9	C10	C11	C6	0.17(18)
C11	C6	C7	C8	-2.49(19)
C12	C13	C14	C15	-0.2(2)
C13	C12	C17	C16	1.12(18)
C13	C14	C15	C16	0.8(2)
C14	C15	C16	C17	-0.5(2)
C15	C16	C17	C12	-0.5(2)
C17	C12	C13	C14	-0.77(18)
C18	N3	C21	C22	68.3(12)
C18	N3	C21	C23	103.14(18)
C18	N3	C21	C24	-168.2(14)
C18	N3	C21	C25	-132.37(14)
C21	N3	C18	C19	-84.32(14)
C21	N3	C18	C20	42.50(16)

Table 6: Hydrogen Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for **4aa**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij}.

Atom	x	y	z	U_{eq}
H3	5066(15)	1735(18)	4030(10)	46(4)
H7	7152(15)	1595(19)	4381(9)	45(4)
H8	8765(16)	2880(20)	4083(10)	54(5)
H9	9114(15)	5239(18)	4517(9)	45(4)
H10	7847(14)	6186(18)	5246(9)	43(4)
H11	6137(15)	4990(20)	5518(10)	51(4)
H13	4254(15)	4791(19)	6440(9)	49(4)
H14	5123(16)	5630(20)	7537(11)	57(5)
H15	6800(16)	4480(20)	8147(10)	55(5)
H16	7612(18)	2470(20)	7623(11)	59(5)
H17	6706(13)	1657(17)	6505(8)	36(4)
H18	2773(14)	2194(15)	7408(8)	33(3)
H19A	842(17)	4120(20)	7295(10)	56(5)
H19B	2074(17)	4370(20)	7762(11)	62(5)
H19C	2032(16)	4330(20)	6923(11)	56(5)
H20A	1593(17)	650(20)	7987(10)	61(5)
H20B	609(19)	1880(20)	8034(11)	62(5)
H20C	1885(17)	2050(20)	8432(11)	58(5)
H21A	-27.24	684.4	6942	46
H21	-174.51	1244.56	6981.92	46
H22A	-642.08	2976.51	6894.92	91
H22B	-1408.85	2221.54	6244.06	91
H22C	-304.86	3183.08	6111.83	91
H23A	-462.13	3202.26	6241.54	89
H23B	-1304.39	1952.72	5923.81	89
H23C	-118.84	2303.8	5587.46	89
H24A	108.5	858.05	5456.67	100
H24B	-788.82	-99.49	5830.22	100
H24C	591.25	-465.7	5922.81	100
H25A	470.39	-279.26	5799.12	76
H25B	-692.75	-557.61	6171.08	76
H25C	582.84	-879.46	6587.46	76

Table 7: Atomic Occupancies for all atoms that are not fully occupied in **4aa**.

Atom	Occupancy
H21A	0.092(6)
H21	0.908(6)
C22	0.092(6)
H22A	0.092(6)
H22B	0.092(6)
H22C	0.092(6)
C23	0.908(6)
H23A	0.908(6)
H23B	0.908(6)
H23C	0.908(6)
C24	0.092(6)
H24A	0.092(6)
H24B	0.092(6)
H24C	0.092(6)
C25	0.908(6)
H25A	0.908(6)
H25B	0.908(6)
H25C	0.908(6)



Crystal data and structure refinement for **5aa**.

Formula	$C_{17}H_{11}FO_2$
$D_{calc.}$/ g cm^{-3}	1.378
m /mm^{-1}	0.823
Formula Weight	266.26
Colour	clear pale colourless
Shape	prism
Size/mm^3	0.61×0.10×0.08
T/K	140.00(10)
Crystal System	monoclinic
Space Group	$P2_1/n$
a/Å	6.12164(16)
b/Å	18.5825(5)
c/Å	11.3690(2)
a/°	90
b/°	97.117(2)
g/°	90
V/Å^3	1283.32(6)
Z	4
Z'	1
Wavelength/Å	1.54184
Radiation type	Cu K_α
Q_{min}/°	4.585
Q_{max}/°	76.661
Measured Refl's.	14068
Indep't Refl's	2685
Refl's I≥2 σ(I)	2402
R_{int}	0.0266
Parameters	226
Restraints	0
Largest Peak	0.221
Deepest Hole	-0.173
GooF	1.035
wR_2 (all data)	0.0920
wR_2	0.0881
R_1 (all data)	0.0369
R_1	0.0328

Reflection Statistics

Total reflections (after filtering)	14354	Unique reflections	2685
Completeness	0.995	Mean I/σ	30.74
hkl_{max} collected	(7, 23, 10)	hkl_{min} collected	(-7, -23, -14)
hkl_{max} used	(7, 23, 14)	hkl_{min} used	(-7, 0, 0)
Lim d_{max} collected	100.0	Lim d_{min} collected	0.77
d_{max} used	11.28	d_{min} used	0.79
Friedel pairs	1097	Friedel pairs merged	1
Inconsistent equivalents	1	R_{int}	0.0266
R_{sigma}	0.0172	Intensity transformed	0
Omitted reflections	0	Omitted by user (OMIT hkl)	0
Multiplicity	(2878, 1688, 851, 441, 214, 142, 61, 39, 34, 27, 20, 16, 6, 4)	Maximum multiplicity	25
Removed systematic absences	286	Filtered off (Shel/OMIT)	0

Table 8: Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for **5aa**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij}.

Atom	x	y	z	U_{eq}
F1	4824.4(15)	9275.7(4)	5555.8(7)	49.1(2)
O1	6295.5(14)	8385.6(4)	6614.7(7)	38.2(2)
O2	8029.7(14)	7524.0(5)	7707.6(7)	43.1(2)
C1	4630(2)	8583.9(6)	5816.3(10)	36.3(2)
C2	6423.5(18)	7668.7(6)	7028.5(9)	33.2(2)
C3	4621.4(16)	7194.0(6)	6587.4(8)	28.9(2)
C4	3016.8(16)	7425.4(6)	5718.8(8)	28.2(2)
C5	3023.4(19)	8162.0(6)	5324.2(9)	33.9(2)
C6	4671.7(16)	6478.5(6)	7171.3(8)	29.3(2)
C7	6471.4(18)	6018.8(7)	7169.4(9)	35.4(2)
C8	6516(2)	5363.1(7)	7758.9(10)	41.3(3)
C9	4777(2)	5162.3(7)	8362.0(10)	42.0(3)
C10	2980(2)	5616.8(7)	8364.1(10)	39.9(3)
C11	2919.3(18)	6272.5(6)	7773.6(9)	32.8(2)
C12	1270.9(16)	6950.2(6)	5120.9(8)	27.8(2)
C13	-824.6(17)	7229.7(6)	4763.7(9)	32.8(2)
C14	-2453.8(19)	6806.1(8)	4143.8(10)	41.0(3)
C15	-2001(2)	6101.6(8)	3872.1(10)	43.3(3)
C16	79(2)	5818.3(7)	4207.4(10)	38.5(3)
C17	1709.8(18)	6239.7(6)	4828.1(9)	31.7(2)

Table 9: Anisotropic Displacement Parameters (×10^4) for **5aa**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2} \times U_{11} + ... + 2hka^* \times b^* \times U_{12}]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
F1	68.5(5)	30.0(4)	50.3(4)	-3.0(3)	13.8(4)	-11.0(3)
O1	40.8(4)	38.9(4)	35.3(4)	-7.1(3)	5.8(3)	-12.0(3)
O2	32.5(4)	59.3(6)	35.5(4)	-4.1(4)	-3.8(3)	-9.9(4)
C1	47.4(6)	30.2(5)	32.9(5)	-3.2(4)	11.2(4)	-4.9(4)
C2	31.7(5)	41.4(6)	26.7(5)	-4.4(4)	4.8(4)	-6.8(4)
C3	27.0(5)	34.3(5)	25.6(4)	-2.4(4)	3.4(4)	-2.7(4)
C4	29.0(5)	30.7(5)	25.2(4)	-2.6(4)	4.5(4)	0.0(4)
C5	40.5(6)	31.4(5)	29.7(5)	-1.0(4)	3.9(4)	0.0(4)
C6	27.5(5)	35.6(5)	23.5(4)	-1.1(4)	-2.1(3)	-1.2(4)
C7	30.4(5)	44.9(6)	30.1(5)	1.5(4)	0.6(4)	3.4(4)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C8	42.7(6)	43.8(6)	35.1(5)	1.7(5)	-4.1(5)	9.8(5)
C9	55.8(7)	37.4(6)	30.8(5)	3.6(4)	-2.4(5)	-0.9(5)
C10	45.6(6)	42.2(6)	32.6(5)	0.5(5)	7.1(4)	-8.7(5)
C11	30.9(5)	37.6(5)	29.8(5)	-1.8(4)	3.0(4)	-3.1(4)
C12	27.3(5)	32.9(5)	23.0(4)	1.3(4)	1.7(3)	-0.1(4)
C13	29.4(5)	40.5(6)	28.2(5)	3.9(4)	2.9(4)	4.1(4)
C14	27.1(5)	63.1(8)	31.5(5)	6.1(5)	-1.3(4)	-2.2(5)
C15	38.0(6)	60.0(8)	30.5(5)	-3.4(5)	-1.7(4)	-16.8(5)
C16	46.2(6)	38.5(6)	30.6(5)	-5.0(4)	3.7(4)	-8.6(5)
C17	32.3(5)	34.1(5)	28.0(5)	-1.2(4)	0.9(4)	-1.2(4)

Table 10: Bond Lengths in Å for **5aa**.

Atom	Atom	Length/Å
F1	C1	1.3280(13)
O1	C1	1.3305(15)
O1	C2	1.4119(14)
O2	C2	1.2030(14)
C1	C5	1.3259(16)
C2	C3	1.4523(14)
C3	C4	1.3728(14)
C3	C6	1.4847(14)
C4	C5	1.4407(14)
C4	C12	1.4846(14)
C6	C7	1.3944(15)

Atom	Atom	Length/Å
C6	C11	1.3959(15)
C7	C8	1.3892(17)
C8	C9	1.387(2)
C9	C10	1.3870(19)
C10	C11	1.3894(16)
C12	C13	1.3968(14)
C12	C17	1.3959(15)
C13	C14	1.3917(16)
C14	C15	1.381(2)
C15	C16	1.3872(18)
C16	C17	1.3901(15)

Table 11: Bond Angles in ° for **5aa**.

Atom	Atom	Atom	Angle/°
C1	O1	C2	119.66(8)
F1	C1	O1	109.74(10)
C5	C1	F1	124.10(11)
C5	C1	O1	126.14(11)
O1	C2	C3	116.72(9)
O2	C2	O1	115.59(10)
O2	C2	C3	127.70(11)
C2	C3	C6	114.62(9)
C4	C3	C2	120.23(10)
C4	C3	C6	125.13(9)
C3	C4	C5	119.48(9)
C3	C4	C12	123.61(9)
C5	C4	C12	116.88(9)
C1	C5	C4	117.45(10)
C7	C6	C3	121.38(10)

Atom	Atom	Atom	Angle/°
C7	C6	C11	119.21(10)
C11	C6	C3	119.37(10)
C8	C7	C6	120.33(11)
C9	C8	C7	120.27(11)
C10	C9	C8	119.63(11)
C9	C10	C11	120.46(11)
C10	C11	C6	120.10(11)
C13	C12	C4	119.68(9)
C17	C12	C4	121.52(9)
C17	C12	C13	118.64(10)
C14	C13	C12	120.77(11)
C15	C14	C13	119.89(11)
C14	C15	C16	120.07(10)
C15	C16	C17	120.18(11)
C16	C17	C12	120.43(10)

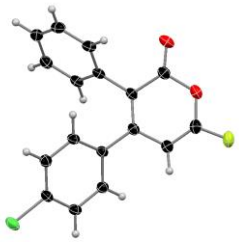
Table 12: Torsion Angles in ° for **5aa**.

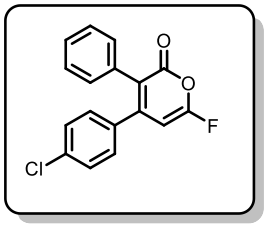
Atom	Atom	Atom	Atom	Angle/°
F1	C1	C5	C4	-178.81(10)
O1	C1	C5	C4	2.62(18)
O1	C2	C3	C4	6.55(14)
O1	C2	C3	C6	-171.92(8)
O2	C2	C3	C4	-173.27(11)
O2	C2	C3	C6	8.27(16)
C1	O1	C2	O2	176.73(10)

Atom	Atom	Atom	Atom	Angle/°
C1	O1	C2	C3	-3.10(14)
C2	O1	C1	F1	179.78(9)
C2	O1	C1	C5	-1.49(17)
C2	C3	C4	C5	-5.57(15)
C2	C3	C4	C12	172.59(9)
C2	C3	C6	C7	-58.04(13)
C2	C3	C6	C11	119.48(10)
C3	C4	C5	C1	1.06(15)
C3	C4	C12	C13	146.16(10)
C3	C4	C12	C17	-38.48(15)
C3	C6	C7	C8	177.63(10)
C3	C6	C11	C10	-177.48(9)
C4	C3	C6	C7	123.58(12)
C4	C3	C6	C11	-58.89(14)
C4	C12	C13	C14	176.44(10)
C4	C12	C17	C16	-176.26(10)
C5	C4	C12	C13	-35.64(14)
C5	C4	C12	C17	139.72(10)
C6	C3	C4	C5	172.72(9)
C6	C3	C4	C12	-9.12(16)
C6	C7	C8	C9	-0.47(17)
C7	C6	C11	C10	0.11(15)
C7	C8	C9	C10	0.63(18)
C8	C9	C10	C11	-0.43(18)
C9	C10	C11	C6	0.06(17)
C11	C6	C7	C8	0.10(16)
C12	C4	C5	C1	-177.22(10)
C12	C13	C14	C15	-0.26(17)
C13	C12	C17	C16	-0.86(15)
C13	C14	C15	C16	-0.54(18)
C14	C15	C16	C17	0.64(18)
C15	C16	C17	C12	0.08(17)
C17	C12	C13	C14	0.95(15)

Table 13: Hydrogen Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for **5aa**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij}.

Atom	x	y	z	U_{eq}
H5	1970(20)	8349(8)	4713(13)	39(4)
H7	7700(30)	6162(8)	6756(14)	46(4)
H8	7780(30)	5043(9)	7770(15)	58(5)
H9	4850(30)	4706(9)	8800(15)	51(4)
H10	1730(30)	5475(9)	8771(15)	52(4)
H11	1620(30)	6600(8)	7757(13)	41(4)
H13	-1160(20)	7721(8)	4941(13)	36(3)
H14	-3870(30)	7013(10)	3887(16)	58(5)
H15	-3130(30)	5796(9)	3437(15)	54(4)
H16	420(30)	5322(9)	4009(14)	49(4)
H17	3190(20)	6042(8)	5041(12)	36(3)





Crystal data and structure refinement for **5ca**.

Formula	$C_{17}H_{10}ClFO_2$
$D_{calc.}$/ g cm^{-3}	1.518
m /mm^{-1}	2.700
Formula Weight	300.70
Colour	colourless
Shape	prism
Size/mm^3	0.36×0.07×0.05
T/K	140.00(10)
Crystal System	monoclinic
Space Group	$P2_1/n$
a/Å	5.82517(17)
b/Å	19.3273(5)
c/Å	11.7017(3)
a/°	90
b/°	92.745(3)
g/°	90
V/Å^3	1315.92(7)
Z	4
Z'	1
Wavelength/Å	1.54184
Radiation type	Cu K_α
Q_{min}/°	4.421
Q_{max}/°	72.602
Measured Refl's.	3810
Indep't Refl's	3810
Refl's I≥2 σ(I)	3335
R_{int}	n/a
Parameters	191
Restraints	0
Largest Peak/e Å^{-3}	0.214
Deepest Hole/e Å^{-3}	-0.232
GooF	1.043
wR_2 (all data)	0.0903
wR_2	0.0880
R_1 (all data)	0.0381
R_1	0.0333

Reflection Statistics

Total reflections (after filtering)	5167	Unique reflections	2595
Completeness	0.994	Mean I/σ	22.65
hkl_{max} collected	(7, 23, 14)	hkl_{min} collected	(-7, -23, -14)
hkl_{max} used	(7, 23, 14)	hkl_{min} used	(-7, 0, 0)
Lim d_{max} collected	100.0	Lim d_{min} collected	0.77
d_{max} used	10.0	d_{min} used	0.81
Friedel pairs	196	Friedel pairs merged	1
Inconsistent equivalents	0	R_{int}	0.0
R_{sigma}	0.0209	Intensity transformed	0
Omitted reflections	0	Omitted by user (OMIT hkl)	0
Multiplicity	(3547, 133)	Maximum multiplicity	0
Removed systematic absences	0	Filtered off (Shel/OMIT)	0

Table 84: Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for **5ca**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij}.

Atom	x	y	z	U_{eq}
Cl1	12775.4(7)	5548.5(2)	6622.0(4)	32.38(14)
F1	4977(2)	9320.0(5)	4276.6(10)	34.2(3)
O1	3335(2)	8511.4(6)	3231.0(11)	27.8(3)
O2	1408(2)	7732.6(7)	2176.5(12)	31.6(3)
C1	3051(3)	7828.5(9)	2812.0(15)	24.3(4)
C2	5013(3)	8651.5(9)	4007.6(15)	26.4(4)
C3	6501(3)	8201.2(9)	4472.7(15)	24.9(4)
C4	6385(3)	7498.3(8)	4052.4(14)	21.1(3)
C5	4773(3)	7324.7(9)	3208.5(14)	21.9(3)
C6	8012(3)	6997.1(8)	4616.3(14)	19.8(3)
C7	7373(3)	6313.2(9)	4822.4(14)	22.2(3)
C8	8831(3)	5864.9(9)	5431.6(15)	23.9(3)
C9	10966(3)	6105.4(9)	5836.4(14)	23.0(3)
C10	11660(3)	6780.0(9)	5652.0(14)	23.1(3)
C11	10173(3)	7221.1(9)	5042.2(14)	21.7(3)
C12	4618(3)	6643.9(9)	2620.0(14)	21.9(3)
C13	2676(3)	6224.3(10)	2687.4(15)	25.2(4)
C14	2553(3)	5591.3(9)	2135.9(16)	27.8(4)
C15	4350(3)	5370.9(9)	1492.8(15)	28.3(4)
C16	6286(3)	5785.8(9)	1411.3(15)	26.7(4)
C17	6425(3)	6417.6(9)	1971.4(15)	23.4(3)

Table 15: Anisotropic Displacement Parameters (×10^4) for **5ca**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2} \times U_{11} + ... + 2hka^* \times b^* \times U_{12}]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cl1	25.3(2)	34.3(2)	36.7(3)	7.57(18)	-6.92(16)	6.34(16)
F1	40.2(6)	22.1(5)	40.4(6)	-0.8(4)	2.9(5)	7.6(4)
O1	26.0(6)	27.3(6)	30.0(7)	3.5(5)	0.6(5)	8.2(5)
O2	22.4(6)	39.4(7)	32.2(7)	4.5(5)	-5.5(5)	5.9(5)
C1	20.4(8)	28.2(9)	24.6(8)	2.4(7)	3.1(7)	3.1(6)
C2	28.2(9)	23.8(8)	27.5(9)	0.0(7)	5.4(7)	2.8(7)
C3	22.8(8)	25.0(8)	26.9(9)	-1.1(7)	0.7(7)	2.1(6)
C4	16.9(7)	23.3(8)	23.2(8)	1.3(6)	3.5(6)	1.0(6)
C5	16.6(7)	25.2(8)	24.0(8)	2.2(6)	1.9(6)	2.9(6)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C6	16.9(7)	23.8(8)	18.8(8)	-0.9(6)	1.2(6)	2.2(6)
C7	16.3(7)	25.9(8)	24.3(8)	-0.8(6)	-0.4(6)	-0.3(6)
C8	22.7(8)	23.0(8)	25.9(8)	1.9(6)	0.8(6)	0.3(6)
C9	19.2(8)	27.4(9)	22.2(8)	1.1(6)	-0.7(6)	5.7(6)
C10	16.6(7)	29.1(8)	23.6(8)	-2.1(7)	-0.1(6)	0.6(6)
C11	18.4(7)	23.4(8)	23.5(8)	-2.3(6)	1.9(6)	-0.3(6)
C12	16.9(7)	27.3(8)	20.9(8)	2.0(6)	-3.2(6)	2.4(6)
C13	18.0(7)	33.4(9)	24.0(8)	0.0(7)	-0.4(6)	0.2(7)
C14	21.8(8)	31.6(9)	29.6(9)	1.0(7)	-3.2(7)	-3.7(7)
C15	31.3(9)	26.3(8)	26.5(9)	-2.4(7)	-6.5(7)	3.2(7)
C16	22.7(8)	31.2(9)	26.1(9)	0.3(7)	0.6(7)	6.7(7)
C17	16.3(7)	29.1(9)	24.9(8)	3.7(7)	0.6(6)	1.8(6)

Table 16: Bond Lengths in Å for **5ca**.

Atom	Atom	Length/Å
Cl1	C9	1.7383(16)
F1	C2	1.330(2)
O1	C1	1.415(2)
O1	C2	1.330(2)
O2	C1	1.198(2)
C1	C5	1.458(2)
C2	C3	1.327(3)
C3	C4	1.445(2)
C4	C5	1.371(2)
C4	C6	1.488(2)
C5	C12	1.486(2)
C6	C7	1.397(2)

Atom	Atom	Length/Å
C6	C11	1.400(2)
C7	C8	1.386(2)
C8	C9	1.390(2)
C9	C10	1.385(3)
C10	C11	1.388(2)
C12	C13	1.397(2)
C12	C17	1.397(2)
C13	C14	1.383(3)
C14	C15	1.385(3)
C15	C16	1.391(3)
C16	C17	1.386(3)

Table 17: Bond Angles in ° for **5ca**.

Atom	Atom	Atom	Angle/°
C2	O1	C1	119.77(13)
O1	C1	C5	116.45(15)
O2	C1	O1	115.86(15)
O2	C1	C5	127.68(17)
F1	C2	O1	109.88(14)
C3	C2	F1	123.87(17)
C3	C2	O1	126.24(17)
C2	C3	C4	117.25(16)
C3	C4	C6	116.27(15)
C5	C4	C3	119.64(15)
C5	C4	C6	124.05(15)
C1	C5	C12	114.74(15)
C4	C5	C1	120.18(16)
C4	C5	C12	125.08(14)
C7	C6	C4	121.54(14)
C7	C6	C11	118.27(15)
C11	C6	C4	119.97(15)

Atom	Atom	Atom	Angle/°
C8	C7	C6	121.20(15)
C7	C8	C9	118.85(16)
C8	C9	Cl1	118.89(13)
C10	C9	Cl1	119.42(13)
C10	C9	C8	121.67(15)
C9	C10	C11	118.58(16)
C10	C11	C6	121.43(16)
C13	C12	C5	121.27(15)
C17	C12	C5	119.89(15)
C17	C12	C13	118.84(16)
C14	C13	C12	120.70(16)
C13	C14	C15	120.14(16)
C14	C15	C16	119.75(17)
C17	C16	C15	120.32(16)
C16	C17	C12	120.24(16)

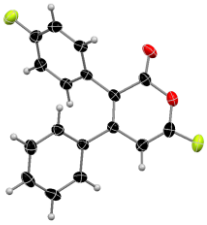
Table 18: Torsion Angles in ° for **5ca**.

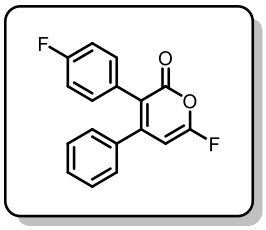
Atom	Atom	Atom	Atom	Angle/°
Cl1	C9	C10	C11	-178.73(13)
F1	C2	C3	C4	-177.27(15)

Atom	Atom	Atom	Atom	Angle/°
O1	C1	C5	C4	8.0(2)
O1	C1	C5	C12	-171.28(13)
O1	C2	C3	C4	3.8(3)
O2	C1	C5	C4	-171.53(17)
O2	C1	C5	C12	9.2(3)
C1	O1	C2	F1	179.70(13)
C1	O1	C2	C3	-1.3(2)
C1	C5	C12	C13	-62.5(2)
C1	C5	C12	C17	116.60(17)
C2	O1	C1	O2	174.94(15)
C2	O1	C1	C5	-4.6(2)
C2	C3	C4	C5	-0.2(2)
C2	C3	C4	C6	-177.82(15)
C3	C4	C5	C1	-5.7(2)
C3	C4	C5	C12	173.51(15)
C3	C4	C6	C7	142.64(16)
C3	C4	C6	C11	-31.9(2)
C4	C5	C12	C13	118.28(19)
C4	C5	C12	C17	-62.6(2)
C4	C6	C7	C8	-174.63(15)
C4	C6	C11	C10	174.86(15)
C5	C4	C6	C7	-34.9(2)
C5	C4	C6	C11	150.58(16)
C5	C12	C13	C14	-179.97(16)
C5	C12	C17	C16	-179.42(15)
C6	C4	C5	C1	171.80(15)
C6	C4	C5	C12	-9.0(3)
C6	C7	C8	C9	-0.3(2)
C7	C6	C11	C10	0.2(2)
C7	C8	C9	Cl1	178.87(13)
C7	C8	C9	C10	0.4(3)
C8	C9	C10	C11	-0.3(3)
C9	C10	C11	C6	0.0(2)
C11	C6	C7	C8	0.0(2)
C12	C13	C14	C15	-1.0(3)
C13	C12	C17	C16	-0.3(2)
C13	C14	C15	C16	0.5(3)
C14	C15	C16	C17	0.1(3)
C15	C16	C17	C12	-0.2(3)
C17	C12	C13	C14	0.9(3)

Table 19: Hydrogen Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for **5ca**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij}.

Atom	x	y	z	U_{eq}
H3	7598.35	8335.19	5057.89	30
H7	5912.21	6152.47	4539.97	27
H8	8377.82	5401.33	5569.85	29
H10	13122.99	6937.56	5936.7	28
H11	10631.19	7684.93	4911.12	26
H13	1425.65	6375.31	3116.6	30
H14	1234.33	5307.24	2198.31	33
H15	4260.3	4937.98	1108.93	34
H16	7518.37	5635.62	969.65	32
H17	7755.05	6697.77	1913.95	28





Crystal data and structure refinement for **5ac**.

Formula	$C_{17}H_{10}F_2O_2$
$D_{calc.}$/ g cm^{-3}	1.458
m /mm^{-1}	0.970
Formula Weight	284.25
Colour	colourless
Shape	plate
Size/mm^3	0.38×0.23×0.04
T/K	140.00(10)
Crystal System	monoclinic
Space Group	$P2_1/n$
a/Å	6.16235(12)
b/Å	18.5749(4)
c/Å	11.4059(2)
a/°	90
b/°	97.2906(17)
g/°	90
V/Å^3	1295.03(4)
Z	4
Z'	1
Wavelength/Å	1.54184
Radiation type	Cu K_α
Q_{min}/°	4.576
Q_{max}/°	72.568
Measured Refl's.	11023
Indep't Refl's	2543
Refl's I≥2 σ(I)	2298
R_{int}	0.0220
Parameters	191
Restraints	0
Largest Peak/e Å^{-3}	0.190
Deepest Hole/e Å^{-3}	-0.191
GooF	1.044
wR_2 (all data)	0.0822
wR_2	0.0784
R_1 (all data)	0.0352
R_1	0.0313

Reflection Statistics

Total reflections (after filtering)	11239	Unique reflections	2543
Completeness	0.989	Mean I/σ	23.68
hkl_{max} collected	(7, 21, 12)	hkl_{min} collected	(-7, -22, -14)
hkl_{max} used	(7, 22, 14)	hkl_{min} used	(-7, 0, 0)
Lim d_{max} collected	100.0	Lim d_{min} collected	0.77
d_{max} used	11.31	d_{min} used	0.81
Friedel pairs	1159	Friedel pairs merged	1
Inconsistent equivalents	8	R_{int}	0.022
R_{sigma}	0.0208	Intensity transformed	0
Omitted reflections	0	Omitted by user (OMIT hkl)	0
Multiplicity	(3226, 1760, 696, 190, 148, 73, 39, 9, 8, 5)	Maximum multiplicity	18
Removed systematic absences	216	Filtered off (Shel/OMIT)	0

Table 20: Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for **5ac**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij}.

Atom	x	y	z	U_{eq}
F1	4986.8(14)	9259.6(4)	5566.5(7)	42.4(2)
F2	4687.1(14)	4517.7(4)	8867.3(7)	43.1(2)
O1	6359.2(14)	8358.5(5)	6626.6(8)	33.4(2)
O2	8026.7(14)	7481.7(5)	7703.4(8)	38.8(2)
C1	6447.3(19)	7639.9(7)	7022.4(10)	29.8(3)
C2	4740(2)	8569.3(7)	5815.2(11)	32.1(3)
C3	3126(2)	8158.7(6)	5311.5(10)	30.0(3)
C4	3058.6(18)	7423.8(6)	5700.8(9)	25.1(2)
C5	4630.7(18)	7177.0(6)	6566.4(9)	25.8(2)
C6	1273.3(18)	6963.7(6)	5101.2(9)	24.8(2)
C7	-786.5(19)	7263.3(7)	4758.7(10)	29.8(3)
C8	-2448(2)	6857.6(8)	4142.7(11)	37.7(3)
C9	-2068(2)	6148.3(8)	3861.2(11)	39.3(3)
C10	-19(2)	5844.0(7)	4186.9(11)	35.5(3)
C11	1645.1(19)	6249.3(7)	4799.1(10)	28.9(3)
C12	4631.8(18)	6460.9(6)	7139.1(9)	26.0(2)
C13	6397.6(19)	5989.8(7)	7137.8(10)	31.1(3)
C14	6416(2)	5332.5(7)	7713.8(11)	34.0(3)
C15	4659(2)	5157.7(7)	8292.5(10)	32.2(3)
C16	2881(2)	5603.6(7)	8309.7(11)	31.9(3)
C17	2875.9(18)	6259.5(6)	7729.5(10)	27.7(3)

Table 91: Anisotropic Displacement Parameters (×10^4) for **5ac**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2} \times U_{11} + ... + 2hka^* \times b^* \times U_{12}]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
F1	53.6(5)	26.6(4)	48.7(5)	-1.4(3)	12.7(4)	-8.5(3)
F2	54.1(5)	33.3(4)	40.9(4)	9.6(3)	2.5(3)	1.9(3)
O1	33.7(4)	34.1(5)	32.4(4)	-5.0(3)	4.2(3)	-10.4(4)
O2	29.2(4)	52.5(6)	32.3(5)	-0.6(4)	-5.8(4)	-9.6(4)
C1	27.9(6)	36.6(6)	24.9(5)	-3.3(5)	3.6(4)	-6.5(5)
C2	38.8(6)	27.2(6)	31.8(6)	-2.7(5)	10.1(5)	-3.9(5)
C3	34.7(6)	27.9(6)	27.0(6)	-0.8(4)	2.2(5)	0.7(5)
C4	25.5(5)	27.1(6)	22.8(5)	-2.7(4)	3.0(4)	0.1(4)
C5	23.0(5)	30.4(6)	23.9(5)	-2.5(4)	2.2(4)	-2.4(4)
C6	24.3(5)	28.7(6)	20.8(5)	0.7(4)	0.1(4)	-0.2(4)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C7	27.6(6)	35.6(6)	25.8(5)	3.4(5)	1.5(4)	4.3(5)
C8	24.5(6)	58.0(9)	28.9(6)	4.7(6)	-3.2(5)	0.1(5)
C9	33.0(6)	53.9(8)	29.4(6)	-5.1(6)	-2.6(5)	-13.8(6)
C10	42.0(7)	34.5(6)	29.2(6)	-5.7(5)	1.6(5)	-7.6(5)
C11	28.6(6)	30.7(6)	26.2(6)	-1.1(4)	-0.7(4)	1.0(5)
C12	22.6(5)	32.2(6)	21.4(5)	-1.4(4)	-4.0(4)	-0.9(4)
C13	24.1(5)	39.9(7)	28.5(6)	1.3(5)	0.3(4)	1.2(5)
C14	30.7(6)	37.1(7)	32.5(6)	1.3(5)	-2.6(5)	7.5(5)
C15	40.1(7)	29.0(6)	25.4(6)	2.7(4)	-3.4(5)	-0.5(5)
C16	32.2(6)	35.0(6)	28.7(6)	-0.9(5)	4.5(5)	-4.3(5)
C17	24.9(5)	30.9(6)	26.6(5)	-2.2(4)	0.5(4)	-0.6(4)

Table 22: Bond Lengths in Å for **5ac**.

Atom	Atom	Length/Å
F1	C2	1.3260(15)
F2	C15	1.3566(14)
O1	C1	1.4080(15)
O1	C2	1.3306(16)
O2	C1	1.2021(15)
C1	C5	1.4544(15)
C2	C3	1.3252(18)
C3	C4	1.4378(16)
C4	C5	1.3714(16)
C4	C6	1.4891(15)
C5	C12	1.4819(16)
C6	C7	1.3956(15)

Atom	Atom	Length/Å
C6	C11	1.3971(16)
C7	C8	1.3884(18)
C8	C9	1.383(2)
C9	C10	1.390(2)
C10	C11	1.3871(17)
C12	C13	1.3965(17)
C12	C17	1.3962(16)
C13	C14	1.3858(18)
C14	C15	1.3768(19)
C15	C16	1.3757(18)
C16	C17	1.3862(17)

Table 23: Bond Angles in ° for **5ac**.

Atom	Atom	Atom	Angle/°
C2	O1	C1	119.80(9)
O1	C1	C5	116.69(10)
O2	C1	O1	115.72(10)
O2	C1	C5	127.59(12)
F1	C2	O1	109.70(10)
C3	C2	F1	124.31(12)
C3	C2	O1	125.98(12)
C2	C3	C4	117.51(11)
C3	C4	C6	116.85(10)
C5	C4	C3	119.62(10)
C5	C4	C6	123.51(10)
C1	C5	C12	114.57(10)
C4	C5	C1	120.08(11)
C4	C5	C12	125.32(10)
C7	C6	C4	119.50(10)
C7	C6	C11	118.78(10)
C11	C6	C4	121.58(10)

Atom	Atom	Atom	Angle/°
C8	C7	C6	120.76(12)
C9	C8	C7	119.90(12)
C8	C9	C10	120.02(11)
C11	C10	C9	120.15(12)
C10	C11	C6	120.38(11)
C13	C12	C5	121.25(11)
C17	C12	C5	119.74(10)
C17	C12	C13	118.97(11)
C14	C13	C12	120.74(11)
C15	C14	C13	118.39(11)
F2	C15	C14	118.41(11)
F2	C15	C16	118.83(12)
C16	C15	C14	122.76(12)
C15	C16	C17	118.42(11)
C16	C17	C12	120.72(11)

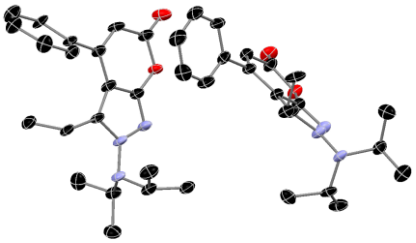
Table 24: Torsion Angles in ° for **5ac**.

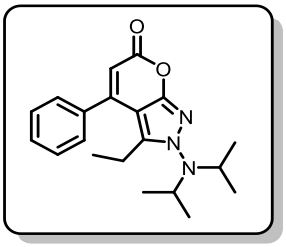
Atom	Atom	Atom	Atom	Angle/°
F1	C2	C3	C4	-178.46(11)
F2	C15	C16	C17	179.39(10)
O1	C1	C5	C4	6.67(16)
O1	C1	C5	C12	-171.42(9)

Atom	Atom	Atom	Atom	Angle/°
O1	C2	C3	C4	2.34(19)
O2	C1	C5	C4	-173.43(12)
O2	C1	C5	C12	8.48(18)
C1	O1	C2	F1	-179.46(9)
C1	O1	C2	C3	-0.16(18)
C1	C5	C12	C13	-58.23(14)
C1	C5	C12	C17	119.44(12)
C2	O1	C1	O2	175.79(11)
C2	O1	C1	C5	-4.30(15)
C2	C3	C4	C5	0.24(17)
C2	C3	C4	C6	-178.23(11)
C3	C4	C5	C1	-4.70(16)
C3	C4	C5	C12	173.16(11)
C3	C4	C6	C7	-36.21(15)
C3	C4	C6	C11	139.39(11)
C4	C5	C12	C13	123.80(13)
C4	C5	C12	C17	-58.53(16)
C4	C6	C7	C8	176.56(11)
C4	C6	C11	C10	-176.68(11)
C5	C4	C6	C7	145.38(11)
C5	C4	C6	C11	-39.02(16)
C5	C12	C13	C14	177.59(10)
C5	C12	C17	C16	-177.53(10)
C6	C4	C5	C1	173.67(10)
C6	C4	C5	C12	-8.47(18)
C6	C7	C8	C9	-0.08(19)
C7	C6	C11	C10	-1.05(17)
C7	C8	C9	C10	-0.5(2)
C8	C9	C10	C11	0.3(2)
C9	C10	C11	C6	0.50(19)
C11	C6	C7	C8	0.84(17)
C12	C13	C14	C15	-0.39(18)
C13	C12	C17	C16	0.19(17)
C13	C14	C15	F2	-179.29(10)
C13	C14	C15	C16	0.81(19)
C14	C15	C16	C17	-0.72(18)
C15	C16	C17	C12	0.20(17)
C17	C12	C13	C14	-0.09(17)

Table 25: Hydrogen Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for **5ac**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij}.

Atom	x	y	z	U_{eq}
H3	2053.23	8343.16	4715.39	36
H7	-1054.75	7750.41	4949.3	36
H8	-3844.86	7066.85	3914.83	45
H9	-3206.49	5868.96	3445.13	47
H10	241.92	5357.42	3989.91	43
H11	3045.56	6039.96	5014.12	35
H13	7599.55	6121.36	6737.59	37
H14	7612.43	5010.36	7709.36	41
H16	1684.81	5465.44	8709.68	38
H17	1664.53	6575.42	7733.75	33





Crystal data and structure refinement for **6ag**.

Formula	$C_{20}H_{25}N_3O_2$
$D_{calc.}$/ g cm^{-3}	1.245
m /mm^{-1}	0.650
Formula Weight	339.43
Colour	clear light yellow
Shape	irregular
Size/mm^3	0.24×0.17×0.12
T/K	140.00(10)
Crystal System	triclinic
Space Group	P-1
a/Å	10.4488(6)
b/Å	13.1778(8)
c/Å	15.6415(10)
a/°	109.270(6)
b/°	97.031(5)
g/°	111.857(6)
V/Å^3	1811.5(2)
Z	4
Z'	2
Wavelength/Å	1.54184
Radiation type	Cu K_α
Q_{min}/°	3.118
Q_{max}/°	72.679
Measured Refl's.	15128
Indep't Refl's	7000
Refl's I≥2 σ(I)	5303
R_{int}	0.0446
Parameters	648
Restraints	0
Largest Peak	0.441
Deepest Hole	-0.248
GooF	1.092
wR_2 (all data)	0.1839
wR_2	0.1676
R_1 (all data)	0.0859
R_1	0.0654

Reflection Statistics

Total reflections (after filtering)	15130	Unique reflections	7000
Completeness	0.971	Mean I/σ	9.33
hkl_{max} collected	(11, 16, 19)	hkl_{min} collected	(-12, -15, -17)
hkl_{max} used	(12, 15, 19)	hkl_{min} used	(-12, -16, 0)
Lim d_{max} collected	100.0	Lim d_{min} collected	0.77
d_{max} used	14.17	d_{min} used	0.81
Friedel pairs	1795	Friedel pairs merged	1
Inconsistent equivalents	7	R_{int}	0.0446
R_{sigma}	0.0548	Intensity transformed	0
Omitted reflections	0	Omitted by user (OMIT hkl)	2
Multiplicity	(4701, 2806, 750, 272, 170, 63, 22, 11, 1)	Maximum multiplicity	10
Removed systematic absences	0	Filtered off (Shel/OMIT)	0

Table 26: Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for **6ag**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij}.

Atom	x	y	z	U_{eq}
O1	11812(2)	8447.1(18)	2840.6(15)	37.8(5)
O2	10547.7(17)	7248.3(15)	3447.5(12)	28.2(4)
N1	9192(2)	6089.0(19)	4144.4(15)	28.2(4)
N2	8031(2)	6080.4(19)	4484.3(15)	27.1(4)
N3	7418(2)	5298.5(18)	4906.0(15)	26.5(4)
C1	10805(3)	8186(2)	3162.2(18)	29.5(5)
C2	9829(3)	8741(2)	3261.2(18)	29.6(5)
C3	8698(2)	8408(2)	3618.2(17)	25.8(5)
C4	8490(2)	7467(2)	3936.6(17)	25.4(5)
C5	9439(2)	6932(2)	3830.3(17)	25.1(5)
C6	7713(3)	8986(2)	3675.1(17)	27.1(5)
C7	8255(3)	10229(2)	4151(2)	33.8(5)
C8	7324(4)	10754(3)	4253(2)	43.7(7)
C9	5859(4)	10060(3)	3875(2)	45.8(7)
C10	5306(3)	8830(3)	3382(2)	39.4(6)
C11	6234(3)	8293(2)	3281.9(19)	31.4(5)
C12	7595(2)	6895(2)	4395.1(17)	26.1(5)
C13	6431(3)	7085(2)	4794(2)	31.0(5)
C14	6980(3)	8302(3)	5617(2)	40.8(7)
C15	8534(3)	5459(2)	5690.6(19)	31.8(5)
C16	9183(3)	6737(3)	6422(2)	40.8(6)
C17	7887(3)	4593(3)	6132(2)	39.5(6)
C18	6530(3)	4054(2)	4188.7(18)	29.6(5)
C19	5361(3)	4019(3)	3488(2)	39.3(6)
C20	7354(3)	3416(3)	3691(2)	39.8(7)
O3	13526.9(18)	5673.9(17)	1968.7(15)	37.1(4)
O4	11793.5(17)	3843.0(15)	1472.4(13)	28.2(4)
N4	9891(2)	1944.6(18)	833.0(15)	26.9(4)
N5	8432(2)	1541.3(18)	489.1(15)	25.4(4)
N6	7483(2)	323.9(17)	127.7(14)	25.2(4)
C21	12250(3)	5059(2)	1681.5(18)	28.3(5)
C22	11156(3)	5480(2)	1583.5(18)	28.3(5)
C23	9723(3)	4752(2)	1261.5(17)	25.8(5)
C24	9291(2)	3489(2)	980.1(17)	25.7(5)
C25	10364(2)	3105(2)	1108.9(17)	25.5(5)
C26	8662(3)	5241(2)	1212.9(17)	26.9(5)

Atom	x	y	z	U_{eq}
C27	8823(3)	6069(2)	810.7(19)	32.5(5)
C28	7804(4)	6496(3)	734(2)	41.3(7)
C29	6620(3)	6117(3)	1071(2)	42.5(7)
C30	6471(3)	5326(3)	1496(2)	38.7(6)
C31	7483(3)	4890(2)	1565.6(19)	31.6(5)
C32	8022(2)	2420(2)	539.2(17)	25.4(5)
C33	6512(3)	2133(2)	94.7(19)	29.0(5)
C34	6386(3)	2492(3)	-738(2)	36.3(6)
C35	7307(3)	-104(2)	898.5(18)	27.8(5)
C36	6809(3)	655(3)	1619(2)	36.1(6)
C37	8592(3)	-199(3)	1380(2)	36.2(6)
C38	7892(3)	-375(2)	-661.1(18)	29.6(5)
C39	7854(3)	91(3)	-1429(2)	39.3(6)
C40	6856(3)	-1695(3)	-1055(2)	38.0(6)

Table 107: Anisotropic Displacement Parameters (×10^4) for **6ag**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2} \times U_{11} + ... + 2hka^* \times b^* \times U_{12}]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O1	30.9(9)	42.5(11)	52.3(12)	28.9(9)	24.0(9)	16.6(8)
O2	25.1(8)	29.0(9)	37.2(9)	17.4(8)	17.8(7)	12.4(7)
N1	23.3(9)	30.9(11)	35.0(11)	15.7(9)	15.5(8)	12.4(8)
N2	24.7(10)	26.8(10)	34.8(11)	15.2(9)	17.2(8)	11.3(8)
N3	26.9(10)	25.4(10)	31.2(10)	14.9(9)	15.5(8)	10.3(8)
C1	25.8(11)	32.2(13)	34.0(13)	17.8(11)	12.8(10)	11.2(10)
C2	27.3(12)	26.3(12)	34.1(13)	15.1(10)	9.1(10)	8.1(10)
C3	22.0(11)	23.7(11)	27.6(11)	8.8(9)	6.1(9)	7.6(9)
C4	22.5(11)	22.9(11)	28.2(11)	8.2(9)	8.4(9)	8.9(9)
C5	19.5(10)	26.1(12)	29.7(11)	11.9(10)	11.5(9)	8.3(9)
C6	26.9(11)	25.3(12)	30.6(12)	12.9(10)	9.4(9)	11.3(10)
C7	33.5(13)	25.9(13)	39.0(14)	12.3(11)	7.9(11)	11.4(11)
C8	59.2(18)	35.2(15)	44.3(16)	16.1(13)	14.6(14)	28.7(14)
C9	50.7(17)	55.3(19)	52.2(18)	25.5(15)	21.4(14)	39.2(16)
C10	30.0(14)	50.4(17)	46.6(16)	22.9(14)	14.7(12)	22.8(13)
C11	26.2(12)	30.9(13)	36.3(13)	13.0(11)	10.4(10)	11.9(10)
C12	22.2(11)	23.4(11)	29.8(12)	9.7(10)	9.8(9)	7.2(9)
C13	26.6(12)	30.0(13)	44.2(15)	18.2(12)	20.0(12)	14.4(10)
C14	45.7(16)	31.6(14)	51.3(17)	16.4(13)	29.3(14)	19.1(13)
C15	29.6(12)	37.6(14)	35.6(13)	18.5(11)	15.8(11)	17.0(11)
C16	34.3(14)	43.9(17)	34.2(14)	9.4(13)	8.2(12)	13.0(13)
C17	39.7(15)	51.1(18)	44.6(16)	28.8(15)	20.8(13)	26.2(14)
C18	28.8(12)	24.3(12)	35.5(13)	13.3(11)	15.0(10)	8.8(10)
C19	34.0(14)	39.2(16)	38.8(15)	15.3(13)	10.0(12)	10.6(13)
C20	45.3(16)	28.2(14)	47.7(16)	13.6(13)	26.9(14)	15.6(12)
O3	23.3(9)	31.2(10)	51.4(12)	15.1(9)	12.8(8)	7.5(8)
O4	20.7(8)	25.5(9)	36.8(9)	12.0(7)	9.8(7)	8.4(7)
N4	21.6(9)	24.9(10)	33.6(11)	12.1(8)	10.0(8)	8.9(8)
N5	20.8(9)	22.1(10)	34.3(11)	12.5(8)	10.1(8)	8.6(8)
N6	23.6(9)	19.0(9)	30.7(10)	9.4(8)	9.6(8)	7.1(8)
C21	24.6(11)	25.0(12)	32.3(12)	10.1(10)	11.3(10)	8.3(10)
C22	27.7(12)	24.0(12)	33.6(13)	12.9(10)	14.1(10)	9.2(10)
C23	27.3(11)	27.2(12)	28.4(11)	13.7(10)	14.4(9)	13.5(10)
C24	22.7(11)	25.5(12)	30.2(12)	12.7(10)	11.5(9)	9.6(9)
C25	20.6(10)	26.6(12)	31.2(12)	13.4(10)	11.5(9)	9.5(9)
C26	27.9(11)	23.5(11)	28.3(11)	8.6(9)	9.7(9)	11.7(10)
C27	40.5(14)	25.6(12)	34.0(13)	13.1(11)	14.9(11)	14.7(11)
C28	61.8(18)	36.0(15)	36.9(14)	17.1(12)	16.3(13)	29.8(14)
C29	46.8(16)	44.8(17)	43.4(16)	13.2(13)	12.2(13)	32.2(14)
C30	33.9(14)	45.3(16)	40.8(15)	14.1(13)	15.0(12)	22.9(13)
C31	32.7(13)	32.2(13)	35.0(13)	15.6(11)	16.1(11)	15.6(11)
C32	24.5(11)	26.4(12)	30.9(12)	15.5(10)	14.1(9)	11.5(9)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C33	22.1(11)	28.4(12)	40.0(14)	17.4(11)	11.4(10)	10.7(10)
C34	30.1(13)	34.1(14)	44.3(15)	22.2(12)	7.1(12)	9.4(11)
C35	25.2(11)	24.7(12)	34.2(13)	14.9(10)	11.9(10)	8.0(10)
C36	38.3(14)	34.2(14)	35.8(14)	14.9(12)	18.5(12)	13.1(12)
C37	29.5(13)	36.0(15)	44.0(15)	22.2(13)	8.5(12)	10.8(12)
C38	25.5(12)	31.7(13)	34.2(13)	12.3(11)	11.8(10)	15.0(10)
C39	39.4(15)	51.9(18)	34.5(14)	21.0(13)	16.8(12)	23.2(14)
C40	31.3(14)	32.2(14)	40.6(15)	6.1(12)	9.1(11)	11.9(11)

Table 28: Bond Lengths in Å for **6ag**.

Atom	Atom	Length/Å
O1	C1	1.206(3)
O2	C1	1.394(3)
O2	C5	1.360(3)
N1	N2	1.381(3)
N1	C5	1.311(3)
N2	N3	1.403(3)
N2	C12	1.352(3)
N3	C15	1.485(3)
N3	C18	1.485(3)
C1	C2	1.455(4)
C2	C3	1.356(3)
C3	C4	1.438(3)
C3	C6	1.486(3)
C4	C5	1.412(3)
C4	C12	1.397(3)
C6	C7	1.400(4)
C6	C11	1.395(4)
C7	C8	1.385(4)
C8	C9	1.381(5)
C9	C10	1.387(5)
C10	C11	1.394(4)
C12	C13	1.496(3)
C13	C14	1.527(4)
C15	C16	1.514(4)
C15	C17	1.516(4)
C18	C19	1.514(4)
C18	C20	1.525(4)
O3	C21	1.203(3)
O4	C21	1.396(3)
O4	C25	1.359(3)
N4	N5	1.379(3)
N4	C25	1.311(3)
N5	N6	1.399(3)
N5	C32	1.359(3)
N6	C35	1.493(3)
N6	C38	1.491(3)
C21	C22	1.457(4)
C22	C23	1.358(3)
C23	C24	1.441(3)
C23	C26	1.482(3)
C24	C25	1.409(3)
C24	C32	1.401(3)
C26	C27	1.398(4)
C26	C31	1.395(3)
C27	C28	1.387(4)
C28	C29	1.390(5)
C29	C30	1.385(5)
C30	C31	1.387(4)
C32	C33	1.494(3)
C33	C34	1.531(4)
C35	C36	1.525(4)
C35	C37	1.526(4)
C38	C39	1.521(4)
C38	C40	1.518(4)

Table 29: Bond Angles in ° for **6ag**.

Atom	Atom	Atom	Angle/°
C5	O2	C1	118.61(19)
C5	N1	N2	101.81(19)
N1	N2	N3	120.87(19)
C12	N2	N1	114.34(19)
C12	N2	N3	124.76(18)
N2	N3	C15	110.09(19)
N2	N3	C18	111.37(19)
C15	N3	C18	116.4(2)
O1	C1	O2	116.3(2)
O1	C1	C2	126.1(2)
O2	C1	C2	117.6(2)
C3	C2	C1	124.1(2)
C2	C3	C4	117.0(2)
C2	C3	C6	121.6(2)
C4	C3	C6	121.4(2)
C5	C4	C3	118.2(2)
C12	C4	C3	138.1(2)
C12	C4	C5	103.6(2)
O2	C5	C4	124.4(2)
N1	C5	O2	120.8(2)
N1	C5	C4	114.8(2)
C7	C6	C3	120.3(2)
C11	C6	C3	120.4(2)
C11	C6	C7	119.3(2)
C8	C7	C6	120.0(3)
C9	C8	C7	120.4(3)
C8	C9	C10	120.3(3)
C9	C10	C11	119.7(3)
C10	C11	C6	120.3(3)
N2	C12	C4	105.4(2)

Atom	Atom	Atom	Angle/°
N2	C12	C13	121.9(2)
C4	C12	C13	132.6(2)
C12	C13	C14	112.9(2)
N3	C15	C16	109.2(2)
N3	C15	C17	110.3(2)
C16	C15	C17	110.3(2)
N3	C18	C19	110.2(2)
N3	C18	C20	115.8(2)
C19	C18	C20	111.5(2)
C25	O4	C21	118.13(19)
C25	N4	N5	101.89(19)
N4	N5	N6	121.46(19)
C32	N5	N4	114.37(19)
C32	N5	N6	124.17(19)
N5	N6	C35	111.15(19)
N5	N6	C38	110.25(17)
C38	N6	C35	115.94(19)
O3	C21	O4	116.1(2)
O3	C21	C22	125.9(2)
O4	C21	C22	117.9(2)
C23	C22	C21	123.9(2)
C22	C23	C24	116.8(2)
C22	C23	C26	121.3(2)
C24	C23	C26	122.0(2)
C25	C24	C23	118.4(2)
C32	C24	C23	137.8(2)
C32	C24	C25	103.7(2)
O4	C25	C24	124.6(2)
N4	C25	O4	120.4(2)
N4	C25	C24	114.9(2)
C27	C26	C23	120.5(2)
C31	C26	C23	121.0(2)
C31	C26	C27	118.5(2)
C28	C27	C26	120.6(2)
C27	C28	C29	120.1(3)
C30	C29	C28	119.8(3)
C29	C30	C31	120.1(3)
C30	C31	C26	120.8(3)
N5	C32	C24	105.0(2)
N5	C32	C33	121.4(2)
C24	C32	C33	133.3(2)
C32	C33	C34	112.5(2)
N6	C35	C36	109.6(2)
N6	C35	C37	116.44(19)
C36	C35	C37	111.1(2)
N6	C38	C39	108.7(2)
N6	C38	C40	110.1(2)
C40	C38	C39	110.0(2)

Table 30: Torsion Angles in ° for **6ag**.

