

Facile Synthesis of Trifluoromethyl Olefins via the Decarboxylation of α -Trifluoromethyl- β -lactones

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General information:

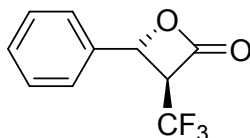
All reactions were conducted under an inert atmosphere. Dichloromethane and pentane were freshly distilled from calcium hydride. Diethyl ether and tetrahydrofuran (THF) were distilled from sodium/benzophenone. All other chemicals were purchased from Aldrich Chemical Co. and used without further purification, unless otherwise noted. Reaction-flasks were dried in oven at 100 °C for 12 h prior to use. ^1H , ^{13}C , and ^{19}F NMR spectra were recorded on Varian ASM 300 MHz spectrometer. Chemical shift (δ) values are reported in parts per million, and are referenced to either tetramethylsilane or dimethyl sulfoxide. Data are reported as: δ value (multiplicity, J -value, integration, where s=singlet, d=doublet, t=triplet, m=multiplet, br=broad). 3,3,3-trifluoropropanoic acid was purchased from Oakwood Products, Inc.; All haloboranes¹ were

1 . (a) H. C. Brown; P. V. Ramachandran; J. Chandrasekharan. *J. Org. Chem.* 1985, **50**, 5446. (b) H. C. Brown; R.

prepared according to literature procedures. Diastereomeric ratios (*syn:anti* ratios) of β -hydroxy- α -trifluoromethylpropanoic acid were determined by ^{19}F NMR analysis.

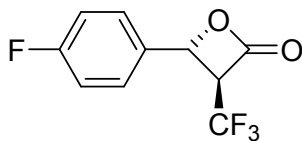
Characterization of compounds

Anti - 4-phenyl-3-(trifluoromethyl)oxetan-2-one (2a)



^1H NMR (300 MHz, CDCl_3): δ 7.48-7.39 (m, 5H), 5.65 (d, $J = 4.5$ Hz, 1H), 4.26 (qd, $J = 4.2$, 8.7 Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3): δ 160.3 (q, $J = 5.4$ Hz), 134.3, 130.0, 129.3, 125.4, 122.0 (q, $J = 277.1$ Hz), 71.8, 62.1 (q, $J = 31.6$ Hz); ^{19}F NMR (282 MHz, CDCl_3): δ -69.2 (d, $J_{\text{H-F}} = 8.5$ Hz, 3F). LRMS (-ve APCI) calcd(M-H) 215, found 215.

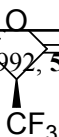
Anti-4-(4-fluorophenyl)-3-(trifluoromethyl)oxetan-2-one (2c)



^1H NMR (300 MHz, CDCl_3): δ 7.40 (dd, $J = 5.1$, 8.7, 2H), 7.17 (t, $J = 8.6$ Hz, 2H), 5.63 (d, $J = 4.5$ Hz, 1H), 4.25 (qd, $J = 4.2$, 8.7 Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3): δ 165.0, 161.7, 159.7, 130.0, 127.3, 126.5, 121.7 (q, $J_{\text{C-F}} = 274.9$ Hz), 116.5, 116.2, 105.4, 71.2, 62.4 (q, $J_{\text{C-F}} = 31.8$ Hz); ^{19}F NMR (282 MHz, CDCl_3): δ -69.3 (d, $J_{\text{H-F}} = 8.5$ Hz, 3F), -111.5 (s, 1H). LRMS (-ve APCI) calcd(M-H) 233, found 233.

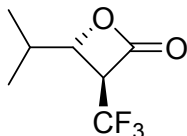
Anti-4-cyclohexyl-3-(trifluoromethyl)oxetan-2-one (2h)

K. Dhar; K. Ganesan; B. Singaram, *J. Org. Chem.* 1992, **57**, 499. (c) H. C. Brown; K. Ganesan; R. K. Dhar, *J. Org. Chem.* 1993, **58**, 147.



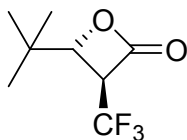
¹H NMR (300 MHz, CDCl₃): δ 4.34 (dd, *J* = 4.5, 8.4Hz, 1H), 4.02 (qd, *J* = 4.2, 8.7 Hz, 1H), 1.86-1.67 (m, 7H), 1.34-1.22 (m, 4H); **¹³C NMR (75 MHz, CDCl₃):** δ 160.4, 121.9 (q, *J* = 274.3 Hz), 75.7, 57.4 (q, 31.6Hz), 40.9, 27.9, 26.6, 25.7, 25.1; **¹⁹F NMR (282 MHz, CDCl₃):** δ -67.75 (d, *J*_{H-F} = 7.1Hz, *syn*-3H), -69.04 (d, *J*_{H-F} = 8.5Hz, 3F) **HRMS LCMS** calcd (M+H) 223.0950, found 223.0943

***Anti*-4-isopropyl-3-(trifluoromethyl)oxetan-2-one (2i)**



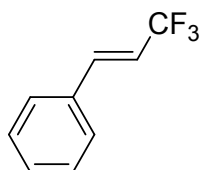
¹H NMR (300 MHz, CDCl₃): δ 4.34 (dd, *J* = 4.5, 8.4, 1H), 4.00 (qd, *J* = 4.2, 8.7Hz, 1H), 2.109-1.969 (m, 1H), 1.10 (d, *J* = 6.6, 3H), 1.02 (d, *J* = 6.6 Hz, 3H) ; **¹³C NMR (75 MHz, CDCl₃):** δ 160.1, 121.9 (q, *J* = 274.5), 73.4, 57.2 (q, *J* = 31.1), 31.7, 17.5, 16.3; **¹⁹F NMR (282 MHz, CDCl₃):** δ -67.1 (d, *J*_{H-F} = 9.0 Hz, *syn*-3F), -69.3 (d, *J*_{H-F} = 8.7Hz, 3H) **HRMS LCMS** calcd (M+H)183.0627, found 183.0622

***Anti*-4-(tert-butyl)-3-(trifluoromethyl)oxetan-2-one (2j)**



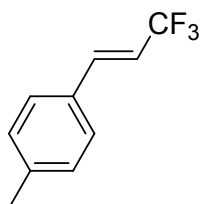
¹H NMR (300 MHz, CDCl₃): δ 4.37 (d, *J* = 4.5 Hz, 1H), 4.03 (qd, *J* = 4.2, 8.7Hz, 1H), 1.05 (s, 9H) ; **¹³C NMR (75 MHz, CDCl₃):** δ 160.4, 122.3 (q, *J* = 274.6 Hz), 79.1, 54.9 (q, 31.4 Hz), 32.8, 24.1; **¹⁹F NMR (282 MHz, CDCl₃):** δ -69.03 (d, *J*_{H-F} = 8.7Hz, 3F) **HRMS LCMS** calcd (M+H)197.0784, found 197.0790

(E)-(3,3,3-trifluoroprop-1-en-1-yl)benzene (3a)



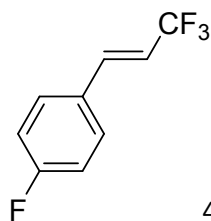
¹H NMR (300 MHz, CDCl₃): δ 7.44-7.36 (m, 5H), 7.14 (dd, *J* = 2.1, 16.2 Hz, 1H), 6.16 (dq, *J* = 6.6, 15.1, 1H); **¹³C NMR (75 MHz, CDCl₃):** δ 137.5, 133.2, 129.8, 128.7, 127.3, 123.4 (q, *J* = 266.7Hz), 115.6 (q, *J* = 33.5Hz); **¹⁹F NMR (282 MHz, CDCl₃):** δ -64.9 (d, *J*_{H-F} = 5.9 Hz, 3F). **LRMS (ESI+)** calcd for [M+Na]⁺ 195.0, found 195.2

(E)-1-methyl-4-(3,3,3-trifluoroprop-1-en-1-yl)benzene (3b)



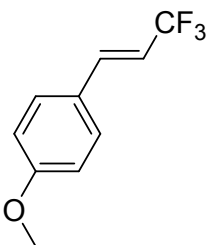
¹H NMR (300 MHz, CDCl₃): δ 7.36 (d, *J* = 8.1Hz, 2H), 7.19 (d, *J* = 7.8 Hz, 2H) 7.11 (dd, *J* = 1.8, 16.2 Hz, 1H), 6.16 (dq, *J* = 6.6, 13.2 Hz, 1H), 2.37 (s, 3H); **¹³C NMR (75 MHz, CDCl₃):** δ 140.0, 137.3, 130.4, 129.4, 127.2, 123.6 (q, *J* = 266.7Hz), 114.6 (q, *J* = 33.3Hz), 21.3; **¹⁹F NMR (282 MHz, CDCl₃):** δ -64.7 (d, *J*_{H-F} = 5.9 Hz, 3F). **LRMS (ESI+)** calcd for [M+Na]⁺ 209.2, found 209.2

(E)-1-fluoro-4-(3,3,3-trifluoroprop-1-en-1-yl)benzene (3c)



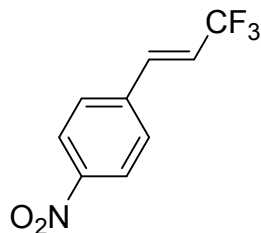
¹H NMR (300 MHz, CDCl₃): δ 7.45-7.40 (m, 2H), 7.13-7.04 (m, 3H), 6.12 (dq, *J* = 6.6, 16.1 Hz, 1H); **¹³C NMR (75 MHz, CDCl₃):** δ 165.2, 161.9, 136.3, 129.9, 129.4 (d, *J* = 7.9 Hz), 127.4, 123.4 (q, *J* = 266.2 Hz), 116.1-115.8 (m), 115.3; **¹⁹F NMR (282 MHz, CDCl₃):** δ -64.9 (d, *J*_{H-F} = 5.6 Hz, 3F), -111.5 (s, 1H). **LRMS (ESI+)** calcd for [M+Na]⁺ 213.1, found 213.3

(*E*)-1-methoxy-4-(3,3,3-trifluoroprop-1-en-1-yl)benzene (3d)



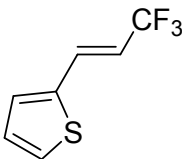
¹H NMR (300 MHz, CDCl₃): δ 7.32 (d, *J* = 8.7 Hz, 2H), 7.04 (dq, *J* = 16.1, 2.2 Hz, 1H), 6.85 (d, *J* = 8.8 Hz, 1H), 6.01 (dq, *J* = 16.1, 6.6 Hz, 1H), 3.76 (s, 3H); **¹³C NMR (75 MHz, CDCl₃):** δ 161.1, 137.2, 132.3, 129.0, 126.0, 124.1 (q, *J* = 266.3 Hz), 114.3, 113.2 (q, *J* = 33.4 Hz), 55.3; **¹⁹F NMR (282 MHz, CDCl₃):** δ -64.4 (d, *J*_{H-F} = 5.9 Hz, 3F) **LRMS (ESI+)** calcd for [M+Na]⁺ 225.2, found 225.3

(*E*)-1-nitro-4-(3,3,3-trifluoroprop-1-en-1-yl)benzene (3e)



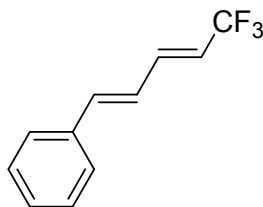
¹H NMR (300 MHz, CDCl₃): δ 8.22 (d, *J* = 2.1 Hz, 1H), 7.64 (d, *J* = 8.5 Hz, 2H), 7.23 (dq, *J* = 16.1, 2.2 Hz, 1H), 6.40 (dq, *J* = 15.9, 6.3 Hz, 1H); **¹³C NMR (75 MHz, CDCl₃):** δ 165.9, 148.4, 141.5, 139.4, 135.5 (q, *J* = 6.8 Hz), 128.3, 124.1, 121.2, 119.8 (q, *J* = 34.3 Hz). **¹⁹F NMR (282 MHz, CDCl₃)** δ -59.32 (d, *J* = 8.5 Hz Z-3F), -65.54 (d, *J* = 5.4 Hz). **LRMS (ESI+)** calcd for [M+Na]⁺ 240.2, found 240.3

(*E*)-2-(3,3,3-trifluoroprop-1-en-1-yl)thiophene (3f)



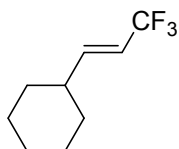
¹H NMR (300 MHz, CDCl₃): δ 7.34 (d, *J* = 5.1 Hz, 1H), 7.26 (dq, *J* = 2.1, 15.9 Hz, 1H) 7.19 (d, *J* = 3.6 Hz, 1H), 7.03(dd, *J* = 3.8, 5.0Hz, 1H), 6.01 (dq, *J* = 6.6, 15.9 Hz, 1H); **¹³C NMR (75 MHz, CDCl₃):** δ 137.8, 130.3, 129.7, 127.7, 127.5, 123.2 (q, *J* = 302.3Hz), 114.3(q, *J* = 33.2Hz), 55.3; **¹⁹F NMR (282 MHz, CDCl₃):** δ -64.6 (d, *J*_{H-F} = 6.3 Hz, 3F). **LRMS (ESI+)** calcd for [M+Na]⁺ 201.4, found 201.1

((1*E*,3*E*)-5,5,5-trifluoropenta-1,3-dien-1-yl)benzene (3g)



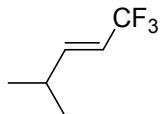
¹H NMR (300 MHz, CDCl₃): δ 7.44-7.29 (m, 5H), 6.94-6.70 (m, 3H), 5.78 (dq, *J* = 7.2, 14.1 Hz, 1H); **¹³C NMR (75 MHz, CDCl₃):** δ 139.1, 137.3, 135.6, 128.7, 127.7, 124.7, 123.3 (q, *J* = 266.3 Hz), 118.1 (q, *J* = 32.9 Hz), 55.3; **¹⁹F NMR (282 MHz, CDCl₃):** δ -64.7 (d, *J*_{H-F} = 6.8 Hz, 3F). **LRMS (ESI+)** calcd for [M+Na]⁺ 221.2, found 221.2

(*E*)-(3,3,3-trifluoroprop-1-en-1-yl)cyclohexane (3h)



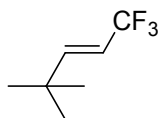
¹H NMR (300 MHz, CDCl₃): δ 6.31 (ddq, *J* = 15.9, 6.5, 2.1 Hz, 1H), 5.53 (dq, *J* = 16.1, 6.4, .5 Hz, 1H), 2.18 – 1.95 (m, 1H), 1.86 – 1.59 (m, 5H), 1.36 – 1.05 (m, 5H); **¹³C NMR (75 MHz, CDCl₃)** δ 145.49 (q, *J* = 6.5 Hz), 123.37 (d, *J* = 268.5 Hz), 116.03 (q, *J* = 33.1 Hz), 39.71, 31.71, 25.93, 25.72, 22.4 (*Z*), 14.0 (*Z*); **¹⁹F NMR (282 MHz, CDCl₃)** δ -59.63 (d, *J* = 8.4 Hz, *Z*-3F), -65.58 (d, *J* = 5.9 Hz, 3F). **LRMS (ESI+)** calcd for [M+Na]⁺ 201.3, found 201.3

(*E*)-1,1,1-trifluoro-4-methylpent-2-ene (3i)



