Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supporting Information

Ligand-free copper-catalyzed borylative defluorination: Access to gem-difluoroallyl boronic acid derivatives

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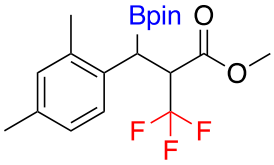
I. Mechanistic Study

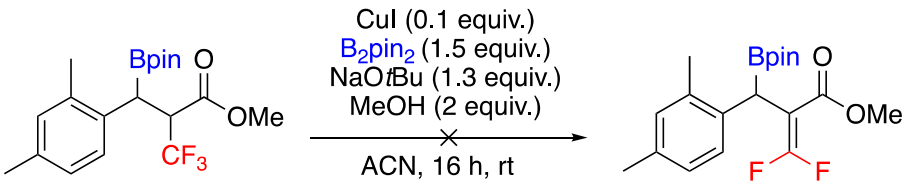
Procedure for the synthesis of borylated product 2b':

To a flame-dried 1 dram vial equipped with a stir bar was added copper iodide (0.1 equiv, 0.050 mmol), bis(pinacolato)diboron (1.5 equiv, 0.75 mmol), and sodium carbonate (1.3 equiv, 0.65 mmol). The vial was capped with a septa and purged with argon. Dry acetonitrile (2.0 mL) was added, followed by the ester **1b** (1.0 equiv, 0.50 mmol) and methanol (2.0 equiv, 1.0 mmol). The argon line was removed and the septum covered with parafilm. The reaction was stirred at room temperature for 16 h. Celite was added to the reaction mixture and the solvent removed *in vacuo*. The reaction mixture was purified via column chromatography (solid loading) to yield the corresponding borylated trifluoroalkene **2b'**.



methyl 2-((2,4-dimethylphenyl)(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)-3,3,3-trifluoropropanoate (2b'). Colorless oil, 23% (44 mg). Purified on silica gel using DCM:Hexanes 1:4. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.07 (d, J = 7.8 Hz, 1H), 6.93 – 6.91 (m, 1H), 6.91 – 6.87 (m, 1H), 3.92 (dq, J = 12.3, 7.8 Hz, 1H), 3.40 (s, 3H), 3.20 (d, J = 12.4 Hz, 1H), 2.34 (s, 3H), 2.23 (s, 3H), 1.14 (s, 6H), 1.10 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ167.7 (q, J = 3.2 Hz), 136.8, 135.7, 132.1, 131.5, 127.6 (br. s), 126.7, 125.1 (q, J = 281.1 Hz), 84.0, 52.5 (q, J = 26.4 Hz), 52.3, 24.44, 24.43, 21.05, 20.18. ^{19}F NMR (376 MHz, $CDCl_3$) δ -67.22 (d, J = 7.7 Hz). ^{11}B NMR (128 MHz, $cdcl_3$) δ 32.4. HRMS: (ESI) m/z: $[M + H]^+$ calcd for $C_{19}H_{27}BF_3O_4$ 387.1952; Found 387.1953.

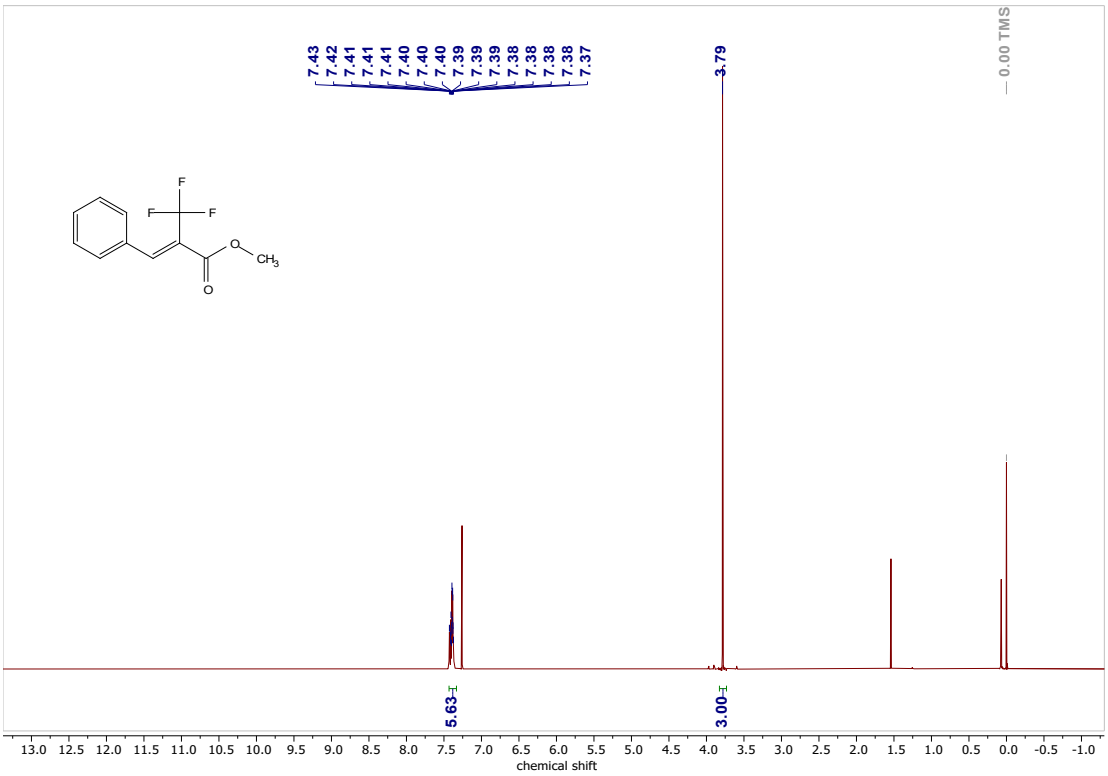
Procedure for the mechanistic study:



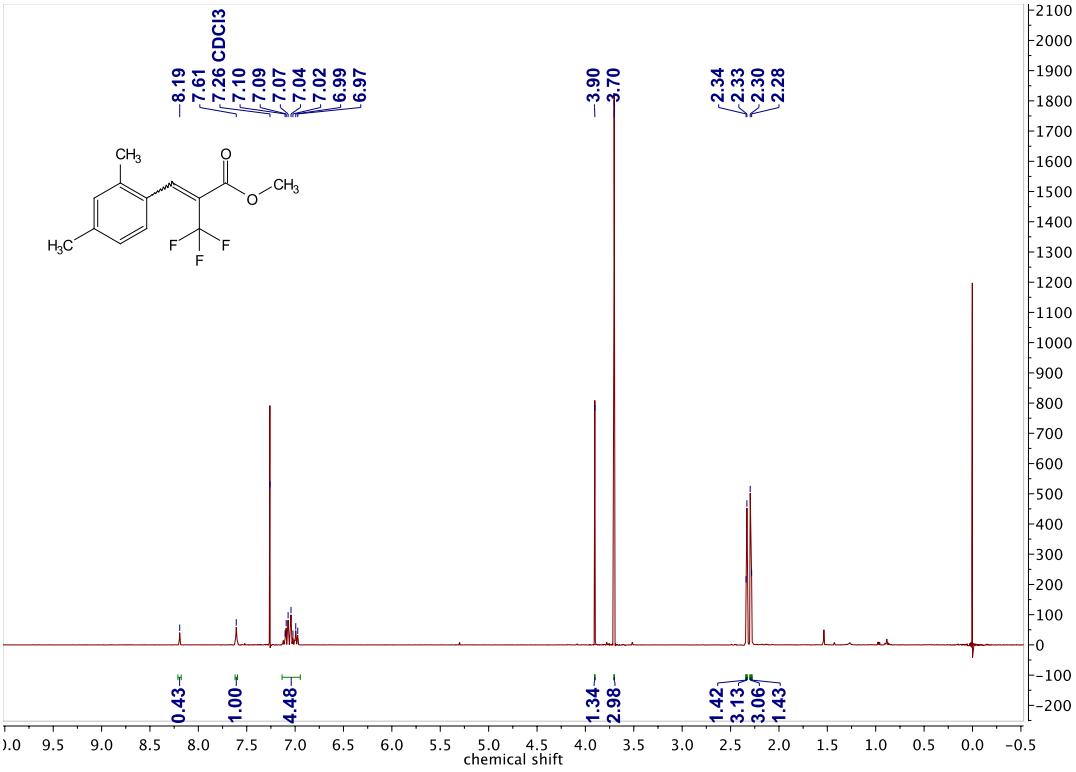
To a flame-dried 1 dram vial equipped with a stir bar was added copper iodide (0.1 equiv, 0.020 mmol), powdered 4 Å molecular sieves (0.050 g/0.20 mmol), bis(pinacolato)diboron (1.5 equiv, 0.30 mmol), and sodium *tert*-butoxide (1.3 equiv, 0.26 mmol). The vial was capped with a septa and purged with argon. Dry acetonitrile (0.80 mL) was added, followed by the ester **1b** (1.0 equiv, 0.20 mmol) and methanol (2.0 equiv, 0.40 mmol). The argon line was removed and the septum covered with parafilm. The reaction was stirred at room temperature for 16 h. The reaction was filtered through a small pad of celite, rinsing with EtOAc, and the solvent removed *in vacuo*. The crude reaction mixture was dissolved in $CDCl_3$ and evaluated by ^{19}F NMR. Only starting material **1b** was observed.

II NMR Spectra

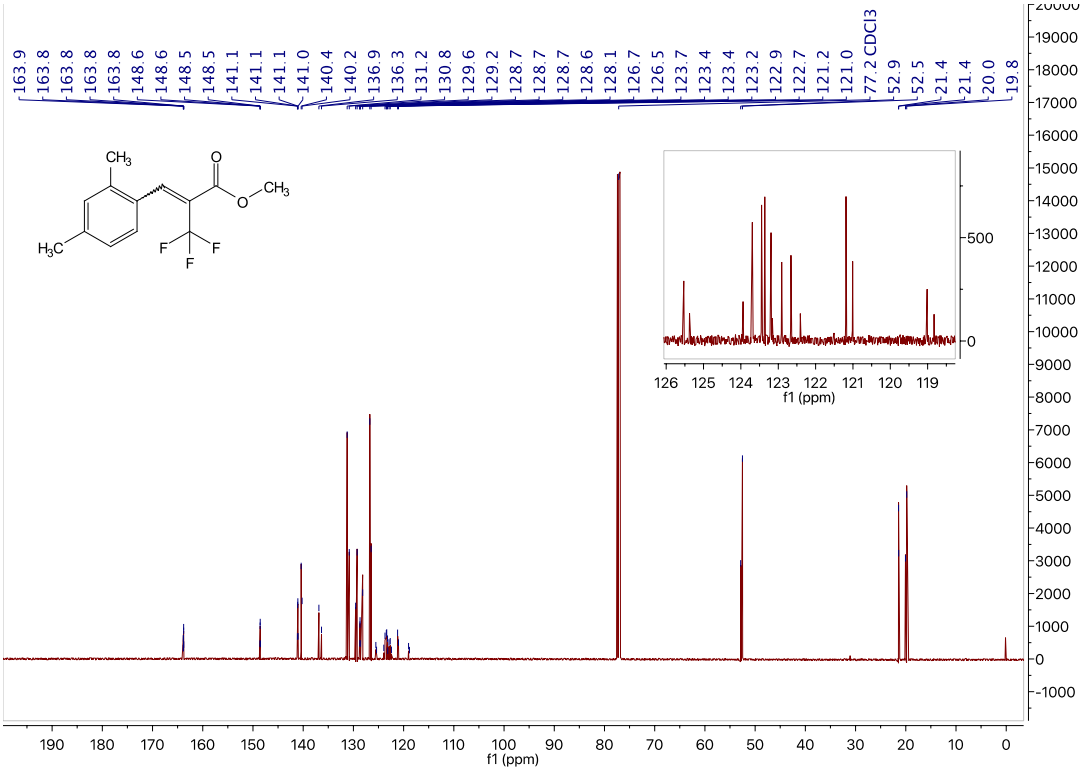
1a – ^{1}H NMR



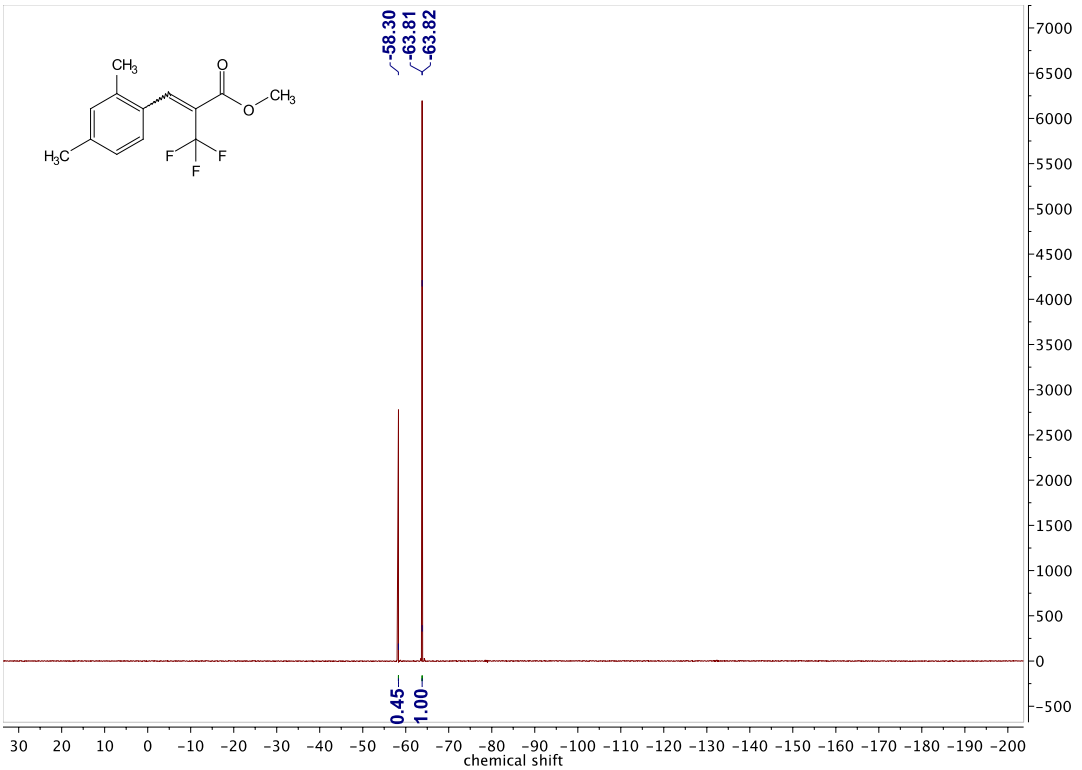
1b – ^{1}H NMR



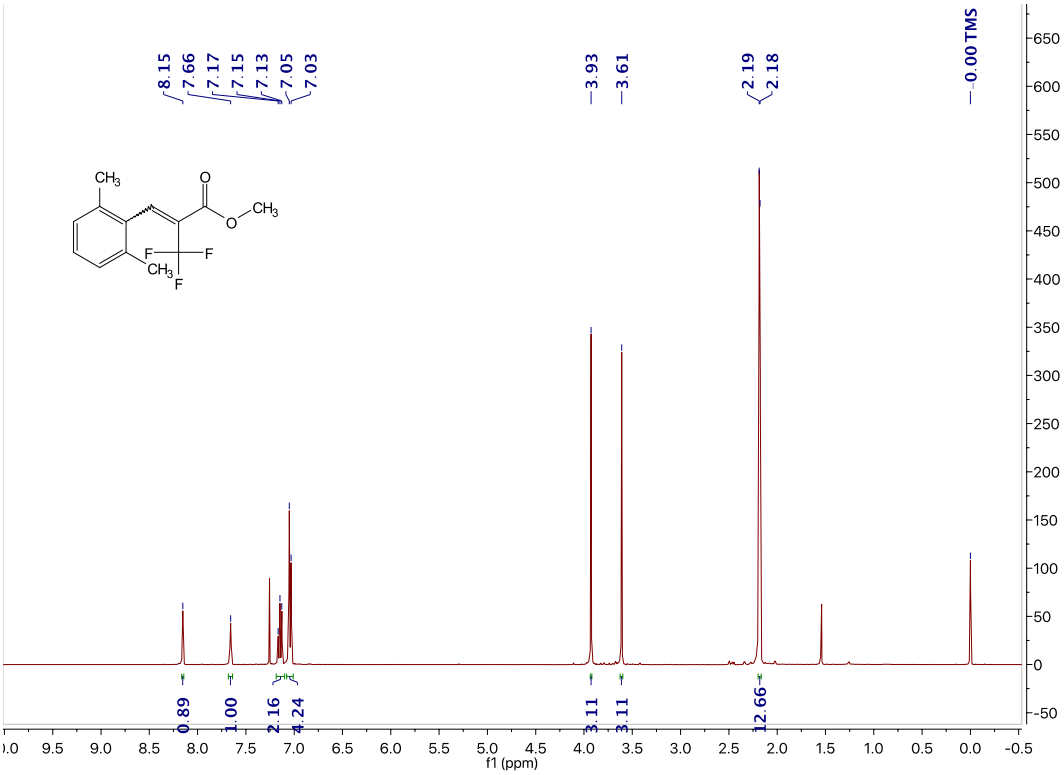
1b – ^{13}C NMR



1b – ^{19}F NMR



1c – ^{1}H NMR



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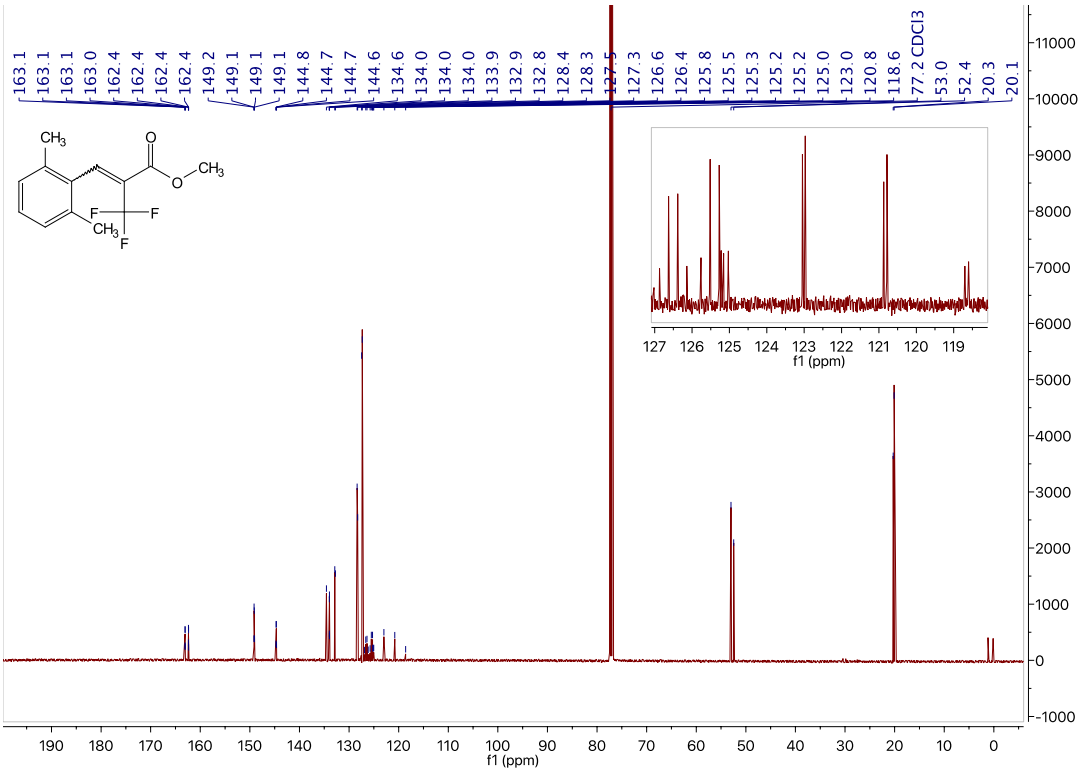

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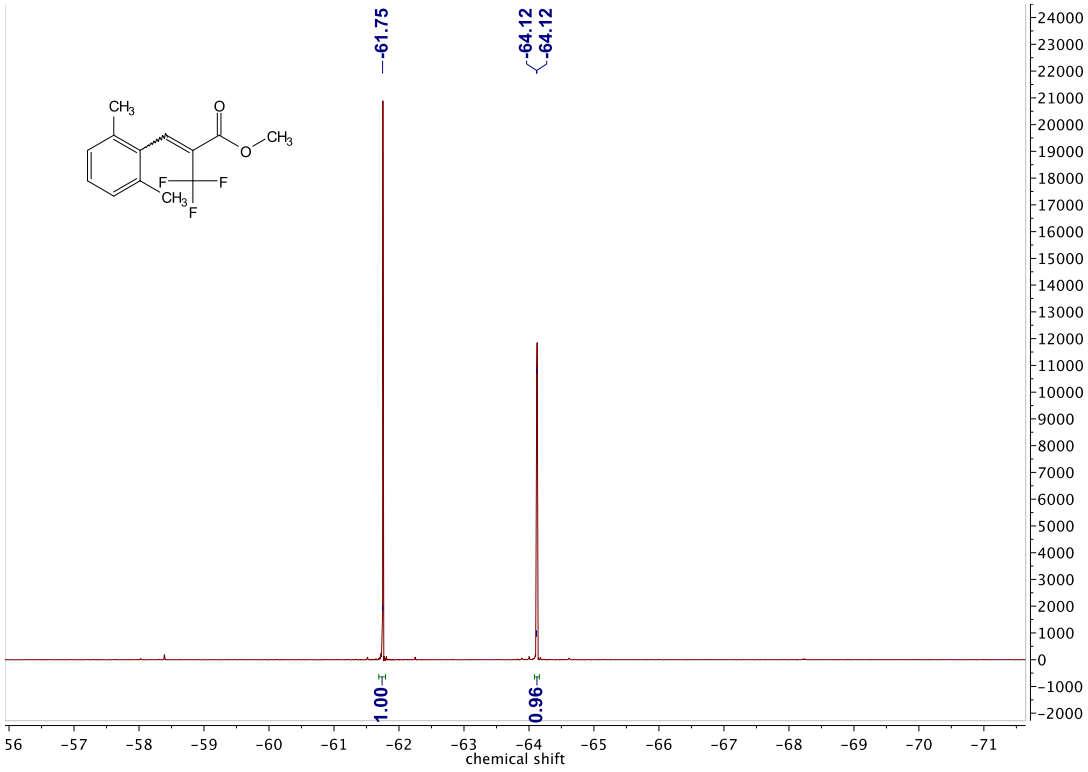
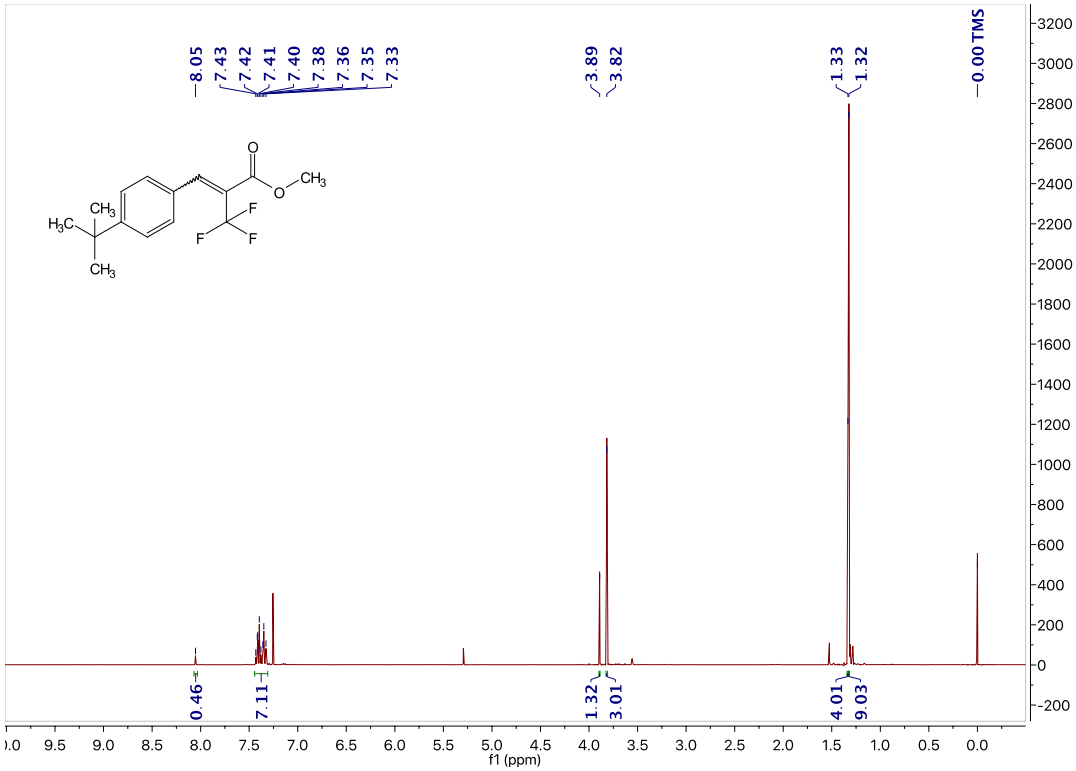


1d – ^{1}H NMR



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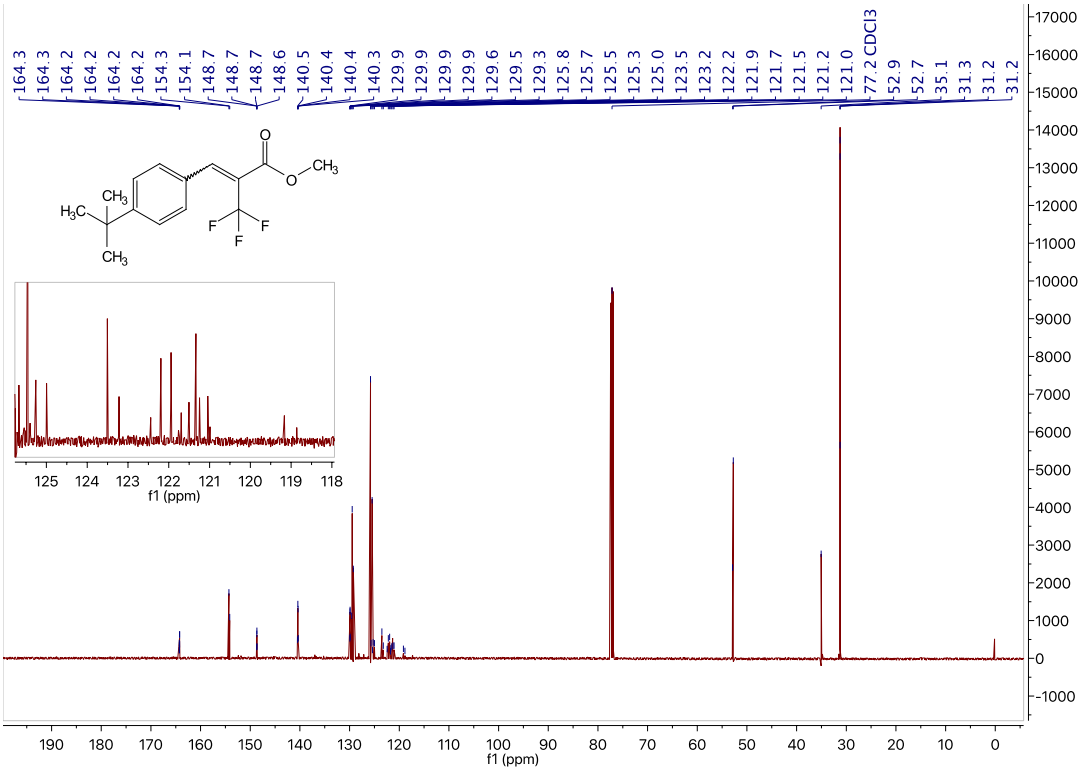

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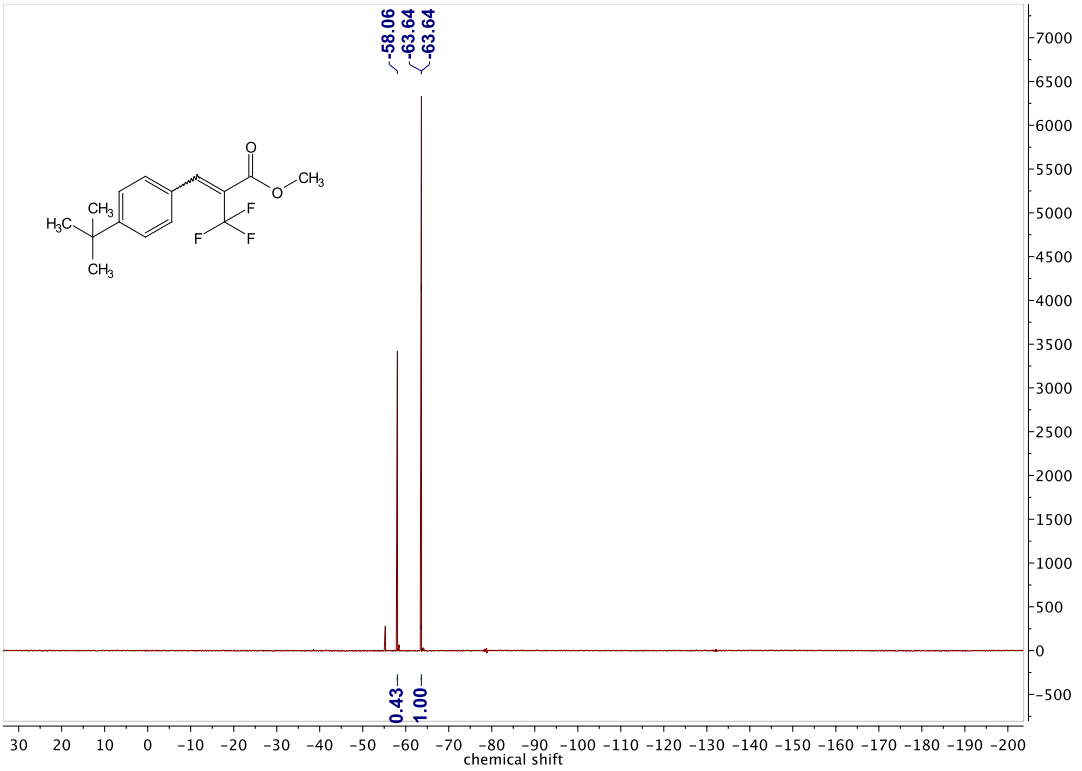
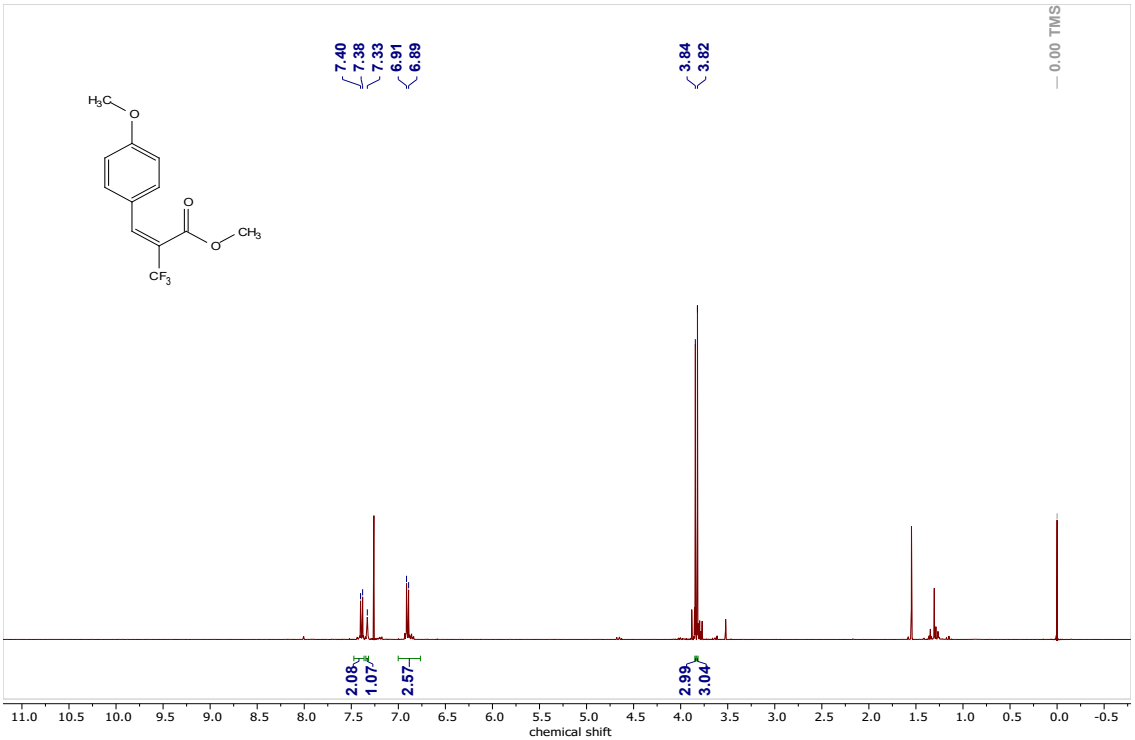


1e – ^{1}H NMR



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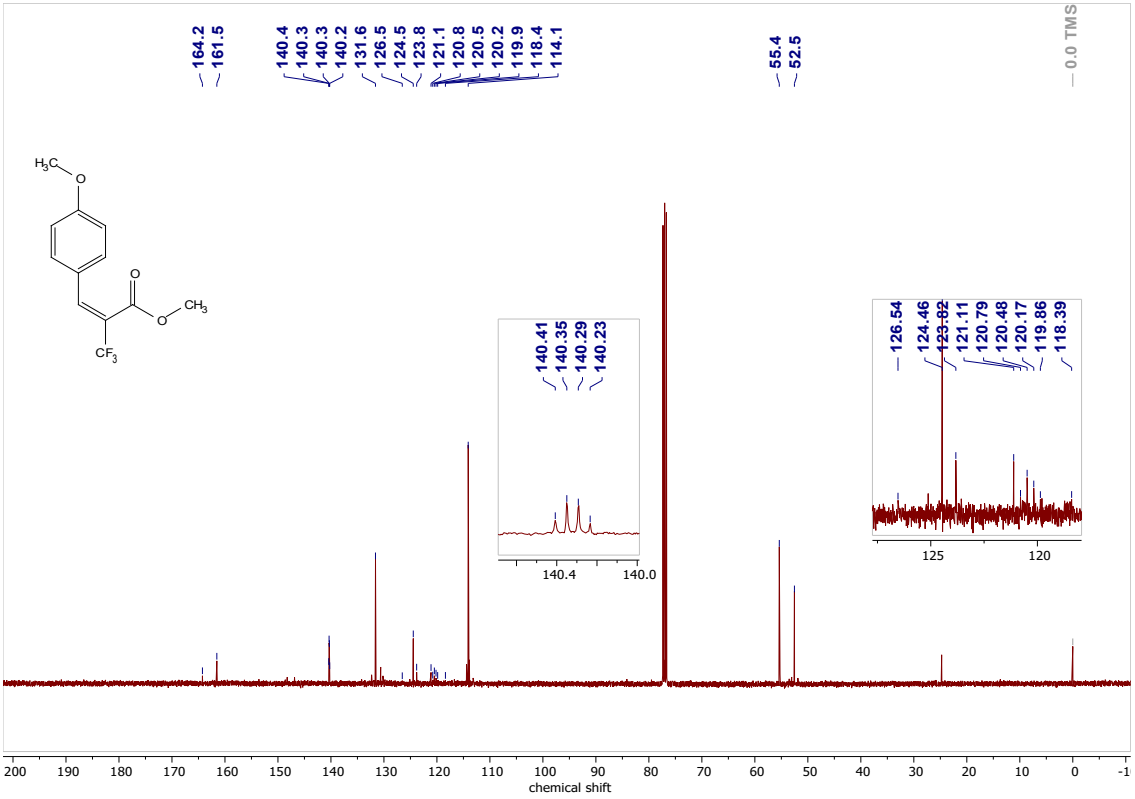
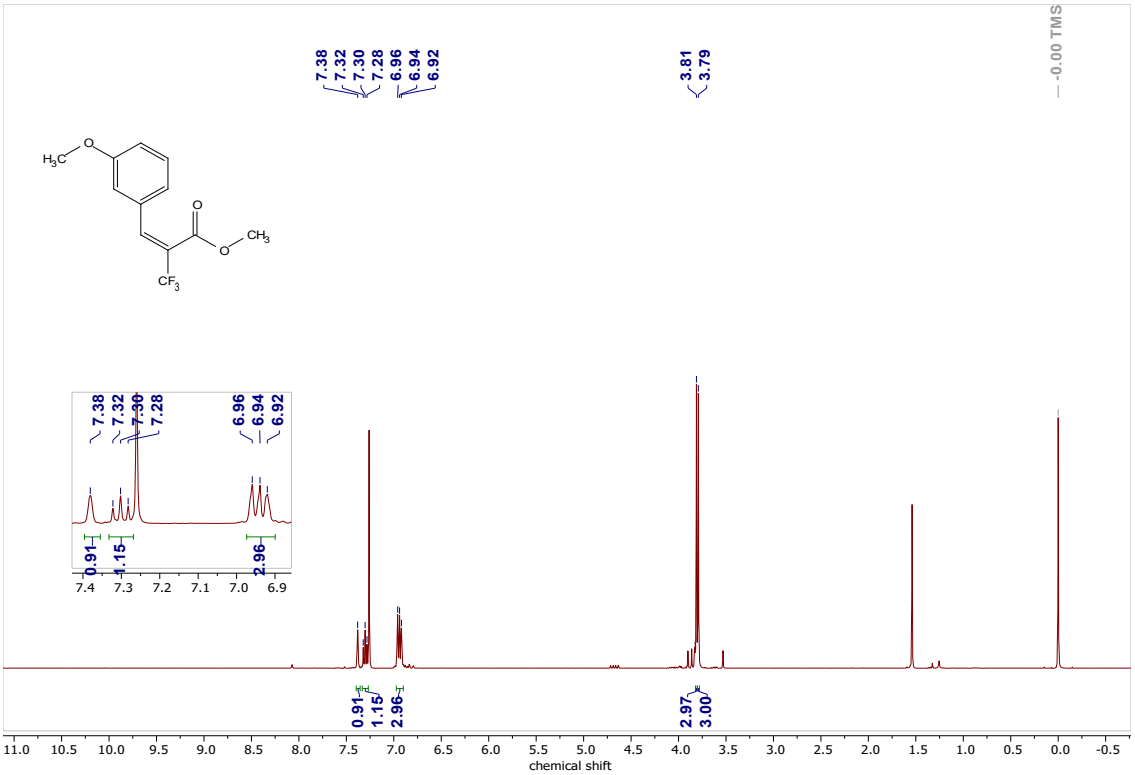
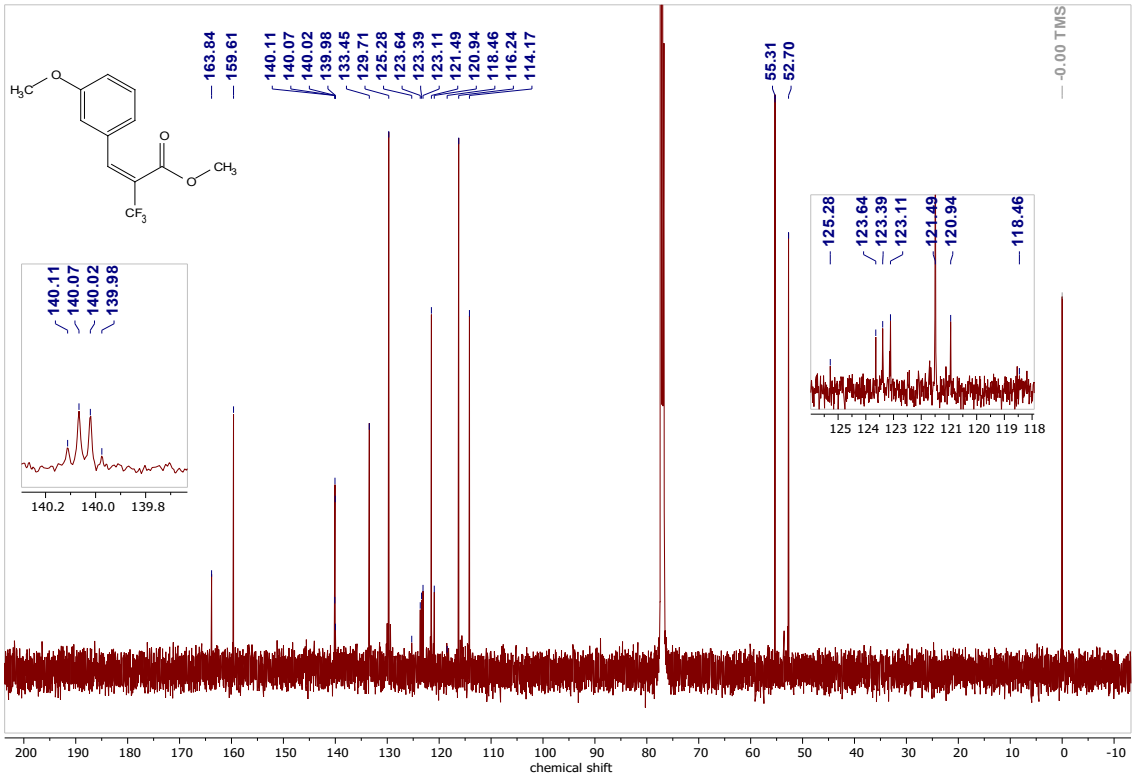


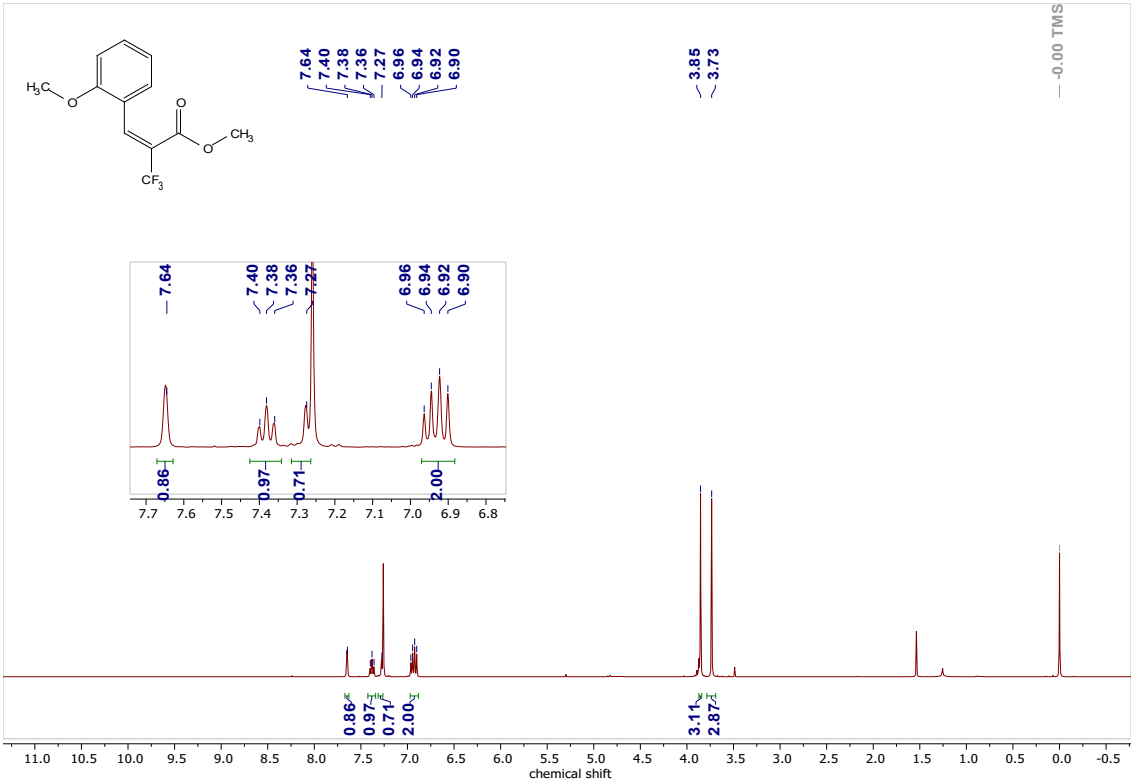
1f – ^{1}H NMR



1f – ^{13}C NMR



1g – ^{1}H NMR



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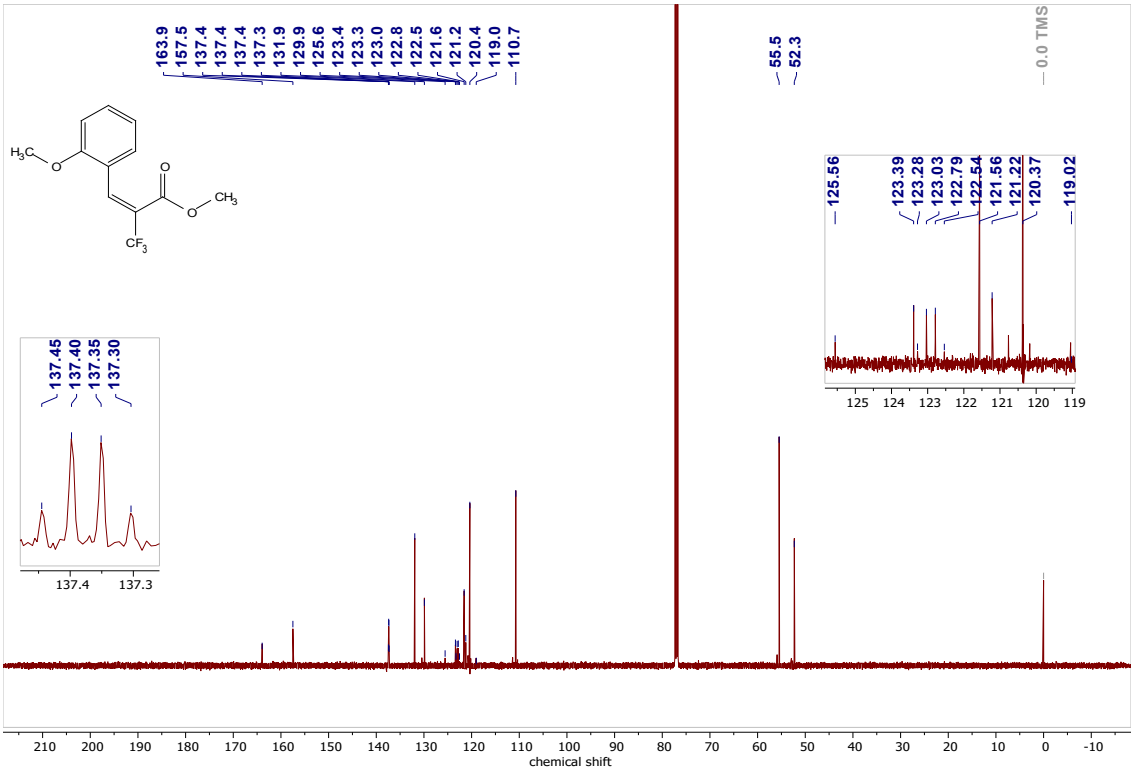
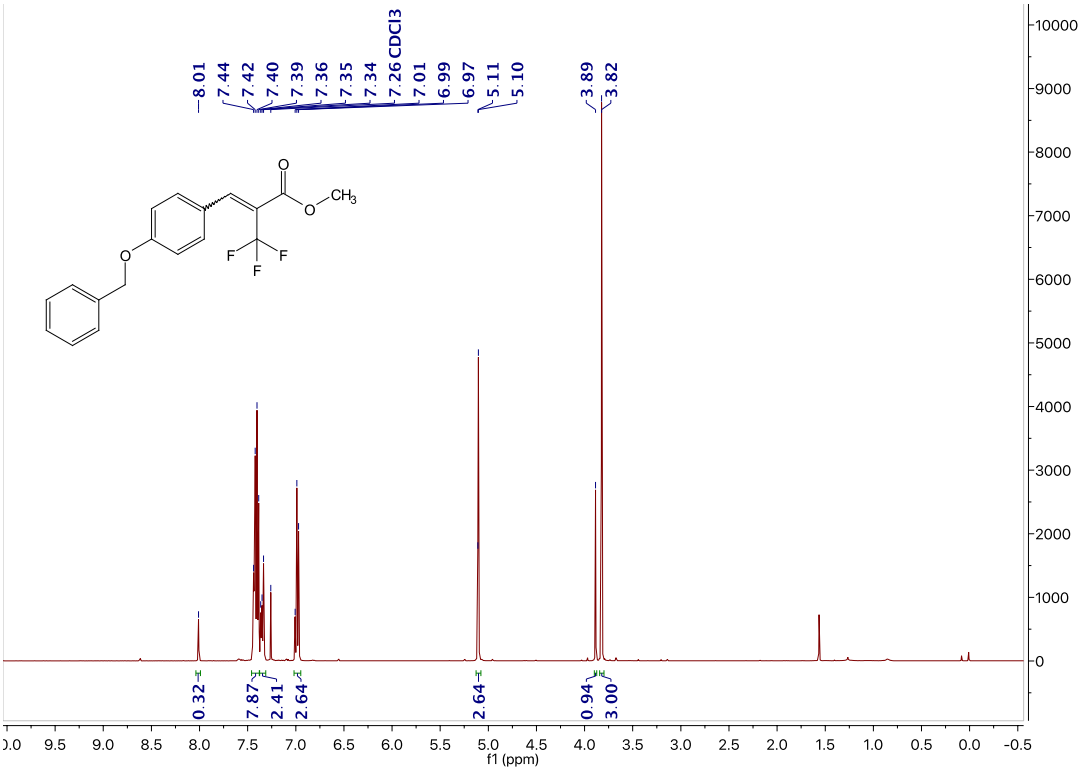


