

Supporting Information

for

Practical tetrafluoroethylene fragment installation through a coupling reaction of (1,1,2,2-tetrafluorobut-3-en-1-yl)zinc bromide with various electrophiles

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Experimental procedures, characterization data (^1H , ^{13}C , ^{19}F NMR, IR and HRMS), copies of ^1H , ^{13}C and ^{19}F NMR spectra

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1. Experimental section

General experimental

Infrared spectra (IR) were determined in a liquid film on a NaCl plate with a JASCO FT/IR-4100 type A spectrometer and all spectra are reported in wavenumber (cm^{-1}). ^1H and ^{13}C NMR spectra were measured with a Bruker AVANCE III 400 NMR spectrometer (^1H : 400 MHz and ^{13}C : 100 MHz) in a chloroform-*d* (CDCl_3) solution and the chemical shifts are reported in parts per million (ppm) using the residual proton or carbon in the NMR solvent. A Bruker AVANCE III 400 NMR spectrometer was used for determining the yield of the products with hexafluorobenzene (C_6F_6) or benzonitrile ($\text{C}_6\text{H}_5\text{N}$). ^{19}F NMR (376.05 MHz) spectra were measured with a Bruker AVANCE III 400 NMR spectrometer in a CDCl_3 solution with trichlorofluoromethane (CFCl_3 , $\delta_{\text{F}} = 0$ ppm) as an internal standard. High-resolution mass spectra (HRMS) were taken on a JEOL JMS-700MS spectrometer by fast atom bombardment (FAB) method.

All reactions were carried out using dried glassware with a magnetic stirrer bar under an atmosphere of argon and routinely monitored by ^{19}F NMR spectroscopy or thin-layer chromatography (TLC).

Materials

All chemicals were of reagent grade and, if necessary, were purified in the usual manner prior to use.

Column chromatography was carried out on silica gel (Wako gel[®] C-200) and TLC was performed on silica gel TLC plates (Merck, Silica gel 60 F₂₅₄).

Preparation of Zn–Ag couple

To a stirred solution of silver acetate (10 mg, 0.060 mmol) in glacial acetic acid (20 mL) at reflux temperature was added zinc powder (10 g, 153 mmol) in one portion, and the whole was stirred at that temperature for additional 30 seconds. After refluxing for 30 seconds, the flask was cooled by dipping in an ice-bath. The Zn–Ag couple formed was separated by vacuum filtration in the open-air, which was washed with Et₂O several times, followed by drying under reduced pressure.

The Zn–Ag couple separated was stored at room temperature under Ar atmosphere. See Figure S1

Preparation of CH₂=CHCF₂CF₂ZnBr in DMF (2-Zn)

In a two-necked round-bottomed flask, equipped with a teflon-coated stirrer bar, was placed Zn–Ag couple (0.66 g, 10 mmol) in DMF (5.0 mL). To the suspension was slowly dropwise added 4-bromo-3,3,4,4-tetrafluorobut-1-ene (**1**, 1.0 g, 5.0 mmol) at 0 °C and the whole was stirred at that temperature for 30 min. The resultant was subjected to a short pad of celite and washed by Et₂O three times. The filtrate was concentrated in vacuo to give the corresponding organozinc reagents **2-Zn** in 86% NMR yield as a 0.70 M DMF solution.

(1,1,2,2-Tetrafluorobut-3-en-1-yl)zinc bromide in DMF (2-Zn)

Yield: 86% (determined by ^{19}F NMR); ^{19}F NMR (CDCl_3): δ -112.10 (brs, 2F, $\text{CF}_2\text{CH=}$), -120.23 (brs, 2F, CF_2Zn).

Typical procedure for Cu(I)-catalyzed cross-coupling reaction of organozinc reagent 2-Zn with iodobenzene (3a)

In a two-necked round-bottomed flask, equipped with a teflon-coated stirrer bar, were added iodobenzene (**3a**, 0.40 mL, 3.6 mmol) and Cu_2O (0.027 g, 0.18 mmol), and a DMF solution of **2-Zn** (0.60 M, 1.0 mL, 0.6 mmol). The whole was heated up at 100 °C and stirred at that temperature for 24 h. After cooling to room temperature, the resultant was filtered through a short pad of silica gel using hexane as an eluent. The filtrate was concentrated in vacuo to give the crude materials, which was purified by silica gel column chromatography using hexanes as an eluent, leading to the corresponding compound **4a** (0.036 g, 0.17 mmol) in 29% isolated yield as a colorless oil.

3,3,4,4-Tetrafluoro-4-phenylbut-1-ene (4a) [S1]

Known compound; Yield: 29% (0.036 g, 0.17 mmol); Colorless oil (hexanes, R_f = 0.57); ^1H NMR (CDCl_3): δ 5.69 (d, J = 11.6 Hz, 1H, *trans*- $\text{CH}_2=\text{CHCF}_2$), 5.83 (dt, J = 17.2, 1.6 Hz, 1H, *cis*- $\text{CH}_2=\text{CHCF}_2$), 6.02 (ddt, J = 17.2, 11.6, 11.5 Hz, 1H, $\text{CF}_2\text{CH=}$), 7.44–7.58 (m, 5H, ArH); ^{13}C NMR (CDCl_3): δ 115.1 (tt, J = 248.8, 37.2 Hz, CF_2), 116.4 (tt, J = 252.1, 35.5 Hz, CF_2), 124.1 (t, J = 9.9

Hz, CH₂=), 126.7 (t, *J* = 24.8 Hz, CF₂CH=), 126.9 (td, *J* = 6.6, 1.7 Hz, Ar), 127.0–127.7 (m, Ar), 128.2 (Ar), 131.0 (t, *J* = 1.7 Hz, Ar); ¹⁹F NMR (CDCl₃): δ –112.56 (s, 2F, CF₂Ar), –114.95 (d, *J* = 11.46 Hz, 2F, CF₂CH=); IR (neat): ν 3071, 1653, 1424, 1286, 1243, 1130, 1070, 949 cm^{–1}; HRMS (FAB) calcd for [M]⁺ C₁₀H₈F₄: 204.0562, found 204.0558.

3,3,4,4-Tetrafluoro-4-(4-methoxyphenyl)but-1-ene (4b) [S1]

Known compound; Yield: 43% (0.065 g, 0.28 mmol); Colorless oil (hexanes, *R_f* = 0.20); ¹H NMR (CDCl₃): δ 3.85 (s, 3H, CH₃), 5.67 (d, *J* = 11.3 Hz, 1H, *trans*-CH₂=CHCF₂), 5.81 (dt, *J* = 17.2, 2.0 Hz, 1H, *cis*-CH₂=CHCF₂), 6.00 (ddt, *J* = 17.2, 11.4, 11.3 Hz, 1H, CF₂CH=), 6.95 (d, *J* = 8.8 Hz, 2H, ArH), 7.48 (d, *J* = 8.8 Hz, 2H, ArH); ¹³C NMR (CDCl₃): δ 55.7 (CH₃), 114.0 (Ar), 115.5 (tt, *J* = 249.0, 38.2 Hz, CF₂), 116.9 (tt, *J* = 251.6, 35.1 Hz, CF₂), 123.2 (t, *J* = 25.4 Hz, Ar), 124.3 (t, *J* = 9.2 Hz, CH₂=), 127.3 (t, *J* = 24.9 Hz, CF₂CH=), 128.7 (t, *J* = 6.3 Hz, Ar), 161.9 (Ar); ¹⁹F NMR (CDCl₃): δ –111.52 (s, 2F, CF₂Ar), –115.01 (d, *J* = 11.4 Hz, 2F, CF₂CH=); IR (neat): ν 2938, 1519, 1420, 1260, 1181, 1095, 1074, 982, 832 cm^{–1}; HRMS (FAB) calcd for [M]⁺ C₁₁H₁₀F₄O: 234.0668, found 234.0672.

3,3,4,4-Tetrafluoro-4-(4-methylphenyl)but-1-ene (4c) [S1]

Known compound; Yield: 36% (0.046 g, 0.21 mmol); Colorless oil (hexanes, *R_f* = 0.37); ¹H NMR (CDCl₃): δ 2.41 (s, 3H, CH₃), 5.68 (d, *J* = 11.2 Hz, 1H, *trans*-CH₂=CHCF₂), 5.82 (dt, *J* = 17.5, 2.0

Hz, 1H, *cis*-CH₂=CHCF₂), 6.01 (ddt, *J* = 17.5, 11.4, 11.2 Hz, 1H, CF₂CH=), 7.26 (d, *J* = 8.4 Hz, 2H, ArH), 7.44 (d, *J* = 8.4 Hz, 2H ArH); ¹³C NMR (CDCl₃): δ 21.3 (CH₃), 115.1 (tt, *J* = 248.4, 37.6 Hz, CF₂), 116.6 (tt, *J* = 251.3, 35.1 Hz, CF₂), 124.0 (t, *J* = 9.5 Hz, CH₂=), 126.8 (t, *J* = 24.8 Hz, CF₂CH=), 126.6–127.1 (m, Ar), 127.9 (t, *J* = 24.8 Hz, Ar), 128.9 (Ar), 141.2 (t, *J* = 1.7 Hz, Ar); ¹⁹F NMR (CDCl₃): δ -112.24 (s, 2F, CF₂Ar), -115.04 (d, *J* = 11.4 Hz, 2F, CF₂CH=); IR (neat): ν 3043, 2927, 1617, 1420, 1288, 1243, 1121, 1074, 982, 818 cm⁻¹; HRMS (FAB) calcd for [M]⁺ C₁₁H₁₀F₄: 218.0719, found 218.0726.

4-(4-Chlorophenyl)-3,3,4,4-tetrafluorobut-1-ene (4d) [S1]

Known compound; Yield: 49% (0.072 g, 0.30 mmol); Colorless oil (hexanes, R_f = 0.50); ¹H NMR (CDCl₃): δ 5.71 (d, *J* = 11.2 Hz, 1H, *trans*-CH₂=CHCF₂), 5.84 (dt, *J* = 17.2, 2.0 Hz, 1H, *cis*-CH₂=CHCF₂), 6.01 (ddt, *J* = 17.2, 11.2, 11.3 Hz, 1H, CF₂CH=), 7.44 (d, *J* = 8.8 Hz, 2H, ArH), 7.50 (d, *J* = 8.8 Hz, ArH); ¹³C NMR (CDCl₃): δ 115.1 (tt, *J* = 249.1, 37.6 Hz, CF₂), 116.2 (tt, *J* = 252.1, 35.6 Hz, CF₂), 124.6 (t, *J* = 9.2 Hz, CH₂=), 126.5 (t, *J* = 24.7 Hz, CF₂CH=), 128.5 (t, *J* = 6.3 Hz, Ar), 128.8 (Ar), 129.4 (t, *J* = 25.3 Hz, Ar), 137.6 (t, *J* = 1.7 Hz, Ar); ¹⁹F NMR (CDCl₃): δ -112.44 (s, 2F, CF₂Ar), -114.80 (d, *J* = 11.3 Hz, 2F, CF₂CH=); IR (neat): ν 2925, 2857, 1604, 1491, 1218, 1135, 1095, 1074, 957, 826 cm⁻¹; HRMS (FAB) calcd for [M]⁺ C₁₀H₇ClF₄: 238.0172, found 238.0170.

3,3,4,4-Tetrafluoro-4-(4-trifluoromethylphenyl)but-1-ene (4e)

Yield: 13% (0.036 g, 0.13 mmol); Colorless oil (hexanes, R_f = 0.57); ^1H NMR (CDCl_3): δ 5.74 (d, J = 11.1 Hz, 1H, *trans*- $\text{CH}_2=\text{CHCF}_2$), 5.86 (dt, J = 17.3, 2.1 Hz, 1H, *cis*- $\text{CH}_2=\text{CHCF}_2$), 6.03 (ddt, J = 17.3, 11.2, 11.1 Hz, 1H, $\text{CF}_2\text{CH=}$), 7.70 (d, J = 8.6 Hz, 2H, ArH), 7.74 (d, J = 8.6 Hz, 2H, ArH); ^{13}C NMR (CDCl_3): δ 115.1 (tt, J = 248.9, 36.9 Hz, CF_2), 116.0 (tt, J = 252.4, 36.1 Hz, CF_2), 123.7 (q, J = 272.6 Hz, CF_3), 124.9 (t, J = 9.3 Hz, $\text{CH}_2=$), 125.5 (q, J = 3.7 Hz, Ar), 126.3 (t, J = 24.6 Hz, $\text{CF}_2\text{CH=}$), 127.7 (t, J = 6.5 Hz, Ar), 133.3 (q, J = 33.0 Hz, Ar), 134.5 (t, J = 25.0 Hz, Ar); ^{19}F NMR (CDCl_3): δ -63.57 (s, 3F, CF_3), -112.81 (s, 2F, CF_2Ar), -114.57 (d, J = 11.2 Hz, 2F, $\text{CF}_2\text{CH=}$); IR (neat): ν 2923, 2870, 1416, 1329, 1220, 1174, 1018, 924, 840 cm^{-1} ; HRMS (FAB) calcd for $[\text{M}]^+$ $\text{C}_{11}\text{H}_7\text{F}_7$: 272.0436, found 272.0428.

Ethyl 4-(1,1,2,2-tetrafluorobut-3-en-1-yl)benzoate (4f) [S1]

Known compound; Yield: 56% (0.095 g, 0.34 mmol); Colorless oil (hexanes/AcOEt = 20/1, R_f = 0.34); ^1H NMR (CDCl_3): δ 1.41 (t, J = 7.2 Hz, 3H, CH_2CH_3), 4.41 (q, J = 7.2 Hz, 2H, CH_2CH_3), 5.71 (d, J = 11.2 Hz, 1H, *trans*- $\text{CH}_2=\text{CHCF}_2$), 5.83 (dt, J = 17.2, 2.0 Hz, 1H, *cis*- $\text{CH}_2=\text{CHCF}_2$), 6.01 (ddt, J = 17.2, 11.5, 11.2 Hz, 1H, $\text{CF}_2\text{CH=}$), 7.63 (d, J = 8.0 Hz, 2H, ArH), 8.13 (d, J = 8.0 Hz, 2H, ArH); ^{13}C NMR (CDCl_3): δ 14.6 (CH_2CH_3), 61.7 (CH_2CH_3), 115.3 (tt, J = 249.4, 36.9 Hz, CF_2), 116.4 (tt, J = 252.3, 35.7 Hz, CF_2), 124.8 (t, J = 9.3 Hz, $\text{CH}_2=$), 126.7 (t, J = 24.7 Hz, $\text{CF}_2\text{CH=}$),

127.3 (t, $J = 6.4$ Hz, Ar), 129.7 (Ar), 133.4 (Ar), 135.2 (t, $J = 24.8$ Hz, Ar), 166.0 (C=O); ^{19}F NMR (CDCl_3): δ -112.88 (s, 2F, CF_2Ar), -114.70 (d, $J = 11.5$ Hz, 2F, $\text{CF}_2\text{CH=}$); IR (neat): ν 2985, 1725, 1412, 1279, 1218, 1136, 1076, 981, 855 cm^{-1} ; HRMS (FAB) calcd for $[\text{M}+\text{H}]^+$ $\text{C}_{13}\text{H}_{13}\text{F}_4\text{O}_2$: 277.0852, found 277.0853.

3,3,4,4-Tetrafluoro-4-(4-nitrophenyl)but-1-ene (4g) [S1]

Known compound; This compound could not be obtained in a pure form, and included the remaining iodoarene; Yield: 65% (determined by ^{19}F NMR); Colorless oil (hexanes/AcOEt = 5/1, R_f = 0.57; ^1H NMR (CDCl_3): δ 5.77 (d, $J = 11.2$ Hz, 1H, *trans*- $\text{CH}_2=\text{CHCF}_2$), 5.88 (dt, $J = 17.3$, 2.0 Hz, 1H, *cis*- $\text{CH}_2=\text{CHCF}_2$), 6.04 (ddt, $J = 17.3$, 11.2, 11.4 Hz, 1H, $\text{CF}_2\text{CH=}$), 7.77 (d, $J = 8.7$ Hz, 2H, ArH), 8.32 (d, $J = 8.7$ Hz, 2H, ArH); ^{13}C NMR (CDCl_3): δ 115.0 (tt, $J = 249.5$, 37.1 Hz, CF_2), 115.8 (tt, $J = 252.9$, 36.5 Hz, CF_2), 123.6 (Ar), 125.2 (t, $J = 9.4$ Hz, $\text{CH}_2=$), 126.0 (t, $J = 24.5$ Hz, $\text{CF}_2\text{CH=}$), 128.5 (t, $J = 6.4$ Hz, Ar), 137.0 (t, $J = 25.0$ Hz, Ar), 149.8 (Ar); ^{19}F NMR (CDCl_3): δ -112.72 (s, 2F, CF_2Ar), -114.25 (d, $J = 11.4$ Hz, 2F, $\text{CF}_2\text{CH=}$); IR (neat): ν 3121, 1613, 1533, 1421, 1284, 1242, 1139, 1077, 945, 849 cm^{-1} ; HRMS (FAB) calcd for $[\text{M}]^+$ $\text{C}_{10}\text{H}_7\text{F}_4\text{NO}_2$: 249.0413, found 249.0422.

4-(3-Chlorophenyl)-3,3,4,4-tetrafluorobut-1-ene (4h)

Yield: 60% (0.142 g, 0.60 mmol); Colorless oil (hexanes, R_f = 0.50); ^1H NMR (CDCl_3): δ 5.72 (d, J

= 11.2 Hz, 1H, *trans*-CH₂=CHCF₂), 5.90 (dt, *J* = 17.3, 2.0 Hz, 1H, *cis*-CH₂=CHCF₂), 6.00 (ddt, *J* = 17.3, 11.2, 11.2 Hz, 1H, CF₂CH=), 7.40 (dd, *J* = 7.8, 7.8 Hz, 1H, ArH), 7.46 (d, *J* = 7.8 Hz, 1H, ArH) 7.50 (d, *J* = 7.8 Hz, 1H, ArH), 7.56 (s, 1H, ArH); ¹³C NMR (CDCl₃): δ 115.1 (tt, *J* = 249.2, 37.3 Hz, CF₂), 115.8 (tt, *J* = 252.5, 35.7 Hz, CF₂), 124.7 (t, *J* = 9.2 Hz, CH₂=), 125.3 (t, *J* = 6.5 Hz, Ar), 126.5 (t, *J* = 24.8 Hz, CF₂CH=), 127.4 (t, *J* = 6.7 Hz, Ar), 129.8 (Ar), 131.4 (Ar), 132.8 (t, *J* = 25.3 Hz, Ar), 134.6 (Ar); ¹⁹F NMR (CDCl₃): δ -112.47 (s, 2F, CF₂Ar), -114.70 (d, *J* = 11.2 Hz, 2F, CF₂CH=); IR (neat): ν 2925, 1420, 1243, 1100, 1011, 981, 886 cm⁻¹; HRMS (FAB) calcd for [M]⁺ C₁₀H₇ClF₄: 238.0172, found 238.0176.

4-(2-Chlorophenyl)-3,3,4,4-tetrafluorobut-1-ene (4i)

Yield: 64% (0.095 g, 0.40 mmol); Colorless oil (hexanes, R_f = 0.50); ¹H NMR (CDCl₃): δ 5.73 (d, *J* = 11.3 Hz, 1H, *trans*-CH₂=CHCF₂), 5.87 (dt, *J* = 17.3, 2.2 Hz, 1H, *cis*-CH₂=CHCF₂), 6.09 (ddtm, *J* = 17.3, 11.3, 11.4 Hz, 1H, CF₂CH=), 7.35 (tm, *J* = 7.7 Hz, 1H, ArH), 7.42 (tm, *J* = 7.7 Hz, 1H, ArH), 7.48 (d, *J* = 7.7 Hz, 1H, ArH), 7.59 (dm, *J* = 7.7 Hz, 1H, ArH); ¹³C NMR (CDCl₃): δ 115.6 (tt, *J* = 250.0, 37.3 Hz, CF₂), 116.4 (tt, *J* = 254.4, 37.0 Hz, CF₂), 124.4 (t, *J* = 9.4 Hz, CH₂=), 126.6 (Ar), 126.7 (t, *J* = 24.6 Hz, CF₂CH=), 128.4 (t, *J* = 23.7 Hz, Ar), 130.4 (t, *J* = 8.4 Hz, Ar), 132.0 (Ar), 132.2 (Ar), 133.4 (t, *J* = 2.8 Hz, Ar); ¹⁹F NMR (CDCl₃): δ -108.47 (s, 2F, CF₂Ar), -113.75 (d, *J* = 11.4 Hz, 2F, CF₂CH=); IR (neat): ν 2929, 1475, 1216, 1154, 1094, 939 cm⁻¹; HRMS (FAB) calcd

for $[M]^+ C_{10}H_7ClF_4$: 238.0172, found 238.0174.

Typical procedure for improved Cu(I)-catalyzed cross-coupling reaction of organozinc reagent 2-Zn with ethyl 2-iodobenzoate (3j)

In a two-necked round-bottomed flask, equipped with a teflon-coated stirrer bar and reflux condenser, was added ethyl 2-iodobenzoate (**3j**, 0.14 g 0.50 mmol), Cu_2O (0.060 g, 0.42 mmol), and a DMF solution of **2-Zn** (0.65 M, 1.54 mL, 1.0 mmol), and the mixture was stirred at 100 °C for 24 h. After being cooled to room temperature, the resulting solution was subjected to a short pad of silica gel using hexanes as an eluent. The filtrate was concentrated in vacuo to give the crude materials, which was purified by silica gel column chromatography to provide the corresponding compound **4j** (0.13 g, 0.48 mmol) in 96% yield as an yellow oil.

Ethyl 2-(1,1,2,2-tetrafluorobut-3-en-1-yl)benzoate (4j)

Yield: 96% (0.13 g, 0.48 mmol); Yellow oil (hexanes/AcOEt = 15/1, R_f = 0.29); 1H NMR ($CDCl_3$): δ 1.35 (t, J = 7.1 Hz, 3H, CH_2CH_3), 4.36 (q, J = 7.1 Hz, 2H, CH_2CH_3), 5.70 (d, J = 11.0 Hz, 1H, *trans*- $CH_2=CHCF_2$), 5.86 (dt, J = 17.3, 2.2 Hz, 1H, *cis*- $CH_2=CHCF_2$), 6.07 (ddt, J = 17.3, 11.4, 11.0 Hz, 1H, $CF_2CH=$), 7.47–7.62 (m, 4H, ArH); ^{13}C NMR ($CDCl_3$): δ 14.1 (CH_2CH_3), 61.9 (CH_2CH_3), 115.2 (tt, J = 250.2, 37.2 Hz, CF_2), 116.6 (tt, J = 253.4, 36.1 Hz, CF_2), 124.2 (t, J = 9.3 Hz, $CH_2=$), 126.8 (t, J = 24.4 Hz, $CF_2CH=$), 127.7 (t, J = 24.5 Hz, Ar), 128.5 (Ar), 128.7–128.9 (m, Ar), 129.7

(Ar), 131.1 (Ar), 133.8 (t, $J = 3.3$ Hz, Ar), 168.6 (C=O); ^{19}F NMR (CDCl_3): δ -106.44 (s, 2F, CF_2Ar), -113.42 (d, $J = 11.4$ Hz, 2F, $\text{CF}_2\text{CH=}$); IR (neat): ν 3076, 2988, 2903, 1739, 1578, 1415, 1370, 1269, 1152 cm^{-1} ; HRMS (FAB) calcd for $[\text{M}+\text{H}]^+$ $\text{C}_{13}\text{H}_{13}\text{F}_4\text{O}_2$: 277.0852, found 277.0847.

3,3,4,4-Tetrafluoro-4-(2-formylphenyl)but-1-ene (4k)

Yield: 83% (0.096 g, 0.41 mmol); Pale yellow oil (hexanes/AcOEt = 15/1, $R_f = 0.40$); ^1H NMR (CDCl_3): δ 5.78 (d, $J = 11.5$ Hz, 1H, *trans*- $\text{CH}_2=\text{CHCF}_2$), 5.90 (dt, $J = 17.3, 2.1$ Hz, 1H, *cis*- $\text{CH}_2=\text{CHCF}_2$), 6.09 (ddtm, $J = 17.3, 11.5, 11.4$ Hz, 1H, $\text{CF}_2\text{CH=}$), 7.63–7.71 (m, 3H, ArH), 8.11–8.13 (m, 1H, ArH), 10.36 (t, $J = 1.7$ Hz, 1H, CHO); ^{13}C NMR (CDCl_3): δ 115.1 (tt, $J = 249.1$ Hz, 37.5 Hz, CF_2), 117.5 (tt, $J = 253.3, 37.7$ Hz, CF_2), 125.3 (t, $J = 9.2$ Hz, Ar), 126.0 (t, $J = 24.7$ Hz, $\text{CF}_2\text{CH=}$), 128.7 (t, $J = 9.5$ Hz, $\text{CH}_2=$), 128.8 (Ar), 131.3 (t, $J = 24.8$ Hz, Ar), 131.7 (Ar), 133.1 (Ar), 135.7 (t, $J = 1.4$ Hz, Ar), 191.0 (tt, $J = 7.3, 3.9$ Hz, C=O); ^{19}F NMR (CDCl_3): δ -103.57 (s, 2F, CF_2Ar), -114.28 (d, $J = 11.4$ Hz, 2F, $\text{CF}_2\text{CH=}$); IR (neat): ν 3075, 2925, 1699, 1597, 1417, 1213, 1128, 922 cm^{-1} ; HRMS (FAB) calcd for $[\text{M}+\text{H}]^+$ $\text{C}_{11}\text{H}_9\text{F}_4\text{O}$: 233.0590, found 233.0593.

3,3,4,4-Tetrafluoro-4-(2-acetylphenyl)but-1-ene (4l)

Yield: 81% (0.123 g, 0.50 mmol); Yellow oil (hexane/AcOEt = 5/2, $R_f = 0.37$); ^1H NMR (CDCl_3): δ 2.52 (s, 3H, CH_3), 5.71 (d, $J = 11.4$ Hz, 1H, *trans*- $\text{CH}_2=\text{CHCF}_2$), 5.86 (dtm, $J = 17.3, 2.3$ Hz, 1H, *cis*- $\text{CH}_2=\text{CHCF}_2$), 6.04 (ddtm, $J = 17.3, 11.36, 11.42$ Hz, 1H, $\text{CF}_2\text{CH=}$), 7.23–7.25 (m, 1H, ArH),

7.47–7.60 (m, 3H, ArH); ^{13}C NMR (CDCl_3): δ 31.8 (CH_3), 115.2 (tt, $J = 249.8, 37.5$ Hz, CF_2), 116.9 (tt, $J = 253.0, 36.3$ Hz, CF_2), 124.6 (t, $J = 9.3$ Hz, $\text{CH}_2=$), 125.8 (Ar), 126.1 (t, $J = 24.7$ Hz, Ar), 126.4 (t, $J = 24.4$ Hz, $\text{CF}_2\text{CH=}$), 128.8 (tt, $J = 7.1, 2.6$ Hz, Ar), 129.0 (Ar), 131.3 (Ar), 142.6 (t, $J = 2.9$ Hz, Ar), 203.8 (C=O); ^{19}F NMR ($\text{CDCl}_3, \text{CFCl}_3$): δ –105.50 (s, 2F, CF_2Ar), –113.53 (d, $J = 11.4$ Hz, 2F, $\text{CF}_2\text{CH=}$); IR (neat): ν 3415, 3072, 2989, 2942, 1709, 1569, 1412, 1250, 1208, 1143, 1108, 1086, 1054, 941, 922 cm^{-1} ; HRMS (FAB) calcd for $[\text{M}+\text{H}]^+ \text{C}_{12}\text{H}_{11}\text{F}_4\text{O}$: 247.0746, Found 247.0749.

3,3,4,4-Tetrafluoro-4-(2-methoxymethylphenyl)but-1-ene (4m)

Yield: 58% (0.069 g, 0.28 mmol); Yellow oil (hexanes/AcOEt = 40/1, $R_f = 0.31$); ^1H NMR (CDCl_3): δ 3.43 (s, 3H, CH_3), 4.65 (s, 2H, ArCH_2), 5.72 (d, $J = 11.24$ Hz, 1H, *trans*- $\text{CH}_2=\text{CHCF}_2$), 5.86 (dt, $J = 17.34, 2.15$ Hz, 1H, *cis*- $\text{CH}_2=\text{CHCF}_2$), 6.05 (dtd, $J = 17.34, 11.24, 11.37$ Hz, 1H, $\text{CF}_2\text{CH=}$), 7.36 (t, $J = 7.37$ Hz, 1H, ArH), 7.49 (d, $J = 7.37$ Hz, 1H, ArH), 7.52 (t, $J = 7.37$ Hz, 1H, ArH), 7.70 (d, $J = 7.37$ Hz, 1H, ArH); ^{13}C NMR (CDCl_3): δ 58.5 (CH_3), 71.3 (tt, $J = 6.56, 3.28$ Hz, ArCH_2), 115.6 (tt, $J = 249.3, 38.1$ Hz, CF_2), 117.9 (tt, $J = 252.98, 36.54$ Hz, CF_2), 124.4 (t, $J = 9.28$ Hz, $\text{CH}_2=$), 126.8 (t, $J = 24.97$ Hz, $\text{CF}_2\text{CH=}$), 127.0 (Ar), 127.7 (t, $J = 23.77$ Hz, Ar), 128.5 (t, $J = 8.09$ Hz, Ar), 128.6 (Ar), 131.3 (Ar), 138.6 (Ar); ^{19}F NMR ($\text{CDCl}_3, \text{CFCl}_3$): δ –106.44 (s, 2F, CF_2Ar), –114.28 (d, $J = 11.37$ Hz, 2F, $\text{CF}_2\text{CH=}$); IR (neat): ν 2987, 2931, 2897, 2827, 1452, 1420, 1213, 1196, 1116, 1097,

1061, 960, 938, 918, 765, 687 cm^{-1} ; HRMS (FAB) calcd for $[\text{M}+\text{Na}]^+$ $\text{C}_{12}\text{H}_{12}\text{F}_4\text{NaO}$: 271.0722, found 271.0715.

3,3,4,4-Tetrafluoro-4-(2-nitrophenyl)but-1-ene (4n)

Yield: 78% (1.3 g, 5.2 mmol); Yellow oil (hexanes/AcOEt = 5/1, R_f = 0.51); ^1H NMR (CDCl_3): δ 5.76 (d, J = 11.4 Hz, 1H, *trans*- $\text{CH}_2=\text{CHCF}_2$), 5.91 (dt, J = 17.0, 2.0 Hz, 1H, *cis*- $\text{CH}_2=\text{CHCF}_2$), 6.1 (ddtm, J = 17.0, 11.4, 11.4 Hz, 1H, $\text{CF}_2\text{CH=}$), 7.55–7.59 (m, 1H, *ArH*), 7.63–7.72 (m, 3H, *ArH*); ^{13}C NMR (CDCl_3): δ 115.1 (tt, J = 250.5, 36.9 Hz, CF_2), 115.5 (tt, J = 254.4, 37.3 Hz, CF_2), 122.6 (t, J = 25.7 Hz, $\text{CF}_2\text{CH=}$), 123.9 (*Ar*), 125.1 (t, J = 9.3 Hz, $\text{CH}_2=$), 125.9 (t, J = 24.4 Hz, *Ar*), 130.1 (tt, J = 6.9, 2.6 Hz, *Ar*), 131.0 (*Ar*), 132.6 (*Ar*), 149.8 (*Ar*); ^{19}F NMR (CDCl_3): δ -107.35 (s, 2F, CF_2Ar), -113.02 (d, J = 11.4 Hz, 2F, $\text{CF}_2\text{CH=}$); IR (neat): ν 3086, 2904, 1609, 1540, 1420, 1372, 1220, 1163, 1119, 980, 851 cm^{-1} ; HRMS (FAB) calcd for $[\text{M}+\text{Na}]^+$ $\text{C}_{10}\text{H}_7\text{F}_4\text{NNaO}_2$: 272.0311, found 272.0313.

3,3,4,4-Tetrafluoro-4-(4-fluoro-2-nitrophenyl)but-1-ene (4o)

Yield: 73% (0.390 g, 1.46 mmol); Yellow oil (hexanes/AcOEt = 5/1, R_f = 0.43); ^1H NMR (CDCl_3): δ 5.74 (d, J = 11.18 Hz, 1H, *trans*- $\text{CH}_2=\text{CHCF}_2$), 5.87 (dt, J = 17.31, 1.84 Hz, 1H, *cis*- $\text{CH}_2=\text{CHCF}_2$), 6.03 (dtd, J = 17.31, 11.32, 11.18 Hz, 1H, $\text{CF}_2\text{CH=}$), 7.29 (dd, J = 7.56, 2.52 Hz, 1H, *ArH*), 7.33–7.37 (m, 1H, *ArH*), 7.70 (dd, J = 8.92, 5.24 Hz, 1H, *ArH*); ^{13}C NMR (CDCl_3): δ 111.99 (d, J =

27.06 Hz, Ar), 115.09 (tt, $J = 250.37, 36.98$, CF₂), 115.37 (tt, $J = 254.39, 37.51$ Hz, CF₂), 118.48 (d, $J = 21.43$ Hz, Ar), 118.70 (Ar), 125.28 (t, $J = 9.83$ Hz, CH₂=), 125.63 (t, $J = 24.44$ Hz, CF₂CH=), 132.27 to 132.51 (m, Ar), 150.66 (Ar), 163.86 (d, $J = 257.69$ Hz, Ar); ¹⁹F NMR (CDCl₃, CFCl₃): δ -104.18 to -104.23 (m, 1F, ArF), -106.94 (s, 2F, CF₂Ar), -112.82 (d, $J = 11.32$ Hz, 2F, CF₂CH=); IR (neat): ν 3087, 2908, 2351, 1929, 1717, 1621, 1550, 1508, 1421, 1369, 1230, 1117, 953, 729 cm⁻¹; HRMS (FAB) calcd for [M]⁺ C₁₀H₆F₅NO₂: 267.0139, found 267.0134.

3,3,4,4-Tetrafluoro-4-(4-methoxy-2-nitrophenyl)but-1-ene (4p)

Yield: 90% (0.510 g, 1.83 mmol); Yellow oil (hexanes/AcOEt = 5/1, $R_f = 0.37$); ¹H NMR (CDCl₃): δ 3.83 (s, 3H, CH₃), 5.70 (d, $J = 11.24$ Hz, 1H, *trans*-CH₂=CHCF₂), 5.83 (dt, $J = 17.33, 1.80$ Hz, 1H, *cis*-CH₂=CHCF₂), 6.00 (dtd, $J = 17.33, 11.67, 11.24$ Hz, 1H, CF₂CH=), 7.00 (d, $J = 2.52$ Hz, 1H, ArH), 7.08 (dm, $J = 8.94$ Hz, 1H, ArH), 7.54 (d, $J = 8.94$ Hz, 1H, ArH); ¹³C NMR (CDCl₃): δ 55.99 (CH₃), 109.47 (Ar), 113.77 (t, $J = 26.23$ Hz, Ar), 115.14 (tt, $J = 250.09, 37.36$ Hz, CF₂), 115.65 (tt, $J = 253.52, 36.90$ Hz, CF₂), 116.30 (Ar), 124.78 (t, $J = 9.31$ Hz, CH₂=), 125.98 (t, $J = 24.43$ Hz, CF₂CH=), 131.25 (t, $J = 7.05$ Hz, Ar), 150.68 (Ar), 162.28 (Ar); ¹⁹F NMR (CDCl₃, CFCl₃): δ -106.74 (s, 2F, CF₂Ar), -113.17 (d, $J = 11.67$ Hz, 2F, CF₂CH=); IR (neat): ν 3095, 2935, 2850, 2370, 2313, 1621, 1546, 1421, 1371, 1098, 1055, 795 cm⁻¹; HRMS (FAB) calcd for [M+Na]⁺ C₁₁H₉F₄NNaO₃: 302.0417, found 302.0418.

3,3,4,4-Tetrafluoro-4-(5-methoxy-2-nitrophenyl)but-1-ene (4q)

Yield: 83% (0.21 g, 0.75 mmol); Yellow oil (hexanes/AcOEt = 5/1, R_f = 0.29); ^1H NMR (CDCl_3): δ 3.87 (s, 3H, CH_3), 5.73 (d, J = 11.22 Hz, 1H, *trans*- $\text{CH}_2=\text{CHCF}_2$), 5.87 (d, J = 17.29 Hz, 1H, *cis*- $\text{CH}_2=\text{CHCF}_2$), 6.05 (dtd, J = 17.29, 11.40, 11.22 Hz, 1H, $\text{CHCF}_2=$), 7.06 (dd, J = 8.92, 2.50 Hz, 1H, ArH), 7.12 (d, J = 2.50 Hz, 1H, ArH), 7.59 (d, J = 8.92 Hz, 1H, ArH); ^{13}C NMR (CDCl_3): δ 56.1 (CH_3), 115.2 (tt, J = 250.8, 36.6 Hz, CF_2), 115.4 (tt, J = 254.5, 37.1 Hz, CF_2), 115.7 (tt, J = 7.8, 2.4 Hz, Ar), 116.5 (Ar), 142.8 (t, J = 21.48 Hz, $\text{CHCF}_2=$), 125.0 (t, J = 8.96 Hz, $\text{CH}_2=$), 126.0 (t, J = 24.29 Hz, Ar), 126.5 (Ar), 143.1 (Ar), 161.2 (Ar); ^{19}F NMR (CDCl_3 , CFCl_3): δ -106.19 (s, 2F, CF_2Ar), -112.46 (d, J = 11.40 Hz, 2F, $\text{CF}_2\text{CH}=$); IR (neat): ν 2947, 2849, 1588, 1538, 1498, 1421, 1364, 1302, 1248, 1117, 963, 859 cm^{-1} ; HRMS (FAB) calcd for $[\text{M}+\text{H}]^+$ $\text{C}_{11}\text{H}_{10}\text{F}_4\text{NNaO}_3$: 280.0597, found 280.0599.

3-(1,1,2,2-Tetrafluorobut-3-en-1-yl)pyridine (4r) [S1]

Known compound: Yield: 57% (0.070 g, 0.34 mmol); Yellow oil (hexanes/AcOEt = 5/1, R_f = 0.29); ^1H NMR (CDCl_3): δ 5.74 (d, J = 11.3 Hz, 1H, *trans*- $\text{CH}_2=\text{CHCF}_2$), 5.86 (dt, J = 17.2, 2.1 Hz, 1H, *cis*- $\text{CH}_2=\text{CHCF}_2$), 6.04 (ddt, J = 17.2, 11.5, 11.3 Hz, 1H, $\text{CF}_2\text{CH}=$), 7.41 (dd, J = 8.0, 4.5 Hz, 1H, ArH), 7.87 (d, J = 8.0 Hz, 1H, ArH), 8.76 (d, J = 4.5 Hz, 1H, ArH), 8.80 (s, 1H, ArH); ^{13}C NMR (CDCl_3): δ 115.0 (tt, J = 249.2, 37.4 Hz, CF_2), 115.8 (tt, J = 252.4, 36.6 Hz, CF_2), 123.2 (Ar), 125.1

(t, J = 9.4 Hz, CH₂=), 126.1 (t, J = 24.6 Hz, CF₂CH=), 127.0 (t, J = 24.9 Hz, Ar), 134.8 (t, J = 6.2 Hz, Ar), 148.2 (t, J = 6.8 Hz, Ar), 152.0 (Ar); ¹⁹F NMR (CDCl₃): δ -113.14 (s, 2F, CF₂Ar), -114.62 (d, J = 11.5 Hz, 2F, CF₂CH=); IR (neat): ν 2928, 2858, 1728, 1424, 1292, 1114, 1094, 965 cm⁻¹; HRMS (FAB) calcd for [M+H]⁺ C₉H₈F₄N: 206.0593, found 206.0586.

Typical procedure for the Amination of **4n**

To a solution of **4n** (0.90 g, 3.6 mmol) in EtOH (5.4 mL) and H₂O (1.8 mL) was added NH₄Cl (0.58 g, 11 mmol) and Fe (1.4 g, 25 mmol). The mixture was heated to reflux (bath temp. 85 °C) and stirred for 16 h. The reaction mixture was cooled to room temperature. Next, the mixture was filtered through silica gel with ethyl acetate, and then concentrated. The **4s** was purified by silica gel column chromatography (0.68 g, 3.1 mmol, 87%).