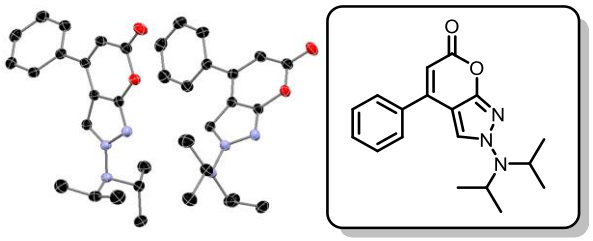
Atom	Atom	Atom	Atom	Angle/°
O1	C1	C2	C3	179.2(3)
O2	C1	C2	C3	0.5(4)
N1	N2	N3	C15	54.8(3)
N1	N2	N3	C18	-75.8(3)
N1	N2	C12	C4	2.0(3)
N1	N2	C12	C13	-175.0(2)
N2	N1	C5	O2	178.5(2)
N2	N1	C5	C4	-0.7(3)
N2	N3	C15	C16	60.2(2)
N2	N3	C15	C17	-178.5(2)
N2	N3	C18	C19	-57.8(2)
N2	N3	C18	C20	69.8(3)
N2	C12	C13	C14	111.8(3)
N3	N2	C12	C4	-179.8(2)
N3	N2	C12	C13	3.2(4)
C1	O2	C5	N1	-177.2(2)
C1	O2	C5	C4	2.0(4)
C1	C2	C3	C4	1.6(4)
C1	C2	C3	C6	-178.1(2)
C2	C3	C4	C5	-2.0(3)
C2	C3	C4	C12	174.4(3)
C2	C3	C6	C7	-55.7(3)
C2	C3	C6	C11	126.4(3)
C3	C4	C5	O2	0.2(4)
C3	C4	C5	N1	179.4(2)
C3	C4	C12	N2	-178.9(3)
C3	C4	C12	C13	-2.4(5)
C3	C6	C7	C8	-175.9(2)
C3	C6	C11	C10	176.4(2)
C4	C3	C6	C7	124.5(3)
C4	C3	C6	C11	-53.4(3)
C4	C12	C13	C14	-64.3(4)
C5	O2	C1	O1	178.9(2)

Atom	Atom	Atom	Atom	Angle/°
C5	O2	C1	C2	-2.2(3)
C5	N1	N2	N3	-179.1(2)
C5	N1	N2	C12	-0.9(3)
C5	C4	C12	N2	-2.2(3)
C5	C4	C12	C13	174.3(3)
C6	C3	C4	C5	177.8(2)
C6	C3	C4	C12	-5.8(5)
C6	C7	C8	C9	-1.0(4)
C7	C6	C11	C10	-1.5(4)
C7	C8	C9	C10	-0.5(5)
C8	C9	C10	C11	1.1(5)
C9	C10	C11	C6	0.0(4)
C11	C6	C7	C8	2.1(4)
C12	N2	N3	C15	-123.2(2)
C12	N2	N3	C18	106.2(3)
C12	C4	C5	O2	-177.3(2)
C12	C4	C5	N1	1.9(3)
C15	N3	C18	C19	174.9(2)
C15	N3	C18	C20	-57.5(3)
C18	N3	C15	C16	-171.90(19)
C18	N3	C15	C17	-50.5(3)
O3	C21	C22	C23	-179.5(3)
O4	C21	C22	C23	-3.0(4)
N4	N5	N6	C35	72.7(2)
N4	N5	N6	C38	-57.3(3)
N4	N5	C32	C24	-2.3(3)
N4	N5	C32	C33	172.5(2)
N5	N4	C25	O4	-177.9(2)
N5	N4	C25	C24	1.1(3)
N5	N6	C35	C36	56.3(3)
N5	N6	C35	C37	-70.9(3)
N5	N6	C38	C39	-59.1(3)
N5	N6	C38	C40	-179.7(2)
N5	C32	C33	C34	-112.8(3)
N6	N5	C32	C24	177.4(2)
N6	N5	C32	C33	-7.7(3)
C21	O4	C25	N4	174.7(2)
C21	O4	C25	C24	-4.1(3)
C21	C22	C23	C24	-1.8(4)
C21	C22	C23	C26	177.6(2)
C22	C23	C24	C25	3.7(3)
C22	C23	C24	C32	-172.4(3)
C22	C23	C26	C27	47.9(3)
C22	C23	C26	C31	-132.1(3)
C23	C24	C25	O4	-0.8(3)
C23	C24	C25	N4	-179.7(2)
C23	C24	C32	N5	179.1(3)
C23	C24	C32	C33	5.2(5)
C23	C26	C27	C28	177.7(2)
C23	C26	C31	C30	-178.3(2)
C24	C23	C26	C27	-132.7(3)
C24	C23	C26	C31	47.4(3)
C24	C32	C33	C34	60.4(4)
C25	O4	C21	O3	-177.3(2)
C25	O4	C21	C22	5.8(3)
C25	N4	N5	N6	-178.9(2)
C25	N4	N5	C32	0.8(3)
C25	C24	C32	N5	2.6(2)
C25	C24	C32	C33	-171.3(2)
C26	C23	C24	C25	-175.7(2)
C26	C23	C24	C32	8.2(4)
C26	C27	C28	C29	1.0(4)

Atom	Atom	Atom	Atom	Angle/°
C27	C26	C31	C30	1.7(4)
C27	C28	C29	C30	0.9(5)
C28	C29	C30	C31	-1.6(5)
C29	C30	C31	C26	0.2(4)
C31	C26	C27	C28	-2.3(4)
C32	N5	N6	C35	-107.0(2)
C32	N5	N6	C38	123.0(2)
C32	C24	C25	O4	176.5(2)
C32	C24	C25	N4	-2.4(3)
C35	N6	C38	C39	173.5(2)
C35	N6	C38	C40	52.9(3)
C38	N6	C35	C36	-176.8(2)
C38	N6	C35	C37	56.0(3)

Table 31: Hydrogen Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for **6ag**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij}.

Atom	x	y	z	U_{eq}
H2	10060(30)	9380(30)	3040(20)	22(6)
H7	9210(40)	10700(30)	4420(20)	41
H8	7740(40)	11640(40)	4580(30)	60(11)
H9	5210(40)	10420(40)	3950(30)	61(11)
H10	4350(40)	8400(30)	3120(20)	35(8)
H11	5840(30)	7410(30)	2920(20)	32(7)
H13A	6110(30)	6480(30)	5020(20)	32(7)
H13B	5750(30)	7030(30)	4340(20)	24(7)
H14A	7420(40)	8920(30)	5450(20)	41(9)
H14B	6200(40)	8470(40)	5860(30)	61(11)
H14C	7780(50)	8370(40)	6150(30)	67(12)
H15	9330(30)	5300(30)	5430(20)	30(7)
H16A	9860(40)	6830(30)	6890(30)	37(8)
H16B	8430(30)	6930(30)	6680(20)	35(8)
H16C	9670(40)	7340(30)	6170(30)	45(9)
H17A	7550(40)	3760(40)	5770(30)	50(10)
H17B	8650(40)	4800(30)	6670(30)	41(8)
H17C	7060(40)	4750(40)	6330(30)	61(11)
H18	6050(30)	3590(30)	4550(20)	32(8)
H19A	4740(40)	3200(40)	3070(30)	47(9)
H19B	4800(40)	4360(40)	3760(30)	54(10)
H19C	5730(40)	4440(40)	3100(30)	53(10)
H20A	7770(40)	3770(30)	3260(30)	48(9)
H20B	8180(40)	3420(30)	4150(30)	50(10)
H20C	6620(50)	2520(40)	3290(30)	70(12)
H22	11500(30)	6370(30)	1790(20)	34
H27	9630(30)	6320(30)	570(20)	32(7)
H28	7890(40)	7020(40)	390(30)	56(10)
H29	5820(40)	6400(40)	960(30)	58(11)
H30	5660(50)	5070(40)	1720(30)	68(12)
H31	7390(30)	4370(30)	1840(20)	35(8)
H33A	5930(30)	1250(30)	-100(20)	25(7)
H33B	6130(30)	2540(30)	570(20)	37(8)
H34A	5380(40)	2190(30)	-1060(20)	40(8)
H34B	6890(40)	3330(30)	-560(20)	42(9)
H34C	6870(40)	2130(40)	-1170(30)	57(11)
H35	6500(30)	-920(30)	580(20)	35(8)
H36A	6590(30)	280(30)	2040(20)	32(7)
H36B	5990(40)	710(30)	1340(30)	45(9)
H36C	7630(40)	1460(30)	1980(20)	40(8)
H37A	9360(40)	560(30)	1830(30)	46(9)
H37B	8890(30)	-710(30)	840(20)	38(8)
H37C	8190(40)	-650(40)	1820(30)	55(10)
H38	8870(30)	-230(30)	-400(20)	23(7)
H39A	6810(40)	20(30)	-1680(30)	47
H39B	8050(40)	-380(30)	-1960(30)	46(9)
H39C	8590(40)	960(40)	-1170(30)	48(9)
H40A	5920(40)	-1790(30)	-1260(20)	39(8)
H40B	6870(40)	-2050(30)	-590(30)	47(9)
H40C	7170(40)	-2100(30)	-1580(30)	50(10)



Crystal data and structure refinement for **6ah**.

Formula	$C_{18}H_{21}N_3O_2$
$D_{calc.}$/ g cm^{-3}	1.273
m /mm^{-1}	0.679
Formula Weight	311.38
Colour	clear pale colourless
Shape	prism
Size/mm^3	0.43×0.14×0.09
T/K	140.00(10)
Crystal System	monoclinic
Space Group	$P2_1/n$
a/Å	10.40586(17)
b/Å	28.8016(4)
c/Å	11.4833(2)
a/°	90
b/°	109.1940(18)
g/°	90
V/Å^3	3250.29(10)
Z	8
Z'	2
Wavelength/Å	1.54184
Radiation type	Cu K_α
Q_{min}/°	3.069
Q_{max}/°	72.781
Measured Refl's.	8186
Indep't Refl's	8186
Refl's I≥2 σ(I)	7212
R_{int}	.
Parameters	586
Restraints	0
Largest Peak	0.300
Deepest Hole	-0.217
GooF	1.068
wR_2 (all data)	0.1136
wR_2	0.1105
R_1 (all data)	0.0417
R_1	0.0371

Reflection Statistics

Total reflections (after filtering)	12183	Unique reflections	6373
Completeness	0.986	Mean I/σ	32.52
hkl_{max} collected	(12, 35, 14)	hkl_{min} collected	(-12, -35, -14)
hkl_{max} used	(11, 35, 14)	hkl_{min} used	(-12, 0, 0)
Lim d_{max} collected	100.0	Lim d_{min} collected	0.77
d_{max} used	14.4	d_{min} used	0.81
Friedel pairs	81	Friedel pairs merged	1
Inconsistent equivalents	0	R_{int}	0.0
R_{sigma}	0.015	Intensity transformed	0
Omitted reflections	0	Omitted by user (OMIT hkl)	0
Multiplicity	(7112, 525, 10)	Maximum multiplicity	0
Removed systematic absences	0	Filtered off (Shel/OMIT)	0

Table 32: Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for **6ah**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij}.

Atom	x	y	z	U_{eq}
O1	10467.8(11)	3884.2(4)	112.6(10)	35.6(3)
O2	10616.0(9)	3624.5(3)	1965.1(9)	25.0(2)
N1	10621.1(11)	3354.0(4)	3864.8(10)	23.2(2)
N2	9620.0(11)	3331.3(4)	4404.5(10)	22.2(2)
N3	9872.6(11)	3153.5(4)	5592.5(10)	22.2(2)
C1	9869.5(14)	3818.3(4)	836.0(13)	25.4(3)
C2	8442.8(14)	3920.9(5)	615.8(12)	25.1(3)
C3	7783.3(13)	3845.1(4)	1441.6(12)	21.2(3)
C4	8580.9(13)	3636.8(4)	2594.7(12)	20.7(3)
C5	9956.9(13)	3537.6(4)	2784.5(12)	21.1(3)
C6	8413.8(13)	3501.0(4)	3697.1(12)	21.5(3)
C7	6323.0(13)	3966.4(4)	1133.8(11)	21.9(3)
C8	5778.8(15)	4327.8(5)	308.3(13)	27.5(3)
C9	4391.5(15)	4421.1(5)	-75.7(14)	31.9(3)
C10	3537.7(15)	4163.8(5)	378.1(14)	31.4(3)
C11	4068.4(15)	3810.9(5)	1217.9(14)	30.8(3)
C12	5454.4(14)	3710.3(5)	1595.8(12)	25.5(3)
C13	10141.1(14)	2643.5(4)	5629.1(13)	25.5(3)
C14	8992.4(17)	2405.9(5)	4637.4(17)	36.1(3)
C15	11525.8(16)	2496.8(5)	5561.2(17)	34.5(3)
C16	10490(2)	3944.4(5)	6390.0(17)	40.9(4)
C17	10932.6(14)	3439.3(5)	6497.2(13)	27.2(3)
C18	11132.5(17)	3263.5(6)	7794.8(14)	35.2(3)
O3	6604.4(11)	5161.0(4)	3153.0(10)	33.9(2)
O4	6404.0(9)	4513.4(3)	4120.3(9)	25.6(2)
N4	6040.7(11)	3836.9(4)	5063.6(11)	23.9(2)
N5	4881.2(11)	3650.1(4)	5209.6(10)	21.9(2)
N6	4896.0(11)	3216.1(4)	5771.0(10)	22.5(2)
C19	5833.2(14)	4907.2(5)	3442.9(13)	25.0(3)
C20	4382.5(14)	4982.7(4)	3148.8(12)	24.2(3)
C21	3531.8(13)	4691.7(4)	3478.8(11)	21.1(3)
C22	4155.3(12)	4292.9(4)	4191.1(11)	20.3(3)
C23	5560.9(13)	4222.0(4)	4460.2(12)	21.7(3)
C24	3751.9(12)	3903.1(4)	4693.7(12)	21.1(3)
C25	2049.9(13)	4781.9(4)	3095.7(12)	22.2(3)
C26	1394.0(14)	4985.5(5)	1950.1(13)	26.9(3)
C27	4.5(15)	5075.8(5)	1573.2(14)	31.5(3)
C28	-740.0(14)	4958.2(5)	2335.7(14)	28.4(3)
C29	-97.4(14)	4758.4(5)	3479.0(14)	26.3(3)

Atom	x	y	z	U_{eq}
C30	1294.9(14)	4670.0(4)	3860.3(13)	23.8(3)
C31	5300.1(15)	2853.0(5)	5039.7(14)	28.3(3)
C32	4282.0(19)	2854.2(5)	3742.6(15)	37.0(4)
C33	5328.7(18)	2377.1(5)	5636.8(17)	36.1(3)
C34	5671.4(15)	3228.8(5)	7115.5(13)	28.1(3)
C35	5075.6(17)	3598.1(6)	7729.2(14)	34.8(3)
C36	7212.7(16)	3283.3(7)	7463.2(17)	40.5(4)

Table 33: Anisotropic Displacement Parameters (×10^4) for **6ah**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2} \times U_{11} + ... + 2hka^* \times b^* \times U_{12}]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O1	36.2(5)	43.8(6)	33.7(6)	4.7(4)	21.0(5)	-1.1(4)
O2	22.0(4)	29.7(4)	26.1(5)	1.5(4)	11.6(4)	-0.5(4)
N1	18.9(5)	28.0(5)	24.0(5)	1.0(4)	8.5(4)	0.2(4)
N2	19.6(5)	27.5(5)	20.3(5)	2.8(4)	7.6(4)	1.6(4)
N3	22.7(5)	24.1(5)	18.9(5)	2.8(4)	5.5(4)	1.3(4)
C1	29.6(7)	24.4(6)	24.3(7)	0.0(5)	11.8(5)	-2.5(5)
C2	27.2(7)	26.2(6)	22.4(6)	0.7(5)	8.8(5)	-0.6(5)
C3	23.3(6)	18.9(5)	20.7(6)	-1.9(4)	6.1(5)	-1.6(5)
C4	19.3(6)	20.7(5)	22.2(6)	-1.3(4)	7.1(5)	-0.6(4)
C5	21.4(6)	21.2(5)	22.0(6)	-1.2(5)	8.8(5)	-2.1(4)
C6	19.3(6)	22.5(6)	22.8(6)	0.6(5)	7.0(5)	1.6(4)
C7	24.3(6)	21.4(6)	19.0(6)	-3.4(5)	5.6(5)	0.5(5)
C8	28.4(7)	24.7(6)	28.5(7)	2.6(5)	8.0(5)	1.8(5)
C9	30.1(7)	29.1(6)	32.3(8)	2.8(6)	4.7(6)	6.7(6)
C10	23.2(6)	34.5(7)	32.7(7)	-3.8(6)	4.3(5)	4.8(5)
C11	23.2(6)	37.6(7)	30.3(7)	0.0(6)	7.2(5)	-1.3(6)
C12	23.3(6)	28.5(6)	23.7(6)	1.9(5)	6.6(5)	0.3(5)
C13	26.8(6)	22.9(6)	26.9(7)	2.9(5)	9.0(5)	0.9(5)
C14	33.1(8)	29.9(7)	43.1(9)	-5.9(6)	9.4(7)	-4.2(6)
C15	30.9(7)	30.2(7)	43.2(9)	5.4(6)	13.5(7)	7.7(6)
C16	54.5(10)	27.8(7)	38.6(9)	-3.4(6)	12.9(8)	-6.0(7)
C17	26.1(6)	30.6(7)	23.1(7)	-1.8(5)	5.7(5)	-5.1(5)
C18	35.3(8)	42.8(8)	23.1(7)	-0.5(6)	3.5(6)	-2.4(6)
O3	30.2(5)	36.5(5)	38.6(6)	7.6(4)	16.1(4)	-6.4(4)
O4	19.7(4)	27.0(5)	32.2(5)	3.2(4)	11.3(4)	-1.5(3)
N4	18.8(5)	25.1(5)	29.1(6)	2.4(4)	9.6(4)	0.9(4)
N5	19.1(5)	20.4(5)	26.6(6)	3.4(4)	8.2(4)	0.4(4)
N6	24.8(5)	19.8(5)	23.4(5)	2.7(4)	8.7(4)	1.5(4)
C19	26.1(6)	25.2(6)	24.9(6)	-0.3(5)	10.1(5)	-3.4(5)
C20	23.6(6)	23.4(6)	25.5(6)	2.8(5)	7.8(5)	-0.8(5)
C21	23.0(6)	21.5(6)	18.9(6)	-0.2(5)	7.0(5)	0.2(5)
C22	18.2(6)	22.5(6)	20.5(6)	-0.7(5)	6.8(5)	-0.2(4)
C23	20.6(6)	23.4(6)	22.4(6)	-1.7(5)	8.9(5)	-1.7(5)
C24	18.5(6)	22.7(6)	22.0(6)	-0.3(5)	6.6(5)	0.4(4)
C25	21.6(6)	19.5(5)	24.4(6)	-1.0(5)	6.2(5)	0.0(4)
C26	25.5(6)	29.2(6)	25.9(7)	4.0(5)	8.2(5)	3.4(5)
C27	29.6(7)	33.6(7)	26.5(7)	4.3(6)	2.7(6)	8.4(6)
C28	21.4(6)	27.5(6)	33.4(7)	-3.4(5)	4.9(5)	3.9(5)
C29	23.7(6)	23.6(6)	32.6(7)	-2.4(5)	10.7(6)	1.1(5)
C30	22.9(6)	22.5(6)	25.2(7)	1.7(5)	7.0(5)	0.7(5)
C31	34.4(7)	23.1(6)	32.2(7)	0.9(5)	17.3(6)	2.8(5)
C32	54.6(10)	31.5(7)	28.0(7)	-1.8(6)	17.8(7)	1.0(7)
C33	48.7(9)	23.1(7)	40.5(9)	2.7(6)	19.8(8)	5.3(6)
C34	29.6(7)	27.8(6)	24.7(7)	3.7(5)	6.1(5)	1.3(5)
C35	39.0(8)	36.6(8)	26.8(7)	-4.3(6)	7.9(6)	0.3(6)
C36	26.8(7)	52.7(10)	35.7(9)	5.9(7)	1.6(6)	4.8(7)

Table 114: Bond Lengths in Å for **6ah**.

Atom	Atom	Length/Å
O1	C1	1.2057(18)
O2	C1	1.3906(17)
O2	C5	1.3574(16)
N1	N2	1.3776(15)
N1	C5	1.3163(17)
N2	N3	1.3989(15)
N2	C6	1.3430(16)
N3	C13	1.4932(16)
N3	C17	1.4900(17)
C1	C2	1.4520(19)
C2	C3	1.3586(19)
C3	C4	1.4421(18)
C3	C7	1.4842(18)
C4	C5	1.4050(17)
C4	C6	1.3895(18)
C7	C8	1.3963(18)
C7	C12	1.3993(19)
C8	C9	1.390(2)
C9	C10	1.384(2)
C10	C11	1.385(2)
C11	C12	1.393(2)
C13	C14	1.516(2)
C13	C15	1.528(2)
C16	C17	1.519(2)
C17	C18	1.522(2)

Atom	Atom	Length/Å
O3	C19	1.2102(17)
O4	C19	1.3930(16)
O4	C23	1.3608(15)
N4	N5	1.3808(15)
N4	C23	1.3161(17)
N5	N6	1.4041(14)
N5	C24	1.3436(16)
N6	C31	1.4859(17)
N6	C34	1.4890(17)
C19	C20	1.4509(19)
C20	C21	1.3602(18)
C21	C22	1.4355(17)
C21	C25	1.4808(17)
C22	C23	1.4068(17)
C22	C24	1.3889(17)
C25	C26	1.3965(19)
C25	C30	1.3947(19)
C26	C27	1.3908(19)
C27	C28	1.388(2)
C28	C29	1.387(2)
C29	C30	1.3923(19)
C31	C32	1.518(2)
C31	C33	1.5286(19)
C34	C35	1.516(2)
C34	C36	1.528(2)

Table 35: Bond Angles in ° for **6ah**.

Atom	Atom	Atom	Angle/°
C5	O2	C1	117.75(10)
C5	N1	N2	101.69(10)
N1	N2	N3	121.91(10)
C6	N2	N1	113.91(10)
C6	N2	N3	124.17(11)
N2	N3	C13	111.17(10)
N2	N3	C17	109.65(10)
C17	N3	C13	115.79(10)
O1	C1	O2	116.67(12)
O1	C1	C2	125.31(13)
O2	C1	C2	118.02(11)
C3	C2	C1	124.60(12)
C2	C3	C4	115.94(12)
C2	C3	C7	120.57(12)
C4	C3	C7	123.49(11)
C5	C4	C3	118.46(11)
C6	C4	C3	138.34(12)
C6	C4	C5	103.17(11)
O2	C5	C4	125.20(12)
N1	C5	O2	119.93(11)
N1	C5	C4	114.86(11)
N2	C6	C4	106.35(11)
C8	C7	C3	119.48(12)
C8	C7	C12	118.82(12)
C12	C7	C3	121.60(11)
C9	C8	C7	120.43(13)
C10	C9	C8	120.37(13)
C9	C10	C11	119.80(13)

Atom	Atom	Atom	Angle/°
C10	C11	C12	120.30(14)
C11	C12	C7	120.25(13)
N3	C13	C14	109.20(11)
N3	C13	C15	116.20(11)
C14	C13	C15	111.13(13)
N3	C17	C16	109.71(12)
N3	C17	C18	109.30(11)
C16	C17	C18	109.76(13)
C23	O4	C19	117.75(10)
C23	N4	N5	101.35(10)
N4	N5	N6	121.63(10)
C24	N5	N4	114.06(10)
C24	N5	N6	124.14(11)
N5	N6	C31	109.24(10)
N5	N6	C34	112.01(10)
C31	N6	C34	116.47(11)
O3	C19	O4	116.47(12)
O3	C19	C20	125.36(13)
O4	C19	C20	118.17(11)
C21	C20	C19	124.43(12)
C20	C21	C22	115.99(12)
C20	C21	C25	121.25(12)
C22	C21	C25	122.75(11)
C23	C22	C21	118.93(11)
C24	C22	C21	137.89(12)
C24	C22	C23	103.06(11)
O4	C23	C22	124.70(11)
N4	C23	O4	120.13(11)

Atom	Atom	Atom	Angle/°
N4	C23	C22	115.15(11)
N5	C24	C22	106.35(11)
C26	C25	C21	119.48(12)
C30	C25	C21	121.31(12)
C30	C25	C26	119.21(12)
C27	C26	C25	120.52(13)
C28	C27	C26	119.79(13)
C29	C28	C27	120.18(13)
C28	C29	C30	120.09(13)
C29	C30	C25	120.21(12)
N6	C31	C32	108.49(12)
N6	C31	C33	110.19(12)
C32	C31	C33	110.28(13)
N6	C34	C35	109.52(11)
N6	C34	C36	115.96(13)
C35	C34	C36	111.15(13)

Table 36: Torsion Angles in ° for **6ah**.

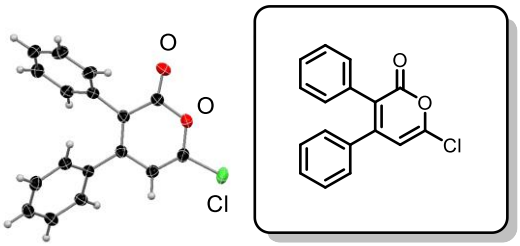
Atom	Atom	Atom	Atom	Angle/°
O1	C1	C2	C3	-179.91(13)
O2	C1	C2	C3	0.7(2)
N1	N2	N3	C13	-68.22(14)
N1	N2	N3	C17	61.11(15)
N1	N2	C6	C4	1.66(15)
N2	N1	C5	O2	178.98(10)
N2	N1	C5	C4	0.19(14)
N2	N3	C13	C14	-52.59(15)
N2	N3	C13	C15	74.05(15)
N2	N3	C17	C16	55.82(15)
N2	N3	C17	C18	176.22(11)
N3	N2	C6	C4	-179.43(11)
C1	O2	C5	N1	179.94(11)
C1	O2	C5	C4	-1.41(18)
C1	C2	C3	C4	-1.66(19)
C1	C2	C3	C7	179.37(12)
C2	C3	C4	C5	1.14(17)
C2	C3	C4	C6	178.71(14)
C2	C3	C7	C8	-28.51(18)
C2	C3	C7	C12	147.77(13)
C3	C4	C5	O2	0.37(18)
C3	C4	C5	N1	179.09(11)
C3	C4	C6	N2	-179.18(14)
C3	C7	C8	C9	174.39(13)
C3	C7	C12	C11	-175.21(13)
C4	C3	C7	C8	152.60(12)
C4	C3	C7	C12	-31.13(18)
C5	O2	C1	O1	-178.59(11)
C5	O2	C1	C2	0.89(17)
C5	N1	N2	N3	179.91(11)
C5	N1	N2	C6	-1.16(14)
C5	C4	C6	N2	-1.37(13)
C6	N2	N3	C13	112.97(13)
C6	N2	N3	C17	-117.71(13)
C6	C4	C5	O2	-177.97(11)
C6	C4	C5	N1	0.75(15)
C7	C3	C4	C5	-179.92(11)
C7	C3	C4	C6	-2.3(2)
C7	C8	C9	C10	1.5(2)
C8	C7	C12	C11	1.1(2)
C8	C9	C10	C11	-0.1(2)

Atom	Atom	Atom	Atom	Angle/°
C9	C10	C11	C12	-0.8(2)
C10	C11	C12	C7	0.3(2)
C12	C7	C8	C9	-2.0(2)
C13	N3	C17	C16	-177.41(12)
C13	N3	C17	C18	-57.01(15)
C17	N3	C13	C14	-178.59(12)
C17	N3	C13	C15	-51.95(17)
O3	C19	C20	C21	179.68(13)
O4	C19	C20	C21	-0.7(2)
N4	N5	N6	C31	-61.13(15)
N4	N5	N6	C34	69.43(15)
N4	N5	C24	C22	-1.64(15)
N5	N4	C23	O4	-179.50(11)
N5	N4	C23	C22	-0.85(15)
N5	N6	C31	C32	-59.40(14)
N5	N6	C31	C33	179.78(12)
N5	N6	C34	C35	56.63(15)
N5	N6	C34	C36	-70.12(15)
N6	N5	C24	C22	-177.01(11)
C19	O4	C23	N4	177.62(12)
C19	O4	C23	C22	-0.90(18)
C19	C20	C21	C22	1.6(2)
C19	C20	C21	C25	-177.22(12)
C20	C21	C22	C23	-2.04(18)
C20	C21	C22	C24	-177.26(15)
C20	C21	C25	C26	34.24(19)
C20	C21	C25	C30	-145.36(13)
C21	C22	C23	O4	1.82(19)
C21	C22	C23	N4	-176.76(11)
C21	C22	C24	N5	176.68(15)
C21	C25	C26	C27	-179.65(13)
C21	C25	C30	C29	179.98(11)
C22	C21	C25	C26	-144.49(13)
C22	C21	C25	C30	35.91(18)
C23	O4	C19	O3	179.92(12)
C23	O4	C19	C20	0.30(17)
C23	N4	N5	N6	177.04(11)
C23	N4	N5	C24	1.54(14)
C23	C22	C24	N5	0.98(14)
C24	N5	N6	C31	113.90(14)
C24	N5	N6	C34	-115.54(14)
C24	C22	C23	O4	178.53(12)
C24	C22	C23	N4	-0.06(15)
C25	C21	C22	C23	176.75(12)
C25	C21	C22	C24	1.5(2)
C25	C26	C27	C28	-0.7(2)
C26	C25	C30	C29	0.38(19)
C26	C27	C28	C29	1.1(2)
C27	C28	C29	C30	-0.7(2)
C28	C29	C30	C25	0.0(2)
C30	C25	C26	C27	0.0(2)
C31	N6	C34	C35	-

Atom	Atom	Atom	Atom	Angle/°
				176.63(12)
C31	N6	C34	C36	56.62(16)
C34	N6	C31	C32	172.50(12)
C34	N6	C31	C33	51.68(16)

Table 37: Hydrogen Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for **6ah**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij}.

Atom	x	y	z	U_{eq}
H2	7974(18)	4040(6)	-214(17)	30(4)
H6	7693(17)	3524(5)	4011(15)	21(4)
H8	6350(20)	4530(7)	-30(20)	45(5)
H9	4050(20)	4678(7)	-650(20)	41(5)
H10	2600(20)	4215(7)	120(20)	43(5)
H11	3460(20)	3625(7)	1539(19)	40(5)
H12	5826(19)	3455(6)	2177(17)	30(4)
H13	10111(18)	2538(6)	6444(18)	30(4)
H14A	8120(30)	2510(8)	4710(20)	53(6)
H14B	9080(20)	2065(8)	4740(20)	47(5)
H14C	9020(20)	2489(7)	3800(20)	50(6)
H15A	11610(20)	2566(8)	4780(20)	52(6)
H15B	11660(20)	2162(8)	5680(20)	46(6)
H15C	12270(30)	2651(9)	6210(30)	65(7)
H16A	9650(20)	3974(8)	6590(20)	50(6)
H16B	10320(20)	4058(7)	5540(20)	41(5)
H16C	11200(20)	4132(8)	6950(20)	47(5)
H17	11810(20)	3415(7)	6298(19)	41(5)
H18A	11770(20)	3472(8)	8400(20)	52(6)
H18B	10290(30)	3265(7)	7960(20)	53(6)
H18C	11540(20)	2940(7)	7956(19)	42(5)
H20	4079(17)	5268(6)	2727(16)	25(4)
H24	2908(18)	3798(6)	4720(15)	23(4)
H26	1920(20)	5056(6)	1361(18)	34(4)
H27	-430(20)	5218(7)	791(19)	38(5)
H28	-1690(20)	5010(7)	2080(20)	49(6)
H29	-600(20)	4694(6)	4022(18)	32(4)
H30	1732(18)	4546(6)	4694(16)	25(4)
H31	6208(18)	2926(6)	4990(16)	25(4)
H32A	4320(20)	3148(7)	3333(18)	36(5)
H32B	3340(20)	2818(7)	3770(20)	49(6)
H32C	4480(20)	2611(7)	3250(20)	43(5)
H33A	5440(20)	2146(7)	5090(20)	45(5)
H33B	6040(20)	2343(7)	6390(20)	40(5)
H33C	4440(20)	2301(7)	5780(20)	47(5)
H34	5456(19)	2919(6)	7431(17)	32(4)
H35A	5470(20)	3572(7)	8630(20)	49(6)
H35B	4090(20)	3564(7)	7510(20)	45(5)
H35C	5270(20)	3912(8)	7460(20)	49(6)
H36A	7460(20)	3607(7)	7240(20)	45(5)
H36B	7600(30)	3243(8)	8340(20)	56(6)
H36C	7580(20)	3050(8)	7010(20)	52(6)



Crystal data and structure refinement for **8**.

Formula	$C_{17}H_{11}ClO_2$
$D_{calc.}$/ g cm^{-3}	1.395
m/mm^{-1}	2.492
Formula Weight	282.71
Colour	colourless
Shape	plate
Size/mm^3	0.21×0.20×0.0 3
T/K	140.00(10)
Crystal System	triclinic
Space Group	$P\bar{1}$
a/Å	7.9105(3)
b/Å	9.8857(3)
c/Å	17.5630(4)
a/°	83.587(2)
b/°	81.245(3)
g/°	85.103(3)
V/Å^3	1345.68(8)
Z	4
Z'	2
Wavelength/Å	1.54184
Radiation type	CuK_α
Q_{min}/°	4.512
Q_{max}/°	72.527
Measured Refl's.	10445
Indep't Refl's	5170
Refl's I≥2 σ(I)	4471
R_{int}	0.0232
Parameters	361
Restraints	0
Largest Peak/e Å^{-3}	0.249
Deepest Hole/e Å^{-3}	-0.262
GooF	1.027
wR_2 (all data)	0.0938
wR_2	0.0888
R_1 (all data)	0.0412

Reflection Statistics

Total reflections (after filtering)	10445	Unique reflections	5170
Completeness	0.97	Mean I/σ	17.3
hkl_{max} collected	(9, 12, 21)	hkl_{min} collected	(-9, -12, -14)
hkl_{max} used	(9, 12, 21)	hkl_{min} used	(-9, -12, 0)
Lim d_{max} collected	100.0	Lim d_{min} collected	0.77
d_{max} used	9.8	d_{min} used	0.81
Friedel pairs	1118	Friedel pairs merged	1
Inconsistent equivalents	1	R_{int}	0.0232
R_{sigma}	0.032	Intensity transformed	0
Omitted reflections	0	Omitted by user (OMIT hkl)	0
Multiplicity	(3527, 1880, 552, 189, 105, 26, 7, 2)	Maximum multiplicity	9
Removed systematic absences	0	Filtered off (Shel/OMIT)	0

Table 38: Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for **8**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij}.

Atom	x	y	z	U_{eq}
Cl1	14493.7(5)	8390.9(4)	5437.6(2)	37.37(11)
O1	12907.3(14)	8210.1(11)	6810.2(6)	30.5(2)
O2	11850.6(15)	8230.2(12)	8043.8(6)	33.2(2)
C1	11649.0(19)	7854.4(15)	7436.2(8)	26.7(3)
C2	12826(2)	7844.9(16)	6099.7(9)	28.6(3)
C3	11587(2)	7127.9(16)	5943.5(9)	28.8(3)
C4	10250.4(19)	6718.8(14)	6555.0(8)	24.8(3)
C5	10249.6(19)	7100.4(14)	7285.7(8)	24.9(3)
C6	8957.1(19)	5861.8(15)	6352.8(8)	25.4(3)
C7	8394(2)	4727.7(15)	6847.6(8)	26.9(3)
C8	7228(2)	3913.7(15)	6638.5(9)	30.6(3)
C9	6599(2)	4221.6(17)	5941.5(10)	33.8(3)
C10	7155(2)	5343.0(17)	5446.2(9)	33.9(3)
C11	8337(2)	6149.6(16)	5646.3(9)	30.2(3)
C12	8851.5(19)	6899.7(14)	7945.6(8)	26.0(3)
C13	7163(2)	7346.8(15)	7852.3(9)	28.0(3)
C14	5868(2)	7292.0(17)	8480.5(9)	33.3(3)
C15	6231(2)	6776.4(17)	9210.3(10)	35.9(4)
C16	7894(2)	6309.6(16)	9306.8(9)	33.9(3)
C17	9203(2)	6367.0(16)	8682.0(9)	29.9(3)
Cl2	11865.1(6)	10052.8(4)	4106.0(2)	40.26(12)
O3	9290.6(15)	8847.4(12)	3896.8(6)	33.3(3)
O4	6977.6(18)	7734.6(15)	3910.7(7)	45.5(3)
C18	8195(2)	8206.5(16)	3508.4(9)	31.1(3)
C19	10709(2)	9395.7(15)	3506.6(9)	29.1(3)
C20	11171(2)	9401.2(14)	2743.5(8)	27.0(3)
C21	10118.0(19)	8768.4(14)	2302.6(8)	24.3(3)
C22	8659(2)	8198.6(14)	2674.0(8)	25.6(3)
C23	10742.4(18)	8744.6(15)	1462.5(8)	24.8(3)
C24	11399.3(19)	9911.4(15)	1036.7(8)	27.2(3)
C25	12047(2)	9904.1(16)	258.4(9)	31.3(3)
C26	12073(2)	8725.0(17)	-103.8(9)	32.5(3)
C27	11453(2)	7551.8(17)	316.5(9)	32.1(3)
C28	10781(2)	7558.3(15)	1091.8(9)	28.6(3)
C29	7443.1(19)	7561.9(15)	2275.5(8)	26.1(3)
C30	7209(2)	6171.3(16)	2423.6(9)	31.7(3)
C31	6149(2)	5566.1(17)	2018.9(10)	35.7(4)

Atom	x	y	z	U_{eq}
C32	5274(2)	6350.5(18)	1480.2(10)	35.5(4)
C33	5452(2)	7744.7(18)	1350.3(9)	35.2(3)
C34	6542(2)	8349.9(16)	1744.1(9)	30.6(3)

Table 39: Anisotropic Displacement Parameters (×10^4) for **8**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2} \times U_{11} + ... + 2hka^* \times b^* \times U_{12}]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cl1	30.56(19)	48.6(2)	32.7(2)	-0.09(16)	-0.27(15)	-14.32(16)
O1	27.7(5)	37.0(6)	28.6(5)	-5.8(4)	-4.2(4)	-9.0(4)
O2	31.5(6)	41.7(6)	29.8(6)	-11.9(4)	-8.0(4)	-6.2(5)
C1	24.8(7)	29.6(7)	26.1(7)	-4.2(5)	-4.6(6)	-1.5(6)
C2	28.3(7)	31.2(7)	26.1(7)	-2.4(6)	-2.0(6)	-4.7(6)
C3	29.7(7)	32.6(7)	24.7(7)	-4.0(6)	-3.2(6)	-5.7(6)
C4	25.1(7)	25.3(6)	24.3(7)	-1.8(5)	-4.6(6)	-2.4(5)
C5	25.5(7)	24.5(6)	25.3(7)	-3.2(5)	-5.6(6)	-2.0(5)
C6	26.0(7)	26.9(7)	24.0(7)	-5.8(5)	-2.9(6)	-2.4(6)
C7	28.9(7)	28.7(7)	23.6(7)	-4.2(5)	-3.2(6)	-3.2(6)
C8	31.3(8)	27.4(7)	33.0(8)	-5.2(6)	-0.5(6)	-5.2(6)
C9	32.0(8)	35.0(8)	37.6(9)	-11.4(6)	-6.5(7)	-8.6(6)
C10	37.7(8)	39.0(8)	28.1(8)	-6.1(6)	-10.2(7)	-7.0(7)
C11	34.5(8)	31.4(7)	25.7(7)	-3.4(6)	-5.2(6)	-6.5(6)
C12	29.2(7)	25.3(7)	25.2(7)	-7.1(5)	-3.7(6)	-5.4(6)
C13	29.4(7)	29.4(7)	27.8(7)	-7.7(6)	-6.1(6)	-5.8(6)
C14	28.2(8)	36.2(8)	37.6(9)	-13.5(6)	-2.0(6)	-6.7(6)
C15	36.6(9)	39.7(8)	31.5(8)	-11.0(7)	5.4(7)	-12.3(7)
C16	43.7(9)	33.3(8)	25.2(7)	-3.7(6)	-2.8(7)	-9.1(7)
C17	33.6(8)	30.3(7)	26.8(7)	-4.6(6)	-5.5(6)	-3.4(6)
Cl2	48.8(2)	47.0(2)	30.5(2)	-6.45(16)	-16.54(17)	-11.97(18)
O3	40.0(6)	40.0(6)	21.1(5)	-2.8(4)	-4.0(4)	-10.4(5)
O4	47.5(7)	62.5(8)	26.6(6)	-1.5(5)	4.5(5)	-25.4(6)
C18	34.1(8)	34.7(8)	24.8(7)	-0.6(6)	-3.6(6)	-9.1(6)
C19	33.3(8)	29.2(7)	26.8(7)	-2.2(6)	-9.6(6)	-5.0(6)
C20	29.4(7)	26.2(7)	26.3(7)	-1.0(5)	-5.7(6)	-6.0(6)
C21	27.8(7)	22.5(6)	22.8(7)	-1.4(5)	-4.4(6)	-2.3(5)
C22	29.0(7)	25.5(7)	22.4(7)	-0.5(5)	-3.8(6)	-4.7(6)
C23	23.8(7)	28.5(7)	22.7(7)	-2.3(5)	-4.4(5)	-3.6(5)
C24	28.9(7)	26.9(7)	25.7(7)	-3.1(5)	-1.9(6)	-4.0(6)
C25	33.1(8)	33.1(8)	25.6(7)	1.0(6)	-0.3(6)	-3.0(6)
C26	32.0(8)	41.9(8)	22.5(7)	-5.0(6)	-2.0(6)	2.1(7)
C27	34.7(8)	34.6(8)	29.2(8)	-10.4(6)	-6.8(6)	-1.6(6)
C28	29.0(7)	29.0(7)	28.3(7)	-3.0(6)	-3.9(6)	-5.2(6)
C29	24.2(7)	30.9(7)	22.9(7)	-2.5(5)	-0.2(5)	-5.9(6)
C30	27.8(7)	31.5(8)	36.4(8)	0.0(6)	-7.1(6)	-5.2(6)
C31	31.1(8)	31.0(8)	46.4(9)	-7.5(7)	-4.7(7)	-7.0(6)
C32	30.1(8)	45.0(9)	34.4(8)	-10.1(7)	-5.0(7)	-10.9(7)
C33	32.3(8)	44.9(9)	28.8(8)	0.6(6)	-7.3(6)	-5.7(7)
C34	31.4(8)	32.5(7)	27.6(7)	1.7(6)	-4.3(6)	-6.7(6)

Table 40: Bond Lengths in Å for **8**.

Atom	Atom	Length/Å
Cl1	C2	1.7026(16)
O1	C1	1.4013(19)
O1	C2	1.3492(19)
O2	C1	1.2053(18)
C1	C5	1.458(2)
C2	C3	1.335(2)
C3	C4	1.437(2)
C4	C5	1.377(2)
C4	C6	1.489(2)
C5	C12	1.484(2)
C6	C7	1.400(2)
C6	C11	1.394(2)
C7	C8	1.389(2)
C8	C9	1.384(2)

Atom	Atom	Length/Å
C9	C10	1.389(2)
C10	C11	1.387(2)
C12	C13	1.398(2)
C12	C17	1.400(2)
C13	C14	1.387(2)
C14	C15	1.388(2)
C15	C16	1.385(3)
C16	C17	1.389(2)
Cl2	C19	1.7073(15)
O3	C18	1.4100(19)
O3	C19	1.345(2)
O4	C18	1.200(2)
C18	C22	1.456(2)
C19	C20	1.334(2)
C20	C21	1.442(2)
C21	C22	1.369(2)
C21	C23	1.485(2)
C22	C29	1.489(2)
C23	C24	1.397(2)
C23	C28	1.399(2)
C24	C25	1.385(2)
C25	C26	1.386(2)
C26	C27	1.388(2)
C27	C28	1.385(2)
C29	C30	1.393(2)
C29	C34	1.390(2)
C30	C31	1.389(2)
C31	C32	1.386(2)
C32	C33	1.387(2)
C33	C34	1.393(2)

Table 121: Bond Angles in ° for **8**.

Atom	Atom	Atom	Angle/°
C2	O1	C1	120.70(12)
O1	C1	C5	117.51(12)
O2	C1	O1	115.09(13)
O2	C1	C5	127.39(14)
O1	C2	Cl1	111.99(11)
C3	C2	Cl1	124.50(12)
C3	C2	O1	123.51(14)
C2	C3	C4	119.24(14)
C3	C4	C6	116.64(13)
C5	C4	C3	119.44(13)
C5	C4	C6	123.90(13)
C1	C5	C12	114.98(12)
C4	C5	C1	119.53(14)
C4	C5	C12	125.33(13)
C7	C6	C4	121.15(13)
C11	C6	C4	120.01(13)
C11	C6	C7	118.79(14)
C8	C7	C6	120.39(14)
C9	C8	C7	120.36(14)
C8	C9	C10	119.60(14)
C11	C10	C9	120.37(14)
C10	C11	C6	120.48(14)
C13	C12	C5	119.87(13)
C13	C12	C17	118.74(14)
C17	C12	C5	121.19(14)
C14	C13	C12	120.66(14)
C13	C14	C15	120.19(16)
C16	C15	C14	119.63(15)
C15	C16	C17	120.61(15)
C16	C17	C12	120.15(15)
C19	O3	C18	120.68(12)
O3	C18	C22	116.84(13)
O4	C18	O3	115.45(14)
O4	C18	C22	127.71(15)
O3	C19	Cl2	111.99(11)
C20	C19	Cl2	124.08(13)
C20	C19	O3	123.92(14)
C19	C20	C21	118.89(14)
C20	C21	C23	116.49(13)
C22	C21	C20	119.33(13)
C22	C21	C23	124.15(13)
C18	C22	C29	115.63(13)
C21	C22	C18	120.30(14)
C21	C22	C29	124.06(13)
C24	C23	C21	119.44(13)
C24	C23	C28	118.74(13)
C28	C23	C21	121.73(13)
C25	C24	C23	120.71(14)
C24	C25	C26	120.06(14)
C25	C26	C27	119.76(14)
C28	C27	C26	120.44(15)
C27	C28	C23	120.27(14)
C30	C29	C22	120.55(13)
C34	C29	C22	120.18(13)
C34	C29	C30	119.27(14)
C31	C30	C29	120.40(15)
C32	C31	C30	120.15(15)
C31	C32	C33	119.72(15)
C32	C33	C34	120.24(15)
C29	C34	C33	120.16(15)

Table 42: Torsion Angles in ° for **8**.

