

Alkyltriflones in the Ramberg–Bäcklund Reaction: An Efficient and Modular Synthesis of *gem*-Difluoroalkenes

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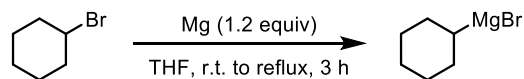
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1. General:

Reactions were performed in oven-dried vials with Teflon-lined caps or flame-dried flasks. All solvents were distilled from either calcium hydride or sodium metal prior to use. Work-ups and purifications were performed using commercial reagent-grade solvents. Other starting materials for the synthesis of alkyl sulfones were purchased from Sigma-Aldrich, Alfa Aesar, Oakwood Chemical, Frontier Scientific, or Cambridge Isotopes Laboratories and used as received.

Thin layer chromatography was performed on aluminum-backed silica plates and visualized by UV (254, 365 nm). Preparative thin layer chromatography (PTLC) was performed on glass-backed silica plates and visualized by UV (254, 365 nm). High-resolution mass spectra (HRMS) were obtained from a Thermo Fisher Scientific Exactive (ESI) or an Applied Biosystems/MDS Sciex QStar XL QqTOF instrument (EI). NMR spectra were recorded on a Bruker Avance 400 (^1H : 400.13, ^{13}C : 100.62) instrument operating at the denoted spectrometer frequency given in mega Hertz (MHz) for the specified nucleus. All NMR samples were prepared using CDCl_3 . To specify the signal multiplicity, the following abbreviations are used: s = singlet, d = doublet, t = triplet, q = quartet, sep = septet, and m = multiplet; br indicates a broad resonance. Shifts are reported in parts per million (ppm) relative to tetramethylsilane (TMS) as an external standard for ^1H - and ^{13}C NMR spectra and calibrated against the solvent residual peak.

Preparation of cyclohexylmagnesium bromide

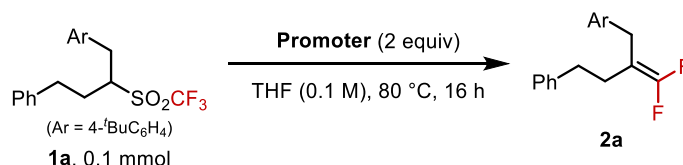


A 250-mL flask containing a magnetic stirring bar was flame-dried under vacuum and filled with argon after cooling to room temperature. To the flask were added magnesium turnings (1.06 g, 44 mmol) in THF (15 mL) and 1,2-dibromoethane (50 μL) to activate the magnesium surface. Bromocyclohexane (5 mL, 40 mmol) in THF (35 mL) was added dropwise to the reaction mixture at room temperature over 1 hour. Then, the reaction mixture was stirred for 2 hours at 75 $^\circ\text{C}$. The reaction was allowed to cool to room temperature and titrated with iodine as an indicator to determine the concentration of the Grignard reagent (0.55–0.57 M in THF).

2. Optimization of Reaction Conditions

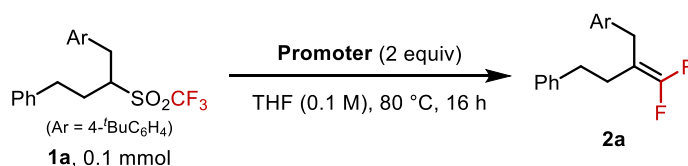
To a flame-dried 1DR vial containing a magnetic stir bar under an atmosphere of dry argon was added alkyltriflone **1a**, promoter, and THF. The reaction mixture was stirred for 16 hours at 80 °C. The reaction mixture was cooled to room temperature, quenched with NH₄Cl (sat. aq.), and diluted with ethyl acetate. 1,3,5-Trimethoxybenzene was added to the mixture as an internal standard. The resulting solution was passed through a small pad of silica gel, washed with ethyl acetate three times. The crude reaction mixture was concentrated under reduced pressure, and analyzed by ¹H NMR spectroscopy with the use of an internal standard.

2.1. Screening of Promoter



Entry	Promoter	Yield (%)
1	ⁱ PrMgBr	60
2	Mg(OEt) ₂	0
3	(TMP) ₂ Mg-LiCl	15
4	ⁿ BuLi	5
5	^t BuONa	0
6	^t BuOK	0
7	Et ₂ Zn	0

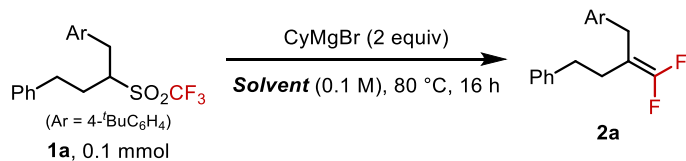
2.2. Screening of Grignard Reagents



Promoter	Yield (%)
H ₃ C-MgBr	82%
	60%
	83%
	80% ^a
	38%
	49%

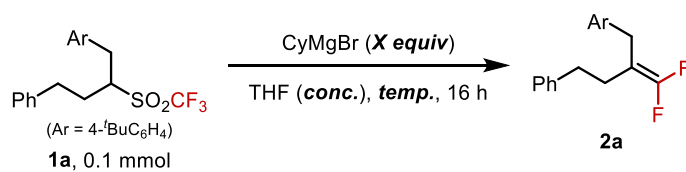
^a 1 equivalent of C₂Mg

2.3. Screening of Solvents



Entry	Solvent	Yield (%)
1	THF	76
2	1,4-dioxane	72
3	Et ₂ O	74
4	toluene	52

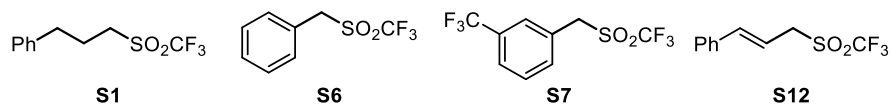
2.4. Screening of Other Parameters



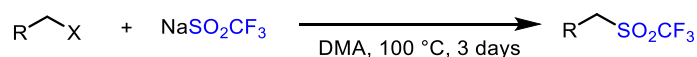
Entry	CyMgBr (X equiv)	temp. (°C)	conc. (M)	Ratio (2a/1a)
1	2.0	80	0.1	86:14
2	1.5	80	0.1	49:51
3	2.0	50	0.1	62:38
4	2.0	80	0.24	87:13

3. Synthesis of Primary Alkyltriflones

S1,¹ S6,² S7,³ and S12⁴ were synthesized using reported procedures.

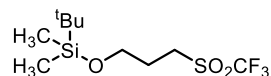


Synthesis of Primary Alkyltriflones (General Procedure A)



To a flame-dried flask containing a magnetic stir bar under an atmosphere of dry argon was added alkyl halide (1.0 equiv.), $NaSO_2CF_3$ (1.5-2 equiv.), KI (0.1 equiv.), and dry dimethylacetamide (DMA) (0.2 M). The reaction mixture was stirred at 100 °C for 3 days. Upon reaction completion, the reaction was cooled to room temperature, filtered and concentrated under reduced pressure. The crude product was purified by column chromatography, distillation, or recrystallization.

tert-Butyldimethyl(3-((trifluoromethyl)sulfonyl)propoxy)silane S2



Prepared from (3-bromopropoxy)(*tert*-butyl)dimethylsilane (1.09 g, 4.3 mmol), $NaSO_2CF_3$ (1.17 g, 7.5 mmol), and potassium iodide (831 mg, 0.5 mmol) in DMA (10 mL) according to General Procedure A. The crude residue was distilled by Kugelrohr to give S2 (894 mg, 62%) as a colorless oil.

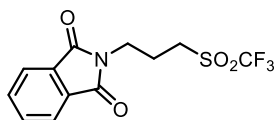
¹H NMR (400 MHz, Chloroform-*d*): δ 3.75 (t, $J = 5.6$ Hz, 2H), 3.40-3.31 (m, 2H), 2.14-2.07 (m, 2H), 0.88 (s, 9H), 0.06 (s, 6H).

¹³C{¹H} NMR (101 MHz, Chloroform-*d*): δ 119.5 (q, $J = 326.9$ Hz), 60.1, 46.8, 25.8, 24.3, 18.2, -5.5.

¹⁹F NMR (376 MHz, Chloroform-*d*): δ -79.1.

HRMS (ESI): m/z calcd for $[C_{10}H_{21}F_3O_3SSi+H]^+$: 307.1006, found 307.1006.

2-(3-((Trifluoromethyl)sulfonyl)propyl)isoindoline-1,3-dione S3



Prepared from *N*-(3-bromopropyl)phthalimide (1.34 g, 5 mmol), NaSO₂CF₃ (1.17 g, 7.5 mmol), and potassium iodide (831 mg, 0.5 mmol) in DMA (10 mL) according to General Procedure A. The crude residue was purified by column chromatography (EtOAc/Hexane = 1:4) to give **S3** (910 mg, 57%) as a colorless solid.

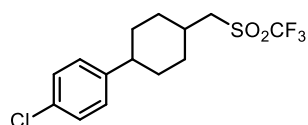
¹H NMR (400 MHz, Chloroform-*d*): δ 7.88 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.76 (dd, *J* = 5.5, 3.0 Hz, 2H), 3.89 (t, *J* = 6.6 Hz, 2H), 3.39-3.28 (m, 2H), 2.33 (dt, *J* = 14.5, 6.6 Hz, 2H),

¹³C{¹H} NMR (101 MHz, Chloroform-*d*): δ 168.1, 134.4, 131.7, 123.5, 119.3 (q, *J* = 327.1 Hz), 47.5, 36.0, 20.8.

¹⁹F NMR (376 MHz, Chloroform-*d*): δ -78.8.

HRMS (ESI): *m/z* calcd for [C₁₂H₁₀F₃NO₄S+H⁺]: 322.0353, found 322.0355.

1-Chloro-4-(4-(((trifluoromethyl)sulfonyl)methyl)cyclohexyl)benzene **S4**



Prepared from 1-chloro-4-(4-(iodomethyl)cyclohexyl)benzene (1 g, 3 mmol) and NaSO₂CF₃ (936 mg, 6 mmol) in DMA (6 mL) according to General Procedure A. The crude residue was purified by column chromatography (EtOAc/Hexane = 1:30) to give **S4** (290 mg, 28%) as a colorless solid.

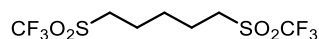
¹H NMR (700 MHz, Chloroform-*d*): δ 7.28 (d, *J* = 8.3 Hz, 2H), 7.14 (d, *J* = 8.3 Hz, 2H), 3.16 (d, *J* = 6.5 Hz, 2H), 2.50 (tt, *J* = 12.2, 3.4 Hz, 1H), 2.32-2.26 (m, 1H), 2.19-2.15 (m, 2H), 1.98-1.96 (m, 2H), 1.55 (qd, *J* = 13.1, 3.4 Hz, 2H), 1.38 (qd, *J* = 12.9, 3.4 Hz, 2H).

¹³C{¹H} NMR (176 MHz, Chloroform-*d*): δ 144.7, 131.8, 128.6, 128.1, 119.3 (q, *J* = 327.2 Hz), 55.3, 42.8, 33.3, 33.2, 31.4.

¹⁹F NMR (376 MHz, Chloroform-*d*): δ -80.0.

HRMS (EI): *m/z* calcd for [C₁₄H₁₆ClF₃O₂S]: 340.0512, found 340.0503.

1,5-Bis(((trifluoromethyl)sulfonyl)pentane **S5**



Prepared from 1,5-diiodopentane (1 mL, 6.7 mmol) and NaSO₂CF₃ (3.1 g, 20 mmol) in DMA (50 mL) according to General Procedure A. The crude residue was purified by column chromatography (EtOAc/Hexane = 1:10) to give **S5** (1.29 g, 57%) as a colorless solid.

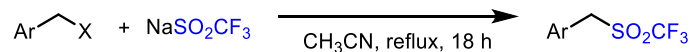
¹H NMR (400 MHz, Chloroform-*d*): δ 3.26 (t, *J* = 7.7 Hz, 4H), 2.04 (p, *J* = 8.0 Hz, 4H), 1.80-1.71 (m, 2H).

¹³C{¹H} NMR (101 MHz, Chloroform-*d*): δ 119.3 (q, *J* = 326.8 Hz), 48.9, 27.0, 20.4.

¹⁹F NMR (376 MHz, Chloroform-*d*): δ -79.1.

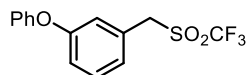
HRMS (ESI): m/z calcd for $[C_7H_{10}F_6O_4S_2+Na^+]$: 358.9817, found 358.9816

Synthesis of Primary Benzyltriflones (General Procedure B)



To a flame-dried flask containing a magnetic stir bar under an atmosphere of dry argon was added alkyl halide (1.0 equiv), NaSO_2CF_3 (1.5-2.0 equiv), KI (0.1 equiv), and dry CH_3CN (0.2 M). The reaction mixture was stirred at 80 °C for 18 hours. Upon reaction completion, the reaction was cooled to room temperature, quenched with $\text{Na}_2\text{S}_2\text{O}_3$ (sat. aq.) and diluted with ethyl acetate. The aqueous layer was extracted with ethyl acetate three times, and the combined organic layer was washed with brine. The organic layer was dried over Na_2SO_4 , filtered, and concentrated under reduced pressure. The crude mixture was purified by column chromatography to give the desired benzyl triflone.

1-Phenoxy-3-(((trifluoromethyl)sulfonyl)methyl)benzene **S8**



Prepared from 3-phenoxybenzyl bromide (750 mg, 2.9 mmol), NaSO_2CF_3 (667 mg, 4.3 mmol), and potassium iodide (47 mg, 0.29 mmol) in CH_3CN (14 mL) according to General Procedure B. The crude residue was purified by column chromatography (EtOAc/Hexane = 1:30) to give **S8** (660 mg, 74%) as a colorless solid.

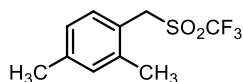
^1H NMR (700 MHz, Chloroform-*d*): δ 7.41-7.33 (m, 3H), 7.21-7.14 (m, 2H), 7.09 (dd, $J = 8.2, 2.5$ Hz, 1H), 7.06 (t, $J = 2.1$ Hz, 1H), 7.04 (d, $J = 7.4$ Hz, 2H), 4.43 (s, 2H),

$^{13}\text{C}\{^1\text{H}\}$ NMR (176 MHz, Chloroform-*d*): δ 158.1, 156.3, 130.5, 129.9, 125.7, 124.7, 124.0, 121.1, 120.0, 119.7 (q, $J = 328.2$ Hz), 119.3, 55.9.

^{19}F NMR (376 MHz, Chloroform-*d*): δ -77.3.

HRMS (ESI): m/z calcd for $[C_{14}H_{11}F_3O_3S+Na^+]$: 339.0273, found 339.0284

2,4-Dimethyl-1-(((trifluoromethyl)sulfonyl)methyl)benzene **S9**



Prepared from 2,4-dimethylbenzyl bromide (816 mg, 4 mmol), NaSO_2CF_3 (1.25 g, 8 mmol), and potassium iodide (66 mg, 0.4 mmol) in CH_3CN (20 mL) according to General Procedure B. The crude residue was purified by column chromatography (EtOAc/Hexane = 1:30) to give **S9** (302 mg, 30%) as a colorless solid.

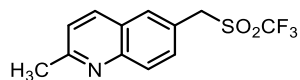
^1H NMR (700 MHz, Chloroform-*d*): δ 7.25 (d, $J = 7.8$ Hz, 1H), 7.12 (s, 1H), 7.08 (d, $J = 7.1$ Hz, 1H), 4.51 (s, 2H), 2.42 (s, 3H), 2.35 (s, 3H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (176 MHz, Chloroform-*d*): δ 140.3, 138.8, 132.3, 132.1, 127.4, 119.9 (q, $J = 328.2$ Hz), 118.2, 53.0, 21.1, 19.5.

^{19}F NMR (376 MHz, Chloroform-*d*): δ -78.4.

HRMS (ESI): m/z calcd for $[\text{C}_{10}\text{H}_{11}\text{F}_3\text{O}_2\text{S}+\text{Na}^+]$: 275.0324, found 275.0323.

2-Methyl-6-(((trifluoromethyl)sulfonyl)methyl)quinolone S10



Prepared from 6-(bromomethyl)-2-methylquinoline (534 mg, 2.3 mmol), NaSO_2CF_3 (718 mg, 4.6 mmol), and potassium iodide (38 mg, 0.23 mmol) in CH_3CN (23 mL) according to General Procedure B. The crude residue was purified by column chromatography (EtOAc/Hexane = 1:3) to give (251 mg, 38%) as an orange solid.

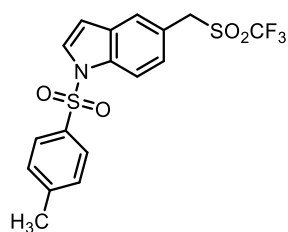
^1H NMR (400 MHz, Chloroform-*d*): δ 8.10 (d, $J = 8.7$ Hz, 1H), 8.07 (d, $J = 8.5$ Hz, 1H), 7.87 (d, $J = 2.1$ Hz, 1H), 7.69 (dd, $J = 8.7, 2.1$ Hz, 1H), 7.35 (d, $J = 8.5$ Hz, 1H), 4.64 (s, 2H), 2.77 (s, 3H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, Chloroform-*d*): δ 160.7, 147.8, 136.4, 131.4, 131.0, 129.8, 126.4, 123.0, 120.5, 119.7 (d, $J = 328.2$ Hz), 55.9, 25.3.

^{19}F NMR (376 MHz, Chloroform-*d*): δ -76.9.

HRMS (ESI): m/z calcd for $[\text{C}_{12}\text{H}_{10}\text{F}_3\text{O}_2\text{S}+\text{H}^+]$: 290.0457, found 290.0462.

1-Tosyl-5-(((trifluoromethyl)sulfonyl)methyl)-1H-indole S11



Prepared from 5-(bromomethyl)-1-tosyl-1H-indole (728 mg, 2 mmol), NaSO_2CF_3 (468 mg, 3 mmol), and potassium iodide (33 mg, 0.2 mmol) in CH_3CN (10 mL) according to General Procedure B. The crude residue was purified by column chromatography (EtOAc/Hexane = 1:10) to give **S11** (681 mg, 82%) as a colorless solid.

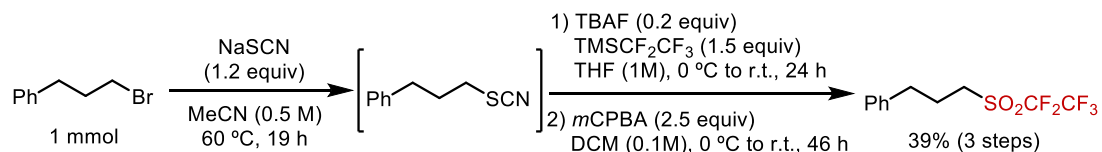
^1H NMR (700 MHz, Chloroform-*d*): δ 8.04 (d, $J = 8.6$ Hz, 1H), 7.77 (d, $J = 8.4$ Hz, 2H), 7.62 (d, $J = 3.7$ Hz, 1H), 7.60 (d, $J = 1.9$ Hz, 1H), 7.33 (dd, $J = 8.6, 1.9$ Hz, 1H), 7.25 (d, $J = 8.4$ Hz, 2H), 6.66 (d, $J = 3.7$ Hz, 1H), 4.54 (s, 2H), 2.35 (s, 3H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (176 MHz, Chloroform-*d*): δ 145.4, 135.4, 135.0, 131.3, 130.1, 127.5, 127.2, 126.8, 126.8, 124.6, 119.8 (q, $J = 328.2$ Hz), 117.0, 114.2, 108.6, 55.9, 21.5.

^{19}F NMR (376 MHz, Chloroform-*d*): δ -77.5.

HRMS (ESI): m/z calcd for $[C_{17}H_{14}F_3O_4NS_2+H^+]$: 418.0389, found 418.0388.

Synthesis of Pentafluoroethyl Sulfone S13



A reaction tube containing a magnetic stirring bar was flame-dried under vacuum and filled with argon after cooling to room temperature. To the tube were added 1-bromo-3-phenylpropane (0.1 mL, 1 mmol), sodium thiocyanate (97 mg, 1.2 mmol), and dry acetonitrile (2 mL, 0.5 M). After stirring the reaction mixture at 60 °C for 19 hours, the reaction was allowed to cool to room temperature and filtered through a pad of Celite.

The solvent was removed under reduced pressure to give the (3-thiocyanatopropyl)benzene. The obtained thiocyanate and TMSCF₂CF₃ (0.35 mL, 2 mmol) were dissolved in THF (1 mL, 1 M). A solution of TBAF (0.2 mL, 0.2 mmol, 1 M in THF) was added to the reaction mixture at 0 °C, and the resulting solution was allowed to warm to room temperature. After stirring for 24 hours, the reaction mixture was diluted with diethyl ether. The organic layer was washed with water twice and brine once, dried over Na₂SO₄, filtered, and concentrated under reduced pressure. The crude mixture was purified by column chromatography (pentane:diethyl ether = 1:75) to give the sulfide. The obtained sulfide was dissolved in CH₂Cl₂ (10 mL), and the solution was cooled to 0 °C. To the solution was added *m*CPBA (560 mg, 2.5 mmol), then the resulting mixture was allowed to warm to room temperature after stirring for 2 hours. The reaction was monitored by ¹⁹F NMR. After stirring for 46 hours, the reaction was quenched with Na₂S₂O₃ (sat. aq.). The organic layer was dried over Na₂SO₄, filtered, and concentrated under reduced to give primary pentafluoroethyl sulfone **S13** (117.9 mg, 39% over 3 steps).

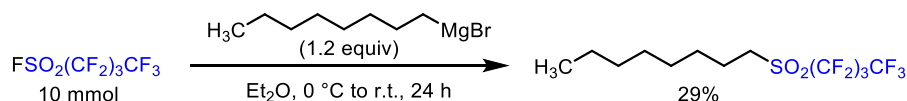
¹H NMR (700 MHz, Chloroform-*d*): 7.35 (t, $J = 7.5$ Hz, 2H), 7.29-7.26 (m, 1H), 7.20 (d, $J = 7.5$ Hz, 2H), 3.24 (t, $J = 7.9$ Hz, 2H), 2.85 (t, $J = 7.4$ Hz, 2H), 2.32 (m, 2H).

¹³C{¹H} NMR (176 MHz, Chloroform-*d*): δ 138.8, 128.8, 128.4, 126.9, 117.2 (qt, $J = 288.5, 31.6$ Hz), 112.4 (tq, $J = 300.9, 40.4$ Hz), 49.6, 34.0, 22.1.

¹⁹F NMR (376 MHz, Chloroform-*d*): δ -79.3 (s, 3F), -118.4 (s, 2F).

HRMS (EI): m/z calcd for $[C_{11}H_{11}F_5O_2S]$: 302.0400, found 302.0405.

Synthesis of 1-((Perfluorobutyl)sulfonyl)octane S14 from Sulfonyl Fluoride



A 50-mL Schlenk flask containing a magnetic stirring bar was flame-dried under vacuum and filled with argon after cooling to room temperature. To the flask were added sulfonyl fluoride (1.8 mL, 10 mmol) and dry Et₂O (50 mL, 0.2 M). A solution of *n*-octyl magnesium bromide (12 mL, 12 mmol, 1 M in Et₂O) was added dropwise to the reaction mixture at 0 °C under argon. The mixture was allowed to warm to room temperature. After stirring for 24 hours, the reaction was quenched with NaHCO₃ (sat. aq.) and diluted with diethyl ether. The aqueous layer was extracted with diethyl ether three times, and the combined organic layer was washed with brine. The organic layer was dried over Na₂SO₄, filtered, and concentrated under reduced pressure. The crude mixture was purified by column chromatography (EtOAc/Hexane = 1:50) to give primary alkyl sulfone **S14** (1.14 g, 29%).

¹H NMR (400 MHz, Chloroform-*d*): δ 3.25 (t, *J* = 8.1 Hz, 2H), 1.91-2.01 (m, 2H), 1.48 (p, *J* = 7.2 Hz, 2H), 1.25-1.36 (m, 8H), 0.88 (t, *J* = 6.5 Hz, 3H),

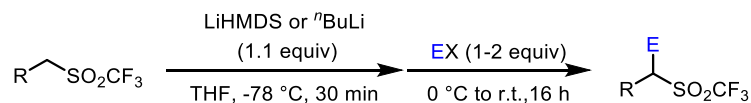
¹³C{¹H} NMR (101 MHz, Chloroform-*d*): δ 122.5-104.7 (m, SO₂(CF₂)₃CF₃), 51.0, 31.6, 28.8, 28.8, 28.4, 22.5 (d, *J* = 1.5 Hz), 20.5, 13.9 (d, *J* = 4.7 Hz),

¹⁹F NMR (376 MHz, Chloroform-*d*): δ -81.9, -114.6, -122.5, -127.1.

HRMS (ESI): *m/z* calcd for [C₁₂H₁₇F₉O₂S+Na⁺]: 419.0698, found 419.0686.

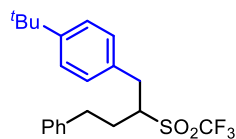
4. Synthesis of Secondary Alkyltriflones

Deprotonation-Alkylation of Primary Alkyltriflones with LiHMDS or *n*-BuLi (General Procedure C)



A 50-mL Schlenk flask containing a magnetic stirring bar was flame-dried under vacuum and filled with argon after cooling to room temperature. To the flask were added primary alkyl triflone and dry THF (0.13 M). A solution of LiHMDS (1.1 equiv, 0.5 M THF solution) or *n*-BuLi (1.1 equiv, 2.5 M Hexane solution) was added dropwise to the reaction mixture at -78 °C under argon. After stirring for 30 min, electrophile (1.5-2.0 equiv) was added to the reaction mixture. The mixture was stirred at -78 °C for 30 min and allowed to warm to room temperature. After stirring for 16 hours, the reaction was quenched with NH₄Cl (sat. aq.) and diluted with ethyl acetate. The aqueous layer was extracted with ethyl acetate three times, and the combined organic layer was washed with brine. The organic layer was dried over Na₂SO₄, filtered, and concentrated under reduced pressure. The crude mixture was purified by column chromatography to give the desired secondary alkyltriflone.

1-(*tert*-Butyl)-4-(4-phenyl-2-((trifluoromethyl)sulfonyl)butyl)benzene **1a**



Prepared from triflone **S1** (398 mg, 2 mmol), *n*-BuLi (0.88 mL, 2.2 mmol, 2.5 M Hexane solution), 4-(*tert*-butyl)benzylbromide (0.48 mL, 2.6 mmol) in THF (20 mL) according to General Procedure C. The crude residue was purified by column chromatography (EtOAc/Hexane = 1:30) to give **1a** (666 mg, 84%) as a colorless oil.

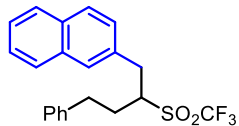
¹H NMR (400 MHz, Chloroform-*d*): δ 7.36 (d, *J* = 8.3 Hz, 2H), 7.27-7.14 (m, 3H), 7.08 (d, *J* = 8.3 Hz, 2H), 6.93 (dd, *J* = 7.7, 1.7 Hz, 2H), 3.56-3.47 (m, 1H), 3.43 (dd, *J* = 14.1, 3.6 Hz, 1H), 2.92 (dd, *J* = 14.1, 10.5 Hz, 1H), 2.78-2.61 (m, 2H), 2.39-2.25 (m, 1H), 2.15-2.01 (m, 1H), 1.34 (s, 9H).

¹³C{¹H} NMR (101 MHz, Chloroform-*d*): δ 150.6, 139.4, 132.1, 128.8, 128.5, 128.3, 126.4, 125.9, 120.0 (q, *J* = 329.8 Hz), 61.5, 34.5, 33.3, 32.3, 31.3, 28.1.

¹⁹F NMR (376 MHz, Chloroform-*d*): δ -75.3.

HRMS (ESI): *m/z* calcd for [C₂₁H₂₅F₃O₂S+Na⁺]: 421.1420, found 421.1418.

2-(4-Phenyl-2-((trifluoromethyl)sulfonyl)butyl)naphthalene **1b**



Prepared from triflone **S1** (252 mg, 1 mmol), LiHMDS (176 mg, 1.05 mmol, 2 mL of THF solution), 2-bromo(methyl)naphthalene (331 mg, 1.5 mmol) in THF (8 mL) according to General Procedure C. The crude residue was purified by column chromatography (EtOAc/Hexane = 1:40) to give **1b** (273 mg, 70%) as a colorless solid.

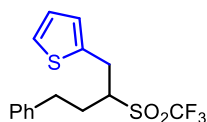
¹H NMR (400 MHz, Chloroform-*d*): δ 7.89-7.75 (m, 3H), 7.60 (s, 1H), 7.56-7.46 (m, 2H), 7.23 (dd, $J = 8.4, 1.9$ Hz, 1H), 7.18-7.08 (m, 3H), 6.93-6.86 (m, 2H), 3.67-3.60 (m, 2H), 3.11 (dd, $J = 14.8, 11.3$ Hz, 1H), 2.81-2.63 (m, 2H), 2.40-2.29 (m, 1H), 2.20-2.06 (m, 1H).

¹³C{¹H} NMR (101 MHz, Chloroform-*d*): δ 139.2, 133.4, 132.6, 132.5, 128.9, 128.1, 127.7, 127.6, 126.6, 126.5, 126.5, 126.2, 120.0 (q, $J = 329.6$ Hz), 61.4, 34.0, 32.4, 28.1.

¹⁹F NMR (376 MHz, Chloroform-*d*): δ -75.2.

HRMS (ESI): m/z calcd for [C₂₁H₁₉F₃O₂S+Na⁺]: 415.0945, found 415.0950.

2-(4-Phenyl-2-((trifluoromethyl)sulfonyl)butyl)thiophene **1c**



Prepared from triflone **S1** (252 mg, 1 mmol), *n*-BuLi (0.44 mL, 1.1 mmol, 2.5 M Hexane solution), 2-(chloromethyl)thiophene (202 mg, 1.3 mmol) in THF (10 mL) according to General Procedure C. The crude residue was purified by column chromatography (EtOAc/Hexane = 1:50) to give **1c** (160 mg, 46%) as a colorless solid.

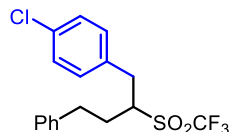
¹H NMR (400 MHz, Chloroform-*d*): δ 7.24-7.08 (m, 4H), 6.96 (d, $J = 7.1$ Hz, 2H), 6.88 (dd, $J = 5.2, 3.5$ Hz, 1H), 6.78 (d, $J = 3.5$ Hz, 1H), 3.49 (dd, $J = 14.8, 3.9$ Hz, 1H), 3.45-3.38 (m, 1H), 3.20 (dd, $J = 14.8, 9.4$ Hz, 1H), 2.66 (t, $J = 8.0$ Hz, 2H), 2.25 (m, 1H), 2.14-2.00 (m, 1H).

¹³C{¹H} NMR (101 MHz, Chloroform-*d*): δ 139.3, 136.7, 128.6, 128.3, 127.3, 127.3, 126.5, 125.3, 119.83 (q, $J = 329.6$ Hz), 61.5, 32.3, 28.3, 27.9.

¹⁹F NMR (376 MHz, Chloroform-*d*): δ -75.7.

HRMS (ESI): m/z calcd for [C₁₅H₁₅F₃O₂S₂+H⁺]: 349.0538, found 349.0538.

1-Chloro-4-(4-phenyl-2-((trifluoromethyl)sulfonyl)butyl)benzene **1d**



Prepared from triflone **S1** (252 mg, 1 mmol), LiHMDS (184 mg, 1.1 mmol, 2 mL of THF solution), 4-chlorobenzyl bromide (267 mg, 1.3 mmol) in THF (3 mL) according to General Procedure C. The crude residue was purified by distillation to remove unreacted bromide (10 mmHg, 120 °C) to afford **1d** (364 mg, 97%) as a colorless oil.

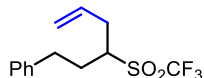
¹H NMR (400 MHz, Chloroform-*d*): δ 7.29 (d, $J = 8.4$ Hz, 2H), 7.24-7.16 (m, 3H), 7.04 (d, $J = 8.4$ Hz, 2H), 6.99-6.91 (m, 2H), 3.53-3.42 (m, 1H), 3.39 (dd, $J = 14.3, 3.9$ Hz, 1H), 2.92 (dd, $J = 14.3, 10.1$ Hz, 1H), 2.71 (t, $J = 7.7$ Hz, 2H), 2.40-2.22 (m, 1H), 2.10-1.96 (m, 1H),

¹³C{¹H} NMR (101 MHz, Chloroform-*d*): δ 139.0, 133.6, 133.5, 130.4, 129.2, 128.7, 128.3, 126.6, 119.9 (q, $J = 329.6$ Hz), 61.2, 33.2, 32.3, 28.0.

¹⁹F NMR (376 MHz, Chloroform-*d*) δ -75.0.

HRMS (EI): m/z calcd for [C₁₇H₁₆ClF₃O₂S]: 376.0512, found 376.0502.

(3-((Trifluoromethyl)sulfonyl)hex-5-en-1-yl)benzene **1e**



Prepared from triflone **S1** (252 mg, 1 mmol), *n*-BuLi (0.44 mL, 1.1 mmol, 2.5 M Hexane solution), and 2-(chloromethyl)thiophene (202 mg, 1.3 mmol) in THF (10 mL) according to General Procedure C. The crude residue was purified by column chromatography (EtOAc/Hexane = 1:50) to give **1e** (126 mg, 43%) as a colorless solid.

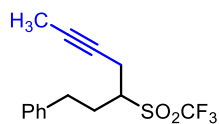
¹H NMR (400 MHz, Chloroform-*d*): δ 7.32 (t, $J = 7.4$ Hz, 2H), 7.25-7.16 (m, 3H), 5.76 (ddt, $J = 19.2, 9.7, 7.0$ Hz, 1H), 5.27-5.22 (m, 2H), 3.36-3.29 (m, 1H), 2.93-2.74 (m, 3H), 2.67-2.60 (m, 1H), 2.33 (dm, $J = 15.3$ Hz, 1H), 2.15 (dm, $J = 15.3$ Hz, 1H).

¹³C{¹H} NMR (101 MHz, Chloroform-*d*): δ 139.4, 131.4, 128.7, 128.4, 126.6, 120.1, 119.8 (q, $J = 329.6$ Hz), 59.6, 32.0, 31.3, 28.0.

¹⁹F NMR (376 MHz, Chloroform-*d*): δ -75.8.

HRMS (EI): m/z calcd for [C₁₃H₁₅F₃O₂S]: 292.0745, found 292.0749.

(3-((Trifluoromethyl)sulfonyl)hept-5-yn-1-yl)benzene **1f**



A 100-mL Schlenk flask containing a magnetic stirring bar was flame-dried under vacuum and filled with argon after cooling to room temperature. To the flask were added primary alkyl triflone **S1** (504 mg, 2 mmol) and dry THF (10 mL). A solution of *n*-BuLi (0.72 mL, 1.8 mmol, 2.5M Hexane solution) was added dropwise to the reaction mixture at 0 °C under argon. After stirring for 30 min, the reaction mixture was transferred to the cooled solution of 1-bromo-2-butyne (0.36 mL, 4 mmol) in THF (10 mL) at 0 °C. The mixture was allowed to warm to room temperature. After stirring for 16 hours, the reaction was quenched with NH₄Cl (sat. aq.) and diluted with ethyl acetate. The aqueous layer was extracted with ethyl acetate three times, and the combined organic layer was washed with brine. The organic layer was dried over Na₂SO₄, filtered, and concentrated under reduced pressure. The crude mixture was purified by column chromatography to give a yellow oil as a mixture of starting material, mono-alkylated, and di-alkylated products (1:0.7:0.4). The mixture was further purified by Kugelrohr distillation (120 °C, 10 mmHg) to give **1f** (70 mg, 12%) as a colorless oil.

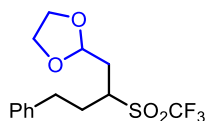
¹H NMR (400 MHz, Chloroform-*d*): δ 7.35-7.30 (m, 2H), 7.25-7.17 (m, 3H), 3.35 (ddd, *J* = 12.1, 7.1, 5.0 Hz, 1H), 3.03-2.87 (m, 1H), 2.87-2.70 (m, 3H), 2.50-2.24 (m, 2H), 1.82 (t, *J* = 2.6 Hz, 3H).

¹³C{¹H} NMR (101 MHz, Chloroform-*d*): δ 139.5, 128.7, 128.4, 126.7, 119.7 (q, *J* = 329.4 Hz), 80.2, 71.8, 59.1, 32.1, 28.1, 18.1, 3.5.

¹⁹F NMR (376 MHz, Chloroform-*d*): δ -76.2.

HRMS (ESI): *m/z* calcd for [C₁₄H₁₅F₃O₂S+H⁺]: 305.0818, found 305.0824.

2-(4-Phenyl-2-((trifluoromethyl)sulfonyl)butyl)-1,3-dioxolane **1g**



Prepared from triflone **S1** (306 mg, 1 mmol), LiHMDS (184 mg, 1.1 mmol, 2 mL of THF solution), 2-(bromomethyl)-1,3-dioxolane (217 mg, 1.3 mmol) in THF (5 mL) and DMPU (0.5 mL) as a co-solevent according to General Procedure C. The crude residue was purified by column chromatography (EtOAc/Hexane = 1:10) to give **1g** (112 mg, 33%) as a colorless solid.

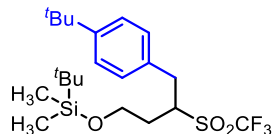
¹H NMR (400 MHz, Chloroform-*d*): δ 7.33-7.29 (m, 2H), 7.25-7.19 (m, 3H), 5.04 (t, *J* = 4.3 Hz, 1H), 3.96-3.79 (m, 4H), 3.63-3.53 (m, 1H), 2.96-2.79 (m, 2H), 2.49-2.33 (m, 2H), 2.29-2.10 (m, 2H).

¹³C{¹H} NMR (176 MHz, Chloroform-*d*): δ 139.8, 128.6, 128.5, 126.5, 119.9 (q, *J* = 329.3 Hz), 101.1, 65.1, 56.5, 32.3, 31.6, 30.1.

¹⁹F NMR (376 MHz, Chloroform-*d*): δ -75.5.

HRMS (ESI): *m/z* calcd for [C₁₄H₁₇F₃O₄S+Na⁺]: 361.0692, found 361.0690.

tert*-Butyl(4-(4-(*tert*-butyl)phenyl)-3-((trifluoromethyl)sulfonyl)butoxy)dimethylsilane **1h*



Prepared from triflone **S2** (306 mg, 1 mmol), LiHMDS (184 mg, 1.1 mmol, 2 mL of THF solution), and 4-(*tert*-butyl)benzylbromide (295 mg, 1.3 mmol) in THF (3 mL) according to General Procedure C. The crude residue was purified by Kugelrohr distillation (120 °C, 10 mmHg) to remove unreacted bromide to afford **1h** (309 mg, 68%) as a colorless oil.

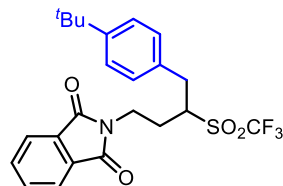
¹H NMR (400 MHz, Chloroform-*d*): δ 7.34 (d, *J* = 8.3 Hz, 2H), 7.15 (d, *J* = 8.3 Hz, 2H), 3.90-3.84 (m, 1H), 3.65 (ddd, *J* = 10.3, 6.6, 5.2 Hz, 1H), 3.44 (dd, *J* = 14.3, 3.9 Hz, 1H), 3.37 (ddd, *J* = 10.3, 6.9, 5.0 Hz, 1H), 2.87 (dd, *J* = 14.3, 10.1 Hz, 1H), 1.95-1.87 (m, 1H), 2.32-2.24 (m, 1H), 0.80 (s, 9H), 1.31 (s, 9H), -0.06 (s, 3H), -0.11 (s, 3H).

¹³C{¹H} NMR (176 MHz, Chloroform-*d*): δ 150.4, 132.4, 128.8, 125.9, 120.0 (q, *J* = 329.4 Hz), 58.9, 58.6, 34.5, 33.6, 31.3, 30.2, 25.7, 18.1, -5.7, -5.7.

¹⁹F NMR (376 MHz, Chloroform-*d*): δ -75.5.

HRMS (ESI): *m/z* calcd for [C₂₁H₃₅F₃O₃SSi+H⁺]: 453.2107, found 453.2101.

2-(4-(4-(*tert*-Butyl)phenyl)-3-((trifluoromethyl)sulfonyl)butyl)isoindoline-1,3-dione **S15**



Prepared from triflone **S3** (647 mg, 2 mmol), LiHMDS (351 mg, 2.1 mmol, 2 mL of THF solution), and 4-(*tert*-butyl)benzylbromide (681 mg, 3 mmol) in THF (18 mL) according to General Procedure C. The crude residue was purified by column chromatography (EtOAc/Hexane = 1:5) to give **S15** (396 mg, 42%) as a colorless solid.

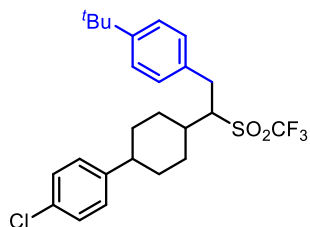
¹H NMR (400 MHz, Chloroform-*d*): δ 7.80 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.72 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.19 (d, *J* = 8.3 Hz, 2H), 7.11 (d, *J* = 8.2 Hz, 2H), 3.83-3.76 (m, 2H), 3.64 (dt, *J* = 14.2, 5.8 Hz, 1H), 3.41 (dd, *J* = 14.1, 3.5 Hz, 1H), 2.86 (dd, *J* = 14.1, 11.0 Hz, 1H), 2.51-2.29 (m, 1H), 2.17-1.98 (m, 1H), 1.19 (s, 9H).

¹³C{¹H} NMR (176 MHz, Chloroform-*d*): δ 168.0, 150.6, 134.1, 131.7, 131.5, 128.8, 125.9, 123.3, 120.0 (q, *J* = 329.8 Hz), 60.3, 35.6, 34.4, 33.6, 31.2, 26.0.

¹⁹F NMR (376 MHz, Chloroform-*d*): δ -75.2.

HRMS (ESI): *m/z* calcd for [C₂₃H₂₄F₃O₄NS+H⁺]: 468.1451, found 468.1462.

1-(*tert*-Butyl)-4-(2-(4-(4-chlorophenyl)cyclohexyl)-2-((trifluoromethyl)sulfonyl)ethyl)benzene **1j**



Prepared from triflone **S4** (272mg, 0.8 mmol), LiHMDS (140 mg, 0.84 mmol, 2 mL of THF solution), and 4-(*tert*-butyl)benzylbromide (272 mg, 1.2 mmol) in THF (6 mL) according to General Procedure C. The crude residue was purified by column chromatography (EtOAc/Hexane = 1:50) to give **1j** (158 mg, 41%) as a colorless solid.

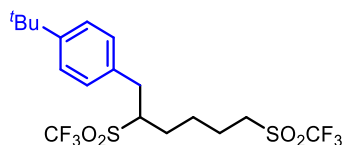
¹H NMR (400 MHz, Chloroform-*d*): δ 7.30 (d, J = 8.4 Hz, 2H), 7.17 (d, J = 8.5 Hz, 2H), 7.07 (d, J = 8.4 Hz, 2H), 7.02 (d, J = 8.5 Hz, 2H), 3.53 (ddd, J = 8.9, 4.5, 2.1 Hz, 1H), 3.28 (dd, J = 15.2, 4.5 Hz, 1H), 3.02 (dd, J = 15.2, 8.9 Hz, 1H), 2.38 (tt, J = 11.8, 3.4 Hz, 1H), 2.24-2.11 (m, 1H), 1.93-1.67 (m, 5H), 1.48-1.32 (m, 3H), 1.26 (s, 9H).

¹³C{¹H} NMR (101 MHz, Chloroform-*d*): δ 150.4, 144.8, 133.4, 131.7, 128.5, 128.4, 128.1, 125.9, 119.8 (q, J = 330.5 Hz), 67.3, 43.0, 37.3, 34.5, 34.3, 33.7, 31.3, 30.8, 30.1, 29.2.

¹⁹F NMR (376 MHz, Chloroform-*d*): δ -76.0.

HRMS (EI): m/z calcd for [C₂₅H₃₀ClF₃O₂S]: 509.1511, found 509.1500.

1-(2,6-Bis((trifluoromethyl)sulfonyl)hexyl)-4-(*tert*-butyl)benzene **S16**



Prepared from triflone **S5** (336 mg, 1 mmol), LiHMDS (184 mg, 1.1 mmol, 2 mL of THF solution), and 4-(*tert*-butyl)benzylbromide (295 mg, 1.2 mmol) in THF (8 mL) according to General Procedure C. The crude residue was purified by column chromatography (EtOAc/Hexane = 1:10) to give **S16** (255 mg, 53%) as a colorless solid.

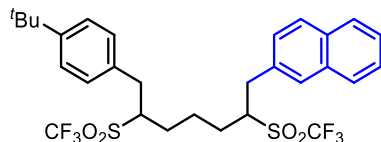
¹H NMR (400 MHz, Chloroform-*d*): δ 7.39 (d, J = 8.3 Hz, 2H), 7.13 (d, J = 8.3 Hz, 2H), 3.58-3.47 (m, 1H), 3.42 (dd, J = 14.1, 3.5 Hz, 1H), 3.11-3.06 (m, 2H), 2.86 (dd, J = 14.1, 11.1 Hz, 1H), 2.03-1.90 (m, 1H), 1.92-1.64 (m, 4H), 1.61-1.45 (m, 1H), 1.32 (s, 9H).

¹³C{¹H} NMR (101 MHz, Chloroform-*d*): δ 151.0, 131.8, 128.6, 126.2, 119.9 (q, J = 329.7 Hz), 119.3 (d, J = 327.1 Hz), 62.1, 48.8, 34.5, 33.0, 31.2, 25.6, 24.9, 20.3.

¹⁹F NMR (376 MHz, Chloroform-*d*): δ -75.7, -79.5.

HRMS (ESI): m/z calcd for [C₁₈H₂₄F₆O₄S₂+H⁺]: 483.1091, found 483.1093.

2-(7-(4-(*tert*-Butyl)phenyl)-2,6-bis((trifluoromethyl)sulfonyl)heptyl)naphthalene **1k**



Prepared from triflone **S16** (241 mg, 0.5 mmol), LiHMDS (88 mg, 0.53 mmol, 1 mL of THF solution), and 2-bromo(methyl)naphthalene (131 mg, 0.6 mmol) in THF (4 mL) according to General Procedure C. The crude residue was purified by column chromatography (EtOAc/Hexane = 1:10) to give **1k** (109 mg, 35%, a mixture of diastereoisomers, dr = 50:50) as a colorless solid.

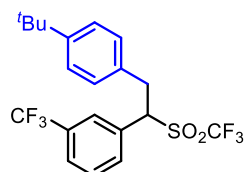
¹H NMR (700 MHz, Chloroform-*d*): δ 7.88-7.79 (m, 3H), 7.63 (dd, $J = 7.4, 1.8$ Hz, 1H), 7.56-7.48 (m, 2H), 7.29 (d, $J = 8.3$ Hz, 1H), 7.26 (d, $J = 8.3$ Hz, 1H), 7.25-7.20 (m, 1H), 6.98 (d, $J = 8.3$ Hz, 1H), 6.93 (d, $J = 8.3$ Hz, 1H), 3.58-3.46 (m, 2H), 3.41-3.23 (m, 2H), 3.01 (dd, $J = 13.9, 10.4$ Hz, 1H), 2.74 (ddd, $J = 14.1, 12.3, 10.7$ Hz, 1H), 1.84-1.53 (m, 6H), 1.29 (s, 4.5H), 1.29 (s, 4.5H).

¹³C{¹H} NMR (176 MHz, Chloroform-*d*): δ 150.8, 150.7, 133.5, 132.6, 132.4, 132.3, 131.9, 131.8, 129.1, 128.6, 128.2, 128.1, 127.8, 127.6, 127.6, 126.8, 126.8, 126.4, 126.4, 126.3, 126.3, 126.1, 126.0, 119.93 (q, $J = 329.8$ Hz), 119.92 (q, $J = 329.6$ Hz), 119.88 (q, $J = 329.7$ Hz), 119.87 (q, $J = 329.7$ Hz), 62.2, 62.0, 61.9, 34.5, 33.5, 33.3, 32.9, 32.5, 31.3, 26.1, 26.0, 25.8, 25.7, 22.9, 22.4.

¹⁹F NMR (376 MHz, Chloroform-*d*): δ -75.38, -75.39, -75.42, -75.58.

HRMS (ESI): m/z calcd for [C₂₉H₃₂F₆O₄S₂+Na⁺]: 645.1539, found 645.1538.

1-(2-(4-(*tert*-Butyl)phenyl)-1-((trifluoromethyl)sulfonyl)ethyl)-3-(trifluoromethyl)benzene **1m**



Prepared from triflone **S7** (262 mg, 0.9 mmol), LiHMDS (159 mg, 0.95 mmol, 2 mL of THF solution), and 4-(*tert*-butyl)benzylbromide (220 mg, 1.2 mmol) in THF (7 mL) according to General Procedure C. The crude residue was purified by column chromatography (EtOAc/Hexane = 1:50) to give **1m** (279 mg, 71%) as a colorless oil.

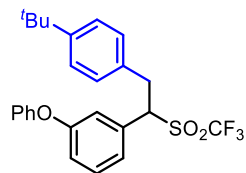
¹H NMR (700 MHz, Chloroform-*d*): δ 7.66 (d, $J = 7.9$ Hz, 1H), 7.61 (d, $J = 7.9$ Hz, 1H), 7.55-7.50 (m, 2H), 7.21 (d, $J = 8.4$ Hz, 2H), 6.86 (d, $J = 8.4$ Hz, 2H), 4.61 (dd, $J = 11.5, 3.3$ Hz, 1H), 3.79 (dd, $J = 13.9, 3.3$ Hz, 1H), 3.37 (dd, $J = 13.9, 11.5$ Hz, 1H), 1.24 (s, 9H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (176 MHz, Chloroform-*d*): δ 150.6, 133.2, 131.4 (q, $J = 32.8$ Hz), 131.1, 130.1, 129.6, 128.6, 127.0 (q, $J = 3.8$ Hz), 126.7 (q, $J = 3.8$ Hz), 123.5 (q, $J = 329.9$ Hz), 119.8 (q, $J = 329.1$ Hz), 68.2, 34.4, 33.8, 31.1.

^{19}F NMR (376 MHz, Chloroform-*d*): δ -63.9, -74.2.

HRMS (ESI): m/z calcd for $[\text{C}_{19}\text{H}_{21}\text{F}_3\text{O}_2\text{S}+\text{NH}_4^+]$: 388.1558, found 388.1553.

1-(2-(4-(*tert*-Butyl)phenyl)-1-((trifluoromethyl)sulfonyl)ethyl)-3-phenoxybenzene 1n



Prepared from triflone **S8** (474 mg, 1.5 mmol), LiHMDS (264 mg, 1.6 mmol, 3 mL of THF solution), and 4-(*tert*-butyl)benzylbromide (356 mg, 2 mmol) in THF (12 mL) according to General Procedure C. The crude residue was purified by column chromatography (EtOAc/Hexane = 1:30) to give **1n** (505 mg, 73%) as a colorless oil.

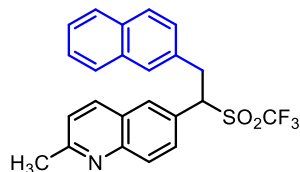
^1H NMR (700 MHz, Chloroform-*d*): δ 7.37-7.28 (m, 3H), 7.22 (d, $J = 8.4$ Hz, 2H), 7.15 (d, $J = 7.7$ Hz, 1H), 7.12 (t, $J = 7.3$ Hz, 1H), 7.03 (dd, $J = 8.2, 2.3$ Hz, 1H), 6.98 (s, 1H), 6.89 (dd, $J = 7.9, 5.8$ Hz, 4H), 4.50 (dd, $J = 11.6, 3.2$ Hz, 1H), 3.70 (dd, $J = 13.9, 3.2$ Hz, 1H), 3.33 (dd, $J = 13.9, 11.6$ Hz, 1H), 1.26 (s, 9H),

$^{13}\text{C}\{^1\text{H}\}$ NMR (176 MHz, Chloroform-*d*): δ 157.4, 156.8, 150.4, 131.6, 130.5, 130.4, 129.8, 128.8, 125.6, 124.9, 123.6, 120.7, 120.5, 119.9 (q, $J = 330.5$ Hz), 118.7, 68.5, 34.4, 33.6, 31.2.

^{19}F NMR (376 MHz, Chloroform-*d*): δ -74.2.

HRMS (ESI): m/z calcd for $[\text{C}_{25}\text{H}_{25}\text{F}_3\text{O}_3\text{S}+\text{Na}^+]$: 485.1369, found 485.1366.

6-(2-(4-(*tert*-Butyl)phenyl)-1-((trifluoromethyl)sulfonyl)ethyl)-2-methylquinoline 1p



Prepared from triflone **S10** (231 mg, 0.8 mmol), LiHMDS (140 mg, 0.84 mmol, 2 mL of THF solution), and 2-bromo(methyl)naphthalene (265 mg, 1.2 mmol, 2 mL of THF solution) in THF (4 mL) according to General Procedure C. The crude residue was purified by column chromatography (EtOAc/Hexane = 1:2) to give **1p** (258 mg, 75%) as an orange solid.

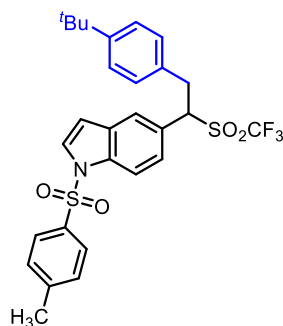
¹H NMR (700 MHz, Chloroform-*d*): δ 8.03 (d, *J* = 8.7 Hz, 1H), 7.95 (d, *J* = 8.4 Hz, 1H), 7.74 (dd, *J* = 8.8, 2.1 Hz, 1H), 7.72-7.68 (m, 2H), 7.65-7.59 (m, 2H), 7.46 (s, 1H), 7.42-7.36 (m, 2H), 7.29 (d, *J* = 8.4 Hz, 1H), 7.03 (dd, *J* = 8.5, 1.9 Hz, 1H), 4.83 (dd, *J* = 11.7, 3.2 Hz, 1H), 4.02 (dd, *J* = 13.9, 3.2 Hz, 1H), 3.68 (dd, *J* = 13.9, 11.7 Hz, 1H), 2.73 (s, 3H).

¹³C{¹H} NMR (176 MHz, Chloroform-*d*): δ 160.8, 148.1, 136.3, 133.2, 132.4, 132.1, 130.1, 129.8, 129.7, 128.6, 128.2, 127.6, 127.5, 126.6, 126.3, 126.1, 126.1, 125.8, 122.9, 119.9 (q, *J* = 330.2 Hz), 68.7, 34.4, 25.4.

¹⁹F NMR (376 MHz, Chloroform-*d*): δ -74.0.

HRMS (ESI): *m/z* calcd for [C₂₃H₁₈F₃O₂NS+H⁺]: 430.1083, found 430.1077.

5-(2-(4-(*tert*-Butyl)phenyl)-1-((trifluoromethyl)sulfonyl)ethyl)-1-tosyl-1H-indole **1q**



Prepared from triflone **S11** (417 mg, 1 mmol), LiHMDS (175 mg, 1.05 mmol, 2 mL of THF solution), and 4-(*tert*-butyl)benzylbromide (272 mg, 1.2 mmol, 2 mL of THF solution) in THF (8 mL) according to General Procedure C. The crude residue was purified by recrystallization from CH₂Cl₂/Hexane to give **1q** (410 mg, 72%) as a colorless solid.

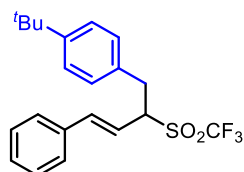
¹H NMR (400 MHz, Chloroform-*d*): δ 7.98 (d, *J* = 8.7 Hz, 1H), 7.75 (d, *J* = 8.4 Hz, 2H), 7.58 (d, *J* = 3.7 Hz, 1H), 7.54 (d, *J* = 1.8 Hz, 1H), 7.30 (dd, *J* = 8.7, 1.8 Hz, 1H), 7.25 (d, *J* = 8.4 Hz, 2H), 7.13 (d, *J* = 8.4 Hz, 2H), 6.83 (d, *J* = 8.4 Hz, 2H), 6.63 (d, *J* = 3.7 Hz, 1H), 4.61 (dd, *J* = 11.4, 3.0 Hz, 1H), 3.72 (dd, *J* = 13.9, 3.0 Hz, 1H), 3.41 (dd, *J* = 13.9, 11.4 Hz, 1H), 2.37 (s, 3H), 1.21 (s, 9H).

¹³C{¹H} NMR (101 MHz, Chloroform-*d*): δ 150.2, 145.3, 135.5, 135.1, 131.8, 131.1, 130.0, 128.6, 127.4, 126.8, 126.2, 125.6, 123.5, 123.3, 120.0 (q, *J* = 330.6 Hz), 114.0, 108.8, 68.9, 34.4, 34.1, 31.2, 21.6.

¹⁹F NMR (376 MHz, Chloroform-*d*): δ -74.1.

HRMS (ESI): *m/z* calcd for [C₂₈H₂₈F₃NO₄S₂+Na⁺]: 586.1304, found 586.1307.

(*E*)-1-(*tert*-Butyl)-4-(4-phenyl-2-((trifluoromethyl)sulfonyl)but-3-en-1-yl)benzene **1s**



Prepared from triflone **S12** (252 mg, 1 mmol), LiHMDS (175 mg, 1.05 mmol, 2 mL of THF solution), and 4-(*tert*-butyl)benzylbromide (272 mg, 1.2 mmol, 2 mL of THF solution) in THF (8 mL) according to General Procedure C. The crude residue was purified by column chromatography (EtOAc/Hexane = 1:30) to give **1s** (250 mg, 63%) as a yellow solid. (It should be noted that **1s** decomposes slowly at room temperature, thus it should be stored at low temperature under inert atmosphere).

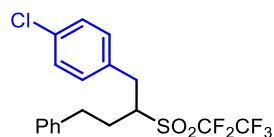
¹H NMR (700 MHz, Chloroform-*d*): δ 7.36-7.29 (m, 7H), 7.13 (d, J = 8.0 Hz, 2H), 6.51 (d, J = 15.6 Hz, 1H), 6.05 (dd, J = 15.6, 9.8 Hz, 1H), 4.20 (d, J = 9.8 Hz, 1H), 3.60 (d, J = 13.8 Hz, 1H), 3.14-3.10 (m, 1H), 1.29 (s, 9H).

¹³C{¹H} NMR (176 MHz, Chloroform-*d*): δ 150.4, 140.3, 135.1, 131.7, 129.1, 129.0, 128.7, 126.9, 125.7, 120.0 (q, J = 330.4 Hz), 117.1, 67.4, 34.5, 32.4, 31.2.

¹⁹F NMR (376 MHz, Chloroform-*d*): δ -73.7.

HRMS (ESI): m/z calcd for [C₂₁H₂₃F₃O₂S+NH₄⁺]: 414.1709, found 414.1710.

1-Chloro-4-(2-((perfluoroethyl)sulfonyl)-4-phenylbutyl)benzene **1u**



Prepared from sulfone **S13** (105.8 mg, 0.35 mmol), LiHMDS (61.2 mg, 0.37 mmol, 1 mL of THF solution), and 4-chlorobenzylbromide (94.5 mg, 0.46 mmol) in THF (1.5 mL) according to General Procedure C. The crude residue was purified by column chromatography (EtOAc/Hexane = 1:30) to give **1u** (41 mg, 27%) as a colorless oil.

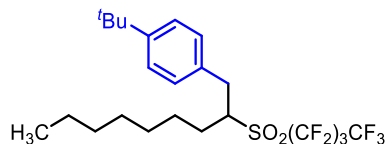
¹H NMR (700 MHz, Chloroform-*d*): δ 7.31 (d, J = 7.9 Hz, 2H), 7.27-7.15 (m, 3H), 7.07 (d, J = 8.1 Hz, 2H), 6.98 (d, J = 7.2 Hz, 2H), 3.62-3.57 (m, 1H), 3.43 (dd, J = 14.5, 3.9 Hz, 1H), 2.97 (dd, J = 14.5, 10.2 Hz, 1H), 2.79-2.67 (m, 2H), 2.41-2.29 (m, 1H), 2.13-2.03 (m, 1H).

¹³C{¹H} NMR (176 MHz, Chloroform-*d*): δ 139.1, 133.7, 133.5, 130.4, 129.2, 128.7, 128.3, 126.6, 117.2 (qt, J = 288.8, 31.6 Hz), 114.0 (tq, J = 303.8, 39.7 Hz), 62.3, 33.4, 32.4, 28.2.

¹⁹F NMR (376 MHz, Chloroform-*d*): δ -79.1, -114.8.

HRMS (EI): m/z calcd for [C₁₈H₁₆F₅O₂SCl]: 426.0480, found 426.0489.

1-(*tert*-Butyl)-4-(2-((perfluorobutyl)sulfonyl)nonyl)benzene **1v**



Prepared from sulfone **S14** (1.14 g, 2.9 mmol), LiHMDS (500 mg, 3 mmol, 5 mL of THF solution), and 4-(*tert*-butyl)benzylbromide (790 mg, 3.5 mmol) in THF (25 mL) according to General Procedure C. The crude residue was purified by column chromatography (EtOAc/Hexane = 1:30) to give **1v** (1.04 g, 67%) as a pale orange oil.

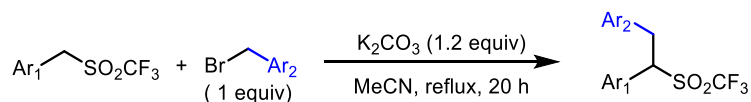
¹H NMR (700 MHz, Chloroform-*d*): δ 7.36 (d, J = 8.1 Hz, 2H), 7.13 (d, J = 8.1 Hz, 2H), 3.63-3.58 (m, 1H), 3.41 (dd, J = 14.3, 3.6 Hz, 1H), 2.93 (dd, J = 14.3, 10.3 Hz, 1H), 1.94 (ddt, J = 15.9, 10.7, 5.3 Hz, 1H), 1.81 (ddt, J = 15.6, 10.7, 5.4 Hz, 1H), 1.45-1.40 (m, 1H), 1.32 (s, 9H), 1.30-1.27 (m, 1H), 1.27-1.21 (m, 2H), 1.18-1.16 (m, 6H), 0.85 (t, J = 7.3 Hz, 3H).

¹³C{¹H} NMR (176 MHz, Chloroform-*d*): δ 150.5, 132.6, 128.7, 125.9, 108.0-121.0 (m, C₄F₉), 64.6, 34.5, 33.1, 31.5, 31.3, 29.1, 28.6, 26.7, 26.1, 22.5, 14.0.

¹⁹F NMR (376 MHz, Chloroform-*d*): δ -81.7 (t, J = 10.2 Hz, 3F), -110.7 (t, J = 14.2 Hz, 2F), -123.1--120.2 (m, 2F), -126.8 (t, J = 14.1 Hz, 2F),

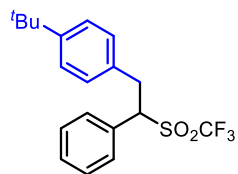
HRMS (ESI): m/z calcd for [C₂₃H₃₁F₉O₂S+Na⁺]: 565.1793, found 565.1801.

Benylation of Benzyl Triflones with K₂CO₃ (General Procedure D)



A 50-mL Schlenk flask containing a magnetic stirring bar was flame-dried under vacuum and filled with argon after cooling to room temperature. To the flask were added primary alkyl triflone, K₂CO₃, benzyl bromide and dry CH₃CN (0.25 M). After stirring the mixture at 80 °C for 30 min, the mixture was allowed to cool to room temperature. The reaction was quenched with water and diluted with ethyl acetate. The aqueous layer was extracted with ethyl acetate two times, and the combined organic layer was washed once with brine. The organic layer was dried over Na₂SO₄, filtered, and concentrated under reduced pressure. The crude mixture was purified by column chromatography to give the desired secondary benzyl triflone.

1-(*tert*-Butyl)-4-(2-phenyl-2-((trifluoromethyl)sulfonyl)ethyl)benzene **11**



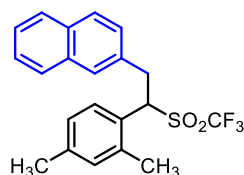
Prepared from triflone **S6** (224 mg, 1 mmol), K₂CO₃ (165 mg, 1.2 mmol), and 4-(*tert*-butyl)benzylbromide (227 mg, 1 mmol) in CH₃CN (4 mL) according to General Procedure D. The crude residue was purified by column chromatography (EtOAc/Hexane = 1:50) to give **11** (332 mg, 90%) as a colorless solid.

¹H NMR (700 MHz, Chloroform-*d*): δ 7.39-7.37 (m, 5H), 7.20 (d, *J* = 8.4 Hz, 2H), 6.89 (d, *J* = 8.3 Hz, 2H), 4.56 (dd, *J* = 11.5, 3.1 Hz, 1H), 3.74 (dd, *J* = 14.0, 3.1 Hz, 1H), 3.40 (dd, *J* = 14.0, 11.5 Hz, 1H), 1.25 (s, 9H).
¹³C{¹H} NMR (176 MHz, Chloroform-*d*): δ 150.2, 131.8, 130.2, 129.9, 129.0, 128.7, 128.6, 125.6, 119.9 (q, *J* = 330.5 Hz), 68.8, 34.4, 33.6, 31.2.

¹⁹F NMR (376 MHz, Chloroform-*d*): δ -74.7.

HRMS (ESI): *m/z* calcd for [C₁₉H₂₁F₃O₂S+Na⁺]: 393.1107, found 393.1121.

2-(2-(2,4-Dimethylphenyl)-2-((trifluoromethyl)sulfonyl)ethyl)naphthalene 1o



Prepared from triflone **S9** (252 mg, 1 mmol), K₂CO₃ (165 mg, 1.2 mmol), and 4-(*tert*-butyl)benzylbromide (227 mg, 1 mmol) in CH₃CN (4 mL) according to General Procedure D. The crude residue was purified by column chromatography (EtOAc/Hexane = 1:50) to give **1o** (182 mg, 46%) as a colorless solid.

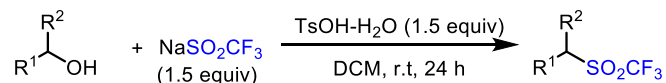
¹H NMR (700 MHz, Chloroform-*d*): δ 7.78-7.75 (m, 1H), 7.70 (d, *J* = 8.1 Hz, 1H), 7.70-7.64 (m, 2H), 7.47-7.40 (m, 3H), 7.16 (d, *J* = 7.9 Hz, 1H), 7.05 (d, *J* = 8.2 Hz, 1H), 6.85 (s, 1H), 5.04 (d, *J* = 11.6 Hz, 1H), 3.91 (d, *J* = 13.7 Hz, 1H), 3.54 (dd, *J* = 13.7, 11.6 Hz, 1H), 2.29 (s, 3H), 1.88 (s, 3H).

¹³C{¹H} NMR (176 MHz, Chloroform-*d*): δ 139.6, 138.2, 133.3, 132.4, 132.4, 131.7, 128.4, 128.4, 128.1, 127.6, 127.6, 127.6, 126.6, 126.2, 126.0, 123.7, 120.1 (q, *J* = 330.3 Hz), 63.5, 35.6, 21.1, 19.1.

¹⁹F NMR (376 MHz, Chloroform-*d*): δ -75.1.

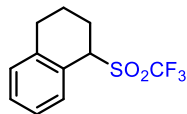
HRMS (ESI): *m/z* calcd for [C₂₁H₁₉F₃O₂S+H⁺]: 393.1131, found 393.1124.

Triflylation of Secondary Alcohol (General Procedure E)



To a flame-dried flask containing a magnetic stir bar under an atmosphere of dry argon was added the secondary alcohol (1.0 equiv), TsOH-H₂O (1.5 equiv), NaSO₂CF₃ (1.5 equiv), and dry CH₂Cl₂ (0.2 M). The reaction mixture was stirred at room temperature for 24 h. Upon reaction completion, the reaction was filtered and concentrated in vacuo. The crude product was purified by column chromatography or recrystallization.

1-((Trifluoromethyl)sulfonyl)-1,2,3,4-tetrahydronaphthalene 1r



Prepared from alcohol (1 g, 6.8 mmol), TsOH-H₂O (1.9 g, 10 mmol), and NaSO₂CF₃ (1.6 g, 10 mmol) in CH₂Cl₂ (34 mL) according to General Procedure E. The crude residue was purified by column chromatography (EtOAc/Hex = 1:75) to give **1r** (776 mg, 43%) as a colorless solid. (It should be noted that **1r** decomposes slowly at room temperature, thus it should be stored at low temperature under inert atmosphere).

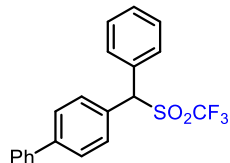
¹H NMR (400 MHz, Chloroform-*d*): δ 7.46 (d, *J* = 7.7 Hz, 1H), 7.34 (td, *J* = 7.5, 1.4 Hz, 1H), 7.26-7.22 (m, 2H), 4.71 (dd, *J* = 6.2, 3.3 Hz, 1H), 2.96 (dt, *J* = 17.0, 5.2 Hz, 1H), 2.80 (ddd, *J* = 16.5, 9.1, 6.0 Hz, 1H), 2.67-2.54 (m, 1H), 2.38-2.14 (m, 2H), 1.88-1.78 (m, 1H),

¹³C{¹H} NMR (176 MHz, Chloroform-*d*): δ 140.2, 132.1, 129.9, 129.7, 126.1, 122.6, 120.3 (q, *J* = 330.7 Hz), 61.9, 28.0, 23.4, 18.4.

¹⁹F NMR (376 MHz, Chloroform-*d*): δ -83.0.

HRMS (ESI): *m/z* calcd for [C₁₁H₁₁F₃O₂S+Na⁺]: 287.0324, found 287.0324.

4-(Phenyl((trifluoromethyl)sulfonyl)methyl)-1,1'-biphenyl **1t**



Prepared from alcohol (1 g, 4 mmol), TsOH-H₂O (912 mg, 4.8 mmol), NaSO₂CF₃ (936 mg, 6 mmol) in CH₂Cl₂ (20 mL) according to General Procedure E. The crude residue was purified by column chromatography (EtOAc/Hex = 1:25) and recrystallization from Hexane/EtOAc to give **1t** (456 mg, 30%) as a colorless solid.

¹H NMR (400 MHz, Chloroform-*d*): δ 7.76-7.63 (m, 6H), 7.58 (d, *J* = 7.6 Hz, 2H), 7.50-7.42 (m, 5H), 7.38 (t, *J* = 7.2 Hz, 1H), 5.68 (s, 1H).

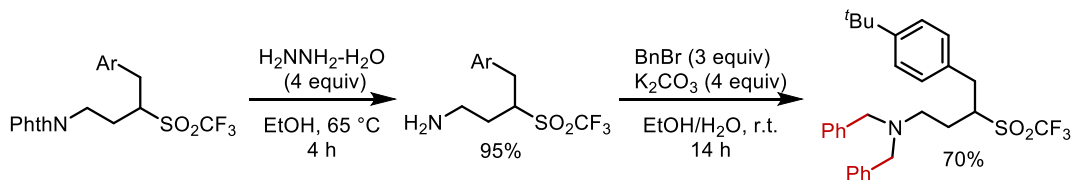
¹³C{¹H} NMR (101 MHz, Chloroform-*d*): δ 142.7, 139.8, 130.4, 130.0, 129.8, 129.5, 129.3, 128.9, 128.2, 127.9, 127.9, 127.1, 121.7 (q, *J* = 330.4 Hz), 71.8.

¹⁹F NMR (376 MHz, Chloroform-*d*): δ -73.7.

HRMS (EI): *m/z* calcd for [C₂₀H₁₅F₃O₂S]: 376.0745, found 376.0742.

Transformation of *N*-Phthalamide to Dibenzylamine

N,N-dibenzyl-4-(4-(tert-butyl)phenyl)-3-((trifluoromethyl)sulfonyl)butan-1-amine **1i**



To a 50 mL flask containing a magnetic stir bar under an atmosphere of dry argon was added triflate **S15** (468 mg, 1 mmol), $\text{H}_2\text{NNH}_2\text{-H}_2\text{O}$ (0.31 mL, 4 mmol) and ethanol (11 mL). The reaction mixture was stirred at 60 °C for 24 h. Upon completion, the reaction was filtered and concentrated in vacuo to give a yellow oil (320 mg, 0.95 mmol, 95%). The crude product (269 mg, 0.8 mmol) was added to a 4 dram vial containing a magnetic stir bar under an atmosphere of dry argon. To the vial was added K_2CO_3 (441 mg, 3.2 mmol), benzyl bromide (0.38 mL, 3.2 mmol), ethanol (4 mL) and water (1 mL). The reaction mixture was stirred at room temperature for 14 hours. The reaction was quenched with water and diluted with ethyl acetate. The aqueous layer was extracted with ethyl acetate twice, and the combined organic layer was washed once with brine. The organic layer was dried over Na_2SO_4 , filtered, and concentrated under reduced pressure. The crude mixture was purified by column chromatography (EtOAc/Hexane = 1:3) to give dibenzylamine **1i** (240 mg, 70%) as a pale yellow oil.

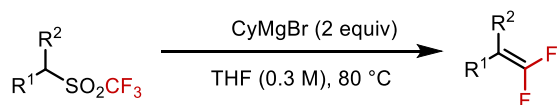
^1H NMR (700 MHz, Chloroform-*d*): δ 7.34-7.31 (m, 4H), 7.28-7.22 (m, 8H), 6.93-6.10 (m, 2H), 3.76-3.74 (m, 1H), 3.50 (d, J = 13.5 Hz, 2H), 3.29 (d, J = 13.5 Hz, 2H), 3.12 (dd, J = 15.0 Hz, 1H), 2.81 (dd, J = 14.5, 9.6 Hz, 1H), 2.50-2.47 (m, 1H), 2.40-2.36 (m, 1H), 2.25-2.22 (m, 1H), 1.90-1.86 (m, 1H), 1.26 (d, J = 4.7 Hz, 9H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (176 MHz, Chloroform-*d*): δ 150.3, 131.8, 129.0, 129.0, 129.0, 128.9, 128.8, 128.4, 128.3, 120.0 (q, J = 330.1 Hz), 60.0, 57.7, 49.7, 34.4, 33.1, 31.2, 24.1.

^{19}F NMR (376 MHz, Chloroform-*d*): δ -75.4.

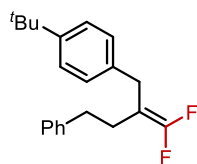
HRMS (ESI): m/z calcd for $[\text{C}_{29}\text{H}_{34}\text{F}_3\text{NO}_2\text{S}+\text{H}^+]$: 518.2329, found 518.2335.

5. Ramberg–Bäcklund Reaction for the Synthesis of *gem*-Difluoroalkenes (General Procedure F)



To a flame-dried 1 dram vial containing a magnetic stir bar under an atmosphere of dry argon was added triflone, and cyclohexyl magnesium bromide (0.57 M in THF). The reaction mixture was stirred at 80 °C. After completion, the reaction mixture was cooled to room temperature, quenched with NH₄Cl (sat. aq.) and diluted with ethyl acetate. The resulting solution was passed through a small pad of silica gel, and washed with ethyl acetate three times. The crude reaction mixture was concentrated under reduced pressure, and purified by PTLC or column chromatography to afford *gem*-difluoroalkene.

1-(*tert*-Butyl)-4-(2-(difluoromethylene)-4-phenylbutyl)benzene **2a**



Prepared from triflone **1a** (398 mg, 1 mmol) and cyclohexyl magnesium bromide (3.5 mL, 2 mmol, 0.57 M in THF solution) according to General Procedure F. The crude residue was purified by column chromatography (Hexane only) to give **2a** (255 mg, 81%) as a colorless oil.

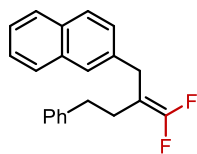
¹H NMR (400 MHz, Chloroform-*d*): δ 7.30 (d, *J* = 8.3 Hz, 2H), 7.24-7.22 (m, 2H), 7.18-7.16 (m, 1H), 7.10-7.07 (m, 4H), 3.26 (s, 2H), 2.61 (dd, *J* = 9.3, 6.6 Hz, 2H), 2.18 (ddt, *J* = 10.1, 6.6, 2.2 Hz, 2H), 1.30 (s, 9H).

¹³C{¹H} NMR (126 MHz, Chloroform-*d*): δ 153.9 (t, *J* = 284.4 Hz), 149.4, 141.2, 135.4 (t, *J* = 2.6 Hz), 128.3, 126.0, 125.4, 88.5 (t, *J* = 17.2 Hz), 34.4, 33.8 (t, *J* = 2.7 Hz), 31.8 (d, *J* = 2.8 Hz), 31.4, 27.8 (d, *J* = 2.1 Hz).

¹⁹F NMR (376 MHz, Chloroform-*d*): δ -96.0 (d, *J* = 56.4 Hz), -96.3 (d, *J* = 54.5 Hz).

HRMS (ESI): *m/z* calcd for [C₂₁H₂₄F₂]: 314.1846, found 314.1851.

2-(2-(Difluoromethylene)-4-phenylbutyl)naphthalene **2b**



Prepared from triflone **1b** (78.4 mg, 0.2 mmol) and cyclohexyl magnesium bromide (0.7 mL, 0.4 mmol, 0.57 M in THF solution) according to General Procedure F. The crude residue was purified by PTLC (Hexane only) to give **2b** (40 mg, 65%) as a colorless oil.

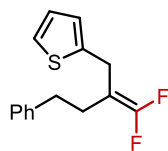
¹H NMR (700 MHz, Chloroform-*d*): δ 7.89-7.75 (m, 3H), 7.64 (s, 1H), 7.54-7.45 (m, 2H), 7.34 (d, $J = 8.3$ Hz, 1H), 7.28 (t, $J = 7.3$ Hz, 2H), 7.24-7.20 (m, 1H), 7.13 (d, $J = 7.5$ Hz, 2H), 3.50 (s, 2H), 2.70 (t, $J = 7.9$ Hz, 2H), 2.25 (t, $J = 7.9$ Hz, 2H).

¹³C{¹H} NMR (176 MHz, Chloroform-*d*): δ 154.0 (t, $J = 284.7$ Hz), 141.1, 135.9, 133.5, 132.3, 128.3, 128.3, 128.2, 127.6, 127.5, 127.0, 127.0, 126.1, 126.0, 125.5, 88.3 (t, $J = 17.2$ Hz), 33.8, 32.6, 27.7.

¹⁹F NMR (376 MHz, Chloroform-*d*): δ -95.9 (d, $J = 52.8$ Hz), -96.2 (d, $J = 52.1$ Hz).

HRMS (ESI): m/z calcd for [C₂₁H₁₈F₂+Na⁺]: 331.1269, found 331.1265.

2-(2-(Difluoromethylene)-4-phenylbutyl)thiophene **2c**



Prepared from triflone **1c** (69.6 mg, 0.2 mmol) and cyclohexyl magnesium bromide (0.7 mL, 0.4 mmol, 0.57 M in THF solution) according to General Procedure F. The crude residue was purified by PTLC (Hexane only) to give **2c** (33.2 mg, 63%) as a colorless oil.

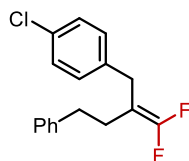
¹H NMR (400 MHz, Chloroform-*d*): δ 7.33-7.24 (m, 2H), 7.21-7.12 (m, 4H), 6.94 (dd, $J = 5.2, 3.4$ Hz, 1H), 6.83 (d, $J = 3.4$ Hz, 1H), 3.49 (s, 2H), 2.67 (dd, $J = 9.3, 6.7$ Hz, 2H), 2.37-2.24 (m, 2H).

¹³C{¹H} NMR (176 MHz, Chloroform-*d*): δ 153.8 (t, $J = 285.4$ Hz), 141.2 (t, $J = 3.1$ Hz), 141.0, 128.4, 128.3, 126.9, 126.1, 125.5, 124.1, 88.4 (d, $J = 16.6$ Hz), 33.8 (t, $J = 2.5$ Hz), 27.7, 26.7.

¹⁹F NMR (376 MHz, Chloroform-*d*): δ -95.5 (d, $J = 52.5$ Hz), -95.7 (d, $J = 52.4$ Hz).

HRMS (EI): m/z calcd for [C₁₅H₁₄F₂S]: 264.0784, found 264.0782.

1-Chloro-4-(2-(difluoromethylene)-4-phenylbutyl)benzene **2d**



Prepared from triflone **1d** (75.3 mg, 0.2 mmol) and cyclohexyl magnesium bromide (0.7 mL, 0.4 mmol, 0.57 M in THF solution) according to General Procedure F. The crude residue was purified by PTLC (Hexane only) to give **2d** (48 mg, 82%) as a colorless oil.

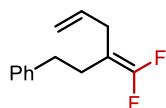
¹H NMR (700 MHz, Chloroform-*d*): δ 7.30-7.26 (m, 4H), 7.21 (t, *J* = 7.4 Hz, 1H), 7.13-7.09 (m, 4H), 3.27 (s, 2H), 2.64 (t, *J* = 7.9 Hz, 2H), 2.19 (t, *J* = 7.9 Hz, 2H).

¹³C{¹H} NMR (176 MHz, Chloroform-*d*): δ 154.0 (t, *J* = 285.0 Hz), 140.9, 136.9, 132.3, 123.0, 128.6, 128.4, 128.3, 126.1, 88.1 (t, *J* = 17.5 Hz), 33.8 (t, *J* = 2.6 Hz), 31.8 (d, *J* = 2.9 Hz), 27.6 (d, *J* = 1.9 Hz).

¹⁹F NMR (376 MHz, Chloroform-*d*): δ -95.6 (d, *J* = 53.6 Hz), -96.1 (d, *J* = 52.7 Hz).

HRMS (EI): *m/z* calcd for [C₁₇H₁₅F₂Cl]: 292.0830, found 292.0822.

(3-(Difluoromethylene)hex-5-en-1-yl)benzene **2e**



Prepared from triflone **1e** (58.4 mg, 0.2 mmol) and cyclohexyl magnesium bromide (0.85 mL, 0.4 mmol, 0.47 M in THF solution) according to General Procedure F. The crude residue was purified by PTLC (Hexane only) to give **2e** (35.8 mg, 86%) as a colorless oil.

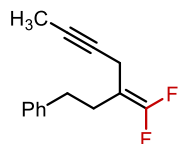
¹H NMR (700 MHz, Chloroform-*d*): δ 7.30 (t, *J* = 7.5 Hz, 2H), 7.21 (t, *J* = 7.5 Hz, 1H), 7.18 (d, *J* = 7.5 Hz, 2H), 5.74 (ddt, *J* = 16.8, 9.9, 6.6 Hz, 1H), 5.14-5.05 (m, 2H), 2.74 (d, *J* = 6.7 Hz, 2H), 2.73-2.67 (m, 2H), 2.28 (t, *J* = 7.9 Hz, 2H).

¹³C{¹H} NMR (176 MHz, Chloroform-*d*): δ 153.6 (t, *J* = 284.6 Hz), 141.2, 134.6, 128.4, 128.3, 126.0, 116.6, 86.9 (t, *J* = 17.3 Hz), 33.8 (t, *J* = 2.9 Hz), 30.7 (d, *J* = 2.7 Hz), 28.0 (d, *J* = 2.2 Hz).

¹⁹F NMR (376 MHz, Chloroform-*d*): δ -95.9 (d, *J* = 54.7 Hz), -96.1 (d, *J* = 55.0 Hz).

HRMS (EI): *m/z* calcd for [C₁₃H₁₄F₂]: 208.1064, found 208.1071.

(3-(Difluoromethylene)hept-5-yn-1-yl)benzene **2f**



Prepared from triflone **1f** (30.4 mg, 0.1 mmol) and cyclohexyl magnesium bromide (0.35 mL, 0.2 mmol, 0.57 M in THF solution) according to General Procedure F. The crude residue was purified by PTLC (Hexane/EtOAc = 60:1) to give **2f** (11.3 mg, 51%) as a colorless oil.

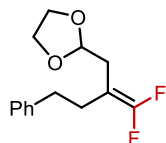
¹H NMR (700 MHz, Chloroform-*d*): δ 7.30 (t, *J* = 7.6 Hz, 2H), 7.22-7.18 (m, 3H), 2.89-2.88 (m, 2H), 2.78-2.75 (m, 2H), 2.42 (tt, *J* = 8.0, 2.2 Hz, 2H), 1.80 (t, *J* = 2.7 Hz, 3H).

¹³C{¹H} NMR (176 MHz, Chloroform-*d*): δ 153.1 (t, *J* = 284.8 Hz), 141.2, 128.4, 128.3, 126.1, 85.8 (dd, *J* = 19.8, 16.1 Hz), 76.7, 74.8 (t, *J* = 3.3 Hz), 33.7 (t, *J* = 2.7 Hz), 27.8, 16.6 (t, *J* = 3.2 Hz), 3.4.

¹⁹F NMR (376 MHz, Chloroform-*d*): δ -95.2 (d, *J* = 51.7 Hz), -95.8 (d, *J* = 51.8 Hz).

HRMS (EI): *m/z* calcd for [C₁₄H₁₄F₂]: 220.1064, found 220.1058.

2-(2-(Difluoromethylene)-4-phenylbutyl)-1,3-dioxolane **2g**



Prepared from triflone **1g** (67.6 mg, 0.2 mmol) and cyclohexyl magnesium bromide (0.85 mL, 0.4 mmol, 0.47 M in THF solution) according to General Procedure F. The crude residue was purified by PTLC (EtOAc/Hexane = 1:10) to give **2g** (33 mg, 65%) as a colorless oil.

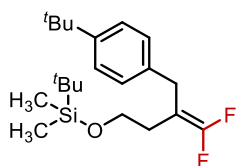
¹H NMR (400 MHz, Chloroform-*d*): δ 7.31-7.24 (m, 2H), 7.23-7.15 (m, 3H), 4.94 (t, J = 4.9 Hz, 1H), 4.04-3.94 (m, 2H), 3.88-3.84 (m, 2H), 2.72 (dd, J = 9.4, 6.6 Hz, 2H), 2.41-2.31 (m, 4H).

¹³C{¹H} NMR (176 MHz, Chloroform-*d*): δ 154.5 (t, J = 285.3 Hz), 141.3, 128.4, 126.0, 103.2 (t, J = 3.5 Hz), 84.4 (dd, J = 20.2, 16.7 Hz), 64.9, 33.8 (t, J = 2.7 Hz), 31.1 (d, J = 2.7 Hz), 28.8 (d, J = 2.0 Hz).

¹⁹F NMR (376 MHz, Chloroform-*d*): δ -94.1 (d, J = 50.2 Hz), -94.3 (d, J = 50.3 Hz).

HRMS (ESI): m/z calcd for [C₁₄H₁₆F₂O₂+Na⁺]: 277.1011, found 277.1012.

tert-Butyl((3-(4-(*tert*-butyl)benzyl)-4,4-difluorobut-3-en-1-yl)oxy)dimethylsilane **2h**



Prepared from triflone **1h** (180 mg, 0.4 mmol) and cyclohexyl magnesium bromide (1.4 mL, 0.8 mmol, 0.57 M in THF solution) according to General Procedure F. The crude residue was purified by column chromatography (EtOAc/Hexane = 1:75) to give **2h** (121.5 mg, 83%) as a colorless oil.

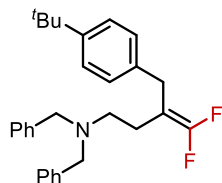
¹H NMR (700 MHz, Chloroform-*d*): δ 7.32 (d, J = 8.1 Hz, 2H), 7.12 (d, J = 8.1 Hz, 2H), 3.56 (t, J = 6.9 Hz, 2H), 3.32 (s, 2H), 2.13 (tt, J = 6.9, 2.0 Hz, 2H), 1.32 (s, 9H), 0.88 (s, 9H), 0.01 (s, 6H).

¹³C{¹H} NMR (176 MHz, Chloroform-*d*): δ 154.4 (t, J = 284.4 Hz), 149.3, 135.5 (t, J = 2.7 Hz), 128.3, 125.4, 86.5 (t, J = 17.7 Hz), 61.0 (t, J = 3.2 Hz), 34.4, 32.3 (d, J = 2.5 Hz), 31.4, 29.5 (d, J = 1.9 Hz), 25.9, 18.2, -5.4.

¹⁹F NMR (376 MHz, Chloroform-*d*): δ -96.1 (d, J = 52.1 Hz), 96.2 (d, J = 53.7 Hz).

HRMS (ESI): m/z calcd for [C₂₁H₃₄F₂OSi+H⁺]: 369.2420, found 369.2405.

N,N*-Dibenzyl-3-(4-(*tert*-butyl)benzyl)-4,4-difluorobut-3-en-1-amine **2i*



Prepared from triflone **1i** (51.7 mg, 0.1 mmol) and cyclohexyl magnesium bromide (0.35 mL, 0.2 mmol, 0.57 M in THF solution) according to General Procedure F. The crude residue was purified by column chromatography (EtOAc/Hexane = 1:75) to give **2i** (27.5 mg, 63%) as a colorless solid.

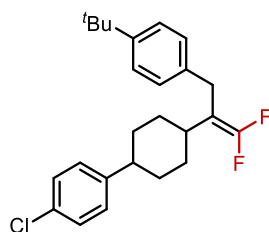
¹H NMR (700 MHz, Chloroform-*d*): δ 7.26-7.24 (m, 7H), 7.19-7.14 (m, 5H), 6.80 (d, J = 7.9 Hz, 2H), 3.44 (s, 4H), 2.94 (s, 2H), 2.36 (t, J = 7.3 Hz, 2H), 2.00 (t, J = 7.3 Hz, 2H), 1.22 (s, 9H).

¹³C{¹H} NMR (176 MHz, Chloroform-*d*): δ 153.9 (t, J = 283.5 Hz), 149.2, 139.6, 135.4, 128.9, 128.9, 128.3, 128.2, 128.2, 126.9, 125.3, 87.5 (t, J = 17.4 Hz), 58.1, 50.3, 34.3, 31.4, 31.2, 23.1.

¹⁹F NMR (376 MHz, Chloroform-*d*): δ -96.8 (d, J = 52.6 Hz), -97.1 (d, J = 55.2 Hz).

HRMS (ESI): m/z calcd for [C₂₉H₃₃F₂NS+H⁺]: 434.2654, found 434.2650.

1-(*tert*-Butyl)-4-(2-(4-(4-chlorophenyl)cyclohexyl)-3,3-difluoroallyl)benzene **2j**



Prepared from triflone **1j** (99.4 mg, 0.2 mmol) and cyclohexyl magnesium bromide (0.7 mL, 0.4 mmol, 0.57 M in THF solution) according to General Procedure F. The crude residue was purified by column chromatography (EtOAc/Hexane = 1:75) to give **2j** (78.5 mg, 97%) as a colorless solid.

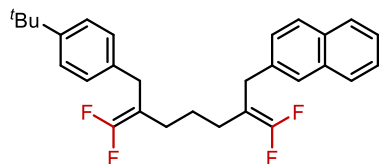
¹H NMR (700 MHz, Chloroform-*d*): δ 7.32 (d, J = 7.9 Hz, 2H), 7.22 (d, J = 7.9 Hz, 2H), 7.14 (d, J = 7.9 Hz, 2H), 7.08 (d, J = 7.9 Hz, 2H), 3.31 (s, 2H), 2.40 (t, J = 11.9 Hz, 1H), 2.22-2.06 (m, 1H), 1.84 (d, J = 12.5 Hz, 2H), 1.68 (d, J = 12.4 Hz, 2H), 1.47-1.43 (m, 2H), 1.43-1.35 (m, 2H), 1.32 (s, 9H).

¹³C{¹H} NMR (176 MHz, Chloroform-*d*): δ 154.1 (t, J = 285.8 Hz), 149.1, 145.7, 136.1, 131.5, 128.4, 128.1, 127.9, 125.3, 92.8 (t, J = 14.6 Hz), 43.1, 36.9, 34.4, 34.1, 31.4, 31.1 (t, J = 2.7 Hz), 30.9 (d, J = 3.7 Hz).

¹⁹F NMR (376 MHz, Chloroform-*d*): δ -94.2 (d, J = 55.0 Hz), -94.5 (d, J = 53.8 Hz).

HRMS (EI): m/z calcd for $[C_{25}H_{29}F_2Cl]$: 402.1926, found 402.1922.

2-(6-(4-(*tert*-Butyl)benzyl)-2-(difluoromethylene)-7,7-difluorohept-6-en-1-yl)naphthalene 2k



Prepared from triflone **1k** (93.4 mg, 0.15 mmol) and cyclohexyl magnesium bromide (0.6 mL, 0.6 mmol, 0.57 M in THF solution) according to General Procedure F. The crude residue was purified by PTLC (Hexane only) to give **2k** (42.9 mg, 67%) as a colorless oil.

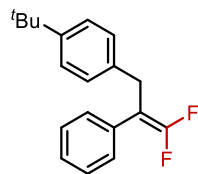
1H NMR (700 MHz, Chloroform-*d*): δ 7.85 (d, $J = 8.0$ Hz, 1H), 7.81 (t, $J = 7.7$ Hz, 2H), 7.60 (s, 1H), 7.51 (t, $J = 7.4$ Hz, 1H), 7.48 (t, $J = 7.4$ Hz, 1H), 7.34-7.28 (m, 3H), 7.04 (d, $J = 7.8$ Hz, 2H), 3.41 (s, 2H), 3.19 (s, 2H), 1.89-1.82 (m, 4H), 1.40 (p, $J = 7.7$ Hz, 2H), 1.33 (s, 9H).

$^{13}C\{^1H\}$ NMR (176 MHz, $CDCl_3$): δ 153.8 (t, $J = 284.2$ Hz), 153.8 (t, $J = 284.2$ Hz), 149.3, 135.9 (t, $J = 2.8$ Hz), 135.3 (t, $J = 2.7$ Hz), 133.5, 132.3, 128.2, 128.2, 127.6, 127.5, 127.0, 126.9, 126.1, 125.5, 125.4, 88.3 (t, $J = 17.2$ Hz), 34.4, 32.3, 31.4, 31.3, 25.2, 25.1, 24.8.

^{19}F NMR (376 MHz, Chloroform-*d*): δ -96.16 (d, $J = 56.4$ Hz), -96.31 (d, $J = 56.4$ Hz), -96.54 (d, $J = 54.8$ Hz), -96.74 (d, $J = 53.2$ Hz).

HRMS (ESI): m/z calcd for $[C_{29}H_{30}F_4+Na^+]$: 477.2176, found 477.2178.

1-(*tert*-Butyl)-4-(3,3-difluoro-2-phenylallyl)benzene 2l



Prepared from triflone **1l** (74 mg, 0.2 mmol) and cyclohexyl magnesium bromide (0.85 mL, 0.4 mmol, 0.47 M in THF solution) according to General Procedure F. The crude residue was purified by PTLC (Hexane only) to give **2l** (49.4 mg, 86%) as a colorless oil.

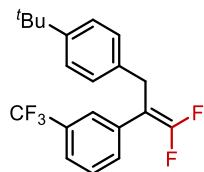
1H NMR (700 MHz, Chloroform-*d*): δ 7.38-7.22 (m, 7H), 7.16-7.04 (m, 2H), 3.74 (s, 2H), 1.31 (s, 9H).

$^{13}C\{^1H\}$ NMR (176 MHz, Chloroform-*d*): δ 154.5 (dd, $J = 292.0, 287.3$ Hz), 149.2, 135.4, 133.8 (t, $J = 4.1$ Hz), 128.3, 128.2, 127.8, 127.2, 125.4, 91.6 (dd, $J = 21.5, 13.3$ Hz), 34.3, 33.3, 31.3.

^{19}F NMR (376 MHz, Chloroform-*d*): δ -91.1 (d, $J = 40.9$ Hz), -91.9 (d, $J = 40.5$ Hz).

HRMS (ESI): m/z calcd for $[C_{19}H_{20}F_2+Na^+]$: 309.1425, found 309.1440.

1-(3-(4-(*tert*-Butyl)phenyl)-1,1-difluoroprop-1-en-2-yl)-3-(trifluoromethyl)benzene 2m



Prepared from triflone **1m** (87.7 mg, 0.2 mmol) and cyclohexyl magnesium bromide (0.7 mL, 0.4 mmol, 0.57 M in THF solution) according to General Procedure F. The crude residue was purified by PTLC (Hexane only) to give **2m** (69 mg, 97%) as a colorless oil.

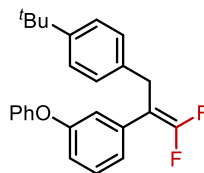
1H NMR (700 MHz, Chloroform-*d*): δ 7.53 (s, 1H), 7.49 (d, $J = 7.8$ Hz, 1H), 7.45 (d, $J = 7.8$ Hz, 1H), 7.41 (t, $J = 7.8$ Hz, 1H), 7.29 (d, $J = 8.1$ Hz, 2H), 7.08 (d, $J = 8.1$ Hz, 2H), 3.73 (s, 2H), 1.30 (s, 9H).

$^{13}C\{^1H\}$ NMR (126 MHz, Chloroform-*d*): δ 154.6 (dd, $J = 292.9, 288.6$ Hz), 149.6, 134.7 (t, $J = 2.6$ Hz), 134.6 (d, $J = 3.9$ Hz), 131.6, 130.8 (q, $J = 32.3$ Hz), 128.9, 127.9, 125.5, 125.1 (m), 124.0 (q, $J = 3.8$ Hz), 124.0 (q, $J = 272.5$ Hz), 91.2 (dd, $J = 22.6, 12.9$ Hz), 34.4, 33.2, 31.3.

^{19}F NMR (376 MHz, Chloroform-*d*): δ -63.7, -89.9 (d, $J = 34.6$ Hz), -90.6 (d, $J = 37.6$ Hz).

HRMS (ESI): m/z calcd for $[C_{20}H_{19}F_5+Na^+]$: 377.1299, found 377.1298.

1-(3-(4-(*tert*-Butyl)phenyl)-1,1-difluoroprop-1-en-2-yl)-3-phenoxybenzene 2n



Prepared from triflone **1n** (92.5 mg, 0.2 mmol) and cyclohexyl magnesium bromide (0.7 mL, 0.4 mmol, 0.57 M in THF solution) according to General Procedure F. The crude residue was purified by PTLC (Hexane only) to give **2n** (58.1 mg, 77%) as a colorless oil.

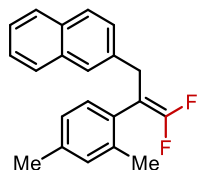
1H NMR (400 MHz, Chloroform-*d*): δ 7.36-7.29 (m, 2H), 7.28-7.21 (m, 3H), 7.10 (tt, $J = 7.4, 1.1$ Hz, 1H), 7.08-7.03 (m, 3H), 6.98-6.93 (m, 3H), 6.87 (ddd, $J = 8.2, 2.5, 1.0$ Hz, 1H), 3.67 (s, 2H), 1.29 (s, 9H).

$^{13}C\{^1H\}$ NMR (176 MHz, Chloroform-*d*): δ 157.1, 157.0, 154.5 (dd, $J = 292.6, 287.5$ Hz), 149.2, 135.5 (t, $J = 4.1$ Hz), 135.1, 129.7, 129.6, 127.8, 125.4, 123.3, 123.2 (t, $J = 3.6$ Hz), 118.8, 117.6, 91.4 (dd, $J = 21.9, 13.0$ Hz), 34.3, 33.2, 31.3.

^{19}F NMR (376 MHz, Chloroform-*d*): δ -90.5 (d, $J = 38.1$ Hz), -90.8 (d, $J = 38.1$ Hz).

HRMS (ESI): m/z calcd for $[C_{25}H_{24}F_2O+Na^+]$: 401.1687, found 401.1692.

2-(2-(2,4-Dimethylphenyl)-3,3-difluoroallyl)naphthalene 2o



Prepared from triflone **1o** (39.2 mg, 0.1 mmol) and ethyl magnesium bromide (0.4 mL, 0.2 mmol, 0.5 M in THF solution) in THF 0.1 mL according to General Procedure F. The crude residue was purified by PTLC (Hexane only) to give **2o** (10.5 mg, 34%) as a colorless oil.

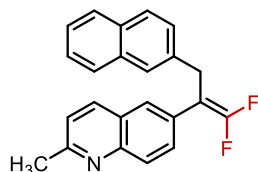
1H NMR (400 MHz, Chloroform-*d*): δ 7.83-7.76 (m, 1H), 7.76-7.67 (m, 2H), 7.49 (s, 1H), 7.49-7.38 (m, 2H), 7.23 (dd, $J = 8.5, 1.8$ Hz, 1H), 6.96 (s, 1H), 6.88 (dd, $J = 7.8, 1.8$ Hz, 1H), 6.83 (d, $J = 7.8$ Hz, 1H), 3.74 (s, 2H), 2.27 (s, 3H), 2.06 (s, 3H).

$^{13}C\{^1H\}$ NMR (176 MHz, Chloroform-*d*): δ 153.0 (dd, $J = 288.3, 286.2$ Hz), 137.5, 136.6, 135.8 (t, $J = 2.8$ Hz), 133.4, 132.2, 130.9, 129.7 (d, $J = 4.4$ Hz), 129.6 (d, $J = 3.4$ Hz), 127.9, 127.6, 127.5, 127.3, 127.2, 126.4, 125.9, 125.4, 90.8 (dd, $J = 20.9, 18.3$ Hz), 35.8 (d, $J = 2.3$ Hz), 21.0, 19.2.

^{19}F NMR (376 MHz, Chloroform-*d*): δ -91.0 (d, $J = 42.7$ Hz), -94.8 (d, $J = 43.8$ Hz).

HRMS (ESI): m/z calcd for $[C_{21}H_{18}F_2+Na^+]$: 331.1269, found 331.1266.

6-(1,1-Difluoro-3-(naphthalen-2-yl)prop-1-en-2-yl)-2-methylquinoline 2p



Prepared from triflone **1p** (215 mg, 0.5 mmol) and cyclohexyl magnesium bromide (1.75 mL, 1 mmol, 0.57 M in THF solution) according to General Procedure F. The crude residue was purified by column chromatography (EtOAc/Hexane = 1:4) to give **2p** (61 mg, 35%) as an orange oil.

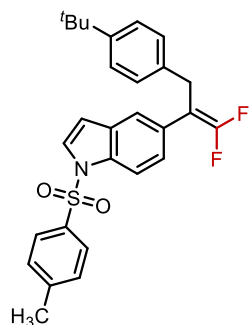
1H NMR (700 MHz, Chloroform-*d*): δ 7.95 (d, $J = 9.3$ Hz, 1H), 7.91 (d, $J = 8.4$ Hz, 1H), 7.77 (d, $J = 6.7$ Hz, 1H), 7.74 (d, $J = 8.4$ Hz, 1H), 7.71 (d, $J = 7.2$ Hz, 1H), 7.66 (d, $J = 6.0$ Hz, 2H), 7.62 (s, 1H), 7.45-7.38 (m, 2H), 7.33 (d, $J = 8.3$ Hz, 1H), 7.23 (d, $J = 8.4$ Hz, 1H), 3.99 (s, 2H), 2.71 (s, 3H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (176 MHz, Chloroform-*d*): δ 159.3, 154.7 (dd, $J = 292.7, 288.4$ Hz), 136.3, 135.7 (t, $J = 2.8$ Hz), 133.5, 132.3, 130.9, 129.6, 128.6, 128.3, 127.6, 127.5, 127.0 (t, $J = 3.7$ Hz), 126.6, 126.6, 126.2, 126.1, 125.5, 122.3, 91.4 (dd, $J = 22.0, 13.2$ Hz), 34.1, 25.2.

^{19}F NMR (376 MHz, Chloroform-*d*): δ -90.0 (d, $J = 37.9$ Hz), -90.9 (d, $J = 38.1$ Hz).

HRMS (ESI): m/z calcd for $[\text{C}_{23}\text{H}_{17}\text{F}_2\text{N}+\text{H}^+]$: 346.1402, found 346.1390.

5-(3-(4-(*tert*-Butyl)phenyl)-1,1-difluoroprop-1-en-2-yl)-1-tosyl-1H-indole 2q



Prepared from triflone **1q** (56.3 mg, 0.1 mmol) and cyclohexyl magnesium bromide (0.4 mL, 0.2 mmol, 0.49 M in THF solution) according to General Procedure F. The crude residue was purified by PTLC (EtOAc/Hexane = 1:10) to give **2q** (10.9 mg, 23%) as a colorless solid.

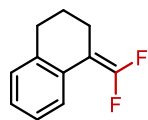
^1H NMR (400 MHz, Chloroform-*d*): δ 7.89 (d, $J = 8.7$ Hz, 1H), 7.76 (d, $J = 8.0$ Hz, 2H), 7.53 (d, $J = 3.7$ Hz, 1H), 7.43 (s, 1H), 7.28-7.19 (m, 5H), 7.08 (d, $J = 8.0$ Hz, 2H), 6.58 (d, $J = 3.8$ Hz, 1H), 3.71 (s, 2H), 2.34 (s, 3H), 1.28 (s, 9H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, Chloroform-*d*): δ 21.5, 31.3, 33.7, 34.3, 91.6 (q, $J = 13.3$ Hz), 108.9, 113.3, 121.2 (t, $J = 3.5$ Hz), 124.9 (t, $J = 3.3$ Hz), 125.4, 126.7, 126.8, 127.8, 128.9 (d, $J = 3.2$ Hz), 129.9, 130.7, 133.8, 135.3, 145.0, 149.2, 154.4 (q, $J = 287.8$ Hz), 149.2, 145.0, 135.3, 133.8, 130.7, 129.9, 128.9 (d, $J = 3.2$ Hz), 127.8, 126.8, 126.7, 125.4, 124.9 (t, $J = 3.3$ Hz), 121.2 (t, $J = 3.5$ Hz), 113.3, 108.9, 91.6 (q, $J = 13.3$ Hz), 34.3, 33.7, 31.3, 21.5.

^{19}F NMR (376 MHz, Chloroform-*d*): δ -91.5 (d, $J = 42.3$ Hz), -92.6 (d, $J = 41.4$ Hz).

HRMS (ESI): m/z calcd for $[\text{C}_{28}\text{H}_{27}\text{F}_2\text{NO}_2+\text{H}^+]$: 480.1803, found 480.1814.

1-(Difluoromethylene)-1,2,3,4-tetrahydronaphthalene 2r



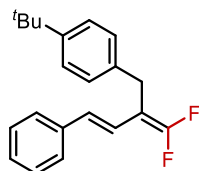
Prepared from triflone **1r** (132 mg, 0.5 mmol) and cyclohexyl magnesium bromide (2 mL, 1 mmol, 0.49 M in THF solution) according to General Procedure F. The crude residue was purified by column chromatography (Hexane only) to give **2r** (70.8 mg, 79%) as a colorless oil. The product is slowly decomposed under argon atmosphere at 0 °C, and in CDCl₃ to give unidentified products (δ 3.0-0.7 in ¹H NMR).

¹H NMR (400 MHz, Chloroform-*d*): δ 7.58 (d, *J* = 7.4 Hz, 1H), 7.24-7.05 (m, 3H), 2.80 (t, *J* = 6.4 Hz, 2H), 2.48 (ddd, *J* = 9.2, 5.6, 2.6 Hz, 2H), 1.85 (pd, *J* = 6.4, 1.8 Hz, 2H),

¹⁹F NMR (376 MHz, Chloroform-*d*): δ -88.6 (d, *J* = 41.6 Hz), -89.0 (d, *J* = 41.6 Hz).

Data were consistent with those reported in the literature.⁵

(*E*)-1-(*tert*-Butyl)-4-(2-(difluoromethylene)-4-phenylbut-3-en-1-yl)benzene 2s



Prepared from triflone **1s** (59.4 mg, 0.15 mmol) and cyclohexyl magnesium bromide (0.46 mL, 0.23 mmol, 0.49 M in THF solution) according to General Procedure F. The crude residue was purified by PTLC (Hexane only) to give **2s** (8 mg, 19%) as a colorless solid.

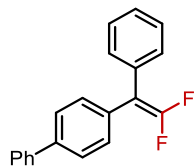
¹H NMR (400 MHz, Chloroform-*d*): δ 7.44-7.27 (m, 6H), 7.24-7.15 (m, 3H), 6.85 (dt, *J* = 16.2, 1.6 Hz, 1H), 6.49 (d, *J* = 16.2 Hz, 1H), 3.62 (s, 2H), 1.30 (s, 9H).

¹³C{¹H} NMR (176 MHz, Chloroform-*d*): δ 155.7 (dd, *J* = 297.4, 292.1 Hz), 149.2, 137.1, 135.3, 129.2 (dd, *J* = 11.7, 3.9 Hz), 128.6, 127.6, 127.5, 126.2, 125.5, 120.0, 91.6 (dd, *J* = 20.9, 12.3 Hz), 34.4, 31.4, 29.1.

¹⁹F NMR (376 MHz, Chloroform-*d*): δ -90.4 (d, *J* = 27.5 Hz), -90.6 (d, *J* = 27.6 Hz).

HRMS (EI): *m/z* calcd for [C₂₁H₂₂F₂]: 312.1689, found 312.1692.

4-(2,2-Difluoro-1-phenylvinyl)-1,1'-biphenyl 2t



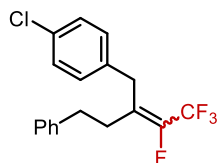
Prepared from triflone **1t** (75.3 mg, 0.2 mmol) and cyclohexyl magnesium bromide (0.82 mL, 0.4 mmol, 0.49 M in THF solution) according to General Procedure F. The crude residue was purified by column chromatography (Hexane only) to give **2t** (15.3 mg, 26%) as a colorless solid.

¹H NMR (400 MHz, Chloroform-*d*): δ 7.63-7.54 (m, 4H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.41-7.28 (m, 8H).

¹⁹F NMR (376 MHz, Chloroform-*d*): δ -88.3 (d, *J* = 31.5 Hz), -88.5 (d, *J* = 32.0 Hz).

Data were consistent with those reported in the literature.⁶

1-Chloro-4-(3,4,4,4-tetrafluoro-2-phenethylbut-2-en-1-yl)benzene **2u**



Prepared from triflone **1u** (38 mg, 0.09 mmol) and cyclohexyl magnesium bromide (0.33 mL, 0.18 mmol, 0.55 M in THF solution) according to General Procedure F. The crude residue was purified by PTLC (Hexane/EtOAc = 30:1) to give **2u** (24.3 mg, 79%, E/Z = 39:61) as a colorless oil.

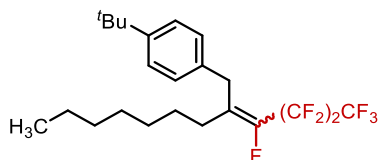
¹H NMR (700 MHz, Chloroform-*d*): δ 7.32-7.26 (m, 4H), 7.24-7.19 (m, 1H), 7.13-7.06 (m, 4H), 3.49 (s, 0.8H), 3.44 (s, 1.2H), 2.70-2.64 (m, 2H), 2.38-2.35 (m, 2H).

¹³C{¹H} NMR (176 MHz, Chloroform-*d*): δ 142.9 (qd, $J = 174.5, 37.9$ Hz, CF of only the major isomer is shown.), 140.4, 140.3, 132.9, 132.8, 130.2, 130.0, 128.9, 128.9, 128.6, 128.5, 128.2, 128.2, 126.4, 126.4, 126.0 (m), 125.7 (m), 119.6 (dq, $J = 273.2, 43.1$ Hz, CF₃ of only the major isomer is shown.), 34.9 (d, $J = 3.5$ Hz), 34.0 (d, $J = 7.2$ Hz), 33.6, 33.4 (m), 30.2 (d, $J = 5.1$ Hz), 29.7 (m).

¹⁹F NMR (376 MHz, Chloroform-*d*): δ -65.1 (d, $J = 10.1$ Hz, CF₃), -66.4 (d, $J = 7.3$ Hz, CF₃), -130.7 (CF), -131.9 (CF).

HRMS (EI): m/z calcd for [C₁₈H₁₅F₄Cl]: 342.0798, found 342.0788.

1-(*tert*-Butyl)-4-(2-(perfluorobutylidene)nonyl)benzene **2v**



Prepared from triflone **1v** (150 mg, 0.28 mmol) and cyclohexyl magnesium bromide (0.98 mL, 0.56 mmol, 0.57 M in THF solution) according to General Procedure F. The crude residue was purified by PTLC (Hexane only) to give **2v** (82.5 mg, 64%, E/Z = 41:59) as a yellow oil.