1h – ^{1}H NMR



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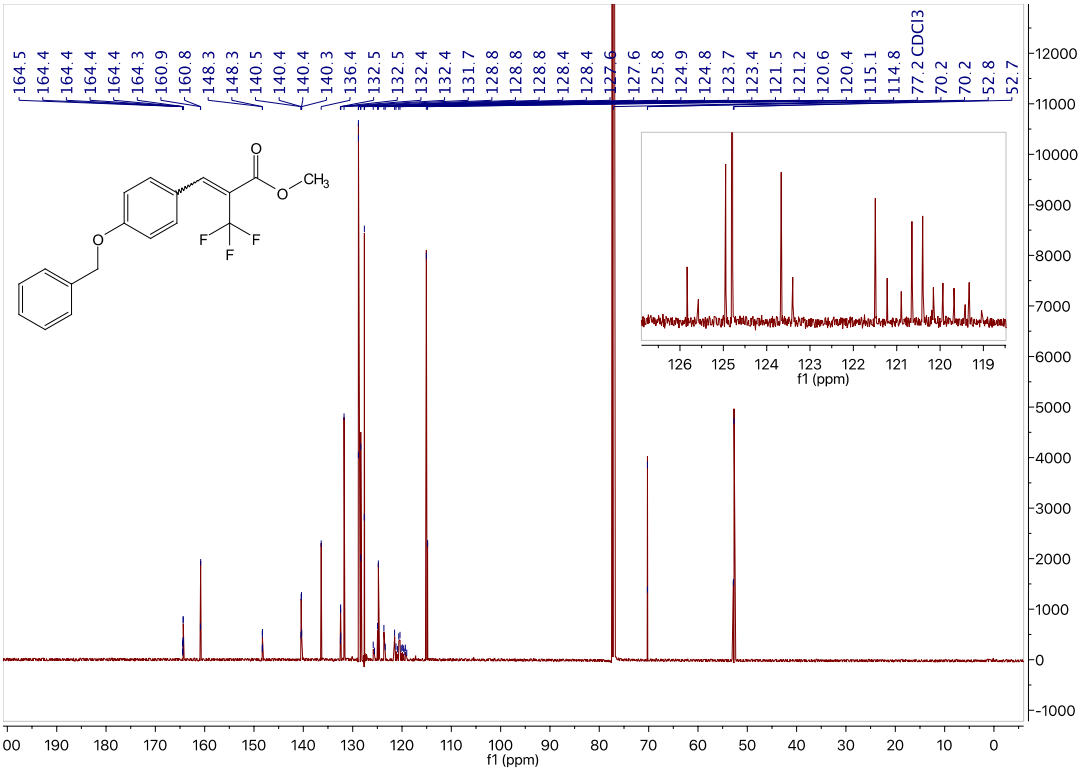
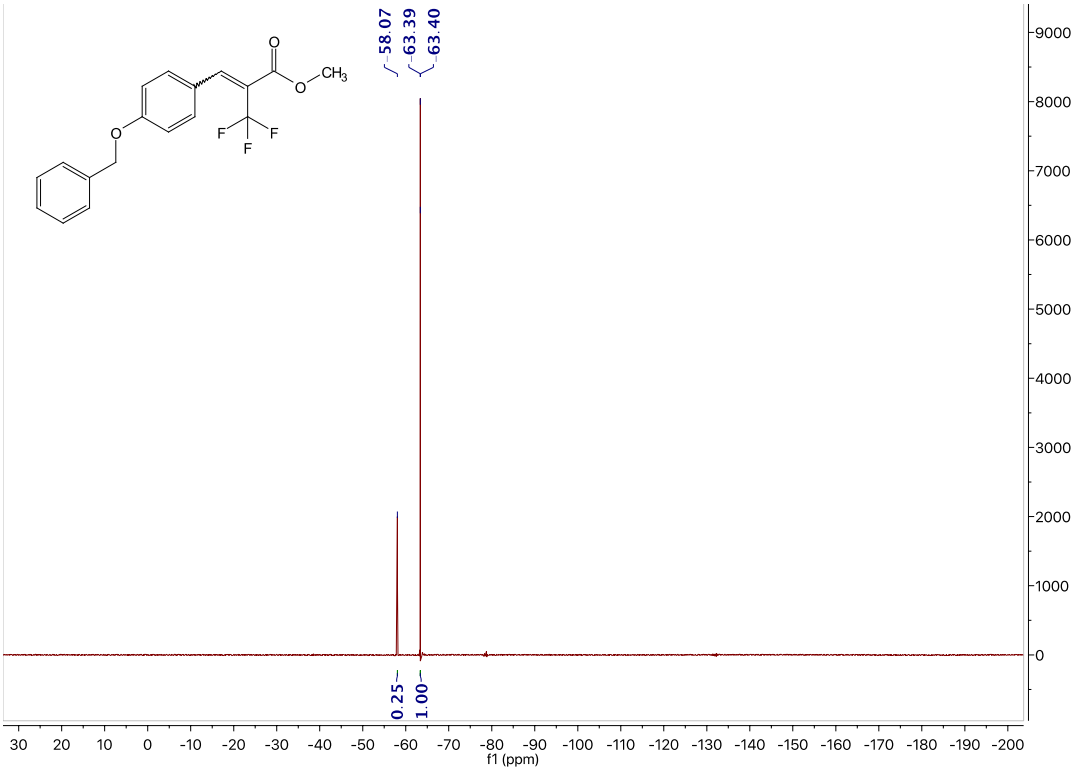
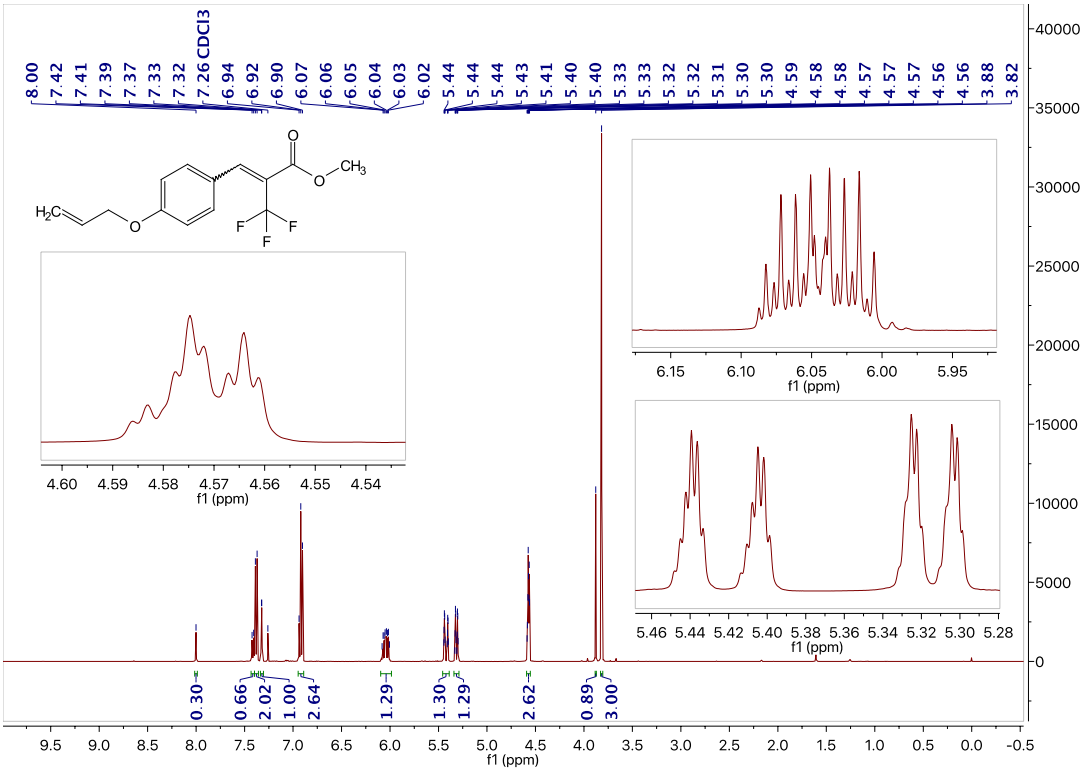


1h – ^{19}F NMR



1i – ^{1}H NMR



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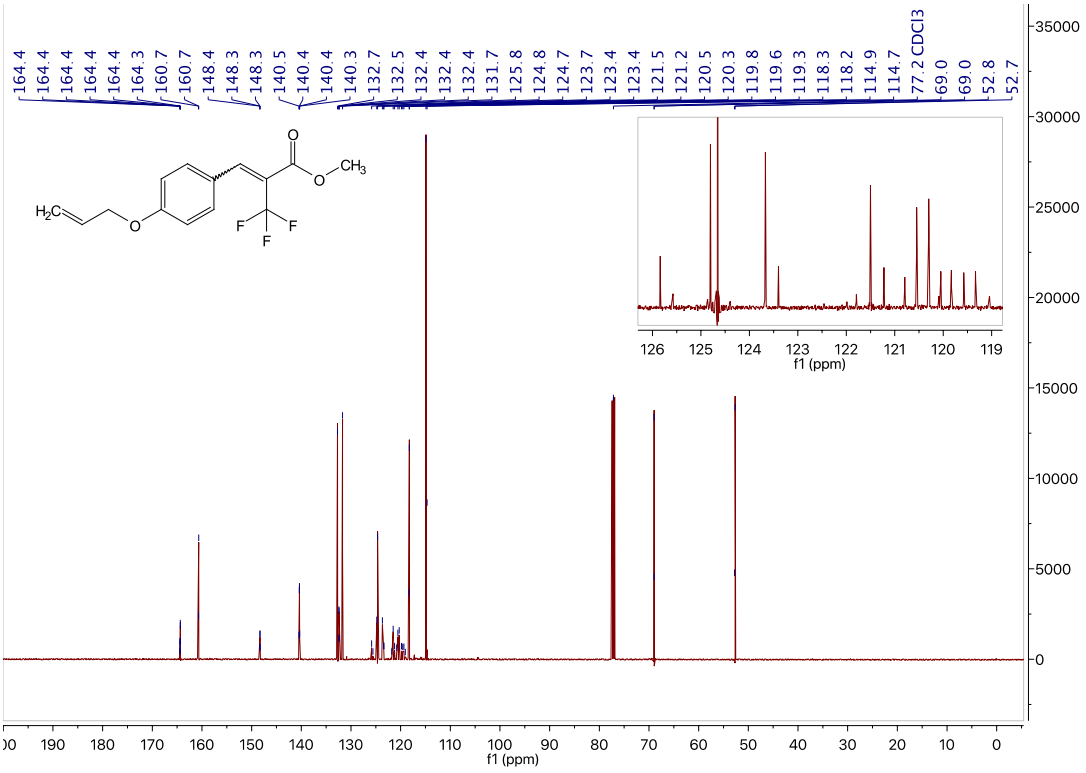

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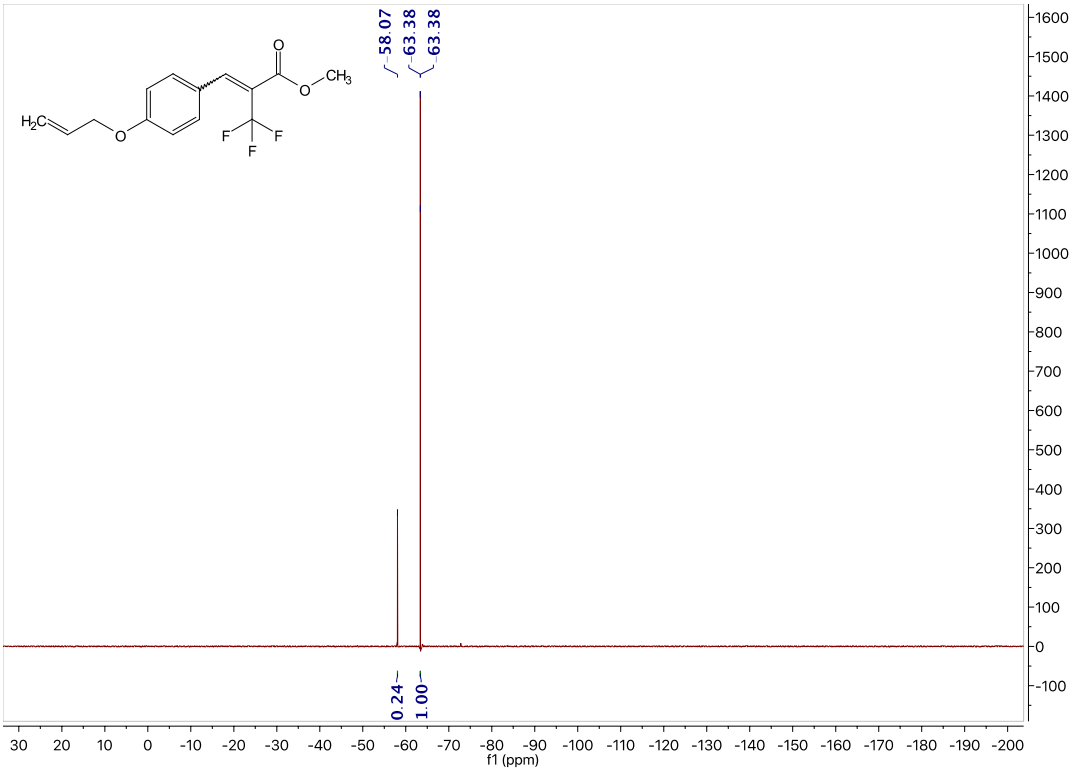

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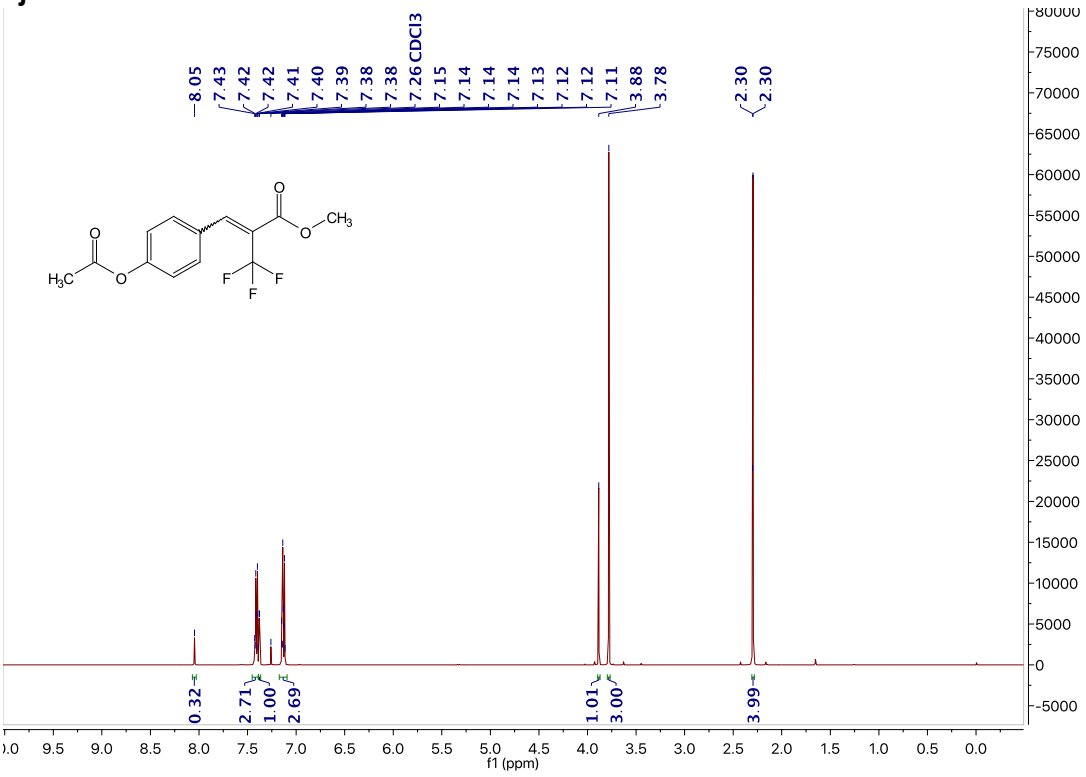

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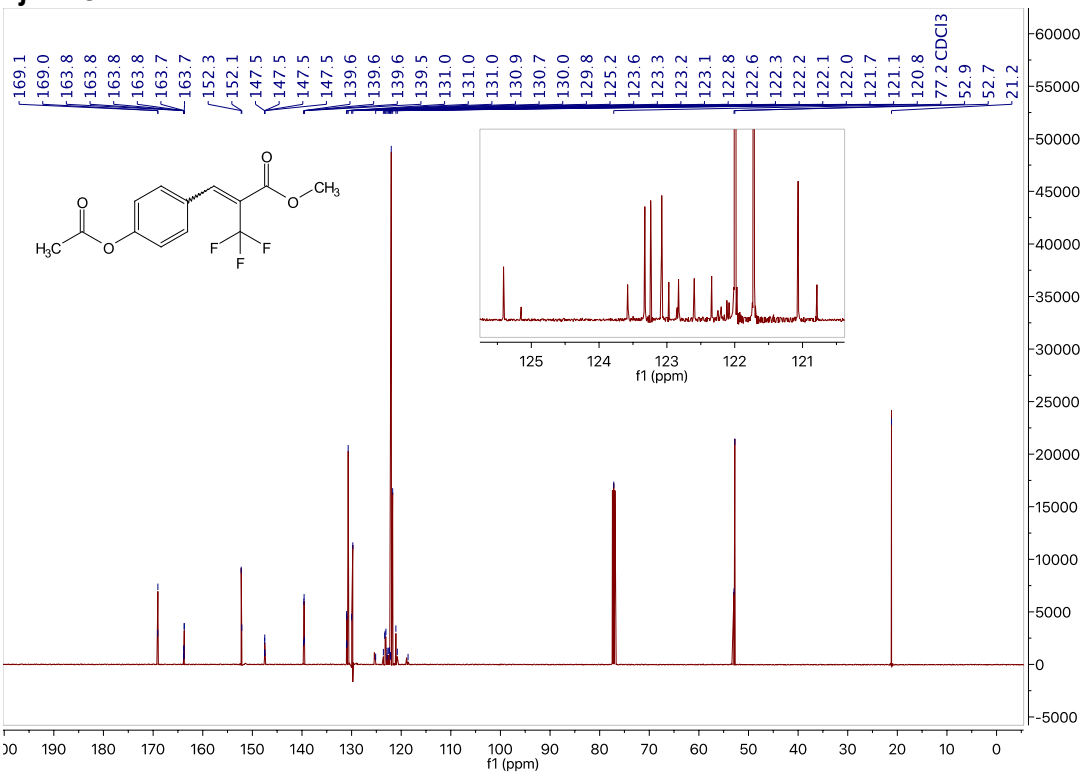

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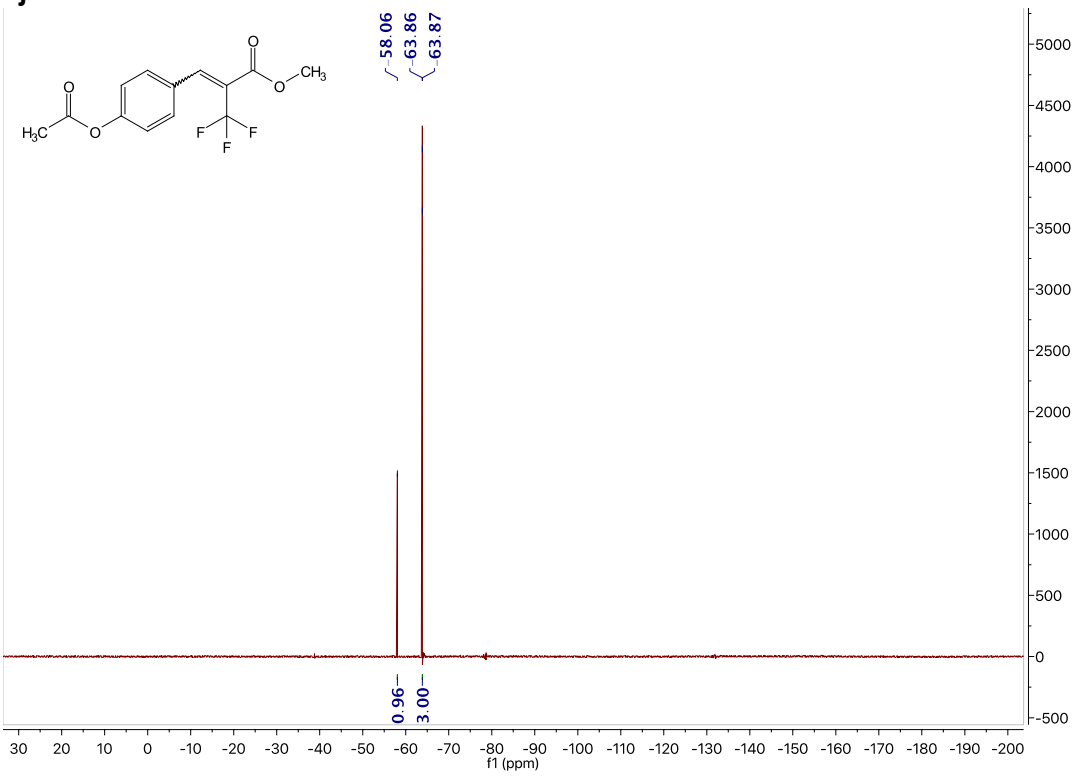
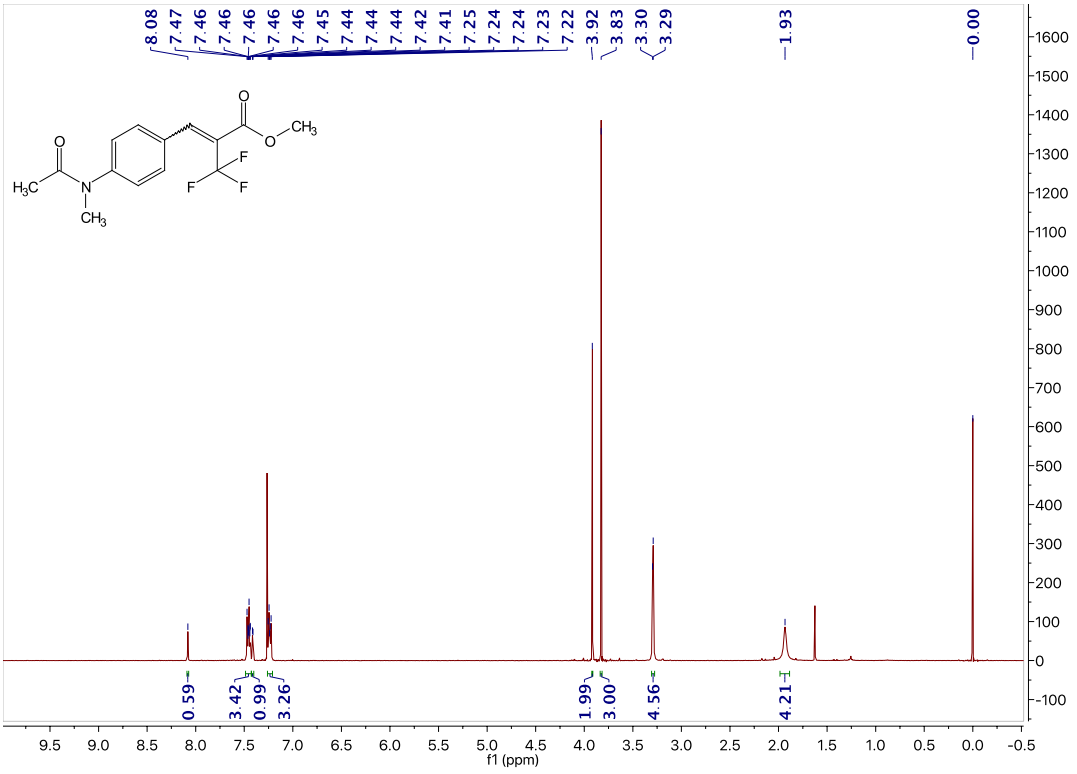


1k – ^{1}H NMR



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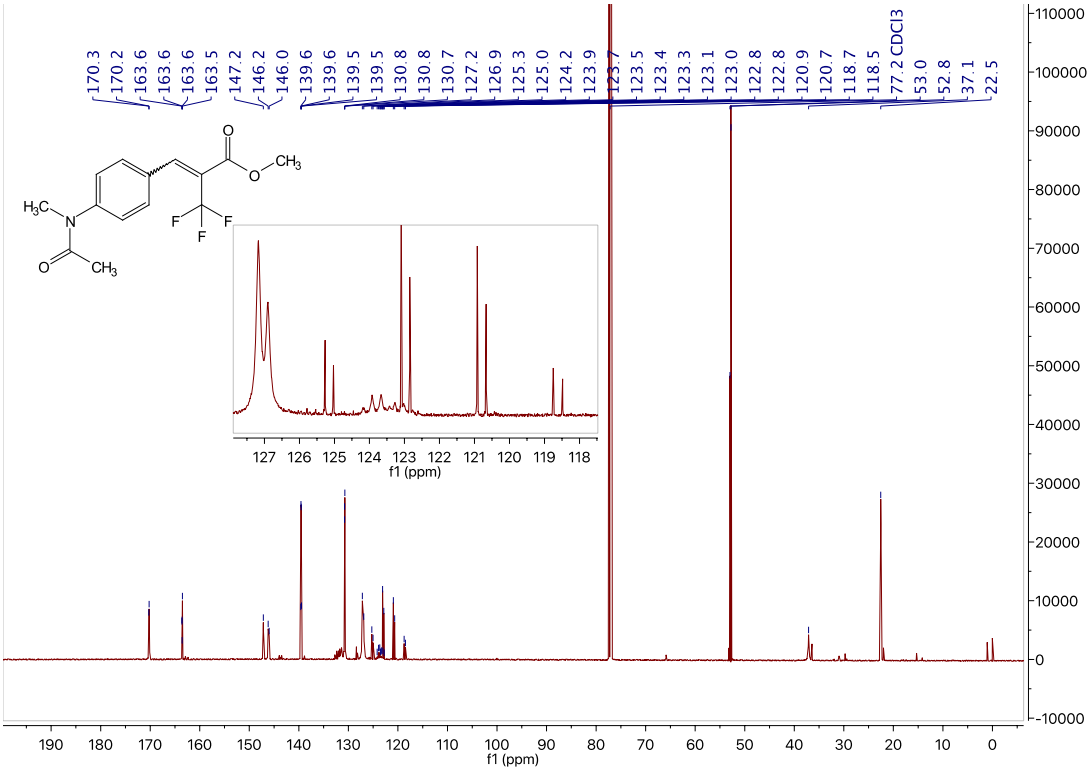

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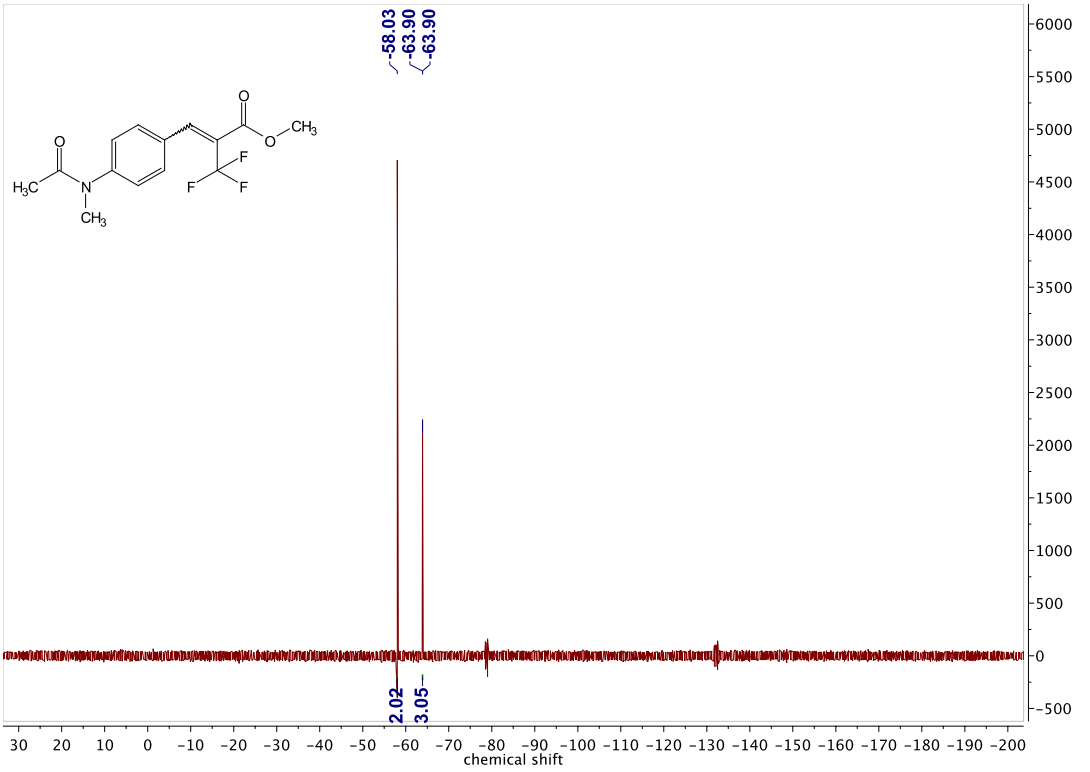

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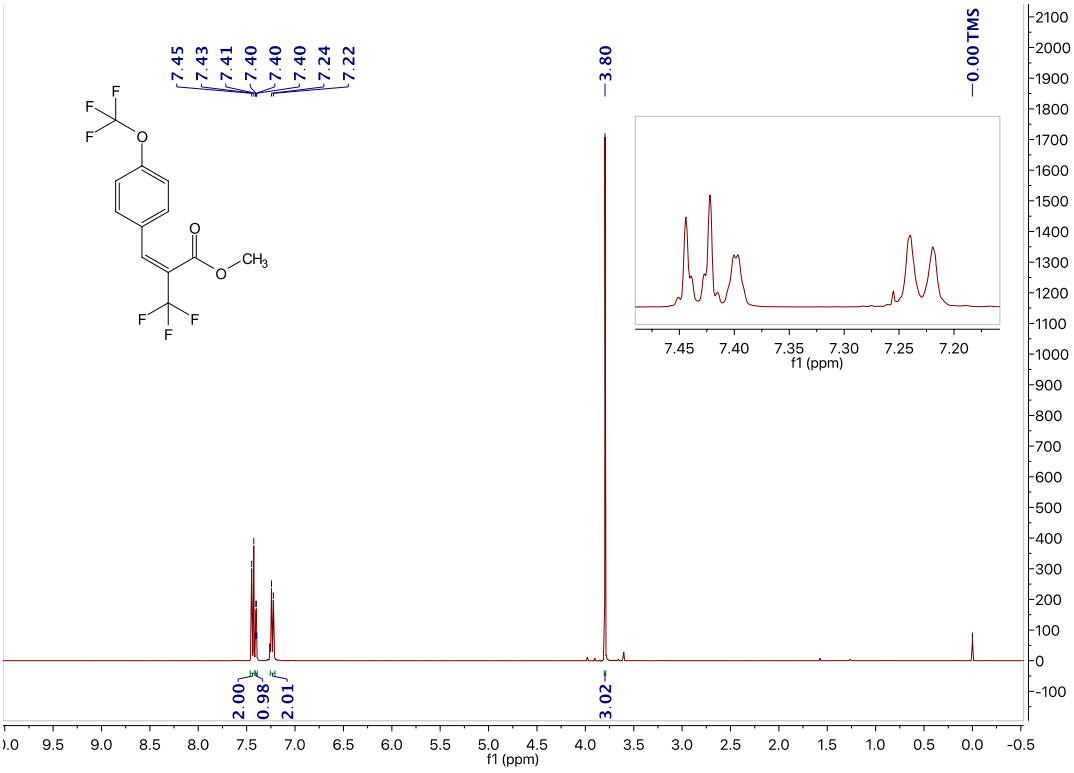

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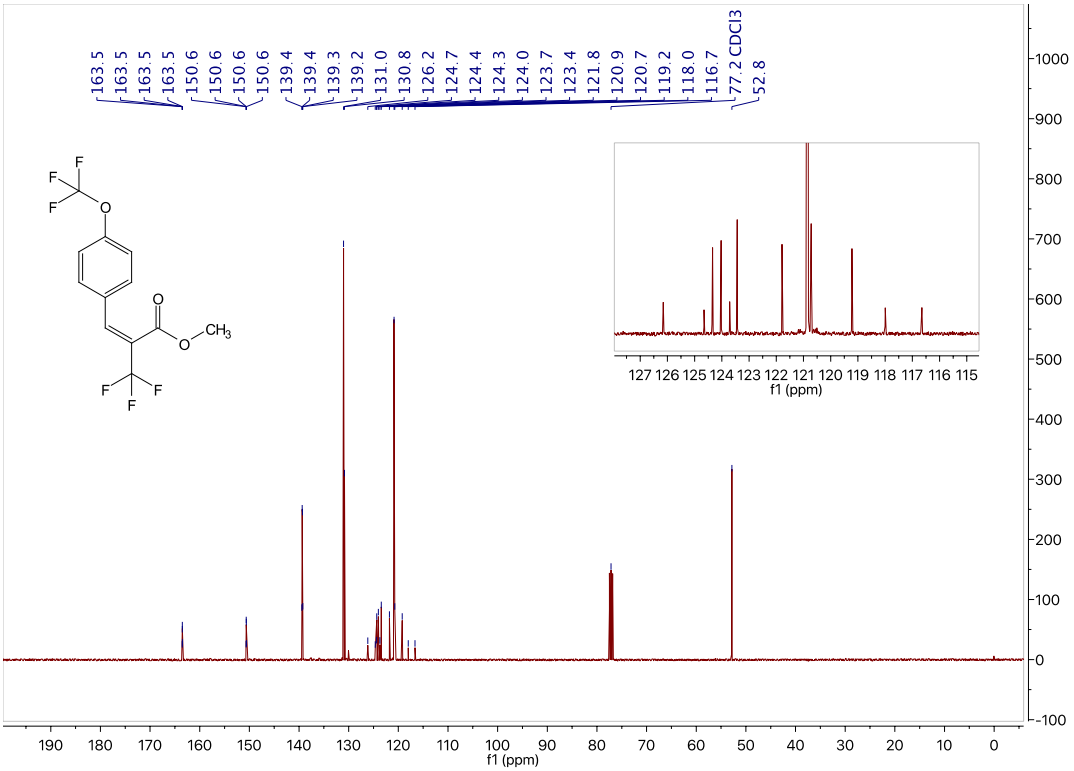

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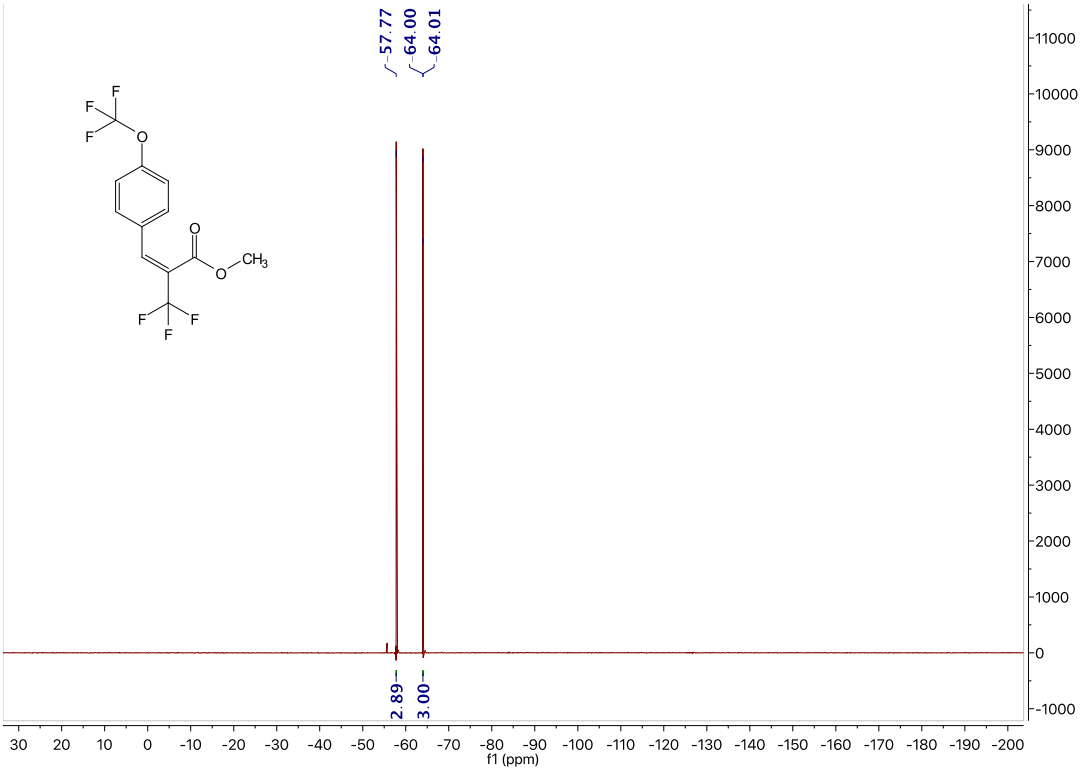

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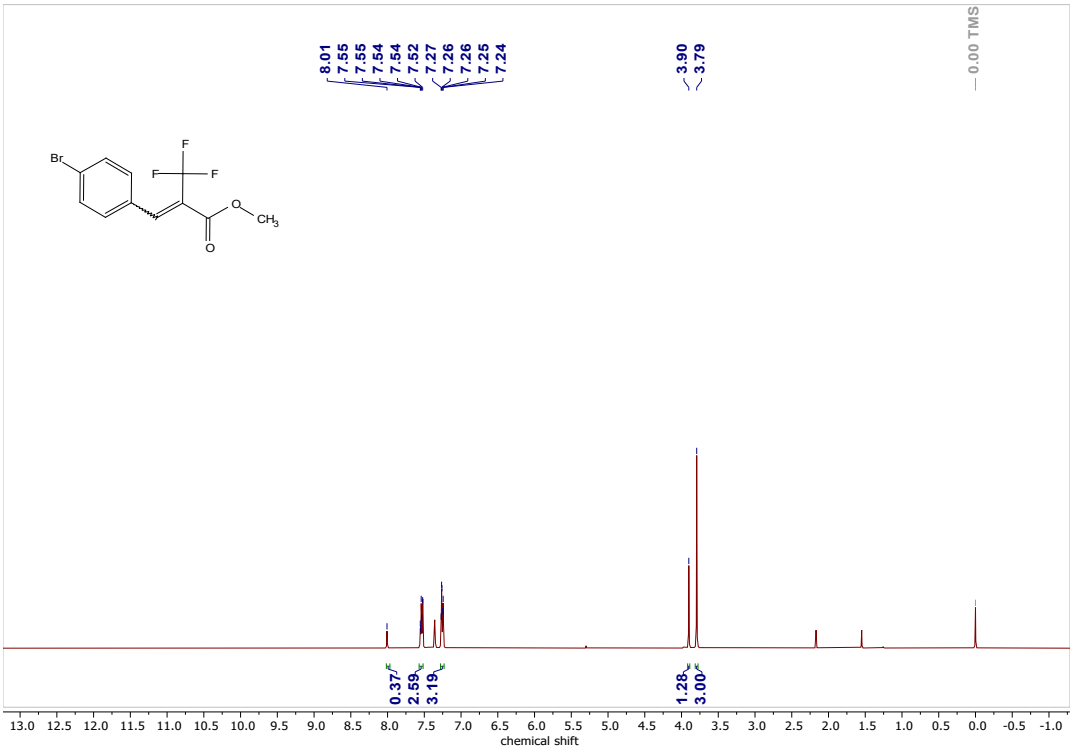

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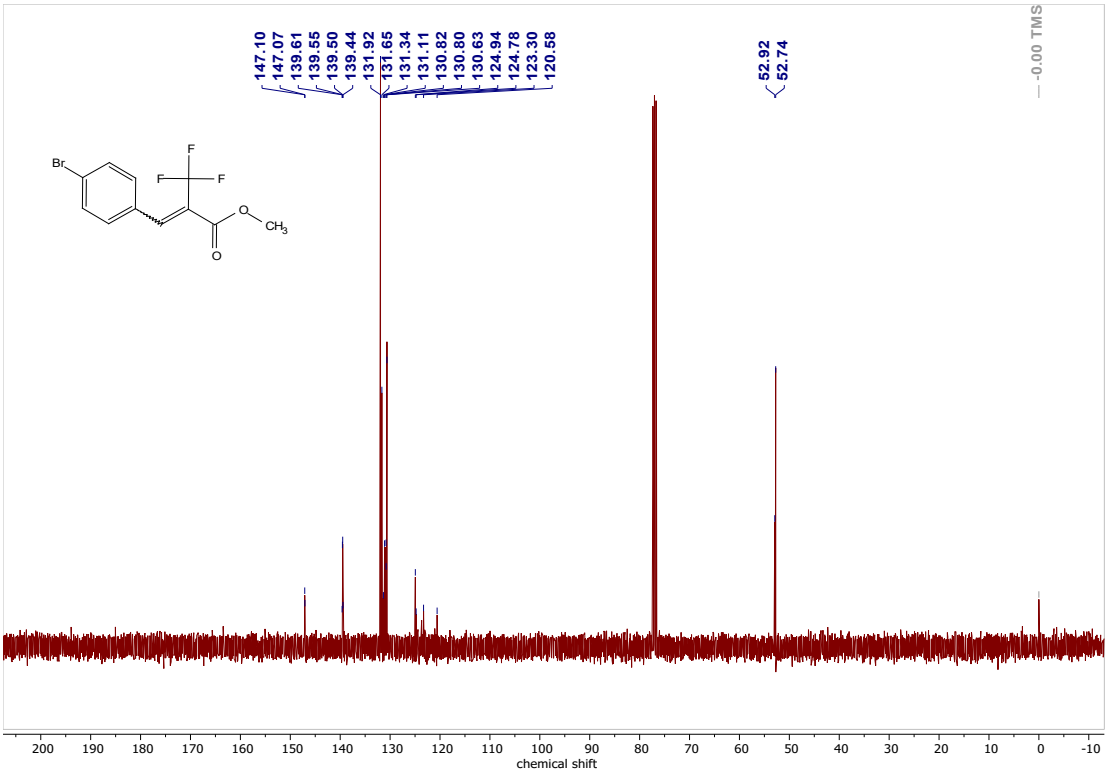

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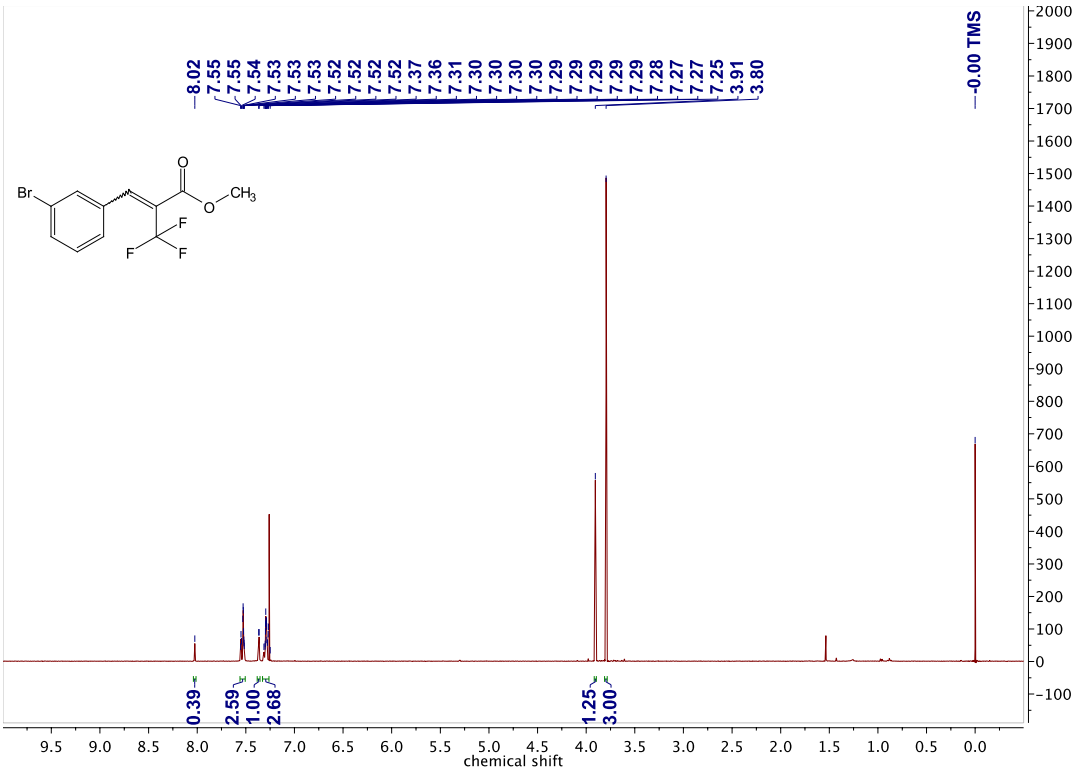

