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Highly Diastereoselective Strain-Release Doyle-Kirmse Reaction: Access to Functionalized Difluoro(methylene)cyclopropanes

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1. General Methods

1.1 Solvents, Reagents, Glassware and Reaction Setup

Unless otherwise specified, all reactions were conducted under an inert atmosphere of nitrogen or argon using hot air oven dried (120 ºC) glassware utilizing standard Schlenk-line technique. Air- and moisture-sensitive liquids and solutions were transferred via syringe into the reaction vessels through a rubber septum under inert atmosphere. Unless otherwise specified, all reagents were purchased of the highest commercial quality and used as received. Non-anhydrous solvents were purchased at the highest commercial quality and used as received. Organic solvents used for carrying out reactions were dried using standard methods. All work up and purification were carried out with reagent grade solvents in air. The temperature described below −5 °C was achieved using an immersion cooler by Julabo.

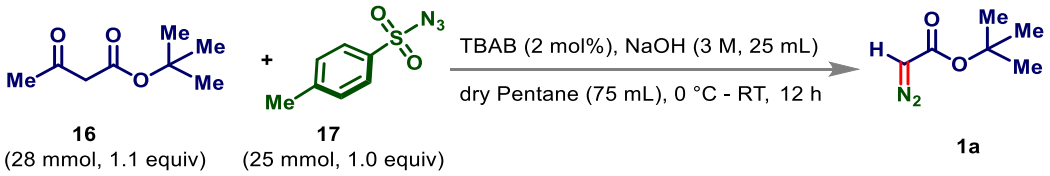
1.2 Analytical Methods:

Chromatography: Column chromatography was carried out using Sigma-Aldrich silica gel (60 Å, 230-400 mesh, 40-63 μm). Reactions were monitored by thin-layer chromatography (TLC), using aluminium-backed Merck Kieselgel 60 F254 fluorescent treated silica gel plates, which were visualized under UV light or by staining with aqueous basic $KMnO_4$, or phosphomolybdic acid solution in ethanol. **IR:** Infrared (FT-IR) spectra were recorded of neat sample on Bruker alfa FT-IR, ν_{max} in cm^{-1} and the bands are characterized as strong (s), medium (m), and weak (w). **Melting Point**: Melting points were measured in open glass capillary on a Buchi M-560 melting point apparatus. **NMR:** NMR spectra were recorded on Bruker Ultrashield spectrometer at 400 MHz (for ^{1}H-NMR), 101 MHz (for ^{13}C-NMR), 376 MHz (for ^{19}F-NMR) and 162 MHz (for ^{31}P-NMR). Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as internal standard ($CDCl_3$: δ 7.26 ppm for ^{1}H-NMR and δ 77.00 ppm for ^{13}C-NMR). For ^{1}H-NMR, data are reported as follows: chemical shift, multiplicity (s = singlet, brs = broad singlet, d = doublet, dd = doublet of doublets, ddd = doublet of doublet of doublets, t = triplet, q = quartet, dt = doublet of triplets, m = multiplet etc.), coupling constants (Hz) and integration. **NMR yields:** Following work up or/and solvent evaporation, dibromomethane (relative to limiting starting material) was added to the crude residue. The resultant mixture was dissolved in $CDCl_3$, and a 0.5 mL sample of the resultant solution taken for 1H NMR analysis. Yields were calculated based on the integrals of known product resonances relative to dibromomethane (2H, at 4.94 ppm in $CDCl_3$). **MS**: High

Resolution Mass Spectrometry (HRMS) was performed on Waters e2695 XEVO G2-XS Q-TOF instrument. Gas Chromatography Mass Spectrometry (GCMS) was performed on SCHIMADZU GC 2010 Plus instrument.

4. Preparation of Diazo Compounds:

Tert-butyl 2-diazoacetate (1a)



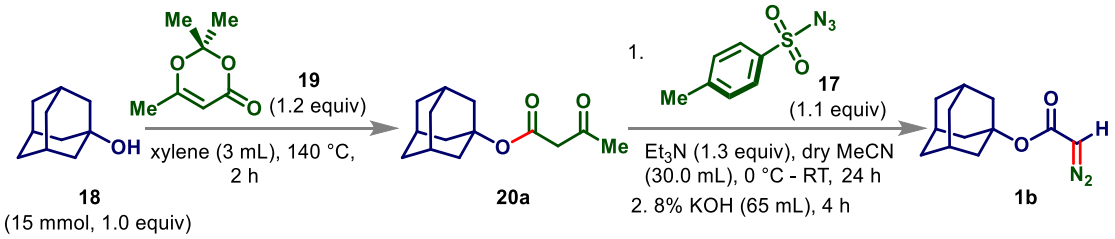
16 (28 mmol, 1.1 equiv) + **17** (25 mmol, 1.0 equiv) → **1a**

Following a slightly modified procedure,[1] *tert*-butyl-acetooacetate (**16**) (4.5 mL, 28 mmol, 1.1 equiv), *tetra-n*-butylammonium bromide (TBAB) (160 mg, 0.500 mmol, 0.02 equiv), tosylazide **17** (4.9 g, 25 mmol, 1.0 equiv), and anhydrous *n*-pentane (75 mL) were mixed, and stirred at 0 °C. Next, pre-cooled NaOH solution (3.0 M, 25 mL) was added dropwise to the reaction mixture over a period of 30 min. After 12 h, the reaction mixture was passed through celite pad, washed with brine solution (2 × 50 mL), dried over anhydrous Na_2SO_4, and concentrated under reduced pressure (upto 300 mbar) at 25 ºC water bath temperature. The crude product was purified by column chromatography using petroleum ether as eluent to afford *tert*-butyl 2-diazoacetate (**1a**) as a yellow oil (3.00 g, 21.1 mmol, 84%).

- **TLC:** R_f = 0.51 (EtOAc:petroleum ether, 1:20 v/v), $KMnO_4$
- **^{1}H NMR (400 MHz, $CDCl_3$):** δ 4.61 (br s, 1H, C*H*N_2), 1.48 (s, 9H, OC(CH_3)$_3$).
- **^{13}C NMR (101 MHz, $CDCl_3$):** δ 166.1, 81.2, 46.5, 28.2.

The characterization data corresponded to the reported values.[1]

Adamantan-1-yl 2-diazoacetate (1b)



18 (15 mmol, 1.0 equiv) → **20a** → **1b**

Step 1: Following a slightly modified procedure,[2] adamantan-1-ol (**18**) (2.28 g, 15.0 mmol, 1.00 equiv), 2,2,6-trimethyl-4*H*-1,3-dioxin-4-one (**19**) (2.13 g, 15.0 mmol, 1.20 equiv), and xylene (3 mL) were mixed, and stirred at 140 °C for 2 h. After cooling to room temperature, xylene was evaporated, and the residue was purified by column chromatography using 1:50 EtOAc:petroleum ether as mobile phase to afford adamantan-1-yl 3-oxobutanoate (**20a)** as a colorless oil (3.11 g, 13.2 mmol, 88%).

- **TLC:** R_f = 0.37 (EtOAc:petroleum ether, 1:20 v/v), $KMnO_4$
- **^{1}H NMR (400 MHz, $CDCl_3$):** δ 12.22 (s, 0.06H, O*H* of enol form), 4.88 (s, 0.06H, vinylic *H* of enol form), 3.34 (s, 1.9H, CH_3COCH_2 of keto form), 2.25 (s, 2.8H, CH_3COCH_2 of keto form), 2.20 – 2.06 (m, 9H, 3 × CH_2 and 3 × C*H* of adamantyl group), 1.91 (s, 0.2H, CH_3 of enol form), 1.73 – 1.57 (m, 6H, 3 × CH_2 of adamantyl group).
- **^{13}C NMR (101 MHz, $CDCl_3$) (Enol form):** δ 174.6, 172.3, 91.1, 80.7, 41.4, 36.0, 21.1. One carbon was not resolved at 101 MHz.
- **^{13}C NMR (101 MHz, $CDCl_3$) (Keto form)**: δ 201.2, 166.0, 81.9, 51.6, 41.0, 35.9, 30.7, 29.9.

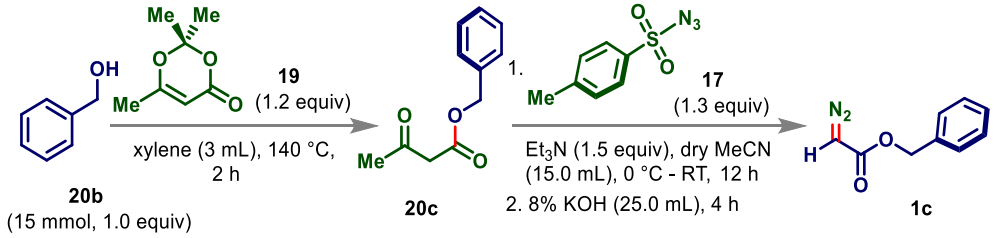
The characterization data corresponded to the reported values.[2]

Step 2: Following a slightly modified procedure,[2] to a solution of adamantan-1-yl 3-oxobutanoate (**20a**) (3.11 g, 13.2 mmol, 1.00 equiv) in anhydrous acetonitrile (15 mL), triethylamine (2.40 mL, 17.1 mmol, 1.30 equiv) was added. The reaction mixture was cooled in an ice bath and a solution of tosyl azide **17** (2.86 g, 14.5 mmol, 1.10 equiv) in anhydrous acetonitrile (15 mL) was added dropwise. Next, the reaction mixture was allowed to warm to room temperature and stirred. After 24 h, 8% aqueous KOH (65 mL) solution was added to the reaction mixture and stirred for 4 h. Next, the reaction mixture was extracted with diethyl ether (3 × 50 mL). The organic layers were combined, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The crude product was purified by column chromatography using 1:25 EtOAc:petroleum ether as eluent to afford adamantan-1-yl 2-diazoacetate (**1b**) as a yellow solid (2.80 g, 12.7 mmol, 97%).

- **TLC:** R_f = 0.55 (EtOAc:petroleum ether, 1:10 v/v), $KMnO_4$
- **^{1}H NMR (400 MHz, $CDCl_3$):** δ 4.60 (br s, 1H, C*H*N_2), 2.22 – 2.06 (m, 9H, 3 × CH_2 and 3 × C*H* of adamantyl group), 1.72 – 1.61 (m, 6H, 3 × CH_2 of adamantyl group).
- **^{13}C NMR (101 MHz, $CDCl_3$):** δ 165.9, 81.4, 46.7, 41.6, 36.1, 30.8.

The characterization data corresponded to the reported values.[2]

Benzyl 2-diazoacetate (1c)



Step 1: Following a slightly modified procedure,[2] phenylmethanol **20b** (1.56 mL, 15.0 mmol, 1.00 equiv), 2,2,6-trimethyl-4*H*-1,3-dioxin-4-one (**19**) (2.56 g, 18.0 mmol, 1.20 equiv) and xylene (3 mL) was mixed and stirred at 140 °C for 2 h. After cooling to room temperature, xylene was evaporated and the residue was purified by column chromatography using 1:25 EtOAc:petroleum ether as eluent to afford benzyl 3-oxobutanoate (**20c)** as a colorless liquid (2.22 g, 11.5 mmol, 77%).

- **TLC:** R_f = 0.33 (EtOAc:petroleum ether, 1:5 v/v), $KMnO_4$
- **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.41 – 7.30 (m, 5H, Ar*H*), 5.18 (s, 2H, OCH_2Ar), 3.50 (s, 2H, COCH_2CO), 2.25 (s, 3H, COCH_3).
- **^{13}C NMR (101 MHz, $CDCl_3$):** δ 200.2, 166.7, 135.1, 128.3, 128.2, 128.1, 66.7, 49.6, 29.8.

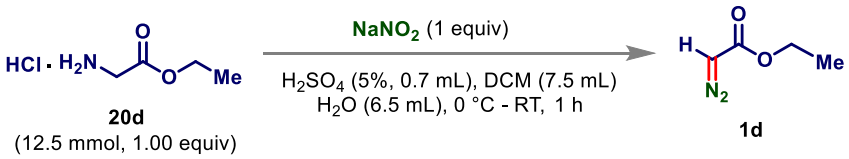
The characterization data corresponded to the reported values.[3]

Step 2: Following a slightly modified procedure,[4] to a solution of benzyl 3-oxobutanoate (**20c**) (961 mg, 5.00 mmol, 1.00 equiv) in anhydrous acetonitrile (7 mL), triethylamine (1.1 mL, 7.5 mmol, 1.5 equiv) was added. Next, a solution of tosyl azide **17** (1.28 g, 6.50 mmol, 1.30 equiv) in anhydrous acetonitrile (8 mL) was added dropwise, at 0 ºC, and the reaction mixture allowed to warm to room temperature. After 12 h, the reaction mixture was treated with 8% aqueous KOH solution (25 mL) and stirred for 4 h. The reaction mixture was extracted with diethyl ether (3 × 30 mL). The organic layers were combined, washed with brine solution (30 mL), dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The crude product was purified by column chromatography using 1:50 EtOAc:petroleum ether as eluent to afford benzyl 2-diazoacetate (**1c**) as a yellow liquid (700 mg, 3.97 mmol, 79%).

- **TLC:** R_f = 0.28 (EtOAc:petroleum ether, 1:20, v/v), $KMnO_4$
- **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.41 – 7.30 (m, 5H, Ar*H*), 5.20 (s, 2H, OCH_2Ar), 4.80 (br s, 1H, C*H*N_2).
- **^{13}C NMR (101 MHz, $CDCl_3$):** δ 166.6, 135.8, 128.5, 128.3, 128.1, 66.4, 46.3.

The characterization data corresponded to the reported values.[5]

Ethyl 2-diazoacetate (1d)

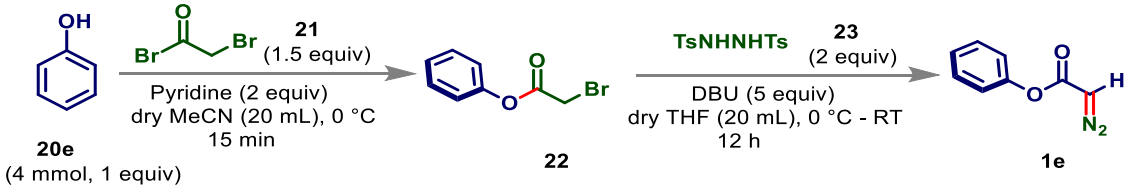


Following a slightly modified procedure,[1] ethyl glycinate hydrochloride (**20d**) (1.74 g, 12.5 mmol, 1.00 equiv), distilled water (3.5 mL), and DCM (7.5 mL) were mixed, and stirred at 0 °C. Next, pre-cooled aqueous solution (3 mL) of $NaNO_2$ (865 mg, 12.5 mmol, 1.00 equiv) was added to the reaction mixture and stirred for 30 min. Subsequently, 5 % H_2SO_4 solution (0.7 mL) was added dropwise over a period of 15 min. After stirring for further 15 min, the reaction mixture was quenched with 5% aqueous $NaHCO_3$ solution (30 mL) and extracted with diethyl ether (3 × 25 mL). The organic layers were combined, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure (upto 350 mbar) at 25 ºC water bath temperature to afford ethyl 2-diazoacetate (**1d**) (1.2 g, 11 mmol, 84%) as a yellow oil.

- **TLC:** R_f = 0.45 (EtOAc:petroleum ether, 1:25, v/v), $KMnO_4$
- **^{1}H NMR (400 MHz, $CDCl_3$):** δ 4.72 (br s, 1H, C*H*N_2), 4.20 (q, *J* = 7.2 Hz, 2H, OC*H*$_2$CH$_3$), 1.26 (t, *J* = 7.1 Hz, 3H, OCH$_2$C*H*$_3$).
- **^{13}C NMR (101 MHz, $CDCl_3$):** δ 166.9, 60.8, 53.4, 14.4.

The characterization data corresponded to the reported values.[1]

Phenyl 2-diazoacetate (1e)



Step 1: Following a slightly modified procedure,[6] to a solution of phenol **20e** (377 mg, 4.00 mmol, 1.00 equiv) and pyridine (0.65 mL, 8.0 mmol, 2.0 equiv) in anhydrous acetonitrile (20 mL) at 0°C, bromoacetyl bromide (**21**) (0.52 ml, 6.0 mmol, 1.5 equiv) was added dropwise over 10 min. After stirring for further 15 min, the reaction mixture was quenched with water (12 mL) and extracted with DCM (3 × 15 mL). The organic layers were combined, washed with brine solution (15 mL),

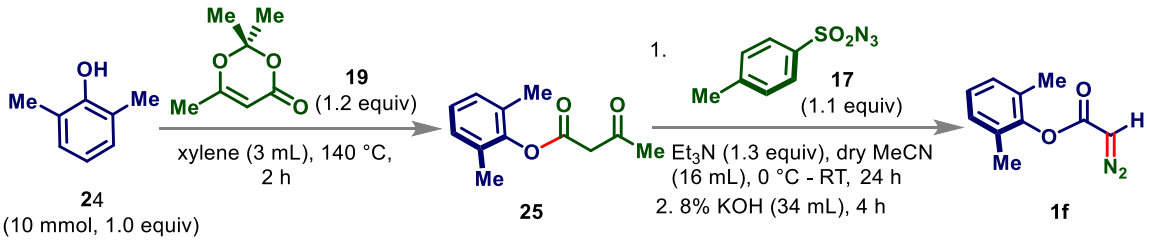
dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The crude product was subjected to the next step without further purification.

Step 2: Following a slightly modified procedure,[6] to a solution of phenyl 2-bromoacetate (**22**) in anhydrous THF (20 mL), *N*,*N*′-ditosylhydrazine (**23**) (2.72 g, 8.00 mmol, 2.00 equiv) was added. Next, 1,8-diazabicycloundec-7-ene (DBU) (3.0 mL, 20 mmol, 5.0 equiv) was added dropwise over 20 min at 0 °C. After 12 h, the reaction mixture was quenched by saturated aqueous Na_2CO_3 solution (30 mL) and extracted with diethyl ether (3 × 20 mL). The organic layers were combined, washed with brine solution (40 mL), dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The crude product was purified by chromatography using 1:40 EtOAc:petroleum ether as mobile phase to afford phenyl 2-diazoacetate (**1e**) as a yellow oil (474 mg, 2.92 mmol, 73%).

- **TLC:** R_f = 0.31 (EtOAc:petroleum ether, 1:20 v/v), $KMnO_4$
- **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.42 – 7.33 (m, 2H, Ar*H*), 7.28 – 7.20 (m, 1H, Ar*H*), 7.17 – 7.09 (m, 2H, Ar*H*), 4.97 (br s, 1H, C*H*N_2).
- **^{13}C NMR (101 MHz, $CDCl_3$):** δ 165.3, 150.4, 129.4, 125.8, 121.6, 46.7.

The characterization data corresponded to the reported values.[6]

2,6-Dimethylphenyl 2-diazoacetate (1f)



Step 1: Following a slightly modified procedure,[6] 2,6-dimethylphenol (**24**) (1.22 g, 10.0 mmol, 1.00 equiv), 2,2,6-trimethyl-4*H*-1,3-dioxin-4-one (**19**) (1.84 g, 13.0 mmol, 1.20 equiv), and xylene (3 mL) were mixed and stirred at 140 °C for 2 h. After cooling to room temperature, xylene was evaporated and the residue was purified by column chromatography using 1:50 EtOAc:petroleum ether as mobile phase to afford 2,6-dimethylphenyl 3-oxobutanoate (**25**) (1.5 g, 7.3 mmol, 73%) as a white solid.

- **TLC:** R_f = 0.38 (EtOAc:petroleum ether, 1:10 v/v), $KMnO_4$

- **^{1}H NMR (400 MHz, $CDCl_3$):** δ 11.98 (s, 0.18H, O*H* of enol form), 7.07 (s, 3H, Ar*H* of keto and enol form), 5.29 (d, *J* = 1.2 Hz, 0.18H, vinylic *H* of enol form), 3.75 (s, 1.76 H, CH_3COCH_2 of keto form), 2.38 (s, *J* = 1.1 Hz, 2.32H, CH_3 of keto form), 2.18 (s, 4.94H, 2 × $ArCH_3$ of keto form), 2.16 (s, 1.06H, 2 × $ArCH_3$ of enol form), 2.05 (s, 0.68H, CH_3 of enol form).
- **^{13}C NMR (101 MHz, $CDCl_3$) (Enol form):** δ 177.5, 170.3, 147.3, 129.9, 128.1, 125.5, 88.2, 20.8, 15.8.
- **^{13}C NMR (101 MHz, $CDCl_3$) (Keto form):** δ 199.6, 164.5, 147.6, 129.7, 128.2, 125.7, 48.8, 29.8, 15.9.

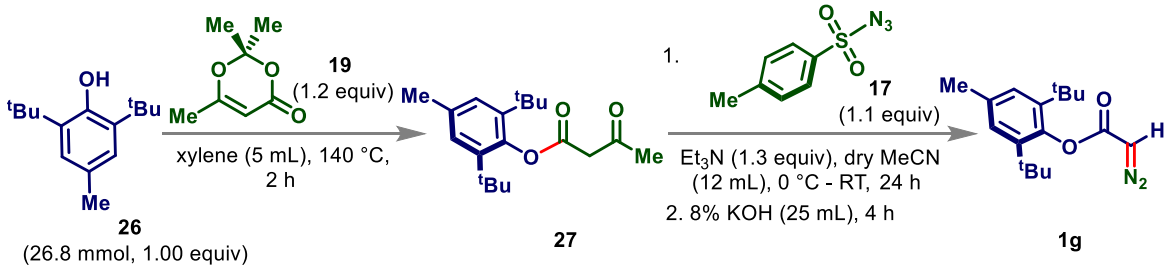
The characterization data corresponded to the reported values.[6]

Step 2: Following a slightly modified procedure,[6] to a solution of 2,6-dimethylphenyl 3-oxobutanoate (**25**) (1.38 g, 6.70 mmol, 1.00 equiv) in anhydrous acetonitrile (8 mL), triethylamine (1.2 mL, 8.7 mmol, 1.3 equiv) was added. Next, the reaction mixture was cooled to 0 ºC, a solution of tosyl azide **17** (1.45 g, 7.36 mmol, 1.10 equiv) in anhydrous acetonitrile (8 mL) was added dropwise, and the reaction mixture was allowed to warm to room temperature. After 24 h, 8% aqueous KOH solution (34 mL) was added to the reaction mixture and stirred. After 4 h, reaction mixture was extracted with diethyl ether (3 × 30 mL). The organic layers were combined, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The crude product was purified by column chromatography using 1:50 EtOAc:petroleum ether as mobile phase to afford 2,6-dimethylphenyl 2-diazoacetate (**1f**) (1.11 g, 6.70 mmol, 87%) as a pale yellow solid.

- **TLC:** R_f = 0.37 (EtOAc:petroleum ether, 1:20 v/v), $KMnO_4$
- **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.07 (s, 3H, Ar*H*), 5.02 (s, 1H, CHN_2), 2.21 (s, 6H, 2 × $ArCH_3$).
- **^{13}C NMR (101 MHz, $CDCl_3$):** δ 164.5, 147.8, 130.5, 128.5, 125.9, 46.2, 16.2.

The characterization data corresponded to the reported values.[6]

2,6-Di-*tert*-butyl-4-methylphenyl 2-diazoacetate (1g)



Step 1: Following a slightly modified procedure,[2] 2,6-di-*tert*-butyl-4-methylphenol (**26**) (5.90 g, 26.8 mmol, 1.00 equiv), 2,2,6-trimethyl-4*H*-1,3-dioxin-4-one (**19**) (4.57 g, 32.1 mmol, 1.20 equiv), and xylene (5 mL) were mixed and stirred at 140 °C for 2 h. After cooling to room temperature, xylene was evaporated and the residue was purified by column chromatography using 1:50 EtOAc:petroleum ether as eluent to afford 2,6-di-*tert*-butyl-4-methylphenyl 3-oxobutanoate (**27**) as a white solid (7.5 g, 25 mmol, 93%).

- **TLC:** R_f = 0.36 (EtOAc:petroleum ether, 1:50 v/v), $KMnO_4$
- **^{1}H NMR (400 MHz, $CDCl_3$):** δ 12.14 (s, 0.55H, O*H* of enol form), 7.12 (s, 2H, Ar*H* of keto and enol form), 5.32 (s, 0.55H, vinylic *H* of enol form), 3.72 (s, 0.9H, CH_3COCH_2 of keto form), 2.39 (s, 1.37H, CH_3COCH_2 of keto form), 2.32 (s, 3H, $ArCH_3$ of keto and enol form), 2.06 (s, 1.63H, CH_3 of enol form), 1.33 (s, 8.1H, $C(CH_3)_3$ of keto form), 1.32 (s, 9.9H, $C(CH_3)_3$ of enol form).
- **^{13}C NMR (101 MHz, $CDCl_3$) (Enol form):** δ 177.4, 173.3, 144.9, 142.2, 134.6, 126.9, 90.4, 35.2, 31.4, 21.5. One carbon of enol form was not resolved in 101 MHz.
- **^{13}C NMR (101 MHz, $CDCl_3$) (Keto form)**: δ 200.2, 167.7, 145.3, 141.8, 135.0, 127.2, 50.7, 35.2, 31.4, 30.8, 21.5.

The characterization data corresponded to the reported values.[2]

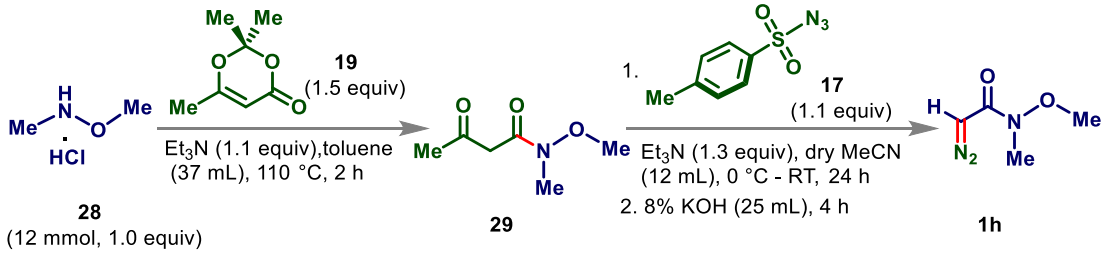
Step 2: Following a slightly modified procedure,[2] to a solution of 2,6-di-*tert*-butyl-4-methylphenyl 3- oxobutanoate (**27**) (1.52 g, 5.00 mmol, 1.00 equiv) in anhydrous acetonitrile (6 mL), triethylamine (0.90 ml, 6.5 mmol, 1.3 equiv) was added. Next, the reaction mixture was cooled to 0 ºC, and a solution of tosyl azide **17** (1.1 g, 5.5 mmol, 1.1 equiv) in anhydrous acetonitrile (6 mL) was added slowly, and the reaction mixture was allowed to warm to room temperature and stirred. After 24 h, 8% aqueous KOH solution (25 mL) was added to that reaction mixture and stirred for further 4 h. Next, the reaction mixture was extracted with diethyl ether (3 × 30 mL). The organic

layers were combined, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The crude product was purified by column chromatography using 1:50 EtOAc:petroleum ether as eluent to afford 2,6-di-*tert*-butyl-4-methylphenyl 2-diazoacetate (**1g**) as a yellow solid (1.20 g, 4.16 mmol, 83%).

- **TLC:** R_f = 0.44 (EtOAc:petroleum ether, 1:50 v/v), $KMnO_4$
- **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.11 (s, 2H, Ar*H*), 5.00 (br s, 1H, C*H*N_2), 2.31 (d, *J* = 2.2 Hz, 3H, ArC*H*$_3$), 1.35 (s, 18H, 2 × C(C*H*$_3$)$_3$).
- **^{13}C NMR (101 MHz, $CDCl_3$):** δ 166.3, 145.1, 142.5, 134.8, 127.1, 47.3, 35.3, 31.5, 21.5.

The characterization data corresponded to the reported values.[2]

2-Diazo-*N*-methoxy-*N*-methylacetamide (1h)



Step 1: Following a reported procedure,[2] *N*,*O*-dimethylhydroxylamine hydrochloride (**28**) (1.17 g, 12.0 mmol, 1.00 equiv), 2,2,6-trimethyl-4*H*-1,3-dioxin-4-one (**19**) (2.56 g, 18.0 mmol, 1.50 equiv), triethylamine (1.90 mL, 13.2 mmol, 1.10 equiv), and toluene (37 mL) were mixed and refluxed for 2 h. Next, the reaction mixture was quenched with aqueous HCl solution (45 mL, 1.0 M), and extracted with ethyl acetate (3 × 50 mL). The organic layers were combined, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The crude product was purified by column chromatography using 1:1 EtOAc:petroleum ether as mobile phase to afford *N*-methoxy-*N*-methyl-3-oxobutanamide (**29)** as a yellow oil (1.1 g, 7.6 mmol, 63%).

- **TLC:** R_f = 0.25 (EtOAc:petroleum ether, 1:1 v/v), $KMnO_4$
- **^{1}H NMR (400 MHz, $CDCl_3$):** δ 13.72 (s, 0.16H, O*H* of enol form), 5.39 (s, 0.16H vinylic H of enol form), 3.66 (s, 3H, OC*H*$_3$), 3.57 (s, 1.65H, CH_3COCH_2 of keto form), 3.20 (s, 2.5H, NC*H*$_3$ of keto form), 3.18 (s, 0.5H, NC*H*$_3$ of enol form), 2.24 (s, 2.5H, C*H*$_3$COCH$_2$ of keto form), 1.96 (s, 0.5H, C*H*$_3$ of enol form).
- **^{13}C NMR (101 MHz, $CDCl_3$) (Keto form):** δ 201.7, 167.8, 61.1, 48.3, 31.8, 30.0.

- **^{13}C NMR (101 MHz, $CDCl_3$) (Enol form):** δ 175.0, 172.2, 86.5, 21.6. Two carbons were not resolved at 101 MHz.

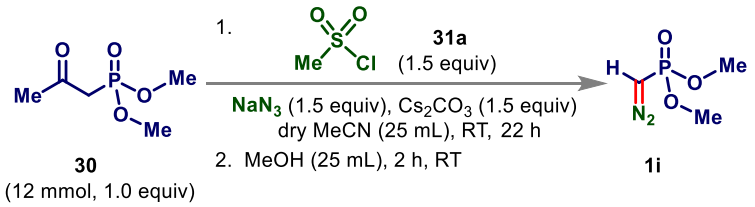
The characterization data corresponded to the reported values.[2]

Step 2: Following a slightly modified procedure,[2] to a solution of *N*-methoxy-*N*-methyl-3-oxobutanamide (**29**) (730 mg, 5.00 mmol, 1.00 equiv) in anhydrous acetonitrile (6 mL) triethylamine (0.91 mL, 6.5 mmol, 1.3 equiv) was added at 0 ºC. Next, a solution of tosyl azide **17** (1.1 g, 5.5 mmol, 1.1 equiv) in anhydrous acetonitrile (6 mL) was added dropwise, and the reaction mixture was allowed to warm to room temperature. After 20 h, 8% aqueous KOH solution (25mL) was added and stirred. After 4 h, water (15 mL) was added, and the reaction mixture was extracted with diethyl ether (3 × 30 mL). The organic layers were combined, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The crude product was purified by column chromatography using 1:1 EtOAc:Petroleum ether as mobile phase to afford 2-diazo-*N*-methoxy-*N*-methylacetamide (**1h**) as a yellow liquid (403 mg, 3.12 mmol, 62%).

- **TLC:** R_f = 0.31 (EtOAc:Petroleum ether, 1:1 v/v), $KMnO_4$
- **^{1}H NMR (400 MHz, $CDCl_3$):** δ 5.32 (s, 1H, C*H*N_2), 3.66 (s, 3H, OC*H*$_3$), 3.18 (s, 3H, NC*H*$_3$).
- **^{13}C NMR (101 MHz, $CDCl_3$):** δ 168.3, 61.4, 46.3, 33.3.

The characterization data corresponded to the reported values.[2]

Dimethyl (diazomethyl)phosphonate (1i):



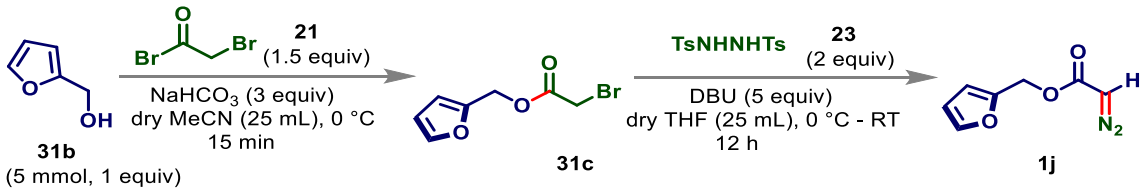
Following a slightly modified procedure,[7] to a solution of NaN_3 (1.17 g, 18.0 mmol, 1.50 equiv) in anhydrous acetonitrile (25 mL), methanesulfonylchloride (**31**) (1.4 mL, 18 mmol, 1.5 equiv) was added dropwise over 15 min at room temperature, and stirred for 1 h. Next, dimethyl-(2-oxopropyl)-phosphonate (**30**) (1.66 mL, 12.0 mmol, 1.00 equiv.) was added dropwise and stirred. After 6 h, Cs_2CO_3 (5.86 g, 18.0 mmol, 1.50 equiv) was added portion-wise to the reaction mixture and stirred for 15 h. Next, MeOH (25 mL) was added to the reaction mixture and stirred. After 2 h, the reaction mixture was quenched by saturated aqueous NH_4Cl solution (20 mL) and extracted

with diethyl ether (3 × 25 mL). The organic layers were combined, washed with brine solution (50 mL), dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The crude product was purified by chromatography using 1:10 EtOAc:petroleum ether mixture as eluent to give the dimethyl (diazomethyl)phosphonate (**1i**) as a yellow oil (1.2 g, 8.0 mmol, 67%).

- **TLC:** R_f = 0.35 (EtOAc:petroleum ether, 1:10 v/v), $KMnO_4$
- **^{1}H NMR (400 MHz, $CDCl_3$):** δ 3.80 (s, 3H, POC*H*$_3$), 3.78 (d, J = 10.8 Hz, 1H, C*H*N_2), 3.77 (s, 3H, POC*H*$_3$)**.**
- **^{13}C NMR (101 MHz, $CDCl_3$):** δ 52.4 (q, *J* = 5.5, 4.6 Hz), 27.9 (d, *J* = 231.8 Hz).
- **^{31}P NMR (162 MHz, $CDCl_3$):** δ 22.44

The characterization data corresponded to the reported values.[8]

Furan-2-ylmethyl 2-diazoacetate (1j)



Step 1: Following a slightly modified procedure,[6] to a solution of furan-2-ylmethanol (**31b**) (491 mg, 5.00 mmol, 1.00 equiv) and $NaHCO_3$ (1.26 g, 15.0 mmol, 3.00 equiv) in anhydrous acetonitrile (25 mL) at 0°C, bromoacetyl bromide (**21**) (0.65 ml, 7.5 mmol, 1.5 equiv) was added dropwise over 10 min. After stirring for further 15 min, the reaction mixture was quenched with water (15 mL) and extracted with DCM (3 × 20 mL). The organic layers were combined, washed with brine solution (20 mL), dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The crude product was subjected to the next step without further purification.

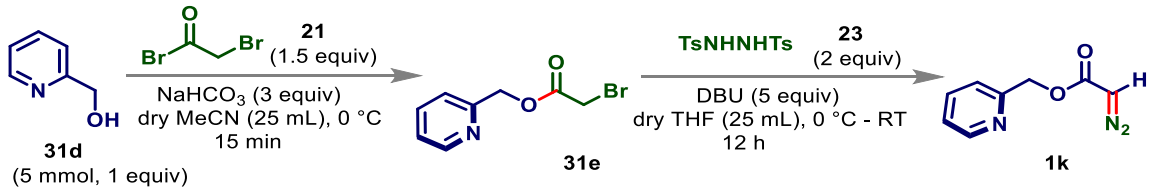
Step 2: Following a slightly modified procedure,[6] to a solution of furan-2-ylmethyl 2-bromoacetate (**31c**) in anhydrous THF (25 mL), *N*,*N*′-ditosylhydrazine (**23**) (3.4 g, 10 mmol, 2.0 equiv) was added. Next, 1,8-diazabicycloundec-7-ene (DBU) (3.7 mL, 25 mmol, 5.0 equiv) was added dropwise over 20 min at 0 °C. After 12 h, the reaction mixture was quenched by saturated aqueous Na_2CO_3 solution (30 mL) and extracted with diethyl ether (3 × 25 mL). The organic layers were combined, washed with brine solution (45 mL), dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The crude product was purified by chromatography using 1:50

EtOAc:petroleum ether as mobile phase to afford furan-2-ylmethyl 2-diazoacetate (**1j**) as a yellow oil (650 mg, 3.91 mmol, 78%).

- **TLC:** R_f = 0.32 (EtOAc:petroleum ether, 1:20 v/v), $KMnO_4$
- **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.42 (dd, *J* = 1.9, 0.9 Hz, 1H, Ar*H*), 6.42 (dd, *J* = 3.3, 0.8 Hz, 1H, Ar*H*), 6.36 (dd, *J* = 3.3, 1.8 Hz, 1H, Ar*H*), 5.14 (s, 2H, CH_2O), 4.78 (br s, 1H, CN_2H).
- **^{13}C NMR (101 MHz, $CDCl_3$):** δ 166.6, 149.5, 143.5, 111.0, 110.7, 58.3, 46.5.

The characterization data corresponded to the reported values.[6]

Pyridin-2-ylmethyl 2-diazoacetate (1k)



Step 1: Following a slightly modified procedure,[9] to a solution of pyridin-2-ylmethanol (**31d**) (546 mg, 5.00 mmol, 1.00 equiv) and $NaHCO_3$ (1.26 g, 15.0 mmol, 3.00 equiv) in anhydrous acetonitrile (25 mL) at 0°C, bromoacetyl bromide (**21**) (0.65 ml, 7.5 mmol, 1.5 equiv) was added dropwise over 10 min. After stirring for further 15 min, the reaction mixture was quenched with water (15 mL), and extracted with DCM (3 × 20 mL). The organic layers were combined, washed with brine solution (20 mL), dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The crude product was subjected to the next step without further purification.

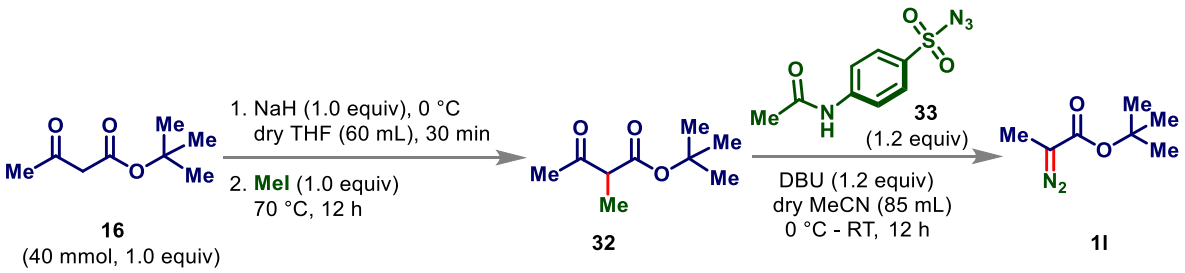
Step 2: Following a slightly modified procedure,[9] to a solution of pyridin-2-ylmethyl 2-bromoacetate (**31c**) in anhydrous THF (25 mL), *N*,*N*′-ditosylhydrazine (**23**) (3.4 g, 10 mmol, 2.0 equiv) was added. Next, 1,8-diazabicycloundec-7-ene (DBU) (3.7 mL, 25 mmol, 5.0 equiv) was added dropwise over 20 min at 0 °C. After 12 h, the reaction mixture was quenched by saturated aqueous Na_2CO_3 solution (30 mL) and extracted with diethyl ether (3 × 25 mL). The organic layers were combined, washed with brine solution (45 mL), dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The crude product was purified by chromatography using 1:5 EtOAc:petroleum ether as mobile phase to afford pyridin-2-ylmethyl 2-diazoacetate (**1k**) as a yellow oil (566 mg, 3.19 mmol, 64%).

- **TLC:** R_f = 0.17 (EtOAc:petroleum ether, 1:5 v/v), $KMnO_4$

- **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.58 (d, *J* = 4.9 Hz, 1H, Ar*H*), 7.69 (t, *J* = 7.7 Hz, 1H, Ar*H*), 7.33 (d, *J* = 7.8 Hz, 1H, Ar*H*), 7.22 (t, *J* = 8.0 Hz, 1H, Ar*H*), 5.30 (s, 2H, CH_2Ar), 4.87 (br s, 1H, CN_2H).
- **^{13}C NMR (101 MHz, $CDCl_3$):** δ 155.7, 149.47, 136.8, 122.9, 121.7, 66.9. Two carbons were not resolved at 101 MHz.

The characterization data corresponded to the reported values.[9]

***Tert*-butyl 2-diazopropanoate (1l)**



Step 1: Following a slightly modified procedure,[10] to a solution of NaH (1.6 g, 40 mmol, 1.0 equiv, 60% dispersion in mineral oil) in 60 ml anhydrous THF at 0 ºC, *tert*-butyl acetoacetate (**16**) (6.6 ml, 40 mmol, 1.0 equiv) was added dropwise and the solution was stirred for 30 min. Next, the reaction mixture was warmed to room temperature, methyl iodide (2.5 mL, 40 mmol, 1.0 equiv) was added, and refluxed at 70 ºC. After 12 h, the reaction mixture was quenched with saturated aqueous NH_4Cl solution (30 ml), extracted with dichloromethane (3 × 30 ml). The organic layers were combined, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The crude product was purified by column chromatography using 1:50 EtOAc:petroleum ether as mobile phase to give *tert*-butyl 2-methyl-3-oxobutanoate (**32**) as a colorless liquid (5.2 g, 30 mmol, 75%).

- **TLC:** R_f = 0.41 (EtOAc:petroleum ether, 1:20 v/v), $KMnO_4$
- **^{1}H NMR (400 MHz, $CDCl_3$):** δ 3.40 (q, *J* = 7.1 Hz, 1H, OCOC*H*(Me)CO), 2.23 (s, 3H, COCH_3), 1.46 (s, 9H, OC(CH_3)$_3$), 1.30 (d, *J* = 4.3 Hz, 3H, COCH(CH_3)CO).
- **^{13}C NMR (101 MHz, $CDCl_3$):** δ 204.0, 169.7, 81.8, 54.7, 28.3, 27.9, 12.6.

The characterization data corresponded to the reported values.[11]

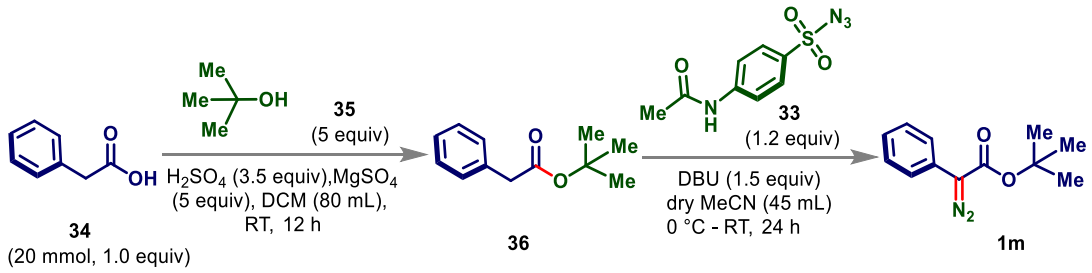
Step 2: Following a slightly modified procedure,[10] *tert*-butyl 2-methyl-3-oxobutanoate (**32**) (4.82 g, 28.0 mmol, 1.00 equiv), 4-acetamidobenzenesulfonyl azide (**33**) (8.10 g, 33.6 mmol, 1.20 equiv), and anhydrous MeCN (85 ml) were mixed and stirred at 0 ºC. Next, DBU (6.30 mL, 42.2 mmol, 1.20 equiv) was added dropwise. After 12 h stirring at room temperature, the reaction

mixture was quenched with saturated aqueous NH_4Cl solution (30 ml) and extracted with hexanes (3 × 30 ml). The organic layers were combined, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The crude product was isolated by column chromatography using petroleum ether as eluent to afford *tert*-butyl 2-diazopropanoate (**1l**) (2.9 g, 28 mmol, 66%) as a yellow liquid.

- **TLC:** R_f = 0.53 (EtOAc:petroleum ether, 1:20 v/v), $KMnO_4$
- **^{1}H NMR (400 MHz, $CDCl_3$):** δ 1.91 (s, 3H, CH_3CN_2), 1.47 (s, 9H, $OC(CH_3)_3$).
- **^{13}C NMR (101 MHz, $CDCl_3$):** δ 167.3, 80.9, 28.3, 14.1. One carbon was not resolved at 101 MHz.

The characterization data corresponded to the reported values.[11]

***Tert*-butyl 2-diazo-2-phenylacetate (1m)**



Step 1: Following a slightly modified procedure,[12] $MgSO_4$ (12.0 g, 100 mmol, 5.00 equiv), concentrated H_2SO_4 (3.6 mL, 70 mmol, 3.5 equiv), and dichloromethane (80 mL) were mixed and stirred at room temperature. Next, phenylacetic acid **34** (2.72 g, 20.0 mmol, 1.00 equiv) and *tert*-butanol (**35**) (9.56 mL, 100 mmol, 5.00 equiv) were added to the reaction mixture. After 12 h, the reaction mixture was quenched with aqueous saturated $NaHCO_3$ (40 ml) solution, extracted with dichloromethane (3 × 30 ml), washed with brine solution (30 mL), dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The crude product was purified by column chromatography using 1:50 EtOAc:petroleum ether as eluent to afford *tert*-butyl phenylacetate (**36**) as clear colorless liquid (3.10 g, 16.2 mmol, 81%).

- **TLC: R_f** = 0.47 (EtOAc:petroleum ether, 1:20 v/v), $KMnO_4$
- **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.35 – 7.21 (m, 5H, Ar*H*), 3.52 (s, 2H, $ArCH_2$), 1.44 (s, 9H, $OC(CH_3)_3$).

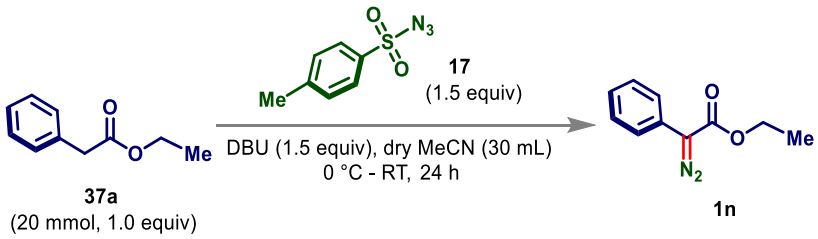
The characterization data corresponded to the reported values.[13]

Step 2: Following a slightly modified procedure,[14] to a solution of *tert*-butyl phenylacetate (**36**) (3.00 g, 15.6 mmol, 1.00 equiv) in anhydrous acetonitrile (45 ml) 4-acetamidobenzenesulfonyl azide (**33)** (4.50 g, 18.7 mmol, 1.20 equiv) was added and stirred. Next, DBU (3.50 mL, 23.4 mmol, 1.50 equiv) was added to the reaction mixture dropwise at 0 ºC. After 24 h, the reaction mixture was quenched with saturated aqueous NH_4Cl (15 ml) solution, extracted with hexanes (3 × 30 ml), and dried over anhydrous Na_2SO_4. The organic layers were combined and concentrated under reduced pressure. The crude product was purified by column chromatography using 1:50 EtOAc:petroleum ether mixture as eluent to give *tert*-butyl 2-diazo-2-phenylacetate (**1m**) as an orange-yellow liquid (2.93 g, 13.4 mmol, 86%).

- **TLC:** R_f = 0.69 (EtOAc:petroleum ether, 1:20, v/v), $KMnO_4$
- **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.47 (d, *J* = 8.8 Hz, 2H, Ar*H*), 7.37 (t, *J* = 7.8 Hz, 2H, Ar*H*), 7.16 (t, *J* = 7.4 Hz, 1H, Ar*H*), 1.55 (s, 9H, OC(C*H*$_3$)$_3$).
- **^{13}C NMR (101 MHz, $CDCl_3$):** δ 164.4, 128.7, 126.0, 125.4, 123.9, 81.8, 63.6, 28.3.

The characterization data corresponded to the reported values.[14]

Ethyl 2-diazo-2-phenylacetate (1n)



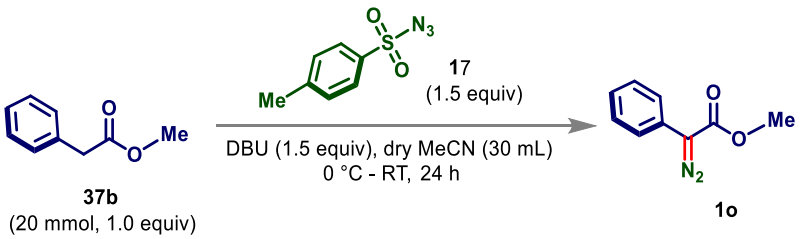
Following a slightly modified procedure,[15] ethyl 2-phenylacetate (**37a**) (3.28 g, 20.0 mmol, 1.00 equiv), tosyl azide **17** (5.92 g, 30.0 mmol, 1.50 equiv), and anhydrous acetonitrile (30 mL) were mixed and stirred. Next, DBU (4.5 mL, 30 mmol, 1.5 equiv) was added dropwise to the reaction mixture at 0 ºC. Next, the reaction mixture was allowed to warm to room temperature and stirred. After 24 h, reaction mixture was quenched with saturated aqueous NH_4Cl (15 mL) solution, extracted with dichloromethane (3 × 30 mL). The organic layers were combined, washed with brine solution (20 mL), dried over Na_2SO_4, and concentrated under reduced pressure. The crude product was purified by chromatography using 1:50 EtOAc:petroleum ether mixture as eluent to afford the ethyl 2-diazo-2-phenylacetate (**1n**) as an orange-yellow oil (3.17 g, 16.7 mmol, 83%).

- **TLC:** R_f = 0.62 (EtOAc:petroleum ether, 1:20 v/v), $KMnO_4$

- **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.52 – 7.46 (m, 2H, Ar*H*), 7.38 (t, *J* = 7.4 Hz, 2H, Ar*H*), 7.18 (t, *J* = 7.6Hz, 1H, Ar*H*), 4.34 (q, *J* = 7.1 Hz, 2H, OCH_2CH_3), 1.34 (t, *J* = 7.1 Hz, 3H, OCH_2CH_3).
- **^{13}C NMR (101 MHz, $CDCl_3$):** δ 165.2, 128.9, 125.7, 125.6, 124.0, 63.4, 61.0, 14.5.

The characterization data corresponded to the reported values.[15]

Methyl 2-diazo-2-phenylacetate (1o)

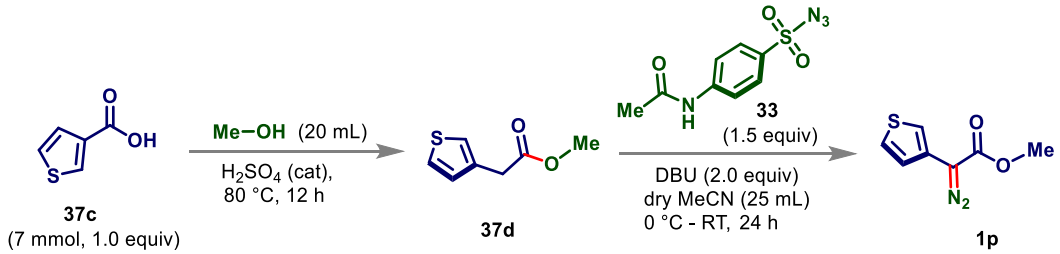


Following a slightly modified procedure,[15] methyl 2-phenylacetate (**37b**) (3.0 g, 20 mmol, 1.0 equiv), tosyl azide **17** (5.92 g, 30.0 mmol, 1.50 equiv), and anhydrous acetonitrile (30 mL) were mixed and stirred. Next, DBU (4.5 mL, 30 mmol, 1.5 equiv) was added dropwise to the reaction mixture at 0 ºC. Next, the reaction mixture was allowed to warm to room temperature and stirred. After 24 h, reaction mixture was quenched with saturated aqueous NH_4Cl (15 mL) solution, extracted with dichloromethane (3 × 30 mL). The organic layers were combined, washed with brine solution (20 mL), dried over Na_2SO_4, and concentrated under reduced pressure. The crude product was purified by chromatography using 1:50 EtOAc:petroleum ether mixture as eluent to afford the methyl 2-diazo-2-phenylacetate (**1o**) as an orange-yellow oil (3.25 g, 18.4 mmol, 92%).

- **TLC:** R_f = 0.55 (EtOAc:petroleum ether, 1:20 v/v), $KMnO_4$
- **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.49 (d, *J* = 8.0 Hz, 2H, Ar*H*), 7.39 (t, *J* = 7.6 Hz, 2H, Ar*H*), 7.19 (t, *J* = 7.4, 1H, Ar*H*), 3.87 (s, 3H, OCH_3).
- **^{13}C NMR (101 MHz, $CDCl_3$):** δ 165.6, 128.9, 125.8, 125.4, 124.0, 51.9. One carbon was not resolved at 101 MHz.

The characterization data corresponded to the reported values.[15]

Methyl 2-diazo-2-(thiophen-3-yl)acetate (1p)



Step 1: Following a slightly modified procedure,[12] a 50 mL round bottom flask was charged with 2-(thiophen-3-yl)acetic acid (**37c**) (1.0 g, 7.0 mmol, 1.0 equiv), methanol (20 mL) and cooled down to 0 °C. Next, 2 drops of concentrated H_2SO_4 were added to the resulting mixture in the ice-cold condition and stirrred for 12h at 80 °C. After completion, the reaction mixture was quenched with water (20 mL), extracted with ethyl acetate (3×30 mL). The organic layers combined, washed with saturated $NaHCO_3$ solution (20 mL), followed by brine solution (20 mL), and dried over anhydrous Na_2SO_4. The collected organic part was concentrated under reduced pressure to obtain compound **37d** as a colorless oil (1.1 g, 6.8 mmol, 96%).

- **TLC: R_f** = 0.47 (EtOAc:petroleum ether, 1:9 v/v), $KMnO_4$
- **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.38 – 7.27 (m, 1H, Ar*H*), 7.15 (d, *J* = 3.0 Hz, 1H, Ar*H*), 7.04 (dd, *J* = 5.0 Hz, 1H, Ar*H*), 3.71 (s, 3H, CO_2CH_3), 3.67 (s, 2H, $ArCH_2$).
- **^{13}C NMR (101 MHz, $CDCl_3$):** δ 171.6, 133.5, 128.4, 125.7, 122.9, 52.0, 35.6.

The characterization data corresponded to the reported values.[16]

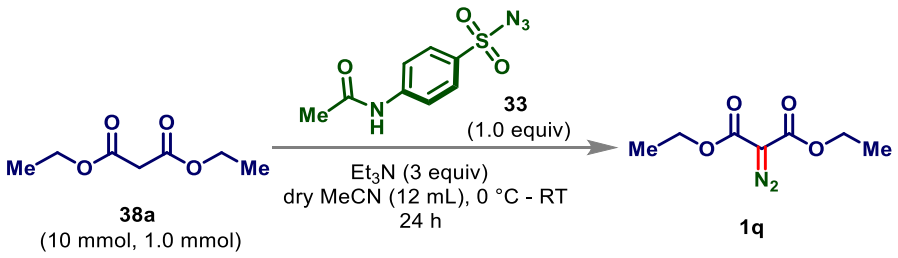
Step 2: Following a slightly modified procedure,[14] methyl 2-(thiophen-3-yl)acetate (**37d**) (1.1 g, 6.8 mmol, 1.0 equiv), *p*-ABSA **33** (2.45 g, 10.2 mmol, 1.50 equiv) and MeCN (25 mL) were added to 50 mL round bottom flask under argon atmosphere. The reaction mixture was cooled down to 0°C in an ice bath and DBU (2.00 mL, 13.6 mmol, 2.00 equiv) was added dropwise. Next, the reaction mixture was allowed to room temperature and stirred. After 12 h, the reaction mixture was quenched with saturated aqueous NH_4Cl (25 mL) solution, extracted with diethyl ether (3 x 40 mL). The organic layers were combined and washed with brine solution (40 mL), dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography using 1:20 v/v EtOAc:petroleum ether as mobile phase to obtain the desired product **1p** as a red liquid (1.1 g, 6.0 mmol 88%).

- **TLC:** R_f = 0.49 (EtOAc:petroleum ether, 1:20, v/v), $KMnO_4$

- **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.44 – 7.35 (m, 2H, Ar*H*), 7.03 (dd, *J* = 5.0, 1.5 Hz, 1H, Ar*H*), 3.87 (s, 3H, CO_2CH_3).
- **^{13}C NMR (101 MHz, $CDCl_3$):** δ 165.9, 126.4, 123.8, 123.4, 117.6, 52.1. One carbon was not resolved at 101 MHz.

The characterization data corresponded to the reported values.[17]

Diethyl 2-diazomalonate (1q):

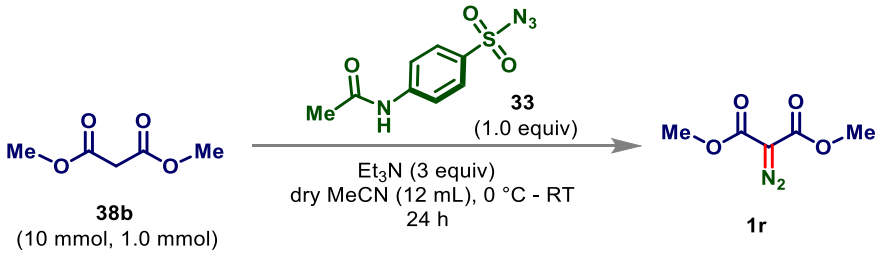


Following a slightly modified procedure,[18] to a solution of diethyl malonate (**38a**) (1.53 mL, 10.0 mmol, 1.00 equiv), and 4- acetamidobenzenesulfonyl azide (**33)** (2.4 g, 10 mmol, 1.0 equiv), in anhydrous acetonitrile (12 mL), Et_3N (4.2 mL, 30 mmol, 3.0 equiv) was added dropwise at 0 ºC over a period of 10 min, and the reaction mixture was allowed to warm to room temperature and stirred. After 24 h, the reaction mixture was quenched with water (25 mL), extracted with diethyl ether (25 mL × 3). The organic layers were combined, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The crude product was purified by column chromatography using 1:10 EtOAc:petroleum ether mixture as mobile phase afforded diethyl 2-diazomalonate (**1q**) (1.57 g, 8.43 mmol, 84%) as a yellow oily liquid.

- **TLC:** R_f = 0.49 (EtOAc:petroleum ether, 1:10 v/v), $KMnO_4$
- **^{1}H NMR (400 MHz, $CDCl_3$):** δ 4.23 (q, *J* = 7.1, 0.9 Hz, 4H, 2 × OCH_2CH_3), 1.25 (t, *J* = 7.2, 0.9 Hz, 6H, 2 × OCH_2CH_3).
- **^{13}C NMR (101 MHz, $CDCl_3$):** δ 160.9, 61.5, 14.2. One carbon was not resolved at 101 MHz.

The characterization data corresponded to the reported values.[18]

Dimethyl 2-diazomalonate (1r):

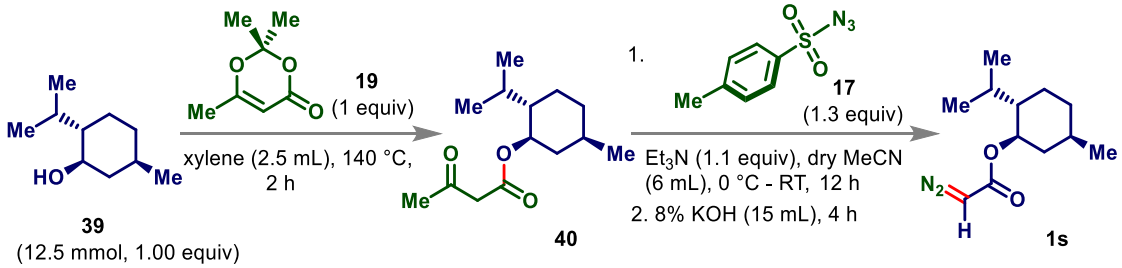


Following a slightly modified procedure,[18] to a solution of dimethyl malonate (**38b**) (1.32 g, 10.0 mmol, 1.00 equiv), and 4- acetamidobenzenesulfonyl azide (**33)** (2.4 g, 10 mmol, 1.0 equiv), in anhydrous acetonitrile (12 mL), Et_3N (4.2 mL, 30 mmol, 3.0 equiv) was added dropwise at 0 ºC over a period of 10 min, and the reaction mixture was allowed to warm to room temperature and stirred. After 24 h, the reaction mixture was quenched with water (25 mL), extracted with diethyl ether (3 × 25 mL). The organic layers were combined, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The crude product was purified by column chromatography using 1:10 EtOAc:petroleum ether mixture as mobile phase afforded dimethyl 2-diazomalonate (**1r**) (1.39 g, 8.79 mmol, 88%) as a pale-yellow liquid.

- **TLC:** R_f = 0.42 (EtOAc:petroleum ether, 1:10 v/v), $KMnO_4$.
- **^{1}H NMR (400 MHz, $CDCl_3$):** δ 3.83 (s, 6H, 2 × OC*H*$_3$).
- **^{13}C NMR (101 MHz, $CDCl_3$):** δ 161.2, 52.3.

The characterization data corresponded to the reported values.[18]

(1*R*,2*S*,5*R*)-2-*Iso*propyl-5-methylcyclohexyl 2-diazoacetate (1s)



Step 1: Following a slightly modified procedure,[2] (1*R*,2*S*,5*R*)-2-*iso*propyl-5- methylcyclohexanol (**39**) (1.95 g, 12.5 mmol, 1.00 equiv), 2,2,6-trimethyl-4H-1,3-dioxin-4-one (**19)** (1.78 g, 12.5 mmol, 1.00 equiv) and xylene (2.5 mL) were mixed and stirred at 140 °C for 2 h. After cooling to room temperature, the xylene was evaporated and the residue was purified by column

chromatography, using 1:25 EtOAc:petroleum ether as eluent in to afford (1*R*,2*S*,5*R*)-2-*iso*propyl-5-methylcyclohexyl 3-oxobutanoate (**40**) as a colorless liquid (1.94 g, 8.06 mmol, 65%).

- **TLC:** R_f = 0.37 (EtOAc:petroleum ether, 1:5, v/v), $KMnO_4$
- **^{1}H NMR (400 MHz, $CDCl_3$)**: δ 12.19 (s, 0.08H, O*H* of enol form), 4.95 (s, 0.08H, vinylic H of enol), 4.73 (td, *J* = 10.9, 4.4 Hz, 1H, OC*H*), 3.43 (s, 1.84H, CH_3COCH_2 of keto form), 2.26 (s, 2.47H, CH_3COCH_2 of keto form), 2.05 – 1.96 (m, 1H), 1.94 (s, 0.22H, CH_3 of enol form), 1.91 – 1.82 (m, 1H), 1.72 – 1.60 (m, 2H), 1.42 – 1.55 (m, 1H), 1.40 – 1.30 (m, 1H), 1.11 – 0.93 (m, 2H), 0.92 – 0.80 (m, 7H), 0.76 (d, *J* = 7.0 Hz, 3H).
- **^{13}C NMR (101 MHz, $CDCl_3$) (Keto form):** δ 200.5, 166.6, 75.4, 50.4, 46.8, 40.6, 34.1, 31.3, 29.9, 26.0, 23.2, 21.9, 20.6, 16.0.
- **^{13}C NMR (101 MHz, $CDCl_3$) (Enol form):** δ 175.2, 172.2, 90.0, 73.8, 47.0, 40.9, 34.1, 26.2, 23.5, 21.9, 21.1, 20.6, 16.3. One carbon was not resolved at 101 MHz.

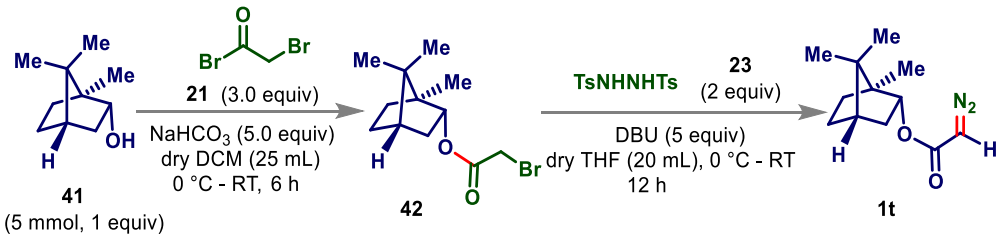
The characterization data corresponded to the reported values.[2]

Step 2: Following a slightly modified procedure,[2] to a solution of (1*R*,2*S*,5*R*)-2-*iso*propyl-5-methylcyclohexyl 3-oxobutanoate (**40**) (720 mg, 3.00 mmol, 1.00 equiv) in anhydrous acetonitrile (3 mL), triethylamine (0.46 mL, 3.3 mmol, 1.1 equiv) was added. Next, a solution of tosyl azide **17** (0.77 g, 3.90 mmol, 1.30 equiv) in anhydrous acetonitrile (3 mL) was added dropwise at 0 ºC. Next, the reaction mixture was allowed to warm to room temperature. After 12 h, the reaction mixture was treated with 8% aqueous KOH solution (15 mL) and stirred for 4 h. The resulting reaction mixture was extracted with diethyl ether (3 × 20 mL). The organic layers were combined, washed with brine solution (25 mL), dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The crude product was purified by column chromatography using 1:50 EtOAc:petroleum ether as mobile phase to afford (1*R*,2*S*,5*R*)-2-*iso*propyl-5-methylcyclohexyl 2-diazoacetate (**1s**) as a yellow solid (500 mg, 2.25 mmol, 75%).

- **TLC:** R_f = 0.25 (EtOAc:Petroleum ether, 1:20 v/v), $KMnO_4$
- **^{1}H NMR (400 MHz, $CDCl_3$):** δ 4.79 – 4.68 (m, 2H, C*H*N_2 and OC*H*), 2.10 – 1.96 (m, 1H), 1.92 – 1.79 (m, 1H), 1.73 – 1.60 (m, 2H), 1.56 – 1.42 (m, 1H), 1.40 – 1.30 (m, 1H), 1.13 – 0.93 (m, 2H), 0.93 – 0.85 (m, 7H), 0.78 (d, *J* = 7.0 Hz, 3H).
- **^{13}C NMR (101 MHz, $CDCl_3$):** δ 116.7, 74.8, 47.1, 46.2, 41.2, 34.2, 31.4, 26.4, 23.6, 22.0, 20.7, 16.5.

The characterization data corresponded to the reported values.[2]

(1*S*,2*R*,4*S*)-1,7,7-Trimethylbicyclo[2.2.1]heptan-2-yl 2-diazoacetate (1t)



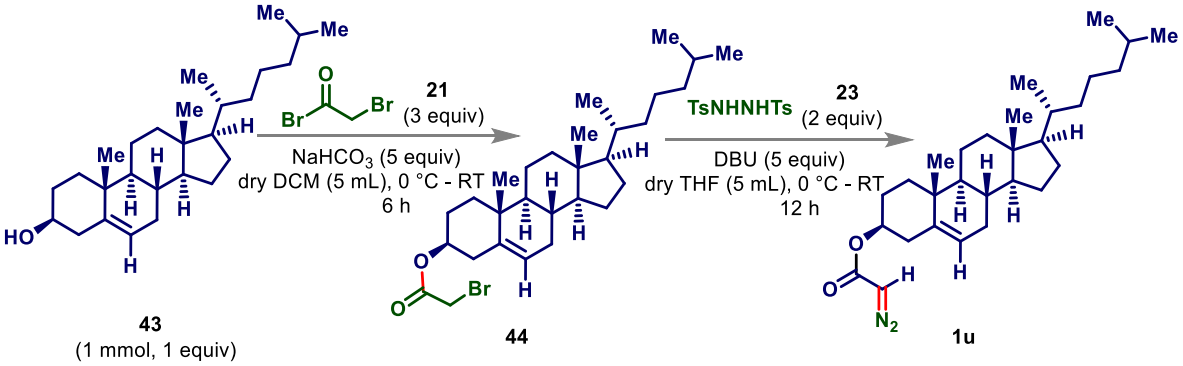
Step 1: Following a slightly modified procedure,[19] borneol **41** (771 mg, 5.00 mmol, 1.00 equiv), $NaHCO_3$ (2.1 g, 25 mmol, 5.0 equiv), and anhydrous dichloromethane (25 mL) were mixed and stirred. Next, bromoacetyl bromide (**21**) (1.31 mL, 15.0 mmol, 3.00 equiv) was added dropwise at 0 °C and the reaction mixture allowed to warm to room temperature. After 6 h, the reaction mixture was quenched with H_2O (30 mL), extracted with dichloromethane (3 × 40 mL). The organic layers were combined, washed with water (30 mL), dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The crude product **42** was subjected to the next step without further purification.

Step 2: Following a slightly modified procedure,[19] to a solution of bromoacetamide **42** in anhydrous THF (20 mL), *N,N′*-ditosylhydrazine (**23**) (3.4 g, 10 mmol, 2.0 equiv) was added. Next, DBU (3.73 mL, 25.0 mmol, 5.00 equiv) was added dropwise at 0 ˚C and stirred. Next, the reaction mixture was allowed to warm to room temperature. After 12 h, the reaction mixture was quenched with the saturated solution of $NaHCO_3$ (30 mL) and extracted with diethyl ether (3 × 30 mL). The organic layers were combined, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The crude product was purified by chromatography using 1:50 EtOAc:petroleum ether as mobile phase to afford (1*S*,2*R*,4*S*)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl 2-diazoacetate (**1t**) (734 mg, 3.30 mmol, 67%) as a pale yellow solid.

- **TLC:** R_f = 0.31 (EtOAc:petroleum ether, 1:20 v/v), $KMnO_4$
- **^{1}H NMR (400 MHz, $CDCl_3$):** δ 5.02 – 4.92 (m, 1H, OC*H*), 4.73 (s, 1H, C*H*N_2), 2.42 – 2.28 (m, 1H), 1.93 – 1.76 (m, 1H), 1.76 – 1.62 (m, 2H), 1.34 – 1.16 (m, 2H), 1.01 (dd, *J* = 13.8, 3.5 Hz, 1H), 0.89 (s, 3H), 0.85 (s, 3H), 0.82 (s, 3H).
- **^{13}C NMR (101 MHz, $CDCl_3$):** δ 166.9, 80.4, 48.8, 47.7, 46.2, 36.7, 27.9, 26.9, 19.6, 18.8, 13.4. One carbon was not resolved in 101 MHz.

The characterization data corresponded to the reported values.[19]

(3*S*,8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-10,13-Dimethyl-17-((*R*)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11, 12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl 2-diazoacetate (1u)



Step 1: Following a slightly modified procedure,[2] cholesterol **43** (387 mg, 1.00 mmol, 1.00 equiv) and $NaHCO_3$ (420 mg, 5.00 mmol, 5.00 equiv), and anhydrous dichloromethane (5 mL) were mixed and stirred. Next, bromoacetyl bromide (**21**) (0.26 mL, 3.00 mmol, 3.00 equiv) was added dropwise at 0 °C and stirred at room temperature. After 6 h, the reaction mixture was quenched with H_2O (15 mL), extracted with dichloromethane (3 × 20 mL). The organic layers were combined, washed with water (25 mL), dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The crude product **44** was used in the next step without further purification.

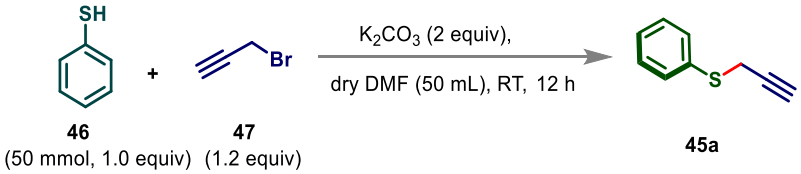
Step 2: Following a slightly modified procedure,[2] bromoacetamide **44**, *N,N′*-ditosylhydrazine (**23**) (681 mg, 2.00 mmol, 2.00 equiv) and anhydrous THF (5 mL) were mixed and stirred at 0 ˚C. Next, DBU (0.75 mL, 5.0 mmol, 5.0 equiv) was added dropwise and stirred at room temperature. After 12 h, the reaction mixture was quenched with saturated aqueous solution of $NaHCO_3$ (10 mL) and extracted with diethyl ether (3 × 20 mL). The organic layers were combined, dried over anhydrous Na_2SO_4. The resulting crude product was purified by chromatography using EtOAc:petroleum ether 1:50 as mobile phase to afford **1u** (232 mg, 0.510 mmol, 51%) as a pale yellow solid.

- **TLC:** R_f = 0.42 (EtOAc:petroleum ether, 1:20, v/v), $KMnO_4$
- **^{1}H NMR (400 MHz, $CDCl_3$):** δ 5.38 (d, *J* = 5.1 Hz, 1H, olefinic *H*), 4.75 – 4.62 (m, 2H, C*H*N_2 and OC*H*), 2.45 – 2.23 (m, 2H), 2.05 – 1.76 (m, 5H), 1.66 – 0.76 (m, 33H), 0.67 (s, 3H).
- **^{13}C NMR (101 MHz, $CDCl_3$):** δ 166.3, 139.5, 122.8, 74.6, 56.7, 56.1, 50.0, 46.3, 42.3, 39.7, 39.5, 38.3, 37.0, 36.5, 36.2, 35.8, 31.9, 31.8, 28.2, 28.0, 28.0, 24.3, 23.8, 22.8, 22.6, 21.0, 19.3, 18.7, 11.8.

The characterization data corresponded to the reported values.[2]

2. Preparation of Propargyl or Allyl Sulfides:

Phenyl(prop-2-yn-1-yl)sulfane (45a)

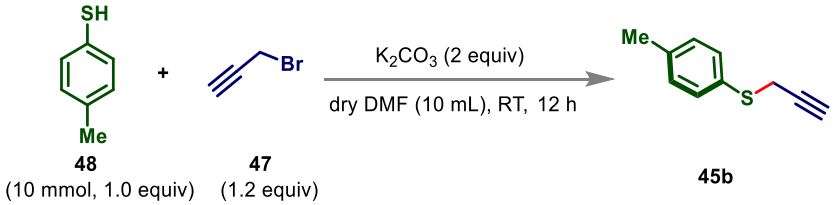


Following a slightly modified procedure,[20] to a solution of thiophenol **46** (5.5 g, 50 mmol, 1.0 equiv) in anhydrous DMF (50 mL), K_2CO_3 (14.0 g, 100 mmol, 2.00 equiv) was added. The reaction mixture was stirred for 30 min at room temperature under argon atmosphere. Next, propargyl bromide **47** (5.7 mL, 60 mmol, 1.2 equiv, 80% solution in toluene) was added dropwise and stirred. After 12 h, the reaction mixture was quenched with water (30 mL) and extracted with diethyl ether (3 × 50 mL). The organic layers were combined, washed with saturated brine solution (50 mL), dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The crude product was purified by column chromatography using petroleum ether as mobile phase to afford phenyl(prop-2-yn-1-yl)sulfane (**45a**) as a light-yellow oil (6.1 g, 41 mmol, 82%).

- **TLC:** R_f = 0.37 (petroleum ether), $KMnO_4$
- **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.45 (d, *J* = 7.5 Hz, 2H, Ar*H*), 7.33 (t, *J* = 7.7 Hz, 2H, Ar*H*), 7.26 (t, *J* = 3.6 Hz, 1H, Ar*H*), 3.61 (d, *J* = 2.6 Hz, 2H, CH_2SAr), 2.24 (t, *J* = 2.6 Hz, 1H, CH_2CCH).
- **^{13}C NMR (101 MHz, $CDCl_3$)**: δ 134.9, 130.0, 129.0, 127.0, 79.8, 71.5, 22.5.

The characterization data corresponded to the reported values.[20]

Prop-2-yn-1-yl(p-tolyl)sulfane (45b)



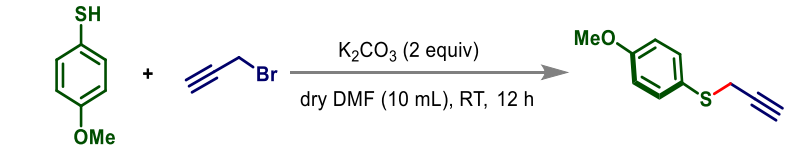
Following a slightly modified procedure,[20] to a solution of *p*-thiocresol **48** (1.24 g, 10.0 mmol, 1.00 equiv) in anhydrous DMF (10 mL), K_2CO_3 (2.76 g, 20.0 mmol, 2.00 equiv) was added. The reaction mixture was stirred for 30 min at room temperature under argon atmosphere. Next,

propargyl bromide **47** (0.90 mL, 12 mmol, 1.2 equiv, 80% solution in toluene) was added dropwise and stirred. After 12 h, the reaction mixture was quenched with water (10 mL) and extracted with diethyl ether (3 × 15 mL). The organic layers were combined, washed with brine solution (15 mL), dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The crude product was purified by column chromatography using petroleum ether as mobile phase to afford prop-2-yn-1-yl(*p*-tolyl)sulfane (**45b**) as a light yellow oil (1.02 g, 6.29 mmol, 63%).

- **TLC:** R_f = 0.62 (EtOAc: petroleum ether, 1:100 v/v), $KMnO_4$
- **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.38 (d, *J* = 8.2 Hz, 2H, Ar*H*), 7.14 (d, *J* = 7.9 Hz, 2H, Ar*H*), 3.56 (d, *J* = 2.7 Hz, 2H, C*H*$_2$SAr), 2.34 (s, 3H, ArC*H*$_3$), 2.23 (t, *J* = 2.6 Hz, 1H, CH$_2$CC*H*).
- **^{13}C NMR (101 MHz, $CDCl_3$):** δ 137.2, 131.0, 129.7, 124.4, 80.0, 71.4, 23.2, 21.0.

The characterization data corresponded to the reported values.[21]

(4-Methoxyphenyl)(prop-2-yn-1-yl)sulfane (45c)



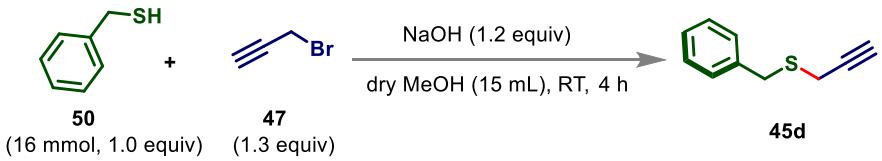
49 (10 mmol, 1.0 equiv) **47** (1.2 equiv) **45c**

Following a slightly modified procedure,[20] to a solution of *p*-thioanisole **49** (1.23 mL, 10.0 mmol, 1.00 equiv) in anhydrous DMF (10 mL), K_2CO_3 (2.76 g, 20.0 mmol, 2.00 equiv) was added. The reaction mixture was stirred for 30 min at room temperature under argon atmosphere. Next, propargyl bromide **47** (0.90 mL, 12 mmol, 1.2 equiv, 80% solution in toluene) was added dropwise and stirred. After 12 h, the reaction mixture was quenched with water (10 mL) and extracted with diethyl ether (3 × 15 mL). The organic layers were combined, washed with saturated brine solution (15 mL), dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The crude product was purified by column chromatography using petroleum ether as mobile phase to afford (4-methoxyphenyl)(prop-2-yn-1-yl)sulfane (**45c**) as a light-yellow oil (1.2 g, 6.7 mmol, 67%).

- **TLC:** R_f = 0.47 (EtOAc:petroleum ether, 1:100 v/v), $KMnO_4$
- **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.48 (d, *J* = 8.8 Hz, 2H, Ar*H*), 6.87 (d, *J* = 8.8 Hz, 2H, Ar*H*), 3.81 (s, 3H, ArOC*H*$_3$), 3.49 (d, *J* = 2.6 Hz, 2H, C*H*$_2$SAr), 2.22 (t, *J* = 2.6 Hz, 1H, CH$_2$CC*H*).

The characterization data corresponded to the reported values.[22]

Benzyl(prop-2-yn-1-yl)sulfane(45d)

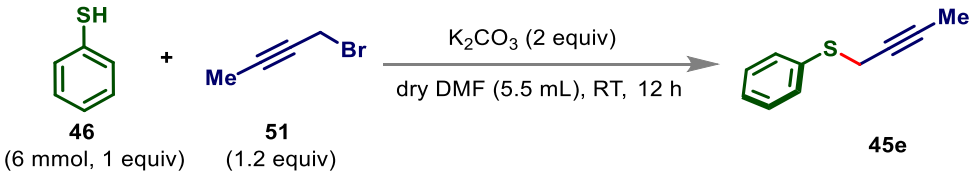


Following a slightly modified procedure,[23] to a solution of phenylmethanethiol **50** (1.9 mL, 16 mmol, 1.0 equiv) in anhydrous methanol (15 mL), NaOH (768 mg, 19.2 mmol, 1.20 equiv) was added. The reaction mixture was stirred for 30 min at room temperature under argon atmosphere. Next, propargyl bromide **47** (2.4 mL, 12 mmol, 1.3 equiv, 80% solution in toluene) was added dropwise and stirred. After 12 h, the reaction mixture was quenched with water (15 mL) and extracted with diethyl ether (3 × 15 mL). The organic layers were combined, washed with saturated brine solution (20 mL), dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The crude product was purified by column chromatography using petroleum ether as an eluent to afford benzyl(prop-2-yn-1-yl)sulfane (**45d**) as a light-yellow oil (1.80 g, 11.1 mmol, 69%).

- **TLC:** R_f = 0.53 (EtOAc:Petroleum ether, 1:100 v/v), $KMnO_4$
- **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.37 – 7.31 (m, 4H, Ar*H*), 7.29 – 7.23 (m, 1H, Ar*H*), 3.87 (s, 2H, ArC*H*$_2$S), 3.08 (d, *J* = 2.6 Hz, 2H, SC*H*$_2$CCH), 2.30 (t, *J* = 2.6 Hz, 1H, SCH$_2$CC*H*).
- **^{13}C NMR (101 MHz, $CDCl_3$):** δ 137.2, 128.7, 128.3, 126.9, 79.6, 71.1, 34.9, 18.1.

The characterization data corresponded to the reported values.[23]

But-2-yn-1-yl(phenyl)sulfane (45e)



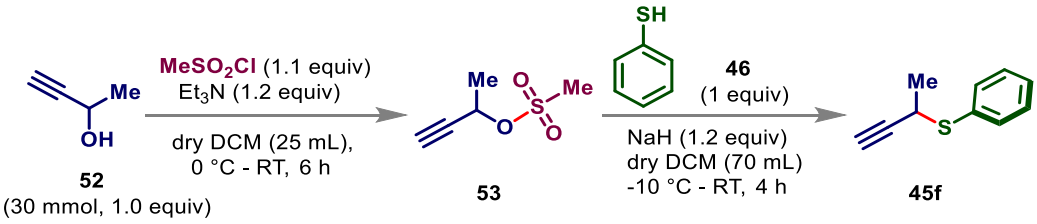
Following a slightly modified procedure,[20] to a solution of thiophenol **46** (0.6 mL, 6 mmol, 1 equiv) in anhydrous DMF (5.5 mL), K_2CO_3 (1.66 g, 12.0 mmol, 2.00 equiv) was added. The reaction mixture was stirred for 30 min at room temperature under argon atmosphere. Next 1-bromobut-2-yne (**51**) (0.63 mL, 7.2 mmol, 1.2 equiv) was added dropwise and stirred. After 12 h reaction mixture was quenched with water (10 mL) and extracted with diethyl ether (3 × 10 mL). The organic layers were combined, washed with saturated brine solution (15 mL), dried over

anhydrous Na_2SO_4, and concentrated under reduced pressure. The crude product was purified by column chromatography using petroleum ether as mobile phase to afford but-2-yn-1-yl(phenyl)sulfane (**45e**) as a light-yellow oil (887 mg, 5.47 mmol, 91%).

- **TLC:** R_f = 0.33 (Petroleum ether), $KMnO_4$
- **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.41 (d, *J* = 1.1 Hz, 2H, Ar*H*), 7.31 (t, *J* = 7.7 Hz, 2H, Ar*H*), 7.25 – 7.20 (t, 1H, Ar*H*), 3.60 (q, *J* = 2.5 Hz, 2H, ArSC*H*$_2$), 1.81 (t, *J* = 2.5 Hz, 3H, CH_2CCCH_3).
- **^{13}C NMR (101 MHz, $CDCl_3$):** δ 135.7, 129.5, 128.9, 126.5, 79.5, 74.6, 22.9, 3.7.

The characterization data corresponded to the reported values.[24]

But-3-yn-2-yl(phenyl)sulfane (45f)



Step 1: Following a slightly modified procedure,[20] to a solution of 3-butyn-2-ol (**52**) (2.4 mL, 30 mmol, 1.0 equiv) in anhydrous dichloromethane (25 mL), triethylamine (5.0 mL, 36 mmol, 1.2 equiv) was added at 0 ºC. Next, methanesulfonyl chloride (2.6 mL, 33 mmol, 1.1 equiv) was added dropwise and stirred at room temperature. After 6 h, the reaction mixture was quenched by saturated aqueous NH_4Cl (15 mL) solution and extracted with dichloromethane (3 × 30 mL). The organic layers were combined, washed with water (50 mL), dried over Na_2SO_4, and concentrated under reduced pressure. The crude mesylated alcohol **53** was used in the next step without further purification.

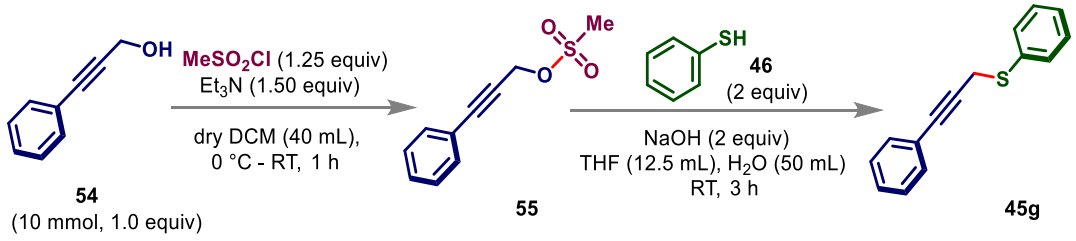
Step 2: Following a slightly modified procedure,[20] thiophenol **46** (3.0 mL, 30 mmol, 1.0 equiv) was dissolved in anhydrous dichloromethane (50 mL) and cooled to - 10 ºC. Next, NaH (1.44 g, 36.0 mmol, 1.20 equiv, 60% in mineral oil) was added portion-wise and stirred for further 15 min. A solution of mesylated alcohol **53** in anhydrous dichloromethane (20 mL) was added slowly at - 10 ºC, and warm-up to room temperature. After 4 h, the reaction mixture was quenched with water (50 mL) and extracted with diethyl ether (3 × 50 mL). The organic layers were combined, washed with water (50 mL), dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The

crude product was purified by column chromatography using petroleum ether to afford the desired but-3- yn-2-yl(phenyl)sulfane (**45f**) as a light-yellow oil (1.5 g, 9.2 mmol, 31%).

- **TLC:** R_f = 0.47 (petroleum ether), $KMnO_4$
- **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.56 – 7.50 (m, 2H, Ar*H*), 7.38 – 7.27 (m, 3H, Ar*H*), 3.89 (qd, *J* = 7.0, 2.4 Hz, 1H, ArSC*H*(CH_3)), 2.33 (d, *J* = 2.4 Hz, 1H, CH(CH_3)CC*H*), 1.53 (d, *J* = 7.0 Hz, 3H, ArSCH(C*H*$_3$)).
- **^{13}C NMR (101 MHz, $CDCl_3$):** δ 133.6, 132.8, 128.8, 127.8, 84.7, 71.4, 32.9, 21.6.

The characterization data corresponded to the reported values.[20]

Phenyl(3-phenylprop-2-yn-1-yl)sulfane (45g)



Step 1: Following a slightly modified procedure,[25] to a solution of 3-phenylprop-2-yn-1-ol (**54**) (1.25 mL, 10.0 mmol, 1.00 equiv) in anhydrous dichloromethane (40 mL), triethylamine (2.1 mL, 15 mmol, 1.5 equiv) was added at 0 ºC. Next, methanesulfonyl chloride (1.00 mL, 12.5 mmol, 1.25 equiv) was added dropwise and stirred for 1 h. To this reaction mixture, 10% aqueous HCl solution (30 mL) was added and extracted with ethyl acetate (3 × 30 mL). The organic layers were combined, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The crude mesylated alcohol **55** was used in the next step without further purification.

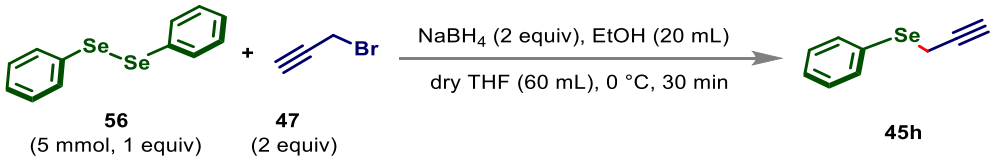
Step 2: Following a slightly modified procedure,[25] thiophenol **46** (2.0 mL, 20 mmol, 2.0 equiv) and NaOH (800 mg, 20.0 mmol, 2.00 equiv) were dissolved in water (50 mL). A solution of mesylated alcohol **55** in THF (12.5 mL) was added dropwise at room temperature and stirred. After 3 h, the reaction mixture was quenched with 10% aqueous NaOH (30 mL) and extracted with diethyl ether (3 × 50 mL). The organic layers were combined, washed with water (50 mL), dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The crude product was purified by column chromatography using petroleum ether as mobile phase to afford the desired phenyl(3-phenylprop-2-yn-1-yl)sulfane (**45g**) as a light-yellow oil (1.15 g, 5.13 mmol, 51%).

- **TLC:** R_f = 0.59 (petroleum ether), $KMnO_4$

- **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.49 (d, *J* = 7.6 Hz, 2H, Ar*H*), 7.37 – 7.21 (m, 8H, Ar*H*), 3.82 (s, 2H, CH_2SAr).
- **^{13}C NMR (101 MHz, $CDCl_3$):** δ 135.1, 131.6, 130.5, 128.9, 128.2, 128.1, 123.0, 127.0, 85.2, 83.6, 23.8.

The characterization data corresponded to the reported values.[26]

Phenyl(prop-2-yn-1-yl)selane (45h)

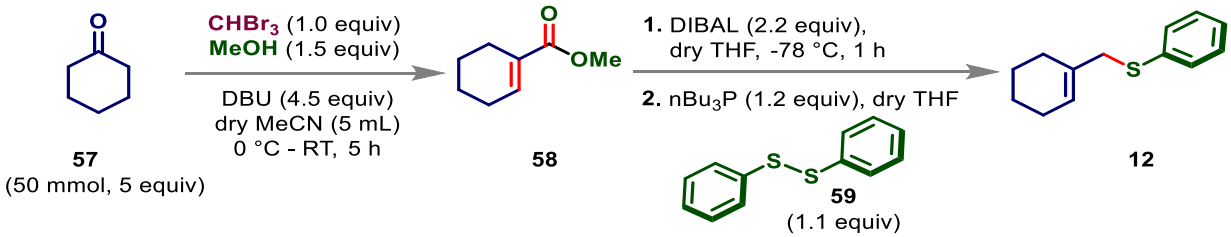


Following a slightly modified procedure,[27] to a solution of $NaBH_4$ (378 mg, 10.0 mmol, 2.00 equiv) in EtOH (20 mL), a solution of diselenide **56** (1.56 g, 5.00 mmol, 1.00 equiv) in anhydrous THF (40 mL) was added dropwise at 0 ºC and stirred. Next, a solution of propargyl bromide **47** (0.95 mL, 10 mmol, 2.0 equiv, 80% solution in toluene) in anhydrous THF (20 mL) was added dropwise and stirred. After 30 min, the reaction mixture was quenched with water (30 mL) and extracted with diethyl ether (3 × 50 mL). The organic layers were combined, dried over $MgSO_4$, and concentrated under reduced pressure. The crude product was purified by column chromatography using petroleum ether as an eluent to afford the desired phenyl(prop-2-yn-1-yl)selane (**45h**) as a light-yellow oil (865 mg, 4.43 mmol, 89%).

- **TLC:** R_f = 0.46 (petroleum ether), $KMnO_4$
- **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.65 – 7.56 (m, 2H, Ar*H*), 7.31 (m, 3H, Ar*H*), 3.49 (d, *J* = 2.7 Hz, 2H, CH_2SeAr), 2.25 (t, *J* = 2.7 Hz, 1H, CH_2CCH).
- **^{13}C NMR (101 MHz, $CDCl_3$):** δ 133.1, 129.4, 129.0, 127.6, 80.7, 71.7, 12.2.

The characterization data corresponded to the reported values.[27]

Cyclohex-1-en-1-ylmethyl (phenyl)sulfane (12)



Step 1: Following a slightly modified procedure,[28] to a solution of cyclohexanone (**57**) (5.2 mL, 50 mmol, 5.0 equiv), anhydrous methanol (0.60 mL, 15 mmol, 1.5 equiv), DBU (6.7 mL, 45 mmol, 4.5 equiv) in anhydrous acetonitrile (5 mL), bromoform (0.90 mL, 10 mmol, 1.0 equiv) was added dropwise at 0 ºC. Next, the reaction mixture was allowed to room temperatureand stirred for 5 h. To this reaction mixture, saturated NH_4Cl solution (20 mL) was added and extracted with ethyl acetate (3 × 25 mL). The organic layers were combined, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The crude product was purified by column chromatography using petroleum ether as eluent to obtain methyl cyclohex-1-ene-1-carboxylate (**58**) as colourless oil (1.35 g, 9.63 mmol, 96%).

- **TLC:** R_f = 0.62 (EtOAc:petroleum ether, 1:20 v/v), $KMnO_4$
- **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.02 – 6.93 (m, 1H, C=C*H*), 3.72 (s, 3H, COOCH_3), 2.30 – 2.22 (m, 2H, CO_2MeCCH_2), 2.21 – 2.15 (m, 2H, C=CHCH_2), 1.71 – 1.54 (m, 4H, aliphatic CH_2).
- **^{13}C NMR (101 MHz, $CDCl_3$):** δ 168.3, 139.9, 130.3, 51.6, 25.9, 24.3, 22.2, 21.6.

The characterization data corresponded to the reported values.[29]

Step 2: Following a slightly modified procedure,[30] to a cooled (-78 °C) solution of **58** (320 mg, 2.28 mmol, 1.00 equiv) in anhydrous THF (5 mL), DIBAL-*H* (1.0 M in hexane, 5.0 mL, 5.0 mmol, 2.2 equiv) was added. After 1 h, saturated aqueous Rochelle salt solution (15 mL) was added to the reaction mixture, stirred at room temperature for 3 h, and extracted with EtOAc (3 × 15 mL). The combined organic layers were washed with brine solution (20 mL), dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The crude was used for the next step without further purification.

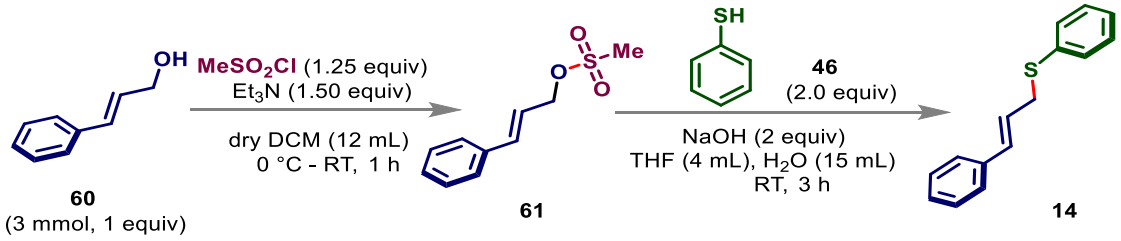
Step 3: To a solution of crude alcohol and diphenyl disulfide (**59**) (548 mg, 2.50 mmol, 1.10 equiv) in anhydrous THF (10 mL), tri-butylphosphine (50 % in EtOAc, 1.4 mL, 2.7 mmol, 1.2 equiv) was added at room temperature and stirred. After 12 h, the reaction mixture was quenched by saturated aqueous $NaHCO_3$ solution (20 mL) and extracted with diethyl ether (3 × 15 mL). The organic layers combined, washed with brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography by using hexane to afford **12** as a colorless oil (435 mg, 2.13 mmol, 93%).

- **TLC:** R_f = 0.55 (EtOAc:petroleum ether, 1:100 v/v), $KMnO_4$

- **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.35 – 7.31 (m, 2H, Ar*H*), 7.29 – 7.23 (m, 2H, Ar*H*), 7.21 – 7.14 (m, 1H, Ar*H*), 5.56 – 5.49 (m, 1H, C=C*H*), 3.47 (s, 2H, CH_2SAr), 2.15 – 2.05 (m, 2H, aliphatic *H*), 2.01 – 1.90 (m, 2H, aliphatic *H*), 1.67 – 1.58 (m, 2H, aliphatic *H*), 1.56 – 1.46 (m, 2H, aliphatic *H*).
- **^{13}C NMR (101 MHz, $CDCl_3$):** δ 136.8, 133.0, 130.1, 128.6, 126.0, 125.6, 42.3, 27.2, 25.3, 22.7, 22.1.

The characterization data corresponded to the reported values.[31]

Cinnamyl(phenyl)sulfane (14)



Step 1: Following a slightly modified procedure,[25] to a solution of (*E*)-3-phenylprop-2-en-1-ol (**60**) (0.40 mL, 3.0 mmol, 1.0 equiv) in anhydrous dichloromethane (12 mL), triethylamine (0.63 mL, 4.5 mmol, 1.5 equiv) was added at 0 ºC. Next, methanesulfonyl chloride (0.30 mL, 3.75 mmol, 1.25 equiv) was added dropwise and stirred for 1 h. To this reaction mixture, 10% aqueous HCl solution (10 mL) was added, extracted with ethyl acetate (3 × 15 mL). The organic layers were combined, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The mesylated alcohol **61** was used in the next step without further purification.

Step 2: Following a slightly modified procedure,[25] thiophenol **46** (0.6 mL, 2 mmol, 2 equiv), NaOH (240 mg, 6.00 mmol, 2.00 equiv) was dissolved in water (15 mL). A solution of mesylated alcohol **61** in THF (4 mL) was added dropwise at room temperature and stirred. After 3 h, the reaction mixture was quenched with 10% aqueous NaOH (10 mL) and extracted with diethyl ether (3 × 15 mL). The organic layers were combined, washed with water (15 mL), dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The crude product was purified by column chromatography using petroleum ether to afford the desired cinnamyl(phenyl)sulfane (**14**) as a light-yellow solid (450 mg, 2.00 mmol, 66%).

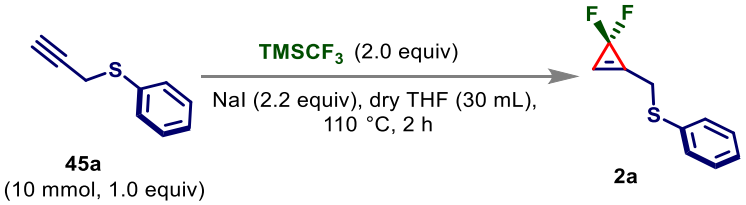
- **TLC:** R_f = 0.57 (EtOAc:petroleum ether, 1:100 v/v), $KMnO_4$

- **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.42-7.35 (m, 2H, Ar*H*), 7.34 – 7.15 (m, 8H, Ar*H*), 6.43 (d, *J* = 15.7 Hz, 1H, ArC*H*CHCH$_2$), 6.25 (dt, *J* = 15.1, 7.1 Hz, 1H, ArCHC*H*CH$_2$), 3.72 (d, *J* = 7.0 Hz, 2H, ArCHC*H*CH$_2$).
- **^{13}C NMR (101 MHz, $CDCl_3$):** δ 136.7, 135.8, 132.8, 130.3, 128.8, 128.5, 127.6, 126.4, 126.3, 125.1, 37.1.

The characterization data corresponded to the reported values.[32]

3. Synthesis of Difluoro Cyclopropenes:

((3,3-Difluorocycloprop-1-en-1-yl)methyl)(phenyl)sulfane (2a)

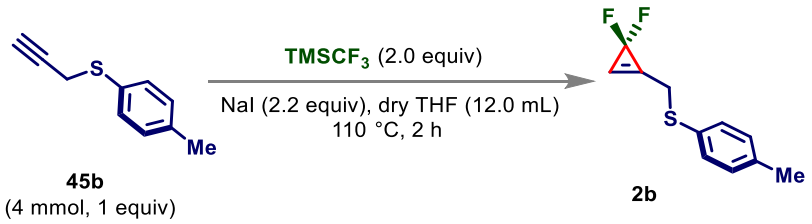


Following a slightly modified procedure,[33] to a 100 mL pressure round bottom flask, phenyl(prop-2-yn-1-yl)sulfane (**45a**) (1.48 g, 10.0 mmol, 1.00 equiv), anhydrous NaI (3.3 g, 22 mmol, 2.2 equiv), freshly distilled anhydrous THF (30 mL) were added and stirred for 30 min under argon atmosphere at room temperature. Next, $TMSCF_3$ (3.2 mL, 20 mmol, 2.0 equiv) was added and heated to 110 ℃. After 2h, the reaction mixture was quenched with saturated K_2CO_3 solution (50 mL) and extracted with diethyl ether (3 × 50 mL). The organic layers were combined, dried over anhydrous K_2CO_3, and concentrated under reduced pressure (up to 200 mbar) at 25 ºC. The crude product was purified by column chromatography using petroleum ether:Et_3N (50:1, v/v) as eluent (the column should be eluted previously with petroleum ether:Et_3N (25:1, v/v)) to afford ((3,3-difluorocycloprop-1-en-1-yl)methyl)(phenyl)sulfane (**2a**) as a light-yellow oil (1.4 g, 7.1 mmol, 71%). **(*See Spectra*)**

- **TLC:** R_f = 0.45 (EtOAc:petroleum ether, 1:100, v/v), $KMnO_4$
- **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.42 – 7.20 (m, 6H, vinylic *H* and 5 × Ar*H*), 3.91 (td, *J* = 2.6, 0.8 Hz, 2H, C*H*$_2$SPh).
- **^{13}C NMR (101 MHz, $CDCl_3$):** δ 134.9 (t, *J* = 10.9 Hz), 134.0, 130.4, 129.2, 127.3, 119.3 (t, *J* = 12.0 Hz), 101.9 (t, *J* = 272.1 Hz), 27.1.
- **^{19}F NMR (376 MHz, $CDCl_3$):** δ -103.49.

- **IR (Neat, ν):** 3066 (w), 2926 (w), 1723 (m), 1582 (w), 1478 (w), 1402 (w), 1312 (s), 1236 (w), 1181 (m), 1030 (s), 881 (w), 743 (m), 694 (w).
- **Mass:** The compound was not detected by HRMS using ESI and CI techniques, but the subsequent product was completely characterized. In addition to this, it was found in GCMS (Calcd. for $C_{10}H_8F_2S^+$ $[M]^+$ 198; found 198).

