Supplementary Information (SI) for RSC Advances.

Electrochemical oxidative CF_3 radical-induced lactonization and etherification of terminal and internal alkenes.

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Supporting Information Placeholder

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1. General information

Commercially available reagents (reagent grade, >99%) were purchased from Sigma Aldrich, Fluorochem and TCI Chemicals and used without any further purification.

Solvents (acetonitrile (ACN), dichloromethane (DCM), diethylether (Et_2O), tetrahydrofuran (THF), ethyl acetate (AcOEt) are commercially available and solvent for reaction were used after degassing.

Acetonitrile used for electrochemical reactions was dried over activated molecular sieves for 24 hours and degassed with N_2 prior to use. The yield of final products was determined using trifluorotoluene ($PhCF_3$) as an internal standard for ^{19}F NMR, unless otherwise noted.

^1H NMR, ^{13}C NMR and ^{19}F NMR spectra were recorded on Varian 400-MR (400 MHz) (equipped with autoswitchable PFG probe) and Bruker Avance Neo 600 MHz (equipped with CryoProbe Prodigy Broadband 5mm) spectrometers. NMR multiplicities are abbreviated as follows: s = singlet, d = doublet, t =triplet, q = quartet, spt = septet, m = multiplet, bs = broad signal. Coupling constants *J* are given in Hz. All ^1H and ^{13}C chemical shifts are calibrated to residual protic-solvents, while ^{19}F chemical shifts were referenced to the internal standard trifluorotoluene.

HRMS spectra were obtained with a G2XS QTof mass spectrometer using either ESI or APCI ionization techniques.

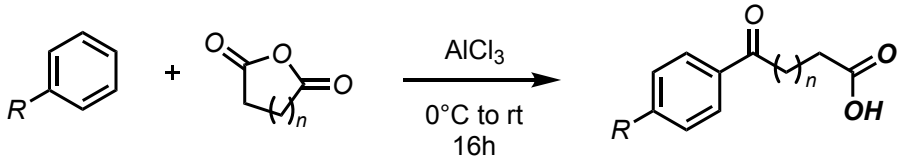
HPLC-UV analyses were recorded with an Agilent 1260 InfinityLab instrument. Column: Zorbax® SB-C18; particle size 5 µm; pore size 100 Å; length 250 mm, internal diameter: 4.6 mm. Mobile phase A: H_2O, mobile phase B: ACN. Gradient (Time(min), %B): 0, 80; 25, 80; 28, 10; 30, 10; flow 0.5 mL min^{-1}column temperature 30°C; injection volume: 10 µL.

GC-MS analyses were recorded with a Hewlett-Packard 5971 spectrometer with GC injection and EI ionization at 70 eV coupled with an Agilent Technologies MSD1100 single-quadrupole mass spectrometer, reported as: m/z (rel. intensity).

Cyclovoltammetry experiments were carried out using the Rodeostat 2.0 apparatus using a Glassy Carbon (GC) as working electrode, Pt as counter electrode and Fc/Fc+ (0.1 M in CH_3CN) as internal standard.

2. Synthesis of starting materials

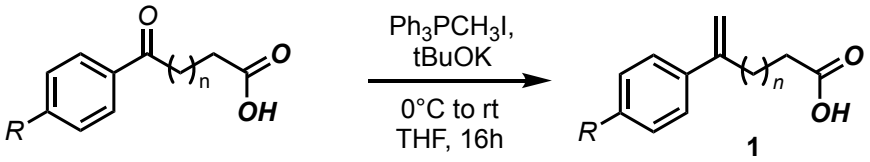
A) Procedure for the synthesis of linear alkenes with acid moiety[1]



1) To an oven-dried 20 mL Schlenk purged under argon atmosphere, the selected arene (8.0 equiv.) was added along with the corresponding anhydride (1.0 equiv). The solution was stirred until the anhydride was fully dissolved. The solution was cooled to 0 °C, and $AlCl_3$ (2.2 equiv) was slowly added. The reaction was

stirred for 30 minutes at room temperature and an additional 30 minutes under reflux, with the reaction progress monitored by TLC.

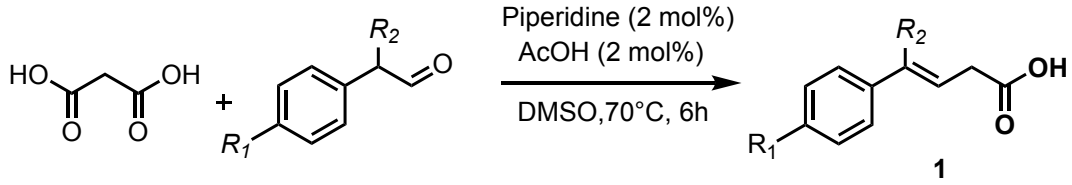
Upon complete consumption of the starting material, the reaction was cooled to room temperature and quenched with the addition of 2M HCl at 0°C. Excess of the arene was removed under reduced pressure. The precipitate was filtered and washed with 1M HCl. The filtrate was dried under vacuum to obtain the selected product without need for any purification.



2) To an oven-dried 20 mL Schlenk purged under argon atmosphere, methyltriphenylphosphonium iodide Ph_3PCH_3I (1.3 equiv) was dissolved in 10 mL of anhydrous THF. Once the solid was fully dissolved, the solution was cooled to 0 °C, and of potassium tert-butoxide tBuOK (2.6 equiv.) was slowly added. The reaction mixture was stirred at room temperature for 30 minutes and then the selected keto acid prepared from Procedure 1) was slowly added. The reaction mixture was stirred for 16h at room temperature.

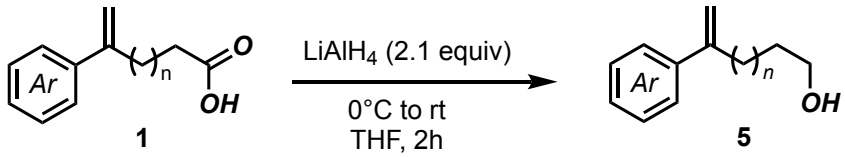
Upon completion, the reaction was quenched and diluted with a 10% w/w aqueous NaOH solution. The THF was evaporated under reduced pressure, and the remaining aqueous solution was basified with $NaHCO_3$ and washed three times with DCM to remove the triphenylphosphine oxide byproduct. It was then acidified to pH close to 1 by the slow addition of 6M HCl. The aqueous phase was washed three more times with DCM. The combined organic phases were evaporated under reduced pressure, and the residue was purified by silica gel column chromatography.

B) Procedure for the synthesis of internal alkenes with acid moiety[2]



To an oven-dried 20 mL Schlenk purged under argon atmosphere, the aldehyde (10.0 mmol, 1.1 equiv) and malonic acid (22.0 mmol, 2.2 equiv) were dissolved in DMSO (10 mL). A catalytic amount of piperidine (2 mol%) and acetic acid (2 mol%) was added. The resulting mixture was stirred at room temperature for 20 minutes and then heated to 70°C for 6 hours. After cooling to room temperature, the reaction was quenched with water, and the product was extracted with diethyl ether (Et_2O). The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure to obtain the crude product. The residue was purified by silica gel column chromatography.

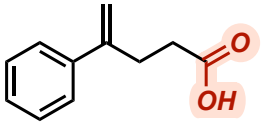
C) Procedure for the synthesis of alkenes with hydroxy moiety[3]



The carboxylic acid **1** was dissolved in 20 mL of THF and added to an oven-dried 50 mL Schlenk purged under argon atmosphere. At this point, 2.1 equiv of $LiAlH_4$ was slowly added to the solution at 0 ºC. The reaction mixture was stirred at 0 ºC for 1 h, allowed to warm to rt and stirred for 2 h. After completion (the progress of the reaction was monitored by TLC, 7:3 Hex:EtOAc.), 10% NaOH was added until no gas evolution was observed. The resultant suspension was stirred for another 30 min at rt. After filtration trough celite and evaporation of the solvent the corresponding alcohol **5** was obtained through flash column chromatography 9:1 to 7:3 Hex:EtOAc.

Substrate characterization

4-phenylpent-4-enoic acid (**1a**)

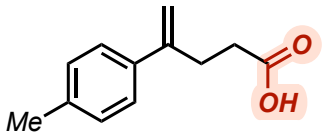


(70%) Compound synthetized following Procedure A

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (m, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 2H), 3.31 (t, *J* = 6.6 Hz, 2H), 2.81 (t, *J* = 6.6 Hz, 2H). **^{13}C NMR** (151 MHz, $CDCl_3$): δ 180.1, 146.4, 140.2, 128.6, 127.9, 126.1, 113.0, 33.1, 30.2.

^{1}H and ^{13}C NMR in agreement with data reported in literature[1]

4-(p-tolyl)pent-4-enoic acid (**1b**)

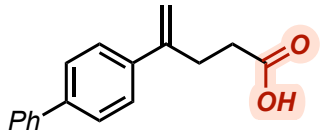


(75%) Compound synthetized following Procedure A

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, J = 8.0 Hz, 2H), 7.26-7.25 (m, 2H), 3.29 (t, J = 6.6, 2H), 2.81 (t, J = 6.6, 2H), 2.41 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 179.9, 146.5, 137.7, 137.6, 129.1, 126.1, 112.1, 33.3, 30.2, 21.2.

^{1}H and ^{13}C NMR in agreement with data reported in literature[1]

4-([1,1'-biphenyl]-4-yl)pent-4-enoic acid (**1c**)

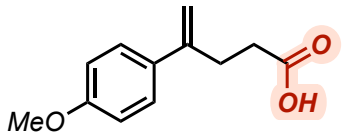


(63%) Compound synthetized following Procedure A

^{1}H NMR (400MHz, DMSO-d_6) δ 12.10 (brs, 1H), 7.66-7.61 (m, 4H), 7.51 (d, J = 8.3Hz, 2H), 7.44 (t, J = 7.7Hz, 2H), 7.33 (t, J = 7.35Hz, 1H), 5.39 (s, 1H), 5.1 (s, 1H), 2.74 (t, J = 7.56Hz, 2H), 2.37 (t, J = 7.56Hz, 2H). **^{13}C NMR** (100 MHz, DMSO-d_6) δ 174.2, 146.4, 140.0, 139.8, 139.5, 129.4, 127.9, 127.1, 126.9, 126.7, 112.9, 33.2, 30.0.

^{1}H and ^{13}C NMR in agreement with data reported in literature[4]

4-(4-methoxyphenyl)pent-4-enoic acid (**1d**)

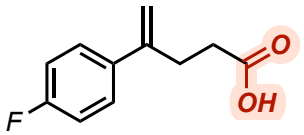


(71%) Compound synthetized following Procedure A

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, J = 8.0 Hz, 2H) 6.87 (d, J = 8.0 Hz, 2H) 5.26 (s, 1H),, 5.03 (s, 1H), 3.82 (s, 3H), 2.83 (t, J = 7.2 Hz, 2H), 2.53 (t, J = 7.2 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 30.1, 32.9, 55.3, 111.4, 113.7, 127.1, 132.7, 145.7, 159.2, 179.0.

^{1}H and ^{13}C NMR in agreement with data reported in literature[1]

4-(4-fluorophenyl)pent-4-enoic acid (**1e**)

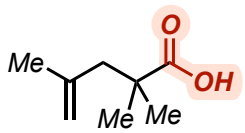


(68%) Compound synthetized following Procedure A

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06-7.97 (m, 2H), 7.20-7.07 (m, 2H), 3.28 (t, J = 6.6 Hz, 2H), 2.80 (t, J = 6.6 Hz, 2H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 179.8, 162.6 (d, J = 246.6 Hz), 145.8, 136.5 (d, J = 3.3 Hz), 127.9 (d, J = 8.0 Hz), 115.5 (d, J = 21.3 Hz), 113.2, 33.1, 30.4.

^{1}H and ^{13}C NMR in agreement with data reported in literature[1]

2,2,4-trimethylpent-4-enoic acid (**1h**)

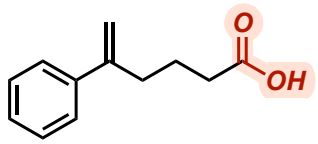


(50%) Compound synthetized following Procedure A

^{1}H NMR (400 MHz, $CDCl_3$): δ 4.82–4.80 (m, 1H), 4.71–4.67 (m, 1H), 2.33 (s, 2H), 1.71–1.68 (m, 3H), 1.21 (s, 6H) **^{13}C NMR** (151 MHz, $CDCl_3$) δ 185.3, 142.2, 114.4, 48.2, 42.0, 25.3, 23.5.

^{1}H and ^{13}C NMR in agreement with data reported in literature[6]

5-phenylhex-5-enoic acid (**1i**)

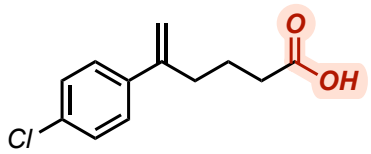


(65%) Compound synthetized following Procedure A

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46-7.42 (m, 2H), 7.38-7.33 (m, 2H), 7.32-7.28 (m, 1H), 5.35 (d, J = 1.3 Hz, 1H), 5.12 (d, J = 1.4 Hz, 1H), 2.62 (td, J = 7.5, 1.2 Hz, 2H), 2.41 (t, J = 7.4 Hz, 2H), 1.82 (p, J = 7.5 Hz, 2H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 180.1, 147.5, 140.9, 128.4, 127.7, 126.4, 113.1, 34.6, 33.5, 23.2.

^{1}H and ^{13}C NMR in agreement with data reported in literature[1]

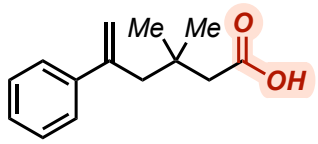
5-(4-chlorophenyl)hex-5-enoic acid (**1j**)



(58%) Compound synthetized following Procedure A

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.76 (bs, 1H), 7.28−7.38 (m, 4H), 5.31 (d, J = 1.3 Hz, 1H), 5.11 (d, J = 2.0 Hz, 1H), 2.55 (t, J = 7.5 Hz, 2H), 2.39 (t, J = 7.4 Hz, 2H), 1.79 (p, J = 7.4 Hz, 2H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 179.6, 146.2, 139.1, 133.3, 128.5, 127.4, 113.6, 34.3, 33.2, 22.9.

3,3-dimethyl-5-phenylhex-5-enoic acid (**1k**)

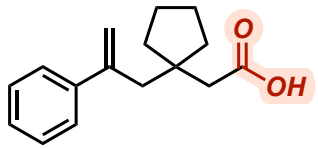


(65%) Compound synthetized following Procedure A

^{1}H NMR (400 MHz, $CDCl_3$): δ= 7.39-7.25 (m, 5H), 5.30 (d, J = 1.8 Hz, 1H), 5.10-5.09 (m, 1H), 2.64 (s, 2H), 2.18 (s, 2H), 0.91 ppm (s, 6H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 179.4, 146.7, 143.2, 128.1, 127.4, 126.6, 117.7, 46.8, 46.0, 34.3, 27.9.

^{1}H and ^{13}C NMR in agreement with data reported in literature[1]

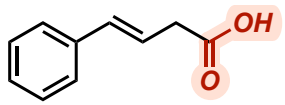
2-(1-(2-phenylallyl)cyclopentyl)acetic acid (**1l**)



(62%) Compound synthetized following Procedure A

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.28 (m, 5H), 5.26 (d, *J* = 2.0 Hz, 1H), 5.14 (d, *J* = 2.0 Hz, 1H), 2.78 (d, J = 0.9 Hz, 2H), 2.29 (s, 2H), 1.58 (d, J = 4.7 Hz, 8H). **^{13}C NMR** (101 MHz, cdcl3) δ 177.75, 140.18, 138.65, 137.06, 129.08, 125.82, 117.69, 34.19, 21.19, 16.39.

(E)-4-phenylbut-3-enoic acid (**1m**)

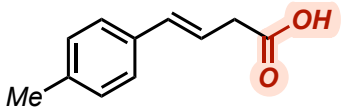


(78%) Compound synthetized following Procedure B

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.02 (br, 1H), 7.38 (d, J = 7.3 Hz, 2H), 7.31 (t, J = 7.7 Hz, 2H), 7.26 – 7.21 (m, 1H), 6.53 (d, J = 15.9 Hz, 1H), 6.35 – 6.24 (m, 1H), 3.30 (dd, J = 7.1, 1.2 Hz, 2H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 178.2, 136.9, 134.2, 128.8, 127.9, 126.6, 121.1, 38.3.

^{1}H and ^{13}C NMR in agreement with data reported in literature[1]

(E)-4-(p-tolyl)but-3-enoic acid (**1n**)

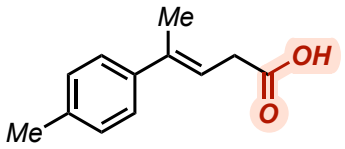


(80%) Compound synthetized following Procedure B

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (d, J = 8.2 Hz, 2H), 7.12 (d, J = 7.8 Hz, 2H), 6.49 (d, J = 15.7 Hz, 1H), 6.33 – 6.12 (m, 1H), 3.28 (d, J = 7.0 Hz, 2H), 2.34 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 177.8, 137.4, 133.9, 129.4, 126.3, 119.8, 38.1, 21.3

^{1}H and ^{13}C NMR in agreement with data reported in literature[1]

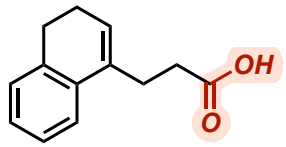
(E)-4-(p-tolyl)pent-3-enoic acid (**1o**)



(45%) Compound synthetized following Procedure B

^{1}H NMR (400 MHz, cdcl3) δ 7.30 (d, J = 8.1 Hz, 2H), 7.13 (d, J = 8.0 Hz, 2H), 5.93 – 5.87 (t, 1H), 3.30 (d, J = 7.1 Hz, 2H), 2.34 (s, 3H), 2.07 – 2.04 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 177.75, 140.18, 138.65, 137.06, 129.08, 125.82, 117.69, 34.19, 21.19, 16.39.

3-(3,4-dihydronaphthalen-1-yl)propanoic acid (**1p**)

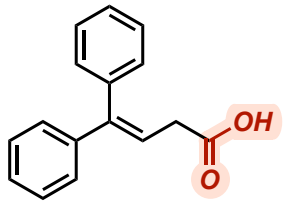


(20%) Compound synthetized following literature procedure[7]

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.25–7.16 (m, 2H), 7.15 (d, J = 0.8 Hz, 2H), 5.90 (t, J = 4.4 Hz, 1H), 2.81 (t, J = 7.6 Hz, 2H), 2.74 (t, J = 7.6 Hz, 2H), 2.62–2.59 (m, 2H), 2.28–2.22 (m, 2H), 1.26 (s, 1H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ: 179.7, 136.8, 134.7, 134.2, 127.8, 126.9, 126.5, 125.3, 122.3, 33.3, 28.3, 27.6, 23.1

^{1}H and ^{13}C NMR in agreement with data reported in literature[7]

4,4-diphenylbut-3-enoic acid (**1q**)

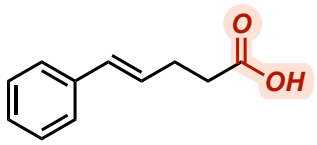


(80%) Compound synthetized following Procedure B

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.14 (m, 10H), 6.23 (t, J = 7.4 Hz, 1H), 3.22 (d, J = 7.4 Hz, 2H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 178.3, 145.4, 141.8, 139.1, 129.8, 128.5, 128.3, 127.6, 127.5, 119.5, 35.3.

^{1}H and ^{13}C NMR in agreement with data reported in literature[1]

(E)-5-phenylpent-4-enoic acid (**1r**)

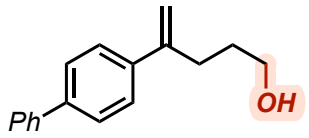


(81%) Compound synthetized following Procedure B

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33-7.35 (m, 2H), 7.28-7.31 (m, 2H), 7.19 (tt, J = 6.5 Hz, 1.5 Hz, 1H), 6.43 (d, J = 16.0 Hz, 1H), 6.18-6.25 (m, 1H), 2.55 (d, J = 3.0 Hz, 4H). **^{13}C NMR** (125 MHz, CDCl3) δ 179.0, 137.4, 131.3, 128.7, 128.1, 127.4, 126.2, 33.8, 28.1.

^{1}H and ^{13}C NMR in agreement with data reported in literature[5]

4-([1,1'-biphenyl]-4-yl)pent-4-en-1-ol (**5a**)

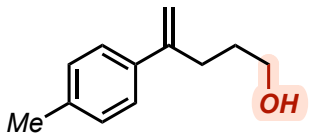


(77%) Compound synthetized following Procedure C

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62–7.51 (m, 4H), 7.48 (d, J = 8.5 Hz, 2H), 7.42 (t, J = 7.5 Hz, 2H), 7.32 (t, J = 7.3 Hz, 1H), 5.36 (s, 1H), 5.13–5.09 (m, 1H), 3.66 (t, J = 6.4 Hz, 2H), 2.62 (t, J = 7.6 Hz, 2H), 1.75 (dt, J = 13.9, 6.5 Hz, 2H), 1.50 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 147.5, 140.7, 140.3, 139.8, 128.7, 127.4, 127.0, 126.5, 112.6, 62.4, 31.5, 31.3

^{1}H and ^{13}C NMR in agreement with data reported in literature[8]

4-(p-tolyl)pent-4-en-1-ol (**5b**)

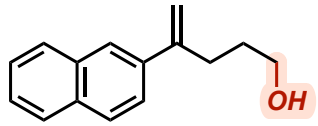


(67%) Compound synthetized following Procedure C

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (d, J = 8.2 Hz, 2H), 7.15 (d, J = 7.9 Hz, 2H), 5.27 (d, J = 1.5 Hz, 1H), 5.05 (q, J = 1.4 Hz, 1H), 3.66 (t, J = 6.4 Hz, 2H), 2.60 (t, J = 7.6 Hz, 2H), 2.35 (s, 3H), 1.77 – 1.69 (m, 2H), 1.63 (br s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 147.7, 138.0, 137.1, 129.0, 125.9, 111.8, 62.4, 31.5, 31.1, 21.0.

^{1}H and ^{13}C NMR in agreement with data reported in literature[9]

4-(naphthalen-2-yl)pent-4-en-1-ol (**5c**)

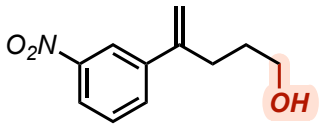


(60%) Compound synthetized following Procedure C

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79-7.84 (m, 4H) 7.59 (dd, J = 1.6, 8.8 Hz, 1H), 7.45-7.48 (m, 2H), 5.45 (d, J = 1.2 Hz, 1H), 5.21 (d, J = 1.2 Hz, 1H), 3.68- 3.72 (m, 2H), 2.73 (t, J = 7.2 Hz, 2H), 1.79 (tt, J = 7.2, 7.2 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 147.8 138.2, 133.4, 132.8, 128.1, 127.9, 127.5, 126.1, 125.8, 124.7, 124.6, 113.1, 62.4, 31.5, 31.2.

^{1}H and ^{13}C NMR in agreement with data reported in literature[9]

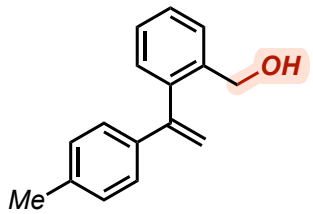
4-(3-nitrophenyl)pent-4-en-1-ol (**5d**)



(86%) Compound synthetized following Procedure C

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (t, J = 2.0 Hz, 1H), 8.12 (m, 1H), 7.74 (m, 1H), 7.50 (t, J = 8.0 Hz, 1H), 5.43 (d, J = 0.8 Hz, 1H), 5.26 (q, J = 1.2 Hz, 1H), 3.70 (t, J = 6.3 Hz, 2H), 2.69 – 2.52 (m, 2H), 1.74 (ddt, J = 8.8, 7.6, 6.4 Hz, 2H).

(2-(1-(p-tolyl)vinyl)phenyl)methanol (**5e**)

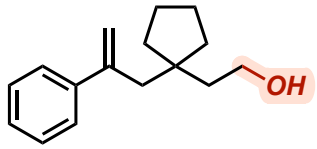


(65%) Compound synthetized following Procedure C

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58-7.49 (m, 1H), 7.46-7.24 (m, 3H), 7.25-7.10 (m, 4H), 5.79 (d, J = 1.2 Hz, 1H), 5.23 (d, J = 1.2 Hz, 1H), 4.47 (d, J = 6.3 Hz, 2H), 2.36 (s, 3H),1.47 (t, J = 6.3 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 148.3, 140.9, 138.8, 138.1, 138.0, 130.4, 129.4, 128.4, 128.2, 127.8, 126.6, 114.9, 63.5, 21.3

^{1}H and ^{13}C NMR in agreement with data reported in literature[10]

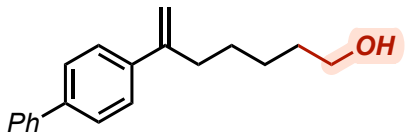
2-(1-(2-phenylallyl)cyclopentyl)ethan-1-ol (**5f**)



(70%) Compound synthetized following Procedure C

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.28 (m, 2H), 7.27 (d, J = 1.6 Hz, 2H), 7.25 – 7.22 (m, 1H), 5.22 (d, J = 1.9 Hz, 1H), 5.12 – 5.04 (m, 1H), 3.60 (t, J = 7.7 Hz, 2H), 2.54 (d, J = 0.9 Hz, 2H), 1.72 – 1.14 (m, 10H).

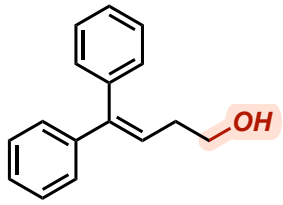
6-([1,1'-biphenyl]-4-yl)hept-6-en-1-ol (**5g**)



(62%) Compound synthetized following Procedure C

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 – 7.54 (m, 4H), 7.51 – 7.40 (m, 4H), 7.34 (t, J = 7.3 Hz, 1H), 5.34 (d, J = 1.4 Hz, 1H), 5.09 (d, J = 1.4 Hz, 1H), 3.68 – 3.59 (m, 2H), 2.56 (t, J = 7.5 Hz, 2H), 1.63 – 1.56 (m, 2H), 1.53 – 1.38 (m, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 147.87, 140.68, 140.12, 140.04, 128.77, 127.25, 126.93, 126.47, 112.22, 62.68, 35.18, 32.50, 28.09, 25.48.

4,4-diphenylbut-3-en-1-ol (**5h**)



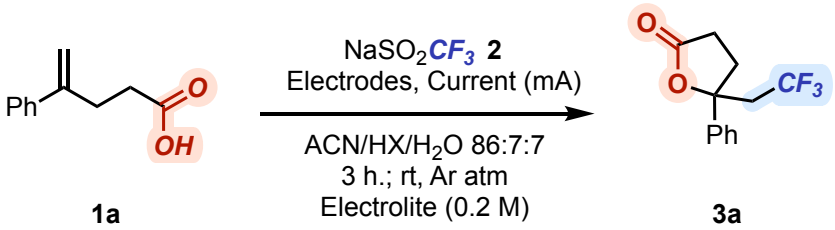
(69%) Compound synthetized following Procedure C

^{1}H NMR (500 MHz, $CDCl_3$) 7.33-7.35 (m, 2H), 7.28-7.31 (m, 2H), 7.19 (tt, J = 6.5 Hz, 1.5 Hz, 1H), 6.43 (d, J = 16.0 Hz, 1H), 6.18-6.25 (m, 1H), 2.55 (d, J = 3.0 Hz, 4H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 179.0, 137.4, 131.3, 128.7, 128.1, 127.4, 126.2, 33.8, 28.1.

^{1}H and ^{13}C NMR in agreement with data reported in literature[11]

3. Optimization study

Table S1:



1a **3a**

Entry[a]	Electrodes	**2** (equiv.)	Current (mA)	HX	Cosolvent	Electrolite	Yield **3a** (%)[b]
1	C(+)/Pt(-)	3	7	-	H_2O (7%)	$LiCLO_4$	34
2	C(+)/Pt(-)	3	7	TFA (7%)	H_2O (7%)	$LiCLO_4$	71
3	C(+)/Ni(-)	3	7	TFA (7%)	H_2O (7%)	$LiCLO_4$	78
4	C(+)/Ni(-)	2	7	TFA (7%)	H_2O (7%)	$LiCLO_4$	76
5	C(+)/Ni(-)	1.5	7	TFA (7%)	H_2O (7%)	$LiCLO_4$	84
6	C(+)/Ni(-)	1.5	7	TFA (5%)	H_2O (7%)	$LiCLO_4$	80
7	C(+)/Ni(-)	1.5	7	TFA (10%)	H_2O (7%)	$LiCLO_4$	85
8	C(+)/Ni(-)	1.5	5	TFA (7%)	H_2O (7%)	$LiCLO_4$	66
9	C(+)/Ni(-)	1.5	10	TFA (7%)	H_2O (7%)	$LiCLO_4$	72
10	RVC(+)/Ni(-)	1.5	7	TFA (7%)	H_2O (7%)	$LiCLO_4$	66
11	Pt(+)/Pt(-)	1.5	7	TFA (7%)	H_2O (7%)	$LiCLO_4$	40
12	C(+)/C(-)	1.5	7	TFA (7%)	H_2O (7%)	$LiCLO_4$	74
13	Pt(+)/Pt(-)	1.5	7	TFA (7%)	H_2O (7%)	$LiCLO_4$	12
14	C(+)/Ni(-)	1.5	7	HFIP (7%)	H_2O (7%)	$LiCLO_4$	60
15	C(+)/Ni(-)	1.5	7	AcOH (7%)	H_2O (7%)	$LiCLO_4$	60
16	C(+)/Ni(-)	1.5	7	TFA (7%)	H_2O (7%)	$TBACLO_4$	81
17	C(+)/Ni(-)	1.5	7	TFA (7%)	H_2O (7%)	$TBAPF_6$	59
18	C(+)/Ni(-)	1.5	7	TFA (7%)	H_2O (7%)	$LiBF_4$	68
19	C(+)/Ni(-)	-	7	TFA (7%)	H_2O (7%)	$LiCLO_4$	-
20	C(+)/Ni(-)	1.5	No current	TFA (7%)	H_2O (7%)	$LiCLO_4$	-
21	C(+)/Ni(-)	1.5	7 (Under air)	TFA (7%)	H_2O (7%)	$LiCLO_4$	65
22	C(+)/Ni(-)	1.5	7	TFA (7%)	-	$LiCLO_4$	89
23	C(+)/Ni(-)	1.5	7	AcOH (7%)	-	$LiCLO_4$	65
24	C(+)/Ni(-)	1.5	7	HFIP (7%)	-	$LiCLO_4$	62
25	C(+)/Ni(-)	1.5	7	-	-	$LiCLO_4$	48
26	C(+)/Ni(-)	1.5	7	TFA (7%)	-	-	60
27	C(+)/Pt(-)	1.5	7	TFA (7%)	-	$LiCLO_4$	67
28	Pt(+)/Pt(-)	1.5	7	TFA (7%)	-	$LiCLO_4$	41
29	C(+)/C(-)	1.5	7	TFA (7%)	-	$LiCLO_4$	64
30	C(+)/Ni(-)	1.5	7 (Divided cell)	TFA (7%)	-	$LiCLO_4$	36

[a]All the reactions were performed with 0.15 mmol scale using IKA electrasyn 2.0. [b]Yield calculated using $PhCF_3$ as internal standard.

General procedure

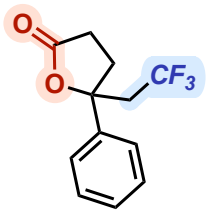
The ElectraSyn vial (10 mL), equipped with a magnetic stir bar, was charged with the electrolyte $LiClO_4$ (0.2 M), the alkene **1** or **5** (0.15 mmol, 1.0 equiv), and the Langlois reagent **2** (0.22 mmol, 1.5 equiv). The ElectraSyn vial cap, fitted with an anode and cathode, was secured to the vial and sealed with a rubber septum. The vessel was evacuated and backfilled with argon three times.

Dry ACN (6 mL) was then added together with the selected percentage of an acid, and the solution was degassed by bubbling with argon under stirring for 1 minute. The reaction mixture was electrolyzed for 3 hours. Upon completion, $PhCF_3$ (0.15 mmol) was added as an internal standard, and the yield was determined via ^{19}F NMR spectroscopy.

Afterward, the ElectraSyn vial cap was removed, and the electrodes and vial were rinsed with EtOAc (10 mL) and aqueous $NaHCO_3$ (10 mL). These rinses were combined with the crude reaction mixture in a separatory funnel. The organic layer was separated, and the aqueous layer was extracted with EtOAc (2 × 10 mL). The combined organic layers were dried over Na_2SO_4, concentrated under reduced pressure, and purified by flash chromatography (Hex:EtOAc from 95:5 to 7:3) to yield the pure products **3** or **6**.

4. Compound characterization

5-phenyl-5-(2,2,2-trifluoroethyl)dihydrofuran-2(3H)-one (**3a**)

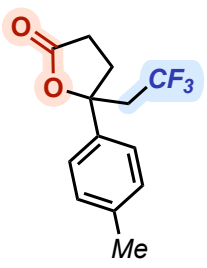


Colorless oil, (80%, 29.3 mg)

^{1}H NMR (600 MHz, CDCl3) δ 7.44 – 7.33 (m, 5H), 2.92 – 2.77 (m, 2H), 2.72 – 2.60 (m, 2H), 2.52 – 2.42 (m, 2H). **^{13}C NMR** δ 175.37, 141.20, 128.95, 128.61, 124.77, 124.70 (q, J = 23.8 Hz), 84.40 (q, J = 2.3 Hz), 45.37 (q, J = 27.7 Hz), 34.25, 28.12. **^{19}F NMR** (565 MHz, $CDCl_3$) δ -60.54 (t, *J* = 10.2 Hz).

GC-MS: 244,189,16. **HRMS (ESI)** m/z calcd for $C_{12}H_{11}F_3O_2$ $[M+H]^+$ 245.0784, found 245.0789.

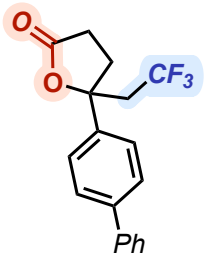
5-(p-tolyl)-5-(2,2,2-trifluoroethyl)dihydrofuran-2(3H)-one (**3b**)



Colorless oil (85%, 32.9 mg)

^{1}H NMR (600 MHz, CDCl3) δ 7.27 (dd, J = 8.1, 6.0 Hz, 2H), 7.22 – 7.16 (m, 2H), 2.90 – 2.74 (m, 2H), 2.66 – 2.57 (m, 3H), 2.52 – 2.41 (m, 1H), 2.35 (s, 3H). **^{13}C NMR** (151 MHz, CDCl3) δ 175.45, 138.48, 138.14, 129.59, 124.73, 124.66 (q, J = 278.5 Hz), 84.48 (q, J = 2.5 Hz), 45.42 (q, J = 27.4 Hz), 34.19, 28.19, 21.14. **^{19}F NMR** (565 MHz, CDCl3) δ -60.53 (t, J = 10.2 Hz). **GC-MS**: 258, 203, 175. **HRMS (ESI)** m/z calcd for $C_{13}H_{13}F_3O_2$ $[M+H]^+$ 259.0940, found 259.0943

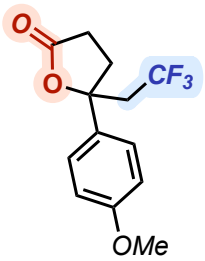
5-([1,1'-biphenyl]-4-yl)-5-(2,2,2-trifluoroethyl)dihydrofuran-2(3H)-one (**3c**)



Colorless oil (87%, 44.5 mg)

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.66 – 7.42 (m, 4H), 7.41 – 7.35 (m, 5H), 2.98 – 2.78 (m, 2H), 2.74 – 2.61 (m, 3H), 2.57 – 2.45 (m, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 175.35, 141.56, 140.18, 140.08, 129.03, 127.87, 127.63, 127.50, 127.23, 125.65, 125.30, 123.81, 121.96, 84.38 (q, J = 2.3 Hz), 45.39 (q, J = 27.6 Hz), 34.21, 28.20. **^{19}F NMR** (565 MHz, $CDCl_3$) δ -60.44 (t, J = 10.2 Hz). **HRMS (ESI)** m/z calcd for $C_{18}H_{15}F_3O_2$ $[M+H]^+$ 321.1102, found 321.1109

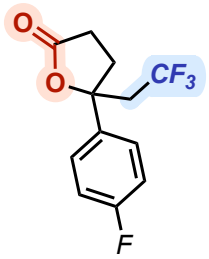
5-(4-methoxyphenyl)-5-(2,2,2-trifluoroethyl)dihydrofuran-2(3H)-one (**3d**)



Colorless oil (52%, 21.3 mg)

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.33 – 7.28 (m, 2H), 6.94 – 6.87 (m, 2H), 3.82 (s, 3H), 2.88 – 2.73 (m, 2H), 2.68 – 2.57 (m, 2H), 2.51 – 2.41 (m, 1H). **^{13}C NMR** (151 MHz, CDCl3) δ 175.46, 159.68, 132.84, 127.48, 126.21, 125.64, 123.80, 121.95, 114.21, 84.40 (q, J = 2.4 Hz), 55.46, 45.55 (q, J = 27.4 Hz), 34.12, 28.27. **^{19}F NMR** (565 MHz, CDCl3) δ -60.59 (t, J = 10.2 Hz). **HRMS (ESI)** m/z calcd for $C_{13}H_{13}F_3O_3$ $[M+H]^+$ 275.0895, found 275.0901

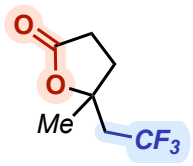
5-(4-fluorophenyl)-5-(2,2,2-trifluoroethyl)dihydrofuran-2(3H)-one (**3e**)



Colorless oil (73%, 28.7 mg)

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.41 – 7.36 (m, 1H), 7.12 – 7.06 (m, 1H), 2.88 – 2.74 (m, 1H), 2.69 – 2.58 (m, 2H), 2.51 – 2.40 (m, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 175.04, 162.70 (d, *J* = 248.3 Hz), 136.85 (d, *J* = 3.4 Hz), 126.82 (d, *J* = 8.2 Hz), 124.60 (q, J = 278.3 Hz), 115.95 (d, *J* = 21.8 Hz), 84.02 (d, *J* = 2.3 Hz), 45.54 (q, *J* = 27.6 Hz), 34.37, 28.08. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -60.62 (t, *J* = 10.2 Hz), -113.32 (m, *J* = 8.8, 5.1 Hz). **GC-MS**: 262, 179, 151. **HRMS (ESI)** m/z calcd for $C_{12}H_{10}F_4O_2$ $[M+H]^+$ 263.0689, found 263.0692

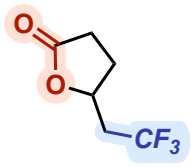
5-methyl-5-(2,2,2-trifluoroethyl)dihydrofuran-2(3H)-one (**3f**)



Colorless oil (38%, 10.3 mg)

^{1}H NMR (600 MHz, $CDCl_3$) δ 2.98 (m, *J* = 15.4, 11.4 Hz, 1H), 2.71 (m, *J* = 15.4, 10.9 Hz, 1H), 2.64 – 2.50 (m, 2H), 2.48 (s, 3H), 2.33 (m, *J* = 13.5, 9.8, 6.6 Hz, 1H), 1.93 (m, *J* = 13.5, 9.8, 7.5, 0.8 Hz, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 172.77, 125.97 (q, *J* = 277.8 Hz), 62.10 (d, *J* = 2.3 Hz), 40.51 (q, *J* = 26.8 Hz), 30.50, 29.85, 27.13. **^{19}F NMR** (565 MHz, $CDCl_3$) δ -61.02 (t, *J* = 11.0 Hz). **GC-MS**: 182, 167, 138. **HRMS (ESI)** m/z calcd for $C_7H_9F_3O_2$ $[M+H]^+$ 183.0627, found 183.0630

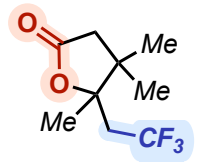
5-(2,2,2-trifluoroethyl)dihydrofuran-2(3H)-one (**3g**)



Colorless oil (33%, 8.3 mg)

^{1}H NMR (400 MHz, $cdcl_3$) δ 4.74 (m, *J* = 8.4, 6.3 Hz, 1H), 2.76 – 2.62 (m, 1H), 2.62 – 2.55 (m, 2H), 2.55 – 2.34 (m, 2H), 2.08 – 1.95 (m, 1H). **^{13}C NMR** (101 MHz, $cdcl_3$) δ 175.89, 125.02 (q, J = 277.9 Hz), 73.89 (q, *J* = 3.5 Hz), 39.64 (q, *J* = 28.6 Hz), 28.39, 28, 38. **^{19}F NMR** (376 MHz, $cdcl_3$) δ -63.96 (t, *J* = 10.5 Hz). **GC-MS**: 168, 125, 124, 111. **HRMS (ESI)** m/z calcd for $C_6H_7F_3O_2$ $[M+H]^+$ 169.0471, found 169.0468

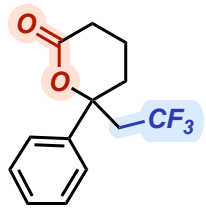
4,4,5-trimethyl-5-(2,2,2-trifluoroethyl)dihydrofuran-2(3H)-one (**3h**)



Colorless oil (40%, 12.0 mg)

^{1}H NMR (600 MHz, $CDCl_3$) δ 2.93 – 2.80 (m, 2H), 2.50 (s, 2H), 2.34 (d, *J* = 13.9 Hz, 1H), 1.86 (dd, *J* = 13.9, 0.9 Hz, 1H), 1.65 (s, 3H), 1.29 (s, 3H), 1.26 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 173.15, 126.13 (q, J = 280.0 Hz), 58.97 (q, *J* = 2.4 Hz), 45.61, 41.87 (q, *J* = 26.1 Hz), 40.34, 28.04, 27.13, 26.86. **^{19}F NMR** (565 MHz, $CDCl_3$) δ -60.23 (t, *J* = 11.0 Hz). **GC-MS**: 210, 209, 194, 182. **HRMS (ESI)** m/z calcd for $C_9H_{13}F_3O_2$ $[M+H]^+$ 211.0940, found 211.0937

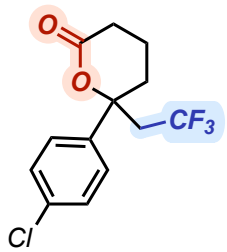
6-phenyl-6-(2,2,2-trifluoroethyl)tetrahydro-2H-pyran-2-one (**3i**)



Colorless oil (50%, 19.3 mg)

^{1}H NMR (400 MHz, $cdcl_3$) δ 7.42 – 7.28 (m, 5H), 2.85 – 2.63 (m, 2H), 2.53 – 2.34 (m, 3H), 2.20 (m, *J* = 13.5, 4.4 Hz, 1H), 1.77 (m, *J* = 15.5, 7.8, 3.9 Hz, 1H), 1.54 (m, *J* = 13.9, 7.5, 4.2 Hz, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 169.15, 140.34, 128.01, 127.26, 126.43, 123.95, 123.71 (q, J = 282.9 Hz), 82.44 (q, *J* = 2.5 Hz), 45.85 (q, *J* = 27.4 Hz), 28.69, 27.87, 15.02. **^{19}F NMR** (376 MHz, $cdcl_3$) δ -59.84 (t, *J* = 10.5 Hz). **GC-MS**: 258, 198, 186. **HRMS (ESI)** m/z calcd for $C_{13}H_{13}F_3O_2$ $[M+H]^+$ 259.0940, found 259.0943

6-(4-chlorophenyl)-6-(2,2,2-trifluoroethyl)tetrahydro-2H-pyran-2-one (**3j**)

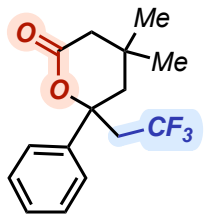


Colorless oil (47%, 20.6 mg)

^{1}H NMR (600 MHz, CDCl3) δ 7.40 – 7.37 (m, 2H), 7.33 – 7.30 (m, 2H), 2.80 – 2.67 (m, 2H), 2.54 – 2.39 (m, 3H), 2.22 (ddd, J = 14.4, 12.5, 4.3 Hz, 1H), 1.86 – 1.79 (m, 1H), 1.61 – 1.51 (m, 1H). **^{13}C NMR** (151 MHz, CDCl3) δ 169.82, 139.94, 134.56, 129.36, 126.70, 124.63 (q, J = 278.3), 83.17 (q, J = 2.4 Hz), 46.92 (q, J =

27.5 Hz), 31.31, 29.02, 16.17. **^{19}F NMR** (565 MHz, CDCl3) δ -59.76 (t, J = 10.2 Hz). **HRMS (ESI)** m/z calcd for $C_{13}H_{12}ClF_3O_2$ $[M+H]^+$ 293.0550, found 293.0553

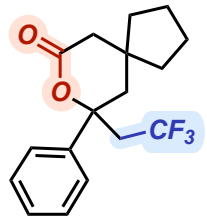
4,4-dimethyl-6-phenyl-6-(2,2,2-trifluoroethyl)tetrahydro-2H-pyran-2-one (**3k**)



Colorless oil (72%, 30.9 mg)

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.44 – 7.41 (m, 1H), 7.38 (dd, *J* = 8.7, 6.9 Hz, 1H), 7.33 – 7.30 (m, 1H), 2.70 (q, *J* = 10.4 Hz, 1H), 2.57 (d, *J* = 14.8 Hz, 1H), 2.23 – 2.08 (m, 2H), 1.09 (s, 2H), 0.80 (s, 2H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 171.09, 142.01, 128.97, 128.34, 125.16, 124.57 (q, J = 277.1 Hz), 82.60 (q, *J* = 2.2 Hz), 48.60 (q, *J* = 27.1 Hz), 44.00, 43.56, 32.57, 30.62, 29.62. **^{19}F NMR** (565 MHz, $CDCl_3$) δ -59.59 (t, *J* = 10.2 Hz). **GC-MS**: 286, 203, 186. **HRMS (ESI)** m/z calcd for $C_{15}H_{17}F_3O_2$ $[M+H]^+$ 287.1253, found 287.1248

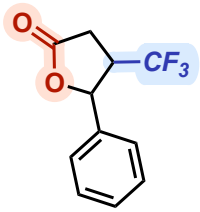
9-phenyl-9-(2,2,2-trifluoroethyl)-8-oxaspiro[4.5]decan-7-one (**3l**)



Waxy solid (60%, 28.1 mg)

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.42 – 7.35 (m, 4H), 7.33 – 7.30 (m, 1H), 2.72 (q, *J* = 10.4 Hz, 2H), 2.55 (d, *J* = 14.6 Hz, 1H), 2.34 (d, *J* = 14.6 Hz, 1H), 2.30 – 2.18 (m, 2H), 1.65 – 1.44 (m, 6H), 1.12 – 1.00 (m, 2H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 170.97, 142.26, 128.88, 128.30, 125.19, 124.63 (q, J = 279.1 Hz), 82.79 (q, *J* = 2.2 Hz), 48.20 (q, *J* = 27.1 Hz), 43.08, 42.03, 41.15, 41.13, 39.06, 23.79, 22.38. **^{19}F NMR** (565 MHz, $CDCl_3$) δ -59.56 (t, *J* = 10.5 Hz). **GC-MS:** 312, 229, 186. **HRMS (ESI)** m/z calcd for $C_{17}H_{19}F_3O_2$ $[M+H]^+$ 313.1410, found 313.1415

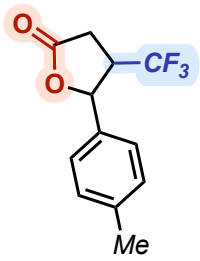
5-phenyl-4-(trifluoromethyl)dihydrofuran-2(3H)-one (**3m**)



White solid (51%, 17.6 mg)

^{1}H NMR (600 MHz, CDCl3) δ 7.45 – 7.38 (m, 3H), 7.33 – 7.31 (m, 2H), 5.62 (d, J = 4.9 Hz, 1H), 3.25 – 3.17 (m, 1H), 2.93 (dd, J = 18.4, 10.0 Hz, 1H), 2.81 (dd, J = 18.4, 6.0 Hz, 1H). **^{13}C NMR** (151 MHz, CDCl3) δ 173.18, 137.69, 129.42, 129.32, 125.75 (q, J = 277.5 Hz), 125.35, 79.26 (q, J = 2.7 Hz), 47.61 (q, J = 28.8 Hz), 28.45 (q, J = 2.6 Hz). **^{19}F NMR** (376 MHz, cdcl3) δ -71.80 (d, J = 8.4 Hz). **GC-MS**: 230, 206, 174. **HRMS (ESI)** m/z calcd for $C_{11}H_9F_3O_2$ $[M+H]^+$ 231.0627, found 231.0633

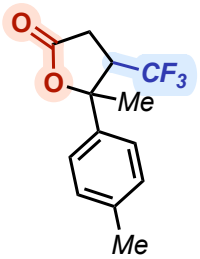
5-phenyl-4-(trifluoromethyl)dihydrofuran-2(3H)-one (**3n**)



White solid (50%, 18.3 mg)

^{1}H NMR (600 MHz, CDCl3) δ 7.25 – 7.19 (m, 4H), 5.58 (d, J = 5.1 Hz, 1H), 3.24 – 3.14 (m, 1H), 2.93 (dd, J = 18.4, 9.9 Hz, 1H), 2.80 (dd, J = 18.4, 6.2 Hz, 1H), 2.37 (s, 3H). **^{13}C NMR** (151 MHz, CDCl3) δ 173.20, 139.45, 134.67, 129.94, 125.8 (q, J = 280.6 Hz), 125.37, 79.34 (q, J = 2.7 Hz), 47.61 (q, J = 28.8 Hz), 28.59 (q, J = 2.5 Hz), 21.30. **^{19}F NMR** (565 MHz, CDCl3) δ -71.70 (d, J = 8.3 Hz). **GC-MS**: 244, 229, 121. **HRMS (ESI)** m/z calcd for $C_{12}H_{11}F_3O_2$ $[M+H]^+$ 245.0784, found 245.0780

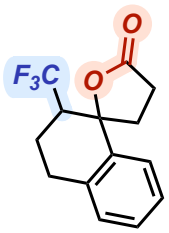
5-methyl-5-(p-tolyl)-4-(trifluoromethyl)dihydrofuran-2(3H)-one (**3o**)



Colorless oil (54%, 20.9 mg)

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.30 – 7.26 (m, 2H), 7.23 – 7.20 (m, 2H), 3.30 (pd, *J* = 9.1, 5.5 Hz, 1H), 2.83 – 2.72 (m, 2H), 2.36 (s, 3H), 1.82 (q, *J* = 2.0 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 172.87, 140.51, 138.51, 129.76, 125.80 (q, J = 281.2 Hz), 124.12, 86.09, 50.06 (q, *J* = 27.7 Hz), 31.73, 29.99 (q, *J* = 2.7 Hz), 24.37 (q, *J* = 2.5 Hz). **^{19}F NMR** (565 MHz, $CDCl_3$) δ -67.09 (d, *J* = 9.4 Hz). **HRMS (ESI)** m/z calcd for $C_{13}H_{13}F_3O_2$ $[M+H]^+$ 259.0940, found 259.0936

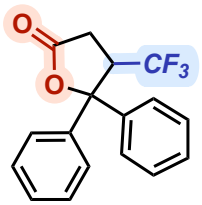
2'-(trifluoromethyl)-3,3',4,4'-tetrahydro-2'H,5H-spiro[furan-2,1'-naphthalen]-5-one (**3p**)



White solid (54%, 21.9 mg)

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.30 – 7.23 (m, 3H), 7.13 – 7.11 (m, 1H), 3.04 – 2.75 (m, 6H), 2.29 (dddd, J = 12.6, 9.7, 7.3, 4.9 Hz, 2H), 1.97 (dddd, J = 13.9, 12.4, 10.8, 6.8 Hz, 1H). **^{13}C NMR** (151 MHz, CDCl3) δ 176.46, 140.31, 134.53, 128.80, 128.49, 127.47, 127.02 (q, J = 281.3 Hz), 125.30, 84.76, 46.95 (q, J = 25.1 Hz), 32.02, 28.72, 27.90, 20.55 (q, J = 2.6 Hz). **^{19}F NMR** (565 MHz, CDCl3) δ -66.13 (d, J = 9.0 Hz). **GC-MS**: 270, 250, 215, 174. **HRMS (ESI)** m/z calcd for $C_{14}H_{13}F_3O_2$ $[M+H]^+$ 271.0940, found 271.0946

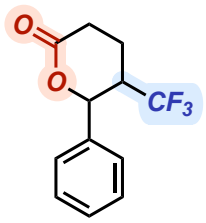
5,5-diphenyl-4-(trifluoromethyl)dihydrofuran-2(3H)-one (**3q**)



Colorless long needle (63%, 28.9 mg)

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.53 – 7.50 (m, 2H), 7.45 – 7.41 (m, 2H), 7.40 – 7.36 (m, 1H), 7.34 – 7.27 (m, 5H), 4.05 (pd, J = 8.6, 4.5 Hz, 1H), 2.97 (dd, J = 18.0, 4.5 Hz, 1H), 2.86 (dd, J = 18.0, 8.8 Hz, 1H). **^{13}C NMR** (151 MHz, CDCl3) δ 172.43, 141.59, 138.16, 129.06, 128.50, 128.25, 126.55, 125.40 (q, J = 280.2 Hz), 89.17, 48.31 (q, J = 27.2 Hz), 31.01 (q, J = 2.6 Hz). **^{19}F NMR** (565 MHz, CDCl3) δ -65.85 (d, J = 8.8 Hz). **GC-MS**: 306, 229, 183. **HRMS (ESI)** m/z calcd for $C_{17}H_{13}F_3O_2$ $[M+H]^+$ 307.0940, found 307.0943

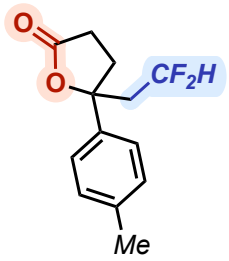
6-phenyl-5-(trifluoromethyl)tetrahydro-2H-pyran-2-one (**3r**)



Colorless long needle (50%, 16.8 mg)

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.45 – 7.35 (m, 3H), 7.34 – 7.31 (m, 2H), 5.50 (d, J = 7.3 Hz, 1H), 2.89 (qq, J = 8.7, 7.0 Hz, 1H), 2.81 – 2.73 (m, 1H), 2.64 (dtd, J = 17.5, 6.6, 0.9 Hz, 1H), 2.28 – 2.13 (m, 2H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 170.04, 137.55, 129.30, 129.03, 128.95, 127.10, 126.59, 125.24, 123.38, 78.82 (q, J = 2.3 Hz), 43.35 (q, J = 26.0 Hz), 27.45, 18.33 (q, J = 2.6 Hz). **^{19}F NMR** (565 MHz, $CDCl^3$) δ -68.60 (d, J = 8.9 Hz). **HRMS (ESI)** m/z calcd for $C_{12}H_{11}F_3O_2$ $[M+H]^+$ 245.0789, found 245.0781

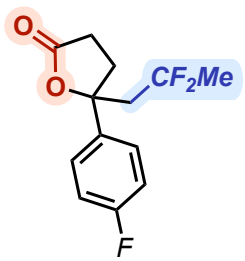
5-(2,2-difluoroethyl)-5-(p-tolyl)dihydrofuran-2(3H)-one (**3s**)



Colorless oil (53%, 20.5 mg)

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.25 (d, *J* = 8.2 Hz, 2H), 7.23 – 7.20 (m, 2H), 5.70 (tt, *J* = 55.6, 4.7 Hz, 1H), 2.63 – 2.41 (m, 6H), 2.36 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 175.79, 138.41, 138.25, 129.76, 124.58, 114.90 (t, *J* = 239.4 Hz), 85.45 (t, *J* = 6.0 Hz), 46.14 (t, *J* = 21.7 Hz), 35.07, 28.22, 21.15. **^{19}F NMR** (565 MHz, $CDCl_3$) δ -113.18 – -114.58 (m). **GC-MS:** 240, 175, 119. **HRMS (ESI)** m/z calcd for $C_{13}H_{14}F_2O_2$ $[M+H]^+$ 241.1034, found 241.1037

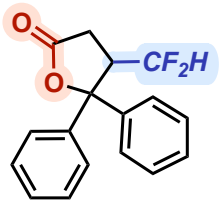
5-(2,2-difluoropropyl)-5-(4-fluorophenyl)dihydrofuran-2(3H)-one (**3t**)



Colorless oil (42%, 16.2 mg)

^{1}H NMR (600 MHz, CDCl3) δ 7.39 – 7.35 (m, 2H), 7.10 – 7.05 (m, 2H), 2.71 – 2.33 (m, 6H), 1.53 (t, J = 19.2 Hz, 3H). **^{13}C NMR** (151 MHz, CDCl3) δ 175.78, 162.46 (d, J = 247.5 Hz), 138.00 (d, J = 3.3 Hz), 126.81 (d, J = 8.3 Hz), 124.46 – 120.77 (dd, J = 241.7 Hz), 115.73 (d, J = 21.5 Hz), 85.58 (dd, J = 4.6, 2.5 Hz), 49.02 (dd, J = 25.0 Hz), 35.28 (dd, J = 2.1 Hz), 28.20, 24.83 (dd, J = 26.9 Hz). **^{19}F NMR** (565 MHz, CDCl3) δ -83.75 – -84.42 (dddq), -84.45 – -85.11 (dddq), -113.96 – -114.04 (m). **GC-MS:** 258, 179, 123. **HRMS (ESI)** m/z calcd for $C_{13}H_{13}F_3O_2$ $[M+H]^+$ 259.0940, found 259.0936

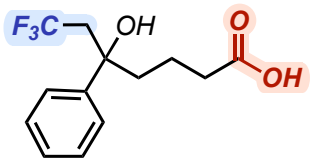
4-(difluoromethyl)-5,5-diphenyldihydrofuran-2(3H)-one (**3u**)



Colorless long needle (35%, 15.1 mg)

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.53 – 7.51 (m, 2H), 7.43 – 7.38 (m, 2H), 7.38 – 7.34 (m, 3H), 7.33 – 7.28 (m, 3H), 5.43 (td, J = 55.0, 3.0 Hz, 1H), 3.73 (dtt, J = 21.9, 8.3, 3.4 Hz, 1H), 2.89 (dd, J = 17.8, 3.7 Hz, 1H), 2.72 (ddd, J = 17.9, 8.6, 1.2 Hz, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 173.66, 141.64, 138.78, 129.01, 128.94, 128.89, 128.51, 126.27, 125.79, 115.51 (dd, J = 243.8, 241.2 Hz), 89.22 (dd, J = 6.8, 2.0 Hz), 46.95 (dd, J = 22.9, 20.1 Hz), 29.25 (dd, J = 5.3, 3.4 Hz). **^{19}F NMR** (565 MHz, $CDCl_3$) δ -118.78 (ddd, J = 291.6, 54.9, 7.6 Hz), -126.92 (ddd, J = 292.0, 54.9, 22.0 Hz). **HRMS (ESI)** m/z calcd for $C_{17}H_{14}F_2O_2$ $[M+H]^+$ 289.1034, found 289.1038

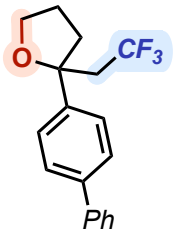
7,7,7-trifluoro-5-hydroxy-5-phenylheptanoic acid (**4h**)



Colorless oil (17%, 7 mg)

^{1}H NMR (600 MHz, DMSO) δ 11.95 (br s), 7.45 (dt, J = 7.0, 1.3 Hz, 2H), 7.31 (dd, J = 8.3, 7.2 Hz, 2H), 7.24 – 7.17 (m, 1H), 5.24 (br s), 2.84 (dq, J = 15.4, 11.5 Hz, 1H), 2.69 (dq, J = 15.5, 11.2 Hz, 1H), 2.14 – 2.01 (m, 2H), 1.85 (ddd, J = 13.6, 11.7, 4.6 Hz, 1H), 1.77 (ddd, J = 13.9, 11.7, 4.6 Hz, 1H), 1.46 (m, J = 13.3, 8.9, 6.6, 4.6 Hz, 1H), 1.07 – 0.97 (m, 1H). **^{13}C NMR** (151 MHz, DMSO) δ 174.32, 144.87, 128.73, 127.63, 126.37 (q, J = 278.3 Hz), 125.32, 72.72 (d, J = 2.3 Hz), 44.92 (q, J = 24.0 Hz), 42.08, 33.81, 18.50. **^{19}F NMR** (565 MHz, DMSO) δ -57.64 (t, J = 11.3 Hz).