¹H NMR (700 MHz, Chloroform-*d*): δ 7.36-7.32 (m, 2H), 7.12-7.09 (m, 2H), 3.56 (s, 0.8H), 3.50 (s, 1.2H), 2.14-2.11 (m, 1.2H), 2.08-2.06 (m, 0.8H), 1.75-1.58 (m, 2H), 1.46-1.37 (m, 2H), 1.32 (s, 9H), 1.26-1.23 (m, 6H), 0.88 (t, $J = 7.0$ Hz, 3H),

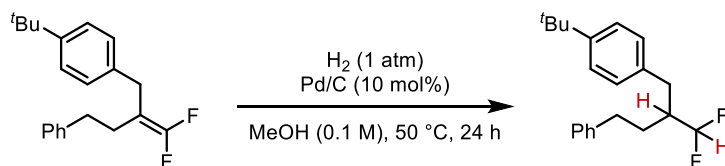
¹³C{¹H} NMR (176 MHz, Chloroform-*d*): δ 149.7, 149.7, 140.6 (td, $J = 245.6, 27.4$ Hz), 134.1, 133.8 (d, $J = 3.0$ Hz), 131.3 (d, $J = 9.2$ Hz), 131.0 (d, $J = 11.4$ Hz), 128.4, 128.4, 125.6, 125.5, 117.8 (tq, $J = 287.4, 33.5$ Hz, CF₃ of only the major isomer is shown.), 108.3-113.6 (m), 43.5, 34.4, 34.0 (d, $J = 8.2$ Hz), 33.0 (q, $J = 4.2$ Hz), 31.6, 31.3, 30.2, 29.4, 29.1, 28.9, 28.6 (d, $J = 6.4$ Hz), 28.4 (d, $J = 3.0$ Hz), 27.4 (d, $J = 4.6$ Hz), 27.3, 26.9 (d, $J = 2.4$ Hz).

^{19}F NMR (376 MHz, Chloroform-*d*): δ -81.7 (m, CF_3), -113.5 (CF_2), -114.5 (CF_2), -128.6 (m, CF_2), -128.7 (CF_2), -129.1 (CF), -129.9 (CF).

HRMS (ESI): m/z calcd for [$\text{C}_{23}\text{H}_{30}\text{F}_8+\text{Na}^+$]: 481.2112, found 481.2109.

6. Synthetic applications

6.1. Hydrogenation



To a reaction tube containing a magnetic stir bar under an atmosphere of hydrogen was added *gem*-difluoroalkene **2a** (62.8 mg, 0.2 mmol), palladium on charcoal (21 mg, 0.02 mmol) and THF (1 mL). The reaction mixture was stirred for 24 hours at 50 °C. After cooling, the reaction mixture was filtered through a Celite pad and concentrated under reduced pressure. The crude residue was purified by PTLC (Hexane only) to give 1-(*tert*-Butyl)-4-(2-(difluoromethyl)-4-phenylbutyl)benzene **3** (50.6 mg, 80%) as a colorless oil.

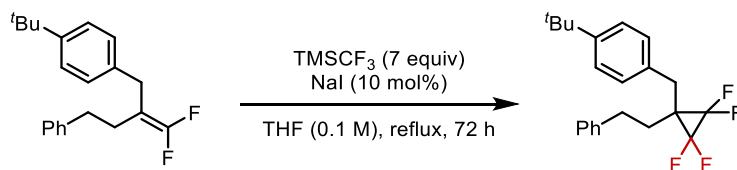
¹H NMR (400 MHz, Chloroform-*d*): δ 7.38-7.31 (m, 2H), 7.29 (td, $J = 7.9, 7.5, 1.7$ Hz, 2H), 7.21 (d, $J = 7.1$ Hz, 1H), 7.18-7.07 (m, 4H), 5.72 (td, $J = 56.6, 2.9$ Hz, 1H), 2.82 (dd, $J = 13.9, 7.1$ Hz, 1H), 2.74-2.64 (m, 3H), 2.20-2.09 (m, 1H), 2.01-1.88 (m, 1H), 1.79-1.65 (m, 1H), 1.35 (s, 9H).

¹³C{¹H} NMR (101 MHz, Chloroform-*d*): δ 149.3, 141.5, 135.5, 128.8, 128.4, 128.3, 126.0, 125.4, 118.1 (t, $J = 242.2$ Hz), 43.2 (t, $J = 18.9$ Hz), 34.4, 33.8 (dd, $J = 6.8, 3.6$ Hz), 33.1, 31.4, δ 28.5 (t, $J = 3.8$ Hz).

¹⁹F NMR (376 MHz, Chloroform-*d*): δ -124.1 (ddd, $J = 279.5, 57.2, 13.6$ Hz), -127.6 (ddd, $J = 279.5, 57.6, 20.4$ Hz).

HRMS (ESI): m/z calcd for [C₂₁H₂₆F₂+Na⁺]: 339.1895, found 339.1895.

6.2. Difluorocyclopropanation



To a reaction tube containing a magnetic stir bar was added *gem*-difluoroalkene **2a** (62.8 mg, 0.2 mmol), sodium iodide (15 mg, 0.1 mmol), TMSCF₃ (74 nL, 0.5 mmol) and THF (0.4 mL). After stirring for 3 and 48 hours at 80 °C, TMSCF₃ (74 nL, 0.5 mmol) was further added to the reaction mixture. The reaction mixture was diluted with CH₂Cl₂. The organic phase was washed with brine, 0.1M Na₂S₂O₃ aq., and brine again. Then the solution was dried over Na₂SO₄, filtered through a pad of silica to give 1-(*tert*-butyl)-4-((2,2,3,3-tetrafluoro-1-phenethyl)cyclopropyl)methyl)benzene **4** (45.8 mg, 70%) as a pale yellow solid.

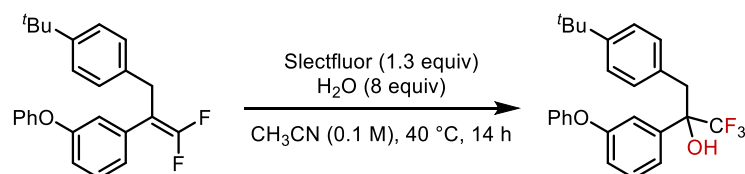
¹H NMR (700 MHz, Chloroform-*d*): δ 7.43-7.38 (m, 1H), 7.29-7.25 (m, 1H), 7.24-7.19 (m, 2H), 7.1-7.06 (m, 1H), 3.03 (s, 2H), 2.74-2.71 (m, 2H), 1.82-1.66 (m, 2H), 1.36 (s, 9H).

¹³C{¹H} NMR (176 MHz, Chloroform-*d*): δ 150.1, 140.6, 132.3, 128.7, 128.5, 128.2, 126.3, 125.8, 108.2 (tt, $J = 310.6, 11.6$ Hz), 39.2 (p, $J = 11.0$ Hz), 34.5, 31.8, 31.3, 28.0 (t, $J = 6.6$ Hz), 24.6 (t, $J = 5.6$ Hz).

¹⁹F NMR (376 MHz, Chloroform-*d*): δ -149.8 (dd, $J = 177.5, 11.5$ Hz), -152.7 (dd, $J = 176.3, 9.7$ Hz).

HRMS (ESI): m/z calcd for [C₂₂H₂₄F₄+H⁺]: 365.1887, found 365.1903.

6.3. Fluorohydroxylation



To a reaction tube containing a magnetic stir bar under an atmosphere of hydrogen was added *gem*-difluoroalkene **2n** (75.7 mg, 0.2 mmol), SelectfluorTM (92 mg, 0.26 mmol), and CH₃CN (2 mL). After adding water (32 mg, 1.6 mmol) to the mixture, the resulting reaction mixture was stirred for 24 hours at 40 °C. The reaction mixture was allowed to cool to room temperature and dried under reduced pressure. The crude residue was purified by PTLC (EtOAc/Hexane = 1:5) to give product **5** (34 mg, 41%) as a colorless solid.

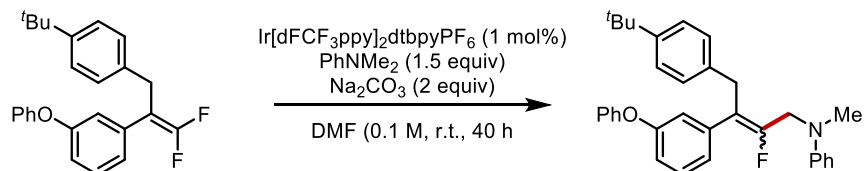
¹H NMR (700 MHz, Chloroform-*d*): δ 7.39-7.30 (m, 4H), 7.30-7.24 (m, 3H), 7.11 (t, $J = 7.0$ Hz, 1H), 7.00 (d, $J = 7.8$ Hz, 1H), 6.96 (d, $J = 7.6$ Hz, 2H), 6.93 (d, $J = 8.2$ Hz, 2H), 3.40 (d, $J = 14.1$ Hz, 1H), 3.36 (d, $J = 14.1$ Hz, 1H), 2.45 (s, 1H), 1.29 (s, 9H).

¹³C{¹H} NMR (176 MHz, Chloroform-*d*): δ 157.1, 157.0, 150.6, 130.4, 129.7, 129.6, 129.5, 125.5, 125.4 (q, $J = 285.7$ Hz), 123.3, 121.5, 119.0, 118.6, 117.8, 76.8 (q, $J = 28.3$ Hz), 41.2, 34.4, 31.2.

¹⁹F NMR (376 MHz, Chloroform-*d*): δ -79.3.

HRMS (ESI): m/z calcd for [C₂₅H₂₅F₃O₂+Na⁺]: 437.1699, found 437.1700.

6.4. Defluoromethylation



To a 1 dram vial containing a magnetic stir bar was added *gem*-difluoroalkene **2n** (75.7 mg, 0.2 mmol), Ir[dFCF₃ppy]₂dtbpyPF₆ (2.2 mg, 0.002 mmol), *N,N*-dimethyl aniline (37.9 μ L, 0.3 mmol), Na₂CO₃ (31.8 mg,

0.3 mmol), and DMF (0.6 mL). After the mixture was degassed through freeze-pump-thaw cycling, the resulting reaction mixture was stirred for 30 hours upon irradiation by blue LED. Water was added to the reaction mixture, and the solution was extracted with ethyl acetate four times. The combined organic phase was dried over Na₂SO₄, and concentrated under reduced pressure. The crude residue was purified by PTLC (EtOAc/Hexane = 1:10) to give product **6** (71.7 mg, 75%, E/Z = 74:26) as a colorless oil.

¹H NMR (400 MHz, Chloroform-*d*): δ 7.36-7.11 (m, 7H), 7.10 (t, *J* = 7.4 Hz, 1H), 7.05 (t, *J* = 7.6 Hz, 1H), 7.01-6.91 (m, 4.2H), 6.88-6.65 (m, 3.4H), 6.57 (d, *J* = 7.7 Hz, 1.4H), 4.26 (d, *J* = 18.5 Hz, 0.5H), 4.05 (d, *J* = 18.9 Hz, 1.5H), 3.77 (s, 0.5H), 3.68 (d, *J* = 3.0 Hz, 1.5H), 2.99 (s, 0.8H), 2.92 (s, 2.2H), 1.29 (s, 2.2H), 1.28 (s, 6.8H).

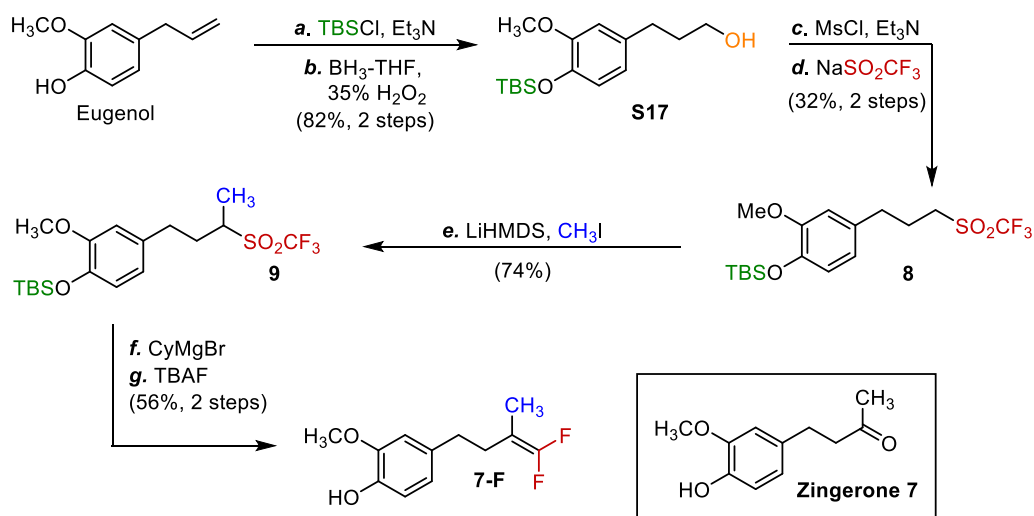
¹³C{¹H} NMR (176 MHz, Chloroform-*d*, major isomer): δ 157.0, 157.0, 154.1 (d, *J* = 257.7 Hz), 149.0, 148.8, 139.4 (d, *J* = 8.1 Hz), 135.5 (d, *J* = 1.6 Hz), 129.7, 129.6, 128.9, 128.3, 125.1, 124.2 (d, *J* = 2.7 Hz), 123.3, 121.5 (d, *J* = 17.9 Hz), 119.8 (d, *J* = 2.8 Hz), 118.7, 118.0, 117.1 113.0, 50.4 (d, *J* = 26.5 Hz), 38.6, 36.0 (d, *J* = 5.8 Hz), 34.3, 31.3.

¹³C NMR (176 MHz, Chloroform-*d*, minor isomer): δ 157.3, 156.6, 154.2 (d, *J* = 259.1 Hz), 149.6, 149.2, 138.5, 135.3 (d, *J* = 2.8 Hz), 129.6, 129.2, 129.1, 127.8, 125.4, 123.8 (d, *J* = 3.7 Hz), 122.9, 120.6 (d, *J* = 41.8 Hz), 119.6 (d, *J* = 3.3 Hz), 118.5, 117.7, 117.6, 113.4, 50.8 (d, *J* = 27.7 Hz), 38.3, 36.0 (d, *J* = 4.3 Hz), 34.3, 31.2.

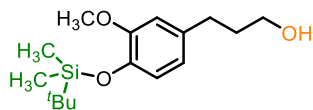
¹⁹F NMR (376 MHz, Chloroform-*d*): δ -110.1 (t, *J* = 18.7 Hz, minor), -115.0 (t, *J* = 18.9 Hz, major).

HRMS (ESI): *m/z* calcd for [C₃₃H₃₄FNO+H⁺]: 480.2697, found 480.2691.

6.5. Synthesis of Fluorinated Analogue of Zingerone



3-(4-((tert-Butyldimethylsilyl)oxy)-3-methoxyphenyl)propan-1-ol **S17**



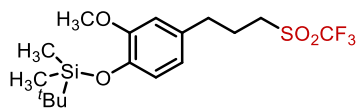
To a 50 mL flask containing a magnetic stir bar under an atmosphere of dry argon was added eugenol (1.54 mL, 10 mmol), *tert*-butyldimethylsilyl chloride (1.58 g, 10.5 mmol) and CH₂Cl₂ (10 mL). Imidazole was added to the solution at 0 °C, and the reaction mixture was stirred at room temperature for 3 h. Upon reaction completion, the reaction was quenched with water, and extracted with CH₂Cl₂ two times to give TBS-protected eugenol. The crude product was added to a 250 mL round-bottom flask containing a magnetic stir bar under an atmosphere of dry argon. Then, to the flask was added THF (58 mL) and BH₃-THF (20 mL, 1.0 M in THF, 20 mmol) at 0 °C. The reaction mixture was stirred at the same temperature for 1 h, and allowed to warm to room temperature. After stirring for an additional 1 h, 1.0 M NaOH aq. (25 mL, 25 mmol) was added to the mixture at 0 °C, thereafter 35% H₂O₂ solution (24 mL) was added dropwise to the resulting mixture. After stirring the reaction for 30 min at 0 °C and 1 h at room temperature, the aqueous layer was extracted with diethyl ether three times. The combined organic layer was washed with brine. The organic layer was dried over Na₂SO₄, filtered, and concentrated under reduced pressure. The crude mixture was purified by column chromatography (EtOAc/Hexane = 1:5) to give alcohol **S17** (2.43 g, 82% over two steps, linear/branched = 92:8) as a pale yellow oil.

¹H NMR (400 MHz, Chloroform-*d*): δ 6.76 (d, *J* = 8.0 Hz, 1H), 6.69 (d, *J* = 2.0 Hz, 1H), 6.64 (dd, *J* = 8.0, 2.0 Hz, 1H), 3.78 (s, 3H), 3.65 (t, *J* = 6.4 Hz, 2H), 2.63 (t, *J* = 7.7 Hz, 2H), 1.93-1.80 (m, 2H), 1.53 (br, 1H), 1.00 (d, *J* = 1.4 Hz, 9H), 0.15 (d, *J* = 1.4 Hz, 6H).

¹³C{¹H} NMR (101 MHz, Chloroform-*d*): δ 150.7, 143.0, 135.2, 120.7, 120.4, 112.5, 62.2, 55.4, 34.3, 31.7, 25.7, 18.4, -4.7.

HRMS (ESI): *m/z* calcd for [C₁₆H₂₈O₃Si+H⁺]: 297.1881, found 297.1866.

tert*-Butyl(2-methoxy-4-(3-((trifluoromethyl)sulfonyl)propyl)phenoxy)dimethylsilane **8*



To a 50 mL round-bottom flask containing a magnetic stir bar under an atmosphere of dry argon was added alcohol **S17** (364 mg, 2 mmol) and CH₂Cl₂ (4 mL). Triethylamine (0.3 mL, 2.2 mmol) was added to the solution at 0 °C, and the reaction mixture was stirred for 10 min. Then methanesulfonyl chloride (0.17 mL, 2.2 mmol) was added dropwise. After stirring the reaction for 3 h, the reaction was quenched with water. The organic layer was washed with *sat.* NaHCO₃ aq. and brine. The organic layer was dried over Na₂SO₄, filtered, and concentrated under reduced pressure to give the mesylated intermediate. To the 100 mL round bottom flask with the crude mixture was added NaSO₂CF₃ (936 mg, 6 mmol) and dimethylacetamide (10 mL). Upon heating the

reaction mixture at 100 °C for 17 h, the reaction was quenched with water at room temperature. The reaction was diluted with ethyl acetate-hexane solution (1:3). The organic layer was washed with water two times and brine, dried over Na₂SO₄, filtered and concentrated under reduced pressure. The crude residue was purified by silica gel column chromatography (EtOAc/Hexane = 1:5) to give primary alkyl triflone **8** (261 mg, 32% over two steps) as a colorless oil.

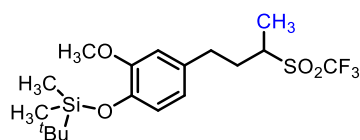
¹H NMR (700 MHz, Chloroform-*d*): δ 6.79 (d, *J* = 8.0 Hz, 1H), 6.66 (d, *J* = 2.1 Hz, 1H), 6.61 (dd, *J* = 8.0, 2.1 Hz, 1H), 3.80 (s, 3H), 3.19-3.14 (m, 2H), 2.75 (t, *J* = 7.4 Hz, 2H), 2.24 (p, *J* = 7.4 Hz, 2H), 1.00 (s, 9H), 0.15 (s, 6H).

¹³C{¹H} NMR (176 MHz, Chloroform-*d*): δ 151.1, 143.9, 132.1, 121.1, 120.6, 119.4 (q, *J* = 326.9 Hz), 112.2, 55.5, 48.6, 33.6, 25.7, 22.4, 18.4, -4.7.

¹⁹F NMR (376 MHz, Chloroform-*d*): δ -79.2.

HRMS (ESI): *m/z* calcd for [C₁₇H₂₇F₃O₄SSi+H⁺]: 413.1424, found 413.1438.

tert*-Butyl(2-methoxy-4-(3-((trifluoromethyl)sulfonyl)butyl)phenoxy)dimethylsilane **9*



A 4 dram vial containing a magnetic stirring bar was flame-dried under vacuum and filled with argon after cooling to room temperature. To the vial were added primary alkyl triflone **7** (148 mg, 0.35 mmol) and dry THF (2 mL). A solution of LiHMDS (59 mg, 0.35 mmol, 0.35 M in THF) was added dropwise to the reaction mixture at 0 °C under argon. After stirring for 30 min, the reaction mixture was added to a 15 mL Schlenk tube with methyl iodide (10 equiv) in THF (2 mL) at -78 °C, and the reaction was allowed to warm to room temperature. After stirring for 17 h, the reaction was quenched with NH₄Cl (sat. aq.) and diluted with ethyl acetate. The aqueous layer was extracted with ethyl acetate three times, and the combined organic layer was washed with brine. The organic layer was dried over Na₂SO₄, filtered, and concentrated under reduced to give secondary alkyl triflone **9** (110 mg, 74%, mixture of starting triflone **8**, **9**, and dimethylated product = 0.13:1.0:0.10) as a pale yellow oil. The crude mixture was used in next step without further purification.

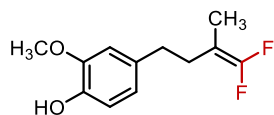
¹H NMR (700 MHz, Chloroform-*d*): δ 6.78 (d, *J* = 8.0 Hz, 1H), 6.66 (d, *J* = 2.2 Hz, 1H), 6.62 (dd, *J* = 8.0, 2.2 Hz, 1H), 3.80 (s, 3H), 3.33-3.25 (m, 1H), 2.86 (ddd, *J* = 14.1, 8.8, 5.4 Hz, 1H), 2.62 (dt, *J* = 14.1, 8.1 Hz, 1H), 2.43 (ddt, *J* = 17.0, 12.4, 5.9 Hz, 1H), 1.97-1.89 (m, 1H), 1.51 (d, *J* = 7.0 Hz, 3H), 0.99 (s, 9H), 0.15 (s, 6H).

¹³C{¹H} NMR (176 MHz, Chloroform-*d*): δ 151.1, 143.8, 132.4, 121.0, 120.5, 119.9 (q, *J* = 329.3 Hz), 112.2, 56.0, 55.5, 31.7, 29.8, 25.7, 18.4, 12.7, -4.7, -4.7.

¹⁹F NMR (376 MHz, Chloroform-*d*): δ -75.2.

HRMS (ESI): *m/z* calcd for [C₁₈H₂₉F₃O₄SSi+Na⁺]: 449.1400, found 449.1411.

4-(4,4-Difluoro-3-methylbut-3-en-1-yl)-2-methoxyphenol 7-F



To a flame-dried 1 dram vial containing a magnetic stir bar under an atmosphere of dry argon was added triflone **9** (85 mg, 0.2 mmol) and cyclohexyl magnesium bromide (0.73 mL, 0.4 mmol, 0.57 M in THF). The reaction mixture was stirred at 80 °C for 5 hours. The reaction mixture was cooled to room temperature, quenched with NH₄Cl (sat. aq.) and diluted with ethyl acetate. The resulting solution was passed through a small pad of silica gel, and washed with ethyl acetate three times. The crude reaction mixture was concentrated under reduced pressure to give the intermediate TBS-protected *gem*-difluoroalkene.

To a flame-dried 1 dram vial containing a magnetic stir bar under an atmosphere of dry argon was added the crude product, and TBAF (0.6 mL, 0.6 mmol, 1M in THF) at 0 °C. After stirring for 1 hour, the reaction mixture was concentrated under reduced pressure, and purified by PTLC (Hexane only) to give *gem*-difluoroalkene **7-F** (26 mg, 57%, over 2 steps) as a colorless oil.

¹H NMR (700 MHz, Chloroform-*d*): δ 6.84 (d, *J* = 8.6 Hz, 1H), 6.68-6.67 (m, 2H), 5.49 (s, 1H), 3.88 (s, 3H), 2.64 (t, *J* = 8.0 Hz, 2H), 2.24 (tt, *J* = 8.0, 2.2 Hz, 2H), 1.58 (t, *J* = 3.1 Hz, 3H),

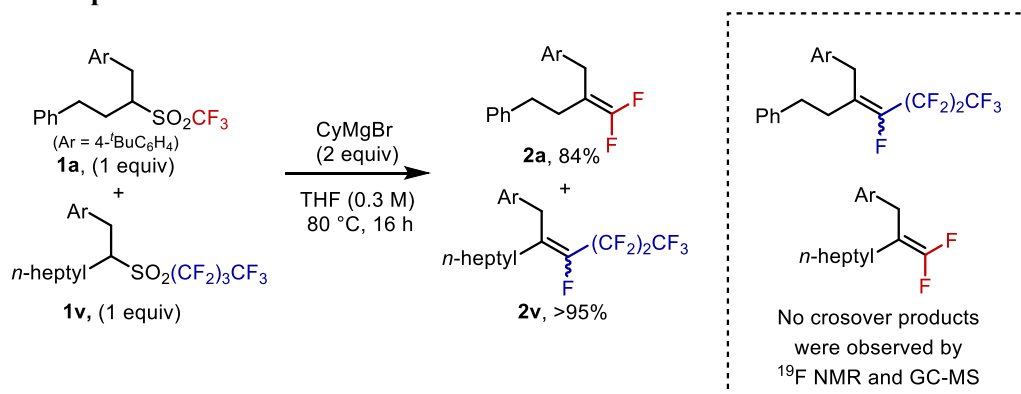
¹³C{¹H} NMR (176 MHz, Chloroform-*d*): δ 153.0 (t, *J* = 281.1 Hz), 146.4, 143.8, 133.2, 120.9, 114.2, 110.8, 84.2 (dd, *J* = 19.5, 18.3 Hz), 55.9, 33.2 (t, *J* = 2.8 Hz), 30.4 (d, *J* = 2.4 Hz), 12.0.

¹⁹F NMR (376 MHz, Chloroform-*d*): δ -97.2 (d, *J* = 58.2 Hz), -97.6 (d, *J* = 58.2 Hz).

HRMS (ESI): *m/z* calcd for [C₁₂H₁₄F₂O₂+Na⁺]: 251.0854, found 251.0846.

7. Mechanistic Study

7.1 Crossover experiment



To a flame-dried 1 dram vial containing a magnetic stir bar under an atmosphere of dry argon was added **1a** (39.8 mg, 0.1 mmol), **1v** (54.2 mg, 0.1 mmol), and cyclohexyl magnesium bromide (0.7 mL, 0.4 mmol, 0.57 M in THF). The reaction mixture was stirred at $80\text{ }^\circ\text{C}$ for 16 hours. The reaction mixture was cooled to room temperature, quenched with sat. NH_4Cl , and diluted with ethyl acetate. Then, 1,3,5-trimethoxybenzene (1.18 mg, 0.078 mmol) was added to the mixture as an internal standard. The resulting solution was passed through a small pad of silica gel, and washed with ethyl acetate three times. The crude reaction mixture was analyzed by ^1H , ^{19}F NMR, and GC-MS showing that alkenes **2a** and **2v** were obtained in 84% and >95%, respectively, without formation of any crossover products.

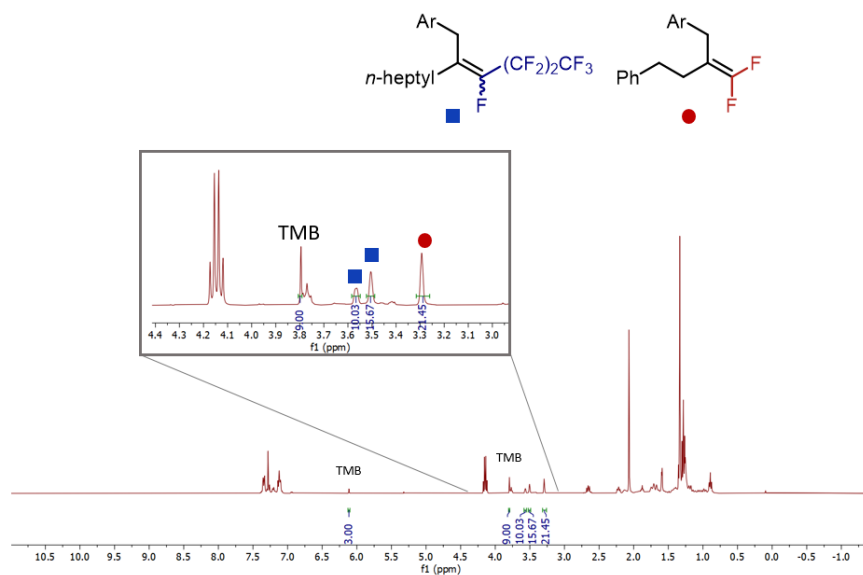


Figure S1. ^1H NMR spectra of the crude mixture for the crossover experiment (TMB = 1,3,5-trimethoxybenzene).

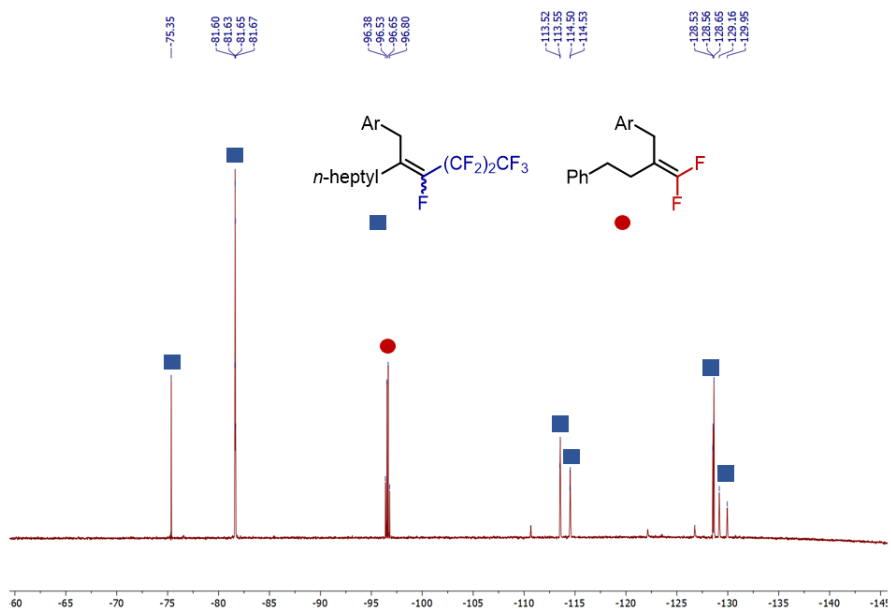


Figure S2. ^{19}F NMR spectra of the crude mixture for the crossover experiment.

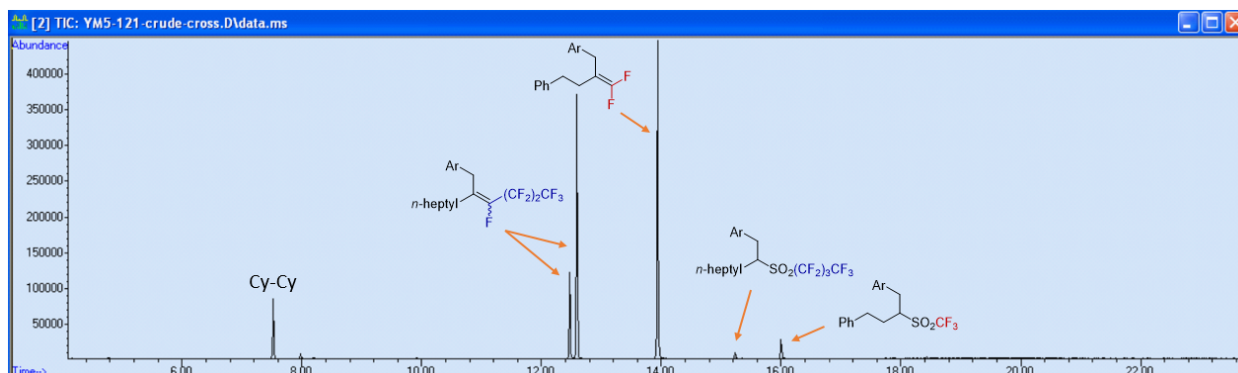
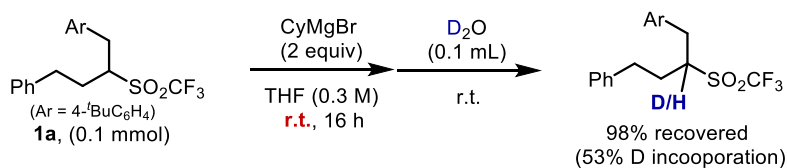


Figure S3. GC-MS spectra of the crude mixture for the crossover experiment.

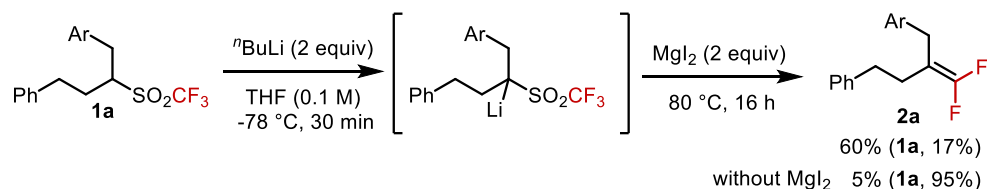
7.2. α -Deuteration of triflone **1a** at room temperature



To a flame-dried 1 dram vial containing a magnetic stir bar under an atmosphere of dry argon was added triflone **1a** (39.8 mg, 0.1 mmol), and cyclohexyl magnesium bromide (0.35 mL, 0.2 mmol, 0.57 M in THF). The reaction mixture was stirred at room temperature for 16 hours. The reaction mixture was quenched with D_2O (0.1 mmol), and diluted with ethyl acetate. Then, 1,3,5-trimethoxybenzene (10.8 mg) was added to the mixture as an internal standard. The resulting solution was passed through a small pad of silica gel, and washed with ethyl acetate three

times. The crude reaction mixture was analyzed by ^1H NMR showing **1a** was recovered in 98% (53% deuterium incorporation). This result indicates that the first step in the *gem*-difluoroolefination process is likely α -deprotonation of the triflone by the Grignard reagent.

7.3. Effect of Magnesium cation



2 Equivalent of *n*-BuLi without MgI_2

To a flame-dried 1 dram vial containing a magnetic stir bar under an atmosphere of dry argon was added triflone **1a** (39.8 mg, 0.1 mmol), and *n*-butyllithium (0.08 mL, 0.2 mmol, 2.5 M in hexane). The reaction mixture was stirred at -78 $^\circ\text{C}$ for 30 min, after which time it turned pale green. The reaction was heated at 80 $^\circ\text{C}$ for 16 hours. The reaction mixture was cooled to room temperature, quenched with NH_4Cl (sat. aq.), and diluted with ethyl acetate. Then, 1,3,5-trimethoxybenzene (1.3 mg) was added to the mixture as an internal standard. The resulting solution was passed through a small pad of silica gel, and washed with ethyl acetate three times. The crude reaction mixture was analyzed by ^1H NMR, which indicated that **2a** was obtained in 5% along with 95% of recovered **1a**.

2 Equivalent of *n*-BuLi and 2 equivalent of MgI_2

To a flame-dried 1 dram vial containing a magnetic stir bar under an atmosphere of dry argon was added triflone **1a** (39.8 mg, 0.1 mmol), and *n*-butyllithium (0.08 mL, 0.2 mmol, 2.5 M in hexane). The reaction mixture was stirred at -78 $^\circ\text{C}$ for 30 min, after which time it turned pale green. Magnesium iodide (55.6 mg, 0.2 mmol) was added to the solution at -78 $^\circ\text{C}$. The reaction became brown, and was heated at 80 $^\circ\text{C}$ for 16 hours. The reaction mixture was cooled to room temperature, quenched with NH_4Cl (sat. aq.), and diluted with ethyl acetate. Then, 1,3,5-trimethoxybenzene (9.0 mg) was added to the mixture as an internal standard. The resulting solution was passed through a small pad of silica gel, washed with ethyl acetate three times. The crude reaction mixture was analyzed by ^1H NMR showing **2a** was obtained in 60% along with 24% of recovered **1a**.

1 Equivalent of *n*-BuLi and 2 equivalent of MgI_2

To a flame-dried 1 dram vial containing a magnetic stir bar under an atmosphere of dry argon was added triflone **1a** (39.8 mg, 0.1 mmol), and *n*-butyllithium (0.04 mL, 0.1 mmol, 2.5 M in hexane). The reaction mixture was stirred at -78 $^\circ\text{C}$ for 30 min. Magnesium iodide (55.6 mg, 0.2 mmol) was added to the solution at -78 $^\circ\text{C}$. The reaction became a white suspension from the originally colorless solution, and was heated at 80 $^\circ\text{C}$ for 16 hours. The reaction mixture was cooled to room temperature, quenched with NH_4Cl (sat. aq.), and diluted with ethyl

acetate. Then, 1,3,5-trimethoxybenzene (9.3 mg) was added to the mixture as an internal standard. The resulting solution was passed through a small pad of silica gel, washed with ethyl acetate three times. The crude reaction mixture was analyzed by ^1H NMR showing **2a** was obtained in 37% along with 58% of recovered **1a**.

7.4. NMR tracking

To a flame-dried J-young tube under an atmosphere of dry argon was added triflone **1a** (30 mg, 0.125 mmol), and cyclohexyl magnesium bromide (0.50 mL, 0.25 mmol, 0.57 M in THF). The reaction mixture was heated to 80 °C. The reaction was monitored by ^{19}F NMR. After 1h, signals corresponding to **2a** and a MgF-containing species⁷ appeared at -98 and -188 ppm, respectively. The signal attributed to the MgF species did not increase during the reaction, presumably, due to its low solubility in THF.

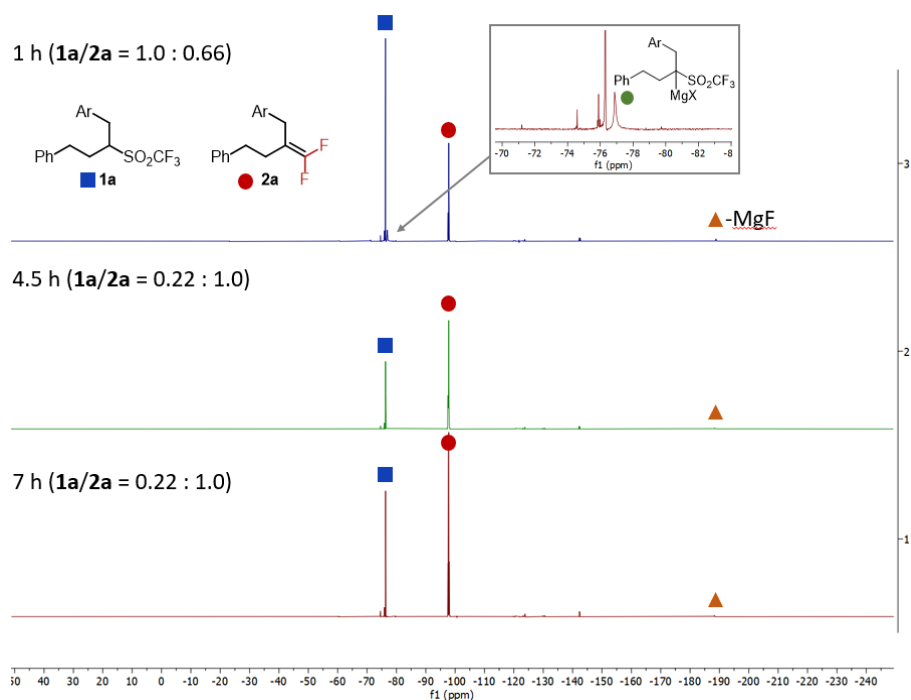
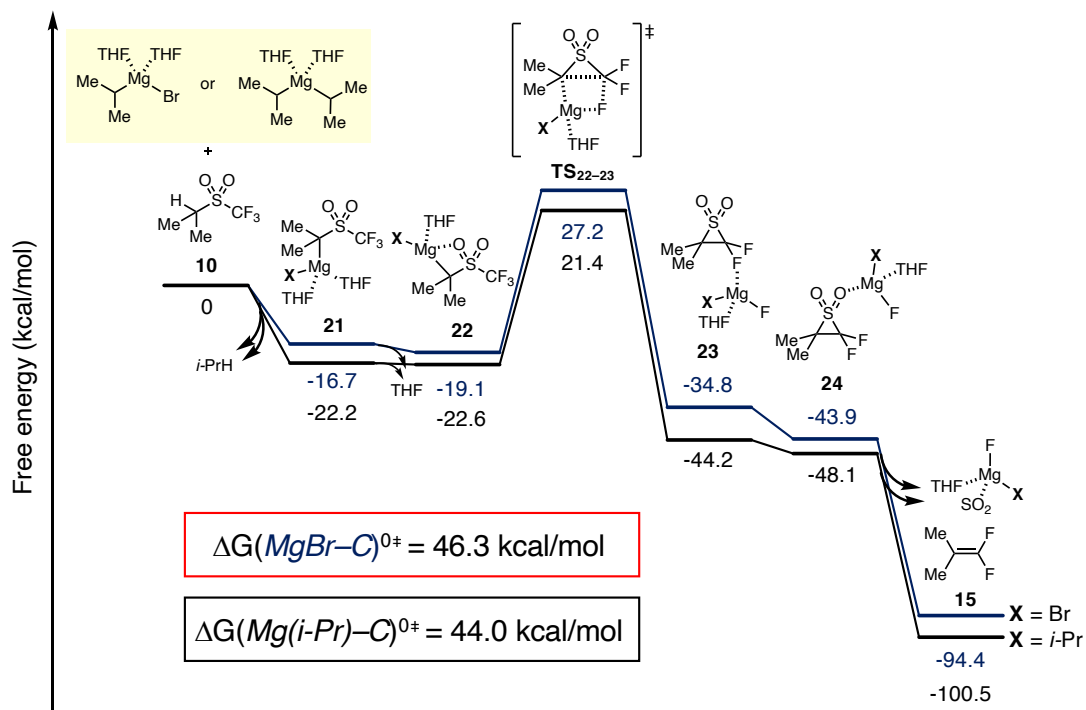


Figure S4. Reaction tracking by ^{19}F NMR spectroscopy.

8. Computational Studies

8.1. Computational Methods

All calculations were performed using Gaussian 09. Geometry optimizations were performed using the B3LYP functional using the 6-31+G(d) basis set all atoms. Stationary points were verified by vibrational frequency analysis. Solvation effects of THF were evaluated with the IEFPCM calculation with radii and non-electrostatic terms for Truhlar and coworkers' SMD solvation model. Thermal corrections were taken from gas phase optimized structures at 353.15K. For free energy calculations, single point calculations were performed using the SCSMP2 (cc-pVDZ basis set for H, C, Mg, and S atoms, and aug-cc-pVDZ basis set for other atoms) with the solvation model.⁷



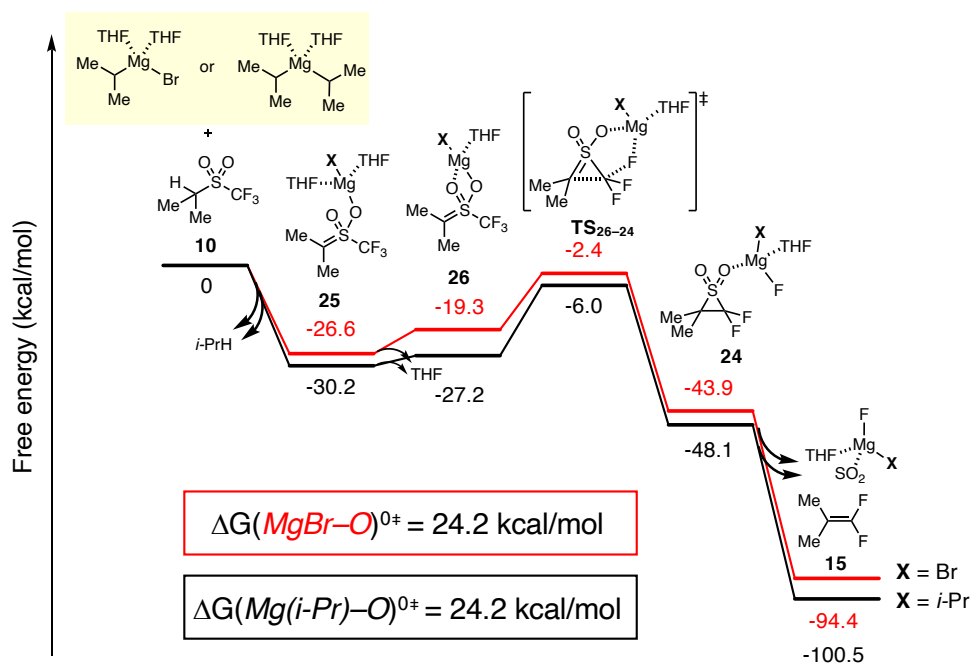
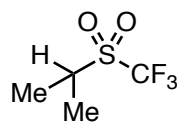


Figure S5. Energy profile for Ramberg-Bäcklund reaction with *i*-Pr₂Mg(THF)₂.

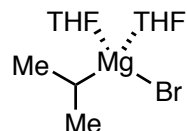
Coordinates of calculated structure for 10



C	-1.50184800	0.46545500	-0.48376200
H	-1.18625900	0.59686400	-1.52428800
S	-0.21110100	-0.65344100	0.22130600
O	-0.33267100	-0.70874000	1.68339200
O	-0.14563900	-1.87265800	-0.59385400
C	-2.82478000	-0.31133300	-0.43088000
H	-3.59934600	0.29933200	-0.90677600
H	-2.75817200	-1.26246800	-0.96475100
H	-3.12827100	-0.50357300	0.60298600
C	-1.55603400	1.80195200	0.25730500
H	-1.76994300	1.65169100	1.31947300
H	-0.62921400	2.37430000	0.16482600
H	-2.36340000	2.40293500	-0.17550400
C	1.43152100	0.24590600	-0.13211600
F	1.43458300	0.72133500	-1.39219600

F	1.61523800	1.27064300	0.71128100
F	2.43301900	-0.62139100	0.01019800

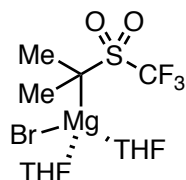
Coordinates of calculated structure for *i*-PrMgBr(THF)₂



C	-1.38870500	3.24055600	-0.63553100
C	-0.03805600	2.52547400	-0.83647800
C	1.10172400	3.47394200	-0.41762300
H	-2.24075700	2.64747800	-1.00143400
H	0.07113500	2.35485000	-1.92581900
H	2.09964400	3.06144800	-0.63111000
H	1.05232600	4.45480500	-0.92605900
H	-1.43867500	4.21639900	-1.15333000
O	-1.65417700	-0.53460500	-0.44567800
O	1.48418200	-0.58964300	-0.81213600
Br	0.23297900	-0.10186700	2.51445800
Mg	0.01900600	0.61540100	0.14621600
C	-2.17313100	-0.48934100	-1.80600600
H	-1.58468300	-1.18763800	-2.41298700
H	-2.03340600	0.52571400	-2.18533500
C	-3.63562300	-0.91968300	-1.69421300
H	-3.99832900	-1.39078500	-2.61234400
H	-4.27296500	-0.05408200	-1.48041300
C	-3.60459500	-1.87466400	-0.48991700
H	-3.23326600	-2.86138400	-0.79136000
H	-4.58399600	-2.00863600	-0.02178800
C	-2.61170800	-1.18960000	0.44494600
H	-3.08638400	-0.41751100	1.05915700
H	-2.04916300	-1.86032400	1.09473100
C	2.44387200	-0.04487100	-1.75945000
H	2.41638400	1.04164600	-1.66558100
H	2.13155000	-0.32746500	-2.77307700
C	3.76945600	-0.69040900	-1.37296700

H	4.21444500	-0.16015100	-0.52354300
H	4.48980900	-0.68886400	-2.19627800
C	3.32649700	-2.10449300	-0.96088300
H	4.03780100	-2.59847100	-0.29310400
H	3.20277900	-2.73633600	-1.84818500
C	1.97715500	-1.86010800	-0.27423700
H	1.23099000	-2.62909600	-0.49332200
H	2.05694300	-1.73720900	0.80826400
H	-1.58253800	3.44684200	0.42740400
H	1.07663900	3.68248800	0.66155200

Coordinates of calculated structure for 11



C	-1.06215500	-1.40865500	-0.96236500
S	-2.67750900	-1.35594500	-0.17620600
O	-3.80202500	-1.57932500	-1.10648400
O	-2.64431400	-2.05688100	1.11842000
C	-0.61594500	-2.89108800	-0.85865500
H	0.34906500	-2.99940000	-1.36733000
H	-0.50128800	-3.22495100	0.17647100
H	-1.31088700	-3.58046000	-1.36140800
C	-1.21181100	-1.02262200	-2.44723900
H	-1.82820300	-1.73986400	-3.00642900
H	-1.66005600	-0.03481900	-2.59273100
H	-0.21616800	-1.00838300	-2.91046700
C	-2.90539300	0.45859400	0.33154400
F	-1.91778500	0.85260400	1.17463000
F	-2.87731700	1.29614100	-0.73325900
F	-4.07285100	0.61475800	0.95542400
Mg	0.50165300	-0.25150100	0.09385600
O	2.26448100	-0.71330800	-1.01605500
O	0.55250900	1.80126700	-0.32005900

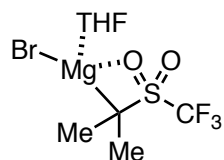
Br	1.49901400	-0.42115000	2.32874900
C	3.27697600	0.31828800	-1.22755000
C	2.92019600	-2.00295200	-0.76350200
C	0.15313200	2.46775900	-1.55675400
C	0.74808500	2.79537100	0.74908500
H	3.30992500	0.94847600	-0.33282500
H	2.96373600	0.91484300	-2.08800400
C	4.58747500	-0.43565200	-1.43769700
C	4.39339500	-1.67214200	-0.54767200
H	2.75686700	-2.62863400	-1.64717400
H	2.44533300	-2.45545100	0.10927700
H	-0.65883800	1.89254300	-2.00258800
H	1.01580600	2.46706200	-2.23431300
C	-0.24150300	3.88070700	-1.13795300
C	0.70691400	4.14664500	0.04150100
H	1.69211200	2.56324200	1.24289200
H	-0.06786300	2.67268500	1.46571000
H	5.45468000	0.16751800	-1.15413300
H	4.70176900	-0.72697900	-2.48833800
H	4.57084200	-1.42191000	0.50338500
H	5.04484200	-2.50669900	-0.82200600
H	-1.28538200	3.89846500	-0.80657600
H	-0.12780200	4.59846800	-1.95523700
H	0.35344500	4.94012700	0.70567200
H	1.70305000	4.42642200	-0.32120800

Coordinates of calculated structure for *i*-PrH

C	0.00000600	0.58685500	-0.00000900
H	-0.00000100	1.24712400	-0.87797700
C	-1.27740400	-0.26005700	0.00002200
H	-2.17654200	0.36706400	-0.00046800
H	-1.32162900	-0.90788300	-0.88441000
H	-1.32194500	-0.90698600	0.88508000
C	1.27739900	-0.26005900	0.00002100
H	1.32157600	-0.90794800	-0.88436500

H	2.17653800	0.36706100	-0.00055300
H	1.32198400	-0.90693700	0.88511600
H	0.00000600	1.24807100	0.87736900

Coordinates of calculated structure for 12



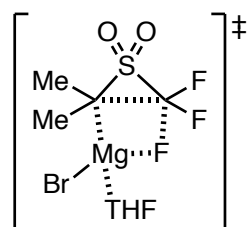
C	1.15829700	-1.29724900	0.93548300
S	1.97190700	-0.58943100	-0.52175100
O	3.02537300	-1.34438200	-1.21622500
C	1.29959800	-2.82729900	0.79359200
H	0.66615200	-3.28205900	1.56366000
H	0.95041100	-3.21062000	-0.17125600
H	2.32923900	-3.18129200	0.94479000
C	1.74217700	-0.82390200	2.27213500
H	2.77614900	-1.15601100	2.44810700
H	1.69639800	0.25948700	2.41417500
H	1.12673000	-1.27089400	3.06178100
C	2.78018500	1.08185000	-0.09779400
F	1.91459300	1.90023700	0.53277100
F	3.84959700	0.89956400	0.68538400
F	3.16378700	1.66513200	-1.23549500
O	0.78844800	-0.14665100	-1.37859200
Mg	-0.73936700	-0.60542500	-0.02460300
O	-1.43123500	1.30629400	0.33052600
Br	-2.74511900	-1.92749300	-0.34408200
C	-1.25671800	2.41232100	-0.61416900
C	-2.62077900	1.53829600	1.16311300
H	-0.91769800	1.98902100	-1.56142100
H	-0.47995000	3.07348700	-0.21602700
C	-2.62159800	3.08754800	-0.66715500
C	-3.11609900	2.93356700	0.78051400
H	-2.31282800	1.45103100	2.20832700

H	-3.33818200	0.74927100	0.92286000
H	-3.28274600	2.55631400	-1.36061100
H	-2.55157800	4.13099700	-0.98730400
H	-4.20245000	3.01563600	0.87267800
H	-2.66145000	3.69661600	1.42244800

Coordinates of calculated structure for THF

O	-0.00010000	-1.25291500	-0.00023000
C	-1.17062300	-0.42902300	-0.13130800
H	-1.94689000	-0.82549300	0.53107700
H	-1.53500700	-0.48732700	-1.16692400
C	-0.73405100	0.99697400	0.22621100
H	-0.79914500	1.15795200	1.30906700
H	-1.34238400	1.76087000	-0.26787500
C	0.73431800	0.99674300	-0.22634700
H	1.34282000	1.76064000	0.26753100
H	0.79947900	1.15735300	-1.30925400
C	1.17046800	-0.42924100	0.13160400
H	1.94707900	-0.82596600	-0.53021400
H	1.53417400	-0.48742400	1.16747800

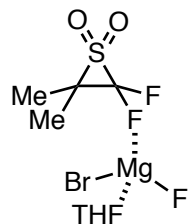
Coordinates of calculated structure for TS₁₂₋₁₃



C	-1.23593400	-0.47254800	1.18255500
S	-2.84730400	-0.22428100	0.57966000
O	-3.80188200	-1.30469800	0.85040100
C	-0.82823100	0.51550900	2.27280900
H	0.25333500	0.46746700	2.44233400
H	-1.08662600	1.54652100	2.02296400
H	-1.31149100	0.25620100	3.22827400
C	-0.90759700	-1.93462600	1.45292000

H	-1.40801400	-2.29690800	2.36213300
H	-1.19143800	-2.59659400	0.62986100
H	0.17180000	-2.03680900	1.60951400
C	-2.32375100	-0.49652400	-1.15851900
F	-0.01233300	-0.74556300	-1.86124100
F	-2.38510300	-1.67536600	-1.67662400
F	-2.34109200	0.46220800	-2.01867500
O	-3.25255000	1.18051000	0.62691700
Mg	0.55346800	0.24235600	-0.43311800
O	2.17080200	-0.86022600	0.21627100
Br	1.15685100	2.57332600	-0.17450600
C	2.57469300	-2.05152500	-0.54795200
C	3.32053600	-0.31076800	0.94002300
H	2.44320100	-1.81884400	-1.60714900
H	1.89685700	-2.86395800	-0.27677400
C	4.03315000	-2.30089100	-0.16072200
C	4.53329400	-0.90045000	0.23160400
H	3.25027900	-0.64336600	1.98231000
H	3.23941300	0.77623800	0.89020100
H	4.59987100	-2.74362000	-0.98446600
H	4.09495200	-2.98140800	0.69632400
H	4.77678400	-0.30996500	-0.65875500
H	5.41536300	-0.92640300	0.87764300

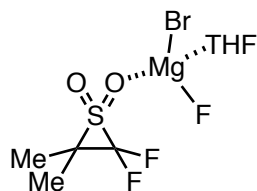
Coordinates of calculated structure for 13



C	2.66227000	-0.69568100	0.71814500
S	3.43486200	-0.27496800	-0.91584300
O	4.61262200	0.60786600	-0.88694600
C	1.99411100	-2.05519400	0.81423400
H	1.18549300	-1.97678000	1.54762400

H	1.58776500	-2.38682800	-0.14440900
H	2.72691500	-2.79357000	1.15346800
C	3.36217700	-0.21197400	1.97549400
H	4.05604200	-0.98169700	2.32576600
H	3.91790600	0.71449600	1.81556300
H	2.60021900	-0.04229600	2.74409200
C	1.94734000	0.40376500	-0.11789900
F	-0.21630700	-0.17310800	2.04139500
F	1.92523800	1.65492000	0.35092200
F	0.70116200	0.11519900	-0.64214300
O	3.16974600	-1.22530600	-2.01100100
Mg	-1.16129900	0.52386400	0.66144000
O	-2.25840500	-1.04555300	-0.03728000
Br	-2.18363800	2.54060300	-0.14398700
C	-2.32124800	-2.33634500	0.65788000
C	-3.28085200	-0.97888400	-1.08671800
H	-2.62424600	-2.13865000	1.68994200
H	-1.31729300	-2.76457900	0.65700400
C	-3.35436800	-3.15582300	-0.11668200
C	-4.27054200	-2.07671900	-0.71796100
H	-2.78760400	-1.17015400	-2.04607200
H	-3.68236300	0.03523600	-1.07811500
H	-3.88506900	-3.85744800	0.53270200
H	-2.86970500	-3.73135600	-0.91343700
H	-4.98496600	-1.71244100	0.02903900
H	-4.83382000	-2.42994900	-1.58612300

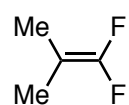
Coordinates of calculated structure for 14



C	3.34739500	0.10935700	0.78809600
S	2.00953300	-0.83528100	-0.06082000

O	2.41903300	-1.95791400	-0.91054800
O	0.74318900	-0.87450400	0.74972300
C	3.06500000	0.63173800	2.18627200
H	2.01491600	0.89226300	2.33057300
H	3.33801200	-0.13073500	2.92176500
H	3.67691300	1.52248400	2.36972800
C	4.76571000	-0.37524200	0.53253200
H	5.03165200	-1.13030800	1.27808400
H	4.88649900	-0.81123700	-0.46121600
H	5.45874700	0.46794400	0.63106100
C	2.64107400	0.83737000	-0.40045900
F	1.87136900	1.89606400	-0.11417800
F	3.34297100	1.06008000	-1.51510200
F	0.04368500	-0.06887000	-1.76812300
Mg	-1.02648400	-0.61000400	-0.37930000
O	-1.79632400	1.21009900	0.22271800
Br	-2.76013400	-2.23047500	0.10902600
C	-3.00158200	1.37615400	1.04284200
C	-1.56102900	2.41464700	-0.57056200
H	-2.71239900	1.25936400	2.09060000
H	-3.68427500	0.56914200	0.76935700
C	-3.53837000	2.77245600	0.70620700
C	-2.93686100	3.05925200	-0.68073100
H	-1.10998600	2.09373600	-1.51029700
H	-0.85410700	3.05048800	-0.02385000
H	-3.18146100	3.51055100	1.43359900
H	-4.63157700	2.79709100	0.71208100
H	-2.87801900	4.12765500	-0.90816900
H	-3.52237600	2.57139700	-1.46820600

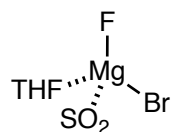
Coordinates of calculated structure for 15



C	0.68993700	0.00000300	-0.00001600
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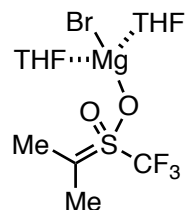
F	1.46941400	-1.09177900	-0.00005400
F	1.46941100	1.09178100	0.00000300
C	-0.63668200	-0.00000100	0.00000600
C	-1.41431400	1.29058800	0.00005600
H	-2.06592000	1.34497400	-0.88214900
H	-2.06598300	1.34487100	0.88221900
H	-0.76671500	2.17006400	0.00012700
C	-1.41430800	-1.29059200	0.00000000
H	-2.06582300	-1.34501300	0.88227000
H	-2.06606900	-1.34484400	-0.88209900
H	-0.76670700	-2.17006600	-0.00017500

Coordinates of calculated structure for MgFBr(SO₂)THF



S	2.15356000	1.41170600	-0.06567800
O	3.46055700	1.40318700	0.59188400
O	0.98268500	1.35294600	0.89689900
Br	1.54174200	-1.19826500	-0.87388300
F	-0.61140900	-1.22681300	2.48575300
O	-1.81257600	0.03188800	0.06945300
C	-3.08036400	-0.44205100	0.63878100
H	-2.98232800	-0.39521700	1.72343000
H	-3.21405300	-1.48527500	0.33365100
C	-4.12990100	0.47732300	0.02646200
H	-4.20338000	1.41023100	0.59718500
H	-5.11931100	0.01208500	0.00343300
C	-3.55828000	0.74067000	-1.37722300
H	-3.95737900	1.64614200	-1.84252500
H	-3.77176900	-0.10460700	-2.04097800
C	-2.05450300	0.84839200	-1.11663800
H	-1.43362400	0.45681100	-1.92622600
H	-1.74460800	1.87171100	-0.88025200
Mg	-0.04965400	-0.42239800	0.98358900

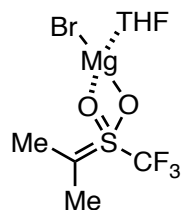
Coordinates of calculated structure for 16



C	3.04357000	-1.47505500	-0.93215000
S	2.03984200	-0.44924000	-0.17731600
O	1.31849400	0.54712600	-1.06438900
O	0.98633200	-1.11501900	0.71034200
C	3.48669400	-2.73219000	-0.21979500
H	2.83932100	-2.98141300	0.62506800
H	3.44551100	-3.57291800	-0.92541600
H	4.52199500	-2.66309000	0.14557200
C	3.82700000	-0.98461600	-2.12811600
H	3.79713300	-1.75424100	-2.91108200
H	3.40650500	-0.06954000	-2.55308100
H	4.88506000	-0.80267400	-1.88827500
C	2.71330800	0.80836600	1.15508900
F	3.33971200	0.12736100	2.13939000
F	3.62087700	1.62541400	0.57891000
F	1.76904100	1.59202100	1.73765700
Mg	-0.62732100	-0.17359400	-0.28521100
O	-1.81618800	-0.54726200	1.41814800
O	-1.23284000	1.81535100	-0.23509000
Br	-1.95621200	-1.20615400	-2.07268900
C	-1.49527500	-1.46571800	2.49748600
C	-3.26547200	-0.56478300	1.30702100
C	-1.41538600	2.68122600	0.92317400
C	-1.11310200	2.61404500	-1.45790800
H	-1.68708700	-0.94558800	3.44530800
H	-0.43574600	-1.70233100	2.41726100
C	-2.44732000	-2.64835200	2.28900600
C	-3.67549800	-2.02435700	1.56773500

H	-3.51773000	-0.20460000	0.30950300
H	-3.66526400	0.11882300	2.06713300
H	-0.70427200	2.37619400	1.69314400
H	-2.43629700	2.53132400	1.29141300
C	-1.19211300	4.10176900	0.40386700
C	-1.63009300	3.99401600	-1.06621300
H	-1.69574300	2.10742900	-2.22955300
H	-0.05715000	2.62765600	-1.74429800
H	-2.71035200	-3.12109700	3.23984800
H	-1.97588100	-3.40523600	1.65599500
H	-4.58367600	-2.07209300	2.17584100
H	-3.87049500	-2.53720200	0.62298600
H	-0.13128000	4.36793300	0.46843300
H	-1.76459700	4.84032600	0.97247300
H	-1.21055500	4.78292000	-1.69676200
H	-2.72251500	4.03492200	-1.14868600

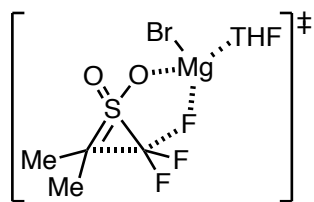
Coordinates of calculated structure for 17



C	2.95950600	-1.26795500	0.34796600
S	1.78617200	-0.19269500	0.02643100
O	0.95844500	-0.49353600	-1.22572100
O	0.77994200	0.02132400	1.16426400
C	3.54905800	-1.30891700	1.74030700
H	2.89508900	-0.84595100	2.48381900
H	3.68758600	-2.35864900	2.03084500
H	4.53381000	-0.82249000	1.79109800
C	3.73233900	-1.87003000	-0.80450600
H	3.86790700	-2.94253300	-0.61229800
H	3.20494600	-1.77167900	-1.75676500
H	4.73292200	-1.42726500	-0.91238200

C	2.18199000	1.67955100	-0.35015600
F	2.78656600	2.22154500	0.72755800
F	3.04502300	1.73392300	-1.38344500
F	1.11443100	2.45147300	-0.65866900
Mg	-0.77086100	-0.65245800	-0.06649000
O	-1.99100500	0.98019200	-0.04979800
Br	-2.22671200	-2.56642900	-0.05498000
C	-1.87789600	2.09984000	0.89326300
C	-3.29849300	1.00475700	-0.71985700
H	-0.89261500	2.54406100	0.75762100
H	-1.96054400	1.69199300	1.90623400
C	-3.04601400	3.01702100	0.54484200
C	-4.11801400	2.02620000	0.06247000
H	-3.69202200	-0.01290400	-0.69651400
H	-3.12737000	1.31572800	-1.75584000
H	-2.76547300	3.70460600	-0.26113700
H	-3.36646300	3.61197200	1.40467000
H	-4.88594600	2.49411100	-0.55971600
H	-4.61341700	1.54753300	0.91471100

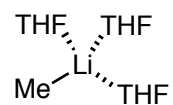
Coordinates of calculated structure for TS₁₇₋₁₄



C	3.39441400	0.23629700	1.02111400
S	2.16777800	-0.56973400	0.22853100
O	2.55317000	-1.80371900	-0.44747400
O	0.83236400	-0.45276600	0.89799300
C	3.07630500	1.30887700	2.02414800
H	2.00393700	1.48673200	2.12779700
H	3.46214500	1.02084900	3.01252800
H	3.56525400	2.25345400	1.74845400
C	4.81642600	-0.19404800	0.78884100

H	5.22466700	-0.65897800	1.69816400
H	4.90766500	-0.91948400	-0.02257100
H	5.44424500	0.67661600	0.55900800
C	2.10507600	0.68910900	-1.01093300
F	1.68396100	1.90319400	-0.75213700
F	2.86509600	0.64153900	-2.06705700
F	0.02031200	0.15636200	-1.78828800
Mg	-0.88203800	-0.54473700	-0.32128500
O	-1.97155900	1.10765500	0.26359700
Br	-2.34027600	-2.43865100	0.05484200
C	-3.18724000	1.04468300	1.08448500
C	-1.92746200	2.36471500	-0.47898900
H	-2.88181400	0.85664500	2.11658700
H	-3.77287200	0.19567500	0.72492100
C	-3.88345300	2.39291500	0.87950000
C	-3.37462900	2.84128300	-0.50116000
H	-1.49202800	2.14749400	-1.45526800
H	-1.27605100	3.05864600	0.06612900
H	-3.57543000	3.10990800	1.64929200
H	-4.97178100	2.29691600	0.92484600
H	-3.45268300	3.92123300	-0.65661600
H	-3.92834100	2.33746000	-1.30145000

Coordinates of calculated structure for MeLi(THF)₂

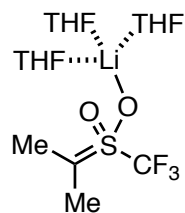


C	0.05930800	0.24413200	2.55047200
H	0.38515000	1.25477800	2.87774500
O	-1.01147200	1.51871000	-0.53678700
O	1.89547300	0.05786600	-0.42902700
C	-0.27256500	2.49883300	-1.28860200
H	-0.82301600	2.75063400	-2.20803800
H	0.68560200	2.04645100	-1.55345900
C	-0.16955600	3.70338300	-0.35577000

H	0.04794600	4.63596700	-0.88629600
H	0.61798300	3.53213000	0.38640600
C	-1.55461900	3.69807300	0.31579600
H	-2.27840100	4.24069600	-0.30362800
H	-1.54744300	4.16232900	1.30600700
C	-1.90833000	2.19950700	0.38625100
H	-1.72326500	1.76127400	1.37031200
H	-2.94176000	1.99975600	0.07885000
C	2.90329400	0.41980500	0.54691000
H	2.36933100	0.76732100	1.43350900
H	3.52691300	1.22731100	0.13554100
C	3.71069700	-0.85643900	0.76162800
H	3.17689400	-1.51702100	1.45416700
H	4.70920400	-0.66369700	1.16609200
C	3.73752500	-1.45445800	-0.65524700
H	3.89927200	-2.53673000	-0.66512900
H	4.53590700	-0.99132000	-1.24719200
C	2.35660900	-1.07017300	-1.21293900
H	2.39203800	-0.77347300	-2.26762900
H	1.62020700	-1.87158200	-1.09621800
O	-0.83660000	-1.69377000	-0.22891800
C	-1.29550100	-2.53411700	0.85632600
C	-1.80714300	-1.70914500	-1.30367900
C	-2.81562600	-2.53680100	0.72257200
H	-0.87943400	-3.54479300	0.73081600
H	-0.91796700	-2.08325800	1.77629300
C	-2.99864700	-2.54790400	-0.80521800
H	-2.07826100	-0.66925000	-1.51035300
H	-1.33756300	-2.13529500	-2.19823100
H	-3.22848300	-1.62004500	1.15917800
H	-3.28348100	-3.39402800	1.21662400
H	-3.95853500	-2.13316200	-1.12792400
H	-2.93412300	-3.57393500	-1.18594200
H	0.74685000	-0.44607200	3.08252400
H	-0.91403600	0.09989500	3.06503100

Li 0.02685800 0.02816500 0.48593200

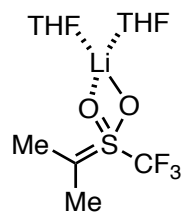
Coordinates of calculated structure for 18



C	-2.43415800	-1.81333000	-0.71628800
S	-1.78250700	-0.37783600	-0.27273200
O	-1.99407300	-0.02407500	1.16225900
O	-0.37779400	-0.19818700	-0.81663300
C	-2.07974100	-2.41124900	-2.05835300
H	-1.14241800	-2.01040400	-2.45392200
H	-1.95992300	-3.50059400	-1.96061700
H	-2.86447500	-2.24828100	-2.81549900
C	-3.73042200	-2.24952900	-0.07072700
H	-3.69605000	-3.32841700	0.14141000
H	-3.91257400	-1.73364700	0.87565900
H	-4.60326500	-2.08353800	-0.72340000
C	-2.53249100	1.21910800	-1.07131500
F	-2.43062700	1.16531200	-2.42331200
F	-3.85084500	1.31107500	-0.77724600
F	-1.95144200	2.38292500	-0.67509500
O	2.63653100	0.11525800	-0.95278600
O	1.23827000	1.84669700	1.30784700
C	2.41078100	0.05397200	-2.38343100
C	3.95798800	-0.38781400	-0.63506800
C	1.94926200	2.96721000	0.74833800
C	0.18062500	2.35383500	2.17415300
H	2.63900900	1.03627200	-2.82045200
H	1.35361700	-0.17057000	-2.53259600
C	3.37832500	-1.01536000	-2.88271100
C	4.59839200	-0.78713000	-1.97391000
H	3.83514700	-1.23995000	0.04194800

H	4.51427700	0.39680100	-0.11083800
H	2.40803900	2.62728300	-0.18276300
H	2.74022500	3.28376900	1.44538200
C	0.88432200	4.04736800	0.57994300
C	0.02752200	3.85487800	1.84670300
H	0.48146500	2.18830500	3.21556300
H	-0.71413400	1.76871300	1.95543000
H	3.61003000	-0.90909100	-3.94664100
H	2.95544200	-2.01420900	-2.72287900
H	5.21345900	0.03158500	-2.36510100
H	5.23809700	-1.66935800	-1.87854200
H	0.29251600	3.84798000	-0.31896500
H	1.31021700	5.05264300	0.50156300
H	-1.01843200	4.12698300	1.68405200
H	0.41210500	4.47119800	2.66694800
O	1.36102700	-1.40840500	1.55060500
C	1.23058600	-2.73491000	0.97753400
C	0.71120700	-1.36650800	2.85435700
C	0.17237300	-3.44612800	1.81909300
H	0.94492800	-2.62117200	-0.07135700
H	2.20771800	-3.23414600	1.04020700
C	0.39332600	-2.82117300	3.20573100
H	1.40114800	-0.88349100	3.55283500
H	-0.20187400	-0.77093800	2.75582400
H	0.29450400	-4.53374000	1.81006500
H	-0.82390300	-3.19839900	1.43806500
H	1.24292000	-3.29495000	3.71297200
H	-0.48179300	-2.90214000	3.85696200
Li	1.10708300	0.13244900	0.31955000

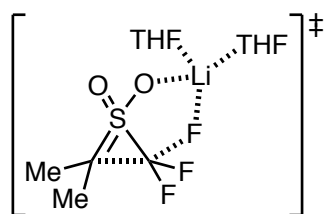
Coordinates of calculated structure for 19



C	2.03065300	1.82929700	0.07079200
S	0.54965200	1.14196500	-0.00652100
O	0.29586800	0.33038700	-1.25587500
O	0.14704700	0.37345200	1.23180600
C	2.49105200	2.41078900	1.38955400
H	1.95846500	1.97528500	2.23941900
H	3.56157200	2.20208800	1.52808300
H	2.37160300	3.50502100	1.43492800
C	2.65633500	2.34950100	-1.20468200
H	3.73473900	2.13545400	-1.19648700
H	2.23311400	1.87417800	-2.09373800
H	2.54935400	3.44031700	-1.31562800
C	-0.98814300	2.31799000	-0.11852400
F	-1.01304200	3.14273600	0.95423300
F	-0.88960800	3.09439200	-1.22207700
F	-2.19273400	1.69117600	-0.17307300
O	-2.02263100	-1.82538900	-0.00579300
C	-2.76941100	-1.66277500	1.23170100
C	-2.89432700	-1.61859300	-1.15093100
H	-2.18907600	-1.01013400	1.88970400
H	-2.87319000	-2.65199000	1.69450100
C	-4.12088100	-1.07476800	0.82352600
C	-4.31643300	-1.64873300	-0.58969200
H	-2.68763100	-2.41441900	-1.87251200
H	-2.64877700	-0.64950300	-1.59890900
H	-4.06362500	0.01771800	0.78777200
H	-4.91981800	-1.35615300	1.51598500
H	-5.01184900	-1.06378400	-1.19845800
H	-4.68894500	-2.67886700	-0.53970800
O	1.28365000	-2.47378400	0.06866200

C	2.06274400	-2.65137000	-1.14952500
C	2.17224100	-2.38637400	1.21360100
C	3.53049700	-2.72409600	-0.70798700
H	1.71426900	-3.56282900	-1.64564800
H	1.86608000	-1.78722300	-1.79212600
C	3.51833600	-1.96772800	0.63092800
H	1.74231200	-1.65901300	1.90607400
H	2.22032600	-3.37243700	1.69492500
H	4.20212300	-2.27849300	-1.44732700
H	3.83750100	-3.76561800	-0.55593700
H	3.52410600	-0.88496800	0.46377700
H	4.35804000	-2.23080900	1.28139100
Li	-0.19803500	-1.22872300	-0.01681800

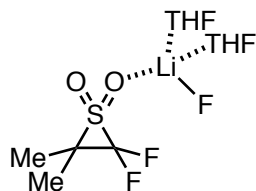
Coordinates of calculated structure for TS₁₉₋₂₀



C	3.29481200	-0.90305900	-0.62326900
S	1.94437400	0.09771500	-0.38712000
O	2.25577500	1.44186300	0.11998500
O	0.78661700	-0.10198400	-1.30249700
C	3.18924300	-2.06529600	-1.57663900
H	2.15386400	-2.34046100	-1.79248700
H	3.67930900	-1.84015300	-2.53638400
H	3.69516100	-2.94201500	-1.15141800
C	4.65854600	-0.37227100	-0.26282200
H	5.20050000	-0.00862700	-1.14975300
H	4.60756400	0.44962400	0.45548000
H	5.26005500	-1.17871700	0.17594900
C	1.69833700	-0.98346300	0.97219000
F	1.27628000	-2.22398700	0.82191000
F	2.25334900	-0.76105000	2.13779100

F	-0.17462900	-0.35956100	1.46537100
O	-2.36924000	-1.22998400	-0.52433900
C	-3.62866300	-0.89974400	-1.15799000
C	-2.54733600	-2.33225400	0.40055700
H	-3.50094900	-0.96981200	-2.24331800
H	-3.87075900	0.13666000	-0.89702700
C	-4.65814000	-1.89787200	-0.60643800
C	-4.03644600	-2.31928800	0.73587300
H	-1.88185100	-2.15008000	1.24668600
H	-2.25553300	-3.26474800	-0.10178400
H	-4.74614200	-2.76529400	-1.27099100
H	-5.65196200	-1.45214600	-0.50356200
H	-4.39641000	-3.28988000	1.09039200
H	-4.24374300	-1.57242500	1.51135600
O	-1.58417300	1.87975000	-0.20808500
C	-1.58769200	2.54697800	1.08986000
C	-1.11478400	2.79326400	-1.22849900
C	-1.13453500	3.98906100	0.82696100
H	-2.60121700	2.48360600	1.49974400
H	-0.90195400	1.99415500	1.73814400
C	-0.32627300	3.86174600	-0.47517100
H	-0.51722500	2.21544800	-1.93793200
H	-1.98424100	3.21890500	-1.74956300
H	-0.54599300	4.38937300	1.65745100
H	-1.99961000	4.64653500	0.67748500
H	0.68525700	3.49923900	-0.26691000
H	-0.25814100	4.80168900	-1.03193200
Li	-0.92840200	0.01769300	-0.09985300

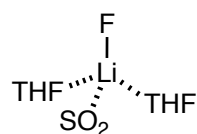
Coordinates of calculated structure for 20



C	3.29736600	-0.50705400	-0.53423700
S	1.72049400	0.37586300	-0.11753600
O	1.92987500	1.65040900	0.59327100
O	0.71495400	0.23204300	-1.21427300
C	3.37032200	-1.23942700	-1.86355700
H	2.39943600	-1.62937400	-2.17535900
H	3.73065700	-0.55383100	-2.63710700
H	4.07712700	-2.07476800	-1.78958200
C	4.59029400	0.14665800	-0.07425100
H	4.95014100	0.82703400	-0.85252700
H	4.46088000	0.71721100	0.84758800
H	5.35621700	-0.62007300	0.09326000
C	2.41617700	-1.15012600	0.57317100
F	1.81723900	-2.32209400	0.30293700
F	2.87421400	-1.15185300	1.83323300
F	-0.16597400	-0.15546000	1.25790200
O	-2.24188200	-1.46187500	-0.62952400
C	-3.63314800	-1.38226100	-1.02188900
C	-2.04338700	-2.57119600	0.28531800
H	-3.69337400	-1.46137000	-2.11271300
H	-4.00841000	-0.39799800	-0.71986200
C	-4.35066100	-2.53190400	-0.29567400
C	-3.42036500	-2.81629900	0.89597900
H	-1.27362600	-2.26012100	0.99487900
H	-1.69489600	-3.44189700	-0.28716900
H	-4.41537200	-3.41392900	-0.94356800
H	-5.36781700	-2.26075700	0.00274700
H	-3.53070000	-3.82973200	1.29378400
H	-3.60256300	-2.10591400	1.71078800
O	-2.03418000	1.78586500	-0.29117100
C	-2.12751600	2.36101500	1.04954900
C	-1.59501900	2.79739000	-1.22603200
C	-1.74715100	3.84082200	0.90507400
H	-3.15251000	2.21579000	1.40720000
H	-1.43253400	1.80215400	1.68300400

C	-0.89121400	3.85002200	-0.37265900
H	-0.94450300	2.31113500	-1.95796200
H	-2.47287400	3.21141800	-1.74243200
H	-1.20687100	4.20925500	1.78169500
H	-2.64082600	4.46242700	0.77068800
H	0.13088500	3.52740000	-0.14934300
H	-0.85503000	4.82974900	-0.85962400
Li	-1.07165400	0.04988900	-0.20520800

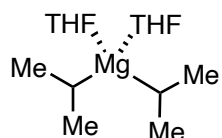
Coordinates of calculated structure for LiF(SO₂)(THF)₂



S	-1.26955400	2.39745100	-0.25532500
O	-2.64561300	2.11857400	0.19728000
O	-0.79822800	1.46803800	-1.34382400
F	-0.20176600	1.46238300	1.10612400
O	2.09884900	-0.11322500	-0.33361100
C	2.80368400	-1.36953600	-0.49557400
C	3.00326400	0.91590100	0.14507600
H	2.62225600	-1.73759800	-1.51002800
H	2.38620900	-2.08639500	0.22088500
C	4.27913600	-1.06086700	-0.21451200
C	4.19336000	0.15465100	0.72367400
H	2.45394900	1.52133300	0.86932800
H	3.29696300	1.54509900	-0.70505100
H	4.79756100	-0.78929700	-1.14136100
H	4.80276000	-1.91349300	0.22746400
H	5.10805100	0.75457500	0.73525900
H	3.97942800	-0.16394700	1.75064200
O	-0.84946600	-1.45115800	0.01245900
C	-1.73126900	-1.80988100	-1.09147100
C	-1.56579200	-1.56764700	1.27212100
C	-3.05935100	-2.23791700	-0.45426600
H	-1.84209900	-0.92327100	-1.72329500

H	-1.24888400	-2.60878100	-1.66406600
C	-3.04242400	-1.49881800	0.89469900
H	-1.30333200	-2.52918500	1.73387200
H	-1.23301200	-0.74894300	1.91456200
H	-3.08116200	-3.32309000	-0.29733300
H	-3.91607800	-1.96880200	-1.07855700
H	-3.68669900	-1.96538100	1.64632900
H	-3.34634500	-0.45443000	0.76885500
Li	0.20373500	0.17926500	-0.18477800

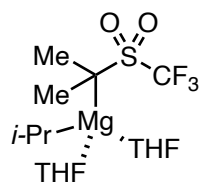
Coordinates of calculated structure for Mg(*i*-Pr)₂(THF)₂



C	-1.43406300	2.23104600	-2.25565800
C	-0.07954200	1.54654500	-1.98744900
C	1.05198900	2.53904400	-2.31578900
H	-2.28777100	1.54888200	-2.12030000
H	0.00488100	0.71919100	-2.72063500
H	2.05186400	2.08392400	-2.24166700
H	0.97721600	2.96547500	-3.33491100
H	-1.52081200	2.64373200	-3.27947600
O	-1.62146300	-0.70995300	0.08728000
O	1.52159400	-0.86120600	-0.13741100
Mg	0.02437100	0.71059100	0.01910800
C	-2.07389400	-1.45937400	-1.07346000
H	-1.44023200	-2.34977000	-1.16868400
H	-1.93938000	-0.82650700	-1.95302900
C	-3.52917500	-1.82369600	-0.77771200
H	-3.83747800	-2.74351100	-1.28327600
H	-4.19780500	-1.01729300	-1.10029100
C	-3.53101400	-1.94171400	0.75520100
H	-3.12409000	-2.91151600	1.06571100
H	-4.52633900	-1.83411400	1.19598400

C	-2.59173800	-0.80843900	1.16597100
H	-3.11729300	0.14958600	1.24547100
H	-2.04289000	-0.98748900	2.09290600
C	2.39736200	-1.07044300	-1.27647700
H	2.44182000	-0.13382600	-1.83391000
H	1.96059700	-1.84802200	-1.91658300
C	3.72336600	-1.51814900	-0.66867900
H	4.30004700	-0.64830800	-0.33396300
H	4.33667500	-2.08578500	-1.37468200
C	3.25513700	-2.35342500	0.53460100
H	4.01614300	-2.45192600	1.31403900
H	2.97310400	-3.36201500	0.20992100
C	2.02667000	-1.57899700	1.02529000
H	1.22670700	-2.22309900	1.40171000
H	2.27463000	-0.83684300	1.78918400
H	-1.60102100	3.07748800	-1.57222800
H	1.05151700	3.39604000	-1.62566700
C	0.20566600	1.43316200	2.06389900
H	0.16987900	0.56373600	2.75088900
C	-0.92903700	2.37980800	2.49838000
H	-1.91921300	1.90318500	2.44597800
H	-0.81407600	2.75100100	3.53533200
H	-0.97807100	3.27448600	1.85942800
C	1.55705700	2.13151400	2.31175800
H	1.67869200	2.49088900	3.35201900
H	2.41816400	1.47708800	2.10478300
H	1.67833600	3.01622600	1.66844500

Coordinates of calculated structure for 21

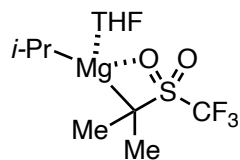


C	-0.85993600	-1.21036400	-1.00186700
S	-2.53258700	-1.25046700	-0.36520300

O	-3.56220800	-1.65847100	-1.34383600
O	-2.54357300	-1.84035700	0.98743800
C	-0.38101900	-2.68527800	-0.94860800
H	0.65995900	-2.72415900	-1.29261300
H	-0.41620400	-3.10093500	0.06329400
H	-0.96114700	-3.34967300	-1.60754800
C	-0.88588200	-0.73523200	-2.46554600
H	-1.48252200	-1.39208800	-3.11488300
H	-1.27261800	0.28118100	-2.58576900
H	0.14036200	-0.73808000	-2.85572000
C	-2.97209200	0.57229300	-0.03992600
F	-2.03187600	1.17957400	0.72963700
F	-3.07456500	1.28916900	-1.18119800
F	-4.13976700	0.63985200	0.60231600
Mg	0.51132900	-0.19520700	0.47169600
O	2.43760000	-0.89096100	-0.27945500
O	0.99746900	1.77378800	-0.23550700
C	3.06223200	-0.59863200	-1.55883700
C	3.30003200	-1.75740900	0.51781600
C	0.34997300	2.61913400	-1.23122300
C	1.90761600	2.57069800	0.58625700
H	3.32941000	0.46455600	-1.56934900
H	2.33033600	-0.78872100	-2.34776800
C	4.29410400	-1.50314400	-1.63308300
C	4.66873400	-1.67387900	-0.15224900
H	2.88979700	-2.77344600	0.48452500
H	3.26918600	-1.39226200	1.54490400
H	-0.70208400	2.33900000	-1.27704700
H	0.82024900	2.42315900	-2.20249800
C	0.59330400	4.04878600	-0.75634800
C	1.97469400	3.93896700	-0.09230200
H	2.86637800	2.04709900	0.62657500
H	1.48785300	2.62204500	1.59465200
H	5.09387400	-1.06270300	-2.23530300
H	4.03150000	-2.47145800	-2.07420500

H	5.22199100	-0.79931400	0.21003600
H	5.27645700	-2.56298400	0.03779300
H	-0.16604500	4.33936200	-0.02180300
H	0.56616600	4.76816200	-1.57970500
H	2.17396400	4.74080300	0.62408000
H	2.76625100	3.95748500	-0.85088000
C	0.80519900	-0.27491600	2.60647900
H	1.85485500	0.02633800	2.80388700
C	0.63432300	-1.69655000	3.17996500
H	0.80653600	-1.74078800	4.27145800
H	-0.38249200	-2.07380000	3.00801700
H	1.32399600	-2.42513000	2.72653100
C	-0.08534000	0.69183000	3.41066100
H	-1.14974400	0.45100000	3.28832000
H	0.11887200	0.65578200	4.49681400
H	0.03621300	1.74233300	3.10404800

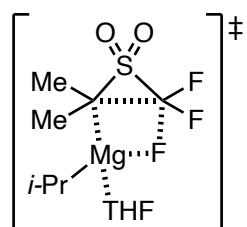
Coordinates of calculated structure for 22



C	-0.79851600	1.35980600	1.00464200
S	-1.70663800	0.85099100	-0.46271600
O	-2.84566600	1.64663000	-0.95199000
C	-0.84828200	2.90436800	1.00167200
H	-0.16341000	3.25498200	1.78258700
H	-0.51214200	3.35066800	0.05871700
H	-1.84796200	3.30617800	1.22270500
C	-1.37514400	0.81582300	2.31629600
H	-2.38290800	1.19144900	2.55114500
H	-1.39673200	-0.27672300	2.36738300
H	-0.71434400	1.15602800	3.12278200
C	-2.45316400	-0.88008800	-0.17975600
F	-1.55093000	-1.74833700	0.32299300

F	-3.49315100	-0.81313000	0.66144200
F	-2.87601400	-1.35057800	-1.35717500
O	-0.60604900	0.57089500	-1.47245700
Mg	1.07532900	0.78008500	-0.16324100
O	1.43645000	-1.28947000	0.02618100
C	1.58830300	-2.15655400	-1.13920400
C	1.74959800	-2.01434000	1.24827200
H	2.16906900	-1.61054000	-1.88724600
H	0.58867300	-2.36134800	-1.53500100
C	2.27939800	-3.41290700	-0.61189000
C	1.77619200	-3.48570600	0.83953100
H	0.98072900	-1.77008500	1.98554800
H	2.72494400	-1.66856400	1.61011200
H	3.36822600	-3.29116200	-0.63523200
H	2.02305900	-4.29871100	-1.19960500
H	2.42276300	-4.08223000	1.48921600
H	0.76687000	-3.91065500	0.87571100
C	2.92850400	1.78000000	-0.54114600
H	3.37298600	1.26557700	-1.41358500
C	2.79906100	3.26541600	-0.92393400
H	2.17023700	3.41245500	-1.81278300
H	2.35120800	3.86008300	-0.11372700
H	3.77657400	3.73315100	-1.14306000
C	3.93464100	1.62283700	0.61607900
H	4.13549100	0.56824400	0.85871400
H	4.91352300	2.08649400	0.39472800
H	3.57484700	2.09986800	1.54065700

Coordinates of calculated structure for TS₂₂₋₂₃

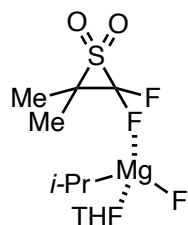


C	1.17188400	-0.44566200	-1.19701000
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S	2.76294700	-0.35006800	-0.50742800
O	3.62703000	-1.51926300	-0.72205800
C	0.94637100	0.51170200	-2.36095700
H	-0.12286500	0.58207300	-2.58896300
H	1.31694500	1.51721100	-2.15120900
H	1.44596400	0.14660500	-3.27298100
C	0.68311100	-1.87068800	-1.41135900
H	1.16732500	-2.33546700	-2.28254900
H	0.85985800	-2.51955200	-0.54873400
H	-0.39558000	-1.85630600	-1.60164700
C	2.14107300	-0.51558800	1.19988200
F	-0.11461700	-0.29457200	1.84971200
F	2.01360400	-1.69164400	1.72788900
F	2.34358600	0.42962000	2.05799200
O	3.30827000	1.00896700	-0.57541300
Mg	-0.62621700	0.60582300	0.31913200
O	-2.26170500	-0.63894000	-0.15163400
C	-2.68230800	-1.69273300	0.77943300
C	-3.34745800	-0.30672700	-1.06362600
H	-2.70538600	-1.25589300	1.78074000
H	-1.92437300	-2.47792400	0.75654100
C	-4.06122100	-2.13401800	0.28694400
C	-4.60103800	-0.86838200	-0.39983300
H	-3.14548900	-0.78938900	-2.02801700
H	-3.34850100	0.77718200	-1.19384600
H	-4.69503200	-2.48009600	1.10820700
H	-3.97113600	-2.95173400	-0.43770900
H	-4.98781300	-0.16030200	0.34182500
H	-5.39524000	-1.07565300	-1.12263600
C	-1.08199900	2.63815800	-0.21316100
H	-1.33967500	2.66670300	-1.28698500
C	0.09392400	3.60631900	0.00185700
H	-0.16601800	4.64677900	-0.26568700
H	0.41331500	3.62992300	1.05372000
H	0.97801800	3.33600300	-0.59022300

C	-2.31429000	3.13156500	0.56804000
H	-3.20961000	2.51776400	0.38703000
H	-2.13889000	3.12206800	1.65379200
H	-2.58857500	4.17079200	0.30982300

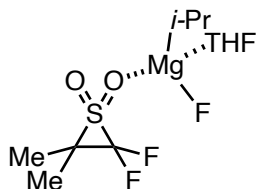
Coordinates of calculated structure for 23



C	2.41753600	-0.76272200	0.76085200
S	3.33368700	-0.50232900	-0.83005000
O	4.53486600	0.35058700	-0.77310800
C	1.69640800	-2.08936600	0.91314600
H	0.83102100	-1.92030500	1.56139000
H	1.36238600	-2.49300400	-0.04570500
H	2.36959700	-2.81535400	1.37934300
C	3.02561700	-0.19314200	2.02929800
H	3.66897600	-0.94502700	2.49603500
H	3.61634900	0.70647500	1.84363600
H	2.20614500	0.05146700	2.71387300
C	1.80094200	0.27315600	-0.22355000
F	-0.45164200	-0.02812900	1.95469200
F	1.79985000	1.56782300	0.13261200
F	0.60509400	-0.01945300	-0.80948800
O	3.14305100	-1.54301700	-1.85895300
Mg	-1.44149300	0.85828700	0.69673600
O	-2.64795900	-0.70285500	0.04209700
C	-2.57028200	-2.06175000	0.57824400
C	-3.77464800	-0.58113100	-0.88177600
H	-2.31766300	-1.97838700	1.63596800
H	-1.76301900	-2.58518500	0.05424100
C	-3.93633000	-2.67008000	0.27845900
C	-4.30212600	-2.00552200	-1.05910000

H	-3.40678300	-0.12335000	-1.80276600
H	-4.51241900	0.08315100	-0.42059200
H	-4.65790400	-2.39610000	1.05683700
H	-3.89730700	-3.76137000	0.21810500
H	-5.37508700	-2.02081200	-1.26943600
H	-3.78655500	-2.50538800	-1.88694500
C	-2.06633300	2.76029400	-0.03162300
H	-3.15859800	2.81048800	0.12984700
C	-1.83160600	2.95406200	-1.54220900
H	-2.19835600	3.93270400	-1.90051100
H	-0.76357200	2.91318900	-1.79972800
H	-2.33447700	2.18785400	-2.15074700
C	-1.44513400	3.93153700	0.75282600
H	-1.67914300	3.88575400	1.82524700
H	-0.34929900	3.94661300	0.66588100
H	-1.79901800	4.91252000	0.38796600

Coordinates of calculated structure for 24

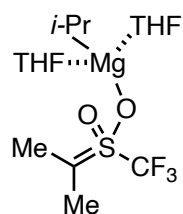


C	3.77385100	-0.68580500	0.01896100
S	2.21783500	0.27475600	-0.26702400
O	1.39418000	0.45504900	0.95635500
O	2.30795600	1.31393300	-1.31080400
C	4.98687700	-0.28886100	-0.80529800
H	5.63908500	-1.15965800	-0.94070400
H	4.71249100	0.09745900	-1.78904400
H	5.55205600	0.48366100	-0.27457900
C	4.05721500	-1.13788900	1.44153700
H	4.63196200	-0.36558200	1.96210800
H	3.14294300	-1.32854000	2.00705800
H	4.65473200	-2.05701900	1.42196600

C	2.62721400	-1.42866700	-0.73445000
F	2.81210500	-1.72232300	-2.03051400
F	2.02936300	-2.45171000	-0.11016400
F	-0.11724400	-0.51729800	-1.09089500
Mg	-1.05952100	-0.07248700	0.47290500
O	-1.26018400	2.02025100	0.17101800
O	-2.93636100	-0.53452000	-0.54610900
C	-0.87185600	3.01099500	1.16548000
C	-1.10269800	2.56184300	-1.17623900
C	-2.98459400	-0.95656800	-1.93644700
C	-4.16337300	-0.91912800	0.13409100
H	0.07321300	2.68794600	1.61300400
H	-1.64768400	3.03208900	1.93516500
C	-0.72632800	4.32257100	0.39274800
C	-0.28533100	3.83885000	-0.99891900
H	-2.10605400	2.76499400	-1.57035400
H	-0.61118300	1.79592300	-1.77828700
H	-1.96335500	-1.20704100	-2.22333400
H	-3.34234900	-0.11431000	-2.54497600
C	-3.98070400	-2.11071200	-1.94707300
C	-5.02112900	-1.63872400	-0.91734600
H	-4.63626200	-0.01631700	0.53298300
H	-3.88587300	-1.56907000	0.96782900
H	-0.00521000	4.99713400	0.86383300
H	-1.68936700	4.84383000	0.33235400
H	0.78325400	3.60094400	-1.00770900
H	-0.48393200	4.56894700	-1.78948100
H	-3.49372000	-3.03412300	-1.61275400
H	-4.40833600	-2.28765700	-2.93866300
H	-5.60114600	-2.45732600	-0.48130700
H	-5.72538000	-0.94058000	-1.38498500
C	-1.47959100	-0.74893000	2.48216200
H	-2.53413100	-0.48571100	2.69417700
C	-1.37846300	-2.28200900	2.60838900
H	-0.35716800	-2.63926400	2.40618700

H	-1.63882100	-2.65311800	3.61862800
H	-2.03639700	-2.80977300	1.90057600
C	-0.63976400	-0.09359900	3.59247900
H	0.43483300	-0.27607900	3.44995000
H	-0.77000400	0.99799600	3.62536000
H	-0.89000900	-0.47192800	4.60254100

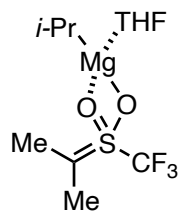
Coordinates of calculated structure for 25



C	-2.59359700	0.15101900	1.76191200
S	-1.91078000	-0.11995600	0.30645800
O	-2.20830300	0.90248300	-0.73312500
O	-0.43662500	-0.53902800	0.45910800
C	-2.16630400	-0.65226600	2.96824000
H	-1.20868400	-1.15683700	2.81727600
H	-2.05475800	0.01508600	3.83432800
H	-2.91310900	-1.41323000	3.24397600
C	-3.92428300	0.86601800	1.81510800
H	-3.90302100	1.61818000	2.61635600
H	-4.15168700	1.38554800	0.88112700
H	-4.75606900	0.18053900	2.04075400
C	-2.39393800	-1.70374600	-0.70043800
F	-2.16405000	-2.82196600	0.03265000
F	-3.71351500	-1.67528100	-0.98390700
F	-1.72675700	-1.85201700	-1.87460500
Mg	1.20426000	0.58136100	0.51806500
O	2.40779000	-0.93991100	-0.29240400
O	0.92793900	1.71112100	-1.21681100
C	1.95298700	-2.26888500	-0.70234200
C	3.86056500	-0.92659100	-0.13653900
C	0.63172100	1.10300800	-2.51637900

C	0.34589200	3.05231700	-1.15067800
H	1.74969200	-2.23983500	-1.77912500
H	1.02587700	-2.47481300	-0.16789300
C	3.11802700	-3.19269700	-0.36557300
C	4.33551300	-2.29331200	-0.63505400
H	4.07878100	-0.76793700	0.92387100
H	4.25415600	-0.08495000	-0.71277000
H	0.13898300	0.14536000	-2.34006000
H	1.59211400	0.94399700	-3.01916300
C	-0.25891400	2.10730900	-3.24961500
C	0.13200200	3.44813900	-2.60668300
H	1.05330600	3.68131700	-0.60644100
H	-0.60200000	2.98640500	-0.60782800
H	3.11278200	-4.10172000	-0.97374200
H	3.08006700	-3.48653400	0.68970500
H	4.55313800	-2.25801200	-1.70881500
H	5.24035300	-2.62414200	-0.11767600
H	-1.30981200	1.88198000	-3.04890100
H	-0.09260800	2.08638100	-4.33074900
H	-0.64354200	4.21210800	-2.71155100
H	1.06059600	3.83781700	-3.04110100
C	2.20043700	1.55384800	2.14427300
H	3.20919700	1.83199100	1.78358900
C	1.53541700	2.85274700	2.63648200
H	0.51142900	2.67628400	2.99645800
H	2.08267000	3.31848400	3.47682800
H	1.46798100	3.61443800	1.84653800
C	2.40565000	0.59932600	3.33756700
H	2.96198900	-0.30997700	3.06222100
H	2.96230000	1.06866400	4.16964400
H	1.44669600	0.26501900	3.75996500

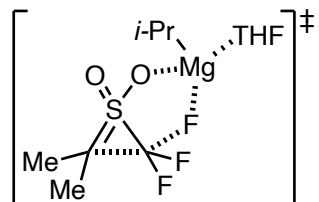
Coordinates of calculated structure for 26



C	-2.94737100	0.95565000	0.04505400
S	-1.55026200	0.12890600	-0.01459700
O	-0.73290200	0.33668900	-1.28598600
O	-0.61752300	0.35684100	1.17294400
C	-3.62936800	1.14398900	1.38148500
H	-2.94682000	0.99242800	2.22176900
H	-4.00640100	2.17364800	1.44432200
H	-4.49160600	0.47303800	1.50913700
C	-3.74925500	1.12612300	-1.22563800
H	-4.13331200	2.15430000	-1.26624900
H	-3.14552700	0.96560400	-2.12263000
H	-4.61768500	0.45220500	-1.26643100
C	-1.55878800	-1.82028700	0.00038300
F	-2.15541300	-2.24562200	1.13462100
F	-2.29405400	-2.25880900	-1.04287200
F	-0.34530400	-2.42035000	-0.07290900
Mg	0.88954200	1.12903700	-0.14008400
O	2.19377100	-0.49199400	-0.04426800
C	2.46533100	-1.26000400	1.17115900
C	2.71781000	-1.18464600	-1.21684200
H	1.53211800	-1.33288000	1.73294600
H	3.20598200	-0.70033600	1.75265200
C	3.00551300	-2.60335400	0.68202500
C	3.67225500	-2.23467600	-0.65387100
H	3.20020300	-0.43693900	-1.85178700
H	1.87437700	-1.63362400	-1.75205500
H	2.18346500	-3.30782700	0.51940900
H	3.70194300	-3.04826800	1.39840600
H	3.78441900	-3.08925000	-1.32684800
H	4.66340000	-1.79886600	-0.48414400

C	1.87319500	3.00364300	-0.32965100
H	2.28150800	3.02399300	-1.35676200
C	0.94017400	4.22125600	-0.19886500
H	0.12609200	4.20171800	-0.93599500
H	0.47092700	4.27276300	0.79441700
H	1.47665300	5.17737700	-0.33821800
C	3.07461800	3.14917200	0.62440400
H	3.80941200	2.34060000	0.49934100
H	3.61895500	4.09922400	0.47448700
H	2.76308100	3.13969100	1.67984900

Coordinates of calculated structure for TS₂₆₋₂₄



C	3.26135400	-0.47182800	-0.87929600
S	2.06286400	0.53455700	-0.28889500
O	2.52738300	1.80158100	0.27089000
O	0.76409500	0.46076900	-1.02666900
C	2.90870100	-1.61312700	-1.79217500
H	1.83091700	-1.72889300	-1.92564800
H	3.35057800	-1.45335600	-2.78653000
H	3.31678800	-2.55654200	-1.40421400
C	4.70189700	-0.11957900	-0.62635700
H	5.18478300	0.22014000	-1.55469500
H	4.81426700	0.67511600	0.11465500
H	5.25125700	-1.00466600	-0.28007500
C	1.83719700	-0.57479100	1.06358400
F	1.33449500	-1.77729000	0.90807800
F	2.52667400	-0.46081600	2.16311500
F	-0.15510200	0.17847300	1.68031900
Mg	-1.03065500	0.81639400	0.13336600
O	-2.08637900	-0.95575200	-0.31654000

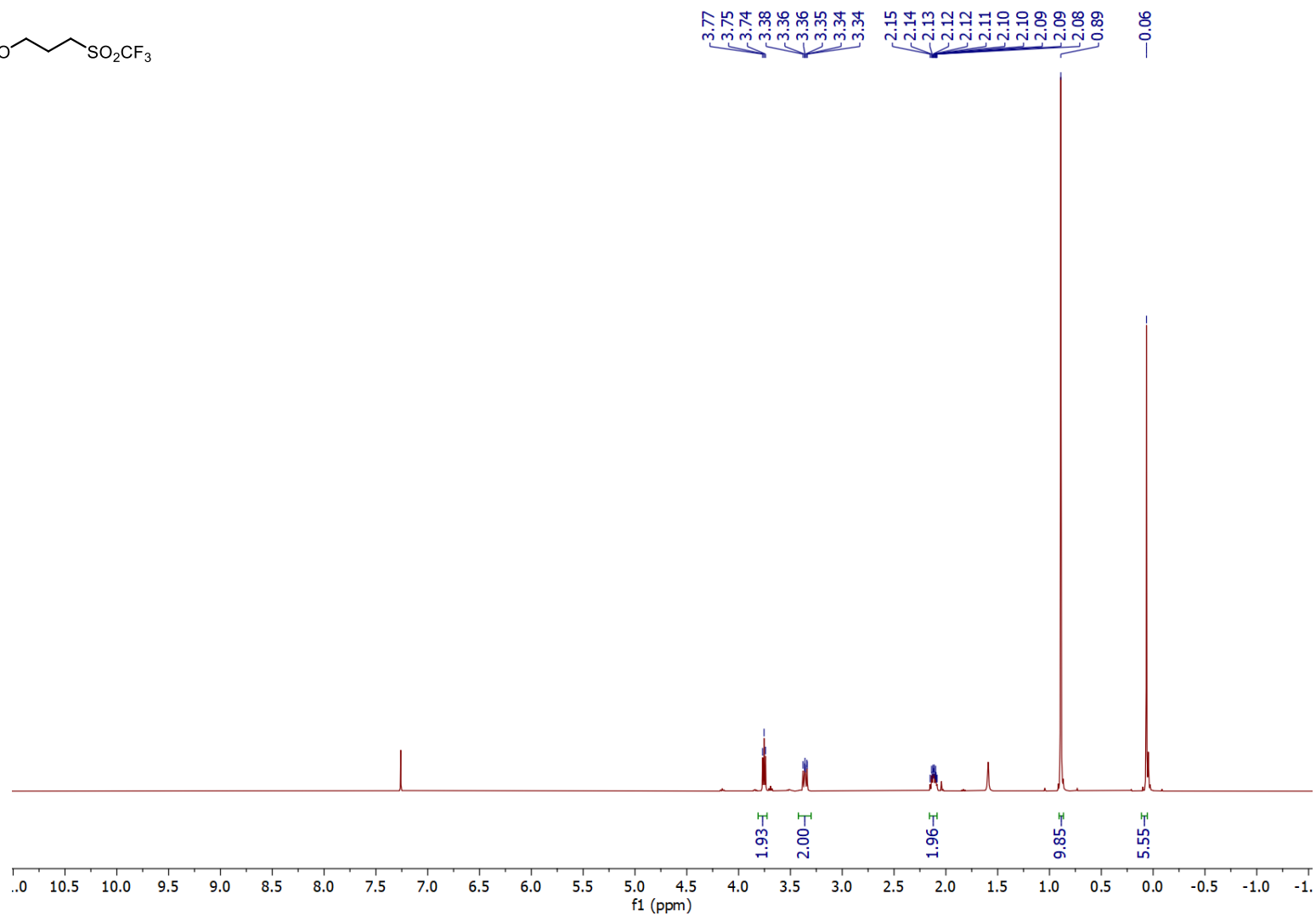
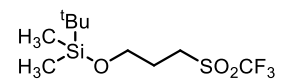
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H	-3.87417800	-0.09165600	-0.90178100
C	-3.99039800	-2.28922500	-0.85065900
C	-3.50168400	-2.61810000	0.57020500
H	-1.62851500	-1.84711200	1.48464600
H	-1.39741600	-2.88473900	0.04973600
H	-3.67697100	-3.07242200	-1.55052300
H	-5.07736000	-2.19133200	-0.92060200
H	-3.58535200	-3.68066500	0.81656600
H	-4.06519100	-2.04706400	1.31696100
C	-2.23931000	2.49999300	-0.39115900
H	-2.64383500	2.30469400	-1.40232400
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H	-0.98707700	4.08355800	0.48184000
H	-0.62345900	3.75377200	-1.21295000
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C	-3.45028800	2.69055800	0.54271600
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9. References

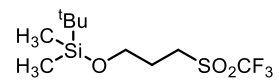
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10. ^1H and ^{13}C NMR Spectra of Products

tert-Butyldimethyl(3-((trifluoromethyl)sulfonyl)propoxy)silane S2 ^1H NMR (400 MHz, Chloroform-*d*)



tert-Butyldimethyl(3-((trifluoromethyl)sulfonyl)propoxy)silane S2 $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, Chloroform-*d*)



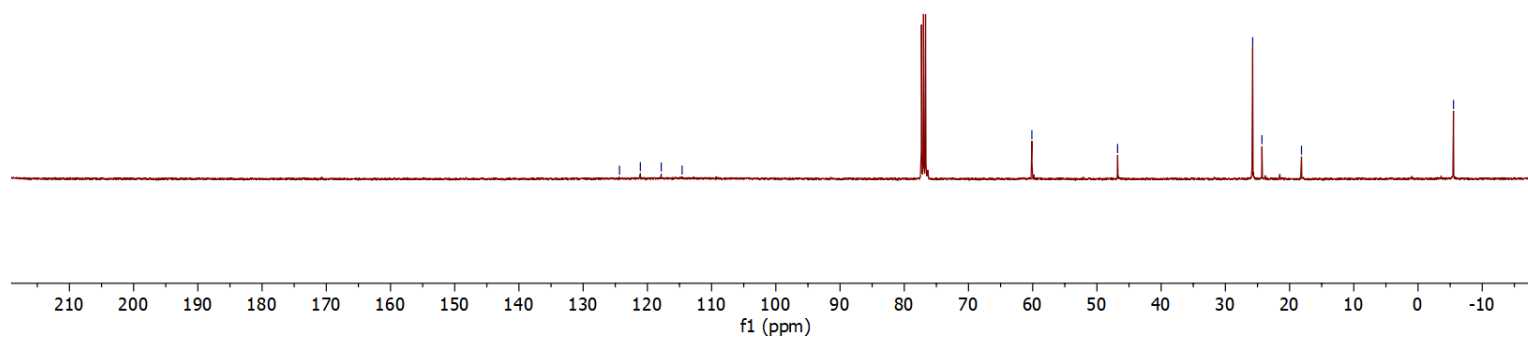
124.34
121.09
117.84
114.60

60.13

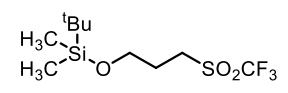
46.78

25.75
24.30
18.15

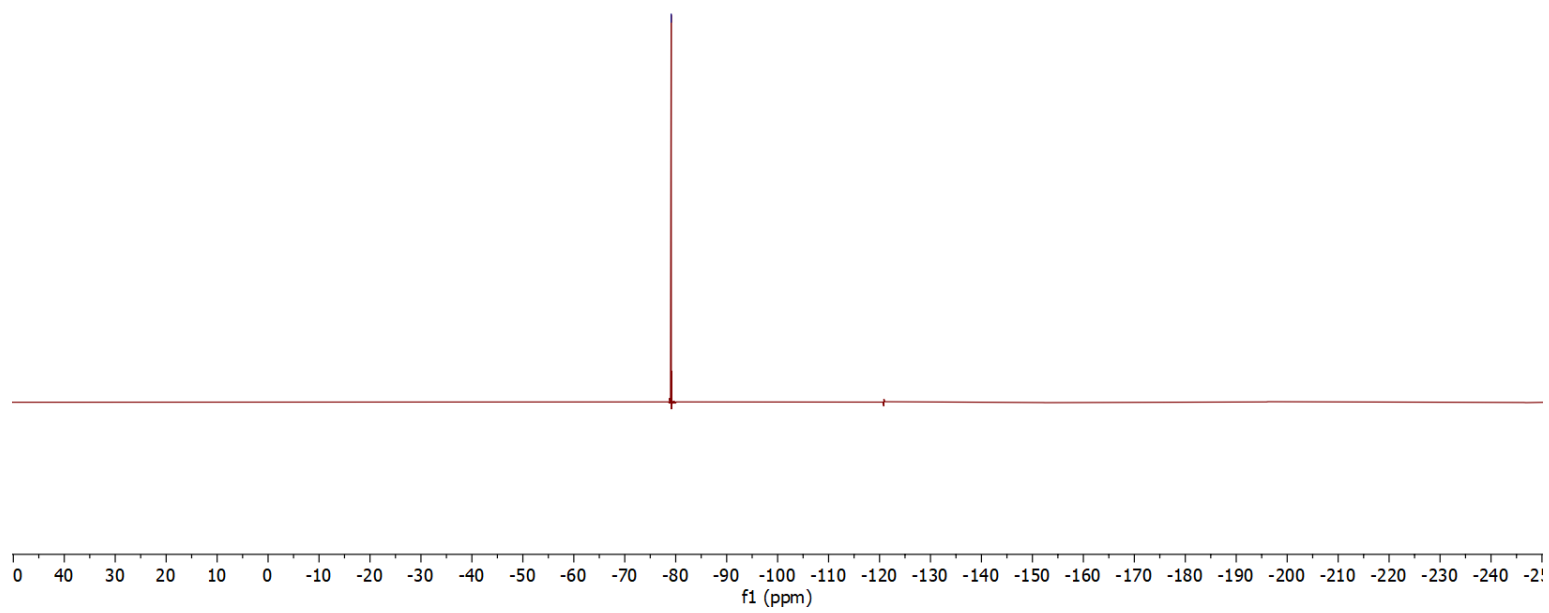
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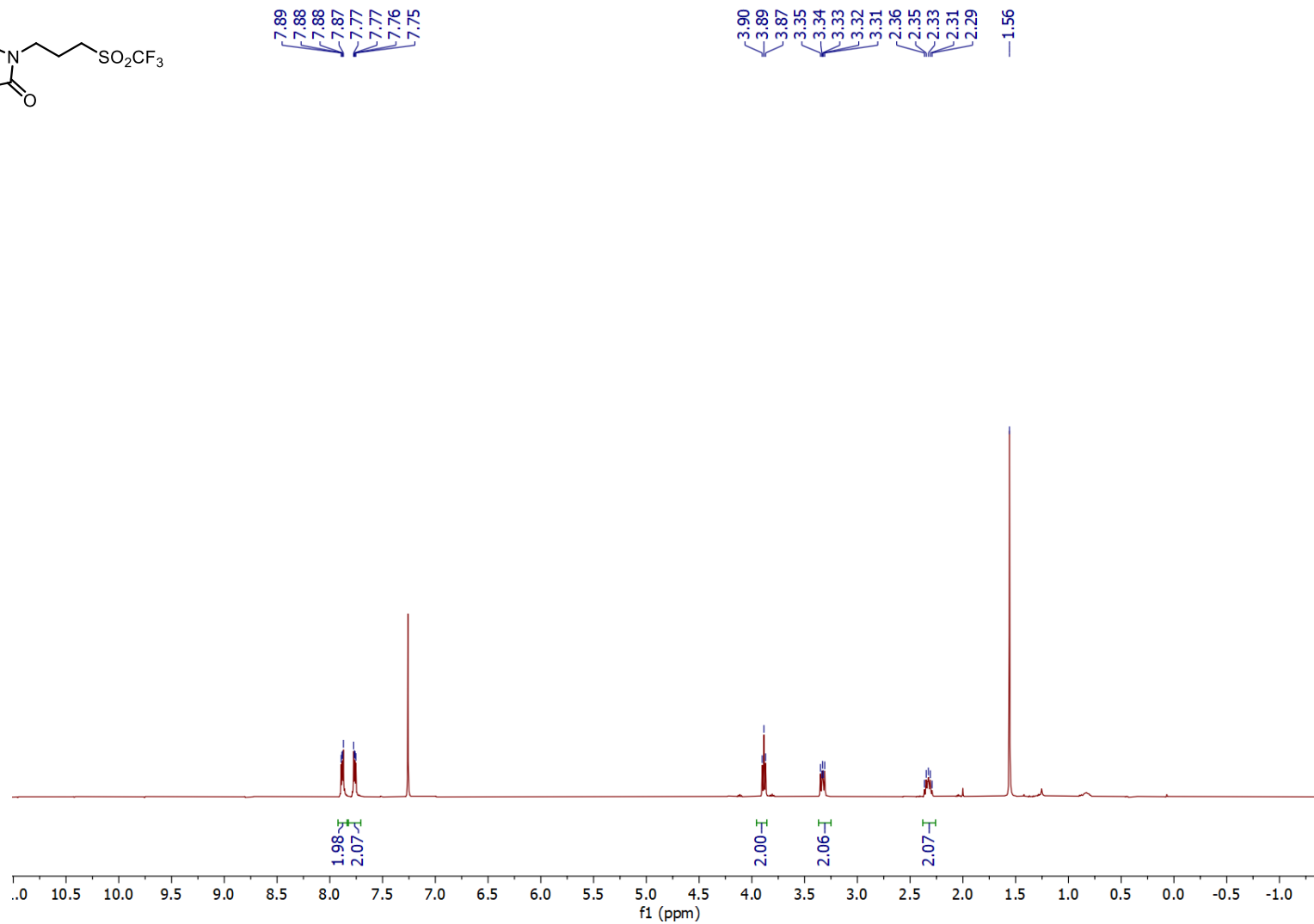
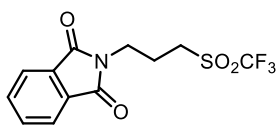
***tert*-Butyldimethyl(3-((trifluoromethyl)sulfonyl)propoxy)silane S2 ¹⁹F NMR (376 MHz, Chloroform-*d*)**