((3,3-Difluorocycloprop-1-en-1-yl)methyl)(p-tolyl)sulfane (2b)

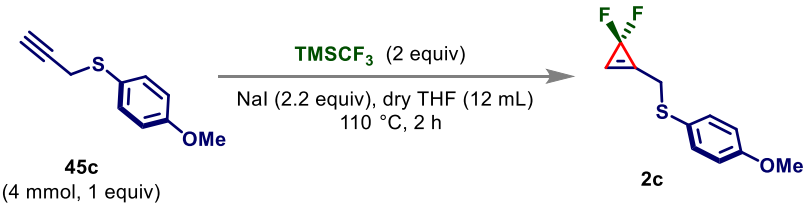


Following a slightly modified procedure,[33] in a 50 mL pressure round bottom flask, prop-2-yn-1-yl(p-tolyl)sulfane (**45b**) (649 mg, 4.00 mmol, 1.00 equiv), anhydrous NaI (1.32 g, 8.80 mmol, 2.20 equiv), and freshly distilled anhydrous THF (12 mL) were mixed at room temperature and stirred for 30 min under argon atmosphere. Next, $TMSCF_3$ (1.3 mL, 8.0 mmol, 2.0 equiv) was added and heated to 110 °C. After 2h, the reaction mixture was quenched with saturated K_2CO_3 solution (20 mL) and extracted with diethyl ether (3 × 20 mL). The organic layers were combined, dried over anhydrous K_2CO_3, and concentrated under reduced pressure (up to 200 mbar) at 25 ºC. The crude product was purified by column chromatography using petroleum ether:Et_3N (50:1, v/v) as eluent (the column should be eluted previously with petroleum ether:Et_3N (25:1, v/v)) to afford ((3,3-difluorocycloprop-1-en-1-yl)methyl)(p-tolyl)sulfane (**2b**) as a light-yellow oil (450 mg, 2.12 mmol, 53%) and store it at -20 ºC. **(***See Spectra***)**

- **TLC:** R_f = 0.47 (EtOAc:petroleum ether, 1:100 v/v), $KMnO_4$
- **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.30 (d, *J* = 8.1 Hz, 2H, Ar*H*), 7.25 (s, 1H, vinylic *H*), 7.13 (d, *J* = 7.9 Hz, 2H, Ar*H*), 3.85 (t, *J* = 2.6 Hz, 2H, CH_2SAr), 2.33 (s, 3H, ArCH_3).
- **^{13}C NMR (101 MHz, $CDCl_3$):** δ 137.8, 135.1 (t, *J* = 11.0 Hz), 131.3, 130.2, 130.0, 119.1 (t, *J* = 12.0 Hz), 101.9 (t, *J* = 271.1 Hz), 27.8, 21.1.
- **^{19}F NMR (376 MHz, $CDCl_3$):** δ -103.47.
- **IR (Neat, ν):** 2922 (s), 2855 (m), 2178 (w), 2050 (w), 1996 (w), 1729 (w), 1458 (w), 1312 (m), 1032 (m), 806 (w), 738 (w).

- **Mass:** The compound was not detected by HRMS using ESI and CI techniques, but the subsequent product was completely characterized. In addition to this, it was found in GCMS (Calcd. for $C_{11}H_8F_2S^+$ $[M]^+$ 212; found 212).

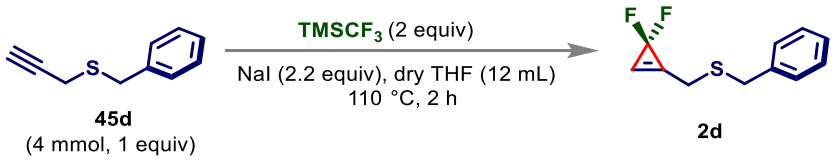
((3,3-Difluorocycloprop-1-en-1-yl)methyl)(4-methoxyphenyl)sulfane (2c)



Following a slightly modified procedure,[33] in a 50 mL pressure round bottom flask, (4-methoxyphenyl)(prop-2-yn-1-yl)sulfane (**45c**) (713 mg, 4.00 mmol, 1.00 equiv), anhydrous NaI (1.32 g, 8.80 mmol, 2.20 equiv), freshly distilled anhydrous THF (12 mL) were mixed at room temperature and stirred for 30 min under argon atmosphere. Next, $TMSCF_3$ (1.3 mL, 8.0 mmol, 2.0 equiv) was added and heated to 110 °C. After 2h, the reaction mixture was quenched with saturated K_2CO_3 solution (20 mL) and extracted with diethyl ether (3 × 20 mL). The organic layers were combined, dried over anhydrous K_2CO_3, and concentrated under reduced pressure (up to 200 mbar) at 25 ºCThe crude product was purified by column chromatography using petroleum ether:Et_3N (50:1, v/v) as eluent (the column should be eluted previously with petroleum ether:Et_3N (25:1, v/v)) to afford ((3,3-difluorocycloprop-1-en-1-yl)methyl)(4-methoxyphenyl)sulfane (**2c**) as light-yellow oil (526 mg, 2.30 mmol, 58%) and store it at -20 ºC. **(*See Spectra*)**

- **TLC:** R_f = 0.35 (EtOAc:petroleum ether, 2:100, v/v), $KMnO_4$
- **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.46 – 7.36 (m, 2H, Ar*H*), 7.23 (s, 1H, vinylic *H*), 6.91 – 6.82 (m, 2H, Ar*H*), 3.80 (s, 3H, OCH_3), 3.78 (td, *J* = 2.6, 0.8 Hz, 2H, CH_2SAr).
- **^{13}C NMR (101 MHz, $CDCl_3$):** δ 159.9, 135.1 (t, *J* = 10.8 Hz), 134.6, 124.1, 118.9 (t, *J* = 12.0 Hz), 114.8, 101.9 (t, *J* = 272.1 Hz), 55.3, 29.0.
- **^{19}F NMR (376 MHz, $CDCl_3$):** δ -103.48.
- **IR (Neat, ν):** 3123 (w), 2943 (w), 2841 (w), 2051 (w), 1720 (w), 1591 (m), 1492 (m), 1458 (w), 1304 (s), 1241 (s), 1176 (m), 1016 (s), 826 (m).
- **Mass:** The compound was not detected by HRMS using ESI and CI techniques, but the subsequent product was completely characterized. In addition to this, it was found in GCMS (Calcd. for $C_{11}H_{10}F_2OS^+$ $[M]^+$ 228; found 228).

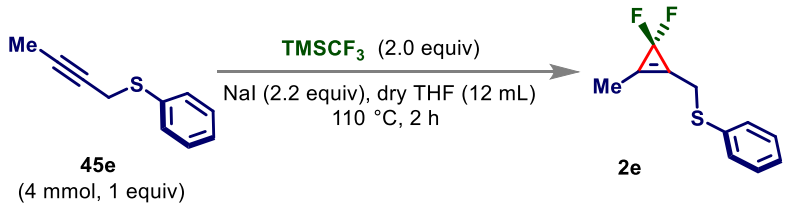
Benzyl((3,3-difluorocycloprop-1-en-1-yl)methyl)sulfane(2d)



Following a slightly modified procedure,[33] in a 50 mL pressure round bottom flask, benzyl(prop-2-yn-1-yl)sulfane (**45d**) (649 mg, 4.00 mmol, 1.00 equiv), anhydrous NaI (1.32 g, 8.80 mmol, 2.20 equiv), and freshly distilled anhydrous THF (12 mL) were mixed at room temperature and stirred for 30 min under argon atmosphere. Next, $TMSCF_3$ (1.3 mL, 8.0 mmol, 2.0 equiv) was added and heated to 110 ℃. After 2h, the reaction mixture was quenched with saturated K_2CO_3 solution (20 mL) and extracted with diethyl ether (3 × 20 mL). The organic layers were combined, dried over anhydrous K_2CO_3, and concentrated under reduced pressure (up to 200 mbar) at 25 ºC. The crude product was purified by column chromatography using petroleum ether:Et_3N (50:1, v/v) as eluent (the column should be eluted previously with petroleum ether:Et_3N (25:1, v/v)) to afford benzyl((3,3-difluorocycloprop-1-en-1-yl)methyl)sulfane (**2d**) as a light-yellow oil (481 mg, 2.27 mmol, 57%) and store it at -20 ºC. **(*See Spectra*)**

- **TLC:** R_f = 0.52 (EtOAc:petroleum ether, 1:100 v/v), $KMnO_4$
- **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.37 – 7.23 (m, 6H, vinylic *H* and 5 × Ar*H*), 3.77 (s, 2H, SCH_2Ar), 3.36 (t, *J* = 2.6 Hz, 2H, CH_2SCH_2Ar).
- **^{13}C NMR (101 MHz, $CDCl_3$):** δ 136.9, 135.1 (t, *J* = 10.8 Hz), 129.0, 128.7, 127.4, 118.3 (t, *J* = 12.0 Hz), 102.1 (t, *J* = 271.7 Hz), 35.7, 22.8.
- **^{19}F NMR (376 MHz, $CDCl_3$):** δ -103.37.
- **IR (Neat, ν):** 3029 (w), 2923 (w), 2160 (w), 1719 (m), 1600 (w), 1406 (w), 1306 (s), 1230 (m), 1014 (s), 761 (m), 701 (s).
- **Mass:** The compound was not detected by HRMS using ESI and CI techniques, but the subsequent product was completely characterized. In addition to this, it was found in GCMS (Calcd. for $C_{11}H_{10}F_2S^+$ $[M]^+$ 212; found 212).

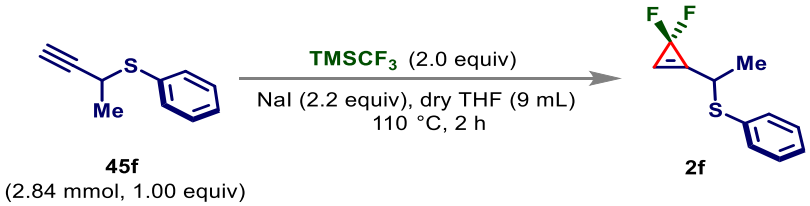
((3,3-Difluoro-2-methylcycloprop-1-en-1-yl)methyl)(phenyl)sulfane (2e)



Following a slightly modified procedure,[33] in a 50 mL pressure round bottom flask, but-2-yn-1-yl(phenyl)sulfane (**45e**) (649 mg, 4.00 mmol, 1.00 equiv), anhydrous NaI (1.32 g, 8.80 mmol, 2.20 equiv), and freshly distilled anhydrous THF (12 mL) were mixed at room temperature and stirred for 30 min under argon atmosphere. Next, $TMSCF_3$ (1.3 mL, 8.0 mmol, 2.0 equiv) was added and heated to 110 °C. After 2h, the reaction mixture was quenched with saturated K_2CO_3 solution (20 mL) and extracted with diethyl ether (3 × 20 mL). The organic layers were combined, dried over anhydrous K_2CO_3, and concentrated under reduced pressure (up to 200 mbar) at 25 ºC. The crude product **2e** was subjected to final step without further purification. **(***See Spectra***)**

- **TLC:** R_f = 0.60 (EtOAc:petroleum ether, 1:100 v/v), $KMnO_4$
- **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.39 – 7.19 (m, 5H, Ar*H*), 3.86 (s, 2H, C*H*$_2$SAr), 1.85 (m, 3H, vinylic C*H*$_3$).
- **^{19}F NMR (376 MHz, $CDCl_3$):** δ -106.42.
- **Mass:** The compound was not detected by HRMS using ESI and CI techniques, but the subsequent product was completely characterized. In addition to this, it was found in GCMS (Calcd. for $C_{11}H_{10}F_2S^+$ $[M]^+$ 212; found 212).

(1-(3,3-Difluorocycloprop-1-en-1-yl)ethyl)(phenyl)sulfane (2f)

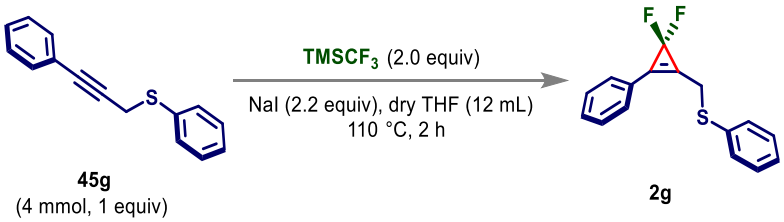


Following a slightly modified procedure,[33] in a 50 mL pressure round bottom flask, but-3-yn-2-yl(phenyl)sulfane (**45f**) (460 mg, 2.84 mmol, 1.00 equiv), anhydrous NaI (935 mg, 6.24 mmol, 2.20 equiv), and freshly distilled anhydrous THF (9 mL) were mixed at room temperature and stirred for 30 min under argon atmosphere. Next, $TMSCF_3$ (0.90 mL, 5.67 mmol, 2.00 equiv) was added and heated to 110 °C. After 2h, the reaction mixture was quenched with saturated K_2CO_3

solution (15 mL) and extracted with diethyl ether (3 × 15 mL). The organic layers were combined, dried over anhydrous K_2CO_3, and concentrated under reduced pressure (up to 200 mbar) at 25 ºC. The crude product was purified by column chromatography using petroleum ether:Et_3N (50:1, v/v) as eluent (the column should be eluted previously with petroleum ether:Et_3N (25:1, v/v)) to afford (1-(3,3-difluorocycloprop-1-en-1-yl)ethyl)(phenyl)sulfane (**2f**) as a light-yellow oil (405 mg, 1.91 mmol, 67%) and store it at -20 ºC. **(***See Spectra***)**

- **TLC:** R_f = 0.55 (EtOAc:petroleum ether, 1:100 v/v), $KMnO_4$
- **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.51 – 7.41 (m, 2H, Ar*H*), 7.39 – 7.28 (m, 3H, Ar*H*), 7.15 (s, 1H, vinylic *H*), 4.24 – 4.12 (m, 1H, CH_3CHSAr), 1.60 – 1.55 (m, 3H, CH_3CHSAr).
- **^{13}C NMR (101 MHz, $CDCl_3$):** δ 138.8 (t, *J* = 10.9 Hz), 133.2, 132.6, 129.1, 128.2, 117.3 (t, *J* = 12.0 Hz), 102.0 (t, *J* = 272.7 Hz), 36.9, 18.7.
- **^{19}F NMR (376 MHz, $CDCl_3$):** δ -103.47.
- **IR (Neat, ν):** 3126 (w), 2923 (m), 2335 (w), 1718 (m), 1582 (w), 1447 (m), 1305 (s), 1024 (s), 834 (m), 747 (s).
- **Mass:** The compound was not detected by HRMS using ESI and CI techniques, but the subsequent product was completely characterized. In addition to this, it was found in GCMS (Calcd. for $C_{11}H_{10}F_2S^+$ $[M]^+$ 212; found 212).

((3,3-Difluoro-2-phenylcycloprop-1-en-1-yl)methyl)(phenyl)sulfane(2g)

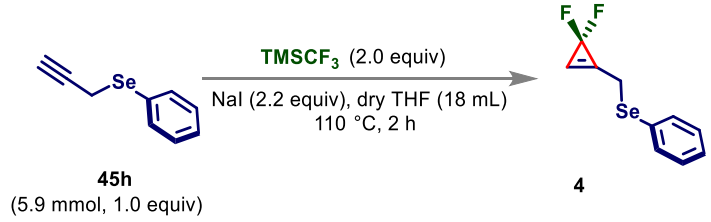


Following a slightly modified procedure,[33] in a 50 mL pressure round bottom flask, phenyl(3-phenylprop-2-yn-1-yl)sulfane (**45g**) (897 mg, 4.00 mmol, 1.00 equiv), anhydrous NaI (1.32 g, 8.80 mmol, 2.20 equiv), and freshly distilled anhydrous THF (12 mL) were mixed at room temperature and stirred for 30 min under argon atmosphere. Next, $TMSCF_3$ (1.3 mL, 8.0 mmol, 2.0 equiv) was added and heated to 110 ℃. After 2h, the reaction mixture was quenched with saturated K_2CO_3 solution (20 mL) and extracted with diethyl ether (3 × 20 mL). The organic layers were combined, dried over anhydrous K_2CO_3, and concentrated under reduced pressure (up to 200 mbar) at 25 ºC. The crude product was purified by column chromatography using petroleum ether:Et_3N (50:1, v/v)

as eluent (the column should be eluted previously with petroleum ether:Et_3N (25:1, v/v)) to afford ((3,3-difluoro-2-phenylcycloprop-1-en-1-yl)methyl)(phenyl)sulfane (**2g**) as a light-yellow oil (792 mg, 2.90 mmol, 72%) and store it at -20 ºC. **(*See Spectra*)**

- **TLC:** R_f = 0.62 (EtOAc:petroleum ether, 1:100 v/v), $KMnO_4$
- **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.55 (d, *J* = 7.1 Hz, 2H, Ar*H*), 7.47 – 7.33 (m, 5H, Ar*H*), 7.29 – 7.15 (m, 3H, Ar*H*), 4.03 (s, 2H, CH_2SAr).
- **^{13}C NMR (101 MHz, $CDCl_3$):** δ 134.5, 131.0, 130.5, 130.1, 129.2, 128.9, 128.0 (t, *J* = 10.7 Hz), 127.2, 123.4, 123.1 (t, *J* = 11.5 Hz), 102.6 (t, *J* = 273.2 Hz), 27.0.
- **^{19}F NMR (376 MHz, $CDCl_3$):** δ -108.49.
- **IR (Neat, ν):** 3062 (w), 2922 (w), 2332 (w), 1795 (m), 1581 (m), 1480 (m), 1284 (s), 1232 (m), 1004 (s), 886 (m), 739 (s), 684 (S).
- **Mass:** The compound was not detected by HRMS using ESI and CI techniques, but the subsequent product was completely characterized. In addition to this, it was found in GCMS (Calcd. for $C_{16}H_{12}F_2S^+$ $[M]^+$ 274; found 274).

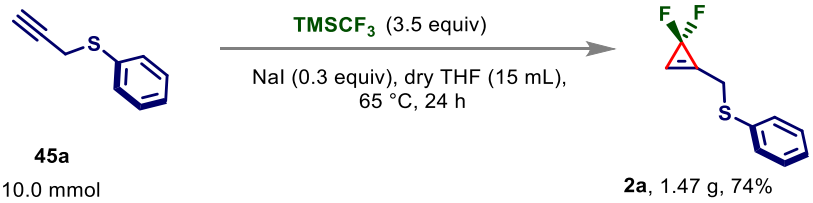
((3,3-Difluorocycloprop-1-en-1-yl)methyl)(phenyl)selane (4)



Following a slightly modified procedure,[33] in a 50 mL pressure round bottom flask, phenyl(prop-2-yn-1-yl)selane (**45h**) (1.15 g, 5.90 mmol, 1.00 equiv), anhydrous NaI (1.94 g, 13.0 mmol, 2.20 equiv), and freshly distilled anhydrous THF (18 mL) were added at room temperature and stirred for 30 min under argon atmosphere. Next, $TMSCF_3$ (1.9 mL, 12 mmol, 2.0 equiv) was added and heated to 110 ℃. After 2h, the reaction mixture was quenched with saturated K_2CO_3 solution (30 mL) and extracted with diethyl ether (3 × 30 mL). The organic layers were combined, dried over anhydrous K_2CO_3, and concentrated under reduced pressure (up to 200 mbar) at 25 ºC. The crude product was purified by column chromatography using petroleum ether:Et_3N (50:1, v/v) as eluent (the column should be eluted previously with petroleum ether:Et_3N (25:1, v/v)) to afford ((3,3-difluoro-2-phenylcycloprop-1-en-1-yl)methyl)(phenyl)sulfane (**4**) as a light-yellow oil (750 mg, 3.06 mmol, 52%) and store it at -20 ºC. **(*See Spectra*)**

- **TLC:** R_f = 0.42 (EtOAc:petroleum ether, 1:100, v/v), $KMnO_4$
- **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.58 – 7.51 (m, 2H, Ar*H*), 7.36 – 7.27 (m, 3H, Ar*H*), 7.13 (s, 1H, vinylic *H*), 3.78 (t, *J* = 2.7 Hz, 2H, C*H*$_2$SeAr).
- **^{13}C NMR (101 MHz, $CDCl_3$):** δ 135.2 (t, *J* = 10.9 Hz), 133.8, 129.3, 128.4, 128.2, 118.2 (t, *J* = 12.0 Hz), 102.1 (t, *J* = 272.5 Hz), 17.0.
- **^{19}F NMR (376 MHz, $CDCl_3$):** δ -103.91.
- **IR (Neat, ν):** 3125 (w), 3063 (w), 2927 (w). 2054 (w), 1718 (m), 1578 (m), 1477 (m), 1302 (s), 1222 (m), 1012 (s), 870 (m), 734 (s).
- **Mass:** The compound was not detected by HRMS using ESI and CI techniques, but the subsequent product was completely characterized. In addition to this, it was found in GCMS (Calcd. for $C_{10}H_8F_2Se^+$ $[M]^+$ 245; found 245).

((3,3-Difluorocycloprop-1-en-1-yl)methyl)(phenyl)sulfane (2a)

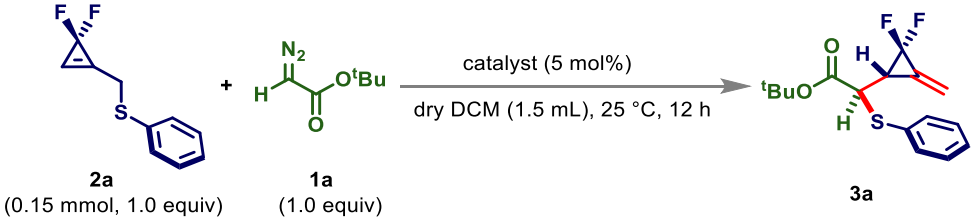


Following a slightly modified procedure,[34] to a 50 mL two-neck round bottom flask, phenyl(prop-2-yn-1-yl)sulfane (**45a**) (1.48 g, 10.0 mmol, 1.00 equiv), anhydrous NaI (450 mg, 3.00 mmol, 0.300 equiv), and freshly distilled anhydrous THF (15 mL) were added and refluxed under argon atmosphere at 65 ºC. To this refluxed reaction mixture, $TMSCF_3$ (5.5 mL, 35 mmol, 3.5 equiv) was added through a syringe pump for 16 h. After 24 h, the reaction mixture was quenched with saturated K_2CO_3 solution (50 mL) and extracted with diethyl ether (3 × 50 mL). The organic layers were combined, dried over anhydrous K_2CO_3, and concentrated under reduced pressure (up to 200 mbar) at 25 ºC. The crude product was purified by column chromatography using petroleum ether:Et_3N (50:1, v/v) as eluent (the column should be eluted previously with petroleum ether:Et_3N (25:1, v/v)) to afford ((3,3-difluorocycloprop-1-en-1-yl)methyl)(phenyl)sulfane (**2a**) as a light-yellow oil (1.47 g, 7.42 mmol, 74%).

5. Optimization of Reaction Conditions:

a) Screening of Catalysts:

A flame dried 5 mL Schlenk tube under nitrogen was charged with catalyst (7.5 µmol, 0.05 equiv), ((3,3-difluorocycloprop-1-en-1-yl)methyl)(phenyl)sulfane (**2a**) (30 mg, 0.15 mmol, 1.0 equiv), and anhydrous dichloromethane (0.5 mL) and stirred at room temperature for 10 min. To this reaction mixture, a solution of *tert*-butyl 2-diazoacetate (**1a**) (21 mg, 0.15 mmol, 1.0 equiv) was added in anhydrous dichloromethane (1 mL) through a syringe pump for 3 h. Next, the reaction mixture was stirred for 12 h at room temperature. After that the reaction mixture was concentrated under reduced pressure, and the crude product was submitted to NMR analysis using CH_2Br_2 (6.0 µl, 0.075 mmol) as an internal standard.

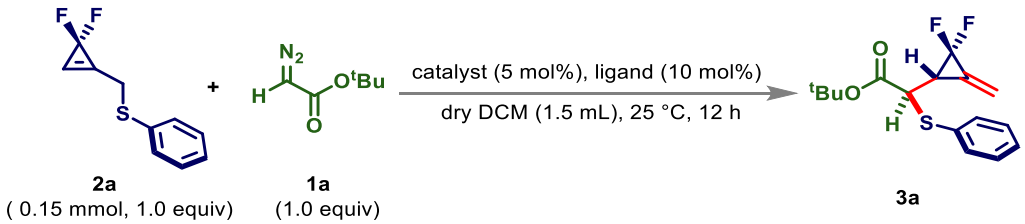


Entry	Catalyst	NMR yield (%)	*dr*
01	$[Rh(OCOCH_3)_2]_2$	22	>20:1
02	$[Rh(OCOCF_3)_2]_2$	05	>20:1
03	$[Rh(esp)]_2$	32	>20:1
04	$[Rh(COD)Cl]_2$	<05	>20:1
05	$[Rh(Cp^*Cl_2)]_2$	ND	-
06	Ag(OTf)	ND	-
07	$HAuCl_4$, H_2O	ND	-
08	$Fe(acac)_3$	ND	-
09	Fe(TPP)Cl	05	>20:1
10	CuCl	30	>20:1
11	$[Cu(MeCN)_4]PF_6$	30	>20:1
12	$CuCl_2$	23	>20:1
13	$CuBr_2$	16	>20:1

14	$Cu(OTf)_2$	ND	-
15	$Cu(acac)_2$	32	>20:1
16	CuCl, $AgNTf_2$	ND	-
17	None	ND	-

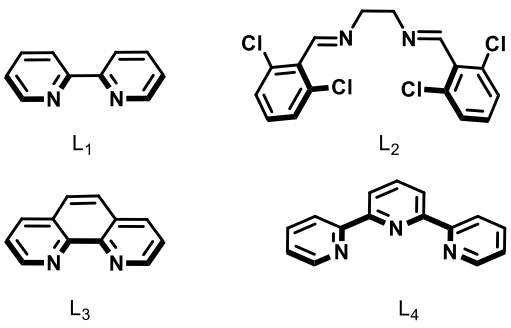
b) Screening of Ligands:

A flame dried 5 mL Schlenk tube under nitrogen was charged with catalyst (7.5 µmol, 0.05 equiv), ligand (15 µmol, 0.10 equiv), ((3,3-difluorocycloprop-1-en-1-yl)methyl)(phenyl)sulfane (**2a**) (30 mg, 0.15 mmol, 1.0 equiv), and anhydrous dichloromethane (0.5 mL) and stirred for 30 min at room temperature. To this reaction mixture, a solution of *tert*-butyl 2-diazoacetate (**1a**) (21 mg, 0.15 mmol, 1.0 equiv) in anhydrous dichloromethane (1 mL) was added through a syringe pump for 3 h. The reaction mixture was stirred for further 9 h. After that the reaction mixture was concentrated under reduced pressure, and the crude product was submitted to NMR analysis using CH_2Br_2 (6.0 µl, 0.075 mmol) as an internal standard.



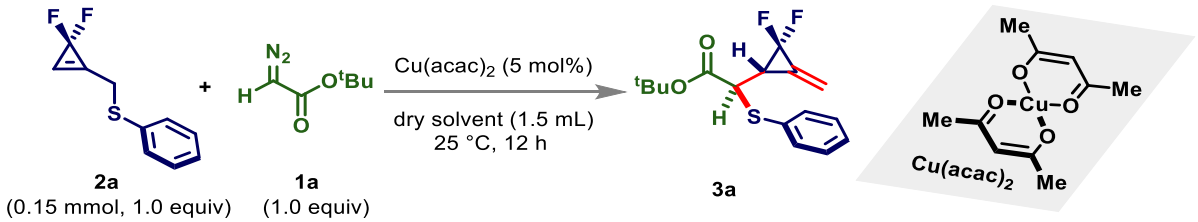
2a (0.15 mmol, 1.0 equiv) **1a** (1.0 equiv) **3a**

Entry	Catalyst	Ligand	NMR yield (%)	*dr*
01	CuCl	L_1	15	>20:1
02	CuCl	L_2	19	>20:1
03	CuCl	L_3	13	>20:1
04	CuCl	L_4	10	>20:1



c) Screening of Solvents:

A flame dried 5 mL Schlenk tube under nitrogen was charged with copper(II) acetylacetonate (2.0 mg, 7.5 µmol, 0.05 equiv) ((3,3-difluorocycloprop-1-en-1-yl)methyl)(phenyl)sulfane (**2a**) (30 mg, 0.15 mmol, 1.0 equiv), anda dry solvent (0.5 mL) and stirred at room temperature for 10 min. To this reaction mixture, a solution of *tert*-butyl 2-diazoacetate (**1a**) (21 mg, 0.15 mmol, 1.0 equiv) in anhydrous solvent (1 mL) was added through a syringe pump for 3 h. The resulting reaction mixture was stirred for 12 h. After that the reaction mixture was concentrated under reduced pressure, and the crude product was submitted to NMR analysis using CH_2Br_2 (6.0 µl, 0.075 mmol) as an internal standard.

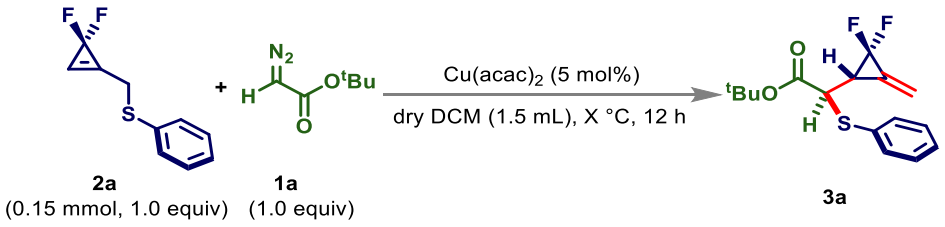


Entry	Solvent	NMR yield (%)	*dr*
01	DCM	32	>20:1
02	DCE	21	>20:1
03	THF	8	>20:1
04	Toluene	19	>20:1
05	MeCN	11	>20:1
06	Hexane	10	>20:1

d) Screening of Temperature:

A flame dried 5 mL Schlenk tube under nitrogen was charged with copper(II) acetylacetonate (2.0 mg, 7.5 µmol, 0.050 equiv), ((3,3-difluorocycloprop-1-en-1-yl)methyl)(phenyl)sulfane (**2a**) (30

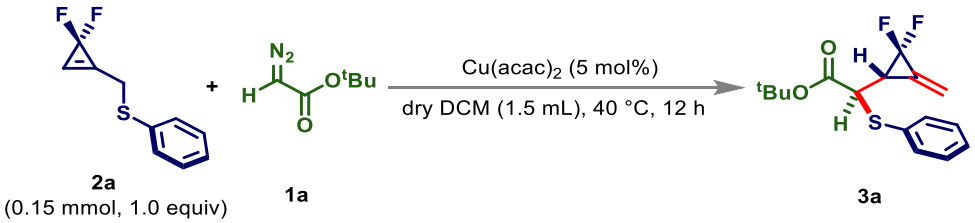
mg, 0.15 mmol, 1.0 equiv),anhydrous dichloromethane (0.5 mL) and stirred at a specific temperature for 10 min. To this reaction mixture, a solution of *tert*-butyl 2-diazoacetate (**1a**) (21 mg, 0.15 mmol, 1.0 equiv) in anhydrous dichloromethane (1 mL) was added through a syringe pump for 3 h. The reaction mixture was stirred 12 h on that specific temperature. After that the reaction mixture was concentrated under reduced pressure, and the crude product was submitted to NMR analysis using CH_2Br_2 (6.0 µl, 0.075 mmol) as an internal standard.



Entry	Temperature (°C)	NMR Yield (%)	*dr*
01	25	32	>20:1
02	0	07	>20:1
03	40	59	>20:1

e) Screening of Diazo Stoichiometry:

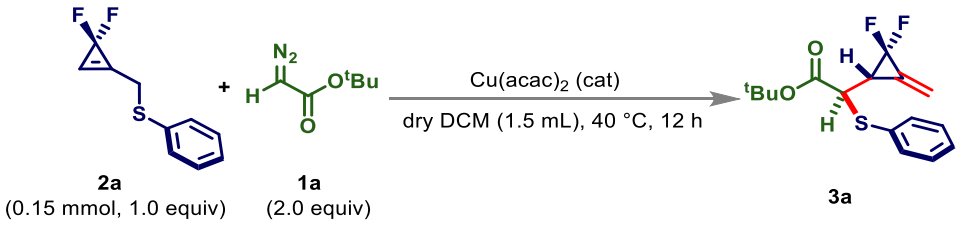
A flame dried 5 mL Schlenk tube under nitrogen was charged with copper(II) acetylacetonate (2.0 mg, 7.5 µmol, 0.050 equiv), ((3,3-difluorocycloprop-1-en-1-yl)methyl)(phenyl)sulfane (**2a**) (30.0 mg, 0.15 mmol, 1.00 equiv), and anhydrous dichloromethane (0.5 mL) and stirred for 10 min at 40 ºC. To this mixture, a solution of *tert*-butyl 2-diazoacetate (**1a**) in anhydrous dichloromethane (1 mL) was added in proper stoichiometry through a syringe pump for 3 h and stirred for 12 h at 40 ºC. After that the reaction mixture was concentrated under reduced pressure, and the crude product was submitted to NMR analysis using CH_2Br_2 (6.0 µl, 0.075 mmol) as an internal standard.



Entry	Diazo (1a) stoichiometry (equiv)	NMR yield (%)	*dr*
01	1.0	59	>20:1
02	1.5	65	>20:1
03	2.0	78	>20:1
04	3.0	75	>20:1

f) Screening of Catalyst Loading:

A flame dried 5 mL Schlenk tube under nitrogen was charged with copper(II) acetylacetonate (x mol%),((3,3-difluorocycloprop-1-en-1-yl)methyl)(phenyl)sulfane (**2a**) (30.0 mg, 0.15 mmol, 1.00 equiv), and anhydrous dichloromethane (0.5 mL) and stirred for 10 min at 40 ºC. To this reaction mixture, a solution of *tert*-butyl 2-diazoacetate (**1a**) (43 mg, 0.30 mmol, 2.0 equiv) in anhydrous dichloromethane (1 mL) was added through a syringe pump for 3 h. The resulting reaction mixture was stirred for 12 h on 40 ºC. After that the reaction mixture was concentrated under reduced pressure, and the crude product was submitted to NMR analysis using CH_2Br_2 (6.0 µl, 0.075 mmol) as an internal standard.

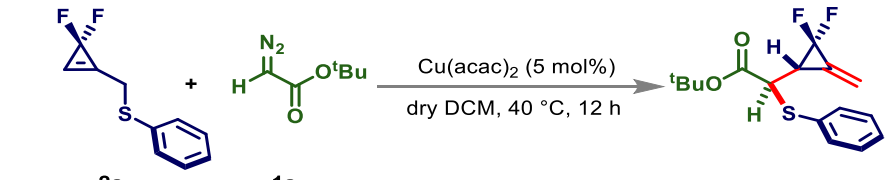


Entry	$Cu(acac)_2$ loading (mol%)	NMR yield (%)	*dr*
01	02	63	>20:1
02	05	78	>20:1
03	10	75	>20:1

g) Screening of Difluorocyclopropene 2a Concentration:

A flame dried 5 mL Schlenk tube under nitrogen was charged with copper(II) acetylacetonate (2.0 mg, 7.5 µmol, 0.050 equiv), ((3,3-difluorocycloprop-1-en-1-yl)methyl)(phenyl)sulfane (**2a**) (30 mg, 0.15 mmol, 1.0 equiv), and anhydrous dichloromethane (1/3 of total amount of solvent) and

stirred for 10 min at 40 ºC. To this reaction mixture, a solution of *tert*-butyl 2-diazoacetate (**1a**) in anhydrous dichloromethane (2/3 of total amount of solvent) was added in proper stoichiometry through a syringe pump for 3 h. The resulting reaction mixture was stirred for 12 h at 40 ºC. After that the reaction mixture was concentrated under reduced pressure, and the crude product was submitted to NMR analysis using CH_2Br_2 (6.0 µl, 0.075 mmol) as an internal standard.

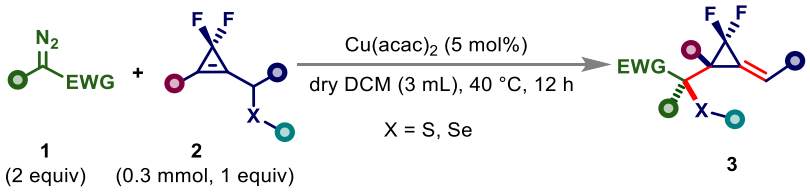


2a (0.15 mmol, 1.0 equiv) **1a** (2.0 equiv) **3a**

Entry	Difluorocyclopropene Concentration (M)	NMR yield (%)	*dr*
01	0.05	73	>20:1
02	0.10	78	>20:1
03	0.20	78	>20:1

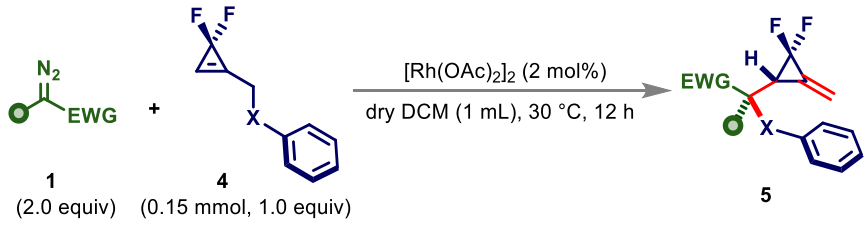
6. Synthesis of Difluoro(methylene)cyclopropanes:

General Procedure A:



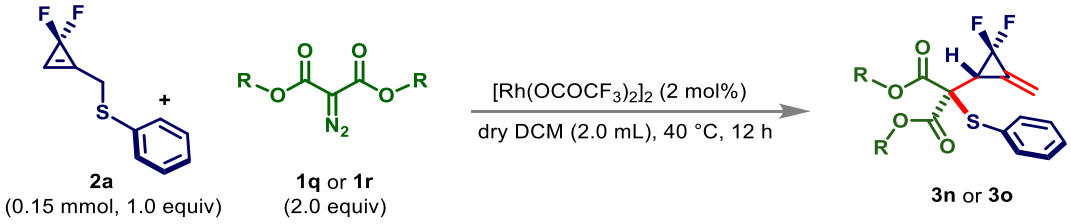
A flame dried 5 mL Schlenk tube under nitrogen was charged with copper (II) acetylacetonate (4.0 mg, 15 µmol, 0.050 equiv), difluorocyclopropene **2** (0.3 mmol, 1 equiv), and anhydrous dichloromethane (1 mL) and stirred for 10 min at 40 ºC. To this reaction mixture, a solution of diazo compound **1** (0.6 mmol, 2 equiv) in anhydrous DCM (2.0 mL) was added through a syringe pump for 3 h. The resulting reaction mixture was stirred for 12 h at 40 ºC. Next, the reaction mixture was concentrated under reduced pressure and the crude product purified by column chromatography using EtOAc:petroleum ether mixture as mobile phase.

General Procedure B:



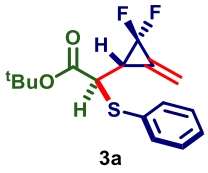
A flame dried 5 mL Schlenk tube under nitrogen was charged with diacetoxy rhodium(II) dimer (1.33 mg, 3.00 µmol, 0.020 equiv), difluorocyclopropene (0.15 mmol, 1.0 equiv), and anhydrous dichloromethane (0.5 mL) and stirred for 10 min at 30 ºC. To this mixture, a solution of diazo compound **1** (0.3 mmol, 2 equiv) in anhydrous dichloromethane (0.5 mL) was added through a syringe pump for 30 min. The resulting reaction mixture stirred for 12 h at 30 ºC. Next, the reaction mixture was concentrated under reduced pressure and the crude product was purified by column chromatography using EtOAc:petroleum ether mixture as mobile phase.

General Procedure C:



A flame dried 5 mL Schlenk tube under nitrogen was charged with bis(2,2,2-trifluoroacetoxy)rhodium (II) (4 mg, 6 µmol, 0.02 equiv), difluorocyclopropene **2a** (60 mg, 0.30 mmol, 1.0 equiv), and anhydrous dichloromethane (1 mL) and stirred for 10 min at 40 ºC. To this reaction mixture, a solution of dialkyl 2-diazomalonate (**1n** or **1o**) (0.60 mmol, 2.0 equiv) in anhydrous dichloromethane (1.0 mL) was added through a syringe pump for 30 min. The resulting reaction mixture was stirred for 12 h at 40 ºC. Next, the reaction mixture was concentrated reduced pressure and the crude product was purified by column chromatography using EtOAc:petroleum ether mixture as mobile phase.

***Tert*-butyl (*r*)-2-((*s*)-2,2-difluoro-3-methylenecyclopropyl)-2-(phenylthio)acetate (3a)**

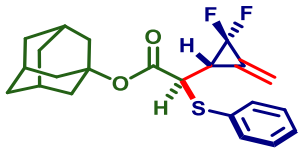


Following general procedure **A**, ((3,3-difluorocycloprop-1-en-1-yl)methyl)(phenyl)sulfane (**2a**) (60 mg, 0.30 mmol, 1.0 equiv) and *tert*-butyl 2-diazoacetate (**1a**) (85 mg, 0.60 mmol, 2.0 equiv) were stirred for 12 h. Next, the reaction mixture was concentrated under reduced pressure and the crude product was purified by column chromatography using EtOAc:petroleum ether (0.1:100) as mobile phase to afford **3a** as a yellow-oil (74.0 mg, 0.236 mmol, 79%, *dr* > 20:1). **(***See Spectra***)**

- **TLC:** R_f = 0.65 (EtOAc:petroleum ether, 1:20, v/v), $KMnO_4$
- **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.56 – 7.47 (m, 2H, Ar*H*), 7.37 – 7.29 (m, 3H, Ar*H*), 6.06 – 6.00 (m, 1H, C=C*H*aHb), 5.81 – 5.75 (m, 1H, C=CHa*H*b) 3.39 (d, *J* = 11.4 Hz, 1H, C*H*SAr), 2.63 – 2.48 (m, 1H, C*H*CF_2), 1.41 (s, 9H, OC(CH_3)$_3$).
- **^{13}C NMR (101 MHz, $CDCl_3$):** δ 169.0, 134.2, 131.8, 130.0 (t, *J* = 7.1 Hz), 129.0, 128.7, 113.7, 106.6 (dd, *J* = 292.9, 291.9 Hz,), 82.3, 49.0 (d, *J* = 3.0 Hz), 29.8 (t, *J* = 12.2 Hz), 27.8.

- **^{19}F NMR (376 MHz, $CDCl_3$) (Major Diastereomer):** δ -126.89 (d, *J* = 178.1 Hz), -139.17 (d, *J* = 177.7 Hz).
- **^{19}F NMR (376 MHz, $CDCl_3$) (Minor Diastereomer):** δ -127.97 (d, *J* = 177.8 Hz), -139.80 (d, *J* = 178.0 Hz).
- **IR (Neat, ν):** 3152 (w), 2925 (m), 2023 (w), 1730 (s), 1581 (w), 1441 (m), 1365 (m), 1260 (s), 1146 (s), 992 (w), 851 (m), 746 (m), 694 (m).
- **HRMS (ESI):** Calcd. for $C_{16}H_{18}F_2O_2SNa^+$, $[M+Na]^+$ 335.0893; found 335.0894.

(1*r*)-Adamantan-1-yl 2-((*s*)-2,2-difluoro-3-methylenecyclopropyl)-2-(phenylthio)acetate (3b)



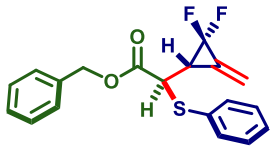
3b

Following general procedure **A**, ((3,3-difluorocycloprop-1-en-1-yl)methyl)(phenyl)sulfane (**2a**) (60 mg, 0.30 mmol, 1.0 equiv) and adamantan-1-yl 2-diazoacetate (**1b**) (132 mg, 0.600 mmol, 2.00 equiv) were stirred for 12 h. Next, the reaction mixture was concentrated under reduced pressure and the crude product was purified by column chromatography using EtOAc:petroleum ether (0.1:100) as mobile phase to afford **3b** as a yellow-oil (108 mg, 0.277 mmol, 92%, *dr* > 20:1). **(***See Spectra***)**

- **TLC:** R_f = 0.78 (EtOAc:petroleum ether, 1:20, v/v), $KMnO_4$
- **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.56 – 7.46 (m, 2H, Ar*H*), 7.37 – 7.28 (m, 3H, Ar*H*), 6.06 – 5.99 (m, 1H, C=C*H*aHb), 5.81 – 5.74 (m, 1H, C=CHa*H*b), 3.38 (dd, *J* = 10.9, 2.0 Hz, 1H, C*H*SAr), 2.61 – 2.48 (m, 1H, C*H*CF_2), 2.20 – 2.11 (m, 3H, adamantyl 3 × C*H*), 2.08 – 2.01 (m, 6H, adamantyl 3 × CH_2), 1.69 – 1.57 (m, 6H, adamantyl 3 × CH_2).
- **^{13}C NMR (101 MHz, $CDCl_3$):** δ 168.7, 134.2, 131.8, 130.0 (t, *J* = 7.2 Hz), 129.0, 128.6, 113.6, 106.6 (dd, *J* = 297.5, 291.1 Hz), 82.3, 49.1 (d, *J* = 2.9 Hz), 41.0, 36.1, 30.8, 29.8 (t, *J* = 12.2 Hz).
- **^{19}F NMR (376 MHz, $CDCl_3$) (Major Diastereomer):** δ -126.83 (d, *J* = 177.7 Hz), -139.08 (d, *J* = 177.8 Hz).
- **^{19}F NMR (376 MHz, $CDCl_3$) (Minor Diastereomer):** δ -127.94 (d, *J* = 177.6 Hz), -139.75 (d, *J* = 177.7 Hz).

- **IR (Neat, ν):** 3066 (w), 2915 (s), 2857 (m), 2350 (w), 2133 (w), 1729 (s), 1582 (w), 1442 (m), 1349 (m), 1251 (s), 1161 (s), 1053 (m), 971 (w), 883 (w), 746 (m).
- **HRMS (ESI):** Calcd. for $C_{22}H_{24}F_2O_2SNa^+$, $[M+Na]^+$ 413.1363; found 413.1363.

Benzyl (*r*)-2-((*s*)-2,2-difluoro-3-methylenecyclopropyl)-2-(phenylthio)acetate (3c)

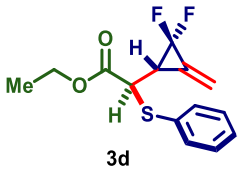


3c

Following general procedure **A**, ((3,3-difluorocycloprop-1-en-1-yl)methyl)(phenyl)sulfane (**2a**) (60 mg, 0.30 mmol, 1.0 equiv) and benzyl 2-diazoacetate (**1c**) (106 mg, 0.600 mmol, 2.00 equiv) were stirred for 12 h. Next, the reaction mixture was concentrated under reduced pressure and the crude product was purified by coloumn chromatography using EtOAc:petroleum ether (0.1:100) as mobile phase to afford **3c** as a yellow-oil (85.0 mg, 0.277 mmol, 82%, *dr* > 20:1). **(*See Spectra*)**

- **TLC:** R_f = 0.45 (EtOAc:petroleum ether, 3:100 v/v), $KMnO_4$
- **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.43 – 7.25 (m, 10H, Ar*H*), 6.10 – 6.04 (m, 1H, C=C*H*aHb), 5.90 – 5.84 (m, 1H, C=CHa*H*b), 5.24 – 5.10 (m, 2H, C*H*$_2$Ar), 3.53 – 3.50 (m, 1H, C*H*SAr), 2.67 – 2.59 (m, 1H, C*H*CF_2).
- **^{13}C NMR (101 MHz, $CDCl_3$):** δ 169.8, 135.2, 134.5, 131.0, 129.6 (d, *J* = 7.3 Hz), 129.2, 129.0, 128.5, 128.4, 128.3, 114.0, 106.5 (dd, *J* = 290.9, 291.9 Hz), 67.4, 48.0 (d, *J* = 3.2 Hz), 29.4 (t, *J* = 12.4 Hz).
- **^{19}F NMR (376 MHz, $CDCl_3$) (Major Diastereomer):** δ -126.69 (d, *J* = 178.2 Hz), -138.76 (d, *J* = 177.7 Hz).
- **^{19}F NMR (376 MHz, $CDCl_3$) (Minor Diastereomer):** δ -128.00 (d, *J* = 177.8 Hz), -139.83 (d, *J* = 177.7 Hz).
- **IR (Neat, ν):** 3066 (w), 2923 (m), 2856 (w), 2328 (w), 1737 (s), 1443 (m), 1251 (s), 1184 (s), 1084 (w), 978 (m), 828 (w), 746 (m), 696 (m).
- **HRMS (ESI):** Calcd. for $C_{19}H_{16}F_2O_2SNa^+$, $[M+Na]^+$ 369.0737; found 369.0741.

Ethyl (*r*)-2-((*s*)-2,2-difluoro-3-methylenecyclopropyl)-2-(phenylthio)acetate (3d)

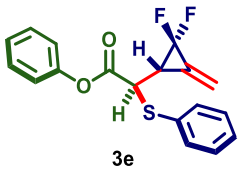


3d

Following general procedure **A**, ((3,3-difluorocycloprop-1-en-1-yl)methyl)(phenyl)sulfane (**2a**) (60 mg, 0.30 mmol, 1.0 equiv) and ethyl 2-diazoacetate (**1d**) (69 mg, 0.60 mmol, 2.0 equiv) were stirred for 12 h. Next, the reaction mixture was concentrated under reduced pressure and the crude product was purified by column chromatography using EtOAc:petroleum ether (0.25:100) as mobile phase to afford **3d** as a yellow-oil (27 mg, 0.095 mmol, 32%, *dr* > 20:1). **(***See Spectra***)**

- **TLC:** R_f = 0.59 (EtOAc:petroleum ether, 1:20 v/v), $KMnO_4$
- **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.54 – 7.45 (m, 2H, Ar*H*), 7.40 – 7.29(m, 3H, Ar*H*), 6.06 (m, 1H, C=C*H*aHb), 5.83 (m, 1H, C=CHa*H*b), 4.18 (qd, *J* = 7.1, 2.9 Hz, 2H, OC*H*$_2$CH$_3$), 3.46 (d, *J* = 10.9 Hz, 1H, C*H*SAr), 2.66 – 2.58 (m, 1H, C*H*CF_2), 1.22 (t, *J* = 7.1 Hz, 3H, OCH$_2$C*H*$_3$).
- **^{13}C NMR (101 MHz, $CDCl_3$):** δ 169.9, 134.4, 131.3, 129.7 (t, *J* = 7.3 Hz), 129.1, 129.0, 114.0, 106.5 (dd, *J* = 297.8, 290.9 Hz), 61.8, 48.1 (d, *J* = 3.2 Hz), 29.6 (t, *J* = 12.3 Hz), 13.9.
- **^{19}F NMR (376 MHz, $CDCl_3$) (Major Diastereomer):** δ -126.85 (d, *J* = 178.0 Hz), -138.95 (d, *J* = 178.1 Hz).
- **^{19}F NMR (376 MHz, $CDCl_3$) (Minor Diastereomer):** δ - 120.71 (d, *J* = 179.7 Hz), -137.57 (d, *J* = 179.7 Hz).
- **IR (Neat, ν):** 2920 (s), 2854 (m), 2357 (w), 1736 (s), 1581 (w), 1444 (m), 1371 (w), 1252 (s), 1154 (s), 1024 (m), 986 (w), 933 (w), 864 (w), 746 (m).
- **HRMS (ESI):** Calcd. for $C_{14}H_{14}F_2O_2SNa^+$, $[M+Na]^+$ 307.0580; found 307.0580.

Phenyl (*r*)-2-((*s*)-2,2-difluoro-3-methylenecyclopropyl)-2-(phenylthio)acetate (3e)

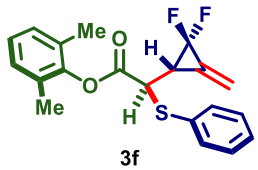


3e

Following general procedure **A**, ((3,3-difluorocycloprop-1-en-1-yl)methyl)(phenyl)sulfane (**2a**) (60 mg, 0.30 mmol, 1.0 equiv) and phenyl 2-diazoacetate (**1e**) (97 mg, 0.60 mmol, 2.0 equiv) were stirred for 12 h. Next, the reaction mixture was concentrated under reduced pressure and the crude product was purified by column chromatography using EtOAc:petroleum ether (0.1:100) as mobile phase to afford **3e** as a yellow-oil (59.0 mg, 0.178 mmol, 59%, *dr* ~ 15:1). **(***See Spectra***)**

- **TLC:** R_f = 0.55 (EtOAc:petroleum ether, 1:20 v/v), $KMnO_4$
- **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.69 – 7.56 (m, 2H, Ar*H*), 7.47 – 7.33 (m, 5H, Ar*H*), 7.31 – 7.21 (m, 1H, ArH), 7.05 (d, *J* = 7.9 Hz, 2H, Ar*H*), 6.19 – 6.12 (m, 1H, C=C*H*aHb), 6.00 - 5.94 (m, 1H, C=CHa*H*b), 3.71 (d, *J* = 11.0 Hz, 1H, C*H*SAr), 2.79 – 2.67 (m, 1H, C*H*CF_2).
- **^{13}C NMR (101 MHz, $CDCl_3$):** δ 168.5, 150.5, 135.2, 134.7, 130.8, 129.5, 129.3, 126.1, 121.2, 114.3, 106.4 (dd, *J* = 297.8, 290.9 Hz), 48.1, 29.7, 29.3 (t, *J* = 12.3 Hz).
- **^{19}F NMR (376 MHz, $CDCl_3$) (Major Diastereomer):** δ -126.66 (d, *J* = 178.3 Hz), -138.64 (d, *J* = 178.1 Hz).
- **^{19}F NMR (376 MHz, $CDCl_3$) (Minor Diastereomer):** δ -127.92 (d, *J* = 178.3 Hz), -139.59 (d, *J* = 178.3 Hz).
- **IR (Neat, ν):** 3067 (w), 2926 9w), 2359 (m), 2160 (w), 1958 (w), 1755 (s), 1590 (w), 1486 (m), 1244 (s), 1192 (s), 1132 (s), 1016 (m), 938 (w), 749 (m).
- **HRMS (ESI):** Calcd. for $C_{18}H_{14}F_2O_2SNa^+$, $[M+Na]^+$ 355.0580; found 355.0580.

2,6-Dimethylphenyl (*r*)-2-((*s*)-2,2-difluoro-3-methylenecyclopropyl)-2-(phenylthio)acetate (3f)



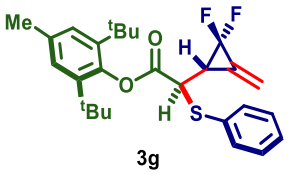
3f

Following general procedure **A**, ((3,3-difluorocycloprop-1-en-1-yl)methyl)(phenyl)sulfane (**2a**) (60 mg, 0.30 mmol, 1.0 equiv) and 2,6-dimethylphenyl 2-diazoacetate (**1f**) (114 mg, 0.600 mmol, 2.00 equiv) were stirred for 12 h. Next, the reaction mixture was concentrated under reduced pressure and the crude product was purified by column chromatography using EtOAc:petroleum ether (0.1:100) as mobile phase to afford **3f** as a yellow-oil (83 mg, 0.23 mmol, 77%, *dr* > 20:1). **(***See Spectra***)**

- **TLC:** R_f = 0. 59 (EtOAc:petroleum ether, 1:20 v/v), $KMnO_4$

- **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.65 – 7.55 (m, 2H, Ar*H*), 7.41 – 7.30 (m, 3H, Ar*H*), 7.06 (s, 3H, Ar*H*), 6.14 – 6.07 (m, 1H, C=C*H*aHb), 5.87 – 5.79 (m, 1H, C=CHa*H*b), 3.78 (dd, *J* = 11.1, 2.2 Hz, 1H, C*H*SAr), 2.83 – 2.67 (m, 1H, C*H*CF_2), 2.16 (s, 6H, 2 × ArCH_3).
- **^{13}C NMR (101 MHz, $CDCl_3$):** δ 167.9, 147.7, 134.5, 133.7, 131.6, 130.2, 129.3, 128.9, 128.7, 126.2, 114.4, 109.4 (dd, *J* =292.9, 291.9 Hz), 48.0 (d, *J* = 3.2 Hz), 29.7 (t, *J* = 12.3 Hz), 16.1.
- **^{19}F NMR (376 MHz, $CDCl_3$) (Major Diastereomer):** δ -126.79 (d, *J* = 178.8 Hz), -138.46 (d, *J* = 178.5 Hz).
- **^{19}F NMR (376 MHz, $CDCl_3$) (Minor Diastereomer):** δ -128.01 (d, *J* = 178.7 Hz), -139.54 (d, *J* = 178.4 Hz).
- **IR (Neat, ν):** 3067 (w), 2886 (m), 2569 (m), 2358 (s), 2205 (m), 1964 (s), 1755 (m), 1587 (w), 1439 (m), 1133 (s), 1084 (w), 925 (m), 857 (w), 772 (s).
- **HRMS (ESI):** Calcd. for $C_{20}H_{18}F_2O_2SNa^+$, $[M+Na]^+$ 383.0893; found 383.0895.

2,6-Di-*tert*-butyl-4-methylphenyl-(*r*)-2-((*s*)-2,2-difluoro-3-methylenecyclopropyl)-2-(phenylthio)acetate (3g)



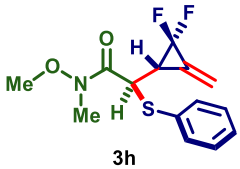
3g

Following general procedure **A**, ((3,3-difluorocycloprop-1-en-1-yl)methyl)(phenyl)sulfane (**2a)** (60 mg, 0.30 mmol, 1.0 equiv) and 2,6-di-*tert*-butyl-4-methylphenyl 2-diazoacetate (**1g**) (173 mg, 0.60 mmol, 2.0 equiv) were stirred for 12 h. Next, the reaction mixture was concentrated under reduced pressure and the crude product was purified column chromatography using petroleum ether as mobile phase to afford **3g** as a yellow-oil (129 mg, 0.281 mmol, 94%, *dr* > 20:1). **(*See Spectra*)**

- **TLC:** R_f = 0.72 (EtOAc:petroleum ether, 1:20 v/v), $KMnO_4$
- **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.62 – 7.55 (m, 2H, Ar*H*), 7.38 – 7.28 (m, 3H, Ar*H*), 7.14 (s, 2H, Ar*H*), 6.10 (s, 1H, C=C*H*aHb), 5.80 (s, 1H, C=CHa*H*b), 3.90 (d, *J* = 10.8 Hz, 1H, C*H*SAr), 2.94 – 2.82 (m, 1H, C*H*CF_2), 2.33 (s, 3H, ArCH_3), 1.37 (s, 9H, ArC(CH_3)$_3$), 1.32 (s, 9H, ArC(CH_3)$_3$).

- **^{13}C NMR (101 MHz, $CDCl_3$):** δ 170.0, 146.3, 142.3, 142.0, 135.0, 133.0, 132.6, 129.1, 128.3, 127.1 (d, *J* = 8.1 Hz), 114.8, 106.2 (dd, *J* = 299.6, 290.6 Hz), 49.3 (d, *J* = 2.9 Hz), 35.3 (d, *J* = 8.4 Hz), 31.4 (d, *J* = 4.3 Hz), 30.7 (t, *J* = 12.2 Hz), 21.4.
- **^{19}F NMR (376 MHz, $CDCl_3$) (Major Diastereomer):** δ -125.90 (d, *J* = 177.5 Hz), -135.91 (d, *J* = 177.6 Hz).
- **^{19}F NMR (376 MHz, $CDCl_3$) (Minor Diastereomer):** δ -128.23 (d, *J* = 177.7 Hz), -137.86 (d, *J* = 177.7 Hz).
- **IR (Neat, ν):** 2960 (m), 2105 (w), 1749 (s), 1593 (w), 1432 (m), 1345 (w), 1242 (s), 1178 (s), 1127 (s), 933 (m), 744 (m), 695 (m).
- **HRMS (ESI):** Calcd. for $C_{27}H_{32}F_2O_2SNa^+$, $[M+Na]^+$ 481.1989; found 481.1987.

(*r*)-2-((*s*)-2,2-Difluoro-3-methylenecyclopropyl)-*N*-methoxy-*N*-methyl-2 (phenylthio)acetamide (3h)

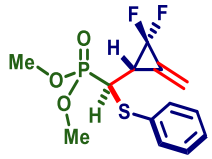


3h

Following general procedure **A**, ((3,3-difluorocycloprop-1-en-1-yl)methyl)(phenyl)sulfane (**2a**) (60 mg, 0.30 mmol, 1.0 equiv) and 2-diazo-*N*-methoxy-*N*-methylacetamide (**1g**) (77 mg, 0.60 mmol, 2.0 equiv) were stirred for 12 h. Next, the reaction mixture was concentrated under reduced pressure and the crude product purified by chromatography using EtOAc:petroleum ether (1:20) as mobile phase to afford **3h** as a yellow-oil (33 mg, 0.11 mmol, 37%, *dr* > 20:1). **(*See Spectra*)**

- **TLC:** R_f = 0.16 (EtOAc:petroleum ether, 1:10 v/v), $KMnO_4$
- **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.59 – 7.45 (m, 2H, Ar*H*), 7.41 – 7.28 (m, 3H, Ar*H*), 6.06 – 6.01 (m, 1H, C=C*H*aHb), 5.78 – 5.72 (m, 1H, C=CHa*H*b), 3.96 (d, *J* = 10.8 Hz, 1H, C*H*SAr), 3.67 (s, 3H, OCH_3), 3.21 (s, 3H, NCH_3), 2.83 – 2.70 (m, 1H, C*H*CF_2).
- **^{13}C NMR (101 MHz, $CDCl_3$):** δ 170.2, 134.9, 130.9, 130.2 (t, *J* = 7.1 Hz), 129.0, 129.0, 113.7, 107.0 (dd, *J* = 298.7, 289.8 Hz), 61.4, 43.8, 32.4, 29.9 (t, *J* = 11.8 Hz).
- **^{19}F NMR (376 MHz, $CDCl_3$):** δ -126.69 (d, *J* = 177.8 Hz), -139.14 (d, *J* = 177.9 Hz).
- **IR (Neat, ν):** 3065 (w), 2924 (s), 2856 (m), 2326 (w), 1730 (m), 1666 (s), 1442 (m), 1270 (s), 1163 (S), 1004 (m), 860 (w), 748 (m), 695 (m).
- **HRMS (ESI):** Calcd. for $C_{14}H_{15}F_2O_2SNa^+$, $[M+Na]^+$ 322.0689; found 322.0689.

Dimethyl ((*r*)-((*s*)-2,2-difluoro-3-methylenecyclopropyl)(phenylthio)methyl)phosphonate (3i)

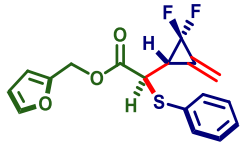


3i

Following general procedure **A**, ((3,3-difluorocycloprop-1-en-1-yl)methyl)(phenyl)sulfane (**2a**) (60 mg, 0.30 mmol, 1.0 equiv) and dimethyl (diazomethyl)phosphonate (**1i**) (90 mg, 0.60 mmol, 2.0 equiv) were stirred for 12 h. Next, the reaction mixture was concentrated under reduced pressure and the crude product was purified by column chromatography using EtOAc:petroleum ether (1:10) as mobile phase to afford **3i** as a yellow-oil (50 mg, 0.16 mmol, 52%, *dr* > 20:1). **(***See Spectra***)**

- **TLC:** R_f = 0.33 (EtOAc:petroleum ether, 1:2 v/v), $KMnO_4$
- **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.61 – 7.50 (m, 2H, Ar*H*), 7.36 – 7.27 (m, 3H, Ar*H*), 6.01 (s, 1H, C=C*H*aHb), 5.72 (s, 1H, C=CHa*H*b), 3.83 (dd, *J* = 10.8, 5.0 Hz, 6H, P(O)(OC*H*$_3$)$_2$), 3.09 (dd, *J* = 16.6, 11.5 Hz, 1H, C*H*SAr), 2.64 – 2.51 (m, 1H, C*H*CF_2).
- **^{13}C NMR (101 MHz, $CDCl_3$):** δ 133.0, 129.4 (dt, *J* = 14.9, 7.1 Hz), 129.1, 128.3, 114.3, 106.2 (ddd, *J* = 292.9, 293.9 Hz), 54.0 (d, *J* = 7.0 Hz), 53.8 (d, *J* = 7.2 Hz), 42.8 (d, *J* = 2.8 Hz), 41.3 (d, *J* = 2.7 Hz), 29.2 (t, *J* = 12.3 Hz).
- **^{19}F NMR (376 MHz, $CDCl_3$) (Major Diastereomer):** δ -126.30 (dd, *J* = 176.7, 3.3 Hz), -137.29 (dd, *J* = 176.4, 7.3 Hz).
- **^{19}F NMR (376 MHz, $CDCl_3$) (Minor Diastereomer):** δ -118.47 (dd, *J* = 177.9, 10.1 Hz), -135.69 (dd, *J* = 178.0, 3.4 Hz),
- **^{31}P NMR (162 MHz, $CDCl_3$):** δ 24.01 (d, *J* = 6.8 Hz).
- **IR (Neat, ν):** 2955 (w), 2854 (w), 2333 (w), 1970 (w), 1752 (w)1580 (w), 1439 (w), 1259 (s), 1185 (m), 1032 (s), 970 (m), 827 (m), 752 (w), 695 (w).
- **HRMS (ESI):** Calcd. for $C_{13}H_{15}F_2O_3PSNa^+$, $[M+Na]^+$ 343.0345; found 343.0348.

Furan-2-ylmethyl (*r*)-2-((*s*)-2,2-difluoro-3-methylenecyclopropyl)-2-(phenylthio)acetate (3j)

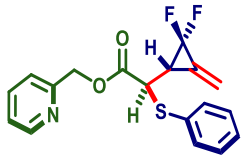


3j

Following general procedure **B**, ((3,3-difluorocycloprop-1-en-1-yl)methyl)(phenyl)sulfane (**2a**) (60 mg, 0.30 mmol, 1.0 equiv) and furan-2-ylmethyl 2-diazoacetate (**1j**) (100 mg, 0.600 mmol, 2.00 equiv) were stirred for 12 h. Next, the reaction mixture was concentrated under reduced pressure and the crude product was purified by column chromatography using EtOAc:petroleum ether (0.5:100) as mobile phase to afford **3j** as a yellow-oil (72 mg, 0.21 mmol, 71%, *dr* > 20:1). **(***See Spectra***)**

- **TLC:** R_f = 0.45 (EtOAc:petroleum ether, 1:20 v/v), $KMnO_4$
- **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.45 – 7.34 (m, 3H, Ar*H*), 7.34 – 7.21 (m, 3H, 2 Ar*H* + 1 furan*H*), 6.44 – 6.31 (m, 2H, furan*H*), 6.06 – 6.02 (m, 1H, C=C*H*aHb), 5.89 – 5.83 (m, 1H, C=CHa*H*b), 5.17 – 5.02 (m, 2H, OCH_2furan), 3.47 – 3.38 (m, 1H, C*H*SAr), 2.63 – 2.52 (m, 1H, C*H*CF_2).
- **^{13}C NMR (101 MHz, $CDCl_3$):** δ 169.6, 148.8, 143.4, 134.8 (d, *J* = 1.9 Hz), 130.7 (d, *J* = 3.5 Hz), 129.5 (t, *J* = 7.3 Hz), 129.1, 114.0 (d, *J* = 2.2 Hz), 111.2 (d, *J* = 1.7 Hz), 110.6, 106.4 (dd, *J* = 297.9, 291.0 Hz), 59.0, 47.8 (d, *J* = 3.2 Hz), 30.9, 29.3 (t, *J* = 12.3 Hz).
- **^{19}F NMR (376 MHz, $CDCl_3$) (Major Diastereomer):** δ -126.76 (d, *J* = 178.0 Hz), -138.87 (d, *J* = 178.0 Hz).
- **^{19}F NMR (376 MHz, $CDCl_3$) (Minor Diastereomer):** δ -128.03 (d, *J* = 178.5 Hz), -139.81 (d, *J* = 178.5 Hz).
- **IR (Neat, ν):** 3061 (w), 2875 (w), 2133 (w), 1985 (m), 1835 (m)1600 (w), 1545 (m), 1259 (s), 1185 (m), 1032 (s), 933 (m), 869 (m).
- **HRMS (ESI):** Calcd. for $C_{17}H_{14}F_2O_3SNa^+$, $[M+Na]^+$ 359.0529; found 359.0533.

Pyridin-2-ylmethyl (*r*)-2-((*s*)-2,2-difluoro-3-methylenecyclopropyl)-2-(phenylthio)acetate (3k)

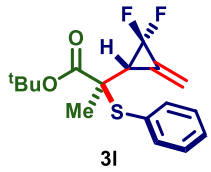


3k

Following general procedure **B**, ((3,3-difluorocycloprop-1-en-1-yl)methyl)(phenyl)sulfane (**2a**) (60 mg, 0.30 mmol, 1.0 equiv) and pyridin-2-ylmethyl 2-diazoacetate (**1k**) (106 mg, 0.600 mmol, 2.00 equiv) were stirred for 12 h. Next, the reaction mixture was concentrated under reduced pressure and the crude product was purified by column chromatography using EtOAc:petroleum ether (10:100) as mobile phase to afford **3k** as a yellow-oil (69 mg, 0.20 mmol, 67%, *dr* > 20:1). **(***See Spectra***)**

- **TLC:** R_f = 0.20 (EtOAc:petroleum ether, 1:5 v/v), $KMnO_4$
- **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.45 (d, *J* = 4.8 Hz, 1H, pyridine*H*), 7.54 (t, *J* = 7.7, 1.8 Hz, 1H, pyridine*H*), 7.35 – 7.28 (m, 2H, pyridine*H*), 7.24 – 7.05 (m, 5H, Ar*H*), 5.98 – 5.93 (m, 1H, C=C*H*aHb), 5.77 – 5.71 (m, 1H, C=CHa*H*b), 5.24 – 5.09 (m, 2H, OCH_2pyridine), 3.49 – 3.40 (m, 1H, C*H*SAr), 2.59 – 2.46 (m, 1H, C*H*CF_2).
- **^{13}C NMR (101 MHz, $CDCl_3$):** δ 169.6, 155.2, 149.3, 136.8, 134.5, 130.9, 129.4 (t, *J* = 7.3 Hz), 129.2, 129.1, 122.9, 121.4, 114.2, 106.4 (dd, *J* = 298.2, 291.0 Hz), 67.6, 47.9 (d, *J* = 3.2 Hz), 29.4 (t, *J* = 12.2 Hz).
- **^{19}F NMR (376 MHz, $CDCl_3$) (Major Diastereomer):** δ -126.67 (d, *J* = 178.1 Hz), -138.65 (d, *J* = 178.4 Hz).
- **^{19}F NMR (376 MHz, $CDCl_3$) (Minor Diastereomer):** δ -128.01 (d, *J* = 178.3 Hz), -139.77 (d, *J* = 178.3 Hz).
- **IR (Neat, ν):** 3059 (w), 2915 (w), 2215 (m), 2000 (w), 1855 (w)1765 (m), 1635 (m), 1457 (s), 1233 (m), 1111 (s), 897 (m), 733 (w).
- **HRMS (ESI):** Calcd. for $C_{18}H_{16}F_2NO_2S^+$, $[M+H]^+$ 348.0870; found 348.0863.

***Tert*-butyl (*r*)-2-((*s*)-2,2-difluoro-3-methylenecyclopropyl)-2-(phenylthio)propanoate (3l)**

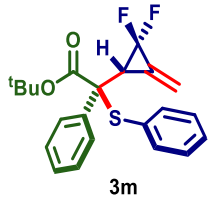


3l

Following general procedure **A**, ((3,3-difluorocycloprop-1-en-1-yl)methyl)(phenyl)sulfane (**2a**) (60 mg, 0.30 mmol, 1.0 equiv) and *tert*-butyl 2-diazopropanoate (**1l**) (94 mg, 0.60 mmol, 2.0 equiv) were stirred for 12 h. Next, the reaction mixture was concentrated under reduced pressure and the crude product was purified by column chromatography using petroleum ether as mobile phase to afford **3l** as a yellow-oil (81 mg, 0.25 mmol, 83%, *dr* > 20:1). **(***See Spectra***)**

- **TLC:** R_f = 0.66 (EtOAc:petroleum ether, 1:20, v/v), $KMnO_4$
- **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.58 – 7.50 (m, 2H, Ar*H*), 7.48 – 7.30 (m, 3H, Ar*H*), 6.08 – 6.02 (m, 1H, C=C*H*aHb), 5.69 – 5.63 (m, 1H, C=CHa*H*b), 2.65 (dq, *J* = 11.8, 3.4 Hz, 1H, C*H*CF_2), 1.45 (s, 9H, OC(CH_3)$_3$), 1.30 (d, *J* = 1.8 Hz, 3H, CH_3C(SAr)).
- **^{13}C NMR (101 MHz, $CDCl_3$):** δ 170.9, 137.2, 132.6, 130.5, 129.8, 128.9, 113.3, 106.9 (dd, *J* = 295.9, 293.9 Hz), 82.1, 53.1, 34.9 (t, *J* = 11.8 Hz), 27.7, 19.6 (d, *J* = 5.8 Hz).
- **^{19}F NMR (376 MHz, $CDCl_3$) (Major Diastereomer):** δ -122.58 (d, *J* = 181.0 Hz), -138.81 (d, *J* = 180.8 Hz).
- **^{19}F NMR (376 MHz, $CDCl_3$) (Minor Diastereomer):** δ -121.17 (d, *J* = 181.1 Hz), -139.97 (d, *J* = 181.2 Hz).
- **IR (Neat, ν):** 3064 (w), 2980 (w), 2933 (w), 1948 (w), 1726 (s), 1440 (w), 1319 (m), 1256 (s), 1167 (s), 1106 (m), 933 (m), 849 (w), 750 (m).
- **HRMS (ESI):** Calcd. for $C_{17}H_{20}F_2O_2SNa^+$, $[M+Na]^+$ 349.1050; found 349.1050.

***Tert*-butyl (*s*)-2-((*s*)-2,2-difluoro-3-methylenecyclopropyl)-2-phenyl-2-(phenylthio)acetate (3m)**



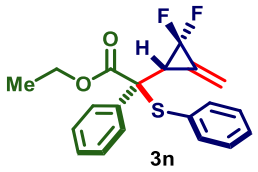
3m

Following general procedure **A**, ((3,3-difluorocycloprop-1-en-1-yl)methyl)(phenyl)sulfane (**2a**) (60 mg, 0.30 mmol, 1.0 equiv) and *tert*-butyl 2-diazo-2-phenylacetate (**1m**) (131 mg, 0.600 mmol,

2.00 equiv) were stirred for 12 h. Next, the reaction mixture was concentrated under reduced pressure, and the crude product was purified by column chromatography using petroleum ether as mobile phase to afford **3m** as a yellow solid (inseparable diastereomeric mixture) (94 mg, 0.24 mmol, 81%, *dr* ~ 4:1). Crystallization using hexane and dichloromethane mixture led to the pure major diastereomer. **(***See Spectra***)**

- **TLC:** R_f = 0.78 (EtOAc:petroleum ether, 1:20, v/v), $KMnO_4$
- **Melting Point (Major Diastereomer):** 127.5 – 129.4 ºC.
- **^{1}H NMR (400 MHz, $CDCl_3$) (Major Diastereomer):** δ 7.42 – 7.36 (m, 2H, Ar*H*), 7.34 – 7.23 (m, 6H, Ar*H*), 7.23 – 7.16 (m, 2H, Ar*H*), 6.07 – 6.00 (m, 1H, C=C*H*aHb), 5.75 – 5.69 (m, 1H, C=CHa*H*b), 2.73 (dq, *J* = 11.5, 3.4 Hz, 1H, C*H*CF_2), 1.37 (s, 9H, OC(CH_3)$_3$).
- **^{13}C NMR (101 MHz, $CDCl_3$) (Major Diastereomer):** δ 168.2, 139.1, 137.2, 130.8, 130.2 (t, *J* = 7.1 Hz), 129.4, 128.6, 128.0, 127.8, 127.7, 113.1, 106.0 (dd, *J* = 295.7, 291.7 Hz), 83.4, 63.5, 34.7 (t, *J* = 12.0 Hz), 27.6.
- **^{19}F NMR (376 MHz, $CDCl_3$) (Major Diastereomer):** δ -122.54 (d, *J* = 180.4 Hz), -139.06 (d, *J* = 180.4 Hz).
- **IR (Neat, ν):** 2921 (s), 2856 (s), 2306 (w), 1729 (m), 1590 (w), 1454 (m), 1370 (w), 1254 (m), 1151 (s), 1025 (w), 843 (m), 746 (s), 696 (s).
- **HRMS (ESI):** Calcd. for $C_{22}H_{22}F_2O_2SNa^+$, $[M+Na]^+$ 411.1206; found 411.1207.

Ethyl (*s*)-2-((*s*)-2,2-difluoro-3-methylenecyclopropyl)-2-phenyl-2-(phenylthio)acetate (3n)



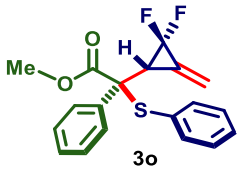
3n

Following general procedure **A**, ((3,3-difluorocycloprop-1-en-1-yl)methyl)(phenyl)sulfane (**2a**) (60 mg, 0.30 mmol, 1.0 equiv) and ethyl 2-diazo-2-phenylacetate (**1n**) (114 mg, 0.600 mmol, 2.00 equiv) were stirred 12 h. The crude reaction mixture was concentrated under reduced pressure and purified by column chromatography using petroleum ether as mobile phase to afford **3n** as a yellow-oil (inseparable diastereomeric mixture) (64 mg, 0.18 mmol, 59%, *dr* ~ 1.1:1). **(***See Spectra***)**

- **TLC:** R_f = 0.69 (EtOAc:petroleum ether, 1:20 v/v), $KMnO_4$

- **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.46 – 7.20 (m, 10H, Ar*H* for both diastereomers), 6.06 – 6.00 (m, 0.6H, C=C*H*aHb for major diastereomer), 5.98 – 5.92 (m, 0.4H, C=C*H*aHb for minor diastereomer), 5.82 – 5.77 (m, 0.6H, C=CHa*H*b for major diastereomer), 5.61 – 5.55 (m, 0.4H, C=CHa*H*b for minor diastereomer), 4.28 – 4.09 (m, 2H, OCH_2CH_3 for both diastereomers), 2.98 – 2.88 (m, 0.4H, C*H*CF_2 for minor diastereomer), 2.86 – 2.76 (m, 0.6H, C*H*CF_2 for major diastereomer), 1.20 (t, *J* = 7.2 Hz, 3H, OCH_2CH_3 for both diastereomers).
- **^{13}C NMR (101 MHz, $CDCl_3$) (for both diastereomers):** δ 170.6, 169.8, 137.8, 137.3, 137.2, 136.9, 130.5, 130.3, 129.8, 129.7, 128.8, 128.7, 128.3, 128.1, 128.0, 128.0, 127.9, 127.8, 114.0, 113.5, 105.9 (dd, *J* = 292.9, 291.9 Hz), 62.9, 62.3, 62.2, 36.1(t, *J* = 12.1 Hz), 34.9 (t, *J* = 13.1 Hz), 13.9, 13.8. Four carbons were not resolved at 101 MHz.
- **^{19}F NMR (376 MHz, $CDCl_3$) (Major Diastereomer):** δ -122.02 (d, *J* = 180.6 Hz), -139.50 (d, *J* = 180.4 Hz).
- **^{19}F NMR (376 MHz, $CDCl_3$) (Minor Diastereomer):** δ -120.80 (d, *J* = 179.0 Hz), -139.22 (d, *J* = 178.9 Hz).
- **IR (Neat, ν):** 3063 (w), 2983 (m), 2926 (m), 2360 (w), 2165 (w), 1957 (w), 1730 (s), 1587 (w), 1441 (m), 1316 (m), 1227 (s), 1164 (s), 1024 (m), 930 (w), 749 (m), 697 (m).
- **HRMS (ESI):** Calcd. for $C_{20}H_{18}F_2O_2SNa^+$, $[M+Na]^+$ 383.0893; found 383.0894.

Methyl (*s*)-2-((*s*)-2,2-difluoro-3-methylenecyclopropyl)-2-phenyl-2-(phenylthio)acetate (3o)



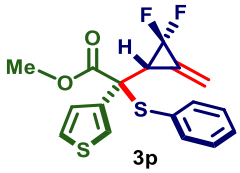
3o

Following general procedure **A**, ((3,3-difluorocycloprop-1-en-1-yl)methyl)(phenyl)sulfane (**2a**) (60 mg, 0.30 mmol, 1.0 equiv) and methyl 2-diazo-2-phenylacetate (**1o**) (106 mg, 0.600 mmol, 2.00 equiv) were stirred 12 h. The crude reaction mixture was concentrated under reduced pressure and purified by column chromatography using petroleum ether as mobile phase to afford **3o** as a yellow-oil (59 mg, 0.17 mmol, 57%, *dr* ~ 1.7:1). **(***See Spectra***)**

- **TLC:** R_f = 0.55 **(**EtOAc:petroleum ether, 1:20 v/v), $KMnO_4$

- **^{1}H NMR (400 MHz, $CDCl_3$) (Major Diastereomer):** δ 7.45 – 7.36 (m, 3H, Ar*H*), 7.34 – 7.26 (m, 6H, Ar*H*), 7.13 – 7.08 (m, 1H, Ar*H*), 6.00 – 5.91 (m, 1H, C=C*H*aHb), 5.54 – 5.46 (m, 1H, C=CHa*H*b), 3.72 (s, 3H, OCH_3), 2.89 – 2.77 (m, 1H, C*H*CF_2).
- **^{1}H NMR (400 MHz, $CDCl_3$) (Minor Diastereomer):** δ 7.43 – 7.26 (m, 8H, Ar*H*), 7.17 – 7.08 (m, 2H, Ar*H*), 6.08 – 6.03 (m, 1H, C=C*H*aHb), 5.87 – 5.82 (m, 1H, C=CHa*H*b), 3.76 (s, 3H, OCH_3), 2.81 – 2.72 (m, 1H, C*H*CF_2).
- **^{13}C NMR (101 MHz, $CDCl_3$) (Minor Diastereomer):** δ 170.2, 137.3, 137.0 (d, J = 2.0 Hz), 130.3 (d, J = 3.9 Hz), 130.0 (d, J = 2.5 Hz), 129.2, 128.9 (d, J = 2.0 Hz), 127.8, 125.2 (d, J = 3.6 Hz), 124.3, 113.9 (d, J = 3.9 Hz), 105.9 (dd, *J* = 293.9, 293.9 Hz), 59.3, 53.0 (d, J = 3.5 Hz), 35.4 – 34.9 (m).
- **^{19}F NMR (376 MHz, $CDCl_3$) (Major Diastereomer):** δ -121.42 (d, *J* = 178.9 Hz), -139.32 (d, *J* = 179.1 Hz).
- **^{19}F NMR (376 MHz, $CDCl_3$) (Minor Diastereomer):** δ -121.99 (d, *J* = 180.3 Hz), -139.60 (d, *J* = 179.6 Hz).
- **IR (Neat, ν):** 3061 (w), 2983 (m), 2825 (m), 2420 (w), 2185 (w), 1957 (w), 1750 (s), 1595 (w), 1437 (m), 1325 (m), 1229 (s), 1167 (s), 1027 (m), 932 (w)**.**
- **HRMS (ESI):** Calcd. for $C_{19}H_{16}F_2O_2SNa^+$, $[M+Na]^+$ 346.0839; not found.

Methyl (S)-2-((S)-2,2-difluoro-3-methylenecyclopropyl)-2-(phenylthio)-2-(thiophen-3-yl)acetate (3p)

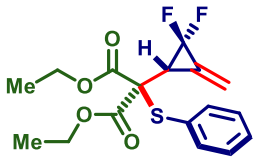


3p

Following general procedure **B**, ((3,3-difluorocycloprop-1-en-1-yl)methyl)(phenyl)sulfane (**2a**) (60 mg, 0.30 mmol, 1.0 equiv) and methyl 2-diazo-2-(thiophen-3-yl)acetate (**1p**) (110 mg, 0.600 mmol, 2.00 equiv) were stirred 12 h. The crude reaction mixture was concentrated under reduced pressure and purified by column chromatography using EtOAc:petroleum ether (0.5:100) as mobile phase to afford **3p** as a yellow-oil (inseparable diastereomeric mixture) (45 mg, 0.13 mmol, 43%, *dr* ~ 1.6:1). **(***See Spectra***)**

- **TLC:** R_f = 0.35 **(**EtOAc:petroleum ether, 1:20 v/v), $KMnO_4$
- **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.47 – 7.24 (m, 6.7H, Ar*H* + thiophene*H* for both diastereomers), 7.17 – 7.07 (m, 1.3H, thiophene*H* for major diastereomer), 6.08 – 6.04 (m, 0.37H, C=C*H*aHb for minor diastereomer), 5.99 – 5.91 (m, 0.63H, C=C*H*aHb for major diastereomer), 5.87 – 5.82 (m, 0.37H, C=CHa*H*b for minor diastereomer), 5.52 – 5.48 (m, 0.63H, C=CHa*H*b for major diastereomer), 3.75 (s, 1.1H, OCH_3 for minor diastereomer), 3.72 (s, 1.9H, OCH_3 for major diastereomer), 2.87 – 2.72 (m, 1H, C*H*CF_2 for both diastereomers).
- **^{13}C NMR (101 MHz, $CDCl_3$) (for both Diastereomers):** δ 170.3, 170.2, 137.4, 137.2, 137.0, 130.3, 130.1, 130.0, 129.9, 129.0, 128.9, 128.1, 127.8, 125.3, 125.2, 124.3, 124.1, 114.0, 113.9, 105.9 (dd, *J* = 289.9, 289.9 Hz), 105.8 (dd, *J* = 290.1, 290.1 Hz), 64.2, 59.3, 58.9, 53.0, 52.9, 35.8 (t, *J* = 12.1 Hz), 35.2 (t, *J* = 12.0 Hz). Two carbons were not resolved at 101 MHz.
- **^{19}F NMR (376 MHz, $CDCl_3$) (Major Diastereomer):** δ -121.41 (d, *J* = 179.1 Hz), -139.32 (d, *J* = 179.1 Hz).
- **^{19}F NMR (376 MHz, $CDCl_3$) (Minor Diastereomer):** δ -121.99 (d, *J* = 179.8 Hz), -139.59 (d, *J* = 179.8 Hz).
- **IR (Neat, ν):** 3265 (w), 3011 (w), 2987 (w), 2665 (m), 2225 (w), 1856 (w), 1695 (s), 1536 (m), 1489 (w), 1269 (s), 1189 (s), 989 (w), 736 (w)**.**
- **HRMS (ESI):** Calcd. for $C_{17}H_{14}F_2O_2S_2Na^+$, $[M+Na]^+$ 375.0301; found 375.0305.

Diethyl (*s*)-2-(2,2-difluoro-3-methylenecyclopropyl)-2-(phenylthio)malonate (3q)

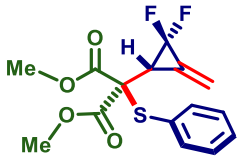


3q

Following general procedure **C**, ((3,3-difluorocycloprop-1-en-1-yl)methyl)(phenyl)sulfane (**2a**) (60 mg, 0.30 mmol, 1.0 equiv) and diethyl 2-diazomalonate (**1q**) (112 mg, 0.600 mmol, 2.00 equiv) were stirred for 12 h. The crude reaction mixture was concentrated under reduced pressure and purified by column chromatography using EtOAc:petroleum ether (1:10) as mobile phase to afford **3q** as a yellow-oil (94 mg, 0.26 mmol, 88%). **(***See Spectra***)**

- **TLC:** R_f = 0.65 (EtOAc:petroleum ether, 1:5 v/v), $KMnO_4$
- **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.60 (d, *J* = 7.3 Hz, 2H, Ar*H*), 7.46 – 7.31 (m, 3H, Ar*H*), 6.04 (m, 1H, C=C*H*aHb), 5.68 – 5.61 (m, 1H, C=CHa*H*b), 4.27 – 4.13 (m, 4H, OC*H*$_2$CH$_3$), 2.76 (dq, *J* = 10.3, 3.5 Hz, 1H, C*H*CF$_2$), 1.24 (td, *J* = 7.1, 4.8 Hz, 6H, OCH$_2$C*H*$_3$).
- **^{13}C NMR (101 MHz, $CDCl_3$):** δ 166.7 (d, *J* = 2.0 Hz), 165.7, 137.5, 130.3, 129.01, 129.0, 128.2 (t, *J* = 7.3 Hz), 114.4, 105.3 (dd, *J* = 297.5, 290.7 Hz), 62.7, 62.6, 62.4 (t, *J* = 2.6 Hz), 32.9 (t, *J* = 12.7 Hz), 13.8 (d, *J* = 3.7 Hz). One carbon was not resolved in 101 MHz.
- **^{19}F NMR (376 MHz, $CDCl_3$):** δ -123.75 (d, *J* = 181.0 Hz), -138.08 (d, *J* = 180.9 Hz).
- **IR (Neat, ν):** 2920 (s), 2854 9m), 2474 (w), 2359 (m), 2161 (w),1890 (w), 1737 (s), 1591 (w), 1452 (m), 12159 (m), 1028 w), 862 (w), 756 (s),
- **HRMS (ESI):** Calcd. for $C_{17}H_{18}F_2O_4SNa^+$, $[M+Na]^+$ 379.0792; found 379.0793.

Dimethyl (*s*)-2-(2,2-difluoro-3-methylenecyclopropyl)-2-(phenylthio)malonate (3r)



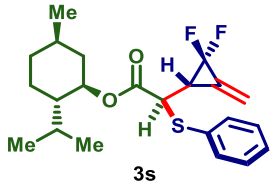
3r

Following general procedure **C**, ((3,3-difluorocycloprop-1-en-1-yl)methyl)(phenyl)sulfane (**2a**) (60 mg, 0.30 mmol, 1.0 equiv) and dimethyl 2-diazomalonate (**1r**) (95 mg, 0.60 mmol, 2.0 equiv) were stirred for 12 h. The crude reaction mixture was concentrated under reduced pressure and purified by column chromatography using EtOAc:petroleum ether (1:10) as mobile phase to afford **3r** as a yellow-oil (66 mg, 0.20 mmol, 67%). **(*See Spectra*)**

- **TLC:** R_f = 0.57 (EtOAc:petroleum ether, 1:5 v/v), $KMnO_4$
- **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.60 – 7.54 (m, 2H, Ar*H*), 7.47 – 7.41 (m, 1H, Ar*H*), 7.41 – 7.31 (m, 2H, Ar*H*), 6.09 – 6.02 (m, 1H, C=C*H*aHb), 5.71 – 5.65 (m, 1H, C=CHa*H*b), 3.74 (s, 3H, OC*H*$_3$), 3.73 (s, 3H, OC*H*$_3$), 2.82 – 2.73 (m, 1H, C*H*CF$_2$).
- **^{13}C NMR (101 MHz, $CDCl_3$):** δ 167.1 (d, *J* = 2.0 Hz), 166.2, 137.5, 130.5, 129.2, 128.8, 127.9 (t, *J* = 7.3 Hz), 114.6, 105.3 (dd, J = 297.8, 290.6 Hz), 62.5, 53.3, 32.8 (t, *J* = 12.8 Hz). One carbon was not resolved in 101 MHz.
- **^{19}F NMR (376 MHz, $CDCl_3$):** δ -123.71 (d, *J* = 181.1 Hz), -138.60 (d, *J* = 181.1 Hz).

- **IR (Neat, ν):** 2895 (s), 2835 (m), 2425 (m), 2225 (w), 2096 (w), 1895 (w), 1725 (s), 1591 (w), 1452 (m), 1215 (m), 1033 (w), 876 (w).
- **HRMS (ESI):** Calcd. for $C_{15}H_{14}F_2O_4SNa^+$, $[M+Na]^+$ 351.0479; found 351.0477.

(1*R*,2*S*,5*R*)-2-*Iso*propyl-5-methylcyclohexyl (*r*)-2-((*s*)-2,2-difluoro-3-methylenecyclopropyl)-2-(phenylthio)acetate (3s)



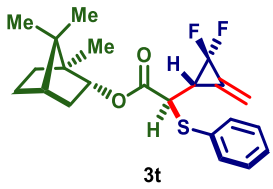
3s

Following general procedure **A**, ((3,3-difluorocycloprop-1-en-1-yl)methyl)(phenyl)sulfane (**2a**) (60 mg, 0.30 mmol, 1.0 equiv) and (1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl 2-diazoacetate (**1s**) (135 mg, 0.600 mmol, 2.00 equiv) were stirred for 12 h. Next, the reaction mixture was concentrated under reduced pressure and the crude product was purified by column chromatography using EtOAc:petroleum ether (0.1:100) as mobile phase to afford **3s** as a yellow oil (inseparable diastereomeric mixture) (102 mg, 0.256 mmol, 86%, *dr* > 20(1:1):1(1:1)). **(***See Spectra***)**

- **TLC:** R_f = 0.68 (EtOAc:petroleum ether, 1:20, v/v), $KMnO_4$
- **^{1}H NMR (400 MHz, $CDCl_3$) (Major Diastereomeric Pair):** δ 7.54 – 7.45 (m, 2H, Ar*H*), 7.37 – 7.29 (m, 3H, Ar*H*), 6.07 – 6.02 (m, 1H, C=C*H*aHb), 5.81 – 5.76 (m, 1H, C=CHa*H*b), 4.71 (td, *J* = 10.6, 4.0 Hz, 1H, OC*H*), 3.52 – 3.40 (m, 1H, C*H*SAr), 2.68 – 2.54 (m, 1H, C*H*CF_2), 2.03 – 1.61 (m, 4H, aliphatic-*H* from menthyl motif), 1.11 – 0.63 (m, 14H, aliphatic-*H* from menthyl motif).
- **^{13}C NMR (101 MHz, $CDCl_3$) (Major Diastereomeric Pair):** δ 169.6, 134.1, 134.0, 131.6, 129.6, 129.1, 128.7, 113.9, 113.8, 75.9, 75.8, 48.4 (d, *J* = 3.0 Hz), 48.3 (d, *J* = 4.0 Hz), 46.9, 46.8, 40.5, 40.4, 34.1, 31.4, 31.3, 29.7, 26.1, 25.6, 23.3, 23.0, 22.0, 20.8, 20.7, 16.2, 15.9. Eight carbons were not resolved at 101 MHz.
- **^{19}F NMR (376 MHz, $CDCl_3$) (Major Diastereomeric Pair):** δ -126.72 (d, *J* = 64.5 Hz), -127.19 (d, *J* = 64.6 Hz), -138.88 (d, *J* = 78.9 Hz), -139.35 (d, *J* = 79.2 Hz).
- **^{19}F NMR (376 MHz, $CDCl_3$) (Minor Diastereomeric Pair):** δ -127.75 (d, *J* = 27.6 Hz), -128.23 (d, *J* = 27.7 Hz), -139.61 (d, *J* = 64.4 Hz), -140.09 (d, *J* = 64.0 Hz).

- **IR (Neat, ν):** 3065 (w), 2953 (s), 2867 (m), 2106 (w), 1729 (s), 1582 (w), 1447 (m), 1258 (s), 1155 (s), 983 (m), 847 (w), 745 (m), 694 (m).
- **HRMS (ESI):** Calcd. for $C_{22}H_{28}F_2O_2SNa^+$, $[M+Na]^+$ 417.1676; found 417.1673.

(1*S*,2*R*,4*S*)-1,7,7-Trimethylbicyclo[2.2.1]heptan-2-yl (*r*)-2-((*s*)-2,2-difluoro-3-methylenecyclopropyl)-2-(phenylthio)acetate (3t)



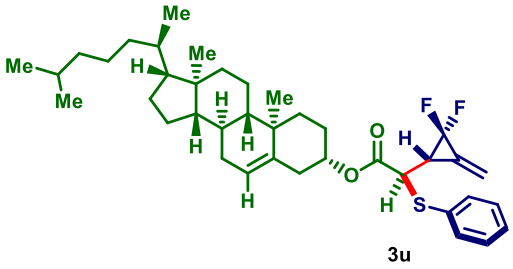
3t

Following general procedure **A**, ((3,3-difluorocycloprop-1-en-1-yl)methyl)(phenyl)sulfane (**2a**) (60 mg, 0.30 mmol, 1.0 equiv) and (1*R*,2*S*,4*R*)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl 2-diazoacetate (**1t**) (135 mg, 0.600 mmol, 2.00 equiv) were stirred for 12 h. Next, the crude reaction mixture was concentrated under reduced pressure and the crude product was purified by column chromatography using EtOAc:petroleum ether (0.1:100) as mobile phase to afford **3t** as a yellow-oil (inseparable diastereomeric mixture) (75 mg, 0.19 mmol, 64%, *dr* > 20(1:1):1(1:1)). **(***See Spectra***)**

- **TLC:** R_f = 0.77 (EtOAc:petroleum ether, 1:20 v/v), $KMnO_4$
- **^{1}H NMR (400 MHz, $CDCl_3$) (Major Diastereomeric Pair):** δ 7.52 – 7.44 (m, 2H, Ar*H*), 7.40 – 7.28 (m, 3H, Ar*H*), 6.09 – 6.02 (m, 1H, C=C*H*aHb), 5.88 – 5.78 (m, 1H, C=CHa*H*b), 4.99 – 4.83 (m, 1H, OC*H*), 3.57 – 3.45 (m, 1H, C*H*SAr), 2.70 – 2.55 (m, 1H, C*H*CF_2), 2.33 (ddt, *J* = 13.8, 8.0, 4.0 Hz, 1H, $CH_2CH(CMe_2)CH_2$), 1.87 – 1.61 (m, 3H, C*H*$_3$), 1.33 – 1.07 (m, 3H, C*H*$_3$), 0.96 – 0.71 (m, 9H, 3 × CH_2 and CH_3).
- **^{13}C NMR (101 MHz, $CDCl_3$) (Major Diastereomeric Pair):** δ 170.3, 170.2, 134.0, 133.9, 131.6, 131.5, 129.8 (t, *J* = 6.7 Hz), 129.2, 128.8 (d, *J* = 1.5 Hz), 114, 113.9, 106.6 (dd, *J* = 294.9, 292.9 Hz), 106.5 (dd, *J* = 292.9, 295.9 Hz), 81.7, 48.9, 48.8, 48.4 (t, *J* = 2.9 Hz), 47.9, 47.8, 44.8, 44.7, 36.5, 36.4, 29.7 (q, *J* = 12.0 Hz), 27.9, 27.8, 26.9, 26.8, 19.6, 18.80, 13.3, 13.2. Six carbons were not resolved at 101 MHz.
- **^{19}F NMR (376 MHz, $CDCl_3$) (Major Diastereomeric Pair):** δ -126.48 (d, *J* = 53.3 Hz), -126.95 (d, *J* = 53.2 Hz), -138.74 (d, *J* = 72.9 Hz), -139.21 (d, *J* = 73.0 Hz).

- **^{19}F NMR (376 MHz, $CDCl_3$) (Minor Diastereomeric Pair):** δ -127.72 (d, *J* = 13.2 Hz), -128.20 (d, *J* = 13.1 Hz), -139.68 (d, *J* = 8.9 Hz), -140.15 (d, *J* = 9.0 Hz).
- **IR (Neat, ν):** 3066 (w), 2954 (m), 2821 (m), 2354 (w), 2205 (w), 2106 (w), 1733 (s), 1582 (w), 1442 (m), 1345 (w), 1255 (s), 1155 (s), 1018 (m), 935 (m), 848 (w), 747 (m).
- **HRMS (ESI):** Calcd. for $C_{22}H_{26}F_2O_2SNa^+$, $[M+Na]^+$ 415.1519; found 415.1518.

(3*S*,8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-10,13-Dimethyl-17-((*R*)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl (*r*)-2-((*s*)-2,2-difluoro-3-methylenecyclopropyl)-2-(phenylthio)acetate (3u)



3u

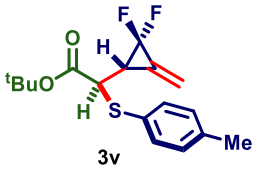
Following general procedure **A**, ((3,3-difluorocycloprop-1-en-1-yl)methyl)(phenyl)sulfane (**2a**) (30 mg, 0.15 mmol, 1.0 equiv) and (3*S*,8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-10,13-dimethyl-17-((*R*)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H cyclopenta [a] phenanthren-3-yl 2-diazoacetate (**1u**) (136 mg, 0.300 mmol, 2.00 equiv) were stirred for 12 h. Next, the crude reaction mixture was concentrated under reduced pressure, and the crude product was purified by column chromatography using EtOAc:petroleum ether (0.1:100) as mobile phase to afford **3u** as a yellow-oil (inseparable diastereomeric mixture) (88 mg, 0.14 mmol, 94%, *dr* > 20(1:1):1(1:1)). **(*See Spectra*)**

- **TLC:** R_f = 0.81 (EtOAc:petroleum ether, 1:20 v/v), $KMnO_4$
- **^{1}H NMR (400 MHz, $CDCl_3$) (Major Diastereomeric Pair):** δ 7.56 – 7.46 (m, 2H, Ar*H*), 7.39 – 7.28 (m, 3H, Ar*H*), 6.09 – 6.02 (m, 1H, C=C*H*aHb), 5.85 – 5.78 (m, 1H, C=CHa*H*b), 5.42 – 5.31 (m, 1H, olefinic *H* of cholesterol motif), 4.69 – 4.54 (m, 1H, OC*H*), 3.45 (dt, *J* = 11.0, 2.4 Hz, 1H, C*H*SAr), 2.68 – 2.53 (m, 1H, C*H*CF_2), 2.34 – 2.17 (m, 2H, *H* of cholesterol motif), 2.06 – 1.91 (m, 2H, aliphatic *H* of cholesterol motif), 1.90 – 1.74 (m, 3H, CH_3), 1.63 – 0.80 (m, 33H, aliphatic *H* of cholesterol motif), 0.68 (s, 3H, CH_3).
- **^{13}C NMR (101 MHz, $CDCl_3$) (Major Diastereomeric Pair):** δ 169.3, 169.3, 139.4, 139.3, 134.4, 134.3, 131.5, 131.4, 129.8 (t, *J* = 7.1 Hz), 129.1, 128.9, 122.9, 113.9 (d, *J* = 2.5 Hz),

106.5 (dd, *J* = 297.5, 290.9 Hz), 75.6, 74.0, 56.7, 56.1, 50.0, 48.3, 42.3, 39.7, 39.5, 37.8, 37.7, 36.9, 36.6, 36.2, 35.8, 31.9, 31.8, 29.6 (t, *J* = 12.2 Hz), 28.2, 28.0, 27.5, 27.4, 24.3, 23.8, 22.8, 22.6, 21.0, 19.3, 18.7, 11.8. Twenty-eight carbons were not resolved at 101 MHz.

- **^{19}F NMR (376 MHz, $CDCl_3$) (Major Diastereomeric Pair):** δ -126.59 (d, *J* = 6.4 Hz), -127.06 (d, *J* = 6.4 Hz), -138.68 (d, *J* = 4.6 Hz), -139.15 (d, *J* = 4.8 Hz).
- **^{19}F NMR (376 MHz, $CDCl_3$) (Minor Diastereomeric Pair):** δ -127.76, -128.23, -139.54 (d, *J* = 13.8 Hz), -140.01 (d, *J* = 13.8 Hz).
- **IR (Neat, ν):** 2938 (s), 2862 (m), 2356 (w), 2068 (w), 1739 (s), 1444 (m), 1253 (s), 1159 (s), 1005 (m), 931 (w), 846 (w), 745 (m), 694 (w).
- **HRMS (ESI):** Calcd. for $C_{39}H_{54}F_2O_2SNa^+$, $[M+Na]^+$ 647.3710; found 647.3708.

***Tert*-butyl (*r*)-2-((*s*)-2,2-difluoro-3-methylenecyclopropyl)-2-(p-tolylthio)acetate (3v)**



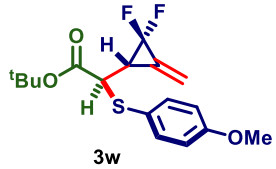
3v

Following general procedure **A**, ((3,3-difluorocycloprop-1-en-1-yl)methyl)(p-tolyl)sulfane (**2b**) (64 mg, 0.30 mmol, 1.0 equiv) and *tert*-butyl 2-diazoacetate (**1a**) (85 mg, 0.60 mmol, 2.0 equiv) were stirred for 12 h. Next, the reaction mixture was concentrated under reduced pressure and the crude product was purified by column chromatography using EtOAc:petroleum ether (0.1:100) as mobile phase to afford **3v** as a yellow-oil (71 mg, 0.22 mmol, 73%, *dr* > 20:1). **(*See Spectra*)**

- **TLC:** R_f = 0.52 (EtOAc:petroleum ether, 3:100 v/v), $KMnO_4$
- **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.39 (d, *J* = 8.1 Hz, 2H, Ar*H*), 7.13 (d, *J* = 7.9 Hz, 2H, Ar*H*), 6.07 – 6.00 (m, 1H, C=C*H*aHb), 5.84 – 5.78 (m, 1H, C=CHa*H*b), 3.30 (dd, *J* = 10.9, 2.1 Hz, 1H, C*H*SAr), 2.59 – 2.47 (m, 1H, C*H*CF_2), 2.34 (s, 3H, ArCH_3), 1.42 (s, 9H, OC(CH_3)$_3$).
- **^{13}C NMR (101 MHz, $CDCl_3$):** δ 169.1, 139.1, 134.7, 130.1 (t, *J* = 7.3 Hz), 129.8, 127.9, 113.5, 106.7 (dd, *J* = 297.4, 291.0 Hz), 82.2, 49.2 (d, *J* = 3.1 Hz), 29.8 (t, *J* = 12.2 Hz), 27.8, 21.2.