Atom	Atom	Atom	Atom	Angle/°
Cl1	C2	C3	C4	179.64(11)
O1	C1	C5	C4	2.8(2)
O1	C1	C5	C12	-172.91(12)
O1	C2	C3	C4	0.4(2)

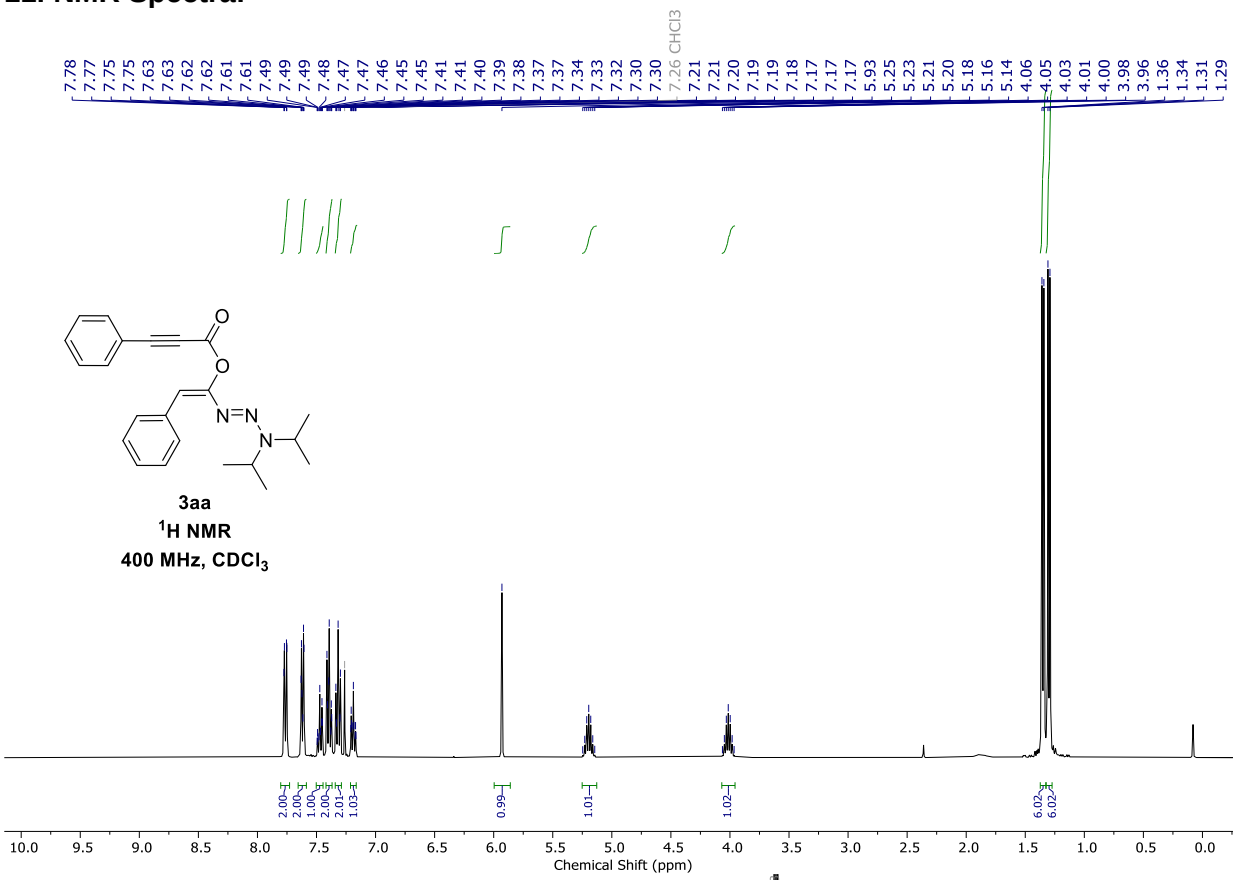
Atom	Atom	Atom	Atom	Angle/°
O2	C1	C5	C4	-178.15(15)
O2	C1	C5	C12	6.2(2)
C1	O1	C2	Cl1	-179.95(10)
C1	O1	C2	C3	-0.6(2)
C1	C5	C12	C13	123.68(15)
C1	C5	C12	C17	-51.15(19)
C2	O1	C1	O2	179.85(13)
C2	O1	C1	C5	-1.0(2)
C2	C3	C4	C5	1.5(2)
C2	C3	C4	C6	-176.99(14)
C3	C4	C5	C1	-3.0(2)
C3	C4	C5	C12	172.17(13)
C3	C4	C6	C7	136.74(15)
C3	C4	C6	C11	-40.6(2)
C4	C5	C12	C13	-51.7(2)
C4	C5	C12	C17	133.47(15)
C4	C6	C7	C8	-177.92(14)
C4	C6	C11	C10	178.84(15)
C5	C4	C6	C7	-41.7(2)
C5	C4	C6	C11	140.96(15)
C5	C12	C13	C14	-173.55(14)
C5	C12	C17	C16	173.84(14)
C6	C4	C5	C1	175.35(13)
C6	C4	C5	C12	-9.5(2)
C6	C7	C8	C9	-0.6(2)
C7	C6	C11	C10	1.4(2)
C7	C8	C9	C10	0.8(2)
C8	C9	C10	C11	0.1(3)
C9	C10	C11	C6	-1.2(3)
C11	C6	C7	C8	-0.5(2)
C12	C13	C14	C15	-0.7(2)
C13	C12	C17	C16	-1.1(2)
C13	C14	C15	C16	-0.4(2)
C14	C15	C16	C17	0.7(2)
C15	C16	C17	C12	0.0(2)
C17	C12	C13	C14	1.4(2)
Cl2	C19	C20	C21	177.70(11)
O3	C18	C22	C21	1.4(2)
O3	C18	C22	C29	-177.75(13)
O3	C19	C20	C21	-1.0(2)
O4	C18	C22	C21	-178.97(17)
O4	C18	C22	C29	1.9(3)
C18	O3	C19	Cl2	-177.68(11)
C18	O3	C19	C20	1.1(2)
C18	C22	C29	C30	-65.76(19)
C18	C22	C29	C34	114.94(16)
C19	O3	C18	O4	179.05(15)
C19	O3	C18	C22	-1.3(2)
C19	C20	C21	C22	1.0(2)
C19	C20	C21	C23	-177.04(13)
C20	C21	C22	C18	-1.3(2)
C20	C21	C22	C29	177.78(13)
C20	C21	C23	C24	-43.40(19)
C20	C21	C23	C28	132.94(15)

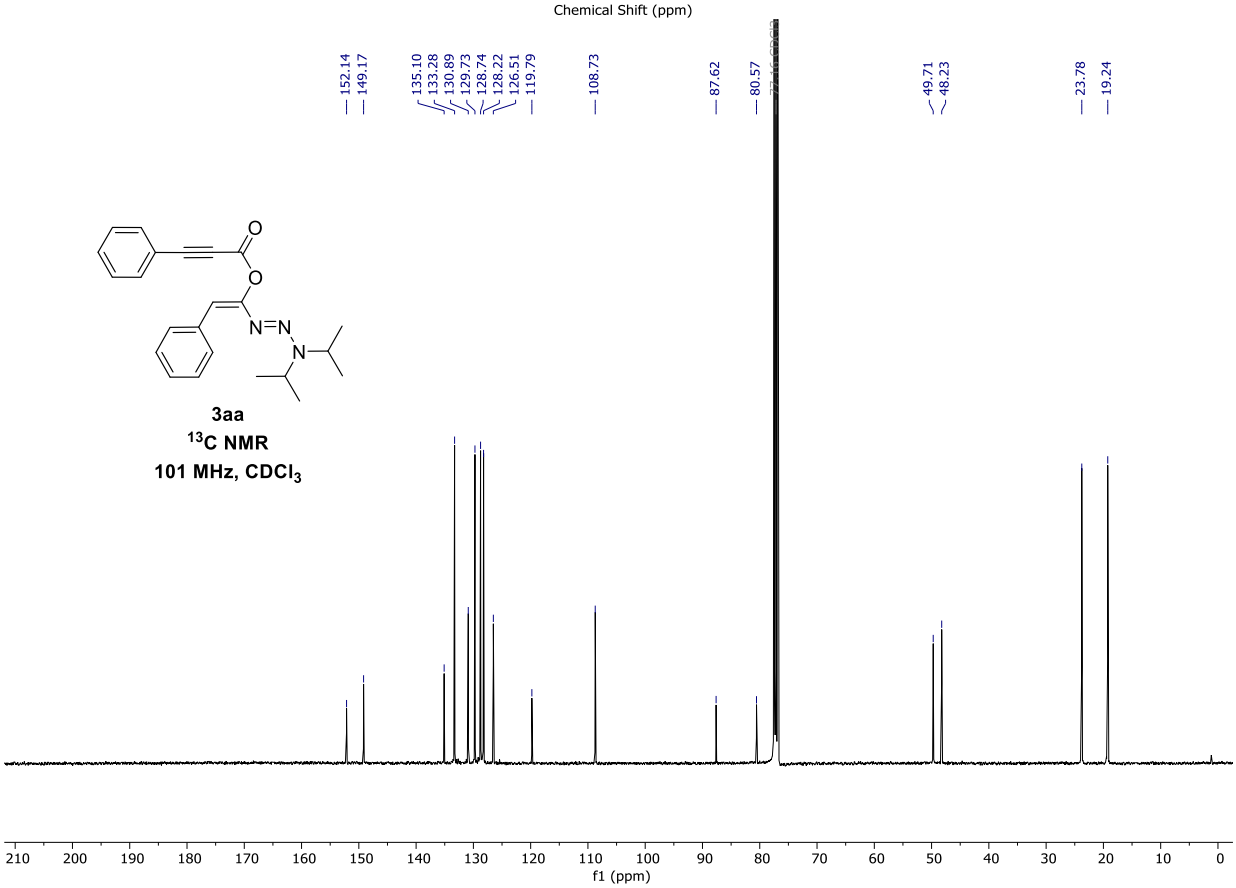
Atom	Atom	Atom	Atom	Angle/°
C21	C22	C29	C30	115.14(17)
C21	C22	C29	C34	-64.2(2)
C21	C23	C24	C25	177.69(14)
C21	C23	C28	C27	-176.66(14)
C22	C21	C23	C24	138.61(15)
C22	C21	C23	C28	-45.0(2)
C22	C29	C30	C31	-176.33(15)
C22	C29	C34	C33	177.64(15)
C23	C21	C22	C18	176.65(14)
C23	C21	C22	C29	-4.3(2)
C23	C24	C25	C26	-1.0(2)
C24	C23	C28	C27	-0.3(2)
C24	C25	C26	C27	-0.2(2)
C25	C26	C27	C28	1.2(2)
C26	C27	C28	C23	-0.9(2)
C28	C23	C24	C25	1.2(2)
C29	C30	C31	C32	-1.9(3)
C30	C29	C34	C33	-1.7(2)
C30	C31	C32	C33	-0.4(3)
C31	C32	C33	C34	1.7(3)
C32	C33	C34	C29	-0.7(3)
C34	C29	C30	C31	3.0(2)

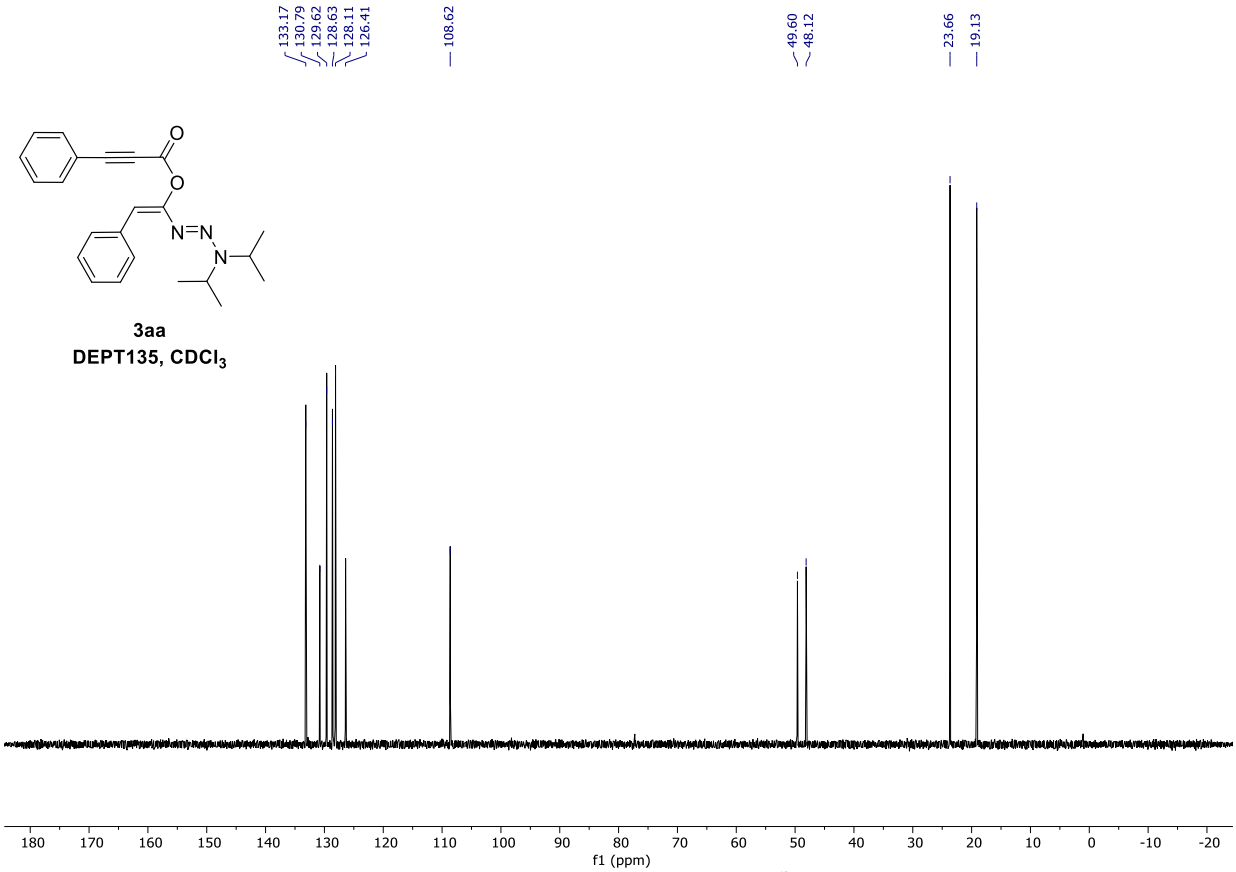
Table 43: Hydrogen Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for **8**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij}.

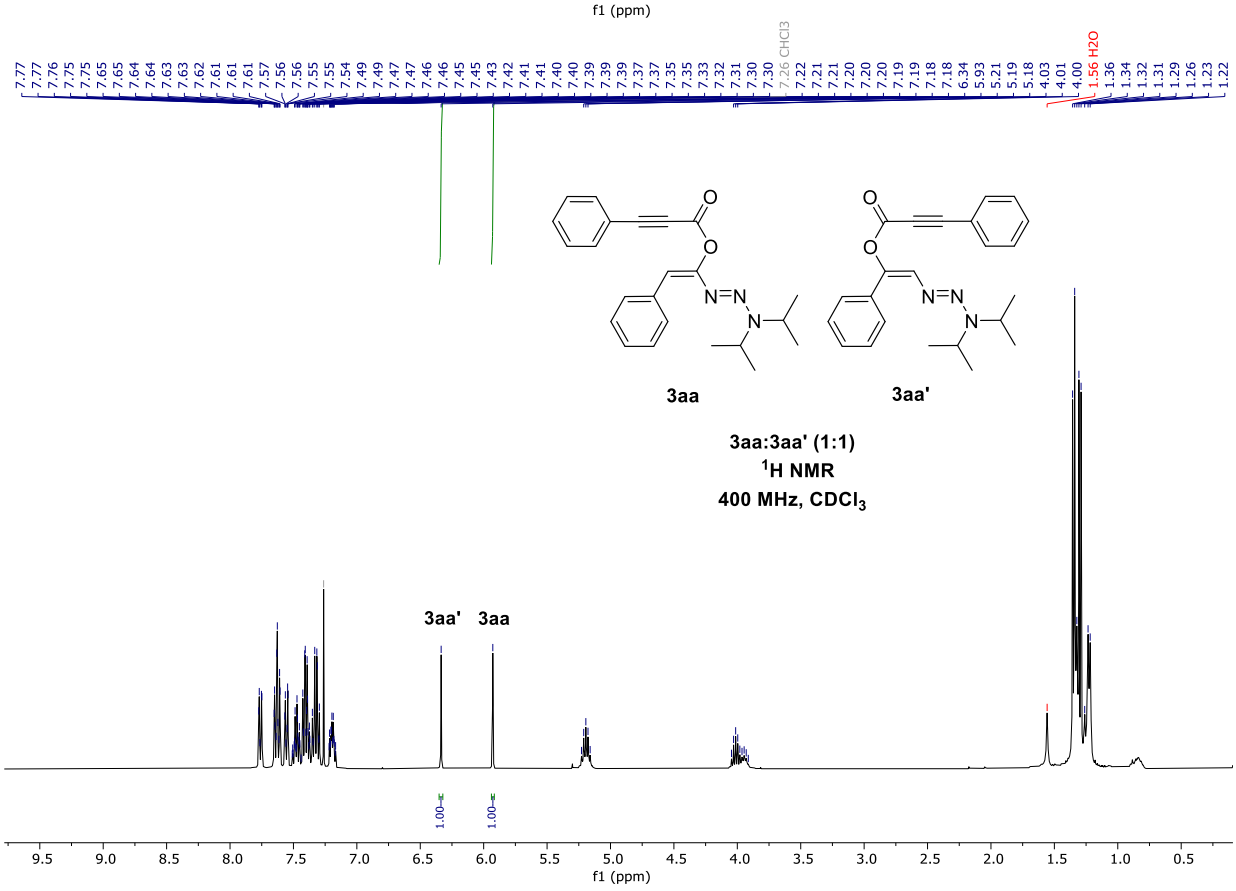
Atom	x	y	z	U_{eq}
H3	11589.71	6890.49	5433.85	35
H7	8812.03	4513.84	7329.13	32
H8	6861.35	3141.29	6975.67	37
H9	5790.66	3669.54	5802.54	41
H10	6723.37	5558.39	4967.94	41
H11	8726.44	6903.65	5299.41	36
H13	6901.71	7691.57	7353.7	34
H14	4727.77	7608.2	8411.15	40
H15	5344.66	6743.93	9641.16	43
H16	8141.42	5946.71	9804.97	41
H17	10338.65	6044.09	8754.62	36
H20	12178.3	9815.12	2494.77	32
H24	11401.92	10718.65	1283.49	33
H25	12473.91	10708.03	-27.31	38
H26	12513.31	8719.97	-637.91	39
H27	11490.23	6738.95	70.77	39
H28	10344.94	6754.16	1373.17	34
H30	7778.86	5633.74	2803.79	38
H31	6024.16	4612.11	2111.63	43
H32	4554.48	5935.38	1201.02	43
H33	4829.41	8288.6	991.57	42
H34	6668.44	9303.49	1649.15	37

11. NMR Spectra:

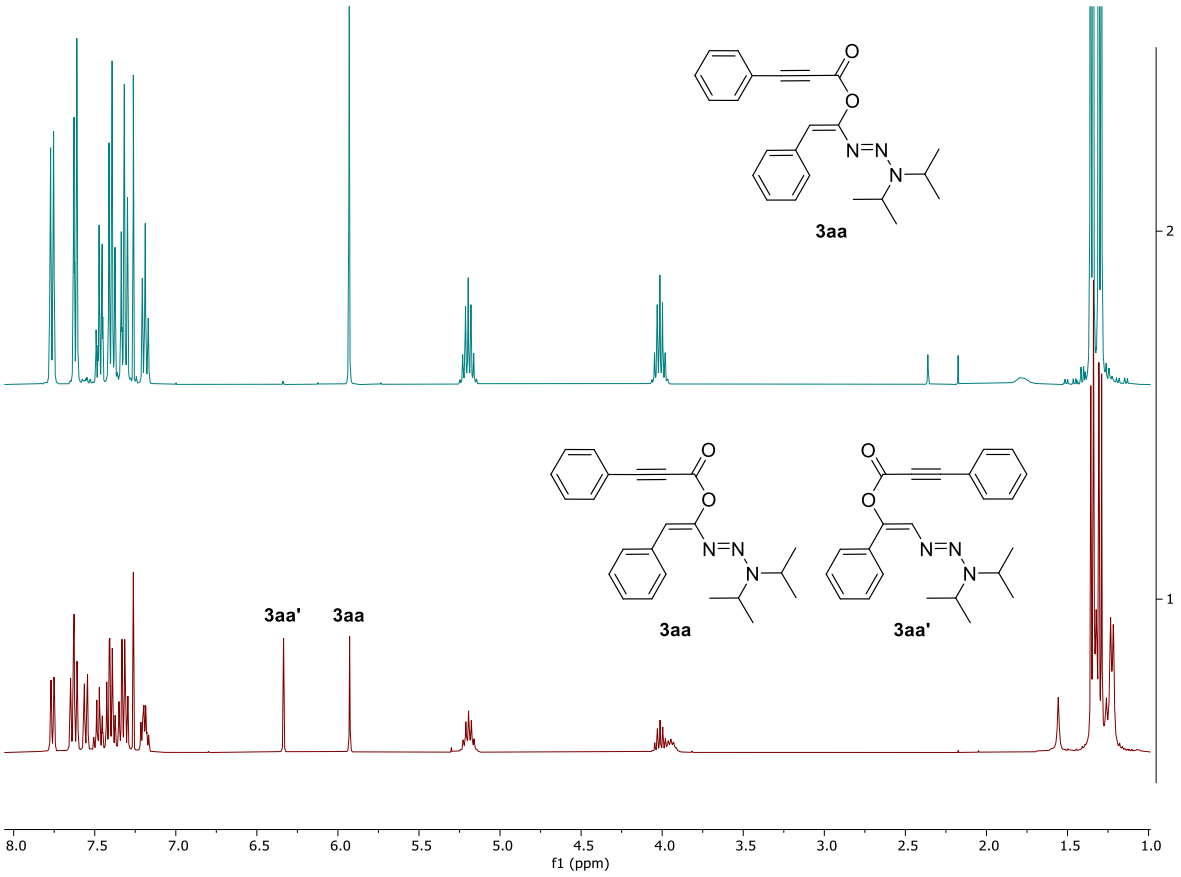


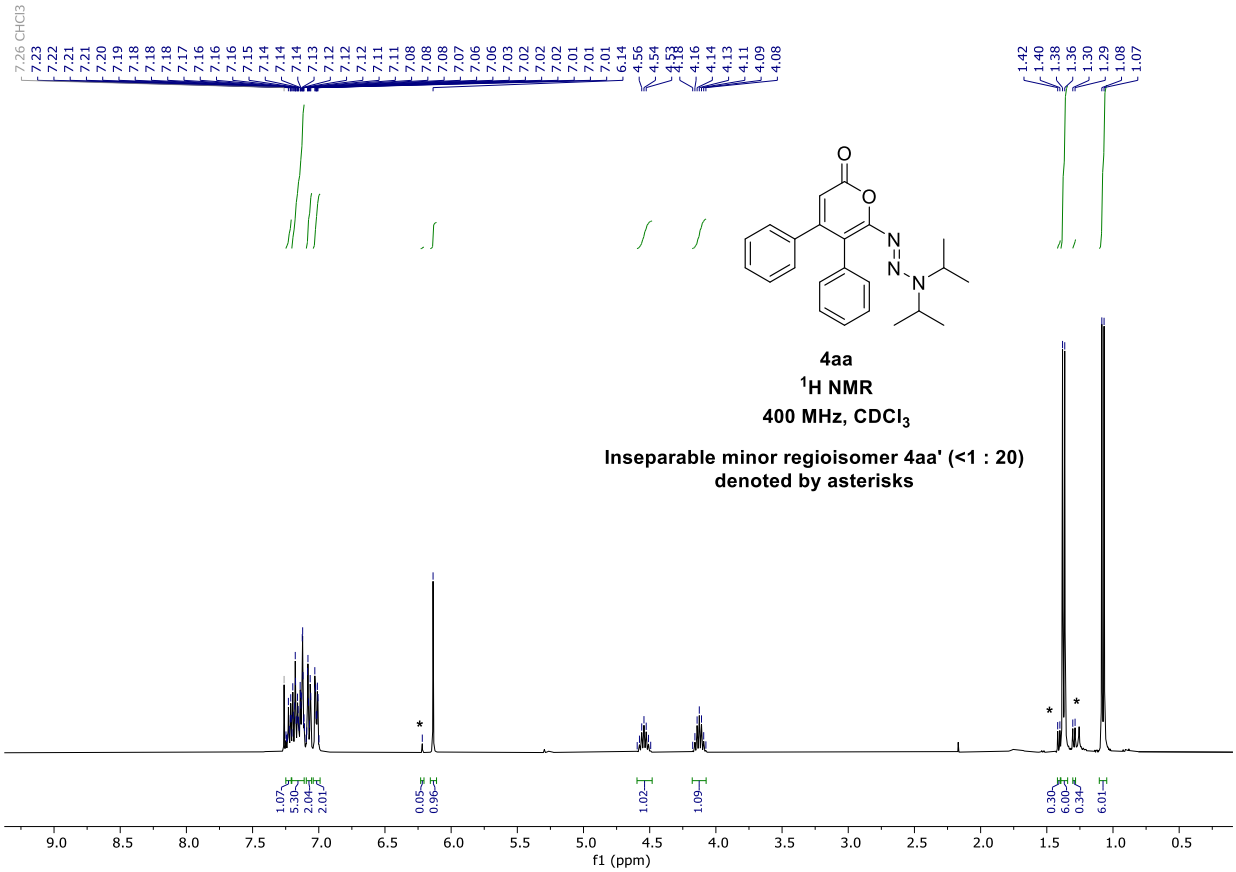



133.17
130.79
129.62
128.63
128.11
126.41
108.62
49.60
48.12
23.66
19.13
3aa
DEPT135, CDCl3
f1 (ppm)


7.26 CHCl3
1.56 H2O
3aa
3aa'
3aa:3aa' (1:1)
1H NMR
400 MHz, CDCl3
3aa'
3aa
1.00
1.00
f1 (ppm)

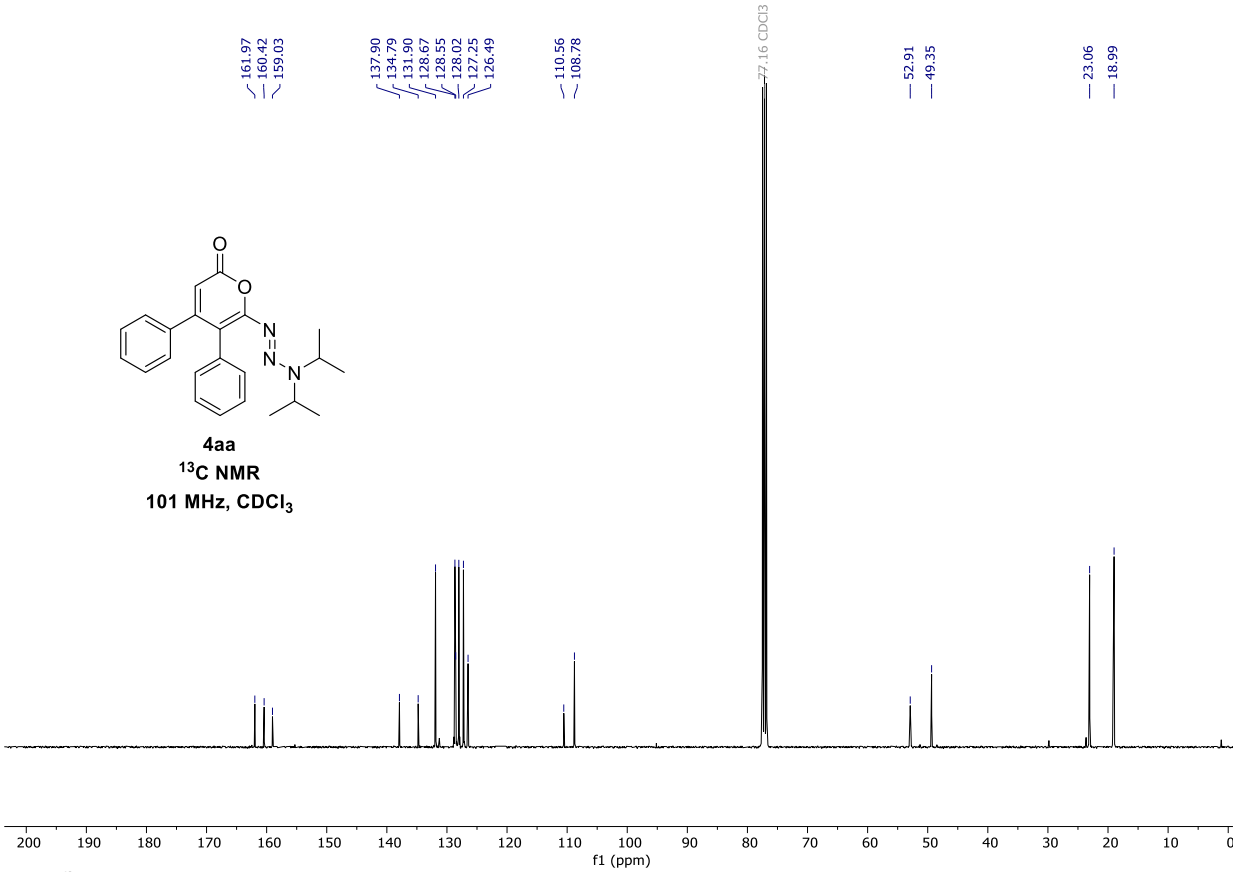
Comparison of ^{1}H NMR spectra of 3aa with 3aa+3aa' mixture





4aa
^{1}H NMR
400 MHz, $CDCl_3$

Inseparable minor regioisomer 4aa' (<1 : 20) denoted by asterisks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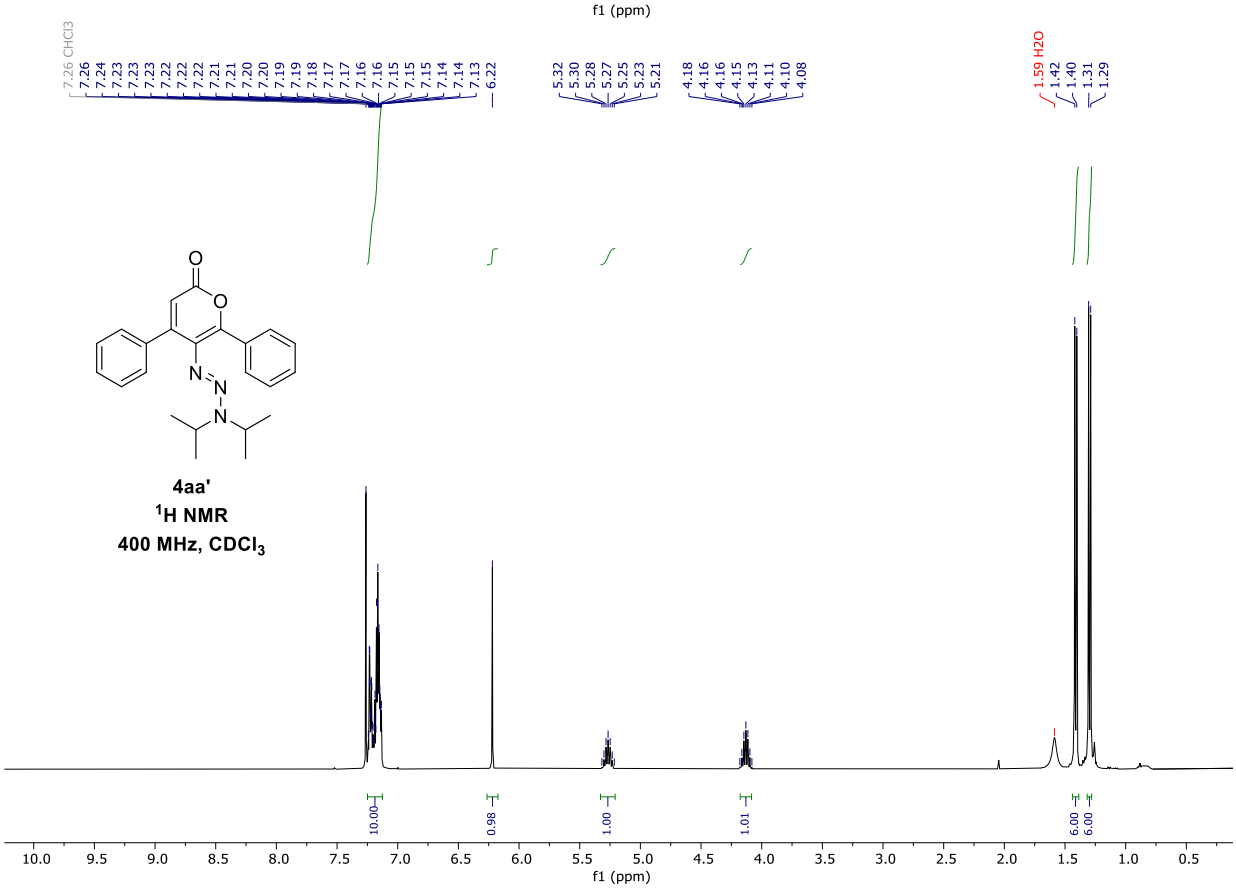
159.03
137.90
134.79
131.90
128.67
128.55
128.02
127.25
126.49
110.56
108.78
77.16 CDCl3
52.91
49.35
23.06
18.99
O
O
N
N
N
4aa
13C NMR
101 MHz, CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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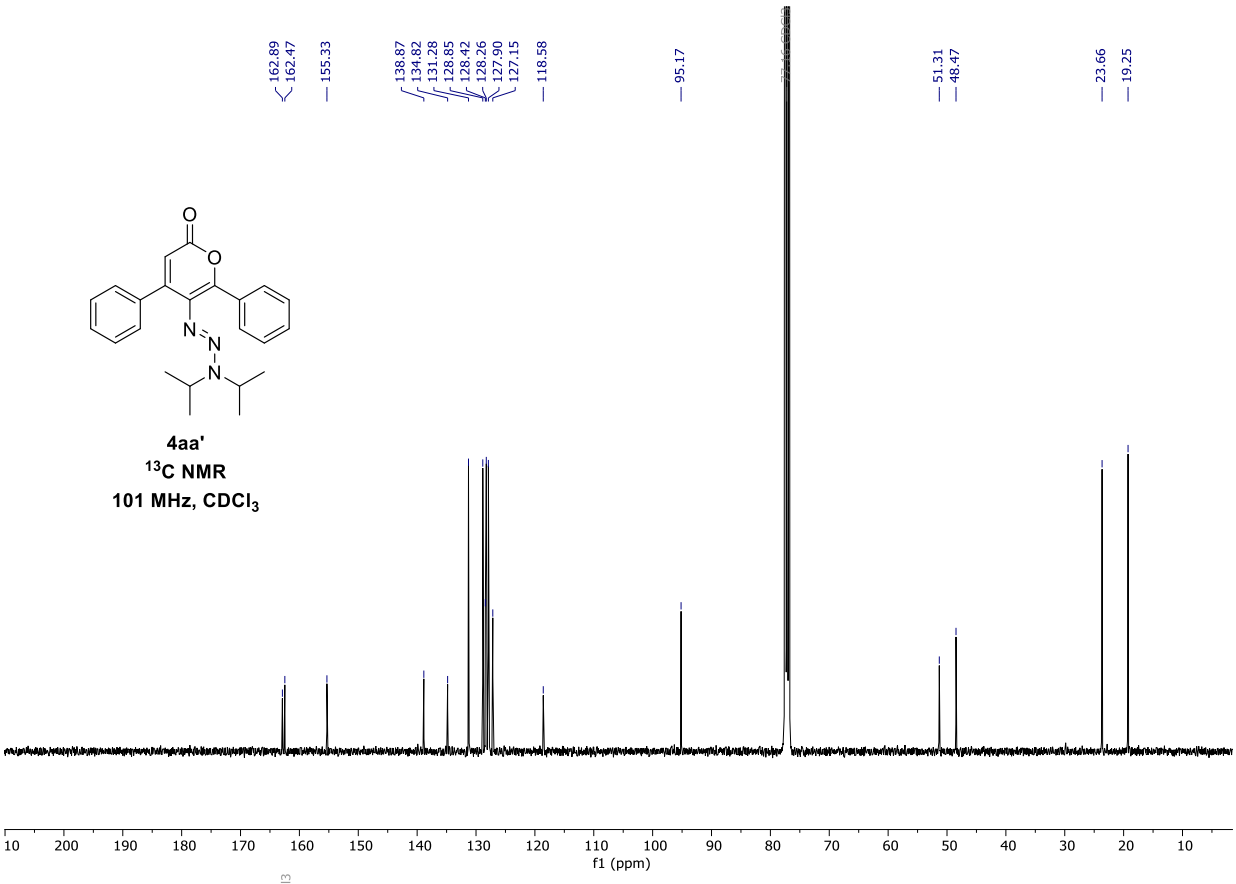
7.26
7.24
7.23
7.23
7.23
7.22
7.22
7.22
7.21
7.21
7.20
7.20
7.19
7.19
7.18
7.17
7.17
7.16
7.16
7.15
7.15
7.15
7.14
7.14
7.13
6.22
5.32
5.30
5.28
5.27
5.25
5.23
5.21
4.18
4.16
4.16
4.15
4.13
4.11
4.10
4.08
1.59 H2O
1.42
1.40
1.31
1.29
O
O
N
N
N
4aa'
1H NMR
400 MHz, CDCl3
10.00
0.98
1.00
1.01
6.00
6.00
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
f1 (ppm)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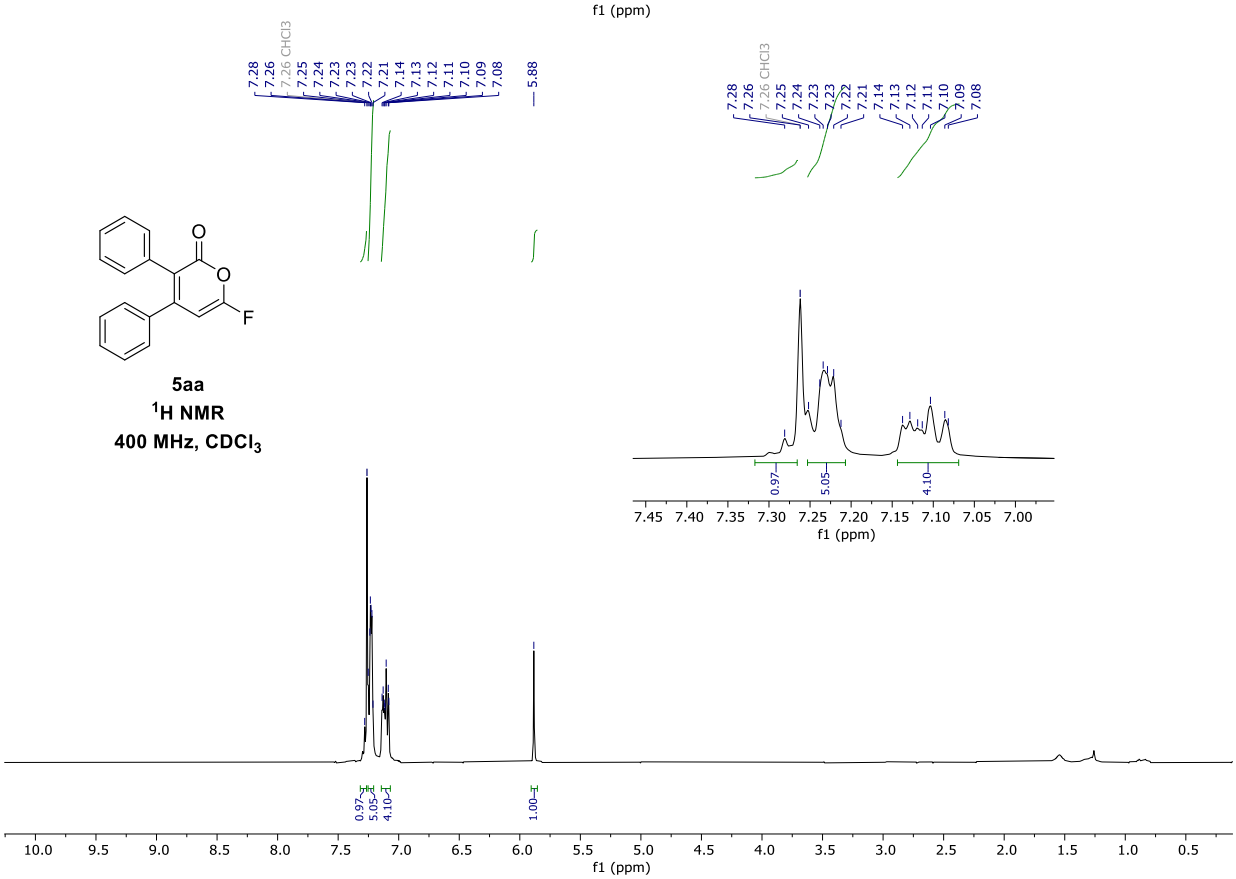
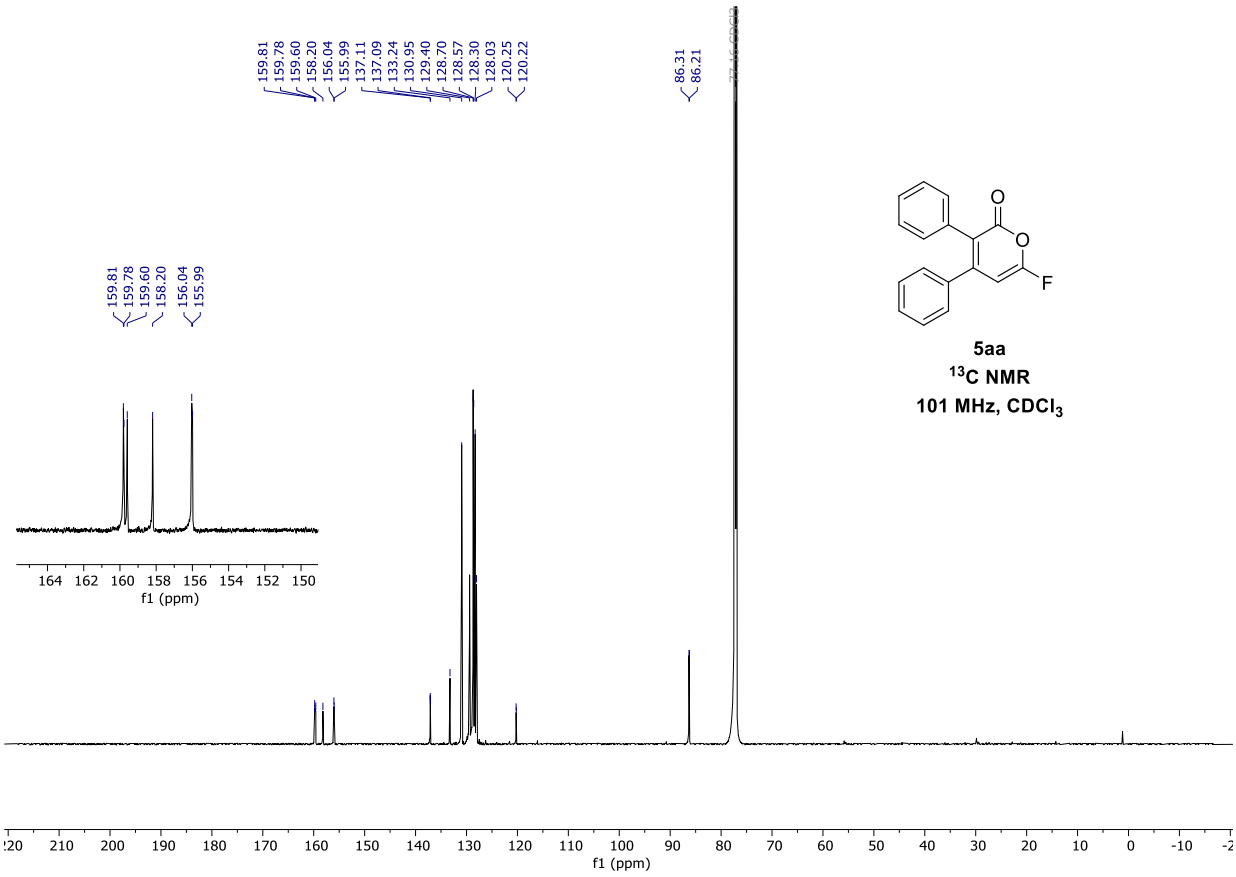
155.33
138.87
134.82
131.28
128.85
128.42
128.26
127.90
127.15
118.58
95.17
77.16 77.00 76.84
51.31
48.47
23.66
19.25
O
O
N
N
N
4aa'
13C NMR
101 MHz, CDCl3
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


7.28
7.26 CHCl3
7.25
7.24
7.23
7.22
7.21
7.14
7.13
7.12
7.11
7.10
7.09
7.08
5.88
O
O
F
5aa
1H NMR
400 MHz, CDCl3
0.97
5.05
4.10
1.00
7.45 7.40 7.35 7.30 7.25 7.20 7.15 7.10 7.05 7.00
f1 (ppm)
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
f1 (ppm)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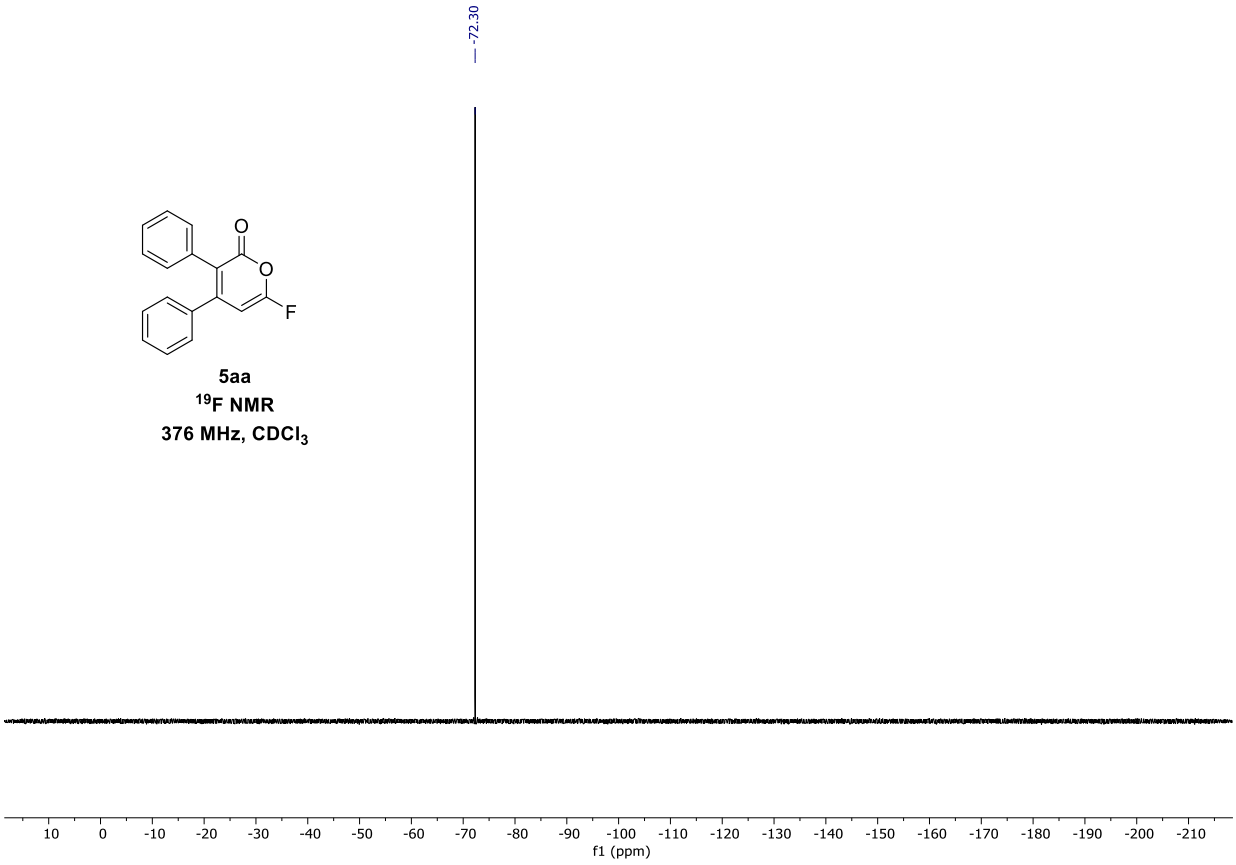
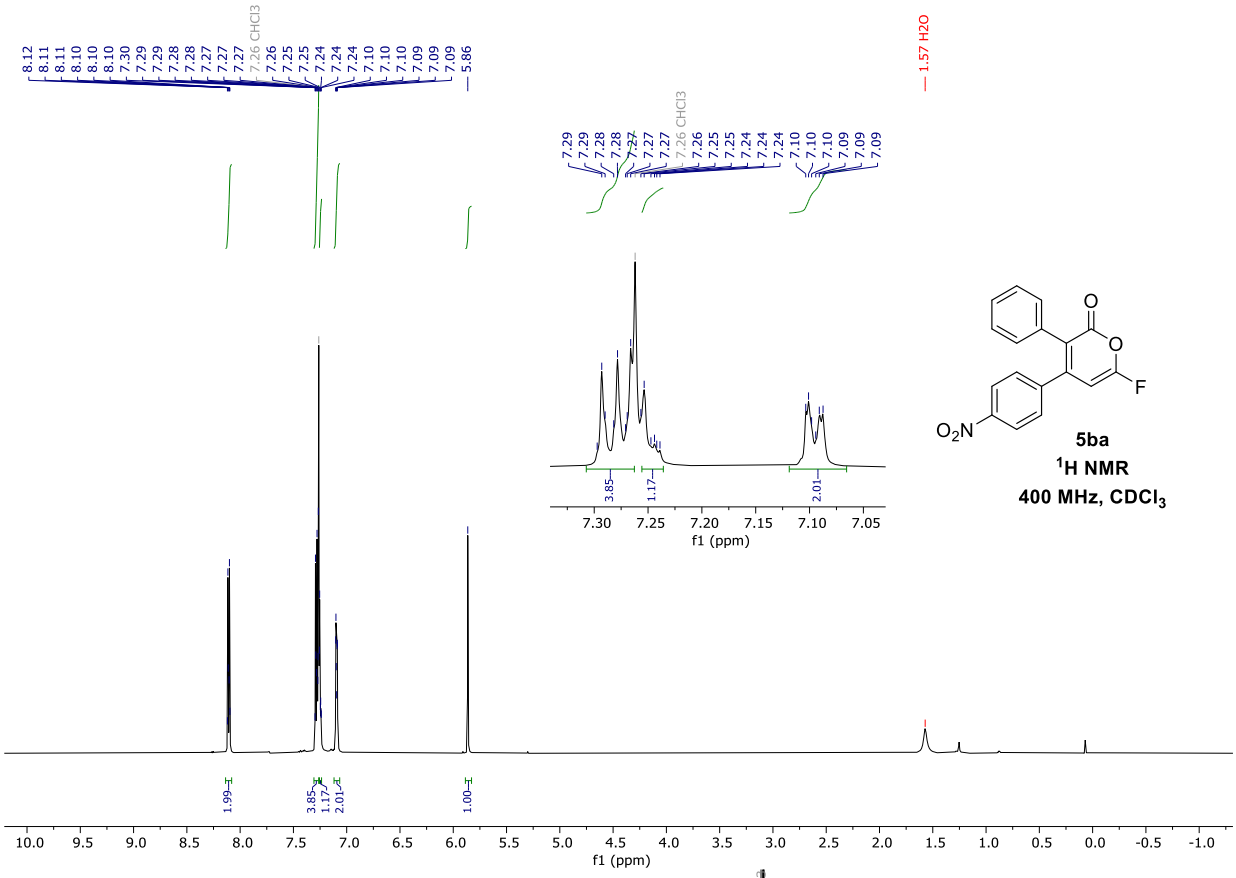
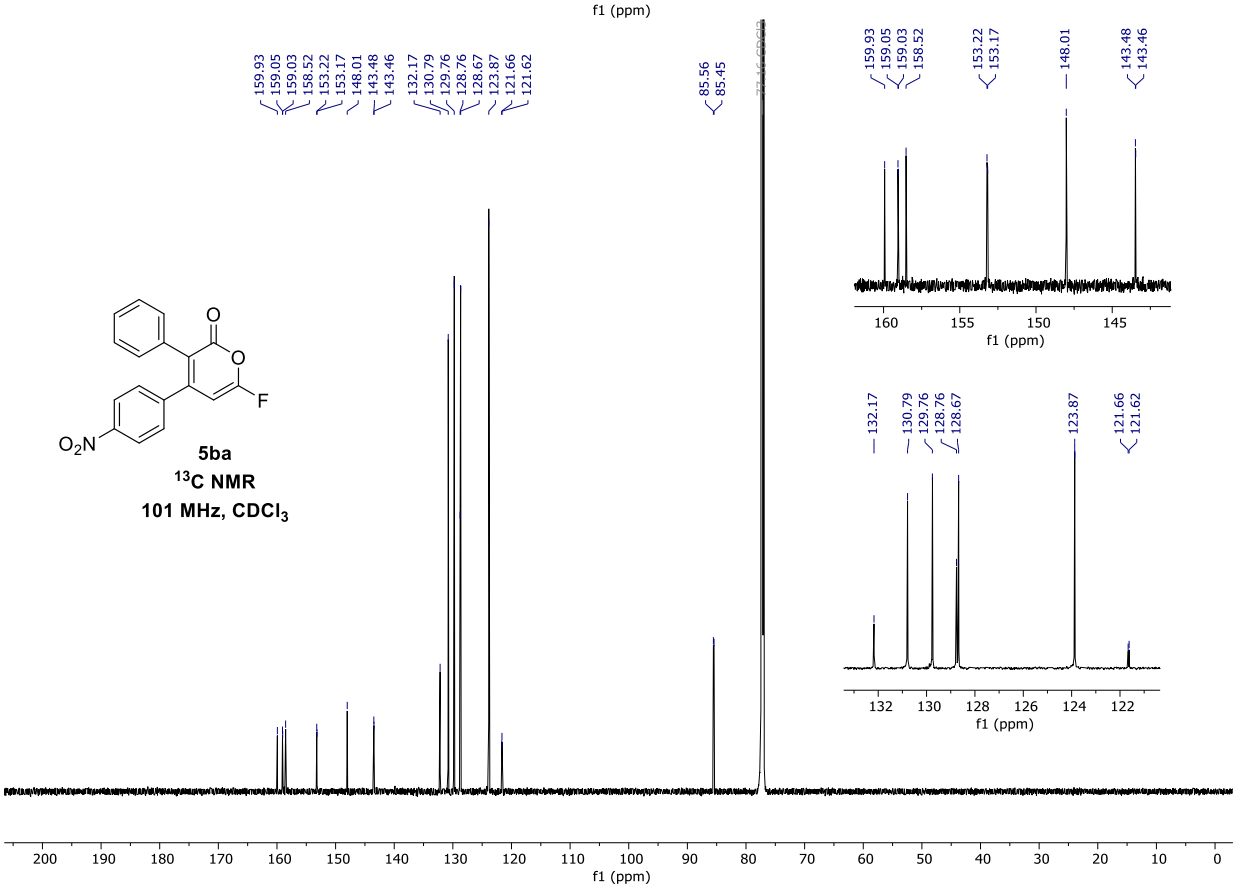
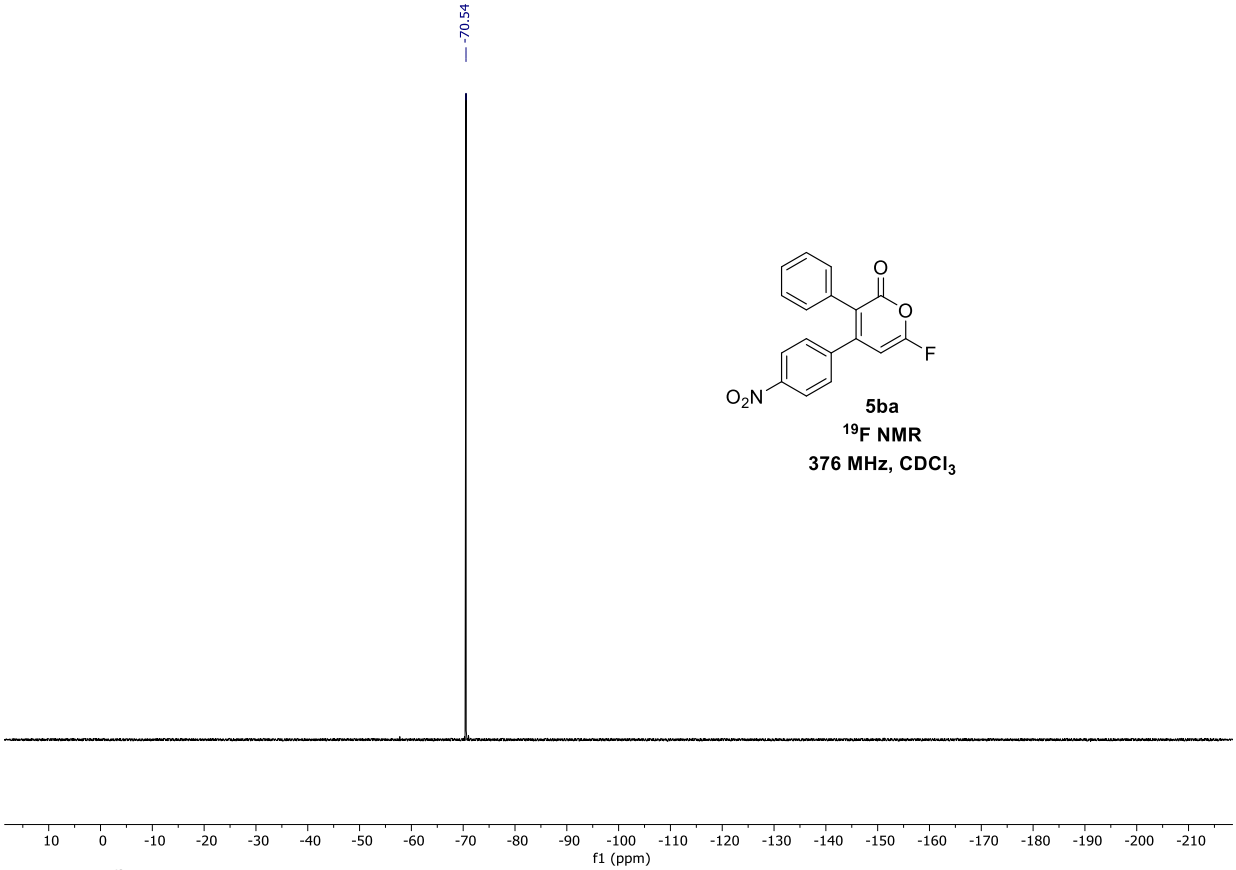
159.78
159.60
158.20
156.04
155.99
137.11
137.09
133.24
130.95
129.40
128.70
128.57
128.30
128.03
120.25
120.22
86.31
86.21
77.16 CDCl3
O
O
F
5aa
13C NMR
101 MHz, CDCl3
f1 (ppm)