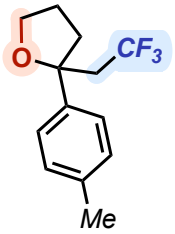
2-([1,1'-biphenyl]-4-yl)-2-(2,2,2-trifluoroethyl)tetrahydrofuran (**6a**)



Colorless oil (52%, 23.9 mg)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 – 7.55 (m, 4H) 7.48 – 7.40 (m, 4H), 7.34 (t, J = 7.5 Hz, 1H), 4.06 (q, J = 7.5 Hz, 1H), 3.94 (td, J = 8.2, 5.5 Hz, 1H), 2.70 (qd, J = 10.8, 8.1 Hz, 2H), 2.37 (ddd, J = 12.6, 7.8, 4.8 Hz, 1H), 2.26 (dt, J = 12.5, 8.2 Hz, 1H), 2.08 – 1.95 (m, 1H), 1.89 – 1.76 (m, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 143.79, 140.80, 140.11, 128.90, 127.90, 127.43, 127.20, 127.09, 126.51, 125.77, 124.66, 122.82, 83.00 (q, J = 2.4 Hz), 67.94, 45.24 (q, J = 26.2 Hz), 38.23, 25.27. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -60.43 (t, J = 10.8 Hz). **HRMS (ESI)** m/z calcd for $C_{18}H_{17}F_3O$ $[M+H]^+$ 307.1309, found 307.1314

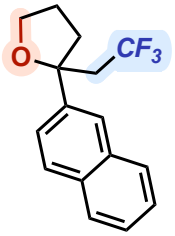
2-(p-tolyl)-2-(2,2,2-trifluoroethyl)tetrahydrofuran (**6b**)



Colorless oil (60%, 22.0 mg)

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.30 – 7.24 (m, 2H), 7.17 – 7.12 (m, 2H), 4.07 – 3.97 (m, 0H), 3.94 – 3.85 (m, 0H), 2.75 – 2.55 (m, 1H), 2.47 (d, J = 1.9 Hz, 0H), 2.37 – 2.15 (m, 2H), 2.07 – 1.91 (m, 0H), 1.78 (dqd, J = 12.4, 8.1, 6.8 Hz, 0H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 141.71, 136.86, 129.06, 128.38, 126.53, 125.24, 124.79, 122.79, 82.99 (d, J = 2.3 Hz), 67.76, 45.33 (q, J = 26.1 Hz), 38.12, 25.22, 21.14. **^{19}F NMR** (565 MHz, $CDCl_3$) δ -60.47 (t, J = 10.9 Hz). **HRMS (ESI)** m/z calcd for $C_{13}H_{15}F_3O$ $[M+H]^+$ 244.1153, found 244.1147

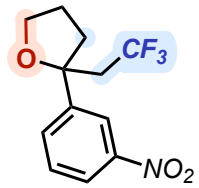
2-(naphthalen-2-yl)-2-(2,2,2-trifluoroethyl)tetrahydrofuran (**6c**)



Colorless oil (40%, 16.8 mg)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 – 7.75 (m, 4H), 7.67 – 7.40 (m, 3H), 4.10 (q, J = 7.5 Hz, 1H), 3.99 (td, J = 8.2, 5.2 Hz, 1H), 2.89 – 2.65 (m, 2H), 2.44 (ddd, J = 12.5, 7.8, 4.7 Hz, 1H), 2.30 (dt, J = 12.5, 8.2 Hz, 1H), 2.02 (dtt, J = 12.9, 7.8, 5.1 Hz, 1H), 1.90 – 1.74 (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.99, 133.23, 132.64, 129.02, 128.33, 128.24, 127.68, 126.98, 126.34, 126.10, 124.21, 124.06, 123.64, 83.24 (q, J = 2.2 Hz), 68.06, 45.15 (q, J = 26.3 Hz), 29.85, 25.26. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -60.45 (t, J = 10.7 Hz). **HRMS (ESI)** m/z calcd for $C_{16}H_{15}F_3O$ $[M+H]^+$ 281.1153, found 281.1158

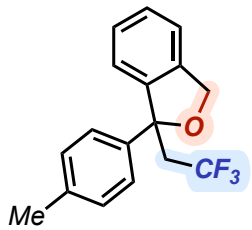
2-(3-nitrophenyl)-2-(2,2,2-trifluoroethyl)tetrahydrofuran (**6d**)



Colorless oil (35%, 14.5 mg)

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.28 (t, J = 2.0 Hz, 1H), 8.14 (ddd, J = 8.2, 2.3, 1.0 Hz, 1H), 7.76 (ddd, J = 7.8, 1.8, 1.0 Hz, 1H), 7.53 (t, J = 8.0 Hz, 1H), 4.08 (dt, J = 8.6, 7.2 Hz, 1H), 3.95 (td, J = 8.2, 5.5 Hz, 1H), 2.78 – 2.62 (m, 2H), 2.36 – 2.24 (m, 2H), 2.04 (dtt, J = 12.9, 7.6, 5.4 Hz, 1H), 1.79 (dqd, J = 12.5, 8.0, 6.9 Hz, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 148.49, 147.02, 131.65, 129.48, 128.00, 126.15, 124.31, 122.53, 122.46, 120.65, 82.60 (q, J = 2.4 Hz), 68.43, 45.11 (q, J = 26.6 Hz), 38.95, 25.18. **^{19}F NMR** (565 MHz, $CDCl_3$) δ -60.39 (t, J = 10.2 Hz). **HRMS (ESI)** m/z calcd for $C_{12}H_{12}F_3NO_3$ $[M+H]^+$ 276.0848, found 276.0841

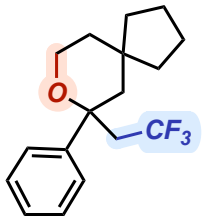
1-(p-tolyl)-1-(2,2,2-trifluoroethyl)-1,3-dihydroisobenzofuran (**6e**)



Colorless oil (34%, 14.9 mg)

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.42 – 7.39 (m, 2H), 7.38 – 7.35 (m, 1H), 7.32 – 7.27 (m, 2H), 7.23 – 7.20 (m, 1H), 7.17 – 7.14 (m, 2H), 5.31 – 5.17 (m, 2H), 3.12 – 2.93 (m, 2H), 2.32 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 142.50, 141.00, 138.54, 137.39, 129.33, 128.21, 128.14, 127.63, 126.29, 124.75, 124.45, 122.60, 122.27, 121.38, 87.48 (q, J = 2.5 Hz), 72.36, 44.41 (q, J = 26.3 Hz), 21.10. **^{19}F NMR** (565 MHz, $CDCl_3$) δ -60.20 (t, J = 10.2 Hz). **HRMS (ESI)** m/z calcd for $C_{17}H_{15}F_3O$ $[M+H]^+$ 293.1153, found 293.1159

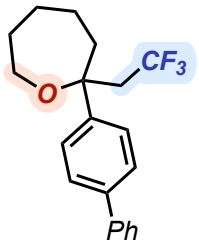
7-phenyl-7-(2,2,2-trifluoroethyl)-8-oxaspiro[4.5]decane (**6f**)



Colorless oil (54%, 24.2 mg)

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.46 – 7.41 (m, 2H), 7.35 (dd, J = 8.5, 7.0 Hz, 2H), 7.30 – 7.25 (m, 1H), 3.84 – 3.71 (m, 2H), 2.58 – 2.40 (m, 2H), 2.26 (dd, J = 14.1, 1.9 Hz, 1H), 1.92 (d, J = 14.1 Hz, 1H), 1.65 – 1.21 (m, 8H), 1.02 (dtd, J = 12.9, 8.3, 0.9 Hz, 1H), 0.97 – 0.89 (m, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 142.14, 128.24, 127.80, 127.18, 126.34, 126.30, 124.50, 122.65, 75.67 (q, J = 2.1 Hz), 60.46, 48.71 (q, J = 25.8 Hz), 44.14, 42.45, 40.63, 35.94, 35.64, 23.91, 22.29. **^{19}F NMR** (565 MHz, $CDCl_3$) δ -59.37 (d, J = 22.4 Hz). **HRMS (ESI)** m/z calcd for $C_{17}H_{21}F_3O$ $[M+H]^+$ 299.1622, found 299.1627

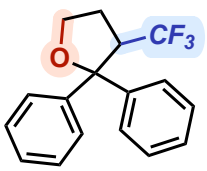
2-([1,1'-biphenyl]-4-yl)-2-(2,2,2-trifluoroethyl)oxepane (**6g**)



Colorless oil (33%, 16.5 mg)

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.64 – 7.56 (m, 4H), 7.51 – 7.44 (m, 4H), 7.36 – 7.31 (m, 1H), 3.87 – 3.76 (m, 1H), 3.54 (ddd, J = 12.9, 8.6, 1.7 Hz, 1H), 2.72 – 2.53 (m, 2H), 2.39 (ddd, J = 15.1, 6.5, 3.1 Hz, 1H), 2.16 – 2.05 (m, 1H), 1.80 – 1.59 (m, 6H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 144.40, 140.86, 139.83, 128.87, 127.37, 127.20, 126.90, 126.58, 126.53, 124.68, 122.84, 78.80 (q, J = 2.2 Hz), 64.53, 45.28 (q, J = 25.7 Hz), 40.00, 31.38, 29.56, 22.51. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -59.75 (t, J = 10.9 Hz). **HRMS (ESI)** m/z calcd for $C_{20}H_{21}F_3O$ $[M+H]^+$ 335.1622, found 335.1626.

2,2-diphenyl-3-(trifluoromethyl)tetrahydrofuran (**6h**)



Colorless oil (51%, 22.4 mg)

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.51 (dd, J = 8.4, 1.3 Hz, 2H), 7.40 – 7.35 (m, 4H), 7.32 – 7.27 (m, 1H), 7.25 – 7.22 (m, 3H), 7.21 – 7.16 (m, 1H), 4.24 (td, J = 8.4, 4.8 Hz, 1H), 3.78 – 3.64 (m, 2H), 2.37 (dddd, J = 13.3,

8.5, 7.3, 4.9 Hz, 1H), 2.26 – 2.14 (m, 1H). **^{19}F NMR** (565 MHz, $CDCl_3$) δ -64.69 (d, J = 9.7 Hz). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 144.79, 141.09, 128.71, 127.71, 127.58, 127.32, 127.27, 126.25, 87.99, 64.76, 51.06 (q, J = 25.6 Hz), 27.57. **^{19}F NMR** (565 MHz, $CDCl_3$) δ -64.69 (d, J = 9.7 Hz). **HRMS (ESI)** m/z calcd for $C_{17}H_{15}F_3O$ $[M+H]^+$ 293.1153, found 293.1145.

5. Cyclic Voltammetry

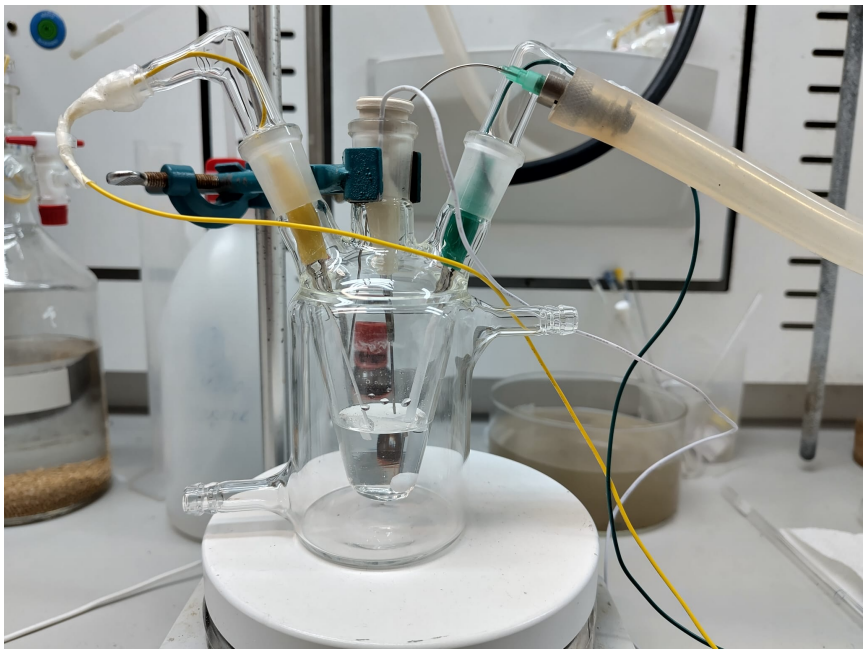


Fig. S1. Setup of the CV with Rodeostat 2.0 instrument

Cyclovoltammetry experiments were carried out using the Rodeostat apparatus using a Glassy Carbon (GC) as working electrode, Pt as counter electrode, Ag wire as a pseudo-reference electrode and [Fc/Fc+] (5 mM in CH_3CN) as internal standard ad 5 mM concentration of reagents.

For **1a**: 8.8 mg of **1a** and 106.1 mg $LiClO_4$ were dissolved in 10 mL of anhydrous ACN, stirred while purging with Ar and then subjected to the CV experiment at 200 mV·s-1 (Figure S2). Then, 9.3 mg of ferrocene were added and the CV experiment was repeated. An irreversible peak is observed. This is then calculated to be +1.40 V vs $E_{1/2}$ of ferrocene.

For **$NaSO_2CF_3$**: 7.8 mg of **2** reagent and 106.1 mg $LiClO_4$ were dissolved in 10 mL of anhydrous ACN, stirred while purging with Ar and then subjected to the CV experiment at 200 mV·s-1. Then, 9.3 mg of ferrocene were added and the CV experiment was repeated. An irreversible peak between is observed. This is then calculated to be +1.17 V vs $E_{1/2}$ of ferrocene.

For **$NaSO_2CF_2H$**: 6.9 mg of reagent and 106.1 mg $LiClO_4$ were dissolved in 10 mL of anhydrous ACN, stirred while purging with Ar and then subjected to the CV experiment at 200 mV·s-1. Then, 9.3 mg of ferrocene were added and the CV experiment was repeated. An irreversible peak between is observed. This is then calculated to be +1.02 V vs $E_{1/2}$ of ferrocene.

For **3a:** 12.2 mg of **3a** and 106.1 mg $LiClO_4$ were dissolved in 10 mL of anhydrous ACN, stirred while purging with Ar and then subjected to the CV experiment at 200 mV·s-1. No cathodic event is observed.

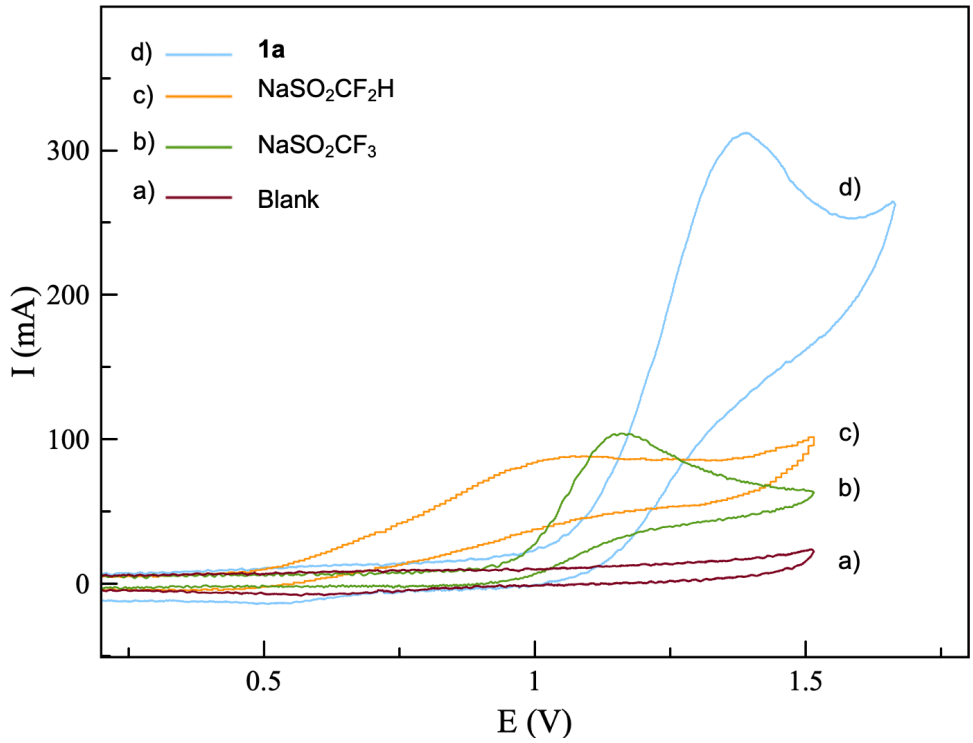


Fig. S2. Cyclic voltammograms of starting materials in 0.1 M $LiClO_4/CH_3CN$, using a Glassy Carbon (GC) as working electrode, Pt as counter electrode and Fc/Fc+ (0.1 M in CH_3CN) as internal standard: (a) background (b) CF_3SO_2Na, (c) CF_2HSO_2Na, (d) alkene **1a**

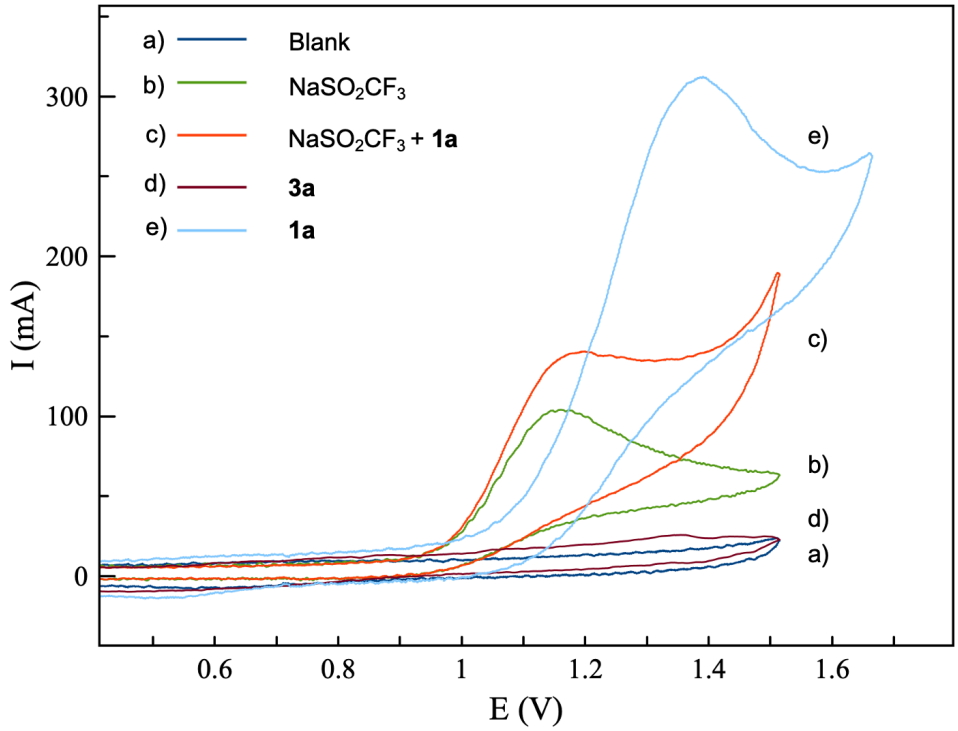
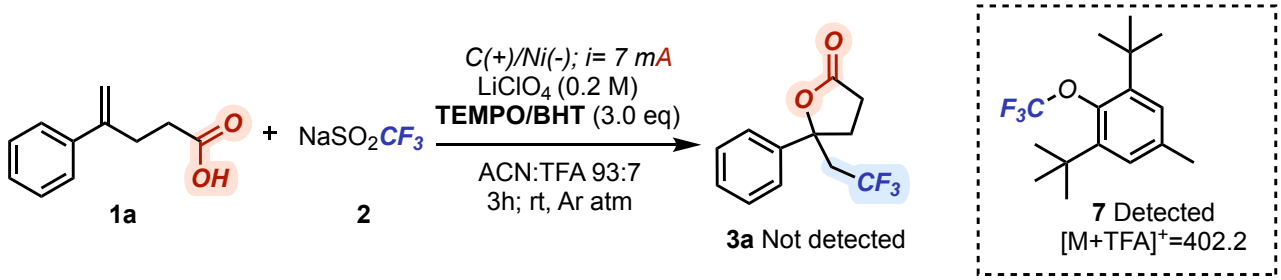


Fig. S3. Cyclic voltammograms of substrates in 0.1 M LiClO4/CH3CN, using a Glassy Carbon (GC) as working electrode, Pt as counter electrode and Fc/Fc+ (0.1 M in CH3CN) as internal standard: (a) background (b) CF_3SO_2Na, (c) CF_3SO_2Na + **1a**, (d) **3a** and e) the alkene **1a**.

6. Control Experiments

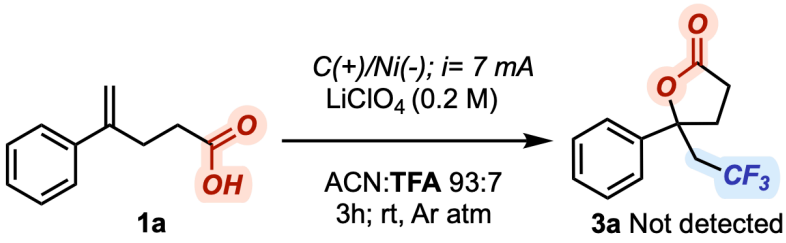
Radical trapping experiment



The ElectraSyn vial (10 mL), equipped with a magnetic stir bar, was charged with the electrolyte $LiClO_4$ (0.2 M), the alkene **1a** (0.15 mmol, 1.0 equiv), the Langlois reagent **2** (0.22 mmol, 1.5 equiv) and the radical trapping reagent (TEMPO or BHT (0.45 mmol, 3.0 equiv).The ElectraSyn vial cap, fitted with an anode and cathode, was secured to the vial and sealed with a rubber septum. The vessel was evacuated and backfilled with argon three times.

Dry ACN (6 mL) was then added together with 6% of TFA, and the solution was degassed by bubbling with argon under stirring for 1 minute. The reaction mixture was electrolyzed for 3 hours. Upon completion, $PhCF_3$ (0.15 mmol) was added as an internal standard, to determine the presence of the product **3b.** We observed no formation of the desired product, which strongly suggests that the reaction proceeds through a radical pathway. Additionally, the [M + TFA] of the BHT adduct **7** adduct was detected using HPLC-MS, further supporting the involvement of trifluoroacetate in the reaction mechanism.

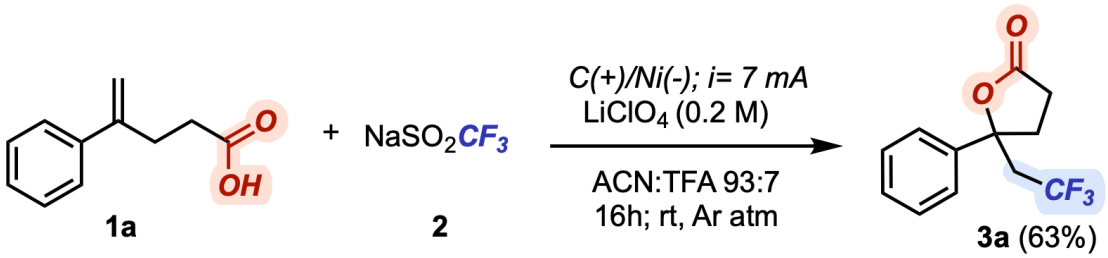
Kolbe type reaction



The ElectraSyn vial (10 mL), equipped with a magnetic stir bar, was charged with the electrolyte $LiClO_4$ (0.2 M) and the alkene **1a** (0.15 mmol, 1.0 equiv).The ElectraSyn vial cap, fitted with an anode and cathode, was secured to the vial and sealed with a rubber septum. The vessel was evacuated and backfilled with argon three times.

Dry ACN (6 mL) was then added together with 6% of TFA, and the solution was degassed by bubbling with argon under stirring for 1 minute. The reaction mixture was electrolyzed for 3 hours. Upon completion, $PhCF_3$ (0.15 mmol) was added as an internal standard, to determine the presence of the product **3b.** No desired product was observed, indicating that TFA is not involved in the reaction mechanism. This observation rules out the possibility of TFA participating directly in the trifluoromethylation process.

1.0 mmol scale reaction



The ElectraSyn vial (20 mL), equipped with a magnetic stir bar, was charged with the electrolyte $LiClO_4$ (0.2 M, 384 mg), the alkene **1a** (1.0 mmol, 1.0 equiv), and the Langlois reagent **2** (1.5 mmol, 1.5 equiv, 234 mg). The ElectraSyn vial cap, fitted with a graphite anode and nickel cathode, was secured to the vial and sealed with a rubber septum. The vessel was evacuated and backfilled with argon three times.

Dry ACN (6 mL) was then added together with 6% of TFA, and the solution was degassed by bubbling with argon under stirring for 1 minute. The reaction mixture was electrolyzed for 16 hours. Upon completion, $PhCF_3$ (1.0 mmol) was added as an internal standard, and the yield was determined via ^{19}F NMR spectroscopy.

Afterward, the ElectraSyn vial cap was removed, and the electrodes and vial were rinsed with EtOAc (3 mL) and aqueous $NaHCO_3$ (20 mL). These rinses were combined with the crude reaction mixture in a separatory funnel. The organic layer was separated, and the aqueous layer was extracted with EtOAc (3 × 15 mL). The combined organic layers were dried over Na_2SO_4, concentrated under reduced pressure, and purified by flash chromatography to achieve product **3a**.

7. NOE experiment

Performed irradiating the frequence corresponding at 3.201 ppm.

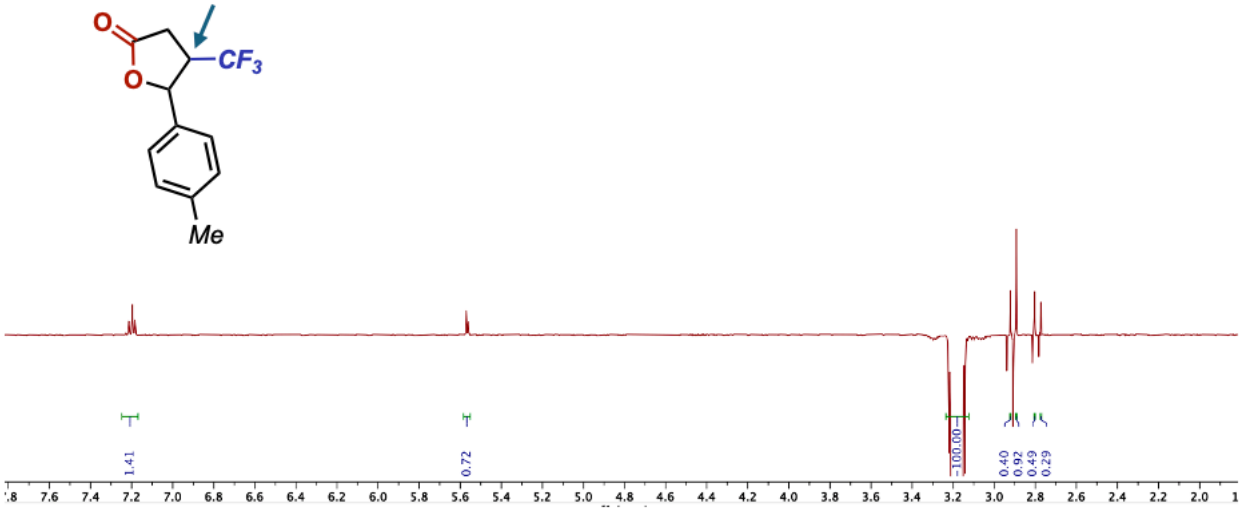


Fig. S4: NOE-1d of compound 3n irradiating the frequency corresponding to the proton alpha to CF3 group.

8. DFT calculations

DFT calculations were conducted at CINECA, through the Italian SuperComputing Resource Allocation – ISCRA, using the Gaussian 16 software package.[12] Geometry optimizations for all reported structures were performed with the dispersion corrected B3LYP-D3 functional with a mixed basis set of LANL2DZ for F and 6-31G(d) (for other atoms).[13] Frequency calculations were performed on all optimized structures to ensure that each local minimum lacked imaginary frequencies and that each transition state contained exactly one imaginary frequency. Solvation in ACN were introduced through single point calculations at optimized gas-phase geometries for all the minima and transition state using def2-TZVP for all atoms and the SMD implicit solvation model.[14] The reported Gibbs free energies were corrected considering the thermal correction computed at 298.15 K.

Charge distribution

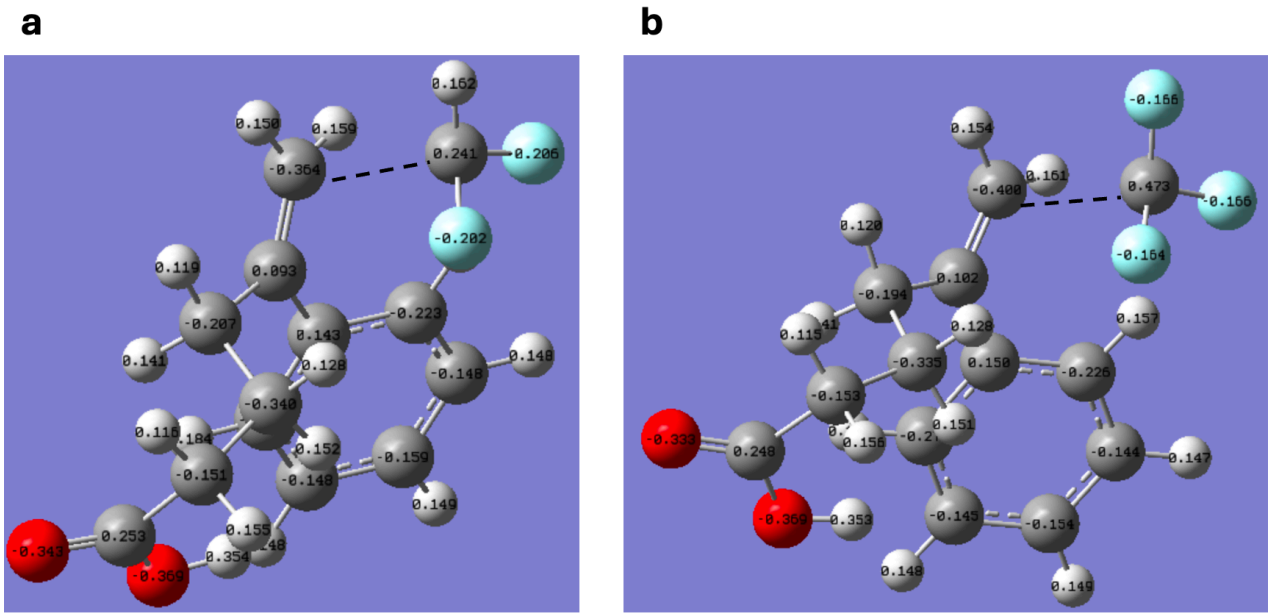


Fig. S5. a) TS1 of CF_2H and alkene **1h:** the presence of the H substituent gives the molecule a more planar structure and therefore the fluorine is able to donate electron density to the carbon. b) TS1 of $CF_3$and alkene **1h:** the CF_3 moiety gives molecule a more pyramidal structure and therefore a worst overlap between the F and the C.

Cartesian Coordinates (Å) of Optimized Structures

IntA (CF_3)

E (ACN) = - 953.971818

C	3.14658300	-1.25736600	-0.21878400
C	1.46669800	-0.28344200	1.84496300
C	0.33722500	0.02530500	1.19315900
H	2.24203700	0.44935200	2.02404100
H	1.61225400	-1.26361800	2.28003400
C	-0.76026100	-0.99504800	1.01139000
C	-2.28452900	-2.15698800	-0.68657000
H	-2.38723100	-2.40548900	-1.74796400
H	-2.26226900	-3.09954400	-0.14028800
F	3.86655900	-0.22261000	-0.63521300
F	2.39729700	-1.73144300	-1.20615500
C	0.12496200	1.36597900	0.59465800
C	-1.14285100	1.96437700	0.59004600
C	1.18230800	2.06418900	-0.00204900
C	-1.34052500	3.21829900	0.02596700
H	-1.98322500	1.46177100	1.05004700
C	0.98398100	3.31660500	-0.56767200
H	2.16334300	1.61065900	-0.04511400
C	-0.27810900	3.90045800	-0.55664500
H	-2.32756900	3.66295800	0.04620400
H	1.81653900	3.83261200	-1.02927200
H	-0.43327100	4.87504500	-1.00139600
C	-0.99836800	-1.35835400	-0.46362900
C	-3.56910300	-1.45508300	-0.27197000
O	-4.48238900	-2.00180800	0.27617500
O	-3.66381900	-0.13269800	-0.57776200
H	-2.85069900	0.19287500	-0.98673300
H	-0.52158500	-1.89983400	1.57341700
H	-1.68886600	-0.60931600	1.44299200
H	-1.00424500	-0.44623900	-1.06978800
H	-0.15026900	-1.93611400	-0.83441400
F	3.92910500	-2.20624400	0.27400600

IntA (CF_2H)

E (ACN) = - 854.670085

C	-2.72911300	2.48891700	-0.37240900
C	-1.68654000	0.75209300	1.95479400
C	-0.68353000	0.19066900	1.26151400
H	-2.62518900	0.23317200	2.12236600
H	-1.58108200	1.73601100	2.40145400
C	0.64276500	0.89681000	1.06887400
C	2.42556900	1.53459900	-0.67027300
H	2.57786000	1.74463700	-1.73734500
H	2.72106700	2.43611100	-0.12754100
F	-2.46324200	1.58269500	-1.33191400
F	-1.69324200	3.33789300	-0.21843000
C	-0.83298300	-1.14545000	0.62140600
C	0.21928100	-2.08044700	0.63199800
C	-2.02280000	-1.49474700	-0.03958500
C	0.07807700	-3.32475400	0.01653200
H	1.15150000	-1.84719900	1.13650200
C	-2.16461200	-2.73994100	-0.65106000
H	-2.82450200	-0.76646600	-0.10043500
C	-1.11515700	-3.66076800	-0.62652100
H	0.90172800	-4.03238000	0.04495200
H	-3.09165500	-2.98488400	-1.16180300
H	-1.22298800	-4.62738200	-1.10972400
C	0.95349200	1.18662200	-0.41488000
C	3.43620800	0.45743700	-0.27974400
O	4.53073800	0.70066700	0.16307300
O	3.06170900	-0.83723100	-0.48089100
H	2.15440800	-0.89323200	-0.81550500
H	0.65381200	1.83461500	1.63344100
H	1.44524700	0.27849100	1.49220600
H	0.65366800	0.32655900	-1.02921500
H	0.32170800	2.00975400	-0.75856300
H	-3.69075000	2.99316300	-0.49902700

IntA (CF_2Me)

E (ACN) = - 854.670085

C	3.22242000	-1.01047800	-0.24329000
C	1.49606600	0.11775000	2.00631500
C	0.35828800	0.19220700	1.29823000
H	2.12413900	0.98783000	2.17073200
H	1.81180000	-0.81230500	2.46886600
C	-0.53656000	-1.01376100	1.10157200
C	-1.83092500	-2.37082400	-0.65713900
H	-1.84925900	-2.64048500	-1.72152200
H	-1.73180100	-3.30537600	-0.09899000
F	2.65635700	-0.30257200	-1.25416800
F	2.66143500	-2.24856400	-0.20603600
C	-0.06417400	1.45670800	0.63542700
C	-1.41290200	1.85964400	0.62694400
C	0.87300200	2.26501600	-0.03020300
C	-1.80471900	3.03732100	-0.01078300
H	-2.16400300	1.26179400	1.13334200
C	0.48124900	3.44386600	-0.66376700
H	1.90676100	1.94019100	-0.07938400
C	-0.85899800	3.83585400	-0.65742900
H	-2.85046700	3.33087200	0.00275800
H	1.22256900	4.04891400	-1.17826500
H	-1.16497300	4.74979600	-1.15801200
C	-0.65329300	-1.42762100	-0.38097400
C	-3.21440800	-1.82033700	-0.31453500
O	-4.11867800	-2.50296300	0.09770700
O	-3.41502100	-0.48903200	-0.52388700
H	-2.60492600	-0.05483800	-0.82991800
H	-0.16152900	-1.85921200	1.68722000
H	-1.53687300	-0.79096700	1.49553700
H	-0.73016100	-0.52962400	-1.00939200
H	0.27824200	-1.90742000	-0.69220100
C	4.71226700	-0.99230700	-0.21401300
H	5.06370600	0.04063400	-0.17264200
H	5.06687900	-1.52962900	0.66776600

H	5.12547900	-1.47223000	-1.11274900

TS1 (CF_3)

E (ACN) = - 953.969852

C	3.05224300	-1.30390400	-0.20174500
C	1.51200400	-0.39178400	1.75057800
C	0.37210600	-0.02286400	1.13956100
H	2.30811800	0.31318700	1.94737000
H	1.61983100	-1.37934100	2.17922100
C	-0.76325100	-1.00182600	0.96747100
C	-2.36554700	-2.08823700	-0.70814300
H	-2.50408800	-2.31361000	-1.77059600
H	-2.35783600	-3.03999100	-0.17787000
F	3.92661500	-0.34743000	-0.50055400
F	2.30222100	-1.58779900	-1.26153100
C	0.19614000	1.33547500	0.57602800
C	-1.05813500	1.96294900	0.57537900
C	1.27507400	2.02719300	0.00915100
C	-1.22177500	3.23639000	0.04563800
H	-1.91482900	1.46752500	1.01210300
C	1.11024100	3.29856400	-0.52280800
H	2.24678200	1.55472400	-0.03864900
C	-0.13862500	3.91057900	-0.50711600
H	-2.19883600	3.70241500	0.06928200
H	1.95870000	3.80819300	-0.96194000
H	-0.26723500	4.90069400	-0.92522300
C	-1.04923500	-1.33308900	-0.50690900
C	-3.61168400	-1.35040600	-0.24320300
O	-4.51032800	-1.86430000	0.35812200
O	-3.68700900	-0.02993500	-0.56420400
H	-2.88777400	0.26622800	-1.01996900
H	-0.54253800	-1.92354400	1.50889300
H	-1.66770600	-0.59285900	1.42806900
H	-1.04200100	-0.41098500	-1.09733600
H	-0.22949200	-1.93055300	-0.90845400
F	3.68230500	-2.39170800	0.22435800

TS1 (CF_2H)

E (ACN) = - 854.665632

C	2.75625200	-2.30790000	-0.09626800
C	1.56083200	-1.03059800	1.74075000
C	0.55526800	-0.35525600	1.13214100
H	2.51385900	-0.56020700	1.95795700
H	1.37778700	-1.99589100	2.20191800
C	-0.80778500	-0.99059200	0.95974600
C	-2.66112100	-1.54981300	-0.73043000
H	-2.85997400	-1.70205400	-1.79964400
H	-2.93498000	-2.47658100	-0.22031900
F	3.74056000	-1.47775700	-0.51701100
F	1.84636600	-2.48312000	-1.08164000
C	0.75639600	1.00132900	0.56655200
C	-0.29423200	1.94092000	0.54191100
C	1.99580300	1.38328200	0.01878900
C	-0.10641700	3.21481000	0.00651100
H	-1.26368400	1.68889100	0.95889400
C	2.18053000	2.65731200	-0.51537800
H	2.80796500	0.66585600	-0.02036100
C	1.13238800	3.58033200	-0.52414200
H	-0.93026800	3.92287900	0.00974900
H	3.14429200	2.92437000	-0.93959500
H	1.27730400	4.57074200	-0.94545200
C	-1.17773600	-1.21420500	-0.52193100
C	-3.63799700	-0.48724800	-0.23257900
O	-4.67182900	-0.73731400	0.33379700
O	-3.29825600	0.81097600	-0.47728800
H	-2.43876600	0.86699600	-0.91992100
H	-0.84463200	-1.94770400	1.49056100
H	-1.56957500	-0.35718800	1.43280700
H	-0.90172500	-0.32478500	-1.10427600
H	-0.55770900	-2.01674700	-0.93051600
H	3.14536600	-3.25422500	0.28995700

TS1 (CF_2Me)

E (ACN) = - 893.985264

C	3.02553500	-1.25645700	-0.21449300
C	1.58159600	-0.44279800	1.66338200
C	0.40874400	-0.05964200	1.09949700
H	2.36914600	0.27068300	1.88058800
H	1.68384700	-1.42872800	2.10584700
C	-0.72492500	-1.04846600	0.93215100
C	-2.37455200	-2.07894100	-0.74883400
H	-2.53942100	-2.26387700	-1.81871200
H	-2.36879200	-3.05360800	-0.25459700
F	3.82757900	-0.18716100	-0.48943700
F	2.17780400	-1.43809300	-1.26472600
C	0.20998300	1.30952800	0.56671100
C	-1.06298900	1.91547600	0.57581500
C	1.28214000	2.03732500	0.01537900
C	-1.25124400	3.20112200	0.06933500
H	-1.91476500	1.39242800	0.99798100
C	1.09084300	3.32231600	-0.48914900
H	2.26341600	1.58027000	-0.04899600
C	-0.17501500	3.91219700	-0.46522300
H	-2.24121400	3.64756000	0.09849600
H	1.93307200	3.85916200	-0.91654300
H	-0.32223800	4.91155800	-0.86405100
C	-1.04273300	-1.34242300	-0.54947400
C	-3.60446400	-1.34397700	-0.22098500
O	-4.52154000	-1.88751600	0.34114800
O	-3.64460300	0.00239000	-0.43399300
H	-2.83816000	0.30835400	-0.87443100
H	-0.48250900	-1.98630600	1.44339800
H	-1.62617900	-0.66371900	1.42715700
H	-1.03734100	-0.40154100	-1.11601000
H	-0.22820300	-1.92859800	-0.98360800
C	3.76677400	-2.48501400	0.19298100
H	4.37798400	-2.26767500	1.07143000
H	3.05347300	-3.27469400	0.43799100

H	4.42043000	-2.83444300	-0.61827600

IntB (CF_3)

E (ACN) = - 954.027223

C	2.47859200	-1.59619800	-0.05788000
C	1.82722800	-0.85619300	1.09922600
C	0.55447800	-0.13320900	0.74127100
H	2.59131300	-0.18675600	1.50228200
H	1.63376100	-1.61843900	1.86183900
C	-0.72161200	-0.93513000	0.72954500
C	-2.68504200	-1.78595800	-0.69274600
H	-3.01387100	-1.96812300	-1.72436000
H	-2.71521300	-2.74095700	-0.16357600
F	2.81516200	-0.76789300	-1.08420100
F	1.65924700	-2.55746500	-0.58014000
C	0.55596200	1.25695800	0.39873000
C	-0.66463200	1.98458600	0.26094400
C	1.76090100	1.98445800	0.17398900
C	-0.66951500	3.33399100	-0.06343300
H	-1.61516900	1.49198000	0.43071700
C	1.74297500	3.33310300	-0.15255400
H	2.71625000	1.47512000	0.21920500
C	0.53097900	4.02325100	-0.27247500
H	-1.61800800	3.85705800	-0.14757800
H	2.68175000	3.85199800	-0.32414100
H	0.52223800	5.07866500	-0.52664300
C	-1.26123200	-1.20184400	-0.69683500
C	-3.70345300	-0.87914400	-0.01282700
O	-4.41597100	-1.21119400	0.89940500
O	-3.76867400	0.40080200	-0.49034700
H	-3.15231200	0.51945300	-1.22713600
H	-0.56761200	-1.89938400	1.22531500
H	-1.49385200	-0.41925500	1.31636300
H	-1.22952800	-0.26792000	-1.27206400
H	-0.58850900	-1.89090400	-1.21339700
F	3.62027600	-2.22702300	0.33556100

IntB (CF_2H)

E (ACN) = - 854.721711

C	-1.92926000	2.59637100	0.05758900
C	-1.56965500	1.62984000	1.17727200
C	-0.63786200	0.51215700	0.78506000
H	-2.51356700	1.25225600	1.58326200
H	-1.11051000	2.23979600	1.96543300
C	0.83896200	0.81213000	0.76035500
C	2.95139700	0.95760100	-0.69550000
H	3.30474000	1.03107600	-1.73262900
H	3.31798900	1.83687700	-0.16105600
F	-2.52773100	1.92990400	-0.99491600
F	-0.78672200	3.19998400	-0.45026300
C	-1.12956800	-0.78132800	0.41641600
C	-0.24747200	-1.89377000	0.26710200
C	-2.51238200	-1.02845300	0.17608400
C	-0.72073300	-3.15144700	-0.08092100
H	0.81467100	-1.77449700	0.44821200
C	-2.97335900	-2.28976000	-0.17413500
H	-3.22016900	-0.20944800	0.22157900
C	-2.08623100	-3.36498300	-0.30357500
H	-0.01979400	-3.97654400	-0.17300700
H	-4.03384800	-2.43699500	-0.35861200
H	-2.45189200	-4.35014600	-0.57646200
C	1.41447200	0.89831400	-0.67359900
C	3.61663600	-0.25161400	-0.04935600
O	4.45210300	-0.19322200	0.81628100
O	3.20216000	-1.47172800	-0.50712200
H	2.53479400	-1.36388700	-1.19993200
H	1.04099800	1.76030300	1.26933800
H	1.38937700	0.04661300	1.32468200
H	1.05259500	0.04171700	-1.25690200
H	1.00807000	1.78390000	-1.16757500
H	-2.60714900	3.39924200	0.37024500

IntB (CF_2Me)