2-(1,1,2,2-Tetrafluorobut-3-en-1-yl)aniline (**4s**)

Yield: 87% (0.682 g, 3.11 mmol); Yellow oil (hexanes/AcOEt = 5/1, R_f = 0.50); ¹H NMR (CDCl₃): δ 4.17 (s, 2H, NH₂), 5.70 (d, J = 11.2 Hz, 1H, *trans*-CH₂=CHCF₂), 5.87 (dtd, J = 17.4, 2.1, 0.7 Hz, 1H, *cis*-CH₂=CHCF₂), 6.03 (dtd, J = 17.4, 11.3, 11.2 Hz, 1H, CHCF₂=), 6.69 (dd, J = 7.9, 0.6 Hz, 1H, ArH), 6.77 (tm, J = 7.9 Hz, 1H, ArH), 7.23–7.30 (m, 2H, ArH); ¹³C NMR (CDCl₃): δ 113.3 (t, J = 22.9 Hz, =CHCF₂), 116.3 (tt, J = 249.7, 37.9 Hz, CF₂), 117.57 (Ar), 117.64 (Ar), 118.3 (tt, J = 252.1, 35.9 Hz, CF₂), 124.2 (t, J = 9.3 Hz, CH₂=), 126.9 (t, J = 24.6 Hz, Ar), 129.2 (t, J = 8.4 Hz,

Ar), 132.2 (Ar), 145.7 (t, $J = 2.2$ Hz, Ar); ^{19}F NMR (CDCl_3): δ -110.60 (s, 2F, CF_2Ar), -115.03 (d, $J = 11.3$ Hz, 2F, $\text{CF}_2\text{CH=}$); IR (neat): ν 3522, 3421, 3236, 3042, 1925, 1582, 1495, 1467, 1420, 1322 cm^{-1} ; HRMS (FAB) calcd for $\text{C}_{10}\text{H}_9\text{F}_4\text{N}$ $[\text{M}]^+$: 219.0671, found 219.0668.

Typical procedure for the Sandmeyer reaction of **4s**

Under an argon atmosphere, to concentrated aqueous HCl (0.75 mL) was slowly added aniline derivative **4s** (0.11 g, 0.49 mmol) and distilled water (0.75 mL) at 0 °C and stirring for 30 min at the same temperature. Then, to this mixture was added a solution of NaNO_2 dissolved in H_2O (1.5 mL) at the 0 °C. After stirring for 10 min at the same temperature, to this mixture was added a solution of KI dissolved in H_2O (1.5 mL) at 0 °C. After gradually warming to room temperature, the mixture was quenched with saturated aqueous sodium thiosulfate and then whole was extracted with ethyl acetate three times. The combined organic layers were dried over anhydrous Na_2SO_4 , then filtered, and concentrated in *vacuo*. The residue was purified by silica gel column chromatography to give the corresponding iodide **4t** (0.11 g, 0.33 mmol) in 67% yield as a pale yellow oil.

3,3,4,4-Tetrafluoro-4-(2-iodophenyl)but-1-ene (**4t**)

Yield: 67% (0.11 g, 0.33 mmol); pale yellow oil (hexanes only, $R_f = 0.50$); ^1H NMR (CDCl_3): δ 5.73 (d, $J = 11.2$ Hz, 1H, *trans*- $\text{CH}_2=\text{CHCF}_2$), 5.87 (dt, $J = 17.3, 2.1$ Hz, 1H, *cis*- $\text{CH}_2=\text{CHCF}_2$), 6.07 (dtd, $J = 17.3, 11.7, 11.2$ Hz, 1H, $\text{CHCF}_2=$), 7.11–7.15 (m, 1H, ArH), 7.41–7.46 (m, 1H, ArH),

7.54 (d, $J = 7.9$ Hz, 1H, ArH), 8.06 (d, $J = 7.9$ Hz, 1H, ArH); ^{13}C NMR (CDCl_3): δ 91.4 (Ar), 115.49 (tt, $J = 250.4, 37.4$ Hz, CF_2), 115.54 (tt, $J = 254.9, 36.8$ Hz, CF_2), 124.6 (t, $J = 9.4$ Hz, $\text{CH}_2=$), 126.8 (t, $J = 24.5$ Hz, $=\text{CHCF}_2$), 127.7, 130.5 (t, $J = 8.4$ Hz), 132.2, 133.2 (t, $J = 23.5$ Hz), 142.9; ^{19}F NMR (CDCl_3): δ -107.37 (s, 2F, CF_2Ar), -112.46 (d, $J = 11.7$ Hz, 2F, $\text{CF}_2\text{CH=}$); IR (neat): ν 3086, 2928, 2850, 1934, 1818, 1716, 1650, 1589, 1567, 1467, 1420 cm^{-1} ; HRMS (FAB) calcd for $[\text{M}]^+ \text{C}_{10}\text{H}_7\text{F}_4\text{I}$: 329.9529, found 329.9520.

Typical procedure for the Sonogashira cross-coupling reaction of **4s** with phenylacetylene

To a solution of **4t** (0.15 g, 0.45 mmol) in Et_3N (0.66 mL) was added $\text{Cl}_2\text{Pd}(\text{PPh}_3)_2$ (0.016 g, 0.0225 mmol), CuI (0.043 g, 0.225 mmol) and ethynylbenzene (0.15 mL 1.35 mmol). The mixture was stirred overnight at the same temperature. Next, the mixture was filtered through silica gel with hexane, and then concentrated. The crude mixture was purified by silica gel column chromatography to afford the corresponding **4u** in a pure form (0.094 g, 0.31 mmol, 69%).

1-(2-Phenylethynyl)-2-(2,2,3,3-tetrafluorobut-3-en-1-yl)benzene (**4u**)

Yield: 69% (0.094 g, 0.31 mmol); Yellow oil (hexanes/ AcOEt = 20/1, $R_f = 0.41$); ^1H NMR (CDCl_3): δ 5.70 (d, $J = 11.3$ Hz, 1H, *trans*- $\text{CH}_2=\text{CHCF}_2$), 5.87 (dt, $J = 16.9, 1.6$ Hz, 1H, *cis*- $\text{CH}_2=\text{CHCF}_2$), 6.13 (ddt, $J = 16.9, 11.3, 11.2$ Hz, 1H, $\text{CHCF}_2=$), 7.37–7.68 (m, 9H, ArH); ^{13}C NMR (CDCl_3): δ 87.5 ($\text{C}\equiv$), 93.6 ($\text{C}\equiv$), 115.7 (tt, $J = 250.4, 36.8$ Hz, CF_2), 116.8 (tt, $J = 254.5, 35.7$ Hz, CF_2), 122.7

(t, $J = 3.5$ Hz, Ar), 123.4 (Ar), 124.1 (t, $J = 9.3$ Hz, $\text{CH}_2=\text{CH}-$), 127.1 (t, $J = 24.5$ Hz, $\text{CF}_2\text{CH}=\text{}$), 127.9 (Ar), 128.5 (Ar), 128.6 (Ar), 128.7 (Ar), 130.8 (Ar), 131.61 (Ar), 131.62 (t, $J = 22.8$ Hz, Ar), 134.3 (Ar); ^{19}F NMR (CDCl_3): δ -109.39 (s, 2F, CF_2Ar), -114.24 (d, $J = 11.2$ Hz, 2F, $\text{CF}_2\text{CH}=\text{}$); IR (neat): ν 3064, 2957, 2926, 2857, 2338, 2224, 1971, 1947, 1918, 1883, 1831, 1725, 1647, 1603, 1498, 1126 cm^{-1} ; HRMS (FAB) calcd for $[\text{M}]^+$ $\text{C}_{18}\text{H}_{12}\text{F}_4$: 304.0875, found 304.0866.

Typical procedure for Cu(I)-catalyzed cross-coupling reaction of organozinc reagent 2-Zn with benzoyl chloride (5a)

In a two-necked round-bottomed flask, equipped with a teflon-coated stirrer bar, were placed benzoyl chloride (**5a**, 0.17 mL, 1.5 mmol), Cu_2O (0.027 g, 0.18 mmol), 2,2'-bipyridyl (0.019 g, 0.12 mmol), and a DMF solution of **2-Zn** (0.61 M, 1.0 mL, 0.61 mmol), and the whole were stirred at room temperature for 20 h. The resultant was poured into water and the organic products were extracted with Et_2O three times. The combined organic layers were dried over anhydrous Na_2SO_4 , then filtered, and concentrated in vacuo. The residue was purified by silica gel column chromatography to give the corresponding **6a** (0.13 g, 0.56 mmol) in 92% yield as a colorless oil.

2,2,3,3-Tetrafluoro-1-phenylpent-4-en-1-one (6a)

Yield: 92% (0.13 g, 0.56 mmol); Colorless oil (hexanes/ AcOEt = 5/1, R_f = 0.70); ^1H NMR (CDCl_3): δ 5.76 (d, $J = 10.4$ Hz, 1H, *cis*- $\text{CH}_2=\text{CH}$), 5.93 (dt, $J = 17.6, 2.4$ Hz, 1H, *trans*- $\text{CH}_2=\text{CH}$), 6.06–6.19

(m, 1H, CH₂=CH), 7.50–7.54 (m, 2H, Ar-H), 7.67 (t, *J* = 7.6 Hz 1H, Ar-H), 8.09 (d, *J* = 6.5 Hz 2H, Ar-H); ¹³C NMR (CDCl₃): δ 112.3 (tt, *J* = 264.5, 36.3 Hz, CF₂), 115.0 (tt, *J* = 250.4, 31.4 Hz, CF₂), 125.1 (t, *J* = 12.0 Hz, CH₂=), 126.6 (t, *J* = 24.0 Hz, CH₂=CH), 129.1 (Ar), 130.6 (m, Ar), 132.6 (m, Ar), 135.2 (Ar), 186.4 (t, *J* = 26.4 Hz, C=O); ¹⁹F NMR (CDCl₃): δ -114.76 (s, 2F, CF₂-C=O), -113.90 (d, *J* = 12.0 Hz, 2F, =CH-CF₂); IR (neat): ν 3066, 2929, 1704, 1450, 1308, 1239, 1153, 1012, 965, 848 cm⁻¹; HRMS (FAB) calcd for C₁₁H₉F₄O [M+H]⁺: 233.0590, found 233.0595.

2,2,3,3-Tetrafluoro-1-(4-methylphenyl)pent-4-en-1-one (6b)

Yield: 97% (0.15 g, 0.59 mmol); Colorless oil (hexanes/AcOEt = 5/1, *R_f* = 0.70); ¹H NMR (CDCl₃): δ 2.42 (s, 3H, CH₃), 5.73 (d, *J* = 11.1 Hz, 1H, *cis*-CH₂=CH), 5.92 (dt, *J* = 17.1, 2.2 Hz, 1H, *trans*-CH₂=CH), 6.11 (ddt, *J* = 17.1, 11.6, 11.1 Hz, 1H, CH₂=CH), 7.29 (d, *J* = 8.1 Hz, 2H, Ar-H), 8.00 (d, *J* = 8.1 Hz, 2H, Ar-H); ¹³C NMR (CDCl₃): δ 21.8 (CH₃), 112.2 (tt, *J* = 265.3, 35.5 Hz, CF₂), 114.8 (tt, *J* = 250.4, 31.0 Hz, CF₂), 124.7 (t, *J* = 9.5 Hz, CH₂=), 126.5 (t, *J* = 23.6 Hz, CH₂=CH), 129.6 (Ar), 129.9 (Ar), 130.5 (t, *J* = 3.3 Hz, Ar), 146.6 (Ar), 185.6 (t, *J* = 26.9 Hz, C=O); ¹⁹F NMR (CDCl₃): δ -114.71 (s, 2F, CF₂-C=O), -113.96 (d, *J* = 11.6 Hz, 2F, =CH-CF₂); IR (neat): ν 2925, 1699, 1420, 1308, 1232, 1153, 1112, 1012, 856 cm⁻¹; HRMS (FAB) calcd for C₁₂H₁₁F₄O [M+H]⁺: 247.0746, found 247.0741.

2,2,3,3-Tetrafluoro-1-(2-methylphenyl)pent-4-en-1-one (6c)

Yield: 83% (0.13 g, 0.53 mmol); Pale yellow oil (hexanes/AcOEt = 20/1, R_f = 0.60); ^1H NMR (CDCl_3): δ 2.46 (s, 3H, CH_3), 5.75 (d, J = 11.3 Hz, 1H, *cis*- $\text{CH}_2=\text{CH}$), 5.91 (dt, J = 17.4, 2.2 Hz, 1H, *trans*- $\text{CH}_2=\text{CH}$), 6.12 (ddtm, J = 17.4, 11.6, 11.3 Hz, 1H, $\text{CH}_2=\text{CH}$), 7.29–7.33 (m, 2H, Ar-*H*), 7.45–7.49 (m, 1H, Ar-*H*), 7.79–7.81 (m, 1H, Ar-*H*); ^{13}C NMR (CDCl_3): δ 20.8 (CH_3), 115.1 (tt, J = 266.6, 35.8 Hz, CF_2), 114.9 (tt, J = 250.5, 31.5 Hz, CF_2), 124.6 (t, J = 9.6 Hz, $\text{CH}_2=$), 125.5 (Ar), 126.4 (t, J = 23.9 Hz, $\text{CH}_2=\text{CH}$), 129.3 (t, J = 5.6 Hz, Ar), 132.0 (Ar), 132.8 (m, 2C, Ar), 140.0 (Ar), 189.6 (t, J = 26.8 Hz, $\text{C}=\text{O}$); ^{19}F NMR (CDCl_3): δ -113.76 (m, 2F, $\text{CF}_2\text{-C}=\text{O}$), -115.08 (s, 2F, $=\text{CH-CF}_2$); IR (neat): ν 3030, 2966, 1715, 1420, 1292, 1247, 1156, 1111, 1013, 860 cm^{-1} ; HRMS (FAB) calcd for $\text{C}_{12}\text{H}_{10}\text{F}_4\text{O}$ $[\text{M}]^+$: 246.0663, found 246.0668.

1-(4-*tert*-Butylphenyl)-2,2,3,3-tetrafluoropent-4-en-1-one (6d)

Yield: 98% (0.17 g, 0.59 mmol); Pale yellow oil (hexanes/AcOEt = 20/1, R_f = 0.60); ^1H NMR (CDCl_3): δ 1.35 (s, 9H, CH_3), 5.74 (d, J = 11.3 Hz, 1H, *cis*- $\text{CH}_2=\text{CH}$), 5.92 (dt, J = 17.4, 2.2 Hz, 1H, *trans*- $\text{CH}_2=\text{CH}$), 6.12 (ddt, J = 17.4, 11.4, 11.3 Hz, 1H, $\text{CH}_2=\text{CH}$), 7.53 (dt, J = 8.7, 2.1 Hz, 2H, Ar-*H*), 8.05 (d, J = 8.7 Hz, 2H, Ar-*H*); ^{13}C NMR (CDCl_3): δ 31.1 (CH_3), 35.5 ($\text{C}(\text{CH}_3)_3$), 112.2 (tt, J = 265.2, 35.7 Hz, CF_2), 114.8 (tt, J = 250.5, 31.1 Hz, CF_2), 124.8 (t, J = 9.5 Hz, $\text{CH}_2=$), 125.9 (Ar), 126.5 (t, J = 23.9 Hz, $\text{CH}_2=\text{CH}$), 129.8 (Ar), 130.5 (t, J = 3.4 Hz, Ar), 159.2 (Ar), 185.7 (t, J =

26.8 Hz, C=O); ^{19}F NMR (CDCl_3): δ -113.98 (dd, J = 11.4, 2.2 Hz, 2F, $\text{CF}_2\text{-C=O}$), -114.76 (s, 2F, =CH-CF_2); IR (neat): ν 2970, 1700, 1600, 1415, 1304, 1114, 888 cm^{-1} ; HRMS (FAB) calcd for $\text{C}_{15}\text{H}_{17}\text{F}_4\text{O}$ $[\text{M}+\text{H}]^+$: 289.1216, found 289.1208.

1-(4-Bromophenyl)-2,2,3,3-tetrafluoropent-4-en-1-one (6e)

Yield: 50% (0.095 g, 0.31 mmol); Colorless oil (hexanes/AcOEt = 20/1, R_f = 0.50); ^1H NMR (CDCl_3): δ 5.77 (d, J = 11.2 Hz, 1H, *cis*- $\text{CH}_2\text{=CH}$), 5.93 (dt, J = 17.3, 2.1 Hz, 1H, *trans*- $\text{CH}_2\text{=CH}$), 6.10 (ddt, J = 17.3, 11.4, 11.2 Hz, 1H, $\text{CH}_2\text{=CH}$), 7.64–7.70 (m, 2H, Ar-*H*), 7.95 (d, J = 8.6 Hz, 2H, Ar-*H*); ^{13}C NMR (CDCl_3): δ 111.9 (tt, J = 265.1, 36.3 Hz, CF_2), 114.6 (tt, J = 250.5, 31.2 Hz, CF_2), 125.0 (t, J = 9.5 Hz, $\text{CH}_2\text{=}$), 126.0 (t, J = 23.9 Hz, $\text{CH}_2\text{=CH}$), 130.7 (Ar), 131.0 (Ar), 131.7 (t, J = 3.5 Hz, Ar), 132.2 (Ar), 185.1 (t, J = 27.3 Hz, C=O); ^{19}F NMR (CDCl_3): δ -114.89 (s, 2F, $\text{CF}_2\text{-C=O}$), -113.80 (dd, J = 11.4, 2.1 Hz, 2F, =CH-CF_2); IR (neat): ν 3125, 1701, 1584, 1420, 1284, 1112, 1012, 883 cm^{-1} ; HRMS (FAB) calcd for $\text{C}_{11}\text{H}_8\text{BrF}_4\text{O}$ $[\text{M}+\text{H}]^+$: 310.9695, found 310.9689.

2,2,3,3-Tetrafluoro-1-(4-trifluoromethylphenyl)pent-4-en-1-one (6f)

Yield: 86% (0.15 g, 0.50 mmol), Pale yellow oil (hexanes/AcOEt = 20/1, R_f = 0.40); ^1H NMR (CDCl_3): δ 5.79 (d, J = 11.1 Hz, 1H, *cis*- $\text{CH}_2\text{=CH}$), 5.95 (dt, J = 17.3, 2.2 Hz, 1H, *trans*- $\text{CH}_2\text{=CH}$), 6.11 (ddt, J = 17.3, 11.9, 11.1 Hz, 1H, $\text{CH}_2\text{=CH}$), 7.78 (d, J = 8.2 Hz, 2H, Ar-*H*), 8.20 (d, J = 8.2

Hz, 2H, Ar-*H*); ^{13}C NMR (CDCl_3): δ 111.9 (tt, J = 265.2, 36.4 Hz, CF_2), 114.8 (tt, J = 250.6, 31.2 Hz, CF_2), 123.4 (q, J = 272.9 Hz, CF_3), 125.5 (t, J = 9.7 Hz, $\text{CH}_2=$), 126.95 (t, J = 23.2 Hz, $\text{CH}_2=\text{CH}$), 125.96 (q, J = 3.6 Hz, Ar), 130.8 (t, J = 3.7 Hz, Ar), 135.1 (Ar), 136.1 (q, J = 27.6 Hz, Ar), 185.6 (t, J = 27.56 Hz, $\text{C}=\text{O}$); ^{19}F NMR (CDCl_3): δ -115.05 (s, 2F, $\text{CF}_2\text{-C}=\text{O}$), -113.63 (dd, J = 11.9, 2.2 Hz, 2F, $=\text{CH-CF}_2$), -64.01 (s, 3F, CF_3); IR (neat): ν 3125, 3075, 1714, 1414, 1330, 1234, 1136, 1069, 965, 852 cm^{-1} ; HRMS (FAB) calcd for $\text{C}_{12}\text{H}_7\text{F}_7\text{O}$ $[\text{M}]^+$: 300.0385, found 300.0393.

2,2,3,3-Tetrafluoro-1-(furan-2-yl)pent-4-en-1-one (6h)

Yield: 83% (0.11 g, 0.50 mmol); Pale yellow oil (hexanes/AcOEt = 5/1, R_f = 0.40); ^1H NMR (CDCl_3): δ 5.69 (d, J = 11.0 Hz, 1H, *cis*- $\text{CH}_2=\text{CH}$), 5.83 (dt, J = 17.0, 2.2 Hz, 1H, *trans*- $\text{CH}_2=\text{CH}$), 5.97 (ddt, J = 17.0, 11.8, 11.0 Hz, 1H, $\text{CH}_2=\text{CH}$), 6.59 (dd, J = 3.8, 1.7 Hz, 1H, Ar-*H*), 7.43–7.45 (m, 1H, Ar-*H*), 7.74 (dd, J = 1.7, 0.6 Hz, 1H, Ar-*H*); ^{13}C NMR (CDCl_3): δ 111.4 (tt, J = 263.3, 36.7 Hz, CF_2), 113.2 (Ar), 114.5 (tt, J = 250.5, 32.0 Hz, CF_2), 124.7 (t, J = 5.8 Hz, Ar), 125.1 (t, J = 9.5 Hz, $\text{CH}_2=$), 125.6 (t, J = 23.8 Hz, $\text{CH}_2=\text{CH}$), 148.6 (Ar), 149.6 (Ar), 173.3 (t, J = 28.0 Hz, $\text{C}=\text{O}$); ^{19}F NMR (CDCl_3): δ -118.56 (s, 2F, $\text{CF}_2\text{-C}=\text{O}$), -114.19 (d, J = 11.8 Hz, 2F, $=\text{CH-CF}_2$); IR (neat): ν 3150, 1692, 1560, 1461, 1397, 1186, 1041, 931, 844 cm^{-1} ; HRMS (FAB) calcd for $\text{C}_9\text{H}_7\text{F}_4\text{O}_2$ $[\text{M}+\text{H}]^+$: 223.0382, found 223.0392.

2,2,3,3-Tetrafluoro-1-(thiophen-2-yl)pent-4-en-1-one (6i)

Yield: 87% (0.13 g, 0.55 mmol); Colorless oil (hexanes/AcOEt = 20/1, R_f = 0.34); ^1H NMR (CDCl_3): δ 5.76 (d, J = 11.1 Hz, 1H, *cis*- $\text{CH}_2=\text{CH}$), 5.92 (dt, J = 17.3, 2.1 Hz, 1H, *trans*- $\text{CH}_2=\text{CH}$), 6.08 (ddt, J = 17.3, 11.4, 11.1 Hz, 1H, $\text{CH}_2=\text{CH}$), 7.21–7.23 (m, 1H, Ar-*H*), 7.85 (dd, J = 4.9, 1.0 Hz, 1H, Ar-*H*), 8.00–8.01 (m, 1H, Ar-*H*); ^{13}C NMR (CDCl_3): δ 114.7 (tt, J = 263.3, 36.4 Hz, CF_2), 114.6 (tt, J = 250.8, 30.8 Hz, CF_2), 125.1 (t, J = 9.5 Hz, $\text{CH}_2=$), 125.9 (t, J = 23.9 Hz, $\text{CH}_2=\text{CH}$), 129.1 (Ar), 136.8 (t, J = 5.5 Hz, Ar), 137.6 (Ar), 138.8 (Ar), 178.8 (t, J = 27.8 Hz, $\text{C}=\text{O}$); ^{19}F NMR (CDCl_3): δ –114.03 to –113.99 (m, 2F, $\text{CF}_2\text{-C}=\text{O}$), –116.59 (s, 2F, $=\text{CH-CF}_2$); IR (neat): ν 3104, 1676, 1411, 1359, 1238, 1165, 1115, 1065, 820 cm^{-1} ; HRMS (FAB) calcd for $\text{C}_9\text{H}_7\text{F}_4\text{OS}$ $[\text{M}+\text{H}]^+$: 239.0153, found 239.0154.

4,4,5,5-Tetrafluoro-1-phenylhept-1,6-diene-3-one (6j)

Yield: 70% (0.11 g, 0.43 mmol); Pale yellow oil (hexanes/AcOEt = 40/1, R_f = 0.37); ^1H NMR (CDCl_3): δ 5.76 (d, J = 10.4 Hz, 1H, *cis*- $\text{CH}_2=\text{CH}$), 5.89–5.95 (m, 1H, *trans*- $\text{CH}_2=\text{CH}$), 6.05 (ddtm, J = 15.5, 13.1, 10.4 Hz, 1H, $\text{CH}_2=\text{CH}$), 7.15 (d, J = 15.6 Hz, 1H), 7.42–7.50 (m, 3H, Ar-*H*), 7.63–7.66 (m, 2H, Ar-*H*), 7.92 (d, J = 15.9 Hz, 1H); ^{13}C NMR (CDCl_3): δ = 111.1 (tt, J = 262.9, 36.8 Hz, CF_2), 114.9 (tt, J = 249.7, 32.2 Hz, CF_2), 118.4, 125.1 (t, J = 9.5 Hz, $\text{CH}_2=$), 125.9 (t, J = 24.0 Hz, $\text{CH}_2=\text{CH}$), 129.28, 129.34, 132.1, 133.8, 148.5, 185.1 (t, J = 26.5 Hz, $\text{C}=\text{O}$); ^{19}F NMR (CDCl_3): δ –

114.48 (d, $J = 13.1$ Hz, 2F, $\text{CF}_2\text{-C=O}$), -122.74 (s, 2F, $=\text{CH-CF}_2$); IR (neat): ν 3068, 2926, 1707, 1608, 1577, 1420, 1147, 1066, 980 cm^{-1} ; HRMS (FAB) calcd for $\text{C}_{13}\text{H}_{11}\text{F}_4\text{O}$ $[\text{M}+\text{H}]^+$: 259.0744, found 259.0746.

3,3,4,4-Tetrafluorododec-1-en-5-one (6k)

Yield: 84% (0.13 g, 0.84 mmol); Colorless oil (hexanes/AcOEt = 20/1, $R_f = 0.57$); ^1H NMR (CDCl_3): δ 0.85 (brs, 3H, CH_3), 1.27 (brs, 8H, $-(\text{CH}_2)_4-$), 1.61 (brs, 2H, COCH_2CH_2), 2.70 (t, $J = 6.7$ Hz, 2H, COCH_2CH_2), 5.69 (d, $J = 10.5$ Hz, 1H, *cis*- $\text{CH}_2=\text{CH}$), 5.84 (d, $J = 17.3$ Hz, 1H, *trans*- $\text{CH}_2=\text{CH}$), 5.96 (dtd, $J = 17.3, 11.4, 10.5$ Hz, 1H, $\text{CH}_2=\text{CH}$); ^{13}C NMR (CDCl_3): δ 14.0 (CH_3), 22.6 (CH_2), 22.7 (CH_2), 28.9 (CH_2), 29.1 (CH_2), 31.8 (CH_2), 38.3 (CH_2), 110.5 (tt, $J = 263.6, 37.3$ Hz, CF_2), 114.9 (tt, $J = 249.4, 32.4$ Hz, CF_2), 124.8 (t, $J = 9.6$ Hz, $\text{CH}_2=\text{CH}$), 125.9 (t, $J = 23.9$ Hz, $=\text{CH-CF}_2$), 197.2 (t, $J = 26.7$ Hz, C=O); ^{19}F NMR (CDCl_3): δ -122.10 (s, 2F, $\text{CF}_2\text{-C=O}$), -114.52 (d, $J = 11.4$ Hz, 2F, $=\text{CH-CF}_2$); IR (neat): ν 2931, 2859, 1751, 1420, 1153, 1117, 1012, 962 cm^{-1} ; HRMS (FAB) calcd for $\text{C}_{12}\text{H}_{19}\text{F}_4\text{O}$ $[\text{M}+\text{H}]^+$: 255.1372, found 255.1364.

Typical procedure for improved Cu(I)-catalyzed cross-coupling reaction of organozinc reagent 2-Zn with 4-nitrobenzoyl chloride (5g)

In a two-necked round-bottomed flask, equipped with a teflon-coated stirrer bar, were placed 4-nitrobenzoyl chloride (**5g**, 0.50 g 2.7 mmol), Cu_2O (0.030 g, 0.21 mmol), 2,2'-bipyridyl (0.020 g,

0.13 mmol), and a DMF solution of **2-Zn** (0.66 M, 1.0 mL, 0.66 mmol), and the whole were stirred at 100 °C for 20 h. The resultant was poured into water and the organic products were extracted with Et₂O three times. The combined organic layers were dried over anhydrous Na₂SO₄, then filtered, and concentrated in *vacuo*. The residue was purified by silica gel column chromatography to give the corresponding **6g** (0.14 g, 0.51 mmol) in 77% yield as a pale yellow oil.

2,2,3,3-Tetrafluoro-1-(4-nitrophenyl)pent-4-en-1-one (6g)

Yield: 77% (0.14 g, 0.51 mmol); Pale yellow oil (hexanes/AcOEt = 5/1, *R_f* = 0.50); ¹H NMR (CDCl₃): δ 5.78 (d, *J* = 11.0 Hz, 1H, *cis*-CH₂=CH), 5.91 (dt, *J* = 17.31, 1.68 Hz, 1H, *trans*-CH₂=CH), 6.07 (dtd, *J* = 17.3, 11.9, 11.0 Hz, 1H, CH₂=CH), 8.21 (d, *J* = 8.4 Hz, 2H, Ar-*H*), 8.30–8.33 (m, 2H, Ar-*H*); ¹³C NMR (CDCl₃): δ 111.7 (tt, *J* = 264.9, 37.4 Hz, CF₂), 114.7 (tt, *J* = 250.6, 31.4 Hz, CF₂), 123.9 (Ar), 125.6 (t, *J* = 23.9 Hz, CH₂=CH), 125.6 (t, *J* = 9.4 Hz, CH₂=), 131.4 (t, *J* = 3.4 Hz, Ar), 136.7 (Ar), 151.2 (Ar), 185.1 (t, *J* = 28.0 Hz, C=O); ¹⁹F NMR (CDCl₃): δ –115.04 (s, 2F, CF₂-C=O), –113.37 (d, *J* = 11.9 Hz, 2F, =CH-CF₂); IR (neat): ν 3057, 1715, 1604, 1531, 1351, 1156, 1014, 834 cm⁻¹; HRMS (FAB) calcd for C₁₁H₈F₄NO₃ [M+H]⁺: 278.0440, found 278.0435.

2. Additional scheme and Figure

Scheme S1:

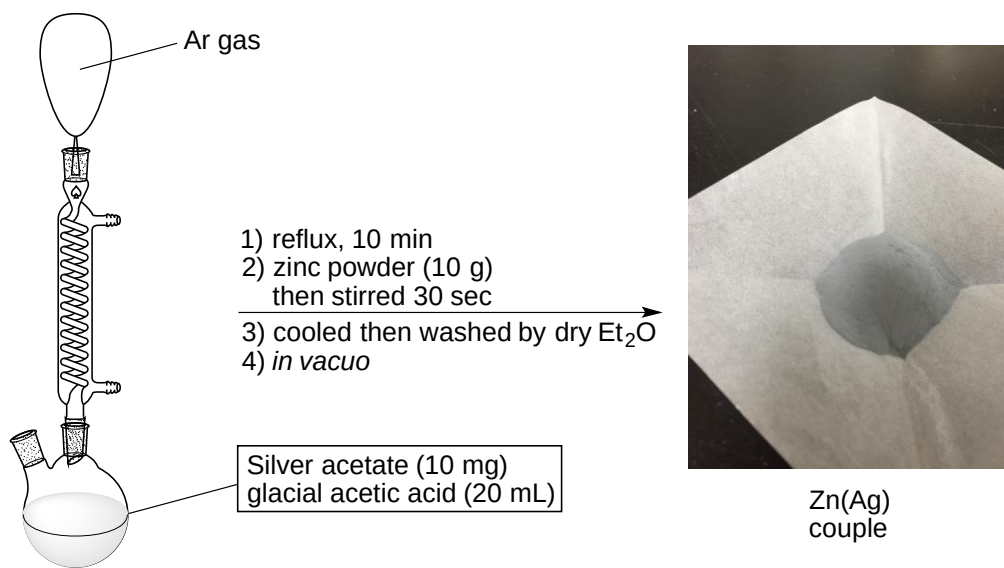
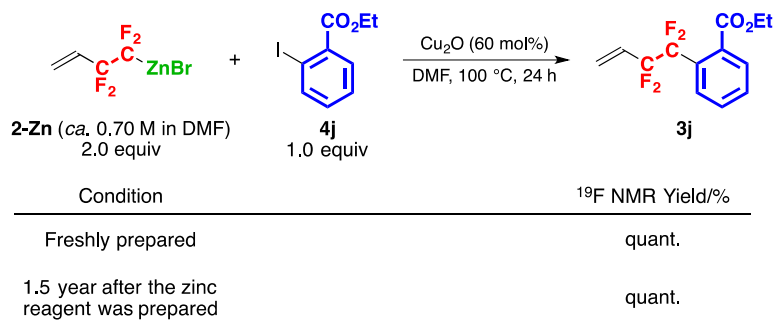


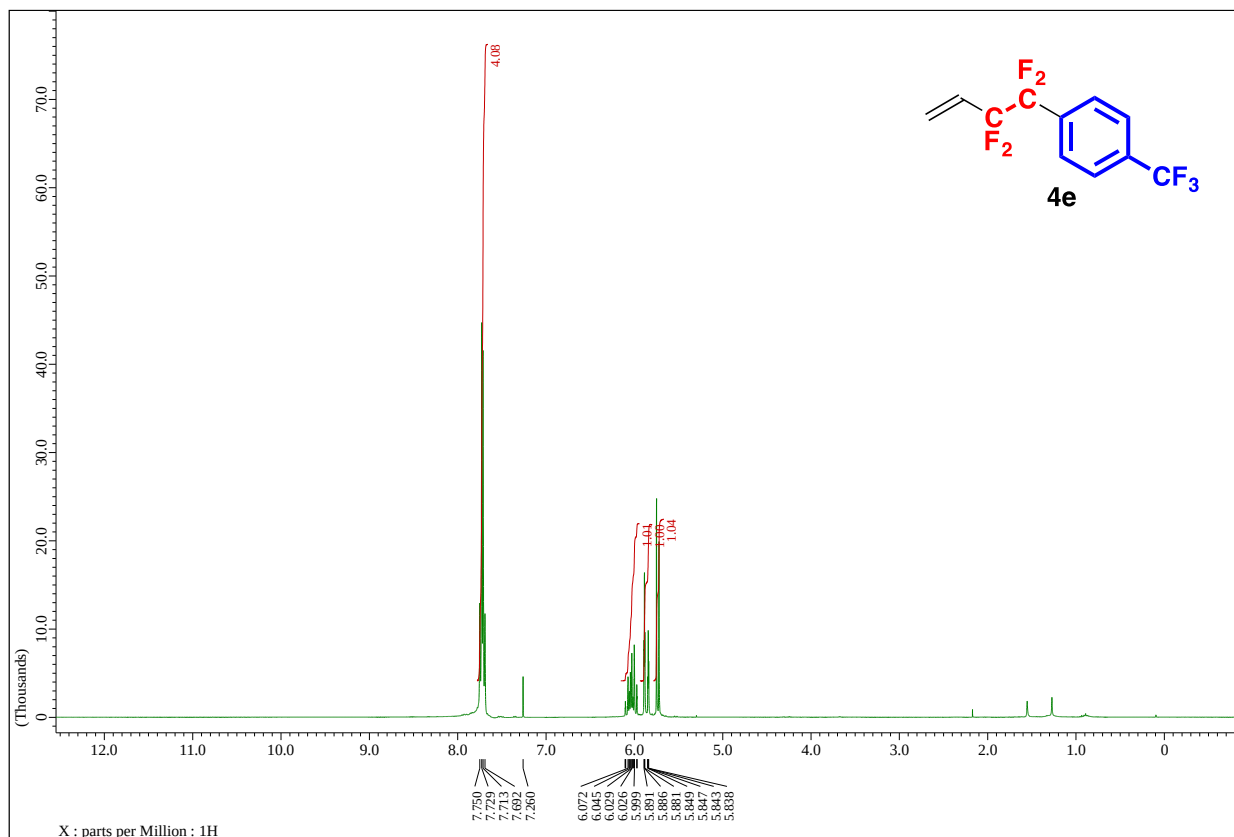
Figure S1: Preparation of Zn-Ag couple

Reference

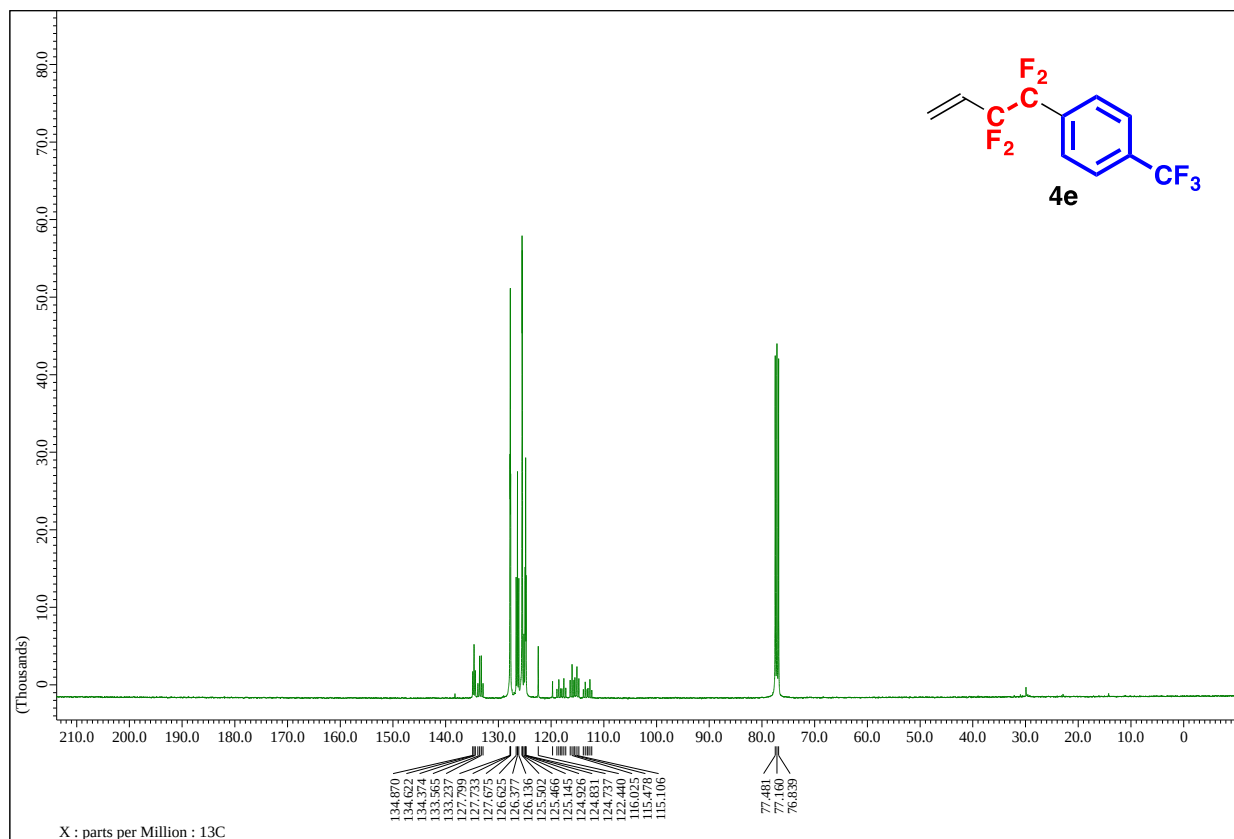
S1 Watanabe, Y.; Konno, T. *J. Fluorine Chem.* **2015**, 174, 102–107. doi:10.1016/j.jfluchem.2014.12.008