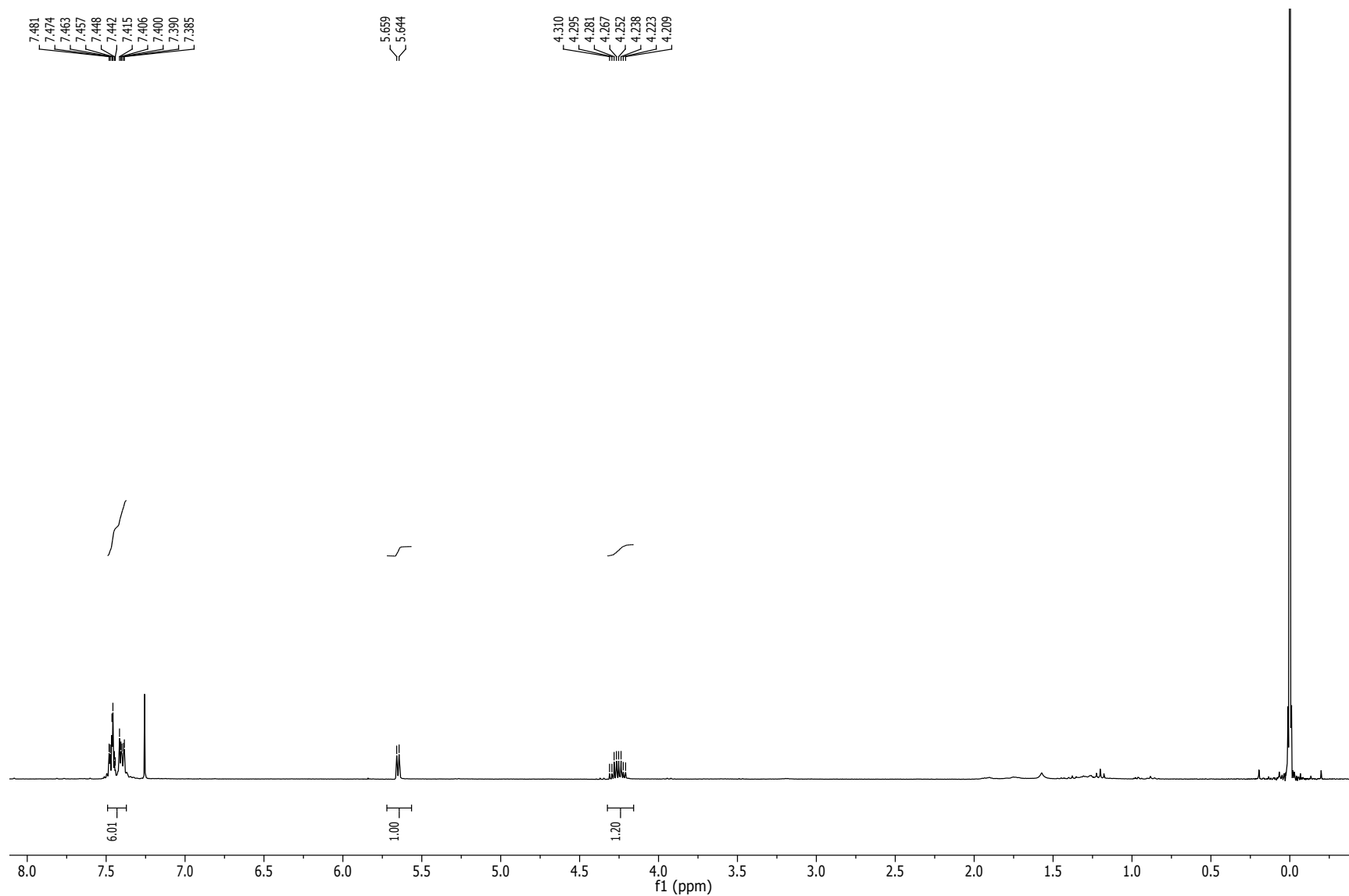
¹H NMR (300 MHz, CDCl₃): δ 6.35 (ddq, *J* = 15.8, 6.5, 2.1 Hz, 1H), 5.545 (dq, *J* = 15.9, 6.3, 1.2 Hz, 1H), 2.48-2.33 (m, 1H), 1.13 (d, *J* = 7.5 Hz, *syn*-6H), 1.06 (d, *J* = 6.6 Hz, 6H); **¹³C NMR (75 MHz, CDCl₃):** δ 146.7, 123.3 (q, *J*_{C-F} = 266.9 Hz), 115.7 (q, *J*_{C-F} = 33 Hz), 30.3, 21.2; **¹⁹F NMR (282 MHz, CDCl₃):** δ -56.6 (d, *J*_{H-F} = 8.5 Hz, *Z*-3F), -65.4 (d, *J*_{H-F} = 5.6 Hz, 3F). **LRMS (ESI+)** calcd for [M+Na]⁺ 161.0, found 161.1

(*E*)-1,1,1-trifluoro-4,4-dimethylpent-2-ene (3j)

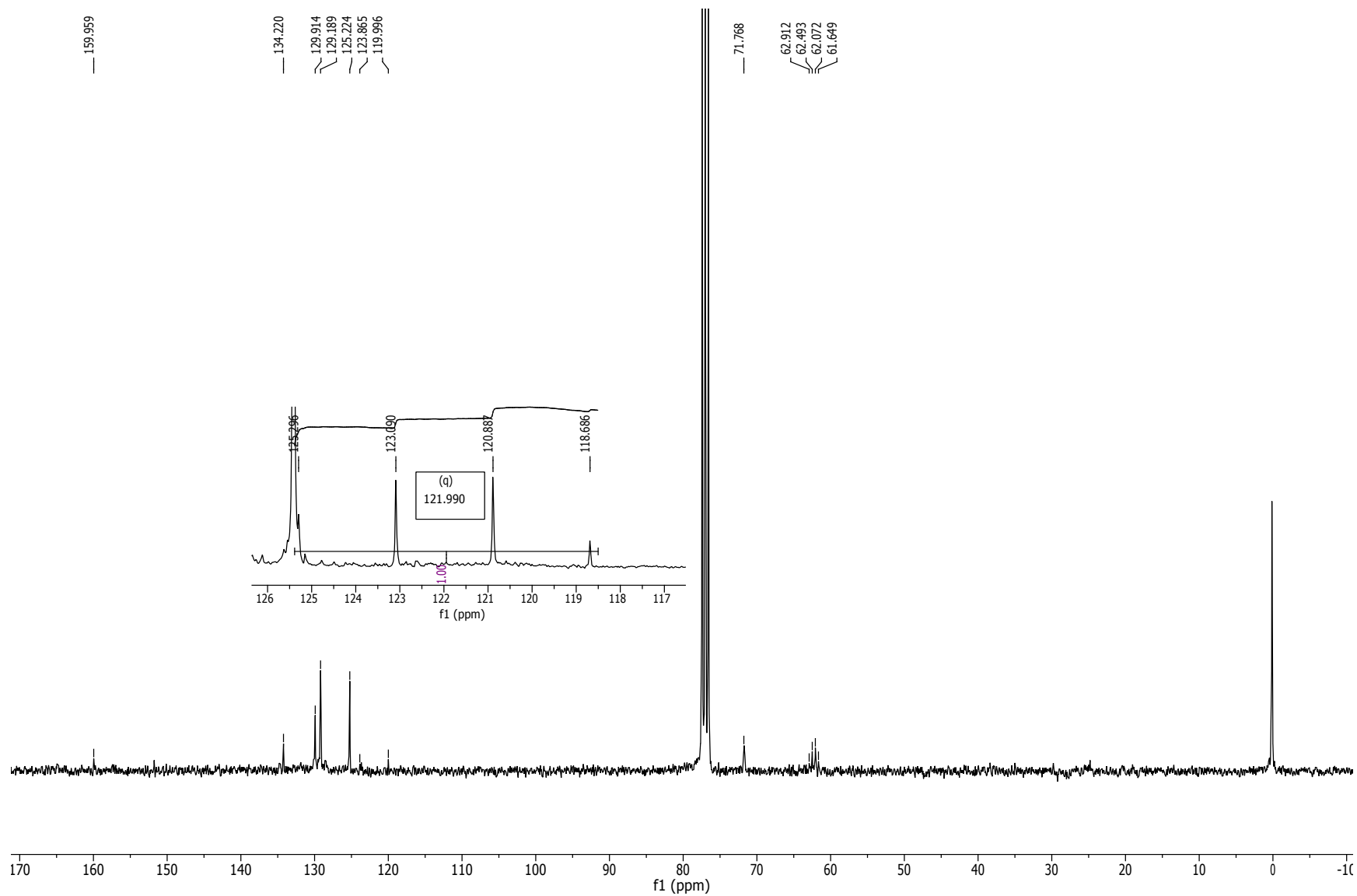


¹H NMR (300 MHz, CDCl₃): δ 6.37 (dq, *J* = 17.0, 2.1 Hz, 1H), 5.5 (dq, *J* = 16.1, 6.2 Hz, 1H), 1.07 (s, 9H); **¹³C NMR (75 MHz, CDCl₃):** δ 150.4 (q, *J*_{C-F} = 5.9 Hz), 123.7 (q, *J*_{C-F} = 266.9 Hz),

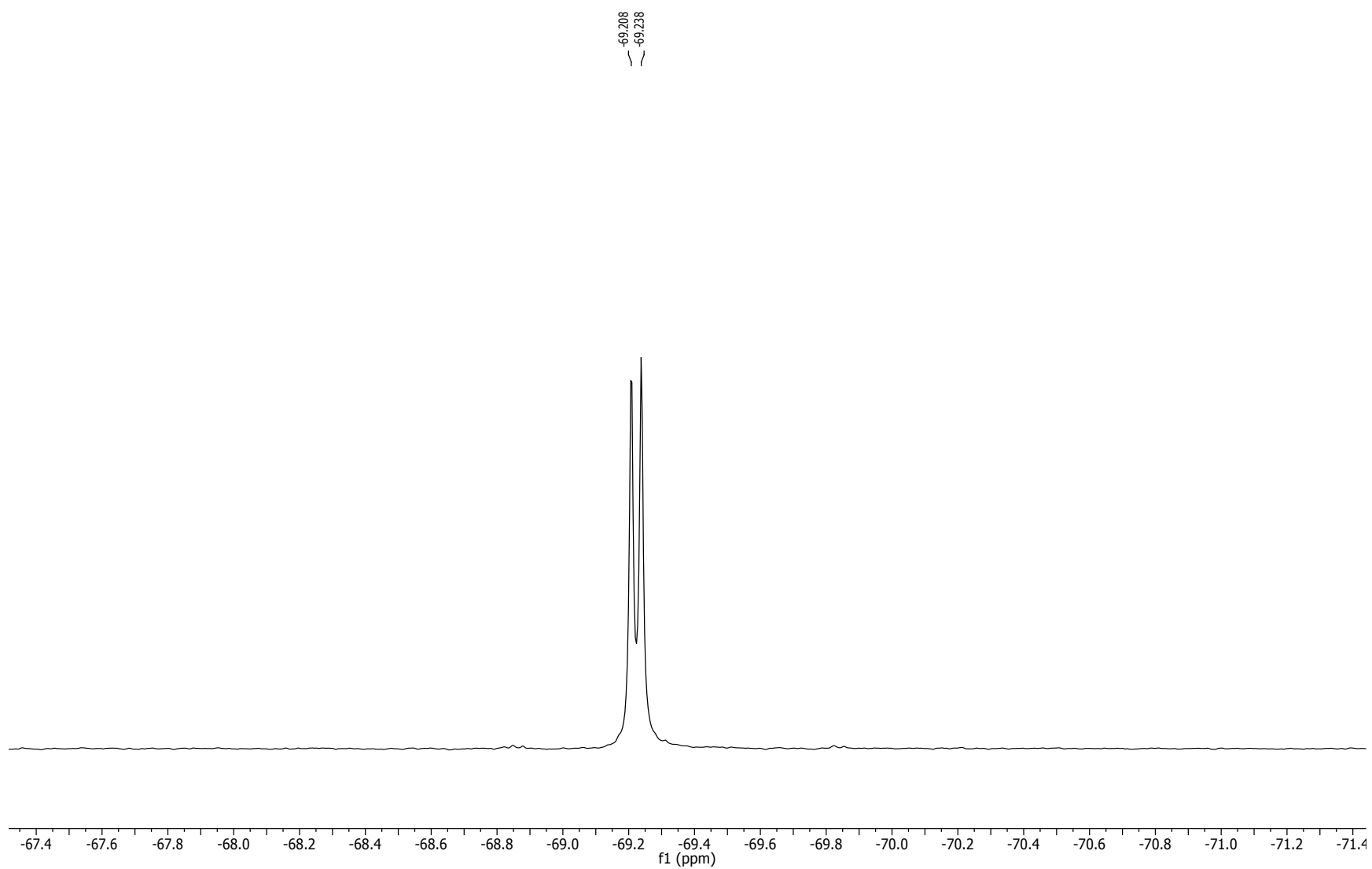
114.07 (q, $J_{C-F} = 33$ Hz), 33.1, 28.6; **^{19}F NMR (282 MHz, CDCl_3):** δ -65.3 (d, $J_{H-F} = 5.6$ Hz, 3F)
. **LRMS** (ESI+) calcd for $[\text{M}+\text{Na}]^+$ 175.2, found 175.4



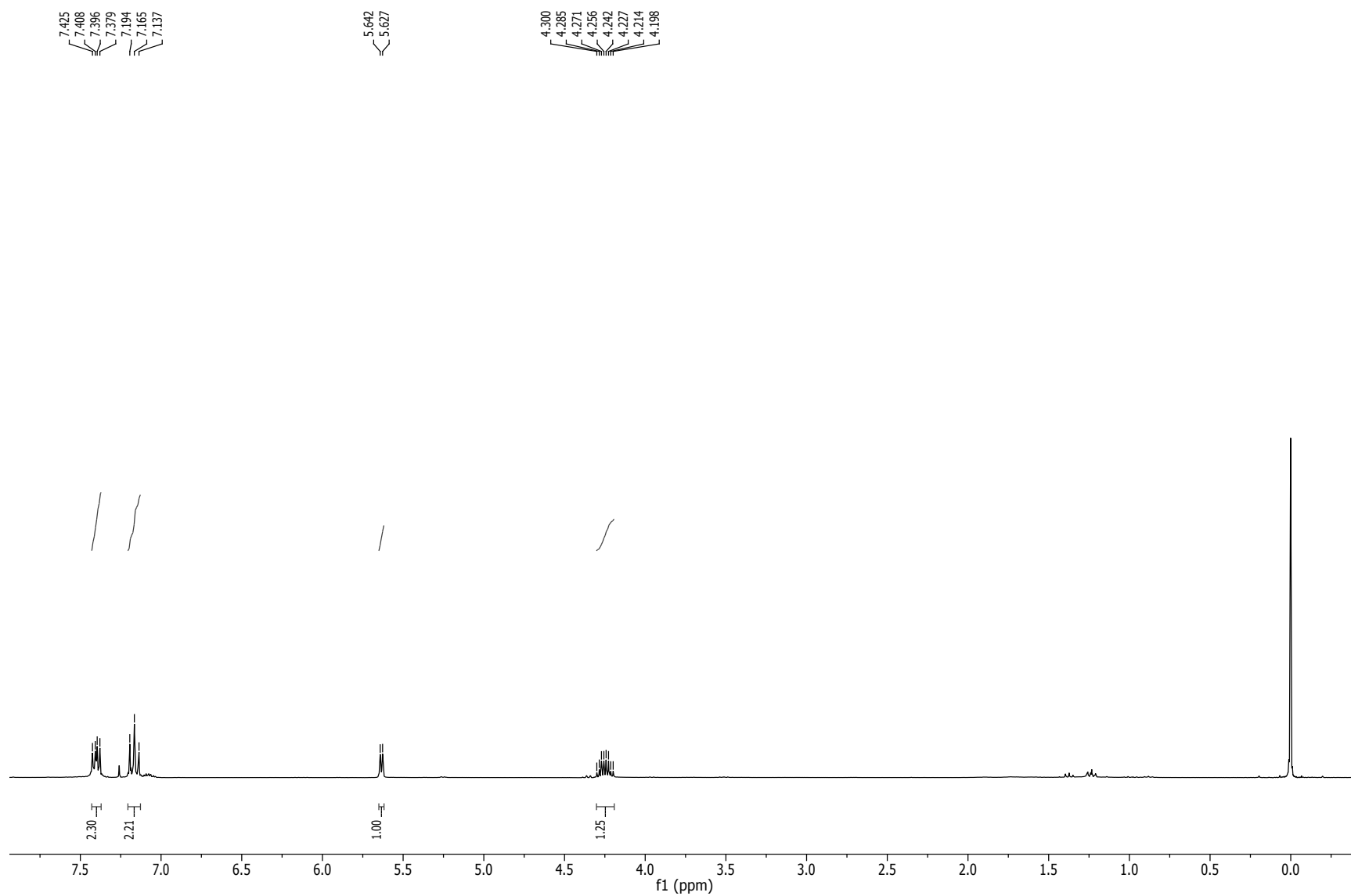
¹H NMR Spectrum of *anti*-4-phenyl-3-(trifluoromethyl)oxetan-2-one (**2a**)