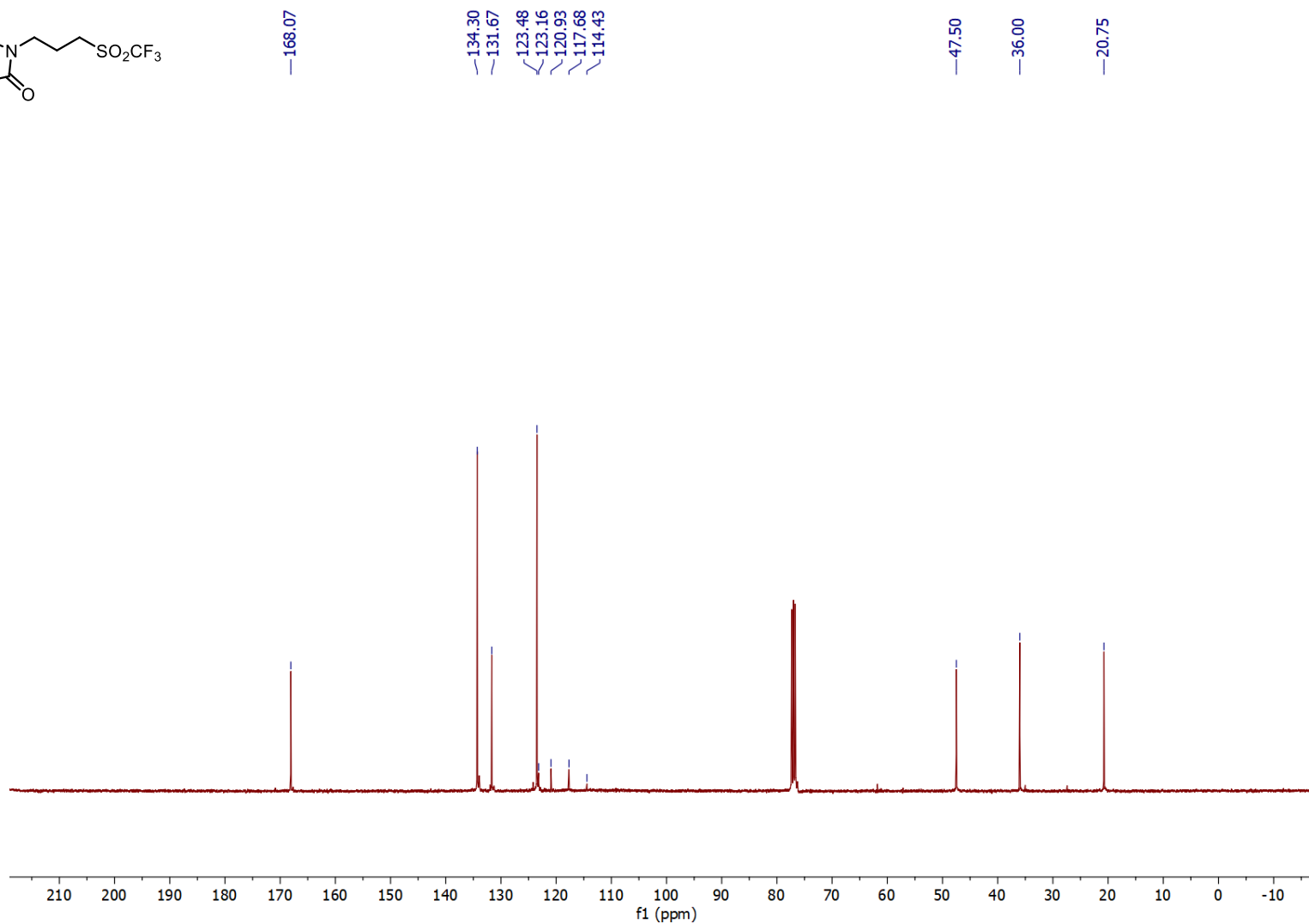
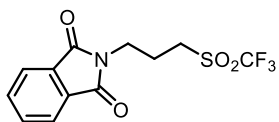
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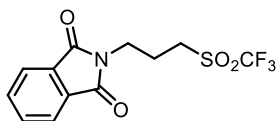
2-(3-((Trifluoromethyl)sulfonyl)propyl)isoindoline-1,3-dione S3 ¹H NMR (400 MHz, Chloroform-*d*)



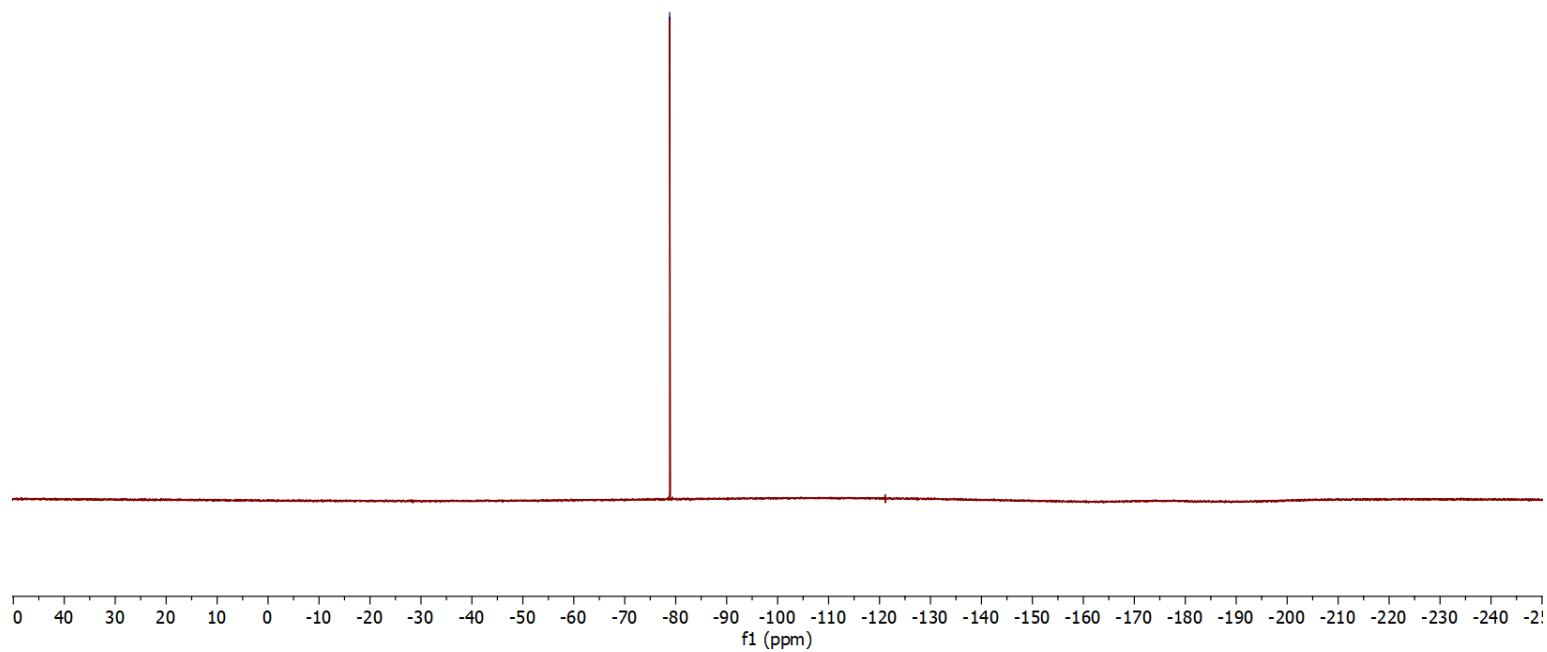
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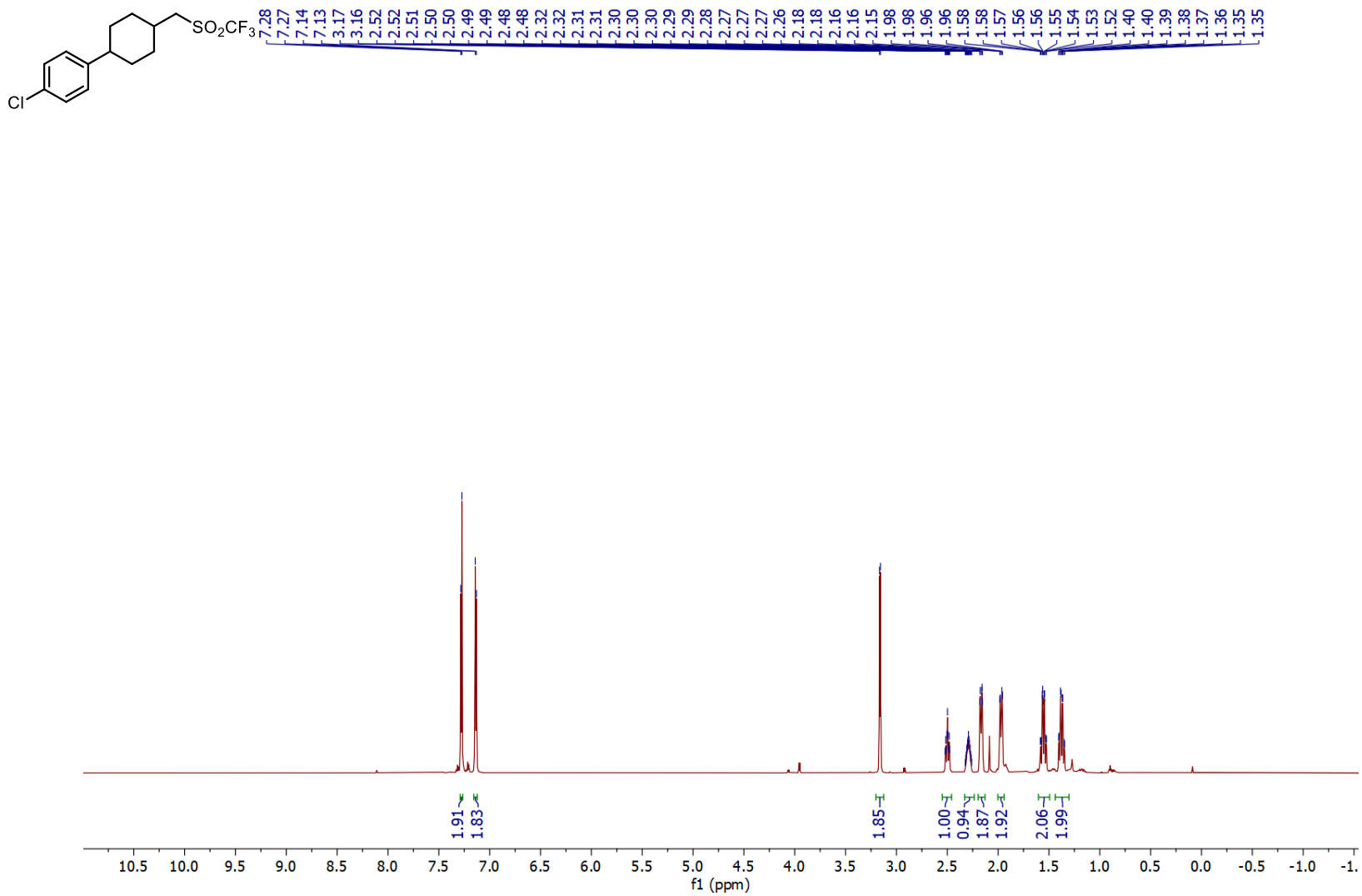
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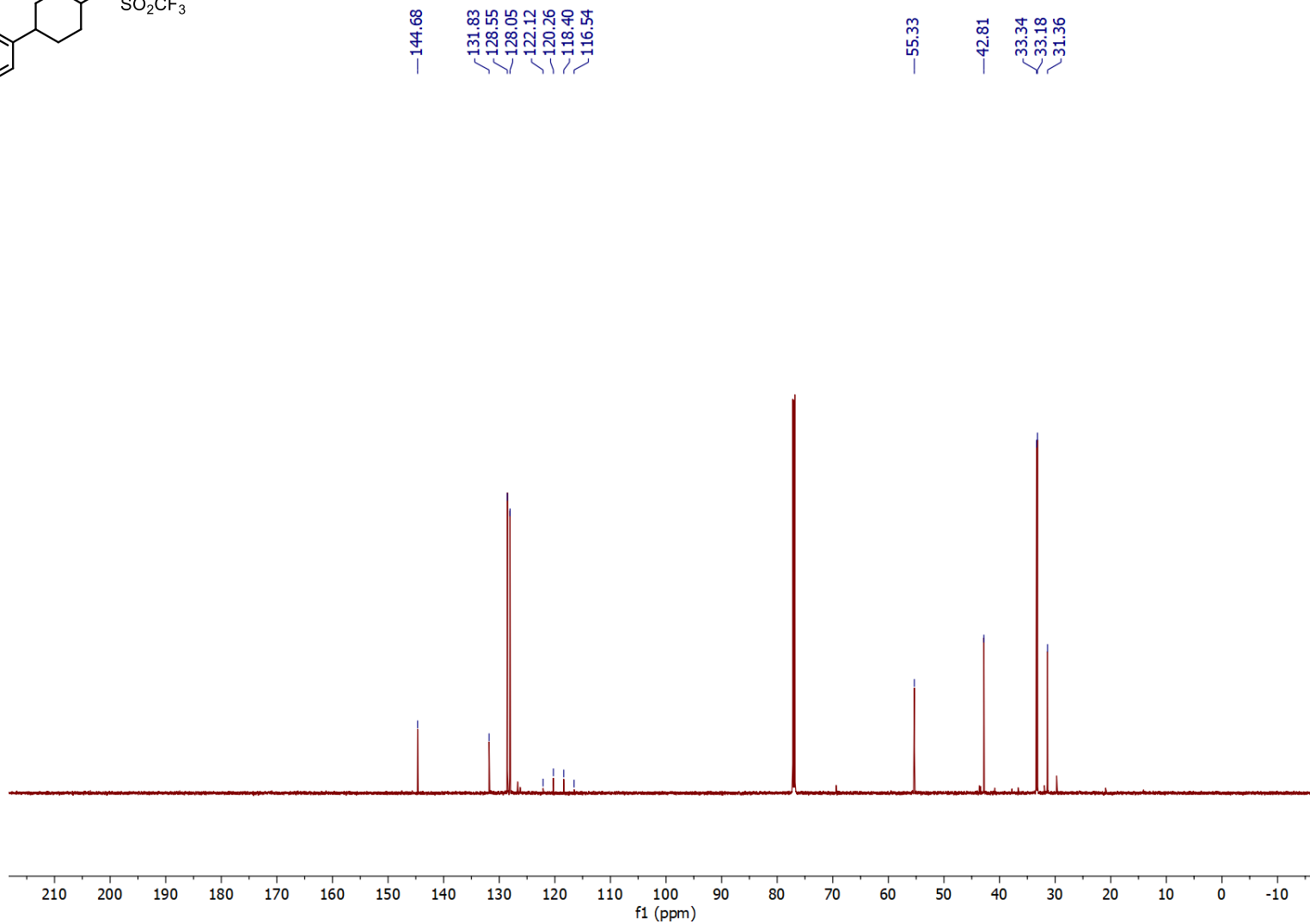
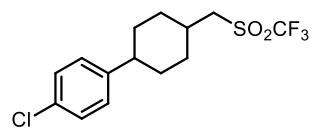
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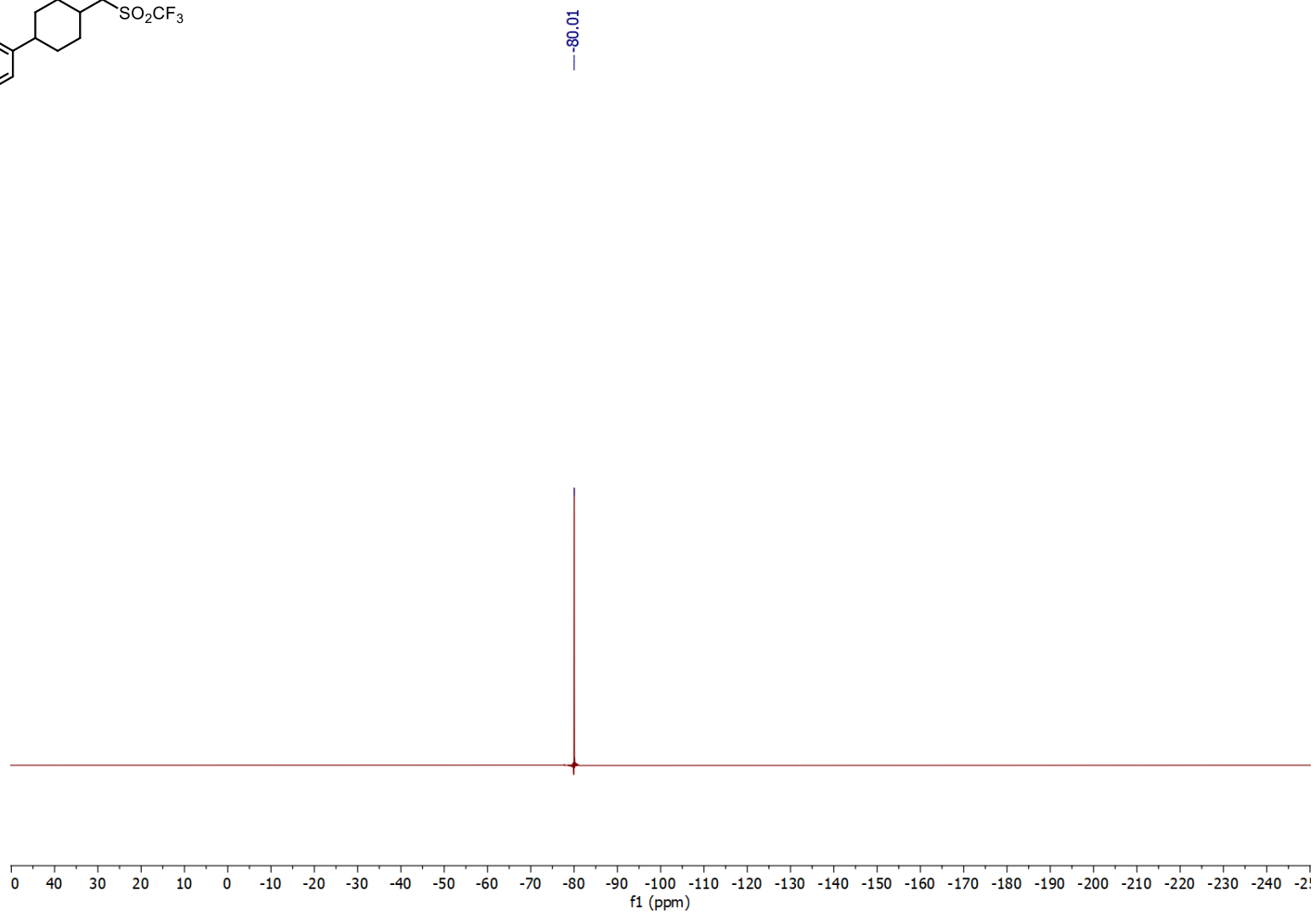
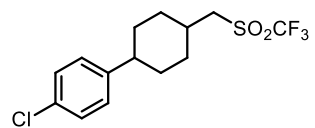
1-Chloro-4-(4-(((trifluoromethyl)sulfonyl)methyl)cyclohexyl)benzene S4 ¹H NMR (700 MHz, Chloroform-*d*)



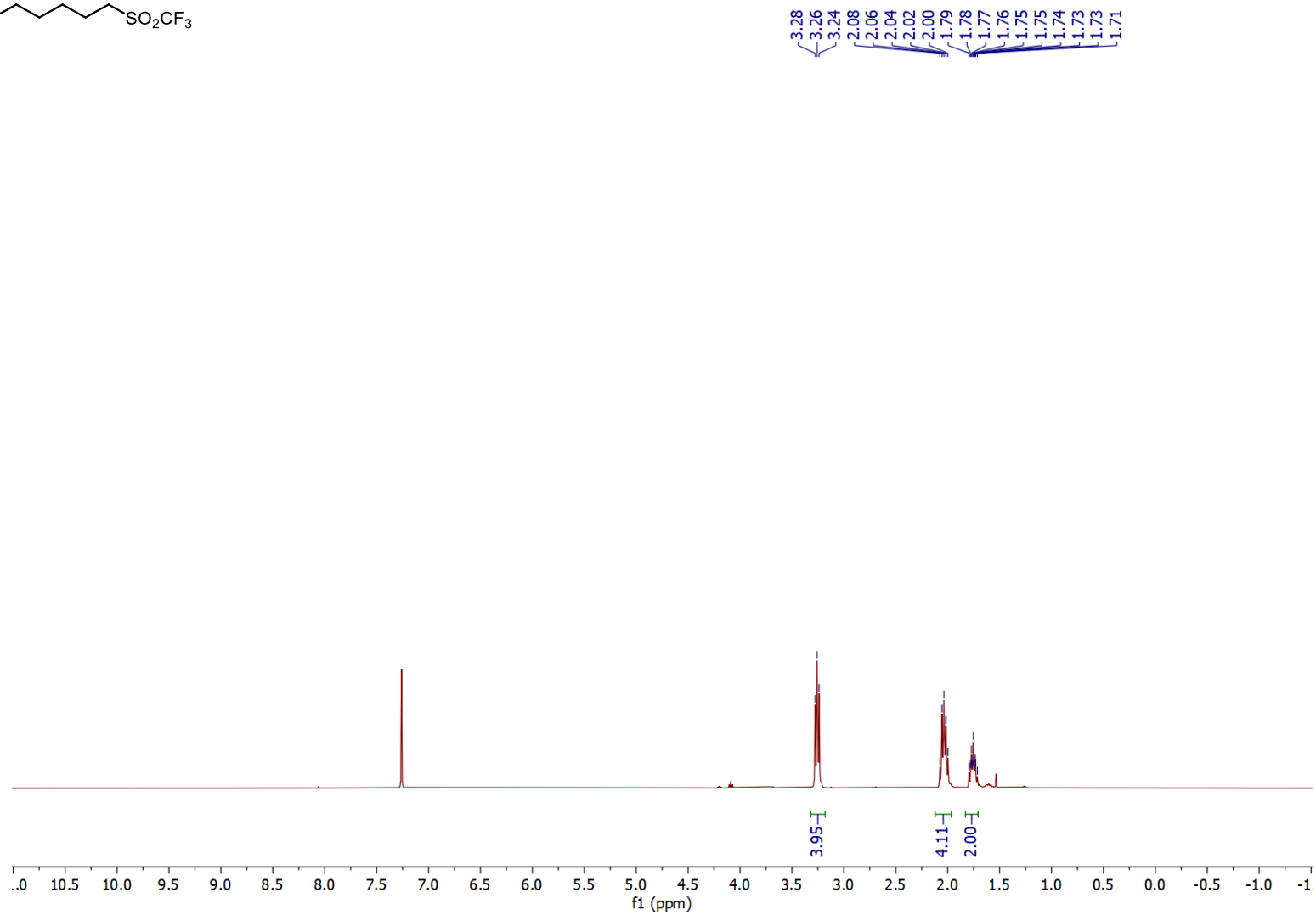
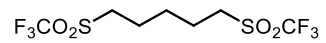
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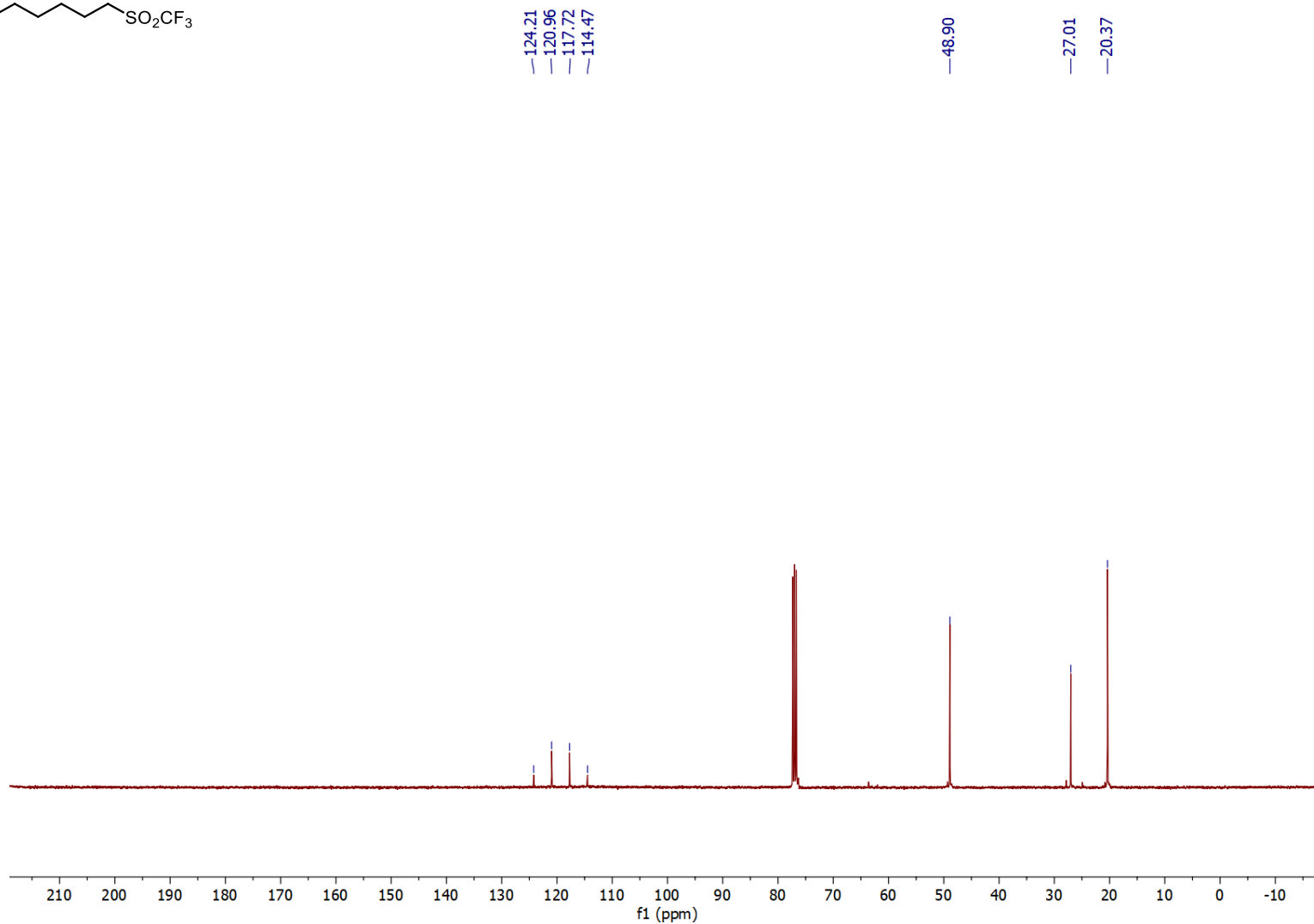
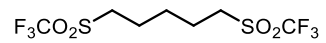
1-Chloro-4-(4-(((trifluoromethyl)sulfonyl)methyl)cyclohexyl)benzene S4 ¹⁹F NMR (376 MHz, Chloroform-*d*)



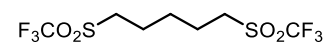
1,5-Bis((trifluoromethyl)sulfonyl)pentane S5 ¹H NMR (400 MHz, Chloroform-*d*)



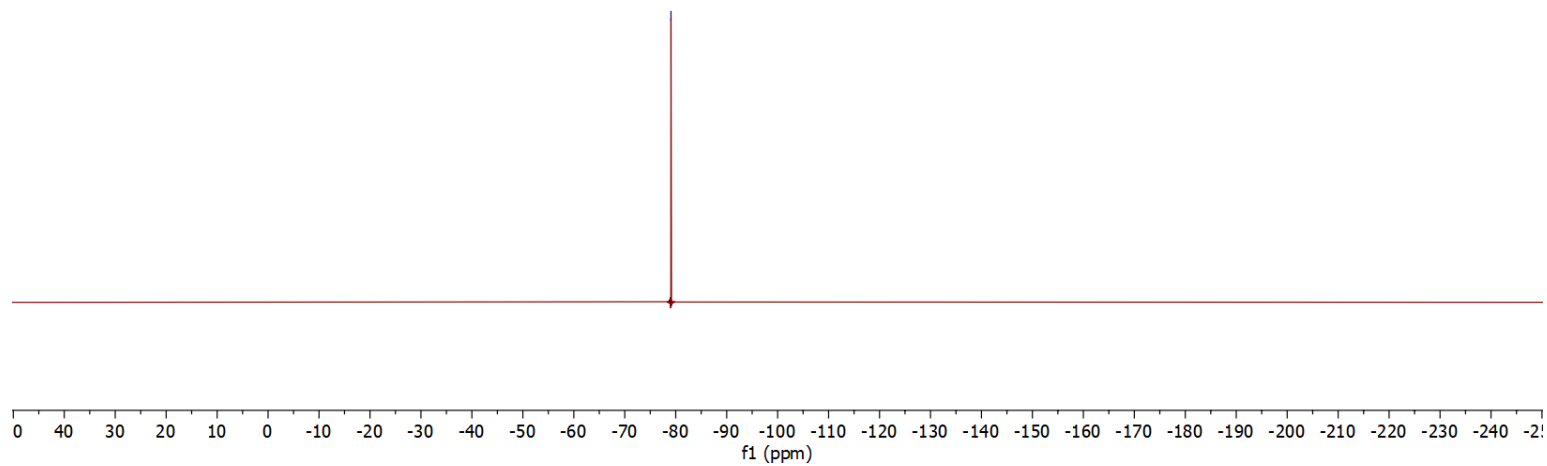
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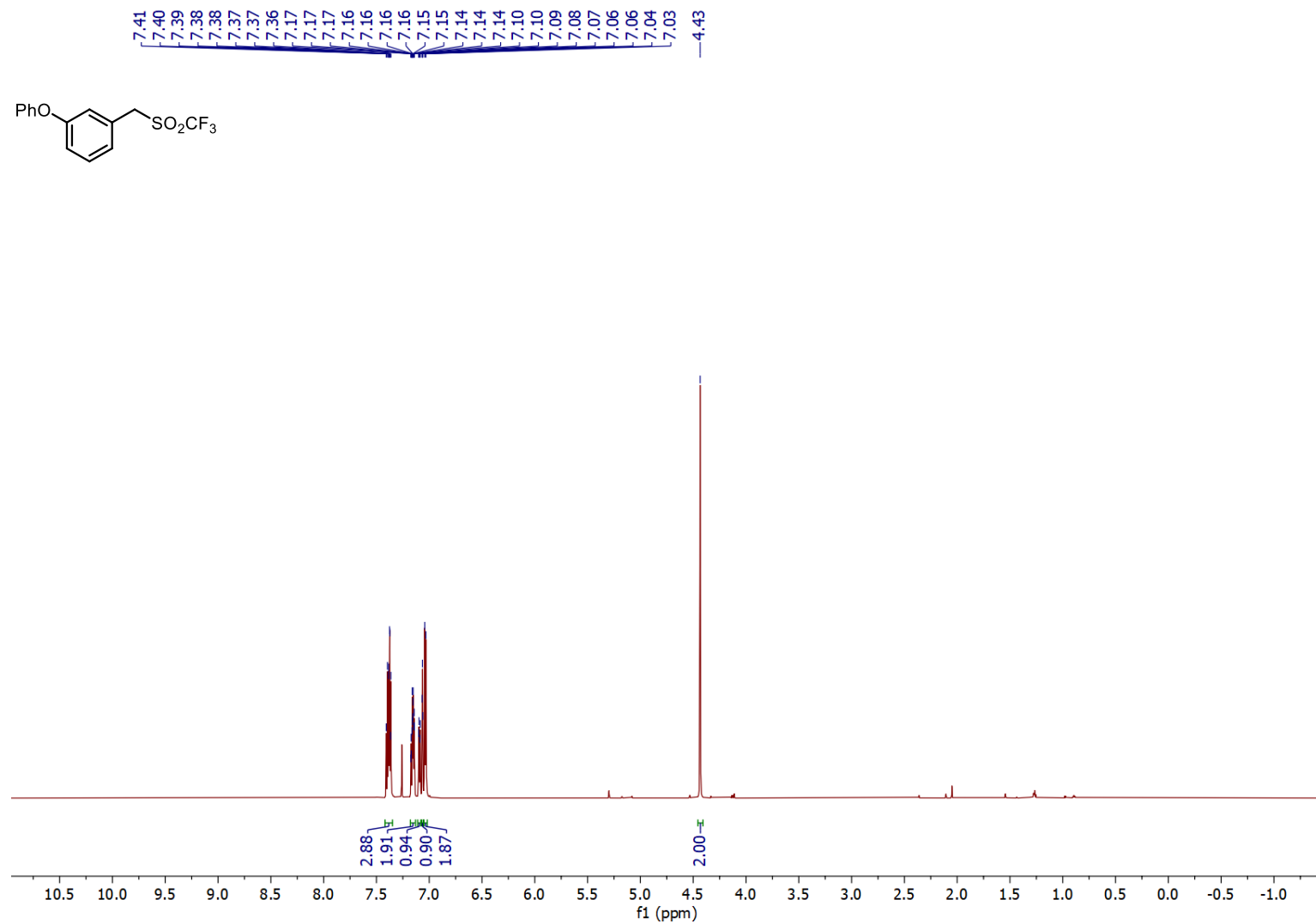
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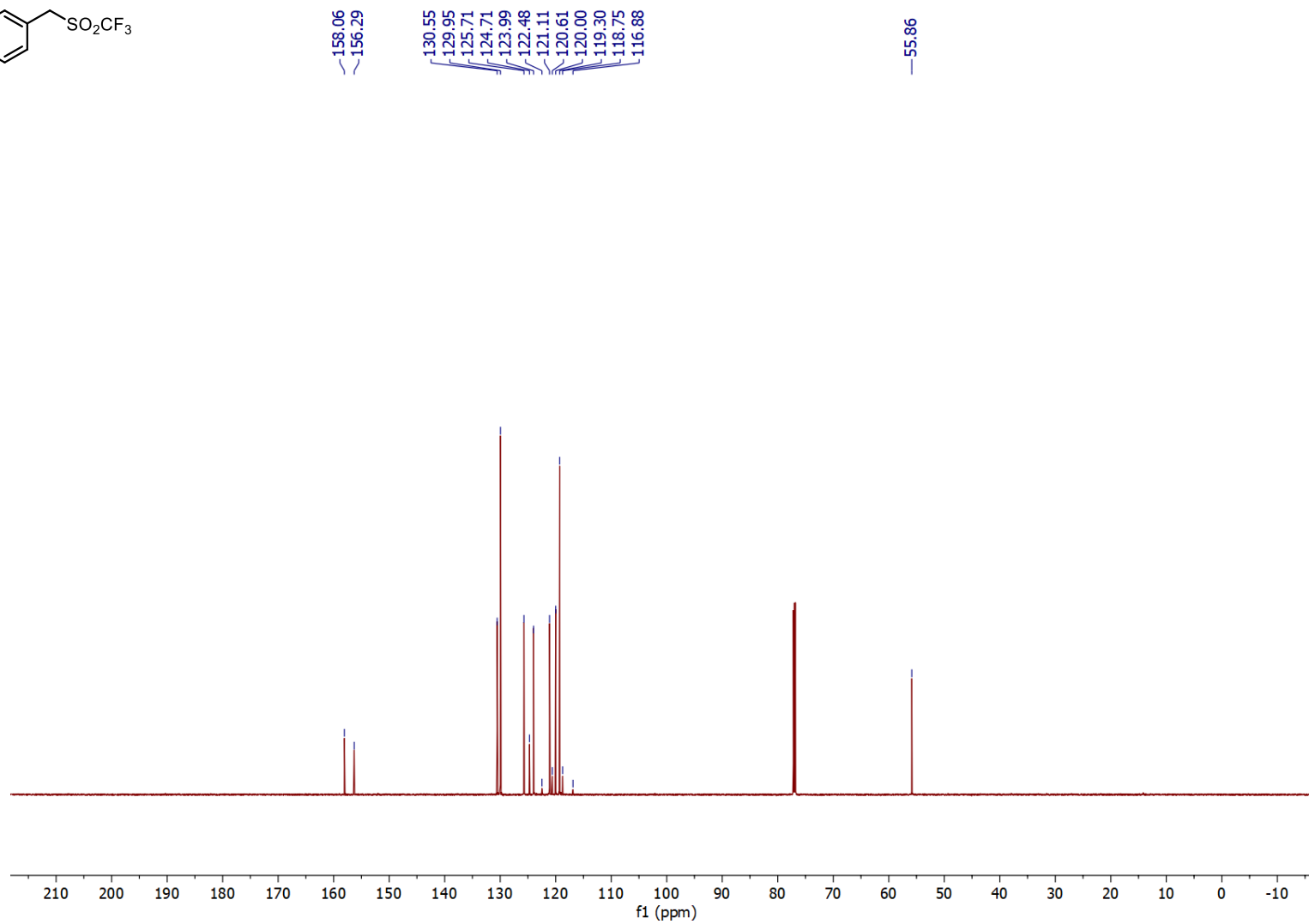
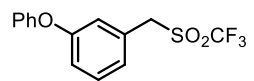
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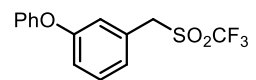
1-Phenoxy-3-(((trifluoromethyl)sulfonyl)methyl)benzene S8 ^1H NMR (700 MHz, Chloroform-*d*)



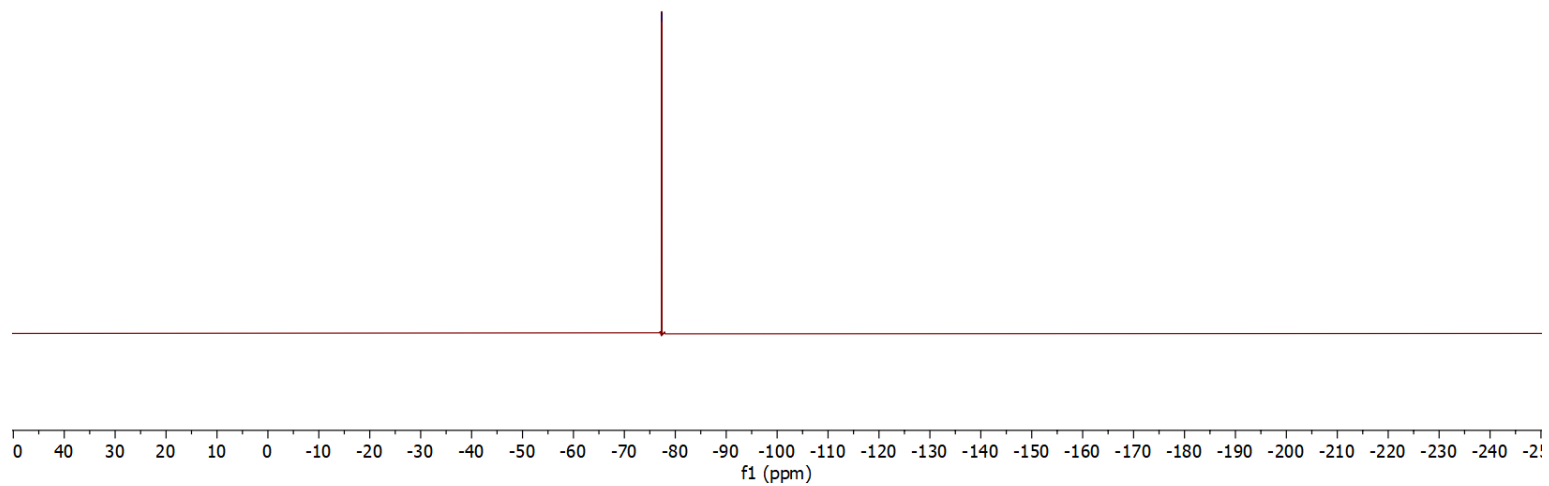
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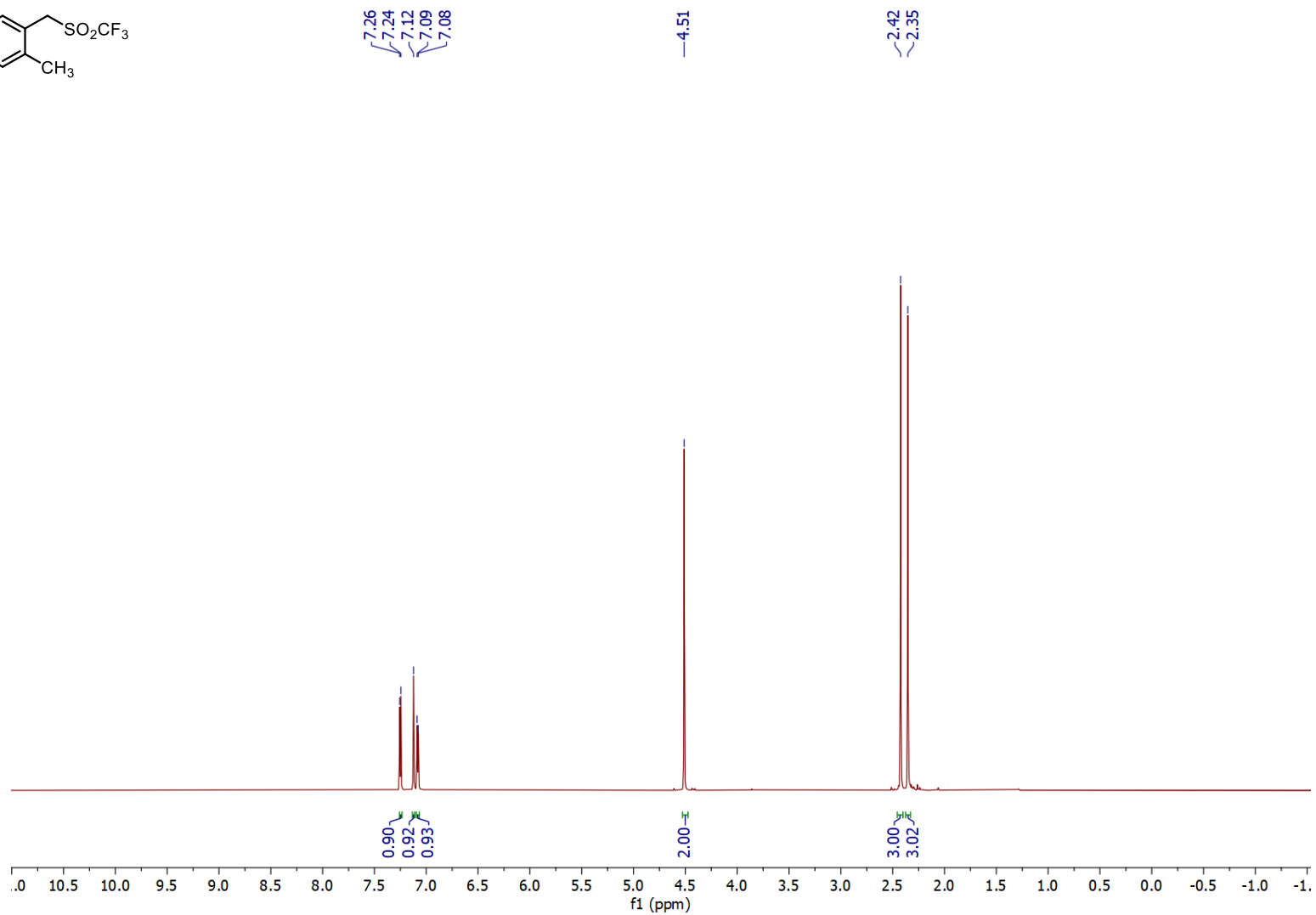
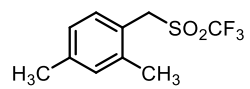
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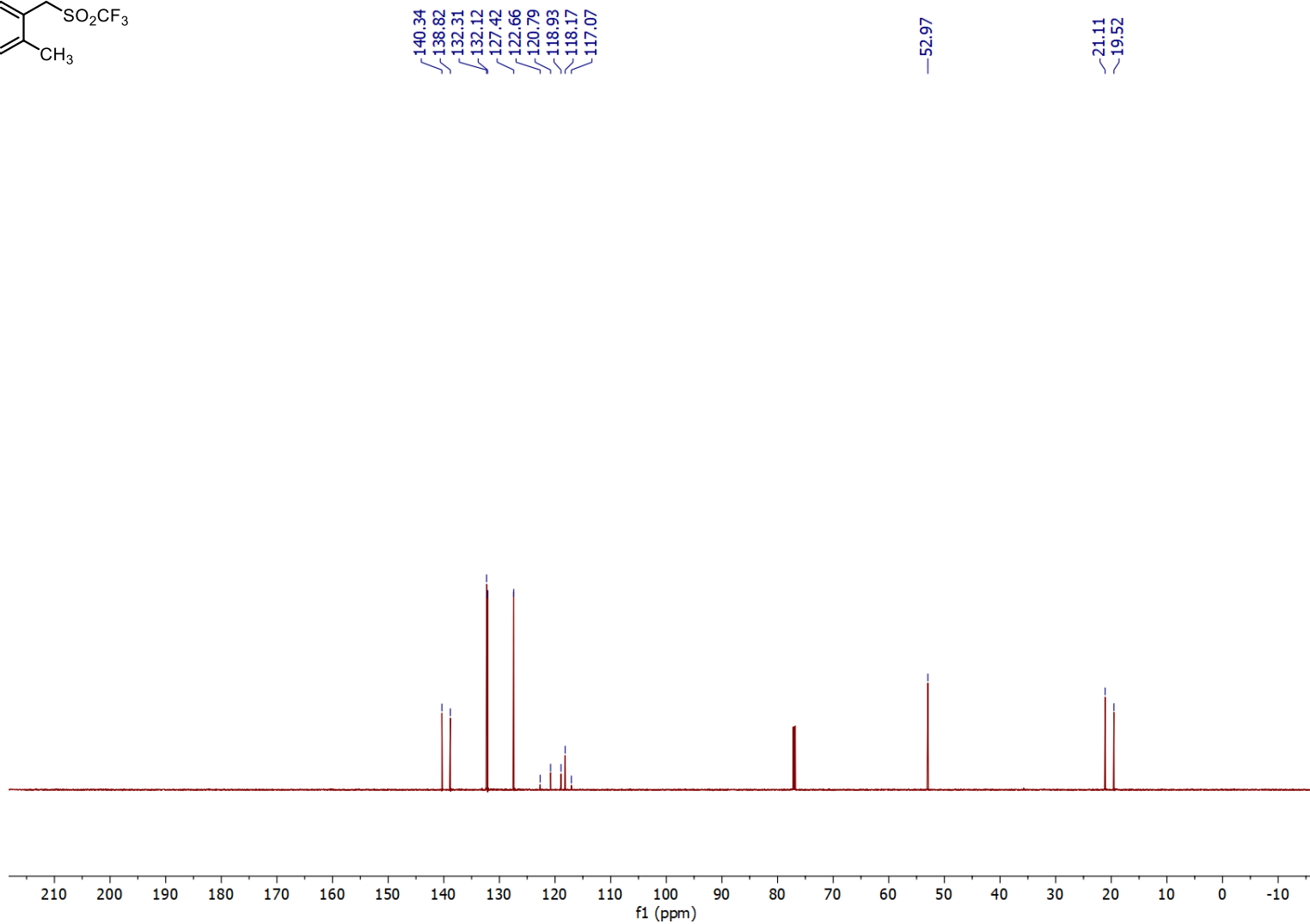
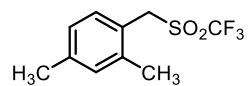
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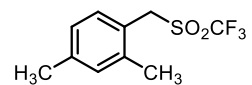
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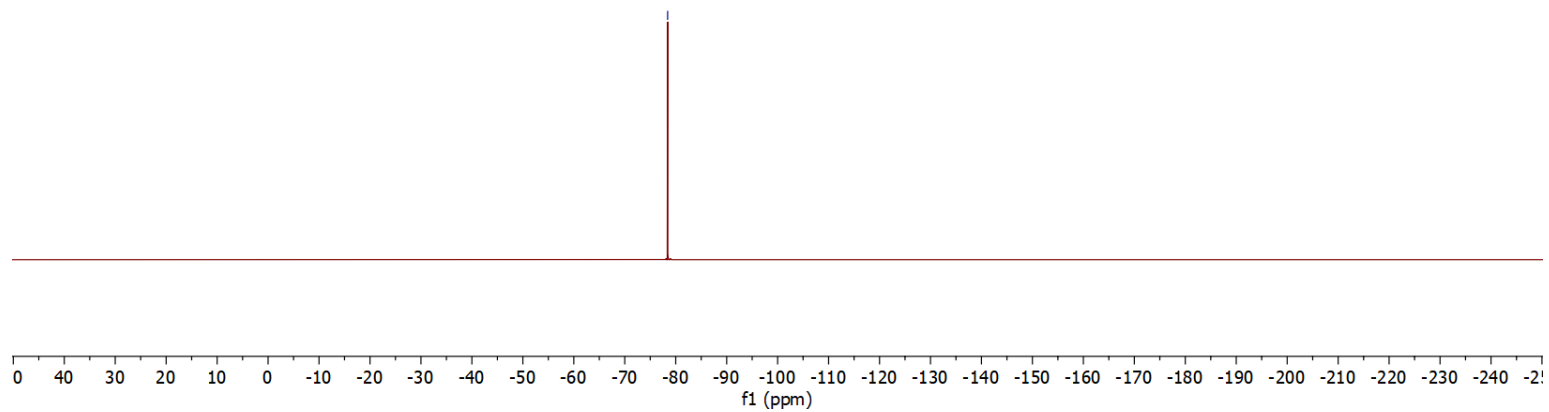
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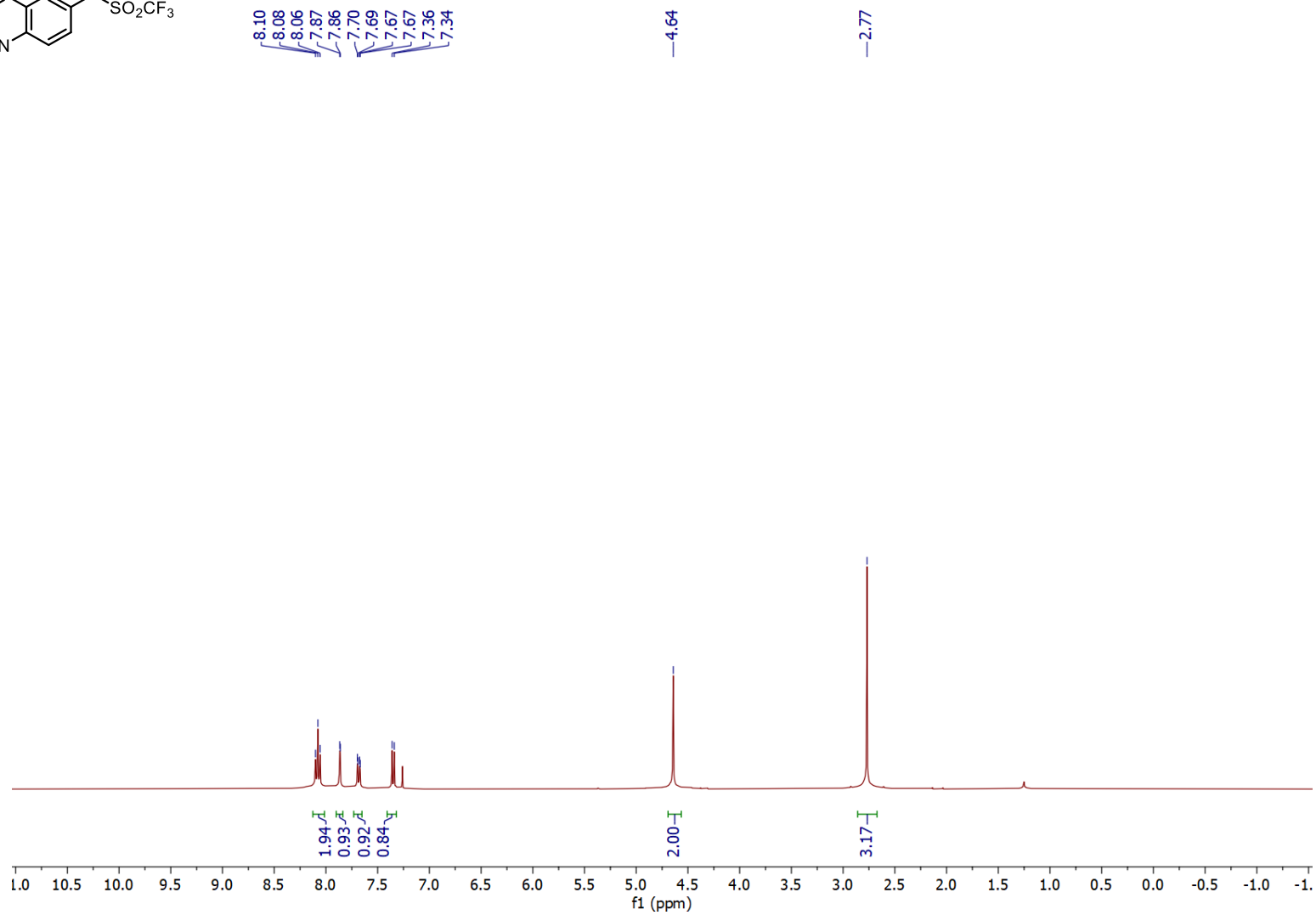
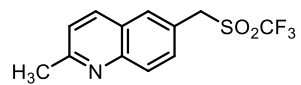
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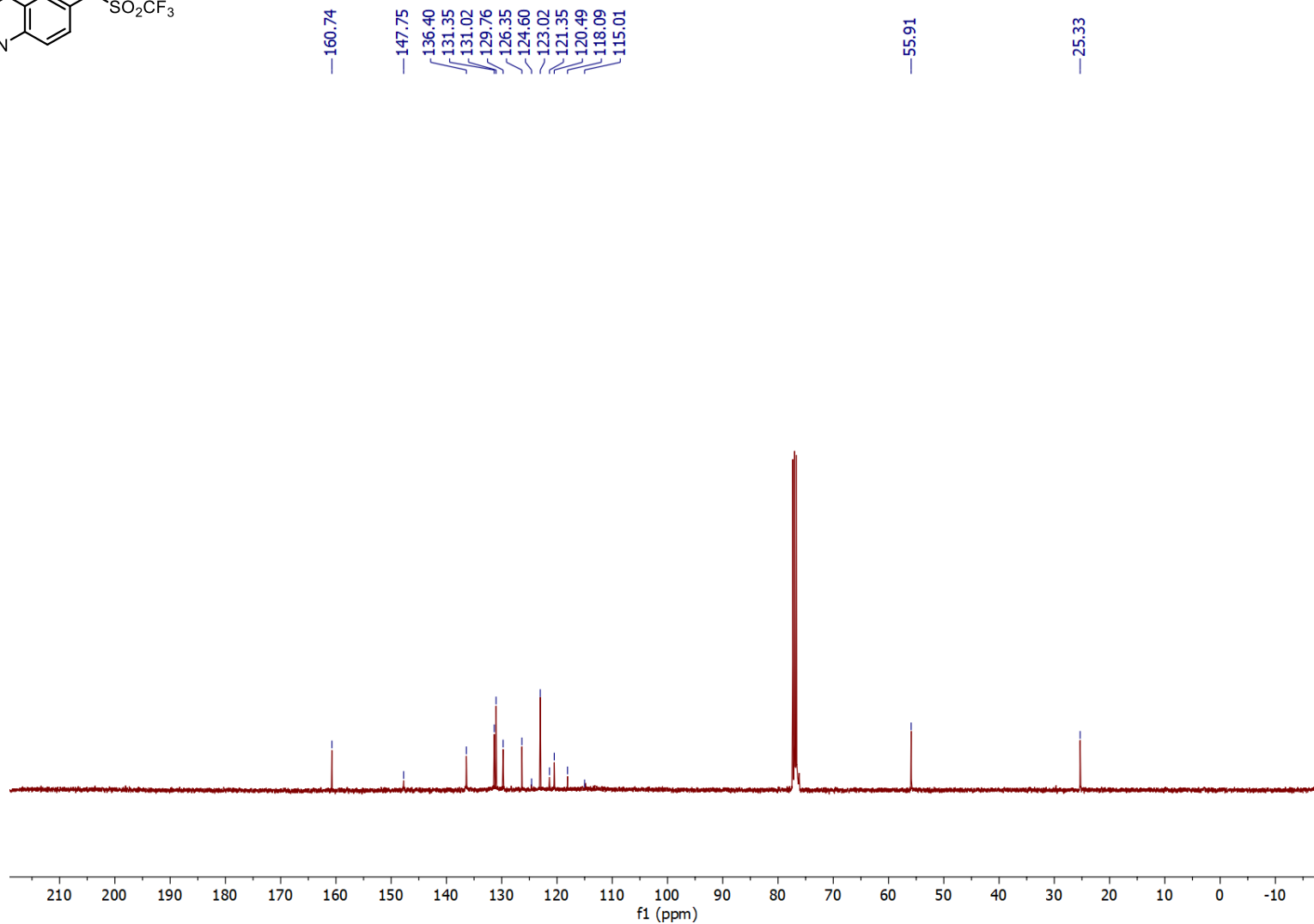
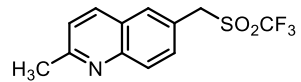
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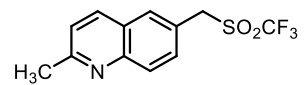
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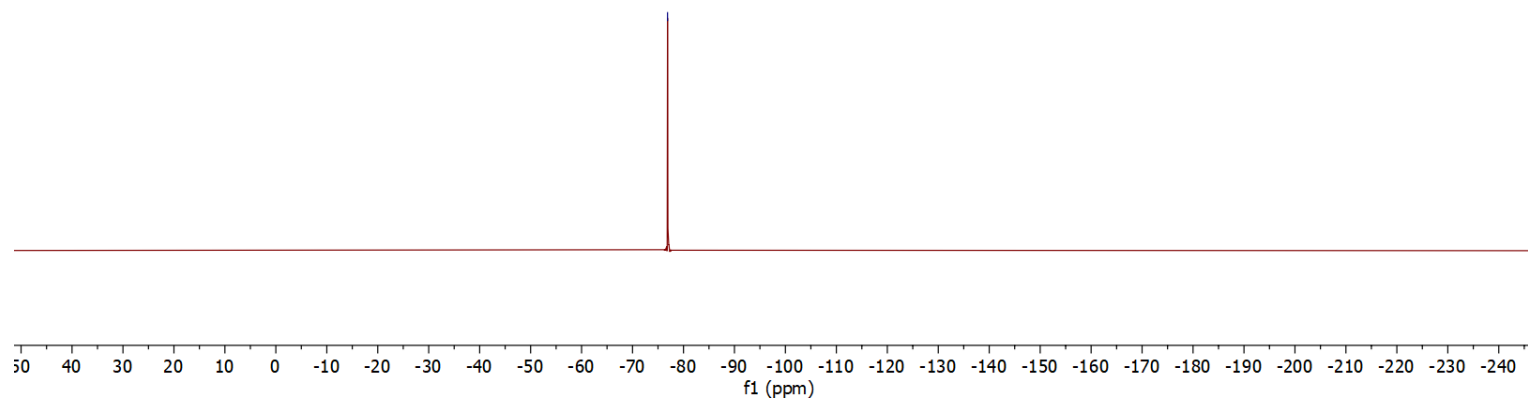
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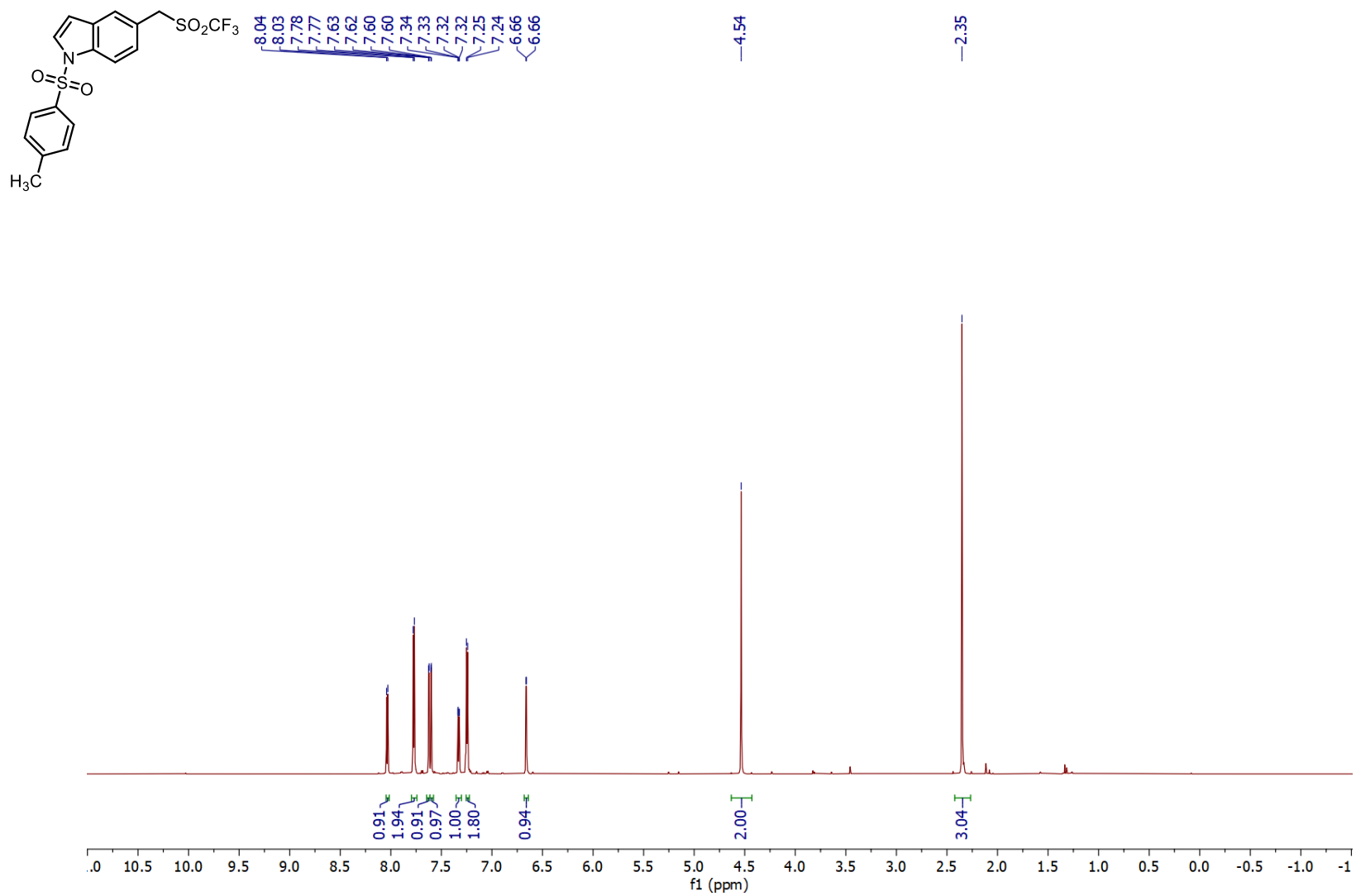
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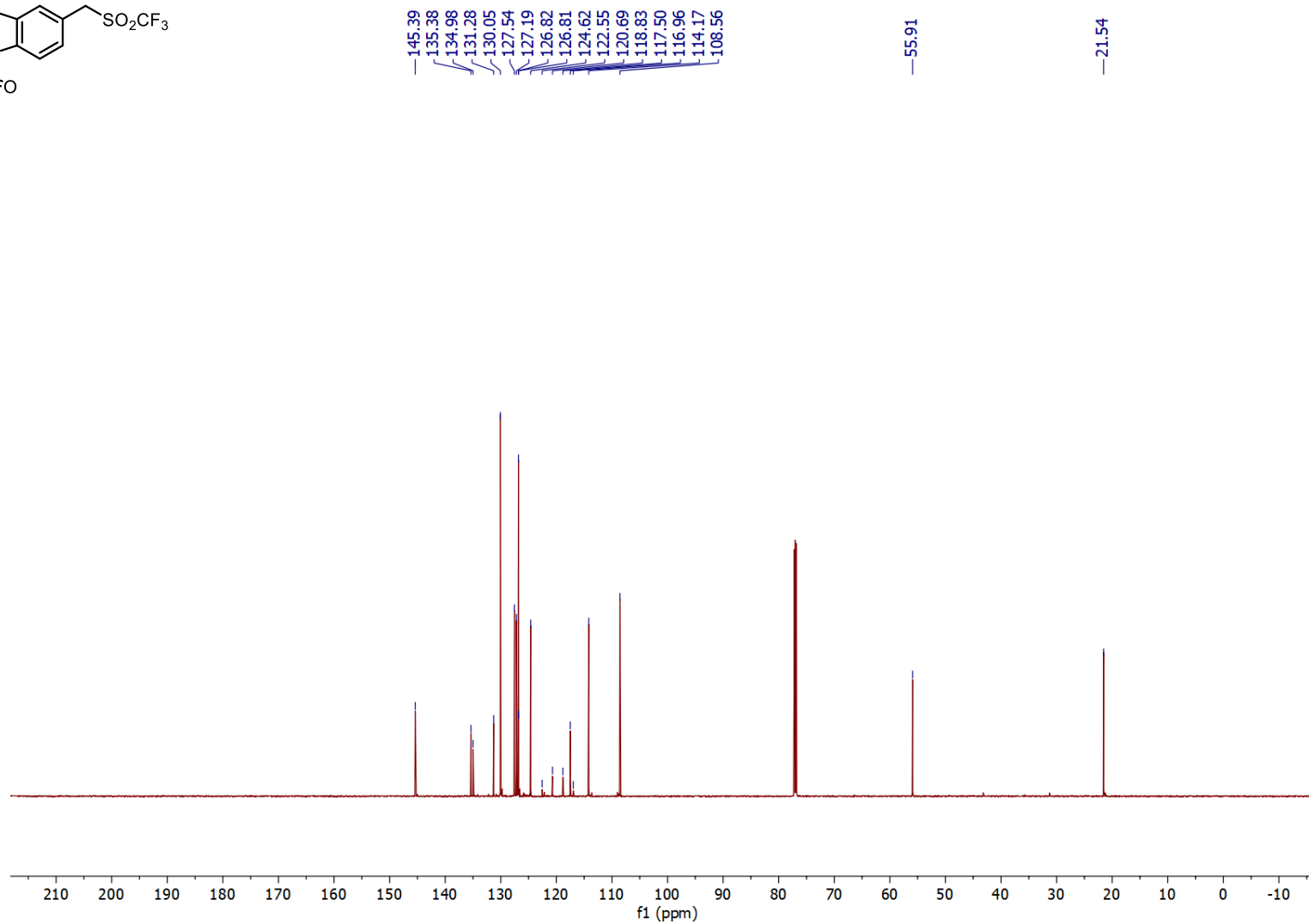
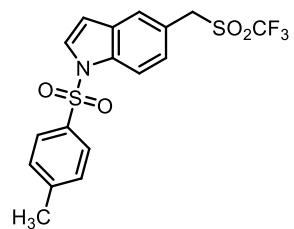
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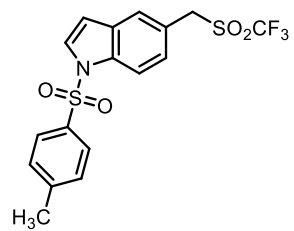
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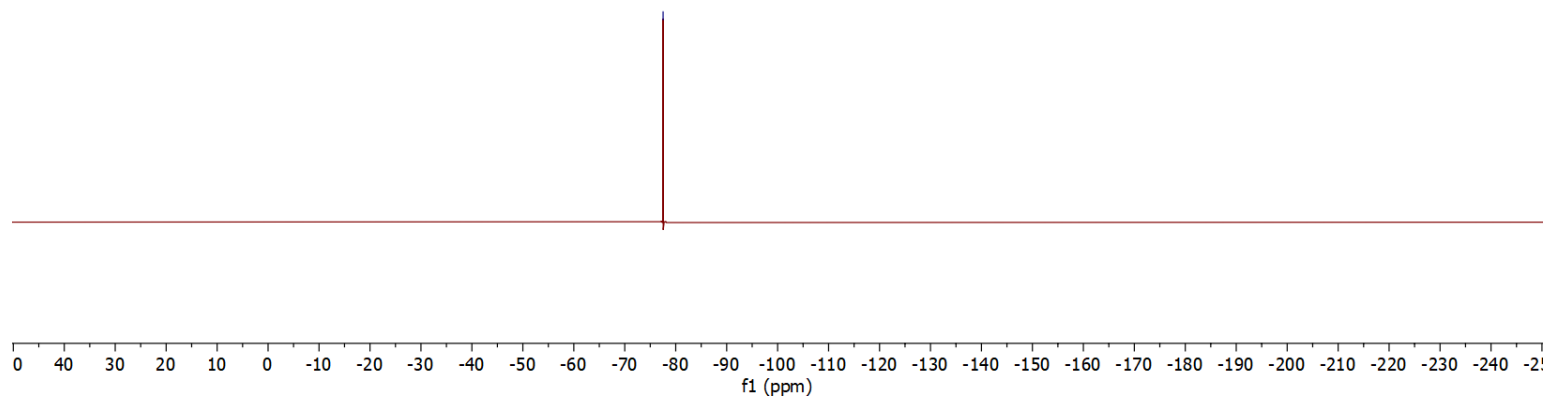
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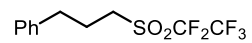
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-77.52

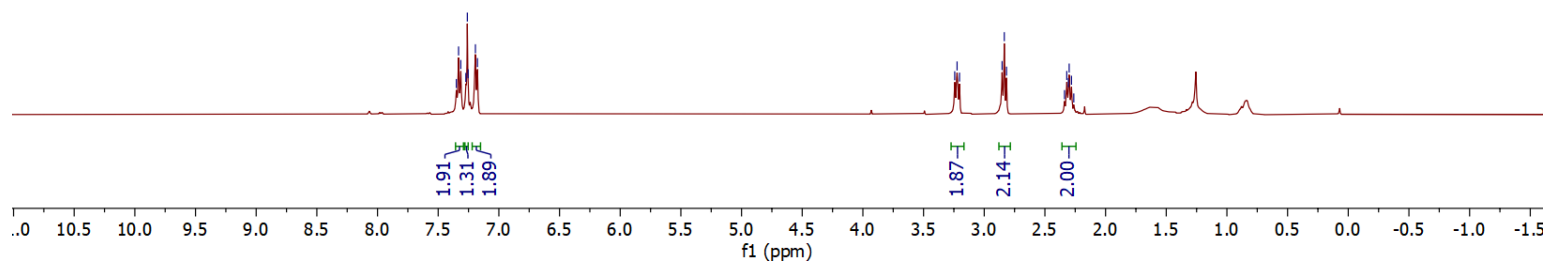


(3-((Perfluoroethyl)sulfonyl)propyl)benzene S13 ¹H NMR (700 MHz, Chloroform-*d*)

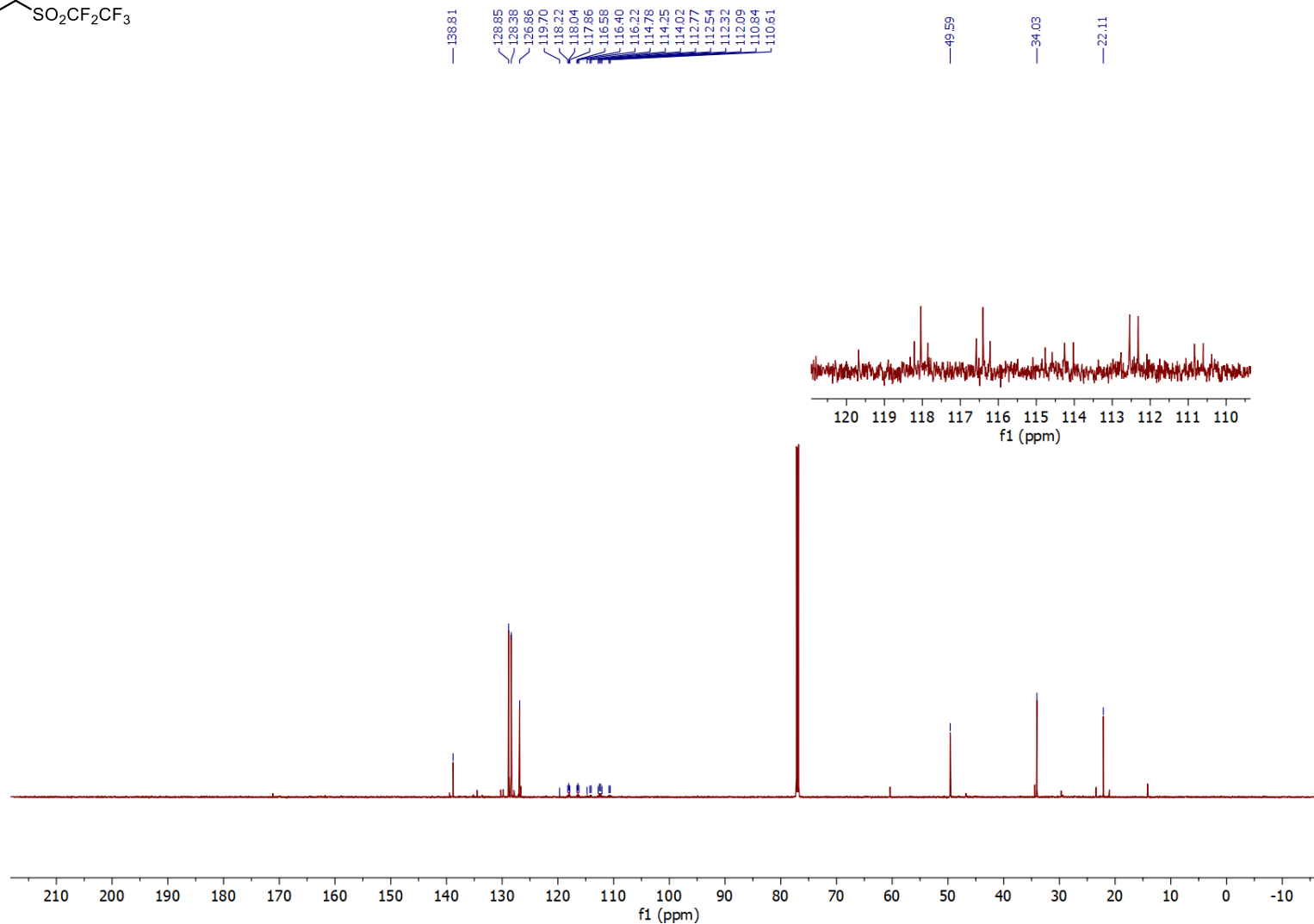
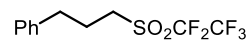


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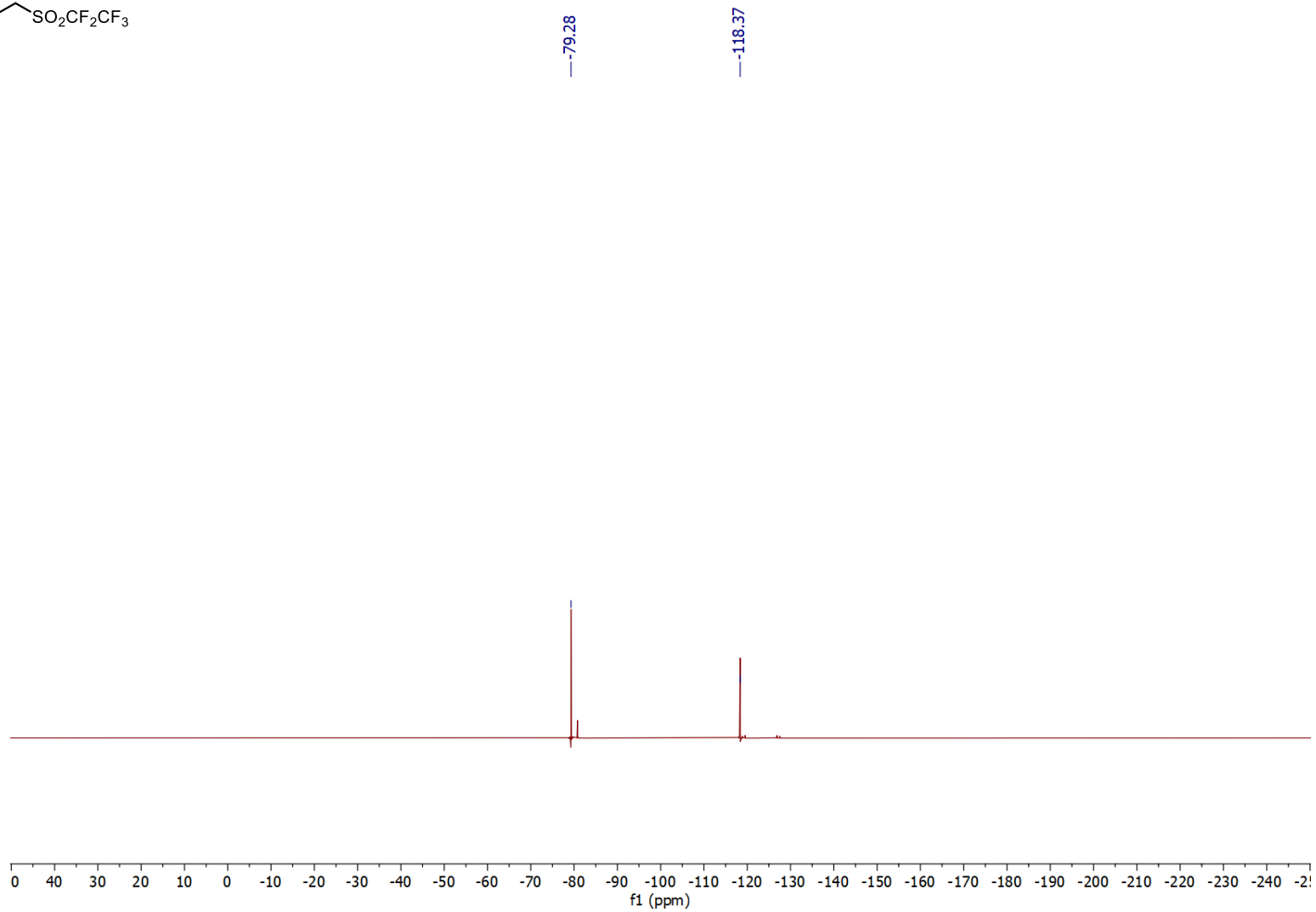
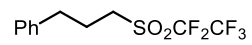
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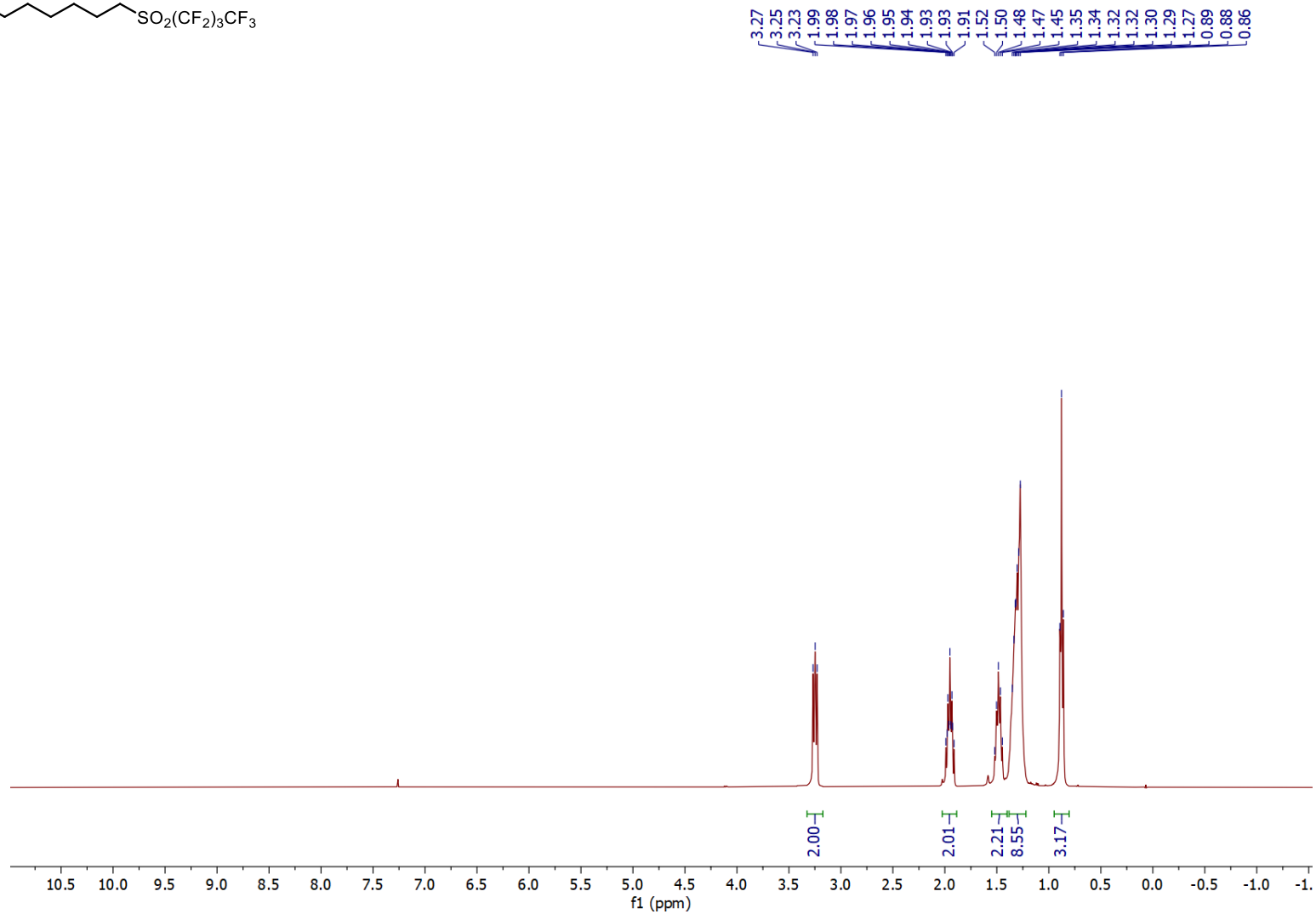
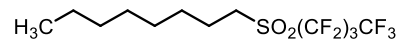
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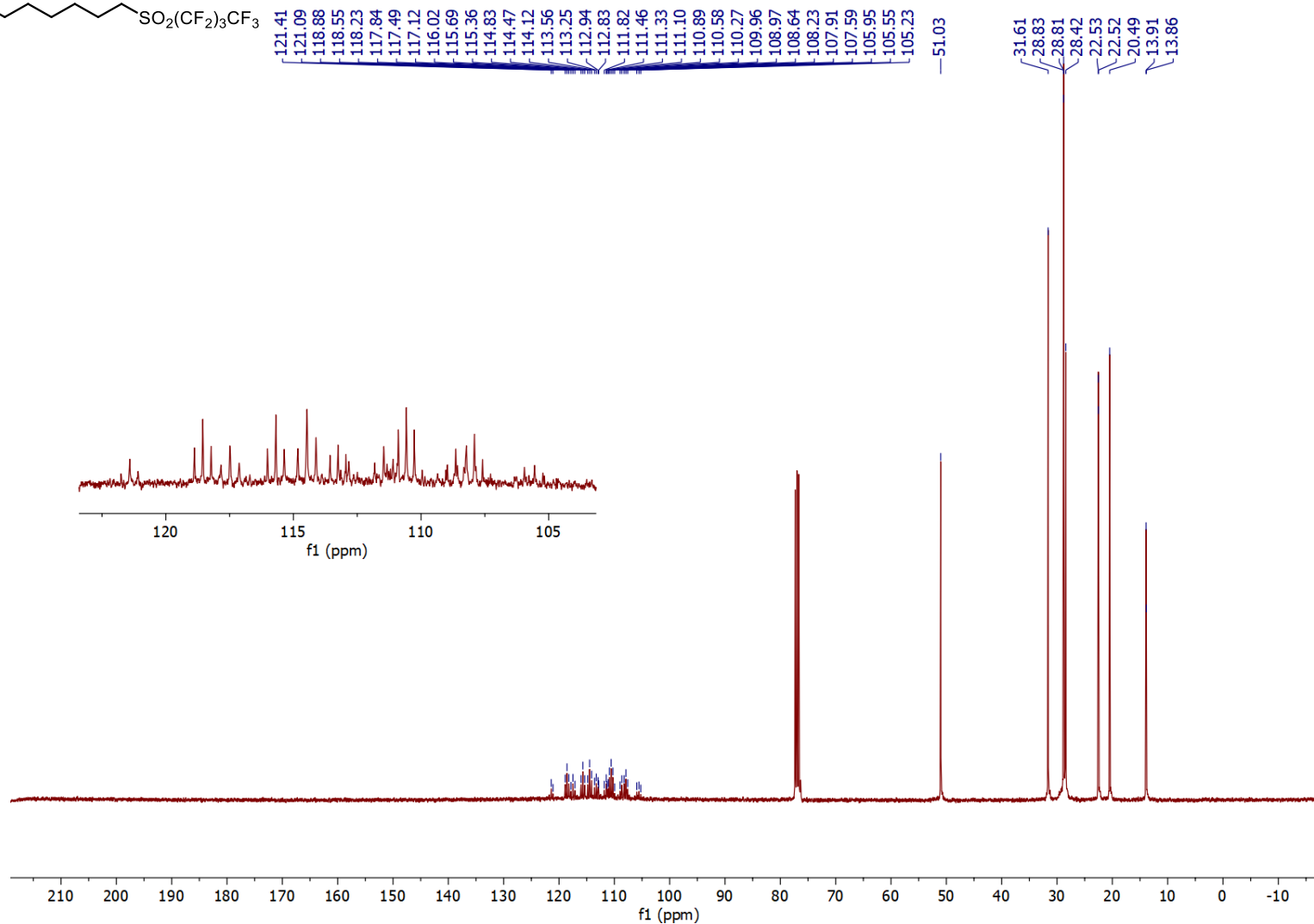
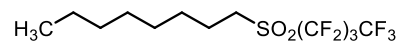
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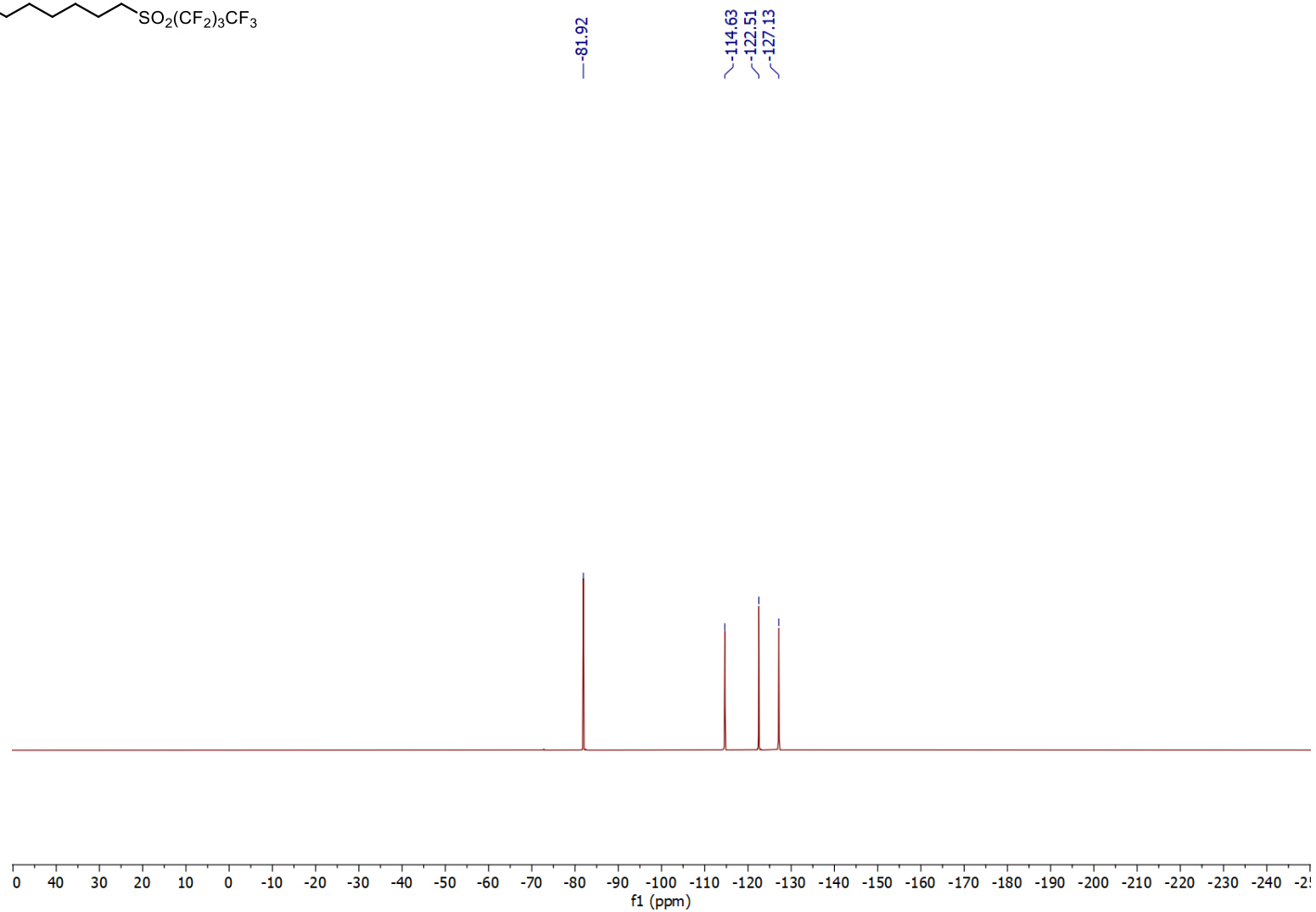
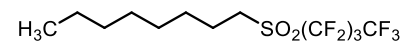
1-((Perfluorobutyl)sulfonyl)octane S14 ¹H NMR (400 MHz, Chloroform-*d*)



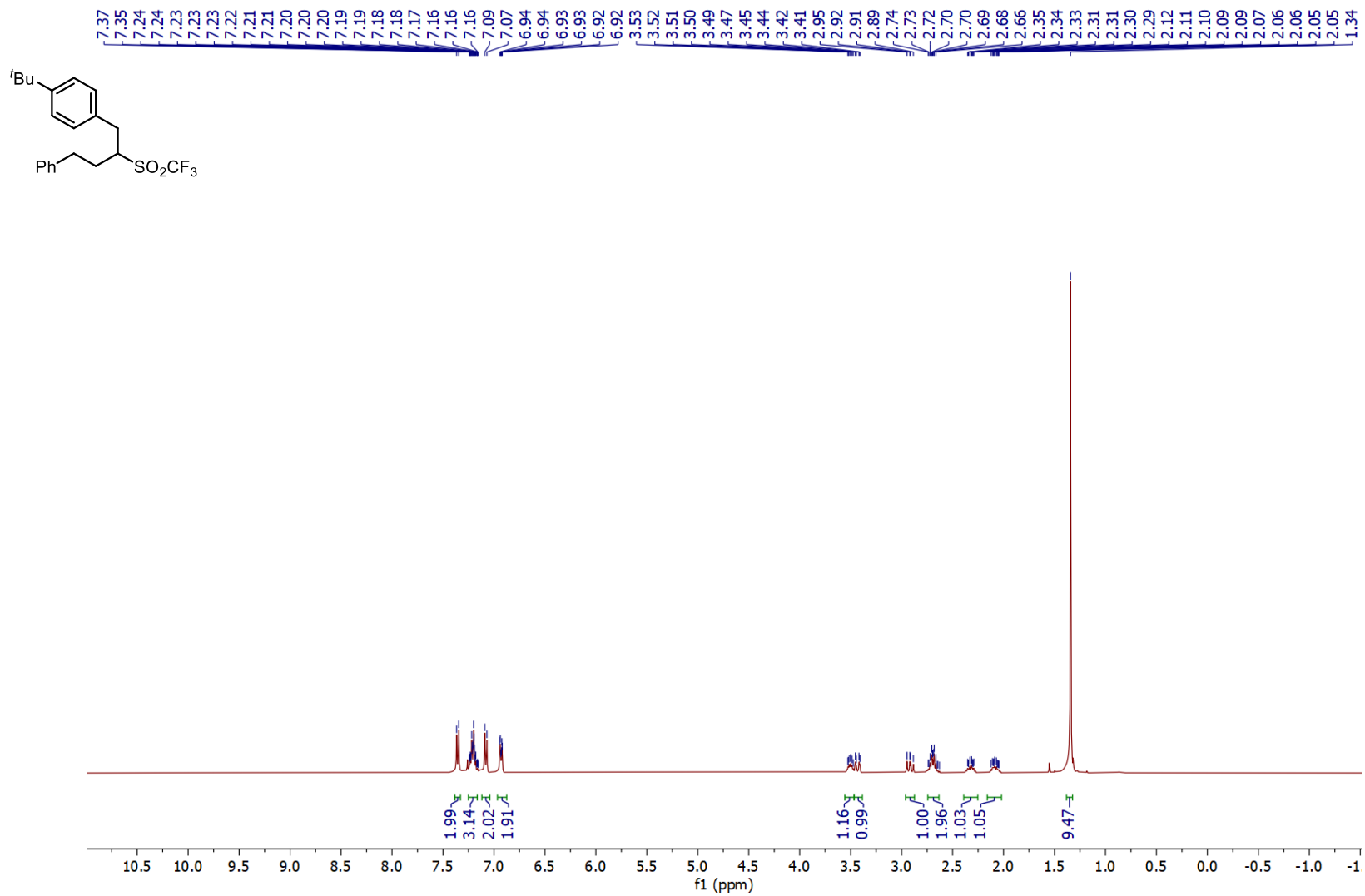
1-((Perfluorobutyl)sulfonyl)octane S14 $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, Chloroform-*d*)



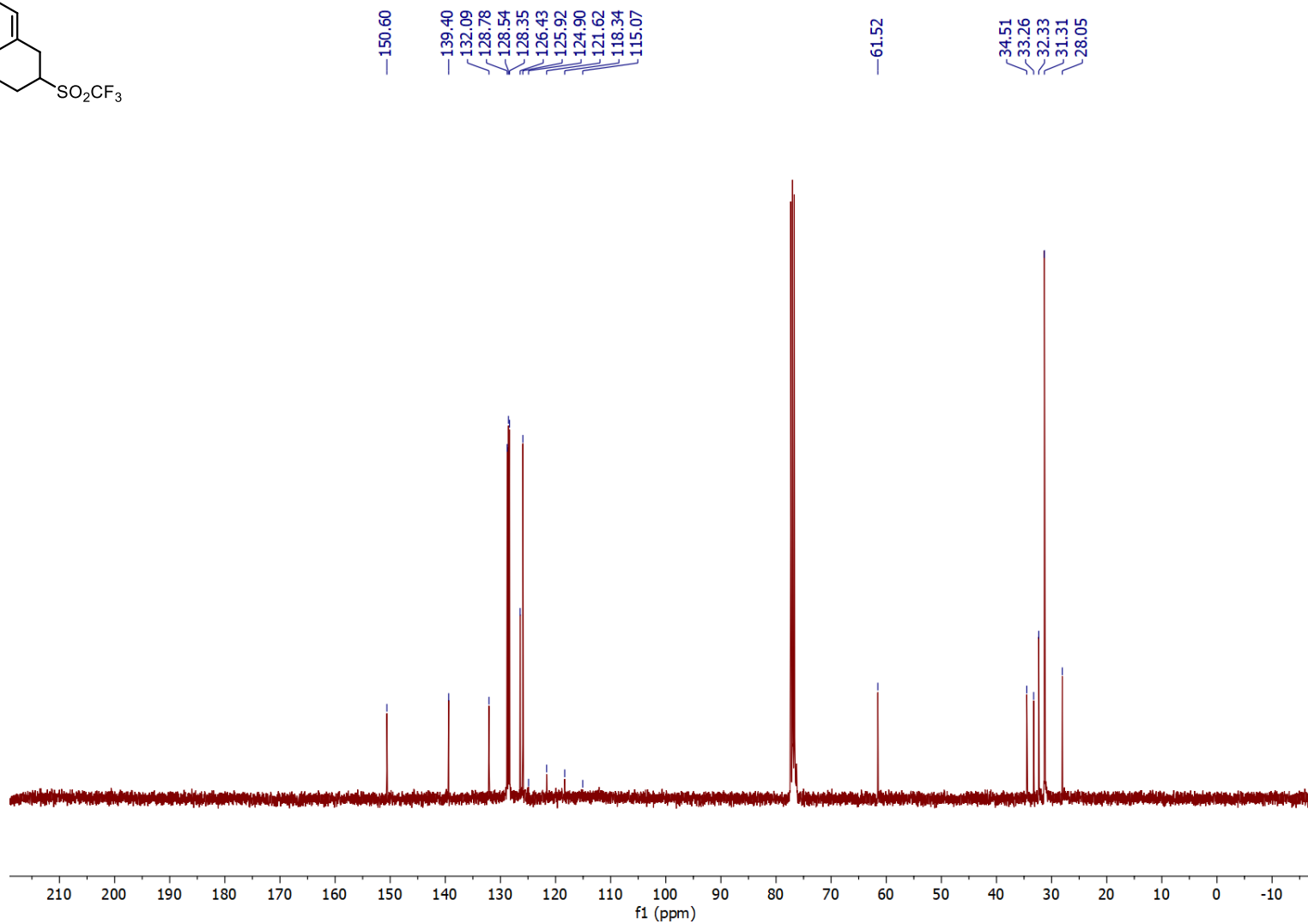
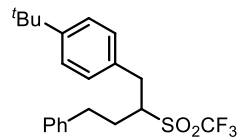
1-((Perfluorobutyl)sulfonyl)octane S14 ¹⁹F NMR (376 MHz, Chloroform-*d*)



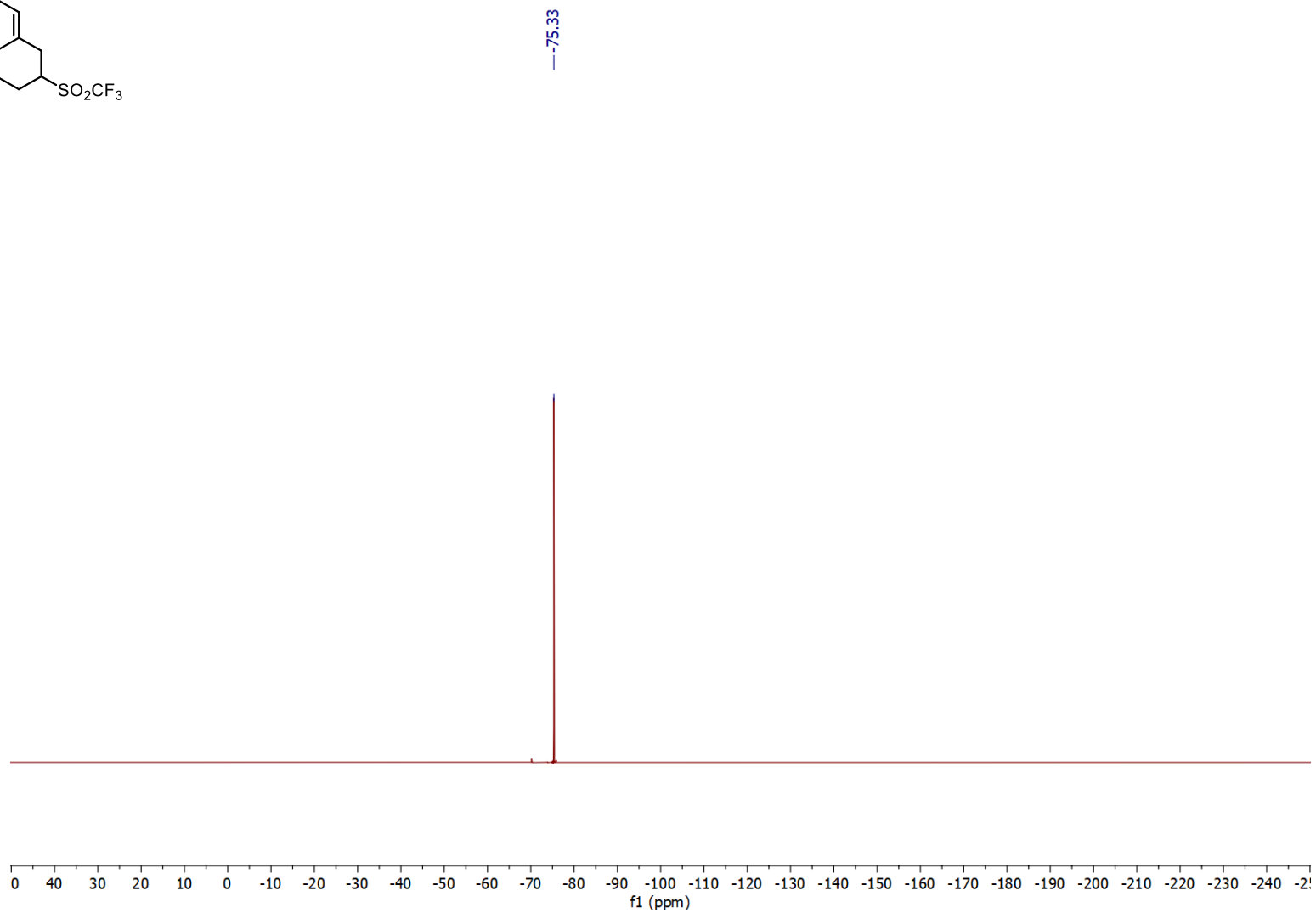
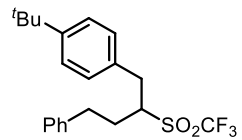
1-(*tert*-Butyl)-4-(4-phenyl-2-((trifluoromethyl)sulfonyl)butyl)benzene 1a ¹H NMR (400 MHz, Chloroform-*d*)



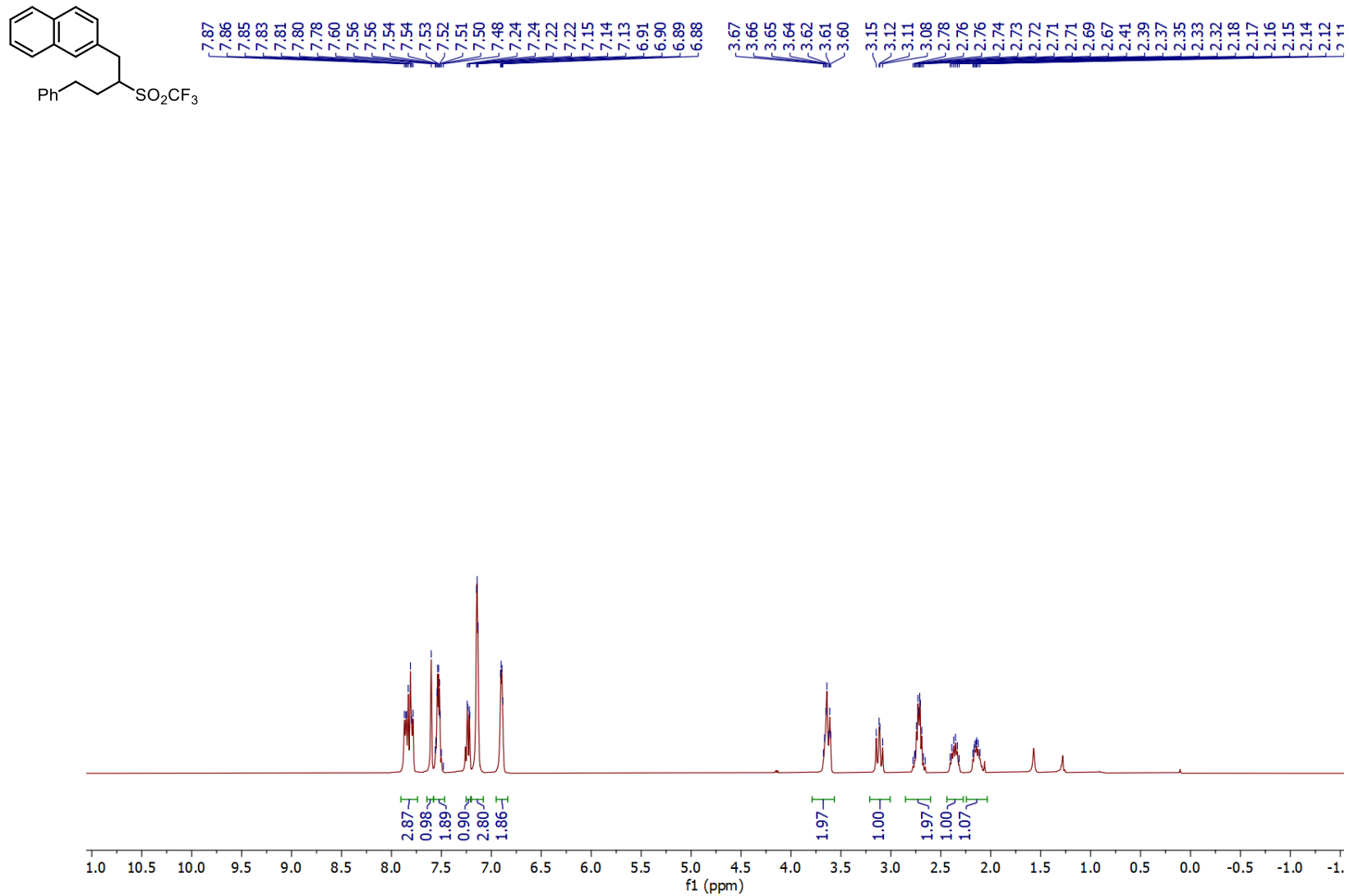
1-(*tert*-Butyl)-4-(4-phenyl-2-((trifluoromethyl)sulfonyl)butyl)benzene 1a $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, Chloroform-*d*)



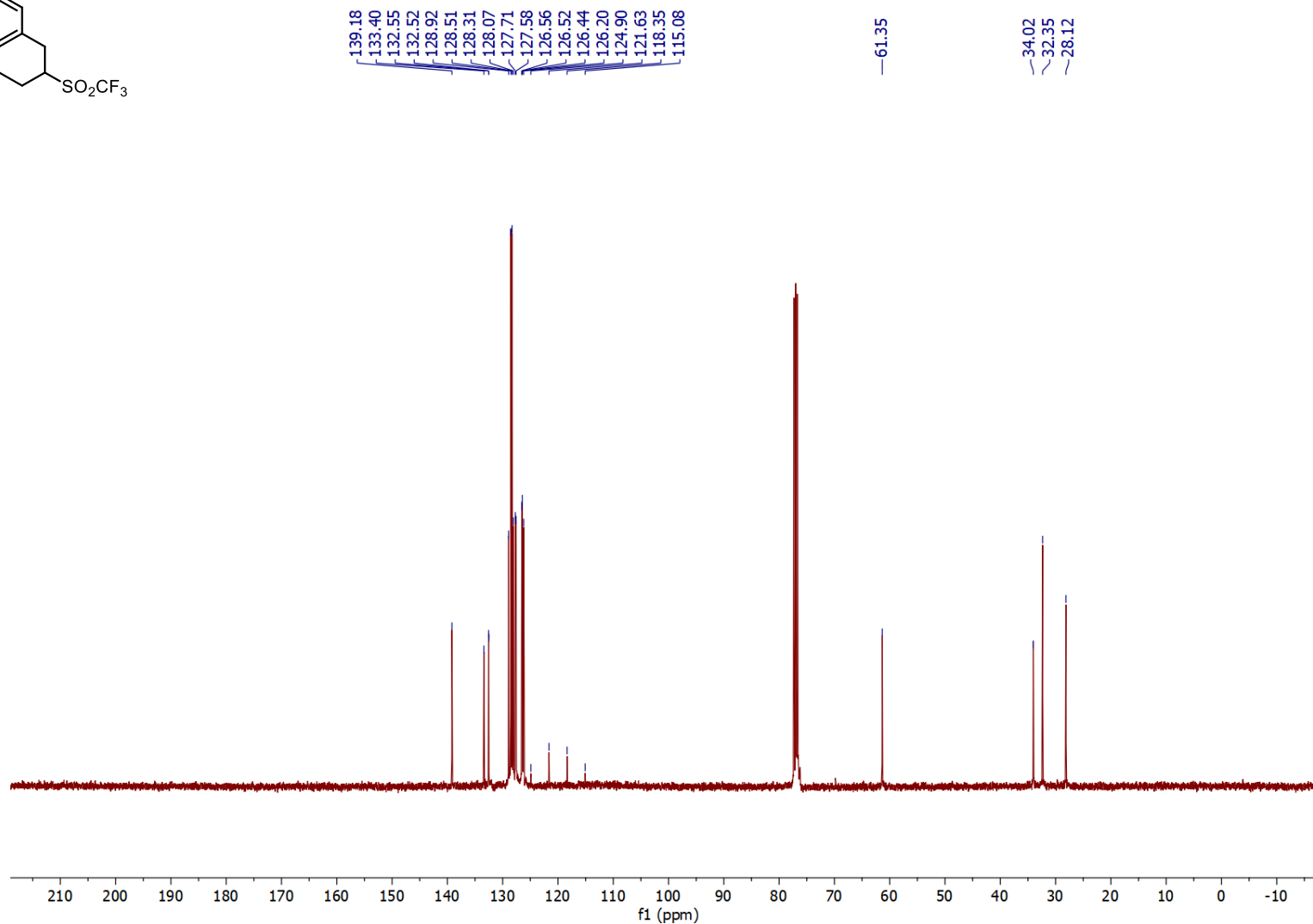
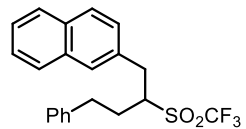
1-(*tert*-Butyl)-4-(4-phenyl-2-((trifluoromethyl)sulfonyl)butyl)benzene 1a ^{19}F NMR (376 MHz, Chloroform-*d*)