3. Copies of ^1H , ^{13}C , and ^{19}F NMR spectra for new compounds

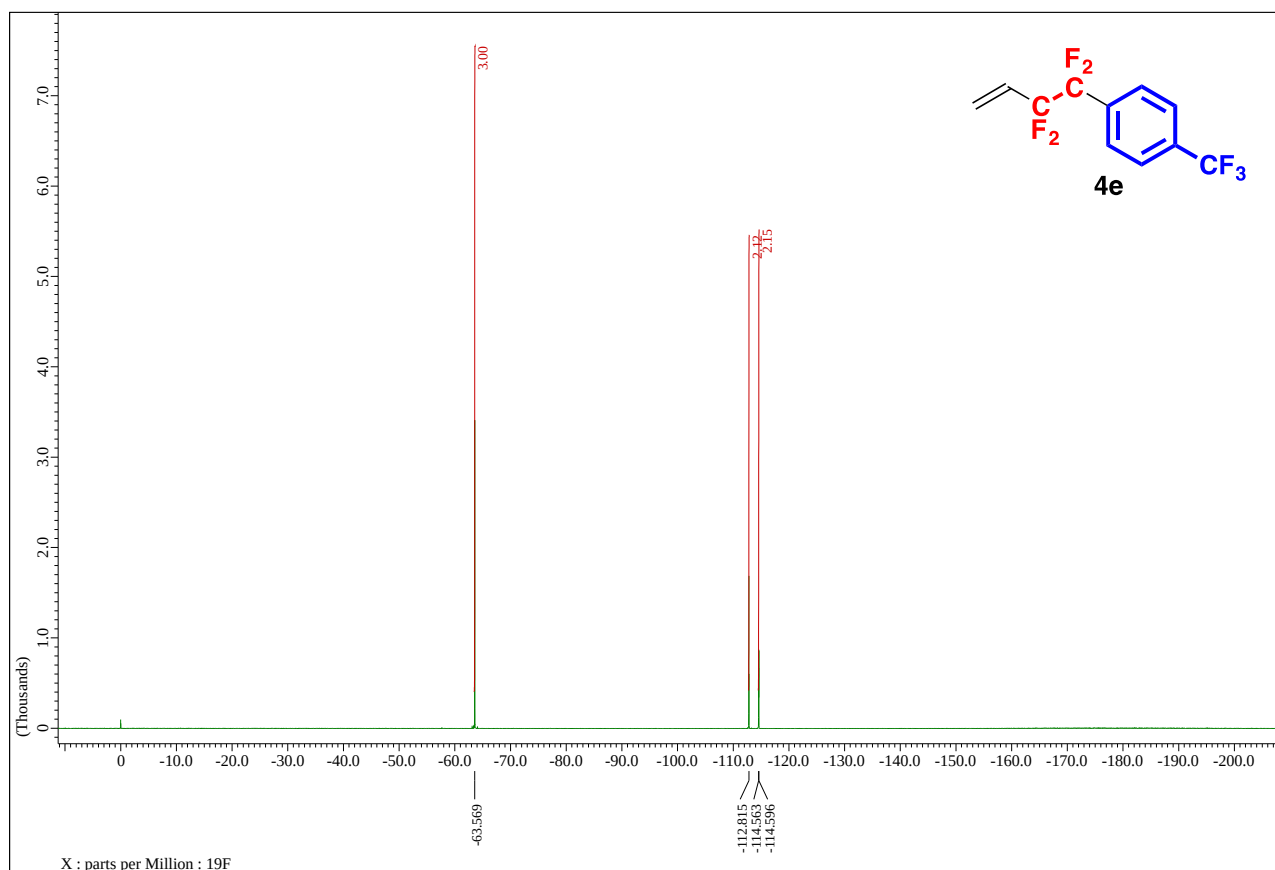
^1H NMR Spectrum of 3,3,4,4-tetrafluoro-4-(4-trifluoromethylphenyl)but-1-ene (**4e**)



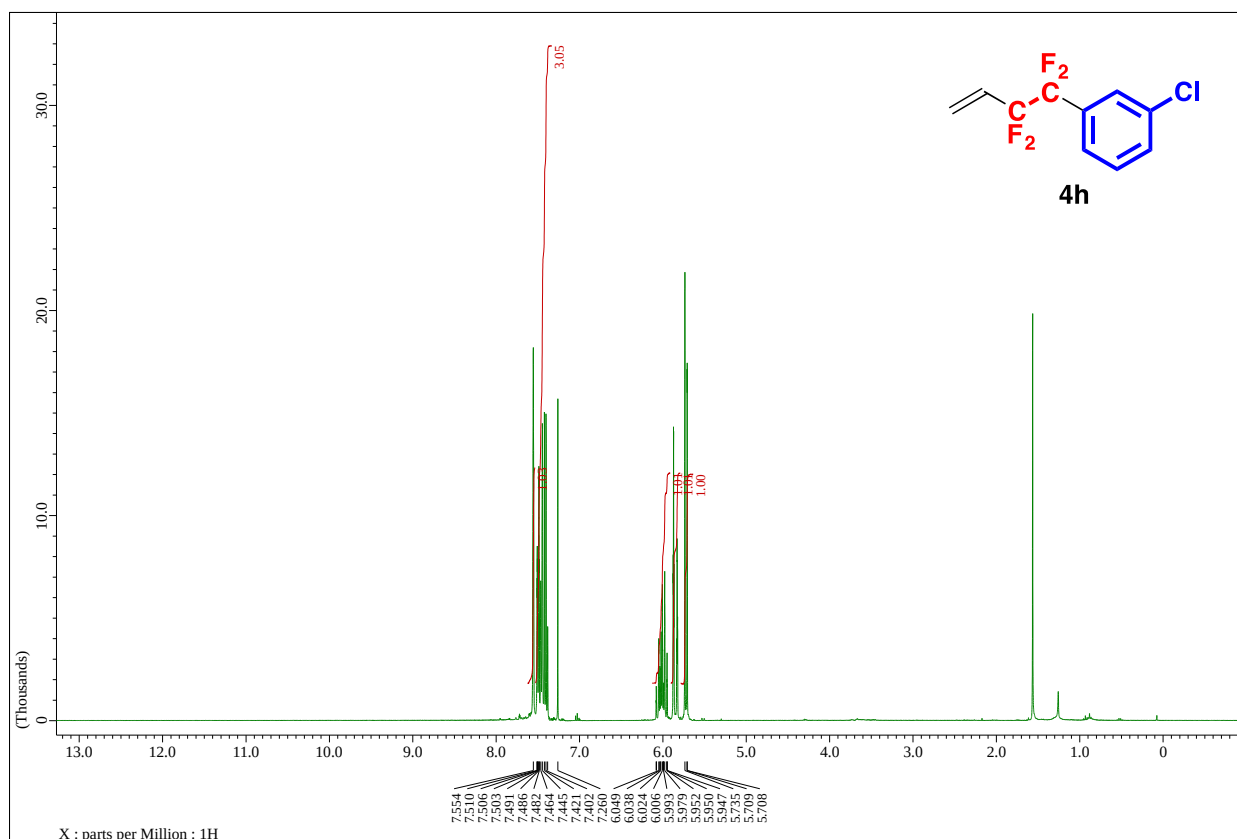
^{13}C NMR Spectrum of 3,3,4,4-tetrafluoro-4-(4-trifluoromethylphenyl)but-1-ene (**4e**)



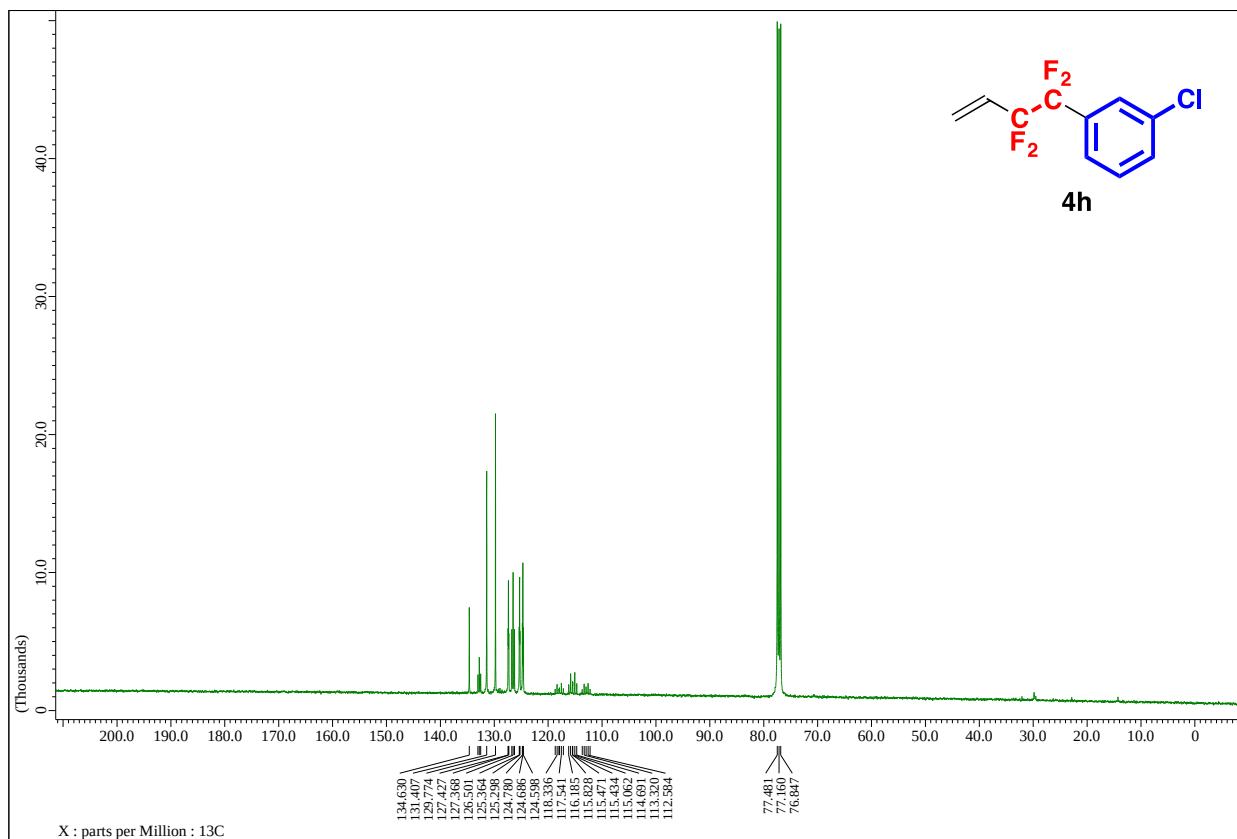
^{19}F NMR Spectrum of 3,3,4,4-tetrafluoro-4-(4-trifluoromethylphenyl)but-1-ene (**4e**)



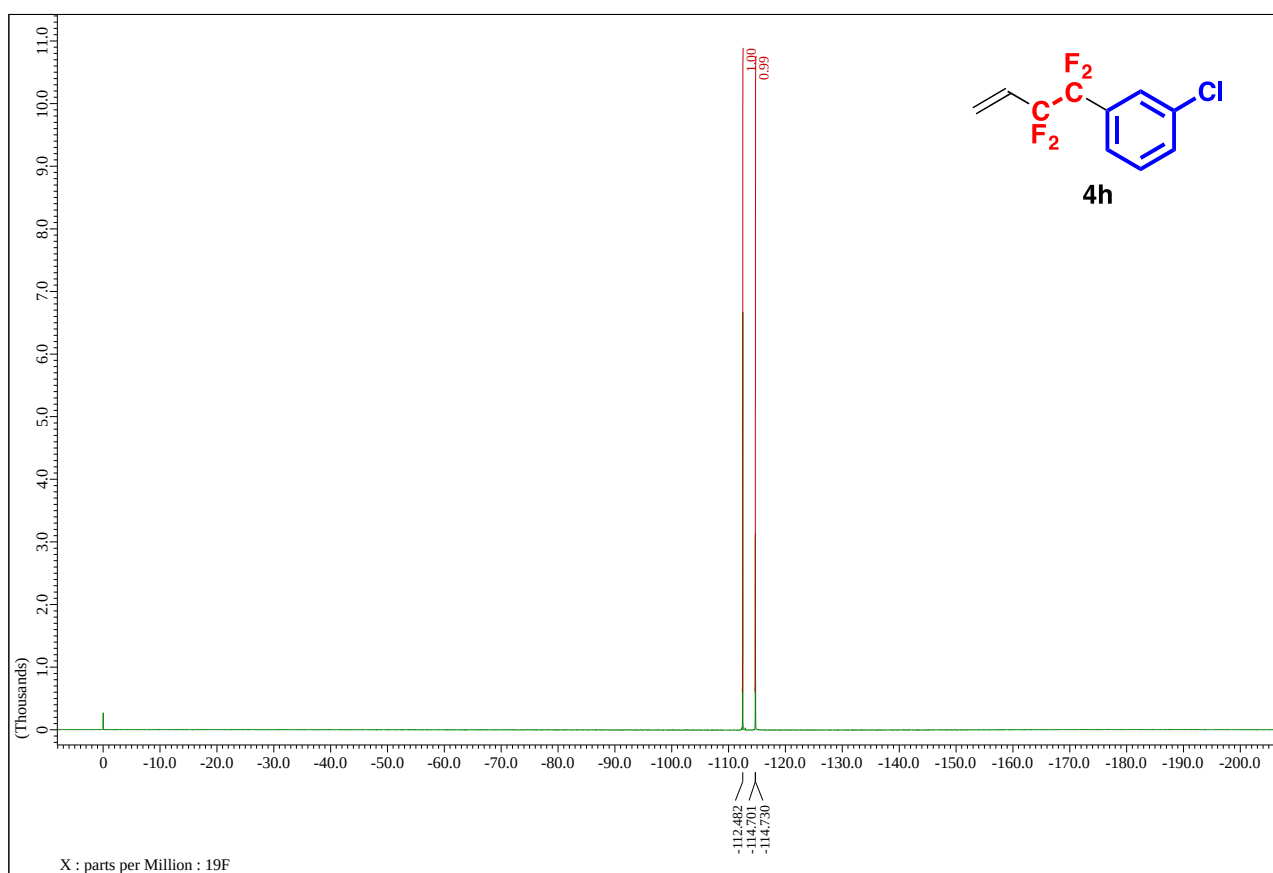
^1H NMR Spectrum of 4-(3-chlorophenyl)-3,3,4,4-tetrafluorobut-1-ene (**4h**)



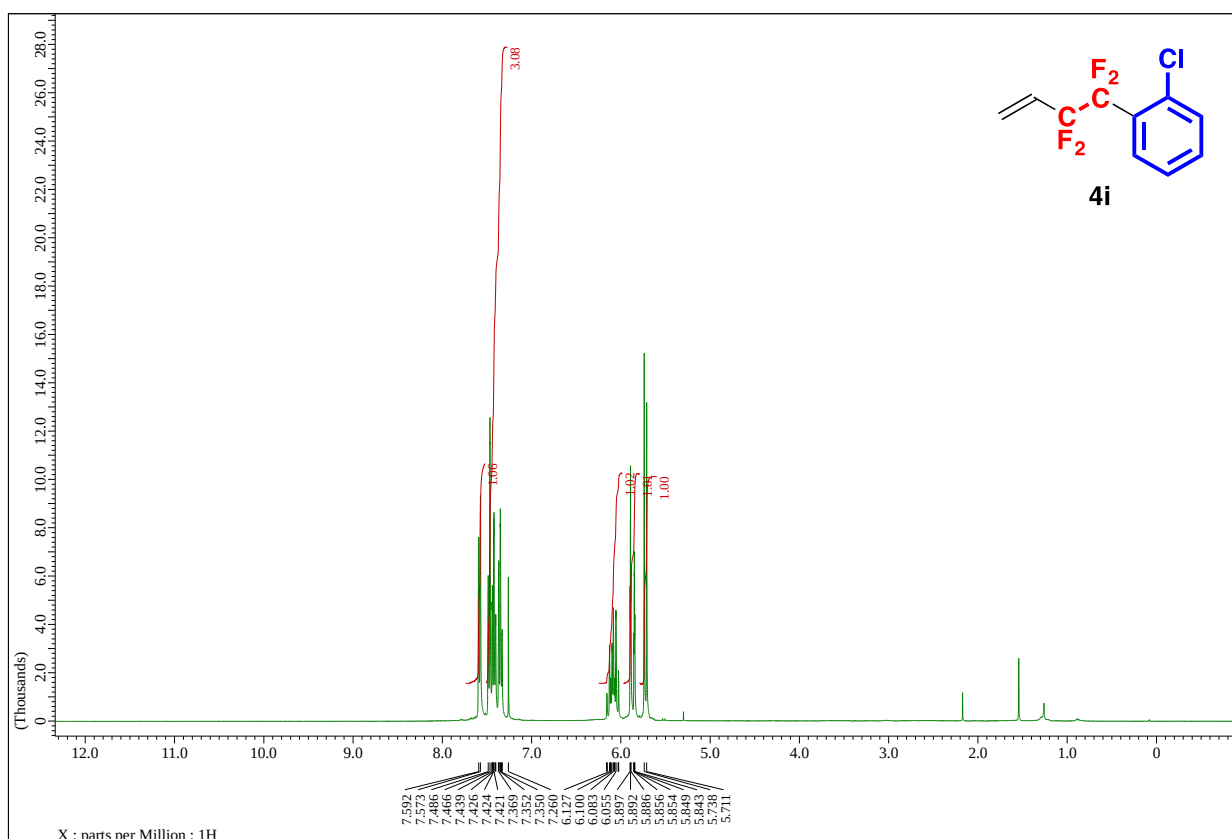
^{13}C NMR Spectrum of 4-(3-chlorophenyl)-3,3,4,4-tetrafluorobut-1-ene (**4h**)



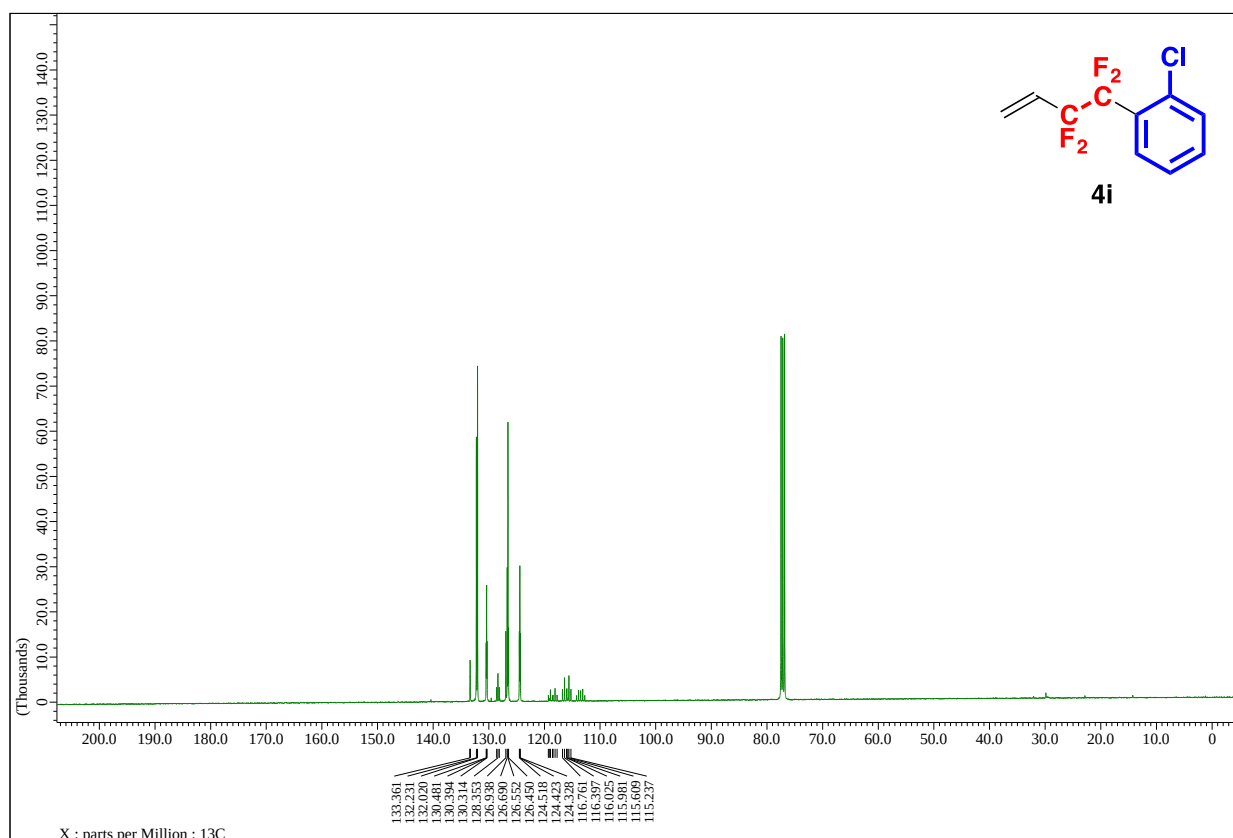
^{19}F NMR Spectrum of 4-(3-chlorophenyl)-3,3,4,4-tetrafluorobut-1-ene (**4h**)



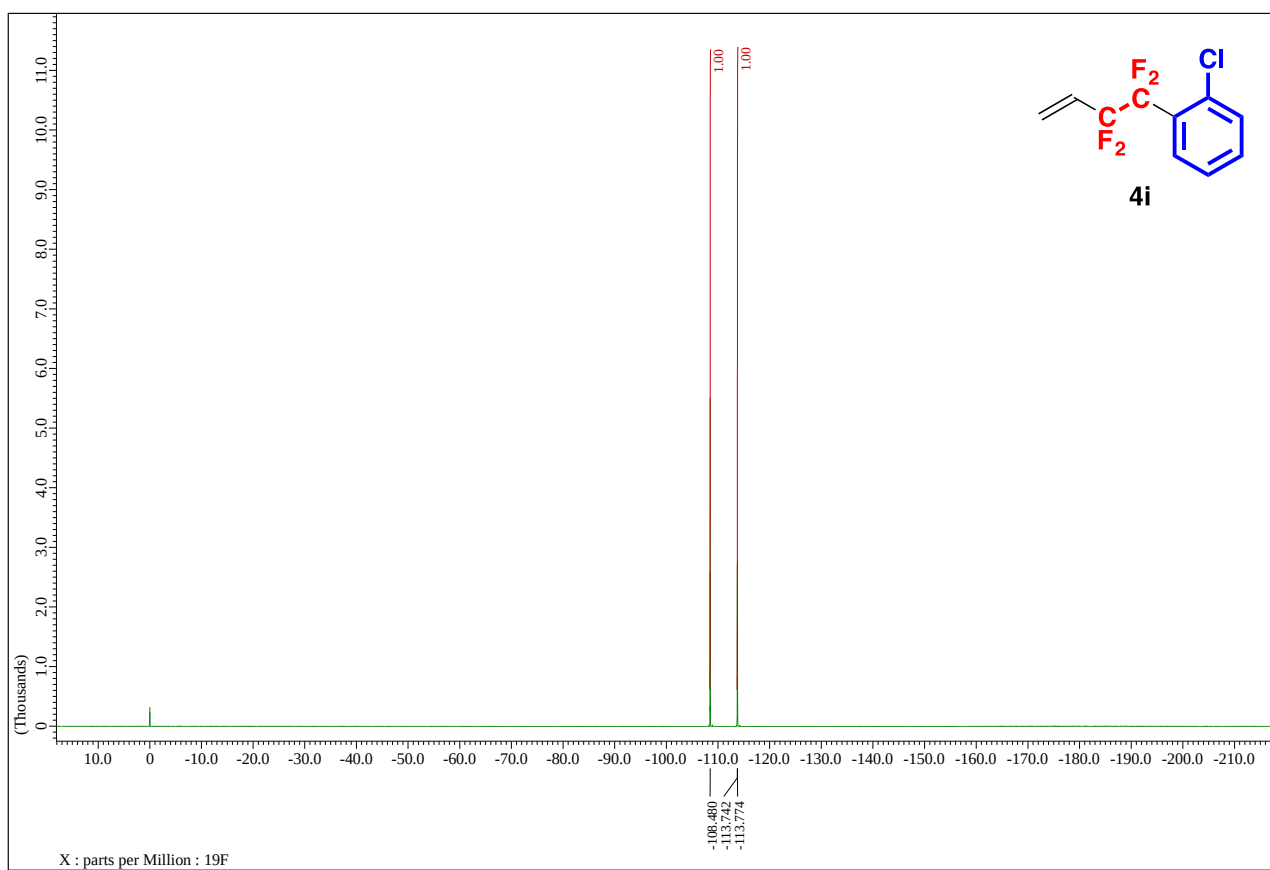
¹H NMR Spectrum of 4-(2-chlorophenyl)-3,3,4,4-tetrafluorobut-1-ene (**4i**)



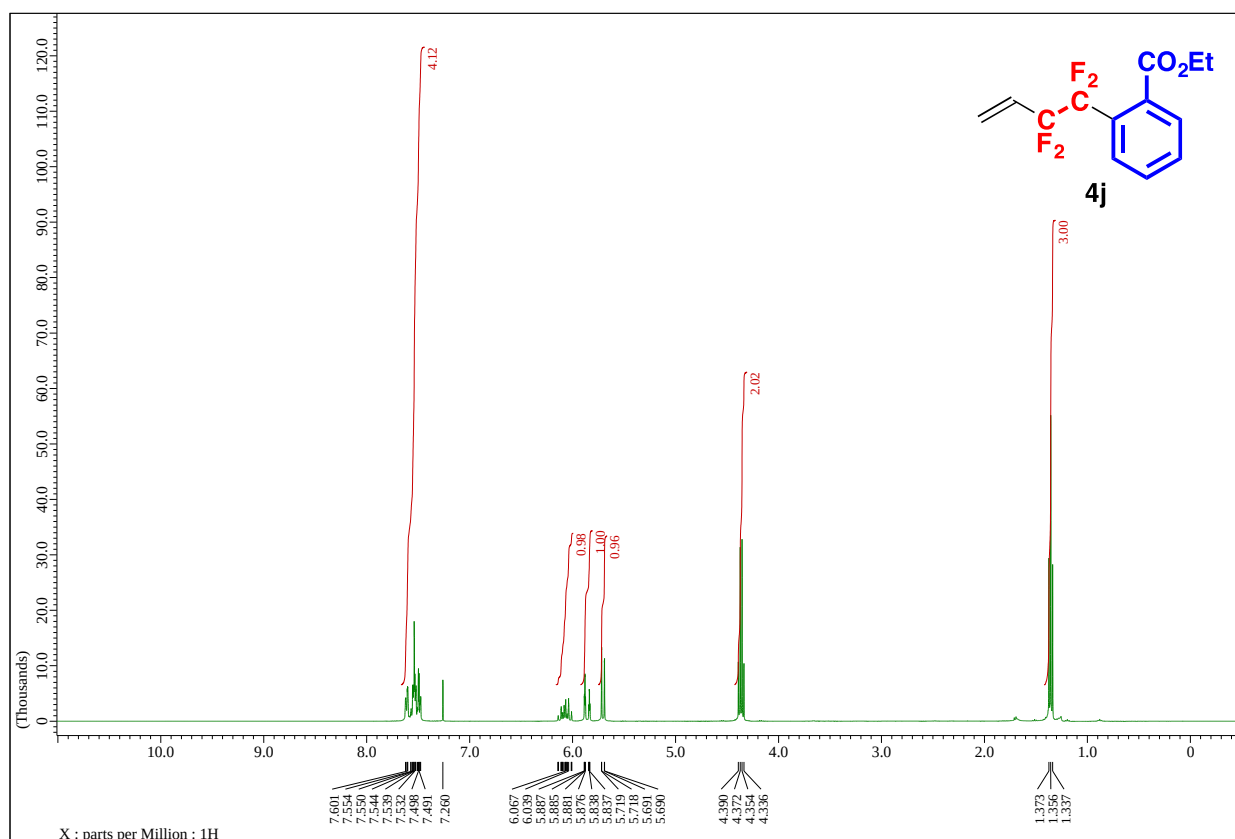
¹³C NMR Spectrum of 4-(2-chlorophenyl)-3,3,4,4-tetrafluorobut-1-ene (**4i**)



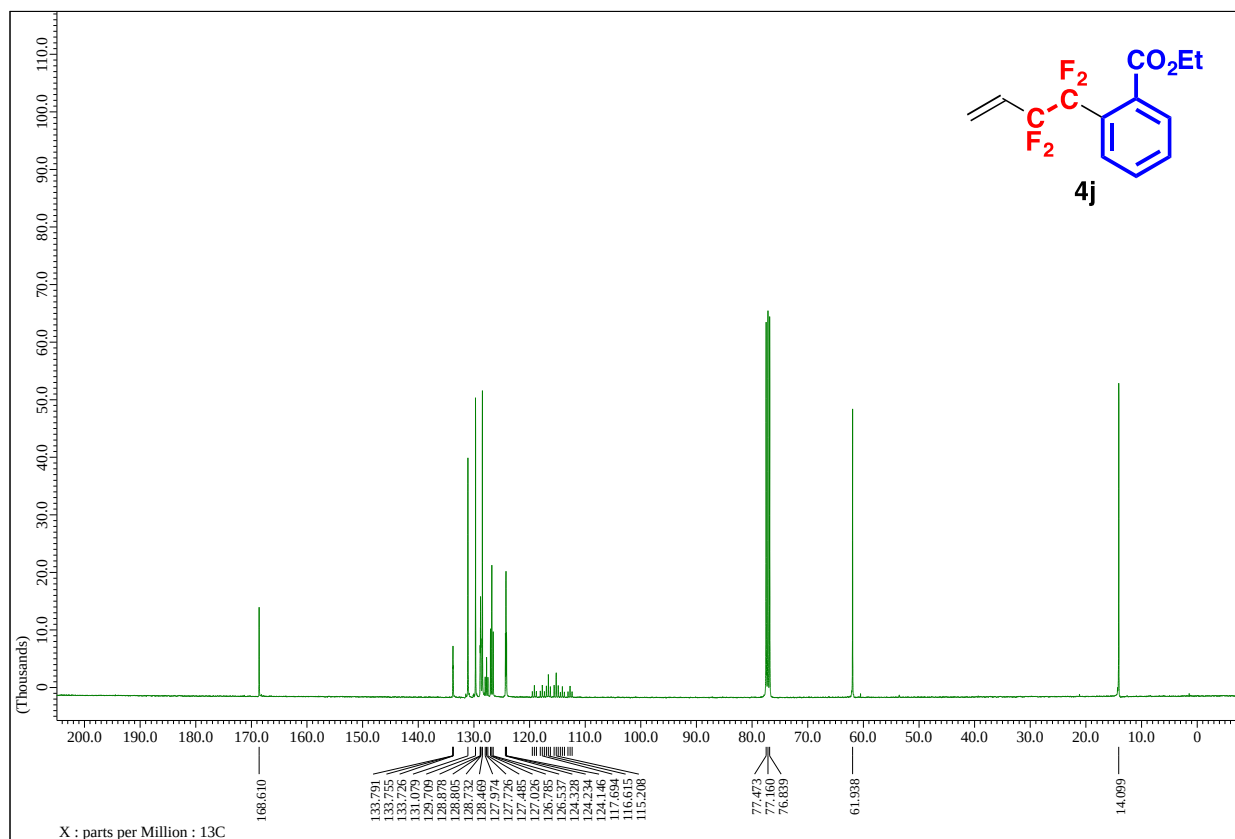
^{19}F NMR Spectrum of 4-(2-chlorophenyl)-3,3,4,4-tetrafluorobut-1-ene (**4i**)



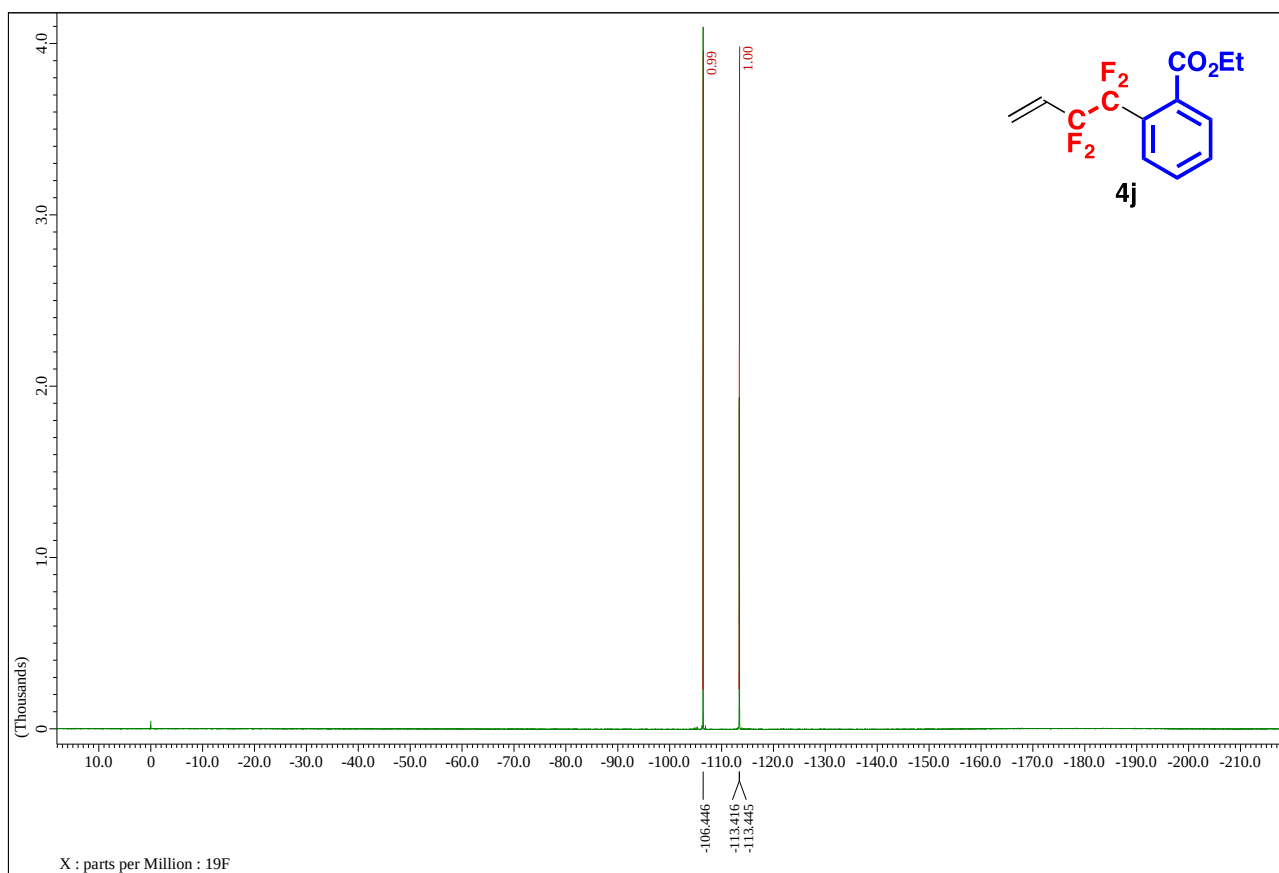
¹H NMR Spectrum of ethyl 2-(1,1,2,2-tetrafluorobut-3-en-1-yl)benzoate (**4j**)



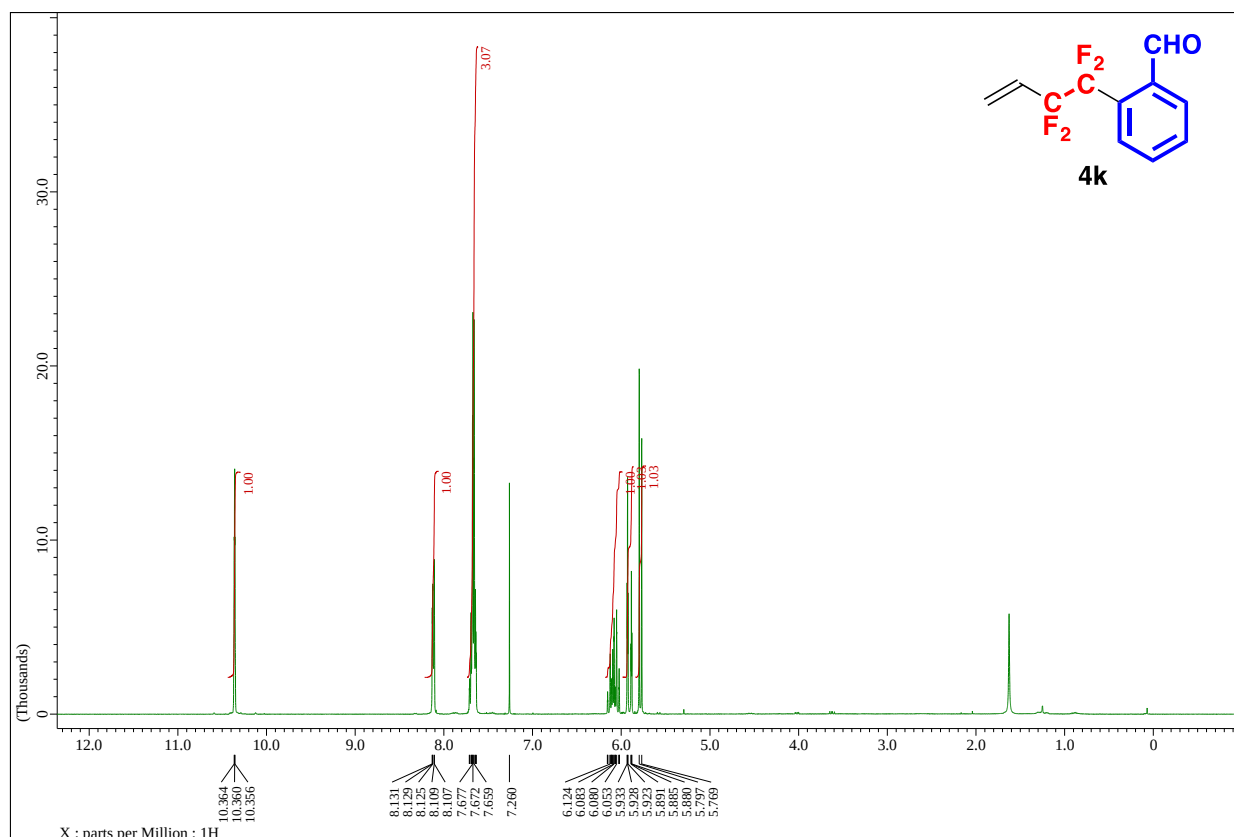
¹³C NMR Spectrum of ethyl 2-(1,1,2,2-tetrafluorobut-3-en-1-yl)benzoate (**4j**)



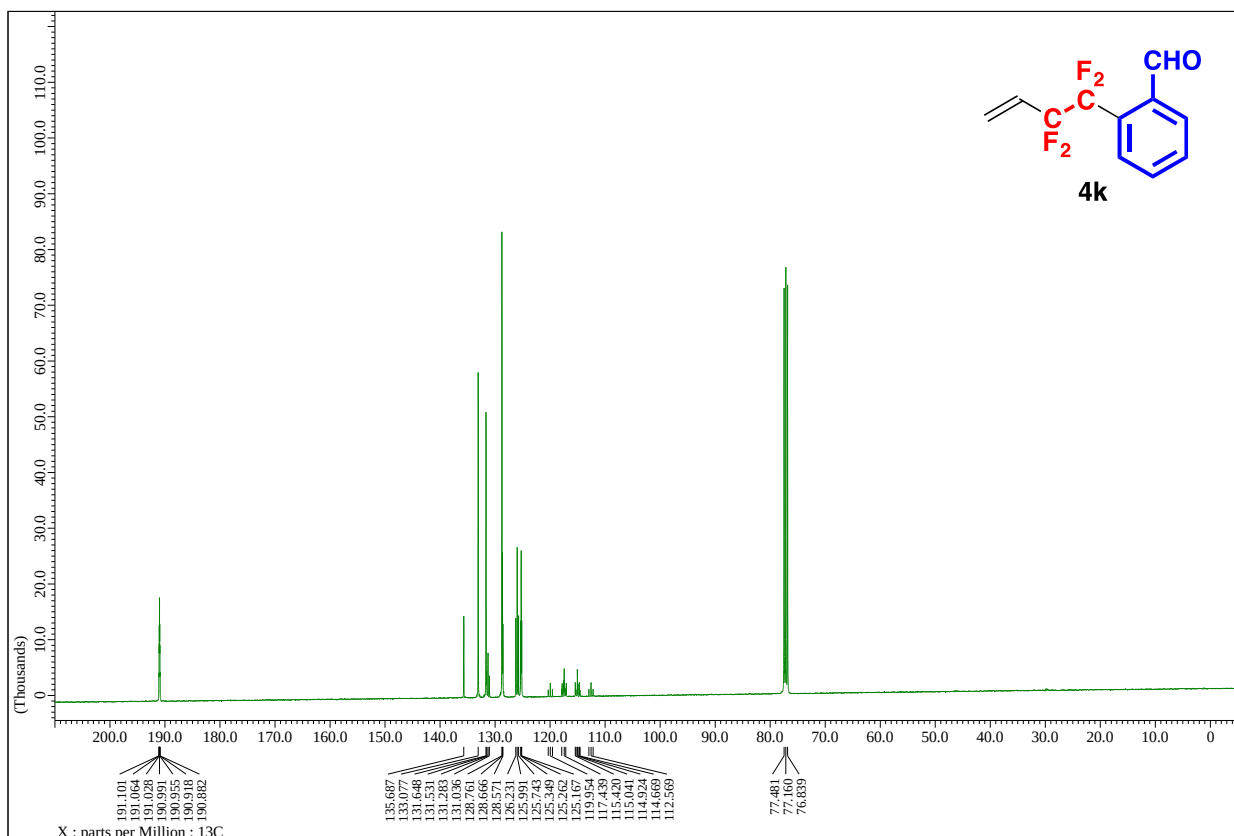
¹⁹F NMR Spectrum of ethyl 2-(1,1,2,2-tetrafluorobut-3-en-1-yl)benzoate (**4j**)



