

Alkali Metal Salts-Assisted Coupling Reaction between Fluorinated Benzyl Electrophiles and Alkenylboronic Acids

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Content

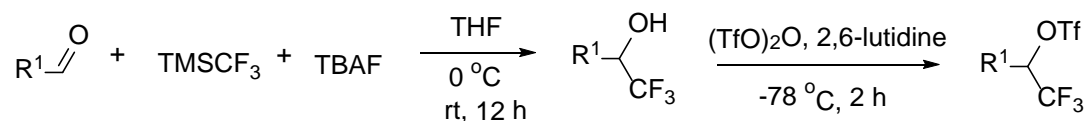
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1. General

Commercial reagents and solvents were obtained from the commercial providers and used without further purification. The products were purified using a commercial flash chromatography system or a regular glass column. TLC was developed on silica gel 60 F254 glass plates. ^1H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded on a Bruker NMR apparatus. The chemical shifts are reported in δ (ppm) values (^1H and ^{13}C NMR relative to CHCl_3 , δ 7.26 ppm for ^1H NMR and δ 77.0 ppm for ^{13}C NMR). Or alternatively, ^1H NMR chemical shifts were referenced to tetramethylsilane signal (0 ppm). Multiplicities are recorded by s (singlet), d (doublet), t (triplet), q (quartet), p (pentet), h (hexet), m (multiplet) and br (broad). Coupling constants (J), are reported in Hertz (Hz). HRMS data were obtained by using Thermo LTQ-Orbitrap XL mass spectrometer with ESI, ACPI or EI ionization sources by the service provided at Indiana University Bloomington Mass Spectral Facility. GC analyses were performed using a Shimadzu GC-2010 ultra gas chromatography–mass spectrometry instrument equipped with a Shimadzu AOC-20s autosampler.

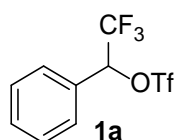
2. Preparation of α -trifluoromethyl benzyl triflates

All α -trifluoromethyl benzyl triflates were prepared according to literature methods.¹

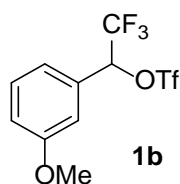


TBAF \cdot 3H₂O (0.6 mmol, 0.12 equiv) was added portion-wise to a solution of TMSCF₃ (6.0 mmol, 1.2 equiv) and the aldehyde (5.0 mmol, 1.0 equiv) in THF (5.0 mL) at 0 °C. The resultant dark solution was warmed to rt and stirred for 16 h, then satd. aq. NH₄Cl (5.0 mL) was added. THF was removed in vacuo, the aqueous layer was extracted with MTBE (3 \times 10.0 mL) and the combined organic extracts were washed sequentially with H₂O (10.0 mL) and brine (10.0 mL) then dried over Na₂SO₄ and concentrated in vacuo. The residue was dissolved in THF (5.0 mL) after which aq 1.0 M HCl (5.0 mL) was added. The reaction mixture was stirred for 8 h before being extracted with EtOAc (3 \times 15.0 mL). The organic layers were combined, washed with brine (10.0 mL), dried over Na₂SO₄ and concentrated in vacuo. The residue was purified by flash silica gel column chromatography (hexanes: EtOAc = 5:1) to give the trifluoromethyl benzylic alcohols. Then, a flame-dried flask was flushed with nitrogen and charged with trifluoromethyl benzylic alcohol (2.0 mmol, 1.0 equiv). Then dry CH₂Cl₂ (5.0 mL) was added, and the mixture was cooled to -78 °C before adding 2, 6-lutidine (0.37 mL, 3.2 mmol, 1.6 equiv). Under stirring, triflic anhydride (0.45 mL, 2.4 mmol, 1.2 equiv) was added dropwise over five minutes, and then the reaction mixture was stirred for another 15 min at -78 °C. Then 0.5 M H₂SO₄ aqueous solution (20.0 mL) and hexanes (15.0 mL) were added. The flask was removed from the cold bath, and the reaction mixture was transferred to a separatory funnel, and the aqueous mixture was extracted of CH₂Cl₂ (15.0 mL \times 5). The organic layers were combined and dried over Na₂SO₄, filtered, and the excess solvents were removed under vacuum, resulting in a clear, yellow liquid residue. This residue was then purified by silica gel column chromatography with 10% EtOAc in petroleum ether.

Two representative α -trifluoromethyl benzyl triflates were synthesized with characterization data.



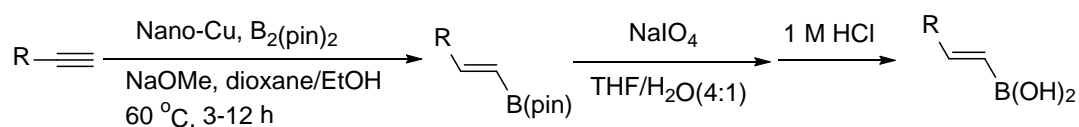
2, 2, 2-trifluoro-1-phenylethyl trifluoromethanesulfonate (1a). Following the standard procedure, the desired product was obtained after flash chromatography (PE:EA = 10% as eluent) as colorless oil (0.55 g, 90 %). ¹H NMR (400 MHz, chloroform-d) δ 7.57 – 7.42 (m, 5H), 5.90 (q, J = 5.9 Hz, 1H). ¹⁹F NMR (376 MHz, chloroform-d) δ -75.07, -76.62 (d, J = 6.1 Hz). ¹³C NMR (100 MHz, chloroform-d) δ 131.4, 129.1, 128.1, 127.9, 121.5 (q, J = 280 Hz), 118.2 (q, J = 318 Hz), 82.6 (q, J = 36 Hz). HRMS (EI) m/z : [M]⁺ Calcd for C₉H₆F₆O₃S 307.9942, found 307.9947.



2, 2, 2-trifluoro-1-(3-methoxyphenyl)ethyl trifluoromethanesulfonate (1b). Following the standard procedure, the desired product was obtained after flash chromatography (PE:EA = 10% as eluent) as colorless oil (0.58 g, 86 %). ¹H NMR (400 MHz, chloroform-d) δ 7.41-7.35 (m, 1H), 7.10 – 6.97 (m, 3H), 5.83 (q, J = 5.9 Hz, 1H), 3.82 (s, 3H). ¹⁹F NMR (376 MHz, chloroform-d) δ -74.85, -76.35 (d, J = 5.7 Hz). ¹³C NMR (100 MHz, chloroform-d) δ 160.00, 130.27, 129.25, 121.41(q, J = 279 Hz), 120.10, 118.31(q, J = 318 Hz), 116.89, 113.37, 82.44 (q, J = 35 Hz), 55.26. HRMS (EI) m/z : [M]⁺ Calcd for C₁₀H₈F₆O₄S 338.0047, found 338.0040.

3. Preparation of alkenylboronic acids

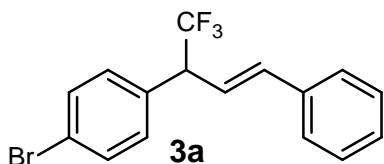
All alkenylboronic acids were prepared according to a literature method.³



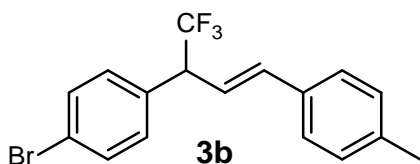
An oven-dried vial was charged with Nano-Cu (0.064 g, 1.0 mmol, 0.2 equiv), MeONa (0.052 g, 1.0 mmol, 1.0 equiv) and bis(pinacolato)diboron (1.9 g, 7.5 mmol, 1.5 equiv). After being sealed with a septum, the vial was connected to an argon-vacuum line and was evacuated and backfilled with argon (x 3). Dioxane (10.0 mL) and EtOH (5.0 mL) were added and the mixture was stirred for 30 min. Then alkyne (5.0 mmol, 1.0 equiv) was added. The mixture was stirred at 60 °C for 3 - 12 h. This was followed by the addition of water; the aqueous phase was then extracted with ethyl acetate (3 x 10.0 mL). The combined organic layers were dried over Na₂SO₄ and concentrated. The crude product was purified by silica gel column chromatography. Alkenylboranes (2.0 mmol) and sodium periodate (1.3 g, 6.0 mmol, 3.0 equiv) were stirred in a 4:1 mixture of THF and H₂O (10.0 mL) for 30 min, at which time aqueous hydrochloric acid (1 N, 1.4 mL) was added to the suspension, and the reaction mixture was stirred at room temperature for 2 - 10 h. The reaction mixture was diluted with water and extracted with EtOAc (3 x 10.0 mL). The combined organic layers were washed with brine, dried over Na₂SO₄ and concentrated in vacuo to yield the desired boronic acid. The obtained boronic acid was used without further purification.

4. General procedure for reaction of α -trifluoromethyl benzyl triflates

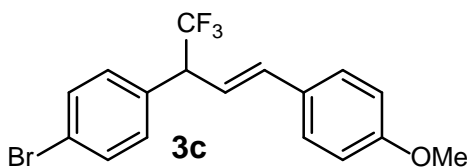
An oven-dried vial was charged with α -trifluoromethyl benzyl triflate **1** (0.2 mmol), alkenylboronic acid **2** (0.30 mmol, 1.5 equiv), K₃PO₄ (0.4 mmol, 0.084g, 2.0 equiv). DCE (1.5 mL) was added and the mixture was stirred at 80 °C for 12 h under air. After that, water were added and the aqueous phase was extracted with ethyl acetate (3 x 5.0 mL). The combined organic layers were dried over Na₂SO₄ and then concentrated. The crude product was purified by silica gel column chromatography to give product **3**.



(E)-1-bromo-4-(1,1,1-trifluoro-4-phenylbut-3-en-2-yl)benzene (3a). Following the standard procedure, the desired product was obtained after flash chromatography (PE as eluent) as colorless oil (49 mg, 73 %). ^1H NMR (400 MHz, chloroform- d) δ 7.57 – 7.46 (m, 2H), 7.41 – 7.35 (m, 2H), 7.35 – 7.29 (m, 2H), 7.31-7.25 (m, 3H), 6.56 (d, J = 15.9 Hz, 1H), 6.39 (dd, J = 15.9, 7.9 Hz, 1H), 4.11 (p, J = 8.9 Hz, 1H). ^{19}F NMR (376 MHz, chloroform- d) δ -69.00 (d, J = 9.6 Hz). ^{13}C NMR (100 MHz, chloroform- d) δ 135.89, 133.67, 131.99, 130.65, 128.64, 128.31, 126.53, 125.70 (q, J = 279 Hz), 122.43, 121.90, 52.83 (q, J = 27 Hz). HRMS (EI) m/z : $[\text{M}]^+$ Calcd for $\text{C}_{16}\text{H}_{12}\text{BrF}_3$ 340.0074, found 340.0070.

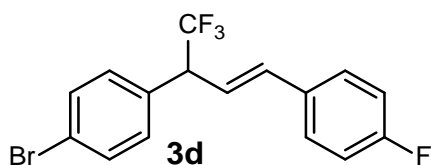


(E)-1-bromo-4-(1,1,1-trifluoro-4-(p-tolyl)but-3-en-2-yl)benzene (3b). Following the standard procedure, the desired product was obtained after flash chromatography (PE as eluent) as colorless oil (56 mg, 80 %). ^1H NMR (400 MHz, chloroform- d) δ 7.50 (d, J = 8.3 Hz, 2H), 7.29 – 7.21 (m, 4H), 7.12 (d, J = 7.9 Hz, 2H), 6.52 (d, J = 15.8 Hz, 1H), 6.33 (dd, J = 15.8, 7.9 Hz, 1H), 4.09 (p, J = 9.0 Hz, 1H), 2.33 (s, 3H). ^{19}F NMR (376 MHz, chloroform- d) δ -69.05 (d, J = 9.4 Hz). ^{13}C NMR (100 MHz, chloroform- d) δ 138.15, 135.63, 133.72, 133.02, 131.82, 130.53, 129.20, 126.31, 125.62 (q, J = 279 Hz), 122.25, 120.71, 52.71 (q, J = 29 Hz), 21.10. HRMS (EI) m/z : $[\text{M}]^+$ Calcd for $\text{C}_{17}\text{H}_{14}\text{BrF}_3$ 354.0321, found 354.0329.

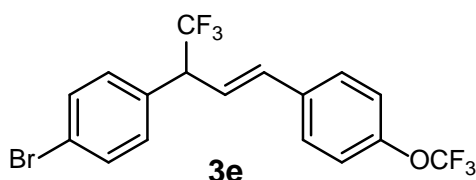


(E)-1-bromo-4-(1,1,1-trifluoro-4-(4-methoxyphenyl)but-3-en-2-yl)benzene (3c). Following the standard procedure, the desired product was obtained after flash chromatography (PE as eluent) as colorless oil (59 mg, 80 %). ^1H NMR (400 MHz, chloroform- d) δ 7.50 (d, J = 8.5 Hz, 2H), 7.30 (d, J = 8.8 Hz, 2H), 7.24 (d, J = 8.3 Hz, 2H), 6.84 (d, J = 8.7 Hz, 2H), 6.49 (d, J = 15.8 Hz, 1H), 6.24 (dd, J = 15.8, 8.0 Hz, 1H), 4.07 (p, J = 8.9 Hz, 1H), 3.79 (s, 3H). ^{19}F NMR (376 MHz, chloroform- d) δ -69.08 (d, J = 9.1 Hz). ^{13}C NMR (100 MHz, chloroform- d) δ 159.65, 135.20, 133.86, 131.85, 130.58, 128.59, 127.73, 125.70 (q, J = 278 Hz), 122.25, 119.52, 113.94, 55.18,

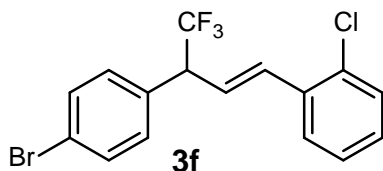
52.78 (q, $J = 27$ Hz). HRMS (EI) m/z : $[M]^+$ Calcd for $C_{17}H_{14}BrF_3O$ 370.0180, found 354.0188.



(E)-1-bromo-4-(1,1,1-trifluoro-4-(4-fluorophenyl)but-3-en-2-yl)benzene (3d). Following the standard procedure, the desired product was obtained after flash chromatography (PE as eluent) as colorless oil (59 mg, 83 %). 1H NMR (400 MHz, chloroform- d) δ 7.50 (d, $J = 8.4$ Hz, 2H), 7.39-7.28 (m, 2H), 7.23 (d, $J = 8.3$ Hz, 2H), 7.02-6.97 (m, 2H), 6.51 (d, $J = 15.8$ Hz, 1H), 6.29 (dd, $J = 15.8, 7.9$ Hz, 1H), 4.08 (p, $J = 8.9$ Hz, 1H). ^{19}F NMR (376 MHz, chloroform- d) δ -69.02 (d, $J = 9.3$ Hz), -113.19 (m, -113.15 - -113.23). ^{13}C NMR (100 MHz, chloroform- d) δ 162.52 (d, $J = 247$ Hz), 134.54, 133.39, 131.85, 131.34, 130.45, 128.00, 125.50 (q, $J = 278$ Hz), 122.32, 121.53, 115.43 (d, $J = 21$ Hz), 52.63 (q, $J = 28$ Hz). HRMS (EI) m/z : $[M]^+$ Calcd for $C_{16}H_{11}BrF_4$ 357.9980, found 357.9985.

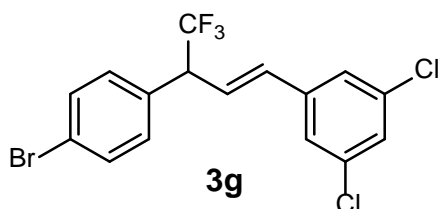


(E)-1-bromo-4-(1,1,1-trifluoro-4-(4-(trifluoromethoxy)phenyl)but-3-en-2-yl)benzene (3e). Following the standard procedure, the desired product was obtained after flash chromatography (PE as eluent) as colorless oil (55 mg, 66 %). 1H NMR (400 MHz, chloroform- d) δ 7.49 (d, $J = 8.5$ Hz, 2H), 7.35 (d, $J = 8.7$ Hz, 2H), 7.21 (d, $J = 8.3$ Hz, 2H), 7.13 (d, $J = 8.2$ Hz, 2H), 6.51 (d, $J = 15.9$ Hz, 1H), 6.34 (dd, $J = 15.9, 7.8$ Hz, 1H), 4.08 (p, $J = 8.9$ Hz, 1H). ^{19}F NMR (376 MHz, chloroform- d) δ -57.95, -69.03 (d, $J = 9.0$ Hz). ^{13}C NMR (100 MHz, chloroform- d) δ 149.01, 134.61, 134.41, 133.36, 132.07, 130.61, 127.85, 125.60 (q, $J = 280$ Hz), 122.57, 122.05 (q, $J = 257$ Hz), 121.68, 121.11, 52.78 (q, $J = 28$ Hz). HRMS (ESI) m/z : $[M+Cl]^+$ Calcd for $C_{17}H_{11}BrClF_6O$ 458.9586, found 458.9582.

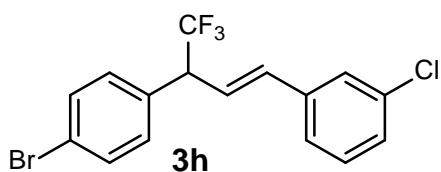


(E)-1-(3-(4-bromophenyl)-4,4,4-trifluorobut-1-en-1-yl)-2-chlorobenzene (3f). Following the standard procedure, the desired product was obtained after flash chromatography (PE as eluent) as colorless oil (58 mg, 78 %). 1H NMR (400 MHz, chloroform- d) δ 7.53 (d, $J = 8.2$ Hz, 3H), 7.40 - 7.32 (m, 1H), 7.30 - 7.20 (m, 4H), 6.99 (d, $J = 15.8$ Hz,

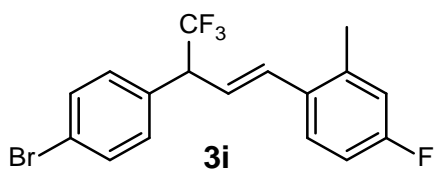
1H), 6.38 (dd, $J = 15.9, 8.1$ Hz, 1H), 4.18 (p, $J = 9.0$ Hz, 1H). ^{19}F NMR (376 MHz, chloroform-d) δ -68.96 (d, $J = 9.0$ Hz). ^{13}C NMR (100 MHz, chloroform-d) δ 134.12, 133.37, 133.24, 132.30, 132.04, 132.02, 130.62, 129.74, 129.31, 126.92, 124.67, 123.22 (q, $J = 280$ Hz), 122.54, 52.92 (q, $J = 28$ Hz). HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{16}\text{H}_{12}\text{BrClF}_3$ 374.9763, found 374.9761.



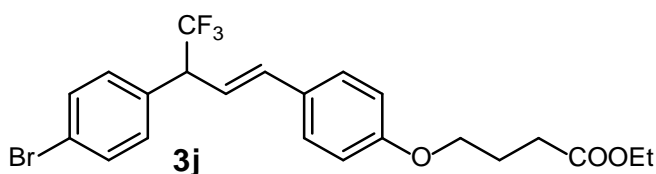
(E)-1-(3-(4-bromophenyl)-4,4,4-trifluorobut-1-en-1-yl)-3,5-dichlorobenzene (3g). Following the standard procedure, the desired product was obtained after flash chromatography (PE as eluent) as colorless oil (57 mg, 70 %). ^1H NMR (400 MHz, chloroform-d) δ 7.32 (d, $J = 8.4$ Hz, 2H), 7.02 (dd, $J = 7.5, 2.7$ Hz, 5H), 6.25-6.16 (m, 2H), 3.90 (q, $J = 8.4$ Hz, 1H). ^{19}F NMR (376 MHz, chloroform-d) δ -69.08 (d, $J = 9.0$ Hz). ^{13}C NMR (100 MHz, chloroform-d) δ 138.70, 135.19, 133.31, 132.81, 132.05, 130.52, 128.00, 125.34 (q, $J = 286$ Hz), 124.97, 124.81, 122.66, 52.59 (q, $J = 29$ Hz). HRMS (ESI) m/z : $[\text{M}-\text{H}]^-$ Calcd for $\text{C}_{16}\text{H}_9\text{BrCl}_2\text{F}_3$ 406.9217, found 406.9220.



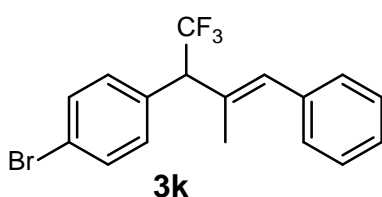
(E)-1-(3-(4-bromophenyl)-4,4,4-trifluorobut-1-en-1-yl)-3-chlorobenzene (3h). Following the standard procedure, the desired product was obtained after flash chromatography (PE as eluent) as colorless oil (57 mg, 77 %). ^1H NMR (400 MHz, chloroform-d) δ 7.54 (d, $J = 8.4$ Hz, 2H), 7.38 (s, 1H), 7.27 (d, $J = 7.2$ Hz, 5H), 6.52 (d, $J = 16.0$ Hz, 1H), 6.42 (dd, $J = 16.0, 8.0$ Hz, 1H), 4.13 (q, $J = 8.4$ Hz, 1H). ^{19}F NMR (376 MHz, chloroform-d) δ -69.06 (d, $J = 9.1$ Hz). ^{13}C NMR (100 MHz, chloroform-d) δ 137.50, 134.42, 134.37, 133.09, 131.88, 130.42, 129.67, 128.07, 126.23, 125.37 (q, $J = 280$ Hz), 124.60, 123.33, 122.39, 52.55 (q, $J = 27$ Hz). HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{16}\text{H}_{12}\text{BrClF}_3$ 374.9592, found 374.9596.



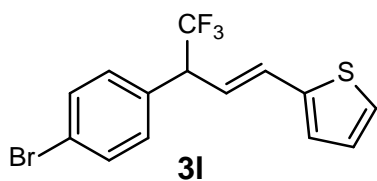
(E)-1-(3-(4-bromophenyl)-4,4,4-trifluorobut-1-en-1-yl)-4-fluoro-2-methylbenzene (3i). Following the standard procedure, the desired product was obtained after flash chromatography (PE as eluent) as colorless oil (53 mg, 72 %). ¹H NMR (400 MHz, chloroform-d) δ 7.64 (d, *J* = 8.5 Hz, 2H), 7.37 (d, *J* = 8.4 Hz, 2H), 7.32 (dd, *J* = 7.3, 2.2 Hz, 1H), 7.29 - 7.25 (m, 1H), 7.09-7.05 (m, 1H), 6.61 (d, *J* = 15.9 Hz, 1H), 6.41 (dd, *J* = 15.9, 7.9 Hz, 1H), 4.21 (p, *J* = 8.8 Hz, 1H), 2.38 (s, 3H). ¹⁹F NMR (376 MHz, chloroform-d) δ -68.89 (d, *J* = 9.0 Hz), -117.26 - -117.33 (m). ¹³C NMR (100 MHz, chloroform-d) δ 161.42(d, *J* = 246 Hz), 135.05, 133.80, 132.15, 130.76, 129.62 (d, *J* = 5 Hz), 125.70 (d, *J* = 8 Hz), 125.84 (q, *J* = 280 Hz). 125.32, 125.14, 122.58, 121.46, 115.34(d, *J* = 22 Hz), 52.95 (q, *J* = 28 Hz), 14.63. HRMS (ESI) *m/z*: [M-H]⁻ Calcd for C₁₇H₁₂BrF₄ 371.0059, found 371.0068.



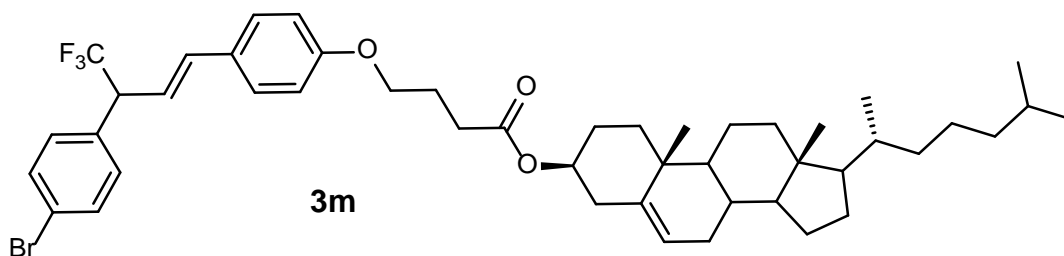
Ethyl (E)-4-(4-(3-(4-bromophenyl)-4,4,4-trifluorobut-1-en-1-yl)phenoxy)butanoate (3j) Following the standard procedure, the desired product was obtained after flash chromatography (PE/EA = 0-5% as eluent) as colorless oil (65 mg, 69 %). ¹H NMR (400 MHz, chloroform-d) δ 7.48 (d, *J* = 8.4 Hz, 2H), 7.30 – 7.18 (m, 4H), 6.80 (d, *J* = 8.7 Hz, 2H), 6.46 (d, *J* = 15.8 Hz, 1H), 6.21 (dd, *J* = 15.8, 8.0 Hz, 1H), 4.11 (q, *J* = 7.1 Hz, 2H), 4.08 – 4.00 (m, 1H), 3.97 (t, *J* = 6.1 Hz, 2H), 2.47 (t, *J* = 7.3 Hz, 2H), 2.07 (p, *J* = 6.7 Hz, 2H), 1.22 (t, *J* = 7.1 Hz, 3H). ¹⁹F NMR (376 MHz, chloroform-d) δ -69.13 (d, *J* = 9.2 Hz). ¹³C NMR (100 MHz, chloroform-d) δ 173.28, 159.12, 135.43, 134.07, 132.08, 130.78, 128.86, 127.92, 125.91 (q, *J* = 279 Hz) 122.46, 119.76, 114.73, 66.92, 60.59, 52.71 (q, *J* = 27 Hz), 30.88, 24.71, 14.35. HRMS (ESI) *m/z*: [M+H]⁺ Calcd for C₂₂H₂₃BrF₃O₃ 471.0783, found 471.0782.



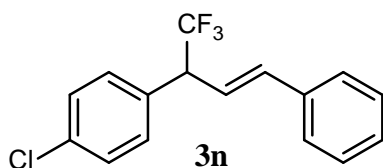
(E)-1-bromo-4-(1,1,1-trifluoro-3-methyl-4-phenylbut-3-en-2-yl)benzene (3k). Following the standard procedure, the desired product was obtained after flash chromatography (PE as eluent) as colorless oil (37 mg, 53 %). ¹H NMR (400 MHz, chloroform-d) δ 7.58 (d, *J* = 8.5 Hz, 2H), 7.41 (dd, *J* = 8.3, 6.9 Hz, 2H), 7.37 – 7.29 (m, 5H), 6.75 (s, 1H), 4.18 (q, *J* = 9.8 Hz, 1H), 1.87 (s, 3H). ¹⁹F NMR (376 MHz, chloroform-d) δ -64.92 (d, *J* = 9.9 Hz). ¹³C NMR (100 MHz, chloroform-d) δ 136.80, 133.17, 131.76, 131.52, 131.03, 130.57, 128.94, 128.10, 126.93, 125.85 (q, *J* = 280 Hz), 122.12, 57.86 (q, *J* = 27 Hz), 16.66. HRMS (EI) *m/z*: [M]⁺ Calcd for C₁₇H₁₄BrF₃ 354.0321, found 354.0329.



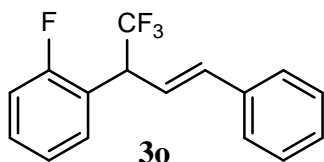
(E)-2-(3-(4-bromophenyl)-4,4,4-trifluorobut-1-en-1-yl)thiophene (3l). Following the standard procedure, the desired product was obtained after flash chromatography (PE as eluent) as colorless oil (52 mg, 76 %). ¹H NMR (400 MHz, chloroform-d) δ 7.52 (d, *J* = 8.5 Hz, 2H), 7.24 (d, *J* = 8.4 Hz, 2H), 7.22 – 7.16 (m, 1H), 7.02 – 6.93 (m, 2H), 6.66 (d, *J* = 15.7 Hz, 1H), 6.22 (dd, *J* = 15.7, 7.8 Hz, 1H), 4.08 (p, *J* = 8.9 Hz, 1H). ¹⁹F NMR (376 MHz, chloroform-d) δ -68.98 (d, *J* = 9.0 Hz). ¹³C NMR (100 MHz, chloroform-d) δ 140.74, 133.39, 132.04, 130.69, 128.88, 127.45, 126.76, 125.58 (q, *J* = 279 Hz), 125.15, 122.52, 121.19, 52.66 (q, *J* = 28 Hz). HRMS (EI) *m/z*: [M]⁺ Calcd for C₁₄H₁₀BrF₃S 345.9639, found 345.9633.



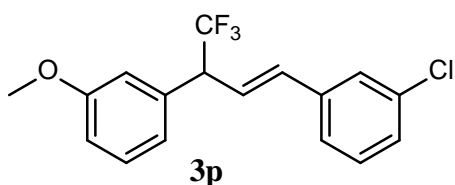
(3S,10R,13R)-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl-4-(4-((E)-3-(4-bromophenyl)-4,4,4-trifluorobut-1-en-1-yl)phenoxy)butanoate (3o). Following the standard procedure, the desired product was obtained after flash chromatography (PE/EA = 0-10% as eluent) as colorless oil (71 mg, 44 %). ¹H NMR (400 MHz, chloroform-d) δ 7.58 (d, *J* = 8.4 Hz, 2H), 7.41 – 7.26 (m, 4H), 6.90 (d, *J* = 8.7 Hz, 2H), 6.56 (d, *J* = 15.9 Hz, 1H), 6.31 (dd, *J* = 15.8, 8.0 Hz, 1H), 5.43 (d, *J* = 4.1 Hz, 1H), 4.74 – 4.66 (m, 1H), 4.15 (dt, *J* = 17.6, 8.8 Hz, 1H), 4.07 (t, *J* = 6.1 Hz, 2H), 2.55 (t, *J* = 7.2 Hz, 2H), 2.37 (d, *J* = 7.7 Hz, 2H), 2.22-2.14 (m, 2H), 2.10 – 2.00 (m, 2H), 1.97 – 1.86 (m, 3H), 1.71 – 1.09 (m, 20H), 1.08 (s, 3H), 1.05 – 1.02 (m, 1H), 0.98 (d, *J* = 6.5 Hz, 3H), 0.94 (d, *J* = 6.6 Hz, 6H), 0.74 (s, 3H). ¹⁹F NMR (376 MHz, chloroform-d) δ -69.01 (d, *J* = 9.2 Hz). ¹³C NMR (100 MHz, chloroform-d) δ 172.32, 158.83, 139.41, 135.12, 133.77, 131.76, 130.46, 129.93, 128.54, 127.60, 125.61 (q, *J* = 278 Hz), 122.48, 119.44, 114.44, 73.91, 66.66, 60.18, 56.49, 55.95, 52.68, 125.74 (q, *J* = 27 Hz), 49.83, 42.12, 39.54, 39.33, 37.95, 36.78, 36.39, 35.99, 35.59, 31.70, 30.91, 30.69, 28.03, 27.81, 27.61, 24.47, 24.09, 23.64, 22.61, 22.36, 20.84, 19.11, 18.52, 14.00, 11.66. HRMS (ESI) *m/z*: [M+Cl]⁺ Calcd for C₄₇H₆₂BrClF₃O₃ 845.3528, found 845.3536.



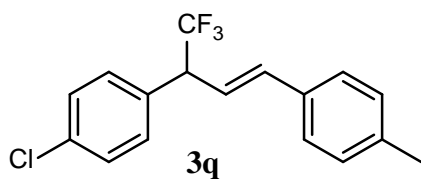
(E)-1-chloro-4-(1,1,1-trifluoro-4-phenylbut-3-en-2-yl)benzene (3n). Following the standard procedure, the desired product was obtained after flash chromatography (PE as eluent) as colorless oil (43 mg, 73 %). ¹H NMR (400 MHz, chloroform-d) δ 7.41 – 7.24 (m, 9H), 6.57 (d, J = 15.9 Hz, 1H), 6.40 (dd, J = 15.9, 7.9 Hz, 1H), 4.13 (p, J = 8.9 Hz, 1H). ¹⁹F NMR (376 MHz, chloroform-d) δ -69.02 (d, J = 9.0 Hz). ¹³C NMR (100 MHz, chloroform-d) δ 135.85, 134.27, 133.13, 130.31, 129.01, 128.62, 128.29, 126.52, 125.75(q, J = 279 Hz), 124.36, 121.97, 52.73(q, J = 27 Hz). HRMS (EI) m/z: [M]⁺ Calcd for C₁₆H₁₂ClF₃ 296.2235, found 296.2233.



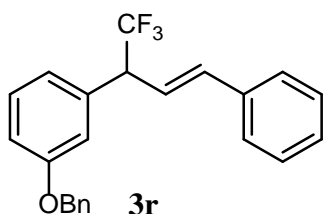
(E)-1-fluoro-2-(1,1,1-trifluoro-4-phenylbut-3-en-2-yl)benzene (3o). Following the standard procedure, the desired product was obtained after flash chromatography (PE as eluent) as colorless oil (35 mg, 68 %). ¹H NMR (400 MHz, chloroform-d) δ 7.51-7.48 (m, 1H), 7.40 (d, J = 7.1 Hz, 2H), 7.36-7.32 (m, 3H), 7.31 – 7.25 (m, 1H), 7.22-7.18 (m, 1H), 7.16-7.11 (m, 1H), 6.64 (d, J = 15.9 Hz, 1H), 6.44 (dd, J = 15.8, 8.2 Hz, 1H), 4.64 (p, J = 8.9 Hz, 1H). ¹⁹F NMR (376 MHz, chloroform-d) δ -68.92 (dd, J = 9.2, 3.9 Hz), -117.54 - -117.62 (m). ¹³C NMR (100 MHz, chloroform-d) δ 160.53(d, J = 247 Hz), 135.93, 129.81, 129.72, 129.52, 128.51, 128.15, 126.46, 125.70(q, J = 284 Hz) 124.35(d, J = 3 Hz), 121.88(d, J = 13 Hz), 121.21, 115.70 (d, J = 23 Hz), 45.68(q, J = 28 Hz). HRMS (EI) m/z: [M]⁺ Calcd for C₁₆H₁₂F₄ 280.0875, found 280.0877.



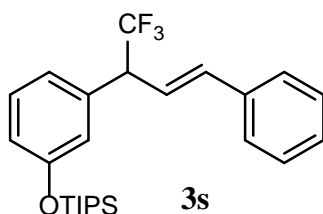
(E)-1-chloro-3-(4,4,4-trifluoro-3-(3-methoxyphenyl)but-1-en-1-yl)benzene (3p). Following the standard procedure, the desired product was obtained after flash chromatography (PE as eluent) as colorless oil (47 mg, 72 %). ¹H NMR (400 MHz, chloroform-d) δ 7.39 (s, 1H), 7.35-7.30 (m, 1H), 7.31-7.26 (m, 3H), 6.98 (d, J = 7.6 Hz, 1H), 6.95 – 6.88 (m, 2H), 6.55 (d, J = 15.9 Hz, 1H), 6.45 (dd, J = 15.9, 7.7 Hz, 1H), 4.13 (p, J = 9.1 Hz, 1H), 3.84 (s, 3H). ¹⁹F NMR (376 MHz, chloroform-d) δ -68.72 (d, J = 9.2 Hz). ¹³C NMR (100 MHz, chloroform-d) δ 159.95, 138.06, 135.85, 134.69, 134.27, 129.99, 129.92, 128.19, 126.54, 125.96(q, J = 280 Hz), 124.90, 124.24, 121.33, 115.16, 113.50, 55.35, 53.45(q, J = 28 Hz). HRMS (ESI) m/z: [M-H]⁻ Calcd for C₁₇H₁₃ClF₃O 325.9977, found 324.9973.



(E)-1-chloro-4-(1,1,1-trifluoro-4-(p-tolyl)but-3-en-2-yl)benzene (3q). Following the standard procedure, the desired product was obtained after flash chromatography (PE as eluent) as colorless oil (49 mg, 83 %). ^1H NMR (400 MHz, chloroform-d) δ 7.37 – 7.23 (m, 6H), 7.12 (d, J = 7.9 Hz, 2H), 6.52 (d, J = 15.9 Hz, 1H), 6.33 (dd, J = 15.9, 7.9 Hz, 1H), 4.10 (p, J = 9.0 Hz, 1H), 2.32 (s, 3H). ^{19}F NMR (376 MHz, chloroform-d) δ -69.02(d, J = 9.0 Hz). ^{13}C NMR (100 MHz, chloroform-d) δ 138.24, 135.71, 134.21, 133.28, 133.13, 130.32, 129.31, 128.98, 126.42, 125.79 (q, J = 280 Hz), 120.90, 52.75(q, J = 28 Hz), 21.19. HRMS (ESI) m/z : $[\text{M}-\text{H}]^-$ Calcd for $\text{C}_{17}\text{H}_{13}\text{ClF}_3$ 308.9780, found 308.9788.

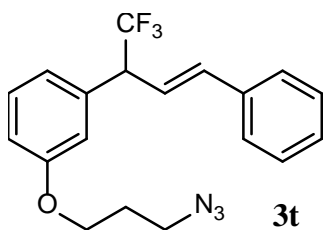


(E)-1-(benzyloxy)-3-(1,1,1-trifluoro-4-phenylbut-3-en-2-yl)benzene (3r). Following the standard procedure, the desired product was obtained after flash chromatography (PE/EA = 0-5% as eluent) as colorless oil (44 mg, 60 %). ^1H NMR (400 MHz, chloroform-d) δ 7.56 (d, J = 6.9 Hz, 2H), 7.53 – 7.48 (m, 4H), 7.47 – 7.40 (m, 4H), 7.39 – 7.35 (m, 1H), 7.15 – 7.06 (m, 3H), 6.70 (d, J = 15.9 Hz, 1H), 6.53 (dd, J = 15.9, 8.1 Hz, 1H), 5.19 (s, 2H), 4.23 (p, J = 9.0 Hz, 1H). ^{19}F NMR (376 MHz, chloroform-d) δ -68.64 (d, J = 9.2 Hz). ^{13}C NMR (100 MHz, chloroform-d) δ 159.04, 136.73, 136.19, 135.54, 129.87, 128.63, 128.18, 128.08, 127.60, 126.01(q, J = 280 Hz), 126.59, 122.51, 121.63, 115.397, 114.26, 70.13, 53.47(q, J = 28 Hz). HRMS (EI) m/z : $[\text{M}]^+$ Calcd for $\text{C}_{23}\text{H}_{19}\text{F}_3\text{O}$ 368.0301, found 368.0300.

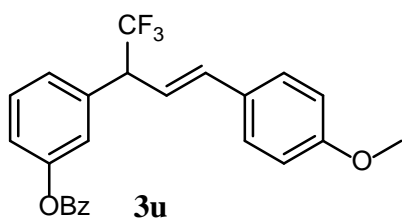


(E)-triisopropyl(3-(1,1,1-trifluoro-4-phenylbut-3-en-2-yl)phenoxy)silane (3s). Following the standard procedure, the desired product was obtained after flash chromatography (PE as eluent) as colorless oil (47 mg, 72 %). ^1H NMR

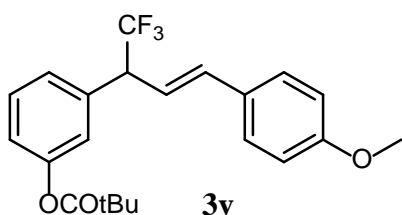
(400 MHz, chloroform-d) δ 7.37 (d, J = 7.1 Hz, 2H), 7.33-7.29 (m, 2H), 7.27 – 7.19 (m, 2H), 6.94 (d, J = 8.3 Hz, 2H), 6.88 – 6.85 (m, 1H), 6.56 (d, J = 15.9 Hz, 1H), 6.41 (dd, J = 15.9, 7.8 Hz, 1H), 4.08 (p, J = 9.0 Hz, 1H), 1.30 – 1.21 (m, 3H), 1.09 (d, J = 7.2 Hz, 18H). ^{19}F NMR (376 MHz, chloroform-d) δ -68.83 (d, J = 9.3 Hz). ^{13}C NMR (100 MHz, chloroform-d) δ 156.29, 136.17, 135.85, 135.34, 129.63, 128.55, 128.05, 126.47, 125.99 (q, J = 279 Hz), 122.64, 121.71, 120.62, 119.71, 53.16(q, J = 27 Hz), 17.82, 12.61. HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{25}\text{H}_{34}\text{F}_3\text{OSi}$ 435.2331, found 435.2328.



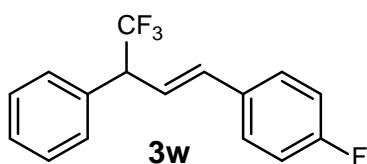
(*E*)-1-(3-azidopropoxy)-3-(1,1,1-trifluoro-4-phenylbut-3-en-2-yl)benzene (3t). Following the standard procedure, the desired product was obtained after flash chromatography (PE as eluent) as colorless oil (44 mg, 61 %). ^1H NMR (400 MHz, chloroform-d) δ 7.37 – 7.31 (m, 2H), 7.27-7.23 (m, 3H), 7.21 (d, J = 4.5 Hz, 1H), 6.94 (d, J = 7.8 Hz, 1H), 6.88 (s, 1H), 6.83 (dd, J = 8.2, 2.4 Hz, 1H), 6.55 (d, J = 15.8 Hz, 1H), 6.38 (dd, J = 15.9, 8.0 Hz, 1H), 4.10 – 4.03 (m, 1H), 4.09-4.01 (m, 2H), 3.48 (t, J = 6.6 Hz, 2H), 2.04-1.98 (m, 2H). ^{19}F NMR (376 MHz, chloroform-d) δ -68.80 (d, J = 9.3 Hz). ^{13}C NMR (100 MHz, chloroform-d) δ 158.91, 136.22, 136.12, 135.54, 129.85, 128.60, 128.16, 126.55, 125.97(q, J = 277 Hz), 122.47, 121.56, 115.55, 113.84, 64.54, 53.42(q, J = 26 Hz), 48.21, 28.77. HRMS (ESI) m/z : $[\text{M}-\text{N}_2+\text{H}]^+$ Calcd for $\text{C}_{19}\text{H}_{19}\text{F}_3\text{NO}$ 334.1419, found 334.1417.



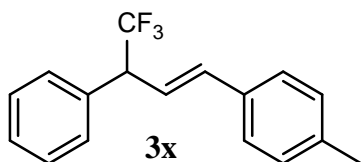
(*E*)-3-(1,1,1-trifluoro-4-(4-methoxyphenyl)but-3-en-2-yl)phenyl benzoate (3u). Following the standard procedure, the desired product was obtained after flash chromatography (PE/EA = 0-10% as eluent) as colorless oil (42 mg, 52 %). ^1H NMR (400 MHz, chloroform-d) δ 8.21 (d, J = 7.6 Hz, 2H), 7.66-7.62 (m, 1H), 7.54-7.50 (m, 2H), 7.47-7.43 (m, 1H), 7.36 – 7.22 (m, 5H), 6.85 (d, J = 8.6 Hz, 2H), 6.56 (d, J = 15.9 Hz, 1H), 6.28 (dd, J = 15.8, 8.1 Hz, 1H), 4.16 (p, J = 9.1 Hz, 1H), 3.80 (s, 3H). ^{19}F NMR (376 MHz, chloroform-d) δ -69.07 (d, J = 9.2 Hz). ^{13}C NMR (100 MHz, chloroform-d) δ 164.70, 159.42, 150.87, 136.26, 135.09, 133.43, 129.93, 129.51, 129.12, 128.34, 127.59, 127.19, 126.23, 125.65 (q, J = 280 Hz), 122.05, 121.38, 119.45, 113.76, 55.04, 52.34 (q, J = 28 Hz). HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{24}\text{H}_{20}\text{F}_3\text{O}_3$ 413.1365, found 413.1361.



(E)-3-(1, 1, 1-trifluoro-4-(4-methoxyphenyl)but-3-en-2-yl)phenyl pivalate (3v). Following the standard procedure, the desired product was obtained after flash chromatography (PE/EA = 0-10% as eluent) as colorless oil (47 mg, 61 %). ^1H NMR (400 MHz, chloroform- d) δ 7.38 (dd, J = 9.0, 6.7 Hz, 1H), 7.32 (d, J = 8.6 Hz, 2H), 7.24 (d, J = 7.9 Hz, 1H), 7.12 – 7.03 (m, 2H), 6.85 (d, J = 8.6 Hz, 2H), 6.53 (d, J = 15.8 Hz, 1H), 6.26 (dd, J = 15.8, 8.1 Hz, 1H), 4.12 (p, J = 9.2 Hz, 1H), 3.80 (s, 3H), 1.36 (s, 9H). ^{19}F NMR (376 MHz, chloroform- d) δ -68.90 (d, J = 9.3 Hz). ^{13}C NMR (100 MHz, chloroform- d) δ 176.89, 159.77, 151.38, 136.43, 135.36, 129.70, 128.90, 127.92, 126.19, 126.05 (q, J = 291 Hz), 122.18, 121.45, 119.89, 114.10, 55.37, 53.03 (q, J = 27 Hz), 39.18, 27.20. HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{22}\text{H}_{24}\text{F}_3\text{O}_3$ 393.1672, found 393.1675.

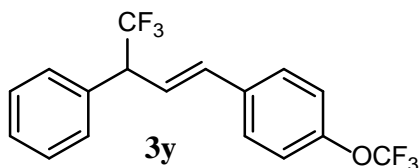


(E)-1-fluoro-4-(4,4,4-trifluoro-3-phenylbut-1-en-1-yl)benzene (3w). Following the standard procedure, the desired product was obtained after flash chromatography (PE as eluent) as colorless oil (44 mg, 79 %). ^1H NMR (400 MHz, chloroform- d) δ 7.41 – 7.33 (m, 6H), 7.03-6.99 (m, 2H), 6.55 (d, J = 15.9 Hz, 1H), 6.37 (dd, J = 15.9, 8.0 Hz, 1H), 4.13 (p, J = 9.1 Hz, 1H). ^{19}F NMR (376 MHz, chloroform- d) δ -68.91 (d, J = 9.3 Hz), -113.52 – -113.59 (m). HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{16}\text{H}_{12}\text{F}_4$ 280.2023, found 280.2028.

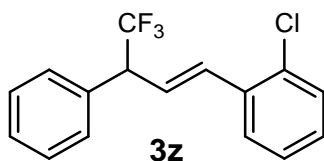


(E)-1-methyl-4-(4,4,4-trifluoro-3-phenylbut-1-en-1-yl)benzene (3x). Following the standard procedure, the desired product was obtained after flash chromatography (PE as eluent) as colorless oil (33 mg, 60 %). ^1H NMR (400 MHz, chloroform- d) δ 7.40 – 7.34 (m, 4H), 7.28 (d, J = 8.0 Hz, 2H), 7.13 (d, J = 7.9 Hz, 2H), 6.55 (d, J = 15.9 Hz, 1H), 6.40 (dd, J = 15.8, 8.0 Hz, 1H), 4.13 (p, J = 9.2 Hz, 1H), 2.34 (s, 3H). ^{19}F NMR (376 MHz, chloroform- d) δ -68.94 (d, J = 9.4 Hz). ^{13}C NMR (100 MHz, chloroform- d) δ 138.06, 135.35, 134.88, 133.39, 129.29, 128.99, 128.78, 128.17, 126.44, 126.09 (q, J = 280 Hz), 121.57, 53.45 (q, J = 27 Hz), 21.20. HRMS (ES) m/z : $[\text{M}]^+$ Calcd

for C₁₇H₁₅F₃ 276.1126, found 276.1127.



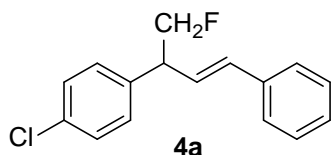
(E)-3-(1,1,1-trifluoro-4-(4-methoxyphenyl)but-3-en-2-yl)phenyl benzoate (3y). Following the standard procedure, the desired product was obtained after flash chromatography (PE as eluent) as colorless oil (42 mg, 63 %). ¹H NMR (400 MHz, chloroform-d) δ 7.43 – 7.36 (m, 6H), 7.17 (d, *J* = 8.4 Hz, 2H), 6.57 (d, *J* = 15.9 Hz, 1H), 6.44 (dd, *J* = 15.9, 7.9 Hz, 1H), 4.15 (p, *J* = 9.1 Hz, 1H). ¹⁹F NMR (376 MHz, chloroform-d) δ -57.91, -68.87 (d, *J* = 9.3 Hz). ¹³C NMR (100 MHz, chloroform-d) δ 148.61, 134.57, 134.11, 133.68, 128.61, 128.02, 127.50, 125.37(q, *J* = 280 Hz), 123.50, 120.75, 115.11 (q, *J* = 257 Hz), 53.07(q, *J* = 27 Hz). HRMS (ESI) *m/z*: [M+H]⁺ Calcd for C₁₇H₁₃F₆O 347.1702, found 347.1703.



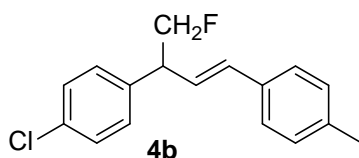
(E)-1-chloro-2-(4,4,4-trifluoro-3-phenylbut-1-en-1-yl)benzene (3z). Following the standard procedure, the desired product was obtained after flash chromatography (PE as eluent) as colorless oil (34 mg, 58 %). ¹H NMR (400 MHz, chloroform-d) δ 7.39 (d, *J* = 7.7 Hz, 1H), 7.32 – 7.12 (m, 6H), 7.09-7.02 (m, 2H), 6.85 (d, *J* = 15.8 Hz, 1H), 6.29 (dd, *J* = 15.8, 8.3 Hz, 1H), 4.06 (p, *J* = 9.0 Hz, 1H). ¹⁹F NMR (376 MHz, chloroform-d) δ -68.86 (d, *J* = 9.3 Hz). ¹³C NMR (100 MHz, chloroform-d) δ 134.26, 134.18, 133.05, 131.71, 129.55, 128.98, 128.79, 128.69, 128.15, 126.80, 126.71, 125.74 (q, *J* = 280 Hz), 125.22, 53.37 (q, *J* = 28 Hz). HRMS (ES) *m/z*: [M]⁺ Calcd for C₁₆H₁₂ClF₃ 296.2723, found 296.2722.