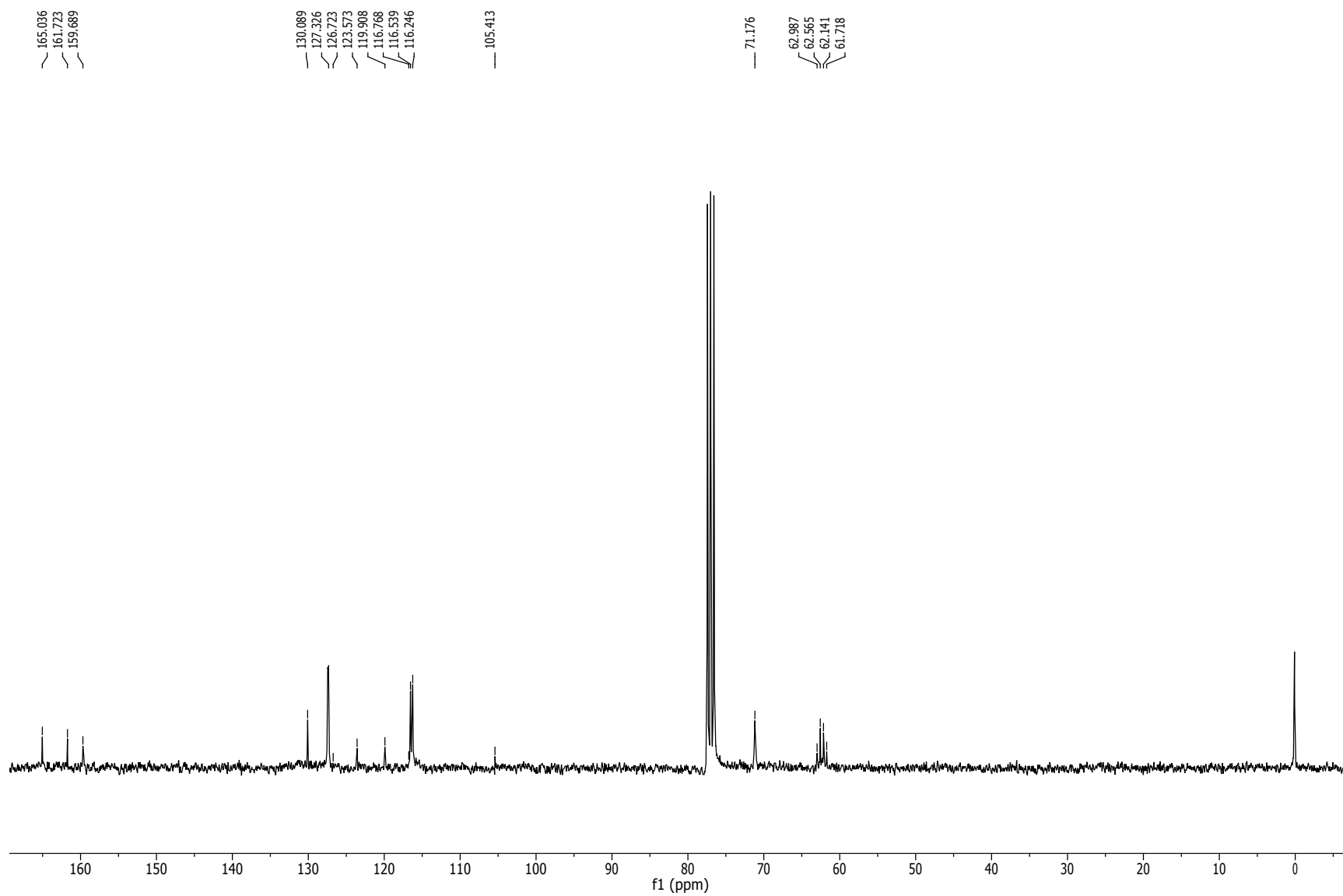
¹³C NMR Spectrum of *anti*-4-phenyl-3-(trifluoromethyl)oxetan-2-one (**2a**)



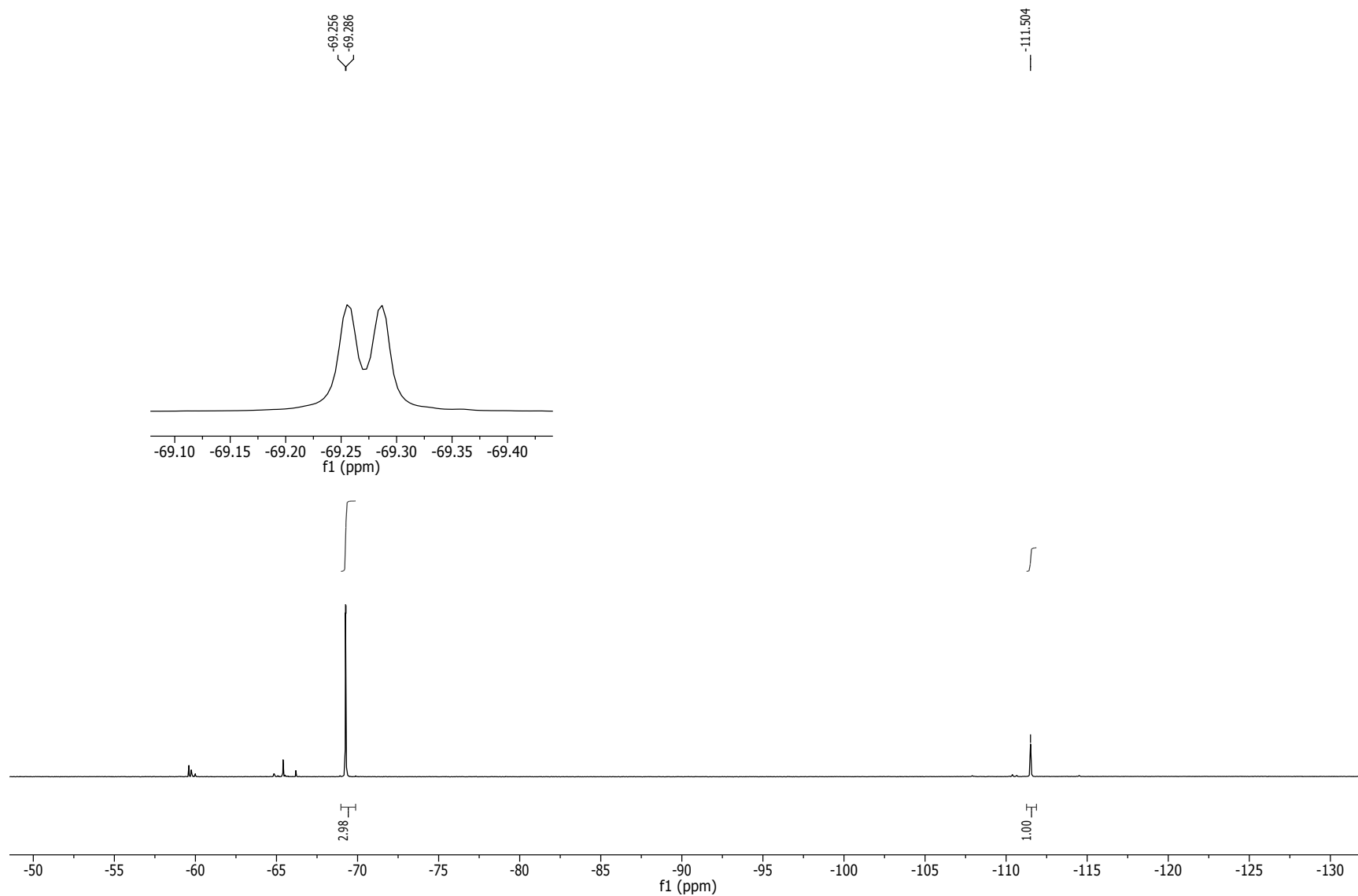
^{19}F NMR Spectrum of *anti*-4-phenyl-3-(trifluoromethyl)oxetan-2-one (**2a**)



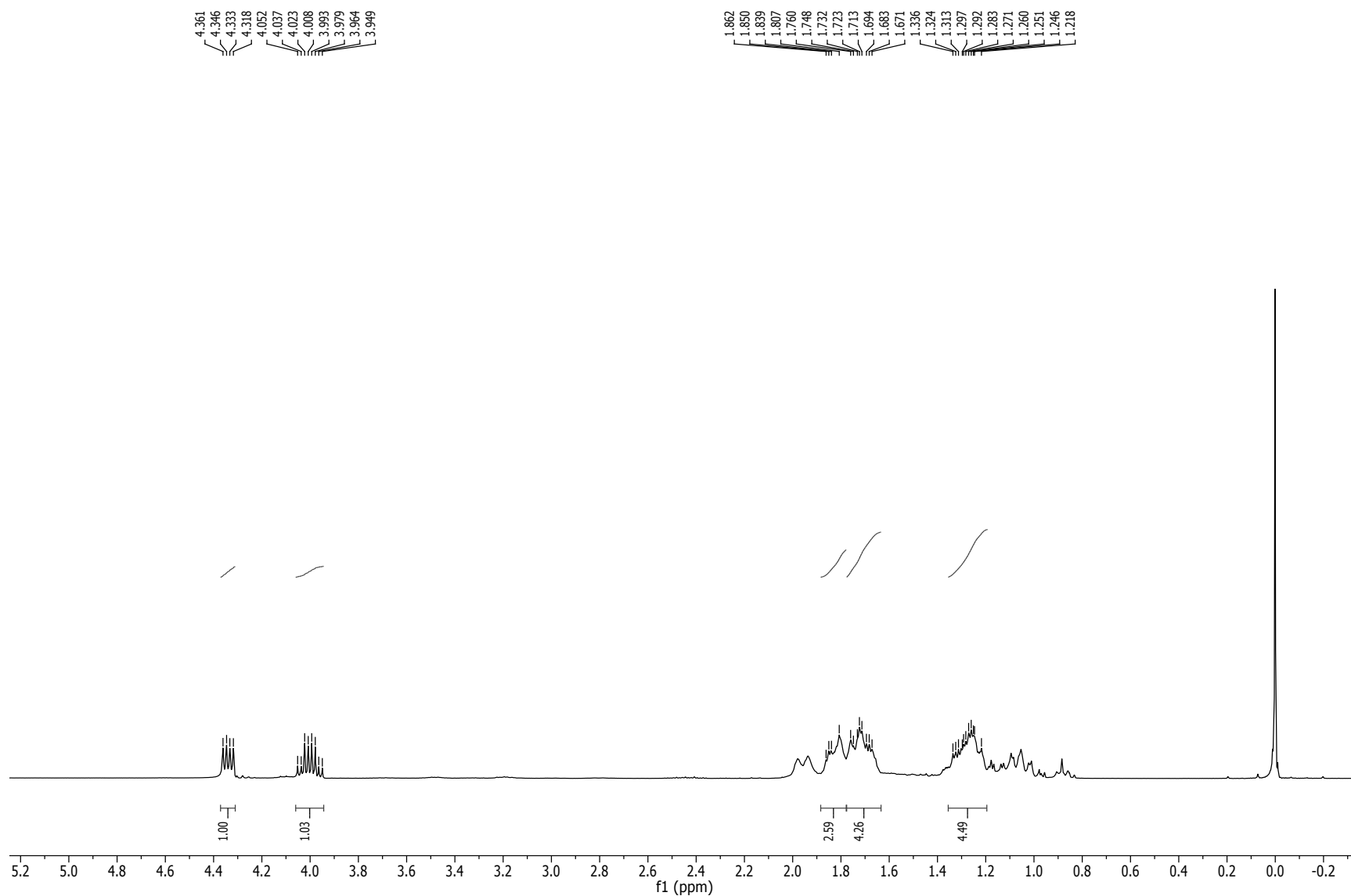
^1H NMR Spectrum of *anti*-4-(4-fluorophenyl)-3-(trifluoromethyl)oxetan-2-one (**2c**)