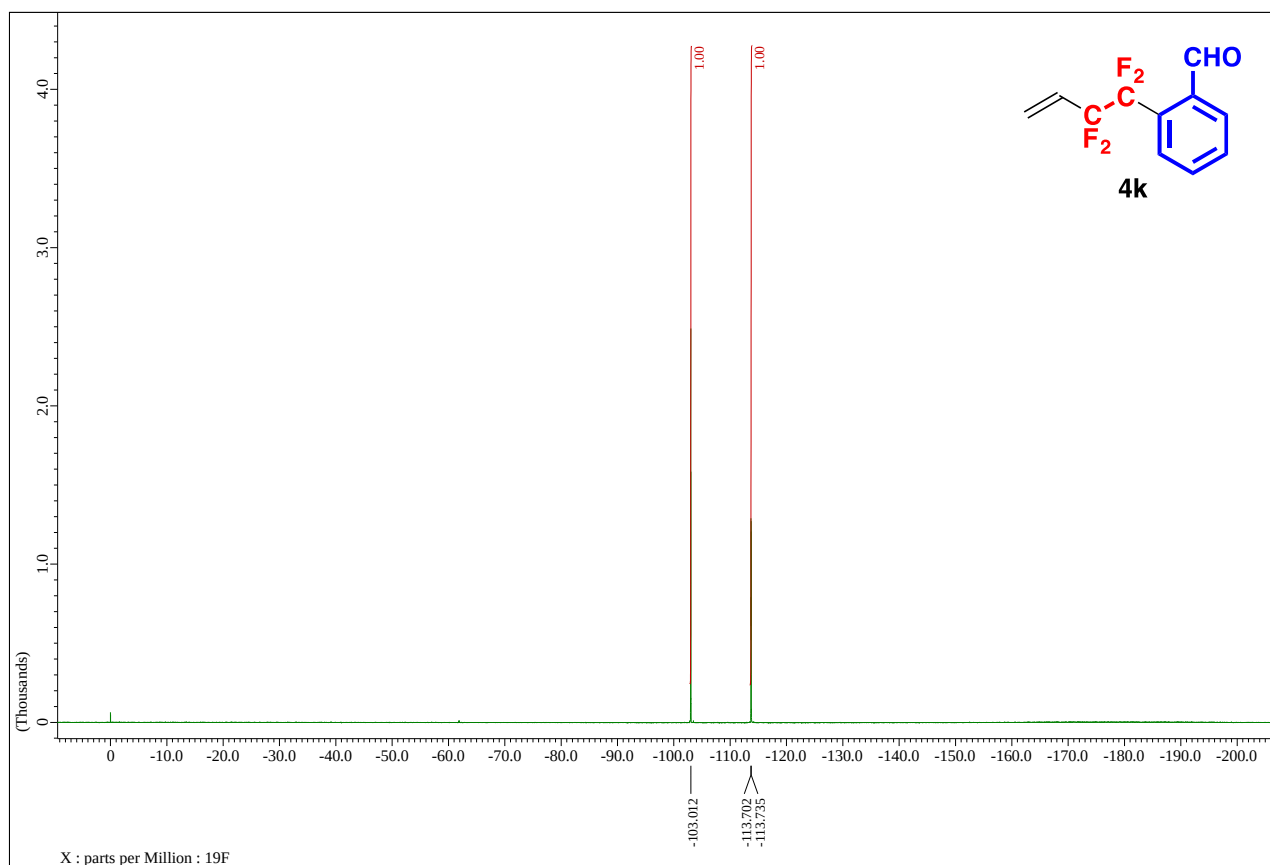
^1H NMR Spectrum of 3,3,4,4-tetrafluoro-4-(2-formylphenyl)but-1-ene (**4k**)



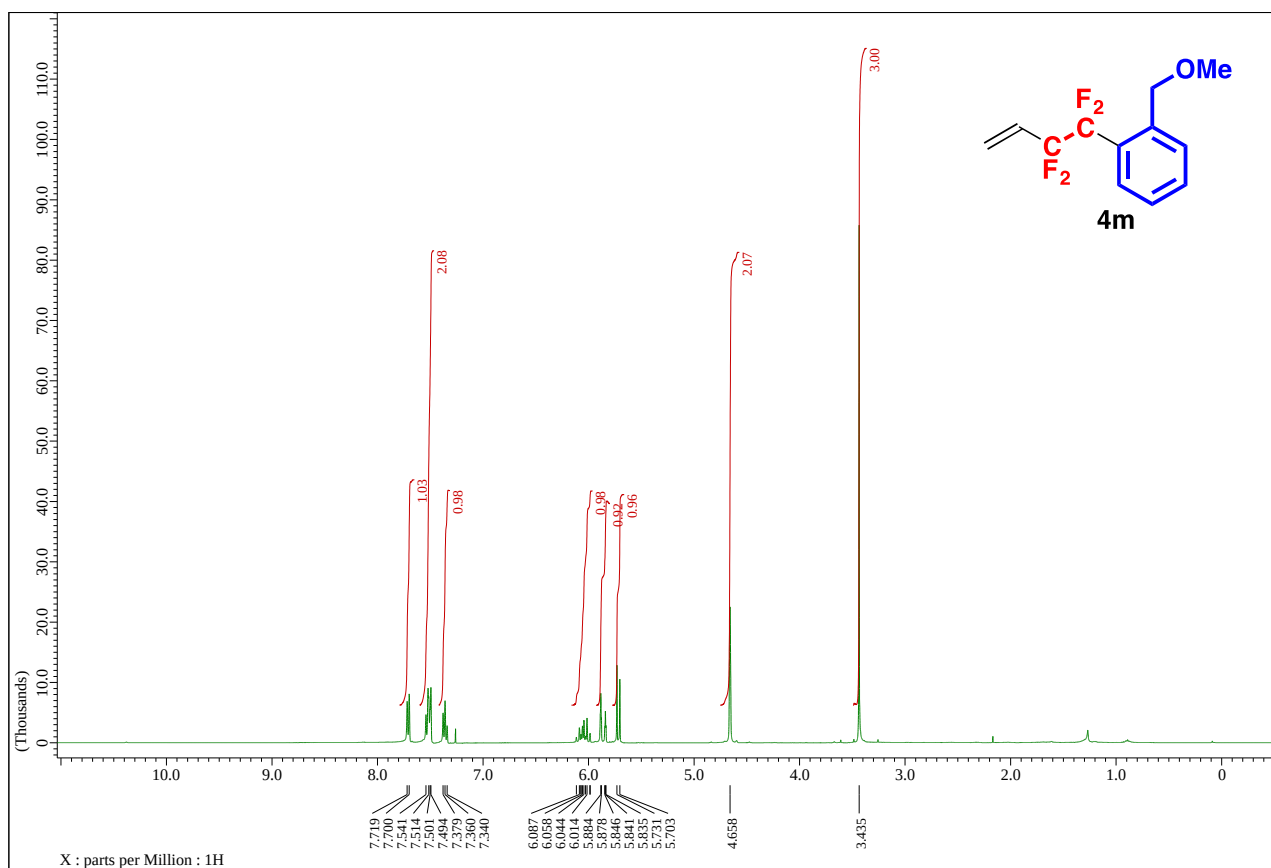
^{13}C NMR Spectrum of 3,3,4,4-tetrafluoro-4-(2-formylphenyl)but-1-ene (**4k**)



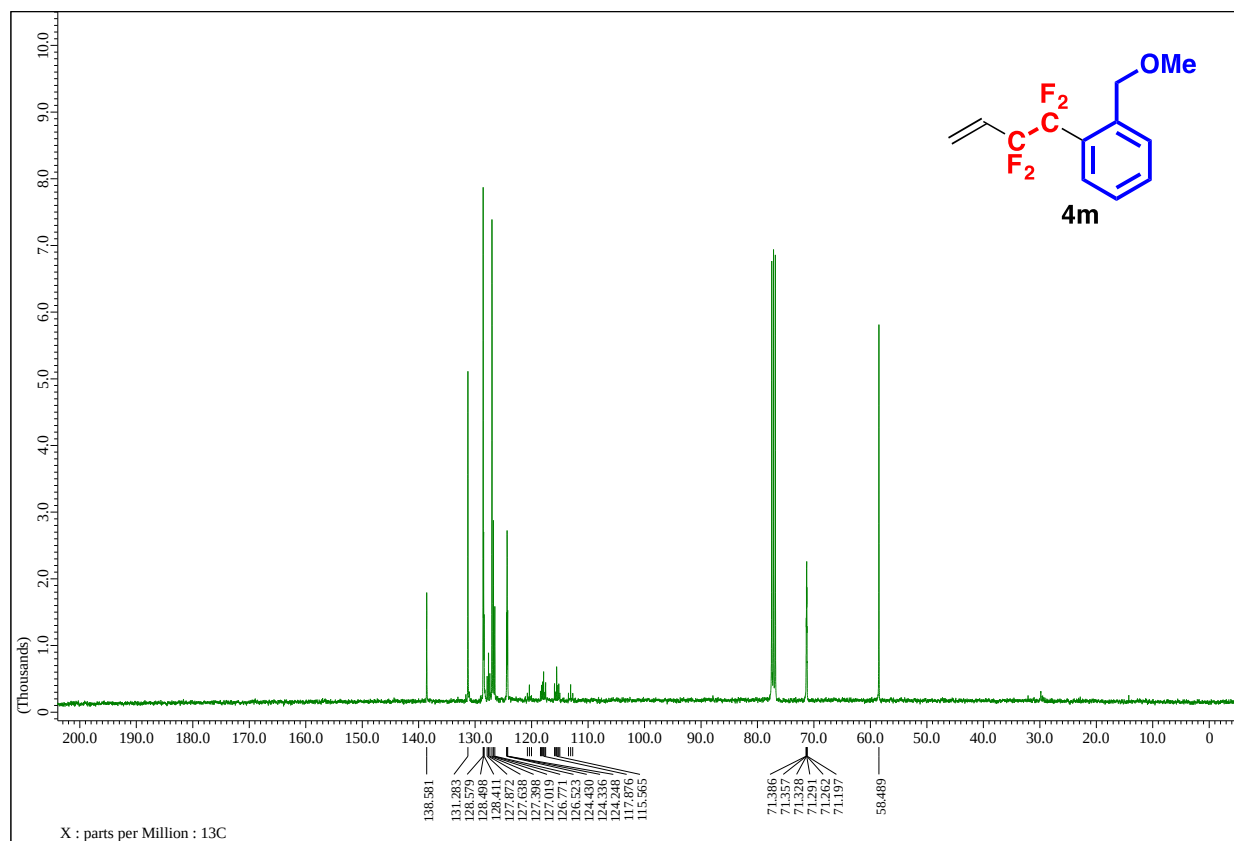
¹⁹F NMR Spectrum of 3,3,4,4-tetrafluoro-4-(2-formylphenyl)but-1-ene (**4k**)



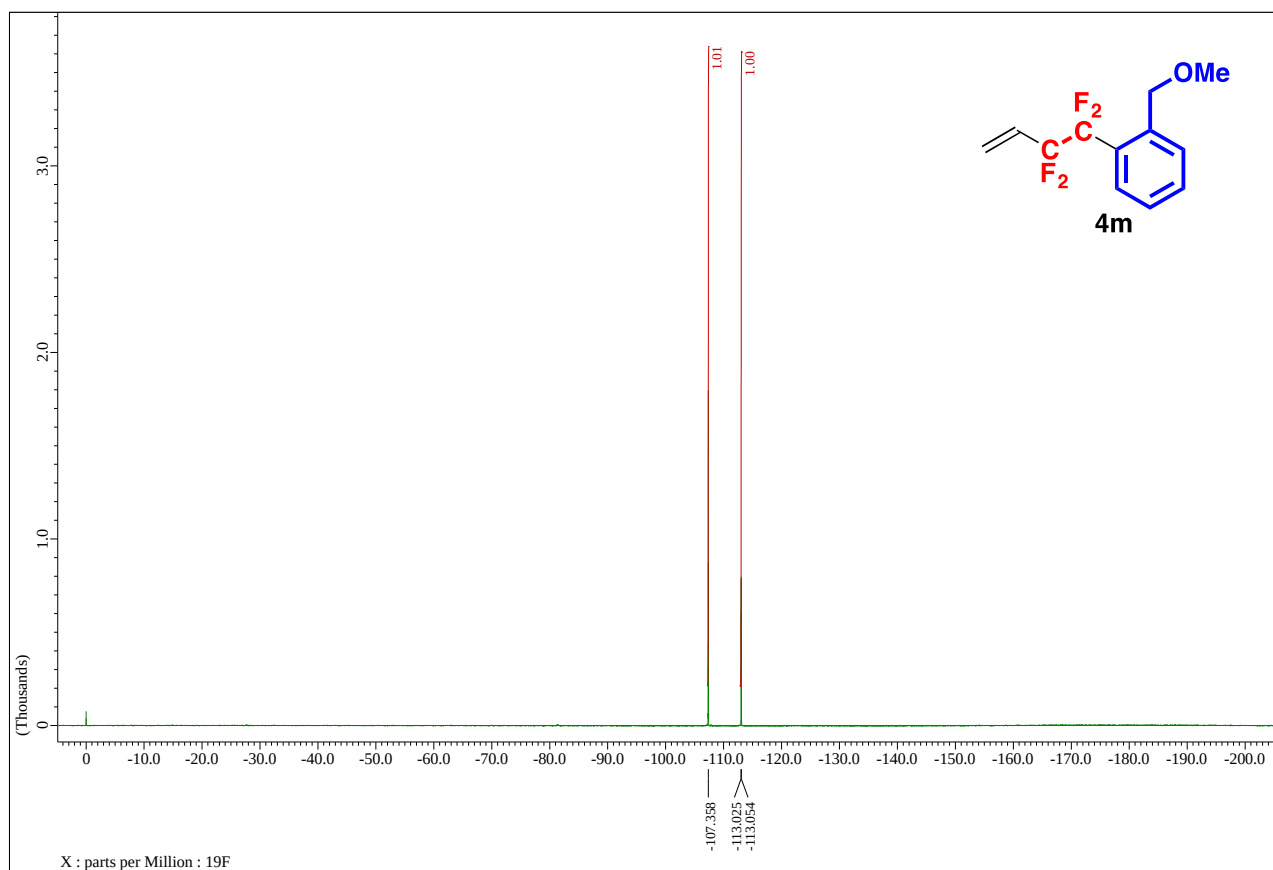
^1H NMR Spectrum of 3,3,4,4-tetrafluoro-4-(2-methoxymethylphenyl)but-1-ene (**4m**)



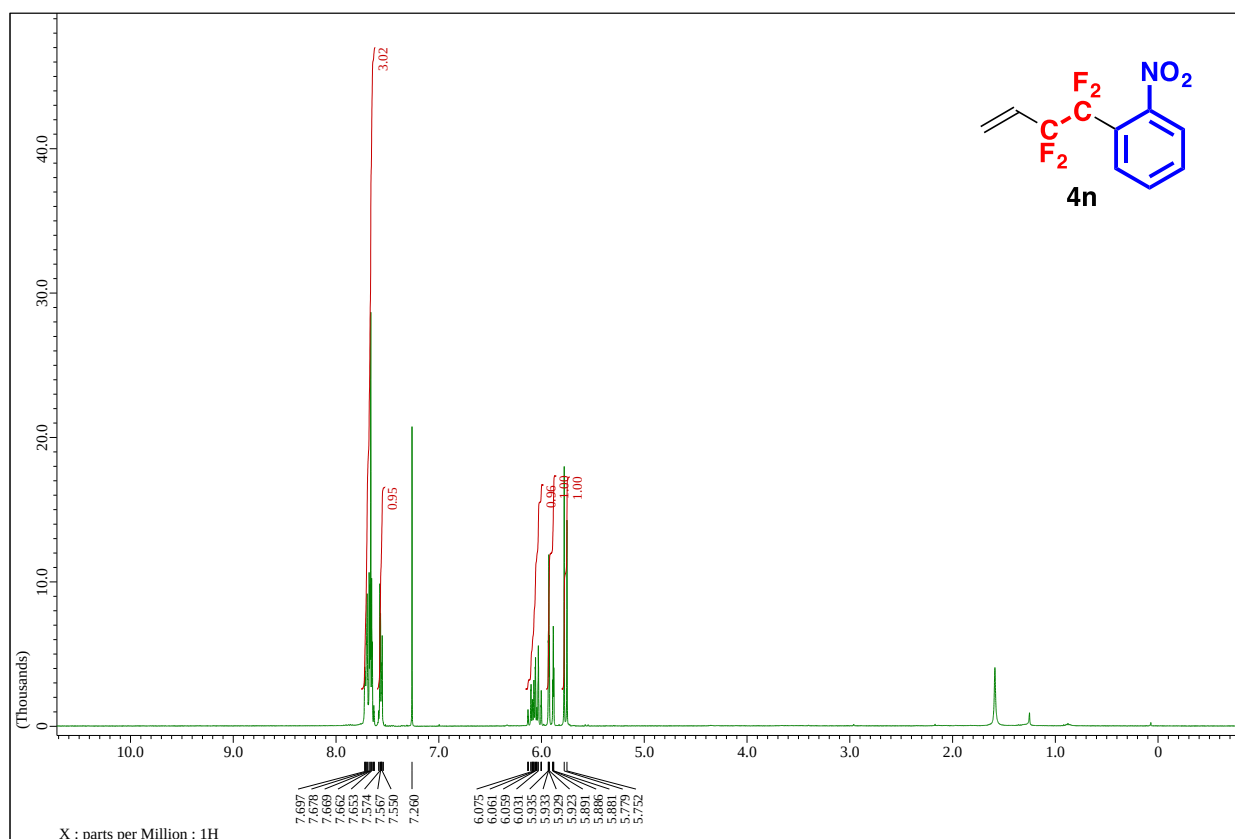
^{13}C NMR Spectrum of 3,3,4,4-tetrafluoro-4-(2-methoxymethylphenyl)but-1-ene (**4m**)



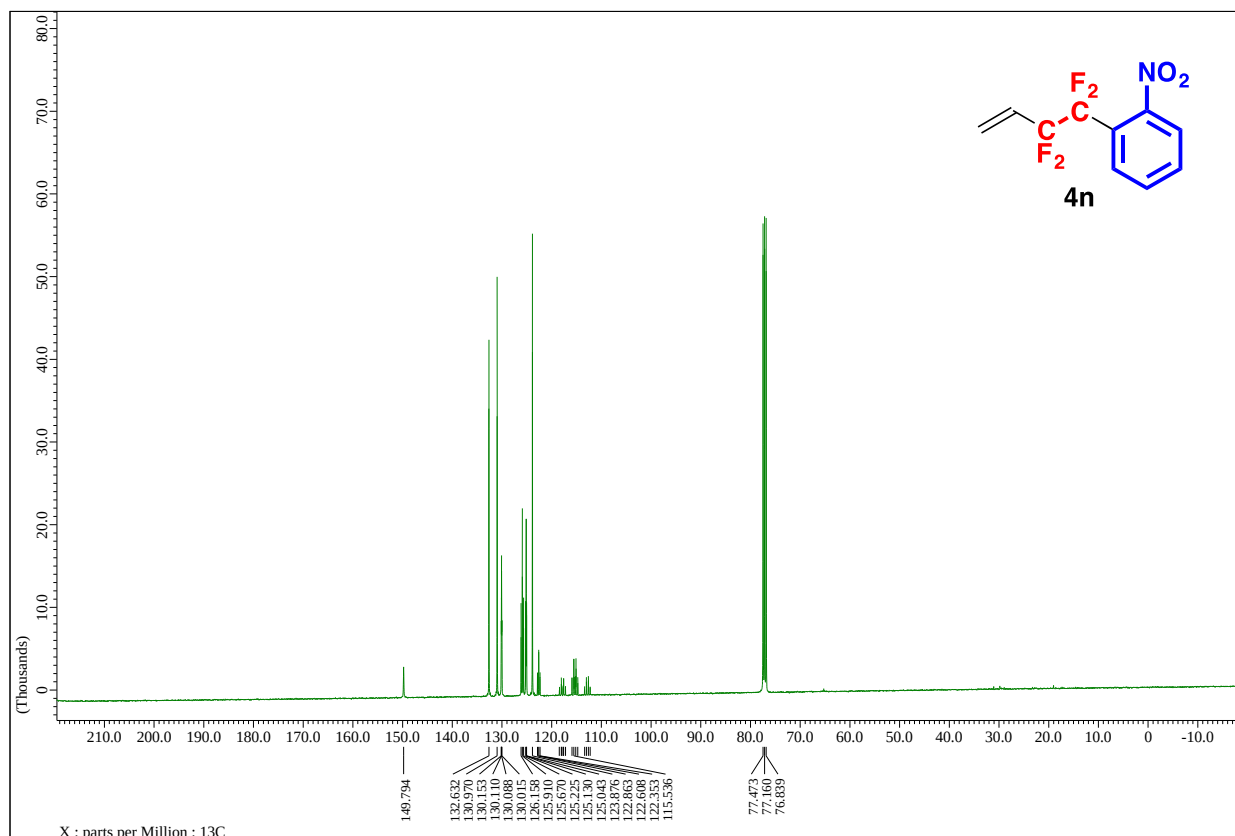
¹⁹F NMR Spectrum of 3,3,4,4-tetrafluoro-4-(2-methoxymethylphenyl)but-1-ene (**4m**)



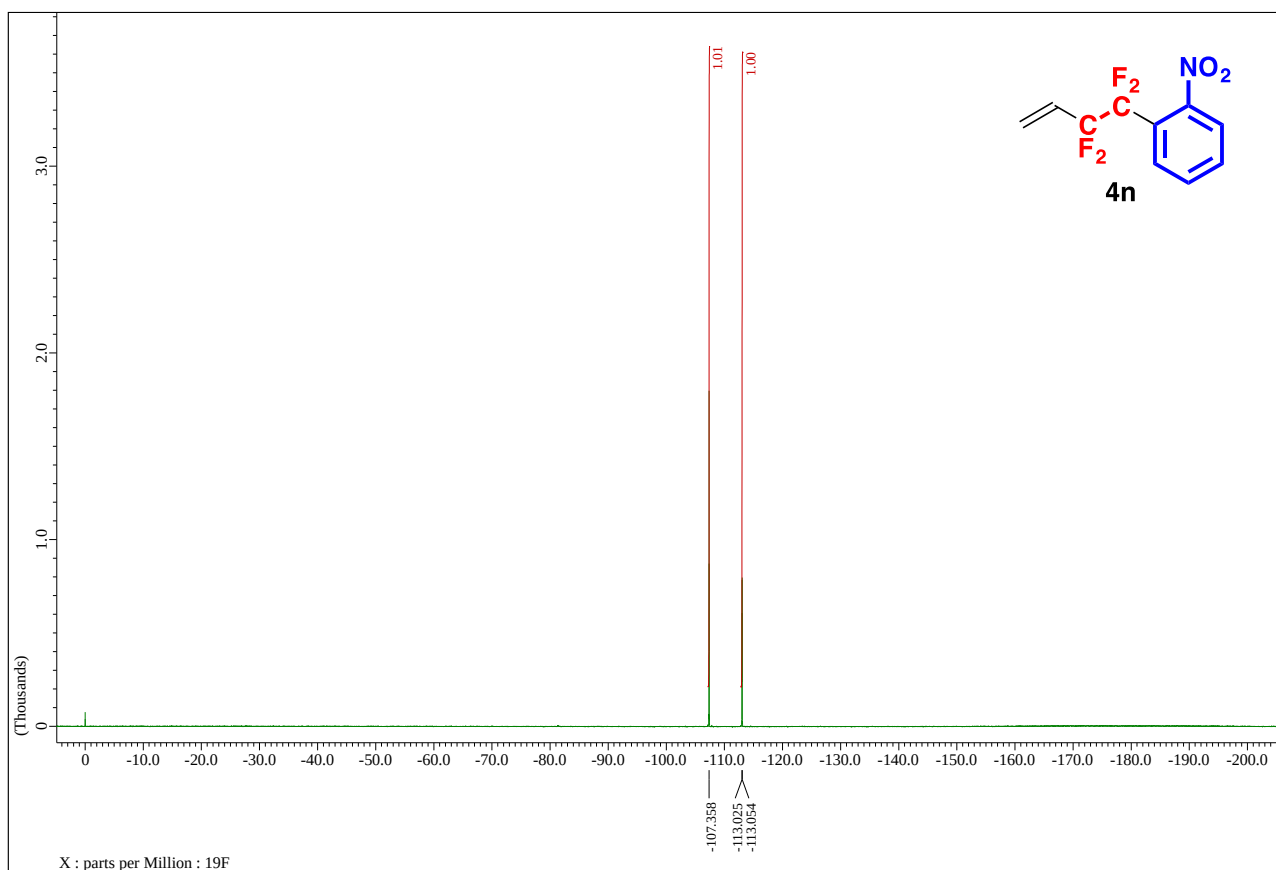
¹H NMR Spectrum of 3,3,4,4-tetrafluoro-4-(2-nitrophenyl)but-1-ene (**4n**)



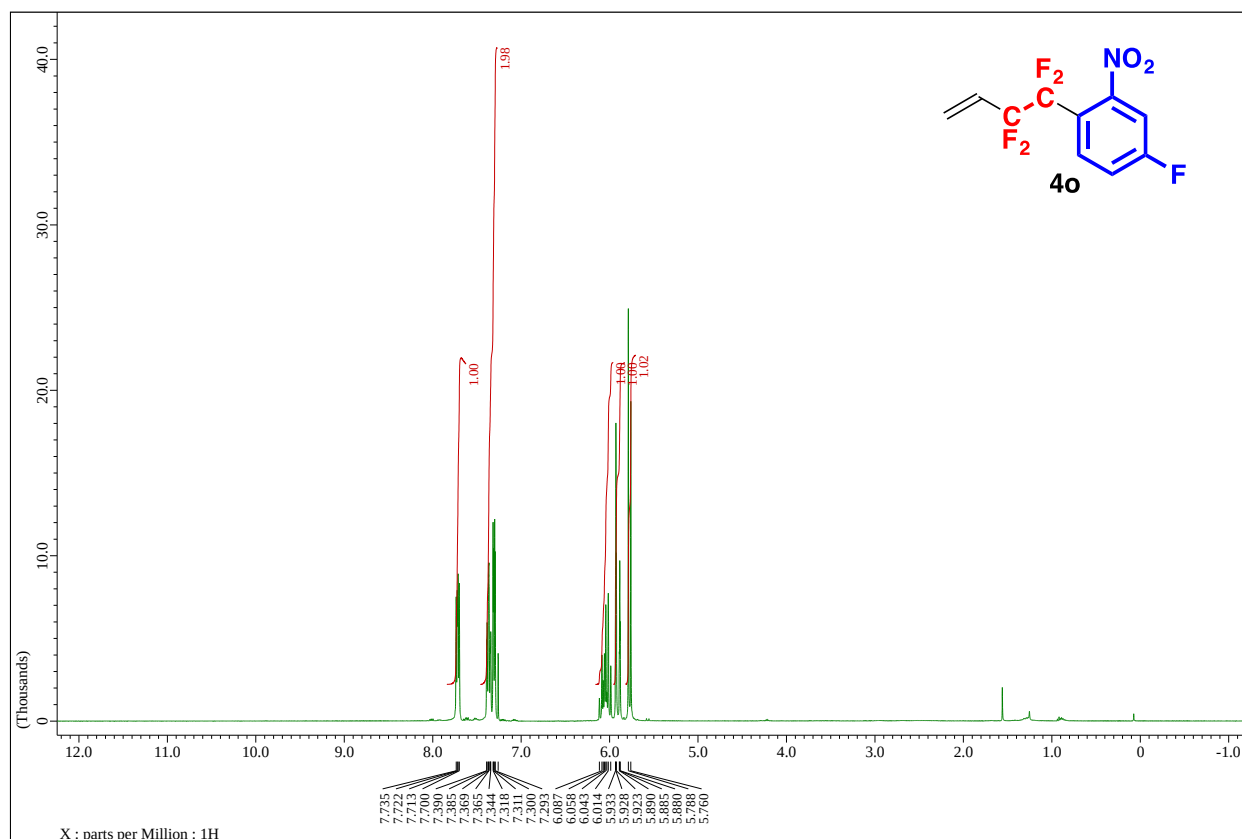
¹³C NMR Spectrum of 3,3,4,4-tetrafluoro-4-(2-nitrophenyl)but-1-ene (**4n**)



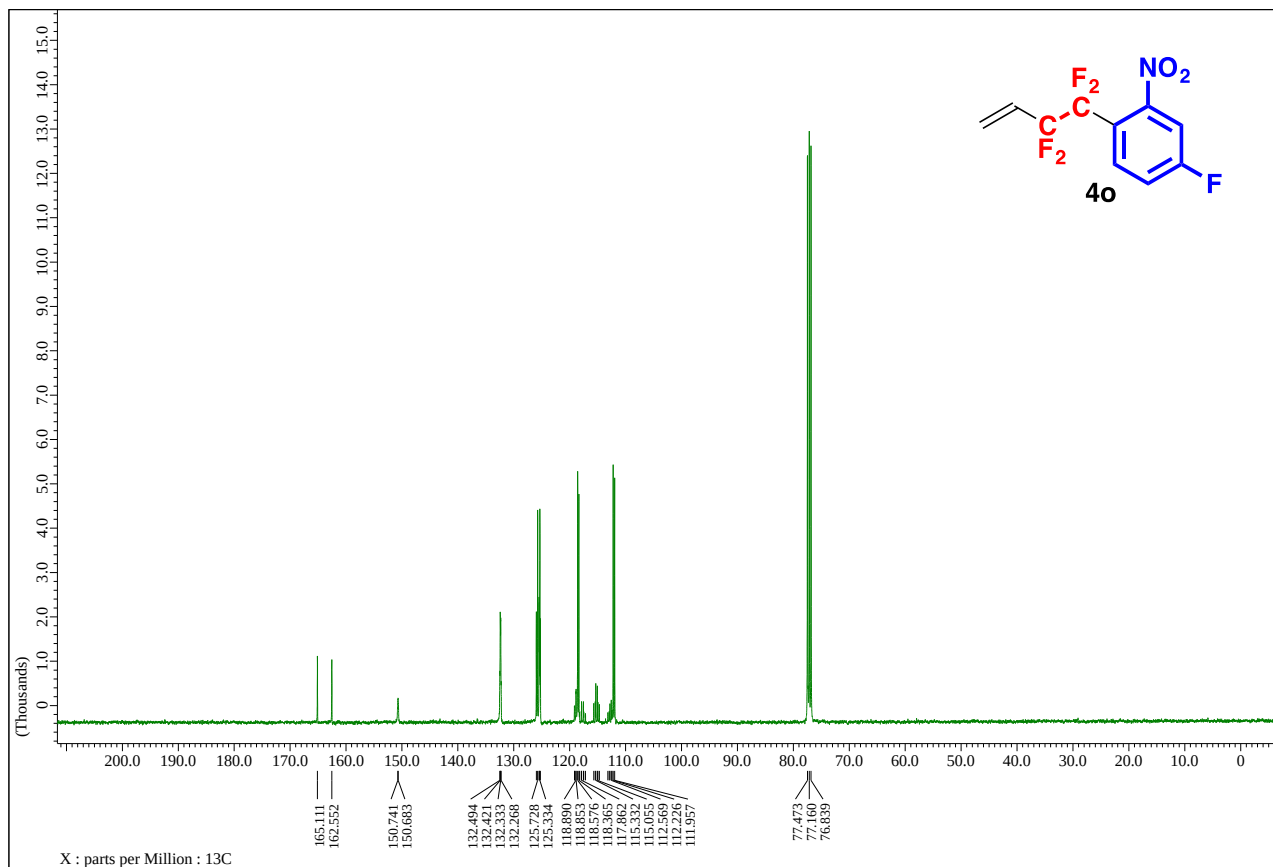
^{19}F NMR Spectrum of 3,3,4,4-tetrafluoro-4-(2-nitrophenyl)but-1-ene (**4n**)



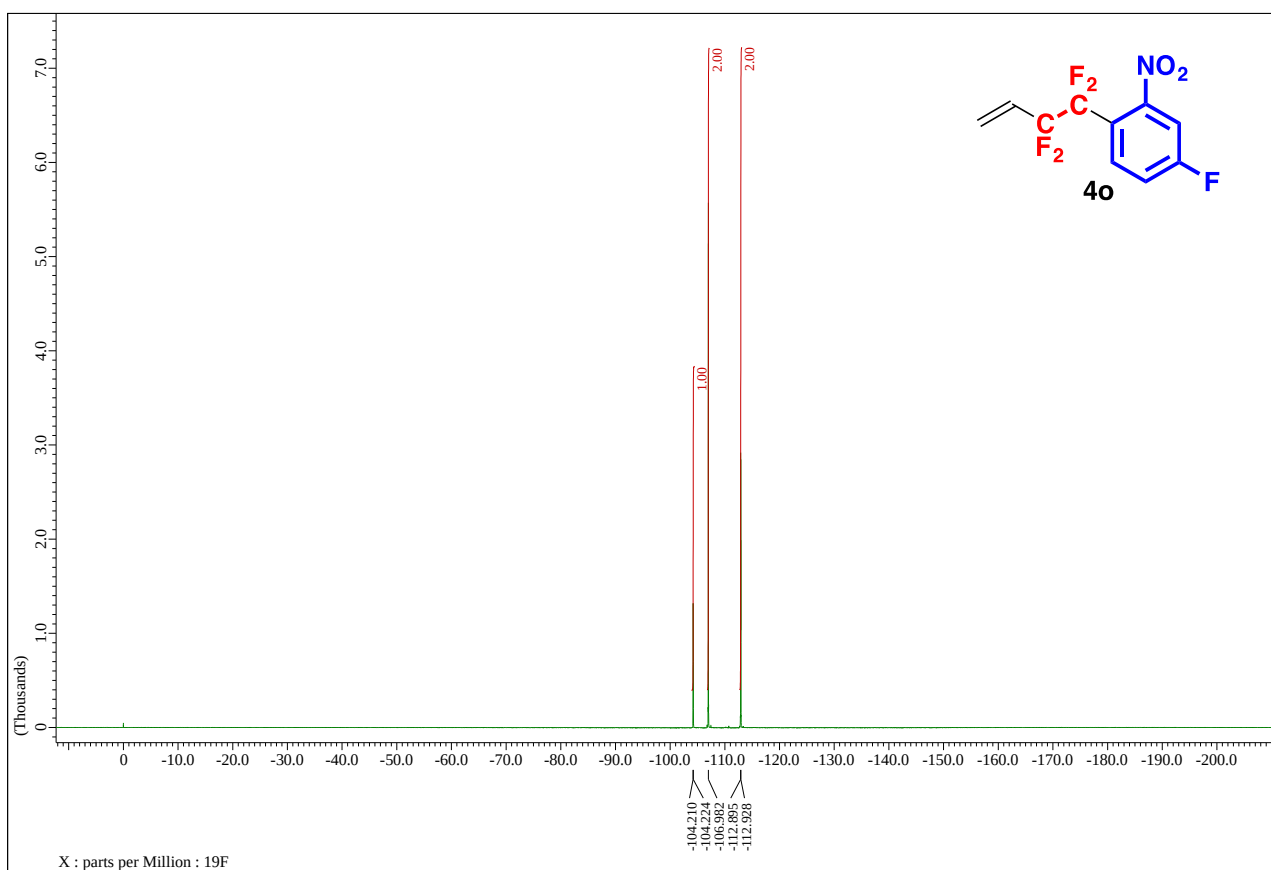
¹H NMR Spectrum of 4-(4-fluoro-2-nitrophenyl)-3,3,4,4-tetrafluorobut-1-ene (**4o**)



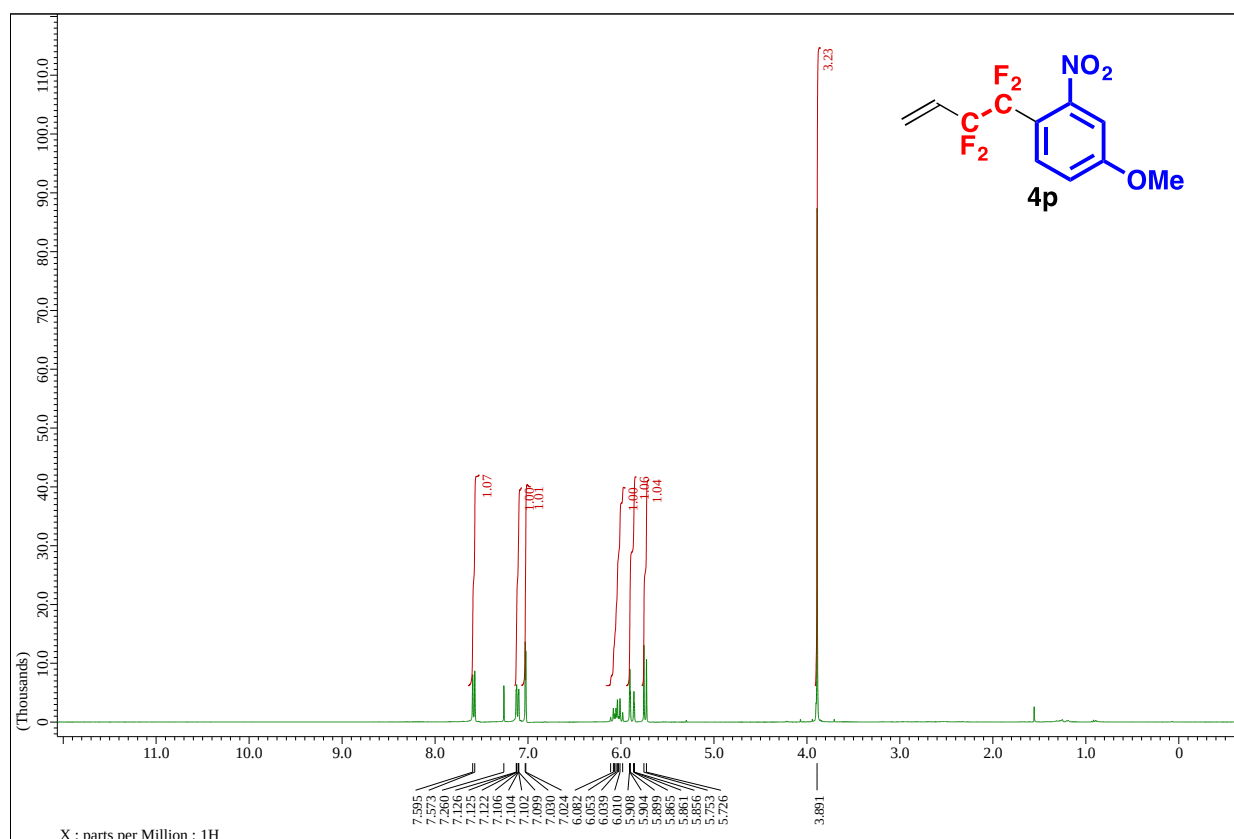
¹³C NMR Spectrum of 4-(4-fluoro-2-nitrophenyl)-3,3,4,4-tetrafluorobut-1-ene (**4o**)