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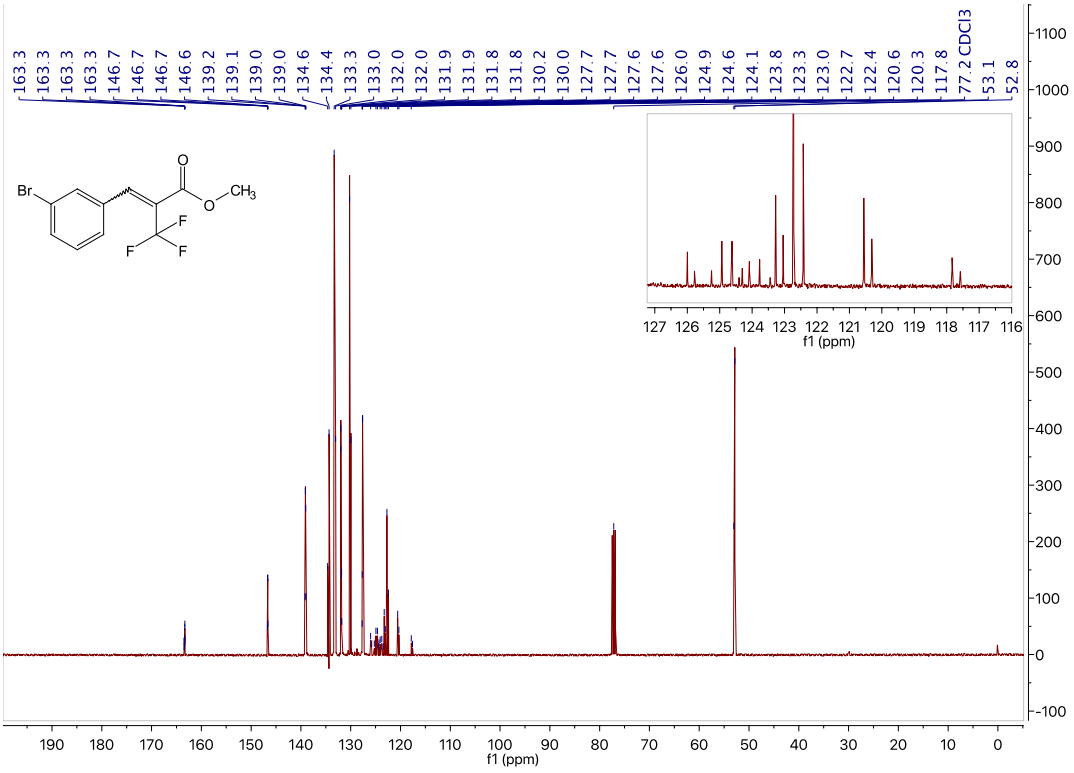

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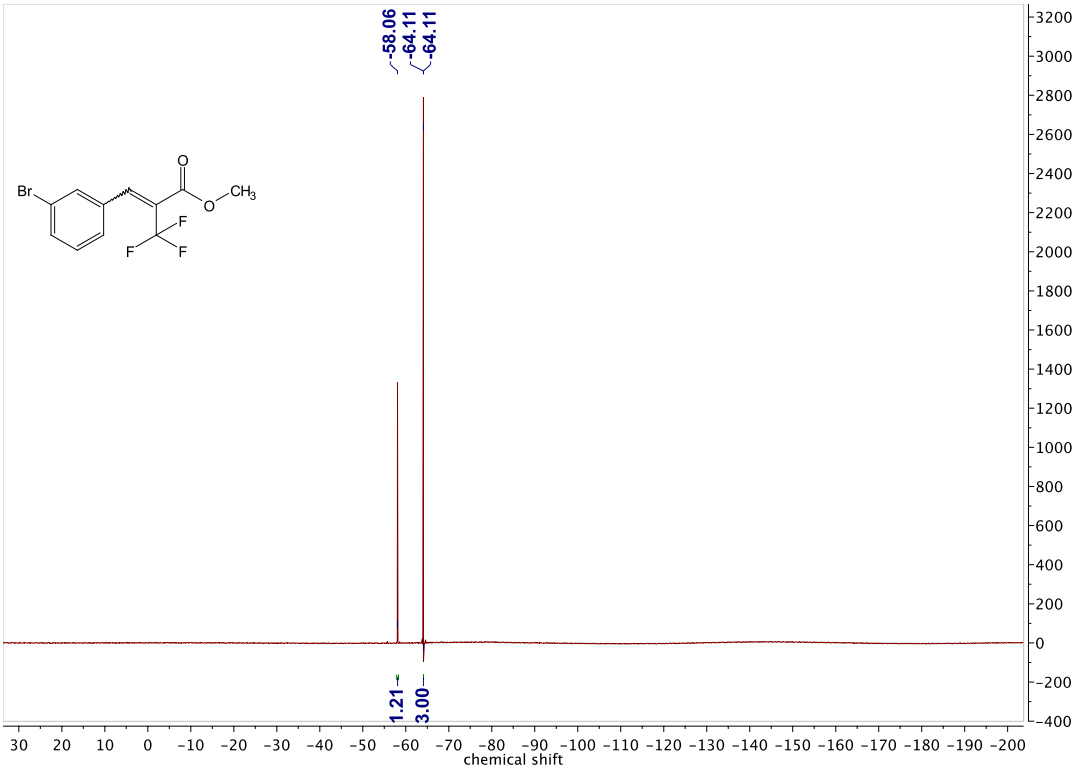
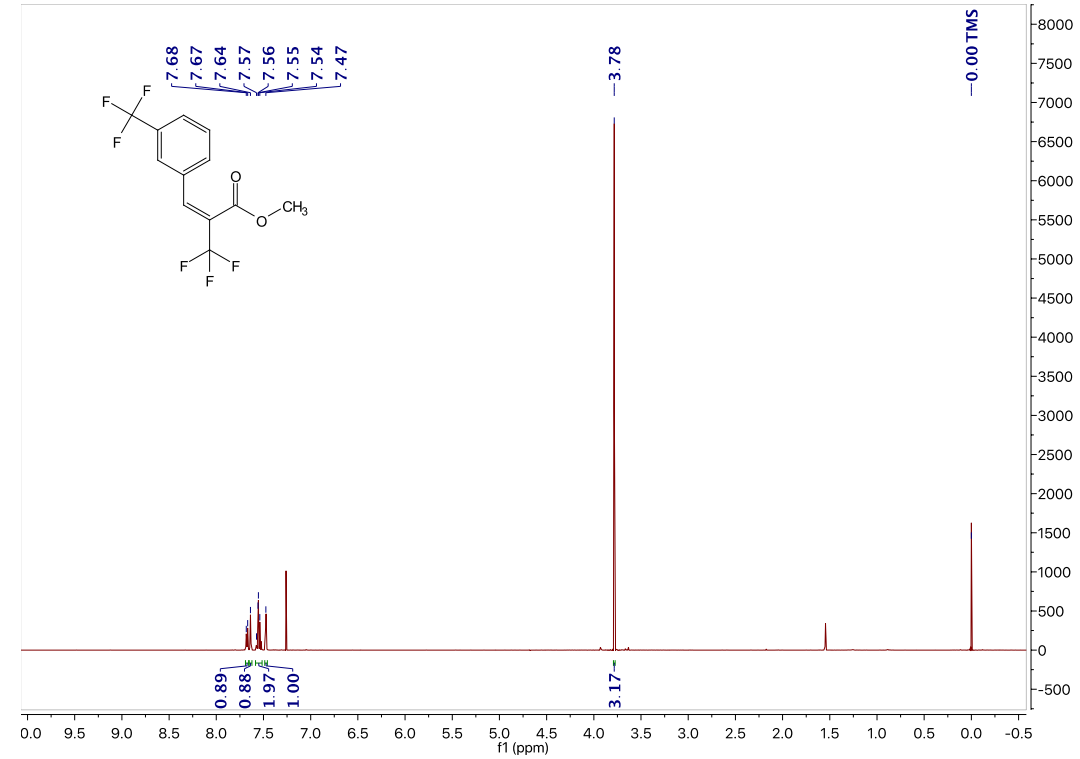


1o – ^{1}H NMR



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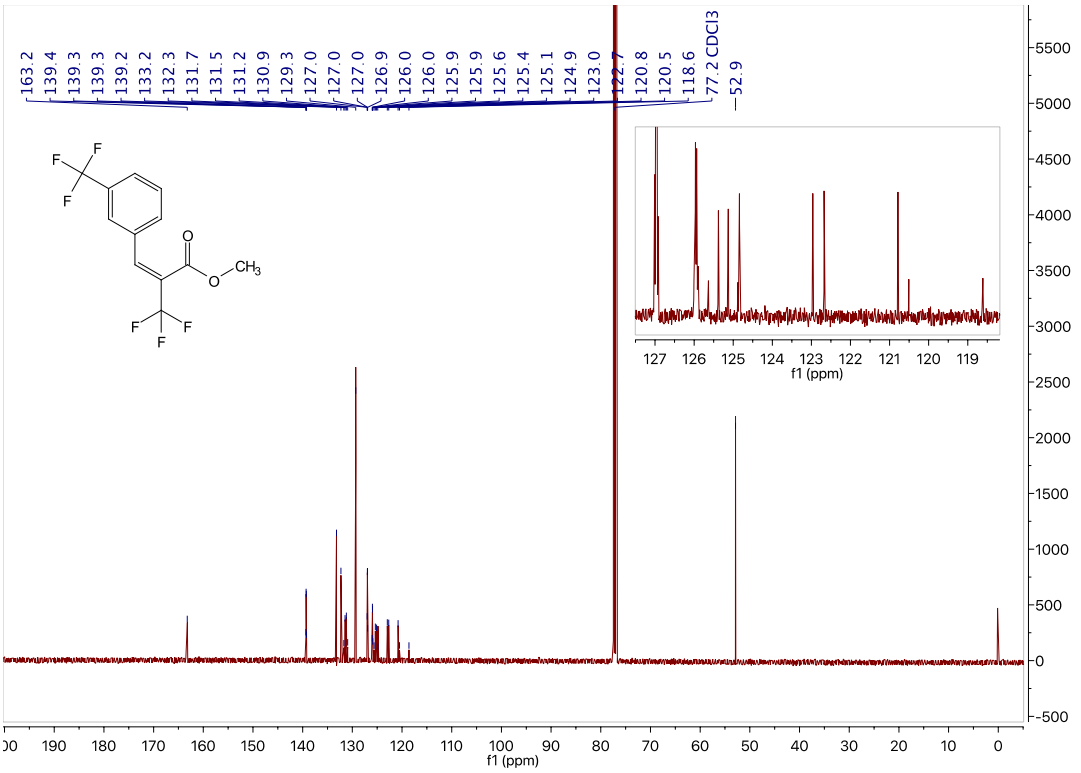
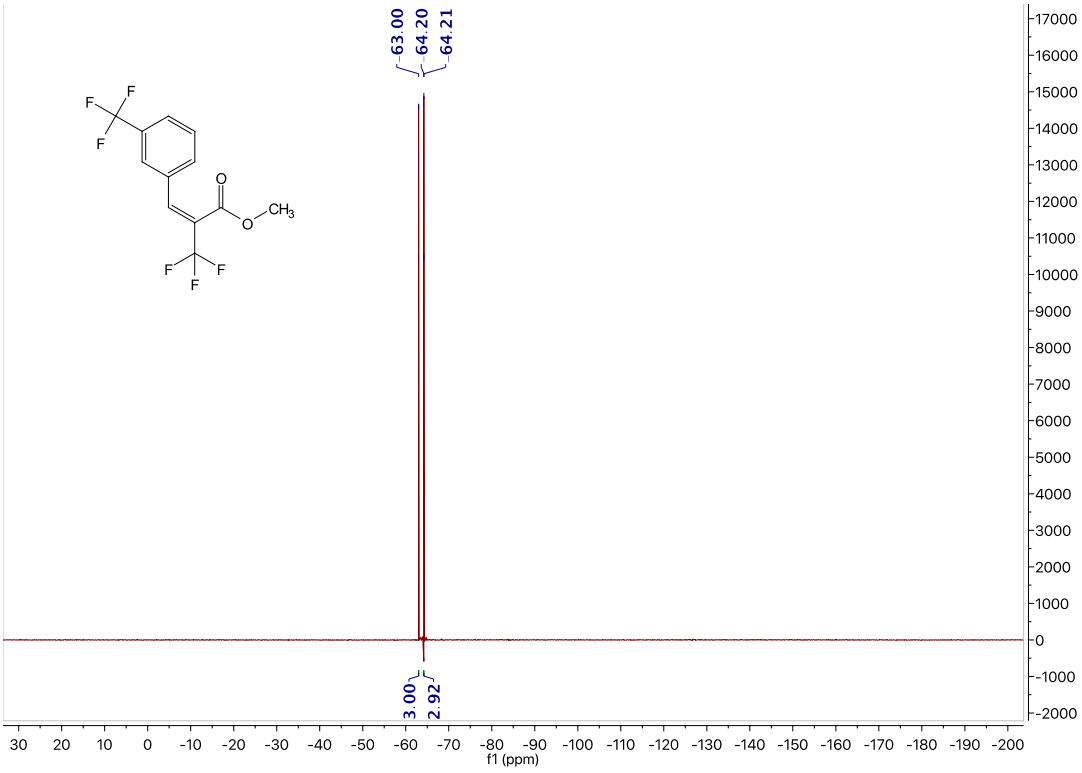
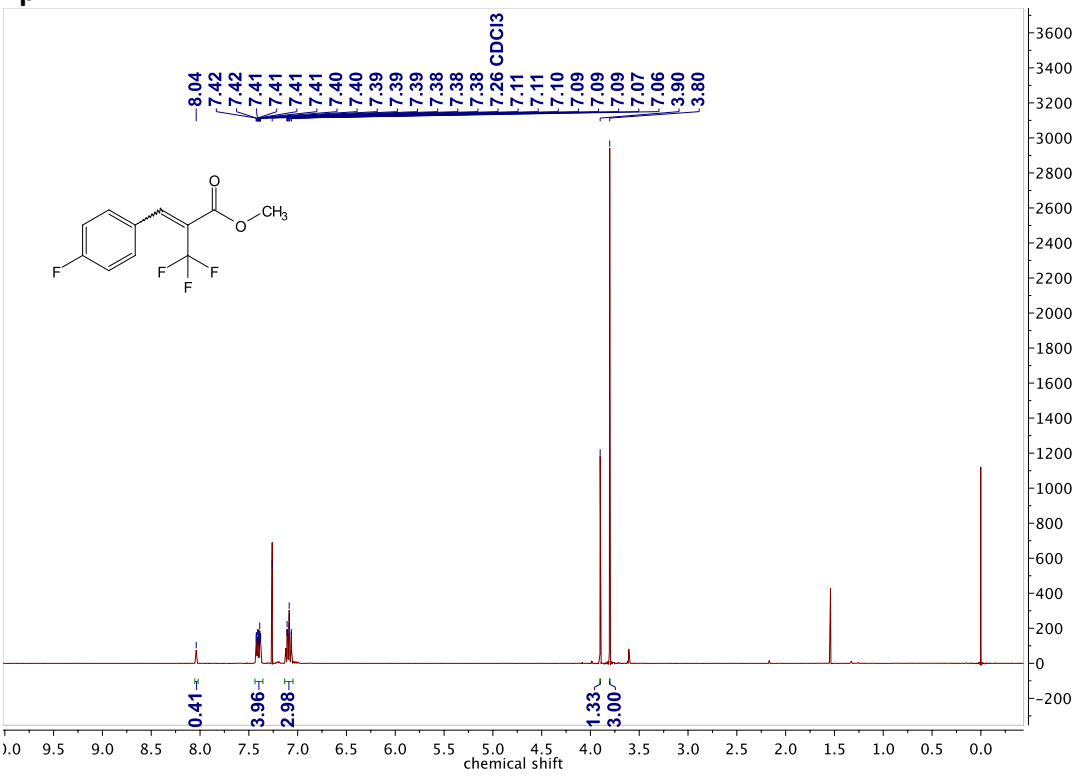


1o – ^{19}F NMR



1p – ^{1}H NMR



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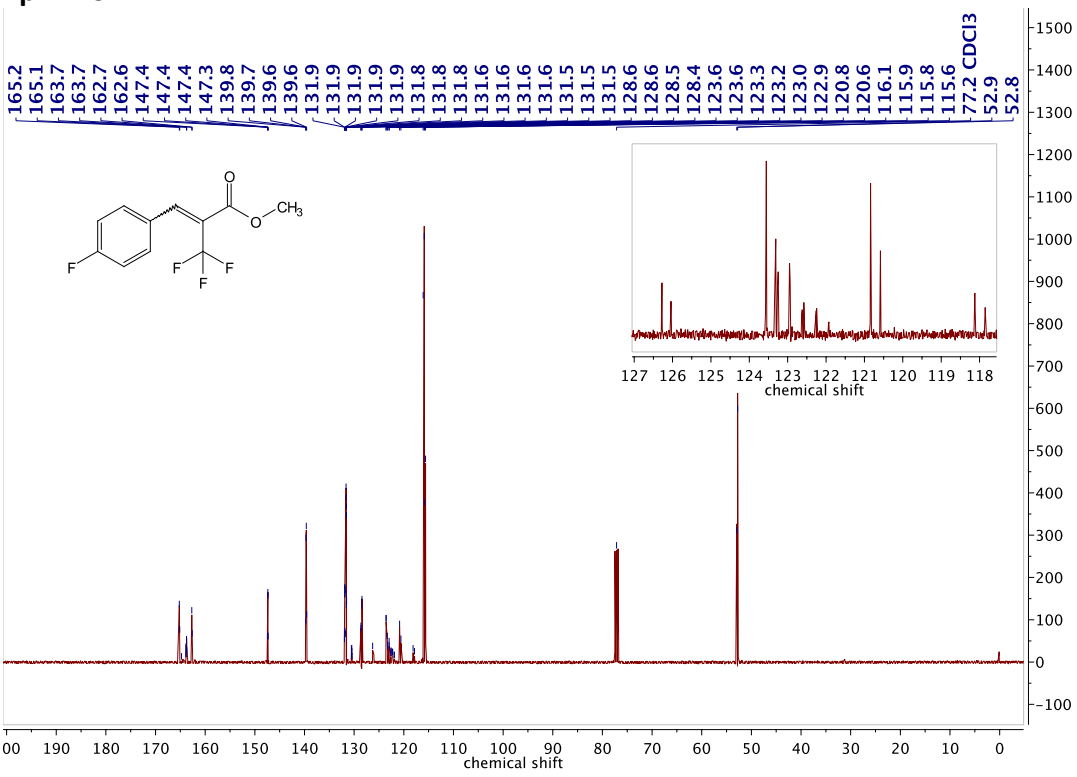
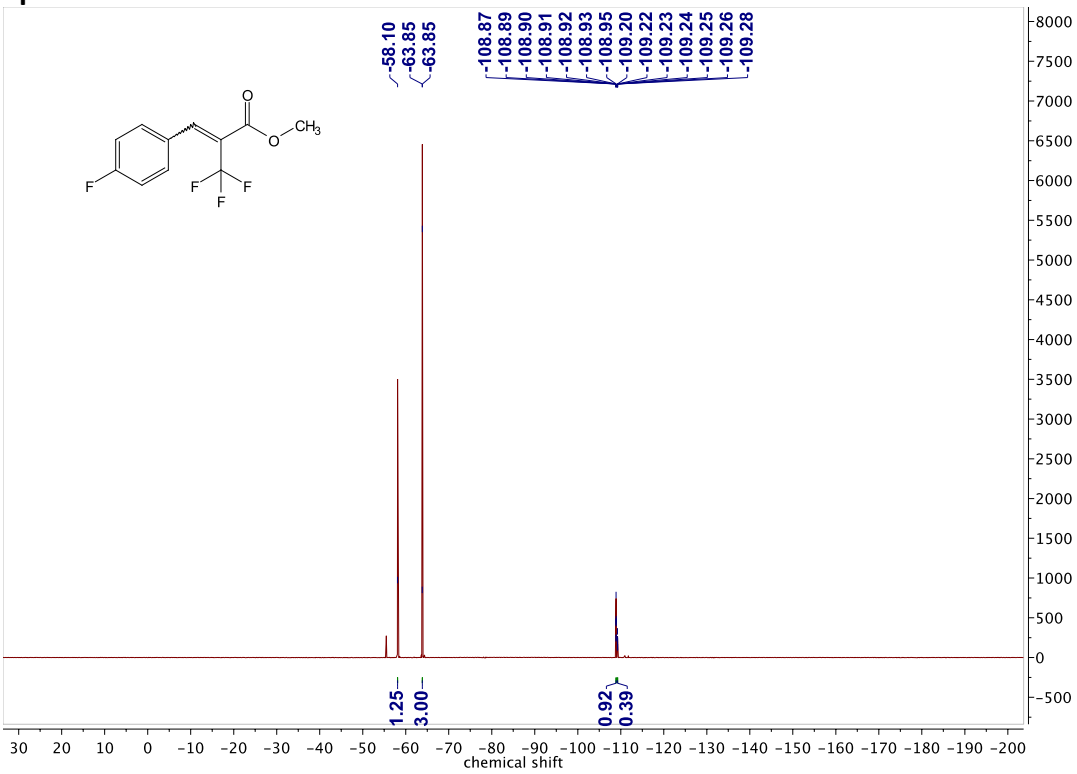
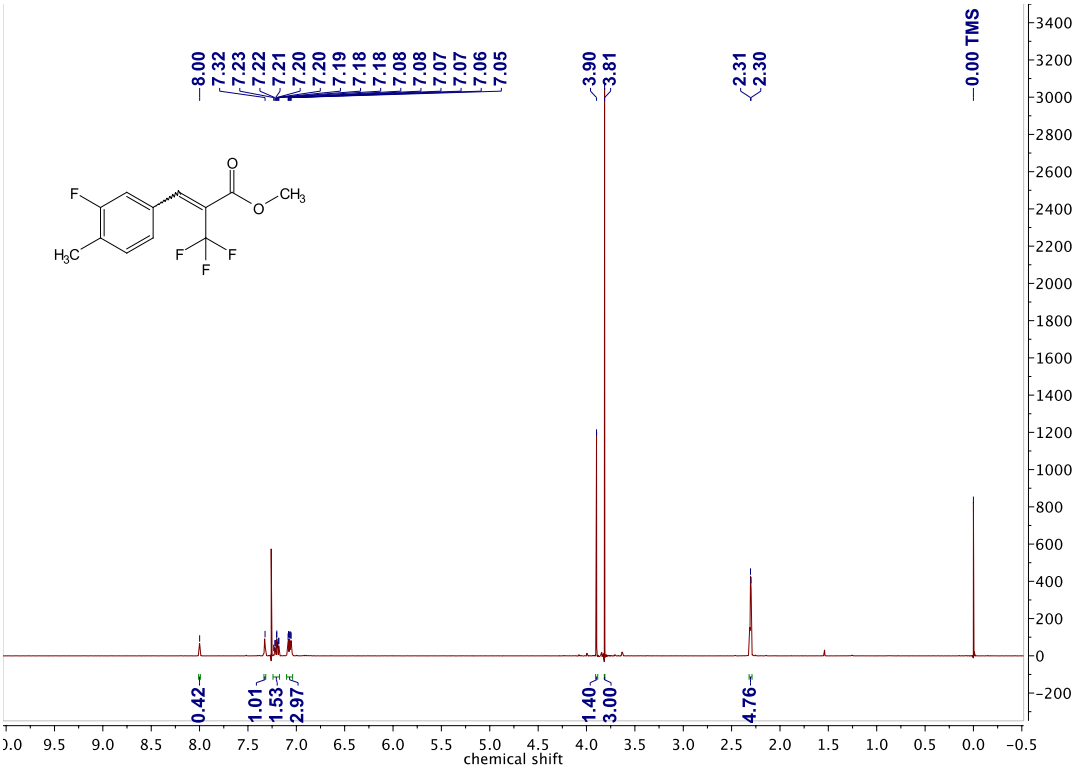


1p – ^{19}F NMR



1q – ^{1}H NMR



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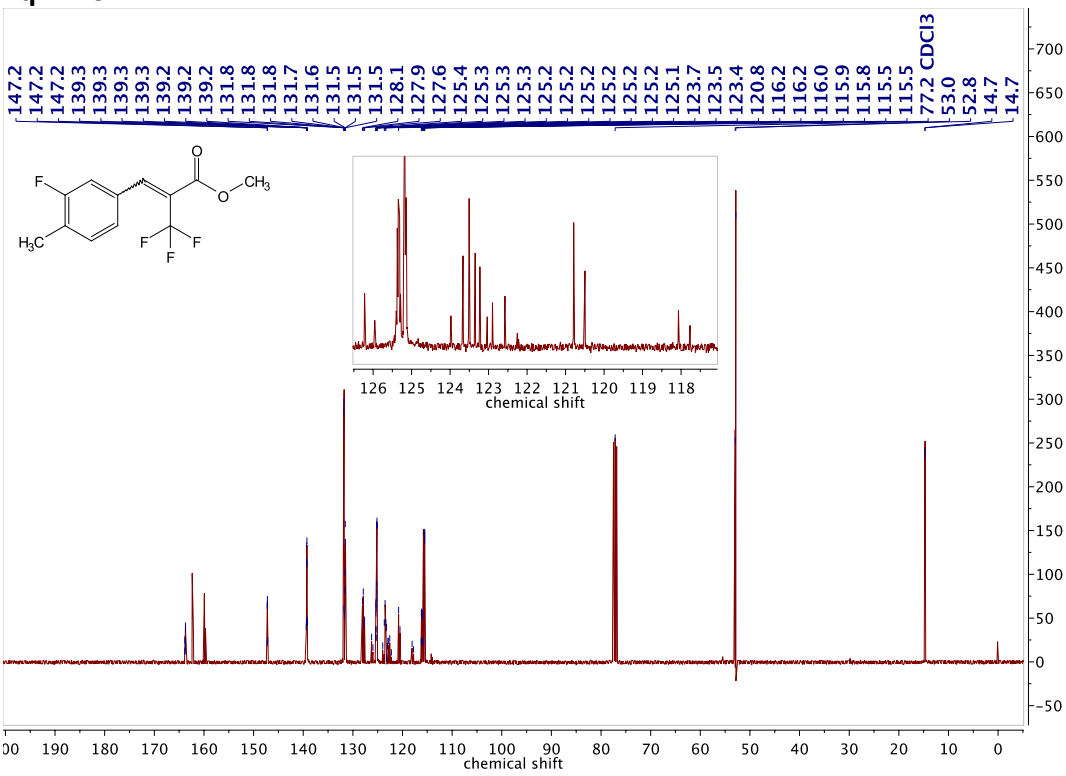
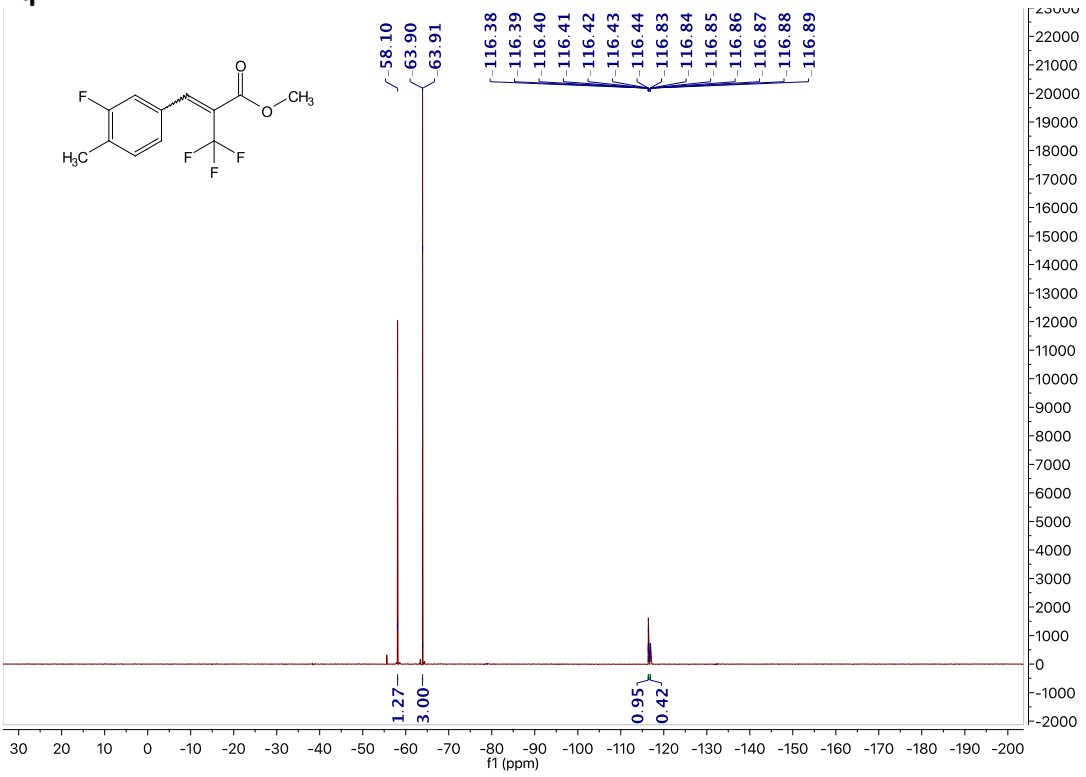
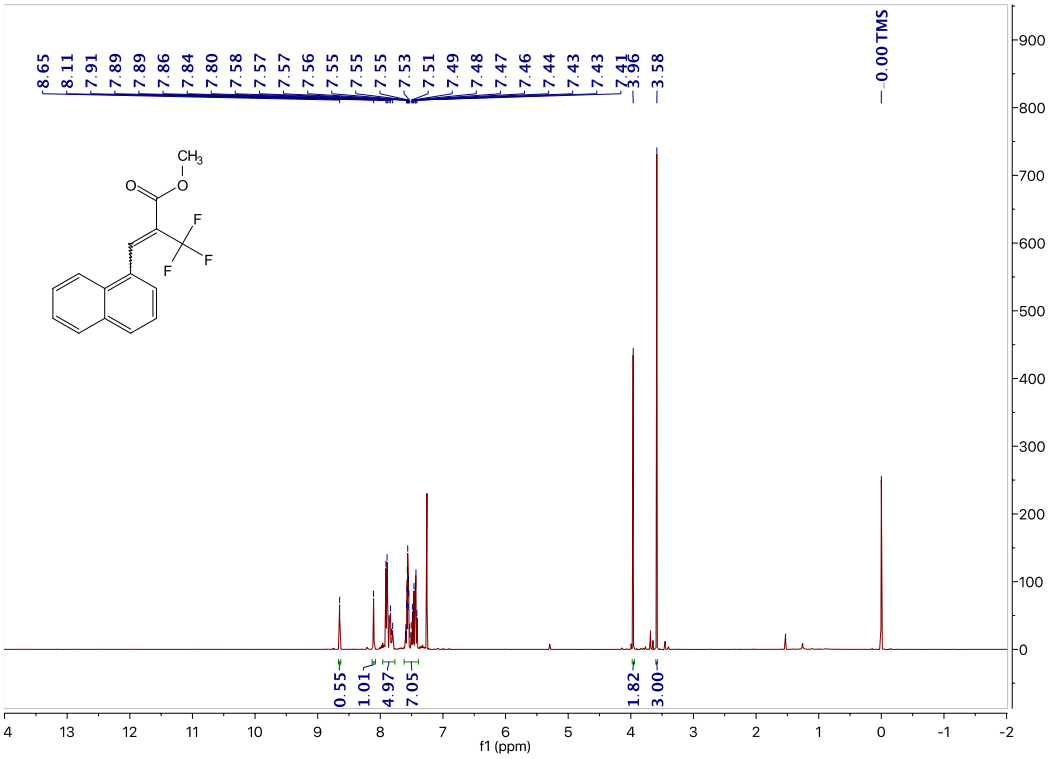


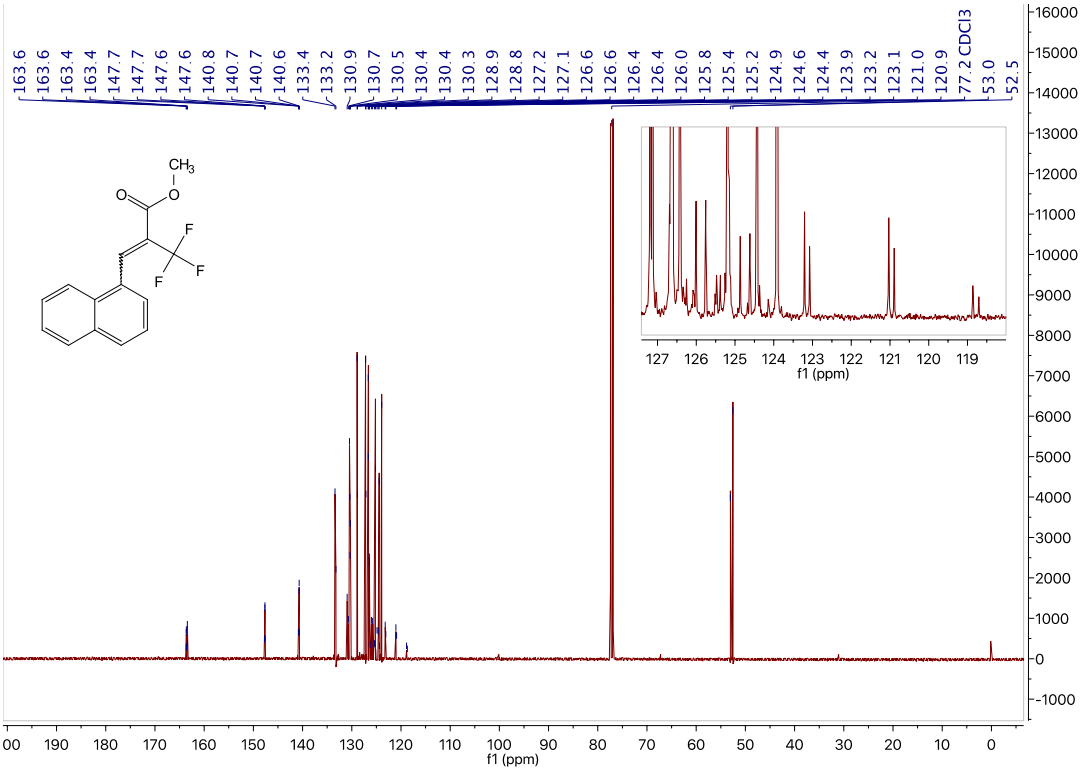
1q – ^{19}F NMR



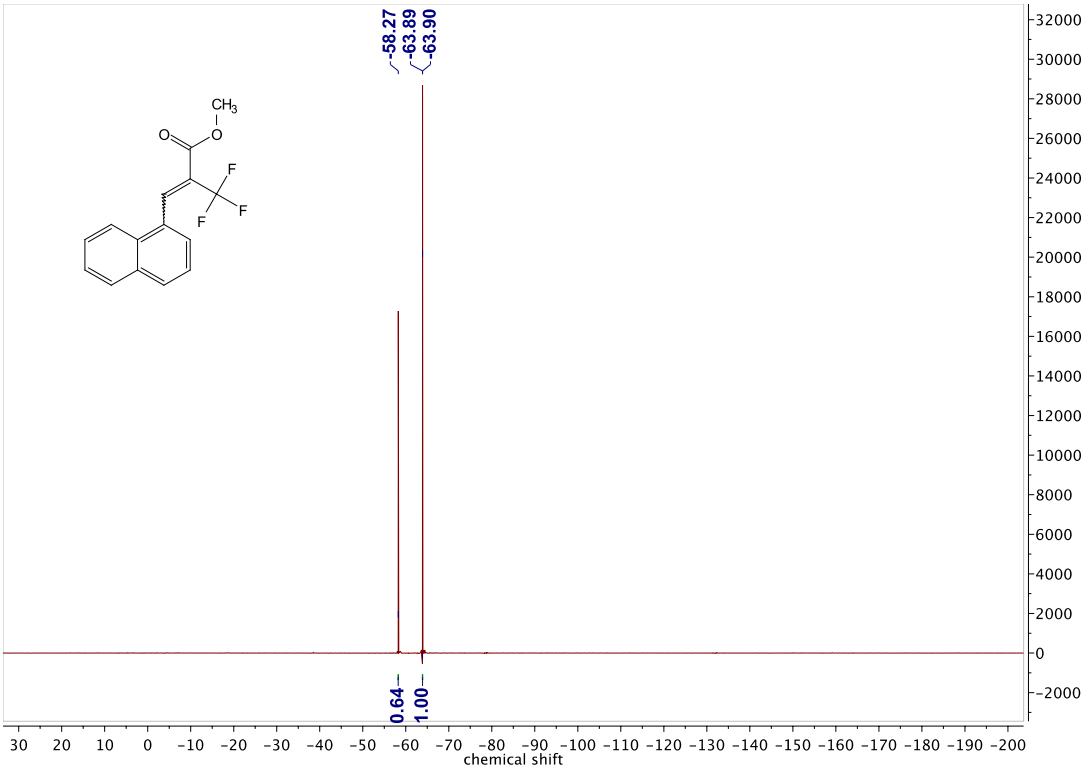
1r – ^{1}H NMR



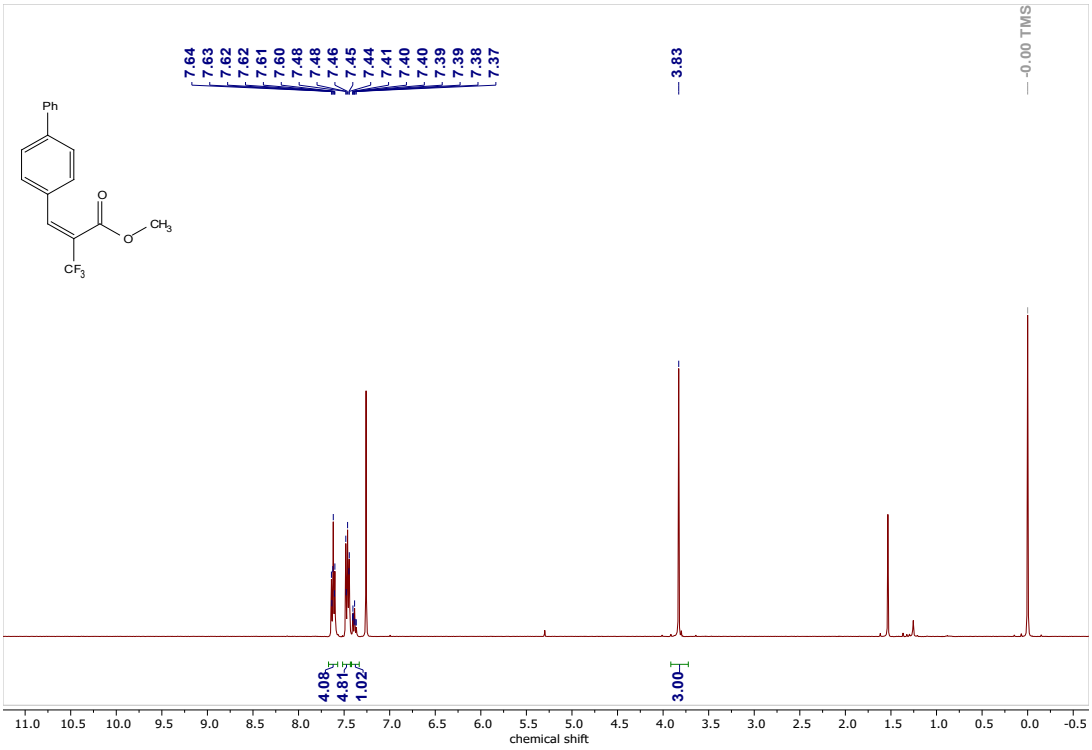
1r – ^{13}C NMR



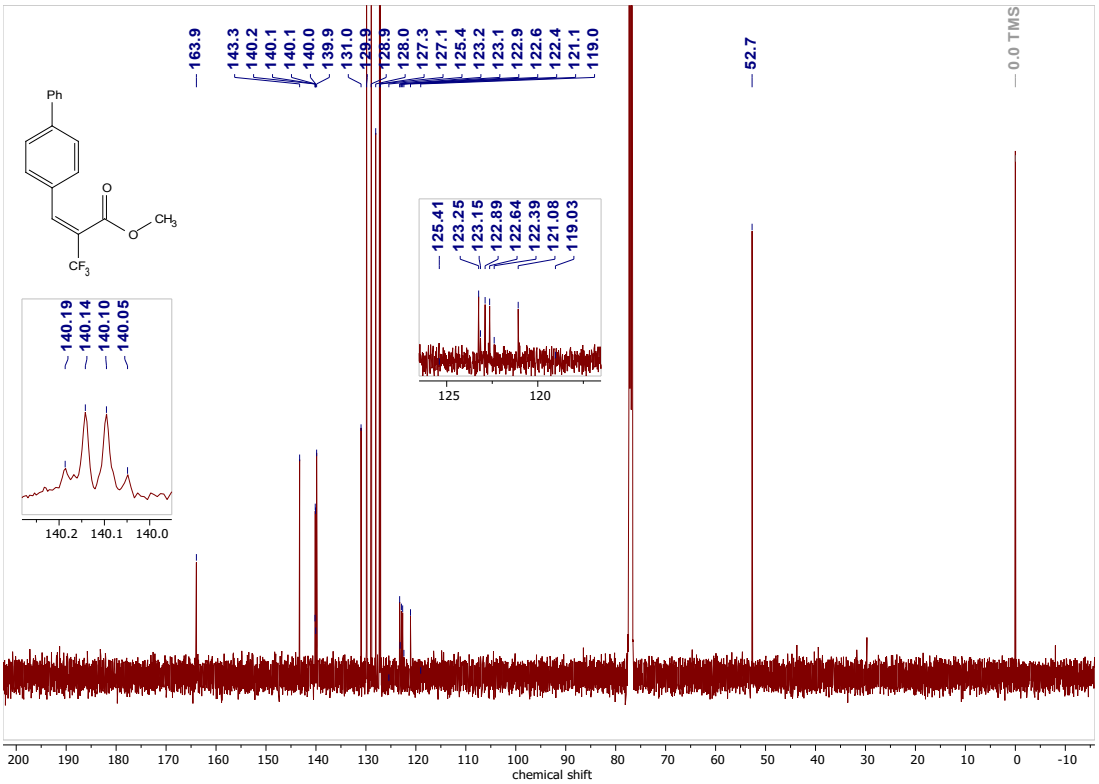
1r – ^{19}F NMR



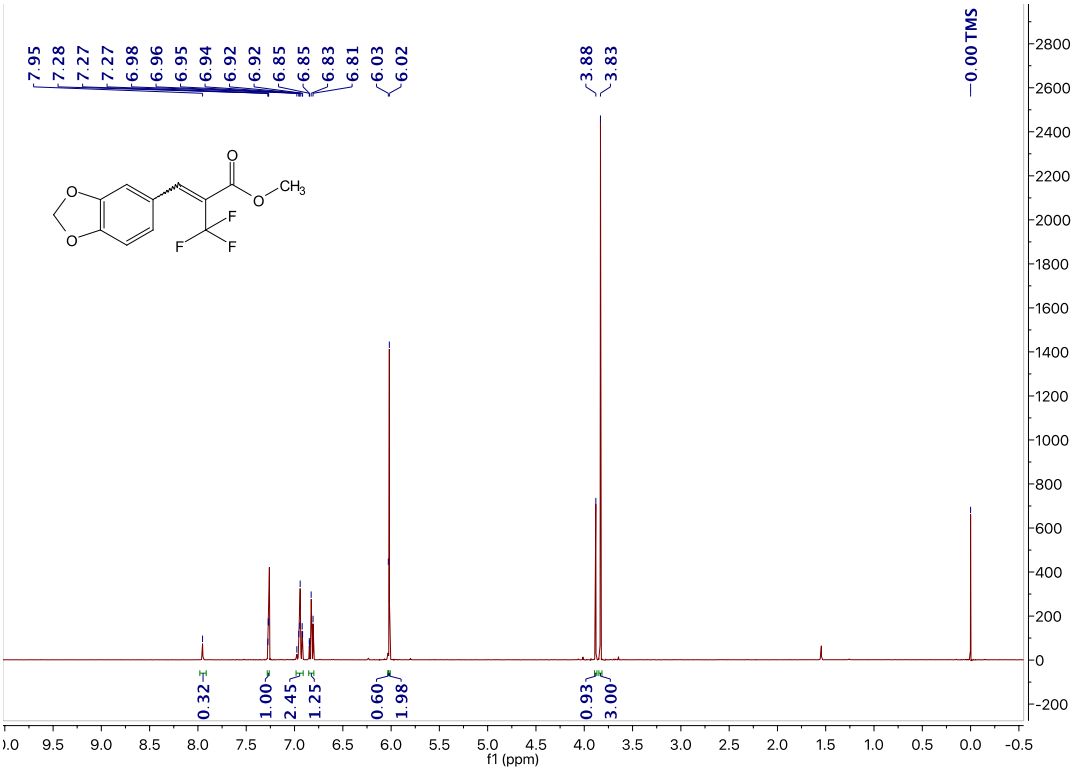
1s – ^{1}H NMR



1s – ^{13}C NMR



1t – ^{1}H NMR



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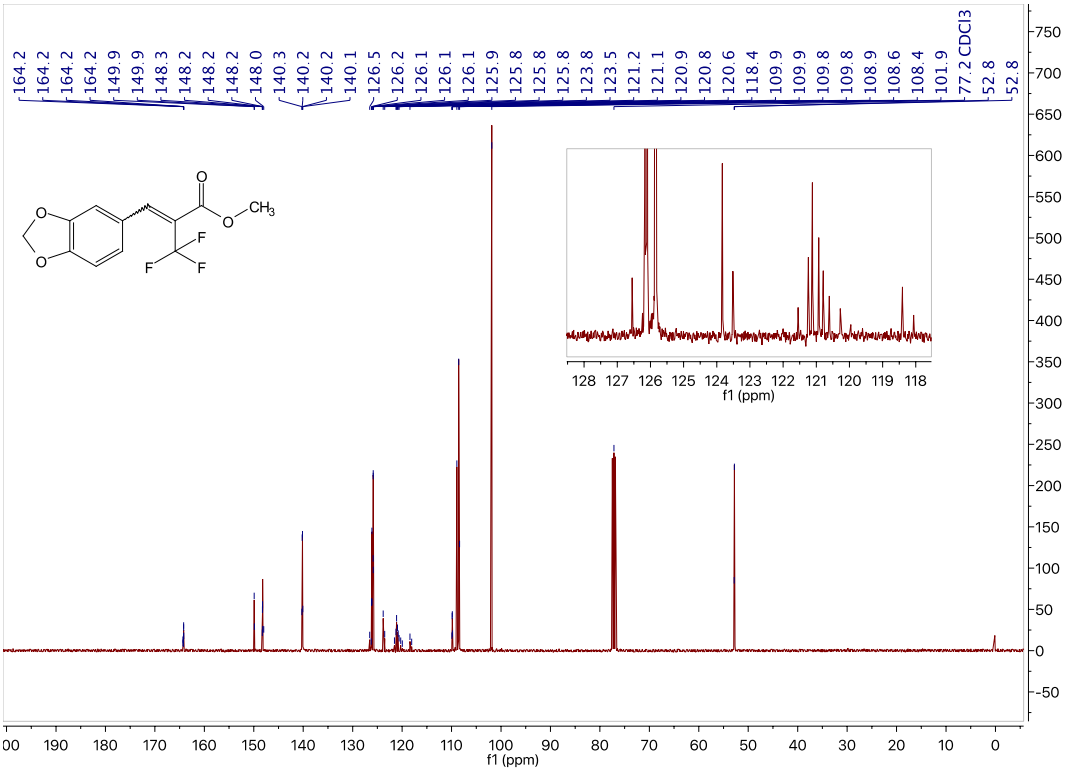
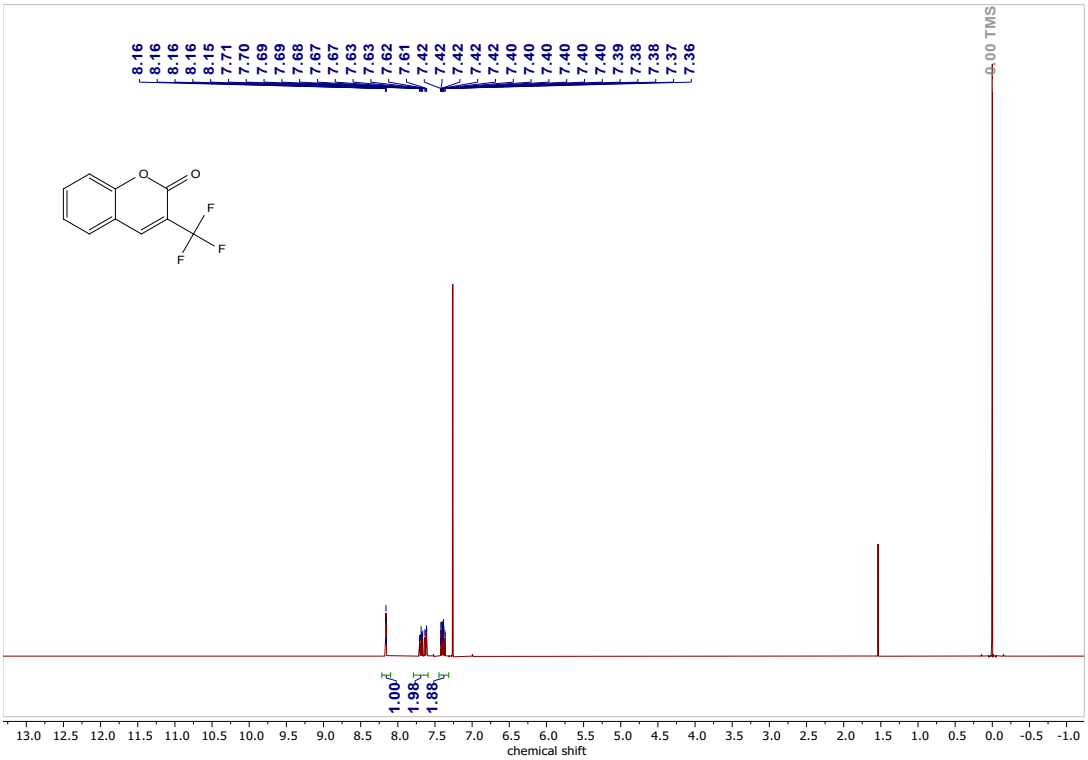
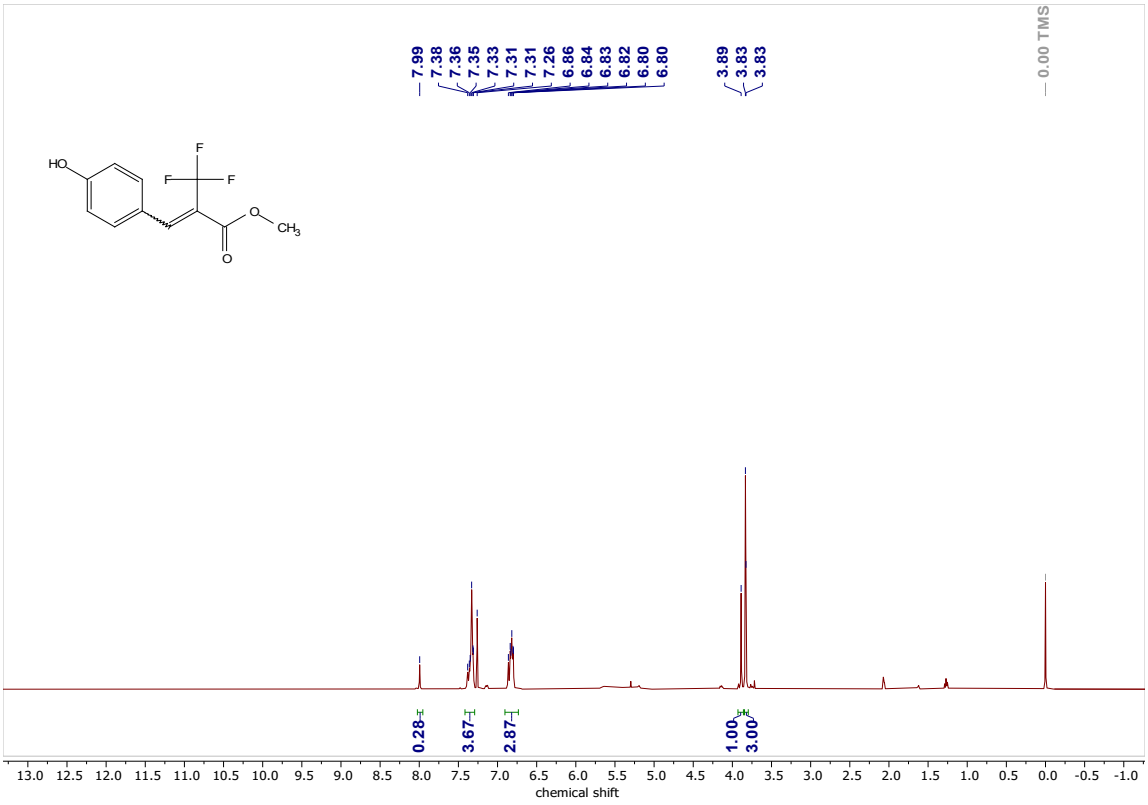