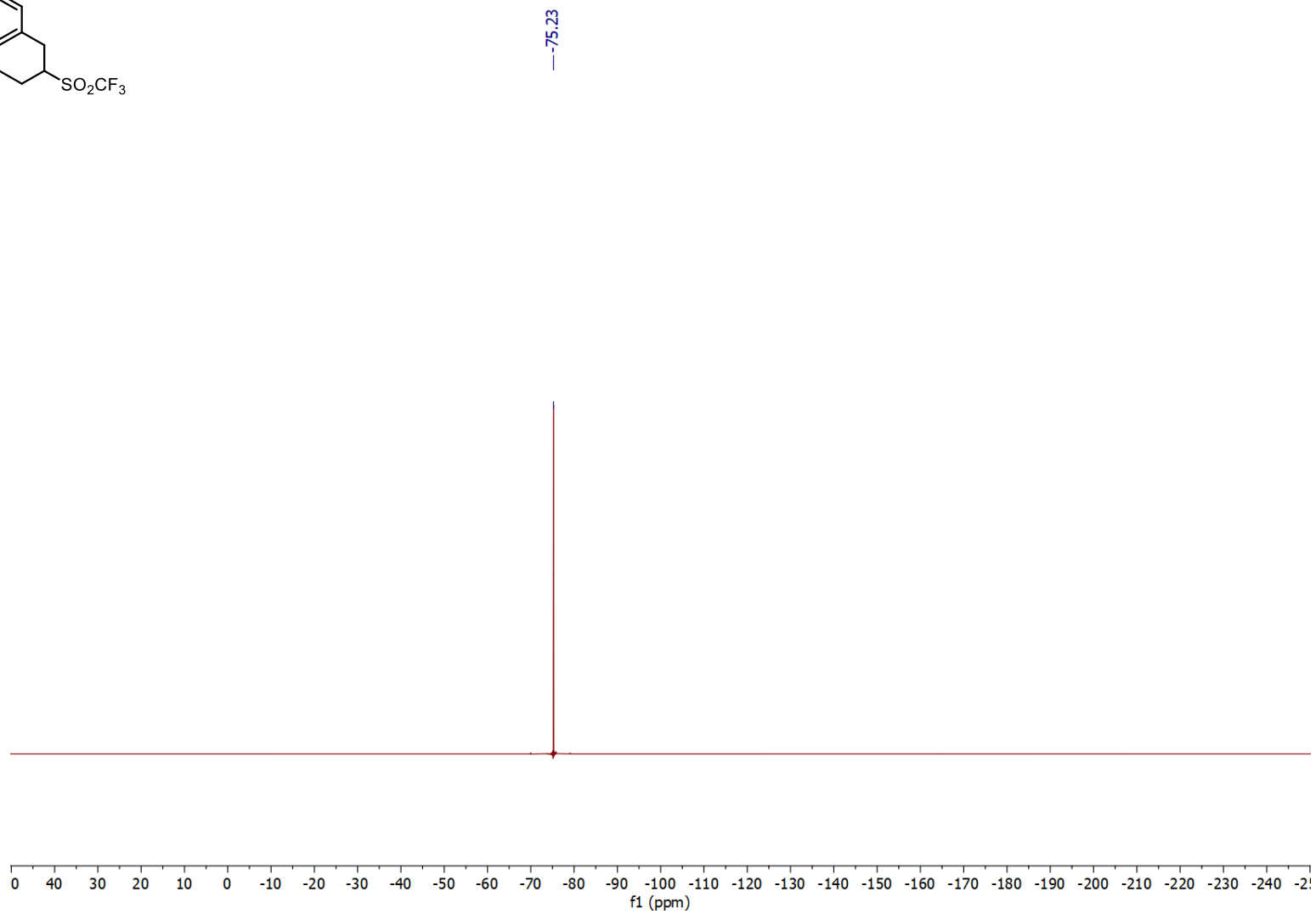
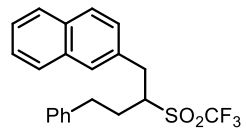
2-(4-Phenyl-2-((trifluoromethyl)sulfonyl)butyl)naphthalene 1b ¹H NMR (400 MHz, Chloroform-*d*)



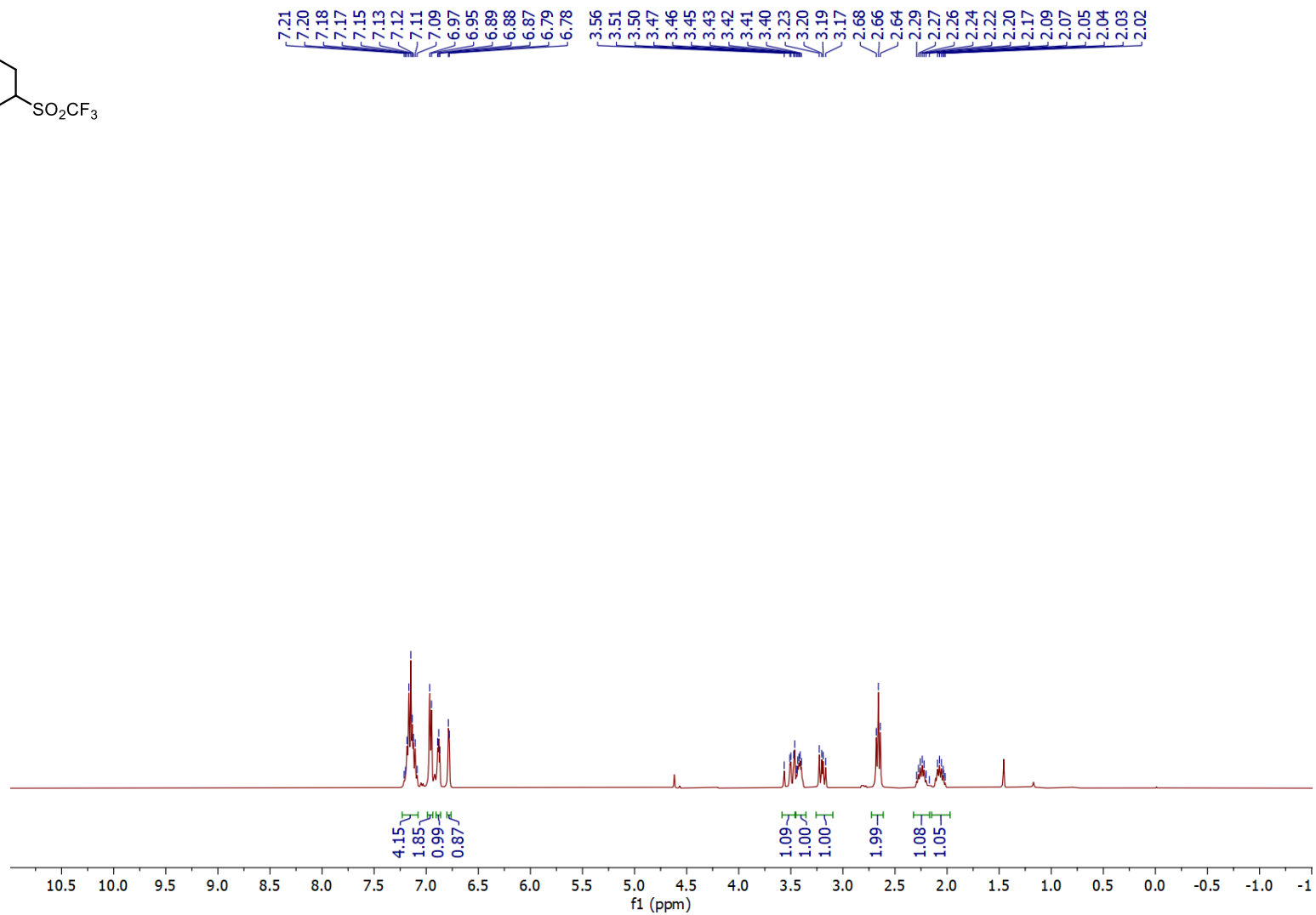
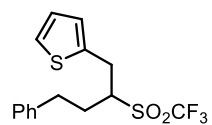
2-(4-Phenyl-2-((trifluoromethyl)sulfonyl)butyl)naphthalene 1b $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, Chloroform-*d*)



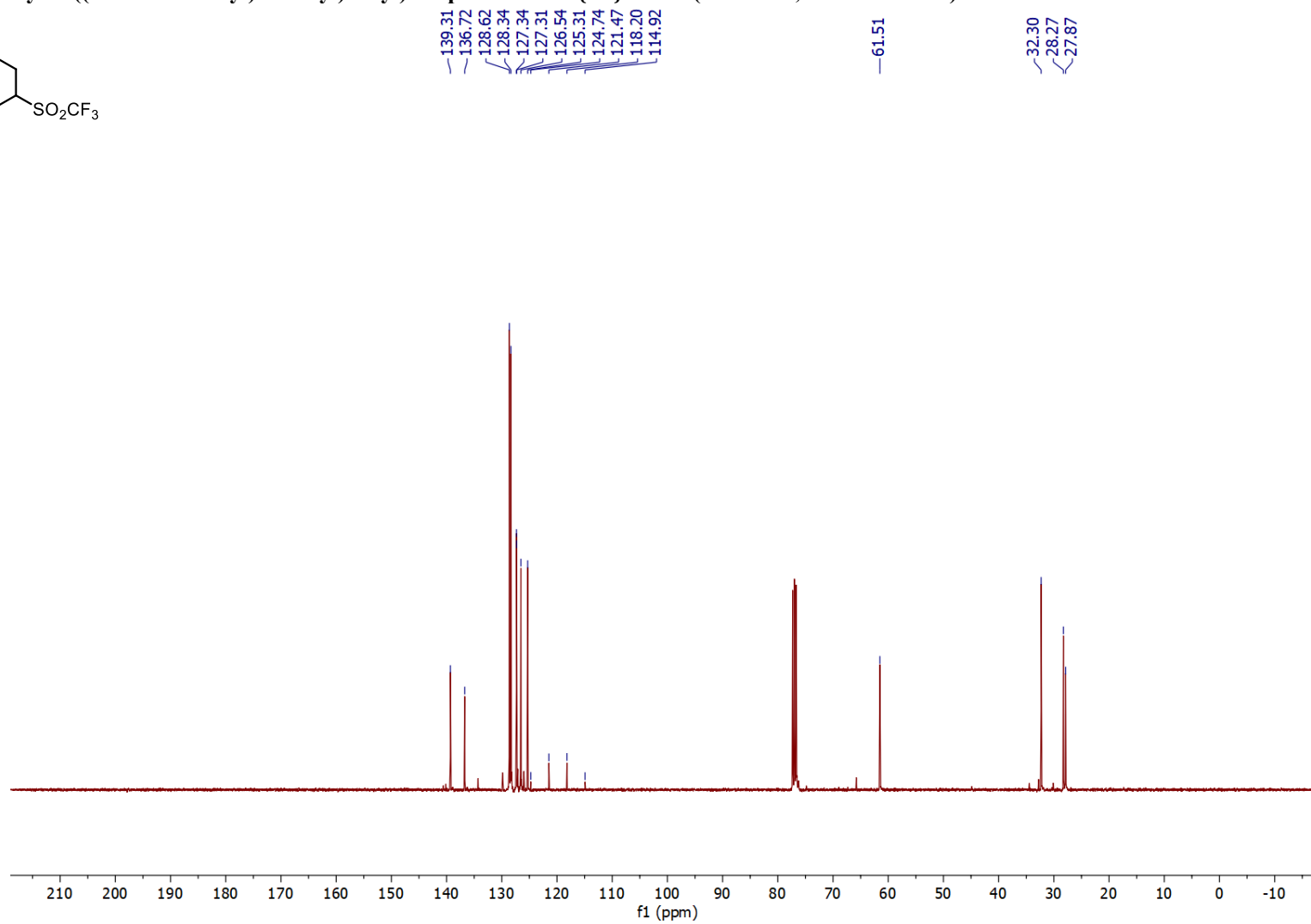
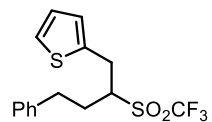
2-(4-Phenyl-2-((trifluoromethyl)sulfonyl)butyl)naphthalene 1b ¹⁹F NMR (376 MHz, Chloroform-*d*)



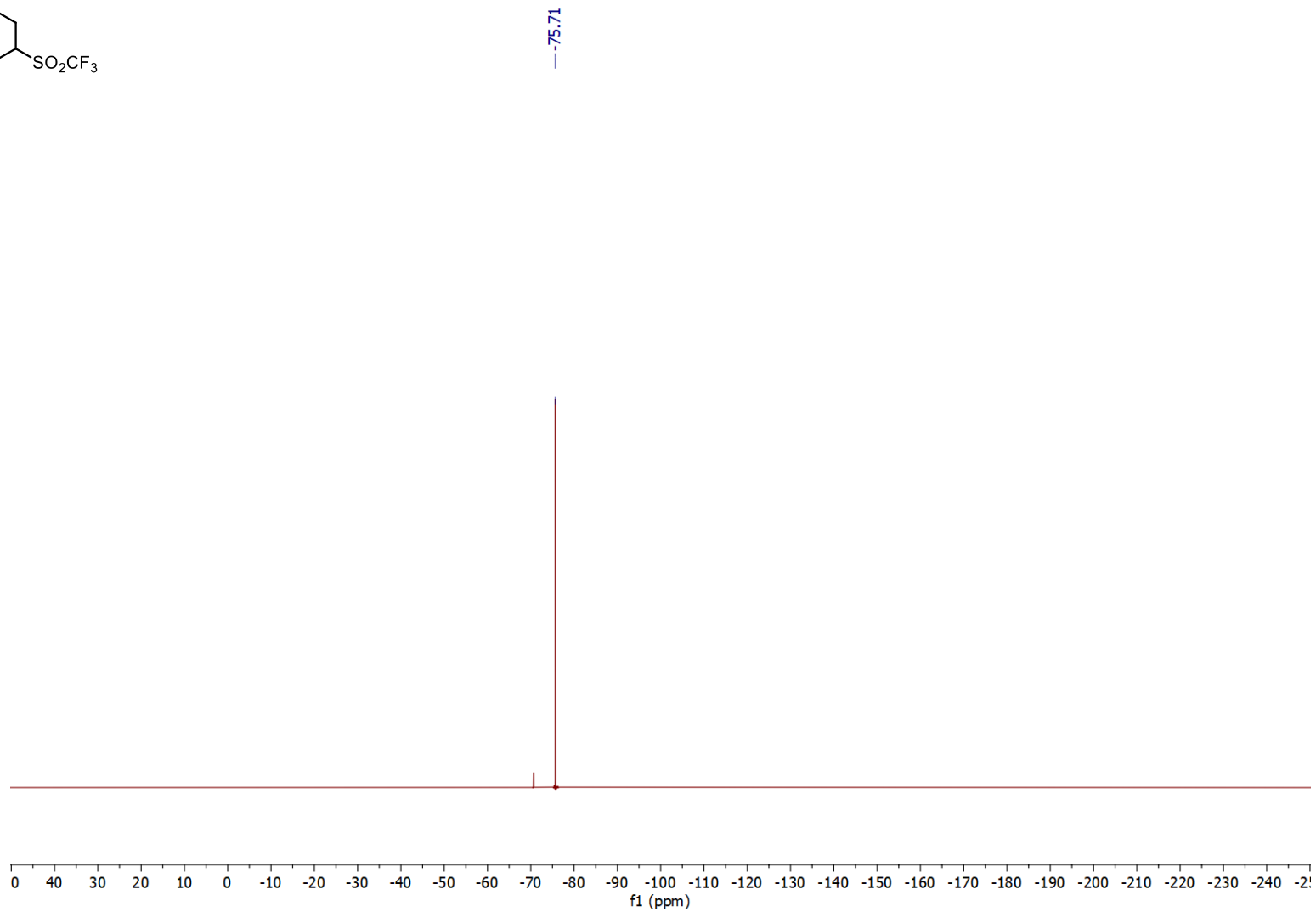
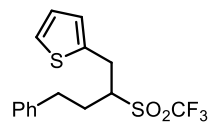
2-(4-Phenyl-2-((trifluoromethyl)sulfonyl)butyl)thiophene 1c ¹H NMR (400 MHz, Chloroform-*d*)



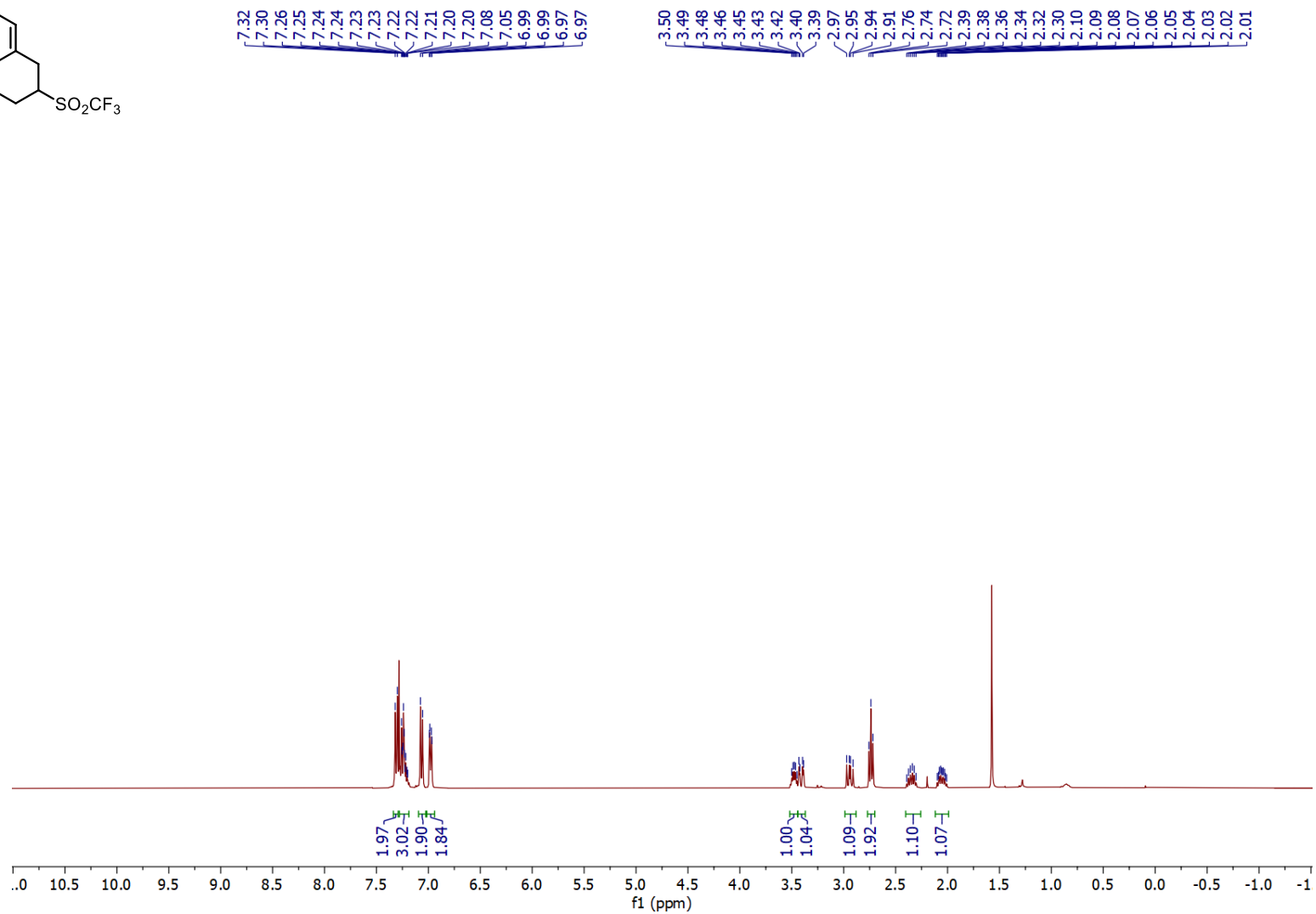
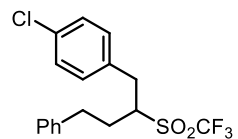
2-(4-Phenyl-2-((trifluoromethyl)sulfonyl)butyl)thiophene 1c $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, Chloroform-*d*)



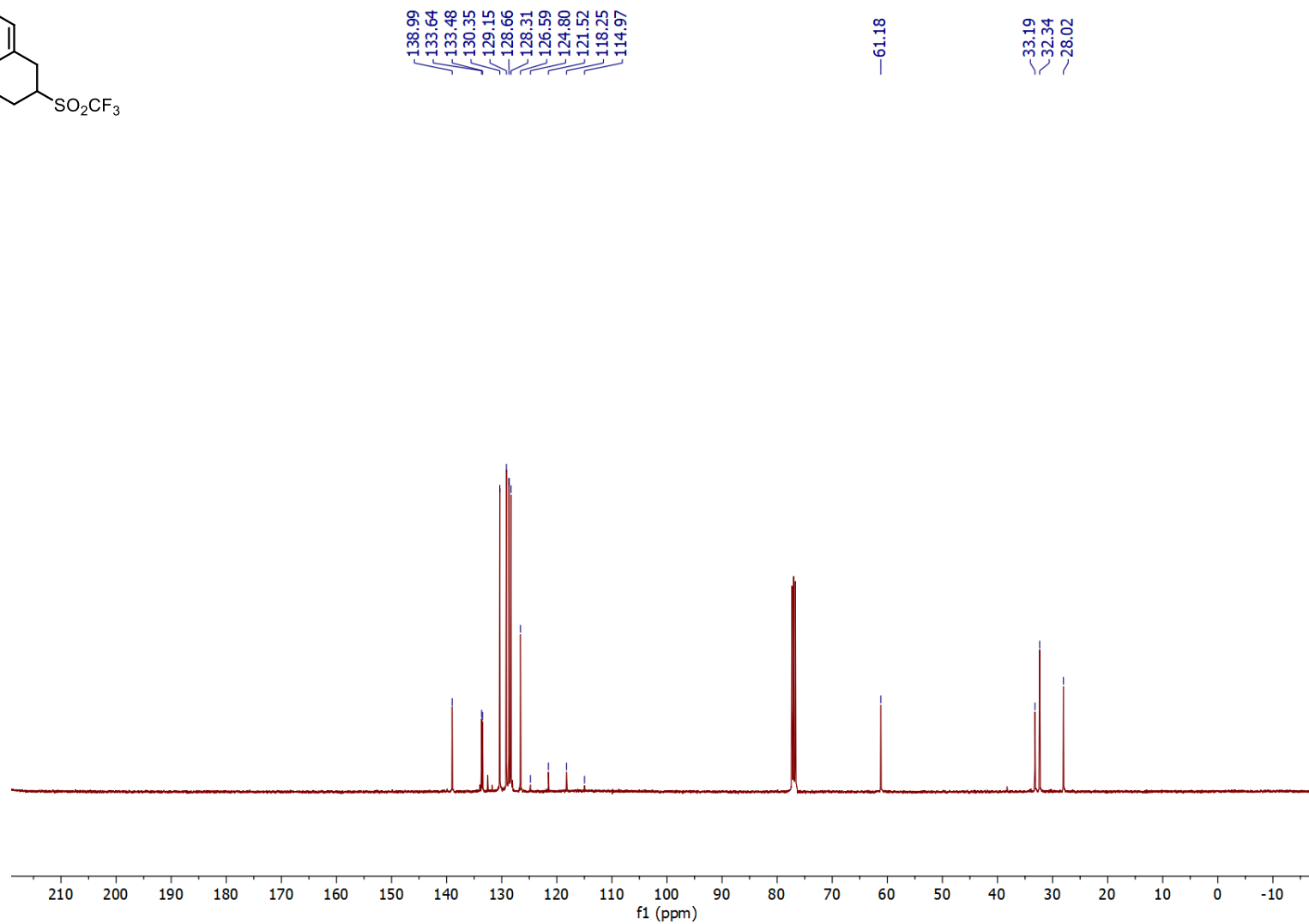
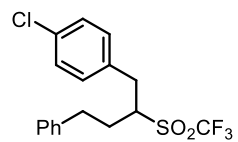
2-(4-Phenyl-2-((trifluoromethyl)sulfonyl)butyl)thiophene 1c ¹⁹F NMR (376 MHz, Chloroform-*d*)



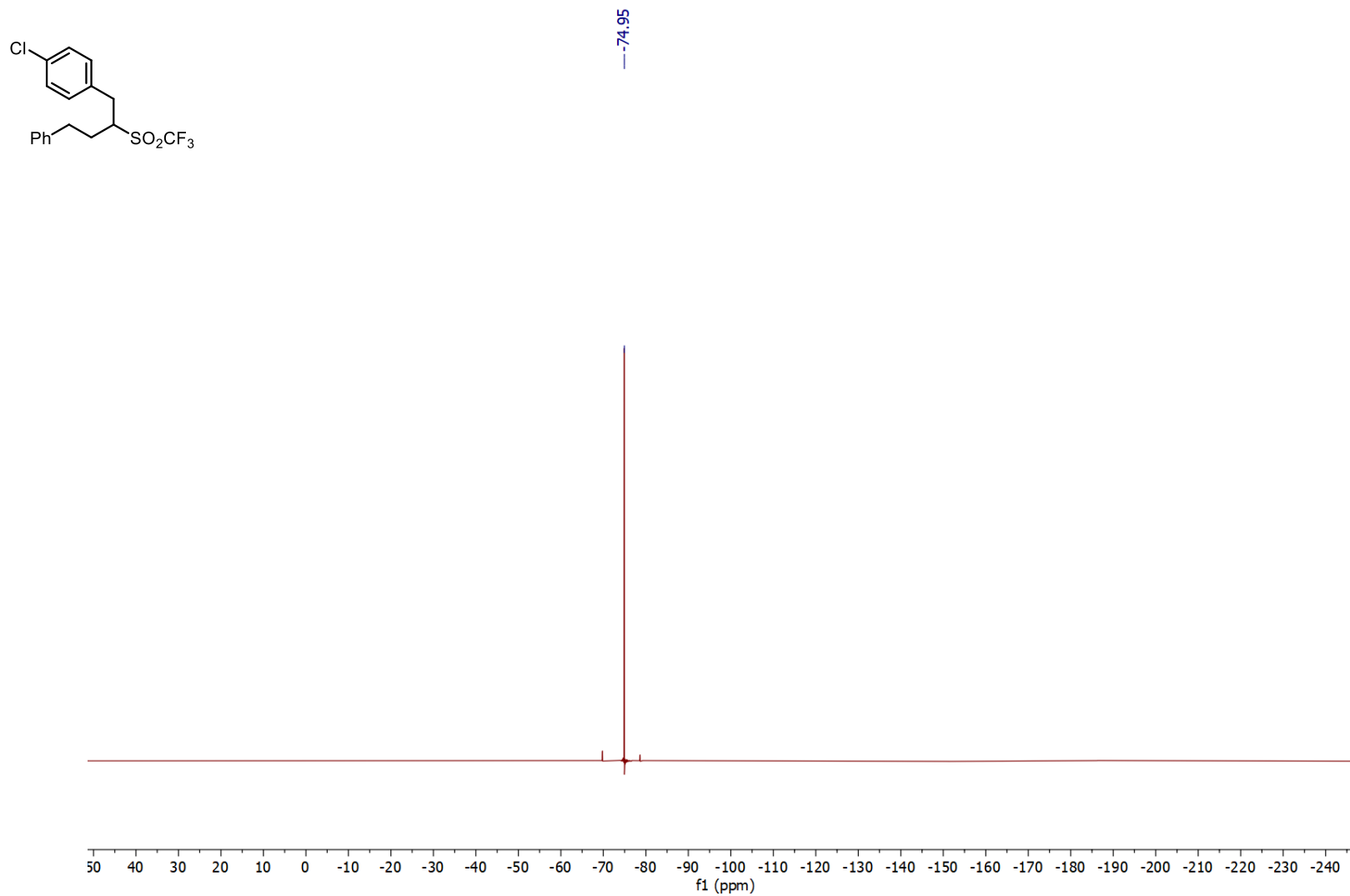
1-Chloro-4-(4-phenyl-2-((trifluoromethyl)sulfonyl)butyl)benzene 1d ¹H NMR (400 MHz, Chloroform-*d*)



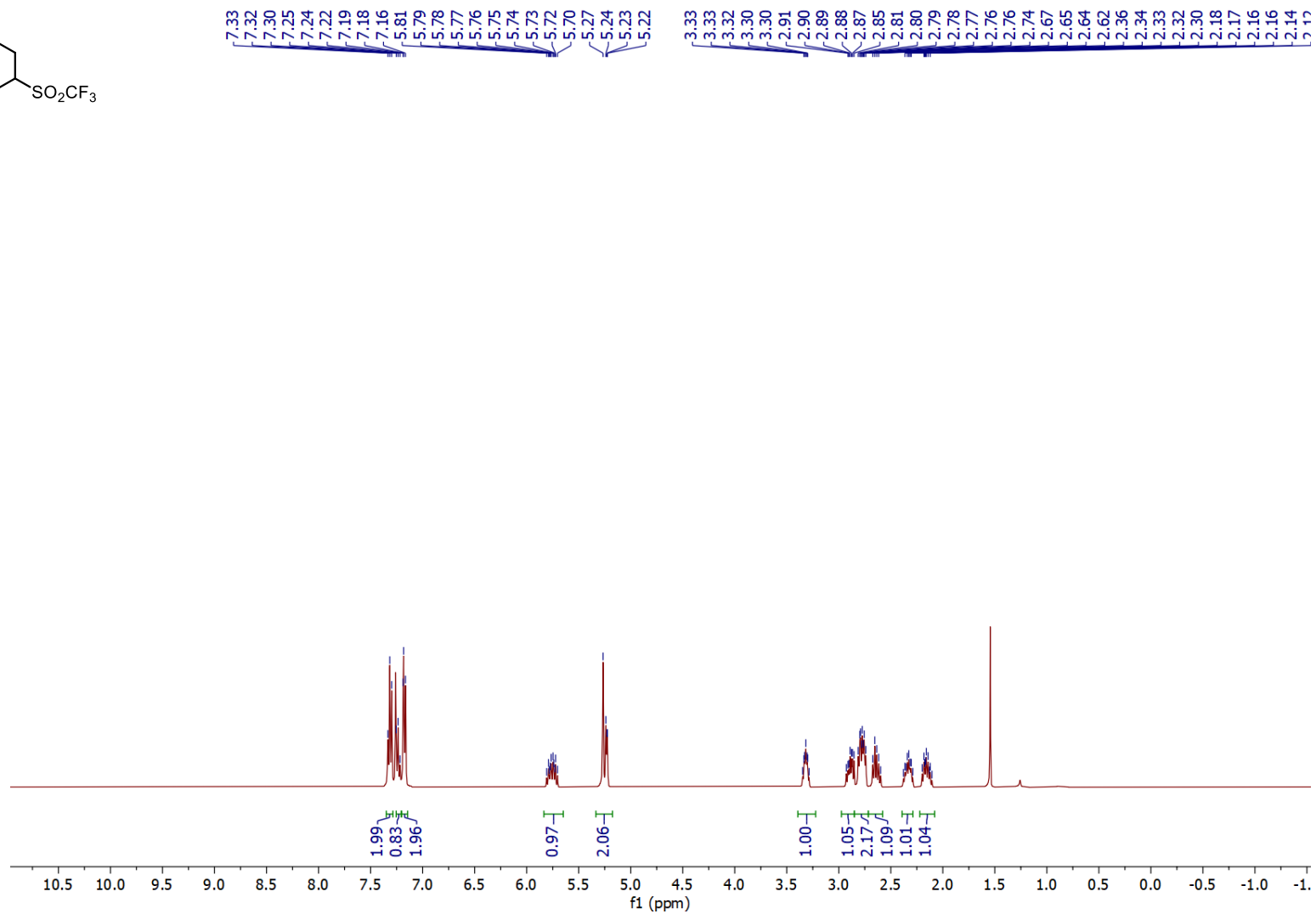
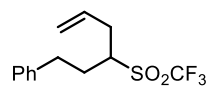
1-Chloro-4-(4-phenyl-2-((trifluoromethyl)sulfonyl)butyl)benzene 1d $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, Chloroform-*d*)



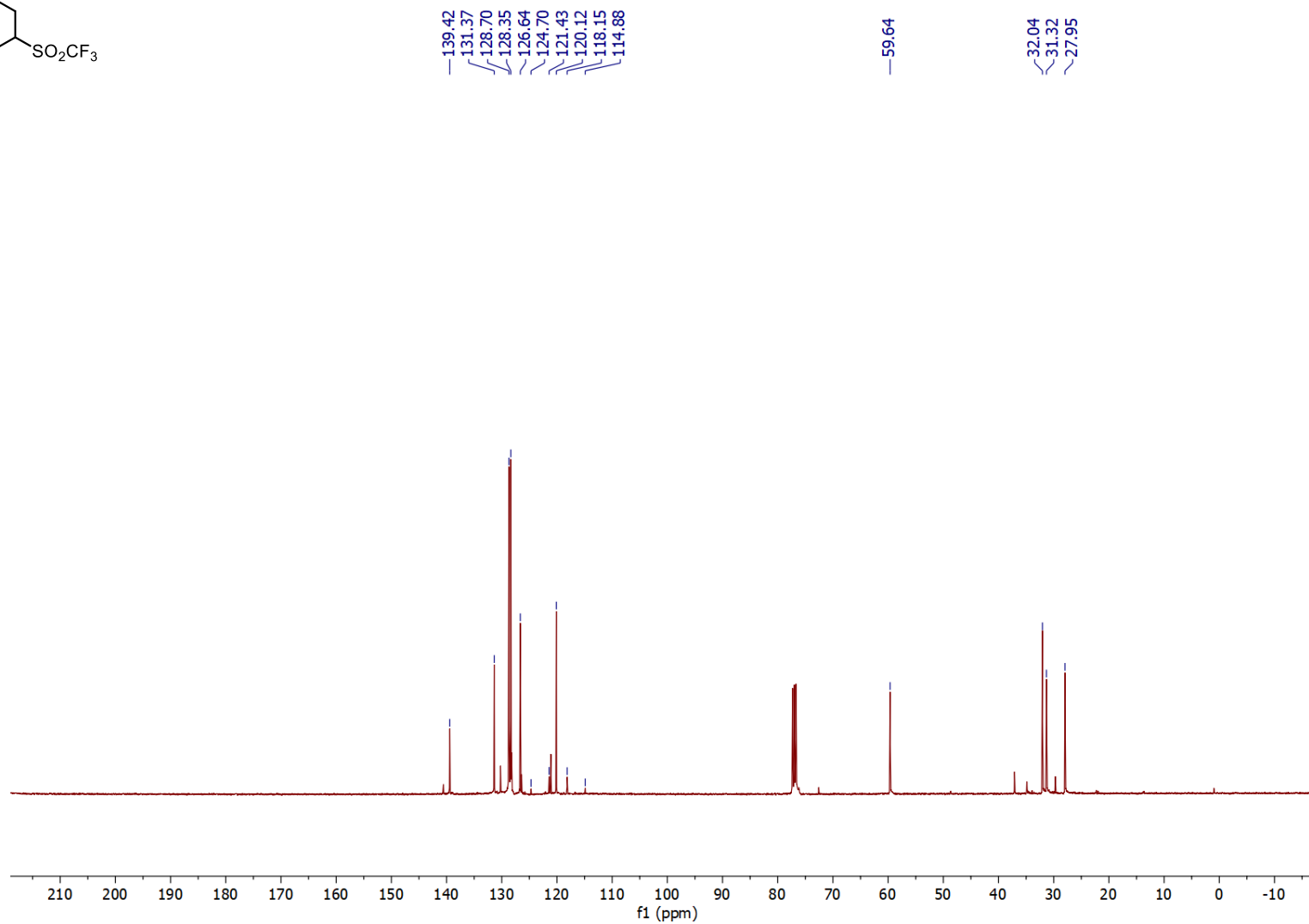
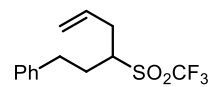
1-Chloro-4-(4-phenyl-2-((trifluoromethyl)sulfonyl)butyl)benzene 1d ^{19}F NMR (376 MHz, Chloroform-*d*)



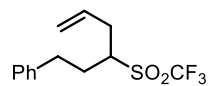
(3-((Trifluoromethyl)sulfonyl)hex-5-en-1-yl)benzene 1e ¹H NMR (400 MHz, Chloroform-*d*)



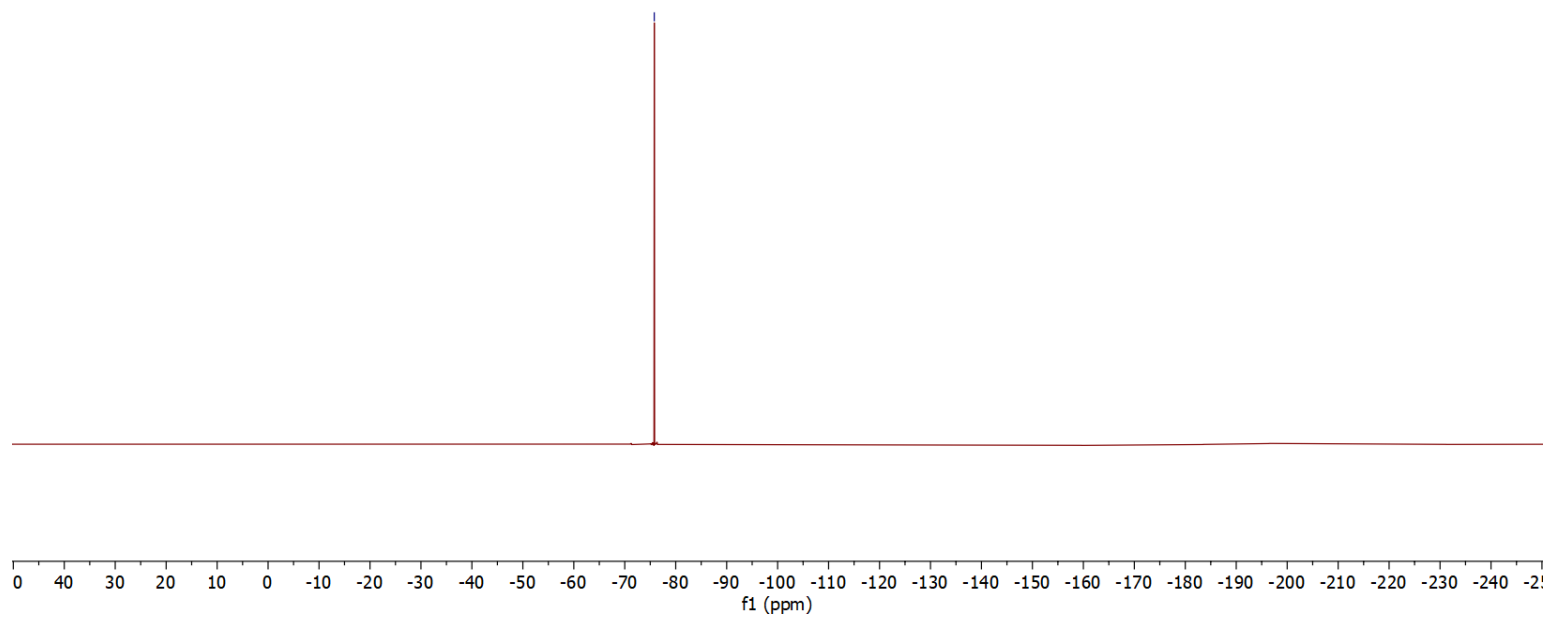
(3-((Trifluoromethyl)sulfonyl)hex-5-en-1-yl)benzene 1e $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, Chloroform-*d*)



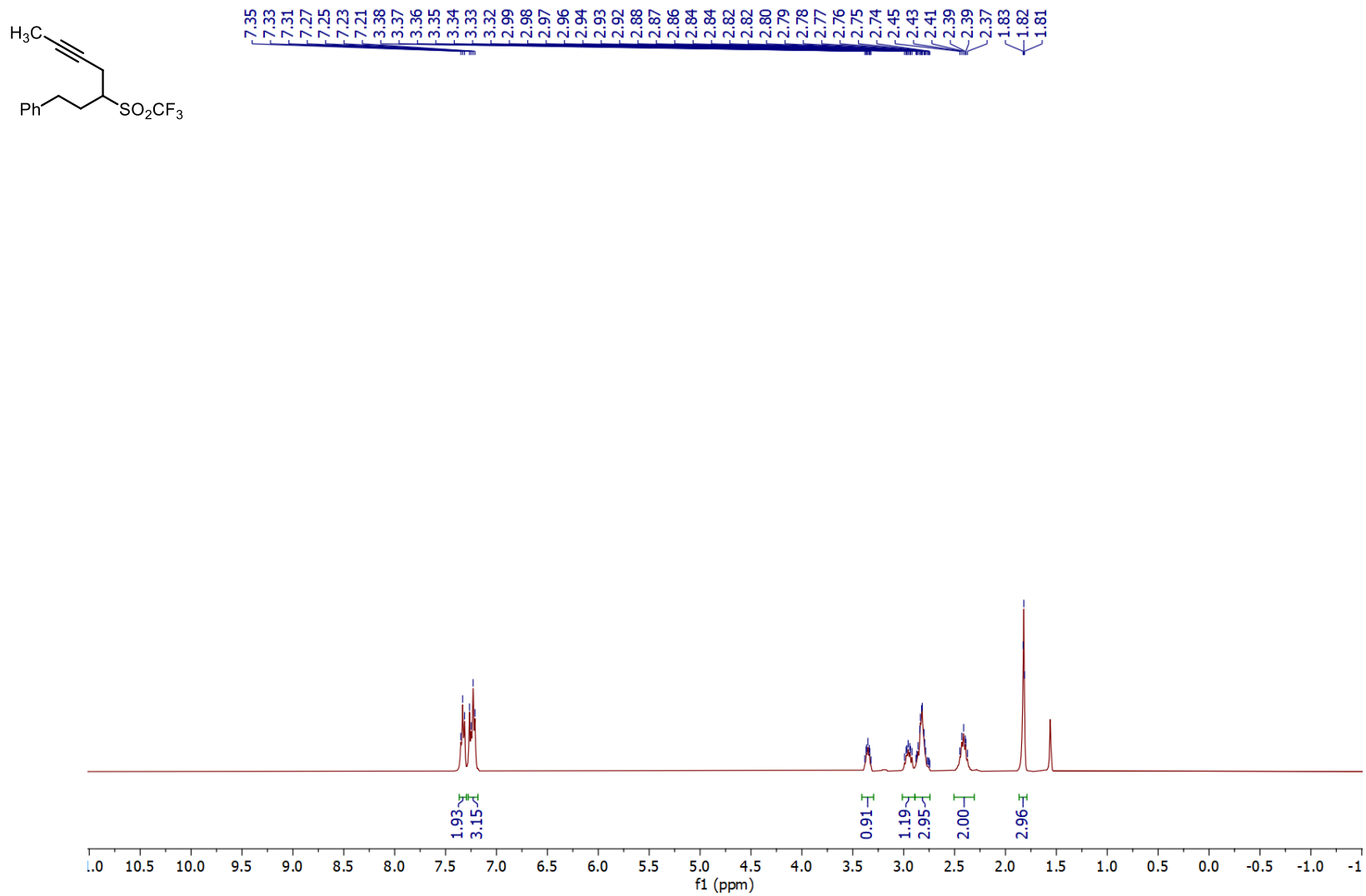
(3-((Trifluoromethyl)sulfonyl)hex-5-en-1-yl)benzene 1e ¹⁹F NMR (376 MHz, Chloroform-*d*)



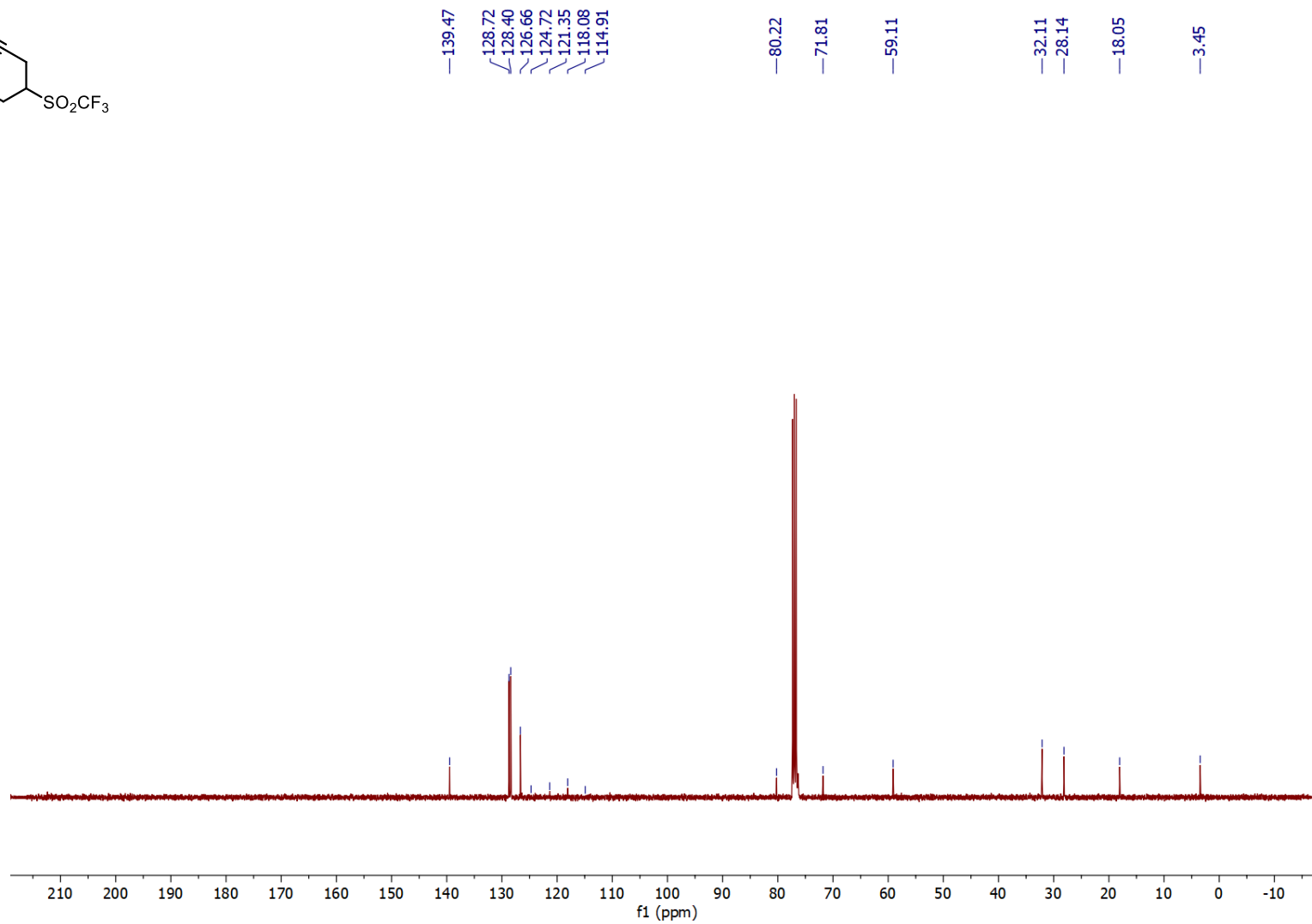
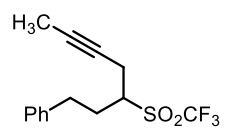
-75.79



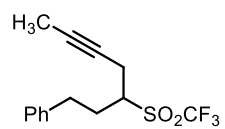
(3-((Trifluoromethyl)sulfonyl)hept-5-yn-1-yl)benzene 1f ¹H NMR (400 MHz, Chloroform-*d*)



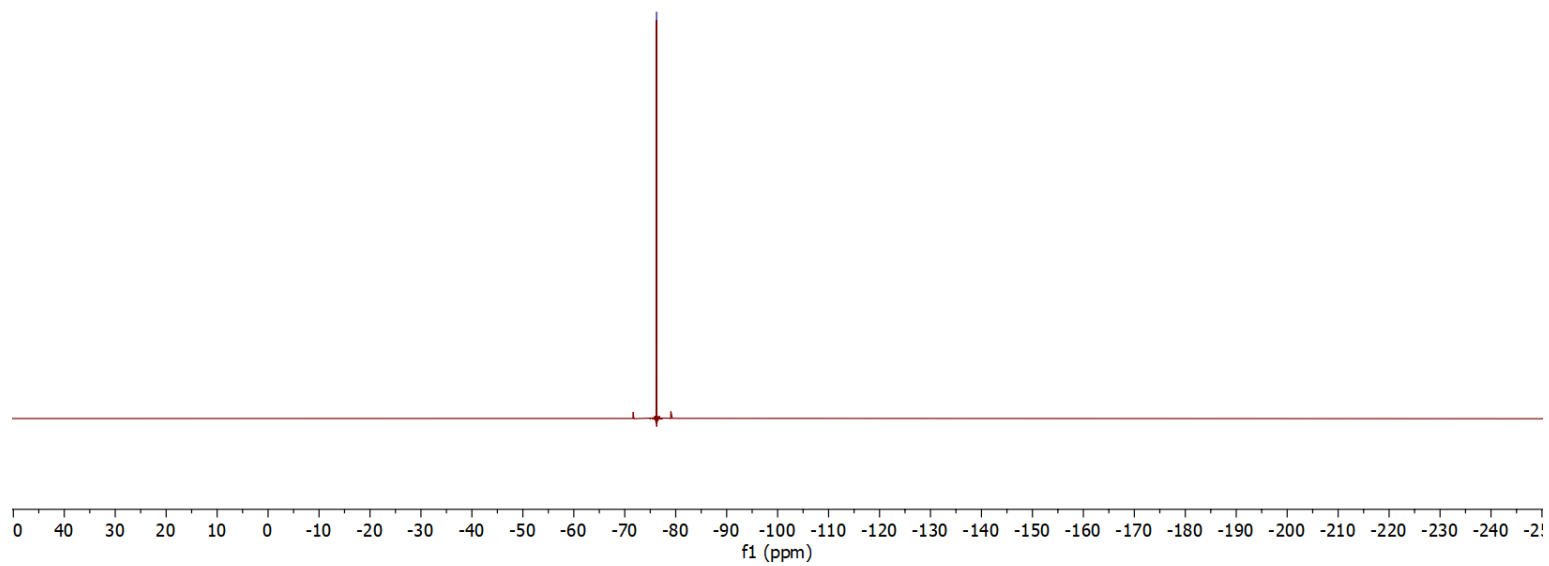
(3-((Trifluoromethyl)sulfonyl)hept-5-yn-1-yl)benzene 1f $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, Chloroform-*d*)



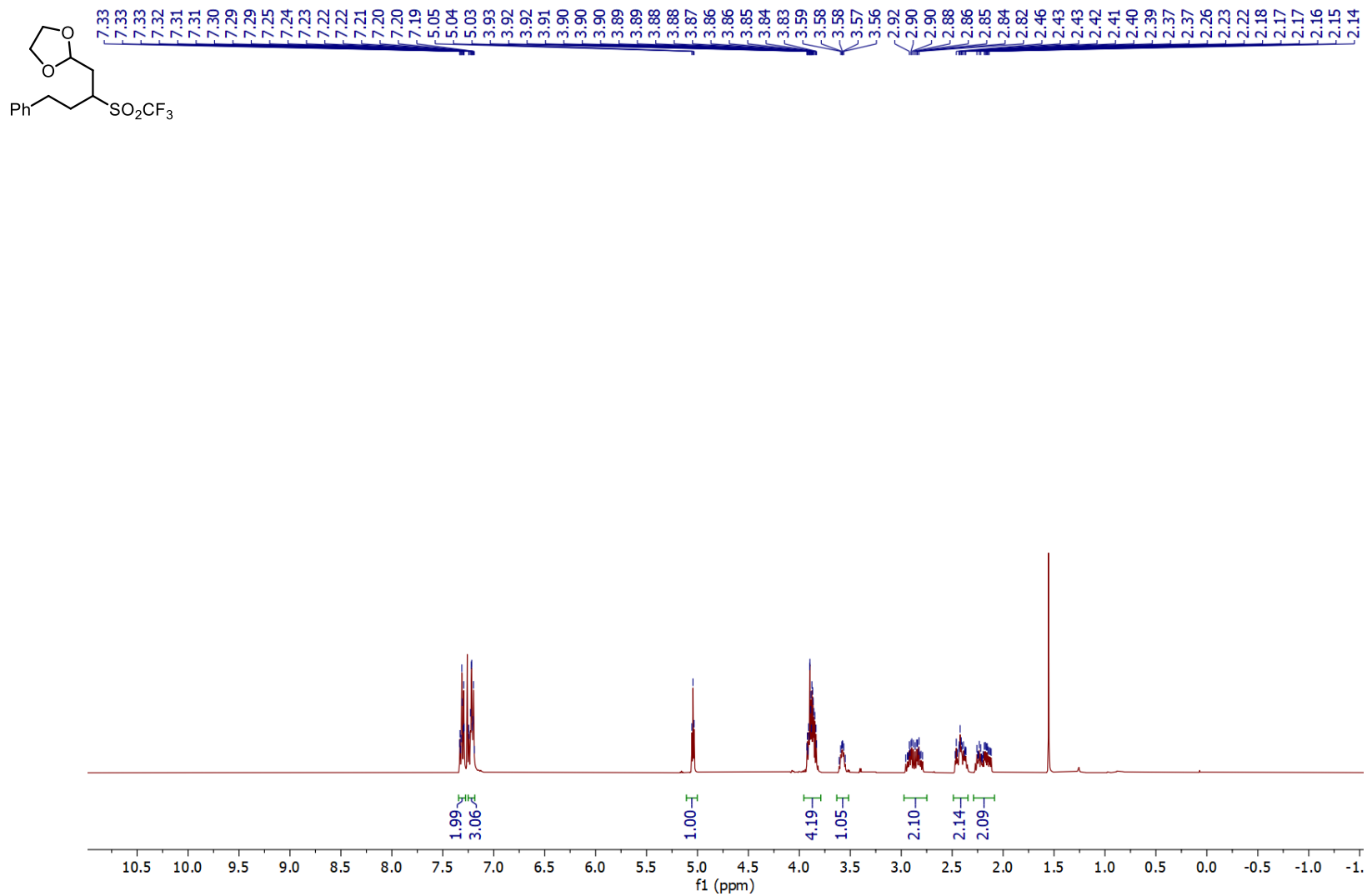
(3-((Trifluoromethyl)sulfonyl)hept-5-yn-1-yl)benzene 1f ¹⁹F NMR (376 MHz, Chloroform-*d*)



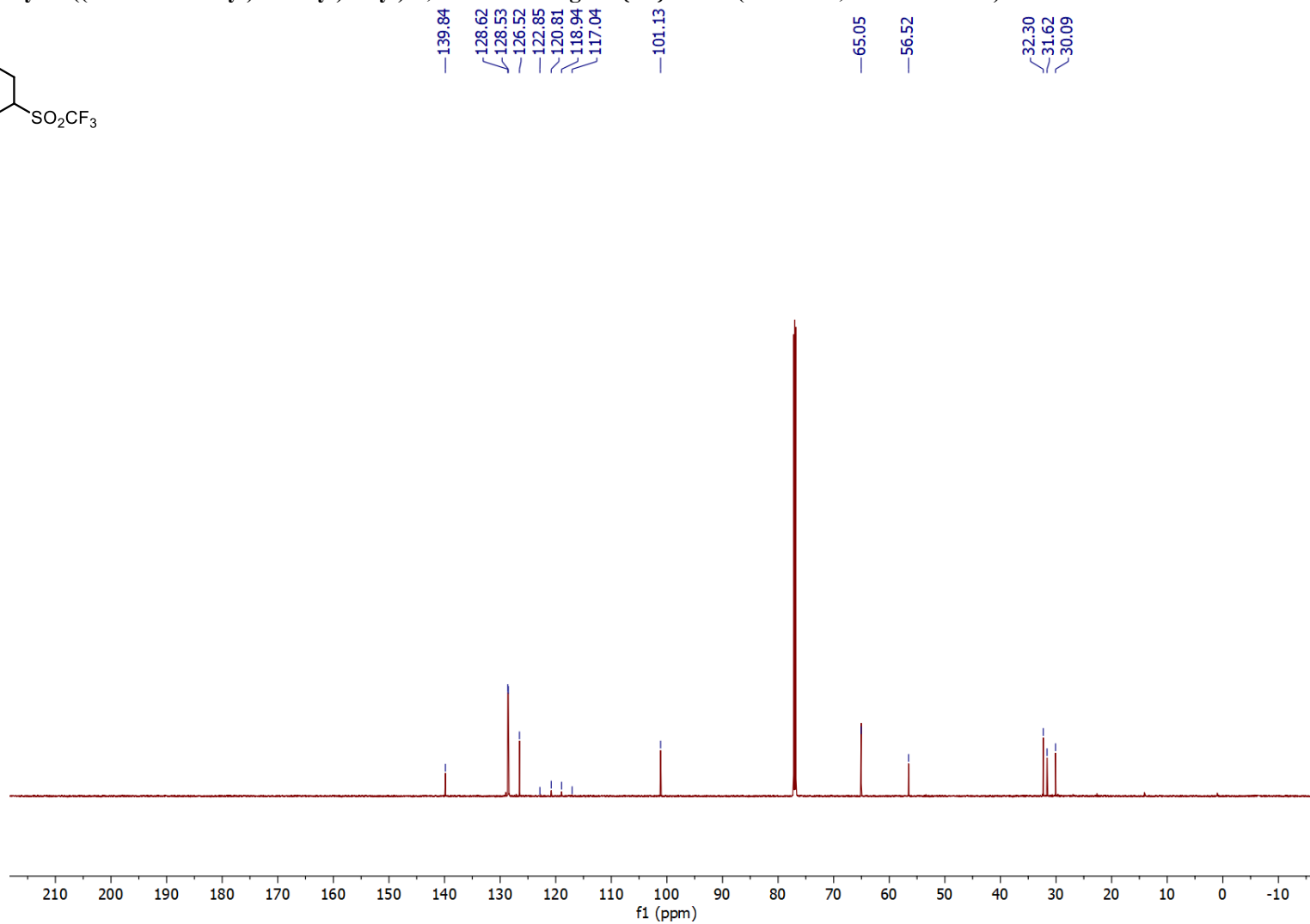
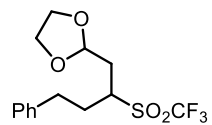
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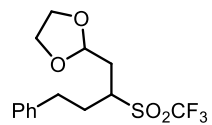
2-(4-Phenyl-2-((trifluoromethyl)sulfonyl)butyl)-1,3-dioxolane 1g ¹H NMR (400 MHz, Chloroform-*d*)



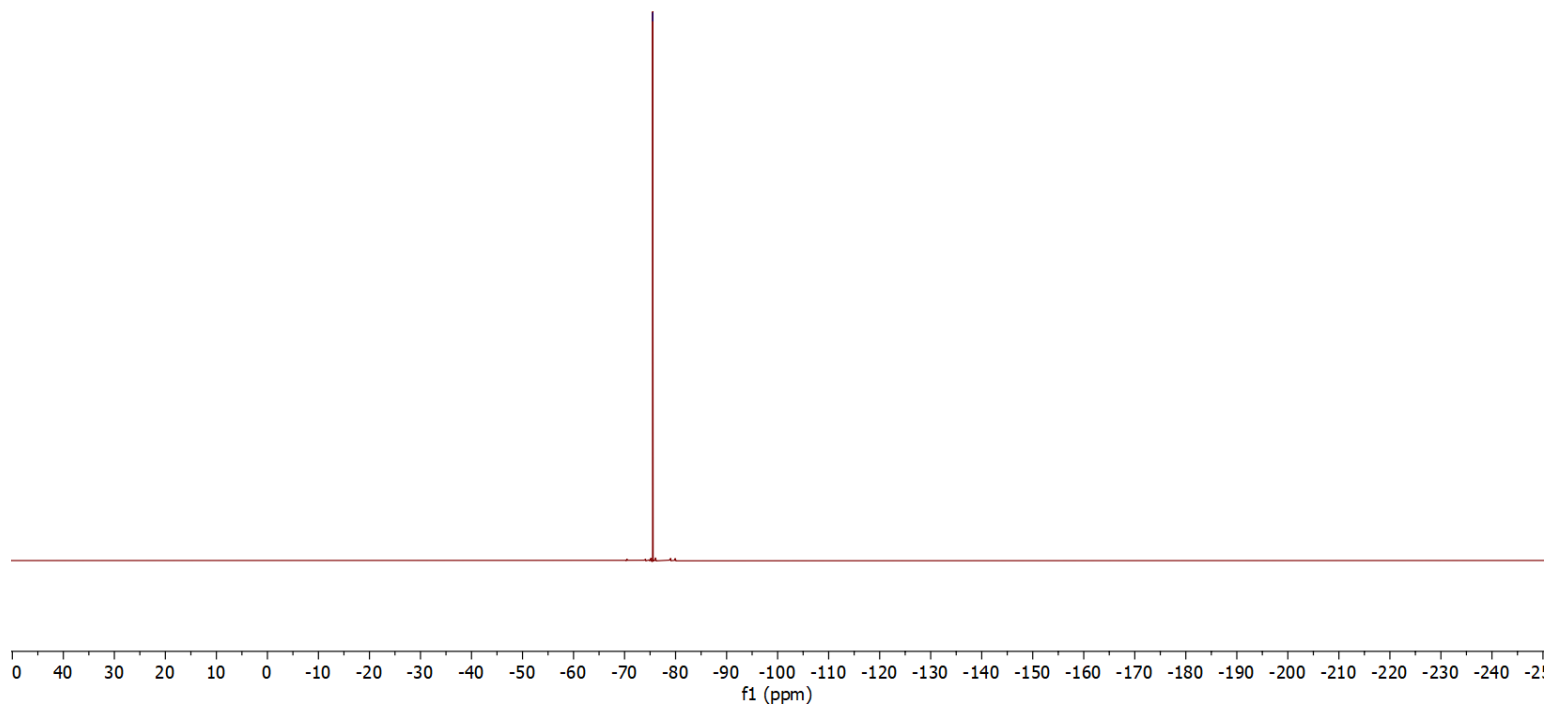
2-(4-Phenyl-2-((trifluoromethyl)sulfonyl)butyl)-1,3-dioxolane 1g $^{13}\text{C}\{^1\text{H}\}$ NMR (176 MHz, Chloroform-*d*)



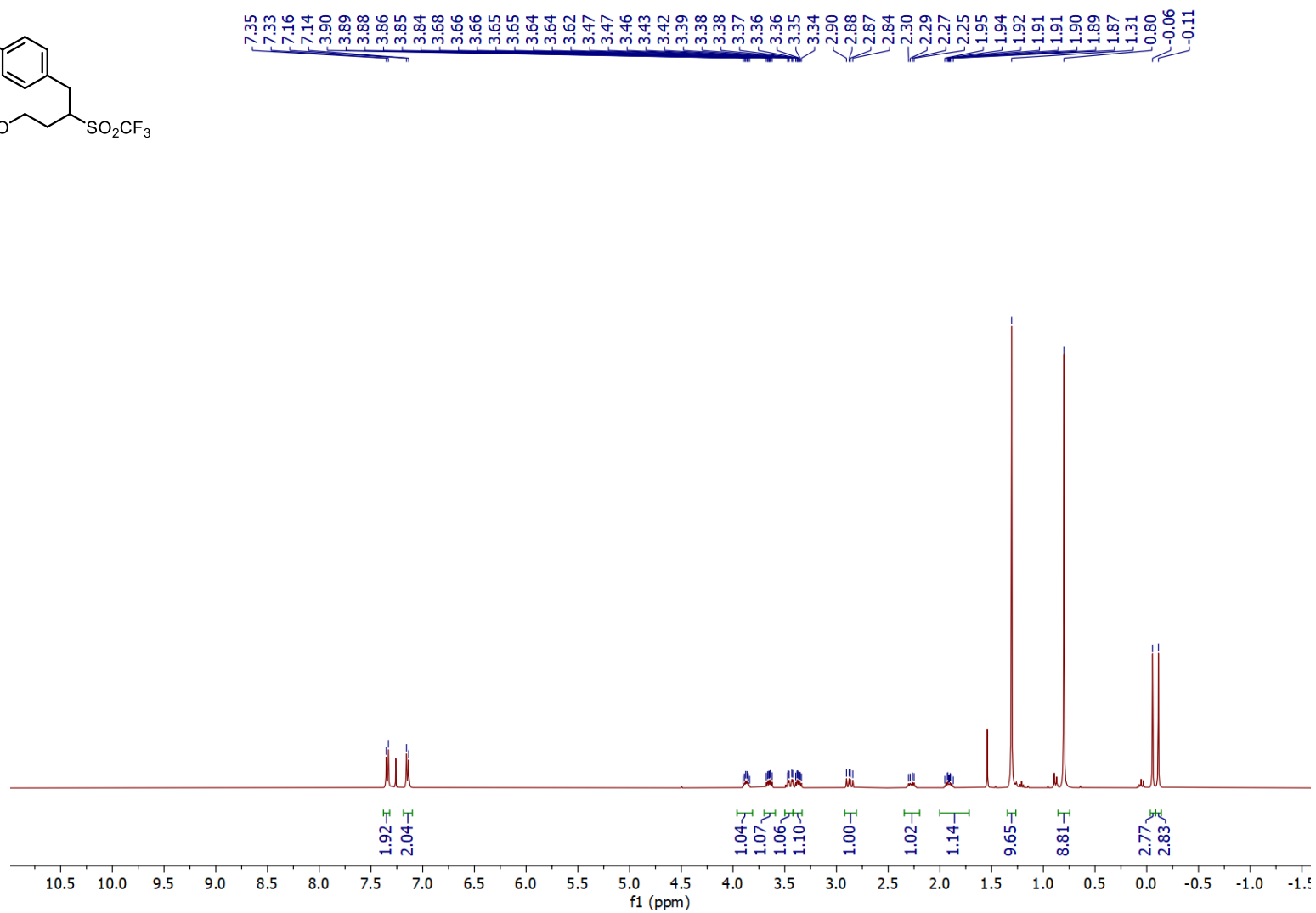
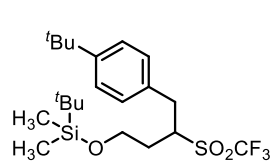
2-(4-Phenyl-2-((trifluoromethyl)sulfonyl)butyl)-1,3-dioxolane 1g ¹⁹F NMR (376 MHz, Chloroform-*d*)



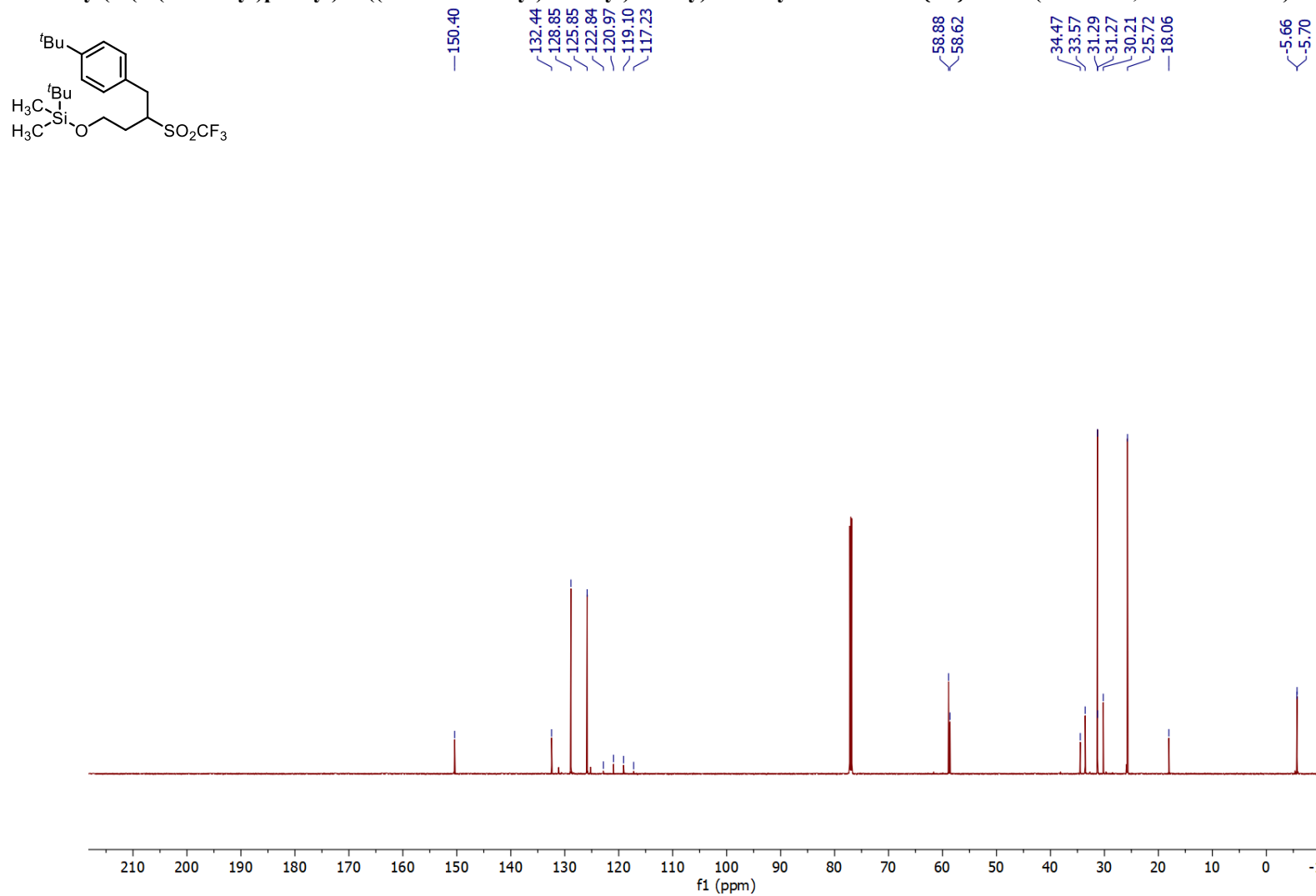
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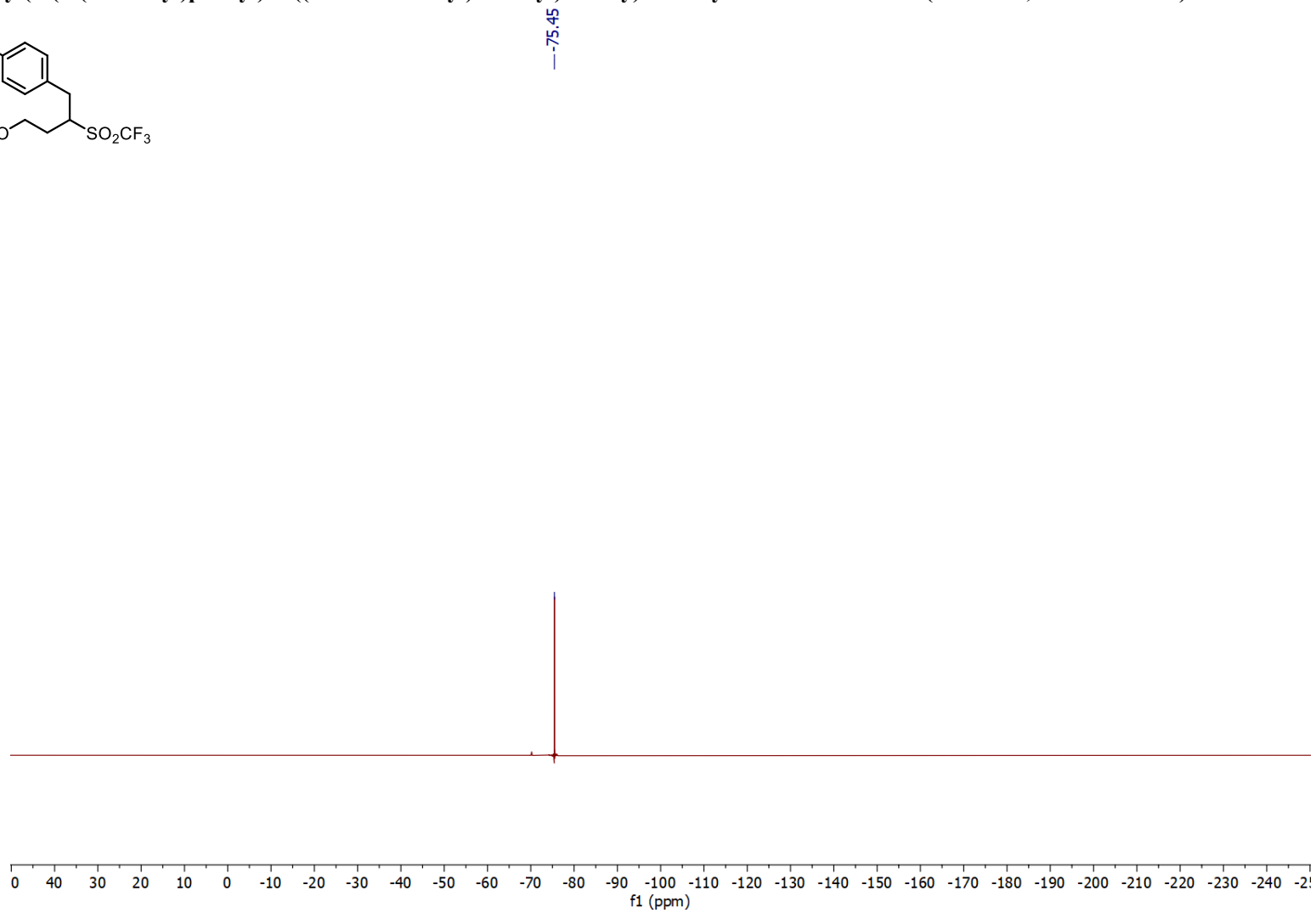
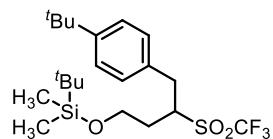
tert-Butyl(4-(4-(*tert*-butyl)phenyl)-3-((trifluoromethyl)sulfonyl)butoxy)dimethylsilane 1h ¹H NMR (400 MHz, Chloroform-*d*)



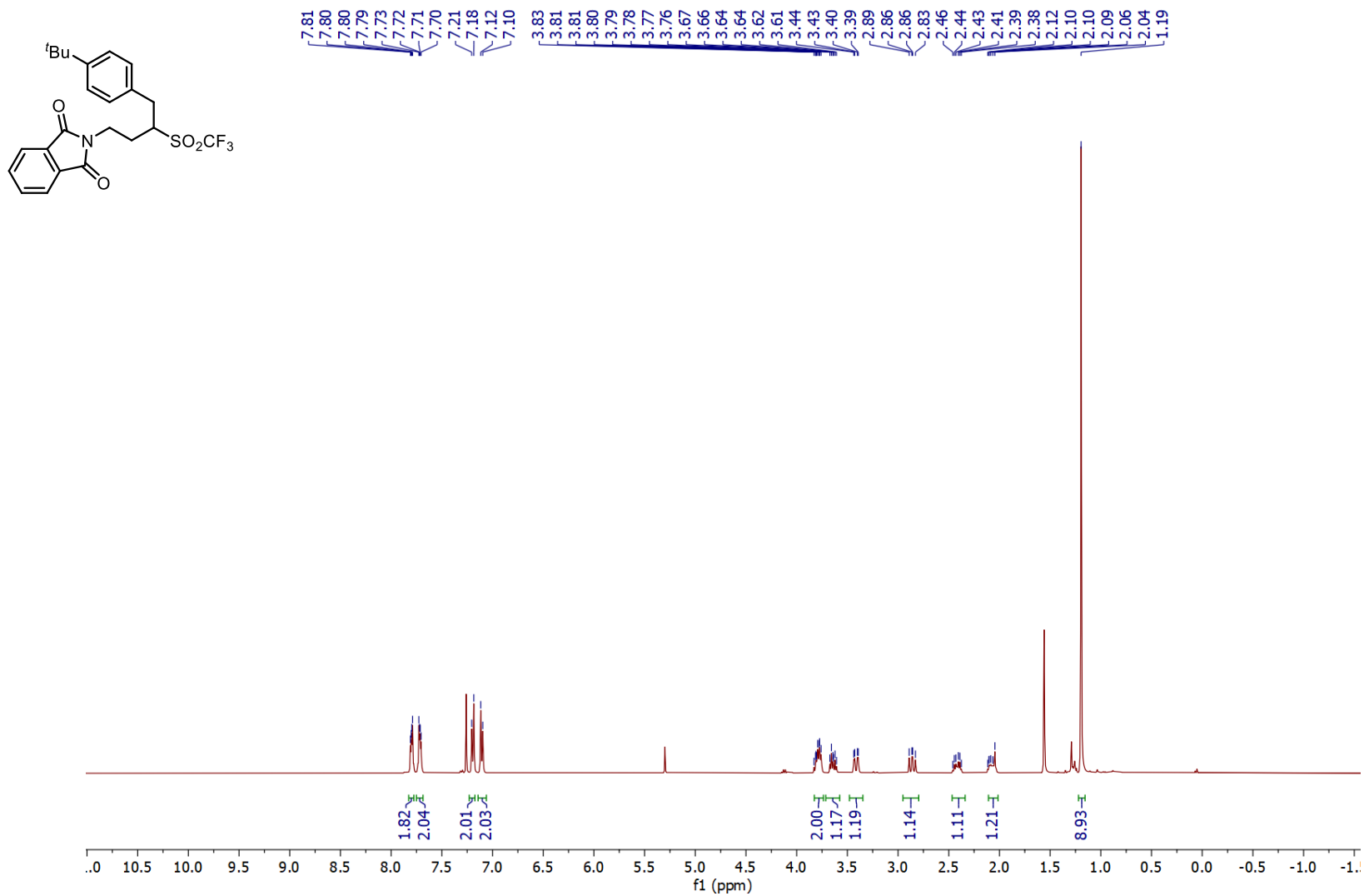
tert-Butyl(4-(4-*tert*-butyl)phenyl)-3-((trifluoromethyl)sulfonyl)butoxy)dimethylsilane 1h $^{13}\text{C}\{^1\text{H}\}$ NMR (176 MHz, Chloroform-*d*)



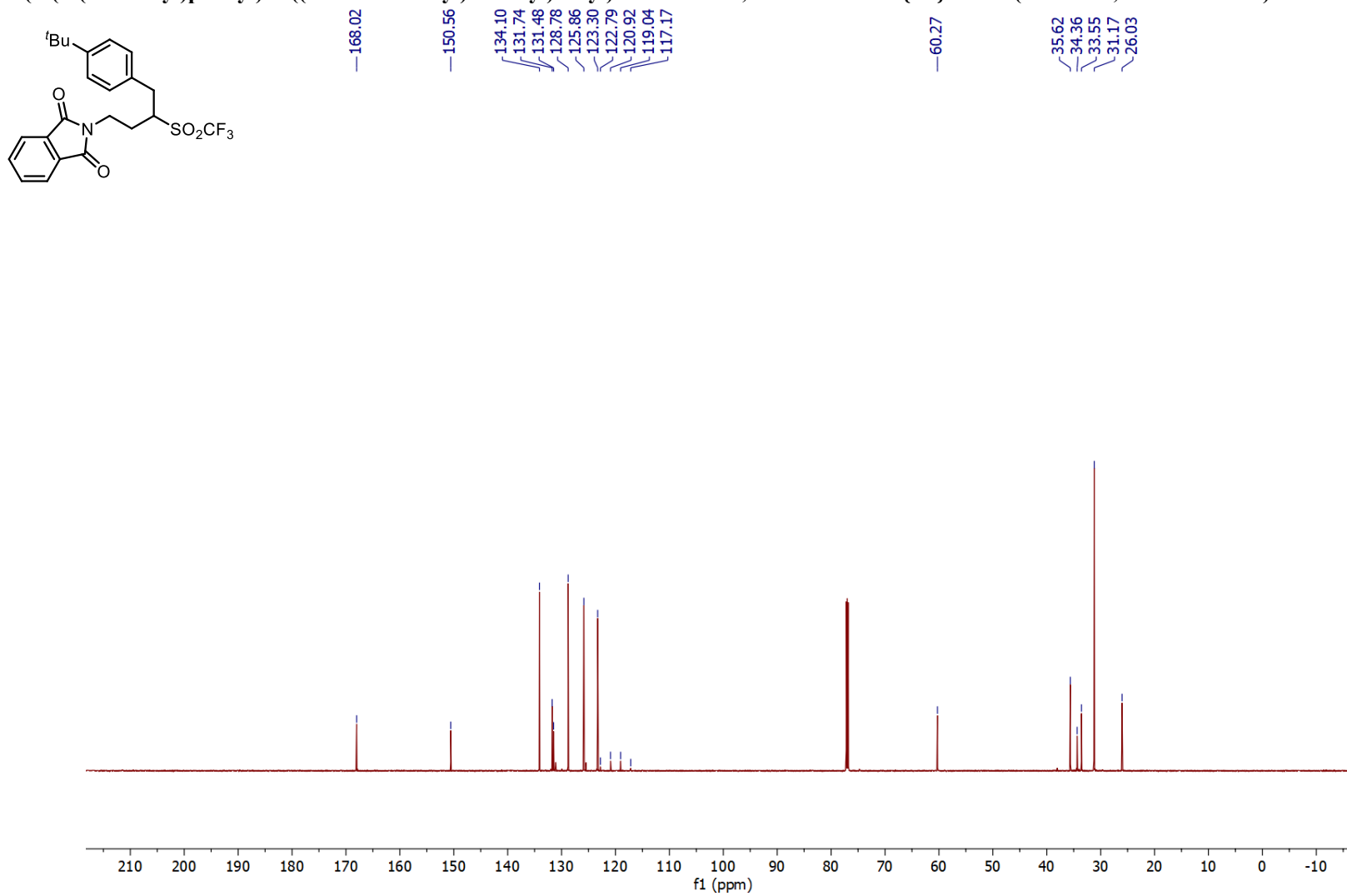
***tert*-Butyl(4-(4-*tert*-butyl)phenyl)-3-((trifluoromethyl)sulfonyl)butoxy)dimethylsilane 1h ¹⁹F NMR (376 MHz, Chloroform-*d*)**



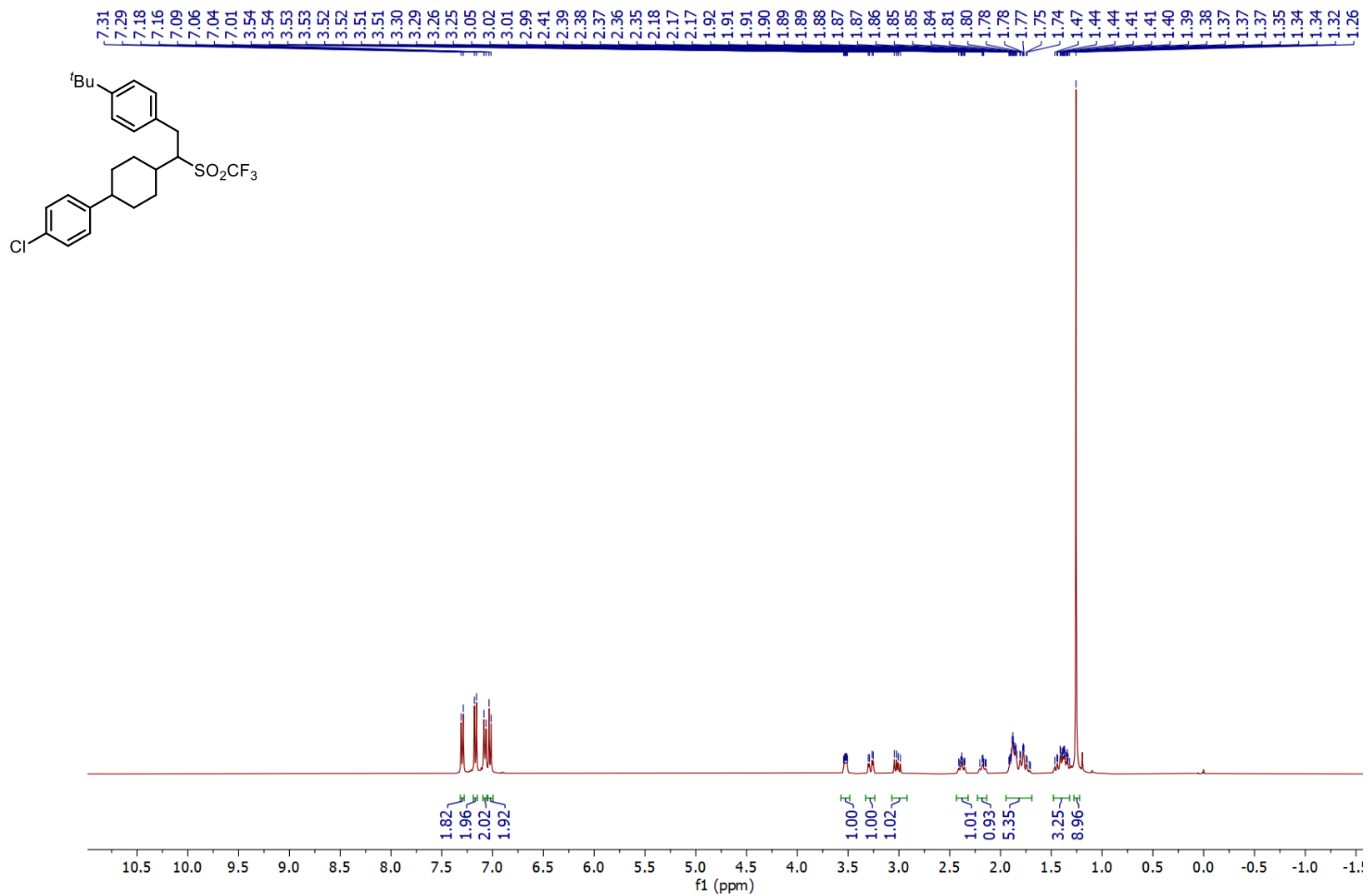
2-(4-(4-*tert*-Butyl)phenyl)-3-((trifluoromethyl)sulfonyl)butylisoindoline-1,3-dione S15 ¹H NMR (400 MHz, Chloroform-*d*)



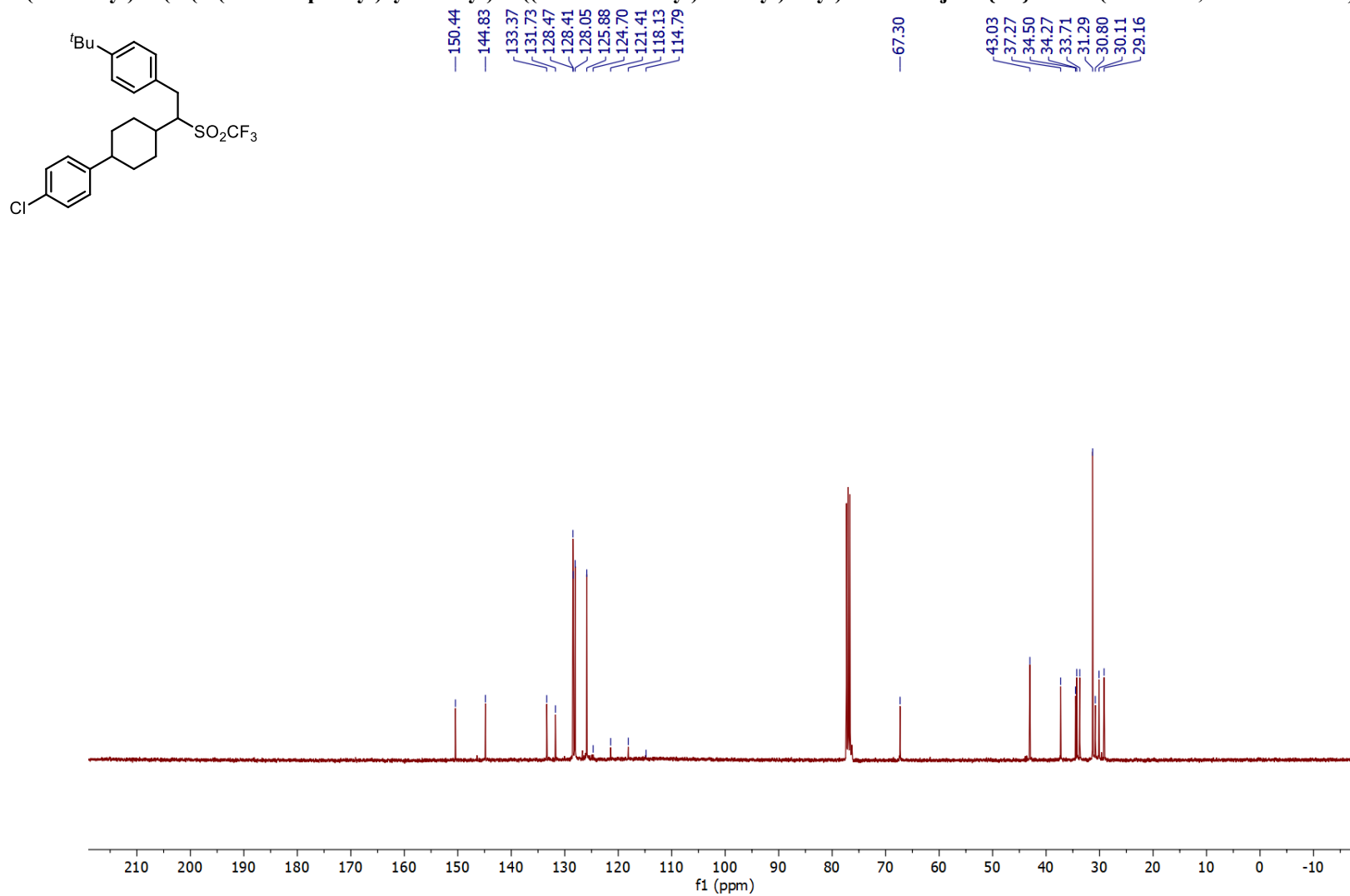
2-(4-(4-(*tert*-Butyl)phenyl)phenyl)-3-((trifluoromethyl)sulfonyl)butylisoindoline-1,3-dione S15 $^{13}\text{C}\{^1\text{H}\}$ NMR (176 MHz, Chloroform-*d*)



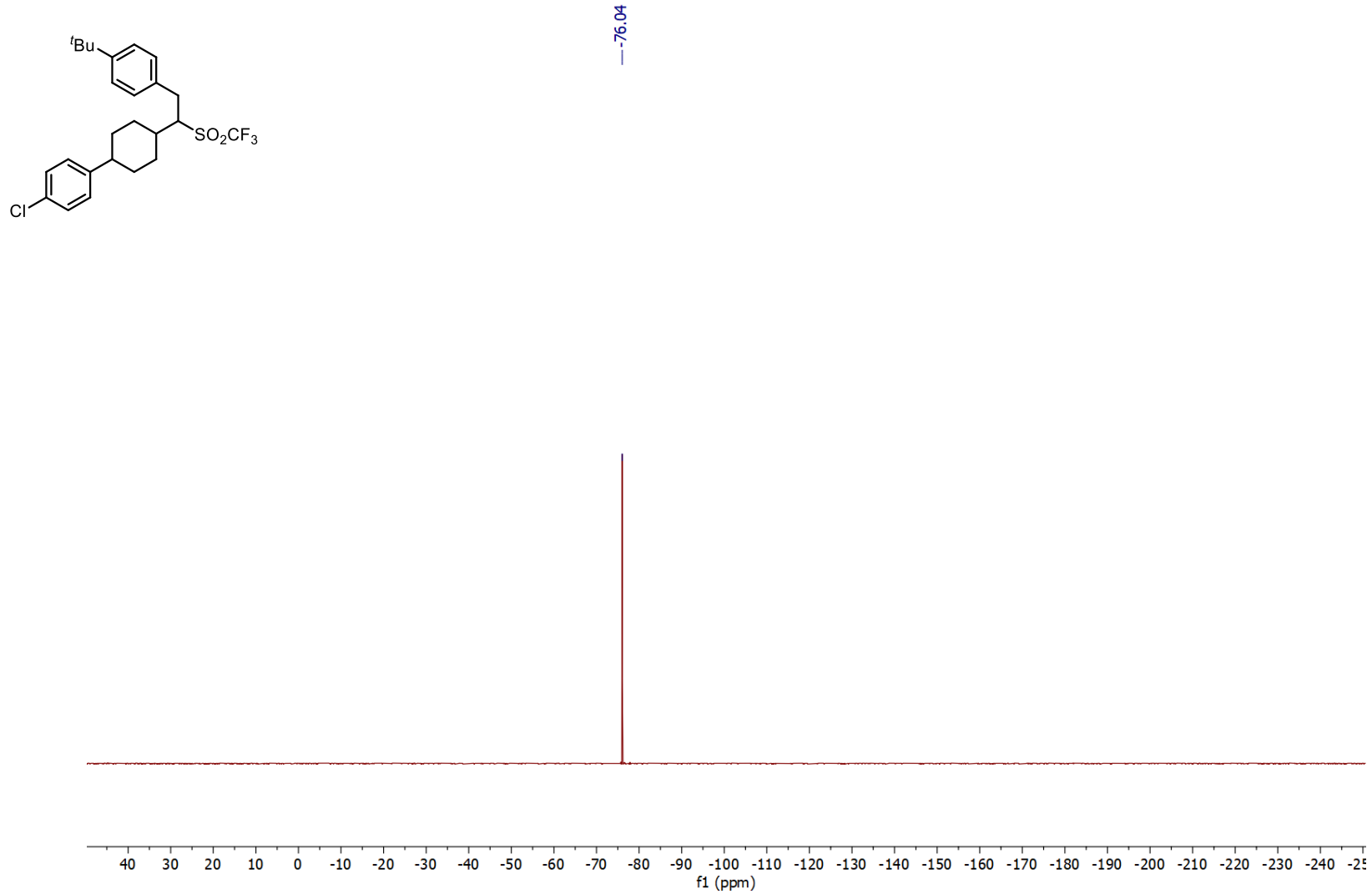
1-(*tert*-Butyl)-4-(2-(4-(4-chlorophenyl)cyclohexyl)-2-((trifluoromethyl)sulfonyl)ethyl)benzene 1j ¹H NMR (400 MHz, Chloroform-*d*)



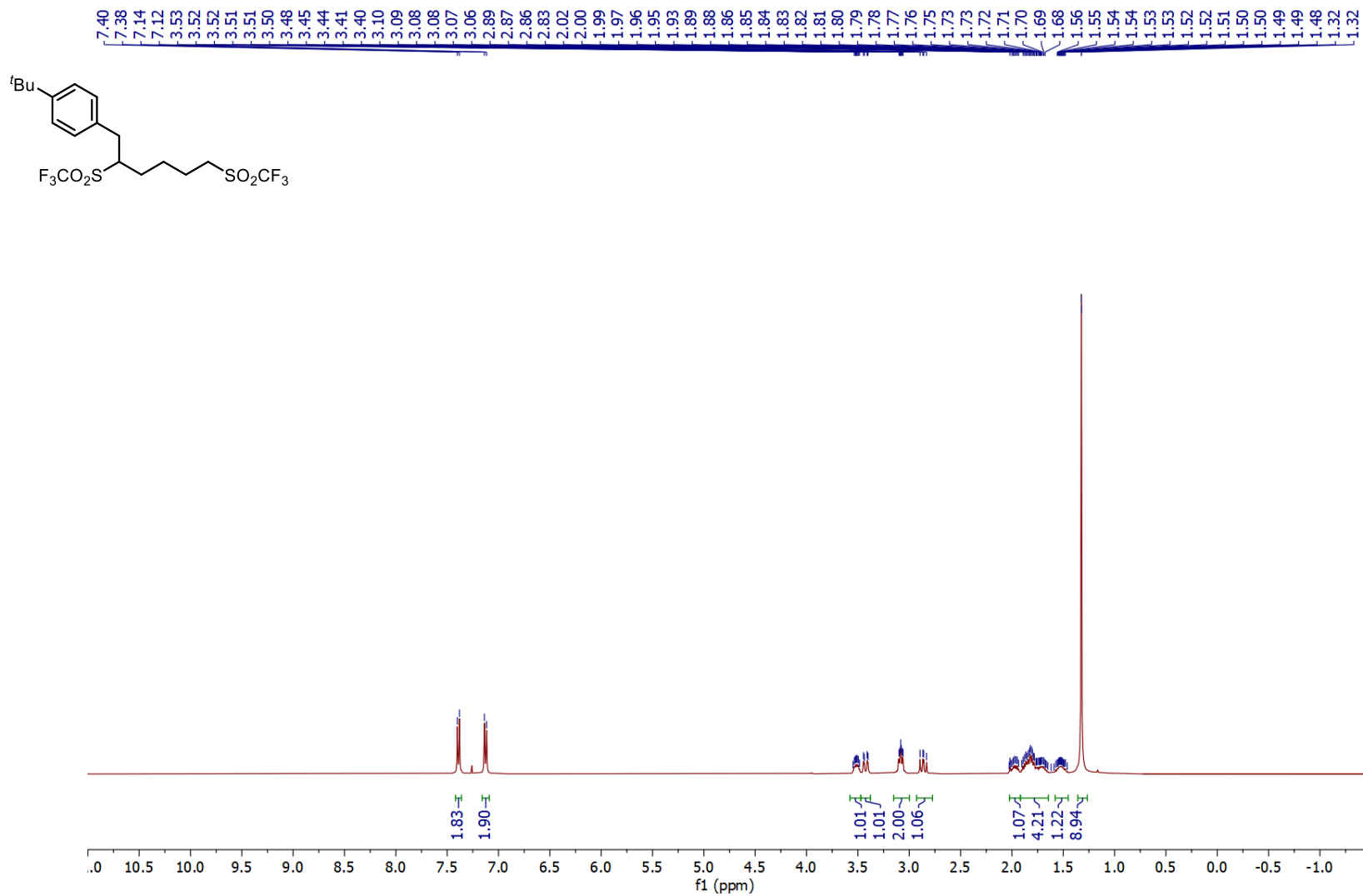
1-(*tert*-Butyl)-4-(2-(4-(4-chlorophenyl)cyclohexyl)-2-((trifluoromethyl)sulfonyl)ethyl)benzene 1j $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, Chloroform-*d*)



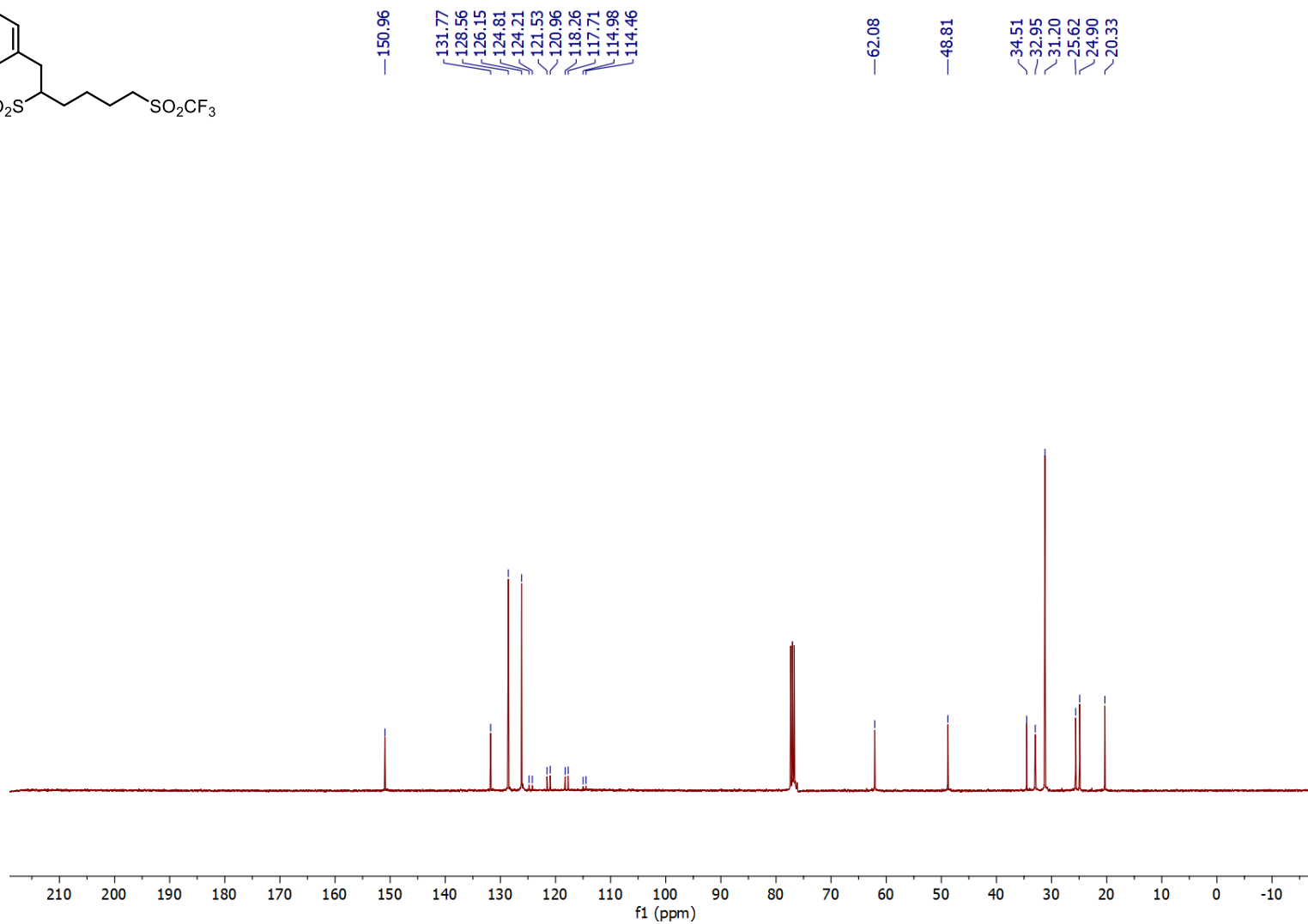
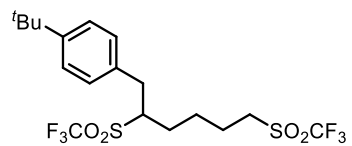
1-(*tert*-Butyl)-4-(2-(4-(4-chlorophenyl)cyclohexyl)-2-((trifluoromethyl)sulfonyl)ethyl)benzene 1j ¹⁹F NMR (376 MHz, Chloroform-*d*)



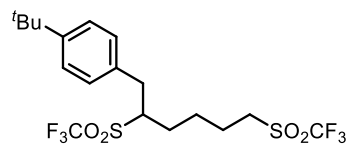
1-(2,6-Bis((trifluoromethyl)sulfonyl)hexyl)-4-(*tert*-butyl)benzene S16 ¹H NMR (400 MHz, Chloroform-*d*)



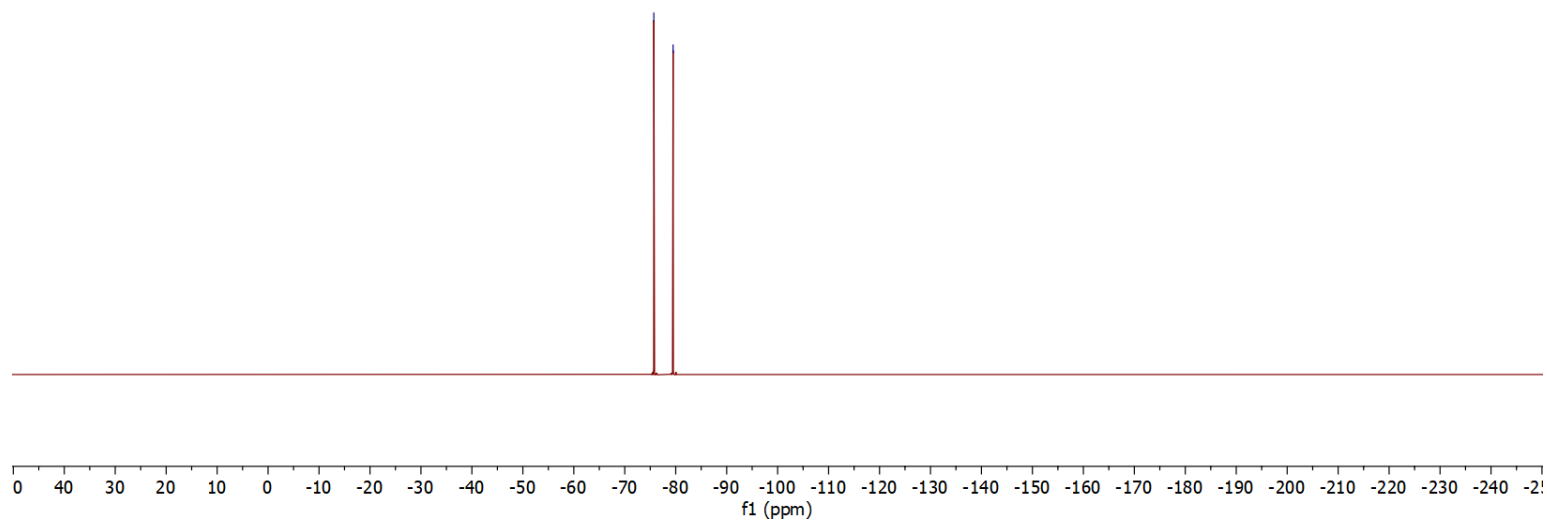
1-(2,6-Bis((trifluoromethyl)sulfonyl)hexyl)-4-(*tert*-butyl)benzene S16 $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, Chloroform-*d*)



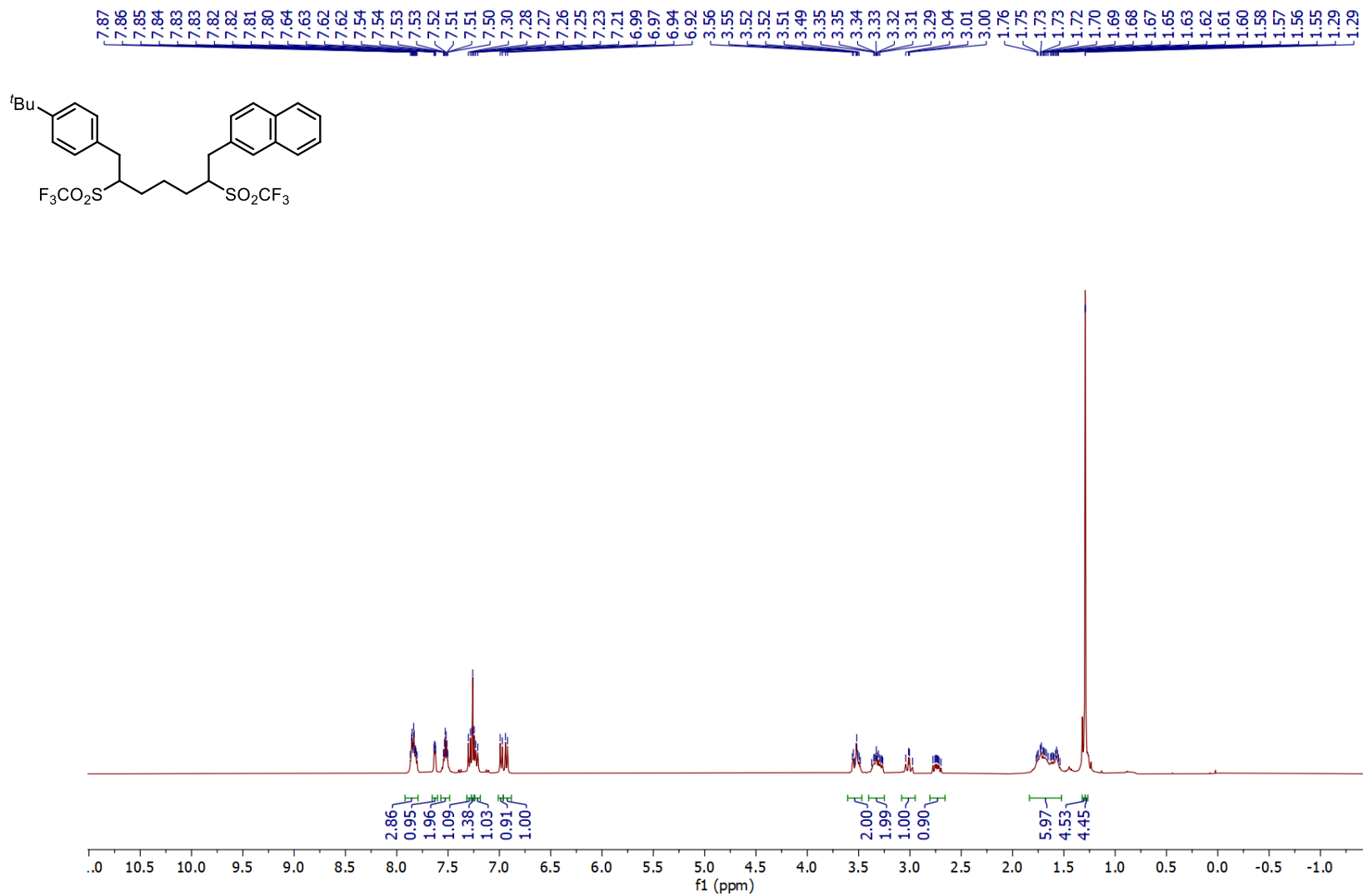
1-(2,6-Bis((trifluoromethyl)sulfonyl)hexyl)-4-(*tert*-butyl)benzene S16 ^{19}F NMR (376 MHz, Chloroform-*d*)



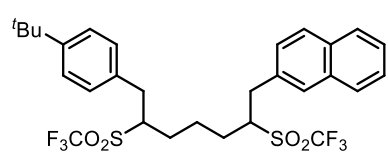
-75.71
-79.49



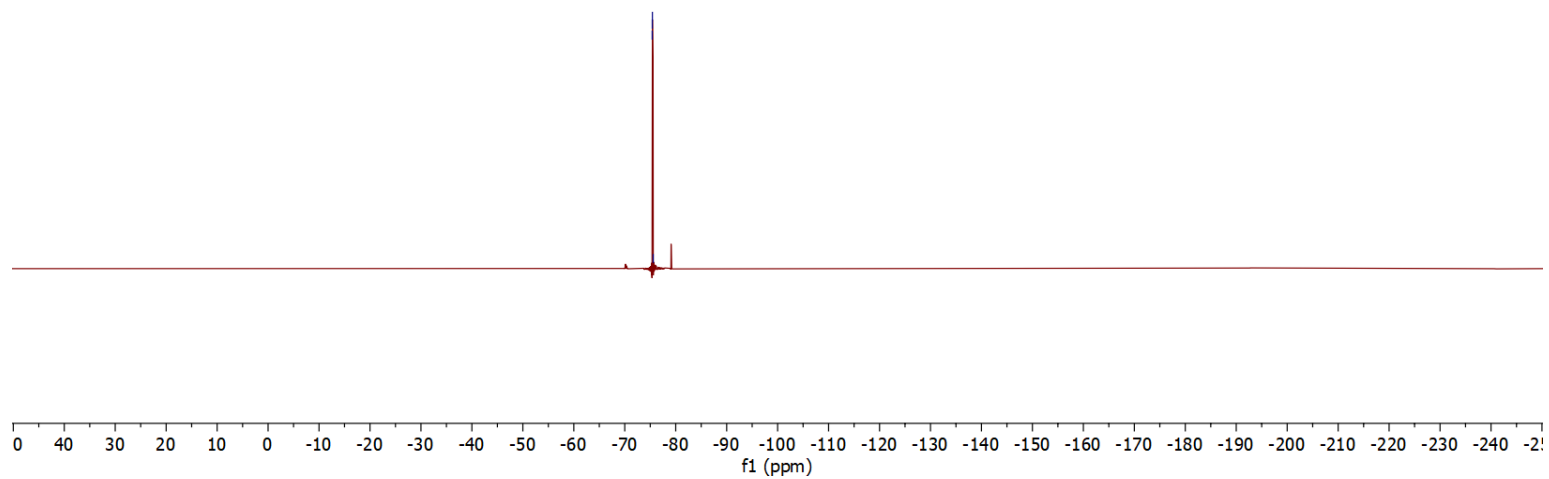
2-(7-(4-(*tert*-Butyl)phenyl)-2,6-bis((trifluoromethyl)sulfonyl)heptyl)naphthalene 1k ¹H NMR (700 MHz, Chloroform-*d*)