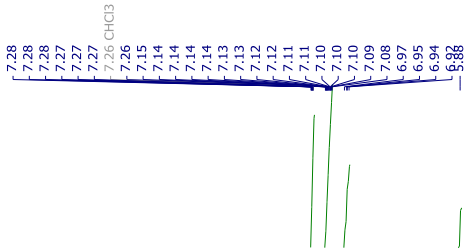

-72.30
O
O
F
5aa
19F NMR
376 MHz, CDCl3
f1 (ppm)

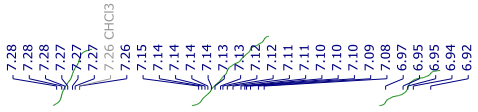

5ba
^{1}H NMR
400 MHz, CDCl$_3$
f1 (ppm)

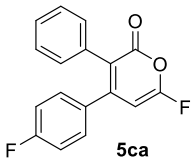

5ba
^{13}C NMR
101 MHz, CDCl$_3$
f1 (ppm)



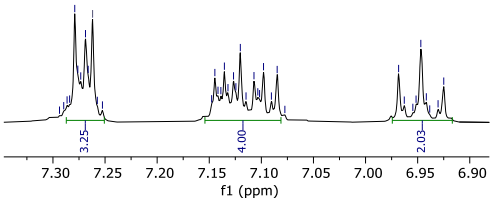
5ba
^{19}F NMR
376 MHz, $CDCl_3$

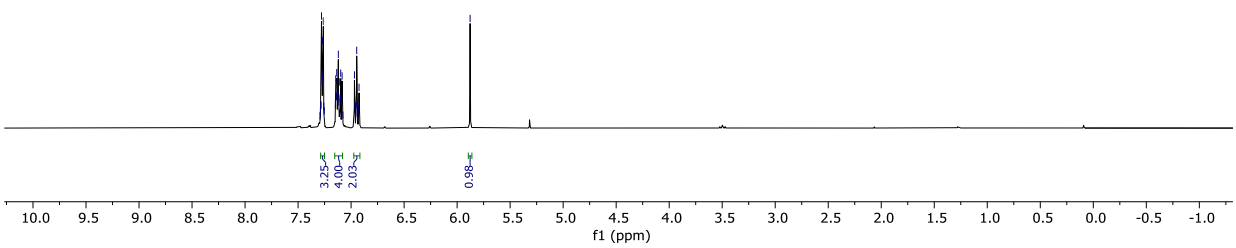


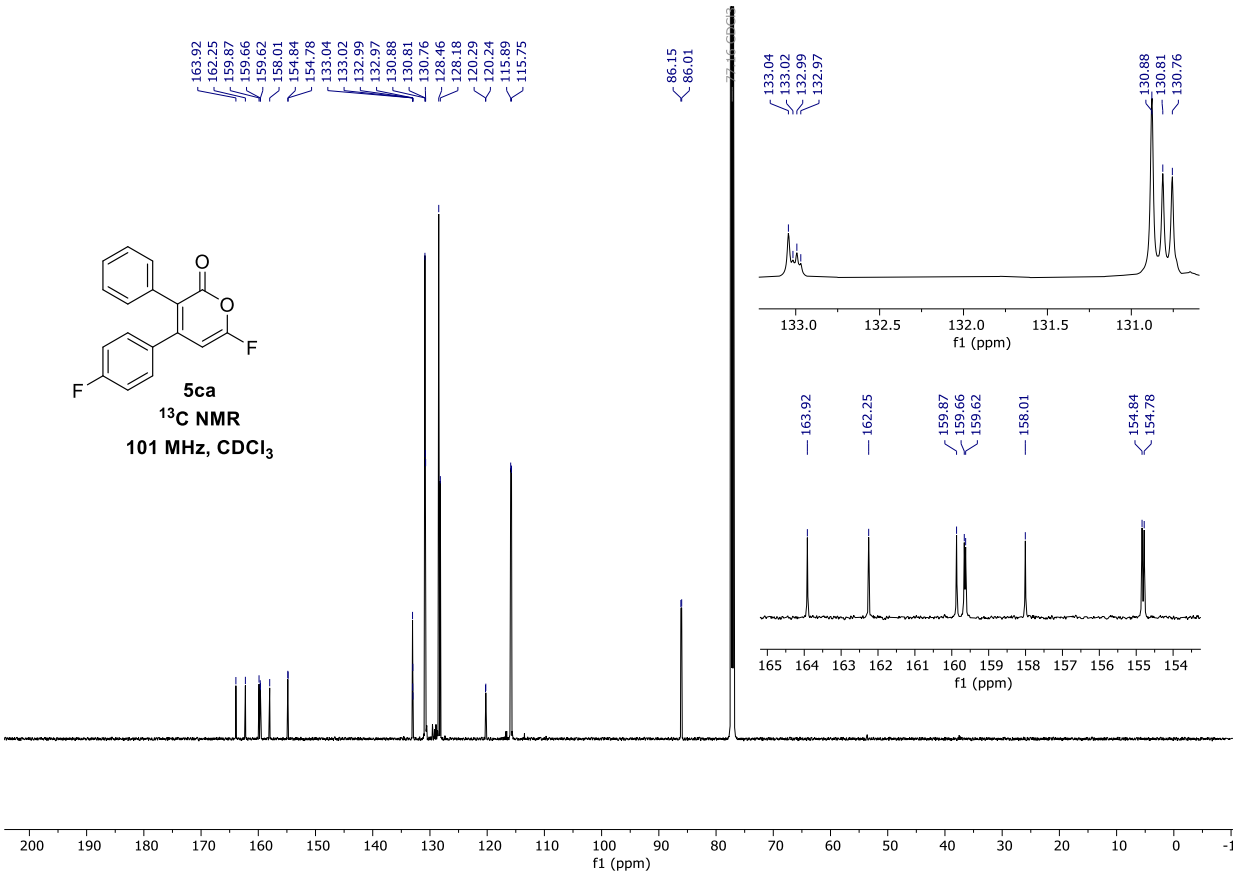




5ca
^{1}H NMR
400 MHz, $CDCl_3$






163.92
162.25
159.87
159.66
159.62
158.01
154.84
154.78
133.04
133.02
132.99
132.97
130.88
130.81
130.76
128.46
128.18
120.29
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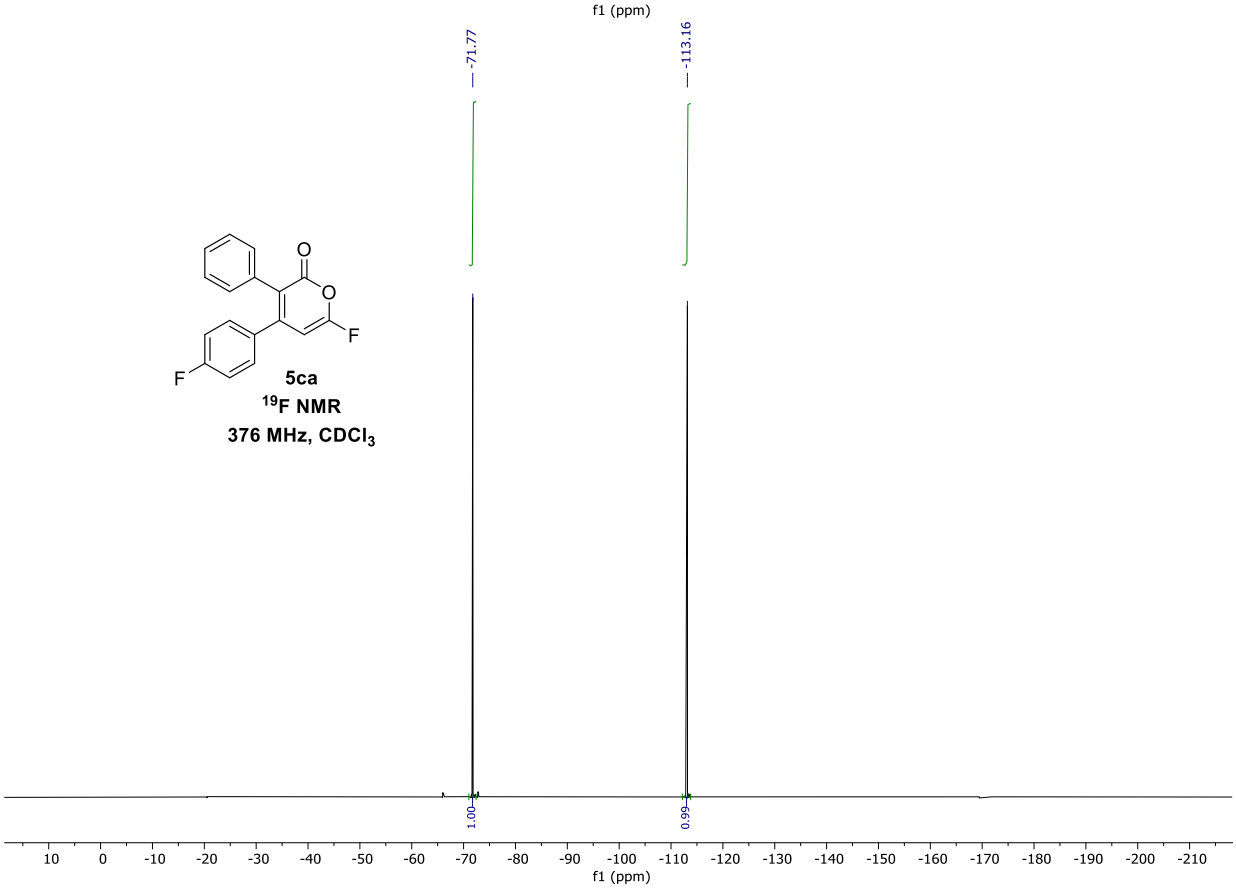
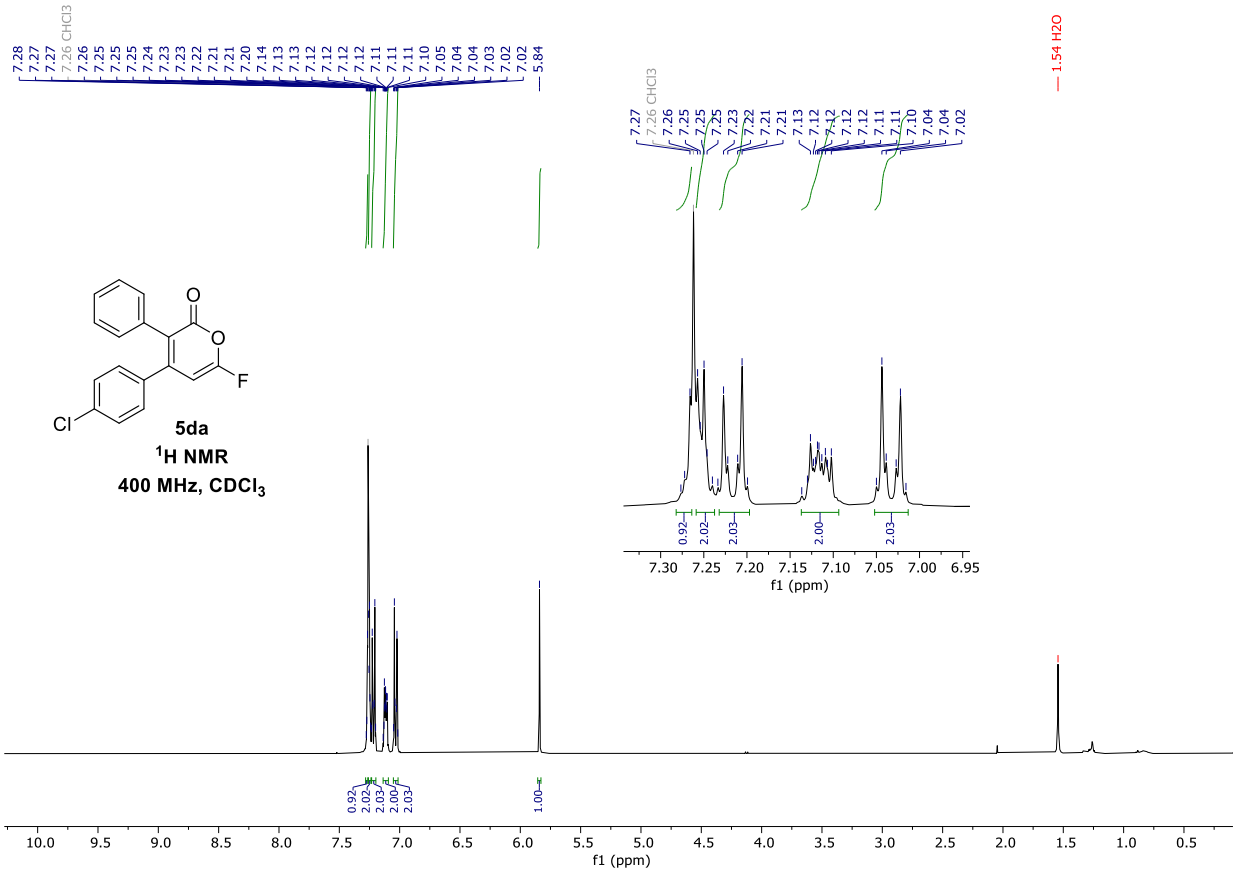
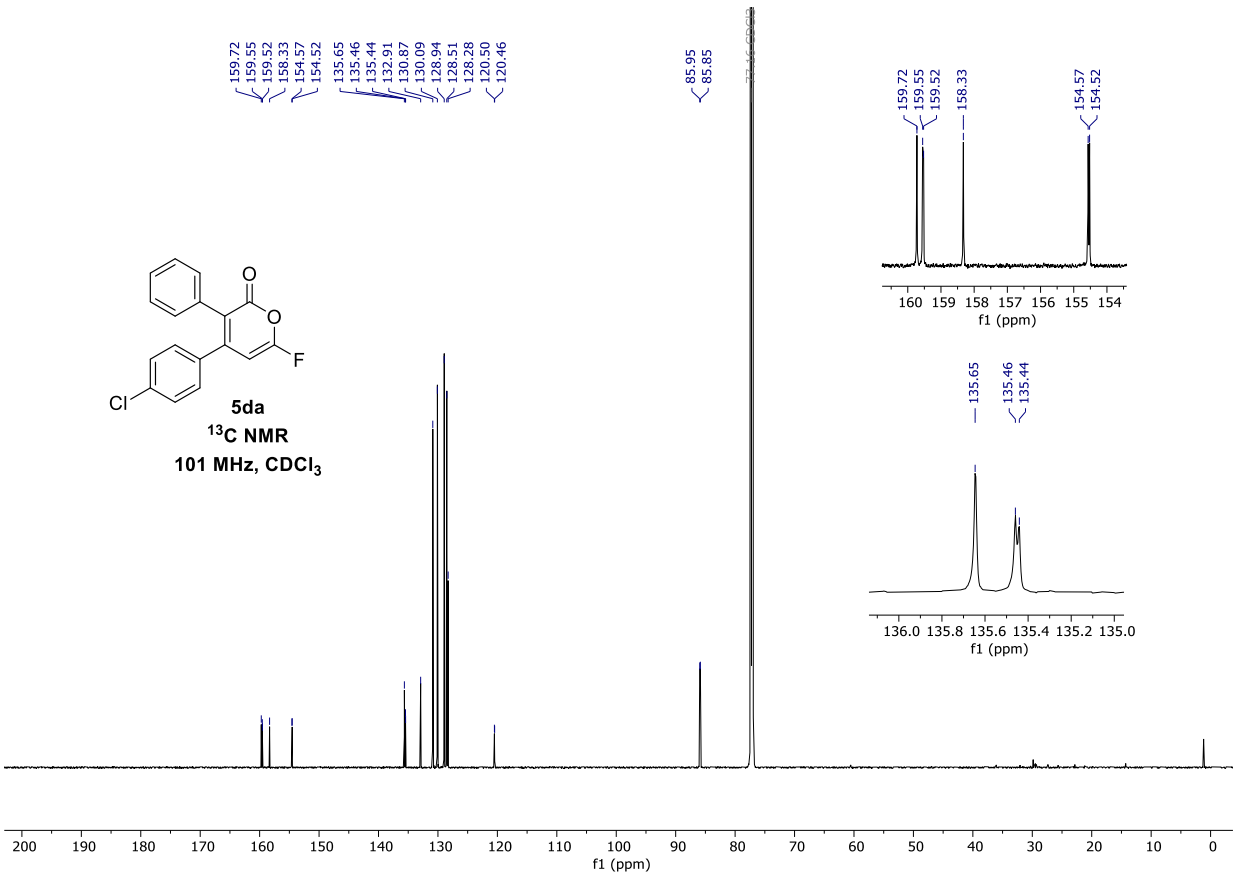
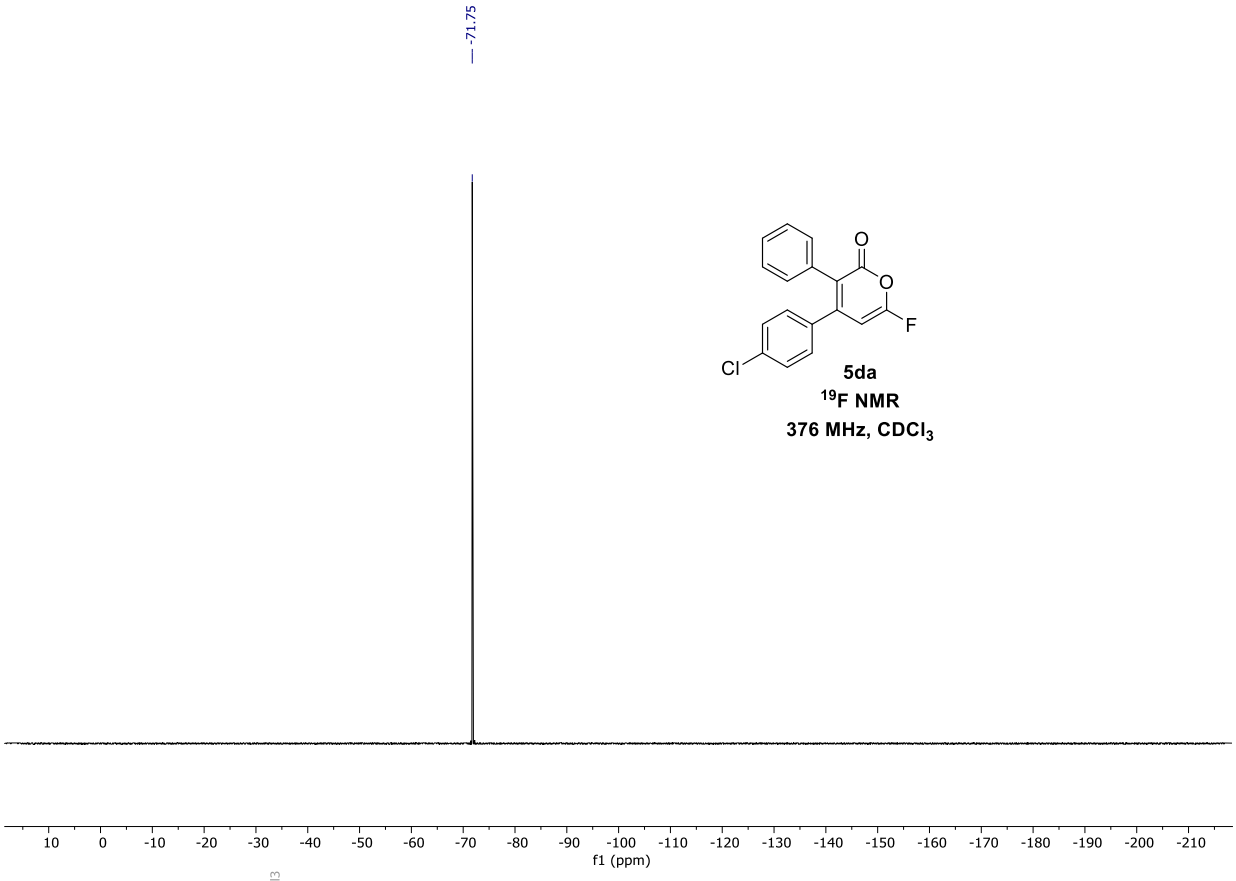
86.15
86.01
O
O
F
F
5ca
13C NMR
101 MHz, CDCl3
f1 (ppm)


-71.77
-113.16
1.00
0.99
O
O
F
F
5ca
19F NMR
376 MHz, CDCl3
f1 (ppm)


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

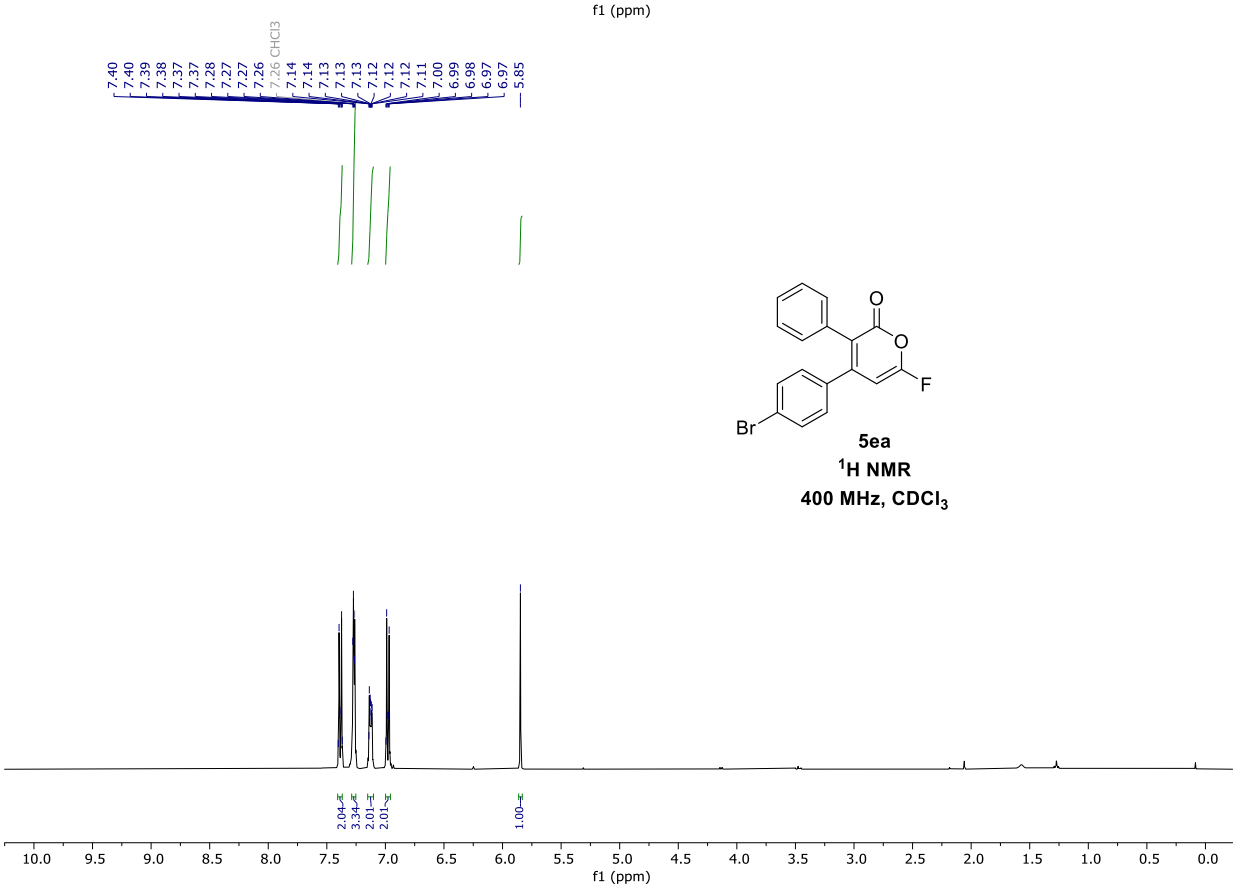

5da
^{13}C NMR
101 MHz, $CDCl_3$
f1 (ppm)



5da

^{19}F NMR

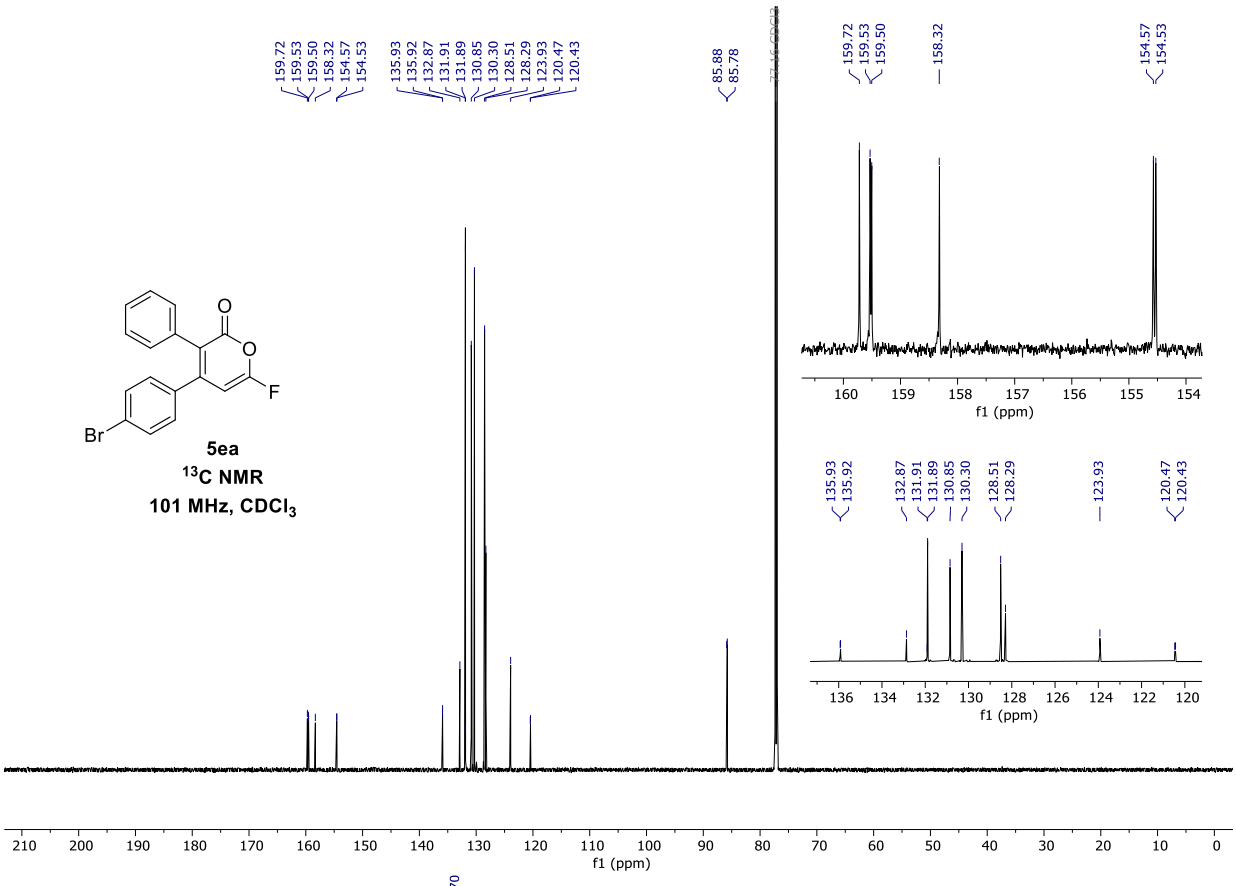
376 MHz, $CDCl_3$

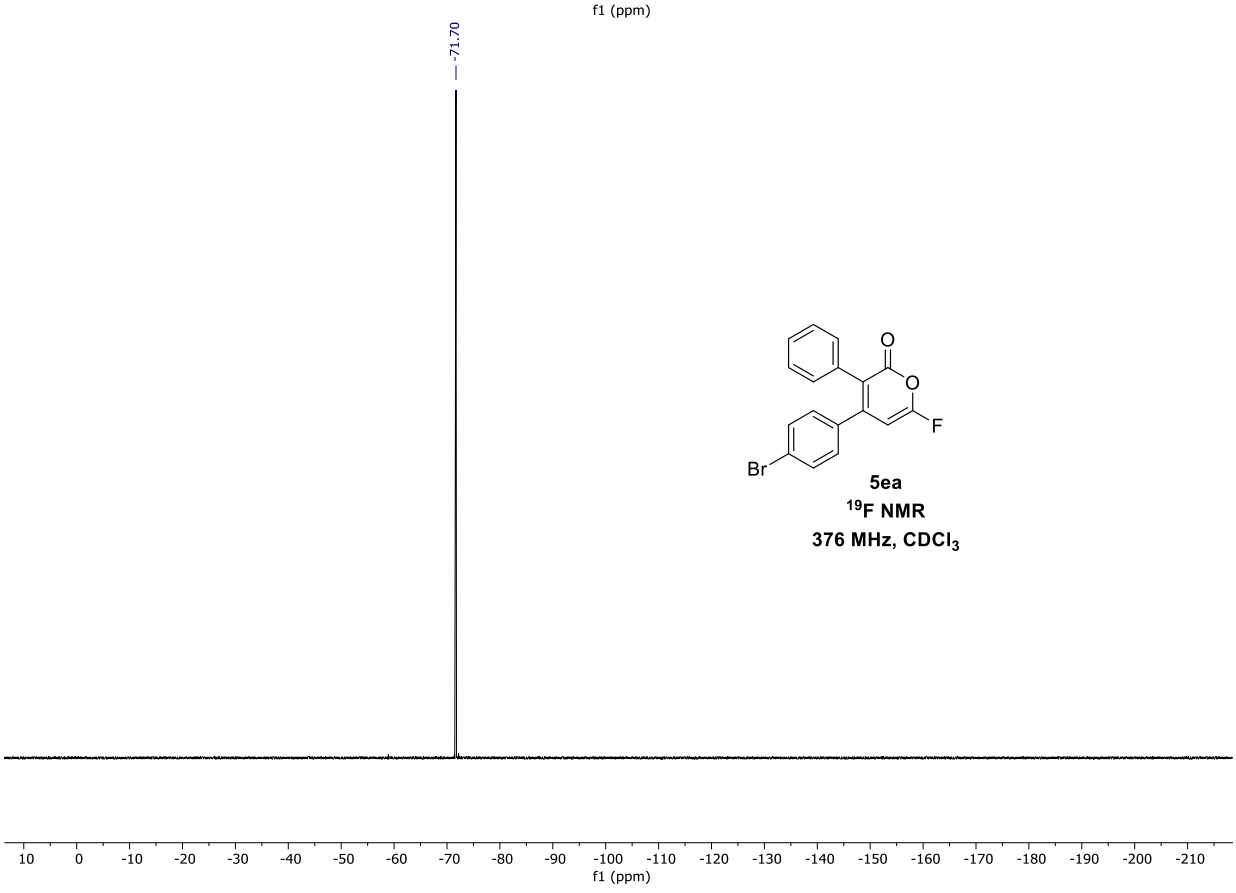


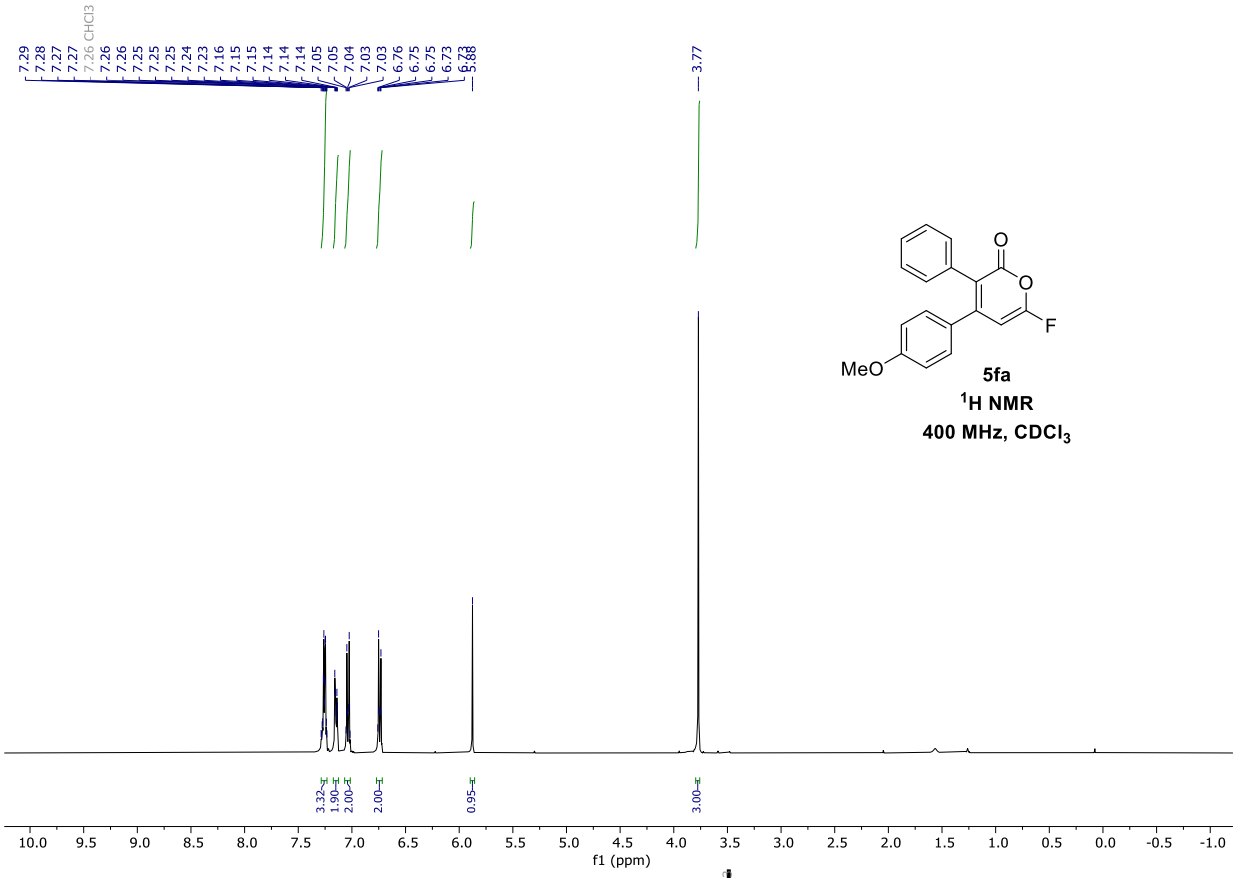
5ea

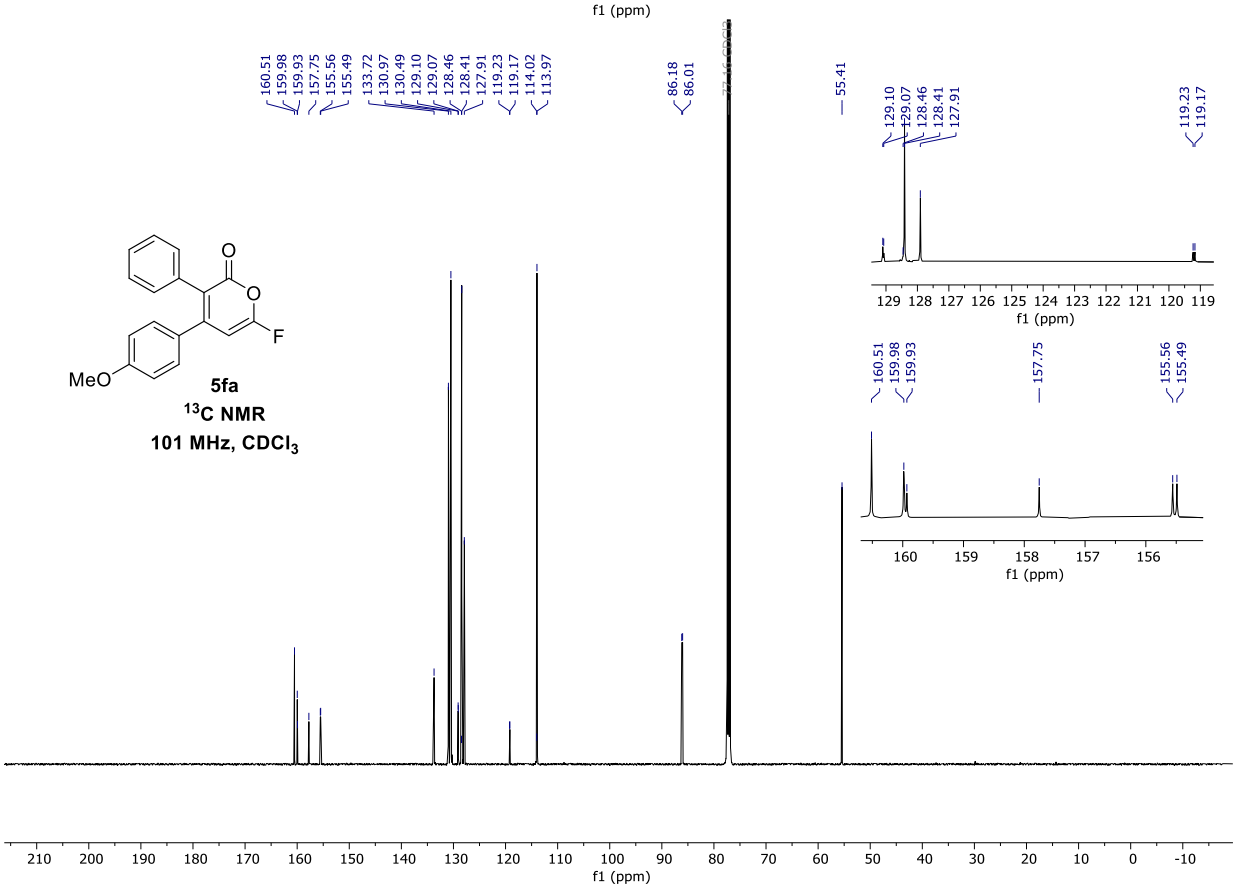
^{1}H NMR

400 MHz, $CDCl_3$


159.72
159.53
159.50
158.32
154.57
154.53
135.93
135.92
132.87
131.91
131.89
130.85
130.30
128.51
128.29
123.93
120.47
120.43
85.88
85.78
77.16 CDCl3
O
O
F
Br
5ea
13C NMR
101 MHz, CDCl3
f1 (ppm)


-71.70
O
O
F
Br
5ea
19F NMR
376 MHz, CDCl3
f1 (ppm)


7.29
7.28
7.27
7.27
7.26 CHCl3
7.26
7.26
7.25
7.25
7.25
7.24
7.23
7.16
7.15
7.15
7.14
7.14
7.14
7.05
7.05
7.04
7.03
7.03
6.76
6.75
6.75
6.73
3.77
3.32
1.90
2.00
2.00
0.95
3.00
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)
O
O
F
MeO
5fa
1H NMR
400 MHz, CDCl3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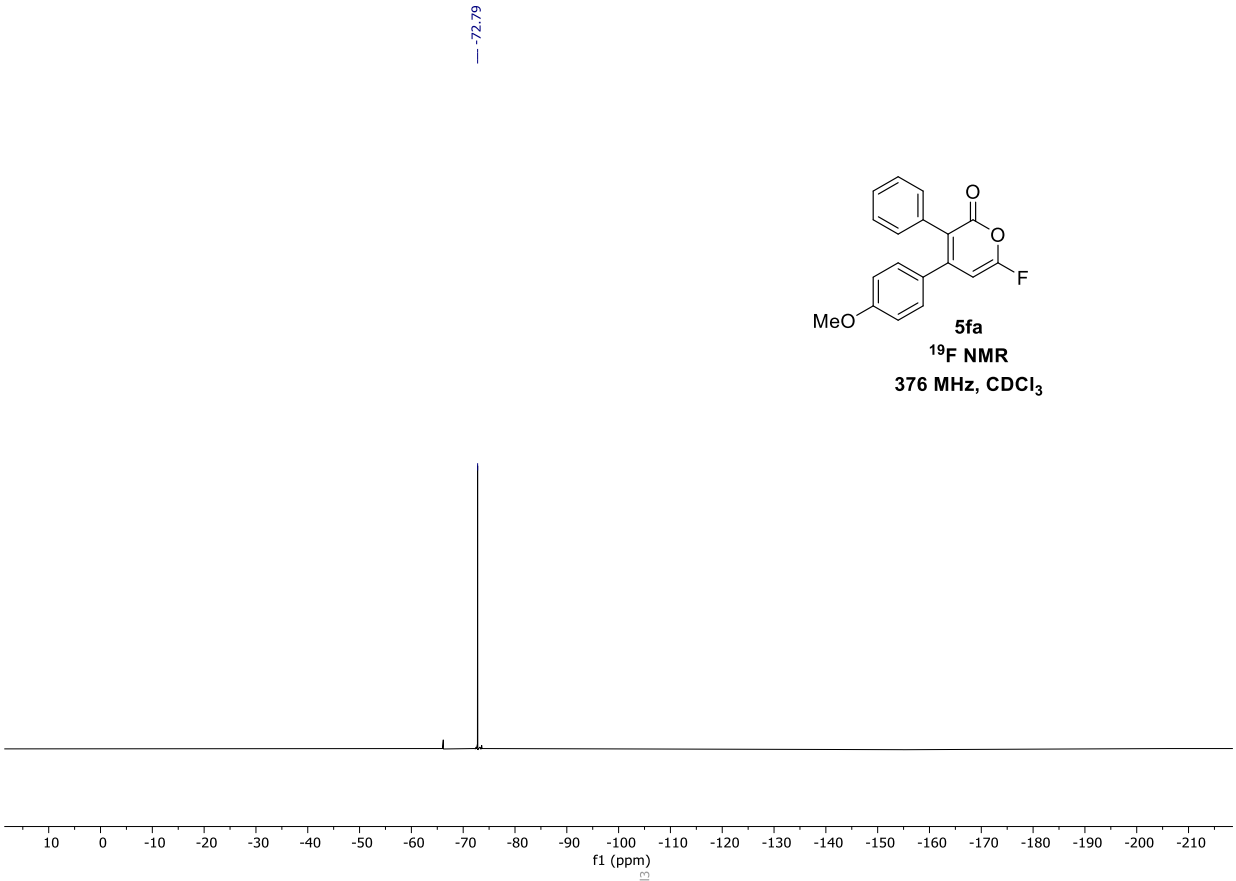
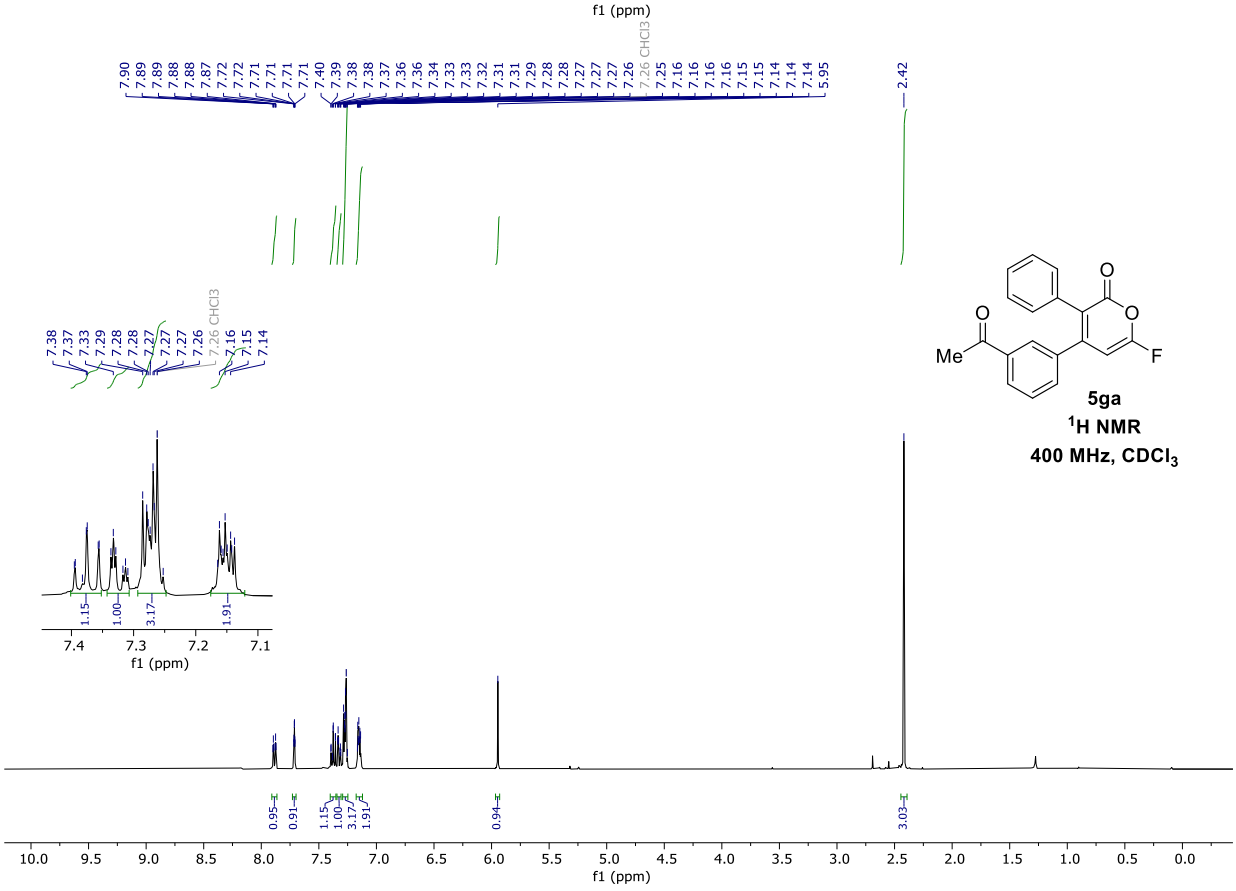
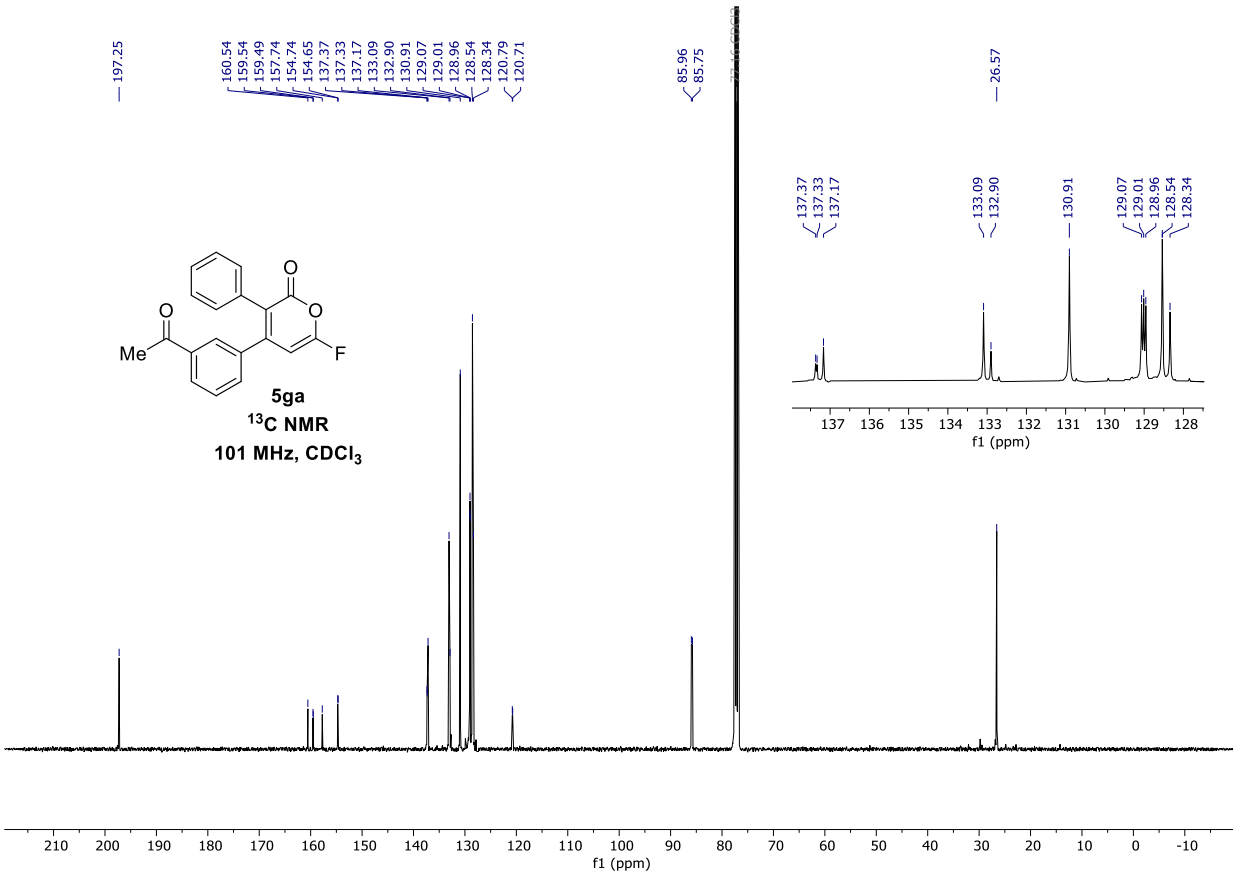
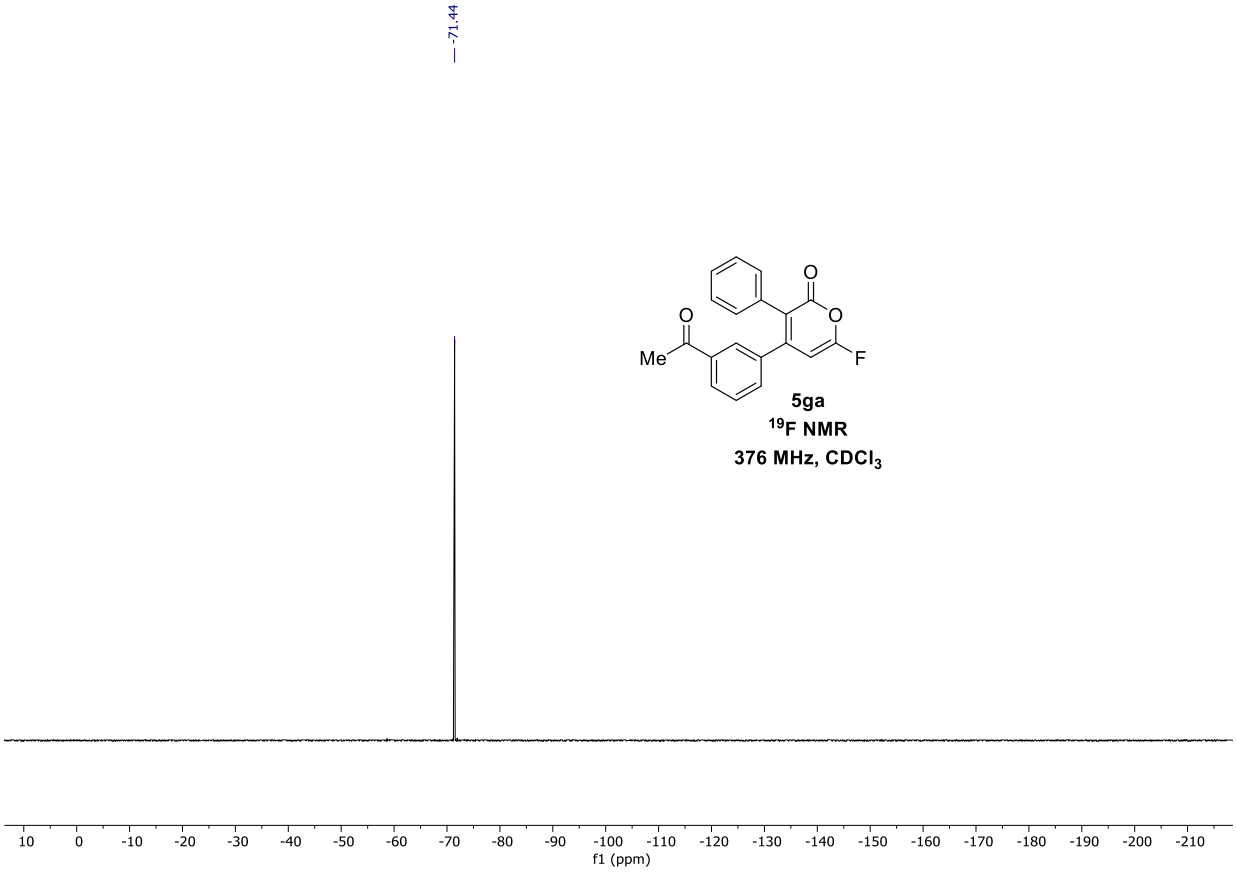
159.93
157.75
155.56
155.49
133.72
130.97
130.49
129.10
129.07
128.46
128.41
127.91
119.23
119.17
114.02
113.97
86.18
86.01
77.16 CDCl3
55.41
129.10
129.07
128.46
128.41
127.91
119.23
119.17
129 128 127 126 125 124 123 122 121 120 119
f1 (ppm)
160.51
159.98
159.93
157.75
155.56
155.49
160 159 158 157 156
f1 (ppm)
O
O
F
MeO
5fa
13C NMR
101 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)