E (ACN) = - 894.029744

C	2.53379600	-1.53593900	-0.04584400
C	1.85453200	-0.77842000	1.09799900
C	0.55899500	-0.09936800	0.74033800
H	2.58841800	-0.06825500	1.49047300
H	1.67831600	-1.51869600	1.88797700
C	-0.69054600	-0.94174500	0.72393500
C	-2.62176500	-1.84477600	-0.71057000
H	-2.94415300	-2.02164800	-1.74537400
H	-2.61198100	-2.81096200	-0.20104300
F	2.73171400	-0.66928600	-1.11731200
F	1.65700300	-2.51758600	-0.52121400
C	0.50956300	1.29085200	0.39893100
C	-0.73302900	1.98630800	0.30109400
C	1.68632000	2.05012400	0.13573200
C	-0.78447100	3.33577800	-0.02074000
H	-1.66362900	1.46840500	0.50363200
C	1.62235600	3.39815400	-0.18808200
H	2.65252800	1.56003400	0.14091500
C	0.38966400	4.05709500	-0.26714000
H	-1.74890700	3.83356800	-0.07311900
H	2.54101800	3.94125400	-0.39201800
H	0.34481800	5.11208200	-0.51965300
C	-1.22435200	-1.20247100	-0.70480600
C	-3.68628300	-1.00101300	-0.01974400
O	-4.42670800	-1.40245600	0.84143600
O	-3.77223700	0.29984200	-0.43213700
H	-3.11928200	0.47835700	-1.12413000
H	-0.49975400	-1.90867300	1.20056500
H	-1.47826200	-0.46228600	1.32196800
H	-1.23091400	-0.25751200	-1.26347900
H	-0.52180700	-1.85127100	-1.23263300
C	3.85079700	-2.19923200	0.28872600
H	4.57751000	-1.44590000	0.60088000
H	3.71020000	-2.92184800	1.09555300

H	4.22551900	-2.71597300	-0.59713400

IntC (CF_3)

E (ACN) = - 953.859013

C	2.07345600	1.68795400	-0.17287100
C	0.67853700	1.25105000	-0.63343500
H	0.76962600	0.87075400	-1.64956100
H	0.08604900	2.16371700	-0.68584500
F	2.94855000	0.65280400	-0.11472800
F	2.03579300	2.25285000	1.06480500
C	0.33823600	-1.13983700	0.21132300
C	-0.23514300	-2.08471000	1.11307100
C	1.23060400	-1.63299600	-0.78577000
C	0.08444800	-3.42830200	1.03538300
H	-0.93920500	-1.76648200	1.87080900
C	1.55309300	-2.97757700	-0.85125900
H	1.68890500	-0.95969300	-1.49642900
C	0.98360800	-3.87817000	0.05774300
H	-0.35962300	-4.13232900	1.73079600
H	2.24508800	-3.33113400	-1.60777700
H	1.23617300	-4.93280500	0.00242500
C	0.01340400	0.25058100	0.28789500
C	-2.86120100	0.38965900	-0.72023300
H	-3.72625200	-0.38522300	-2.20944800
C	-1.89702600	1.78400900	1.15754000
H	0.06687700	1.44988400	1.97374300
C	-3.12393400	1.05680500	0.60308600
H	-3.96391400	1.74643000	0.47336600
H	-3.47769100	0.28274800	1.29737000
C	-0.70077100	0.85004800	1.46350400
H	-1.02017900	0.09155200	2.17670800
H	-2.17440700	2.26703700	2.09784100
H	-1.60247200	2.58808700	0.47671600
O	-3.96429300	0.05426100	-1.37320200
O	-1.73754700	0.15845400	-1.16613100
F	2.56697600	2.60264100	-1.03140100

IntC (CF_2H)

E (ACN) = - 854.557431

C	0.91167100	2.73806000	-0.55102100
C	0.01238200	1.54531100	-0.90707500
H	0.33050000	1.15056400	-1.87185700
H	-0.98976200	1.95105500	-1.04759800
F	2.20587100	2.32851300	-0.32819200
F	0.46769100	3.33798100	0.60932000
C	0.96762400	-0.57094800	0.16700800
C	0.89259700	-1.64154900	1.10544200
C	2.04950700	-0.57533900	-0.75985400
C	1.84950000	-2.64014900	1.12486600
H	0.06693200	-1.70300600	1.80288100
C	3.01562000	-1.56722700	-0.72055600
H	2.15553800	0.22013500	-1.48363700
C	2.91868000	-2.60133800	0.21808700
H	1.77289900	-3.45134000	1.84084500
H	3.84471900	-1.54167700	-1.41925200
H	3.67339300	-3.38169000	0.24129800
C	-0.02264300	0.46161900	0.14511000
C	-2.61381000	-1.00167200	-0.63001700
H	-3.01184100	-2.29104000	-1.94999800
C	-2.42896000	0.90555000	1.03007200
H	-0.54233600	1.67290600	1.72704200
C	-3.14403500	-0.39032200	0.64021200
H	-4.21802300	-0.22248500	0.51168400
H	-3.05441300	-1.14776700	1.43053500
C	-0.91972400	0.72441400	1.31639300
H	-0.79101200	-0.01981900	2.10181600
H	-2.88641400	1.29137100	1.94465600
H	-2.59269300	1.66797000	0.26304300
O	-3.41814400	-1.92342200	-1.14469100
O	-1.54055800	-0.70227000	-1.14914900
H	0.91962100	3.49345800	-1.34287900

IntC (CF_2Me)

E (ACN) = - 893.873525

C	1.91309500	1.86321400	-0.14696100
C	0.64816500	1.17208200	-0.69861300
H	0.88612500	0.72130700	-1.66115900
H	-0.07386200	1.96444000	-0.89210700
F	2.80285800	0.89248900	0.29397000
F	1.55478200	2.58523900	0.98809900
C	0.42493200	-1.22410900	0.16039400
C	-0.28958400	-2.22380800	0.87959500
C	1.52683800	-1.63732500	-0.63909700
C	0.08391400	-3.55437800	0.80943500
H	-1.16465600	-1.95869900	1.45997000
C	1.91367900	-2.96762500	-0.68041900
H	2.11387900	-0.90928200	-1.18133600
C	1.19282400	-3.92880300	0.03745700
H	-0.48101100	-4.30591700	1.35040300
H	2.77427600	-3.26151100	-1.27148600
H	1.49101500	-4.97190500	-0.00718700
C	0.03878500	0.15450900	0.23614200
C	-2.88955300	0.31097300	-0.69383000
H	-3.81340200	-0.45605700	-2.15007000
C	-1.84390800	1.68537600	1.17273500
H	0.09171300	1.21686700	1.98957500
C	-3.10904400	1.02980100	0.61159600
H	-3.90295600	1.76819700	0.46224800
H	-3.51774800	0.29413900	1.31758600
C	-0.69321700	0.68844100	1.42689100
H	-1.03983200	-0.11469700	2.07793300
H	-2.09377700	2.14872200	2.13054700
H	-1.51654400	2.49982400	0.52076600
O	-4.01966100	0.02741700	-1.33001000
O	-1.78987500	-0.01042000	-1.14060500
C	2.60881900	2.78261900	-1.12015500
H	1.92750300	3.57147500	-1.44549200
H	3.46632800	3.23301500	-0.61649700

H	2.95600300	2.21874700	-1.98841400

TS2 (CF_3)

E (ACN) = - 953.855572

C	-0.73224700	2.44079600	-0.16209200
C	-0.69770700	1.05448600	-0.80368100
H	-0.12646000	1.12251100	-1.72888600
H	-1.72939400	0.84010700	-1.08283400
F	0.44374300	2.77798700	0.42498700
F	-1.69477700	2.51367300	0.80116300
C	1.30370900	-0.31377600	0.07868200
C	1.82215500	-1.45001600	0.73874500
C	2.20254700	0.54645700	-0.58315100
C	3.18594400	-1.70912800	0.74460900
H	1.15539900	-2.15598400	1.22259100
C	3.57214900	0.29697800	-0.55285200
H	1.85615200	1.43968600	-1.08587300
C	4.06699400	-0.82970100	0.10541700
H	3.56545300	-2.59304600	1.24641400
H	4.25152100	0.98403400	-1.04601700
H	5.13446400	-1.02573900	0.11949600
C	-0.15087800	-0.05912000	0.09100200
C	-1.70040700	-2.16283500	-0.63130400
H	-1.39544100	-3.25883200	-2.14345600
C	-2.37286600	-0.62333000	1.25409700
H	-0.76862300	0.65451500	1.96166600
C	-2.55368200	-1.99048300	0.58569900
H	-3.59054000	-2.19248400	0.29979600
H	-2.26867000	-2.80519400	1.26669400
C	-0.88469000	-0.27795800	1.39798300
H	-0.37860200	-1.04569600	1.98671600
H	-2.82961900	-0.65244200	2.24579300
H	-2.90417100	0.15272900	0.69715700
O	-2.00835800	-3.18574300	-1.38715000
O	-0.73181600	-1.43375900	-0.95119800
F	-1.01743300	3.37029900	-1.09630600

TS2 (CF_2H)

E (ACN) = - 854.552925

C	-0.40952400	2.70710700	-0.55286900
C	-0.54010400	1.26761300	-1.05072200
H	0.06560800	1.14235600	-1.94942700
H	-1.58151300	1.15579200	-1.35715500
F	0.78554300	2.90260600	0.10176700
F	-1.41618500	2.97952100	0.35644900
C	1.21894600	-0.28231100	0.03651800
C	1.53558200	-1.43573400	0.78557400
C	2.25781100	0.39123500	-0.63220600
C	2.84344300	-1.89549100	0.86555900
H	0.75166300	-1.99824600	1.28241800
C	3.57271300	-0.05770500	-0.52806500
H	2.06484900	1.29510900	-1.19423900
C	3.86878200	-1.20124700	0.21414200
H	3.06702100	-2.79147800	1.43522500
H	4.36494000	0.48829000	-1.02930300
H	4.89302700	-1.55328200	0.28548200
C	-0.18404900	0.18987800	-0.02427400
C	-2.01819700	-1.72299900	-0.52219100
H	-1.86589300	-3.02169300	-1.88901900
C	-2.46410700	0.11007300	1.15450800
H	-0.68350600	1.20606600	1.73473100
C	-2.84650100	-1.28308500	0.64320600
H	-3.89924700	-1.36081900	0.35451700
H	-2.69381800	-2.04629700	1.41983100
C	-0.94172500	0.24058000	1.28643700
H	-0.55721700	-0.52164000	1.96804300
H	-2.92374600	0.26557400	2.13302900
H	-2.86607900	0.88786400	0.50094400
O	-2.47031000	-2.76983800	-1.16506700
O	-0.94642400	-1.19169100	-0.89855000
H	-0.48486100	3.43801200	-1.36379700

TS2 (CF_2Me)

E (ACN) = - 893.868941

C	1.04121500	2.33193900	0.14864700
C	0.80240600	0.96916000	0.81945300
H	0.21655900	1.10734100	1.72868400
H	1.78695500	0.61771400	1.13062300
F	-0.06678700	2.67429000	-0.61674000
F	2.08522200	2.18001200	-0.76570100
C	-1.34318600	-0.16989600	-0.05999100
C	-1.98188400	-1.28193800	-0.64747100
C	-2.13973900	0.83568000	0.51681700
C	-3.36709900	-1.38329100	-0.65890400
H	-1.39371700	-2.09047400	-1.06976300
C	-3.52961400	0.74379300	0.48060900
H	-1.69137000	1.71930800	0.95086400
C	-4.14630100	-0.36446200	-0.10053400
H	-3.84136300	-2.25214100	-1.10334600
H	-4.12931600	1.54045500	0.90811600
H	-5.22911600	-0.43703700	-0.11902500
C	0.13741900	-0.08345000	-0.06905300
C	1.41747200	-2.34694000	0.63290600
H	0.98485900	-3.39230300	2.14832600
C	2.26203400	-0.90136900	-1.25449700
H	0.81166300	0.56108900	-1.93865400
C	2.28258500	-2.27979700	-0.58547000
H	3.28794700	-2.60521200	-0.30090400
H	1.89911200	-3.05584600	-1.26351000
C	0.82466600	-0.38345200	-1.38478000
H	0.22295800	-1.08569900	-1.96664300
H	2.70538000	-0.98501800	-2.24920800
H	2.88101600	-0.19115900	-0.70171600
O	1.60417500	-3.39605500	1.39389200
O	0.54023400	-1.51023600	0.95311300
C	1.37355600	3.46189100	1.09069600
H	2.25766800	3.21208400	1.68137800
H	1.57688300	4.35766100	0.50097600

H	0.53151500	3.65362300	1.75916100

IntD (CF_3)

E (ACN) = - 953.857085

C	-1.03573100	2.29895700	-0.17061200
C	-0.80333000	0.95447700	-0.85544300
H	-0.20245000	1.12670300	-1.74872400
H	-1.78964100	0.63195800	-1.19313800
F	0.03784800	2.72440800	0.54285000
F	-2.08640500	2.23376600	0.69762800
C	1.34218100	-0.19136800	0.03793900
C	1.97600500	-1.31437100	0.60274900
C	2.13656800	0.83894000	-0.48624300
C	3.36283100	-1.40317400	0.64429800
H	1.38693700	-2.13913900	0.99354500
C	3.52827600	0.75635200	-0.42535700
H	1.69491100	1.73004000	-0.91262300
C	4.14431700	-0.36177400	0.13470200
H	3.83447600	-2.28042200	1.07497000
H	4.12743400	1.57071100	-0.81898900
H	5.22702800	-0.42452900	0.17481400
C	-0.16082500	-0.13931200	0.01741700
C	-1.42956900	-2.28342400	-0.59660500
H	-0.95257300	-3.30397900	-2.11902400
C	-2.27372300	-0.84388100	1.28236400
H	-0.76201100	0.59066400	1.91334800
C	-2.31858700	-2.21528200	0.59852500
H	-3.32245900	-2.51951700	0.28531000
H	-1.96372200	-3.00974800	1.27168200
C	-0.82305300	-0.35891100	1.37561200
H	-0.22800300	-1.07049200	1.95373200
H	-2.69833000	-0.93115500	2.28459300
H	-2.89559900	-0.12430600	0.74458900
O	-1.58944800	-3.31067900	-1.37782700
O	-0.52908400	-1.44566800	-0.89680700
F	-1.32698700	3.23967200	-1.09193300

IntD (CF_2H)

E (ACN) = - 854.554156

C	-0.59292900	2.65088300	-0.55560300
C	-0.61033200	1.21820900	-1.08444800
H	0.03298500	1.15177200	-1.96395500
H	-1.63225300	1.04898200	-1.43122500
F	0.53780700	2.89986500	0.19001200
F	-1.67613900	2.85234500	0.28275700
C	1.23866100	-0.23911300	0.00437100
C	1.61274200	-1.41589400	0.68015100
C	2.24112800	0.55885500	-0.56499300
C	2.94941200	-1.78446800	0.78205900
H	0.85577700	-2.06419300	1.11226300
C	3.58366400	0.19736200	-0.44424800
H	2.00026300	1.48524200	-1.06901000
C	3.94141900	-0.97302800	0.22311100
H	3.21873300	-2.70021600	1.29825200
H	4.34790600	0.83597300	-0.87478300
H	4.98622400	-1.25370900	0.30951000
C	-0.21863700	0.12353600	-0.07496700
C	-1.89082800	-1.79018100	-0.49287800
H	-1.62060900	-3.05180700	-1.87782700
C	-2.44357600	-0.00568300	1.18739100
H	-0.68503500	1.16872200	1.70058600
C	-2.75540300	-1.41153800	0.66184800
H	-3.79786400	-1.54736200	0.35667800
H	-2.56805200	-2.17655200	1.42985600
C	-0.92676800	0.19182700	1.27460000
H	-0.49082900	-0.55171000	1.94725300
H	-2.88778600	0.11098300	2.17813200
H	-2.90011800	0.75569900	0.55122900
O	-2.25217100	-2.84798800	-1.16083400
O	-0.83982300	-1.18958700	-0.85712400
H	-0.64971600	3.39427400	-1.35657900

IntD (CF_2Me)

E (ACN) = - 893.870159

C	1.20977900	-2.22842200	-0.15480100
C	0.86560800	-0.90151500	-0.84779800
H	0.27099400	-1.09941300	-1.74097100
H	1.81989000	-0.49630200	-1.18977800
F	0.16126200	-2.61489200	0.67144000
F	2.28405400	-1.99372500	0.70676600
C	-1.35617000	0.10038600	0.03568400
C	-2.06820400	1.19608300	0.55840400
C	-2.07586400	-1.00084700	-0.44946800
C	-3.45821700	1.19157200	0.59328500
H	-1.53744700	2.07163400	0.92116500
C	-3.47009700	-1.01199400	-0.39542000
H	-1.56674800	-1.87484900	-0.83299300
C	-4.16430300	0.08162300	0.12004900
H	-3.99076300	2.04944400	0.99086400
H	-4.01067000	-1.88012900	-0.75798800
H	-5.24901300	0.07167600	0.15481300
C	0.14637000	0.14489100	0.02088300
C	1.24860800	2.39267900	-0.61266600
H	0.71073100	3.36281700	-2.14565400
C	2.19186100	1.03458000	1.27902900
H	0.80514200	-0.51776900	1.91129600
C	2.12853800	2.40319200	0.59160000
H	3.10628000	2.79020500	0.28771700
H	1.70028500	3.16595400	1.25871000
C	0.78589400	0.43348700	1.37424200
H	0.13302200	1.09753500	1.94720700
H	2.60756200	1.15864400	2.28122600
H	2.86634600	0.36274600	0.74405900
O	1.34045700	3.42583100	-1.40155900
O	0.41901800	1.48883400	-0.91284400
C	1.56492900	-3.36394400	-1.08189500
H	2.40411300	-3.08010000	-1.72087300
H	1.84850800	-4.22923000	-0.48002700

H 0.70572400 -3.62325600 -1.70418100

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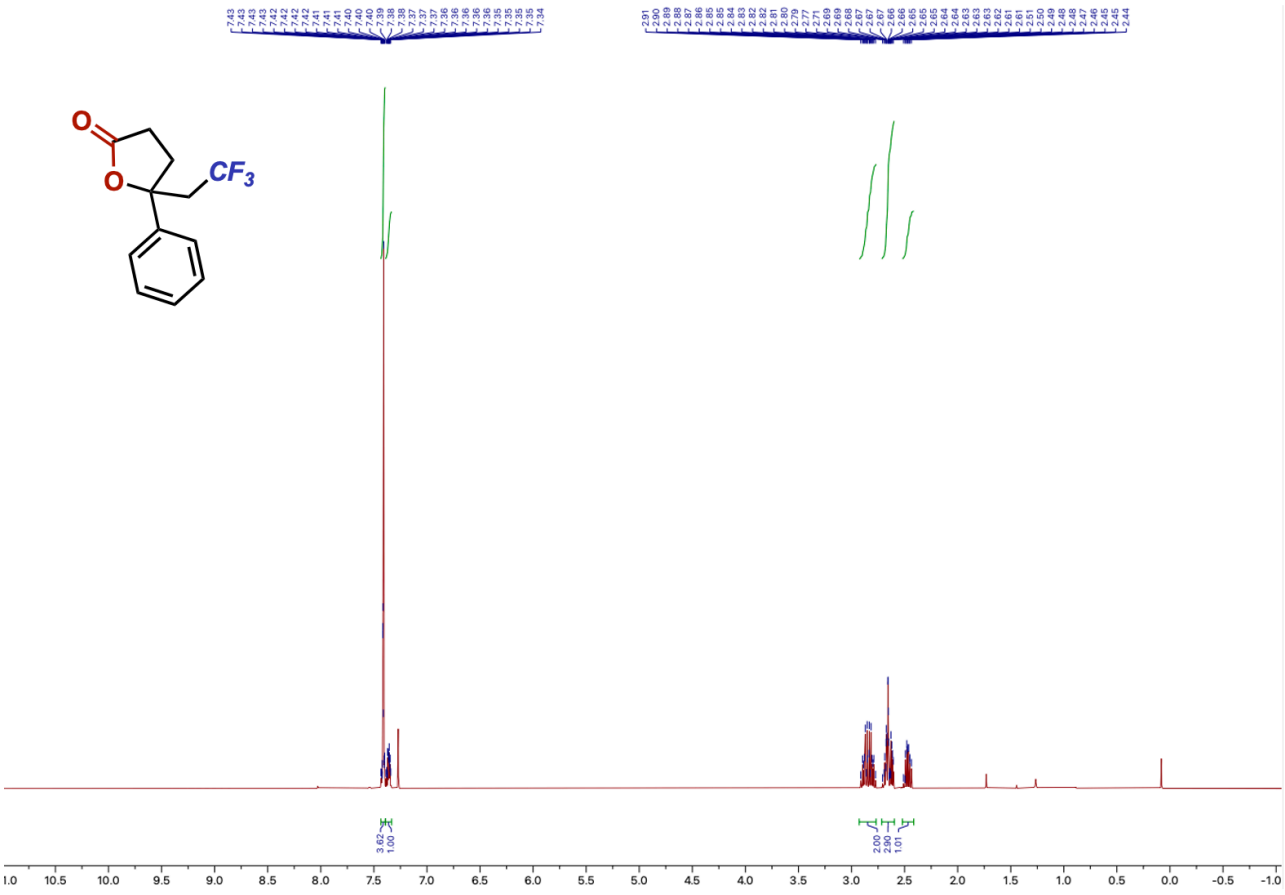
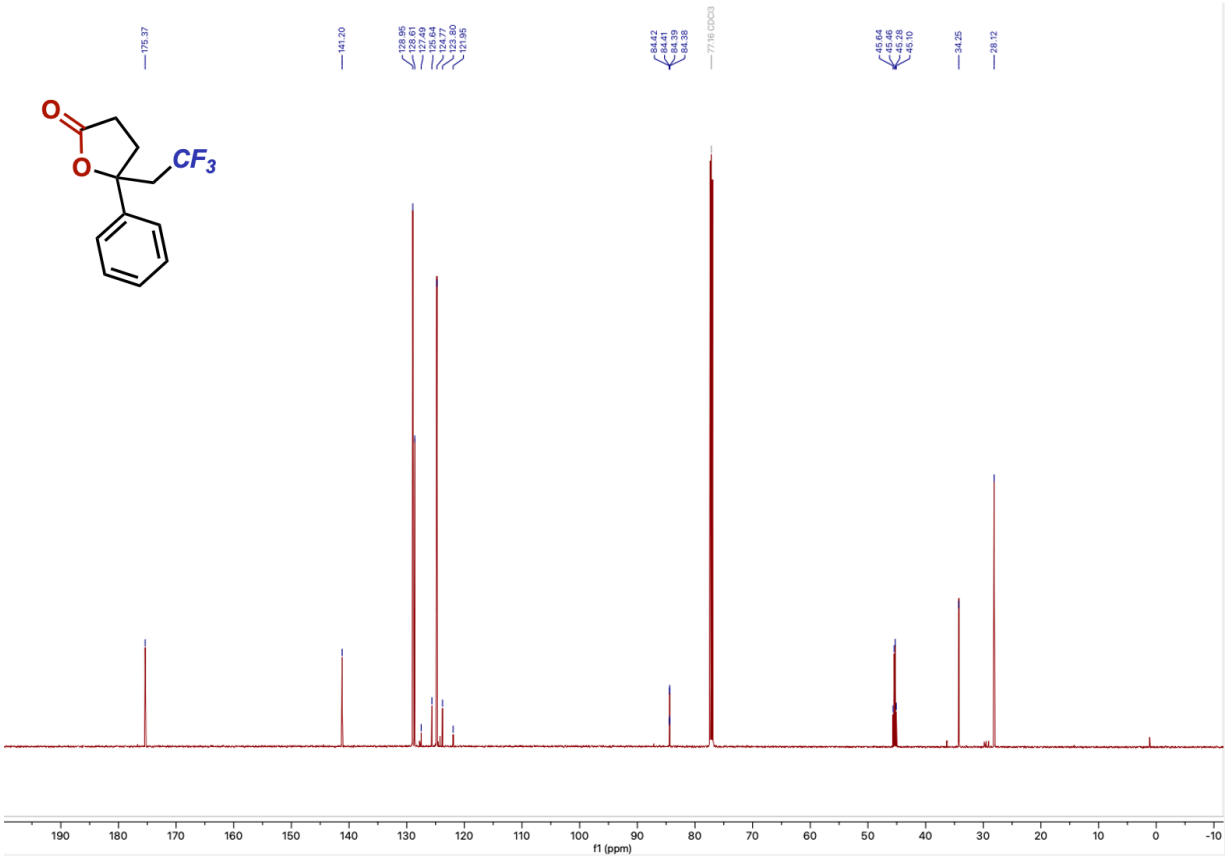
10. ^{1}H, ^{13}C and ^{19}F spectra

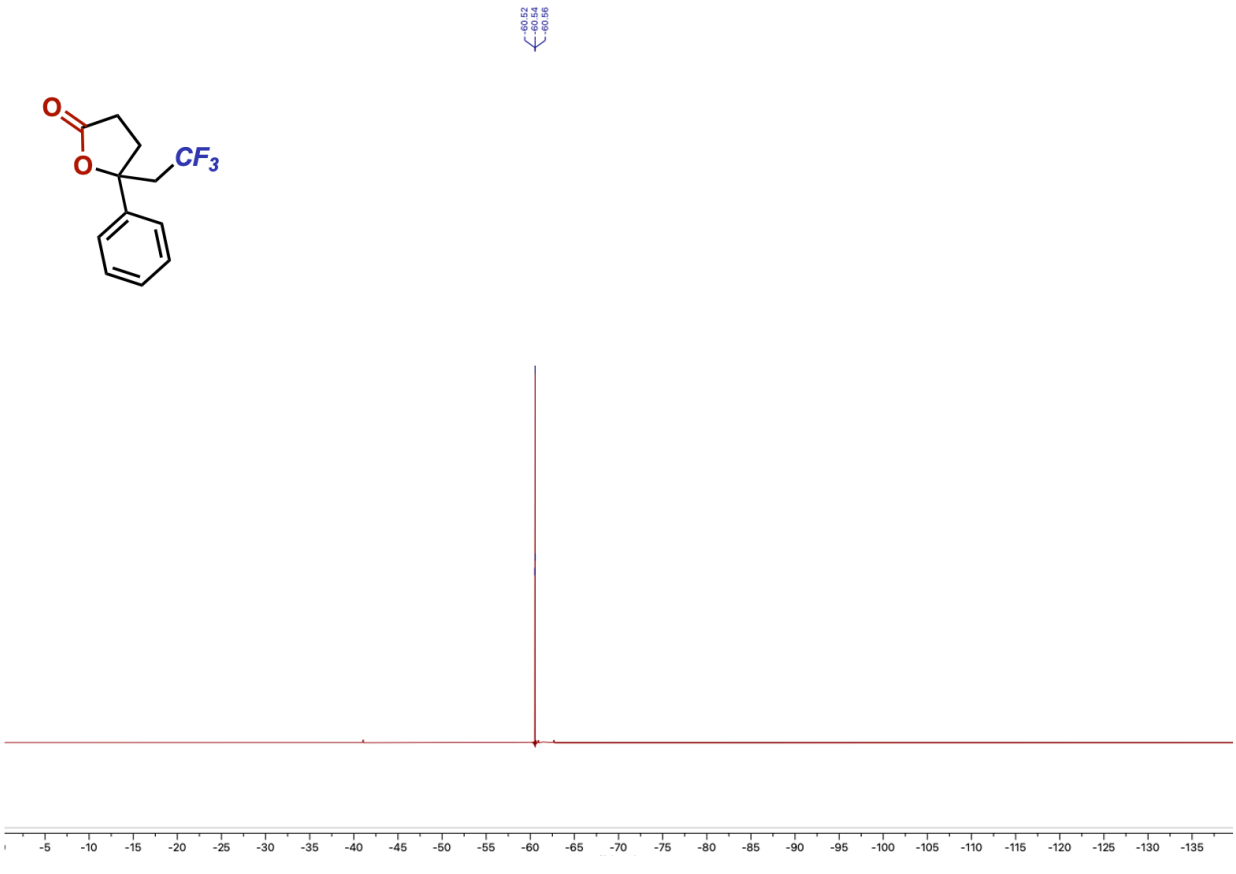
3a ^{1}H NMR (600 MHz, $CDCl_3$)



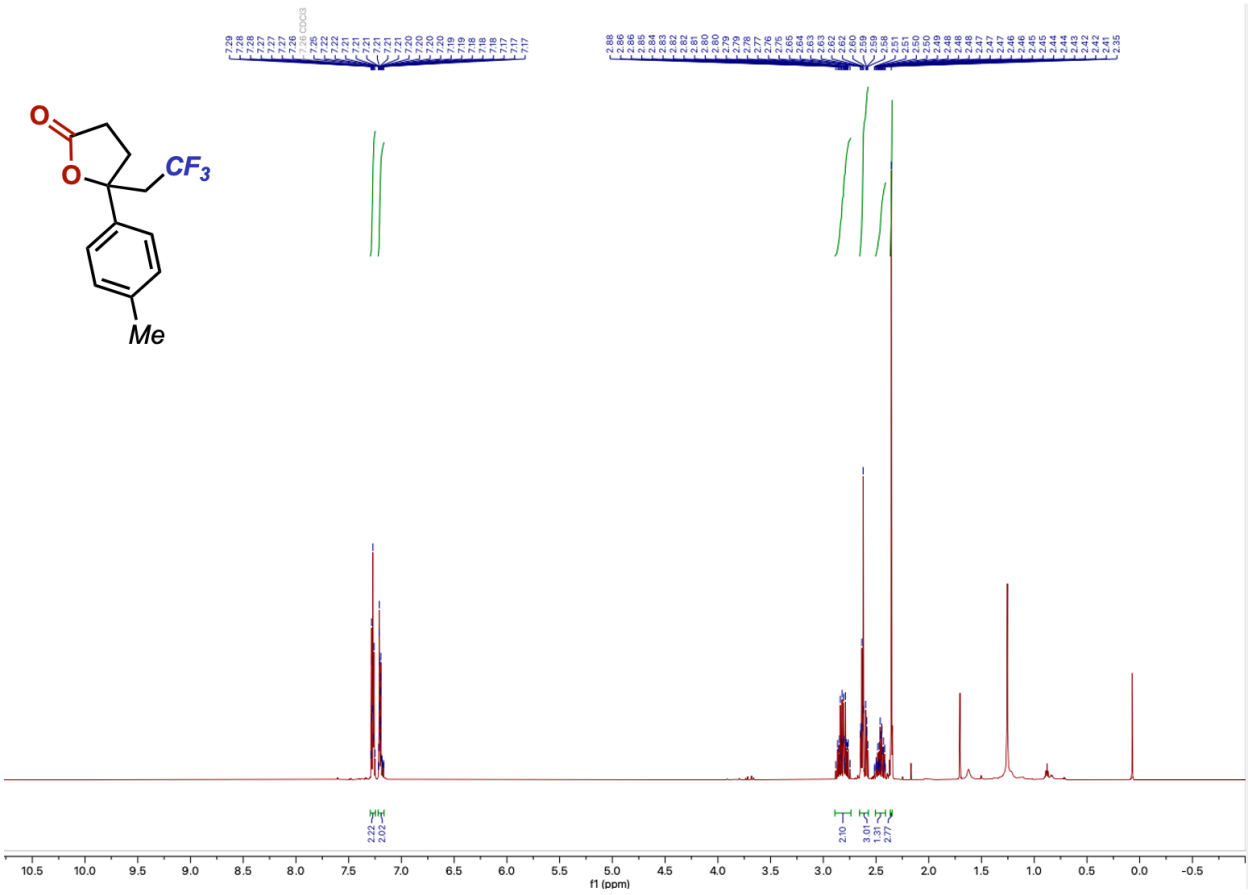
^{13}C NMR (151 MHz, $CDCl_3$)



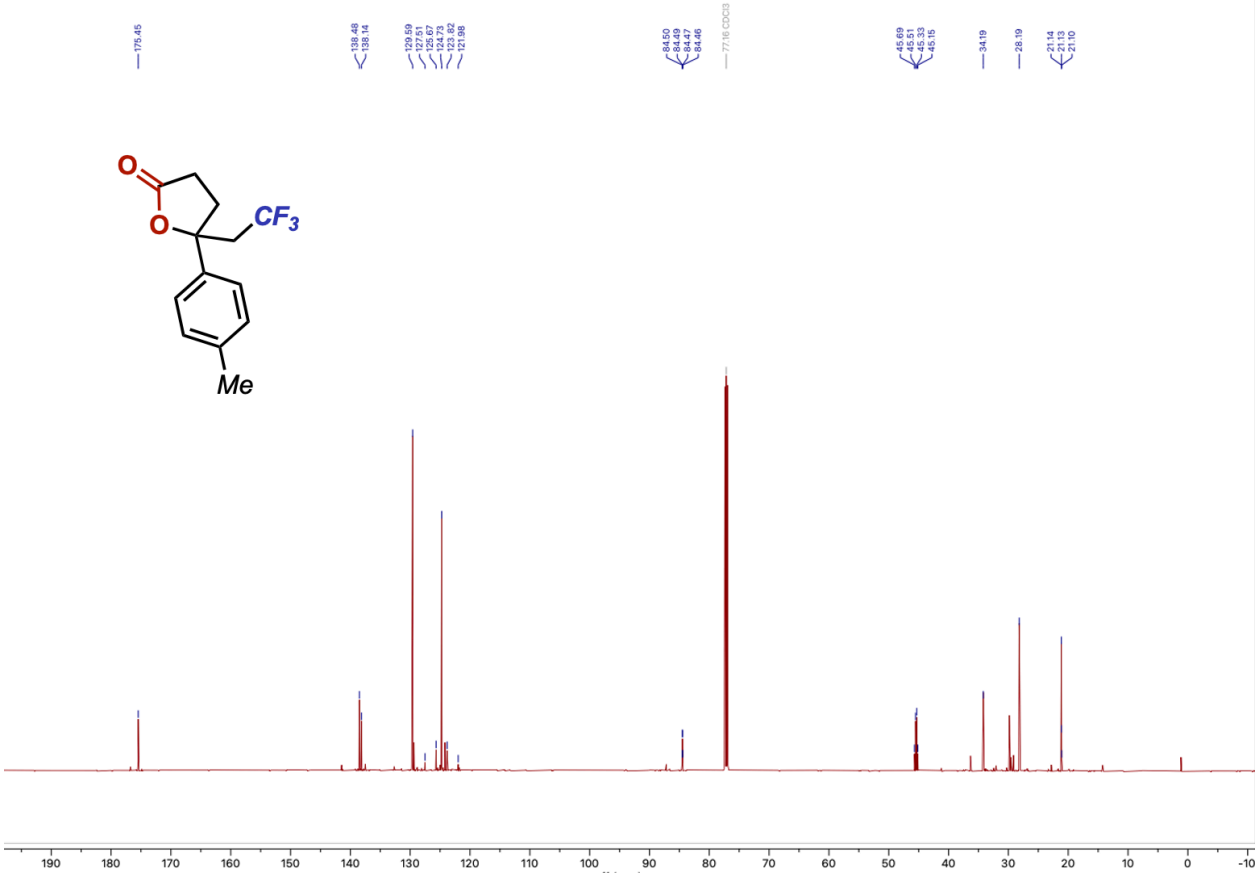
^{19}F NMR (565 MHz, $CDCl_3$)



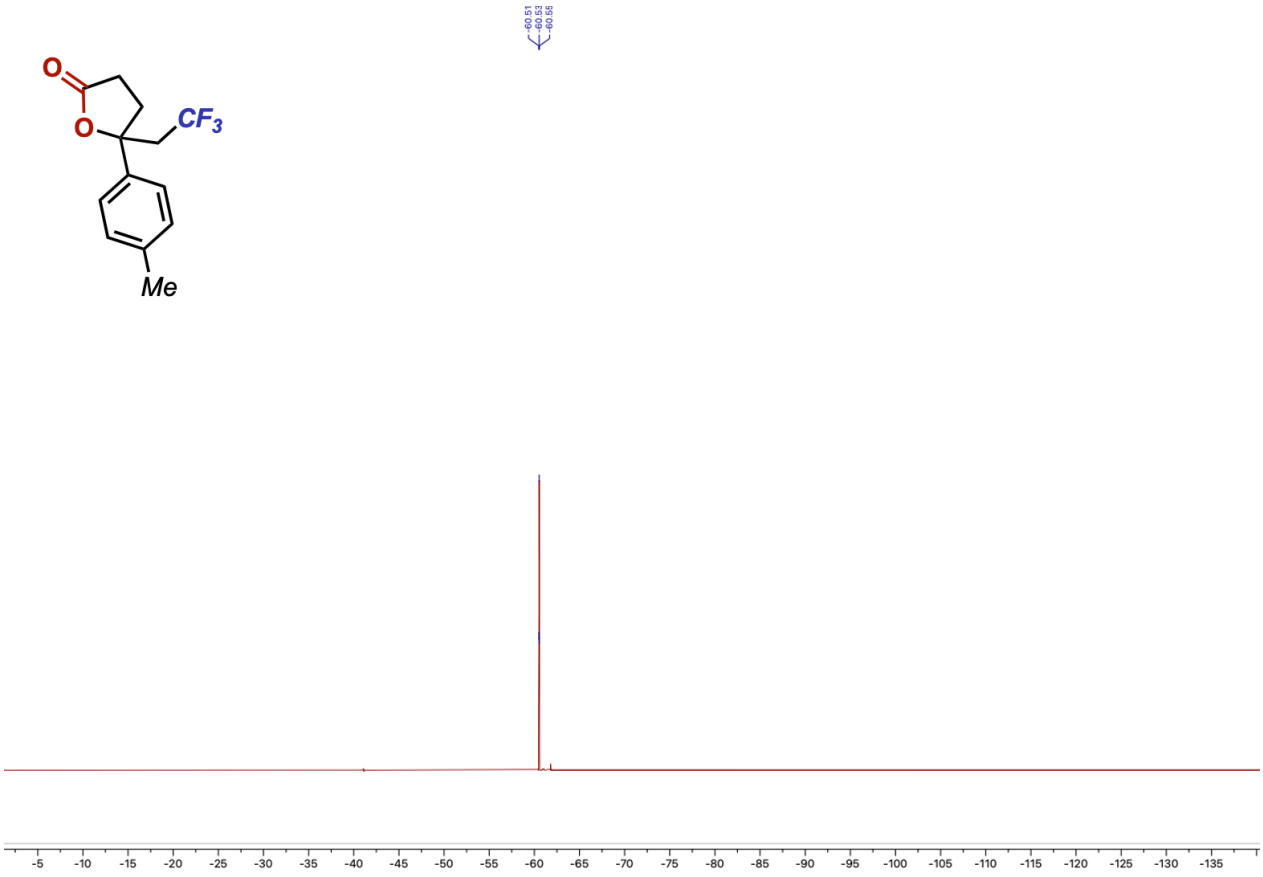
3b ^{1}H NMR (600 MHz, $CDCl_3$)



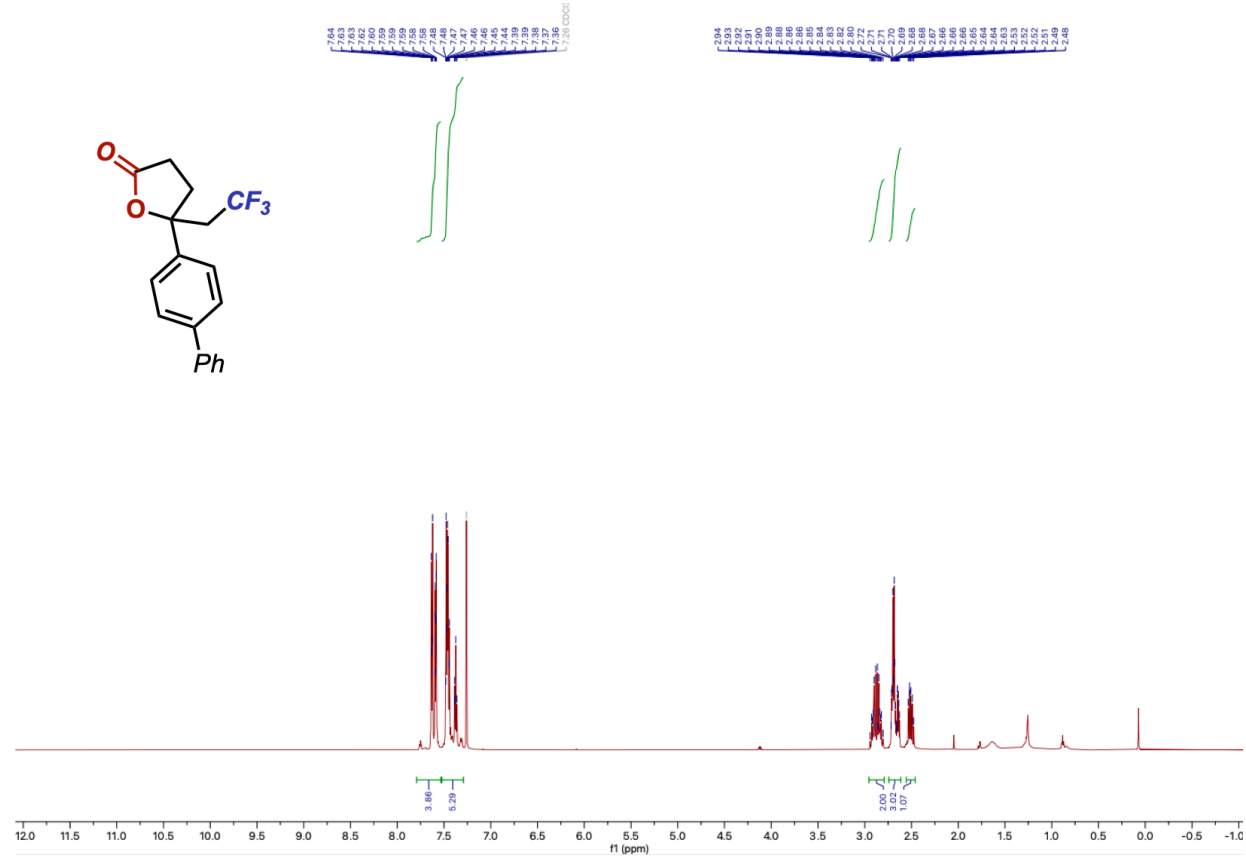
^{13}C NMR (151 MHz, $CDCl_3$)



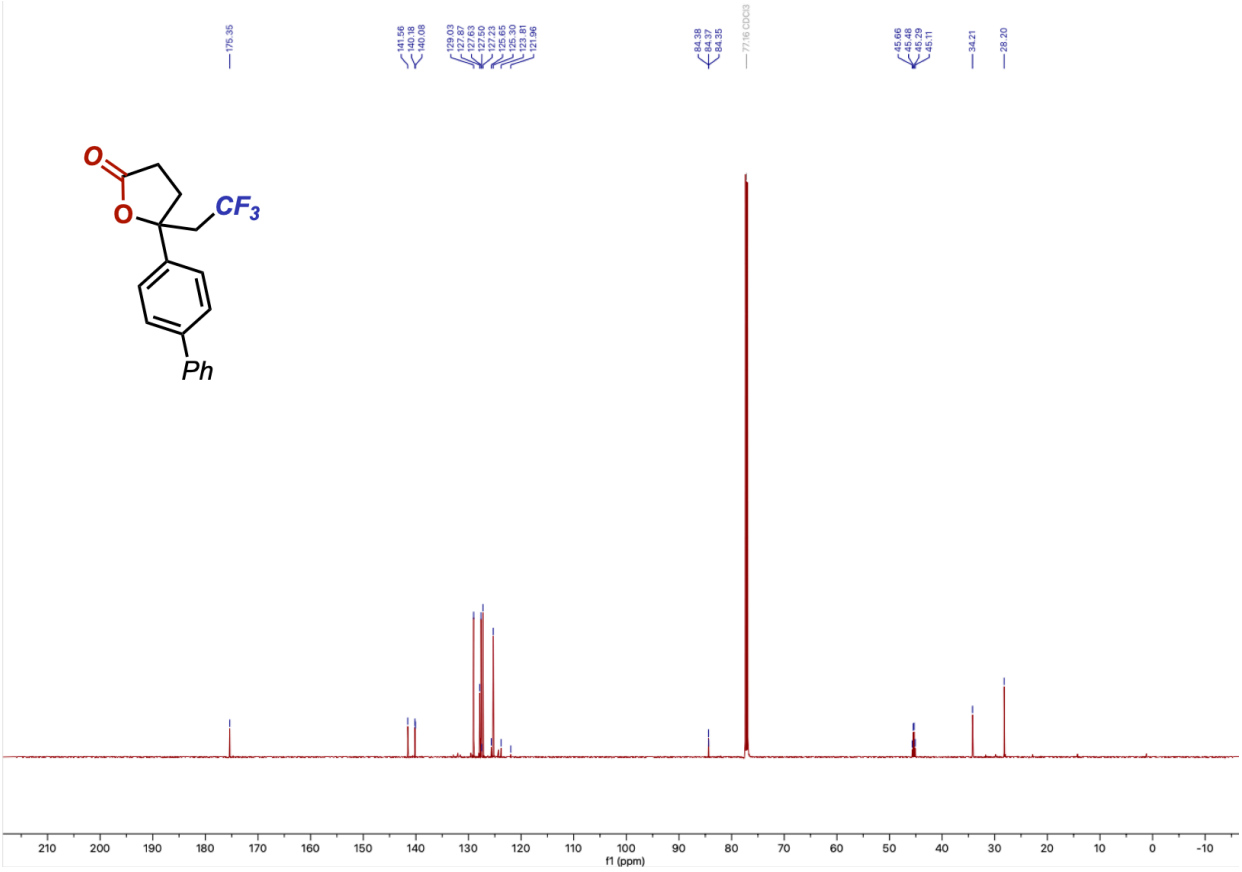
^{19}F NMR (565 MHz, $CDCl_3$)



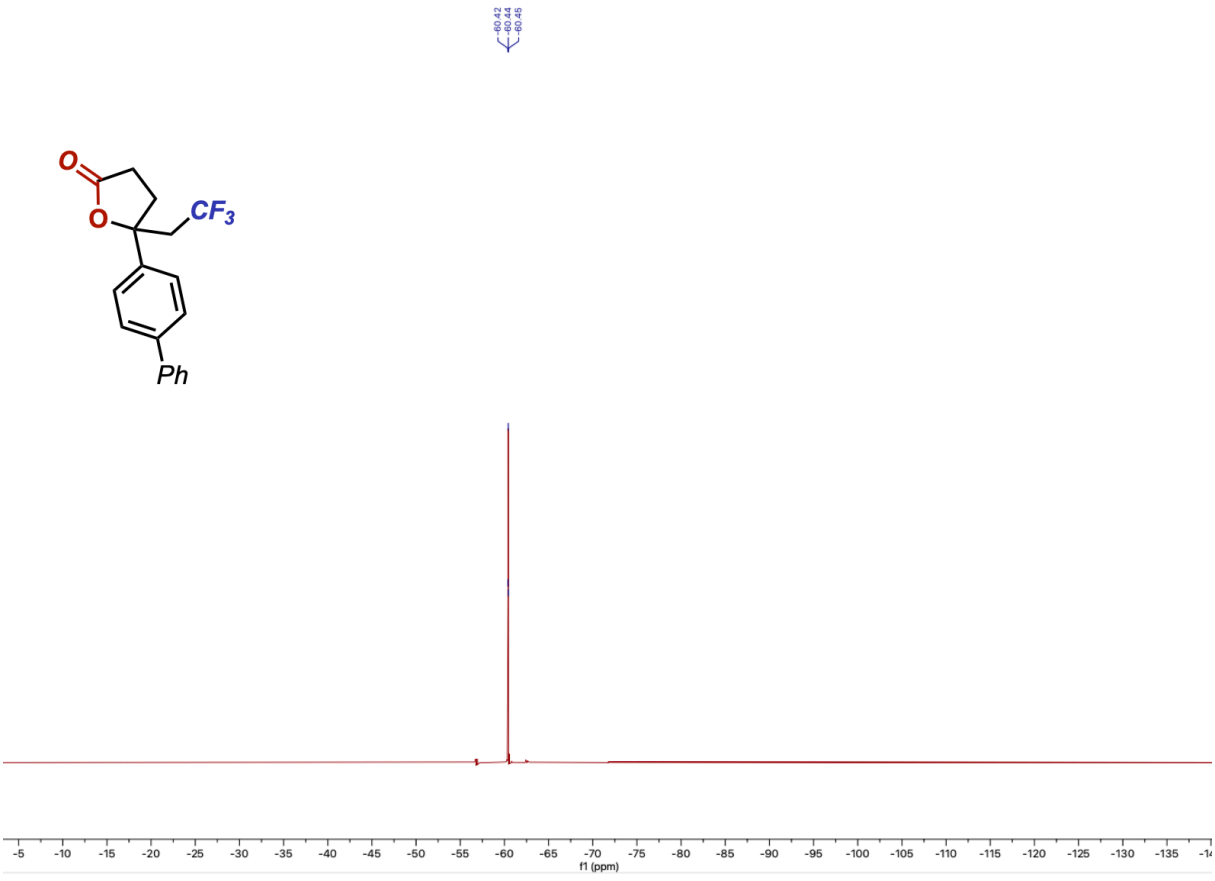
3c ^{1}H NMR (600 MHz, $CDCl_3$)



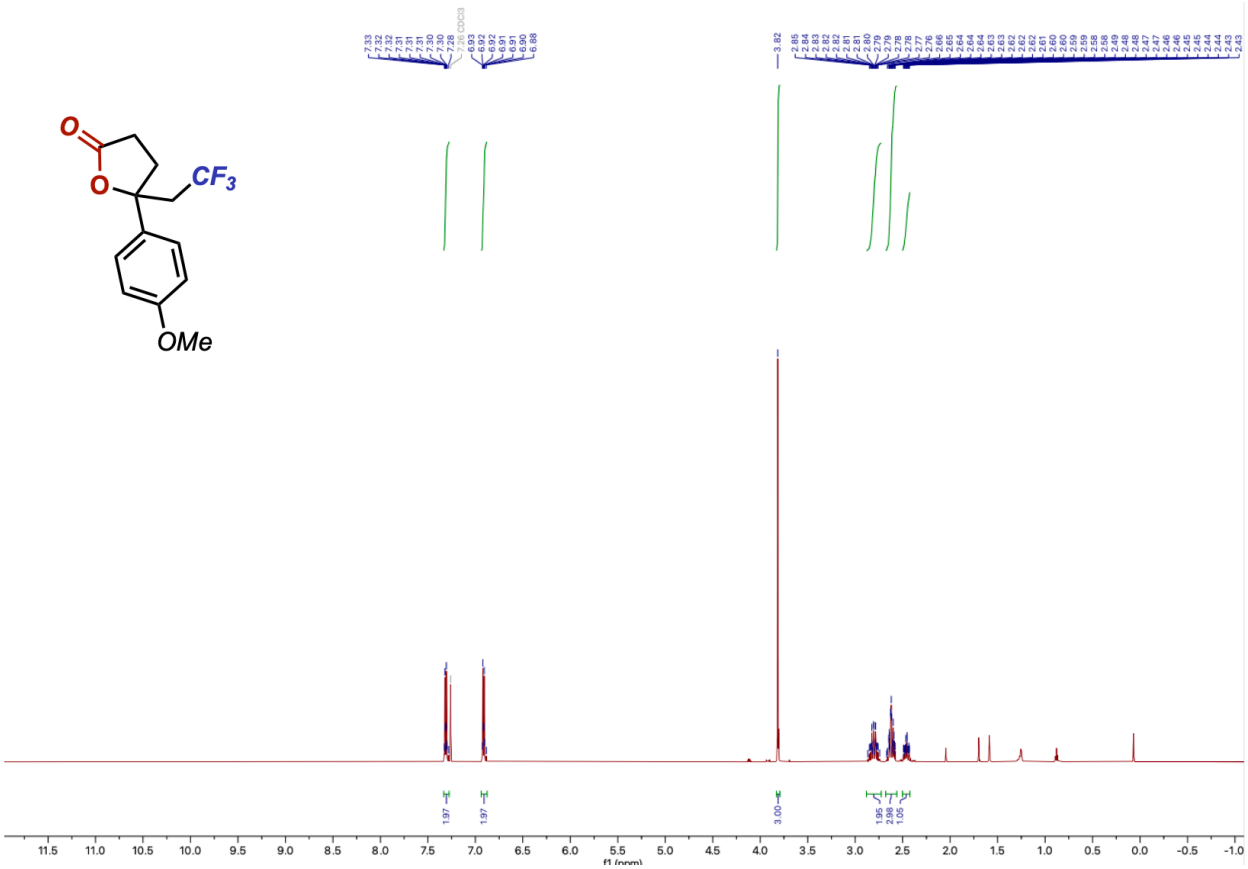
^{13}C NMR (151 MHz, $CDCl_3$)