- **^{19}F NMR (376 MHz, $CDCl_3$) (Major Diastereomer):** δ -126.90 (d, *J* = 177.7 Hz), -139.22 (d, *J* = 177.7 Hz).
- **^{19}F NMR (376 MHz, $CDCl_3$) (Minor Diastereomer):** δ -127.96 (d, *J* = 177.8 Hz), -139.86 (d, *J* = 178.1 Hz).
- **IR (Neat, ν):** 2923 (m), 2857 (w), 2364 (w), 2024 (w), 1731 (s), 1443 (m), 1367 (m), 1260 (s), 1146 (s), 852 (m), 743 (w).
- **HRMS (ESI):** Calcd. for $C_{17}H_{20}F_2O_2SNa^+$, $[M+Na]^+$ 349.1050; found 349.1052.

***Tert*-butyl (*r*)-2-((*s*)-2,2-difluoro-3-methylenecyclopropyl)-2-((4-methoxyphenyl)thio)acetate (3w)**

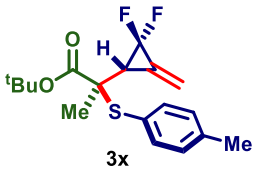


3w

Following general procedure **A**, ((3,3-difluorocycloprop-1-en-1-yl)methyl)(4-methoxyphenyl)sulfane (**2c**) (68 mg, 0.30 mmol, 1.0 equiv) and tert-butyl 2-diazoacetate (**1a**) (85 mg, 0.60 mmol, 2.0 equiv) were stirred for 12 h. Next, the reaction mixture was concentrated under reduced pressure and the crude product was purified by column chromatography using EtOAc:petroleum ether (0.2:100) as mobile phase to afford **3w** as a yellow-oil (79 mg, 0.23 mmol, 77%, *dr* > 20:1). **(***See Spectra***)**

- **TLC:** R_f = 0.55 (EtOAc:petroleum ether, 1:20, v/v), $KMnO_4$
- **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.45 (d, *J* = 8.7 Hz, 2H, Ar*H*), 6.86 (d, *J* = 8.7 Hz, 2H, Ar*H*), 6.07 – 6.02 (m, 1H, C=C*H*aHb), 5.87 – 5.80 (m, 1H, C=CHa*H*b), 3.81 (s, 3H, ArOCH_3), 3.23 (dd, *J* = 10.9, 2.1 Hz, 1H, C*H*SAr), 2.55 – 2.42 (m, 1H, C*H*CF_2), 1.43 (s, 9H, OC(CH_3)$_3$).
- **^{13}C NMR (101 MHz, $CDCl_3$):** δ 169.1, 160.6, 137.1, 130.3 (t, *J* = 7.1 Hz), 121.7, 114.6, 113.4, 106.8 (dd, *J* = 297.2, 290.9 Hz), 82.1, 55.3, 49.5 (d, *J* = 3.1 Hz), 29.7 (t, *J* = 12.1 Hz), 27.8.
- **^{19}F NMR (376 MHz, $CDCl_3$):** δ -126.89 (d, *J* = 177.9 Hz), -139.26 (d, *J* = 177.8 Hz).
- **IR (Neat, ν):** 2922 (s), 2855 (m), 2327 (w), 1731 (s), 1592 (m), 1455 (m), 1368 (m), 1253 (s), 1146 (s), 1031 (w), 986 (w), 831 (m), 740 (w).
- **HRMS (ESI):** Calculated for $C_{17}H_{20}F_2O_3SNa^+$, $[M+Na]^+$ 365.0999; found 365.0997.

***Tert*-butyl (*r*)-2-((*s*)-2,2-difluoro-3-methylenecyclopropyl)-2-(p-tolylthio)propanoate (3x)**

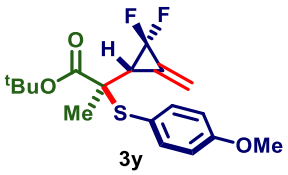


3x

Following general procedure **A**, ((3,3-difluorocycloprop-1-en-1-yl)methyl)(p-tolyl)sulfane (**2b**) (64 mg, 0.30 mmol, 1.0 equiv) and *tert*-butyl 2-diazopropanoate (**1l**) (94 mg, 0.60 mmol, 2.0 equiv) were stirred for 12 h. Next, the reaction mixture was concentrated under reduced pressure and the crude product was purified by column chromatography using EtOAc:petroleum ether (0.1:100) as mobile phase to afford **3x** as a yellow-oil (62 mg, 0.18 mmol, 61%, *dr* > 20:1). In ^{19}F NMR we observed an additional peak corresponding to a unidentified impurity. **(***See Spectra***)**

- **TLC:** R_f = 0.82 (EtOAc:petroleum ether, 1:20 v/v), $KMnO_4$
- **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.41 (d, *J* = 8.0 Hz, 2H, Ar*H*), 7.16 (d, *J* = 7.8 Hz, 2H, Ar*H*), 6.11 – 6.01 (m, 1H, C=C*H*aHb), 5.73 – 5.64 (m, 1H, C=CHa*H*b), 2.63 (dq, *J* = 11.8, 3.3 Hz, 1H, C*H*CF_2), 2.36 (s, 3H, ArCH_3), 1.46 (s, 9H, OC(CH_3)$_3$), 1.28 (d, *J* = 1.8 Hz, 3H, CH_3CSAr).
- **^{13}C NMR (101 MHz, $CDCl_3$):** δ 171.0, 140.2, 137.2, 133.9, 129.7, 129.0 (t, *J* = 6.8 Hz), 113.2, 107.0 (dd, *J* = 294.92, 292.90 Hz), 82.0, 52.9, 34.8 (t, *J* = 11.8 Hz), 29.7, 21.3, 19.5 (d, *J* = 5.5 Hz).
- **^{19}F NMR (376 MHz, $CDCl_3$) (Major Diastereomer):** δ -122.64 (d, *J* = 180.4 Hz), -138.82 (d, *J* = 180.8 Hz).
- **^{19}F NMR (376 MHz, $CDCl_3$) (Minor Diastereomer):** δ -121.22 (d, 176.7 Hz), -140.02 (d, *J* = 181.0 Hz).
- **IR (Neat, ν):** 2976 (w), 2928 (m), 2583 (w), 2204 (w), 2024 (w), 1725 (s), 1599 (w), 1445 (m), 1319 (w), 1257 (s), 1168 (s), 1106 (m), 932 (w), 810 (m), 767 (w).
- **HRMS (ESI):** Calcd. for $C_{18}H_{22}F_2O_2SNa^+$, $[M+Na]^+$ 363.1206; found 363.1203.

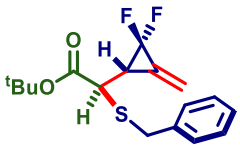
***Tert*-butyl (*r*)-2-((*s*)-2,2-difluoro-3-methylenecyclopropyl)-2-((4-methoxyphenyl)thio)propanoate (3y)**



Following general procedure **A**, (3,3-difluorocycloprop-1-en-1-yl)methyl)(4-methoxyphenyl)sulfane (**2c**) (68.5 mg, 0.30 mmol, 1.00 equiv) and *tert*-butyl 2-diazopropanoate (**1l**) (94 mg, 0.60 mmol, 2.0 equiv) were stirred for 12 h. Next, the reaction mixture was concentrated under reduced pressure and the crude product was purified by column chromatography using EtOAc:petroleum ether (0.1:100) as mobile phase to afford **3y** as a yellow-oil (66 mg, 0.19 mmol, 62%, *dr* > 20:1). In ^{19}F NMR we observed an additional peak corresponding to an unidentified impurity. **(***See Spectra***)**

- **TLC:** R_f = 0.51 (EtOAc:petroleum ether, 3:100 v/v), $KMnO_4$
- **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.44 (d, *J* = 8.7 Hz, 2H, Ar*H*), 6.87 (d, *J* = 8.7 Hz, 2H, Ar*H*), 6.10 – 6.02 (m, 1H, C=C*H*aHb), 5.74 – 5.68 (m, 1H, C=CHa*H*b), 3.82 (s, 3H, ArOCH_3), 2.61 (dq, *J* = 11.9, 3.3 Hz, 1H, C*H*CF_2), 1.46 (s, 9H, OC(CH_3)$_3$), 1.26 (d, *J* = 1.9 Hz, 3H, CH_3CSAr).
- **^{13}C NMR (101 MHz, $CDCl_3$):** δ 171.0, 161.1, 138.9, 129.1, 121.2, 114.4, 113.2, 82.0, 55.3, 52.9, 34.7 (t, *J* = 11.9 Hz), 27.8, 19.4 (d, *J* = 5.7 Hz). One carbon was not resolved at 101 MHz.
- **^{19}F NMR (376 MHz, $CDCl_3$) (Major Diastereomer):** δ -122.70 (d, *J* = 180.6 Hz), -138.85 (d, *J* = 180.5 Hz).
- **^{19}F NMR (376 MHz, $CDCl_3$) (Minor Diastereomer):** δ -121.08 (d, *J* = 180.6 Hz), -140.00 (d, *J* = 180.7 Hz).
- **IR (Neat, ν):** 2976 (w), 2932 (w), 2361 (w), 1889 (w), 1724 (s), 1592 (m), 1492 (m), 1252 (s), 1169 (s), 1106 (m), 1028 (m), 933 (w), 853 (m), 757 (w).
- **HRMS (ESI):** Calculated for $C_{18}H_{22}F_2O_3SNa^+$, $[M+Na]^+$ 379.1155; found 379.1157.

***Tert*-butyl (*r*)-2-(benzylthio)-2-((*s*)-2,2-difluoro-3-methylenecyclopropyl)acetate (3z)**

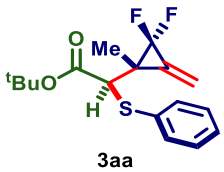


3z

Following general procedure **A**, benzyl((3,3-difluorocycloprop-1-en-1-yl)methyl)sulfane (**2d**) (64 mg, 0.30 mmol, 1.0 equiv) and *tert*-butyl 2-diazoacetate (**1a**) (85 mg, 0.60 mmol, 2.0 equiv) were stirred for 12 h. Next, the reaction mixture was concentrated under reduced pressure and the crude product was purified by column chromatography using EtOAc:petroleum ether (0.25:100) as mobile phase to afford **3z** as a yellow-oil (65 mg, 0.20 mmol, 66%, *dr* > 20:1). **(***See Spectra***)**

- **TLC:** R_f = 0.51 (EtOAc:Petroleum ether, 3:100 v/v), $KMnO_4$
- **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.39 – 7.20 (m, 5H, Ar*H*), 5.97 – 5.91 (m, 1H, C=C*H*aHb), 5.79 – 5.73 (m, 1H, C=CHa*H*b), 3.95 – 3.81 (m, 2H, SCH_2Ar), 3.05 – 2.89 (m, 1H, C*H*SAr), 2.63 – 2.49 (m, 1H, C*H*CF_2), 1.52 (s, 9H, OC(CH_3)$_3$).
- **^{13}C NMR (101 MHz, $CDCl_3$):** δ 169.7, 137.1, 129.8 (t, *J* = 7.3 Hz), 129.1, 128.5, 127.4, 113.3, 106.5 (dd, *J* = 297.1, 291.4 Hz), 82.2, 44.4 (d, *J* = 3.3 Hz), 35.8, 29.2 (t, *J* = 12.4 Hz), 27.9.
- **^{19}F NMR (376 MHz, $CDCl_3$) (Major Diastereomer):** δ -126.79 (d, *J* = 177.3 Hz), -139.68 (d, *J* = 177.2 Hz).
- **^{19}F NMR (376 MHz, $CDCl_3$) (Minor Diastereomer):** δ -121.11 (d, *J* = 178.9 Hz), -136.13 (d, *J* = 179.2 Hz).
- **IR (Neat, ν):** 2920 (s), 2854 (m), 2329 (w), 2030 (w), 1732 (m), 1259 (m), 1145 (m), 1008 (w), 853 (w), 704 (m).
- **HRMS (ESI):** Calcd. for $C_{17}H_{20}F_2O_2SNa^+$, $[M+Na]^+$ 349.1050; found 349.1049.

***Tert*-butyl (*r*)-2-((*s*)-2,2-difluoro-1-methyl-3-methylenecyclopropyl)-2-(phenylthio)acetate (3aa)**

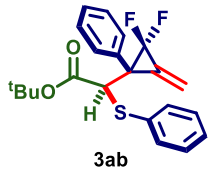


3aa

Following general procedure **A**, ((3,3-difluoro-2-methylcycloprop-1-en-1-yl)methyl)(phenyl)sulfane (**2e**) (64 mg, 0.30 mmol, 1.0 equiv) and *tert*-butyl 2-diazoacetate (**1a**) (85 mg, 0.60 mmol, 2.0 equiv) were stirred for 12 h. Next, the reaction mixture was concentrated under reduced pressure and the crude product was purified by column chromatography using petroleum ether as mobile phase to afford **3aa** as a yellow-oil (inseparable diastereomeric mixture) (70 mg, 0.21 mmol, 71%, *dr* ~ 10:1). **(***See Spectra***)**

- **TLC:** R_f = 0.62 (EtOAc:petroleum ether, 3:100 v/v), $KMnO_4$
- **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.54 – 7.44 (m, 2H, Ar*H* for both diastereomers), 7.36 – 7.20 (m, 3H, Ar*H* for both diastereomers), 5.97 (s, 0.1H, C=C*H*aHb for minor diastereomer), 5.82 (s, 0.9H, C=C*H*aHb for major diastereomer), 5.72 (s, 0.1H, C=CHa*H*b for minor diastereomer), 5.33 (s, 0.9H, C=CHa*H*b for major diastereomer), 3.76 (d, *J* = 2.8 Hz, 0.9H, C*H*SAr for major diastereomer), 3.66 (d, *J* = 1.6 Hz, 0.1H, C*H*SAr for minor diastereomer), 1.57 (s, 2.7 H, CH_3CCF$_2$ for major diastereomer), 1.49 (s, 0.3 H, CH_3CCF$_2$ for minor diastereomer),1.44 (s, 8.1H, OC(CH_3)$_3$ for major diastereomer), 1.42 (s, 0.9H, OC(CH_3)$_3$ for minor diastereomer).
- **^{13}C NMR (101 MHz, $CDCl_3$) (Major Diastereomer):** δ 168.5, 135.3 (t, *J* = 6.3 Hz), 134.0, 132.6, 129.1, 127.9, 112.3, 108.1 (dd, *J* = 300.2, 295.5 Hz), 82.4, 54.7 (d, *J* = 3.6 Hz), 33.1 (t, *J* = 11.7 Hz), 27.8, 12.8 (t, *J* = 3.2 Hz).
- **^{13}C NMR (101 MHz, $CDCl_3$) (Minor Diastereomer):** δ 133.3, 129.0, 128.1, 112.4, 53.7, 30.9, 29.7, 27.9, 12.7 (t, *J* = 3.6 Hz). Four carbons were not resolved at 101 MHz.
- **^{19}F NMR (376 MHz, $CDCl_3$) (Major Diastereomer):** δ -134.96 (d, *J* = 176.7 Hz), -136.58 (d, *J* = 176.8 Hz).
- **^{19}F NMR (376 MHz, $CDCl_3$) (Minor Diastereomer):** δ -136.16 (d, *J* = 176.7Hz), -138.18 (d, *J* = 174.1 Hz).
- **IR (Neat, ν):** 2922 (s), 2853 (m), 2361 (w), 2028 (w), 1735 (m), 1458 (m), 1373 (w), 1254 (w), 1151 (m), 1029 (w), 849 (w), 745 (w), 696 (w).
- **HRMS (ESI):** Calcd. for $C_{17}H_{20}F_2O_2SNa^+$, $[M+Na]^+$ 349.1050; found 349.1054.

***Tert*-butyl (*r*)-2-((*s*)-2,2-difluoro-3-methylene-1-phenylcyclopropyl)-2-(phenylthio)acetate (3ab)**

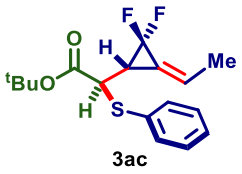


3ab

Following general procedure **A**, ((3,3-difluoro-2-phenylcycloprop-1-en-1-yl)methyl)(phenyl)sulfane (**2g**) (82 mg, 0.30 mmol, 1.0 equiv) and *tert*-butyl 2-diazoacetate (**1a**) (85 mg, 0.60 mmol, 2.0 equiv) were stirred for 12 h. Next, the reaction mixture was concentrated under reduced pressure and the crude product was purified by column chromatography using petroleum ether as mobile phase to afford **3ab** as a yellow-oil (inseparable diastereomeric mixture) (70 mg, 0.18 mmol, 60%, *dr* ~ 7:1). **(***See Spectra***)**

- **TLC:** R_f = 0.62 (EtOAc:petroleum ether, 1:20, v/v), $KMnO_4$
- **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.55 – 7.20 (m, 10H, Ar*H* for both diastereomers), 6.15 (s, 0.15H, C=C*H*aHb for minor diastereomer), 6.12 (s, 0.15H, C=CHa*H*b for minor diastereomer), 6.08 (s, 0.85H, C=C*H*aHb for major diastereomer), 5.95 (s, 0.85H, C=CHa*H*b for major diastereomer), 4.08 – 4.03 (m, 0.85H, C*H*SAr for major diastereomer), 3.97 – 3.93 (m, 0.15H, C*H*SAr for minor diastereomer), 1.36 (s, 8.0H, OC(C*H*$_3$)$_3$ for major diastereomer), 1.32 (s, 1.0H, OC(C*H*$_3$)$_3$ for minor diastereomer).
- **^{13}C NMR (101 MHz, $CDCl_3$) (Major Diastereomer):** δ 168.0, 134.5, 132.1, 131.7, 131.1, 130.8 (d, *J* = 1.9 Hz), 129.0, 128.4, 128.0, 127.6, 113.9, 106.8 (dd, *J* = 274.7, 295.9 Hz) 82.5, 56.1 (d, *J* = 4.3 Hz), 53.41, 27.75.
- **^{13}C NMR (101 MHz, $CDCl_3$) (Minor Diastereomer):** δ 134.6, 133.8, 132.7, 129.0, 127.9, 40.0, 30.9, 29.7, 28.0. Seven peaks were not resolved at 101 MHz.
- **^{19}F NMR (376 MHz, $CDCl_3$) (Major Diastereomer):** δ -127.26 (d, *J* = 171.9 Hz), -131.23 (d, *J* = 171.9 Hz).
- **^{19}F NMR (376 MHz, $CDCl_3$) (Minor Diastereomer):** δ -129.40 (d, *J* = 169.5 Hz), -134.43 (d, *J* = 169.3 Hz).
- **IR (Neat, ν):** 2922 (s), 2855 (m), 2360 (w), 2024 (w), 1738 (w), 1459 (m), 1373 (w), 1154 (w), 873 (w), 696 (w).
- **HRMS (ESI):** Calcd. for $C_{22}H_{22}F_2O_2SNa^+$, $[M+Na]^+$ 411.1206; found 411.1204.

***Tert*-butyl (*r*)-2-((*s, Z*)-3-ethylidene-2,2-difluorocyclopropyl)-2-(phenylthio)acetate (3ac):**

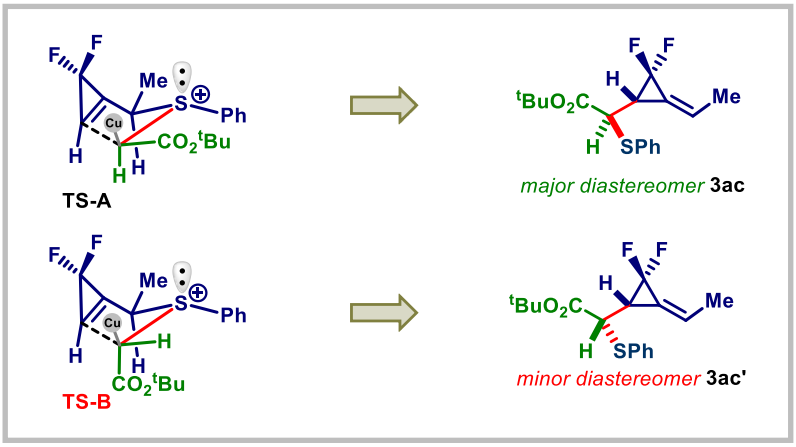


3ac

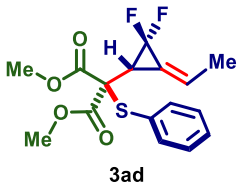
Following general procedure **A**, (1-(3,3-difluorocycloprop-1-en-1-yl)ethyl)(phenyl)sulfane (**2f**) (64.0 mg, 0.30 mmol, 1.00 equiv) and *tert*-butyl 2-diazoacetate (**1a**) (85 mg, 0.60 mmol, 2.0 equiv) were stirred for 12 h. Next, the reaction mixture was concentrated under reduced pressure and the crude product was purified by column chromatography using petroleum ether as mobile phase to afford **3ac** as a yellow-oil (inseparable diastereomeric mixture) (68 mg, 0.21 mmol, 69%, *Z/E* > 20:1, *dr* ~ 1.75:1). **(*See Spectra*)**

- **TLC:** R_f = 0.55 (EtOAc:petroleum ether, 3:100 v/v), $KMnO_4$
- **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.56 – 7.45 (m, 2H, Ar*H* for both diastereomers), 7.36 – 7.29 (m, 3H, Ar*H* for both diastereomers), 6.59 (qd, *J* = 6.9, 3.0 Hz, 0.4H, C=C*H*CH_3 for minor diastereomer), 6.16 (qd, *J* = 6.9, 4.4, 2.4 Hz, 0.6H, C=C*H*CH_3 for major diastereomer), 3.44 – 3.35 (m, 1H, C*H*SAr for both diastereomers), 2.64 – 2.54 (m, 1H, C*H*CF_2 for both diastereomers), 2.13 – 2.06 (m, 1.2H, C=CHC*H*$_3$ for minor diastereomer), 1.94 (dq, *J* = 6.9, 2.2 Hz, 1.8H, C=CHC*H*$_3$ for major diastereomer), 1.39 (s, 5.4H, OC(C*H*$_3$)$_3$ for major diastereomer), 1.37 (s, 3.6H, OC(C*H*$_3$)$_3$ for minor diastereomer).
- **^{13}C NMR (101 MHz, $CDCl_3$) (Major Diastereomer):** δ 169.2, 134.0, 132.1, 128.0, 129.0, 126.9, 121.3 (d, *J* = 11.6 Hz), 107.4 (dd, *J* =290.9, 290.9 Hz), 82.1, 49.2 (d, *J* = 3.4 Hz), 29.7 (t, *J* = 12.1 Hz), 27.8, 18.2.
- **^{13}C NMR (101 MHz, $CDCl_3$) (Minor Diastereomer):** δ 169.5, 133.2, 132.8, 128.3, 126.0, 121.3 (d, *J* = 11.6 Hz), 106.9 (dd, *J* =290.9, 290.9 Hz), 82.1, 29.5 (t, *J* = 13.1 Hz), 27.7, 17.3. Two carbons were not resolved at 101 MHz.
- **^{19}F NMR (376 MHz, $CDCl_3$) (Major Diastereomer):** δ -126.50 (d, *J* = 175.4 Hz), -138.98 (d, *J* = 174.9 Hz).
- **^{19}F NMR (376 MHz, $CDCl_3$) (Minor Diastereomer):** δ -125.82 (d, *J* = 173.4 Hz), -137.81 (d, *J* = 173.5 Hz).
- **IR (Neat, ν):** 3067 (w), 2923 (s), 2856 (m), 2200 (w), 2055 (w), 1966 (w), 1733 (s), 1584 (w), 1456 (m), 1378 (m), 1259 (m), 1147 (s), 1016 (w), 845 (w), 745 (m).

- **HRMS (ESI):** Calcd. for $C_{17}H_{20}F_2O_2SNa^+$, $[M+Na]^+$ 349.1050; found 349.1049.
- **Stereochemical Model:**



Dimethyl (*s*, *Z*)-2-(3-ethylidene-2,2-difluorocyclopropyl)-2-(phenylthio)malonate (3ad):

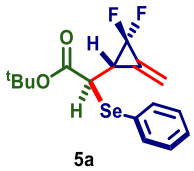


Following general procedure **C**, (1-(3,3-difluorocycloprop-1-en-1-yl)ethyl)(phenyl)sulfane (**2f**) (32.0 mg, 0.15 mmol, 1.00 equiv) and dimethyl 2-diazomalonate (**1r**) (47 mg, 0.30 mmol, 2.0 equiv) were stirred for 12 h. Next, the reaction mixture was concentrated under reduced pressure and the crude product was purified by column chromatography using petroleum ether as mobile phase to afford **3ad** as a yellow-oil (18 mg, 0.05 mmol, 35%, *Z*/*E* ~ 16:1). **(***See Spectra***)**

- **TLC:** R_f = 0.27 (EtOAc:petroleum ether, 1:10 v/v), $KMnO_4$
- **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.62 – 7.52 (m, 2H, Ar*H*), 7.47 – 7.32 (m, 3H, Ar*H*), 6.15 – 6.02 (m, 1H, C=C*H*CH$_3$), 3.73 (s, 6H, 2 × OC*H*$_3$), 2.80 – 2.70 (m, 1H, C*H*CF$_2$), 1.97 – 1.87 (m, 3H, C=CHC*H*$_3$).
- **^{13}C NMR (101 MHz, $CDCl_3$):** δ 137.4, 130.4, 129.1, 128.9, 128.1, 53.3, 53.2, 32.8 (t, *J* = 13.1 Hz), 31.0, 29.7, 18.2. Two carbons were not resolved at 101 MHz.
- **^{19}F NMR (376 MHz, $CDCl_3$) (Major Diastereomer):** δ -123.32 (d, *J* = 178.3 Hz), -138.41 (d, *J* = 178.3 Hz).
- **^{19}F NMR (376 MHz, $CDCl_3$) (Minor Diastereomer):** δ -123.24 (d, *J* = 177.4 Hz), -137.68 (d, *J* = 177.4 Hz).

- **IR (Neat, ν):** 3225 (m), 3127 (s), 2915 (w), 2150 (s), 1987 (w), 1733 (s), 1584 (w), 1456 (m), 1387 (w), 1295 (w), 1215 (m), 1027 (s), 864 (m), 733 (m).
- **HRMS (ESI):** Calcd. for $C_{16}H_{16}F_2O_4SH^+$, $[M+H]^+$ 343.0816; found 343.0815.

***Tert*-butyl (*r*)-2-((*s*)-2,2-difluoro-3-methylenecyclopropyl)-2-(phenylselanyl)acetate (5a)**

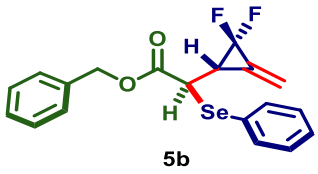


5a

Following general procedure **B**, ((3,3-difluorocycloprop-1-en-1-yl)methyl)(phenyl)selane (**4**) (37 mg, 0.15 mmol, 1.0 equiv) and *tert*-butyl 2-diazoacetate (**1a**) (43 mg, 0.30 mmol, 2.0 equiv) were stirred for 12 h. Next, the reaction mixture was concentrated under reduced pressure and the crude product was purified by column chromatography using EtOAc:petroleum ether (0.1:100) as mobile phase to afford **5a** as a yellow-oil (35.0 mg, 0.097 mmol, 65%, *dr* > 20:1). **(*See Spectra*)**

- **TLC:** R_f = 0.57 (EtOAc:petroleum ether, 1:20 v/v), $KMnO_4$
- **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.67 – 7.60 (m, 2H, Ar*H*), 7.39 – 7.28 (m, 3H, Ar*H*), 6.03 – 5.96 (m, 1H, C=C*H*aHb), 5.82 – 5.75 (m, 1H, C=CHa*H*b), 3.46 – 3.35 (m, 1H, C*H*SeAr), 2.65 – 2.48 (m, 1H, C*H*CF_2), 1.41 (s, 9H, OC(CH_3)$_3$).
- **^{13}C NMR (101 MHz, $CDCl_3$):** δ 170.0, 136.2, 130.6 (t, *J* = 7.0 Hz), 129.2, 128.9, 126.8, 113.1, 107.1 (dd, *J* = 298.4, 291.0 Hz), 82.0, 40.7 (d, *J* = 3.6 Hz), 30.1 (t, *J* = 12.1 Hz), 27.8.
- **^{19}F NMR (376 MHz, $CDCl_3$) (Major Diastereomer):** δ -126.29 (d, *J* = 177.0 Hz), -139.67 (d, *J* = 177.0 Hz).
- **^{19}F NMR (376 MHz, $CDCl_3$) (Minor Diastereomer):** δ -127.85 (d, *J* = 177.4 Hz), -140.27 (d, *J* = 177.5 Hz).
- **IR (Neat, ν):** 2921 (s), 2853 (s), 2014 (w), 1731 (m), 1459 (m), 1369 (m), 1173 (m), 1141 (m), 986 (w), 855 (w), 738 (w).
- **HRMS (ESI):** Calcd. for $C_{16}H_{18}F_2O_2SNa^+$, $[M+Na]^+$ 383.0338; found 383.0335.

Benzyl (*r*)-2-((*s*)-2,2-difluoro-3-methylenecyclopropyl)-2-(phenylselanyl)acetate (5b)

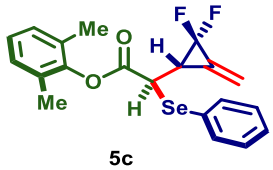


5b

Following general procedure **B**, ((3,3-difluorocycloprop-1-en-1-yl)methyl)(phenyl)selane (**4**) (37 mg, 0.15 mmol, 1.0 equiv) and benzyl 2-diazoacetate (**1c**) (53 mg, 0.30 mmol, 2.0 equiv) were stirred for 12 h. Next, the reaction mixture was concentrated under reduced pressure and the crude product was purified by column chromatography using EtOAc:petroleum ether (0.2:100) as mobile phase to afford **5b** as a yellow-oil (41 mg, 0.10 mmol, 69%, *dr* > 20:1). **(***See Spectra***)**

- **TLC:** R_f = 0.45 (EtOAc:petroleum ether, 1:20 v/v), $KMnO_4$
- **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.48 (d, *J* = 7.2 Hz, 2H, Ar*H*), 7.39 – 7.20 (m, 8H, Ar*H*), 6.07 – 5.98 (m, 1H, C=C*H*aHb), 5.90 – 5.79 (m, 1H, C=CHa*H*b), 5.19 – 5.07 (m, 2H, OCH_2Ar), 3.56 – 3.47 (m, 1H, C*H*SeAr), 2.62 (m, 1H, C*H*CF_2).
- **^{13}C NMR (101 MHz, $CDCl_3$):** δ 170.6, 136.5, 135.3, 130.2 (t, *J* = 7.2 Hz), 129.2, 128.5, 128.3, 128.2, 126.0, 113.4 (d, *J* = 1.6 Hz), 106.9 (dd, *J* = 299.1, 291.1 Hz), 67.2, 39.2 (d, *J* = 3.6 Hz), 29.7 (t, *J* = 12.2 Hz). One carbon was not resolved at 101 MHz.
- **^{19}F NMR (376 MHz, $CDCl_3$):** δ -126.19 (d, *J* = 177.5 Hz), -139.24 (d, *J* = 177.5 Hz).
- **IR (Neat, ν):** 2924 (s), 2856 (m), 1730 (s), 1581 (w), 1445 (m), 1372 (w), 1319 (w), 1254 (s), 1169 (s), 1107 (m), 1014 (m), 932 (m), 850 (m), 746 (m), 695 (w).
- **HRMS (ESI):** Calcd. for $C_{19}H_{16}F_2O_2SeNa^+$, $[M+Na]^+$ 417.0182; found 417.0182.

2,6-Dimethylphenyl (*r*)-2-((*s*)-2,2-difluoro-3-methylenecyclopropyl)-2-(phenylselanyl)acetate (5c)



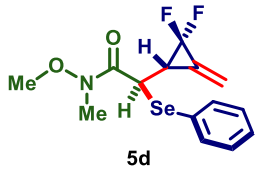
5c

Following general procedure **B**, ((3,3-difluorocycloprop-1-en-1-yl)methyl)(phenyl)selane (**4**) (37 mg, 0.15 mmol, 1.0 equiv) and 2,6-dimethylphenyl 2-diazoacetate (**1f)** (57 mg, 0.30 mmol, 2.0 equiv) were stirred for 12 h. Next, the reaction mixture was concentrated under reduced pressure and the crude product was purified by column chromatography using EtOAc:petroleum ether

(0.1:100) as mobile phase to afford **5c** as a pale-yellow solid (37 mg, 0.09 mmol, 61%, *dr* > 20:1). **(***See Spectra***)**

- **TLC: R_f** = 0.45 (EtOAc:petroleum ether, 3:100, v/v), $KMnO_4$
- **Melting Point:** 100.9 – 102.7 ºC.
- **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.74 – 7.62 (m, 2H, Ar*H*), 7.43 – 7.20 (m, 3H, Ar*H*), 7.07 (s, 3H, Ar*H*), 6.10 – 6.04 (m, 1H, C=C*H*aHb), 5.90 – 5.82 (m, 1H, C=CHa*H*b), 3.81 – 3.68 (m, 1H, C*H*SeAr), 2.80 – 2.67 (m, 1H, C*H*CF_2), 2.21 (s, 6H, ArCH_3).
- **^{13}C NMR (101 MHz, $CDCl_3$):** δ 168.9, 147.7, 135.8, 130.4, 130.0 (t, *J* = 7.2 Hz), 129.4, 129.2, 128.7, 126.7, 126.1, 113.7, 106.9 (dd, *J* = 299.2, 290.9 Hz), 38.9 (d, *J* = 3.6 Hz), 30.0 (t, *J* = 12.2 Hz), 16.2.
- **^{19}F NMR (376 MHz, $CDCl_3$) (Major Diastereomer):** δ -126.22 (d, *J* = 177.9 Hz), -139.07 (d, *J* = 178.1 Hz).
- **^{19}F NMR (376 MHz, $CDCl_3$) (Minor Diastereomer):** δ -127.89 (d, *J* = 178.2 Hz), -140.19 (d, *J* = 178.1 Hz).
- **IR (Neat, ν):** 2923 (m), 2855 (w), 2081 (w), 1746 (s), 1579 (w), 1472 (m), 1438 (m), 1351 (w), 1237 (s), 1125 (s), 985 (m), 932 (m), 737 (m), 691 (m).
- **HRMS (ESI):** Calculated for $C_{20}H_{18}F_2O_2SeNa^+$, $[M+Na]^+$ 431.0338; found 431.0336.

(*r*)-2-((*s*)-2,2-Difluoro-3-methylenecyclopropyl)-*N*-methoxy-*N*-methyl-2-(phenylselanyl) acetamide (5d)



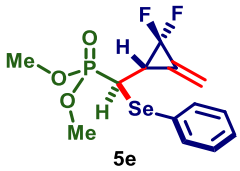
5d

Following general procedure **B**, ((3,3-difluorocycloprop-1-en-1-yl)methyl)(phenyl)selane (**4**) (37.0 mg, 0.15 mmol, 1.00 equiv) and 2-diazo-*N*-methoxy-*N*-methylacetamide (**1h**) (39 mg, 0.30 mmol, 2.0 equiv) were stirred for 12 h. Next, the reaction mixture was concentrated under reduced pressure and the crude product was purified by column chromatography using EtOAc:petroleum ether (1:20) as mobile phase to afford **5d** as a yellow-oil (30 mg, 0.09 mmol, 58%, *dr* > 20:1). **(***See Spectra***)**

- **TLC:** R_f = 0.39 (EtOAc:petroleum ether, 1:5 v/v), $KMnO_4$

- **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.66 – 7.58 (m, 2H, Ar*H*), 7.39 – 7.24 (m, 3H, Ar*H*), 6.05 – 5.97 (m, 1H, C=C*H*aHb), 5.86 – 5.75 (m, 1H, C=CHa*H*b), 4.04 – 3.88 (m, 1H, C*H*SeAr), 3.65 (s, 3H, OCH_3), 3.19 (s, 3H, NCH_3), 2.84 - 2.72 (m, 1H, C*H*CF_2).
- **^{13}C NMR (101 MHz, $CDCl_3$):** δ 171.0, 136.5, 130.9 (t, *J* = 7.1 Hz), 129.1 (d, *J* = 5.9 Hz), 126.2, 113.1, 107.5 (dd, *J* = 291.9, 290.9 Hz), 61.3, 53.4, 35.8, 32.7, 30.2 (t, *J* = 11.9 Hz).
- **^{19}F NMR (376 MHz, $CDCl_3$) (Major Diastereomer):** δ -123.35 (d, *J* = 177.2 Hz), -139.50 (d, *J* = 177.4 Hz).
- **^{19}F NMR (376 MHz, $CDCl_3$) (Minor Diastereomer):** δ -133.78 (d, *J* = 172.6 Hz). One peak was not resolved at 376 MHz.
- **IR (Neat, ν):** 3063 (w), 2927 (m), 2364 (w), 2064 (w), 1751 (w), 1660 (s), 1578 (w), 1439 (s), 1271 (s), 1167 (s), 1005 (m), 860 (w), 741 (m).
- **HRMS (ESI):** Calculated for $C_{14}H_{15}F_2NO_2SeNa^+$, $[M+Na]^+$ 370.0134; found 370.0133.

Dimethyl ((*r*)-((*s*)-2,2-difluoro-3-methylenecyclopropyl)(phenylselanyl)methyl)phosphonate (5e)



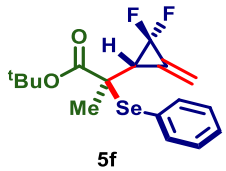
5e

Following general procedure **B**, ((3,3-difluorocycloprop-1-en-1-yl)methyl)(phenyl)selane (**4**) (37 mg, 0.15 mmol, 1.0 equiv) and dimethyl (diazomethyl)phosphonate (**1i**) (45 mg, 0.30 mmol, 2.0 equiv) were stirred for 12 h. Next, the reaction mixture was concentrated under reduced pressure and the crude product was purified by column chromatography using EtOAc:petroleum ether (1:20) as mobile phase to afford **5e** as a yellow-oil (24 mg, 0.065 mmol, 43%, *dr* > 20:1). **(*See Spectra*)**

- **TLC:** R_f = 0.29 (EtOAc:petroleum ether, 2:5 v/v), $KMnO_4$
- **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.75 – 7.65 (m, 2H, Ar*H*), 7.38 – 7.24 (m, 3H, Ar*H*), 6.02 – 5.95 (m, 1H, C=C*H*aHb), 5.83 – 5.75 (s, 1H, C=CHa*H*b), 3.83 (dd, *J* = 10.8, 3.9 Hz, 6H, OP(OCH_3)$_2$), 3.07 – 2.95 (m, 1H, C*H*SeAr), 2.62 – 2.49 (m, 1H, C*H*CF_2).
- **^{13}C NMR (101 MHz, $CDCl_3$):** δ 135.2, 129.2, 128.7, 113.7, 106.7 (ddd, *J* = 292.9, 288.9 Hz), 54.1 (d, *J* = 7.0 Hz), 53.7 (d, *J* = 7.1 Hz), 34.5, 33.0, 29.5 (t, *J* = 12.3 Hz).

- **^{19}F NMR (376 MHz, $CDCl_3$) (Major Diastereomer):** δ -125.63 (dd, *J* = 175.7, 3.7 Hz), -137.68 (dd, *J* = 175.8, 7.1 Hz).
- **^{19}F NMR (376 MHz, $CDCl_3$) (Minor Diastereomer):** δ -129.09 (dd, *J* = 87.3, 4.5 Hz), -143.42 (dd, *J* = 156.3, 6.6 Hz).
- **^{31}P NMR (162 MHz, $CDCl_3$):** δ 25.37 – 25.03 (m).
- **IR (Neat, ν):** 2922 (w), 2854 (w), 2357 (w), 1960 (w), 1823 9w), 1753 (w), 1439 (m), 1257 (s), 1149 (m), 1031 (s), 969 (m), 823 (m), 745 9m), 694 (w).
- **HRMS (ESI):** Calcd. for $C_{13}H_{15}F_2O_3PSeNa^+$, $[M+Na]^+$ 390.9790; found 390.9790.

***Tert*-butyl (*r*)-2-((*s*)-2,2-difluoro-3-methylenecyclopropyl)-2-(phenylselanyl)propanoate (5f)**



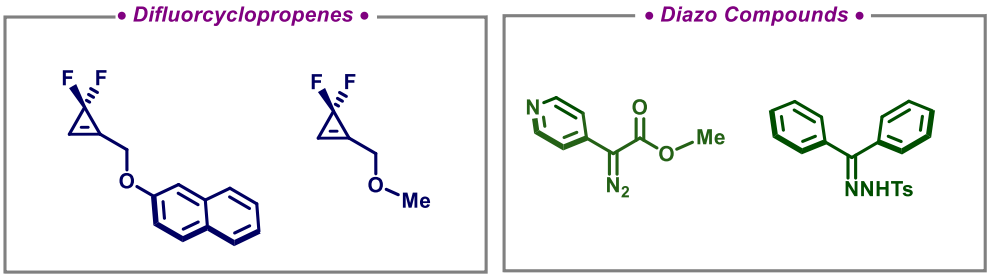
5f

Following general procedure **B**, ((3,3-difluorocycloprop-1-en-1-yl)methyl)(phenyl)selane (**4**) (37 mg, 0.15 mmol, 1.0 equiv) and *tert*-butyl 2-diazopropanoate (**1j**) (47 mg, 0.30 mmol, 2.0 equiv) were stirred for 12 h. Next, the reaction mixture was concentrated under reduced pressure and the crude product was purified by column chromatography using EtOAc:petroleum ether (0.1:100) as mobile phase to afford **5f** as a yellow-oil (36 mg, 0.096 mmol, 64%, *dr* > 20:1). **(*See Spectra*)**

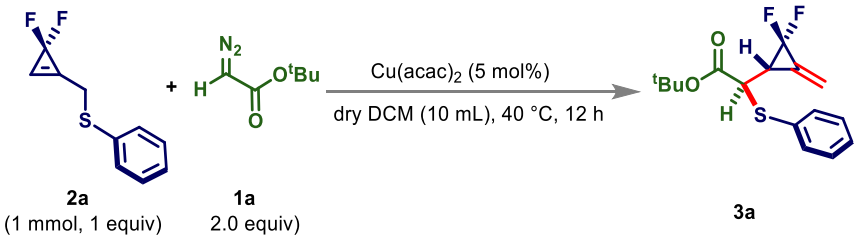
- **TLC:** R_f = 0.51 (EtOAc:petroleum ether, 3:100 v/v), $KMnO_4$
- **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.64 (d, *J* = 4.1 Hz, 2H, Ar*H*), 7.43 (t, *J* = 7.3 Hz, 1H, Ar*H*), 7.38 – 7.31 (m, 2H, Ar*H*), 6.08 – 5.98 (m, 1H, C=C*H*aHb), 5.66 – 5.57 (m, 1H, C=CHa*H*b), 2.71 (dq, *J* = 11.4, 3.3 Hz, 1H, C*H*CF_2), 1.45 (s, 9H, OC(CH_3)$_3$), 1.38 (s, 3H, CH_3CSeAr).
- **^{13}C NMR (101 MHz, $CDCl_3$):** δ 171.7, 138.1, 129.7, 129.2 (t, *J* = 6.9 Hz), 129.0, 127.1, 113.2, 107.2 (dd, *J* = 293.9, 293.9 Hz), 81.9, 46.6, 35.4 (t, *J* = 11.6 Hz), 27.8, 19.8 (d, *J* = 5.2 Hz).
- **^{19}F NMR (376 MHz, $CDCl_3$) (Major Diastereomer):** δ -122.34 (d, *J* = 180.0 Hz), -138.72 (d, *J* = 179.8 Hz).
- **^{19}F NMR (376 MHz, $CDCl_3$) (Minor Diastereomer):** δ -121.06 (d, *J* = 180.3 Hz), -140.16 (d, *J* = 179.9 Hz).

- **IR (Neat, ν):** 2924 (s), 2856 (m), 2363 (w), 2177 (w), 1726 (m), 1580 (w), 1451 (m), 1318 (m), 1256 (s), 1169 (s), 1104 (m), 1016 (w), 932 (w), 853 (m), 741 (m).
- **HRMS (ESI):** Calcd. for $C_{17}H_{20}F_2NO_2SeNa^+$, $[M+Na]^+$ 397.0495; found 397.0494.

Failed Substrate Scope:



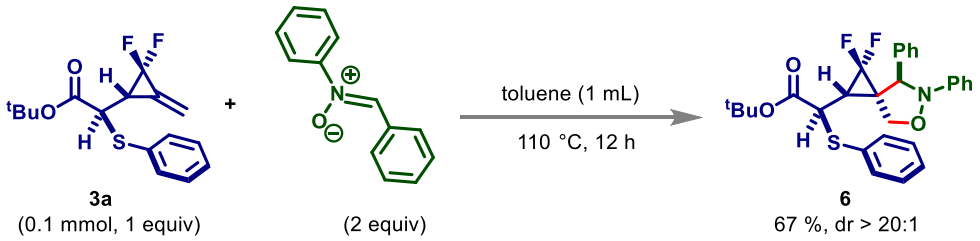
7. Scale-up Reaction:



A oven dried 25 mL round bottom flask under nitrogen was charged with copper (II) acetylacetonate (13 mg, 50 μmol, 0.05 equiv), difluorocyclopropene **2a** (198 mg, 1.00 mmol, 1.00 equiv) and anhydrous dichloromethane (4 mL). The resulting solution was stirred for 10 min at 40 ºC, and a solution of diazo compound **1a** (284 mg, 1.00 mmol, 2.00 equiv) with anhydrous dichloromethane (6 mL) was added through a syringe pump for 3 h. The resulting reaction mixture was stirred for 12 h at 40 ºC. Next, the reaction mixture was concentrated under reduced pressure, and the crude product was purified by column chromatography using EtOAc:petroleum ether (0.1:100) as mobile phase to afford **3a** as a yellow-oil (188 mg, 0.602 mmol, 60%, *dr* > 20:1).

8. Synthetic Utility:

Tert-butyl (*r*)-2-((1*s*,3*s*,7*r*)-2,2-difluoro-6,7-diphenyl-5-oxa-6-azaspiro[2.4]heptan-1-yl)-2-(phenylthio)acetate (6)

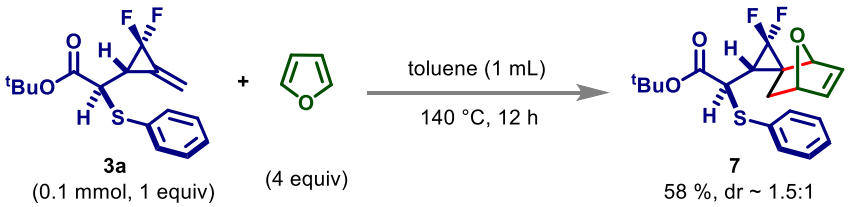


3a (0.1 mmol, 1 equiv) + (2 equiv) → **6** 67 %, dr > 20:1

Following a slightly modified procedure,[35] *tert*-butyl (*r*)-2-((*s*)-2,2-difluoro-3-methylenecyclopropyl)-2-(phenylthio)acetate (**3a**) (31 mg, 0.10 mmol, 1.0 equiv), nitrone (39 mg, 0.20 mmol, 2.0 equiv), toluene (1 mL) were mixed in a 25 mL pressure round bottom flask, and heated at 110 °C. After 12 h, the reaction mixture was extracted with diethyl ether (4 × 5 mL). The organic layers were combined, concentrated under reduced pressure, and the crude product was purified by column chromatography using EtOAc:petroleum ether (2:100) mixture as mobile phase to afford *tert*-butyl (*r*)-2-((1*s*,3*s*,7*r*)-2,2-difluoro-6,7-diphenyl-5-oxa-6-azaspiro[2.4]heptan-1-yl)-2-(phenylthio)acetate (**6**) as a light-yellow oil (34 mg, 0.07 mmol, 67%, *dr* > 20:1). **(*See Spectra*)**

- **TLC:** R_f = 0.22 (EtOAc:Petroleum ether, 1:20, v/v), $KMnO_4$
- **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.56 – 7.50 (m, 2H, Ar*H*), 7.48 – 7.36 (m, 3H, Ar*H*), 7.31 – 7.16 (m, 7H, Ar*H*), 7.05 – 6.97 (m, 3H, Ar*H*), 4.57 – 4.48 (m, 2H, OCH_2), 4.28 (d, *J* = 8.3 Hz, 1H, NC*H*Ar), 3.13 (d, *J* = 11.8, 2.0 Hz, 1H, C*H*SAr), 1.59 (t, 1H, C*H*CF_2), 1.27 (s, 9H, OC(CH_3)$_3$).
- **^{13}C NMR (101 MHz, $CDCl_3$):** δ 168.6, 149.5, 137.7, 133.6, 131.7, 129.2, 129.0, 128.8, 128.6, 128.5, 128.4, 123.1, 116.3, 108.1 (dd, *J* =291.89, 291.89 Hz), 82.4, 70.8, 64.6 (d, *J* =6.06 Hz), 46.6 (d, *J* = 2.8 Hz), 44.6 (t, *J* = 8.3 Hz), 27.6, 27.2 (t, *J* = 9.8 Hz).
- **^{19}F NMR (376 MHz, $CDCl_3$) (Major Diastereomer):** δ -133.94 (d, *J* = 159.5 Hz), -144.24 (d, *J* = 159.5 Hz).
- **^{19}F NMR (376 MHz, $CDCl_3$) (Minor Diastereomer):** δ -131.70 (d, *J* = 164.6 Hz), -138.54 (d, *J* = 164.7 Hz).
- **IR (Neat, ν):** 3135 (s), 2965 (m), 2655 (m), 2223 (w), 2145 (m), 1655 (s), 1565 (w), 1445 (w), 1331 (m), 1057 (m), 965 (w), 915 (w), 877 (m), 693 (w).
- **HRMS (ESI):** Calcd. for $C_{29}H_{29}F_2NO_3SNa^+$, $[M+Na]^+$ 532.1734; found 532.1733.

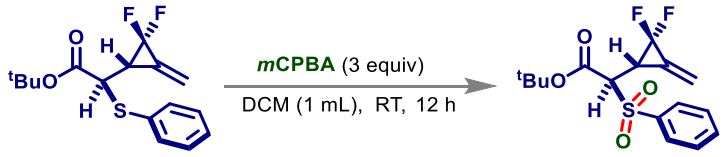
***Tert*-butyl (2*r*)-2-((1*r*)-2',2'-difluoro-7-oxaspiro[bicyclo[2.2.1]heptane-2,1'-cyclopropan]-5-en-3'-yl)-2-(phenylthio)acetate (7)**



Following a slightly modified procedure,[36] *tert*-butyl (*r*)-2-((*s*)-2,2-difluoro-3-methylenecyclopropyl)-2-(phenylthio)acetate (**3a**) (31 mg, 0.10 mmol, 1.0 equiv), furan (29 µL, 0.40 mmol, 4.0 equiv), toluene (1 mL) were mixed in a 25 mL pressure round bottom flask, and heated at 140 °C. After 12 h, the reaction mixture was extracted with diethyl ether (4 × 5 mL). The organic layers were combined, concentrated under reduced pressure, and the crude product was purified by column chromatography using EtOAc:petroleum ether (0.2:100) mixture as mobile phase to afford *tert*-butyl (2*r*)-2-((1*r*)-2',2'-difluoro-7-oxaspiro[bicyclo[2.2.1]heptane-2,1'-cyclopropan]-5-en-3'-yl)-2-(phenylthio)acetate (**7**) as a light-yellow oil (22 mg, 0.058 mmol, 58%, *dr* ~ 1.5:1). **(*See Spectra*)**

- **TLC:** R_f = 0.72 (EtOAc:Petroleum ether, 1:20, v/v), $KMnO_4$
- **^{1}H NMR (400 MHz, $CDCl_3$) (Major Diastereomer):** δ 7.60 – 7.51 (m, 2H, Ar*H*), 7.39 – 7.28 (m, 3H, Ar*H*), 6.53 – 6.45 (m, 2H, *H*C=C*H*), 5.23 (d, *J* = 4.5 Hz, 1H, OC*H*), 4.51 (s, 1H, OC*H*), 3.12 (dd, *J* = 11.5, 2.1 Hz, 1H, C*H*SAr), 2.46 – 2.38 (m, 1H, C*H*CF_2), 1.92 (dd, *J* = 13.9, 11.5 Hz, 1H, CF_2CC*H*aHbCOH), 1.46 (dd, *J* = 11.0, 1.6 Hz, 1H, CF_2CCHa*H*bCOH), 1.41 (s, 9H, OC(CH_3)$_3$).
- **^{13}C NMR (101 MHz, $CDCl_3$) (Major Diastereomer):** δ 169.3, 136.9, 135.3, 134.3, 130.7, 129.0, 128.9, 115.0 (dd, *J* = 291.9, 289.6 Hz), 82.6 (d, *J* = 2.4 Hz), 82.1, 79.7, 46.7, 37.9 (t, *J* = 8.1 Hz), 28.4 (t, *J* = 9.8 Hz), 28.0, 27.8.
- **^{19}F NMR (376 MHz, $CDCl_3$) (Major Diastereomer):** δ -131.45 (d, *J* = 164.4 Hz), -142.56 (d, *J* = 164.4 Hz).
- **IR (Neat, ν):** 2921 (s), 2852 (m), 2358 (w), 2032 (w), 1972 (w), 1733 (s), 1465 (s), 1369 (m), 1277 (m), 1148 (m), 1071 (w), 902 (w), 848 (w), 693 (m).
- **HRMS (ESI):** Calcd. for $C_{20}H_{22}F_2O_3SNa^+$, $[M+Na]^+$ 403.1155; found 403.1154.

***Tert*-butyl (*r*)-2-((*s*)-2,2-difluoro-3-methylenecyclopropyl)-2-(phenylsulfonyl)acetate (8)**



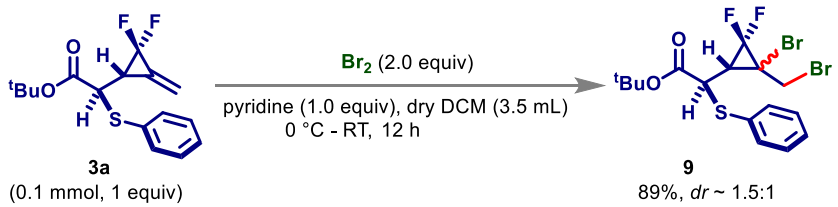
3a
(0.1 mmol, 1 equiv)

8
95%, *dr* >20:1

Following a slightly modified procedure,[37] in a flame dried 5 mL Schlenk tube, *tert*-butyl (*r*)-2-((*s*)-2,2-difluoro-3-methylenecyclopropyl)-2-(phenylthio)acetate (**3a**) (31 mg, 0.10 mmol, 1.0 equiv), dichloromethane (2.5 mL), *meta*-chloroperoxy benzoic acid (*m*CPBA) (104 mg, 0.300 mmol, 3.00 equiv, 50 % assay) were mixed at room temperature, and stirred for overnight. The reaction mixture was quenched with water (5 mL), washed with saturated Na_2SO_3 solution (3 × 4 mL), washed with saturated $NaHCO_3$ solution (3 × 5 mL), dried over anhydrous Na_2SO_4, and concentrated under reduced pressure to get the final compound **8** as a pale-yellow oil (33 mg, 0.096 mmol, 95%, *dr* > 20:1). **(*See Spectra*)**

- **TLC:** R_f = 0.15 (EtOAc:petroleum ether, 1:10 v/v), $KMnO_4$
- **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.91 (m, *J* = 8.0 Hz, 2H, Ar*H*), 7.72 (t, *J* = 4.0 Hz, 1H, Ar*H*), 7.61 (t, *J* = 7.7 Hz, 2H, Ar*H*), 6.23 – 6.15 (m, 1H, C=C*H*aHb), 6.00 – 5.94 (m, 1H, C=C*H*aHb), 3.74 – 3.62 (m, 1H, C*H*SAr), 2.87 – 2.70 (m, 1H, C*H*CF_2), 1.37 (s, 9H, OC(CH_3)$_3$).
- **^{13}C NMR (101 MHz, $CDCl_3$):** δ 162.9, 137.5, 134.5, 129.2 (d, *J* = 10.2 Hz), 127.4 (t, *J* = 6.6 Hz), 116.8, 105.30 (dd, *J* =290.9, 288.9 Hz), 84.1, 68.6 (d, *J* = 3.2 Hz), 27.7, 27.5, 25.1 (t, *J* = 13.3 Hz).
- **^{19}F NMR (376 MHz, $CDCl_3$):** δ -128.85 (d, *J* = 177.3 Hz), -137.51 (d, *J* = 177.5 Hz).
- **IR (Neat, ν):** 2921 (s), 2855 (m), 2359 (w), 2027 (w), 1738 (m), 1456 (m), 1332 (w), 1265 (m), 1147 (m), 1084 (w), 991 (w), 847 (w), 725 (w).
- **HRMS (ESI):** Calculated for $C_{16}H_{18}F_2O_4SNa^+$, $[M+Na]^+$ 367.0792; found 367.0790.

***Tert*-butyl (2*r*)-2-((1*s*)-2-bromo-2-(bromomethyl)-3,3-difluorocyclopropyl)-2-(phenylthio)acetate (9)**

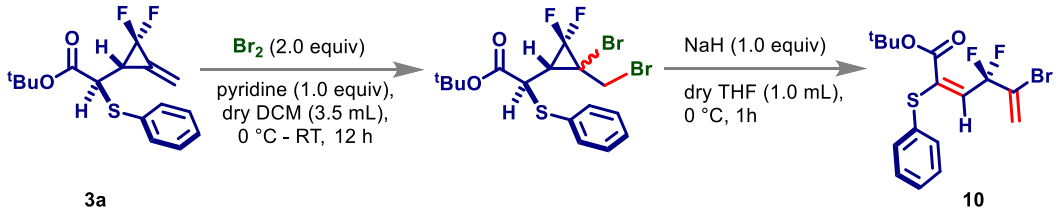


Following a slightly modified procedure,[38] pyridine (8 µL, 0.1 mmol, 1 equiv) was added to a solution of *tert*-butyl (*r*)-2-((*s*)-2,2-difluoro-3-methylenecyclopropyl)-2-(phenylthio)acetate (**3a**) (31 mg, 0.10 mmol, 1.0 equiv) in anhydrous dichloromethane (3.5 mL) under nitrogen atmosphere at 0 ºC. Next, bromine (10.5 µL, 0.200 mmol, 2.00 equiv) was added dropwise to the reaction mixture and stirred for further 11 h at room temperature. Next, the reaction mixture was quenched with water (5 mL) and extracted with dichloromethane (3 × 5 mL). The organic layers were combined, washed with brine (10 mL) solution, dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. The crude product was purified by column chromatography using petroleum ether as mobile phase to afford *tert*-butyl (2*r*)-2-((1*s*)-2-bromo-2-(bromomethyl)-3,3-difluorocyclopropyl)-2-(phenylthio)acetate (**9**) as a yellow liquid (inseparable diastereomeric mixture) (42 mg, 0.089 mmol, 89%, *dr* ~ 1.5:1). **(*See Spectra*)**

- **TLC:** R_f = 0.71 (EtOAc:petroleum ether, 1:20, v/v), $KMnO_4$
- **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.63 – 7.53 (m, 2H, Ar*H* for both diastereomers), 7.45 – 7.29 (m, 3H, Ar*H* for both diastereomers), 3.84 – 3.64 (m, 2H, BrCC*H*$_2$Br for both diastereomers), 3.49 (d, *J* = 11.1 Hz, 0.6H, C*H*SAr for major diastereomer), 3.41 (d, *J* = 11.5 Hz, 0.4H, C*H*SAr for minor diastereomer), 2.48 (td, *J* = 11.4, 2.8 Hz, 0.4H, C*H*CF_2 for minor diastereomer), 1.98 (td, *J* = 13.9, 2.6 Hz, 0.6H, for major diastereomer), 1.42 (s, 3.6H, OC(C*H*$_3$)$_3$ for minor diastereomer), 1.39 (s, 5.4H, OC(C*H*$_3$)$_3$ for major diastereomer).
- **^{13}C NMR (101 MHz, $CDCl_3$) (Major Diastereomer):** δ 168.5, 134.8, 131.2, 129.3, 129.0, 111.0 (dd, *J* = 297.9, 292.9 Hz), 82.8, 49.4, 38.7 (t, *J* = 9.5 Hz), 35.8 (d, *J* = 5.4 Hz), 34.9 (t, *J* = 9.9 Hz), 27.7.
- **^{13}C NMR (101 MHz, $CDCl_3$) (Minor Diastereomer):** δ 167.6, 135.3, 130.0, 129.6, 110.5 (dd, *J* = 297.9, 292.9 Hz), 83.2, 46.1, 42.1 (t, *J* = 11.0 Hz), 31.6 (d, *J* = 6.8 Hz), 27.5. Two carbons were not resolved at 101 MHz.

- **^{19}F NMR (376 MHz, $CDCl_3$) (Major Diastereomer):** δ -133.23 (d, *J* = 157.4 Hz), -135.02 (d, *J* = 157.2 Hz).
- **^{19}F NMR (376 MHz, $CDCl_3$) (Minor Diastereomer):** δ -125.76 (d, *J* = 157.1, 3.1 Hz), -147.82 (d, *J* = 157.2 Hz).
- **IR (Neat, ν):** 2921 (s), 2854 (m), 2360 (w), 2032 (w), 1731 (s), 1581 (w), 1446 (s), 1371 (m), 1281 (m), 1149 (s), 974 (w), 846 (w), 745 (m).
- **HRMS (ESI):** Calculated for $C_{16}H_{18}Br_2F_2O_2SNa^+$, $[M+Na]^+$ 494.9240; found 494.9243.

***Tert*-butyl (*E*)-5-bromo-4,4-difluoro-2-(phenylthio)hexa-2,5-dienoate (10)**



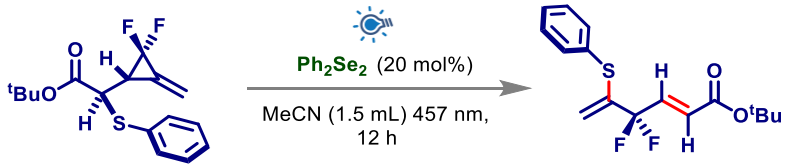
Step 1: Following a slightly modified procedure,[38] pyridine (8 µL, 0.1 mmol, 1 equiv) was added to a solution of *tert*-butyl (*r*)-2-((*s*)-2,2-difluoro-3-methylenecyclopropyl)-2-(phenylthio)acetate (**3a**) (31 mg, 0.10 mmol, 1.0 equiv) in anhydrous dichloromethane (3.5 mL) under nitrogen atmosphere at 0 ºC. Next, bromine (10.5 µL, 0.200 mmol, 2.00 equiv) was added dropwise to the reaction mixture and stirred for further 11 h at room temperature. Next, the reaction mixture was quenched with water (5 mL) and extracted with dichloromethane (3 × 5 mL). The organic layers were combined, washed with brine (10 mL) solution, dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. The crude product was subjected to the next step without further purification.

Step 2: The crude dibromo compound was dissolved in dry THF (1 mL) and this solution was added dropwise to the NaH (60 % dispersed in mineral oil, 4 mg, 0.1 mmol,1 equiv) at 0 ºC and stirred for 1 h. After completion, the reaction mixture was quenched with saturated ammonium chloride solution (3 mL) and extracted with DCM (3 × 5 mL). The organic layers were combined, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography using petroleum ether as eluent to afford *tert*-butyl (*E*)-5-bromo-4,4-difluoro-2-(phenylthio)hexa-2,5-dienoate **(10)** as a light-yellow oil (33 mg, 0.08 mmol, 85%, *E:Z* > 20:1). **(***See Spectra***)**

- **TLC:** R_f = 0.67 (EtOAc:petroleum ether, 1:20, v/v), $KMnO_4$

- **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.35 – 7.26 (m, 5H, Ar*H*), 6.84 (t, *J* = 11.7 Hz, 1H, CF_2CH), 6.49 – 6.44 (m, 1H, C*H*aHbCBr), 6.00 – 5.95 (m, 1H, CHa*H*bCBr)), 1.15 (s, 9H, $OC(CH_3)3$.
- **^{13}C NMR (101 MHz, $CDCl_3$):** δ 162.8, 134.0, 133.7, 133.6 (t, *J* = 30.3 Hz), 130.9, 129.1, 127.7, 122.9 (t, *J* = 5.5 Hz), 68.2, 27.3. Two carbons were not resolved at 101 MHz.
- **^{19}F NMR (376 MHz, $CDCl_3$):** δ -87.76.
- **IR (Neat, ν):** 3031 (s), 2989 (s), 2550 (m), 2223 (w), 1753 (m), 1687 (w), 1422 (m), 1222 (w), 1165 (w), 1045 (w), 972 (w), 865 (w), 715 (m).
- **HRMS (ESI):** Calculated for $C_{16}H_{17}BrF_2O_2SNa^+$, $[M+Na]^+$ 412.9998; found 412.9988.

***Tert*-butyl (*E*)-4,4-difluoro-5-(phenylthio)hexa-2,5-dienoate (11)**

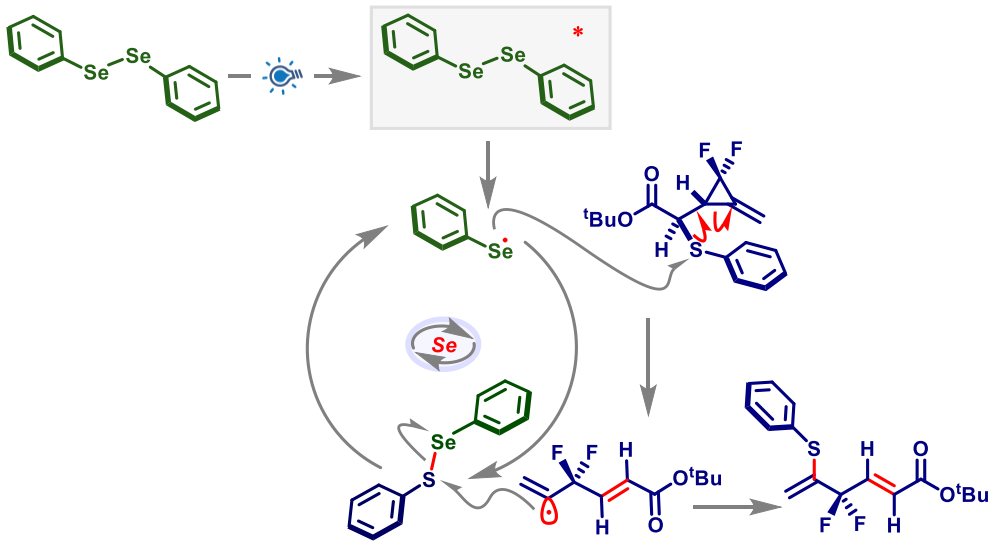


In an oven dry 5.0 mL glass vial, catalytic amount of diphenyl diselenide (6.2 mg, 0.20 equiv, 0.02 mmol), *tert*-butyl (*r*)-2-((*s*)-2,2-difluoro-3-methylenecyclopropyl)-2-(phenylthio)acetate (**3a**) (31 mg, 0.10 mmol, 1.0 equiv), and anhydrous acetonitrile (1.5 mL) were mixed at room temperature under argon atmosphere. Then the reaction mixture was irradiated under 457 nm wavelength blue light, 100% intensity in PhotoCube^{TM} (ThalesNano) instrument. After 12 h, the reaction mixture was concentrated and the crude product was purified by column chromatography using petroleum ether as mobile phase to afford *tert*-butyl (*E*)-4,4-difluoro-5-(phenylthio)hexa-2,5-dienoate (**11**) a light-yellow liquid (25 mg, 0.080 mmol, 80%). **(*See Spectra*)**

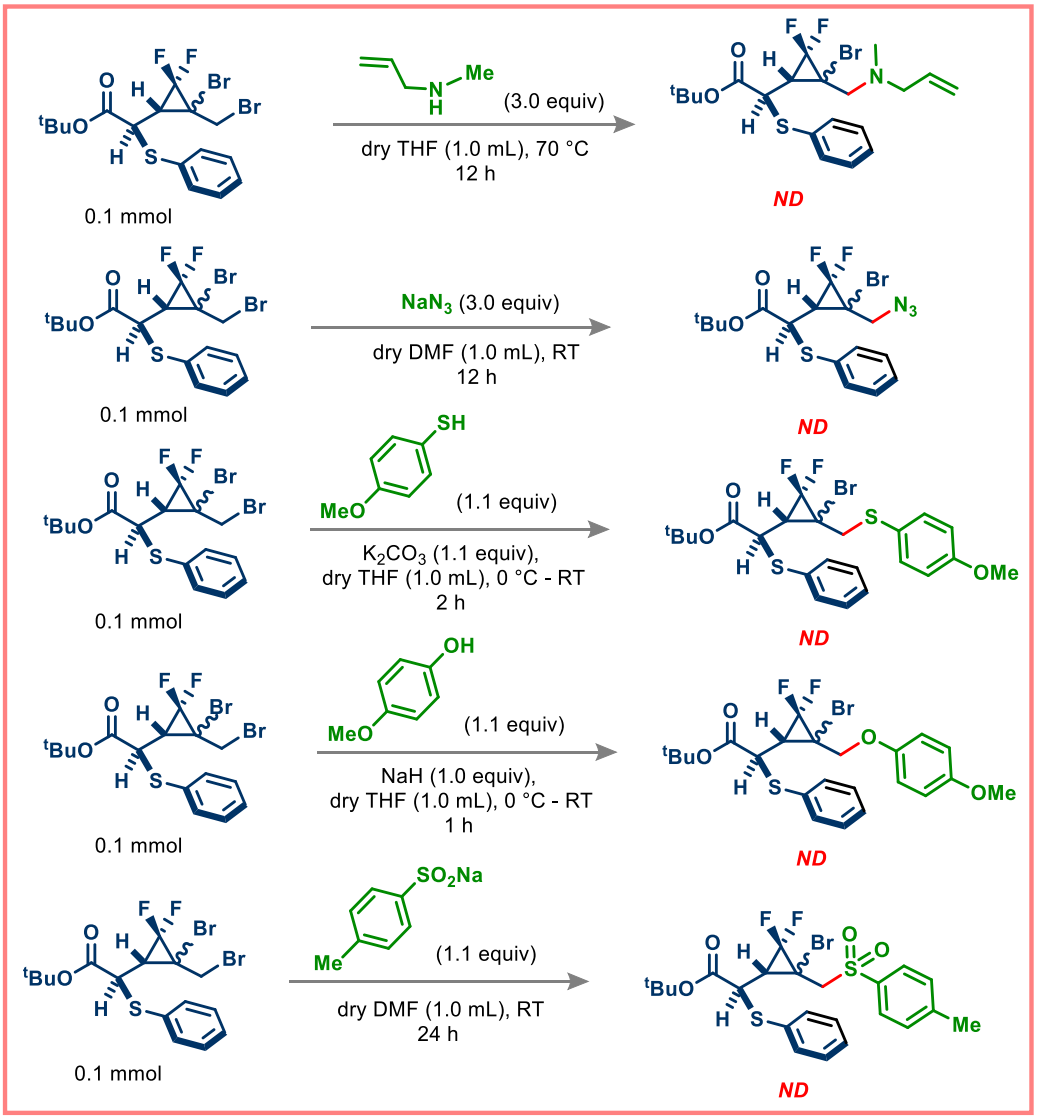
- **TLC:** R_f = 0.57 (EtOAc:petroleum ether, 1:20, v/v), $KMnO_4$
- **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.67 – 7.56 (m, 2H, Ar*H*), 7.42 – 7.32 (m, 3H, Ar*H*), 6.89 – 6.73 (m, 1H, CF_2CH=CH), 6.28 (d, *J* = 15.8 Hz, 1H, CF_2CH=C*H*), 6.15 (s, 1H, C=C*H*aHb), 5.45 (s, 1H, C=CHa*H*b), 1.52 (s, 9H, $OC(CH_3)_3$).
- **^{13}C NMR (101 MHz, $CDCl_3$):** δ 164.1, 137.4 (t, *J* = 14.4 Hz), 136.9 (t, *J* = 29.2 Hz), 135.1, 129.6, 128.7, 127.6 (t, *J* = 6.4 Hz), 127.6, 122.6 (t, *J* = 7.3 Hz), 117.9 (t, *J* = 241.6 Hz), 81.7, 28.0.
- **^{19}F NMR (376 MHz, $CDCl_3$);** δ -93.79.

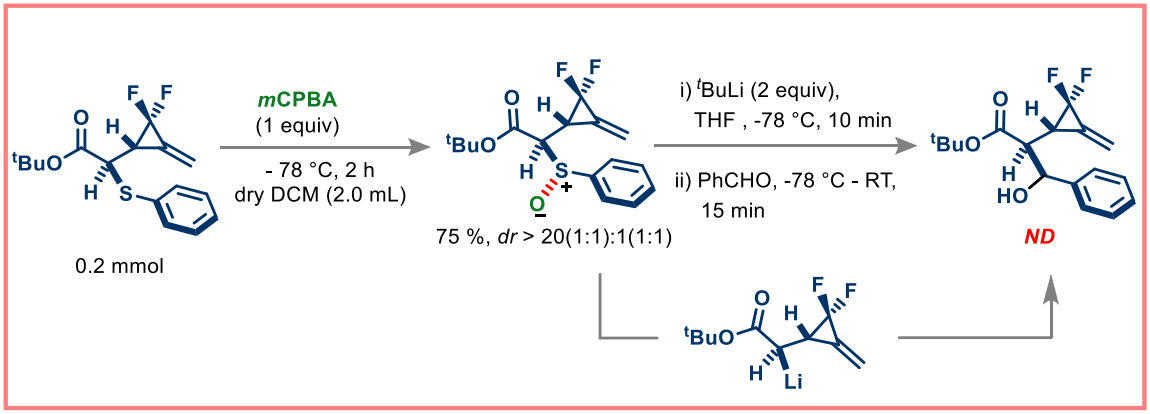
- **IR (Neat, ν):** 2920 (s), 2854 (s), 2360 (w), 2028 (w), 1735 (m), 1458 (m), 1373 (w), 1252 (w), 1157 (m), 1045 (w), 972 (w), 861 (w), 739 (m), 692 (w).
- **HRMS (ESI):** The compound was not detected by HRMS using ESI and CI techniques, but it was found in GCMS (Calcd. for $C_{16}H_{18}F_2O_2S^+$, $[M]^+$ 312; found 312).

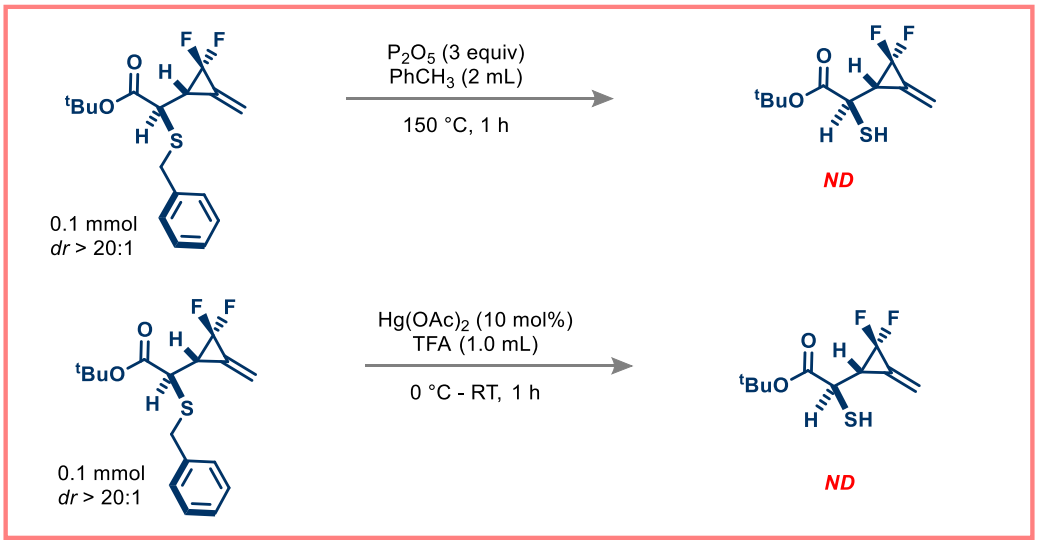
Mechanism of Difluoro-skipped-diene Synthesis:



Failed Experiments:



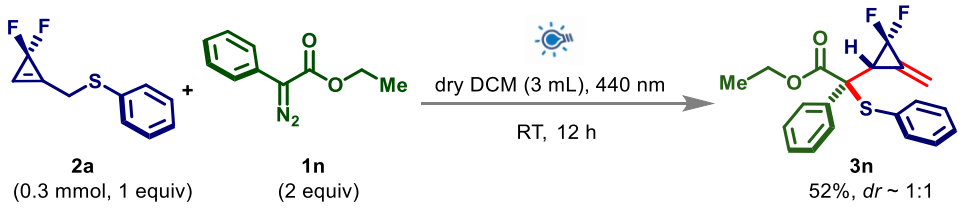




9. Mechanistic Studies:

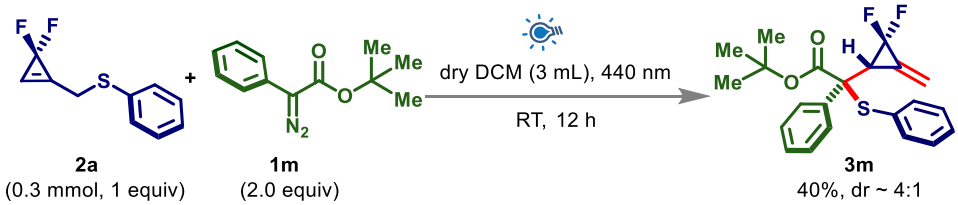
- **Experiment to Support Unbound Ylide for Donor-acceptor Diazo Compound:**

Ethyl (*s*)-2-((*s*)-2,2-difluoro-3-methylenecyclopropyl)-2-phenyl-2-(phenylthio)acetate (3n)



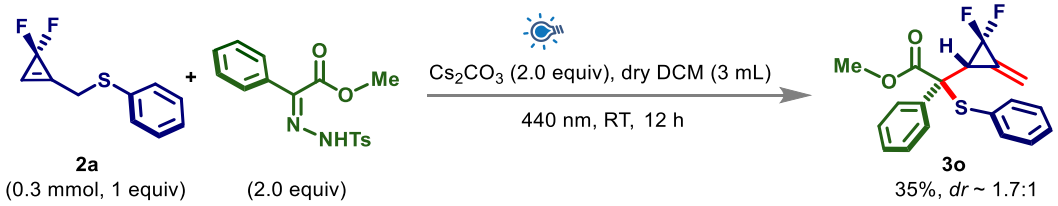
In an oven dry 5.0 mL glass vial, ethyl 2-diazo-2-phenylacetate (**1n**) (114 mg, 2.00 equiv, 0.600 mmol), ((3,3-difluorocycloprop-1-en-1-yl)methyl)(phenyl)sulfane (**2a**) (60 mg, 0.30 mmol, 1.0 equiv), and anhydrous dichloromethane (3 mL) were mixed at room temperature under argon atmosphere. Then the closed vial reaction mixture was irradiated under 440 nm wavelength (Kessil LED) light, 100% intensity. After 12 h, the reaction mixture was concentrated under reduced pressure and the residue was purified by column chromatography using petroleum ether as mobile phase to afford ethyl (*s*)-2-((*s*)-2,2-difluoro-3-methylenecyclopropyl)-2-phenyl-2-(phenylthio)acetate (**3n**) as a light-yellow liquid (inseparable diastereomeric mixture) (56 mg, 0.16 mmol, 52%, *dr* ~ 1:1).

***Tert*-butyl (*s*)-2-((*s*)-2,2-difluoro-3-methylenecyclopropyl)-2-phenyl-2-(phenylthio)acetate (3m)**



In an oven dry 5.0 mL glass vial, *tert*-butyl 2-diazo-2-phenylacetate (**1m**) (131 mg, 0.600 mmol, 2.00 equiv), ((3,3-difluorocycloprop-1-en-1-yl)methyl)(phenyl)sulfane (**2a**) (60 mg, 0.30 mmol, 1.0 equiv), and anhydrous dichloromethane (3 mL) were mixed at room temperature under argon atmosphere. Then the closed vial reaction mixture was irradiated under 440 nm wavelength (Kessil LED) light, 100% intensity. After 12 h, the reaction mixture was concentrated under reduced pressure, and the residue was purified by column chromatography using petroleum ether as mobile phase to afford *tert*-butyl (*s*)-2-((*s*)-2,2-difluoro-3-methylenecyclopropyl)-2-phenyl-2-(phenylthio)acetate (**3m**) as a light-yellow solid (inseparable diastereomeric mixture) (47 mg, 0.12 mmol, 40%, *dr* ~ 4:1).

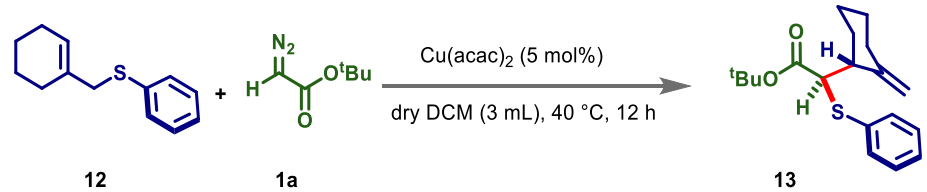
Methyl (*s*)-2-((*s*)-2,2-difluoro-3-methylenecyclopropyl)-2-phenyl-2-(phenylthio)acetate (3o)



In an oven dry 10.0 mL glass vial, methyl-2-phenyl-2-(2-tosylhydrazineylidene)acetate (200 mg, 0.600 mmol, 2.00 equiv), ((3,3-difluorocycloprop-1-en-1-yl)methyl)(phenyl)sulfane (**2a**) (60 mg, 0.30 mmol, 1.0 equiv), Cs_2CO_3 (195 mg, 0.600 mmol, 2.00 equiv) and anhydrous dichloromethane (3 mL) were mixed at room temperature under argon atmosphere. Then the closed vial reaction mixture was irradiated under 440 nm wavelength (Kessil LED) light, 100% intensity. After 12 h, the reaction mixture was concentrated under reduced pressure, and the residue was purified by column chromatography using EtOAc:petroleum ether (0.25:100) as mobile phase to afford *methyl* (*s*)-2-((*s*)-2,2-difluoro-3-methylenecyclopropyl)-2-phenyl-2-(phenylthio)acetate (**3o**) as a light-yellow oil (inseparable diastereomeric mixture) (37 mg, 0.11 mmol, 36%, *dr* ~ 1.7:1).

- **Control Experiment with strain-free substrates**

***Tert*-butyl (*r*)-2-((*r*)-2-methylenecyclohexyl)-2-(phenylthio)acetate (13)**

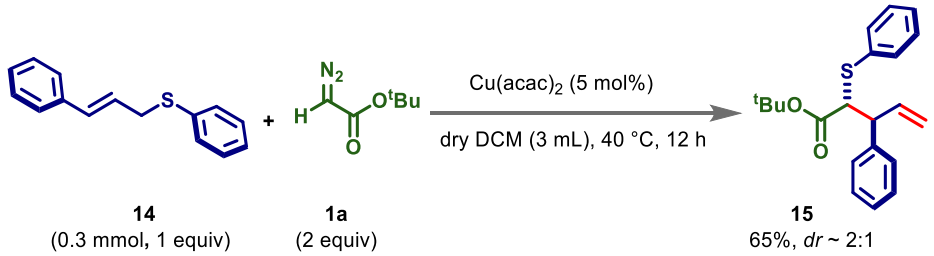


12 (0.3 mmol, 1 equiv) **1a** (2 equiv) **13** 19%, *dr* ~ 4:1

A flame dried 5 mL Schlenk tube under nitrogen was charged with copper (II) acetylacetonate (4.0 mg, 15 μmol, 0.05 equiv), (cyclohex-1-en-1-ylmethyl)(phenyl)sulfane (**12**) (61 mg, 0.30 mmol, 1.0 equiv), and anhydrous dichloromethane (1 mL) and stirred at 40 ºC for 10 min. To this reaction mixture, a solution of *tert*-butyl 2-diazoacetate (**1a**) (85 mg, 0.60 mmol, 2.0 equiv) in anhydrous dichloromethane (2 mL) was added through a syringe pump for 3 h. The resulting reaction mixture was stirred for 12 h at 40 ºC. Next, the reaction mixture was concentrated under reduced pressure, and the crude product was purified by column chromatography using petroleum ether as mobile phase to obtain *tert*-butyl (*r*)-2-((*r*)-2-methylenecyclohexyl)-2-(phenylthio)acetate (**13**) as yellow-oil (inseparable diastereomeric mixture) (18 mg, 0.057 mmol, 19%, *dr* ~ 4:1). **(*See Spectra*)**

- **TLC:** R_f = 0.55 (EtOAc:petroleum ether, 1:20 v/v), $KMnO_4$
- **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.54 – 7.42 (m, 2H, Ar*H* for both diastereomers), 7.32 – 7.19 (m, 3H, Ar*H* for both diastereomers), 4.90 – 4.78 (m, 1.6H, C=C*H*a*H*b for major diatereomer), 4.75 – 4.70 (m, 0.2H, C=C*H*aHb for minor diatereomer), 4.69 – 4.65 (m, 0.2H, C=CHa*H*b for minor diatereomer), 3.95 (d, *J* = 11.1 Hz, 0.8H, C*H*SAr for major diastereomer), 3.82 (d, *J* = 11.5 Hz, 0.2H, C*H*SAr for minor diastereomer), 2.72 – 2.56 (m, 1H, $CH_2CHC=CH_2$ for both diastereomers), 2.32 – 2.10 (m, 2H, aliphatic CH_2 for both diastereomers), 1.77 – 1.36 (m, 6H, aliphatic CH_2 for both diastereomers), 1.29 (s, 7.2H, $OC(CH_3)_3$ for major diastereomer), 1.25 (s, 1.8H, $OC(CH_3)_3$ for minor diastereomer).
- **^{13}C NMR (101 MHz, $CDCl_3$) (for both Diastereomers):** δ 171.2, 149.1, 147.7, 134.3, 132.7, 130.0, 129.0, 128.9, 128.8, 128.7, 127.5, 127.4, 110.3, 109.0, 81.4, 81.1, 54.0, 52.5, 45.1, 44.7, 33.5, 32.7, 31.3, 30.1, 29.7, 28.4, 28.0, 27.8, 22.6, 22.2.
- **HRMS (ESI):** Calculated for $C_{19}H_{26}O_2SNa^+$, $[M+Na]^+$ 341.1551; found 341.1558.

***Tert*-butyl (2*r*,3*s*)-3-phenyl-2-(phenylthio)pent-4-enoate (15)**



A flame dried 5 mL Schlenk tube under nitrogen was charged with copper (II) acetylacetonate (4.0 mg, 15 µmol, 0.05 equiv), cinnamyl(phenyl)sulfane (**14**) (68 mg, 0.30 mmol, 1.0 equiv), anhydrous dichloromethane (1 mL) and stirred at 40 ºC for 10 min. To this reaction mixture a solution of *tert*-butyl 2-diazoacetate (**1a**) (85 mg, 0.60 mmol, 2.0 equiv) in anhydrous dichloromethane (2 mL) was added through a syringe pump for 3 h. The resulting reaction mixture was stirred for 12 h at 40 ºC. Next, the reaction mixture was concentrated under reduced pressure, and the crude product was purified by column chromatography using petroleum ether as mobile phase to obtain *tert*-butyl (2R,3S)-3-phenyl-2-(phenylthio)pent-4-enoate (**15**) as yellow-oil (inseparable diastereomeric mixture) (66 mg, 0.19 mmol, 65%, *dr* ~ 2:1).

- **TLC:** R_f = 0.55 (EtOAc:petroleum ether, 1:20 v/v), $KMnO_4$
- **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.39 – 7.16 (m, 10H, ArH of both diastereomers), 6.20 – 6.08 (m, 0.75H, CH_2=C*H* for major diastereomer), 6.08 – 5.96 (m, 0.25H, CH_2=C*H* for minor diastereomer), 5.22 – 5.16 (m, 1.5H, C*H*$_2$=CH for major diastereomer), 5.16 – 5.09 (m, 0.5H, C*H*$_2$=CH for minor diastereomer), 3.95 (d, *J* = 11.4 Hz, 1H, C*H*SAr for both diastereomers), 3.80 – 3.63 (m, 1H, C*H*Ar for both diastereomer), 1.33 (s, 2.25H, OC(C*H*$_3$)$_3$ for minor diastereomer), 1.02 (s, 6.75H, OC(C*H*$_3$)$_3$ for major diastereomer).
- **^{13}C NMR (101 MHz, $CDCl_3$) (Major Diastereomer):** δ 169.8, 140.8, 138.1, 134.5, 133.1, 128.7, 128.4, 128.1, 127.7, 126.9, 117.3, 81.1, 56.4, 51.8, 27.3.
- **^{13}C NMR (101 MHz, $CDCl_3$) (Minor Diastereomer):** δ 170.3, 140.0, 138.0, 133.8, 133.0, 128.6, 128.5, 128.2, 127.6, 127.0, 116.8, 81.6, 56.6, 51.9, 27.7.

The characterization data corresponded to the reported values.[39]

10. Crystal Structures:

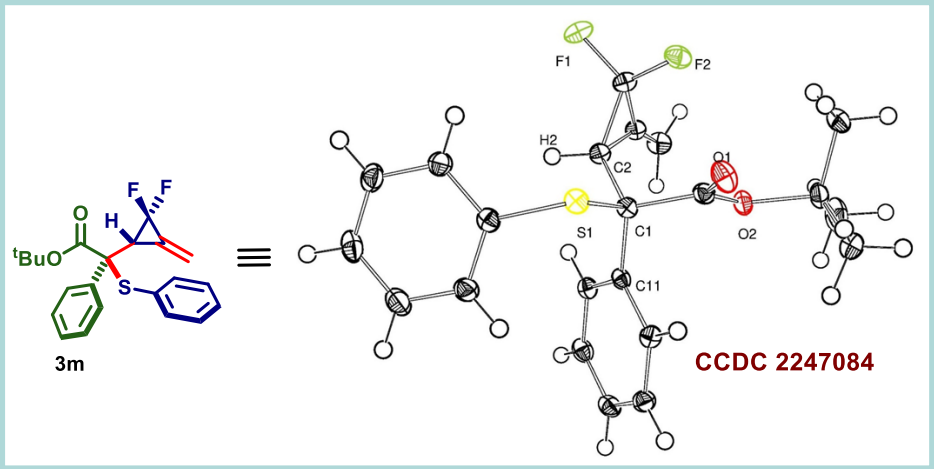


***Figure 1*:** ORTEP diagram of the compound **3m** with 50% thermal ellipsoidal probability. Out of two molecules present in the asymmetric unit, only one is shown here as a representative. Torsional angle between H2-C2-C1-C11 is 61.76(0.91) deg for the first residue and 68.44(0.91) deg for second residue.

Table 1: Crystal Data and Structure Refinement for **3m:**

CCDC number	**2247084**
Identification code	DKR-117
Empirical formula	C_{22} H_{22} F_2 O_2 S
Formula weight	388.45
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	*P* -1
Unit cell dimensions	a = 10.1488(5) Å, b = 13.7389(7) Å, c = 15.2173(8) Å **α** = 68.135(2)°, β = 83.265(2)°, γ = 86.091(2)°
Volume	1954.89(17) $Å^3$
Z	4
Density (calc)(mg/m^3)	1.320
Absorption coefficient(mm^{-1})	0.198
F(000)	816

Crystal size(mm^3)	0.498 x 0.244 x 0.132
Theta range for data collection	1.449 to 30.137°.
Index ranges	-14<=h<=14, -19<=k<=19, -21<=l<=21
Reflections collected	96899
Independent reflections	11514 [R(int) = 0.0507]
Completeness to theta = 25.242°	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7460 and 0.7118
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	11514 / 0 / 663
Goodness-of-fit on F^2	1.034
Final R indices [I>2sigma(I)]	R1 = 0.0358, wR2 = 0.0899
R indices (all data)	R1 = 0.0499, wR2 = 0.0983
Extinction coefficient	n/a
Largest diff. peak and hole	0.482 and -0.331 e.$Å^{-3}$

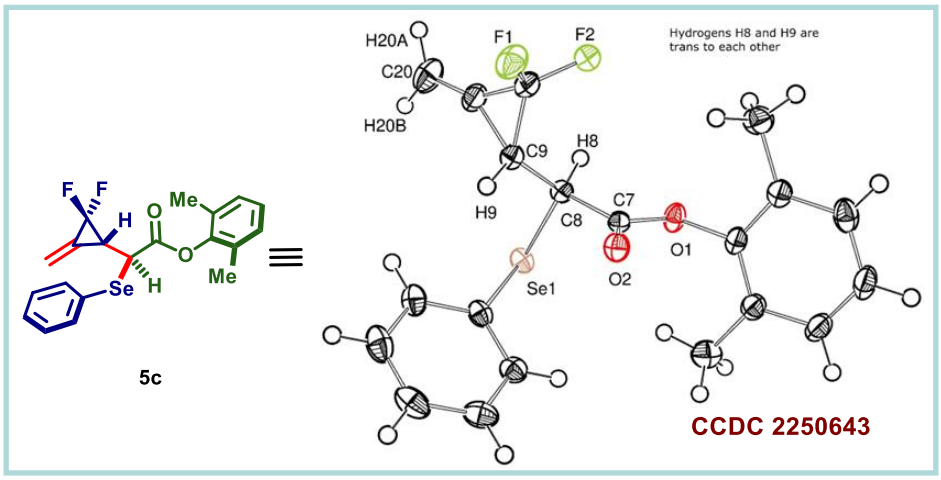


Figure 2: ORTEP plot of compound **5c** with 50% thermal ellipsoidal probability. Molecule sits in Centro-symmetric Space Group $P2_1/n$.