5. General procedure for reaction of α -monofluoromethyl benzyl methanesulfonates

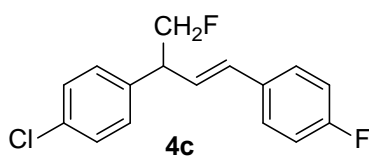
An oven-dried vial was charged with α -monofluoromethyl benzyl methanesulfonates **1'** (0.2 mmol), alkenylboronic acid **2** (0.30 mmol, 1.5 equiv), K₃PO₄ (0.4 mmol, 0.084g, 2.0 equiv), PhCF₃ (1.5 mL) was added and the mixture was stirred at 80 °C for 12 h under air. After that, water were added and the aqueous phase was extracted with ethyl acetate (3 x 5.0 mL). The combined organic layers were dried over Na₂SO₄ and then concentrated. The crude product was purified by silica gel column chromatography to give product **4**.



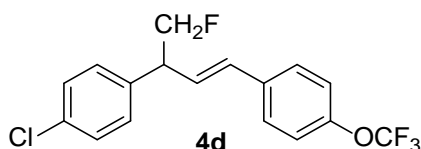
(E)-1-chloro-4-(1-fluoro-4-phenylbut-3-en-2-yl)benzene (4a). Following the standard procedure, the desired product was obtained after flash chromatography (PE as eluent) as colorless oil (42 mg, 83 %). ^1H NMR (400 MHz, chloroform-d) δ 7.46 – 7.28 (m, 6H), 7.28 – 7.21 (m, 3H), 6.51 (d, J = 16.0 Hz, 1H), 6.36 (dd, J = 16.0, 7.2 Hz, 1H), 4.79 – 4.72 (m, 1H), 4.67 – 4.60 (m, 1H), 3.94 – 3.83 (m, 1H). ^{19}F NMR (376 MHz, chloroform-d) δ -217.51 - -217.81 (m). ^{13}C NMR (100 MHz, chloroform-d) δ 138.13, 138.09, 136.65, 132.89, 132.51, 129.38, 128.78, 128.47, 127.59, 126.20, 85.38(d, J = 179 Hz), 48.55 (d, J = 19 Hz). HRMS (ES) m/z : $[\text{M}]^+$ Calcd for $\text{C}_{16}\text{H}_{14}\text{ClF}$ 260.0768, found 260.0762.



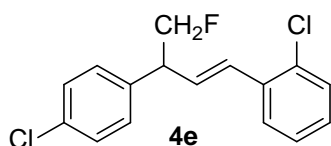
(E)-1-chloro-4-(1-fluoro-4-(p-tolyl)but-3-en-2-yl)benzene (4b). Following the standard procedure, the desired product was obtained after flash chromatography (PE as eluent) as colorless oil (44 mg, 81 %). ^1H NMR (400 MHz, chloroform-d) δ 7.35 (d, J = 8.4 Hz, 2H), 7.33 – 7.21 (m, 4H), 7.14 (d, J = 7.9 Hz, 2H), 6.49 (d, J = 16.0 Hz, 1H), 6.31 (dd, J = 16.0, 7.3 Hz, 1H), 4.79 – 4.59 (m, 2H), 3.92-3.83 (m, 1H), 2.36 (s, 3H). ^{19}F NMR (376 MHz, chloroform-d) δ -217.44 – -217.74 (m). ^{13}C NMR (100 MHz, chloroform-d) δ 138.38, 137.58, 133.98, 132.94, 132.48, 129.53, 129.31, 128.88, 126.54, 126.24, 85.58 (d, J = 175 Hz), 48.68 (d, J = 20 Hz), 21.21. HRMS (ES) m/z : $[\text{M}]^+$ Calcd for $\text{C}_{17}\text{H}_{16}\text{ClF}$ 274.0925, found 274.0920.



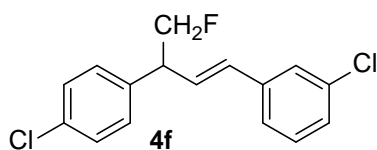
(E)-1-chloro-4-(1-fluoro-4-(4-fluorophenyl)but-3-en-2-yl)benzene (4c). Following the standard procedure, the desired product was obtained after flash chromatography (PE as eluent) as colorless oil (43 mg, 78 %). ^1H NMR (400 MHz, chloroform-d) δ 7.36-7.32 (m, 4H), 7.25 (d, J = 8.3 Hz, 2H), 7.03-6.99 (m, 2H), 6.47 (d, J = 16.0 Hz, 1H), 6.28 (dd, J = 16.0, 7.2 Hz, 1H), 4.78-4.59 (m, 2H), 3.91-3.82 (m, 1H). ^{19}F NMR (376 MHz, chloroform-d) δ -114.37 – -218.05 (m). ^{13}C NMR (100 MHz, chloroform-d) δ 162.23 (d, J = 246 Hz), 137.98, 132.92, 132.78, 131.30, 129.31, 128.78, 127.68 (d, J = 7 Hz), 127.38, 115.33 (d, J = 22 Hz), 85.29 (d, J = 165 Hz), 48.50 (d, J = 20 Hz). HRMS (ES) m/z : $[\text{M}]^+$ Calcd for $\text{C}_{16}\text{H}_{13}\text{ClF}_2$ 278.0674, found 278.0670.



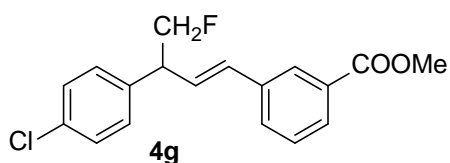
(E)-1-chloro-4-(1-fluoro-4-(4-(trifluoromethoxy)phenyl)but-3-en-2-yl)benzene (4d). Following the standard procedure, the desired product was obtained after flash chromatography (PE as eluent) as colorless oil (61 mg, 90 %). ^1H NMR (400 MHz, chloroform-d) δ 7.40-7.34 (m, 4H), 7.24 (d, J = 8.4 Hz, 2H), 7.17 (d, J = 8.4 Hz, 2H), 6.50 (d, J = 16.0 Hz, 1H), 6.35 (dd, J = 16.0, 7.1 Hz, 1H), 4.76-4.62 (m, 2H), 3.93-3.83 (m, 1H). ^{19}F NMR (376 MHz, chloroform-d) δ -57.92, -217.79 – -218.09 (m). ^{13}C NMR (100 MHz, chloroform-d) δ 148.58, 137.87, 135.51, 133.13, 131.14, 129.42, 128.93, 128.86, 127.52, 121.03, 120.44 (d, J = 256 Hz), 85.32 (d, J = 175 Hz), 48.61 (d, J = 20 Hz). HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{17}\text{H}_{14}\text{ClF}_4\text{O}$ 345.0669, found 345.0663.



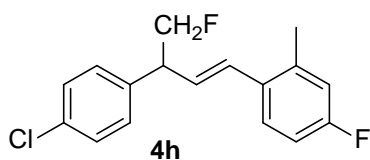
(E)-1-chloro-2-(3-(4-chlorophenyl)-4-fluorobut-1-en-1-yl)benzene (4e). Following the standard procedure, the desired product was obtained after flash chromatography (PE as eluent) as colorless oil (45 mg, 78 %). ^1H NMR (400 MHz, chloroform-d) δ 7.53 (dd, J = 7.4, 1.8 Hz, 1H), 7.39 – 7.33 (m, 3H), 7.25 (s, 2H), 7.24 – 7.16 (m, 2H), 6.93 (d, J = 16.0 Hz, 1H), 6.34 (dd, J = 16.0, 7.4 Hz, 1H), 4.80 - 4.62 (m, 2H), 3.97 - 3.88 (m, 1H). ^{19}F NMR (376 MHz, chloroform-d) δ -218.03 – -218.33 (m). ^{13}C NMR (100 MHz, chloroform-d) δ 137.97, 137.94, 134.98, 133.12, 133.05, 130.62, 130.57, 129.71, 129.48, 128.95, 128.72, 126.84, 85.43 (d, J = 175 Hz), 48.84 (d, J = 20 Hz). HRMS (ES) m/z : $[\text{M}]^+$ Calcd for $\text{C}_{16}\text{H}_{13}\text{Cl}_2\text{F}$ 294.0378, found 294.0371.



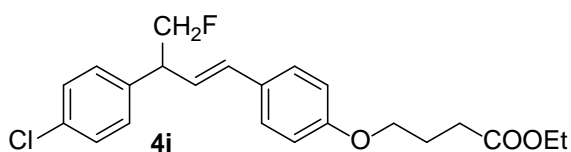
(E)-1-chloro-3-(3-(4-chlorophenyl)-4-fluorobut-1-en-1-yl)benzene (4f). Following the standard procedure, the desired product was obtained after flash chromatography (PE as eluent) as colorless oil (45 mg, 77 %). ^1H NMR (400 MHz, chloroform-d) δ 7.41 – 7.30 (m, 3H), 7.26 – 7.19 (m, 5H), 6.45 (d, J = 16.1 Hz, 1H), 6.37 (dd, J = 16.0, 6.6 Hz, 1H), 4.75 - 4.61 (m, 2H), 3.91 - 3.82 (m, 1H). ^{19}F NMR (376 MHz, chloroform-d) δ -217.70 – -218.00 (m). ^{13}C NMR (100 MHz, chloroform-d) δ 138.62, 137.76, 134.57, 133.16, 131.32, 129.78, 129.46, 129.35, 128.97, 127.63, 126.21, 124.58, 85.32 (d, J = 175 Hz), 48.62 (d, J = 19 Hz). HRMS (ES) m/z : $[\text{M}]^+$ Calcd for $\text{C}_{16}\text{H}_{13}\text{Cl}_2\text{F}$ 294.0378, found 294.0371.



Methyl (*E*)-3-(3-(4-chlorophenyl)-4-fluorobut-1-en-1-yl)benzoate (4g). Following the standard procedure, the desired product was obtained after flash chromatography (PE/EA = 0-5% as eluent) as colorless oil (49 mg, 77 %). ¹H NMR (400 MHz, chloroform-d) δ 8.03 (s, 1H), 7.93 – 7.86 (m, 1H), 7.52 (d, *J* = 7.4 Hz, 1H), 7.39 – 7.32 (m, 3H), 7.27 – 7.19 (m, 2H), 6.51 (d, *J* = 16.1 Hz, 1H), 6.42 (dd, *J* = 16.1, 6.8 Hz, 1H), 4.74 – 4.61 (m, 2H), 3.91 (s, 3H). ¹⁹F NMR (376 MHz, chloroform-d) δ -217.83 – -218.12 (m). ¹³C NMR (100 MHz, chloroform-d) δ 166.86, 137.83, 137.05, 133.11, 131.64, 130.64, 130.53, 129.43, 129.11, 128.91, 128.61, 127.24, 85.31 (d, *J* = 175 Hz), 52.08, 48.64 (d, *J* = 20 Hz). HRMS (ESI) *m/z*: [M+H]⁺ Calcd for C₁₈H₁₇ClFO₂ 319.0901, found 319.0903.

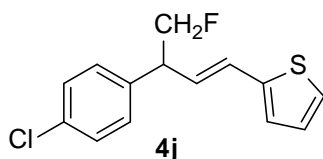


(*E*)-1-(3-(4-chlorophenyl)-4-fluorobut-1-en-1-yl)-4-fluoro-2-methylbenzene (4h). Following the standard procedure, the desired product was obtained after flash chromatography (PE as eluent) as colorless oil (42 mg, 72 %). ¹H NMR (400 MHz, chloroform-d) δ 7.34 (d, *J* = 8.4 Hz, 2H), 7.26 – 7.23 (m, 2H), 7.19 (d, *J* = 7.4 Hz, 1H), 7.16 – 7.13 (m, 1H), 6.96 – 6.92 (m, 1H), 6.47 – 6.38 (m, 1H), 6.25 (dd, *J* = 16.0, 7.2 Hz, 1H), 4.79 – 4.57 (m, 2H), 3.90 – 3.78 (m, 1H), 2.26 (s, 3H). ¹⁹F NMR (376 MHz, chloroform-d) δ -118.52 – -118.54 (m), -217.59 – -217.88 (m). ¹³C NMR (100 MHz, chloroform-d) δ 161.45 (d, *J* = 245 Hz), 138.18, 133.01, 132.58, 131.61, 129.46, 129.28, 128.90, 127.10, 125.21 (d, *J* = 8 Hz), 124.90 (d, *J* = 17 Hz), 115.10 (d, *J* = 23 Hz), 85.55 (d, *J* = 175 Hz), 48.63 (d, *J* = 20 Hz), 14.55. HRMS (ES) *m/z*: [M]⁺ Calcd for C₁₇H₁₅ClF₂ 292.0830, found 292.0831.



Ethyl (*E*)-4-(4-(3-(4-chlorophenyl)-4-fluorobut-1-en-1-yl)phenoxy)butanoate (4i). Following the standard procedure, the desired product was obtained after flash chromatography (PE/EA = 0-10% as eluent) as colorless oil (53 mg, 69 %). ¹H NMR (400 MHz, chloroform-d) δ 7.35 – 7.13 (m, 6H), 6.87 – 6.73 (m, 2H), 6.40 (d, *J* = 16.0 Hz, 1H), 6.20 – 6.11 (m, 1H), 4.73 – 4.54 (m, 2H), 4.15 – 4.09 (m, 2H), 4.02 – 3.91 (m, 2H), 3.86 – 3.76 (m, 1H), 2.56 – 2.40 (m, 2H), 2.15 – 2.01 (m, 2H), 1.25 – 1.21 (m, 2H). ¹⁹F NMR (376 MHz, chloroform-d) δ -217.63 – -217.93 (m). ¹³C NMR (100 MHz, chloroform-d) δ 172.97, 158.34, 138.23, 132.68, 131.78, 129.36, 129.26, 128.63, 127.25, 125.13, 114.35, 85.40 (d, *J* = 174 Hz), 66.57, 60.24, 48.45 (d, *J* = 20 Hz), 30.57, 24.41, 14.02. HRMS (ESI) *m/z*: [M+H]⁺ Calcd for

C₂₂H₂₅ClFO₃ 391.1476, found 391.1473.



(E)-2-(3-(4-chlorophenyl)-4-fluorobut-1-en-1-yl)thiophene (4j). Following the standard procedure, the desired product was obtained after flash chromatography (PE as eluent) as colorless oil (40 mg, 76 %). ¹H NMR (400 MHz, chloroform-d) δ 7.35 (d, *J* = 8.4 Hz, 2H), 7.24 (d, *J* = 8.4 Hz, 2H), 7.17 - 7.15 (m, 1H), 6.97 - 6.94 (m, 2H), 6.61 (d, *J* = 15.8 Hz, 1H), 6.20 (dd, *J* = 15.8, 7.2 Hz, 1H), 4.76 - 4.58 (m, 2H), 3.89 - 3.80 (m, 1H). ¹⁹F NMR (376 MHz, chloroform-d) δ -217.43 - -217.73 (m). ¹³C NMR (100 MHz, chloroform-d) δ 141.78, 137.88, 133.04, 129.47, 128.88, 127.31, 127.20, 125.79, 125.69, 124.22, 85.29 (d, *J* = 176 Hz), 48.46 (d, *J* = 20 Hz). HRMS (ES) *m/z*: [M]⁺ Calcd for C₁₄H₁₂ClFS 266.0332, found 266.0333.

6. Investigation of the metal contamination using coupled plasma mass spectroscopy

(ICP-MS)

Because it has been reported that trace transition-metal contaminants in reagents were able to catalyze coupling reactions, we investigated the metal contamination using coupled plasma mass spectroscopy (ICP-MS) (Table 1). The content of various transition-metals such as Pd, Ni in the styryl boronic acid was below the detection limit. Pd, Ni and Co content in K₃PO₄ are also very low. Cu and Fe contamination are slightly higher, but they are not likely able to catalyze coupling reaction.

Table 1. ICP-MS analysis of trace transition metals

Metal ^a	Pd	Ni	Cu	Co	Fe
K ₃ PO ₄ ^b	< 0.02	< 0.02	0.18	< 0.02	0.49
Ph(CH) ₂ B(OH) ₂ ^c	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02

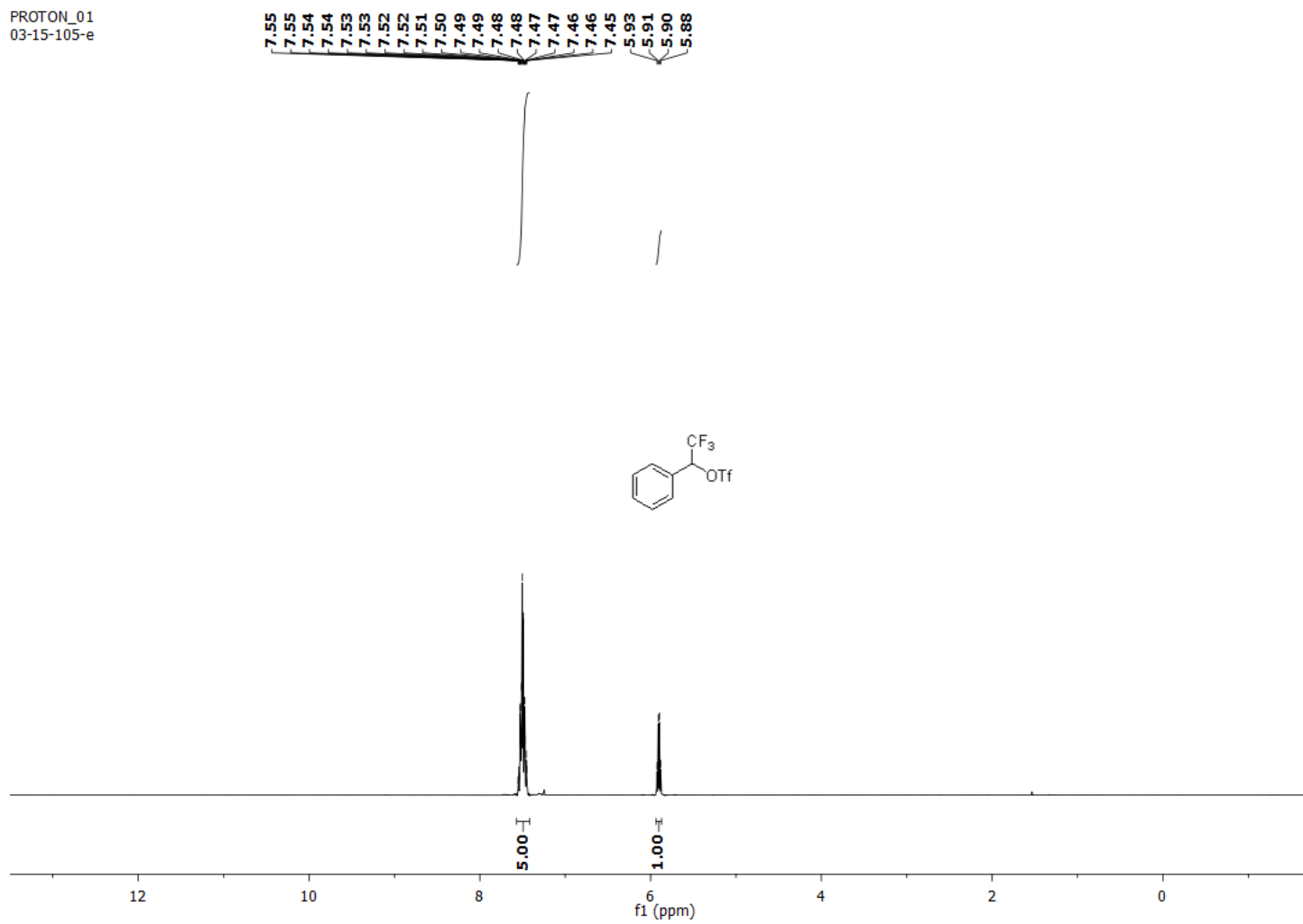
^a 1 unit = 1 mg/g, ^b K₃PO₄ (99%) was purchased from J&K. ^c Ph(CH)₂B(OH)₂ was synthesized through

Cu-catalyzed borylation of alkynes.

7. Copies of NMR Spectra

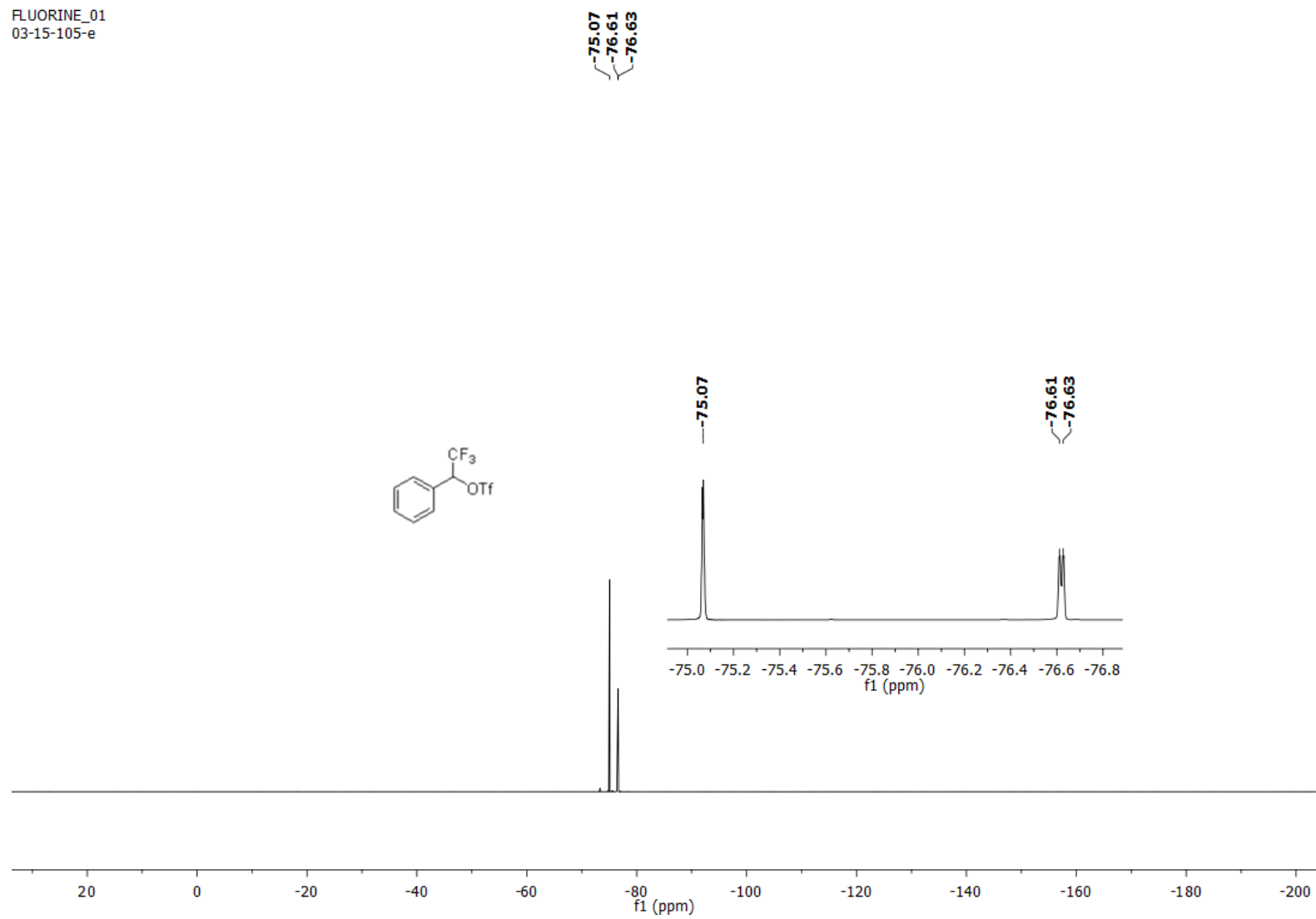
^1H NMR (400 MHz, CDCl_3) of 1a

PROTON_01
03-15-105-e



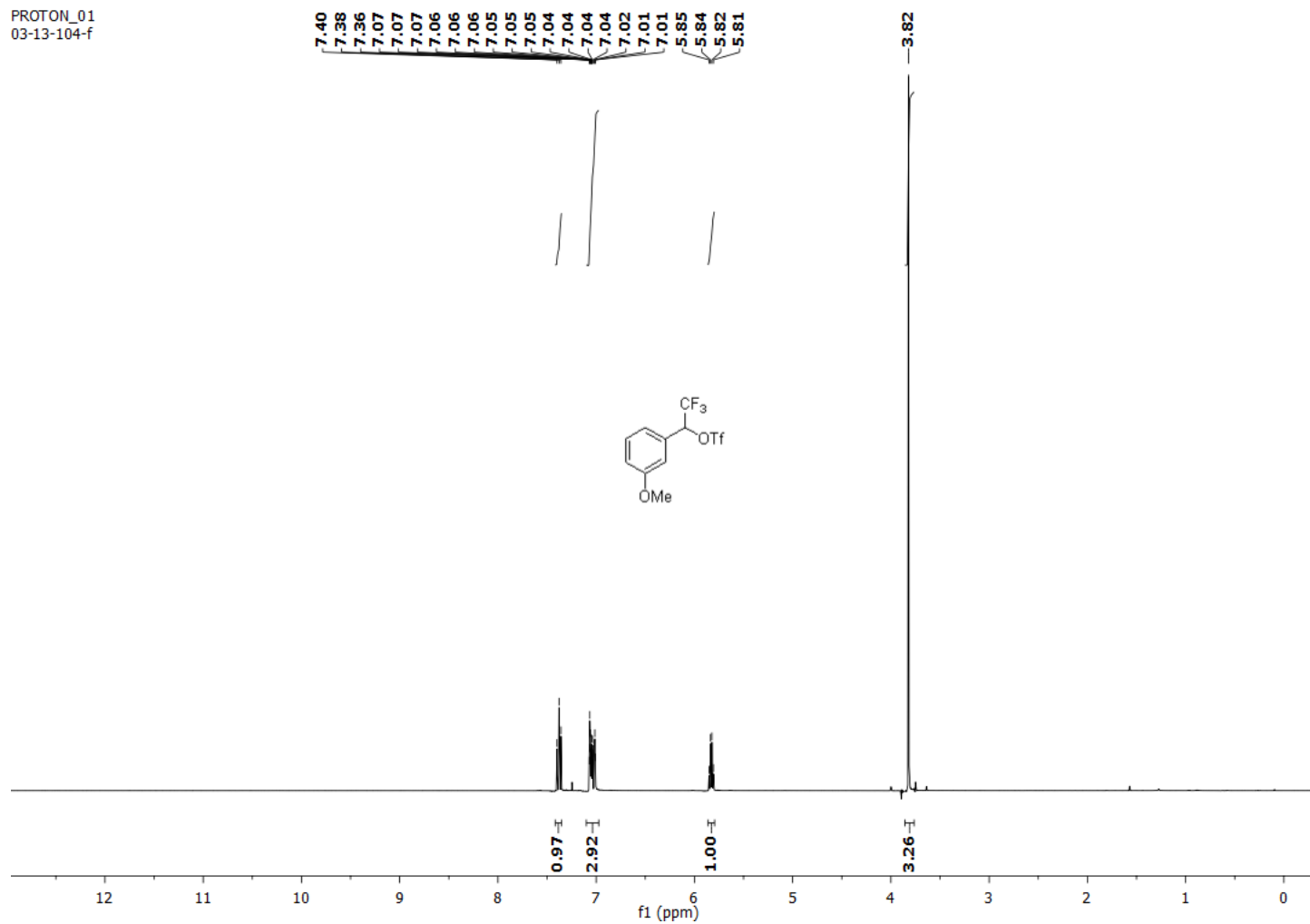
¹⁹F NMR (376 MHz, CDCl₃) of 1a

FLUORINE_01
03-15-105-e



¹H NMR (400 MHz, CDCl₃) of 1b

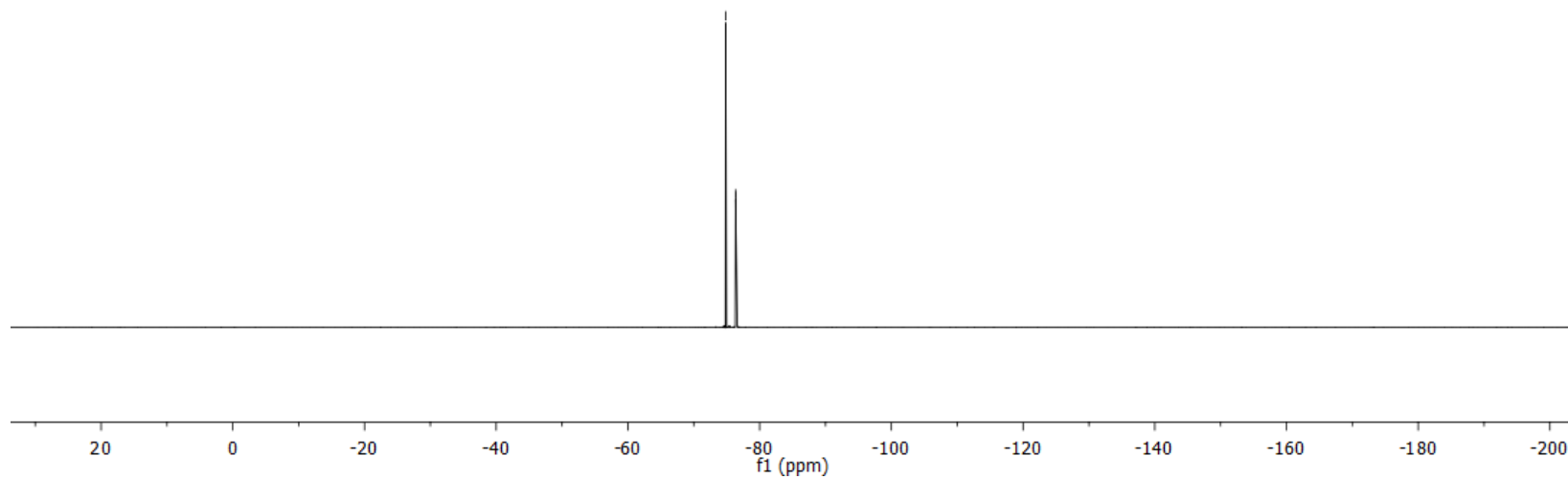
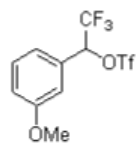
PROTON_01
03-13-104-f



¹⁹F NMR (376 MHz, CDCl₃) of 1b

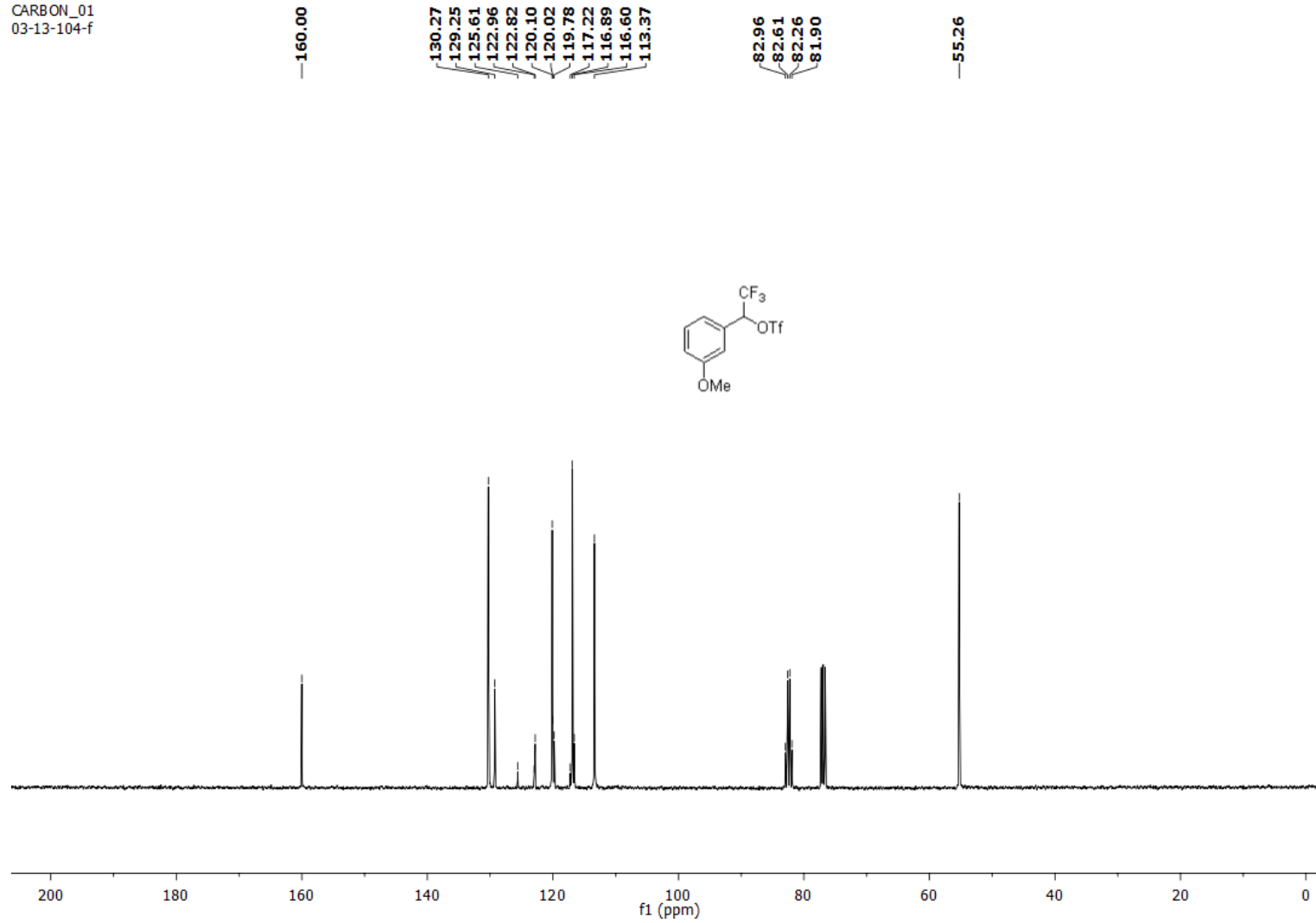
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-74.85
-76.34
-76.36

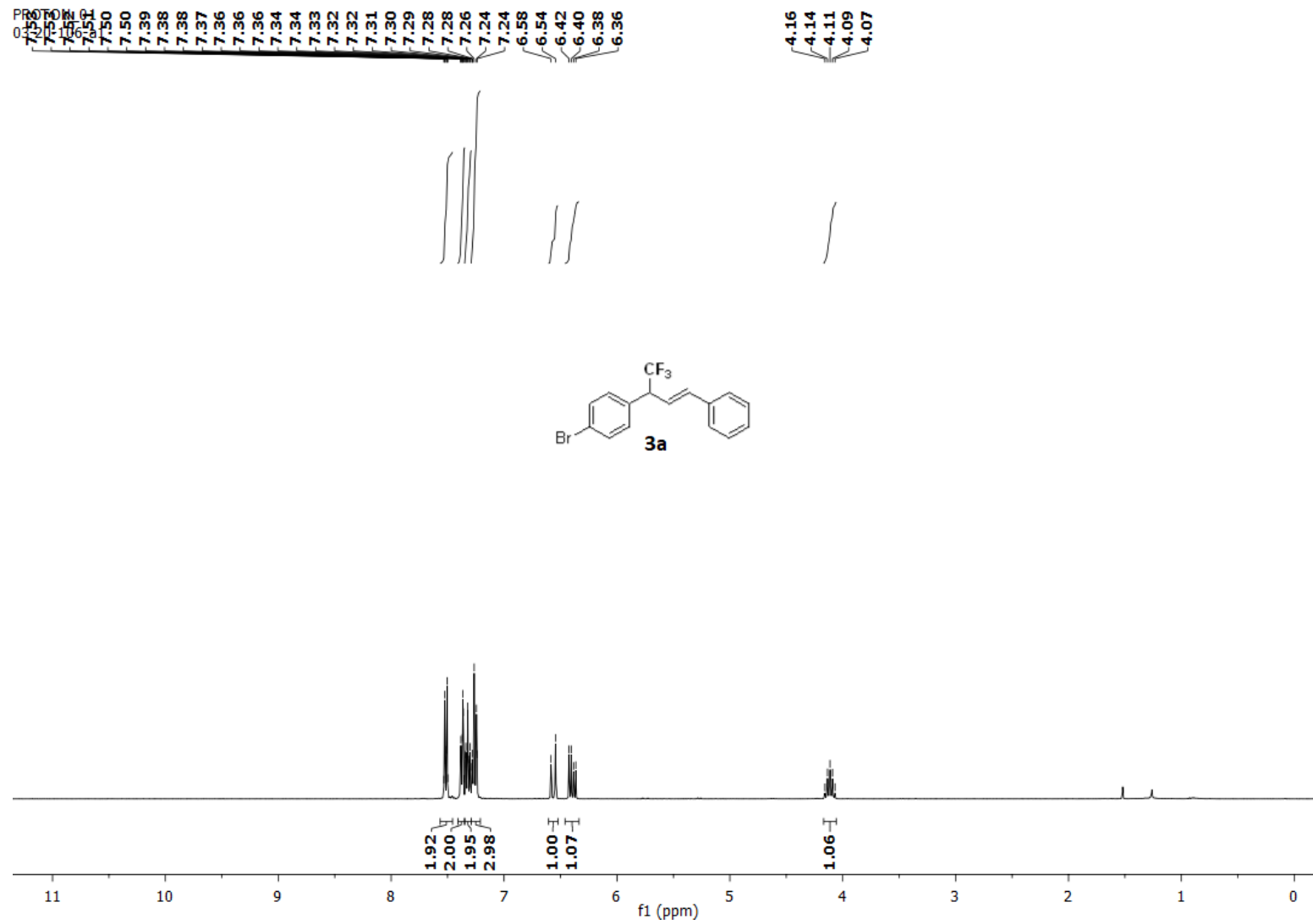


¹³C NMR (100 MHz, CDCl₃) of 1b

CARBON_01
03-13-104-f



¹H NMR (400 MHz, CDCl₃) of 3a

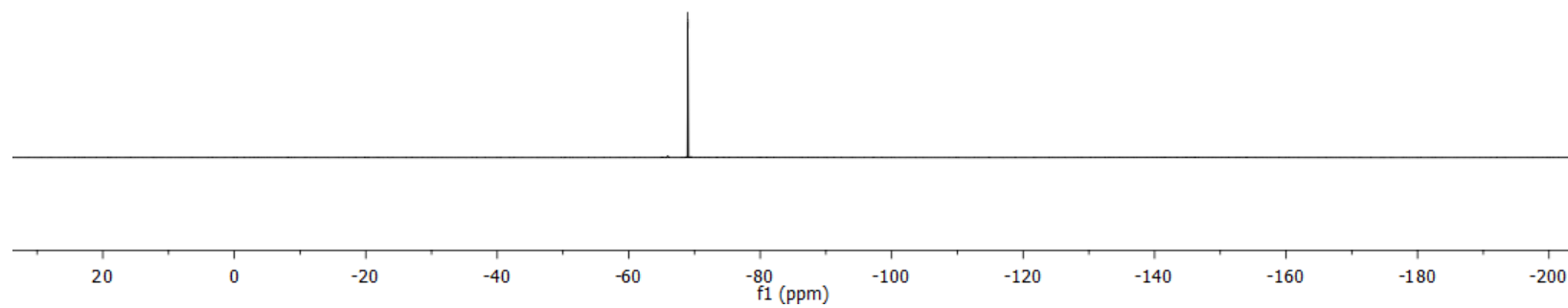
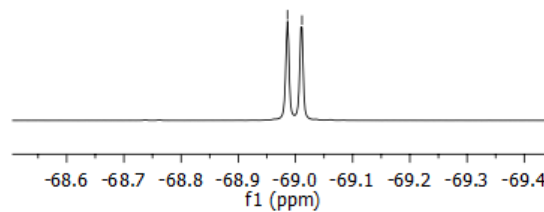
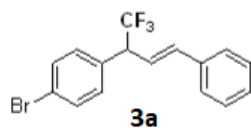


¹⁹F NMR (376 MHz, CDCl₃) of 3a

FLUORINE_01
03-20-106-a1

-68.99
-69.01

-68.99
-69.01

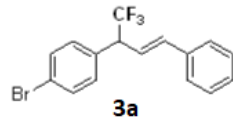


¹³C NMR (100 MHz, CDCl₃) of 3a

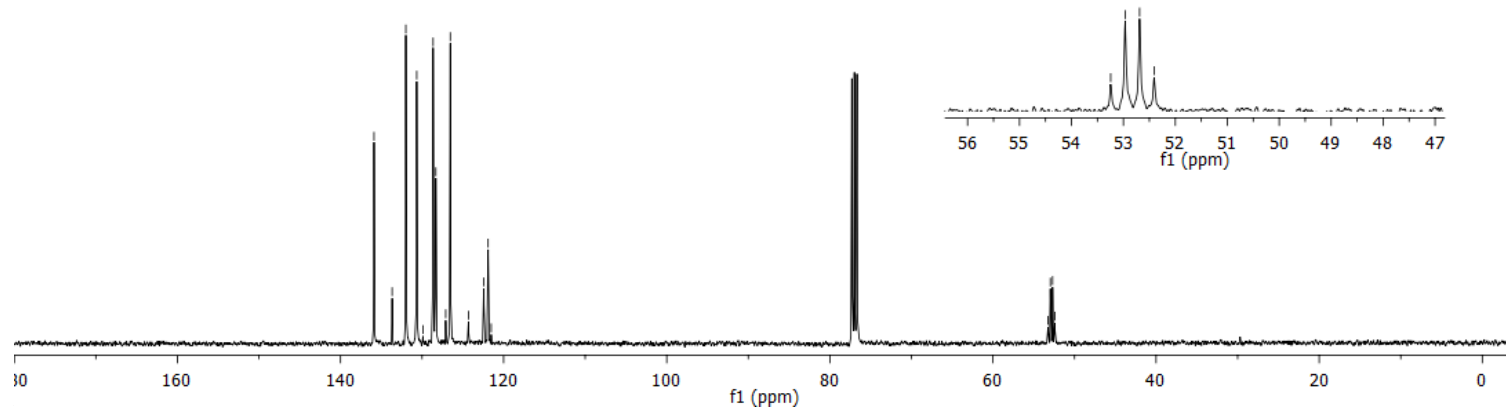
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03-20-106-a11

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133.67
131.99
130.65
129.89
128.64
128.31
127.10
126.53
124.31
122.43
121.90
121.52

53.24
52.97
52.69
52.41

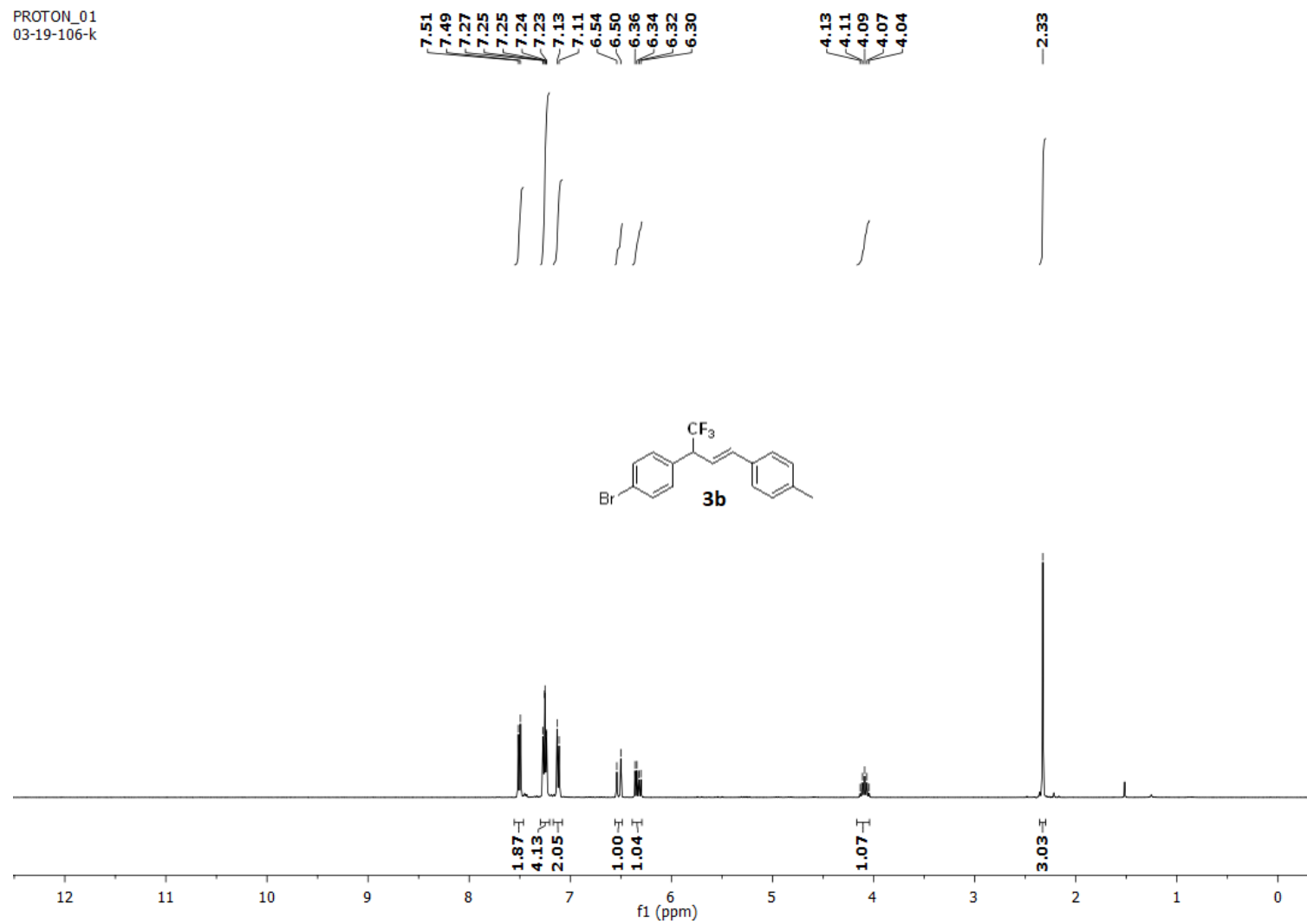


53.24
52.97
52.69
52.41



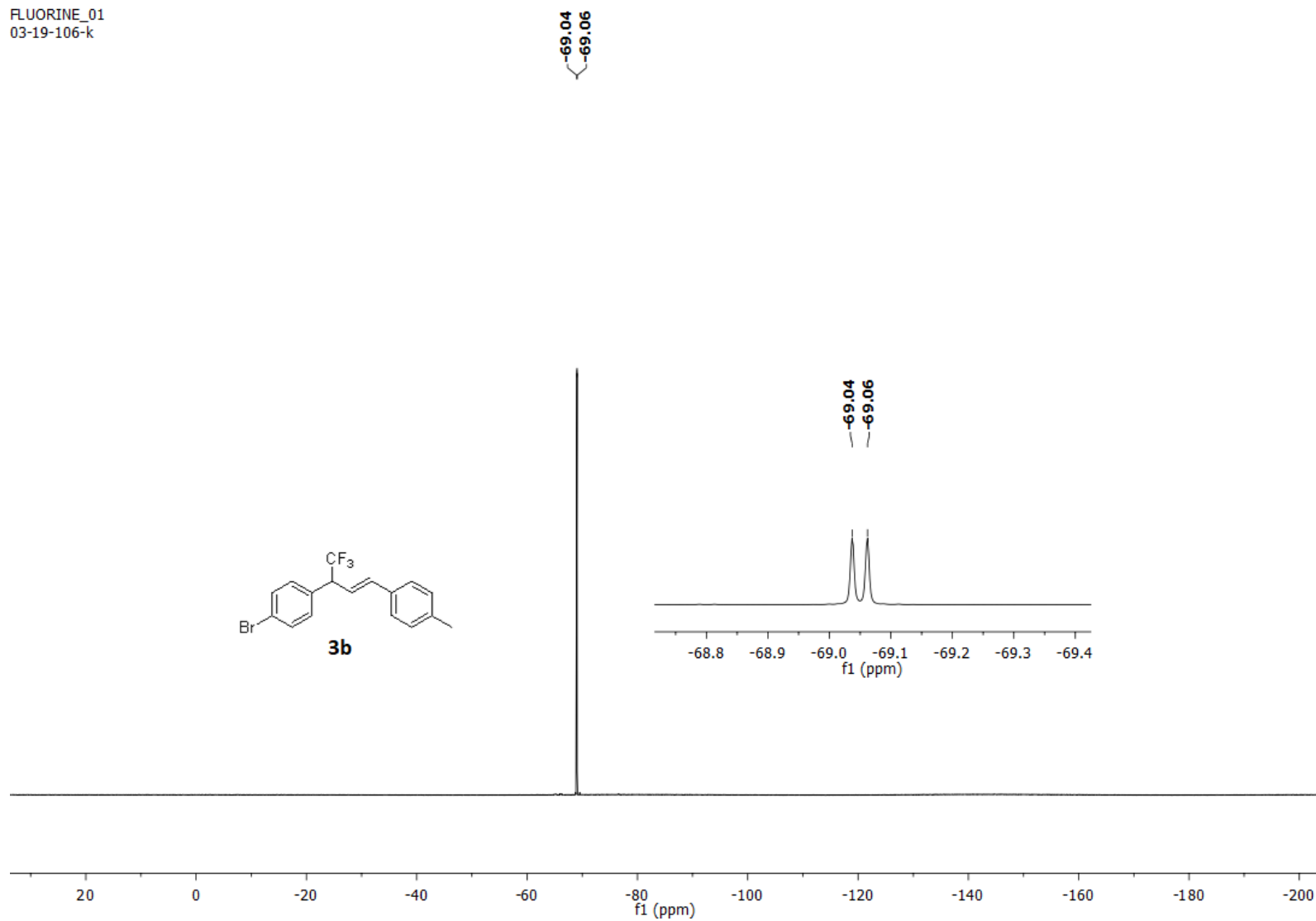
PROTON_01
03-19-106-k

¹H NMR (400 MHz, CDCl₃) of 3b



¹⁹F NMR (376 MHz, CDCl₃) of 3b

FLUORINE_01
03-19-106-k



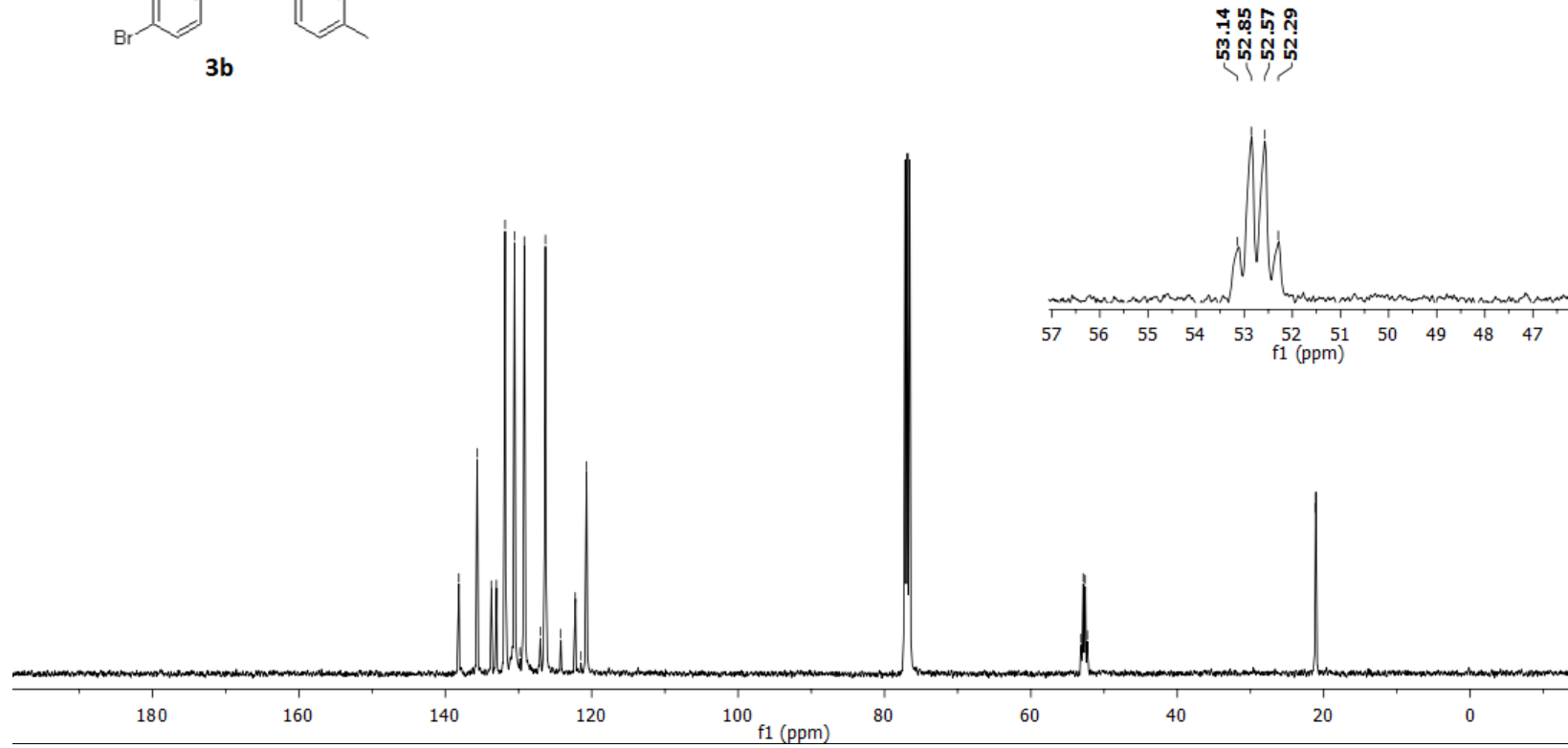
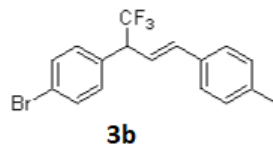
¹³C NMR (100 MHz, CDCl₃) of 3b