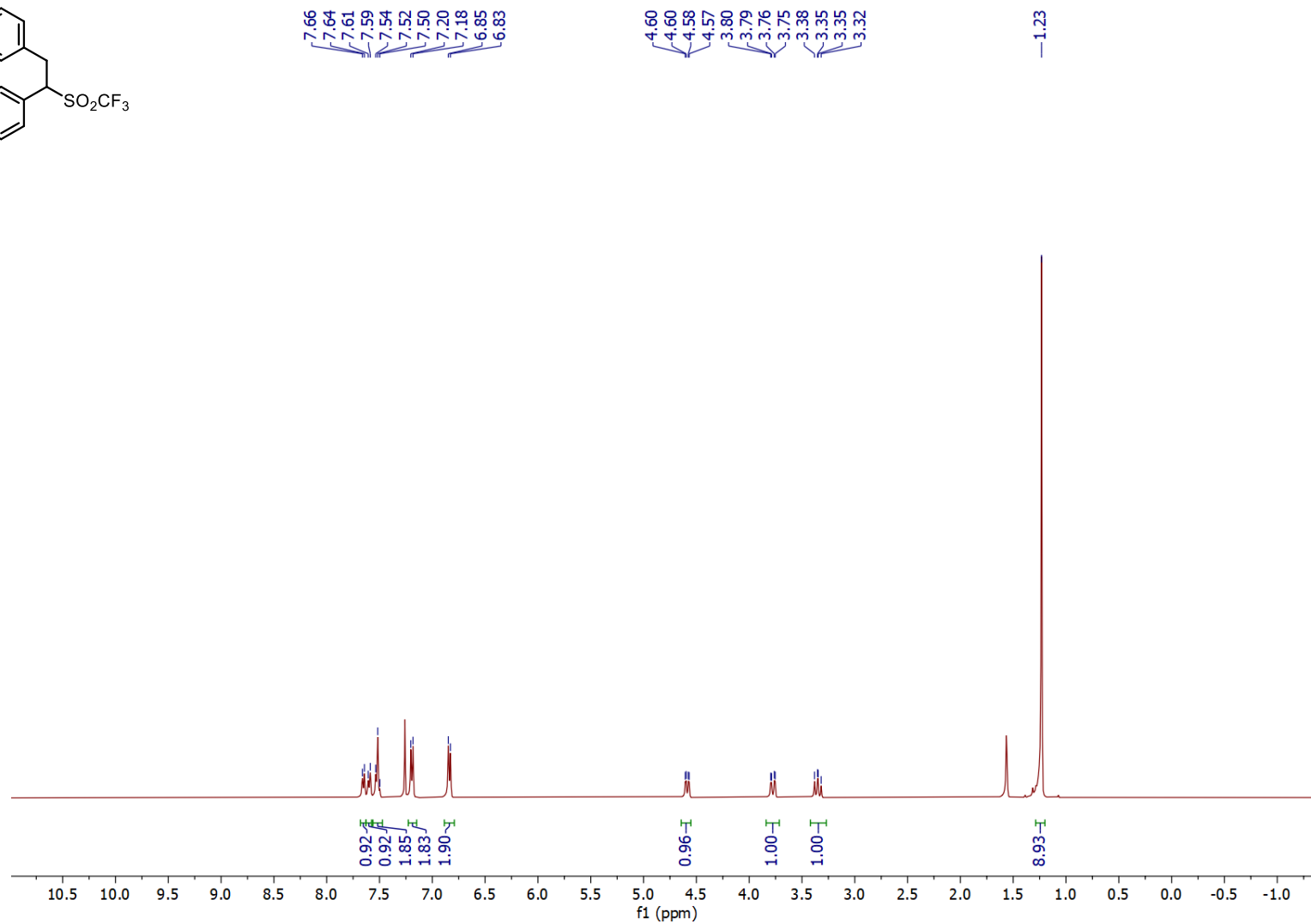
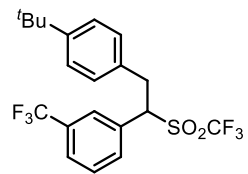
2-(7-(4-(*tert*-Butyl)phenyl)-2,6-bis((trifluoromethyl)sulfonyl)heptyl)naphthalene 1k ^{19}F NMR (376 MHz, Chloroform-*d*)



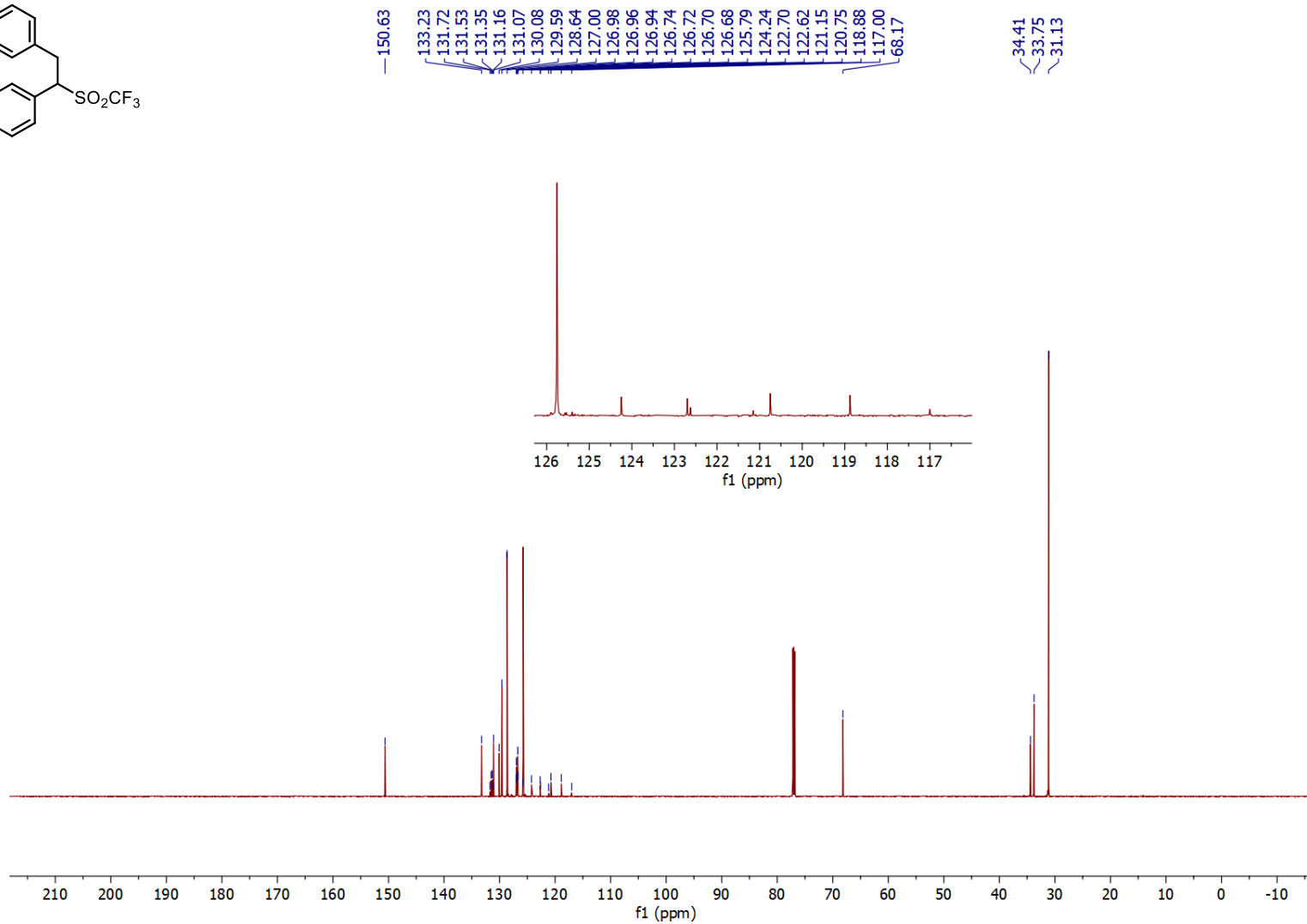
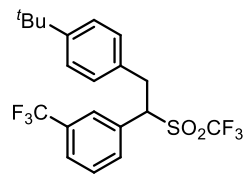
-75.38
-75.39
-75.42
-75.58



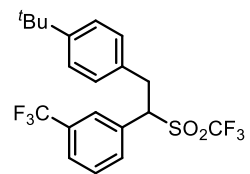
1-(2-(4-(*tert*-Butyl)phenyl)-1-((trifluoromethyl)sulfonyl)ethyl)-3-(trifluoromethyl)benzene 1m ¹H NMR (700 MHz, Chloroform-*d*)



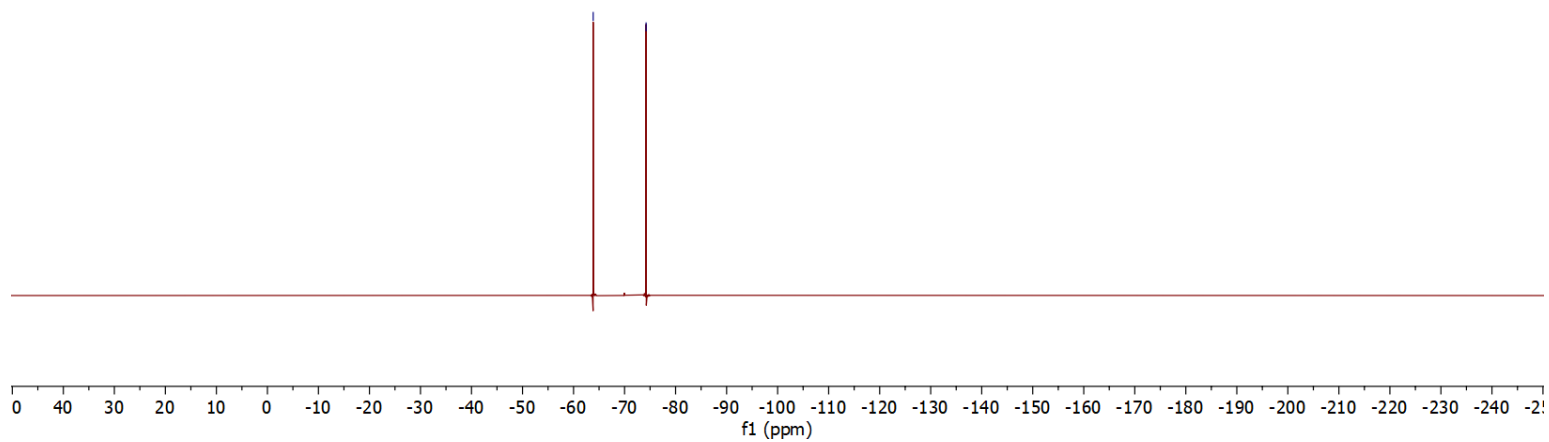
1-(2-(4-(*tert*-Butyl)phenyl)-1-((trifluoromethyl)sulfonyl)ethyl)-3-(trifluoromethyl)benzene 1m $^{13}\text{C}\{^1\text{H}\}$ NMR (176 MHz, Chloroform-*d*)



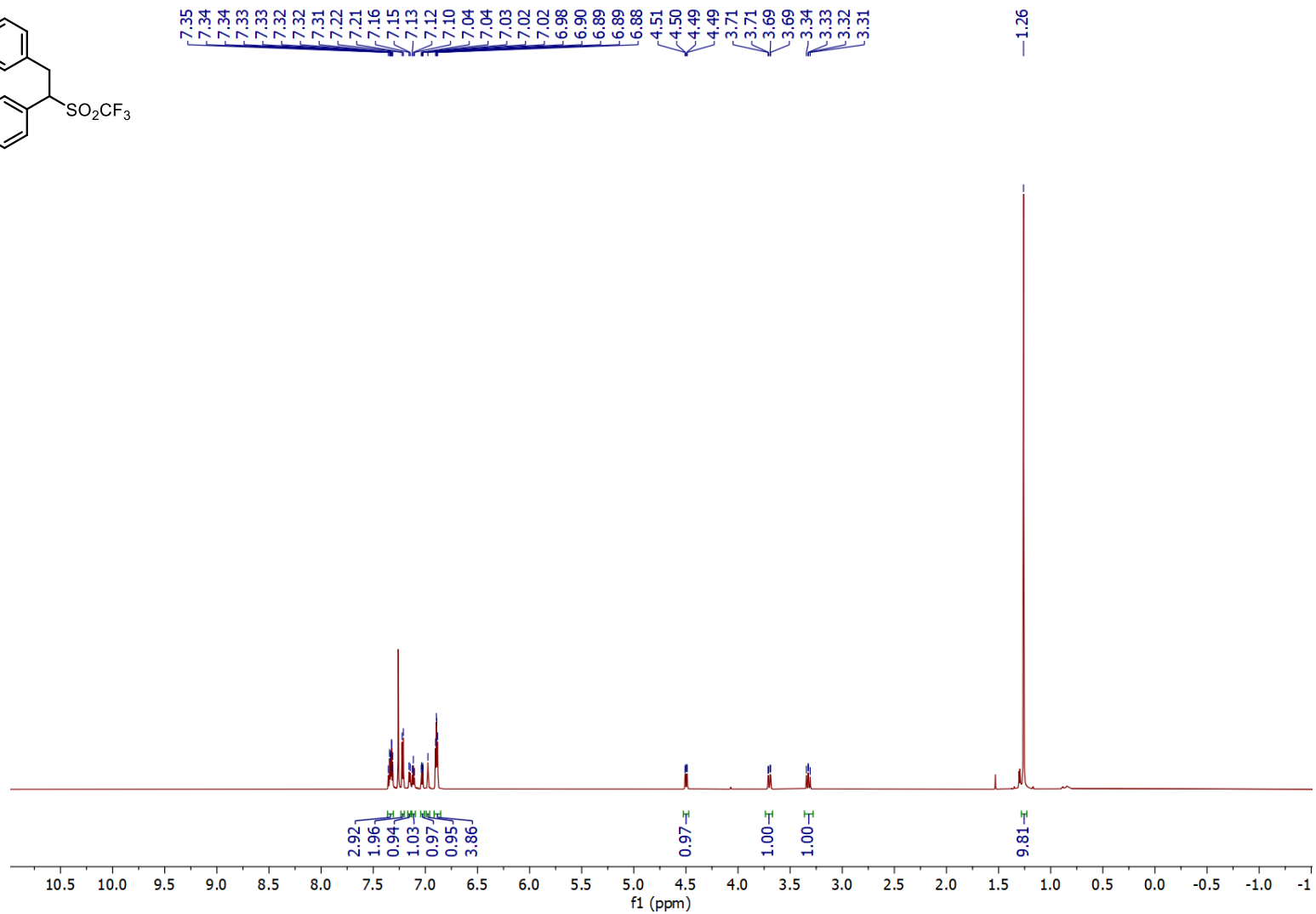
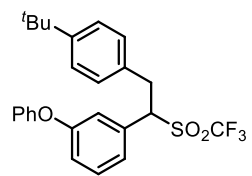
1-(2-(4-(*tert*-Butyl)phenyl)-1-((trifluoromethyl)sulfonyl)ethyl)-3-(trifluoromethyl)benzene 1m ¹⁹F NMR (376 MHz, Chloroform-*d*)



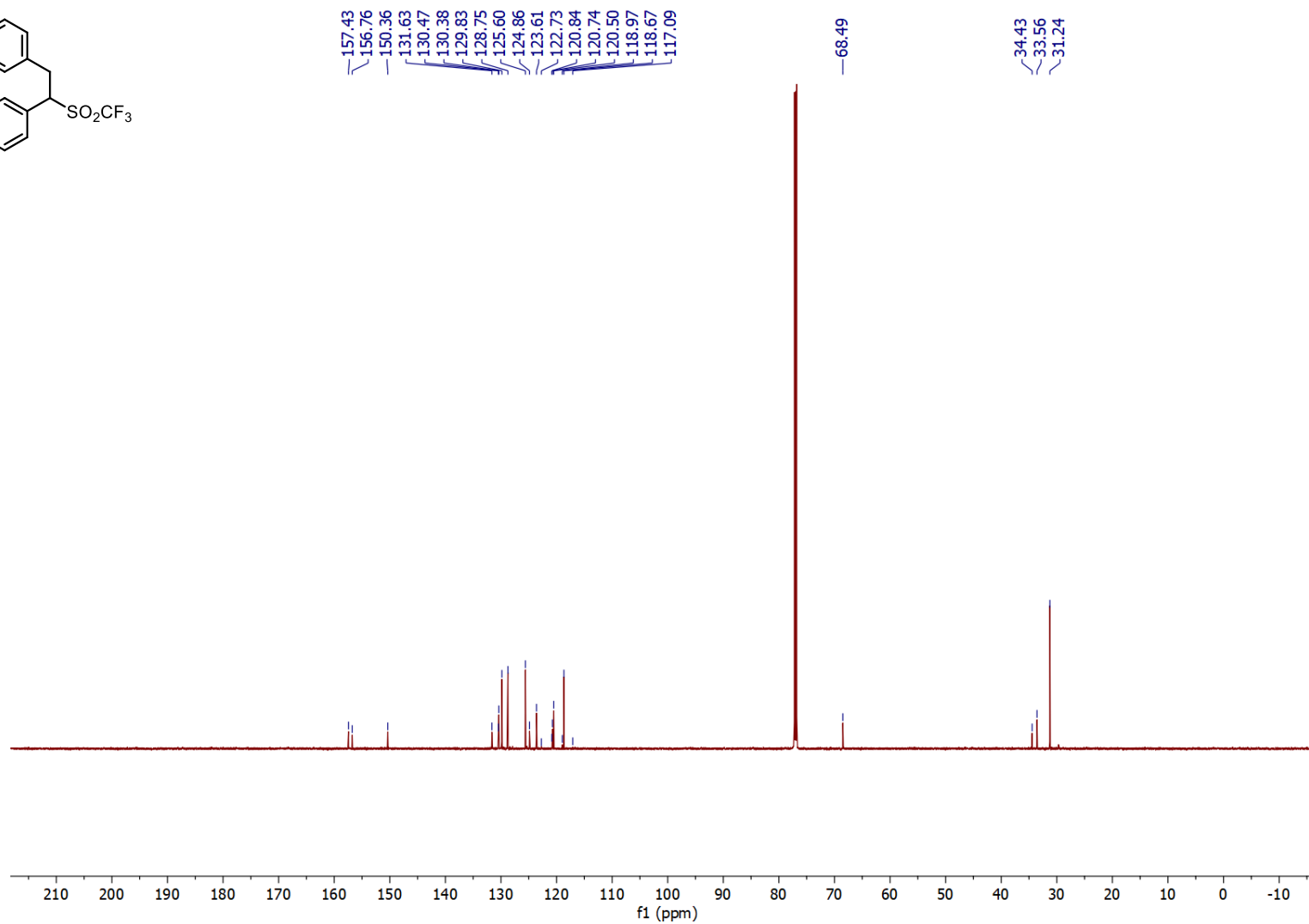
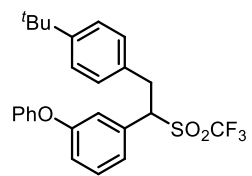
— -63.85
— -74.22



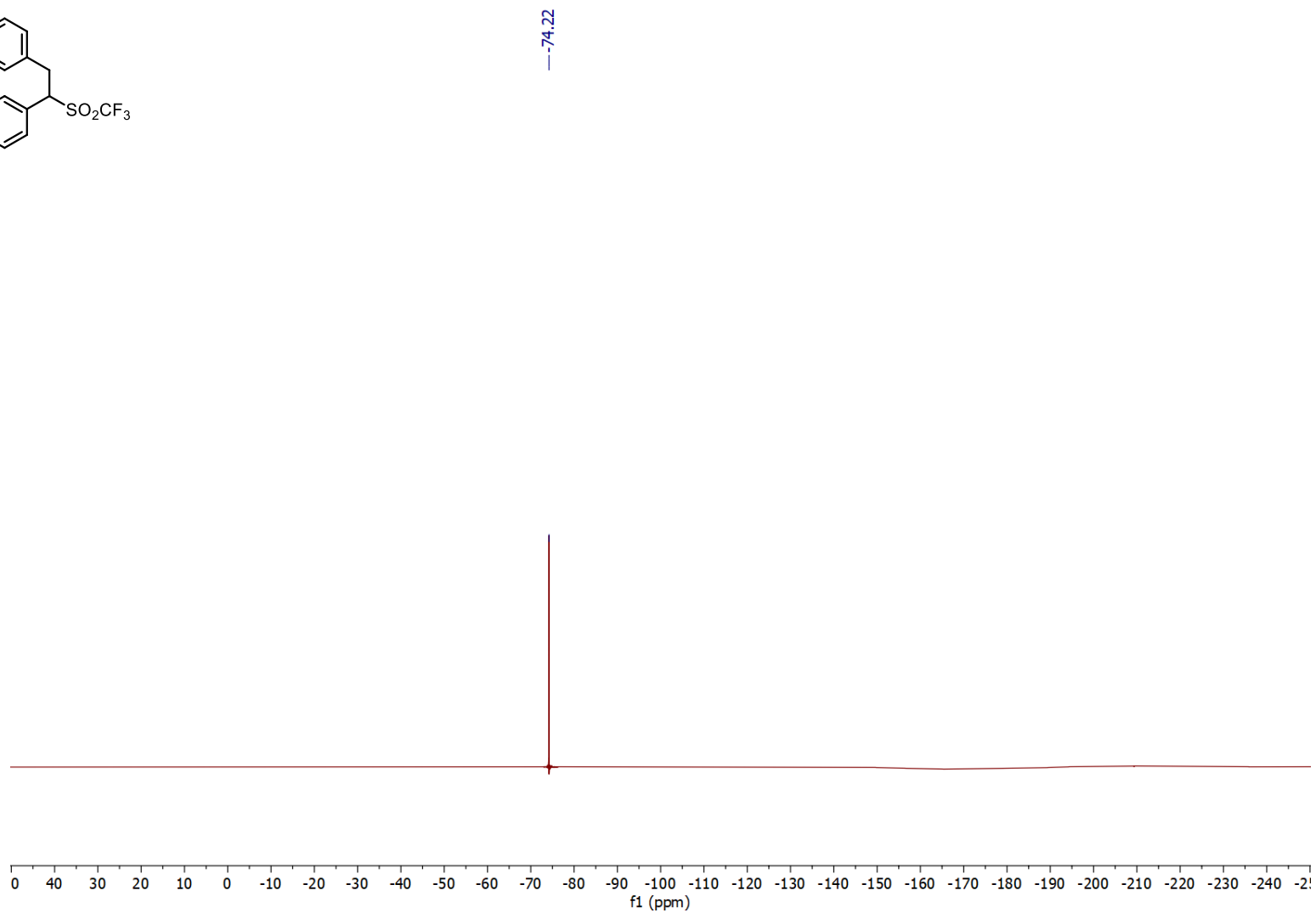
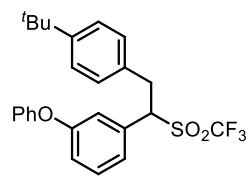
1-(2-(4-(*tert*-Butyl)phenyl)phenyl)-1-((trifluoromethyl)sulfonyl)ethyl)-3-phenoxybenzene 1n ¹H NMR (700 MHz, Chloroform-*d*)



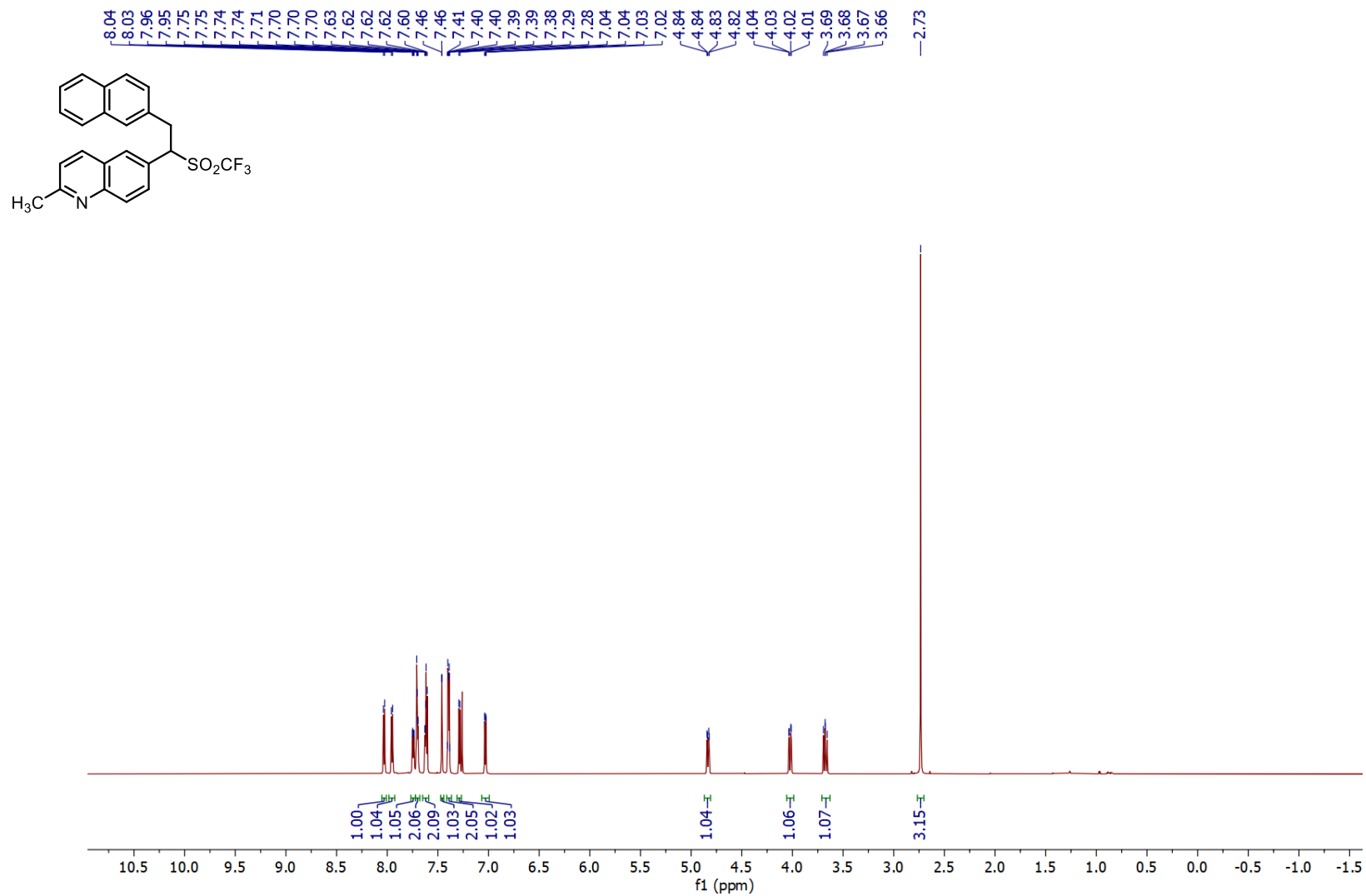
1-(2-(4-(*tert*-Butyl)phenyl)-1-((trifluoromethyl)sulfonyl)ethyl)-3-phenoxybenzene 1n $^{13}\text{C}\{^1\text{H}\}$ NMR (176 MHz, Chloroform-*d*)



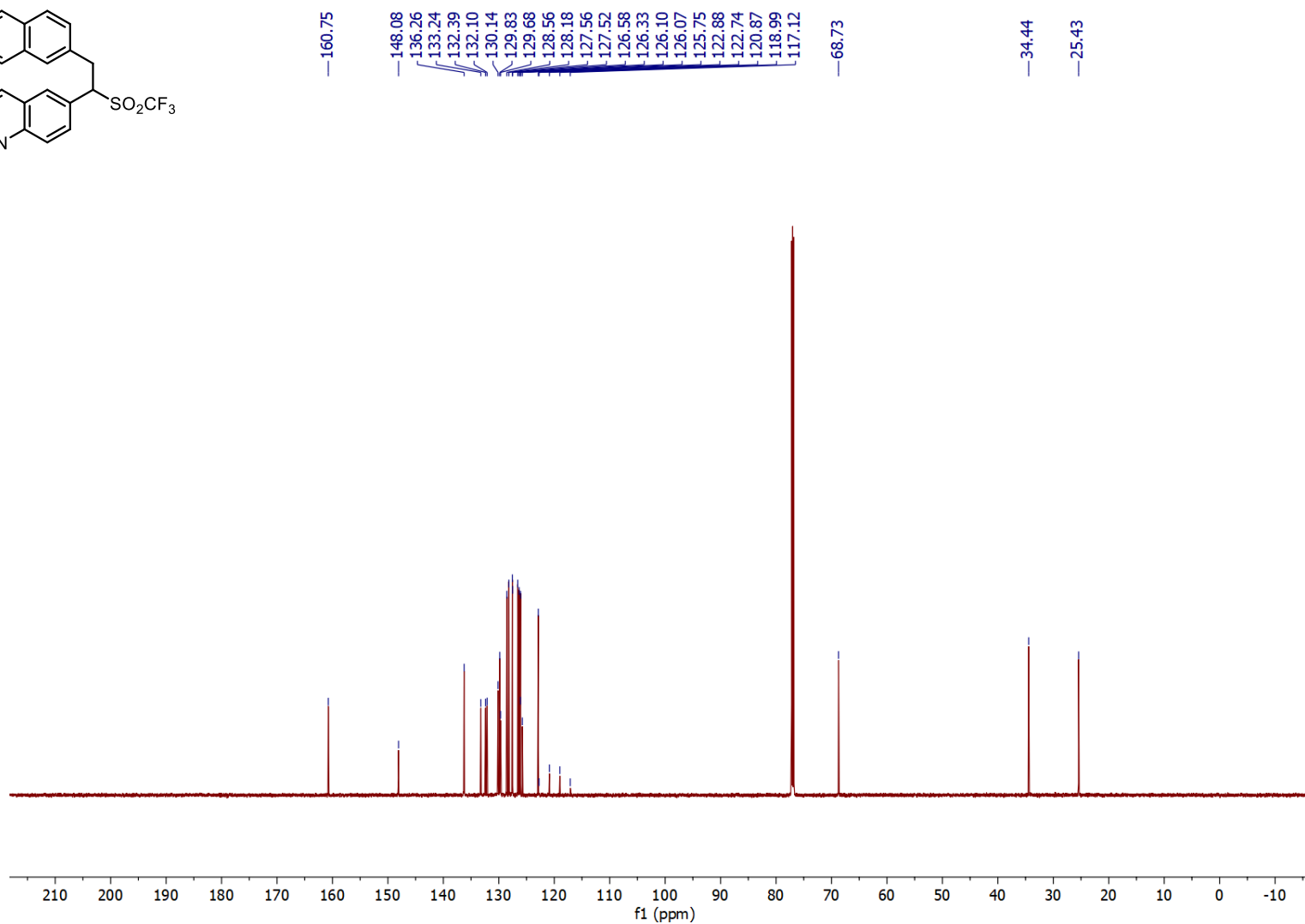
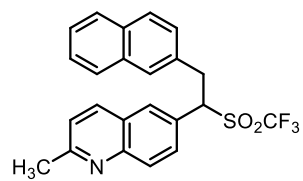
1-(2-(4-(*tert*-Butyl)phenyl)-1-((trifluoromethyl)sulfonyl)ethyl)-3-phenoxybenzene 1n ¹⁹F NMR (376 MHz, Chloroform-*d*)



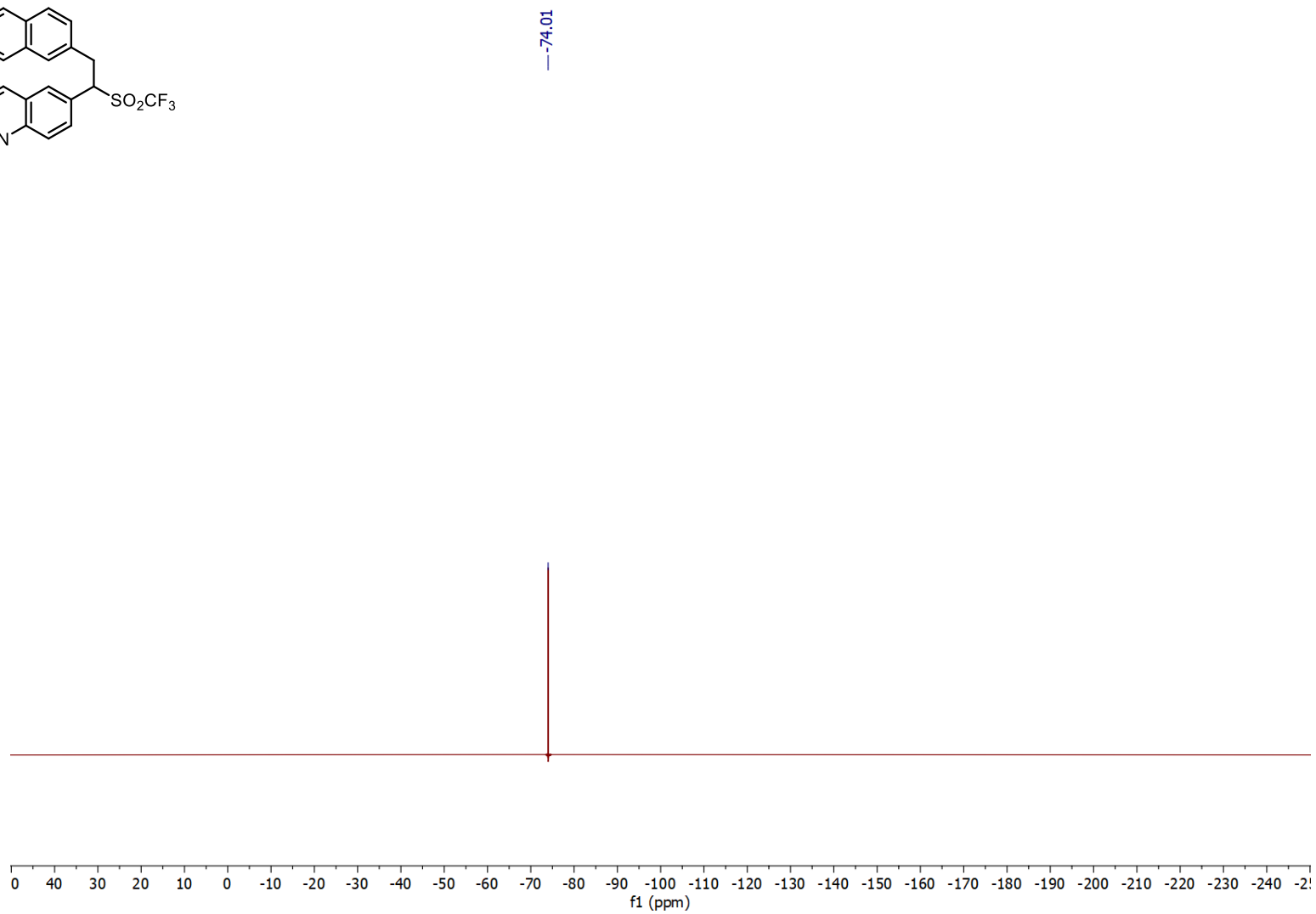
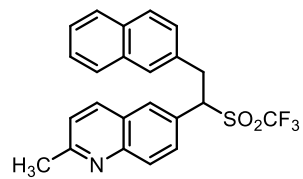
6-(2-(4-(*tert*-Butyl)phenyl)-1-((trifluoromethyl)sulfonyl)ethyl)-2-methylquinoline 1p ¹H NMR (700 MHz, Chloroform-*d*)



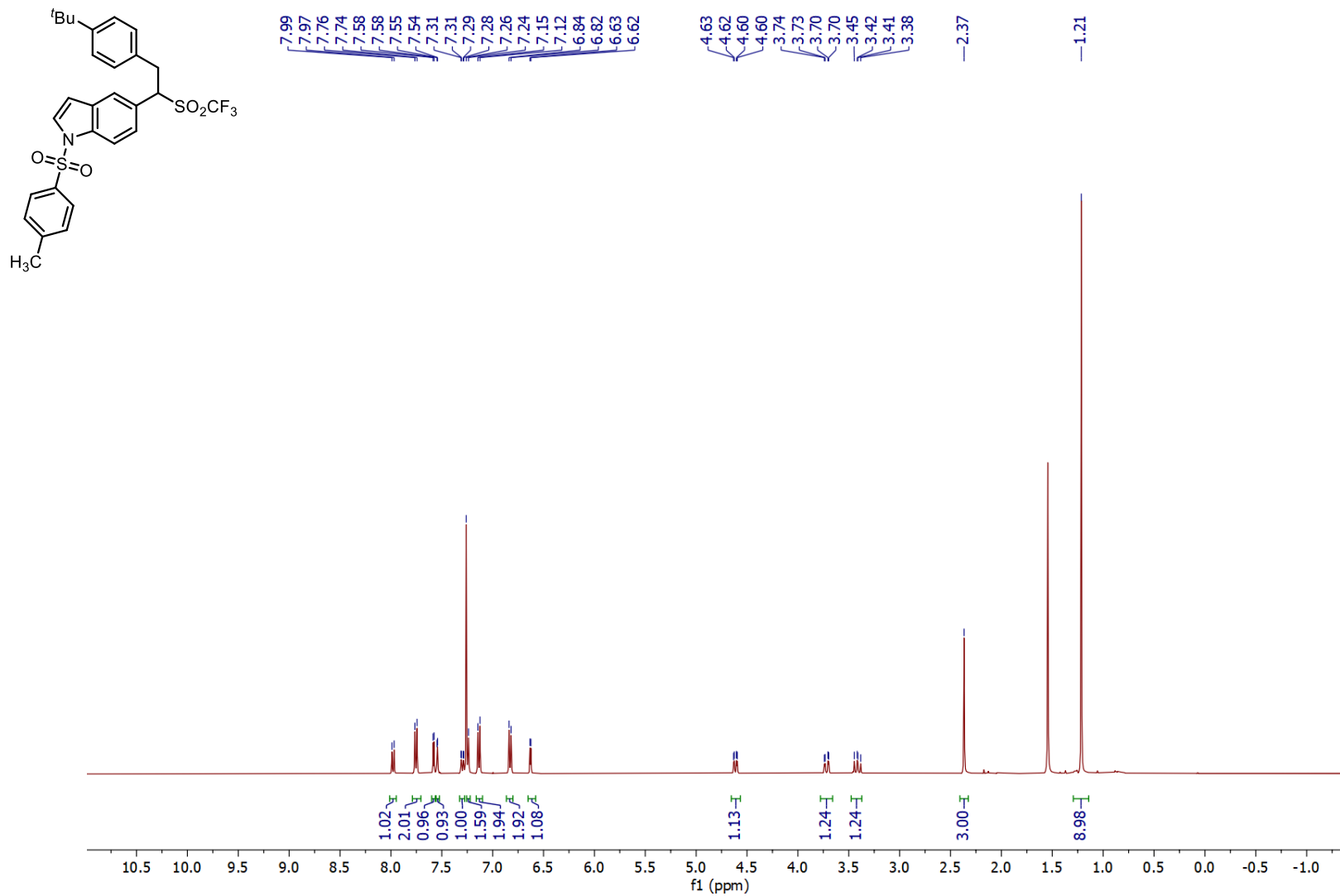
6-(2-(4-(*tert*-Butyl)phenyl)-1-((trifluoromethyl)sulfonyl)ethyl)-2-methylquinoline 1p $^{13}\text{C}\{^1\text{H}\}$ NMR (176 MHz, Chloroform-*d*)



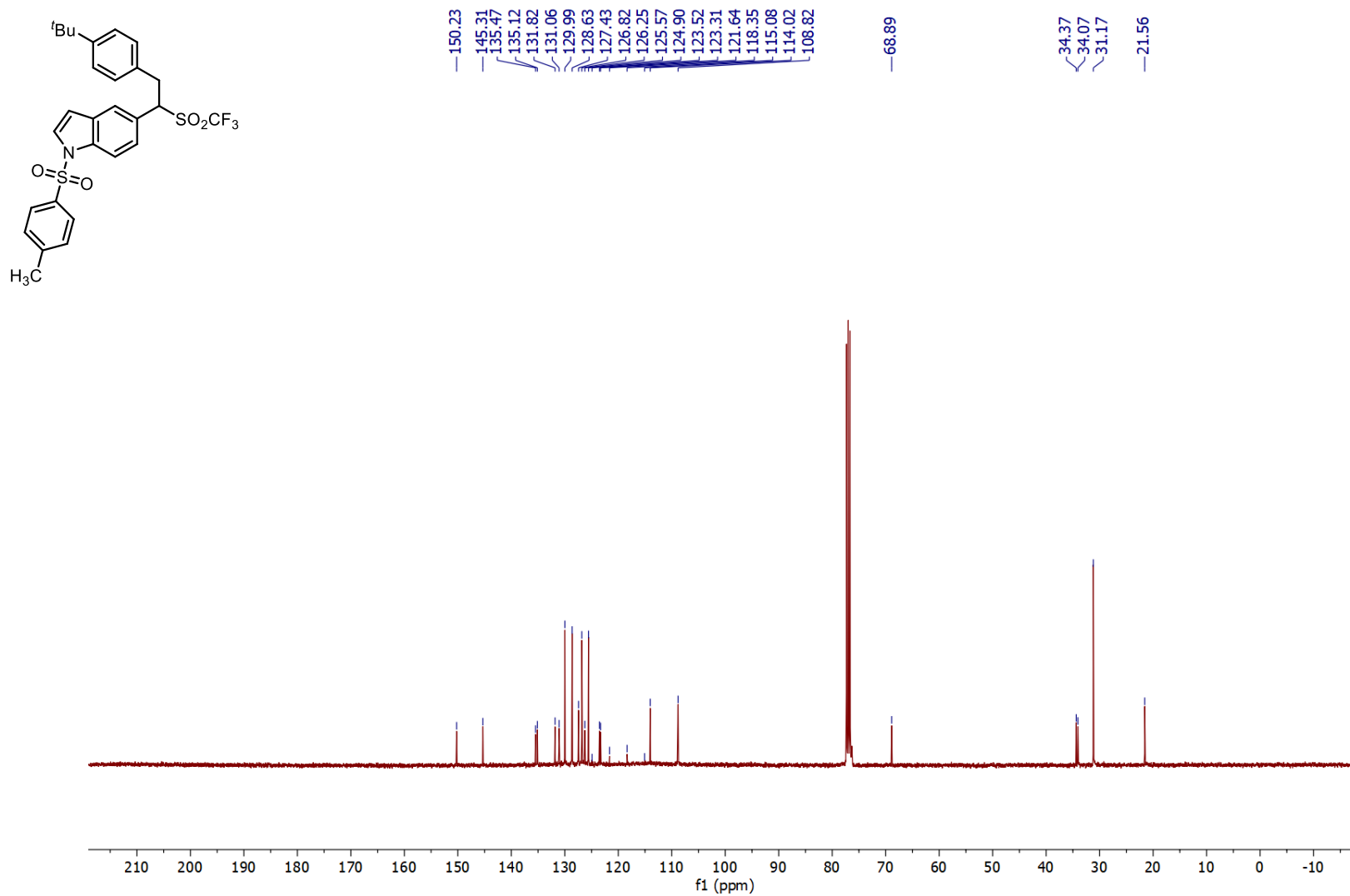
6-(2-(4-(*tert*-Butyl)phenyl)-1-((trifluoromethyl)sulfonyl)ethyl)-2-methylquinoline 1p ¹⁹F NMR (376 MHz, Chloroform-*d*)



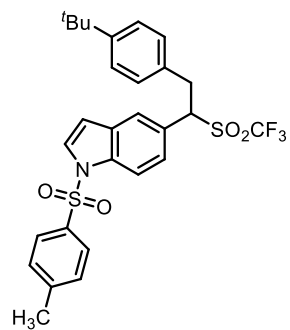
5-(2-(4-(*tert*-Butyl)phenyl)-1-((trifluoromethyl)sulfonyl)ethyl)-1-tosyl-1H-indole 1q ¹H NMR (400 MHz, Chloroform-*d*)



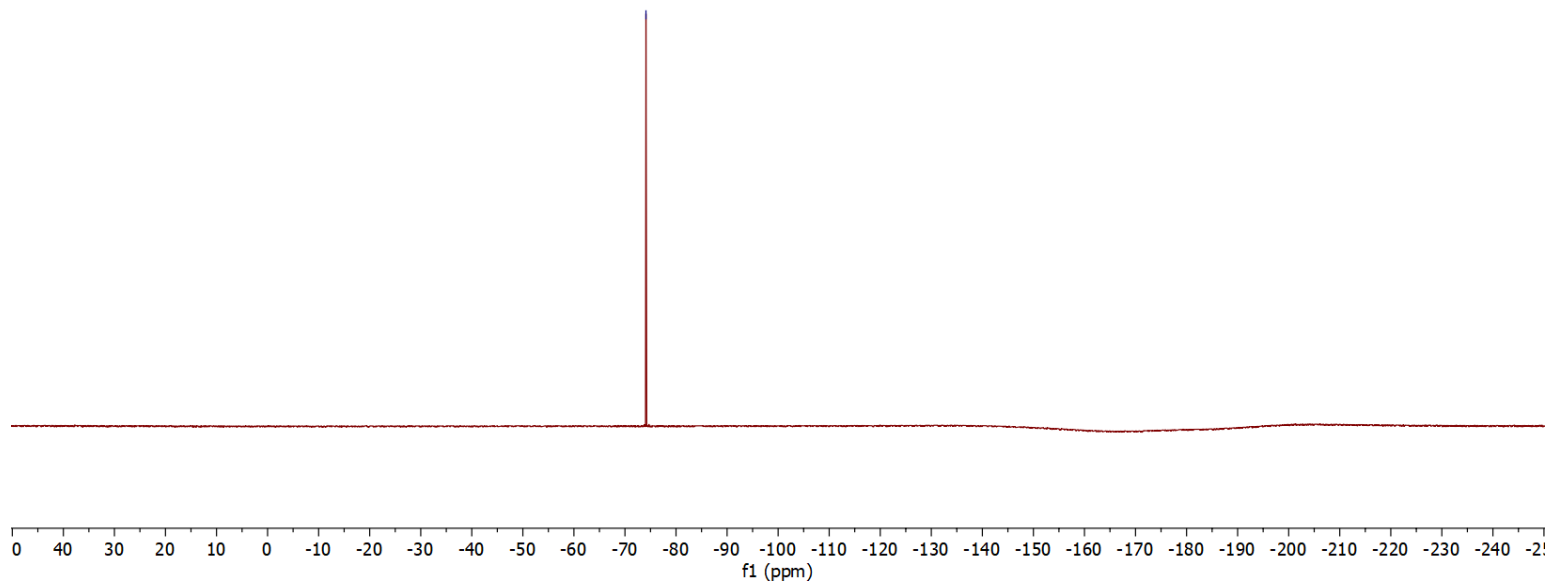
5-(2-(4-(*tert*-Butyl)phenyl)-1-((trifluoromethyl)sulfonyl)ethyl)-1-tosyl-1H-indole 1q $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, Chloroform-*d*)



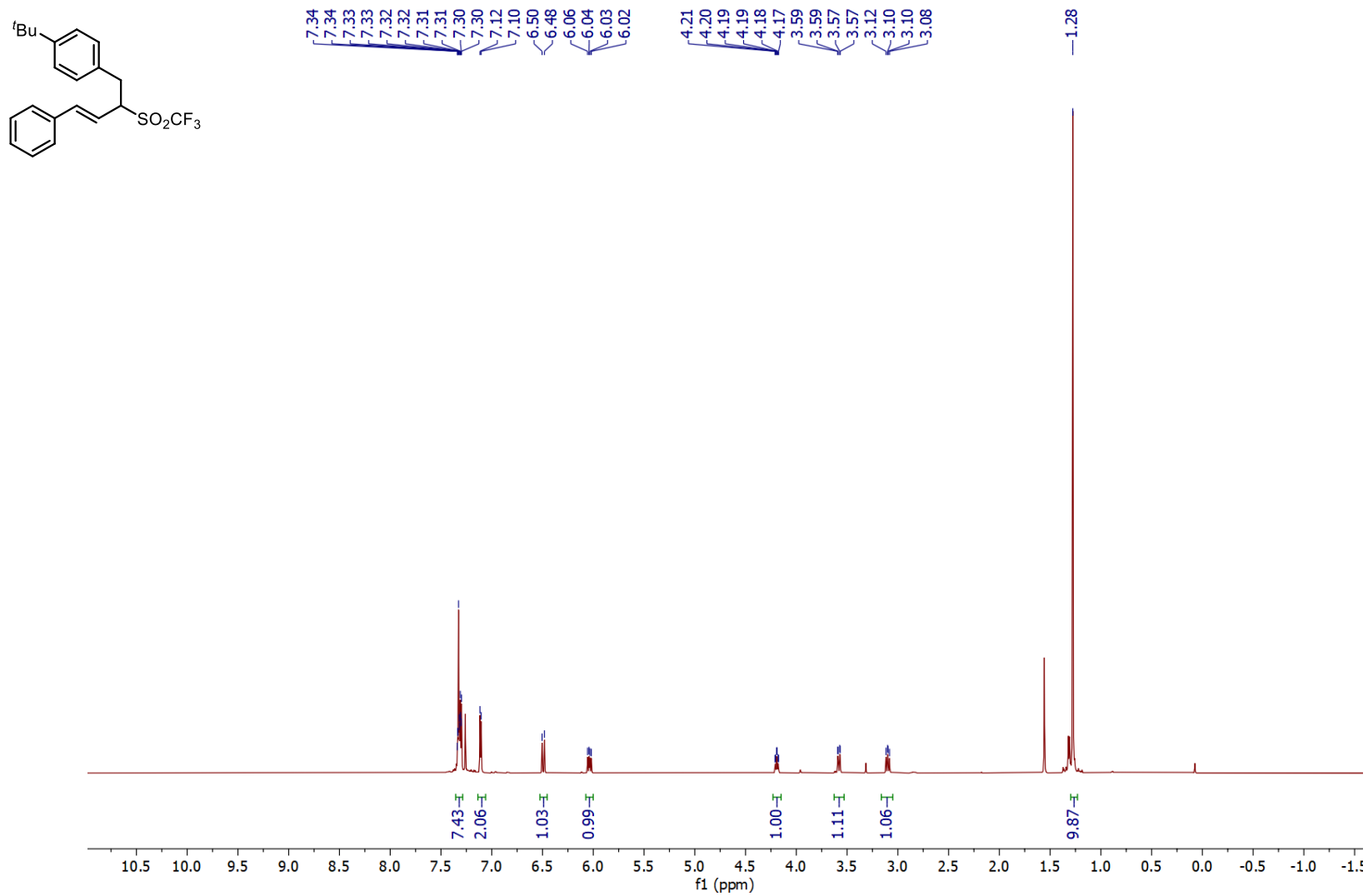
5-(2-(4-(*tert*-Butyl)phenyl)-1-((trifluoromethyl)sulfonyl)ethyl)-1-tosyl-1H-indole 1q ^{19}F NMR (376 MHz, Chloroform-*d*)



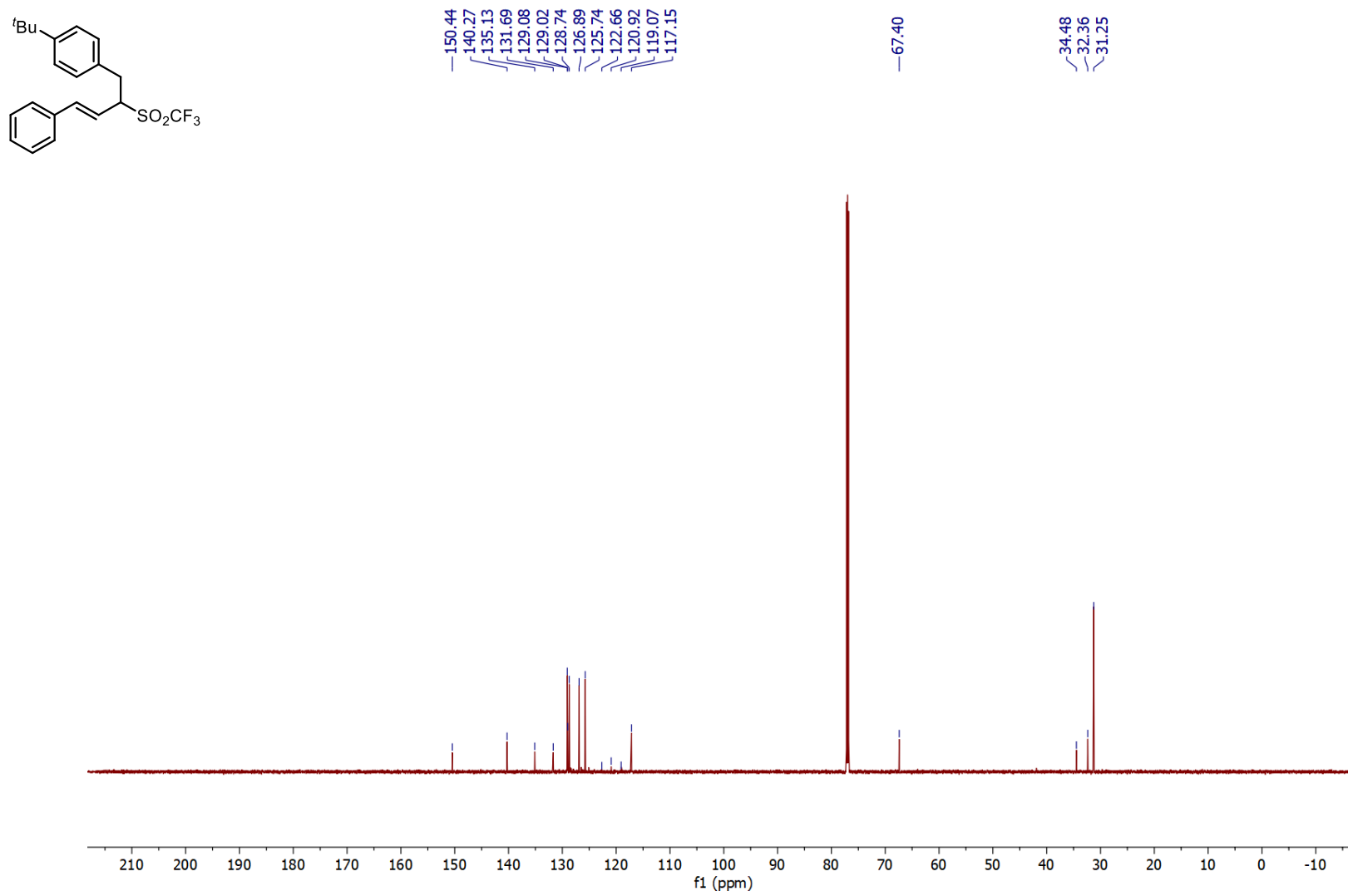
-74.11



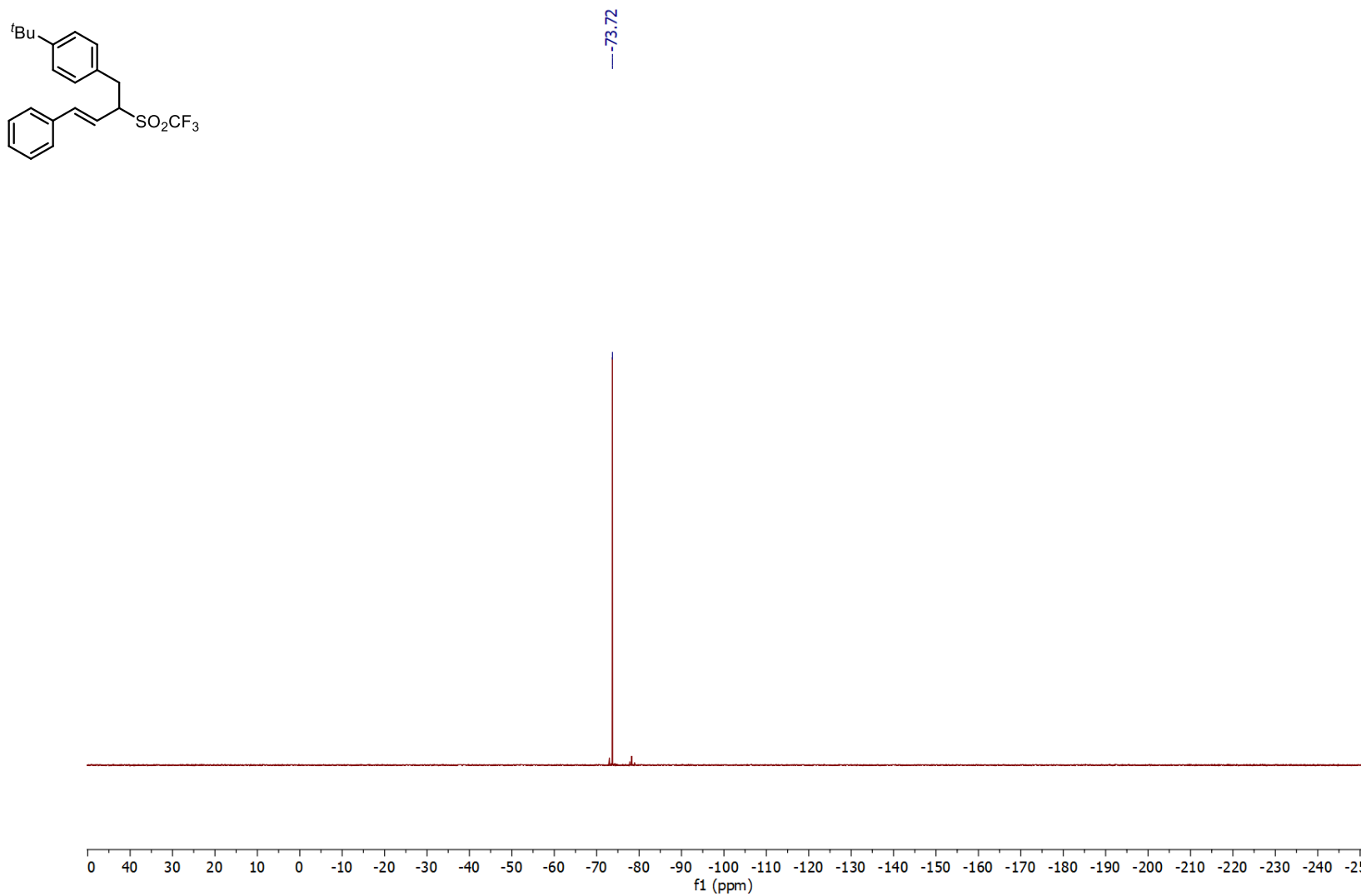
(E)-1-(tert-Butyl)-4-(4-phenyl-2-((trifluoromethyl)sulfonyl)but-3-en-1-yl)benzene 1s ¹H NMR (700 MHz, Chloroform-d)



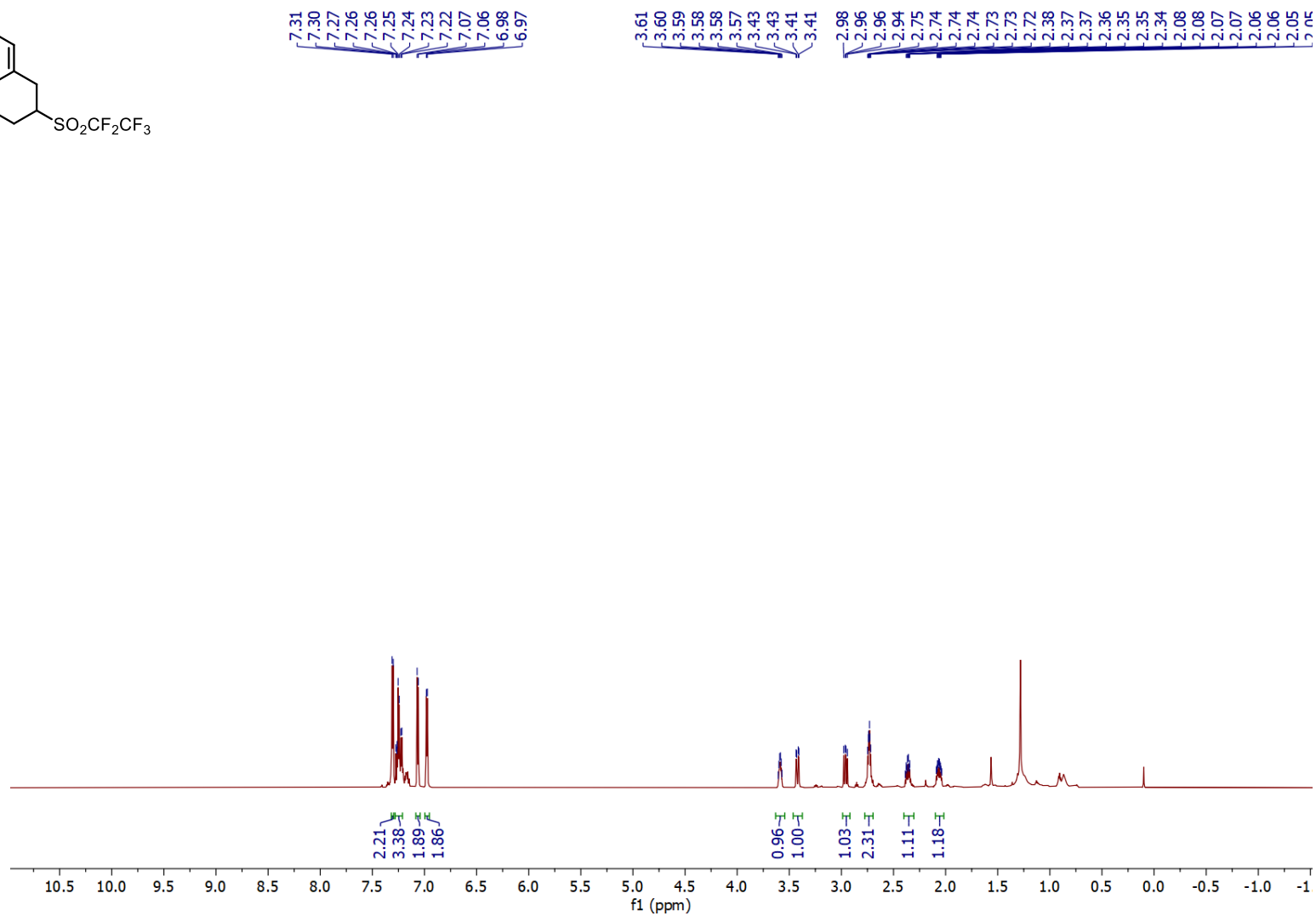
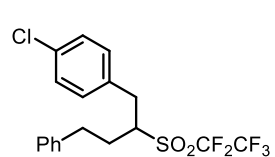
(E)-1-(tert-Butyl)-4-(4-phenyl-2-((trifluoromethyl)sulfonyl)but-3-en-1-yl)benzene 1s $^{13}\text{C}\{^1\text{H}\}$ NMR (176 MHz, Chloroform-*d*)



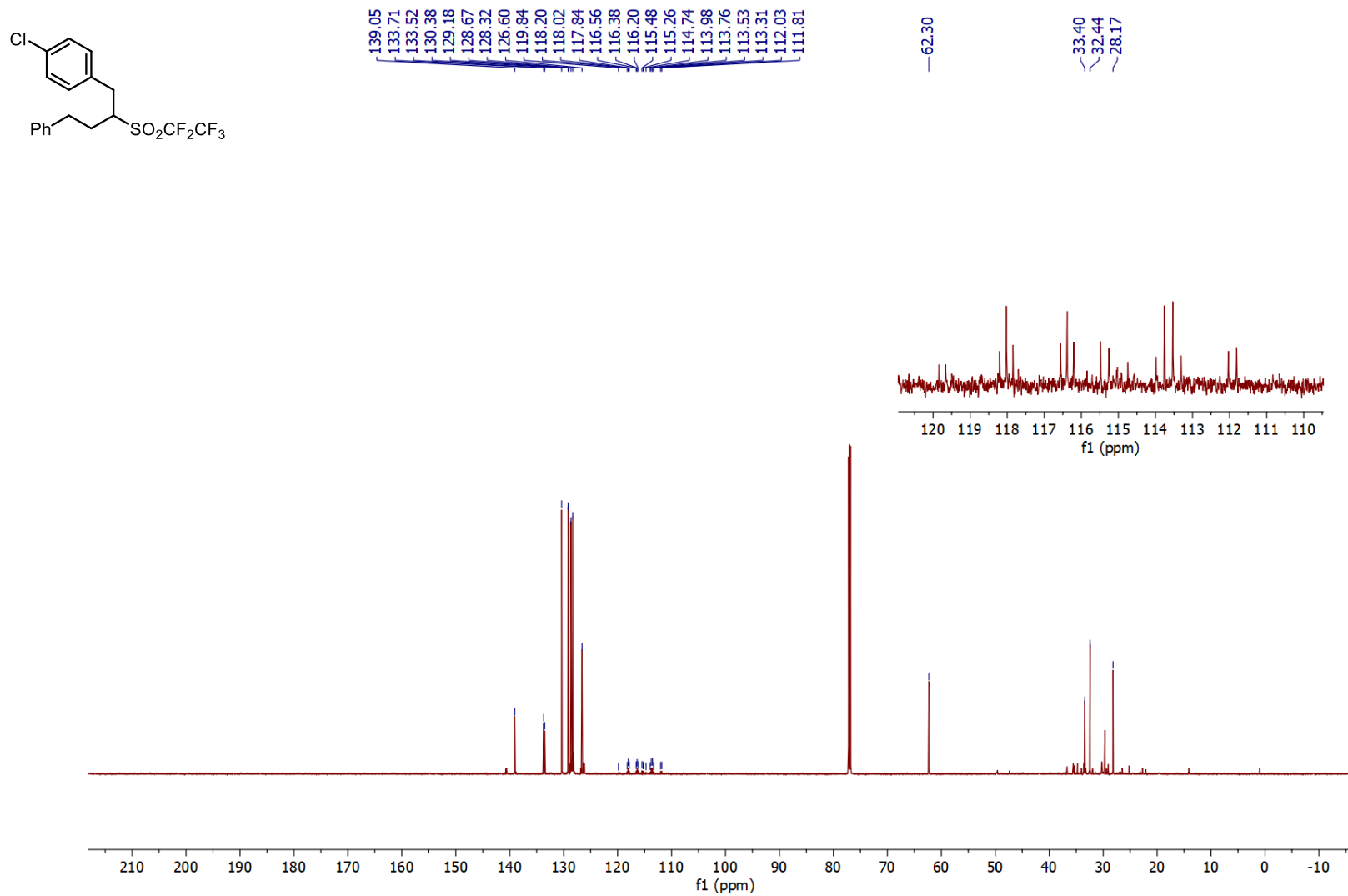
(E)-1-(tert-Butyl)-4-(4-phenyl-2-((trifluoromethyl)sulfonyl)but-3-en-1-yl)benzene 1s ¹⁹F NMR (376 MHz, Chloroform-*d*)



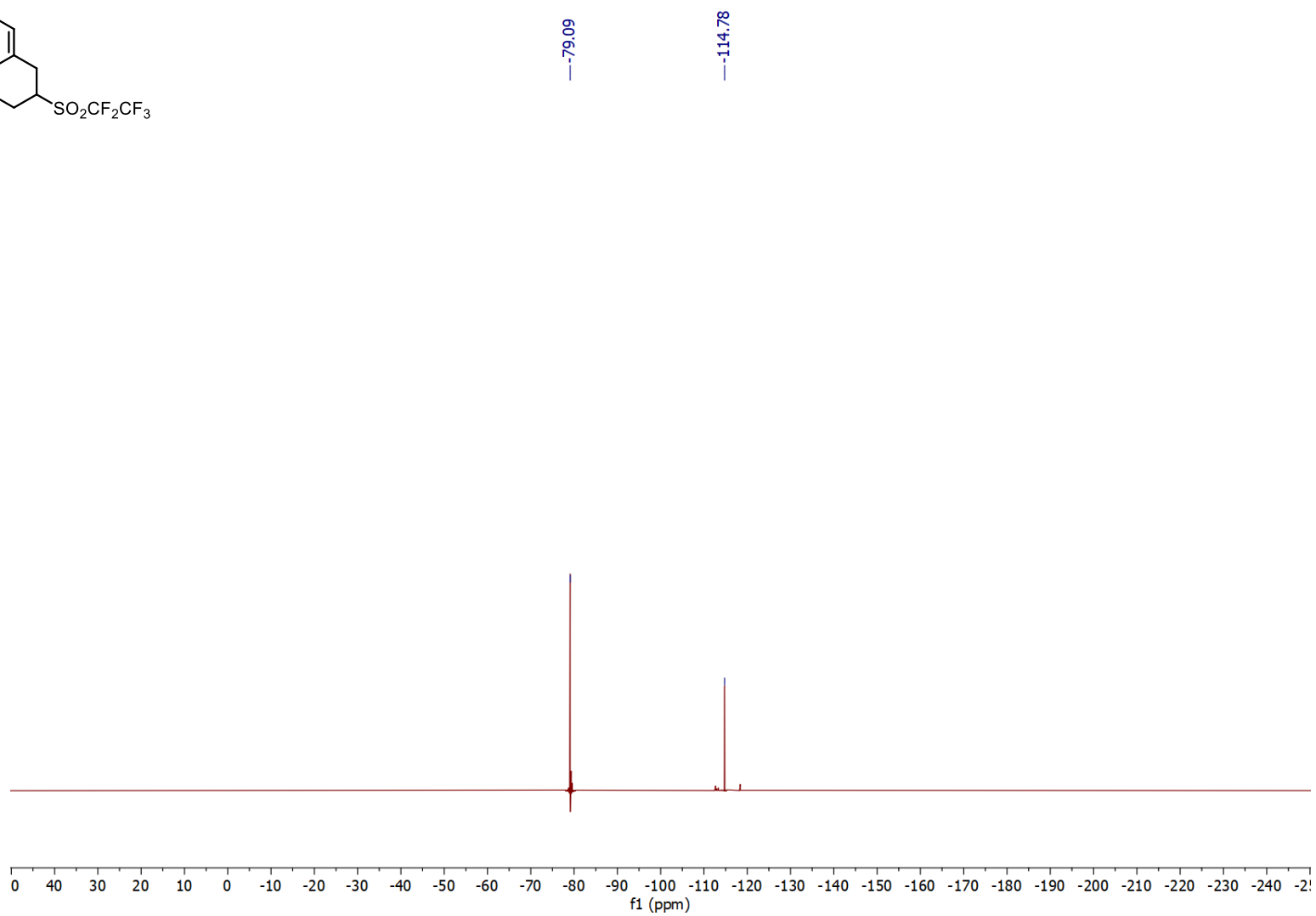
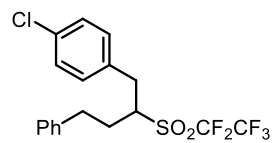
1-Chloro-4-(2-((perfluoroethyl)sulfonyl)-4-phenylbutyl)benzene 1u ¹H NMR (700 MHz, Chloroform-*d*)



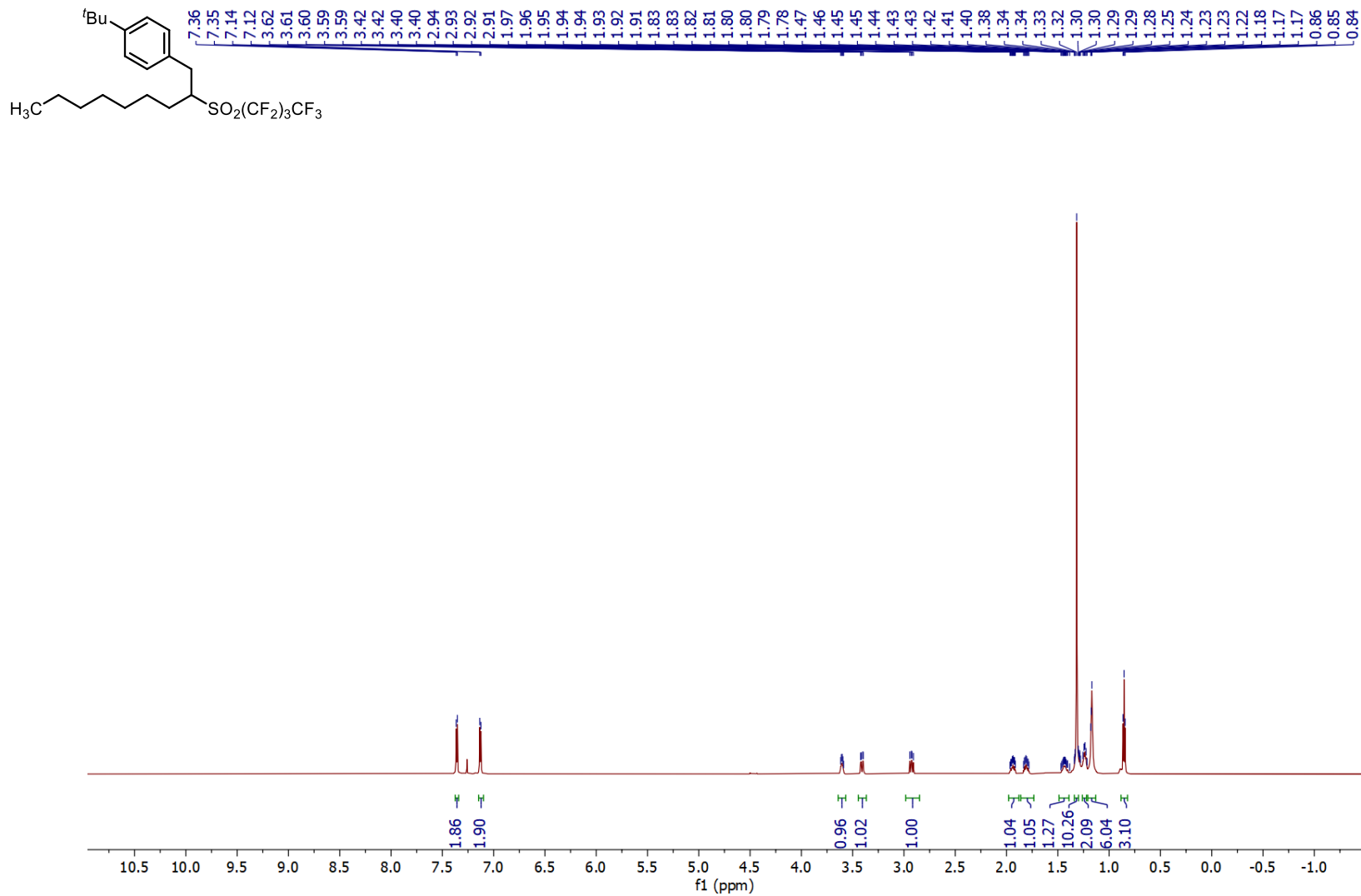
1-Chloro-4-(2-((perfluoroethyl)sulfonyl)-4-phenylbutyl)benzene 1u $^{13}\text{C}\{^1\text{H}\}$ NMR (176 MHz, Chloroform-*d*)



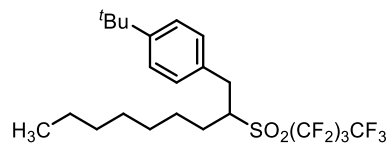
1-Chloro-4-(2-((perfluoroethyl)sulfonyl)-4-phenylbutyl)benzene 1u ¹⁹F NMR (376 MHz, Chloroform-*d*)



1-(*tert*-Butyl)-4-(2-((perfluorobutyl)sulfonyl)nonyl)benzene 1v ¹H NMR (700 MHz, Chloroform-*d*)



1-(*tert*-Butyl)-4-(2-((perfluorobutyl)sulfonyl)nonyl)benzene 1v $^{13}\text{C}\{^1\text{H}\}$ NMR (176 MHz, Chloroform-*d*)



150.50

132.60

128.73

125.85

117.36

116.31

115.62

112.14

110.61

64.56

34.50

33.13

31.52

31.28

29.06

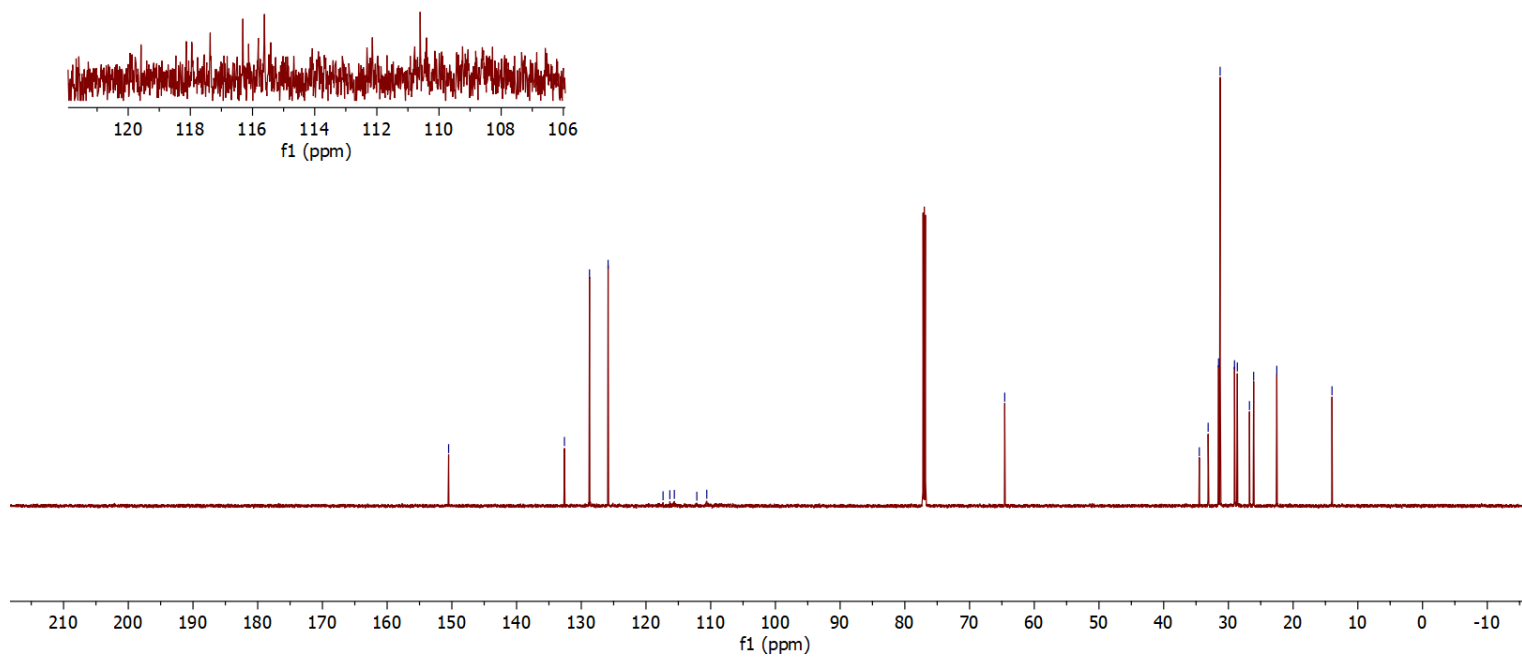
28.62

26.74

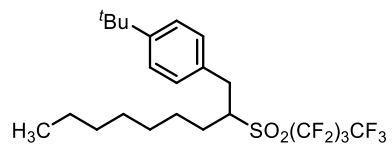
26.10

22.52

13.99

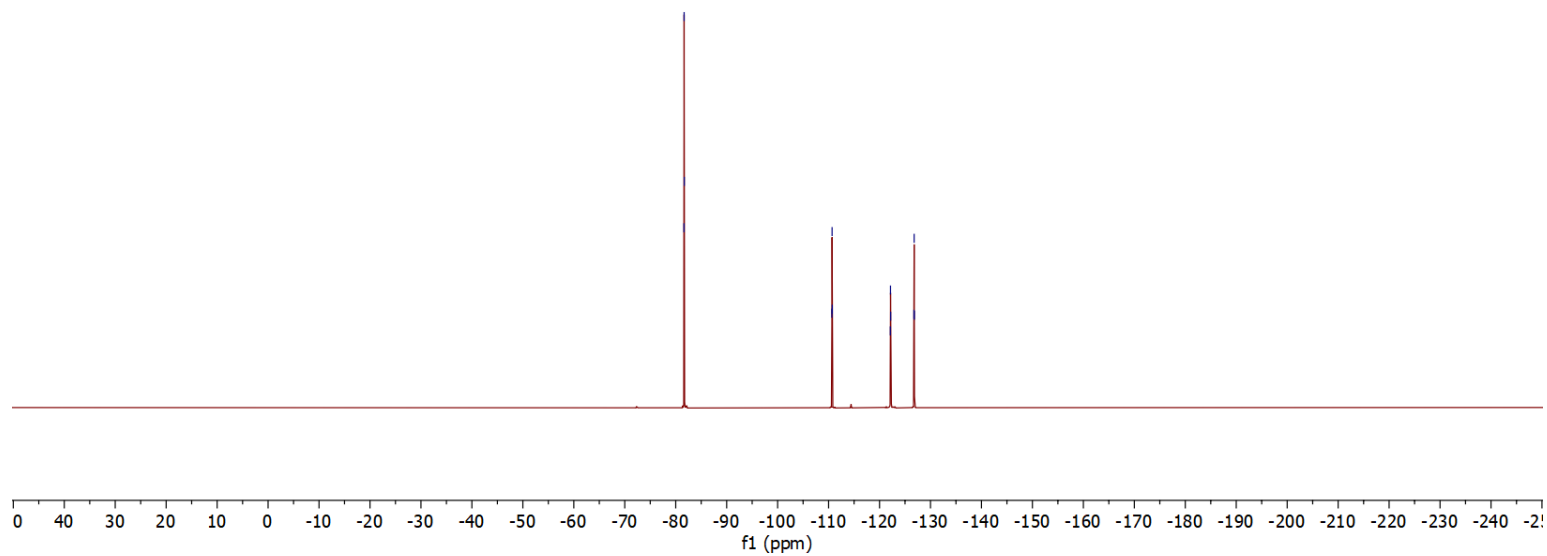


1-(*tert*-Butyl)-4-(2-((perfluorobutyl)sulfonyl)nonyl)benzene 1v ¹⁹F NMR (376 MHz, Chloroform-*d*)

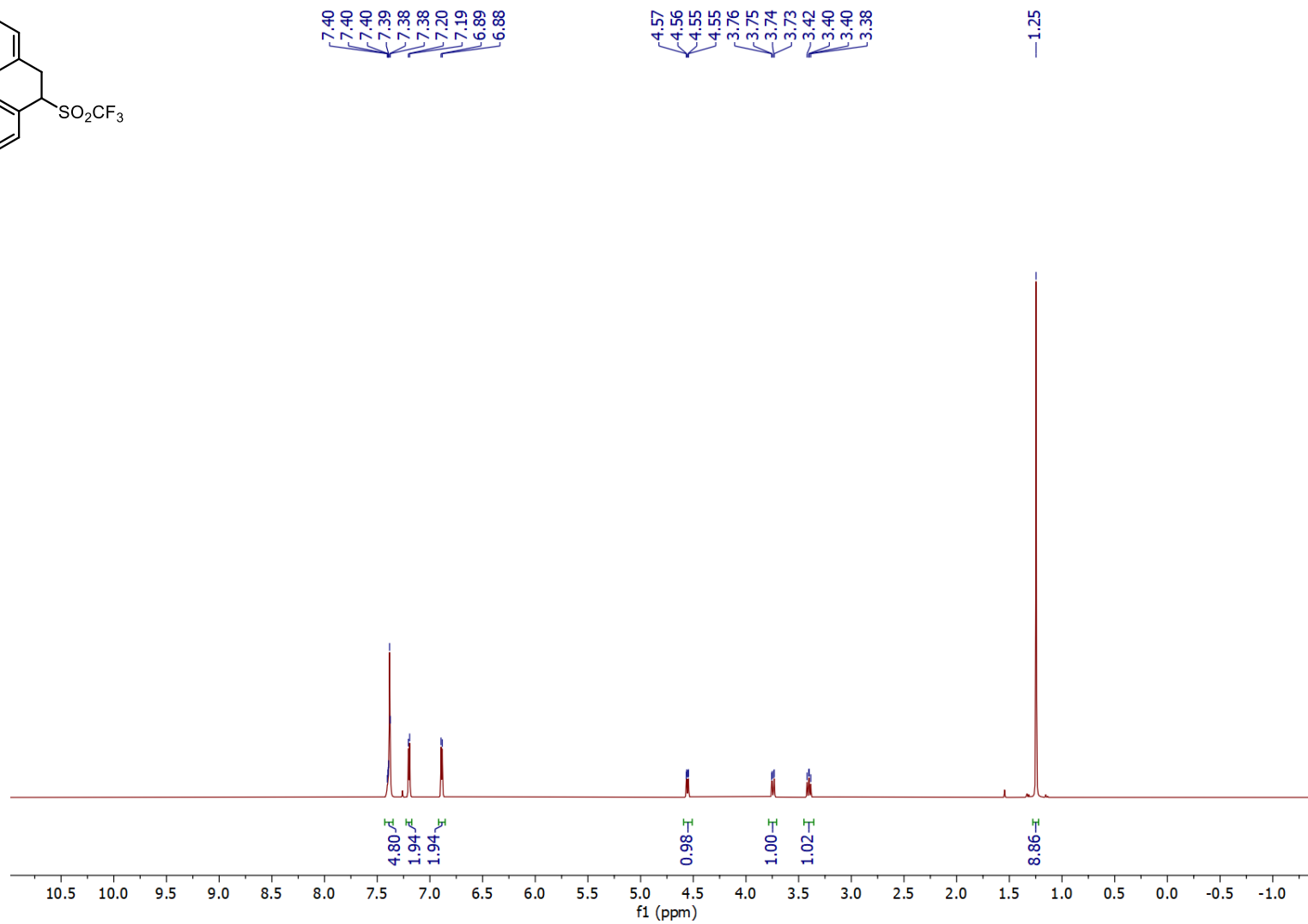
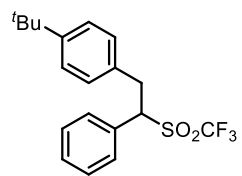


Chemical shift values (ppm) for the ¹⁹F NMR spectrum:

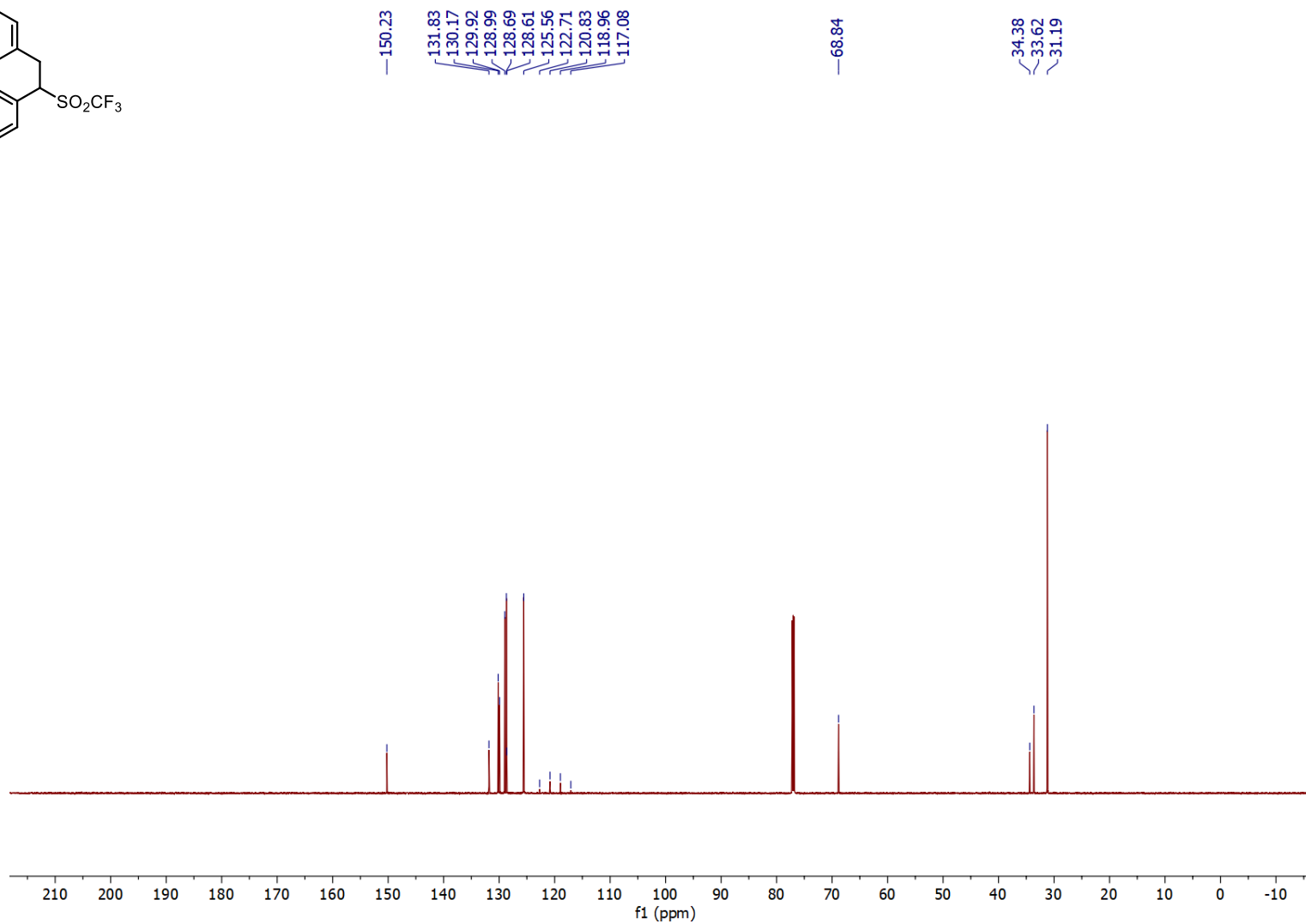
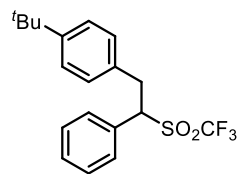
- 81.62
- 81.65
- 81.68
- 110.65
- 110.69
- 110.72
- 122.12
- 122.15
- 122.18
- 126.75
- 126.79
- 126.83



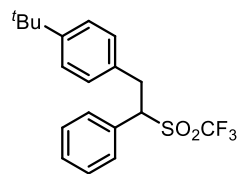
1-(*tert*-Butyl)-4-(2-phenyl-2-((trifluoromethyl)sulfonyl)ethyl)benzene 11 ^1H NMR (700 MHz, Chloroform-*d*)



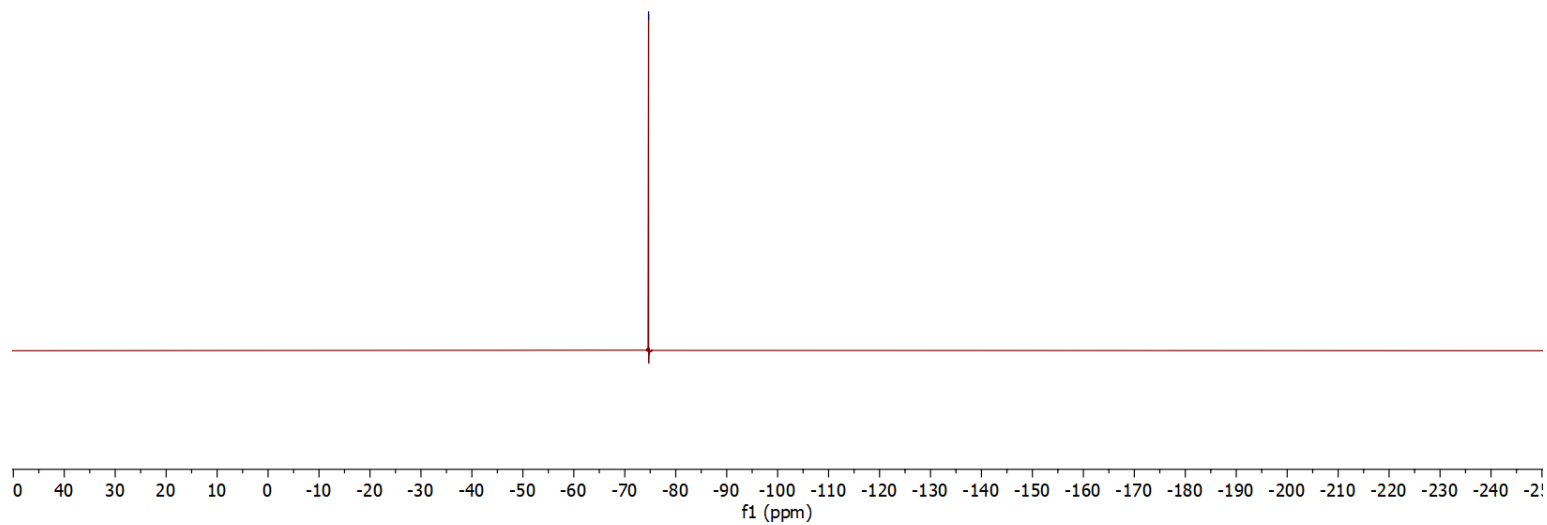
1-(*tert*-Butyl)-4-(2-phenyl-2-((trifluoromethyl)sulfonyl)ethyl)benzene 11 $^{13}\text{C}\{^1\text{H}\}$ NMR (176 MHz, Chloroform-*d*)



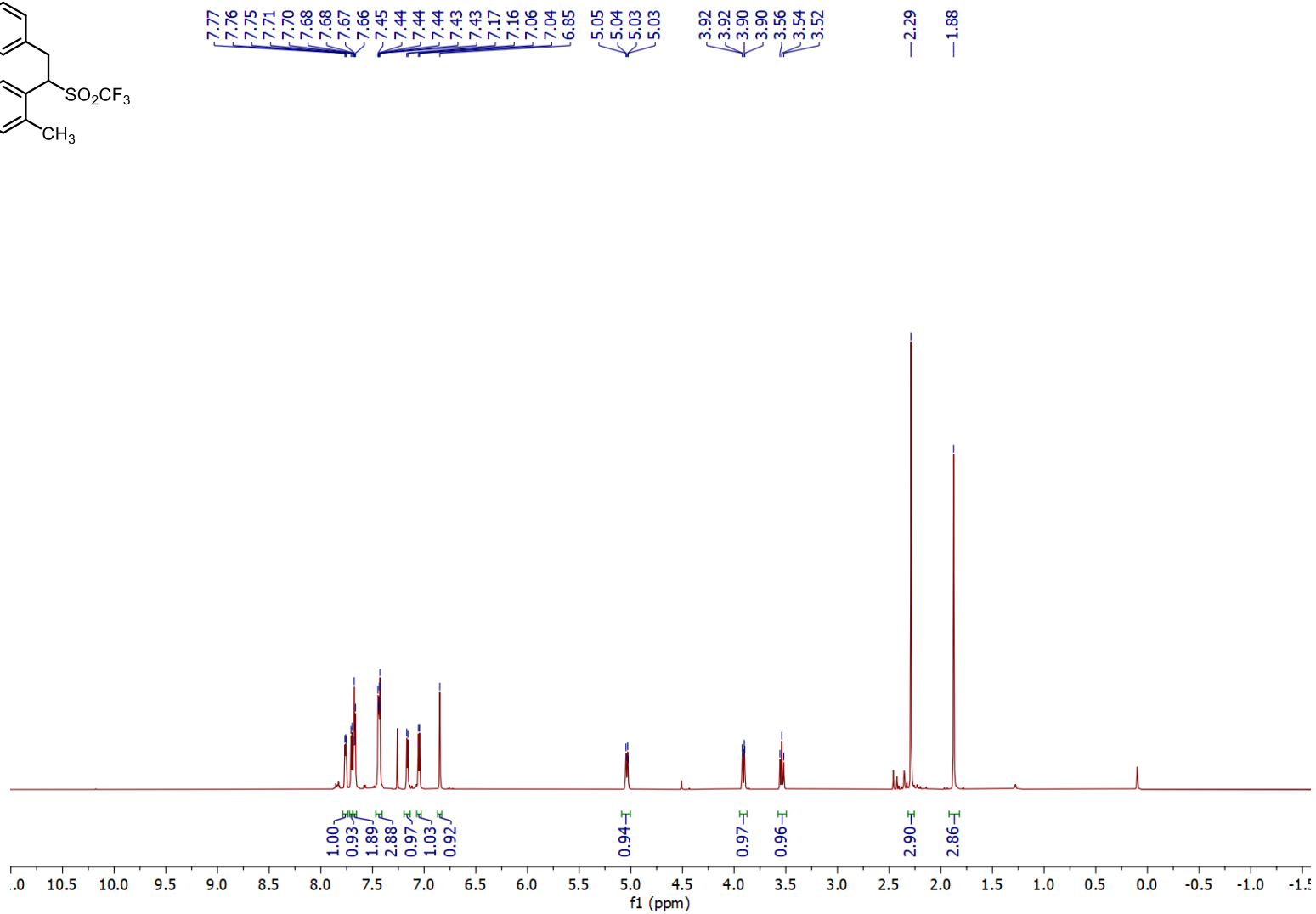
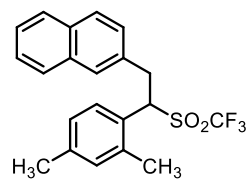
1-(*tert*-Butyl)-4-(2-phenyl-2-((trifluoromethyl)sulfonyl)ethyl)benzene 11 ^{19}F NMR (376 MHz, Chloroform-*d*)



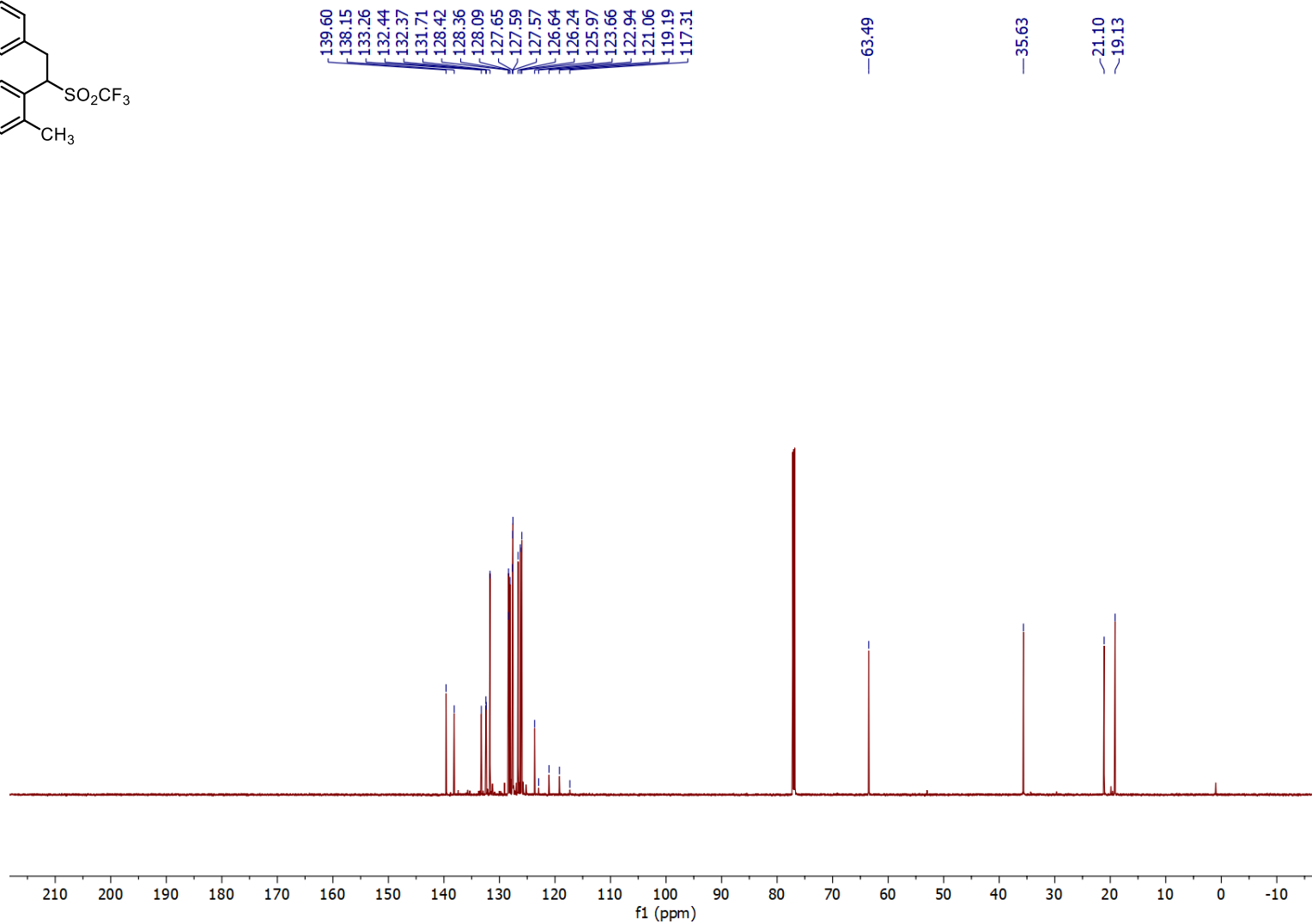
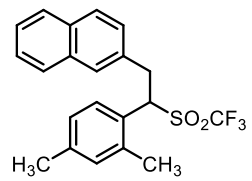
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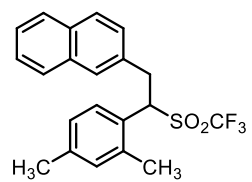
2-(2-(2,4-Dimethylphenyl)-2-((trifluoromethyl)sulfonyl)ethyl)naphthalene 1o ¹H NMR (700 MHz, Chloroform-*d*)



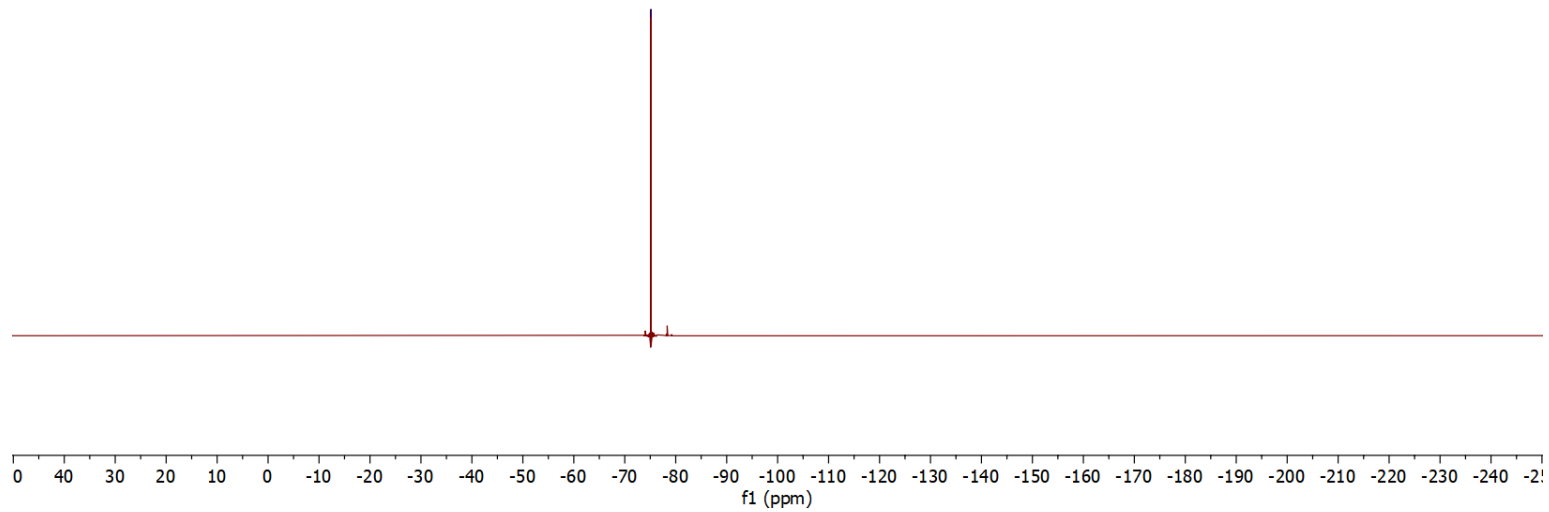
2-(2-(2,4-Dimethylphenyl)-2-((trifluoromethyl)sulfonyl)ethyl)naphthalene 1o $^{13}\text{C}\{^1\text{H}\}$ NMR (176 MHz, Chloroform-*d*)



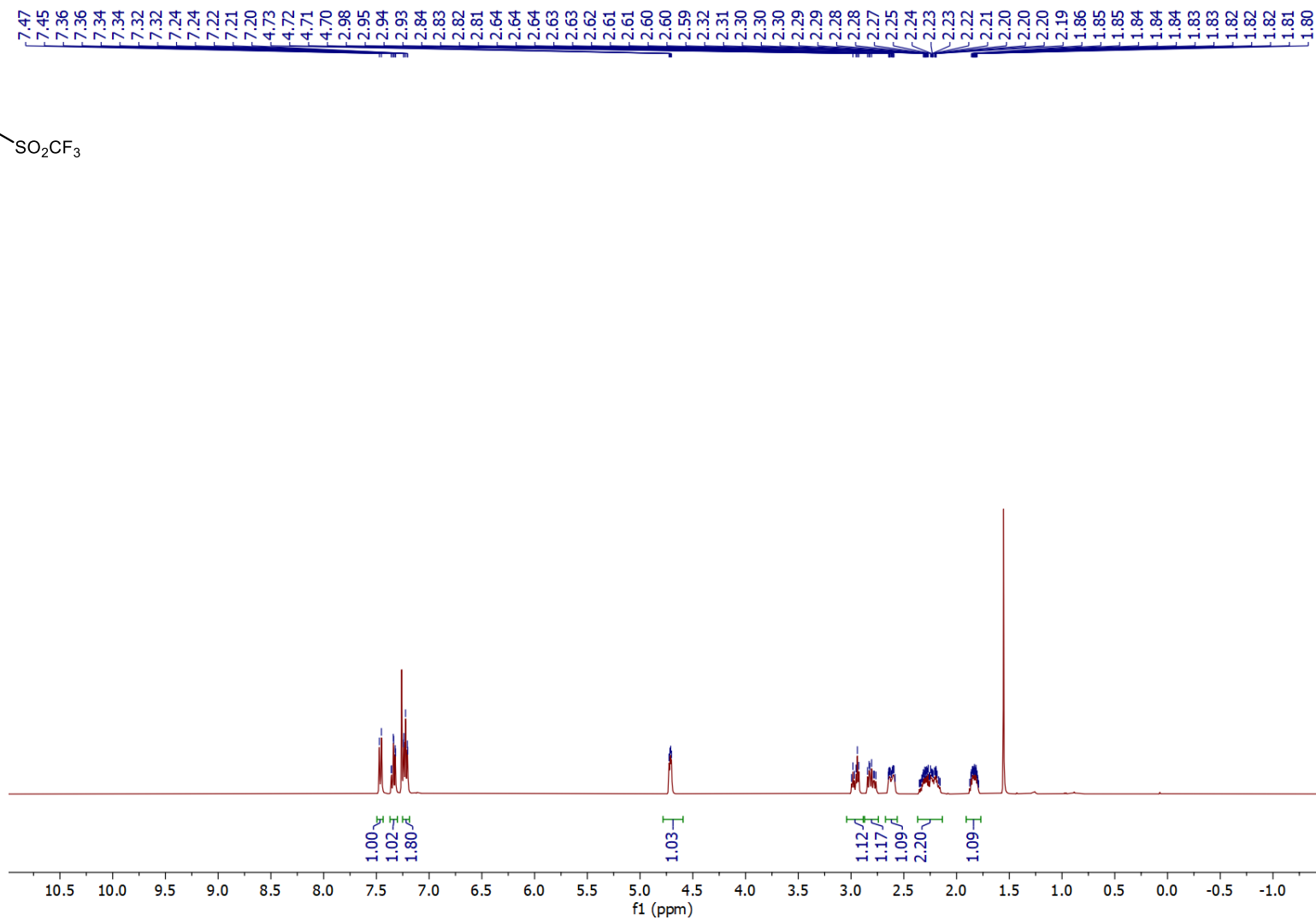
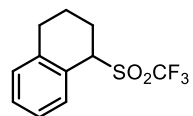
2-(2-(2,4-Dimethylphenyl)-2-((trifluoromethyl)sulfonyl)ethyl)naphthalene 1o ¹⁹F NMR (376 MHz, Chloroform-*d*)



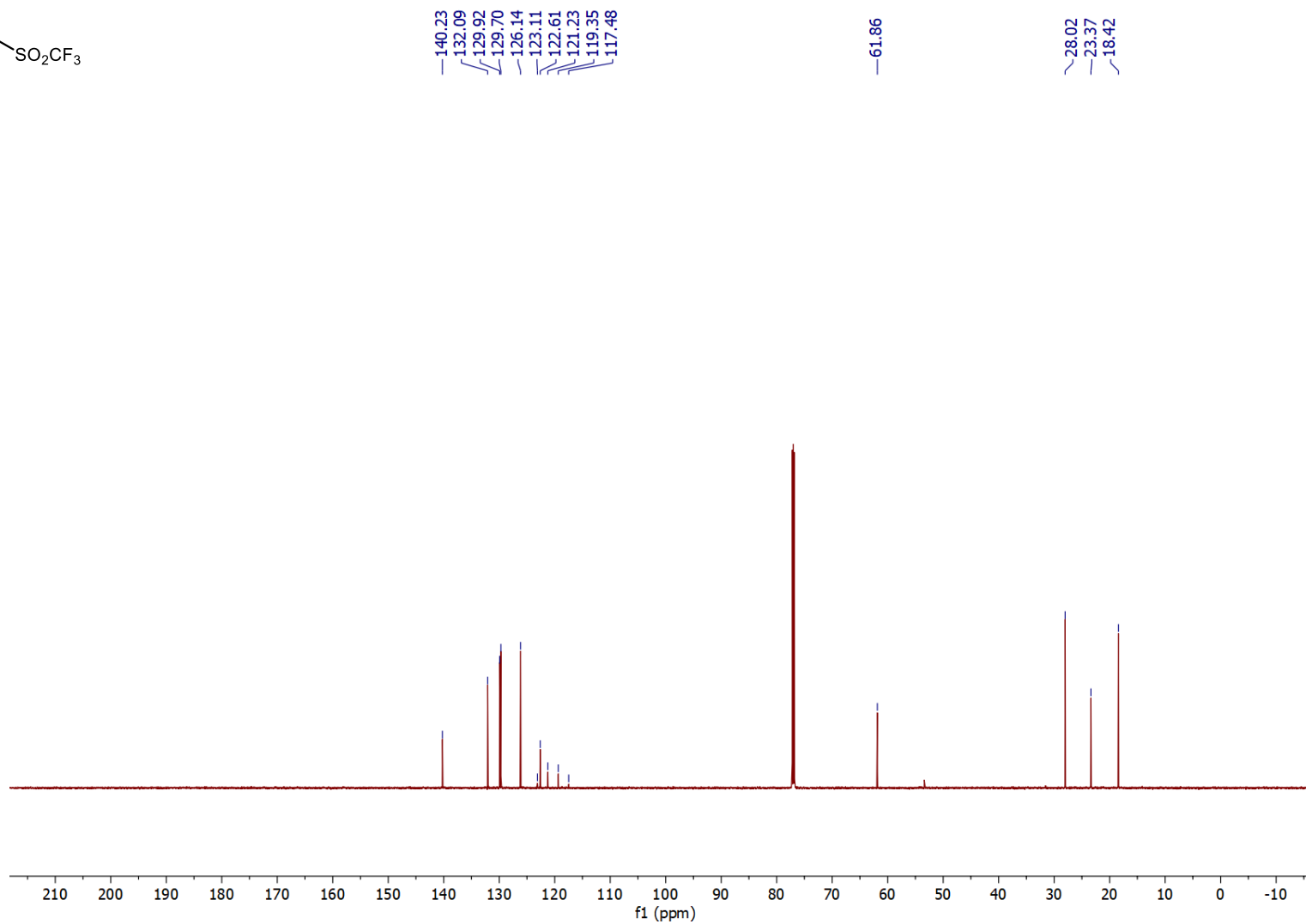
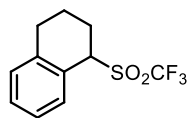
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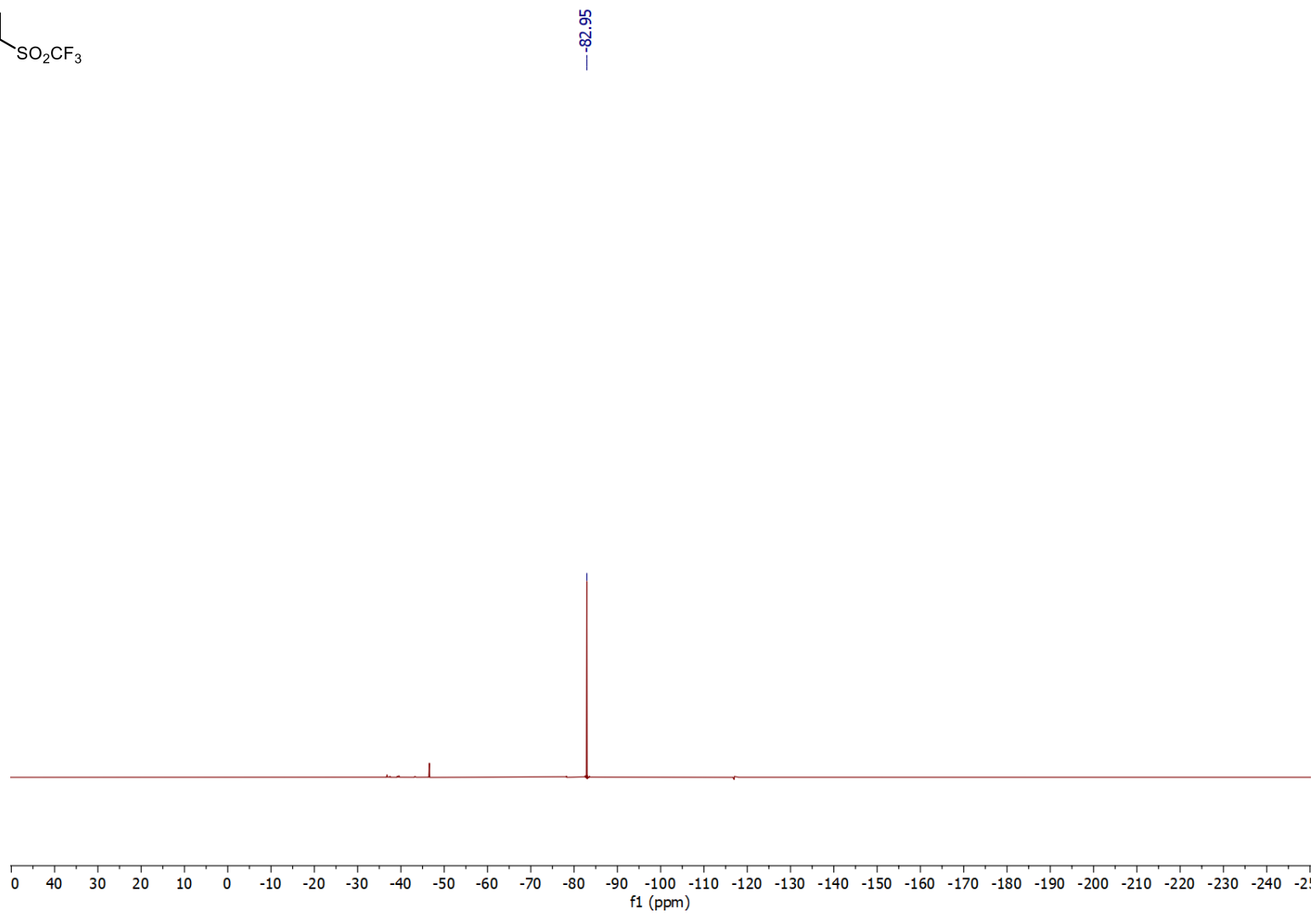
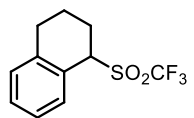
1-((Trifluoromethyl)sulfonyl)-1,2,3,4-tetrahydronaphthalene 1r ¹H NMR (400 MHz, Chloroform-*d*)