Table 2: Crystal Data and Structure Refinement for **5c:**

CCDC Number	**2250643**
Identification code	DKR-153
Empirical formula	$C_{20}\ H_{18}\ F_2\ O_2\ Se$
Formula weight	407.30
Temperature	113(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	*P* $2_1/n$
Unit cell dimensions	a = 10.8764(10) Å, b = 12.9635(12) Å, c = 12.9906(12) Å, b= 92.134(4)°.
Volume	1830.4(3) $Å^3$
Z	4
Density (calculated)	1.478 Mg/m^3
Absorption coefficient	2.080 mm^{-1}
F(000)	824
Crystal size mm^3	0.380 x 0.230 x 0.070

Theta range for data collection	3.143 to 29.590°.
Index ranges	-15<=h<=15, -17<=k<=17, -18<=l<=18
Reflections collected	92660
Independent reflections	5120 [R(int) = 0.0359]
Completeness to theta = 25.242°	99.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7459 and 0.6517
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5120 / 0 / 228
Goodness-of-fit on F^2	1.044
R indices (all data)	R1 = 0.0296, wR2 = 0.0674
Extinction coefficient	n/a
Largest diff. peak and hole	0.966 and -0.668 e.$Å^{-3}$

11. References:

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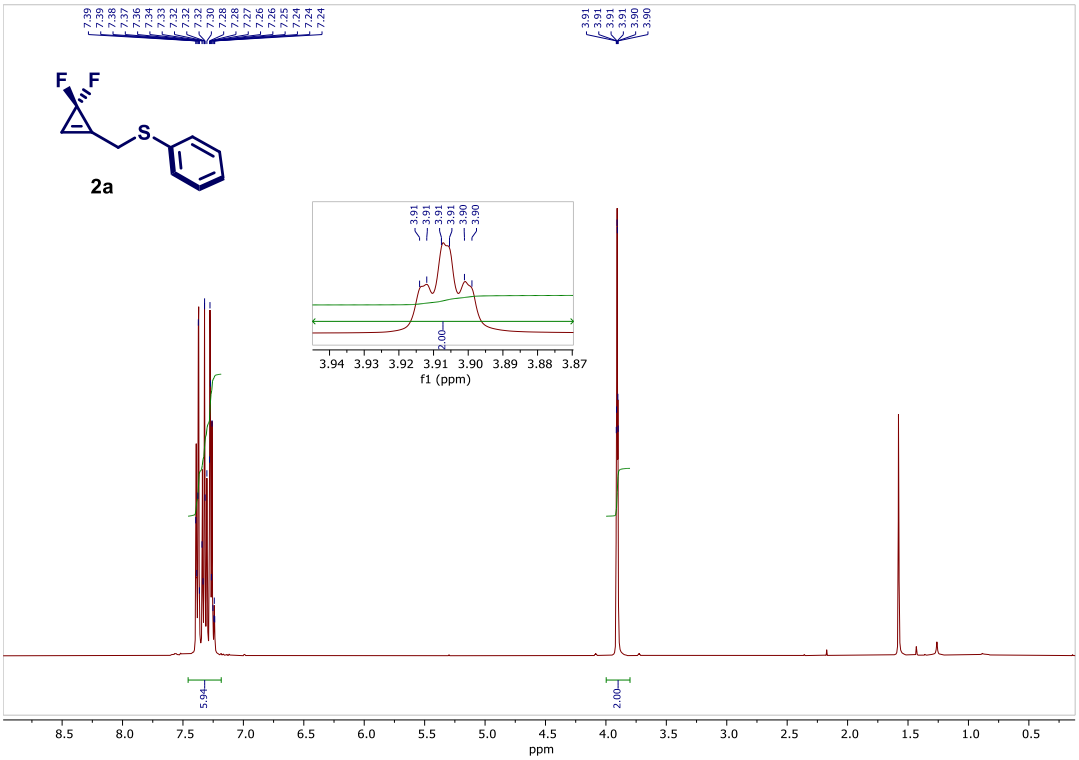
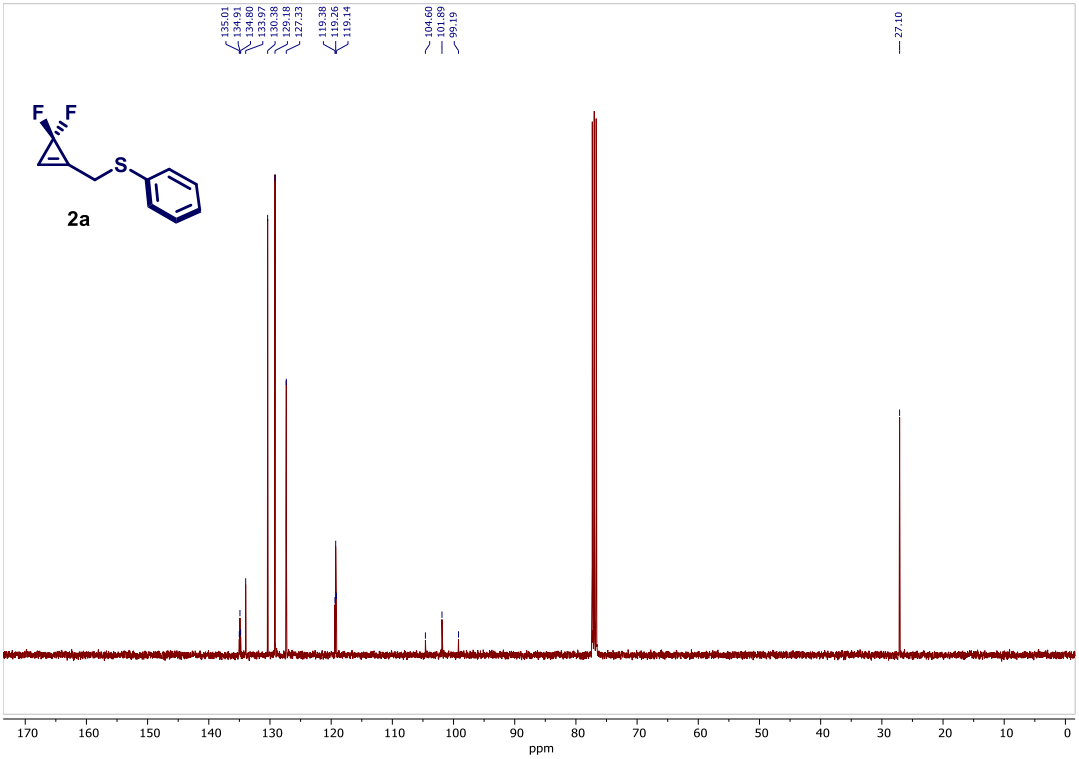
12. NMR Spectra of new compounds:

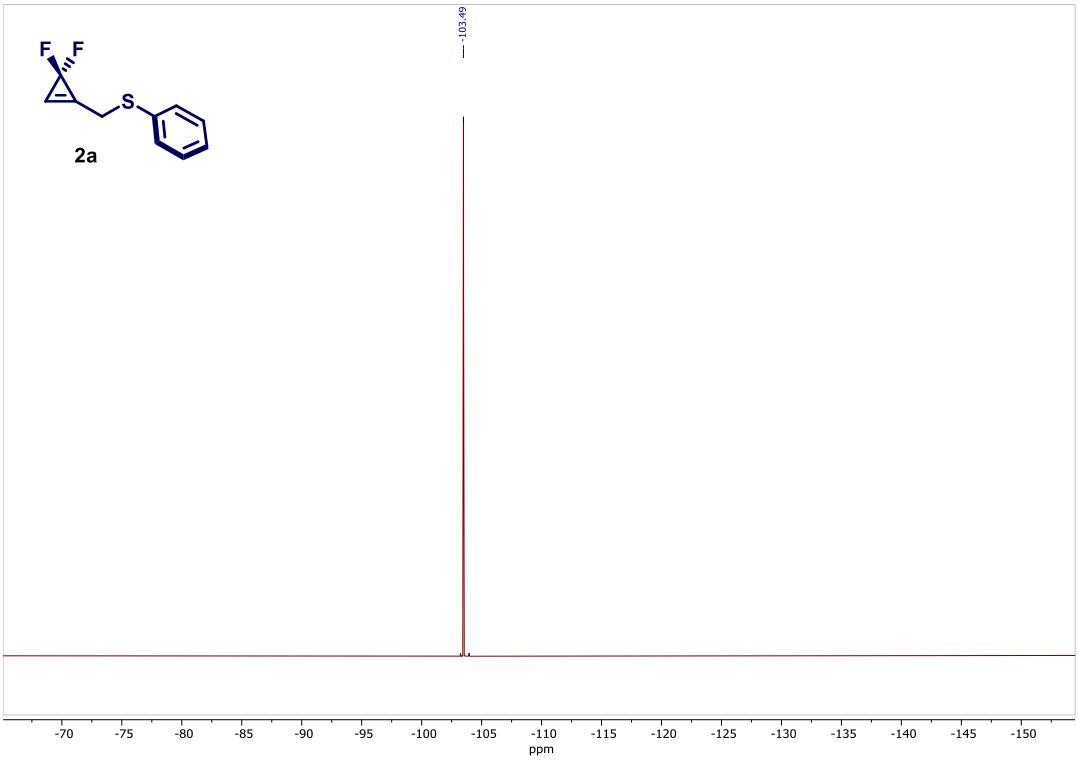
^{1}H NMR (400 MHz, $CDCl_3$) of compound **2a: (***See Procedure***)**



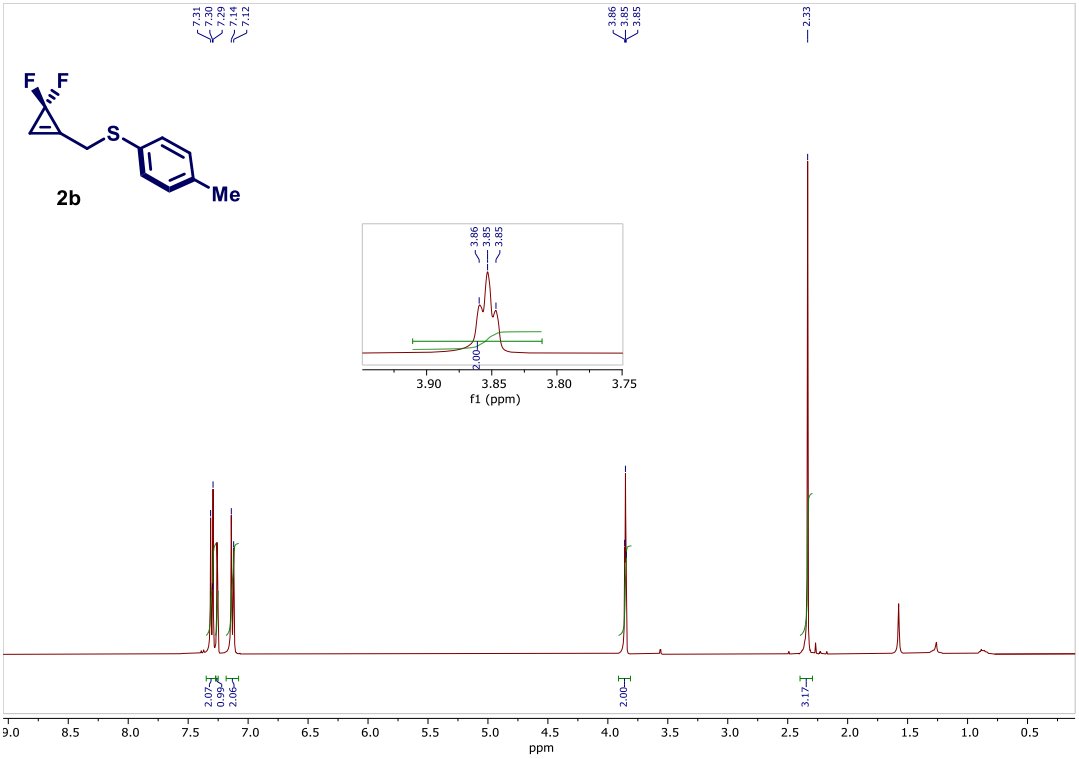
^{13}C NMR (101 MHz, $CDCl_3$) of Compound **2a**:



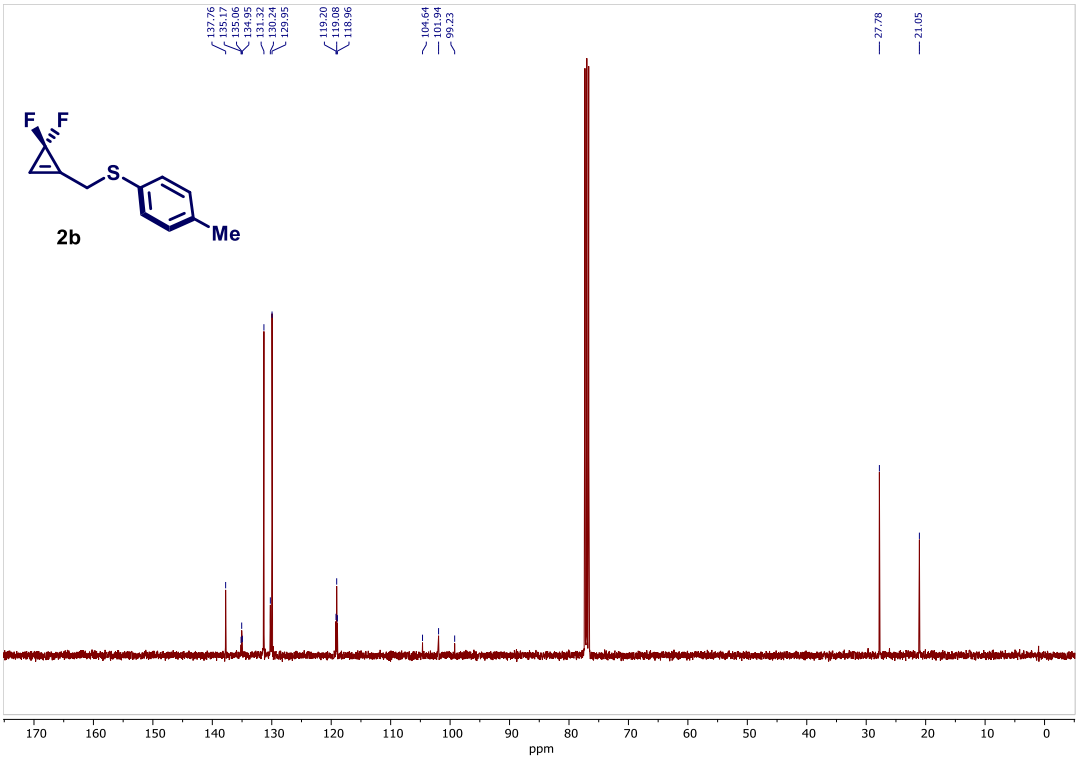
^{19}F NMR (376 MHz, $CDCl_3$) of compound **2a:**



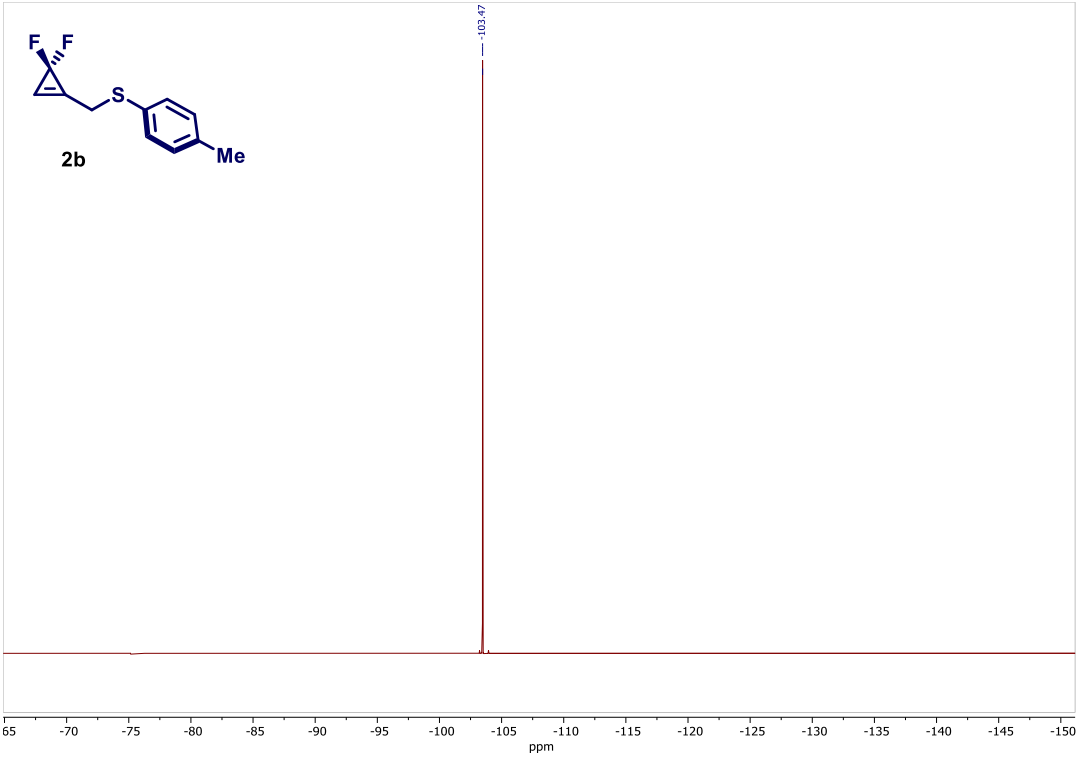
^{1}H NMR (400 MHz, $CDCl_3$) of compound **2b**: **(*See Procedure*)**



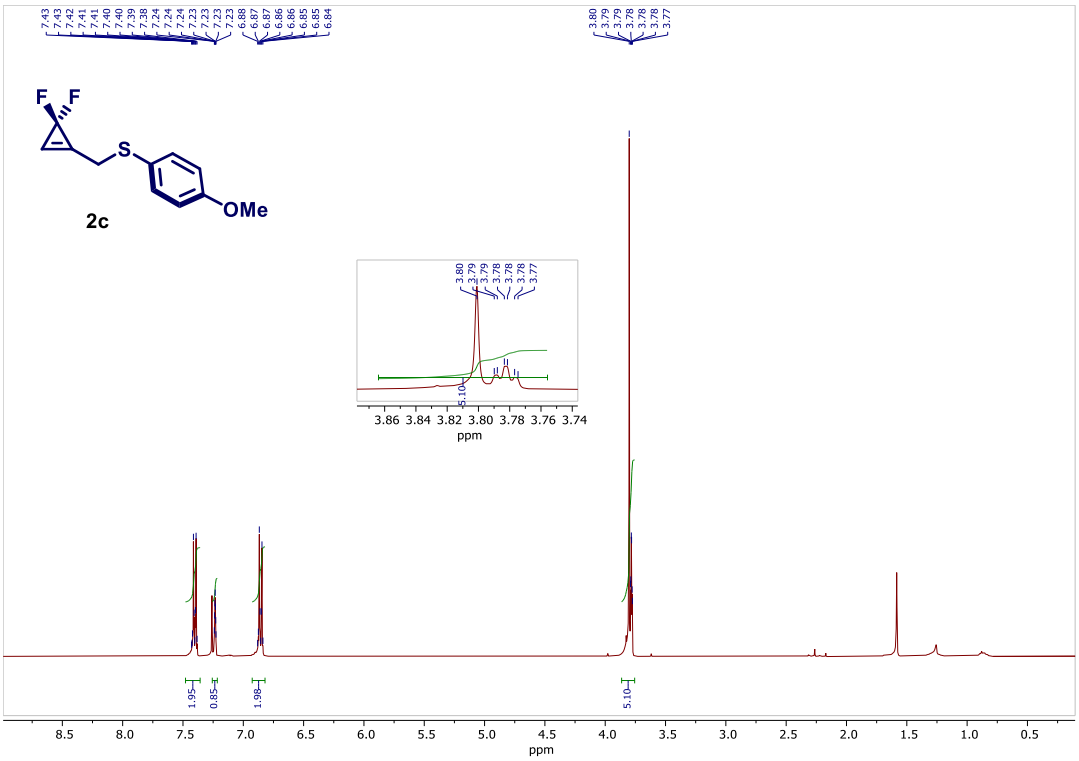
^{13}C NMR (101 MHz, $CDCl_3$) of Compound **2b**:



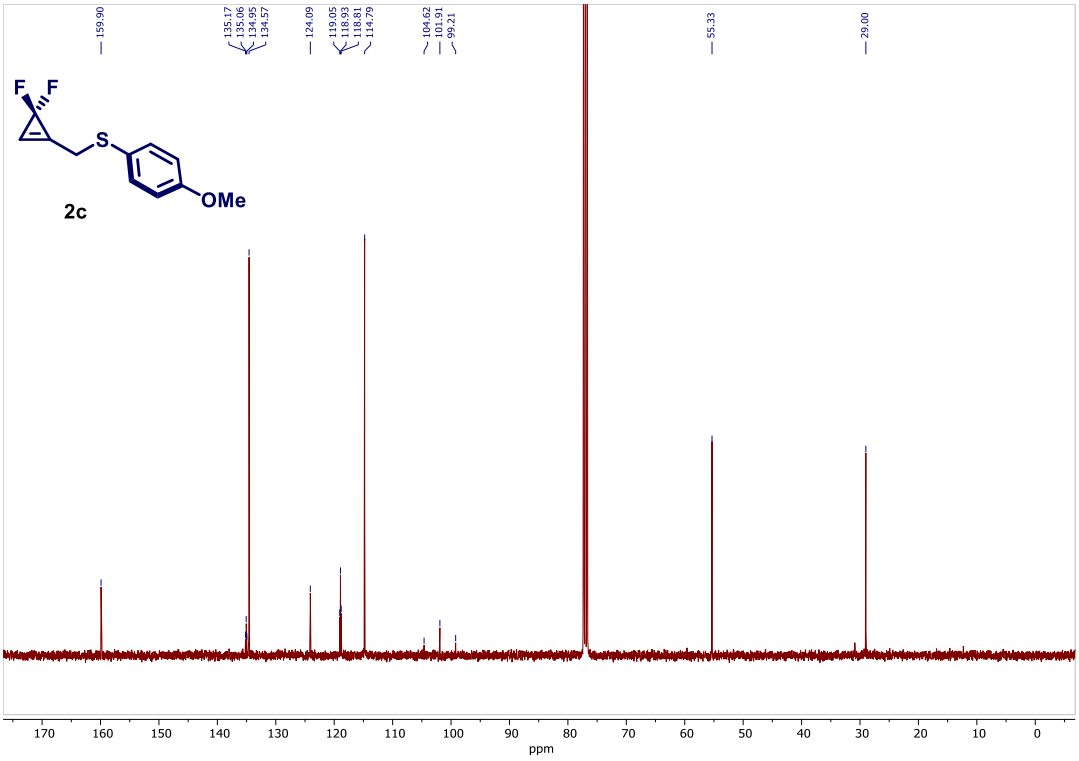
^{19}F NMR (376 MHz, $CDCl_3$) of compound **2b:**



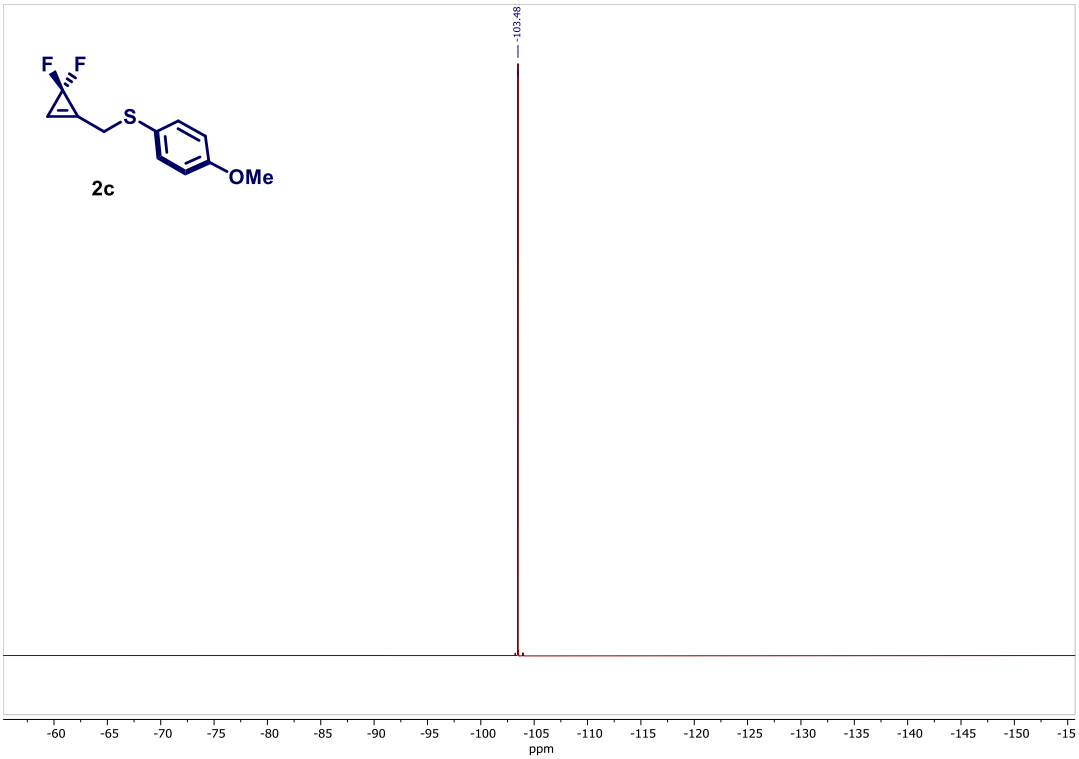
^{1}H NMR (400 MHz, $CDCl_3$) of compound**2c**: **(***See Procedure***)**



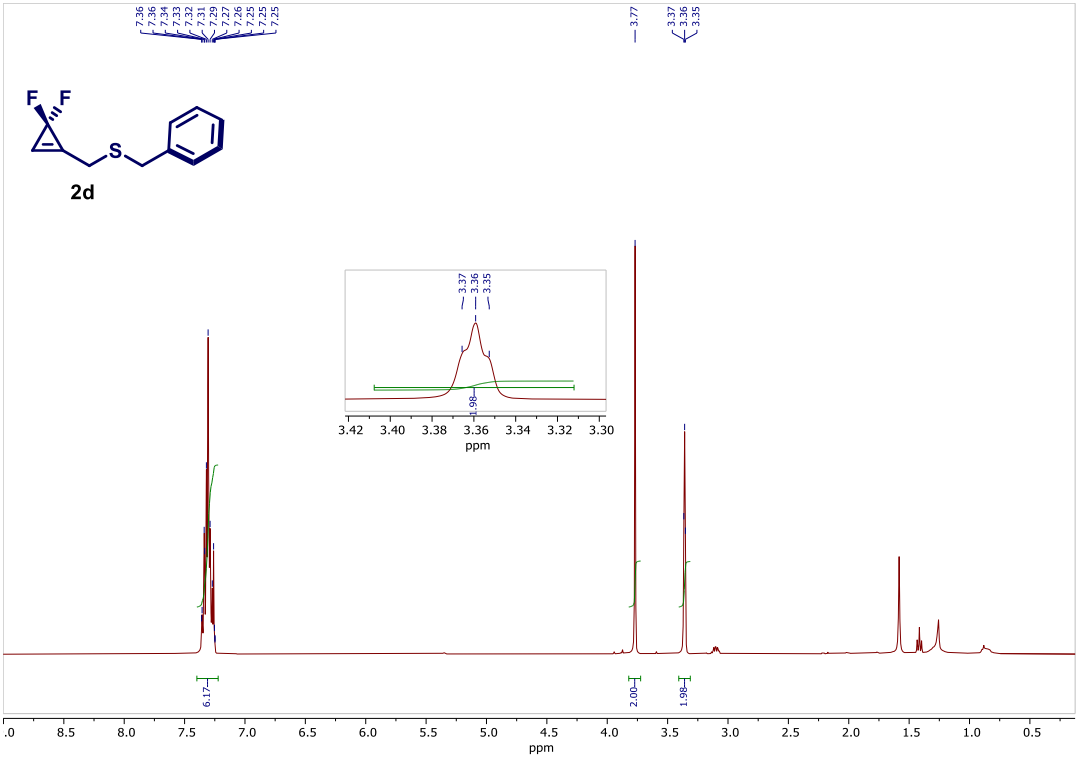
^{13}C NMR (101 MHz, $CDCl_3$) of Compound **2c**:



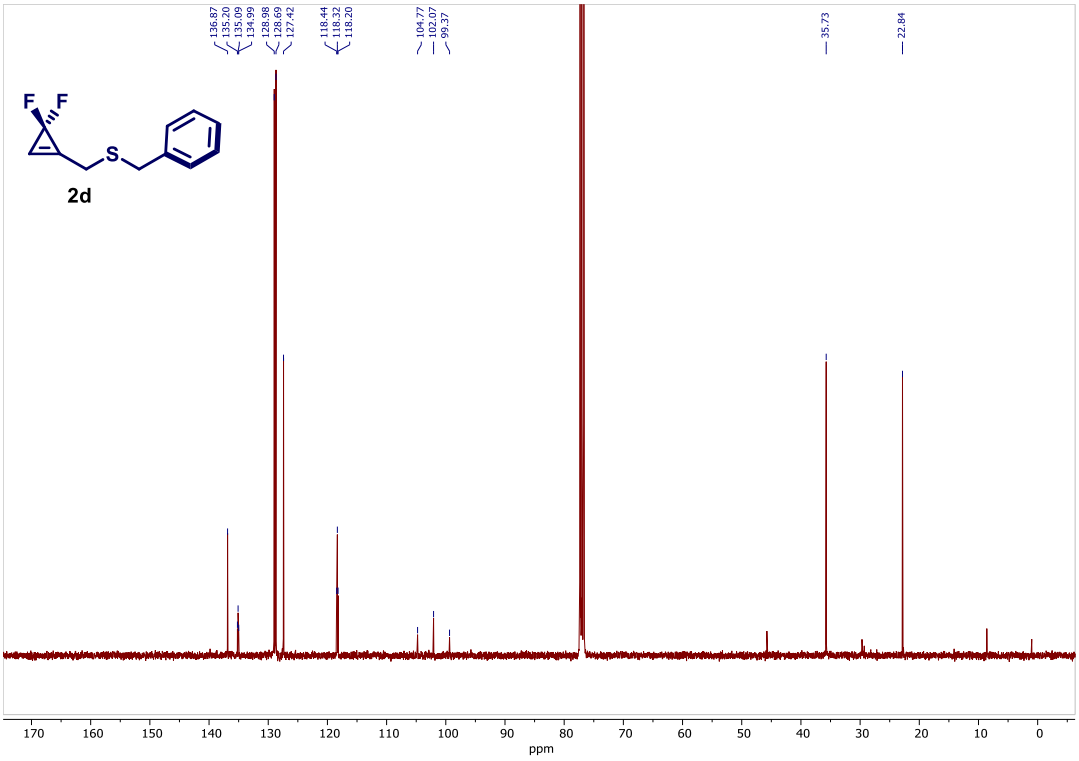
^{19}F NMR (376 MHz, $CDCl_3$) of compound **2c:**



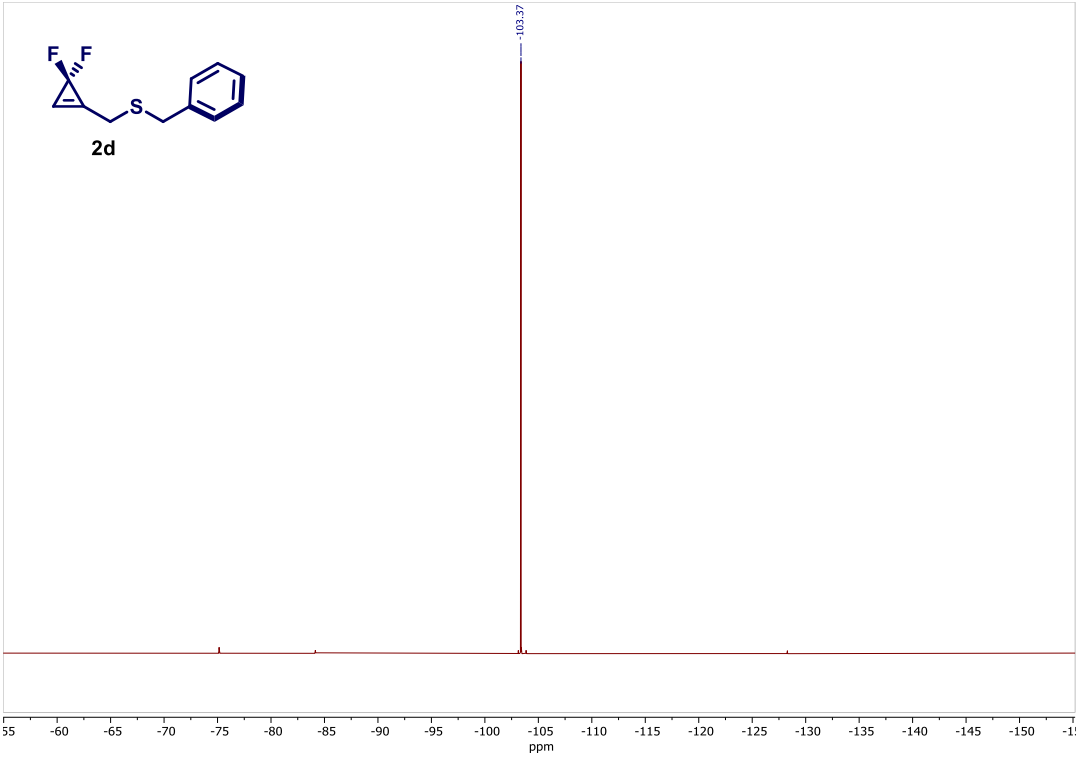
^{1}H NMR (400 MHz, $CDCl_3$) of compound **2d**: **(*See Procedure*)**



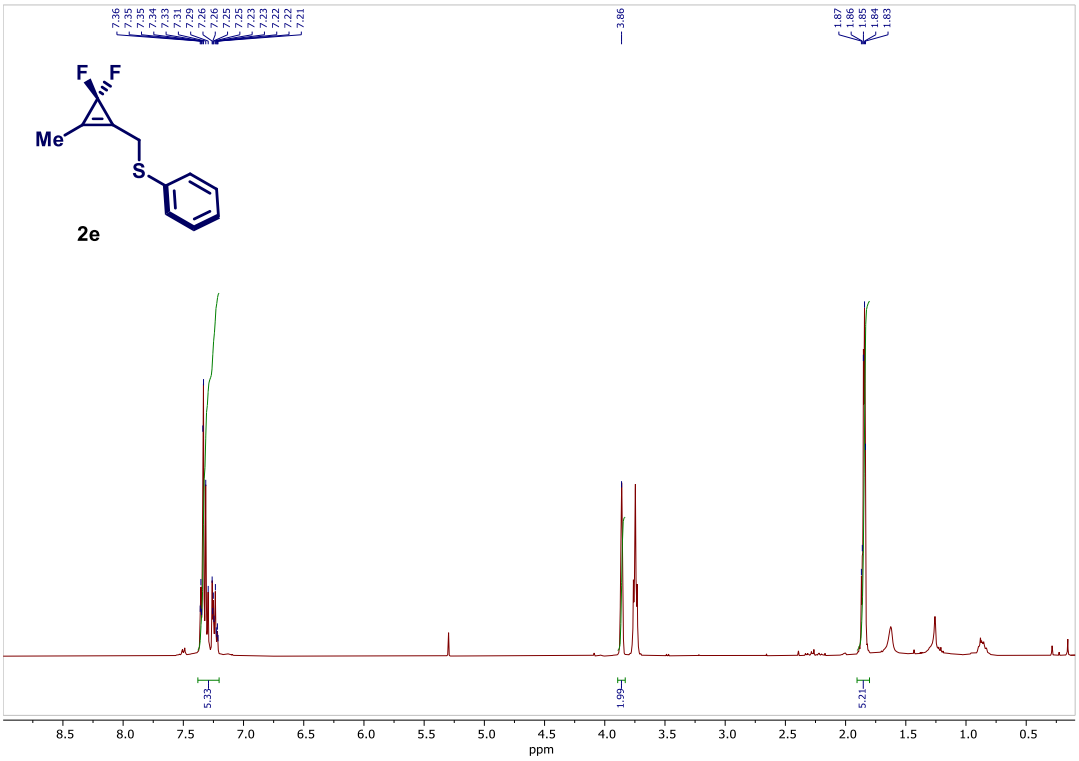
^{13}C NMR (101 MHz, $CDCl_3$) of Compound **2d:**



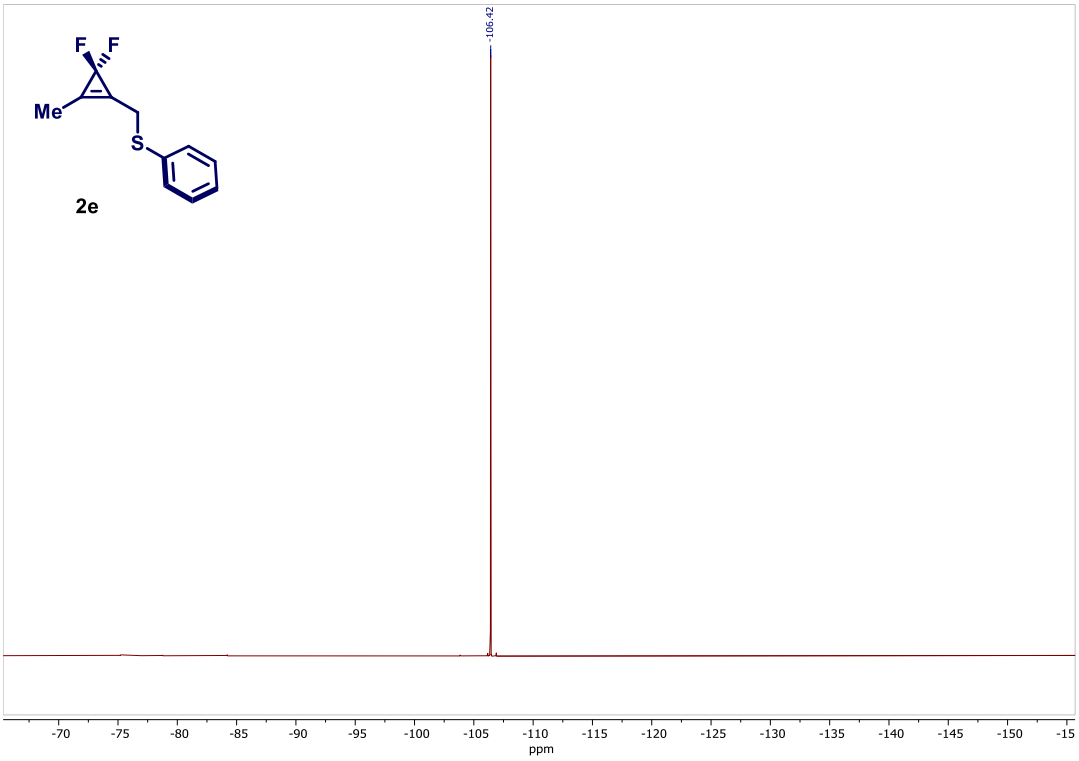
^{19}F NMR (376 MHz, $CDCl_3$) of compound **2d:**



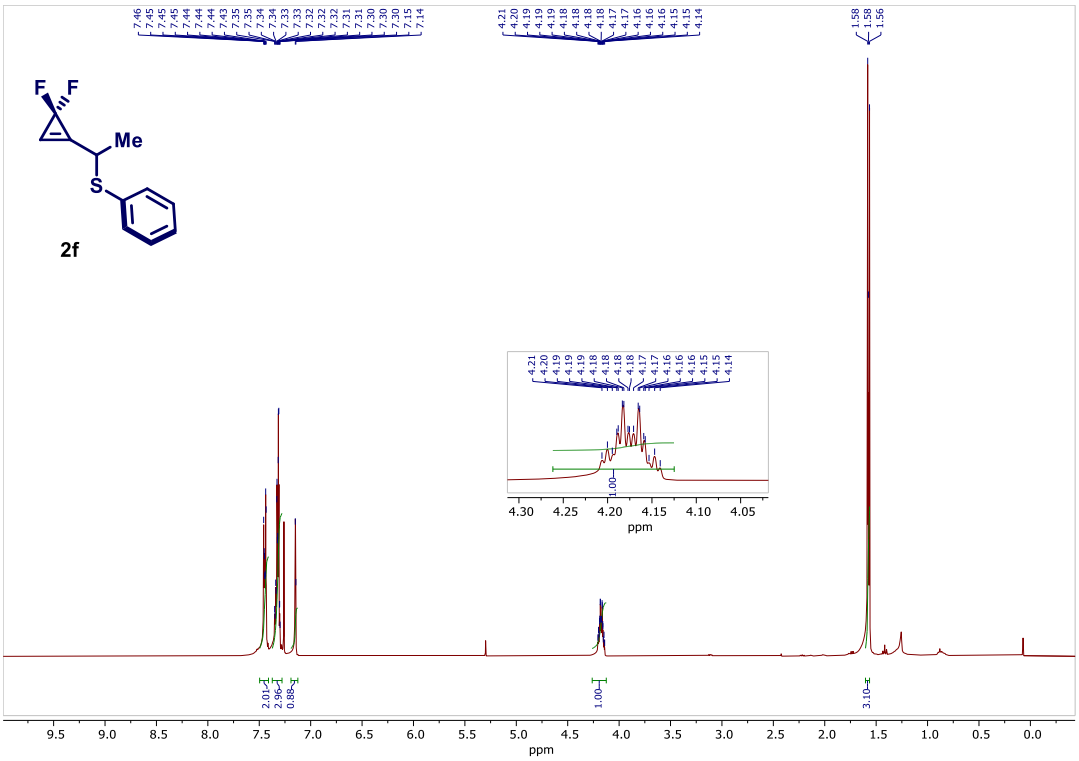
^{1}H NMR (400 MHz, $CDCl_3$) of compound **2e** (in crude reaction mixture)**: (***See Procedure***)**



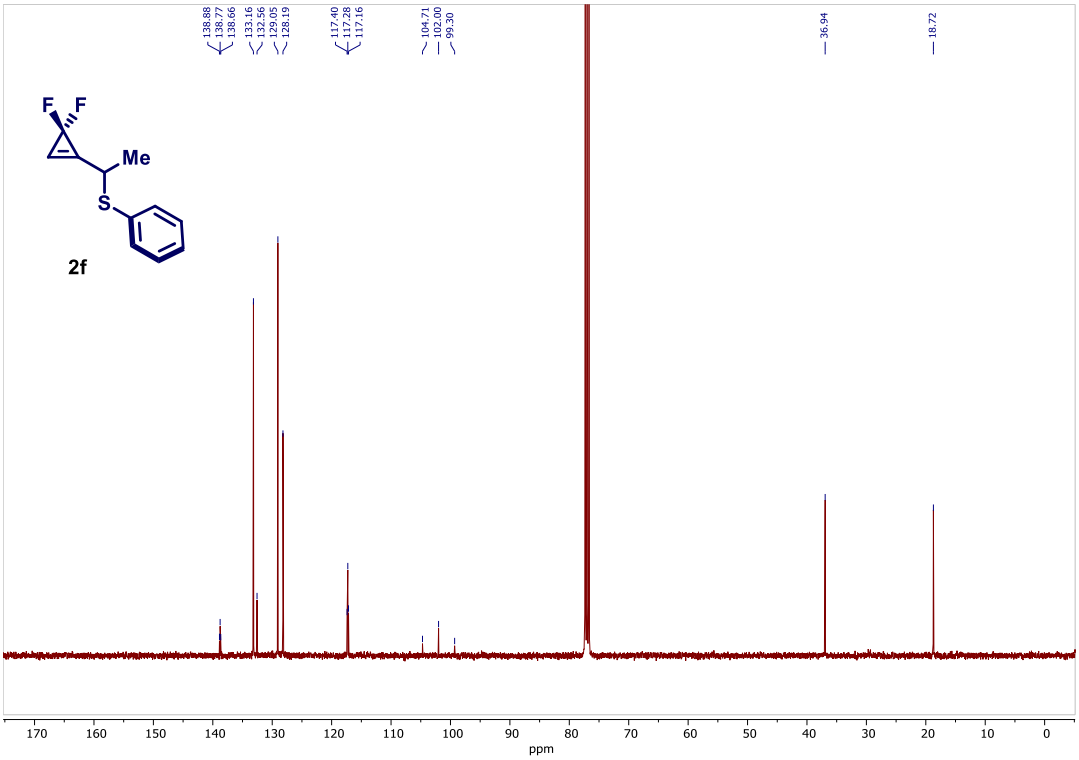
^{19}F NMR (376 MHz, $CDCl_3$) of compound **2e** (in crude reaction mixture):



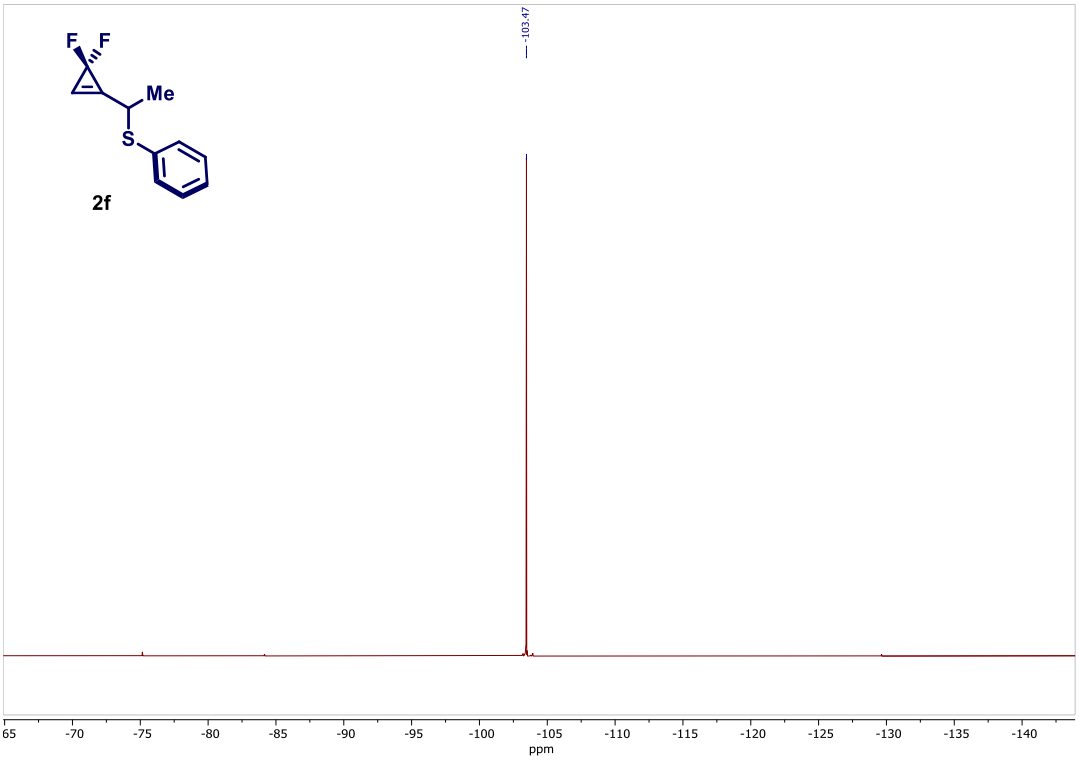
^{1}H NMR (400 MHz, $CDCl_3$) of compound **2f**: (*See Procedure*)



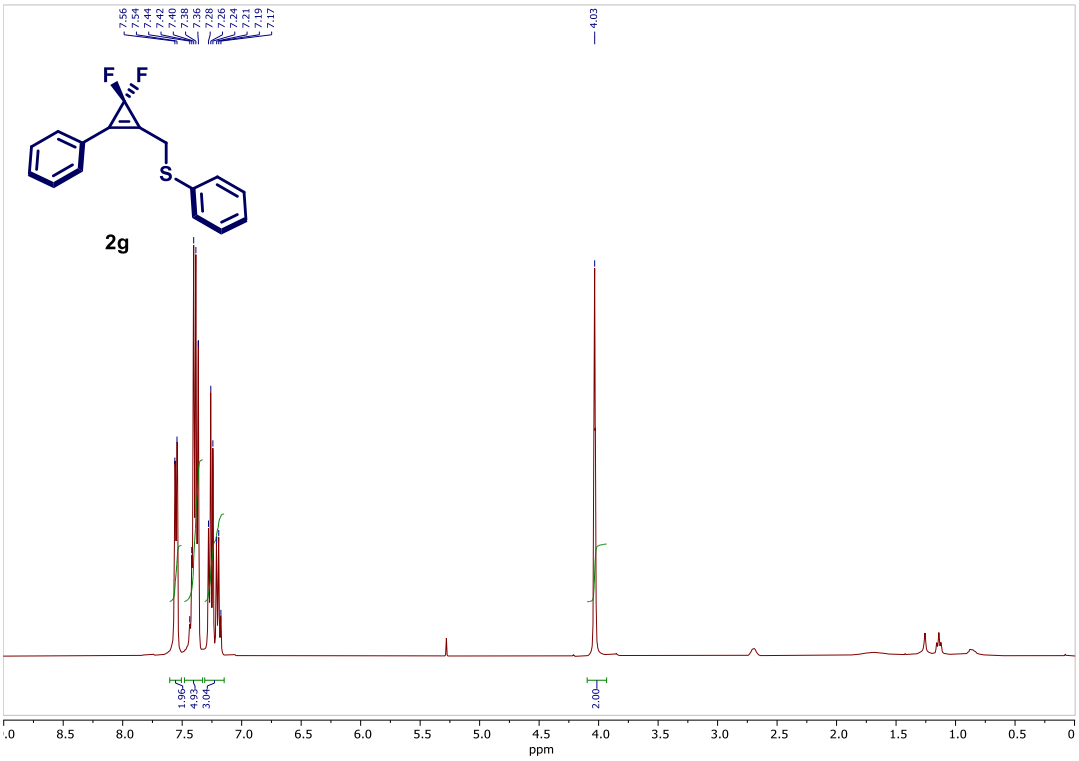
^{13}C NMR (101 MHz, $CDCl_3$) of Compound **2f:**



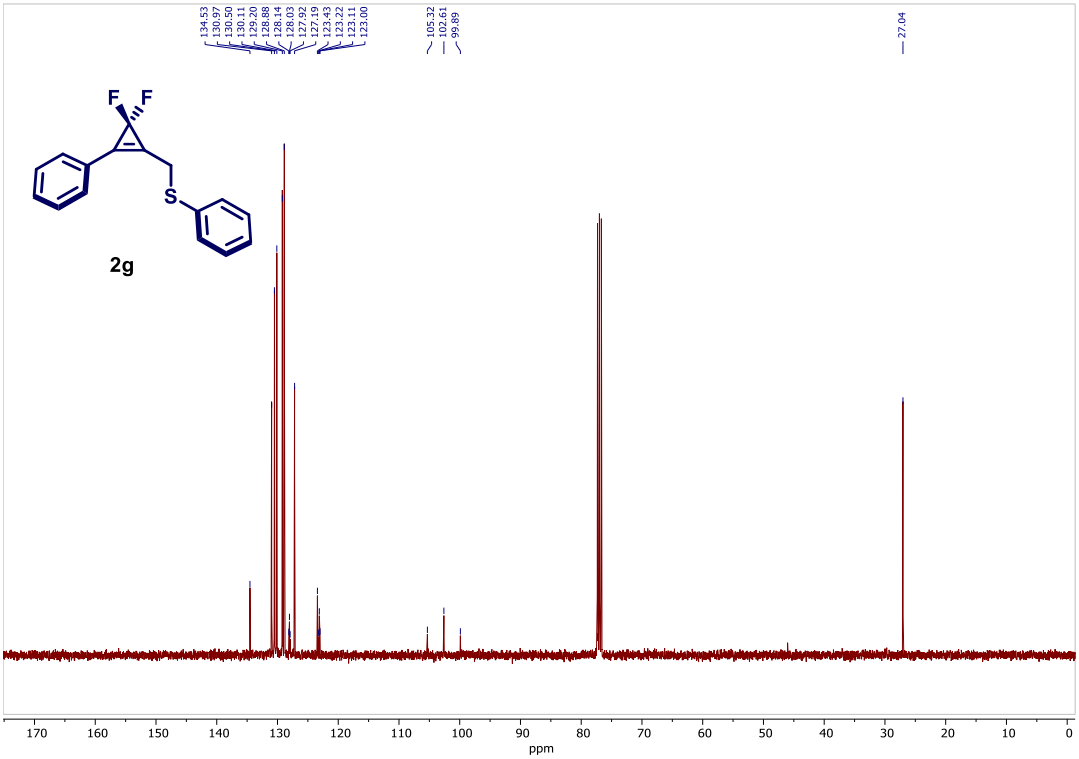
^{19}F NMR (376 MHz, $CDCl_3$) of compound **2f:**



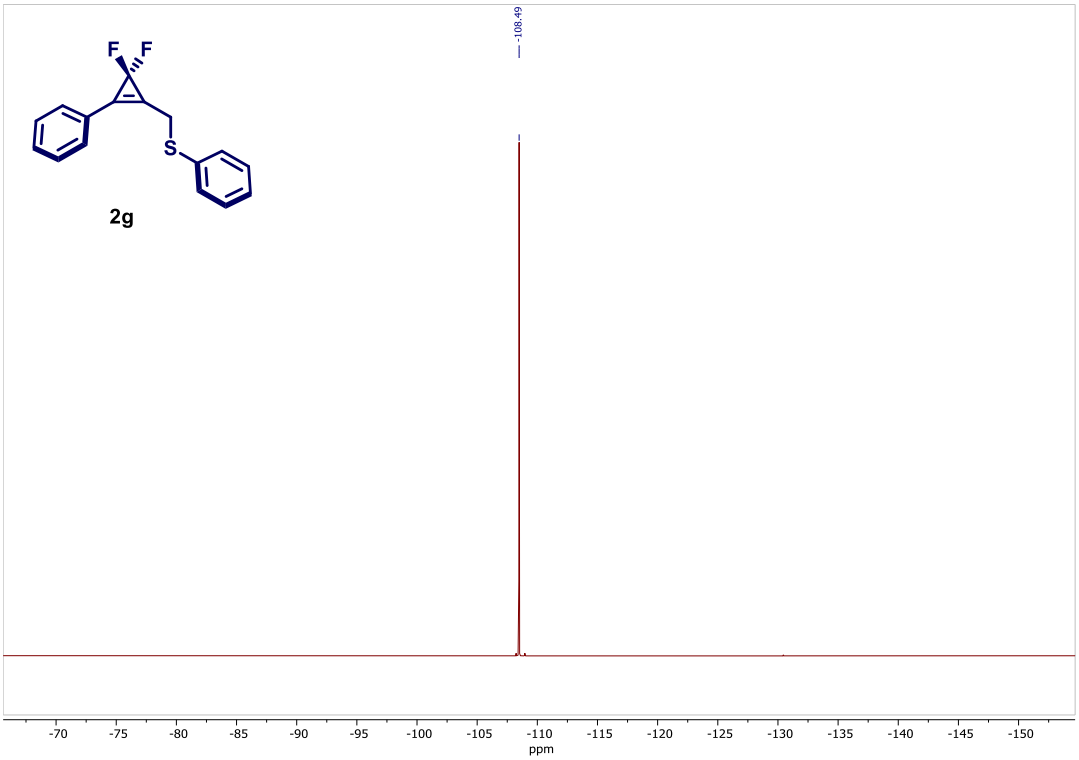
^{1}H NMR (400 MHz, $CDCl_3$) of compound **2g: (*See Procedure*)**



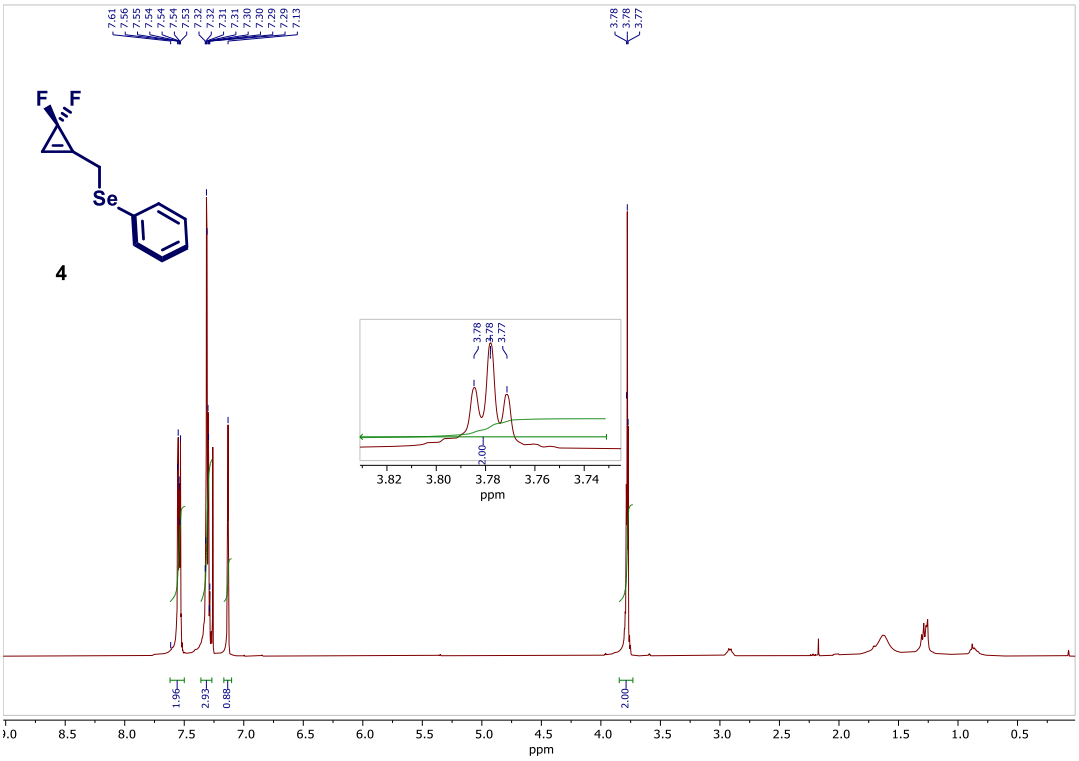
^{13}C NMR (101 MHz, $CDCl_3$) of Compound **2g:**



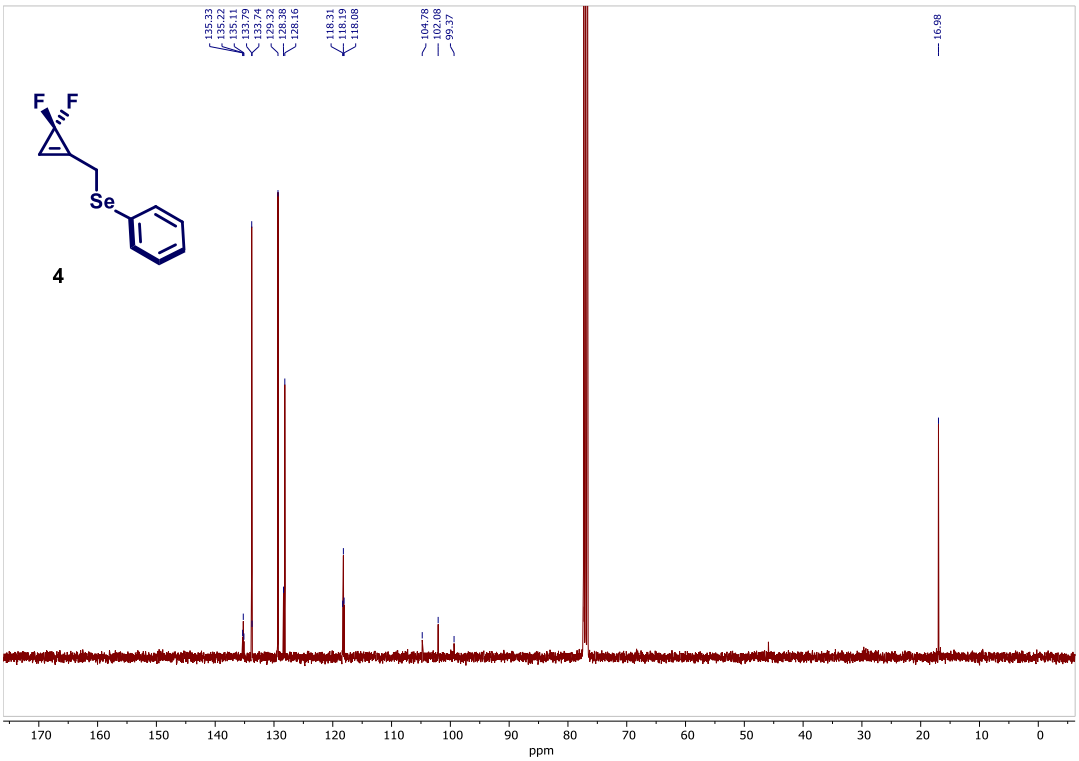
^{19}F NMR (376 MHz, $CDCl_3$) of compound **2g:**



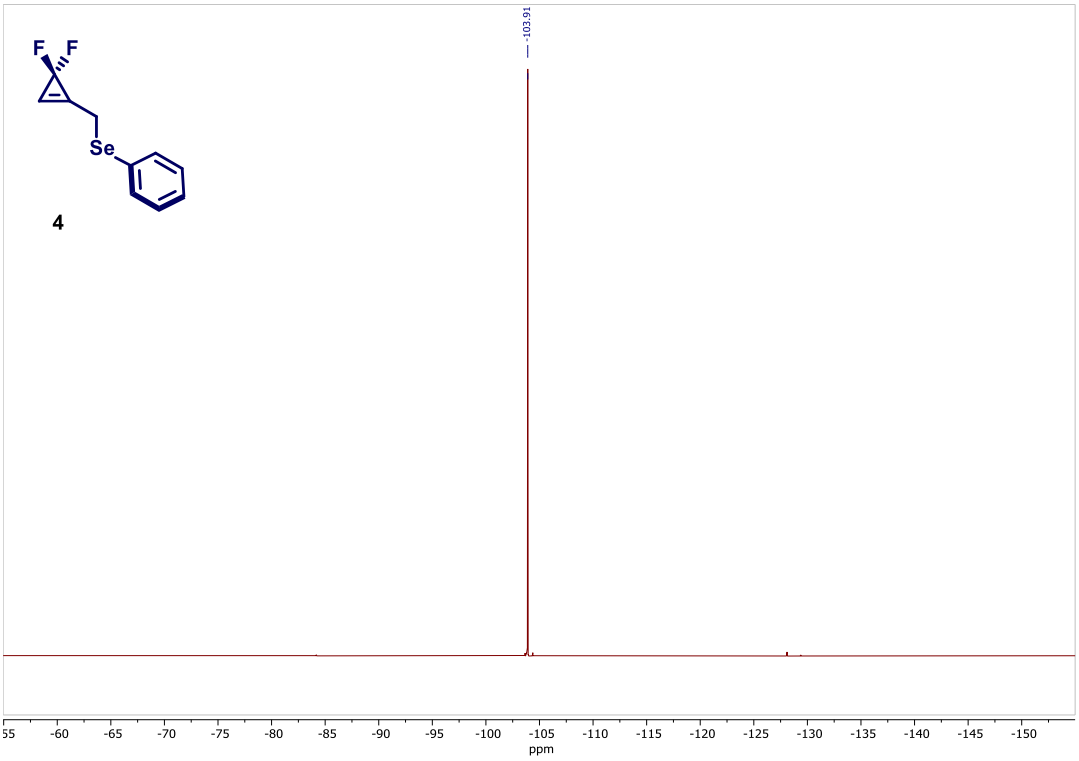
^{1}H NMR (400 MHz, $CDCl_3$) of compound **4: (*See Procedure*)**



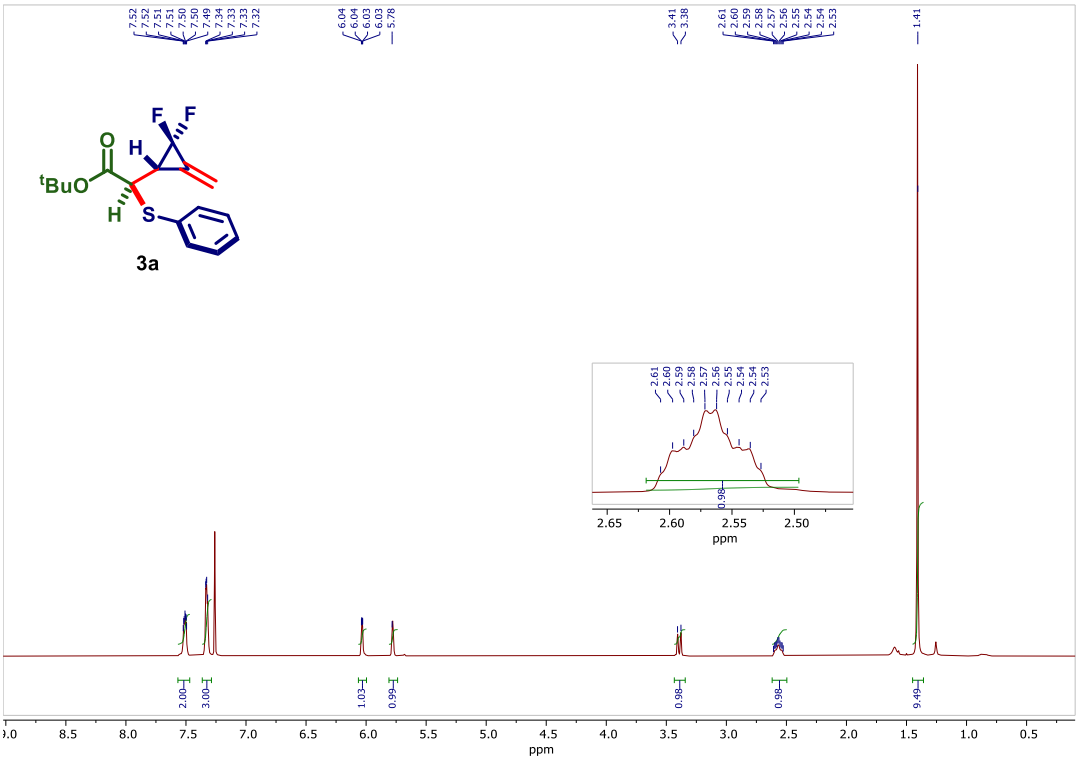
^{13}C NMR (101 MHz, $CDCl_3$) of Compound **4:**



^{19}F NMR (376 MHz, $CDCl_3$) of compound **4:**



^{1}H NMR (400 MHz, $CDCl_3$) of compound **3a: (*See Procedure*)**



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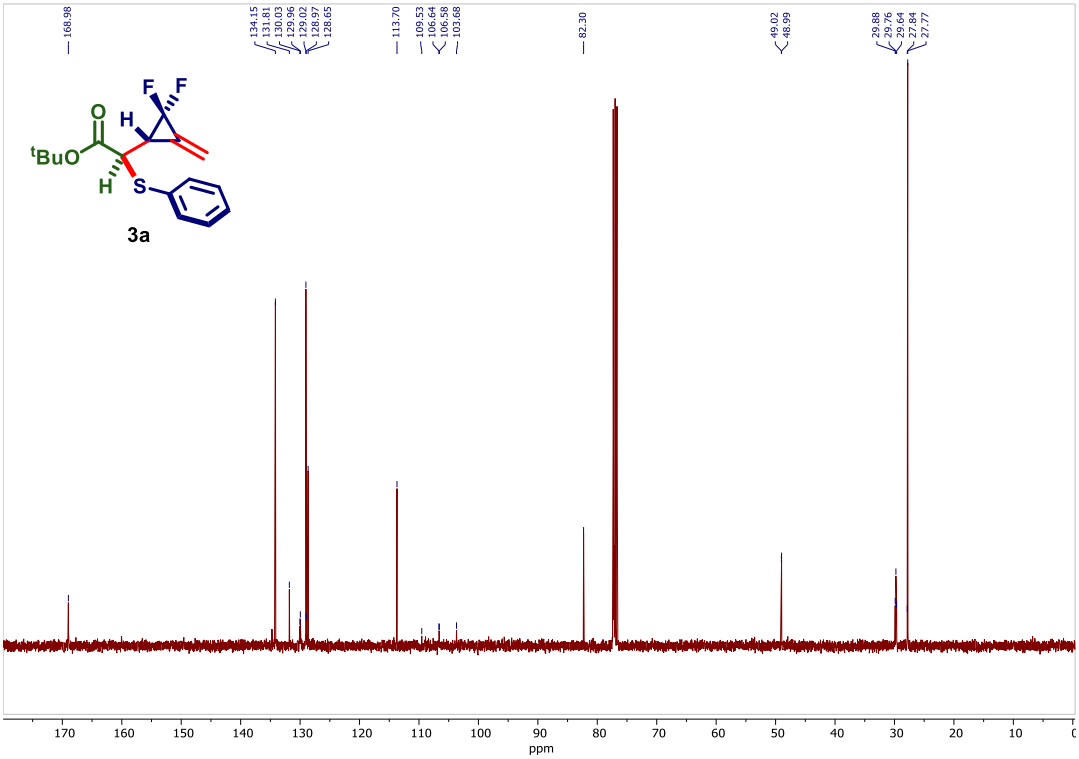

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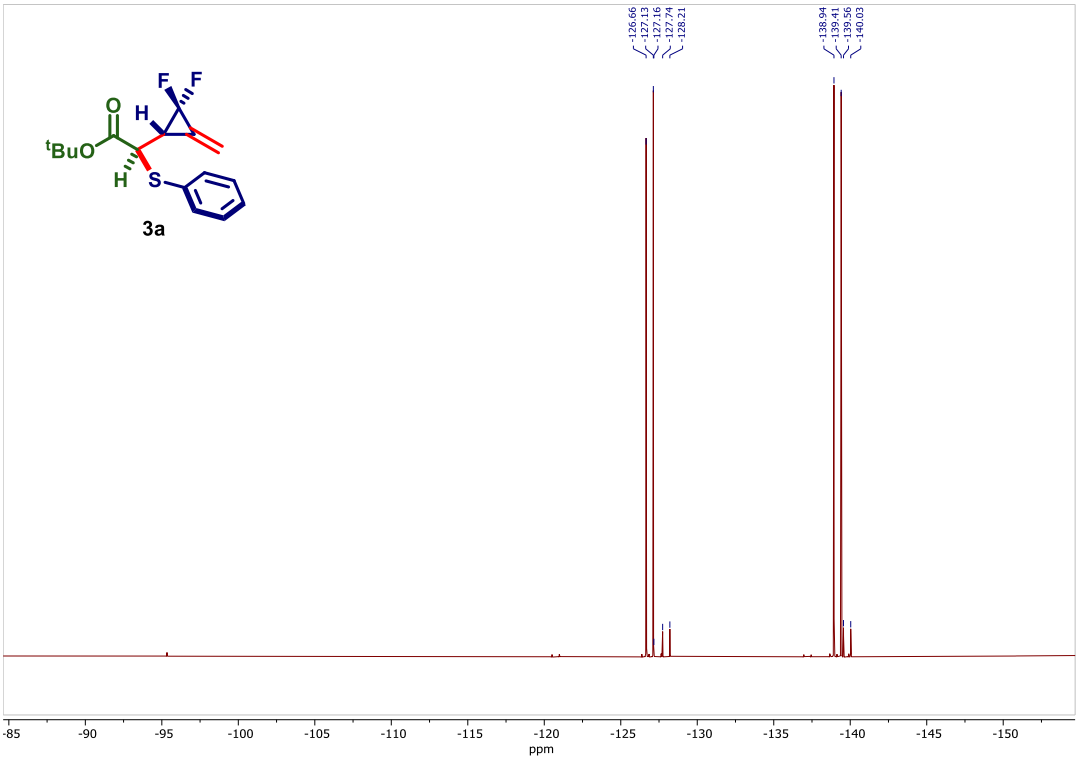
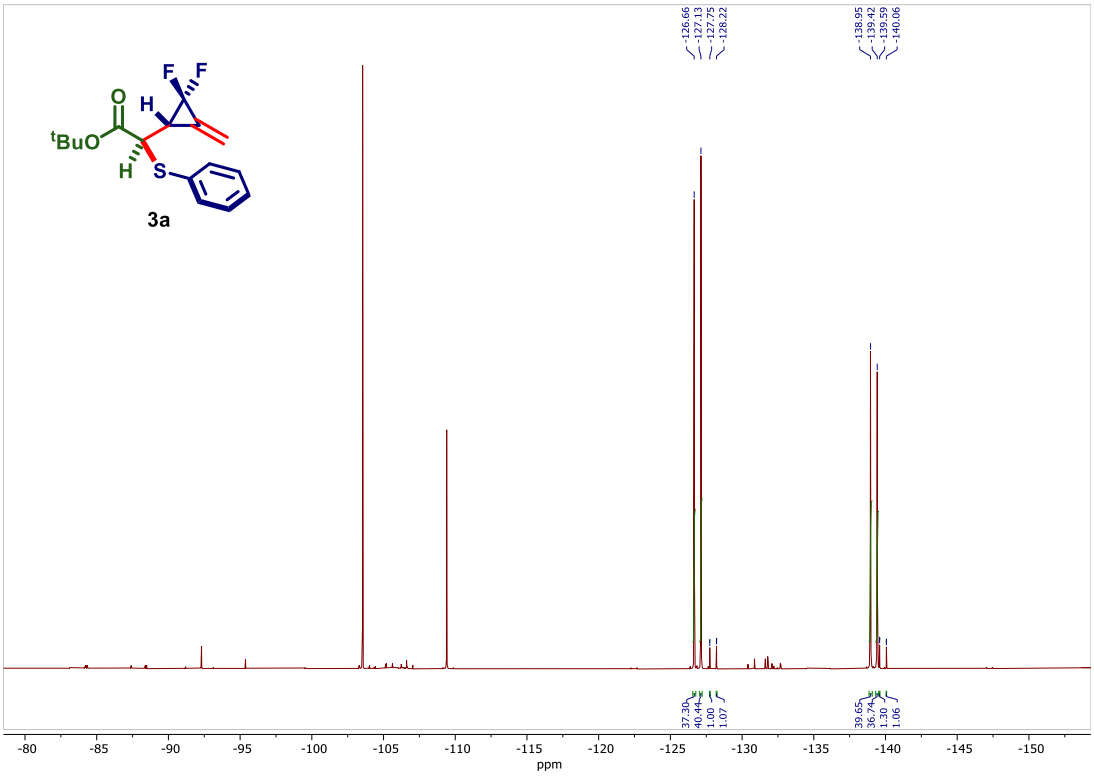
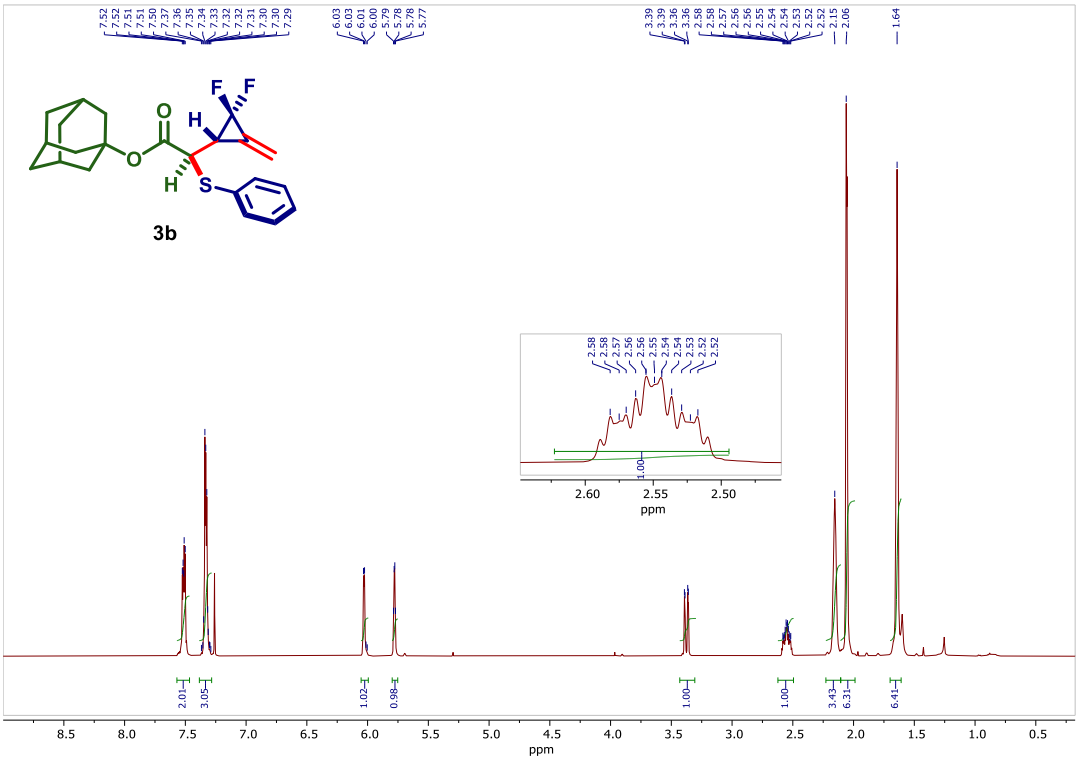


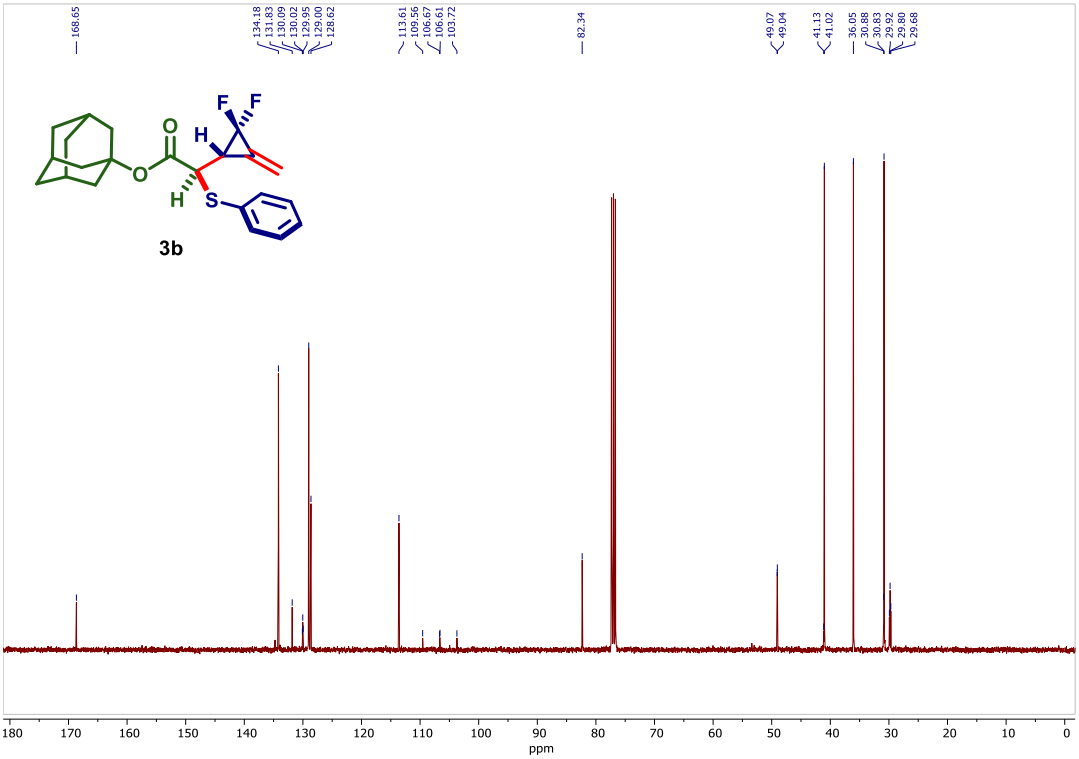
^{19}F NMR (376 MHz, $CDCl_3$) of Crude Reaction Mixture (compound **3a**)**:**



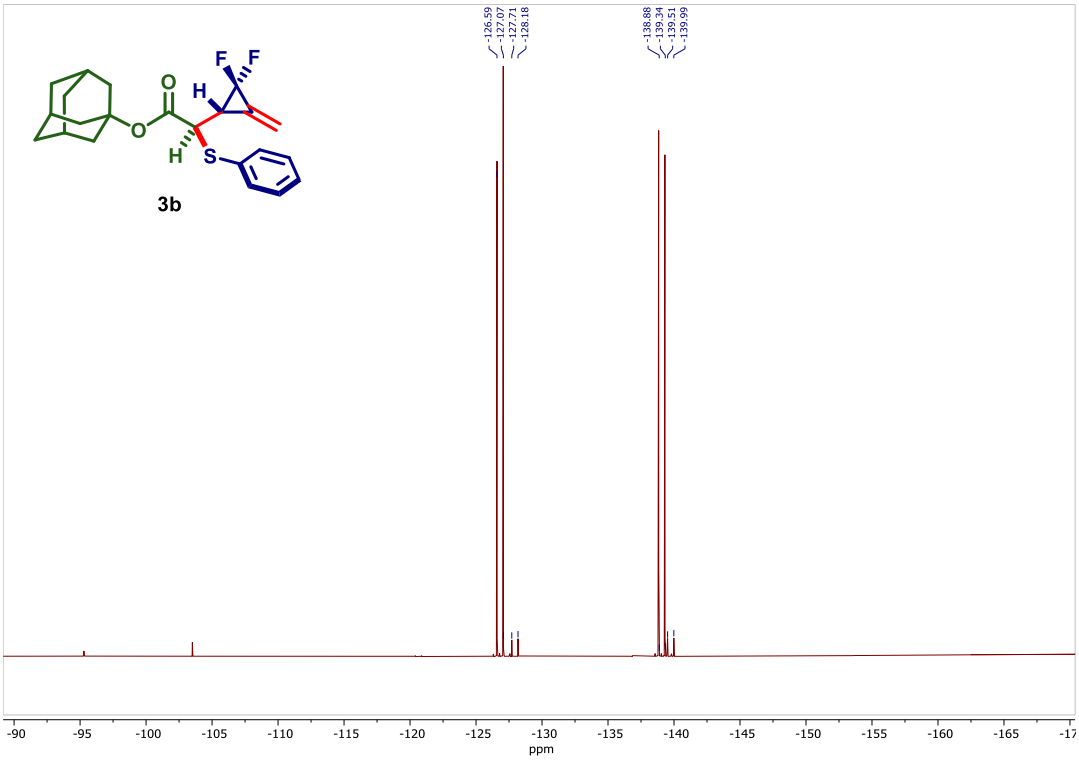
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3b: (*See Procedure*)**



^{13}C NMR (101 MHz, $CDCl_3$) of Compound **3b:**



^{19}F NMR (376 MHz, $CDCl_3$) of compound **3b:**



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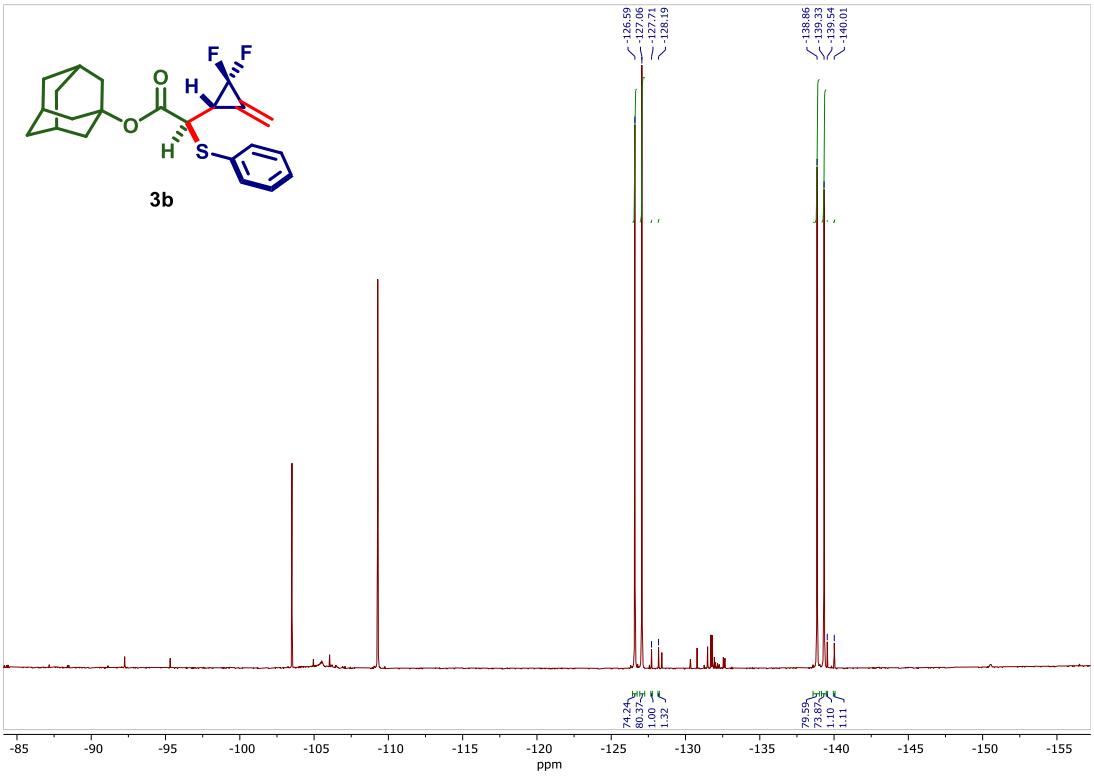

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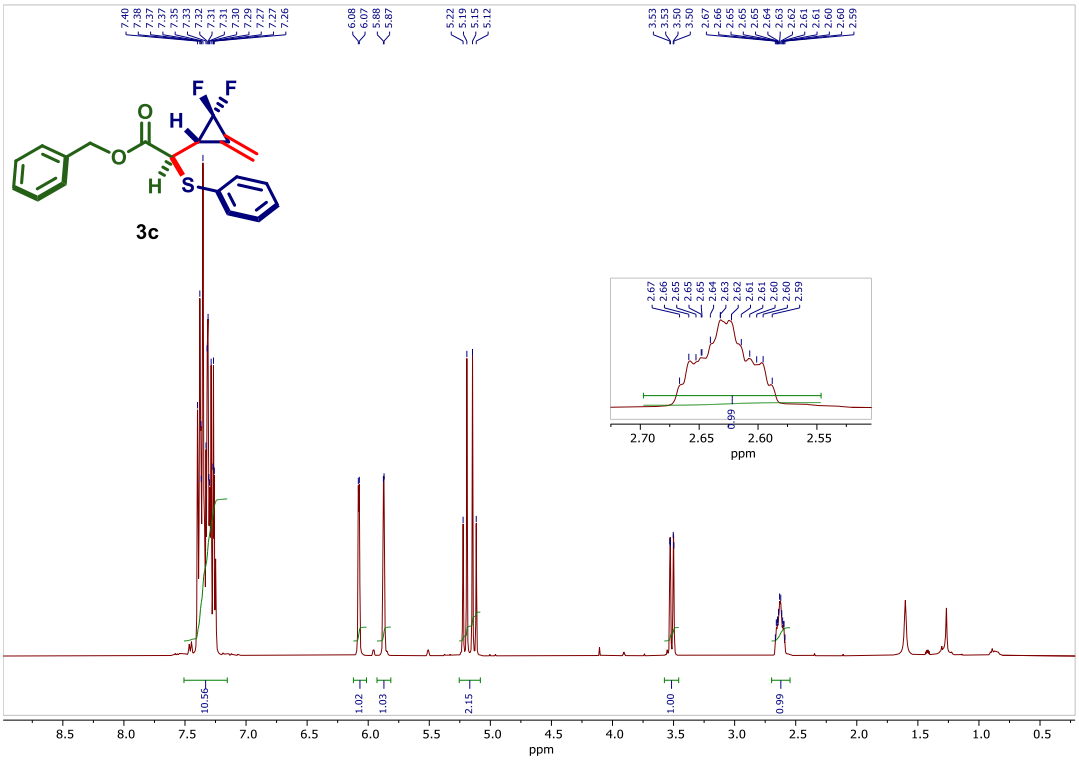

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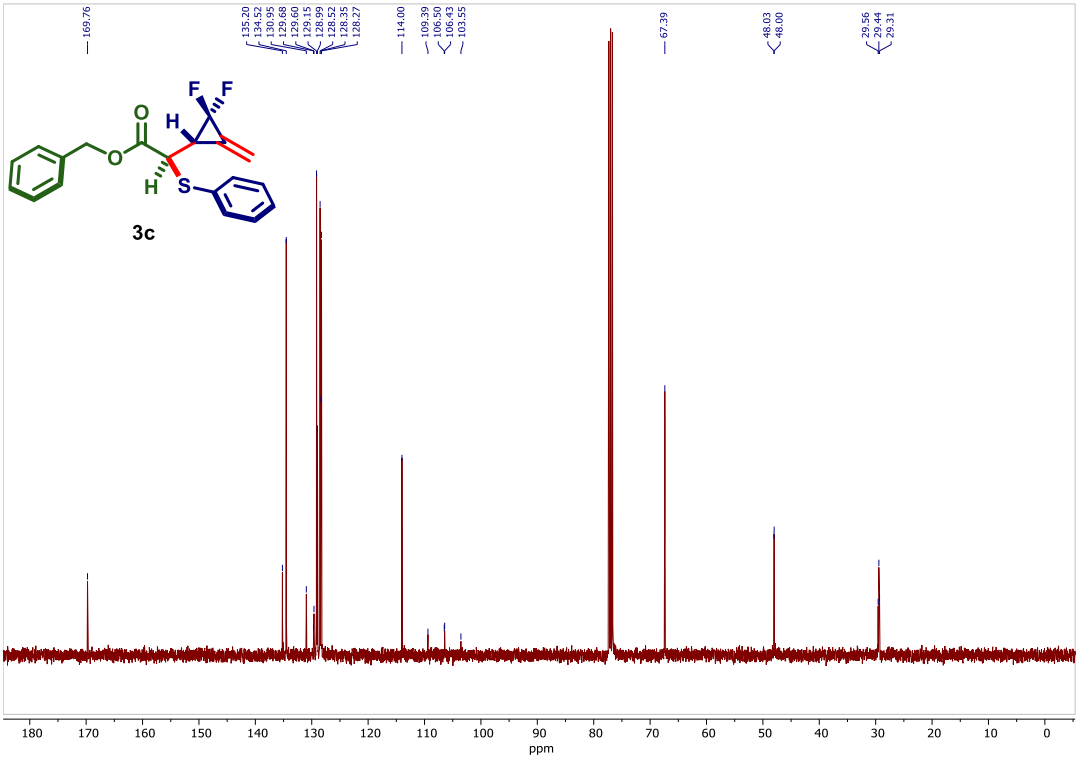

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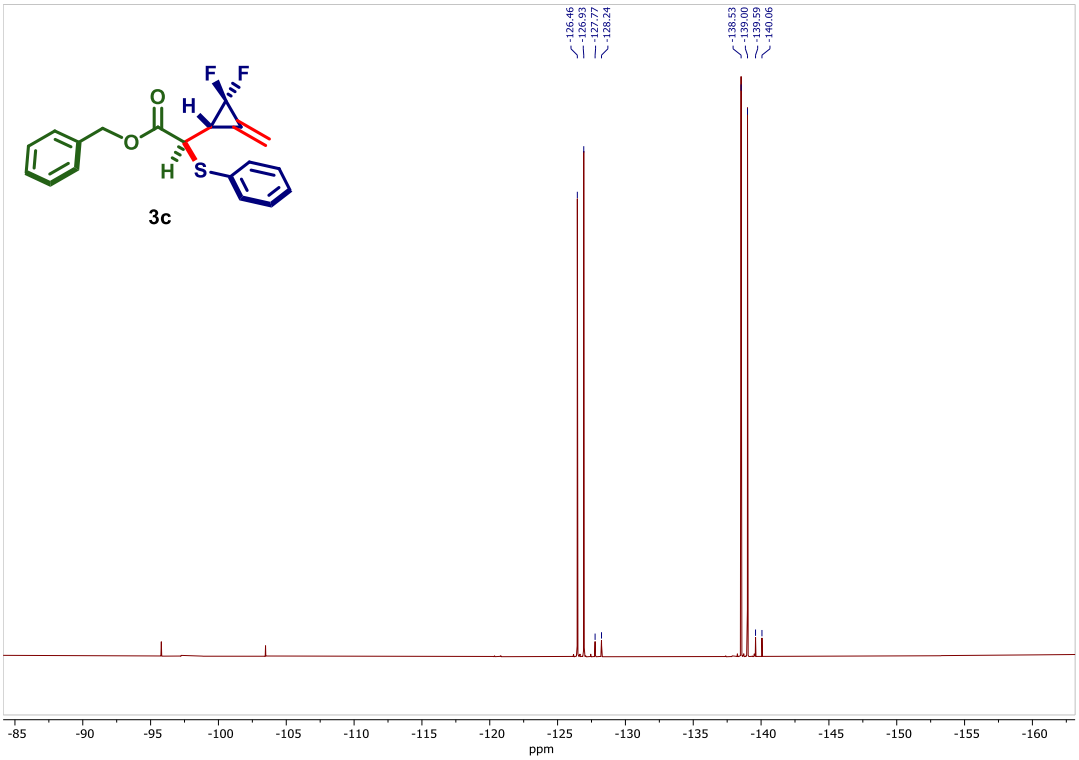
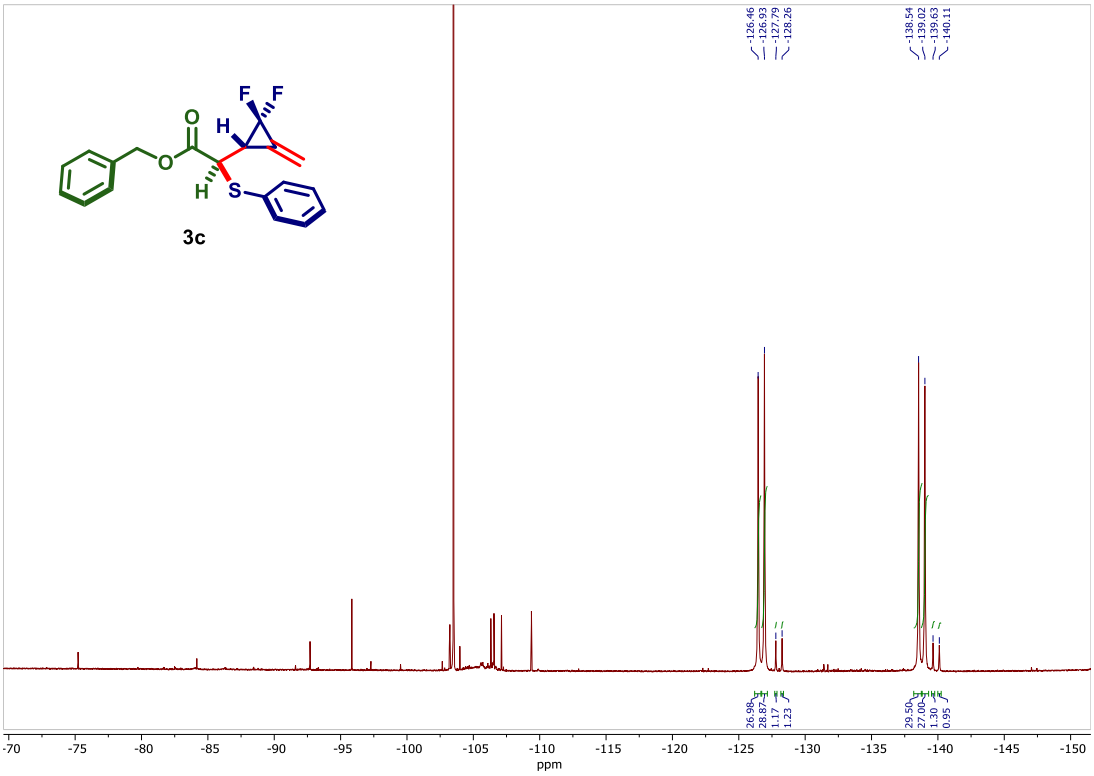


^{19}F NMR (376 MHz, $CDCl_3$) of Crude Reaction Mixture (compound **3c**)**:**



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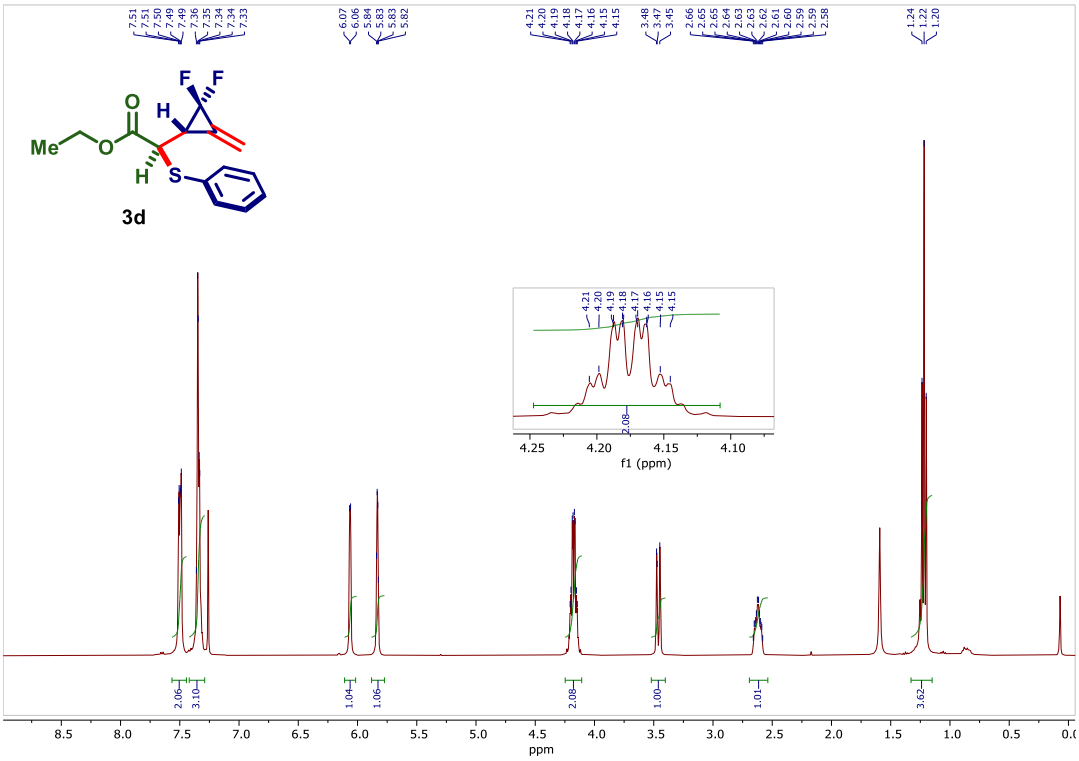
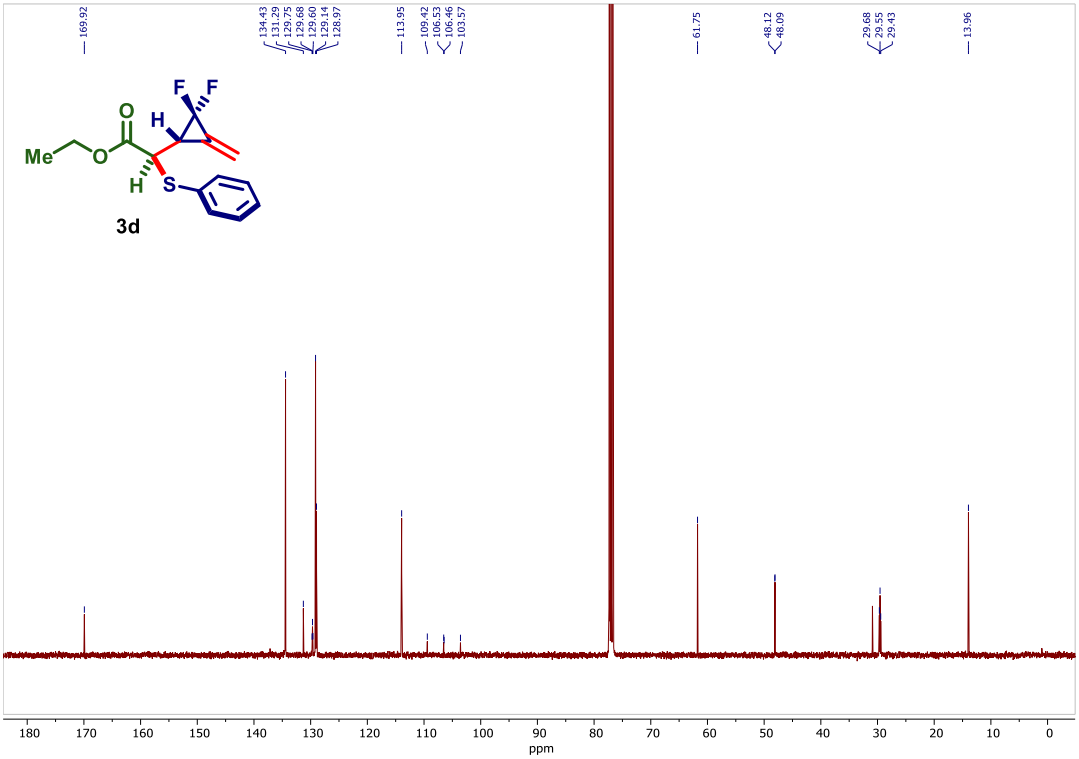
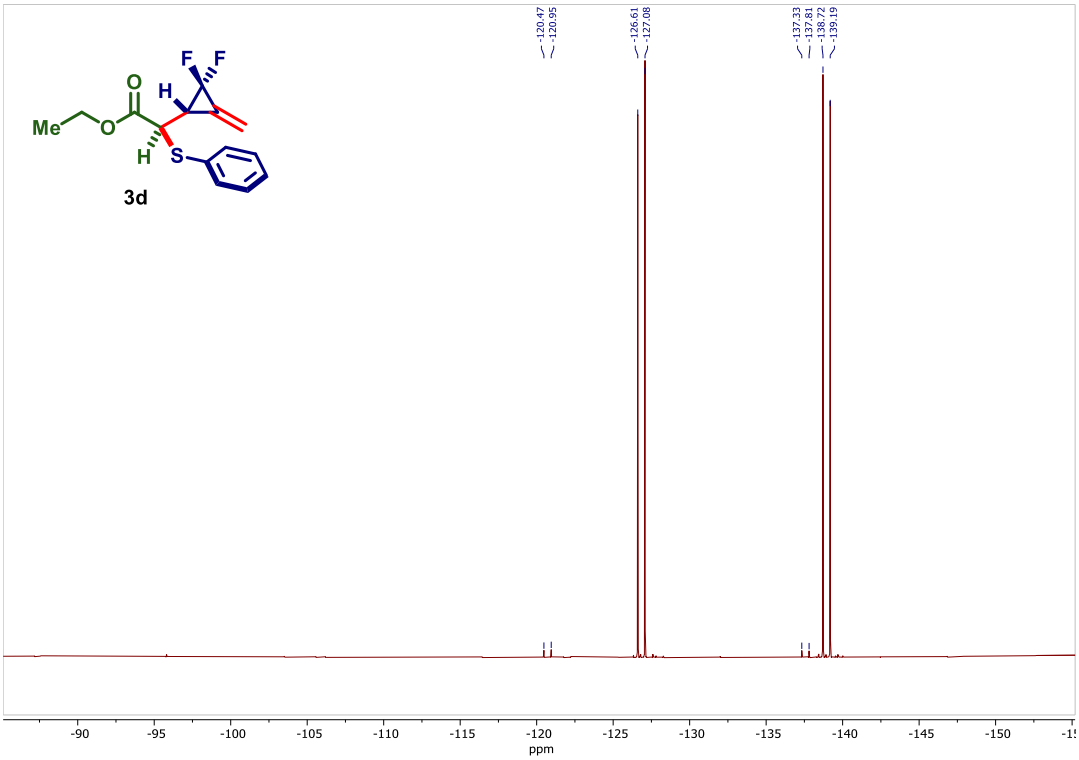


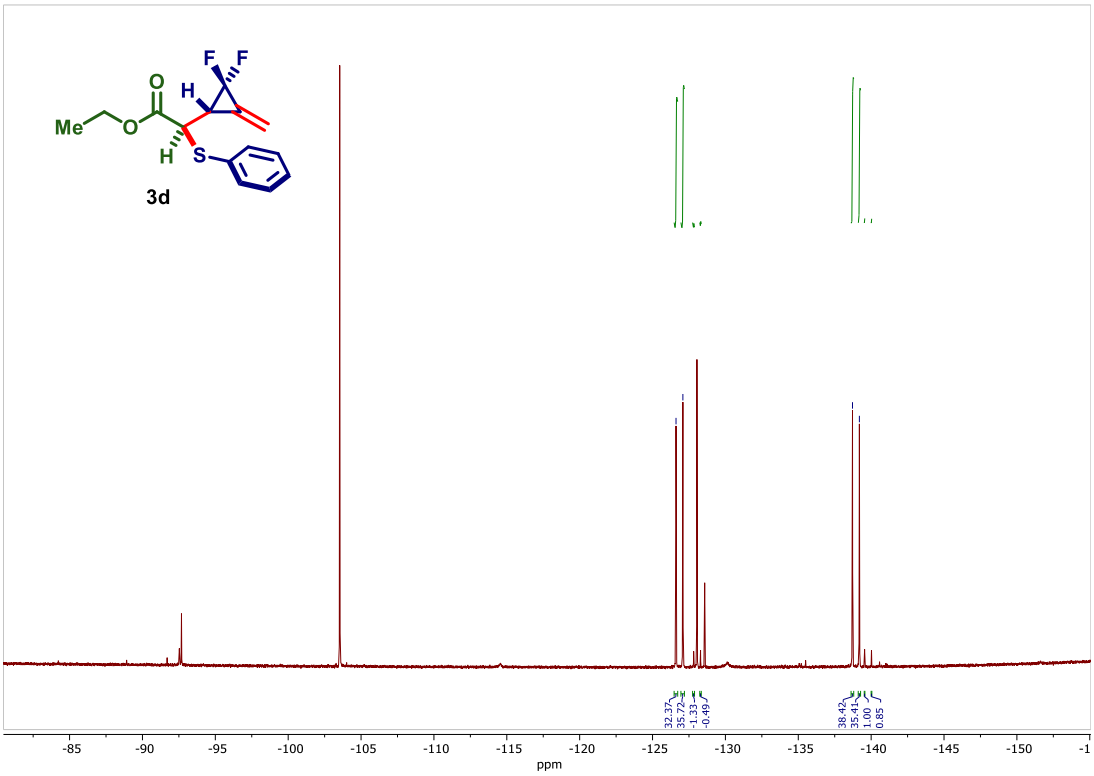
^{13}C NMR (101 MHz, $CDCl_3$) of Compound **3d:**



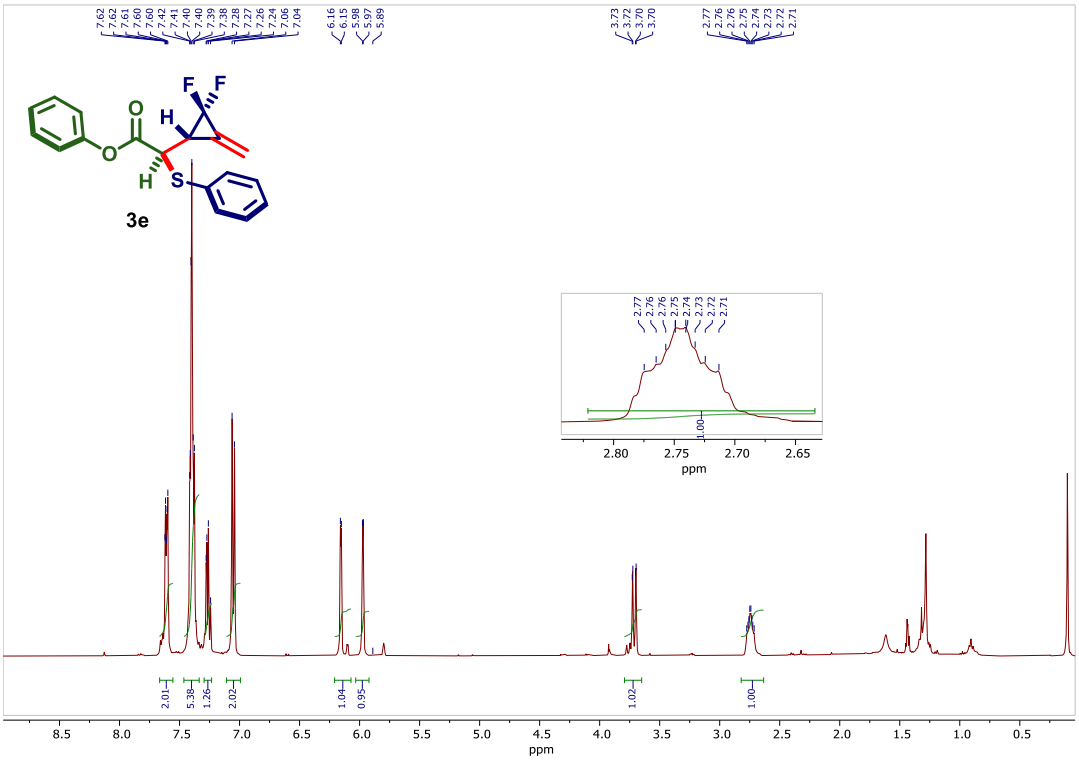
^{19}F NMR (376 MHz, $CDCl_3$) of compound **3d:**



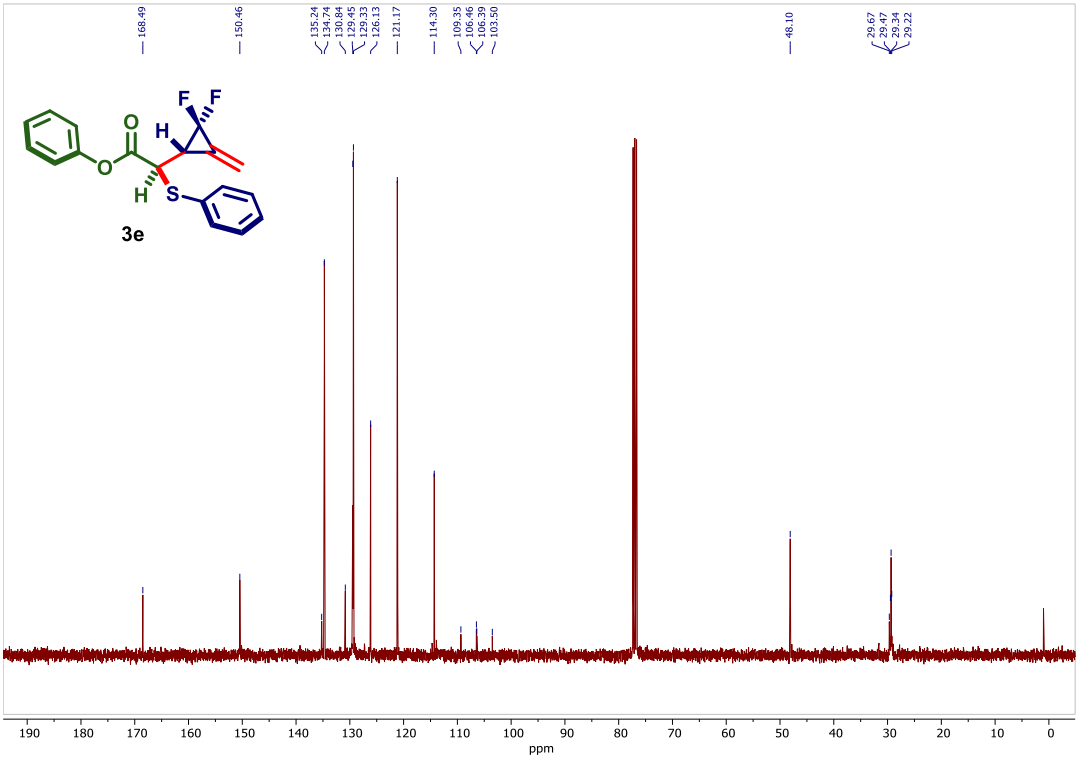
^{19}F NMR (376 MHz, $CDCl_3$) of Crude Reaction Mixture (compound **3d**)**:**