CARBON_01
03-24-106-k

138.15
135.63
133.72
133.02
131.82
130.53
129.81
129.20
127.02
126.31
124.23
122.25
121.46
120.71

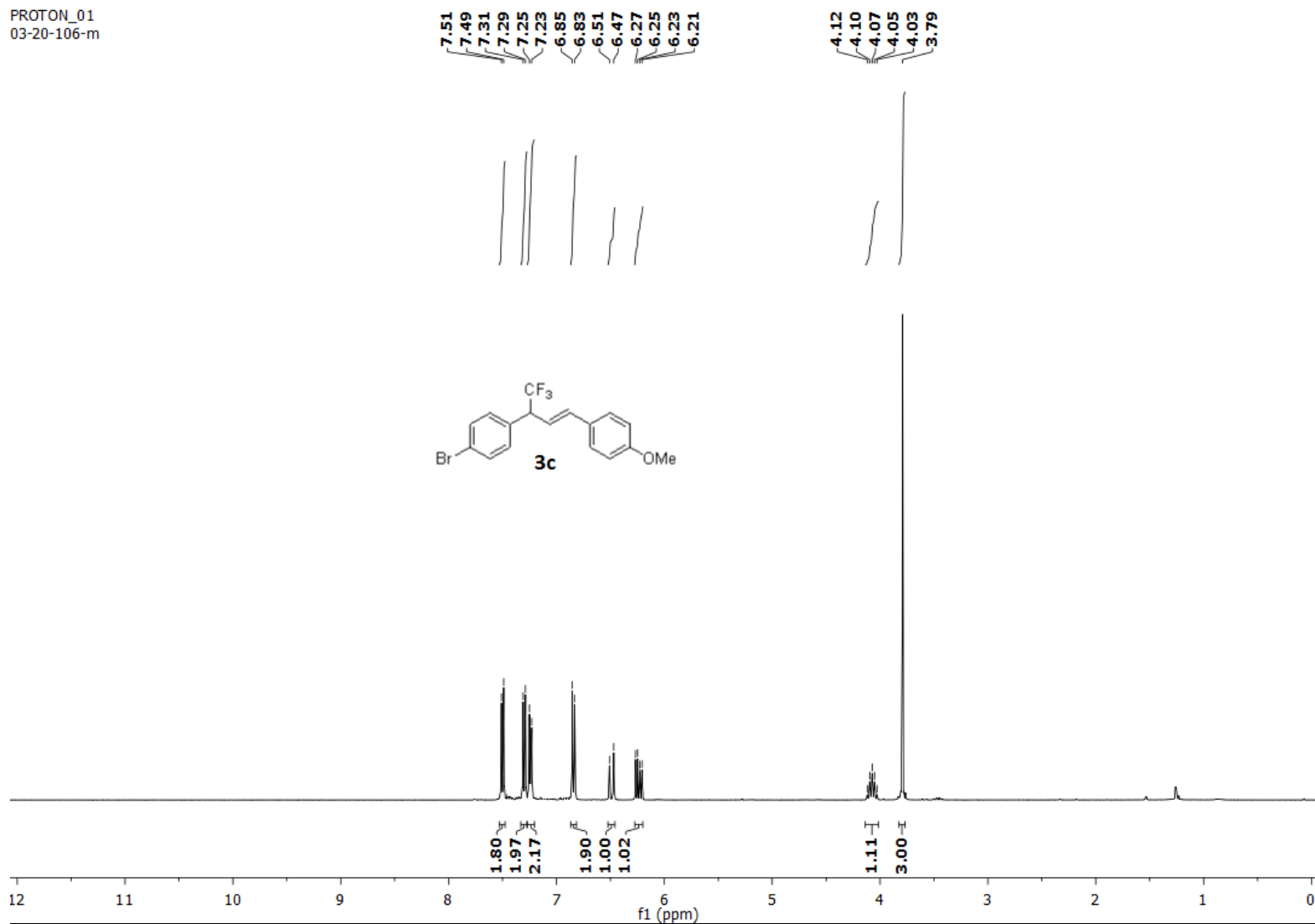
53.14
52.85
52.57
52.29

21.10



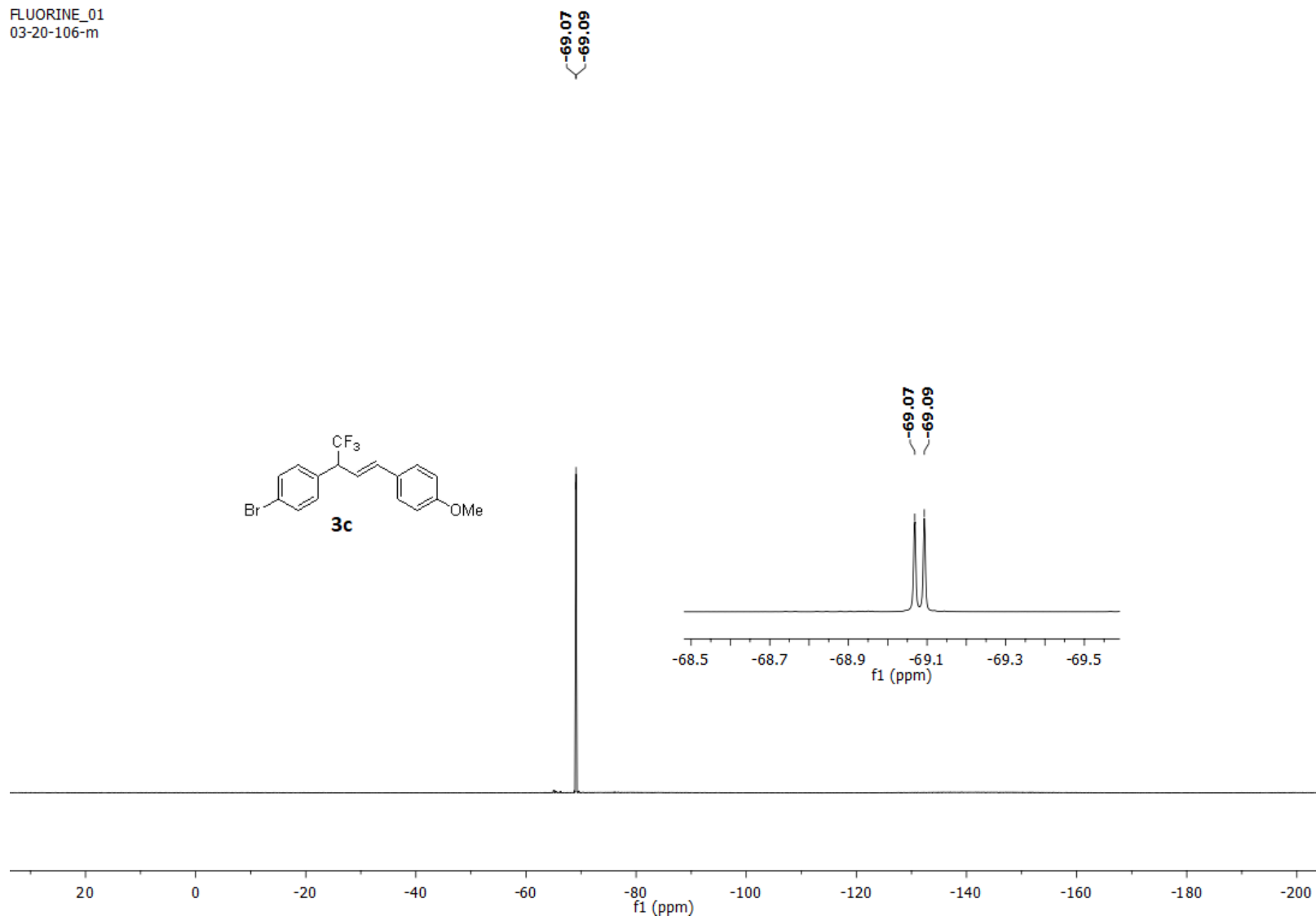
PROTON_01
03-20-106-m

¹H NMR (400 MHz, CDCl₃) of 3c



FLUORINE_01
03-20-106-m

^{19}F NMR (376 MHz, CDCl_3) of **3c**



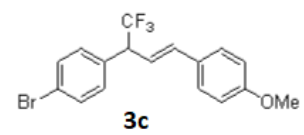
CARBON_01
03-25-106-m

¹³C NMR (100 MHz, CDCl₃) of 3c

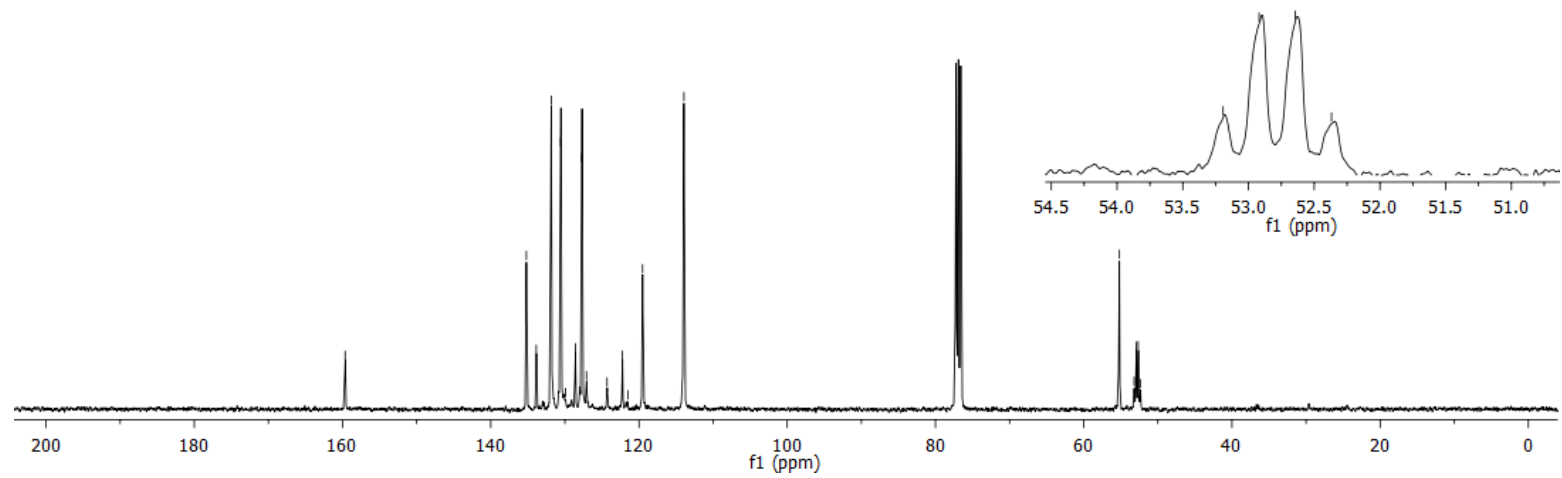
—159.65

135.20
133.86
131.85
130.58
129.91
128.59
127.73
127.09
124.31
122.25
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119.52
114.00
113.94

55.18
53.19
52.92
52.65
52.37

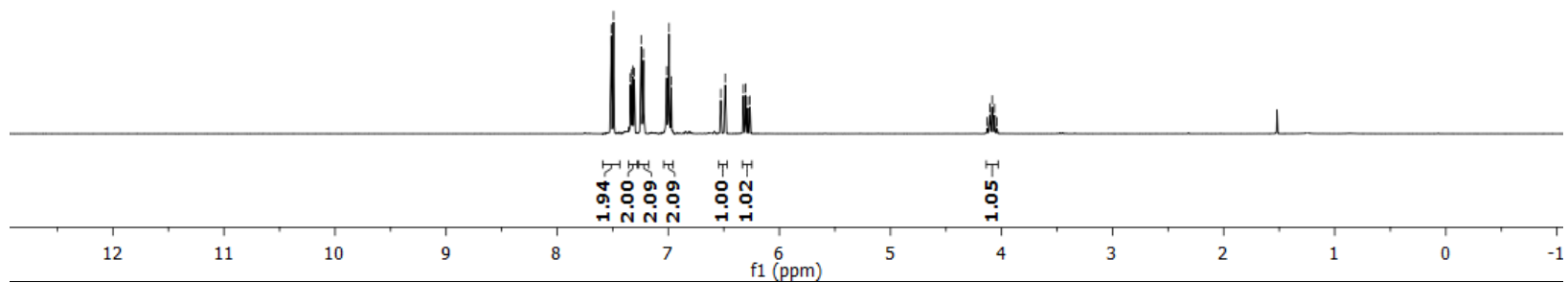
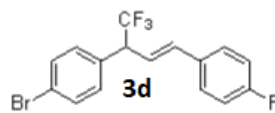
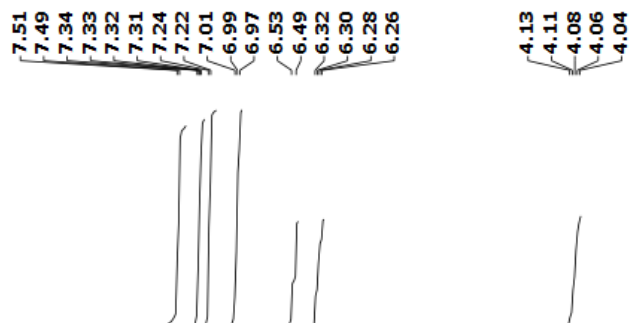


53.19
52.92
52.65
52.37



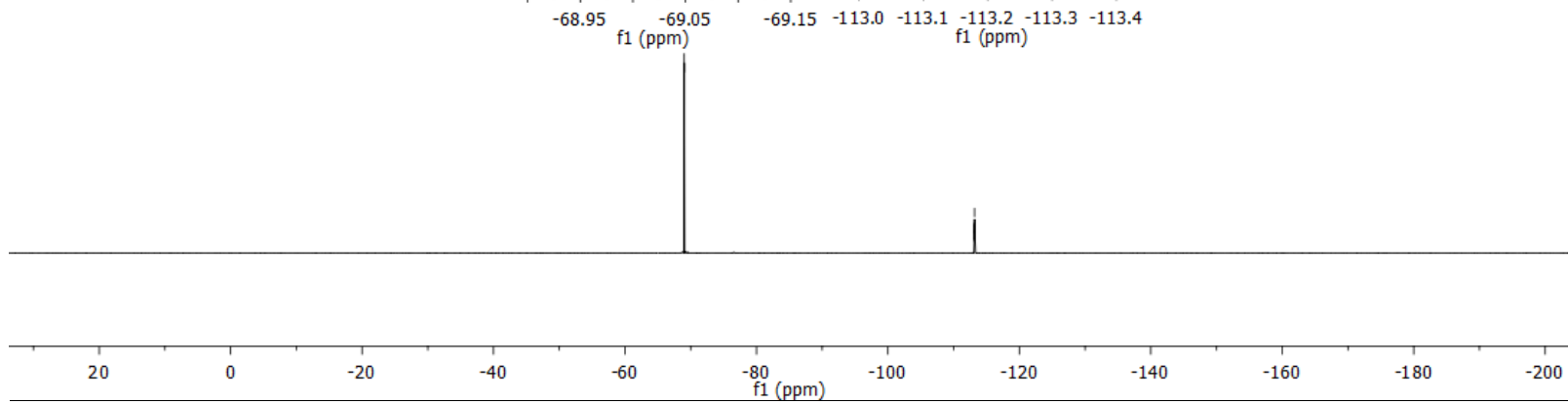
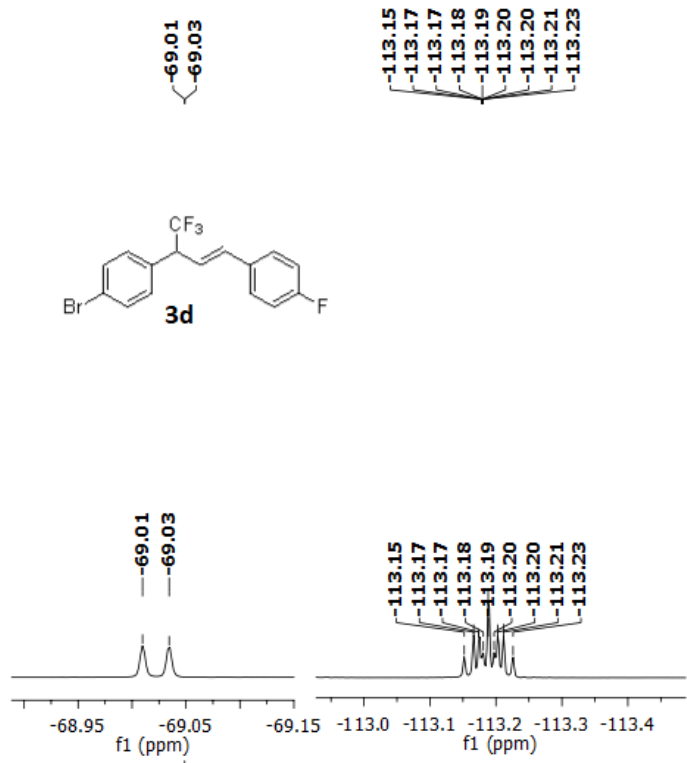
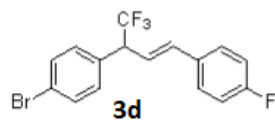
PROTON_01
03-30-107-g

^1H NMR (400 MHz, CDCl_3) of **3d**



FLUORINE_01
03-30-107-g

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



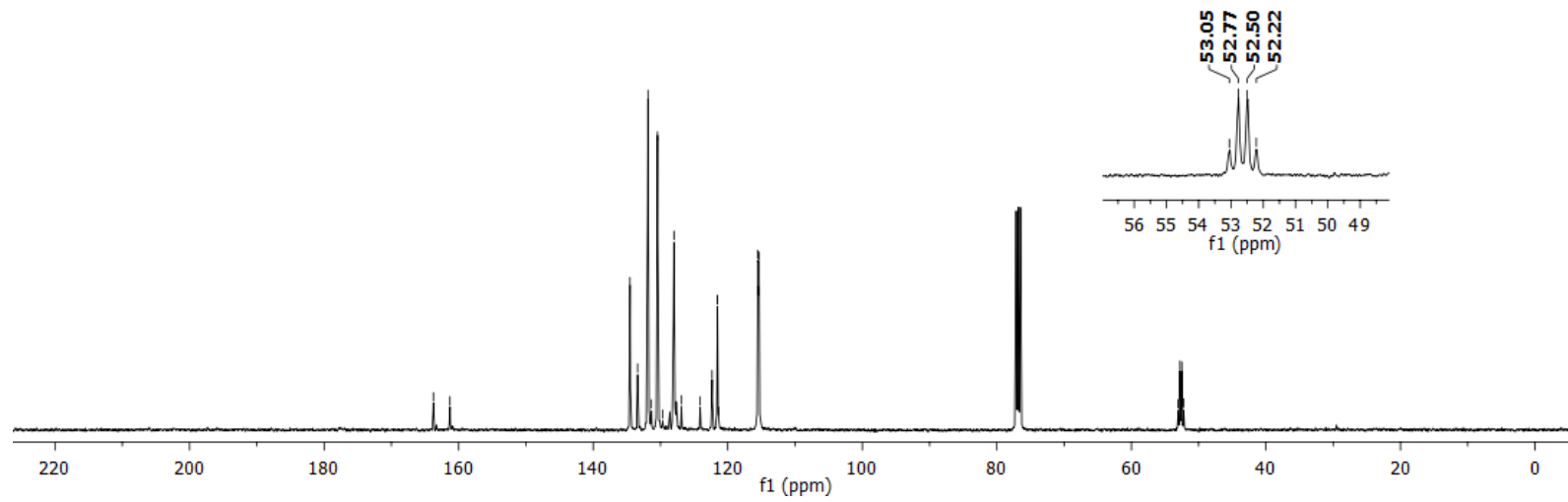
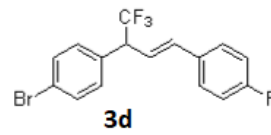
¹³C NMR (100 MHz, CDCl₃) of 3d

CARBON_01
03-31-107-g

163.76
161.29

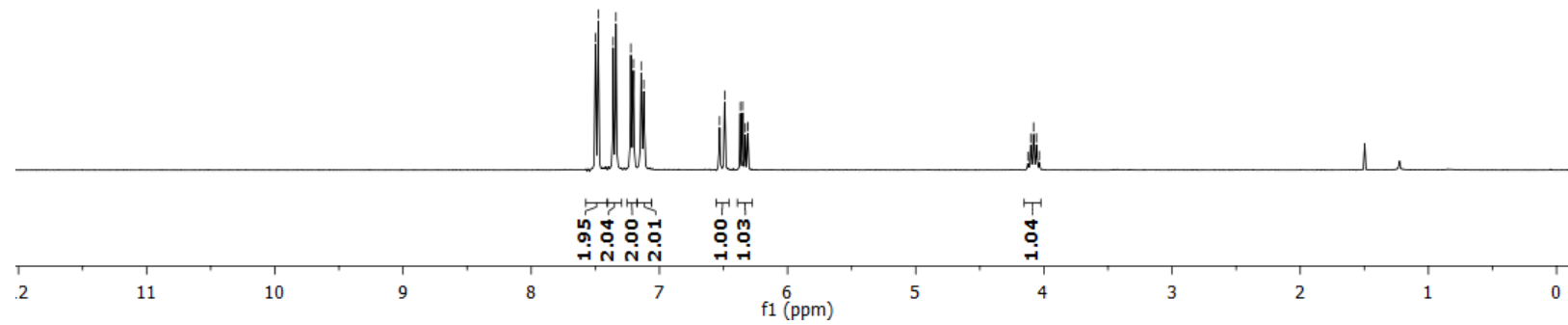
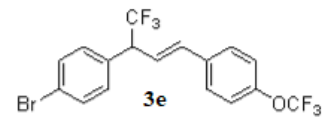
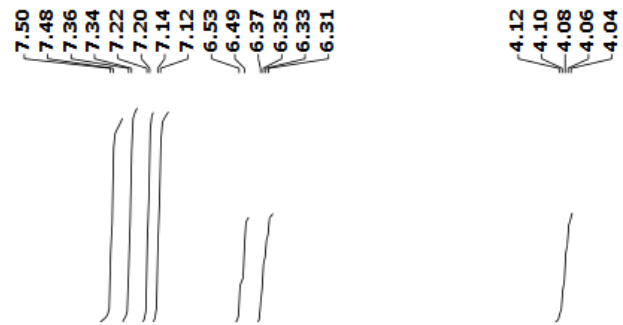
134.54
133.39
131.85
131.34
130.45
129.69
128.00
126.89
124.11
122.32
121.53
121.53
121.33
115.58
115.53
115.36
115.32

53.05
52.77
52.50
52.22



¹H NMR (400 MHz, CDCl₃) of 3e

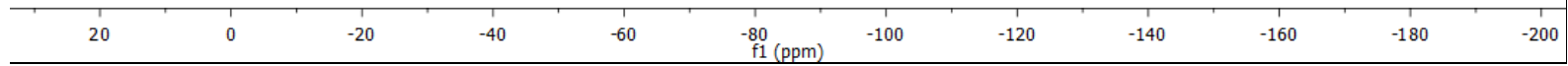
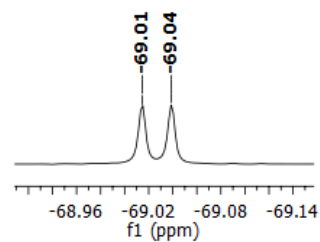
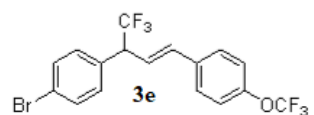
PROTON_01
03-30-107-h



¹⁹F NMR (376 MHz, CDCl₃) of 3e

FLUORINE_01
03-30-107-h

-57.95
-69.01
-69.04

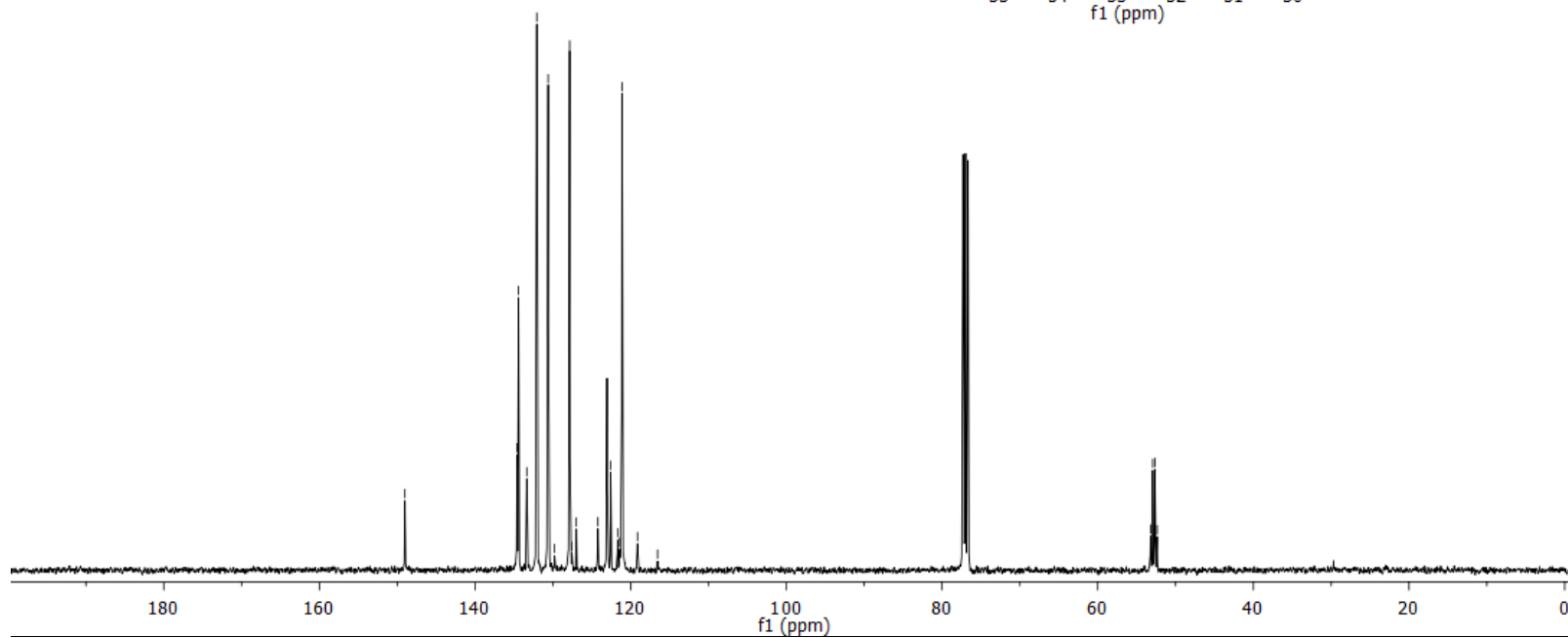
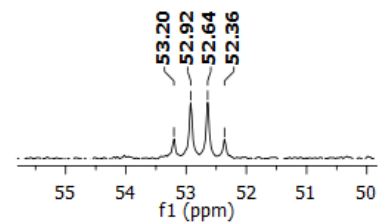
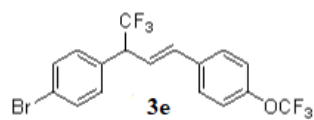


¹³C NMR (100 MHz, CDCl₃) of 3e

CARBON_01
03-30-107-h1

149.01
134.61
134.41
133.36
132.07
130.61
129.79
127.85
127.56
126.99
124.21
122.57
121.68
121.41
121.11
119.12
116.55

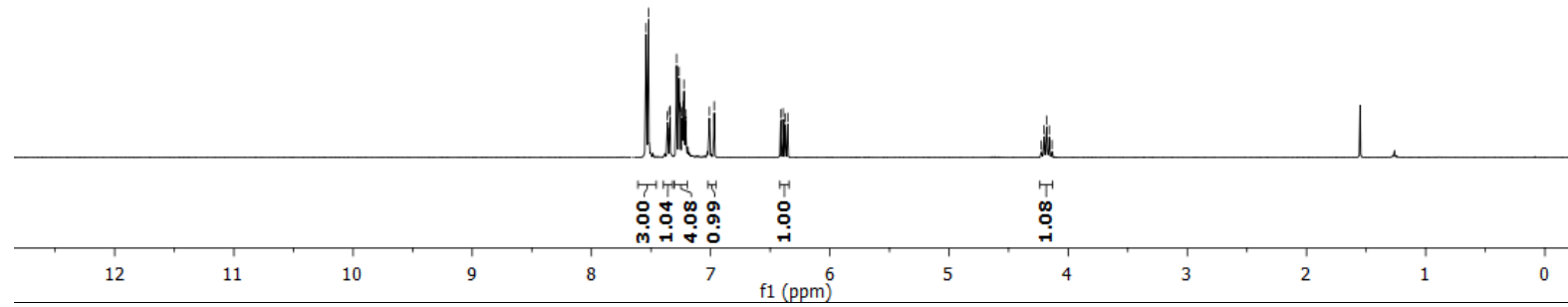
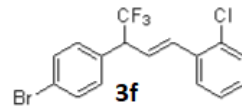
53.20
52.92
52.64
52.36



¹H NMR (400 MHz, CDCl₃) of 3f

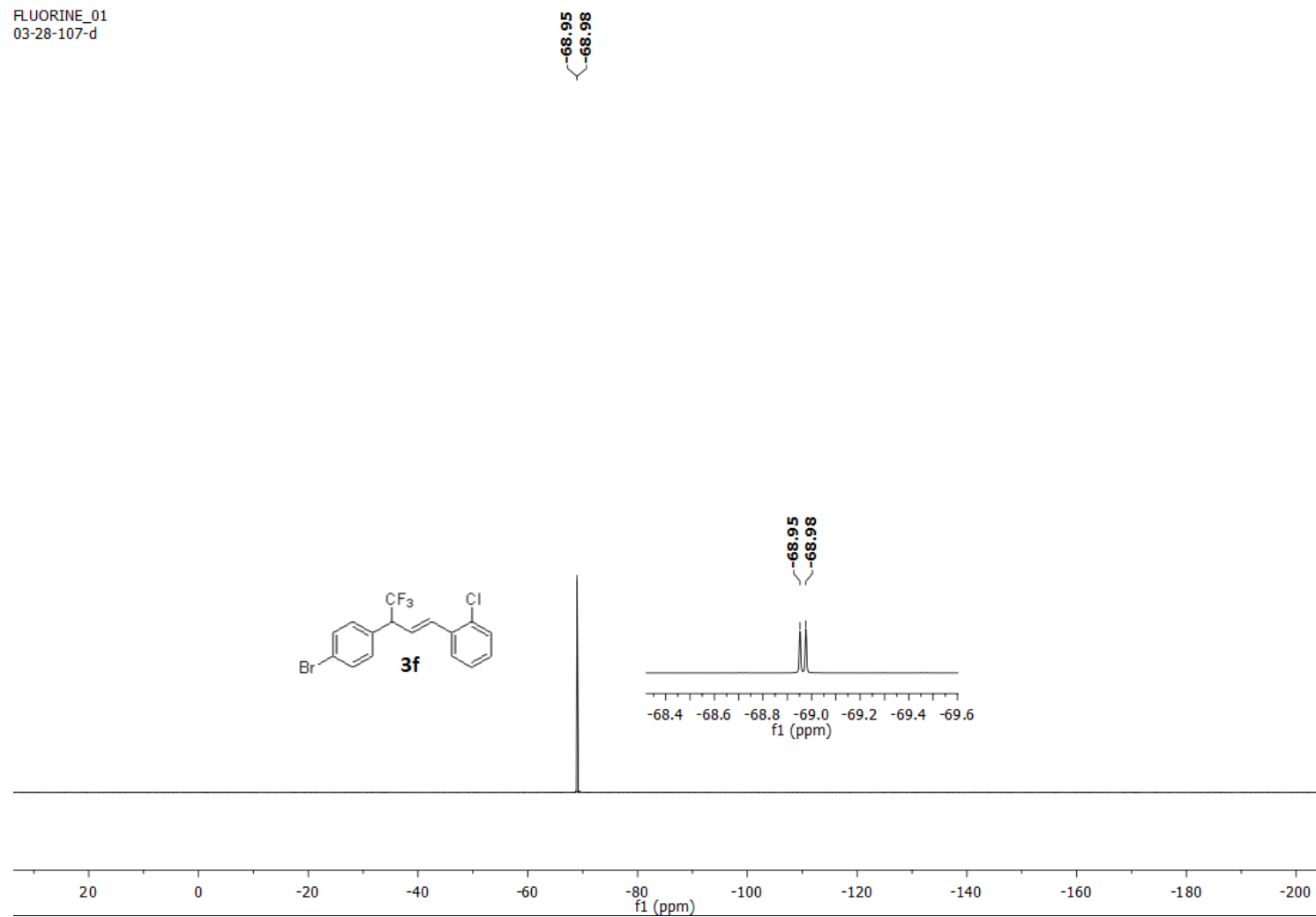
PROTON_01
03-28-107-d

7.54
7.52
7.36
7.36
7.34
7.34
7.28
7.26
7.24
7.24
7.23
7.22
7.22
7.21
7.20
7.01
6.97
6.41
6.39
6.37
6.35
4.23
4.20
4.18
4.16
4.14



FLUORINE_01
03-28-107-d

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

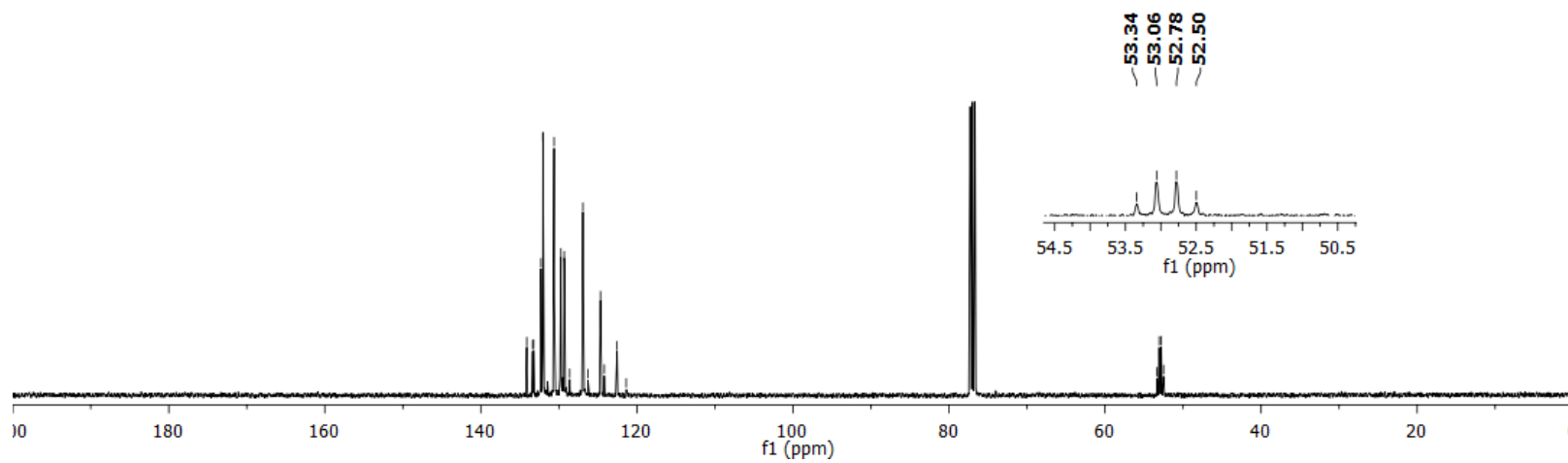
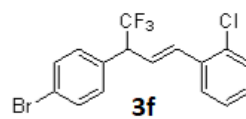


CARBON_01
03-28-107-d0

^{13}C NMR (100 MHz, CDCl_3) of **3f**

134.12
133.37
133.24
132.30
132.04
132.02
130.62
129.74
129.31
128.61
126.92
126.27
124.67
124.17
122.54
121.37

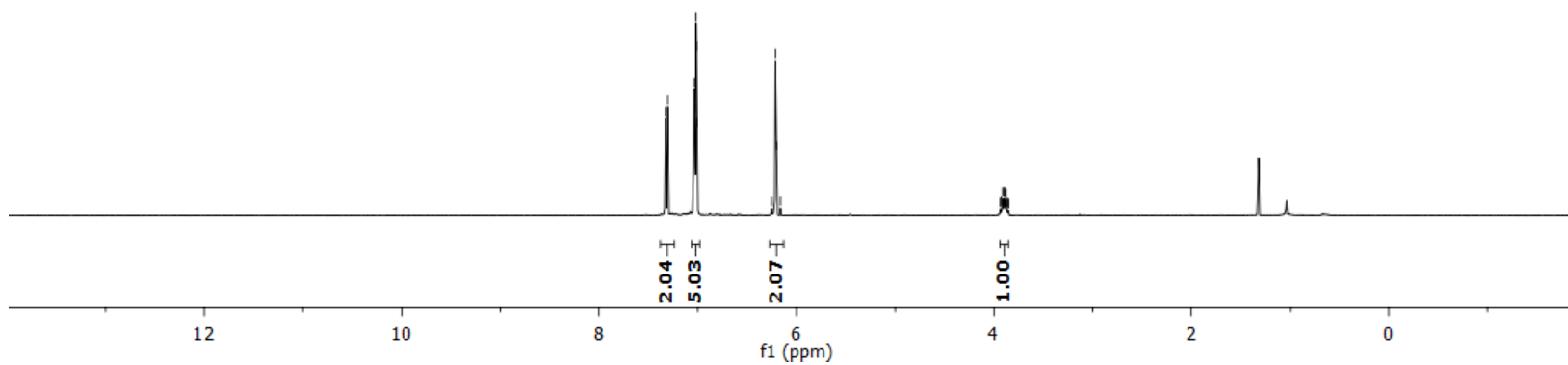
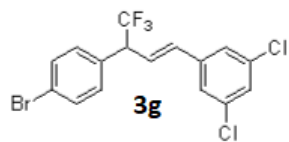
53.34
53.06
52.78
52.50



PROTON_01
03-31-108-d

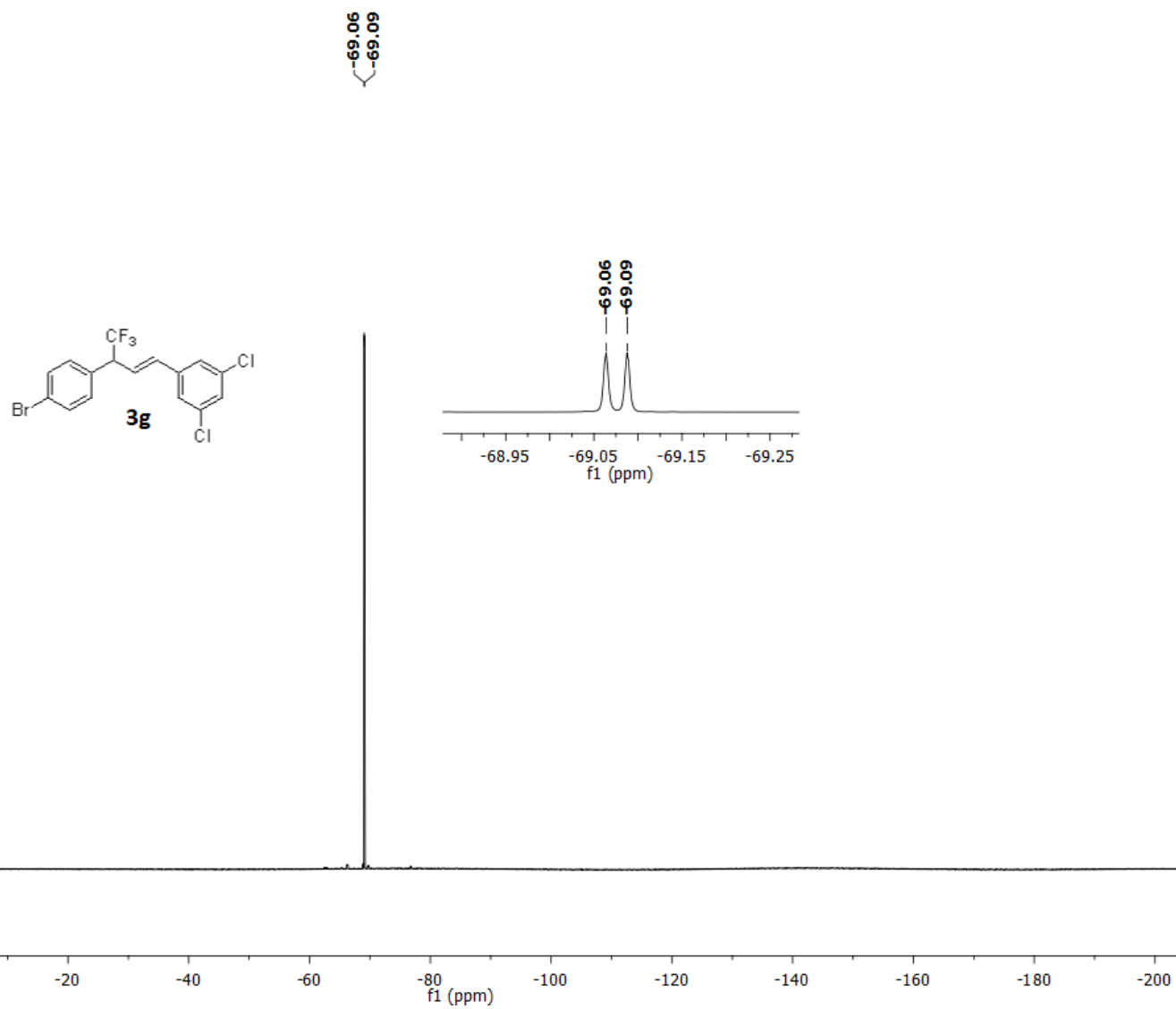
¹H NMR (400 MHz, CDCl₃) of 3g

7.33 7.30 7.04 7.03 7.02 7.01 7.01 6.25 6.21 6.20 6.16 3.94 3.92 3.91 3.90 3.89 3.89 3.88 3.87 3.86 3.85



FLUORINE_01
03-31-108-d

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

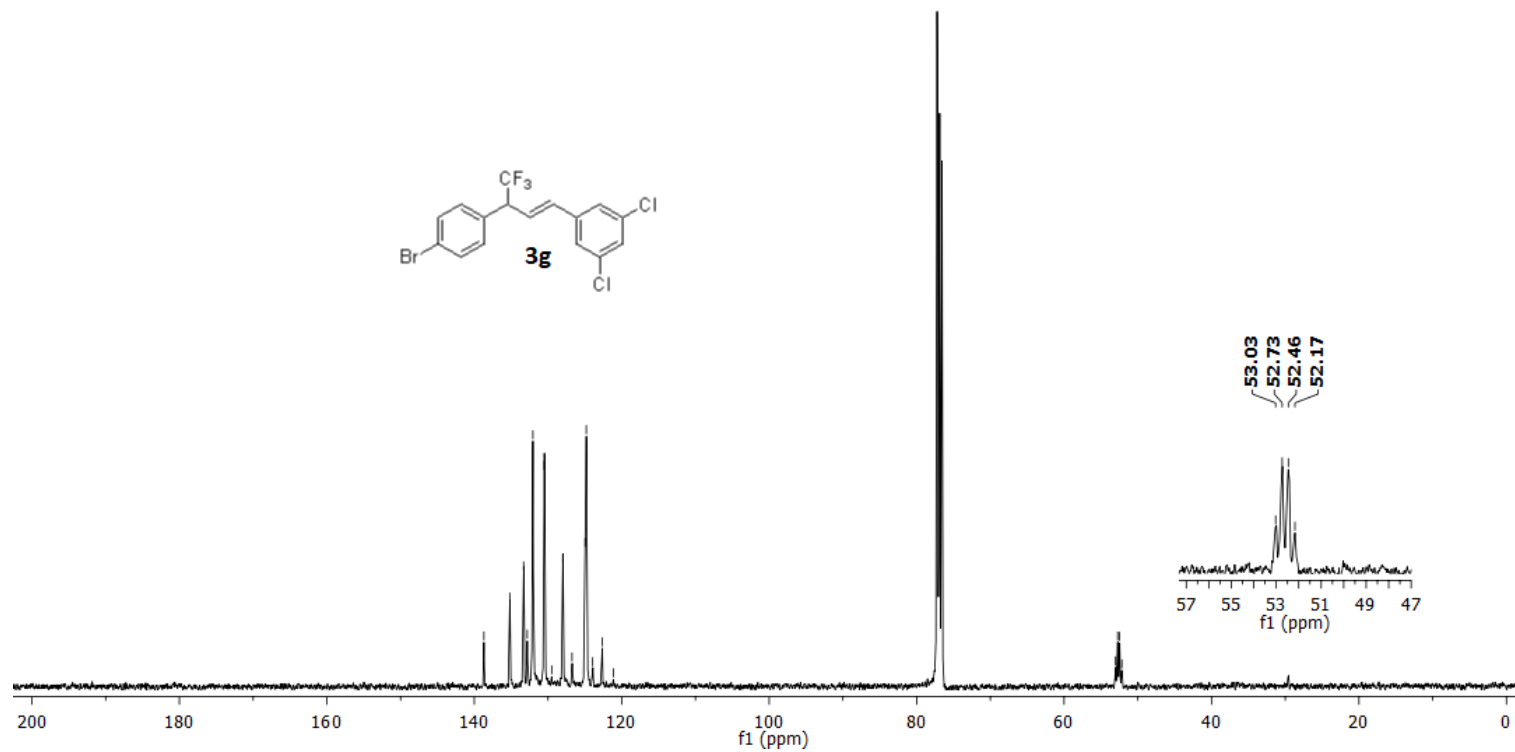
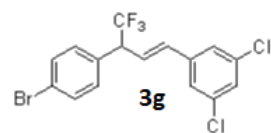