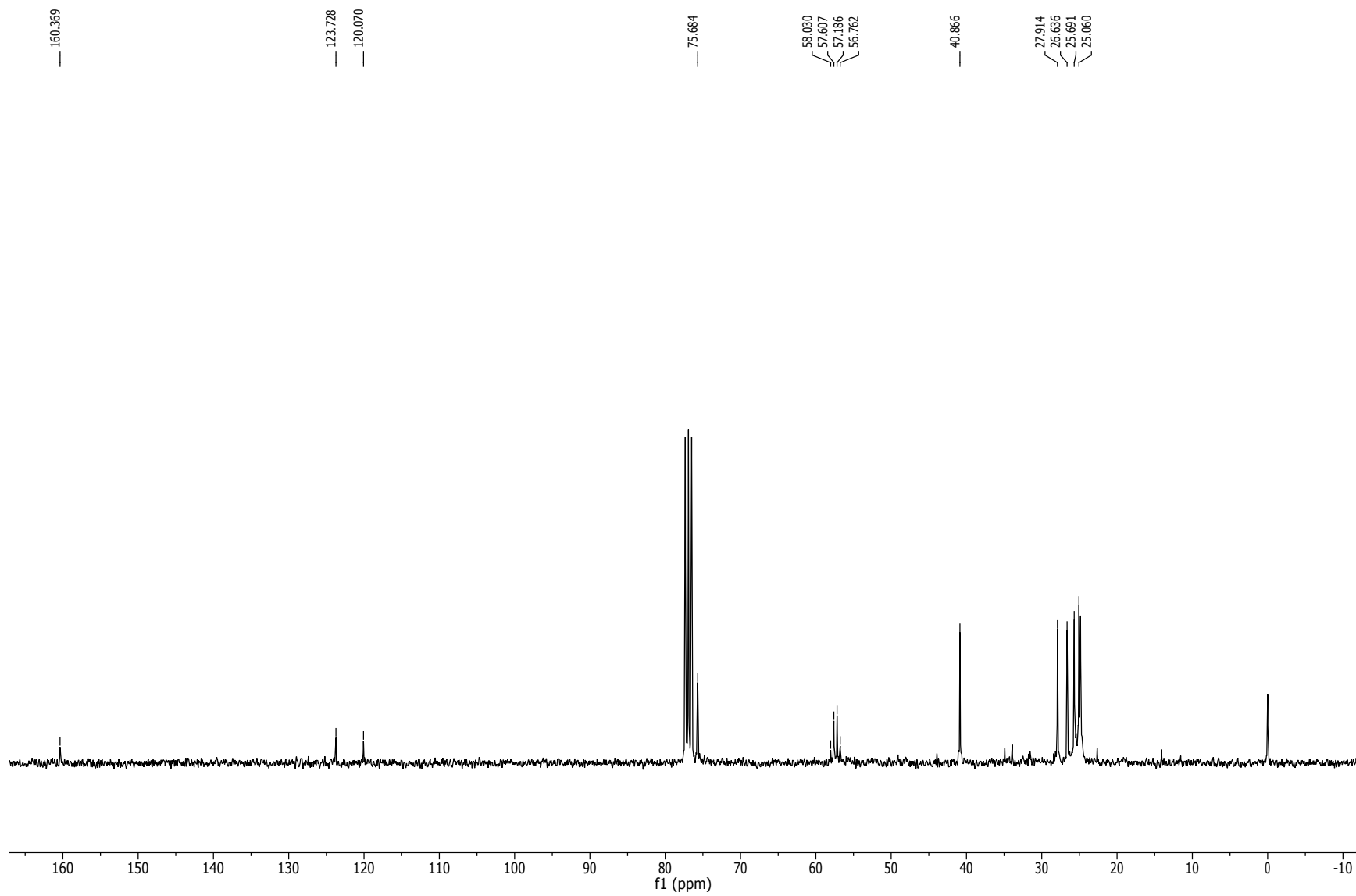
^{13}C NMR Spectrum of *anti*-4-(4-fluorophenyl)-3-(trifluoromethyl)oxetan-2-one (**2c**)



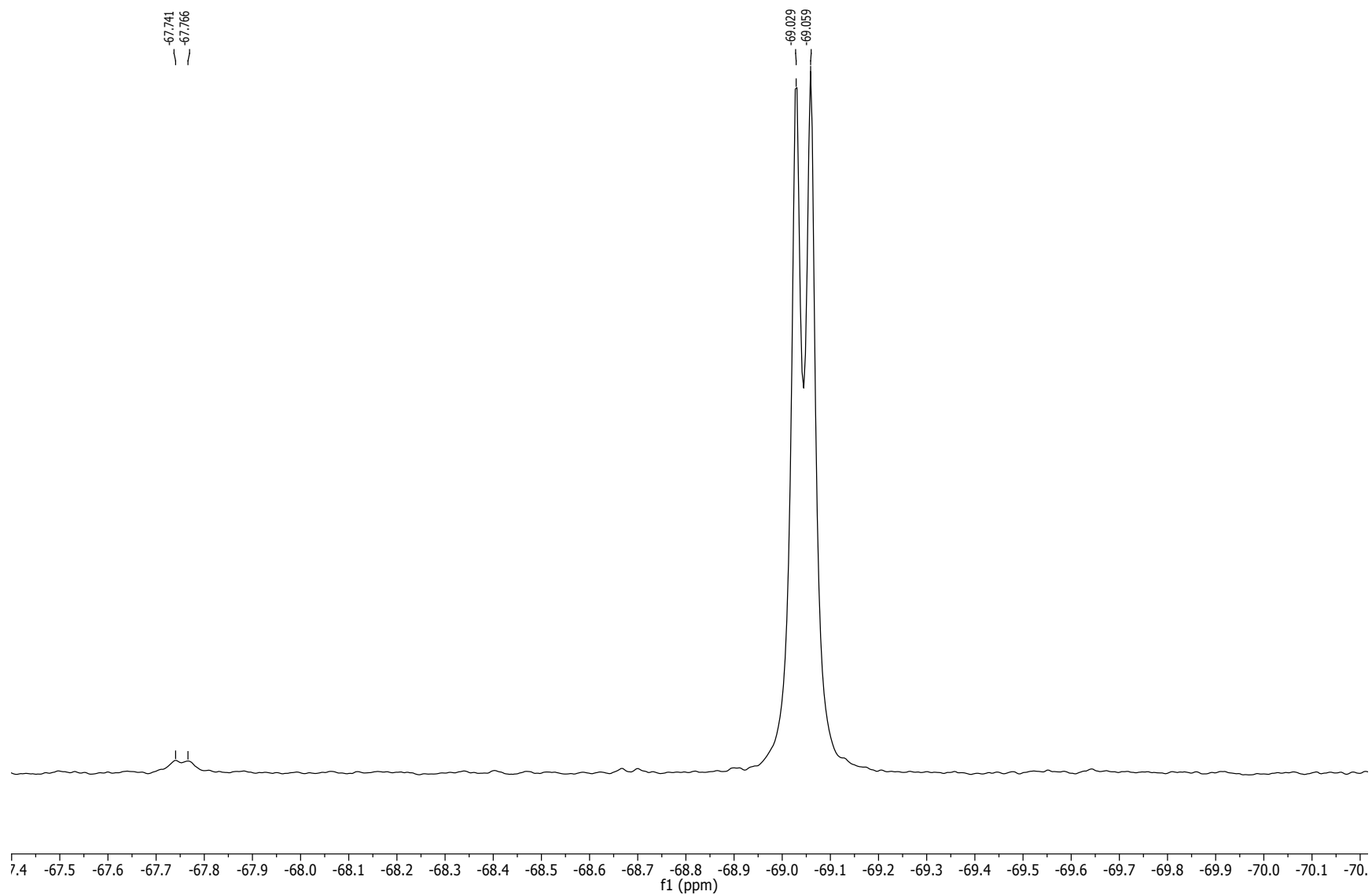
^{19}F NMR Spectrum of *anti*-4-(4-fluorophenyl)-3-(trifluoromethyl)oxetan-2-one (**2c**)



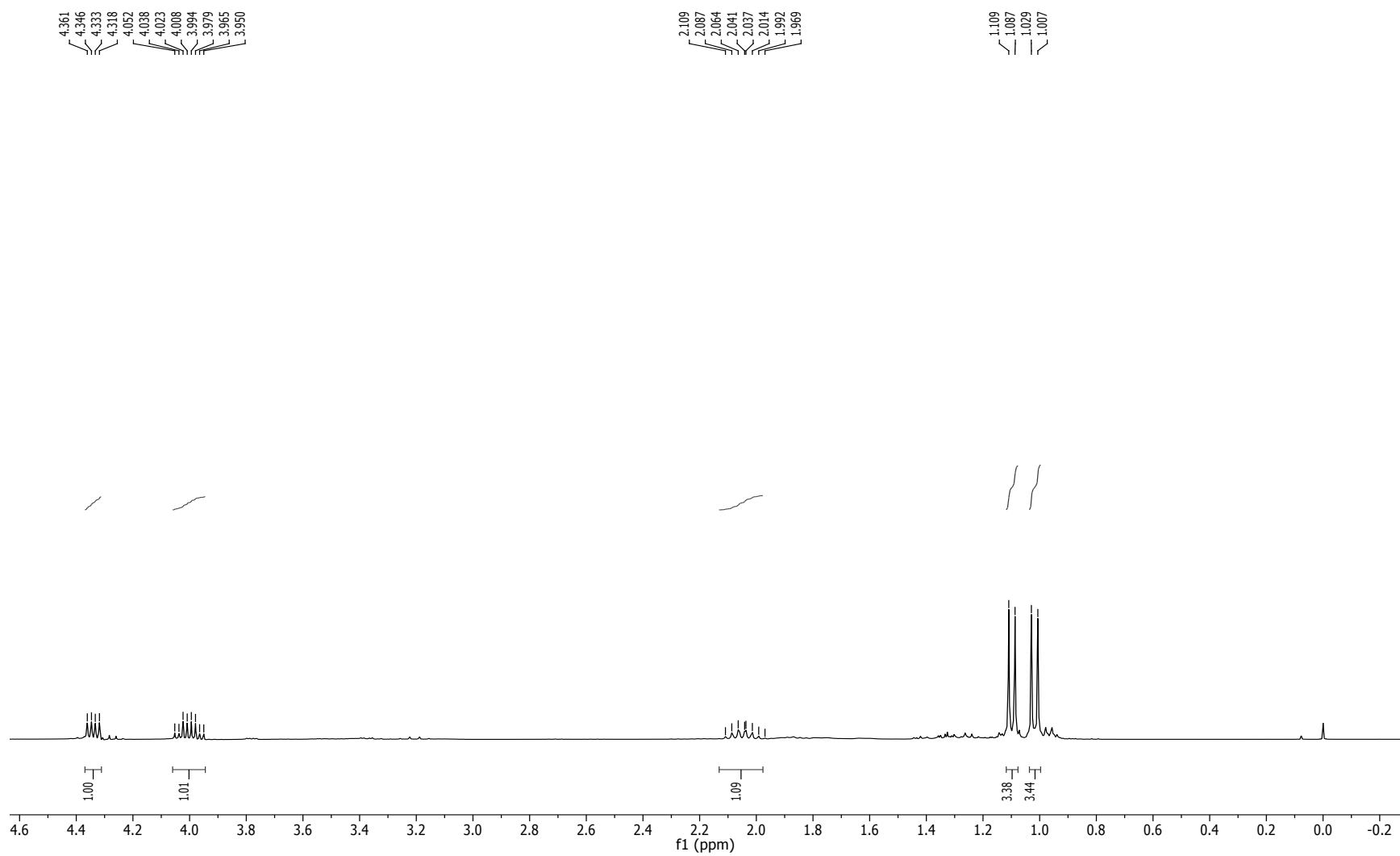
^1H NMR Spectrum of *anti*-4-cyclohexyl-3-(trifluoromethyl)oxetan-2-one (**2h**)



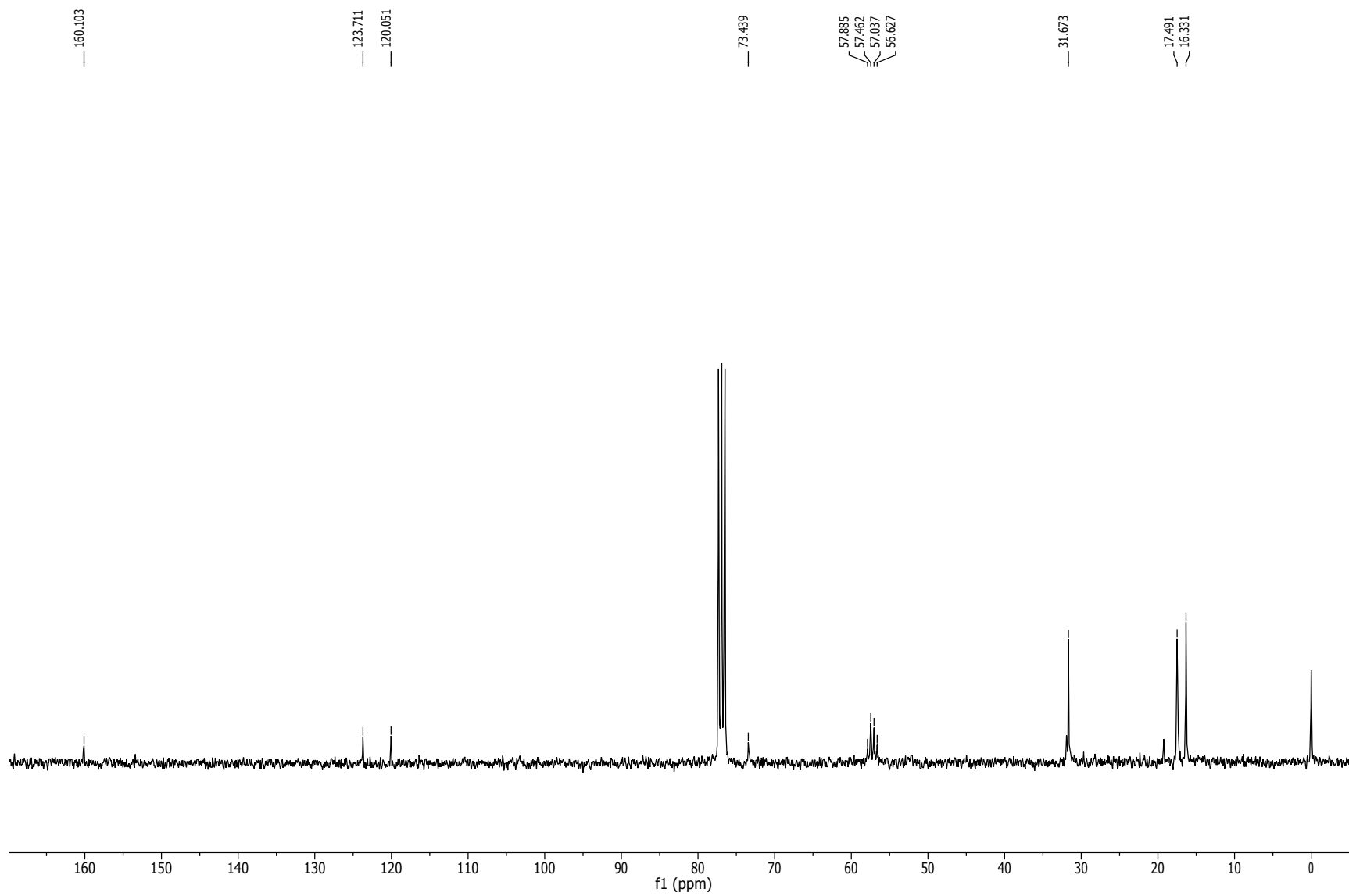
^{13}C NMR Spectrum of *anti*-4-cyclohexyl-3-(trifluoromethyl)oxetan-2-one (**2h**)