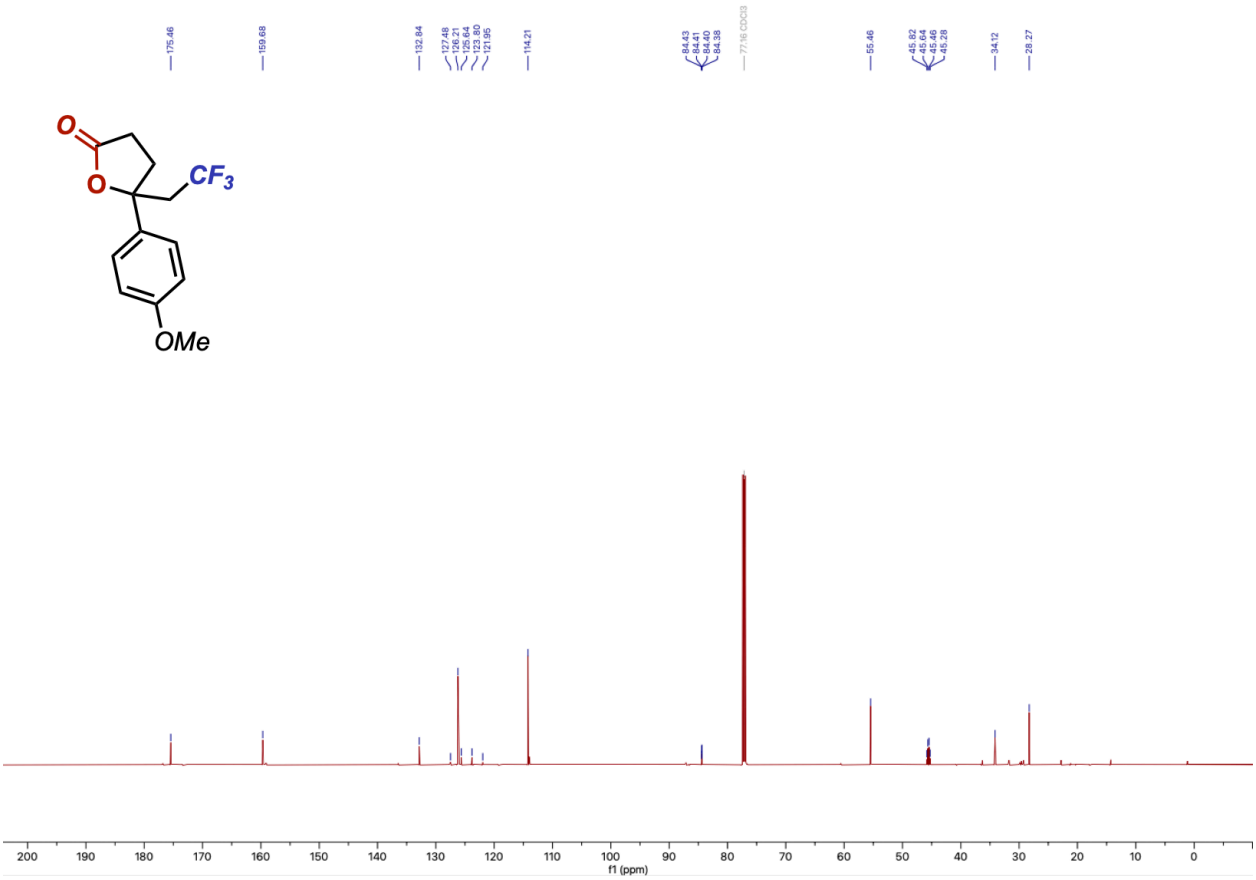
^{19}F NMR (565 MHz, $CDCl_3$)



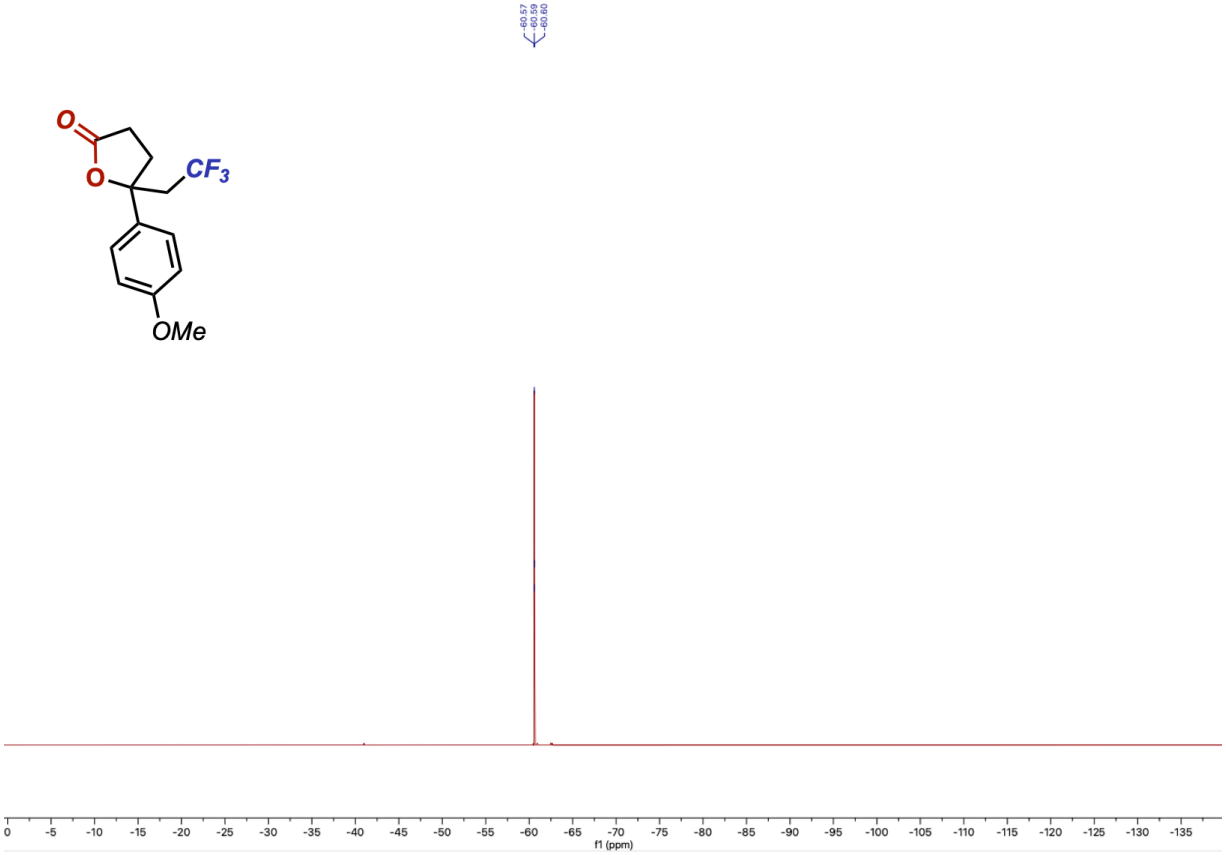
3d ^{1}H NMR (600 MHz, $CDCl_3$)



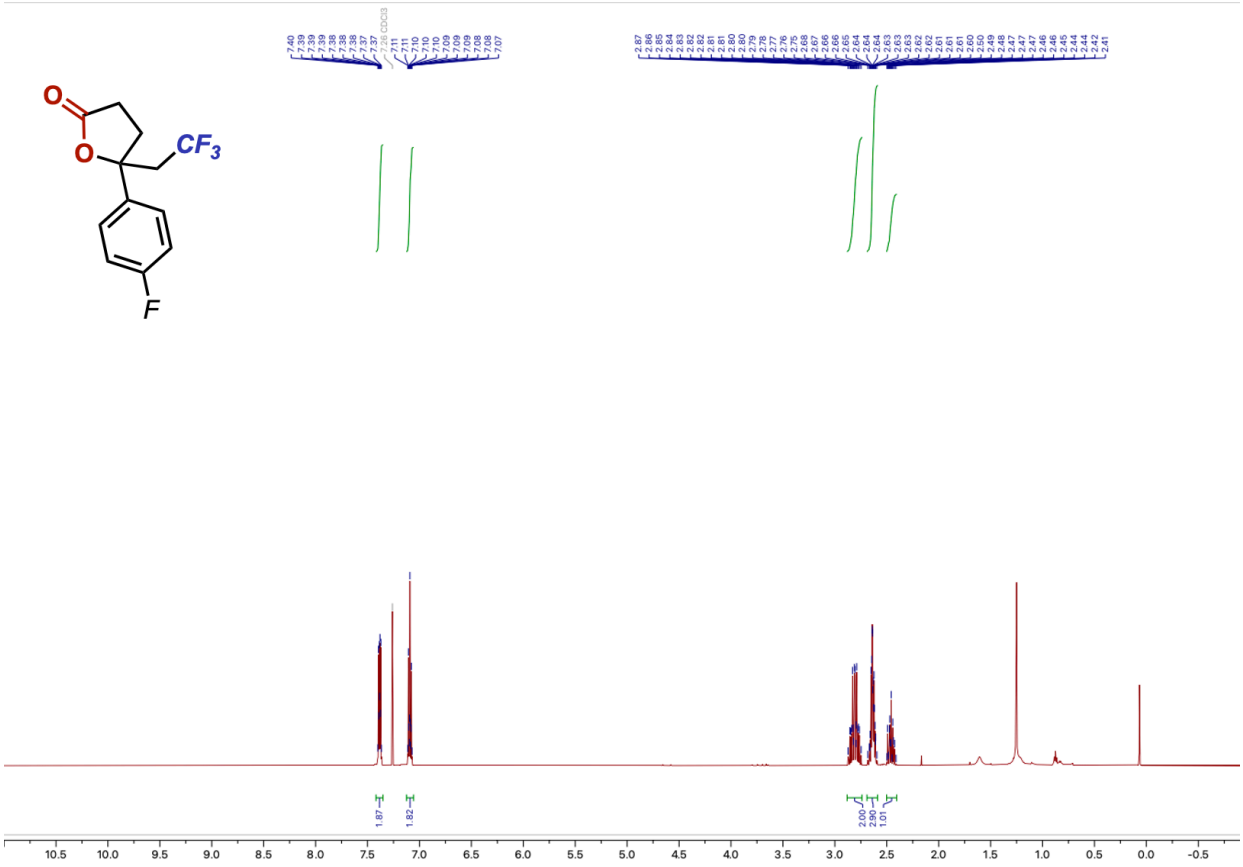
^{13}C NMR (151 MHz, $CDCl_3$)



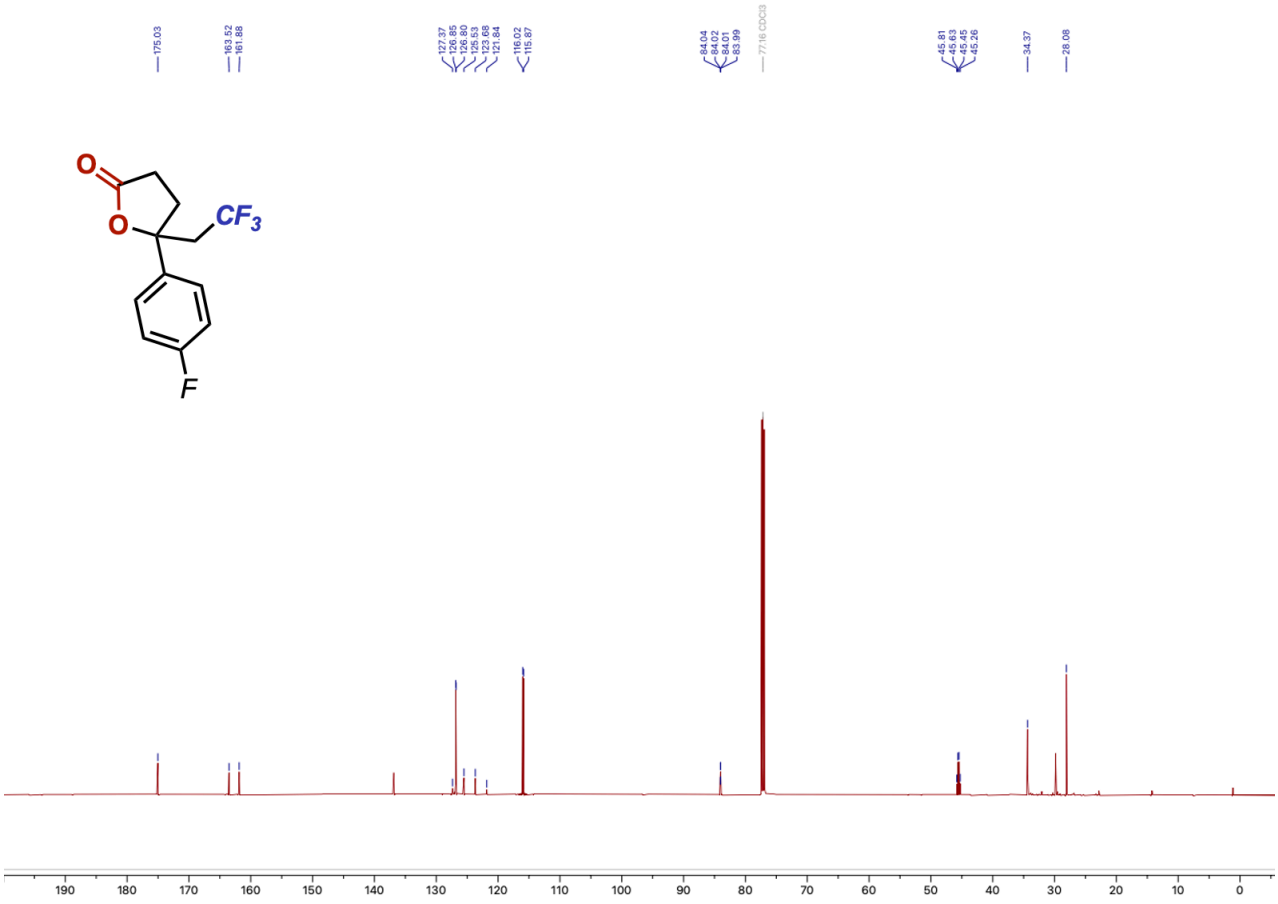
^{19}F NMR (565 MHz, $CDCl_3$)



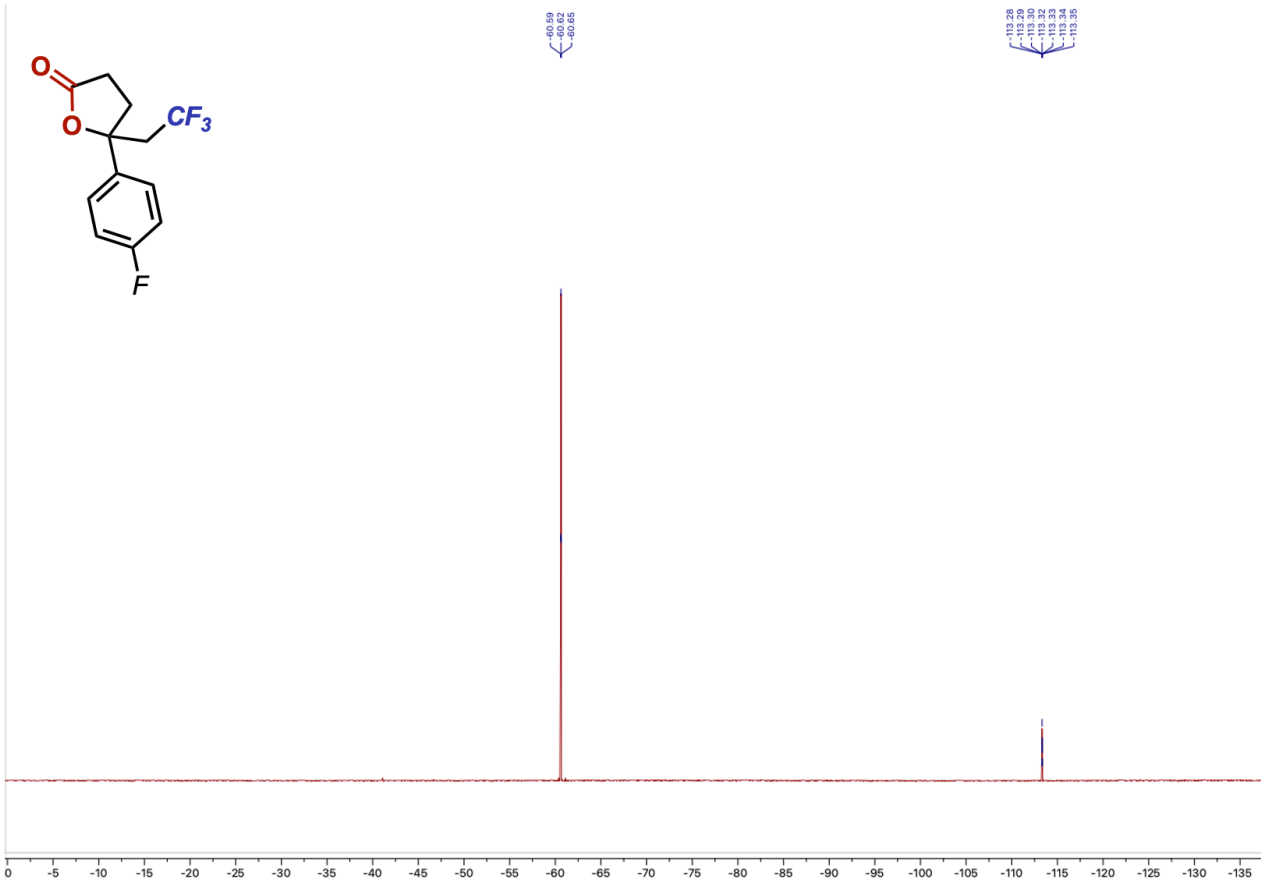
3e ^{1}H NMR (600 MHz, $CDCl_3$)



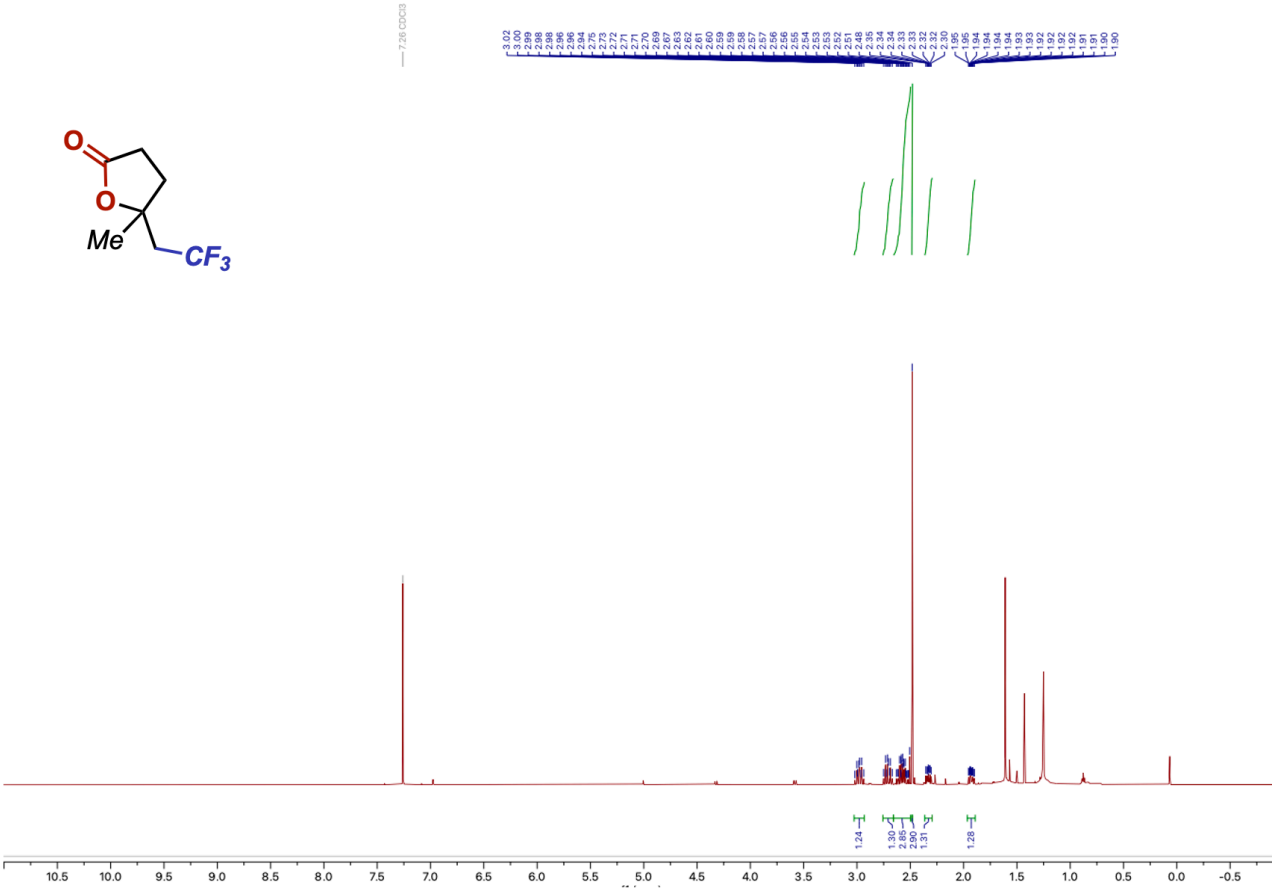
^{13}C NMR (151 MHz, $CDCl_3$)



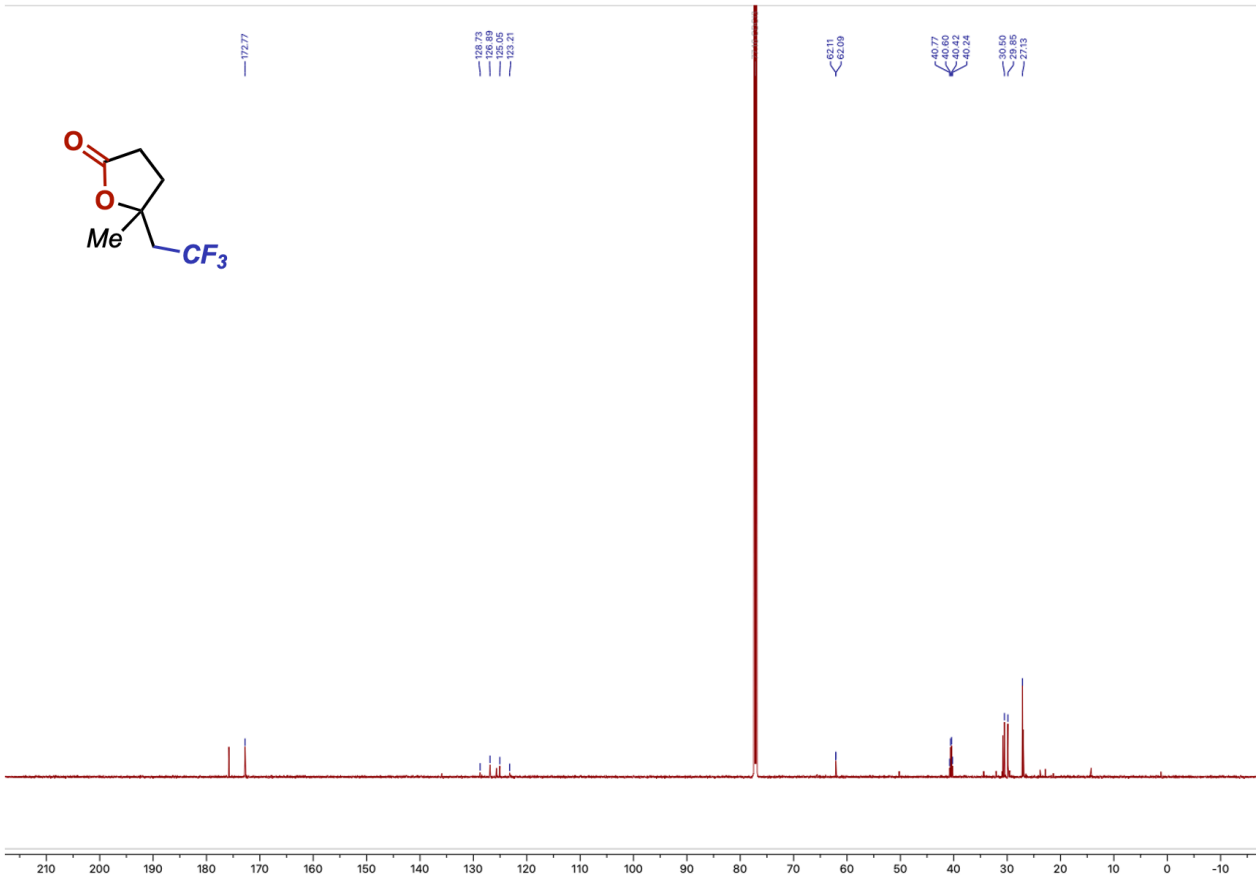
^{19}F NMR (565 MHz, $CDCl_3$)



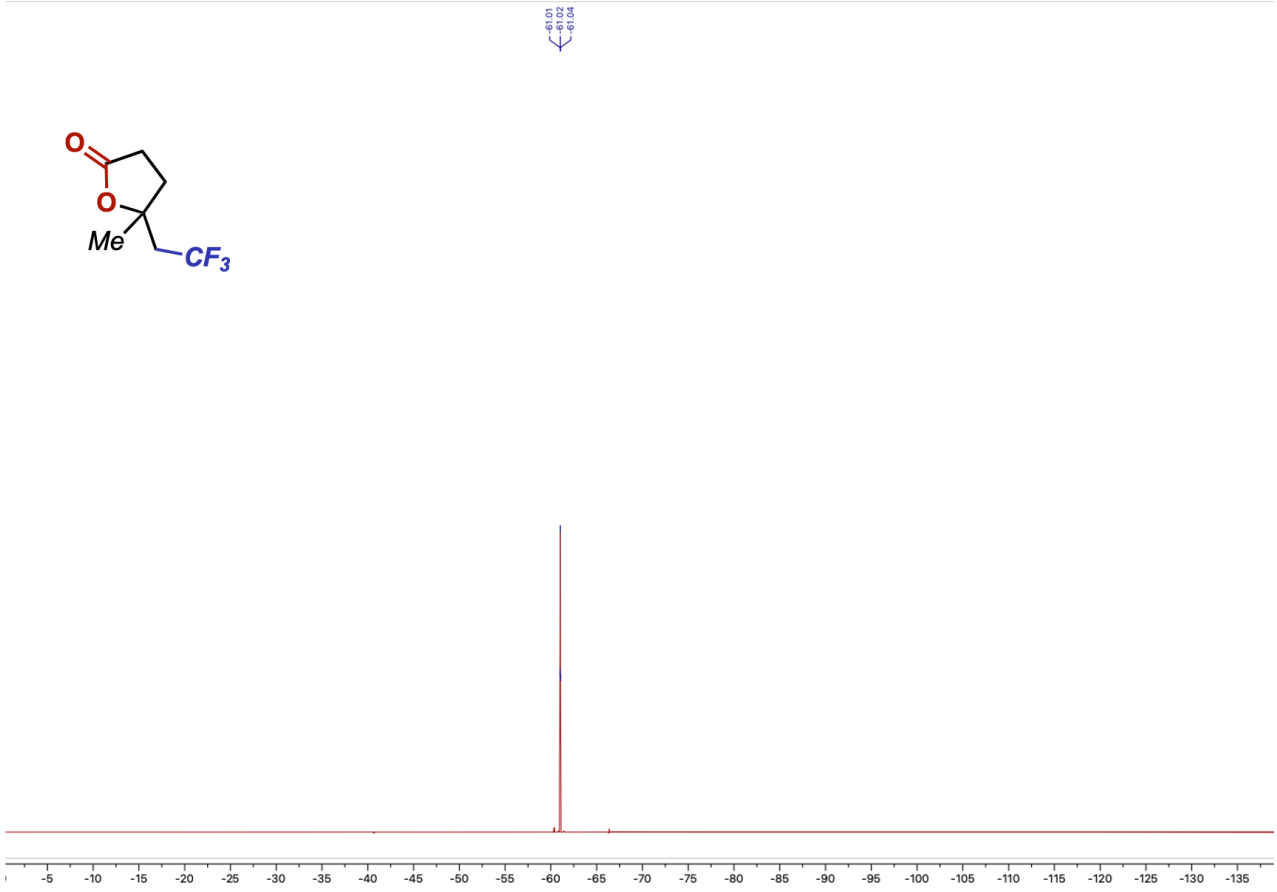
3f ^{1}H NMR (600 MHz, $CDCl_3$)



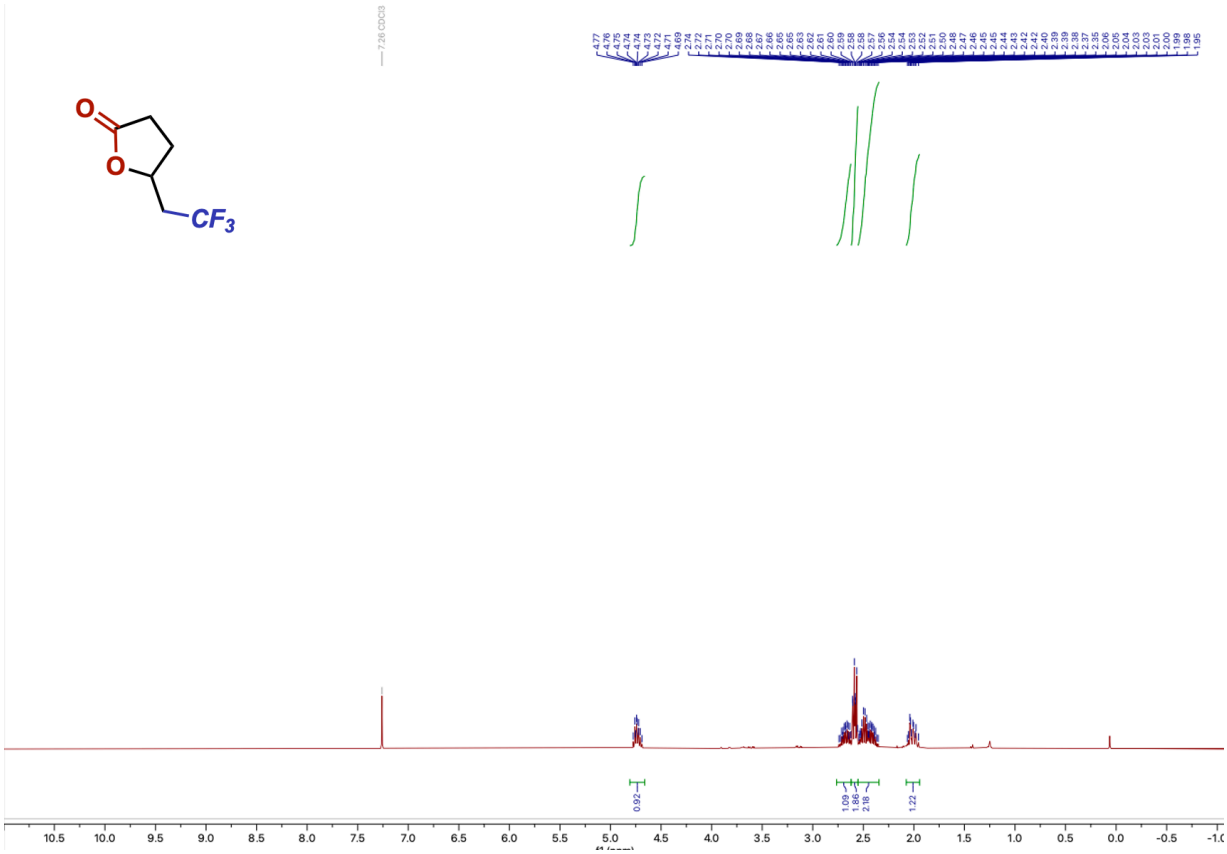
^{13}C NMR (151 MHz, $CDCl_3$)



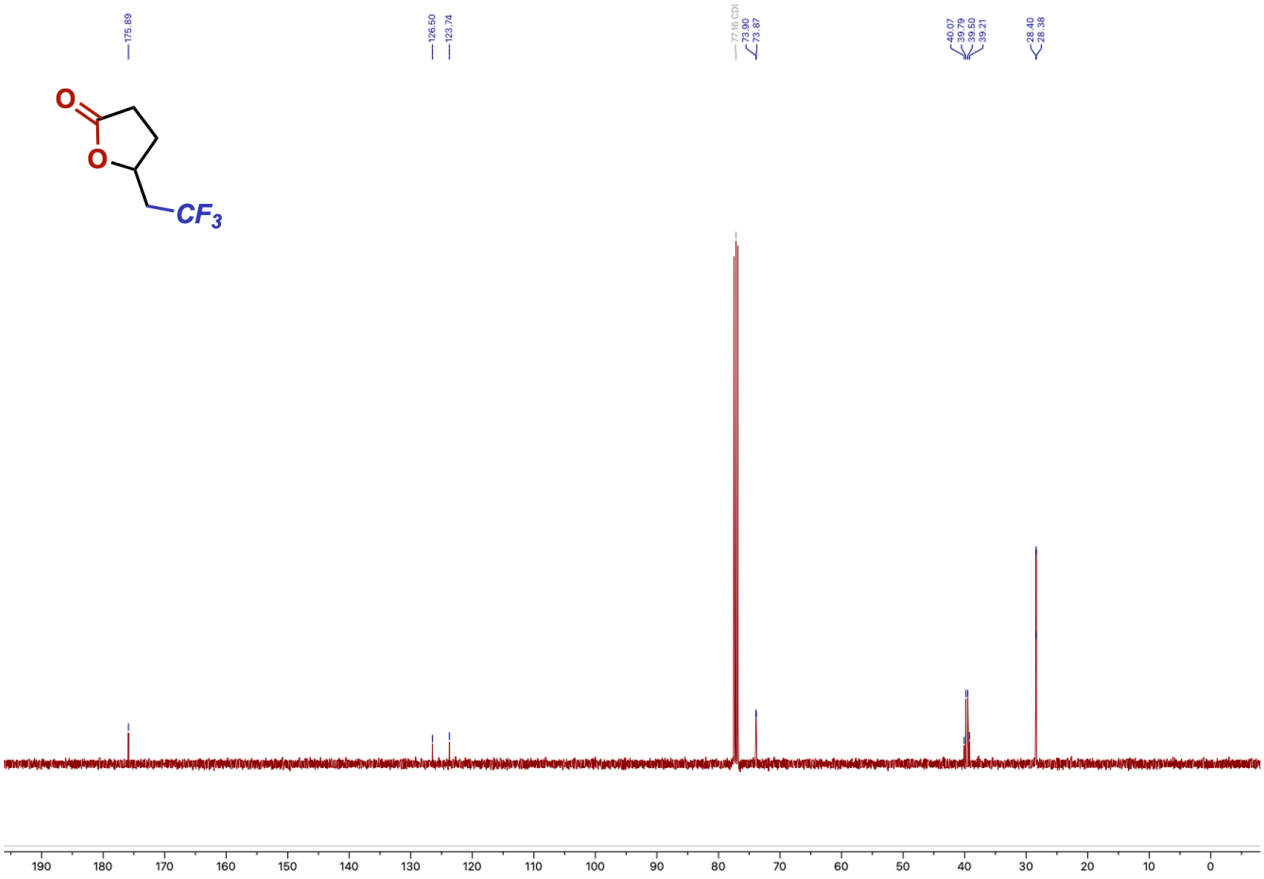
^{19}F NMR (565 MHz, $CDCl_3$)



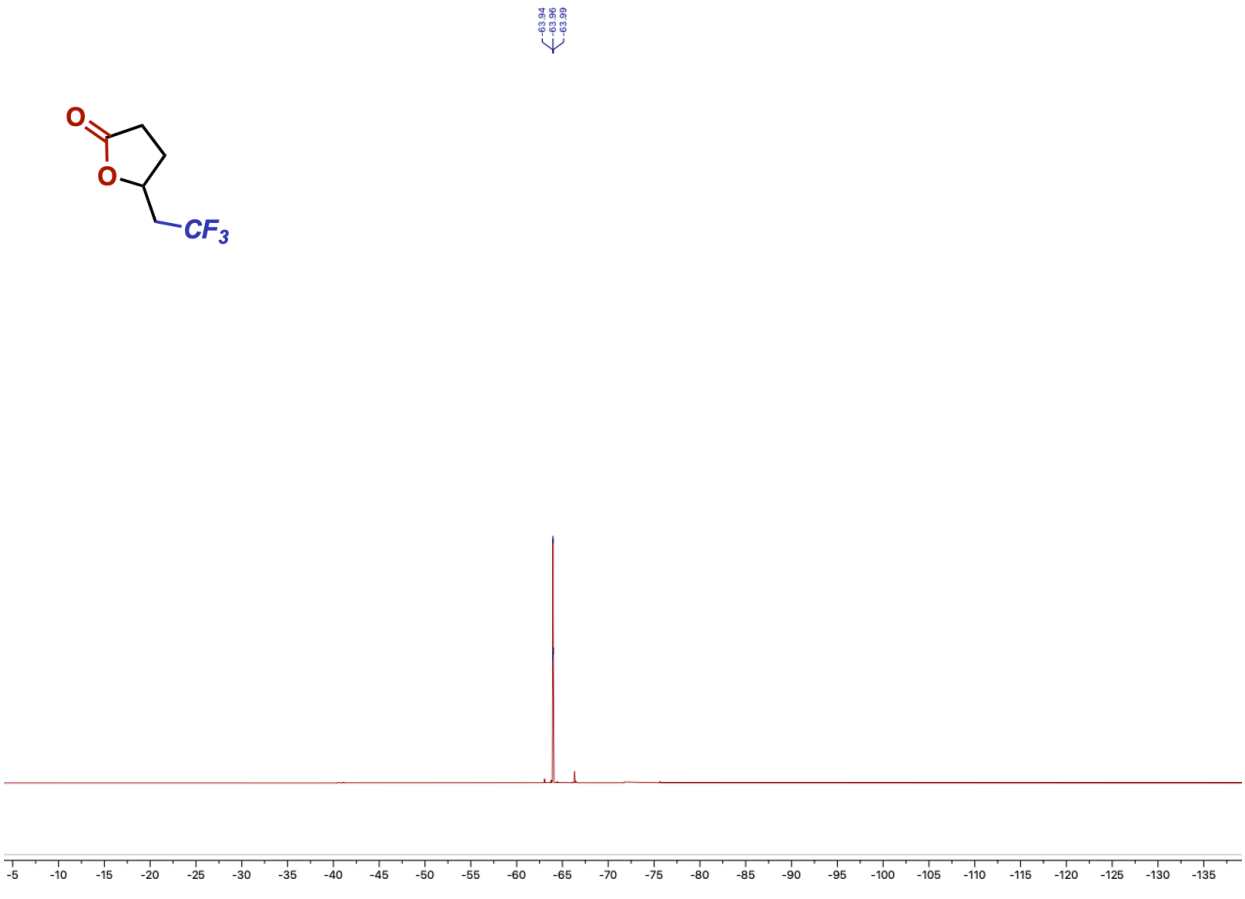
3g ^{1}H NMR (600 MHz, $CDCl_3$)



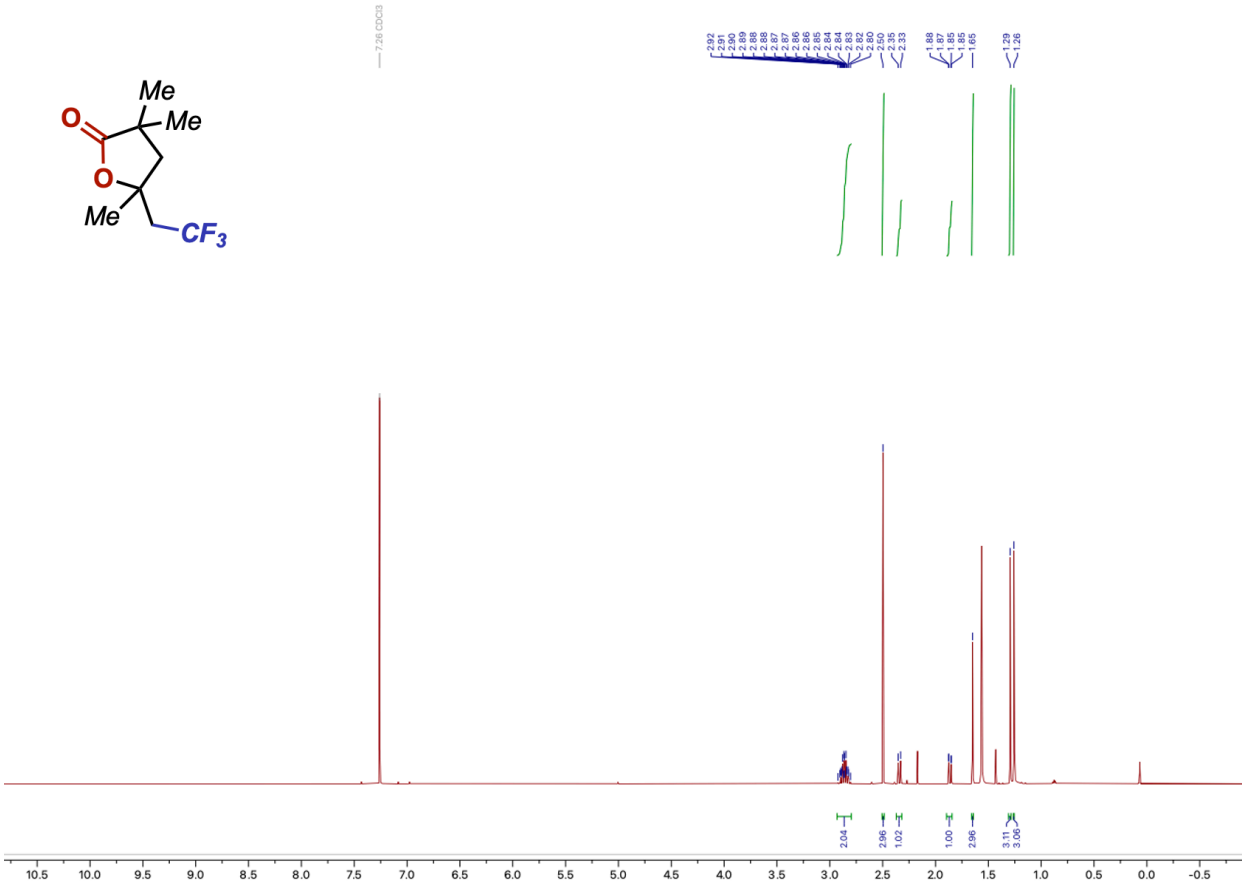
^{13}C NMR (151 MHz, $CDCl_3$)



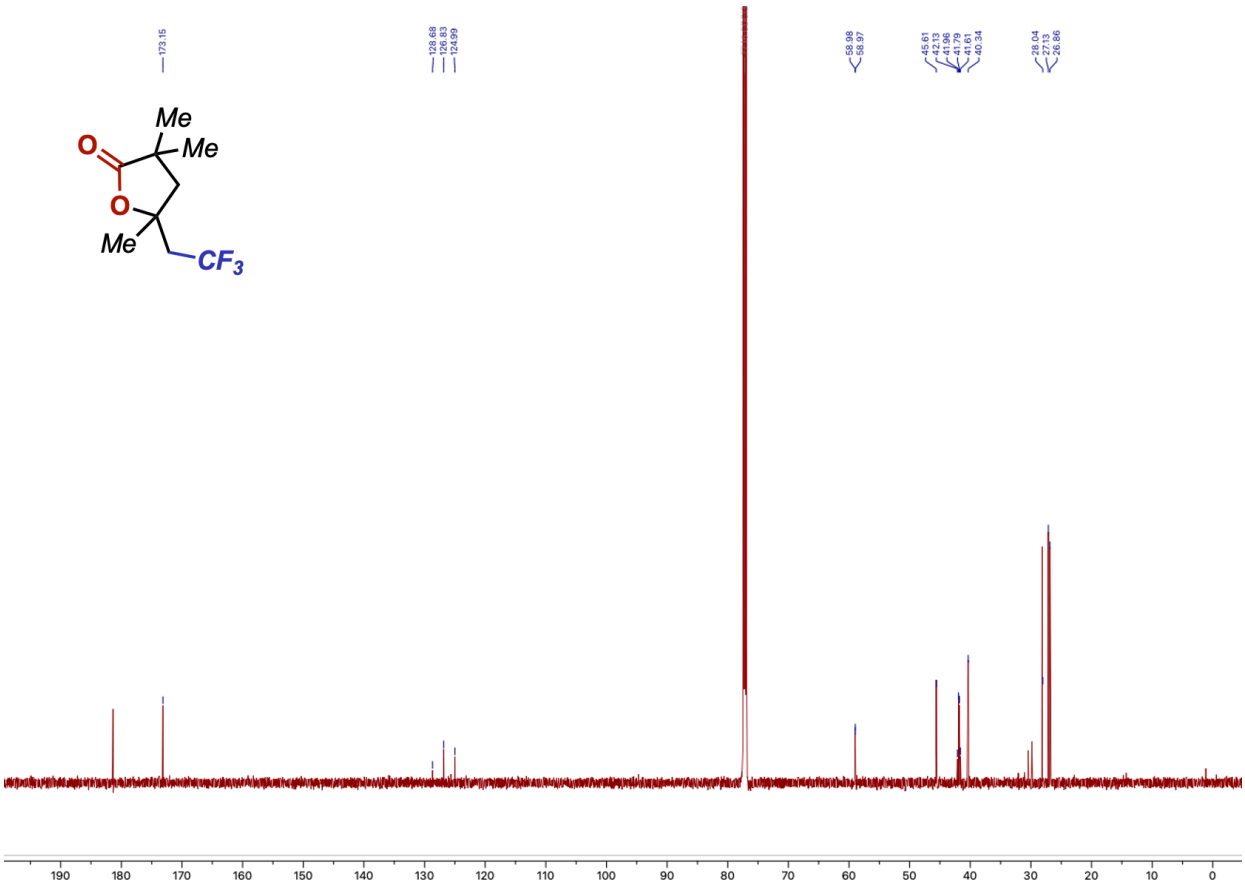
^{19}F NMR (565 MHz, $CDCl_3$)



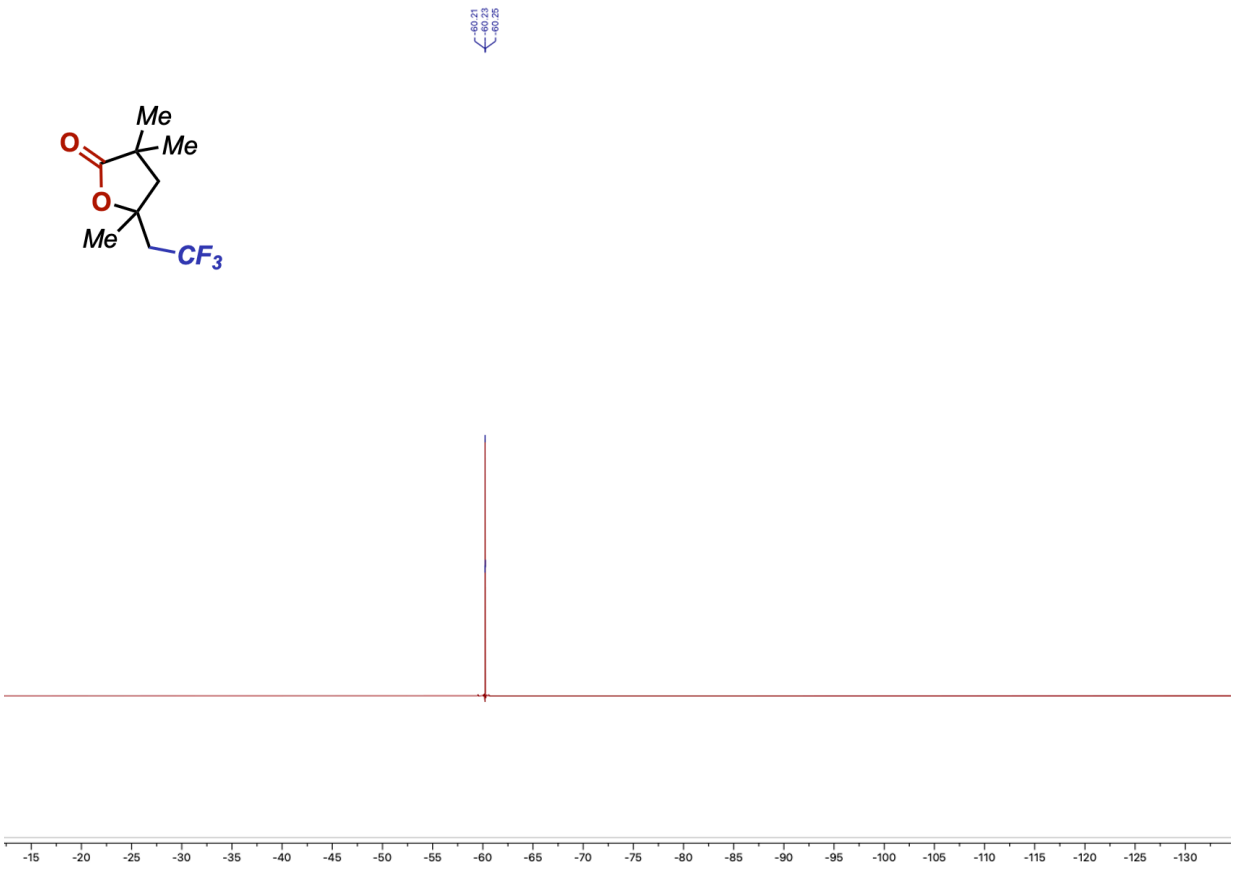
3h ^{1}H NMR (600 MHz, $CDCl_3$)



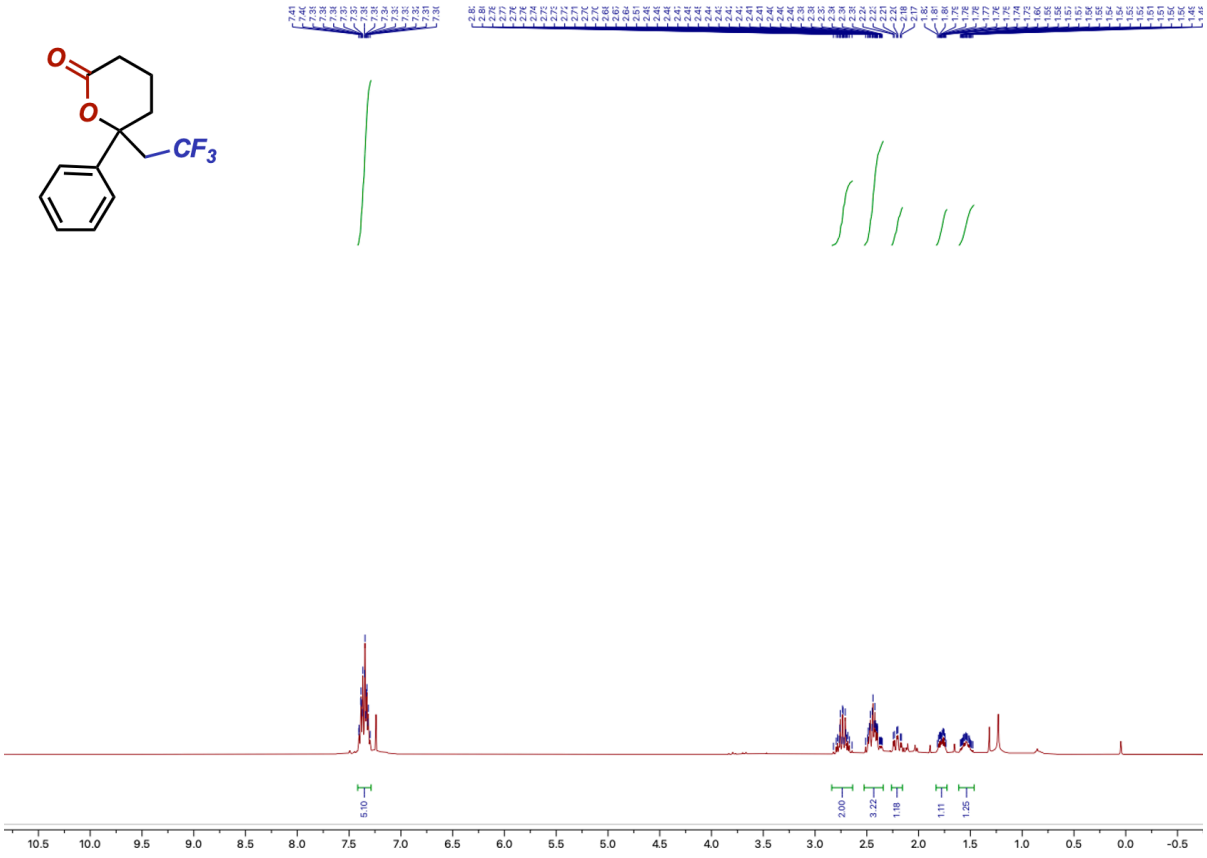
^{13}C NMR (151 MHz, $CDCl_3$)