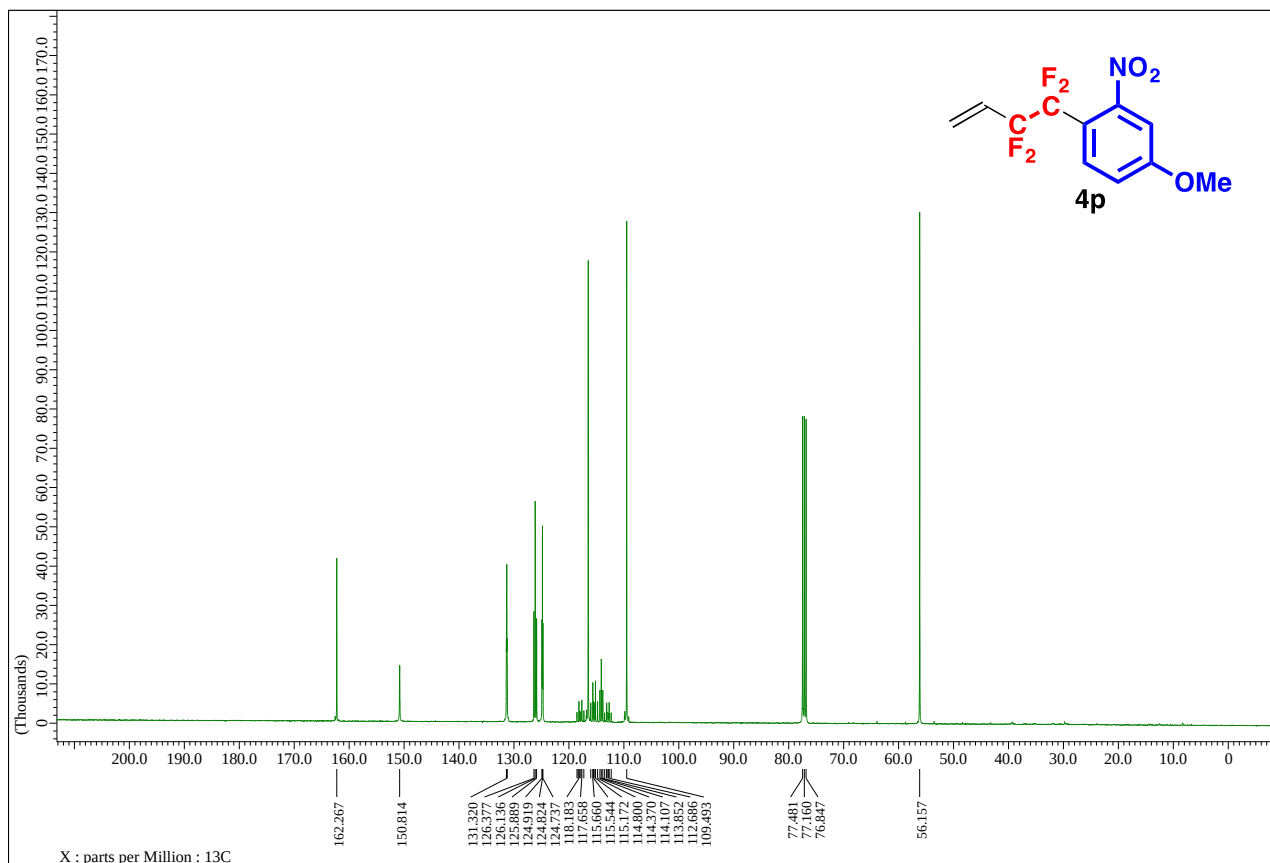
¹⁹F NMR Spectrum of 4-(4-fluoro-2-nitrophenyl)-3,3,4,4-tetrafluorobut-1-ene (**4o**)



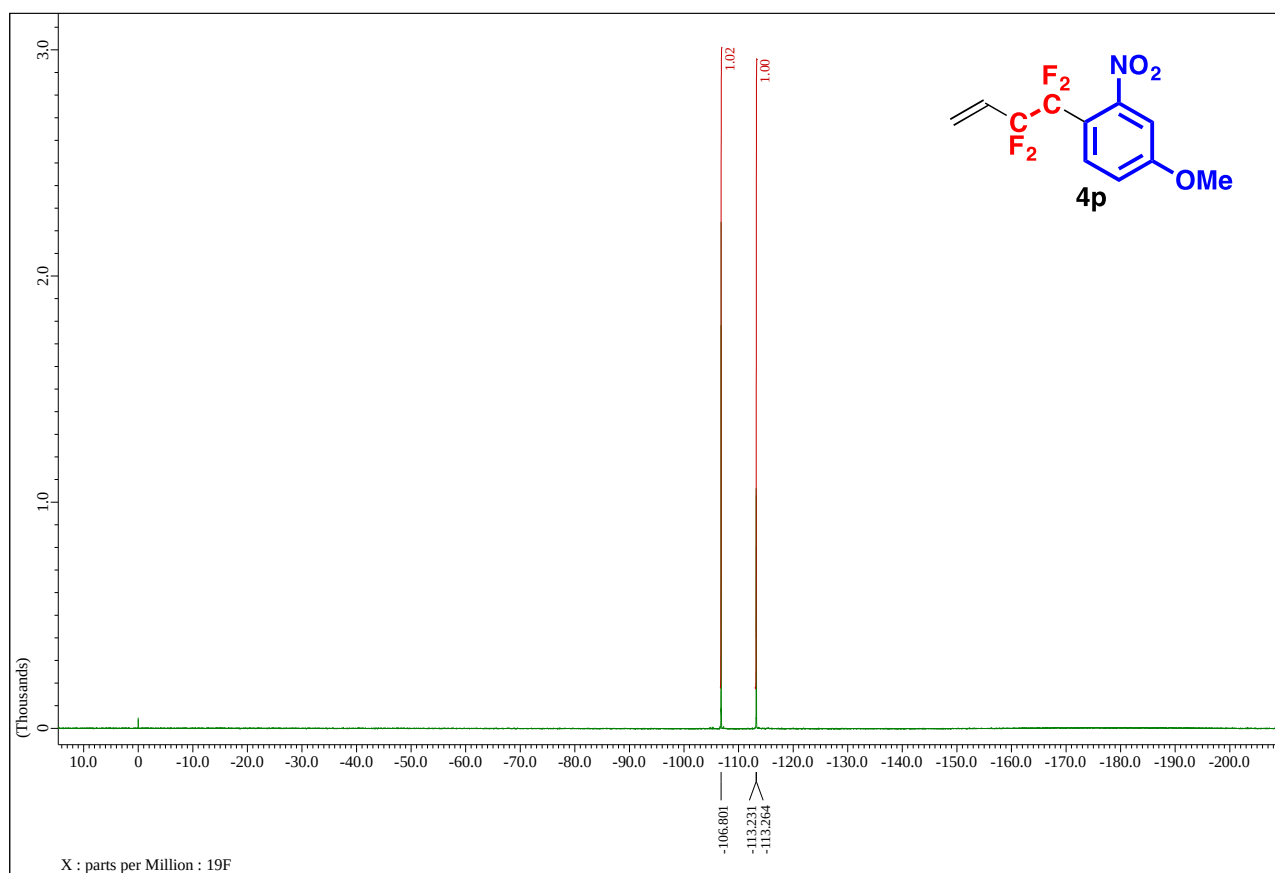
^1H NMR Spectrum of 3,3,4,4-tetrafluoro-4-(4-methoxy-2-nitrophenyl)but-1-ene (**4p**)



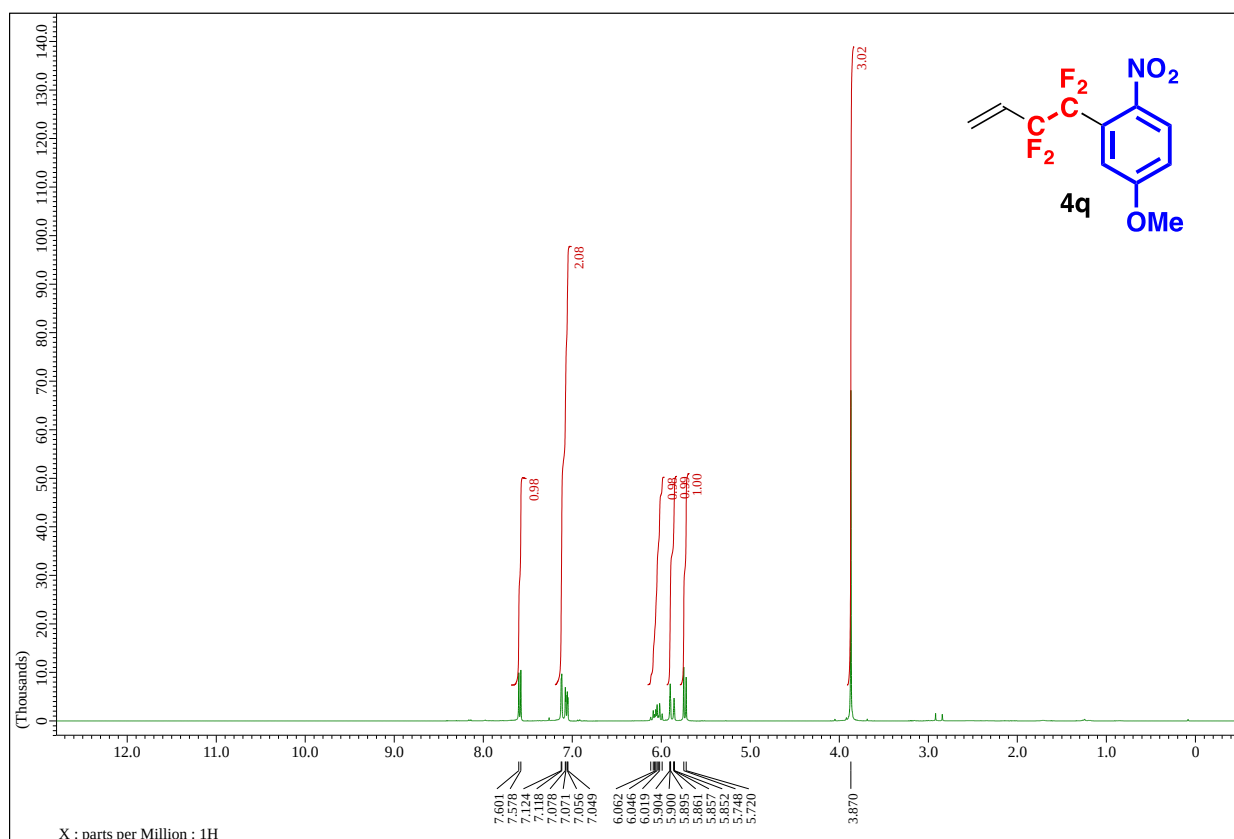
^{13}C NMR Spectrum of 3,3,4,4-tetrafluoro-4-(4-methoxy-2-nitrophenyl)but-1-ene (**4p**)



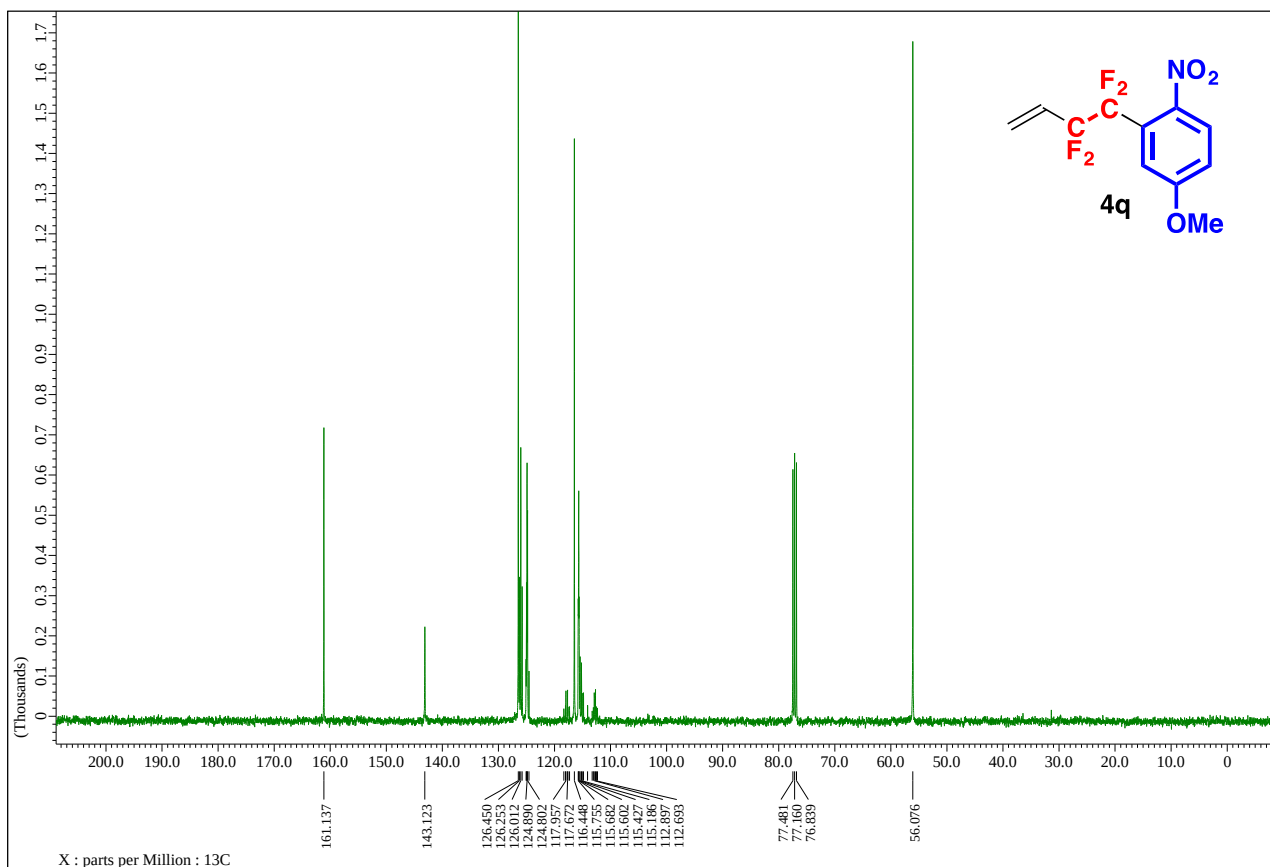
¹⁹F NMR Spectrum of 3,3,4,4-tetrafluoro-4-(4-methoxy-2-nitrophenyl)but-1-ene (**4p**)



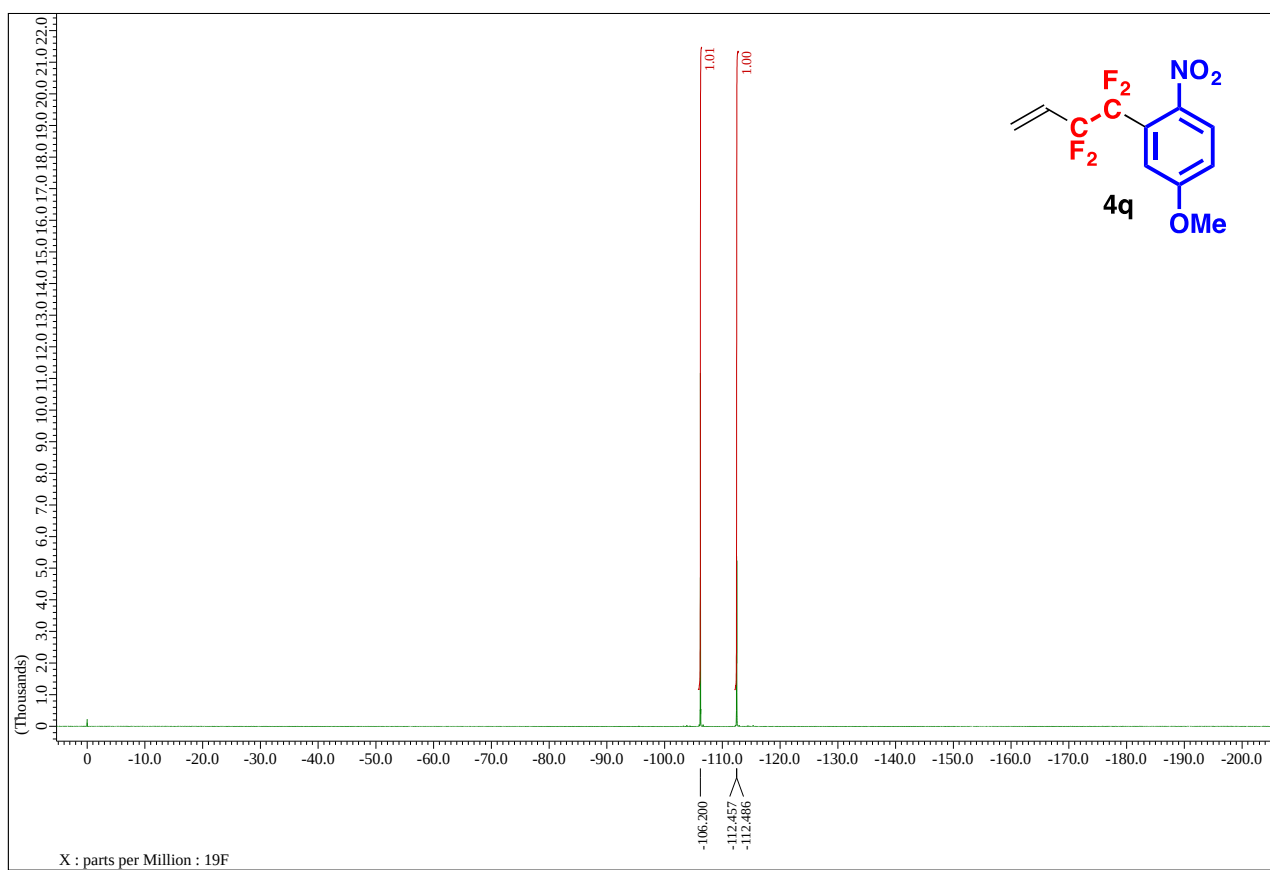
^1H NMR Spectrum of 3,3,4,4-tetrafluoro-4-(5-methoxy-2-nitrophenyl)but-1-ene (**4q**)



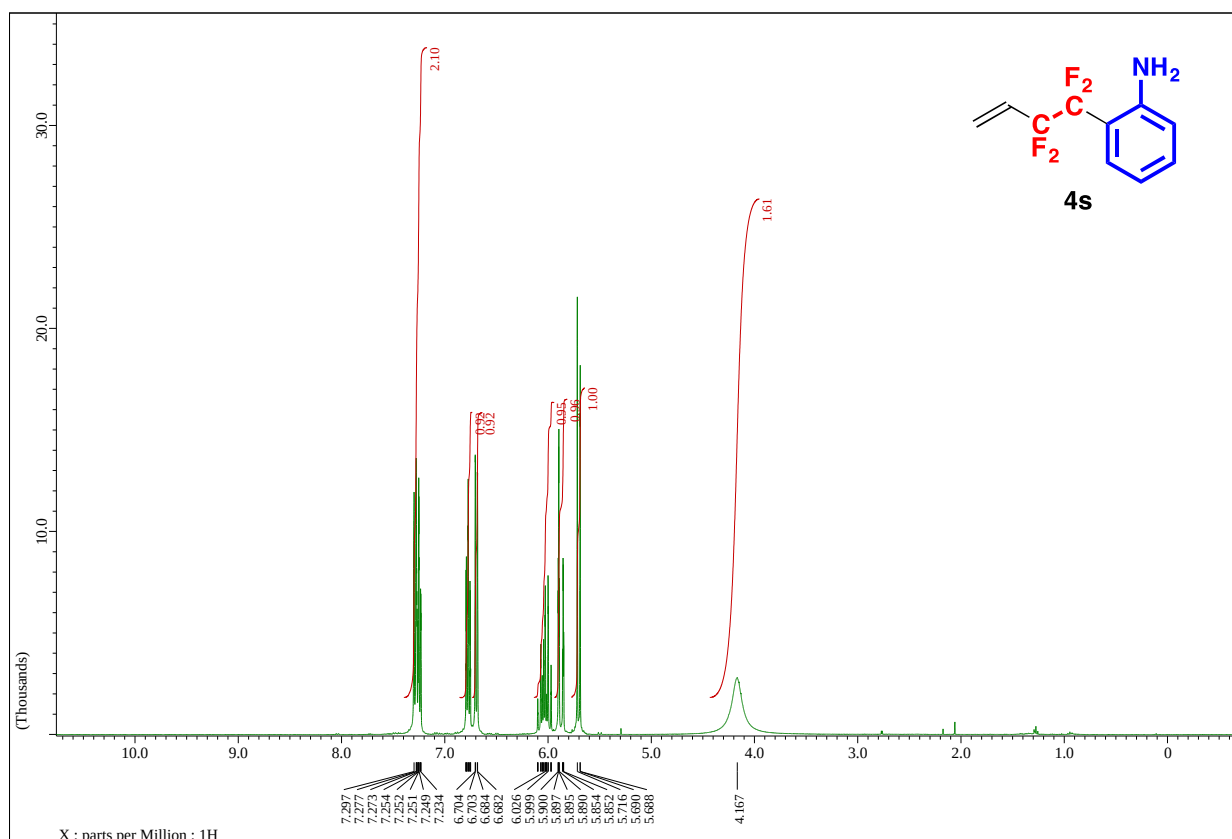
^{13}C NMR Spectrum of 3,3,4,4-tetrafluoro-4-(5-methoxy-2-nitrophenyl)but-1-ene (**4q**)



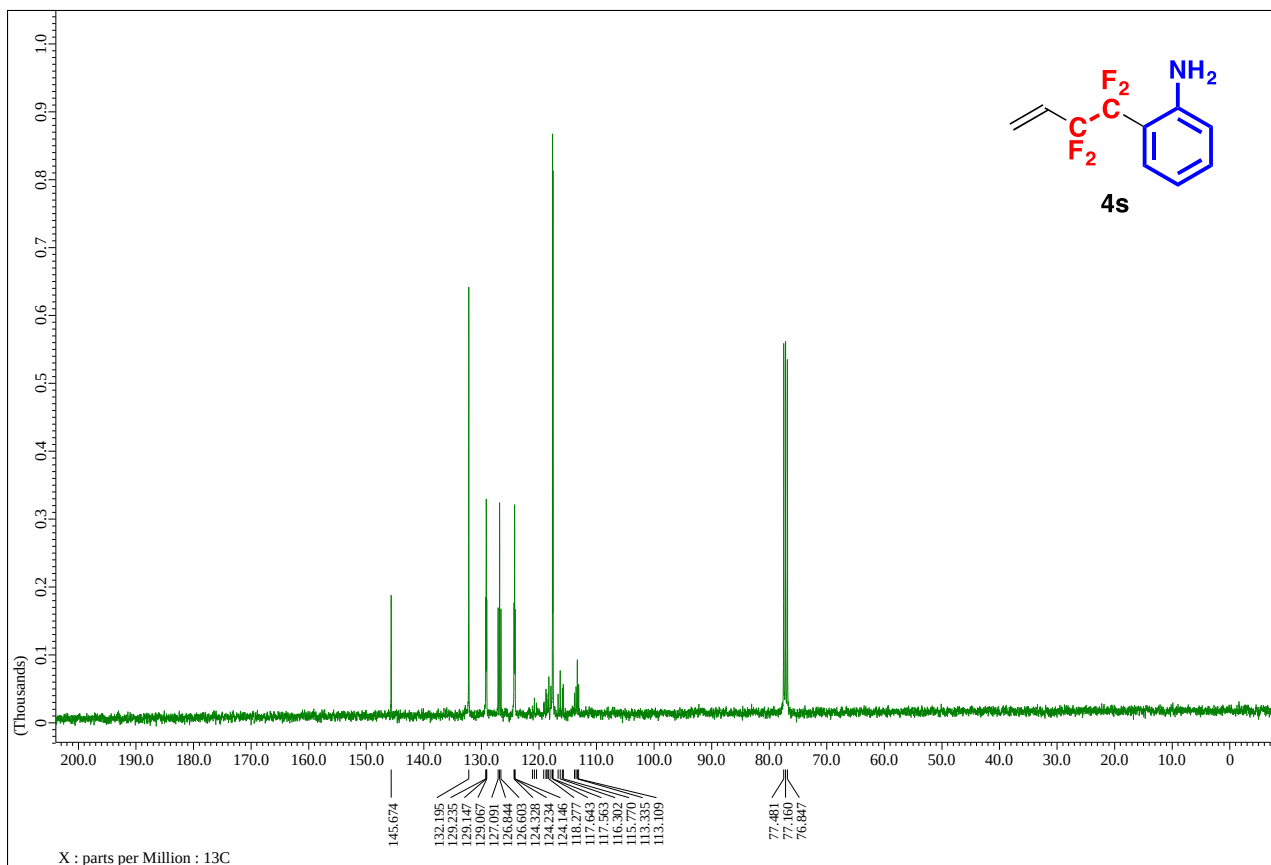
¹⁹F NMR Spectrum of 3,3,4,4-tetrafluoro-4-(5-methoxy-2-nitrophenyl)but-1-ene (**4q**)



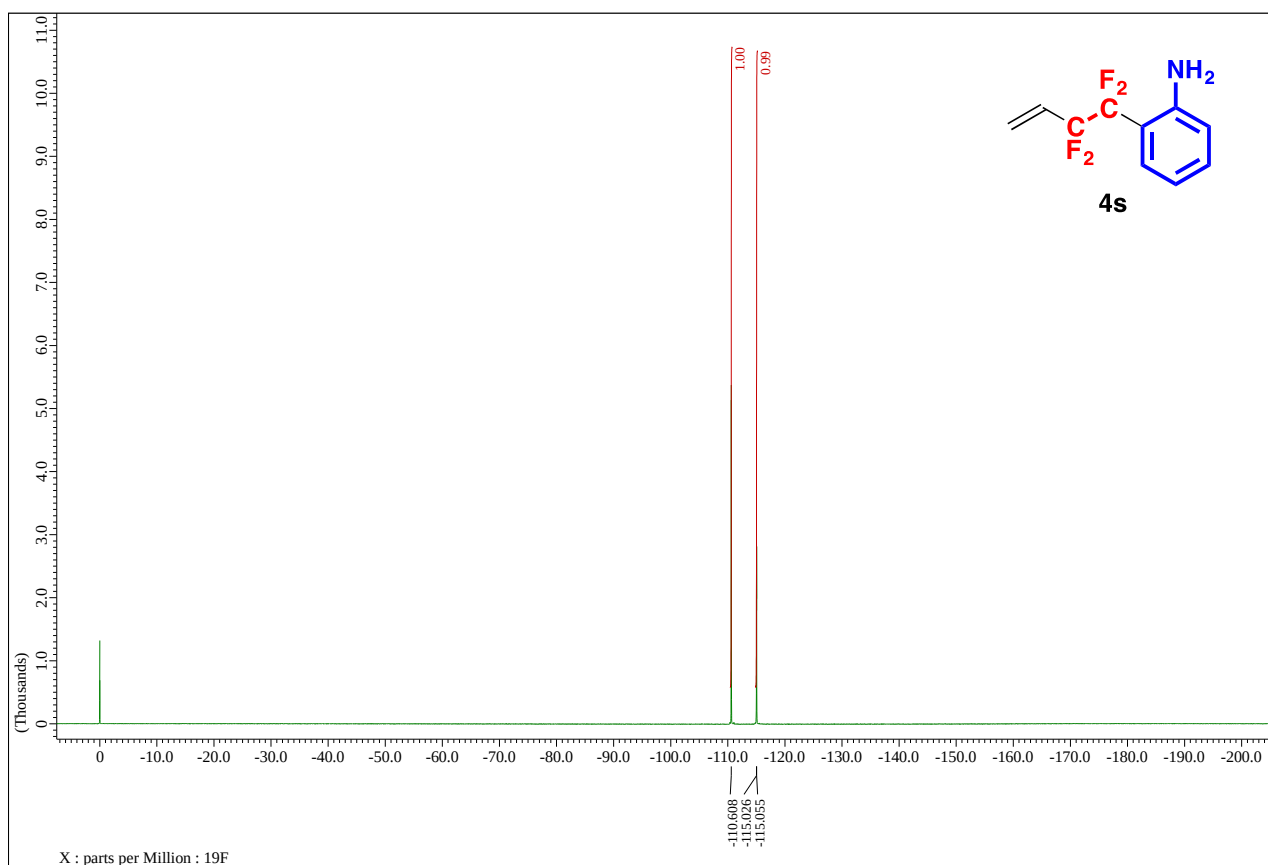
^1H NMR Spectrum of 2-(1,1,2,2-tetrafluorobut-3-en-1-yl)aniline (**4s**)



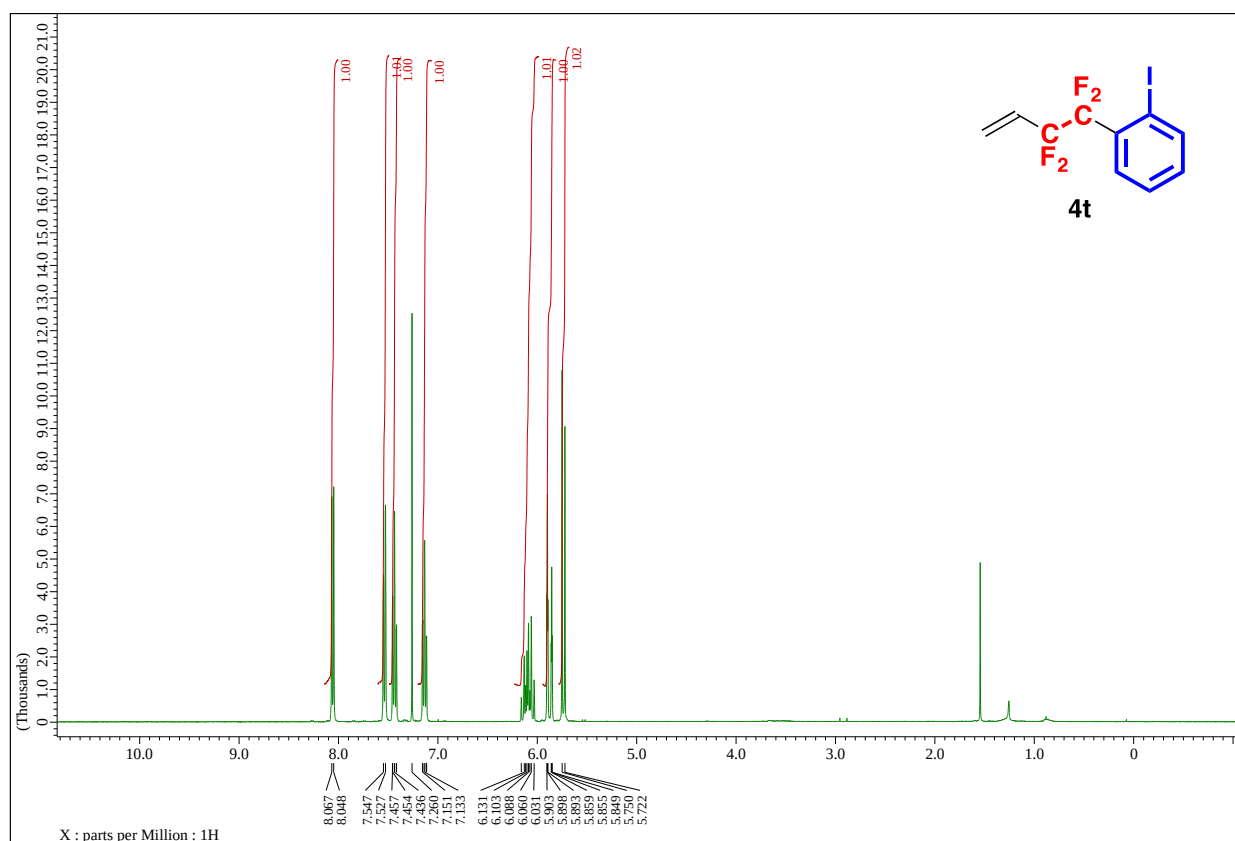
^{13}C NMR Spectrum of 2-(1,1,2,2-tetrafluorobut-3-en-1-yl)aniline (**4s**)



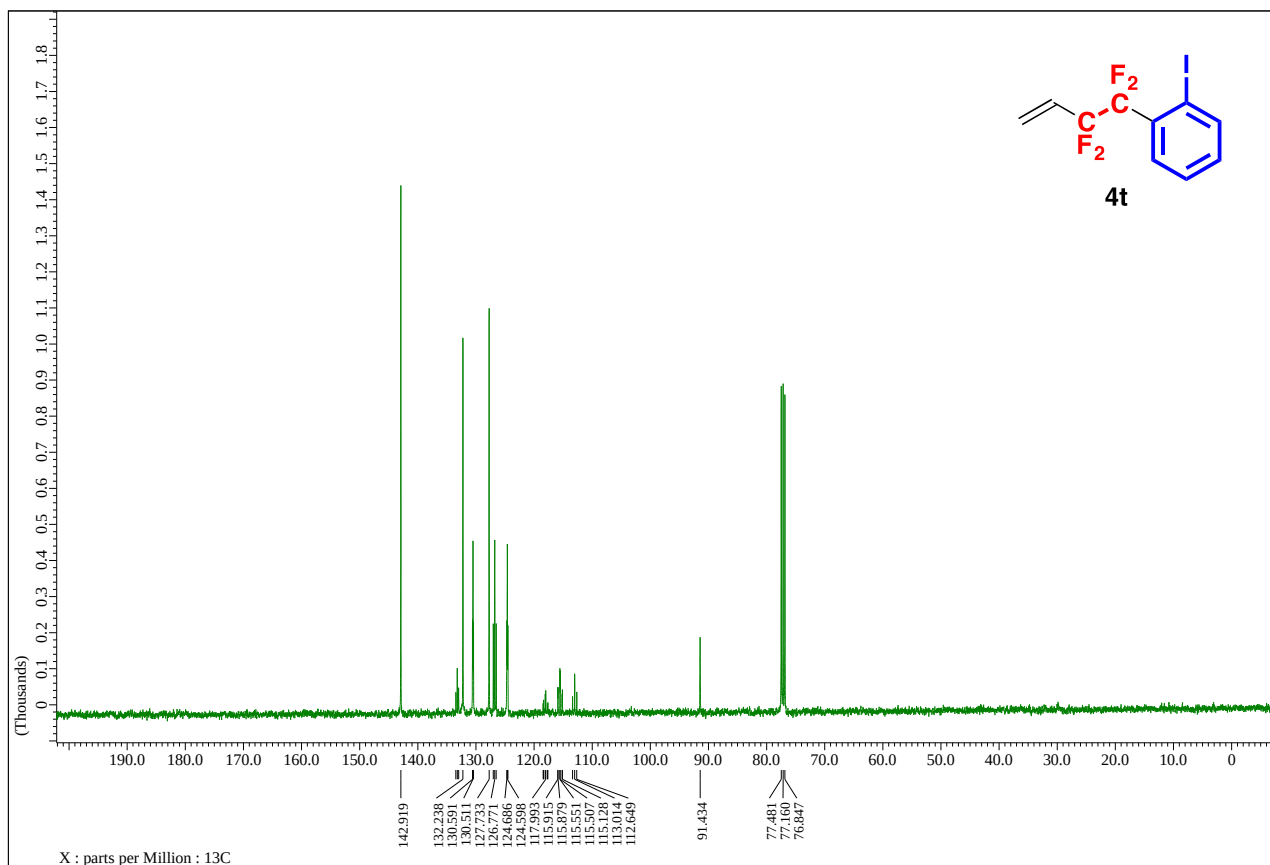
^{19}F NMR Spectrum of 2-(1,1,2,2-tetrafluorobut-3-en-1-yl)aniline (**4s**)



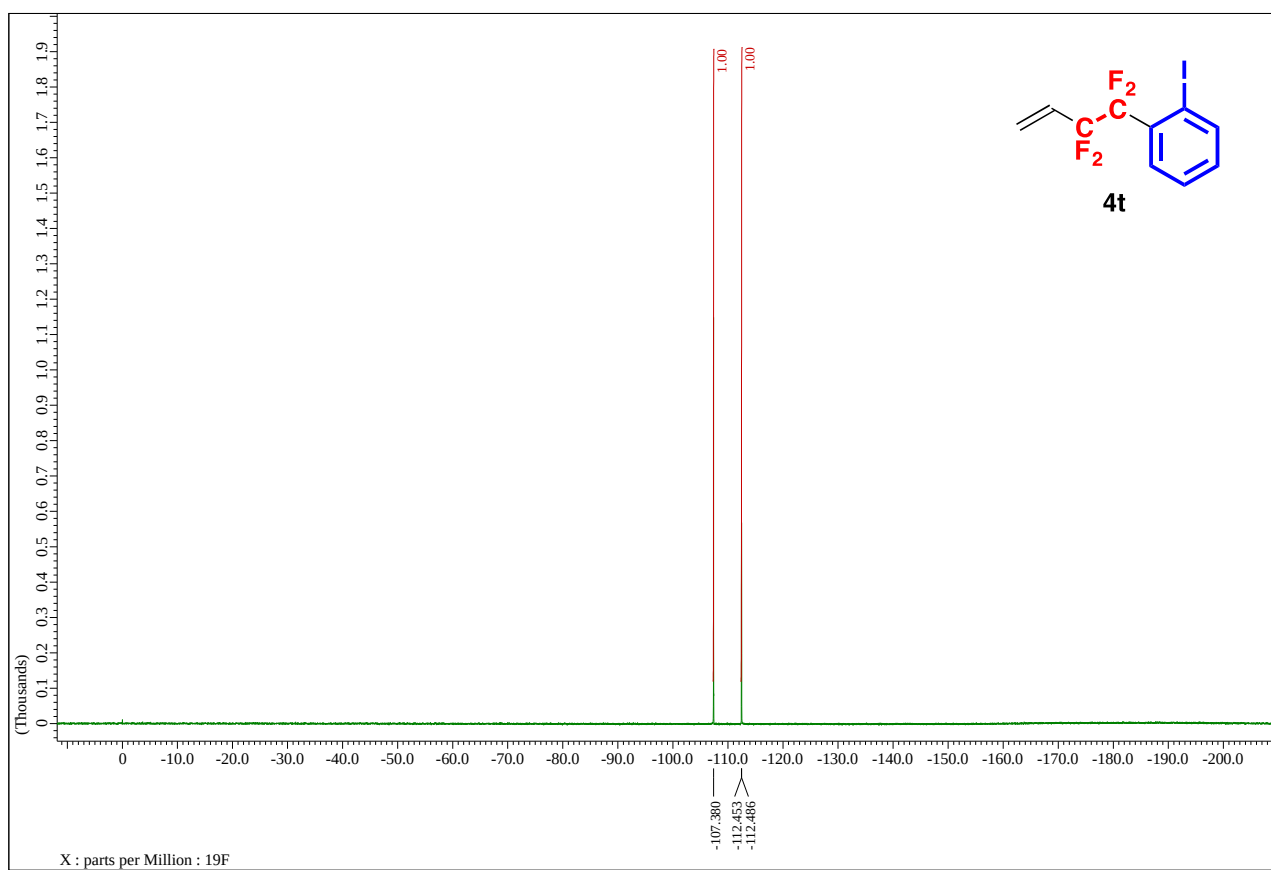
^1H NMR Spectrum of 3,3,4,4-tetrafluoro-4-(2-iodophenyl)but-1-ene (**4t**)