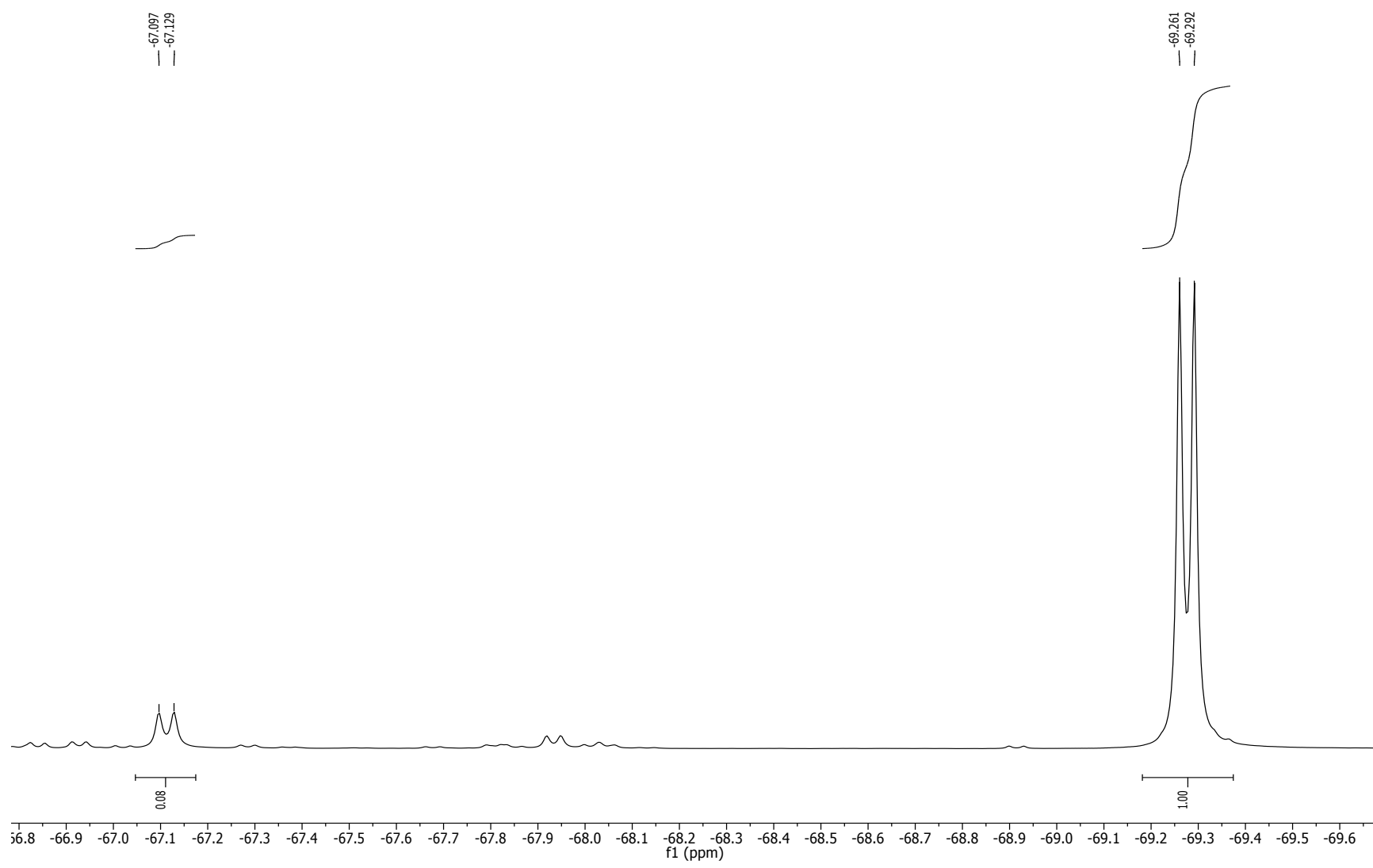
^{19}F NMR Spectrum of *anti*-4-cyclohexyl-3-(trifluoromethyl)oxetan-2-one (**2h**)



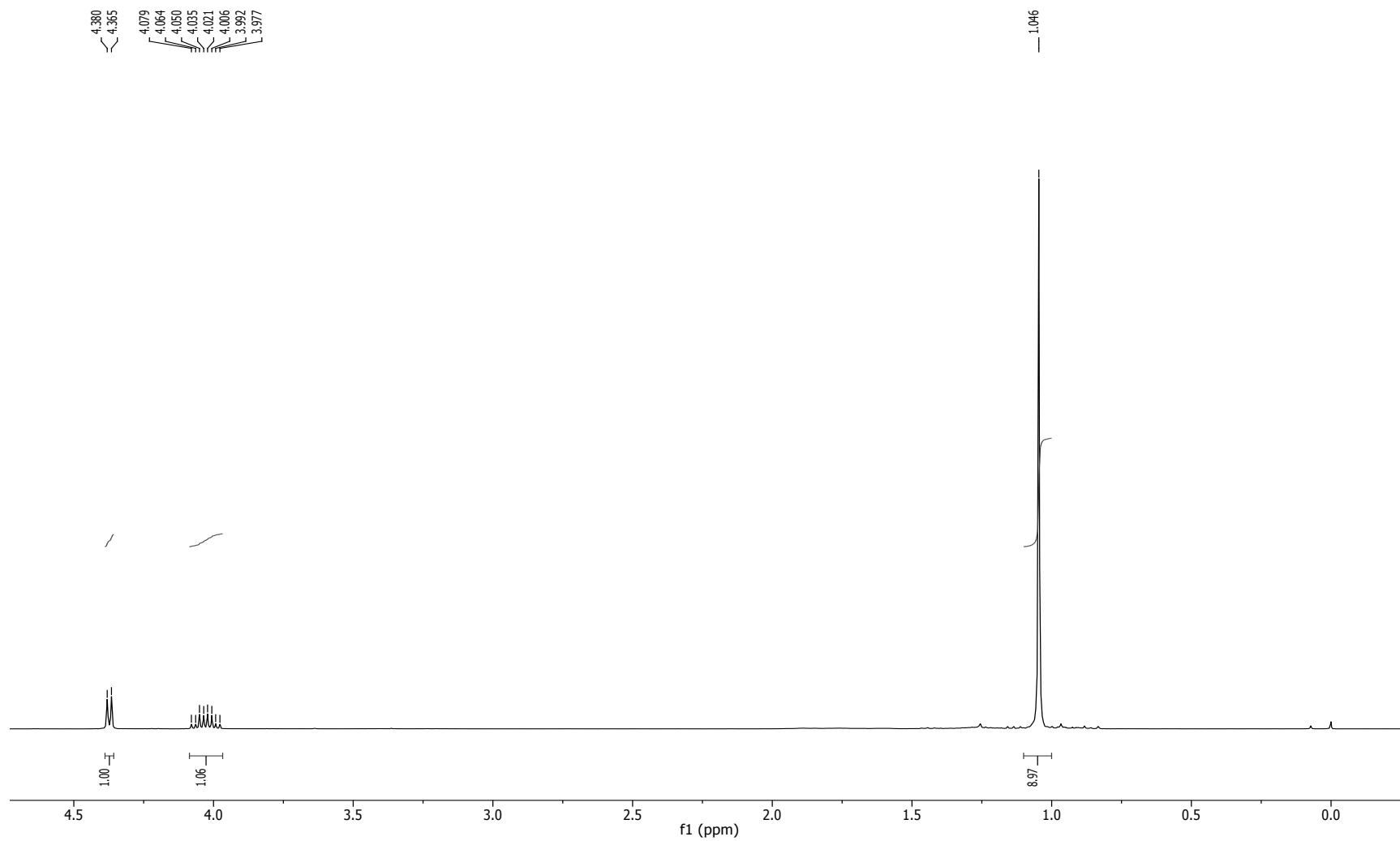
^1H NMR Spectrum of *anti*-4-isopropyl-3-(trifluoromethyl)oxetan-2-one (**2i**)



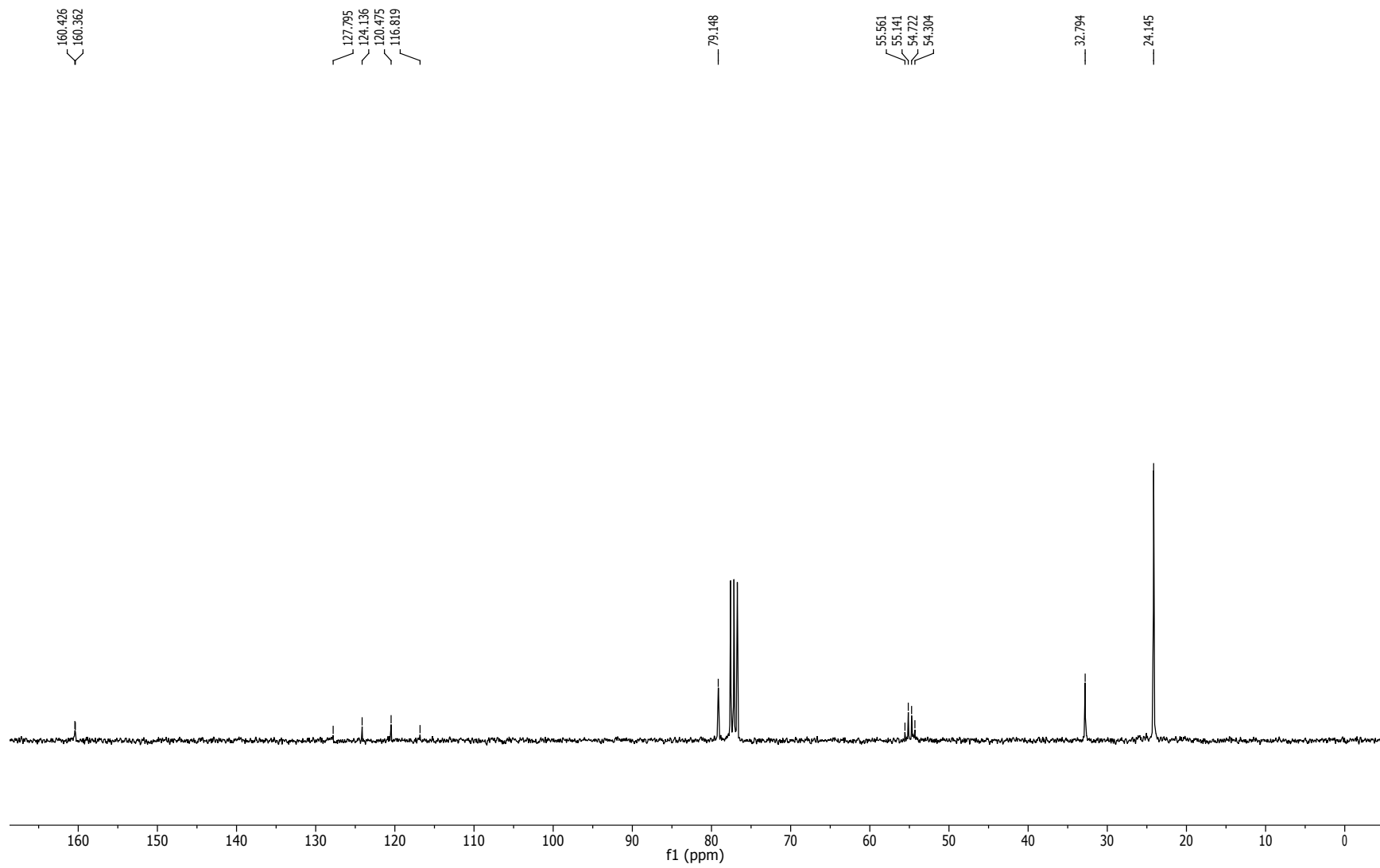
¹³C NMR Spectrum of *anti*-4-isopropyl-3-(trifluoromethyl)oxetan-2-one (**2i**)



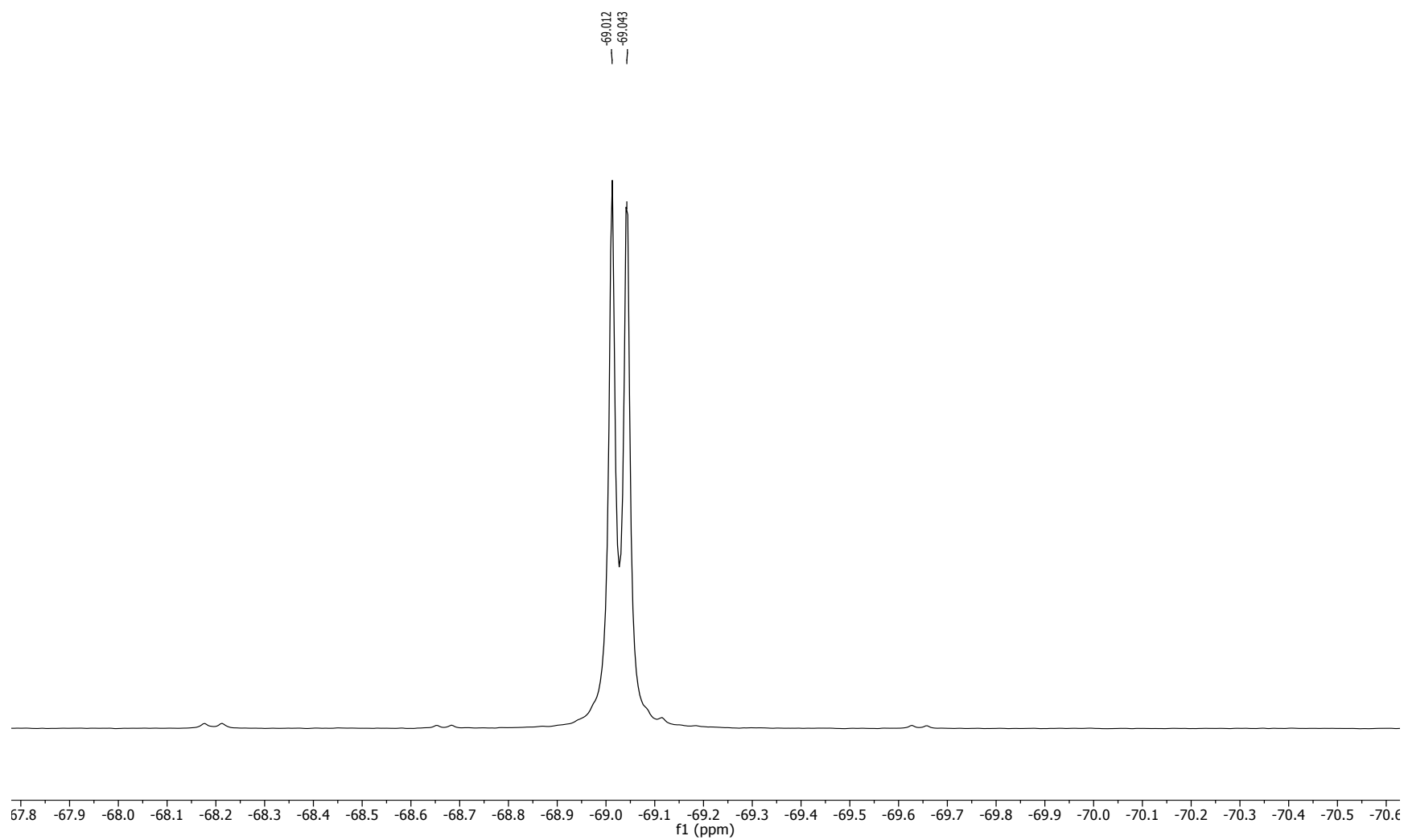
¹⁹F NMR Spectrum of *anti*-4-isopropyl-3-(trifluoromethyl)oxetan-2-one (**2i**)