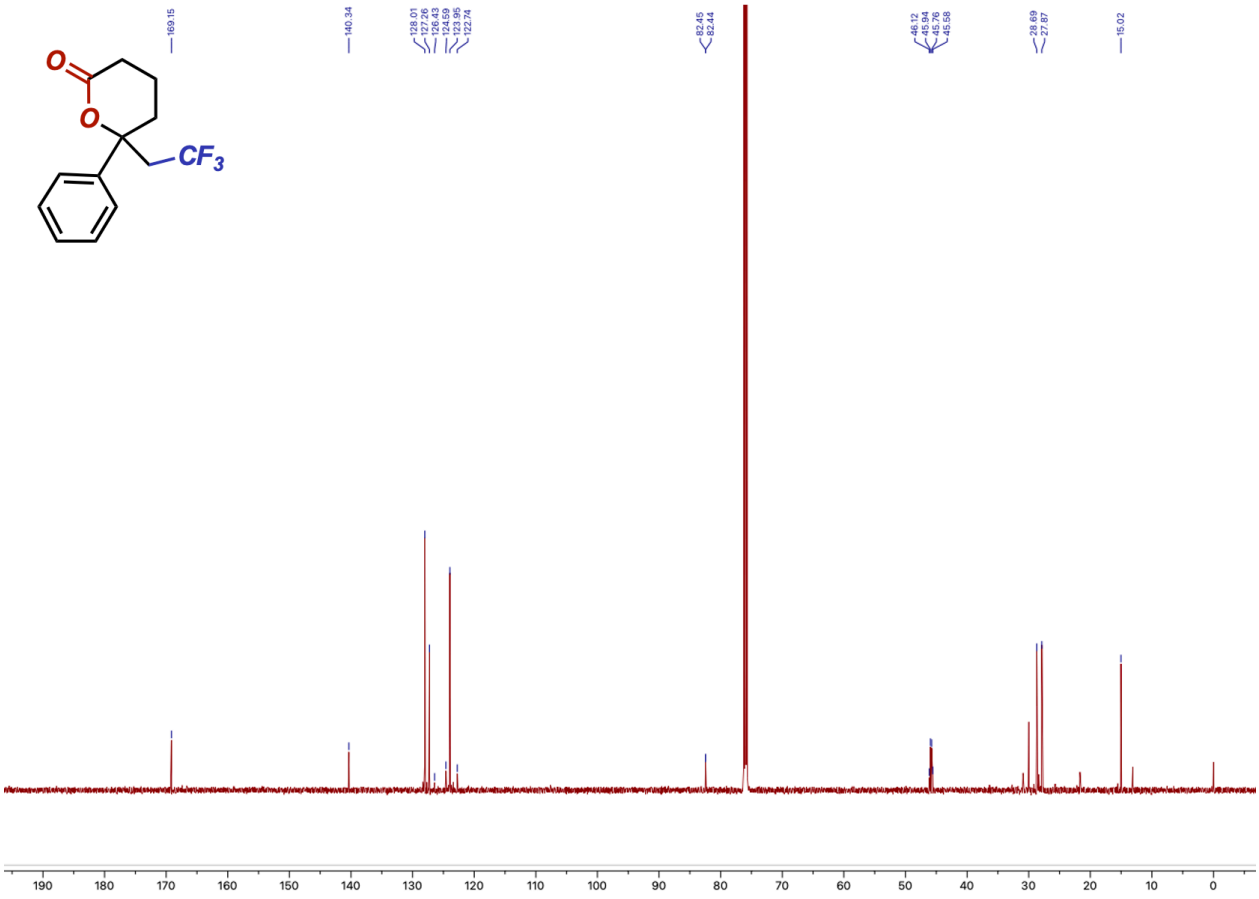
^{19}F NMR (565 MHz, $CDCl_3$)



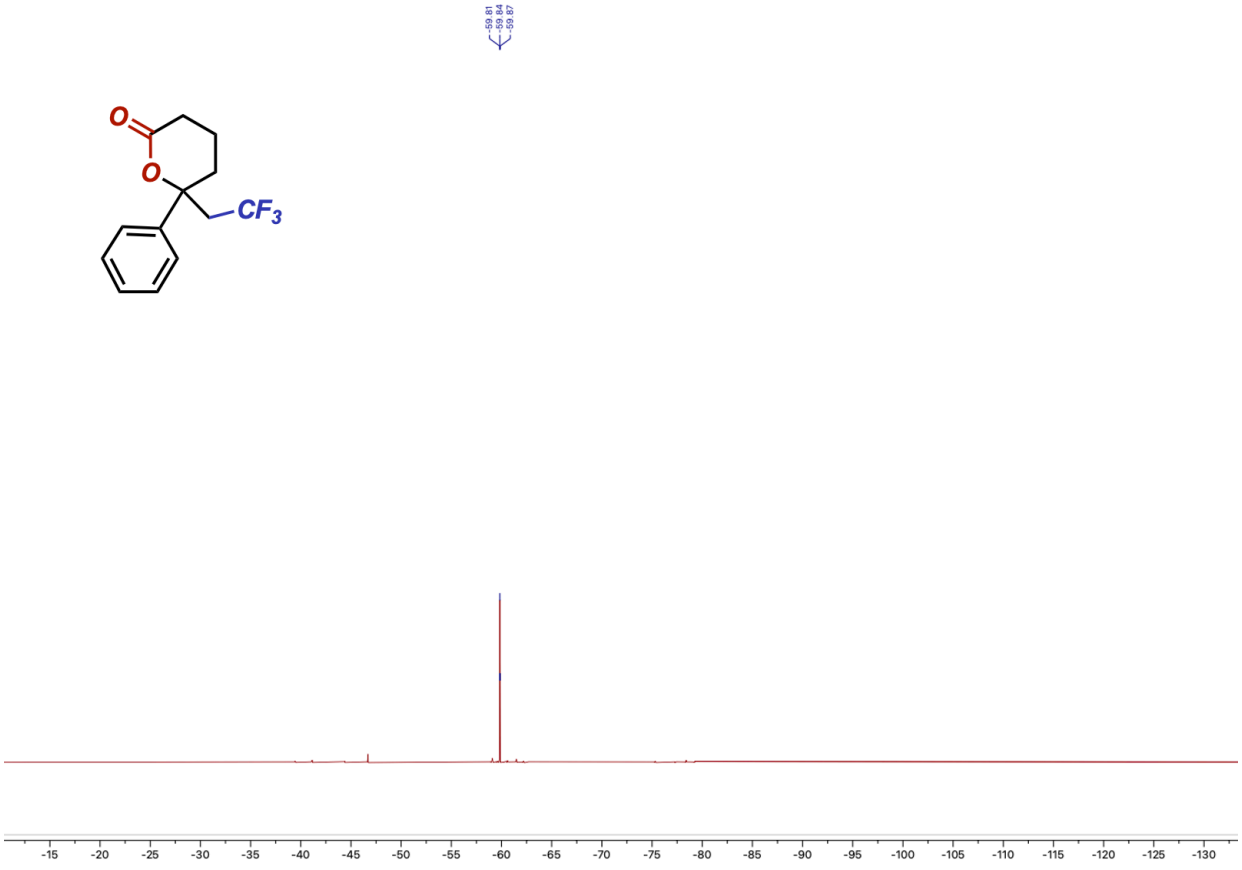
3i ^{1}H NMR (600 MHz, $CDCl_3$)



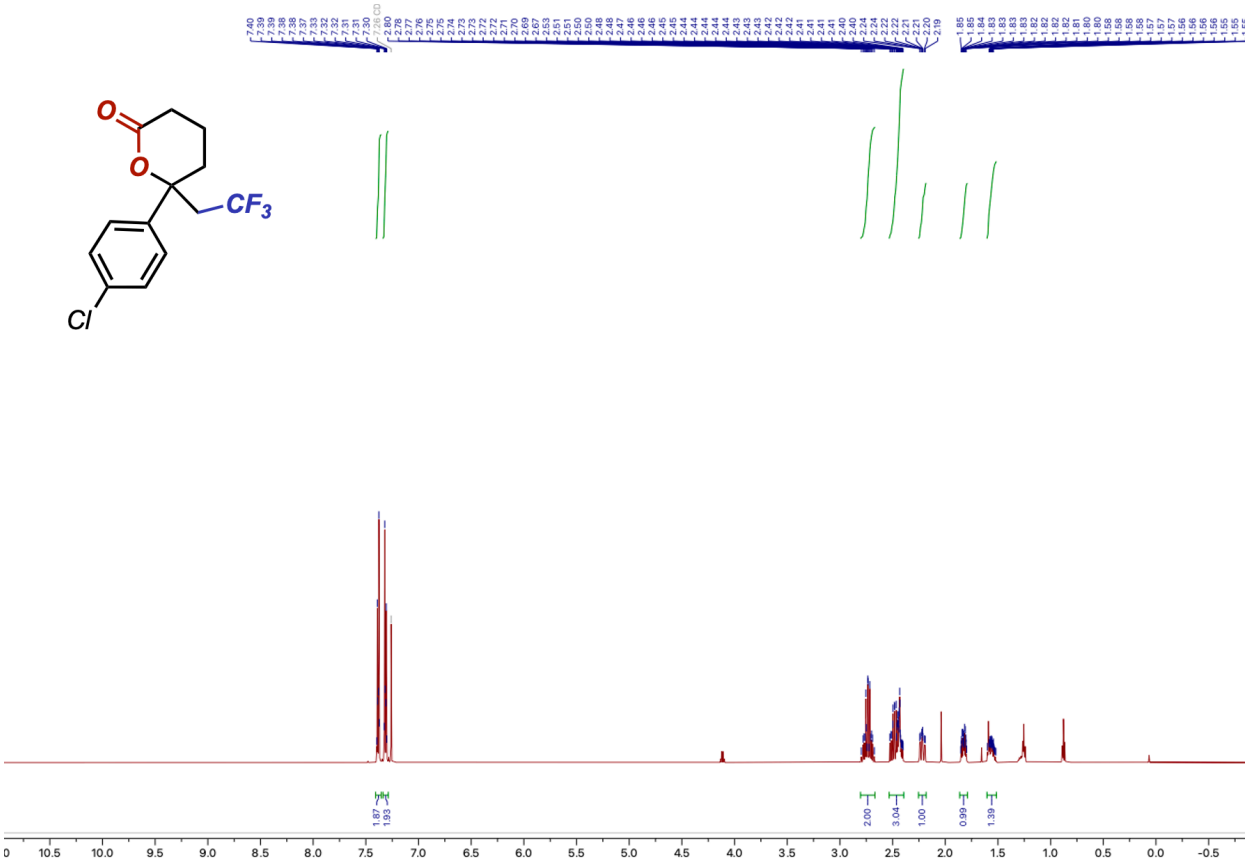
^{13}C NMR (151 MHz, $CDCl_3$)



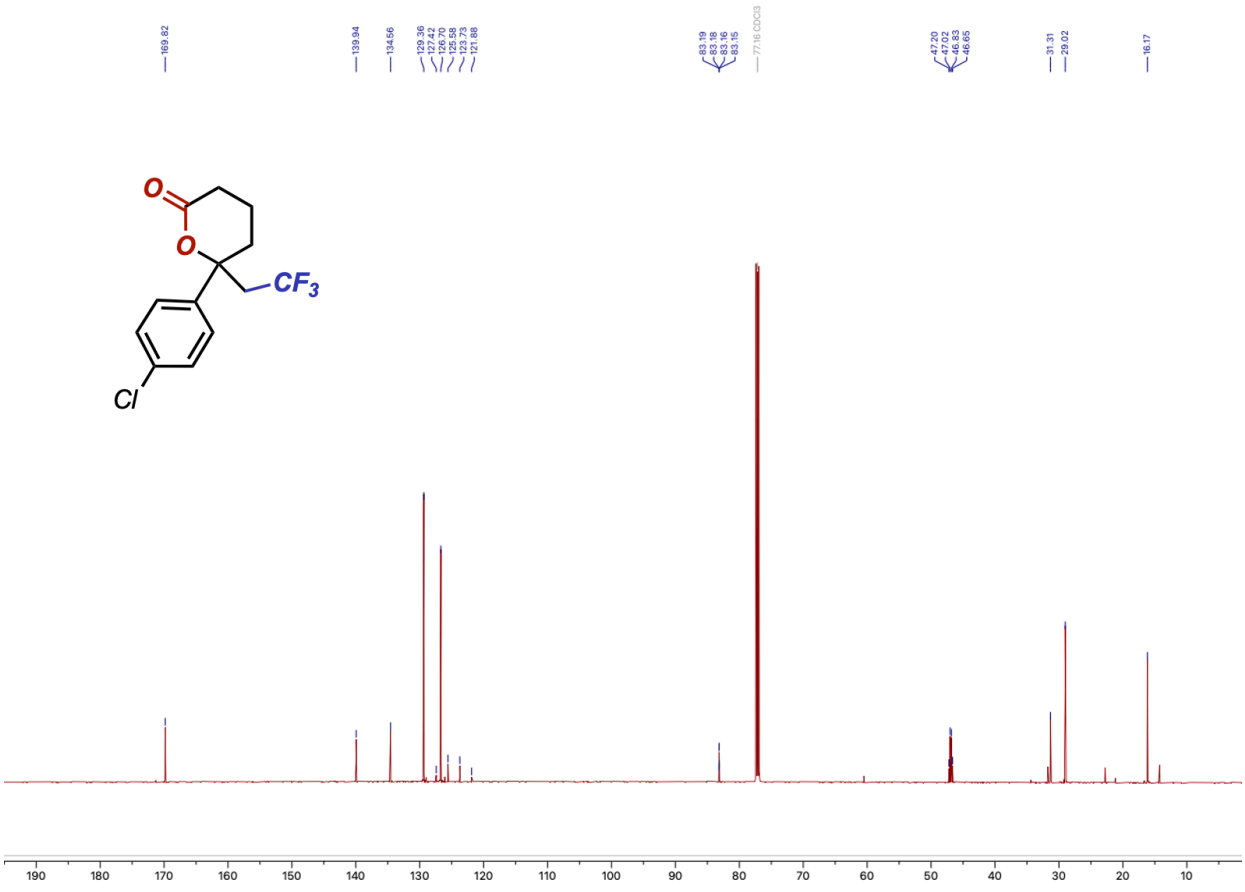
^{19}F NMR (565 MHz, $CDCl_3$)



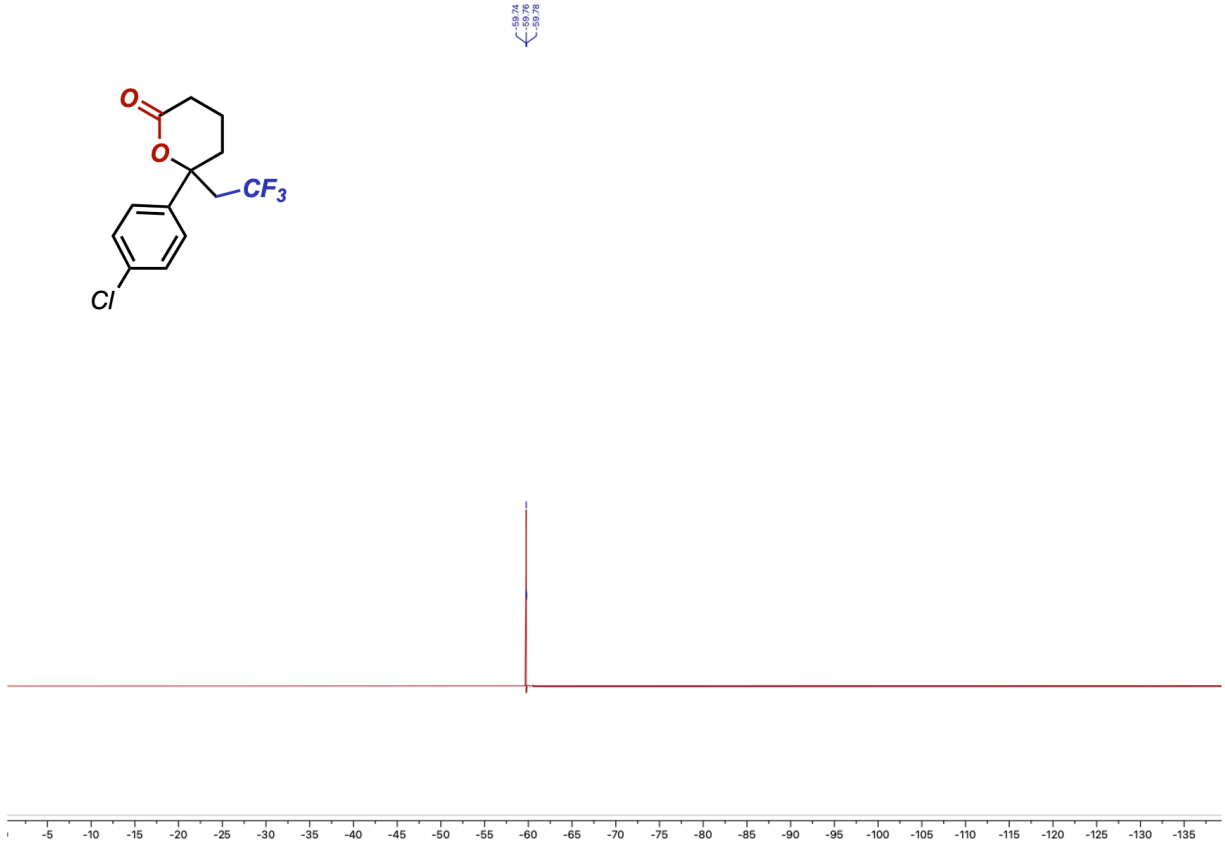
3j ^{1}H NMR (600 MHz, $CDCl_3$)



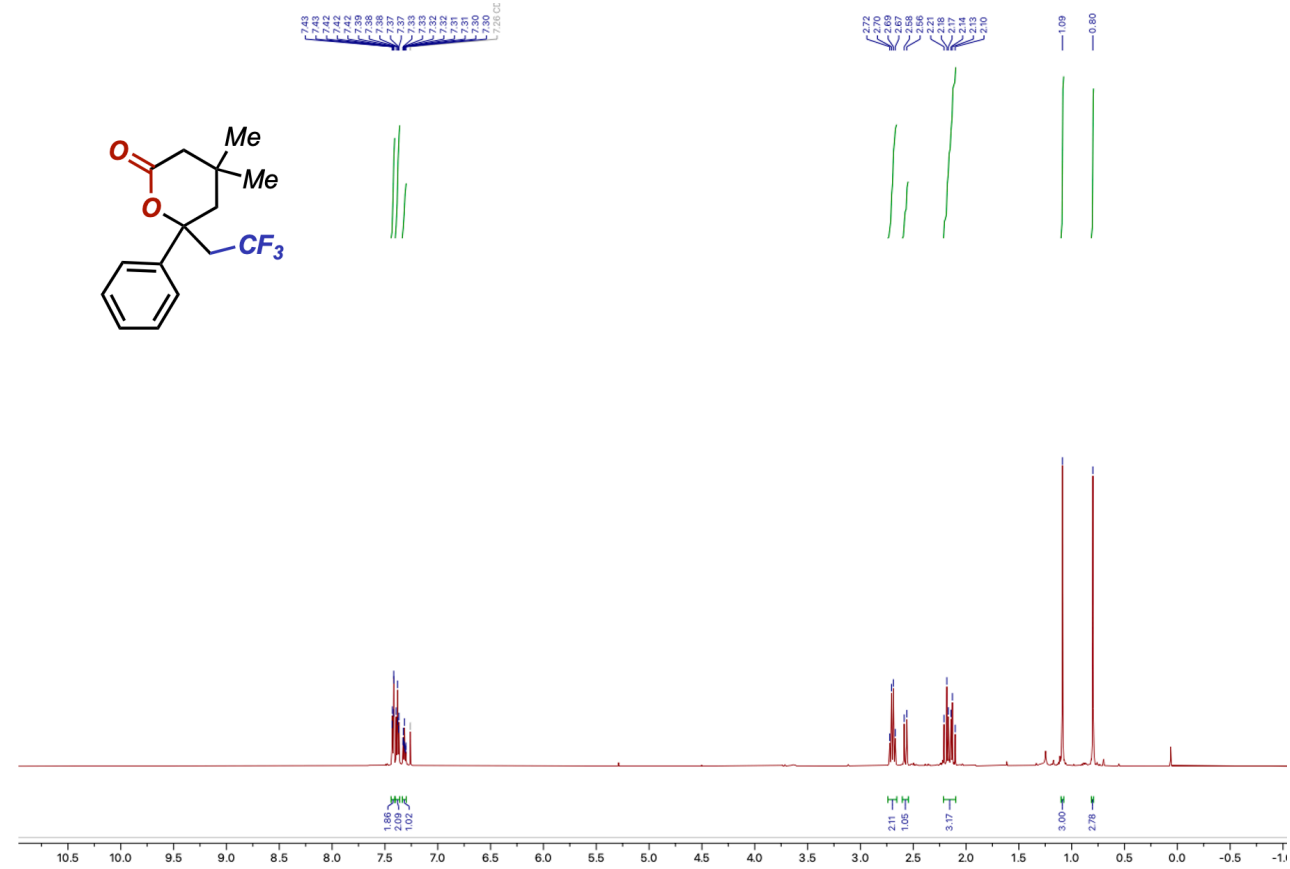
^{13}C NMR (151 MHz, $CDCl_3$)



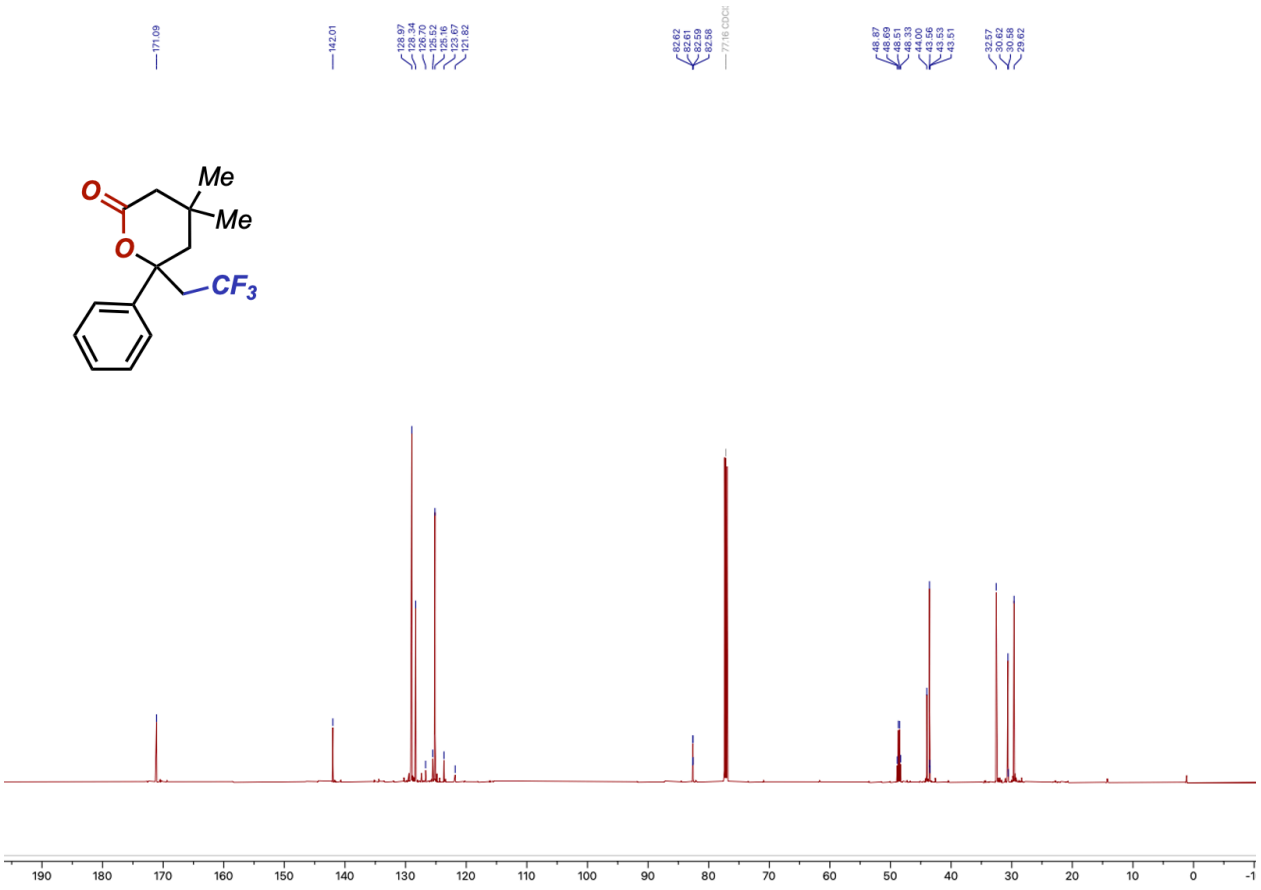
^{19}F NMR (565 MHz, $CDCl_3$)



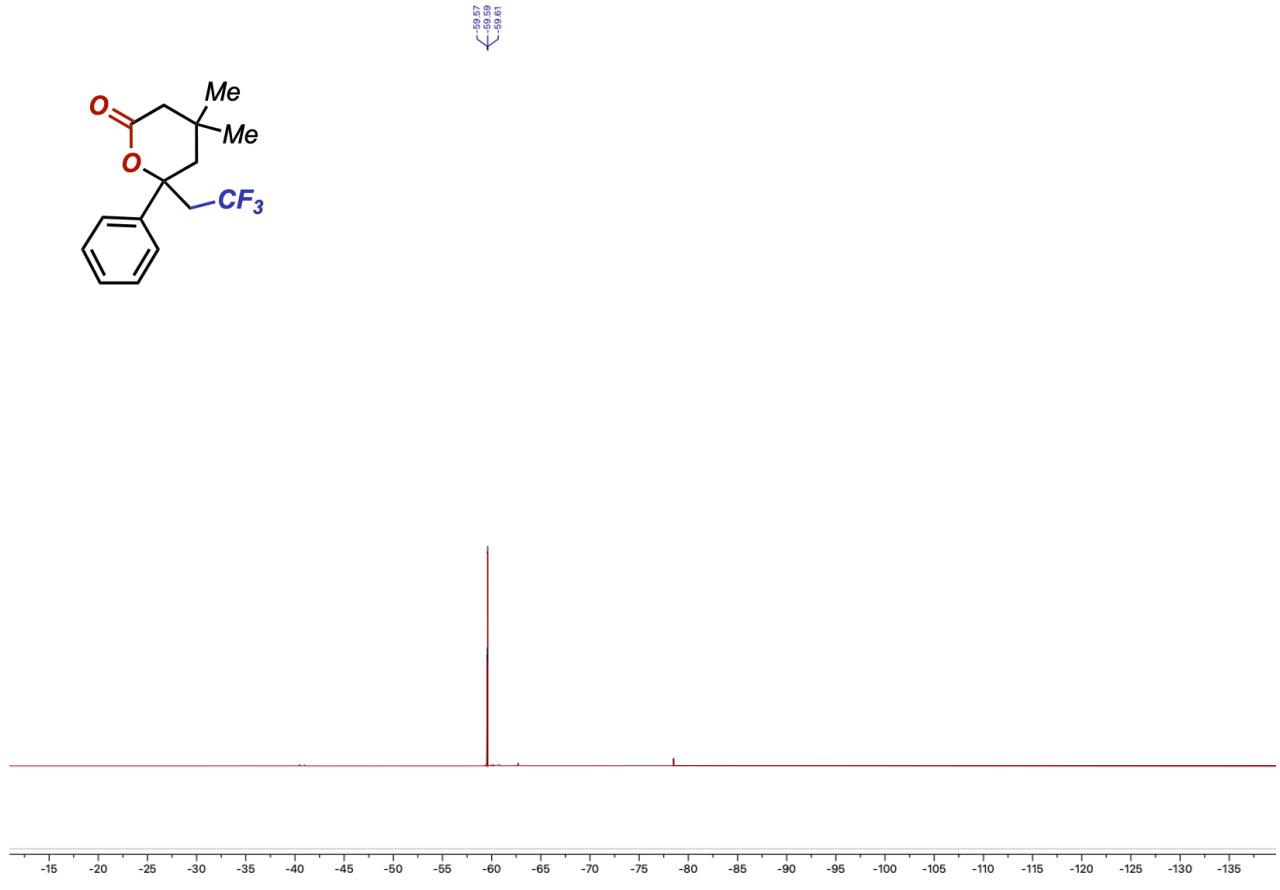
3k ^{1}H NMR (600 MHz, $CDCl_3$)



^{13}C NMR (151 MHz, $CDCl_3$)

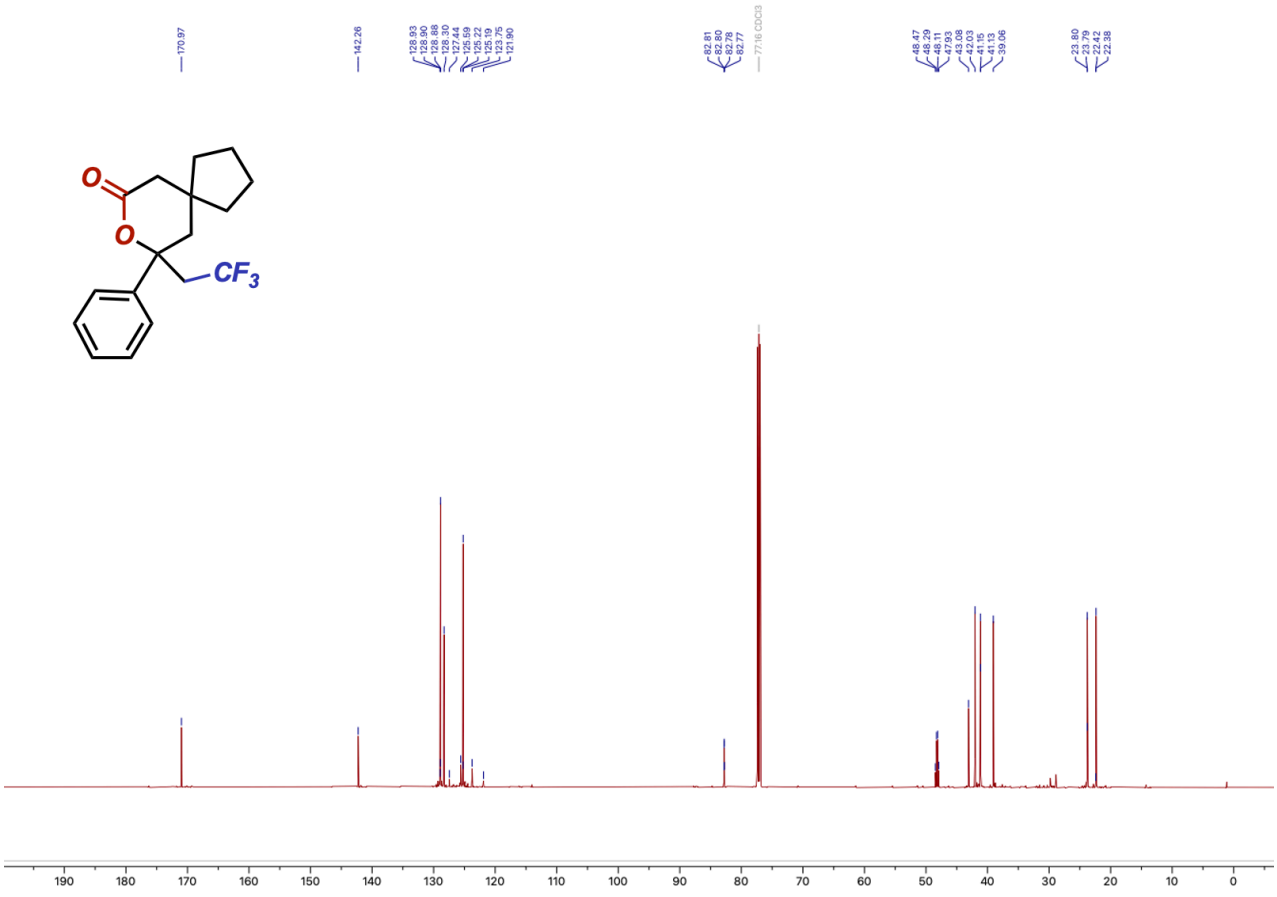


^{19}F NMR (565 MHz, $CDCl_3$)

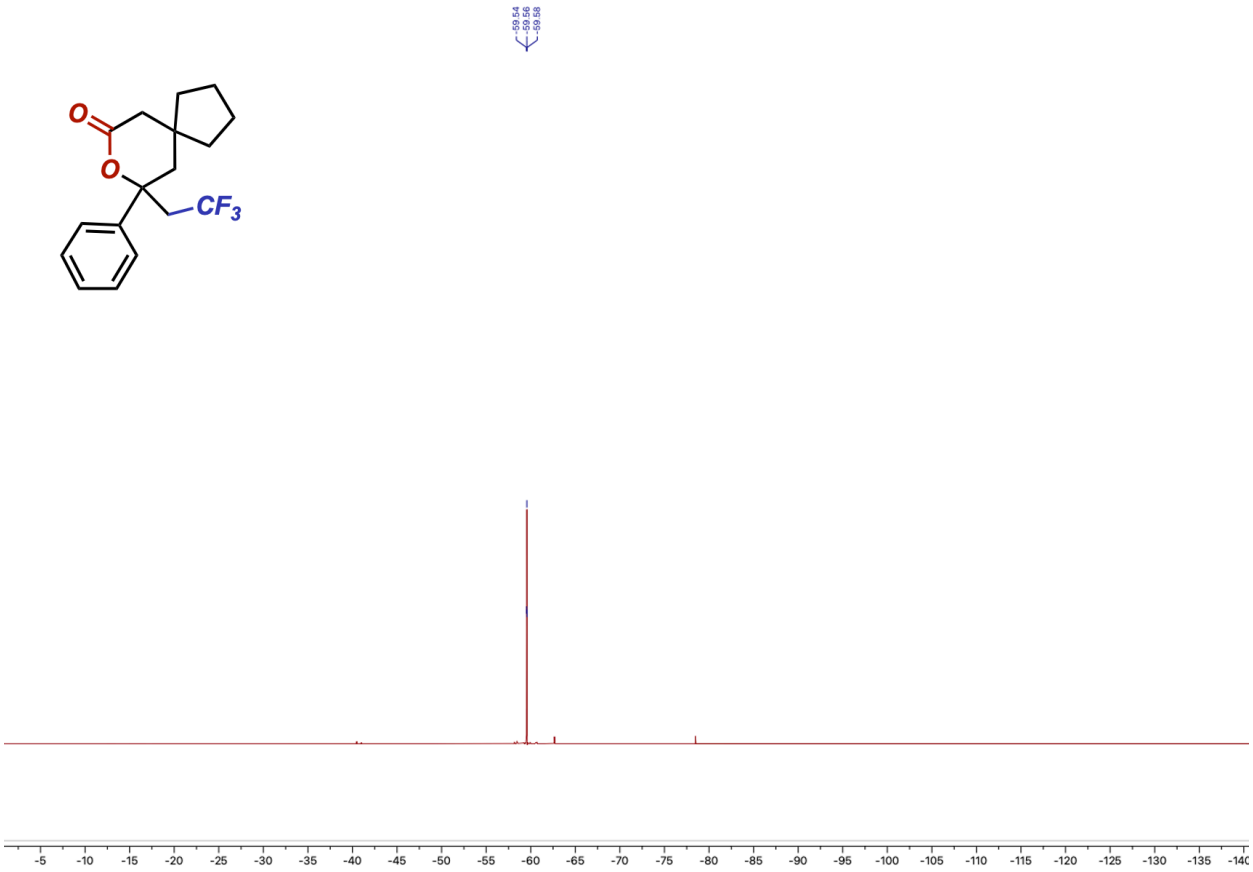


31 ^{1}H NMR (600 MHz, $CDCl_3$)

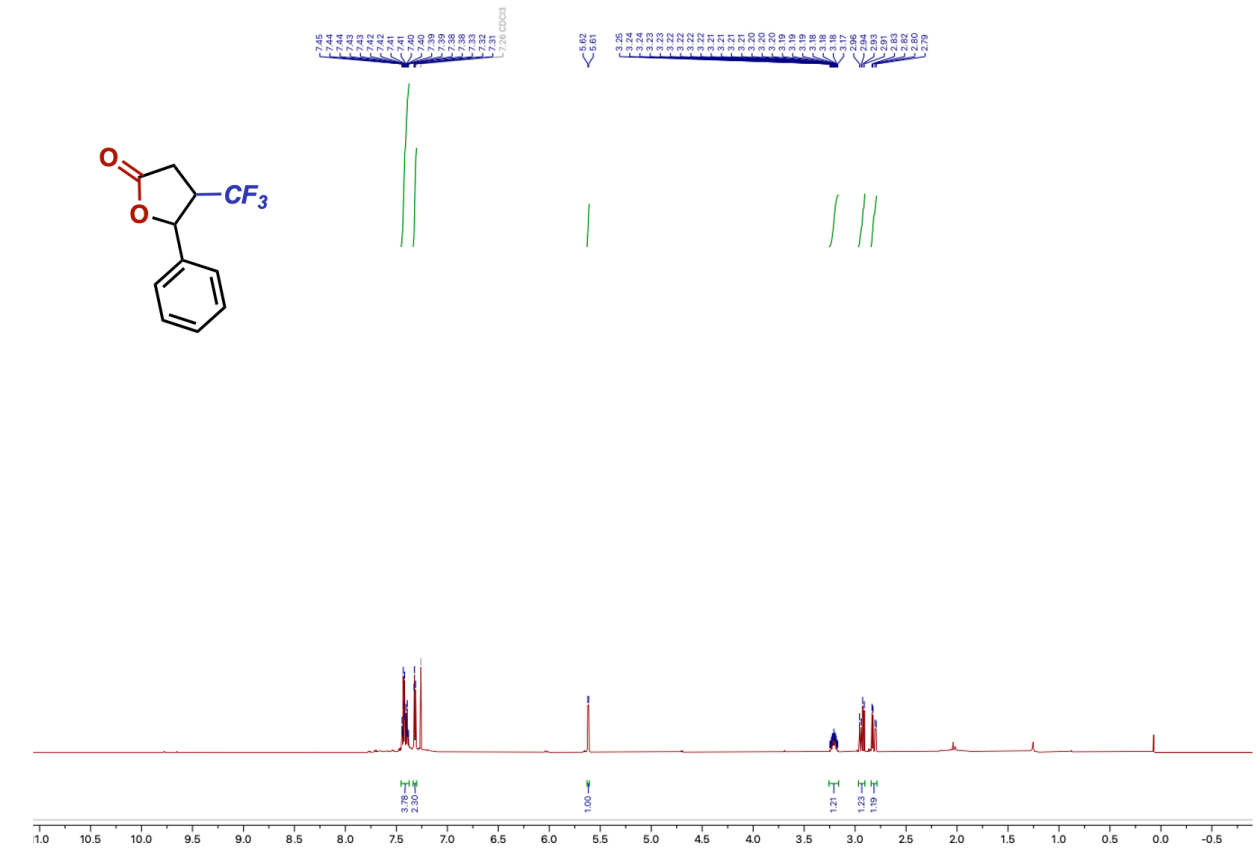
^{13}C NMR (151 MHz, $CDCl_3$)



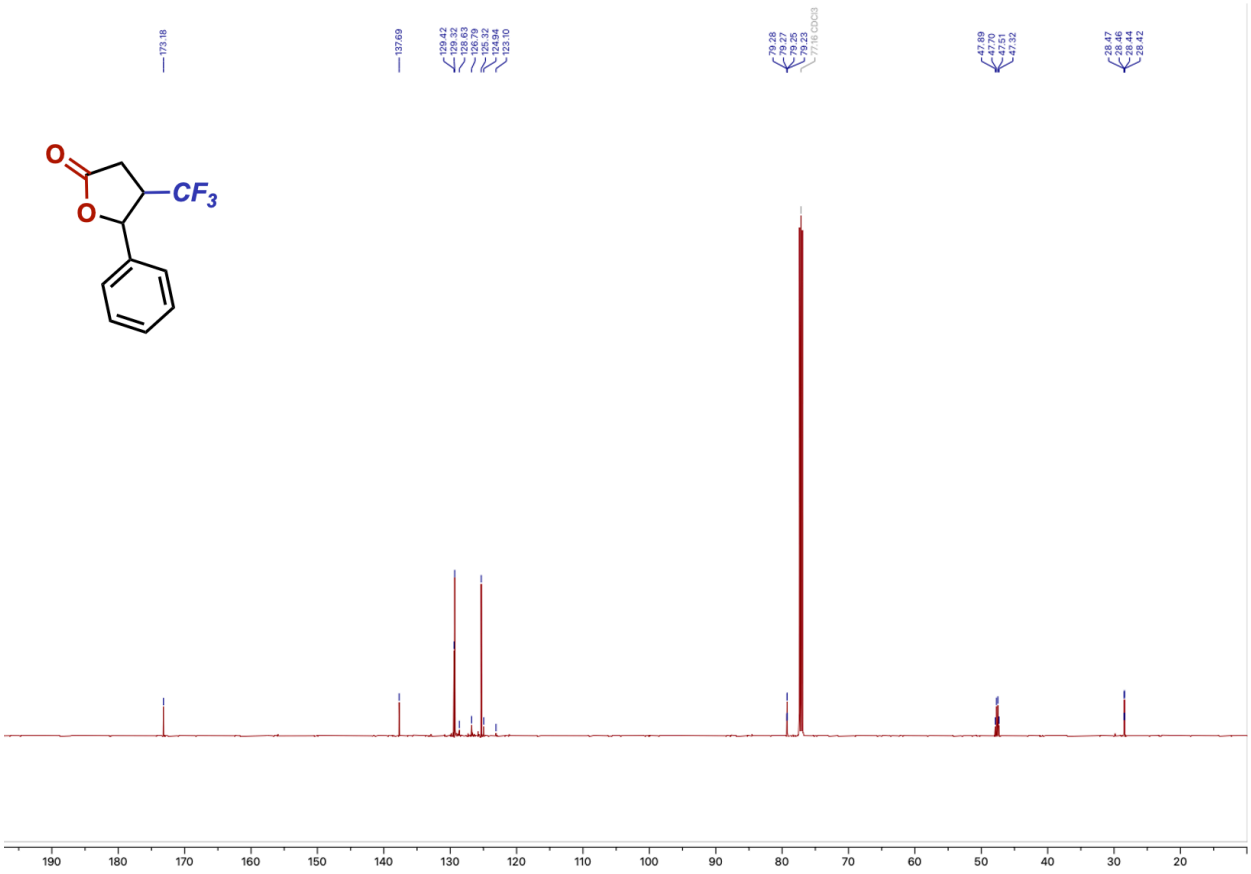
^{19}F NMR (565 MHz, $CDCl_3$)



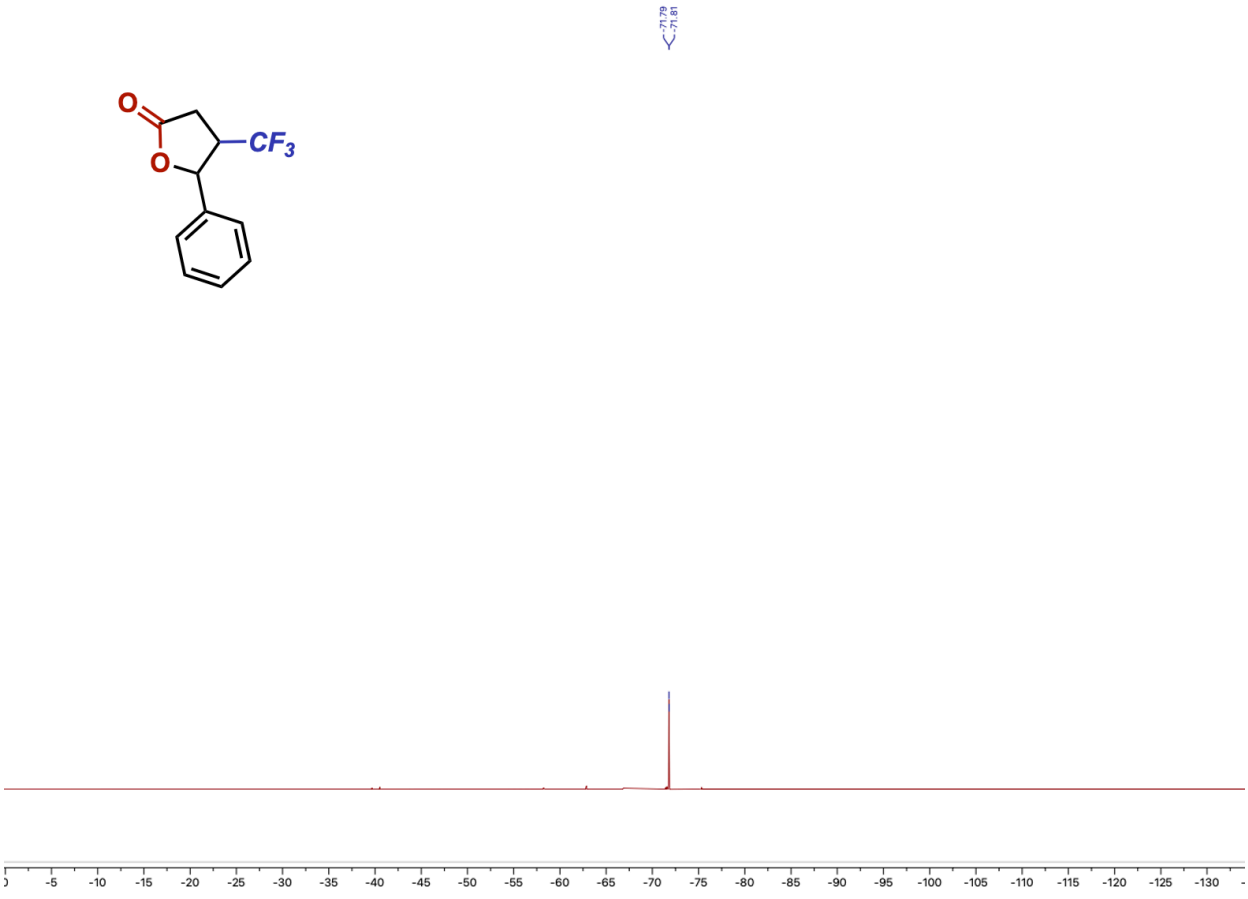
3m ^{1}H NMR (600 MHz, $CDCl_3$)



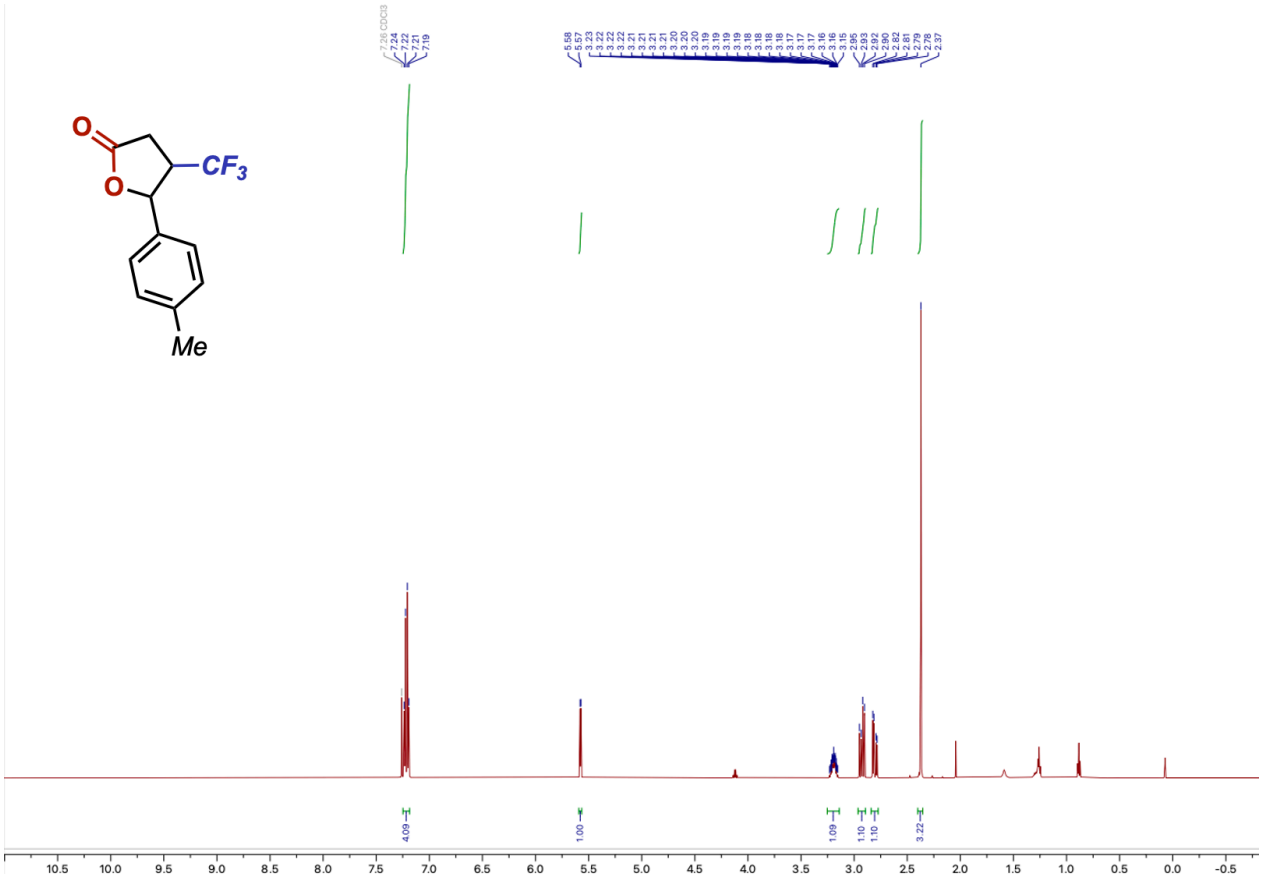
^{13}C NMR (151 MHz, $CDCl_3$)



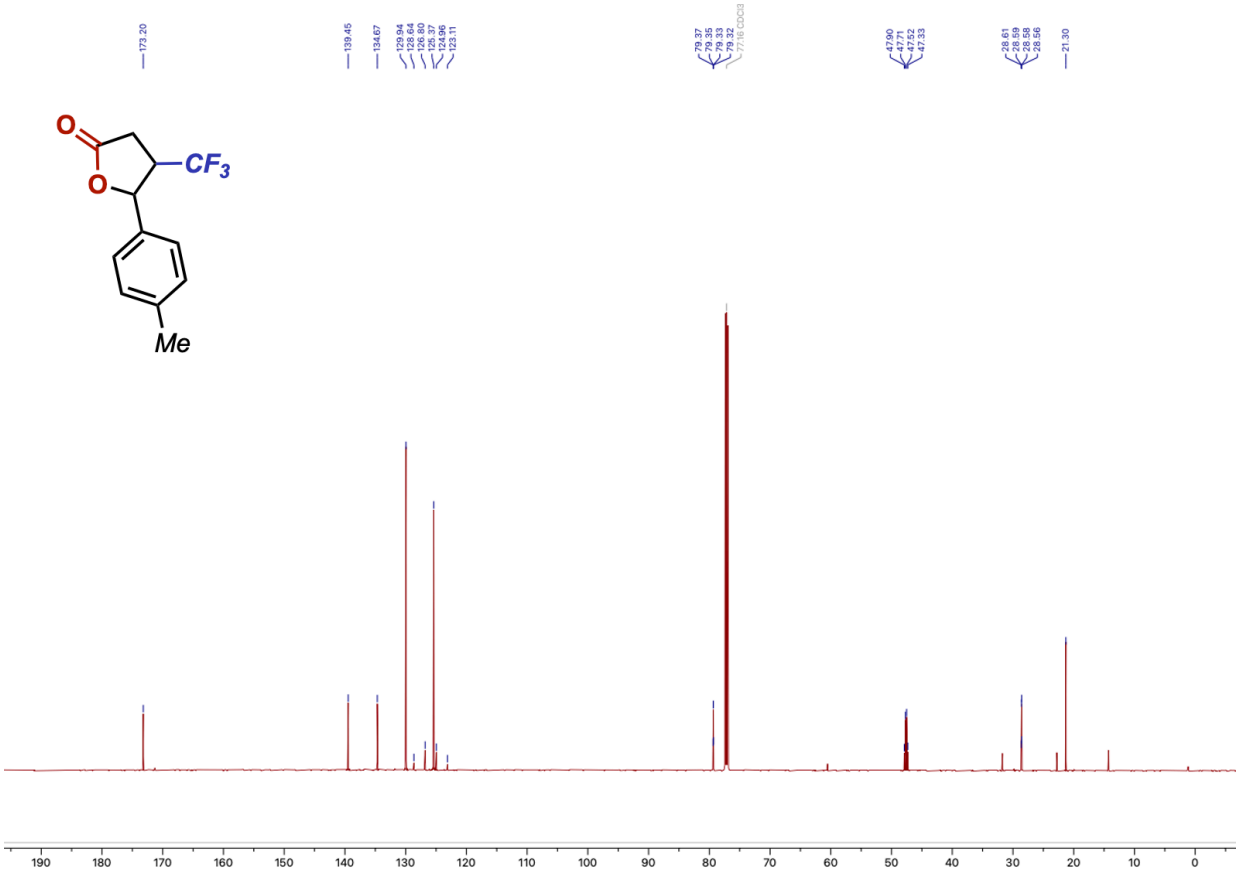
^{19}F NMR (565 MHz, $CDCl_3$)



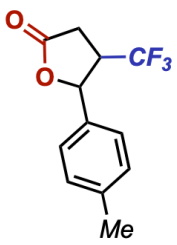
3n ^{1}H NMR (600 MHz, $CDCl_3$)



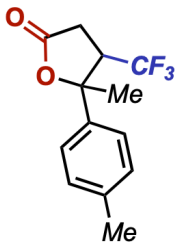
^{13}C NMR (151 MHz, $CDCl_3$)