-72.79
MeO
O
O
F
5fa
19F NMR
376 MHz, CDCl3
f1 (ppm)


7.26 CHCl3
2.42
Me
O
O
O
F
5ga
1H NMR
400 MHz, CDCl3
f1 (ppm)


197.25
160.54
159.54
159.49
157.74
154.74
154.65
137.37
137.33
137.17
133.09
132.90
130.91
129.07
129.01
128.96
128.54
128.34
120.79
120.71
85.96
85.75
26.57
137.37
137.33
137.17
133.09
132.90
130.91
129.07
129.01
128.96
128.54
128.34
O
O
Me
O
F
5ga
13C NMR
101 MHz, CDCl3
f1 (ppm)
f1 (ppm)


-71.44
O
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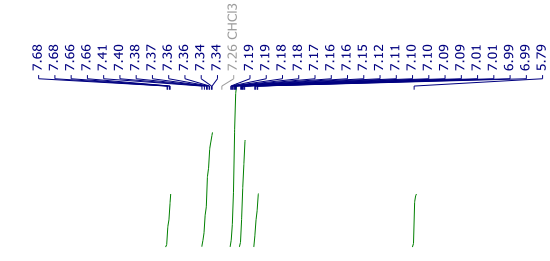
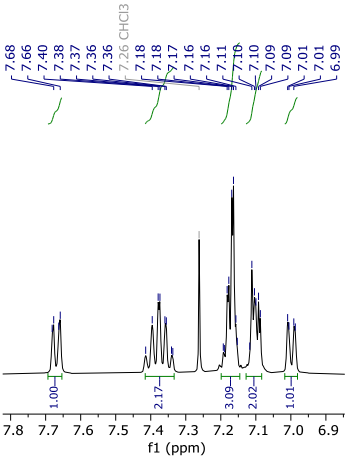
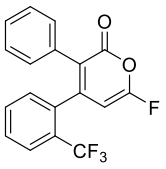
Me
O
F
5ga
19F NMR
376 MHz, CDCl3
f1 (ppm)



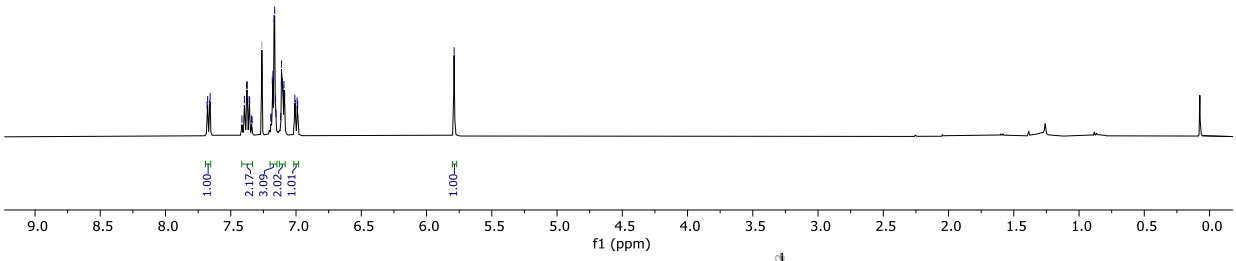


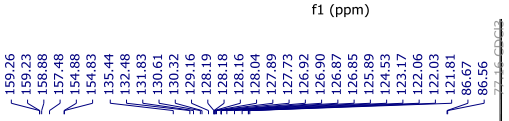


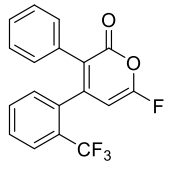
5ha

^{1}H NMR

400 MHz, $CDCl_3$



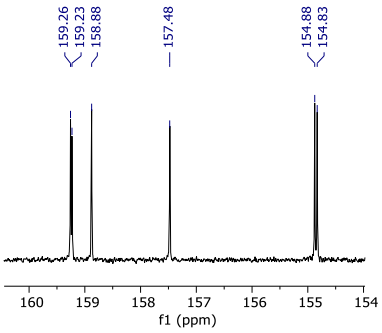


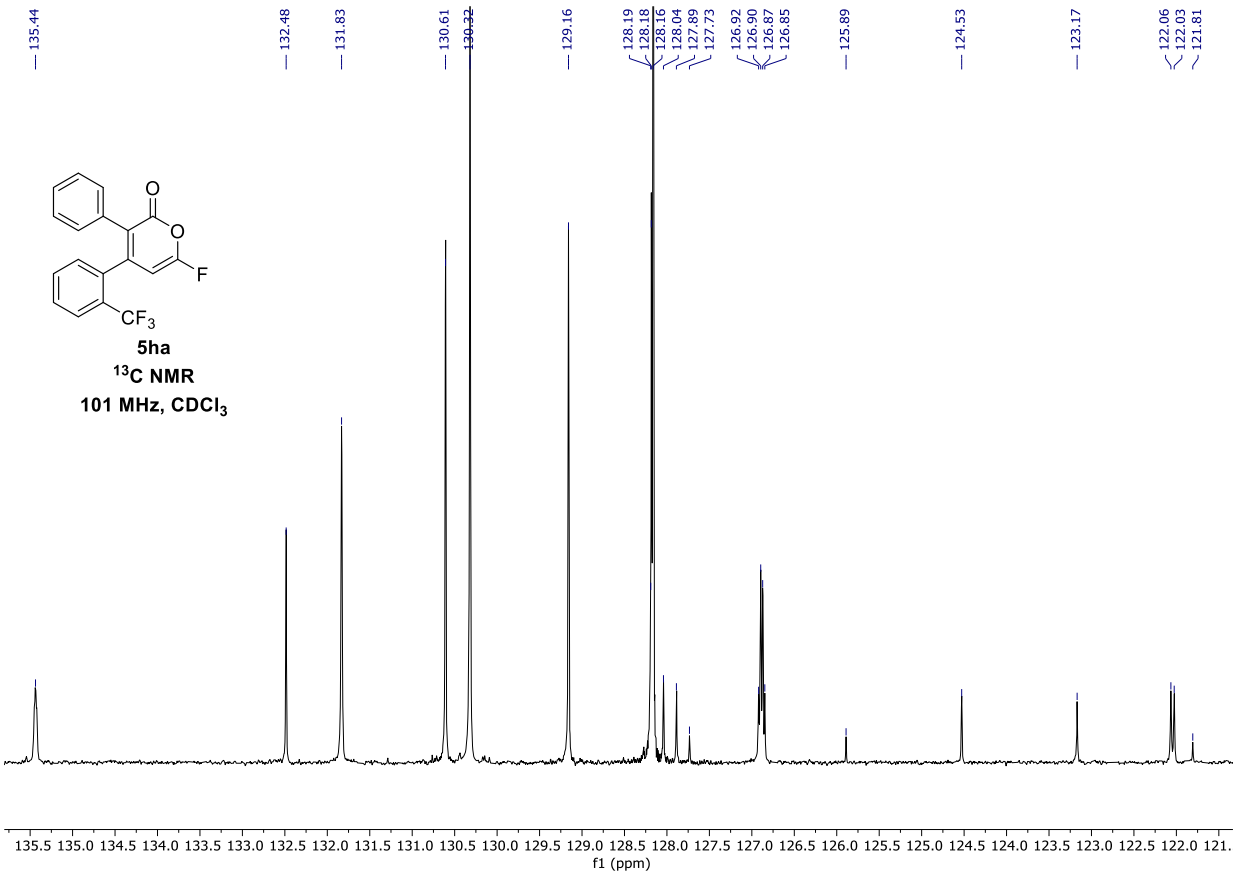


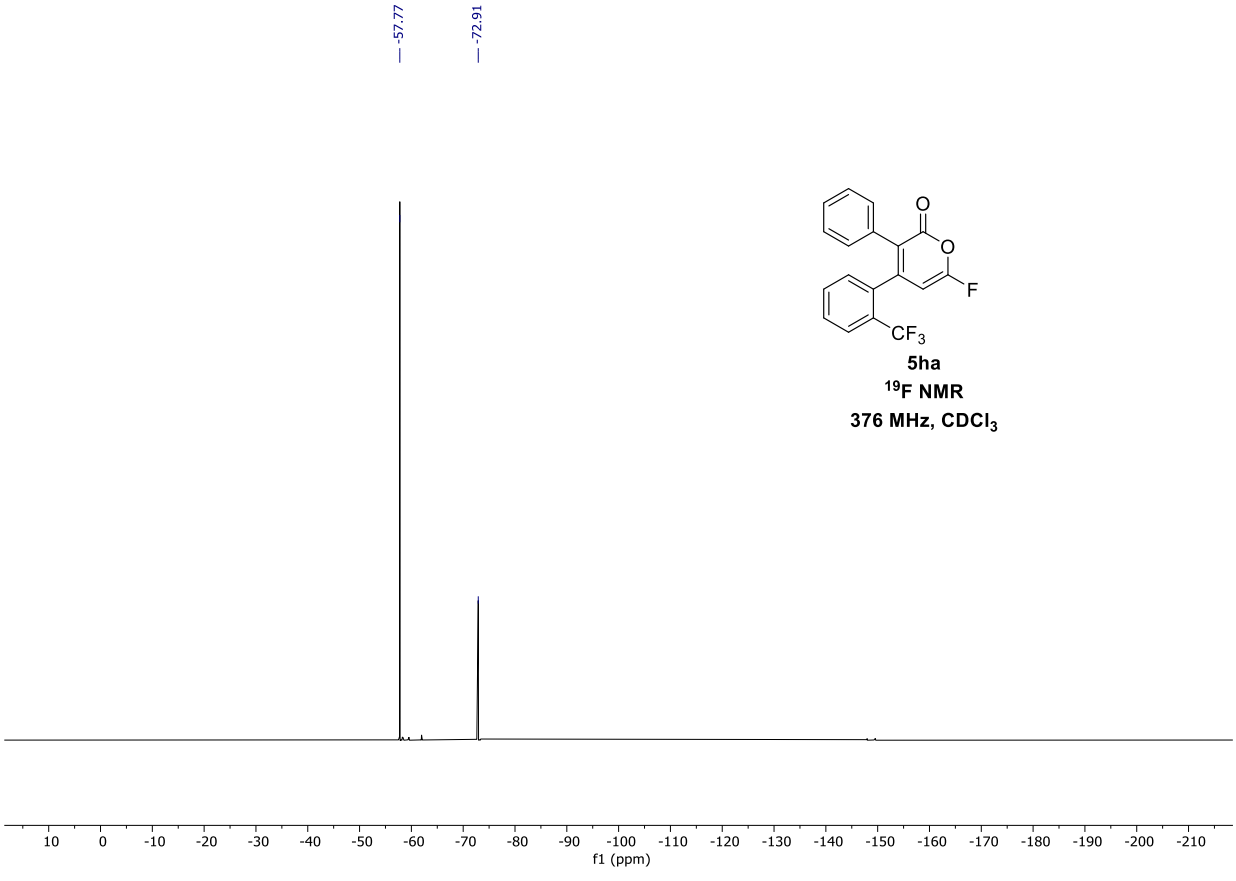
5ha

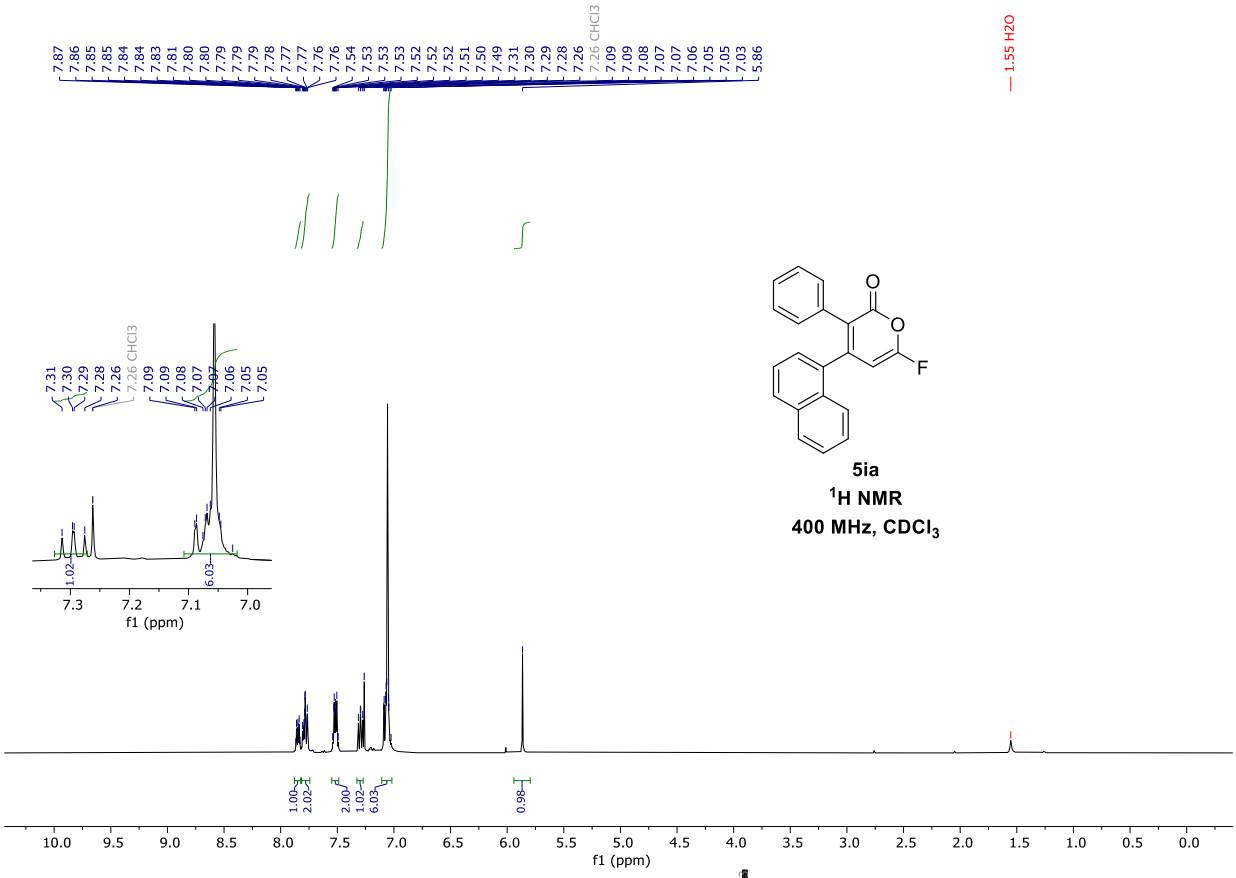
^{13}C NMR

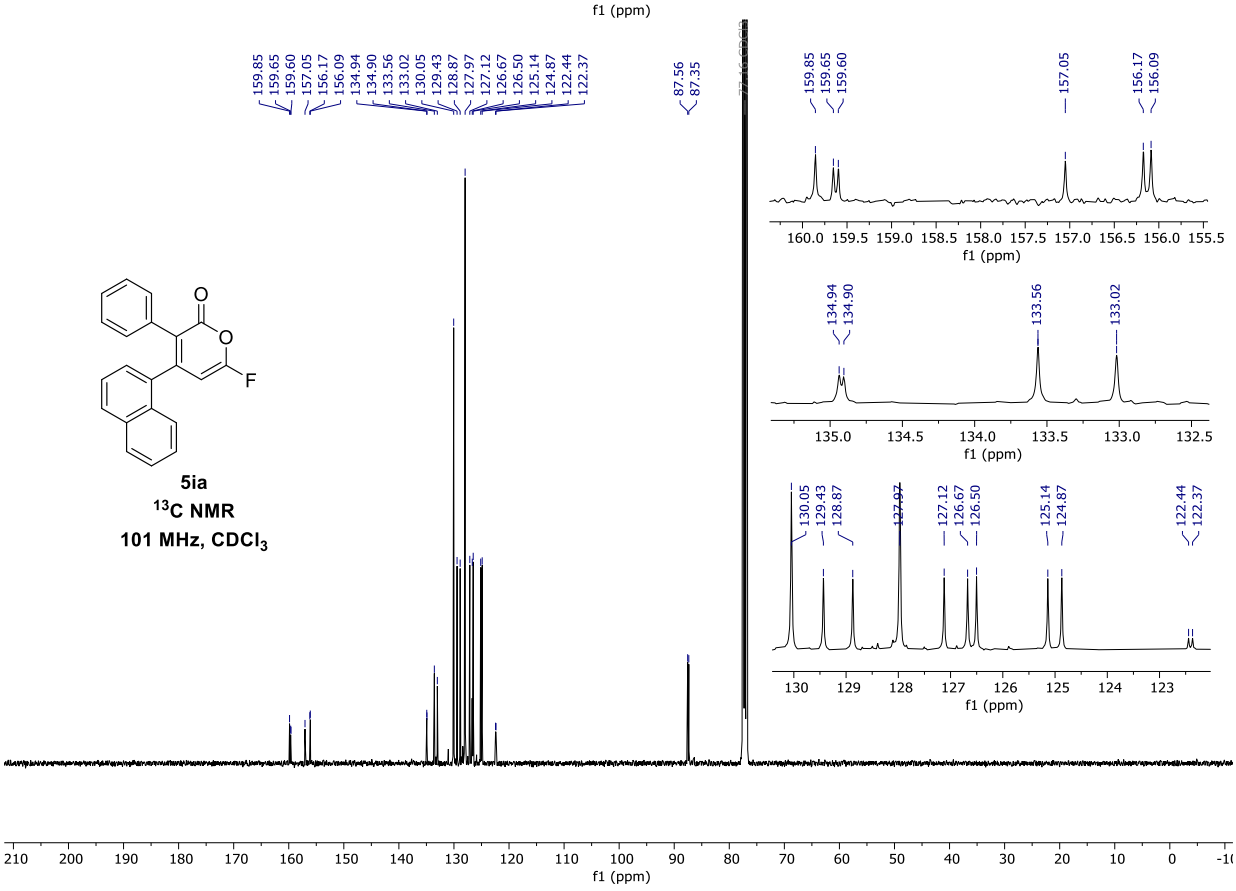
101 MHz, $CDCl_3$

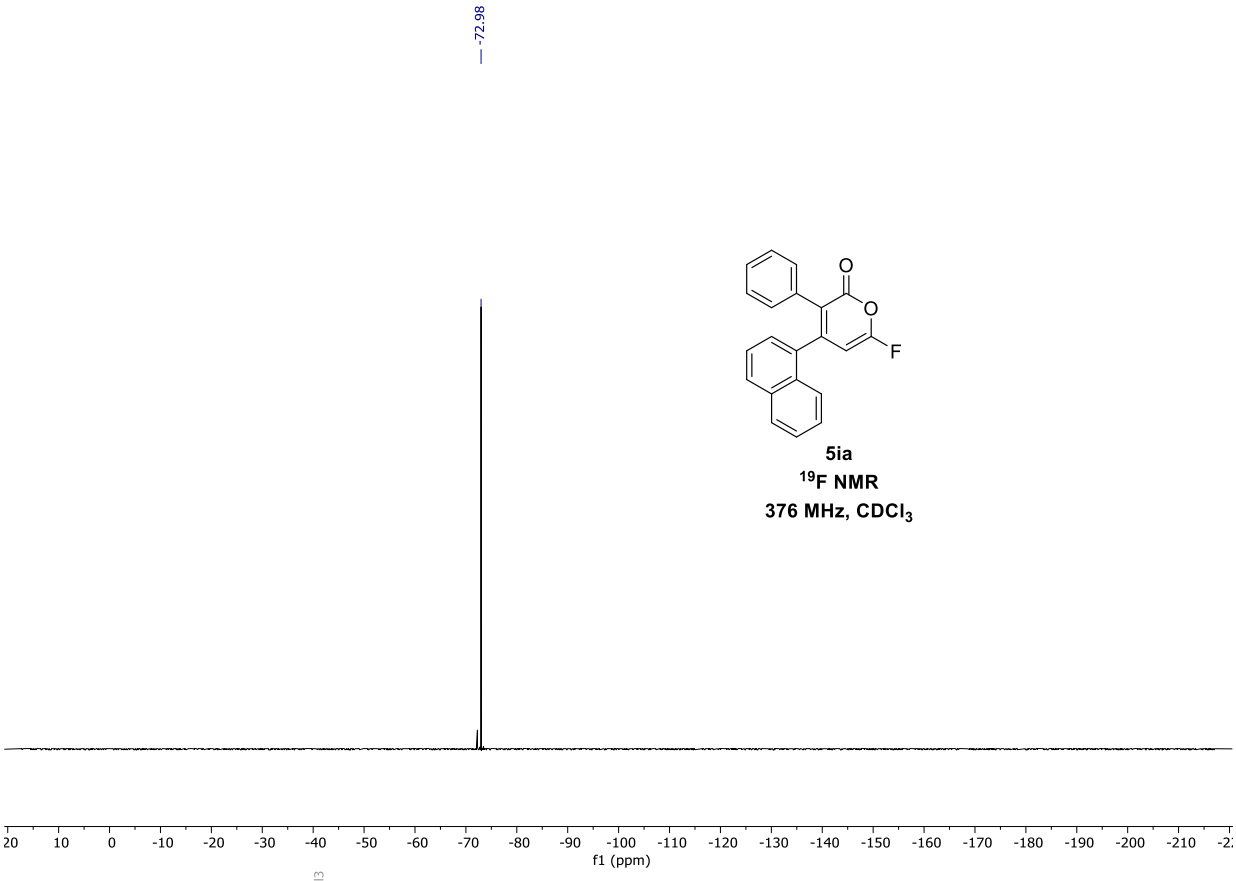



135.44
132.48
131.83
130.61
130.32
129.16
128.19
128.18
128.16
128.04
127.89
127.73
126.92
126.90
126.87
126.85
125.89
124.53
123.17
122.06
122.03
121.81
O
O
F
CF3
5ha
13C NMR
101 MHz, CDCl3
135.5 135.0 134.5 134.0 133.5 133.0 132.5 132.0 131.5 131.0 130.5 130.0 129.5 129.0 128.5 128.0 127.5 127.0 126.5 126.0 125.5 125.0 124.5 124.0 123.5 123.0 122.5 122.0 121.
f1 (ppm)

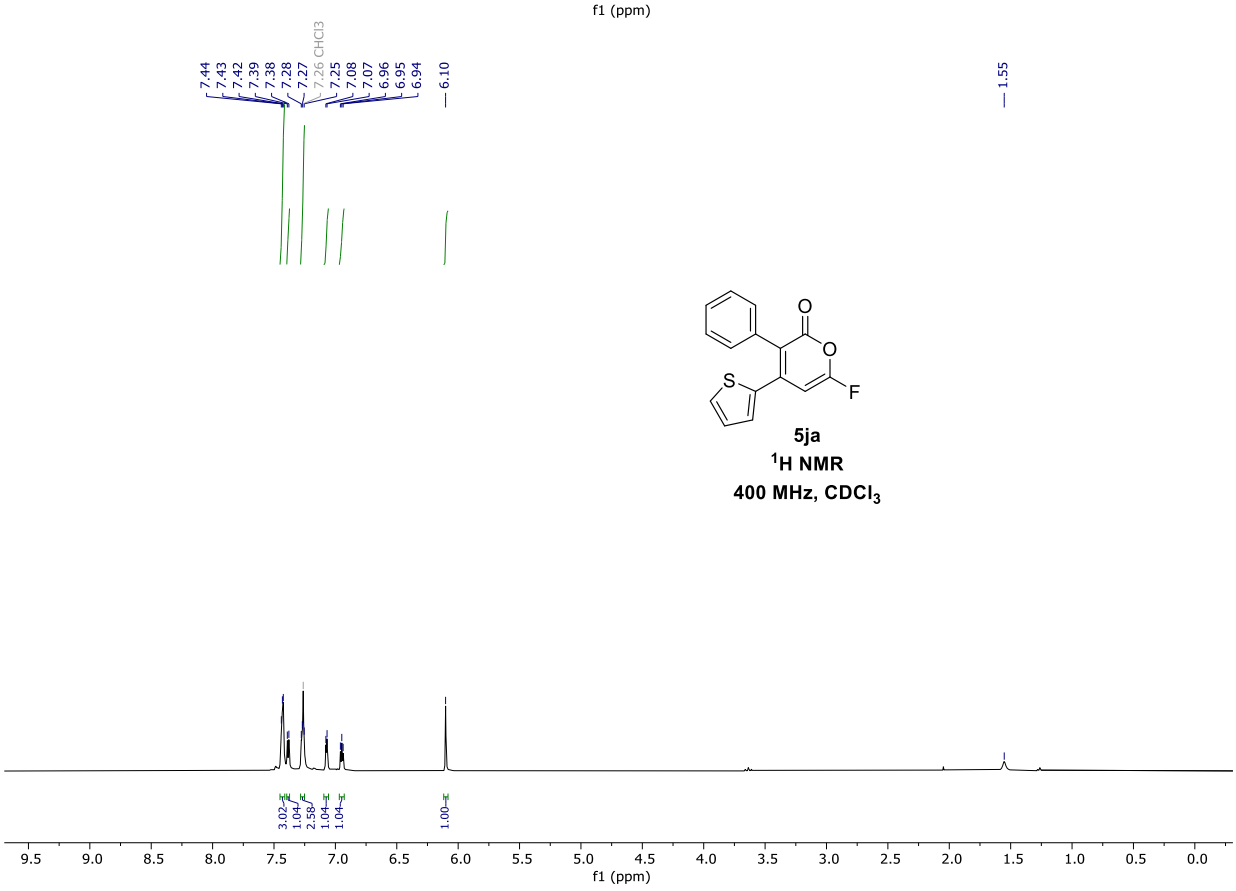

-57.77
-72.91
O
O
F
CF3
5ha
19F NMR
376 MHz, CDCl3
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


7.87 7.86 7.85 7.85 7.84 7.84 7.83 7.81 7.80 7.80 7.79 7.79 7.79 7.78 7.77 7.77 7.76 7.76 7.54 7.53 7.53 7.53 7.52 7.52 7.51 7.50 7.49 7.31 7.30 7.29 7.28 7.26 7.26 CHCl3 7.09 7.09 7.08 7.07 7.07 7.06 7.05 7.05 7.03 5.86
1.55 H2O
7.31 7.30 7.29 7.28 7.26 7.26 CHCl3 7.09 7.09 7.08 7.07 7.07 7.06 7.05 7.05
1.02
6.03
7.3 7.2 7.1 7.0
f1 (ppm)
O
O
F
5ia
1H NMR
400 MHz, CDCl3
1.00 2.02 2.00 1.02 6.03 0.98
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)

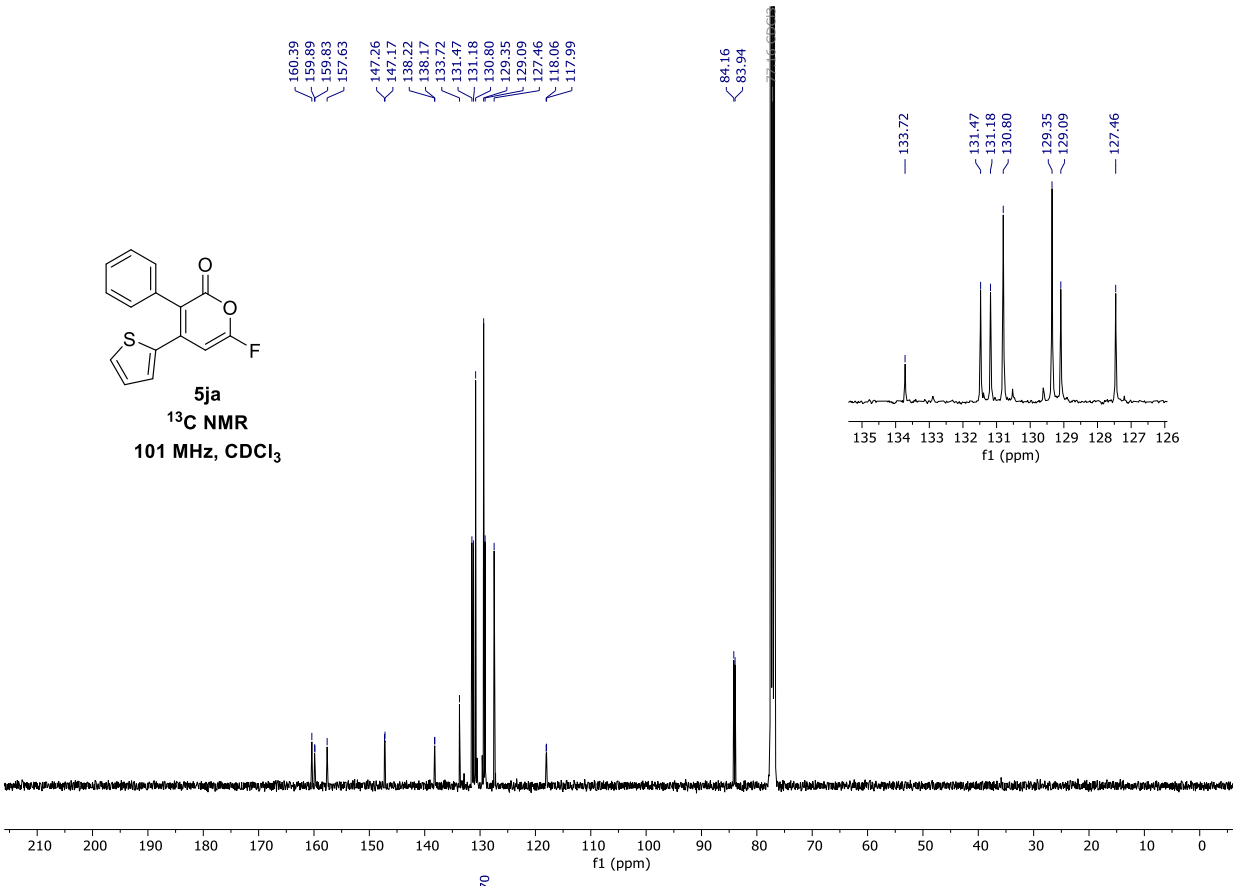

159.85 159.65 159.60 157.05 156.17 156.09 134.94 134.90 133.56 133.02 130.05 129.43 128.87 127.97 127.12 126.67 126.50 125.14 124.87 122.44 122.37
87.56 87.35
159.85 159.65 159.60
157.05
156.17 156.09
160.0 159.5 159.0 158.5 158.0 157.5 157.0 156.5 156.0 155.5
f1 (ppm)
134.94 134.90
133.56
133.02
135.0 134.5 134.0 133.5 133.0 132.5
f1 (ppm)
130.05 129.43 128.87 127.97 127.12 126.67 126.50 125.14 124.87 122.44 122.37
130 129 128 127 126 125 124 123
f1 (ppm)
O
O
F
5ia
13C NMR
101 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)

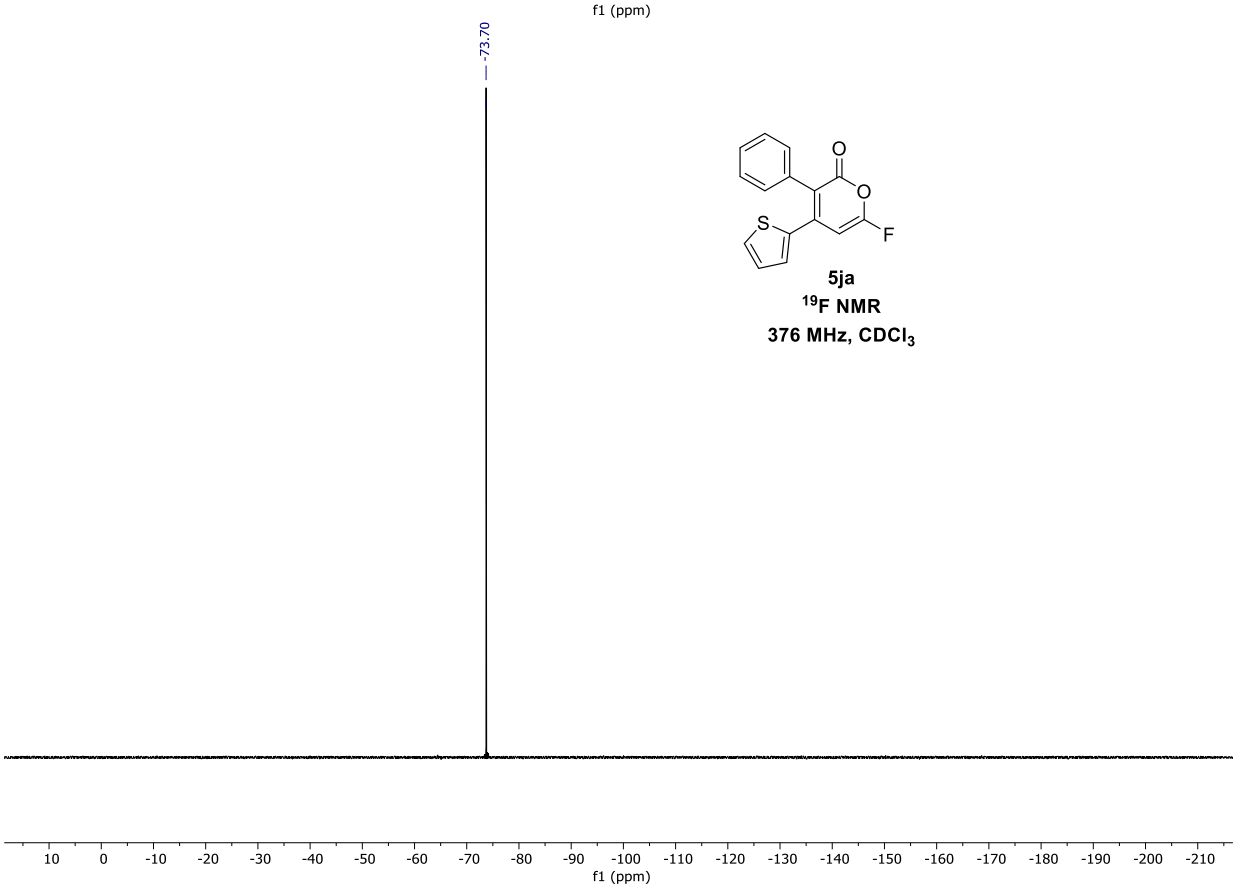


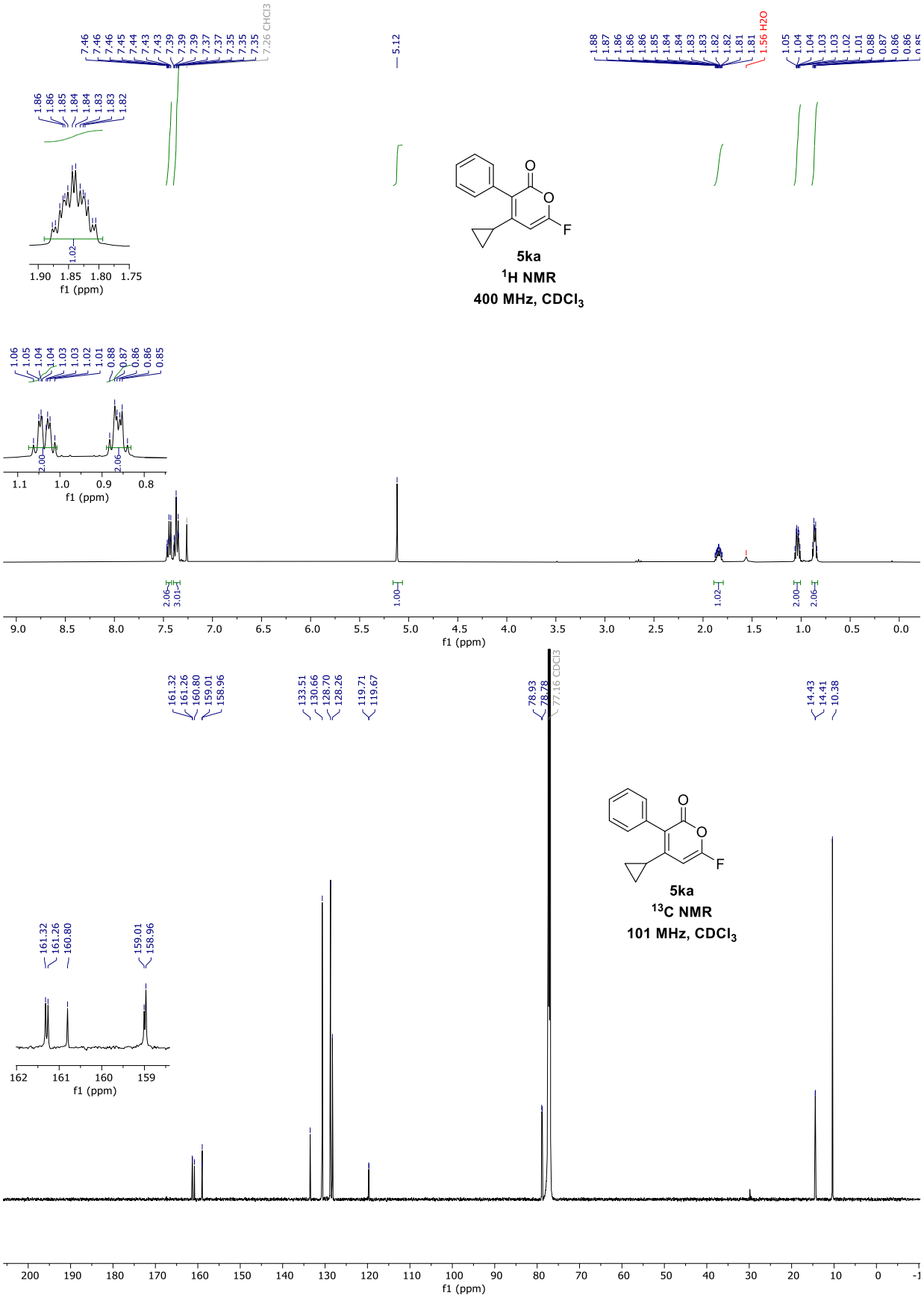
5ia
^{19}F NMR
376 MHz, $CDCl_3$

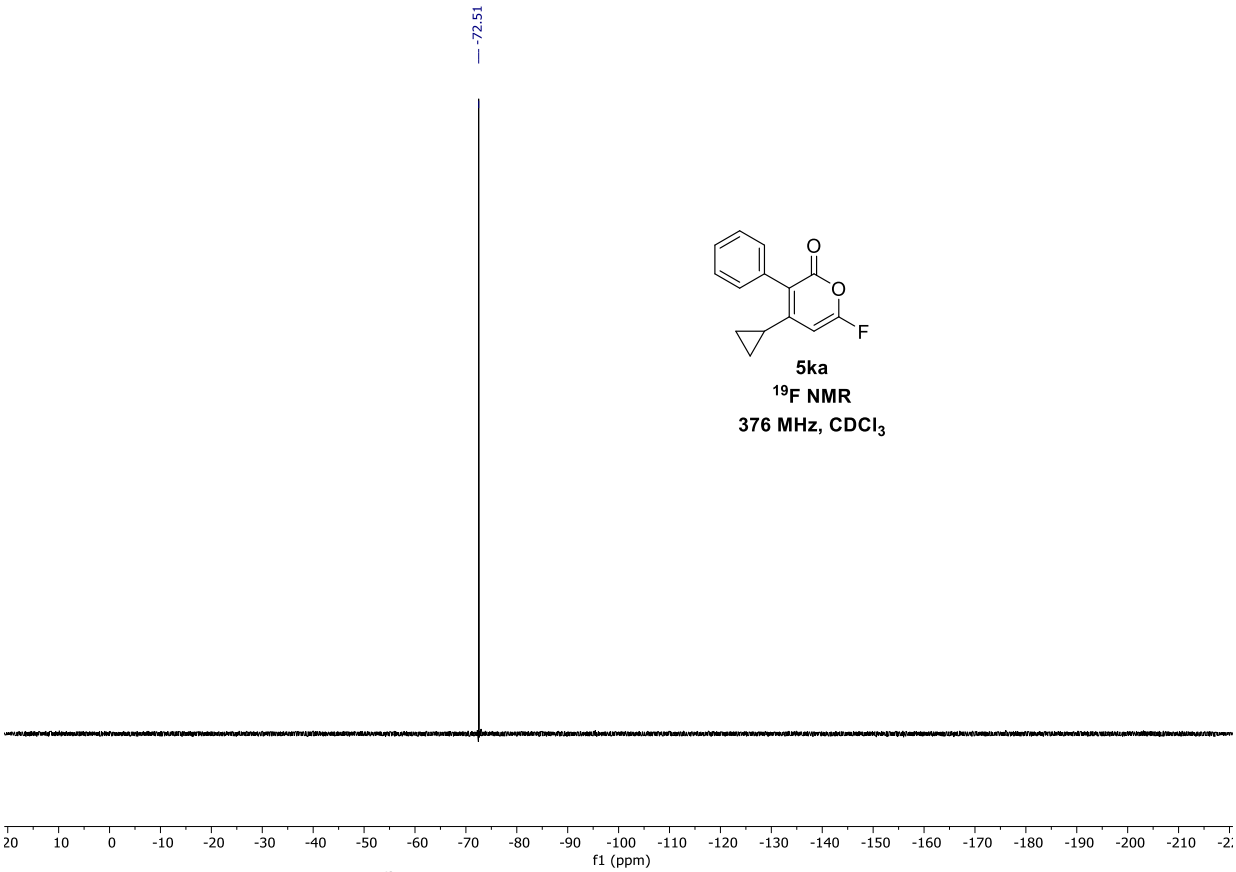


5ja
^{1}H NMR
400 MHz, $CDCl_3$

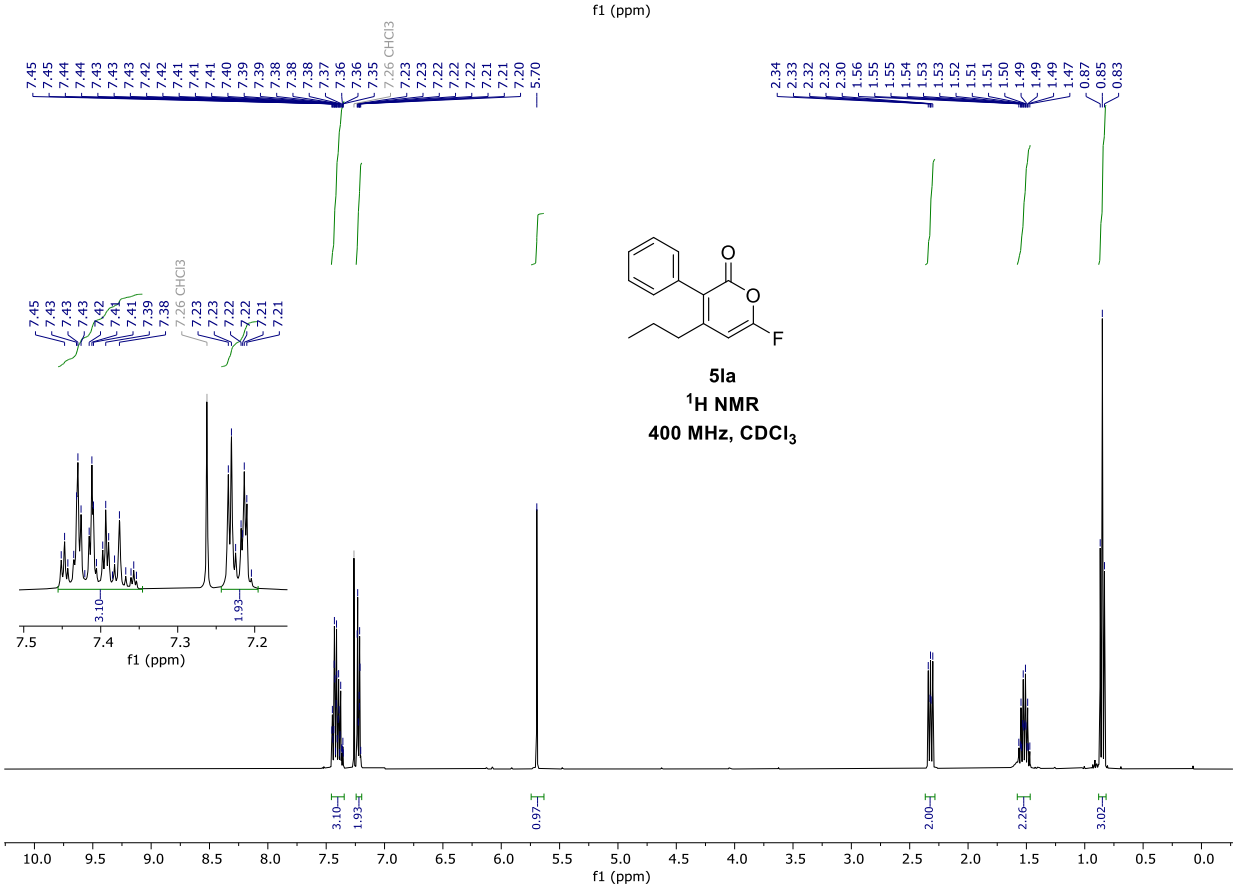

160.39
159.89
159.83
157.63
147.26
147.17
138.22
138.17
133.72
131.47
131.18
130.80
129.35
129.09
127.46
118.06
117.99
84.16
83.94
133.72
131.47
131.18
130.80
129.35
129.09
127.46
O
O
S
F
5ja
13C NMR
101 MHz, CDCl3
f1 (ppm)
f1 (ppm)


-73.70
O
O
S
F
5ja
19F NMR
376 MHz, CDCl3
f1 (ppm)

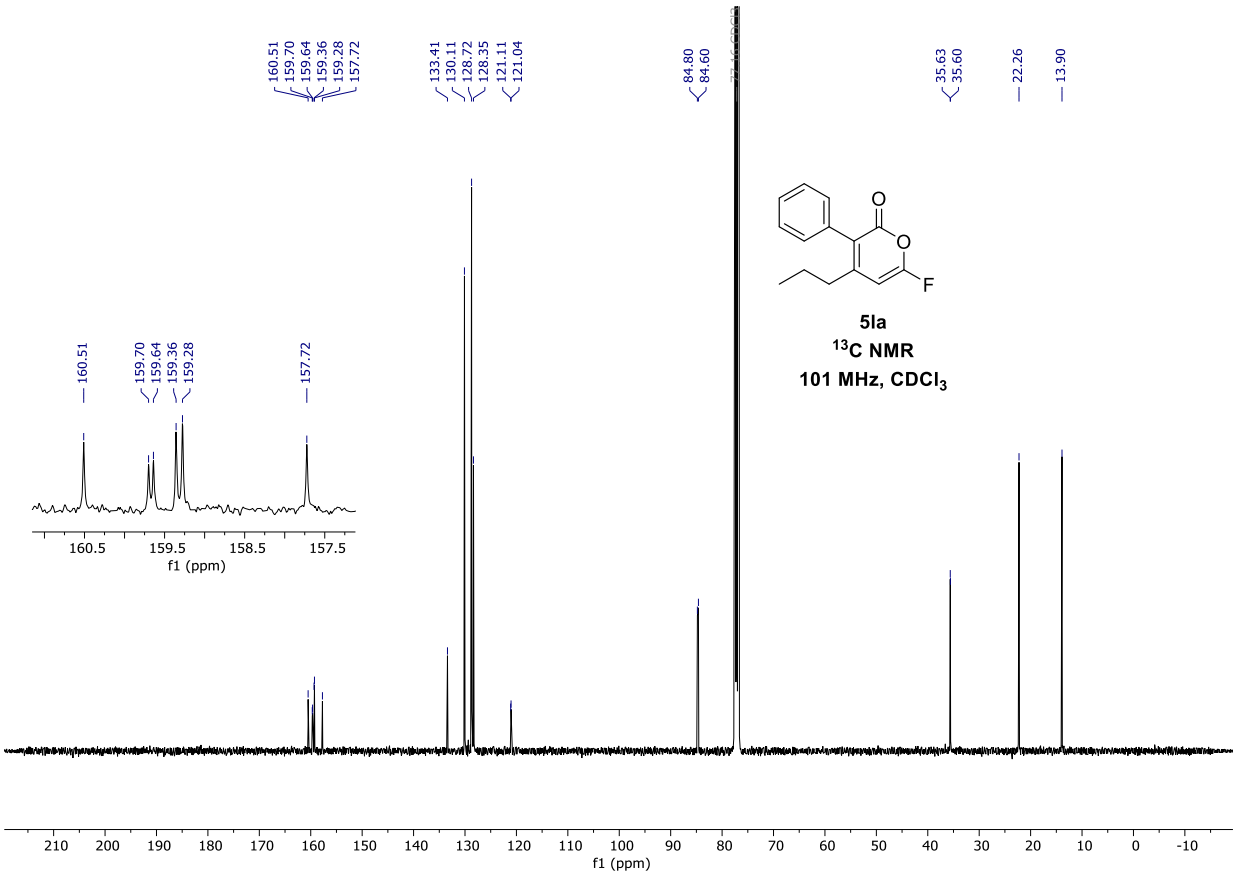

5ka
1H NMR
400 MHz, CDCl3
5ka
13C NMR
101 MHz, CDCl3
f1 (ppm)