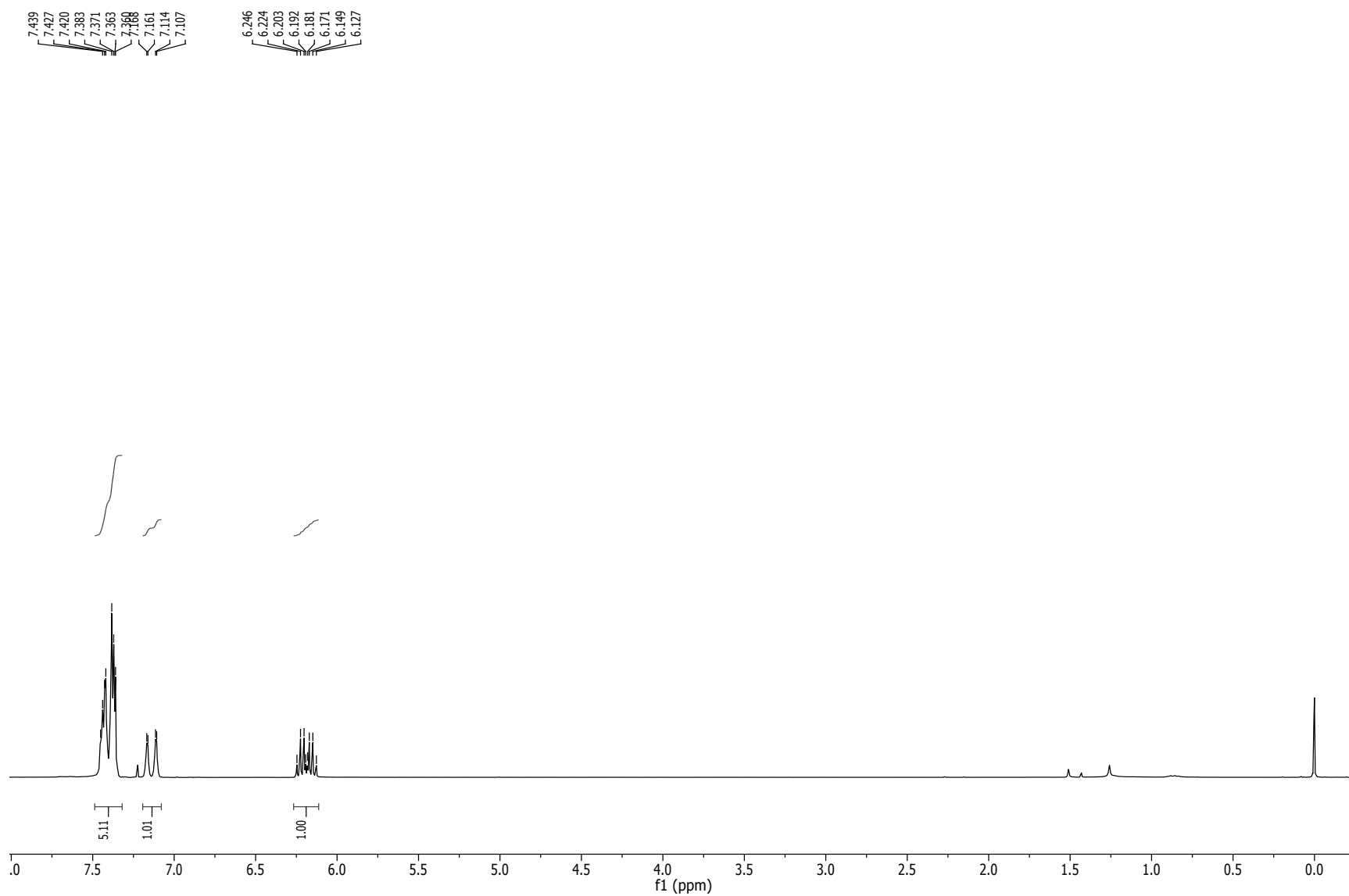
^1H NMR Spectrum of *anti*-4-(tert-butyl)-3-(trifluoromethyl)oxetan-2-one (**2j**)



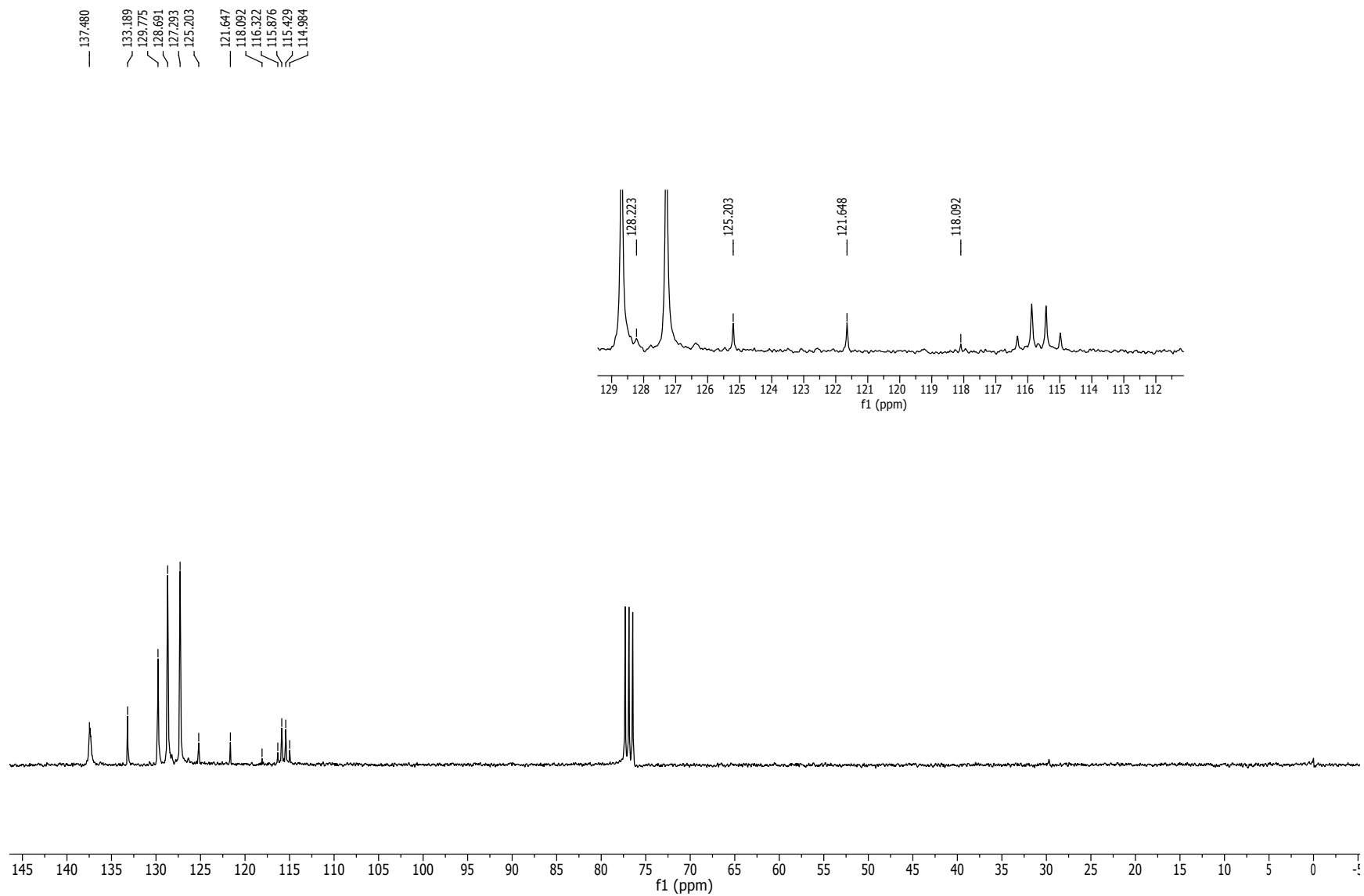
^{13}C NMR Spectrum of *anti*-4-(tert-butyl)-3-(trifluoromethyl)oxetan-2-one (**2j**)



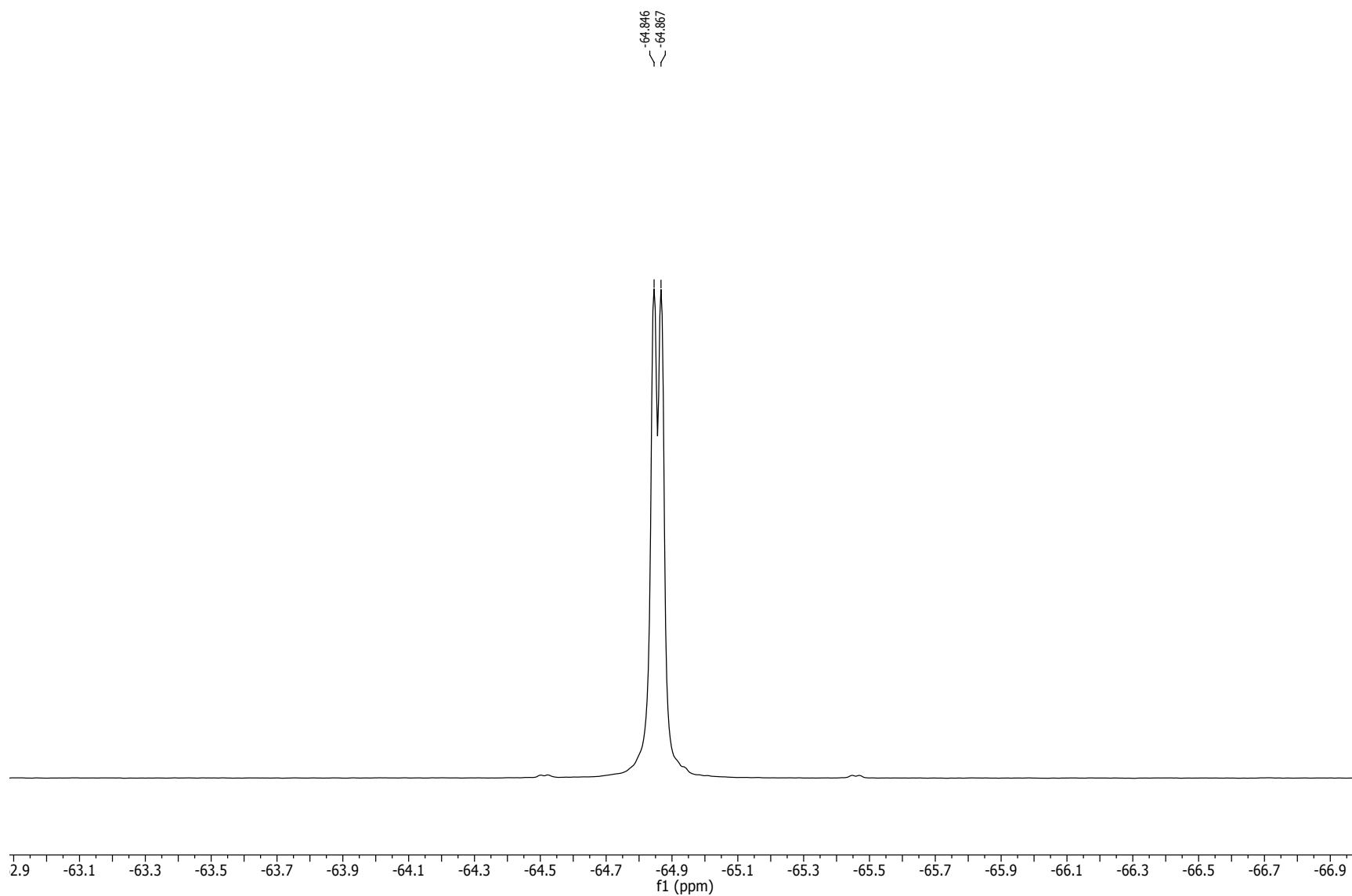
^{19}F NMR Spectrum of *anti*-4-(tert-butyl)-3-(trifluoromethyl)oxetan-2-one (**2j**)



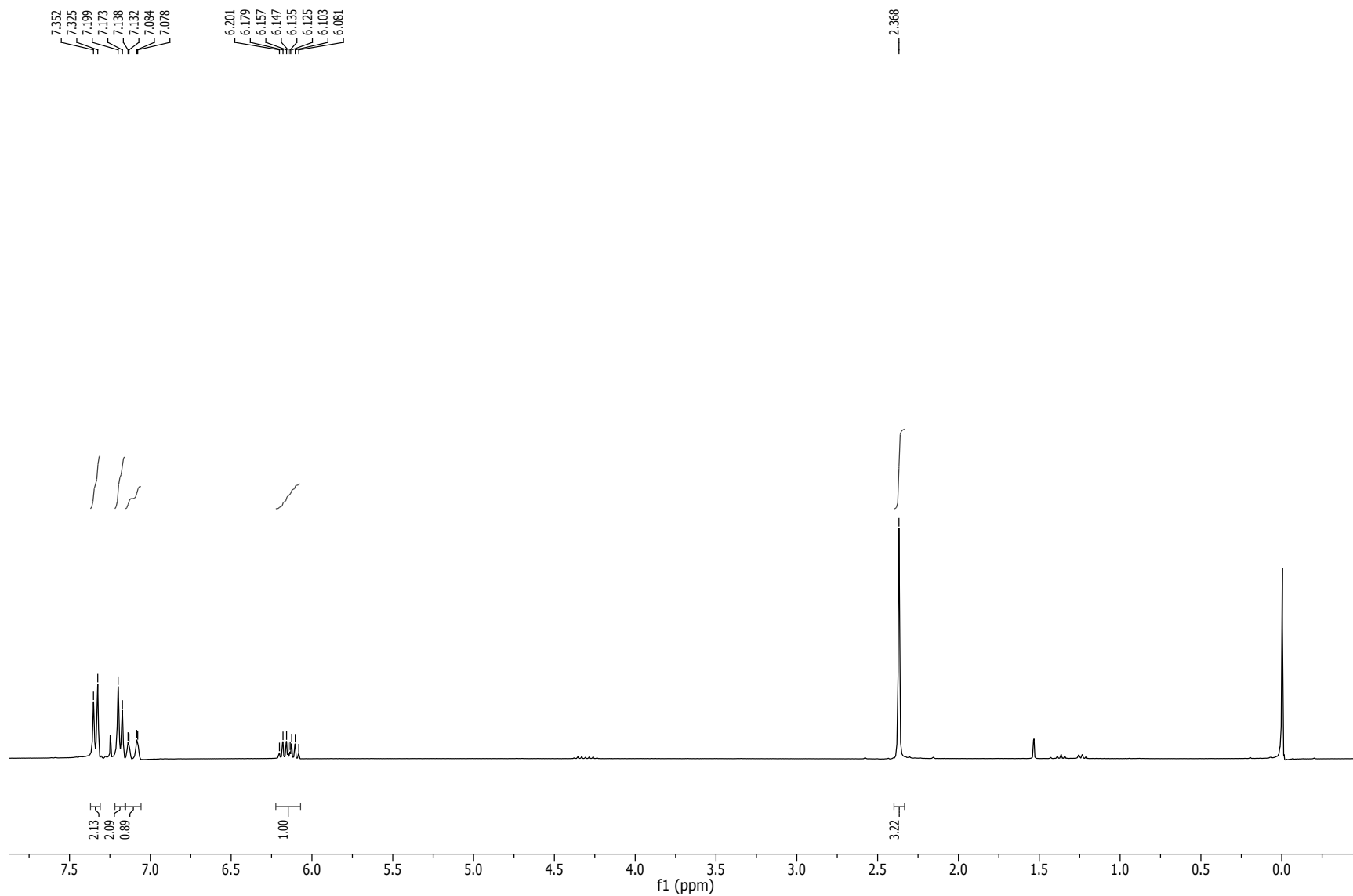
^1H NMR Spectrum of (*E*)-(3,3,3-trifluoroprop-1-en-1-yl)benzene (**3a**)