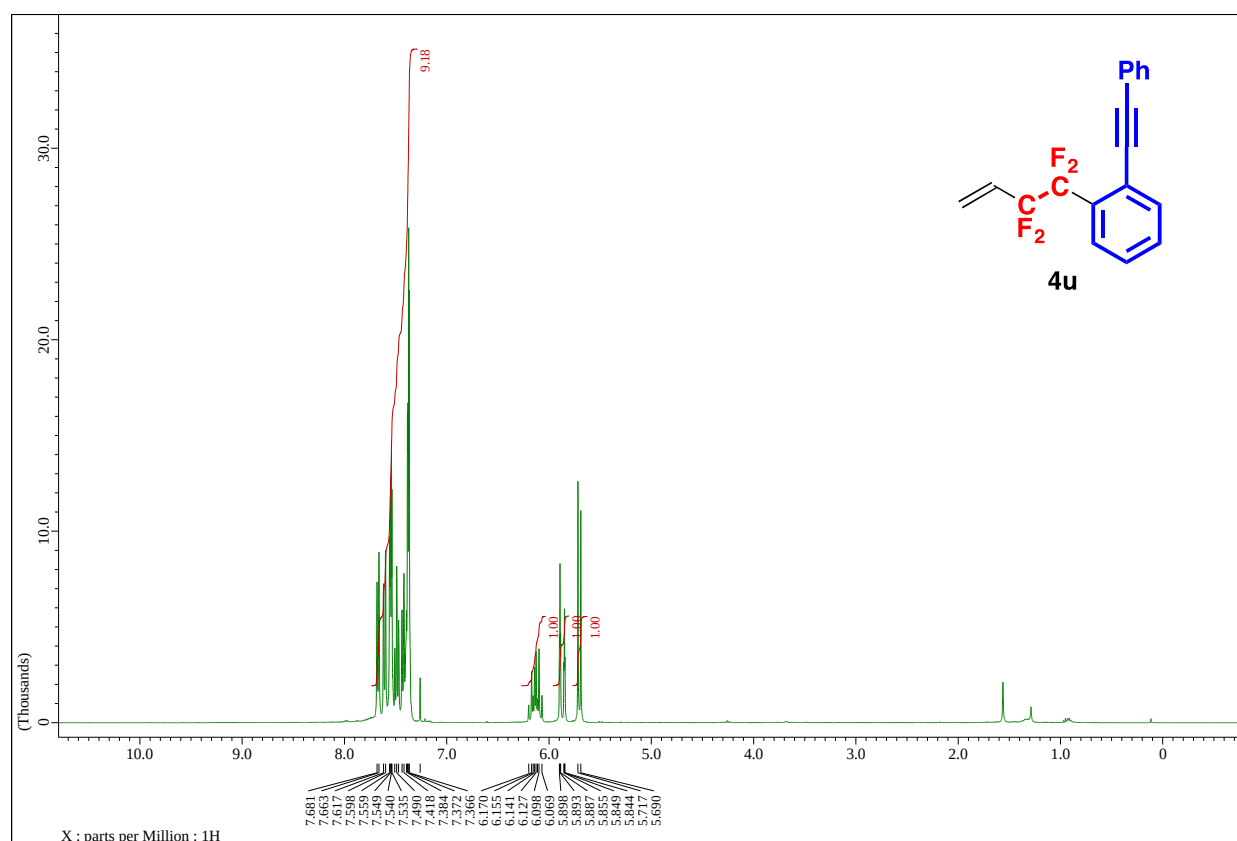
^{13}C NMR Spectrum of 3,3,4,4-tetrafluoro-4-(2-iodophenyl)but-1-ene (**4t**)



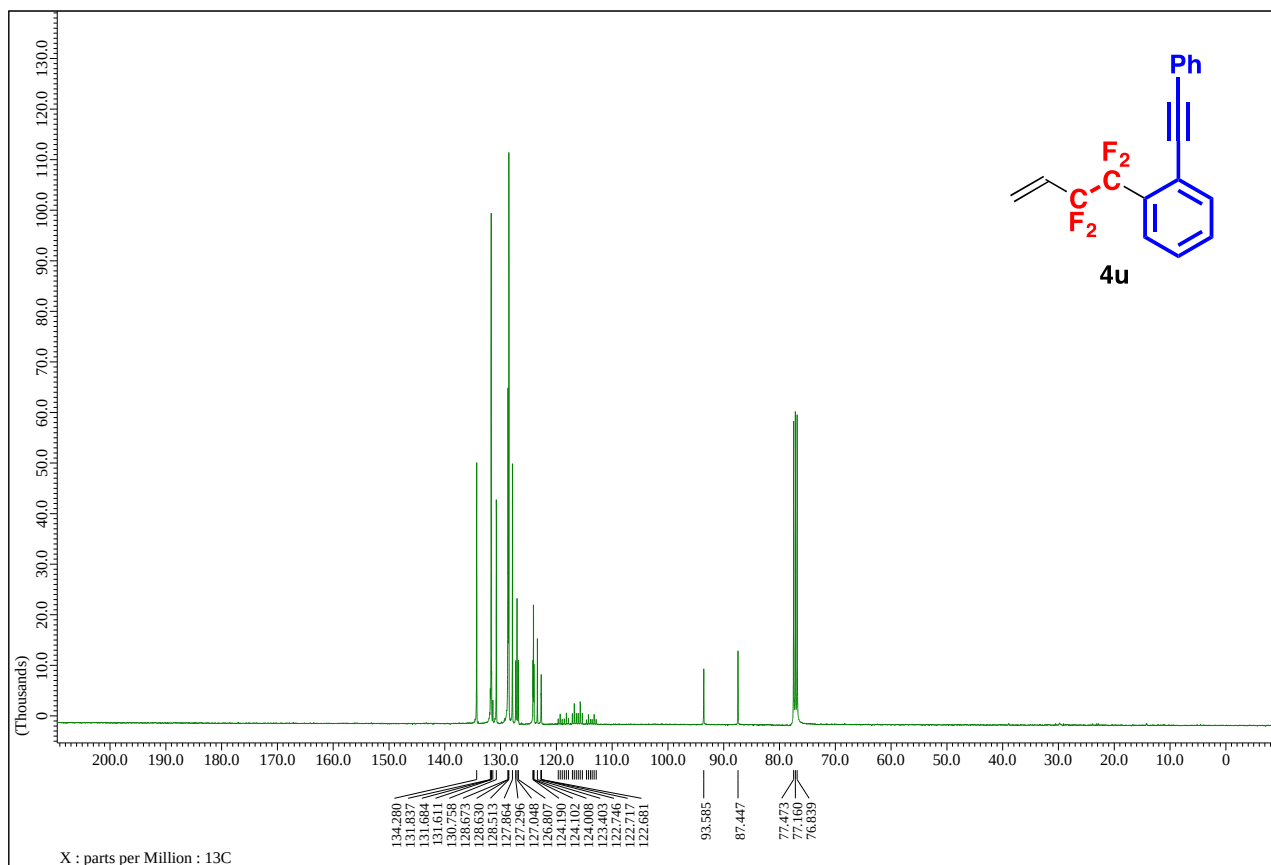
^{13}C NMR Spectrum of 3,3,4,4-tetrafluoro-4-(2-iodophenyl)but-1-ene (**4t**)



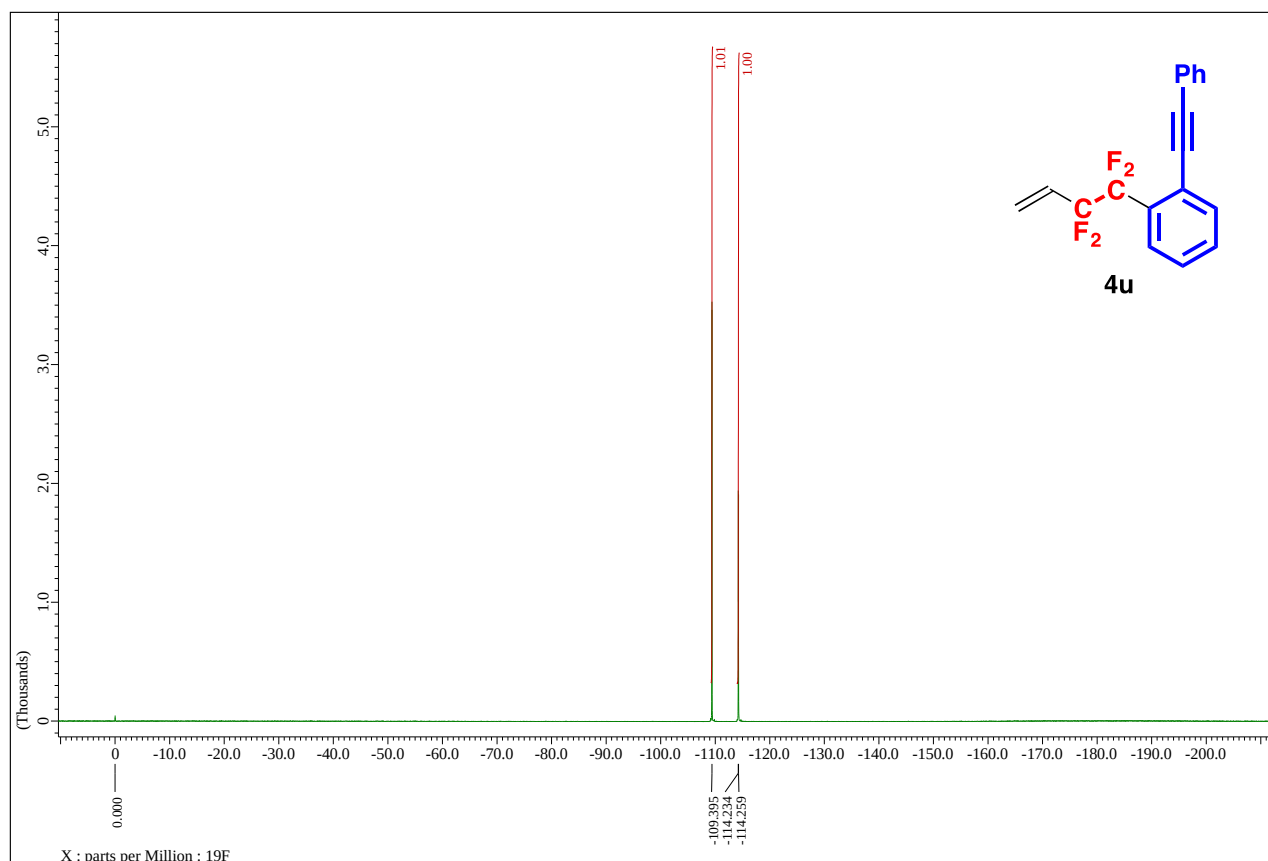
^1H NMR Spectrum of 1-(2-phenylethynyl)-2-(2,2,3,3-tetrafluorobut-3-en-1-yl)benzene (**4u**)



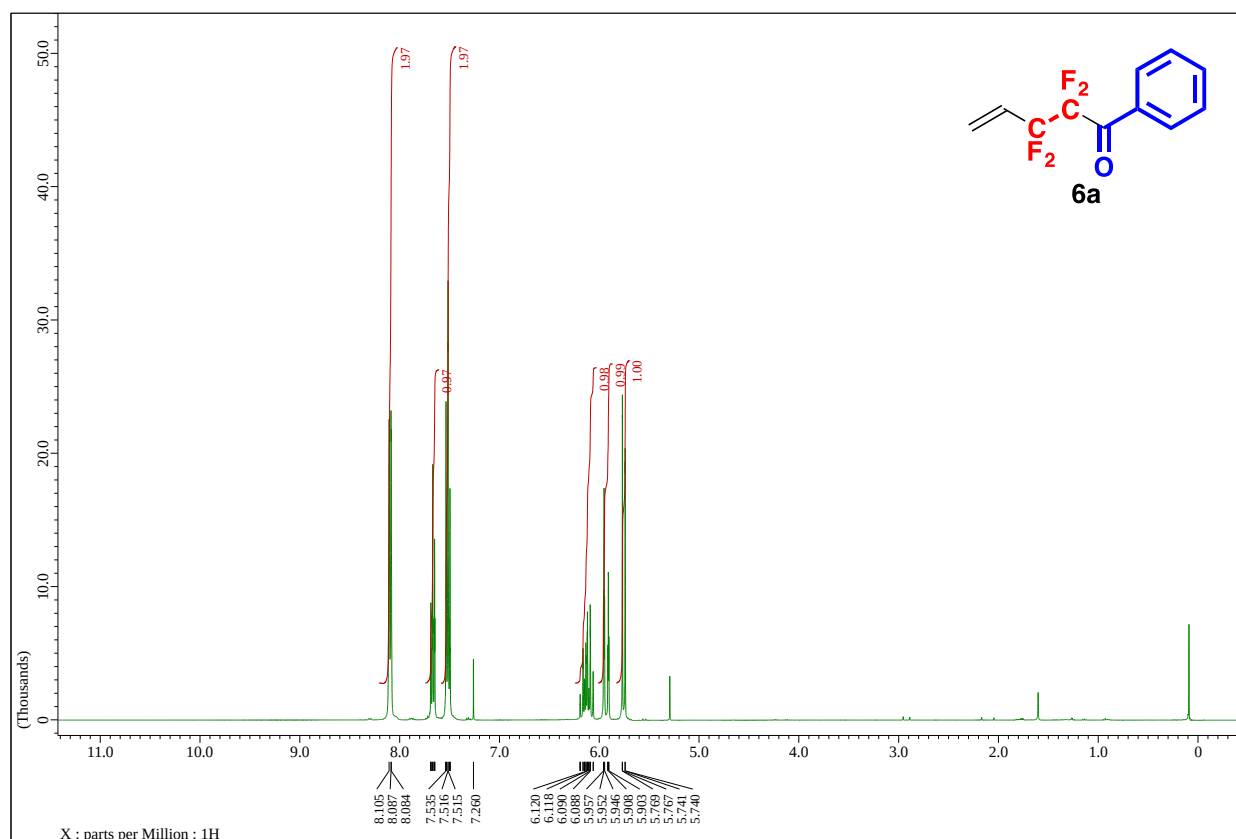
^{13}C NMR Spectrum of 1-(2-phenylethynyl)-2-(2,2,3,3-tetrafluorobut-3-en-1-yl)benzene (**4u**)



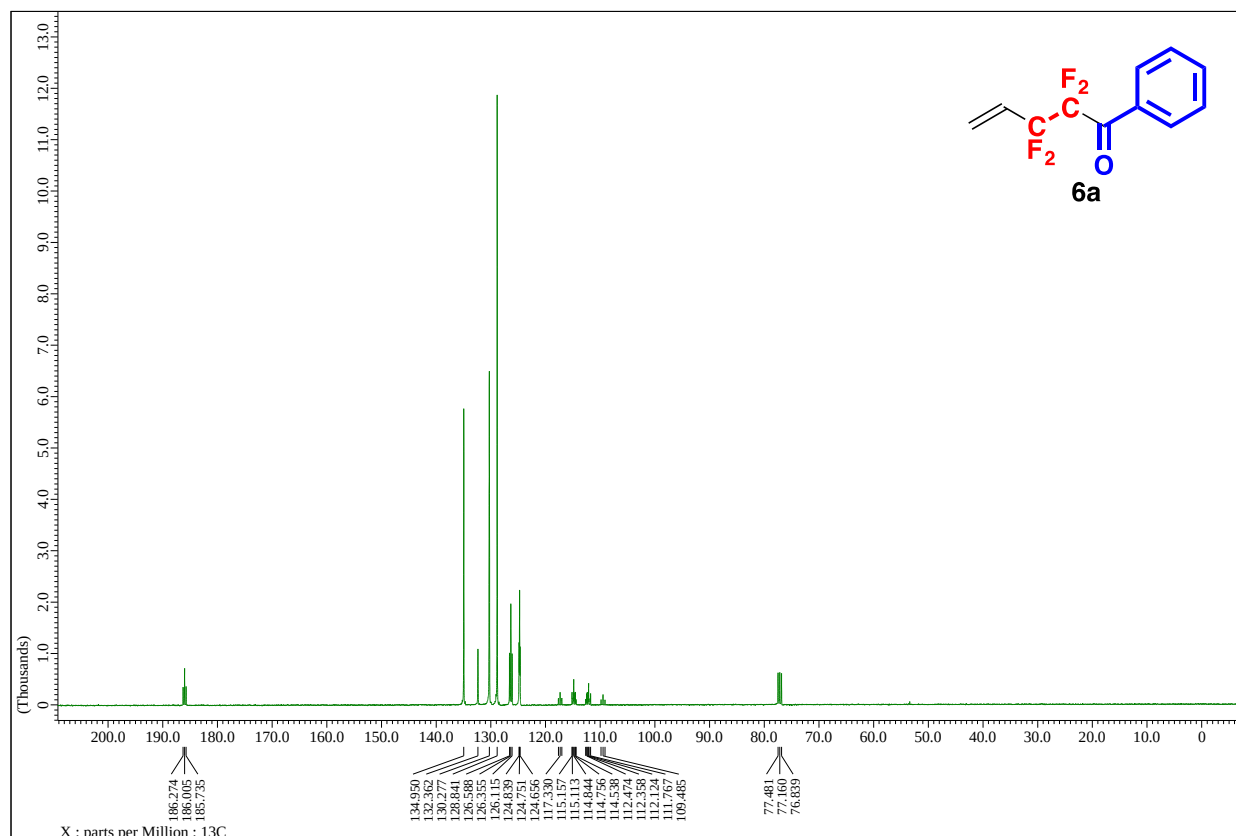
¹⁹F NMR Spectrum of 1-(2-phenylethynyl)-2-(2,2,3,3-tetrafluorobut-3-en-1-yl)benzene (**4u**)



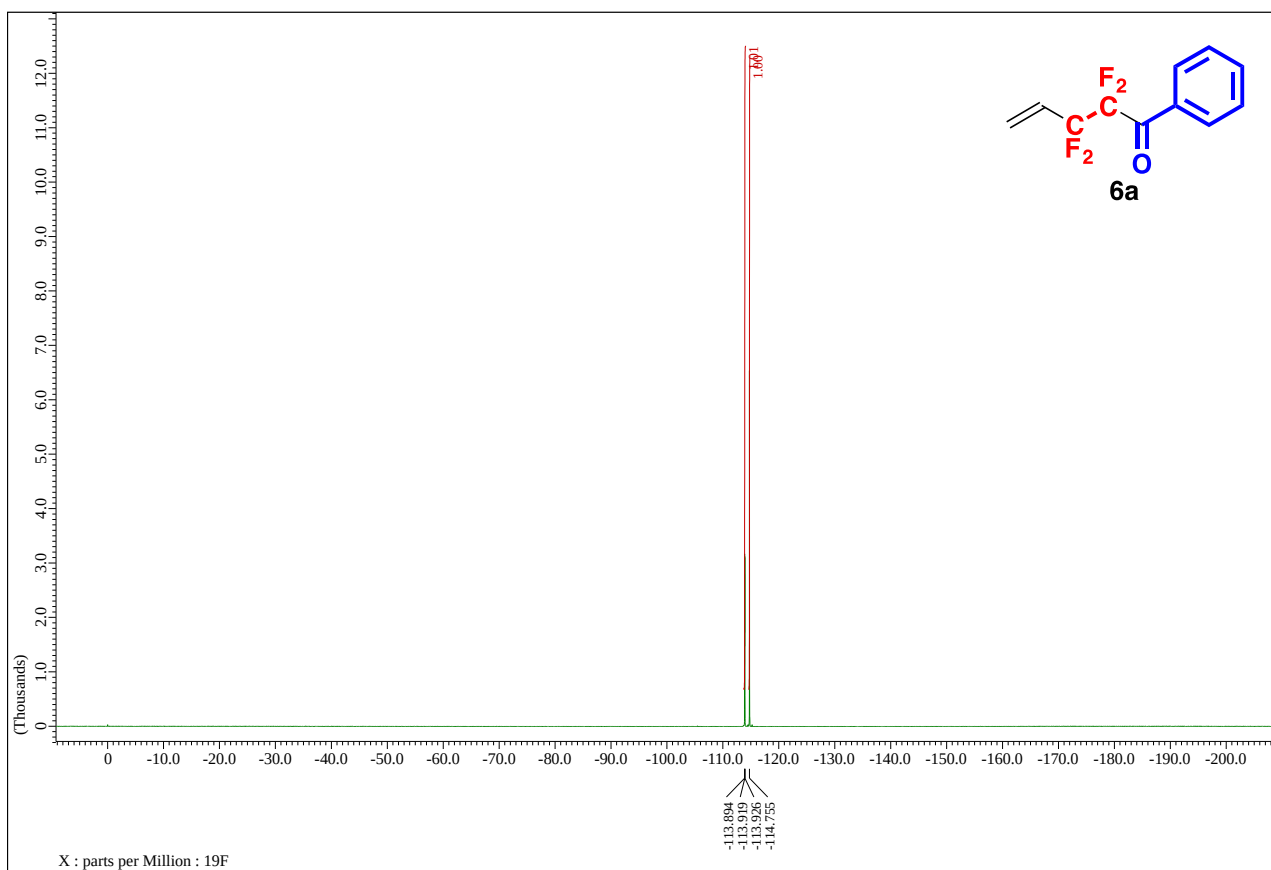
¹H NMR Spectrum of 2,2,3,3-tetrafluoro-1-phenylpent-4-en-1-one (6a)



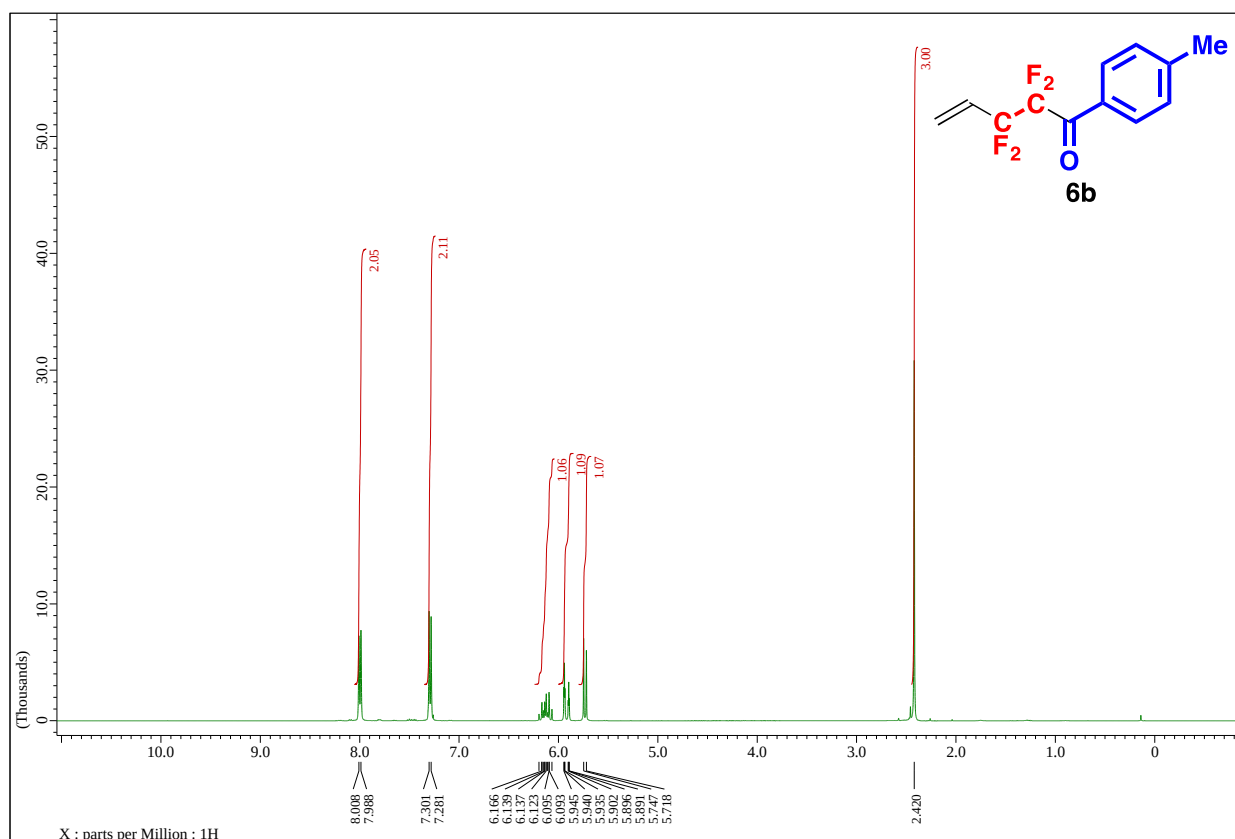
¹³C NMR Spectrum of 2,2,3,3-tetrafluoro-1-phenylpent-4-en-1-one (6a)



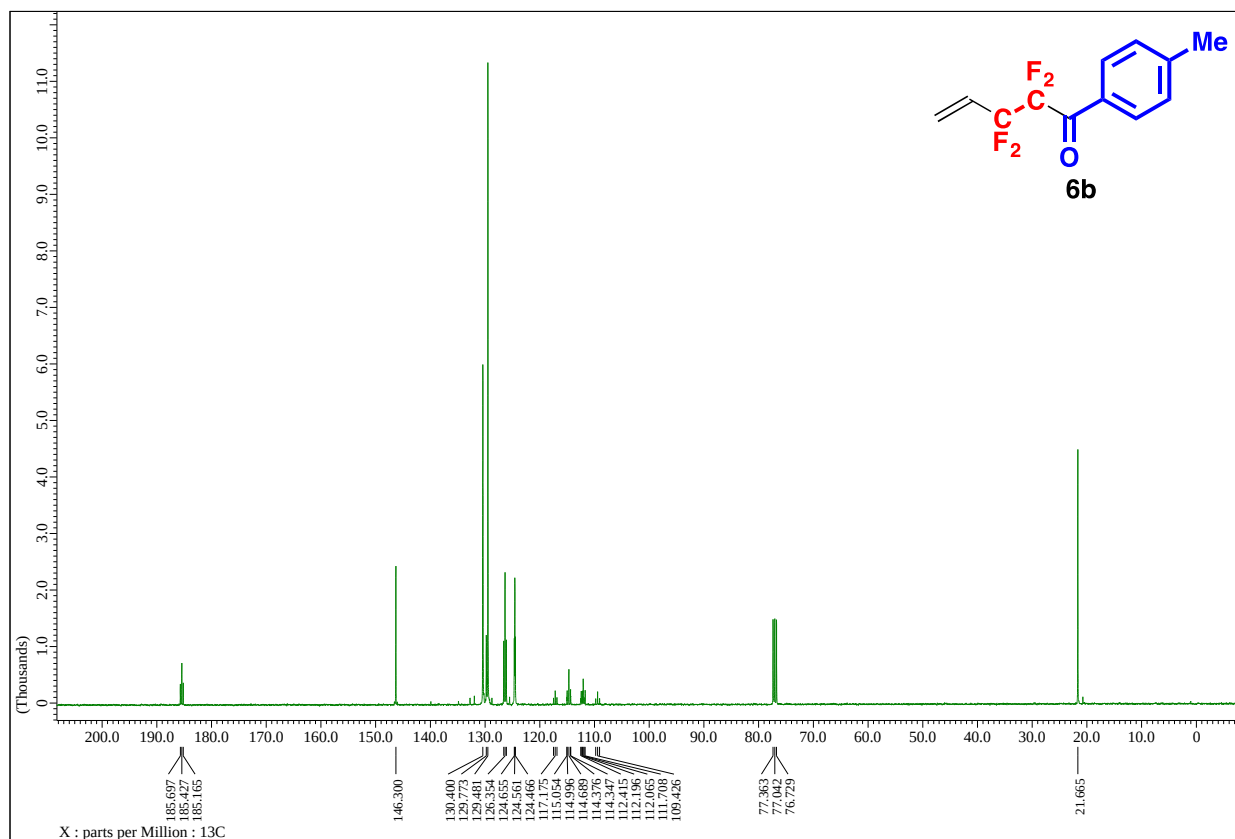
^{19}F NMR Spectrum of 2,2,3,3-tetrafluoro-1-phenylpent-4-en-1-one (**6a**)



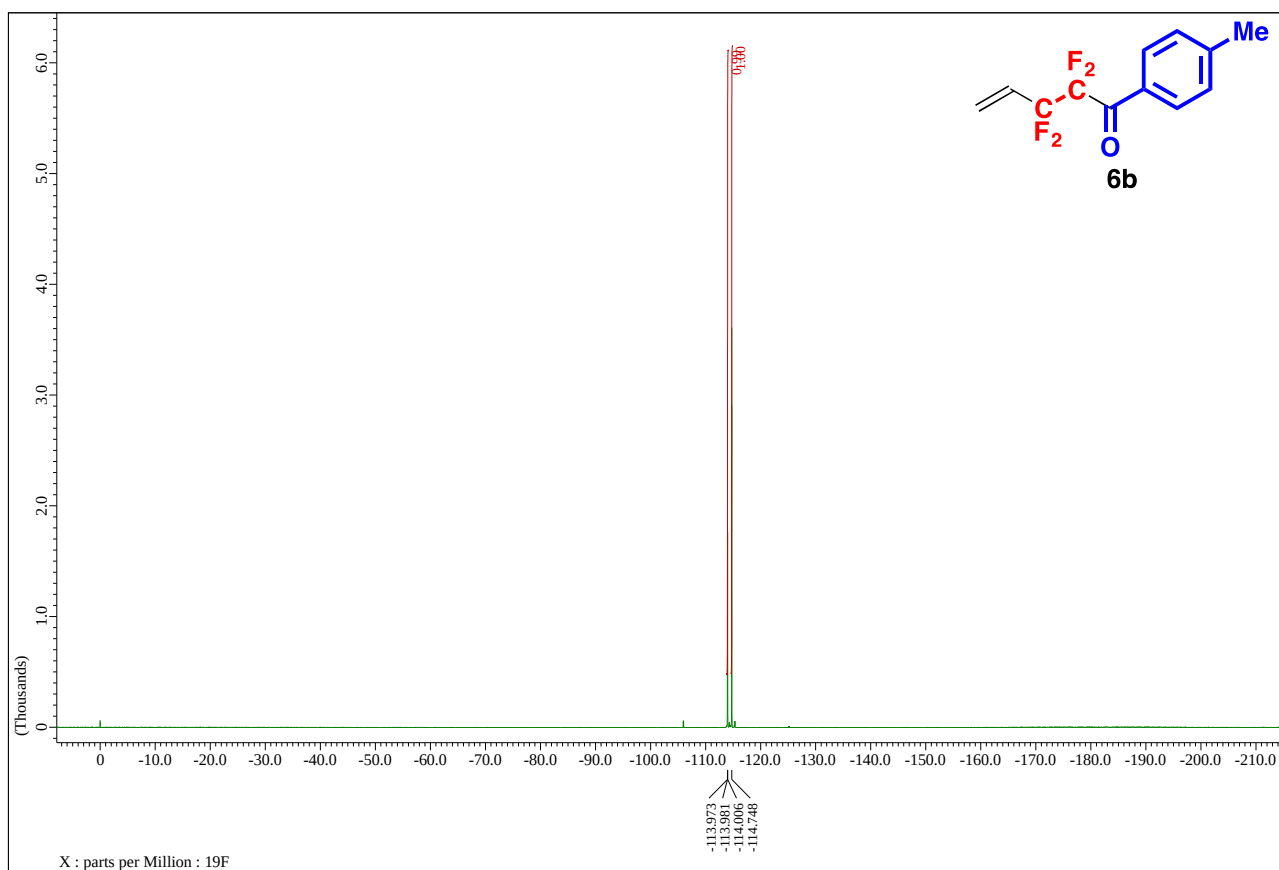
¹H NMR Spectrum of 2,2,3,3-tetrafluoro-1-(4-methylphenyl)pent-4-en-1-one (**6b**)



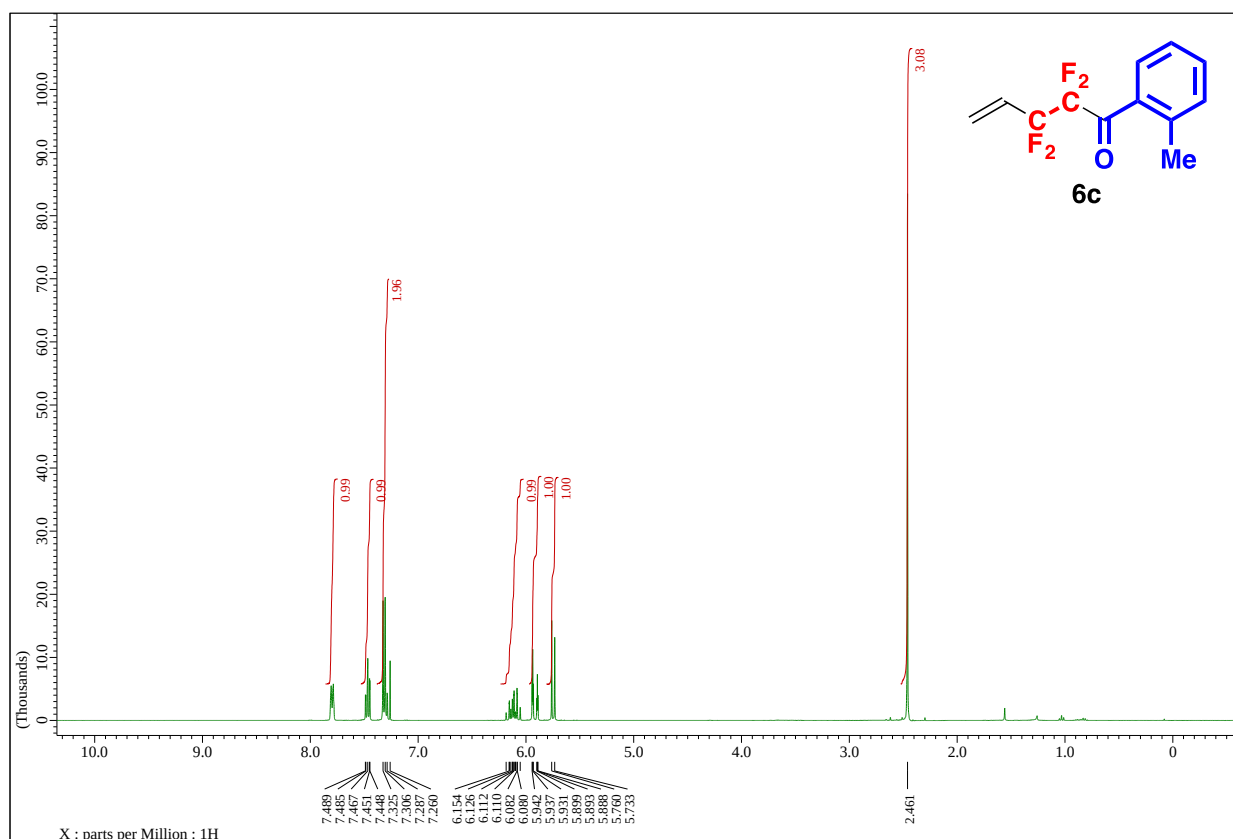
¹³C NMR Spectrum of 2,2,3,3-tetrafluoro-1-(4-methylphenyl)pent-4-en-1-one (**6b**)



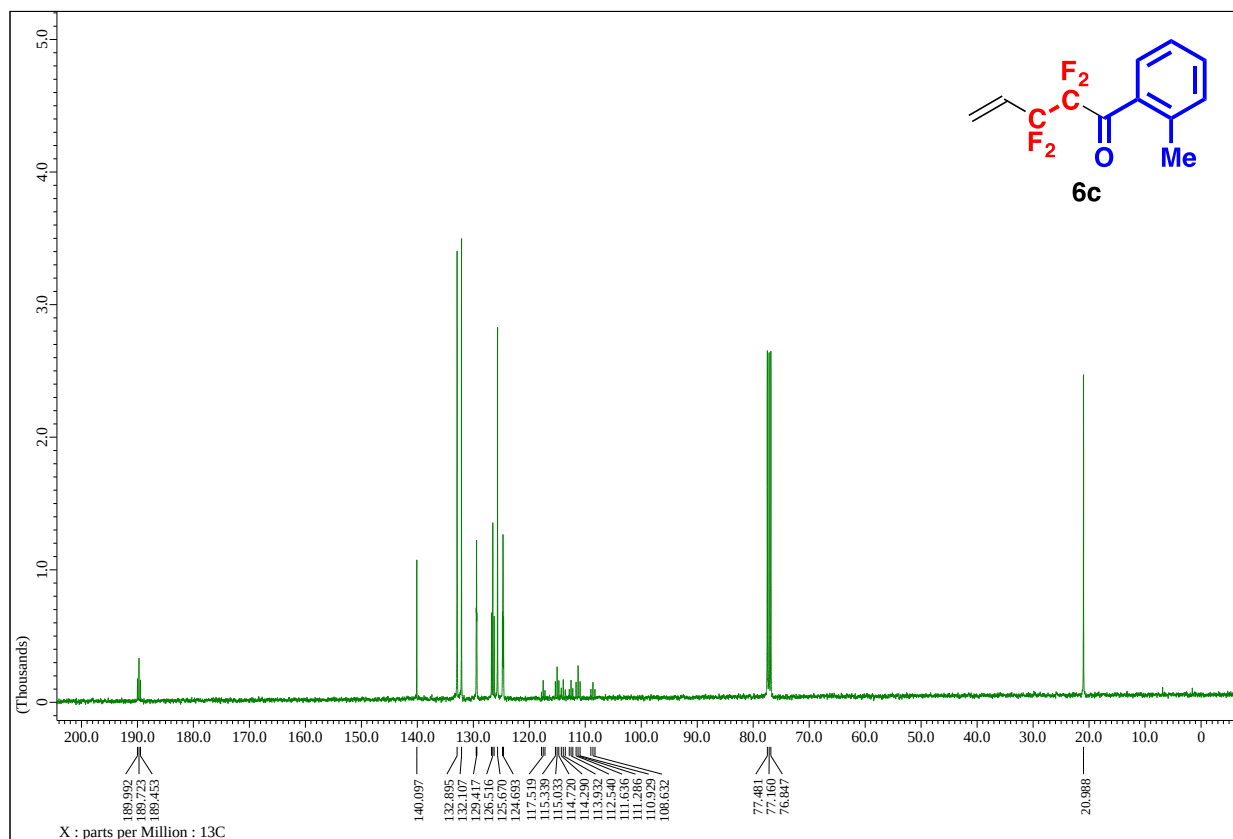
¹⁹F NMR Spectrum of 2,2,3,3-tetrafluoro-1-(4-methylphenyl)pent-4-en-1-one (**6b**)



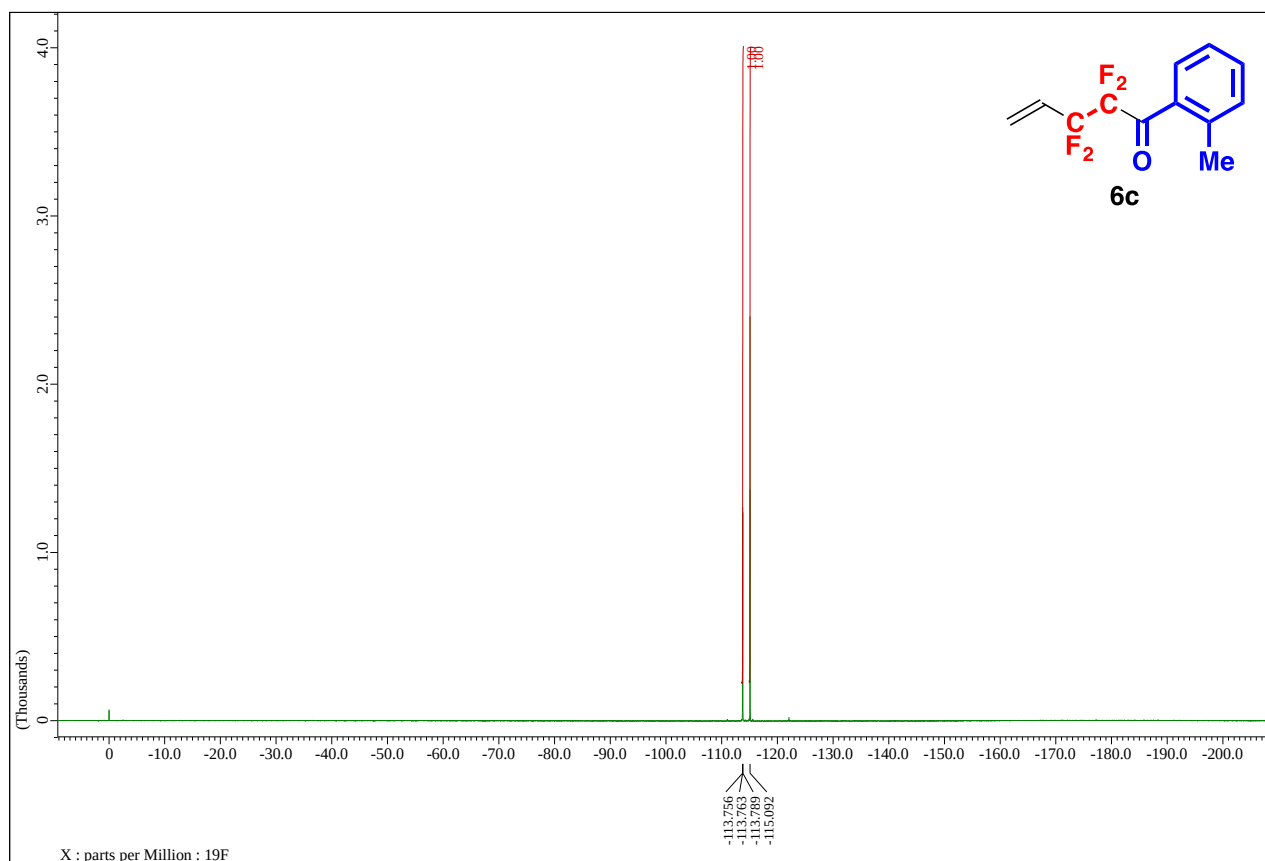
^1H NMR Spectrum of 2,2,3,3-tetrafluoro-1-(2-methylphenyl)pent-4-en-1-one (**6c**)