¹³C NMR (100 MHz, CDCl₃) of 3g

CARBON_01
04-01-108-d

138.70
135.19
133.31
132.81
132.05
130.52
129.50
128.00
126.74
124.97
124.81
123.95
122.66
121.14

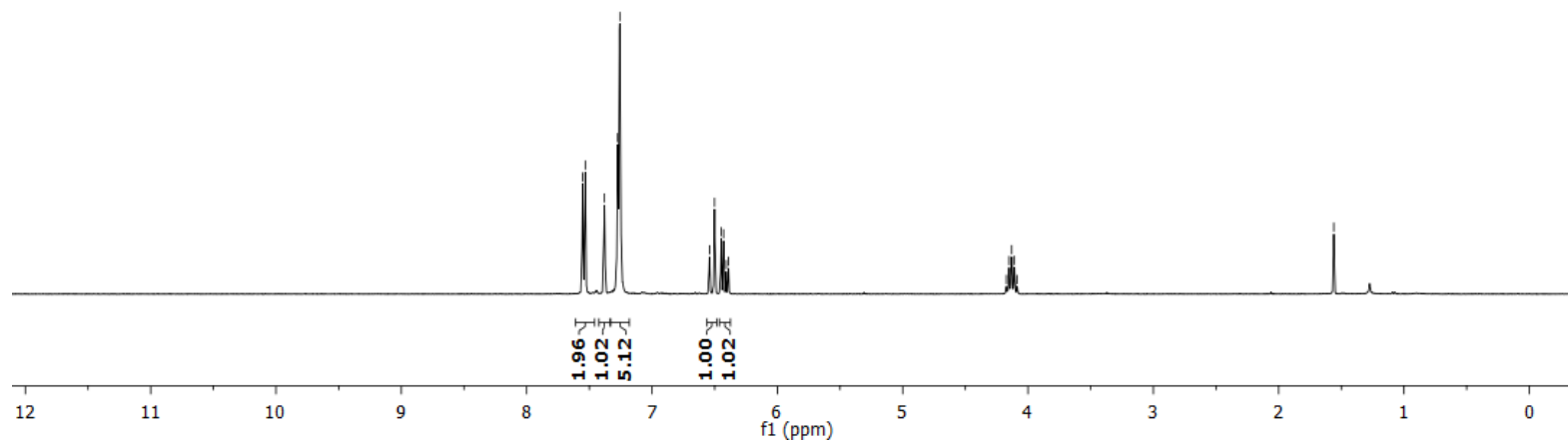
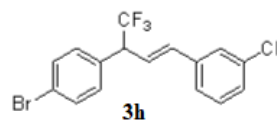
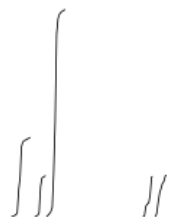
53.03
52.73
52.46
52.17



¹H NMR (400 MHz, CDCl₃) of 3h

PROTON_01
04-23-107-f

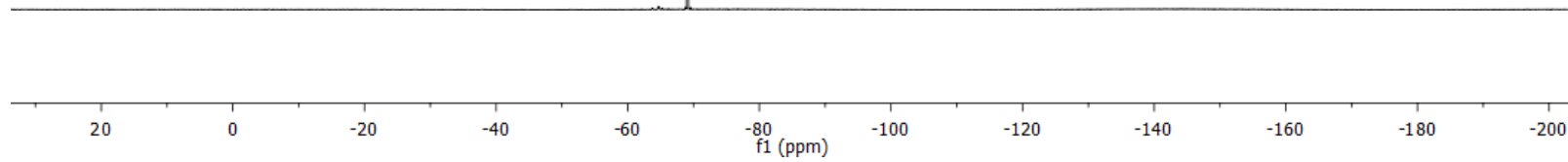
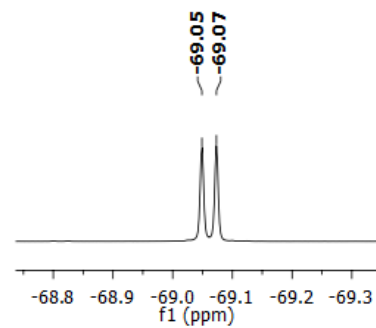
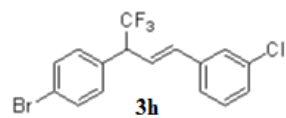
7.55
7.53
7.38
7.27
7.26
6.54
6.50
6.45
6.43
6.41
6.39
4.17
4.15
4.13
4.11
4.09
-1.56



FLUORINE_01
04-23-107-f

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

-69.05
-69.07

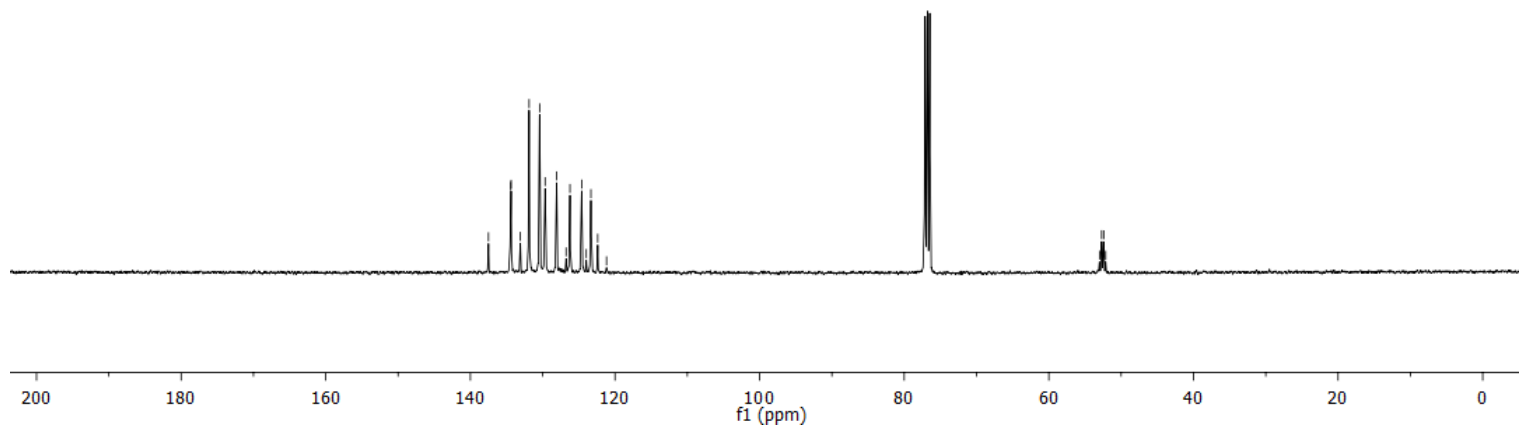
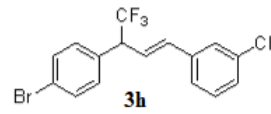


¹³C NMR (100 MHz, CDCl₃) of 3h

CARBON_02
04-23-107-f

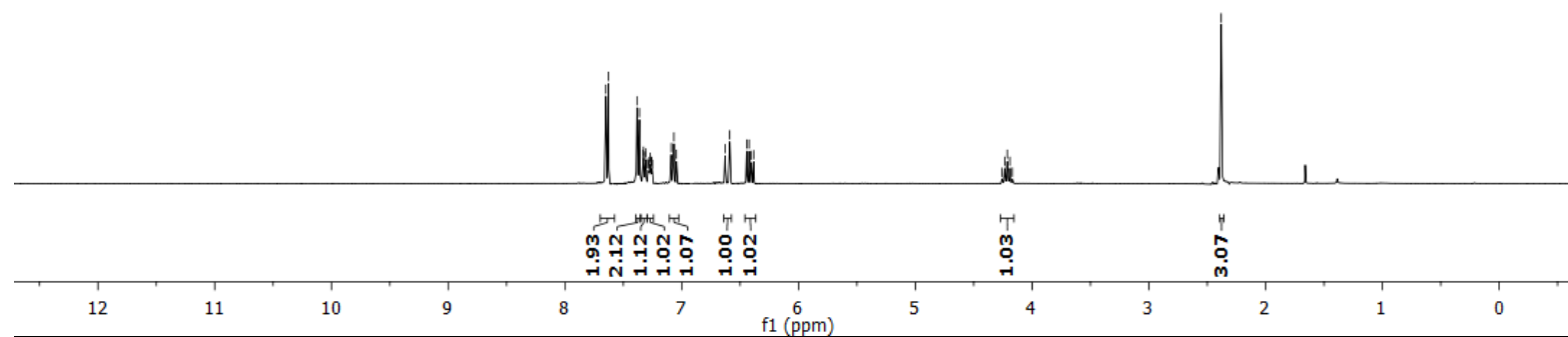
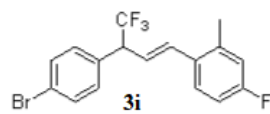
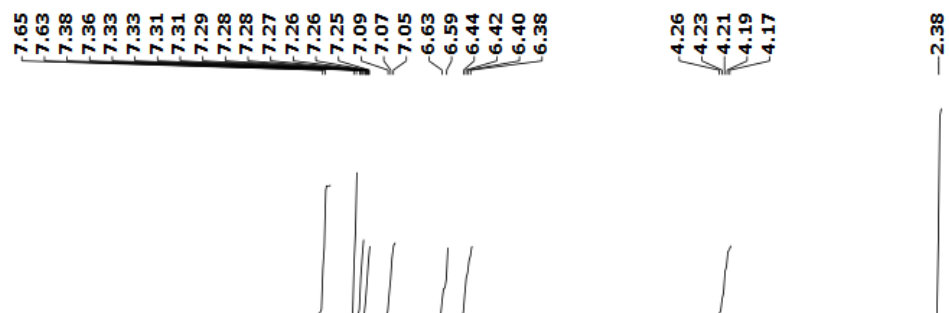
137.50
134.42
134.37
133.09
131.88
130.42
129.67
128.07
126.77
126.23
124.60
123.97
123.33
122.39
121.17

52.99
52.70
52.41
52.14



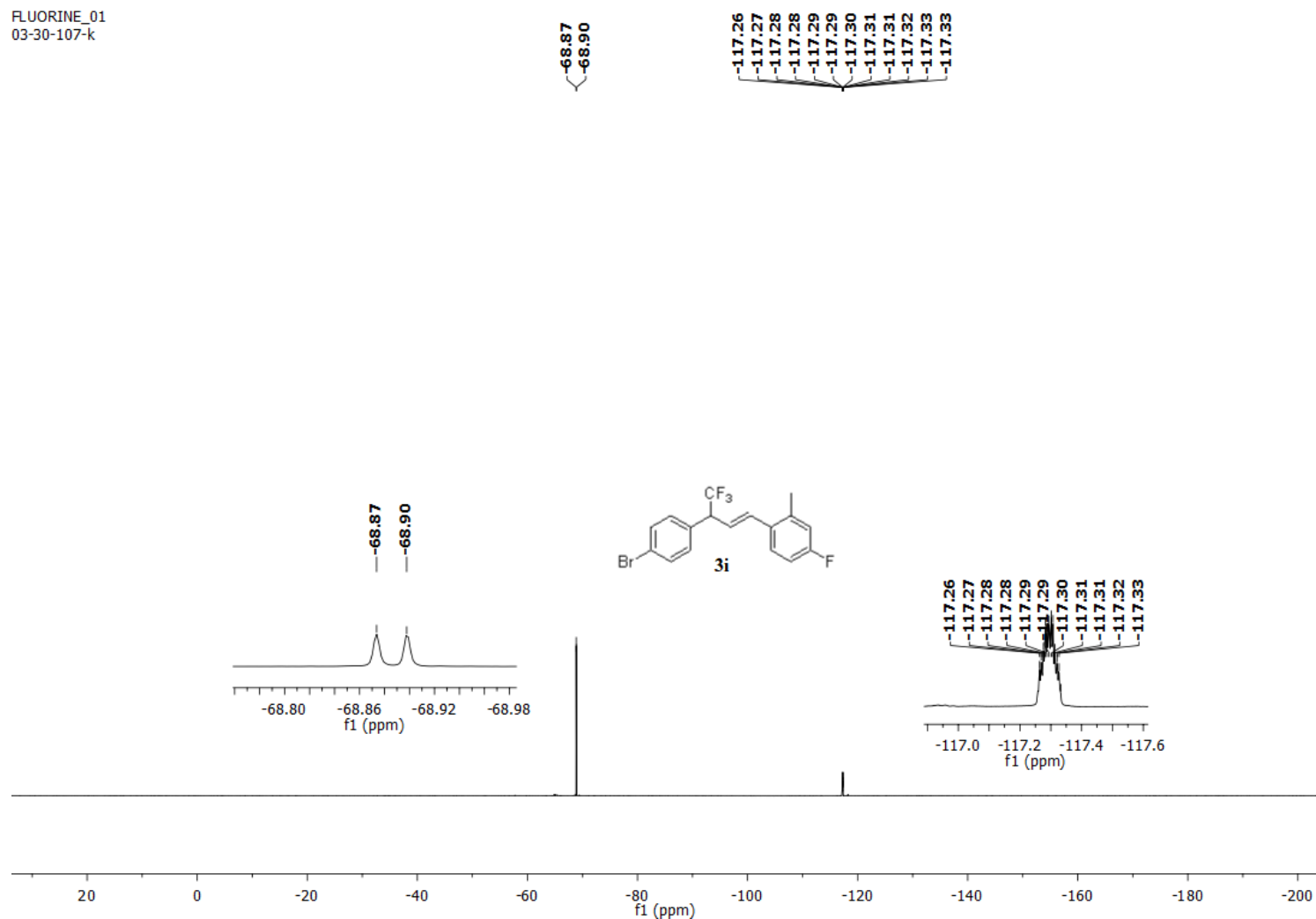
PROTON_01
03-30-107-k

^1H NMR (400 MHz, CDCl_3) of **3i**



FLUORINE_01
03-30-107-k

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



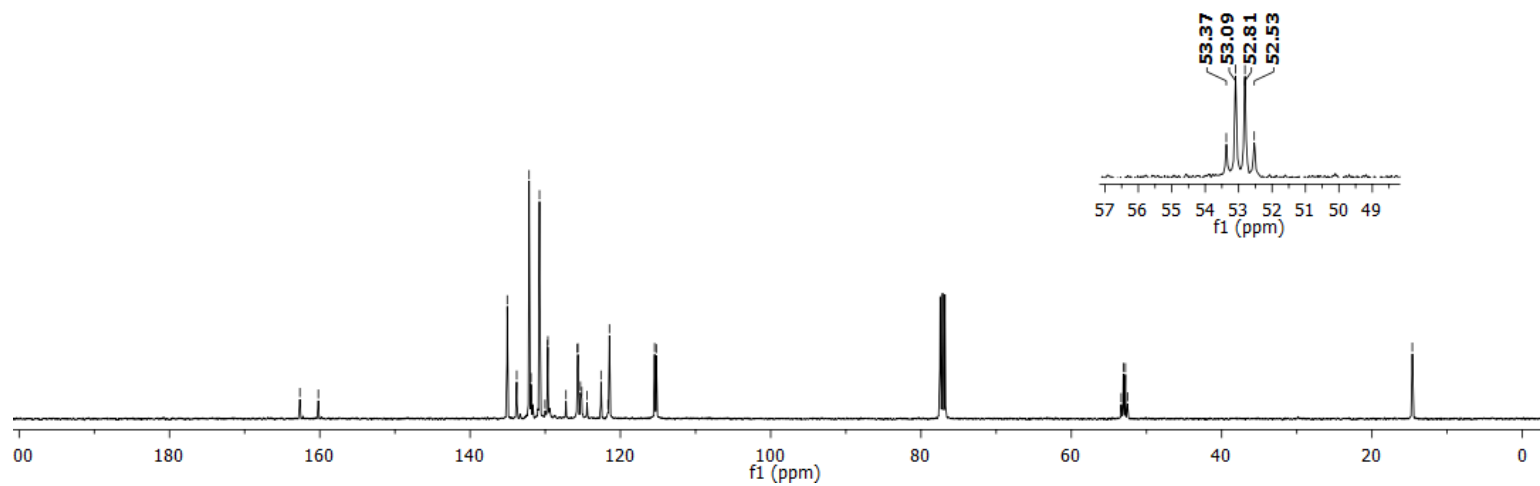
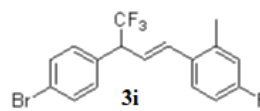
¹³C NMR (100 MHz, CDCl₃) of **3i**

CARBON_01
03-31-107-k

162.65
160.19
135.05
133.80
132.15
131.90
130.76
130.02
129.70
129.65
127.24
125.74
125.66
125.32
125.14
124.45
122.58
121.65
121.46
115.45
115.23

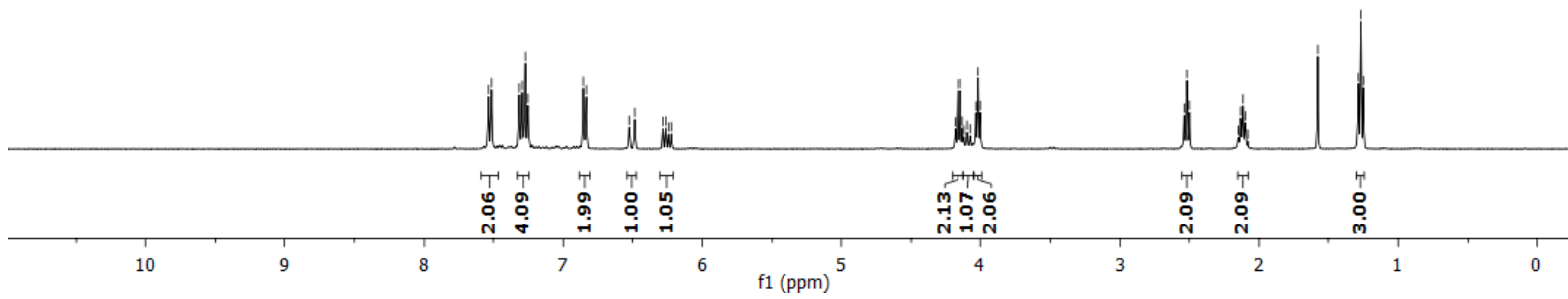
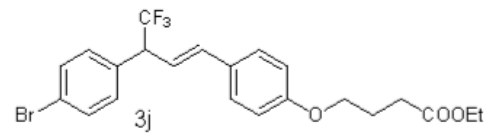
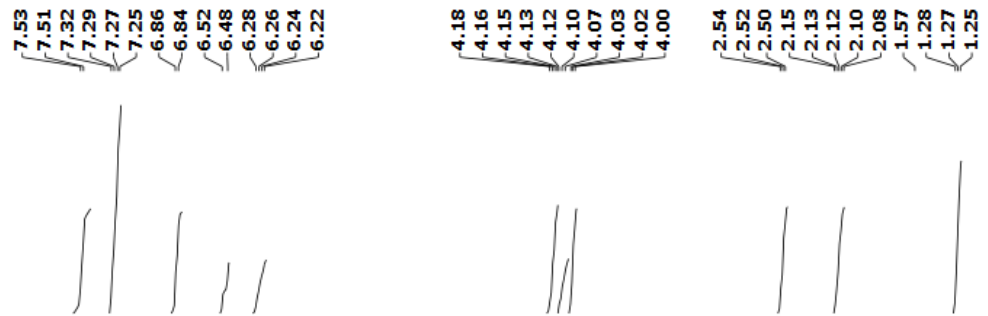
53.37
53.09
52.81
52.53

14.63



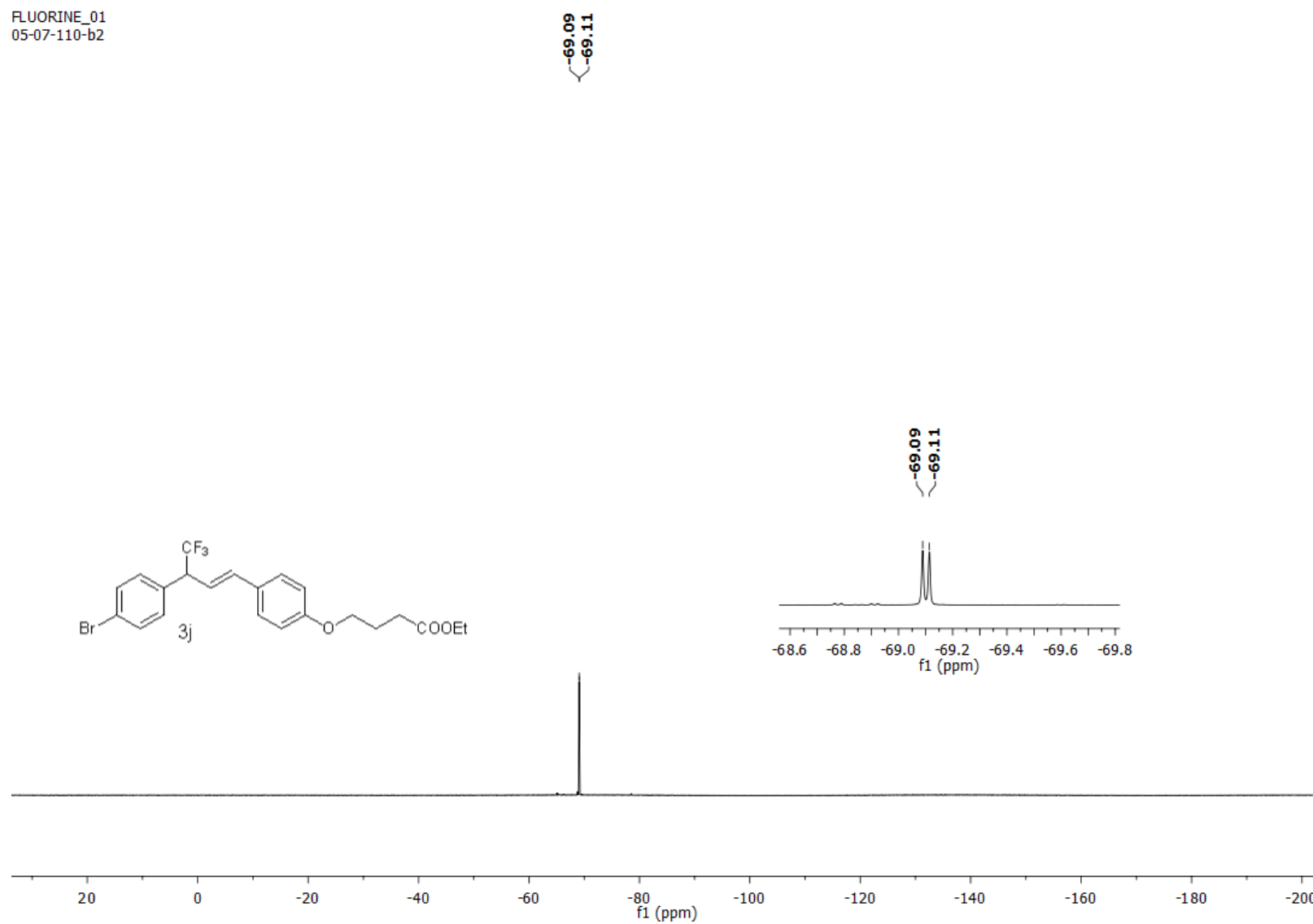
PROTON_01
05-07-110-b2

¹H NMR (400 MHz, CDCl₃) of 3j



FLUORINE_01
05-07-110-b2

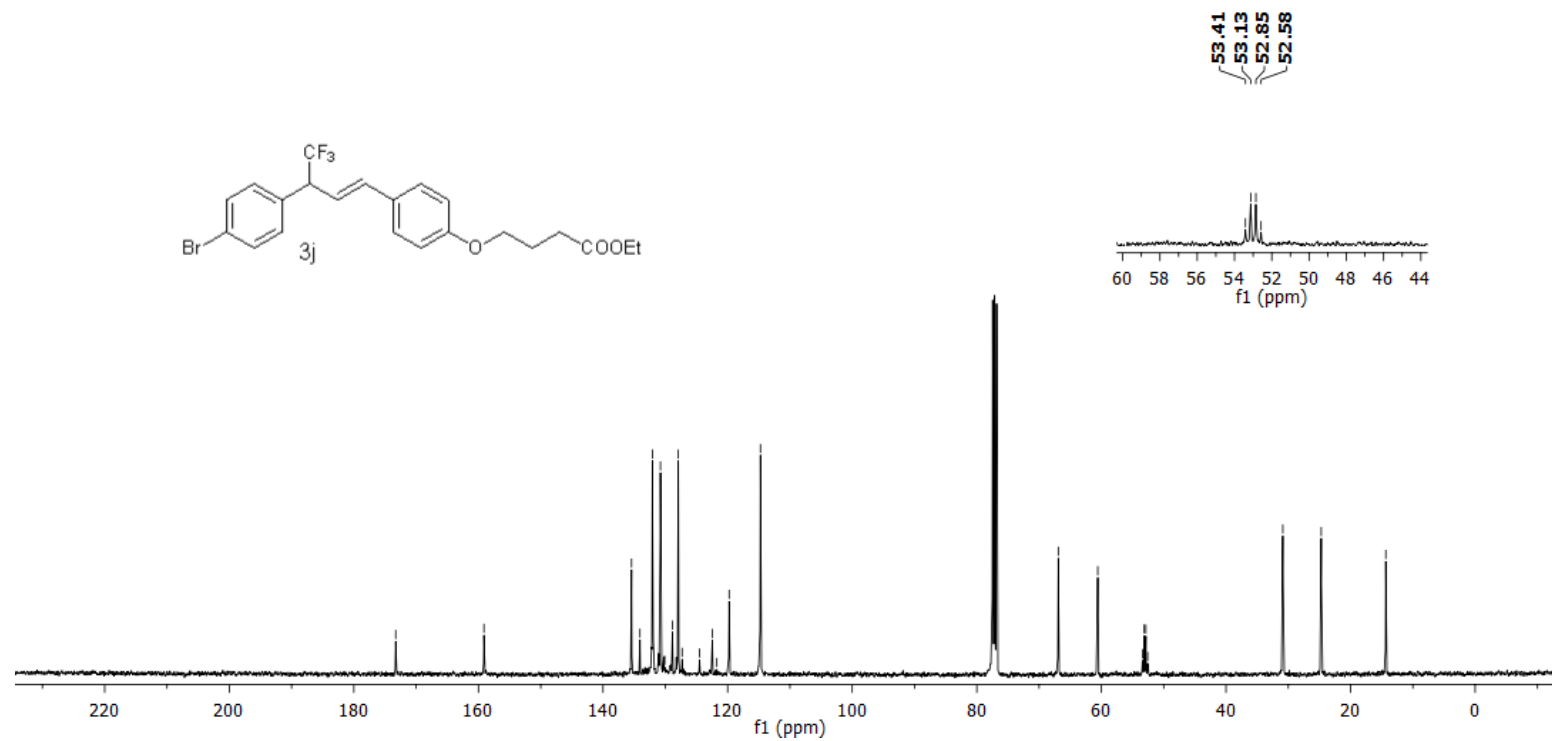
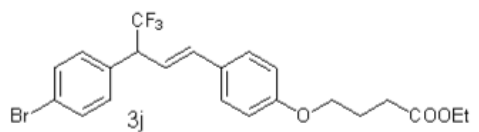
¹⁹F NMR (376 MHz, CDCl₃) of 3j



CARBON_01
05-19-110-b

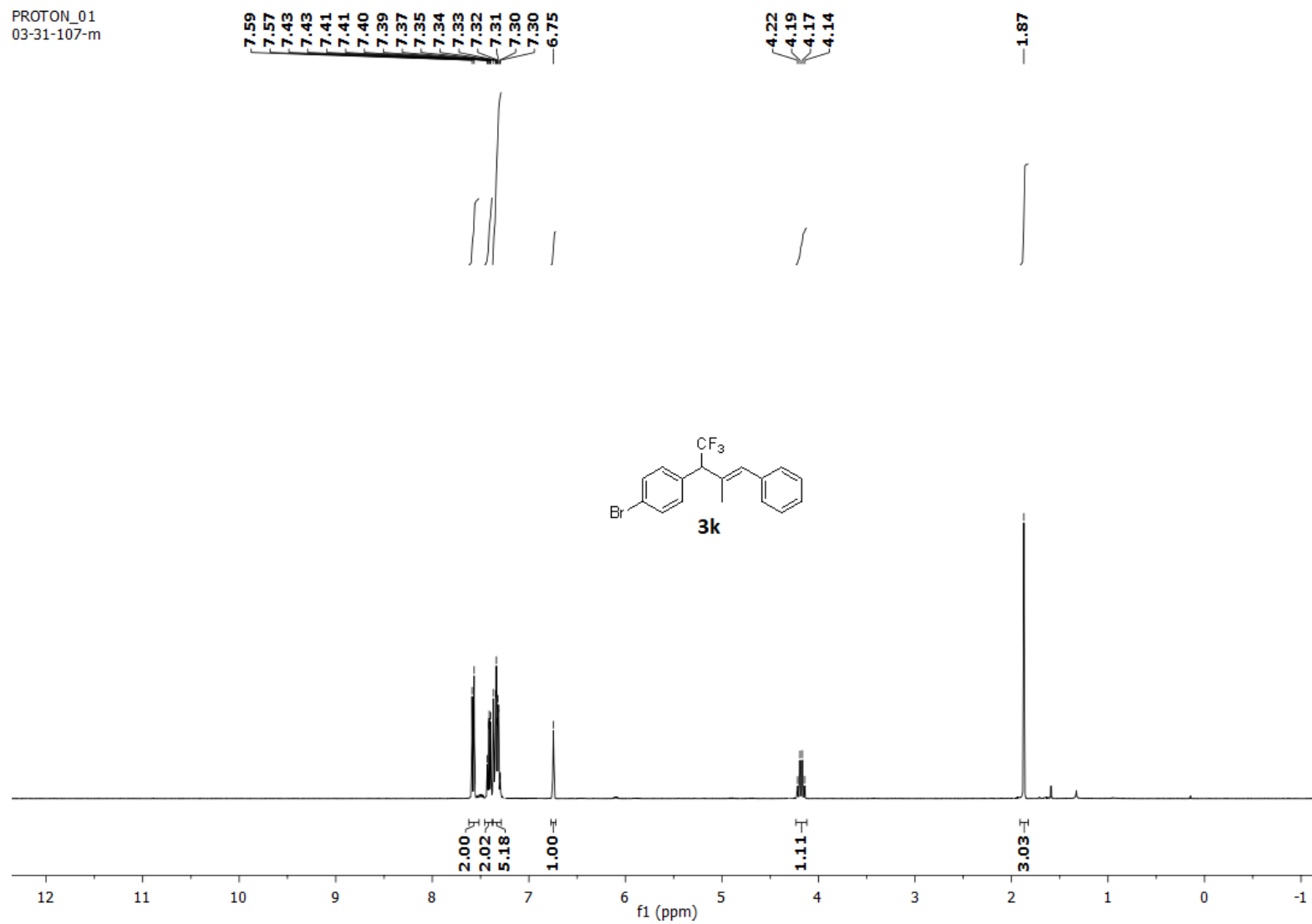
^{13}C NMR (100 MHz, CDCl_3) of 3j

—173.28 —159.12 —135.43 —134.07 —132.08 —130.78 —130.09 —128.86 —127.92 —127.31 —124.52 —122.46 —121.73 —119.76 —114.73 —66.92 —60.59 —53.41 —53.13 —52.85 —52.58 —30.88 —24.71 —14.35



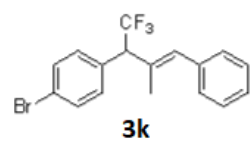
¹H NMR (400 MHz, CDCl₃) of 3k

PROTON_01
03-31-107-m

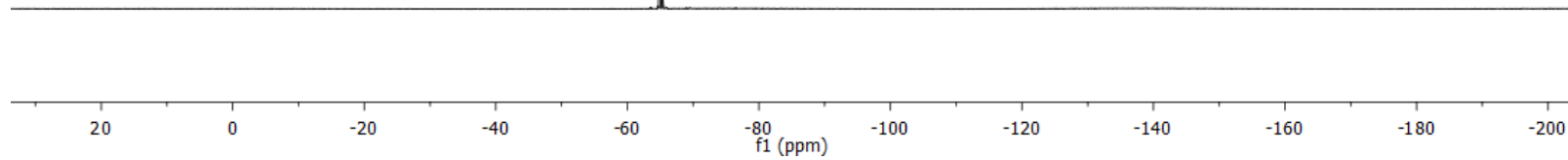
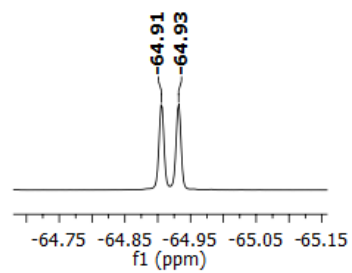


FLUORINE_01
03-31-107-m

¹⁹F NMR (376 MHz, CDCl₃) of 3k



-64.91
-64.93



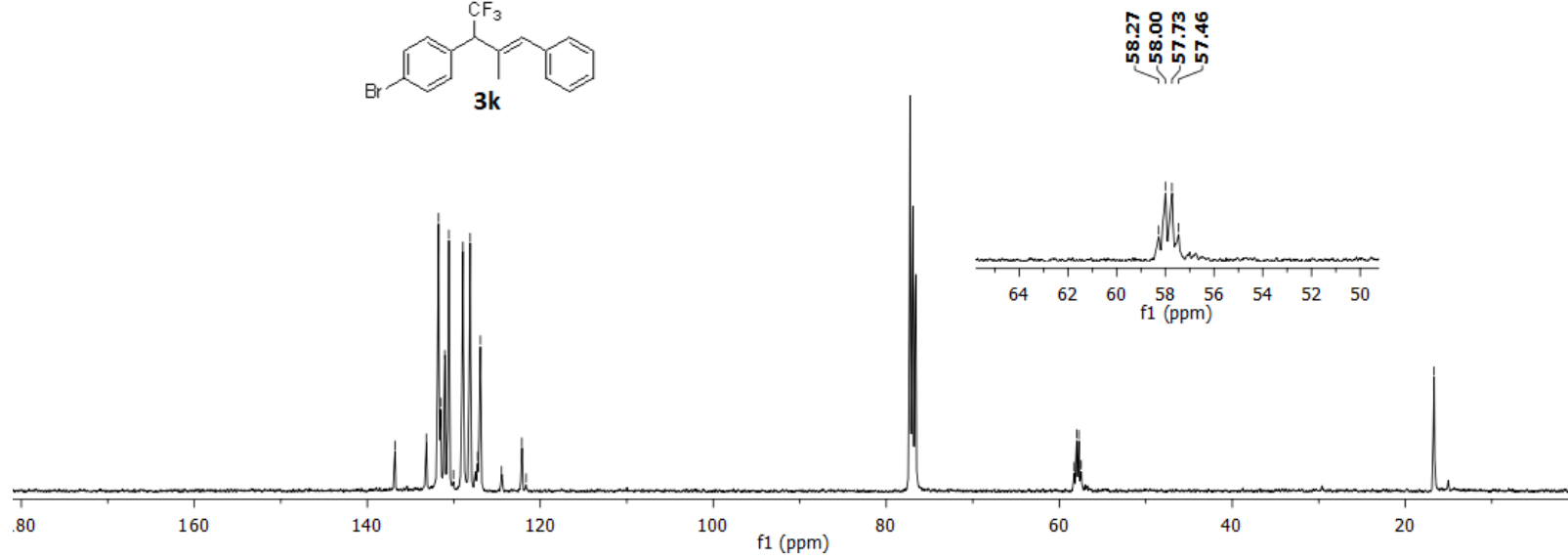
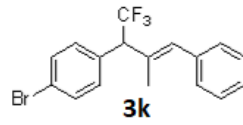
¹³C NMR (100 MHz, CDCl₃) of 3k

CARBON_01
03-31-107-m

136.80
133.17
131.78
131.76
131.52
131.03
130.57
130.04
128.94
128.10
127.23
126.93
124.47
122.12
121.63

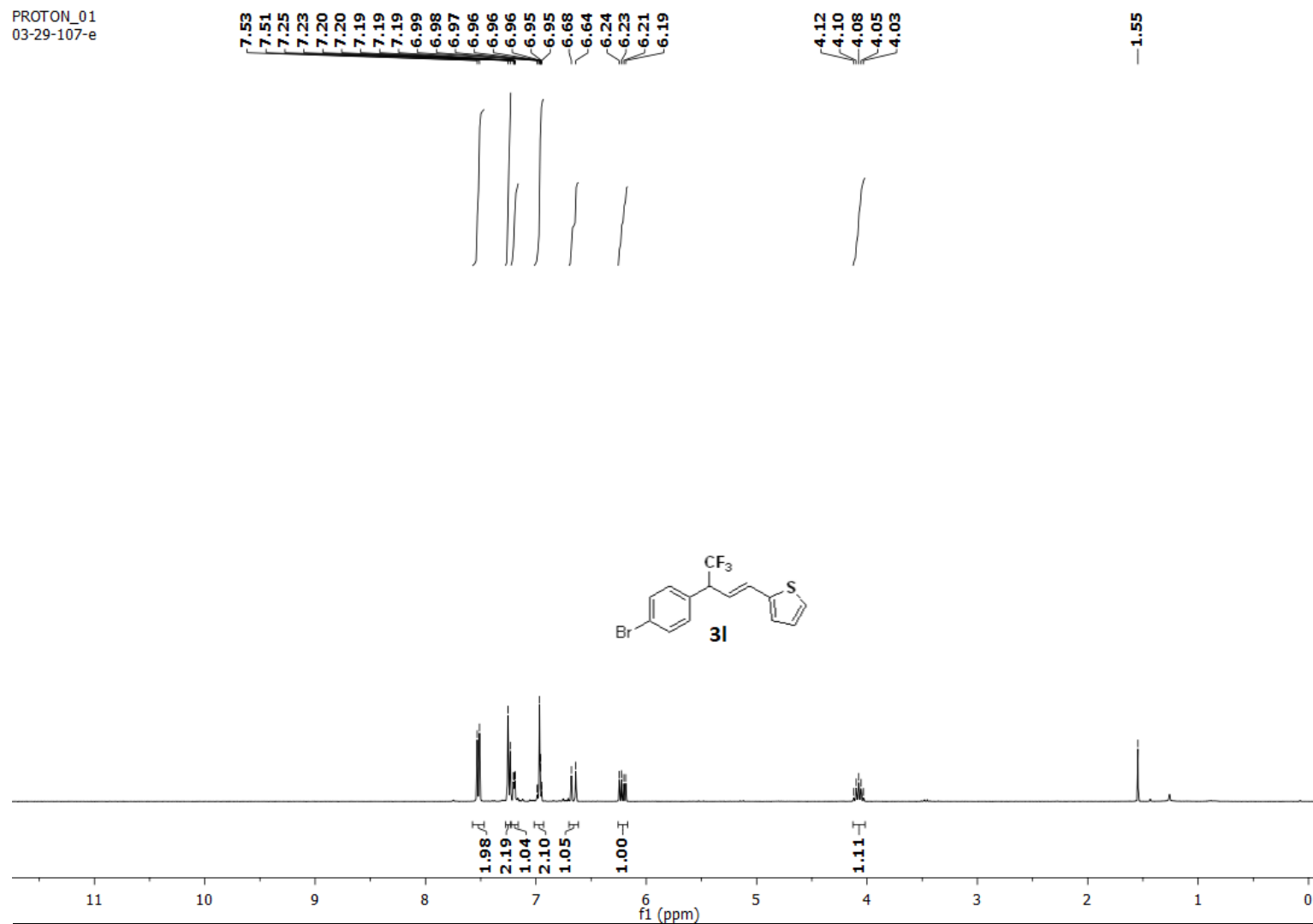
58.27
58.00
57.73
57.46

16.66



PROTON_01
03-29-107-e

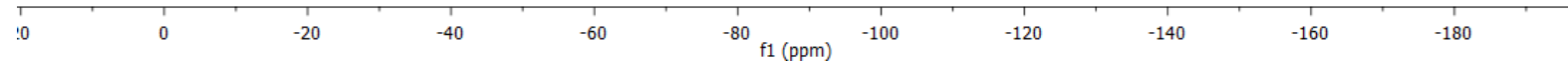
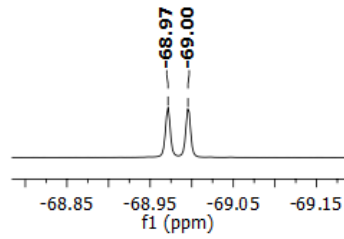
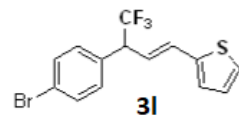
¹H NMR (400 MHz, CDCl₃) of 31



^{19}F NMR (376 MHz, CDCl_3) of 3I

FLUORINE_01
03-29-107-e

-68.97
-69.00

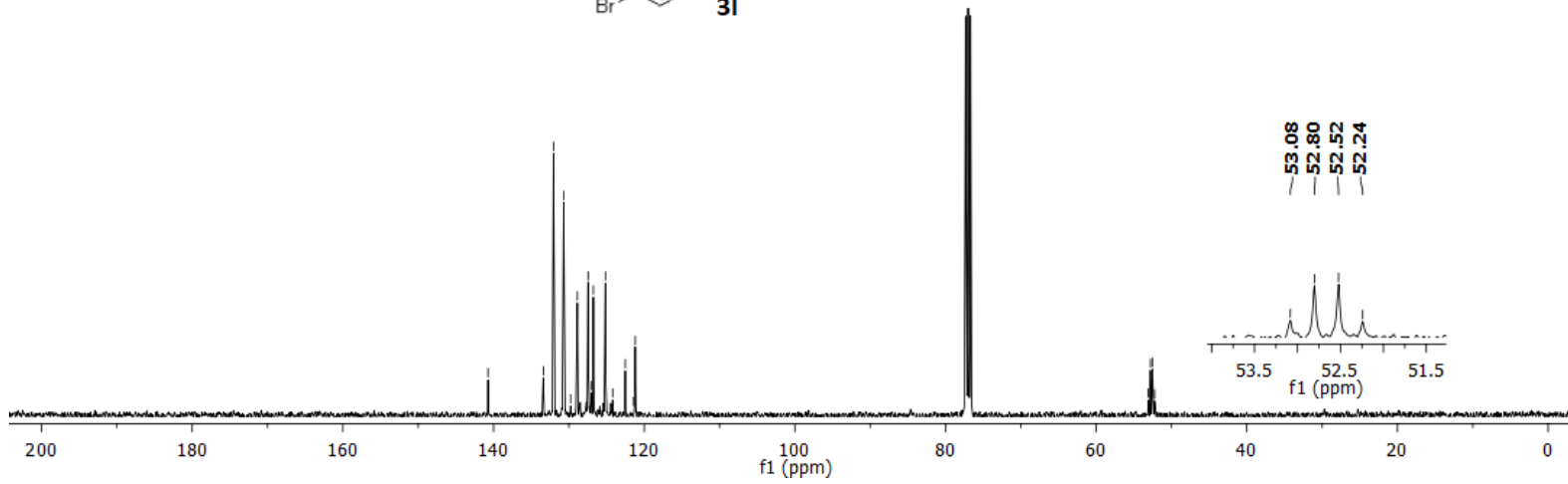
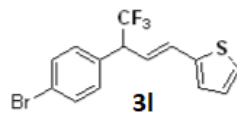


¹³C NMR (100 MHz, CDCl₃) of 3I

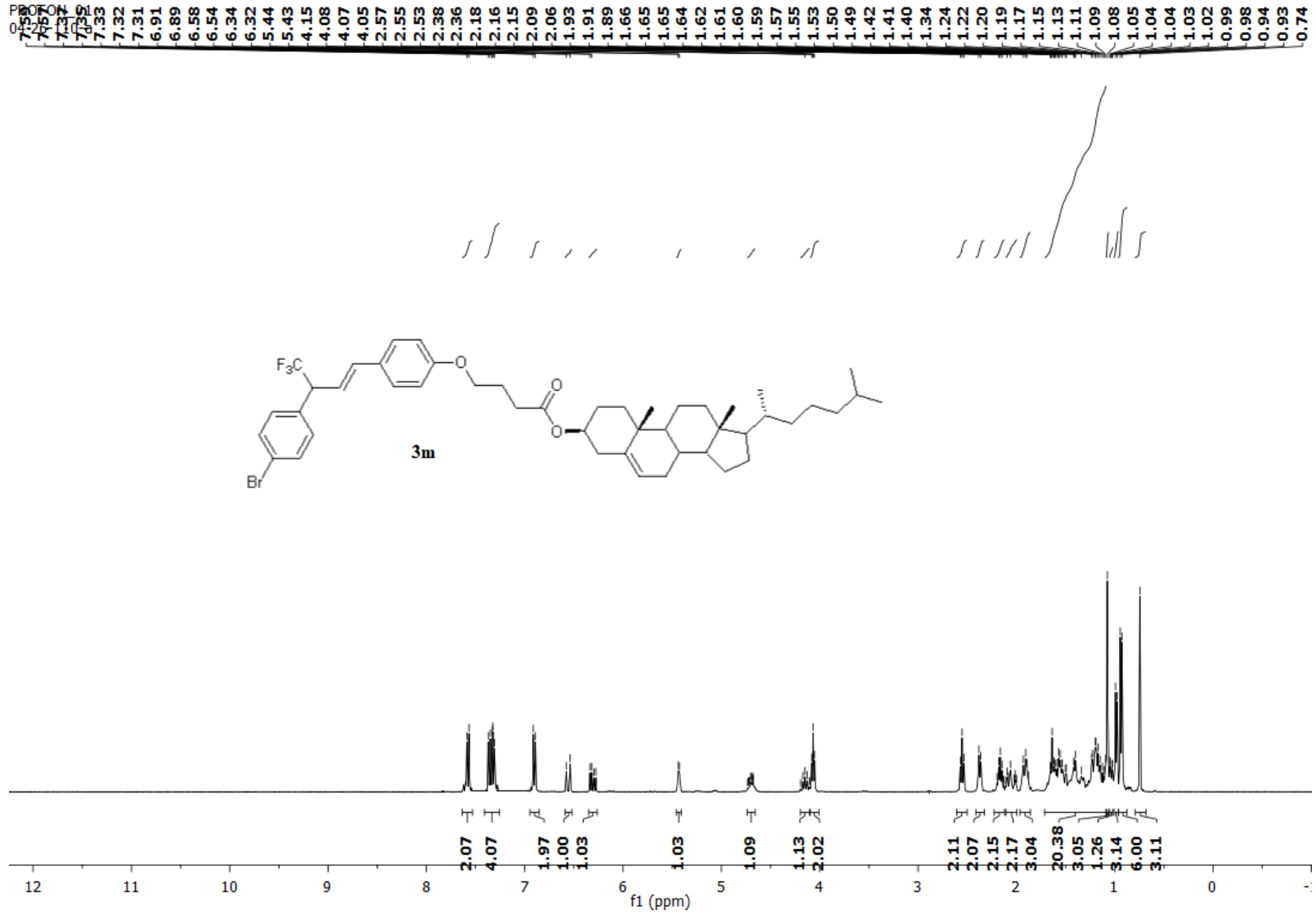
CARBON_01
03-29-107-e

140.74
133.39
132.04
130.69
129.78
128.88
127.45
126.98
126.76
125.15
124.19
122.52
121.40
121.19

53.08
52.80
52.52
52.24



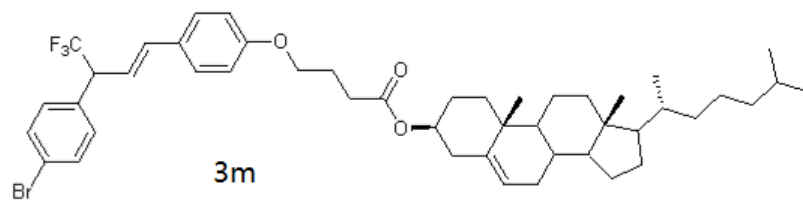
¹H NMR (400 MHz, CDCl₃) of 3m



¹⁹F NMR (376 MHz, CDCl₃) of 3m

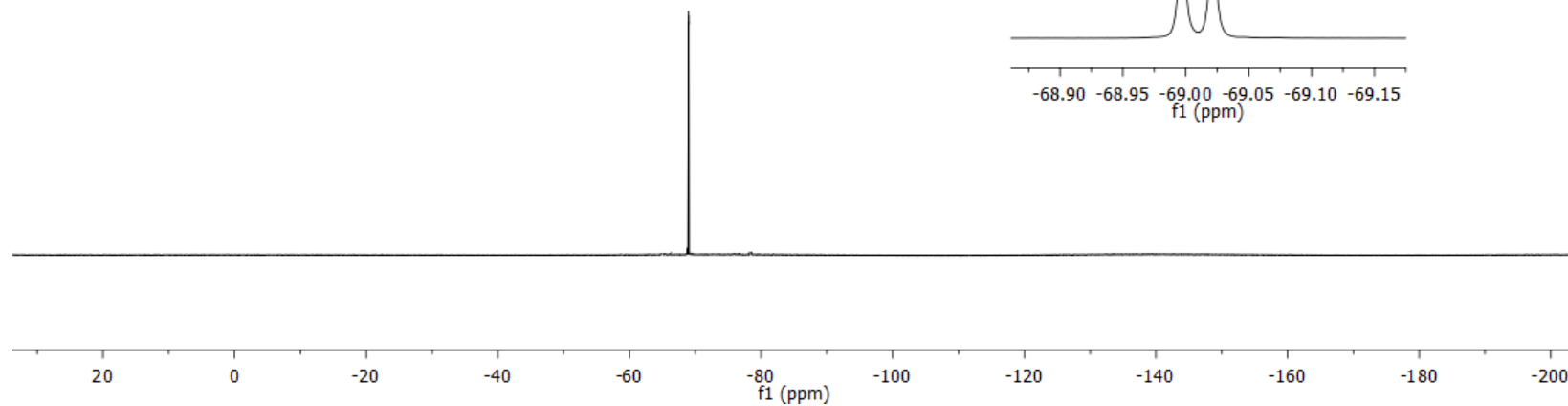
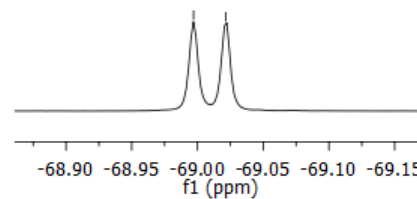
FLUORINE_01
04-26-110-a