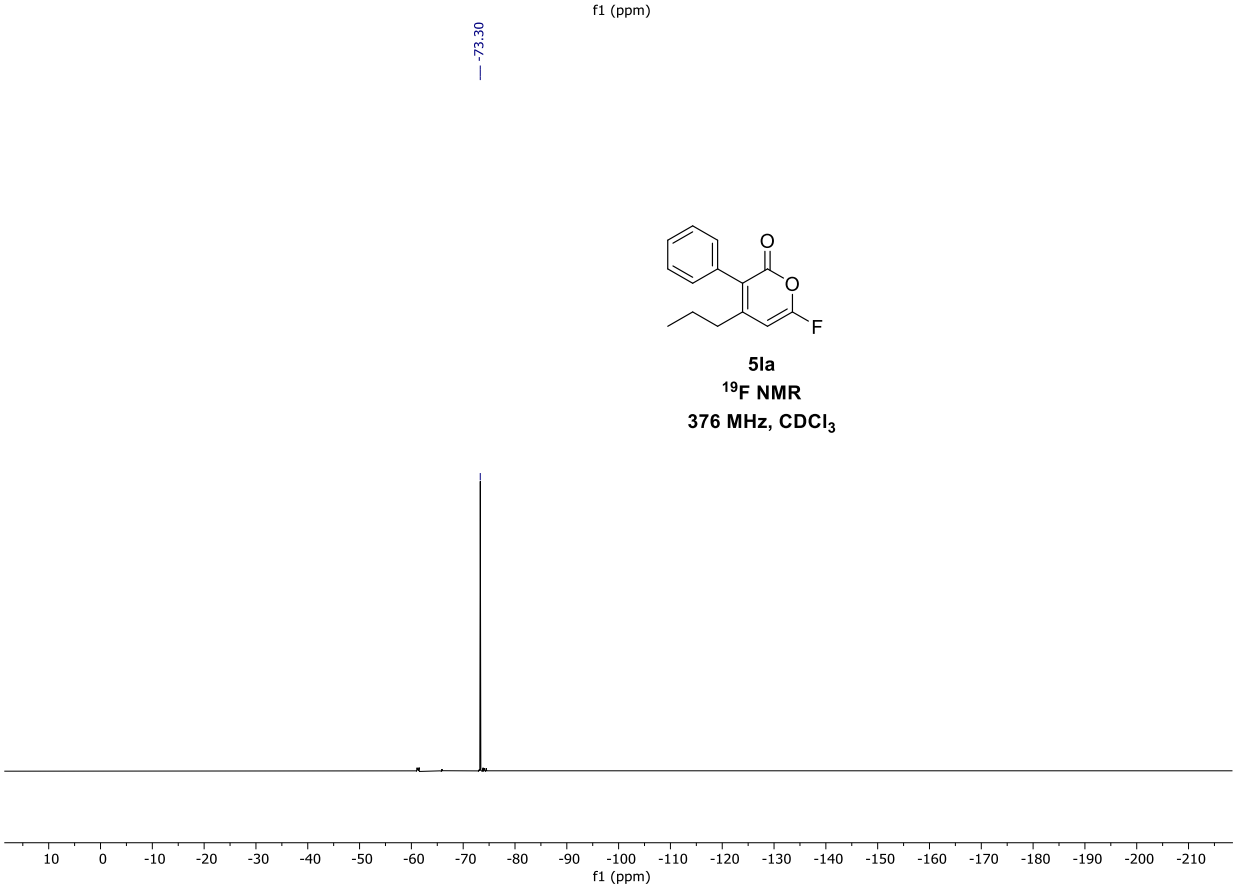
5ka
^{19}F NMR
376 MHz, $CDCl_3$



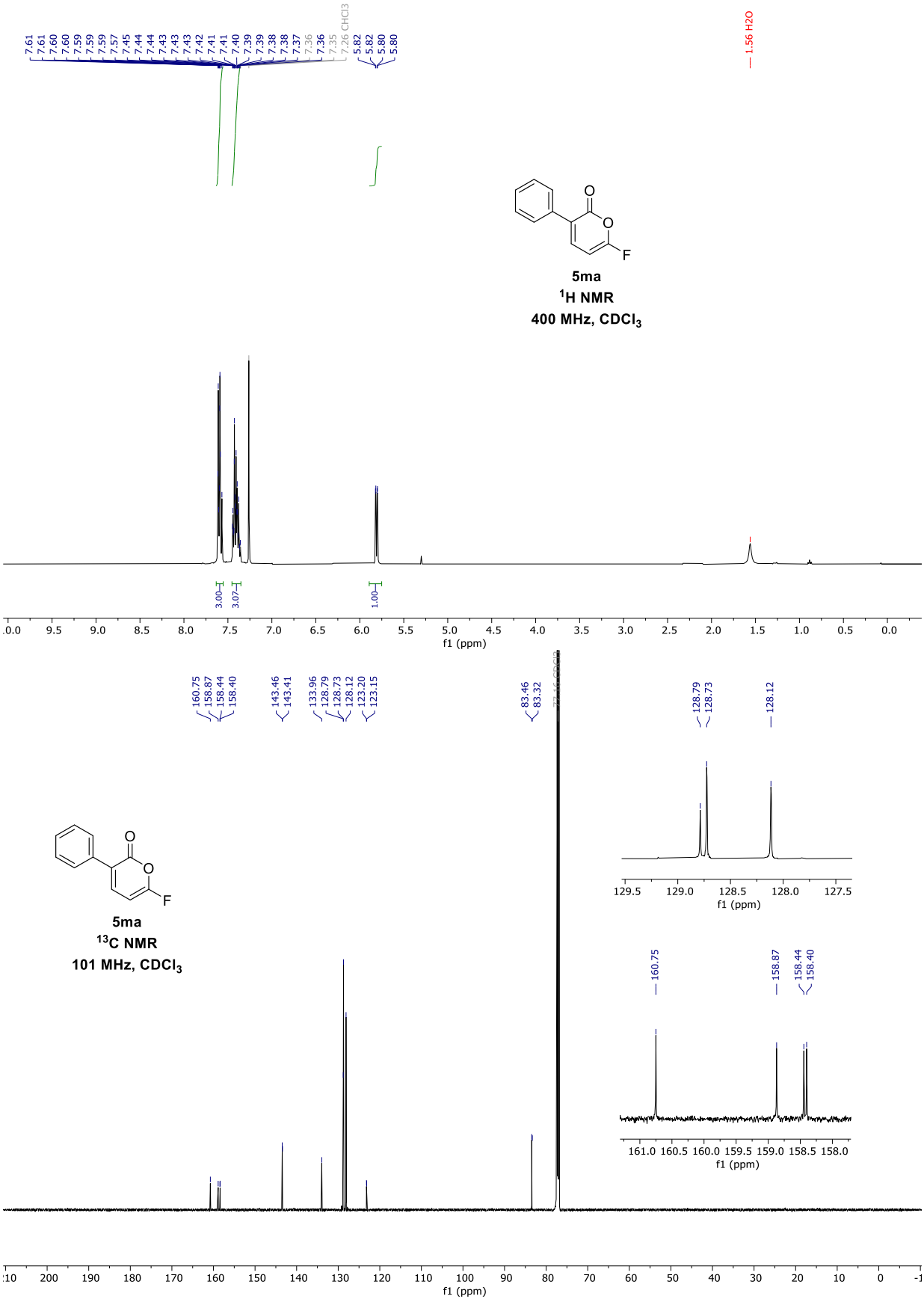
5la
^{1}H NMR
400 MHz, $CDCl_3$

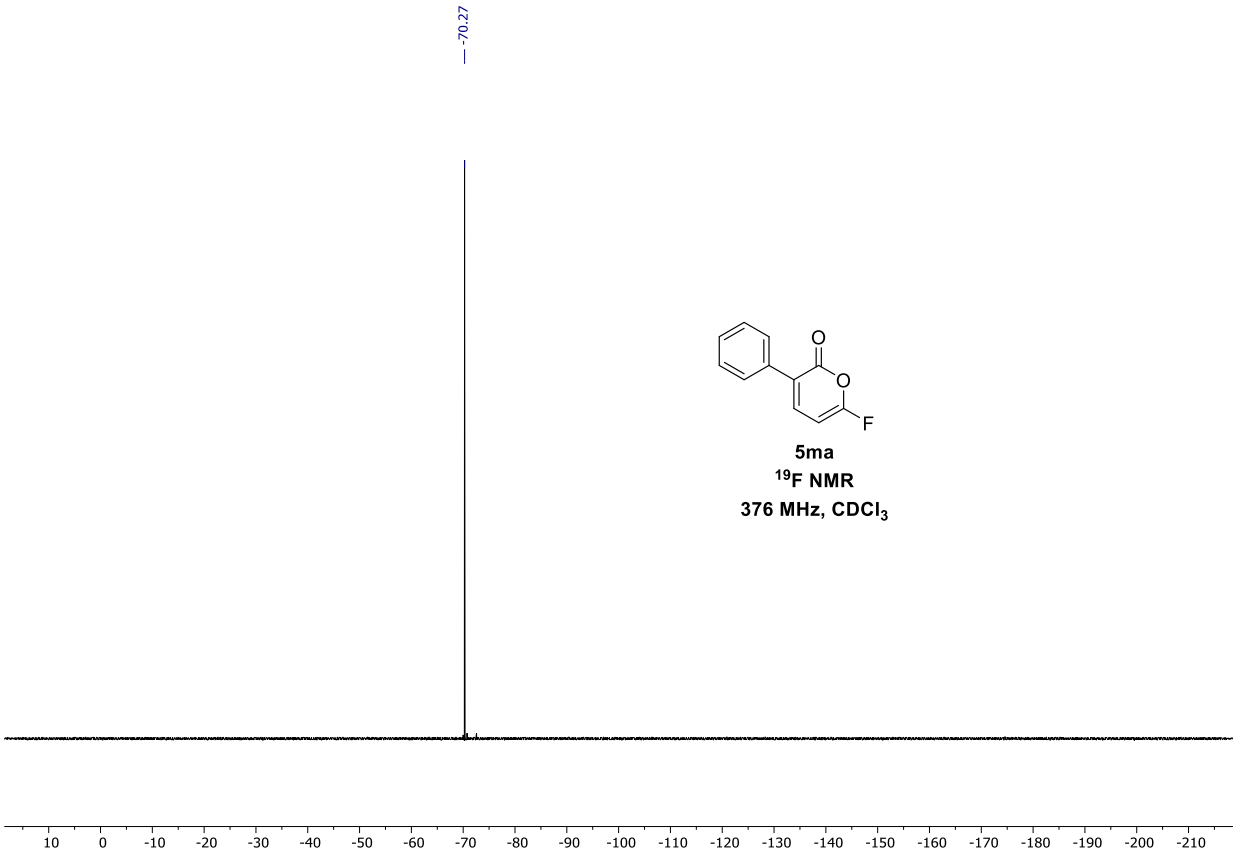


5la
^{13}C NMR
101 MHz, $CDCl_3$

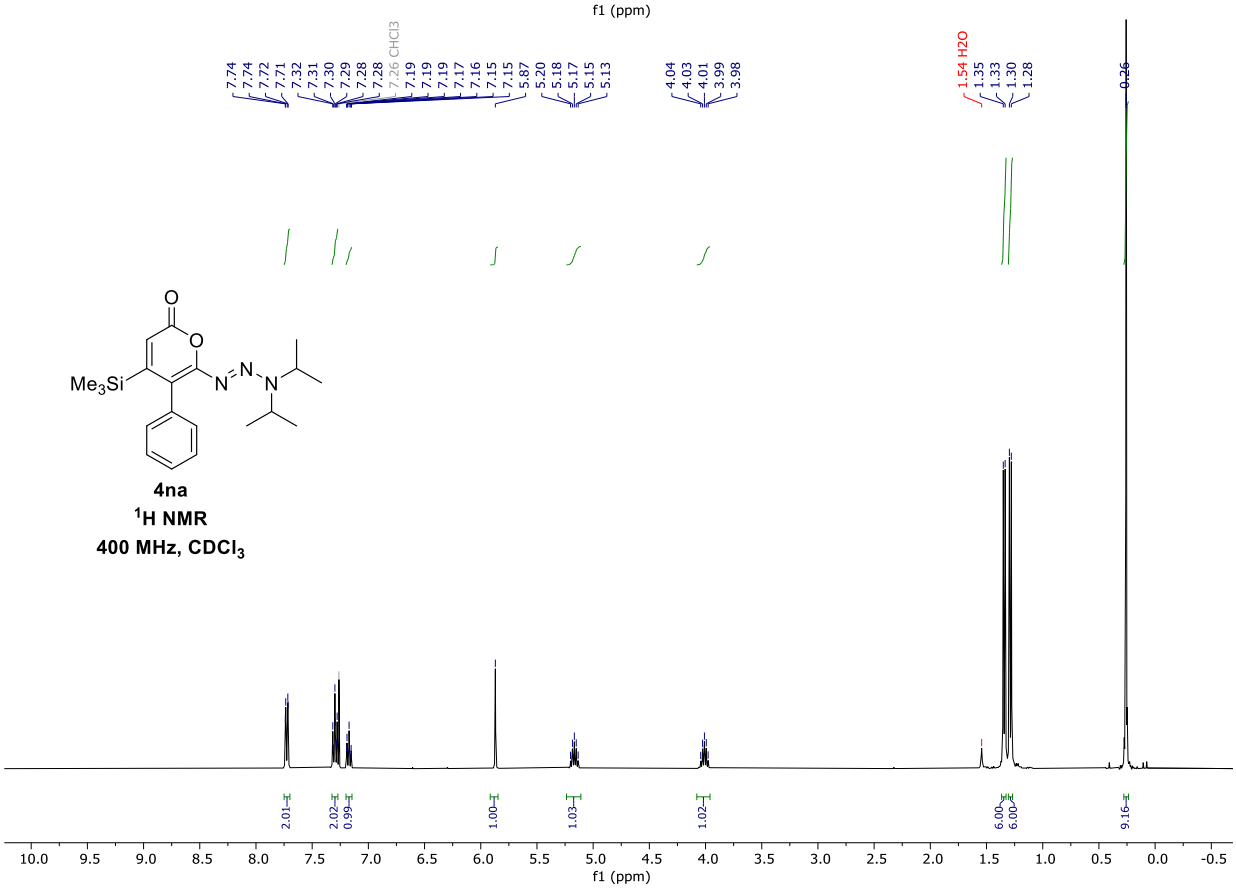


5la
^{19}F NMR
376 MHz, $CDCl_3$

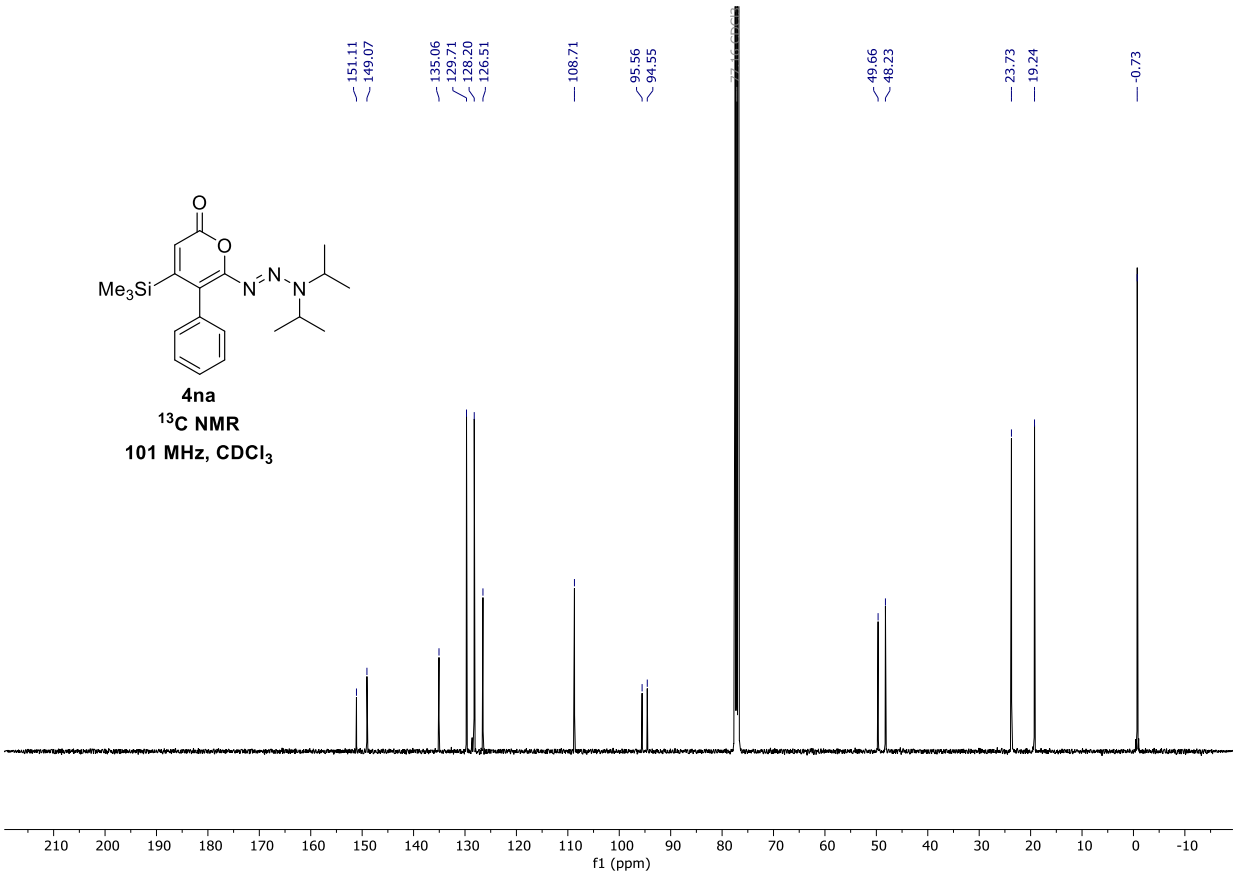

7.61 7.61 7.60 7.60 7.59 7.59 7.59 7.57 7.45 7.44 7.44 7.43 7.43 7.43 7.42 7.41 7.41 7.40 7.39 7.39 7.38 7.38 7.37 7.36 7.36 7.35 7.26 CHCl3
5.82 5.82 5.80 5.80
1.56 H2O
O
O
F
5ma
1H NMR
400 MHz, CDCl3
3.00
3.07
1.00
f1 (ppm)
160.75 158.87 158.44 158.40
143.46 143.41
133.96 128.79 128.73 128.12 123.20 123.15
83.46 83.32
128.79 128.73
128.12
129.5 129.0 128.5 128.0 127.5
f1 (ppm)
160.75
158.87
158.44 158.40
161.0 160.5 160.0 159.5 159.0 158.5 158.0
f1 (ppm)
5ma
13C NMR
101 MHz, CDCl3
f1 (ppm)

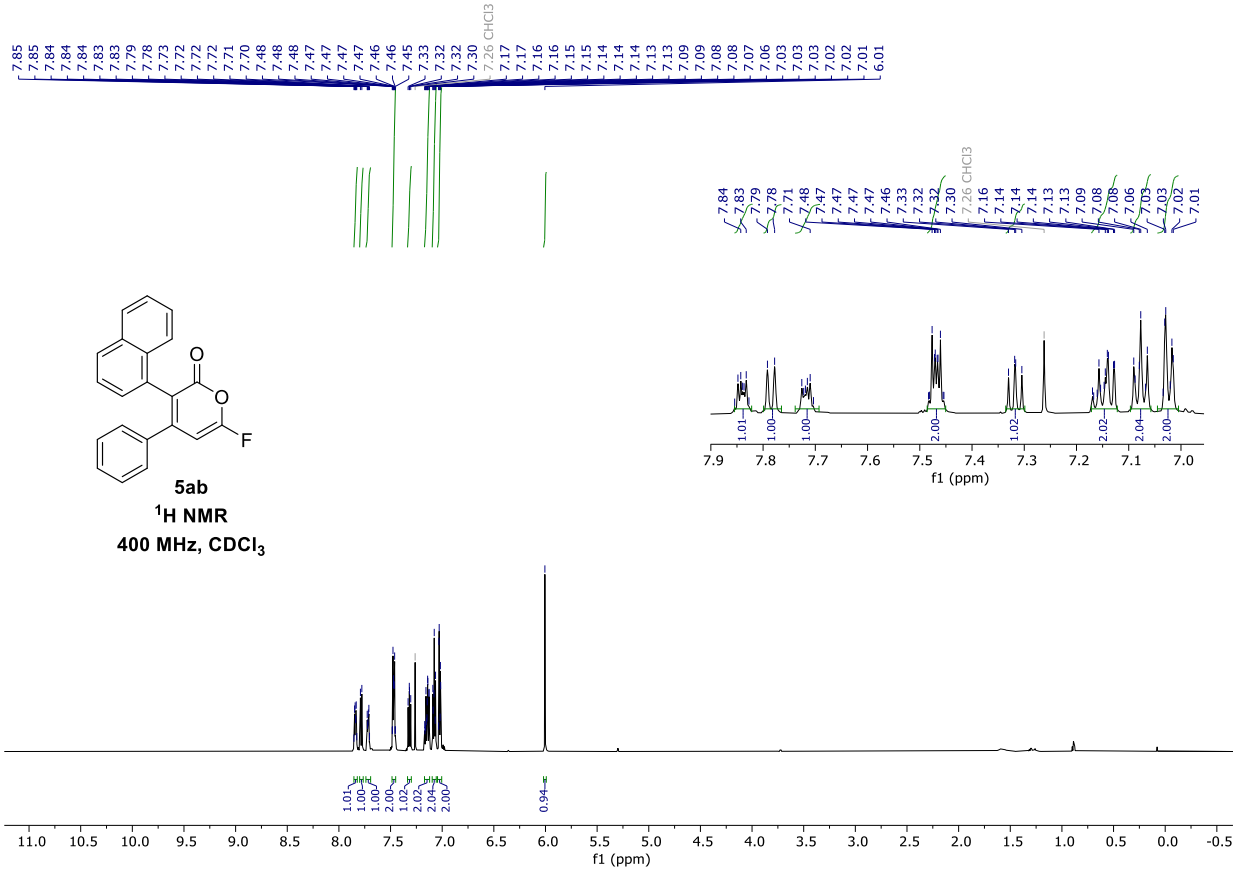


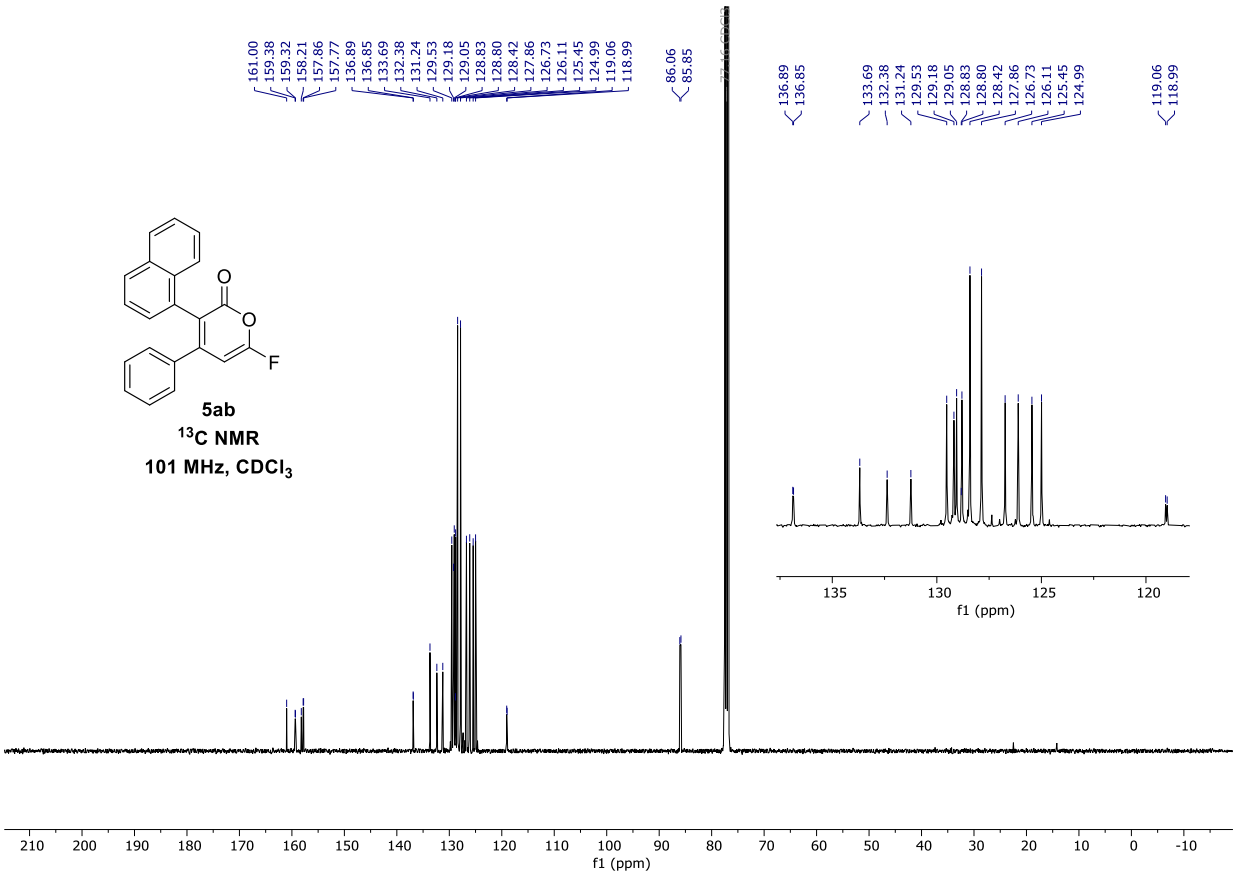
5ma
^{19}F NMR
376 MHz, $CDCl_3$

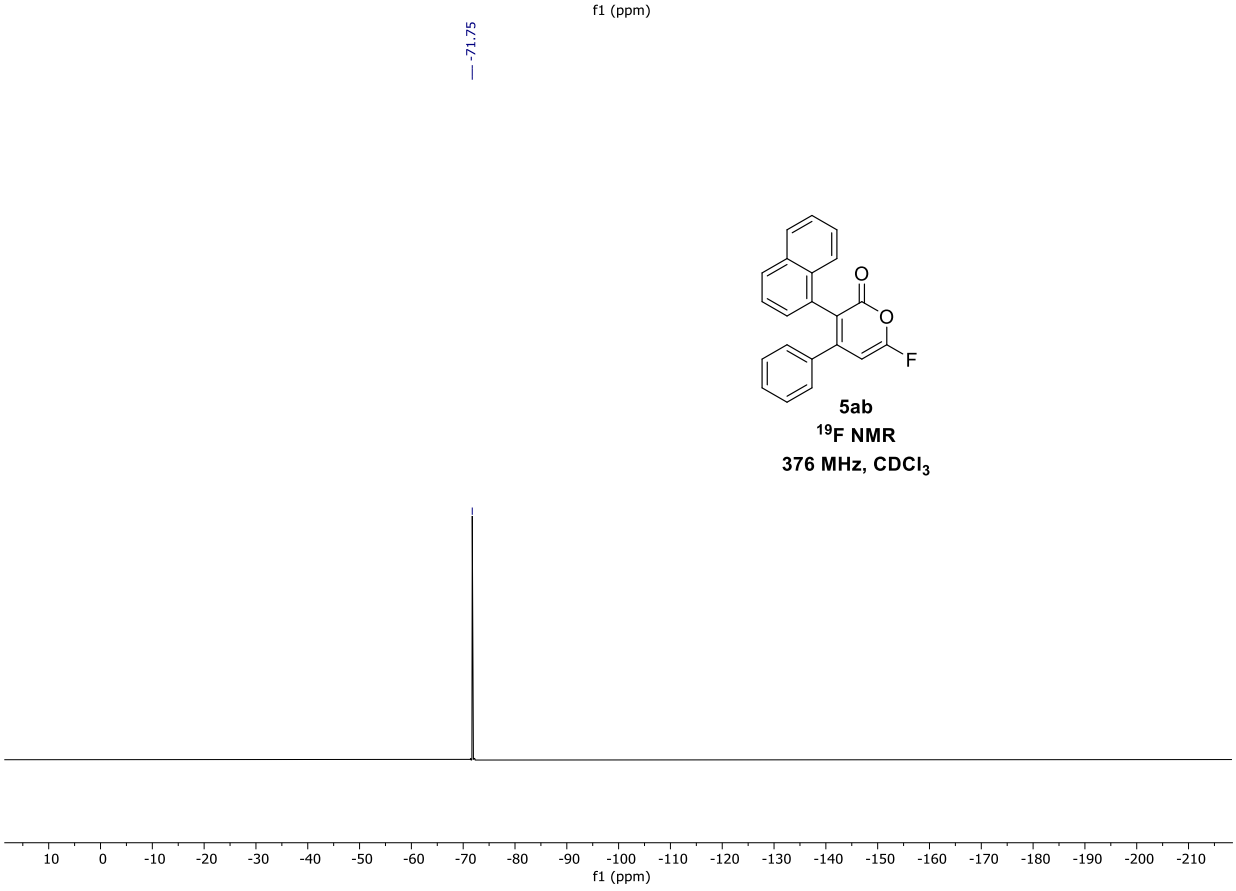


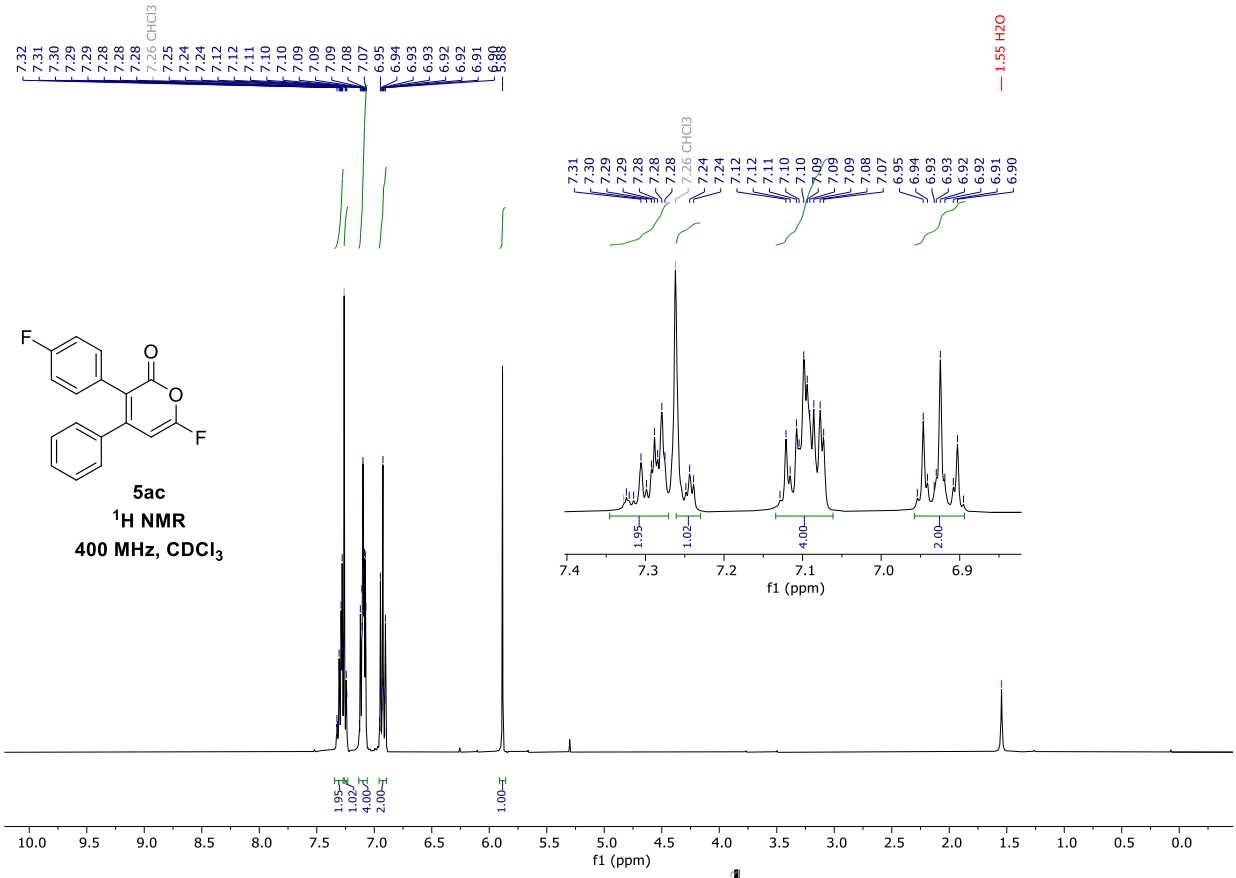
4na
^{1}H NMR
400 MHz, $CDCl_3$

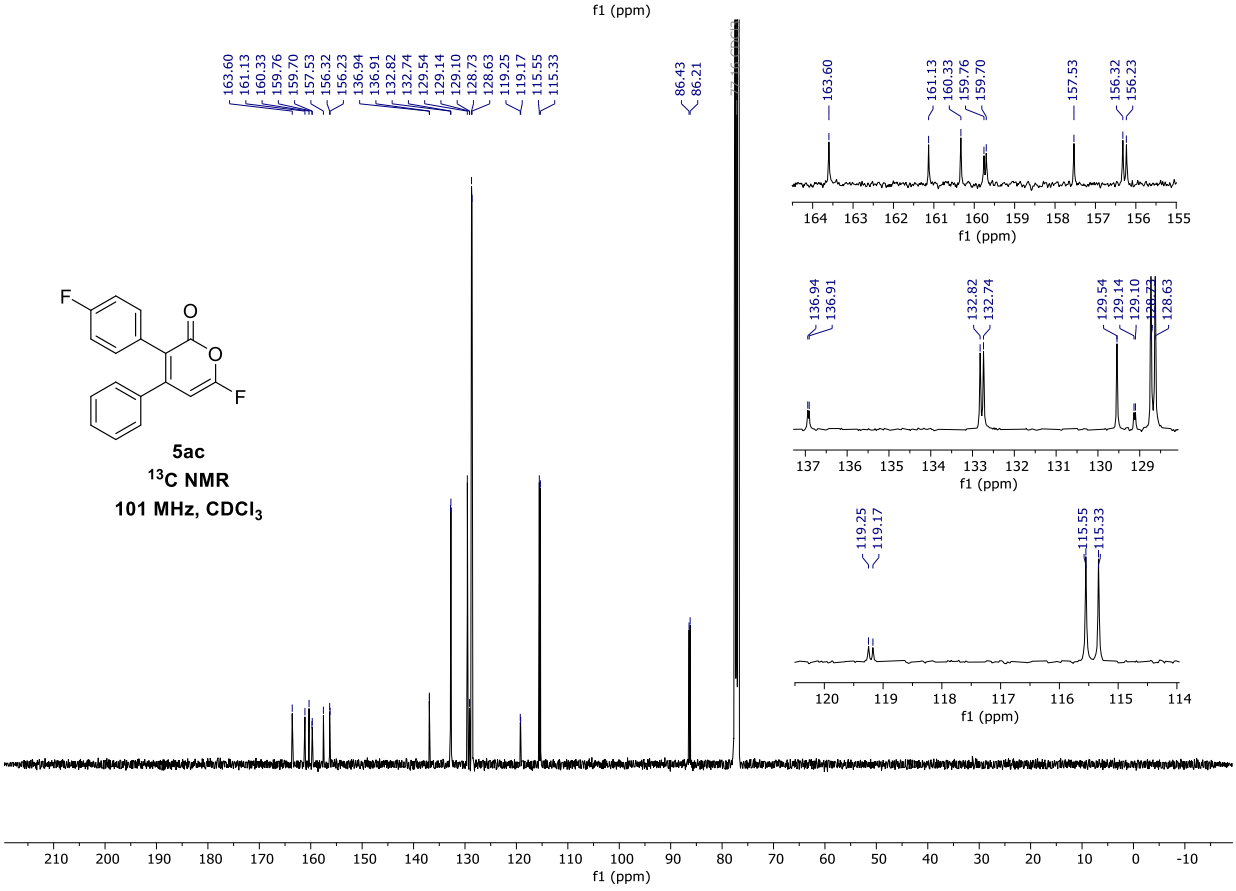

151.11
149.07
135.06
129.71
128.20
126.51
108.71
95.56
94.55
77.16 CDCl3
49.66
48.23
23.73
19.24
-0.73
Me3Si
O
O
N
N
N
4na
13C NMR
101 MHz, CDCl3
f1 (ppm)

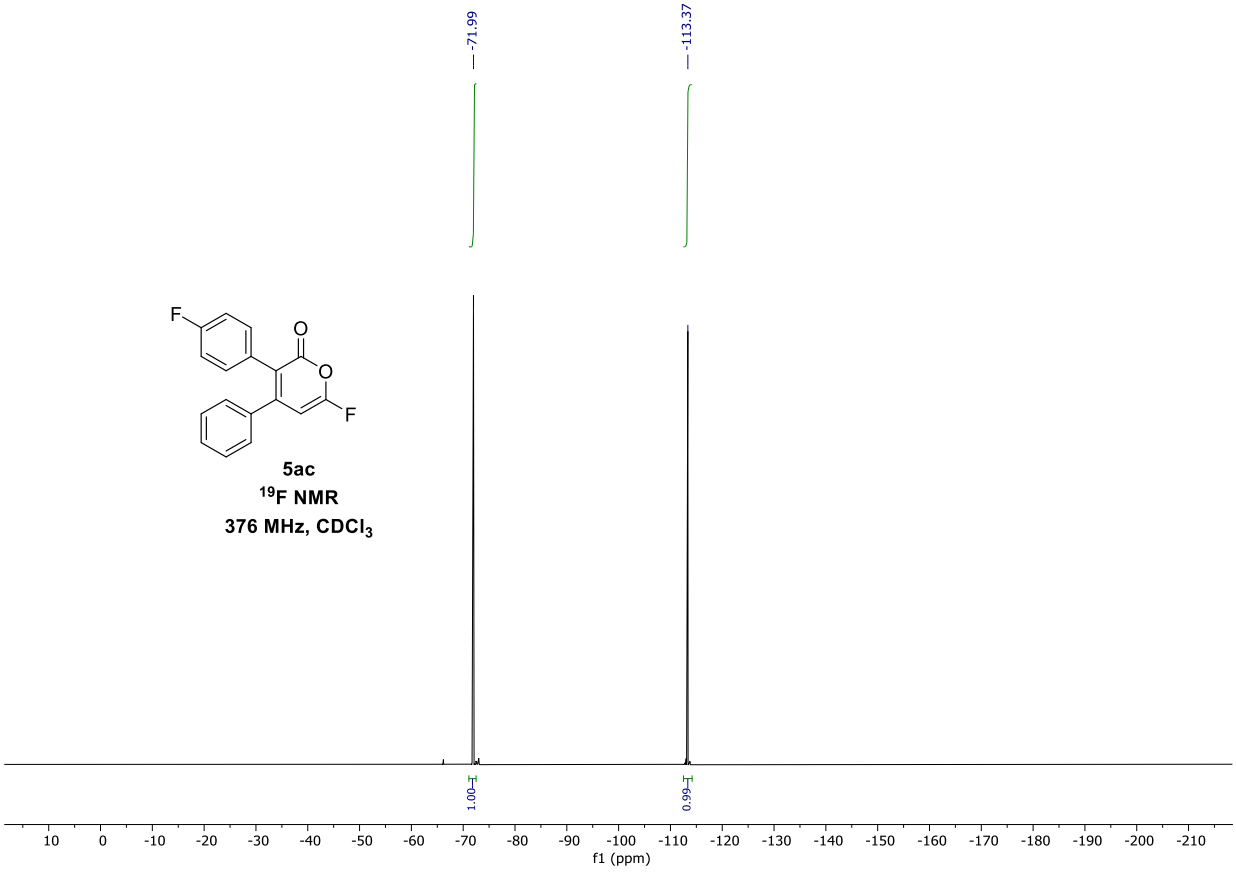

7.26 CHCl3
O
O
F
5ab
1H NMR
400 MHz, CDCl3
1.01
1.00
1.00
2.00
1.02
2.02
2.04
2.00
0.94
f1 (ppm)


161.00
159.38
159.32
158.21
157.86
157.77
136.89
136.85
133.69
132.38
131.24
129.53
129.18
129.05
128.83
128.80
128.42
127.86
126.73
126.11
125.45
124.99
119.06
118.99
86.06
85.85
77.16 CDCl3
136.89
136.85
133.69
132.38
131.24
129.53
129.18
129.05
128.83
128.80
128.42
127.86
126.73
126.11
125.45
124.99
119.06
118.99
O
O
F
5ab
13C NMR
101 MHz, CDCl3
135
130
125
120
f1 (ppm)
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)

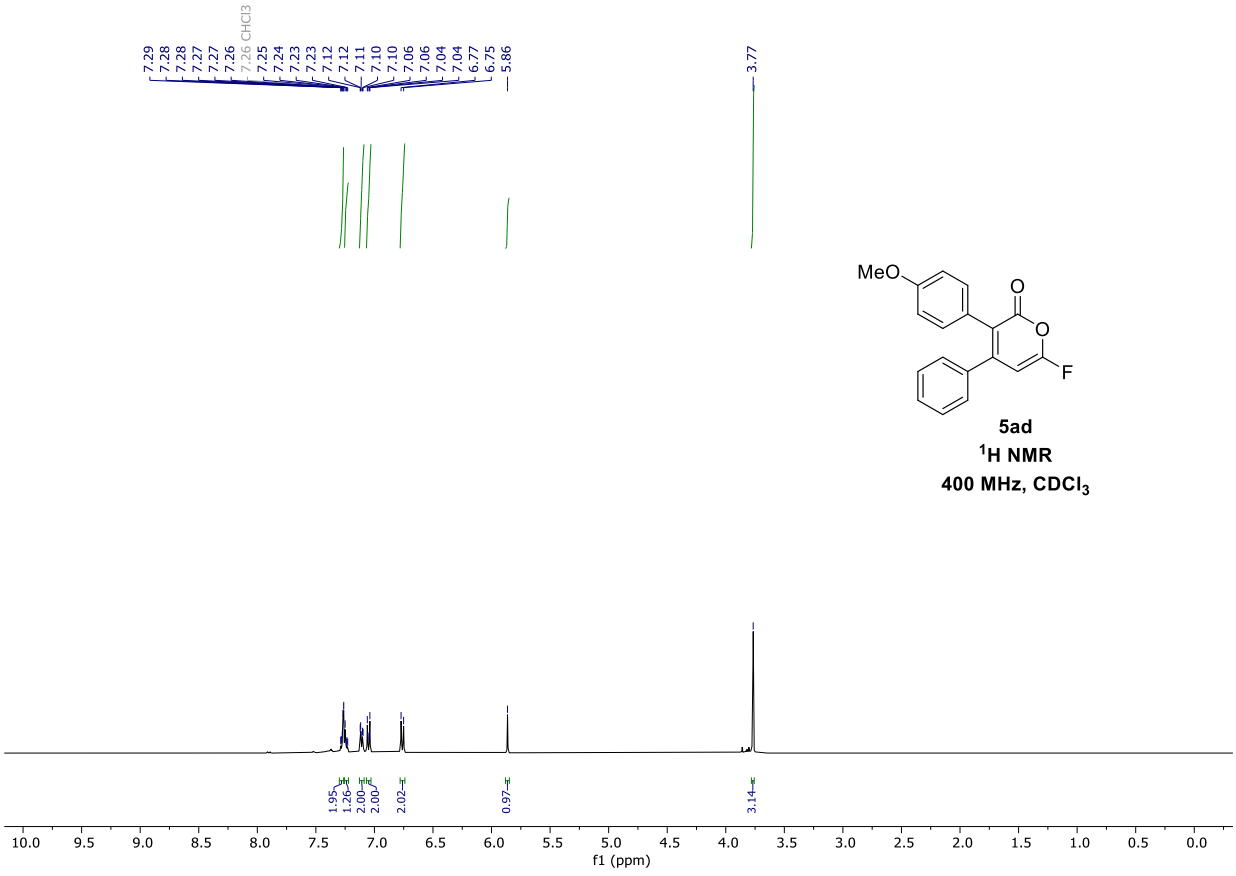

-71.75
O
O
F
5ab
19F NMR
376 MHz, CDCl3
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)


5ac
^{1}H NMR
400 MHz, CDCl$_3$
f1 (ppm)

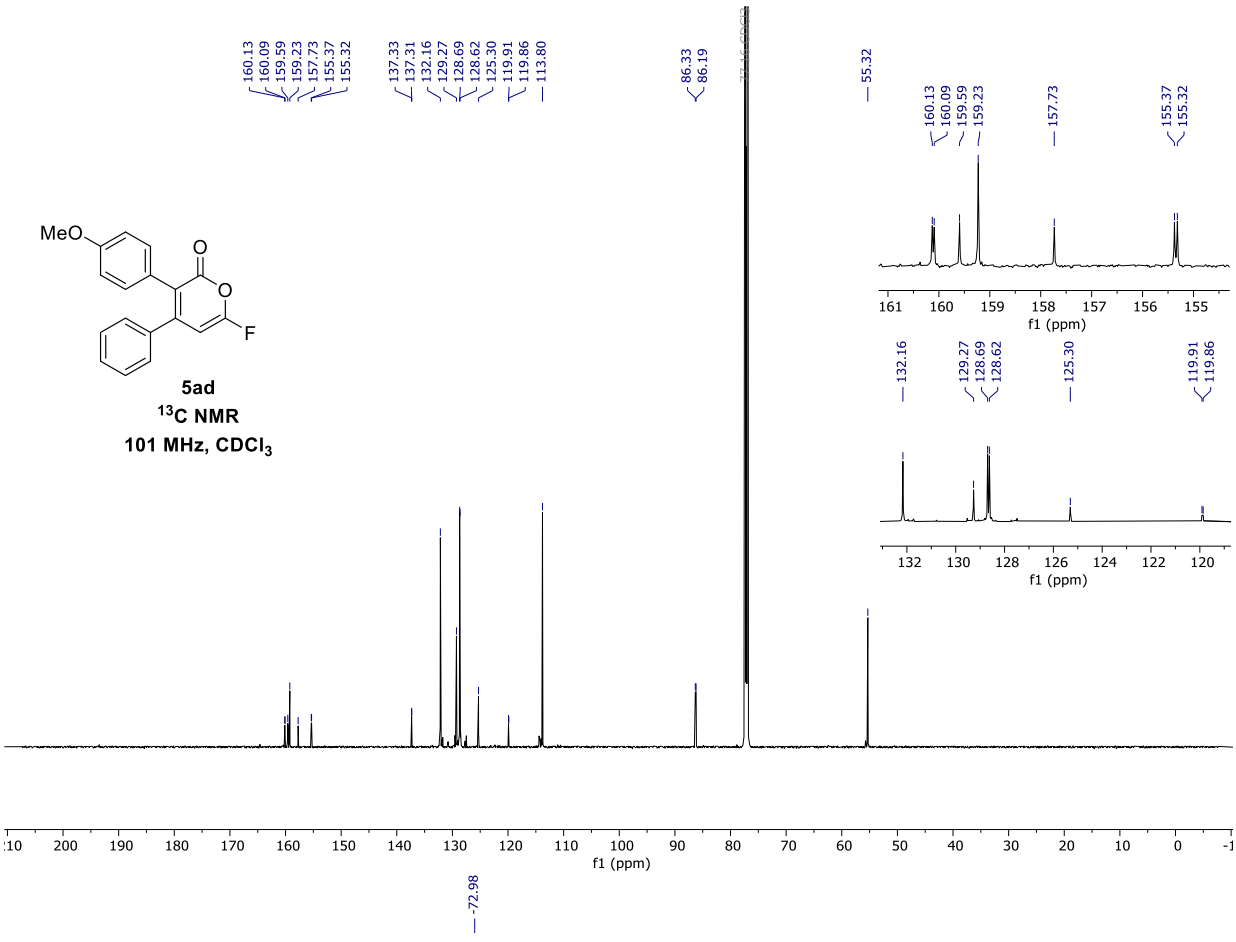

5ac
^{13}C NMR
101 MHz, CDCl$_3$
f1 (ppm)