1t – ^{19}F NMR

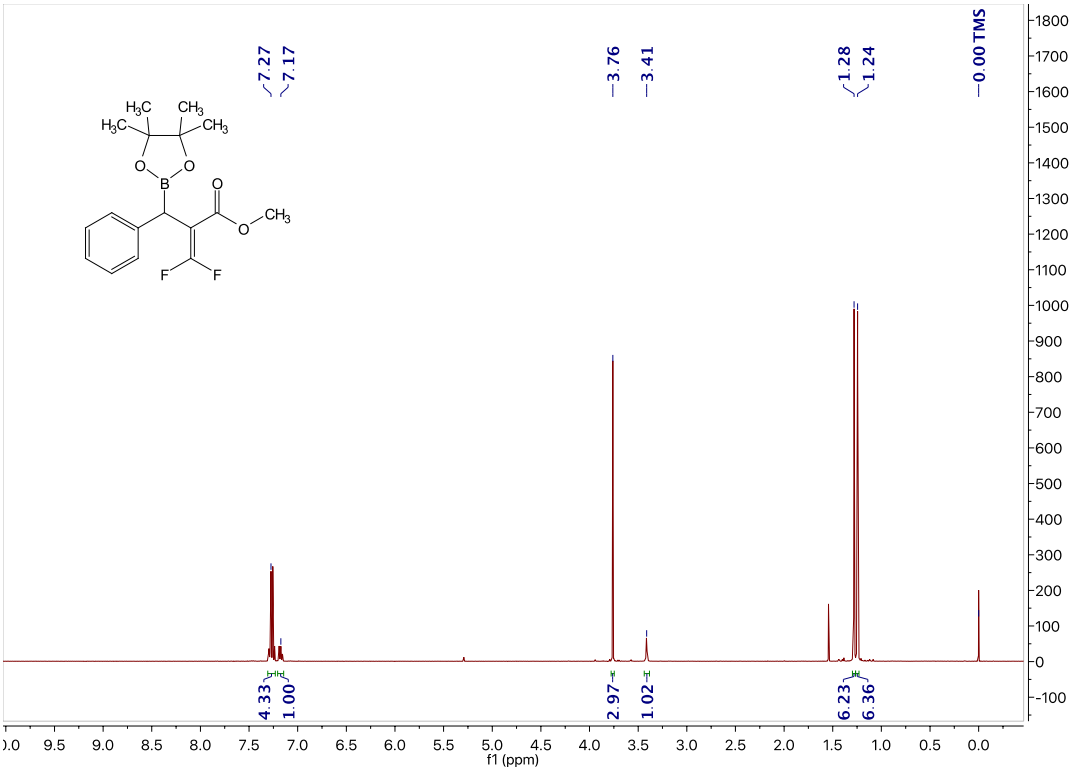
1u – ^{1}H NMR



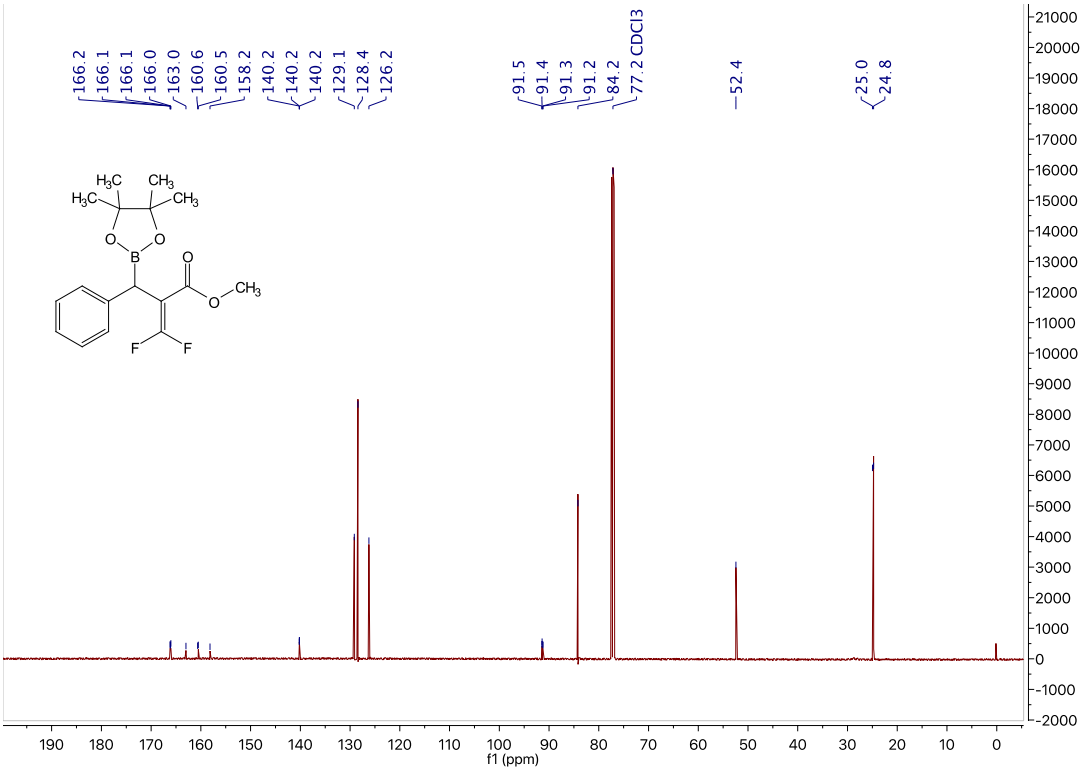
1v – ^{1}H NMR



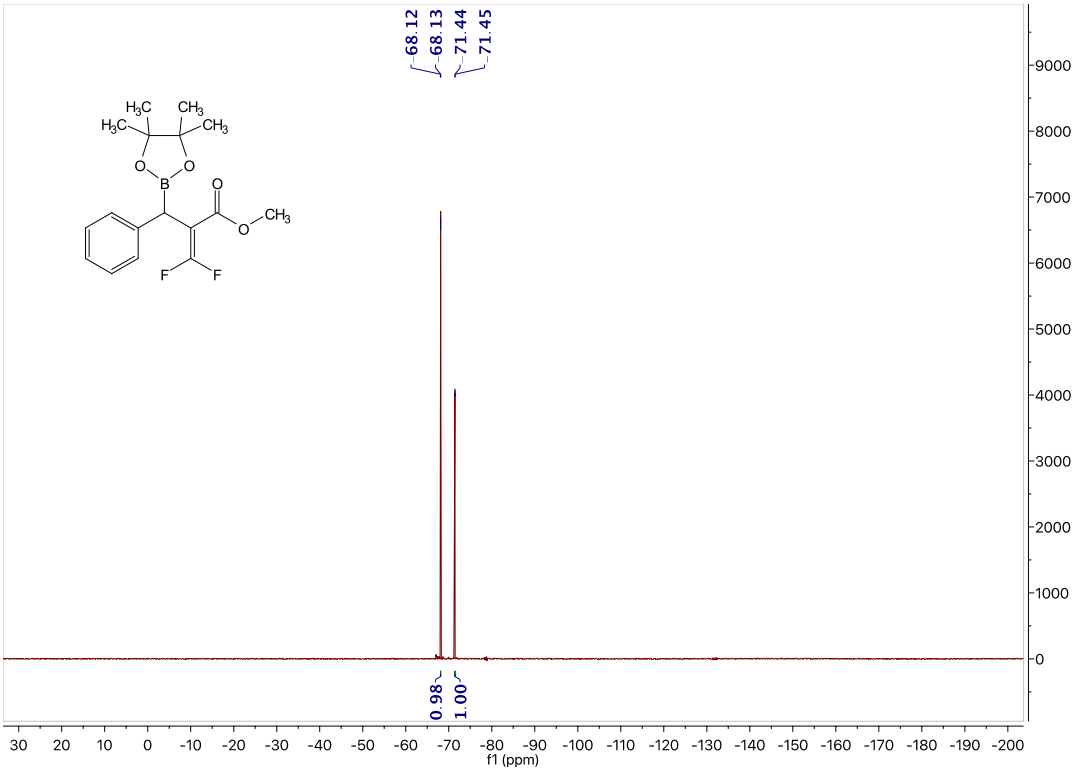
2a – ^{1}H NMR



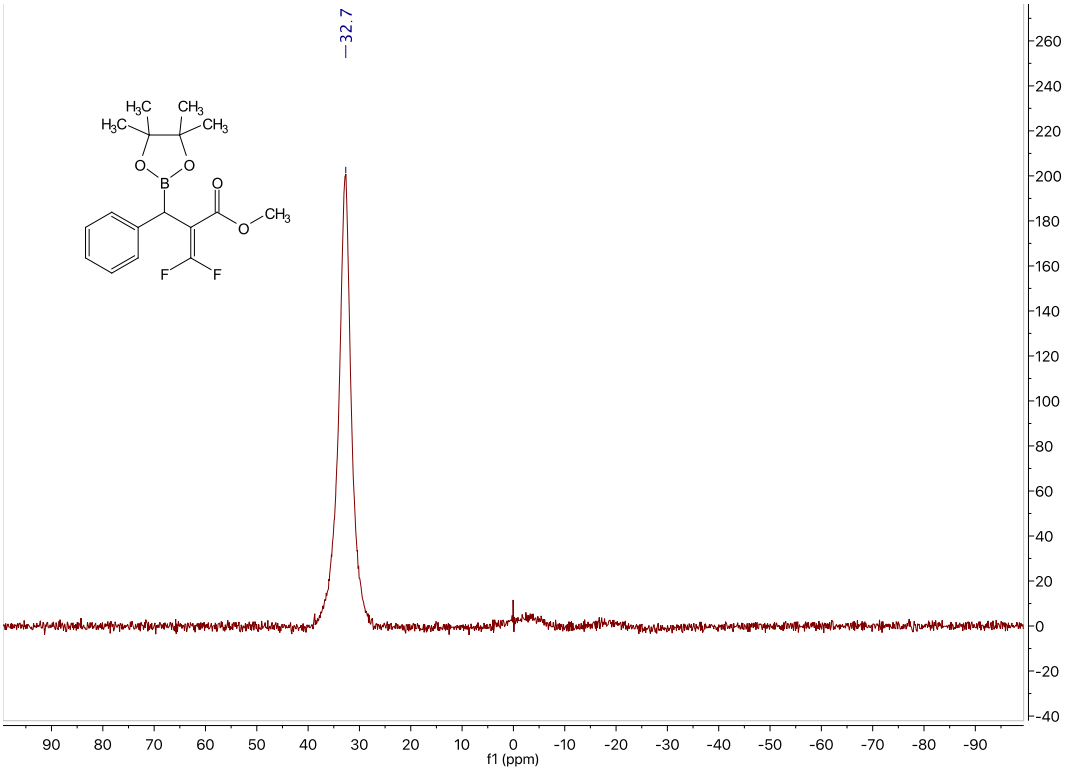
2a – ^{13}C NMR



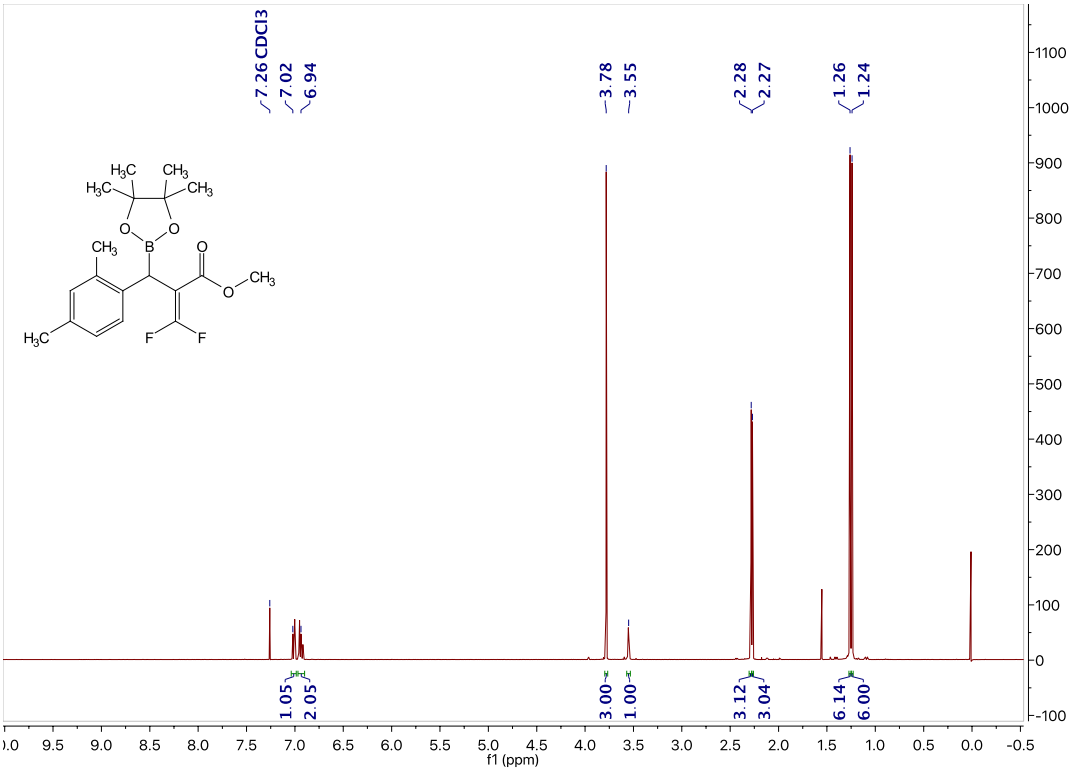
2a – ^{19}F NMR



2a – ^{11}B NMR



2b – ^{1}H NMR



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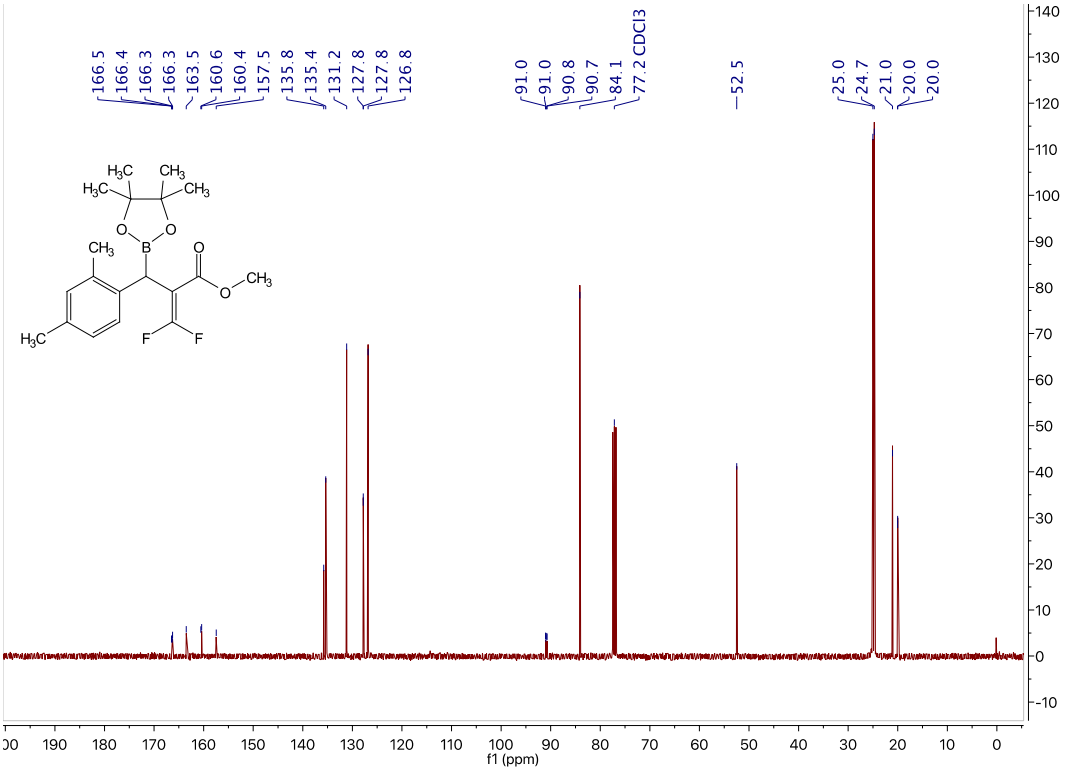
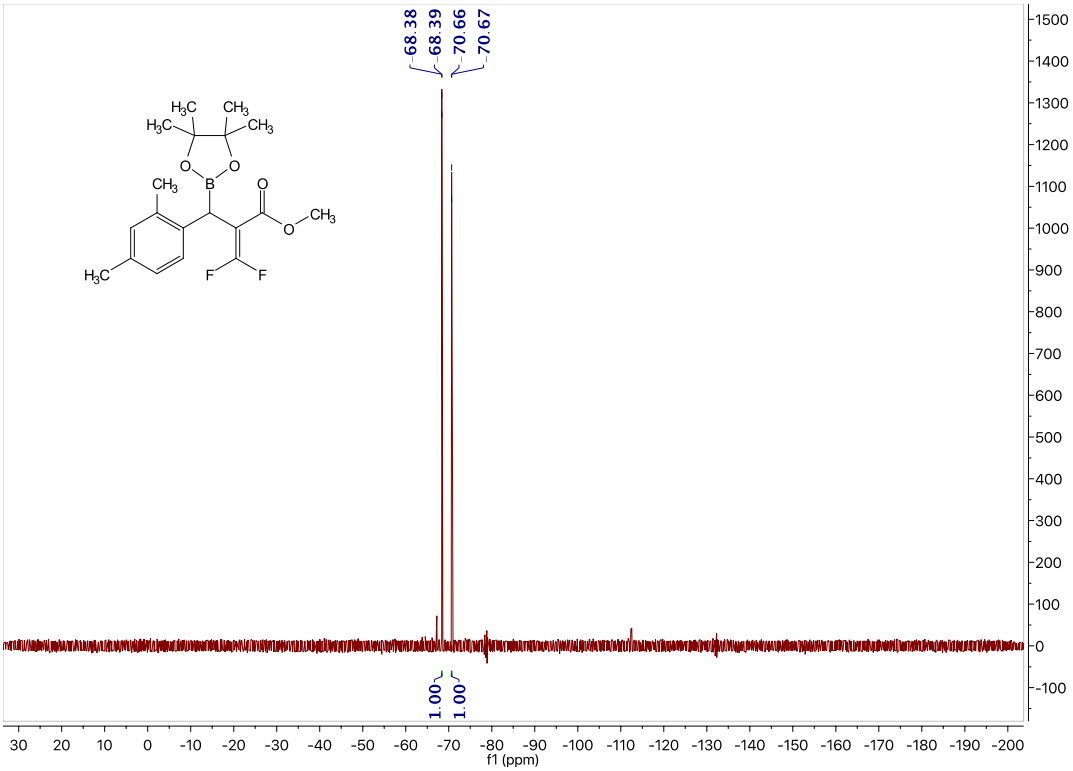
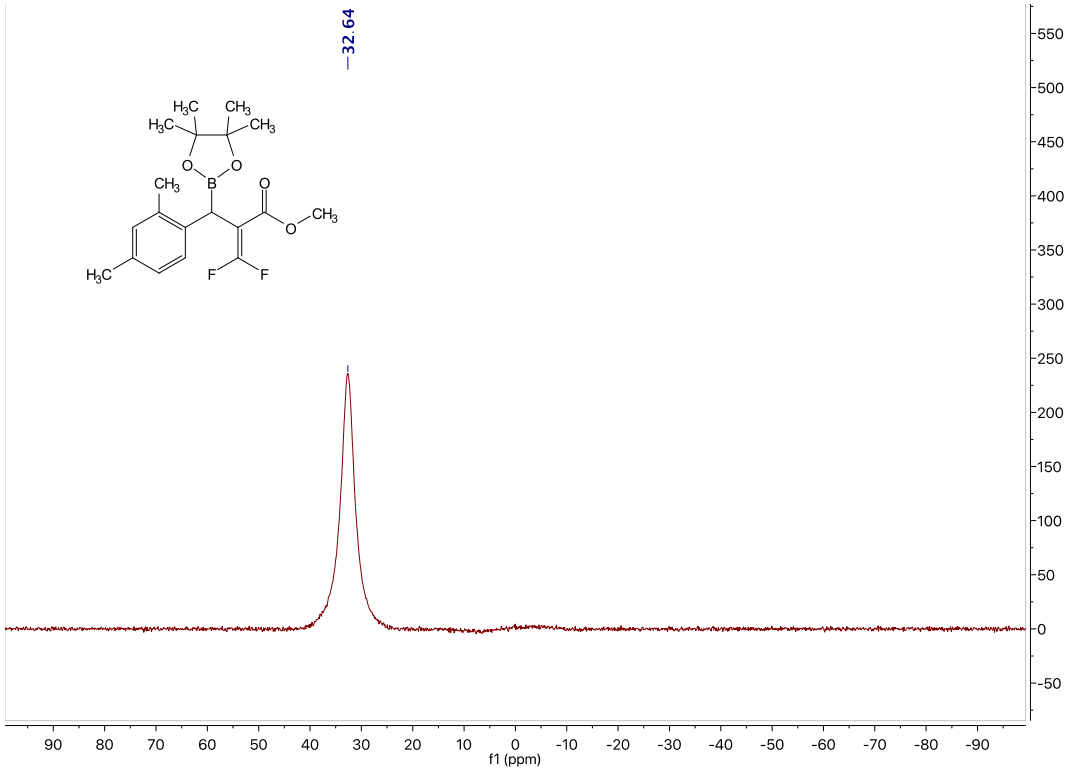


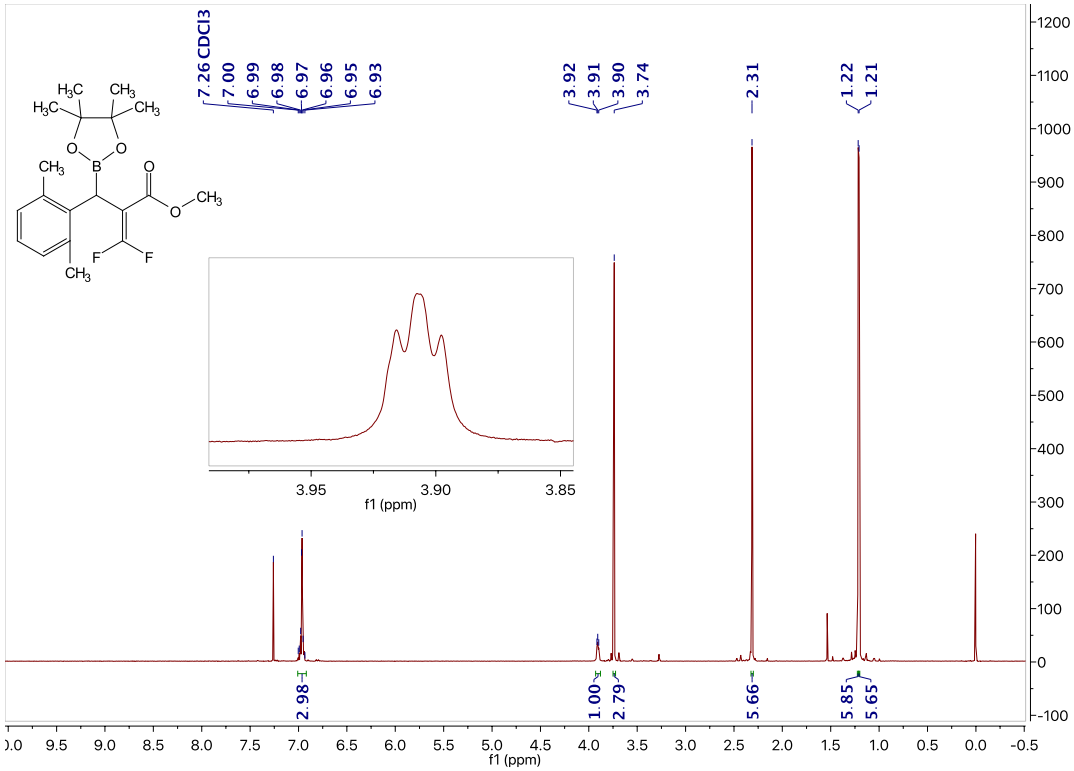
2b – ^{19}F NMR



2b – ^{11}B NMR



2c – ^{1}H NMR



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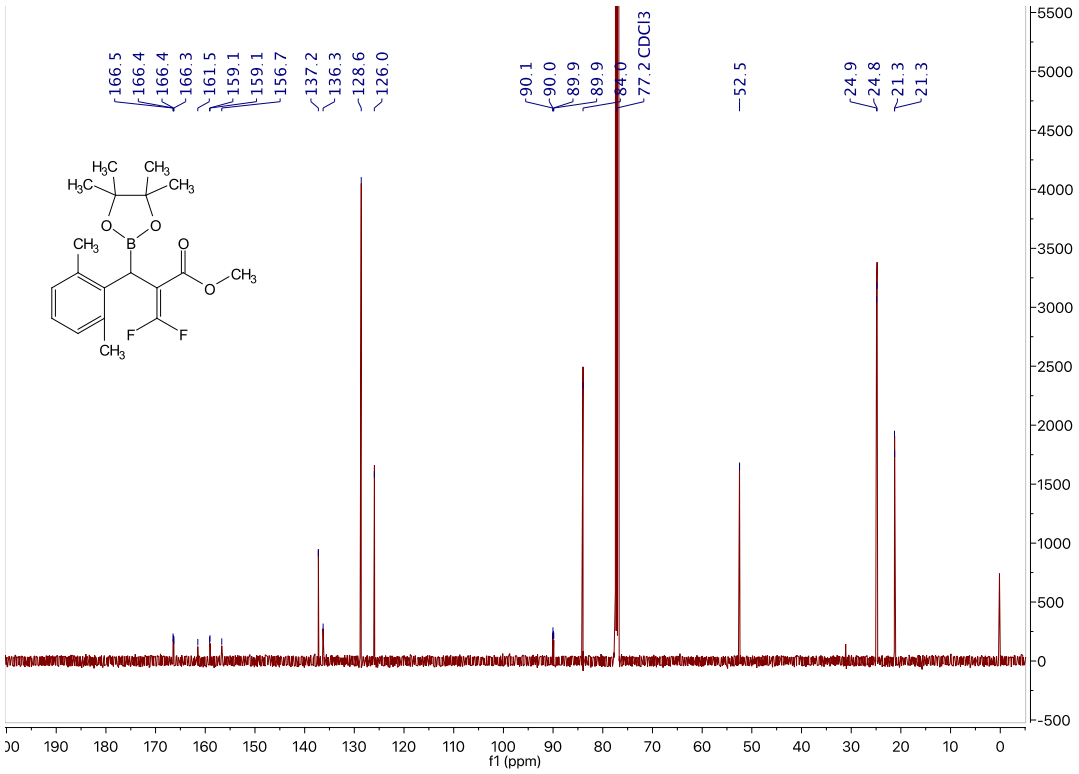

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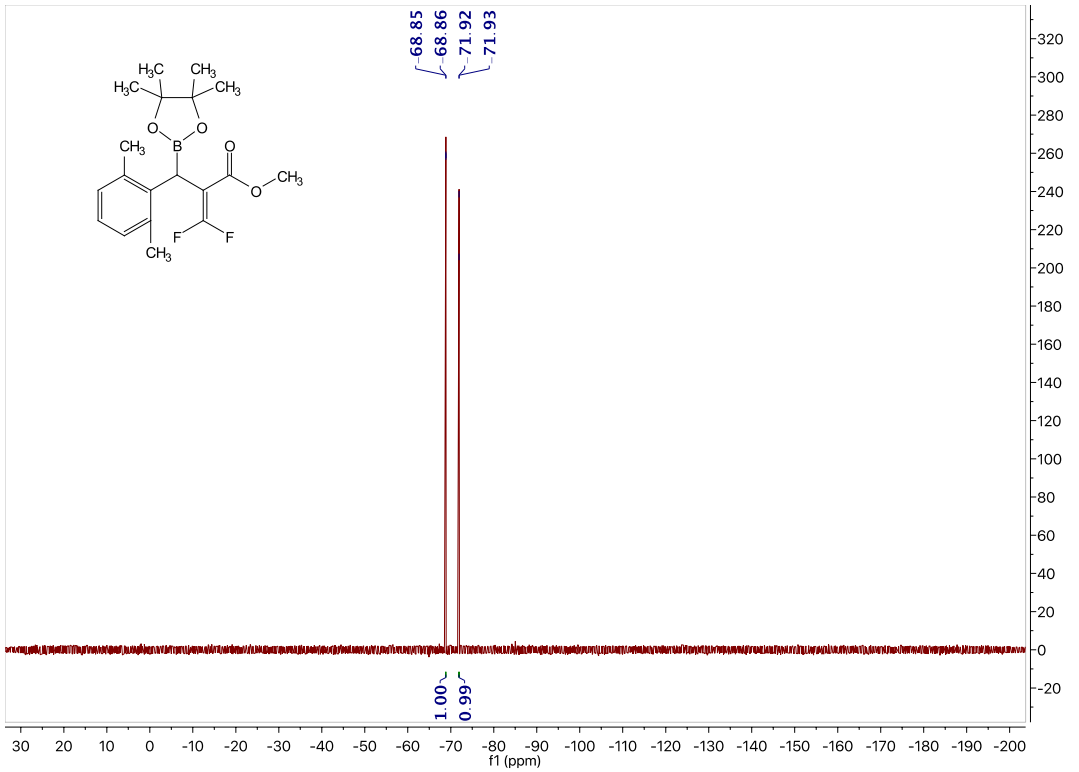

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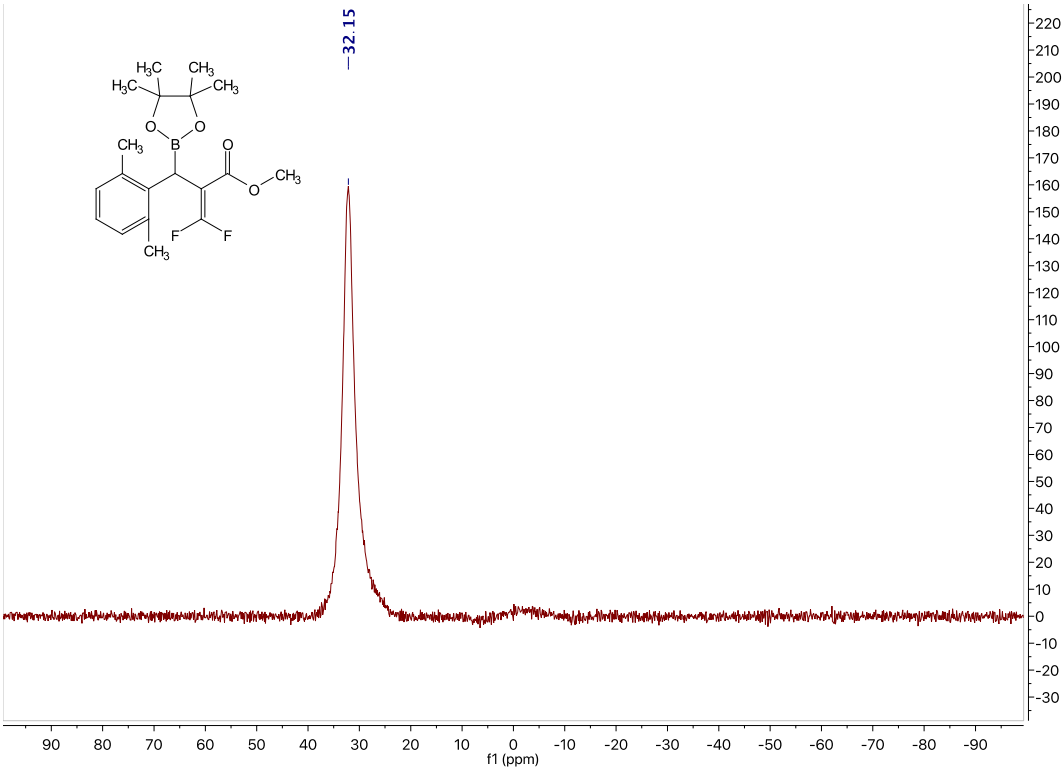

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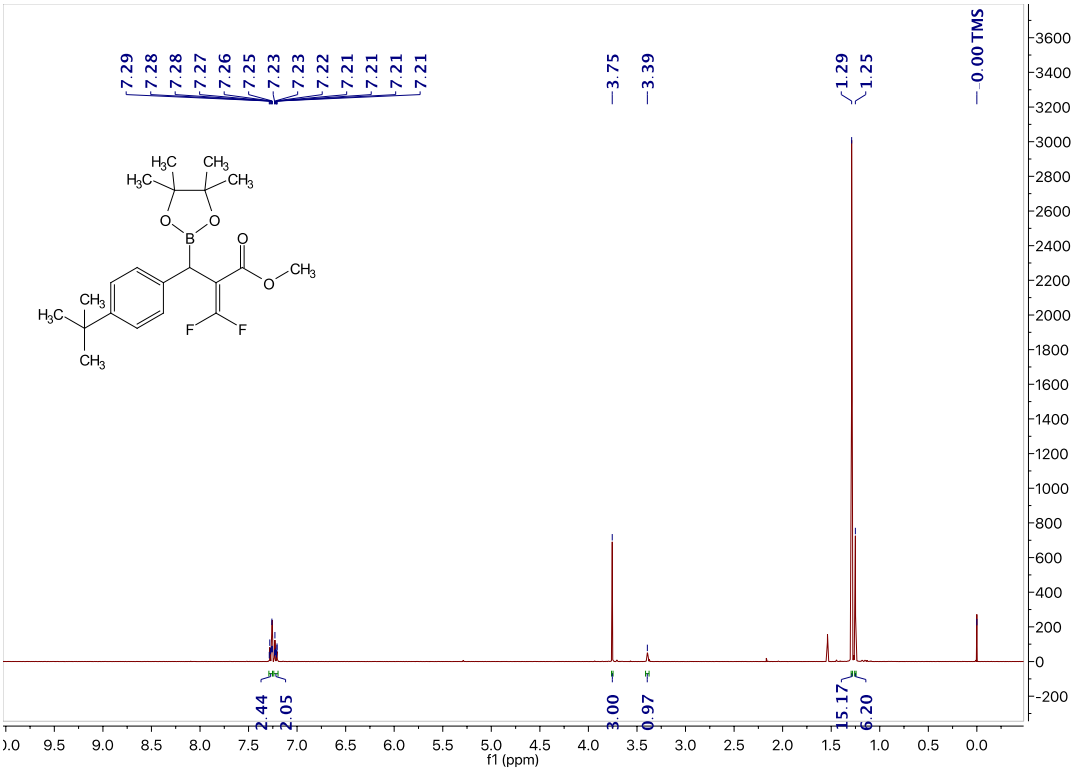
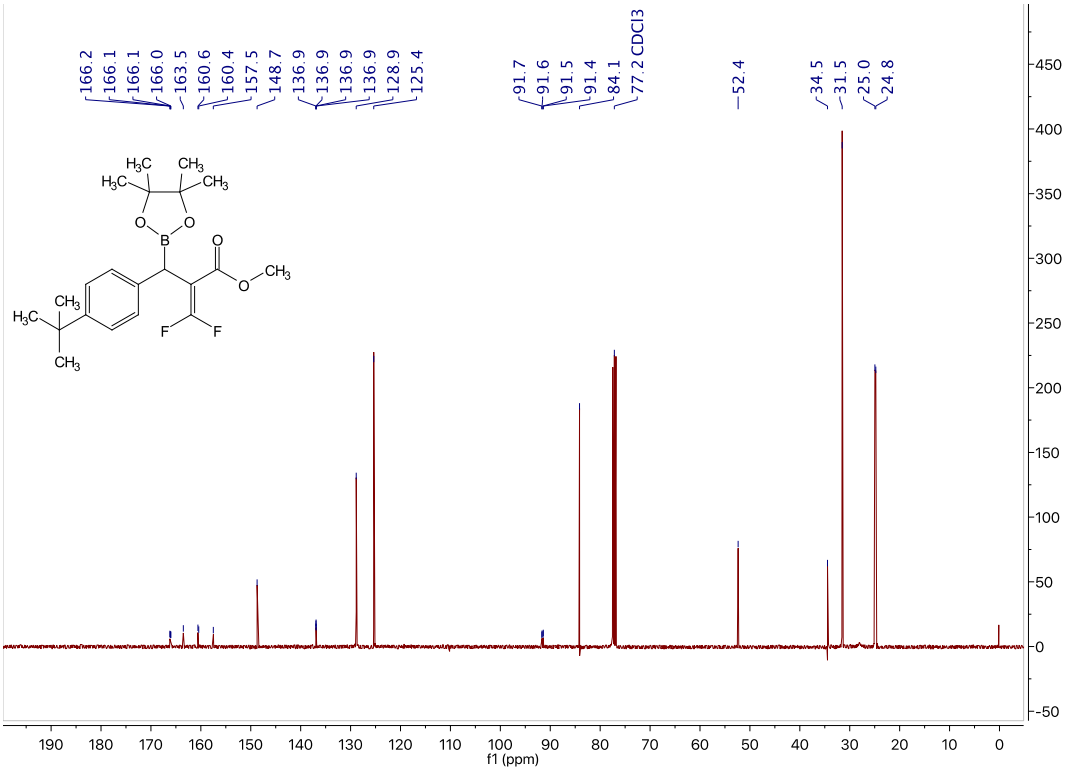
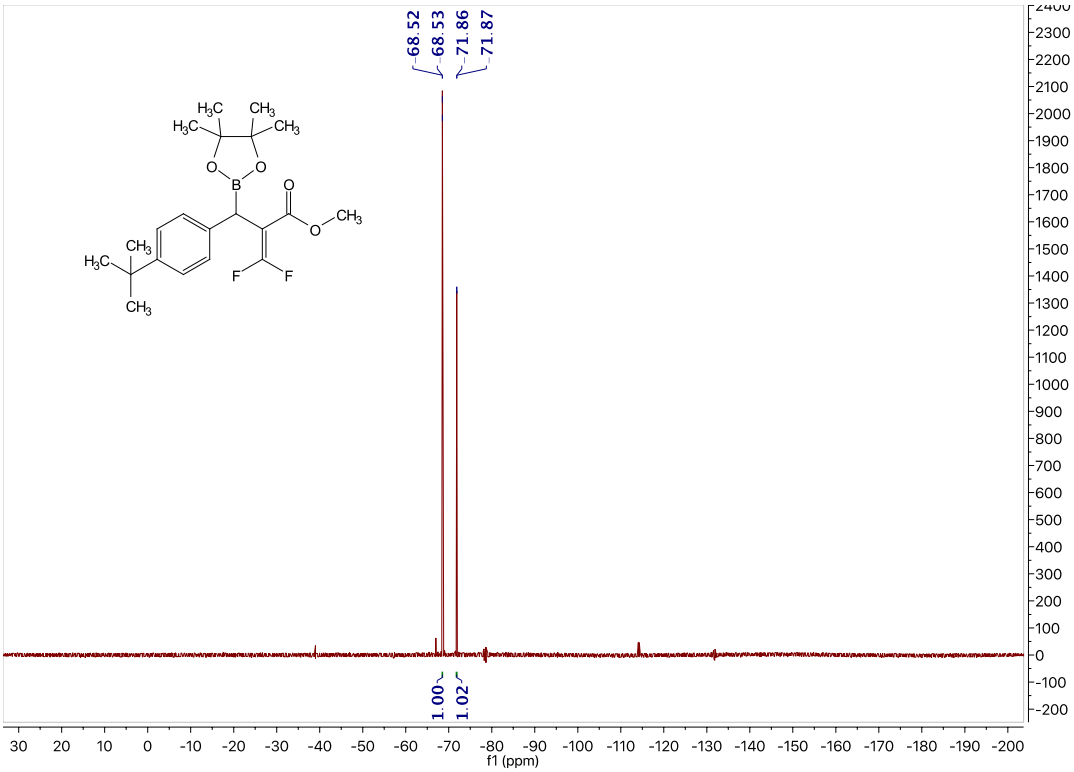