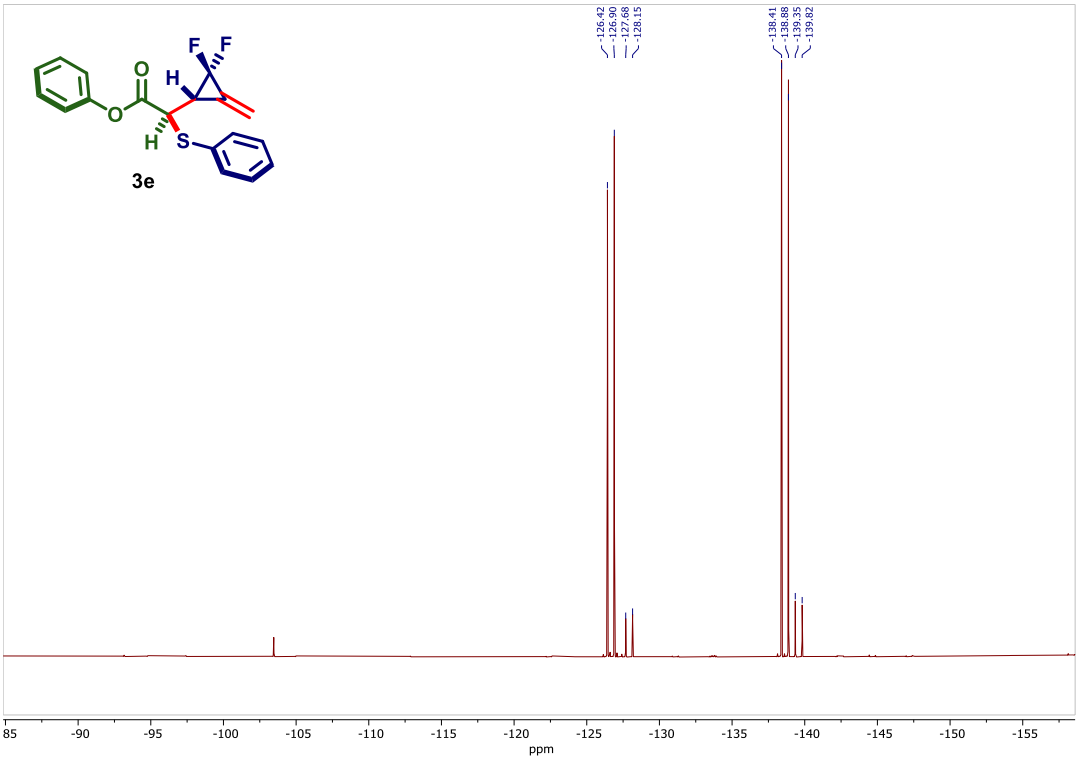
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3e: (*See Procedure*)**



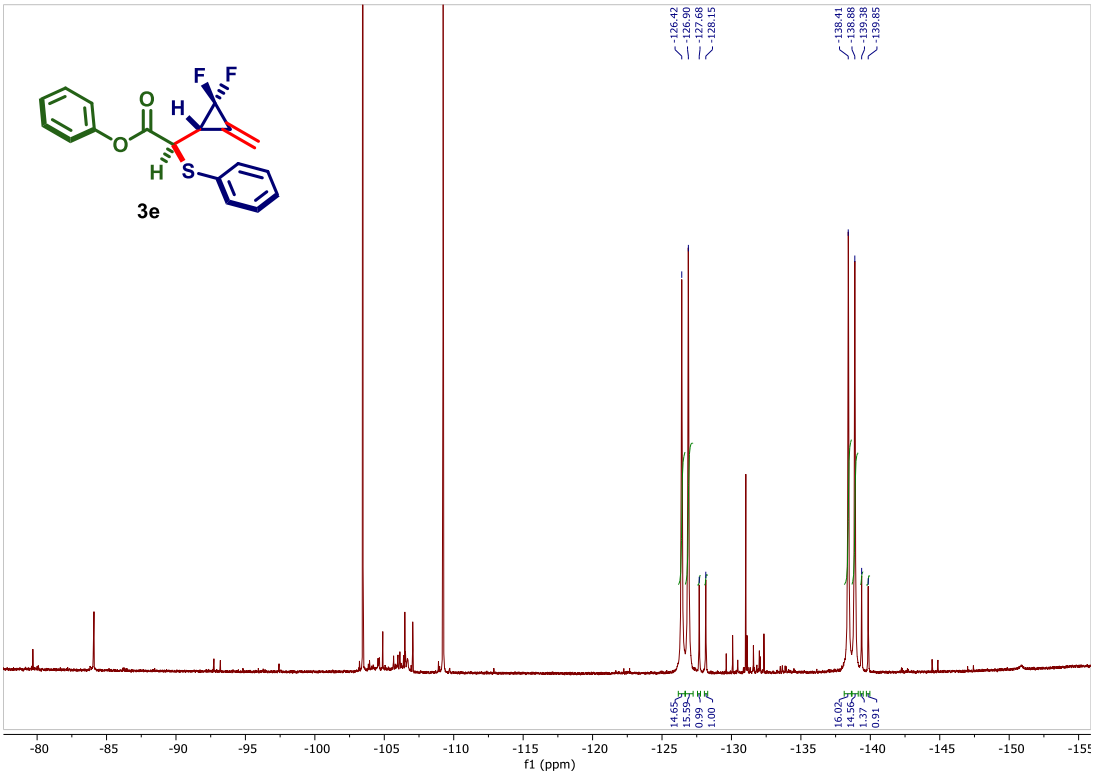
^{13}C NMR (101 MHz, $CDCl_3$) of Compound **3e:**



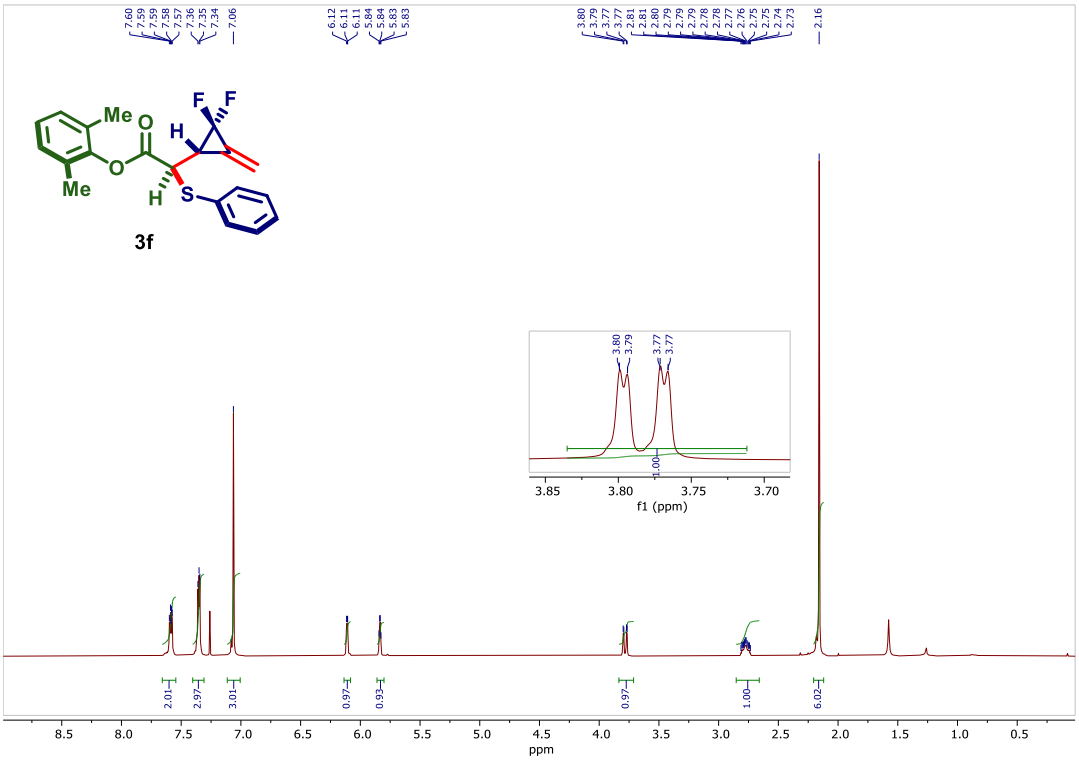
^{19}F NMR (376 MHz, $CDCl_3$) of compound **3e:**



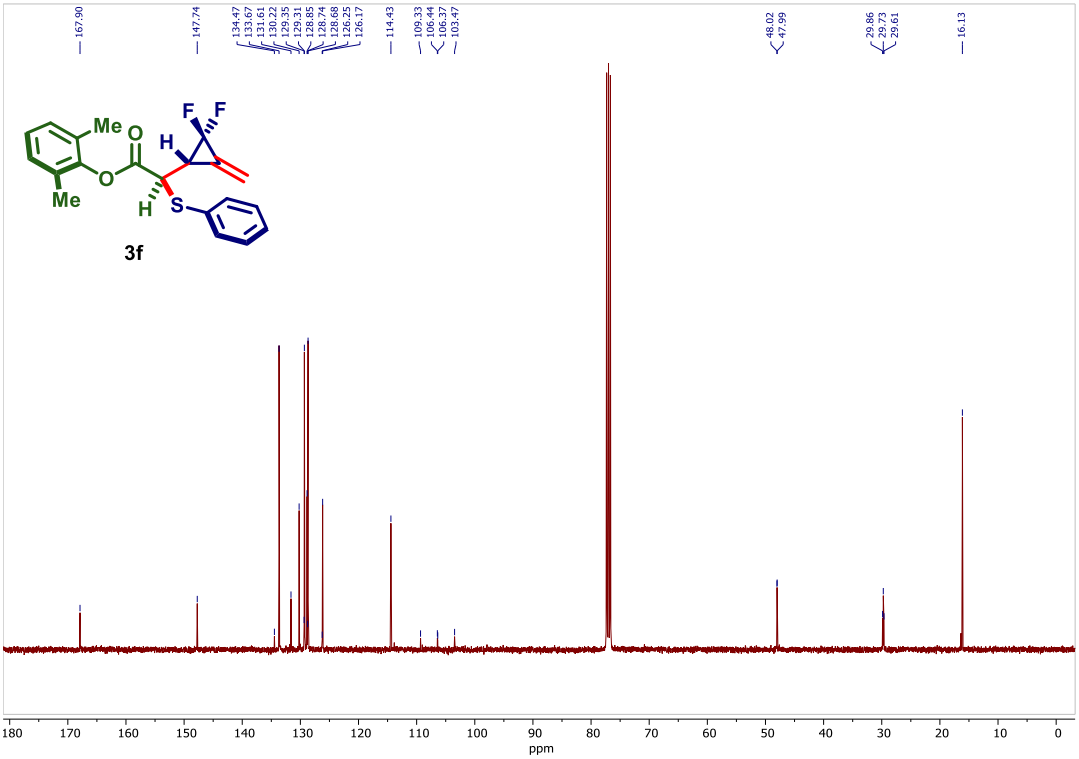
^{19}F NMR (376 MHz, $CDCl_3$) of Crude Reaction Mixture (compound **3e**)**:**



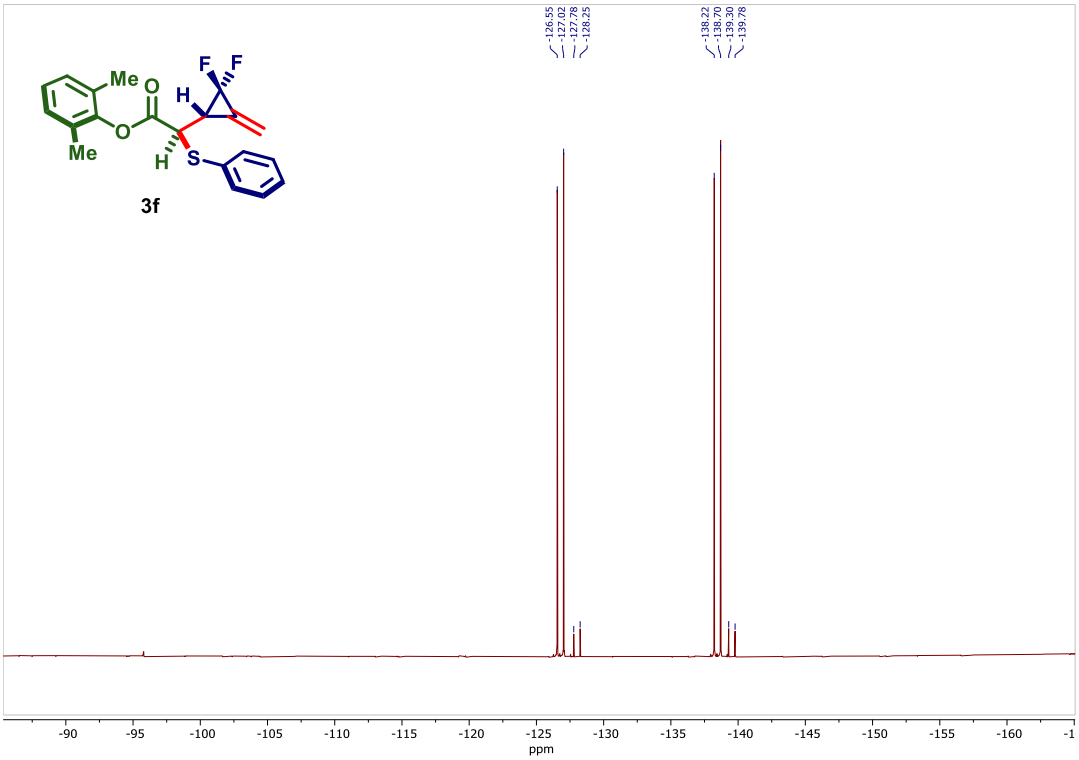
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3f: (*See Procedure*)**



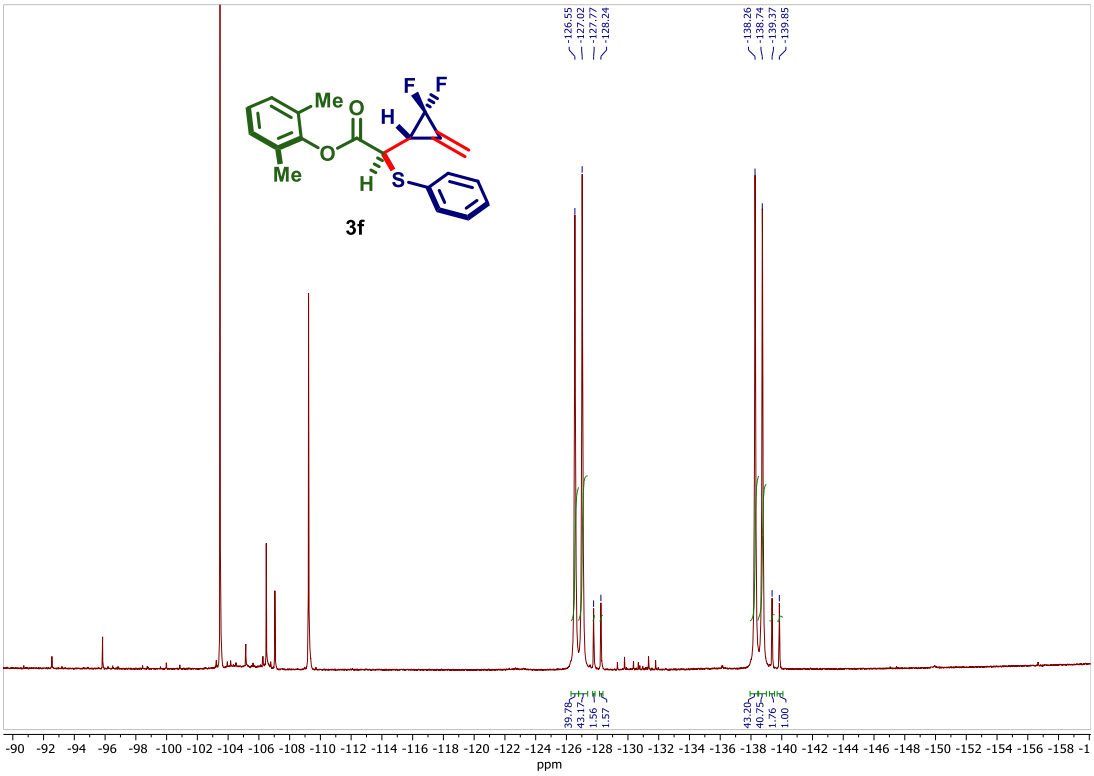
^{13}C NMR (101 MHz, $CDCl_3$) of Compound **3f:**



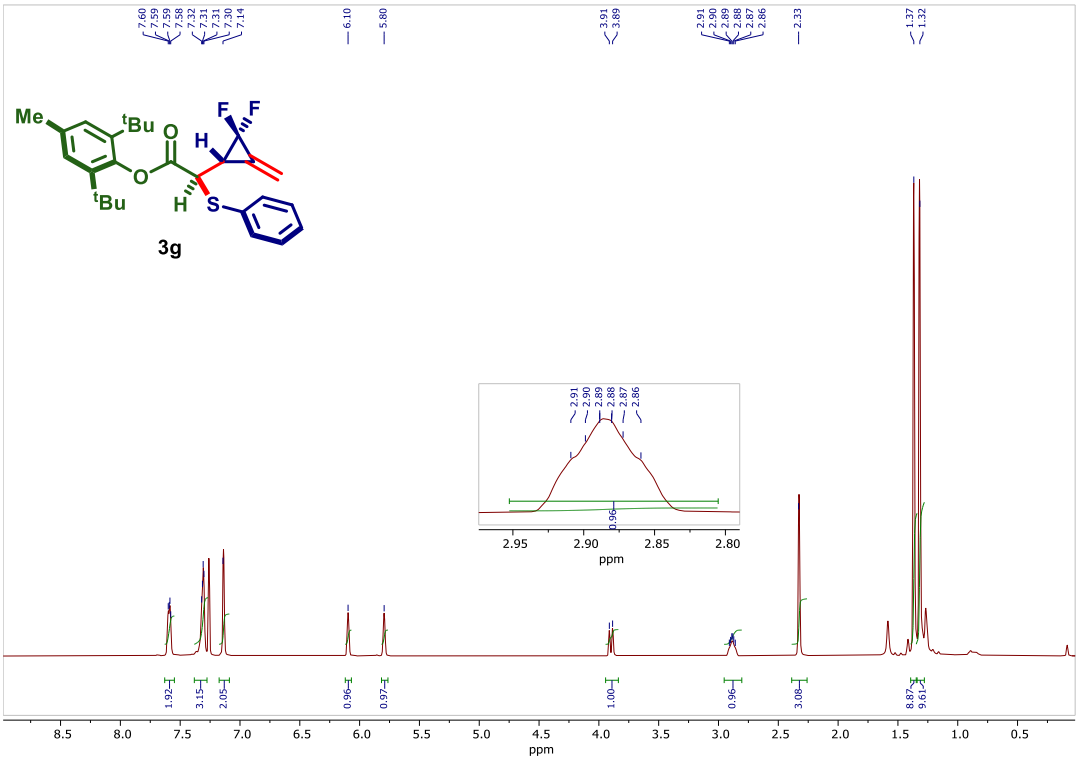
^{19}F NMR (376 MHz, $CDCl_3$) of compound **3f:**



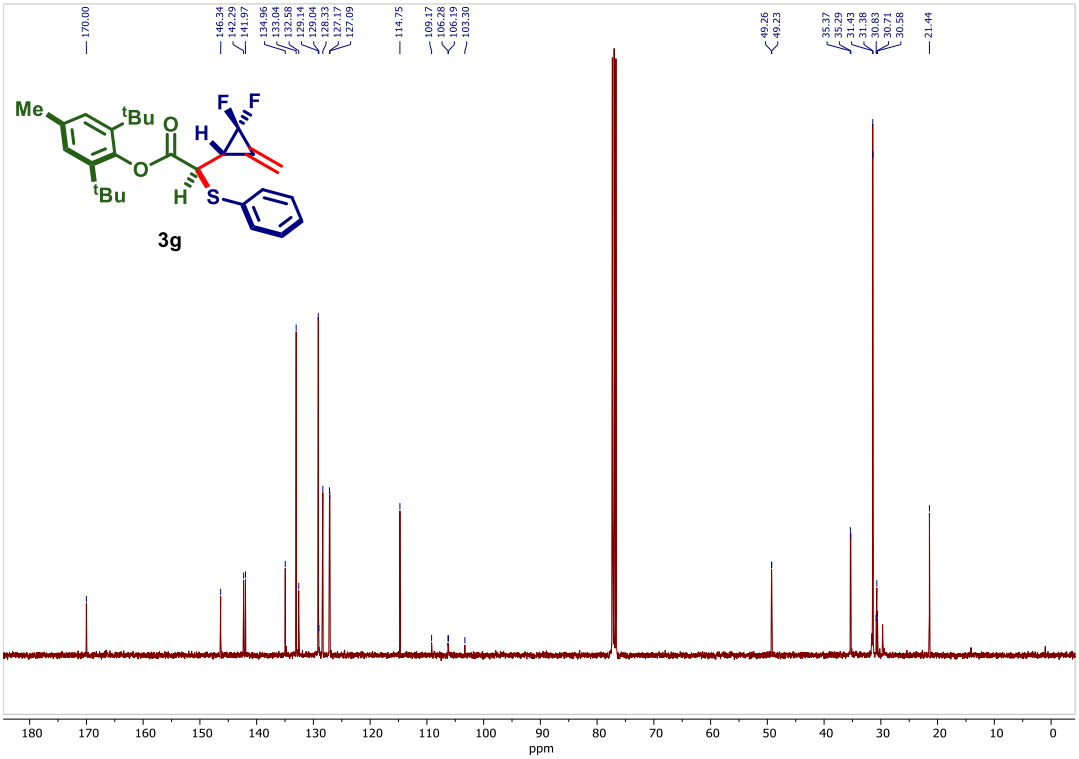
^{19}F NMR (376 MHz, $CDCl_3$) of crude reaction mixture (compound **3f):**



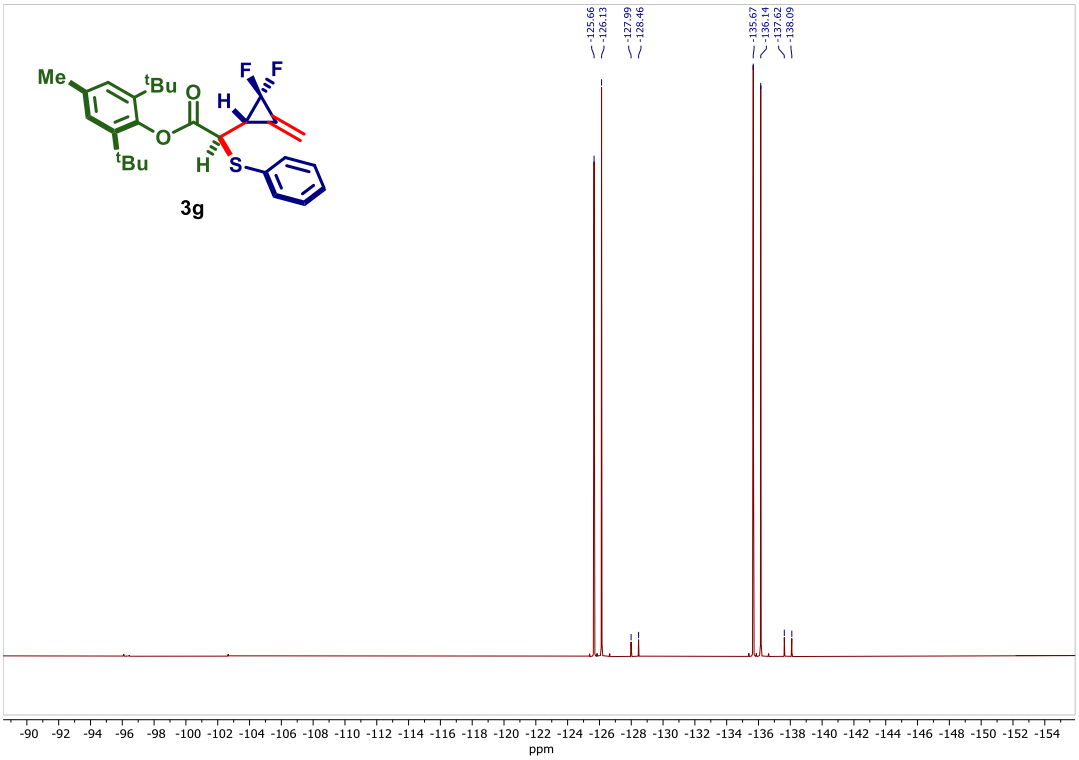
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3g: (***See Procedure*)



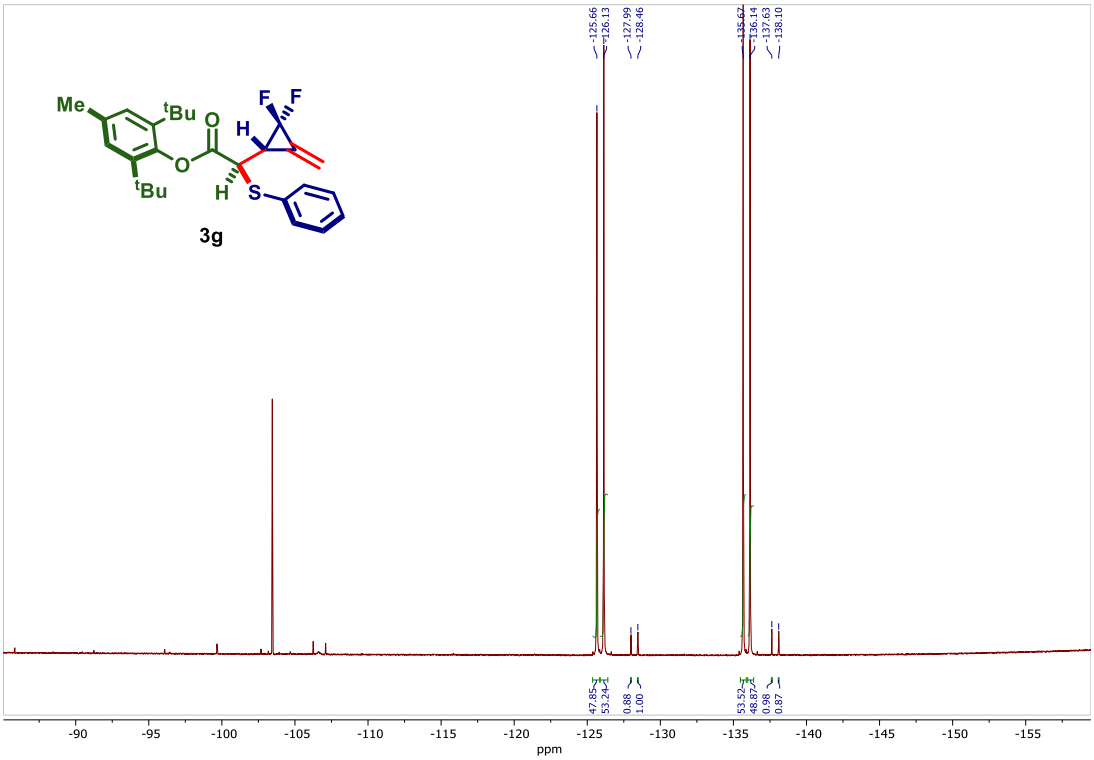
^{13}C NMR (101 MHz, $CDCl_3$) of Compound **3g:**



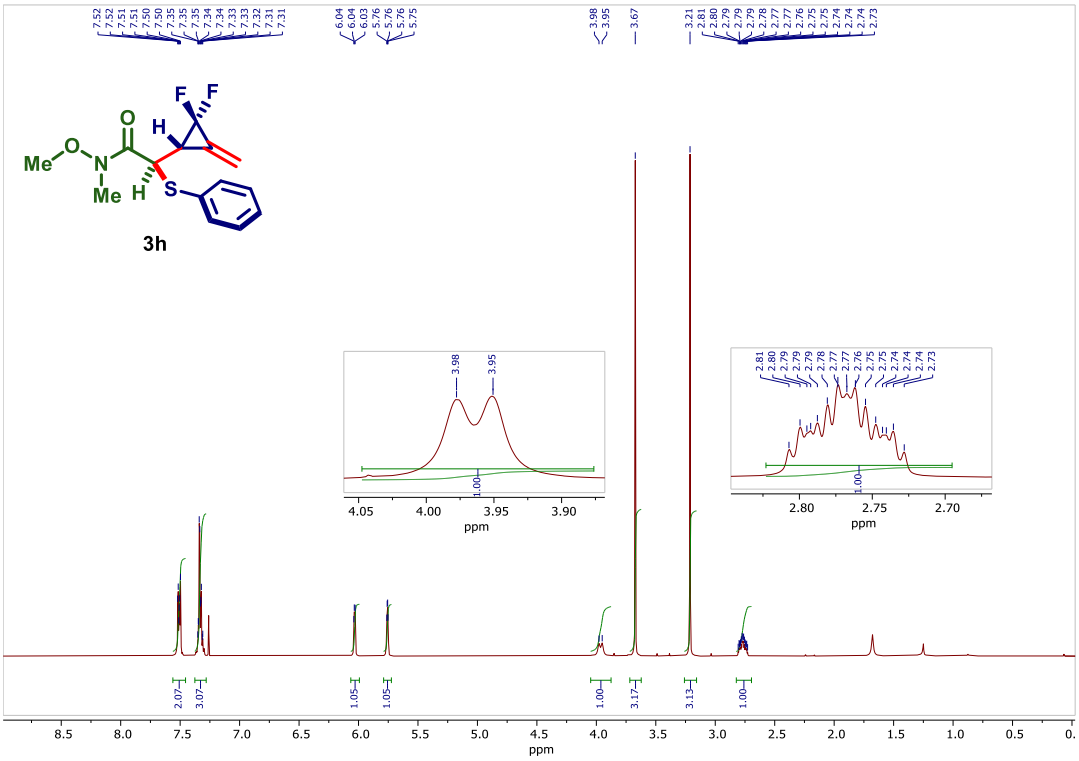
^{19}F NMR (376 MHz, $CDCl_3$) of compound **3g:**



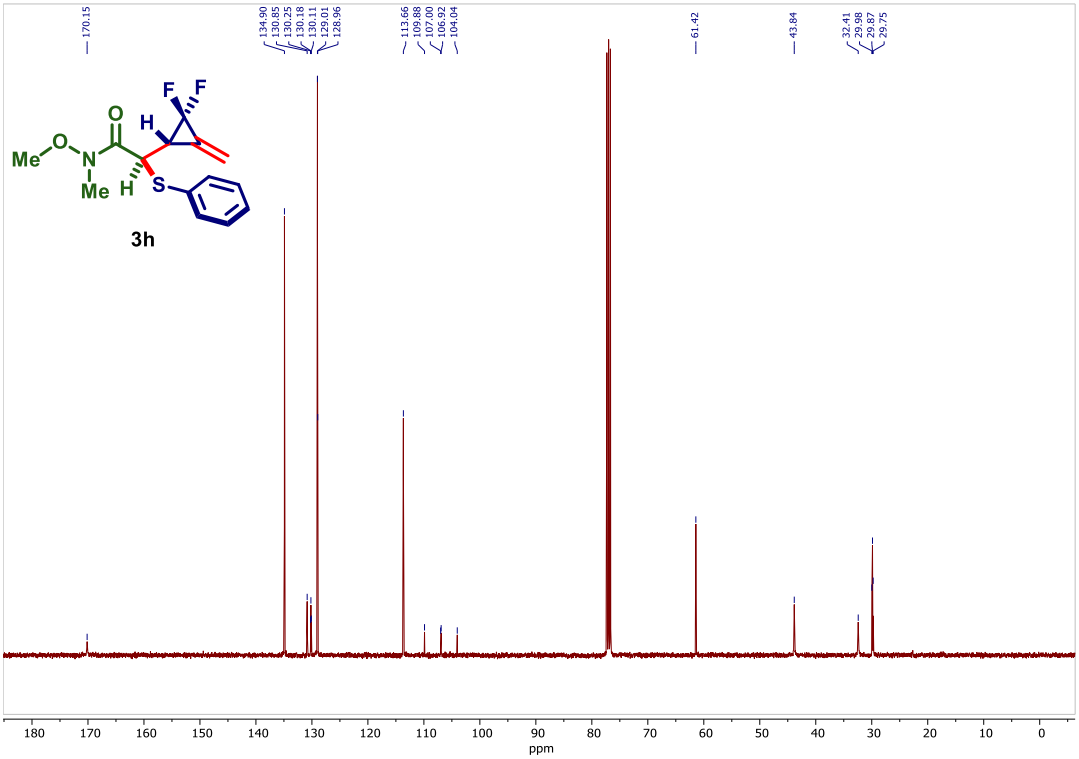
^{19}F NMR (376 MHz, $CDCl_3$) of crude reaction mixture (compound **3g**)**:**



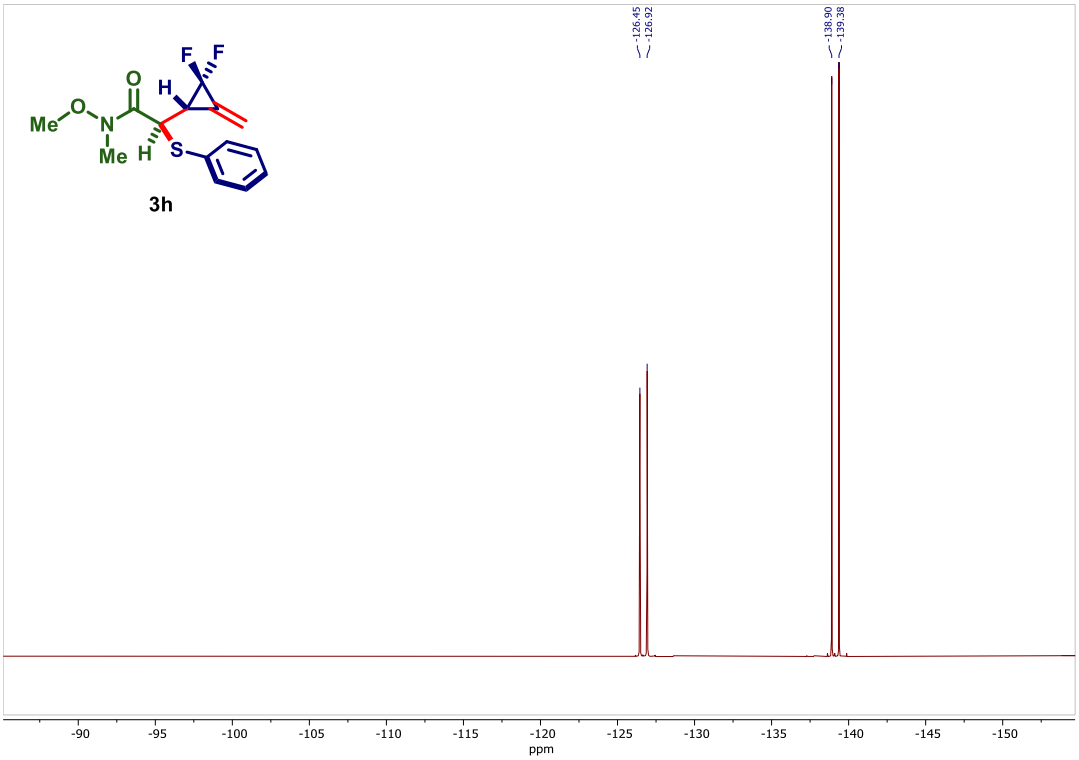
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3h: (***See Procedure***)**



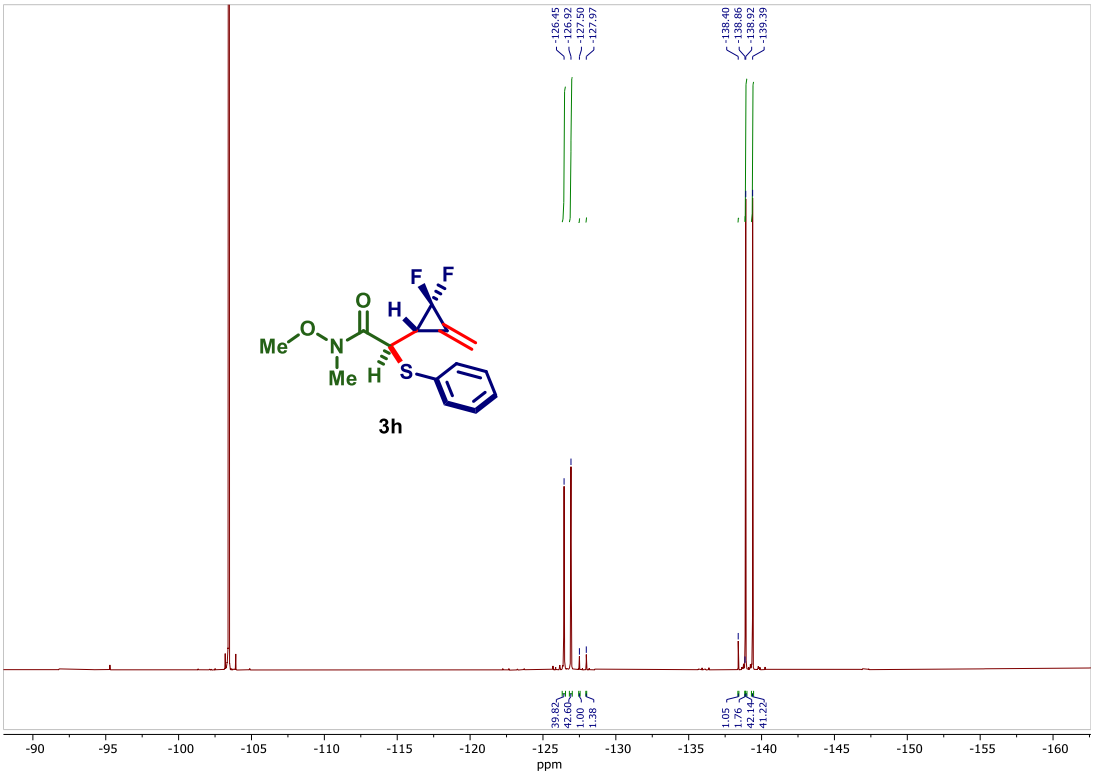
^{13}C NMR (101 MHz, $CDCl_3$) of Compound **3h:**



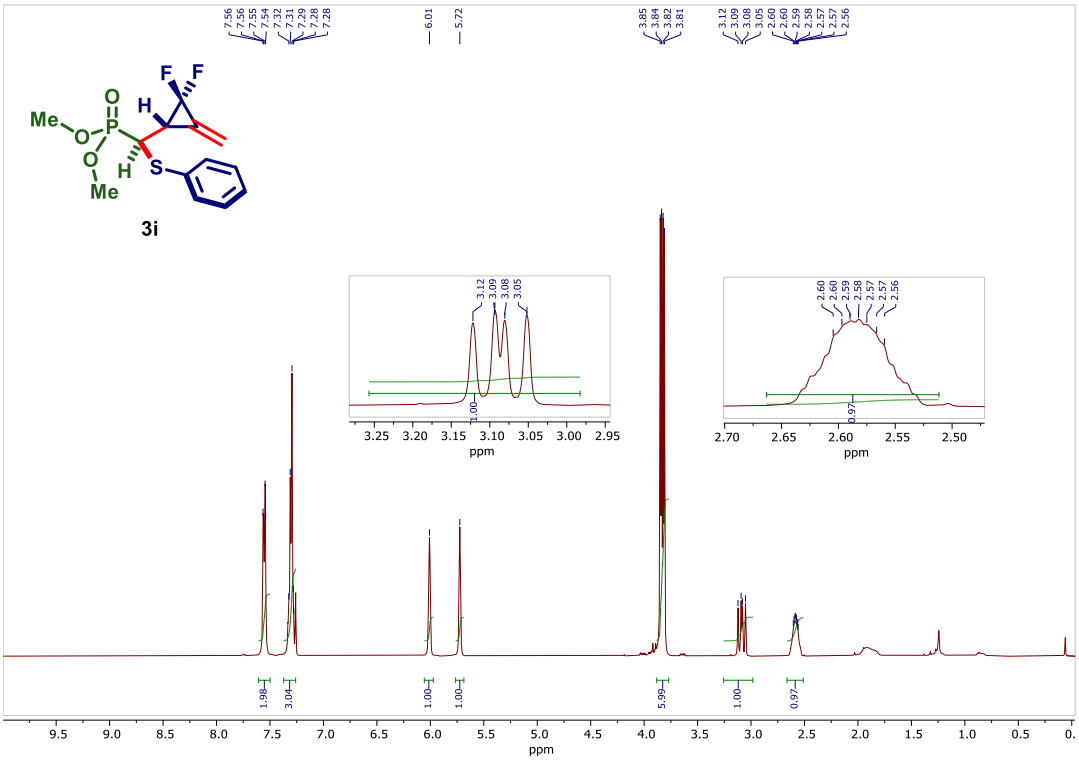
^{19}F NMR (376 MHz, $CDCl_3$) of compound **3h:**



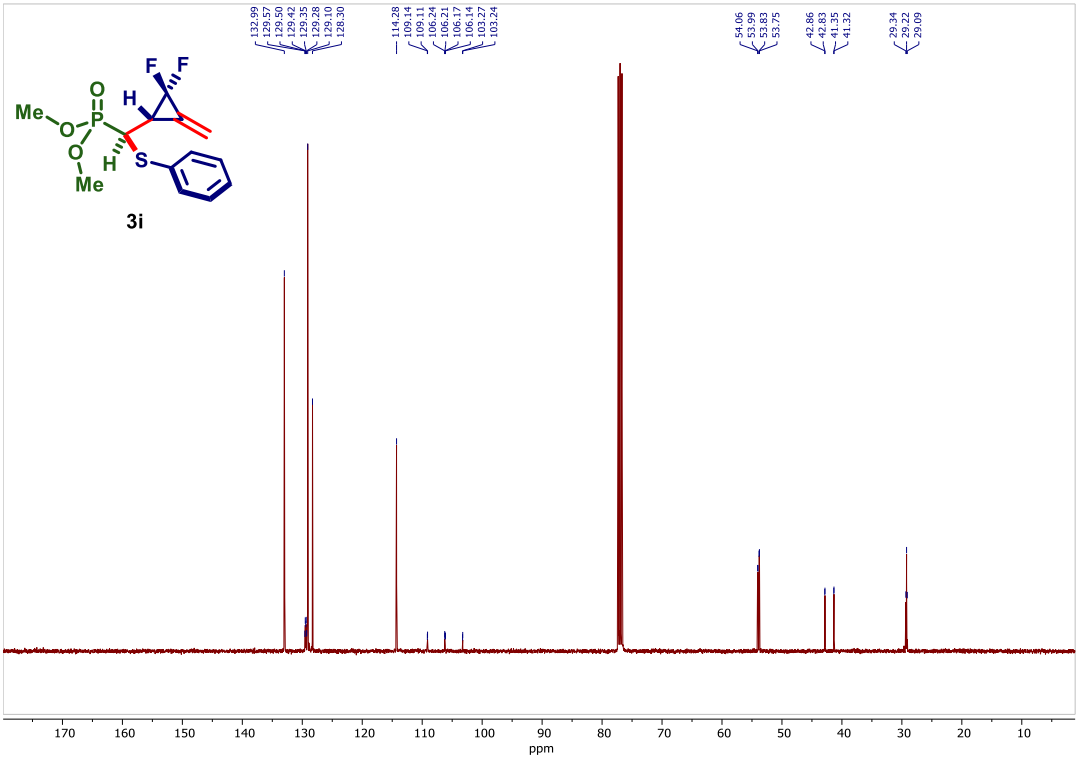
^{19}F NMR (376 MHz, $CDCl_3$) of crude reaction mixture (compound **3h**)**:**



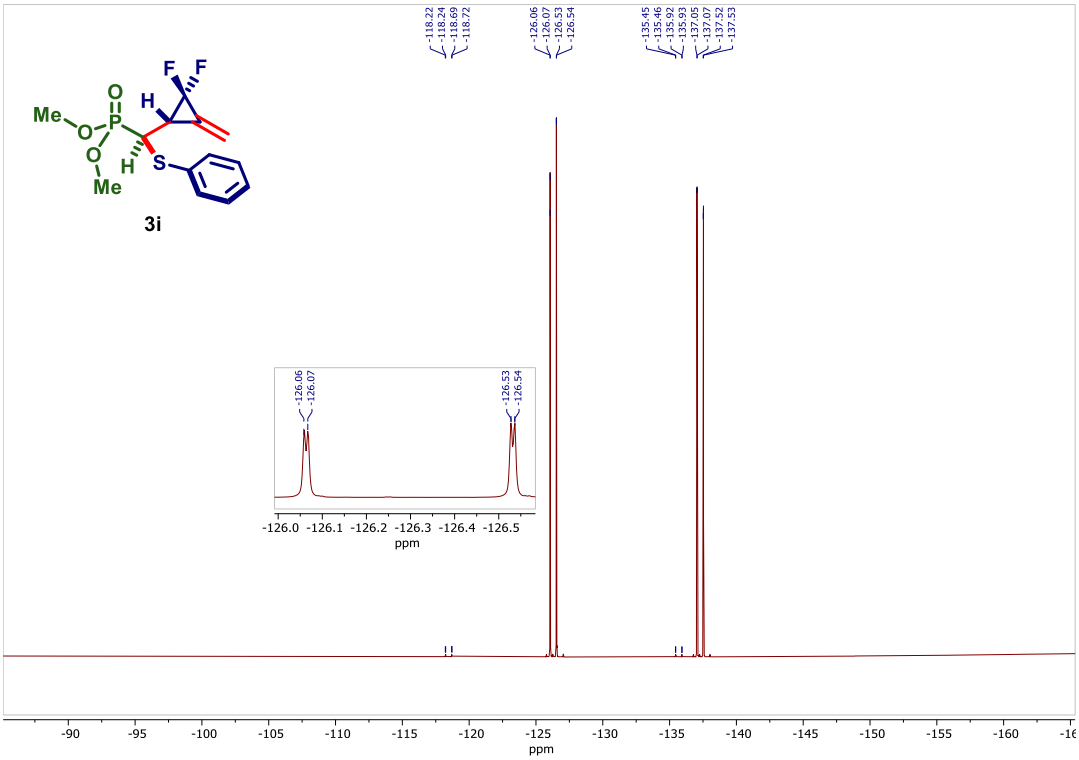
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3i: (*See Procedure*)**



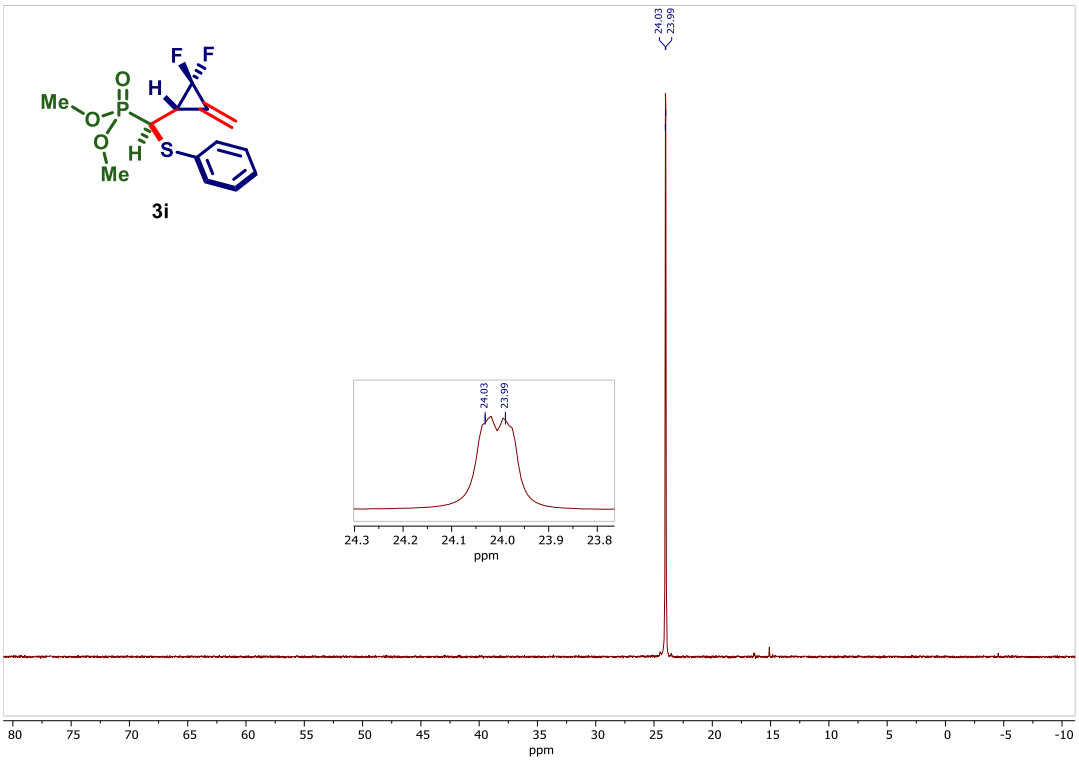
^{13}C NMR (101 MHz, $CDCl_3$) of Compound **3i:**



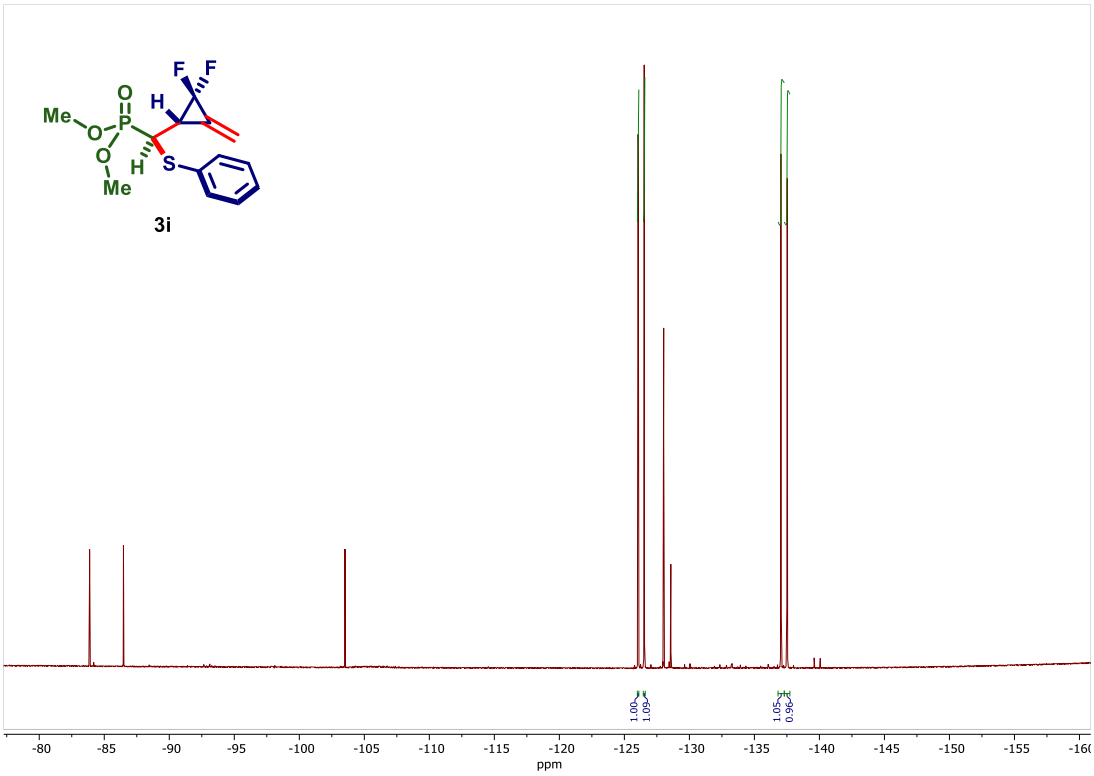
^{19}F NMR (376 MHz, $CDCl_3$) of compound **3i:**



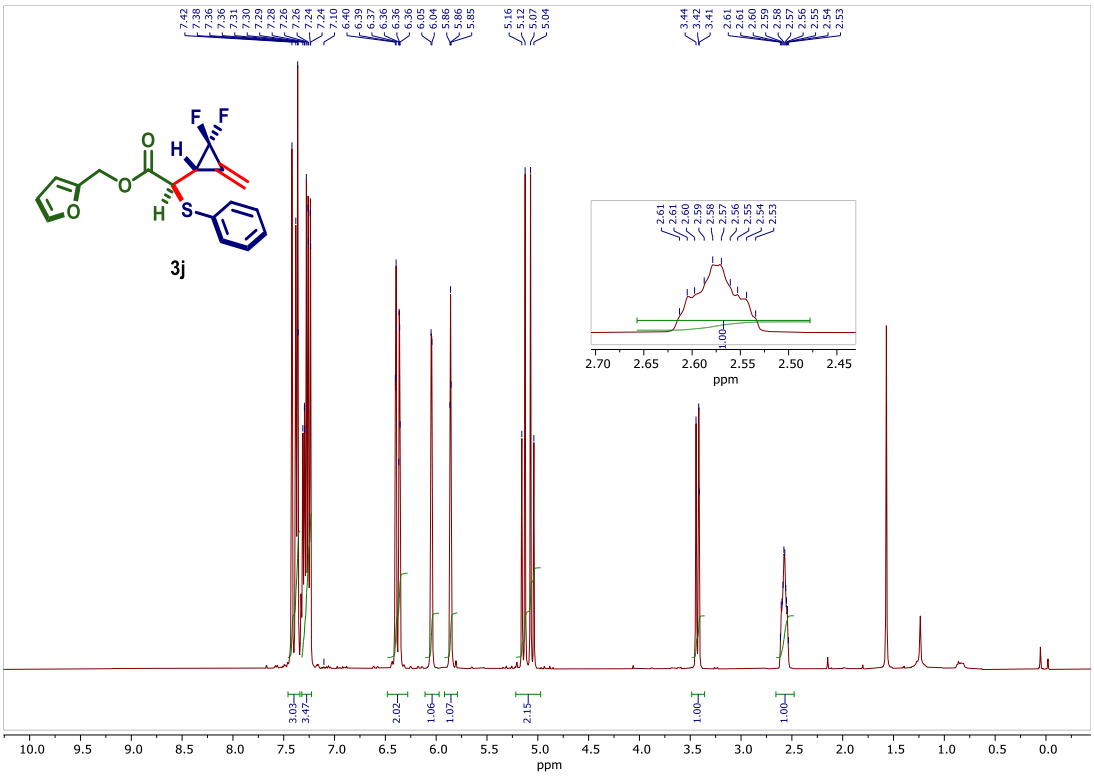
^{31}P NMR (162 MHz, $CDCl_3$) of compound **3i:**



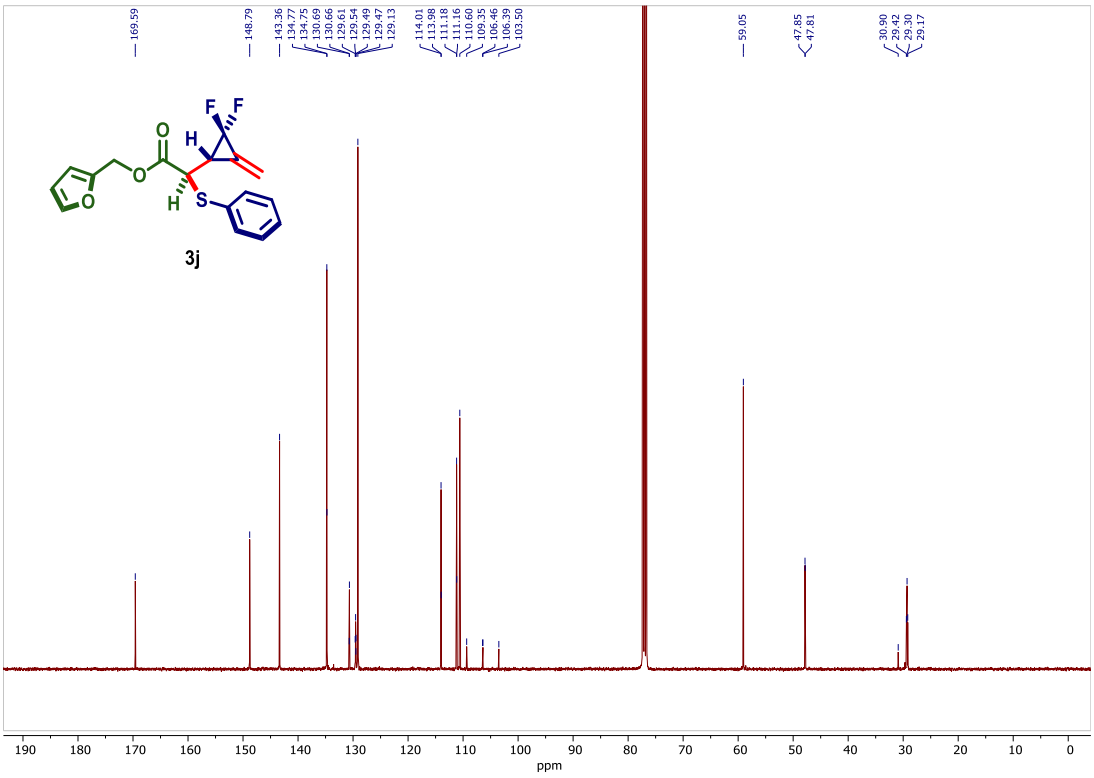
^{19}F NMR (376 MHz, $CDCl_3$) of crude reaction mixture (compound **3i**)**:**



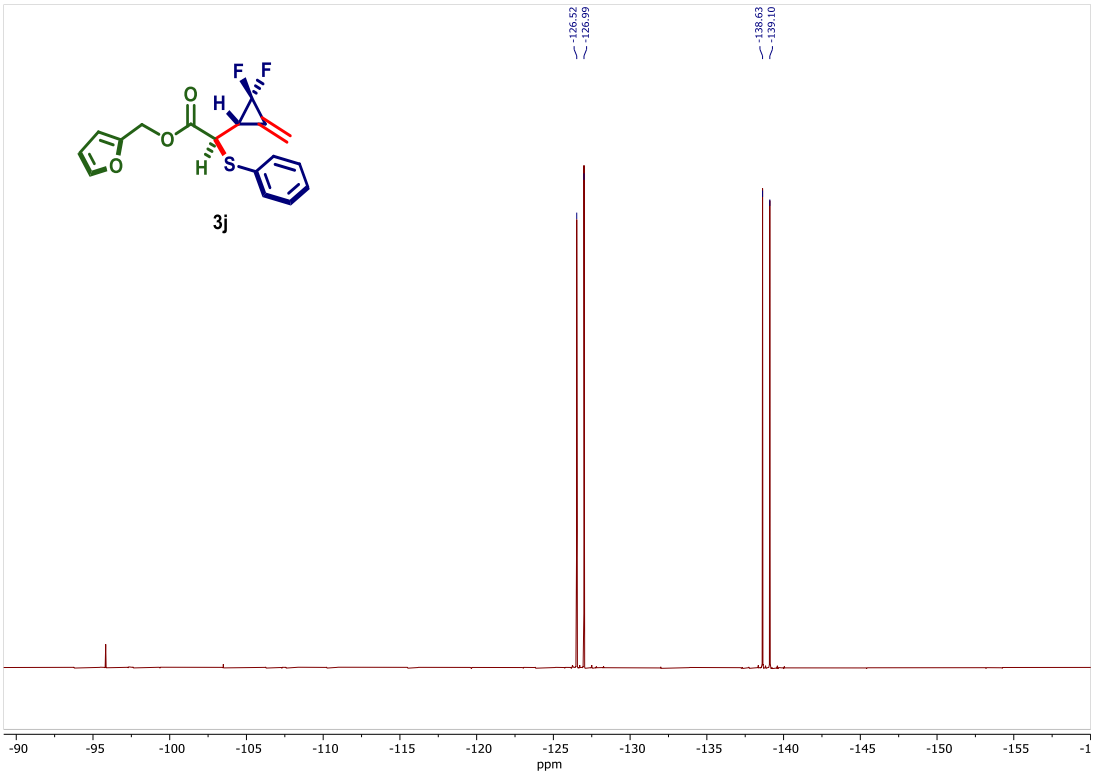
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3j: (*See Procedure*)**



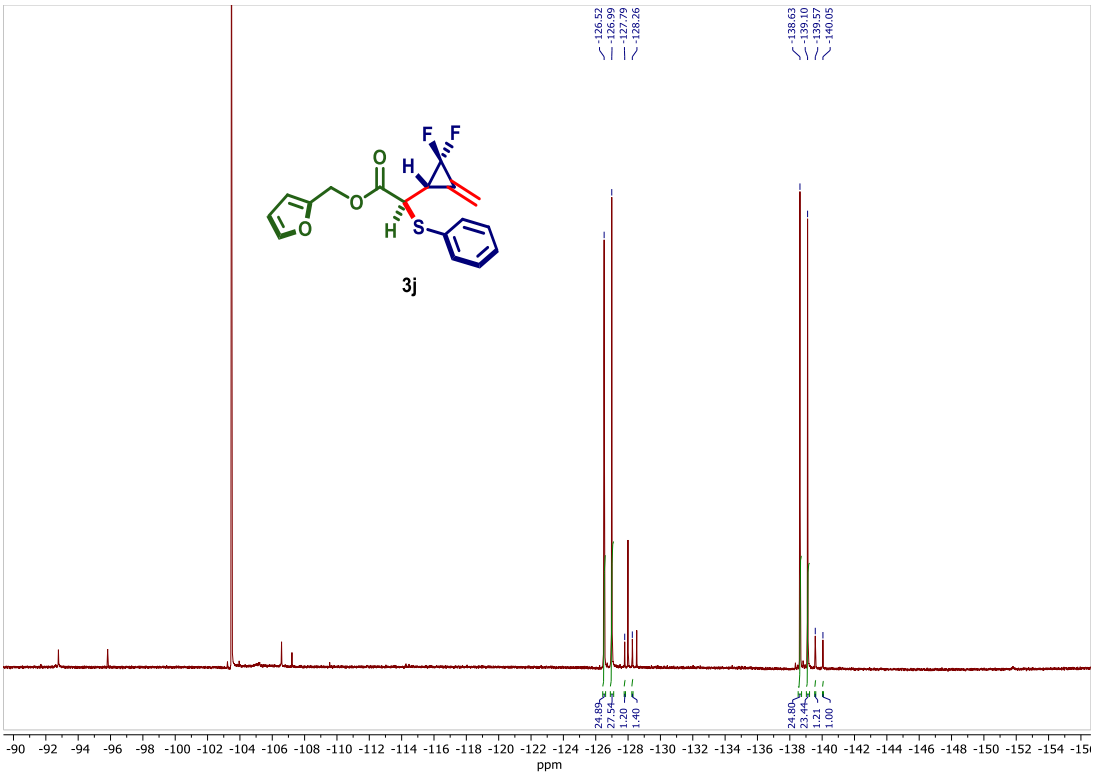
^{13}C NMR (101 MHz, $CDCl_3$) of Compound **3j:**



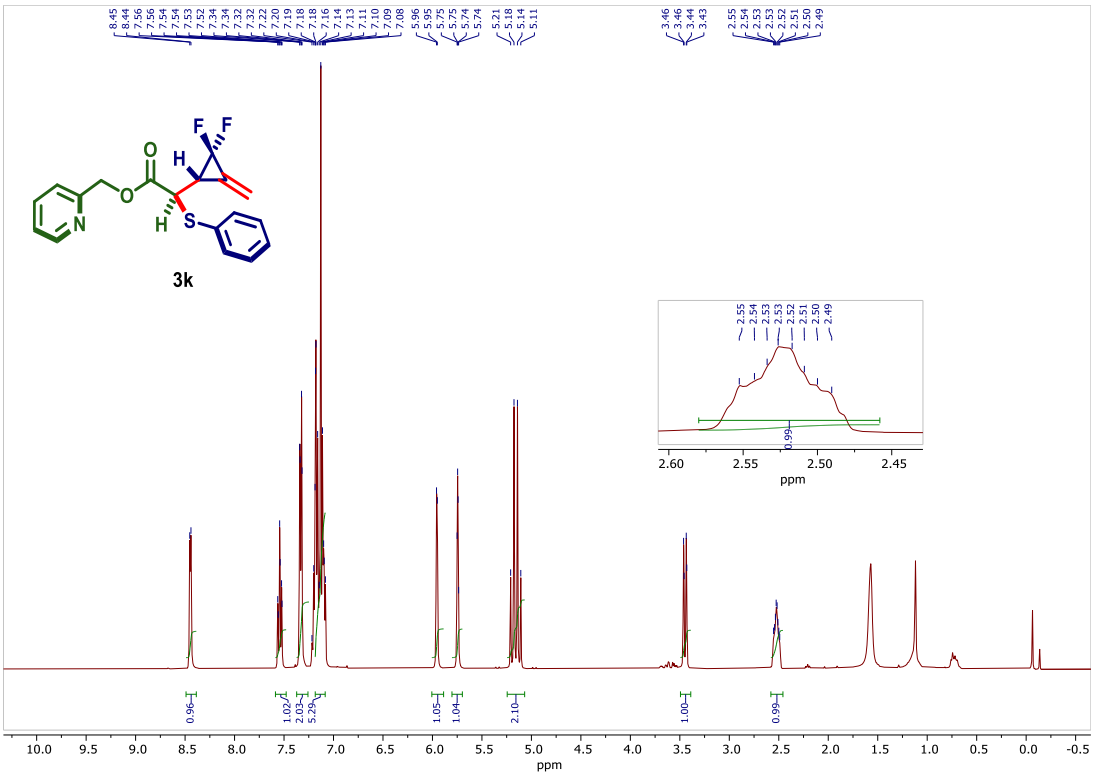
^{19}F NMR (376 MHz, $CDCl_3$) of compound **3j:**



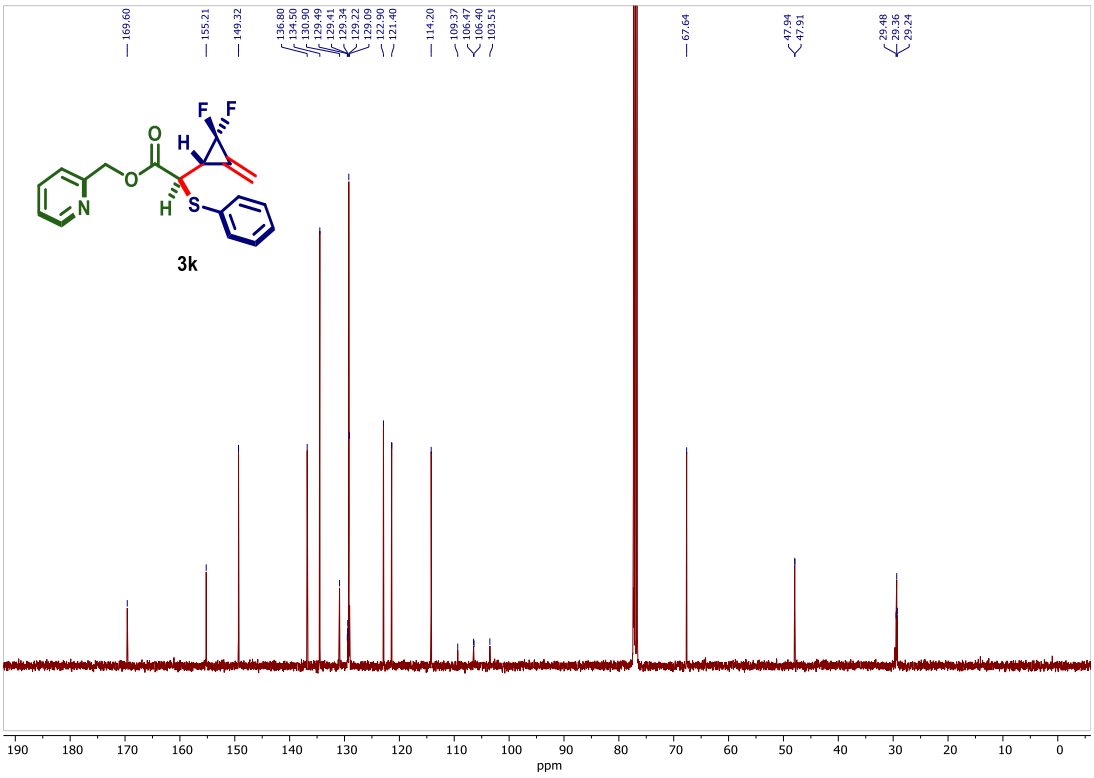
^{19}F NMR (376 MHz, $CDCl_3$) of crude reaction mixture (compound **3j**)**:**



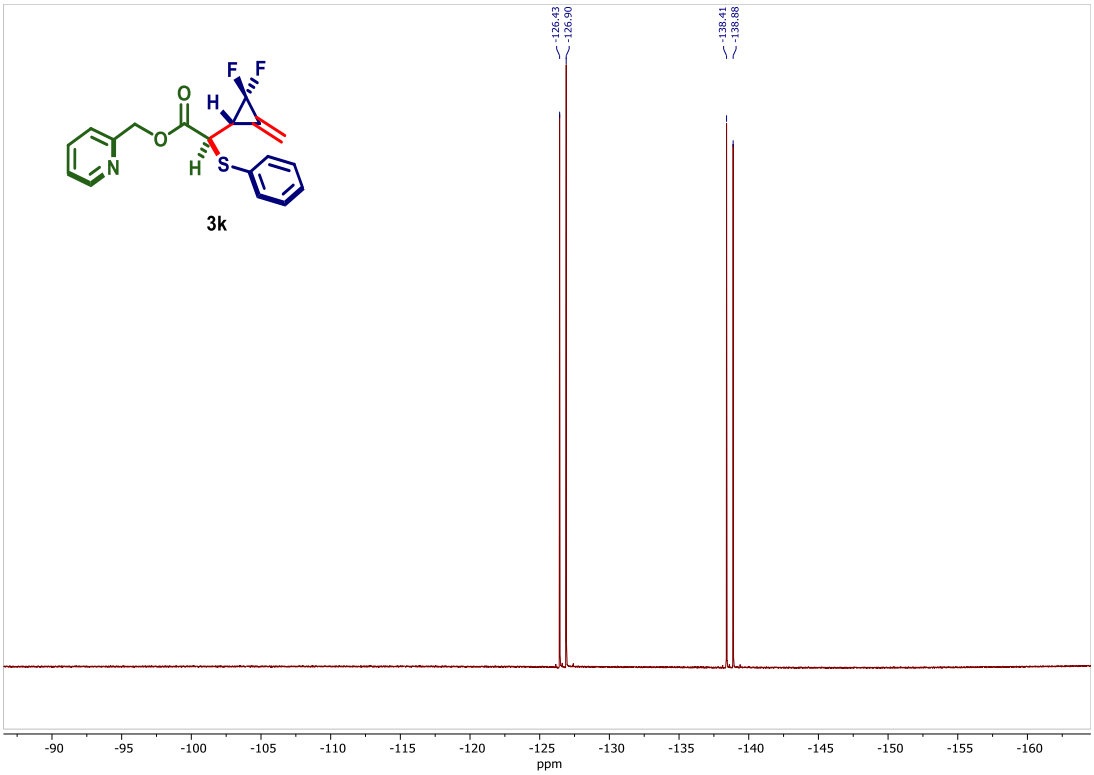
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3k: (*See Procedure*)**



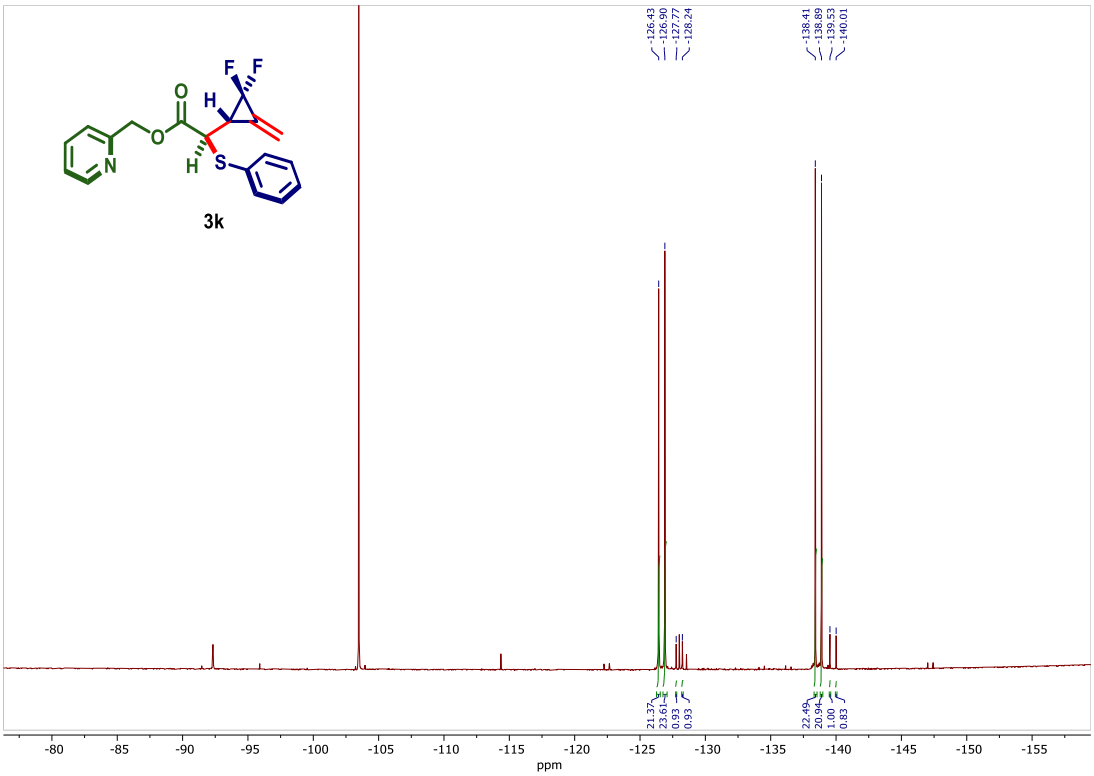
^{13}C NMR (101 MHz, $CDCl_3$) of Compound **3k:**



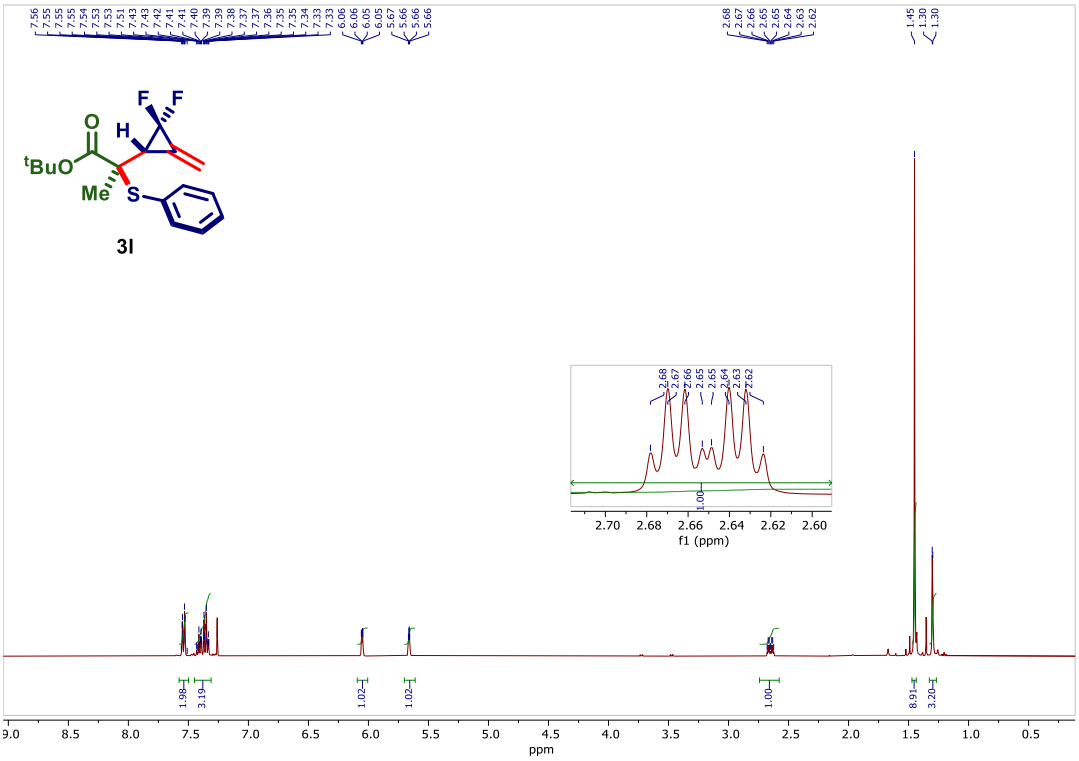
^{19}F NMR (376 MHz, $CDCl_3$) of compound **3k:**



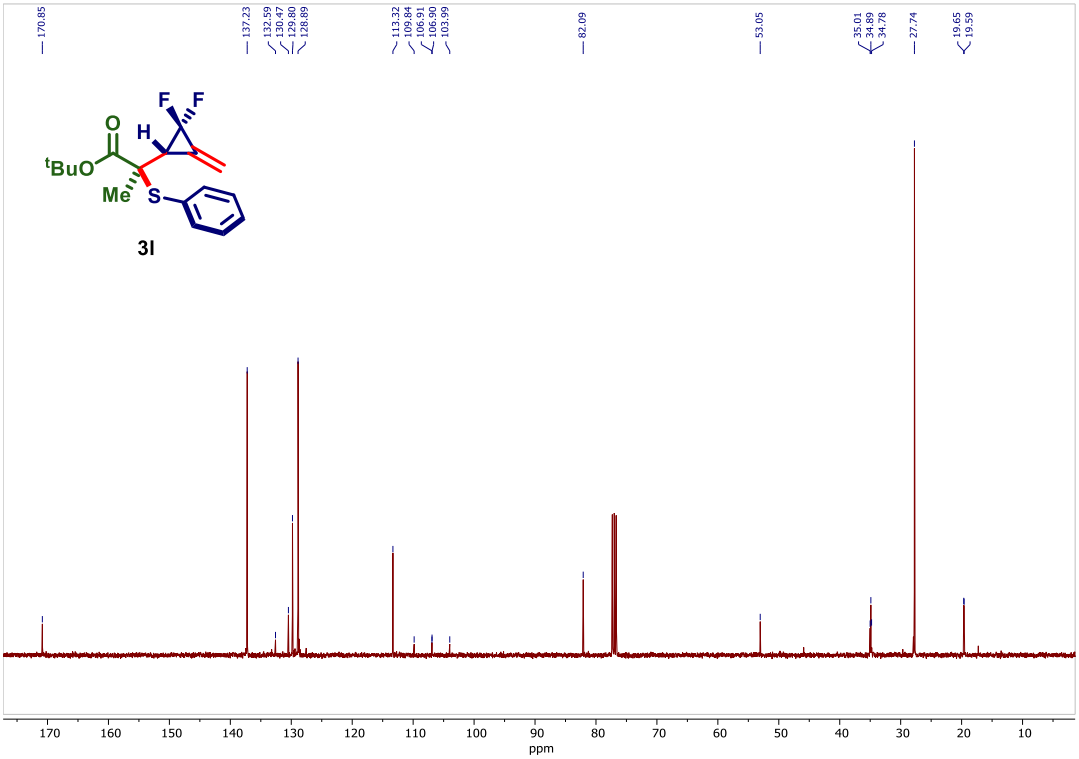
^{19}F NMR (376 MHz, $CDCl_3$) of crude reaction mixture (compound **3k**)**:**



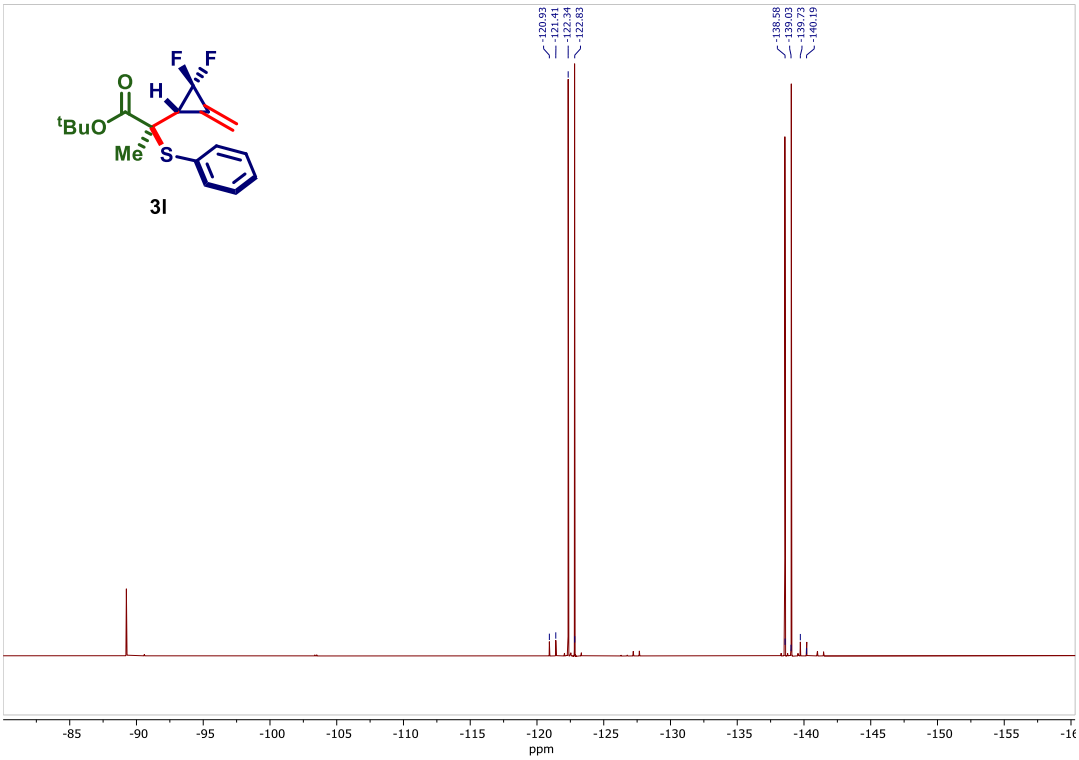
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3l: (***See Procedure***)**



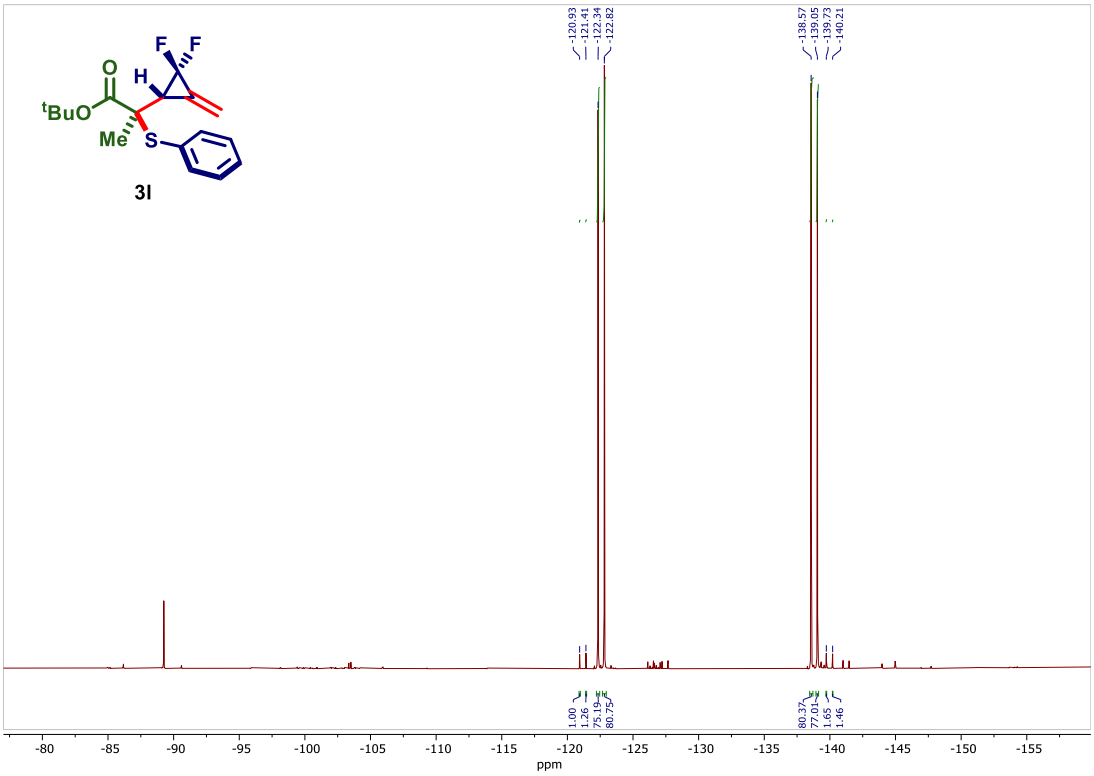
^{13}C NMR (101 MHz, $CDCl_3$) of Compound **3l:**



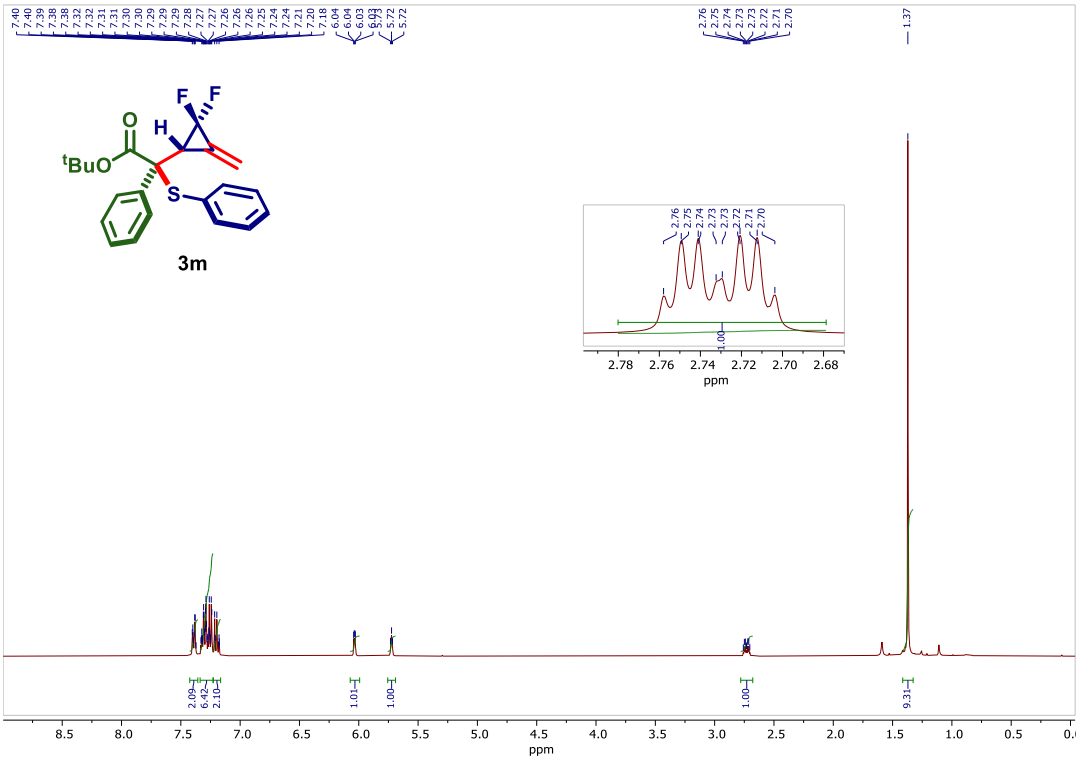
^{19}F NMR (376 MHz, $CDCl_3$) of compound **3l:**



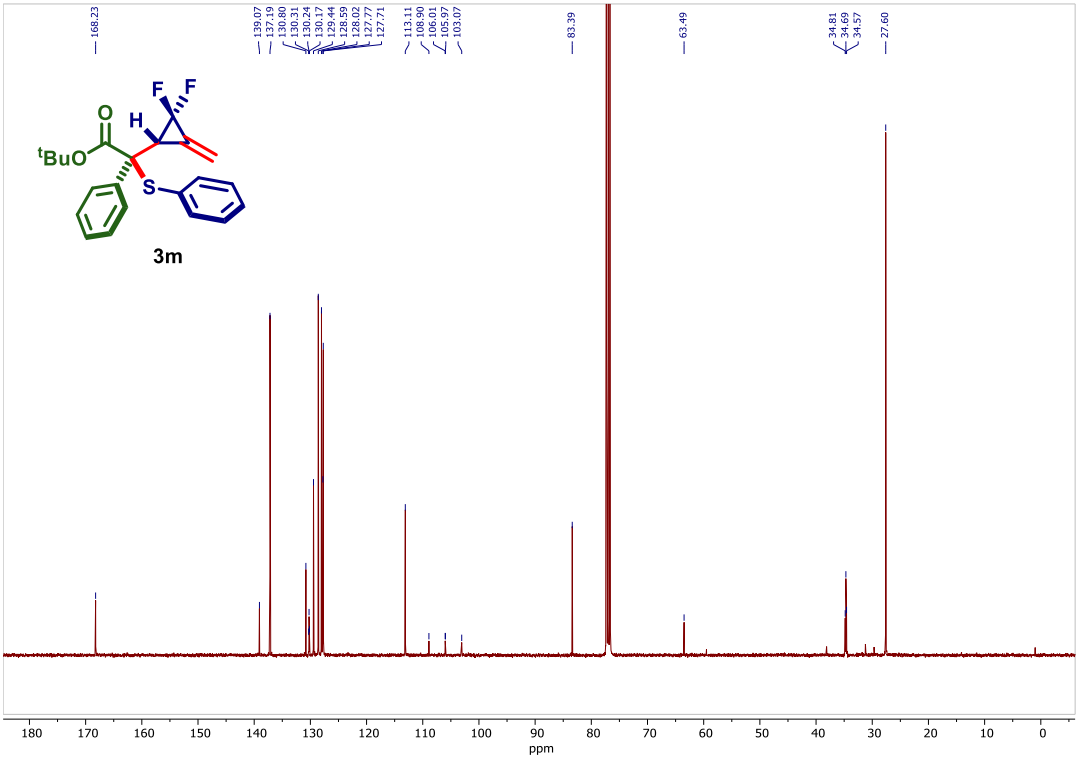
^{19}F NMR (376 MHz, $CDCl_3$) of Crude Reaction Mixture (compound **3l**)**:**



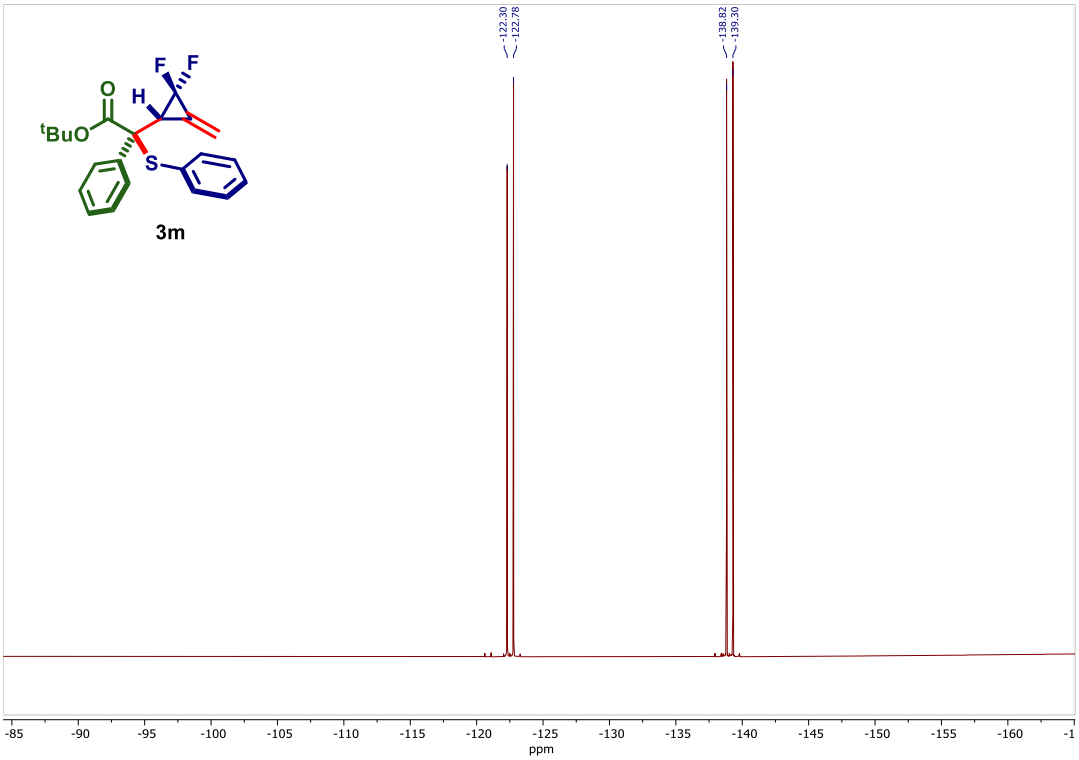
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3m: (*See Procedure*)**



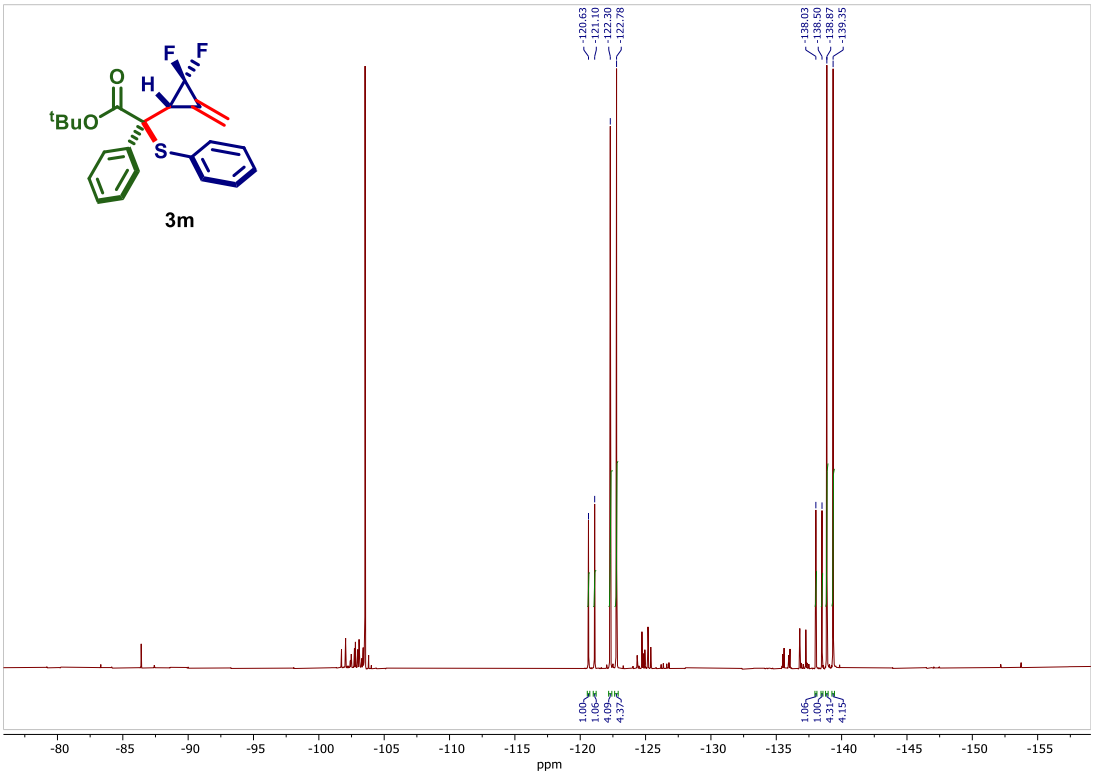
^{13}C NMR (101 MHz, $CDCl_3$) of Compound **3m:**



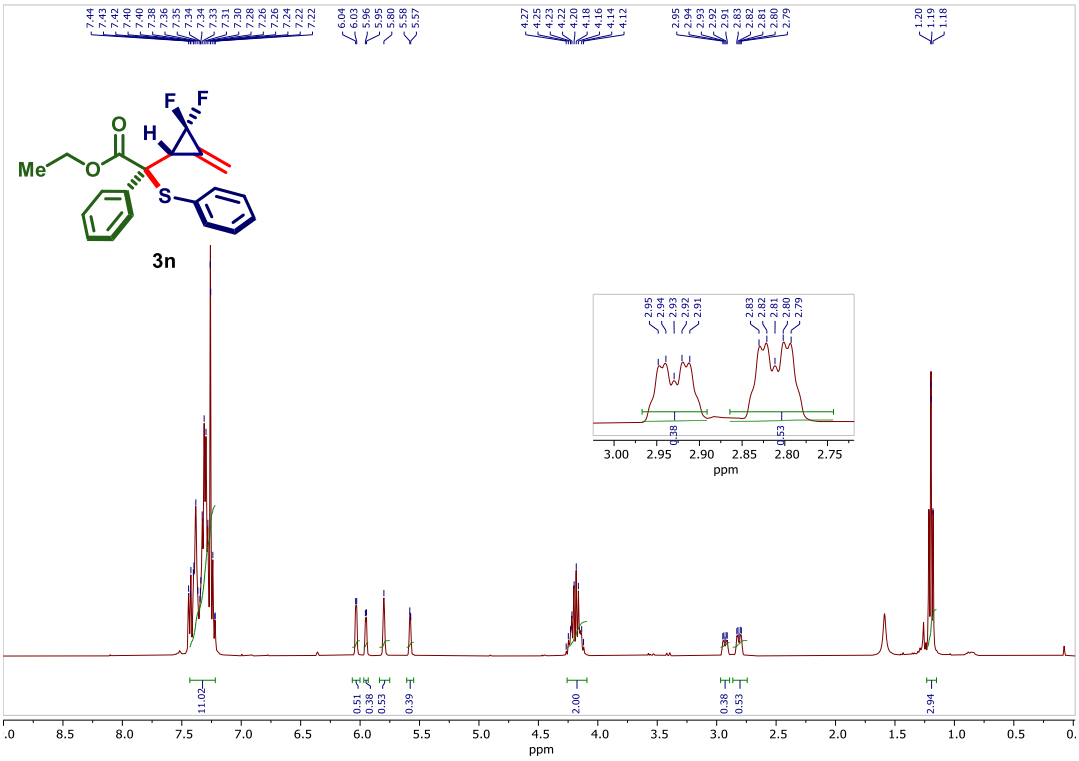
^{19}F NMR (376 MHz, $CDCl_3$) of compound **3m:**



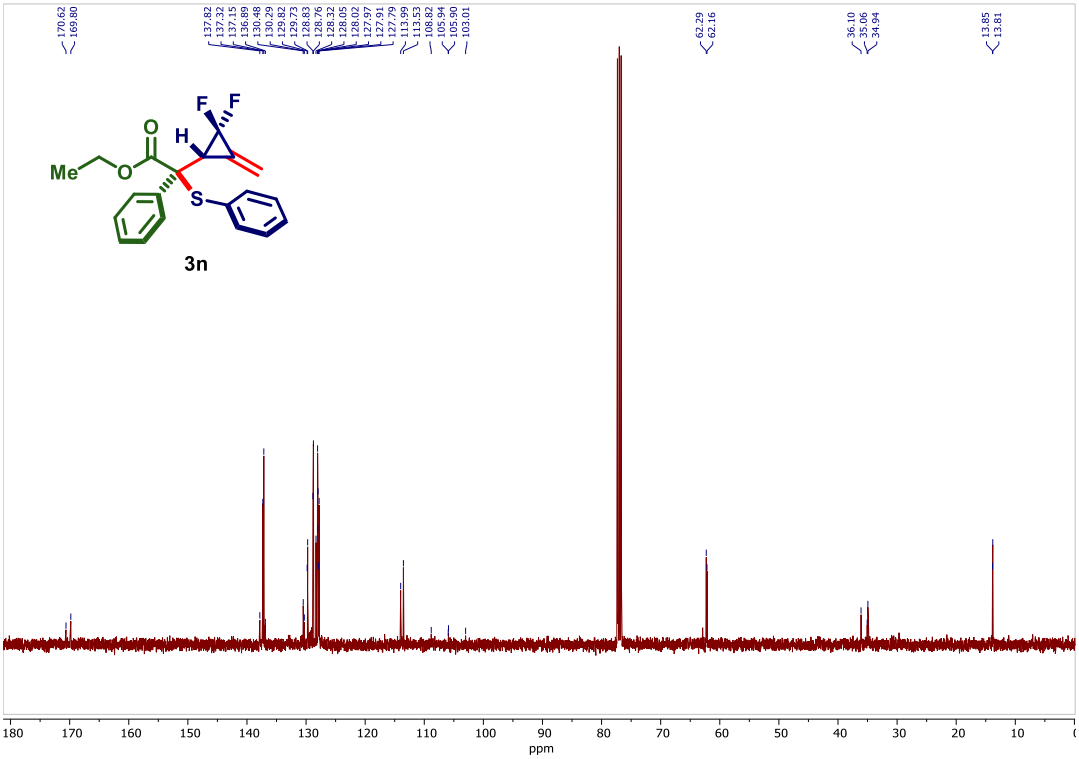
^{19}F NMR (376 MHz, $CDCl_3$) of Crude Reaction Mixture (compound **3m**)**:**



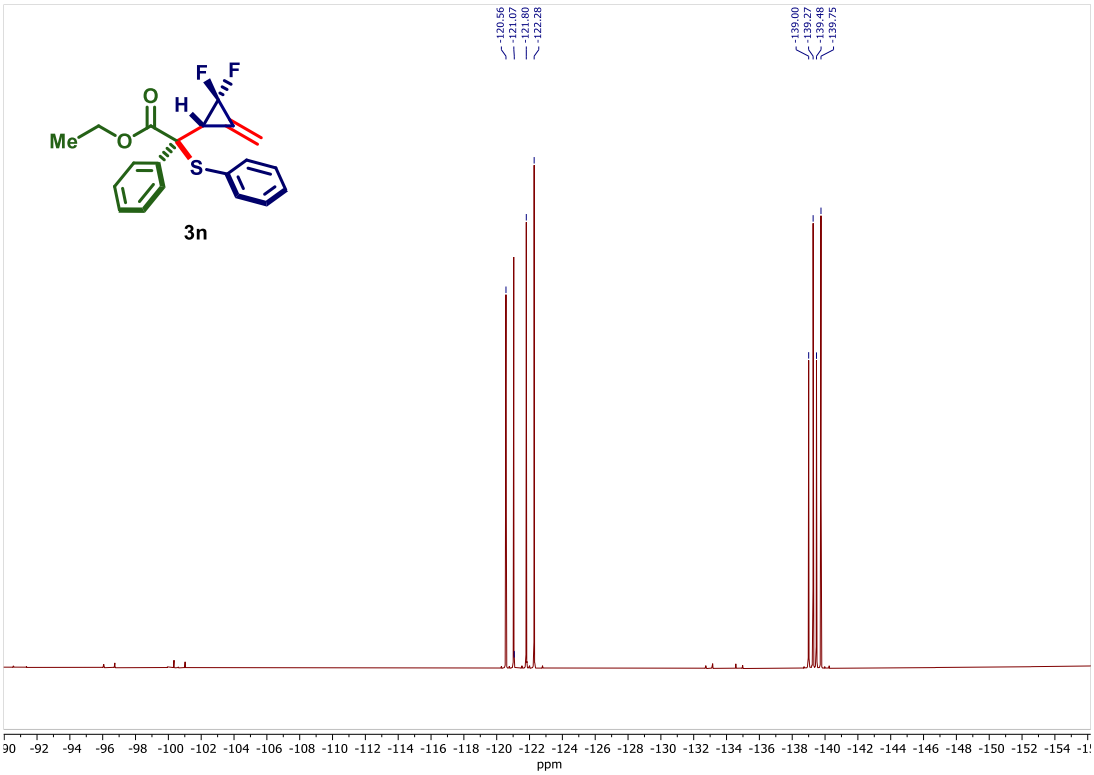
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3n: (*See Procedure*)**