-69.00
-69.02



3m

-69.00
-69.02



¹³C NMR (100 MHz, CDCl₃) of 3m

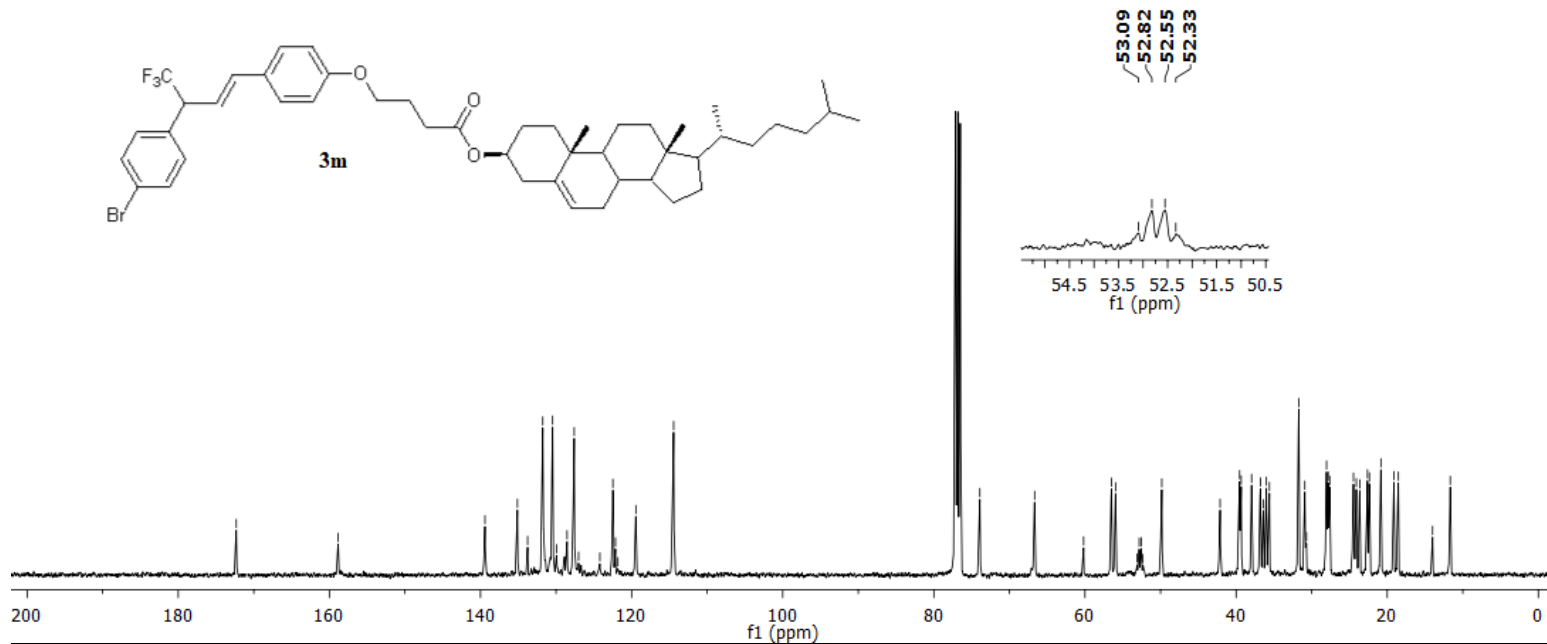
CARBON_01
05-05-110-a

—172.32

—158.83

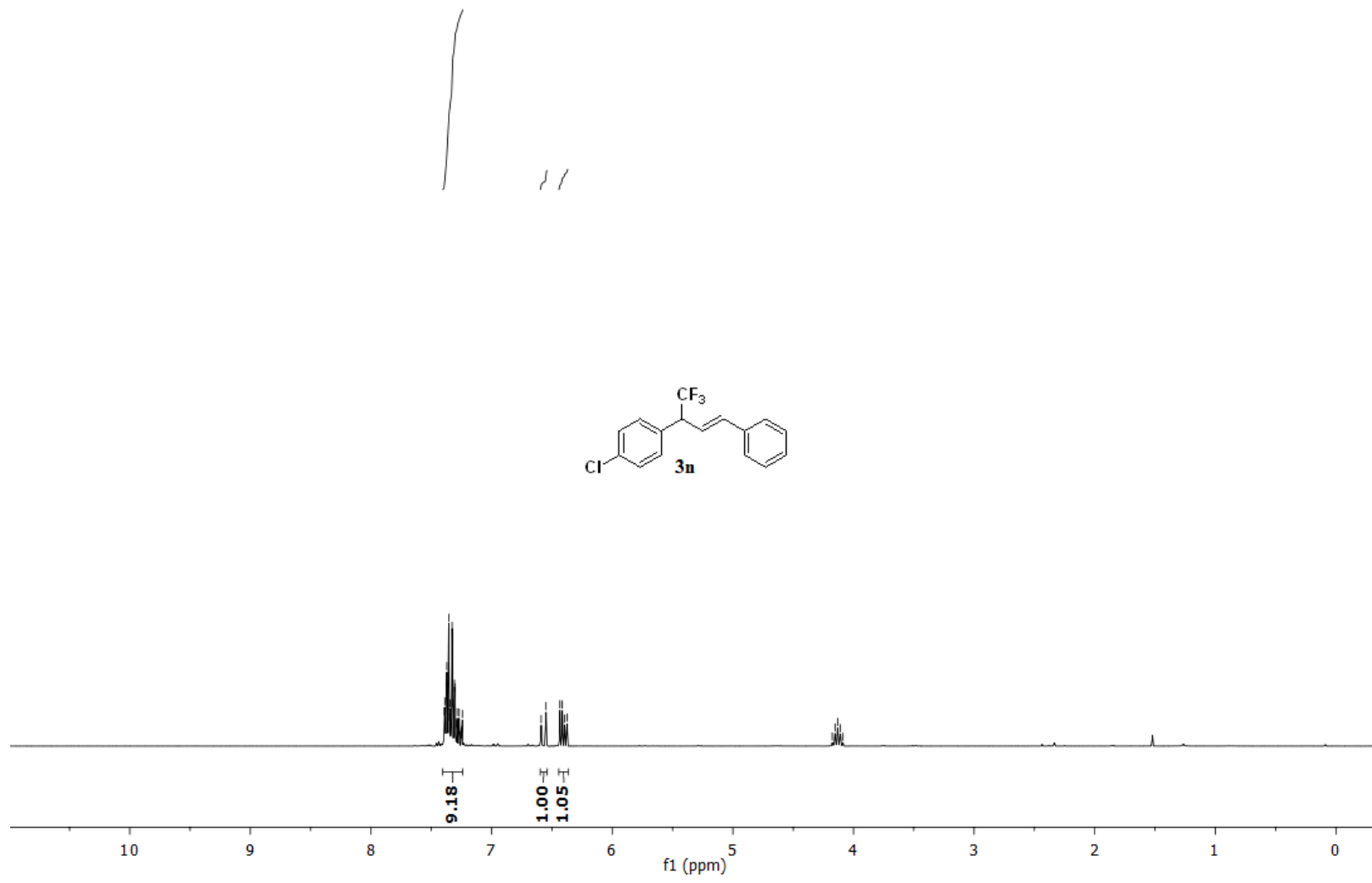
139.41
135.12
133.77
131.76
130.46
129.93
128.54
127.60
127.02
124.20
122.48
122.14
121.81
119.44
114.44

73.91
66.66
60.18
56.49
55.95
53.09
52.82
52.55
52.33
49.83
42.12
39.54
39.33
37.95
36.78
36.39
35.99
35.59
31.70
30.91
30.69
28.03
27.81
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23.64
22.61
22.36
20.84
19.11
18.52
14.00
11.66



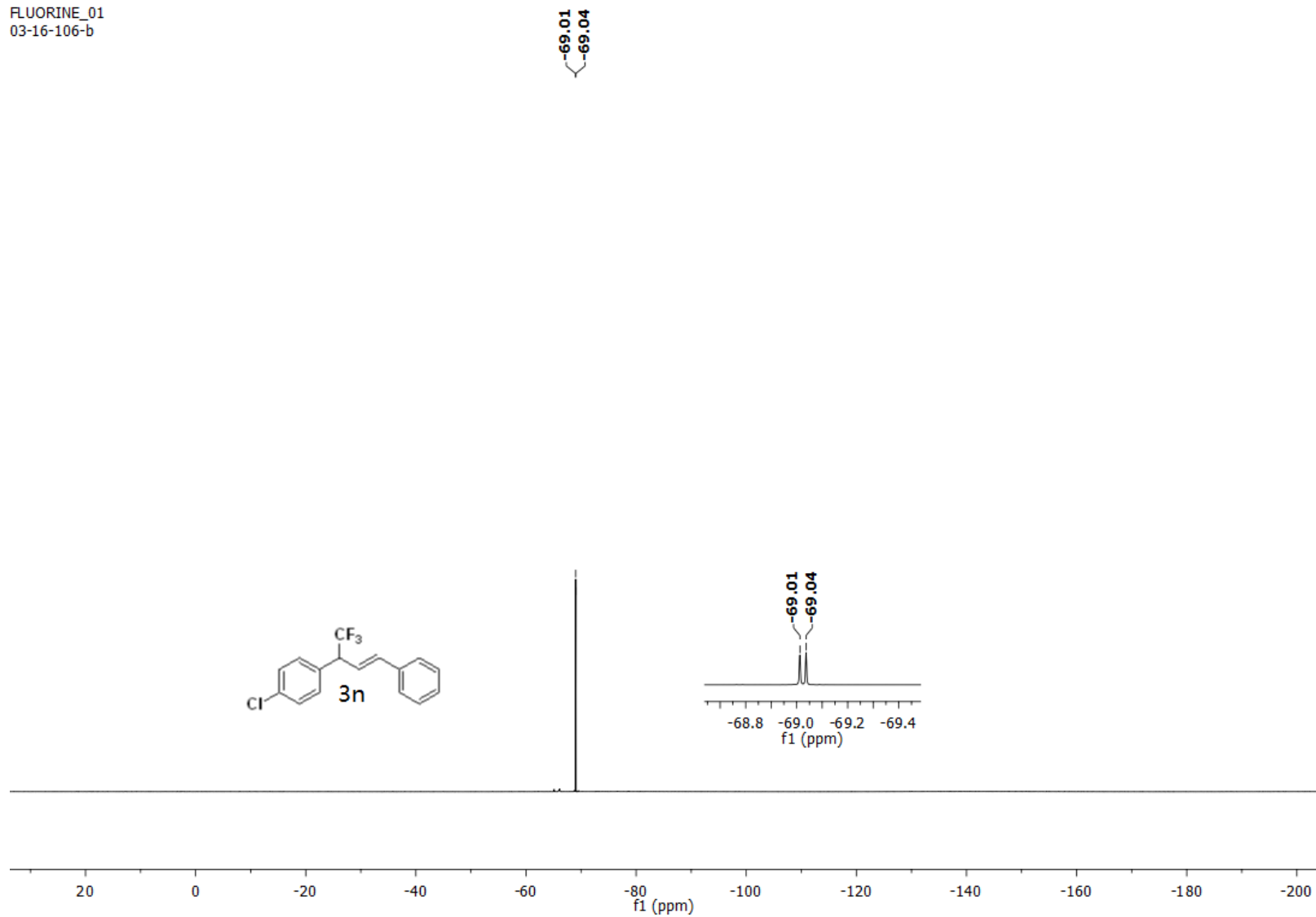
¹H NMR (400 MHz, CDCl₃) of 3n

PROB
03-1
7.38
7.38
7.38
7.38
7.37
7.37
7.36
7.36
7.35
7.35
7.34
7.34
7.33
7.33
7.32
7.31
7.31
7.29
7.29
7.28
7.27
7.24
6.55
6.43
6.41
6.39
6.37
4.18
4.15
4.13
4.11
4.09



FLUORINE_01
03-16-106-b

¹⁹F NMR (376 MHz, CDCl₃) of 3n

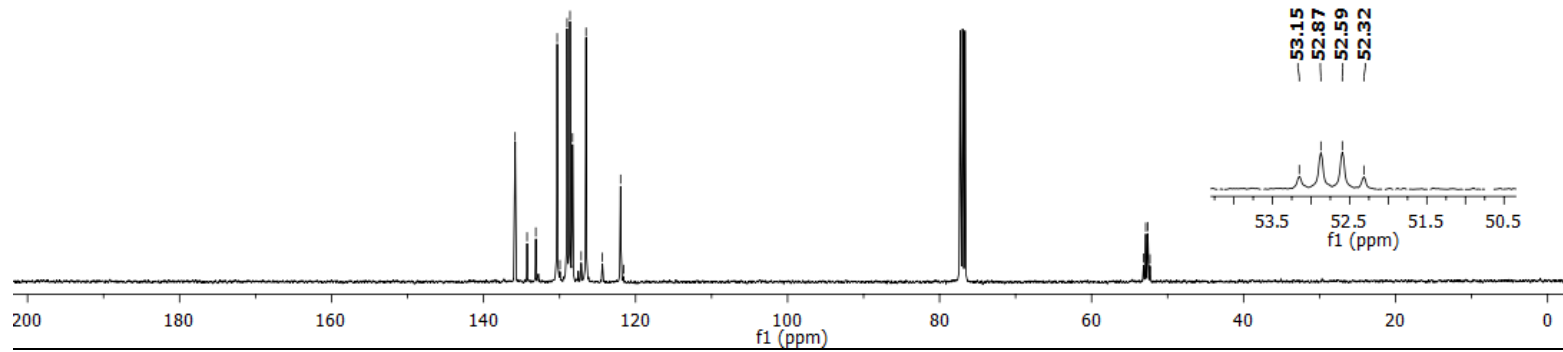
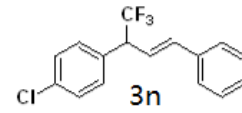


¹³C NMR (100 MHz, CDCl₃) of 3n

CARBON_01
03-16-106-b

135.85
134.27
133.13
130.31
129.94
129.01
128.62
128.29
127.15
126.52
124.36
121.97
121.57

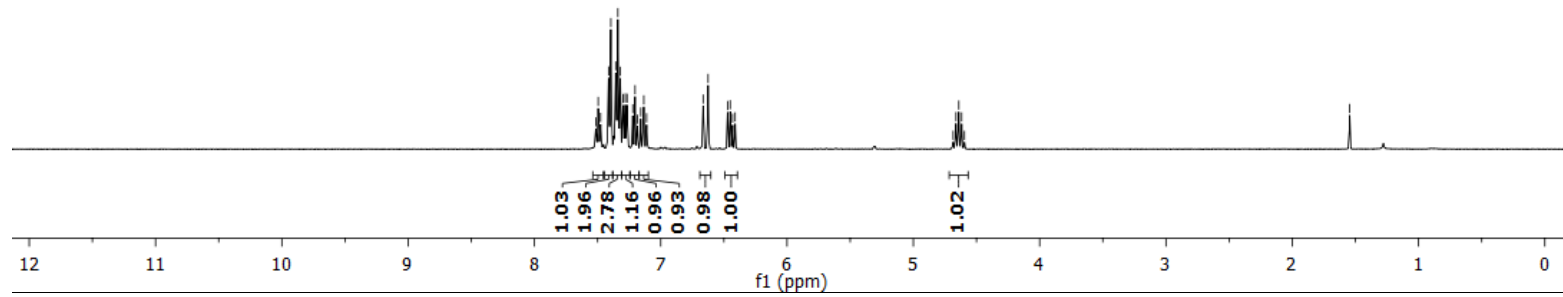
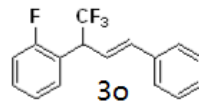
53.15
52.87
52.59
52.32



¹H NMR (400 MHz, CDCl₃) of 3o

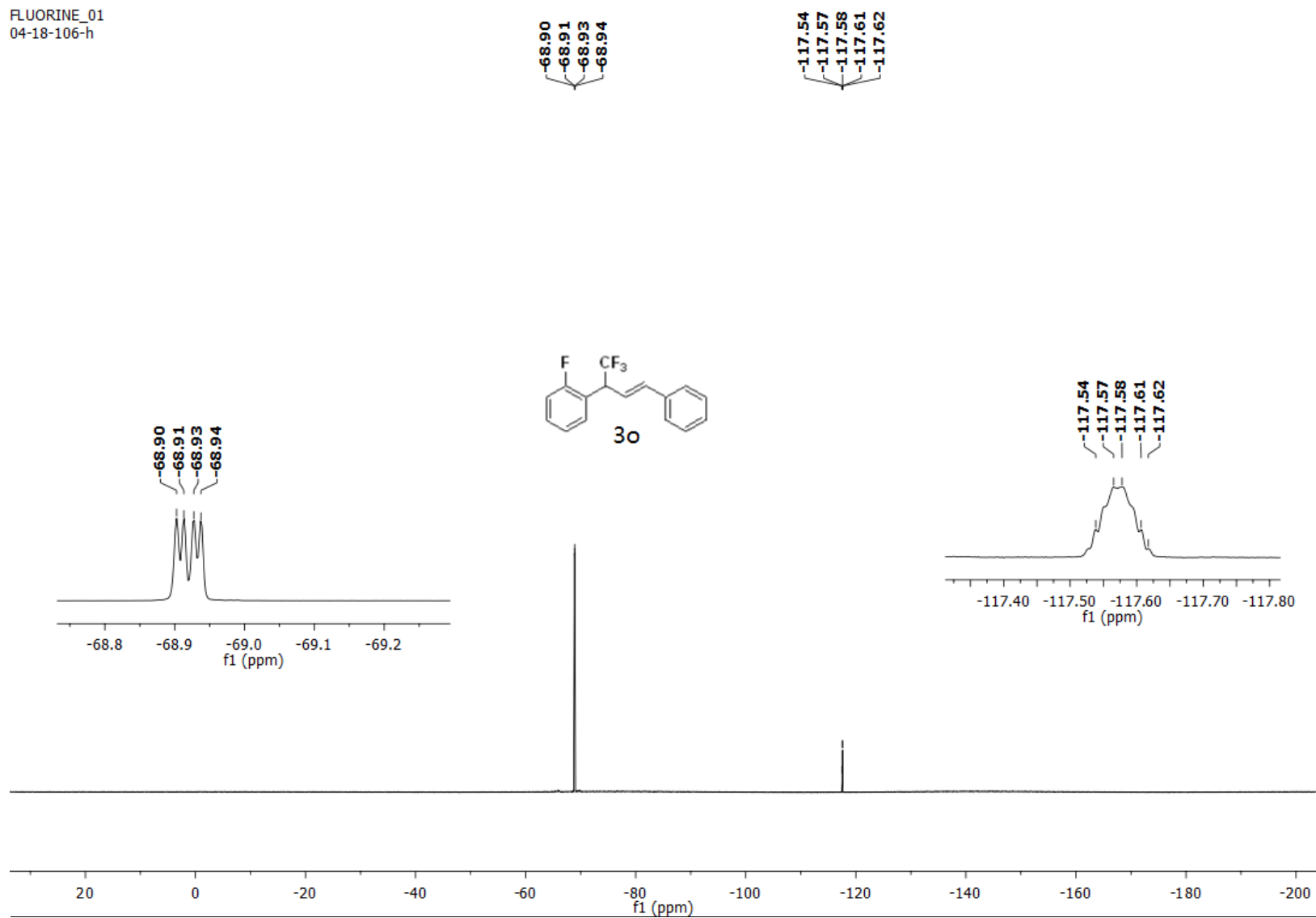
PROTON_01
04-18-106-h

7.51
7.50
7.48
7.41
7.40
7.36
7.34
7.32
7.30
7.28
7.27
7.22
7.20
7.18
7.16
7.13
7.11
6.66
6.62
6.47
6.45
6.43
6.41
4.68
4.66
4.64
4.62
4.60
-1.55



FLUORINE_01
04-18-106-h

¹⁹F NMR (376 MHz, CDCl₃) of 3o



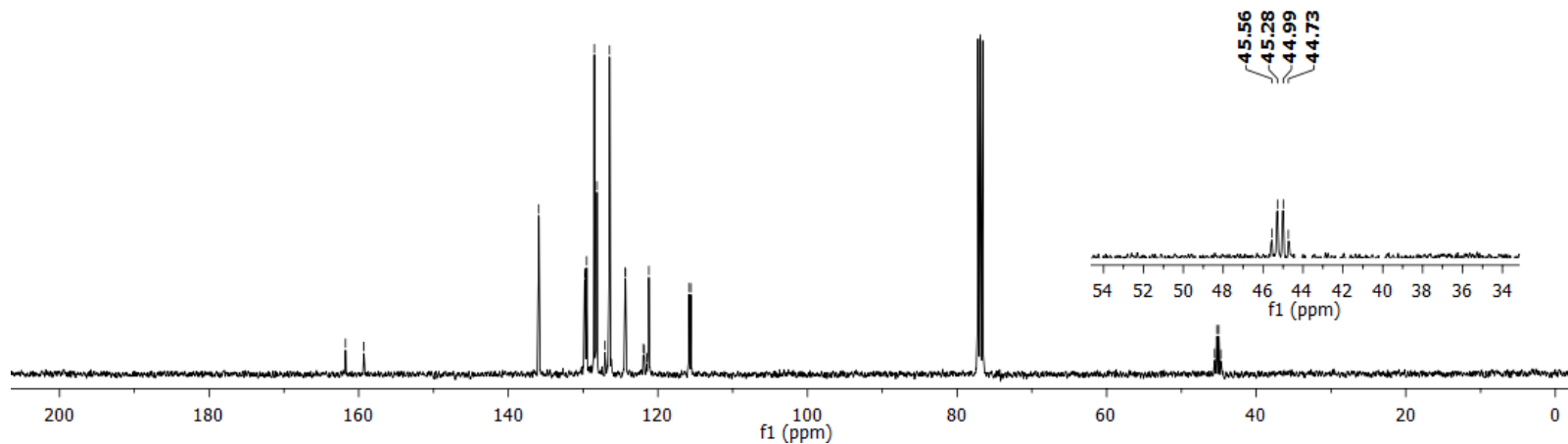
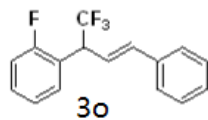
CARBON_01
04-19-106-h

^{13}C NMR (100 MHz, CDCl_3) of 3o

161.77
159.30

135.93
129.81
129.72
129.52
128.51
128.15
127.07
126.46
124.36
124.33
121.95
121.82
121.49
121.21
115.82
115.59

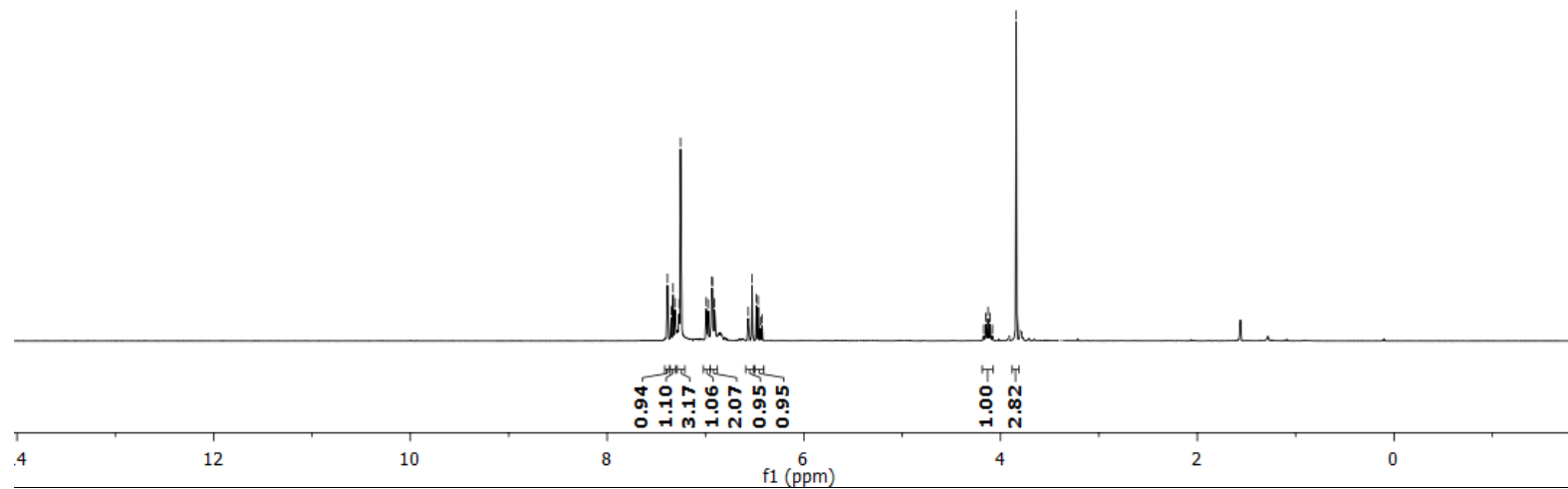
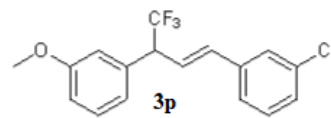
45.56
45.28
44.99
44.73



PROTON_01
04-26-109-t

¹H NMR (400 MHz, CDCl₃) of 3p

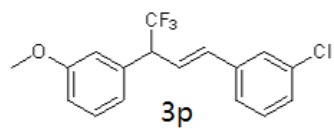
7.39
7.35
7.33
7.31
7.27
7.25
6.99
6.97
6.93
6.93
6.91
6.57
6.53
6.48
6.46
6.44
6.42
4.17
4.15
4.13
4.11
4.08
3.84



¹⁹F NMR (376 MHz, CDCl₃) of 3p

FLUORINE_01
04-26-109-t

-68.71
-68.74



-68.71
-68.74

-68.3 -68.5 -68.7 -68.9 -69.1
f1 (ppm)

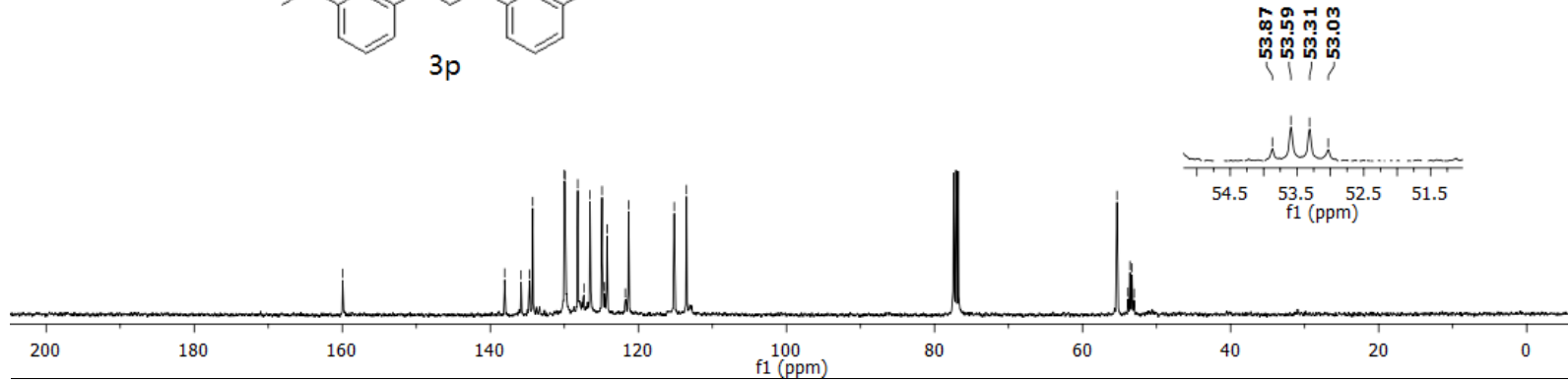
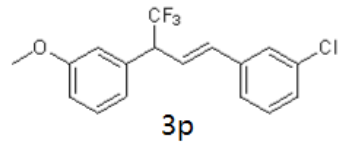
20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200
f1 (ppm)

¹³C NMR (100 MHz, CDCl₃) of 3p

CARBON_01
05-02-109-t

159.95
138.06
135.85
134.69
134.27
129.99
129.92
128.19
127.36
126.54
124.90
124.57
124.24
121.77
121.33
115.16
113.50

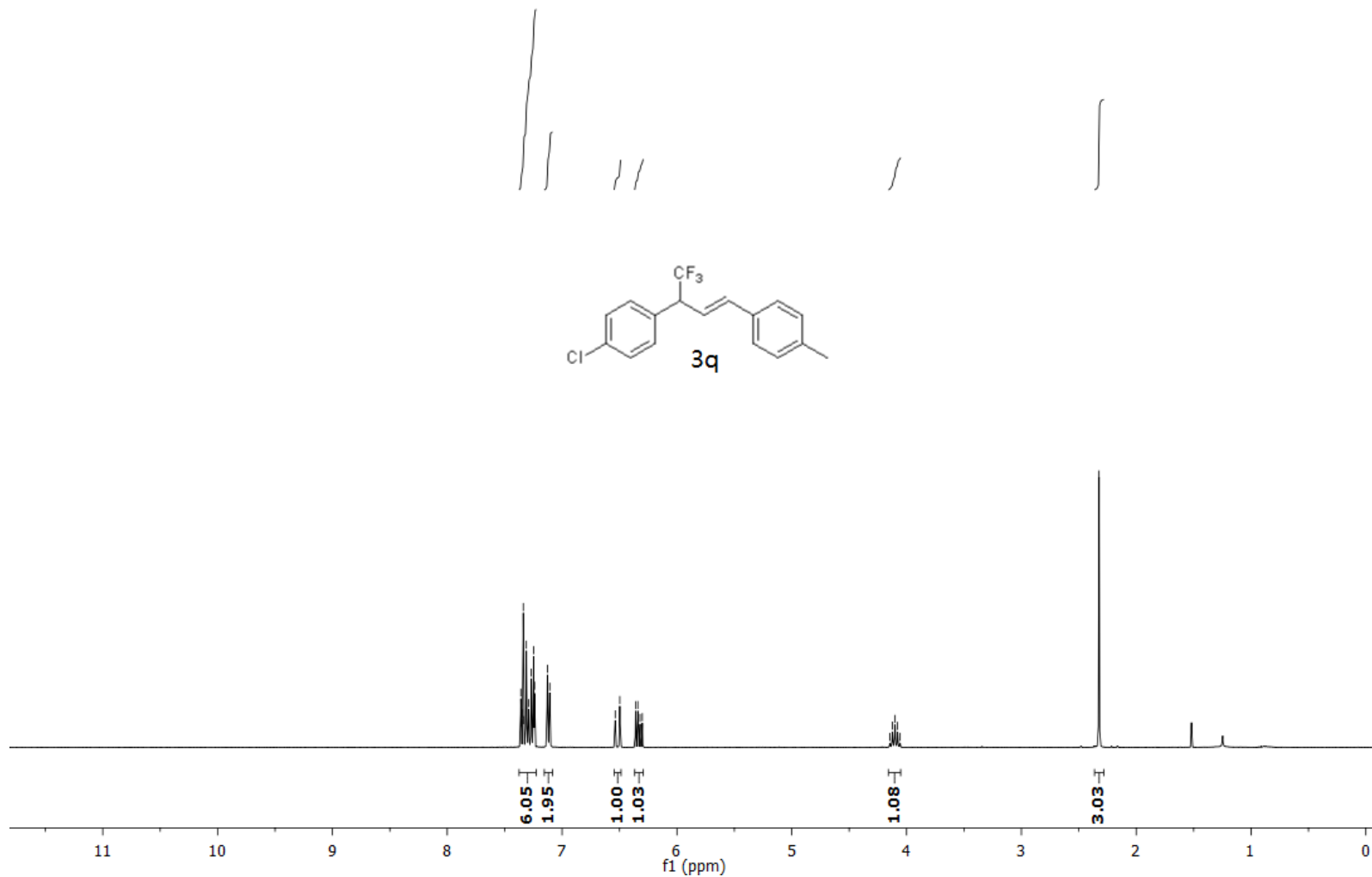
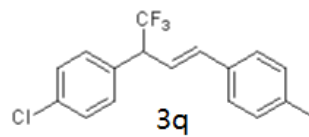
55.35
53.87
53.59
53.31
53.03



PROTON_01
03-23-106-c

¹H NMR (400 MHz, CDCl₃) of 3q

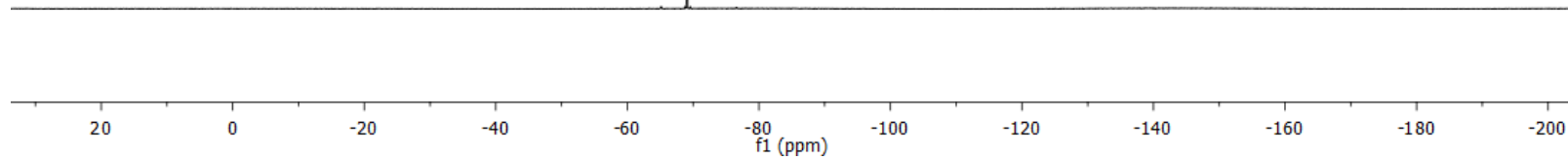
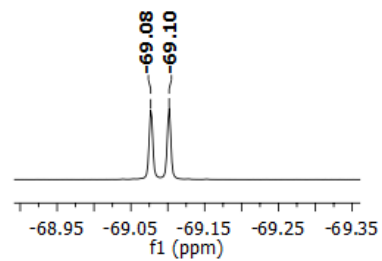
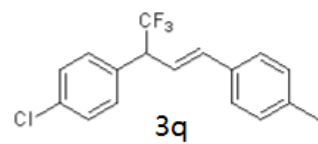
7.36
7.35
7.34
7.34
7.33
7.31
7.29
7.27
7.25
7.24
7.13
7.11
6.54
6.50
6.36
6.34
6.32
6.30
4.15
4.12
4.10
4.08
4.06
-2.32



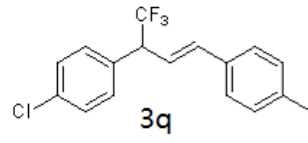
¹⁹F NMR (376 MHz, CDCl₃) of 3q

FLUORINE_01
03-23-106-c

-69.08
-69.10



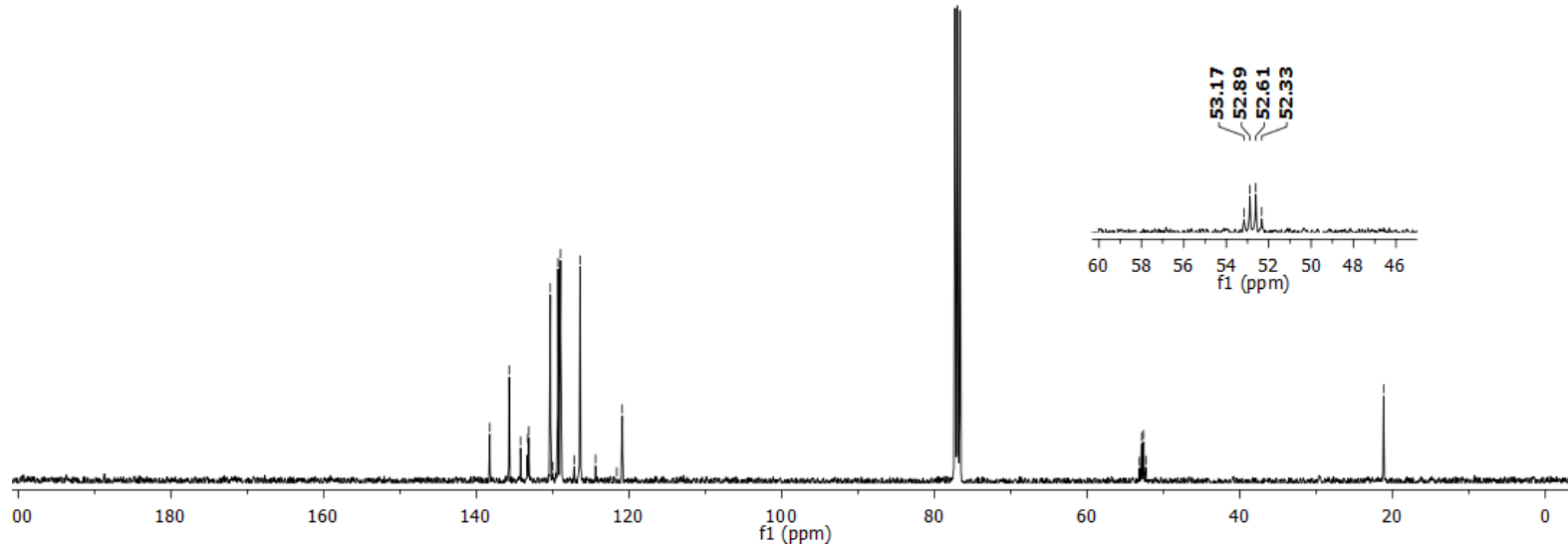
¹³C NMR (100 MHz, CDCl₃) of 3q



138.24
135.71
134.21
133.28
133.13
130.32
129.98
129.31
128.98
127.19
126.42
124.40
121.60
120.90

53.17
52.89
52.61
52.33

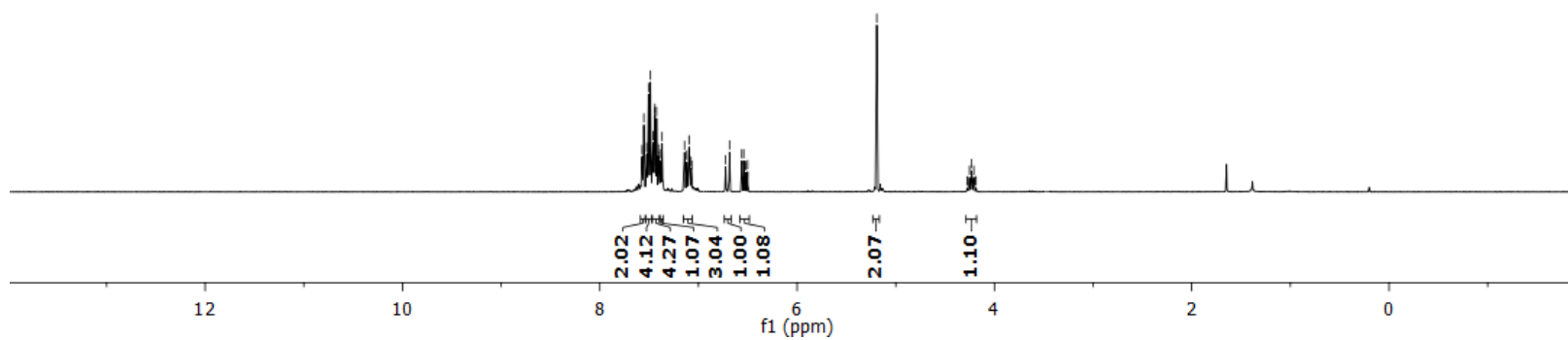
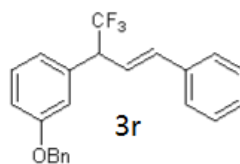
21.19



PROTON_01
04-19-bn3

¹H NMR (400 MHz, CDCl₃) of 3r

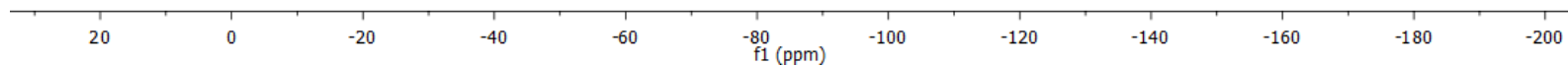
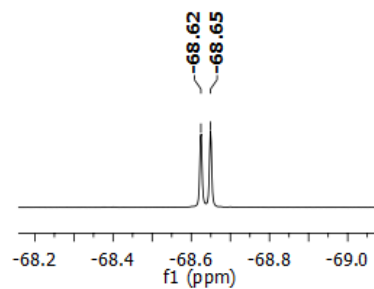
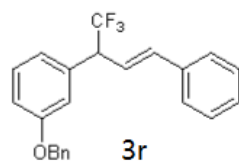
7.57
7.55
7.52
7.52
7.51
7.49
7.46
7.45
7.45
7.44
7.43
7.41
7.40
7.39
7.38
7.37
7.14
7.12
7.10
7.09
7.07
7.07
6.72
6.69
6.56
6.54
6.52
6.50
5.19
4.28
4.25
4.23
4.21
4.19



¹⁹F NMR (376 MHz, CDCl₃) of 3r

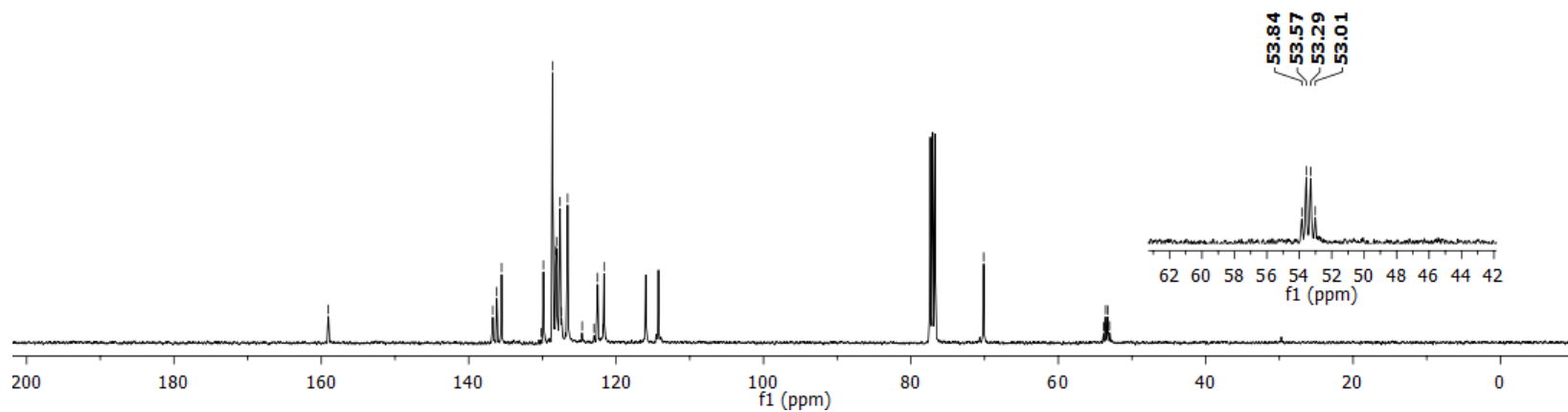
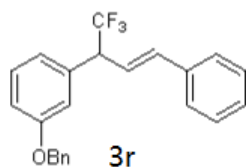
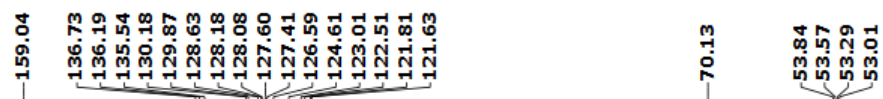
FLUORINE_01
04-19-bn3

-68.62
-68.65



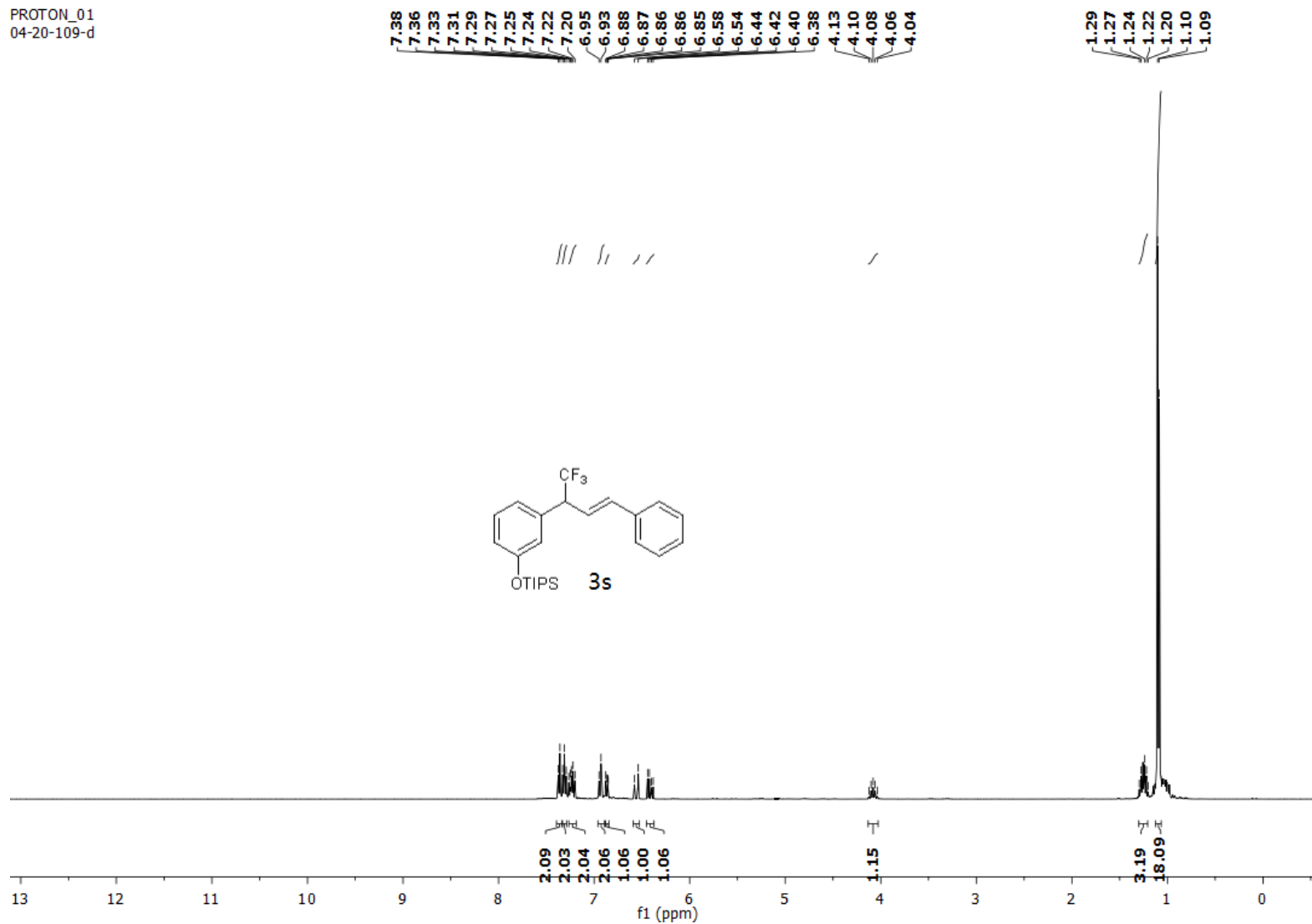
¹³C NMR (100 MHz, CDCl₃) of 3r

CARBON_02
04-24-109-b



PROTON_01
04-20-109-d

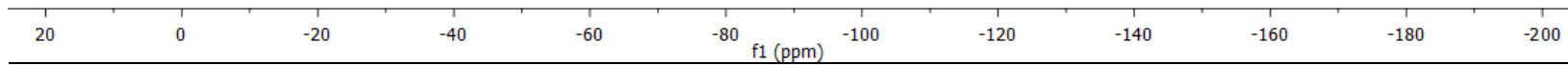
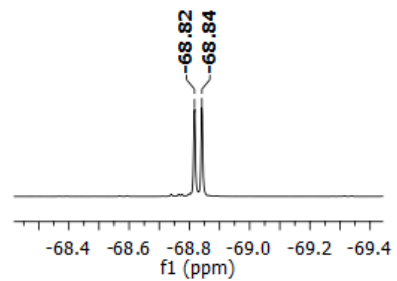
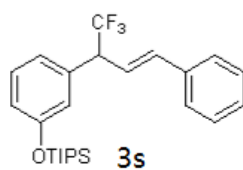
¹H NMR (400 MHz, CDCl₃) of 3s



¹⁹F NMR (376 MHz, CDCl₃) of 3s

FLUORINE_01
04-20-109-d

-68.82
-68.84



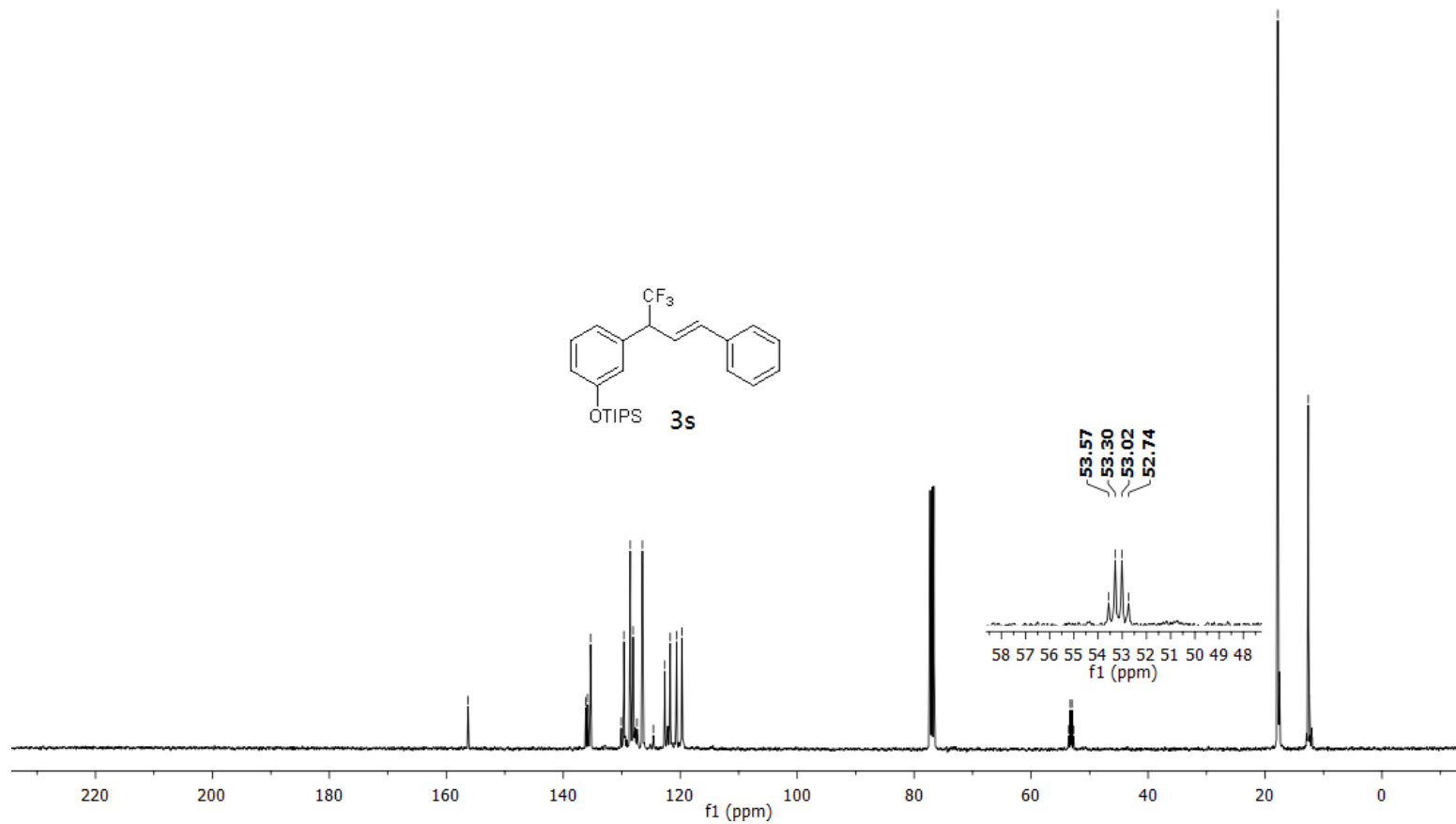
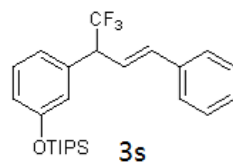
CARBON_01
04-20-109-d