5ac
^{19}F NMR
376 MHz, $CDCl_3$



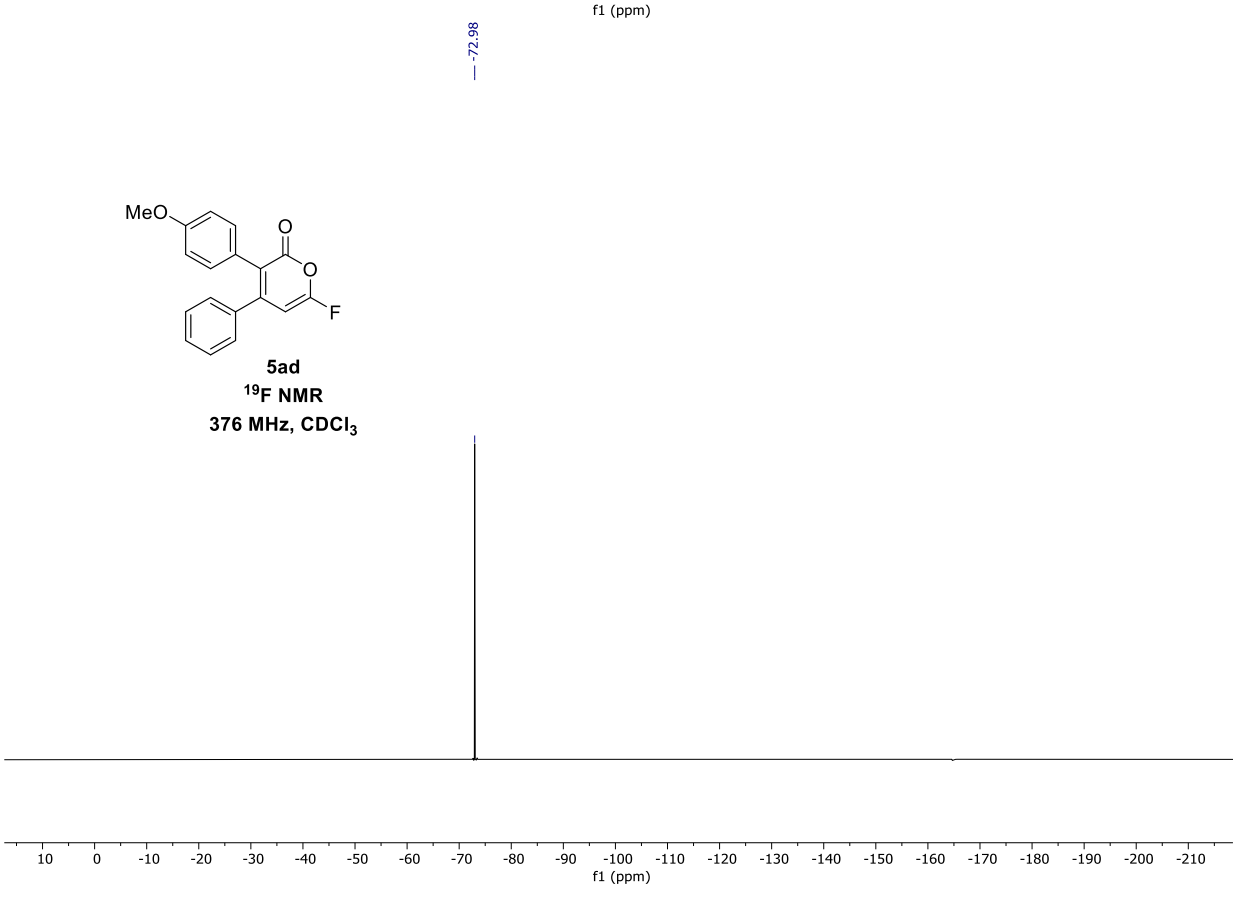
5ad
^{1}H NMR
400 MHz, $CDCl_3$



5ad

^{13}C NMR

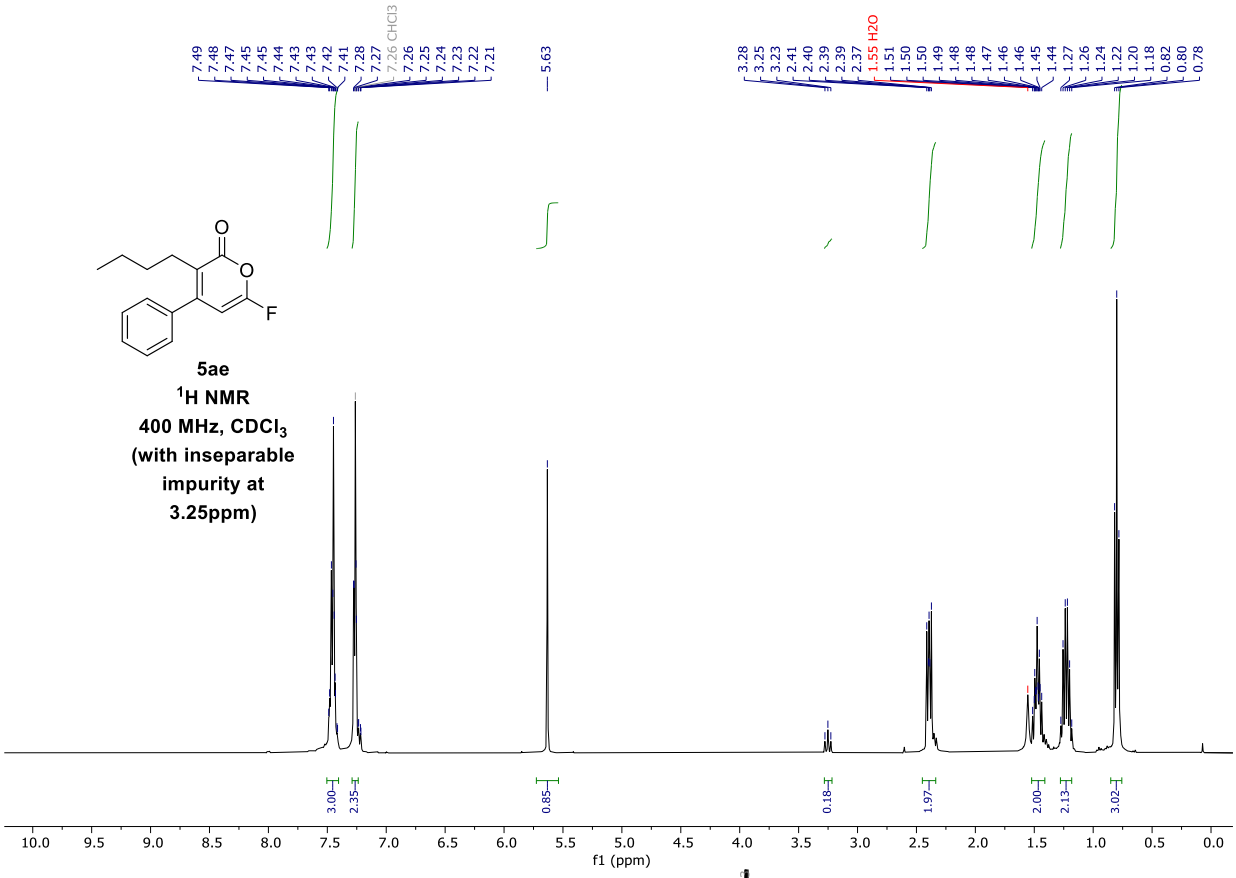
101 MHz, $CDCl_3$

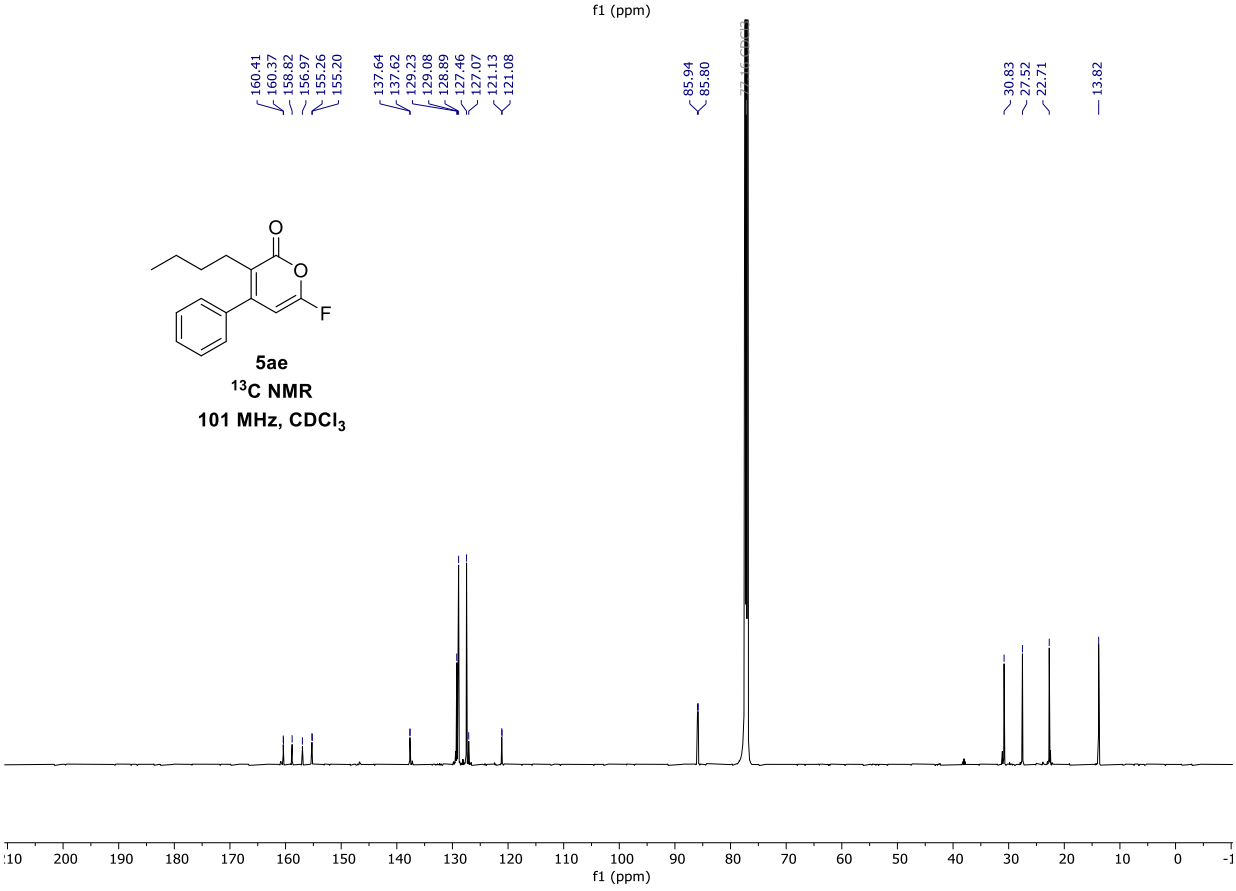


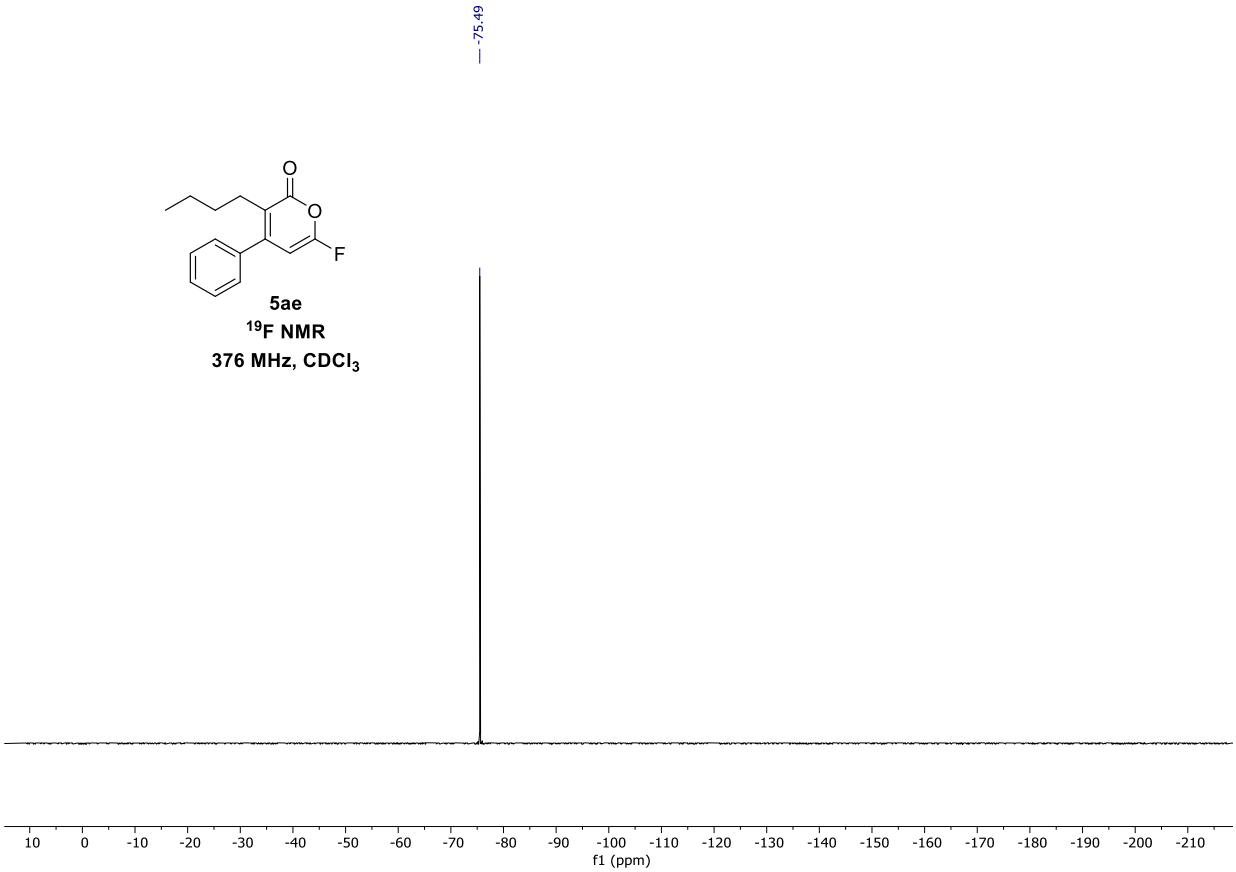
5ad

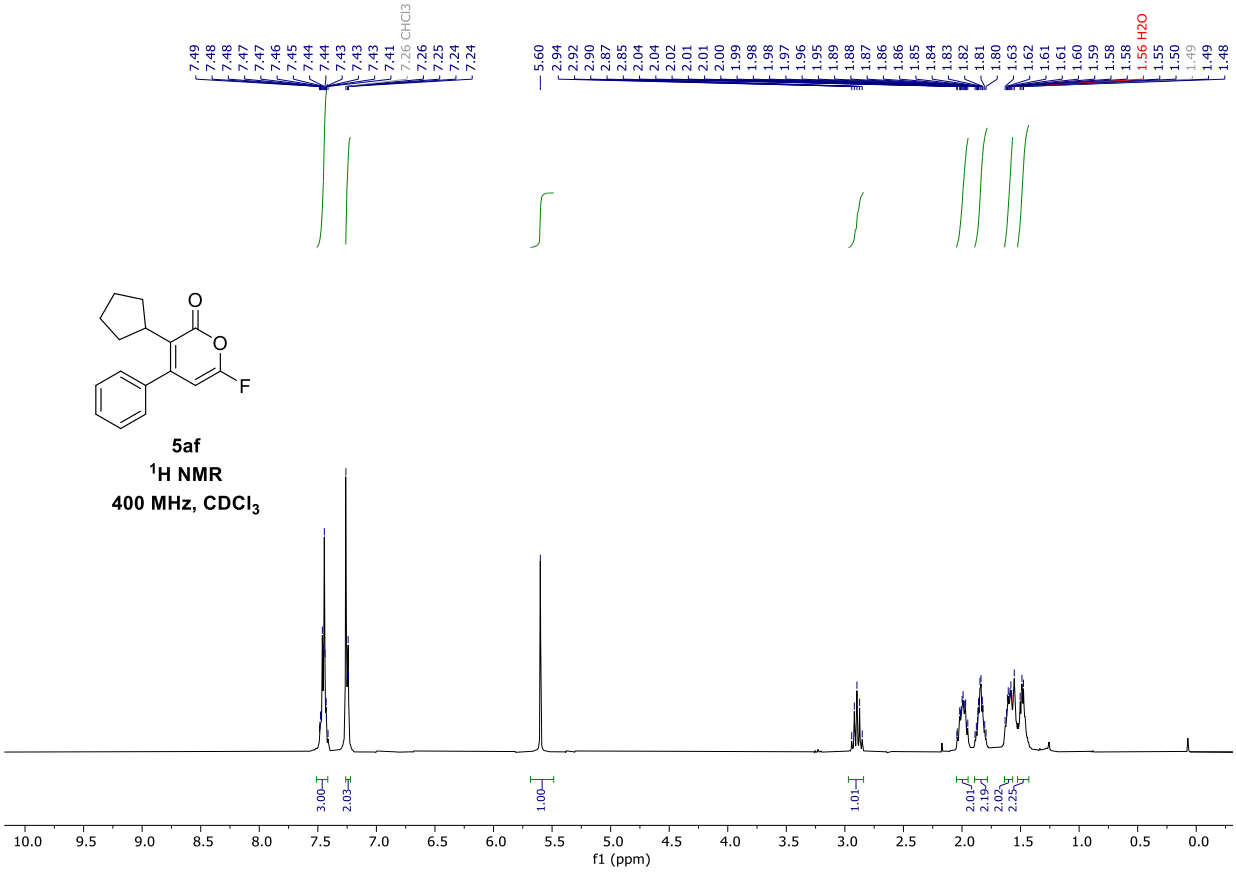
^{19}F NMR

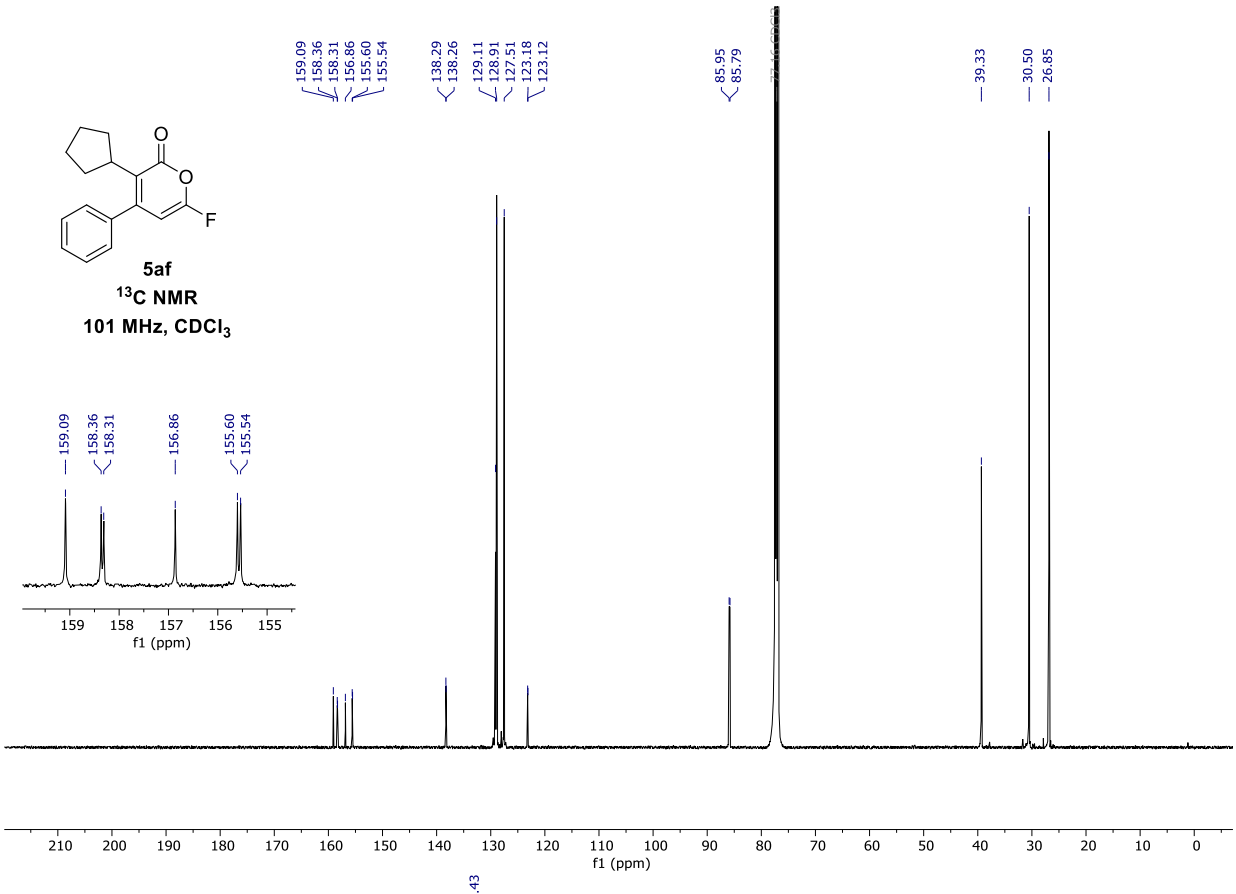
376 MHz, $CDCl_3$

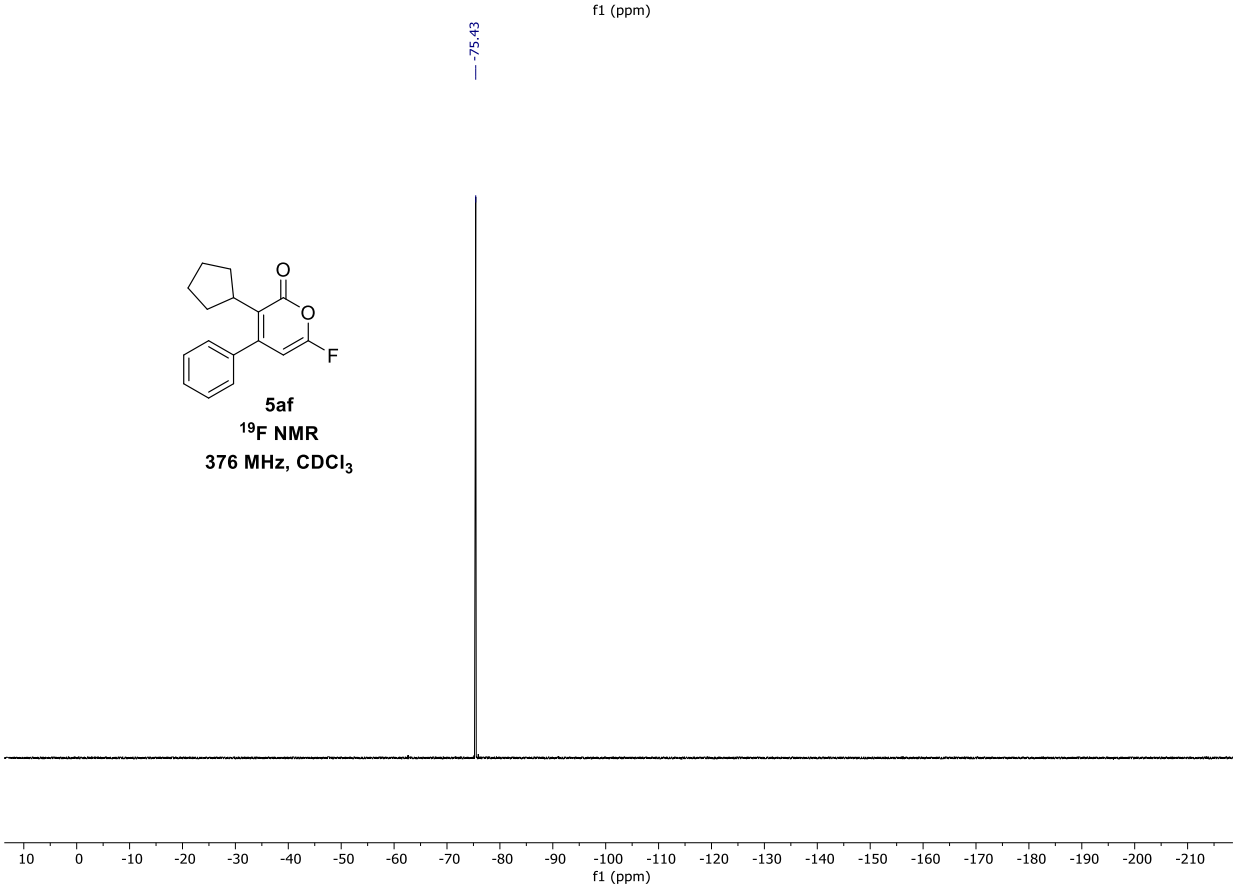

7.49
7.48
7.47
7.45
7.45
7.44
7.43
7.43
7.42
7.41
7.28
7.27
7.26 CHCl3
7.26
7.25
7.24
7.23
7.22
7.21
5.63
3.28
3.25
3.23
2.41
2.40
2.39
2.39
2.37
1.55 H2O
1.51
1.50
1.50
1.49
1.49
1.48
1.48
1.47
1.46
1.46
1.45
1.44
1.27
1.26
1.24
1.22
1.20
1.18
0.82
0.80
0.78
O
O
F
5ae
1H NMR
400 MHz, CDCl3
(with inseparable
impurity at
3.25ppm)
3.00
2.35
0.85
0.18
1.97
2.00
2.13
3.02
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)

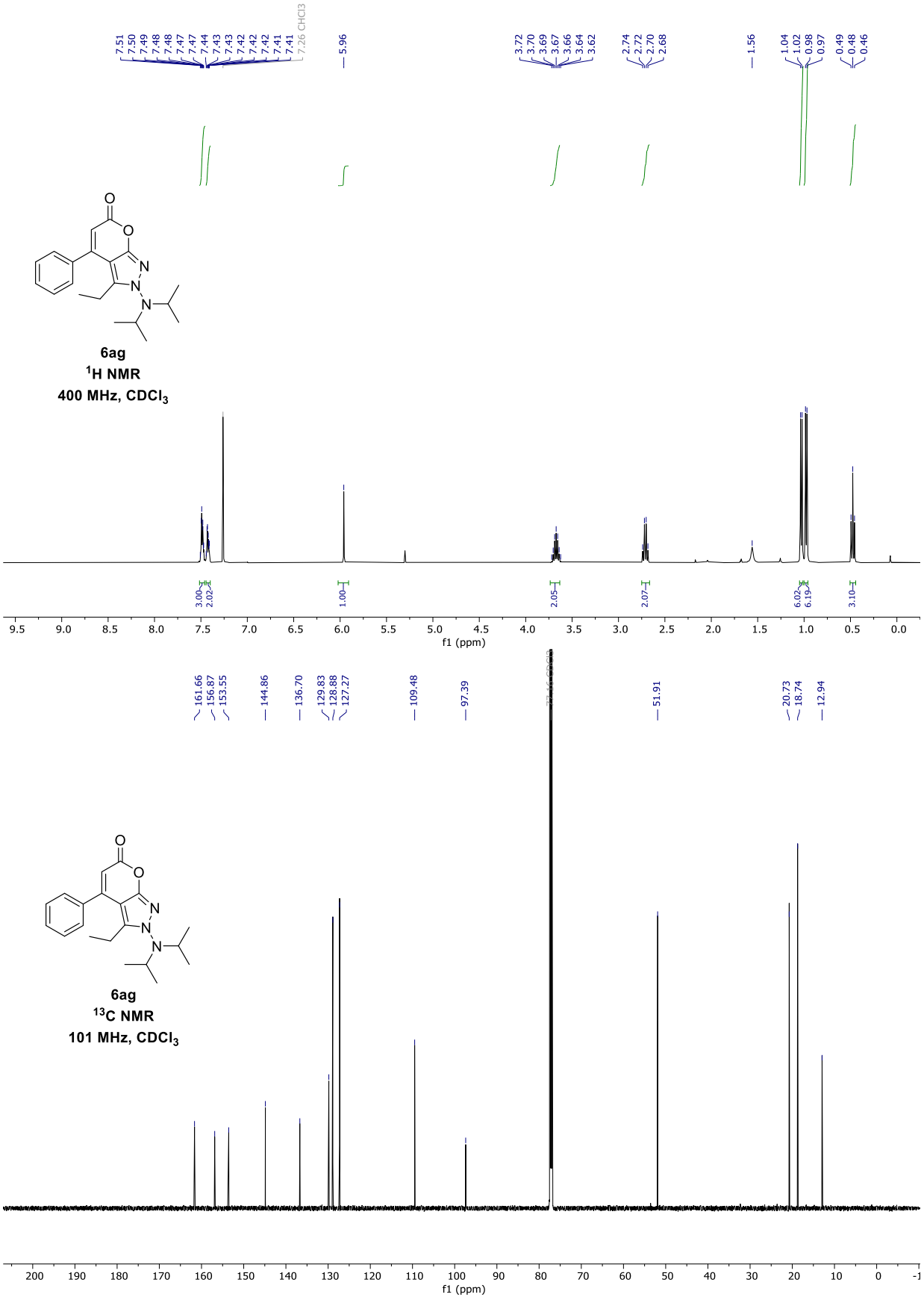

160.41
160.37
158.82
156.97
155.26
155.20
137.64
137.62
129.23
129.08
128.89
127.46
127.07
121.13
121.08
85.94
85.80
30.83
27.52
22.71
13.82
O
O
F
5ae
13C NMR
101 MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)

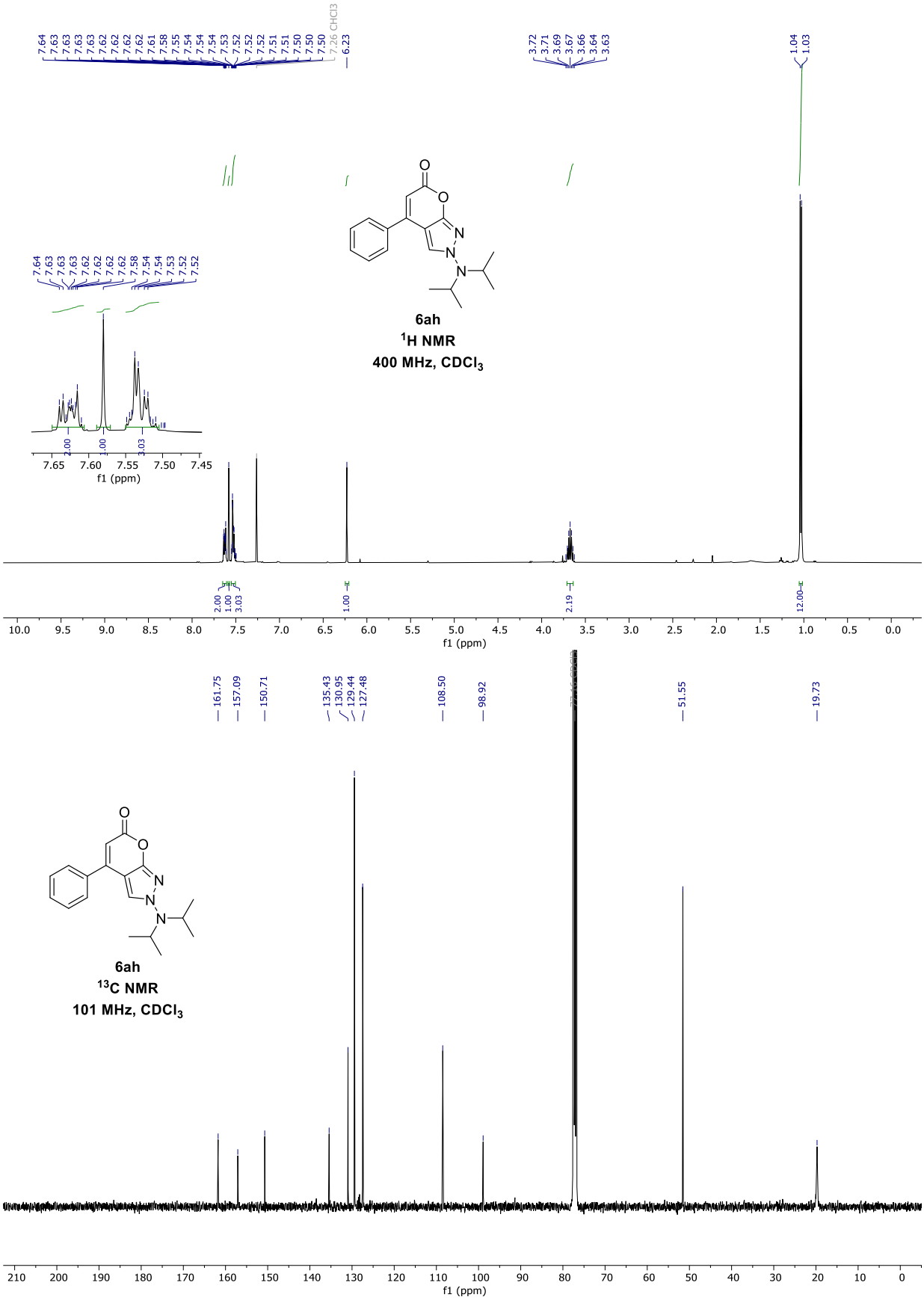

-75.49
O
O
F
5ae
19F NMR
376 MHz, CDCl3
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

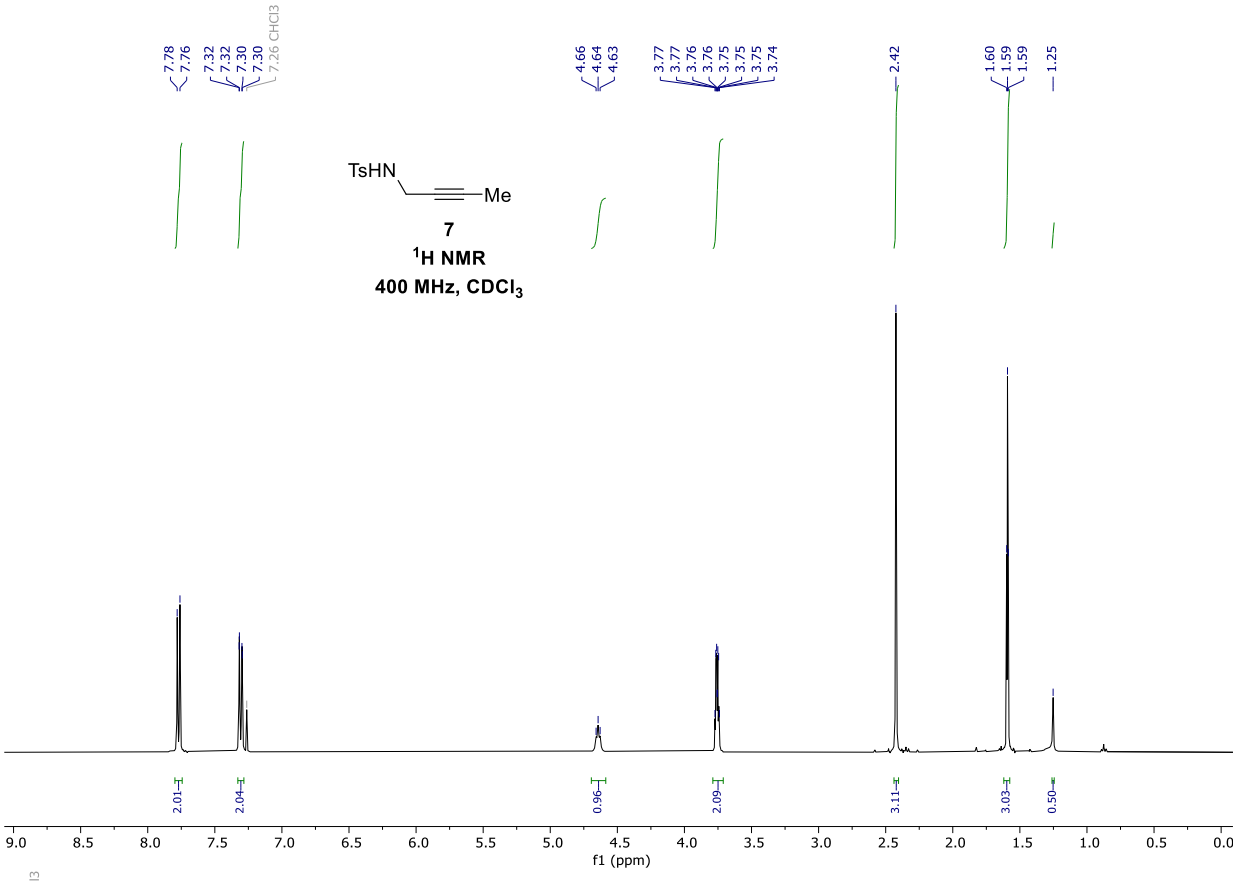

7.49 7.48 7.48 7.47 7.47 7.46 7.45 7.44 7.44 7.43 7.43 7.43 7.41 7.26 CHCl3 7.26 7.25 7.24 7.24
5.60 2.94 2.92 2.90 2.87 2.85 2.04 2.04 2.02 2.01 2.01 2.00 1.99 1.98 1.98 1.97 1.96 1.95 1.89 1.88 1.87 1.86 1.86 1.85 1.84 1.83 1.82 1.81 1.80 1.63 1.62 1.61 1.61 1.60 1.59 1.58 1.58 1.56 H2O 1.55 1.50 1.49 1.49 1.48
O
O
F
5af
1H NMR
400 MHz, CDCl3
3.00 2.03 1.00 1.01 2.01 2.19 2.02 2.25
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)

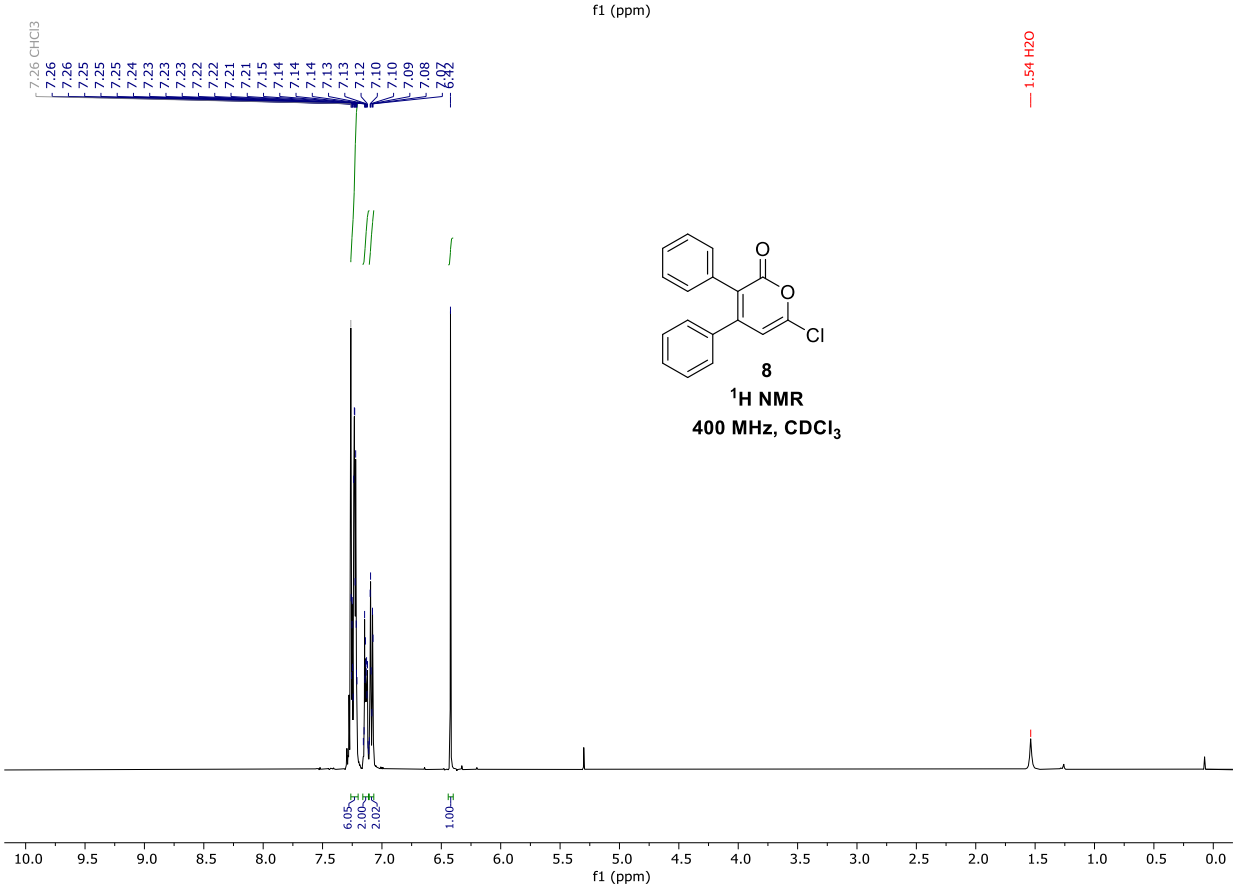

159.09
158.36
158.31
156.86
155.60
155.54
138.29
138.26
129.11
128.91
127.51
123.18
123.12
85.95
85.79
39.33
30.50
26.85
O
O
F
5af
13C NMR
101 MHz, CDCl3
159.09
158.36
158.31
156.86
155.60
155.54
159
158
157
156
155
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

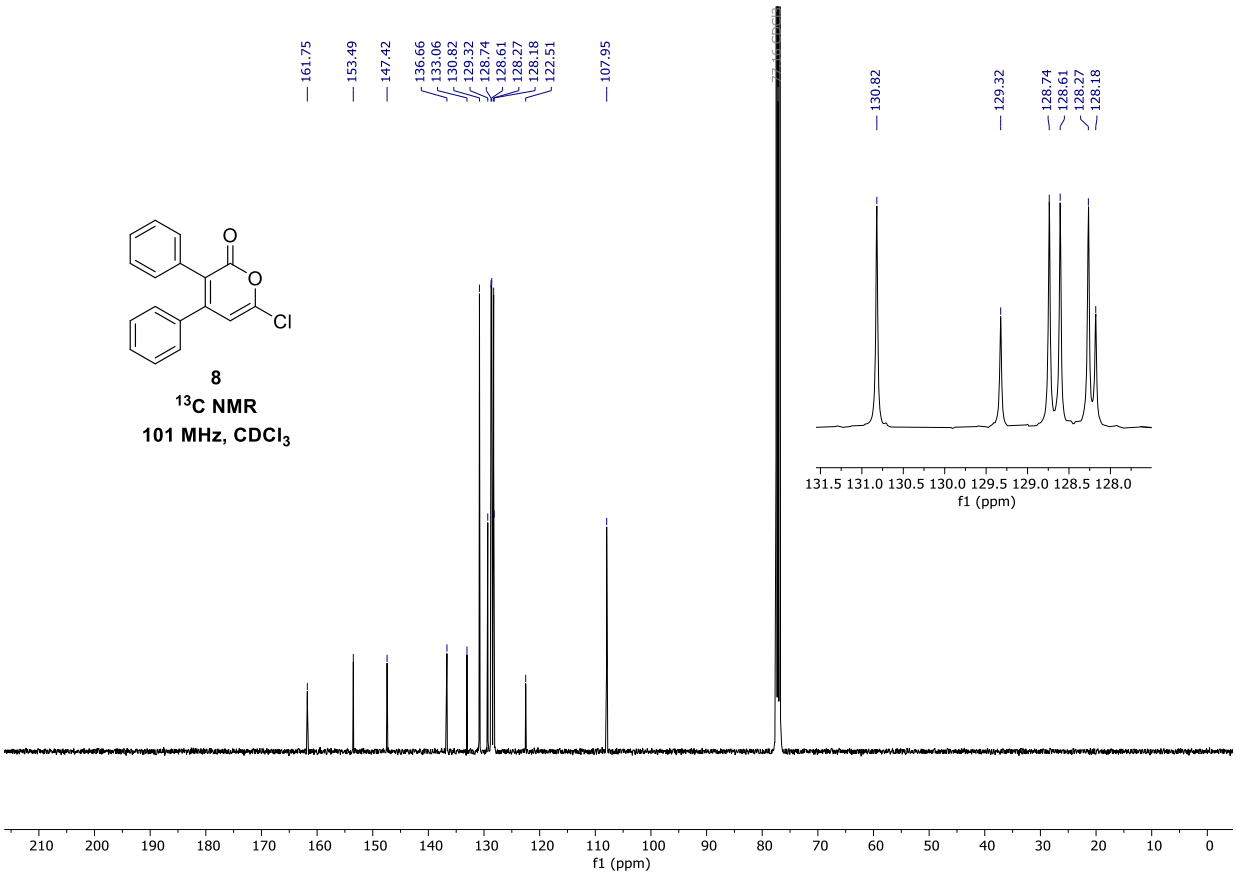

-75.43
O
O
F
5af
19F NMR
376 MHz, CDCl3
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

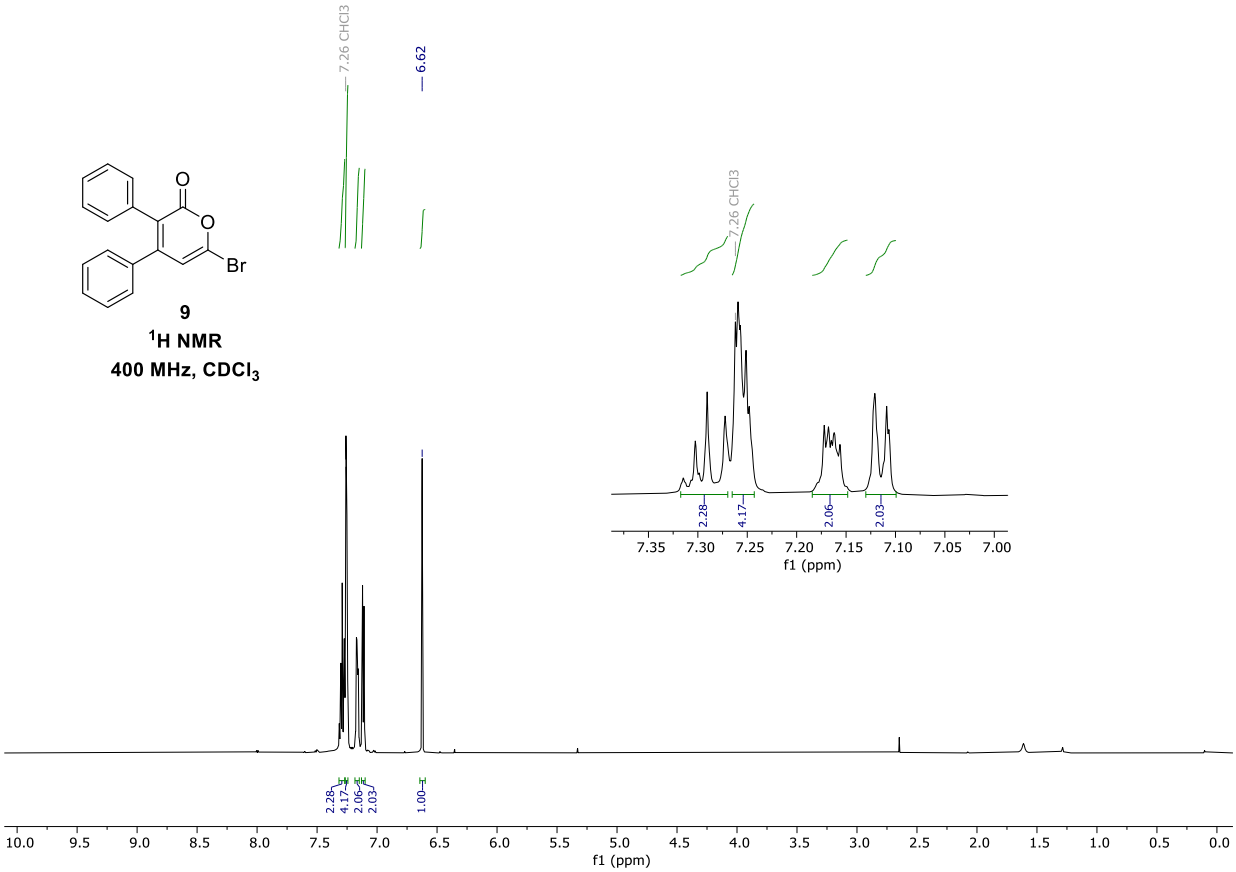

7.51
7.50
7.49
7.48
7.48
7.47
7.47
7.44
7.43
7.43
7.42
7.42
7.42
7.41
7.41
7.26 CHCl3
5.96
3.72
3.70
3.69
3.67
3.66
3.64
3.62
2.74
2.72
2.70
2.68
1.56
1.04
1.02
0.98
0.97
0.49
0.48
0.46
O
O
N
N
N
6ag
1H NMR
400 MHz, CDCl3
3.00
2.02
1.00
2.05
2.07
6.02
6.19
3.10
f1 (ppm)
161.66
156.87
153.55
144.86
136.70
129.83
128.88
127.27
109.48
97.39
77.16 CDCl3
51.91
20.73
18.74
12.94
O
O
N
N
N
6ag
13C NMR
101 MHz, CDCl3
f1 (ppm)

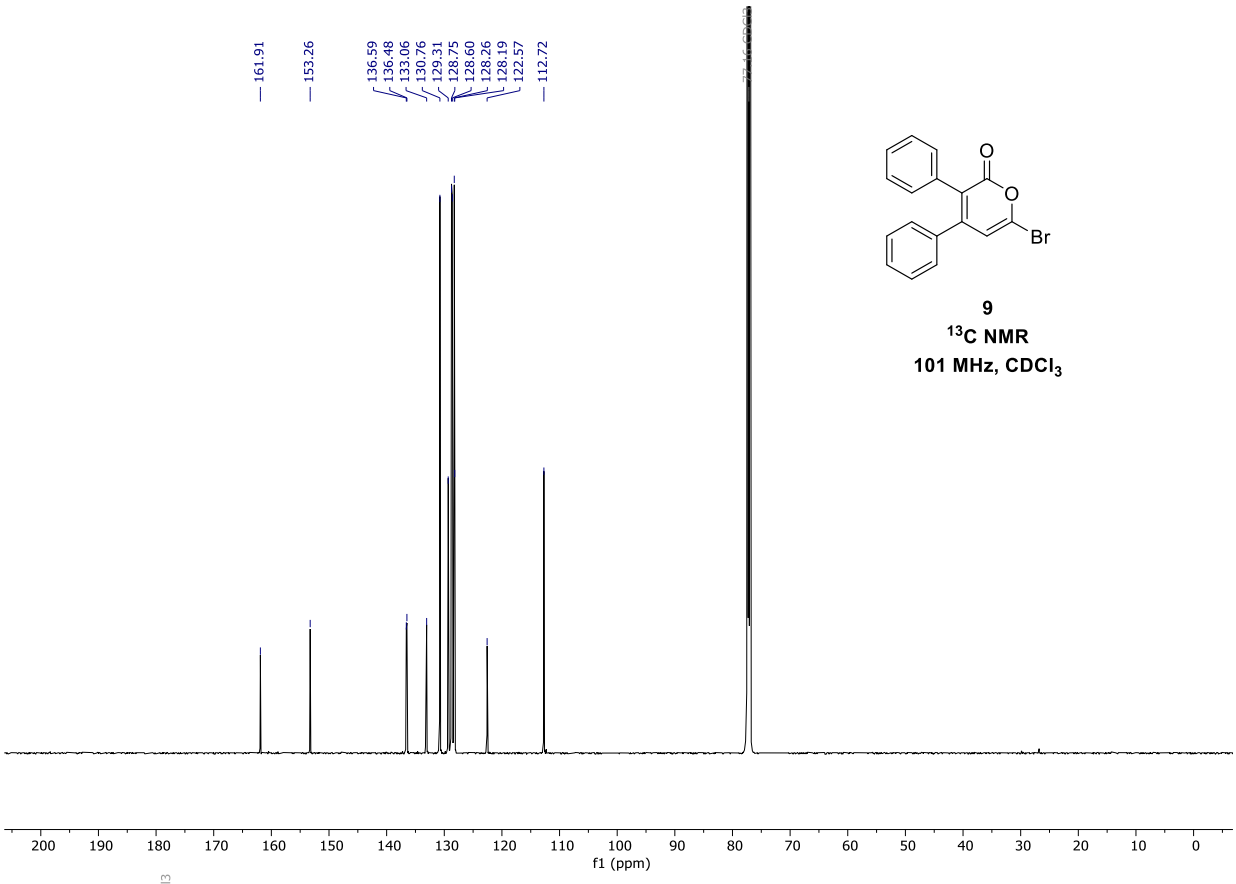

6ah
1H NMR
400 MHz, CDCl3
f1 (ppm)
6ah
13C NMR
101 MHz, CDCl3
f1 (ppm)


7.78
7.76
7.32
7.32
7.30
7.30
7.26 CHCl3
4.66
4.64
4.63
3.77
3.77
3.76
3.76
3.75
3.75
3.75
3.74
2.42
1.60
1.59
1.59
1.25
TsHN
Me
7
1H NMR
400 MHz, CDCl3
2.01
2.04
0.96
2.09
3.11
3.03
0.50
f1 (ppm)


7.26 CHCl3
7.26
7.26
7.25
7.25
7.25
7.24
7.23
7.23
7.23
7.22
7.22
7.21
7.21
7.15
7.14
7.14
7.14
7.13
7.13
7.12
7.10
7.10
7.09
7.08
7.07
6.42
1.54 H2O
O
O
Cl
8
1H NMR
400 MHz, CDCl3
6.05
2.00
2.02
1.00
f1 (ppm)


161.75
153.49
147.42
136.66
133.06
130.82
129.32
128.74
128.61
128.27
128.18
122.51
107.95
77.16 CDCl3
O
O
Cl
8
13C NMR
101 MHz, CDCl3
130.82
129.32
128.74
128.61
128.27
128.18
131.5 131.0 130.5 130.0 129.5 129.0 128.5 128.0
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

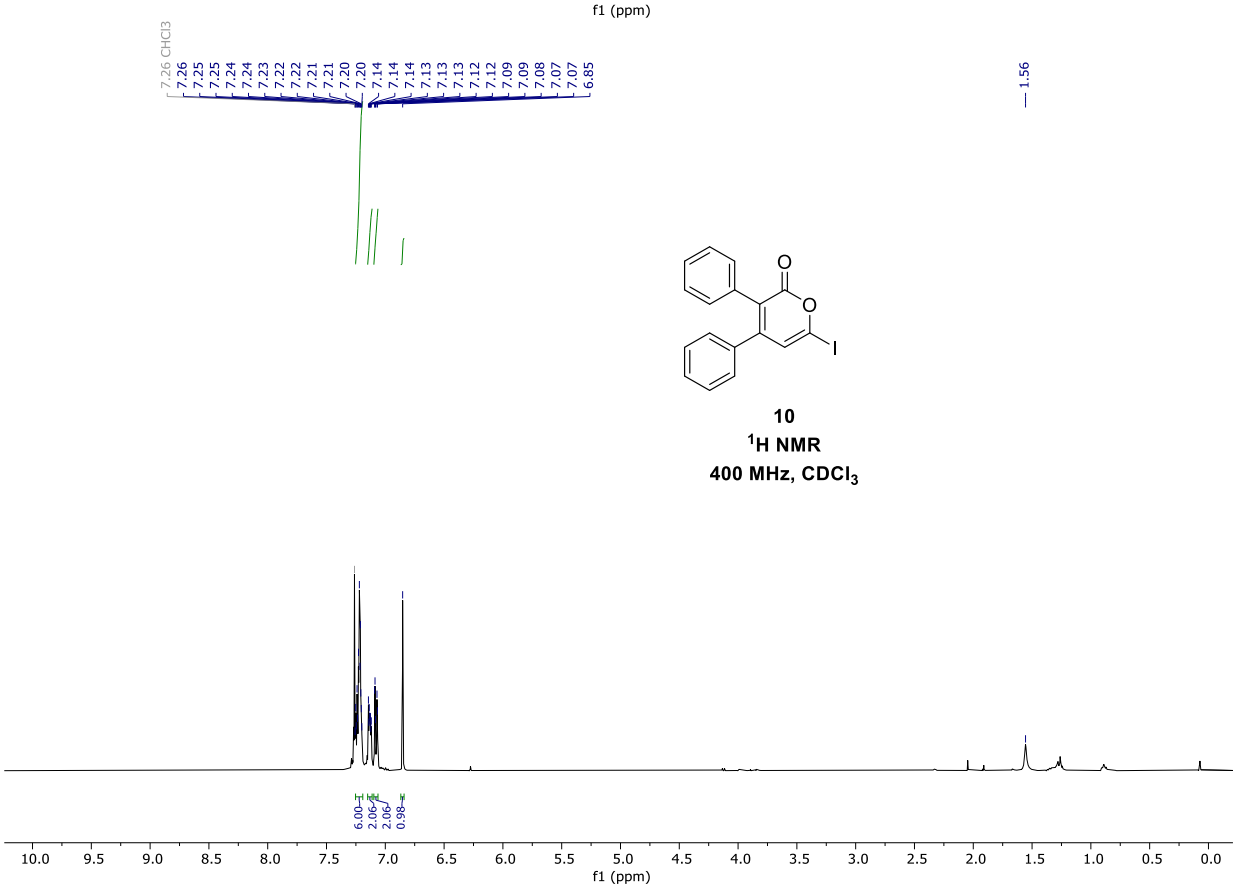

7.26 CHCl3
6.62
O
O
Br
9
1H NMR
400 MHz, CDCl3
7.26 CHCl3
2.28
4.17
2.06
2.03
7.35 7.30 7.25 7.20 7.15 7.10 7.05 7.00
f1 (ppm)
2.28
4.17
2.06
2.03
1.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)