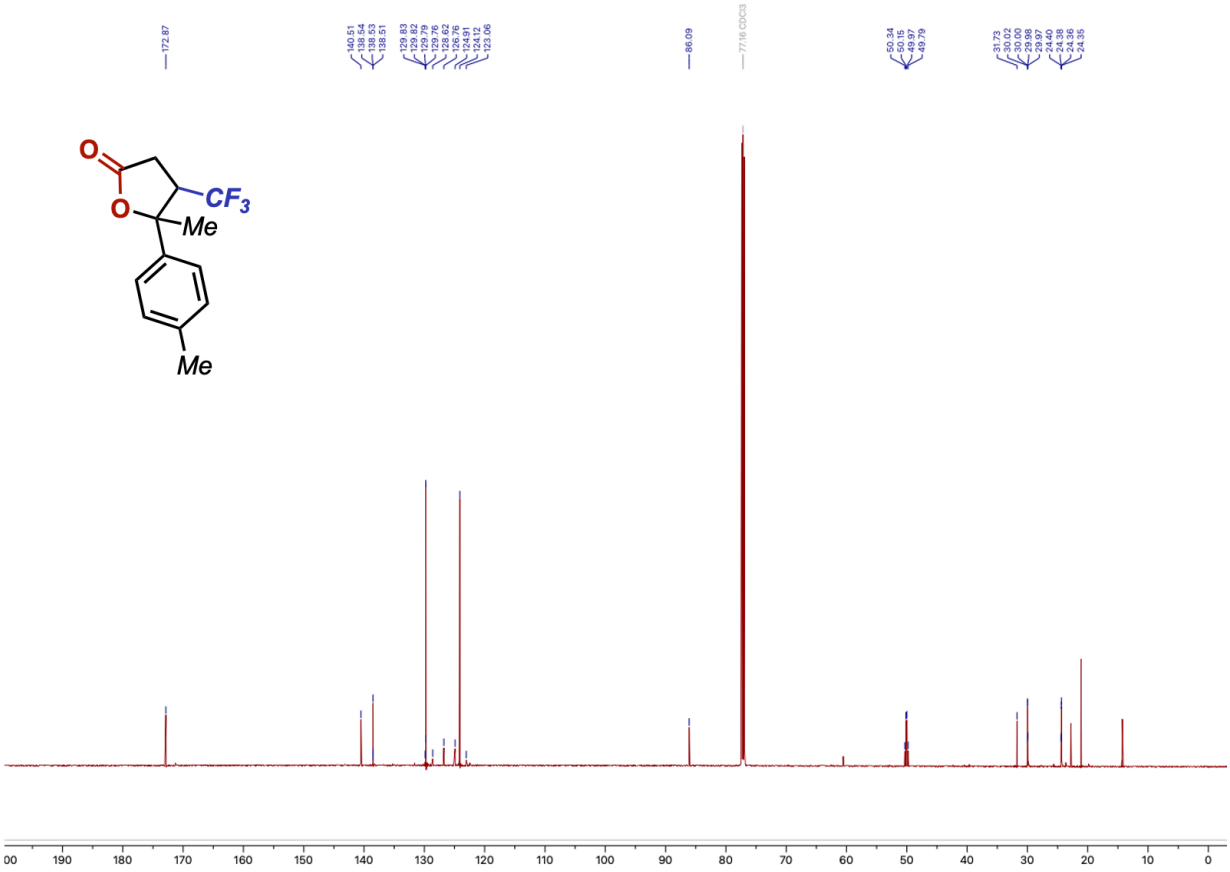
^{19}F NMR (565 MHz, $CDCl_3$)



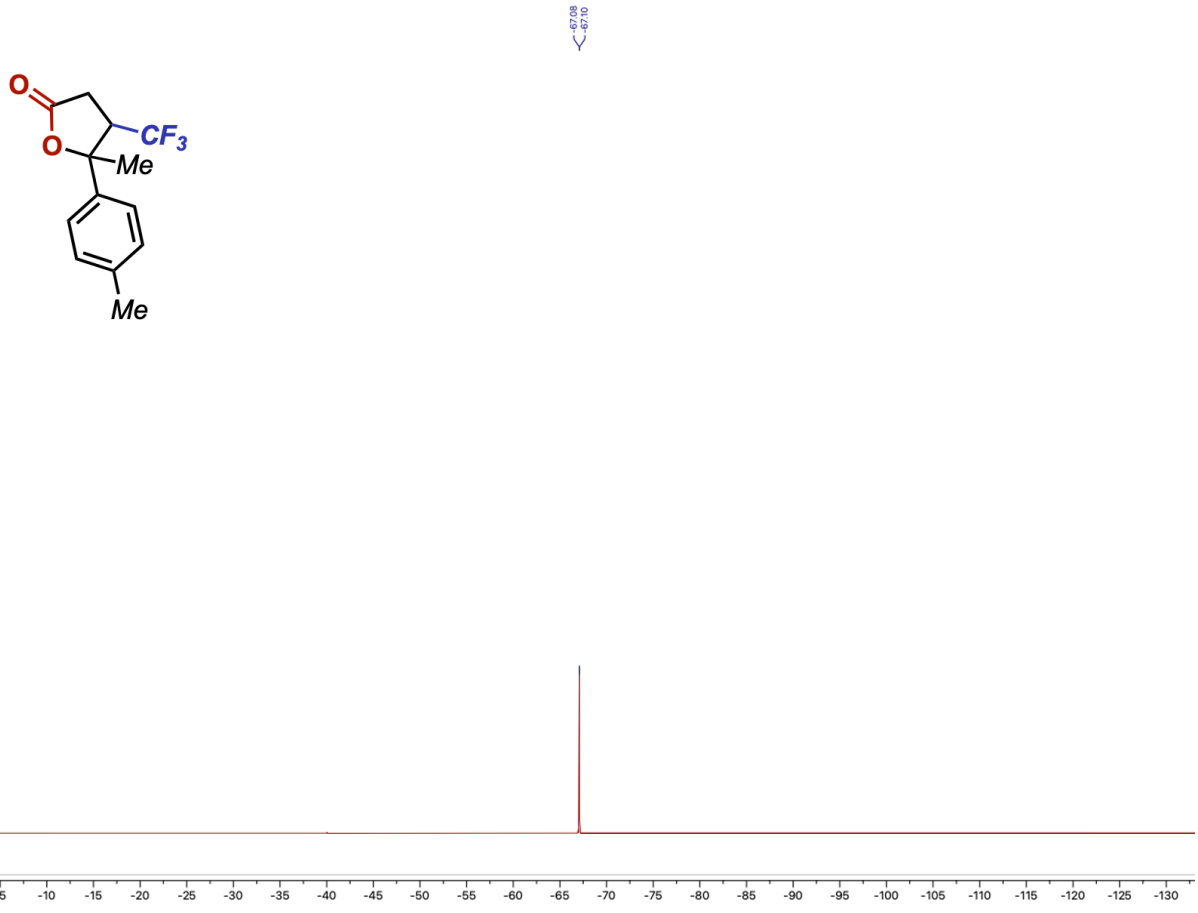
3o ^{1}H NMR (600 MHz, $CDCl_3$)



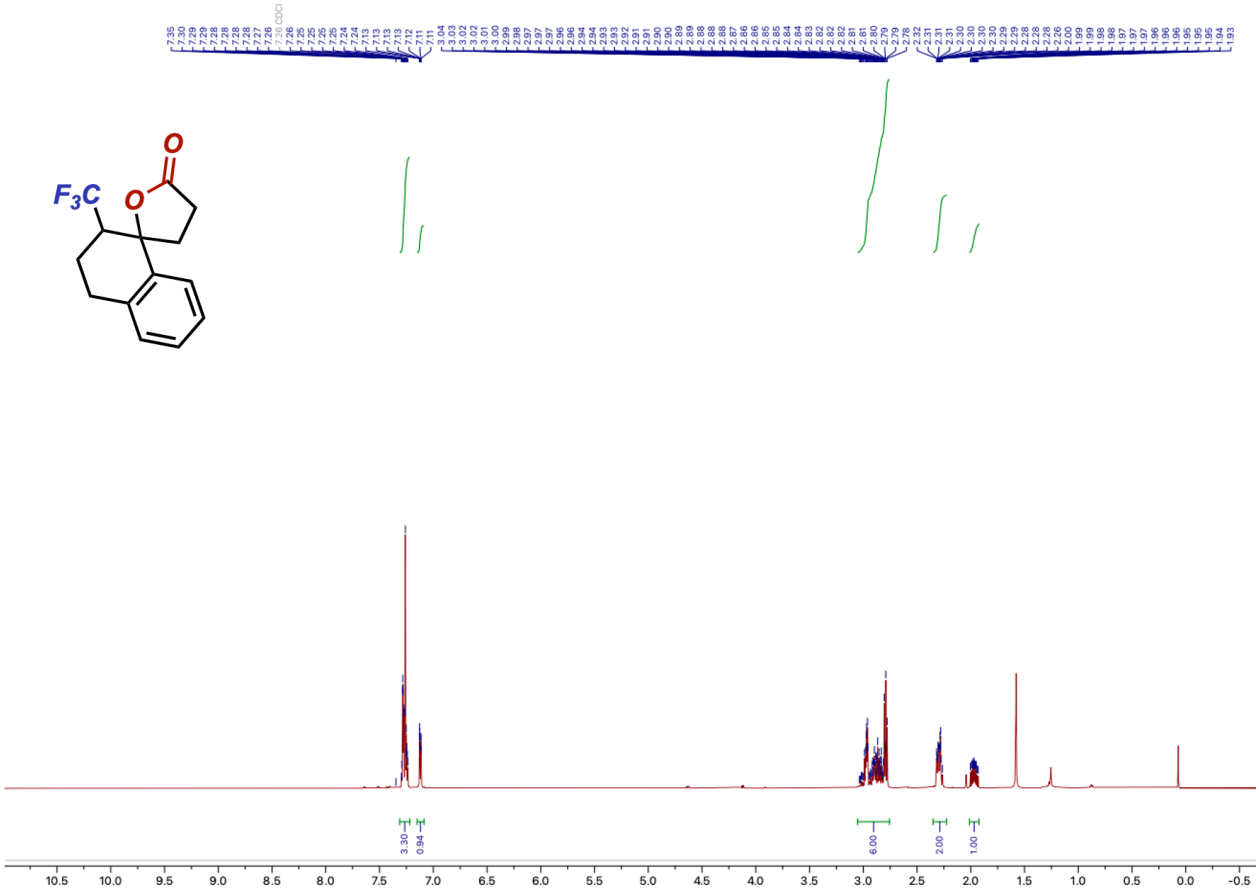
^{13}C NMR (151 MHz, $CDCl_3$)



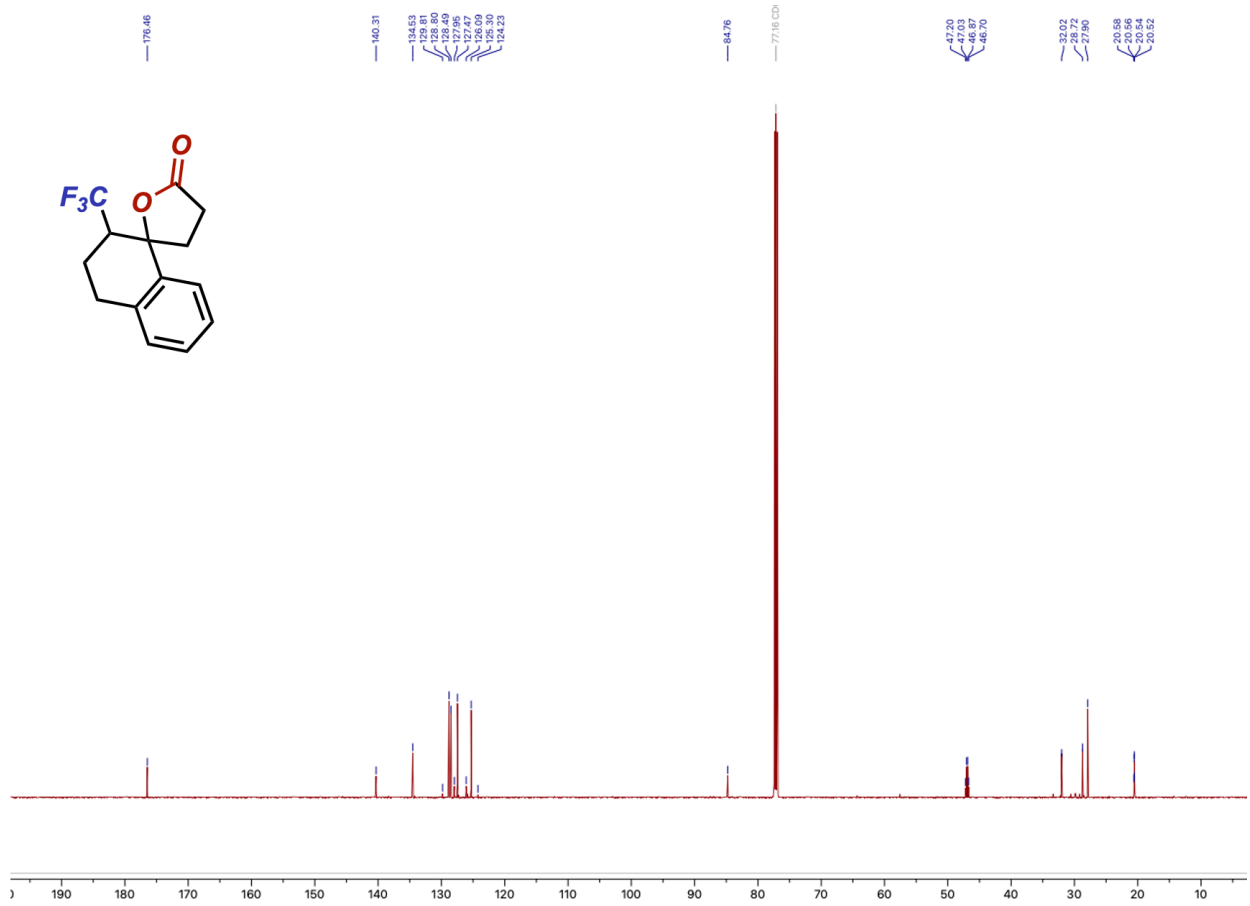
^{19}F NMR (565 MHz, $CDCl_3$)



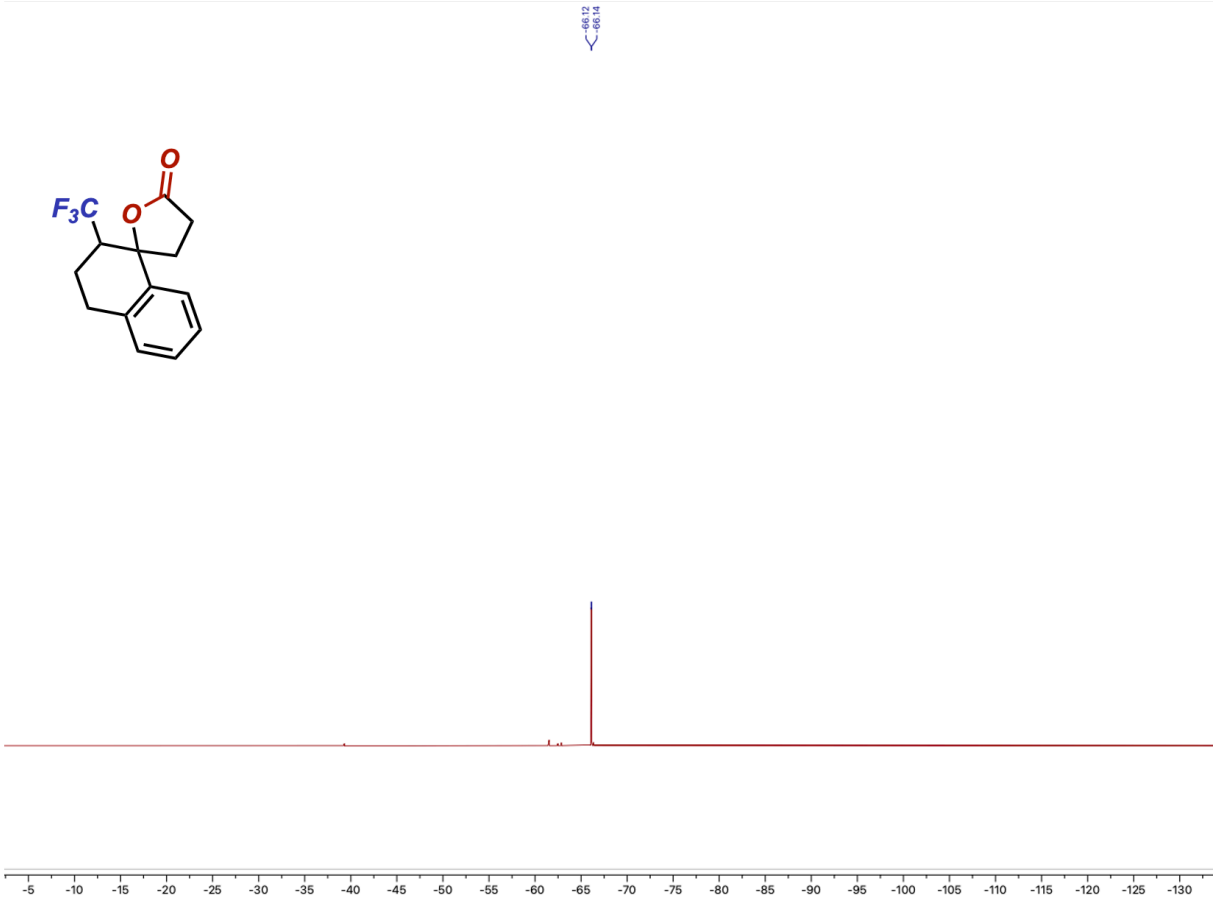
3p ^{1}H NMR (600 MHz, $CDCl_3$)



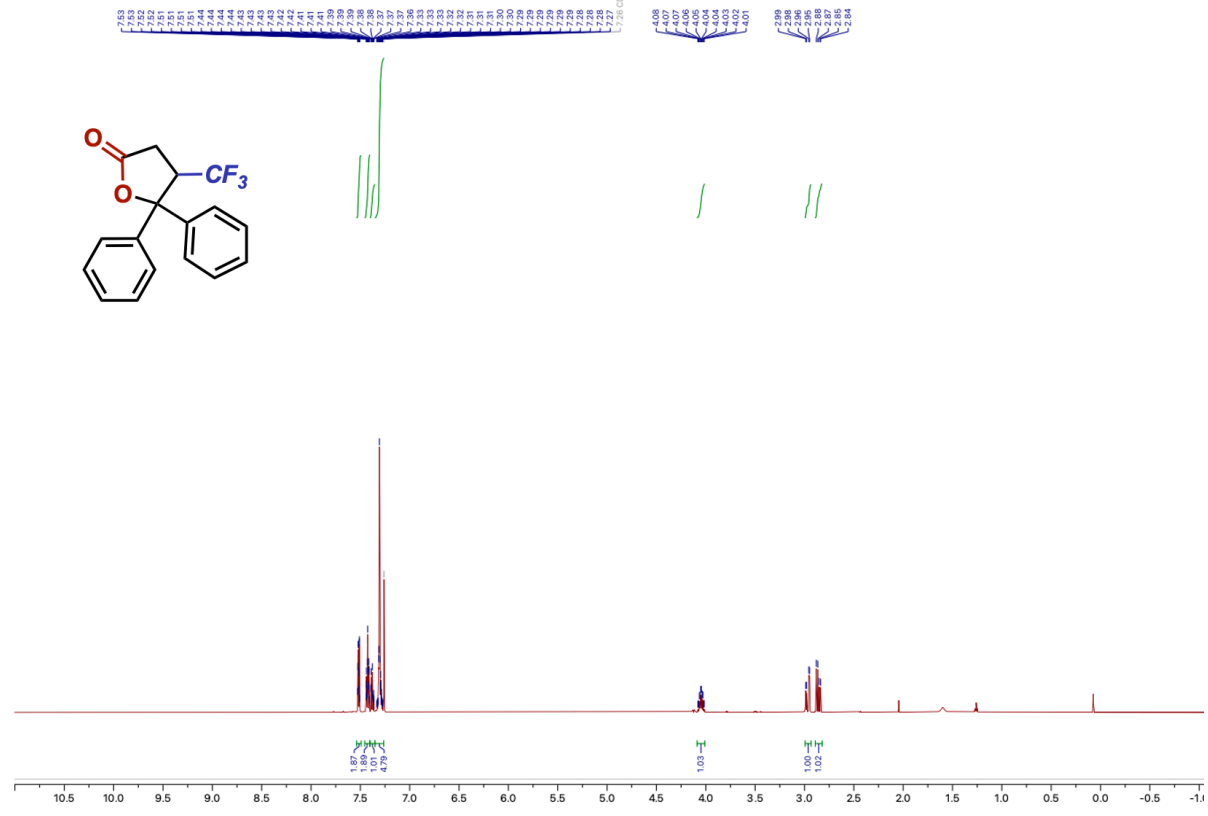
^{13}C NMR (151 MHz, $CDCl_3$)



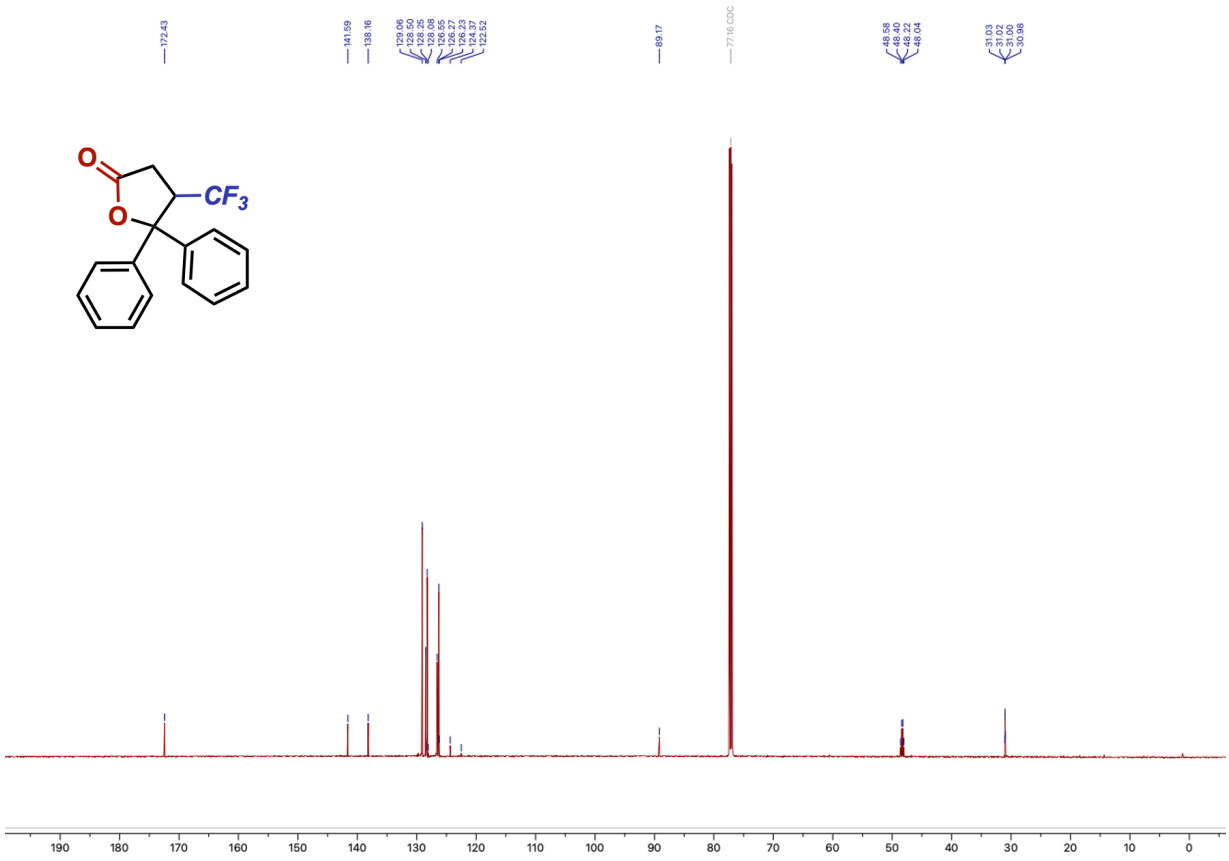
^{19}F NMR (565 MHz, $CDCl_3$)



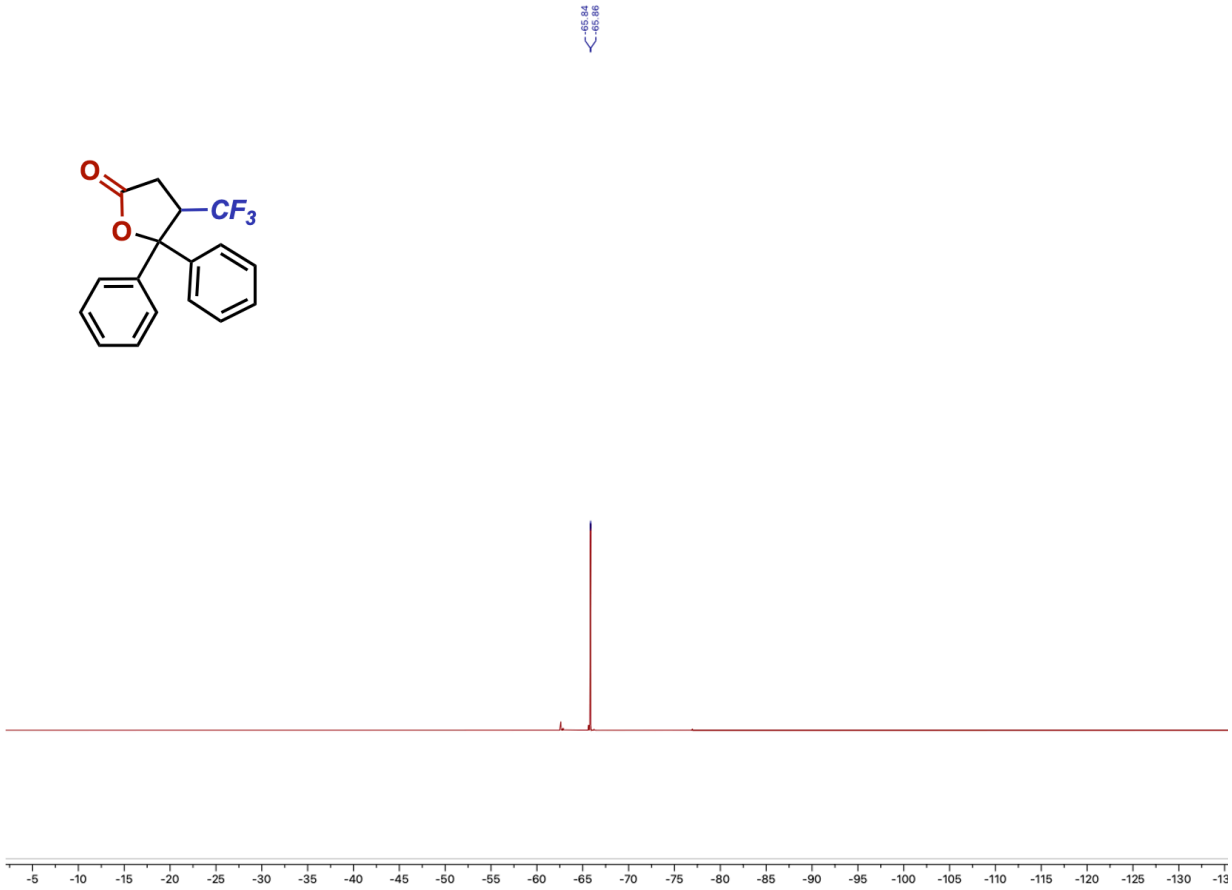
3q ^{1}H NMR (600 MHz, $CDCl_3$)



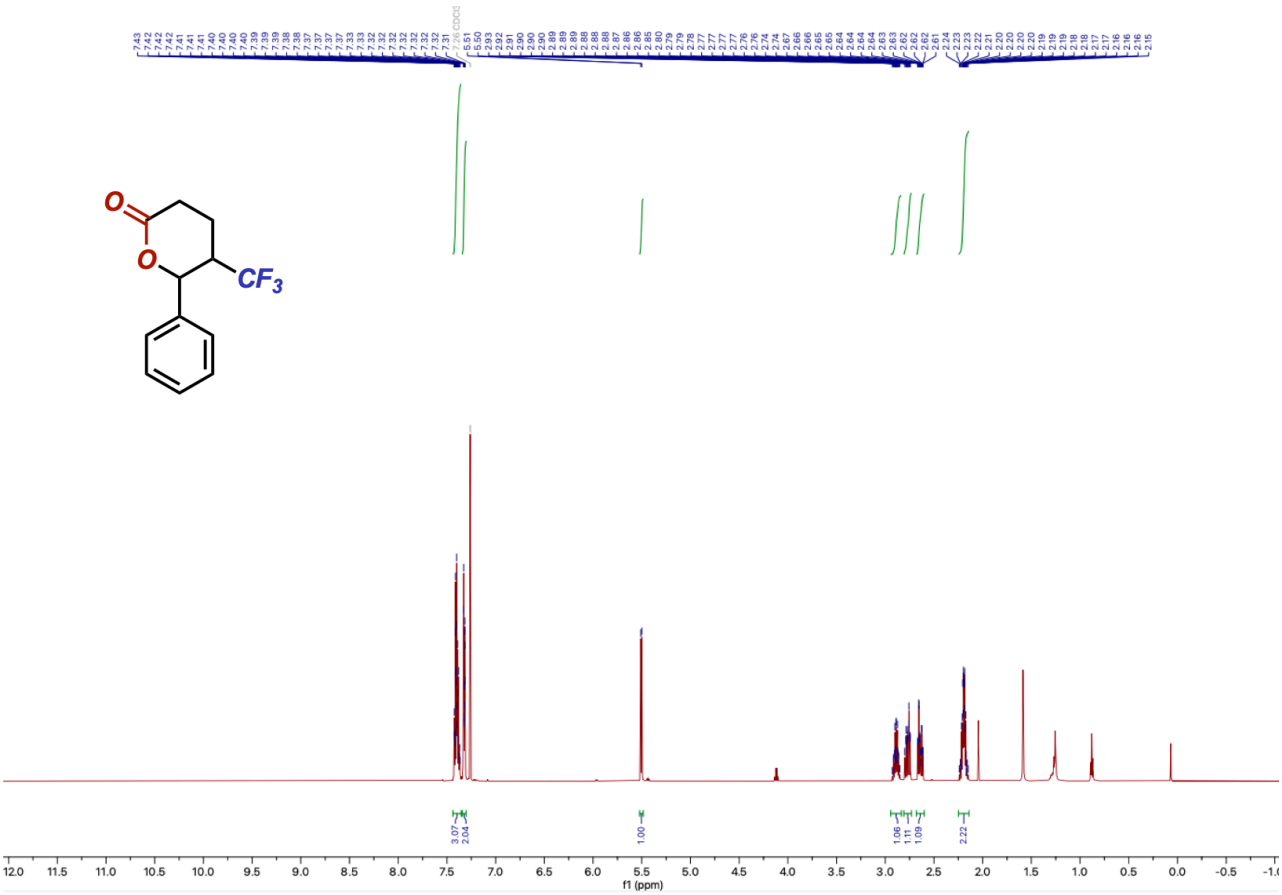
^{13}C NMR (151 MHz, $CDCl_3$)



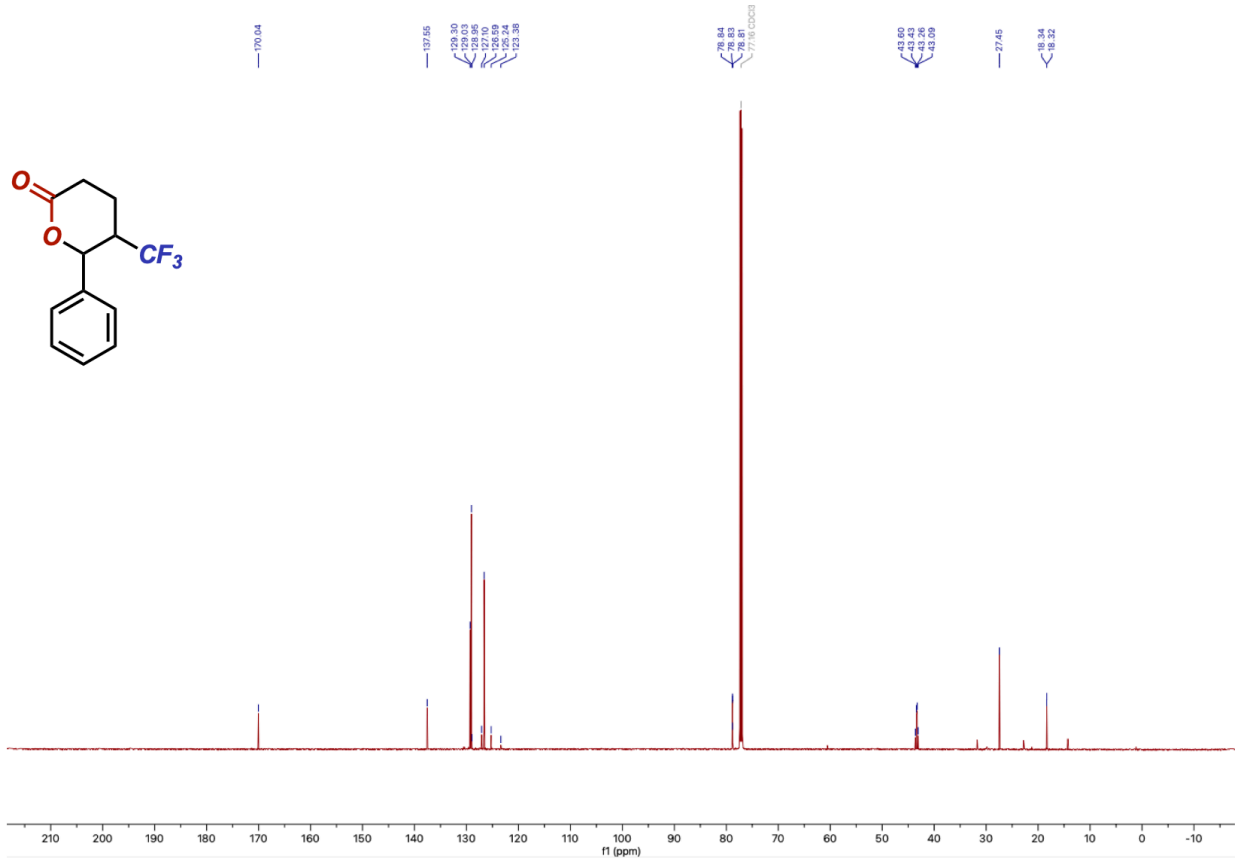
^{19}F NMR (565 MHz, $CDCl_3$)



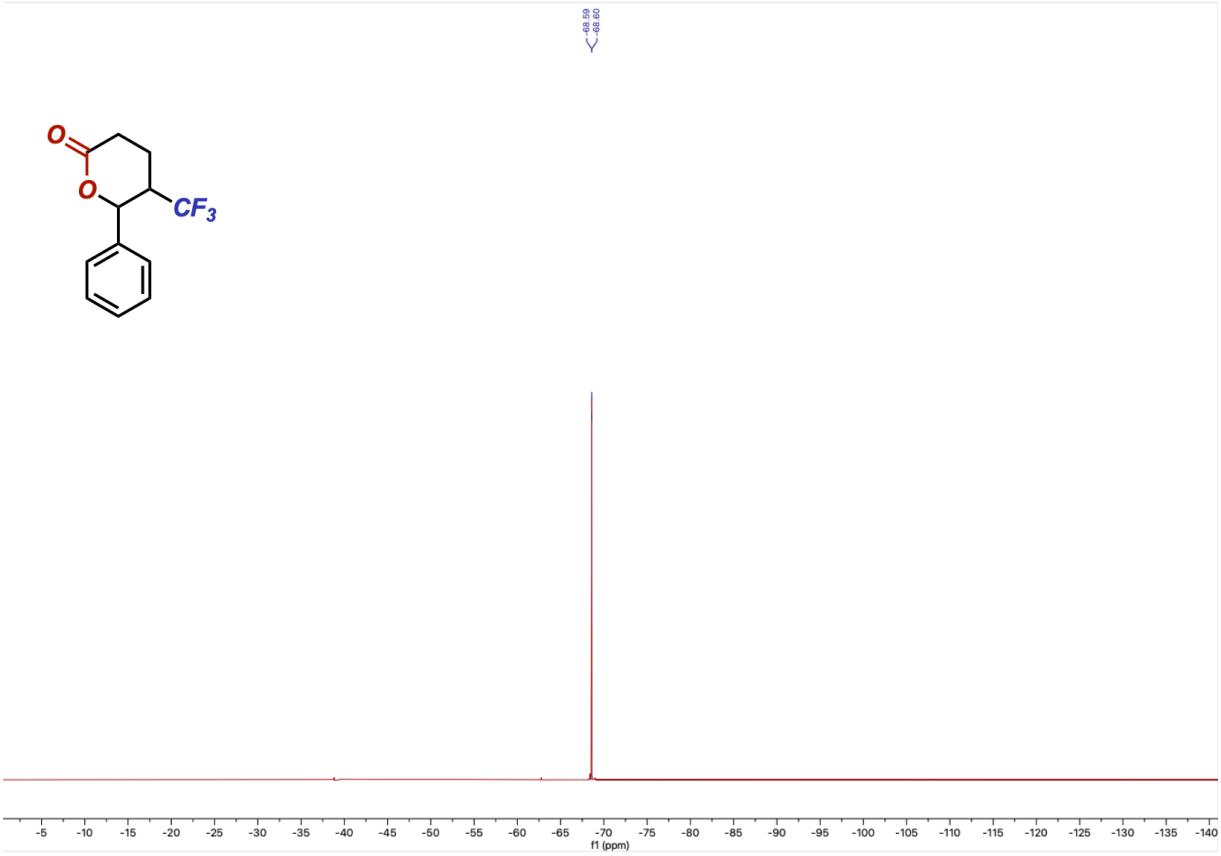
3r ^{1}H NMR (600 MHz, $CDCl_3$)



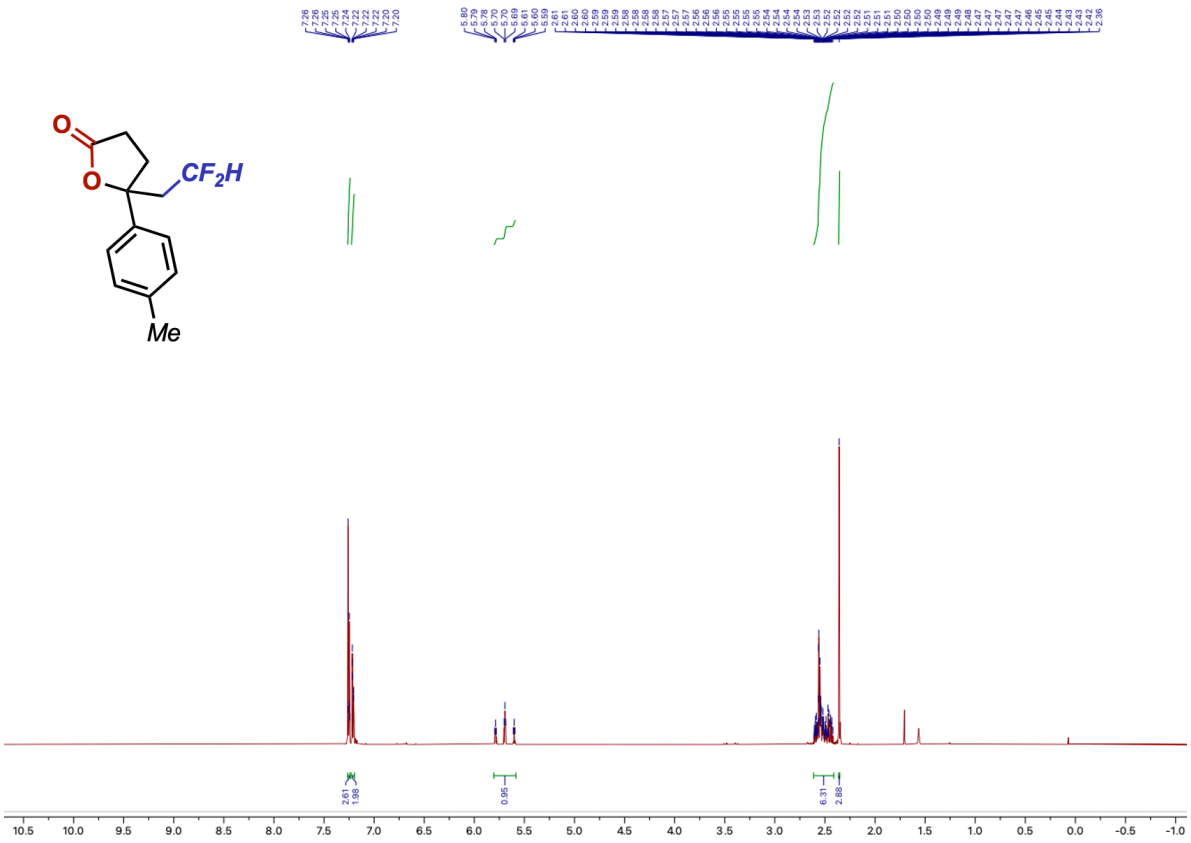
^{13}C NMR (151 MHz, $CDCl_3$)



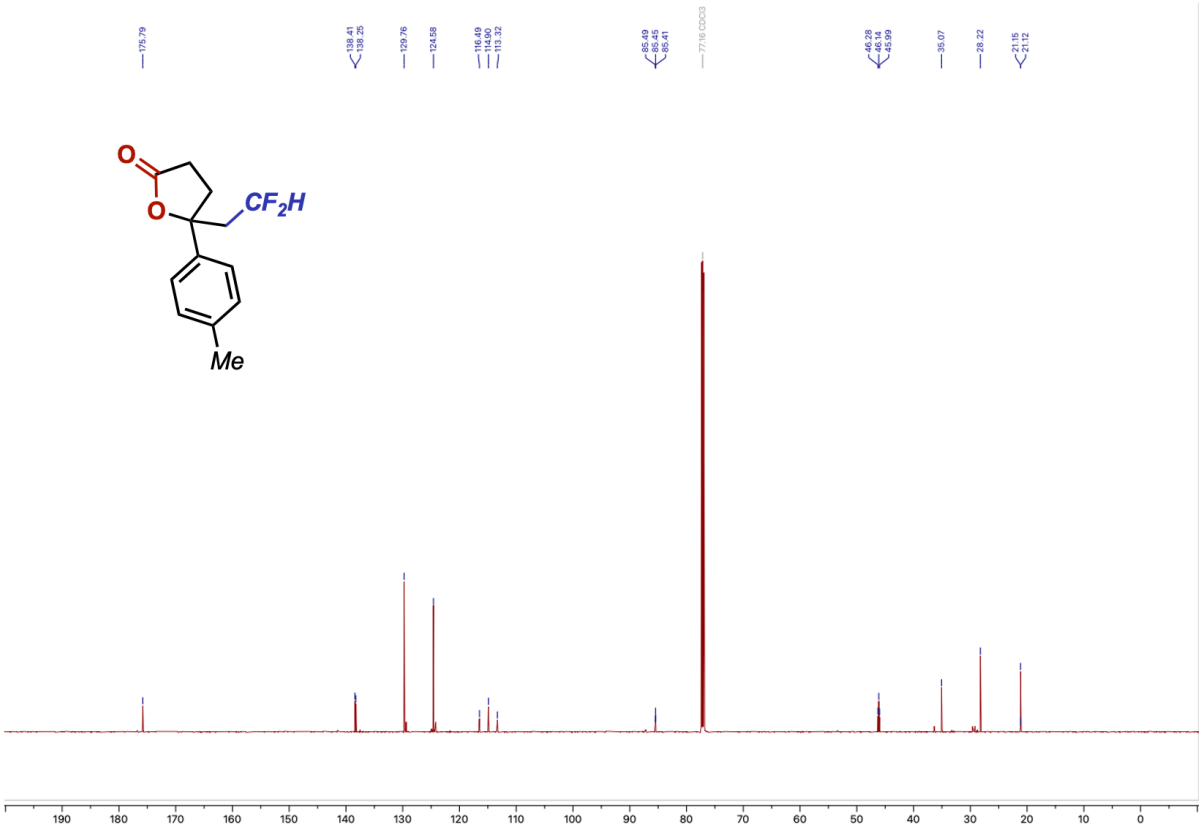
^{19}F NMR (565 MHz, $CDCl_3$)



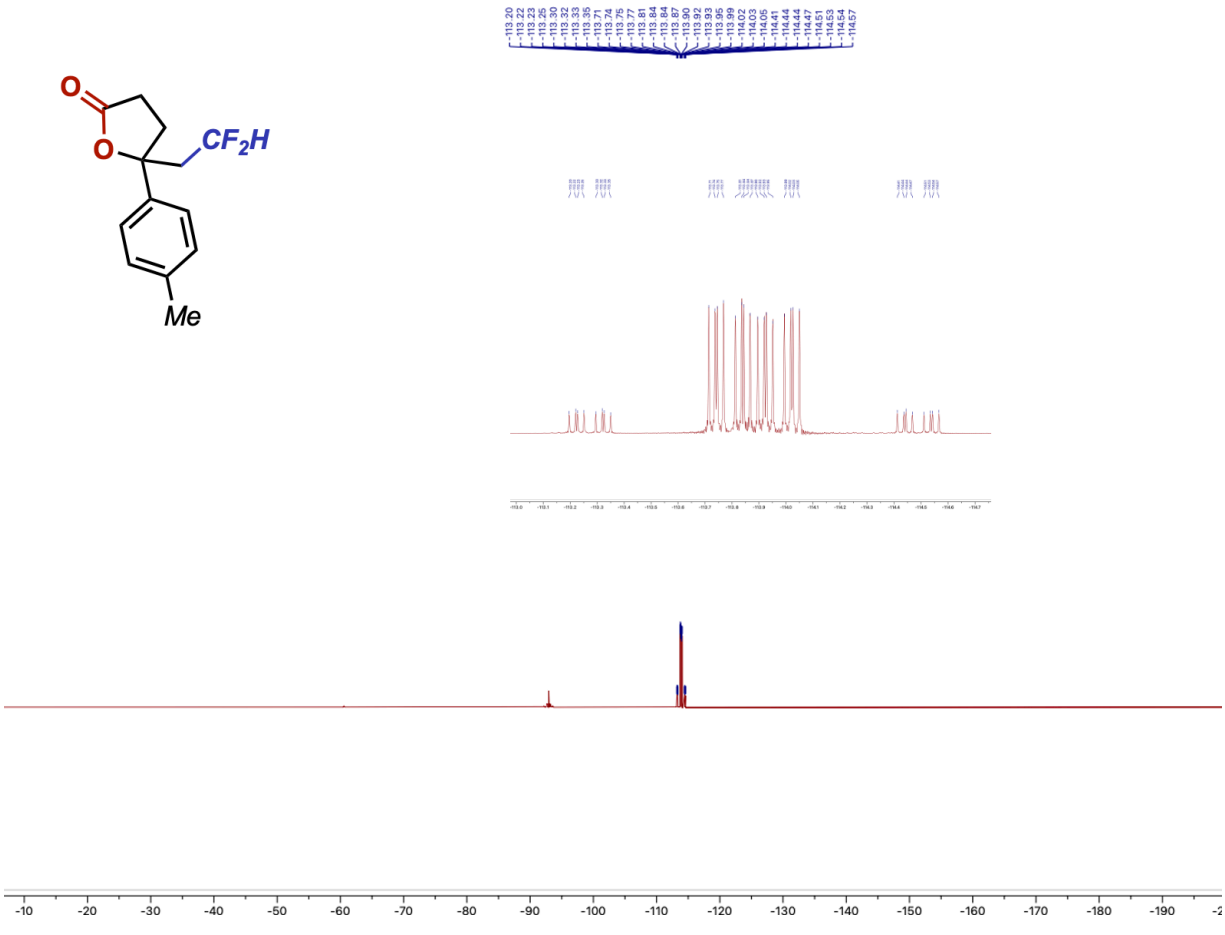
3s ^{1}H NMR (600 MHz, $CDCl_3$)



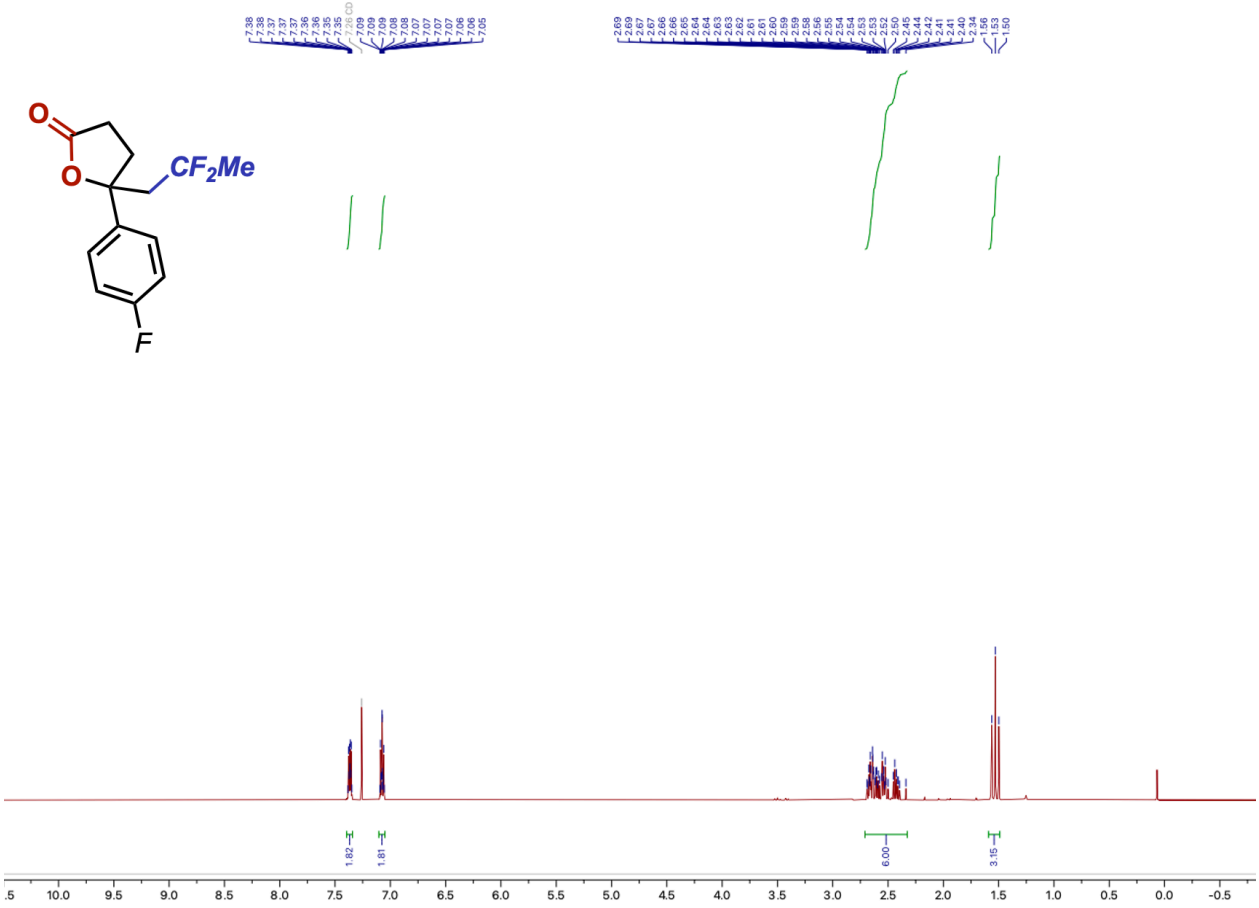
^{13}C NMR (151 MHz, $CDCl_3$)