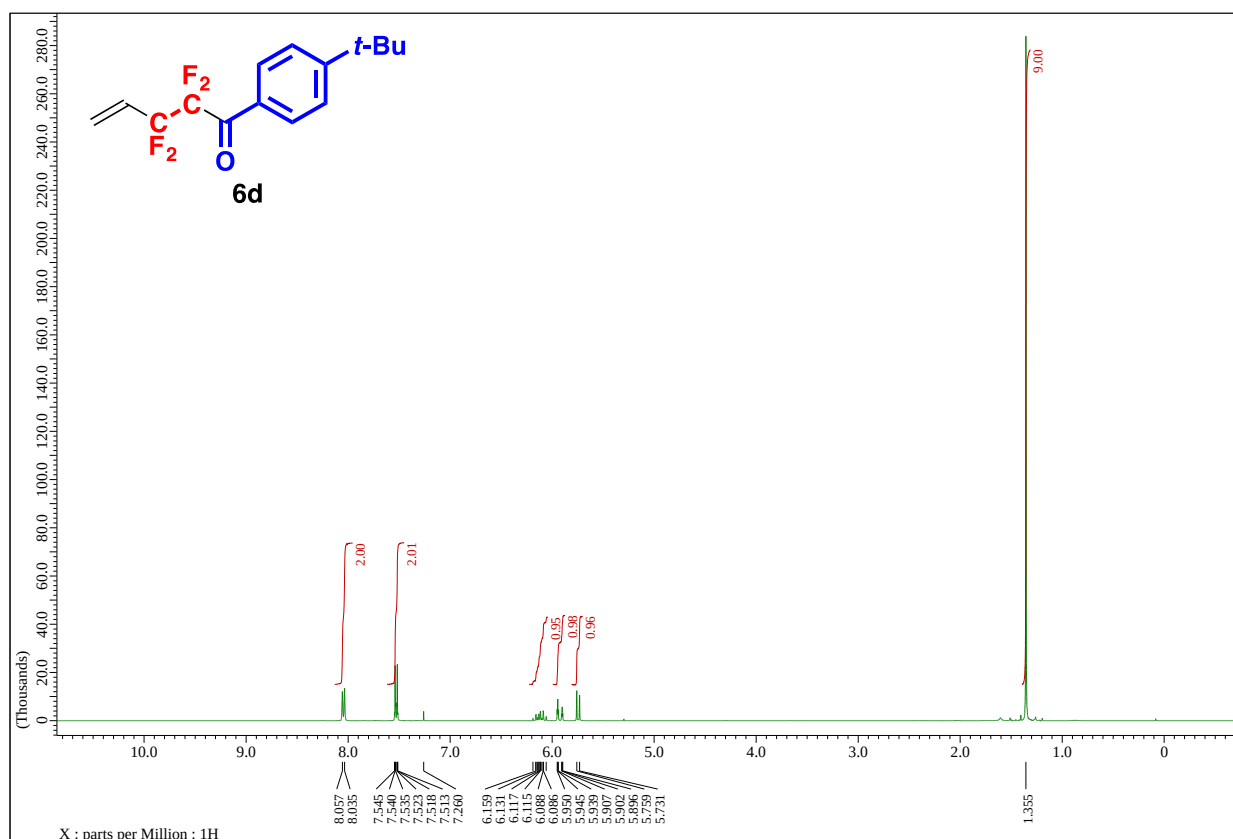
^{13}C NMR Spectrum of 2,2,3,3-tetrafluoro-1-(2-methylphenyl)pent-4-en-1-one (**6c**)



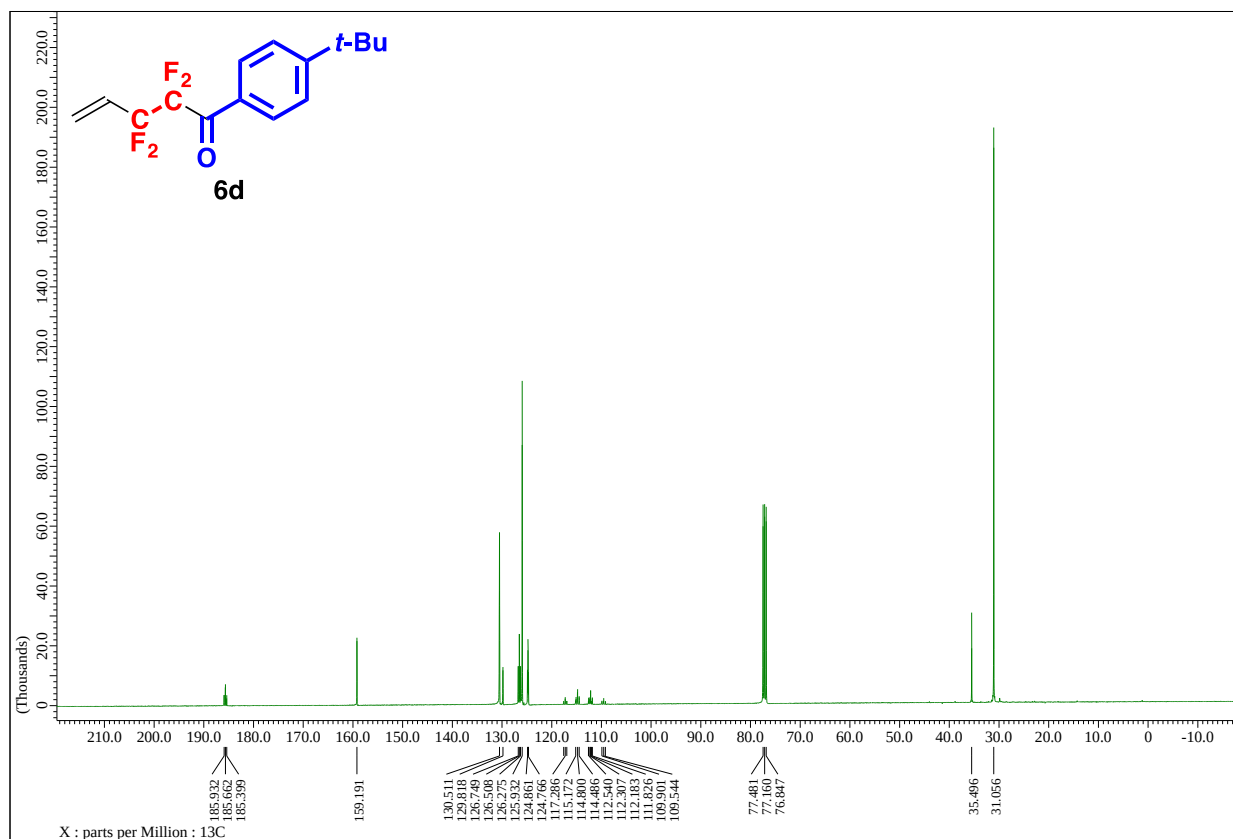
¹⁹F NMR Spectrum of 2,2,3,3-tetrafluoro-1-(2-methylphenyl)pent-4-en-1-one (**6c**)



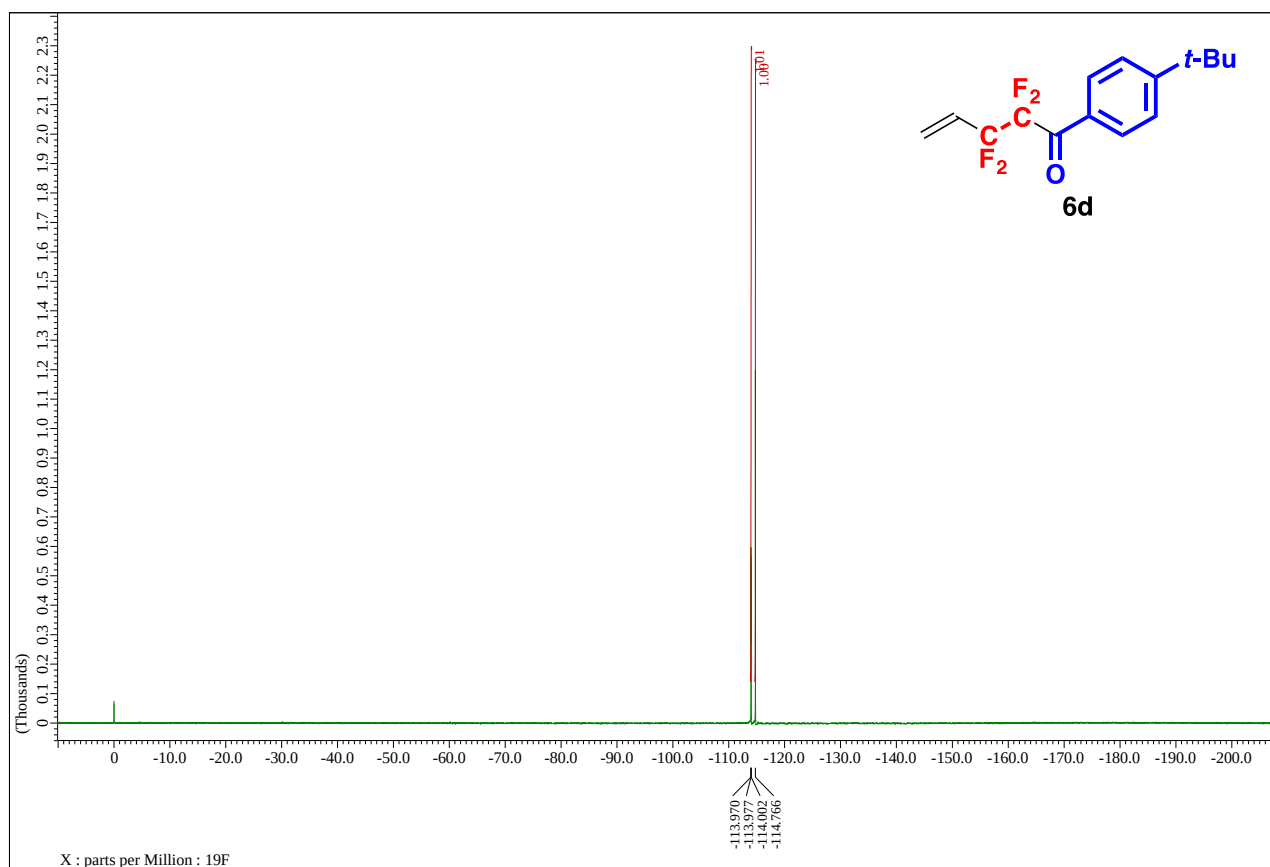
¹H NMR Spectrum of 1-(4-*tert*-butylphenyl)-2,2,3,3-tetrafluoropent-4-en-1-one (**6d**)



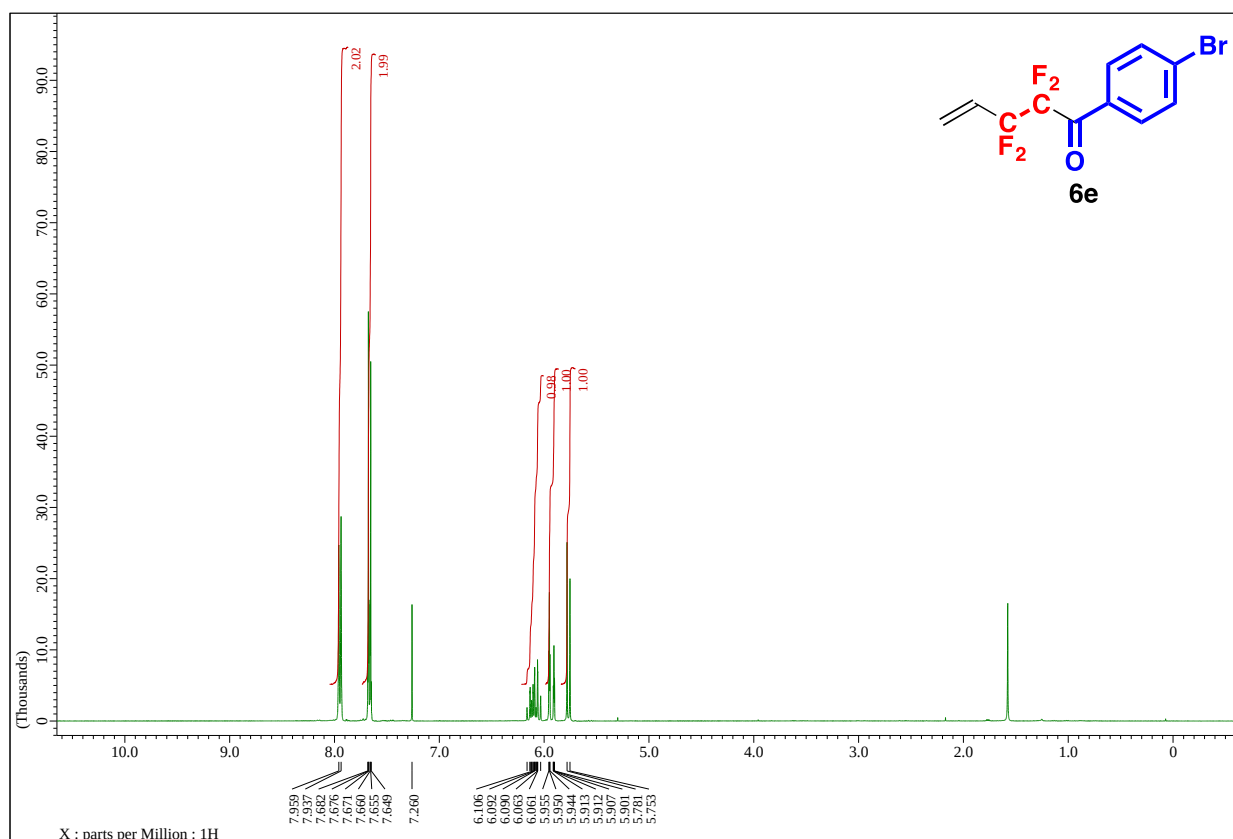
¹³C NMR Spectrum of 1-(4-*tert*-butylphenyl)-2,2,3,3-tetrafluoropent-4-en-1-one (**6d**)



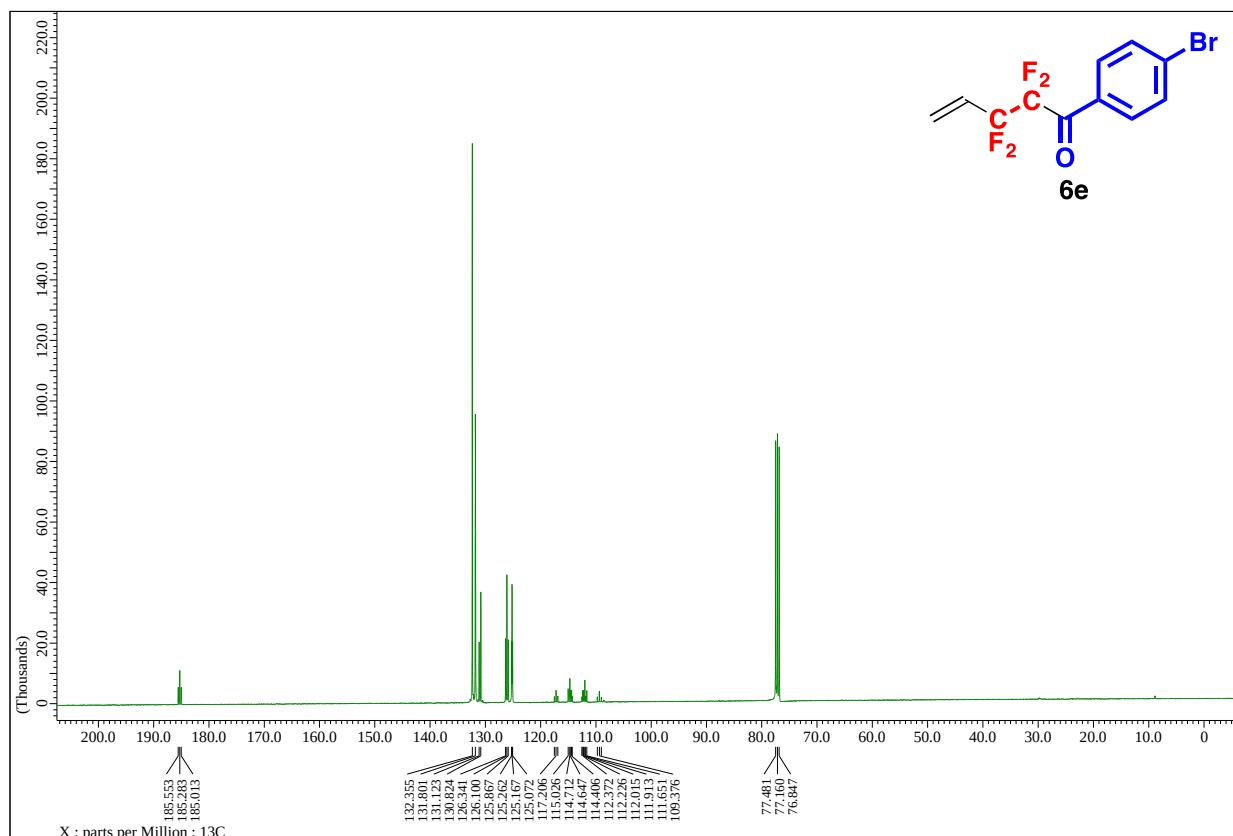
^{19}F NMR Spectrum of 1-(4-*tert*-butylphenyl)-2,2,3,3-tetrafluoropent-4-en-1-one (**6d**)



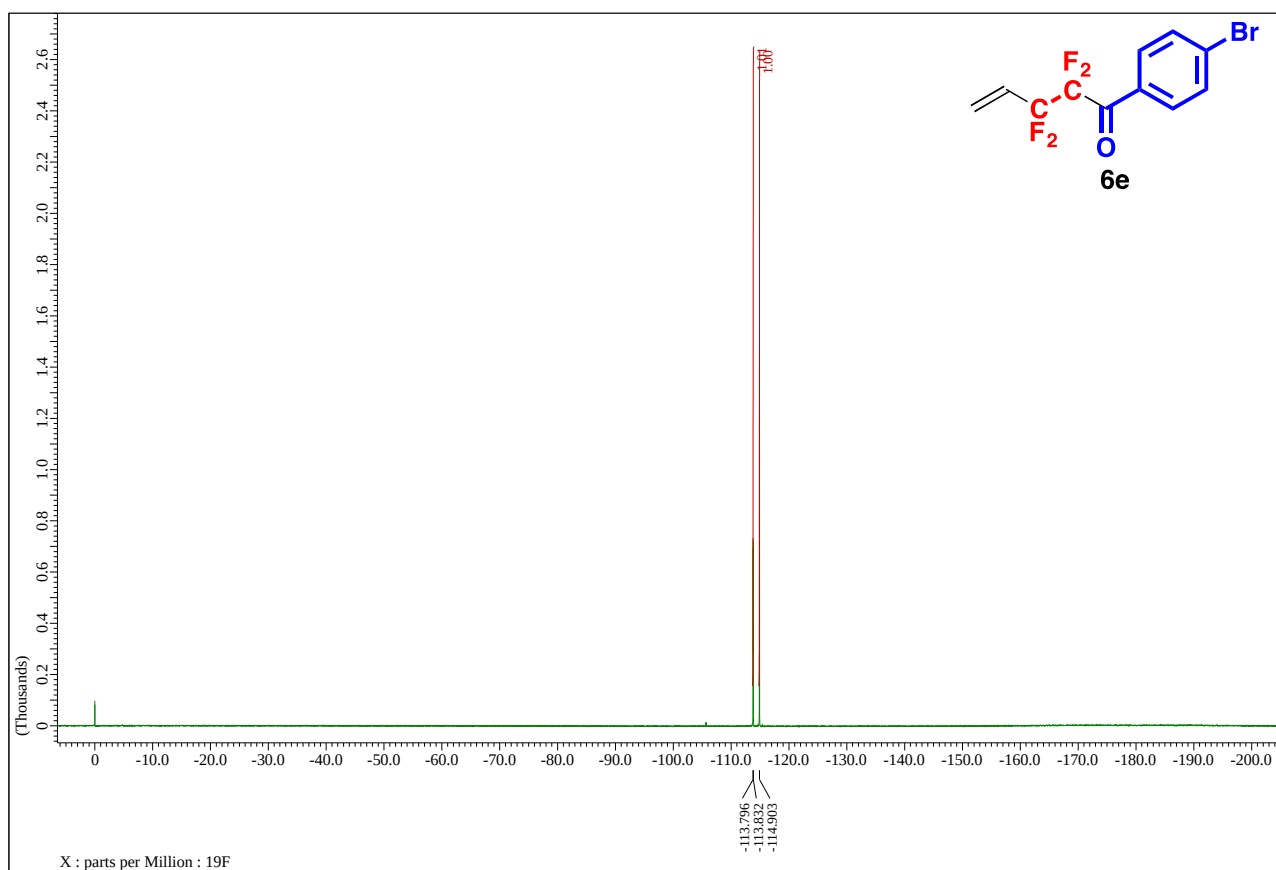
¹H NMR Spectrum of 1-(4-bromophenyl)-2,2,3,3-tetrafluoropent-4-en-1-one (**6e**)



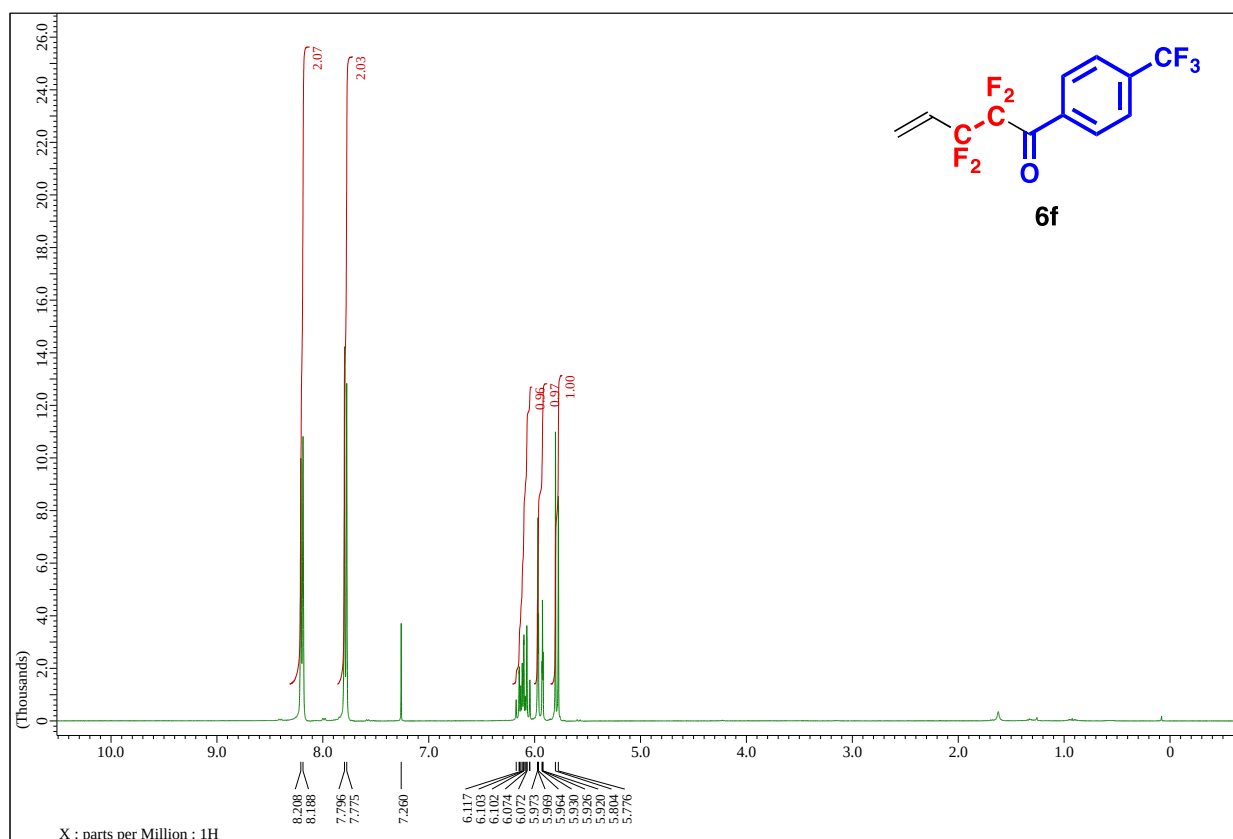
¹³C NMR Spectrum of 1-(4-bromophenyl)-2,2,3,3-tetrafluoropent-4-en-1-one (**6e**)



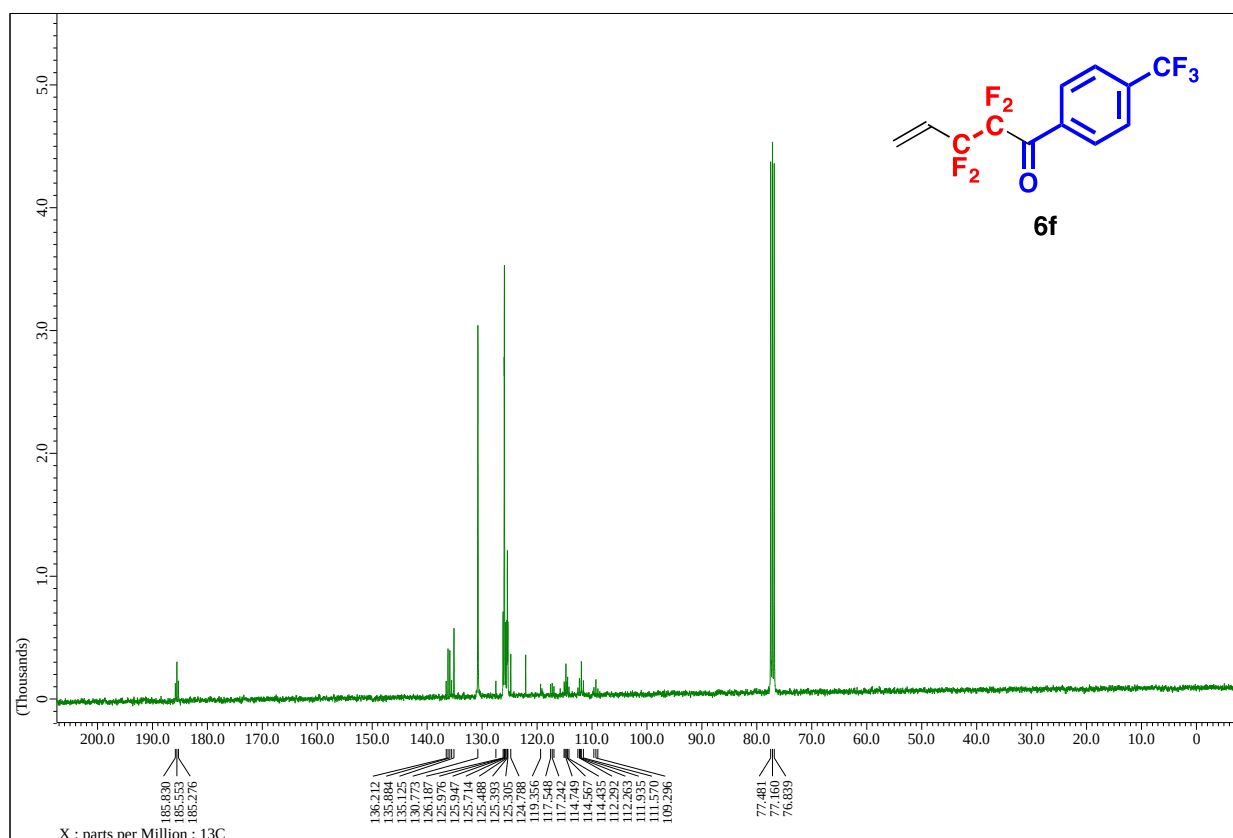
¹⁹F NMR Spectrum of 1-(4-bromophenyl)-2,2,3,3-tetrafluoropent-4-en-1-one (**6e**)



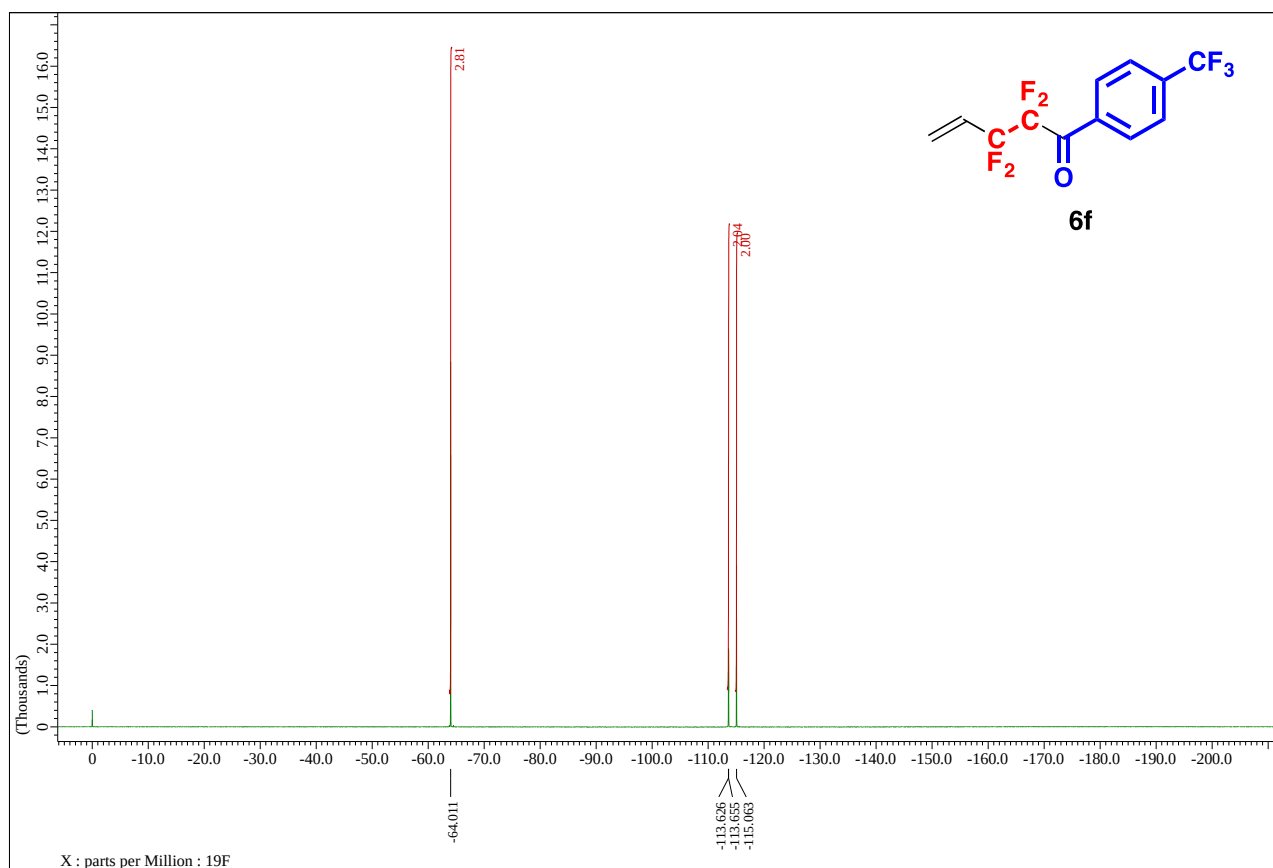
^1H NMR Spectrum of 2,2,3,3-tetrafluoro-1-(4-trifluoromethylphenyl)pent-4-en-1-one (**6f**)



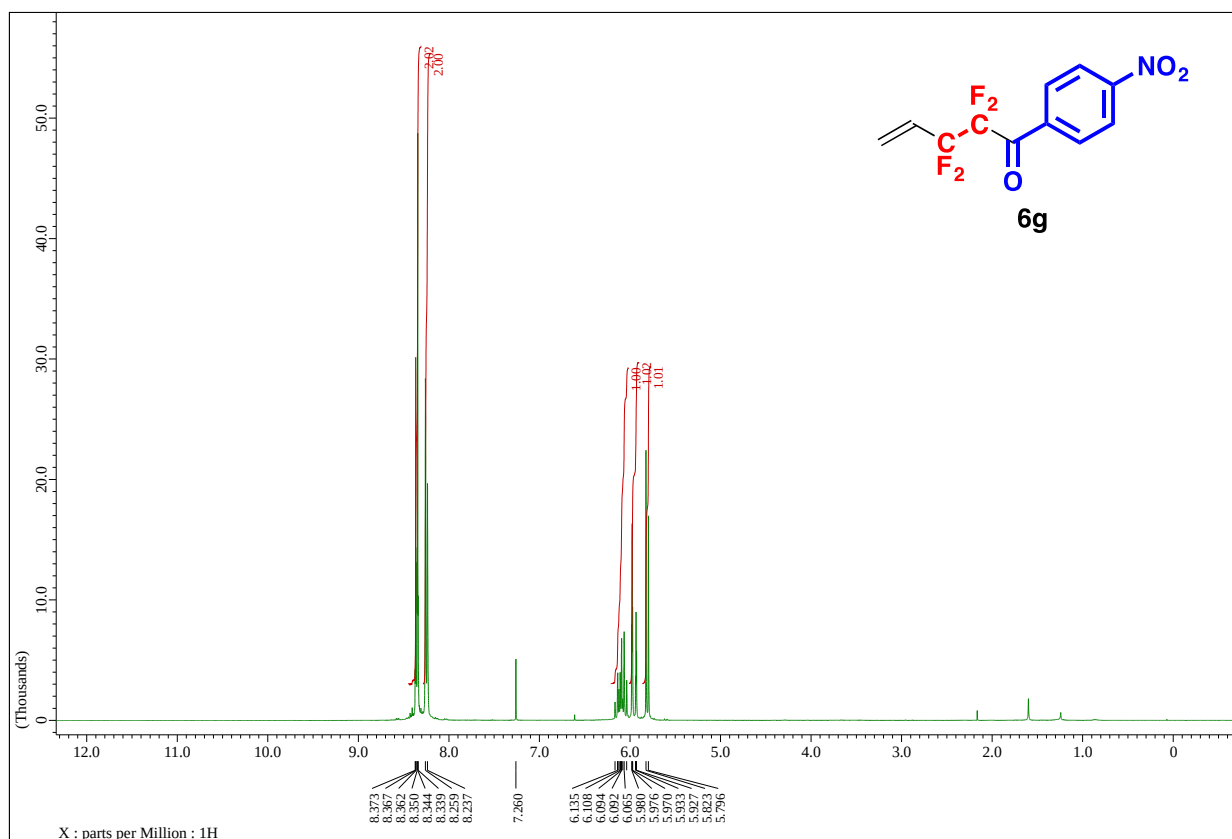
^{13}C NMR Spectrum of 2,2,3,3-tetrafluoro-1-(4-trifluoromethylphenyl)pent-4-en-1-one (**6f**)



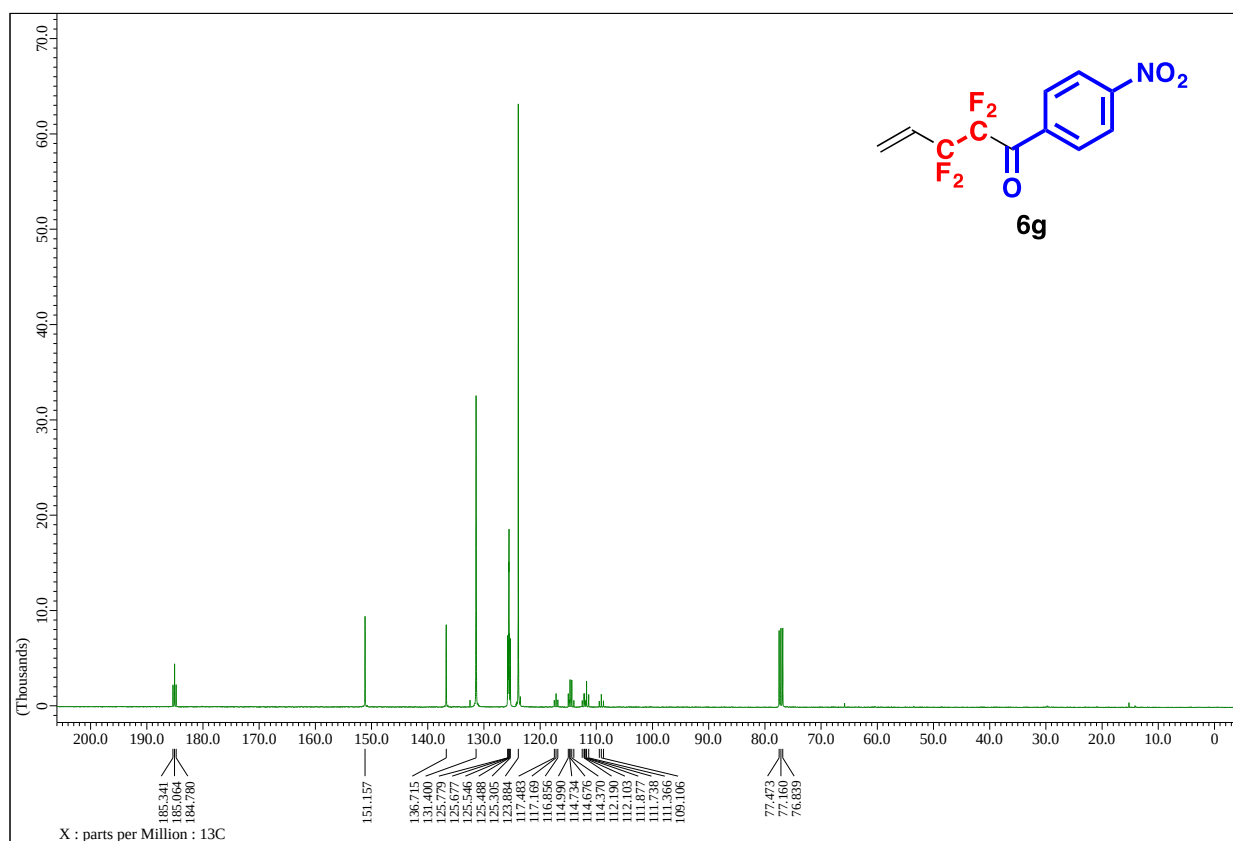
^{19}F NMR Spectrum of 2,2,3,3-tetrafluoro-1-(4-trifluoromethylphenyl)pent-4-en-1-one (**6f**)