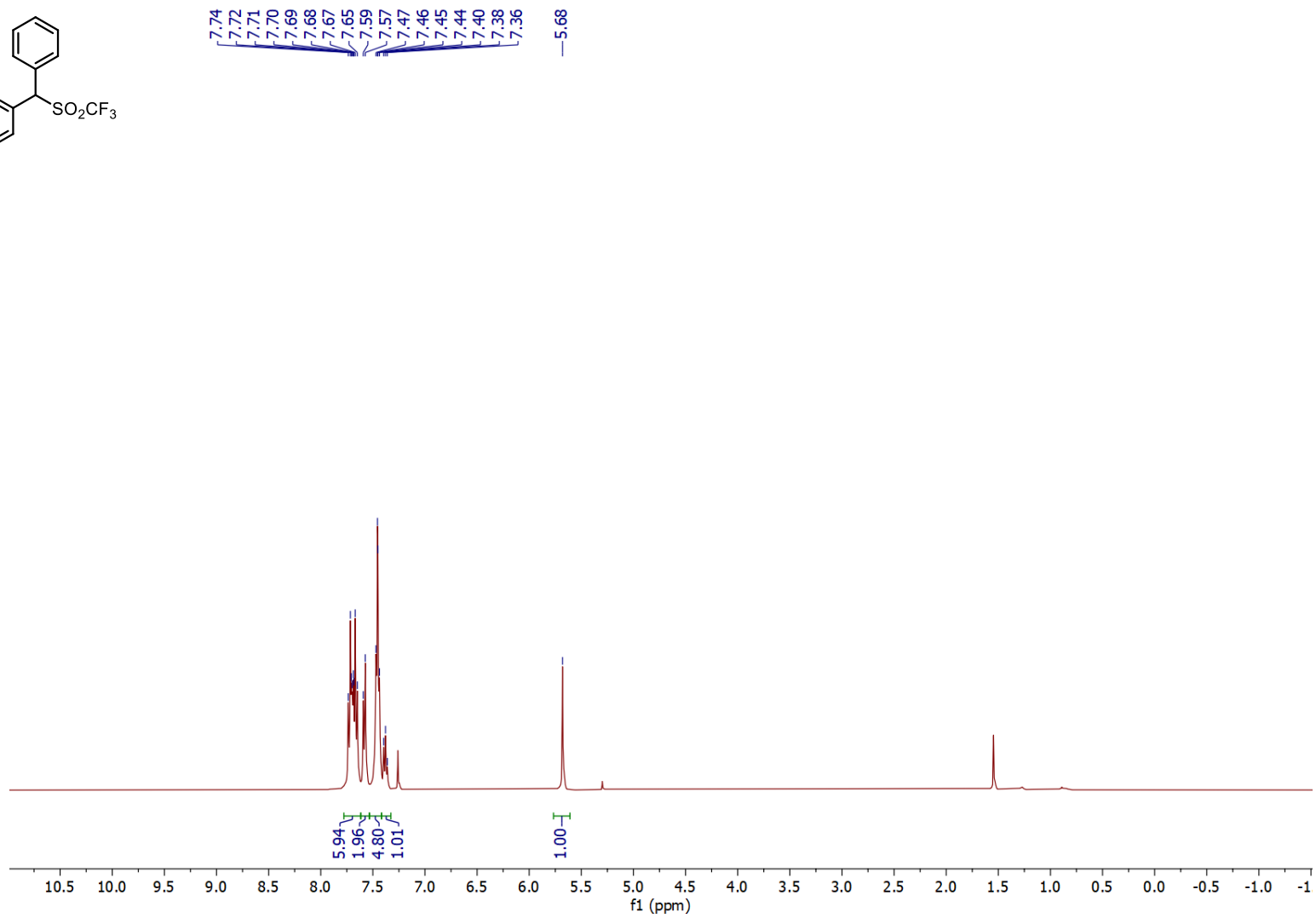
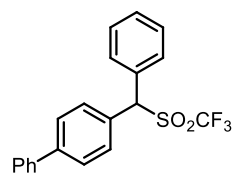
1-((Trifluoromethyl)sulfonyl)-1,2,3,4-tetrahydronaphthalene 1r $^{13}\text{C}\{^1\text{H}\}$ NMR (176 MHz, Chloroform-*d*)



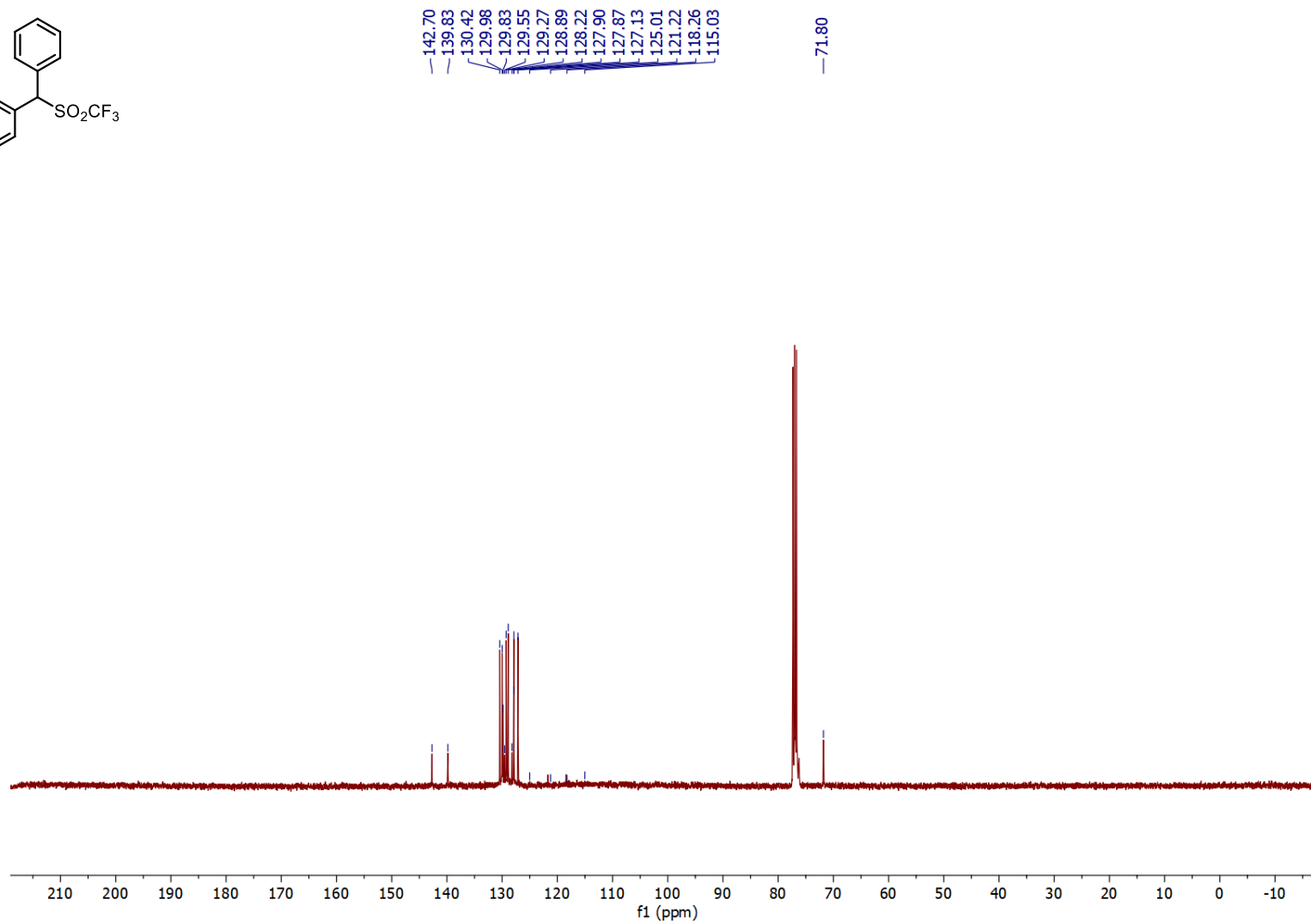
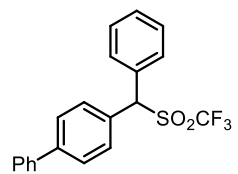
1-((Trifluoromethyl)sulfonyl)-1,2,3,4-tetrahydronaphthalene 1r ¹⁹F NMR (376 MHz, Chloroform-*d*)



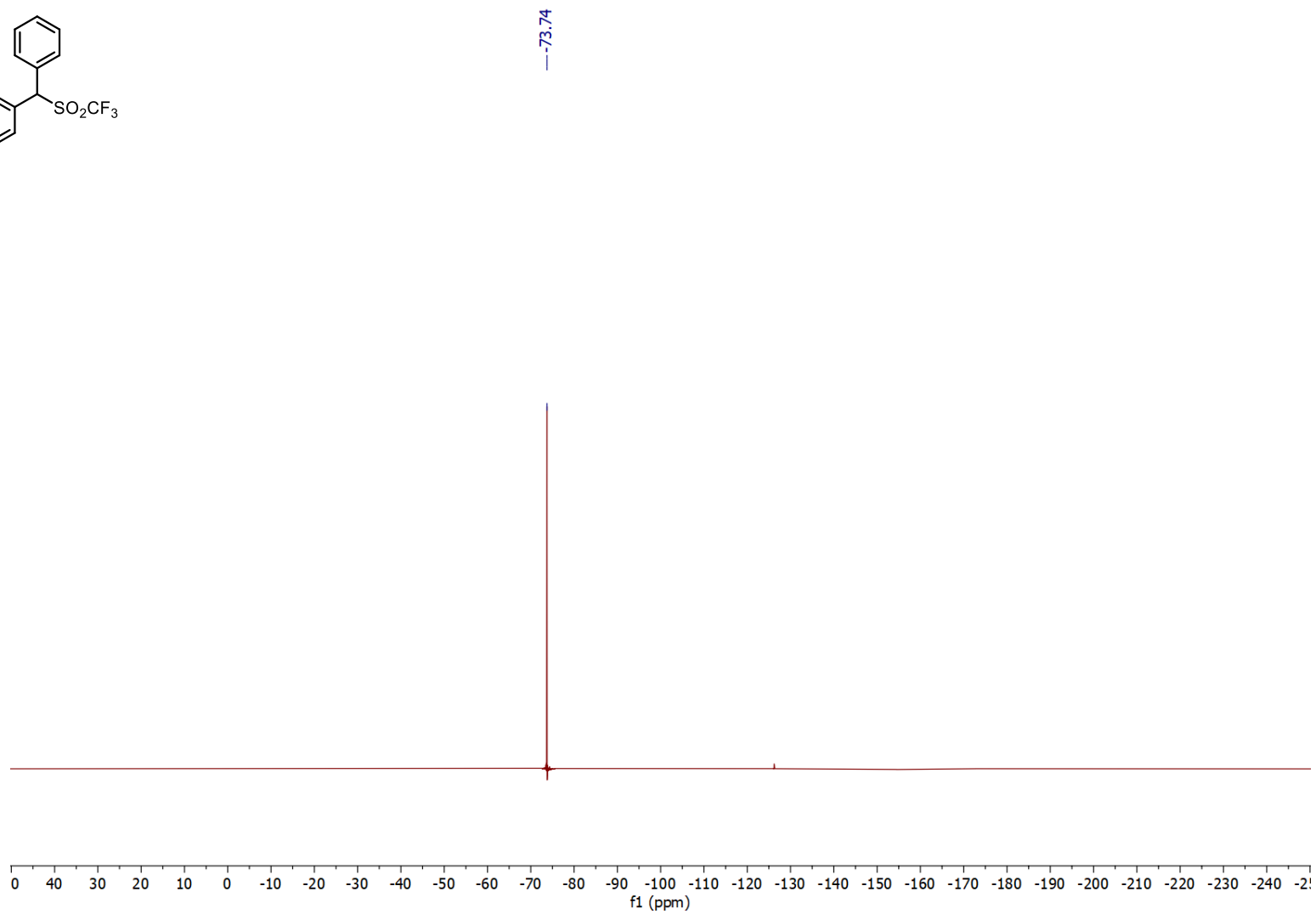
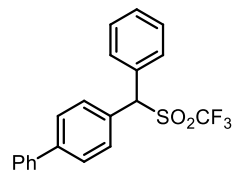
4-(Phenyl((trifluoromethyl)sulfonyl)methyl)-1,1'-biphenyl 1t ¹H NMR (400 MHz, Chloroform-*d*)



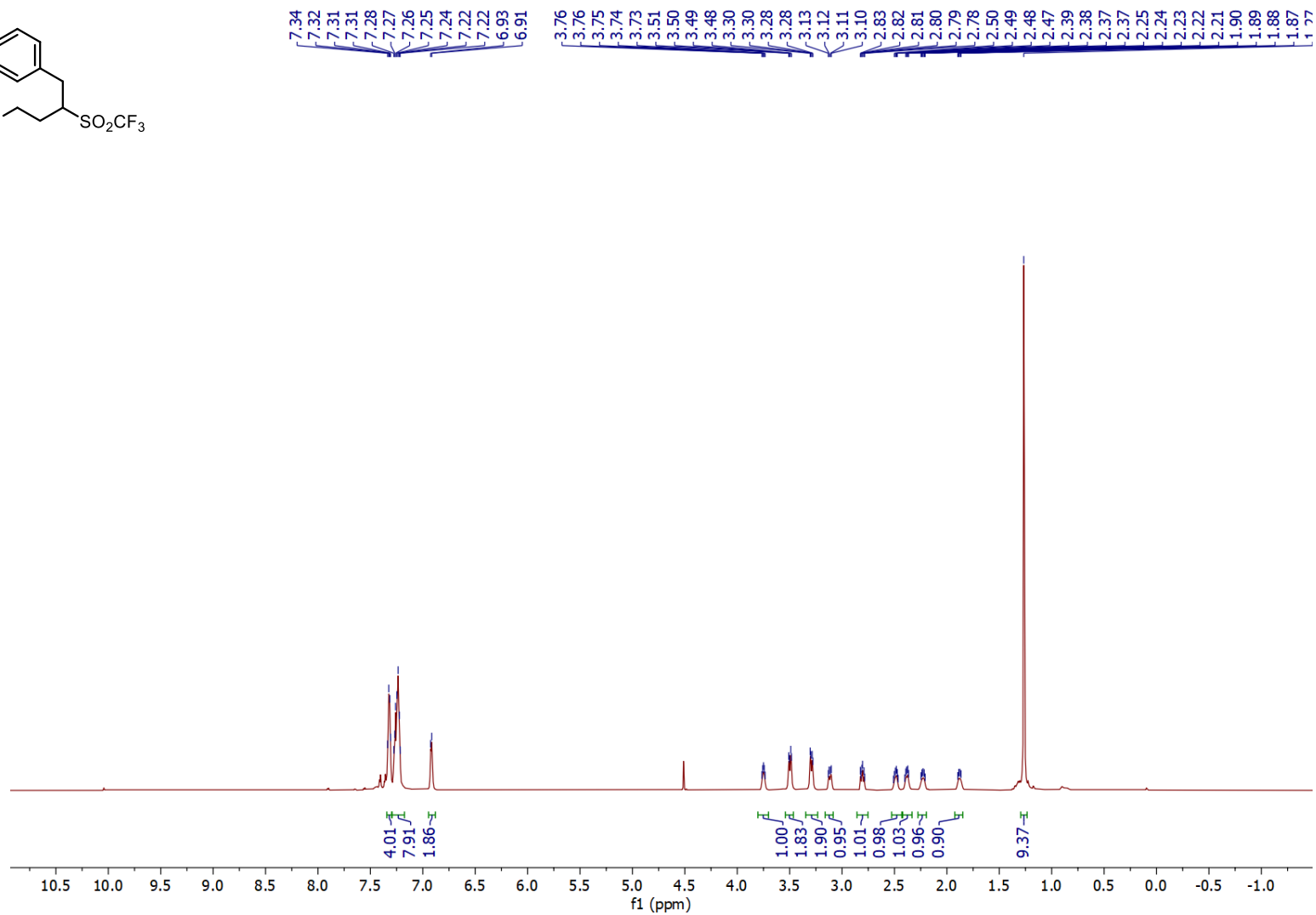
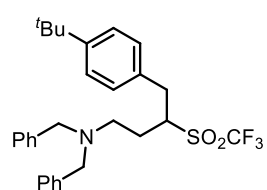
4-(Phenyl((trifluoromethyl)sulfonyl)methyl)-1,1'-biphenyl 1t $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, Chloroform-*d*)



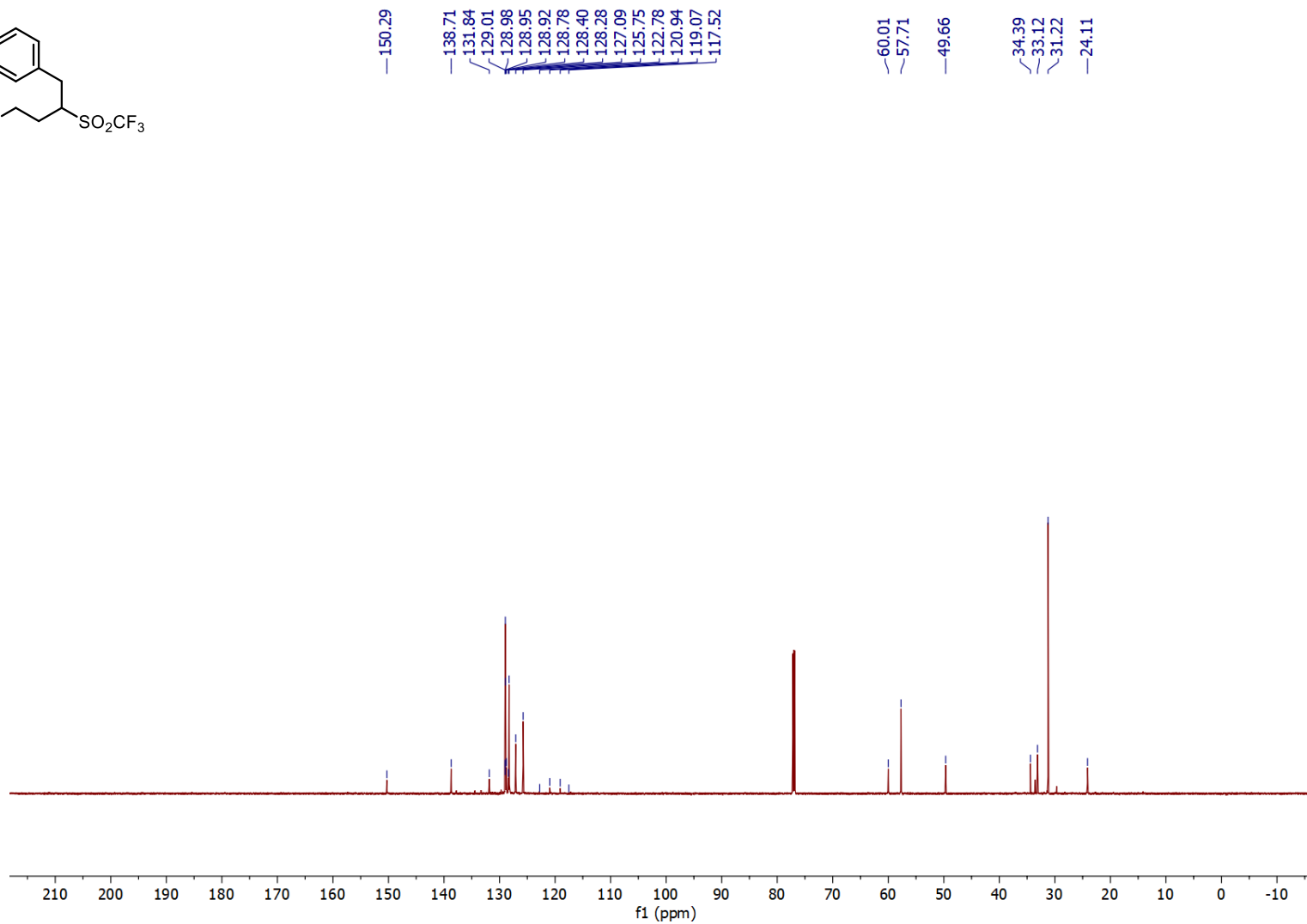
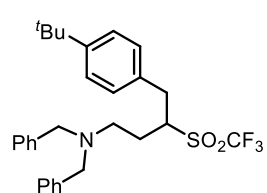
4-(Phenyl((trifluoromethyl)sulfonyl)methyl)-1,1'-biphenyl 1t ¹⁹F NMR (376 MHz, Chloroform-*d*)



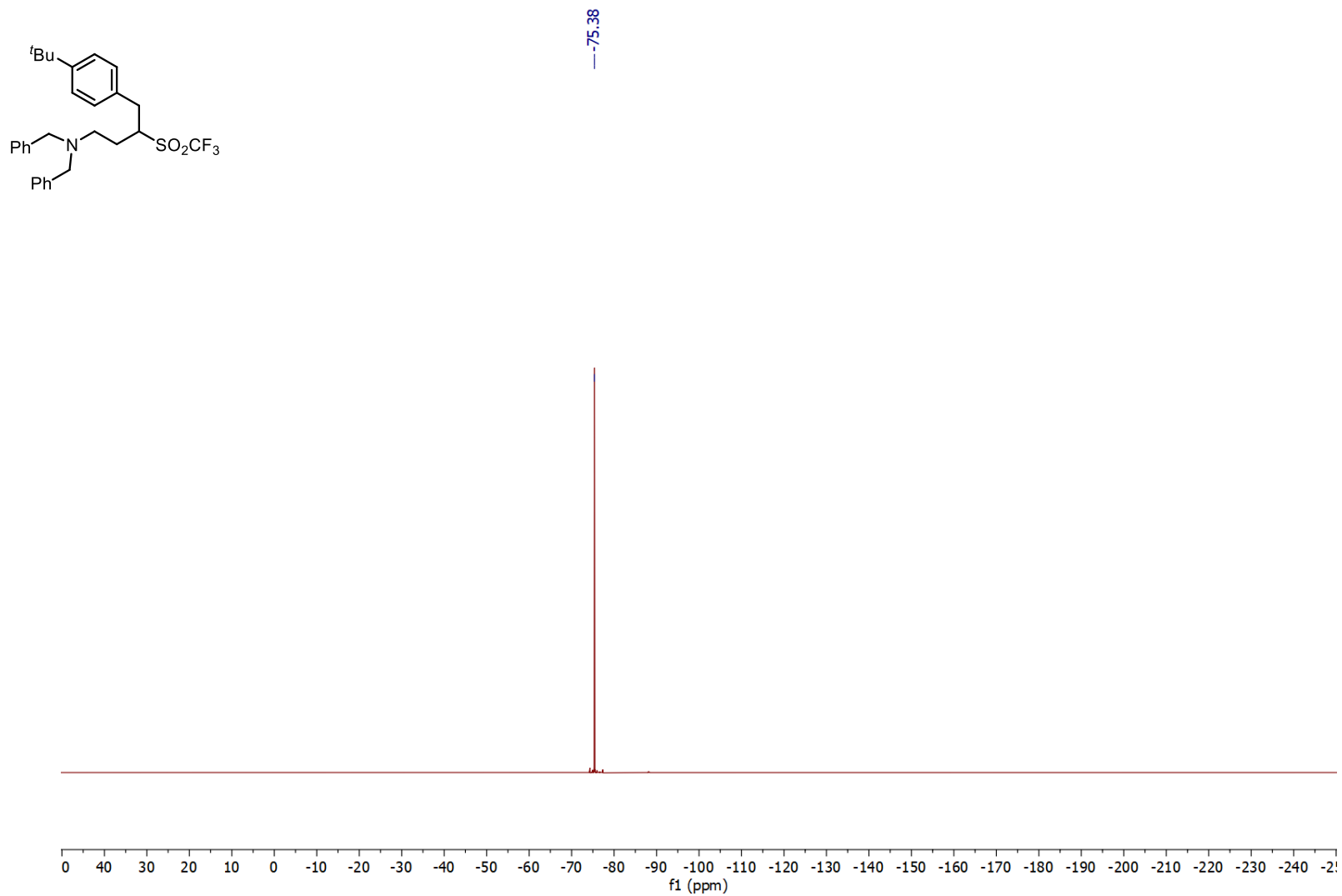
N,N-Dibenzyl-4-(4-(tert-butyl)phenyl)-3-((trifluoromethyl)sulfonyl)butan-1-amine 1i ¹H NMR (700 MHz, Chloroform-*d*)



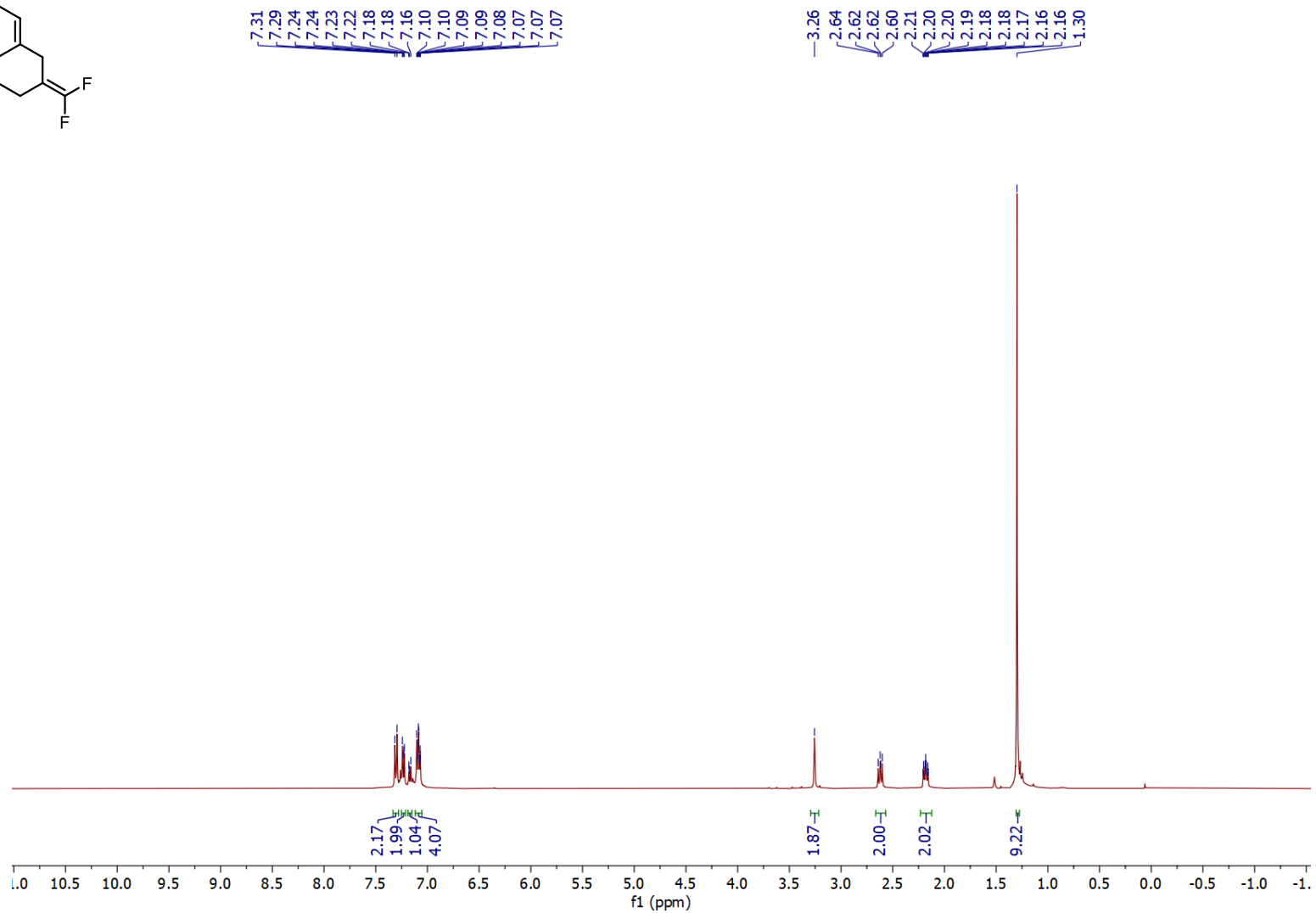
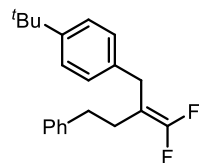
N,N-Dibenzyl-4-(4-(tert-butyl)phenyl)-3-((trifluoromethyl)sulfonyl)butan-1-amine **1i** $^{13}\text{C}\{^1\text{H}\}$ NMR (176 MHz, Chloroform-*d*)



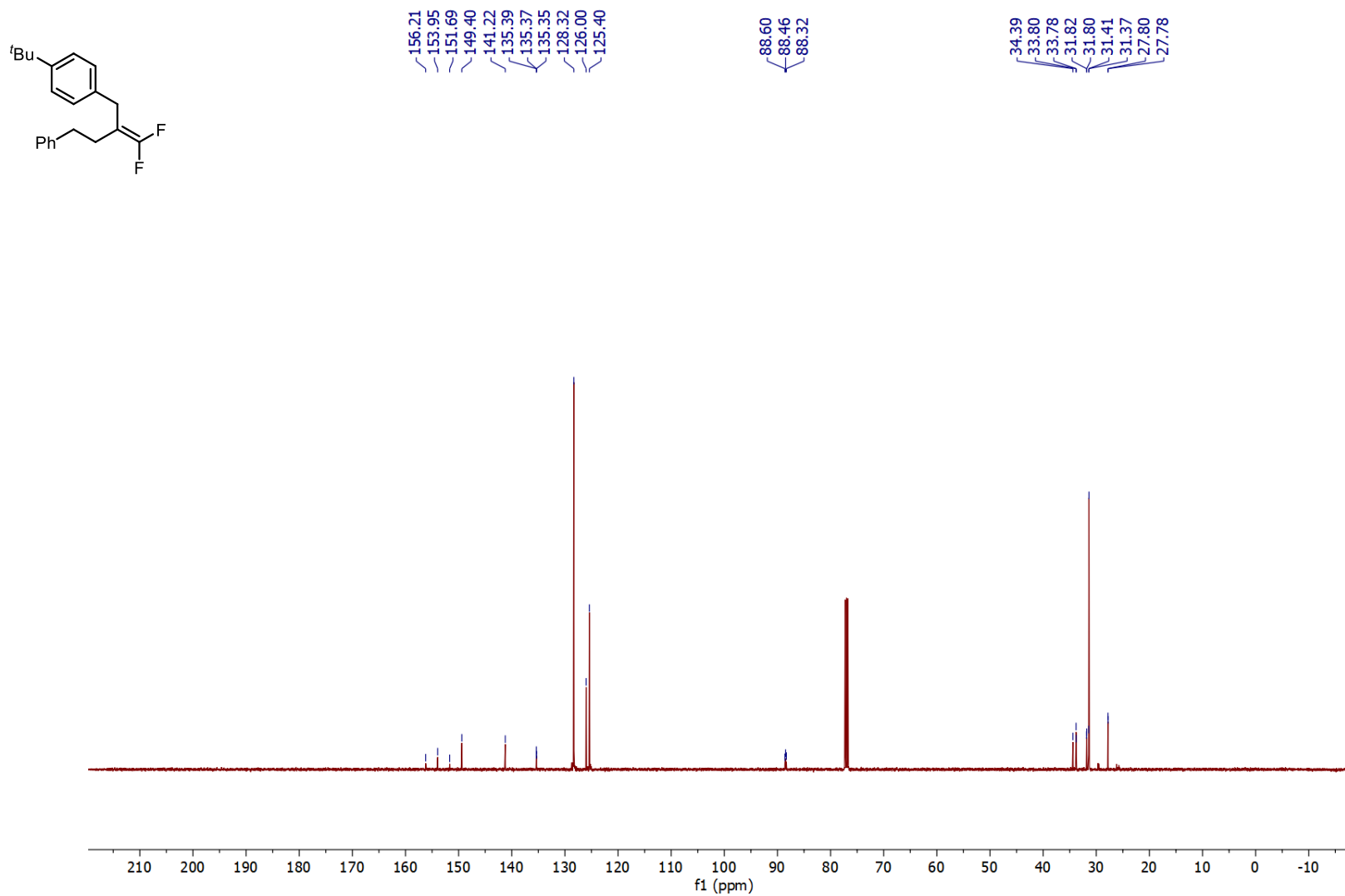
N,N-Dibenzyl-4-(4-(tert-butyl)phenyl)-3-((trifluoromethyl)sulfonyl)butan-1-amine **1i** ^{19}F NMR (376 MHz, Chloroform-*d*)



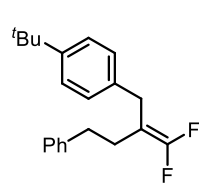
1-(*tert*-Butyl)-4-(2-(difluoromethylene)-4-phenylbutyl)benzene 2a ^1H NMR (400 MHz, Chloroform-*d*)



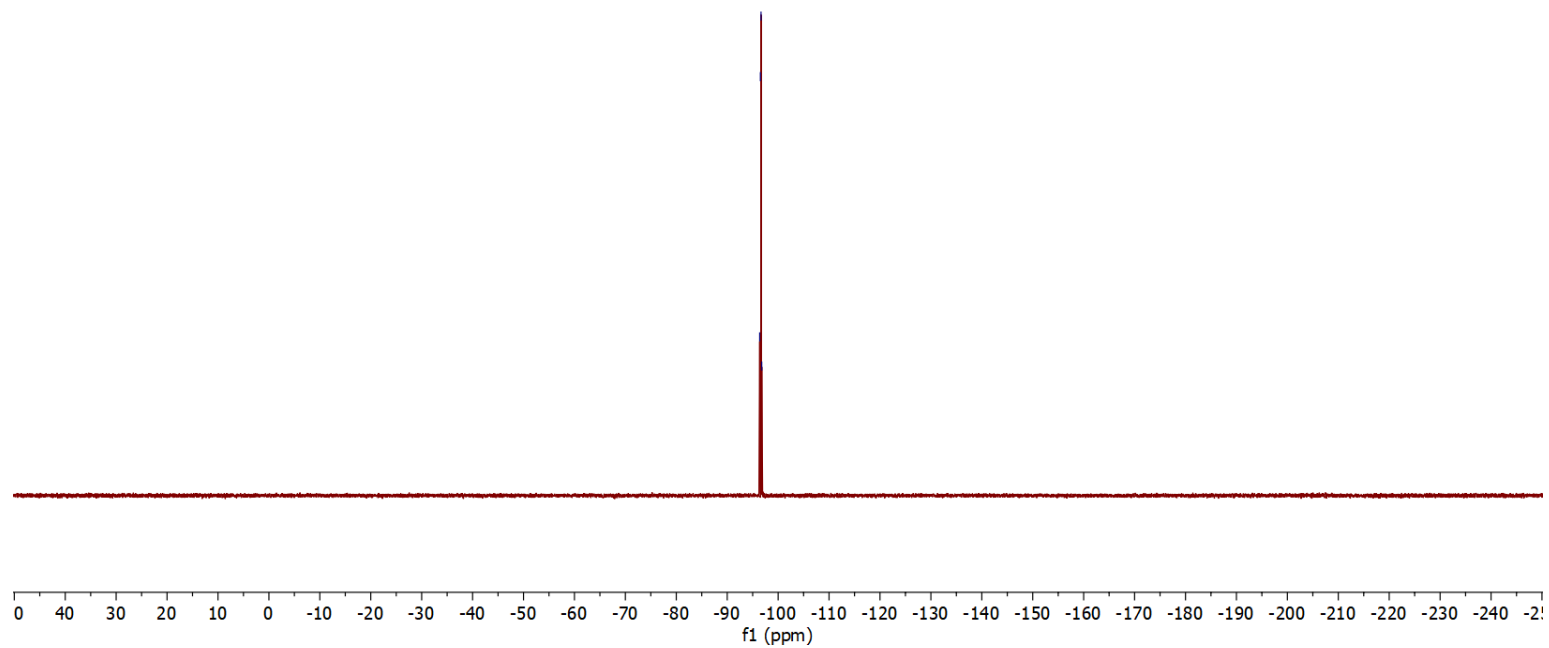
1-(*tert*-Butyl)-4-(2-(difluoromethylene)-4-phenylbutyl)benzene 2a $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, Chloroform-*d*)



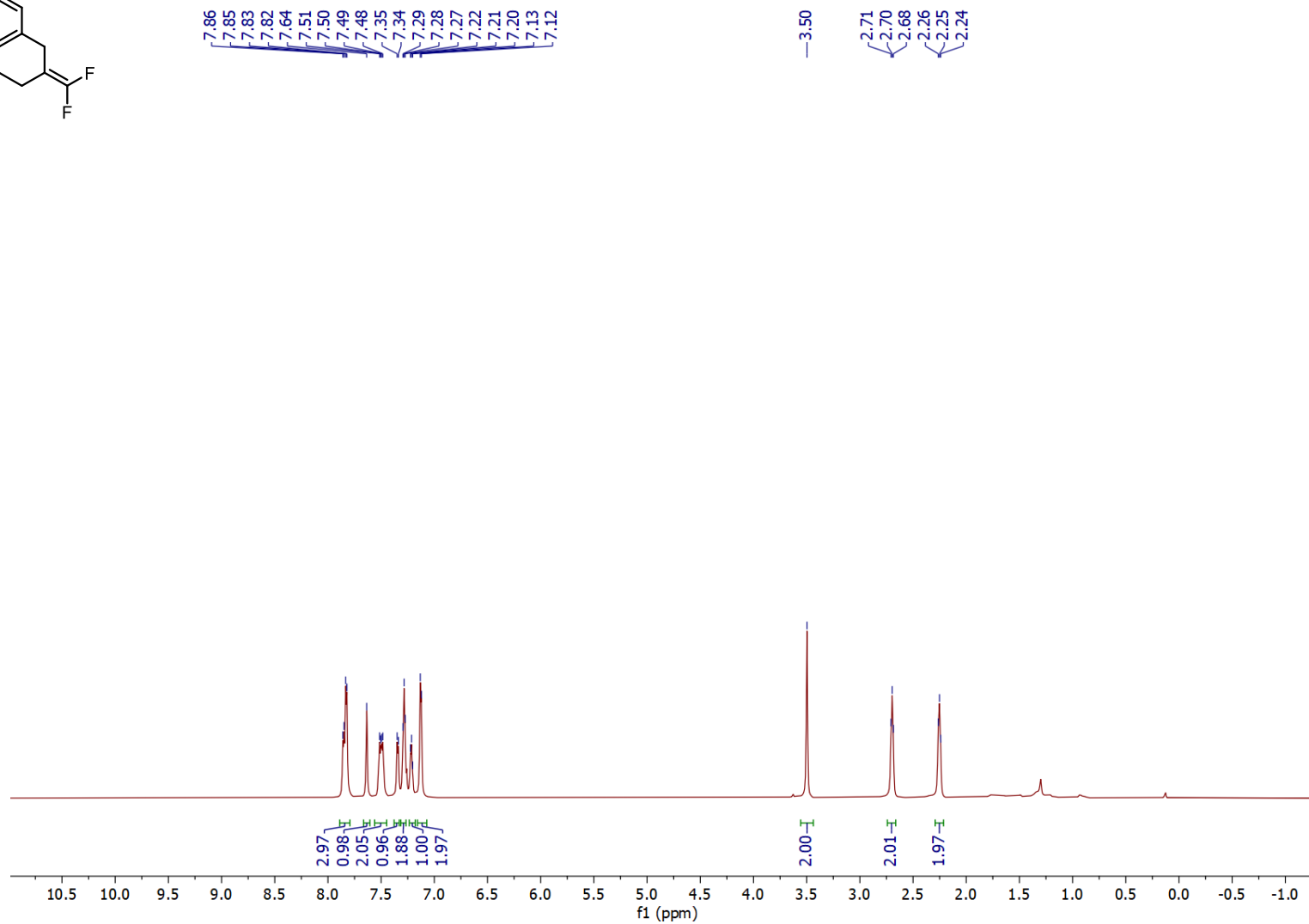
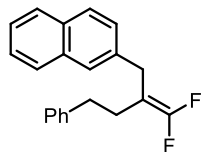
1-(*tert*-Butyl)-4-(2-(difluoromethylene)-4-phenylbutyl)benzene 2a ^{19}F NMR (376 MHz, Chloroform-*d*)



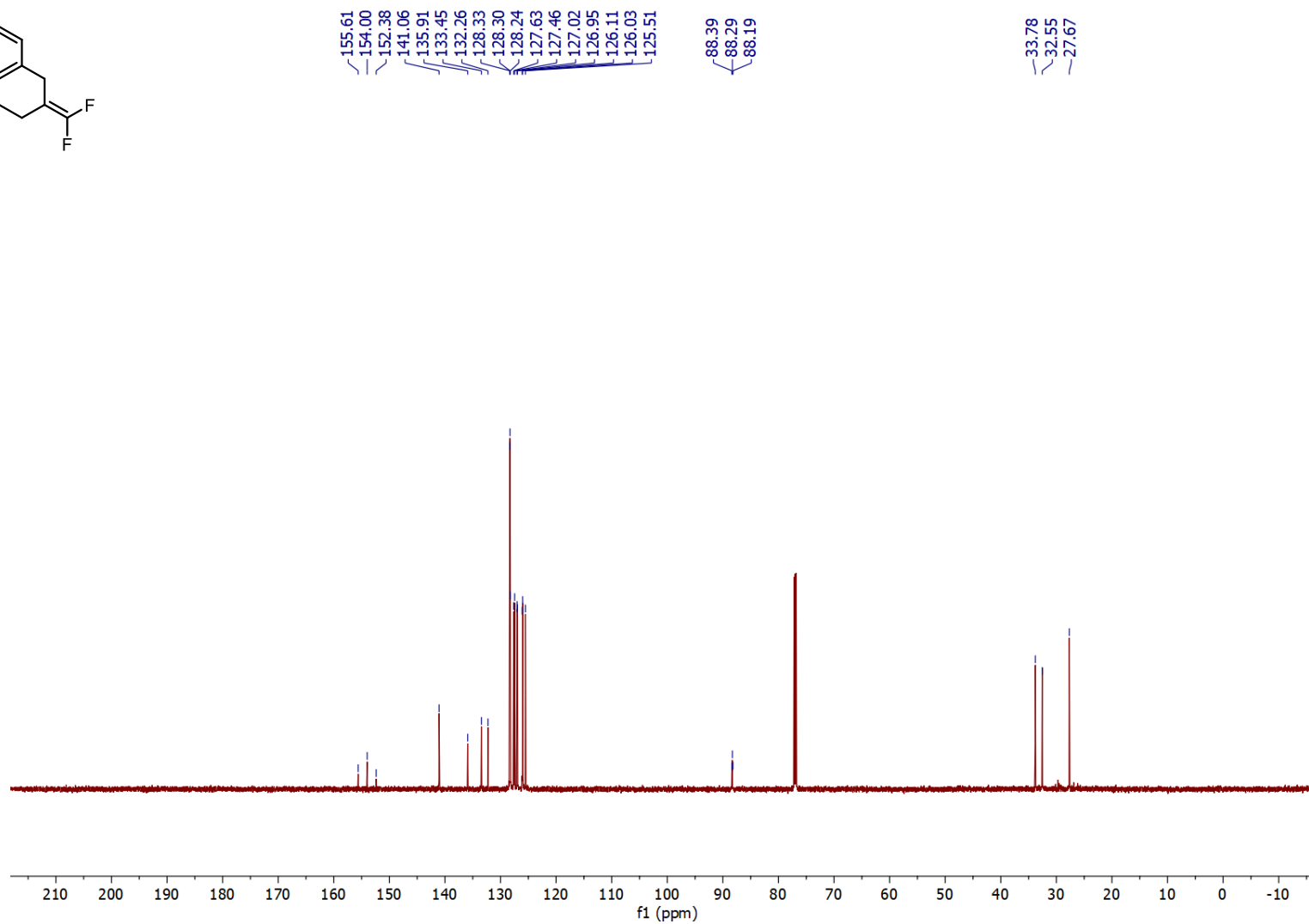
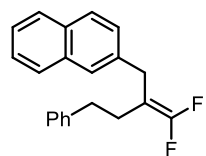
-96.37
-96.52
-96.64
-96.78



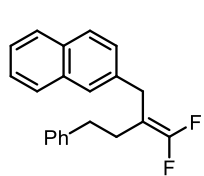
2-(2-(Difluoromethylene)-4-phenylbutyl)naphthalene 2b ¹H NMR (700 MHz, Chloroform-*d*)



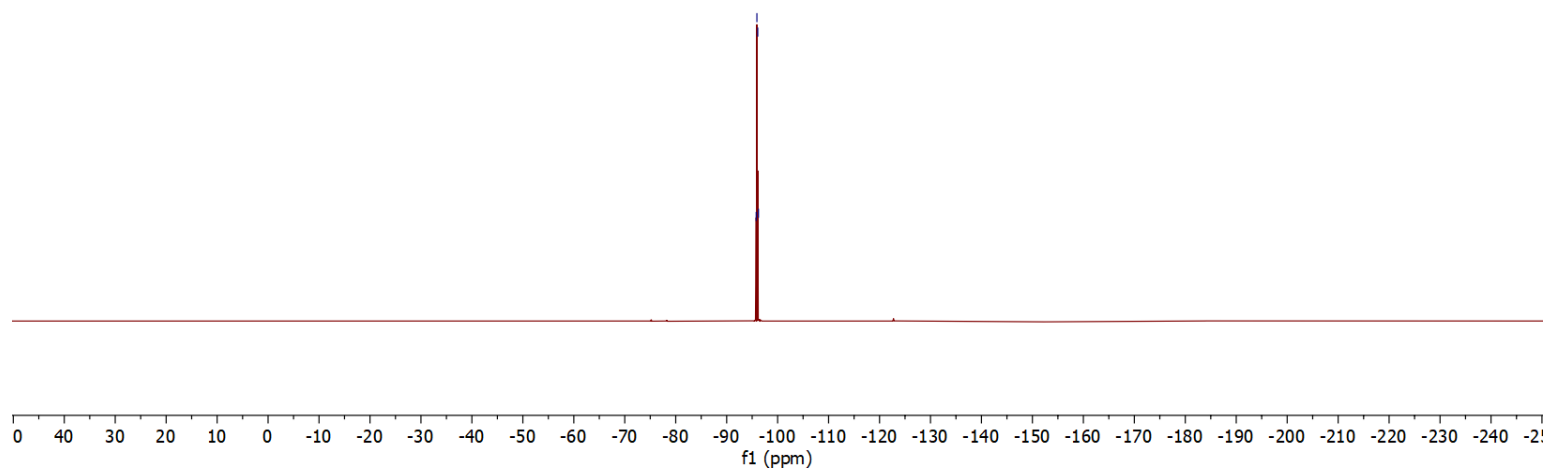
2-(2-(Difluoromethylene)-4-phenylbutyl)naphthalene 2b $^{13}\text{C}\{^1\text{H}\}$ NMR (176 MHz, Chloroform-*d*)



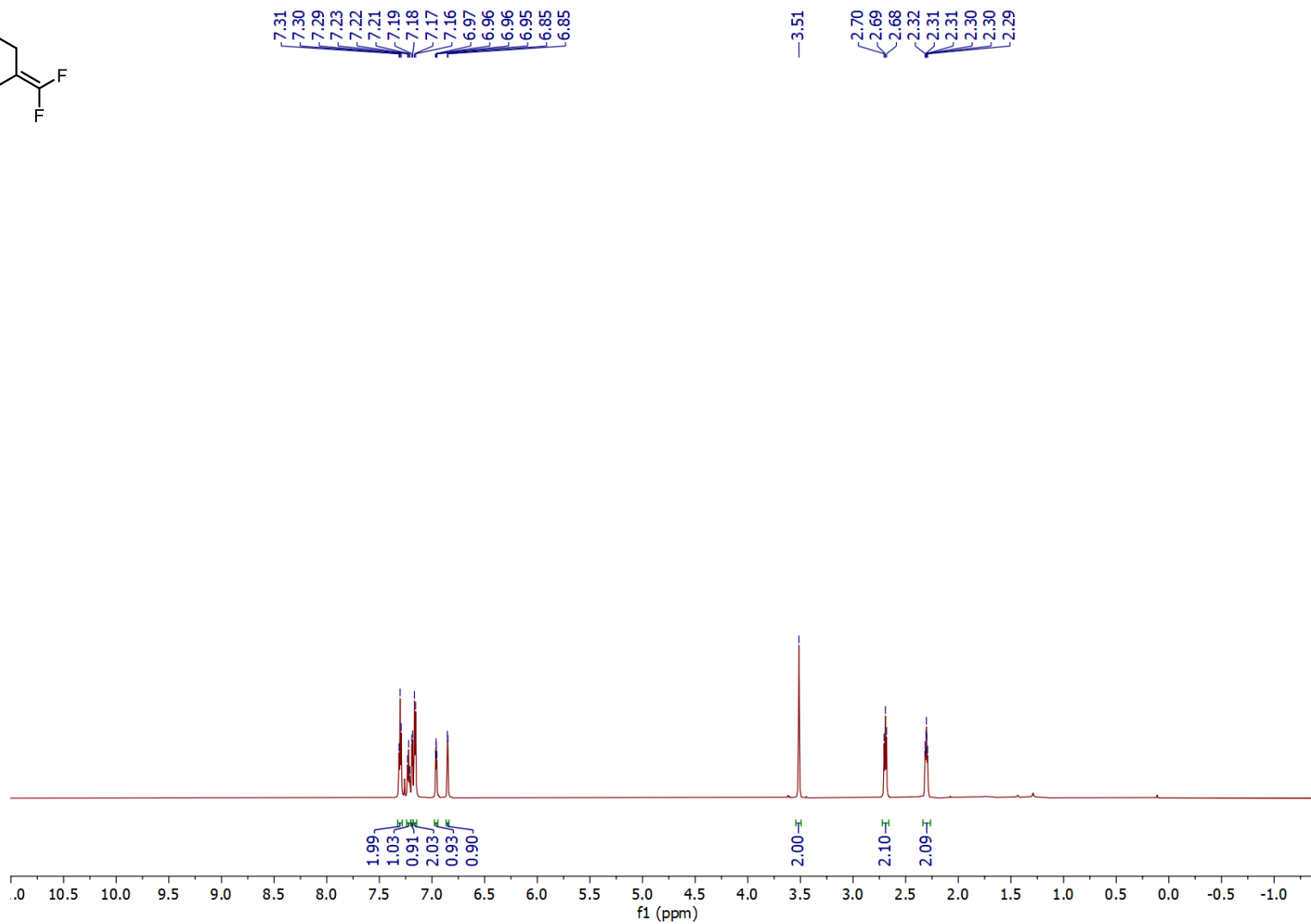
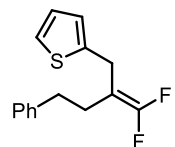
2-(2-(Difluoromethylene)-4-phenylbutyl)naphthalene 2b ¹⁹F NMR (376 MHz, Chloroform-*d*)



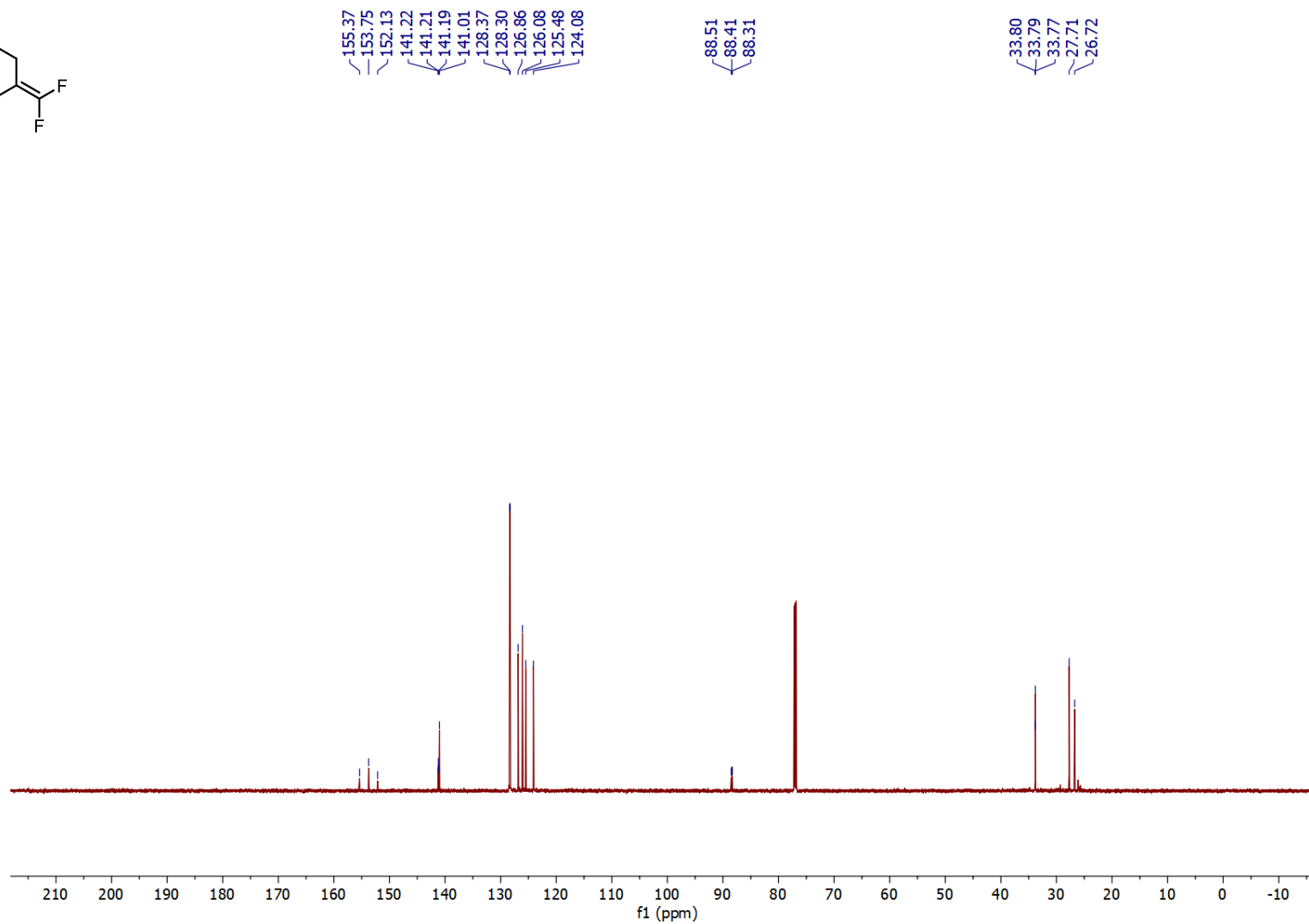
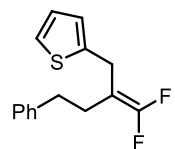
-95.79
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-96.10
-96.24



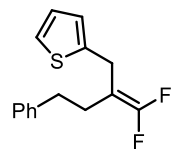
2-(2-(Difluoromethylene)-4-phenylbutyl)thiophene 2c ¹H NMR (400 MHz, Chloroform-*d*)



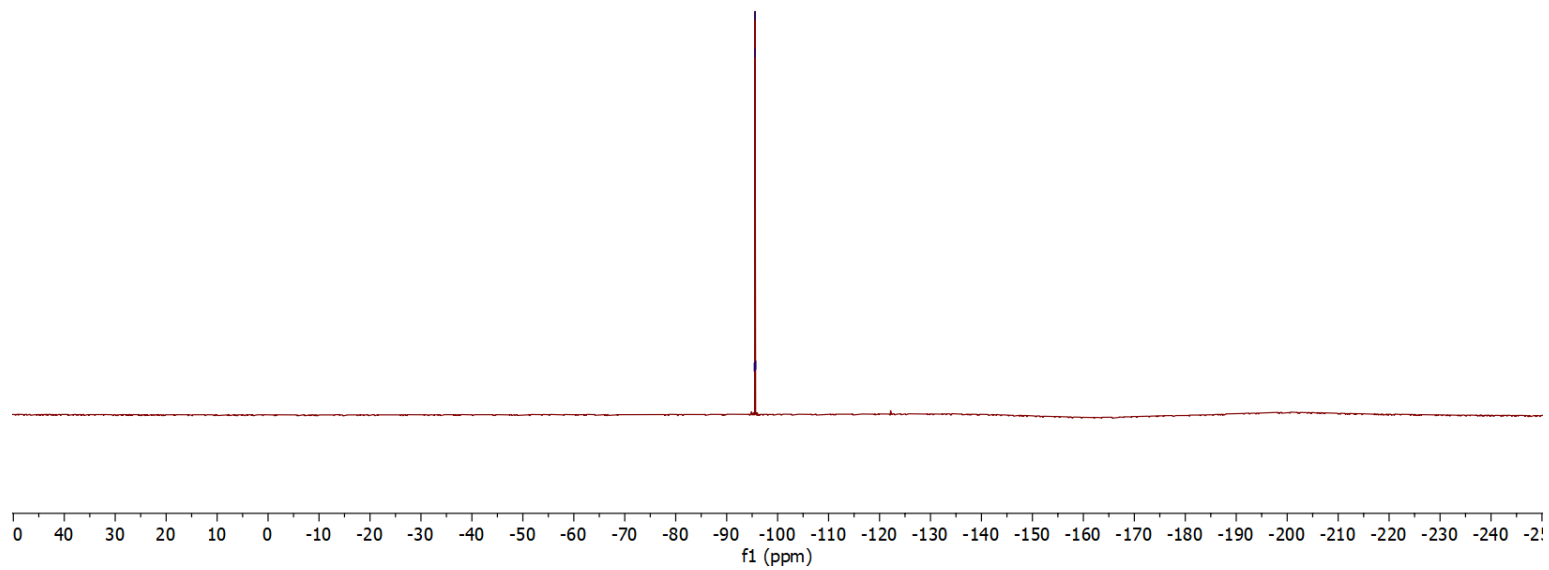
2-(2-(Difluoromethylene)-4-phenylbutyl)thiophene 2c $^{13}\text{C}\{^1\text{H}\}$ NMR (176 MHz, Chloroform-*d*)



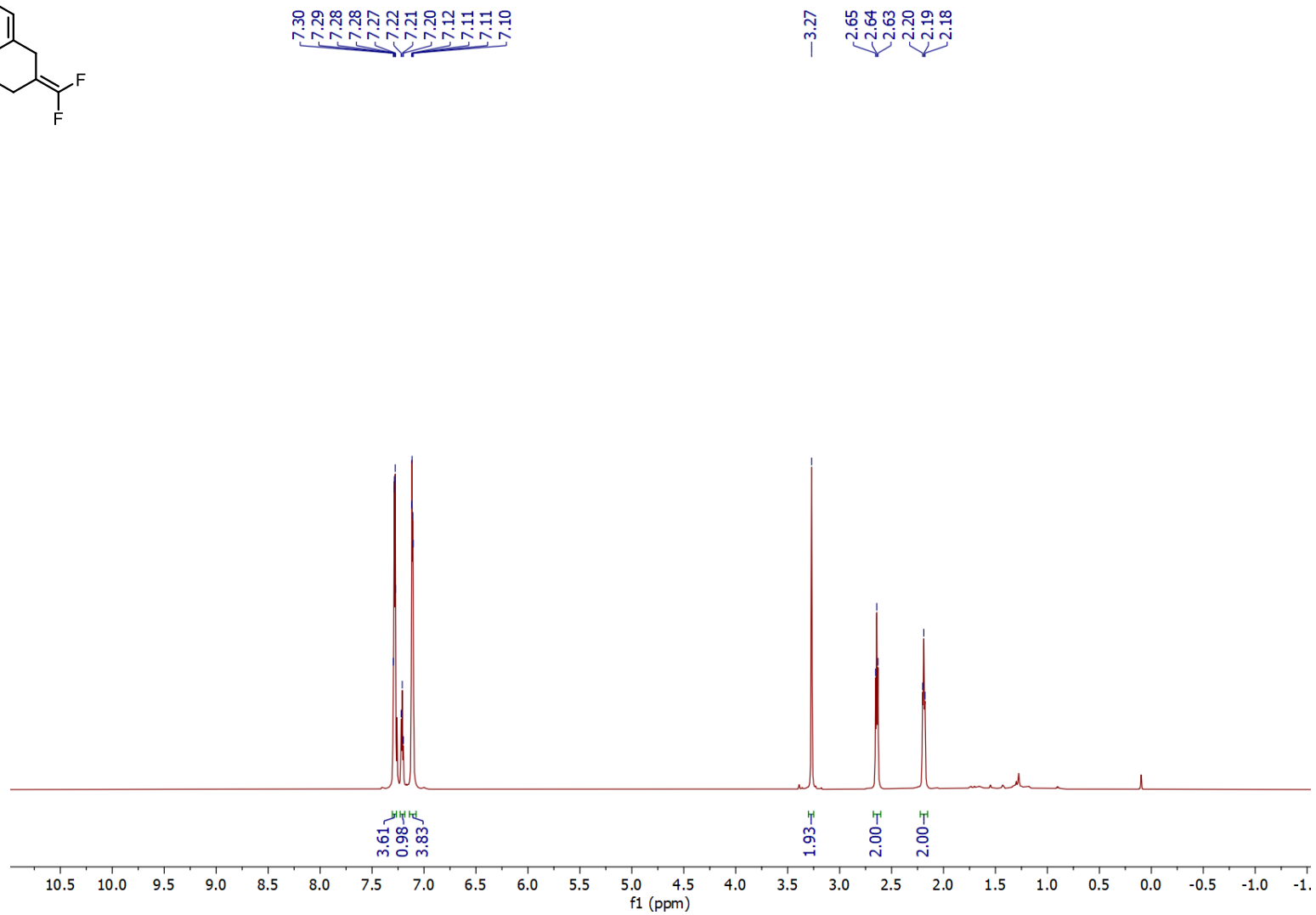
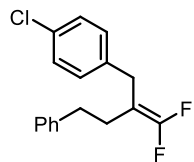
2-(2-(Difluoromethylene)-4-phenylbutyl)thiophene 2c ¹⁹F NMR (376 MHz, Chloroform-*d*)



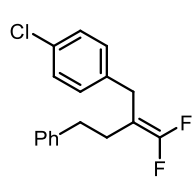
-95.41
-95.55
-95.58
-95.71



1-Chloro-4-(2-(difluoromethylene)-4-phenylbutyl)benzene 2d ^1H NMR (700 MHz, Chloroform-*d*)



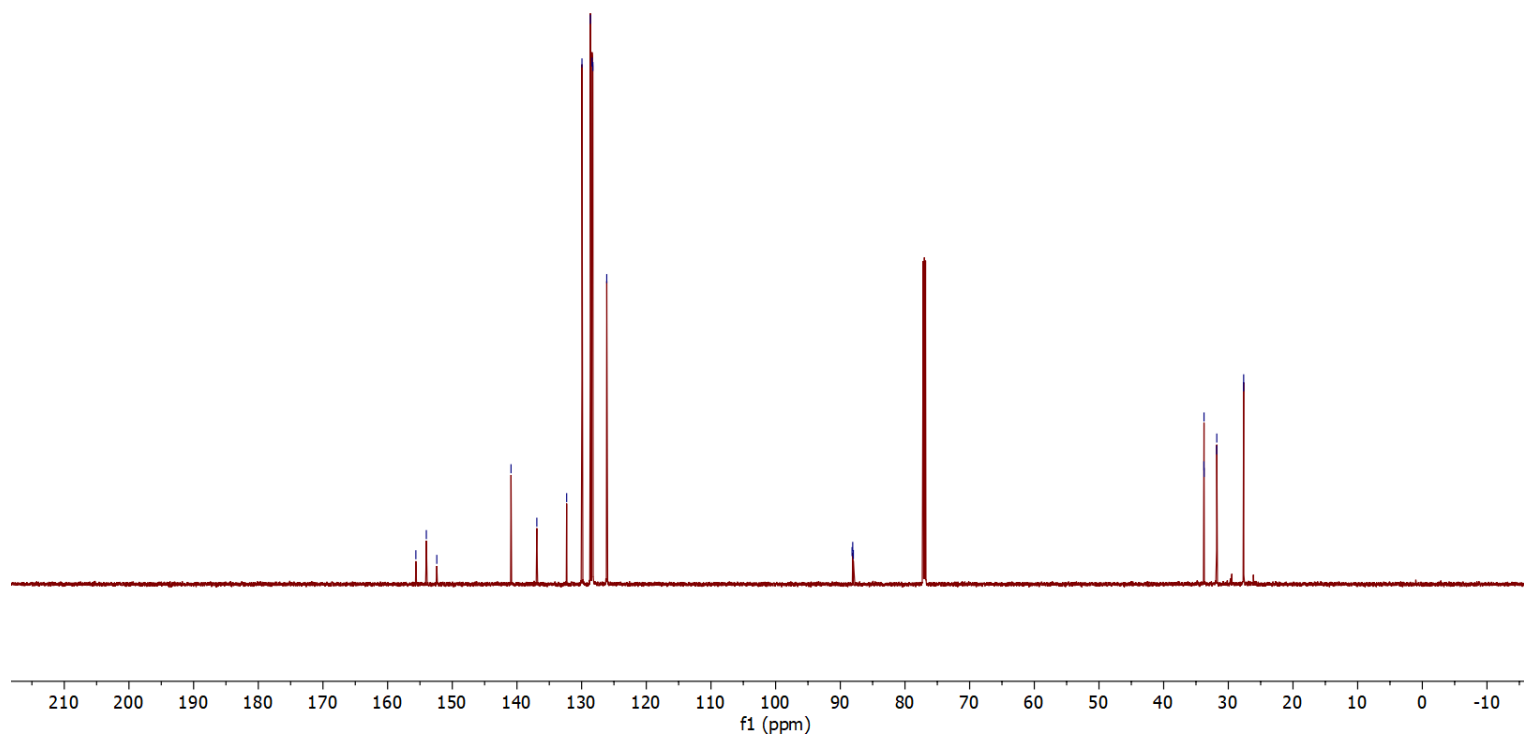
1-Chloro-4-(2-(difluoromethylene)-4-phenylbutyl)benzene 2d $^{13}\text{C}\{^1\text{H}\}$ NMR (176 MHz, Chloroform-*d*)



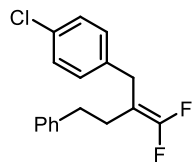
155.63
154.01
152.39
140.92
136.93
132.32
129.95
128.64
128.39
128.26
126.11

88.18
88.08
87.98

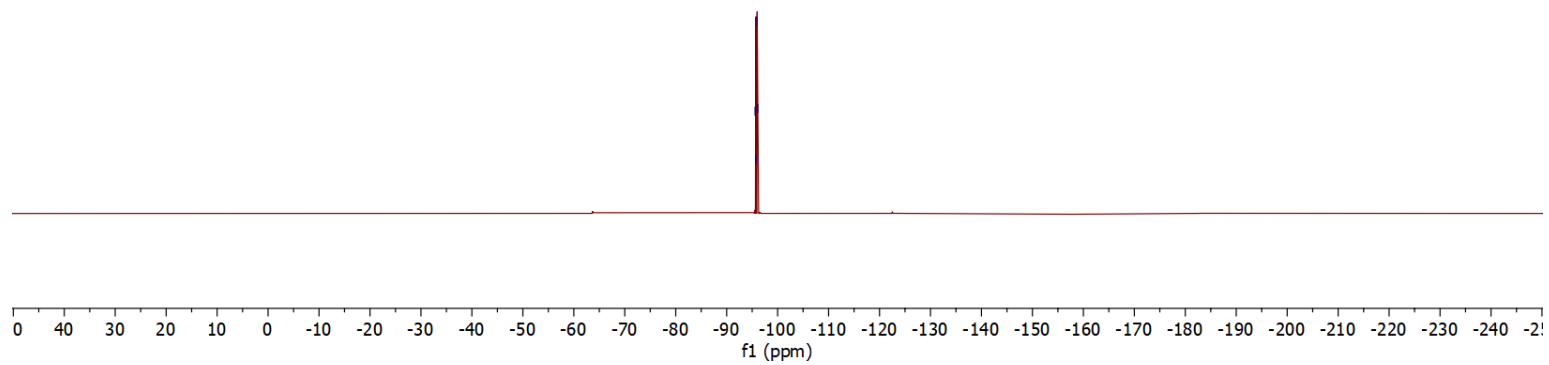
33.77
33.76
33.74
31.80
31.78
27.64
27.63



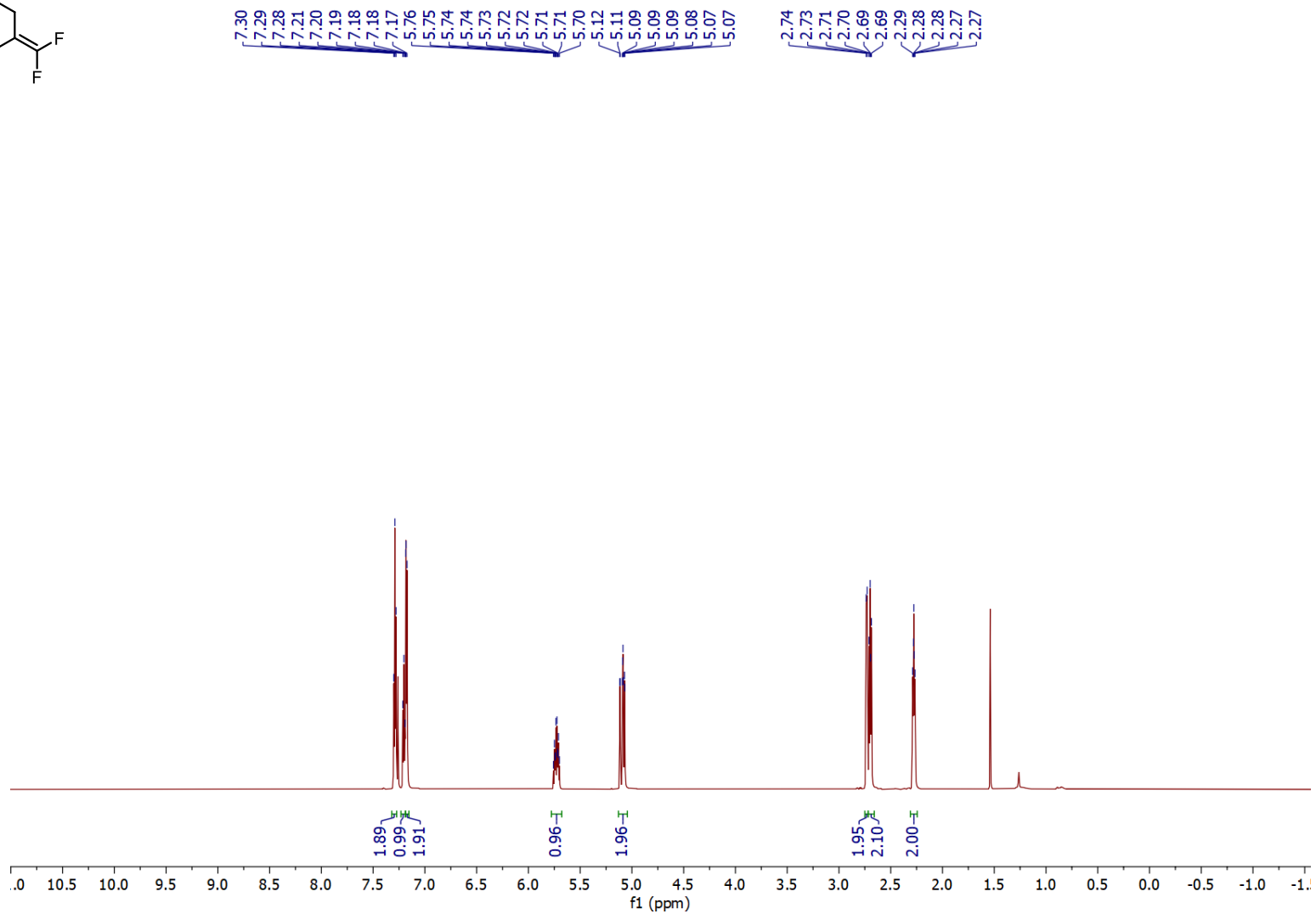
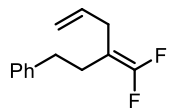
1-Chloro-4-(2-(difluoromethylene)-4-phenylbutyl)benzene 2d ^{19}F NMR (376 MHz, Chloroform-*d*)



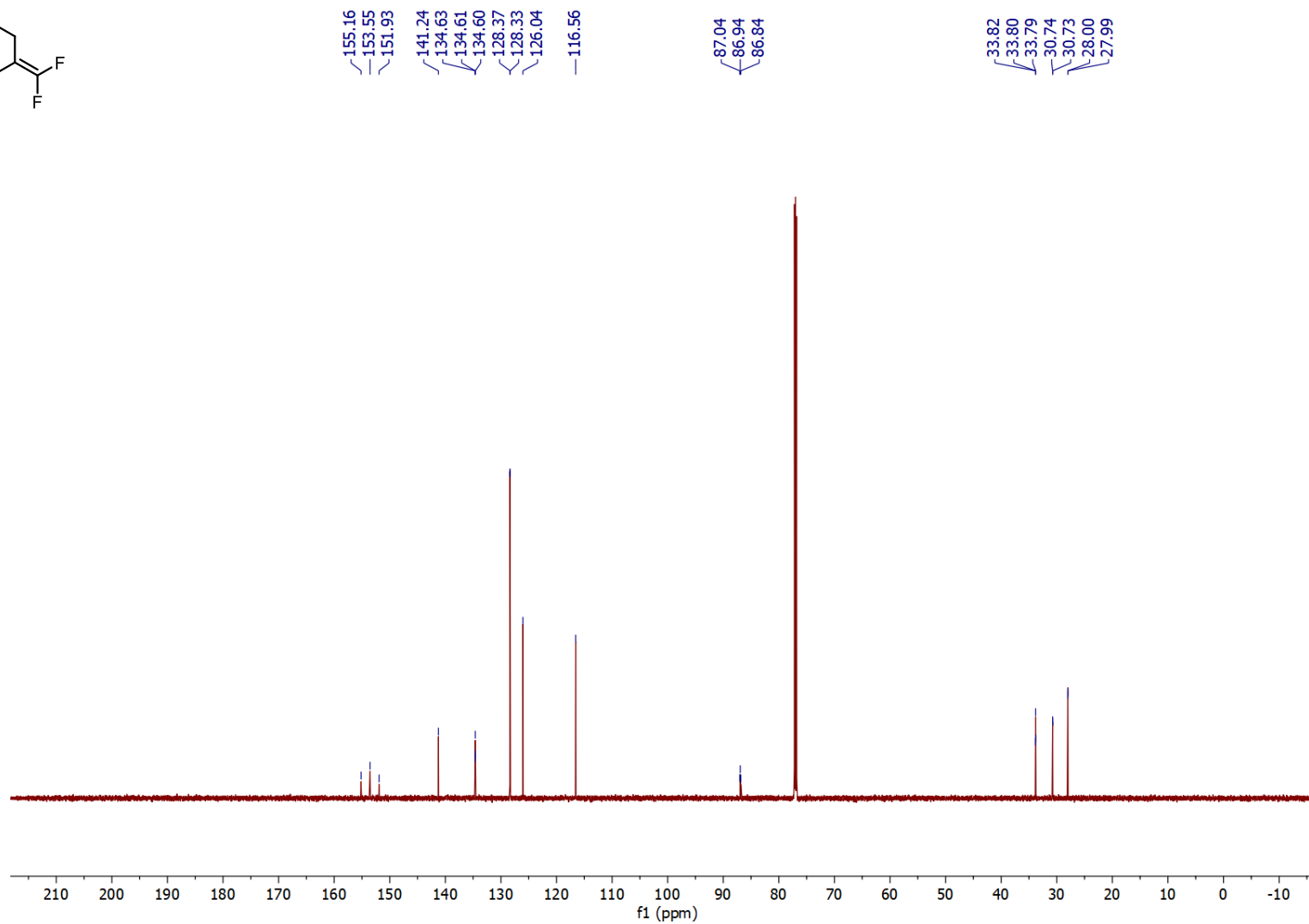
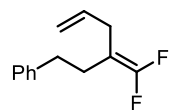
-95.57
-95.73
-95.98
-96.12



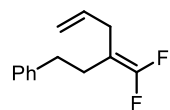
(3-(Difluoromethylene)hex-5-en-1-yl)benzene 2e ¹H NMR (700 MHz, Chloroform-*d*)



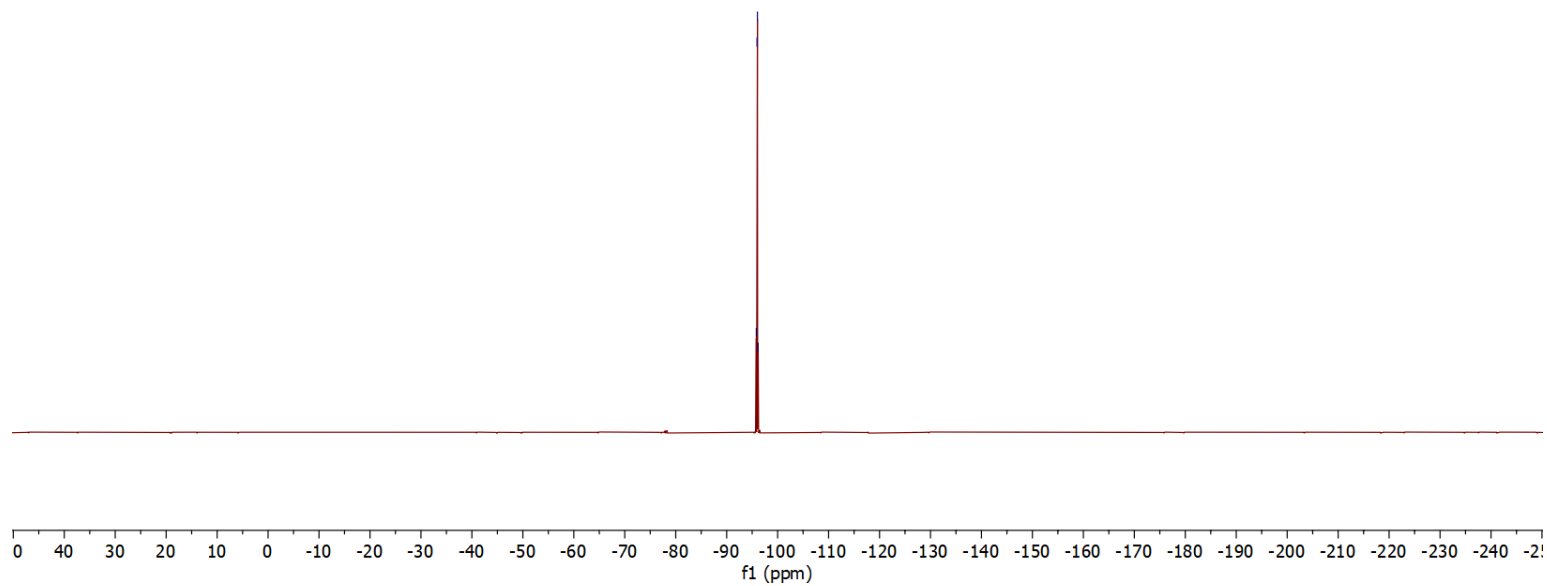
(3-(Difluoromethylene)hex-5-en-1-yl)benzene 2e $^{13}\text{C}\{^1\text{H}\}$ NMR (176 MHz, Chloroform-*d*)



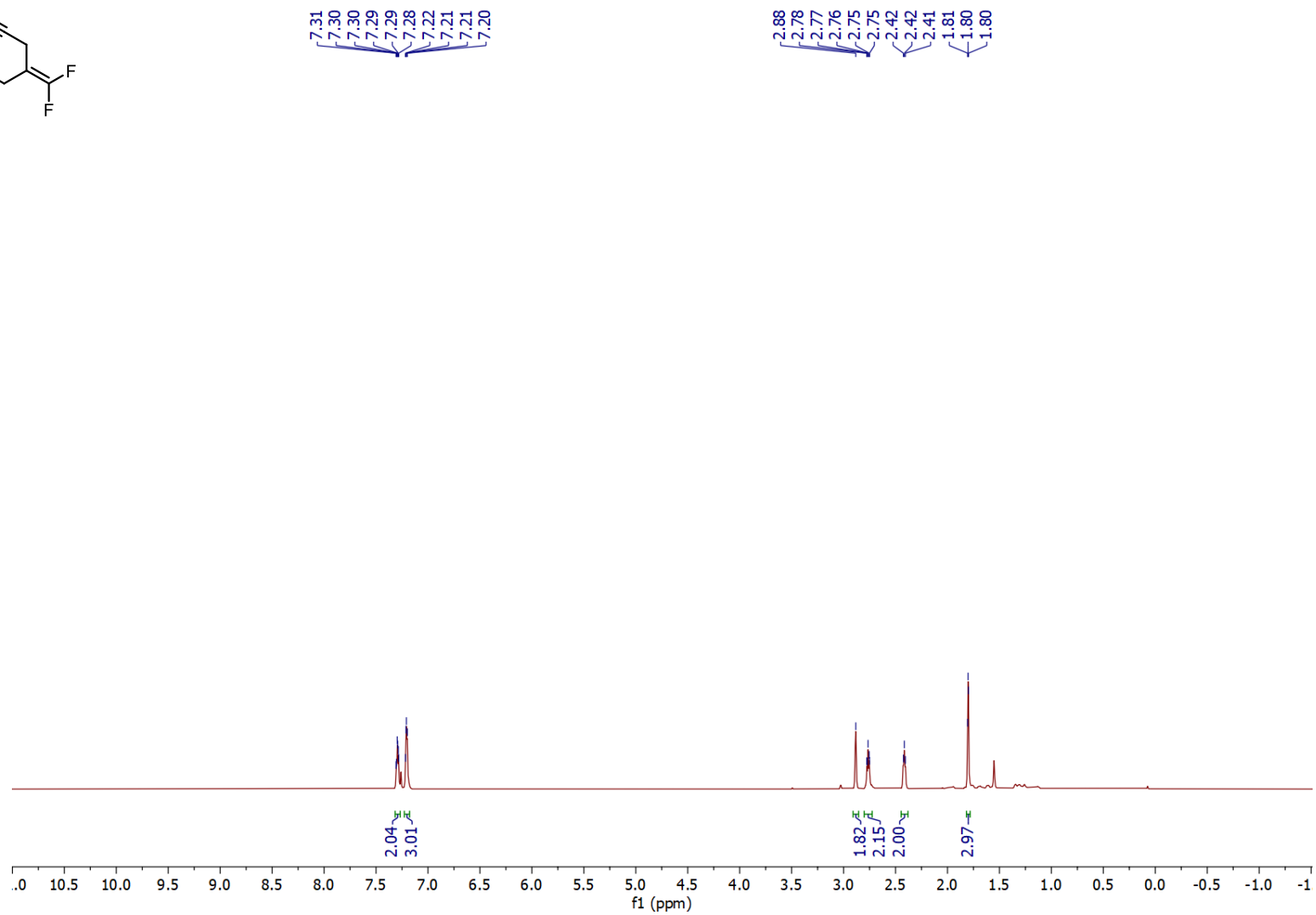
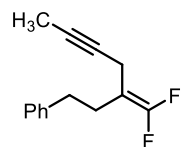
(3-(Difluoromethylene)hex-5-en-1-yl)benzene 2e ¹⁹F NMR (376 MHz, Chloroform-*d*)



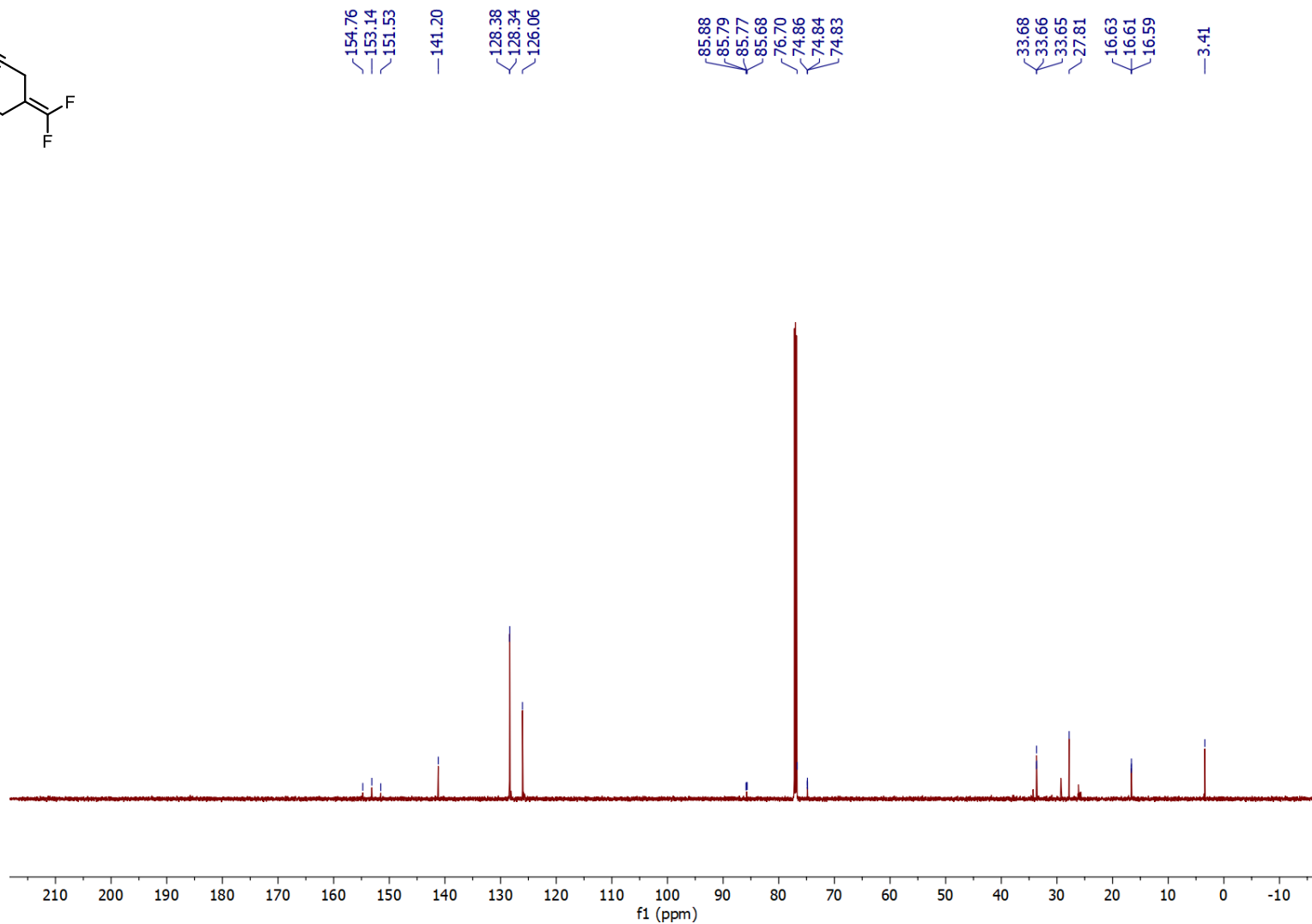
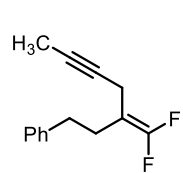
-95.81
-95.95
-96.04
-96.18



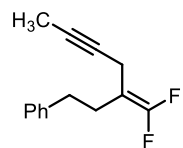
(3-(Difluoromethylene)hept-5-yn-1-yl)benzene 2f ^1H NMR (700 MHz, Chloroform-*d*)



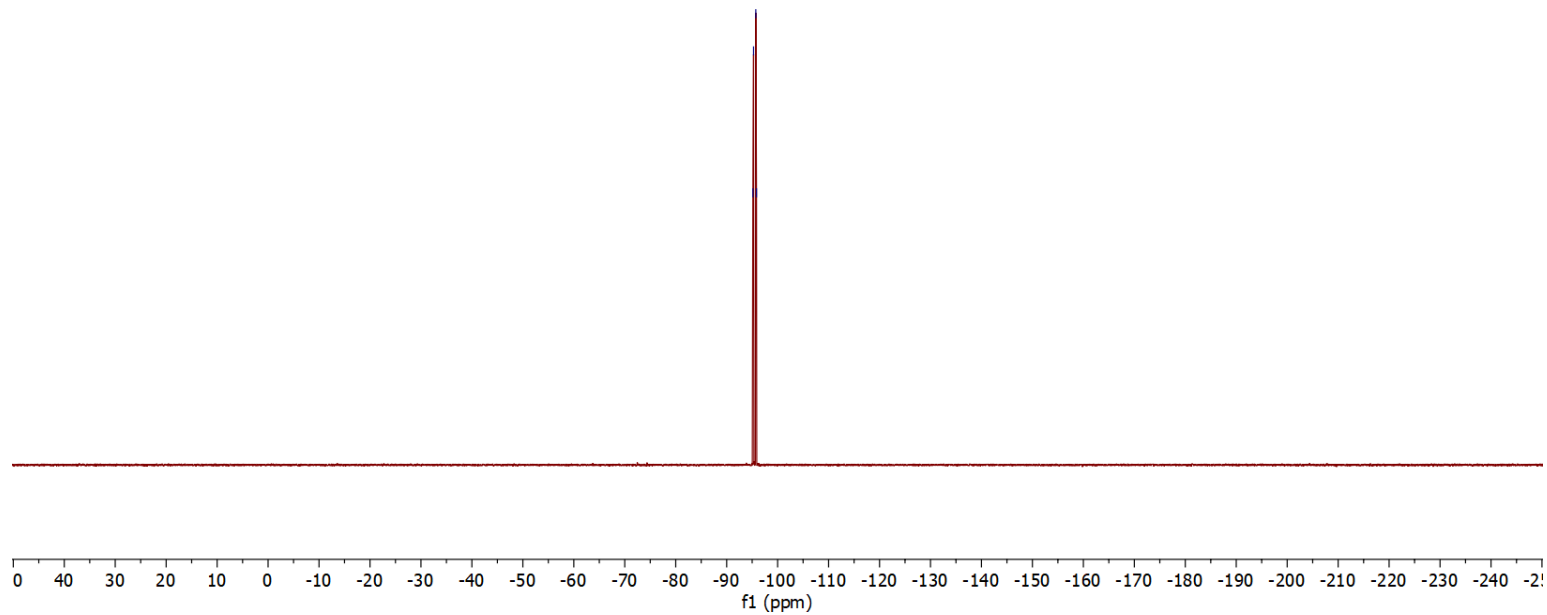
(3-(Difluoromethylene)hept-5-yn-1-yl)benzene 2f $^{13}\text{C}\{^1\text{H}\}$ NMR (176 MHz, Chloroform-*d*)



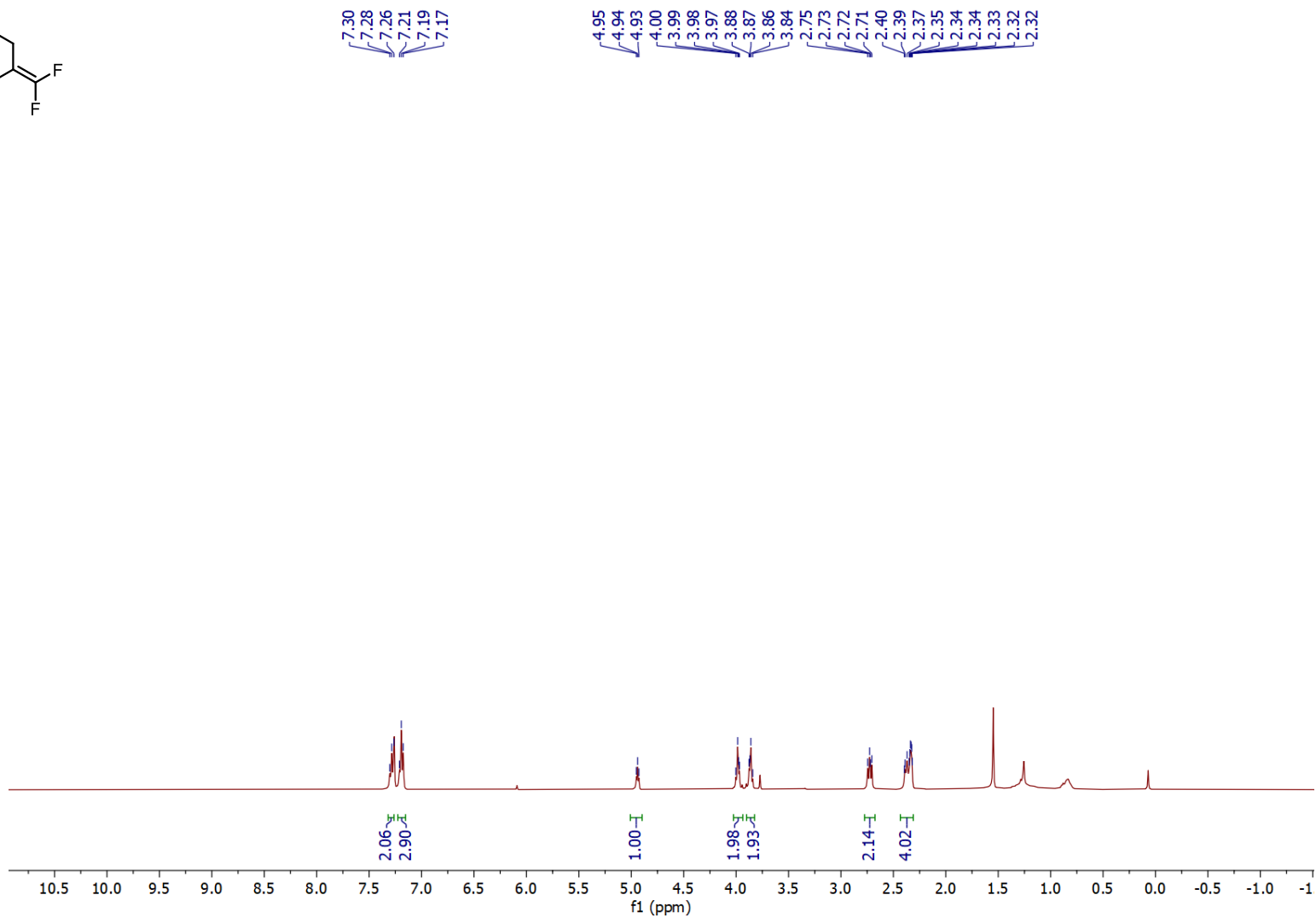
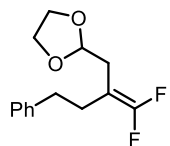
(3-(Difluoromethylene)hept-5-yn-1-yl)benzene 2f ^{19}F NMR (376 MHz, Chloroform-*d*)



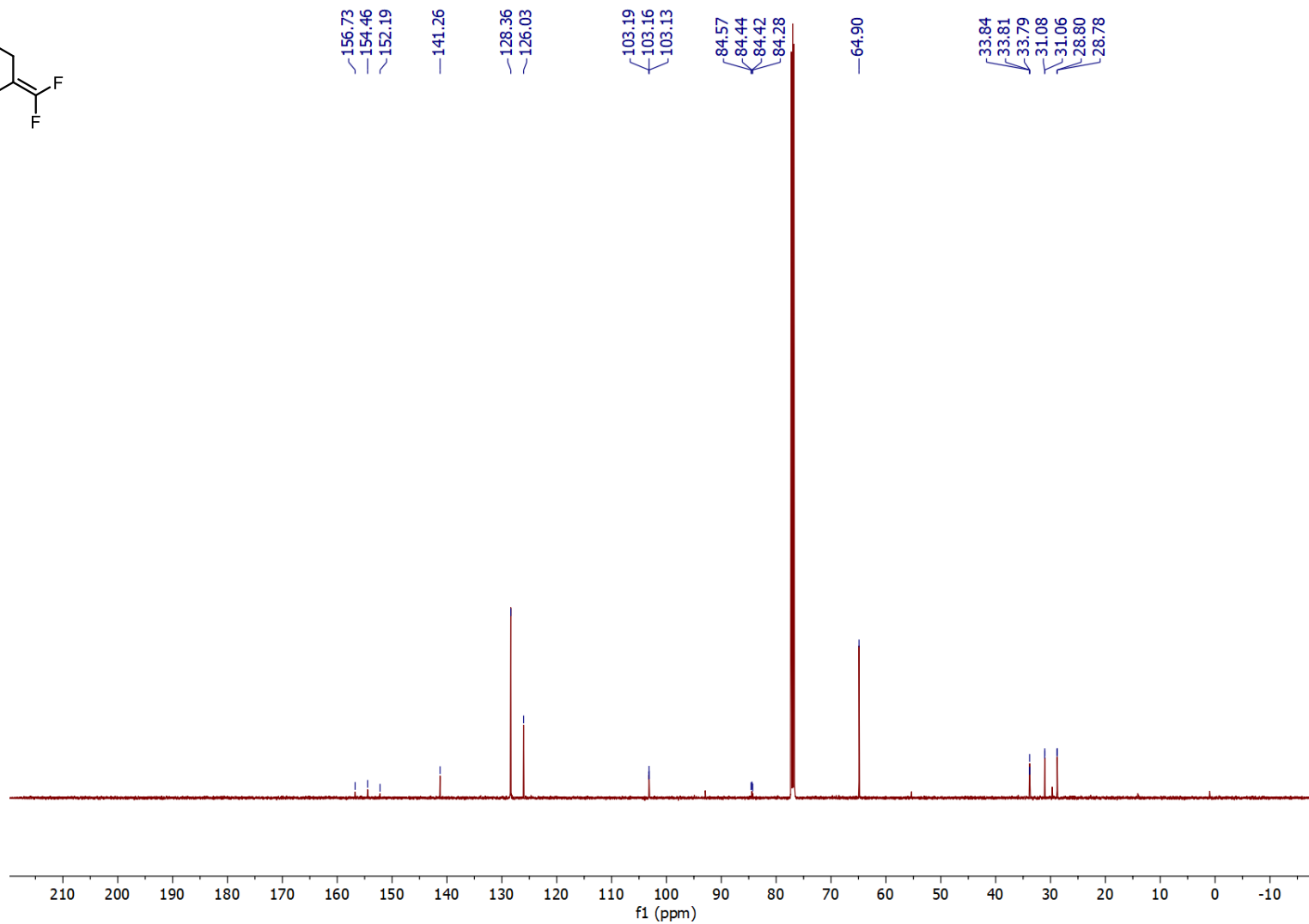
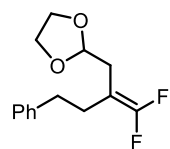
-95.14
-95.27
-95.71
-95.85



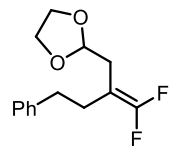
2-(2-(Difluoromethylene)-4-phenylbutyl)-1,3-dioxolane 2g ¹H NMR (700 MHz, Chloroform-*d*)



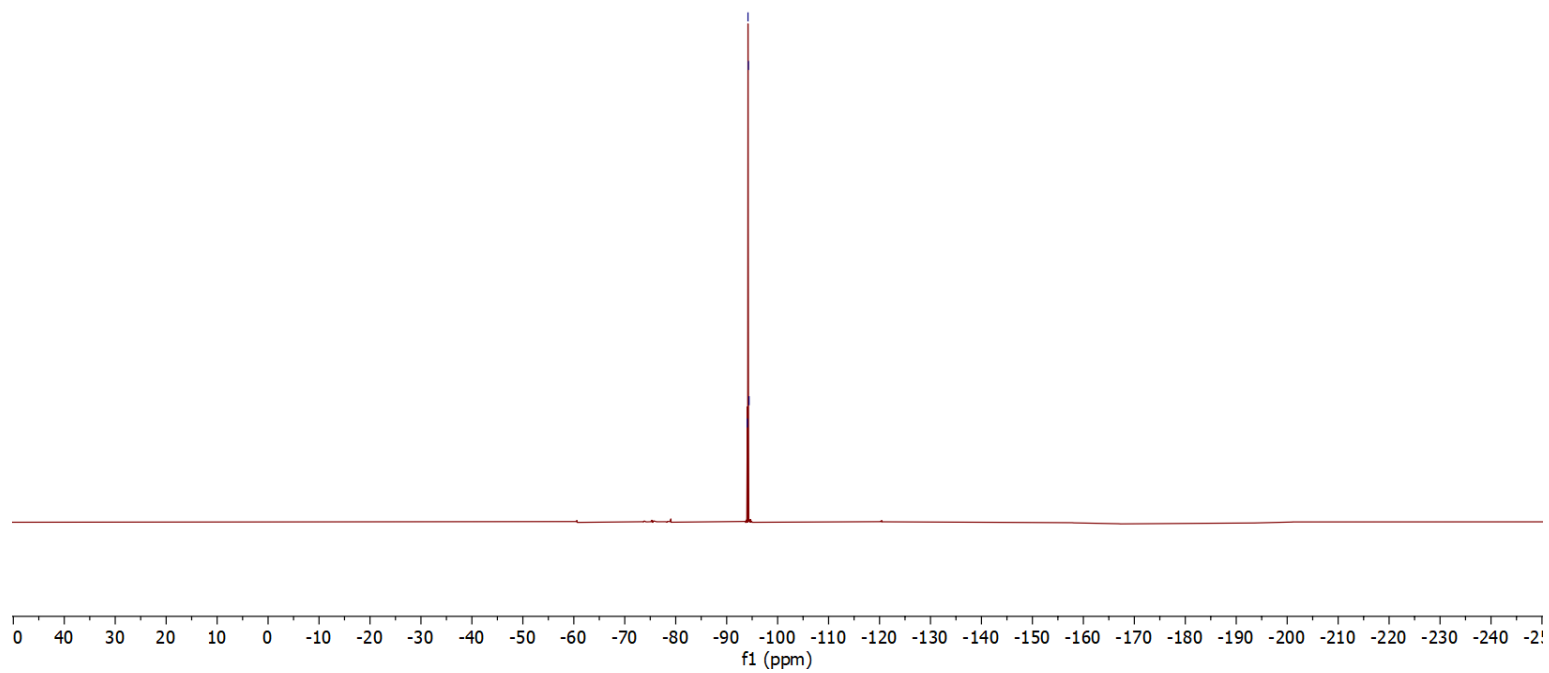
2-(2-(Difluoromethylene)-4-phenylbutyl)-1,3-dioxolane 2g $^{13}\text{C}\{^1\text{H}\}$ NMR (176 MHz, Chloroform-*d*)



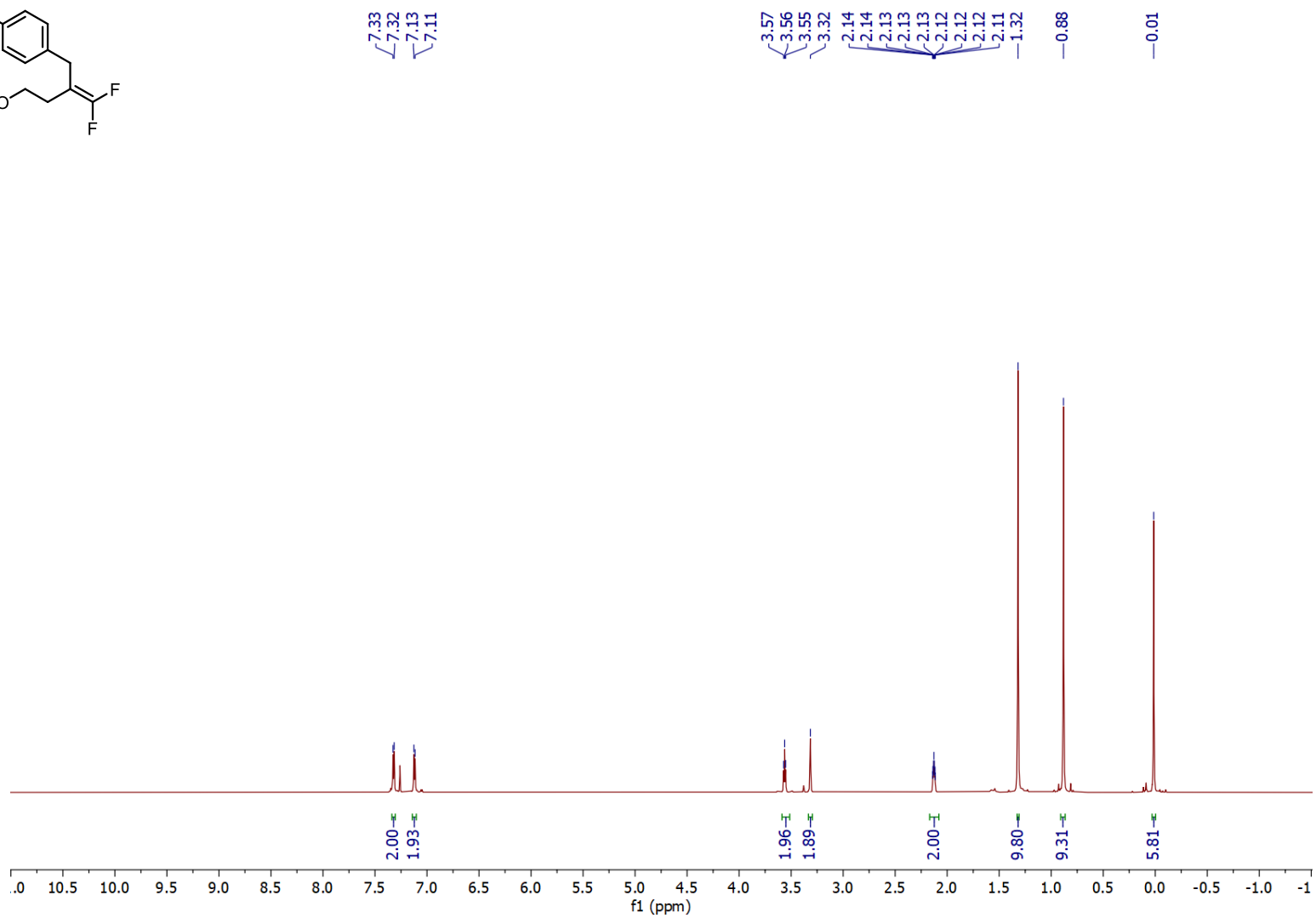
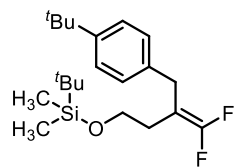
2-(2-(Difluoromethylene)-4-phenylbutyl)-1,3-dioxolane 2g ^{19}F NMR (376 MHz, Chloroform-*d*)



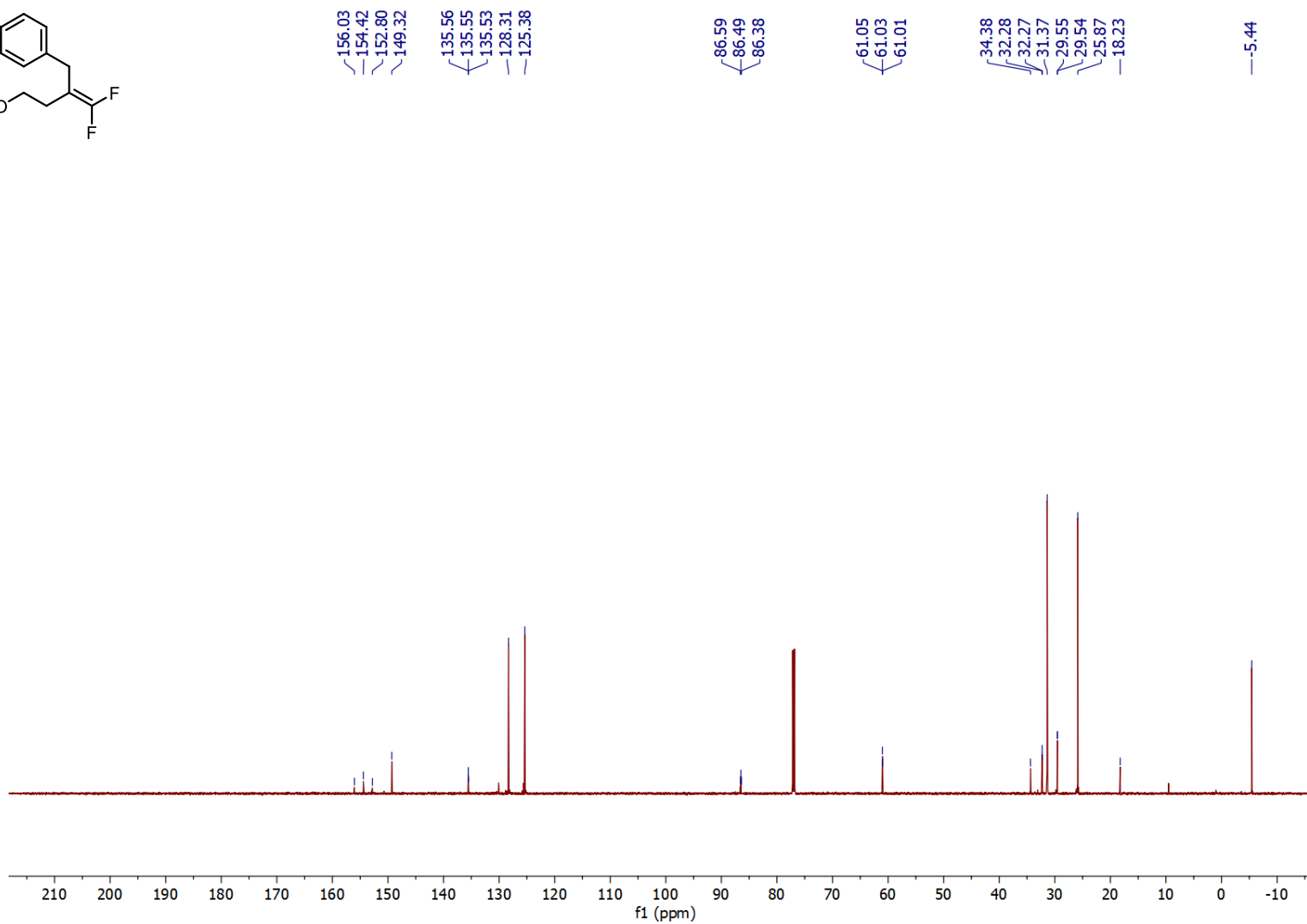
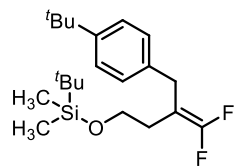
-94.05
-94.18
-94.26
-94.39



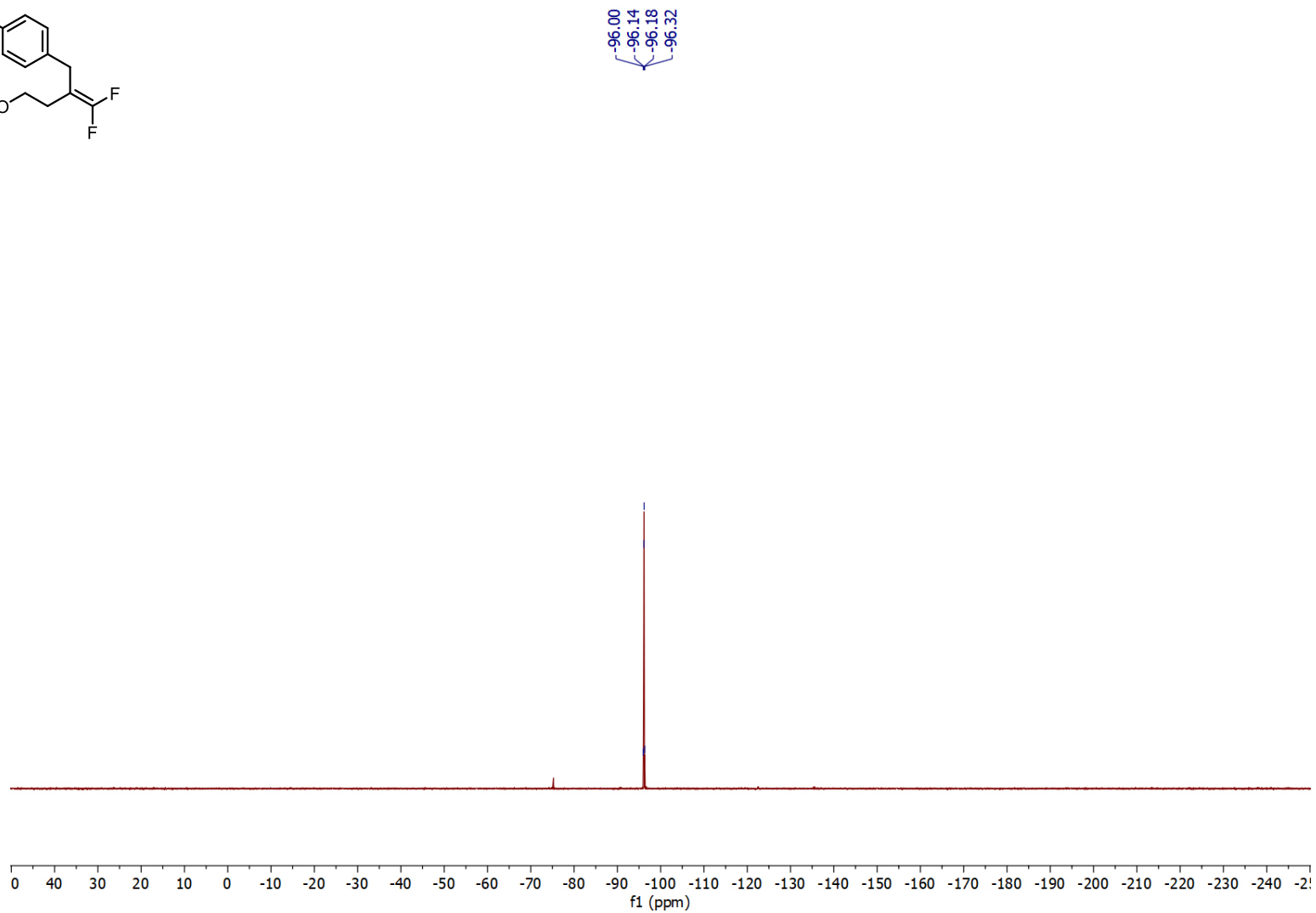
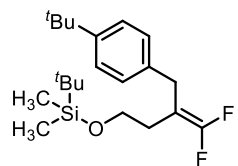
tert-Butyl((3-(4-(*tert*-butyl)benzyl)-4,4-difluorobut-3-en-1-yl)oxy)dimethylsilane 2h ¹H NMR (700 MHz, Chloroform-*d*)