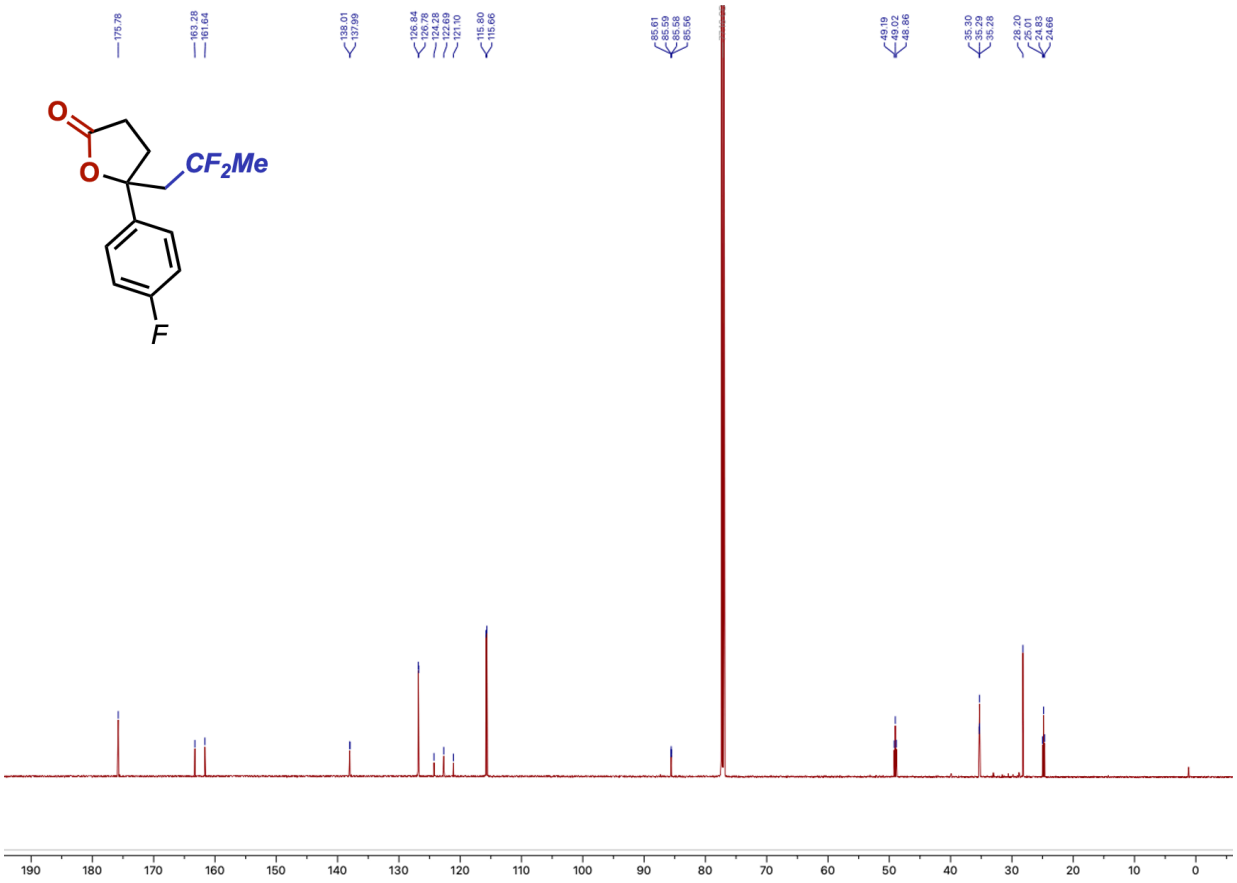
^{19}F NMR (565 MHz, $CDCl_3$)



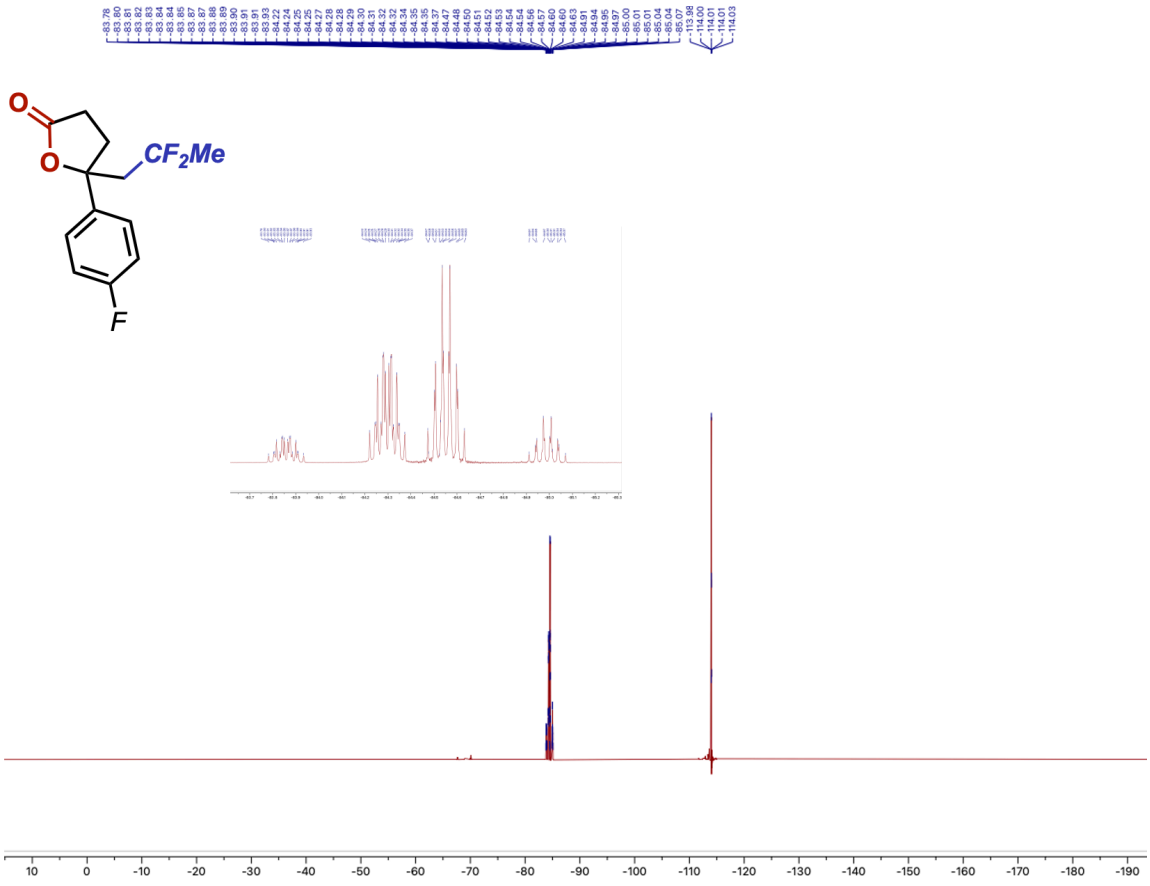
3t ^{1}H NMR (600 MHz, $CDCl_3$)



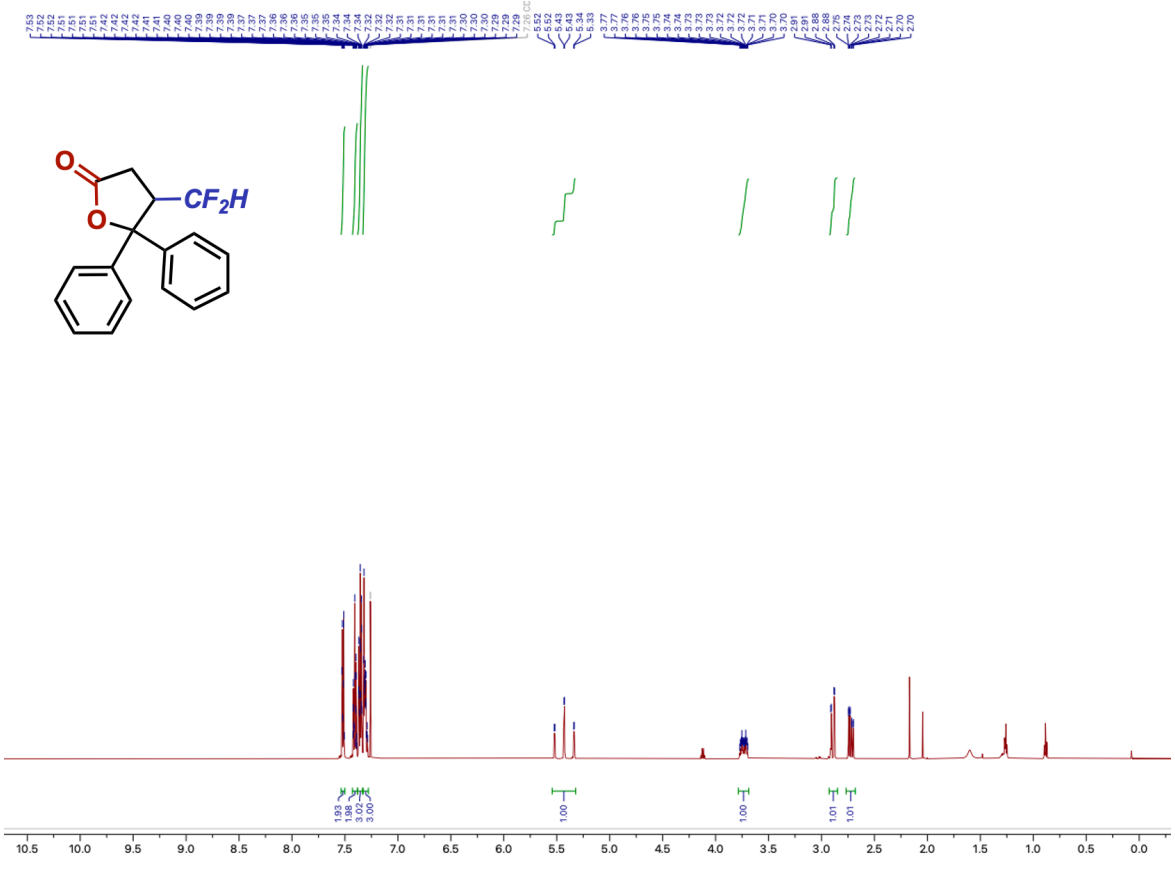
^{13}C NMR (151 MHz, $CDCl_3$)



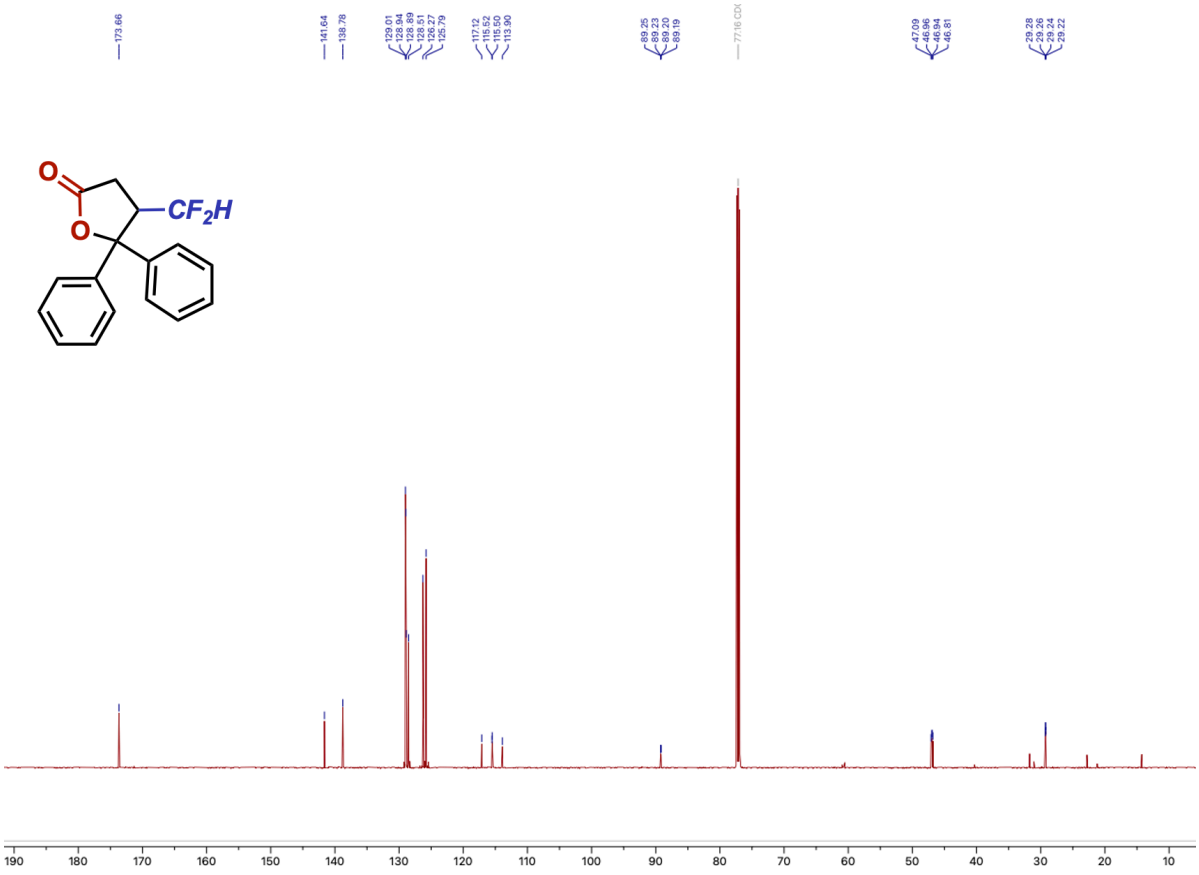
^{19}F NMR (565 MHz, $CDCl_3$)



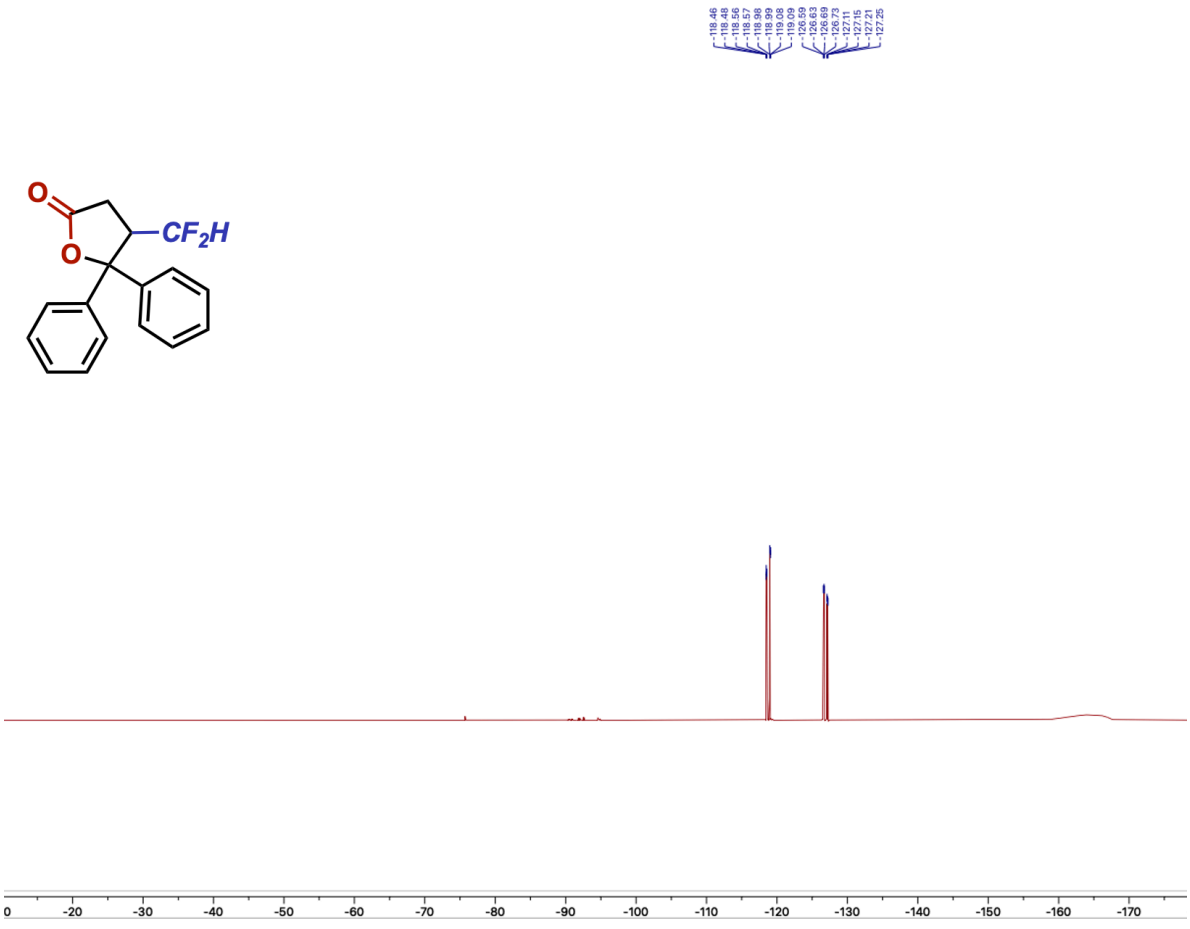
3u ^{1}H NMR (600 MHz, $CDCl_3$)



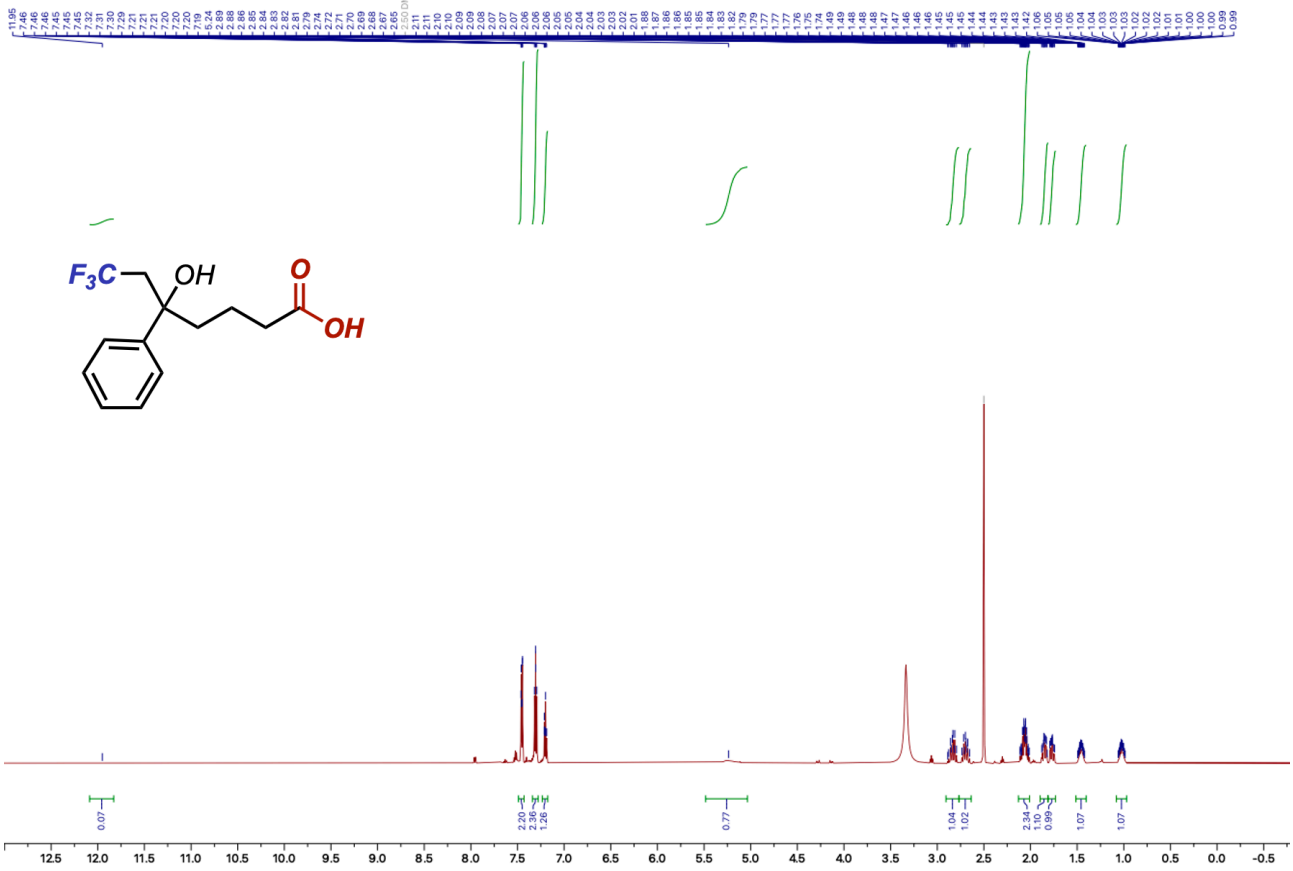
^{13}C NMR (151 MHz, $CDCl_3$)



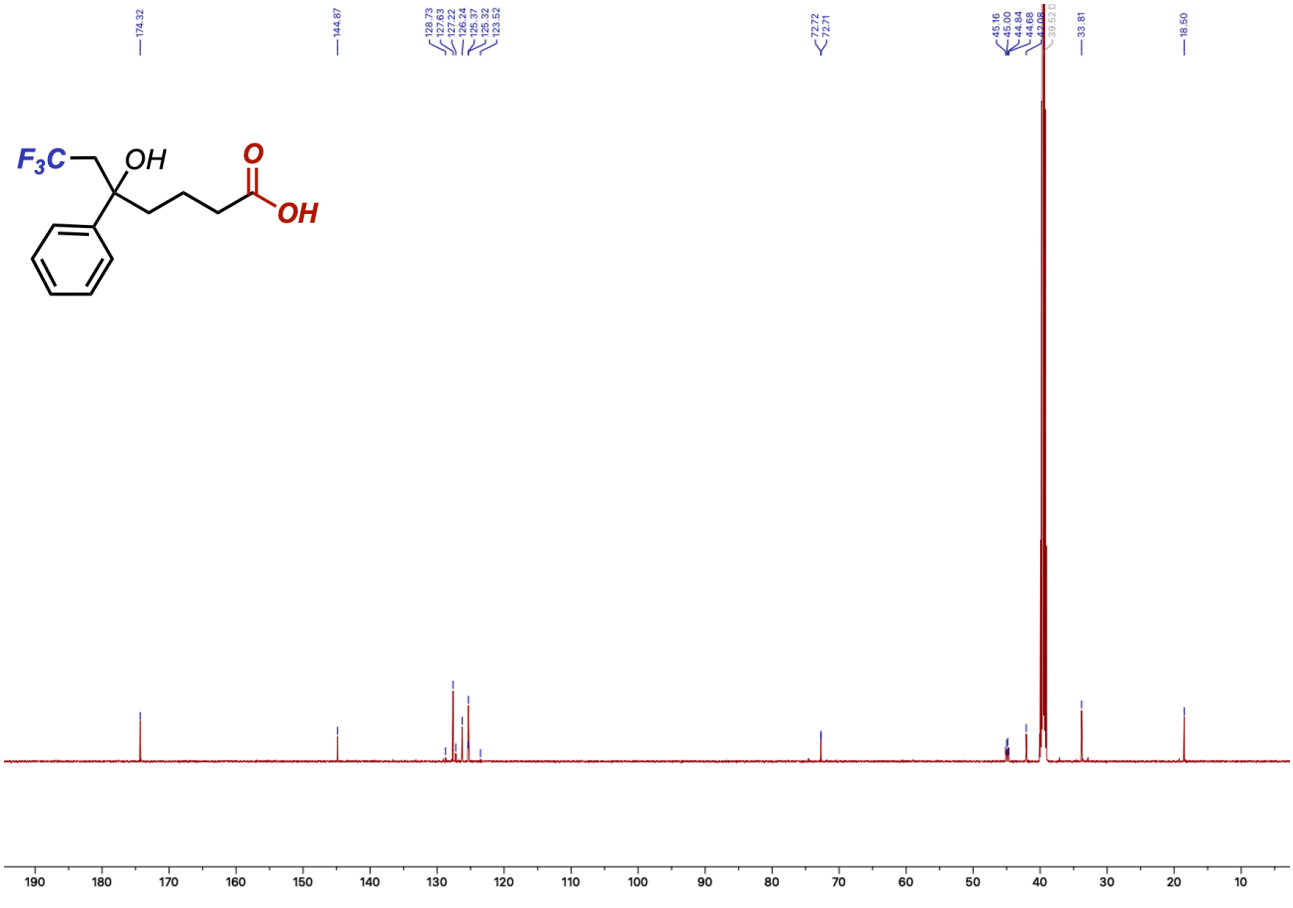
^{19}F NMR (565 MHz, $CDCl_3$)



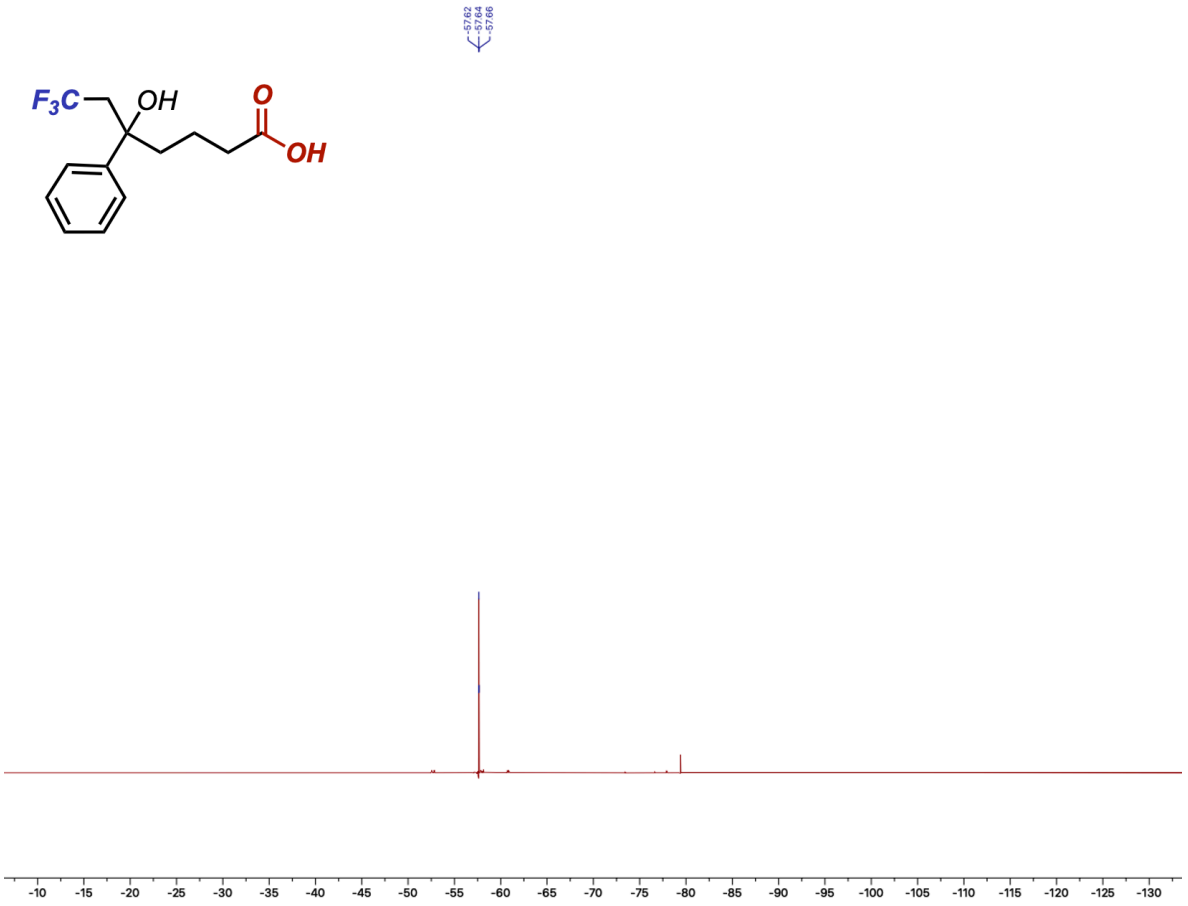
4h ^{1}H NMR (600 MHz, DMSO-d6)



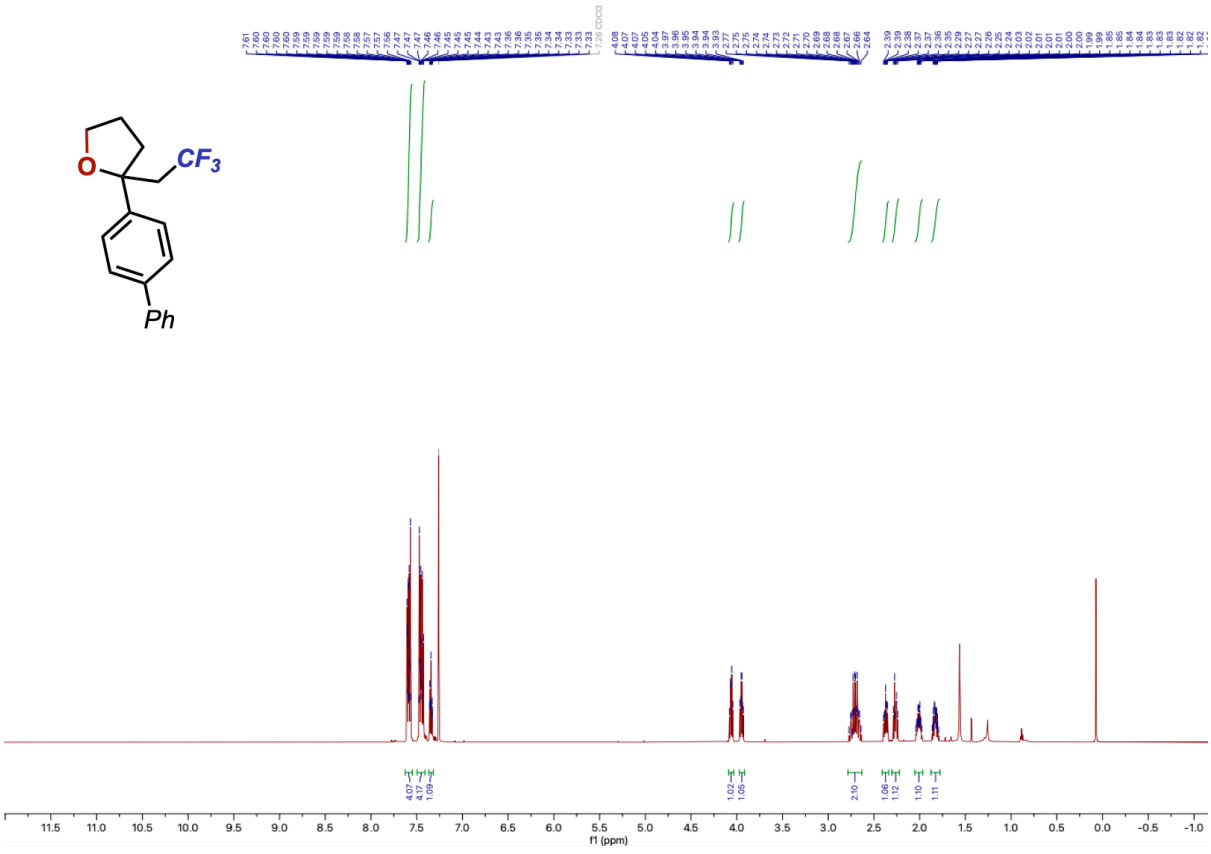
^{13}C NMR (151 MHz, DMSO-d6)



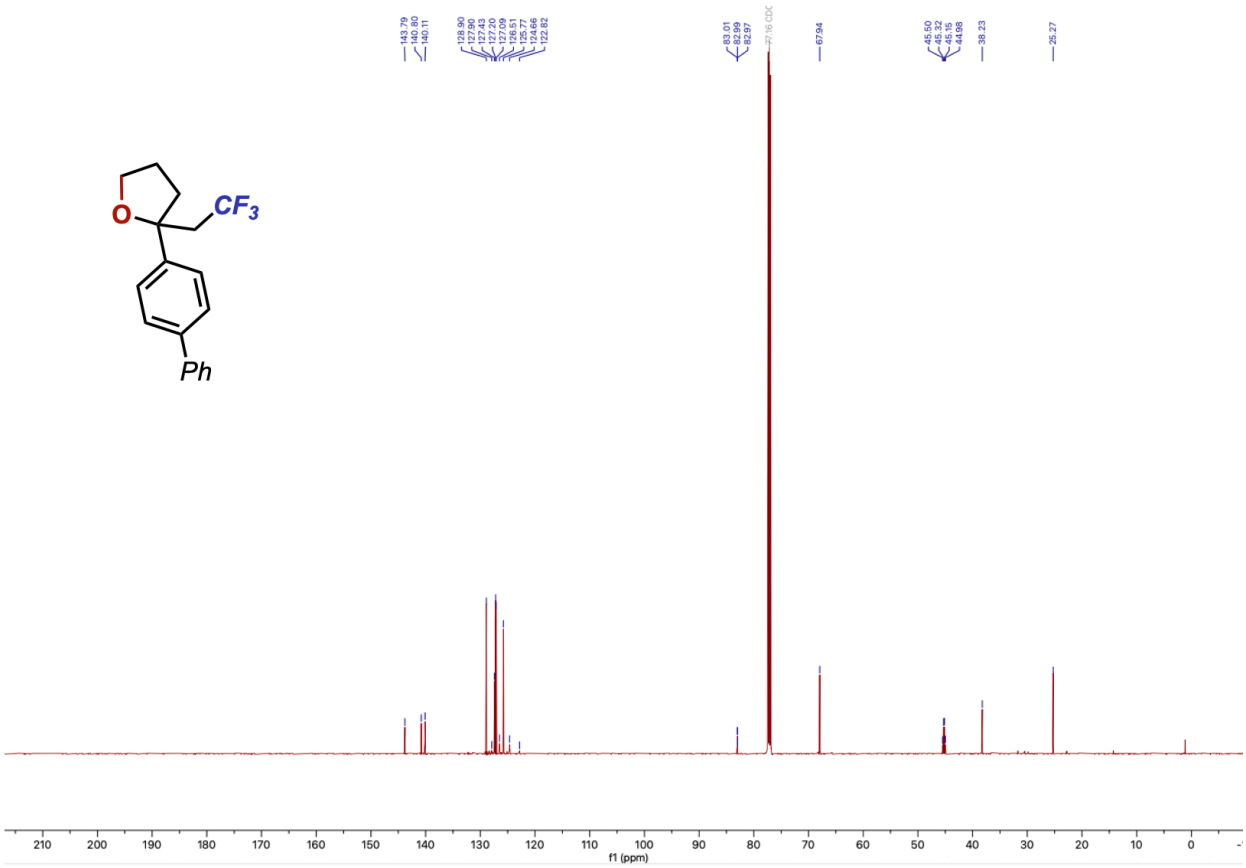
^{19}F NMR (565 MHz, DMSO-d6)



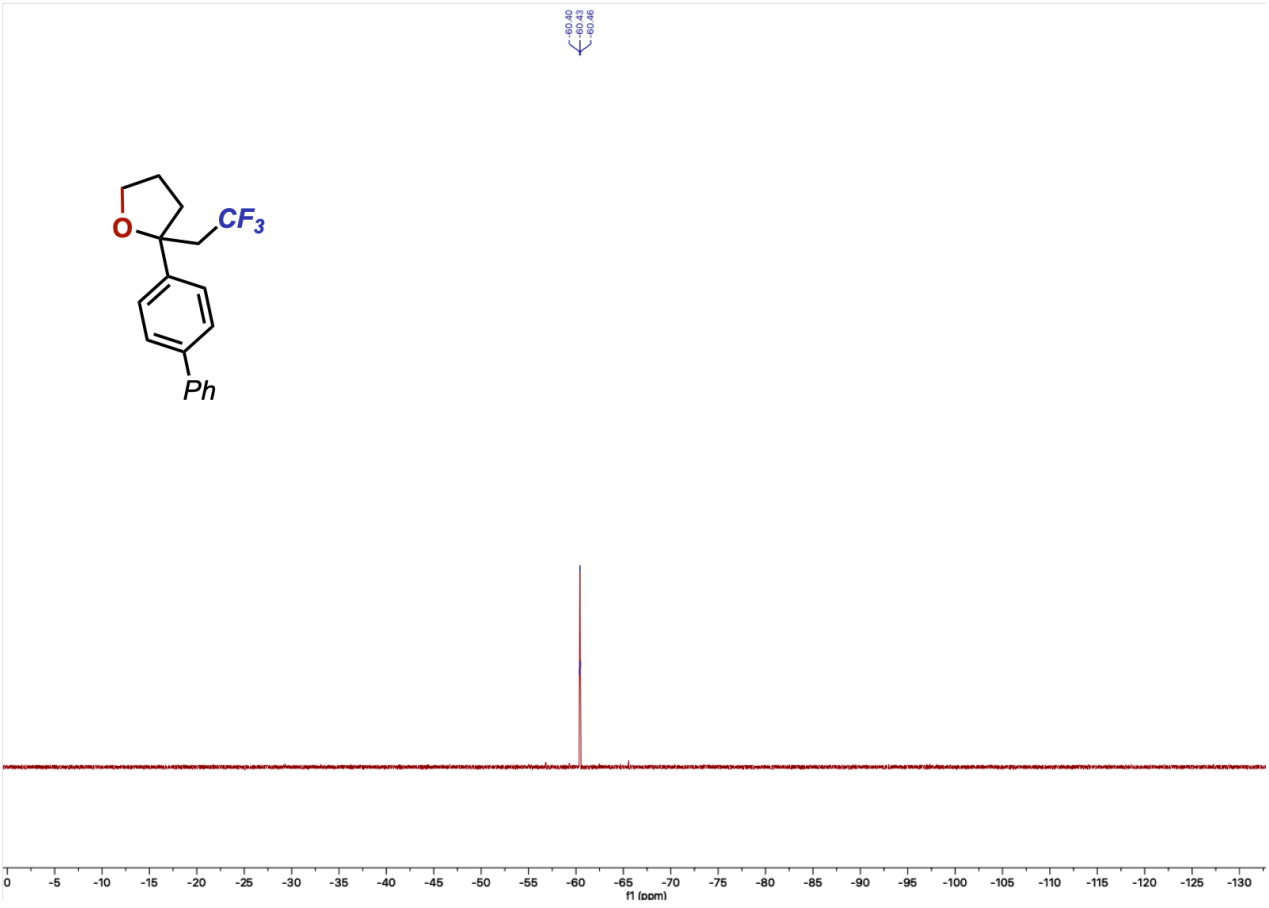
6a ^{1}H NMR (600 MHz, $CDCl_3$)



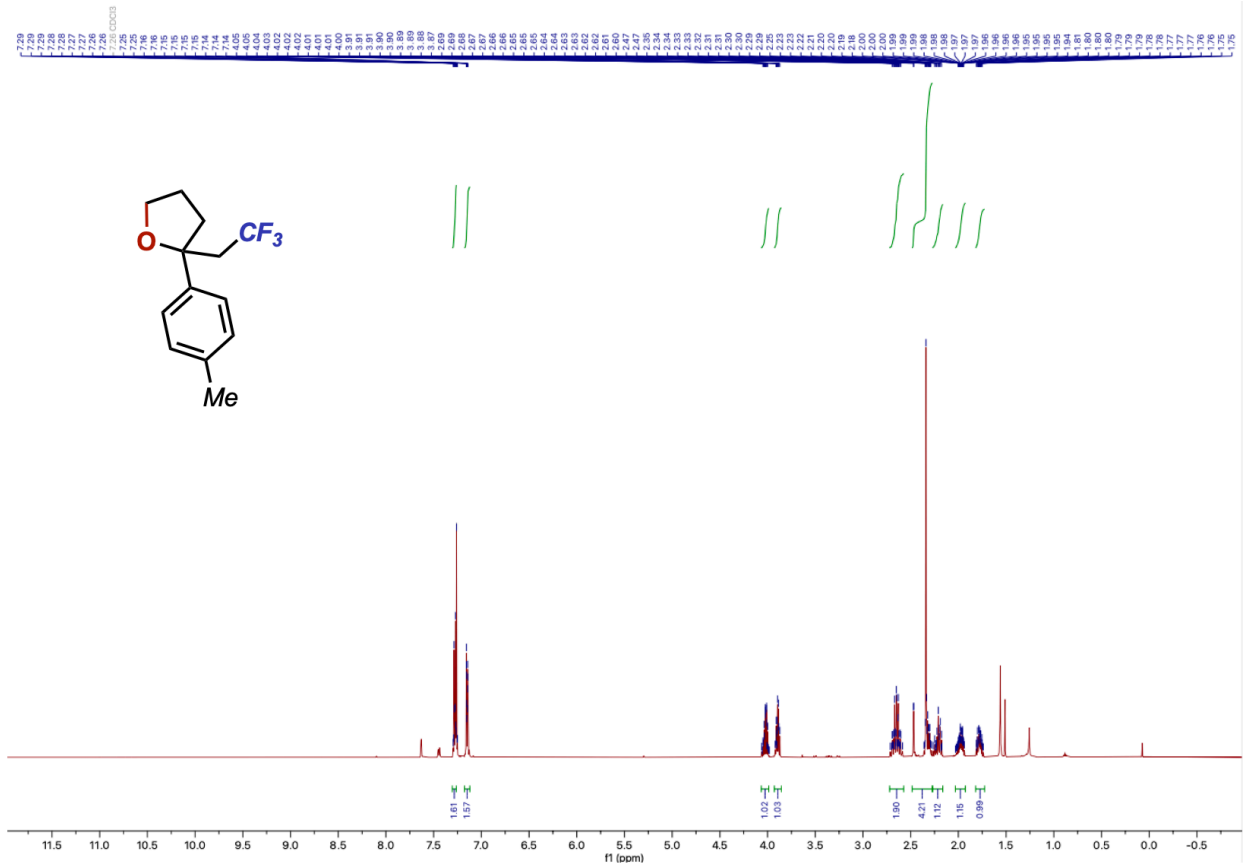
^{13}C NMR (151 MHz, $CDCl_3$)



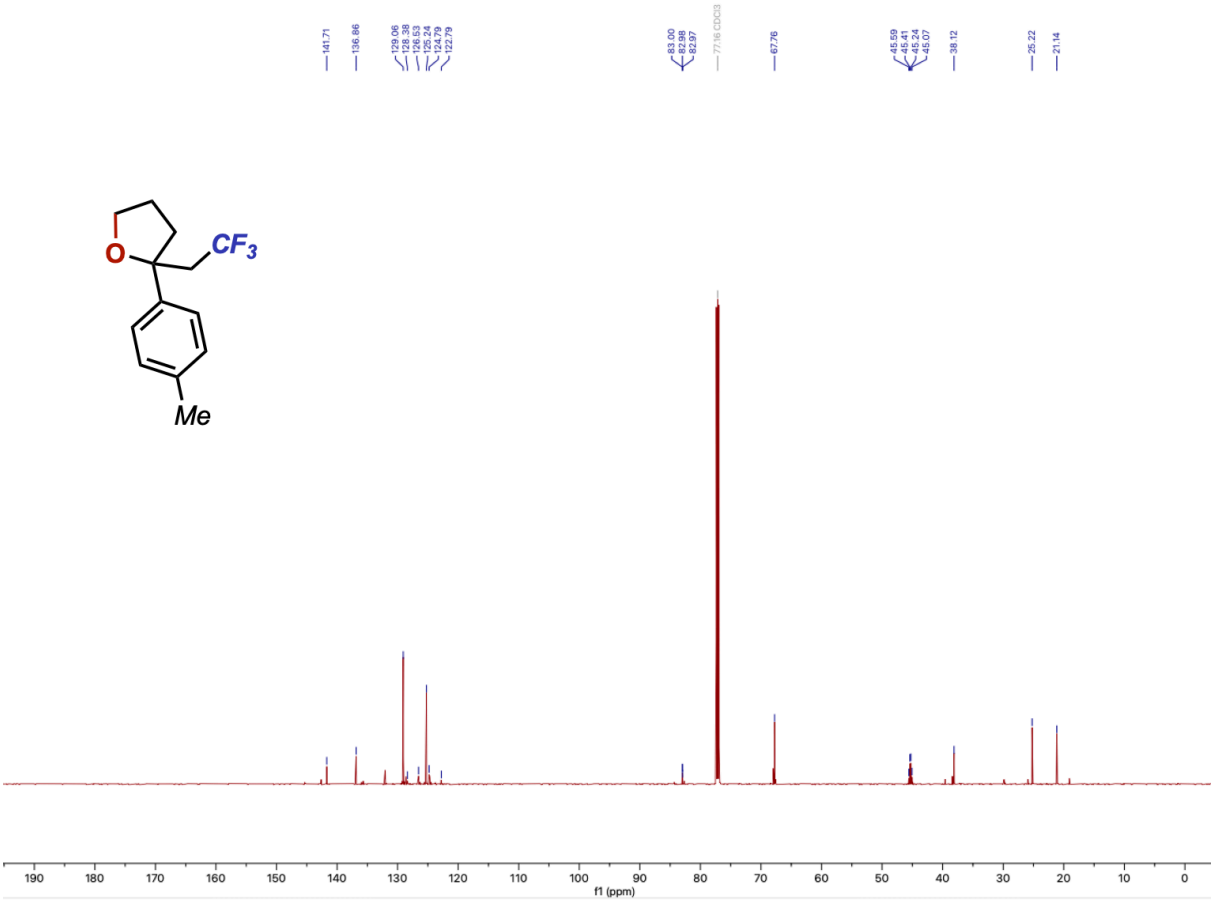
^{19}F NMR (565 MHz, $CDCl_3$)



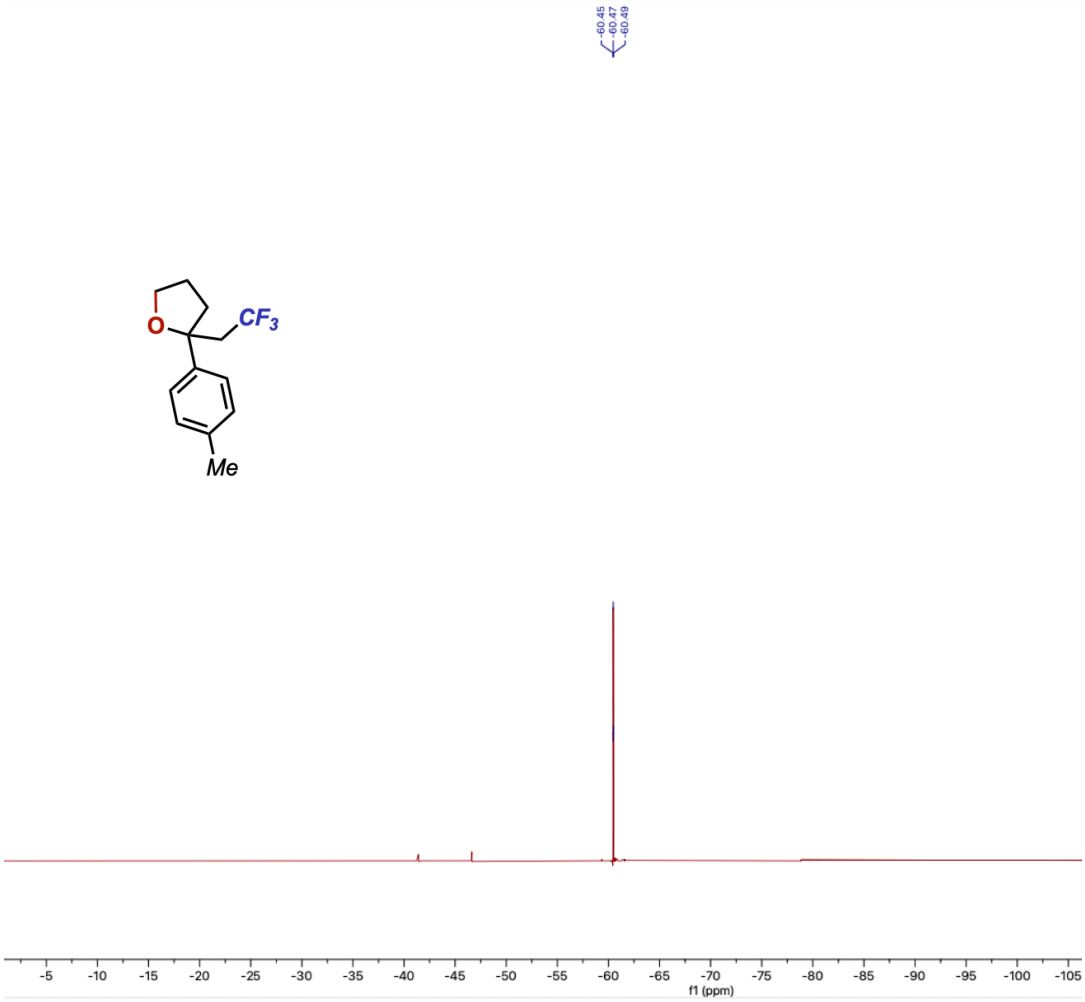
3b ^{1}H NMR (600 MHz, $CDCl_3$)



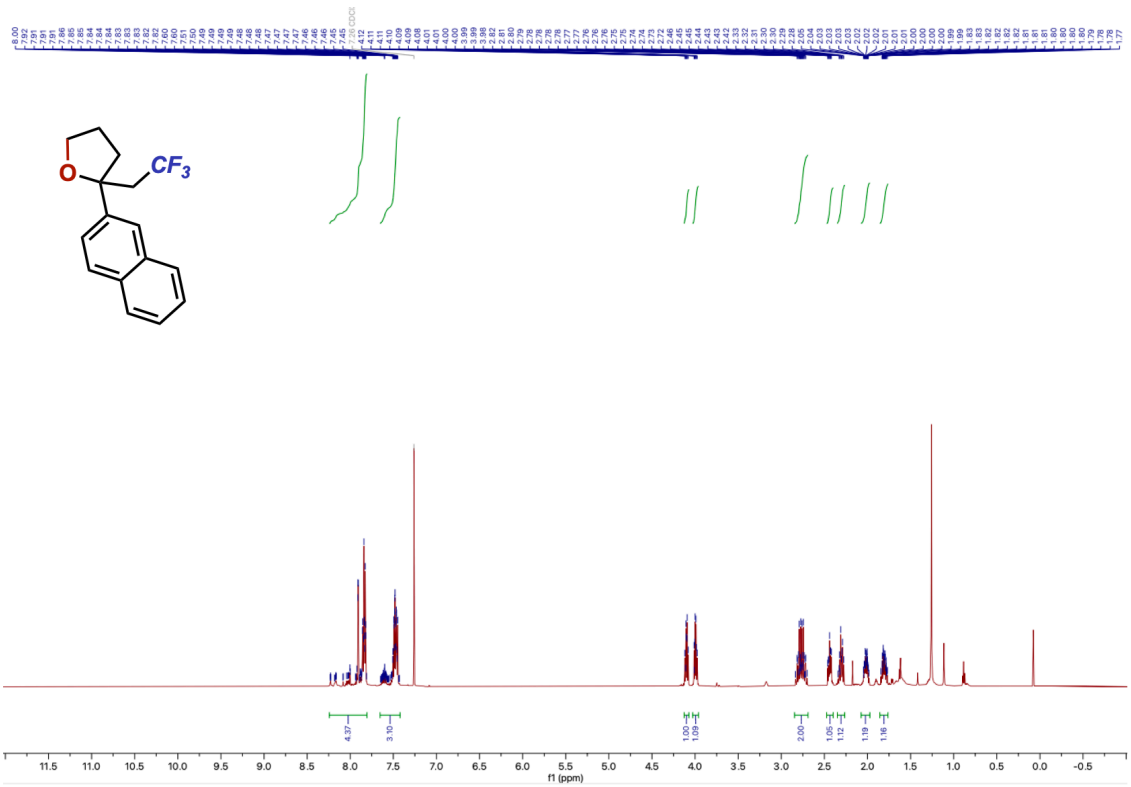
^{13}C NMR (151 MHz, $CDCl_3$)



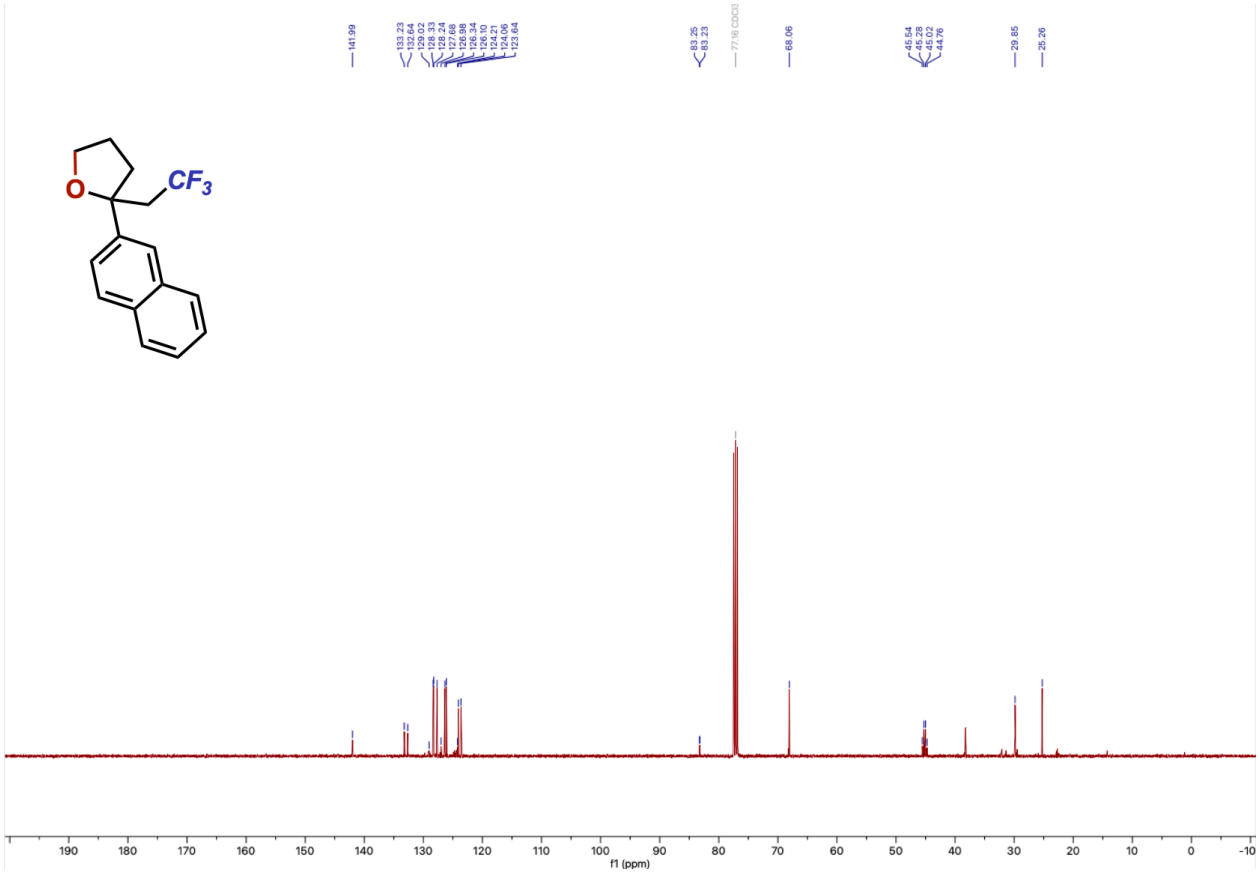
^{19}F NMR (565 MHz, $CDCl_3$)