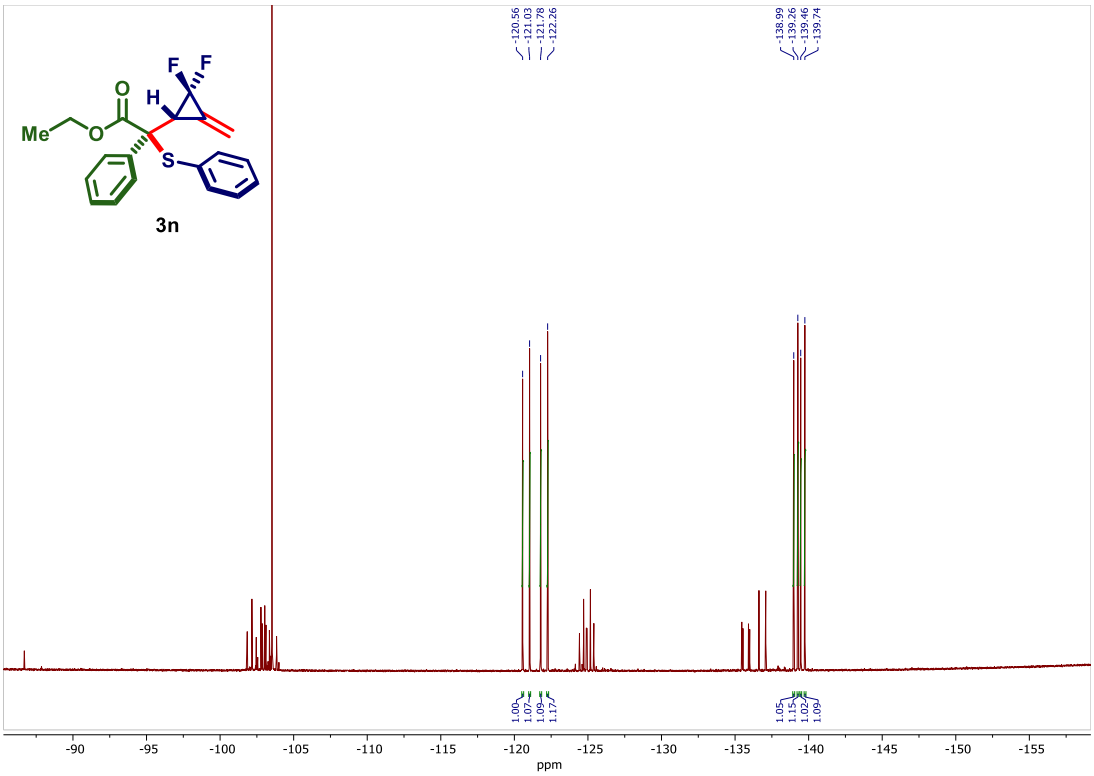
^{13}C NMR (101 MHz, $CDCl_3$) of Compound **3n:**



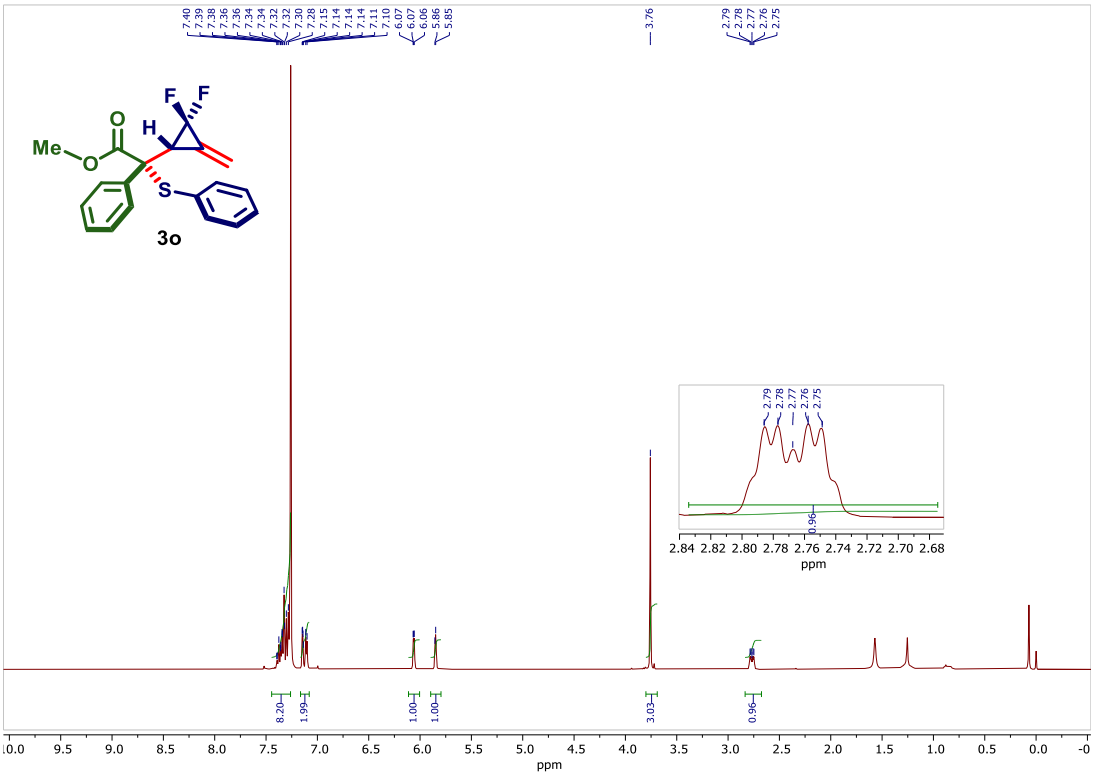
^{19}F NMR (376 MHz, $CDCl_3$) of compound **3n:**



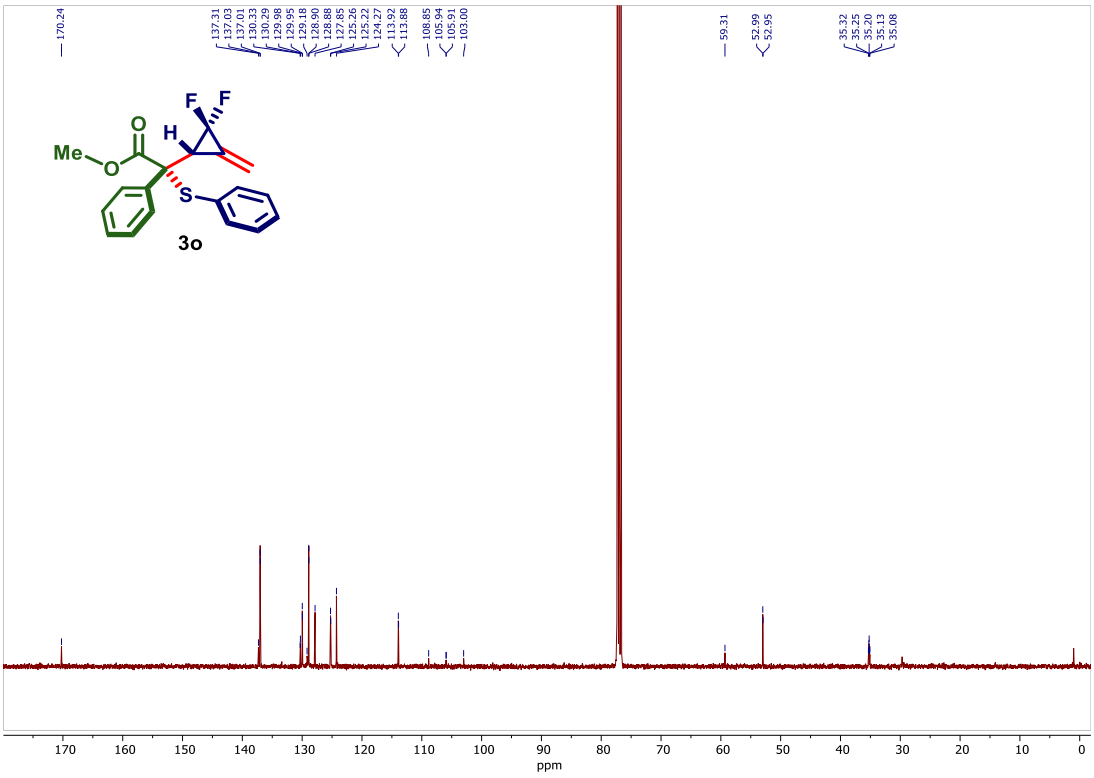
^{19}F NMR (376 MHz, $CDCl_3$) of Crude Reaction Mixture (compound **3n**)**:**



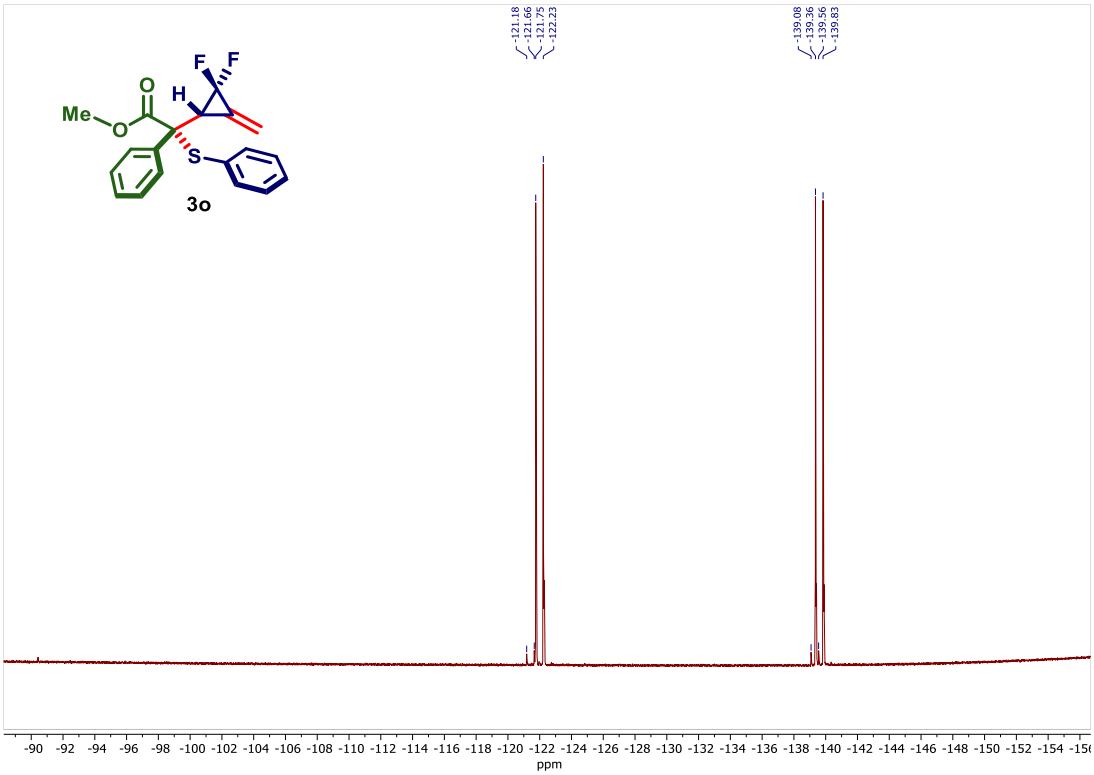
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3o: (*See Procedure*)**



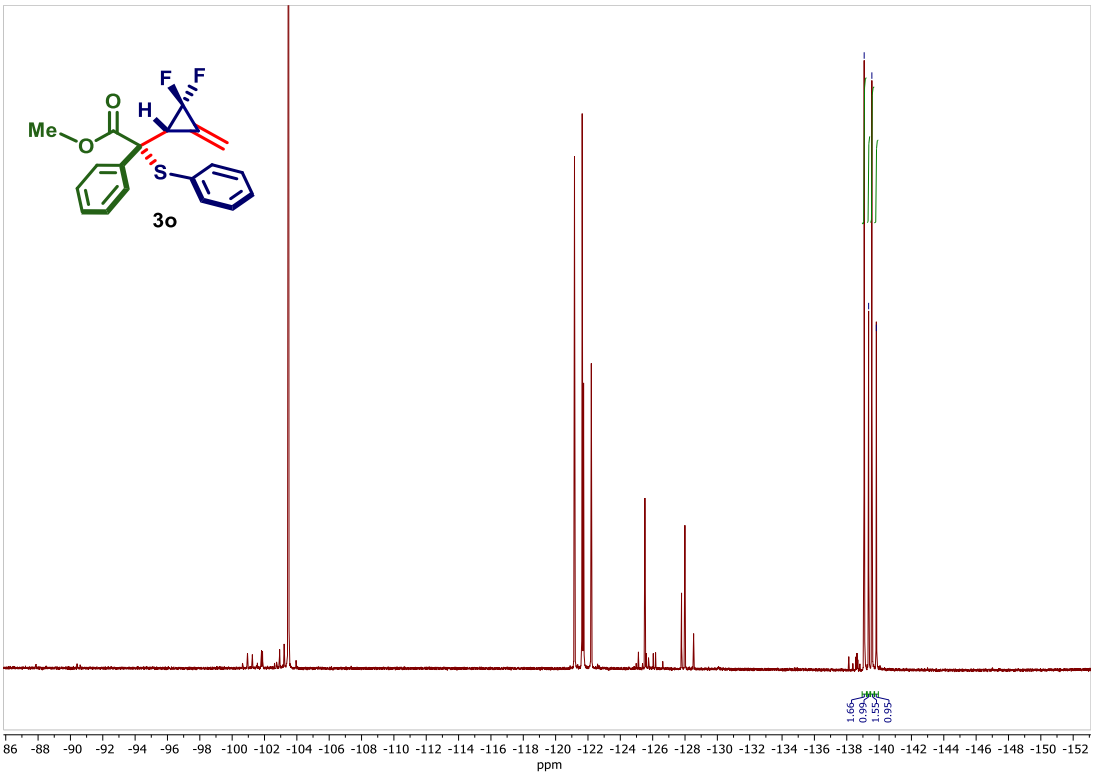
^{13}C NMR (101 MHz, $CDCl_3$) of Compound **3o**:



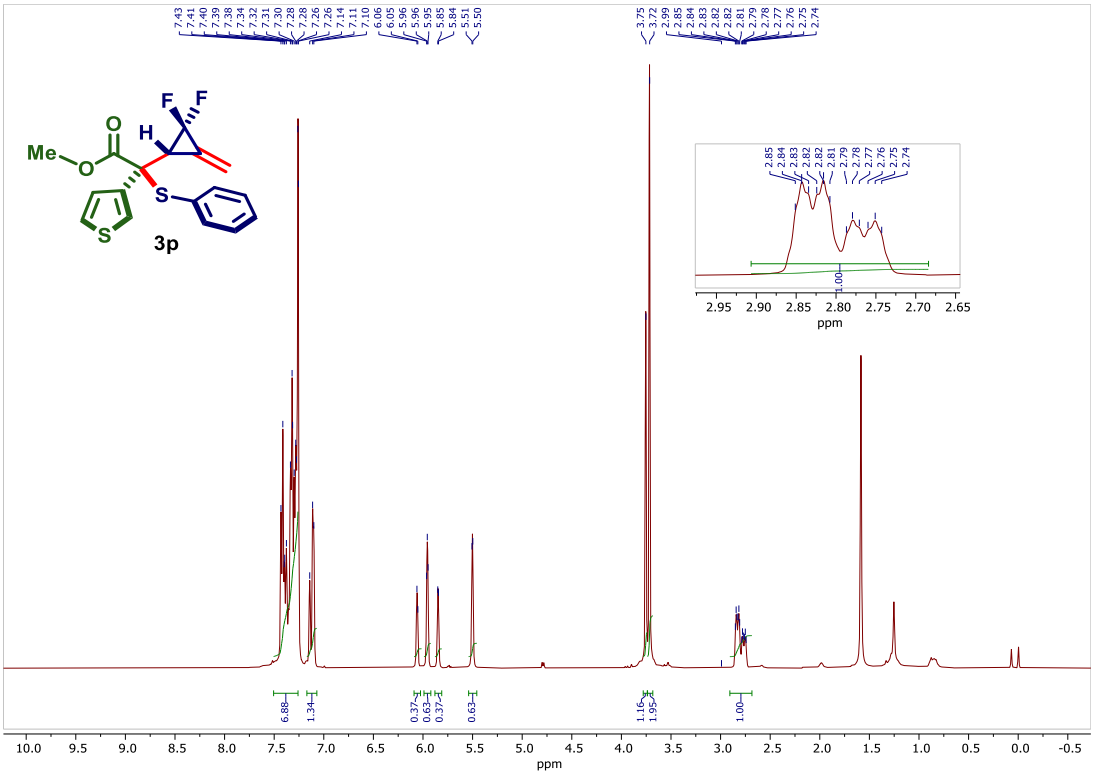
^{19}F NMR (376 MHz, $CDCl_3$) of compound **3o:**



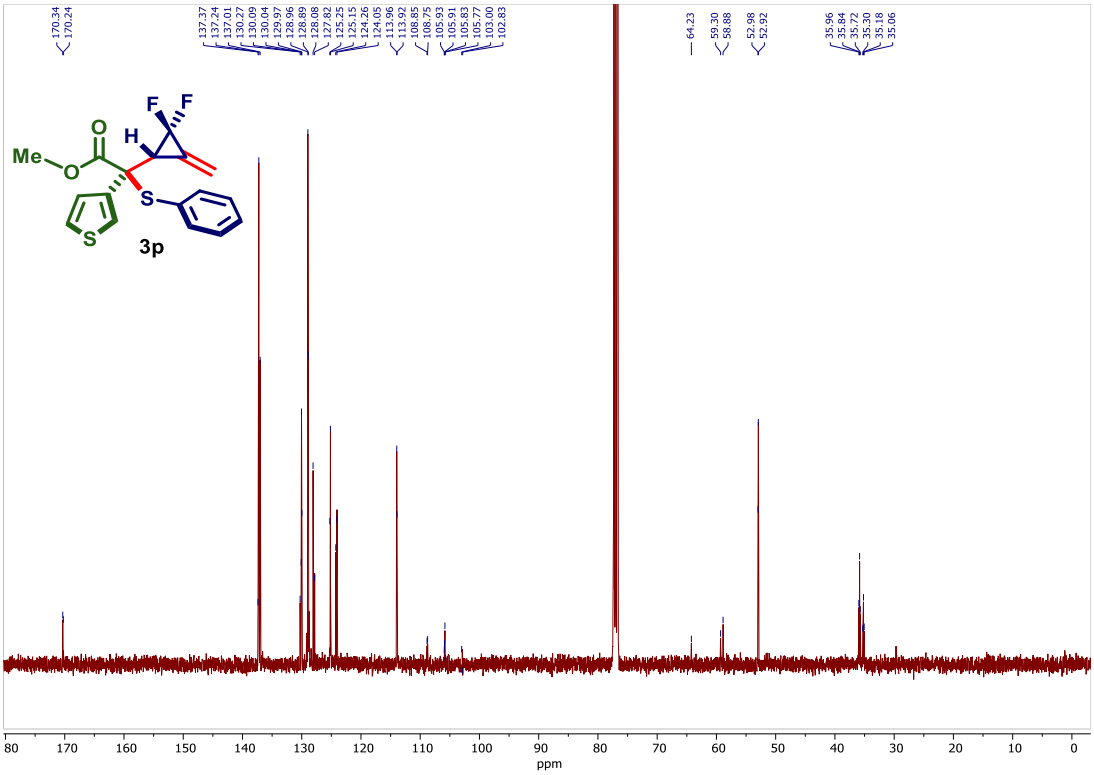
^{19}F NMR (376 MHz, $CDCl_3$) of Crude Reaction Mixture (compound **3o):**



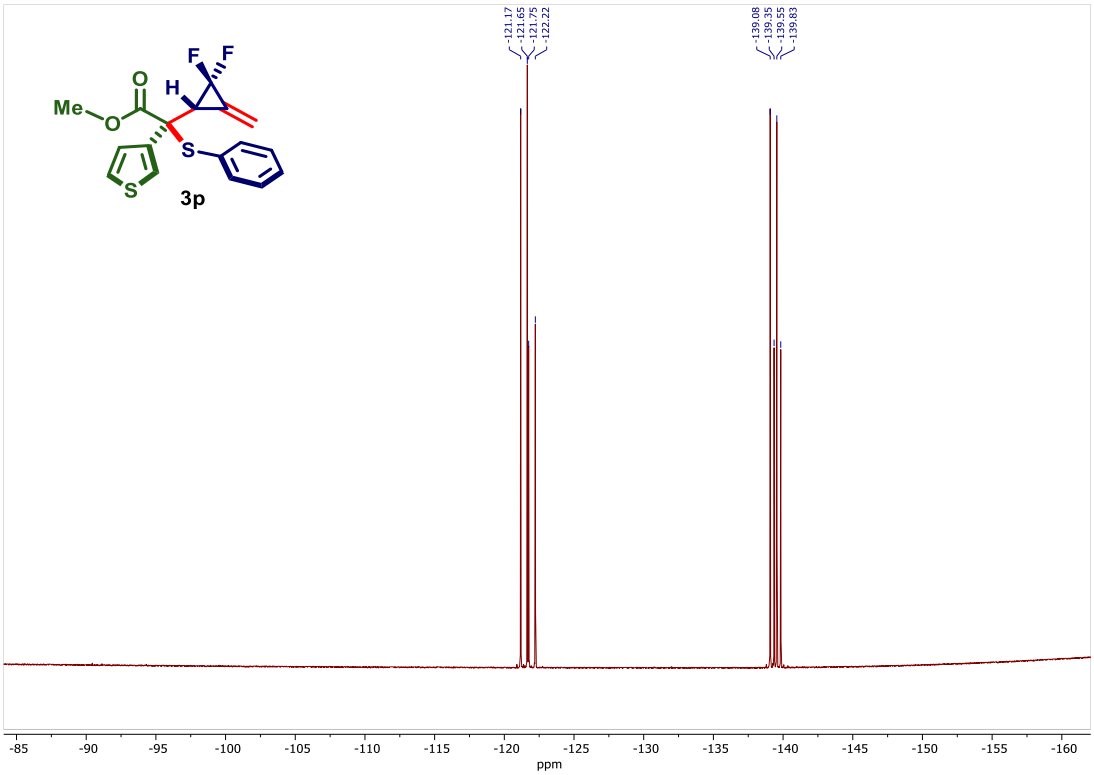
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3p: (*See Procedure*)**



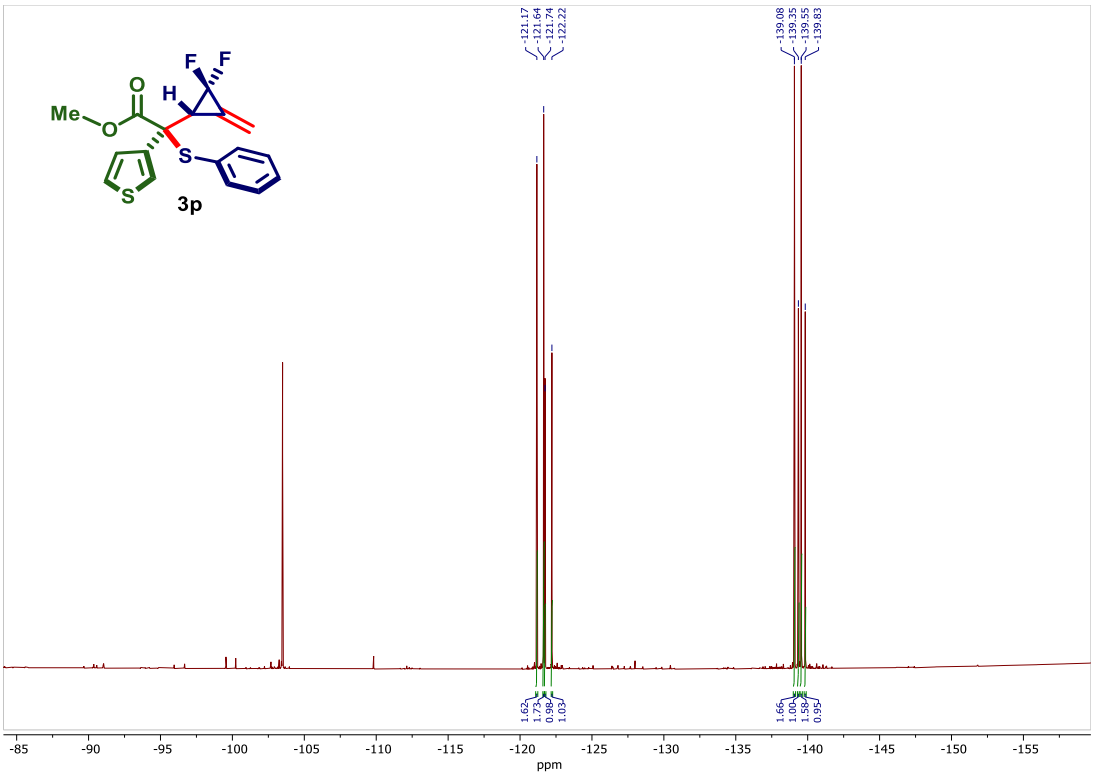
^{13}C NMR (101 MHz, $CDCl_3$) of Compound **3p**:



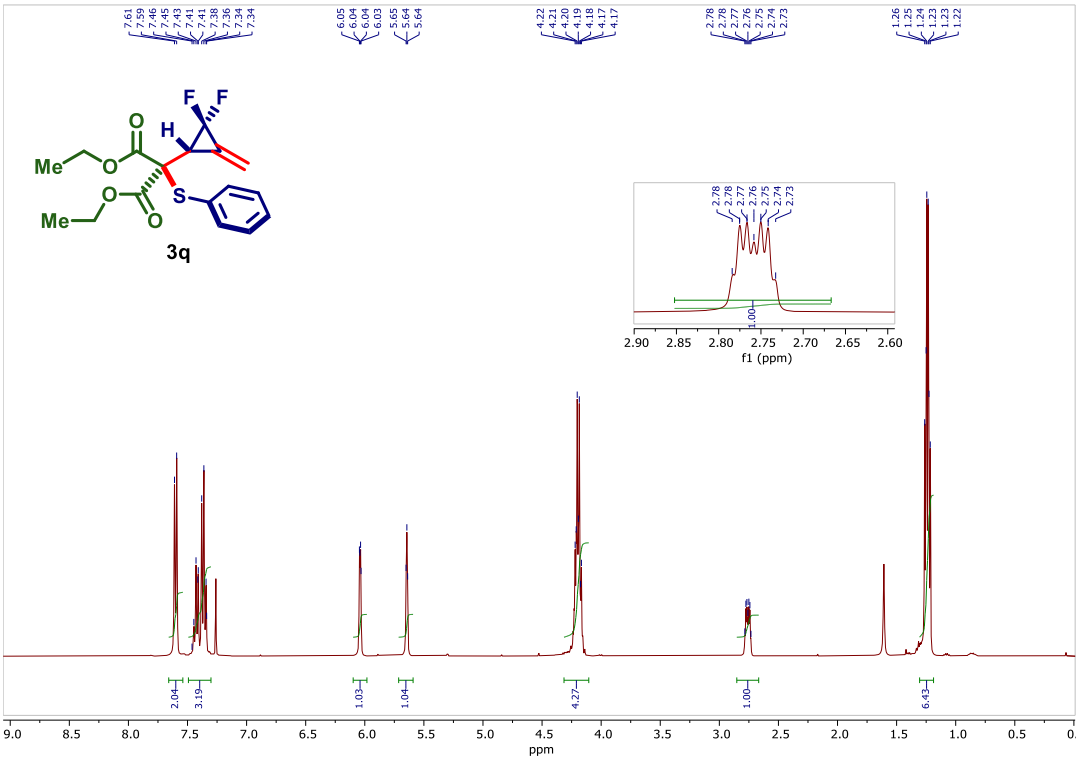
^{19}F NMR (376 MHz, $CDCl_3$) of compound **3p:**



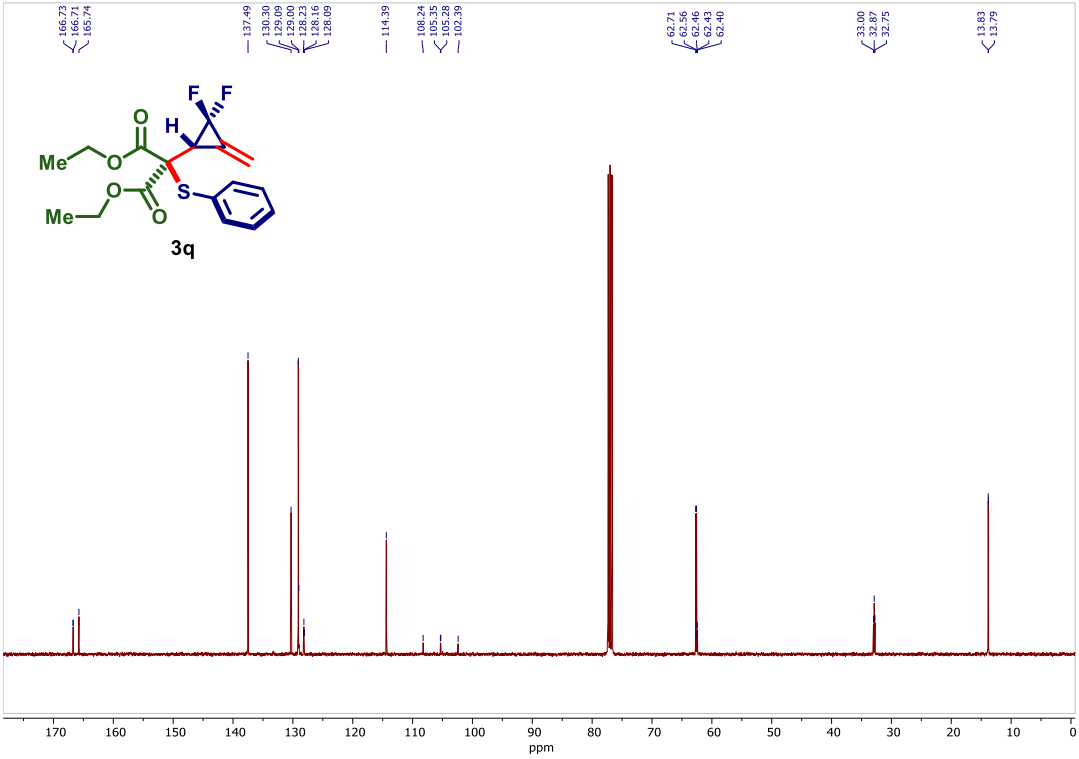
^{19}F NMR (376 MHz, $CDCl_3$) of Crude Reaction Mixture (compound **3p**)**:**



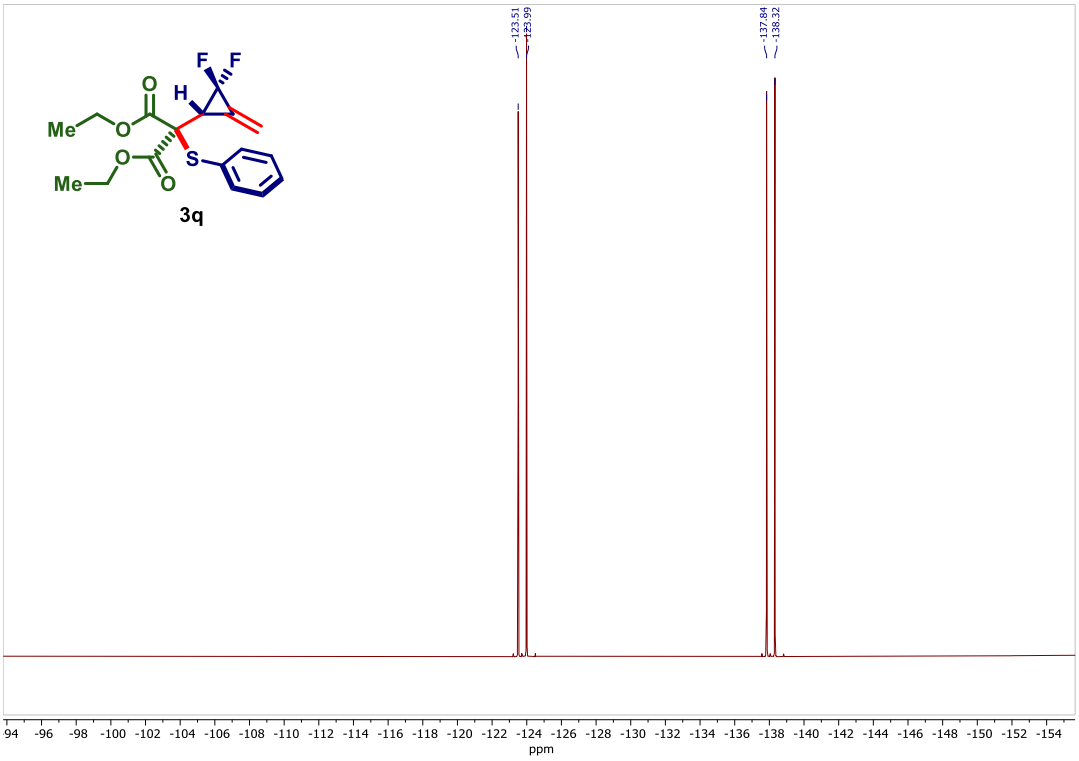
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3q: (*See Procedure*)**



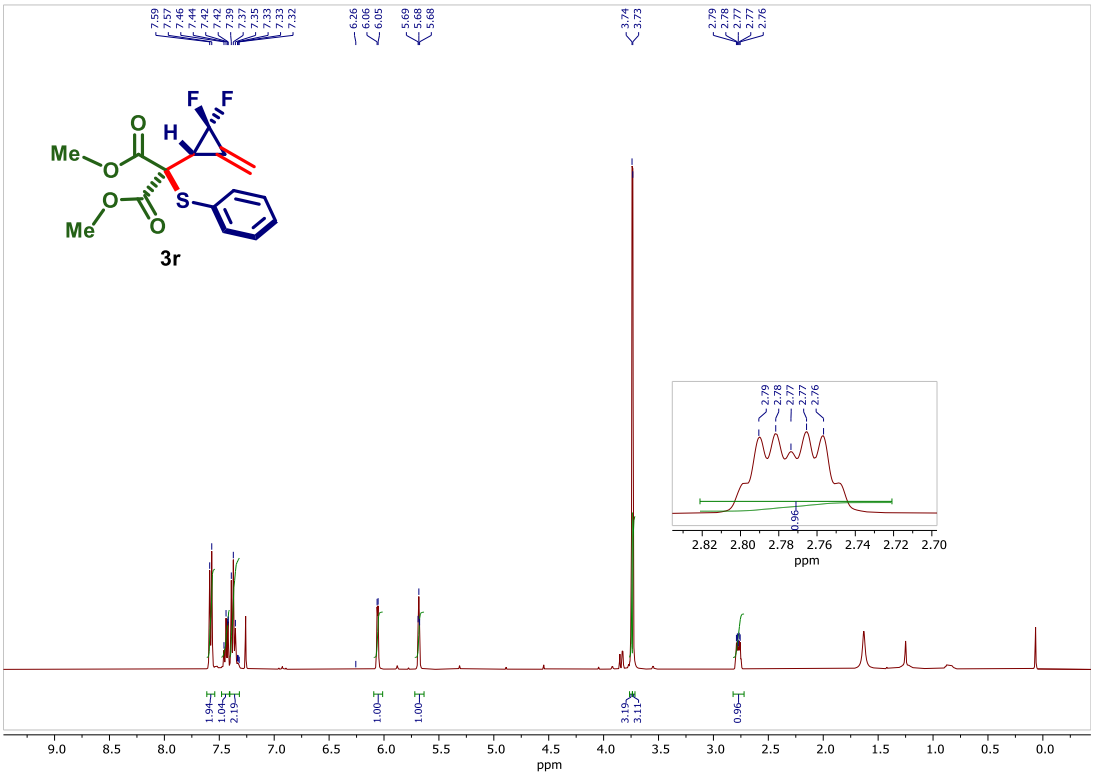
^{13}C NMR (101 MHz, $CDCl_3$) of Compound **3q:**



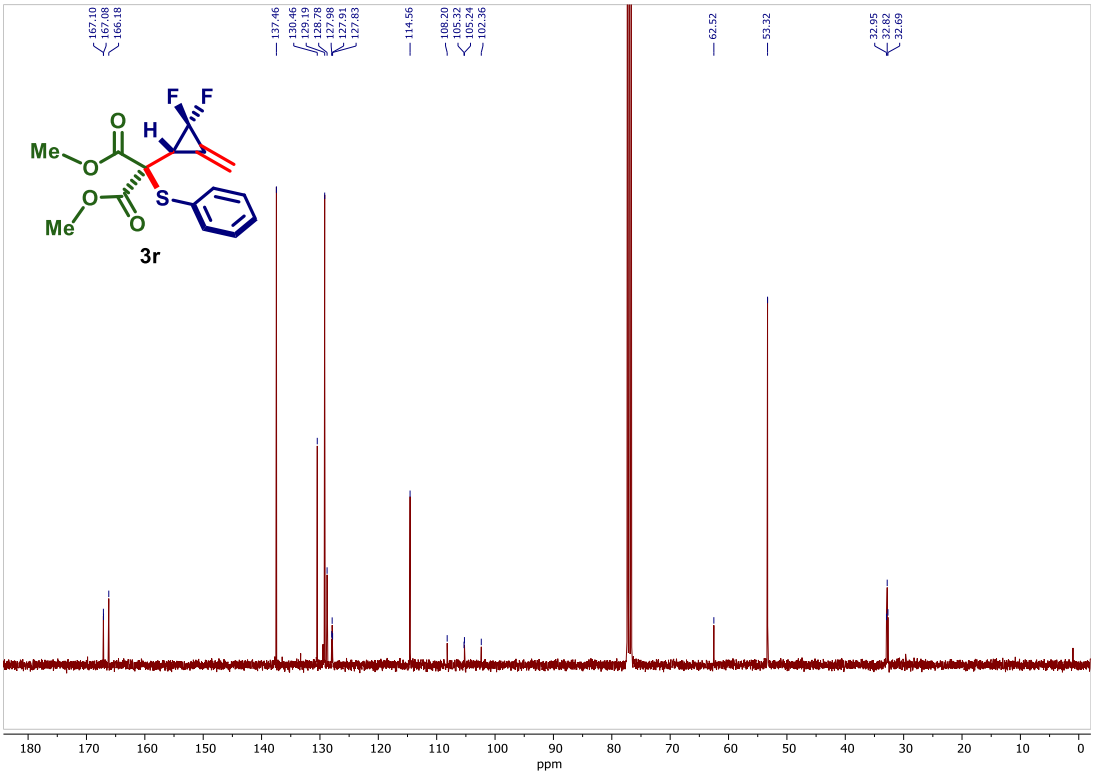
^{19}F NMR (376 MHz, $CDCl_3$) of compound **3q:**



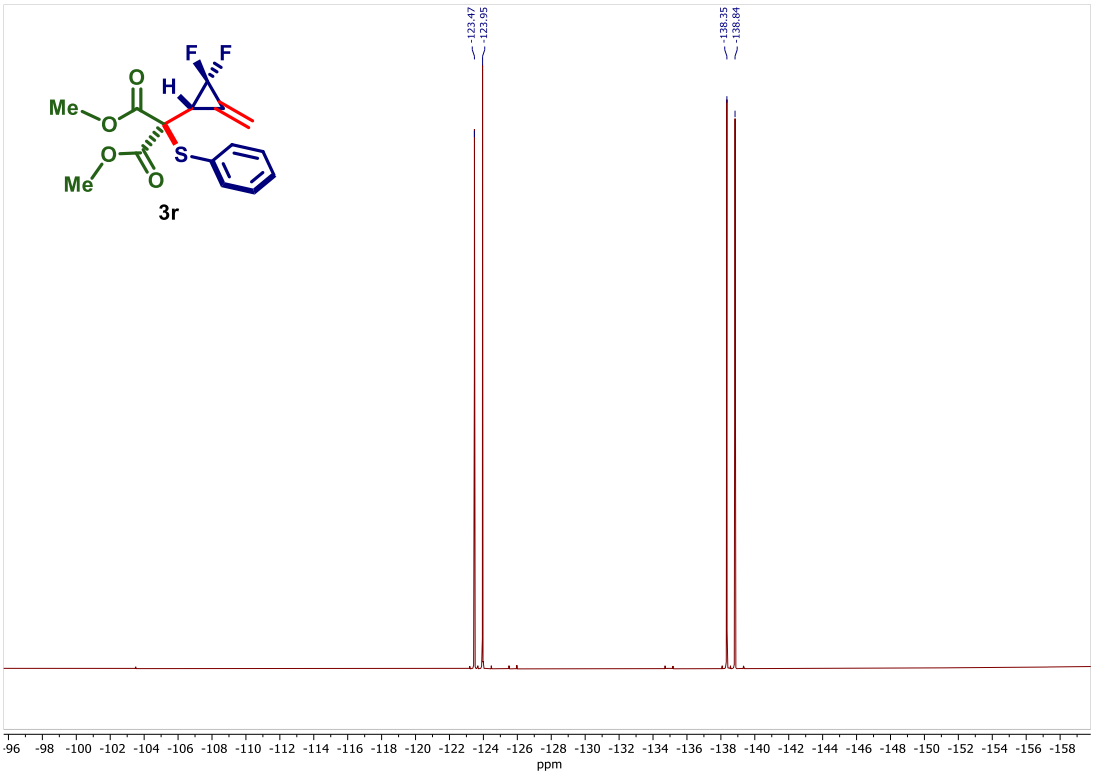
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3r: (*See Procedure*)**



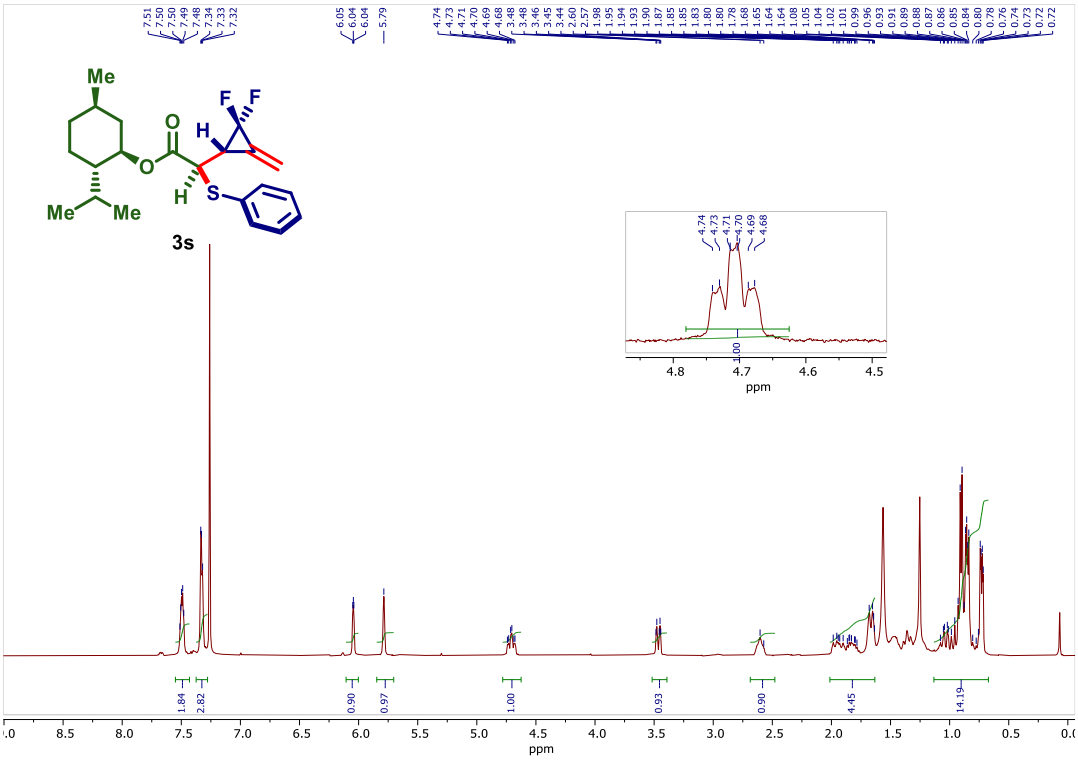
^{13}C NMR (101 MHz, $CDCl_3$) of Compound **3r:**



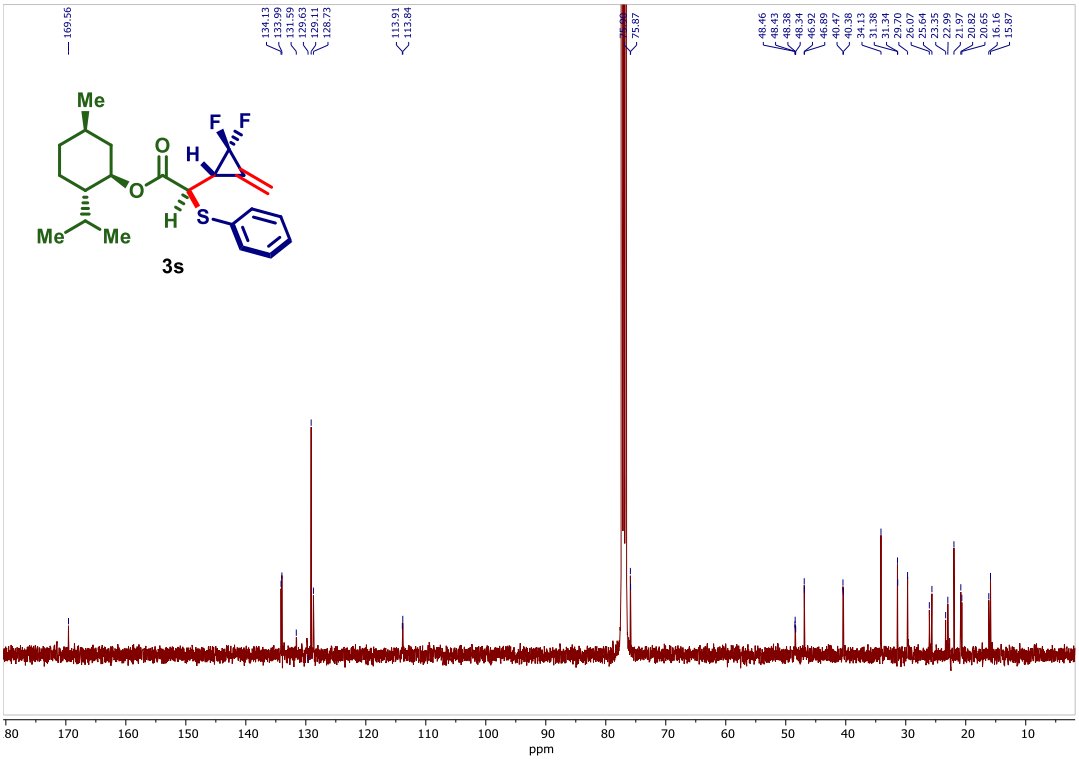
^{19}F NMR (376 MHz, $CDCl_3$) of compound **3r:**



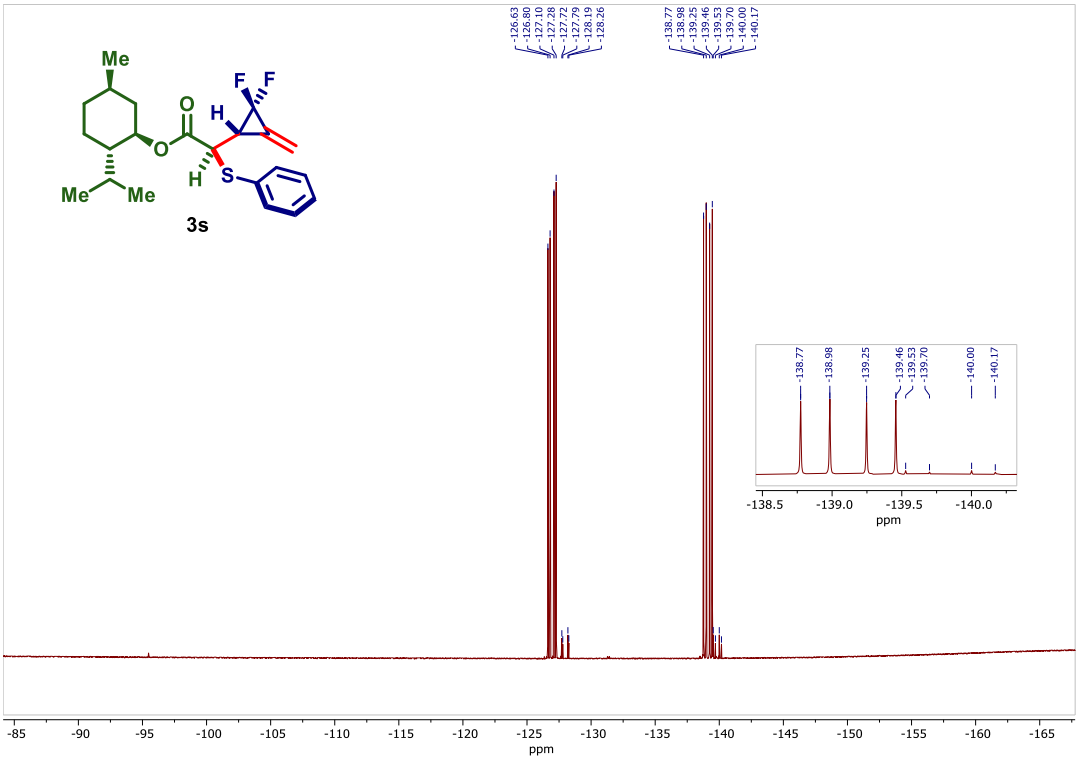
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3s: (***See Procedure***)**



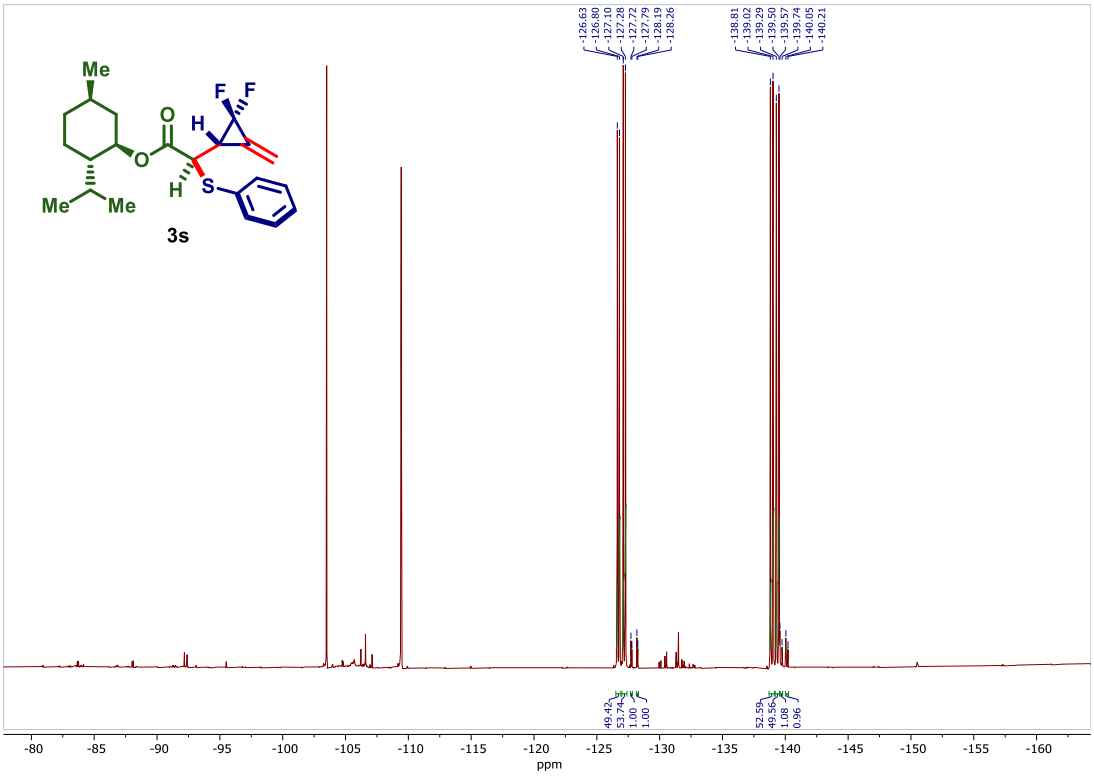
^{13}C NMR (101 MHz, $CDCl_3$) of Compound **3s:**



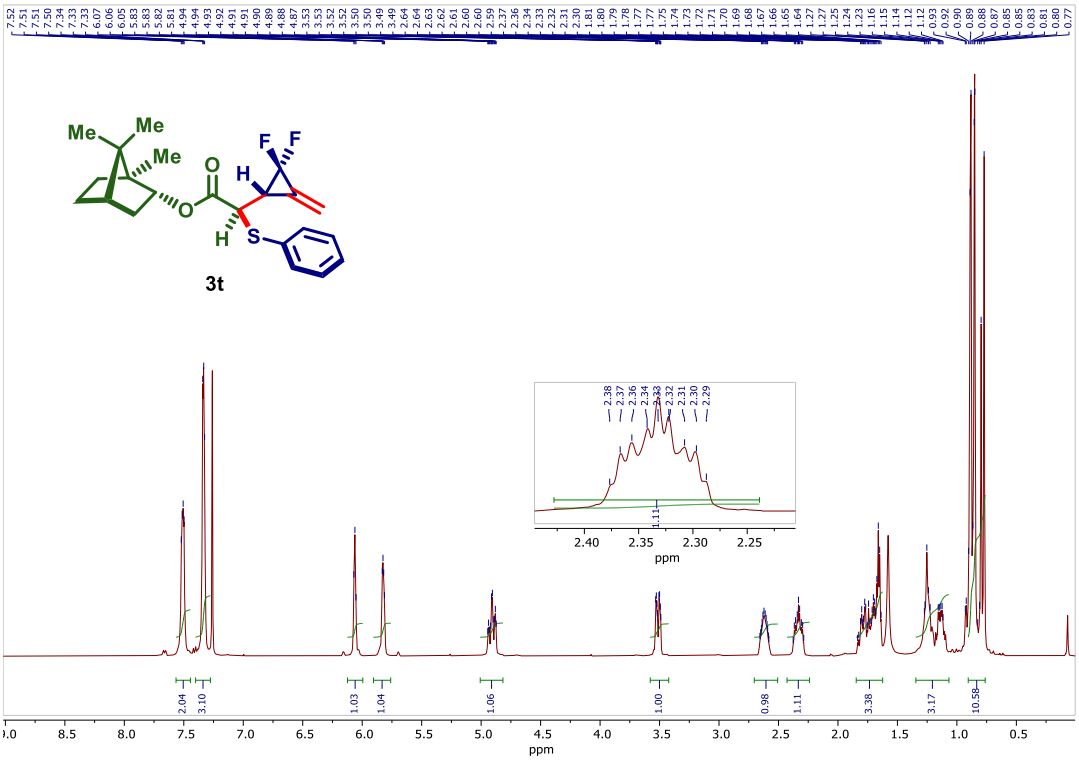
^{19}F NMR (376 MHz, $CDCl_3$) of compound **3s:**



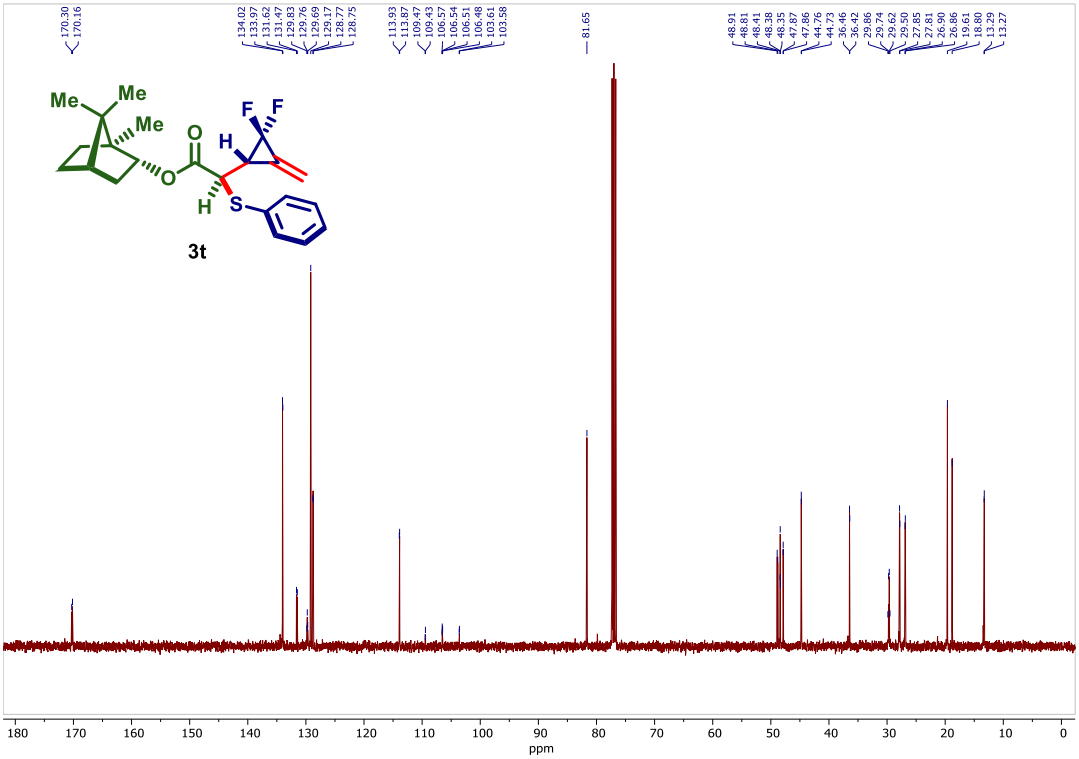
^{19}F NMR (376 MHz, $CDCl_3$) of Crude Reaction Mixture (compound **3s**)**:**



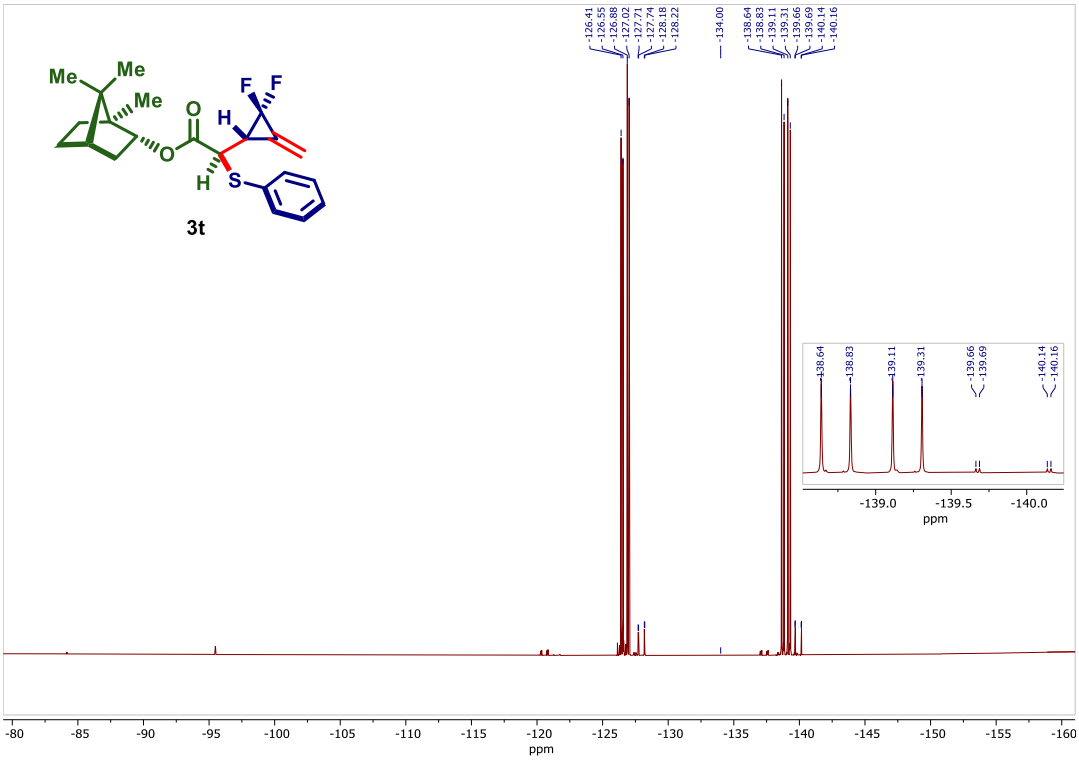
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3t: (*See Procedure*)**



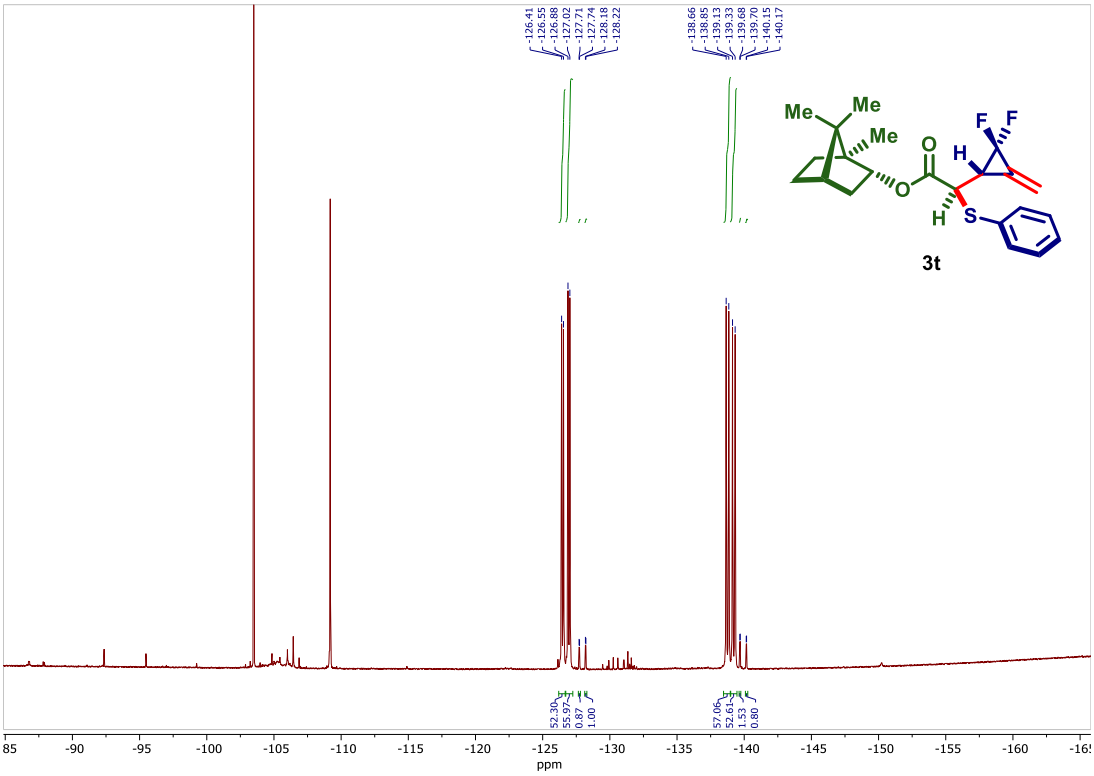
^{13}C NMR (101 MHz, $CDCl_3$) of Compound **3t:**



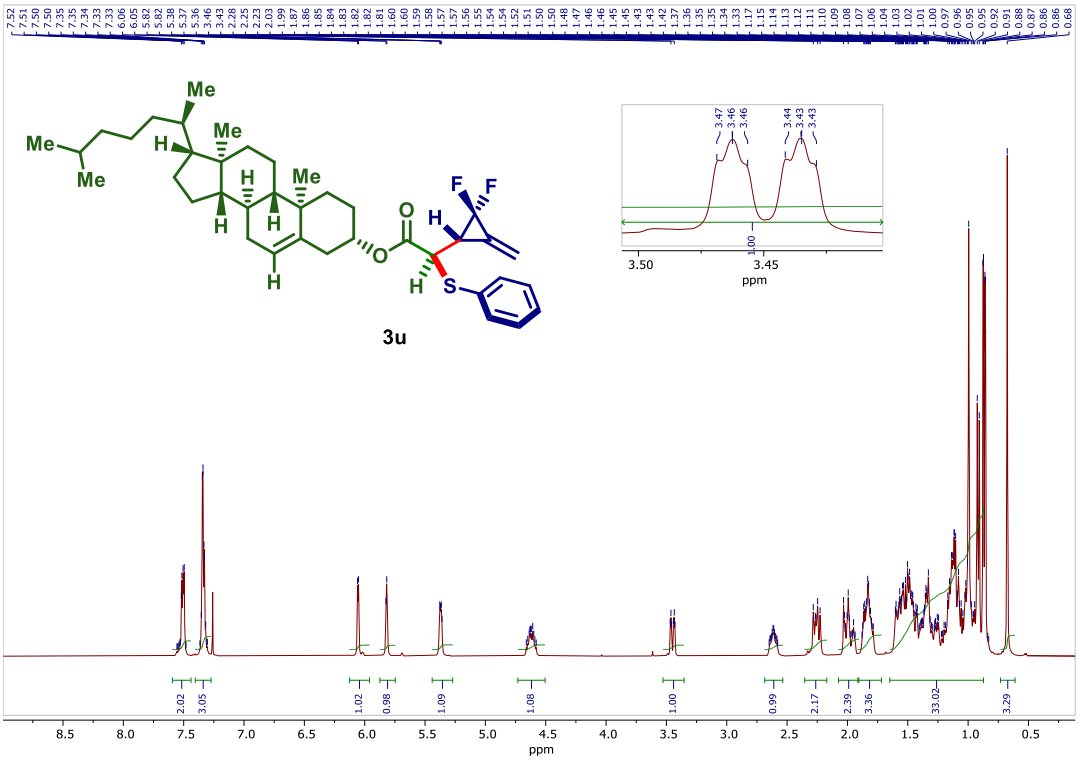
^{19}F NMR (376 MHz, $CDCl_3$) of compound **3t:**



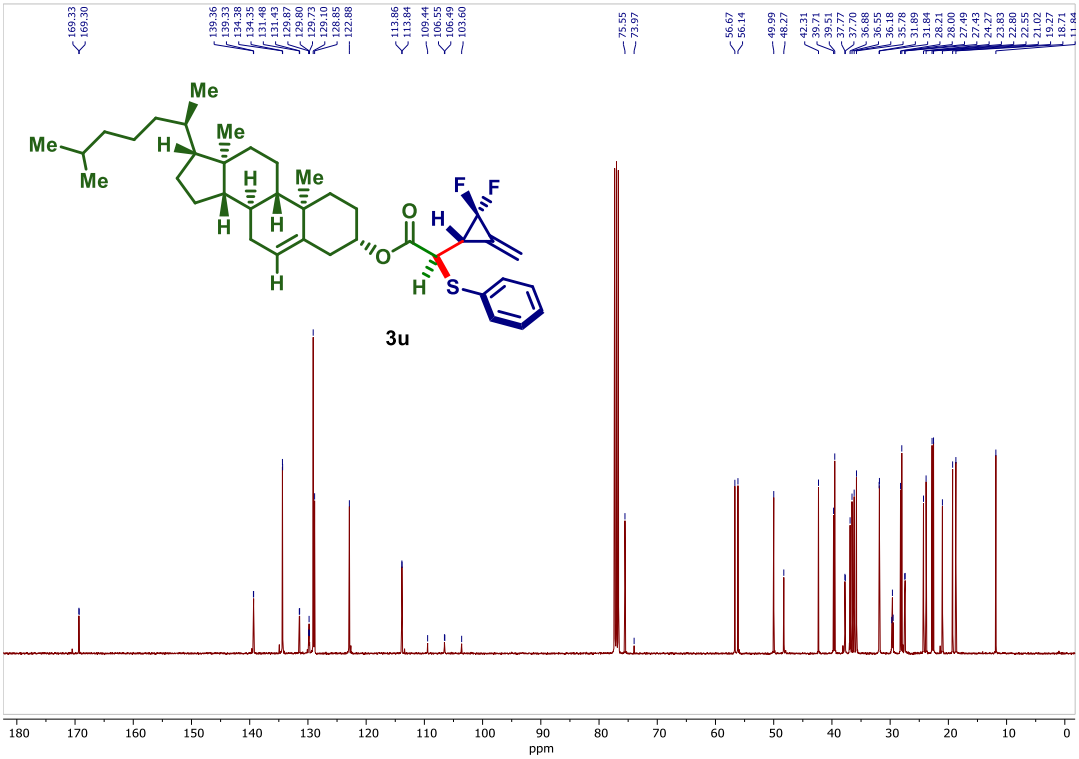
^{19}F NMR (376 MHz, $CDCl_3$) of Crude Reaction Mixture (compound **3t**)**:**



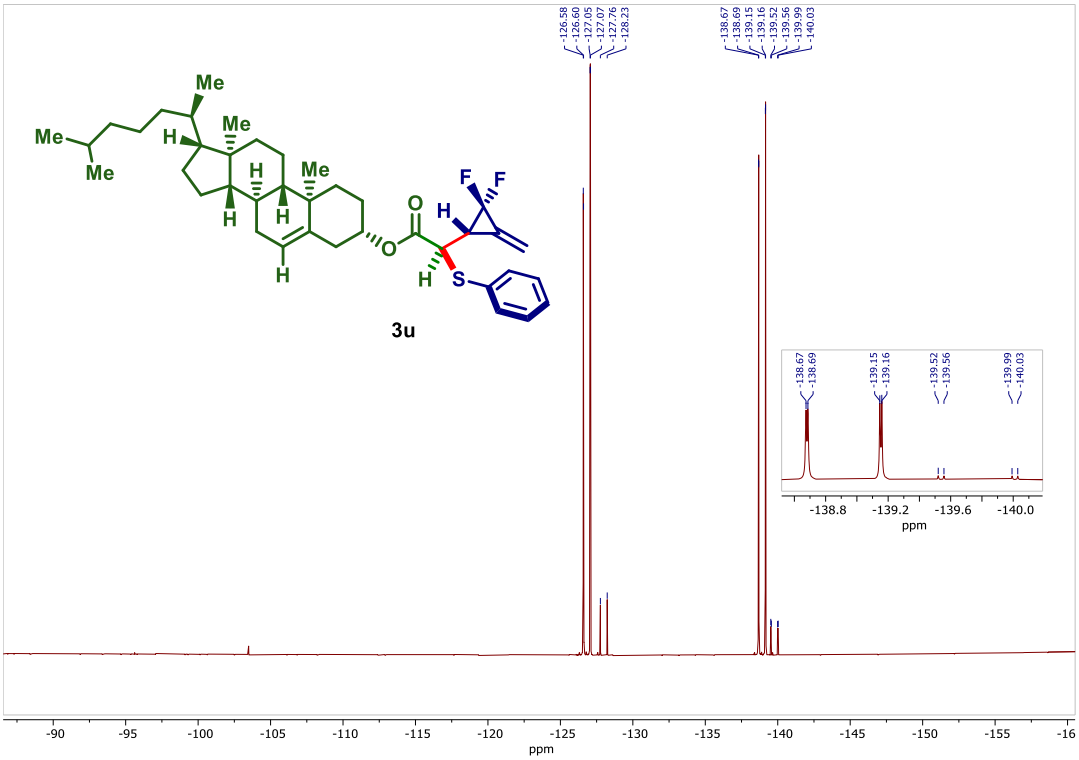
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3u: (*See Procedure*)**



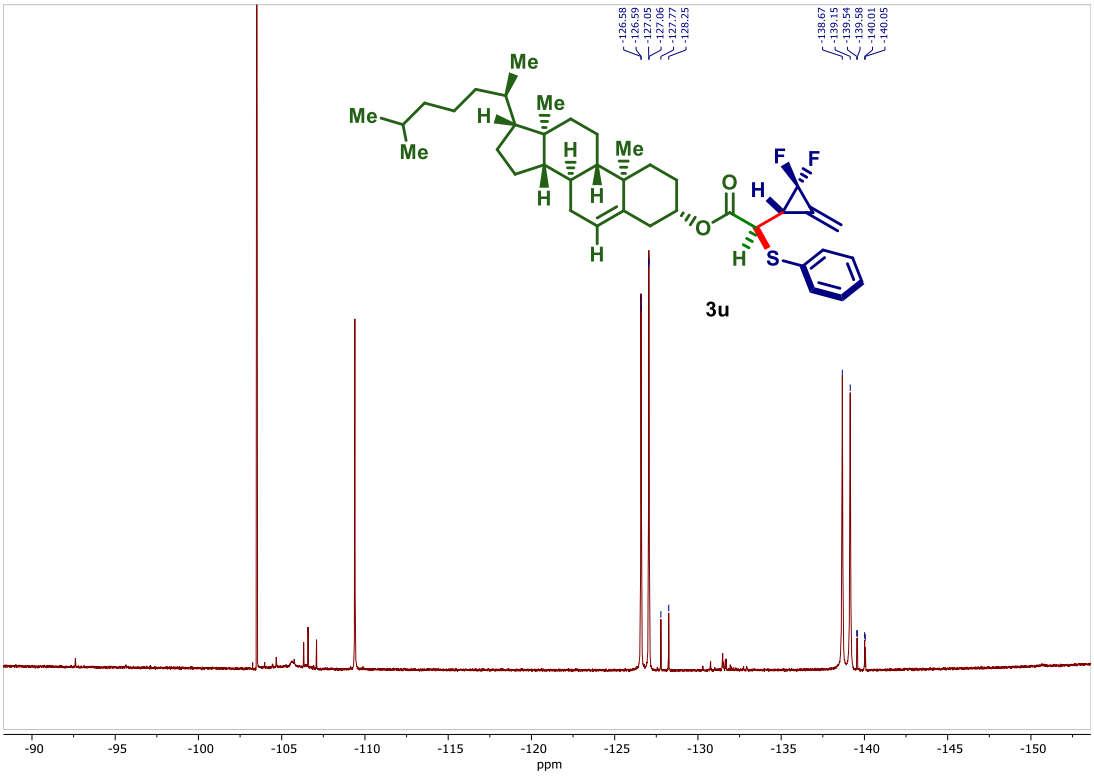
^{13}C NMR (101 MHz, $CDCl_3$) of Compound **3u:**



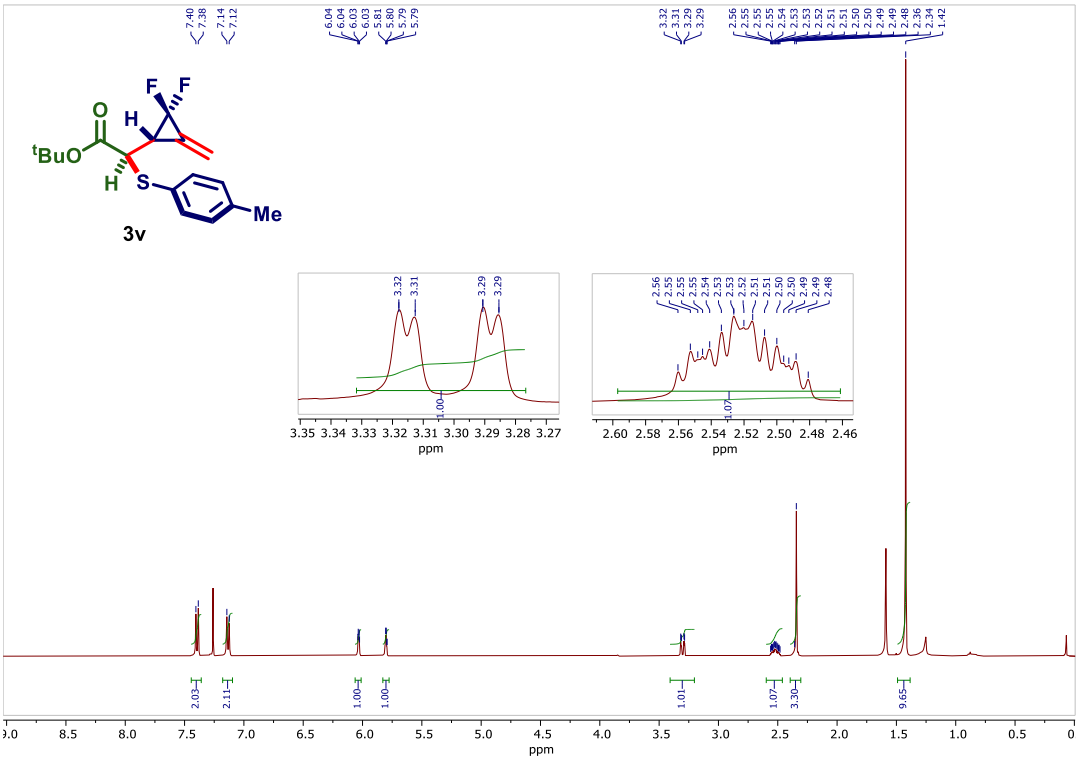
^{19}F NMR (376 MHz, $CDCl_3$) of compound **3u:**



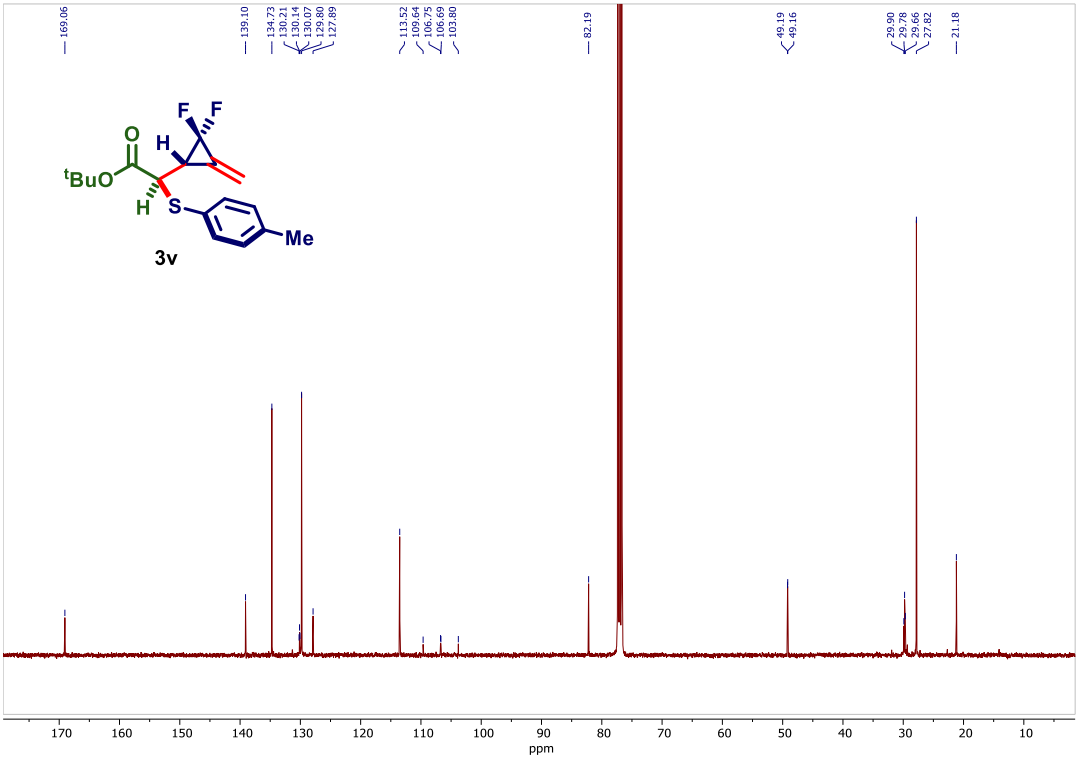
^{19}F NMR (376 MHz, $CDCl_3$) of crude reaction mixture (compound **3u**)**:**



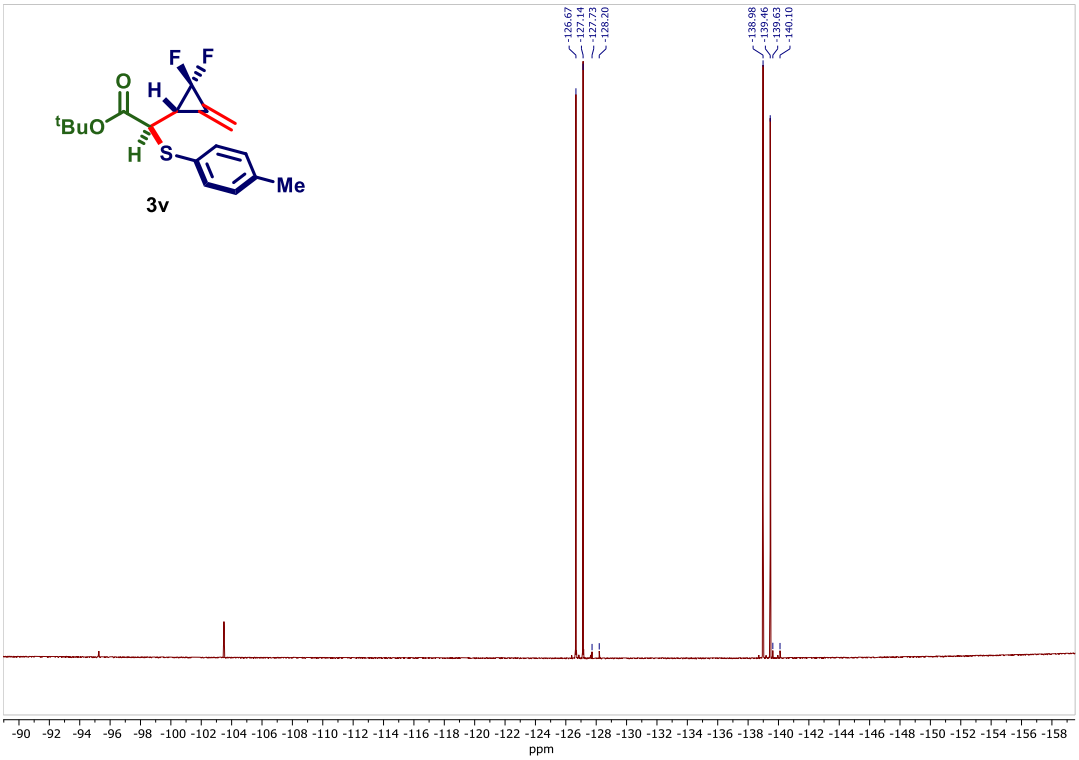
H NMR (400 MHz, $CDCl_3$) of compound **3v: (***See Procedure***)**



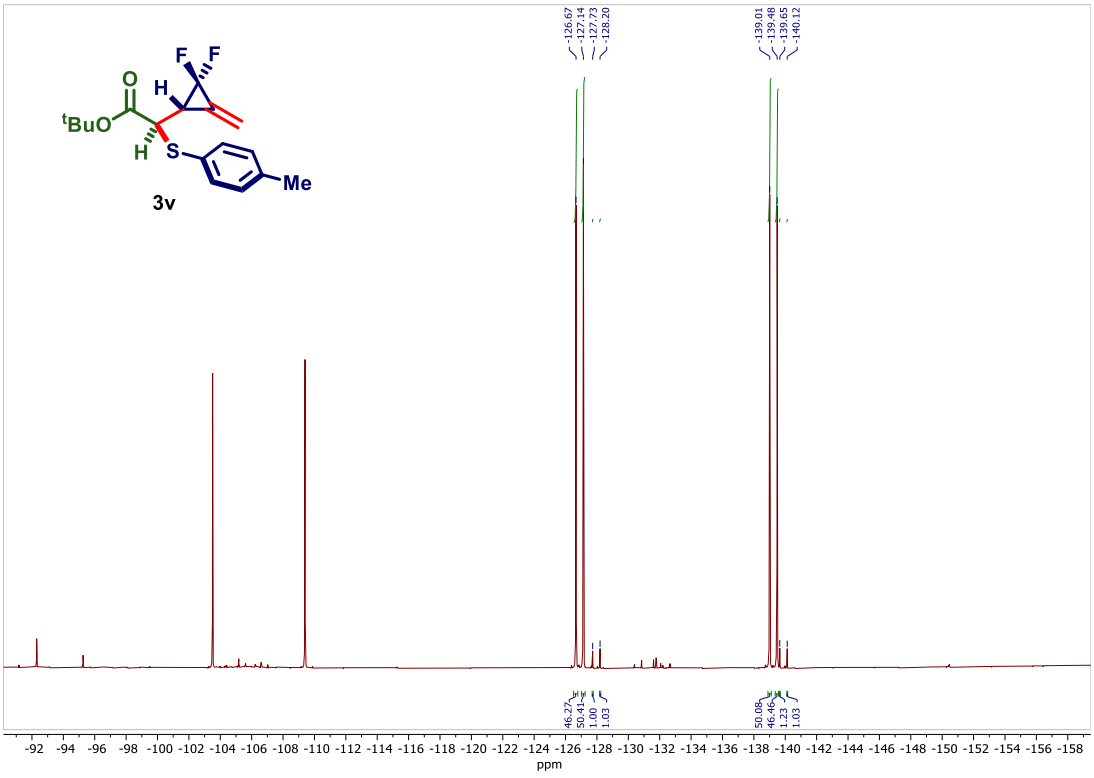
^{13}C NMR (101 MHz, $CDCl_3$) of Compound **3v:**



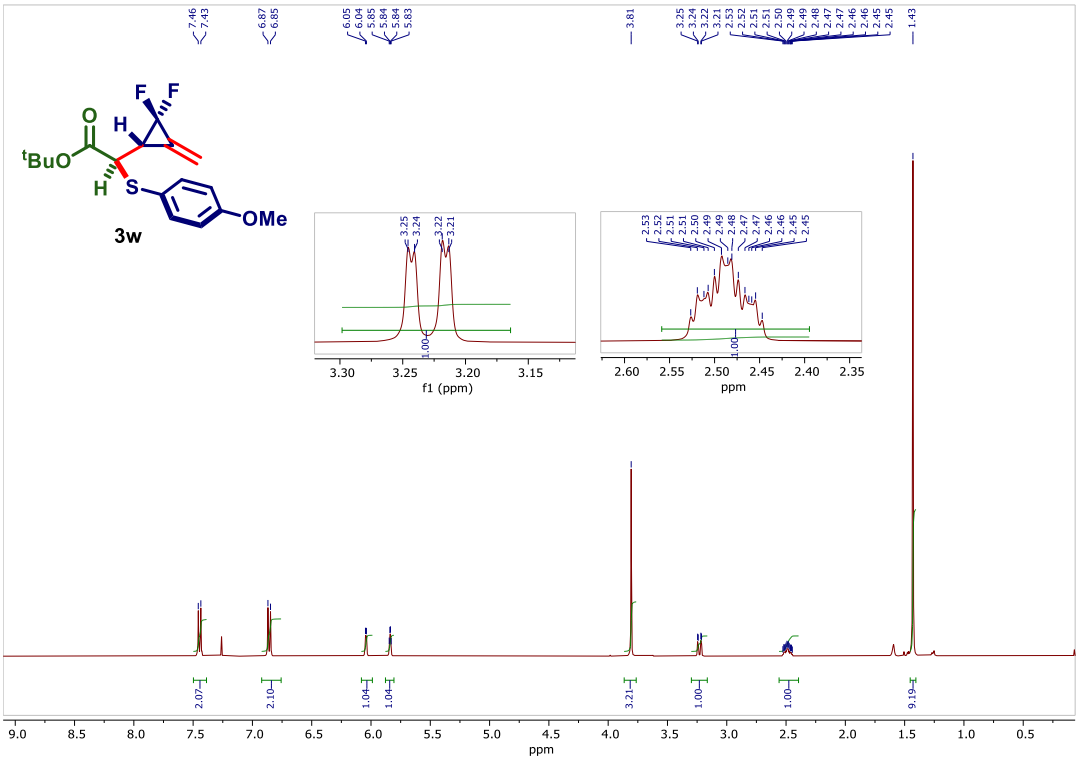
^{19}F NMR (376 MHz, $CDCl_3$) of compound **3v:**



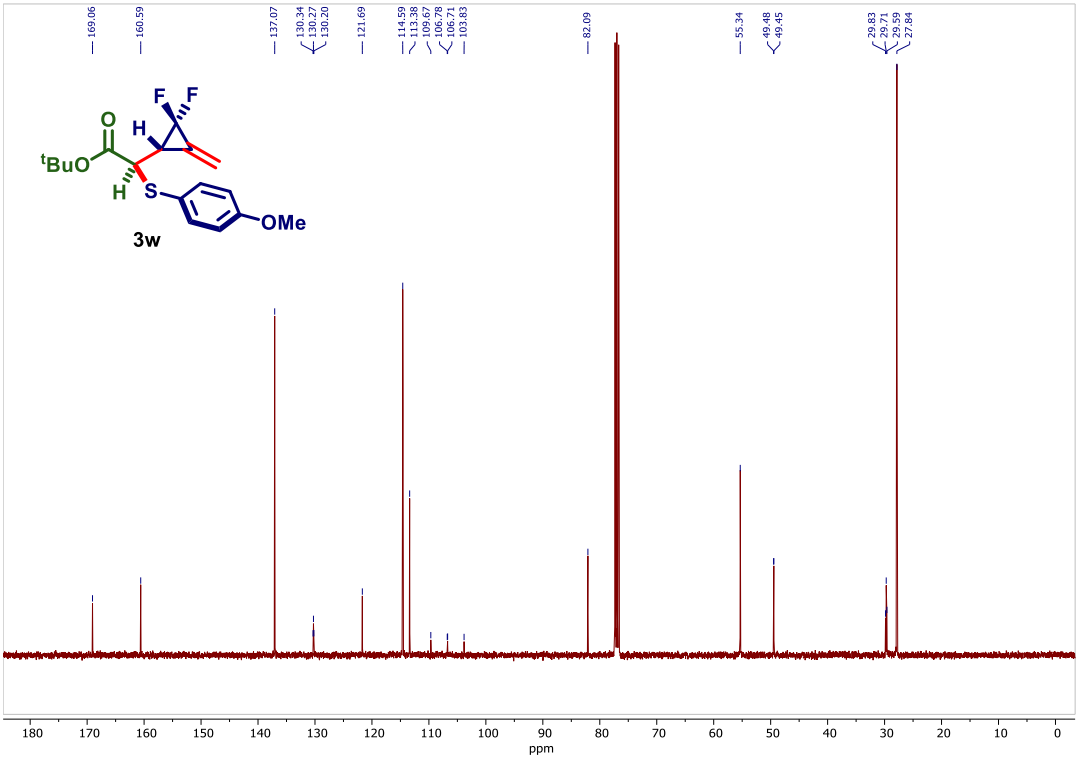
^{19}F NMR (376 MHz, $CDCl_3$) of crude reaction mixture (compound **3v**)**:**



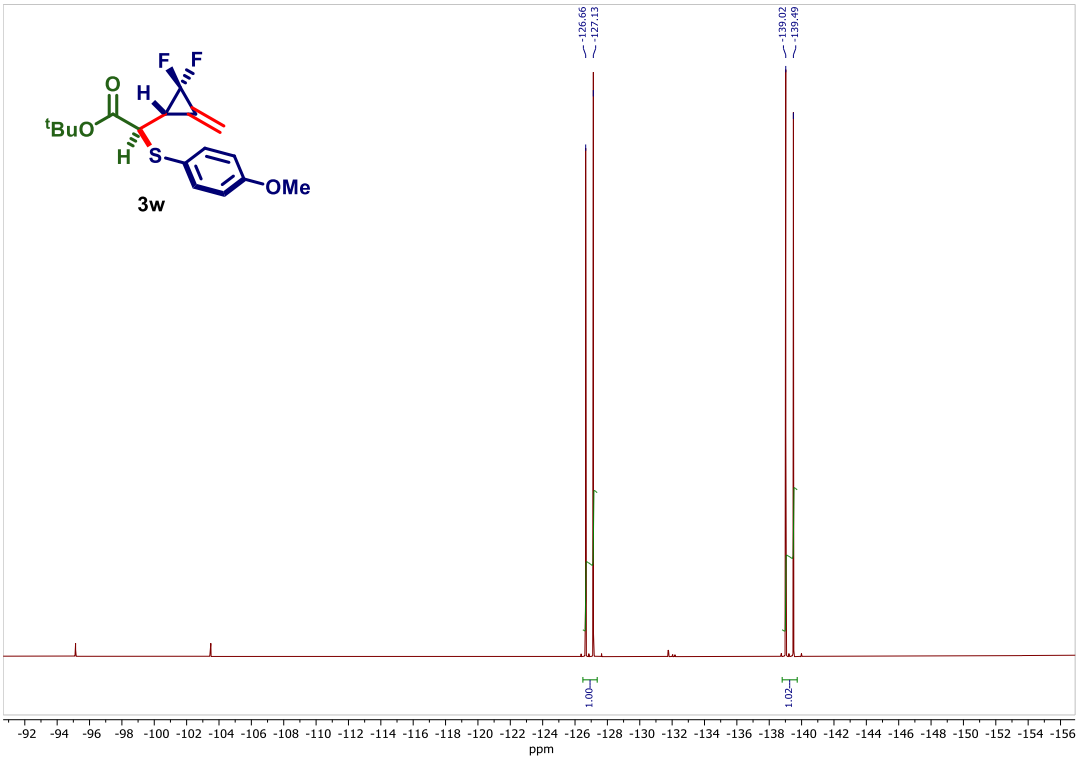
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3w: (*See Procedure*)**



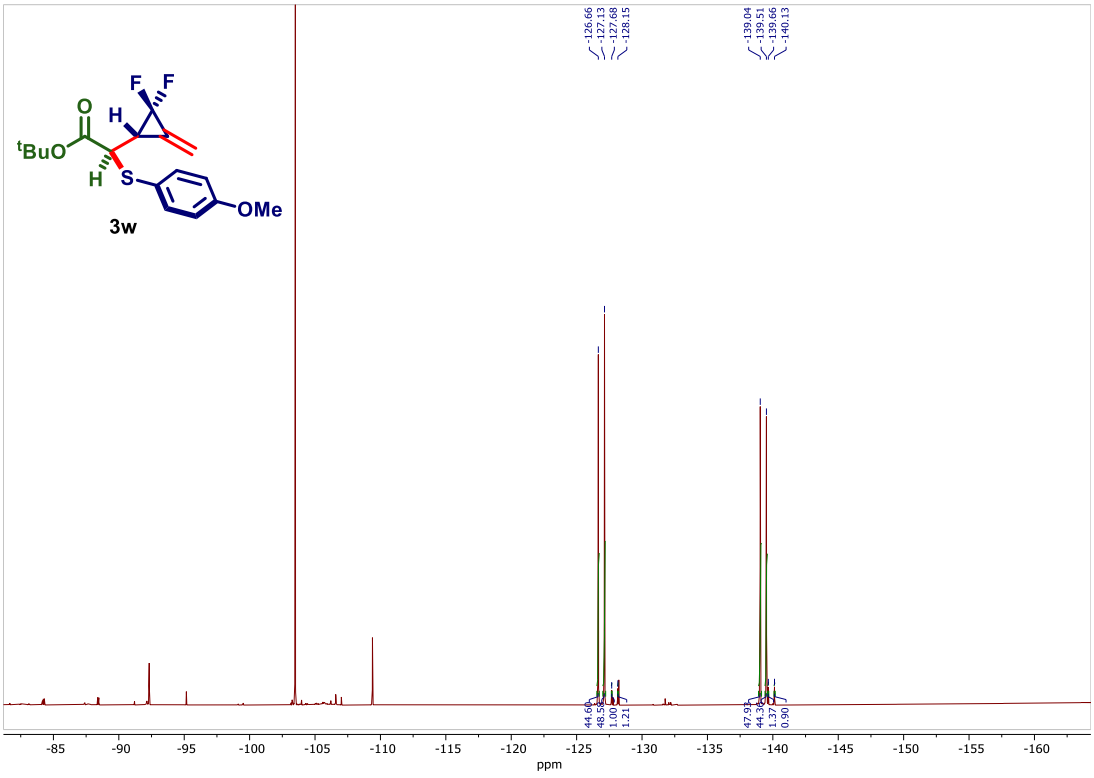
^{13}C NMR (101 MHz, $CDCl_3$) of Compound **3w:**



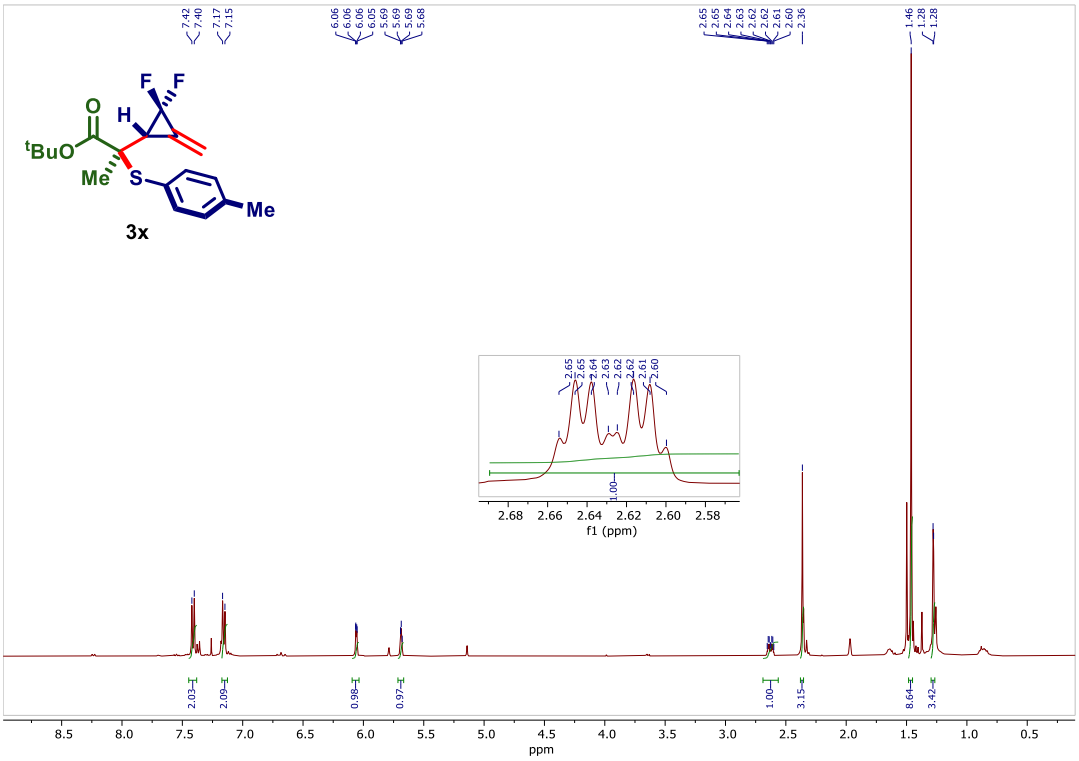
^{19}F NMR (376 MHz, $CDCl_3$) of compound **3w:**



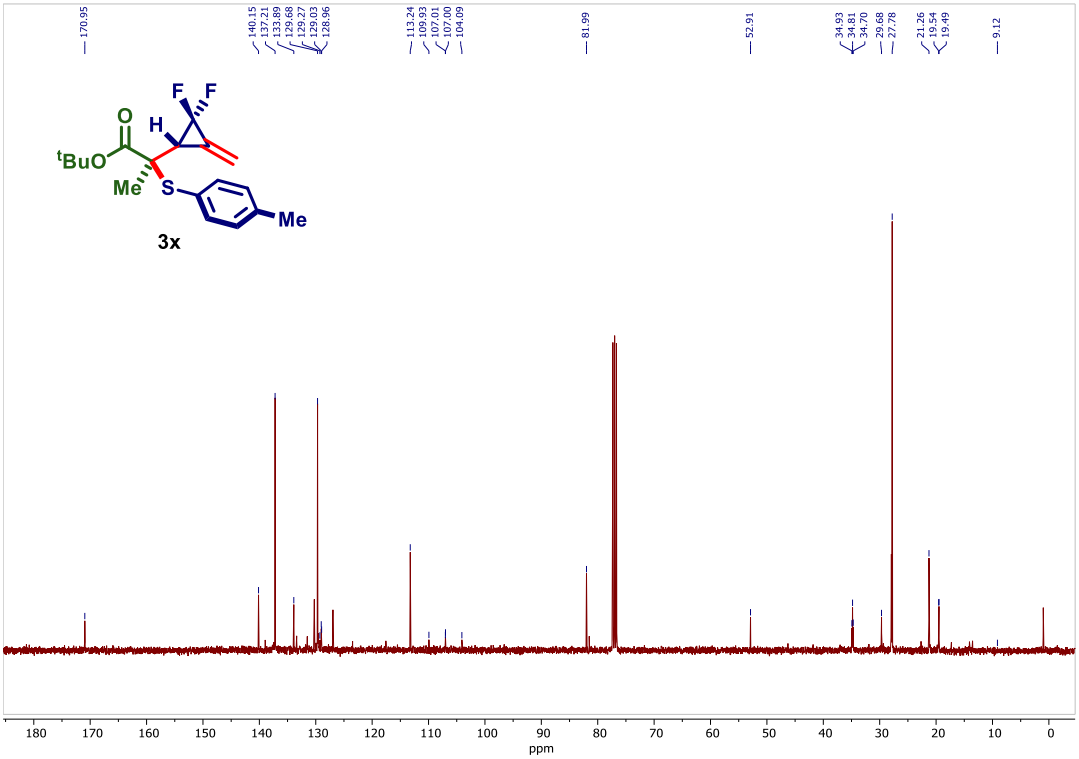
^{19}F NMR (376 MHz, $CDCl_3$) of Crude Reaction Mixture (compound **3w**)**:**



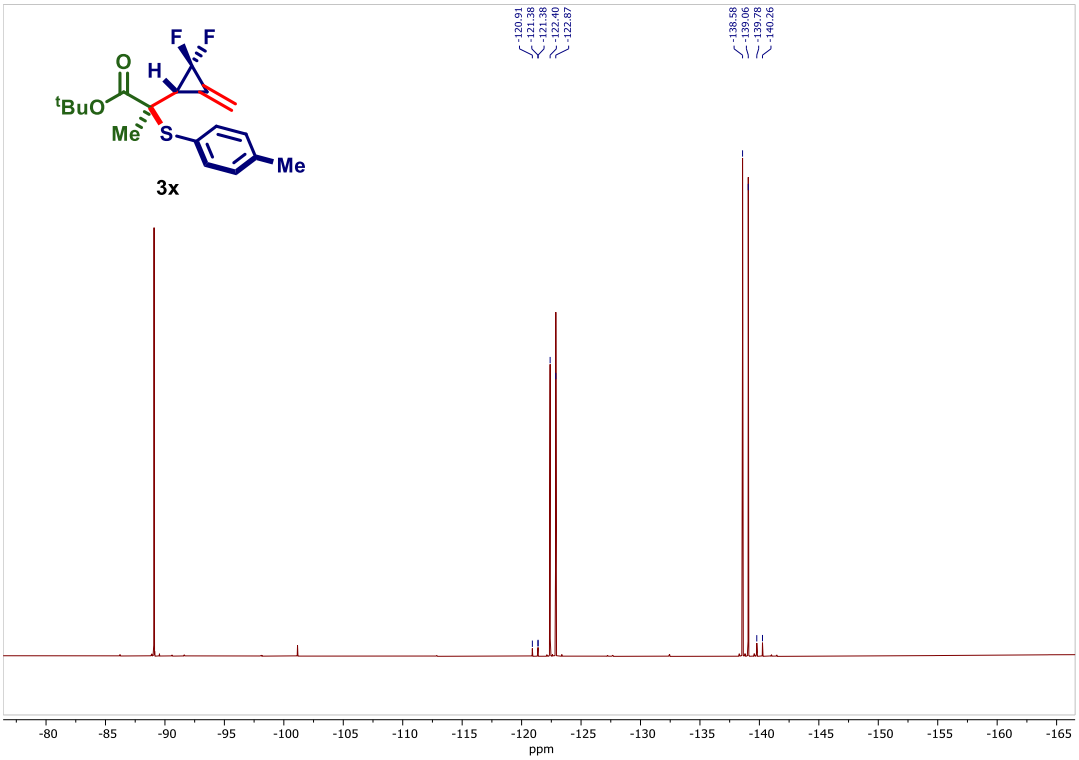
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3x: (*See Procedure*)**