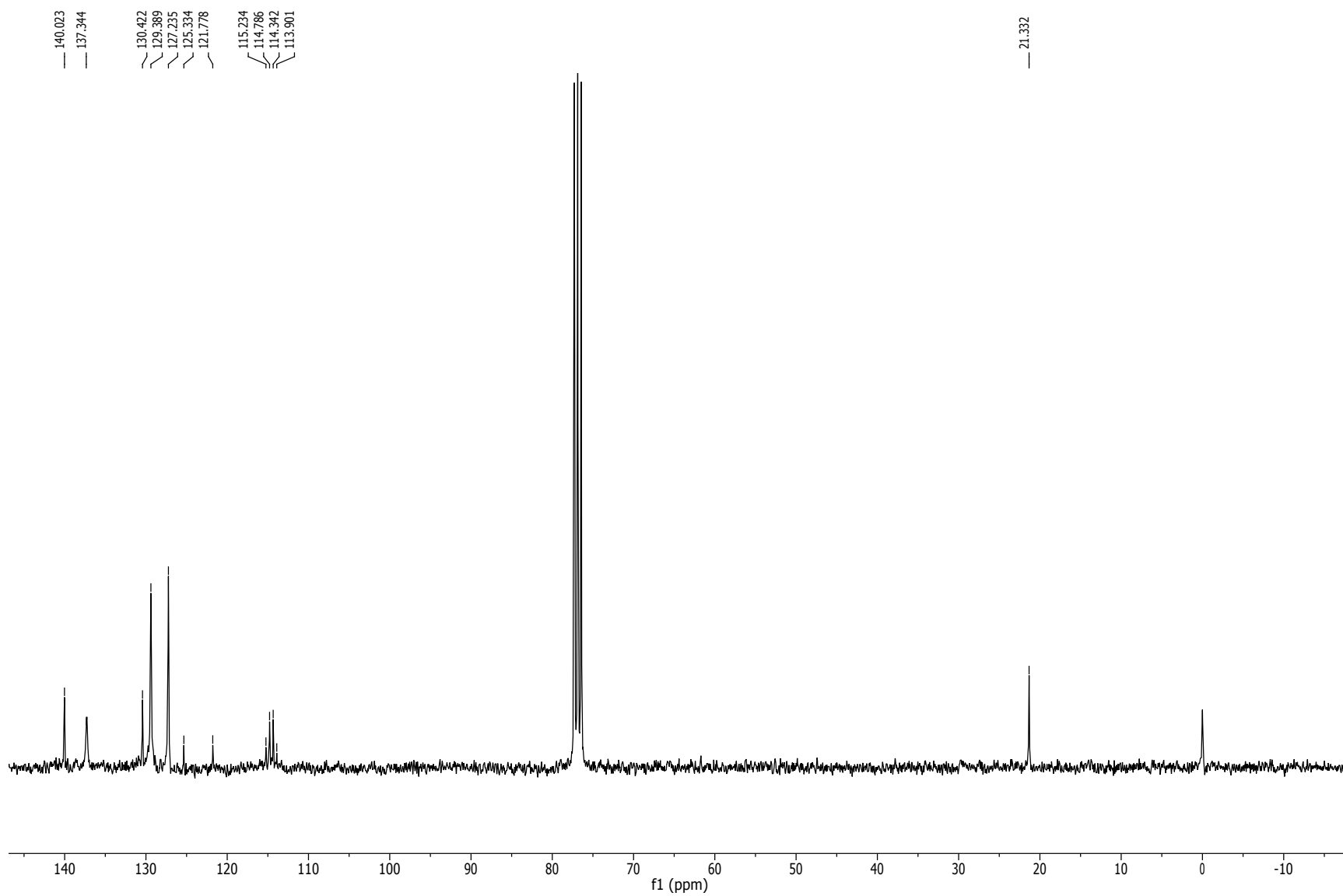
¹³C NMR Spectrum of (*E*)-(3,3,3-trifluoroprop-1-en-1-yl)benzene (**3a**)



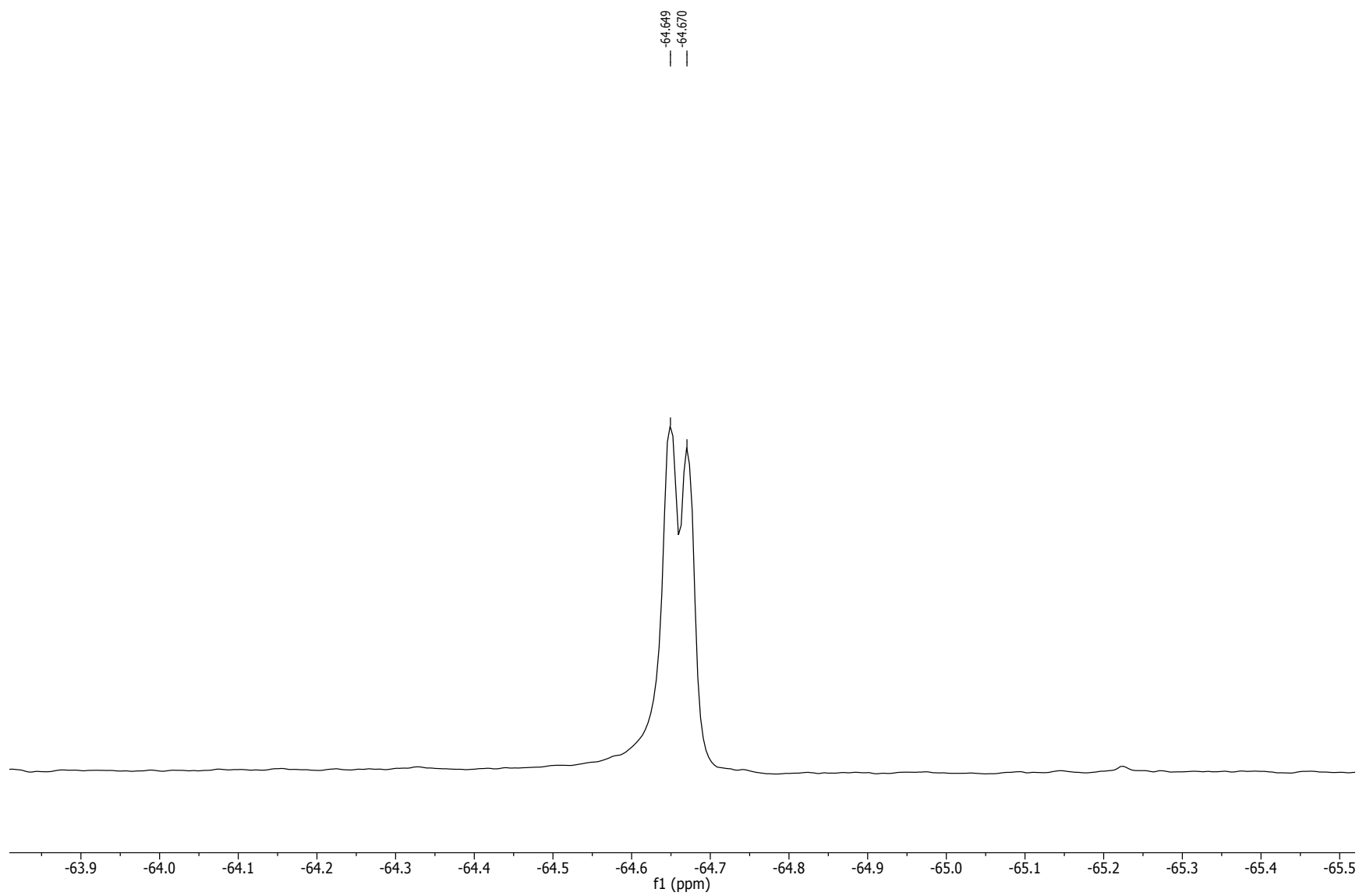
^{19}F NMR Spectrum of (*E*)-(3,3,3-trifluoroprop-1-en-1-yl)benzene (**3a**)



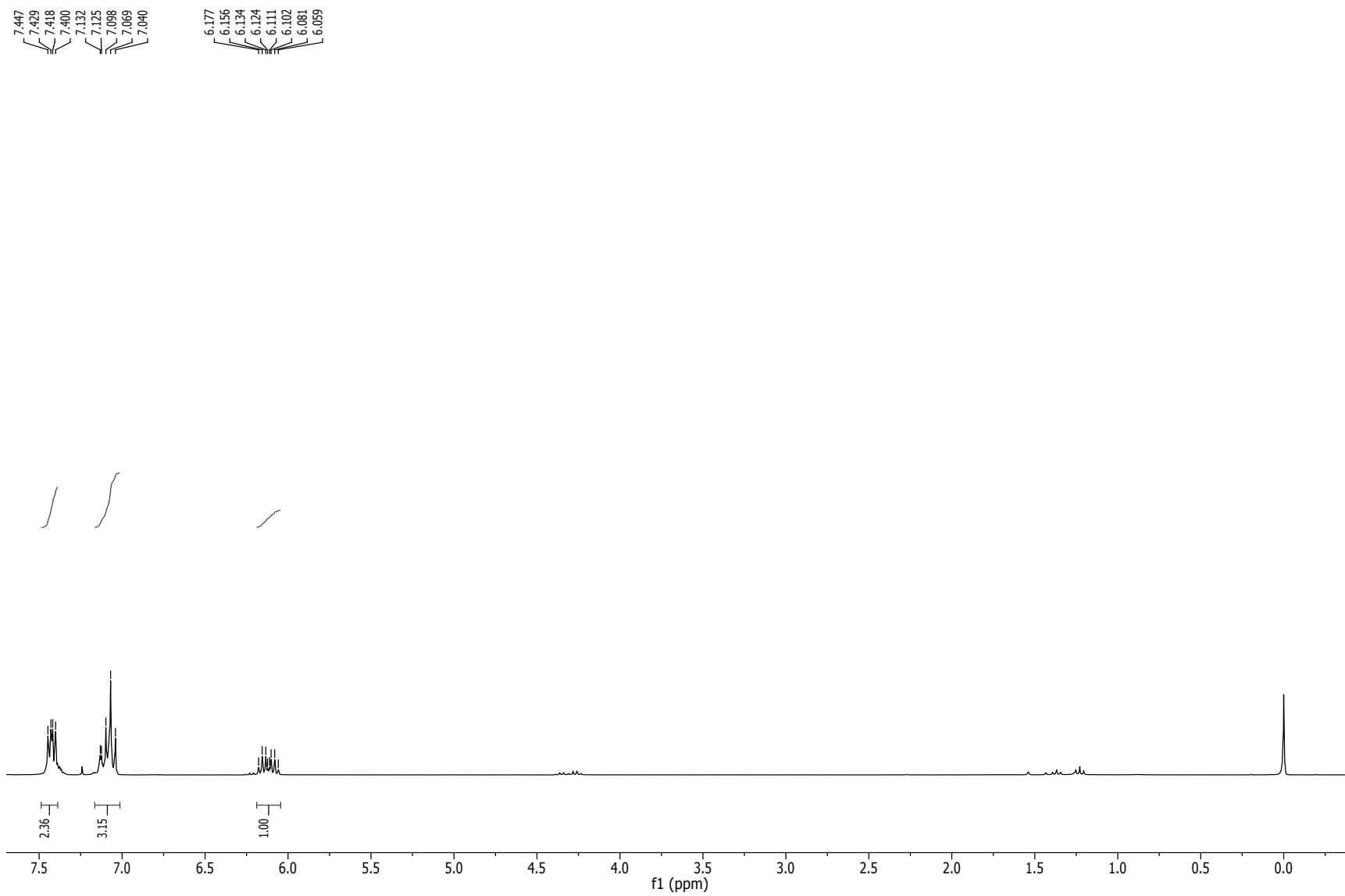
^1H NMR Spectrum of (*E*)-1-methyl-4-(3,3,3-trifluoroprop-1-en-1-yl)benzene (**3b**)



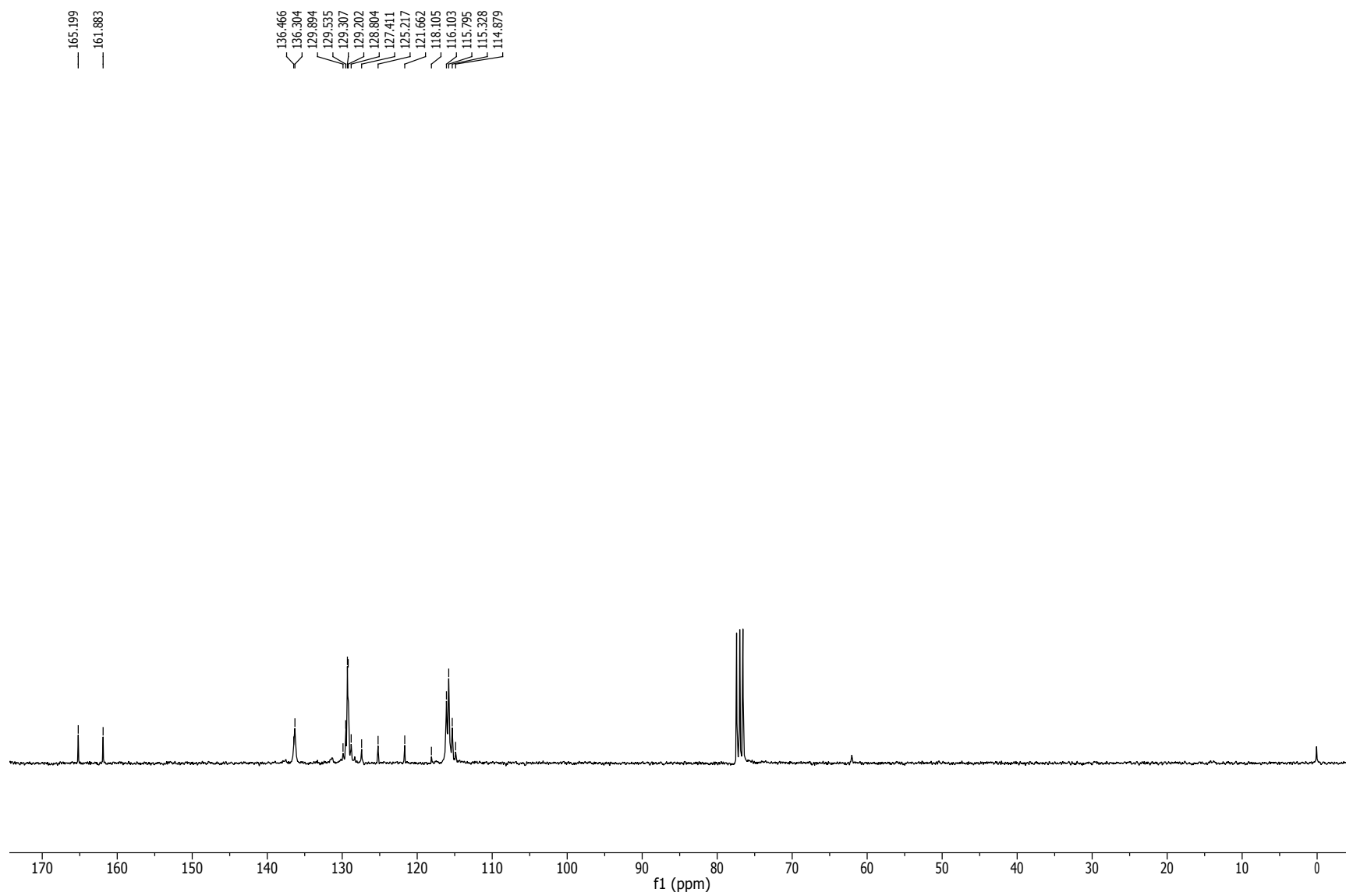
^{13}C NMR Spectrum of (*E*)-1-methyl-4-(3,3,3-trifluoroprop-1-en-1-yl)benzene (**3b**)