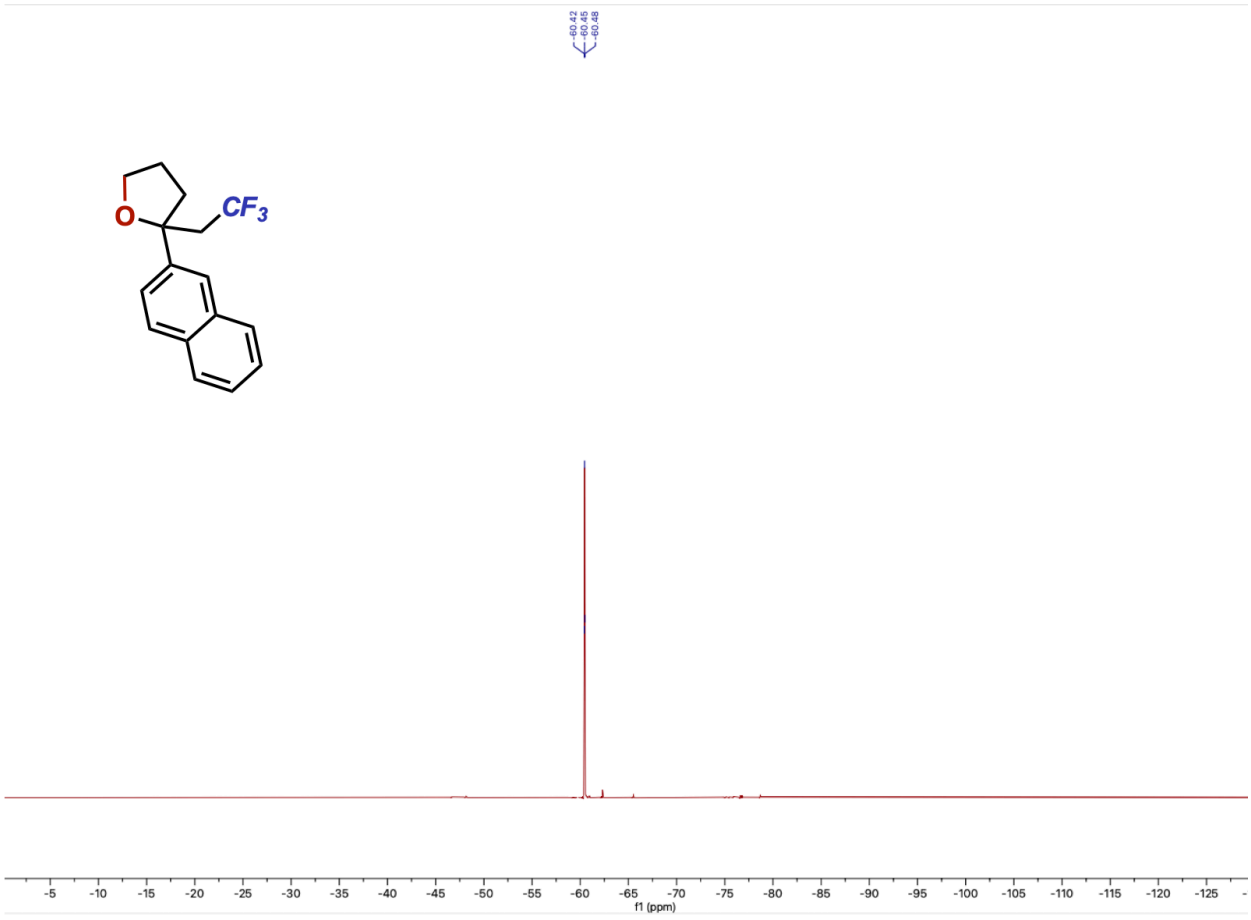
6c ^{1}H NMR (600 MHz, $CDCl_3$)



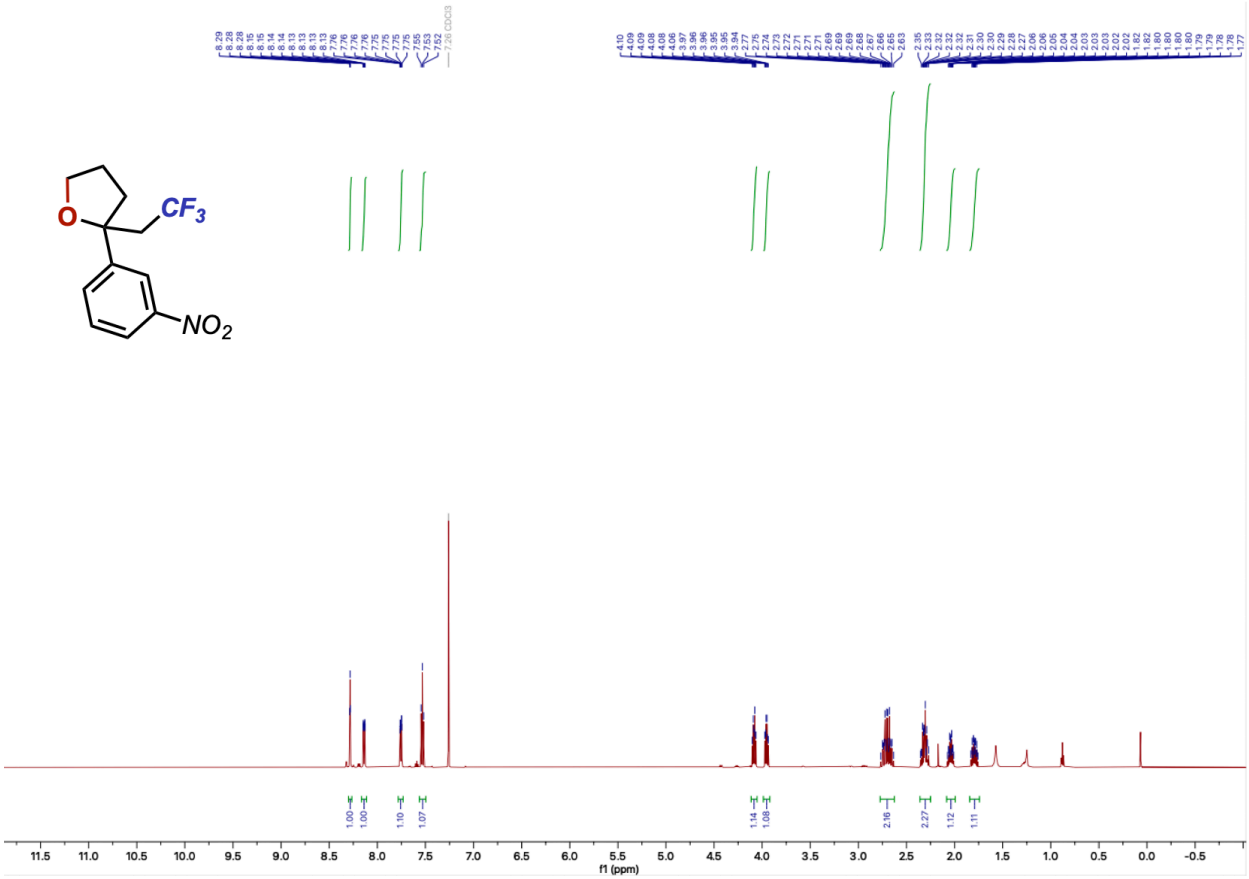
^{13}C NMR (151 MHz, $CDCl_3$)



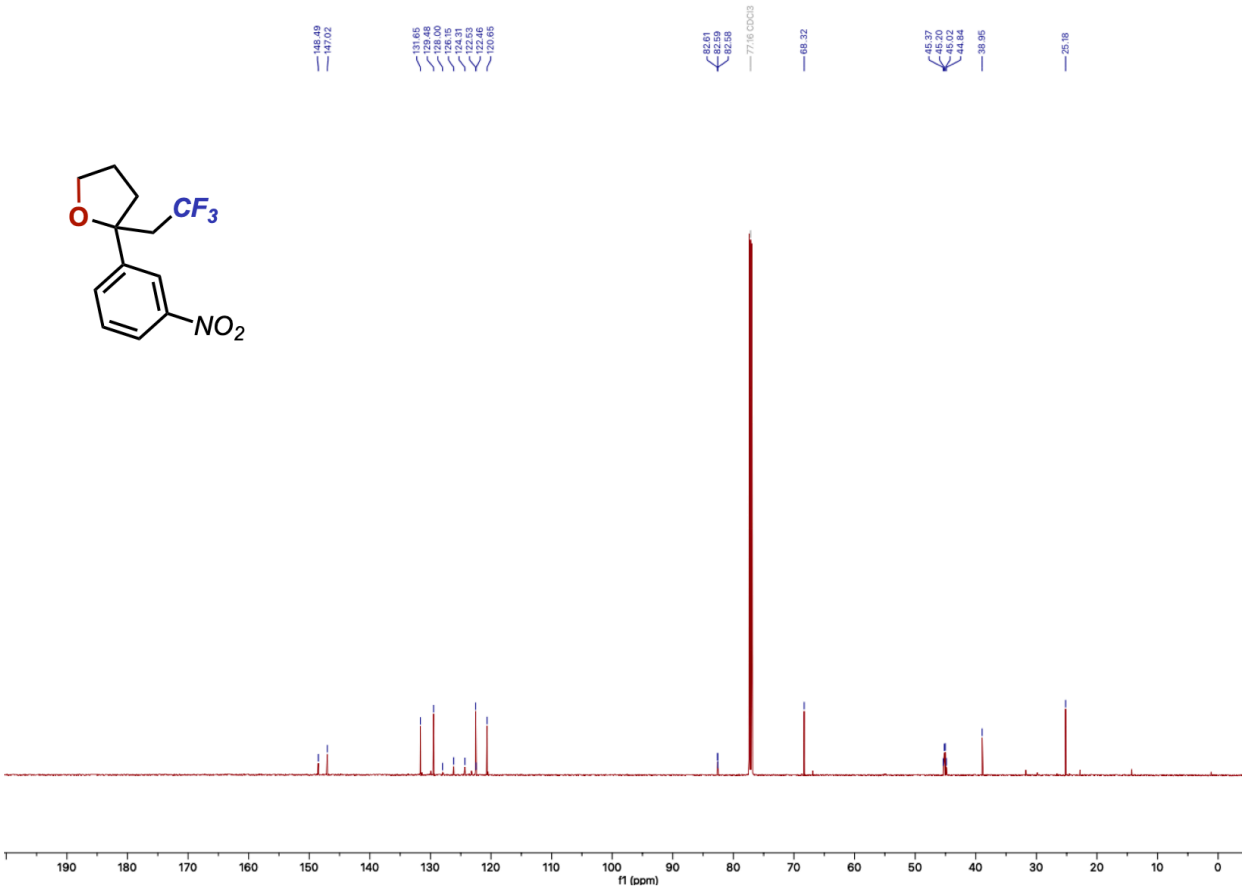
^{19}F NMR (565 MHz, $CDCl_3$)



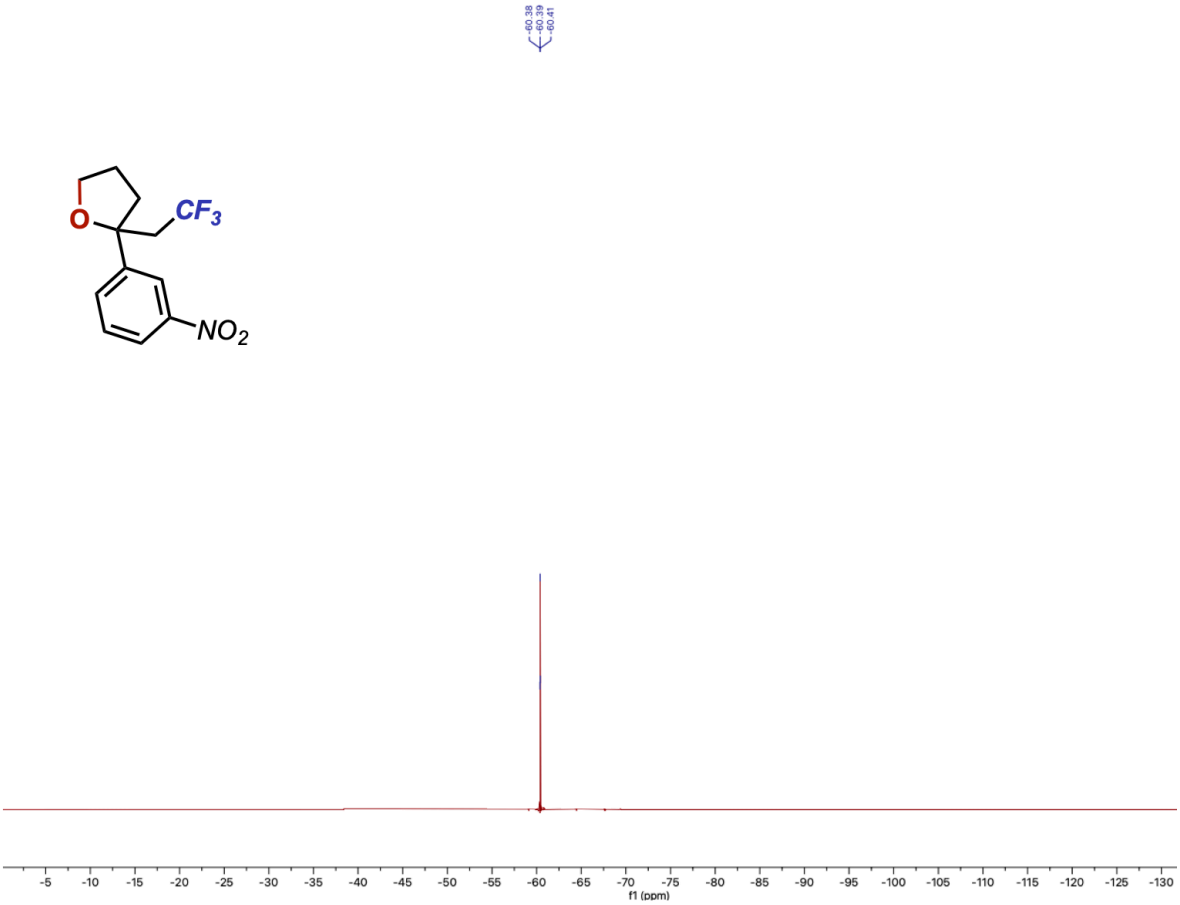
6d ^{1}H NMR (600 MHz, $CDCl_3$)



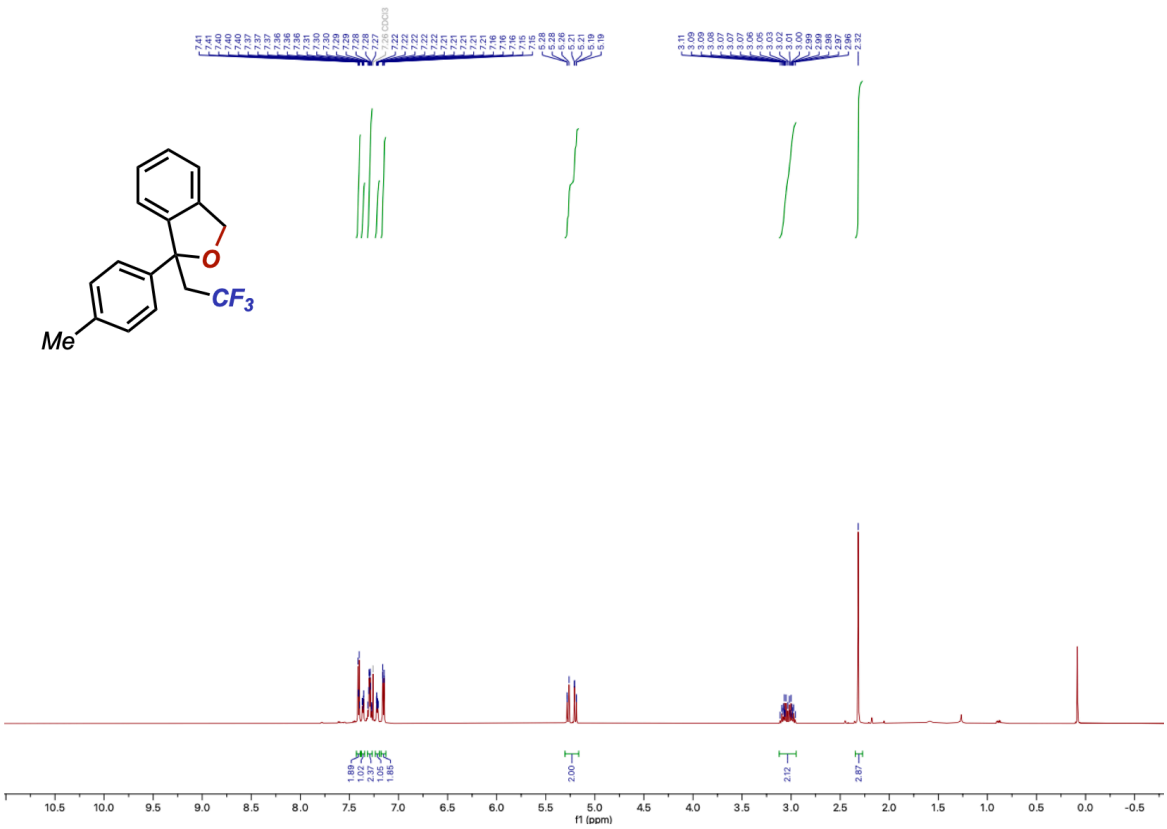
^{13}C NMR (151 MHz, $CDCl_3$)



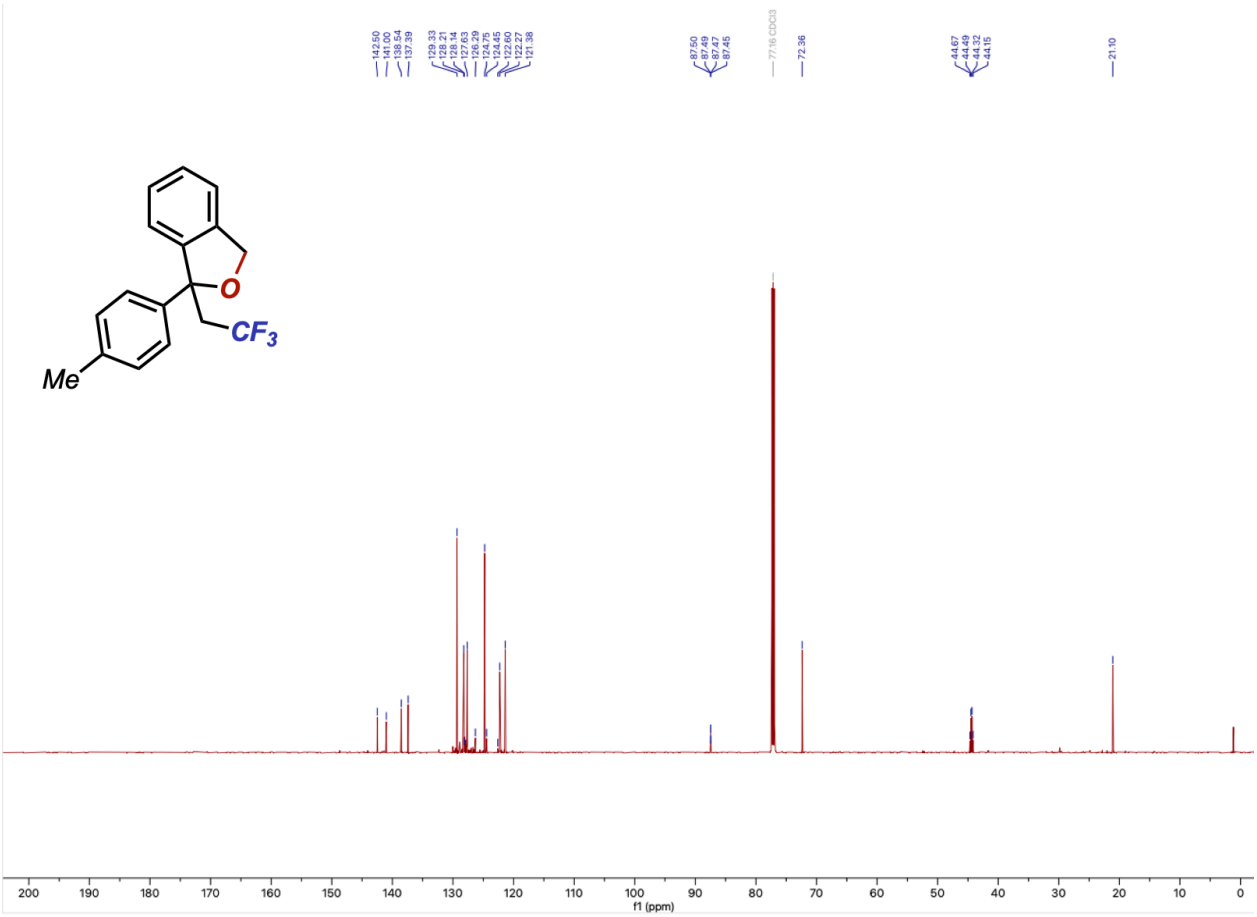
^{19}F NMR (565 MHz, $CDCl_3$)



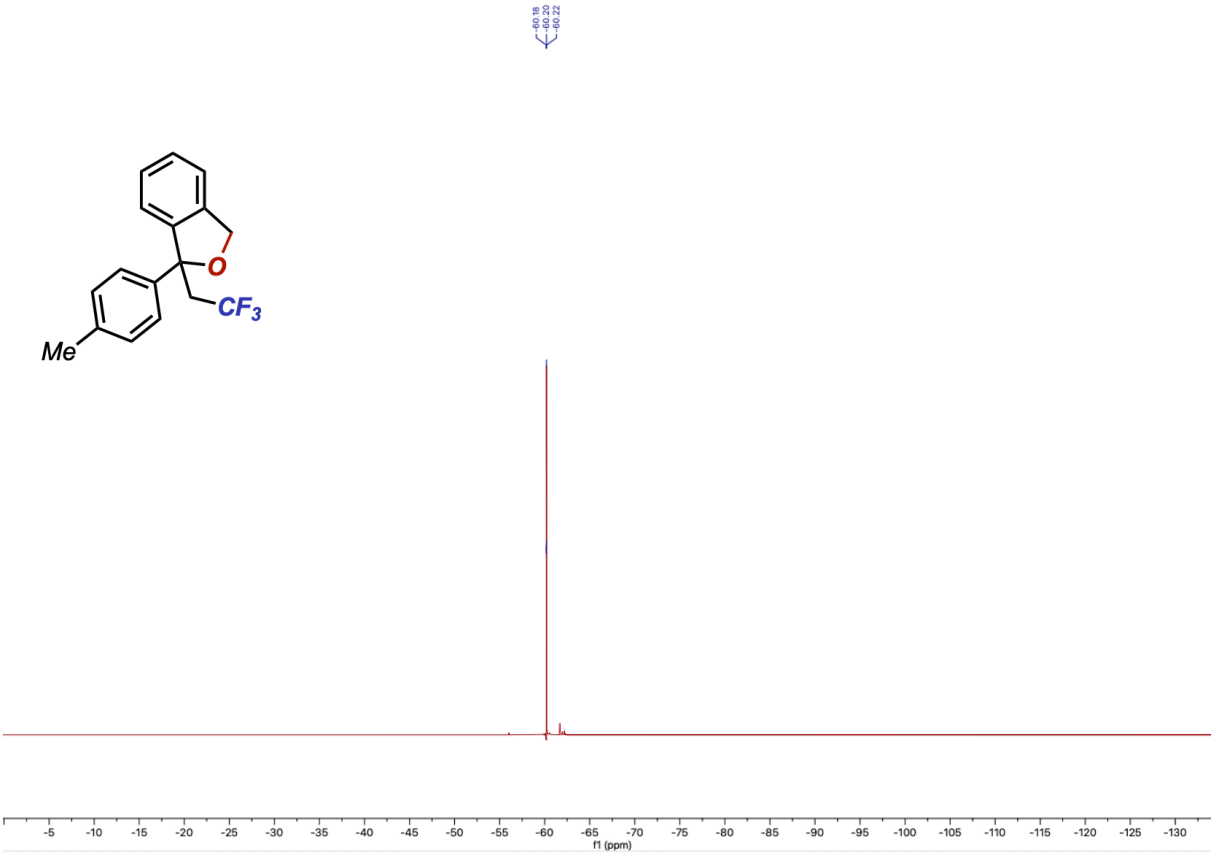
6e ^{1}H NMR (600 MHz, $CDCl_3$)



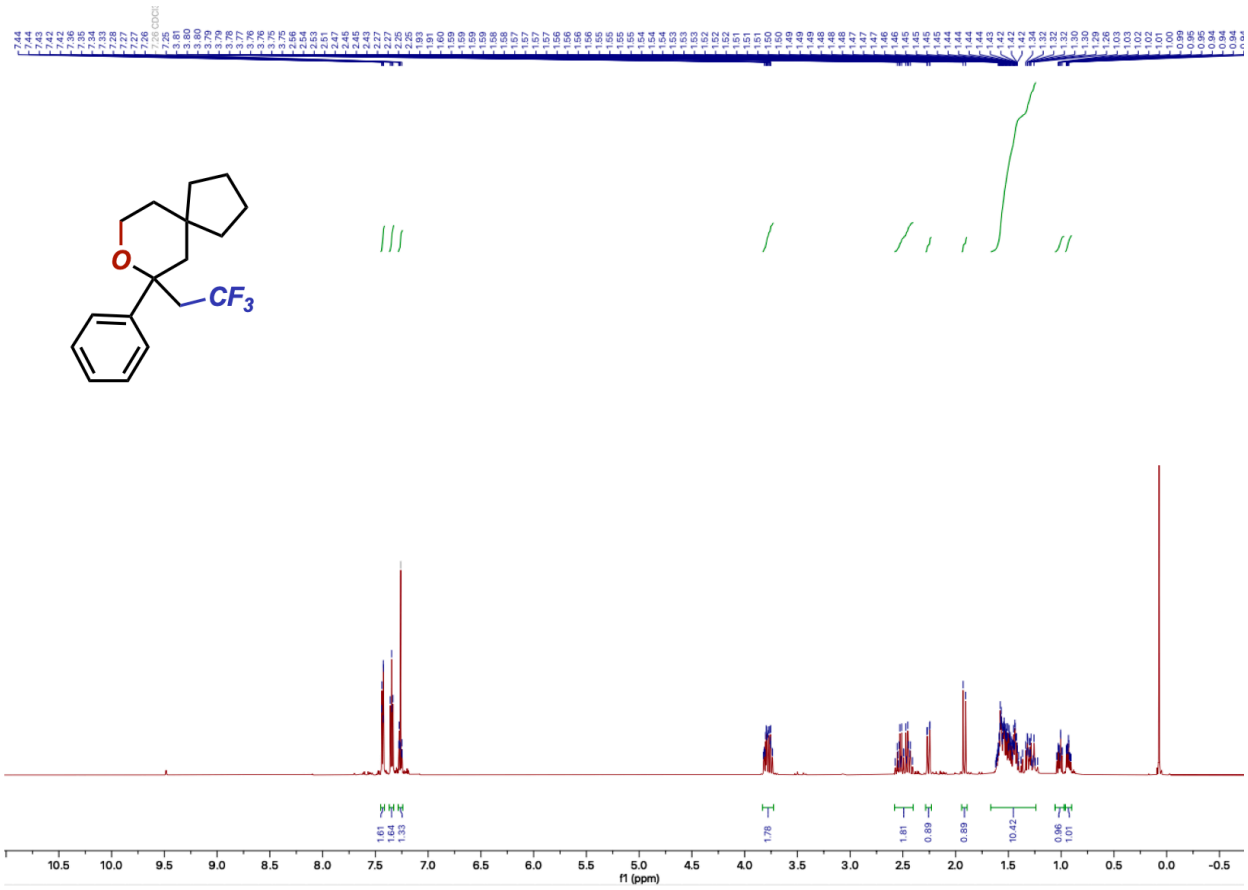
^{13}C NMR (151 MHz, $CDCl_3$)



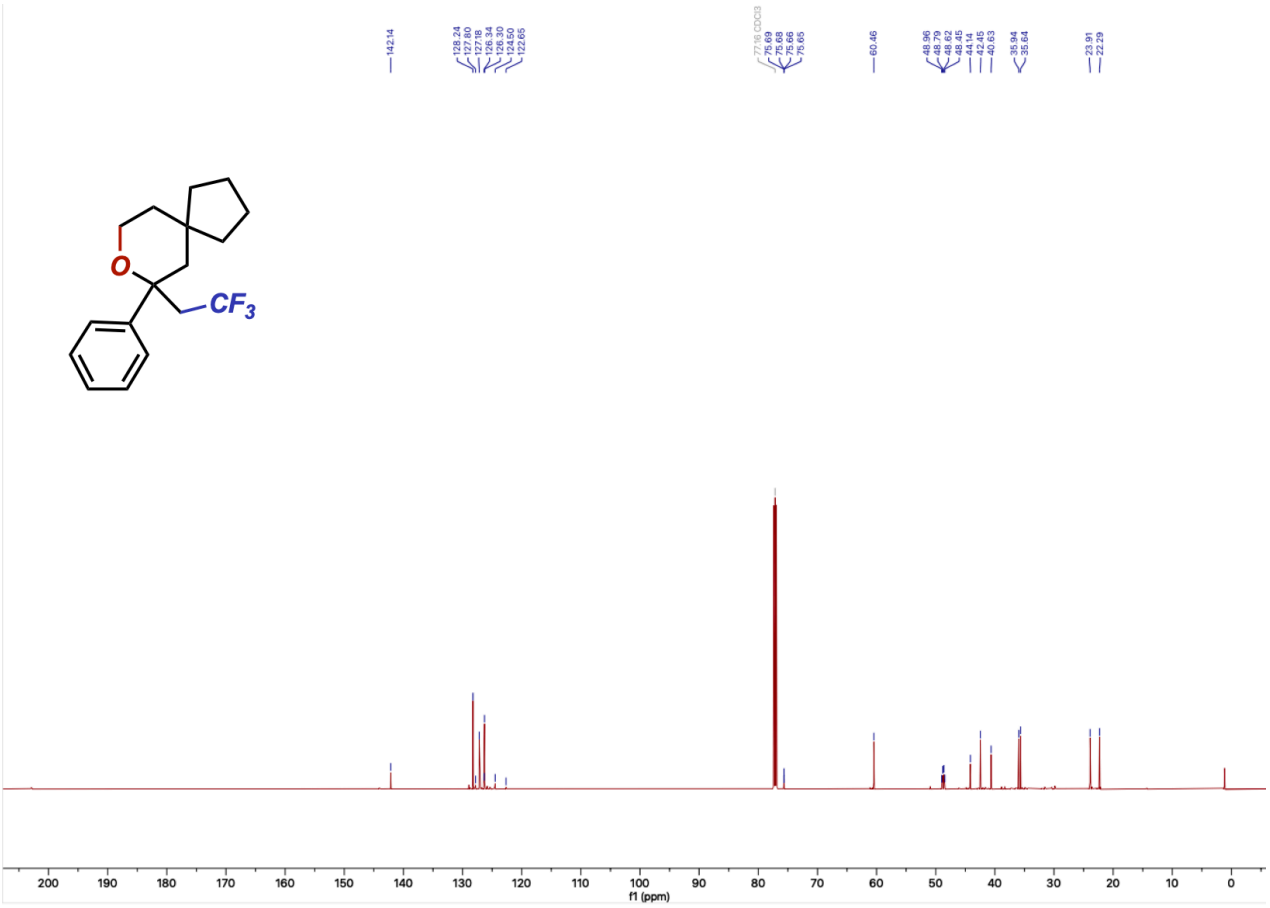
^{19}F NMR (565 MHz, $CDCl_3$)



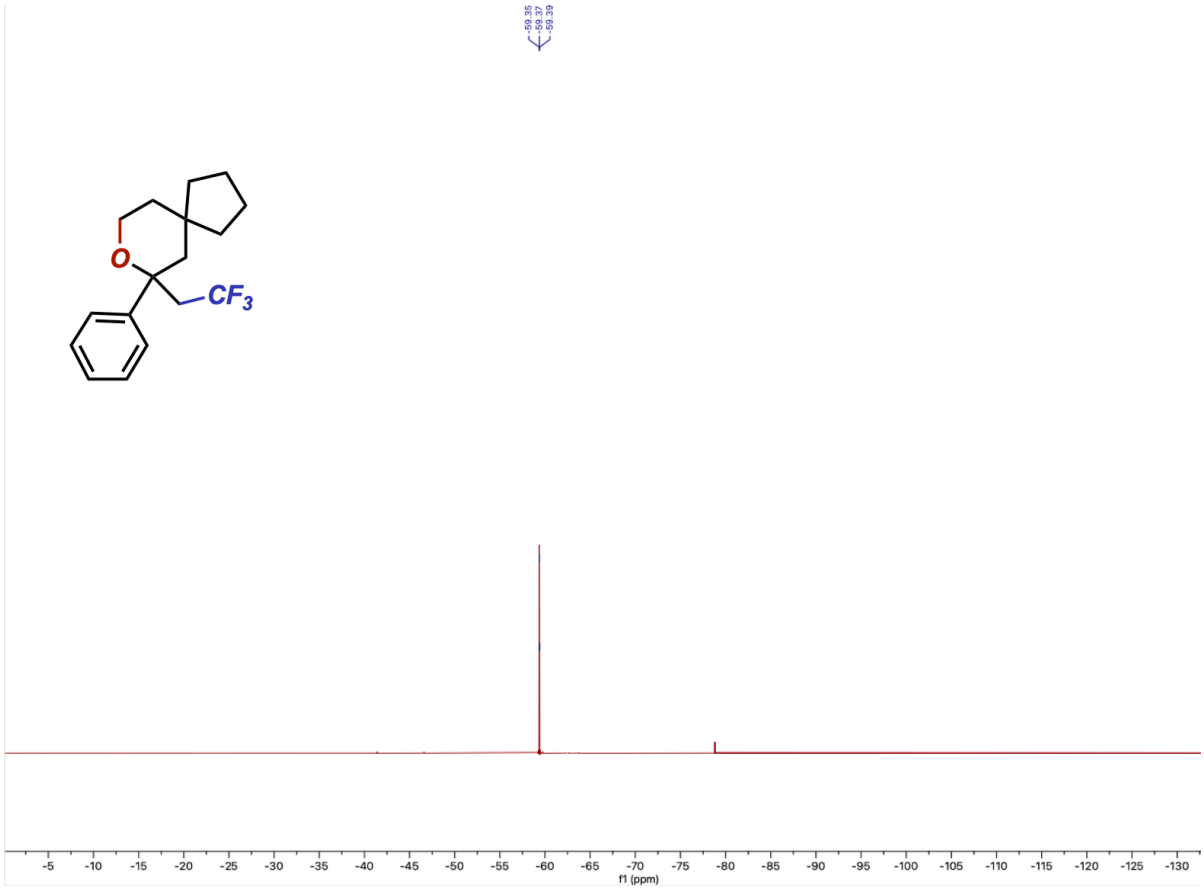
6f ^{1}H NMR (600 MHz, $CDCl_3$)



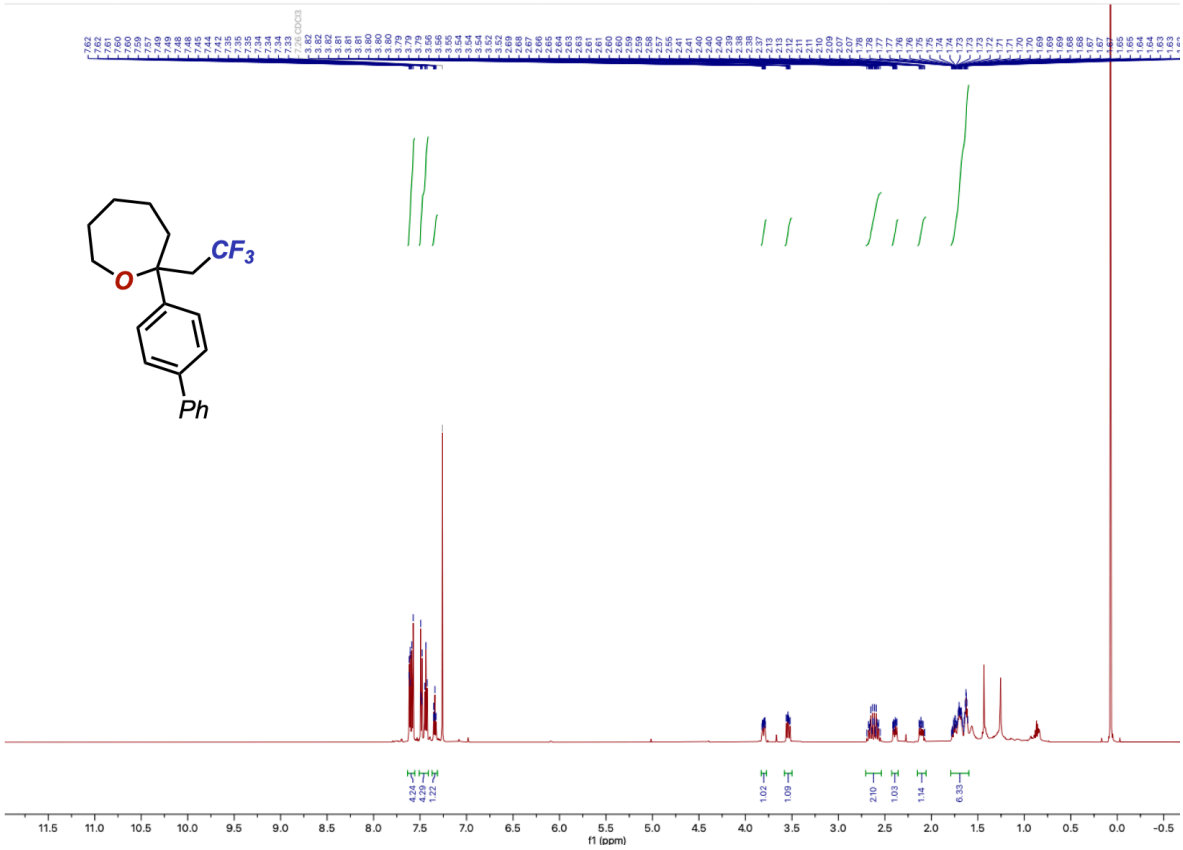
^{13}C NMR (151 MHz, $CDCl_3$)



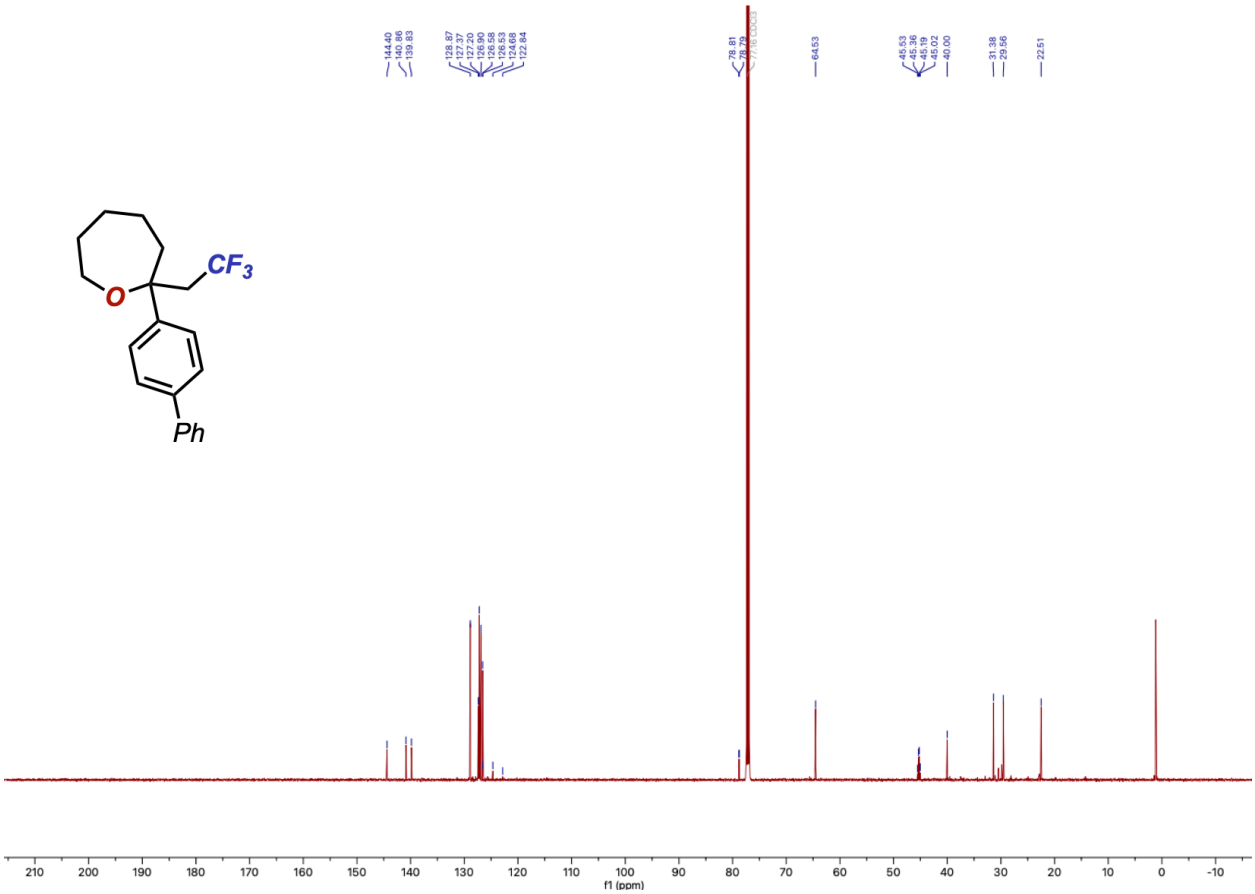
^{19}F NMR (565 MHz, $CDCl_3$)



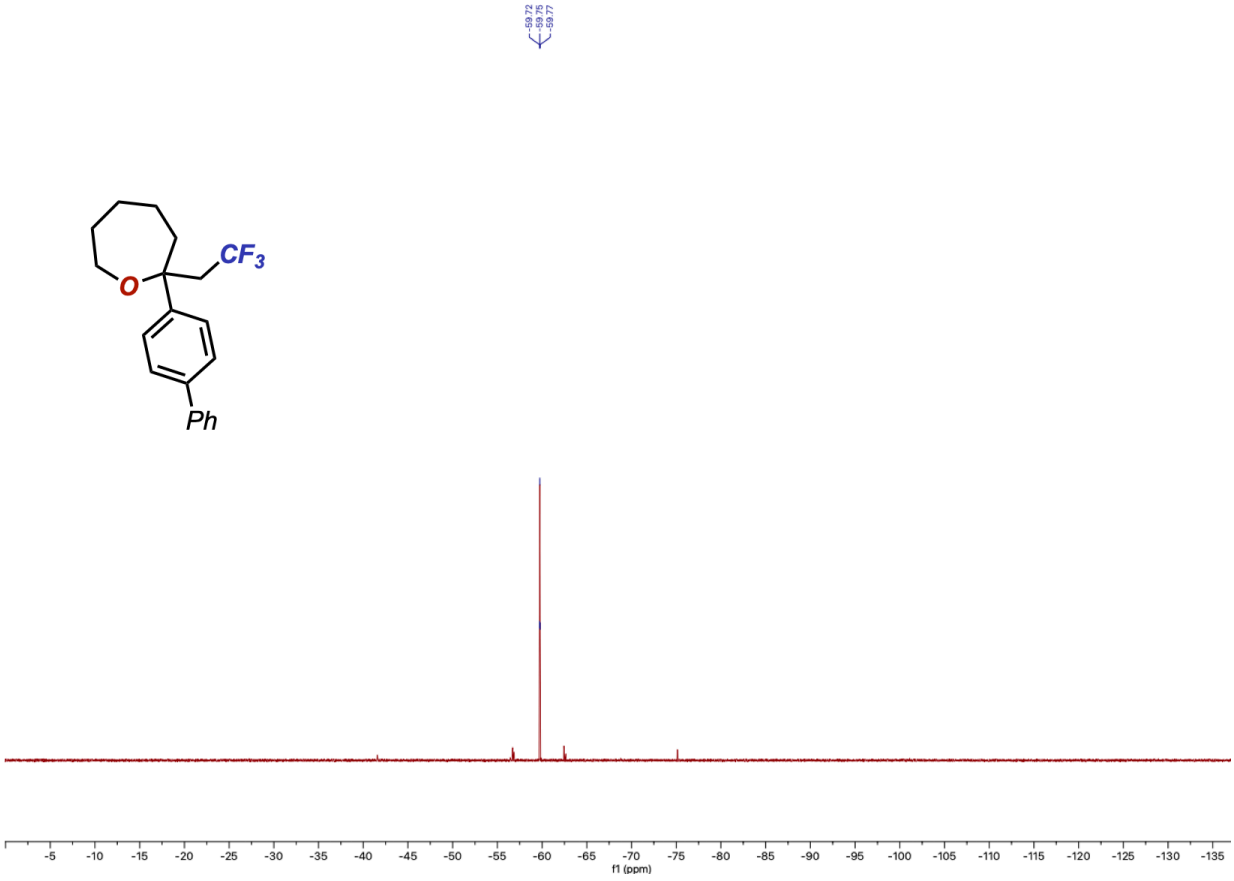
6g ^{1}H NMR (600 MHz, $CDCl_3$)



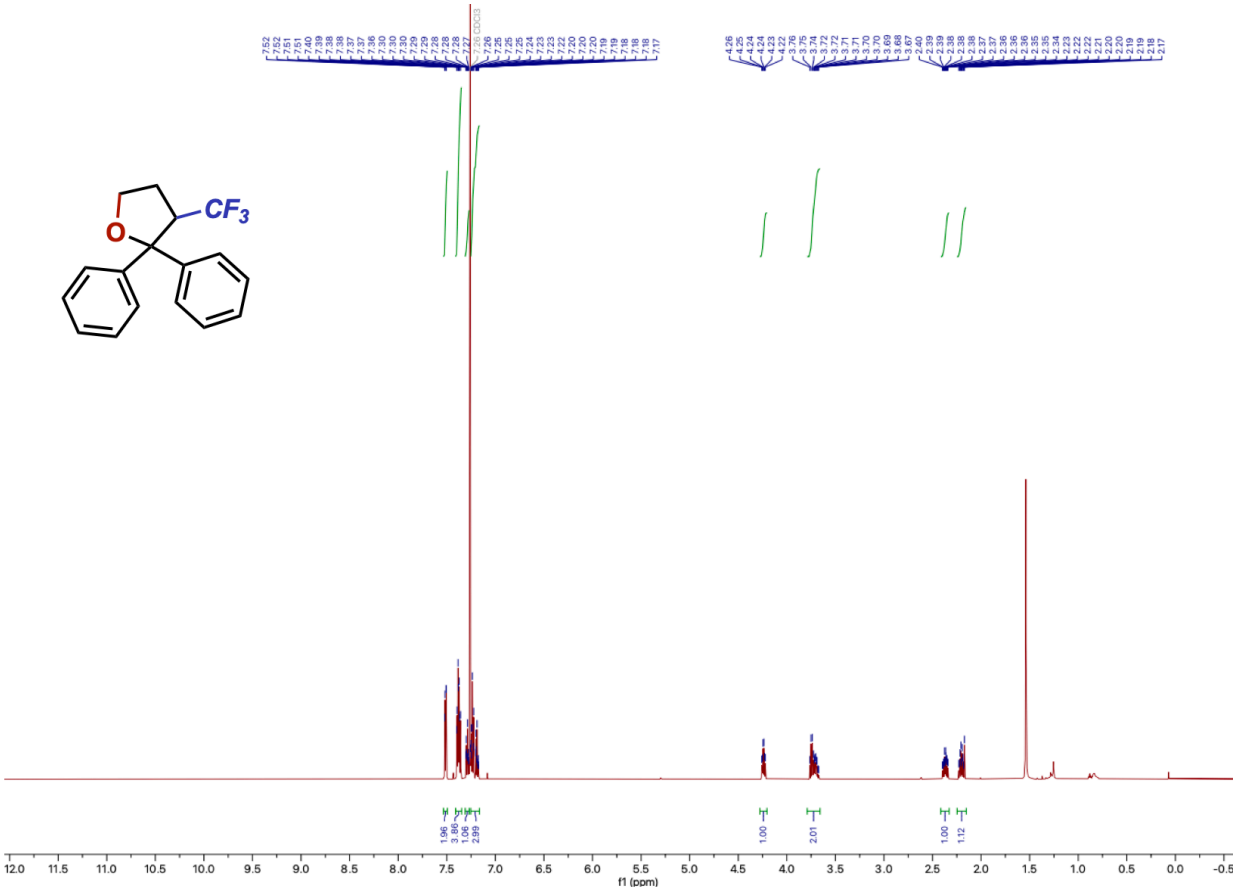
^{13}C NMR (151 MHz, $CDCl_3$)



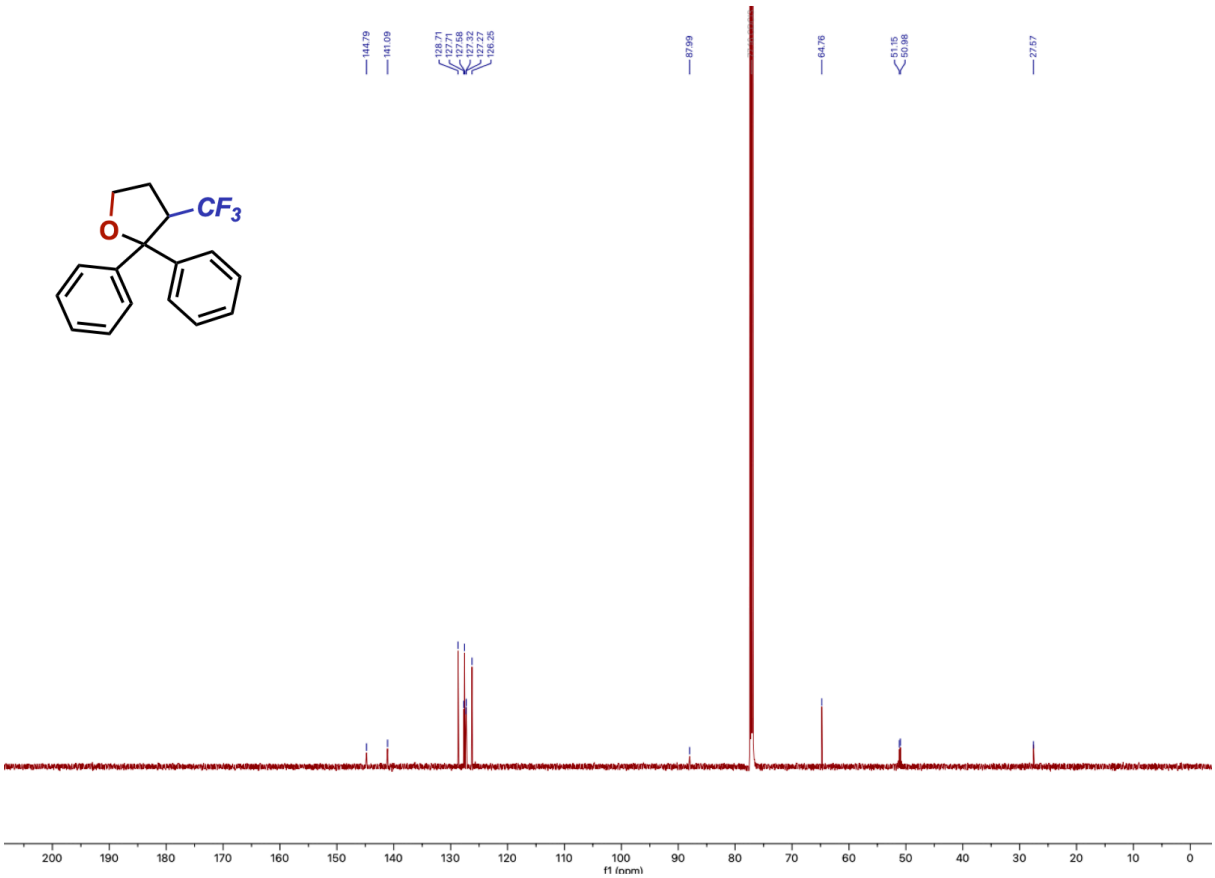
^{19}F NMR (565 MHz, $CDCl_3$)



6h ^{1}H NMR (600 MHz, $CDCl_3$)



^{13}C NMR (151 MHz, $CDCl_3$)



^{19}F NMR (565 MHz, $CDCl_3$)