2d – ^{13}C NMR



2d – ^{19}F NMR



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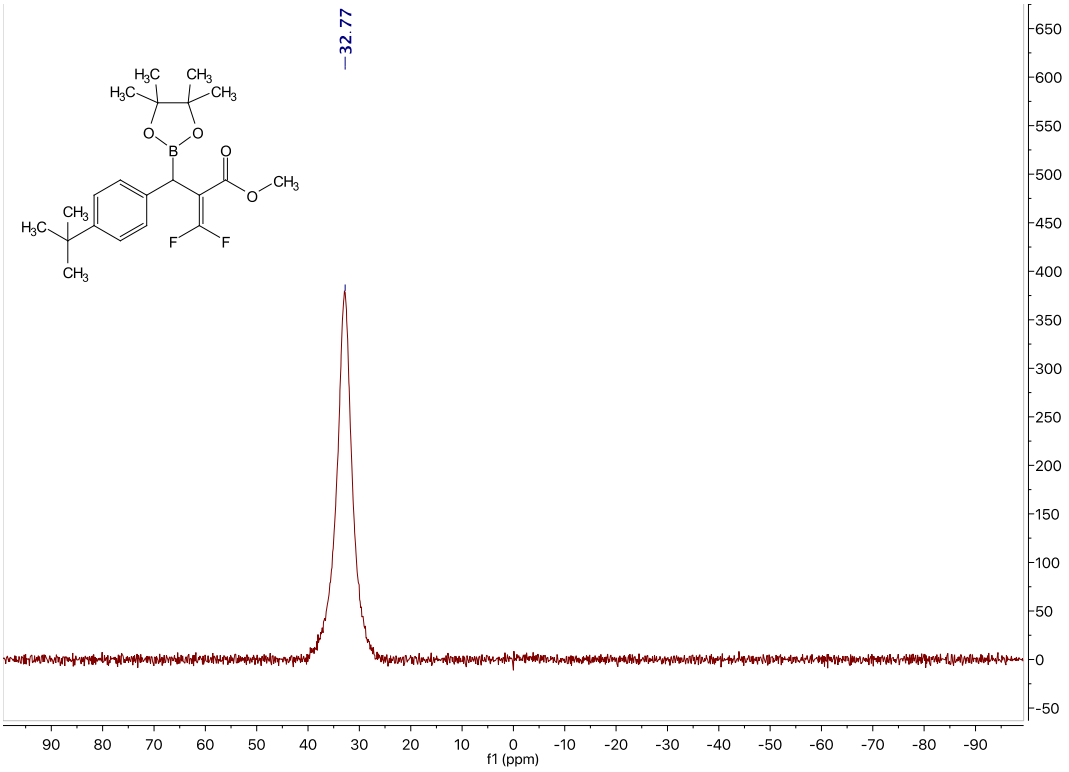
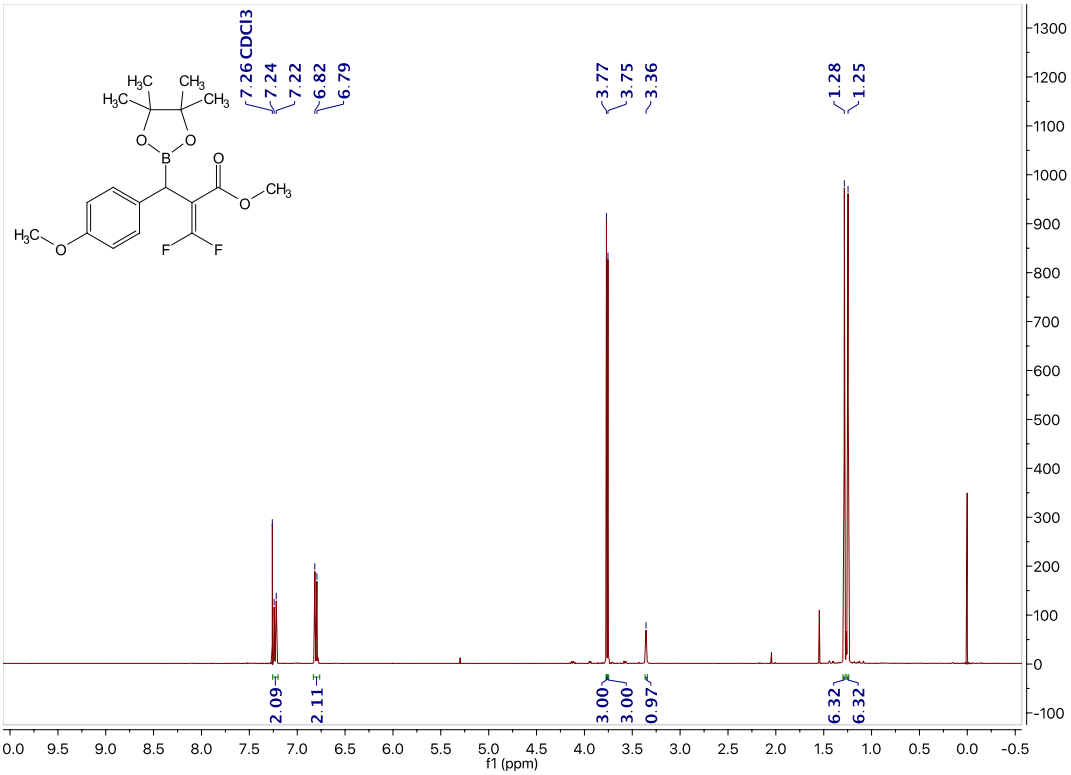


2e – ^{1}H NMR



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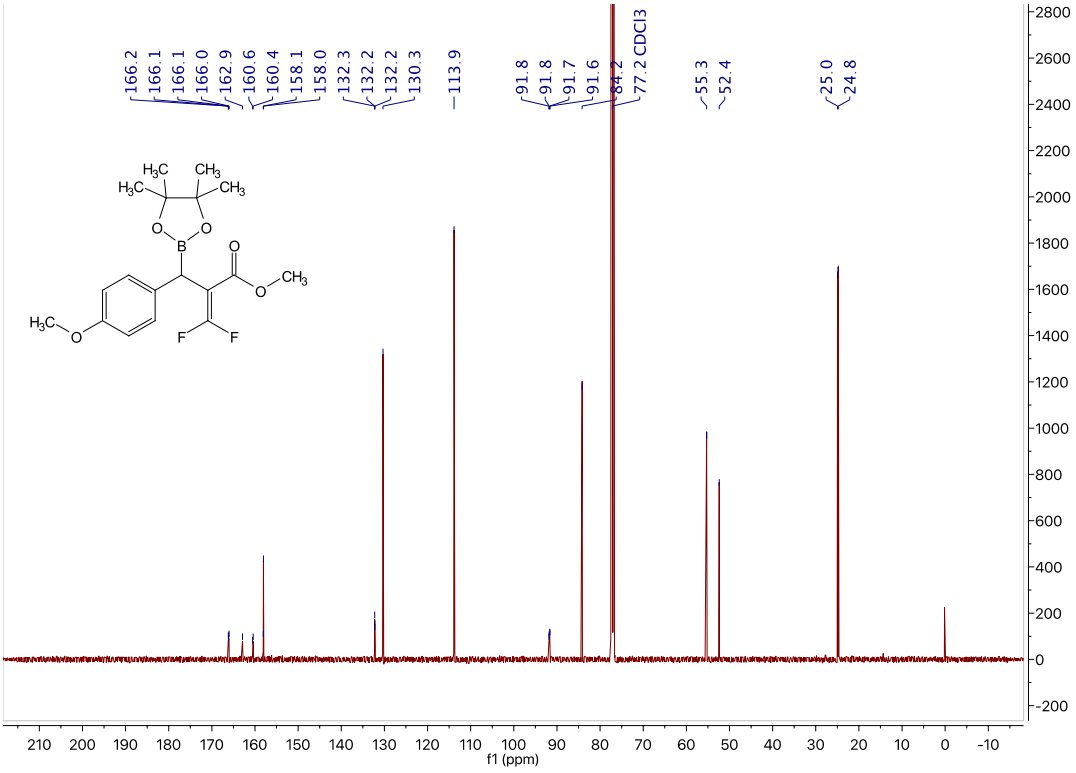

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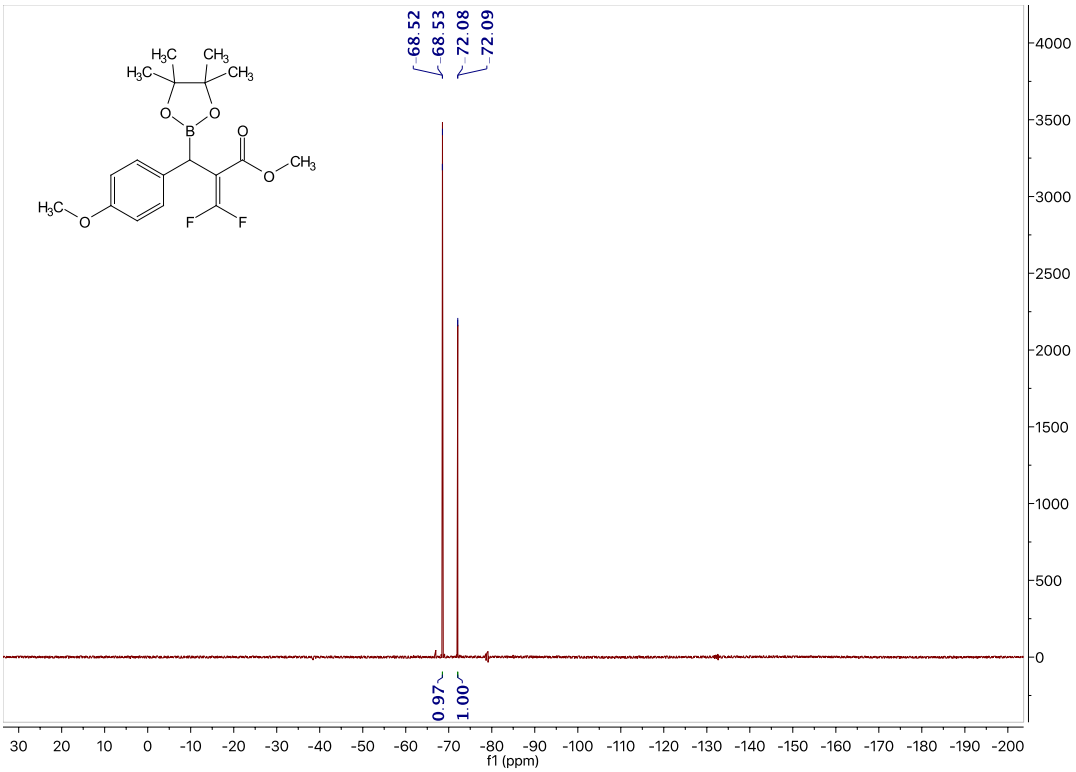

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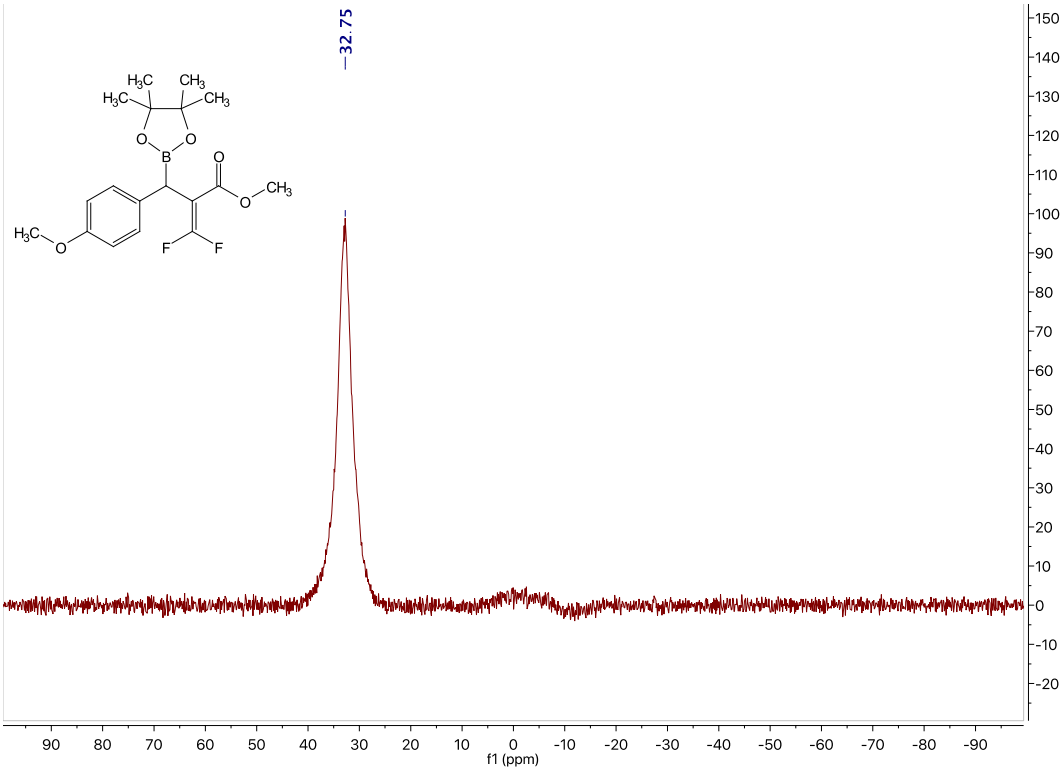

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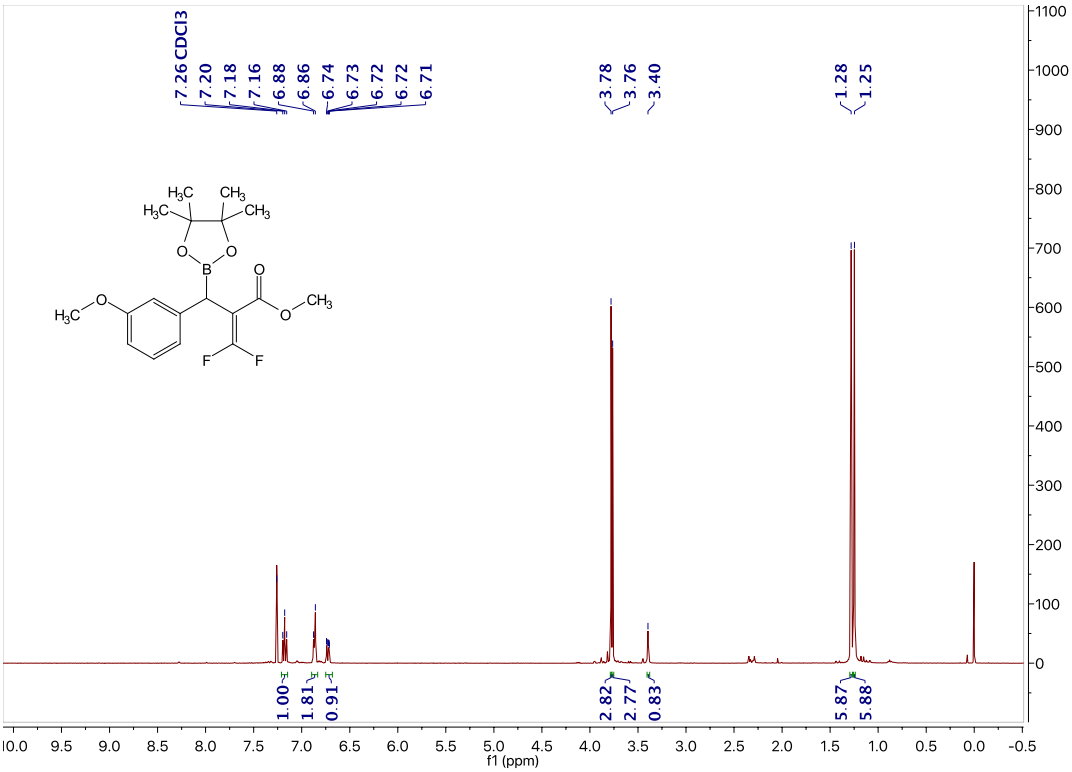
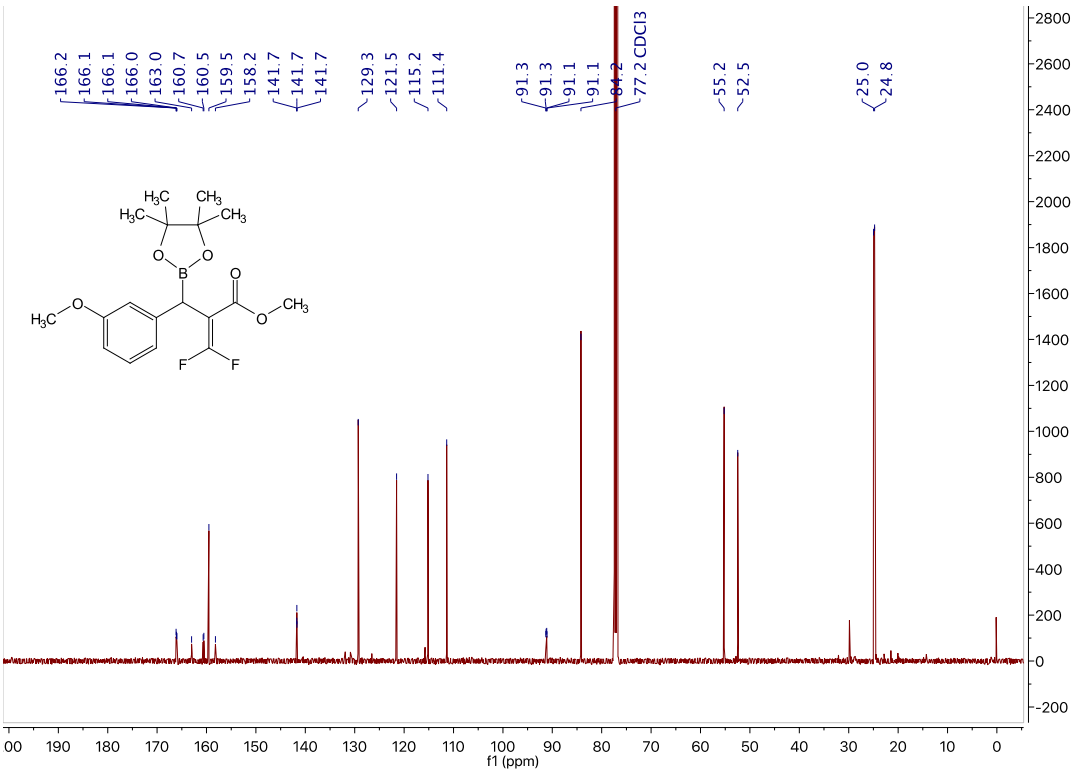
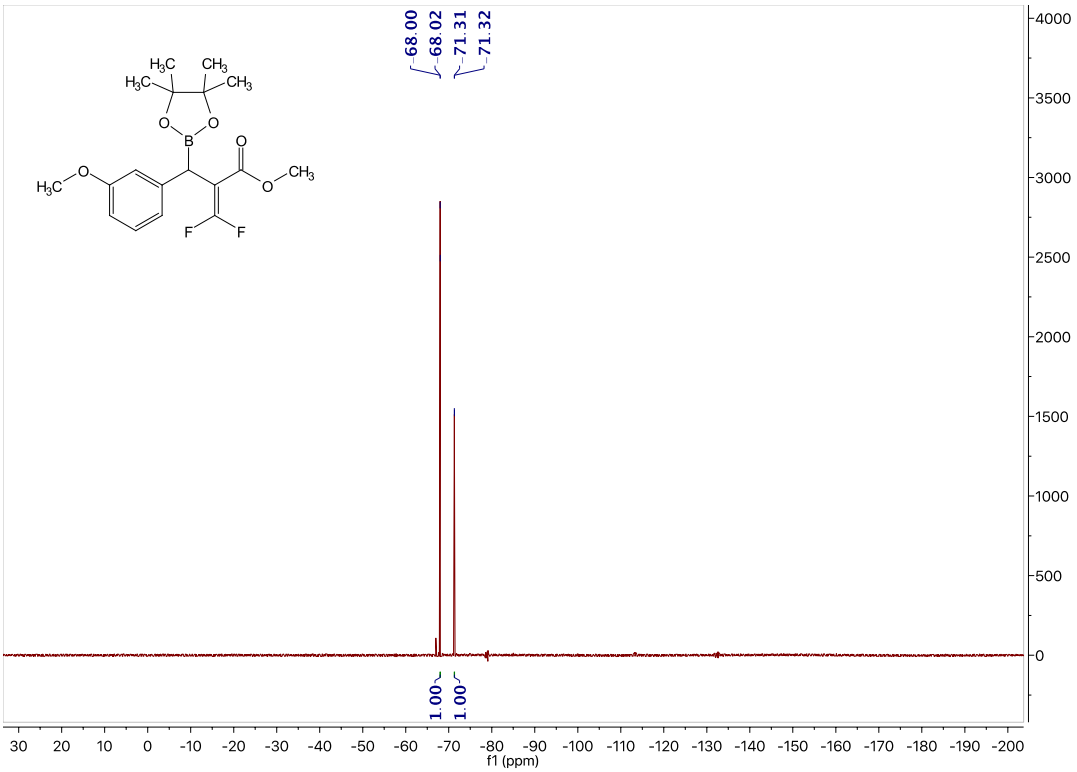


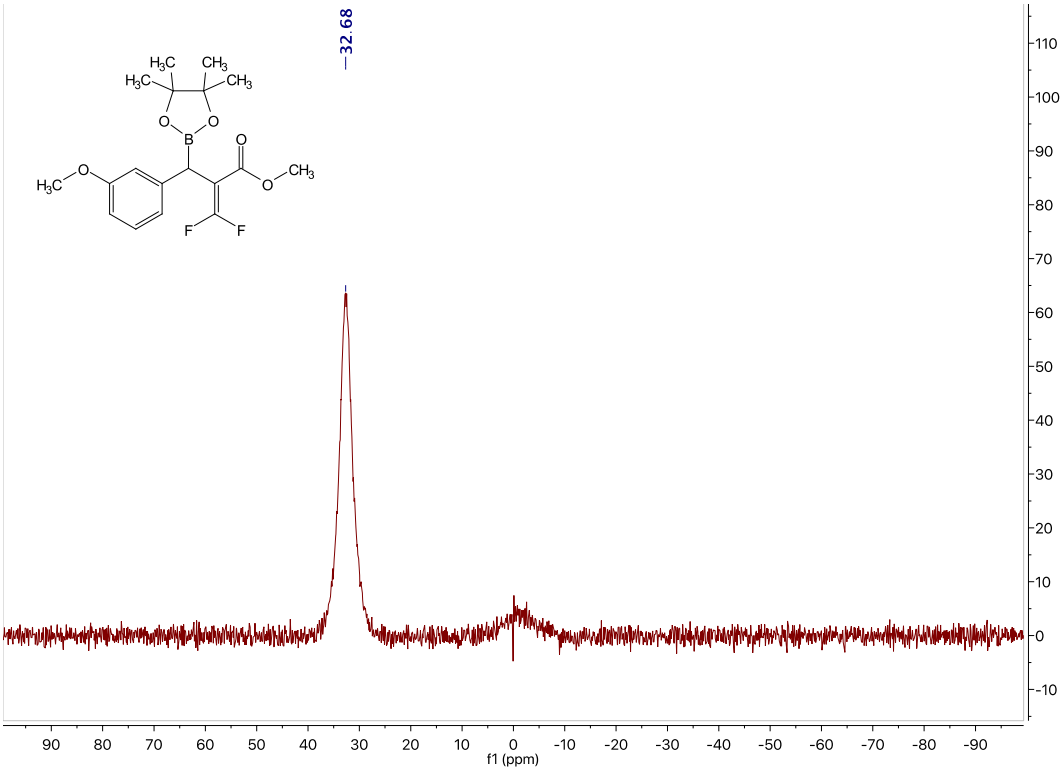
2f – ^{13}C NMR



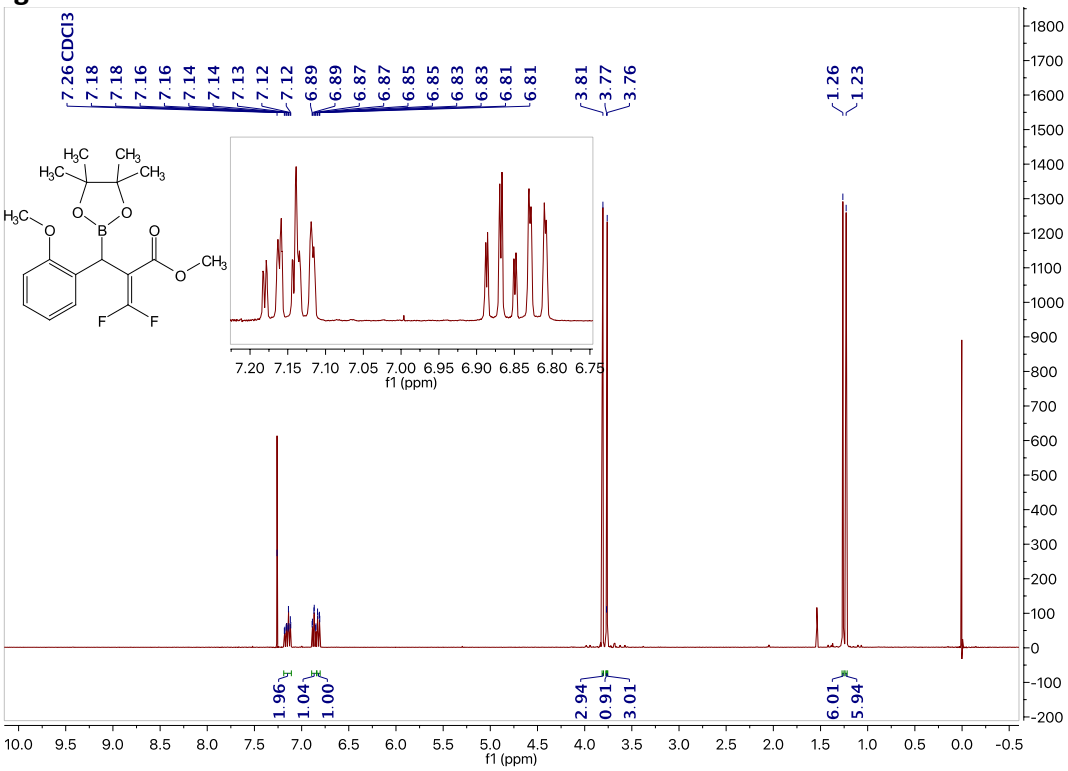
2f – ^{19}F NMR



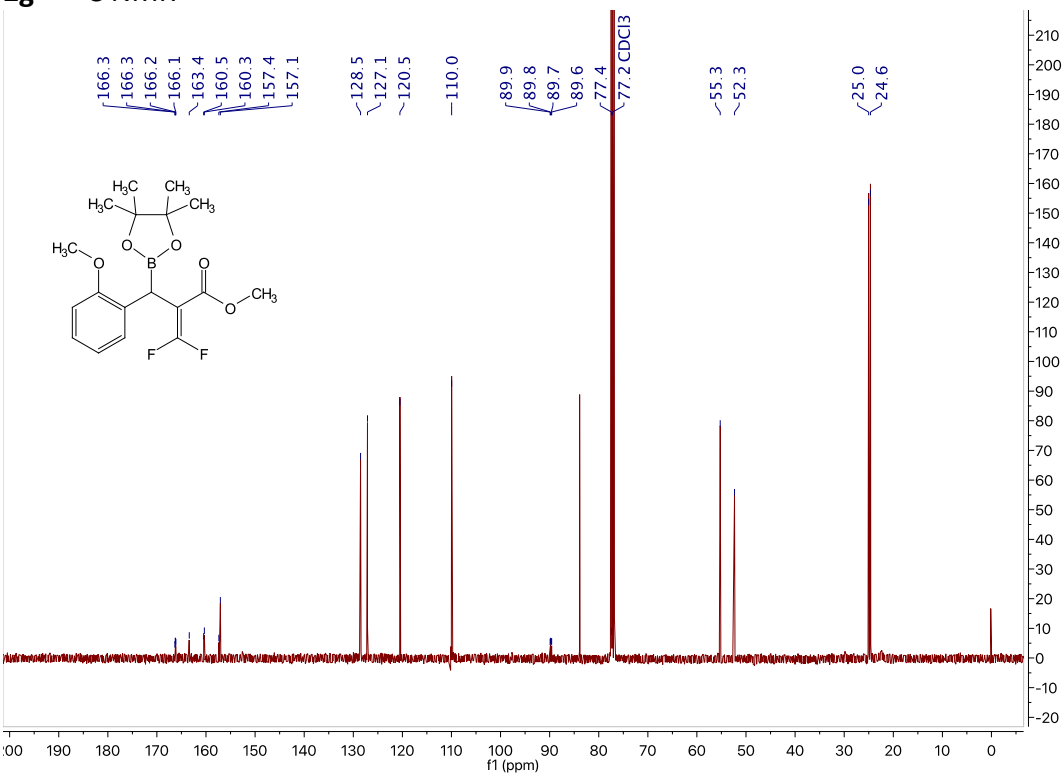
2f – ^{11}B NMR



2g – ^{1}H NMR



2g – ^{13}C NMR



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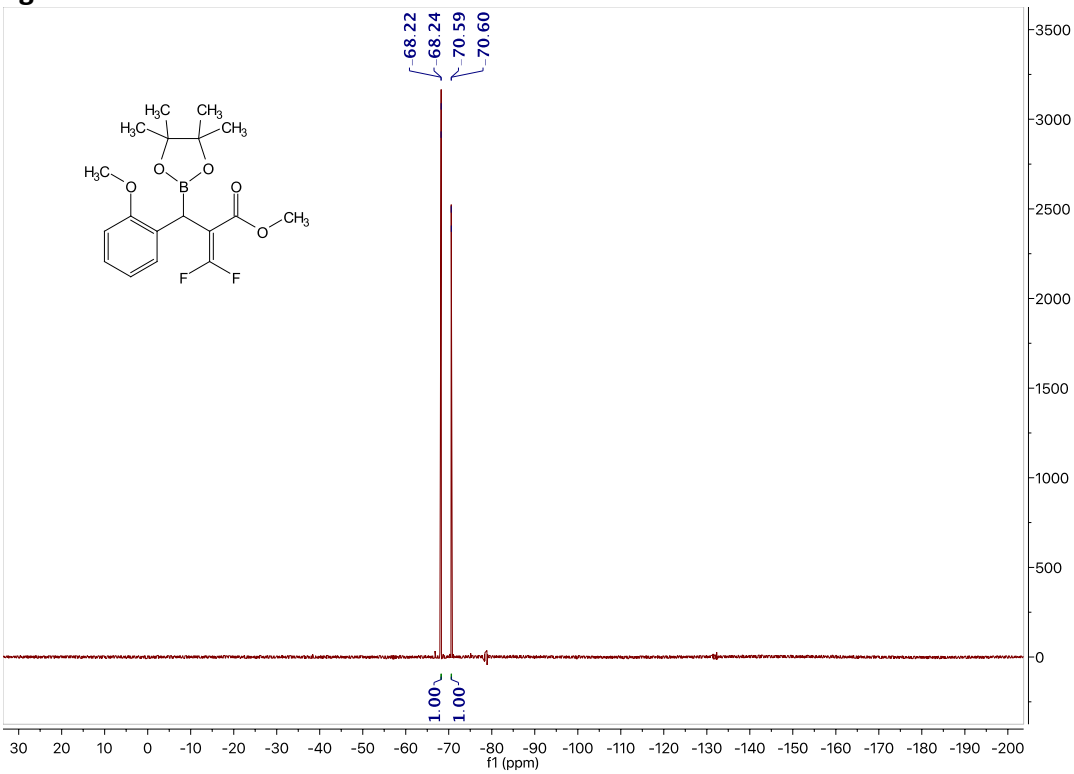

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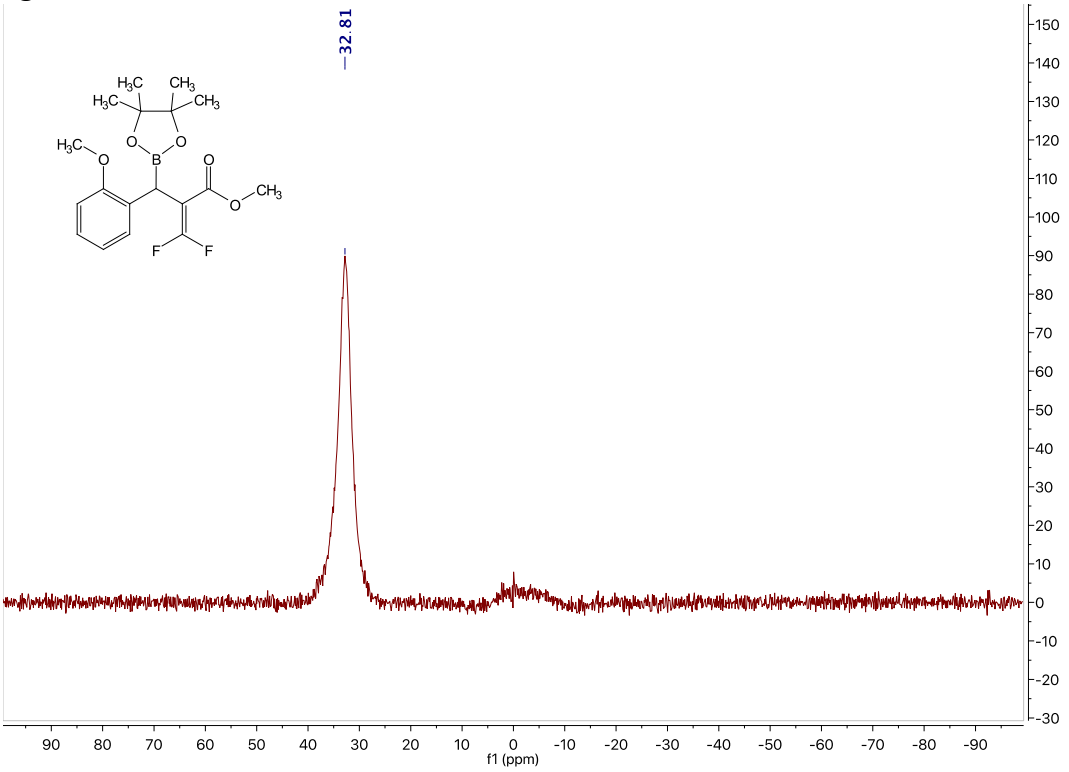
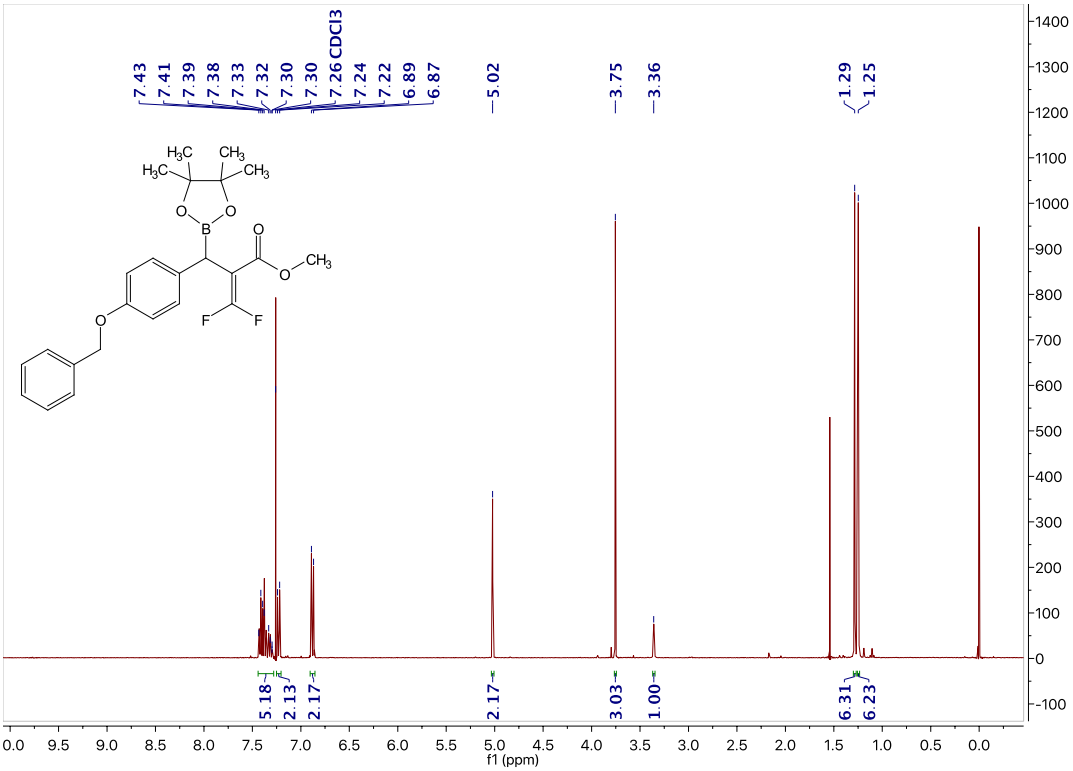


2h – ^{1}H NMR



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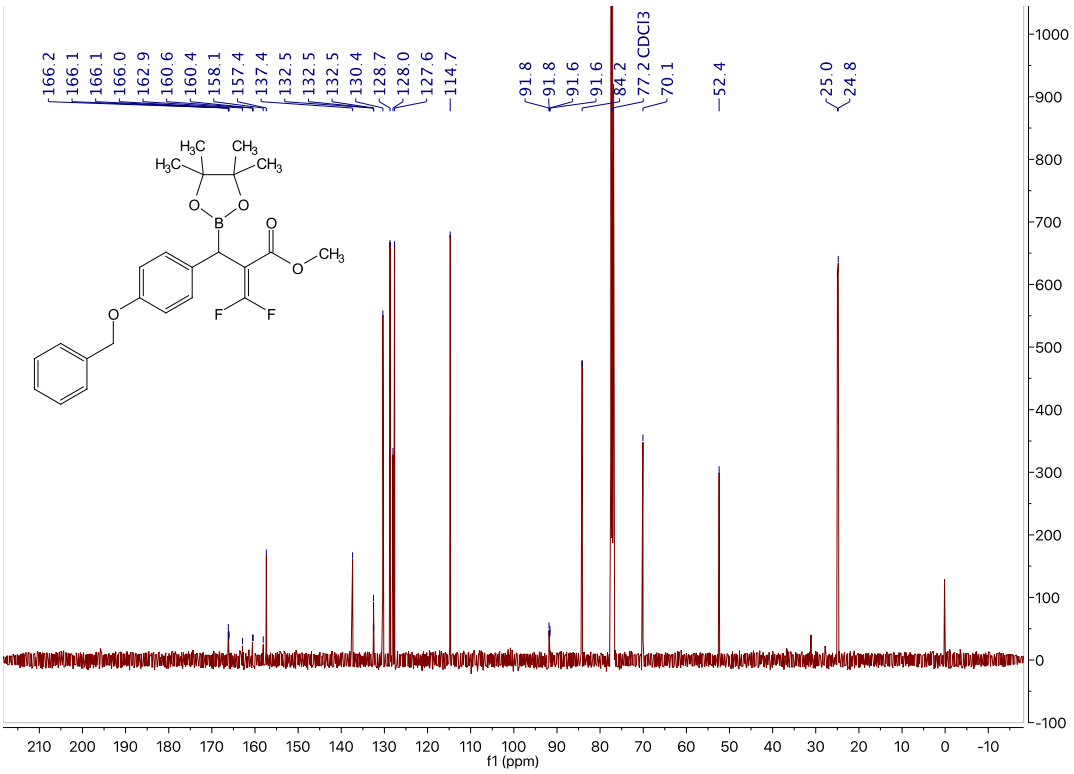
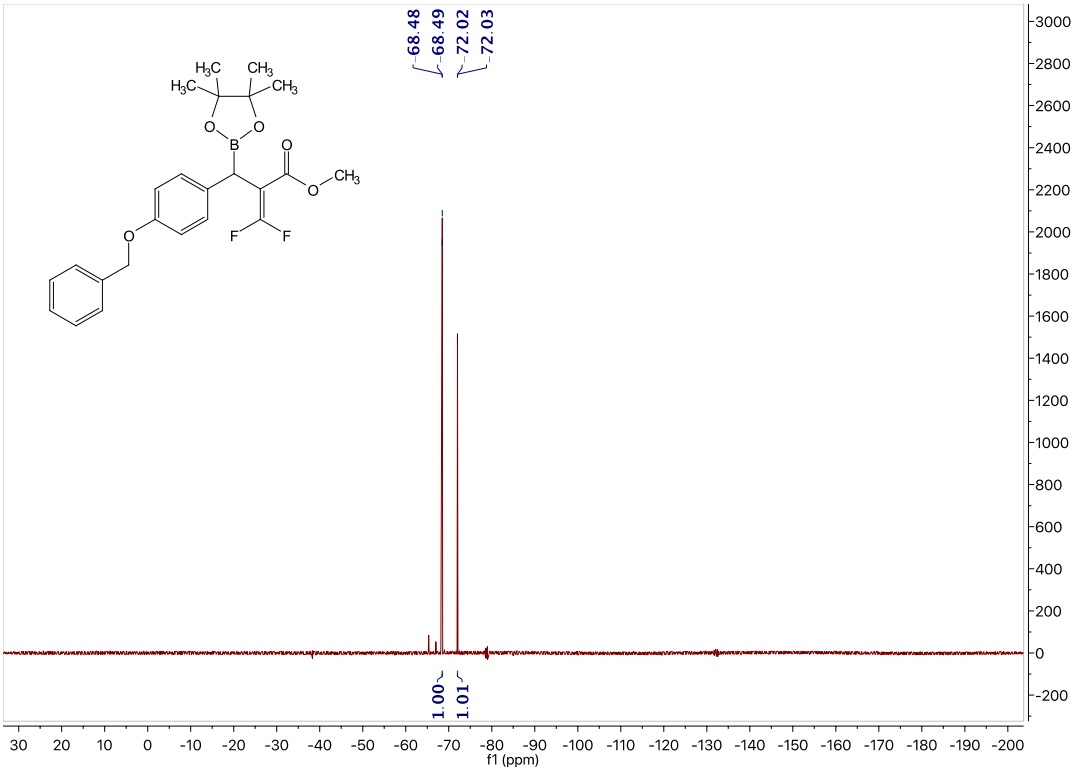
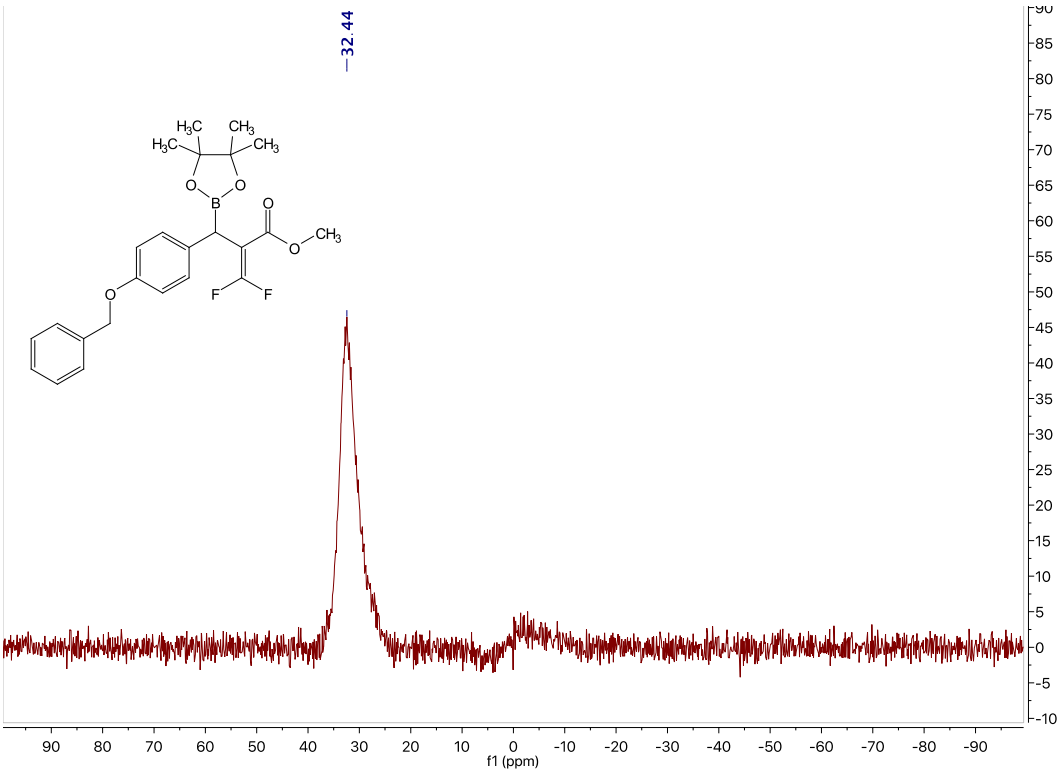