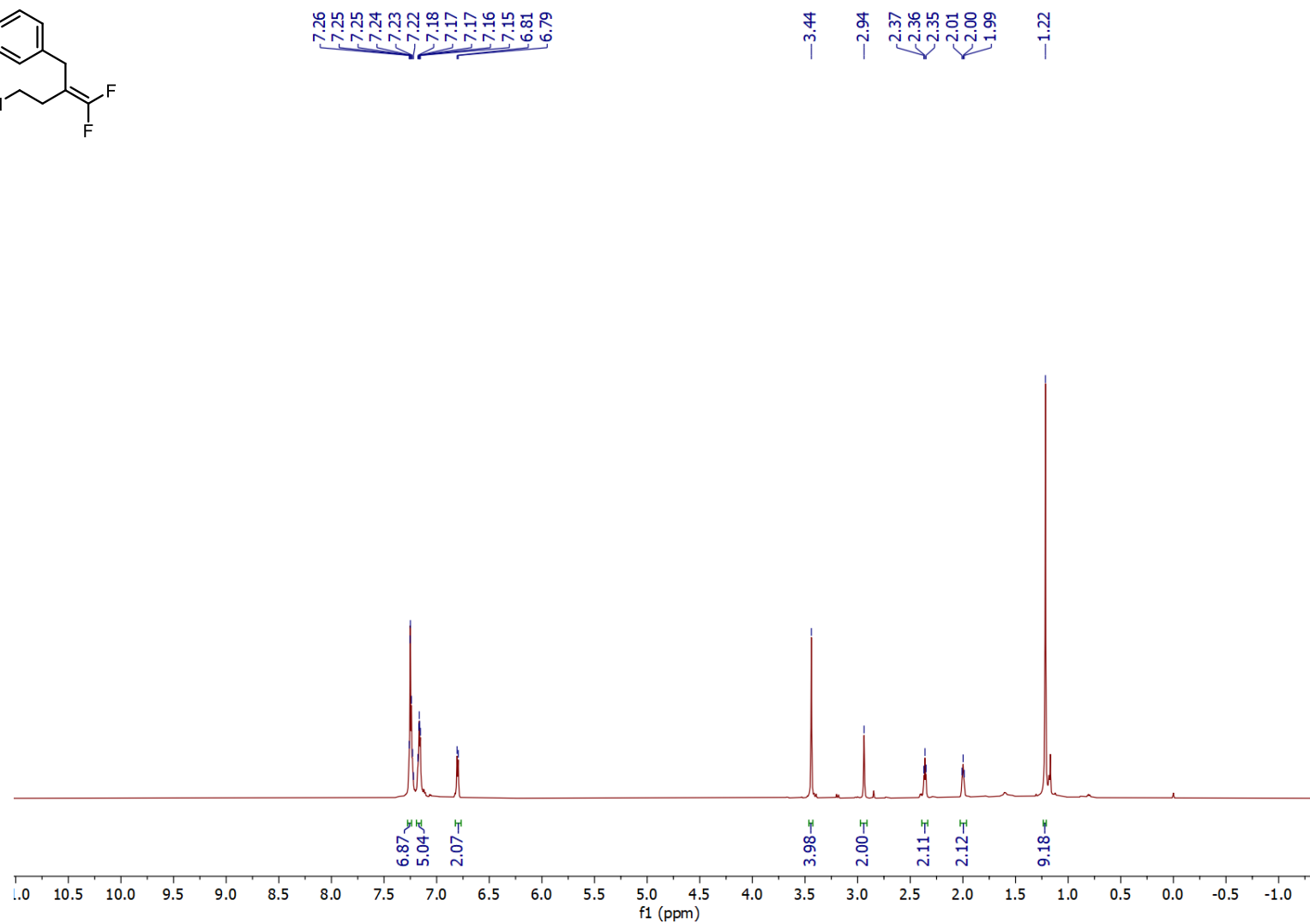
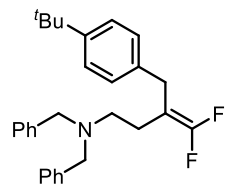
tert-Butyl((3-(4-(*tert*-butyl)benzyl)-4,4-difluorobut-3-en-1-yl)oxy)dimethylsilane 2h $^{13}\text{C}\{^1\text{H}\}$ NMR (176 MHz, Chloroform-*d*)



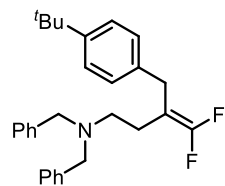
tert-Butyl((3-(4-(*tert*-butyl)benzyl)-4,4-difluorobut-3-en-1-yl)oxy)dimethylsilane 2h ^{19}F NMR (376 MHz, Chloroform-*d*)



N,N-Dibenzyl-3-(4-(*tert*-butyl)benzyl)-4,4-difluorobut-3-en-1-amine 2i ¹H NMR (700 MHz, Chloroform-*d*)



N,N-Dibenzyl-3-(4-(*tert*-butyl)benzyl)-4,4-difluorobut-3-en-1-amine 2i $^{13}\text{C}\{^1\text{H}\}$ NMR (176 MHz, Chloroform-*d*)

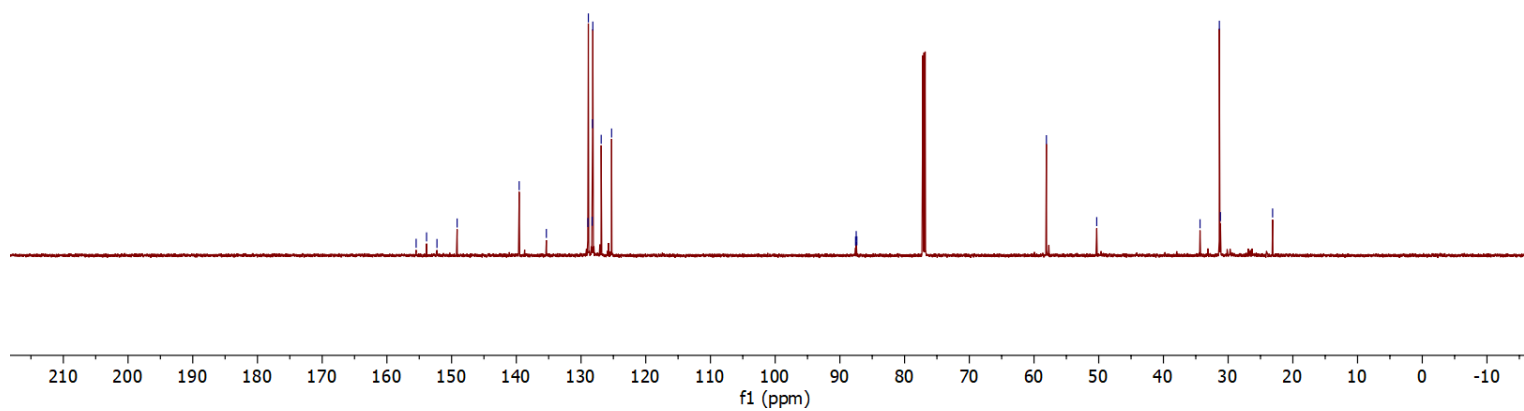


155.48
153.87
152.26
149.15
139.56
135.36
128.93
128.87
128.28
128.22
128.17
126.88
125.27

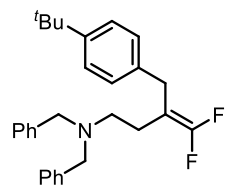
87.57
87.48
87.38

58.09
50.31

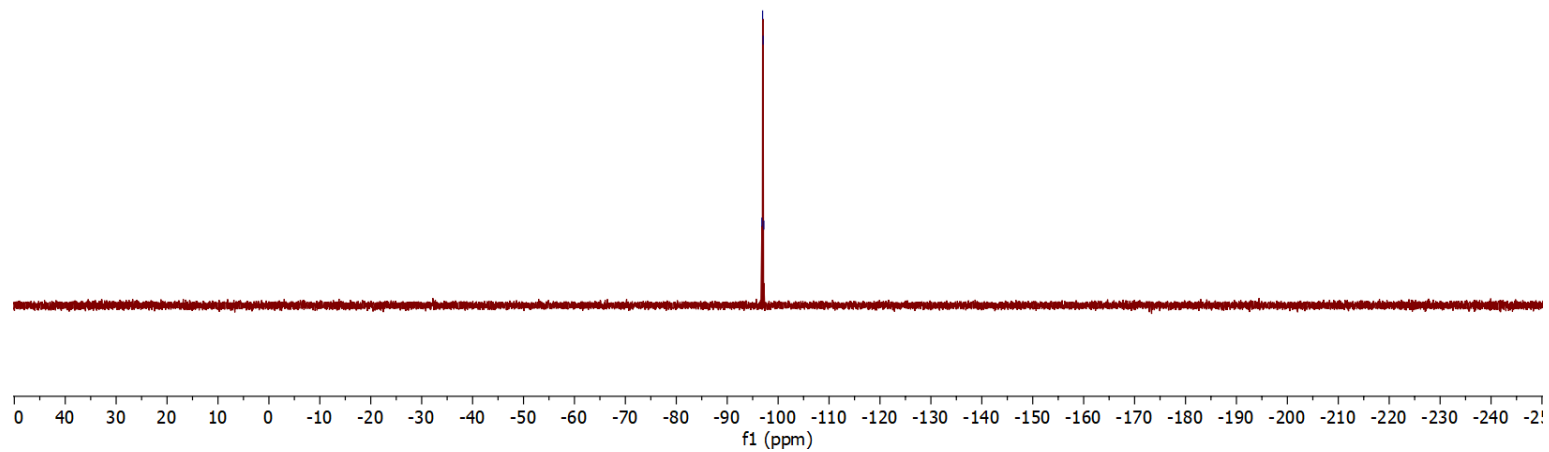
34.34
31.56
31.19
23.13



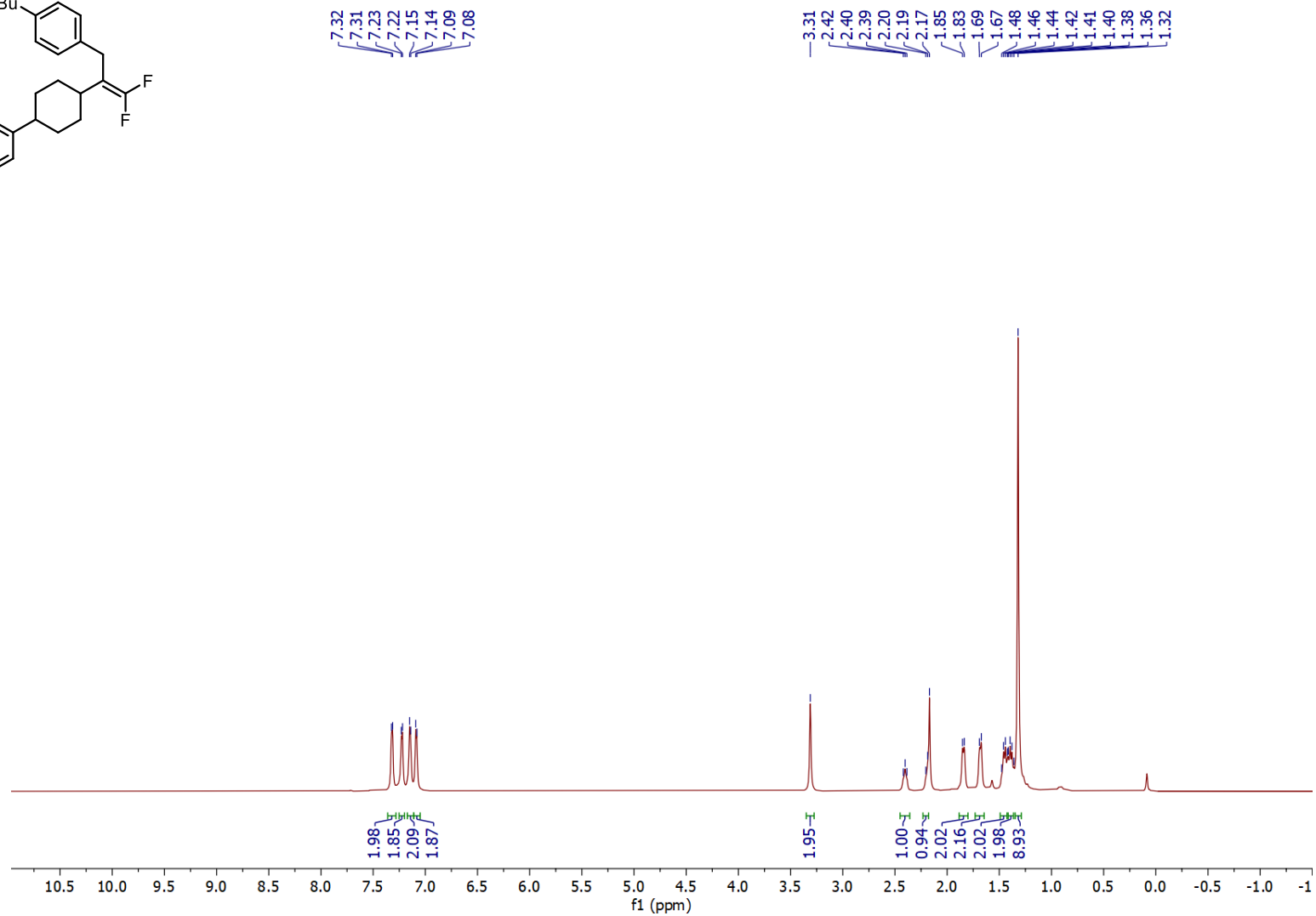
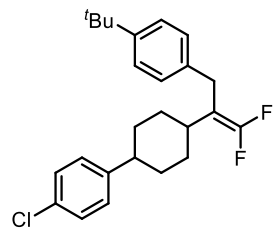
N,N-Dibenzyl-3-(4-(*tert*-butyl)benzyl)-4,4-difluorobut-3-en-1-amine $2i$ ^{19}F NMR (376 MHz, Chloroform-*d*)



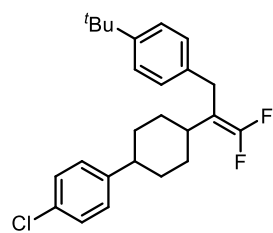
-96.80
-96.95
-97.06
-97.20



1-(*tert*-Butyl)-4-(2-(4-(4-chlorophenyl)cyclohexyl)-3,3-difluoroallyl)benzene 2j ¹H NMR (700 MHz, Chloroform-*d*)



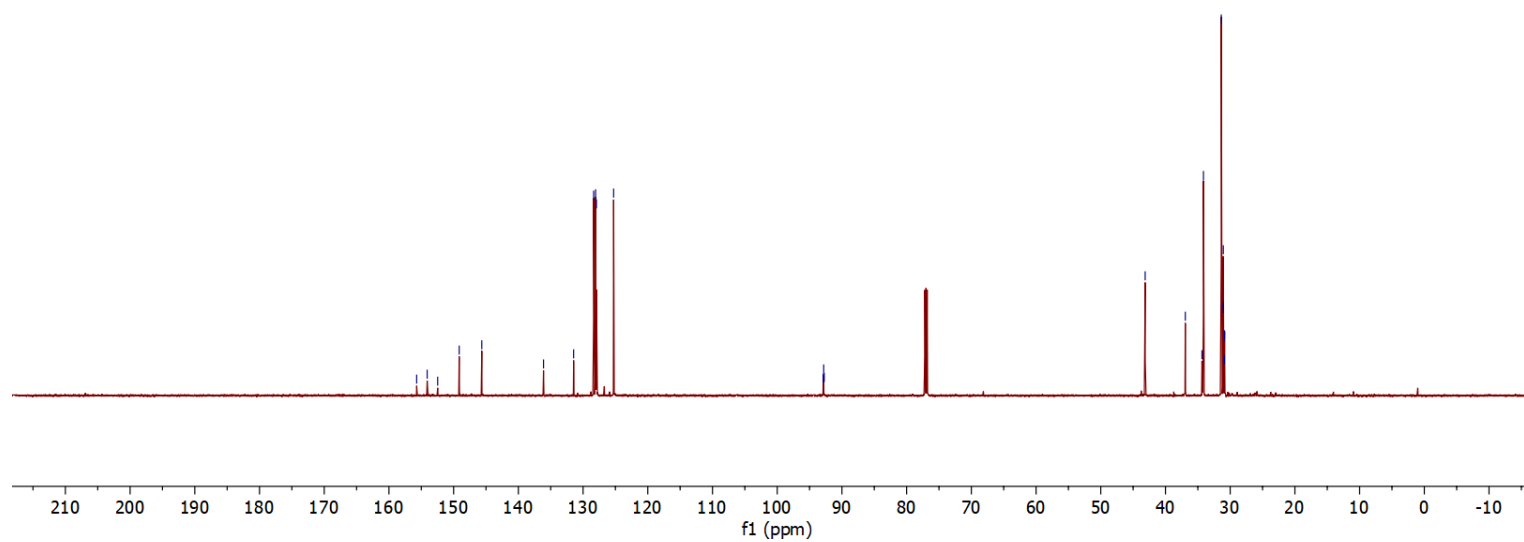
1-(*tert*-Butyl)-4-(2-(4-(4-chlorophenyl)cyclohexyl)-3,3-difluoroallyl)benzene 2j $^{13}\text{C}\{^1\text{H}\}$ NMR (176 MHz, Chloroform-*d*)



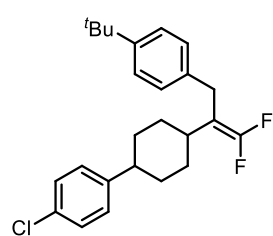
155.71
154.09
152.47
149.14
145.65
136.11
131.46
128.36
128.06
127.94
125.28

92.90
92.82
92.73

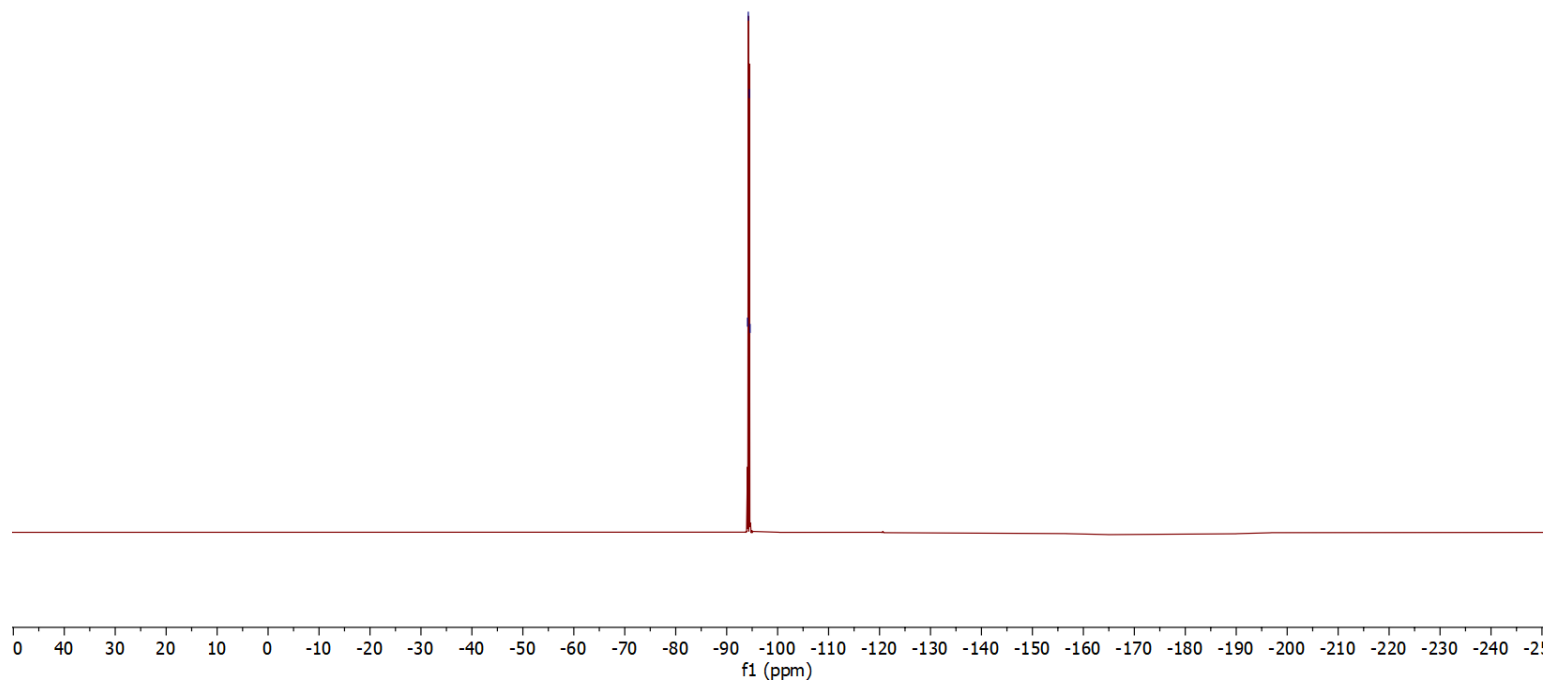
43.14
36.94
34.36
34.13
31.38
31.08
31.06
31.05
30.89
30.87
30.85



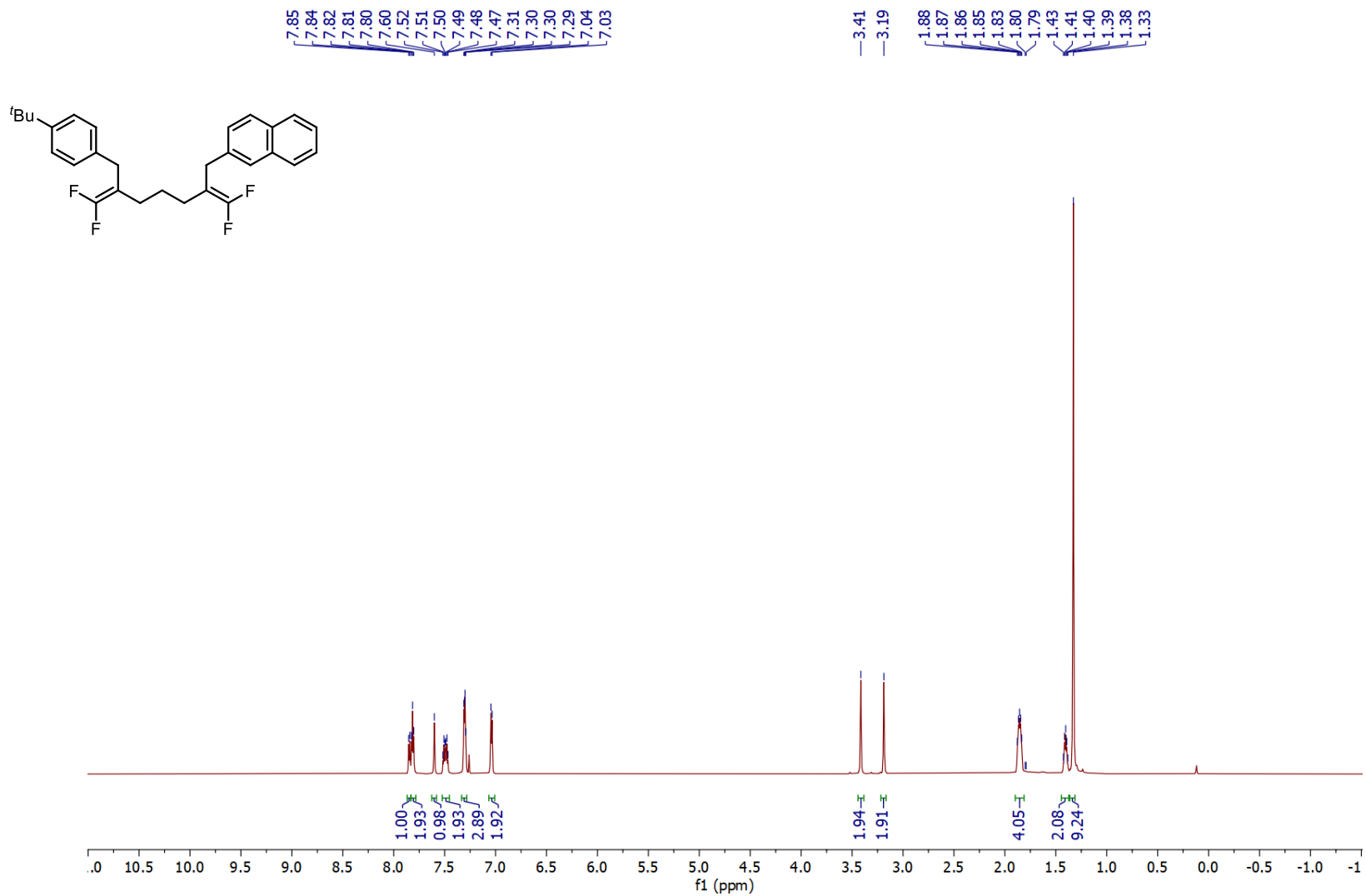
1-(*tert*-Butyl)-4-(2-(4-(4-chlorophenyl)cyclohexyl)-3,3-difluoroallyl)benzene 2j ^{19}F NMR (376 MHz, Chloroform-*d*)



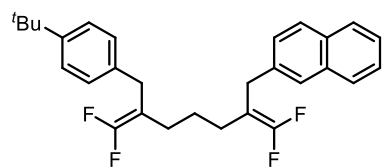
-94.09
-94.24
-94.45
-94.60



2-(6-(4-(*tert*-Butyl)benzyl)-2-(difluoromethylene)-7,7-difluorohept-6-en-1-yl)naphthalene 2k ¹H NMR (700 MHz, Chloroform-*d*)

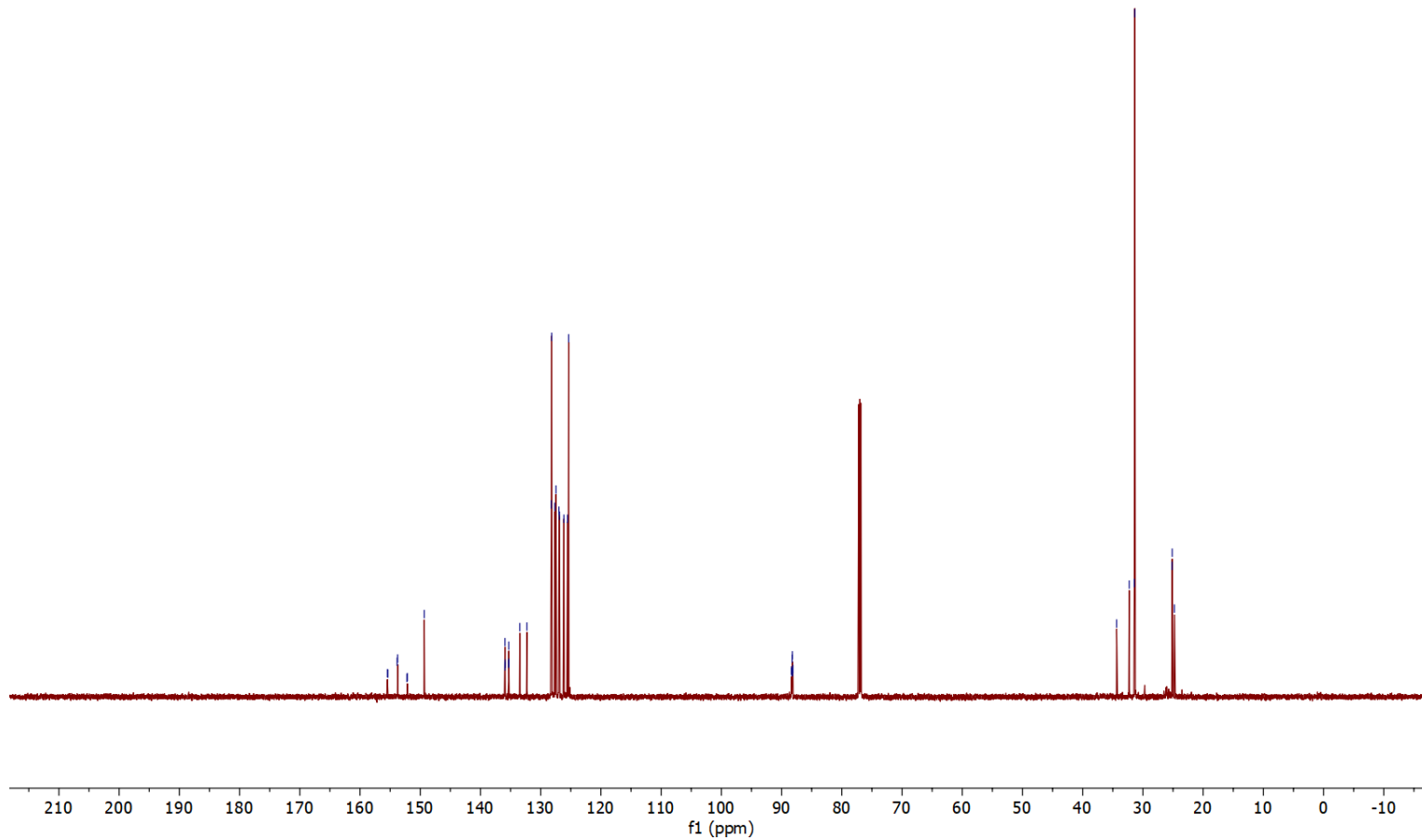


2-(6-(4-(*tert*-Butyl)benzyl)-2-(difluoromethylene)-7,7-difluorohept-6-en-1-yl)naphthalene 2k $^{13}\text{C}\{^1\text{H}\}$ NMR (176 MHz, Chloroform-*d*)

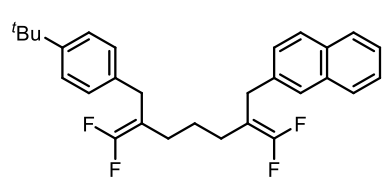


155.45
155.37
153.84
153.76
152.22
152.14
149.33
135.95
135.94
135.92
135.31
135.30
135.28
133.47
132.29
128.24
128.17
127.65
127.46
126.97
126.90
126.15
125.54
125.36
88.36
88.31
88.26
88.21
88.16
88.12

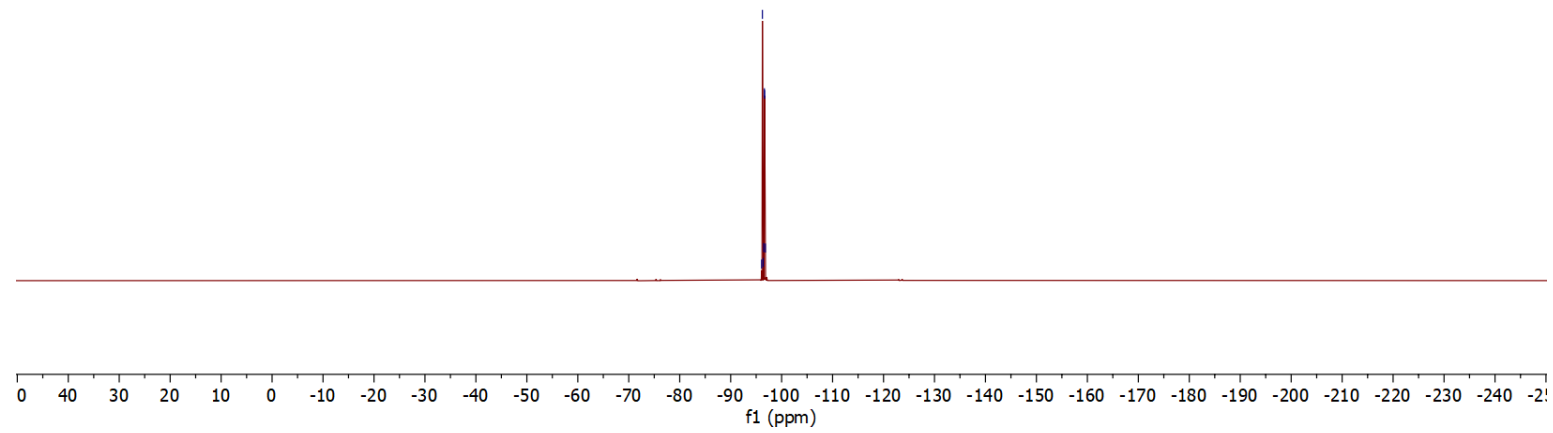
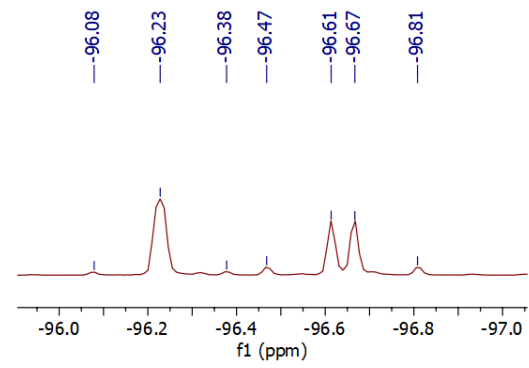
34.36
32.28
31.44
31.35
25.17
25.13
24.77



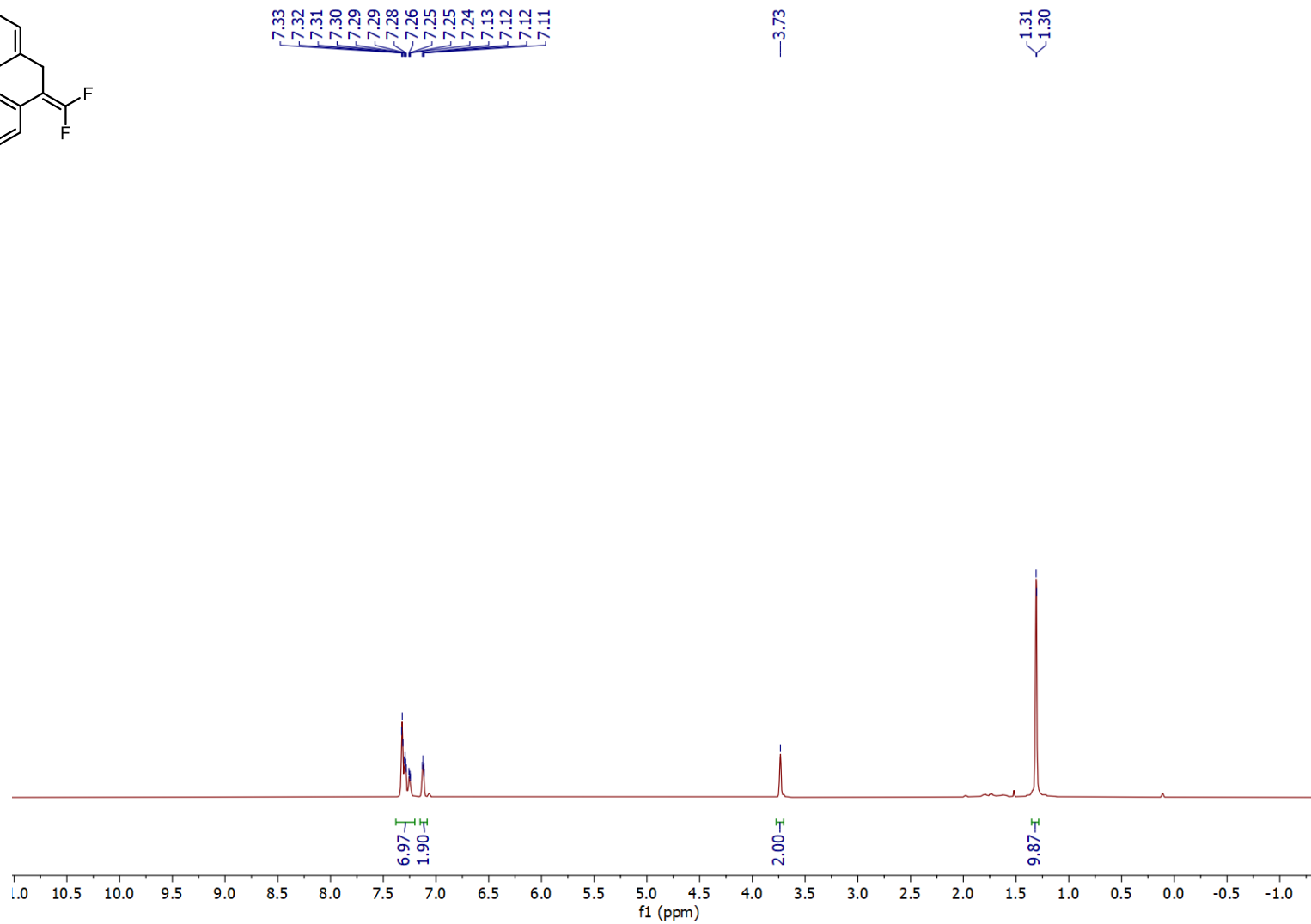
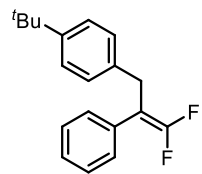
2-(6-(4-(*tert*-Butyl)benzyl)-2-(difluoromethylene)-7,7-difluorohept-6-en-1-yl)naphthalene 2k ^{19}F NMR (376 MHz, Chloroform-*d*)



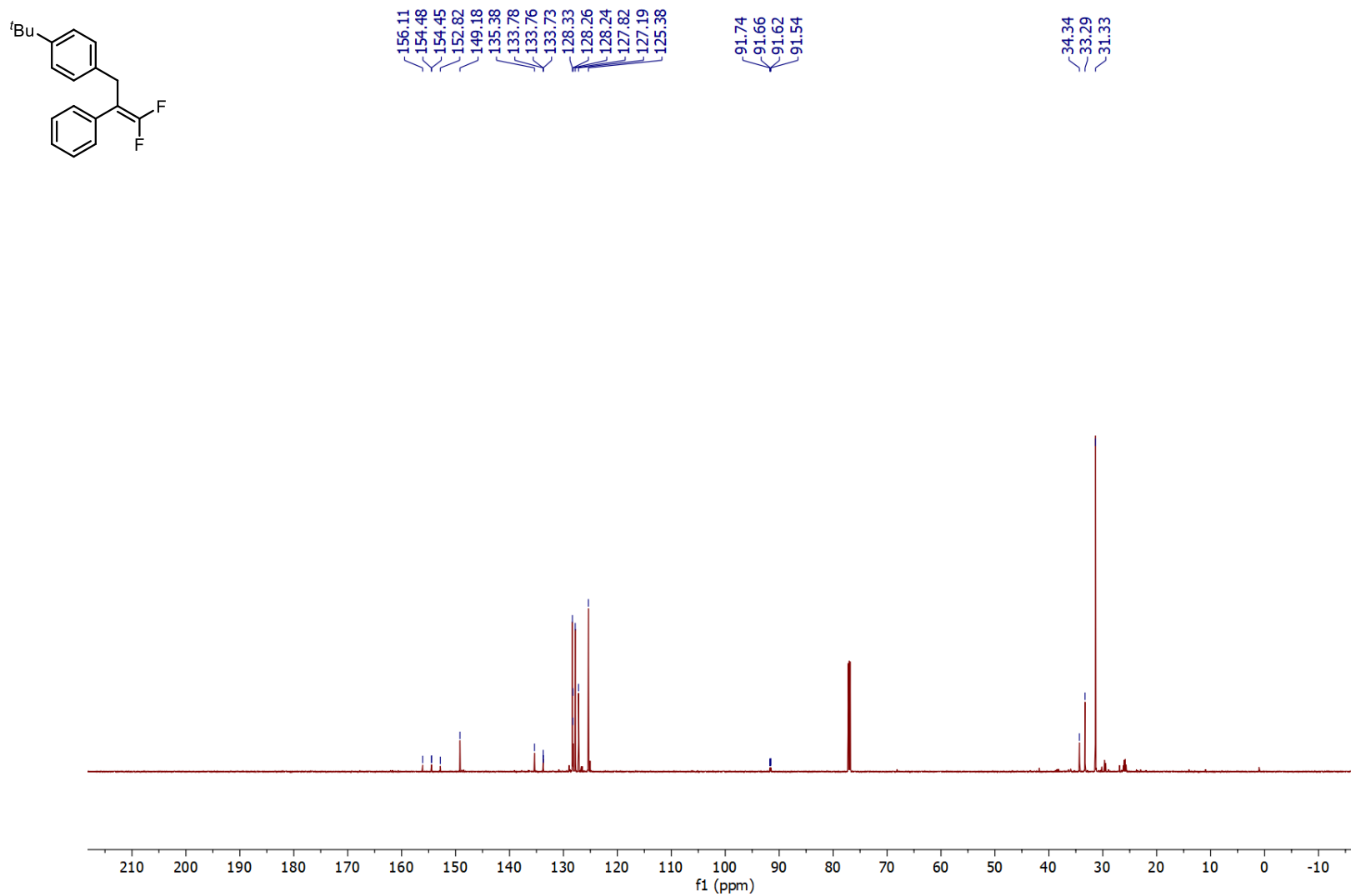
-96.08
-96.23
-96.38
-96.47
-96.61
-96.67
-96.81



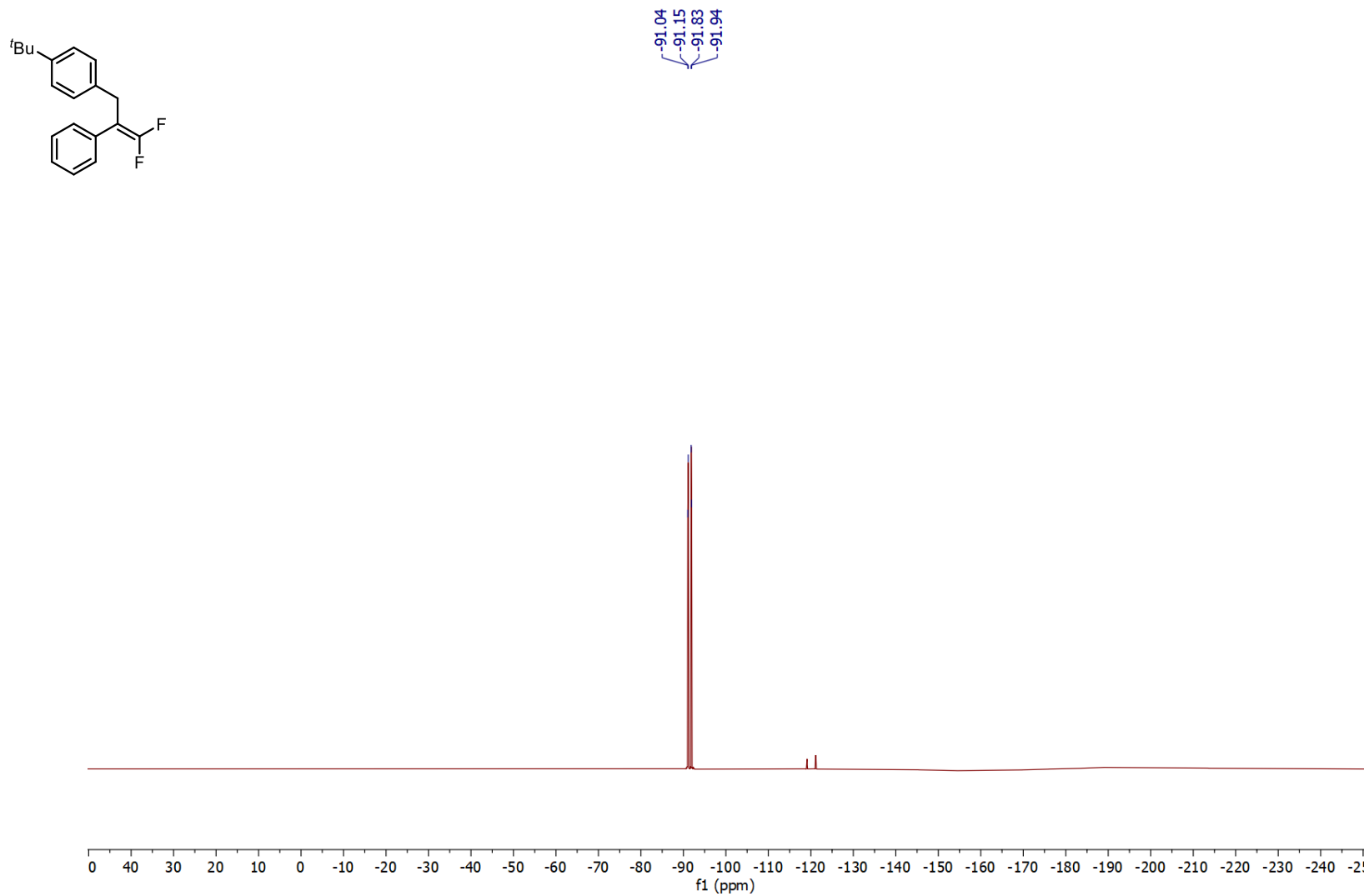
1-(*tert*-Butyl)-4-(3,3-difluoro-2-phenylallyl)benzene 21 ¹H NMR (700 MHz, Chloroform-*d*)



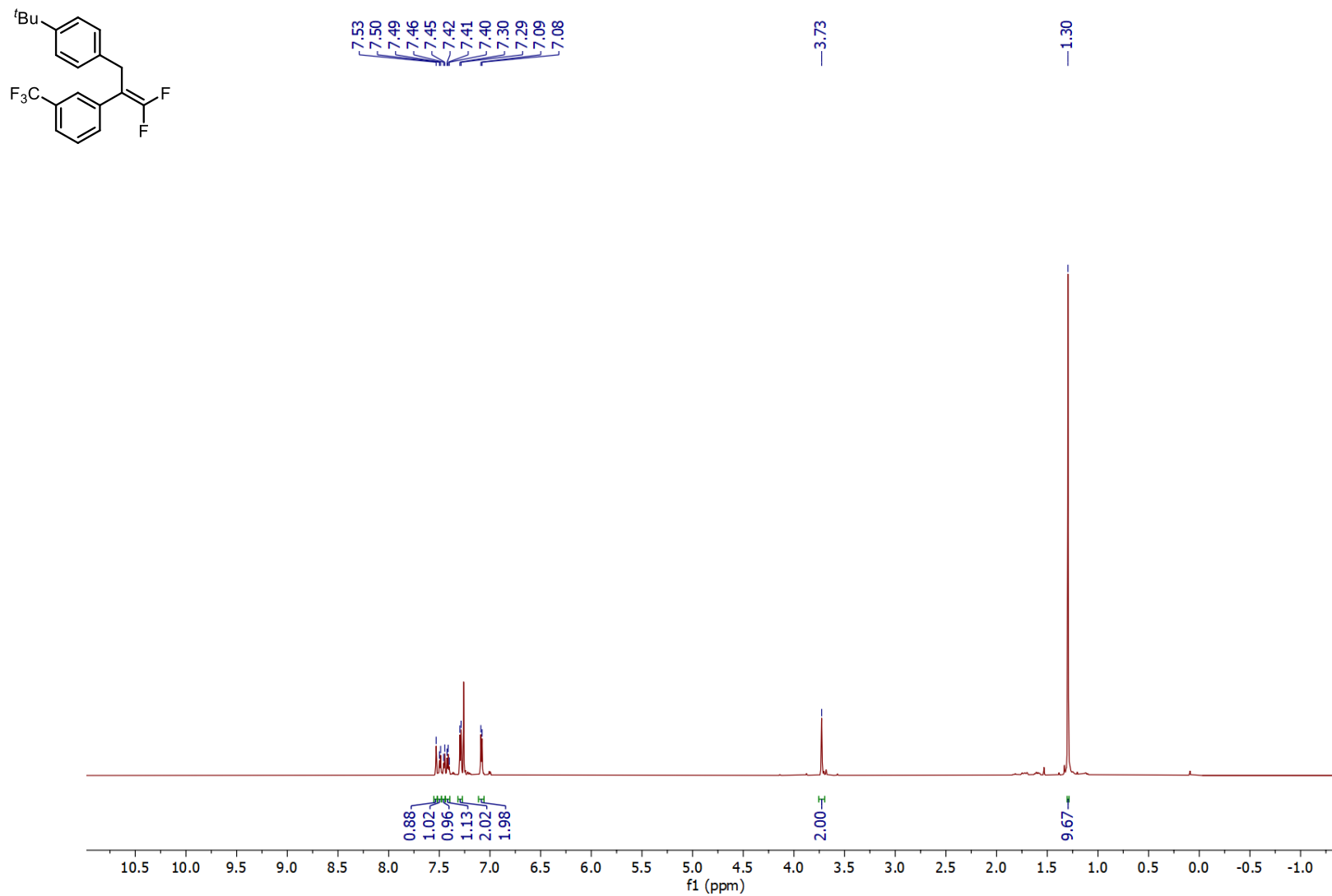
1-(*tert*-Butyl)-4-(3,3-difluoro-2-phenylallyl)benzene 21 $^{13}\text{C}\{^1\text{H}\}$ NMR (176 MHz, Chloroform-*d*)



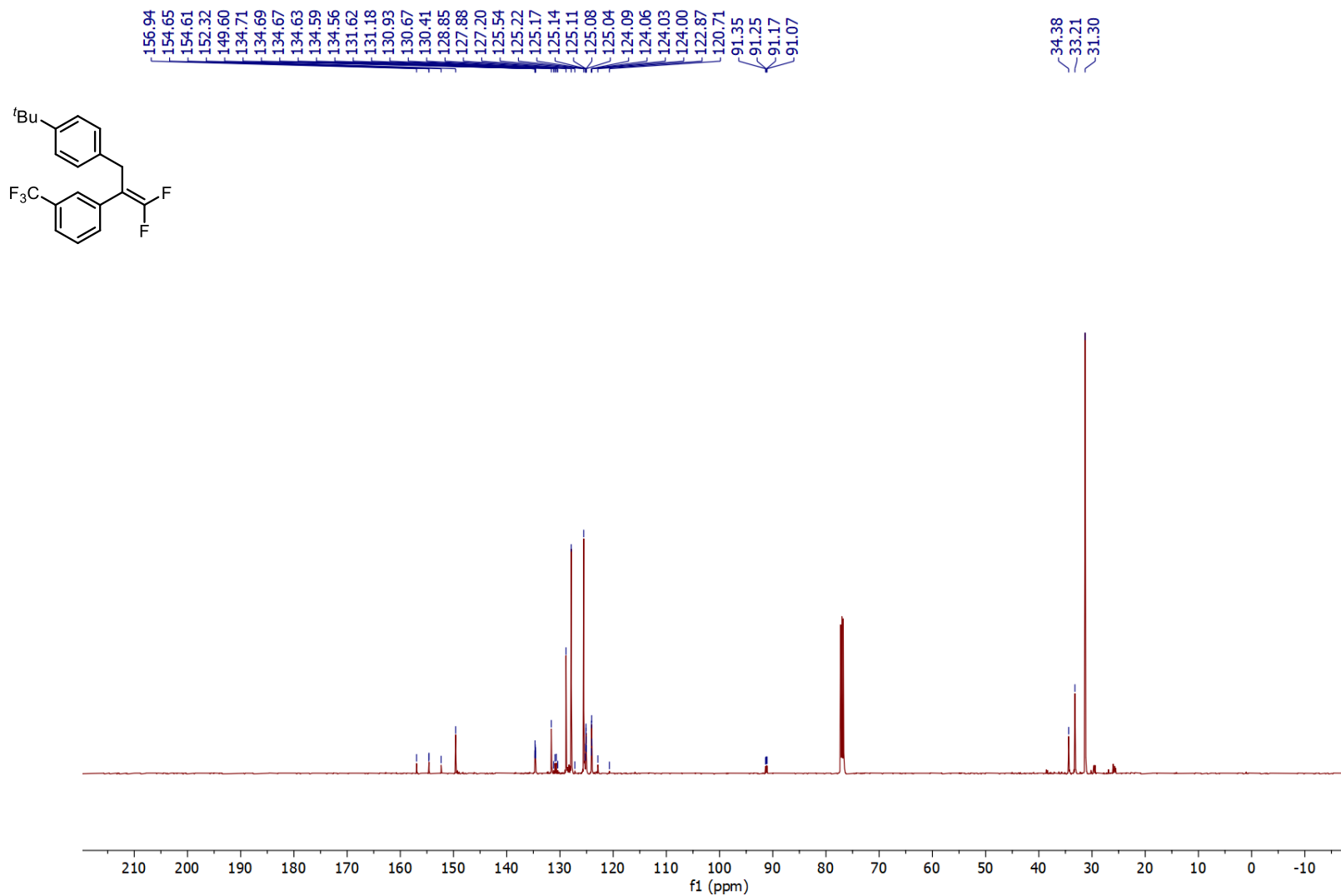
1-(*tert*-Butyl)-4-(3,3-difluoro-2-phenylallyl)benzene 21 ^{19}F NMR (376 MHz, Chloroform-*d*)



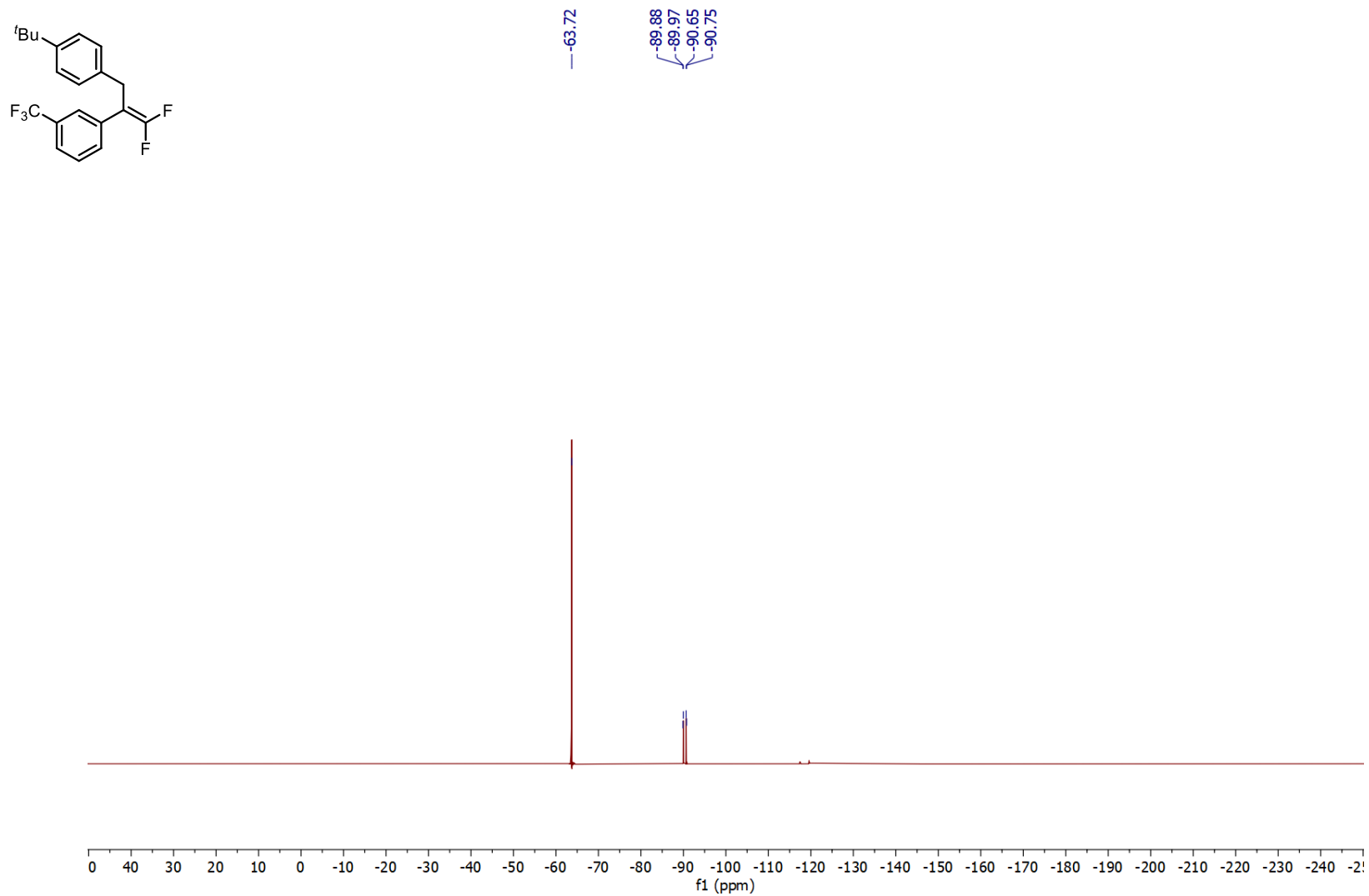
1-(3-(4-(*tert*-Butyl)phenyl)-1,1-difluoroprop-1-en-2-yl)-3-(trifluoromethyl)benzene 2m ¹H NMR (700 MHz, Chloroform-*d*)



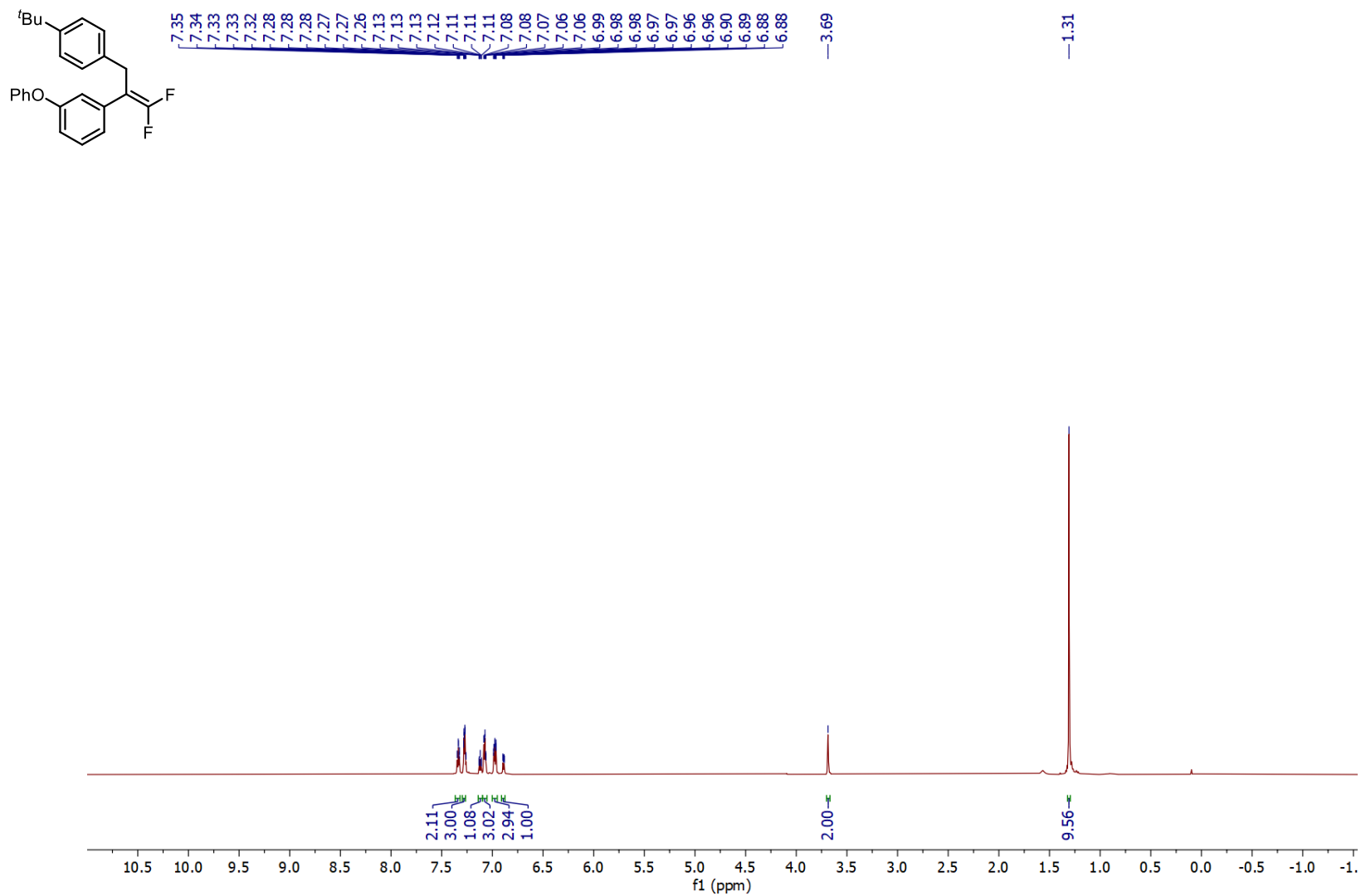
1-(3-(4-(*tert*-Butyl)phenyl)-1,1-difluoroprop-1-en-2-yl)-3-(trifluoromethyl)benzene 2m $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, Chloroform-*d*)



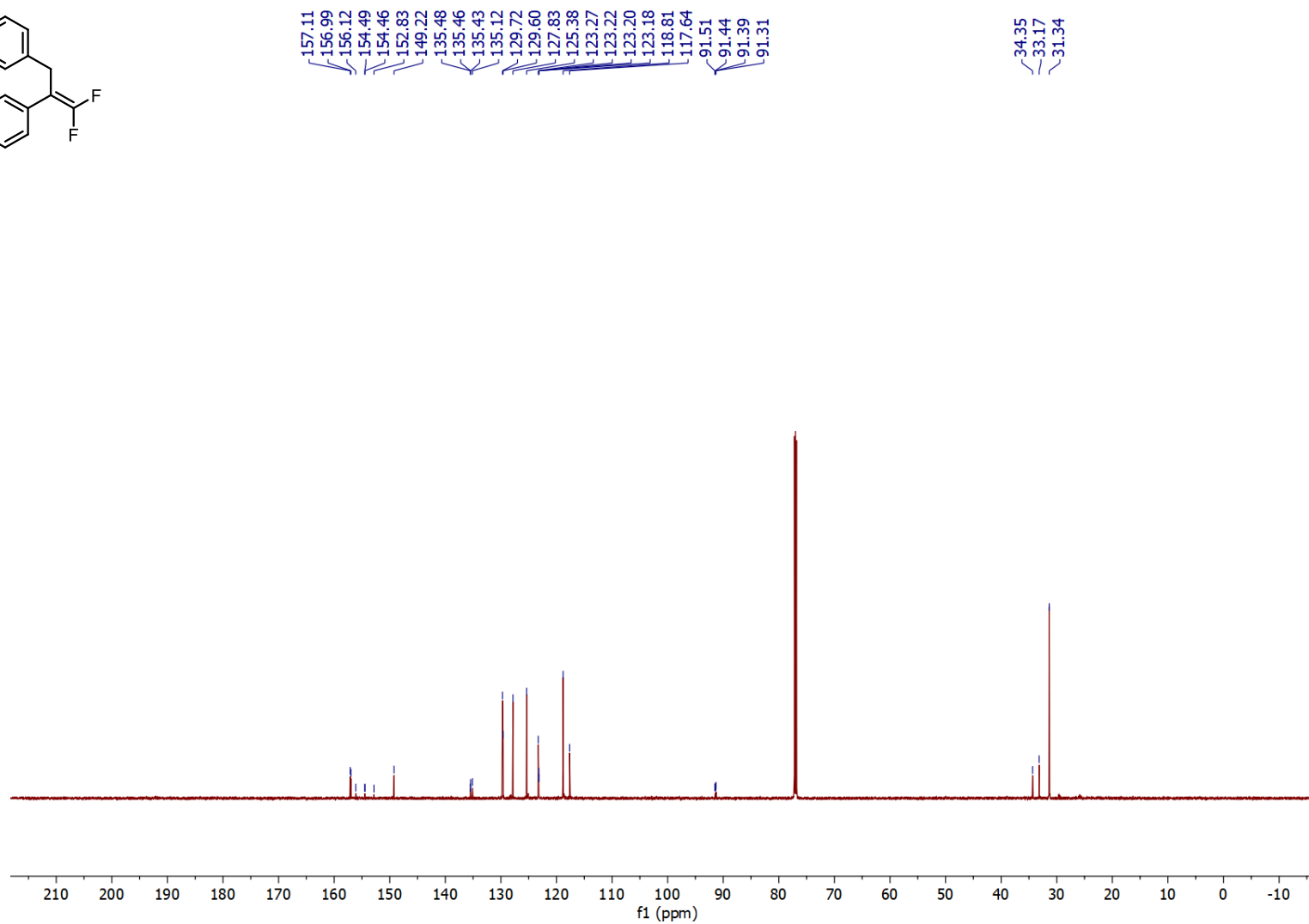
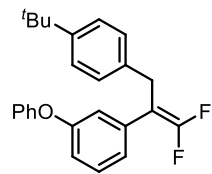
1-(3-(4-(*tert*-Butyl)phenyl)-1,1-difluoroprop-1-en-2-yl)-3-(trifluoromethyl)benzene 2m ^{19}F NMR (376 MHz, Chloroform-*d*)



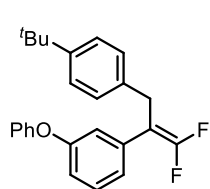
1-(3-(4-(*tert*-Butyl)phenyl)-1,1-difluoroprop-1-en-2-yl)-3-phenoxybenzene 2n ¹H NMR (400 MHz, Chloroform-*d*)



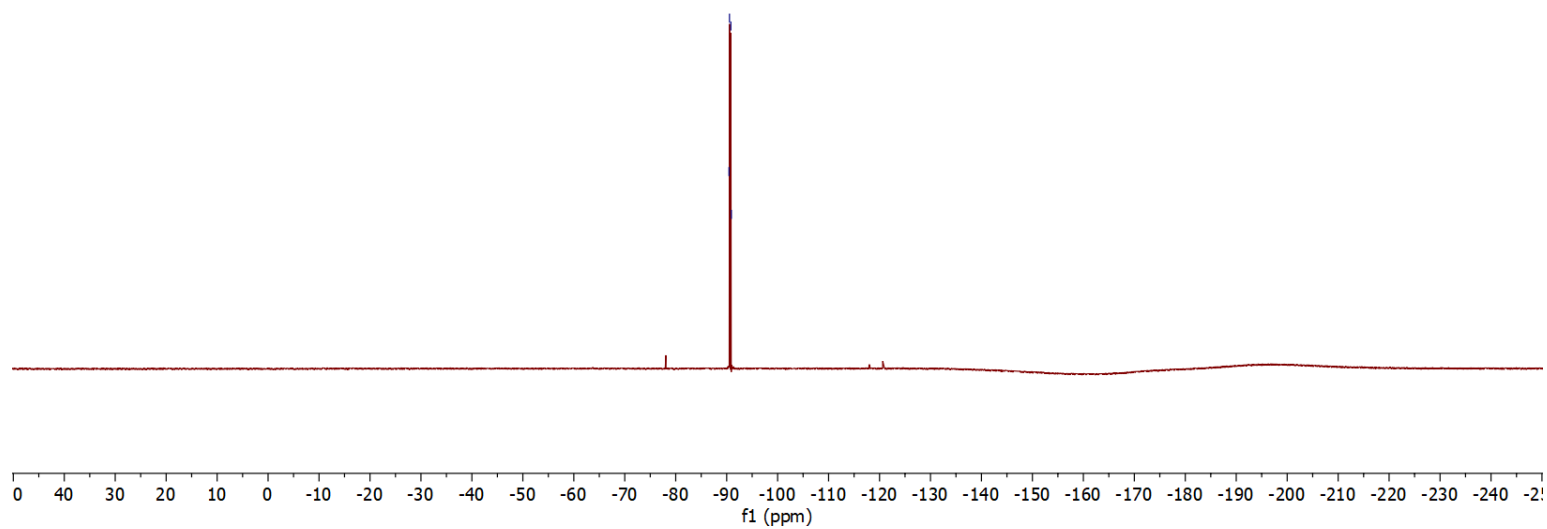
1-(3-(4-(*tert*-Butyl)phenyl)-1,1-difluoroprop-1-en-2-yl)-3-phenoxybenzene 2n $^{13}\text{C}\{^1\text{H}\}$ NMR (176 MHz, Chloroform-*d*)



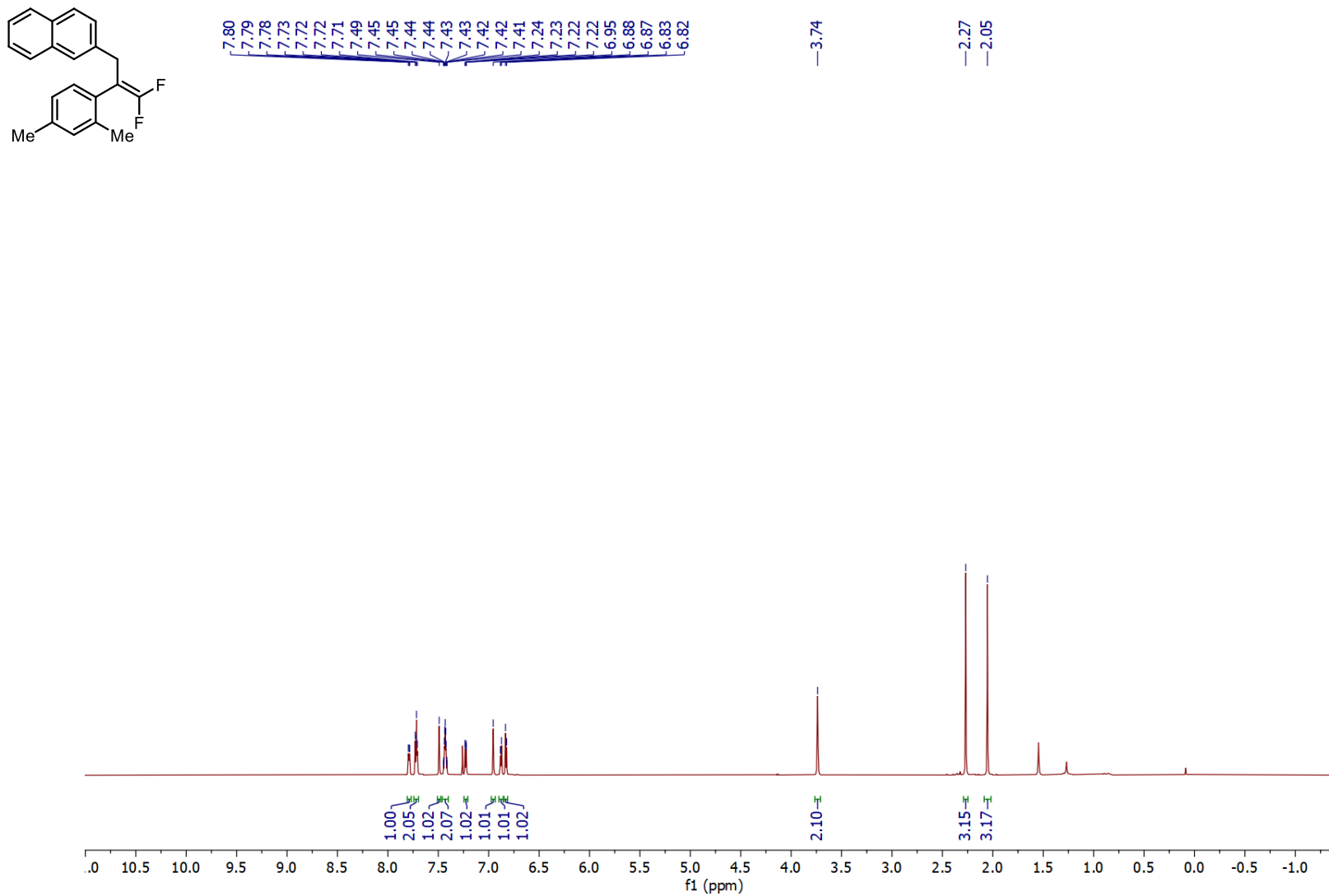
1-(3-(4-(*tert*-Butyl)phenyl)-1,1-difluoroprop-1-en-2-yl)-3-phenoxybenzene 2n ^{19}F NMR (376 MHz, Chloroform-*d*)



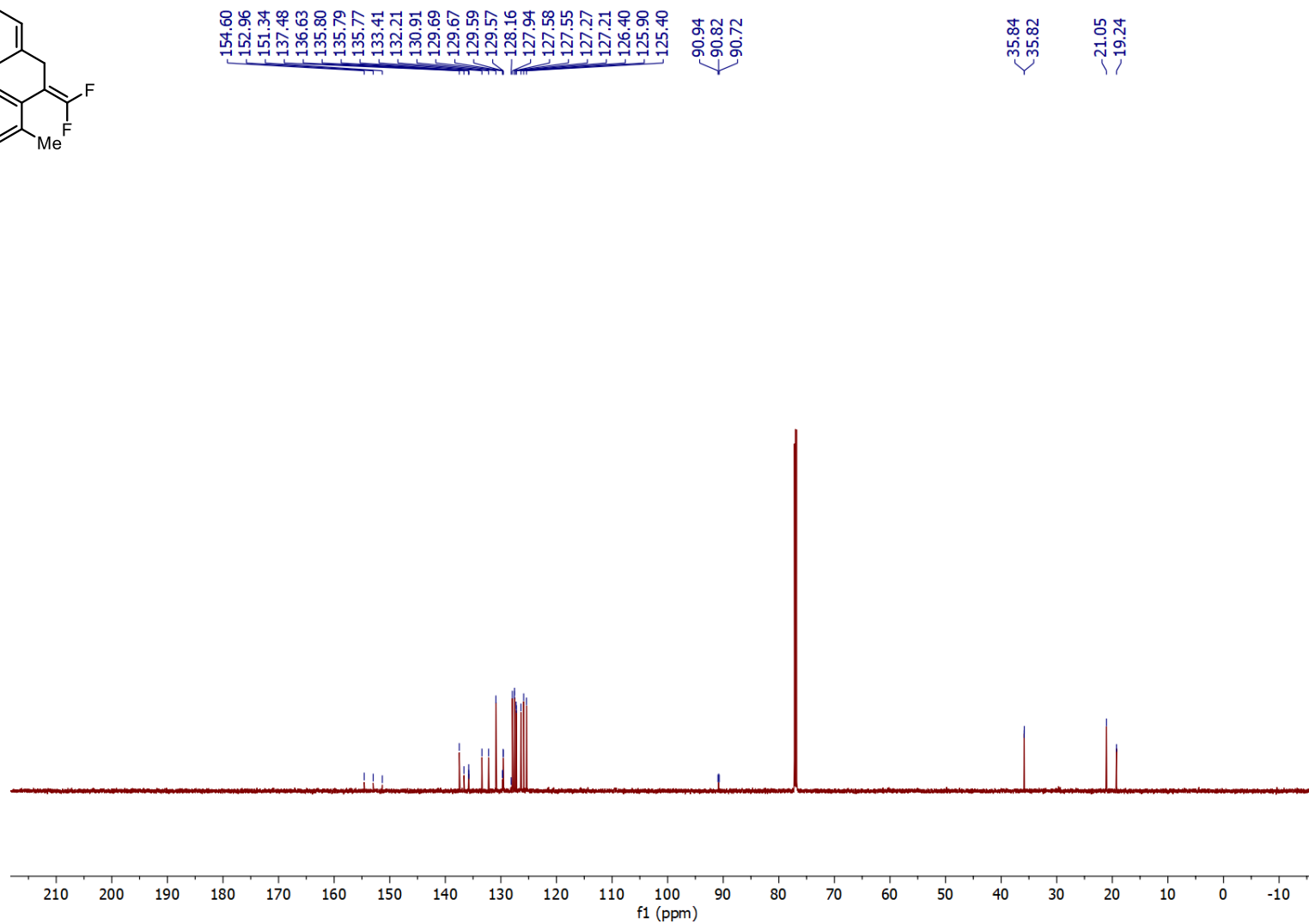
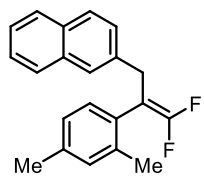
-90.45
-90.55
-90.82
-90.92



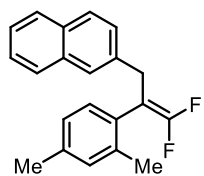
2-(2-(2,4-Dimethylphenyl)-3,3-difluoroallyl)naphthalene 2o ¹H NMR (400 MHz, Chloroform-*d*)



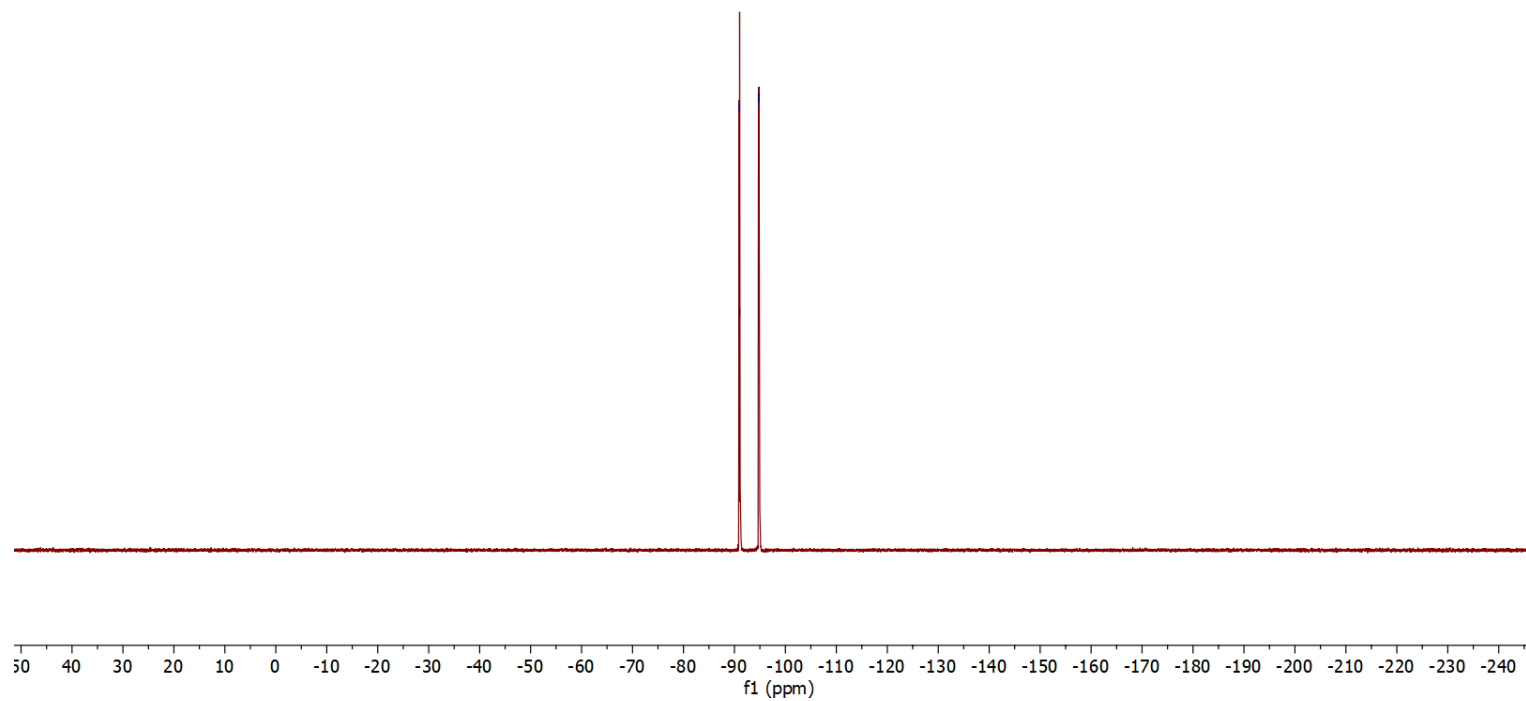
2-(2-(2,4-Dimethylphenyl)-3,3-difluoroallyl)naphthalene 2o $^{13}\text{C}\{^1\text{H}\}$ NMR (176 MHz, Chloroform-*d*)



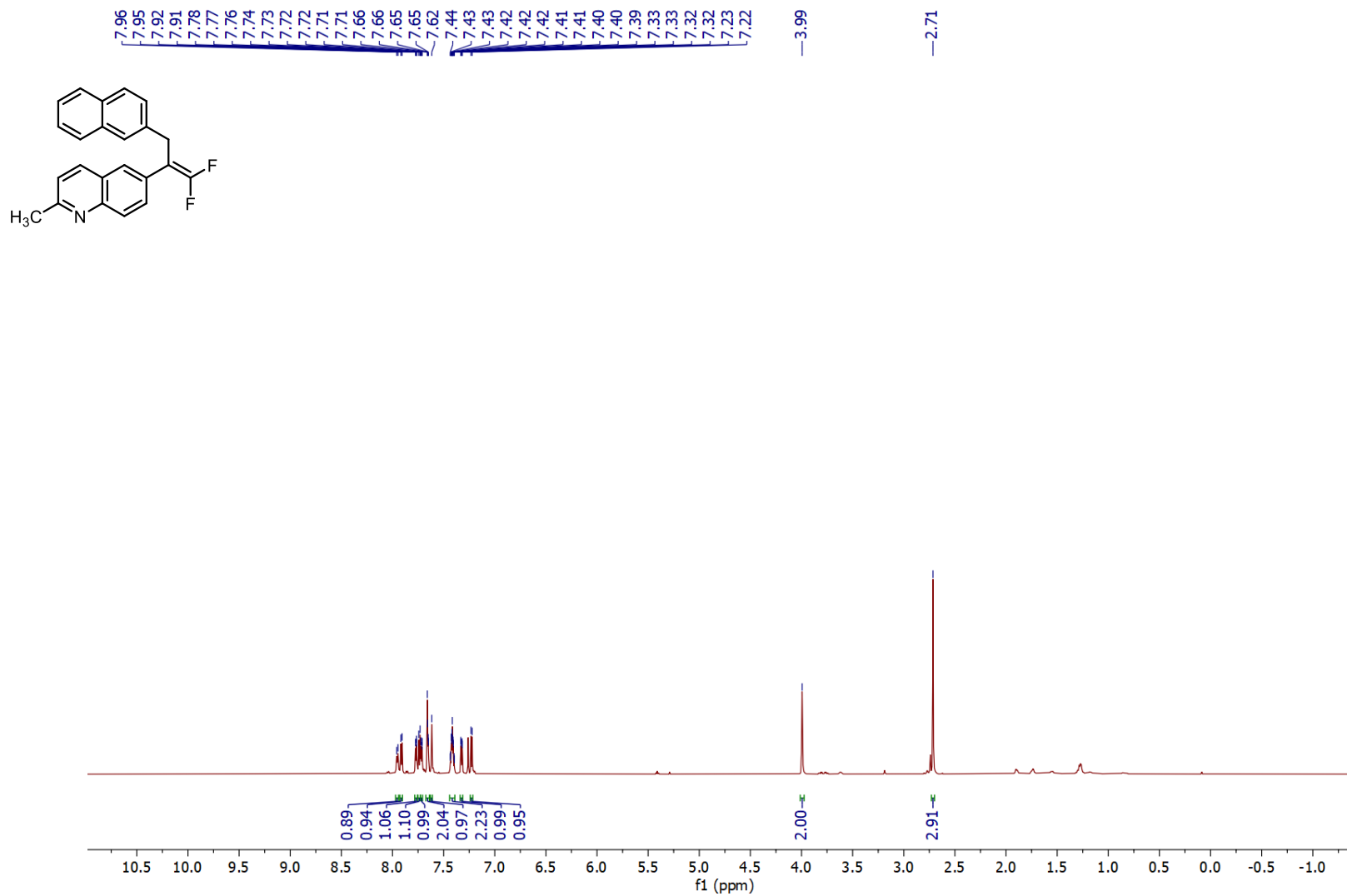
2-(2-(2,4-Dimethylphenyl)-3,3-difluoroallyl)naphthalene 2o ^{19}F NMR (376 MHz, Chloroform-*d*)



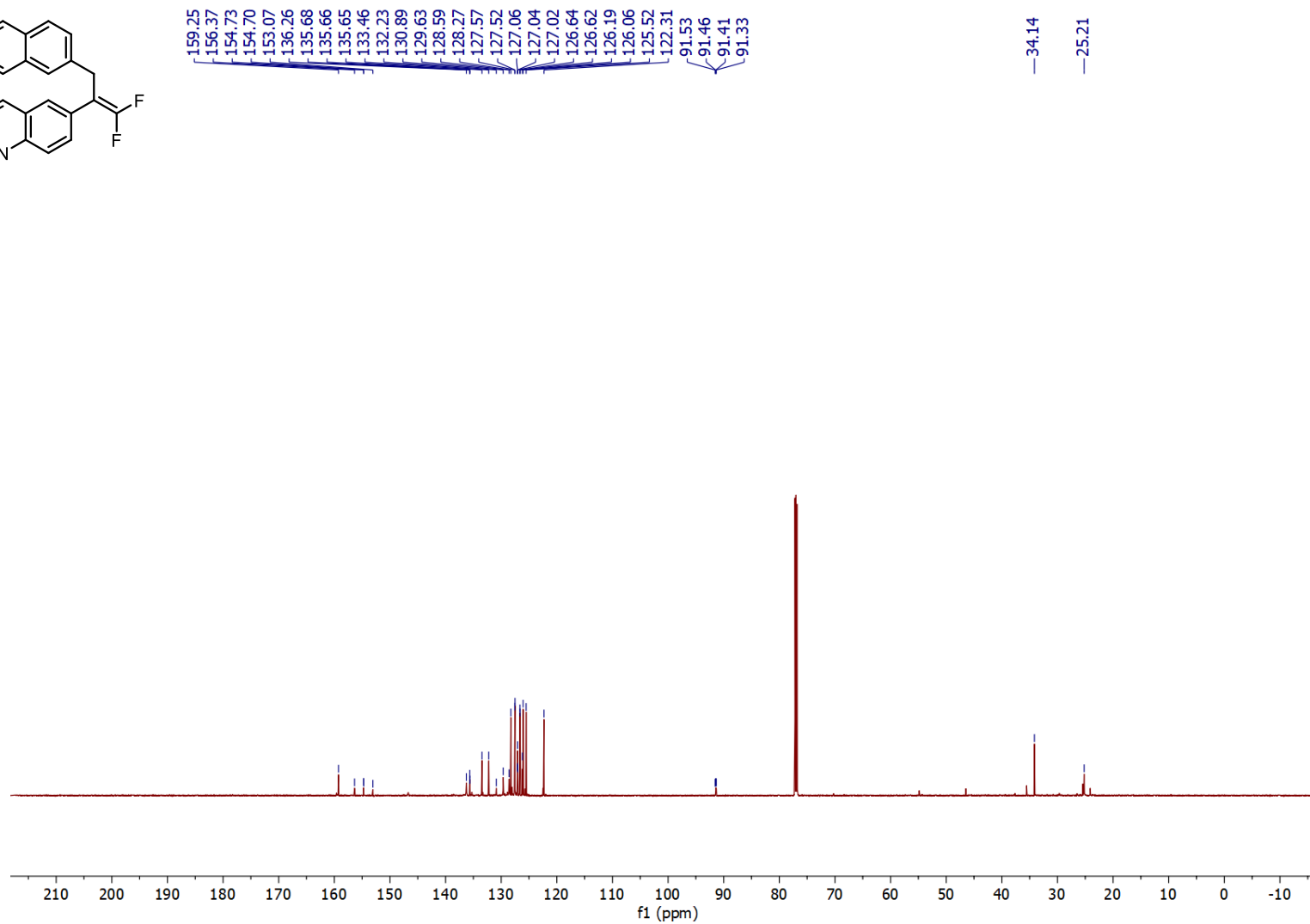
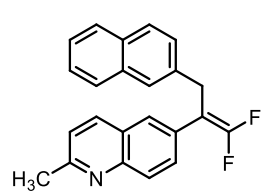
-90.91
-91.04
-94.71
-94.83



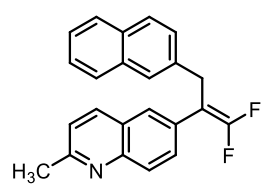
6-(1,1-Difluoro-3-(naphthalen-2-yl)prop-1-en-2-yl)-2-methylquinoline 2p ¹H NMR (700 MHz, Chloroform-*d*)



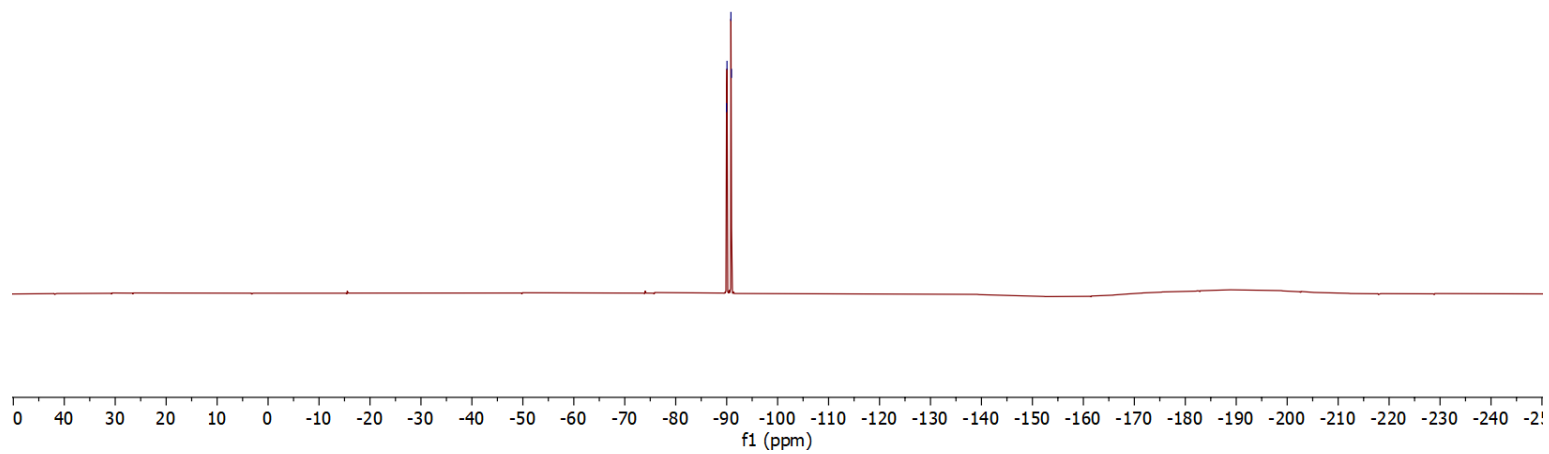
6-(1,1-Difluoro-3-(naphthalen-2-yl)prop-1-en-2-yl)-2-methylquinoline 2p $^{13}\text{C}\{^1\text{H}\}$ NMR (176 MHz, Chloroform-*d*)



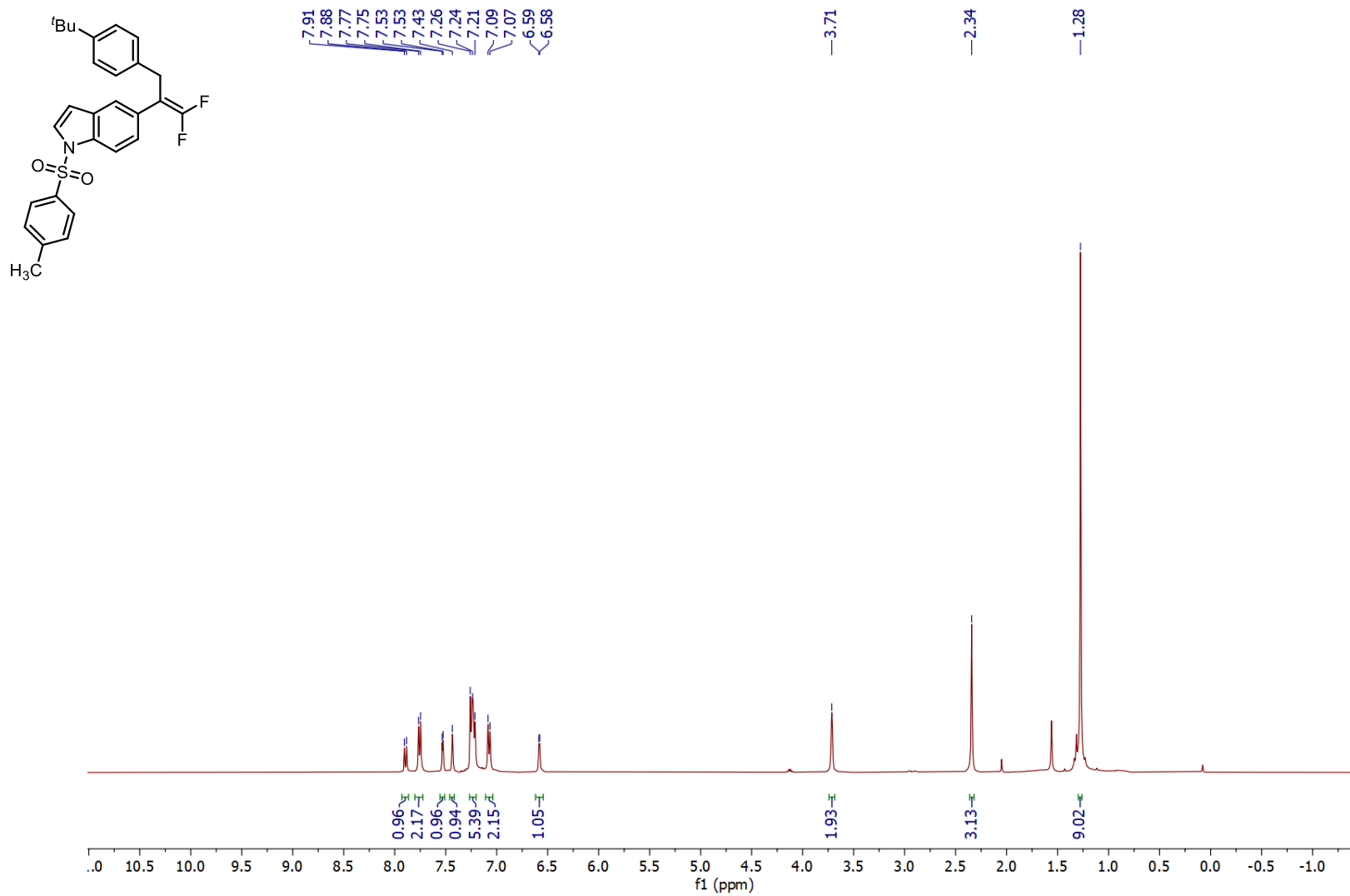
6-(1,1-Difluoro-3-(naphthalen-2-yl)prop-1-en-2-yl)-2-methylquinoline 2p ¹⁹F NMR (376 MHz, Chloroform-*d*)



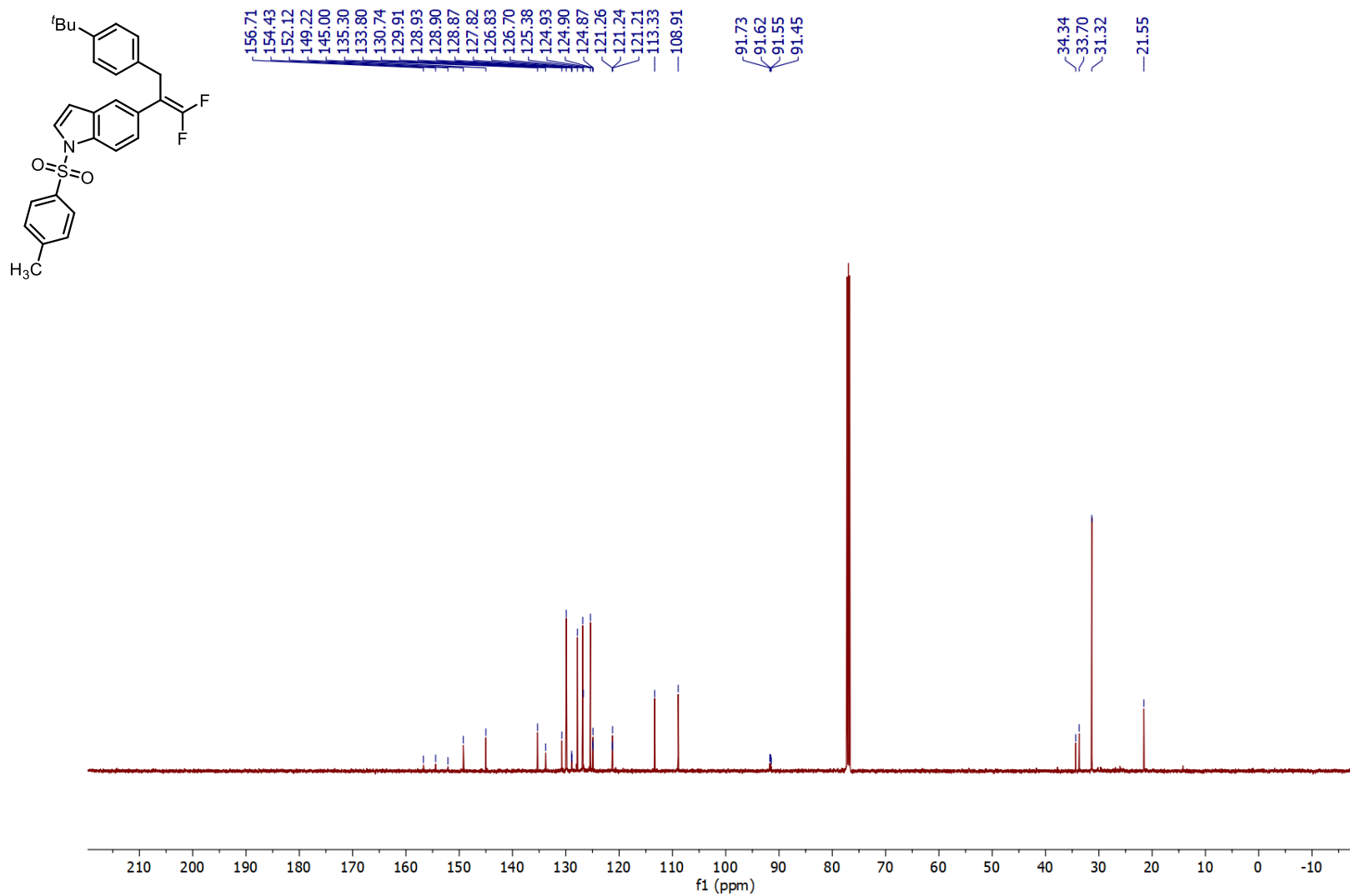
-89.96
-90.07
-90.84
-90.94



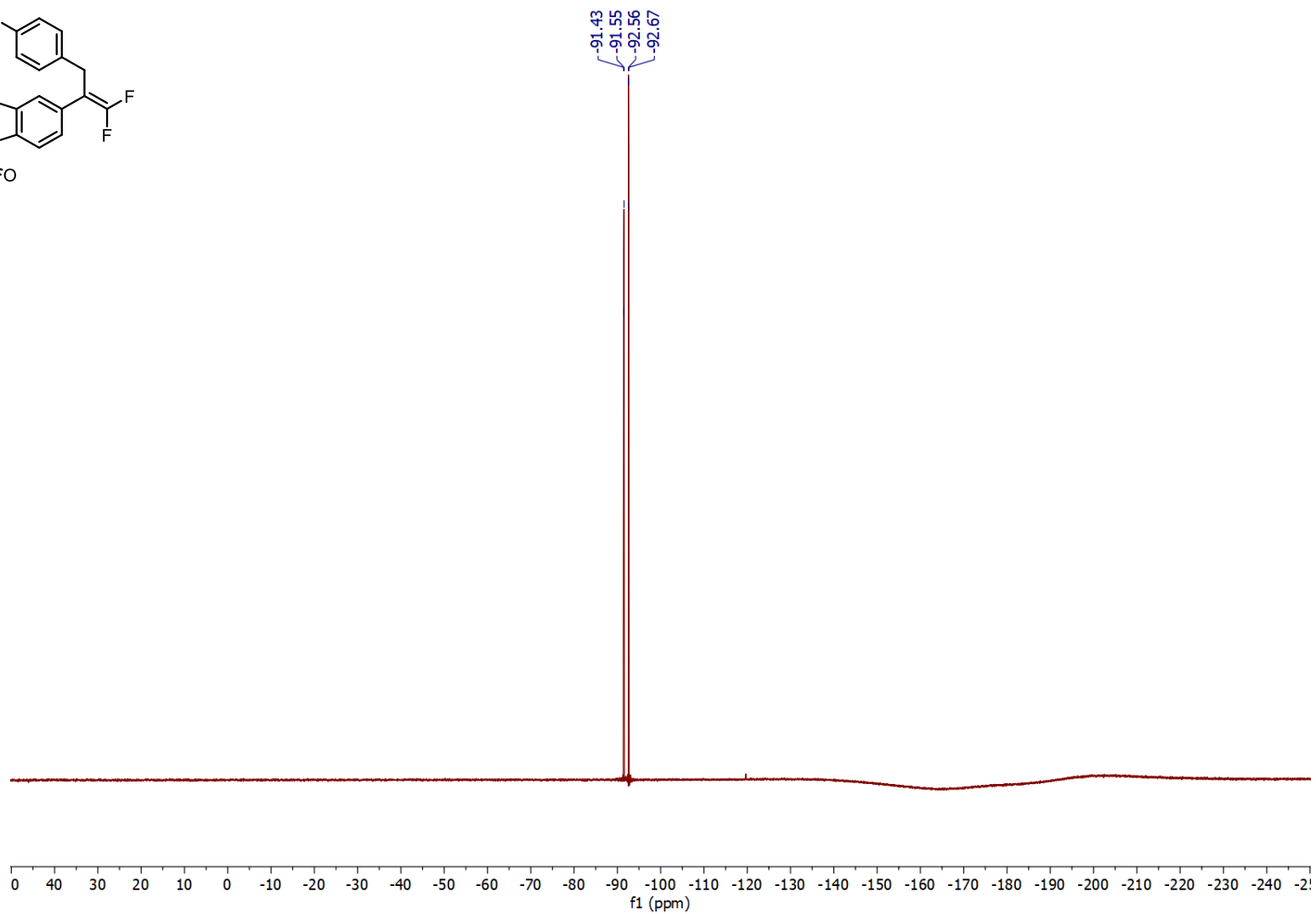
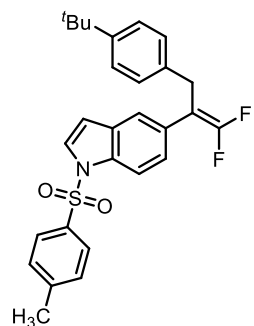
5-(3-(4-(*tert*-Butyl)phenyl)-1,1-difluoroprop-1-en-2-yl)-1H-indole 2q ¹H NMR (400 MHz, Chloroform-*d*)



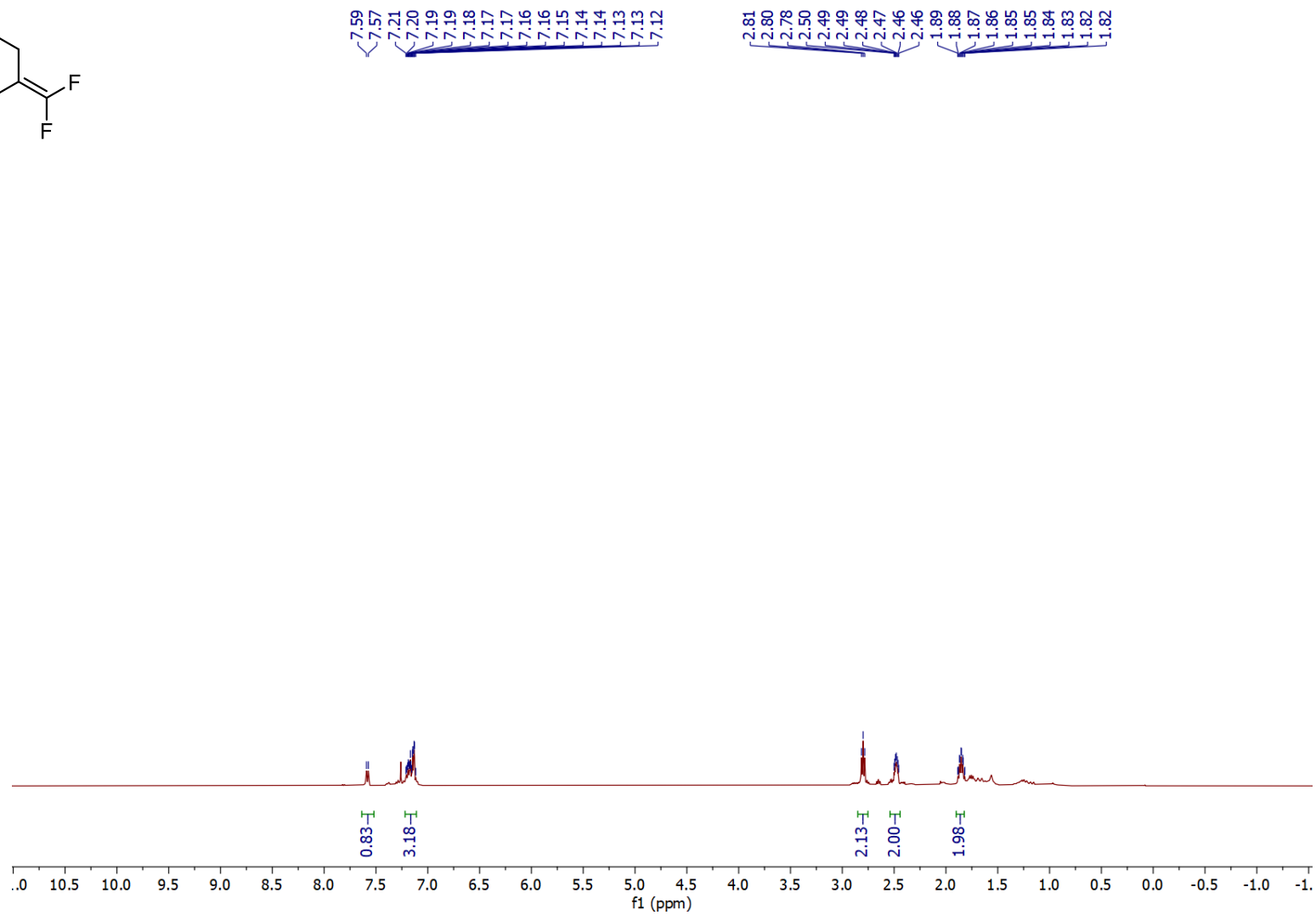
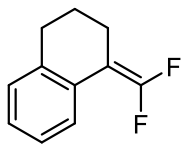
5-(3-(4-(*tert*-Butyl)phenyl)-1,1-difluoroprop-1-en-2-yl)-1H-indole 2q $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, Chloroform-*d*)



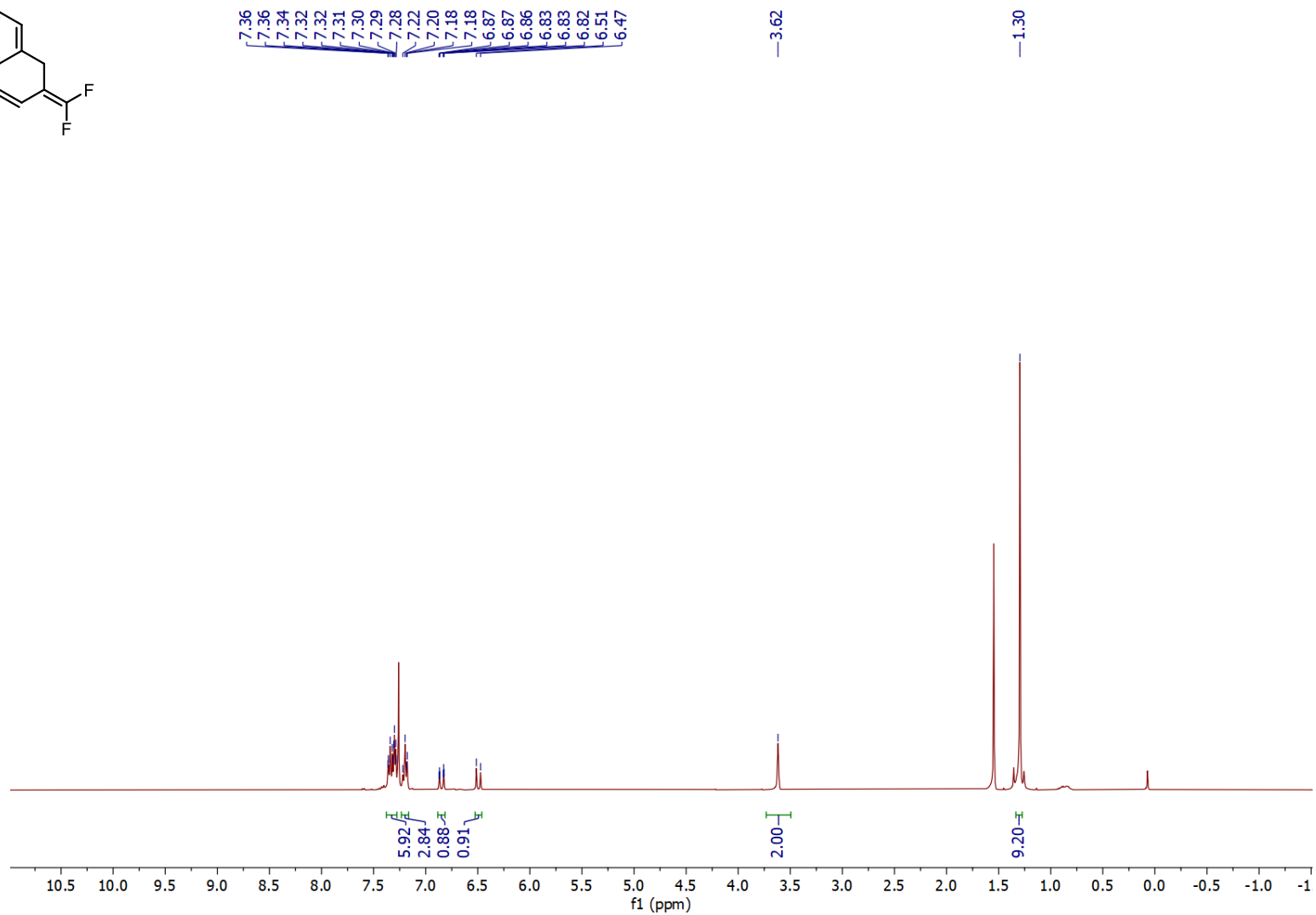
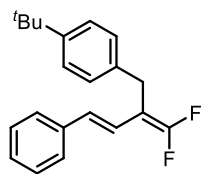
5-(3-(4-(*tert*-Butyl)phenyl)-1,1-difluoroprop-1-en-2-yl)-1H-indole 2q ¹⁹F NMR (376 MHz, Chloroform-*d*)