¹³C NMR (100 MHz, CDCl₃) of 3s

156.29
136.17
135.85
135.34
130.11
129.63
128.55
128.05
127.39
126.47
124.60
122.64
121.71
120.62
119.71

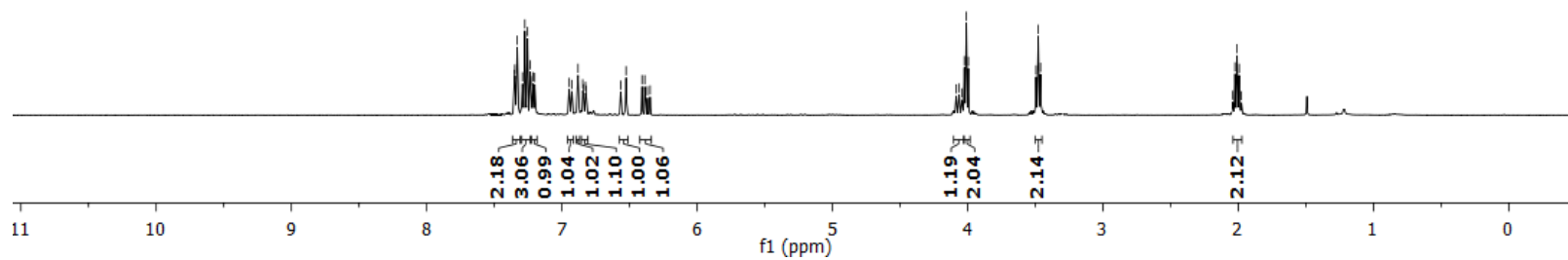
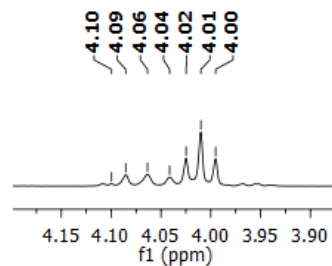
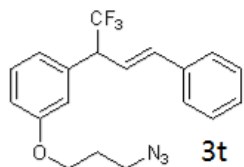
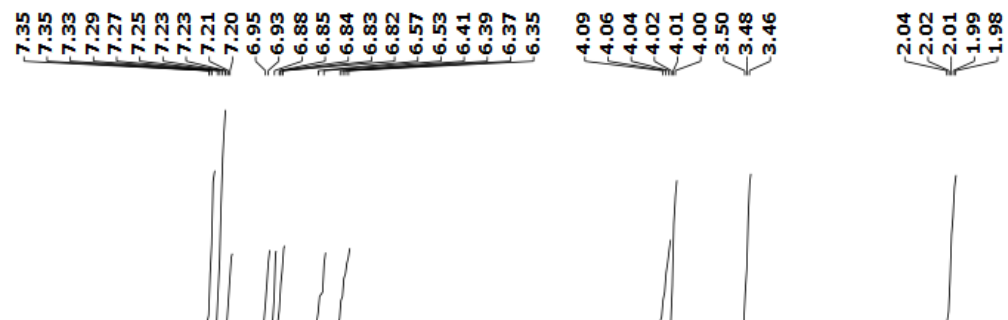
53.57
53.30
53.02
52.74

17.82
12.61



PROTON_01
04-08-109-a

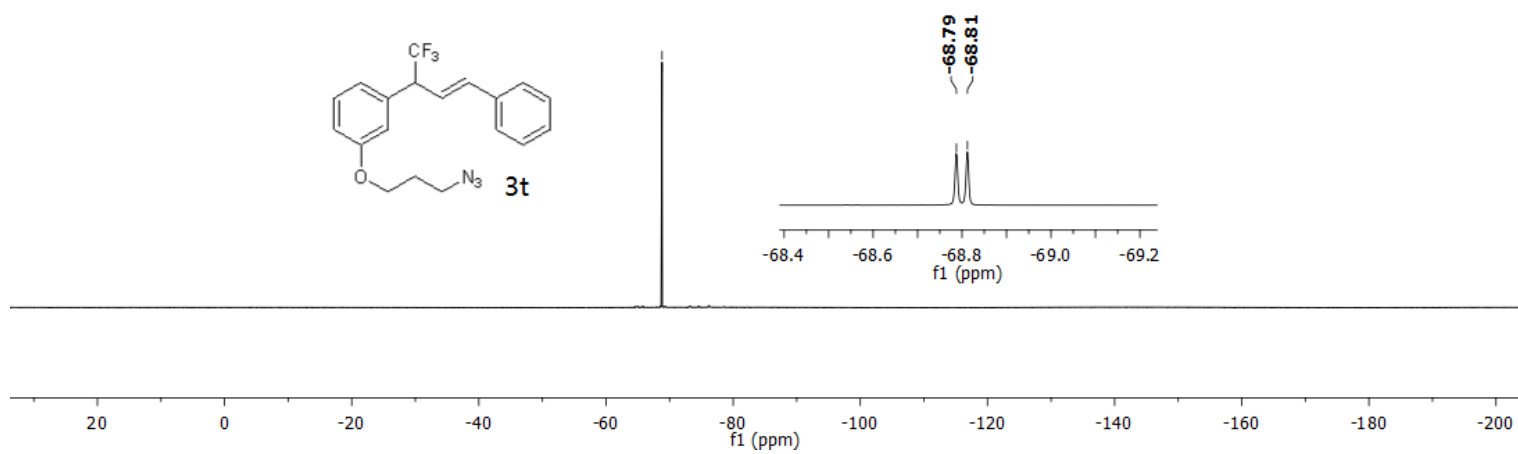
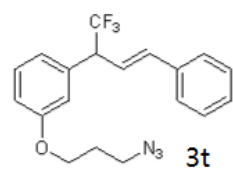
¹H NMR (400 MHz, CDCl₃) of 3t



¹⁹F NMR (376 MHz, CDCl₃) of 3t

FLUORINE_01
04-08-109-a

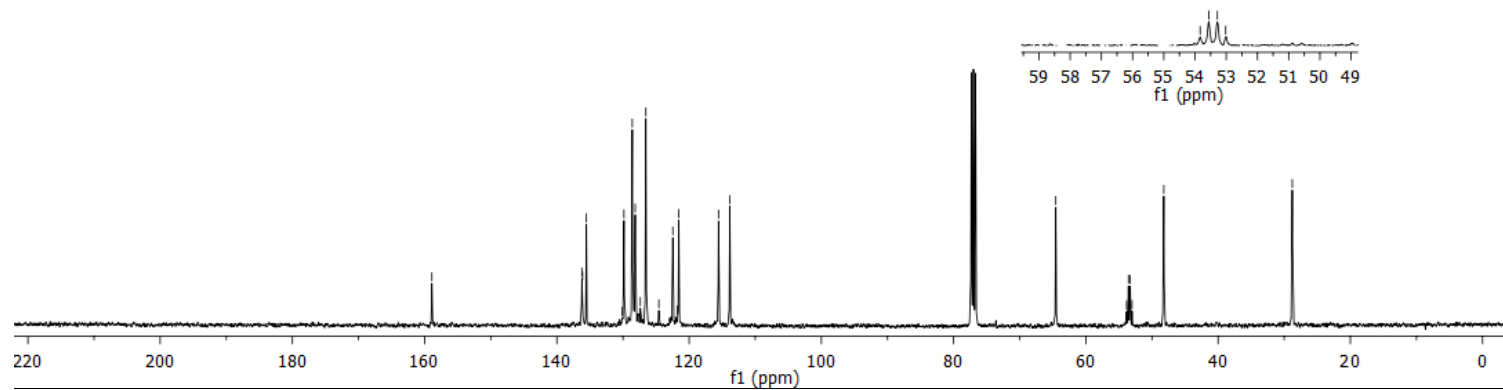
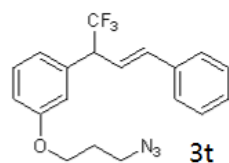
-68.79
-68.81



¹³C NMR (100 MHz, CDCl₃) of 3t

CARBON_01
04-12-109-a

—158.91
—136.22
—136.12
—135.54
—130.15
—129.85
—128.60
—128.16
—127.37
—126.55
—124.58
—122.47
—121.81
—121.56
—115.55
—113.84
—64.54
53.84
53.56
53.28
53.02
48.21
—28.77

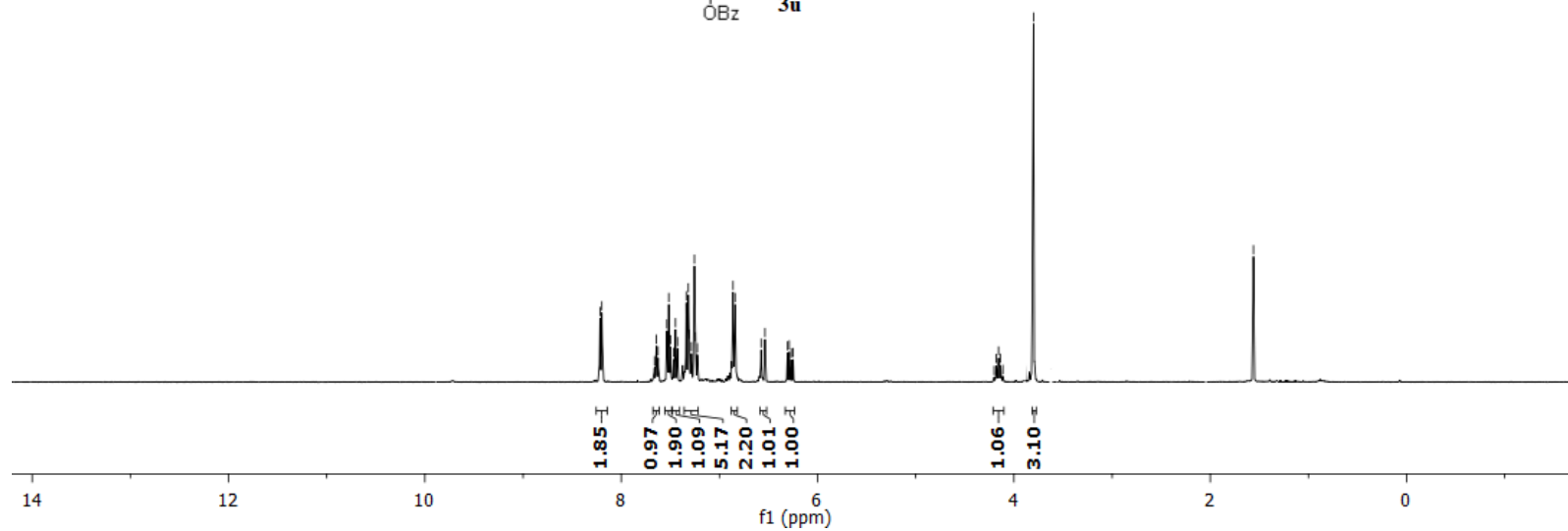
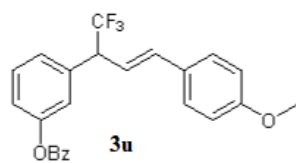


PROTON_01
04-24-109-f

¹H NMR (400 MHz, CDCl₃) of 3u

8.22
8.20
7.66
7.64
7.62
7.54
7.52
7.50
7.47
7.45
7.43
7.34
7.32
7.31
7.29
7.25
7.24
7.22
6.86
6.84
6.58
6.54
6.31
6.29
6.27
6.25
4.20
4.18
4.16
4.14
4.11
3.80

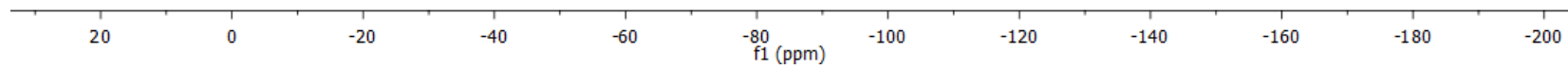
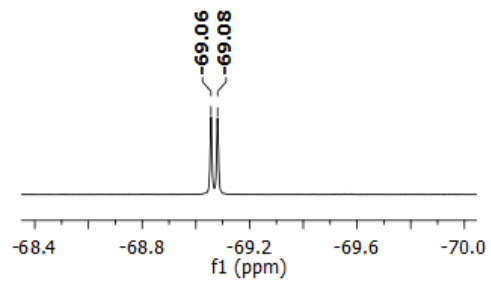
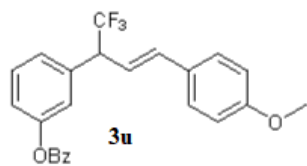
—1.56



¹⁹F NMR (376 MHz, CDCl₃) of **3u**

FLUORINE_01
04-24-109-f

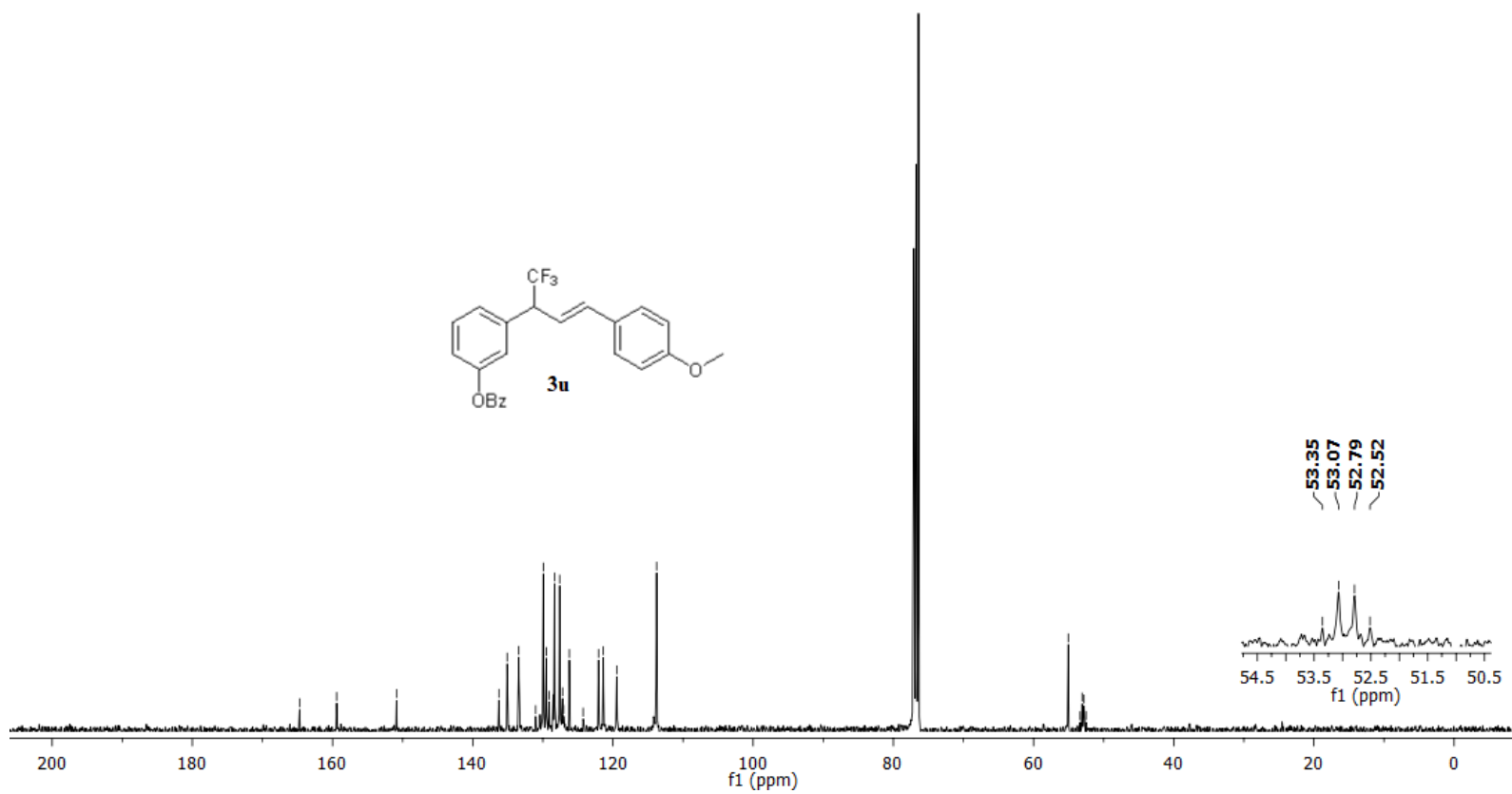
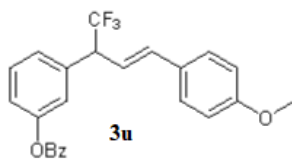
-69.06
-69.08



¹³C NMR (100 MHz, CDCl₃) of 3t

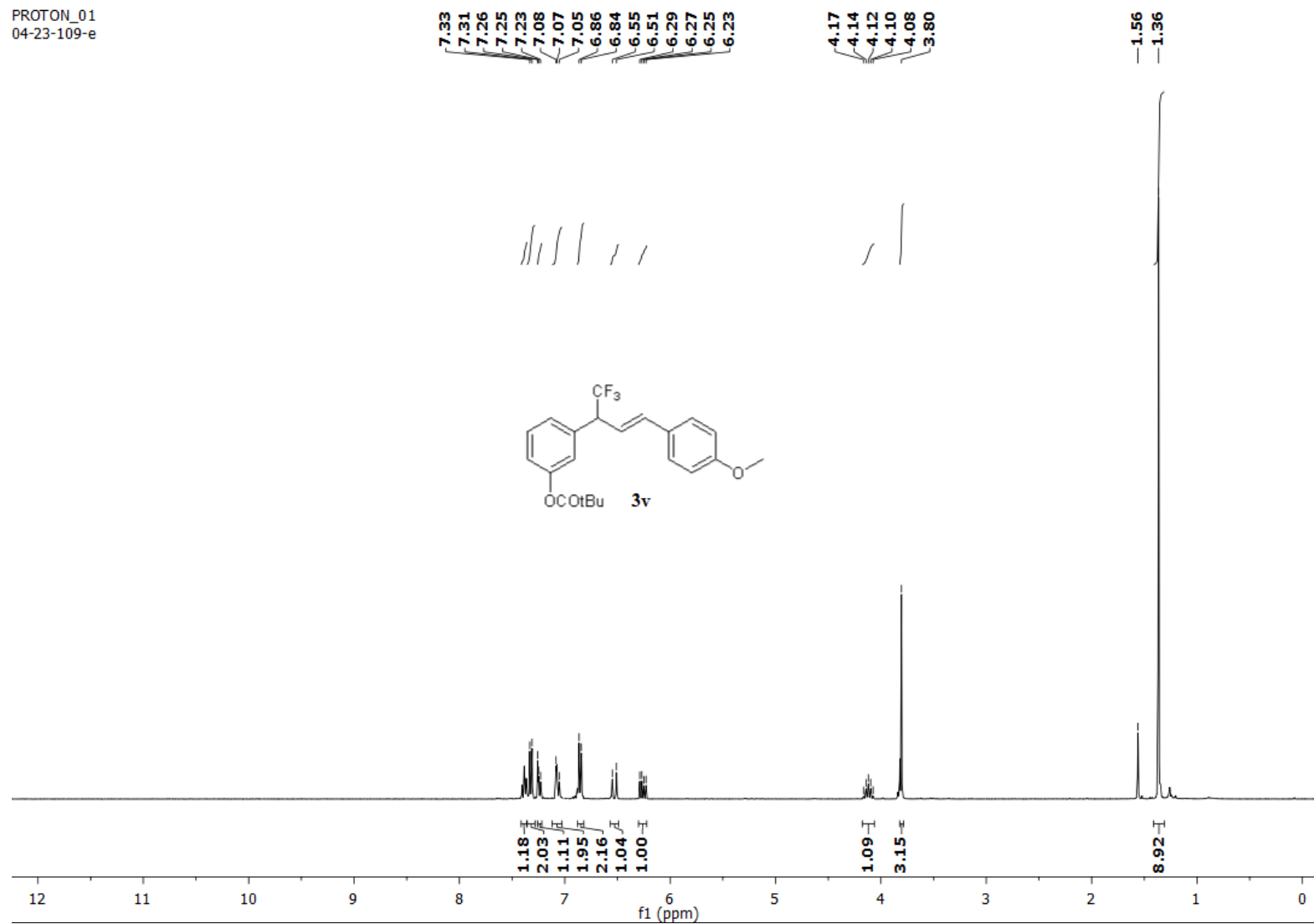
CARBON_01
04-24-109-f

- 164.70
- 159.42
- 150.87
- 136.26
- 135.09
- 133.43
- 131.02
- 129.93
- 129.51
- 129.12
- 128.34
- 127.59
- 127.19
- 127.05
- 126.23
- 124.25
- 122.05
- 121.38
- 119.45
- 113.76
- 55.04
- 53.35
- 53.07
- 52.79
- 52.52



PROTON_01
04-23-109-e

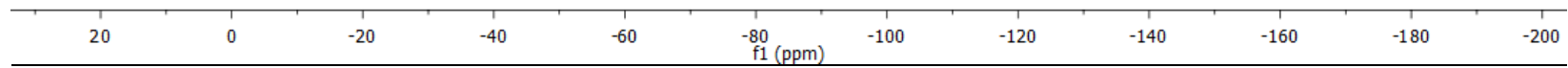
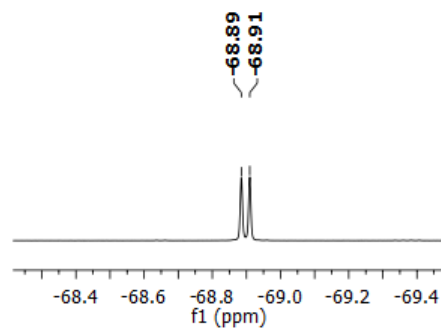
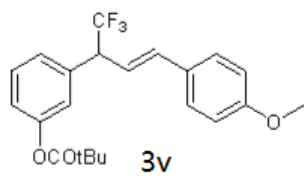
¹H NMR (400 MHz, CDCl₃) of 3v



¹⁹F NMR (376 MHz, CDCl₃) of 3v

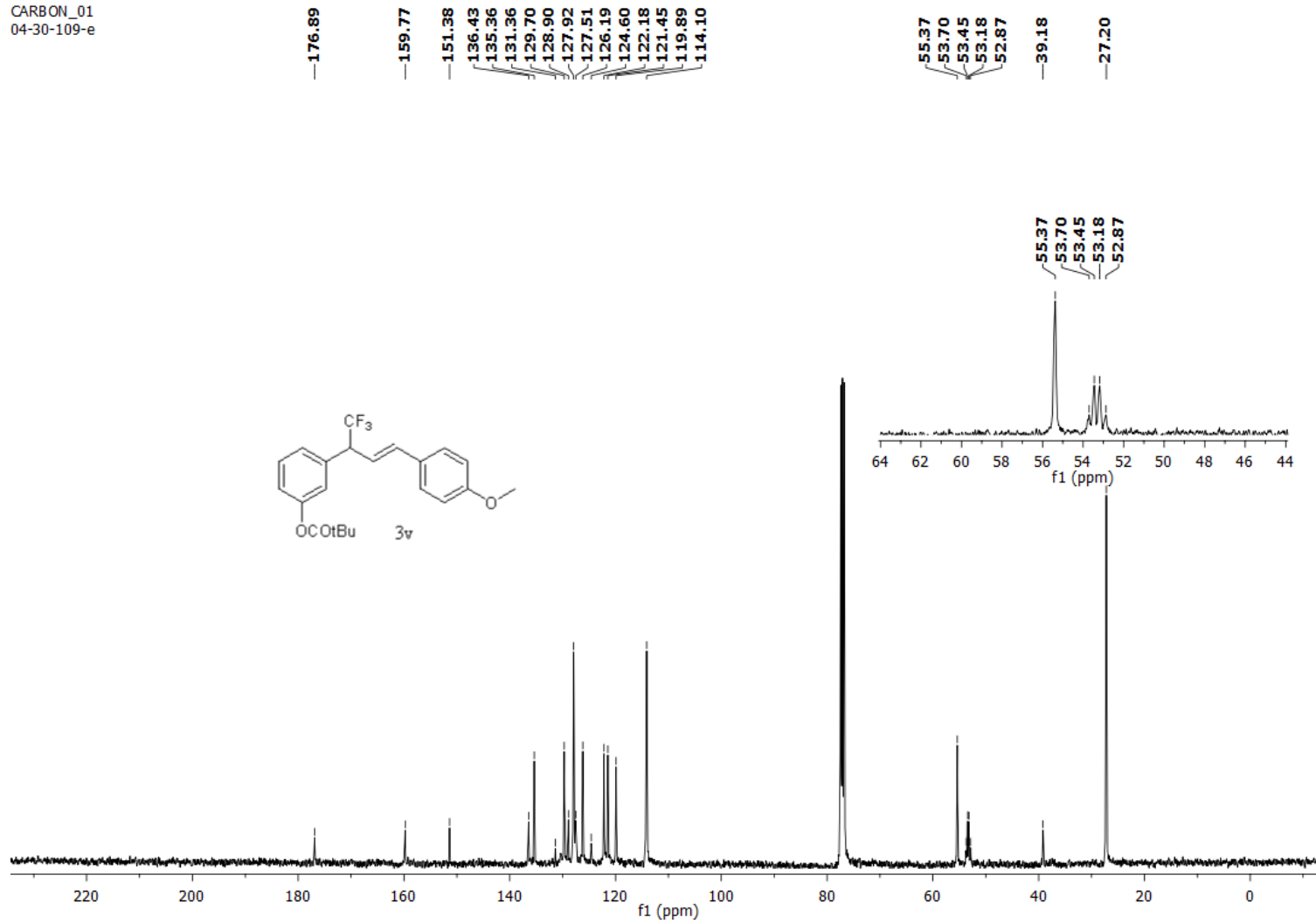
FLUORINE_01
04-23-109-e

-68.89
-68.91



¹³C NMR (100 MHz, CDCl₃) of 3v

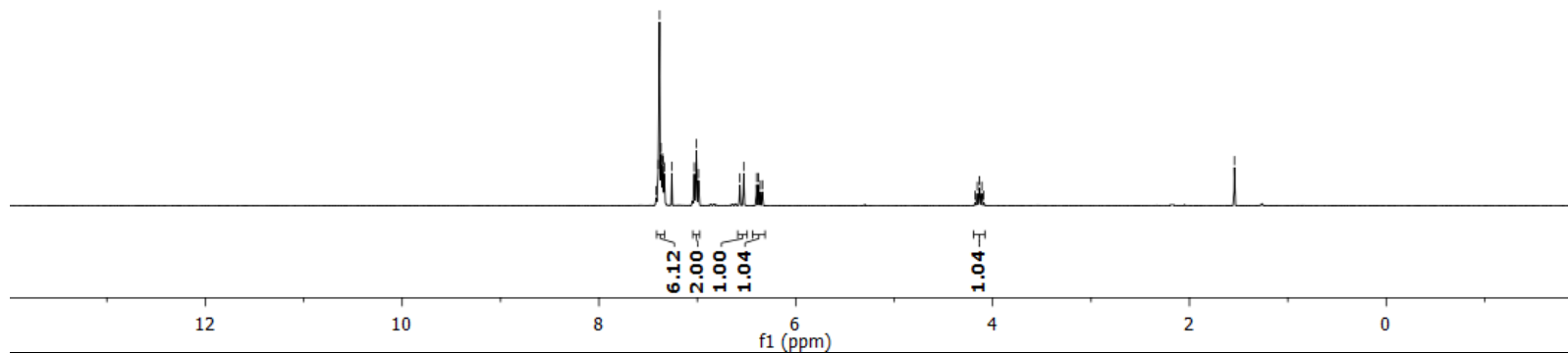
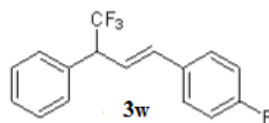
CARBON_01
04-30-109-e



PROTON_01
04-30-109-k1

¹H NMR (400 MHz, CDCl₃) of 3w

7.42
7.40
7.39
7.37
7.36
7.35
7.33
7.26
7.03
7.01
6.99
6.57
6.53
6.40
6.38
6.36
6.34
4.18
4.16
4.13
4.11
4.09
—1.54

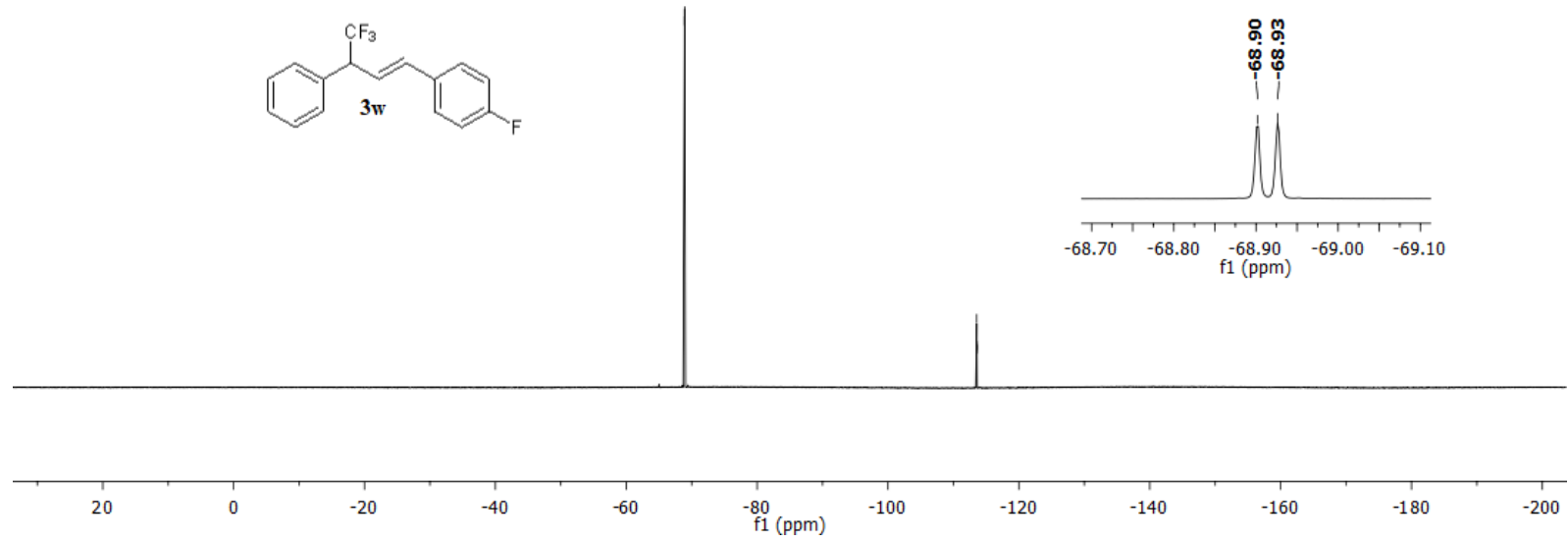
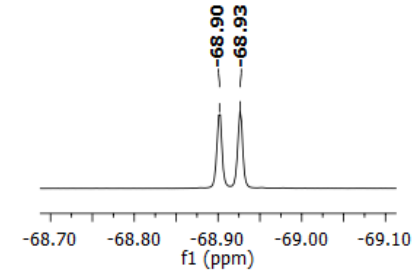
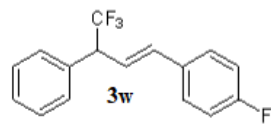


¹⁹F NMR (376 MHz, CDCl₃) of 3w

FLUORINE_01
04-30-109-k1

-68.90
-68.93

-113.54
-113.55
-113.57
-113.58

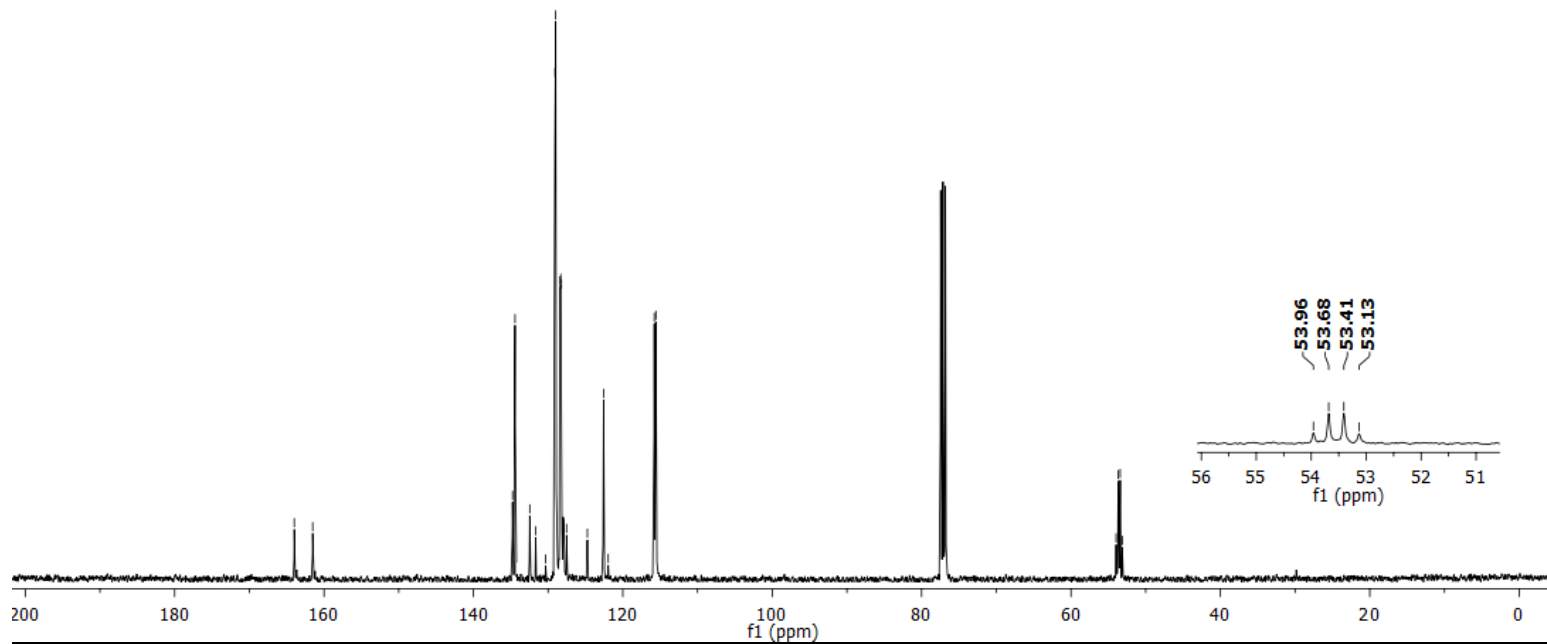
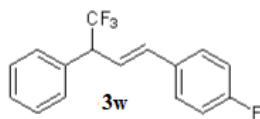


¹³C NMR (100 MHz, CDCl₃) of 3w

CARBON_01
04-18-108-f

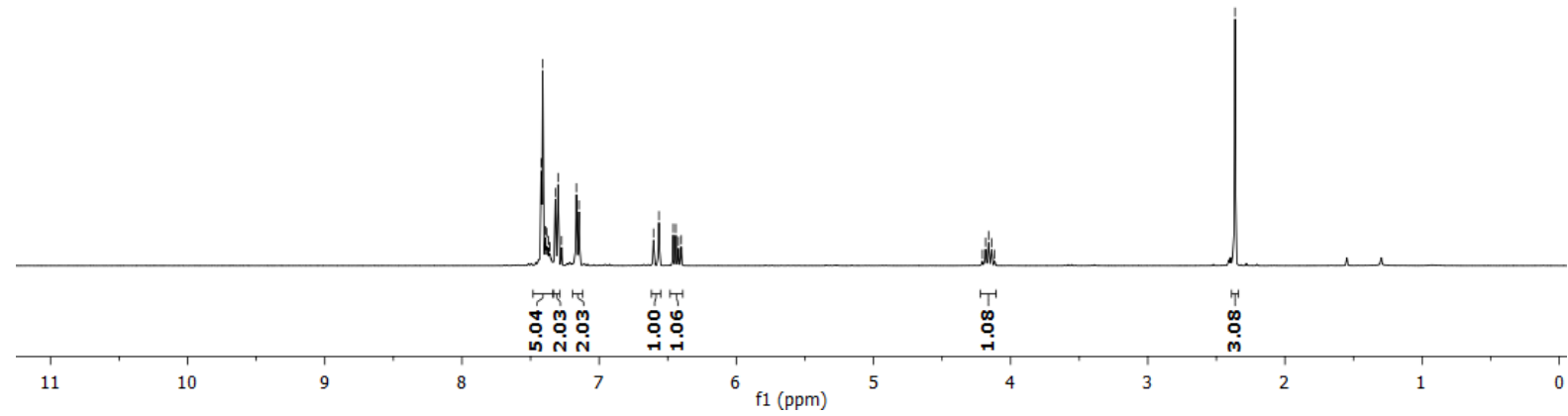
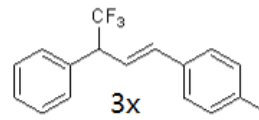
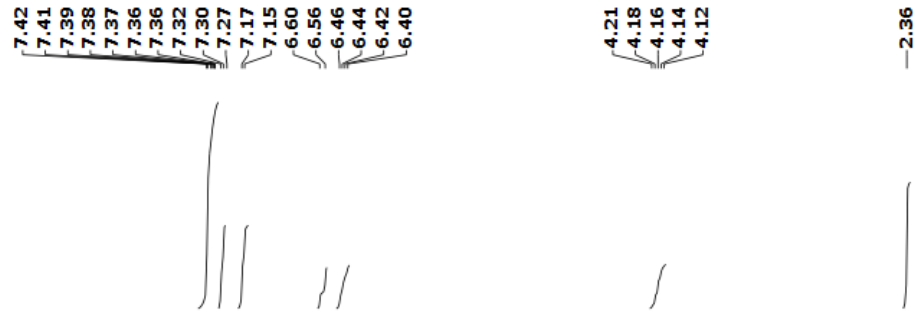
- 163.98
- 161.52
- 134.76
- 134.43
- 132.46
- 131.66
- 130.32
- 129.08
- 128.98
- 128.41
- 128.30
- 128.22
- 127.53
- 124.74
- 122.57
- 121.95
- 115.79
- 115.57

- 53.96
- 53.68
- 53.41
- 53.13



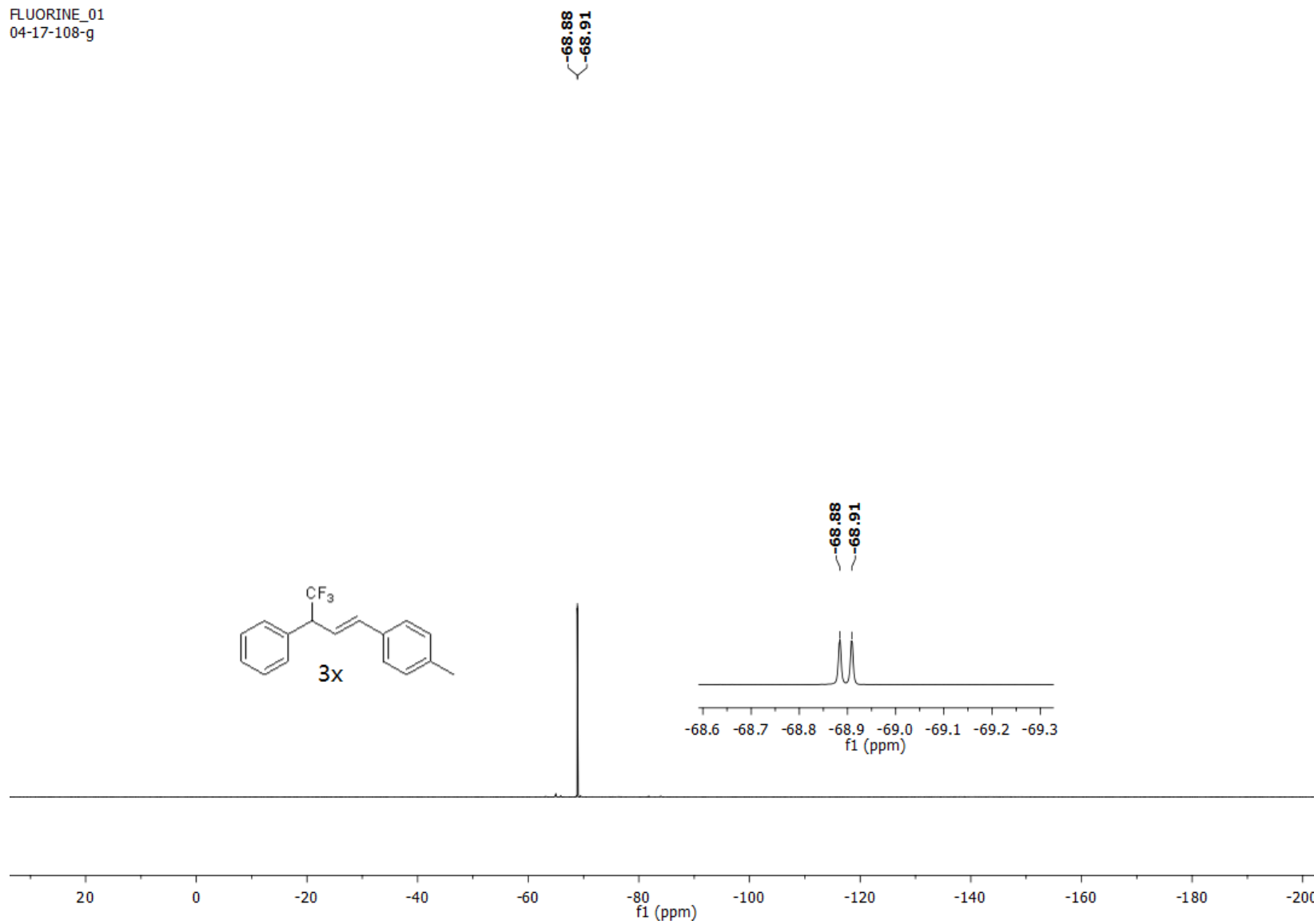
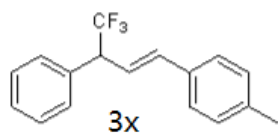
¹H NMR (400 MHz, CDCl₃) of 3x

PROTON_01
04-17-108-g



¹⁹F NMR (376 MHz, CDCl₃) of 3x

FLUORINE_01
04-17-108-g



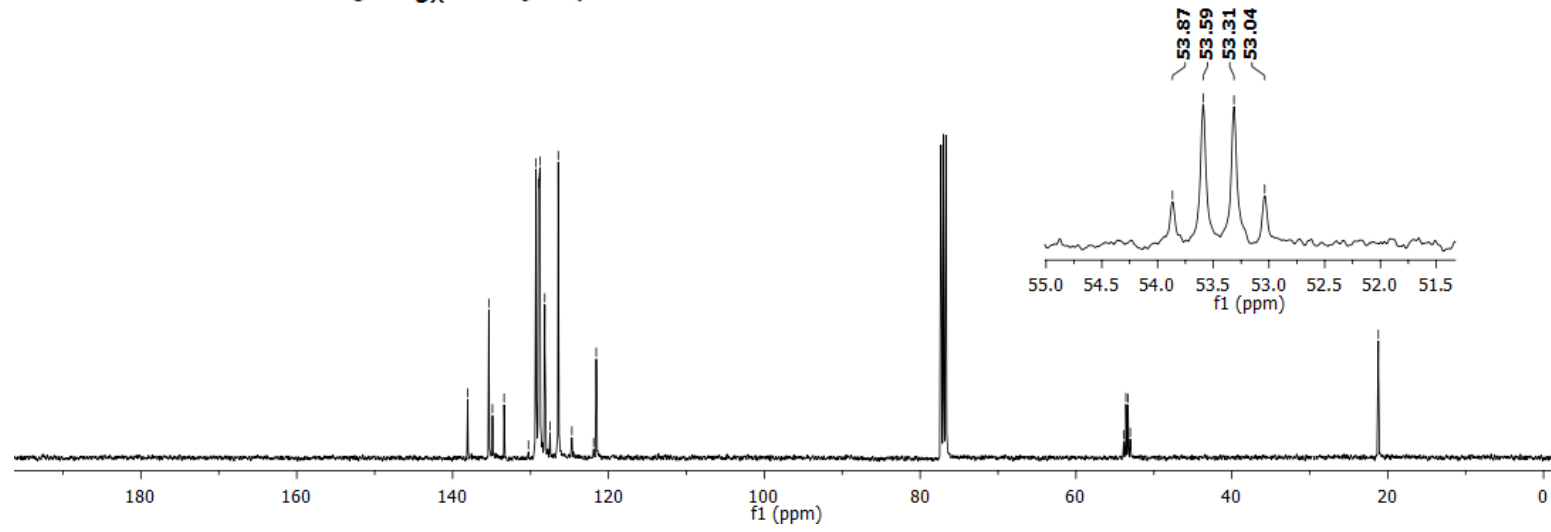
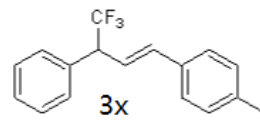
¹³C NMR (100 MHz, CDCl₃) of 3x

CARBON_01
04-17-108-g

138.06
135.35
134.88
133.39
130.27
129.29
128.99
128.78
128.17
127.49
126.44
124.69
121.90
121.57

53.87
53.59
53.31
53.04

21.20

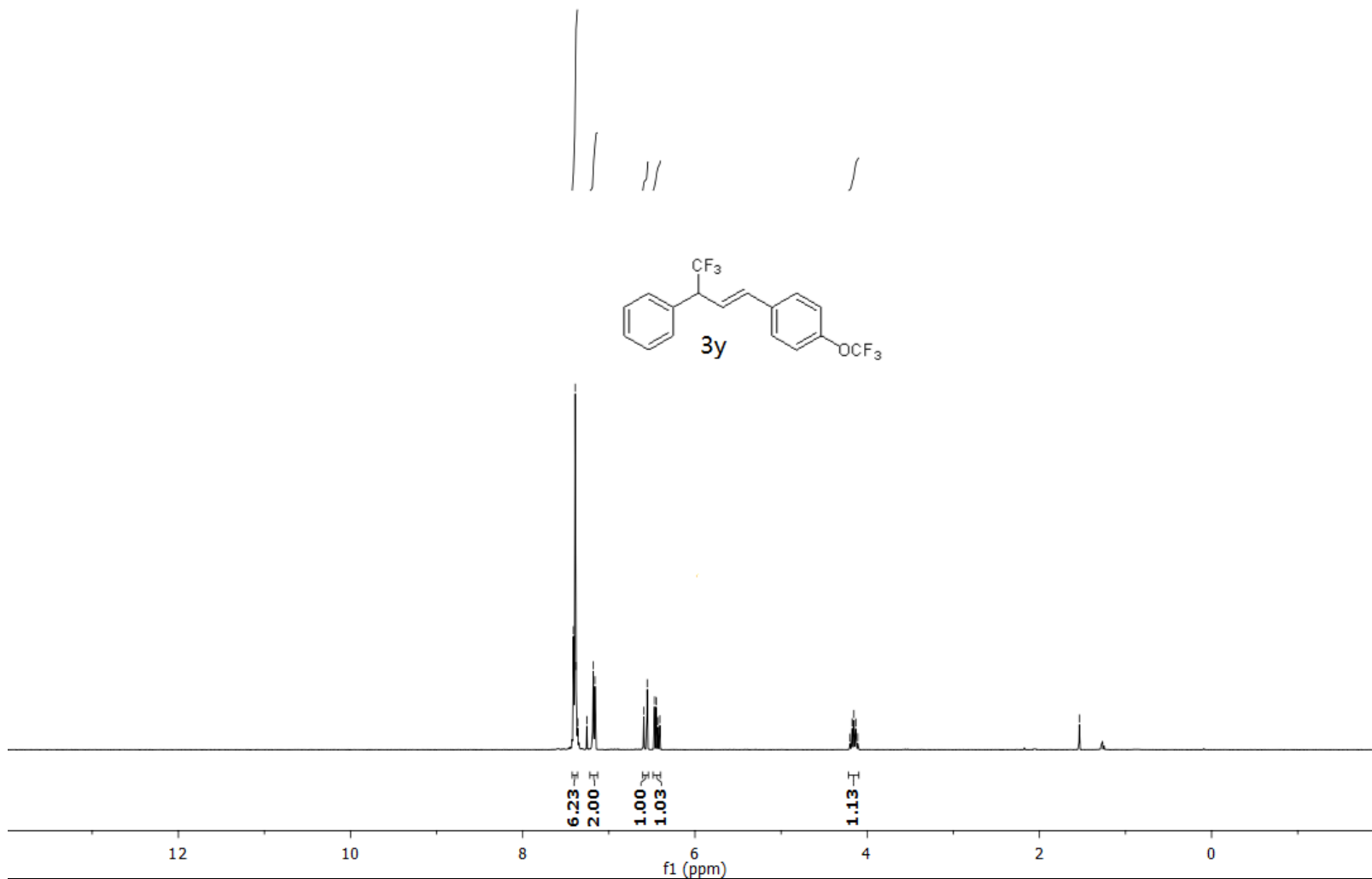
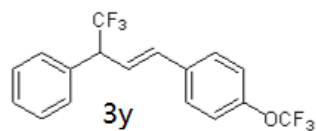