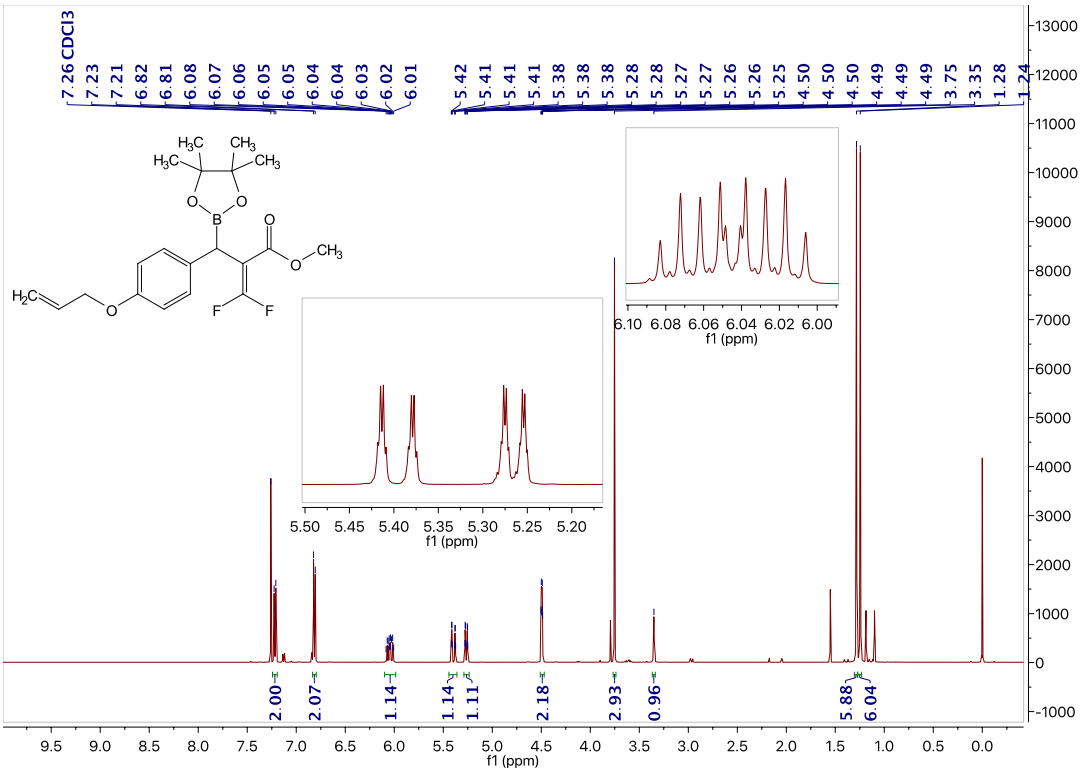
2h – ^{19}F NMR



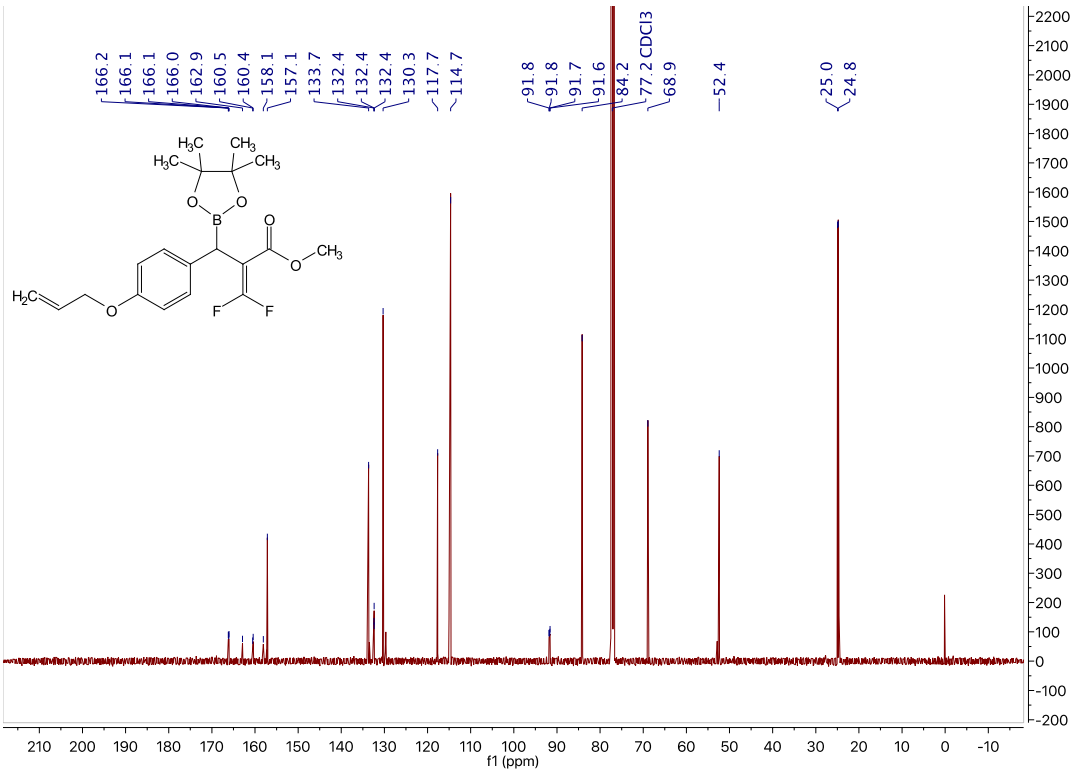
2h – ^{11}B NMR



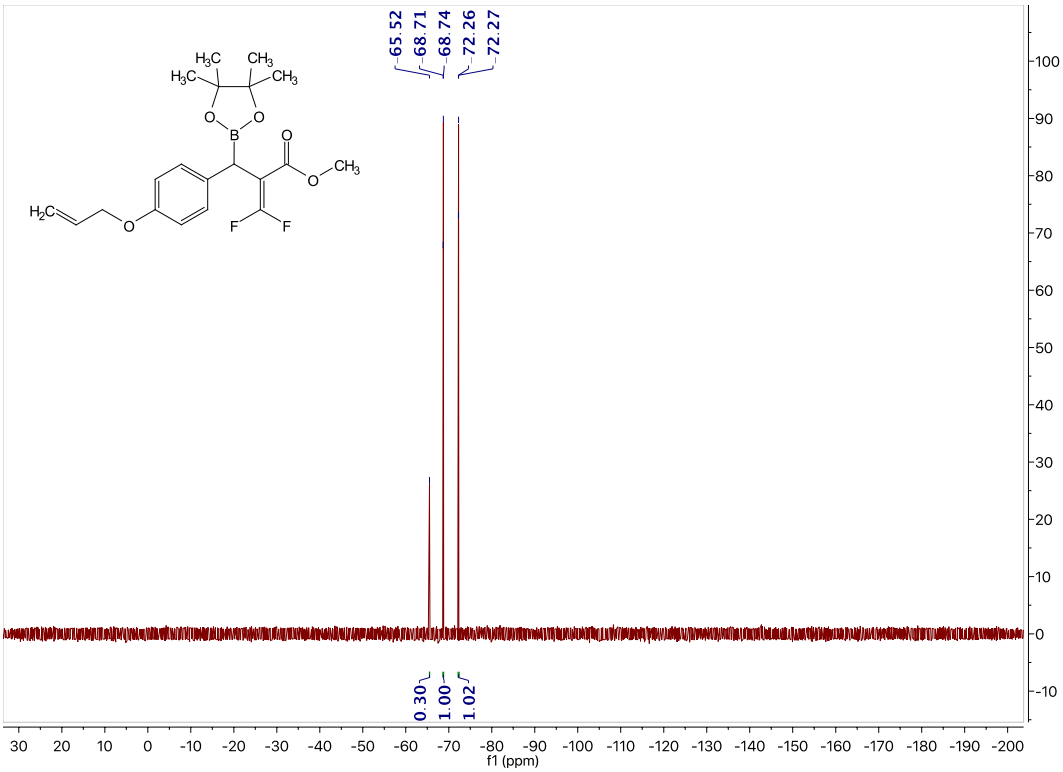
2i – ^{1}H NMR



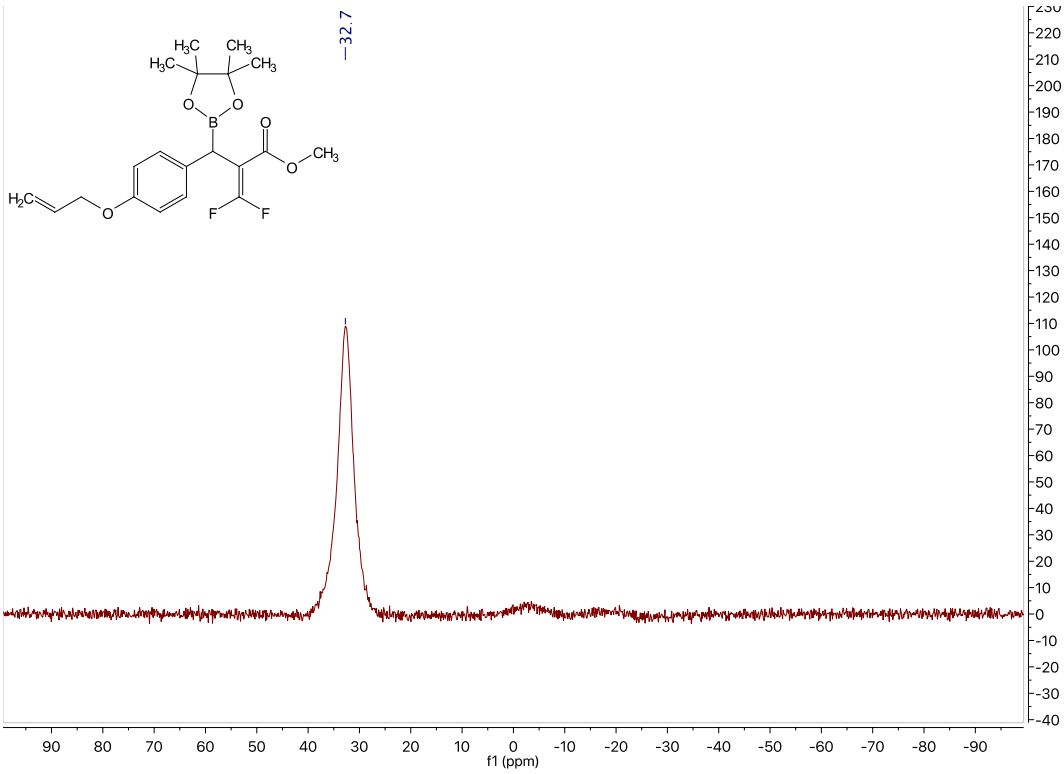
2i – ^{13}C NMR



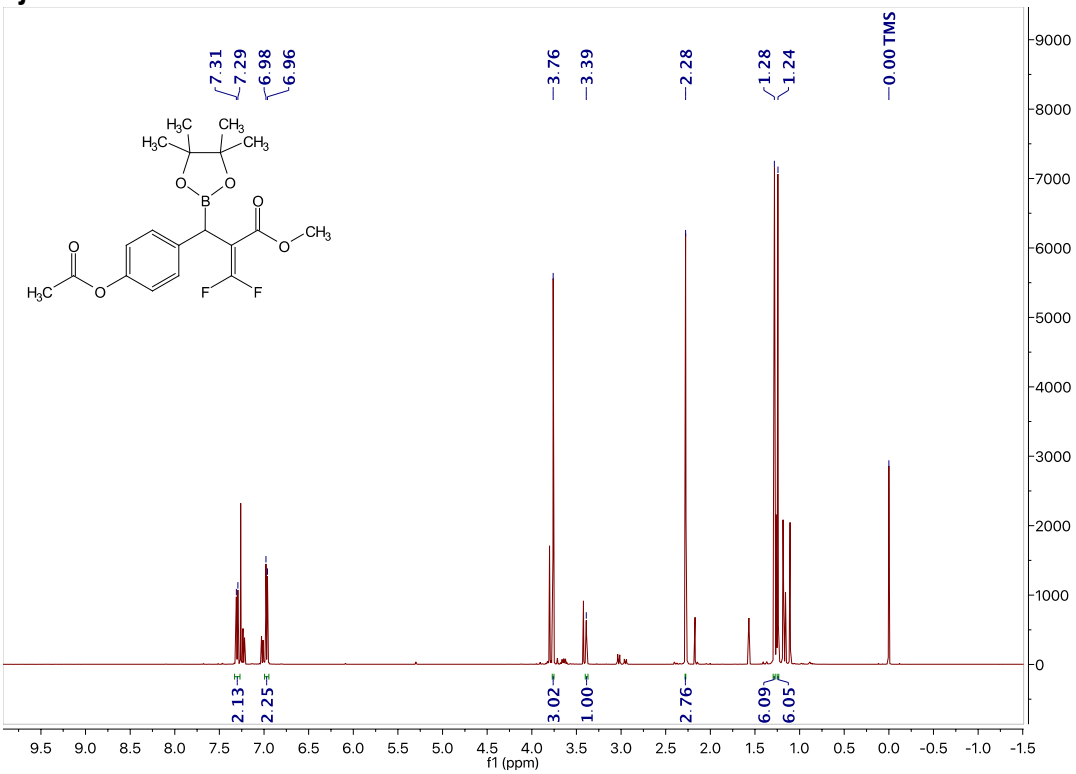
2i – ^{19}F NMR



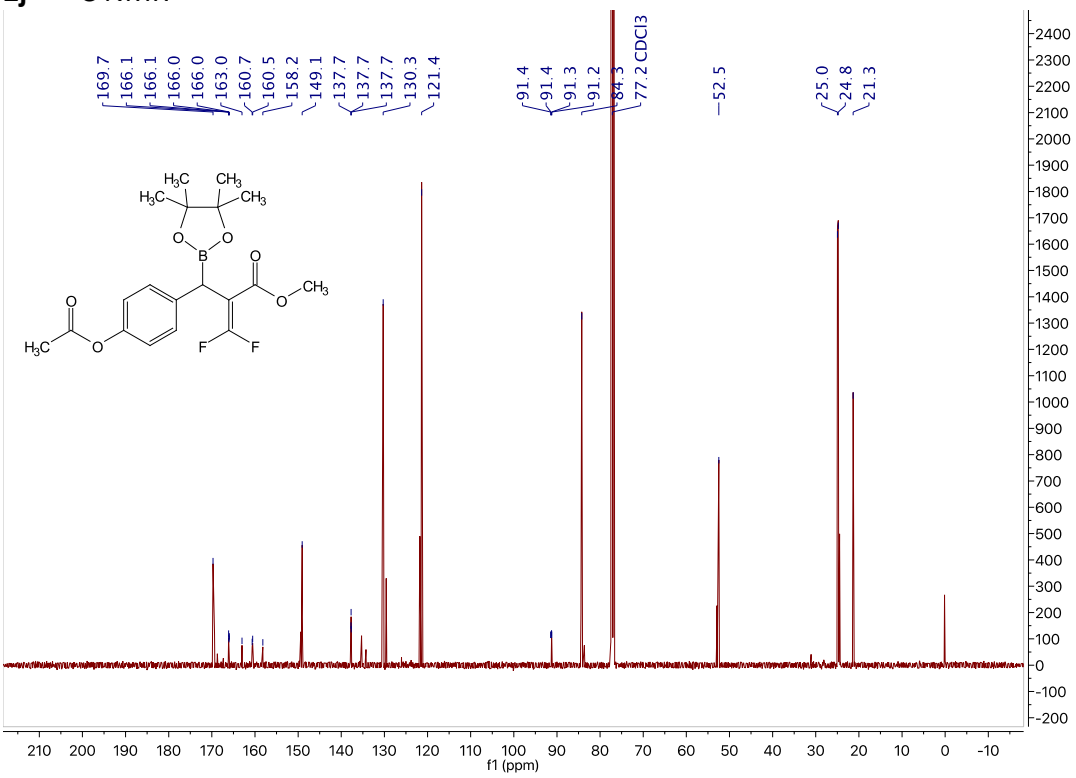
2i – ^{11}B NMR



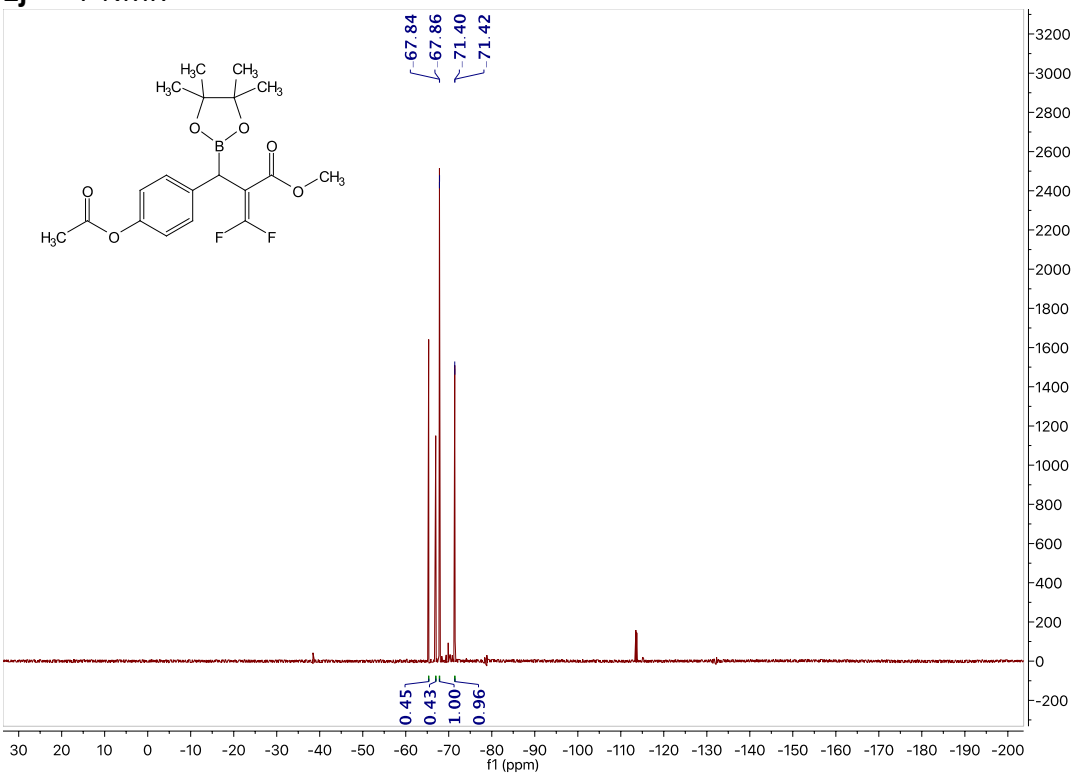
2j – ^{1}H NMR



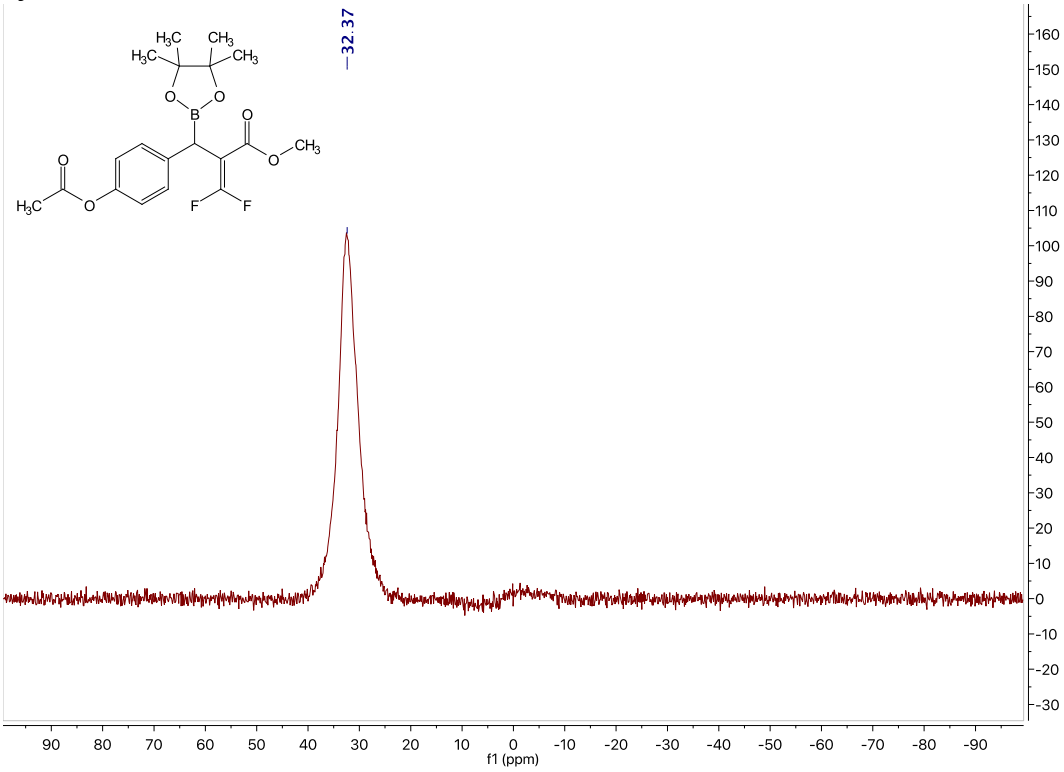
2j – ^{13}C NMR



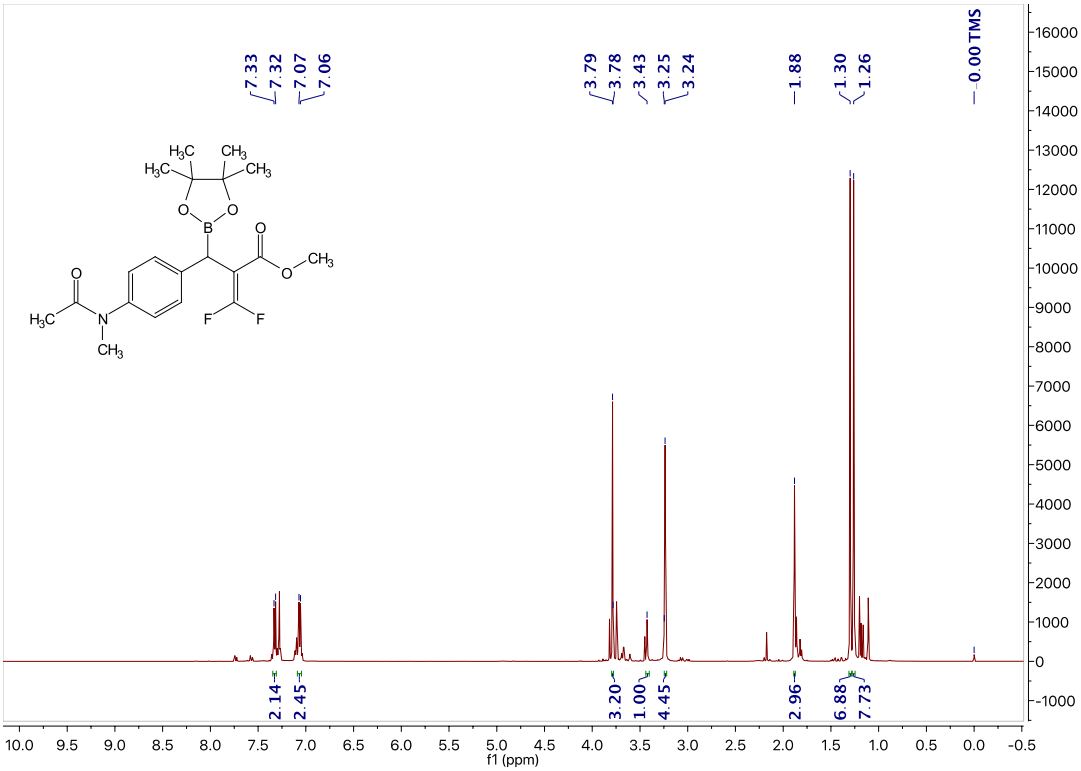
2j – ^{19}F NMR



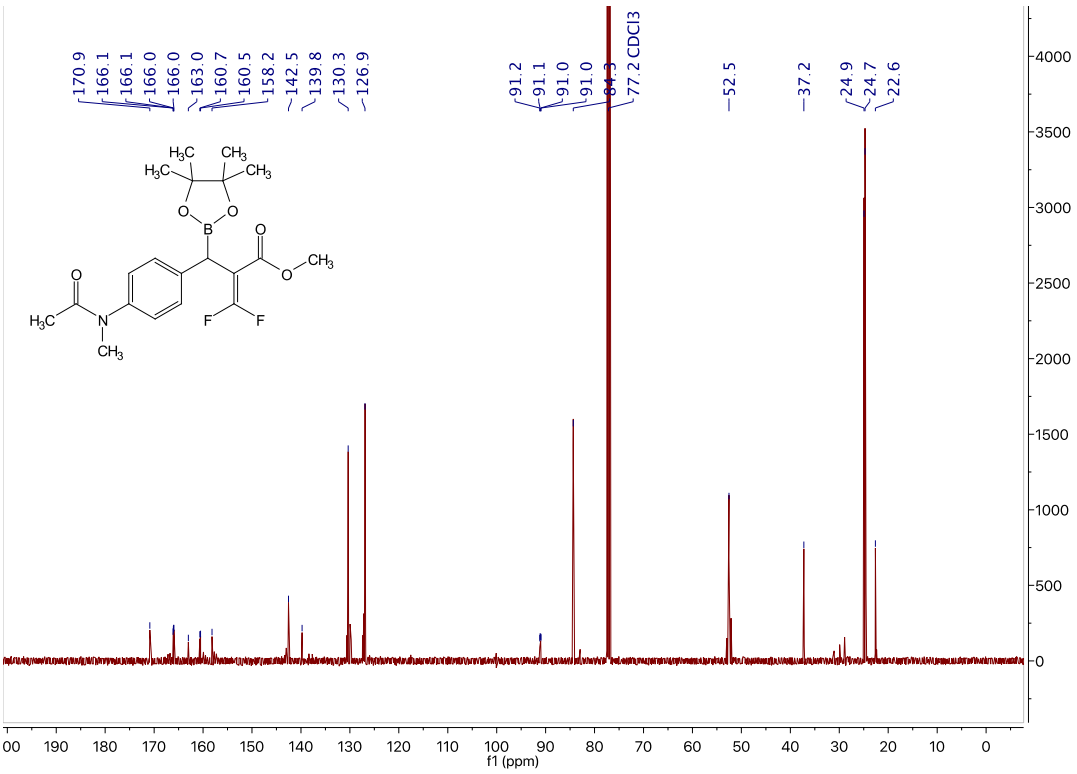
2j – ^{11}B NMR



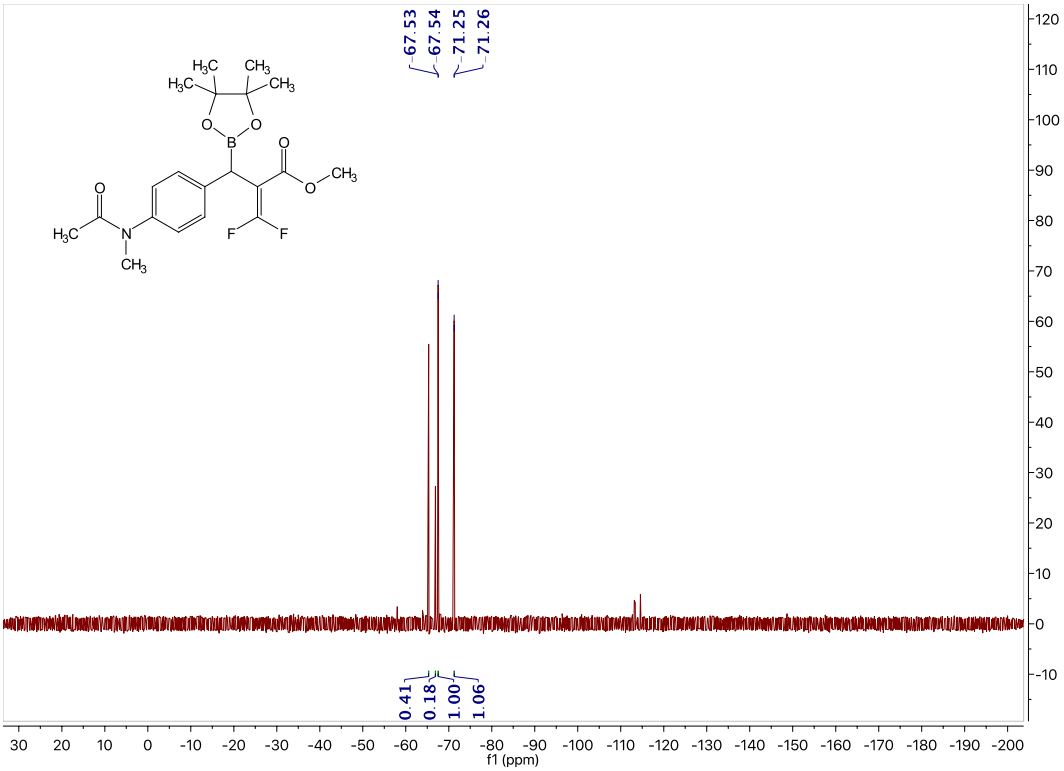
2k – ^{1}H NMR



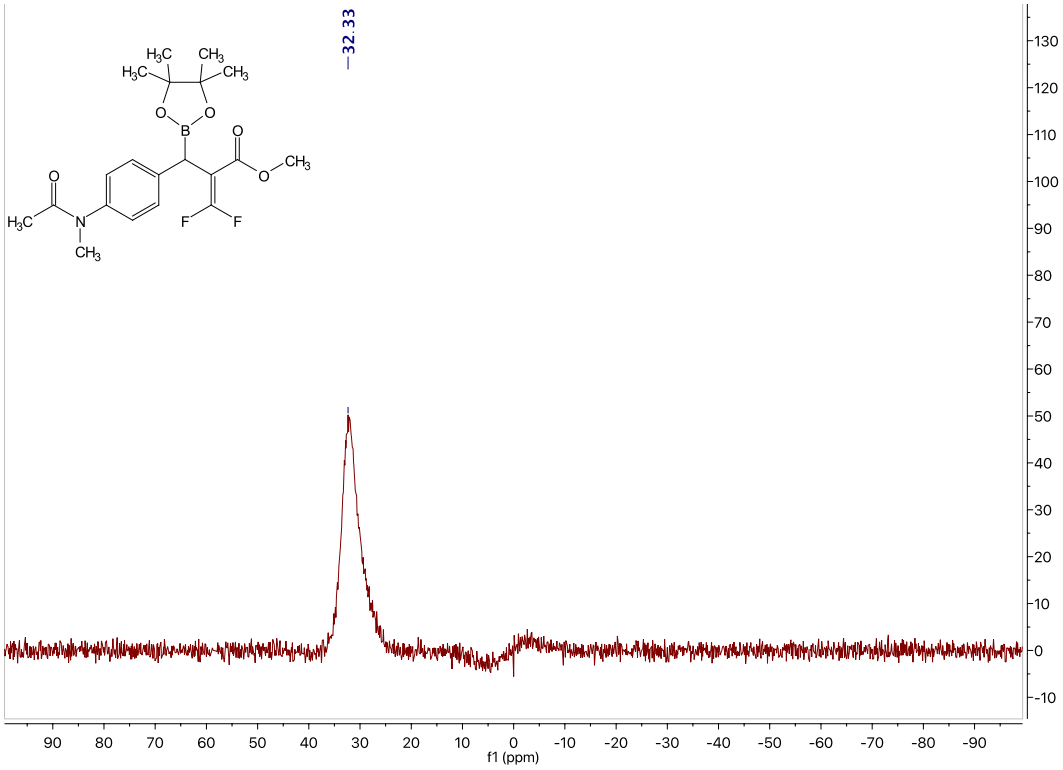
2k – ^{13}C NMR



2k – ^{19}F NMR



2k – ^{11}B NMR



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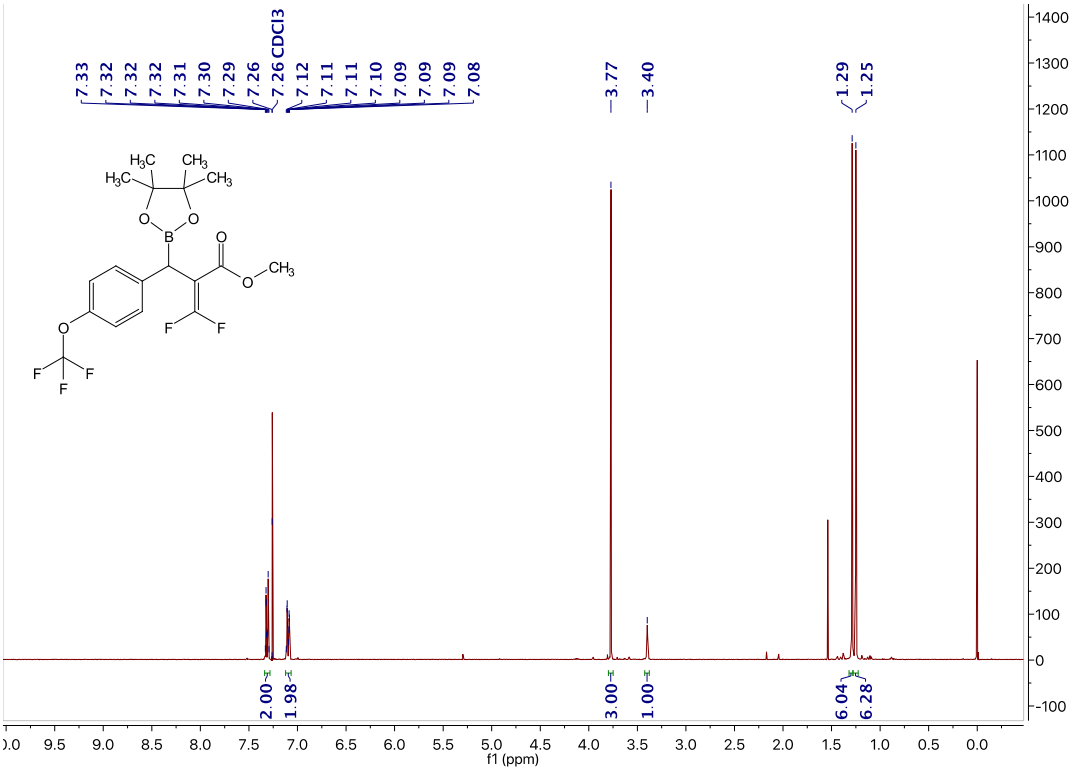
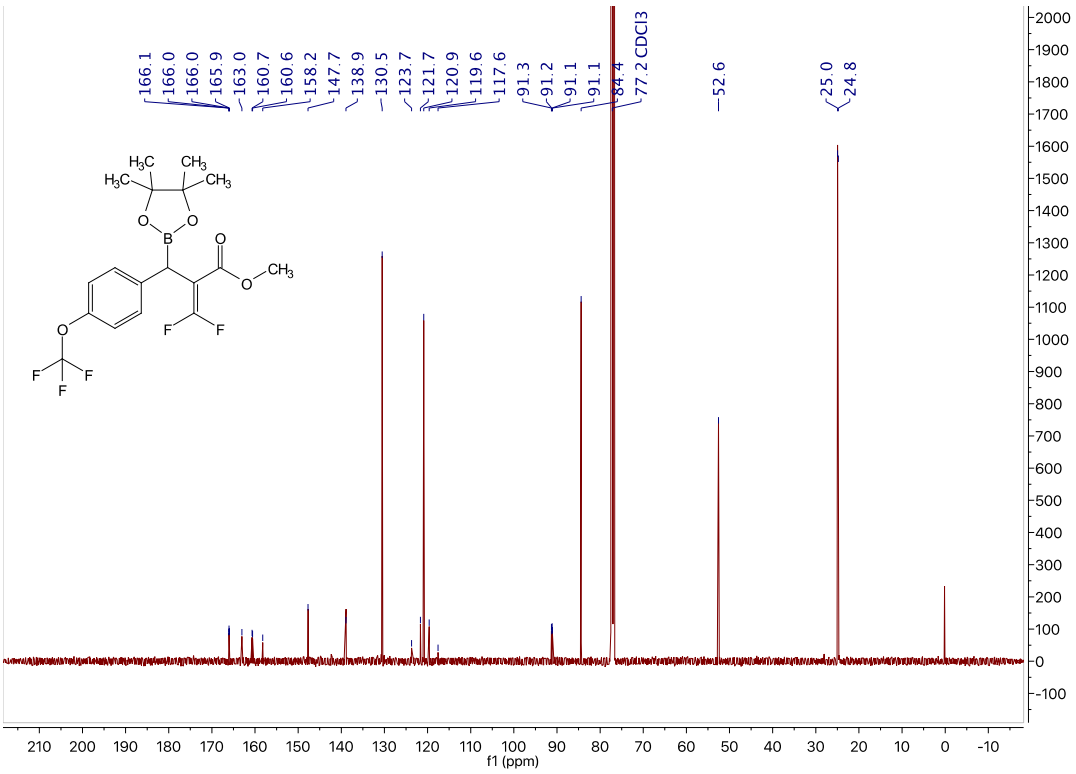
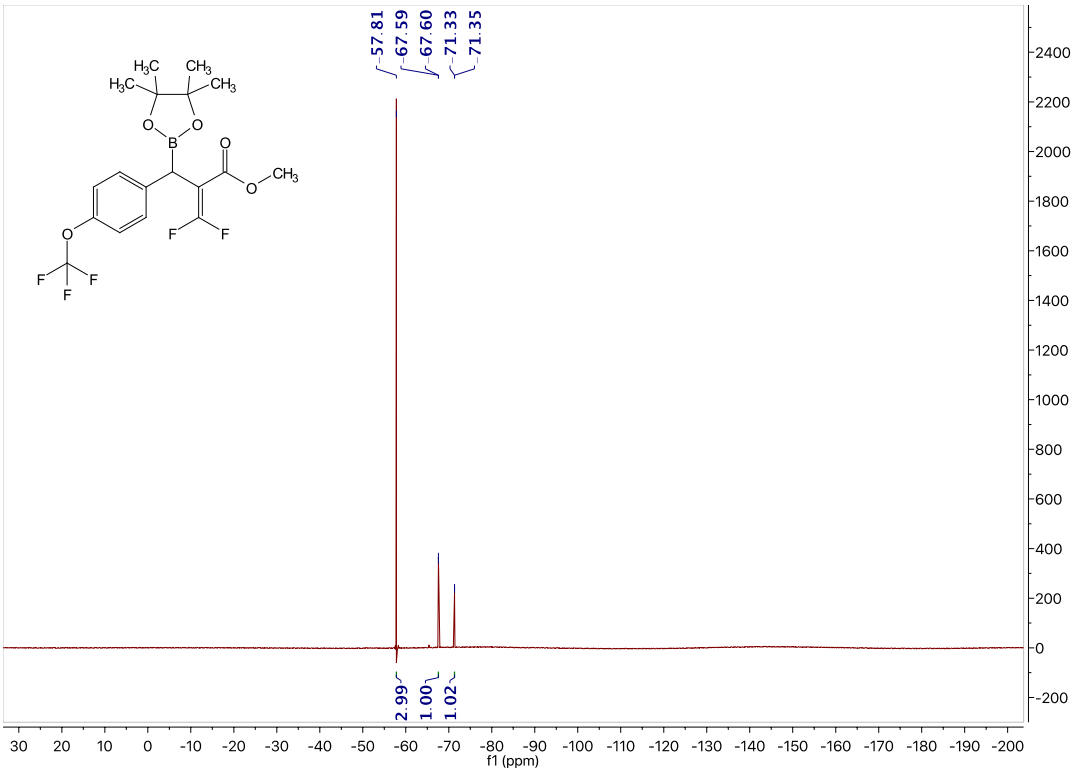