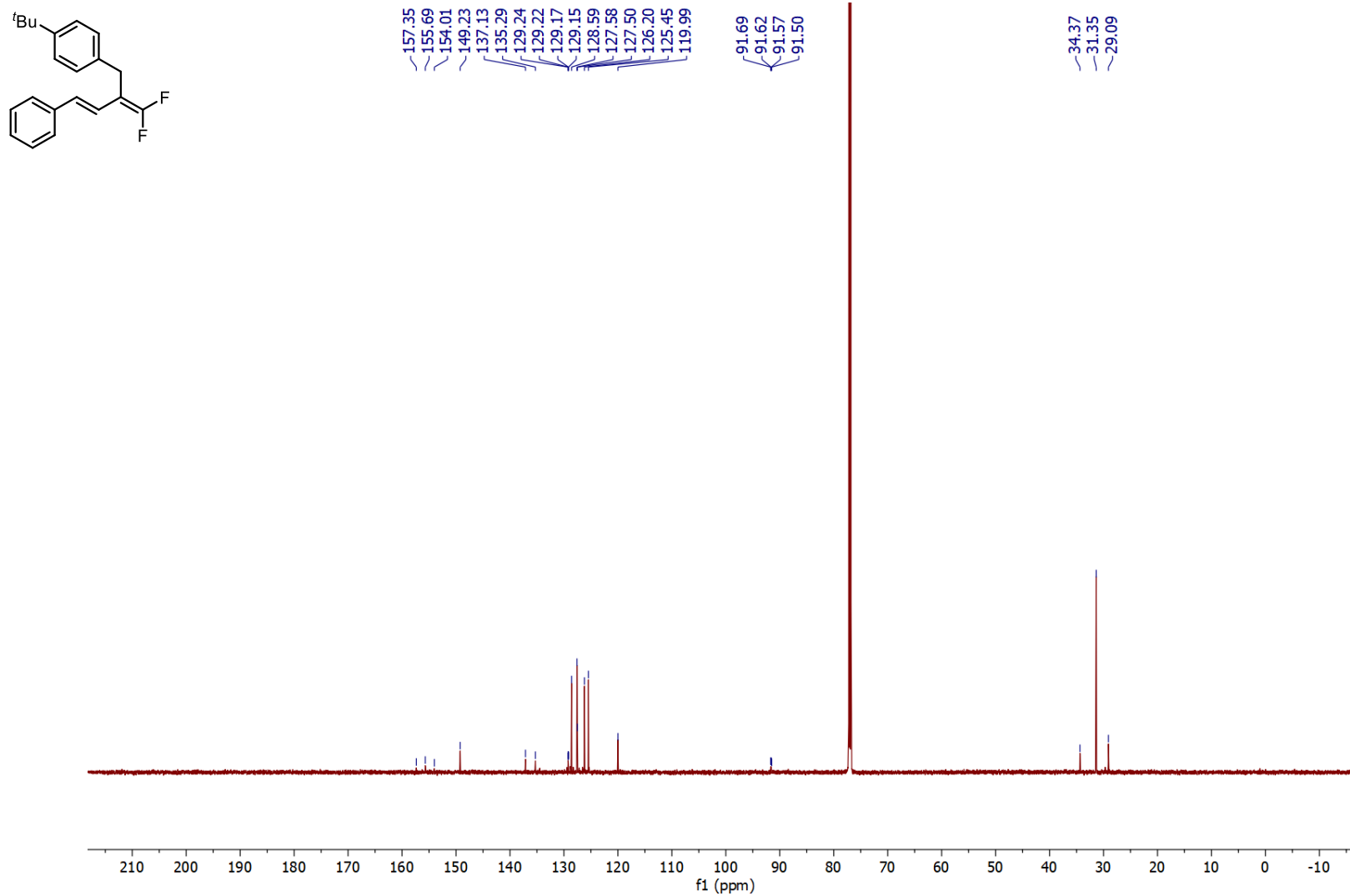
1-(Difluoromethylene)-1,2,3,4-tetrahydronaphthalene 2r ¹H NMR (400 MHz, Chloroform-*d*)



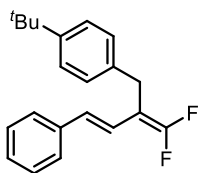
(E)-1-(*tert*-Butyl)-4-(2-(difluoromethylene)-4-phenylbut-3-en-1-yl)benzene 2s ¹H NMR (400 MHz, Chloroform-*d*)



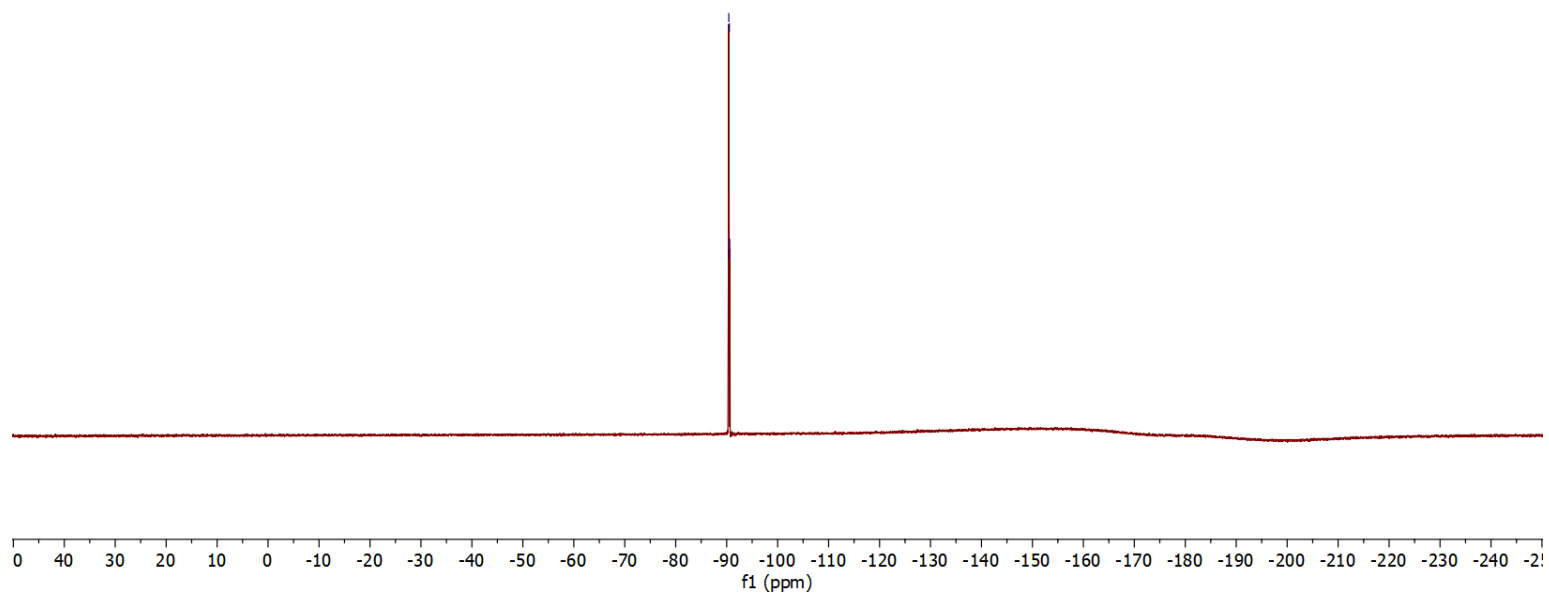
(E)-1-(tert-Butyl)-4-(2-(difluoromethylene)-4-phenylbut-3-en-1-yl)benzene 2s $^{13}\text{C}\{^1\text{H}\}$ NMR (176 MHz, Chloroform-*d*)



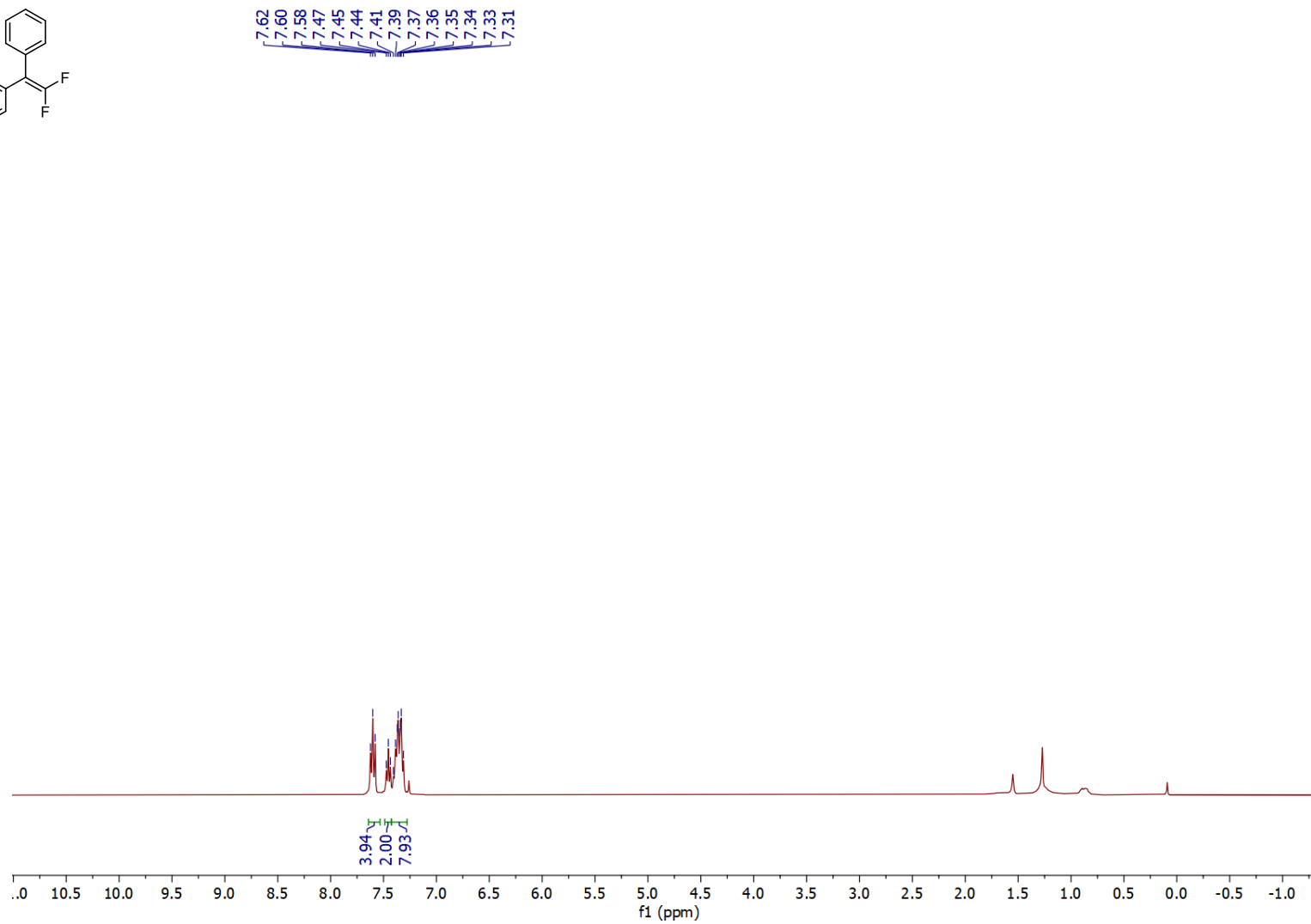
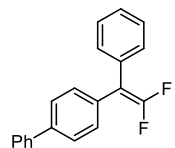
(E)-1-(tert-Butyl)-4-(2-(difluoromethylene)-4-phenylbut-3-en-1-yl)benzene 2s ^{19}F NMR (376 MHz, Chloroform-*d*)



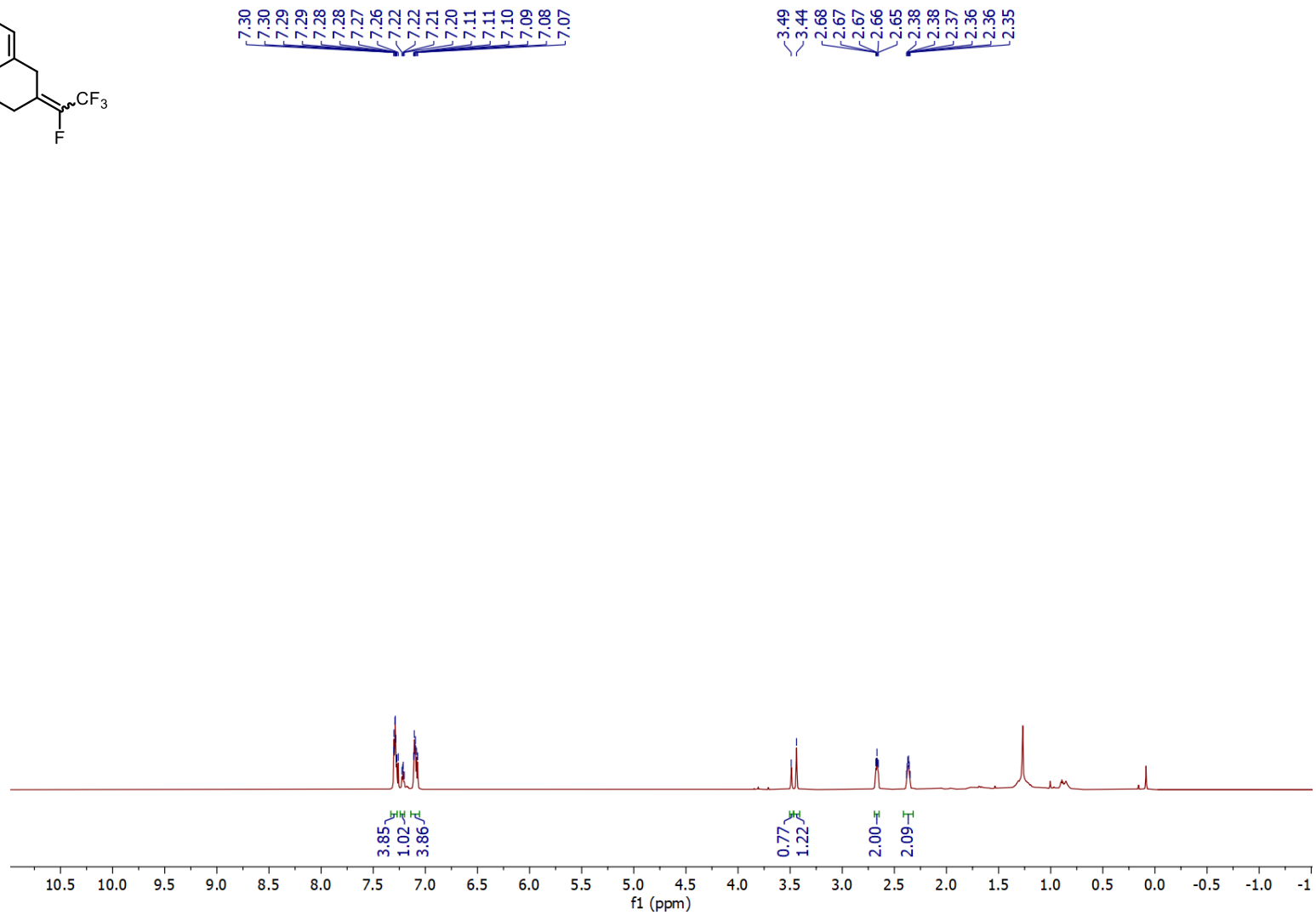
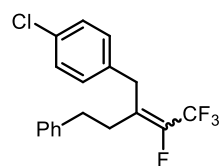
-90.34
-90.41
-90.52
-90.60



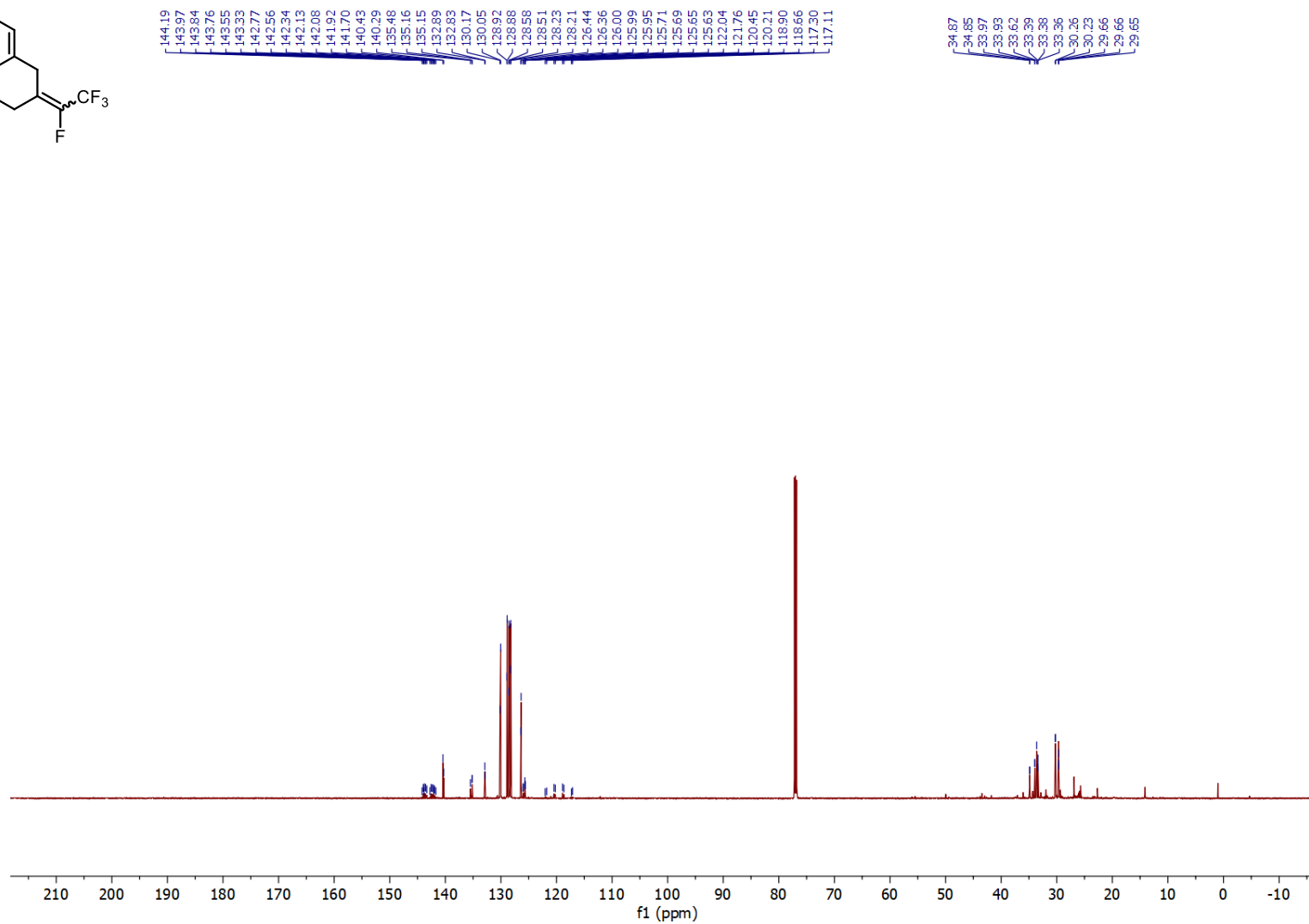
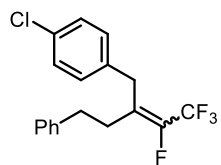
4-(2,2-Difluoro-1-phenylvinyl)-1,1'-biphenyl 2t ¹H NMR (400 MHz, Chloroform-d)



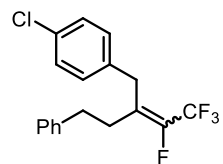
1-Chloro-4-(3,4,4,4-tetrafluoro-2-phenethylbut-2-en-1-yl)benzene 2u ¹H NMR (700 MHz, Chloroform-*d*)



1-Chloro-4-(3,4,4,4-tetrafluoro-2-phenethylbut-2-en-1-yl)benzene 2u $^{13}\text{C}\{^1\text{H}\}$ NMR (176 MHz, Chloroform-*d*)

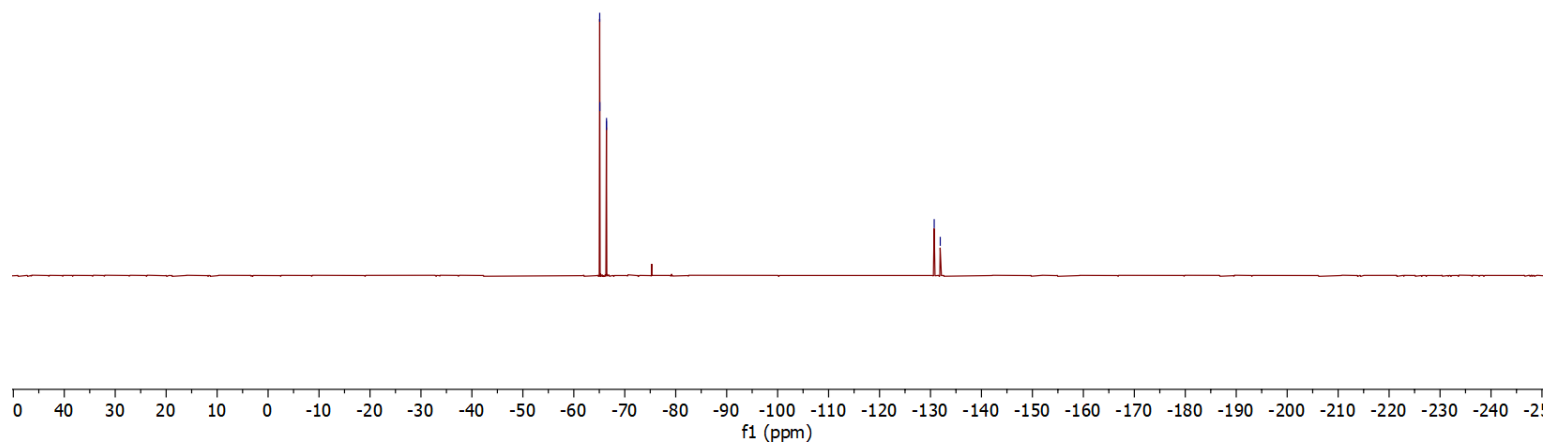


1-Chloro-4-(3,4,4,4-tetrafluoro-2-phenethylbut-2-en-1-yl)benzene 2u ¹⁹F NMR (376 MHz, Chloroform-*d*)

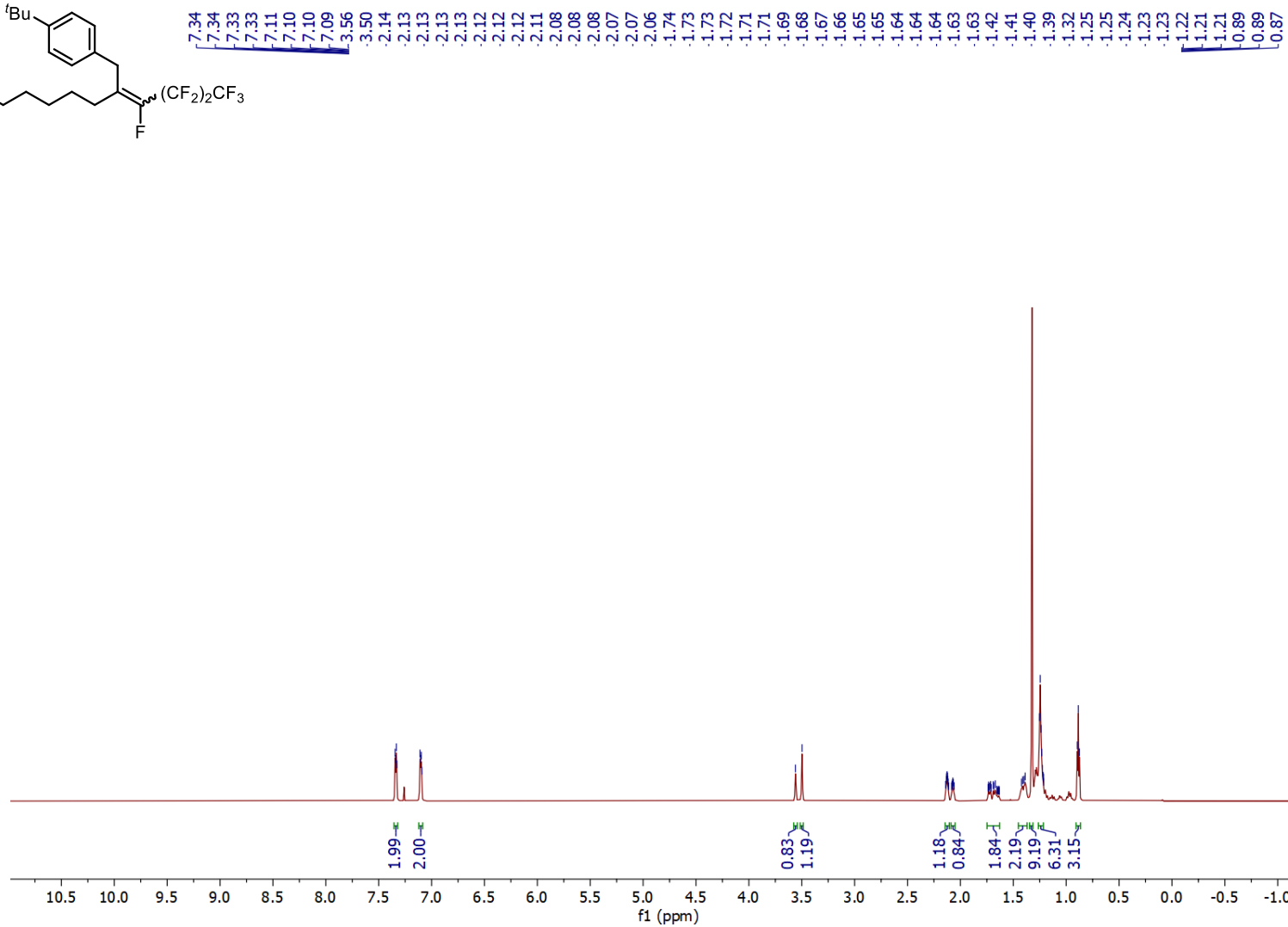
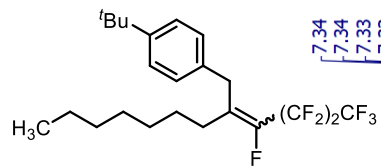


-65.08
-65.11
-66.40
-66.42

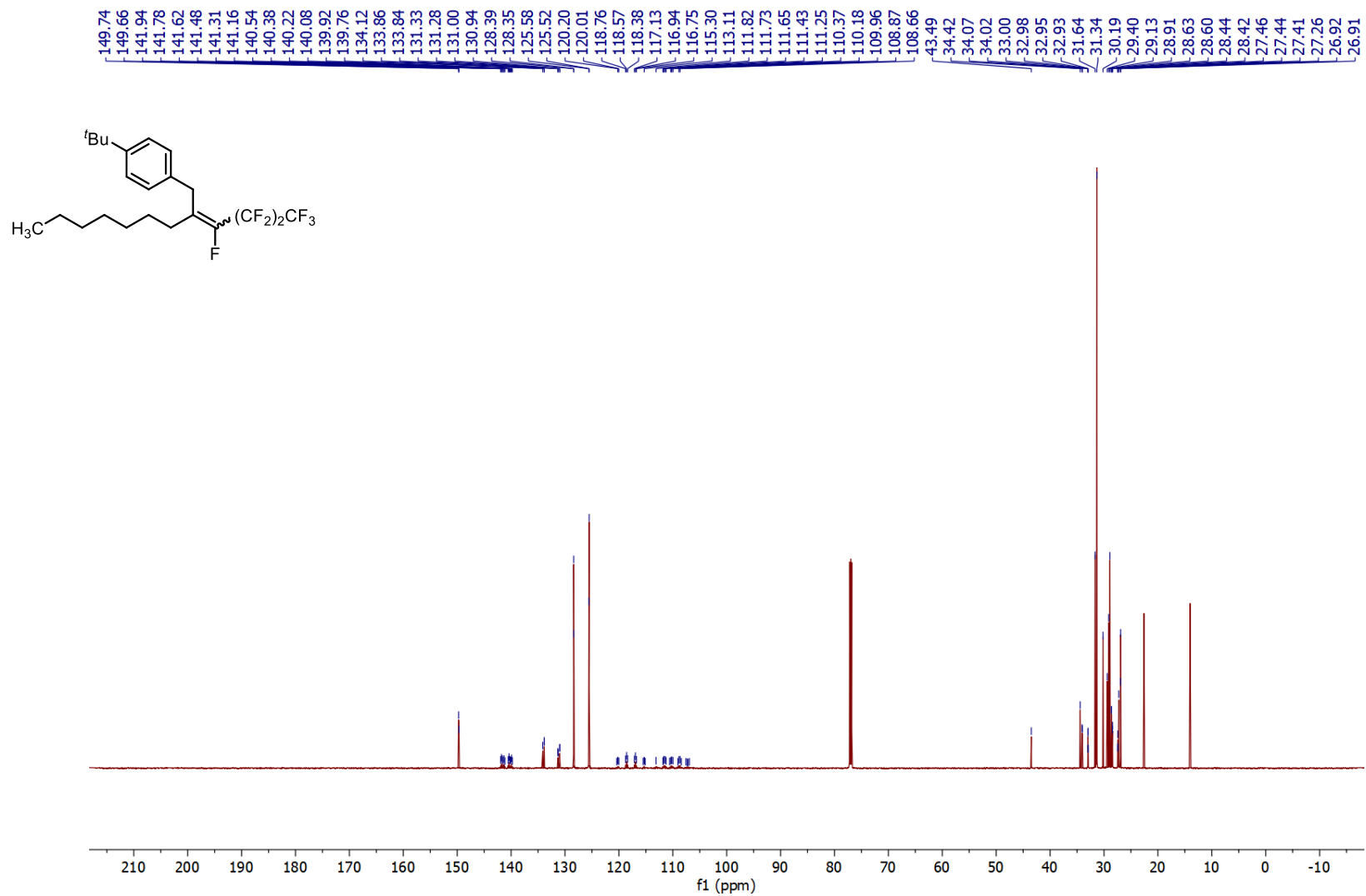
-130.73
-131.92



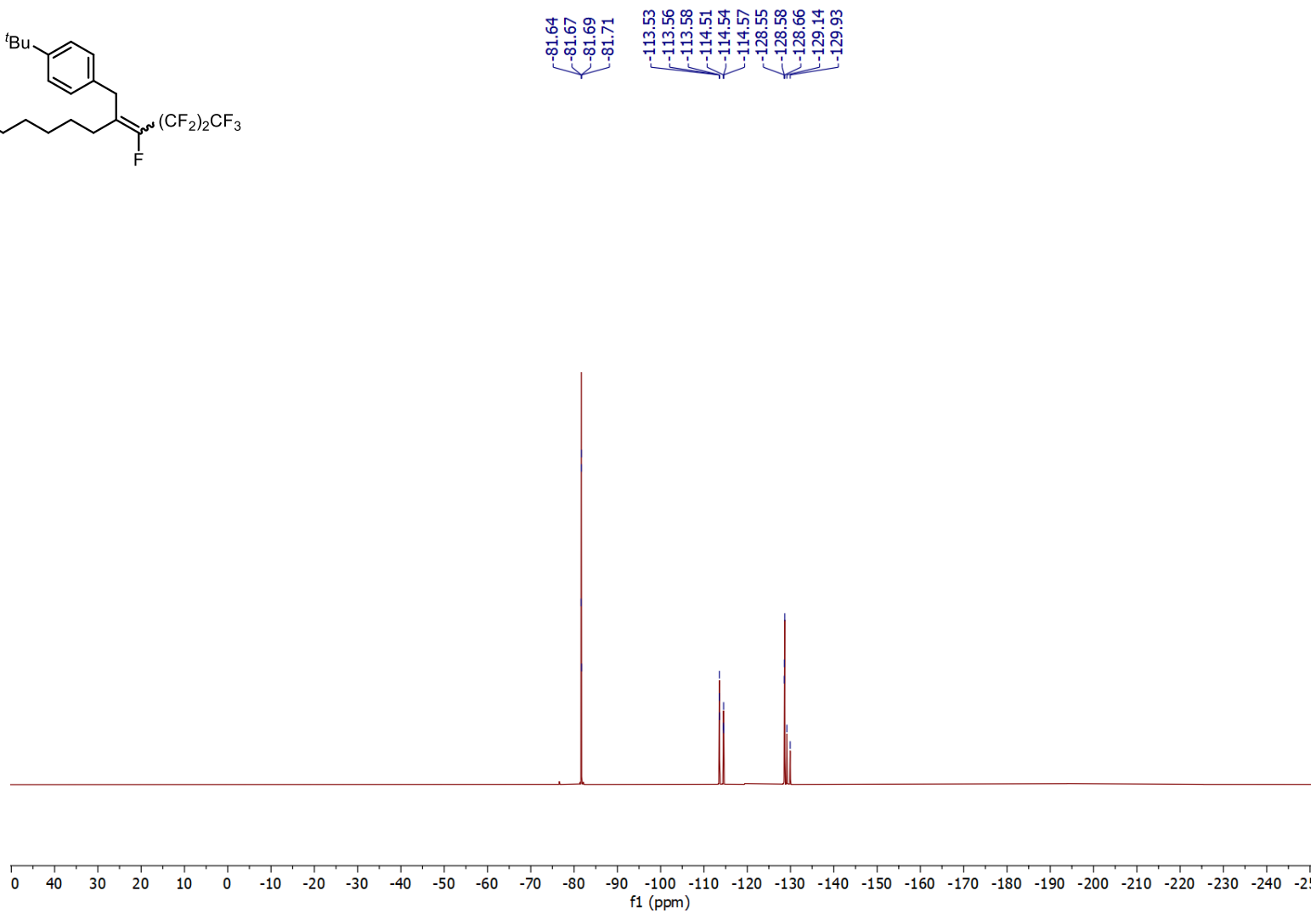
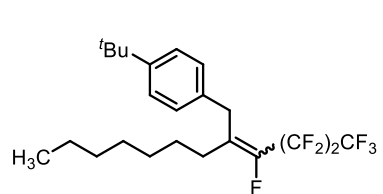
1-(*tert*-Butyl)-4-(2-(perfluorobutylidene)nonyl)benzene 2v ¹H NMR (700 MHz, Chloroform-*d*)



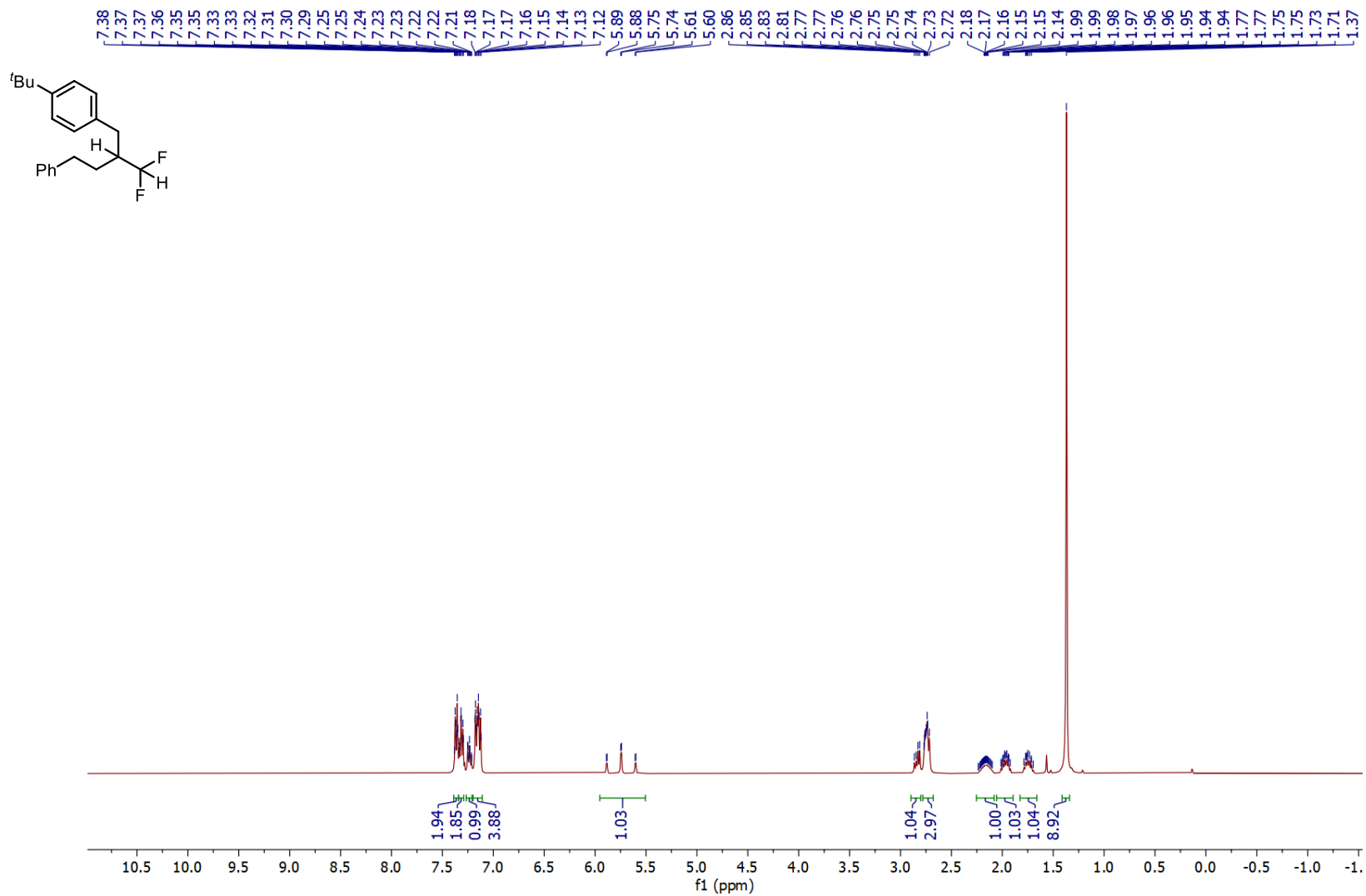
1-(*tert*-Butyl)-4-(2-(perfluorobutylidene)nonyl)benzene 2v $^{13}\text{C}\{^1\text{H}\}$ NMR (176 MHz, Chloroform-*d*)



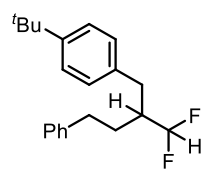
1-(*tert*-Butyl)-4-(2-(perfluorobutylidene)nonyl)benzene 2v ^{19}F NMR (376 MHz, Chloroform-*d*)



1-(*tert*-Butyl)-4-(2-(difluoromethyl)-4-phenylbutyl)benzene 3 ¹H NMR (400 MHz, Chloroform-*d*)

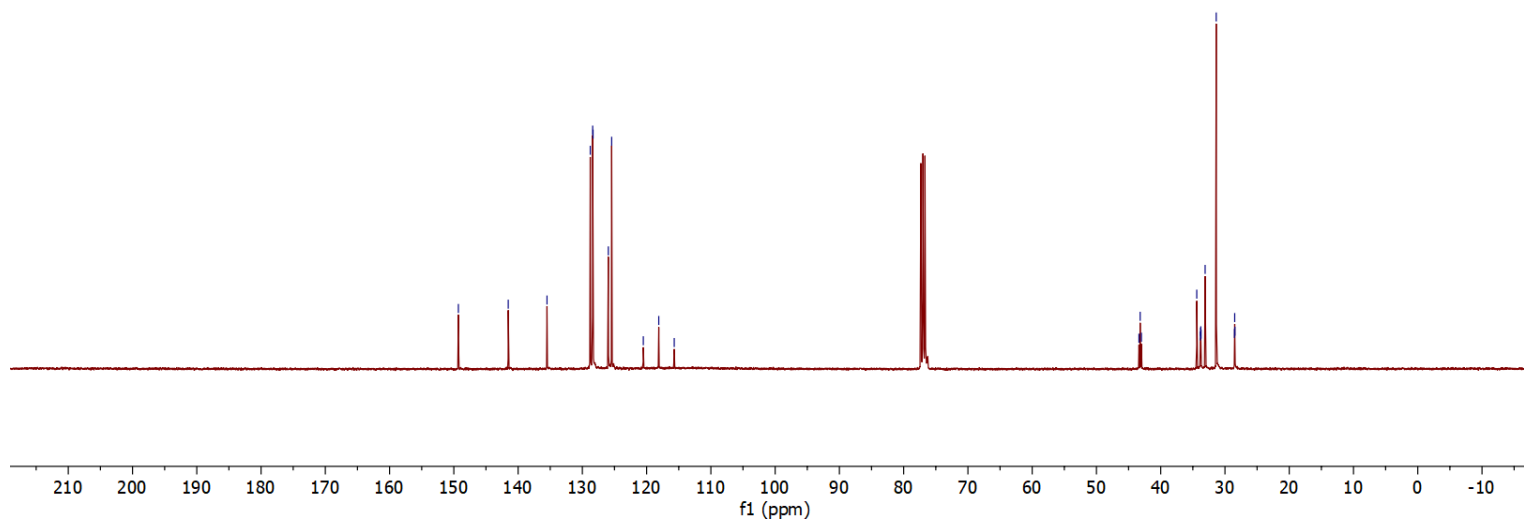


1-(*tert*-Butyl)-4-(2-(difluoromethyl)-4-phenylbutyl)benzene $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, Chloroform-*d*)

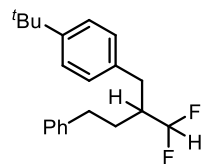


149.29
141.53
135.50
128.77
128.39
128.33
125.96
125.44
120.52
118.11
115.70

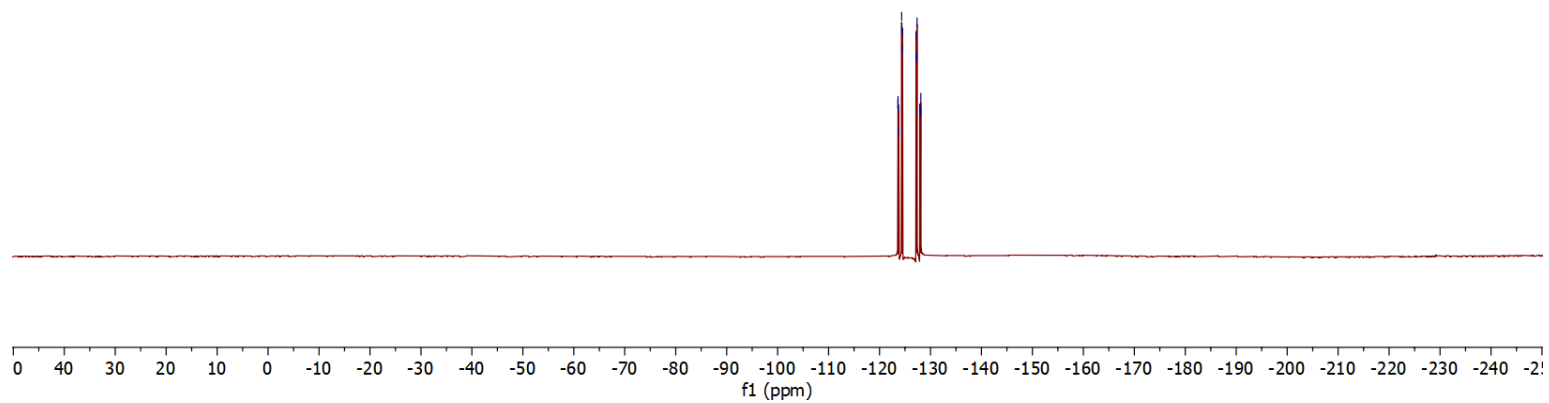
43.38
43.19
43.01
34.39
33.82
33.79
33.76
33.72
33.09
31.36
28.52
28.49
28.45



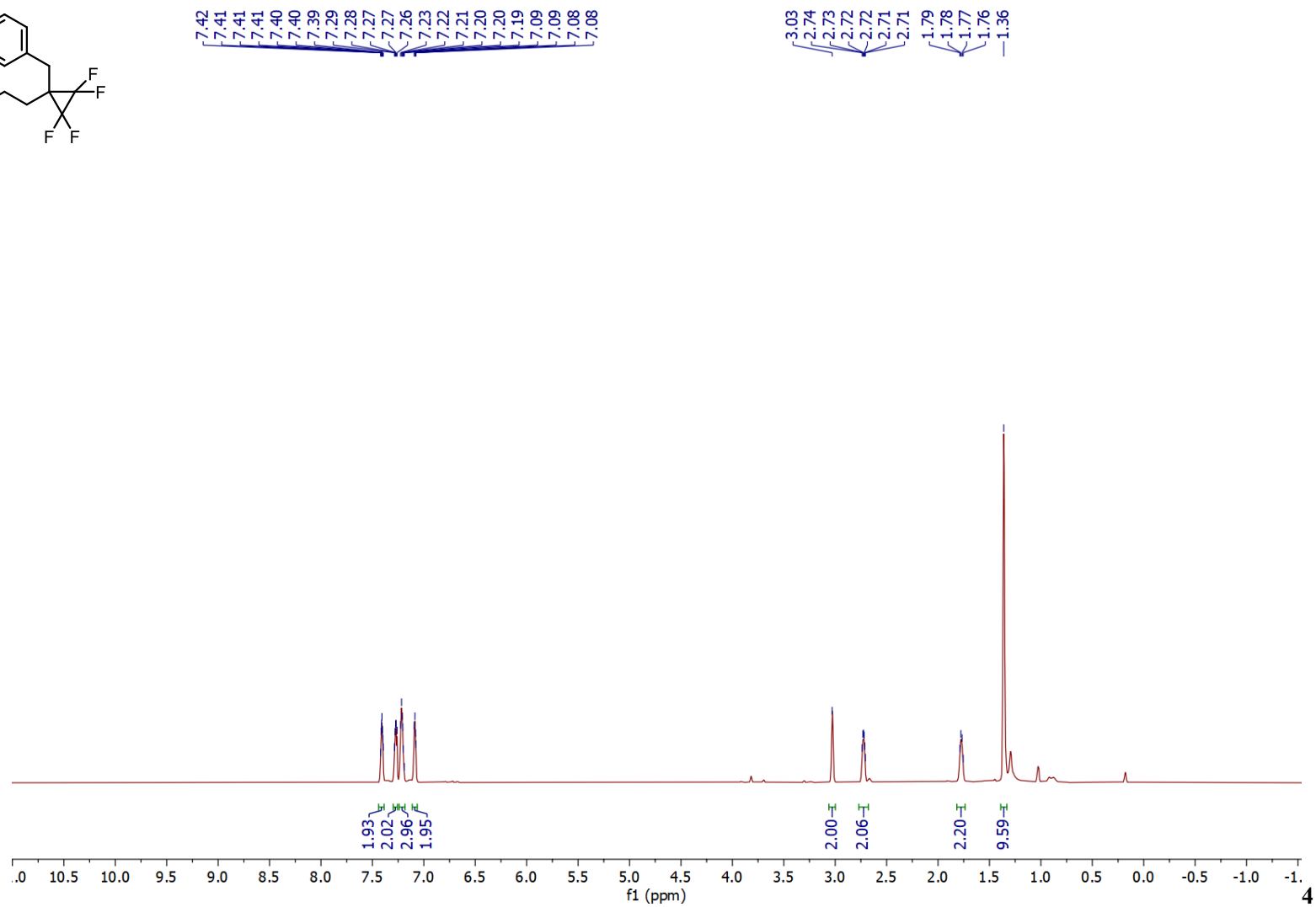
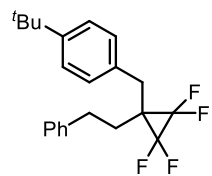
1-(*tert*-Butyl)-4-(2-(difluoromethyl)-4-phenylbutyl)benzene 3 ¹⁹F NMR (376 MHz, Chloroform-*d*)



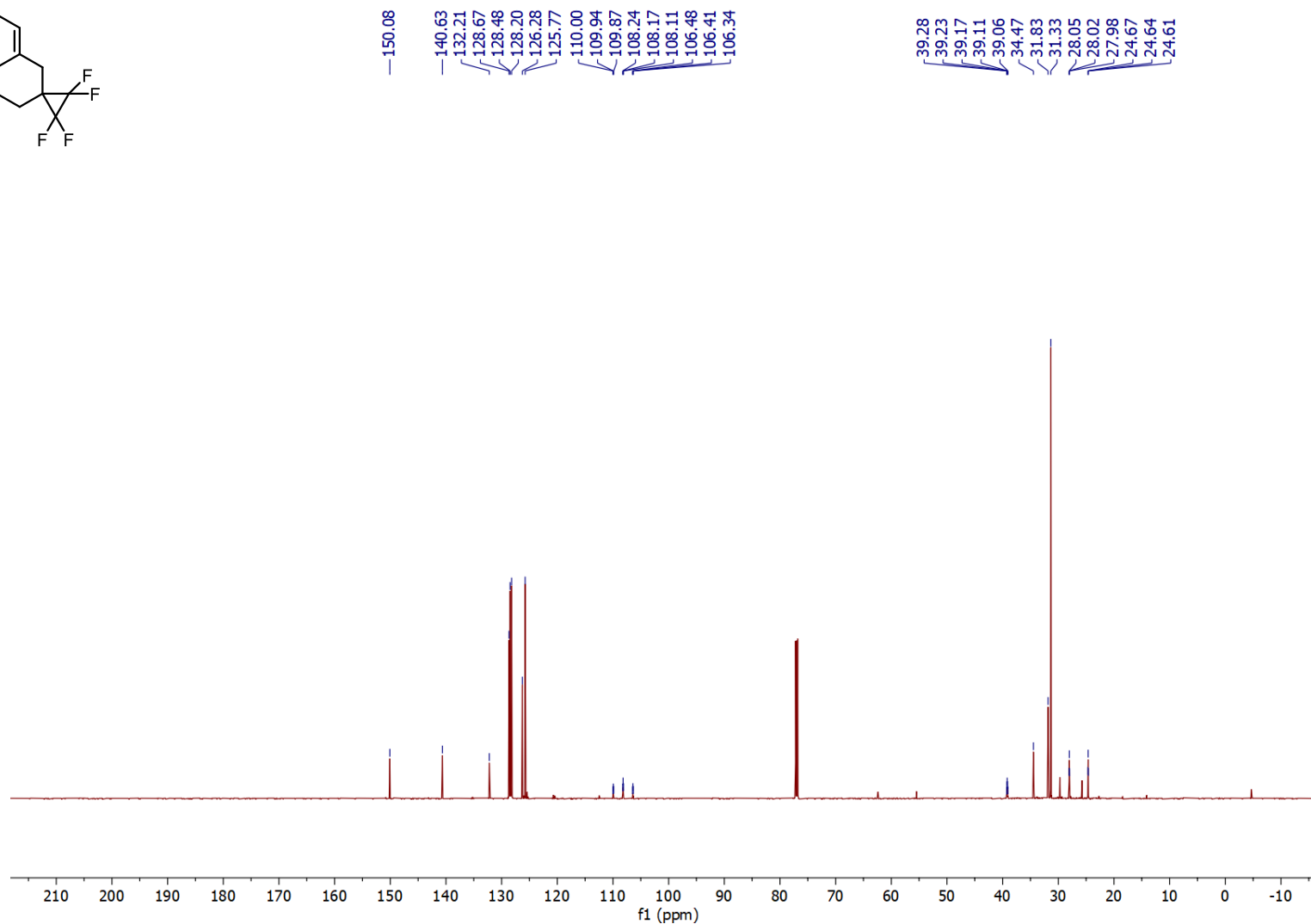
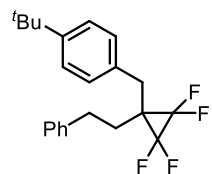
123.60
123.64
123.75
123.79
124.34
124.38
124.49
124.53
127.16
127.21
127.31
127.36
127.90
127.95
128.05
128.10



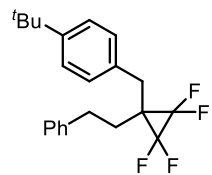
1-(*tert*-Butyl)-4-((2,2,3,3-tetrafluoro-1-phenethylcyclopropyl)methyl)benzene 4 ¹H NMR (700 MHz, Chloroform-*d*)



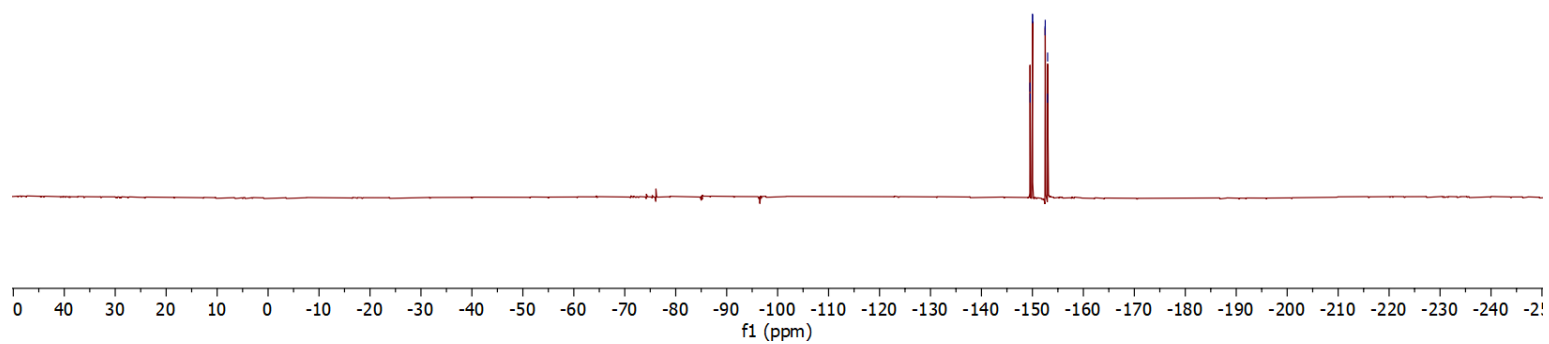
1-(*tert*-Butyl)-4-((2,2,3,3-tetrafluoro-1-phenethyl)cyclopropyl)methyl)benzene $^{13}\text{C}\{^1\text{H}\}$ NMR (176 MHz, Chloroform-*d*)



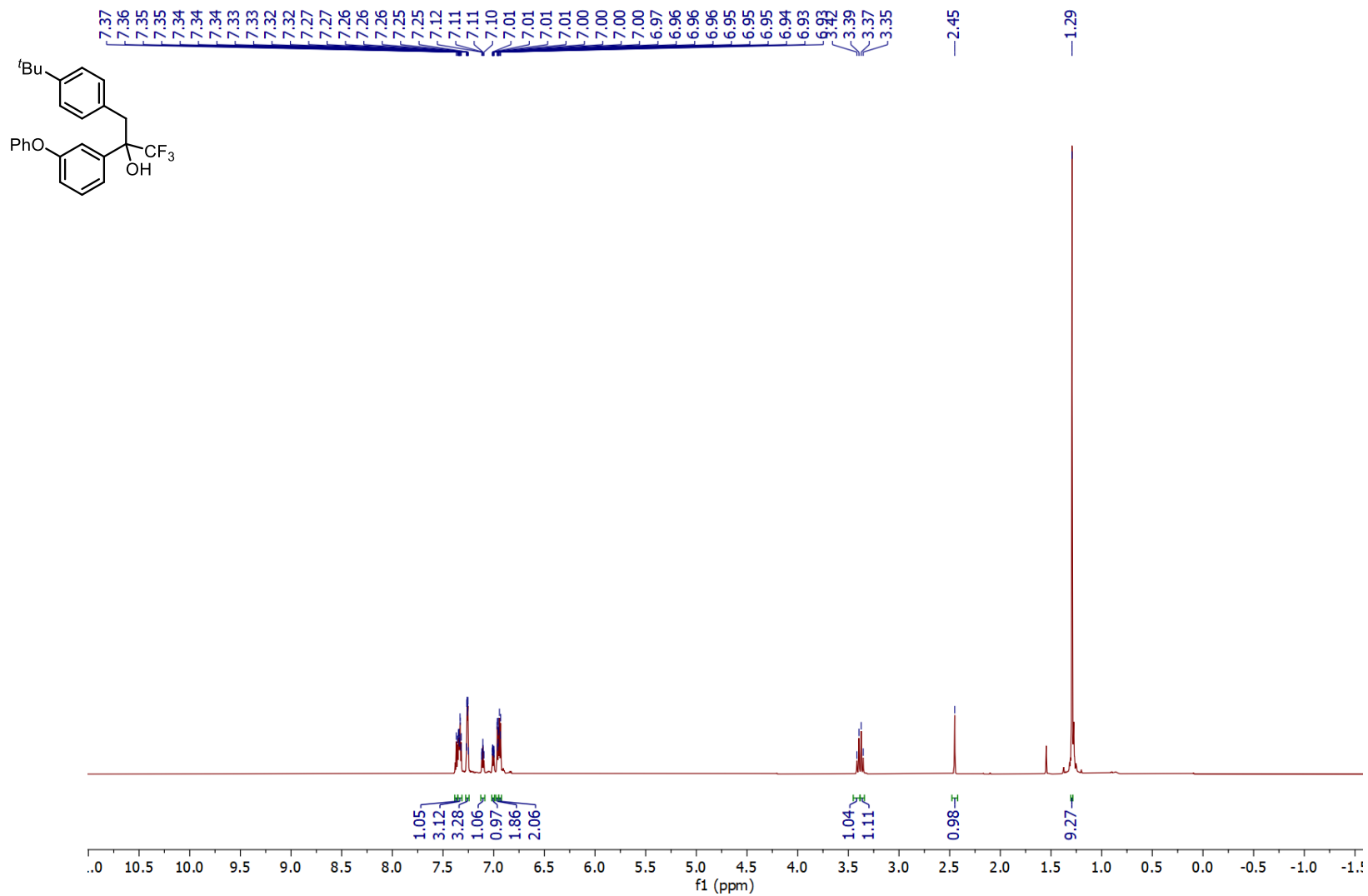
1-(*tert*-Butyl)-4-((2,2,3,3-tetrafluoro-1-phenethyl)cyclopropyl)methyl)benzene 4 ^{19}F NMR (376 MHz, Chloroform-*d*)



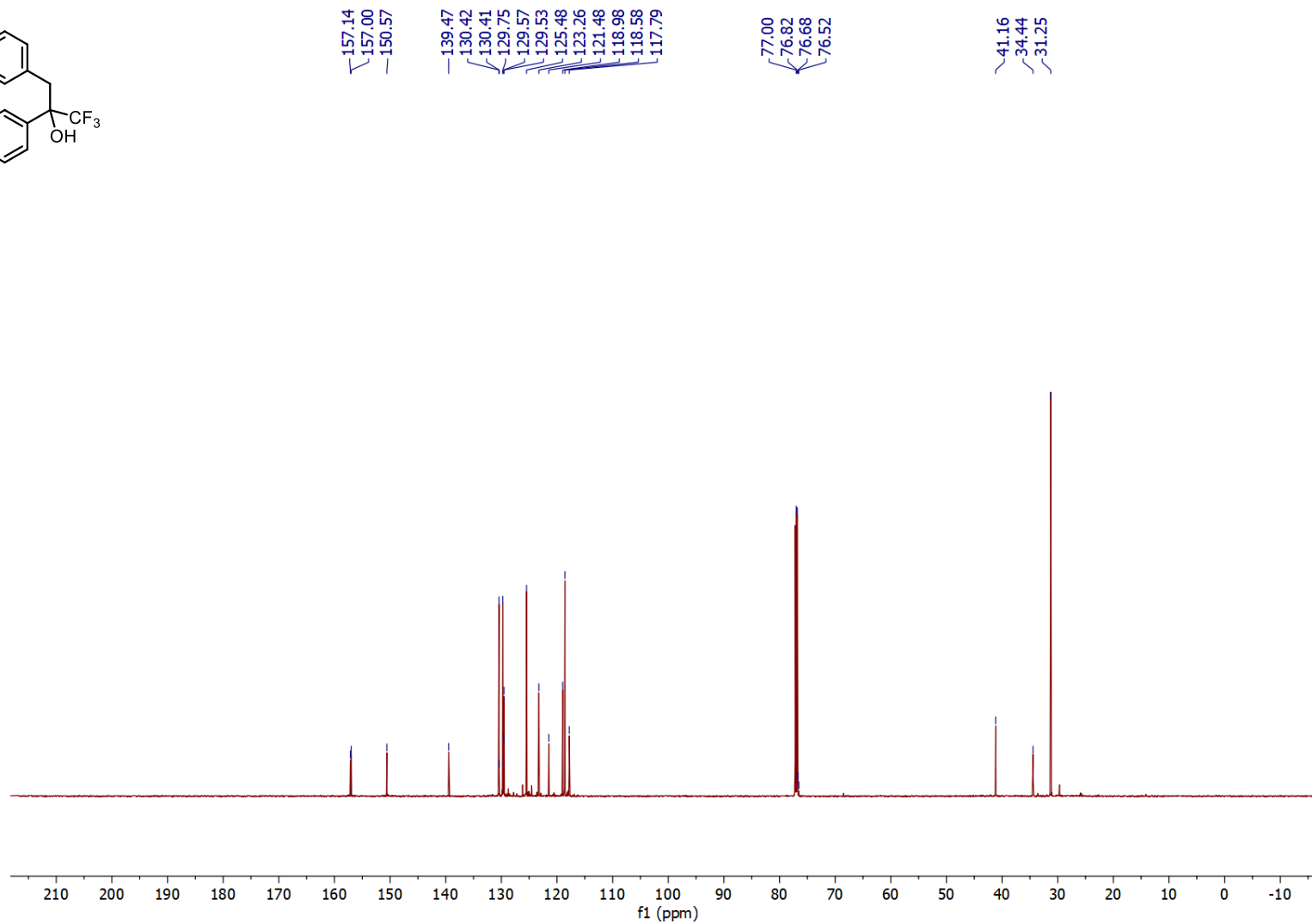
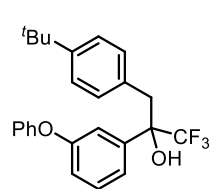
149.53
149.57
150.01
150.03
152.49
152.52
152.96
152.99



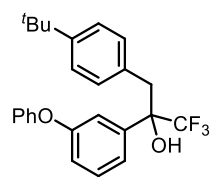
3-(4-(*tert*-Butyl)phenyl)-1,1,1-trifluoro-2-(3-phenoxyphenyl)propan-2-ol ^1H NMR (700 MHz, Chloroform-*d*)



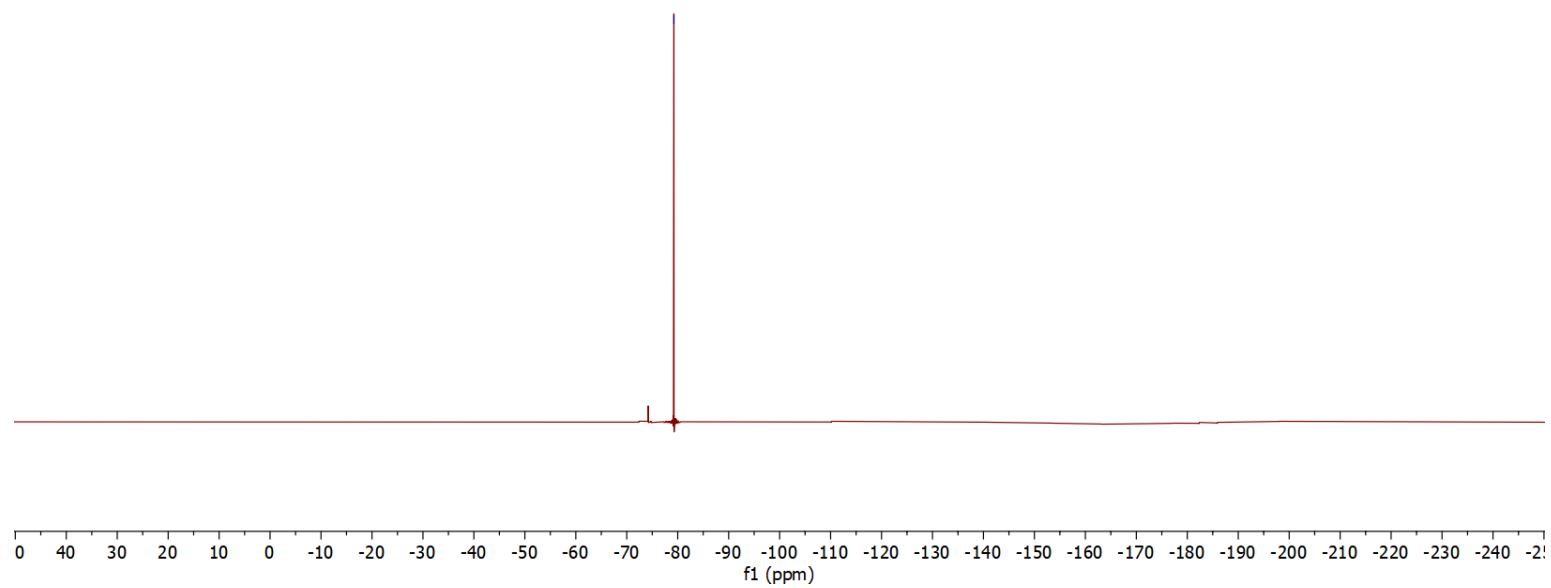
3-(4-(*tert*-Butyl)phenyl)-1,1,1-trifluoro-2-(3-phenoxyphenyl)propan-2-ol $^{13}\text{C}\{^1\text{H}\}$ NMR (176 MHz, Chloroform-*d*)



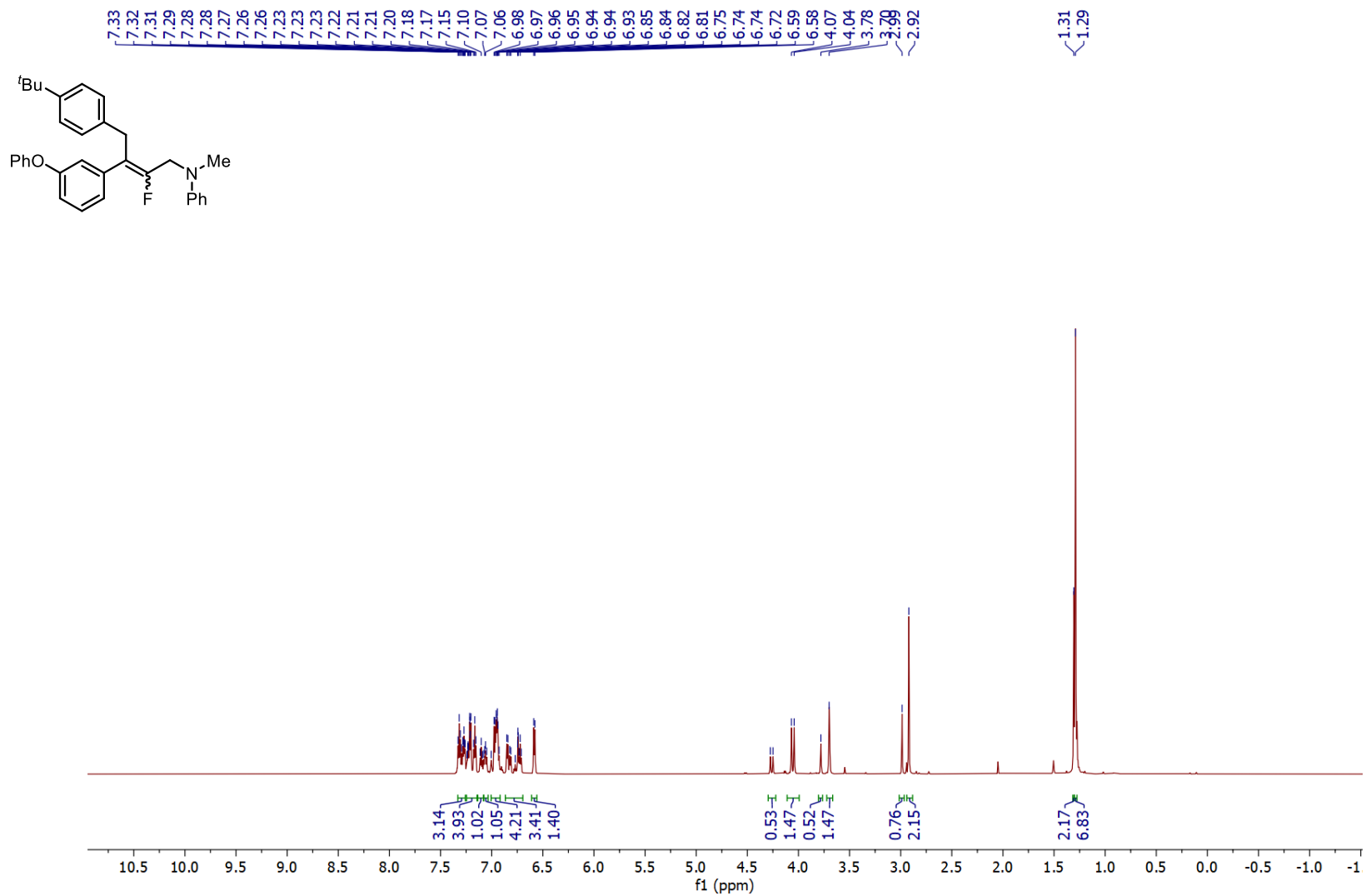
3-(4-(*tert*-Butyl)phenyl)-1,1,1-trifluoro-2-(3-phenoxyphenyl)propan-2-ol ¹⁹F NMR (376 MHz, Chloroform-*d*)



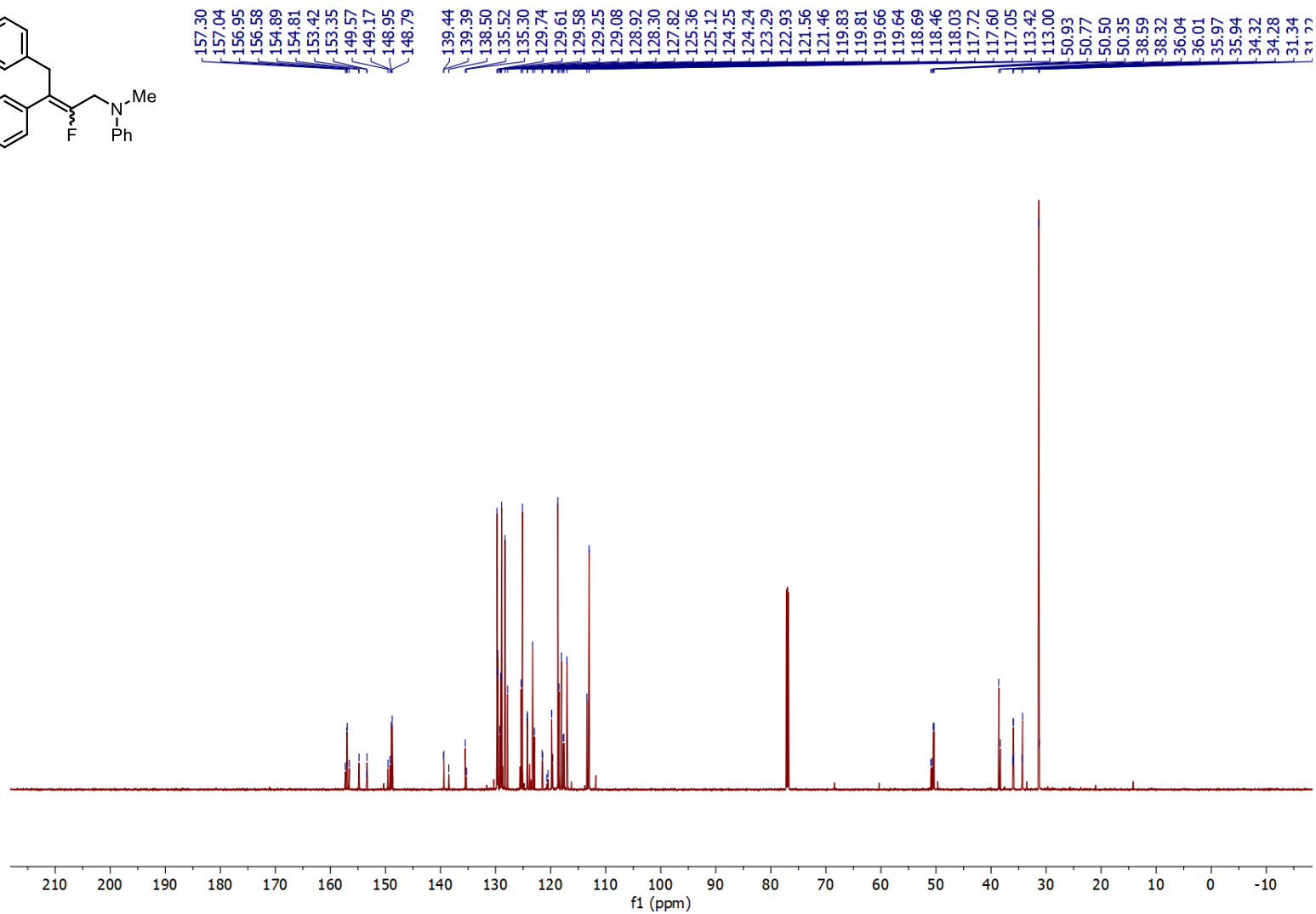
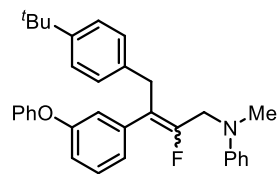
-79.25



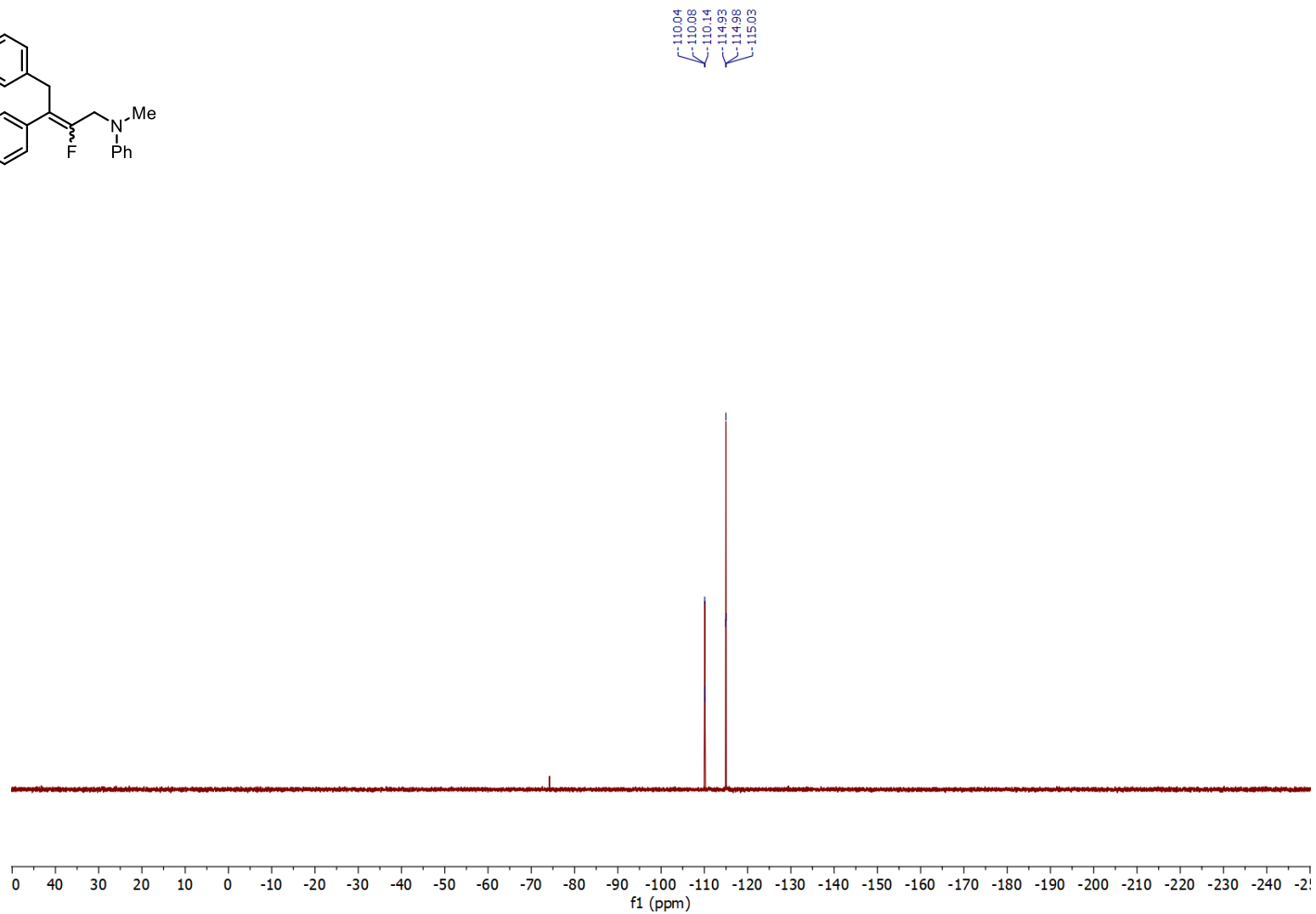
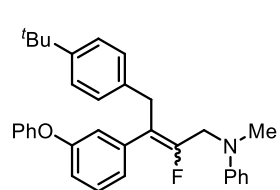
N-(4-(4-*tert*-Butyl)phenyl)-2-fluoro-3-(3-phenoxyphenyl)but-2-en-1-yl)-N-methylaniline ¹H NMR (400 MHz, Chloroform-*d*)



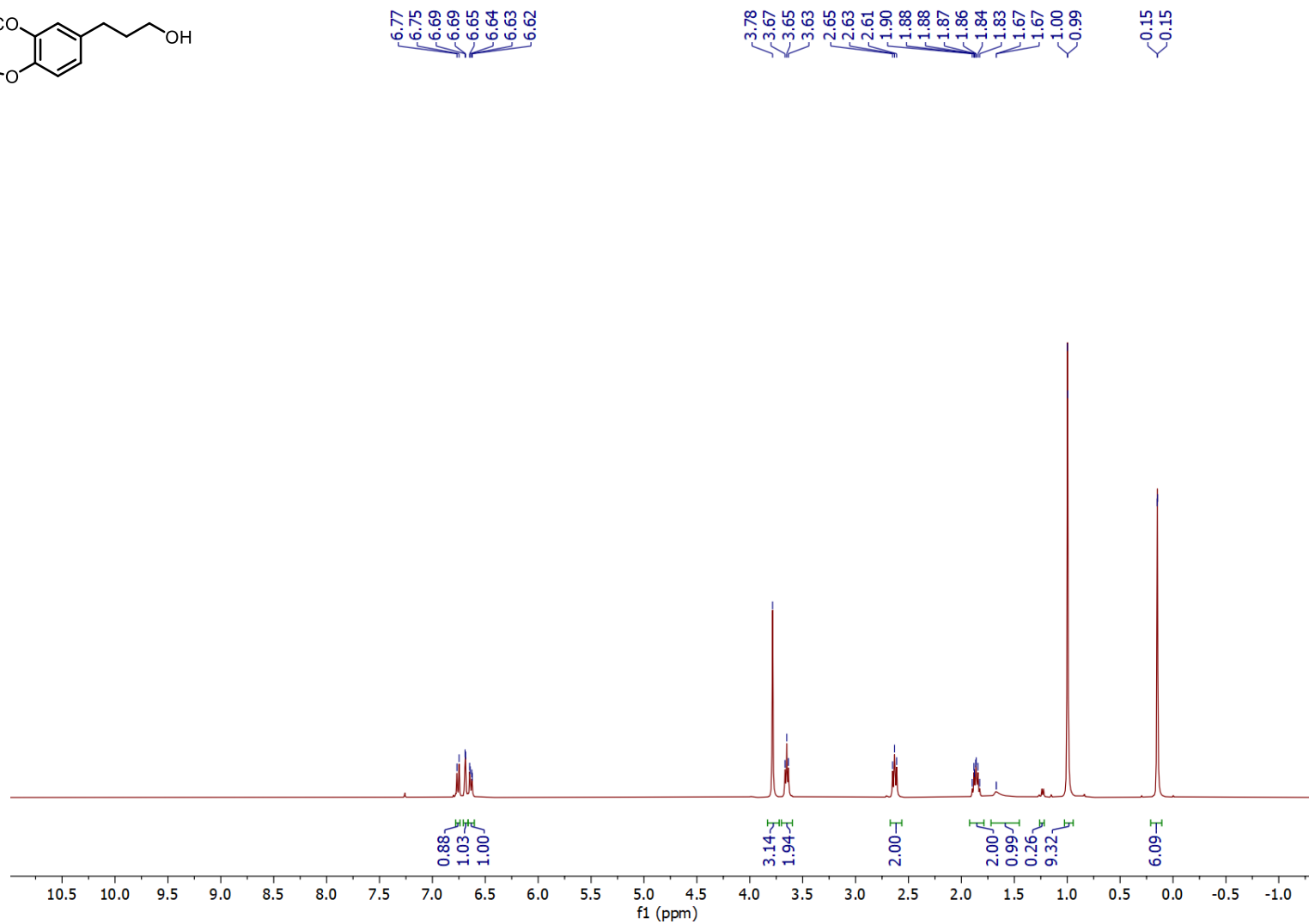
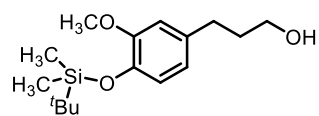
N-(4-(4-*tert*-Butylphenyl)-2-fluoro-3-(3-phenoxyphenyl)but-2-en-1-yl)-N-methylaniline $^{13}\text{C}\{^1\text{H}\}$ NMR (176 MHz, Chloroform-*d*)



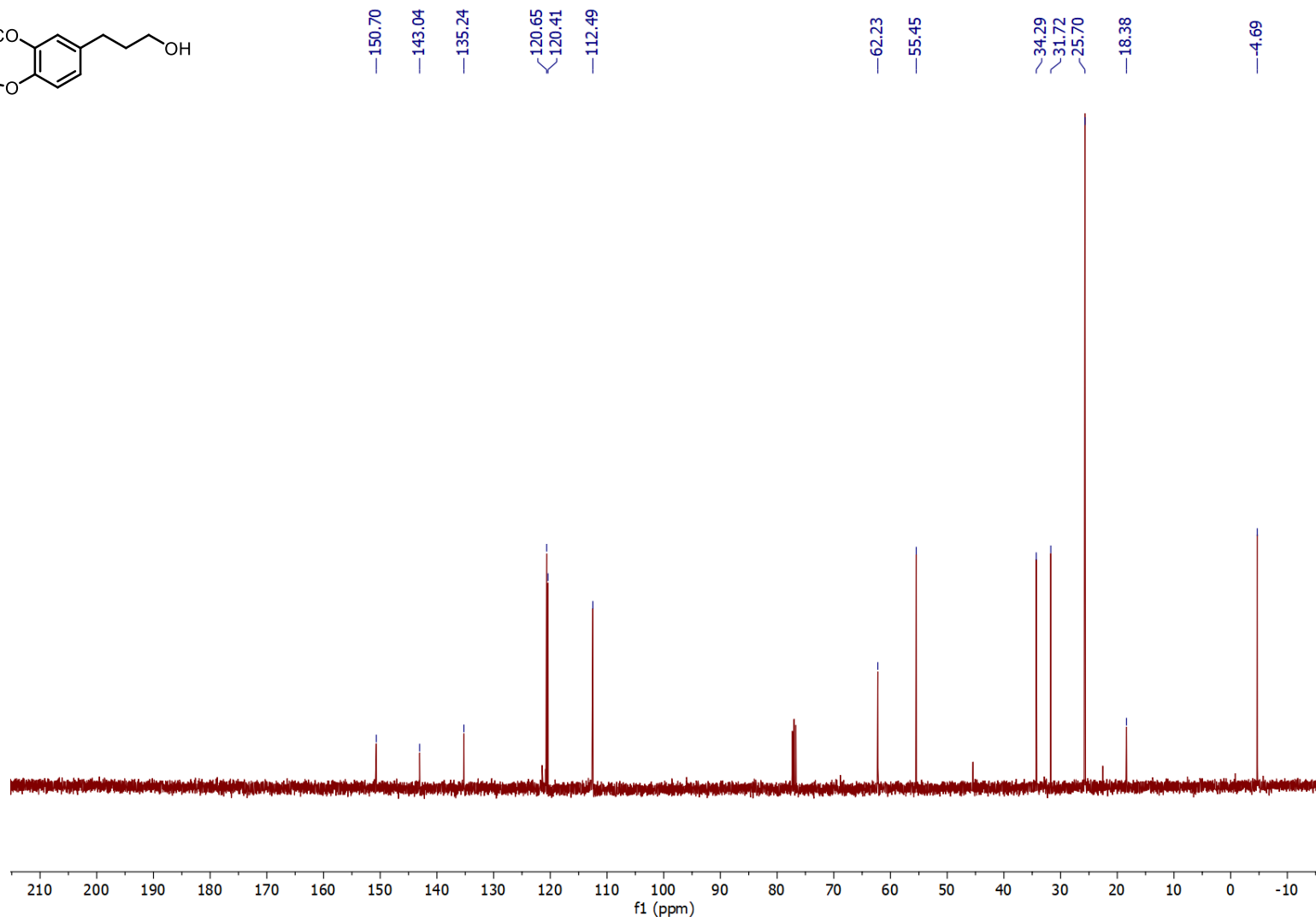
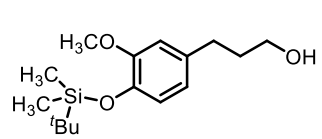
N-(4-(4-*tert*-Butylphenyl)-2-fluoro-3-(3-phenoxyphenyl)but-2-en-1-yl)-N-methylaniline 6 ^{19}F NMR (376 MHz, Chloroform-*d*)



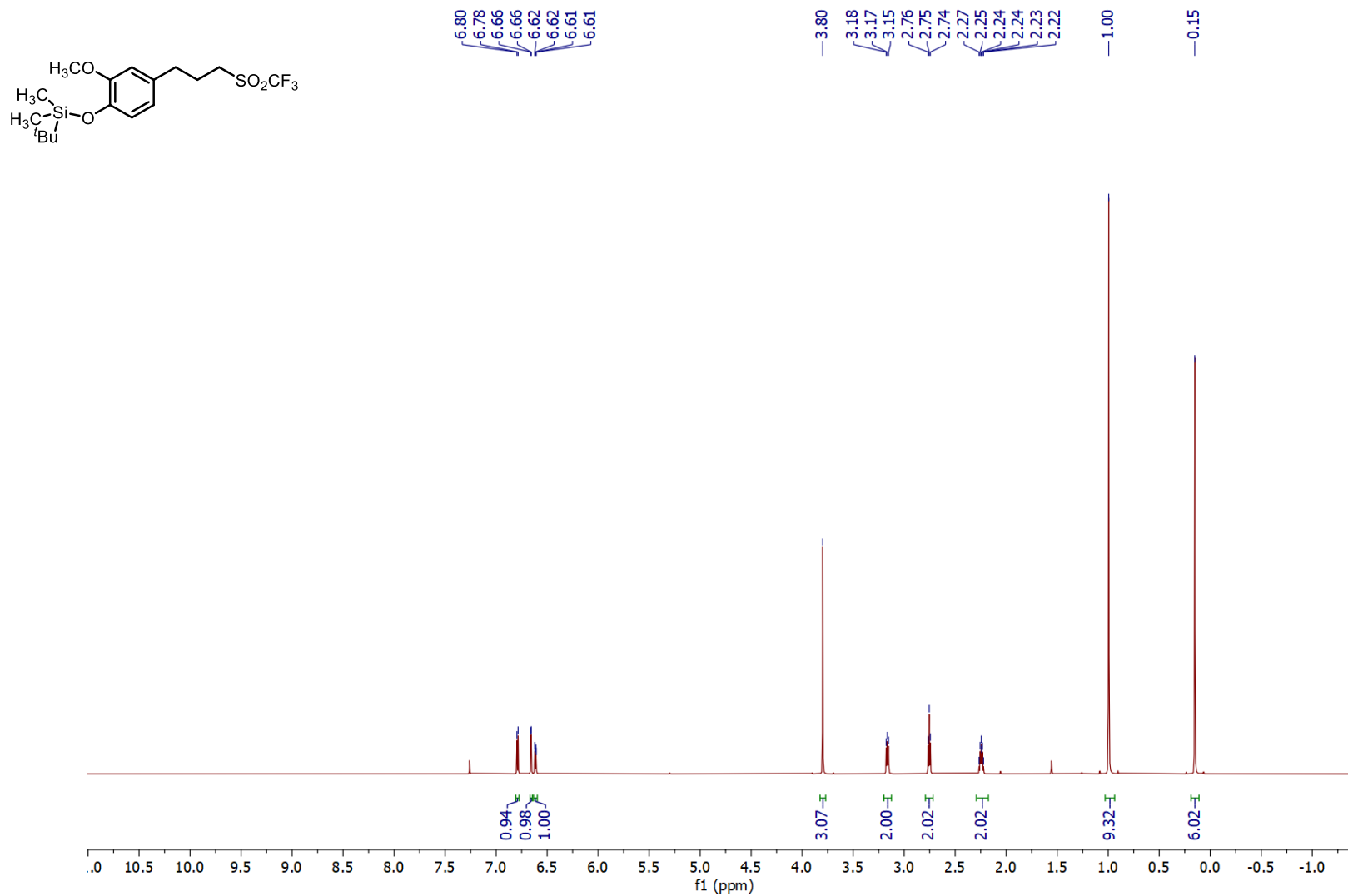
3-(4-((*tert*-Butyldimethylsilyl)oxy)-3-methoxyphenyl)propan-1-ol S17 ¹H NMR (400 MHz, Chloroform-*d*)



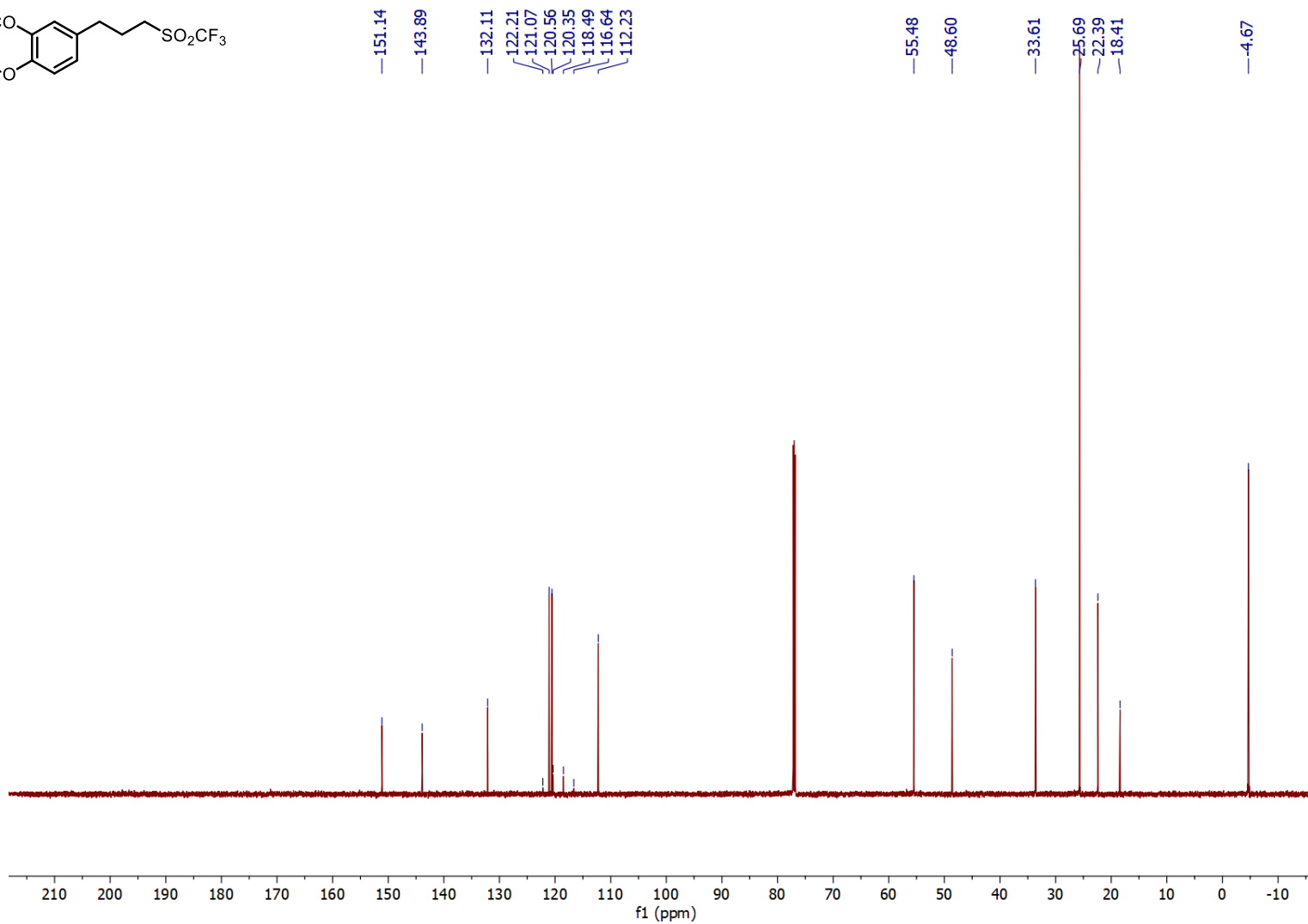
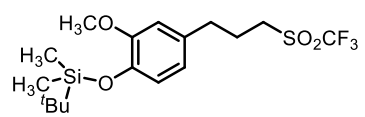
3-(4-((*tert*-Butyldimethylsilyl)oxy)-3-methoxyphenyl)propan-1-ol S17 $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, Chloroform-*d*)



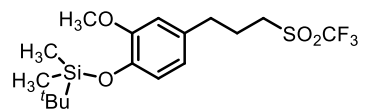
tert-Butyl(2-methoxy-4-(3-((trifluoromethyl)sulfonyl)propyl)phenoxy)dimethylsilane **8** ¹H NMR (700 MHz, Chloroform-*d*)



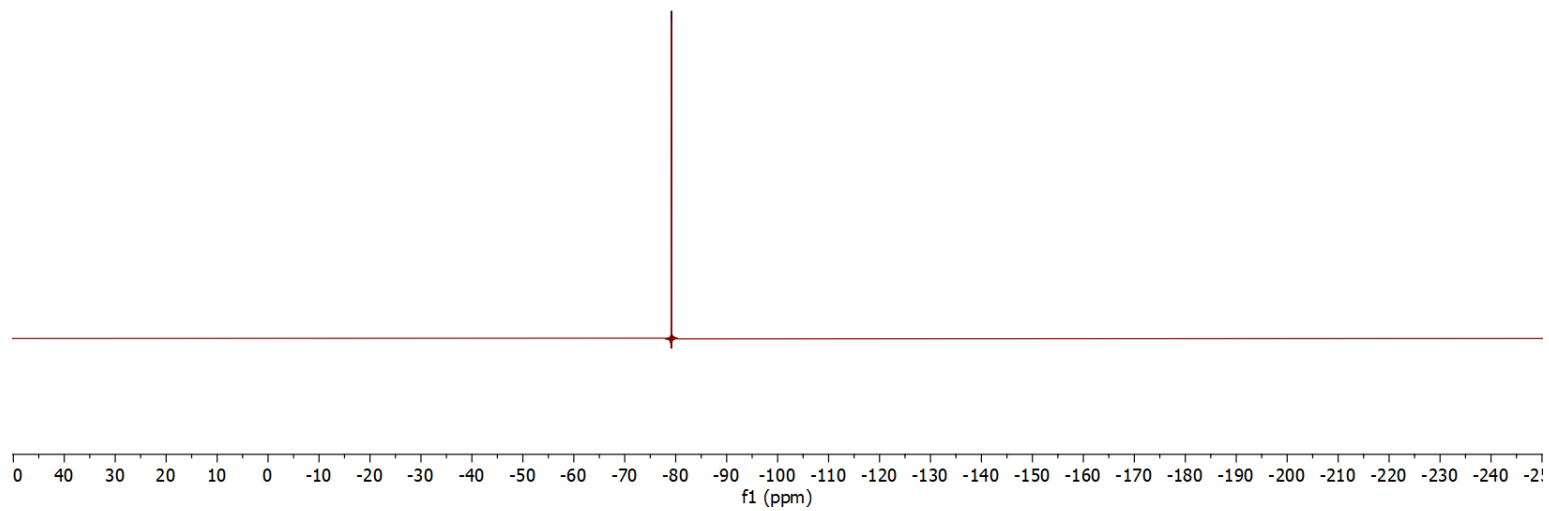
tert-Butyl(2-methoxy-4-(3-((trifluoromethyl)sulfonyl)propyl)phenoxy)dimethylsilane **8** $^{13}\text{C}\{^1\text{H}\}$ NMR (176 MHz, Chloroform-*d*)



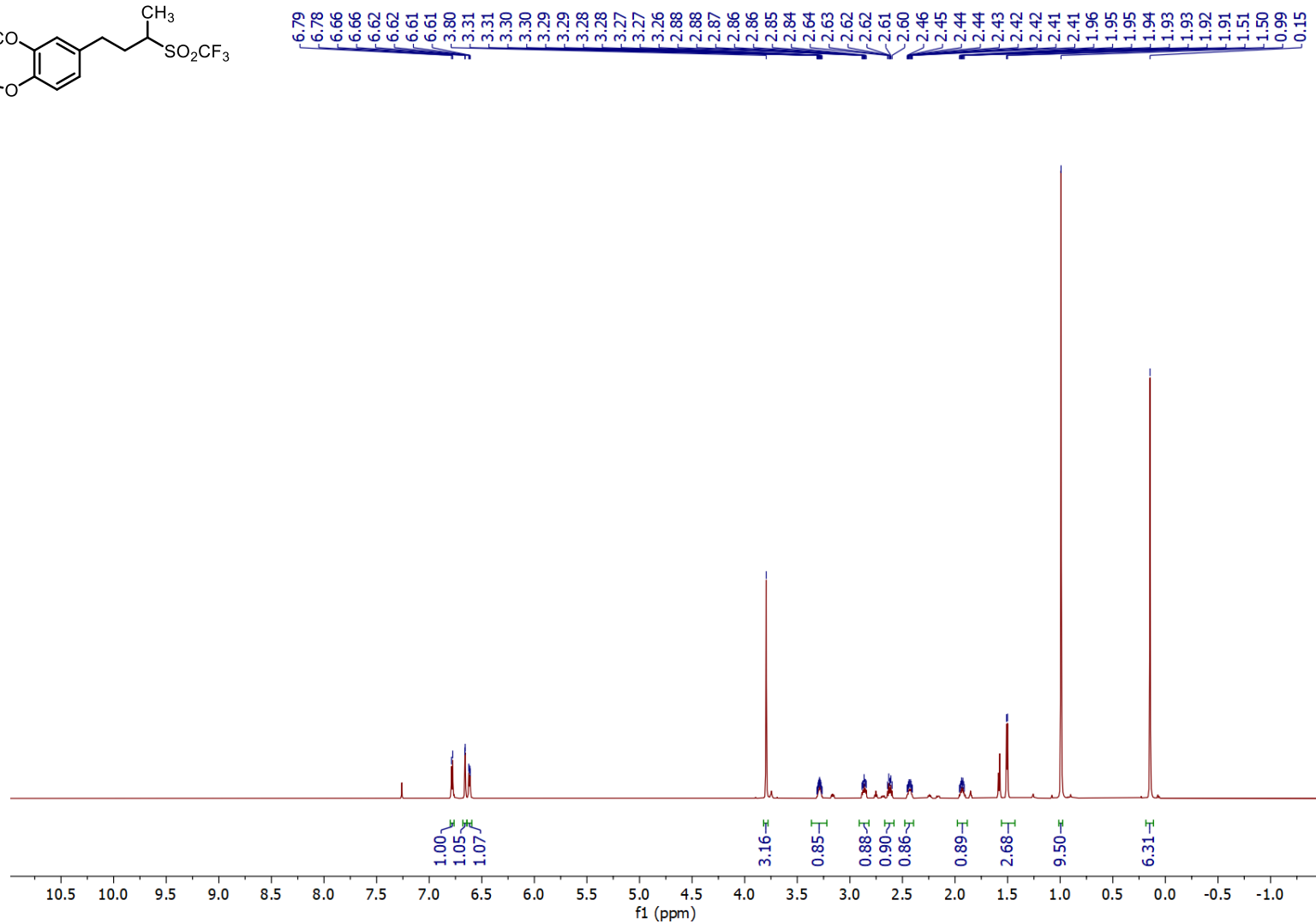
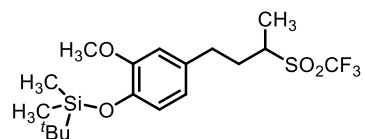
***tert*-Butyl(2-methoxy-4-(3-((trifluoromethyl)sulfonyl)propyl)phenoxy)dimethylsilane 8** ^{19}F NMR (376 MHz, Chloroform-*d*)



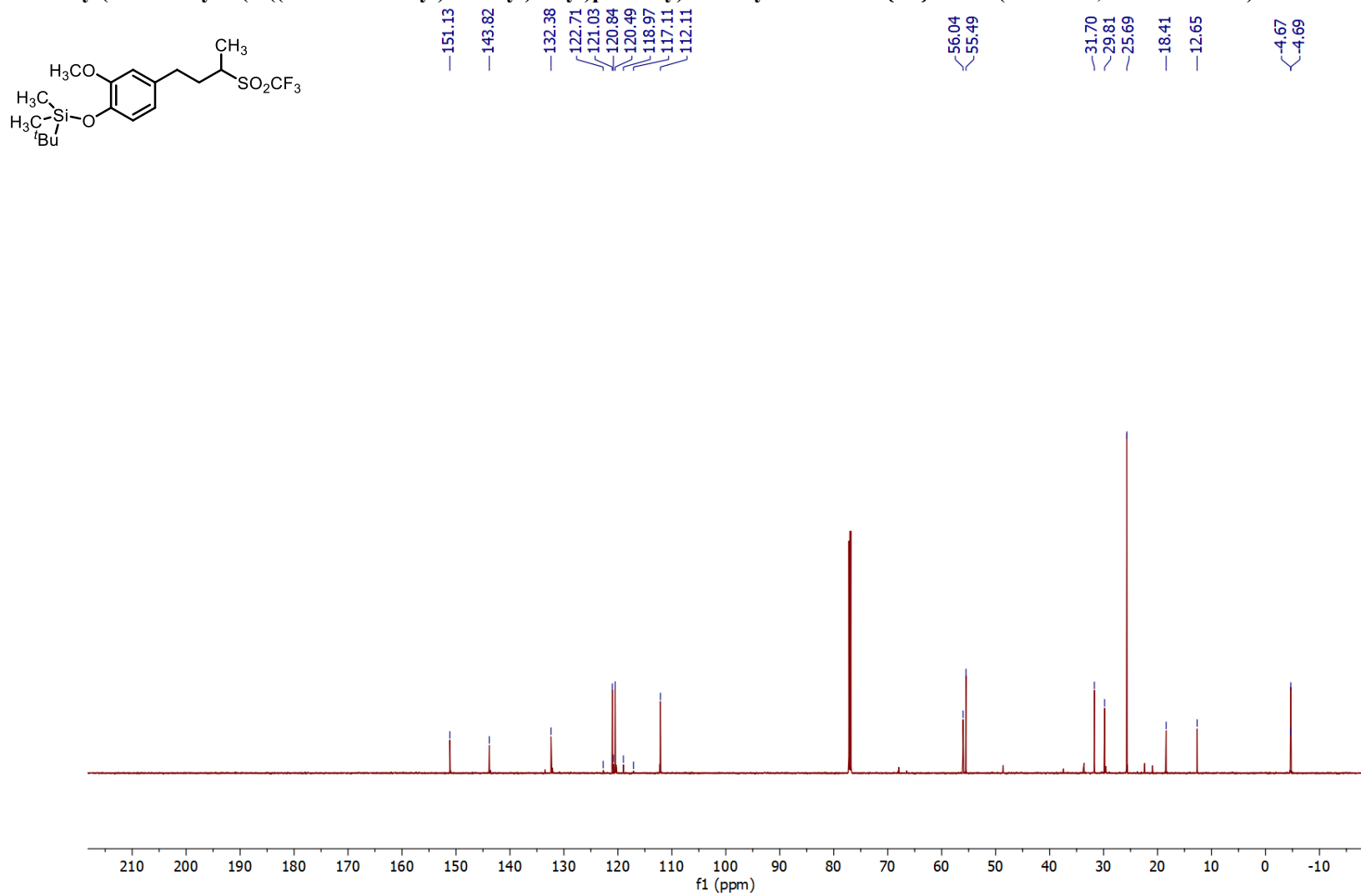
-79.15



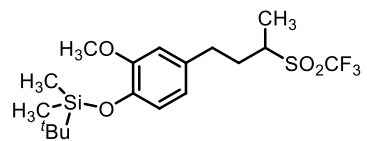
***tert*-Butyl(2-methoxy-4-(3-((trifluoromethyl)sulfonyl)butyl)phenoxy)dimethylsilane 9** ¹H NMR (700 MHz, Chloroform-*d*)



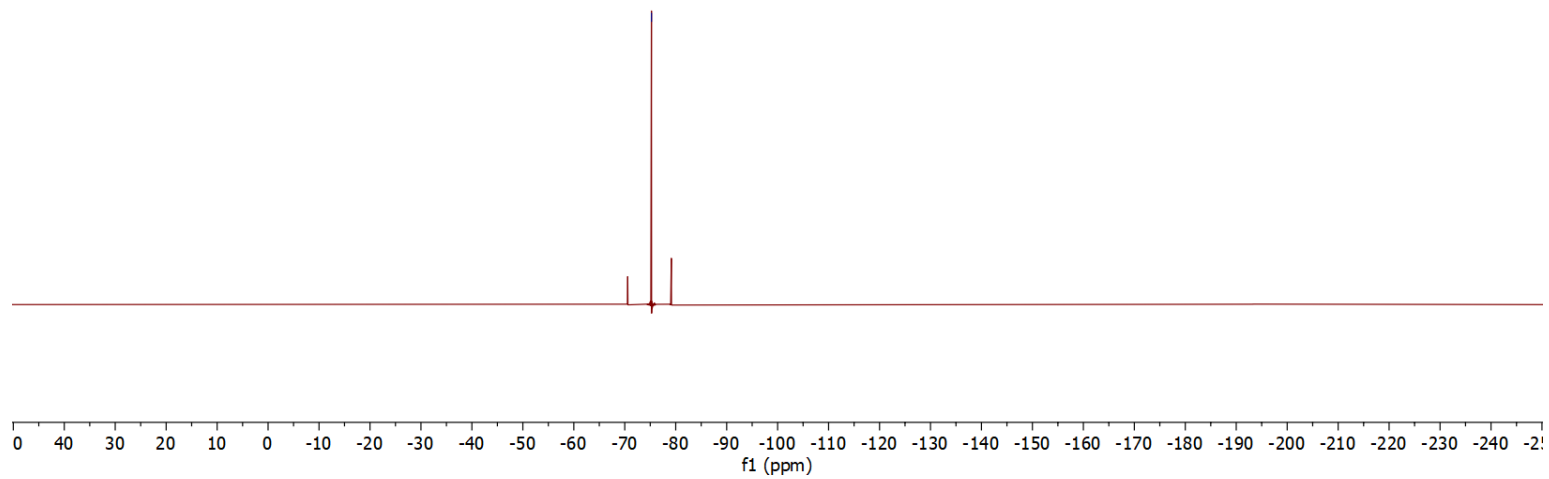
***tert*-Butyl(2-methoxy-4-(3-((trifluoromethyl)sulfonyl)butyl)phenoxy)dimethylsilane 9** $^{13}\text{C}\{^1\text{H}\}$ NMR (176 MHz, Chloroform-*d*)



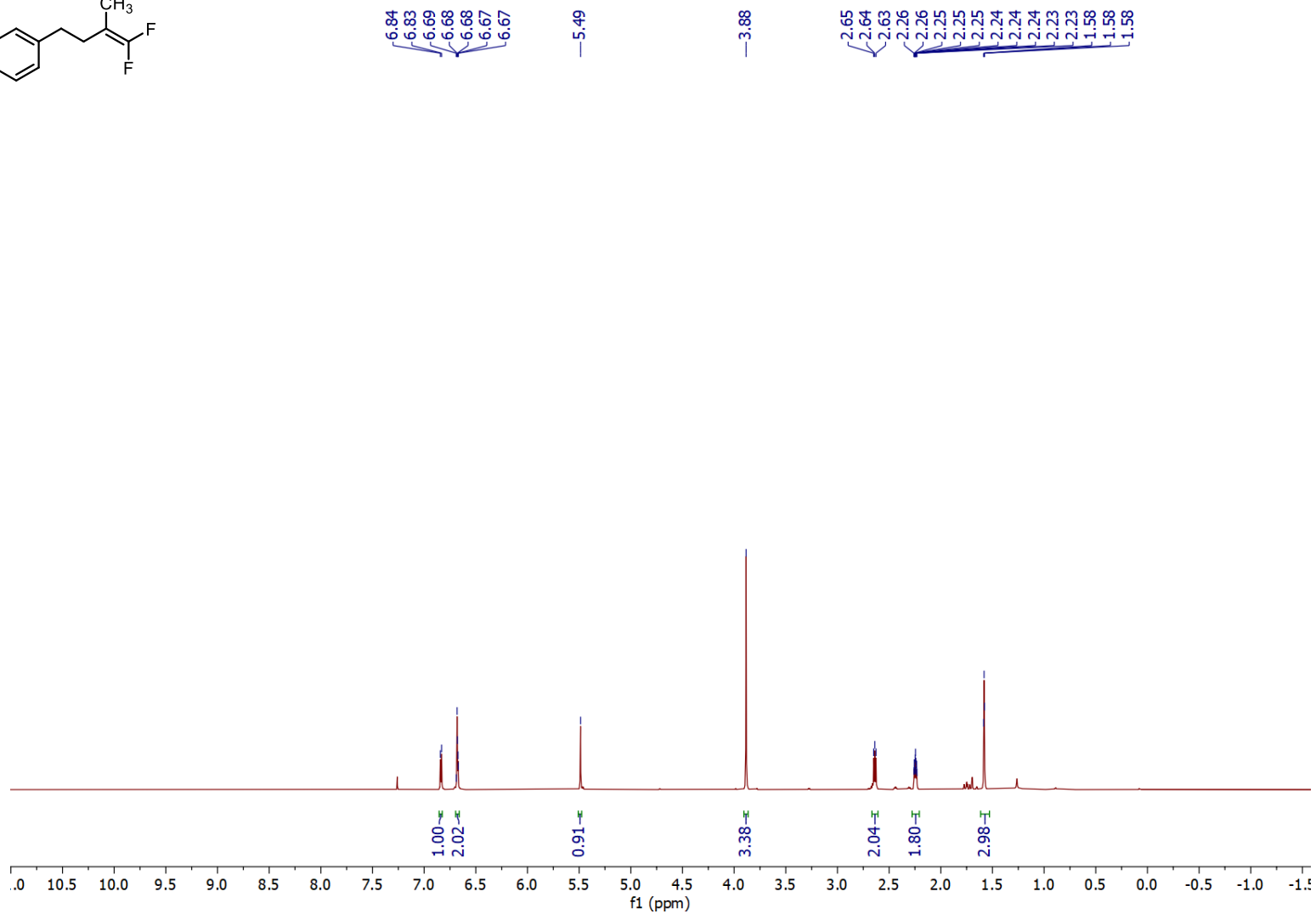
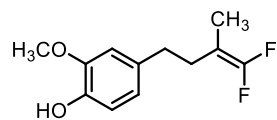
***tert*-Butyl(2-methoxy-4-(3-((trifluoromethyl)sulfonyl)butyl)phenoxy)dimethylsilane 9** ^{19}F NMR (376 MHz, Chloroform-*d*)



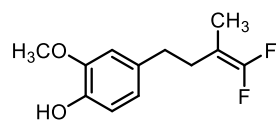
---75.23



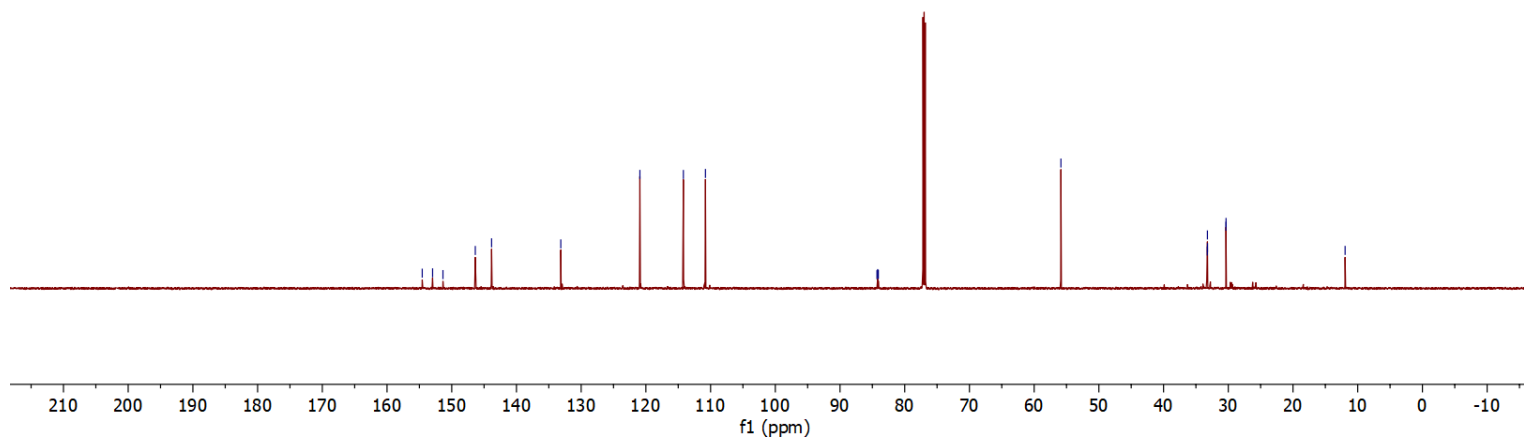
4-(4,4-Difluoro-3-methylbut-3-en-1-yl)-2-methoxyphenol 7-F ^1H NMR (700 MHz, Chloroform-*d*)



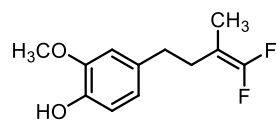
4-(4,4-Difluoro-3-methylbut-3-en-1-yl)-2-methoxyphenol 7-F $^{13}\text{C}\{^1\text{H}\}$ NMR (176 MHz, Chloroform-*d*)



154.56
152.96
151.36
146.36
143.84
— 133.15
120.92
114.21
110.79
84.29
84.18
84.08
— 55.86
33.24
33.22
33.21
30.36
30.35
— 11.95



4-(4,4-Difluoro-3-methylbut-3-en-1-yl)-2-methoxyphenol 7-F ^{19}F NMR (376 MHz, Chloroform-*d*)



-97.16
-97.32
-97.49
-97.64