9

^{13}C NMR

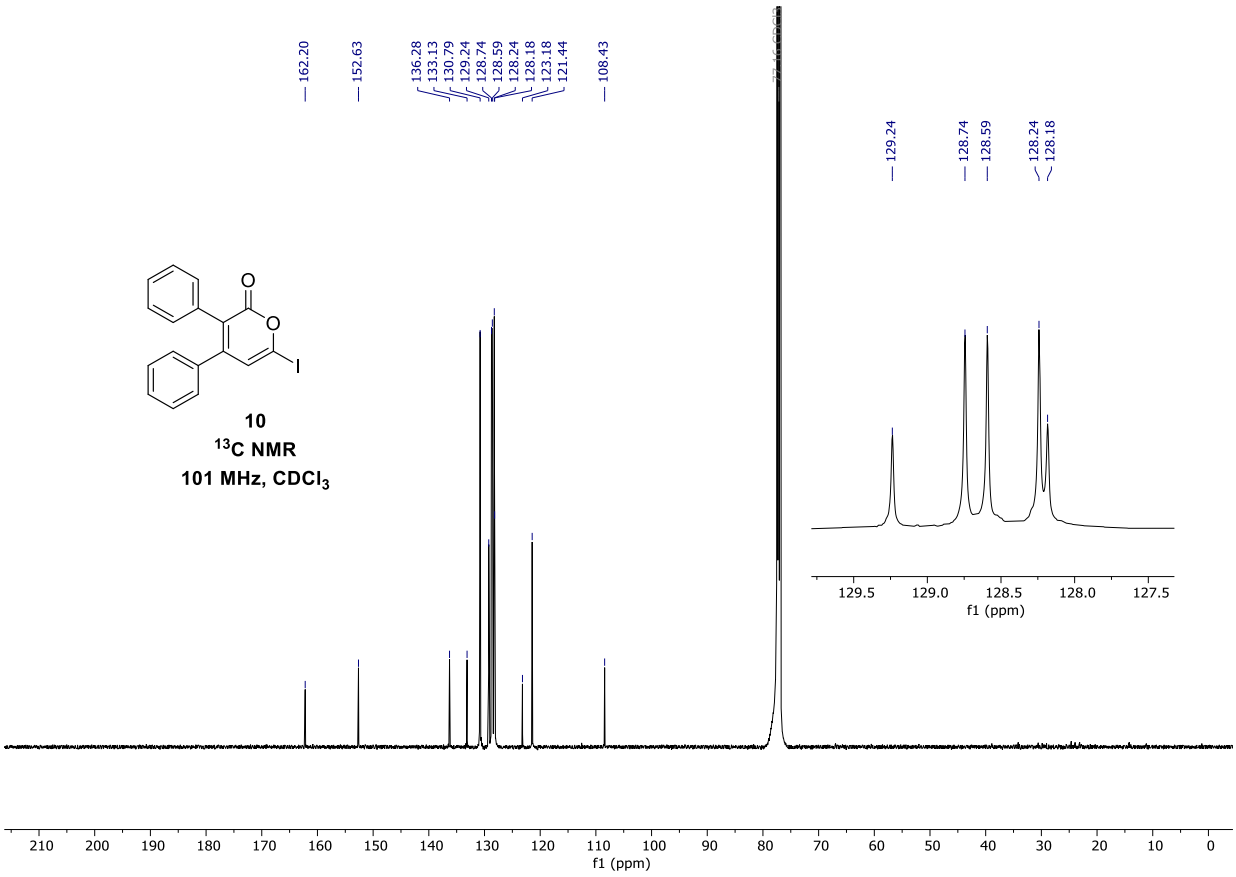
101 MHz, $CDCl_3$

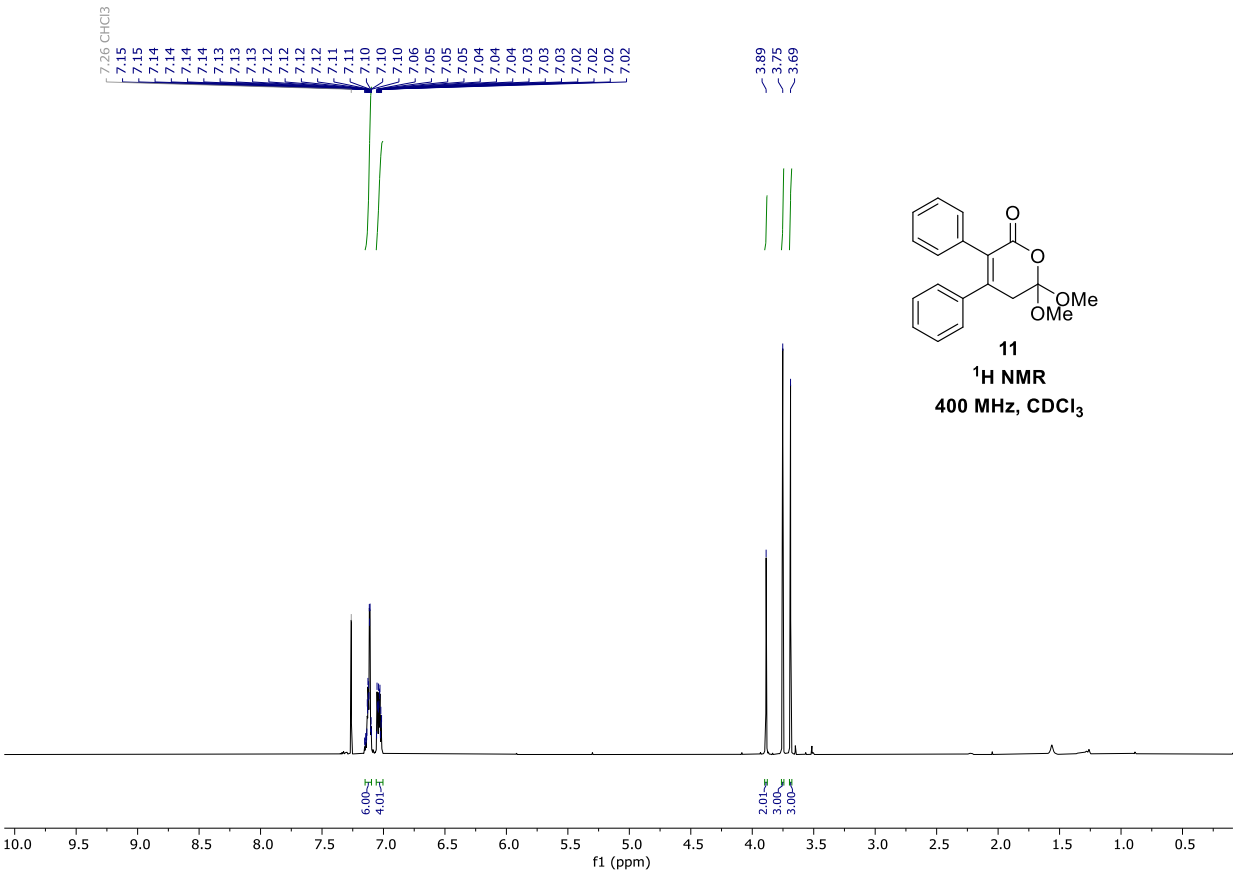


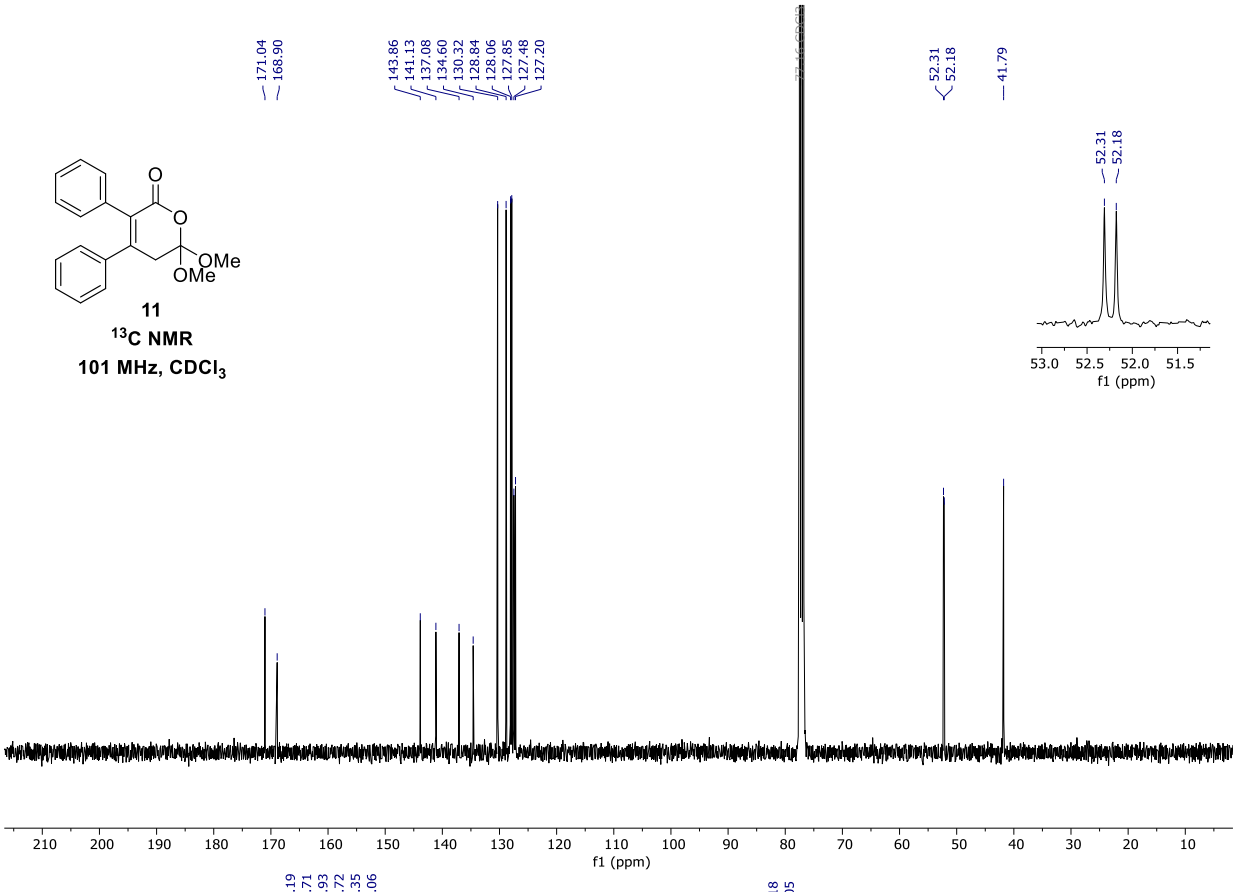
10

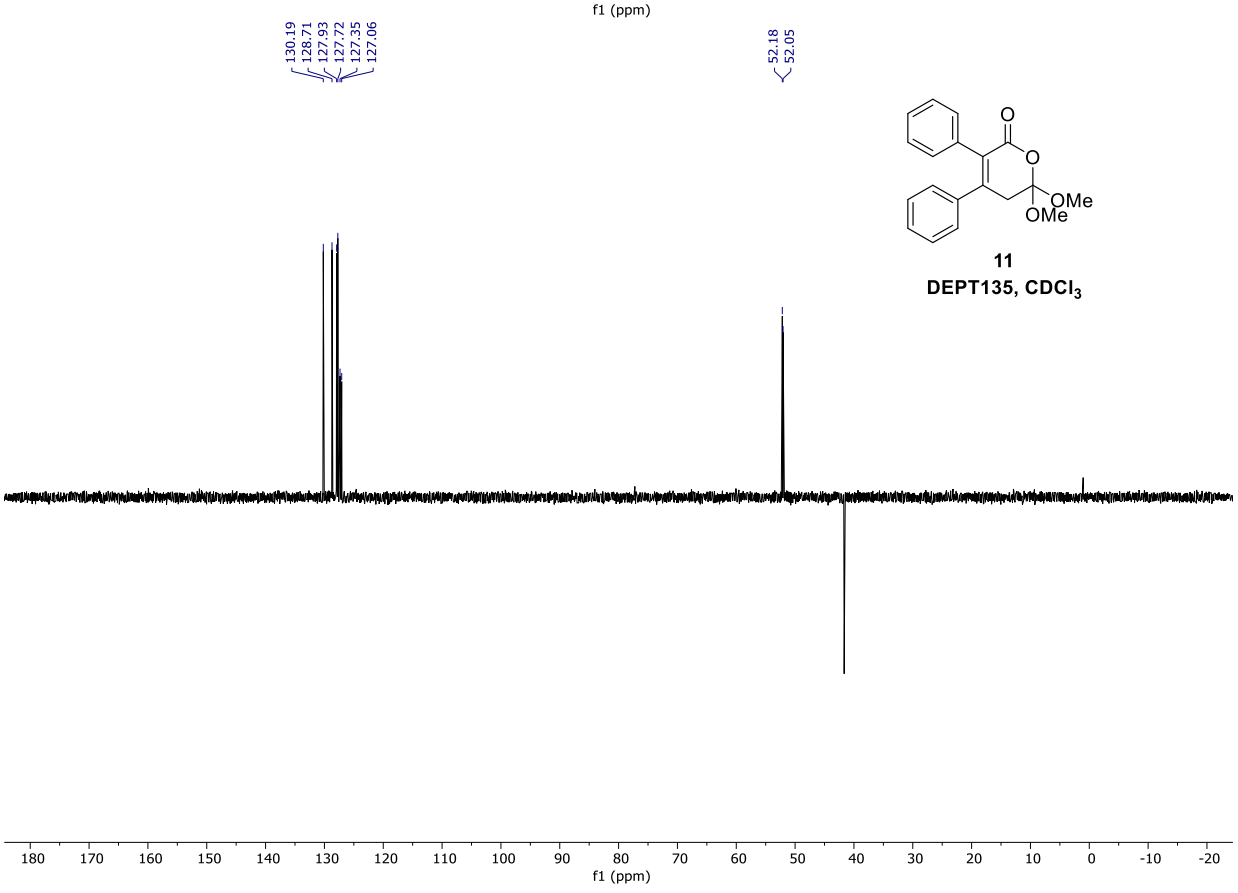
^{1}H NMR

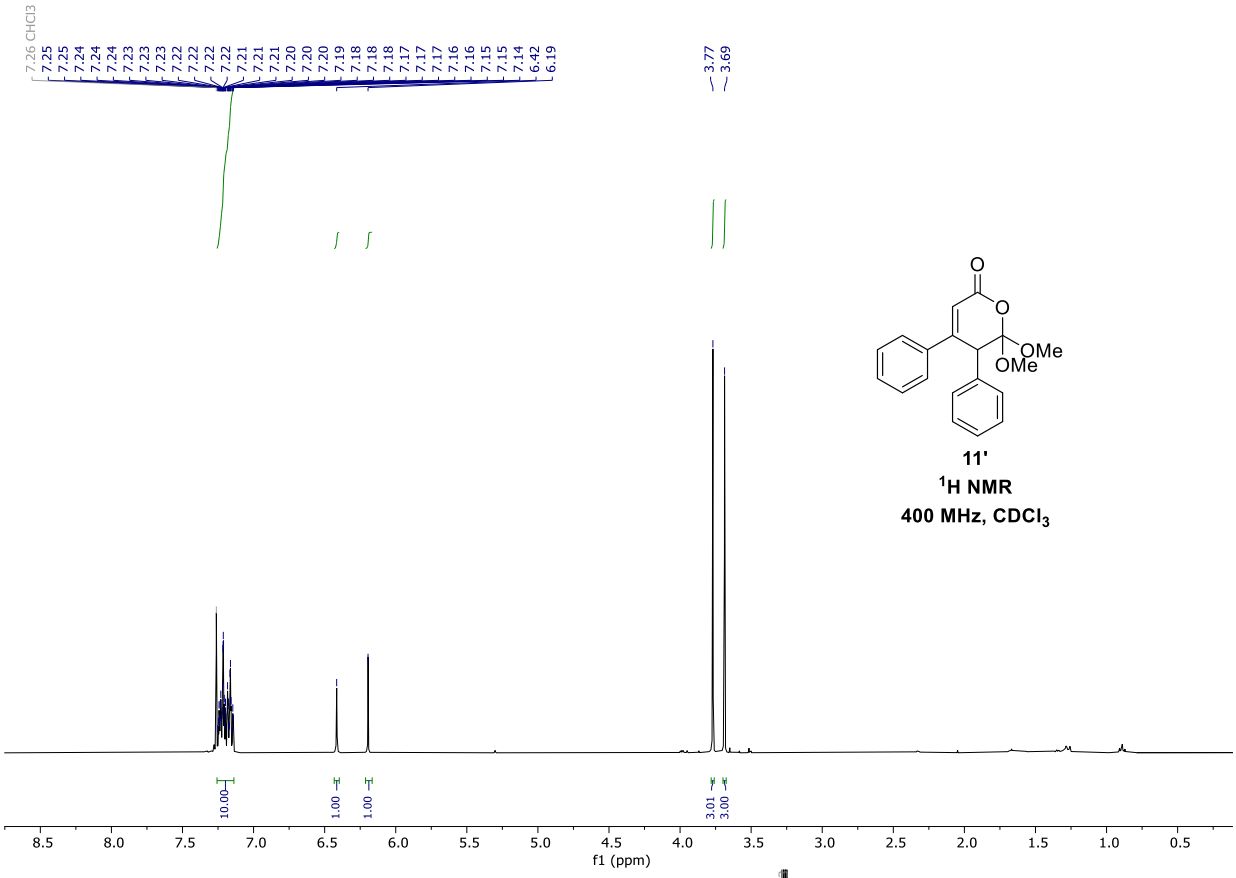
400 MHz, $CDCl_3$

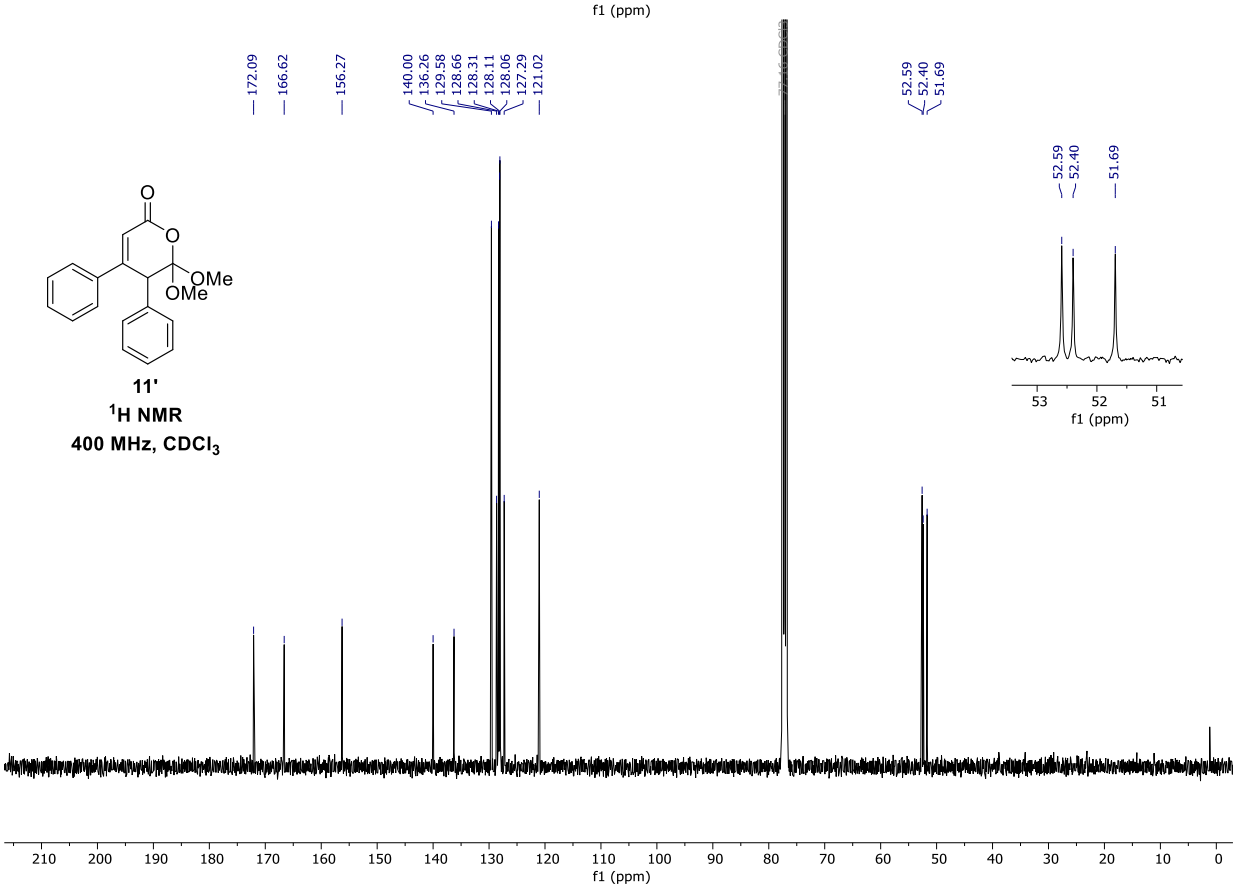

162.20
152.63
136.28
133.13
130.79
129.24
128.74
128.59
128.24
128.18
123.18
121.44
108.43
77.16 CDCl3
129.24
128.74
128.59
128.24
128.18
O
O
I
10
13C NMR
101 MHz, CDCl3
129.5
129.0
128.5
128.0
127.5
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

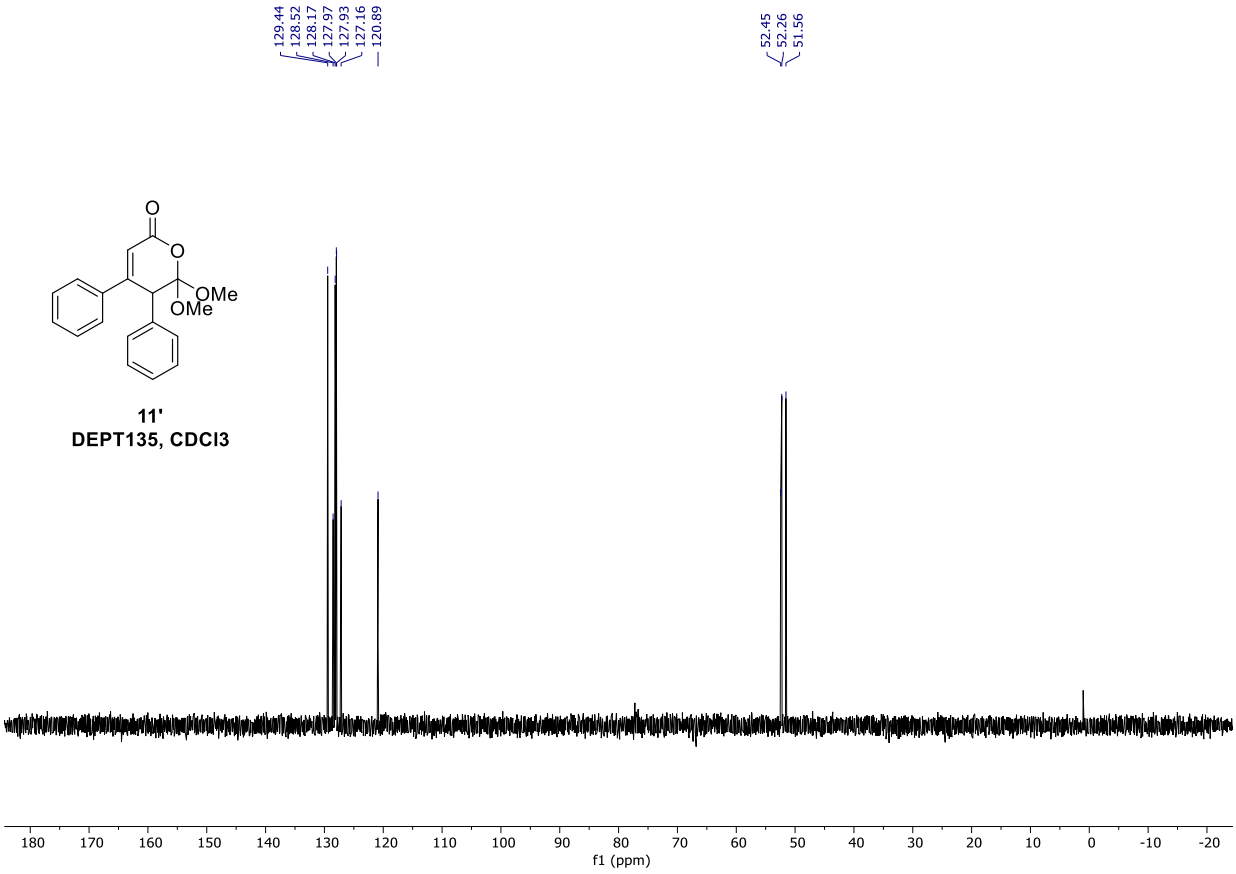

7.26 CHCl3
7.15
7.15
7.14
7.14
7.14
7.14
7.13
7.13
7.12
7.12
7.12
7.11
7.11
7.10
7.10
7.10
7.06
7.05
7.05
7.05
7.04
7.04
7.04
7.03
7.03
7.03
7.02
7.02
7.02
7.02
3.89
3.75
3.69
O
O
OMe
OMe
11
1H NMR
400 MHz, CDCl3
6.00
4.01
2.01
3.00
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

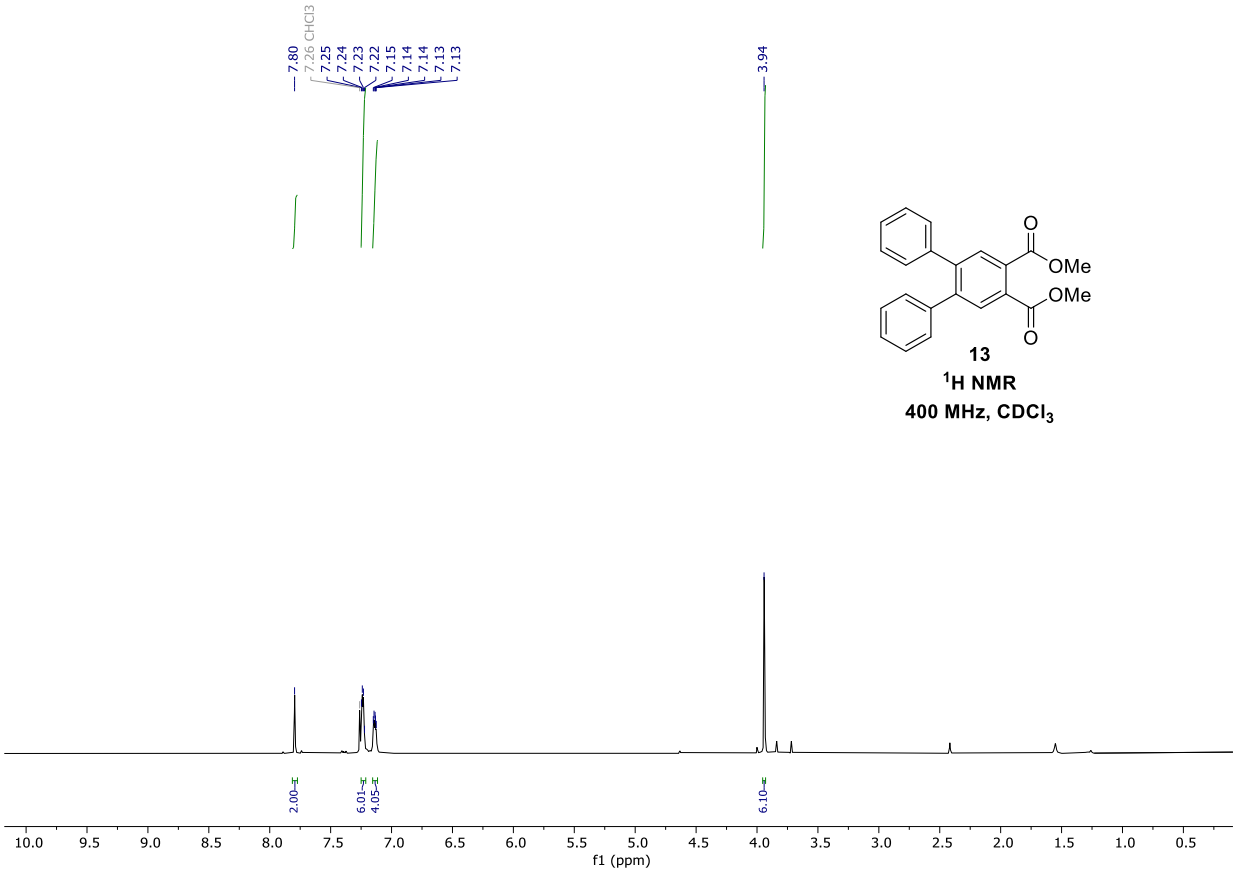

171.04
168.90
143.86
141.13
137.08
134.60
130.32
128.84
128.06
127.85
127.48
127.20
52.31
52.18
41.79
O
O
OMe
OMe
11
13C NMR
101 MHz, CDCl3
52.31
52.18
53.0
52.5
52.0
51.5
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

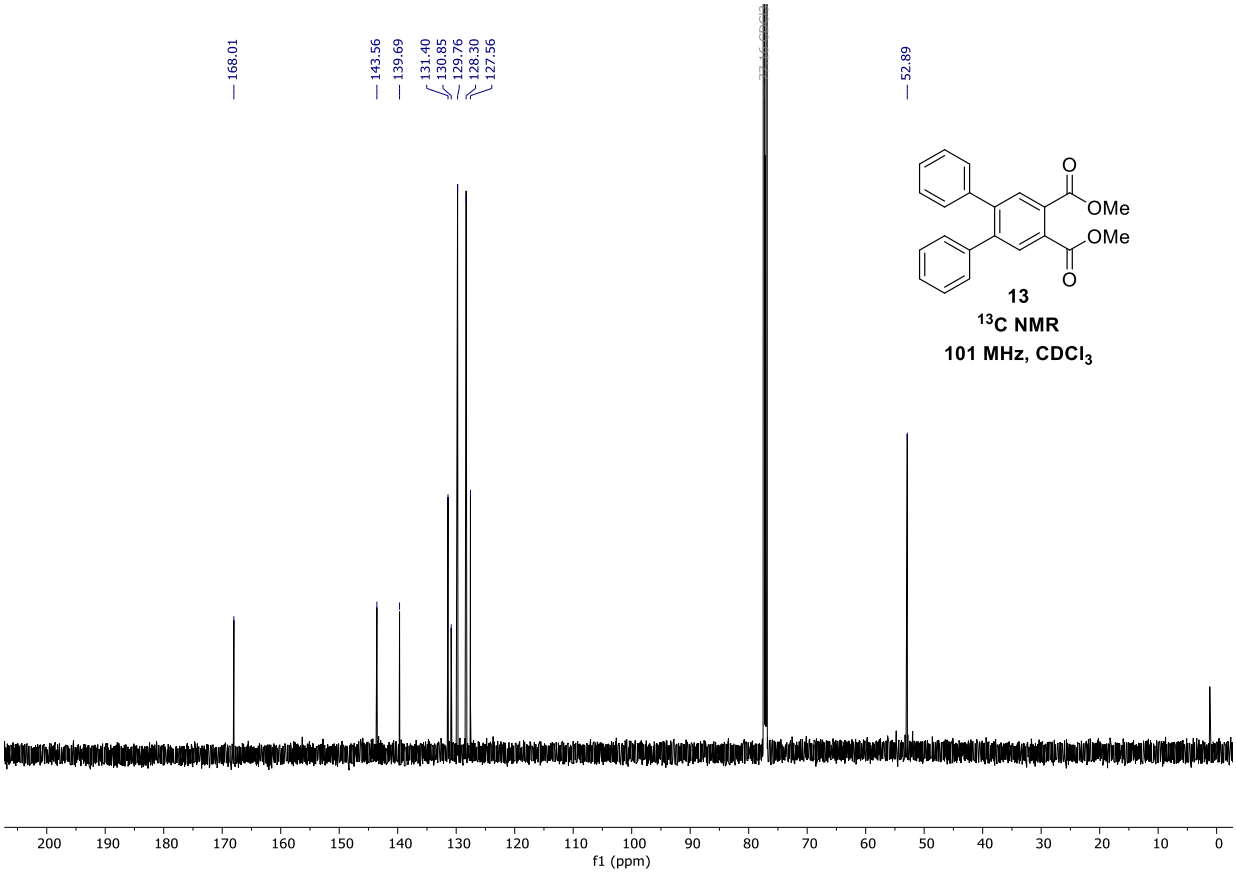

130.19
128.71
127.93
127.72
127.35
127.06
52.18
52.05
O
O
OMe
OMe
11
DEPT135, CDCl3
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)


7.26 CHCl3
7.25
7.24
7.23
7.22
7.21
7.20
7.19
7.18
7.17
7.16
7.15
7.14
6.42
6.19
3.77
3.69
O
O
OMe
OMe
11'
1H NMR
400 MHz, CDCl3
10.00
1.00
1.00
3.01
3.00
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
f1 (ppm)


172.09
166.62
156.27
140.00
136.26
129.58
128.66
128.31
128.11
128.06
127.29
121.02
52.59
52.40
51.69
O
O
OMe
OMe
11'
1H NMR
400 MHz, CDCl3
53
52
51
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


129.44
128.52
128.17
127.97
127.93
127.16
120.89
52.45
52.26
51.56
O
O
OMe
OMe
11'
DEPT135, CDCl3
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

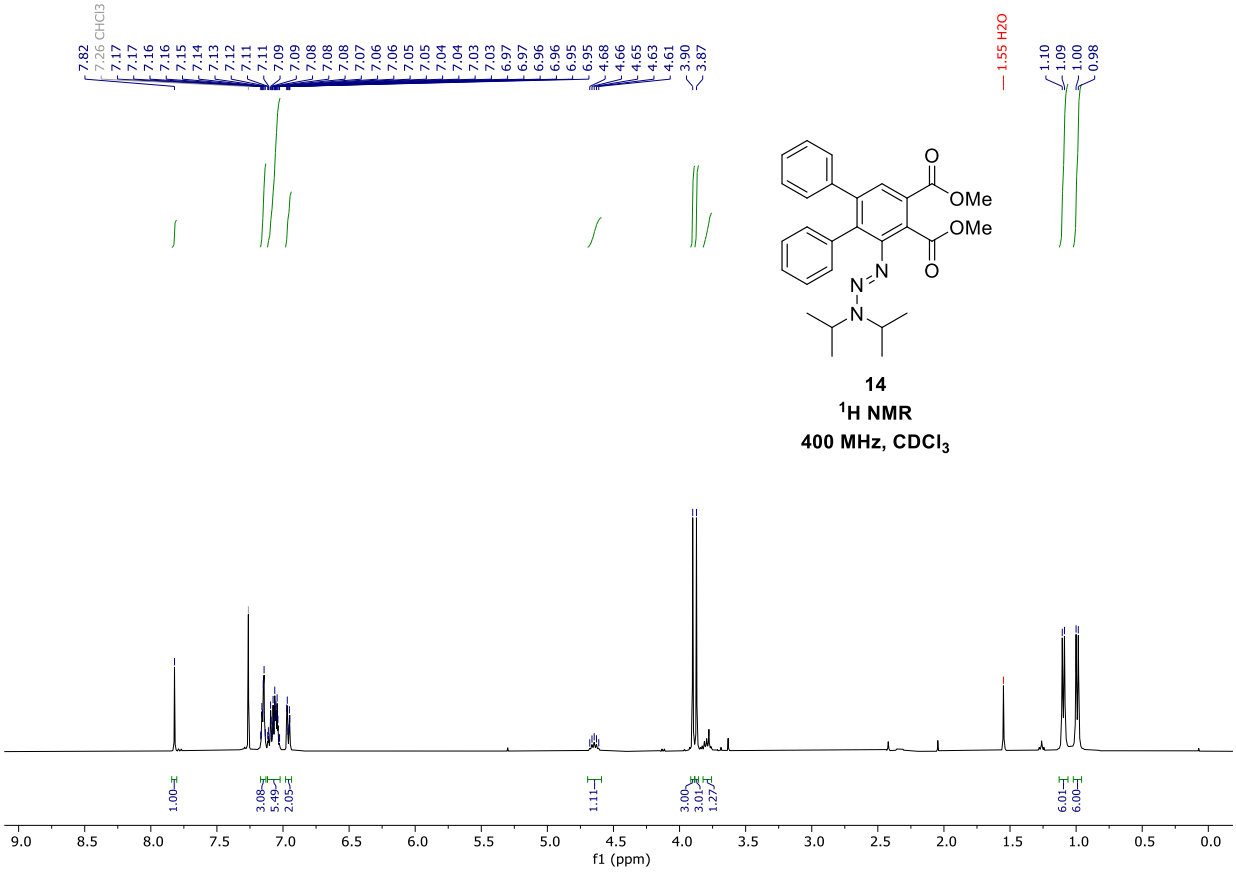

7.80
7.26 CHCl3
7.25
7.24
7.23
7.22
7.15
7.14
7.14
7.13
7.13
3.94
O
OMe
OMe
O
13
1H NMR
400 MHz, CDCl3
2.00
6.01
4.05
6.10
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)



13

^{13}C NMR

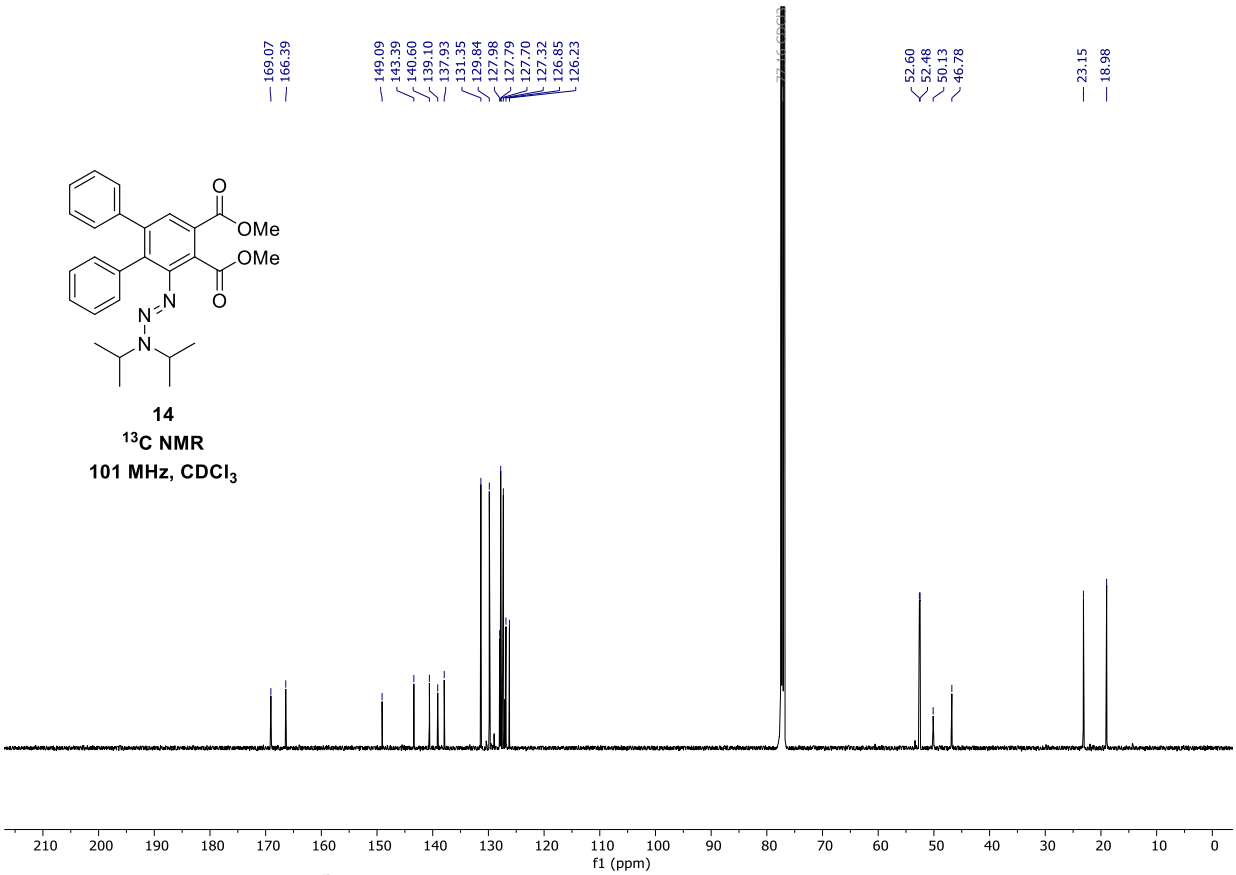
101 MHz, $CDCl_3$



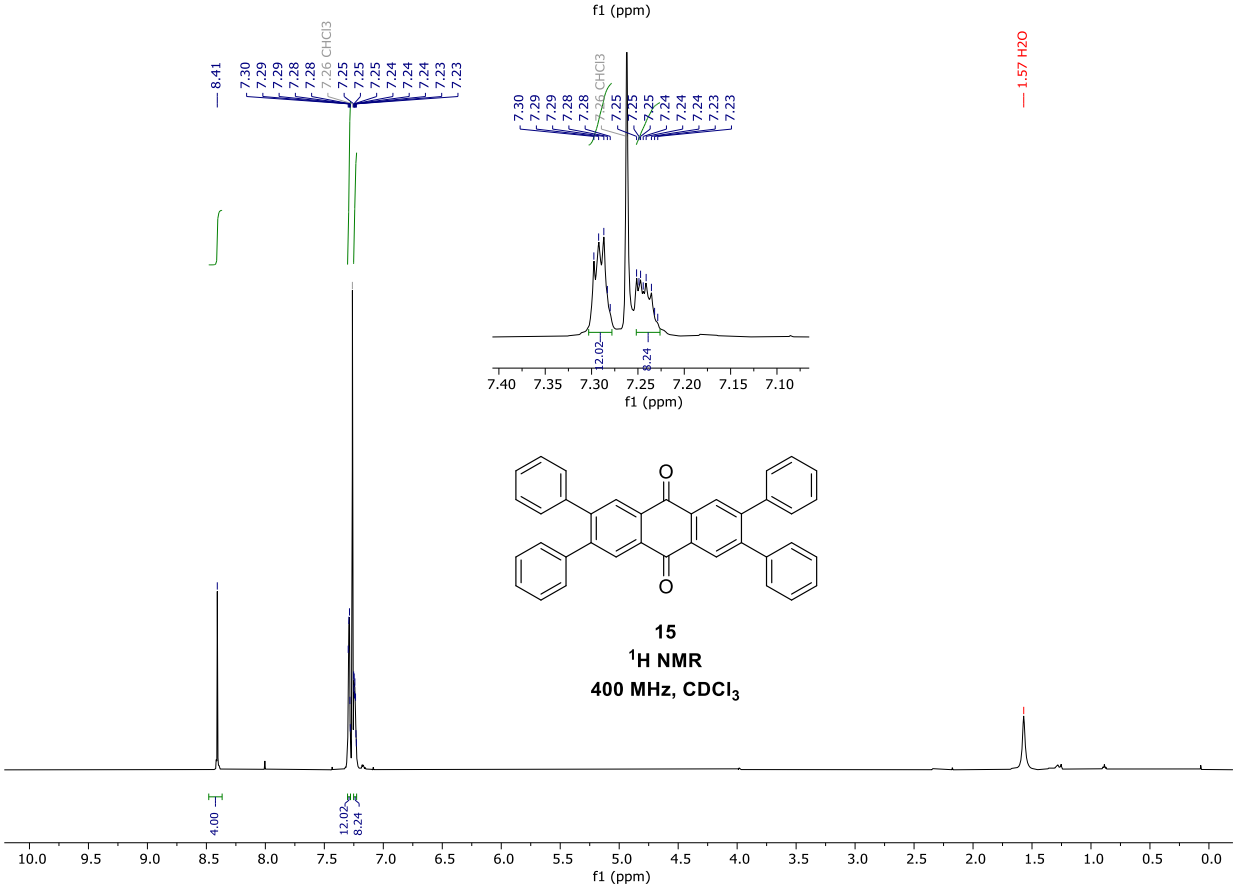
14

^{1}H NMR

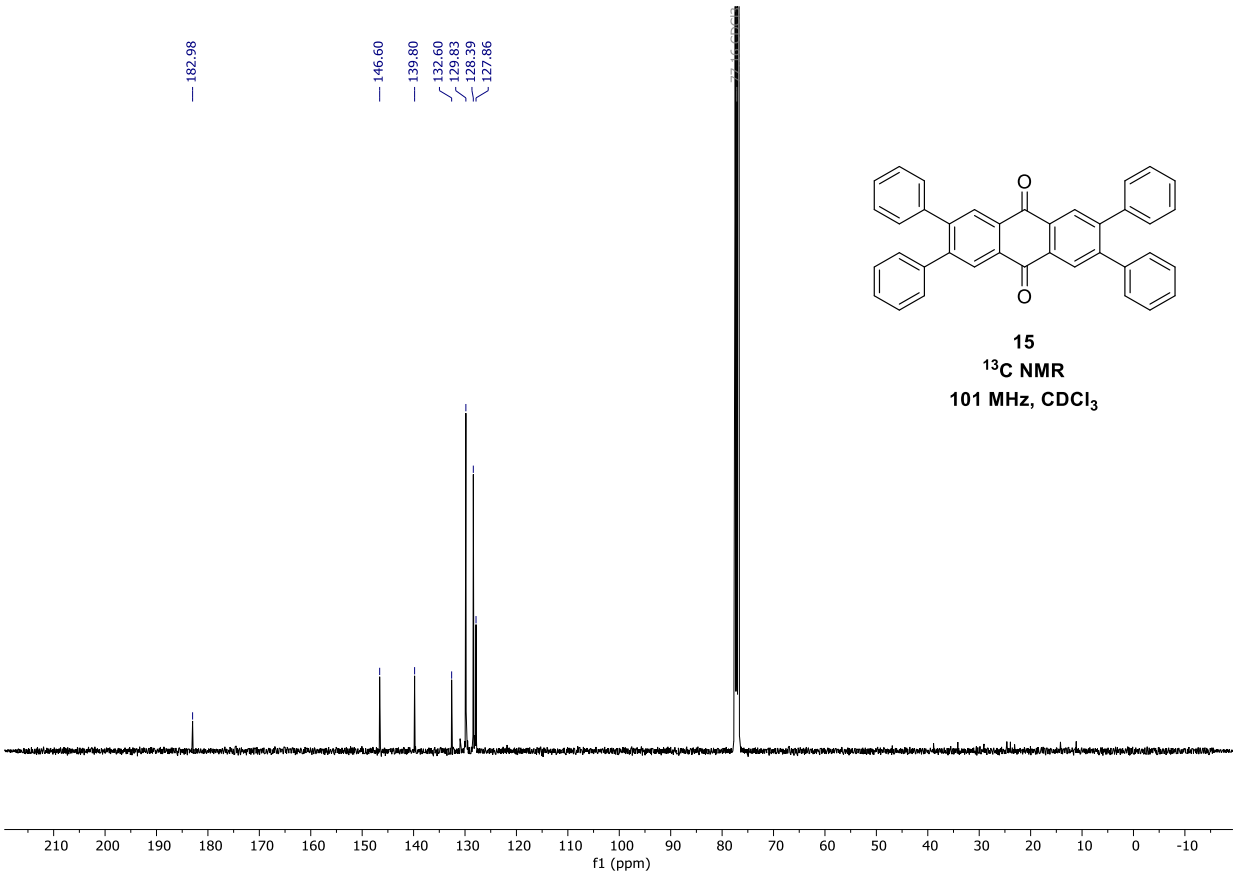
400 MHz, $CDCl_3$



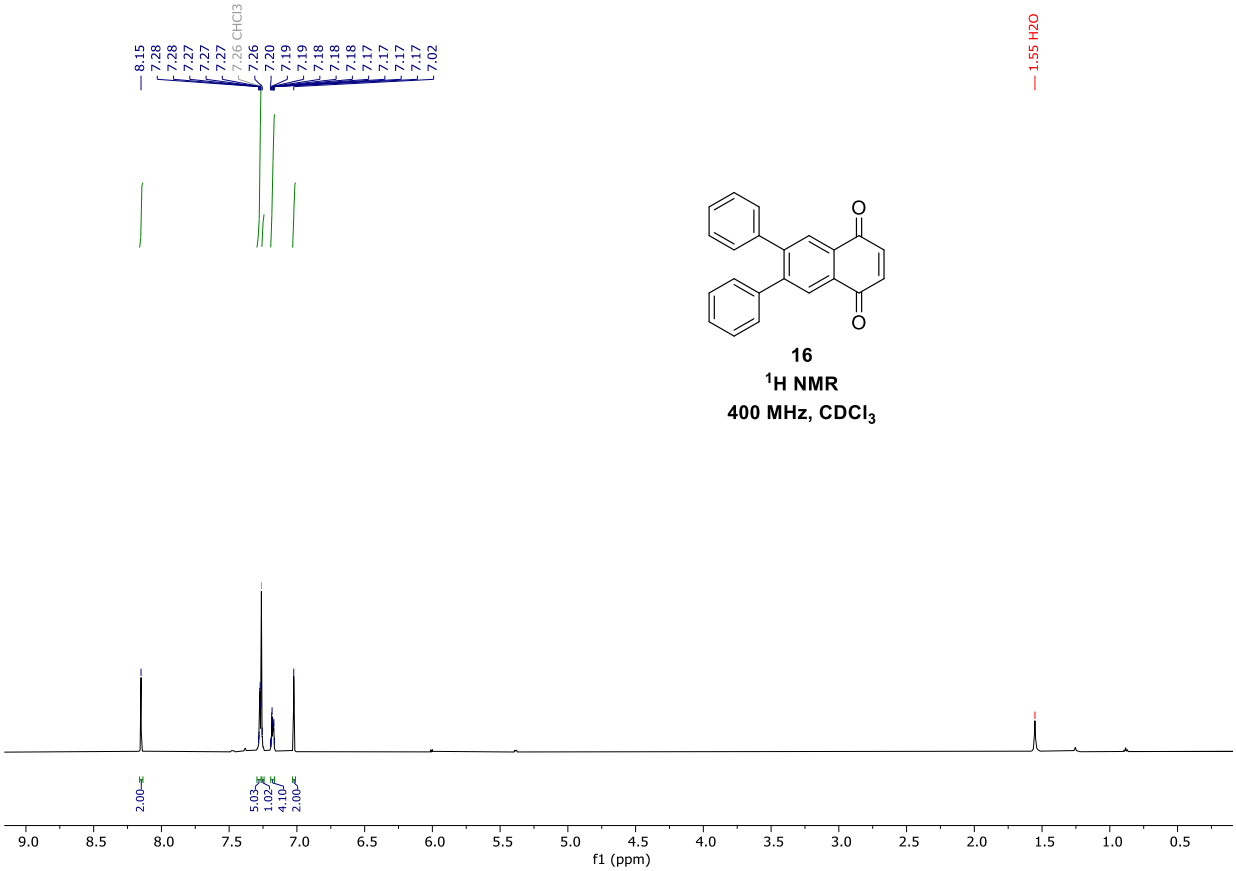
14
^{13}C NMR
101 MHz, $CDCl_3$



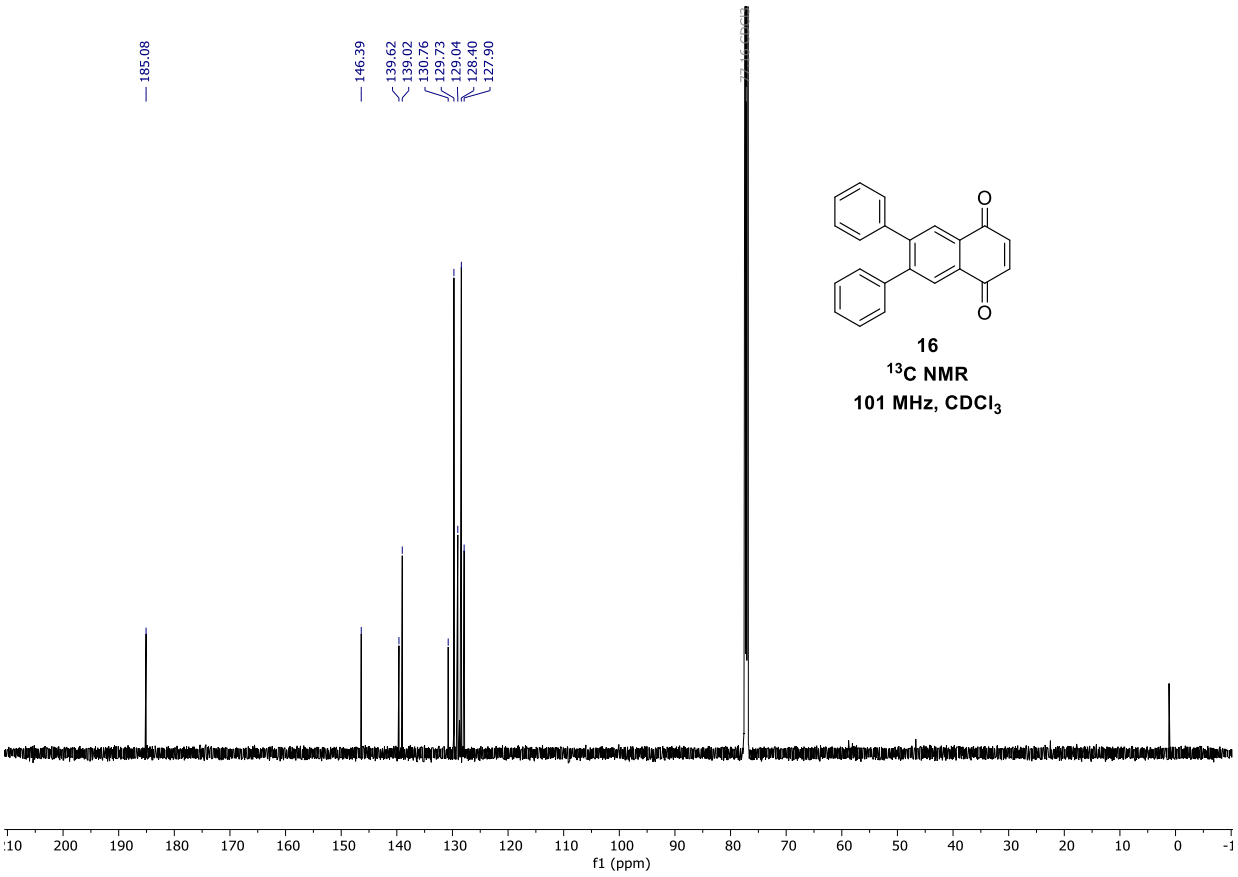
15
^{1}H NMR
400 MHz, $CDCl_3$



15
^{13}C NMR
101 MHz, $CDCl_3$



16
^{1}H NMR
400 MHz, $CDCl_3$


185.08
146.39
139.62
139.02
130.76
129.73
129.04
128.40
127.90
O
O
16
13C NMR
101 MHz, CDCl3
f1 (ppm)

12. References:

(1) L. Jia, Y. Wang, Y. Wang, Y Qin, C. Hu, J. Sheng and S. Ma, *Bioorg. Med. Chem. Lett.*, 2018, **28**, 2471−2476.

(2) M. Ohashi, K. Gamo, Y. Tanaka, M. Waki, Y. Beniyama, K. Matsuno, J. Wada, M. Tenta, J. Eguchi, M. Makishima, N. Matsuura, T. Oyama and H. Miyachi, *Eur. J. Med. Chem.*, 2015, **90**, 53−67.

(3) J.-L. Pan, T.-Q. Liu, C. Chen, Q.-Z. Li, W. Jiang, T.-M. Ding, Z.-Q. Yan and G.-D. Zhu, *Org. Biomol. Chem.*, 2019, **17**, 8589–8600.

(4) Y. Yun, J. Yang, Y. Miao, X. Wang and J. Sun, *Bioorg. Med. Chem. Lett.*, 2020**, 30**, 126900

(5) G. Kiefer, T. Riedel, P. J. Dyson, R. Scopelliti and K. Severin, *Angew. Chem. Int. Ed.*, 2015, **54**, 302−305; *Angew. Chem.*, 2015, **127**, 306–310.

(6) J.-F. Tan, C. T. Bormann, F. G. Perrin, F. M. Chadwick, K. Severin and N. Cramer, *J. Am. Chem. Soc.*, 2019, **141**, 10372–10383.

(7) S. Fu, N.-Y. Chen, X. Liu, Z. Shao, S.-P. Luo and Q. Liu, *J. Am. Chem. Soc.*, 2016, **138**, 8588–8594.

(8) D. Bailey and V. E. Williams, *Tetrahedron Lett.*, 2004, **45**, 2511–2513.