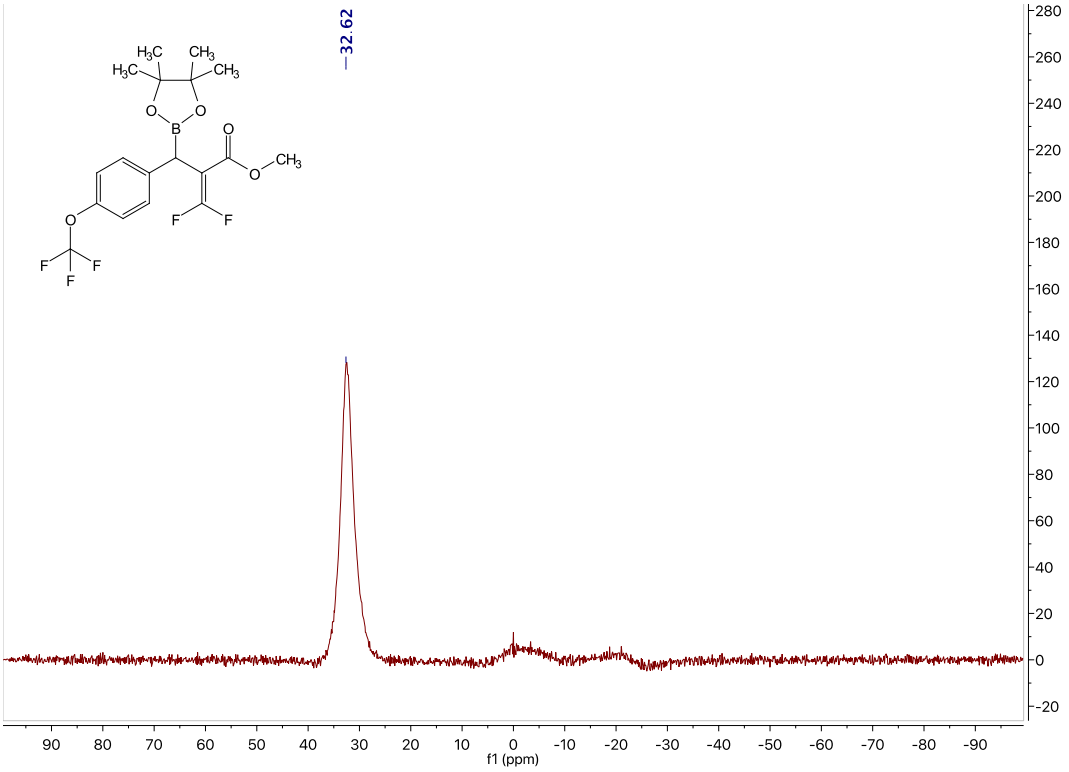
2l – ^{13}C NMR



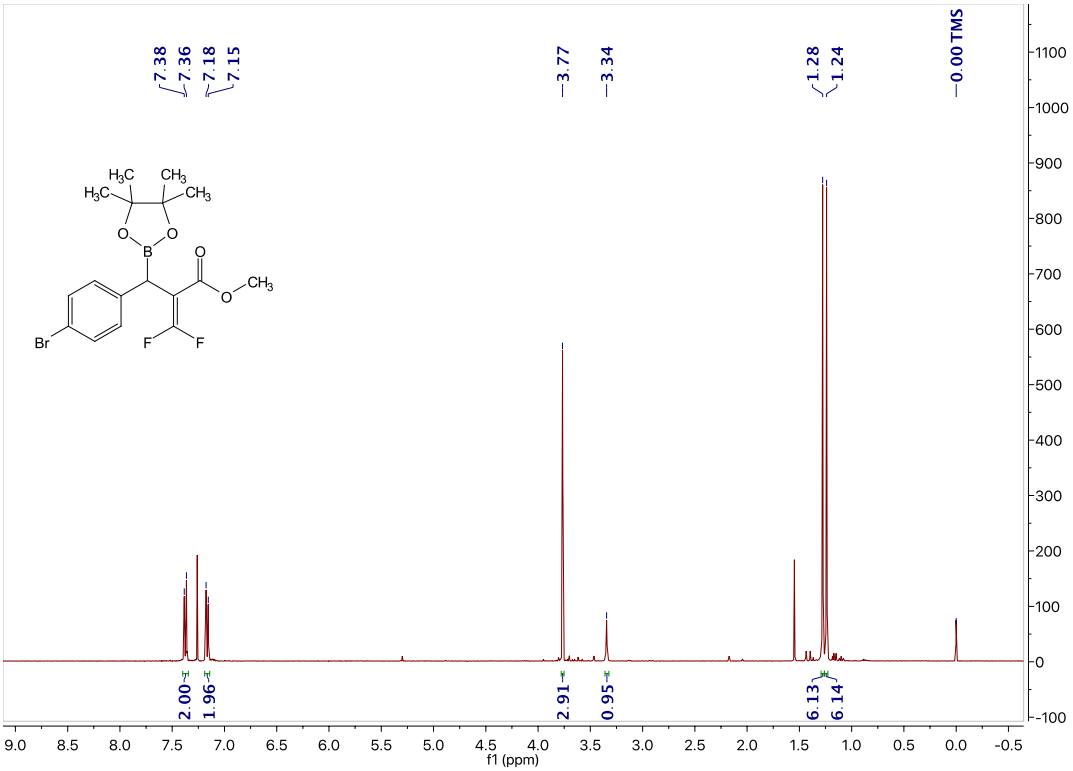
2l – ^{19}F NMR



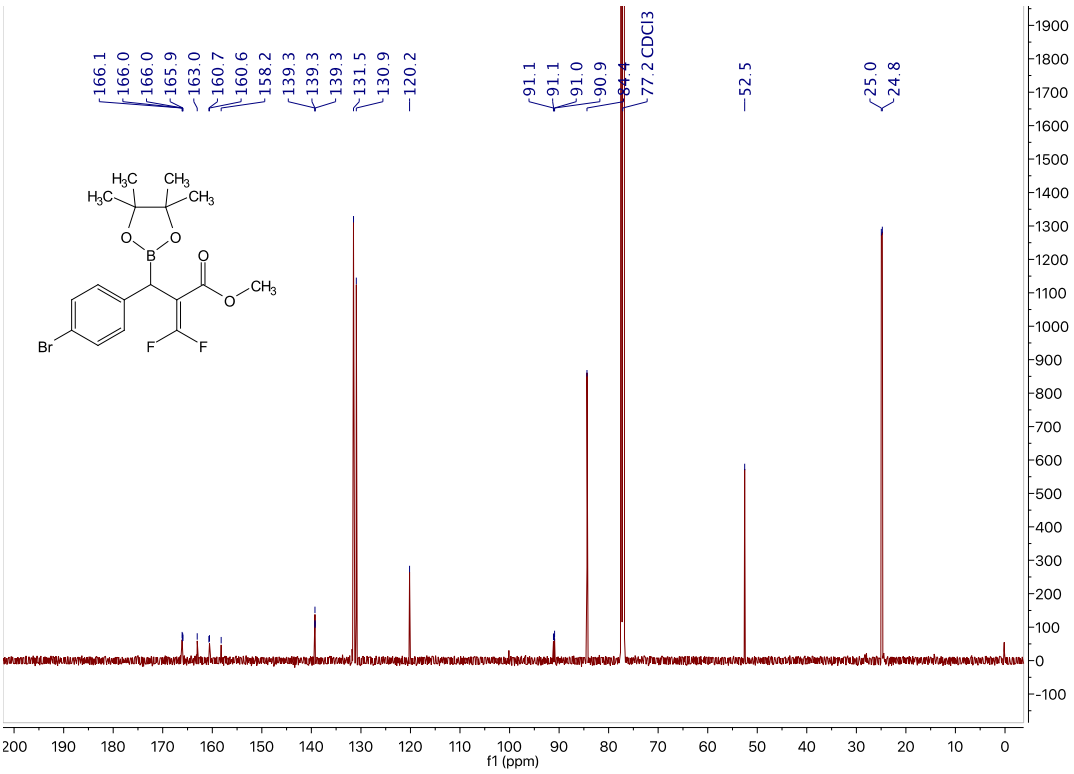
2l – ^{11}B NMR



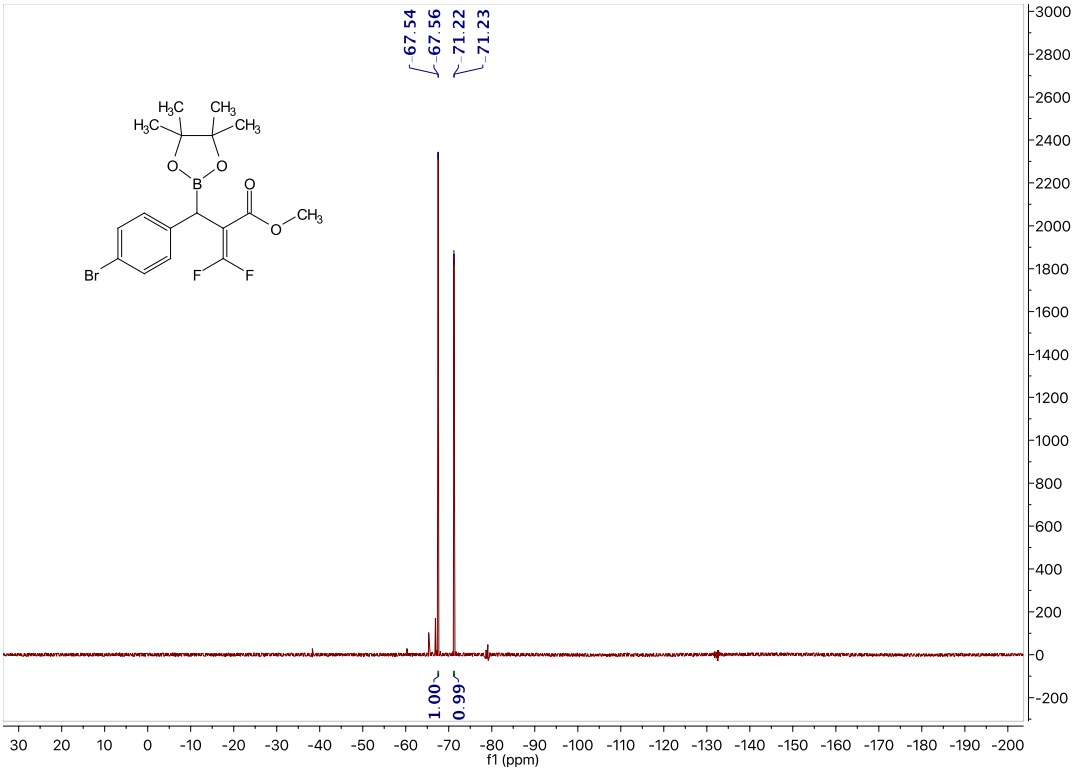
2m – ^{1}H NMR



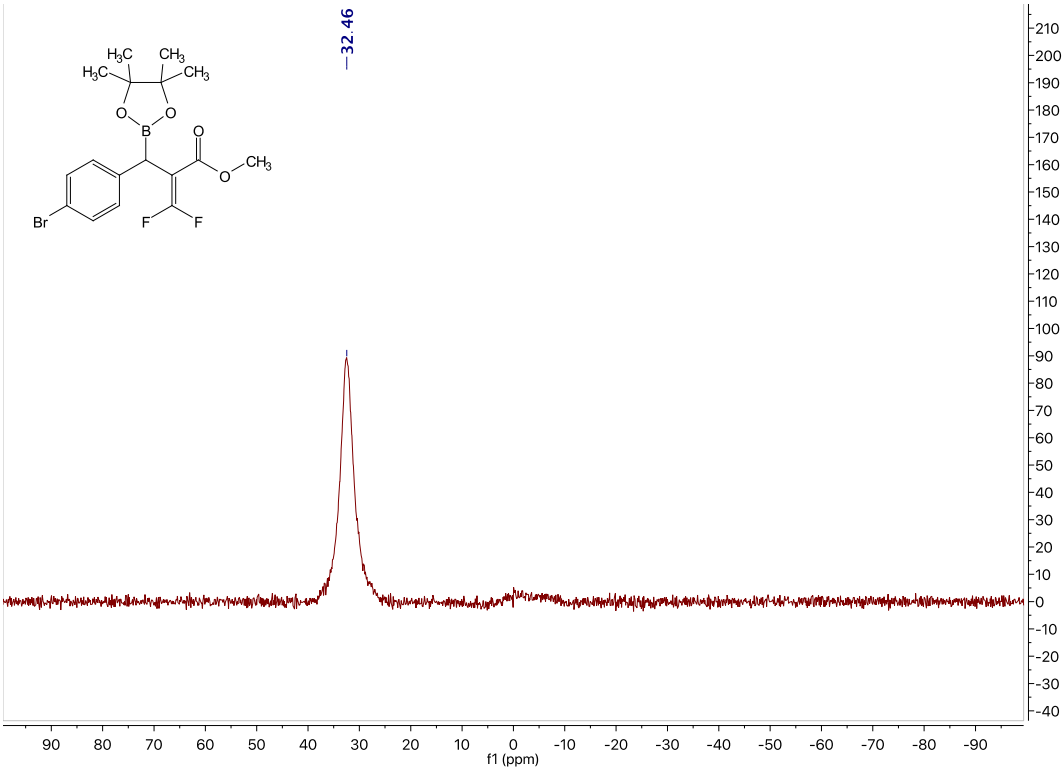
2m – ^{13}C NMR



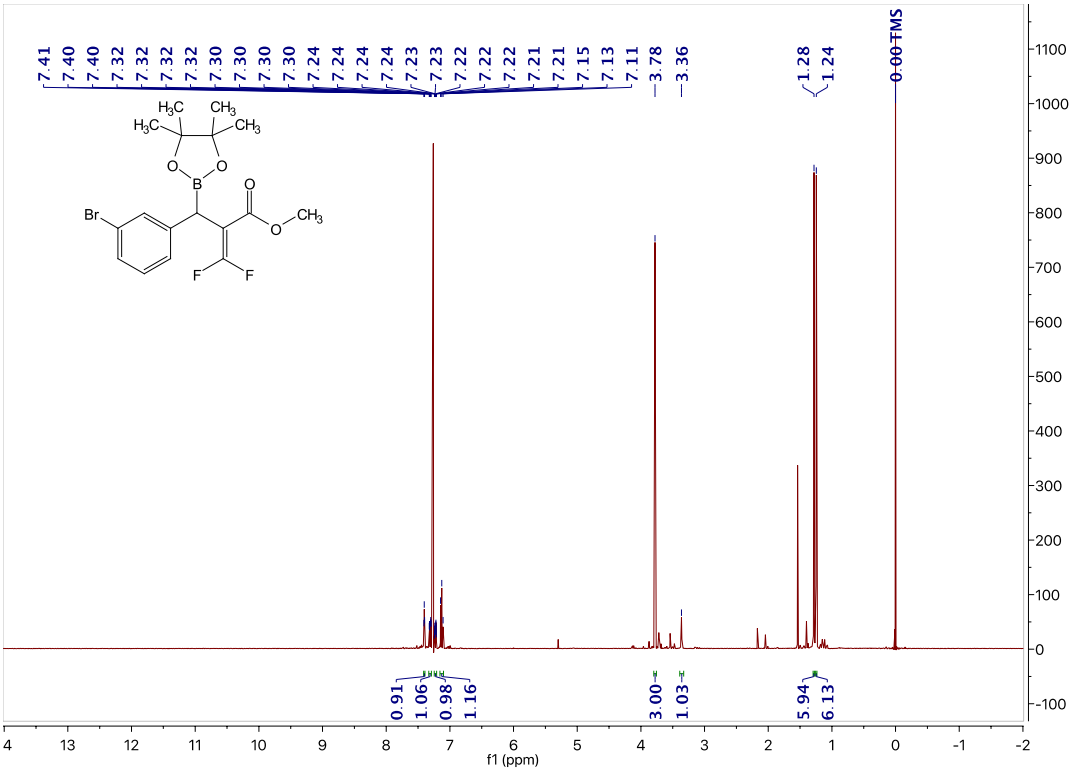
2m – ^{19}F NMR



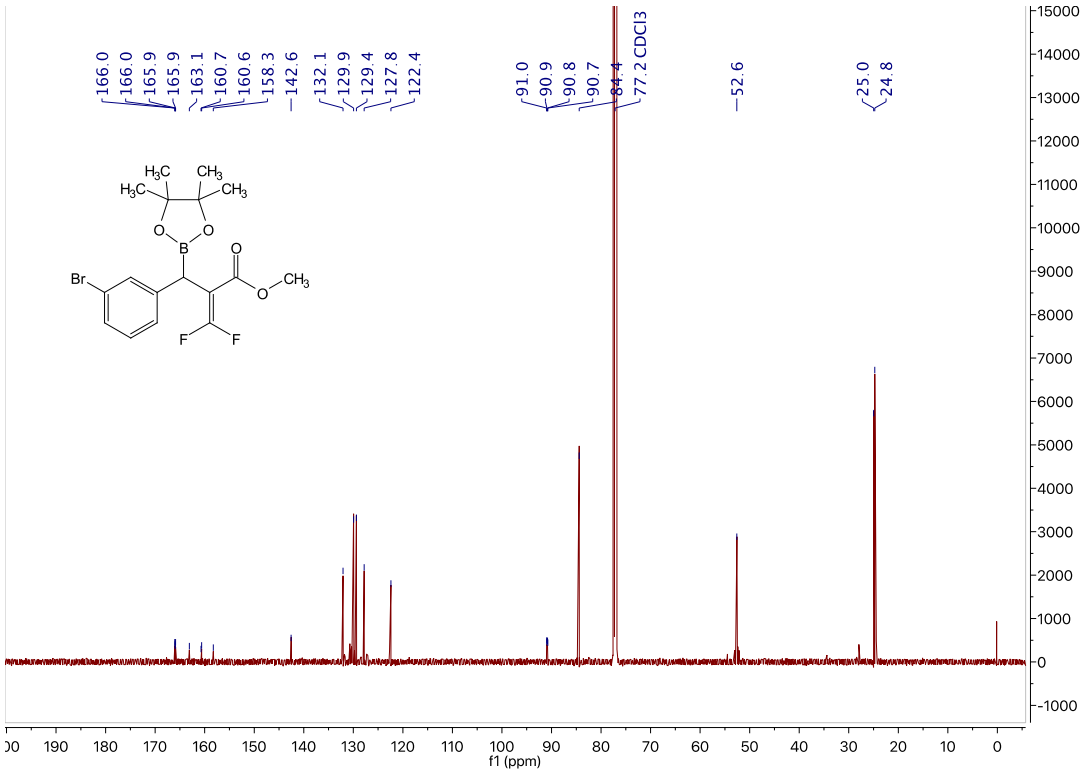
2m – ^{11}B NMR



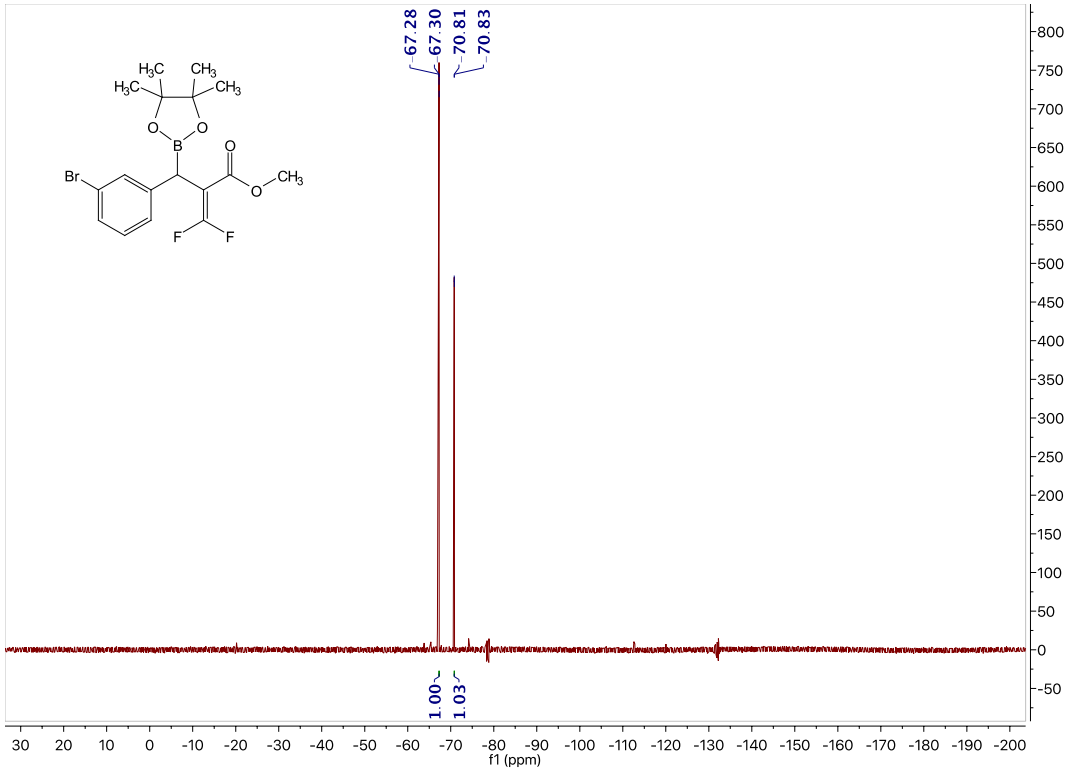
2n – ^{1}H NMR



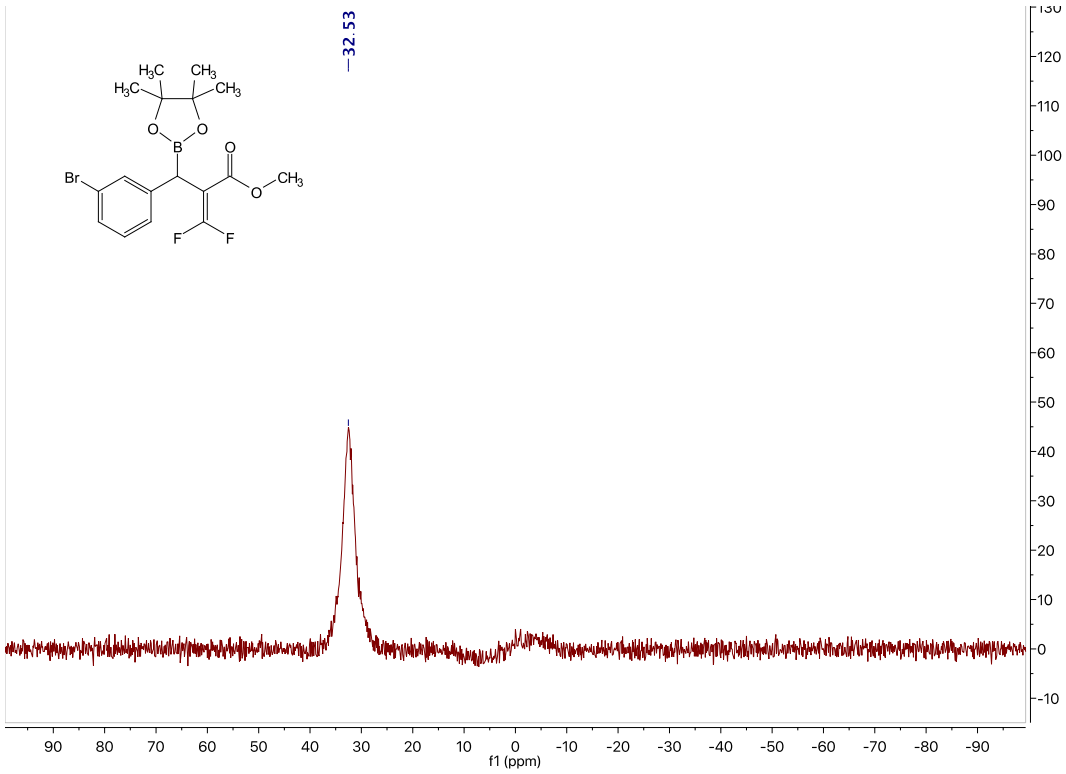
2n – ^{13}C NMR



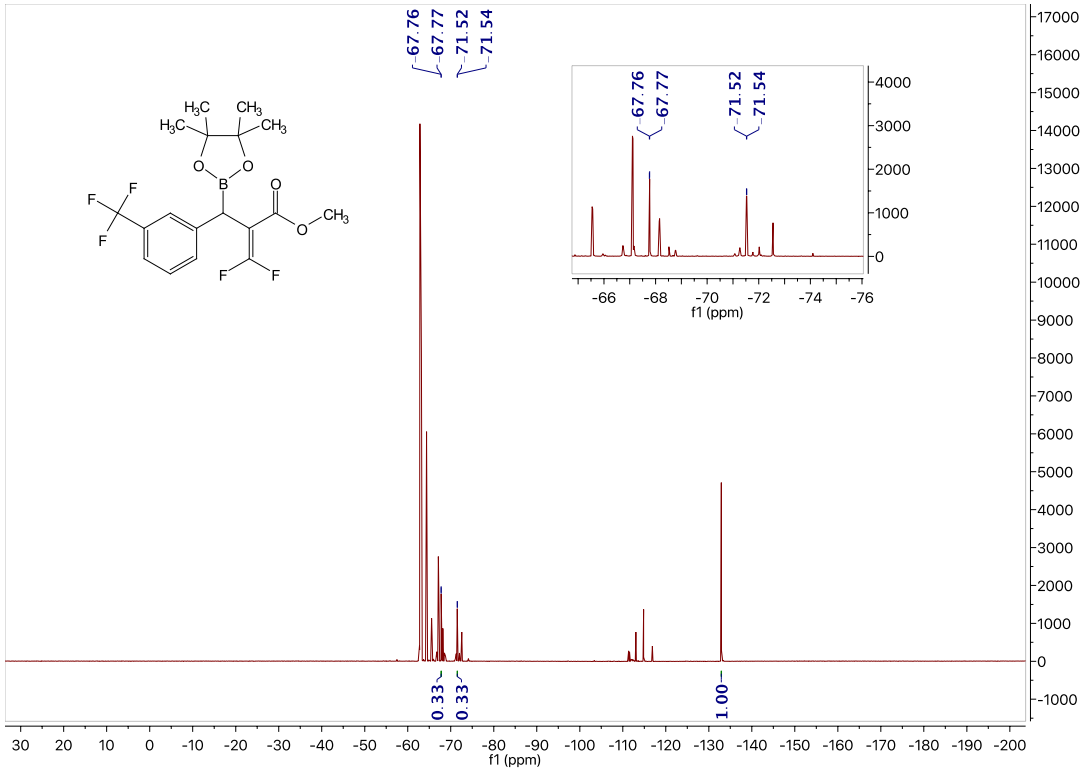
2n – ^{19}F NMR



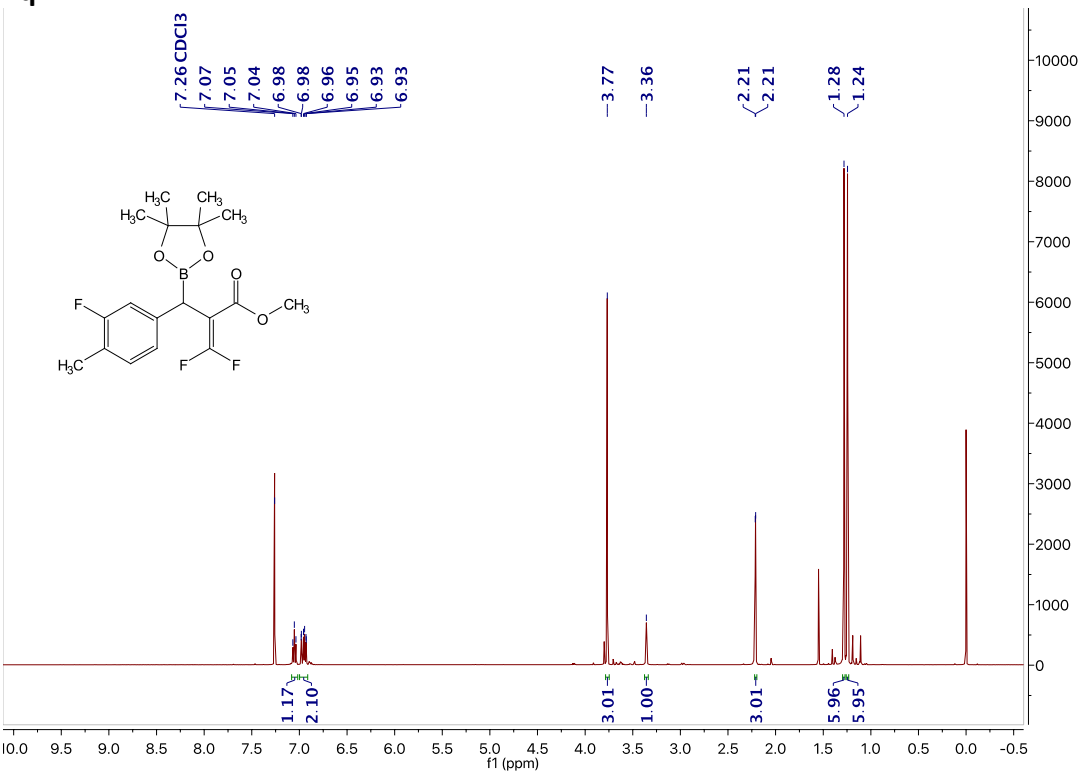
2n – ^{11}B NMR



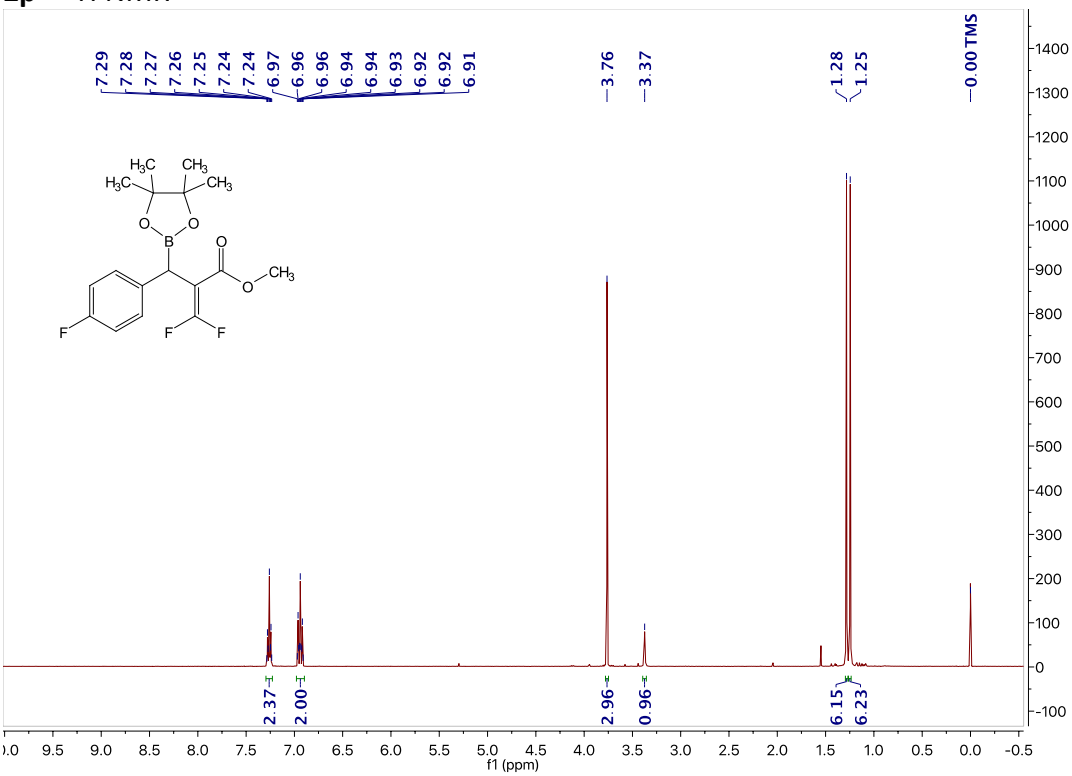
2o – ^{19}F NMR



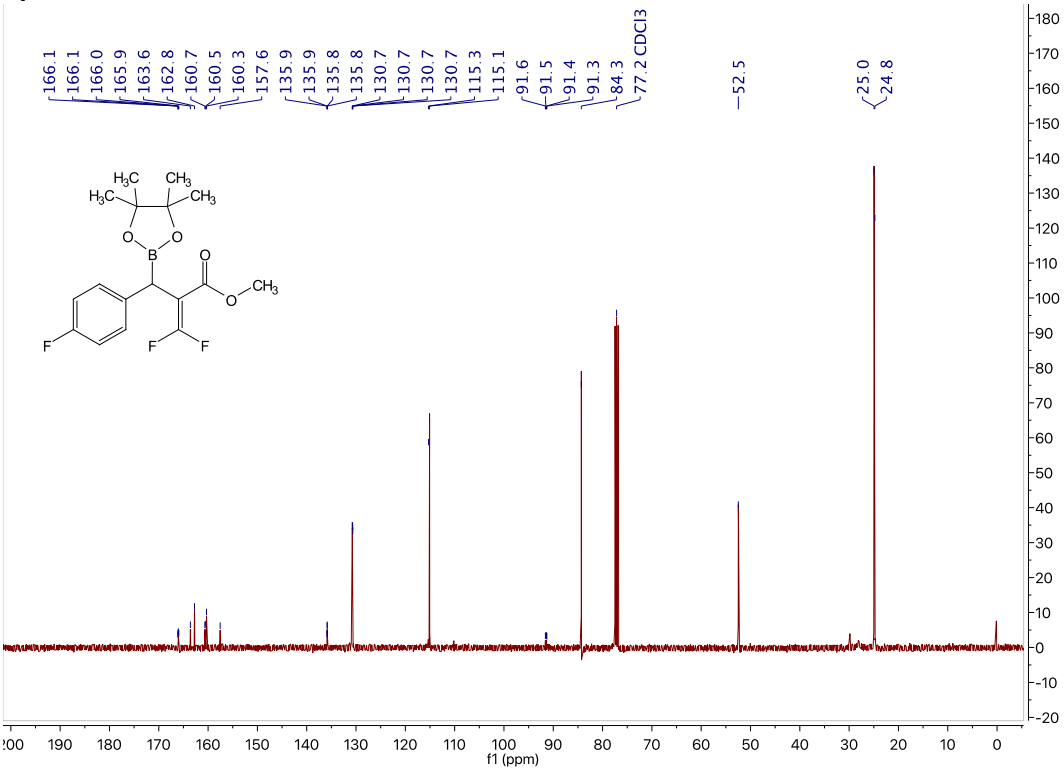
2q – ^{1}H NMR



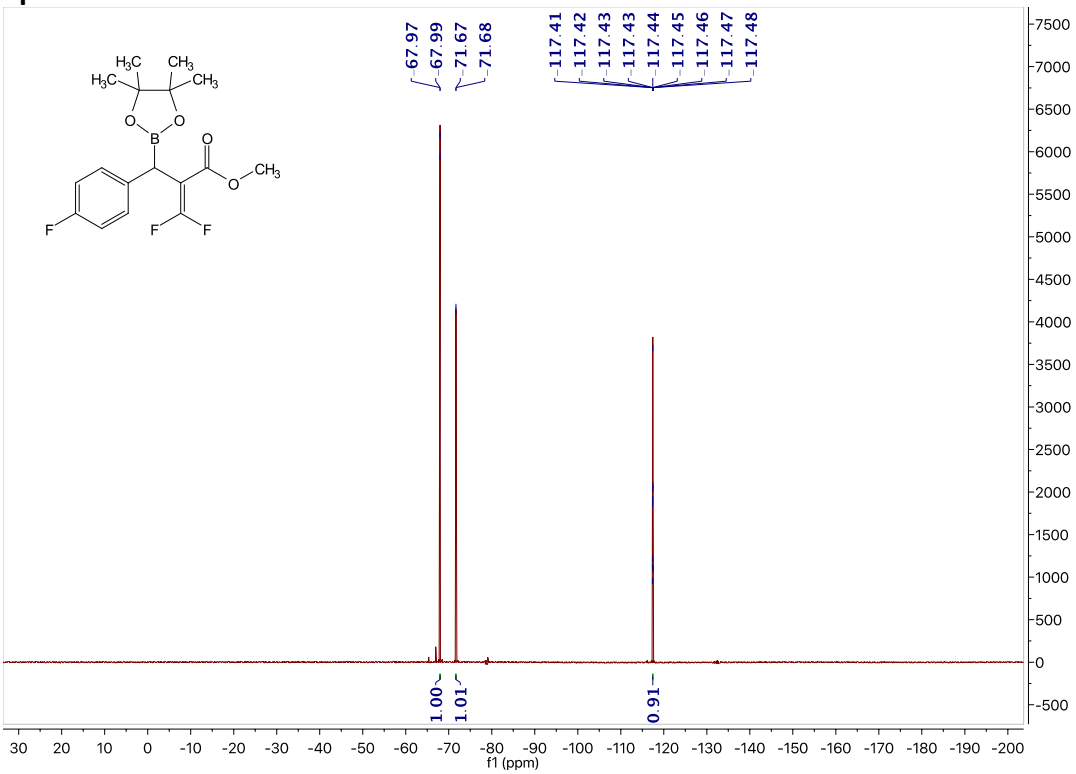
2p – ^{1}H NMR



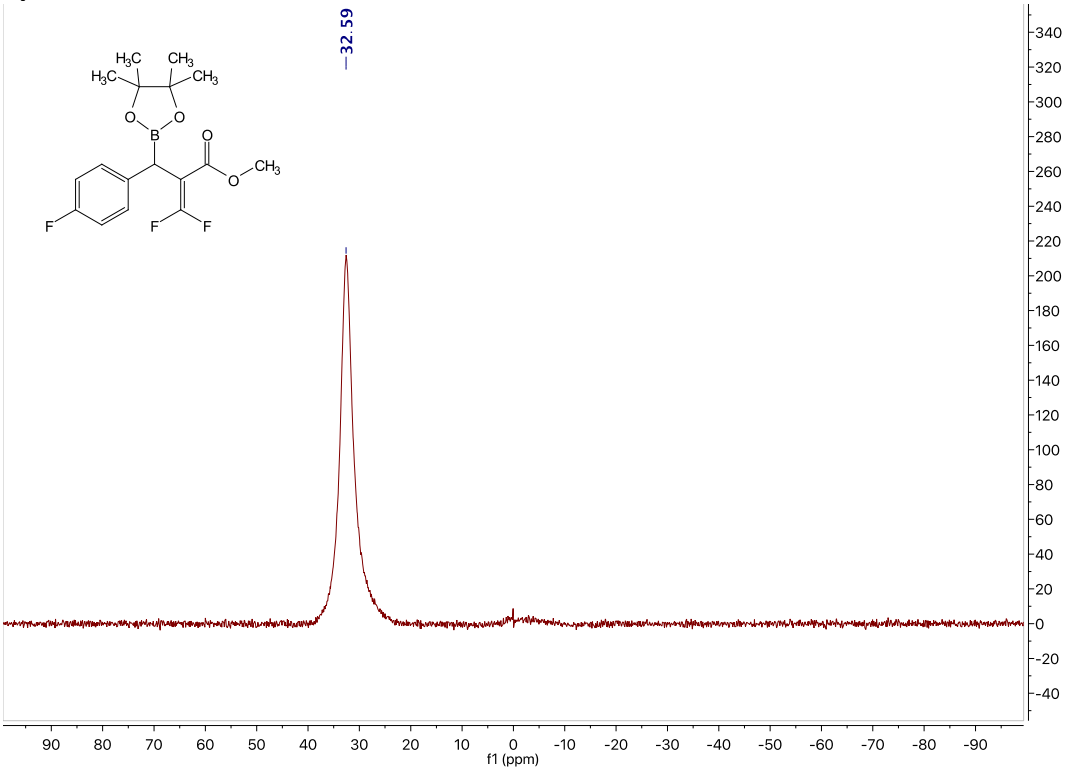
2p – ^{13}C NMR



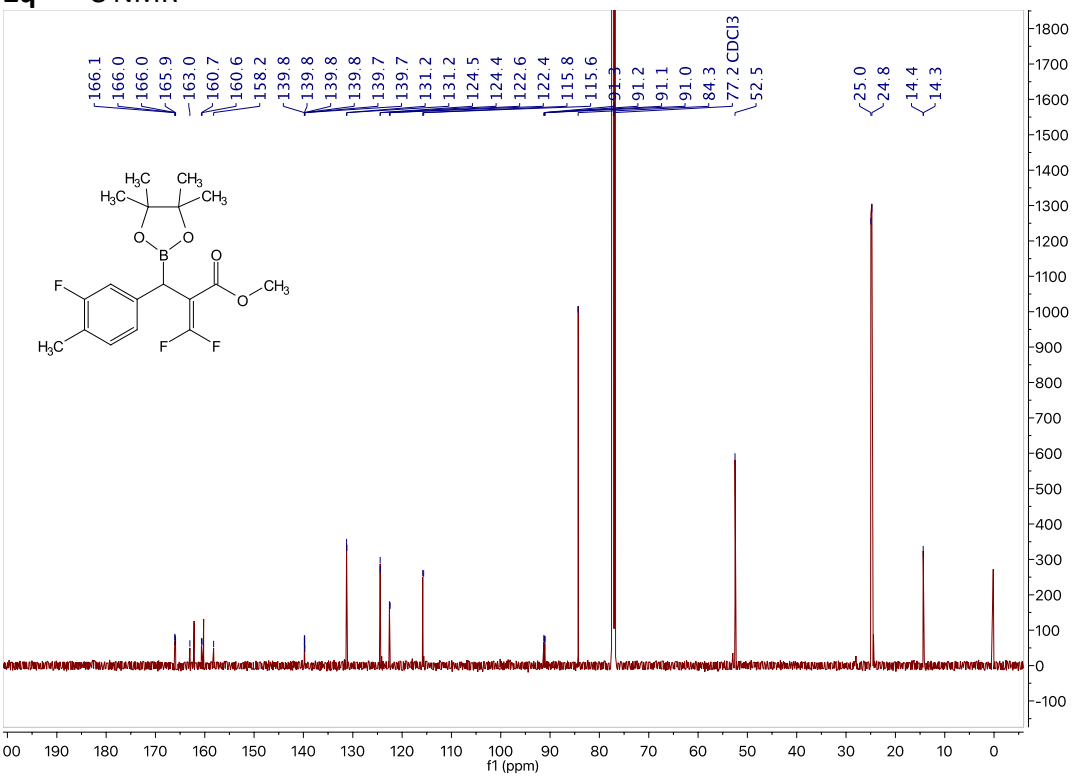
2p – ^{19}F NMR



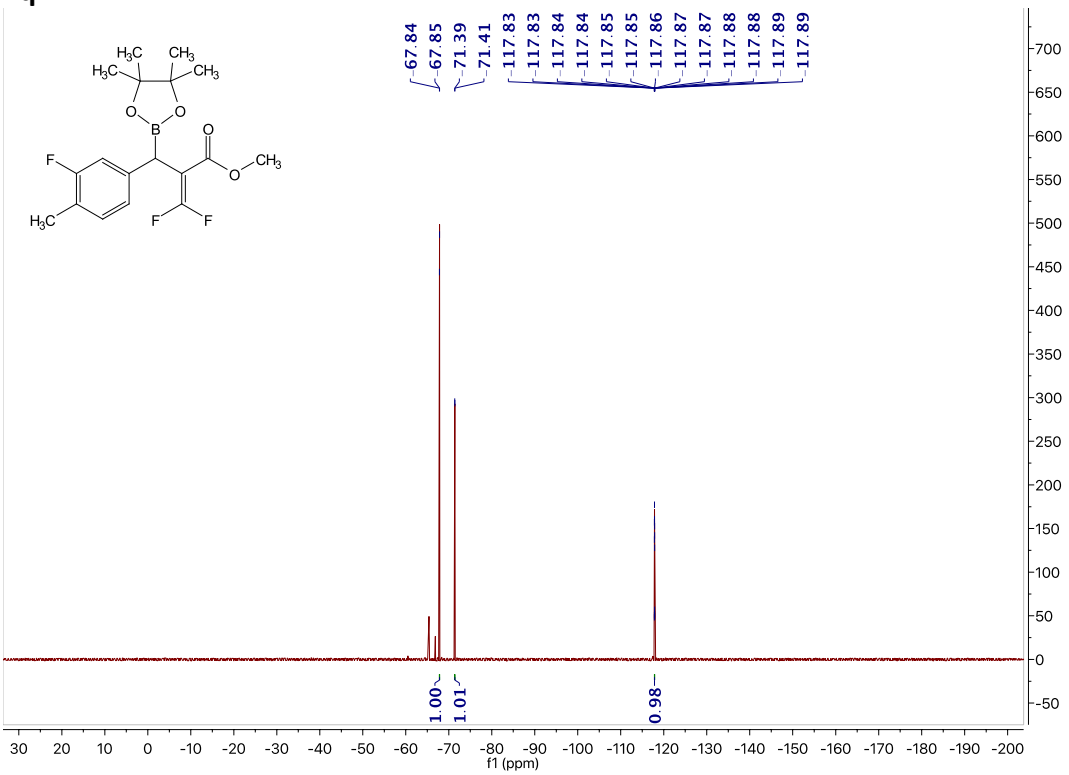
2p – ^{11}B NMR



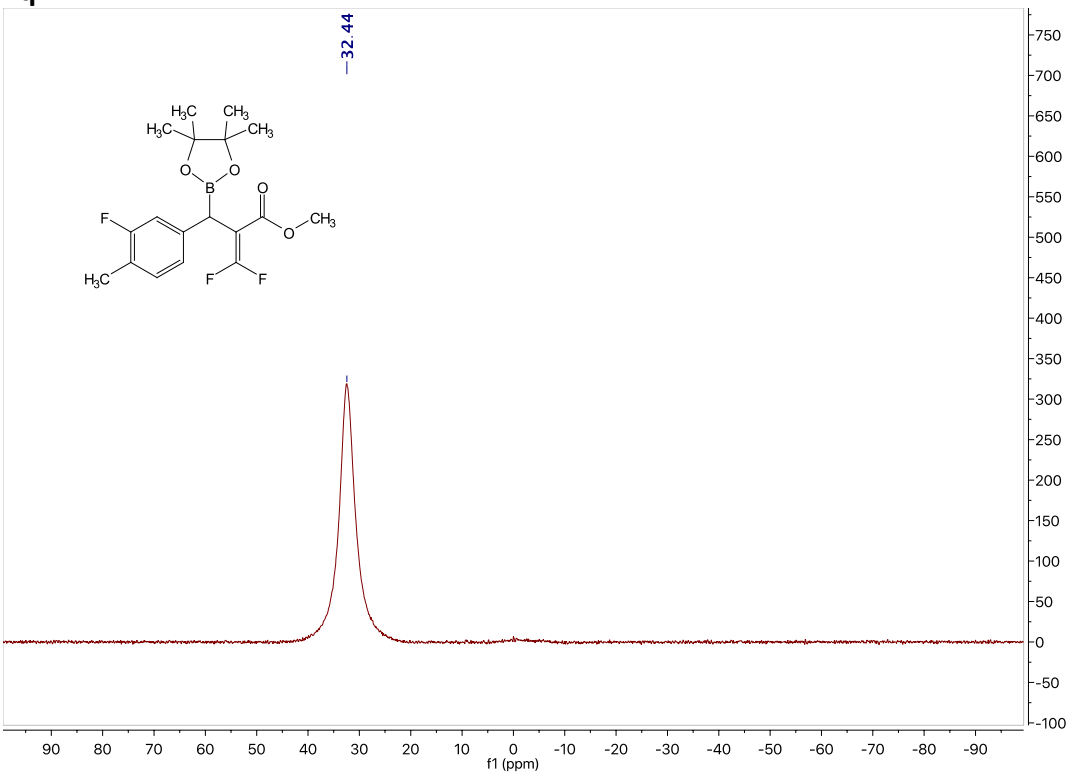
2q – ^{13}C NMR



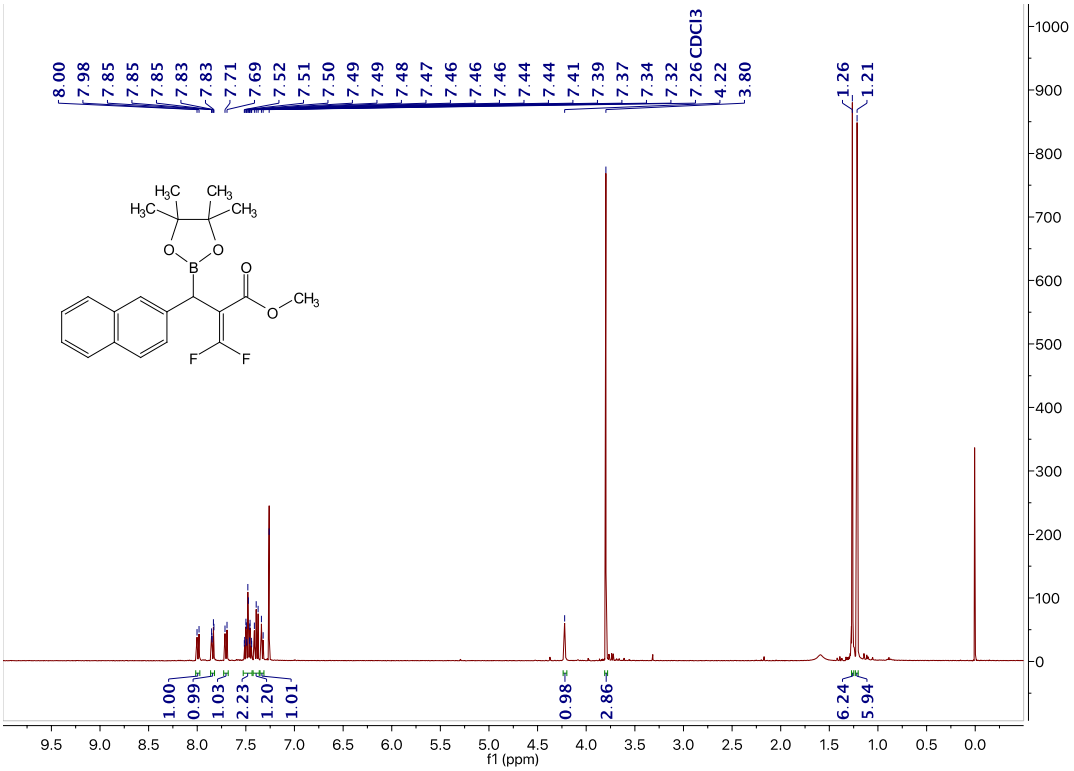
2q – ^{19}F NMR



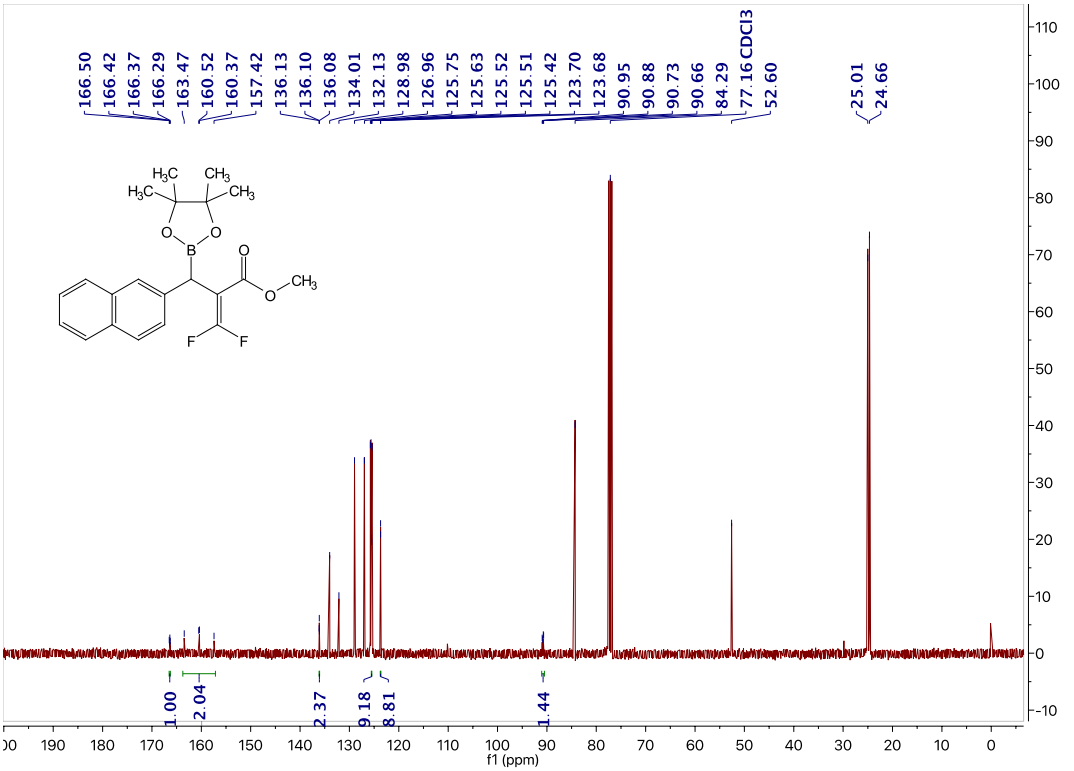
2q – ^{11}B NMR



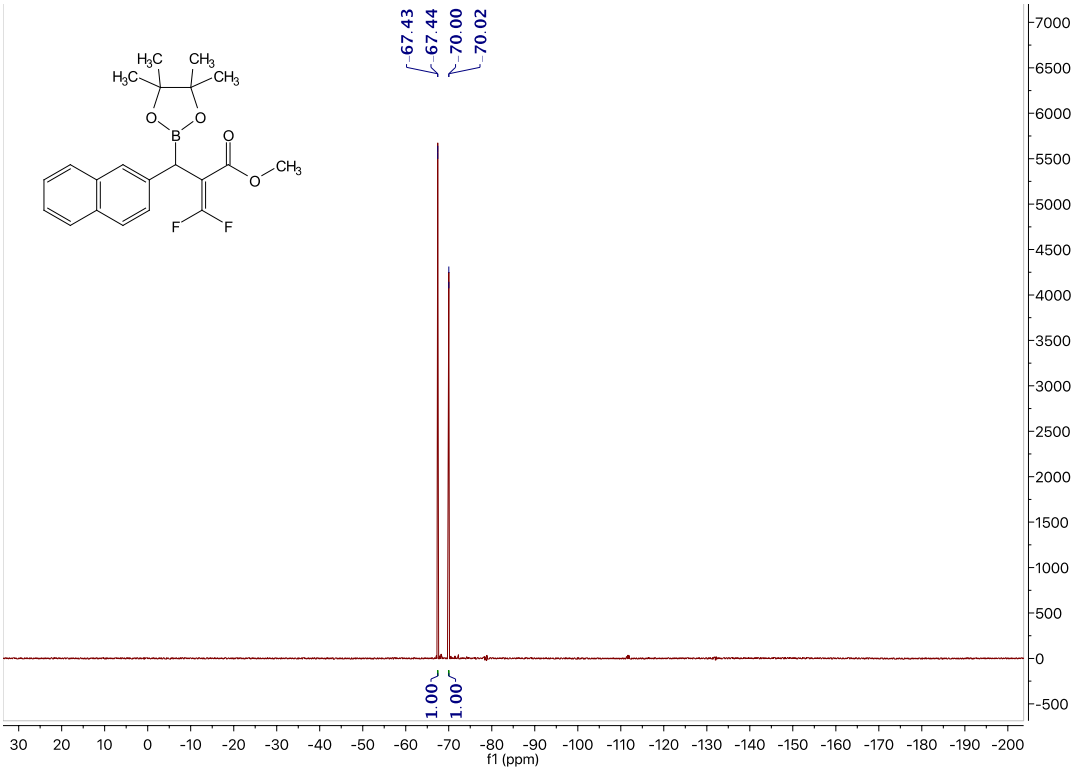