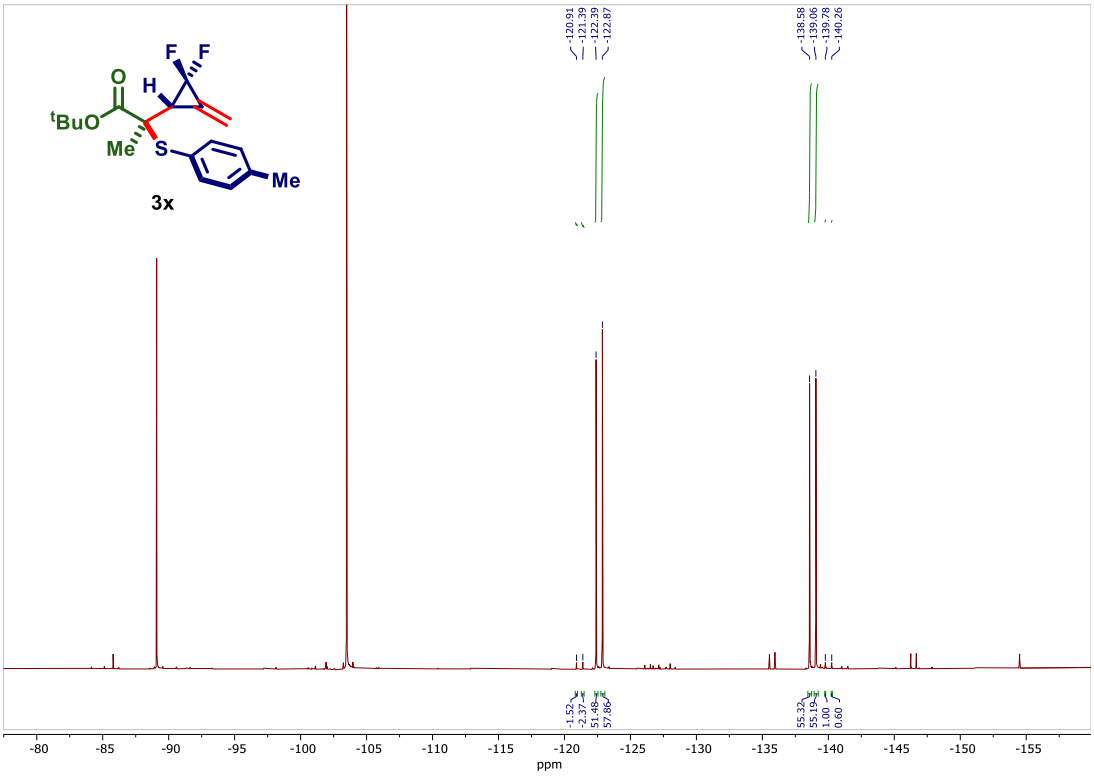
^{13}C NMR (101 MHz, $CDCl_3$) of Compound **3x:**



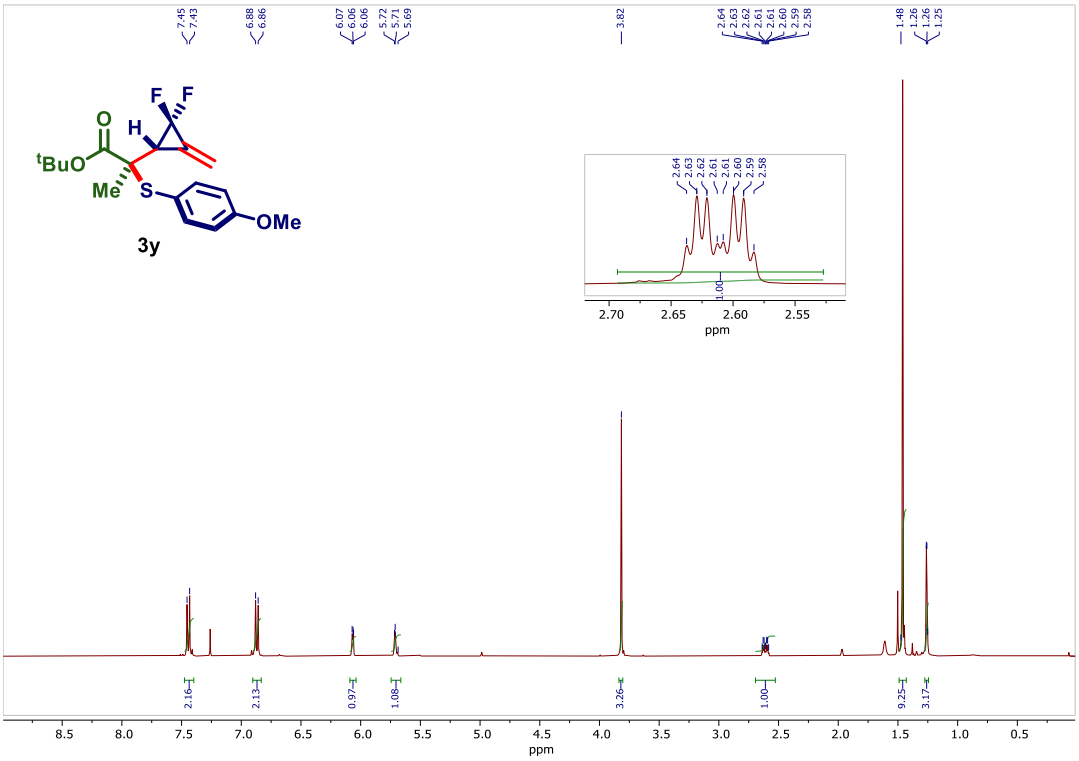
^{19}F NMR (376 MHz, $CDCl_3$) of compound **3x:**



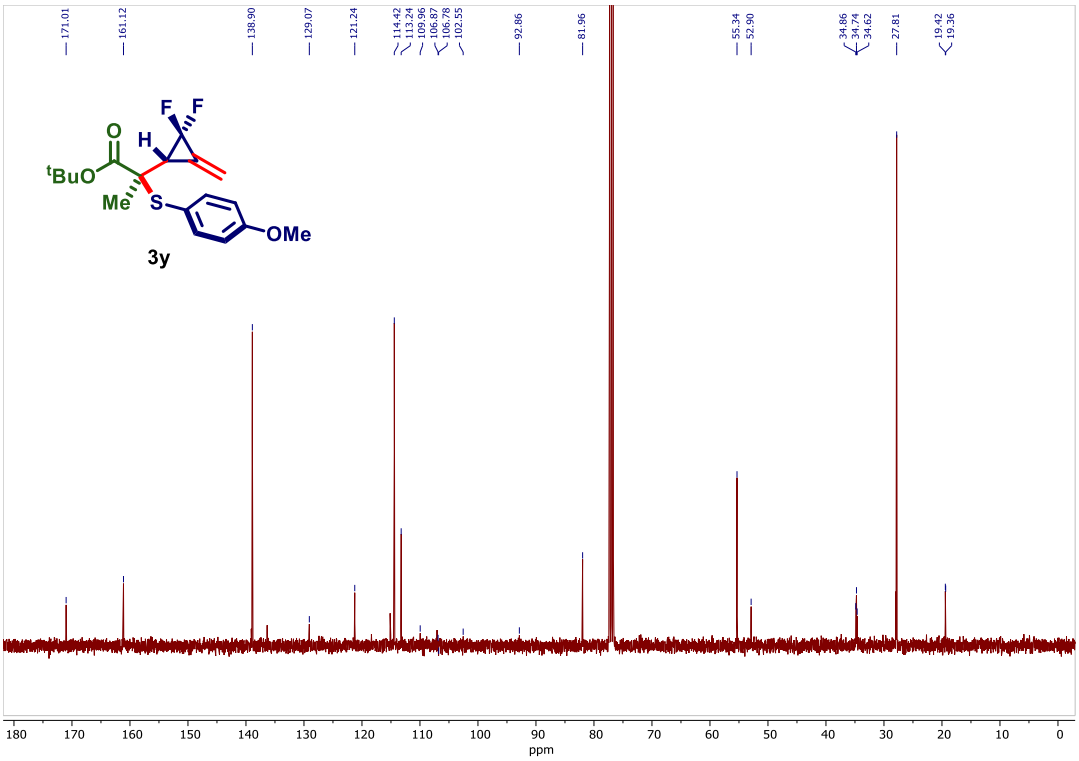
^{19}F NMR (376 MHz, $CDCl_3$) of Crude Reaction Mixture (compound **3x):**



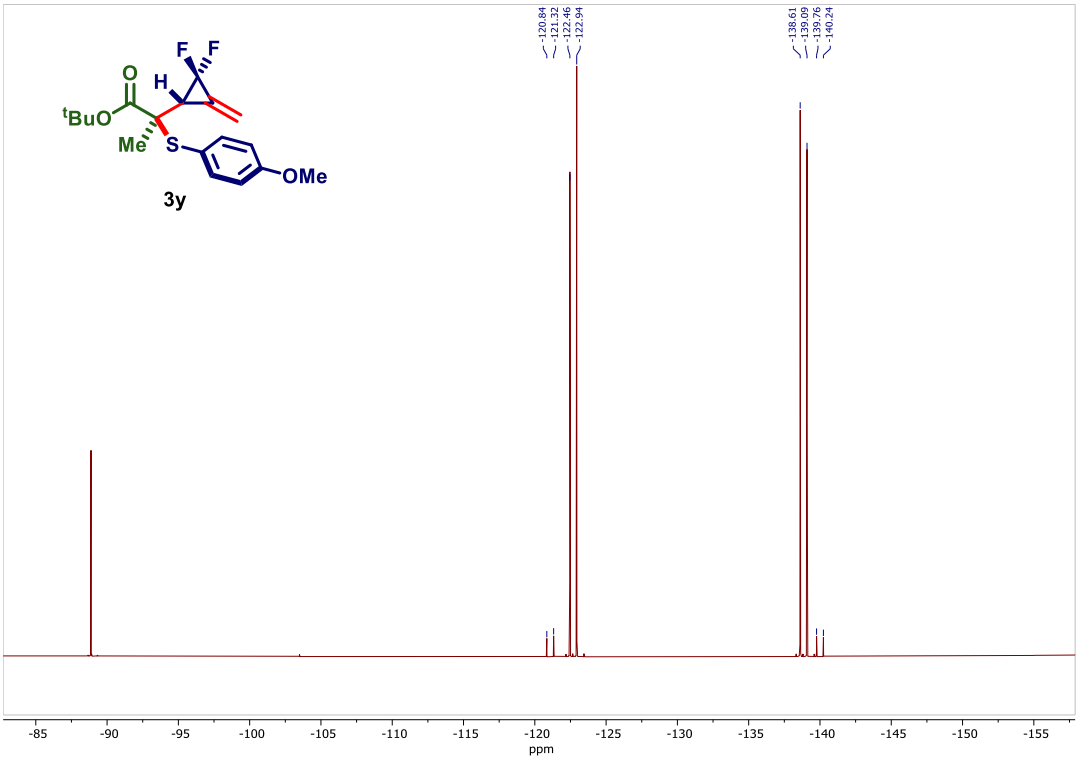
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3y: (*See Procedure*)**



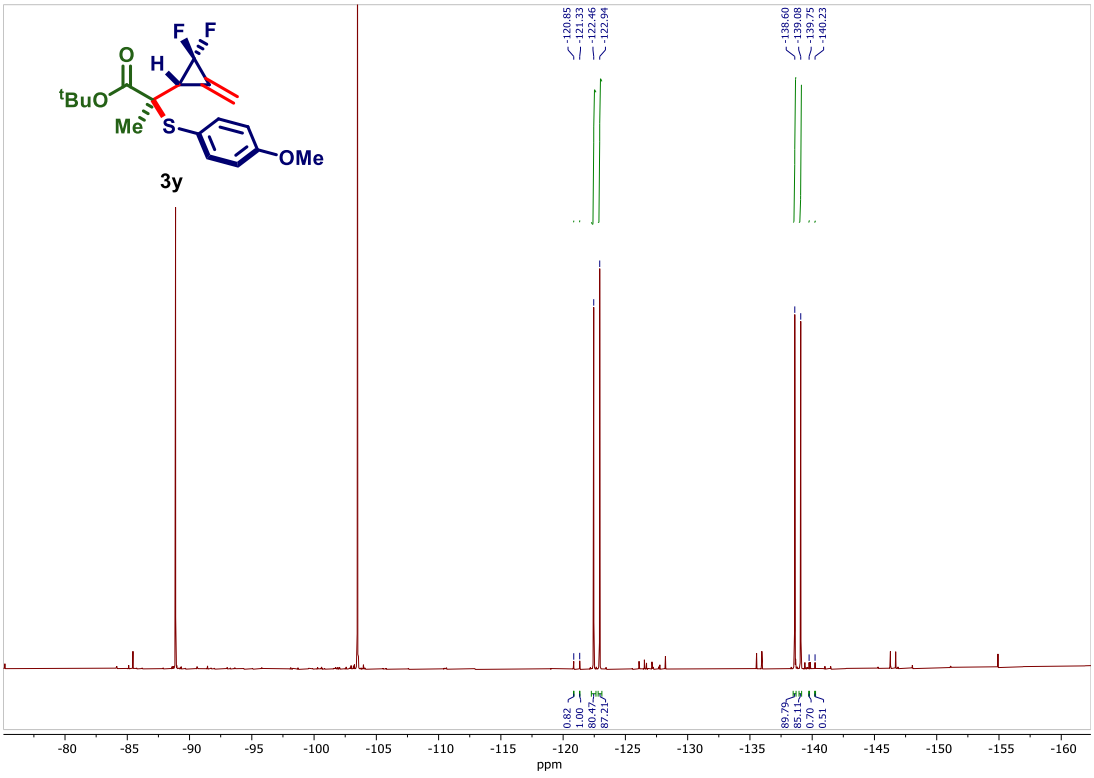
^{13}C NMR (101 MHz, $CDCl_3$) of Compound **3y:**



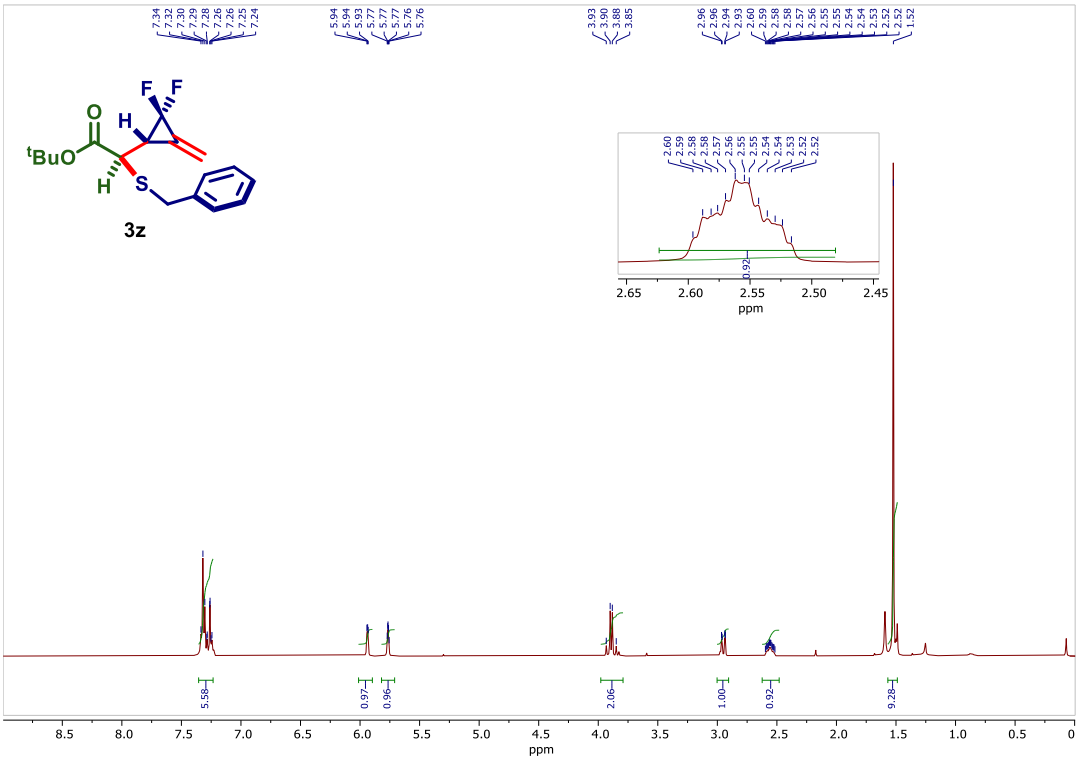
^{19}F NMR (376 MHz, $CDCl_3$) of compound **3y:**



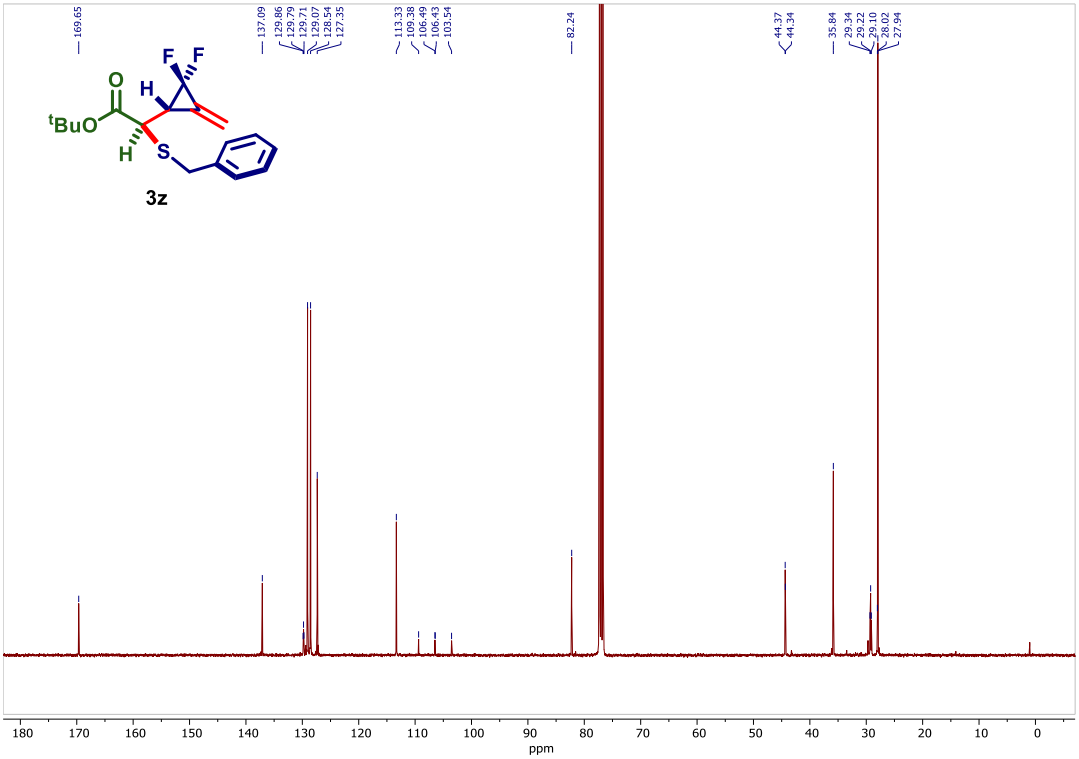
^{19}F NMR (376 MHz, $CDCl_3$) of Crude Reaction Mixture (compound **3y**)**:**



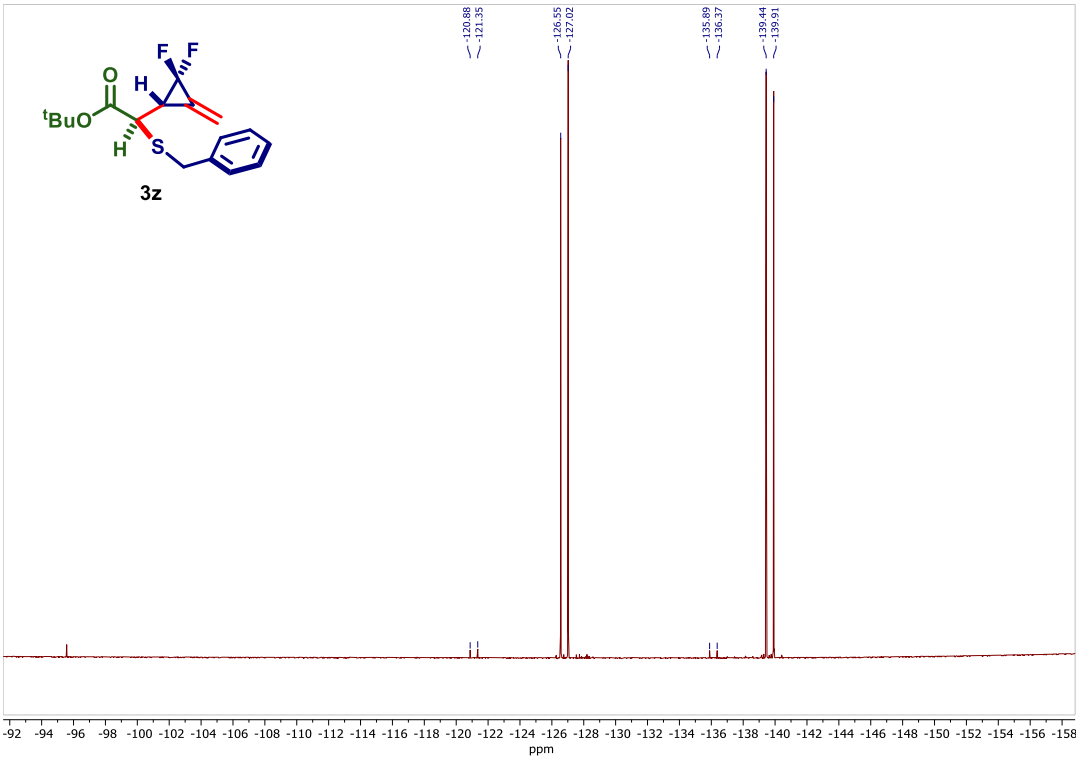
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3z: (*See Procedure*)**



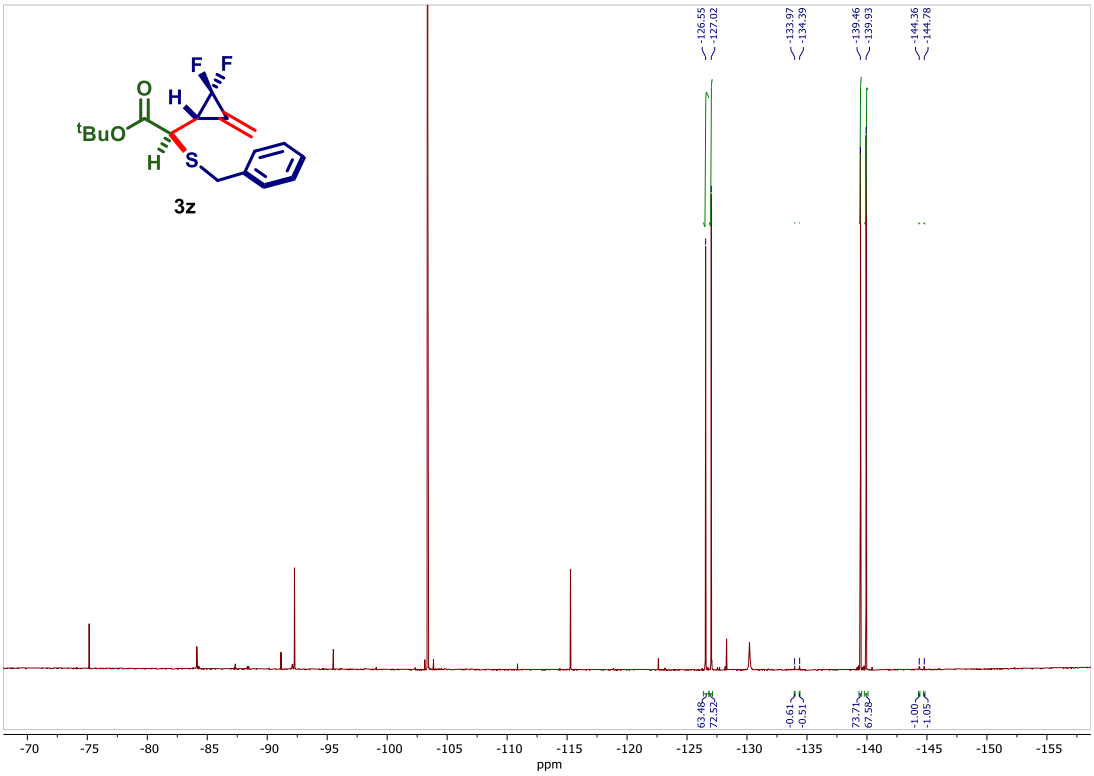
^{13}C NMR (101 MHz, $CDCl_3$) of Compound **3z:**



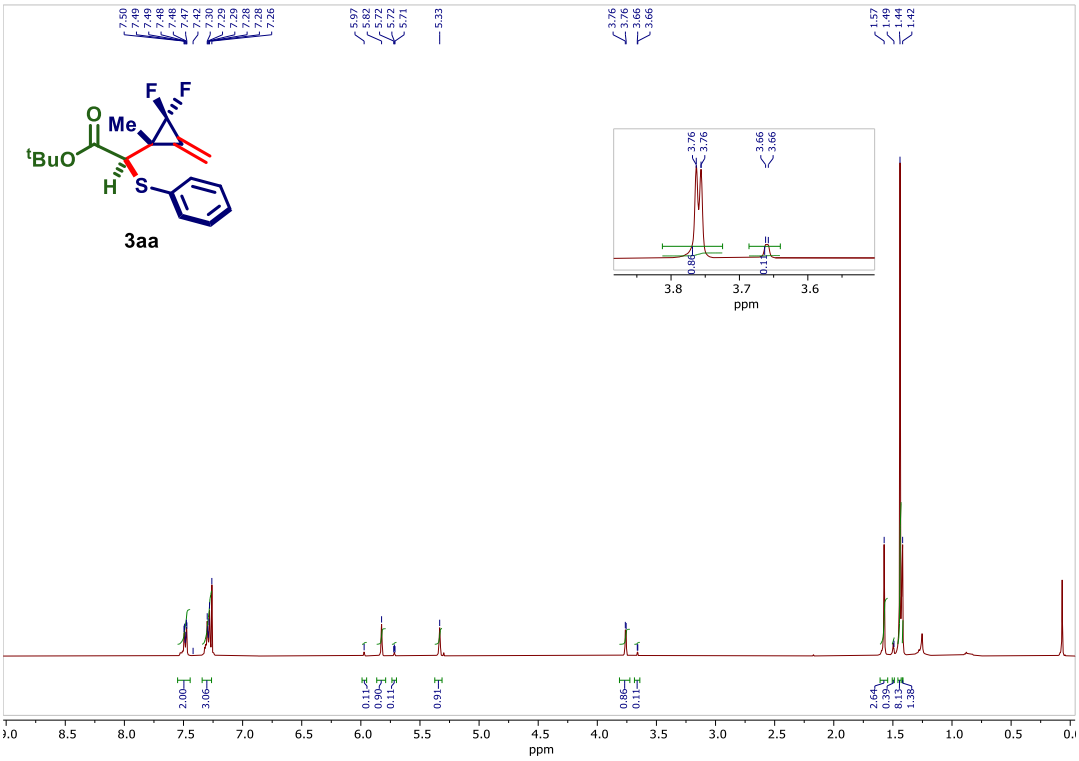
^{19}F NMR (376 MHz, $CDCl_3$) of compound **3z:**



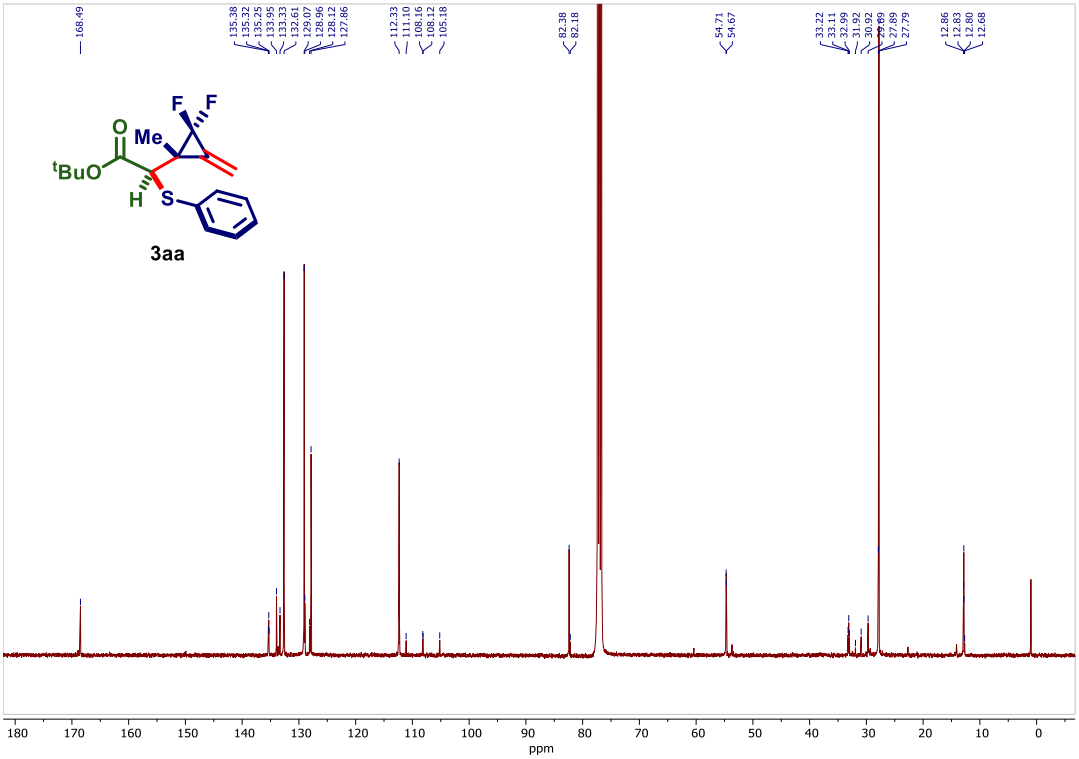
^{19}F NMR (376 MHz, $CDCl_3$) of crude reaction mixture (compound **3z**)**:**



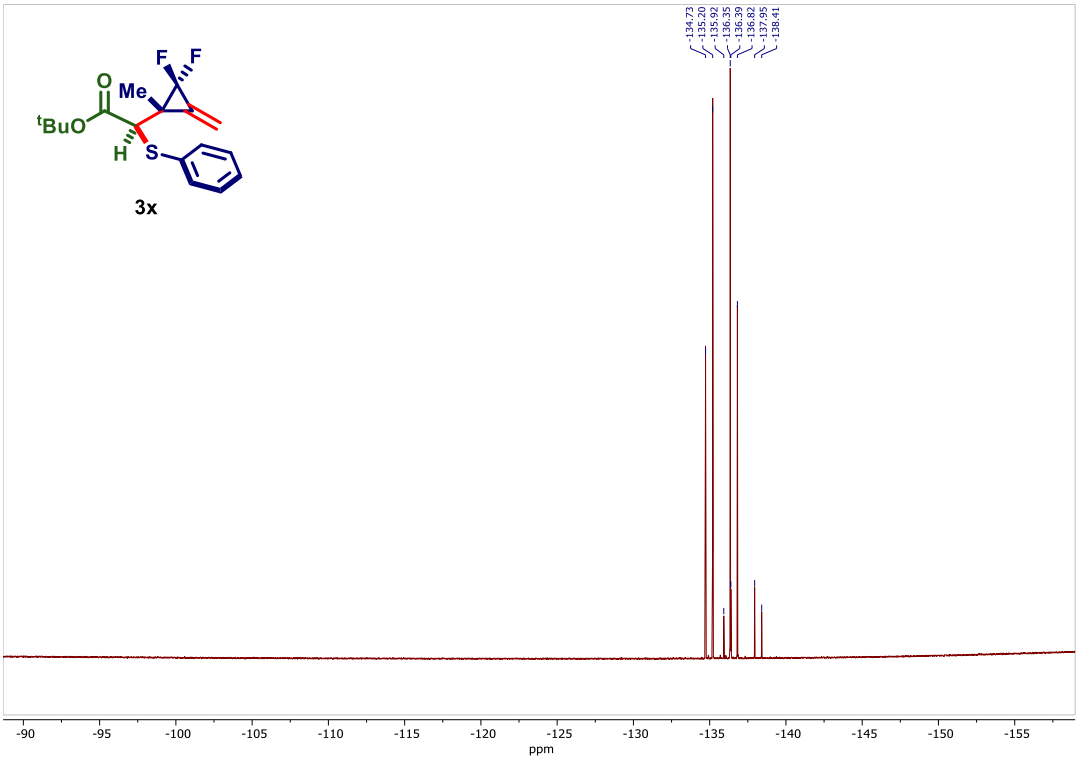
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3aa: (*See Procedure*)**



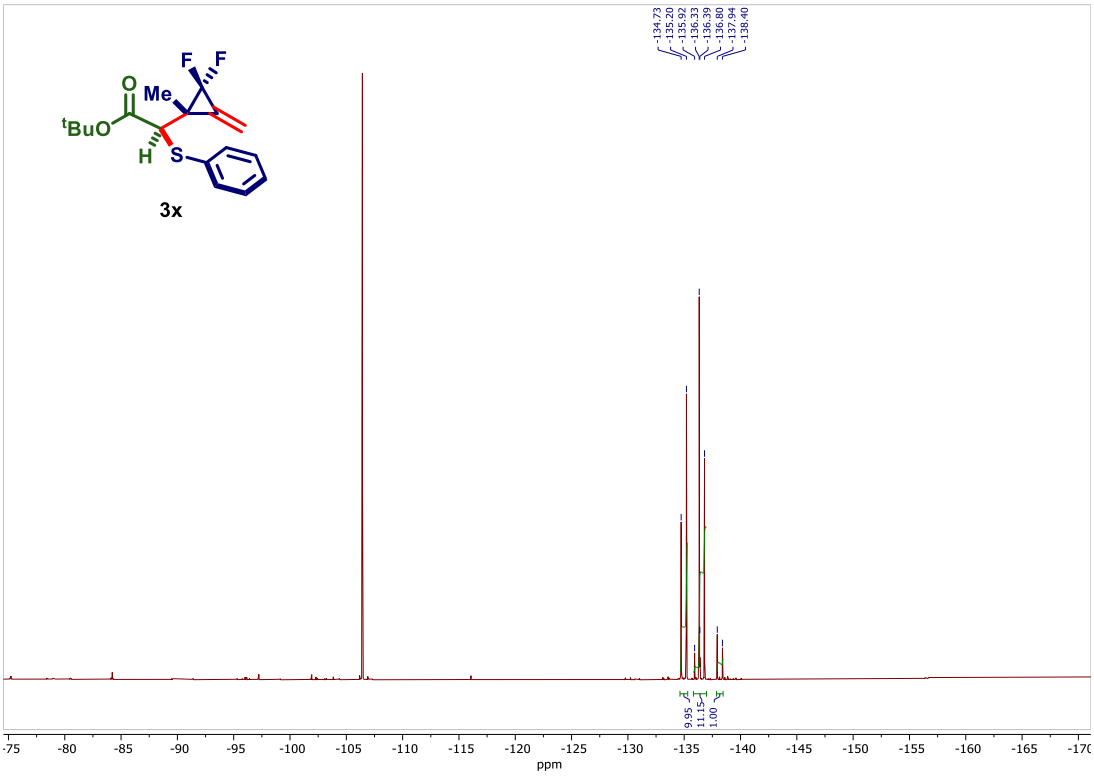
^{13}C NMR (101 MHz, $CDCl_3$) of Compound **3aa:**



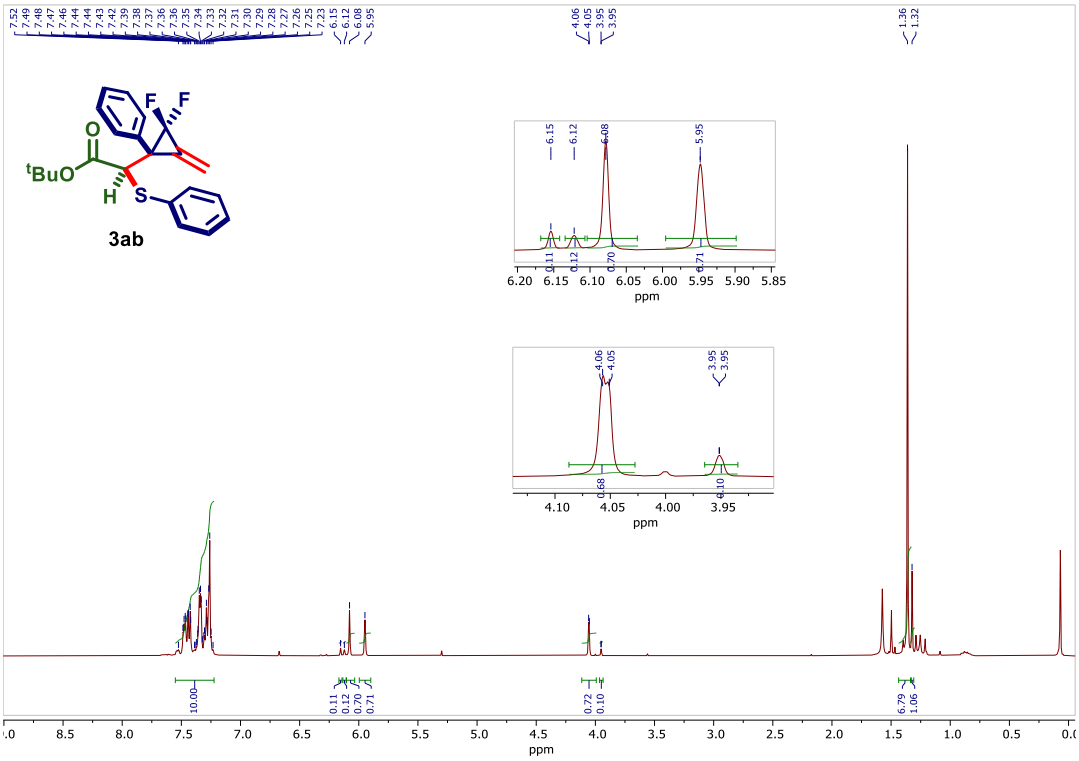
^{19}F NMR (376 MHz, $CDCl_3$) of compound **3aa:**



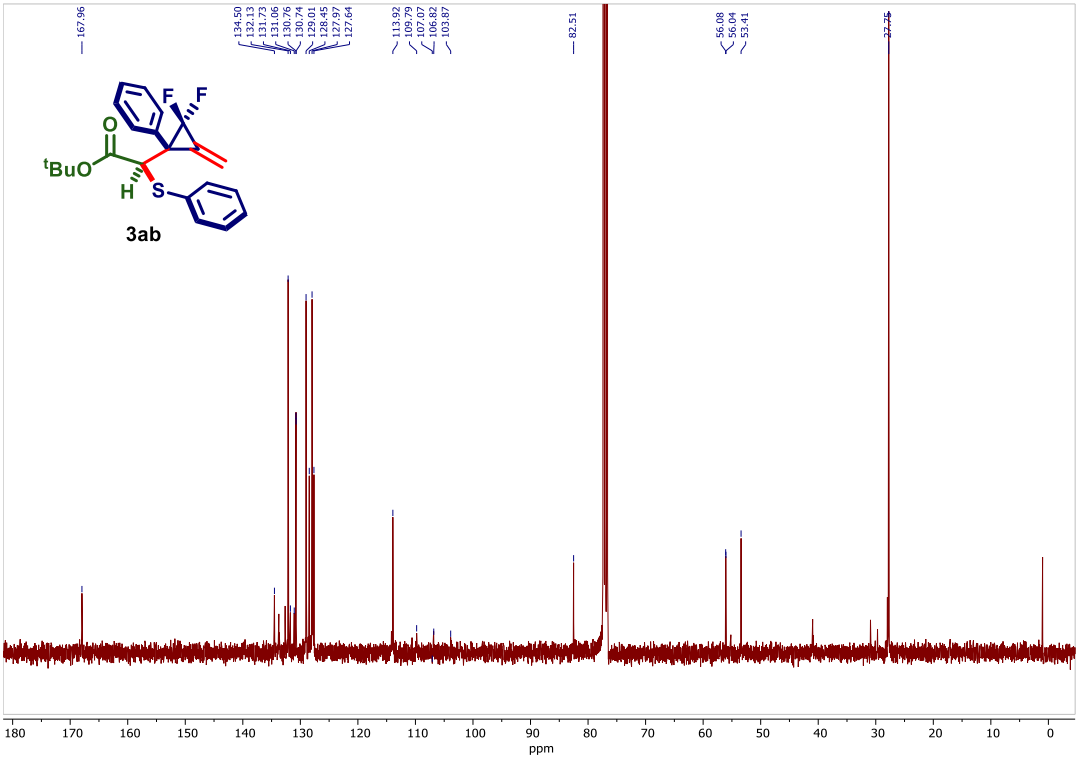
^{19}F NMR (376 MHz, $CDCl_3$) of crude reaction mixture (compound **3aa**)**:**



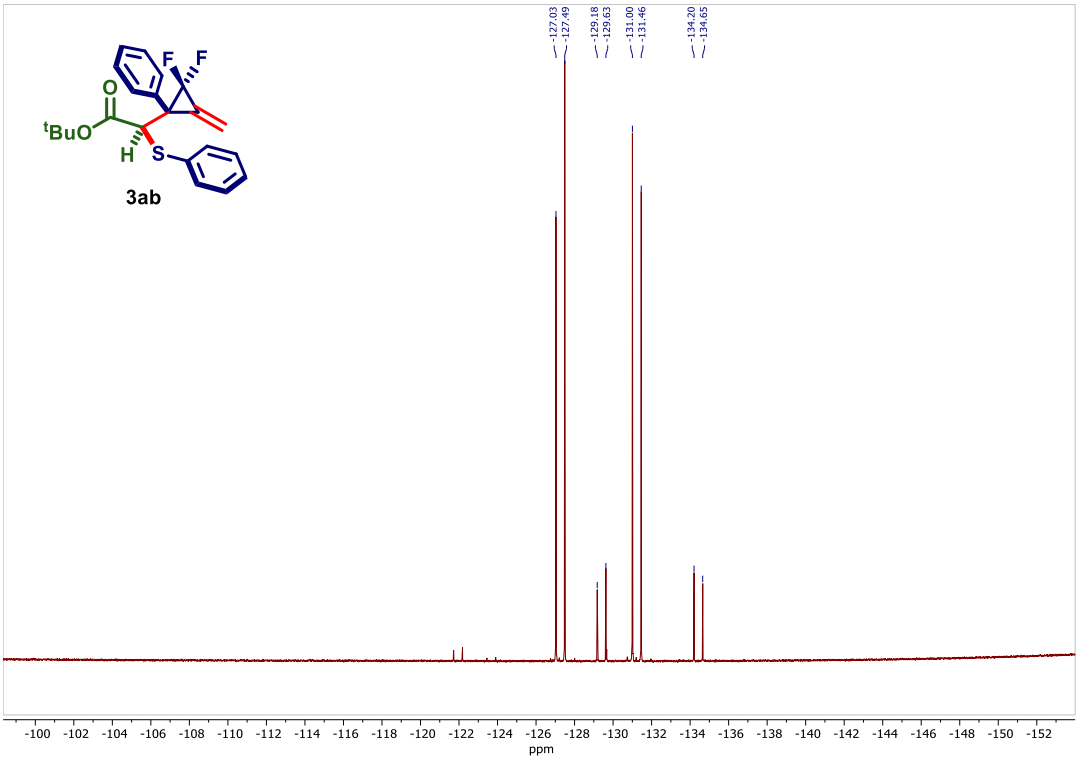
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3ab: (***See Procedure***)**



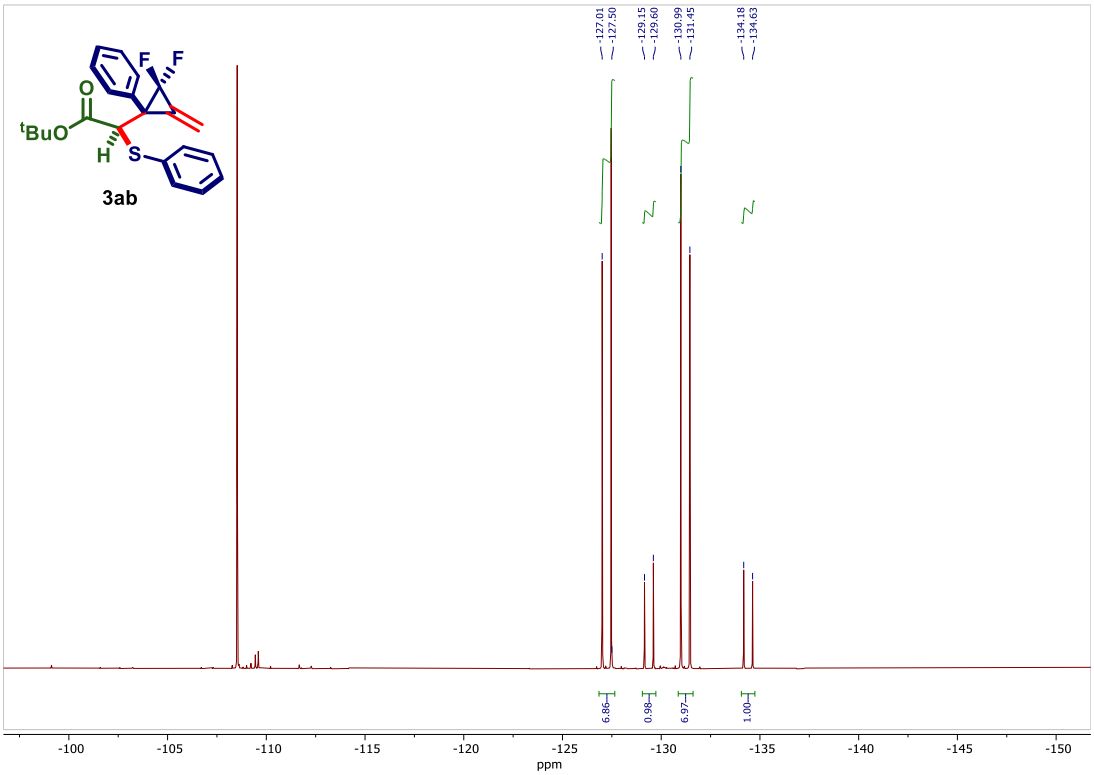
^{13}C NMR (101 MHz, $CDCl_3$) of Compound **3ab:**



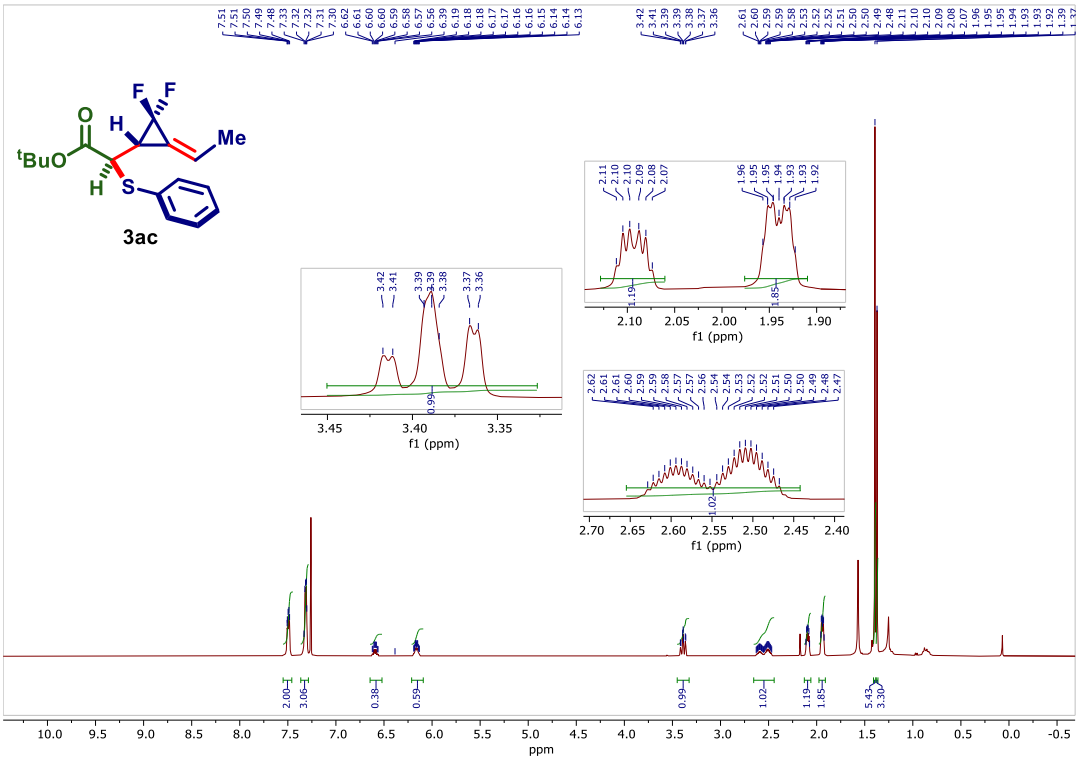
^{19}F NMR (376 MHz, $CDCl_3$) of compound **3ab:**



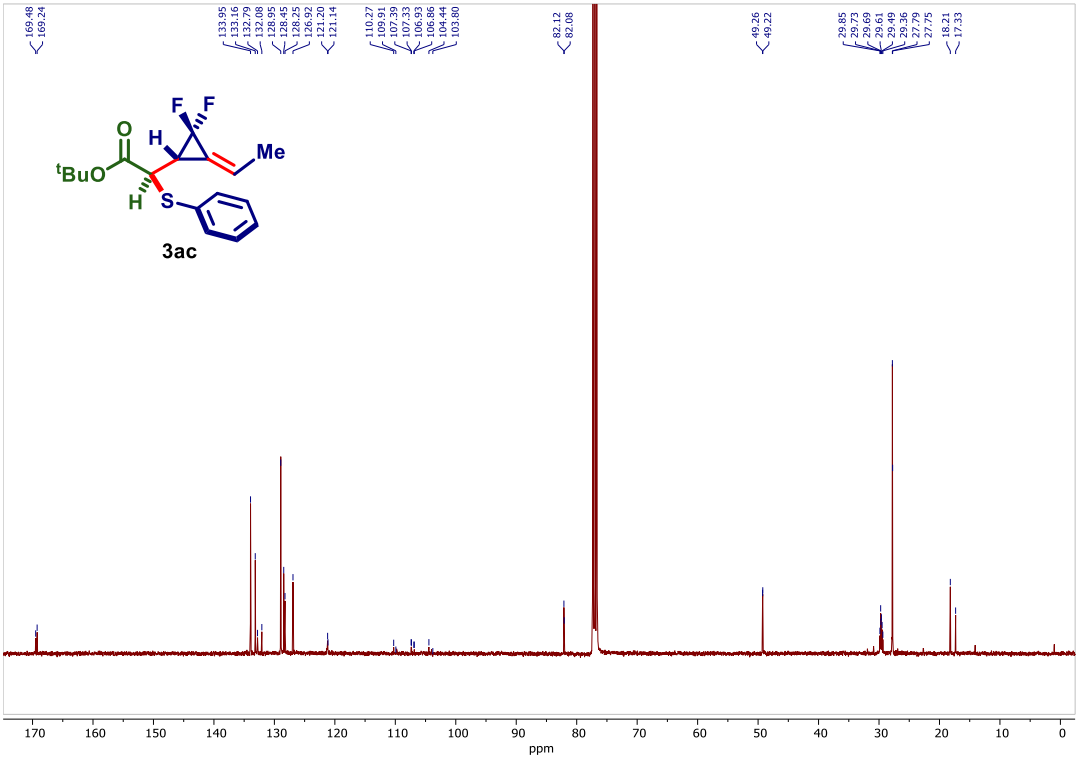
^{19}F NMR (376 MHz, $CDCl_3$) of crude reaction mixture (compound **3ab**)**:**



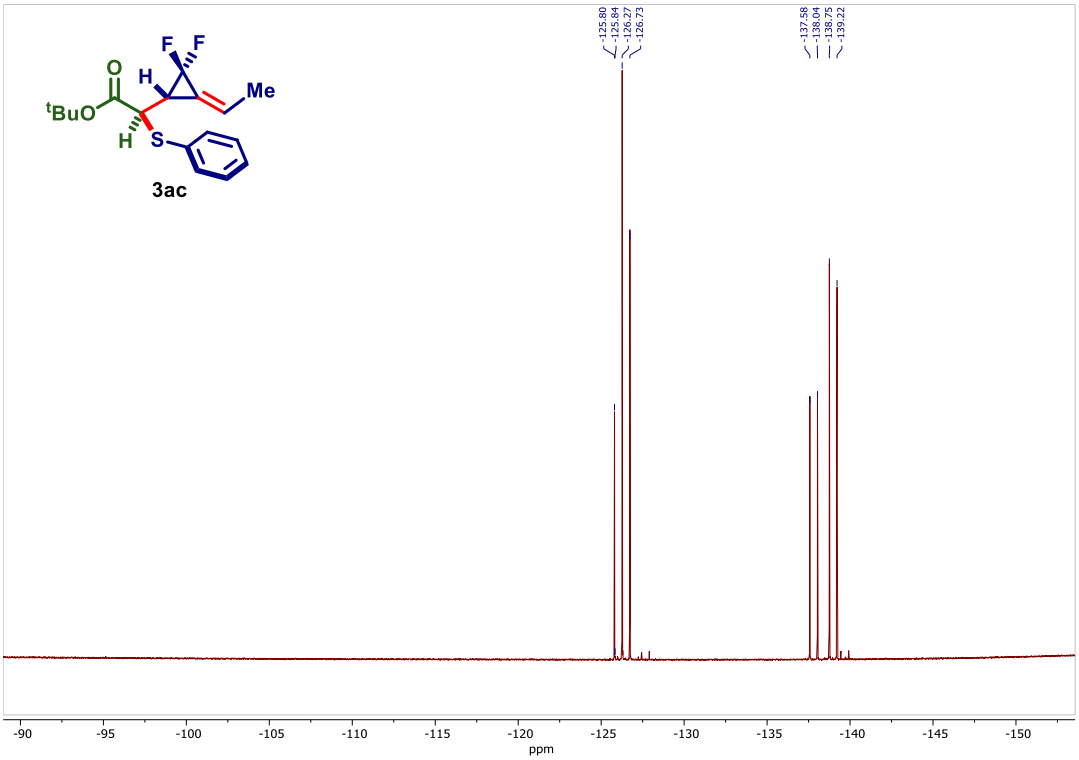
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3ac: (*See Procedure*)**



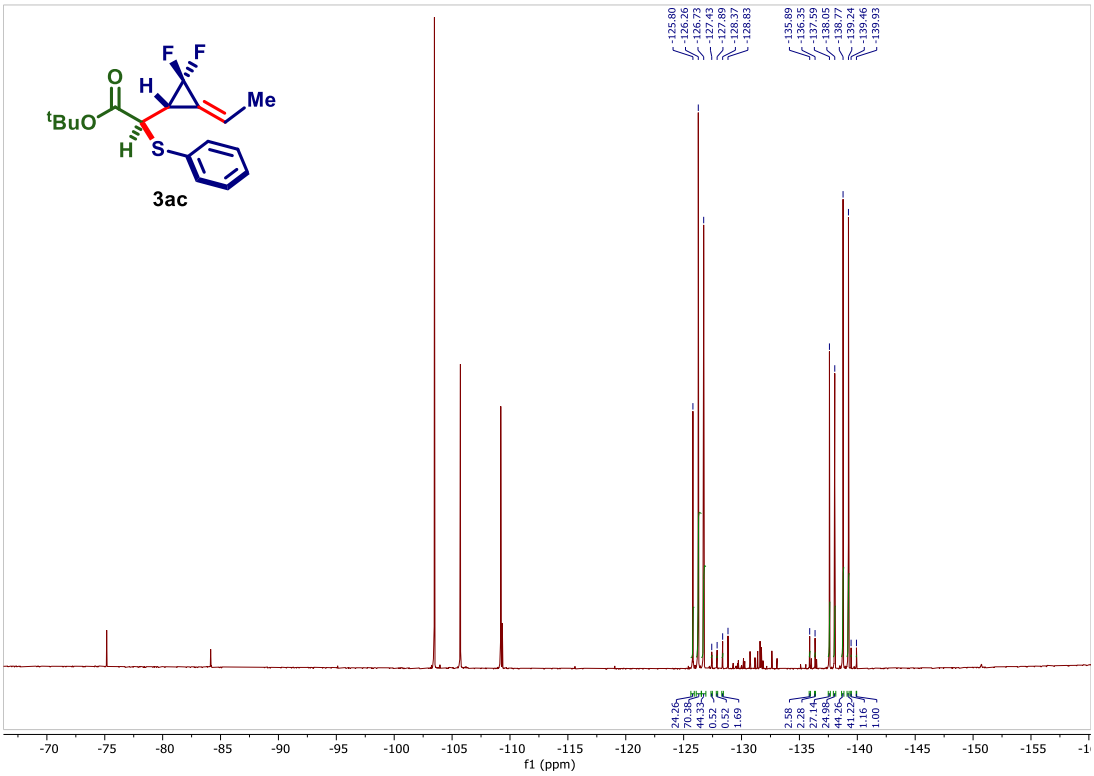
^{13}C NMR (101 MHz, $CDCl_3$) of Compound **3ac:**



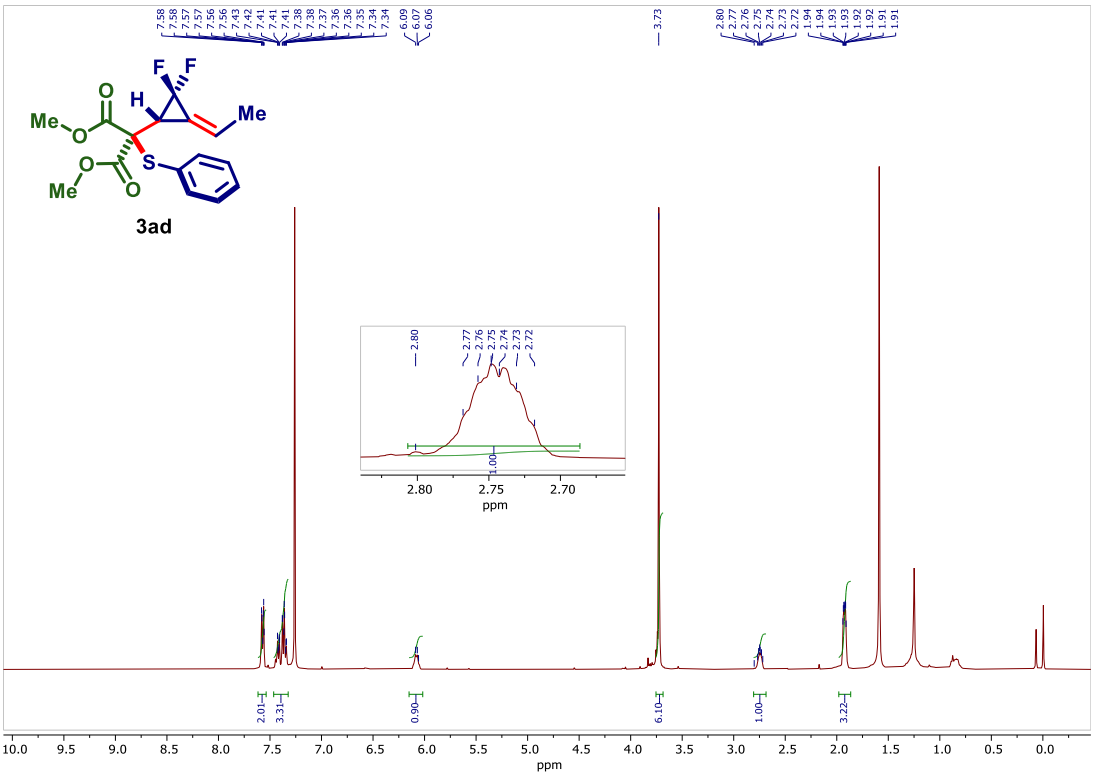
^{19}F NMR (376 MHz, $CDCl_3$) of compound **3ac:**



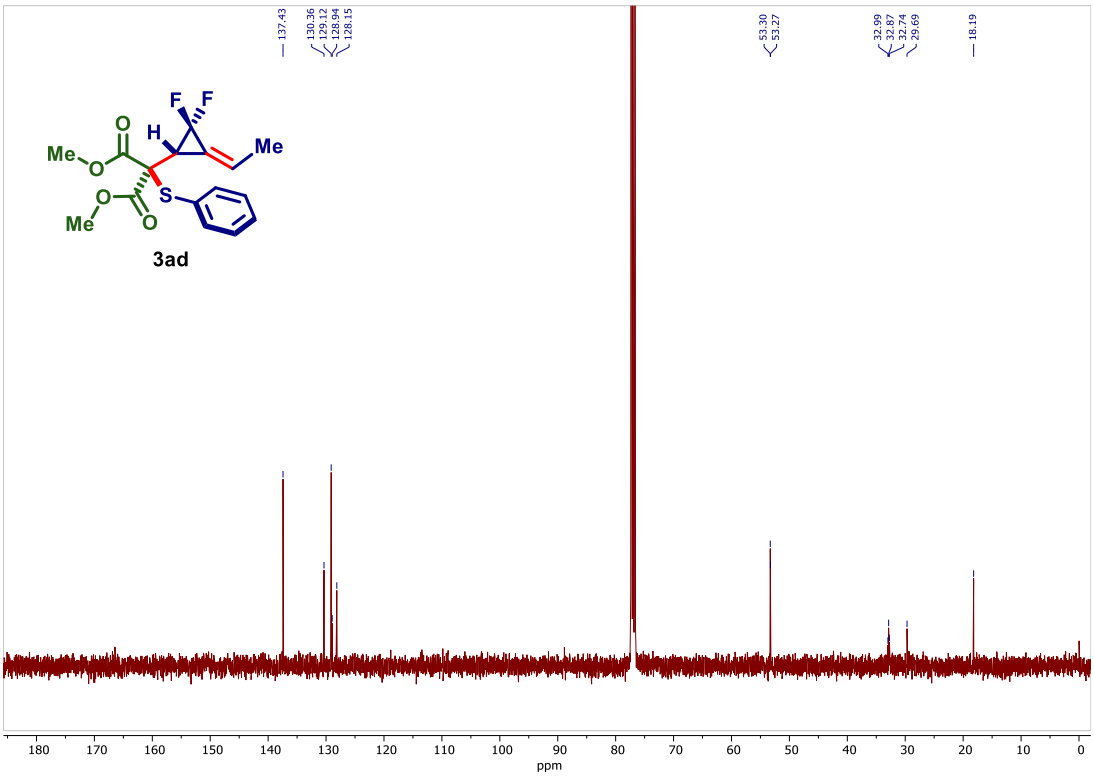
^{19}F NMR (376 MHz, $CDCl_3$) of crude reaction mixture (compound **3ac**)**:**



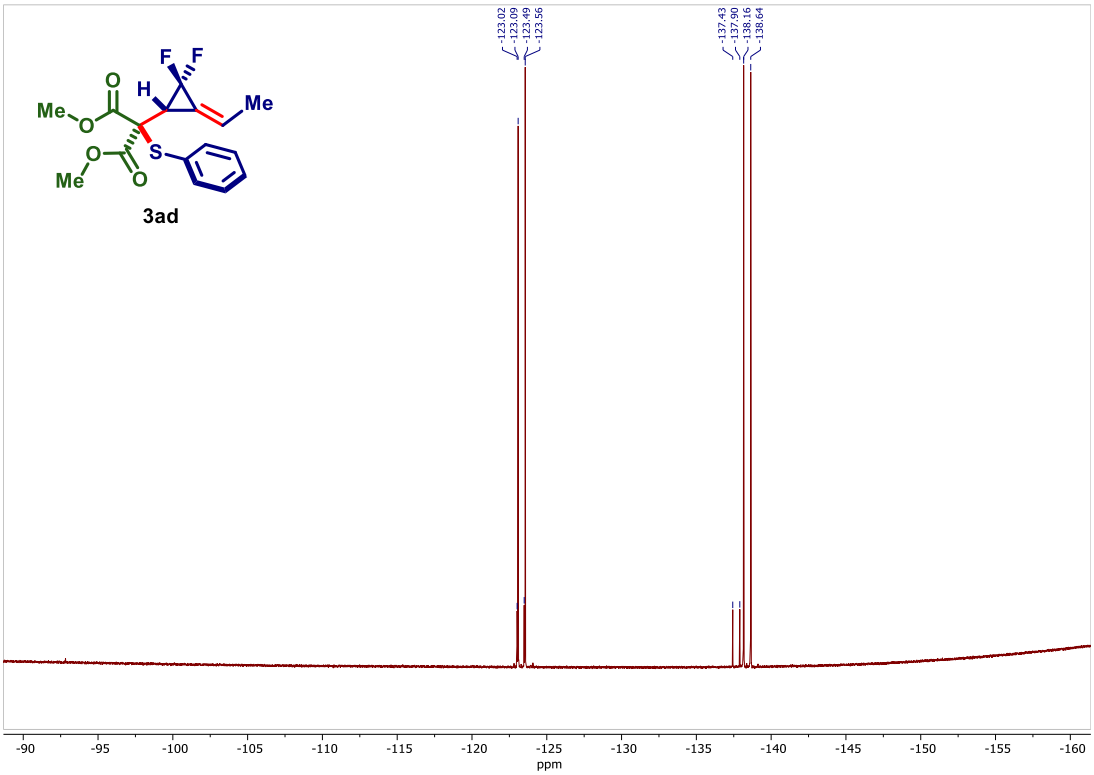
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3ad: (*See Procedure*)**



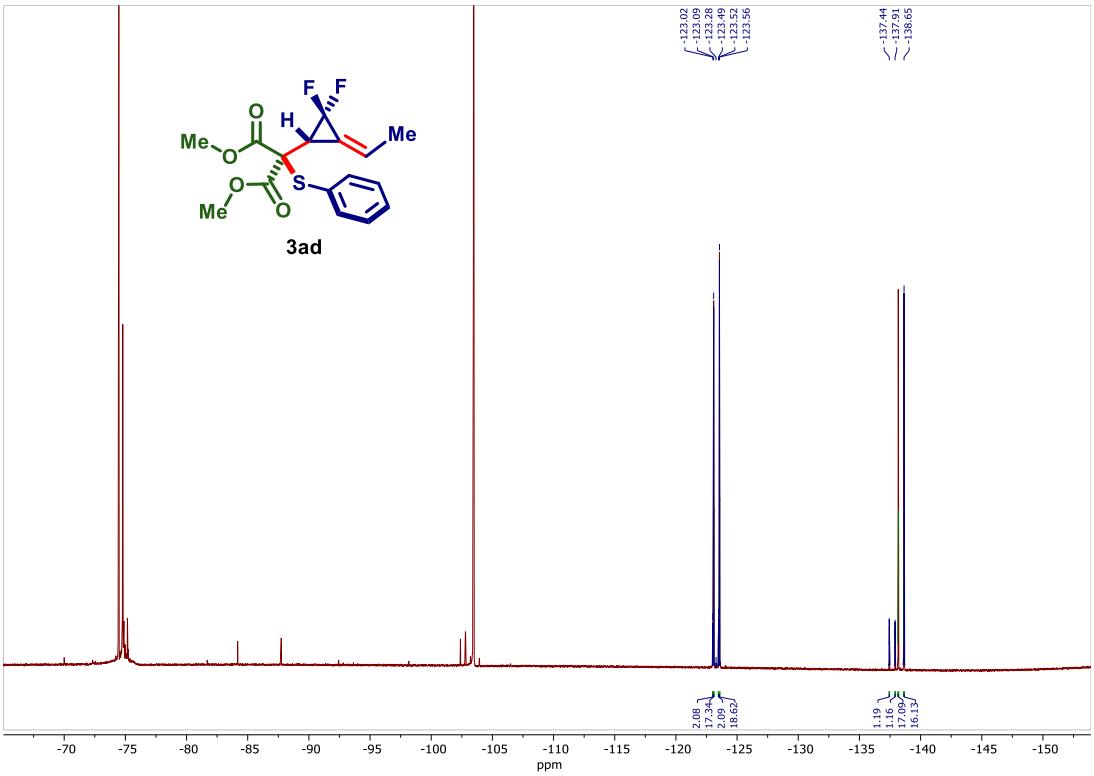
^{13}C NMR (101 MHz, $CDCl_3$) of Compound **3ad:**



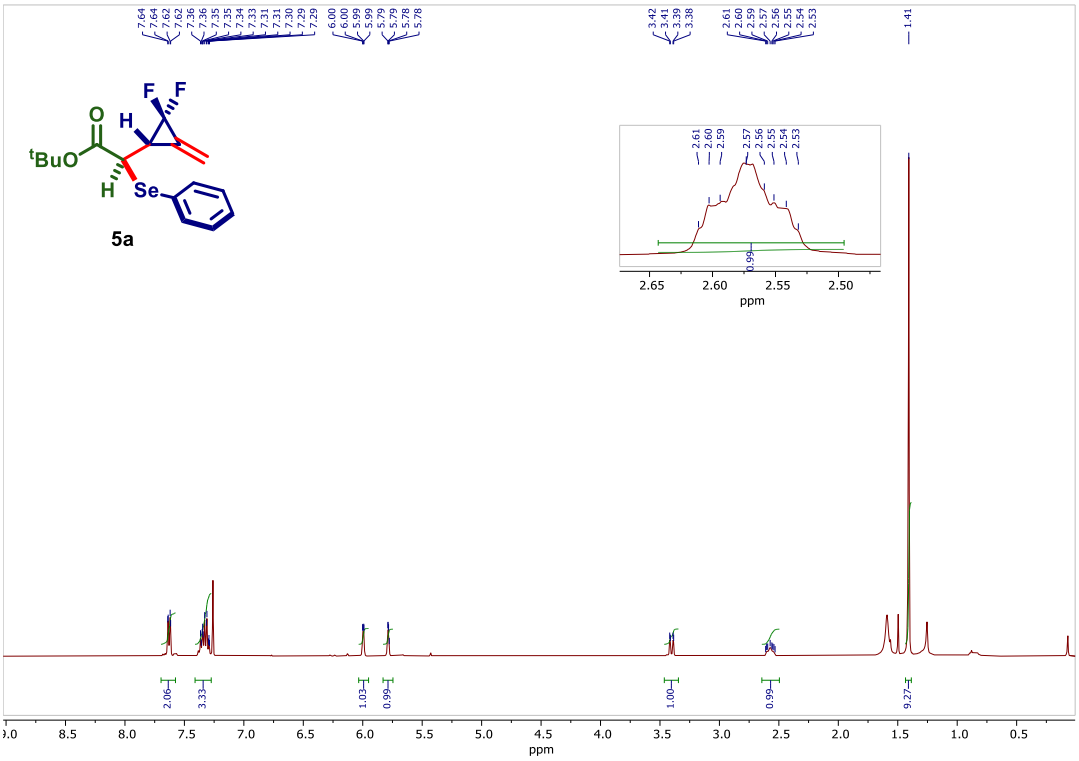
^{19}F NMR (376 MHz, $CDCl_3$) of compound **3ad:**



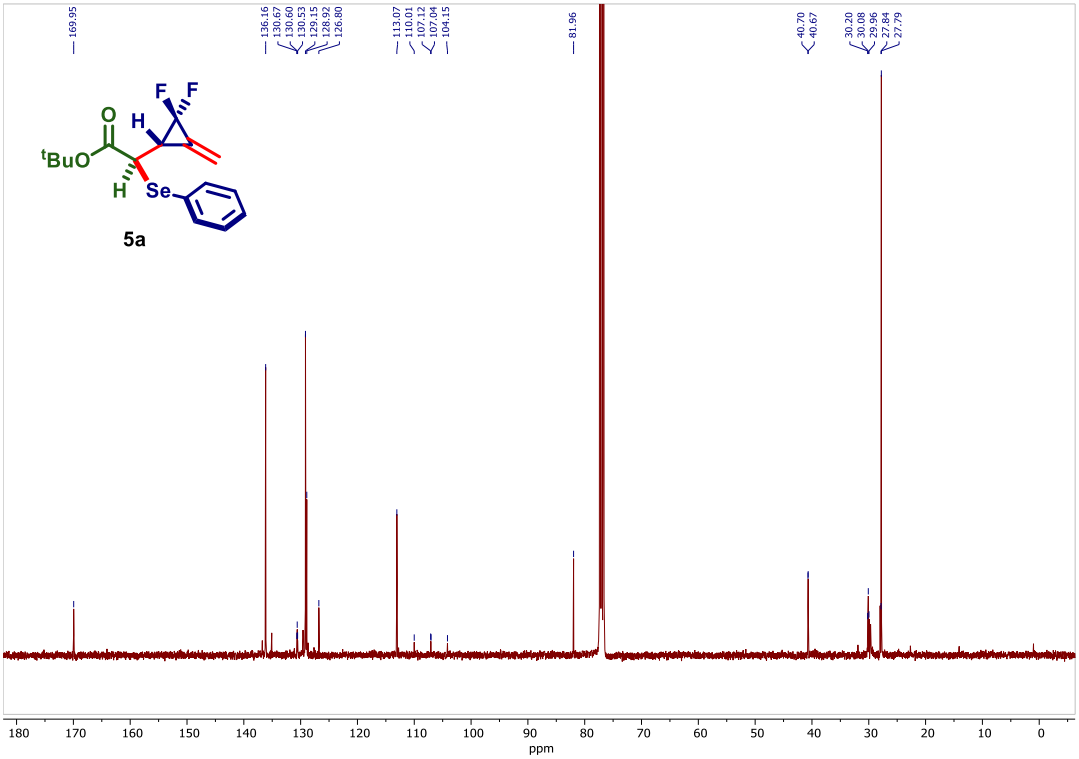
^{19}F NMR (376 MHz, $CDCl_3$) of crude reaction mixture (compound **3ad):**



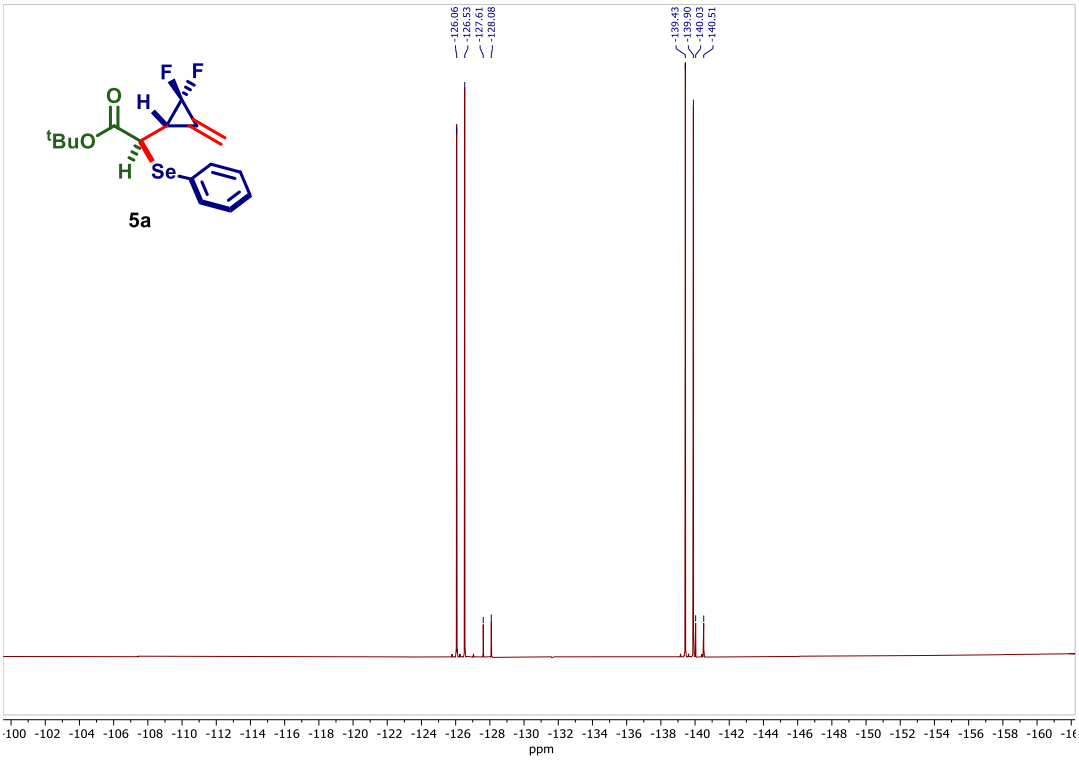
^{1}H NMR (400 MHz, $CDCl_3$) of compound **5a: (*See Procedure*)**



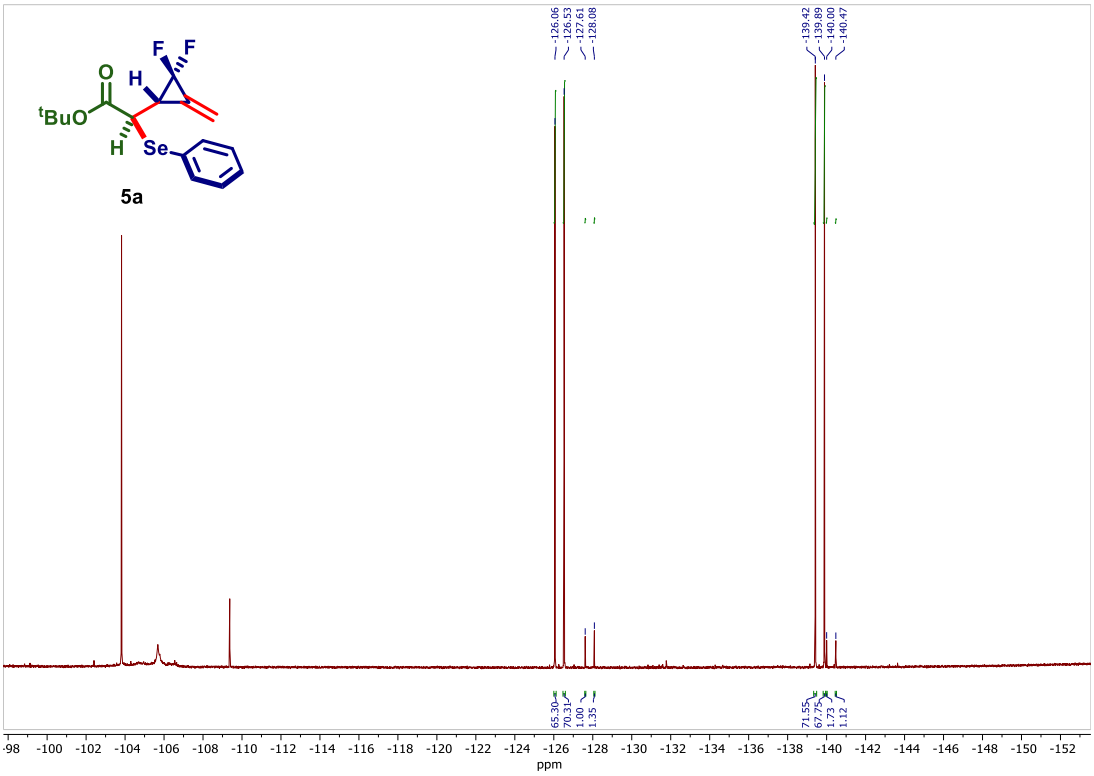
^{13}C NMR (101 MHz, $CDCl_3$) of Compound **5a:**



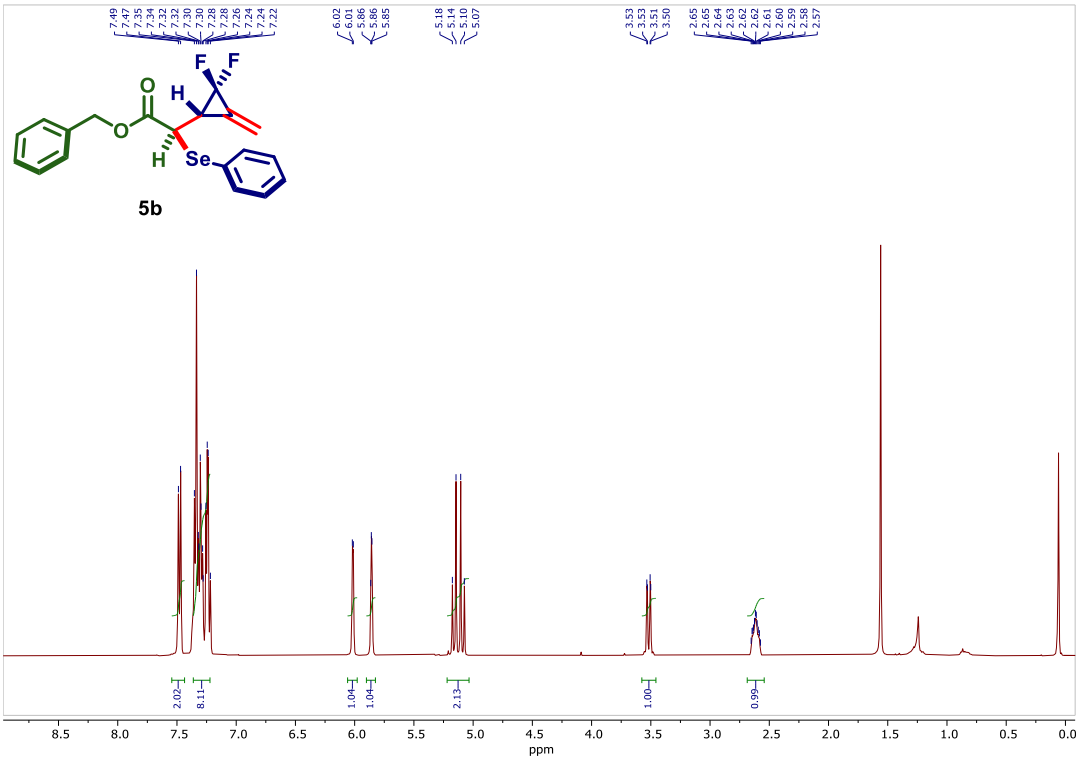
^{19}F NMR (376 MHz, $CDCl_3$) of compound **5a:**



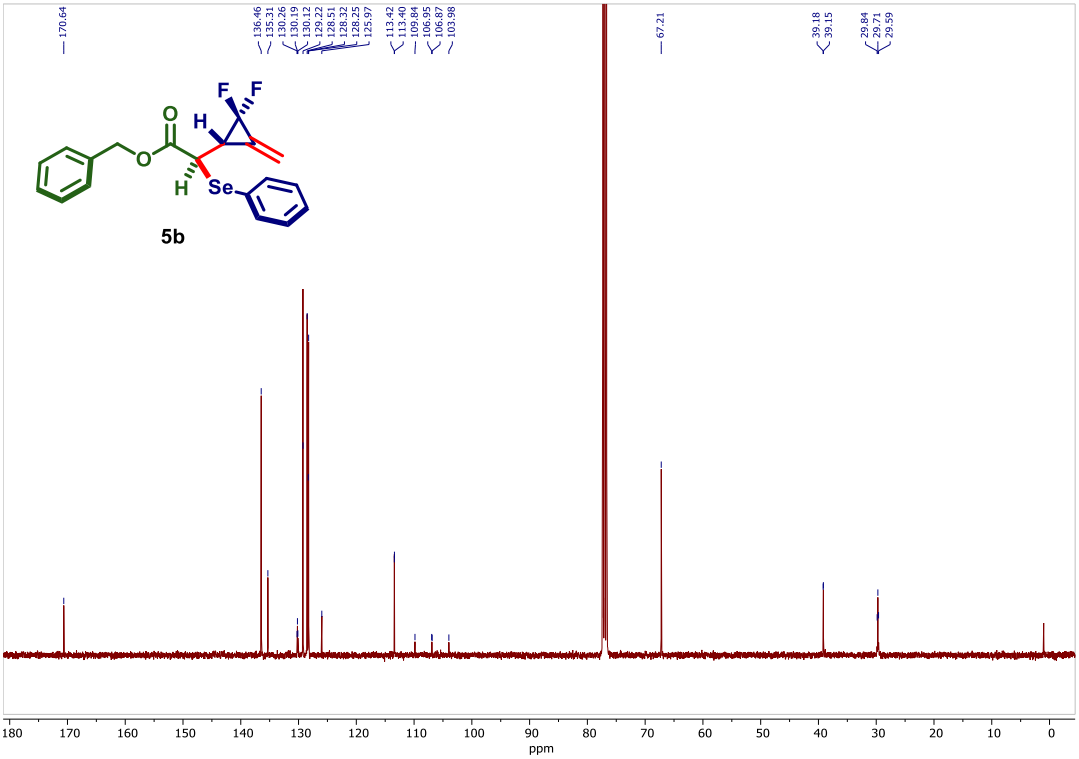
^{19}F NMR (376 MHz, $CDCl_3$) of crude reaction mixture (compound **5a):**



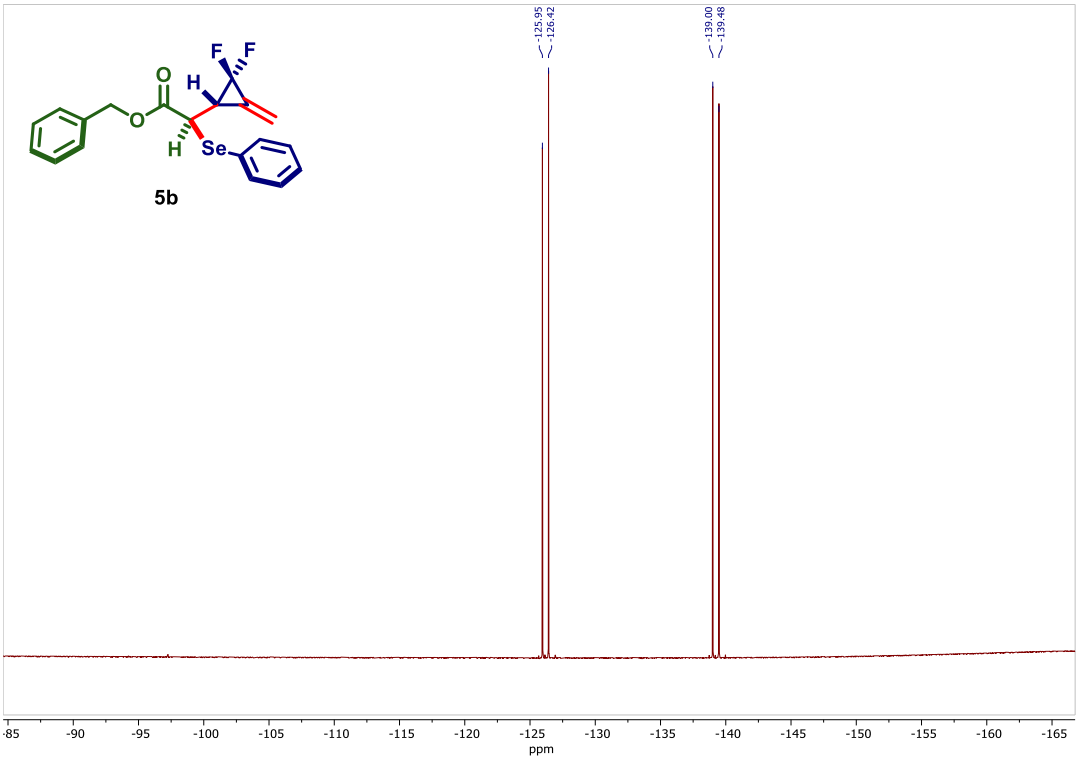
^{1}H NMR (400 MHz, $CDCl_3$) of compound **5b: (***See Procedure***)**



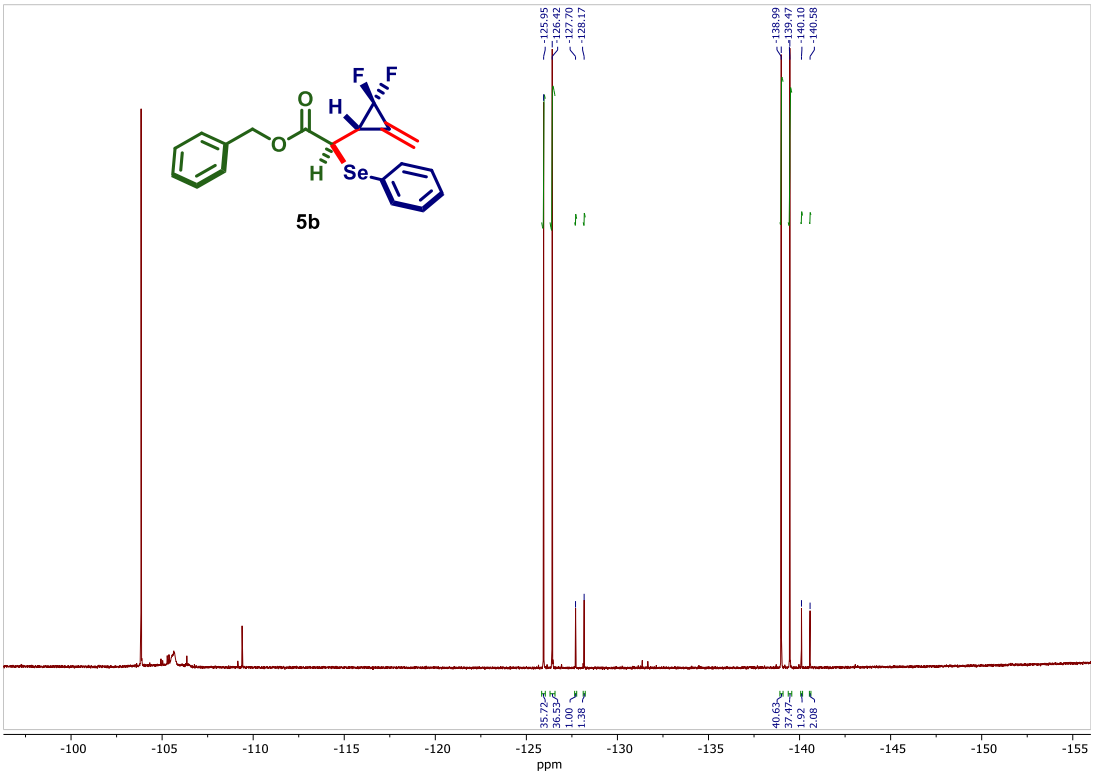
^{13}C NMR (101 MHz, $CDCl_3$) of Compound **5b:**



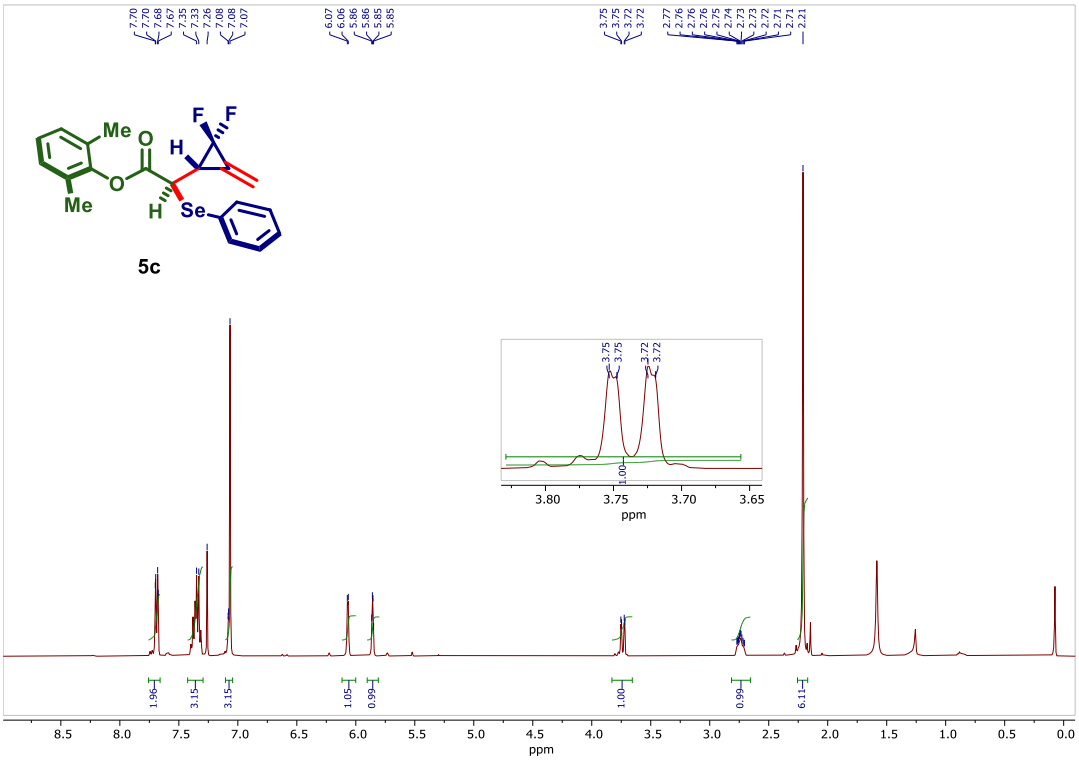
^{19}F NMR (376 MHz, $CDCl_3$) of compound **5b:**



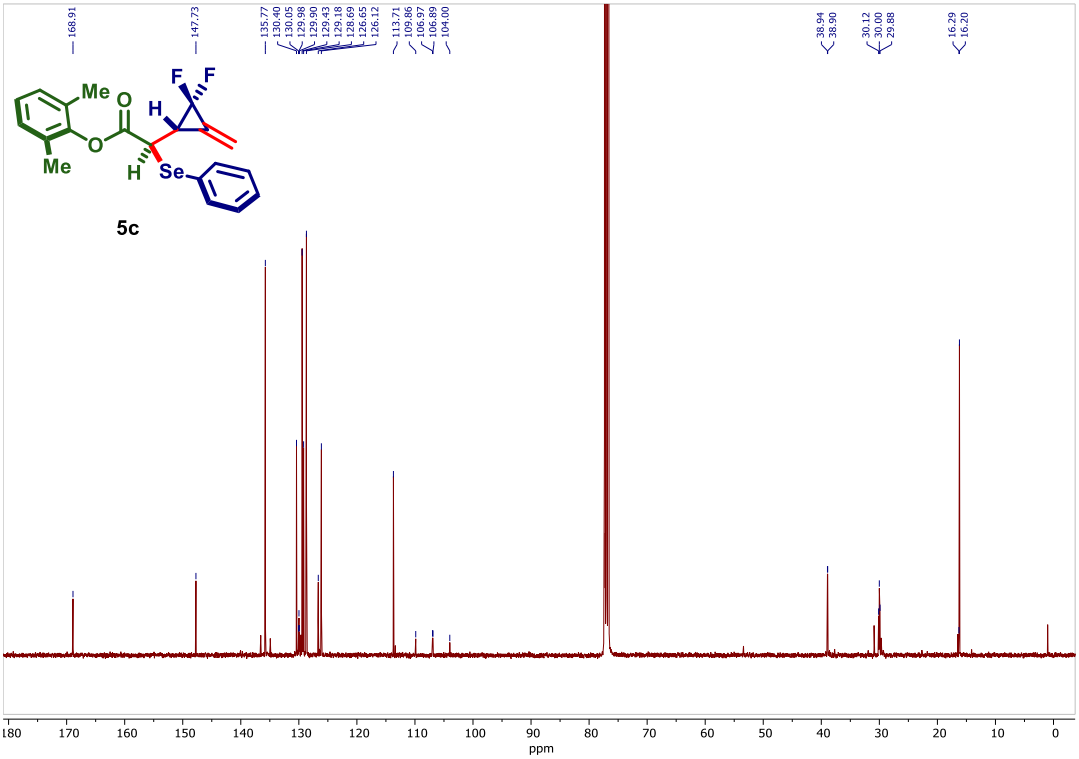
^{19}F NMR (376 MHz, $CDCl_3$) of crude reaction mixture (compound **5b):**



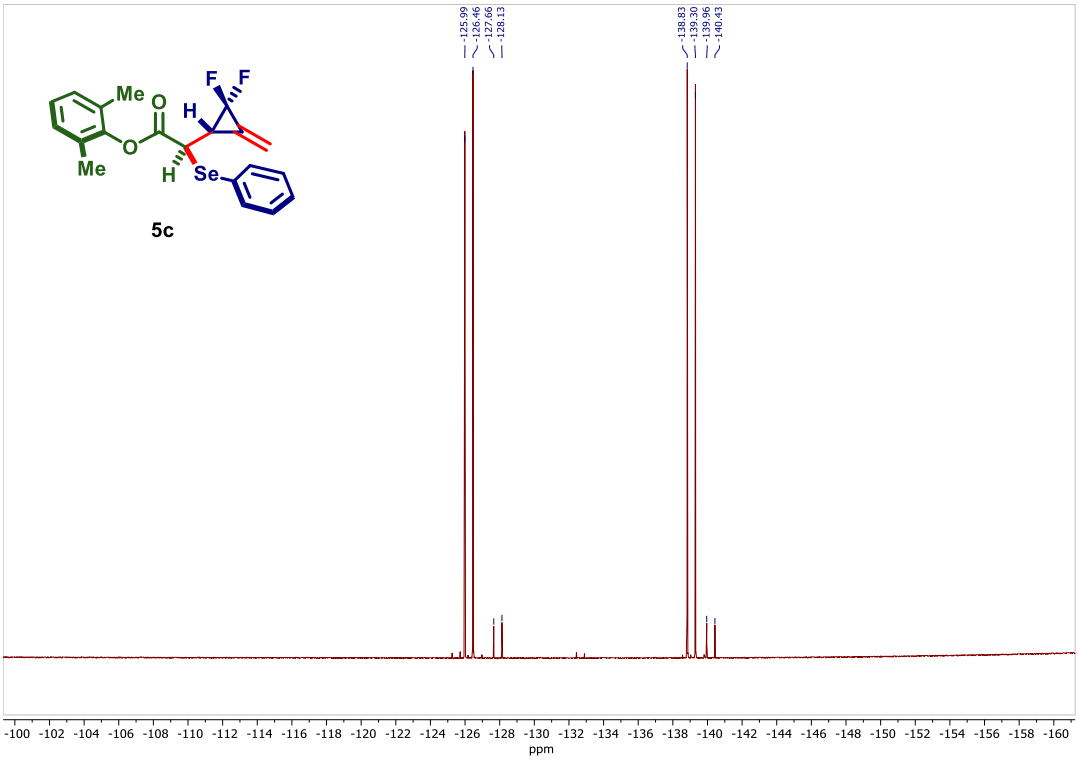
^{1}H NMR (400 MHz, $CDCl_3$) of compound **5c: (*See Procedure*)**



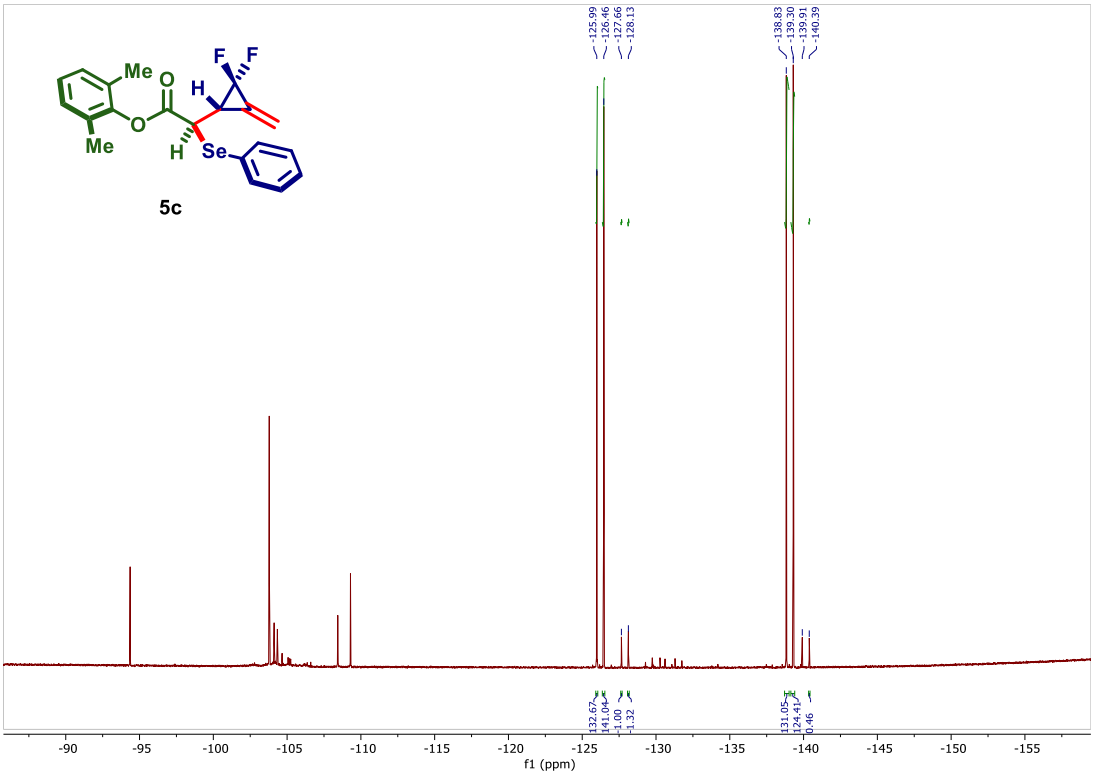
^{13}C NMR (101 MHz, $CDCl_3$) of Compound **5c:**



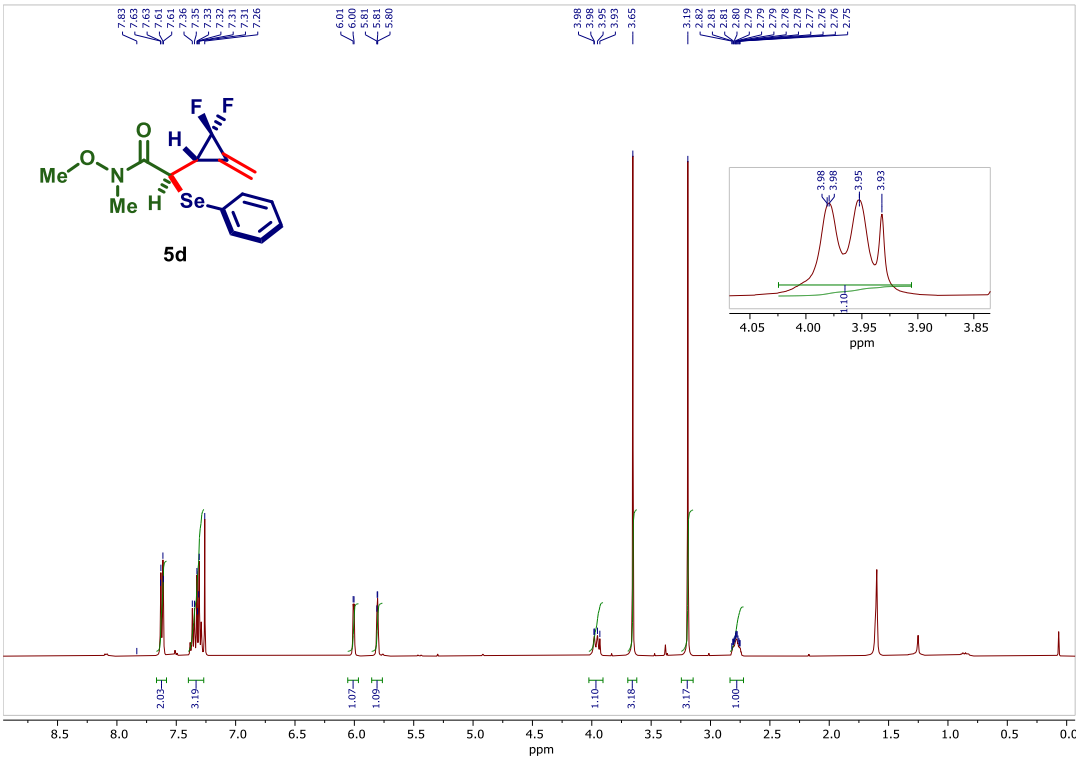
^{19}F NMR (376 MHz, $CDCl_3$) of compound **5c:**