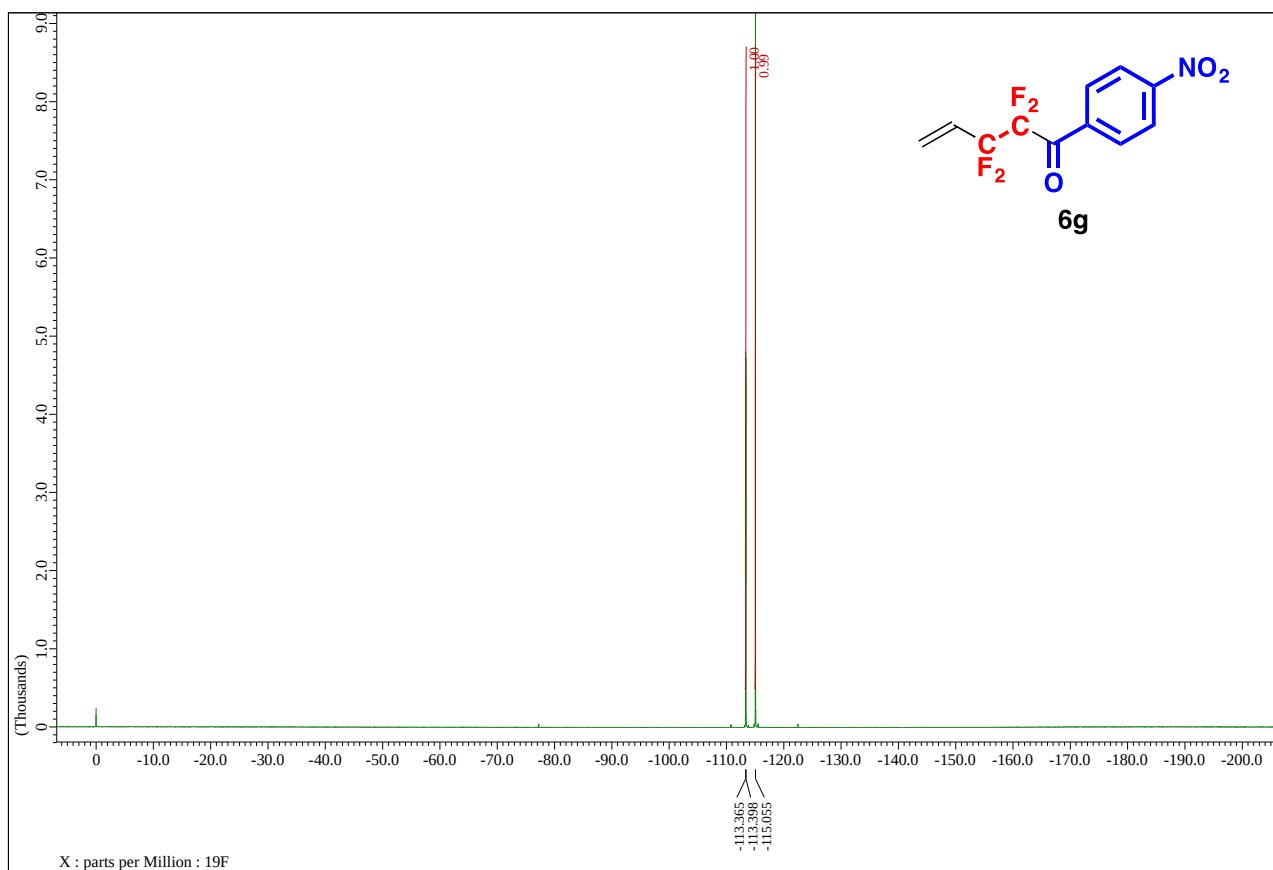
¹H NMR Spectrum of 2,2,3,3-tetrafluoro-1-(4-nitrophenyl)pent-4-en-1-one (**6g**)



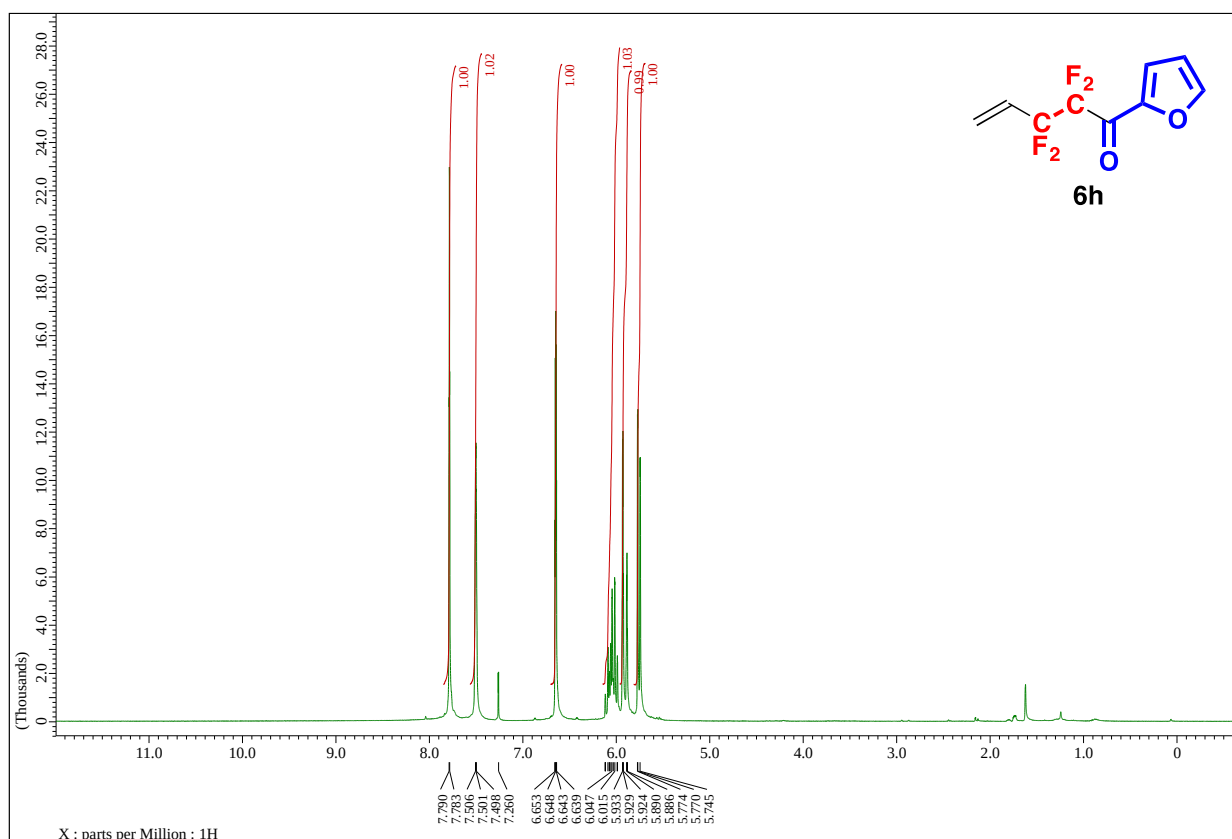
¹³C NMR Spectrum of 2,2,3,3-tetrafluoro-1-(4-nitrophenyl)pent-4-en-1-one (**6g**)



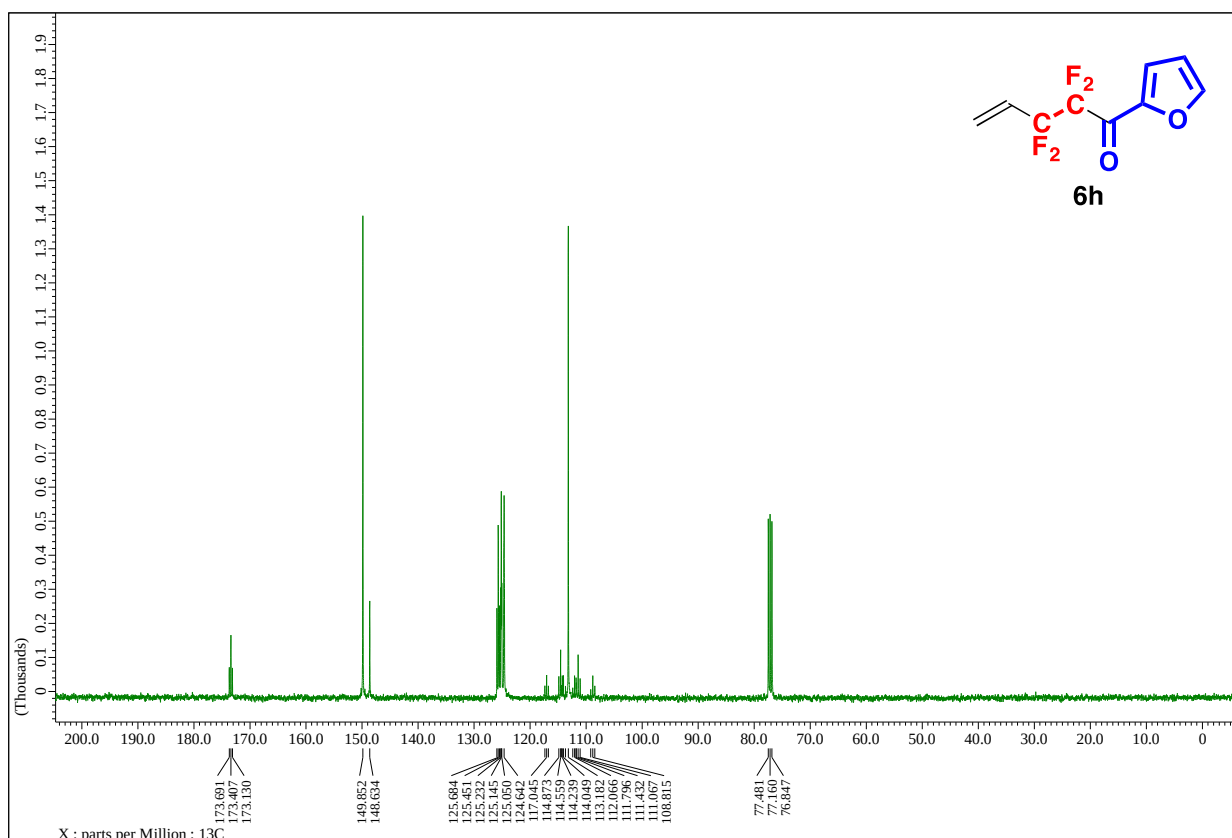
^{19}F NMR Spectrum of 2,2,3,3-tetrafluoro-1-(4-nitrophenyl)pent-4-en-1-one (**6g**)



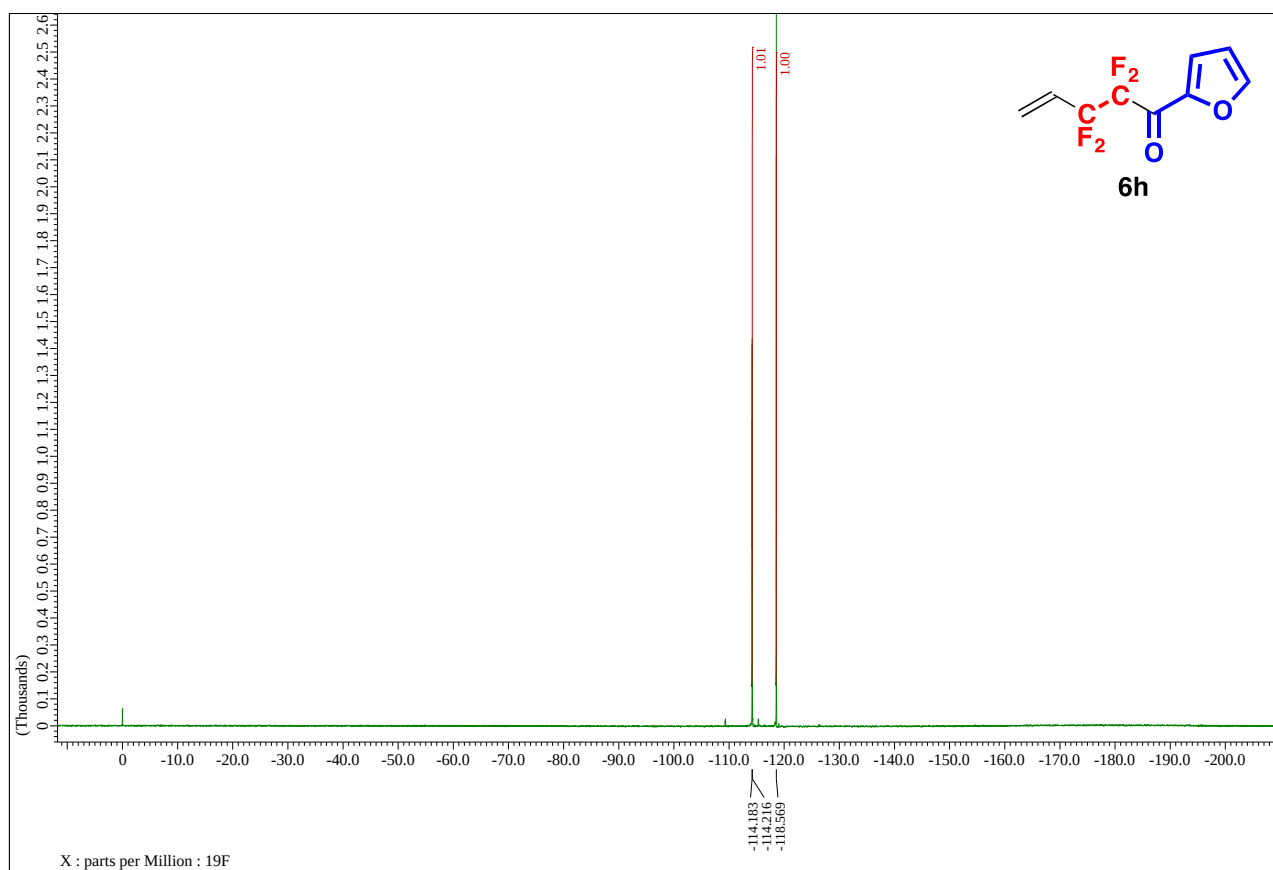
^1H NMR Spectrum of 2,2,3,3-tetrafluoro-1-(furan-2-yl)pent-4-en-1-one (**6h**)

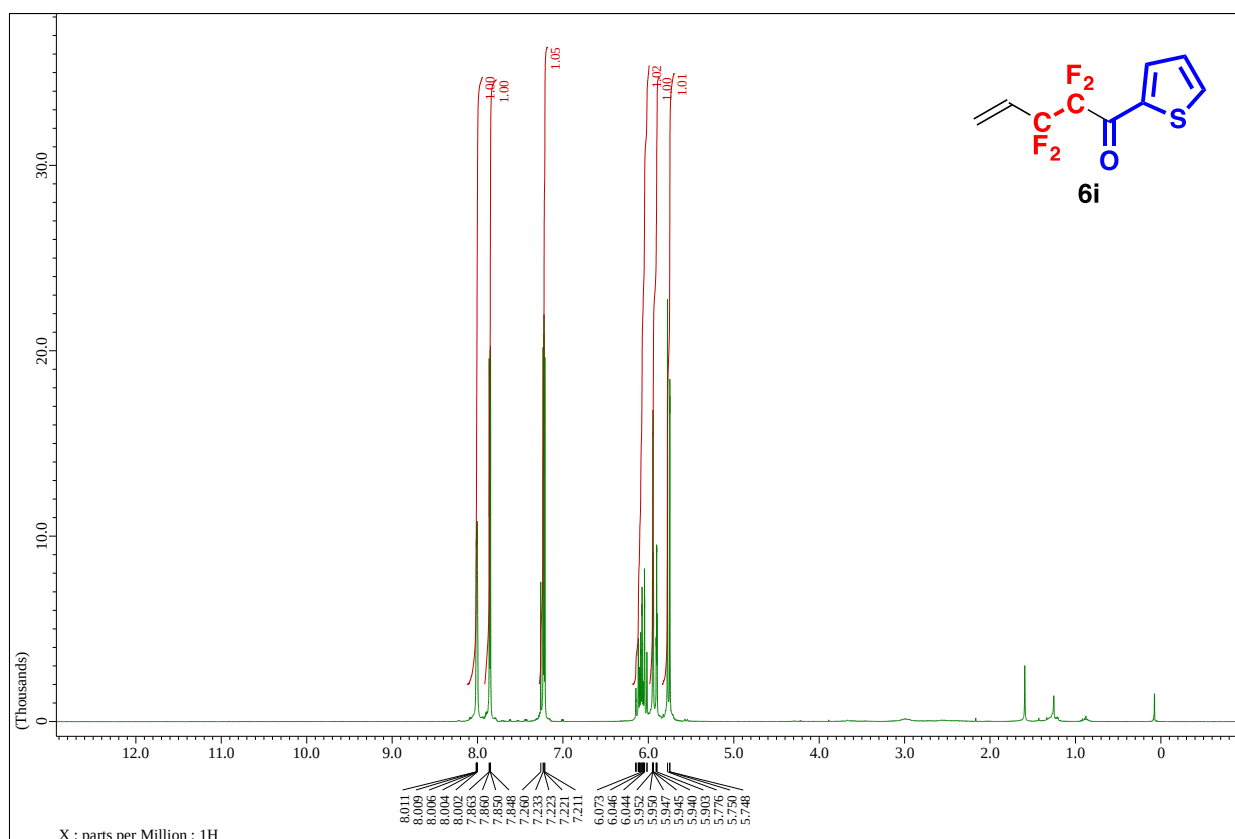


^{13}C NMR Spectrum of 2,2,3,3-tetrafluoro-1-(furan-2-yl)pent-4-en-1-one (**6h**)

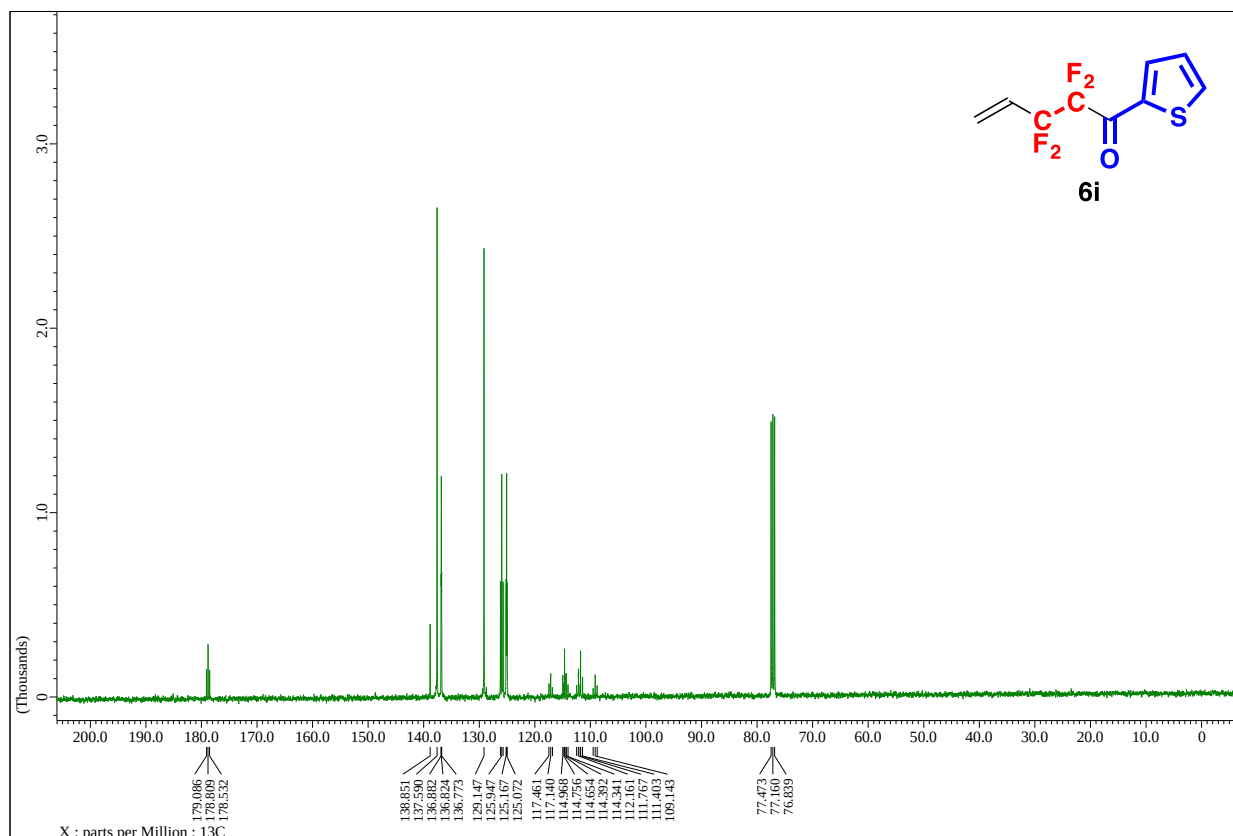


¹⁹F NMR Spectrum of 2,2,3,3-tetrafluoro-1-(furan-2-yl)pent-4-en-1-one (**6h**)

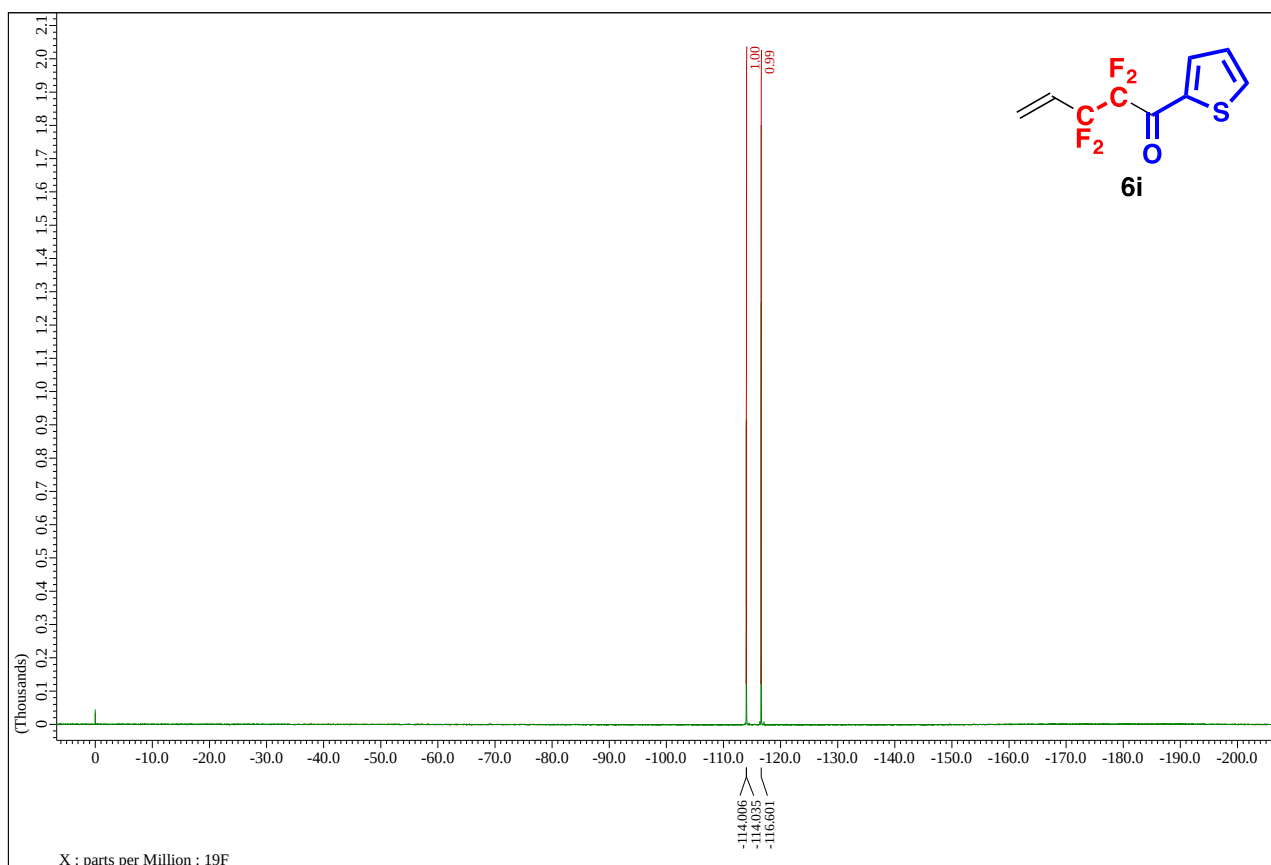


¹H NMR Spectrum of 2,2,3,3-tetrafluoro-1-(thiophen-2-yl)pent-4-en-1-one (**6i**)

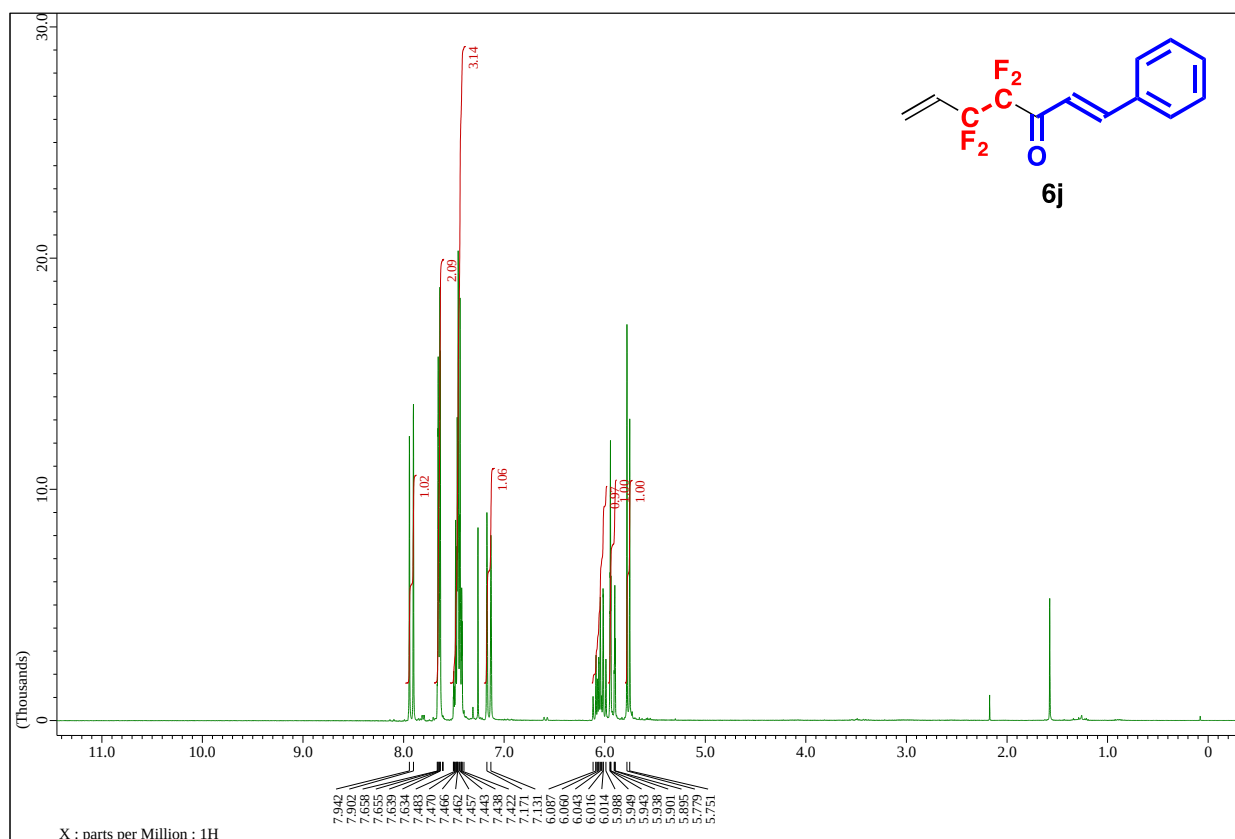
¹³C NMR Spectrum of 2,2,3,3-tetrafluoro-1-(thiophen-2-yl)pent-4-en-1-one (**6i**)



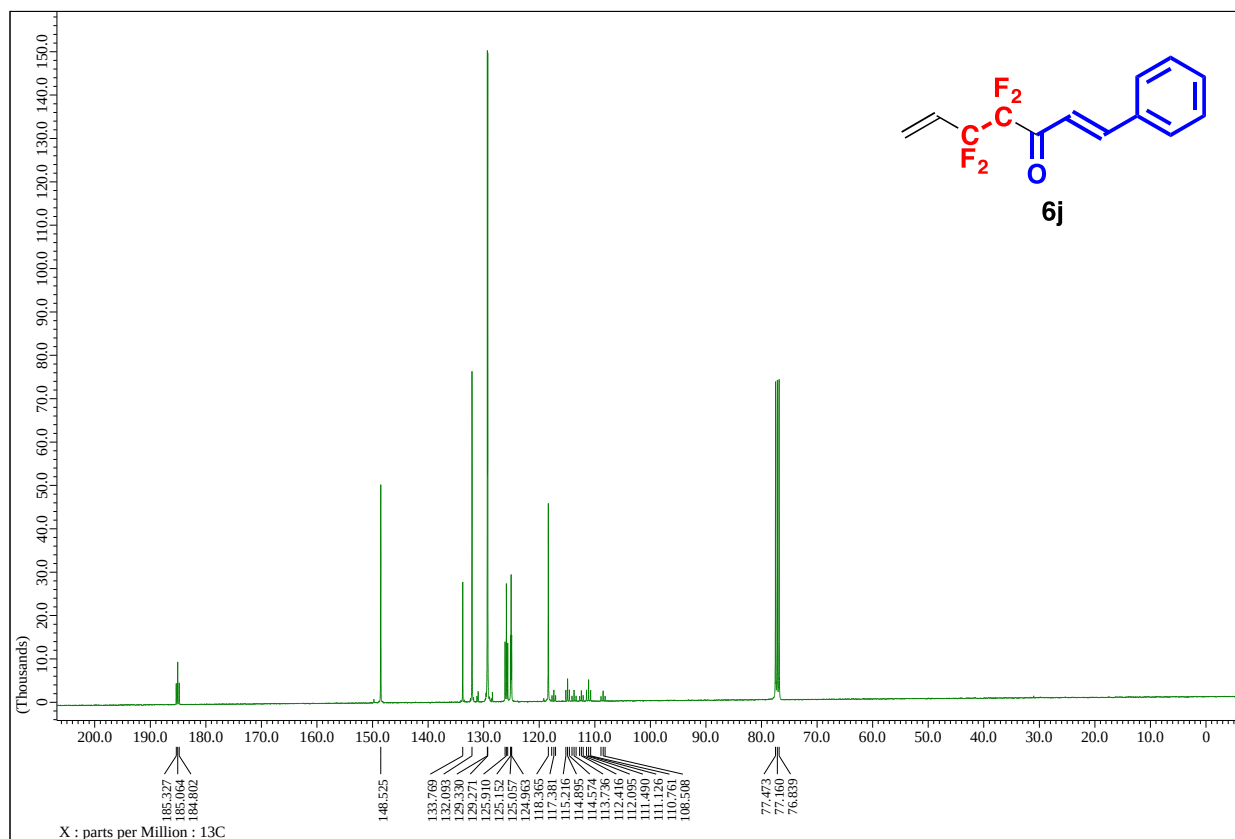
^{19}F NMR Spectrum of 2,2,3,3-tetrafluoro-1-(thiophen-2-yl)pent-4-en-1-one (**6i**)



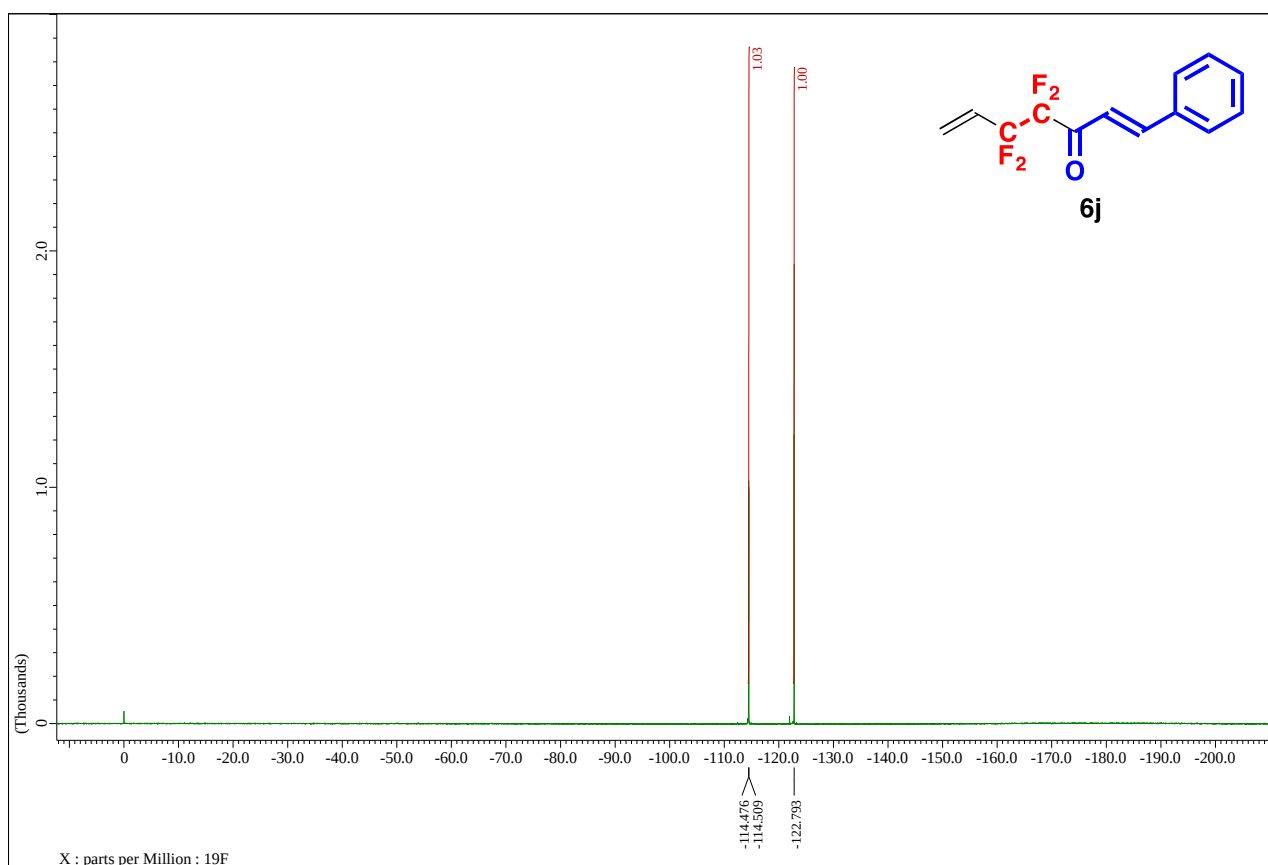
^1H NMR Spectrum of 4,4,5,5-tetrafluoro-1-phenylhept-1,6-dien-3-one (**6j**)



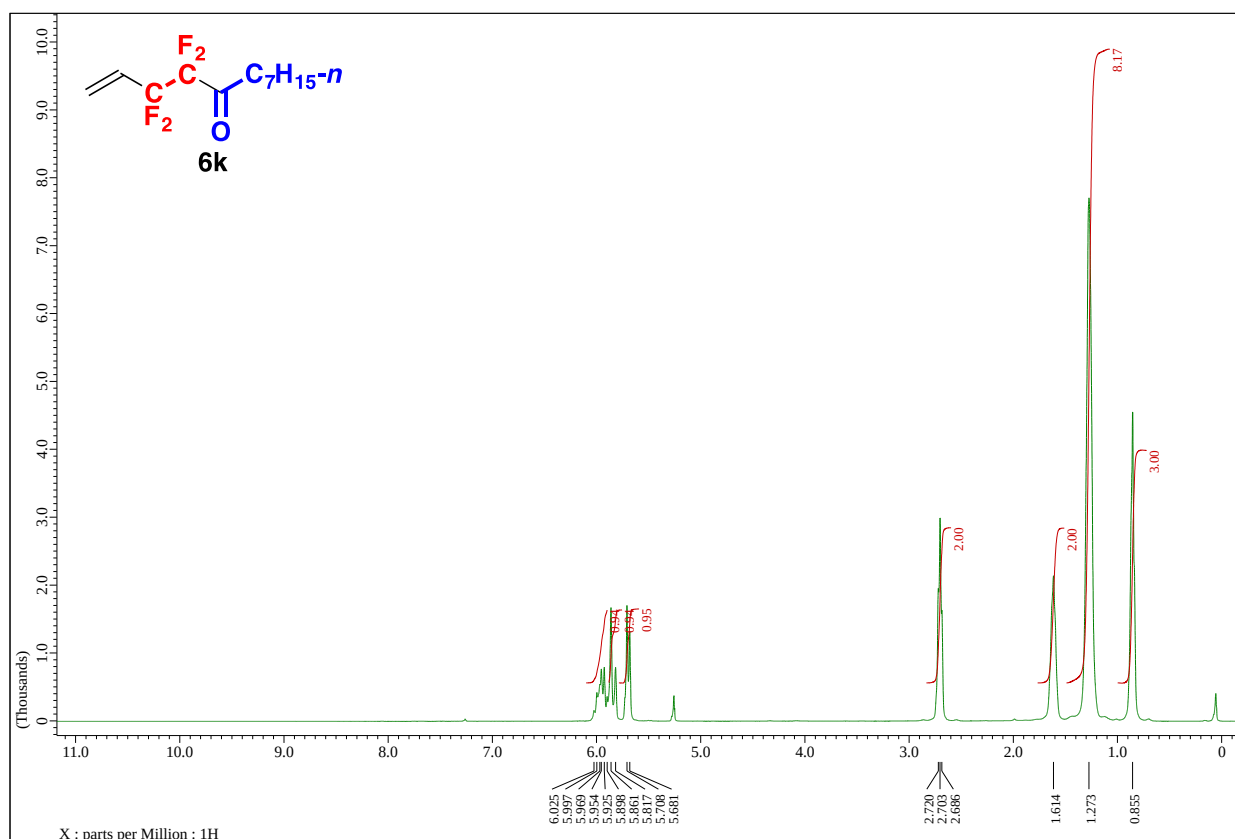
^{13}C NMR Spectrum of 4,4,5,5-tetrafluoro-1-phenylhept-1,6-dien-3-one (**6j**)



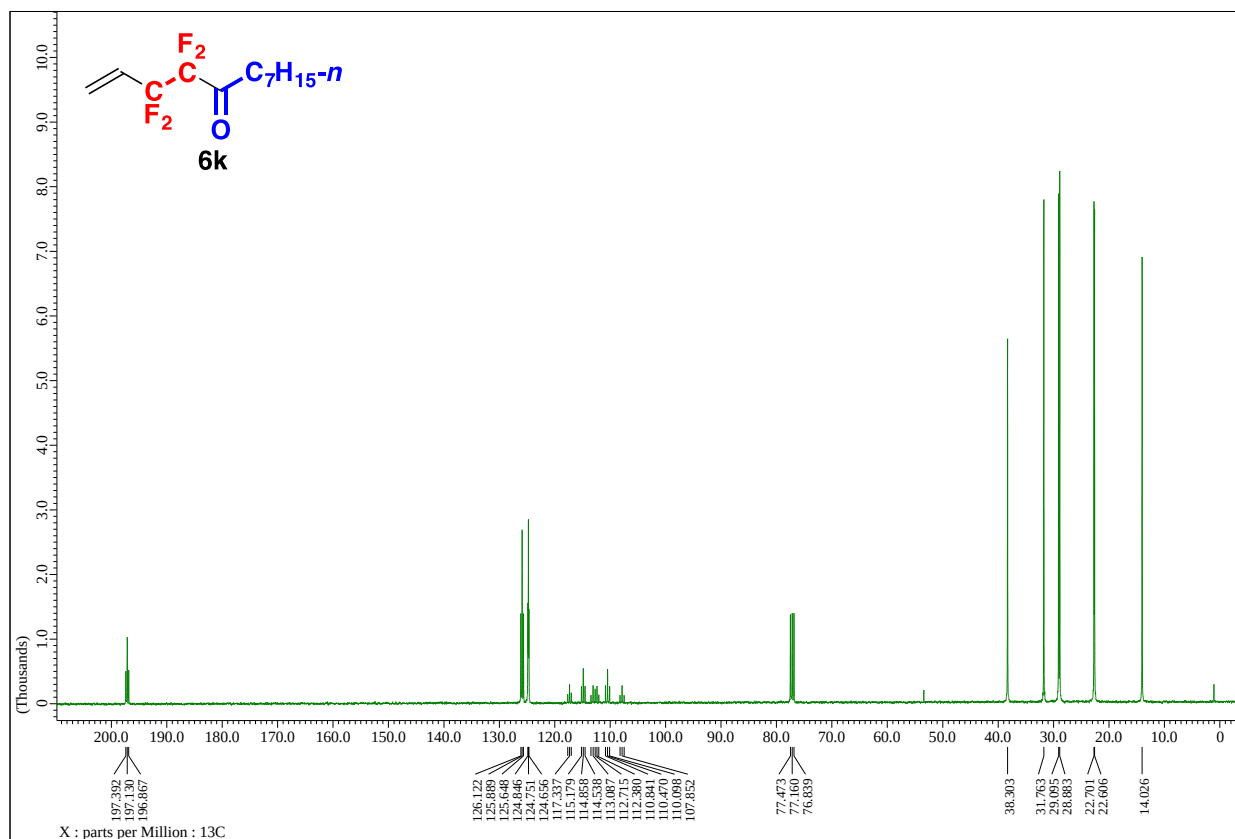
^{19}F NMR Spectrum of 4,4,5,5-tetrafluoro-1-phenylhept-1,6-dien-3-one (**6j**)



¹H NMR Spectrum of 3,3,4,4-tetrafluorododec-1-en-5-one (6k)



¹³C NMR Spectrum of 3,3,4,4-tetrafluorododec-1-en-5-one (6k)



^{19}F NMR Spectrum of 3,3,4,4-tetrafluorododec-1-en-5-one (**6k**)