2r – ^{1}H NMR



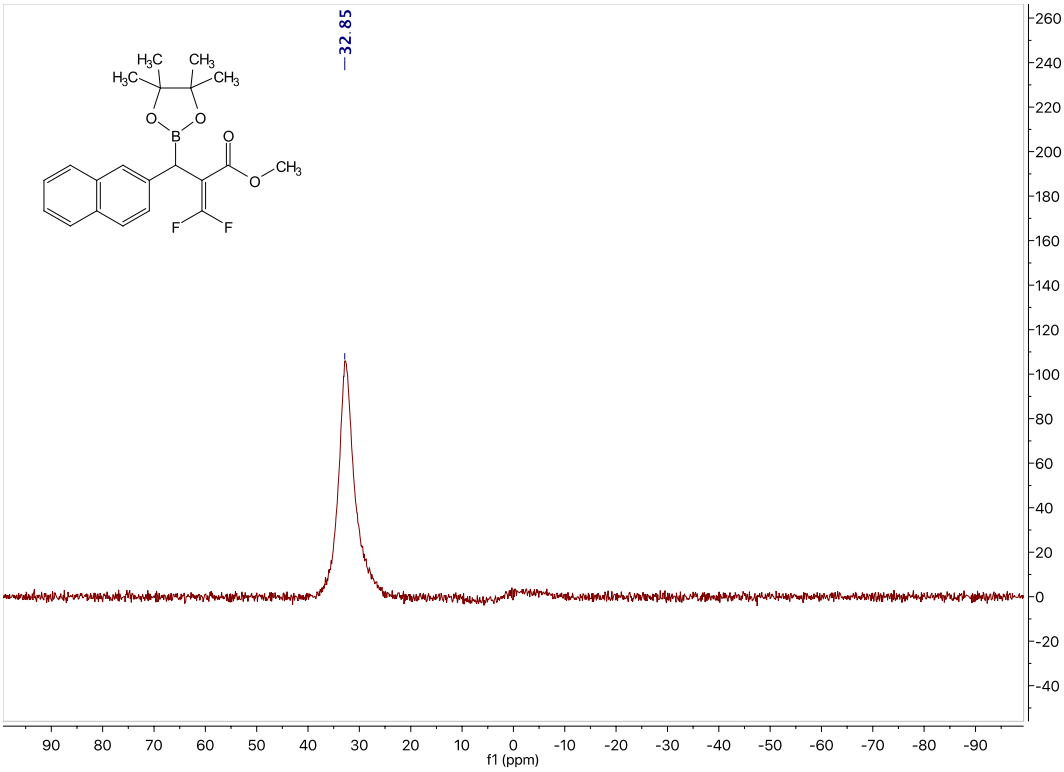
2r – ^{13}C NMR



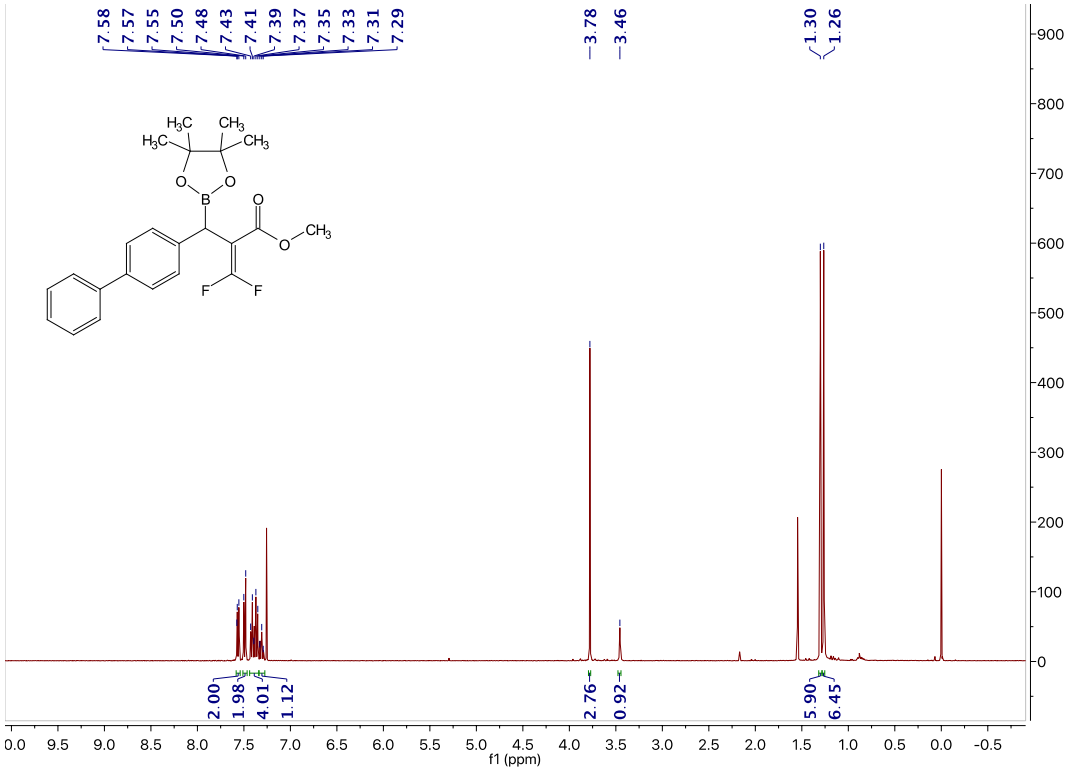
2r – ^{19}F NMR



2r – ^{11}B NMR



2s – ^{1}H NMR



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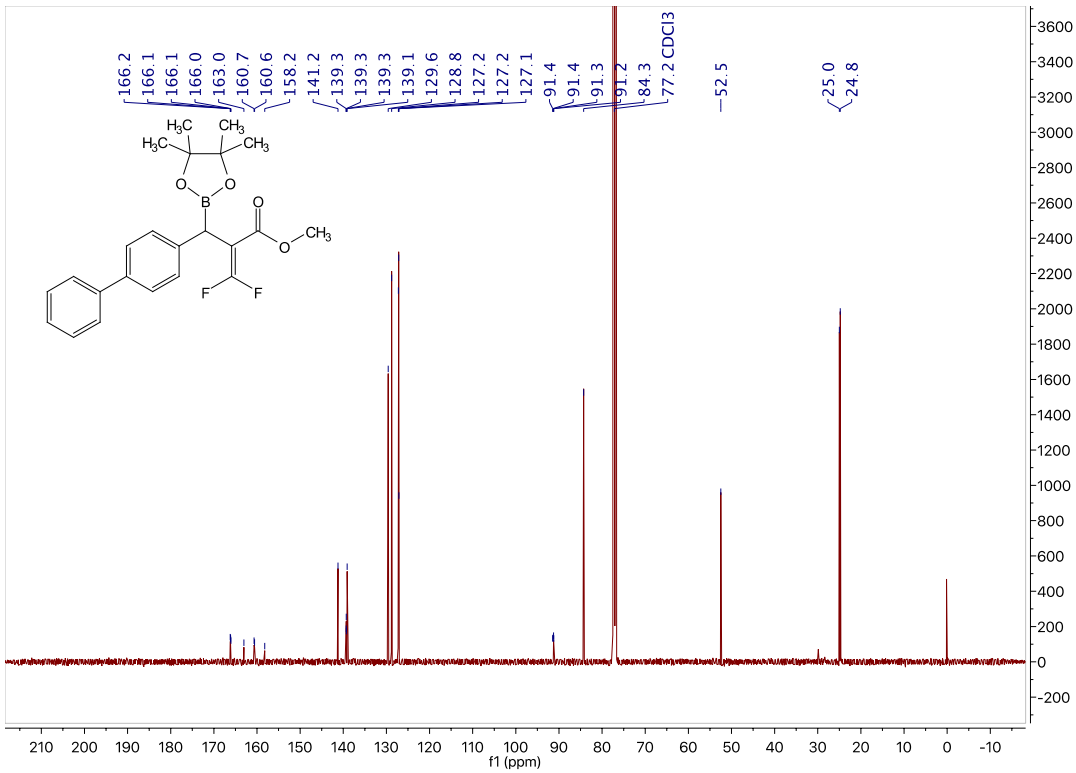
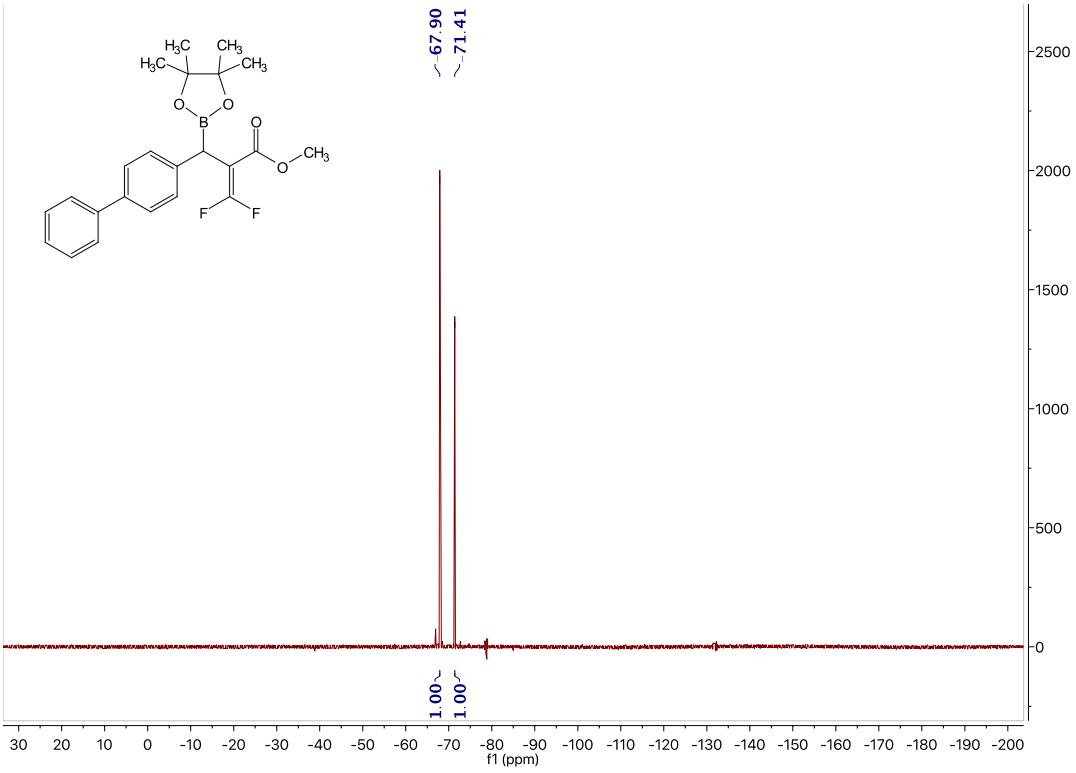
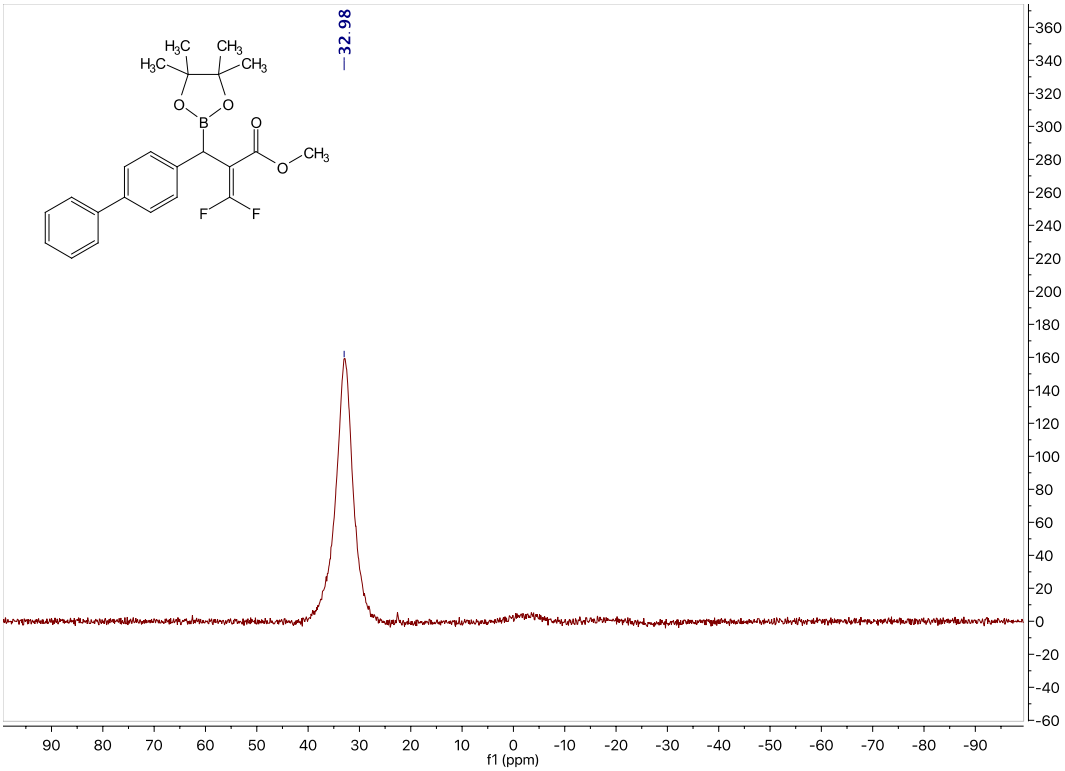


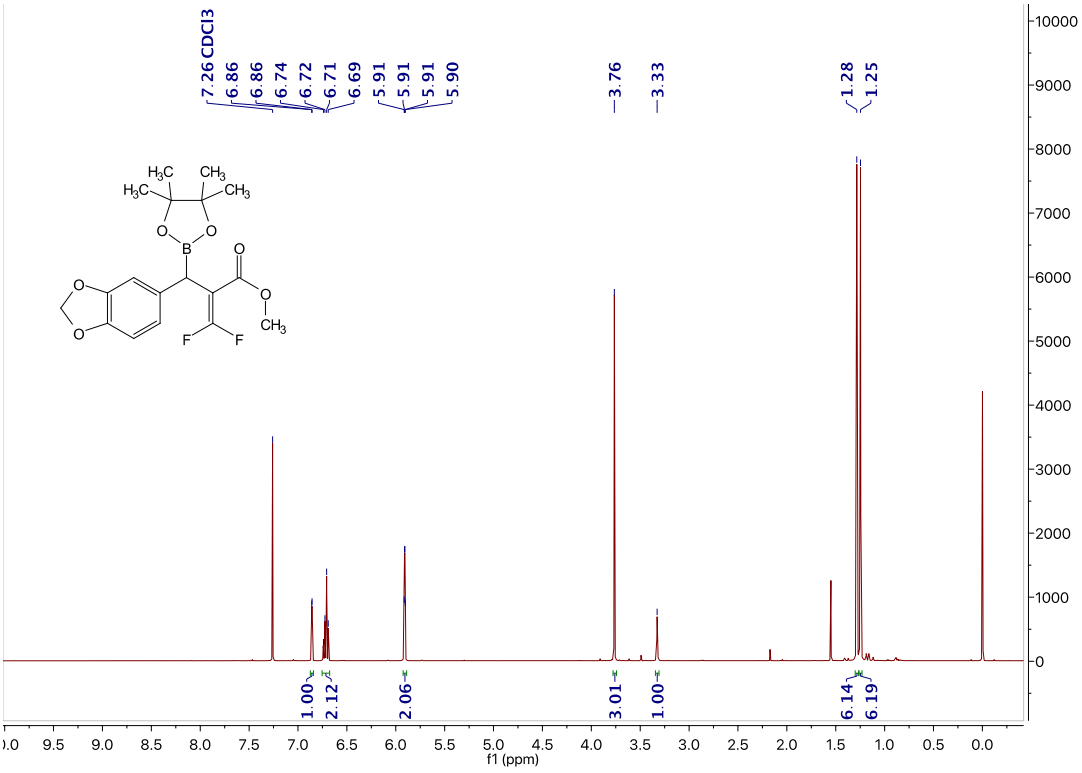
2s – ^{19}F NMR



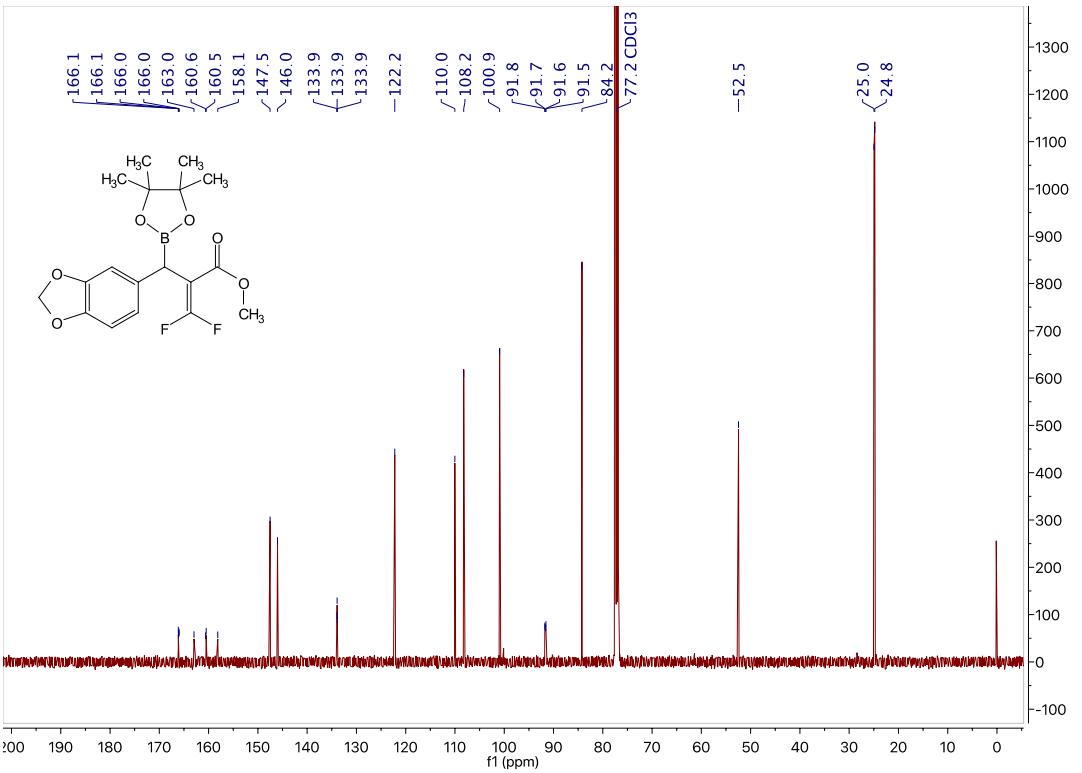
2s – ^{11}B NMR



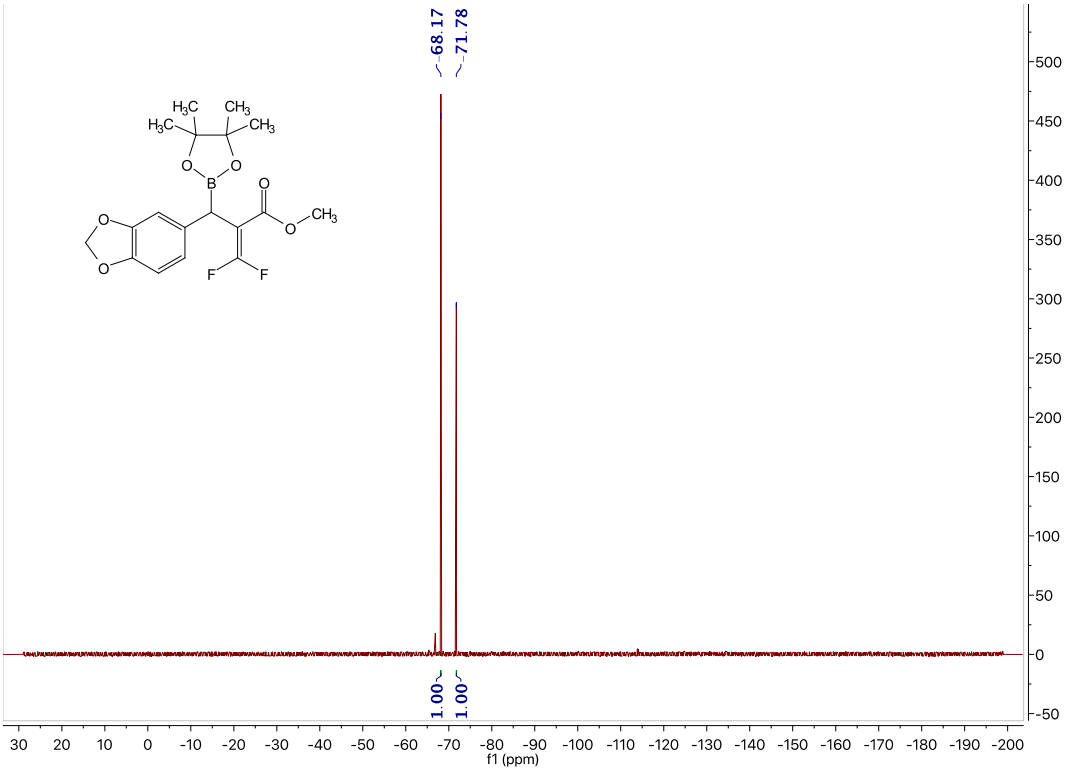
2t – ^{1}H NMR



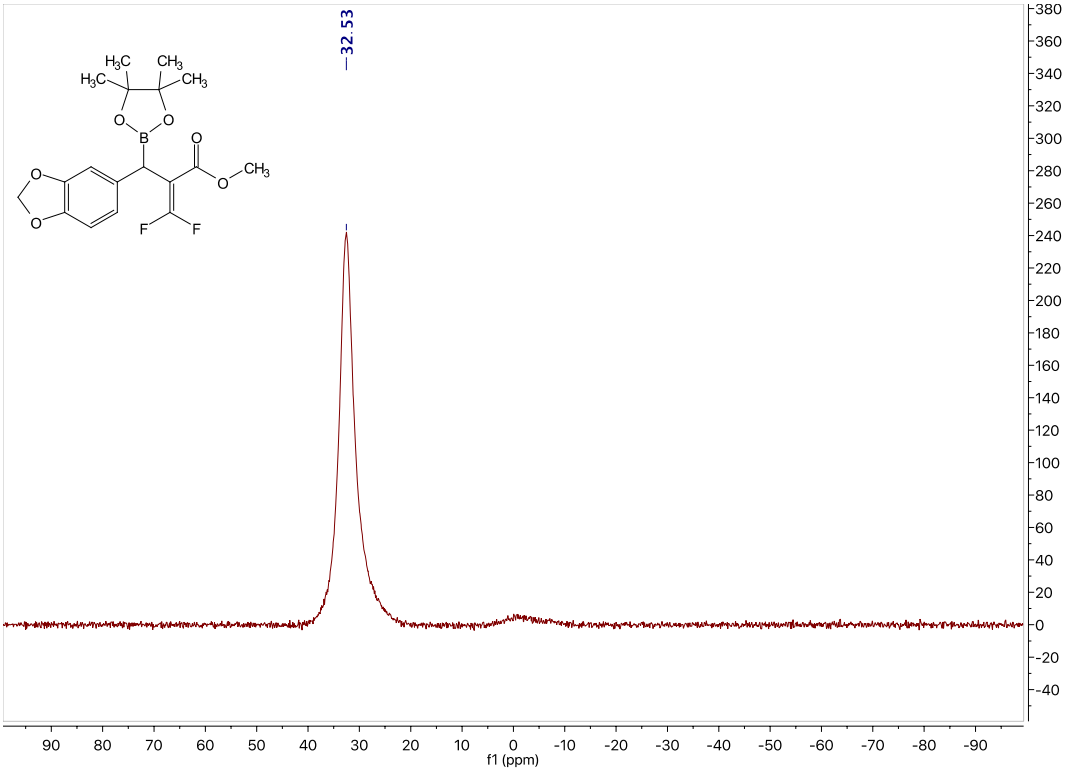
2t – ^{13}C NMR



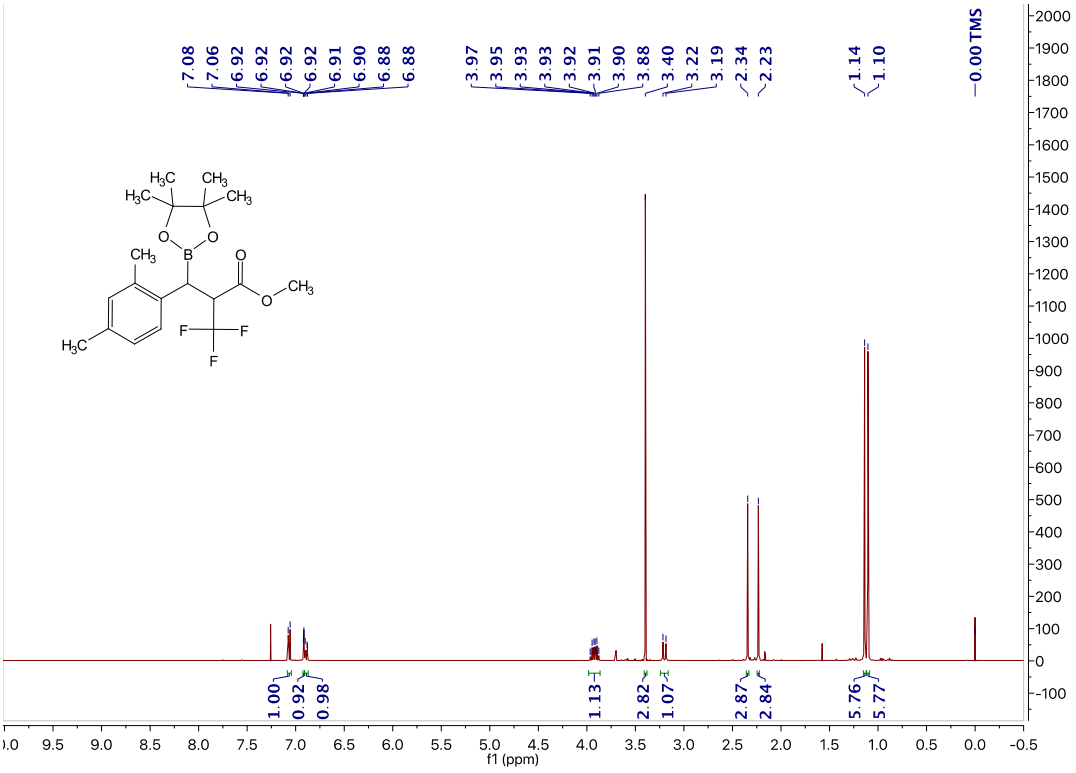
2t – ^{19}F NMR



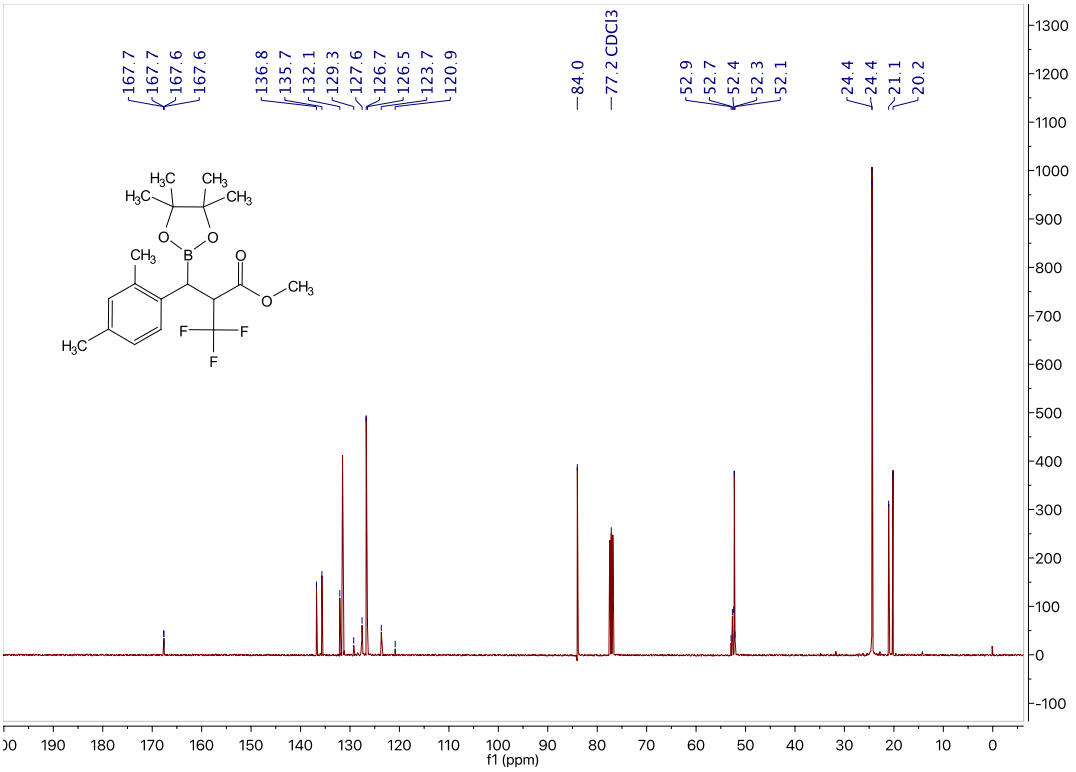
2t – ^{11}B NMR



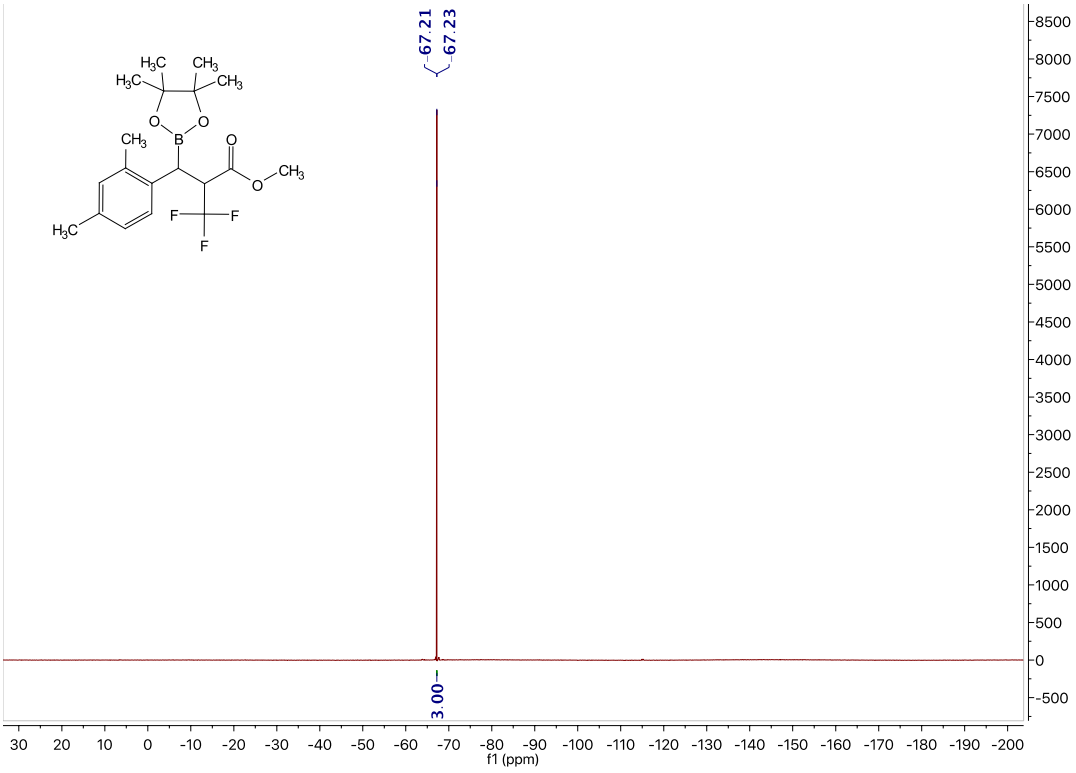
2b' – ^{1}H NMR



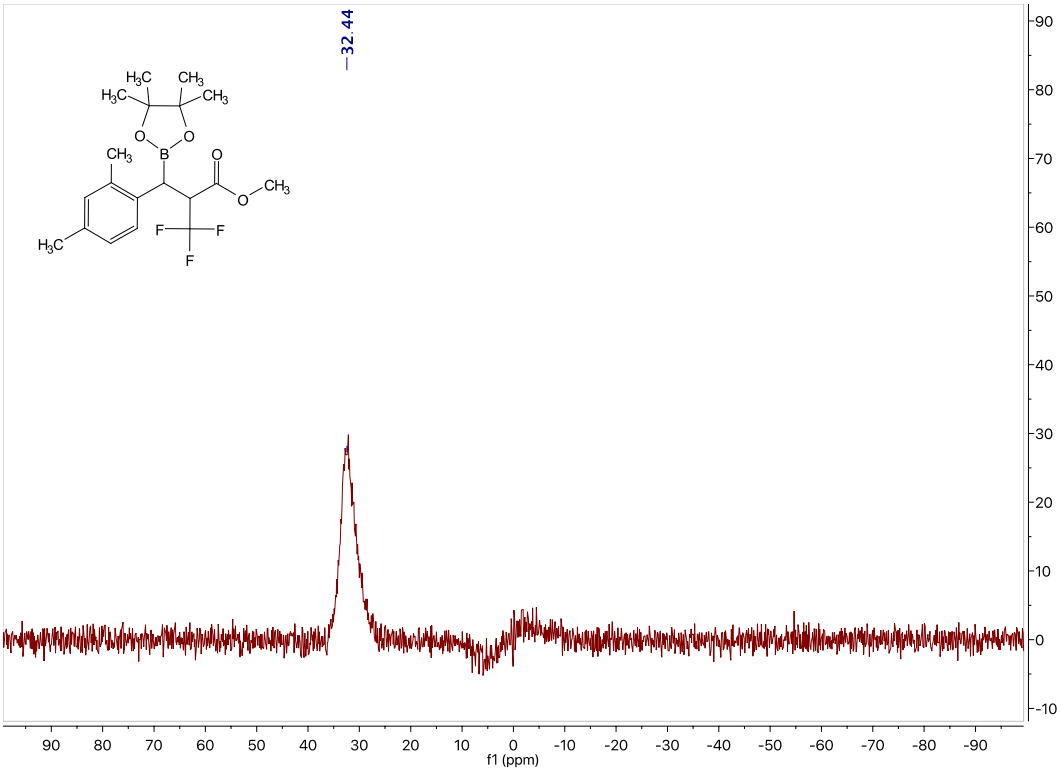
2b' – ^{13}C NMR



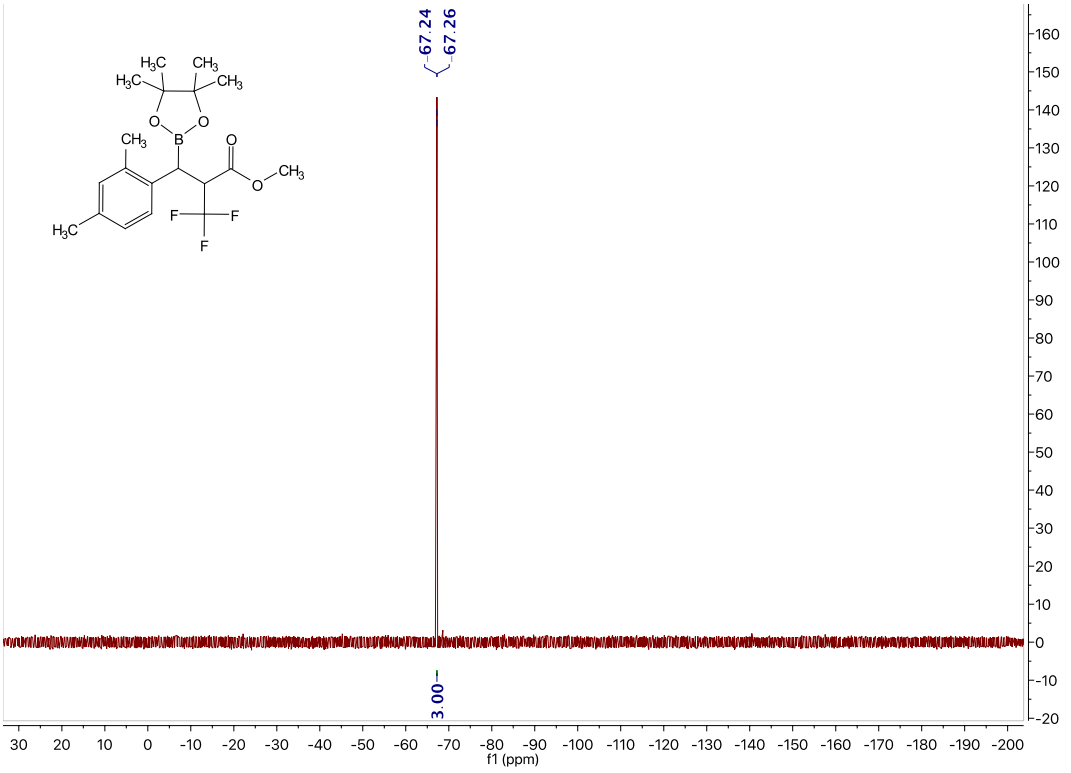
2b' – ^{19}F NMR



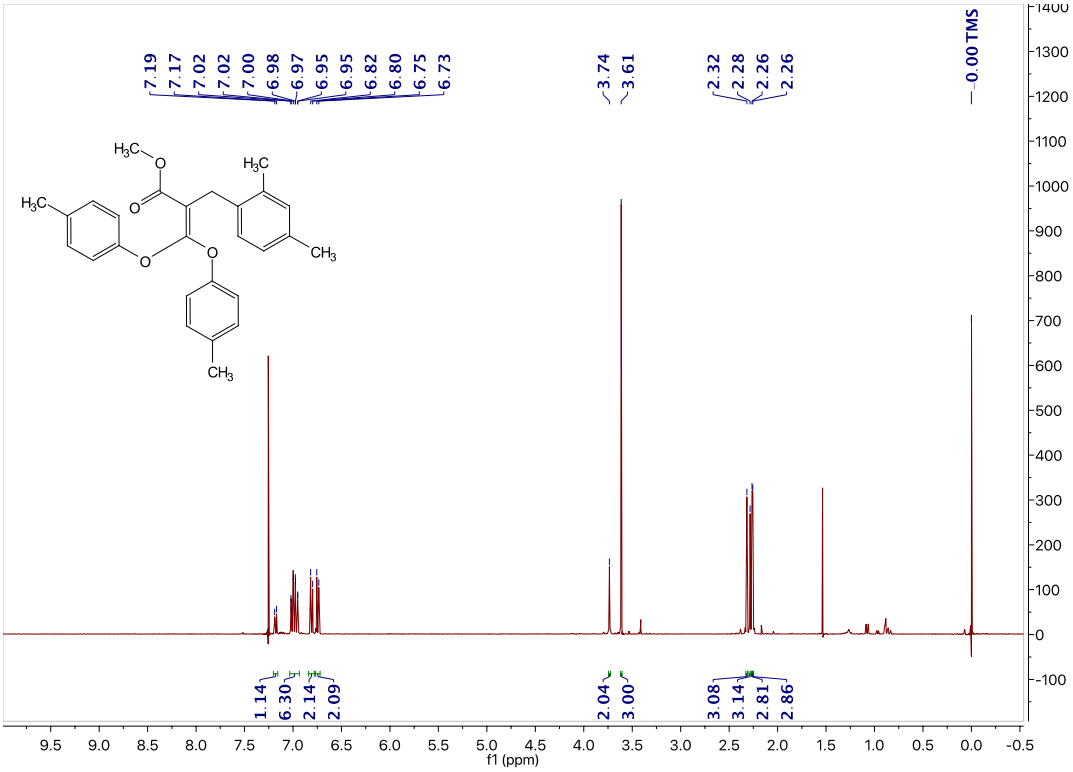
2b' – ^{11}B NMR



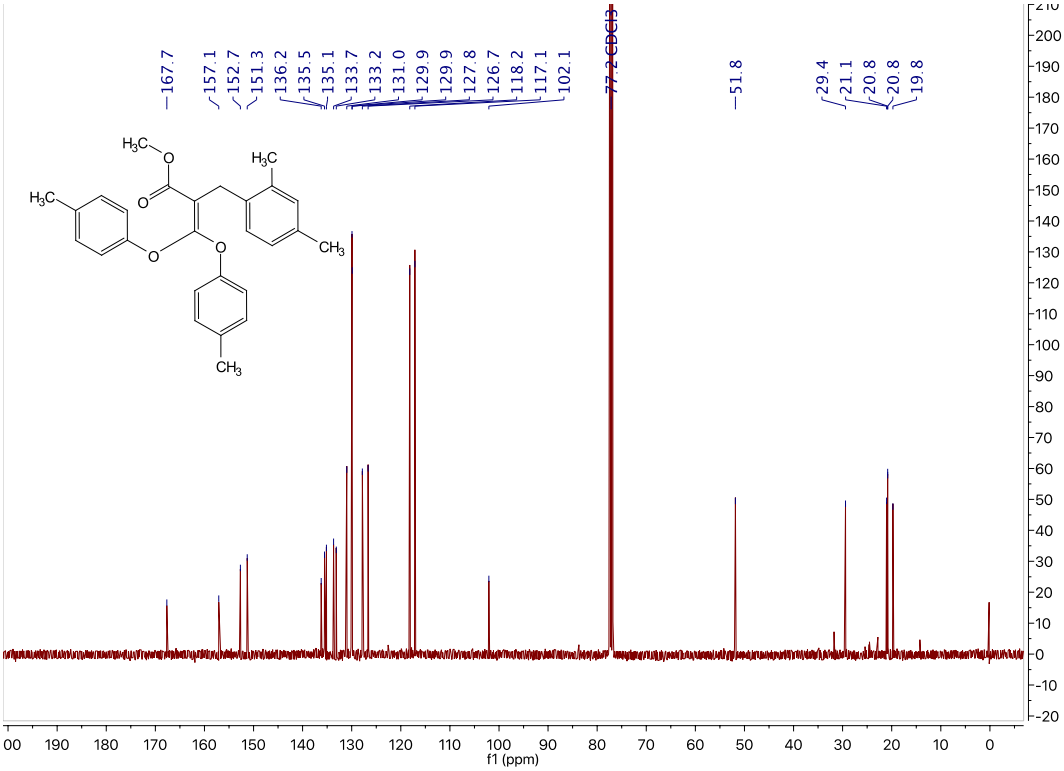
Mechanistic Study – Crude ^{19}F NMR



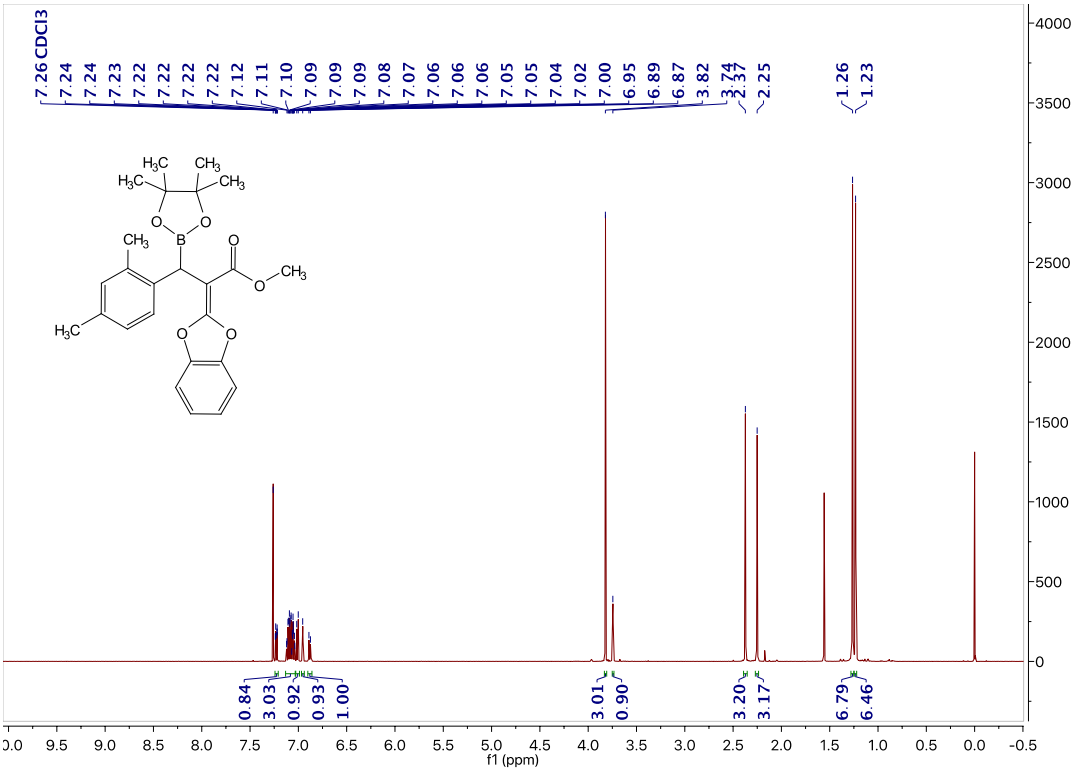
3 – ^{1}H NMR



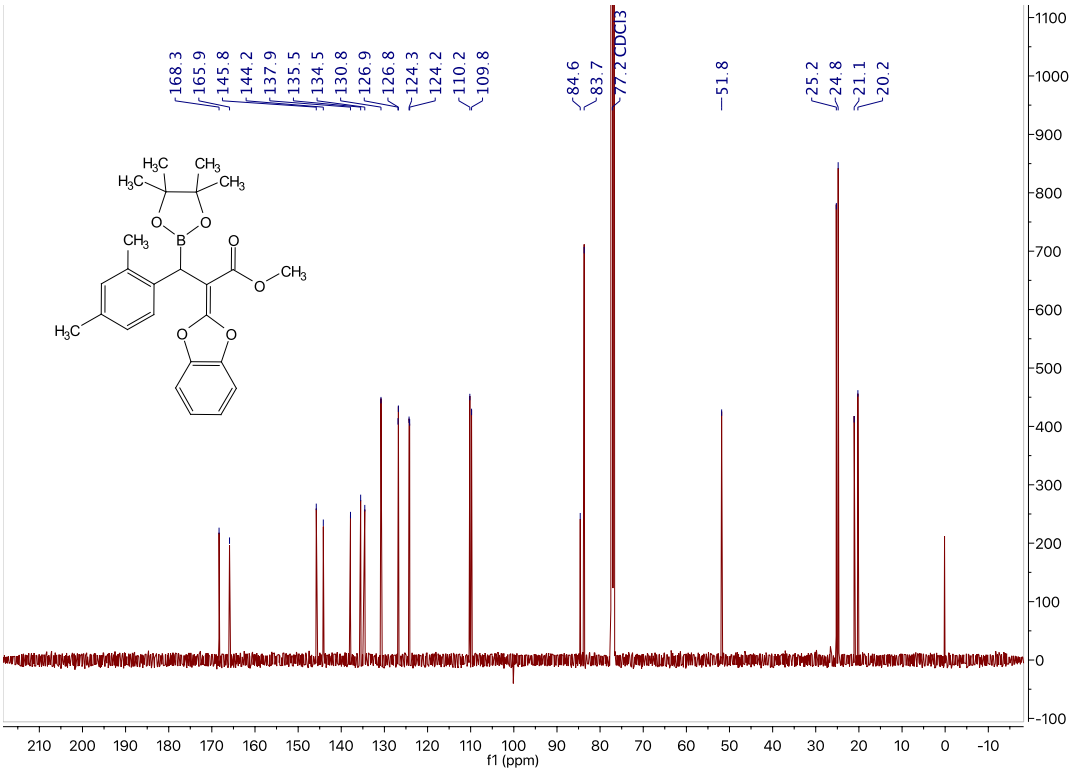
3 – ^{13}C NMR



4 – ^{1}H NMR



4 – ^{13}C NMR



4 – ^{11}B NMR