PROTON_01
04-30-109-p

¹H NMR (400 MHz, CDCl₃) of 3y

7.41 7.41 7.39 7.38 7.36 7.26 7.18 7.16 6.59 6.55 6.47 6.45 6.43 6.41 4.20 4.18 4.15 4.13 4.11

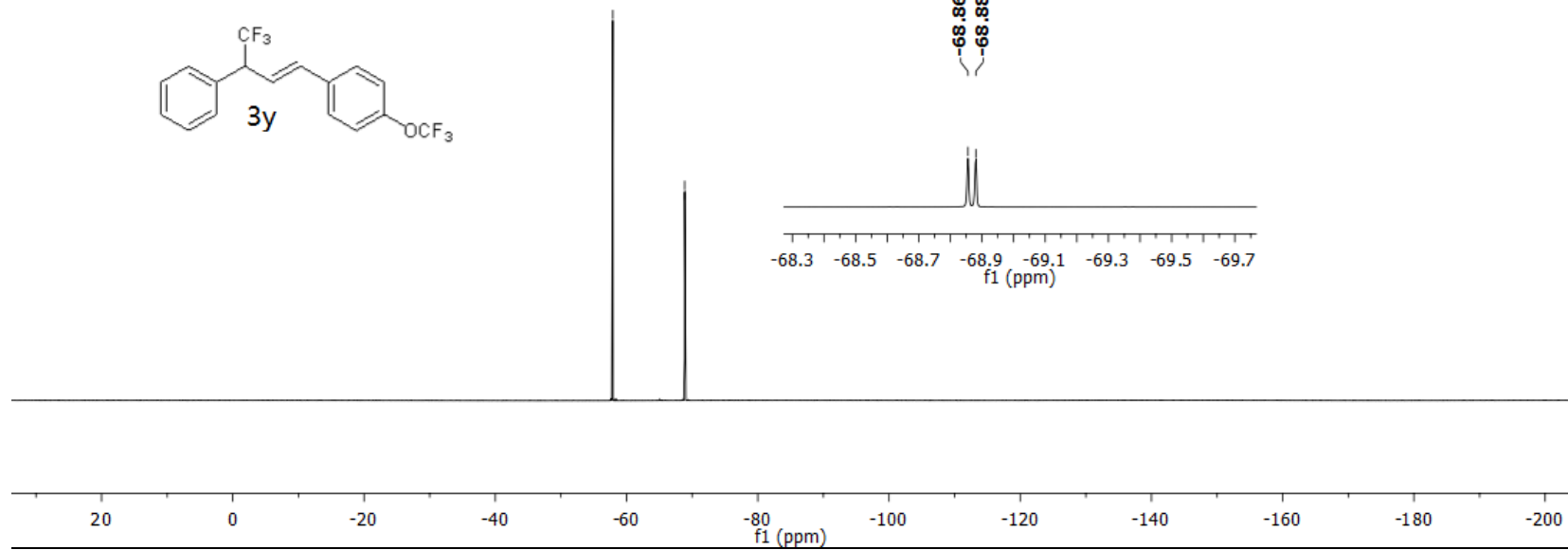
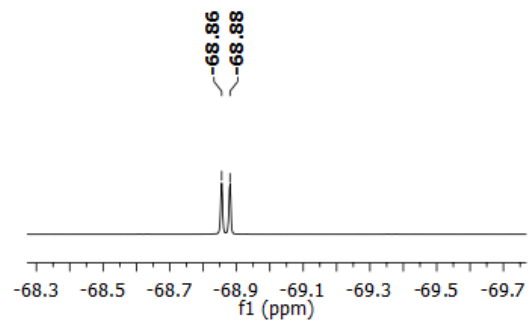
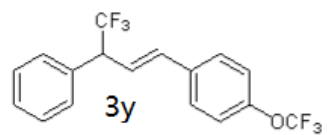
—1.54



FLUORINE_01
04-30-109-p

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

-57.91
-68.86
-68.88

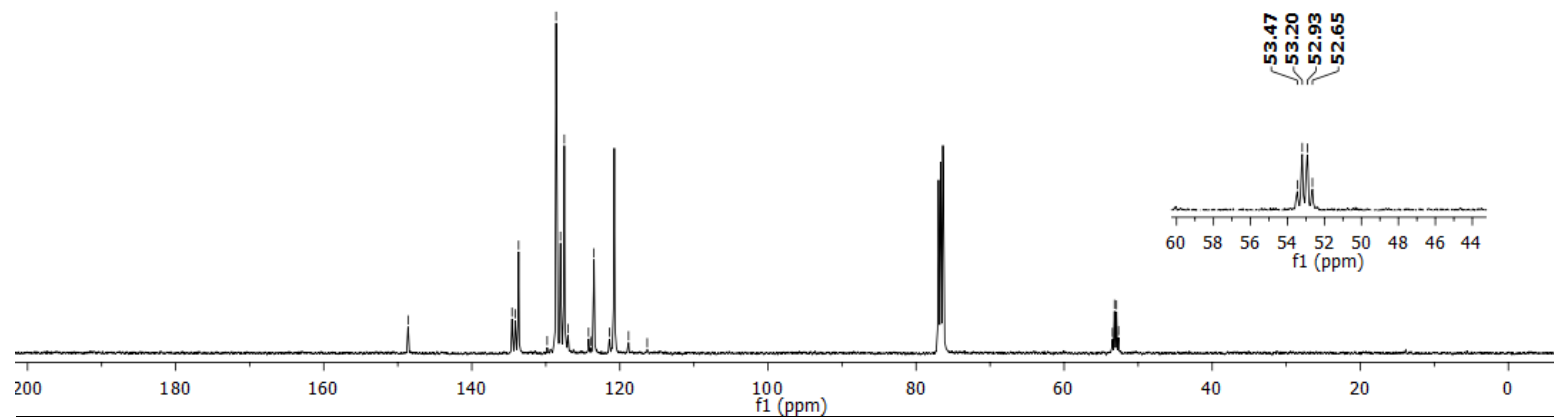
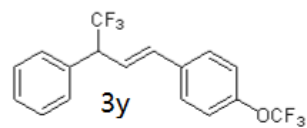


CARBON_01
05-05-109-p

^{13}C NMR (100 MHz, CDCl_3) of 3w

148.61
134.57
134.11
133.68
129.81
128.61
128.02
127.50
127.01
124.23
123.95
123.50
121.40
118.83
116.30

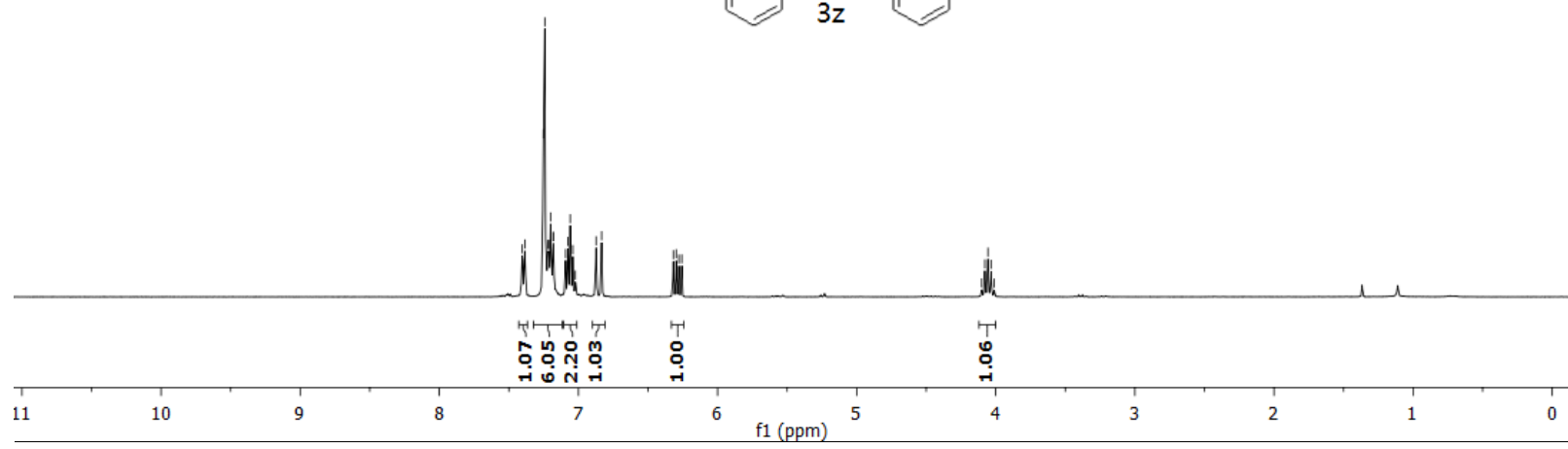
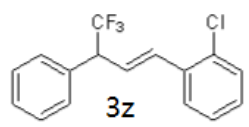
53.47
53.20
52.93
52.65



PROTON_01
04-17-108-k

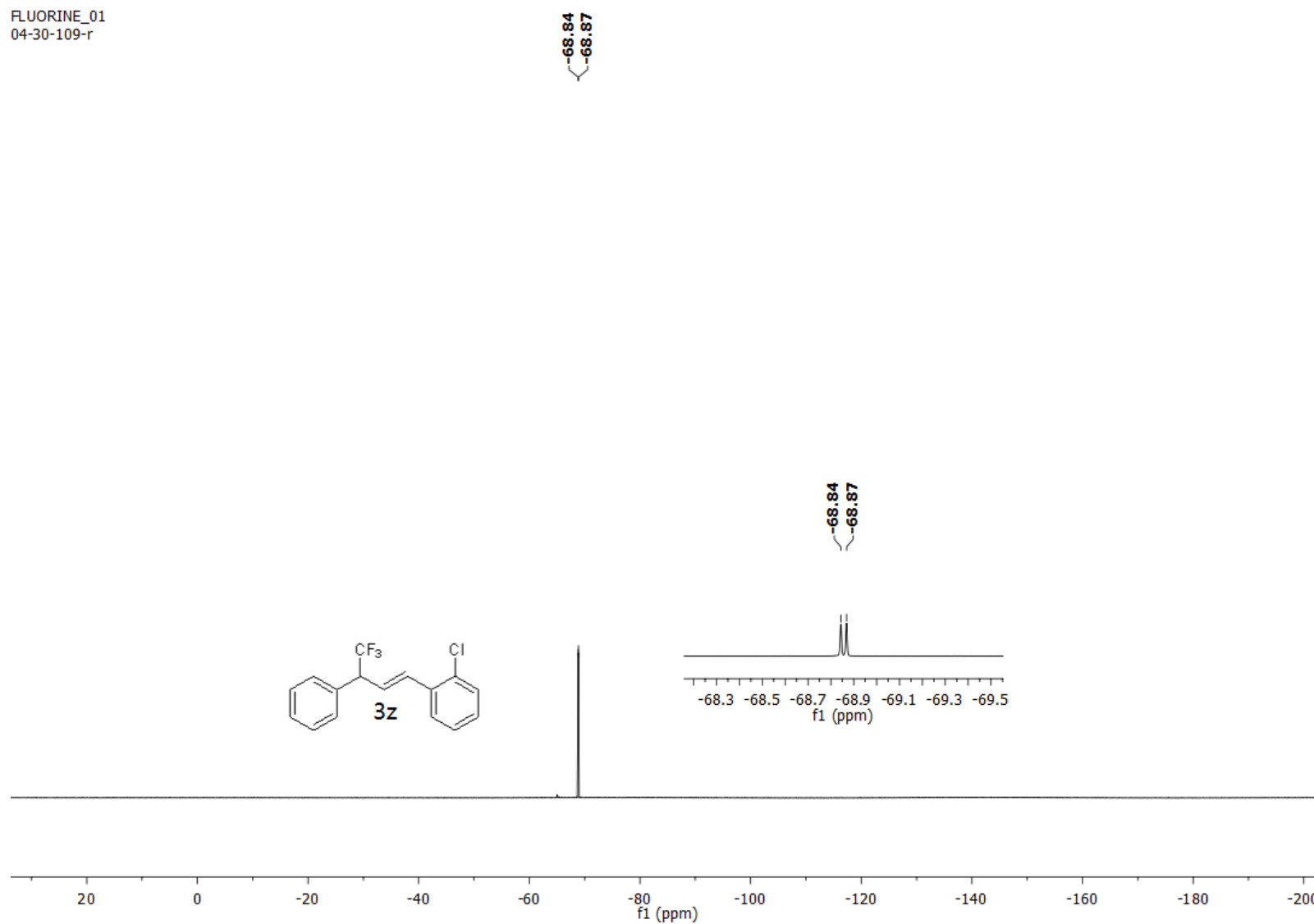
¹H NMR (400 MHz, CDCl₃) of 3z

7.40
7.39
7.25
7.24
7.22
7.21
7.20
7.18
7.18
7.09
7.08
7.06
7.04
7.02
6.87
6.83
6.32
6.30
6.28
6.26
4.10
4.08
4.06
4.03
4.01



¹⁹F NMR (376 MHz, CDCl₃) of 3z

FLUORINE_01
04-30-109-r

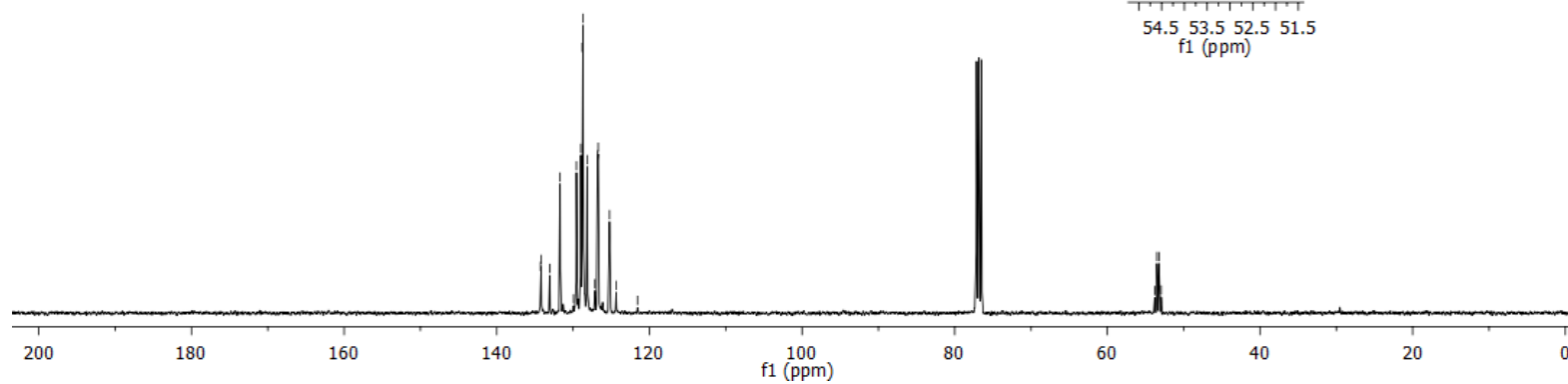
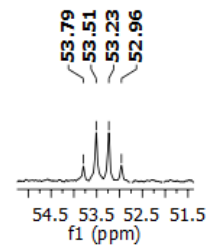
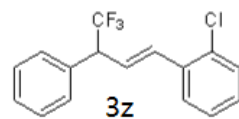


¹³C NMR (100 MHz, CDCl₃) of 3z

CARBON_01
04-17-108-k

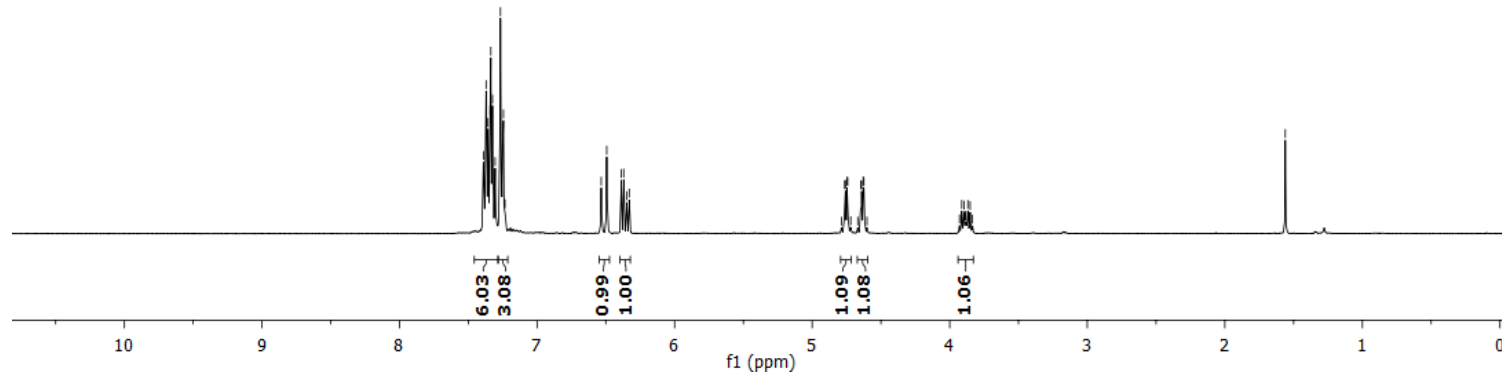
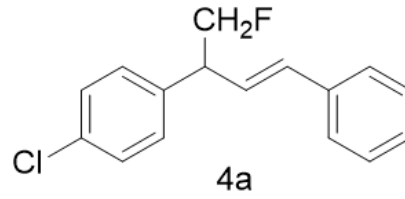
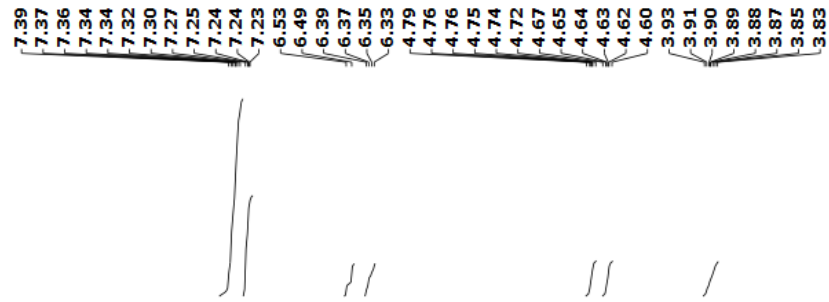
134.26
134.18
133.05
131.71
129.93
129.55
128.98
128.79
128.69
128.15
127.14
126.80
126.71
125.22
124.35
121.55

53.79
53.51
53.23
52.96



¹H NMR (400 MHz, CDCl₃) of 4a

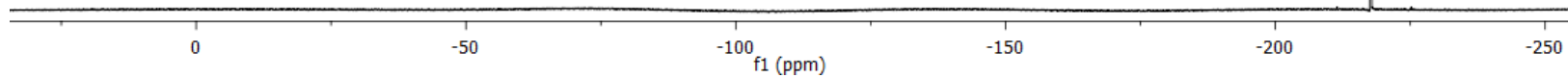
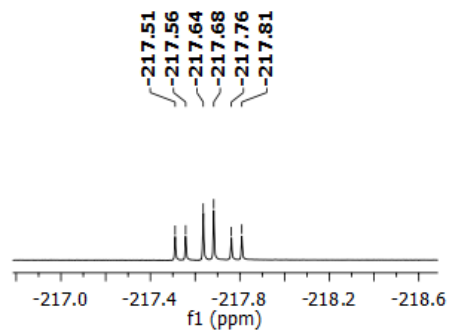
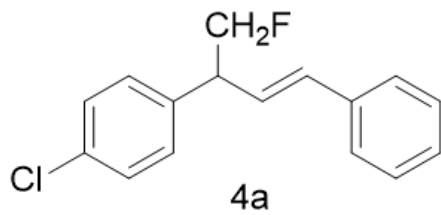
PROTON_01
06-09-112-a3



¹⁹F NMR (376 MHz, CDCl₃) of 4a

FLUORINE_01
STANDARD FLUORINE PARAMETERS

-217.51
-217.56
-217.64
-217.68
-217.76
-217.81



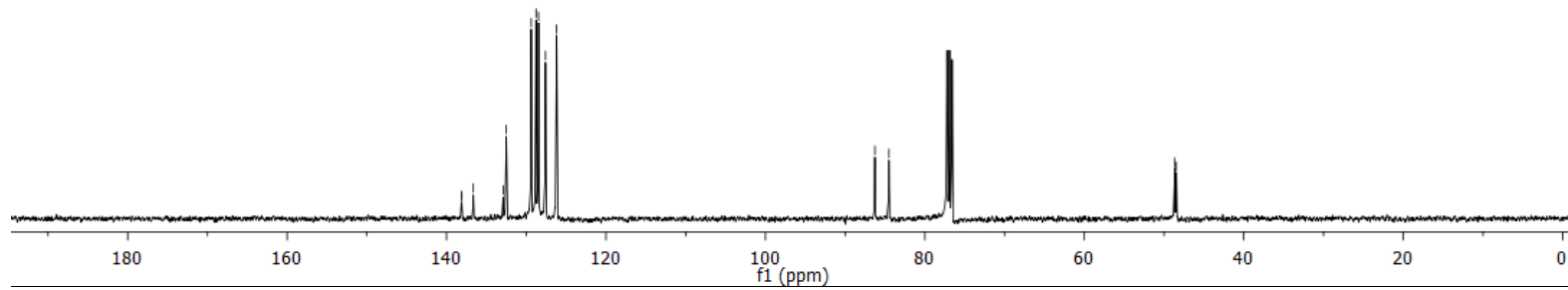
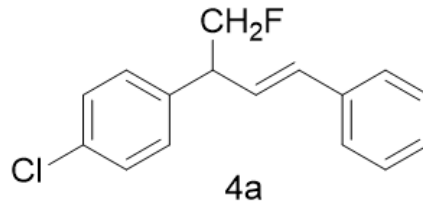
¹³C NMR (100 MHz, CDCl₃) of 4a

CARBON_02
06-09-112-a3

138.13
138.09
136.65
132.89
132.51
129.38
128.78
128.47
127.59
126.20

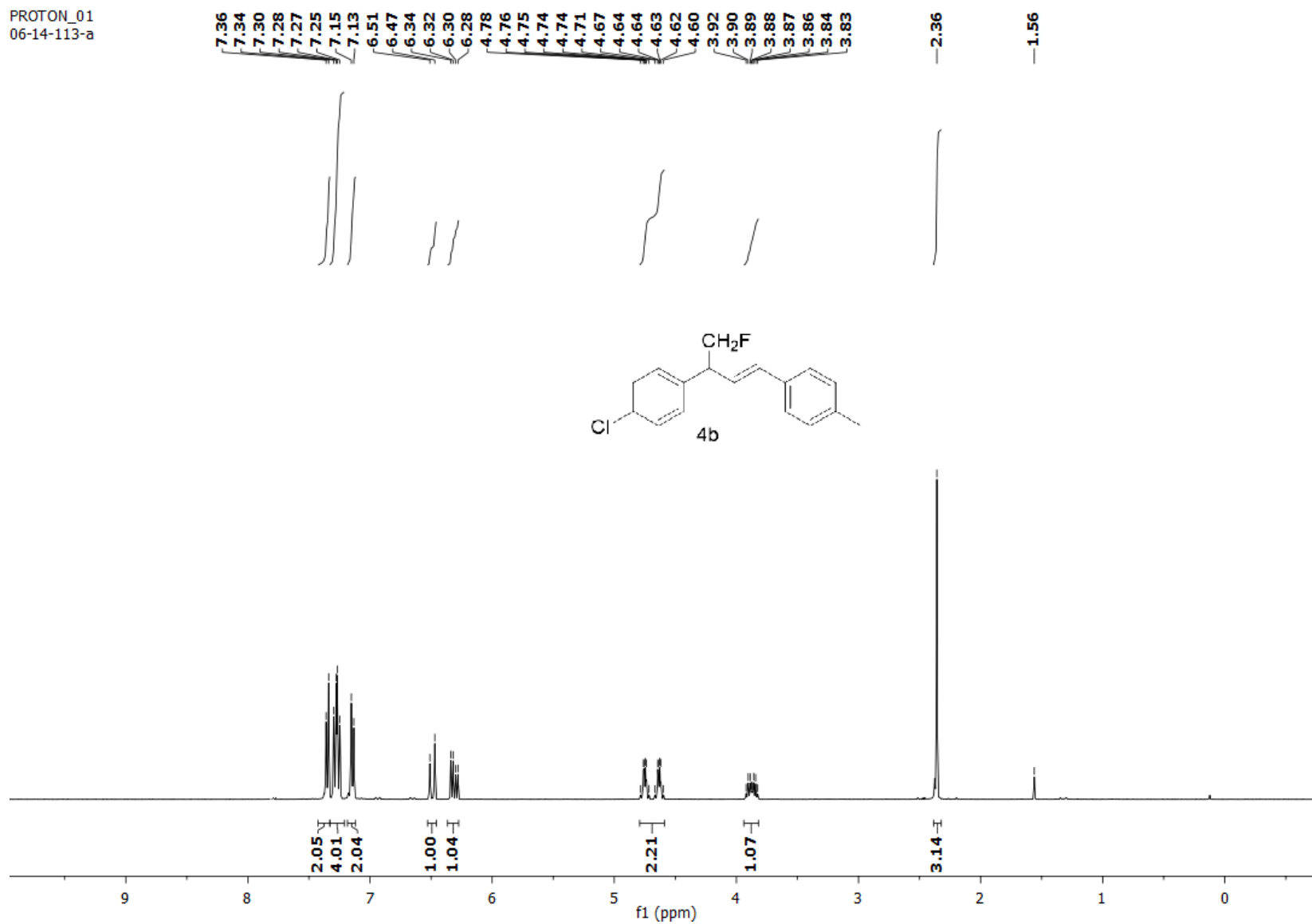
86.26
84.51

48.65
48.46



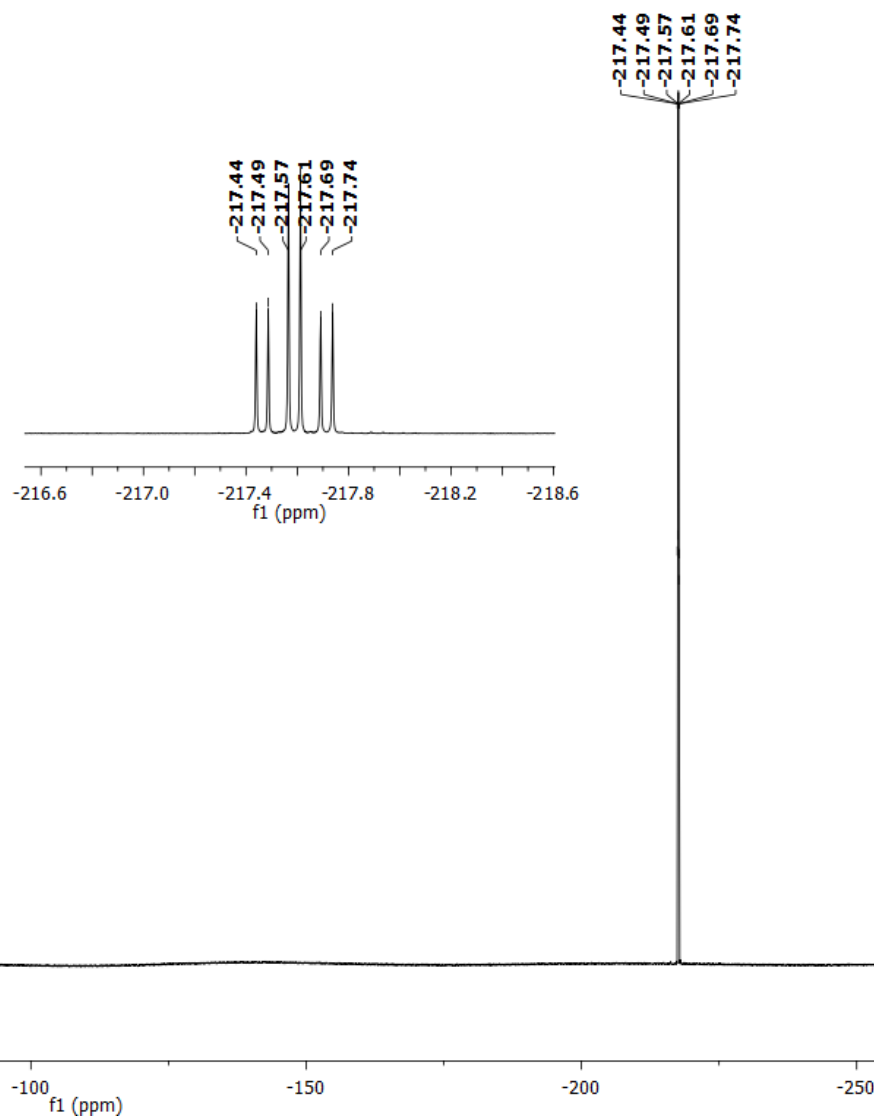
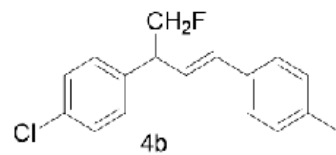
¹H NMR (400 MHz, CDCl₃) of 4b

PROTON_01
06-14-113-a



¹⁹F NMR (376 MHz, CDCl₃) of 4b

FLUORINE_01
STANDARD FLUORINE PARAMETERS



¹³C NMR (100 MHz, CDCl₃) of 4b

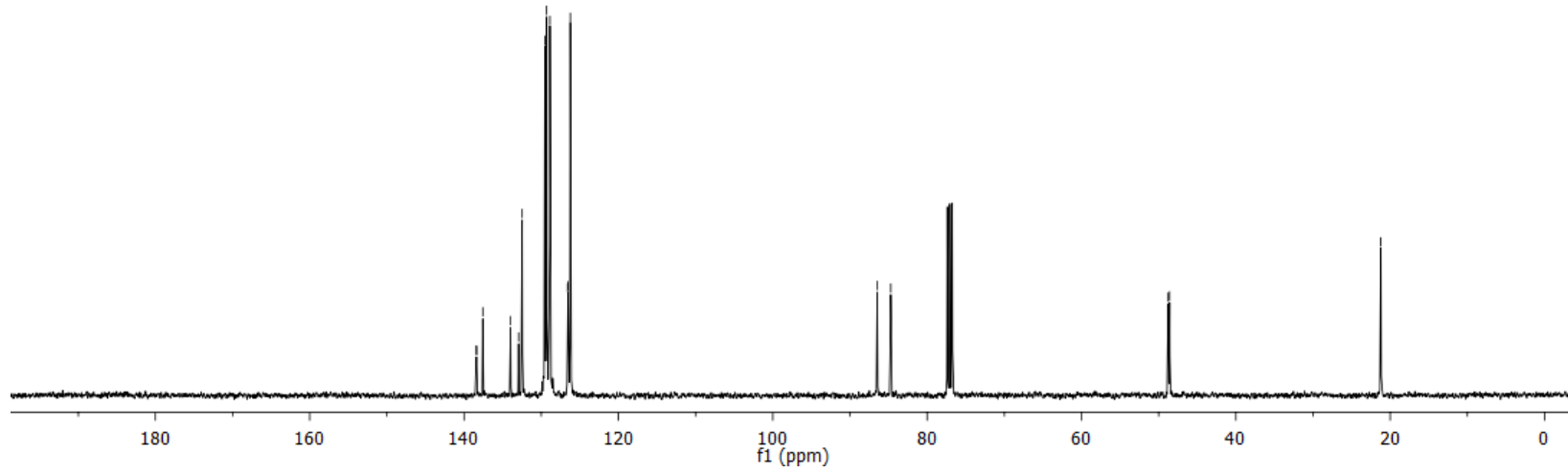
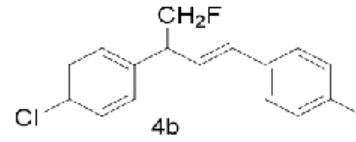
CARBON_01
06-14-113-a

138.42
138.38
137.58
133.98
132.94
132.48
129.53
129.31
128.88
126.59
126.54
126.24

86.46
84.71

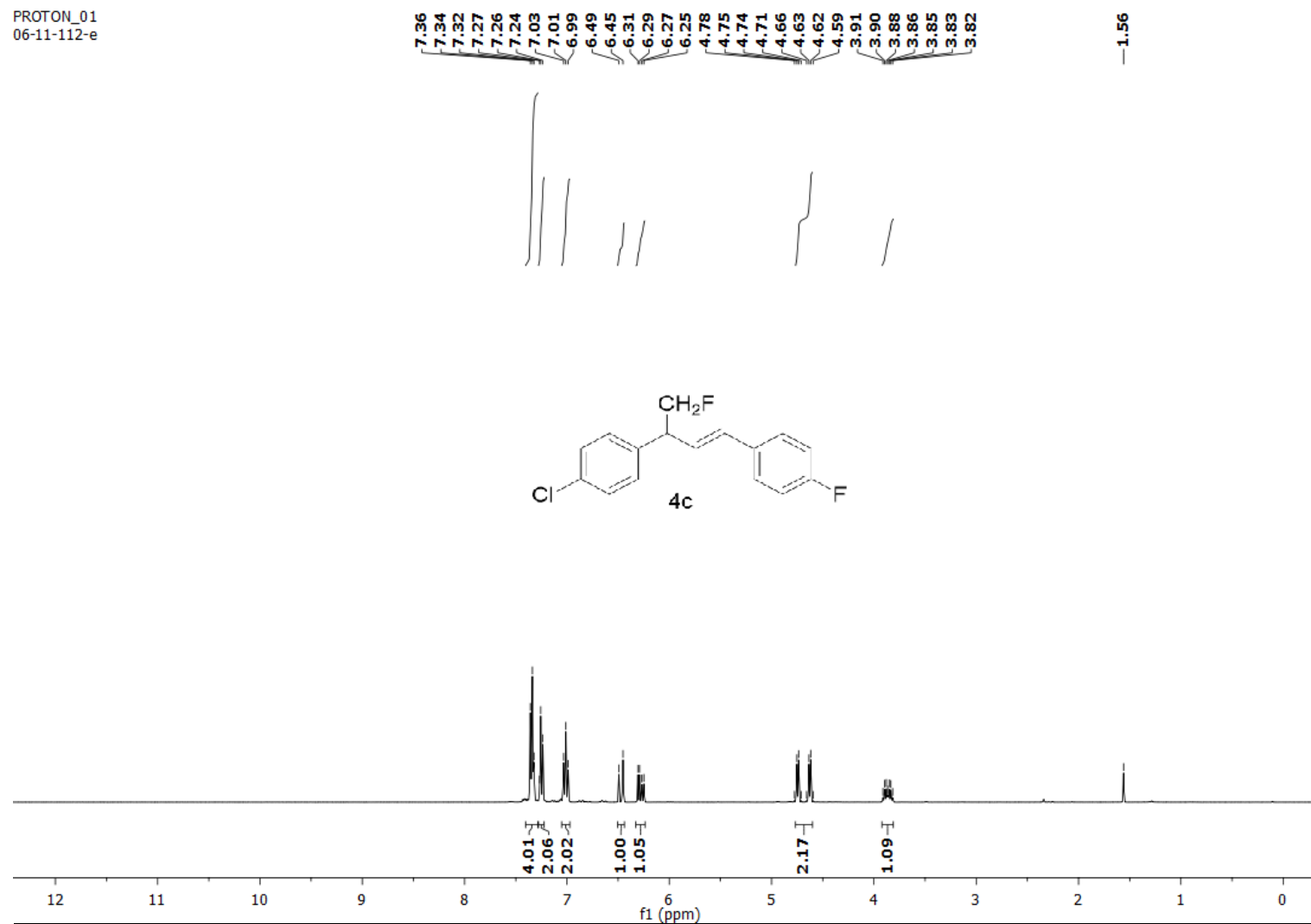
48.78
48.58

21.21



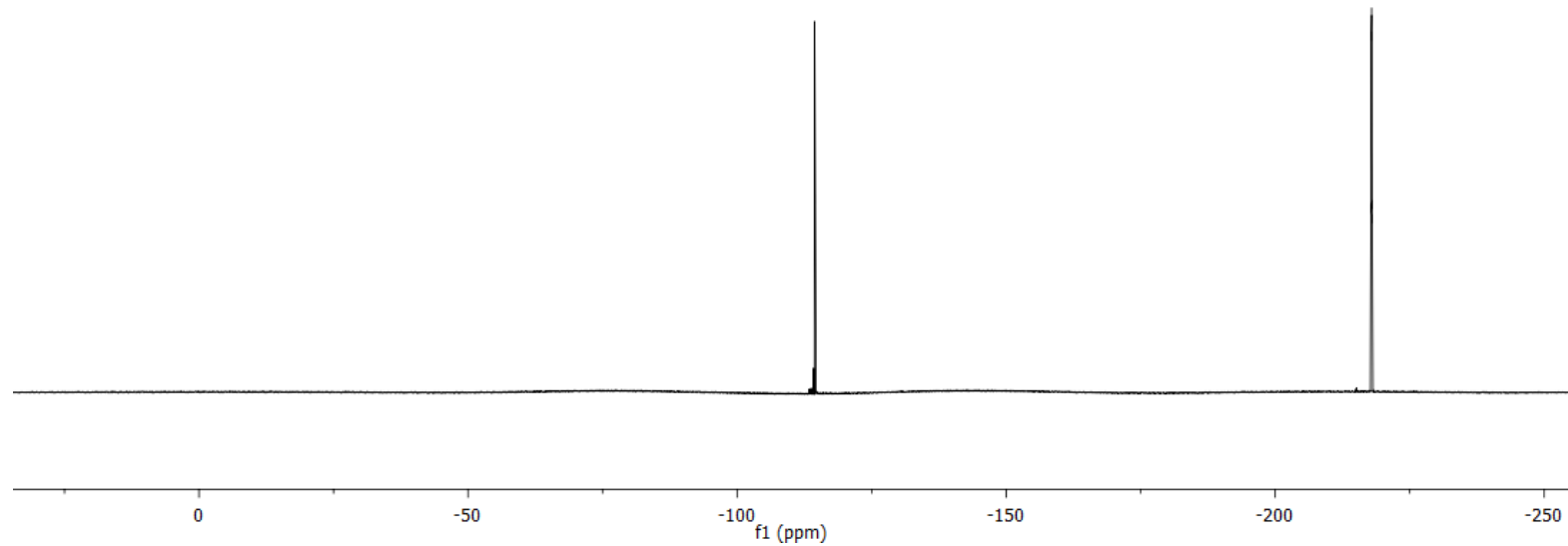
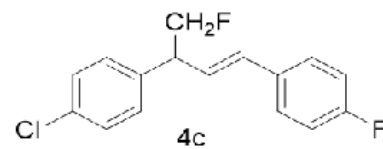
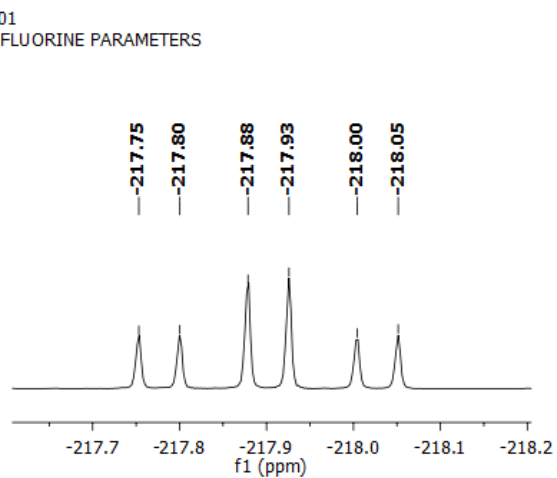
PROTON_01
06-11-112-e

¹H NMR (400 MHz, CDCl₃) of 4c



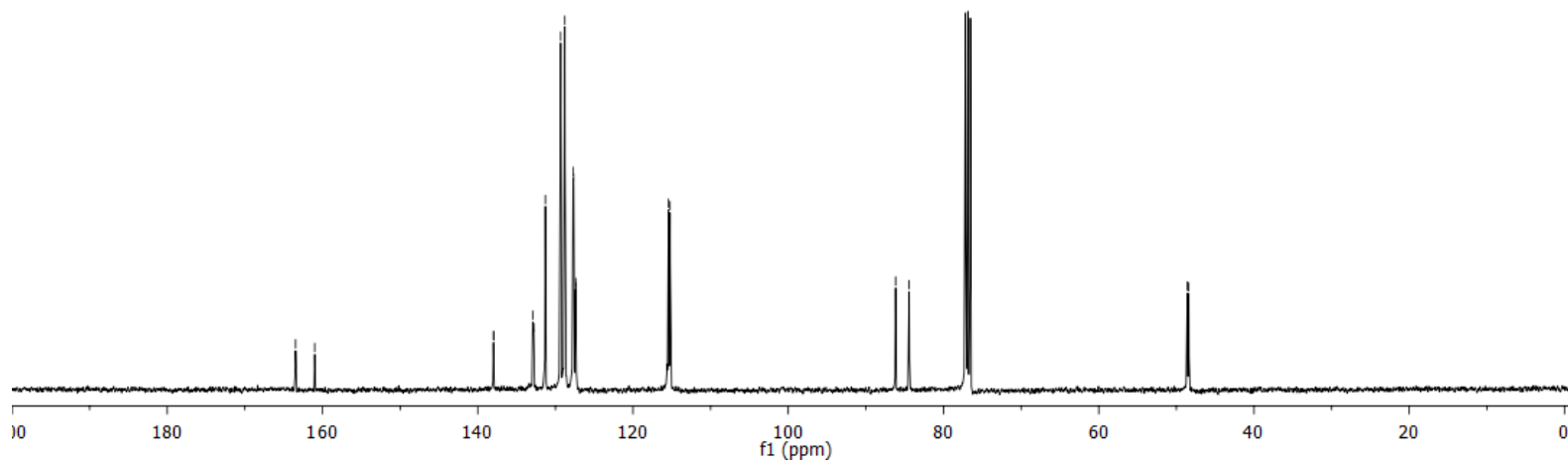
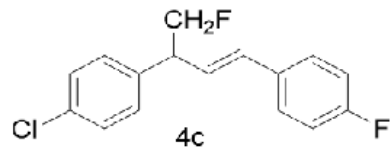
¹⁹F NMR (376 MHz, CDCl₃) of 4c

FLUORINE_01
STANDARD FLUORINE PARAMETERS



¹³C NMR (100 MHz, CDCl₃) of 4c

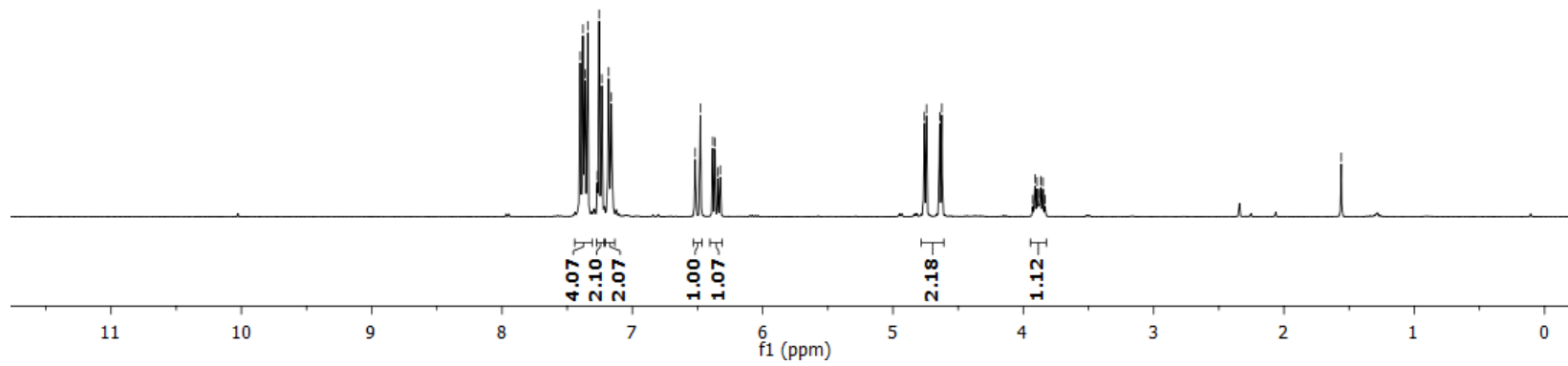
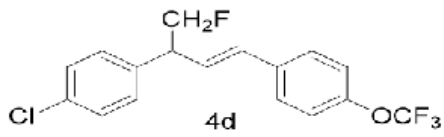
CARBON_01
06-11-112-e



PROTON_01
06-11-112-g

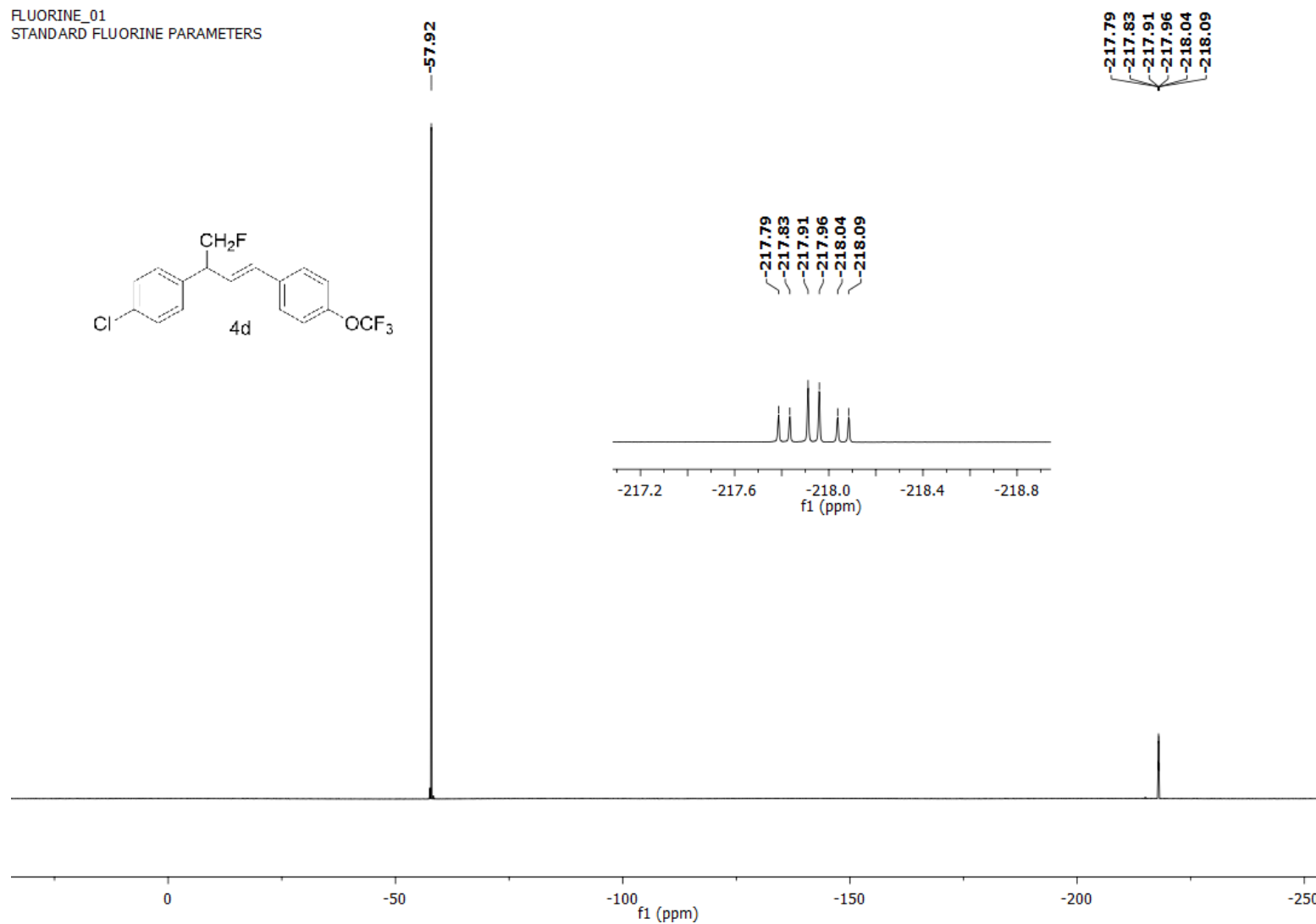
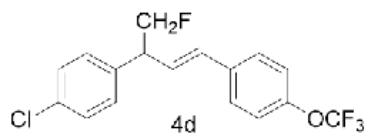
¹H NMR (400 MHz, CDCl₃) of 4d

7.40 7.38 7.36 7.34 7.27 7.26 7.23 7.18 7.16 6.52 6.48 6.38 6.37 6.34 6.32 4.76 4.74 4.64 4.62 3.93 3.91 3.89 3.88 3.87 3.85 3.83 —1.56