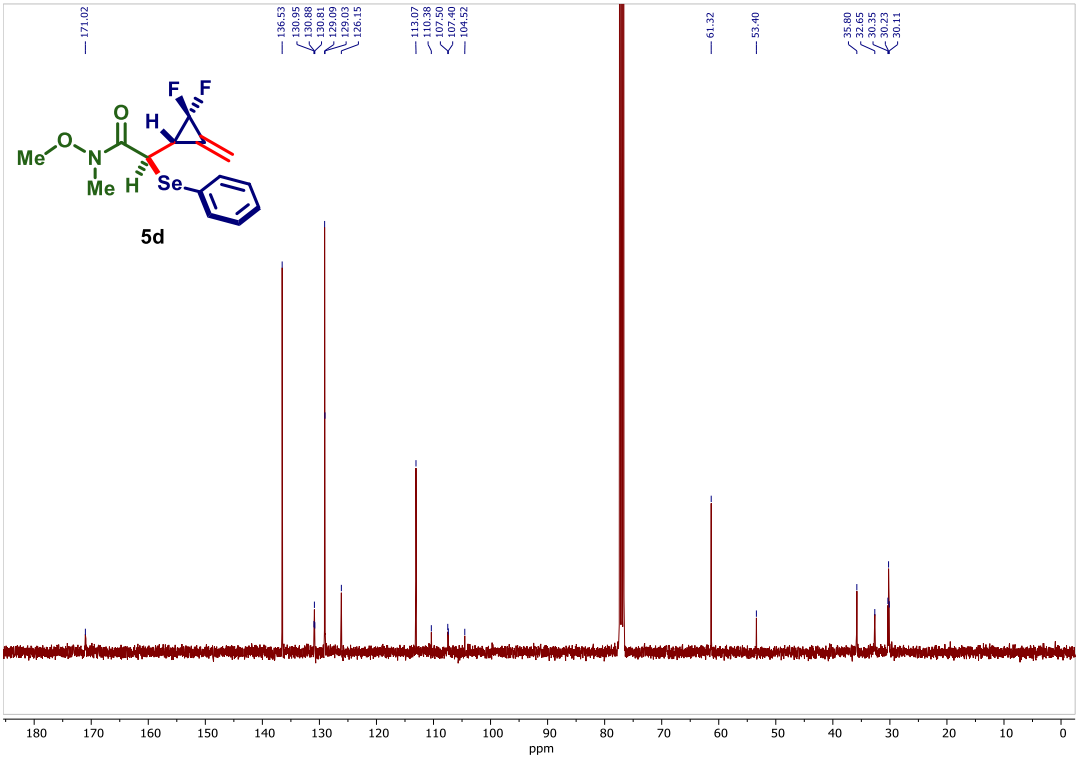
^{19}F NMR (376 MHz, $CDCl_3$) of crude reaction mixture (compound **5c):**



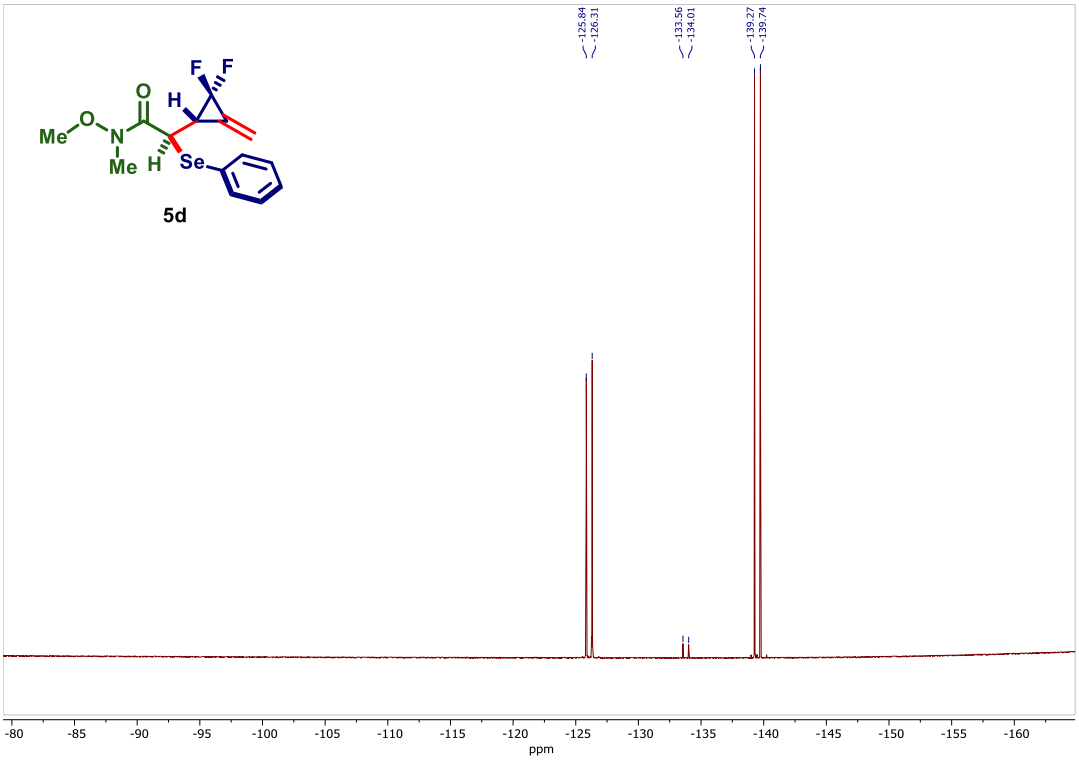
^{1}H NMR (400 MHz, $CDCl_3$) of compound **5d: (*See Procedure*)**



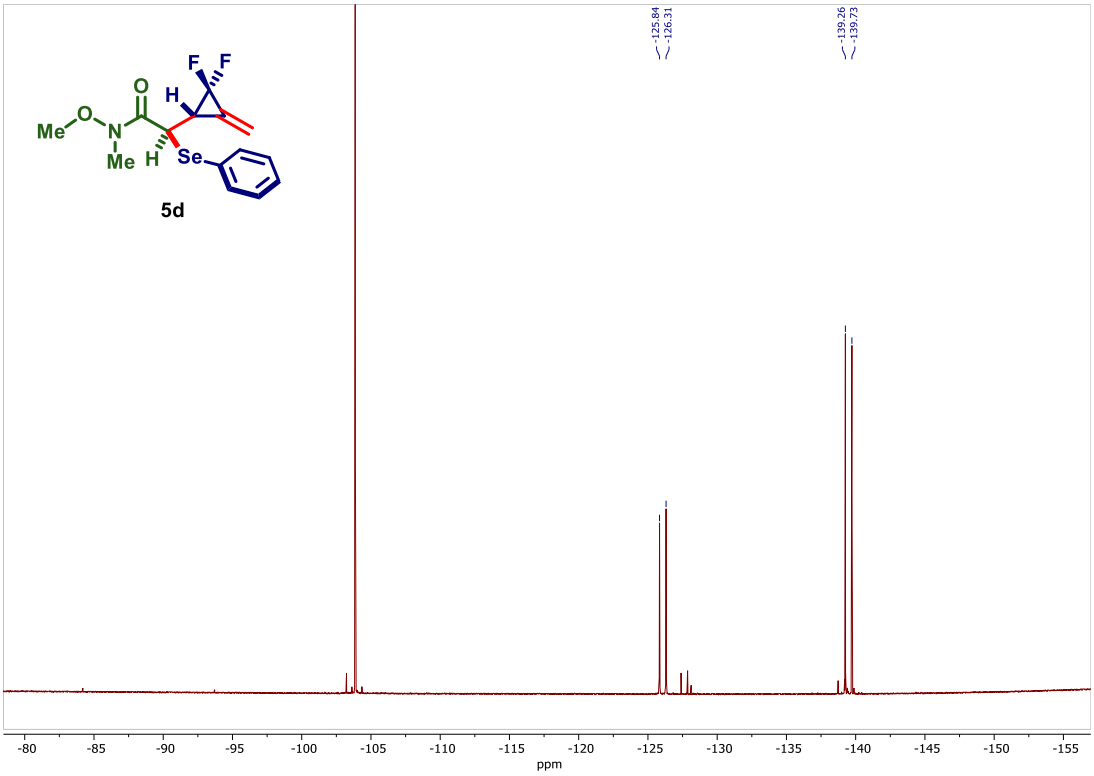
^{13}C NMR (101 MHz, $CDCl_3$) of Compound **5d:**



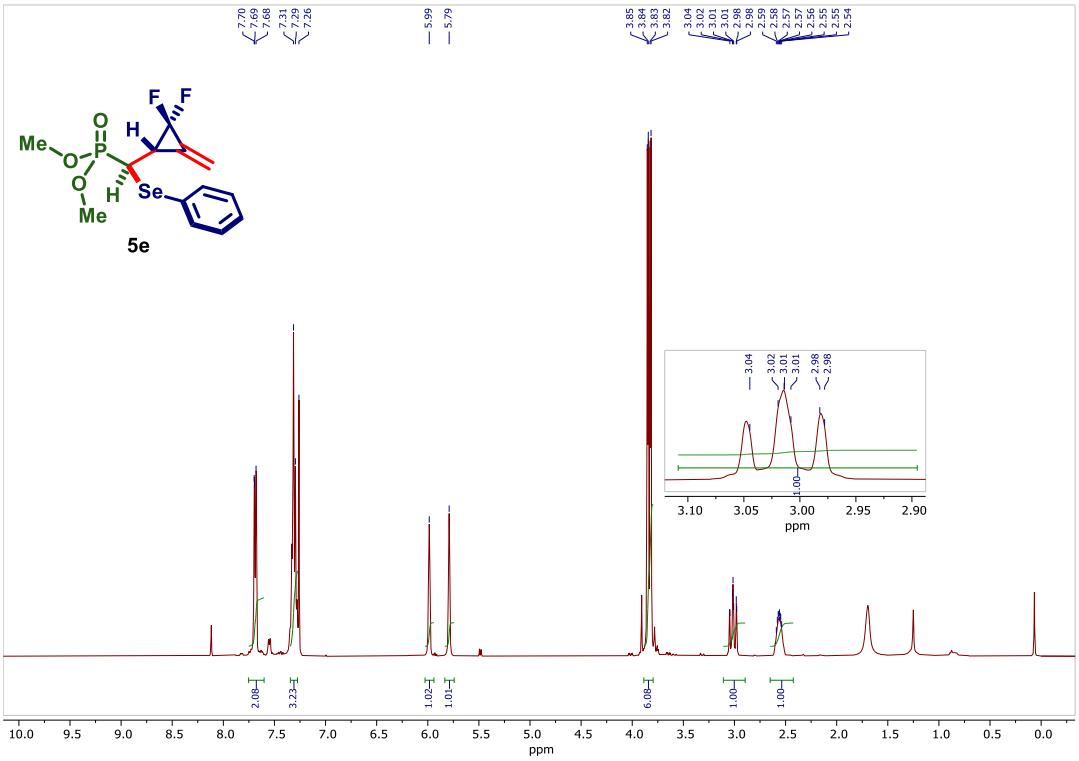
^{19}F NMR (376 MHz, $CDCl_3$) of compound **5d:**



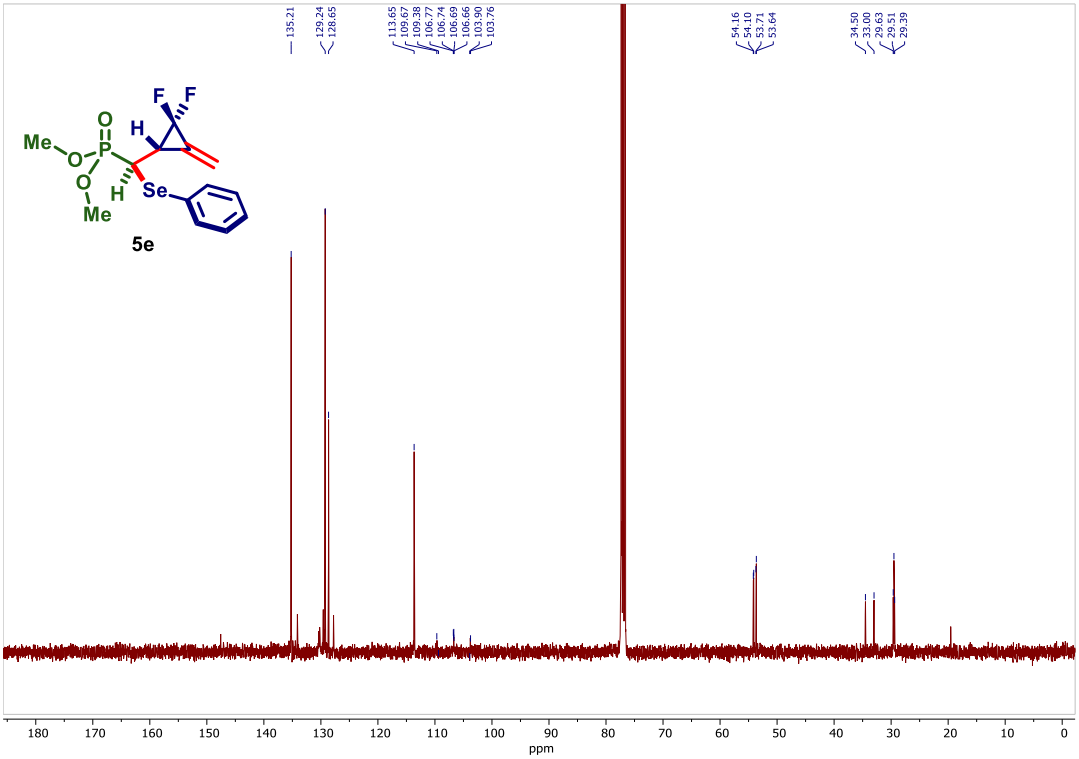
^{19}F NMR (376 MHz, $CDCl_3$) of crude reaction mixture (compound **5d):**



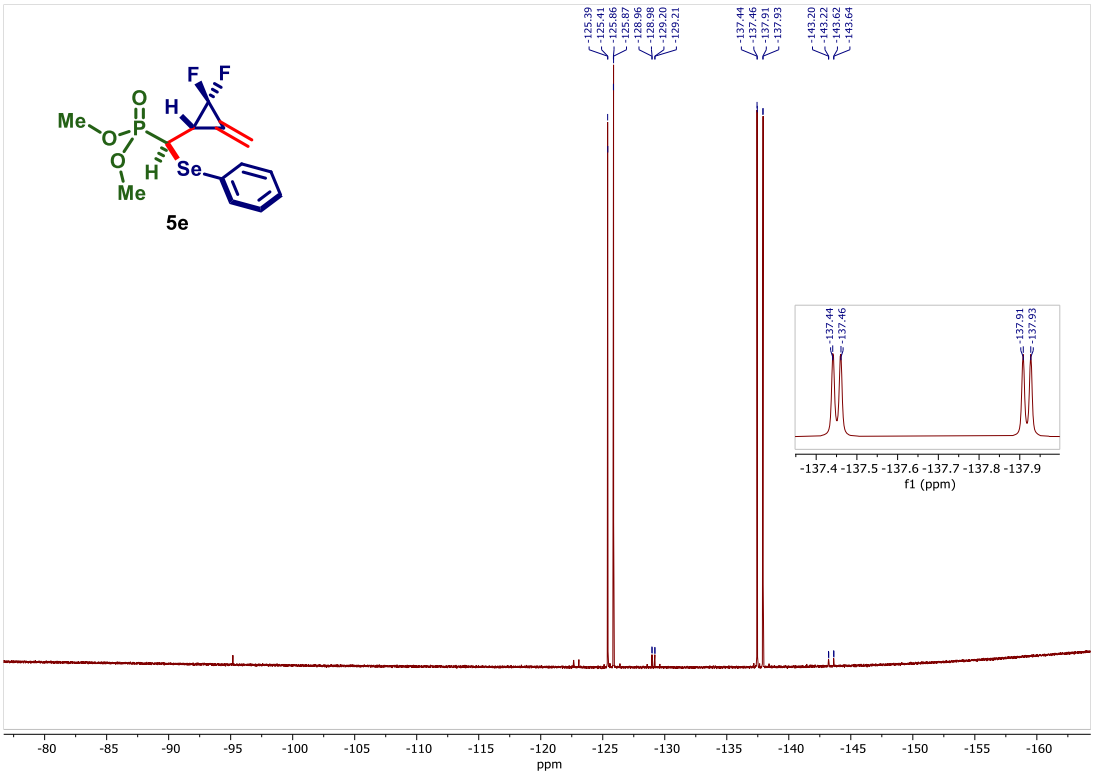
^{1}H NMR (400 MHz, $CDCl_3$) of compound **5e: (*See Procedure*)**



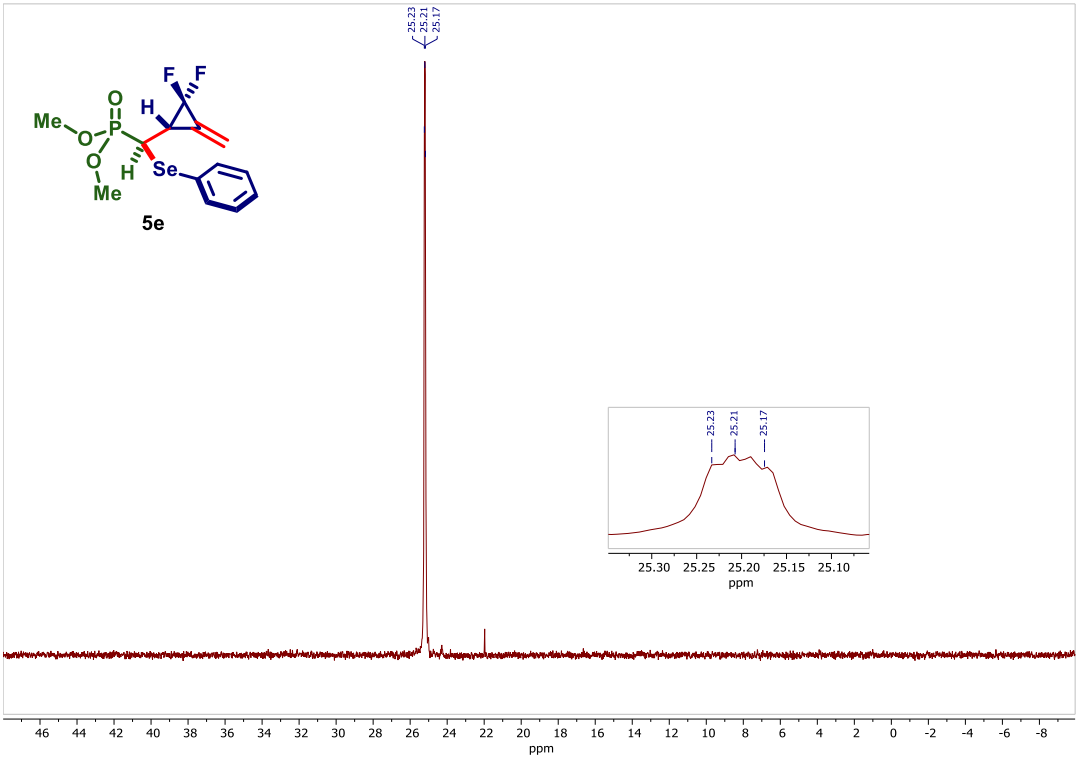
^{13}C NMR (101 MHz, $CDCl_3$) of Compound **5e:**



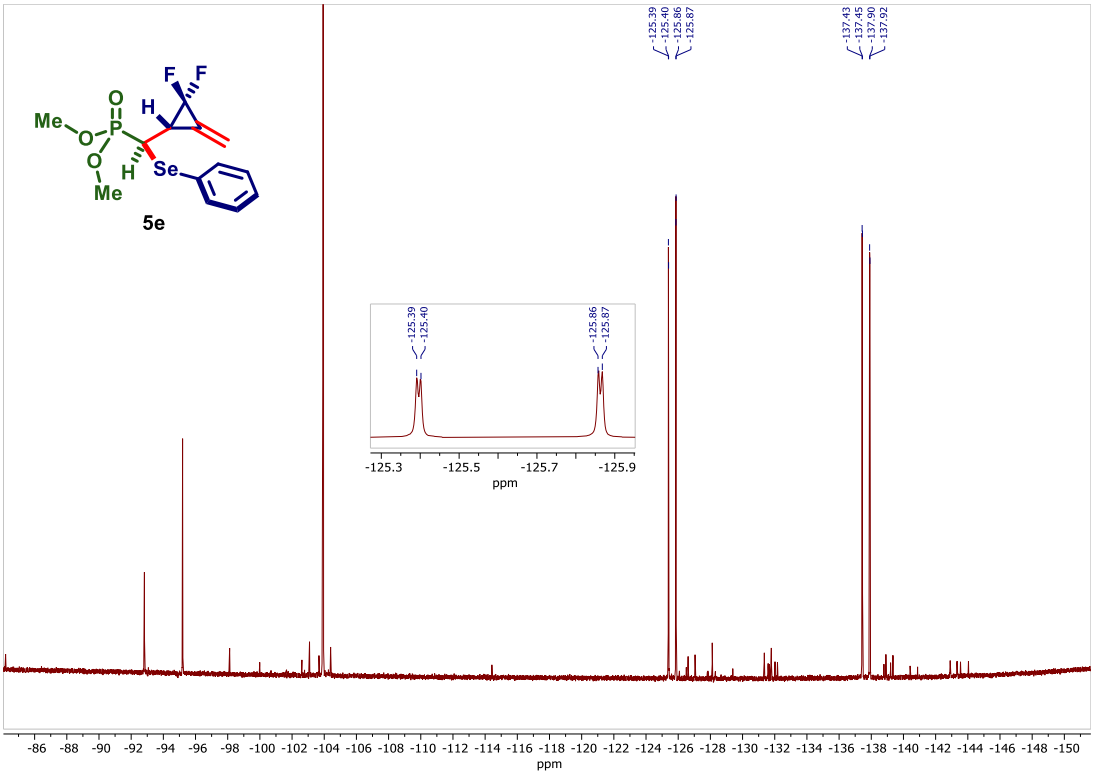
^{19}F NMR (376 MHz, $CDCl_3$) of compound **5e:**



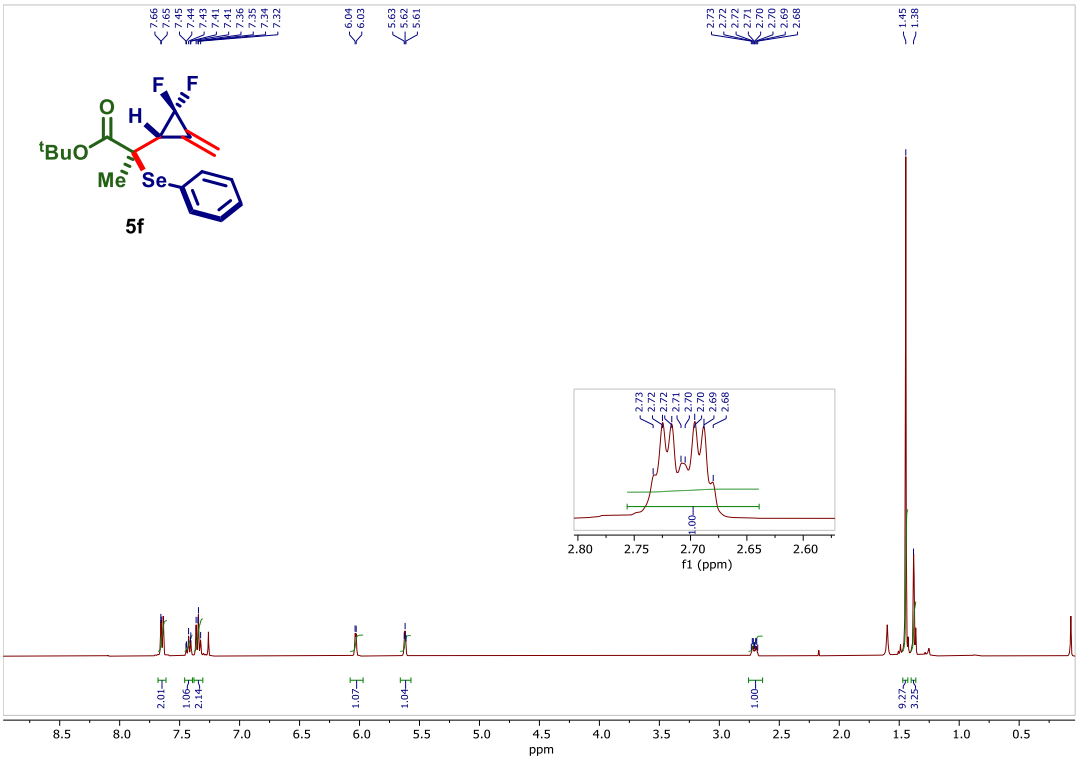
^{31}P NMR (162 MHz, $CDCl_3$) of compound **5e:**



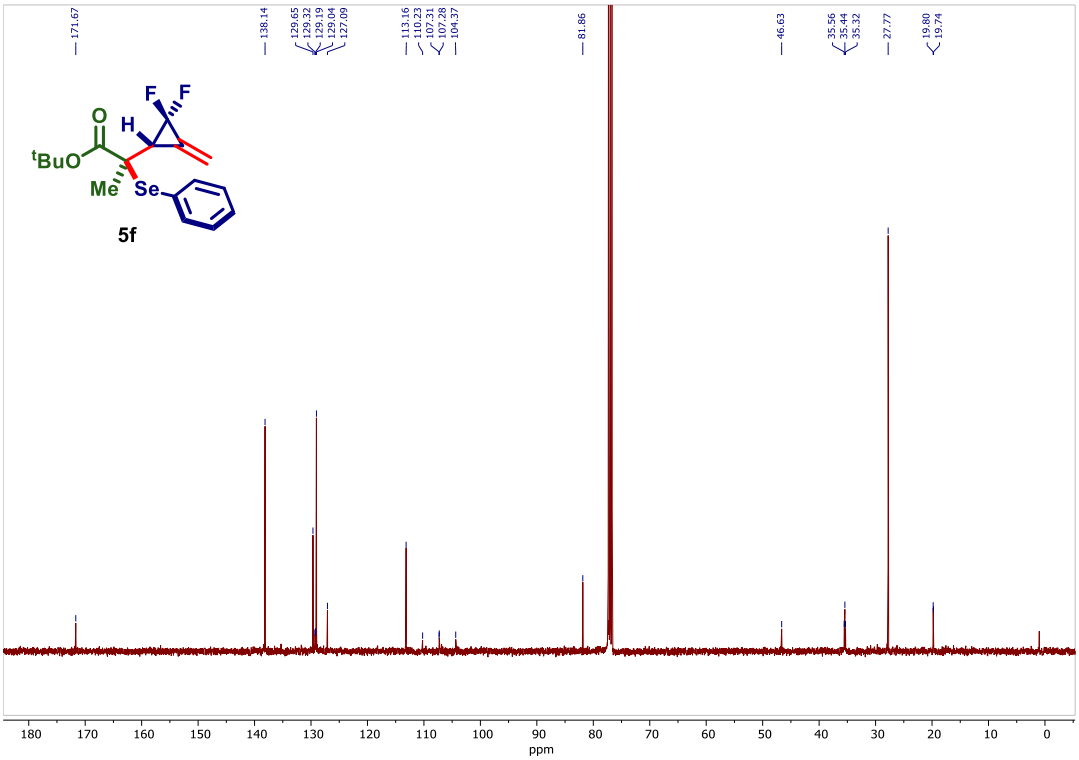
^{19}F NMR (376 MHz, $CDCl_3$) of crude reaction mixture (compound **5e):**



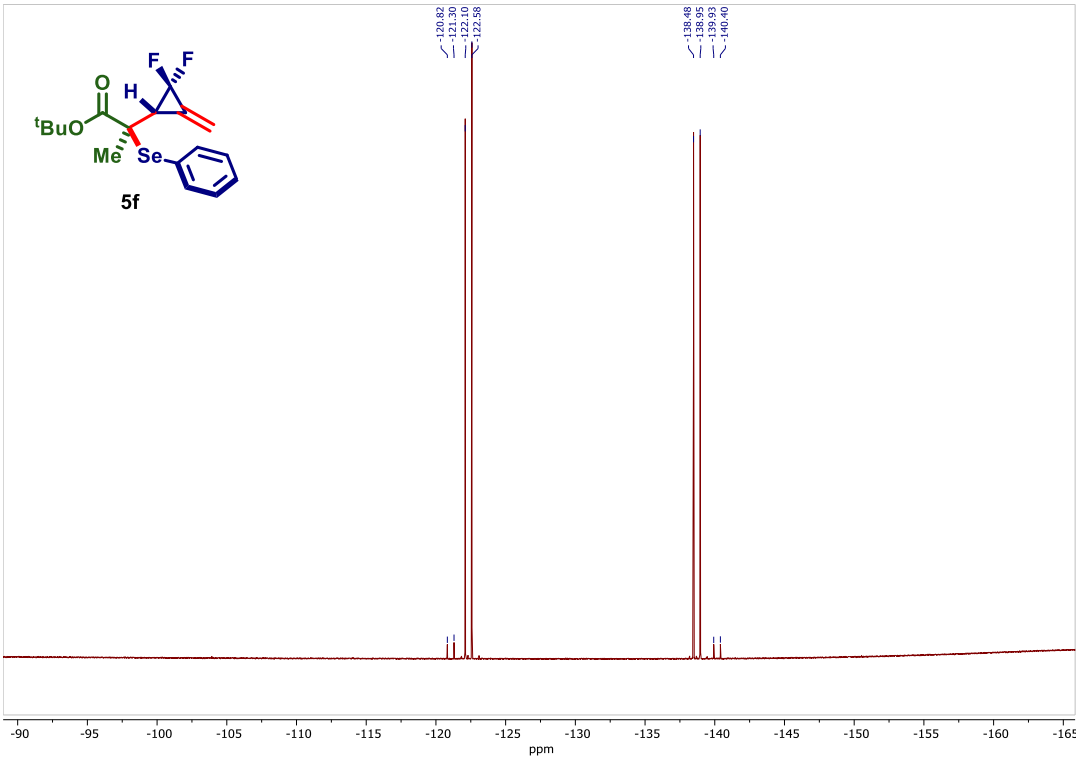
^{1}H NMR (400 MHz, $CDCl_3$) of compound **5f: (*See Procedure*)**



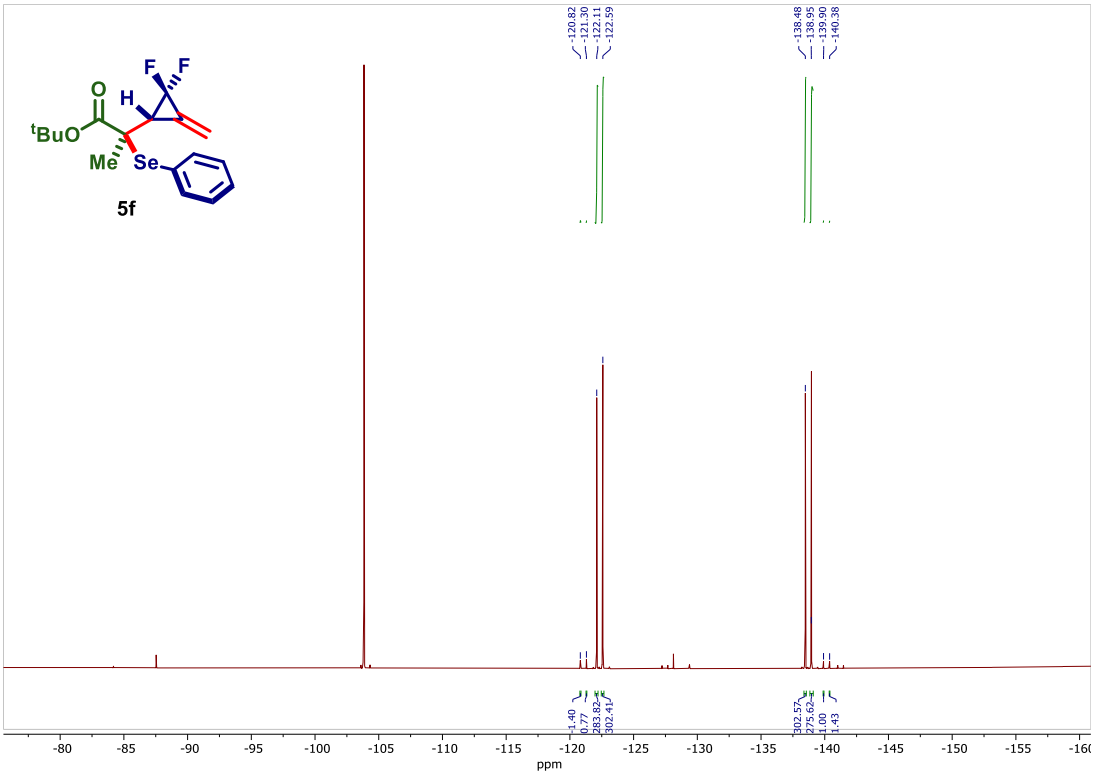
^{13}C NMR (101 MHz, $CDCl_3$) of Compound **5f:**



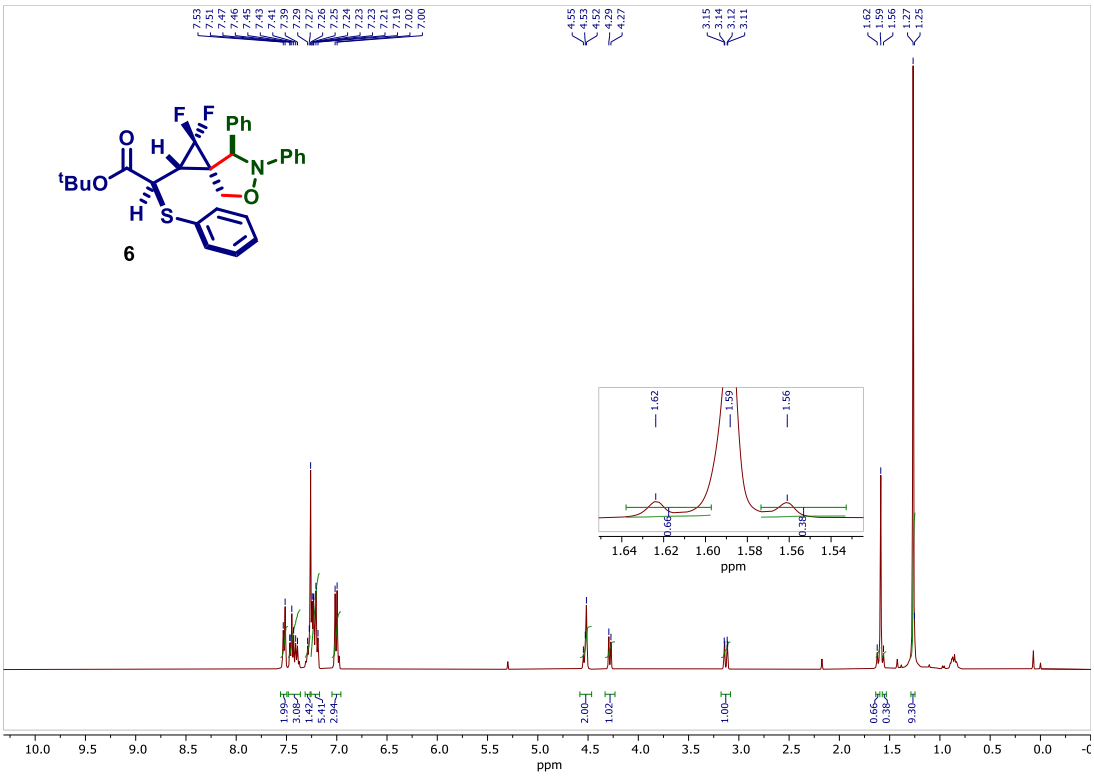
^{19}F NMR (376 MHz, $CDCl_3$) of compound **5f:**



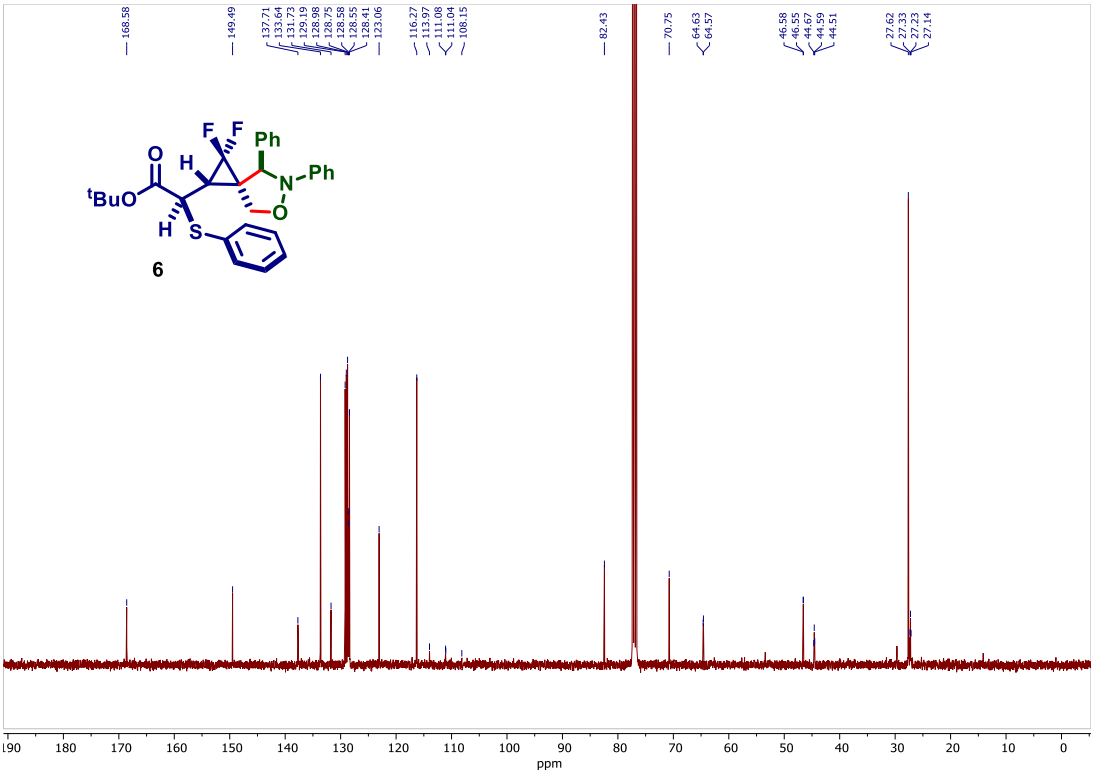
^{19}F NMR (376 MHz, $CDCl_3$) of crude reaction mixture (compound **5f):**



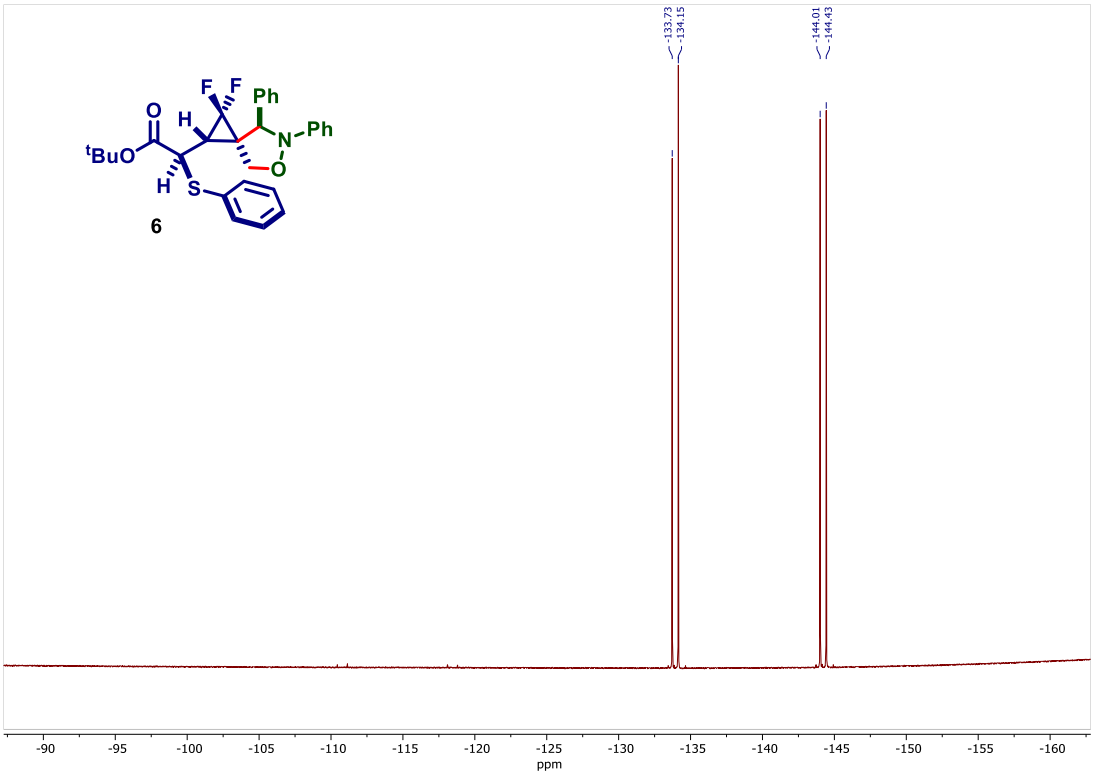
^{1}H NMR (400 MHz, $CDCl_3$) of compound **6: (*See Procedure*)**



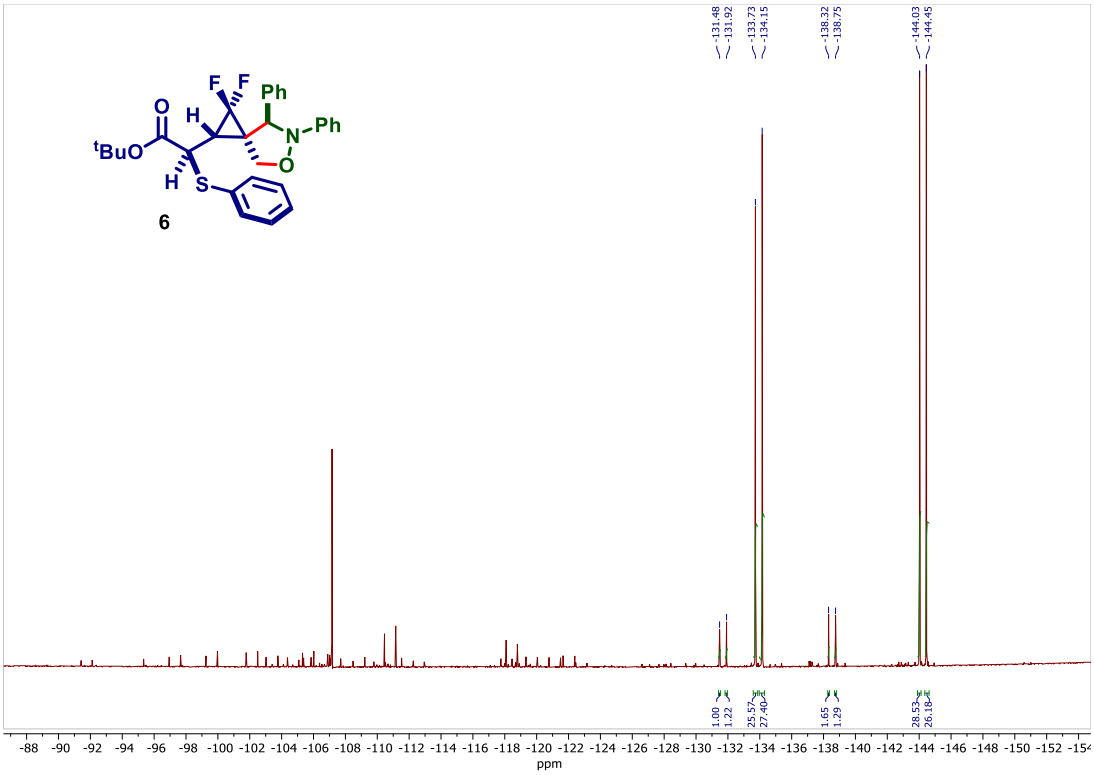
^{13}C NMR (101 MHz, $CDCl_3$) of Compound **6:**



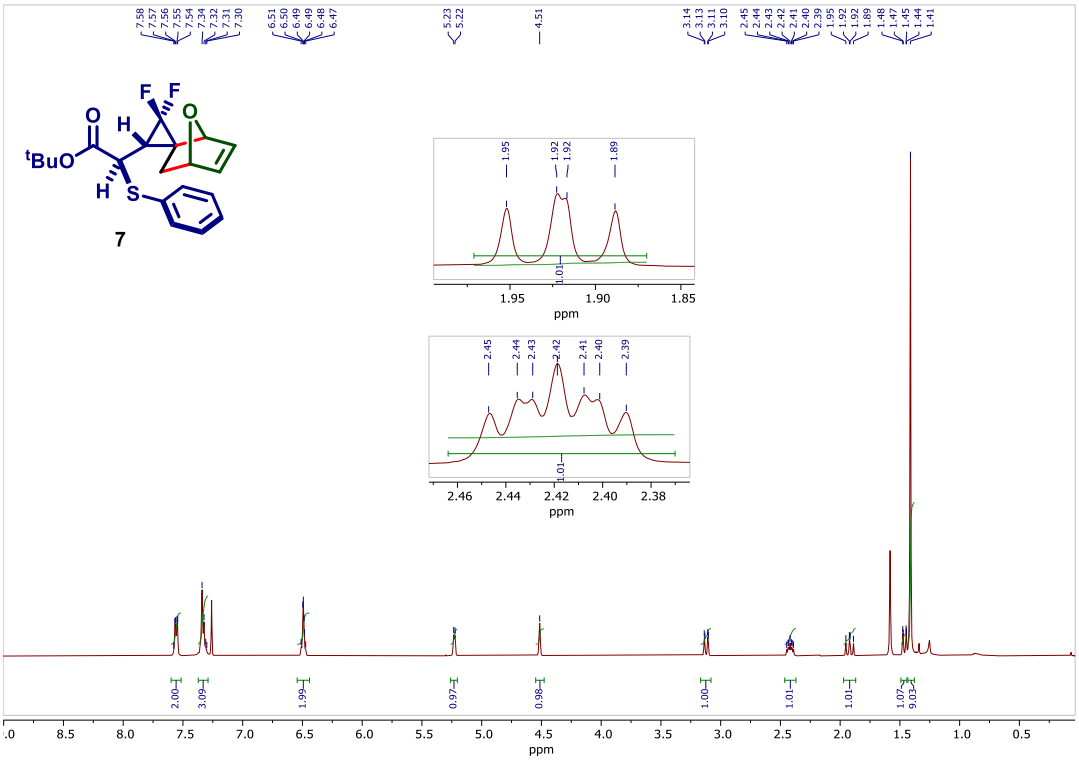
^{19}F NMR (376 MHz, $CDCl_3$) of compound **6:**



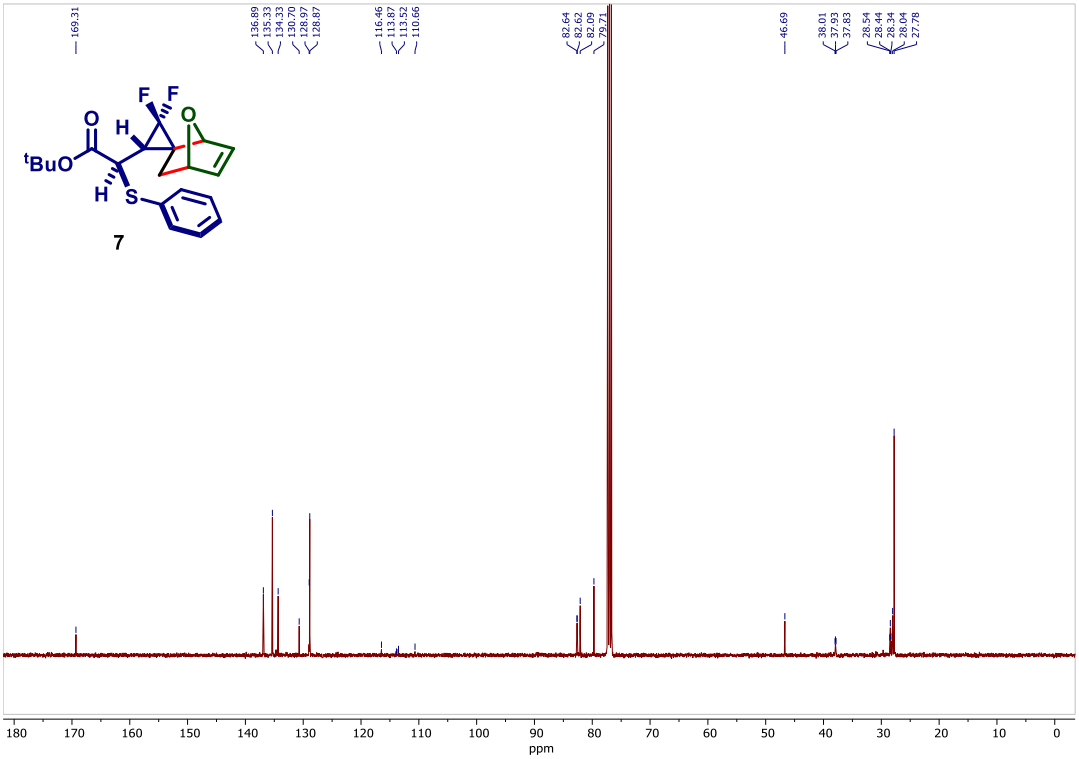
^{19}F NMR (376 MHz, $CDCl_3$) of crude reaction mixture (compound **6**)**:**



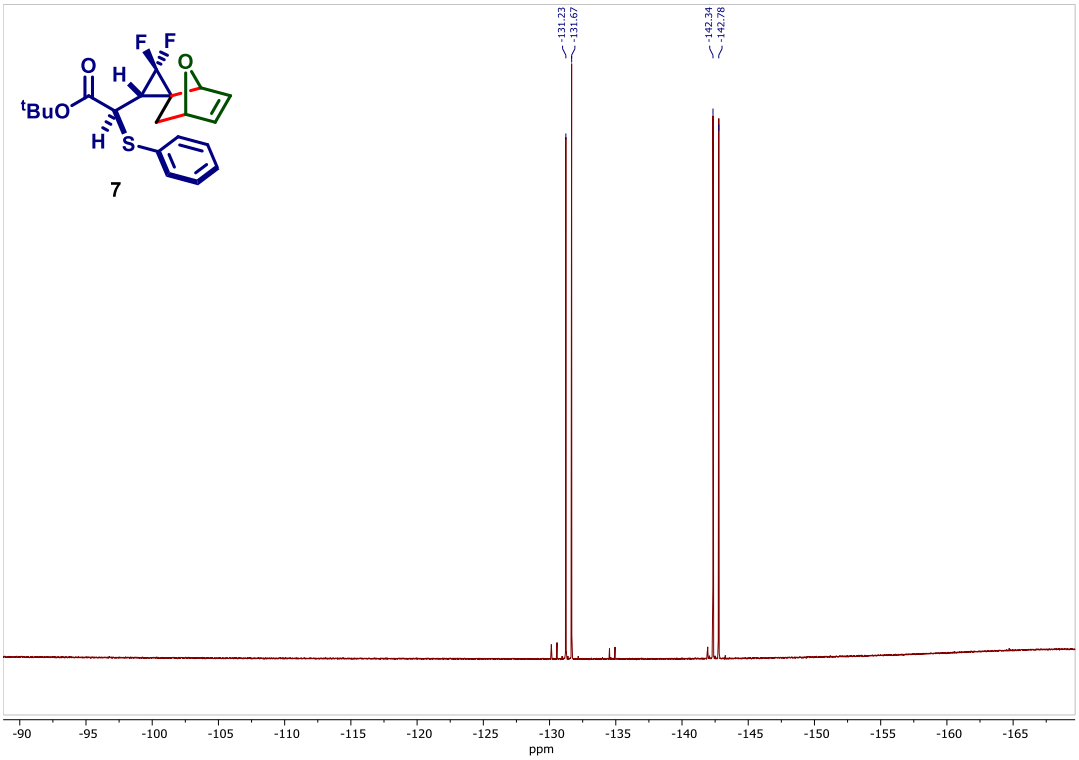
^{1}H NMR (400 MHz, $CDCl_3$) of compound **7: (*See Procedure*)**



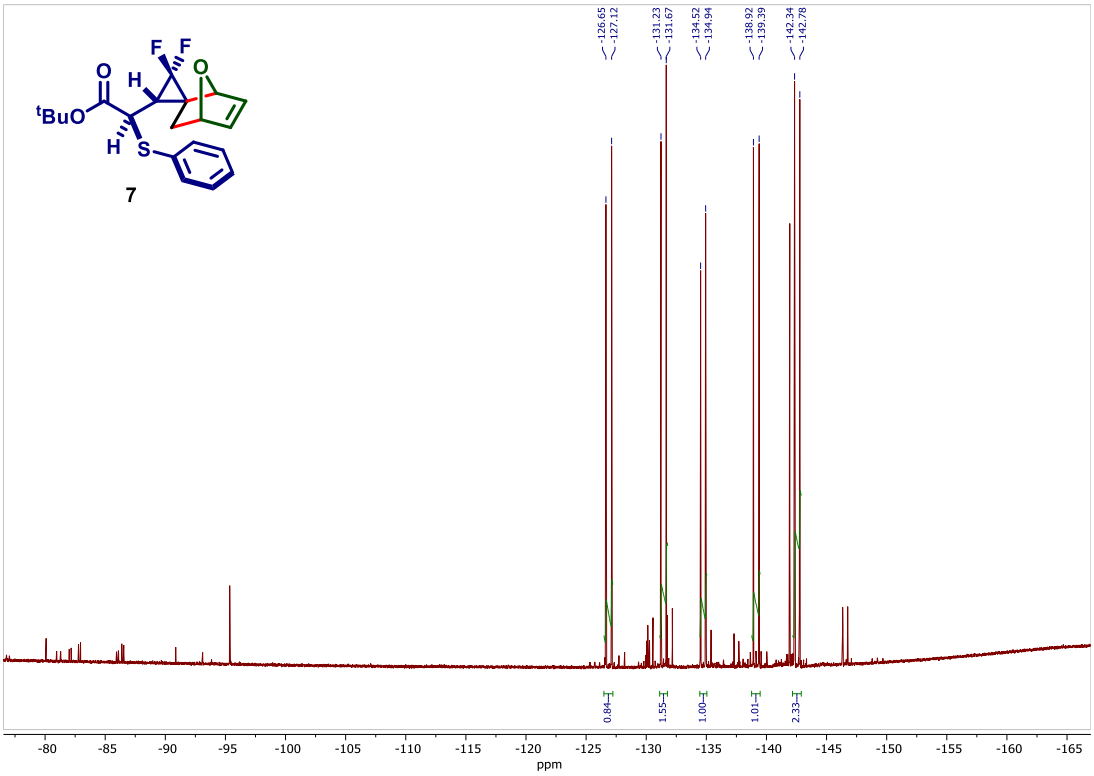
^{13}C NMR (101 MHz, $CDCl_3$) of Compound **7:**



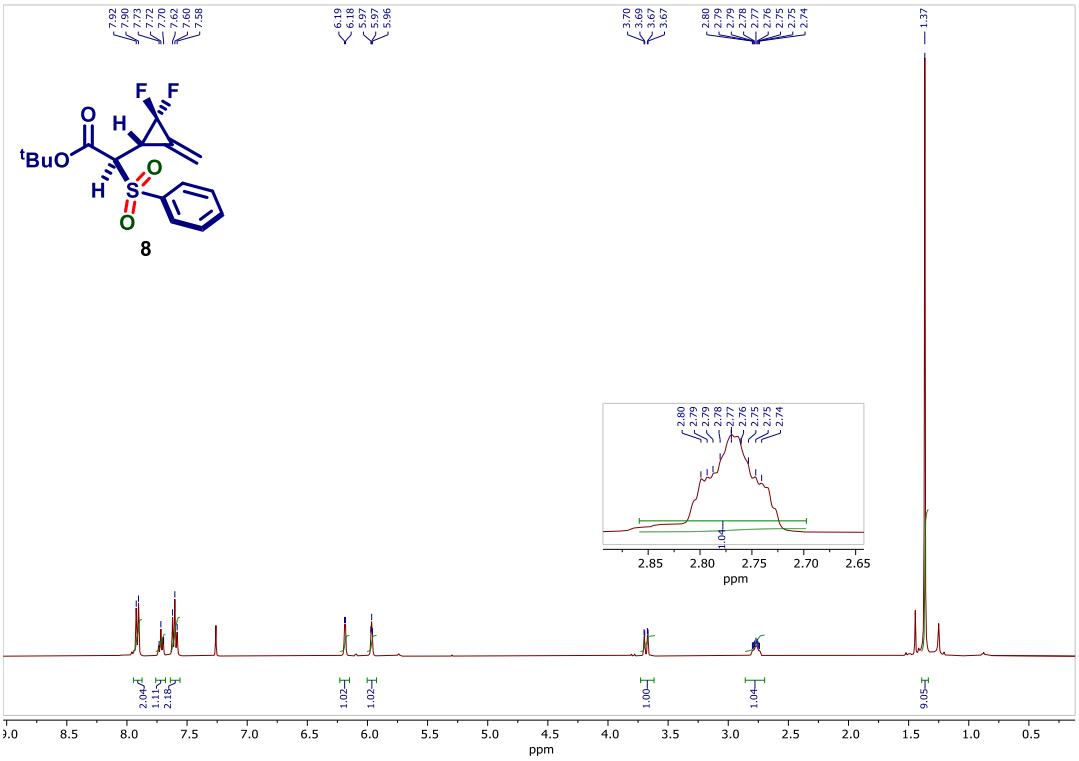
^{19}F NMR (376 MHz, $CDCl_3$) of compound **7:**



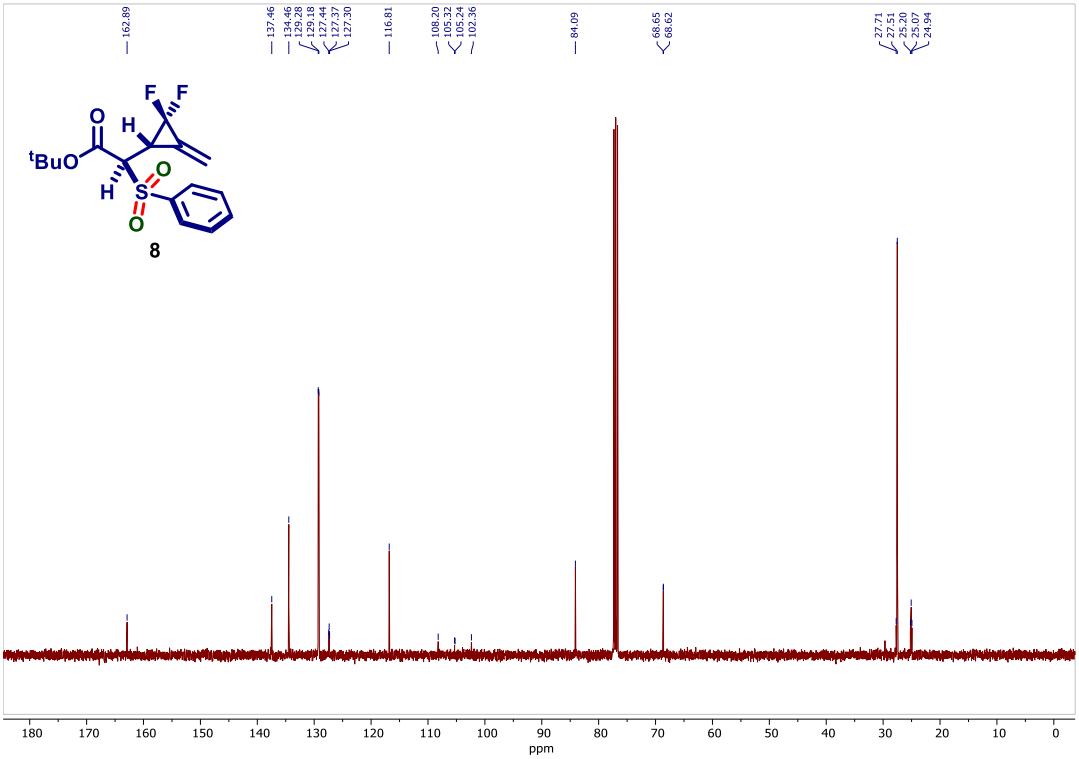
^{19}F NMR (376 MHz, $CDCl_3$) of crude reaction mixture (compound **7):**



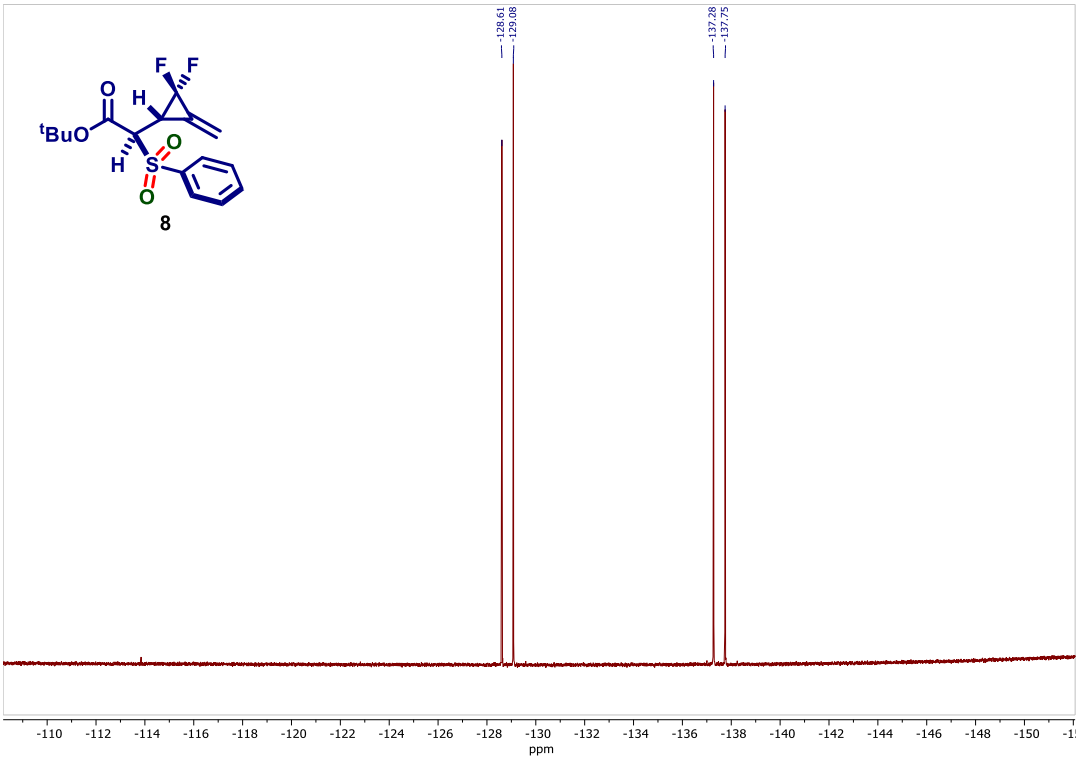
^{1}H NMR (400 MHz, $CDCl_3$) of compound **8: (***See Procedure***)**



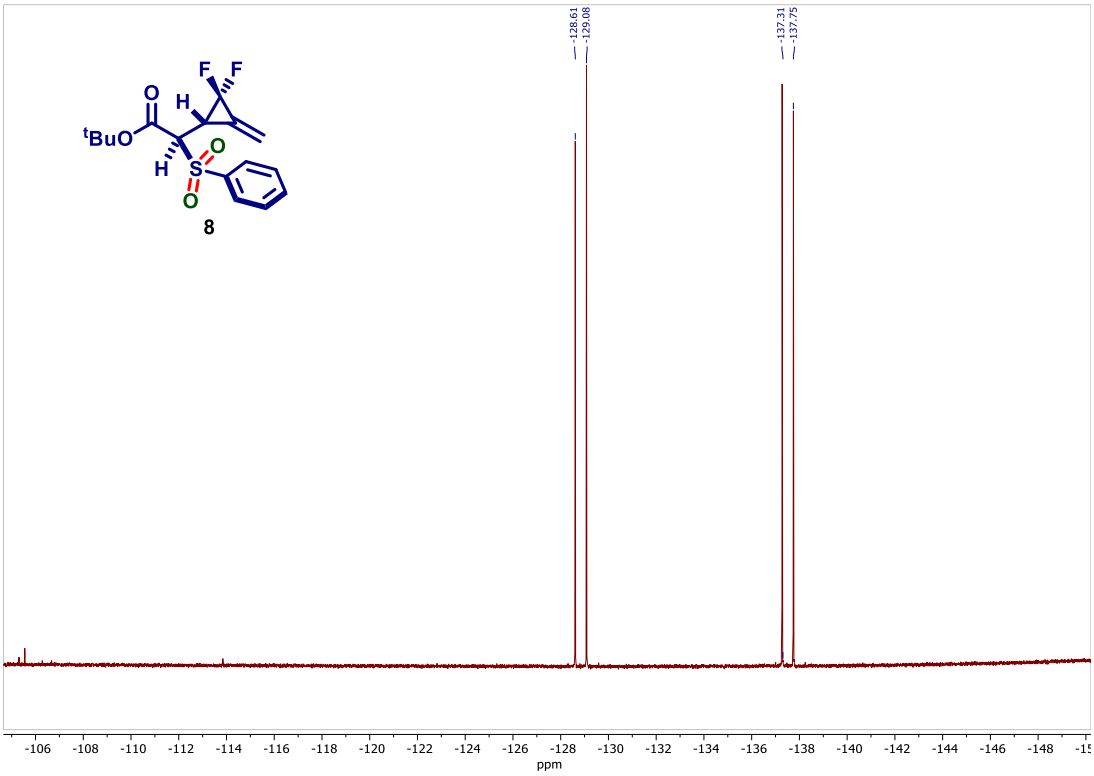
^{13}C NMR (101 MHz, $CDCl_3$) of Compound **8:**



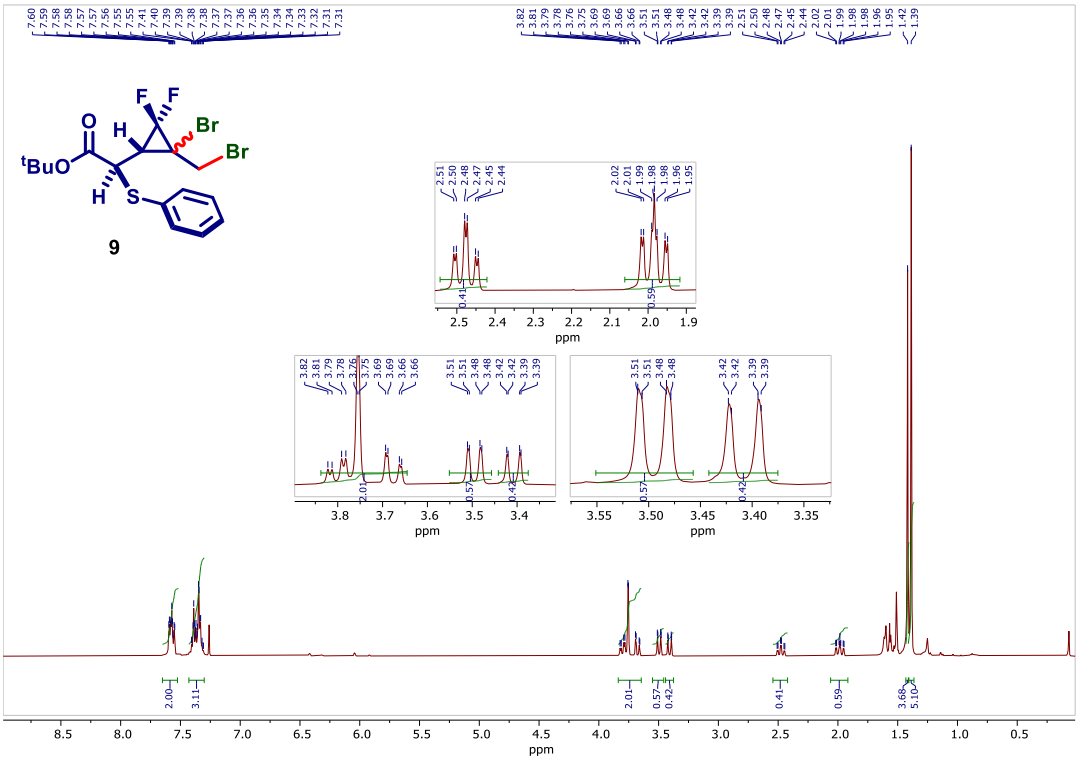
^{19}F NMR (376 MHz, $CDCl_3$) of compound **8:**



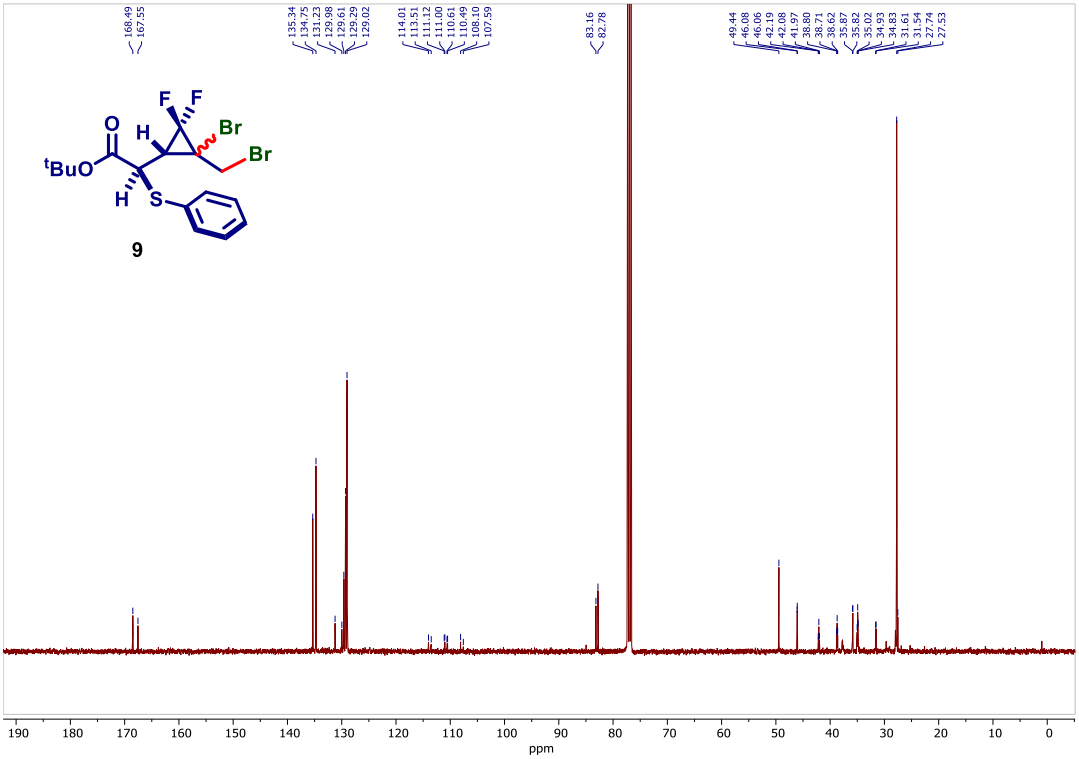
^{19}F NMR (376 MHz, $CDCl_3$) of crude reaction mixture (compound **8):**



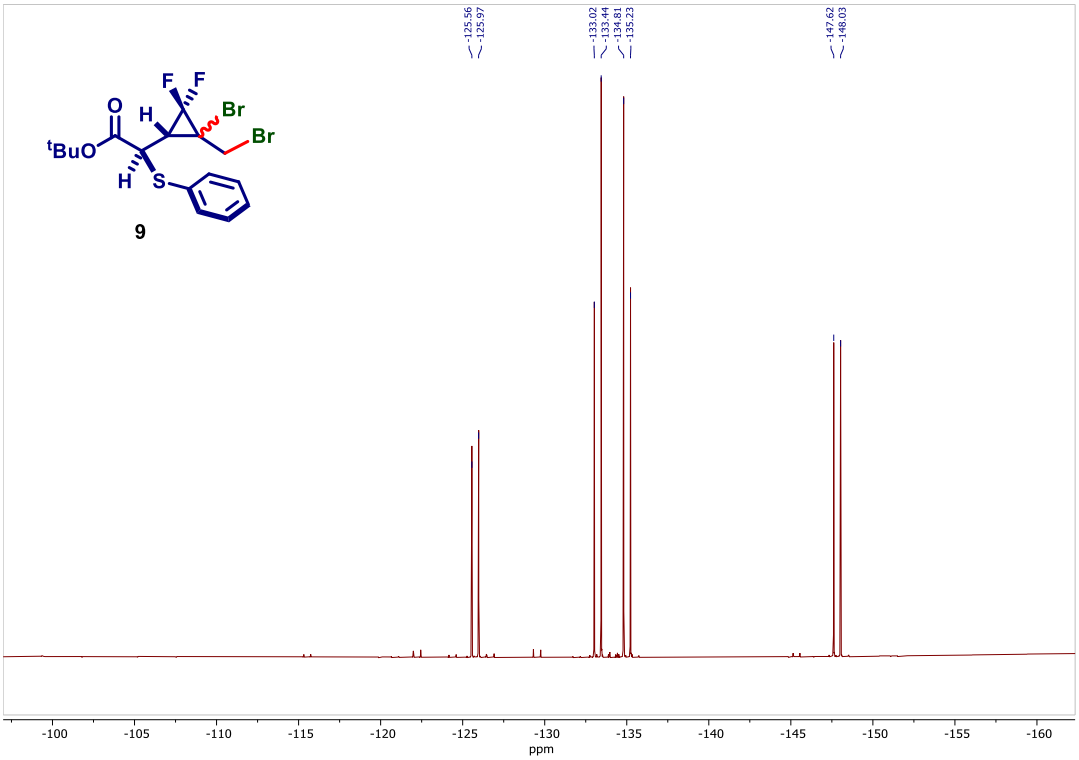
^{1}H NMR (400 MHz, $CDCl_3$) of compound **9: (*See Procedure*)**



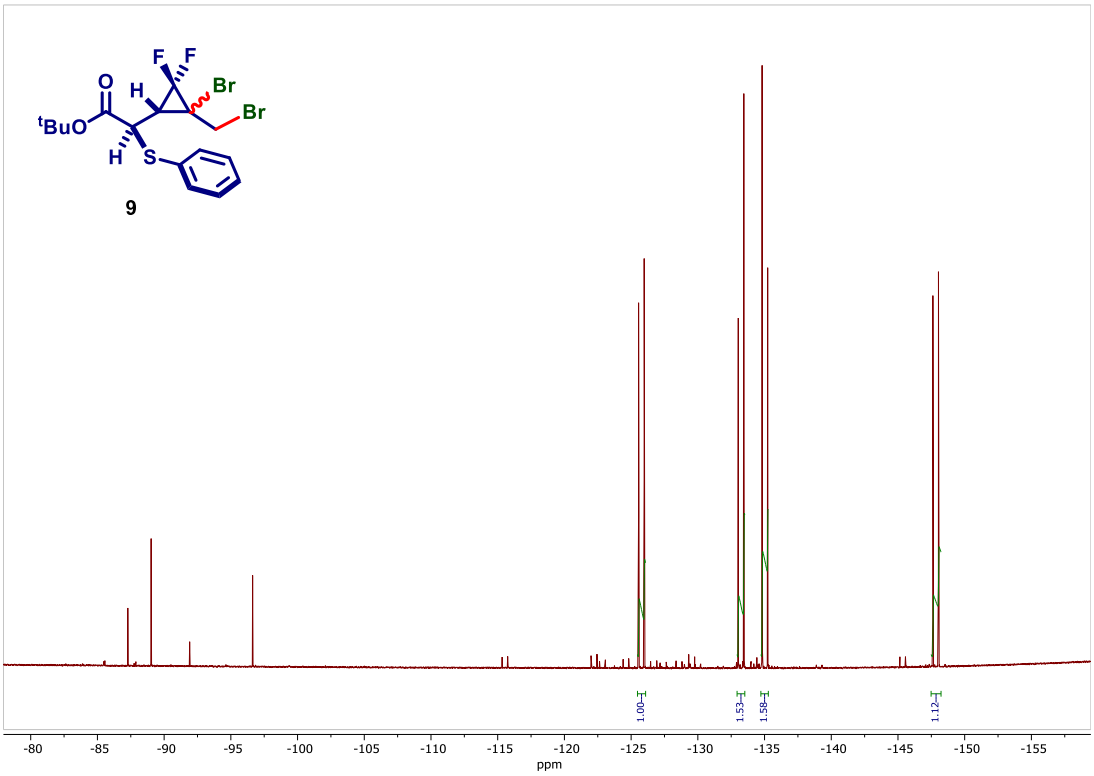
^{13}C NMR (101 MHz, $CDCl_3$) of Compound **9:**



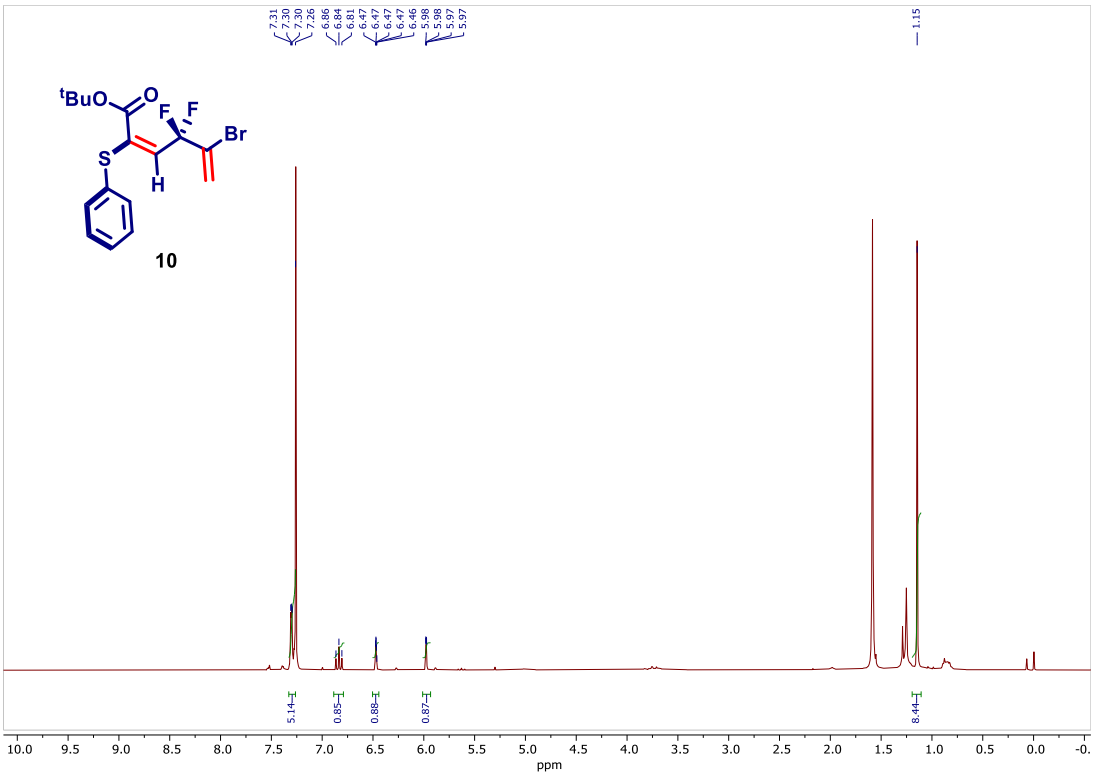
^{19}F NMR (376 MHz, $CDCl_3$) of compound **9:**



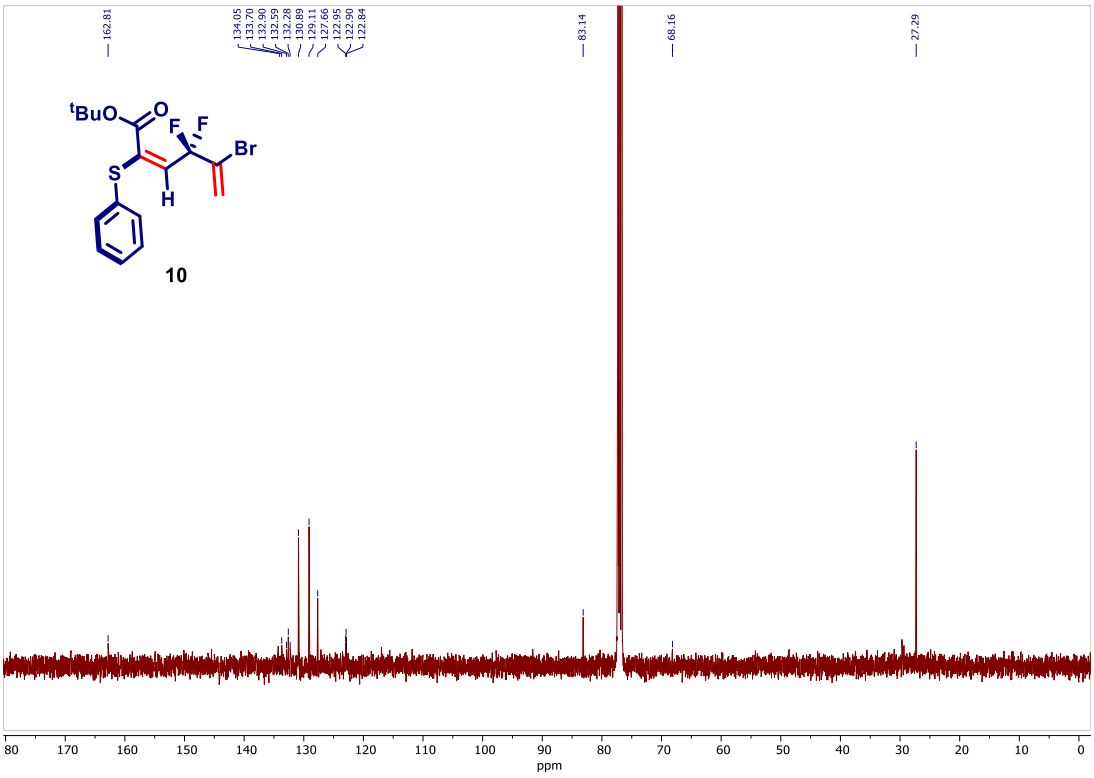
^{19}F NMR (376 MHz, $CDCl_3$) of crude reaction mixture (compound **9):**



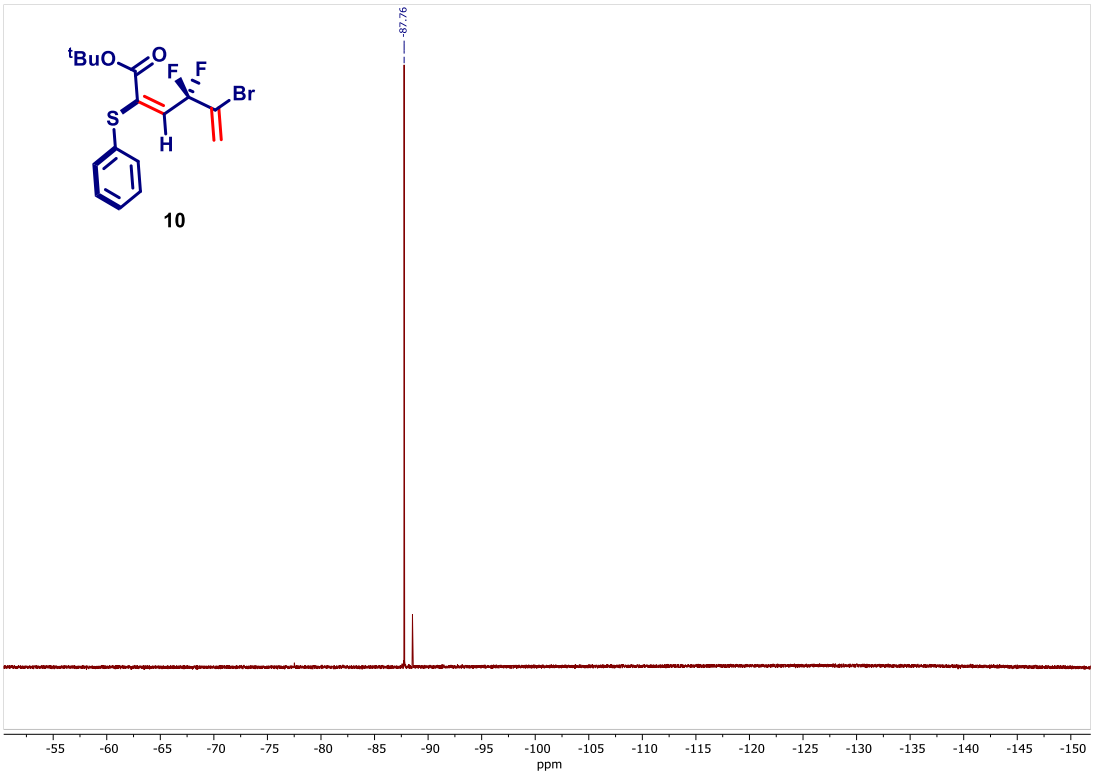
^{1}H NMR (400 MHz, $CDCl_3$) of compound **10: (*See Procedure*)**



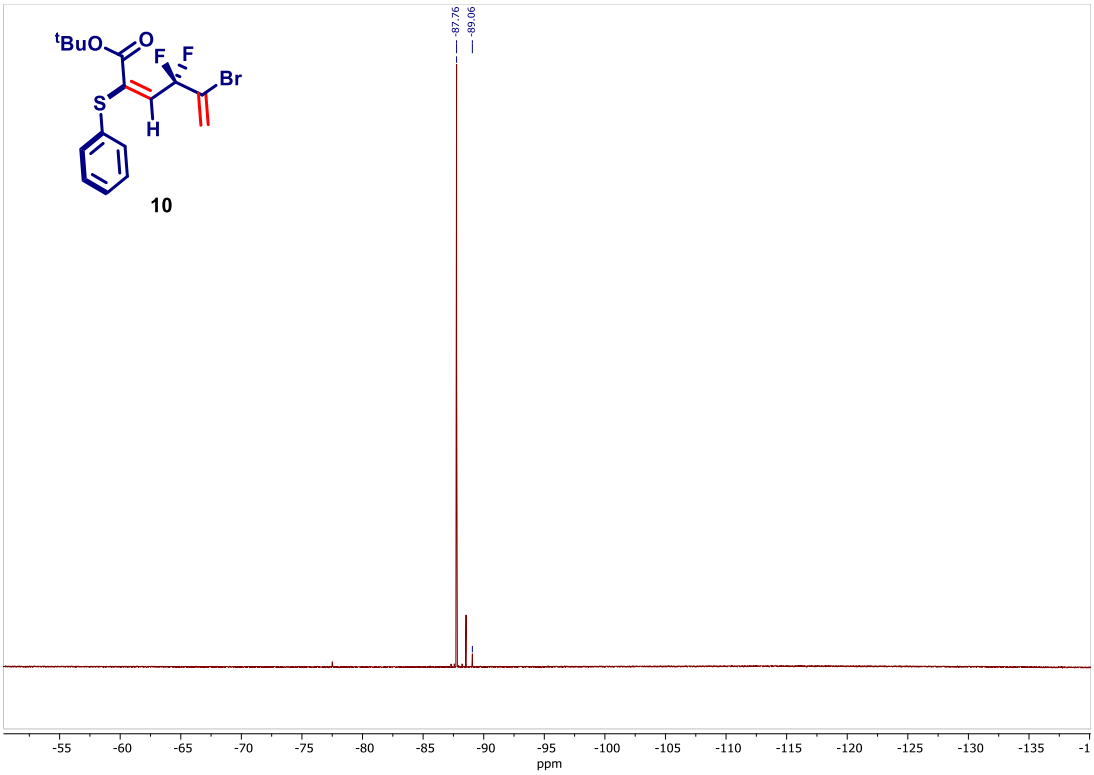
^{13}C NMR (101 MHz, $CDCl_3$) of Compound **10:**



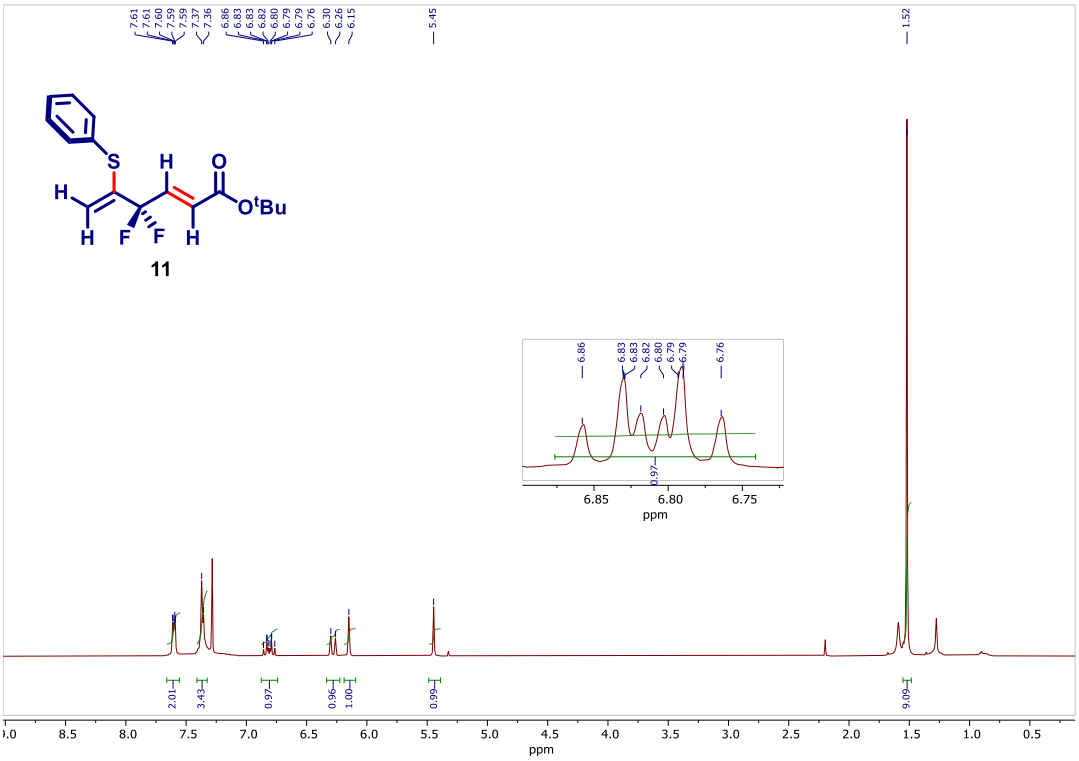
^{19}F NMR (376 MHz, $CDCl_3$) of compound **10:**



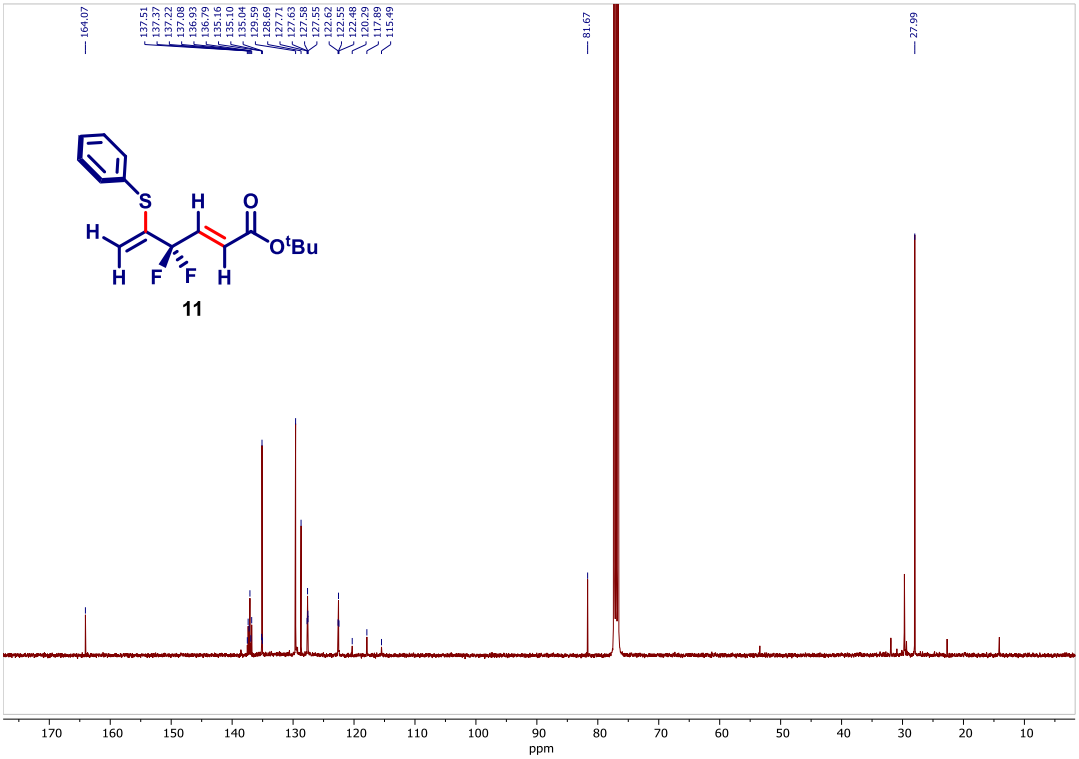
^{19}F NMR (376 MHz, $CDCl_3$) of crude reaction mixture (compound **10**)**:**



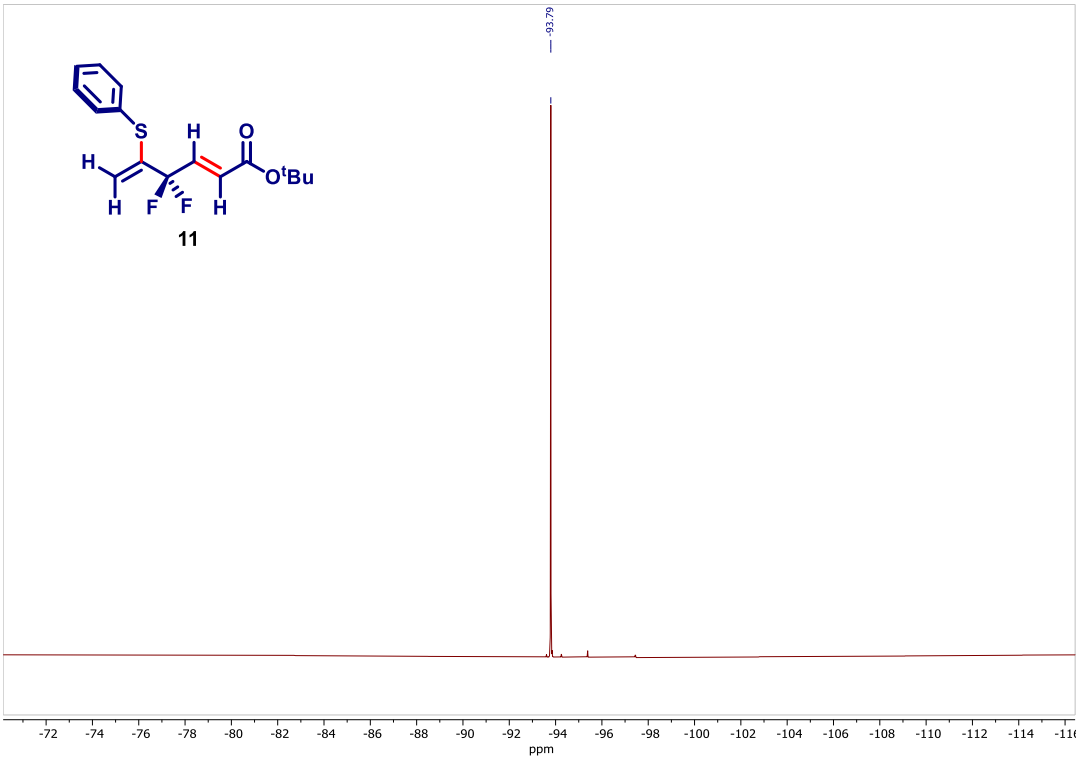
^{1}H NMR (400 MHz, $CDCl_3$) of compound **11: (***See Procedure***)**



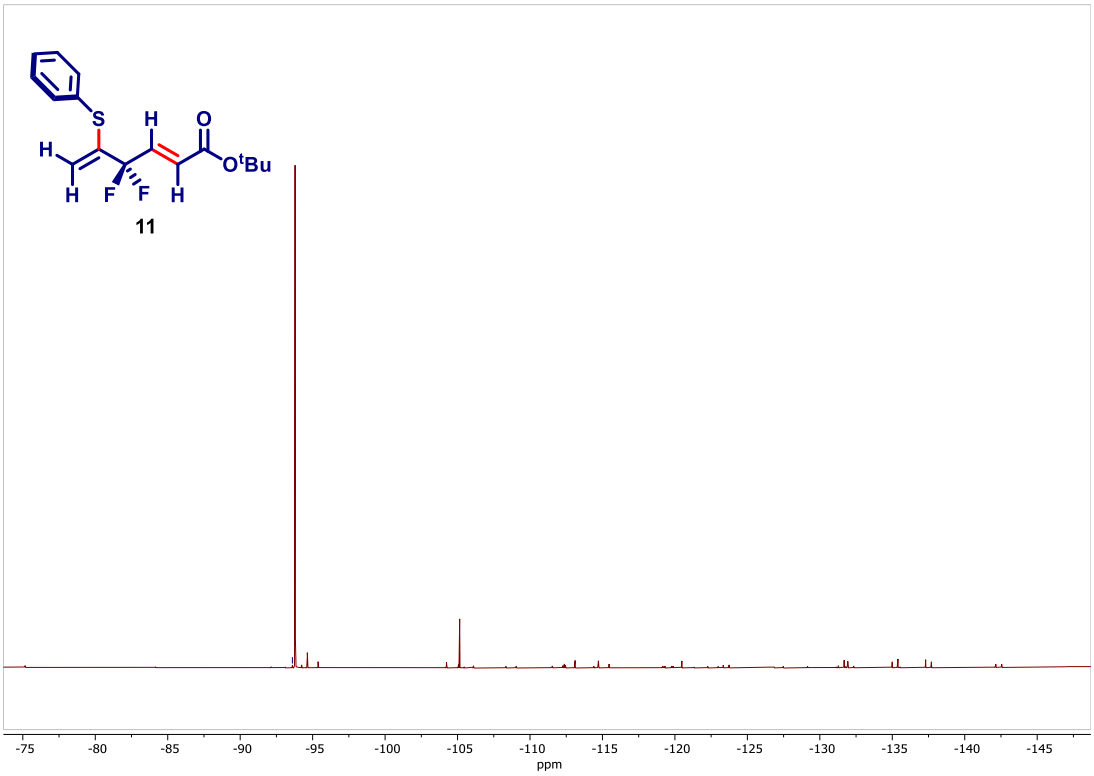
^{13}C NMR (101 MHz, $CDCl_3$) of Compound **11:**



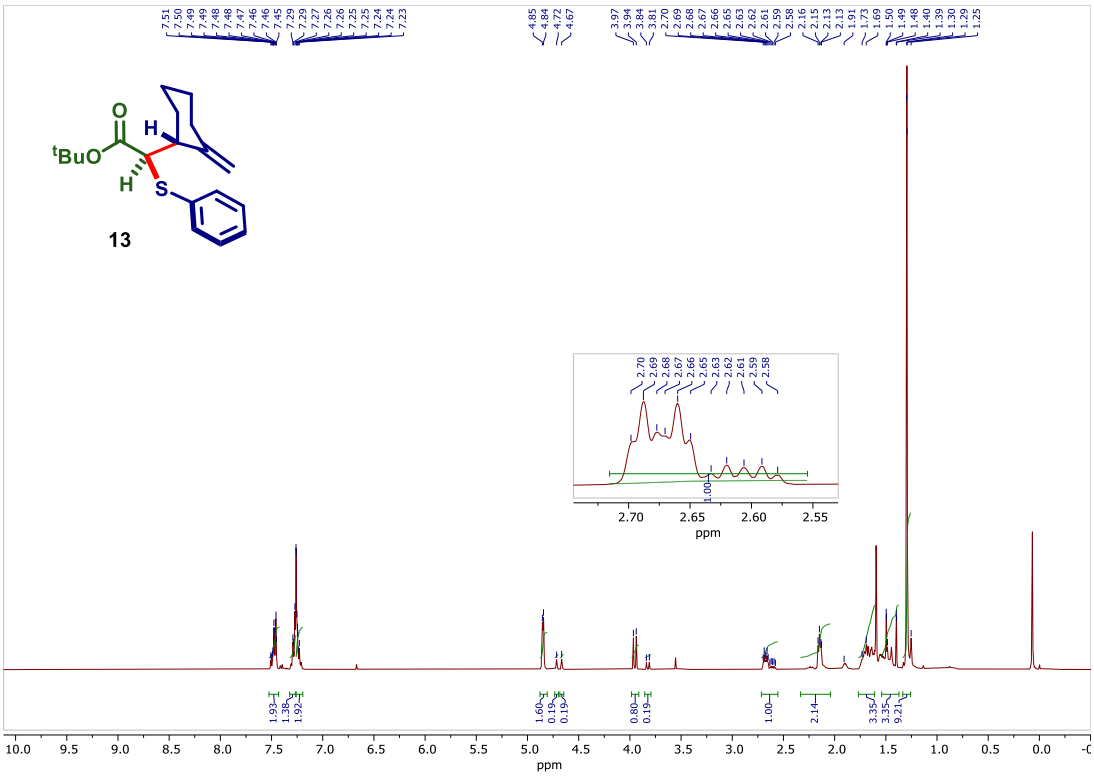
^{19}F NMR (376 MHz, $CDCl_3$) of compound **11:**



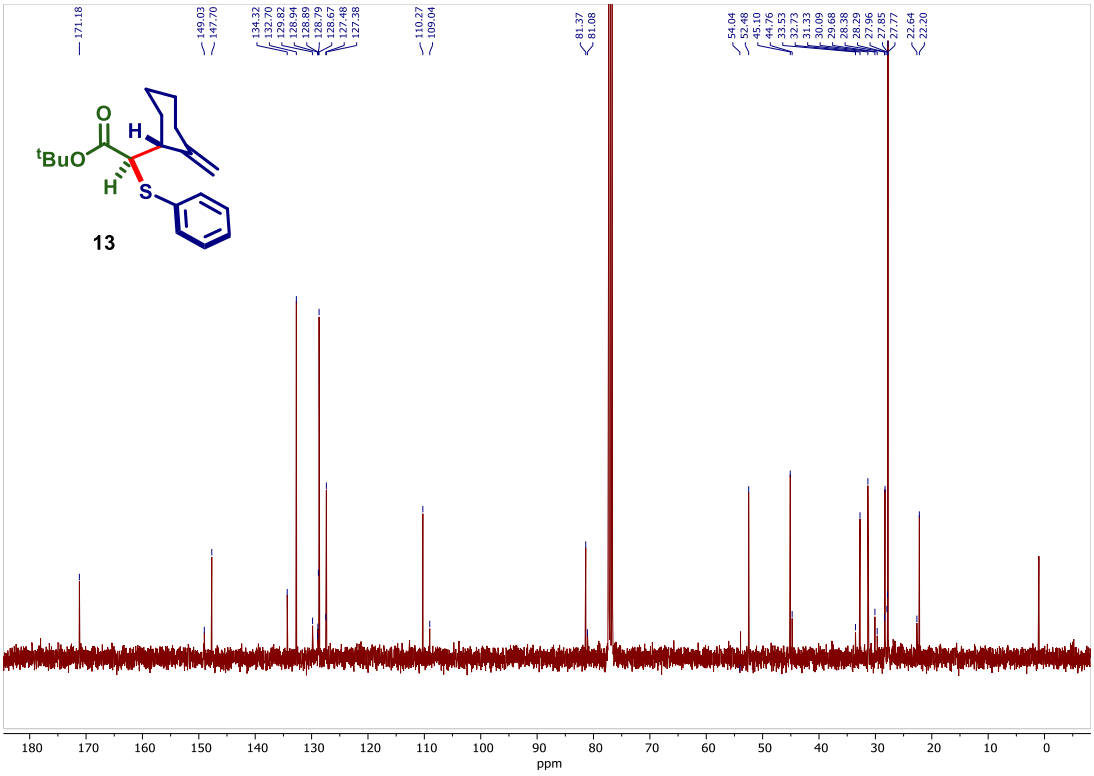
^{19}F NMR (376 MHz, $CDCl_3$) of crude reaction mixture (compound **11):**



^{1}H NMR (400 MHz, $CDCl_3$) of compound **13: (*See Procedure*)**



^{13}C NMR (101 MHz, $CDCl_3$) of Compound **13:**



^{1}H NMR (400 MHz, $CDCl_3$) of crude reaction mixture (compound **13**)**:**