¹⁹F NMR (376 MHz, CDCl₃) of 4d

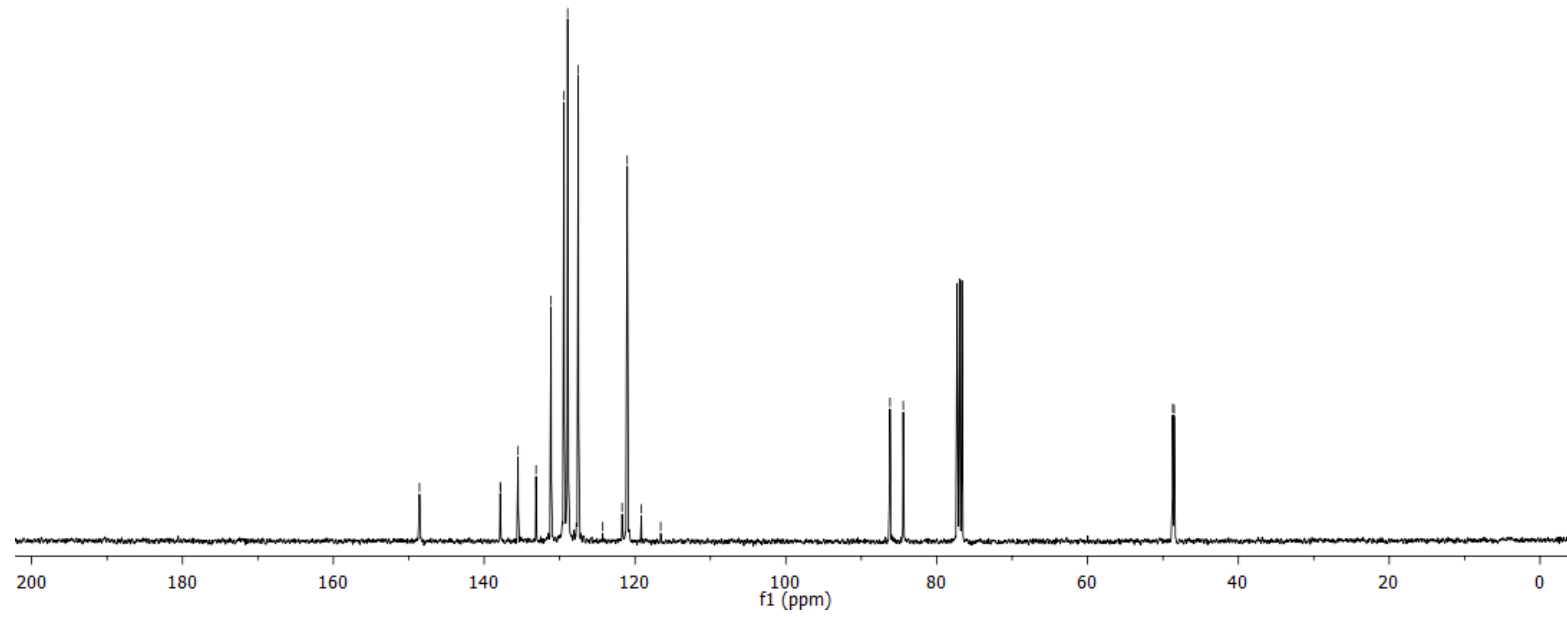
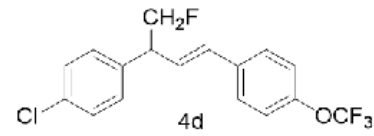
FLUORINE_01
STANDARD FLUORINE PARAMETERS



¹³C NMR (100 MHz, CDCl₃) of 4d

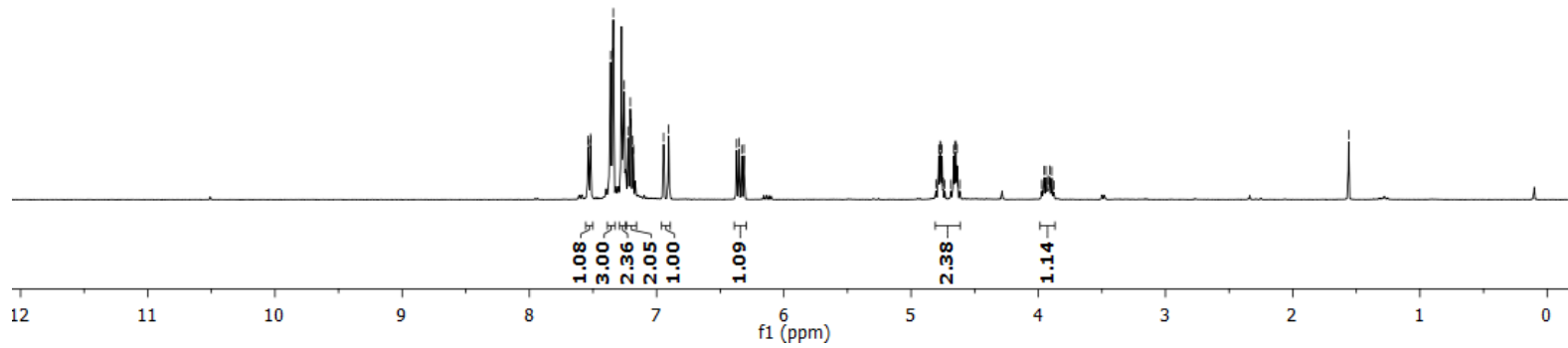
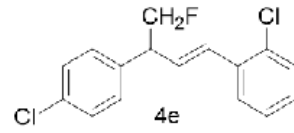
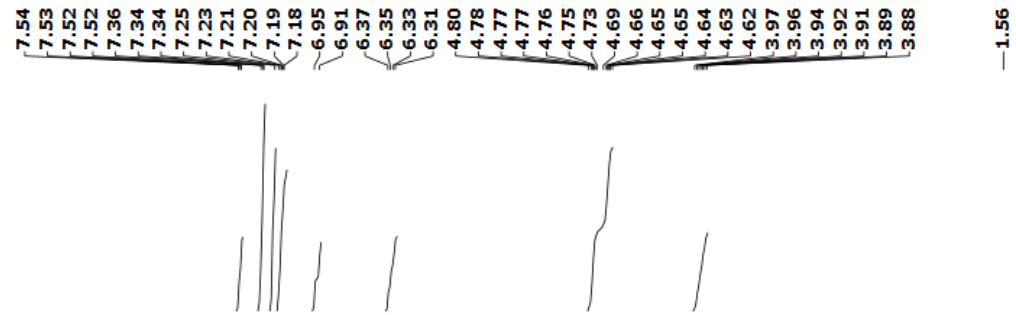
CARBON_01
06-11-112-g

148.58
137.87
137.82
135.51
133.13
131.14
129.42
128.93
128.86
127.52
124.28
121.72
121.03
119.16
116.60
86.19
84.44
48.71
48.51



¹H NMR (400 MHz, CDCl₃) of 4e

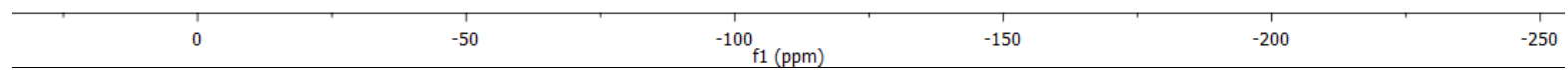
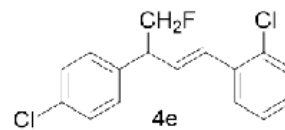
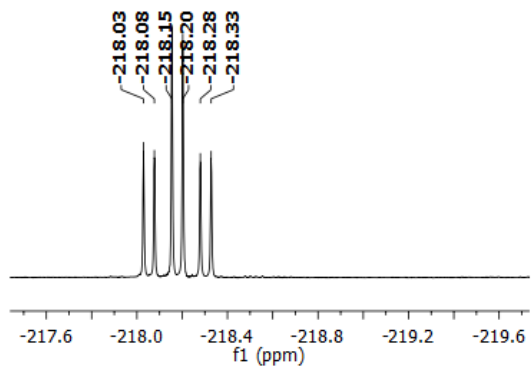
PROTON_01
06-12-112-h



¹⁹F NMR (376 MHz, CDCl₃) of 4e

FLUORINE_01
STANDARD FLUORINE PARAMETERS

-218.03
-218.08
-218.15
-218.20
-218.28
-218.33



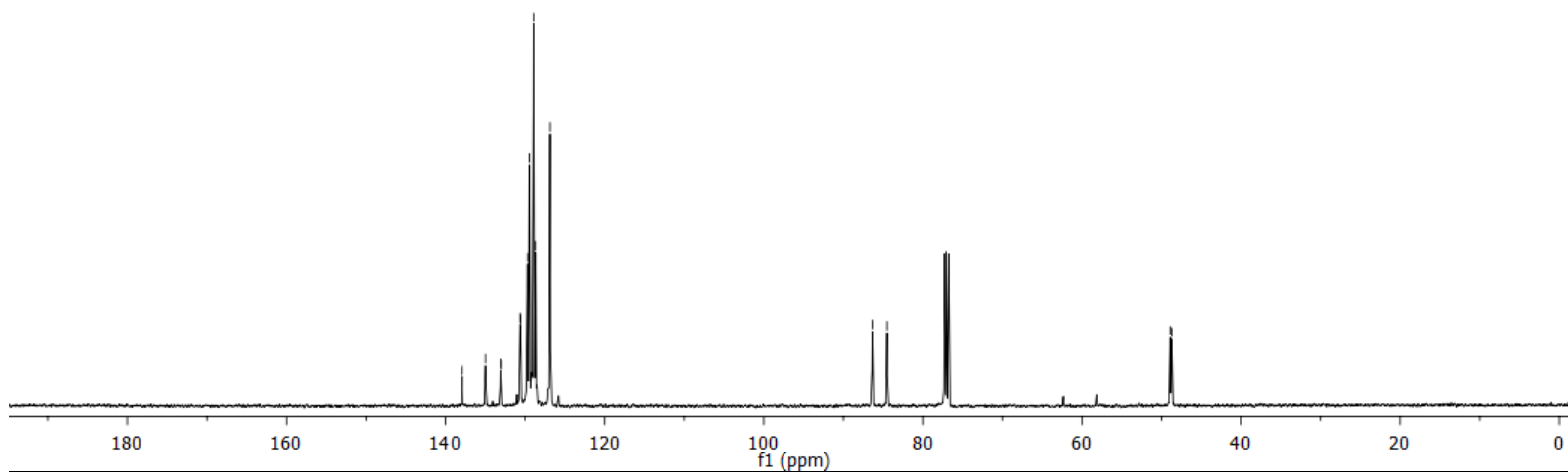
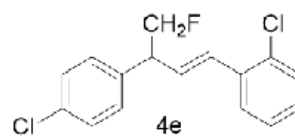
CARBON_01
06-12-112-h

^{13}C NMR (100 MHz, CDCl_3) of 4e

137.97
137.94
134.98
133.12
133.05
130.62
130.57
129.71
129.48
128.95
128.72
126.84

86.30
84.55

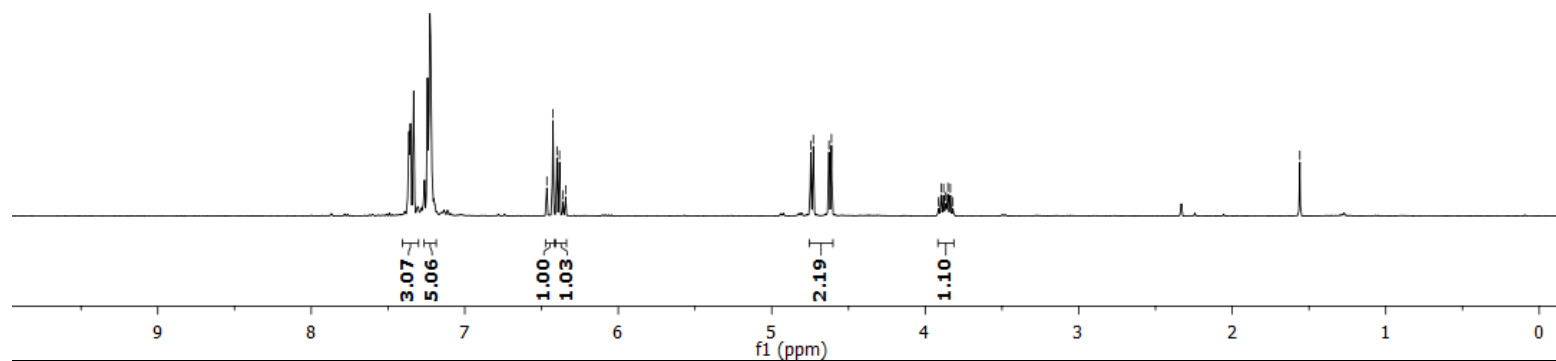
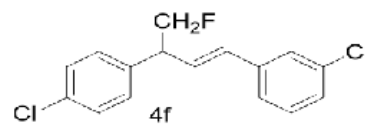
48.94
48.74



¹H NMR (400 MHz, CDCl₃) of 4f

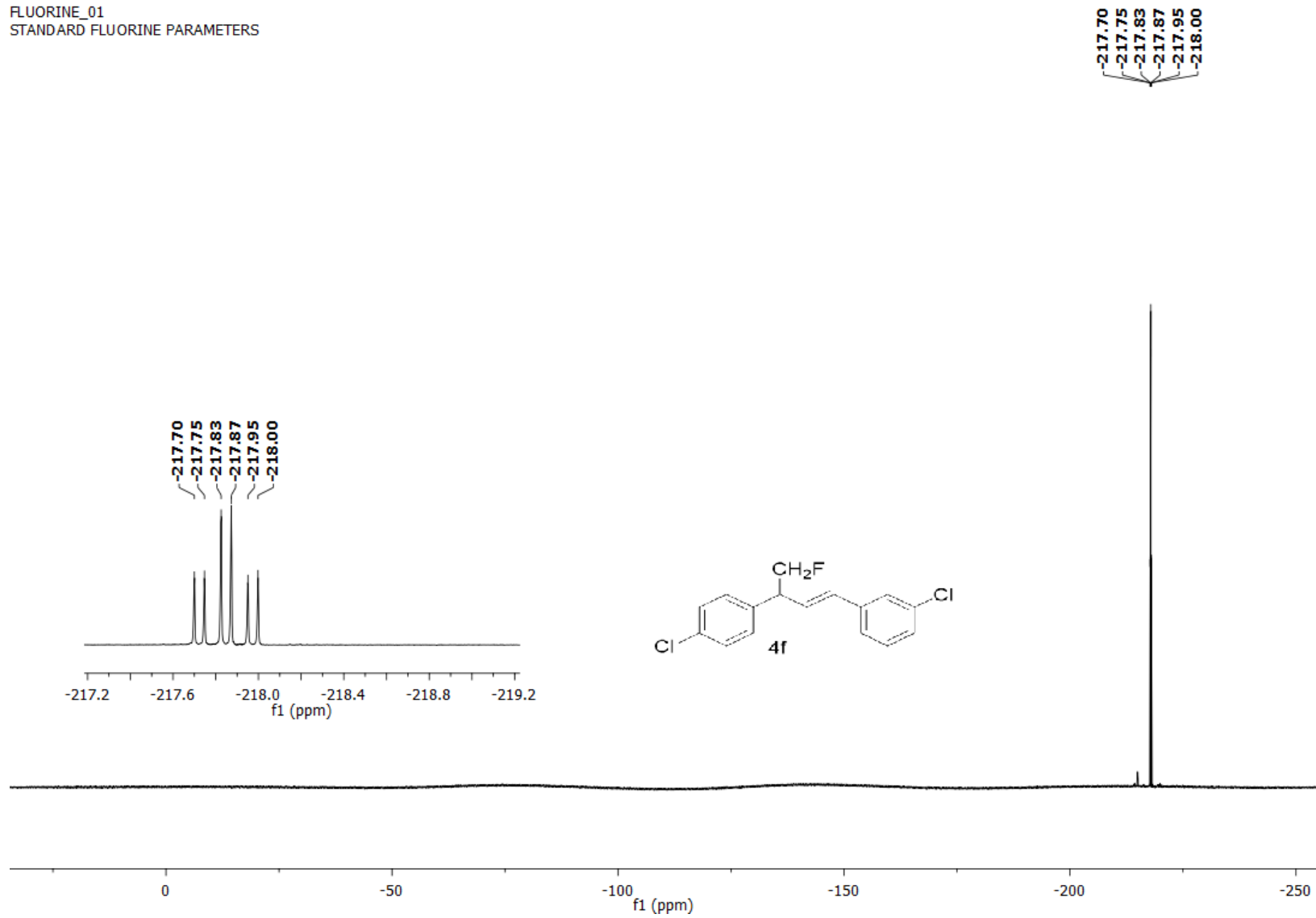
PROTON_01
06-12-112-L

6.47
6.42
6.40
6.38
6.36
6.34
4.75
4.73
4.63
4.61
3.91
3.90
3.88
3.87
3.85
3.84
-1.56



¹⁹F NMR (376 MHz, CDCl₃) of 4f

FLUORINE_01
STANDARD FLUORINE PARAMETERS



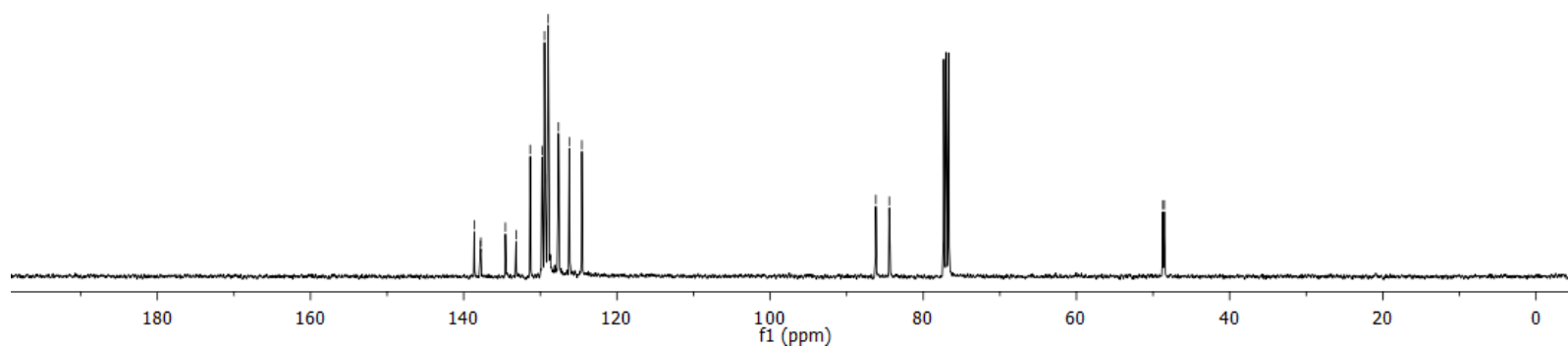
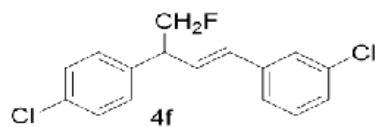
¹³C NMR (100 MHz, CDCl₃) of 4f

CARBON_01
06-12-112-L

138.62
137.81
137.76
134.57
133.16
131.32
129.78
129.46
129.40
129.35
128.97
127.63
126.21
124.58

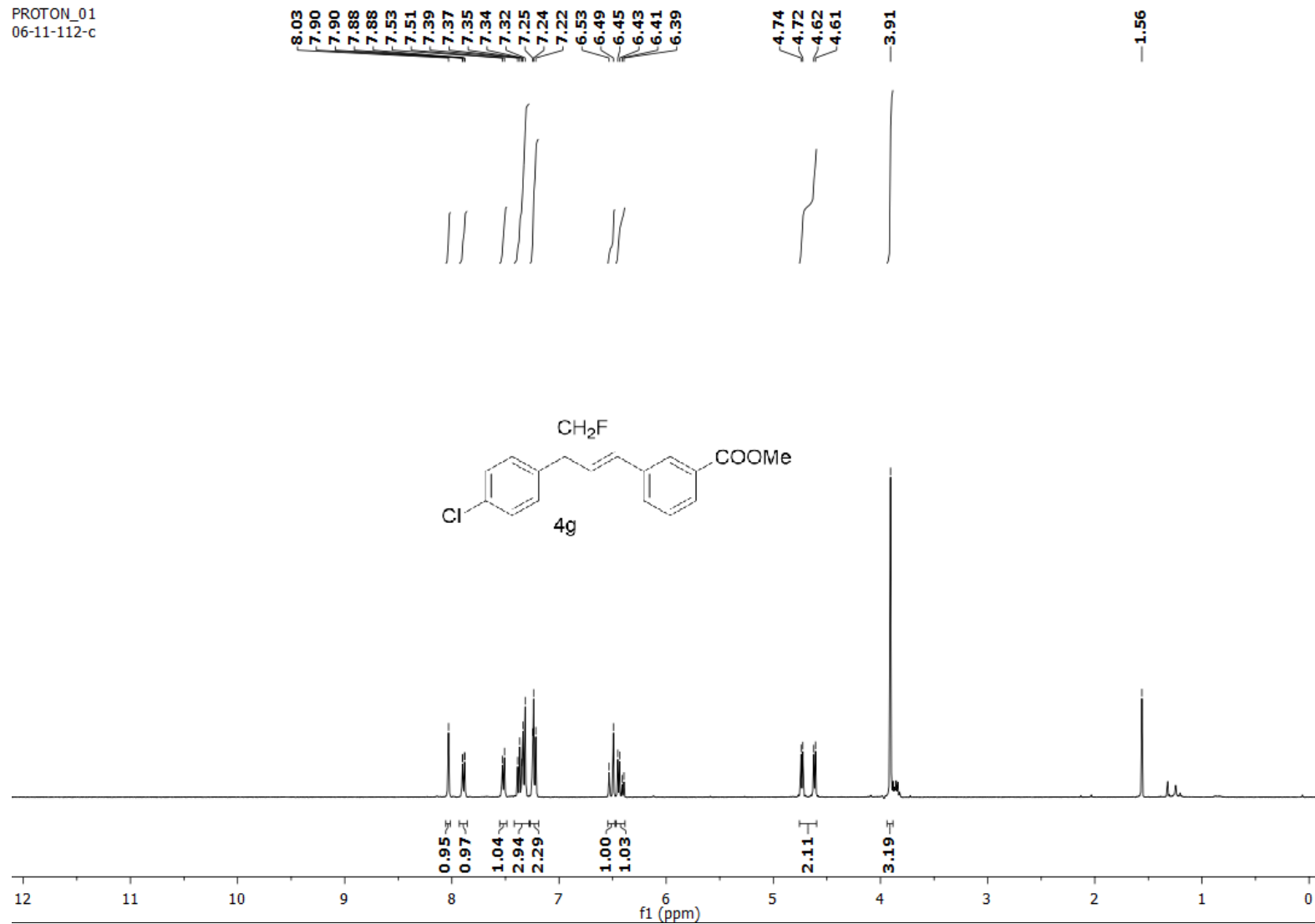
86.19
84.44

48.72
48.53



PROTON_01
06-11-112-c

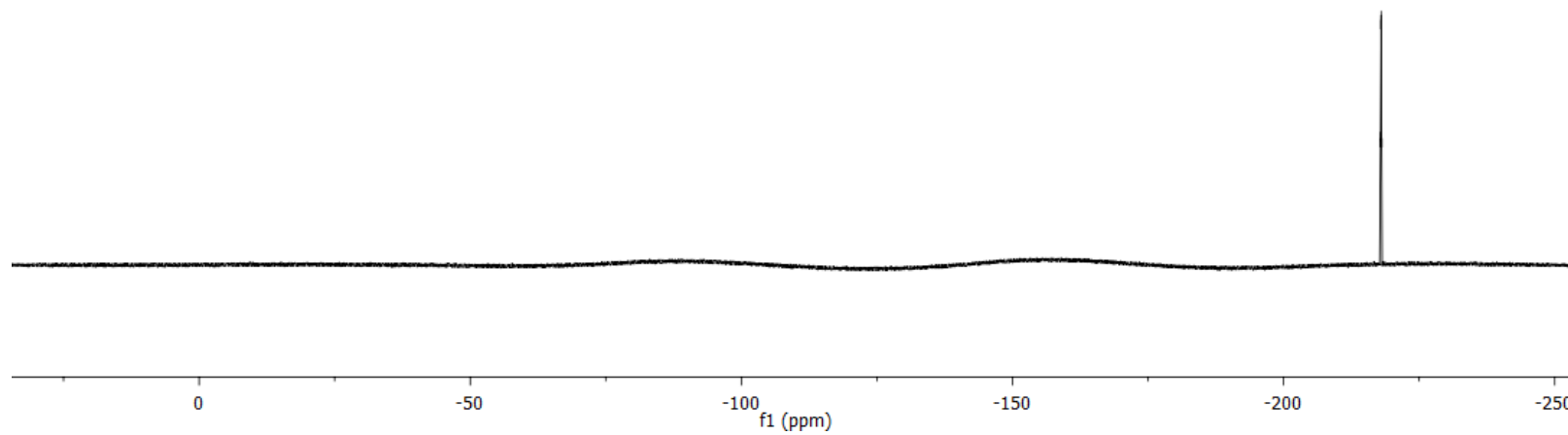
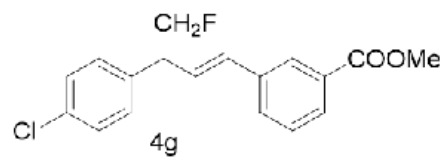
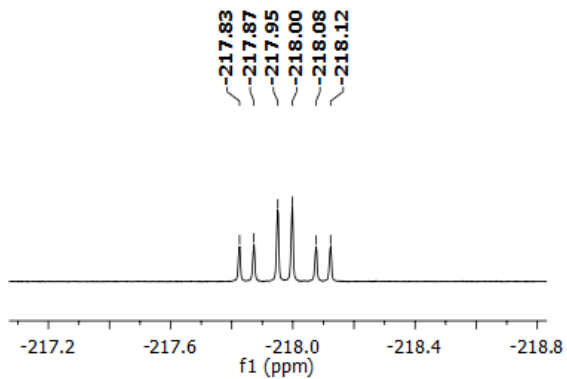
¹H NMR (400 MHz, CDCl₃) of 4g



¹⁹F NMR (376 MHz, CDCl₃) of 4g

FLUORINE_01
STANDARD FLUORINE PARAMETERS

-217.83
-217.87
-217.95
-218.00
-218.08
-218.12



¹³C NMR (100 MHz, CDCl₃) of 4g

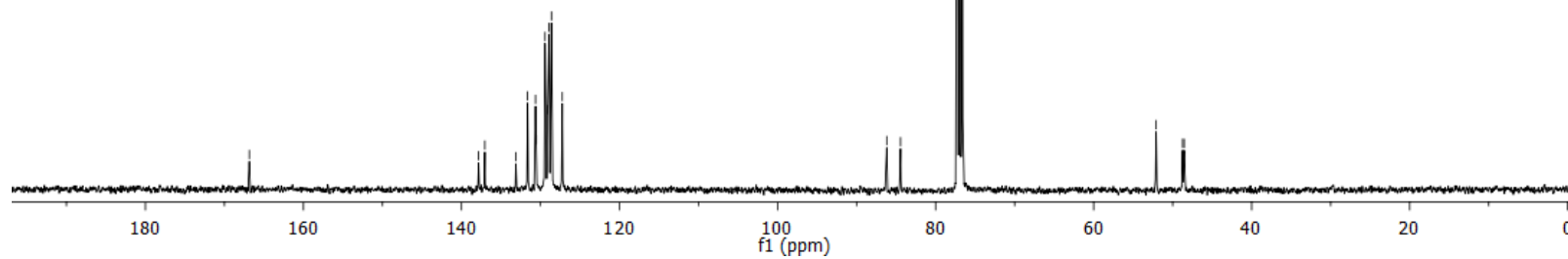
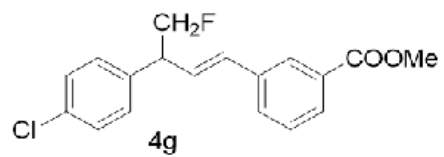
CARBON_01
06-11-112-c1

— 166.86

137.83
137.05
133.11
131.64
130.64
130.53
129.43
129.11
128.91
128.61
127.24

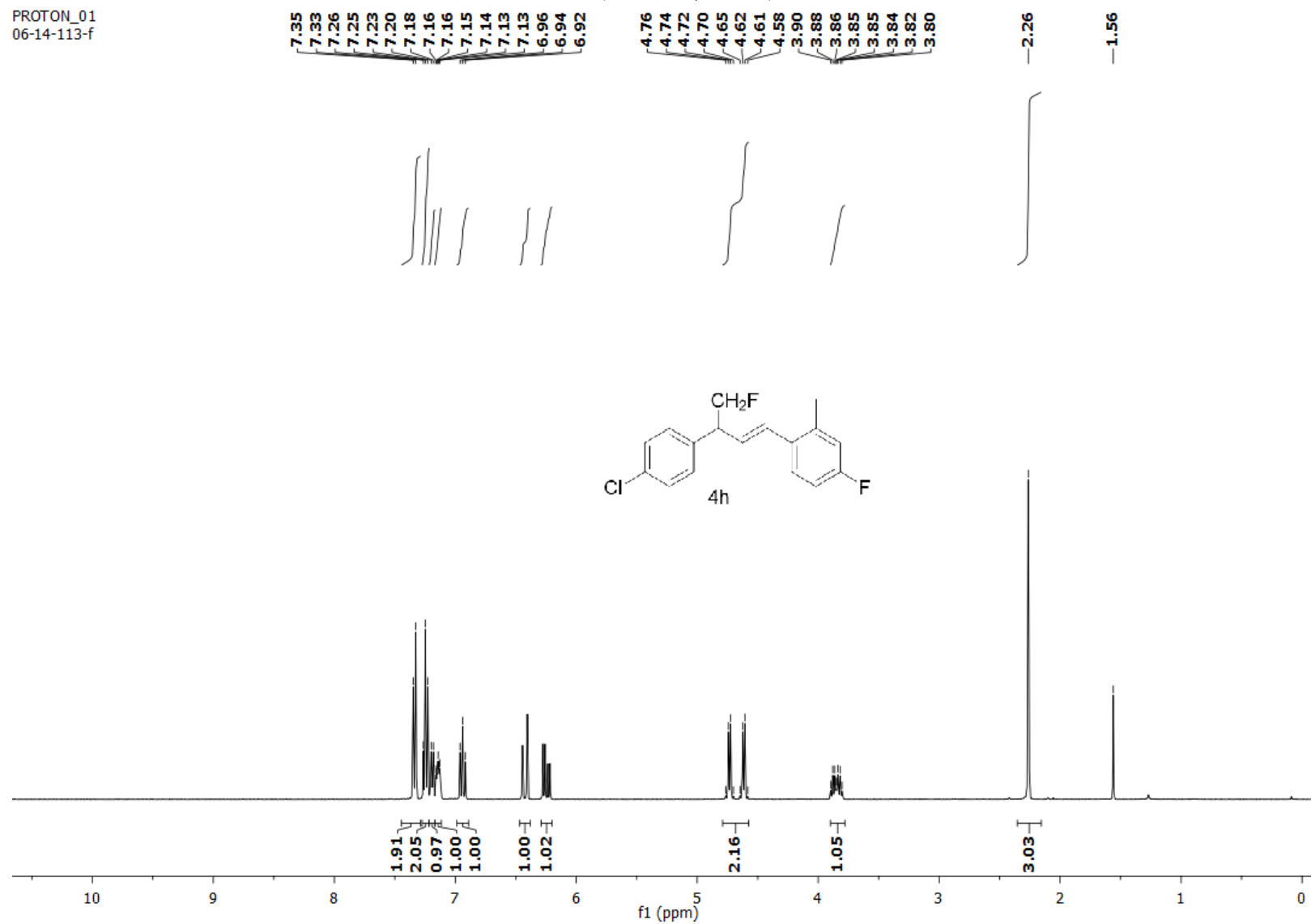
86.18
84.43

52.08
48.74
48.54



PROTON_01
06-14-113-f

¹H NMR (400 MHz, CDCl₃) of 4h



¹⁹F NMR (376 MHz, CDCl₃) of 4h

FLUORINE_01
STANDARD FLUORINE PARAMETERS



¹³C NMR (100 MHz, CDCl₃) of 4h

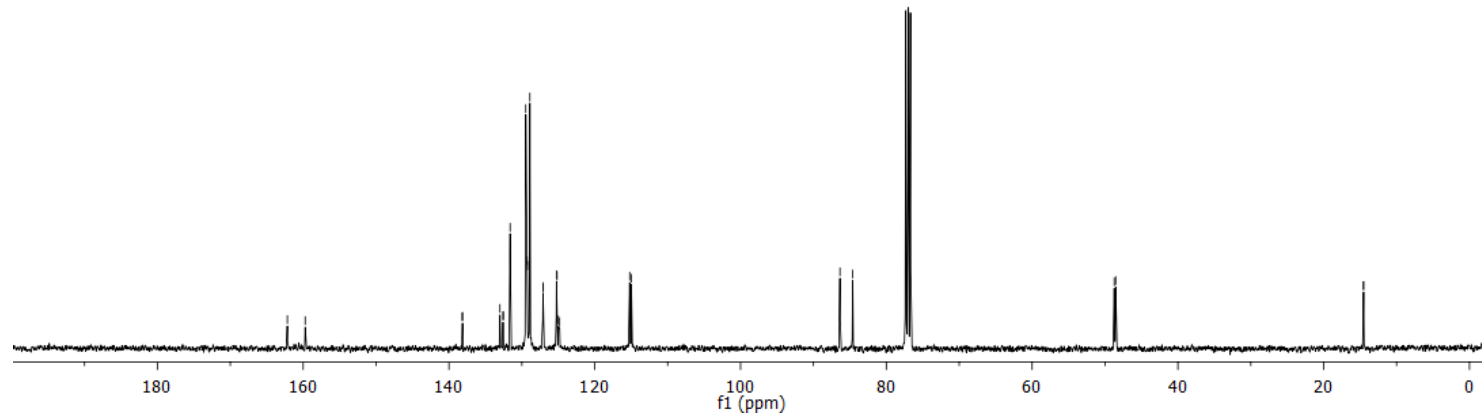
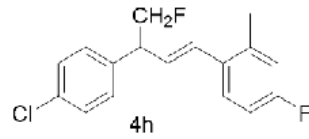
CARBON_01
06-14-113-f

162.17
159.72
138.18
138.14
133.01
132.58
132.55
131.61
129.46
129.28
129.23
128.90
127.10
127.06
125.25
125.17
124.99
124.82
115.21
114.98

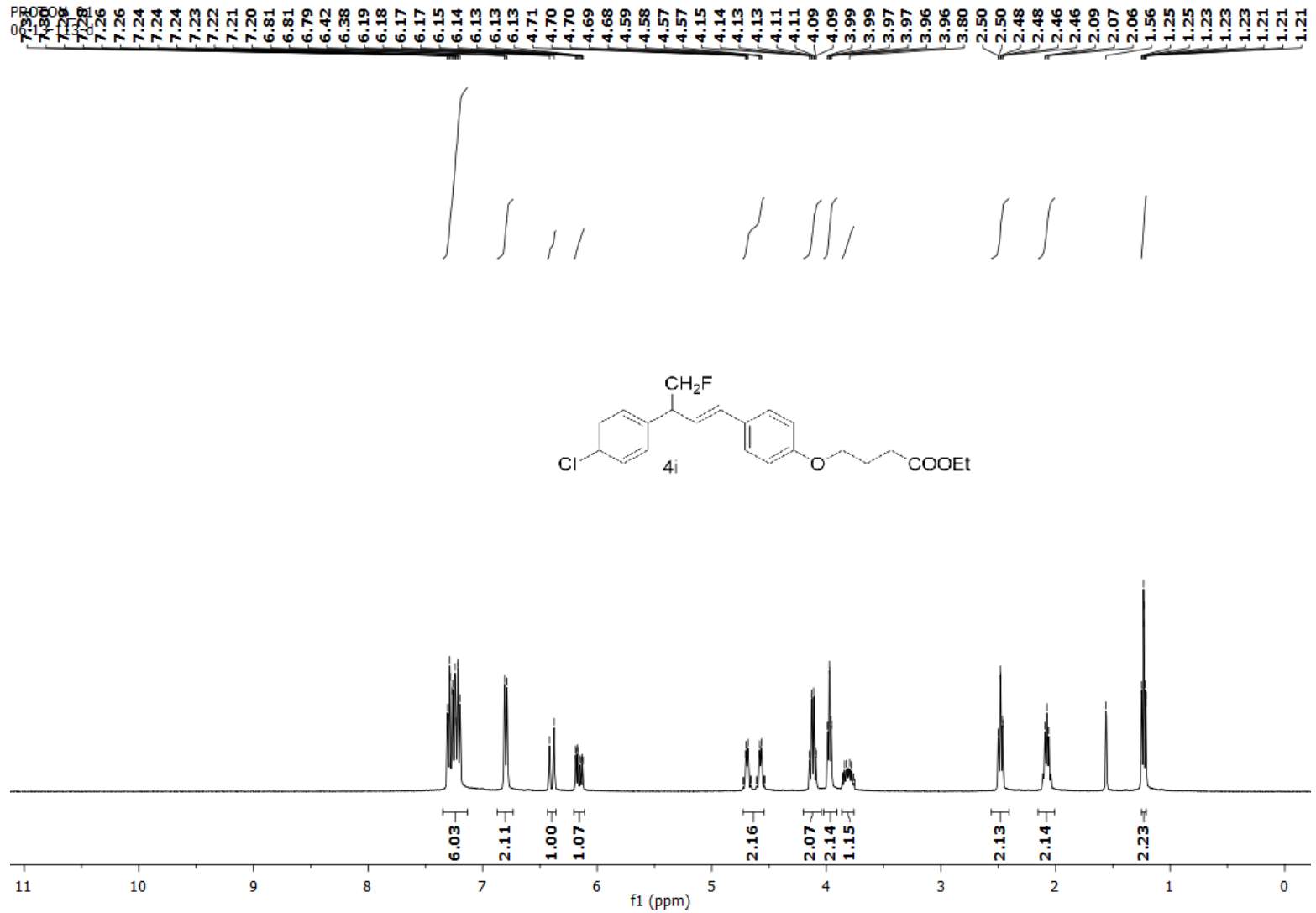
86.37
84.62

48.73
48.53

14.55
14.52

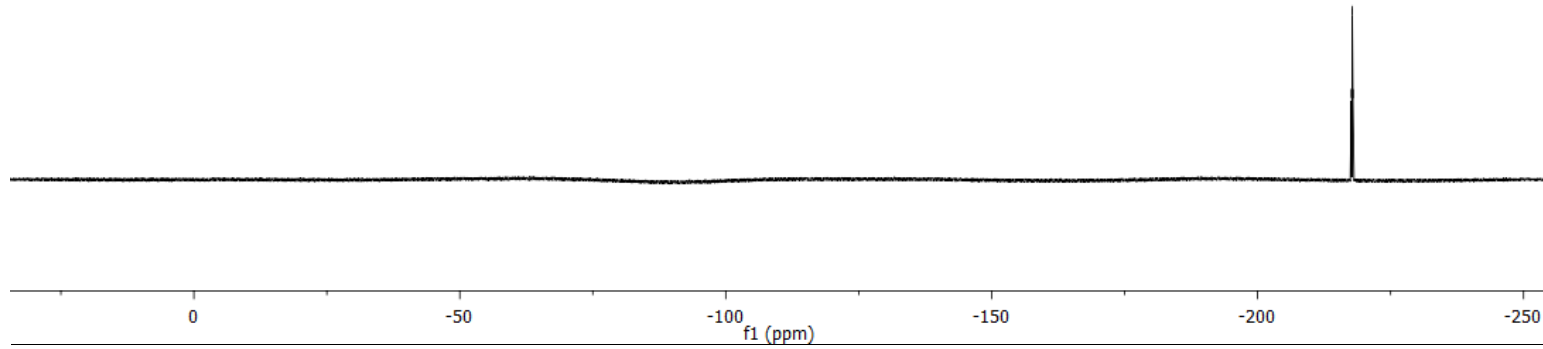
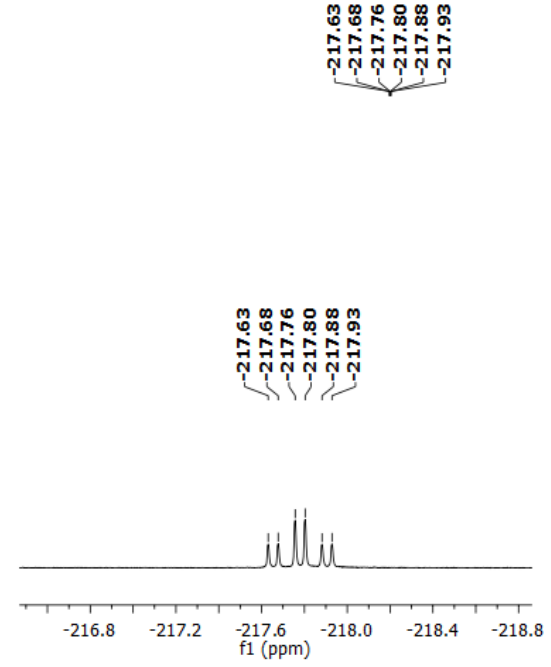
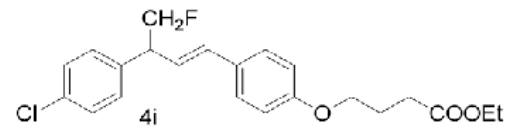


¹H NMR (400 MHz, CDCl₃) of 4i



¹⁹F NMR (376 MHz, CDCl₃) of 4i

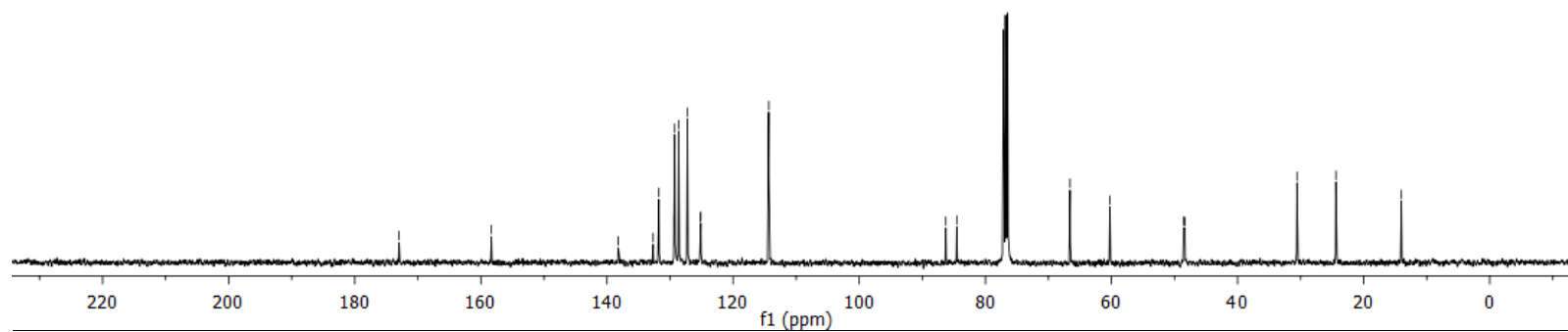
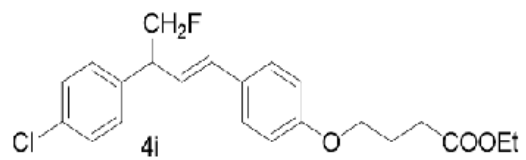
FLUORINE_01
STANDARD FLUORINE PARAMETERS



¹³C NMR (100 MHz, CDCl₃) of 4i

CARBON_01
06-13-113-d

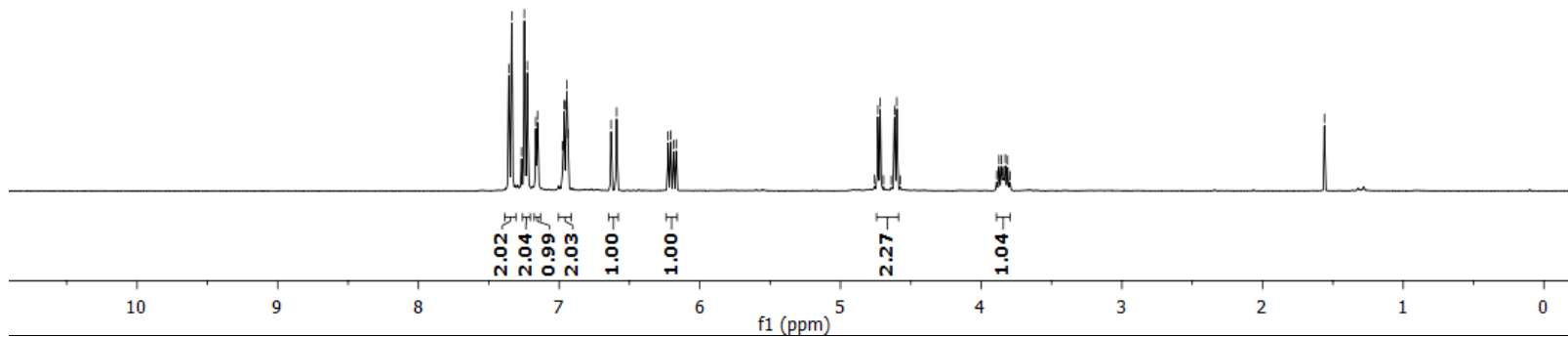
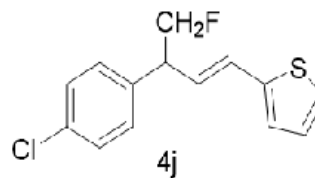
—172.97
—158.34
138.23
132.68
131.78
129.36
129.26
128.63
127.25
125.19
125.13
—114.35
86.27
84.53
—66.57
—60.24
48.55
48.35
—30.57
—24.41
—14.02



¹H NMR (400 MHz, CDCl₃) of 4j

PROTON_01
06-12-113-c

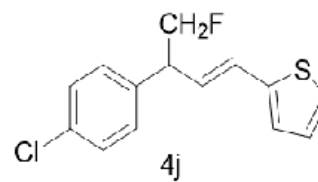
7.36 7.34 7.27 7.25 7.23 7.17 7.15 6.97 6.96 6.95 6.94 6.63 6.59 6.23 6.21 6.19 6.17 4.76 4.73 4.72 4.69 4.64 4.62 4.60 4.58 3.87 3.86 3.84 3.83 3.81 3.80 —1.56



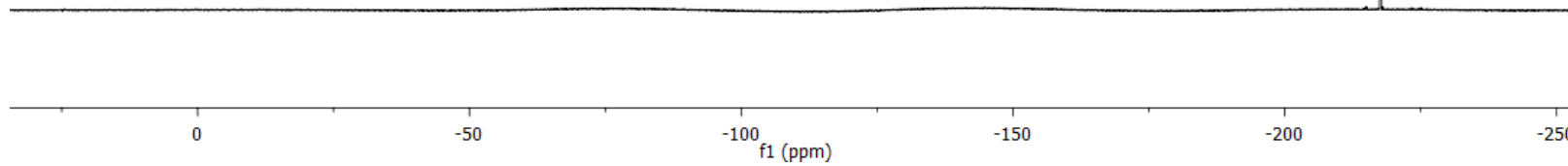
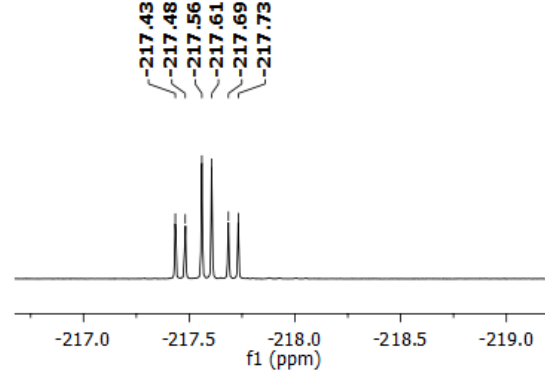
FLUORINE_01
STANDARD FLUORINE PARAMETERS

^{19}F NMR (376 MHz, CDCl_3) of 4j

-217.43
-217.48
-217.56
-217.61
-217.69
-217.73



-217.43
-217.48
-217.56
-217.61
-217.69
-217.73



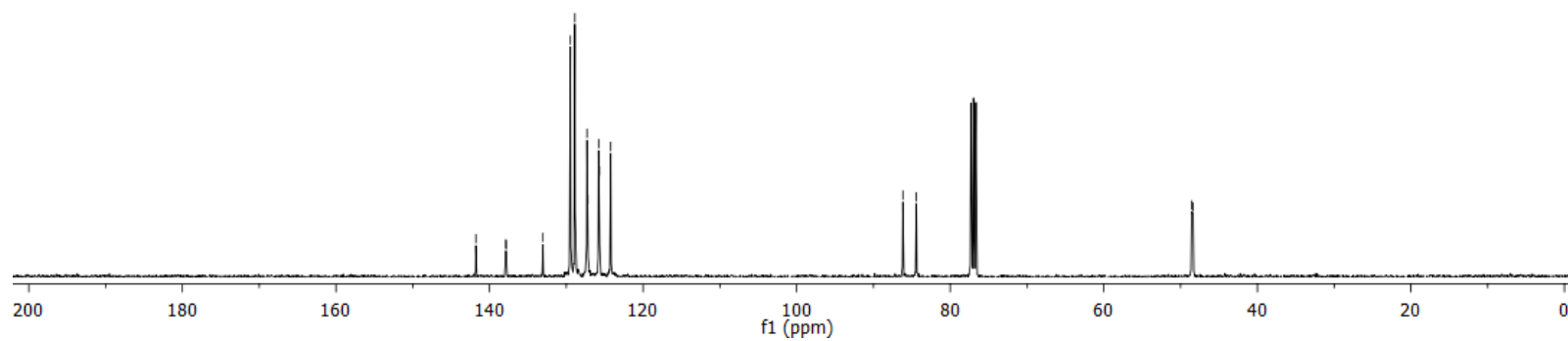
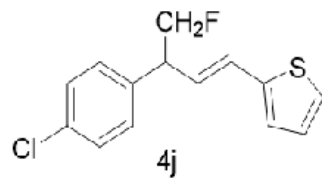
¹³C NMR (100 MHz, CDCl₃) of 4j

CARBON_01
06-12-113-c

141.78
137.88
137.84
133.04
129.47
128.88
127.31
127.26
127.20
125.79
125.69
124.22

86.17
84.41

48.56
48.36



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