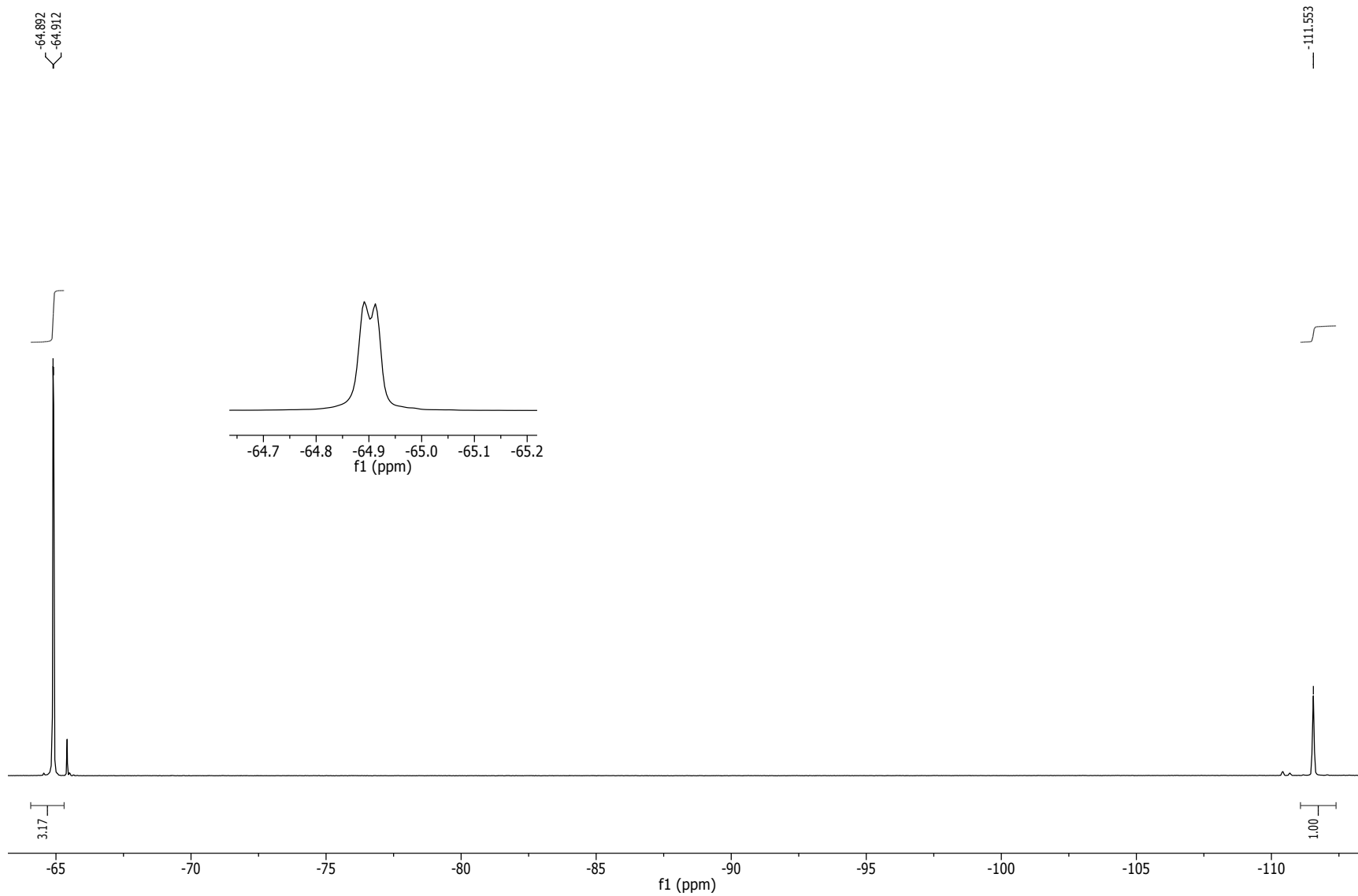
^{19}F NMR Spectrum of (*E*)-1-methyl-4-(3,3,3-trifluoroprop-1-en-1-yl)benzene (**3b**)



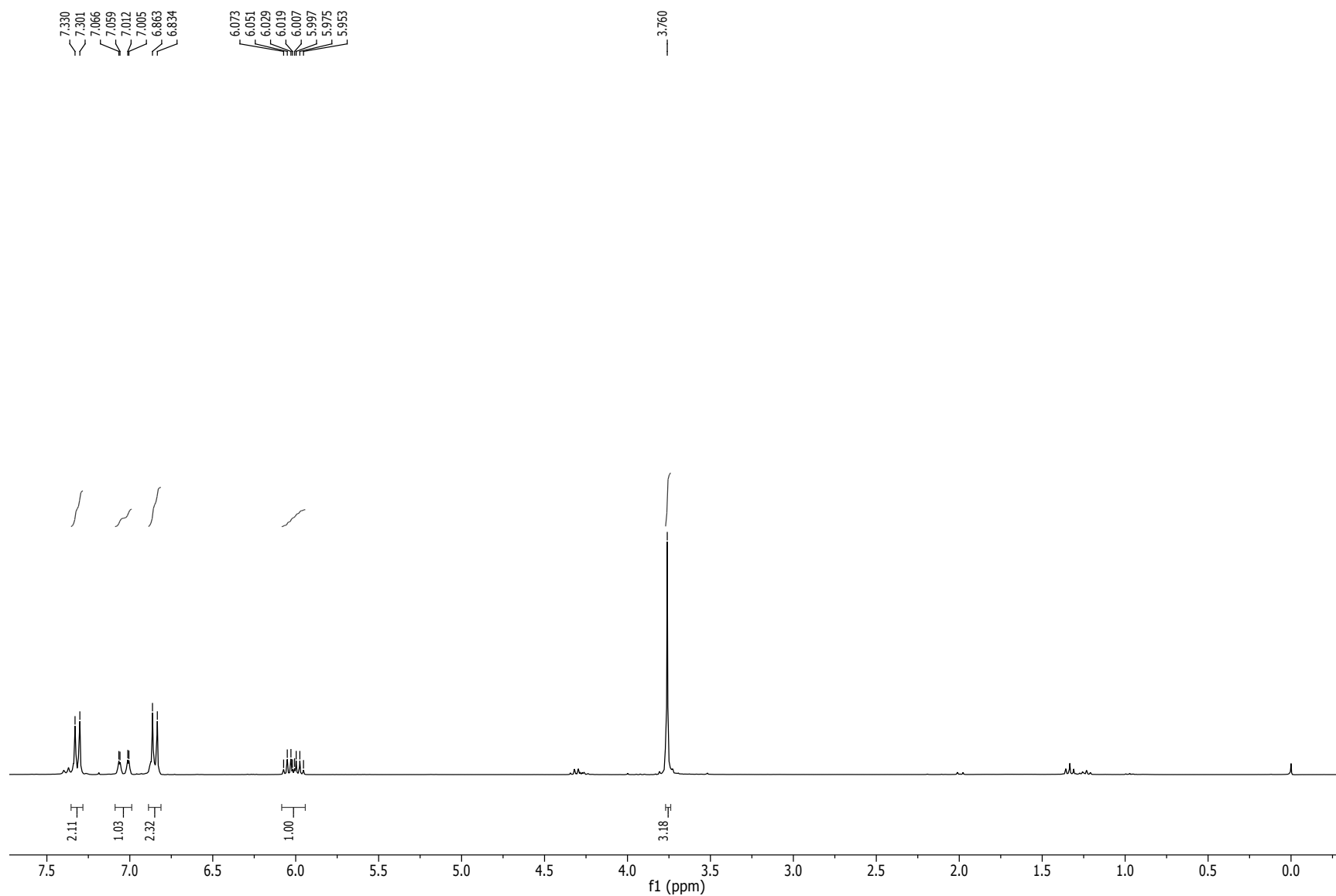
^1H NMR Spectrum of (*E*)-1-fluoro-4-(3,3,3-trifluoroprop-1-en-1-yl)benzene (**3c**)



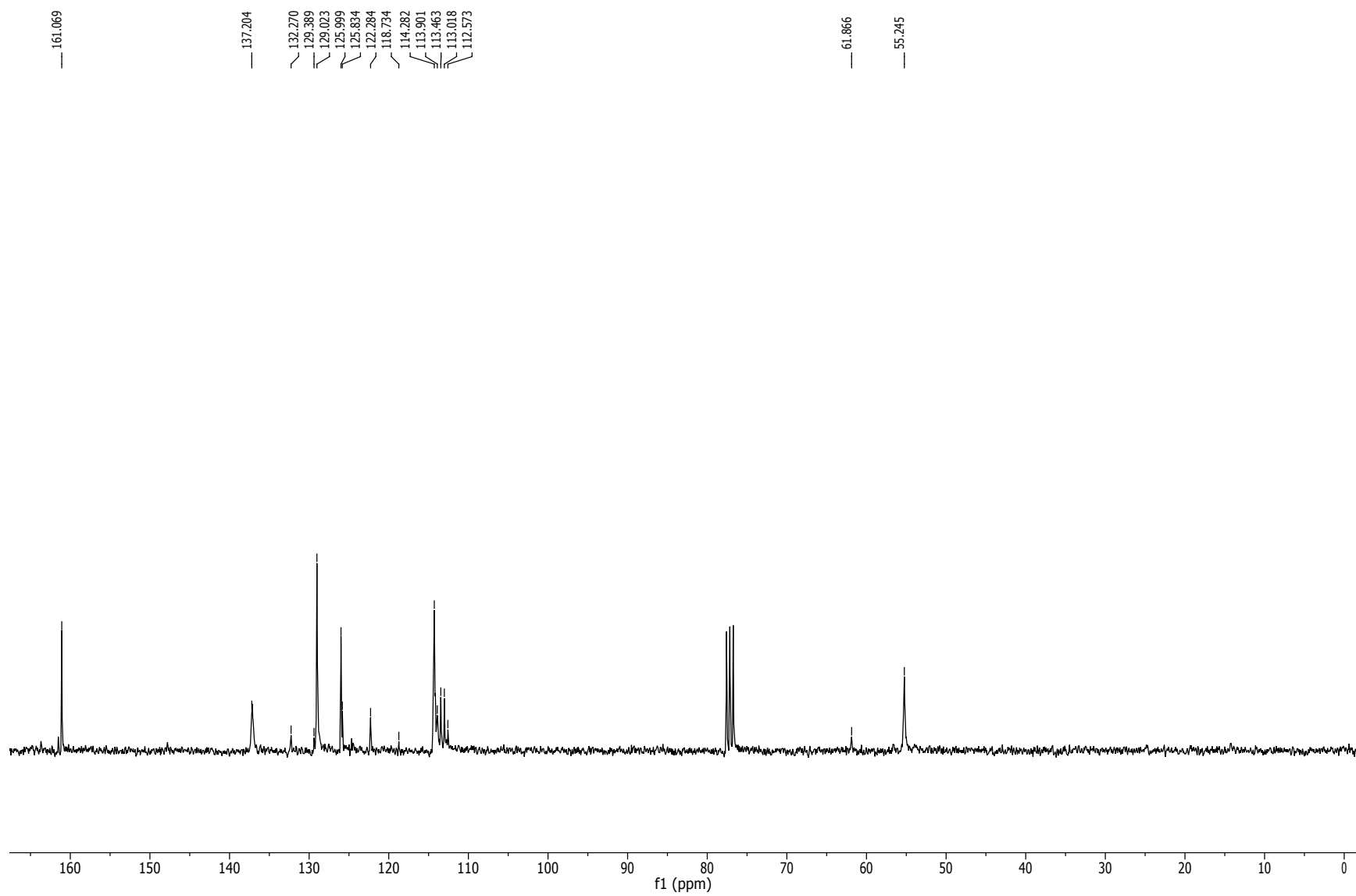
¹³C NMR Spectrum of (*E*)-1-fluoro-4-(3,3,3-trifluoroprop-1-en-1-yl)benzene (**3c**)



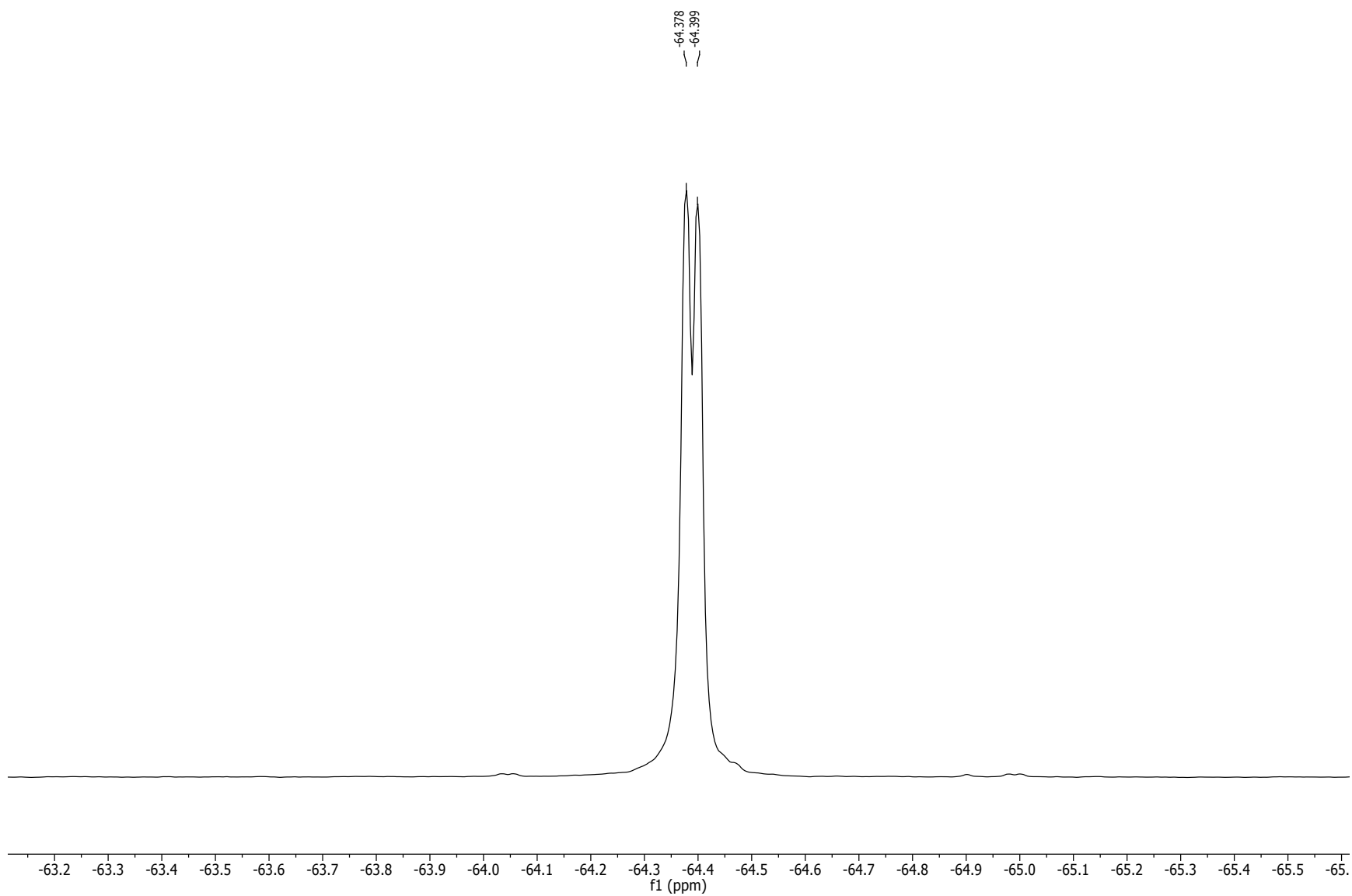
^{19}F NMR Spectrum of *(E)*-1-fluoro-4-(3,3,3-trifluoroprop-1-en-1-yl)benzene (**3c**)



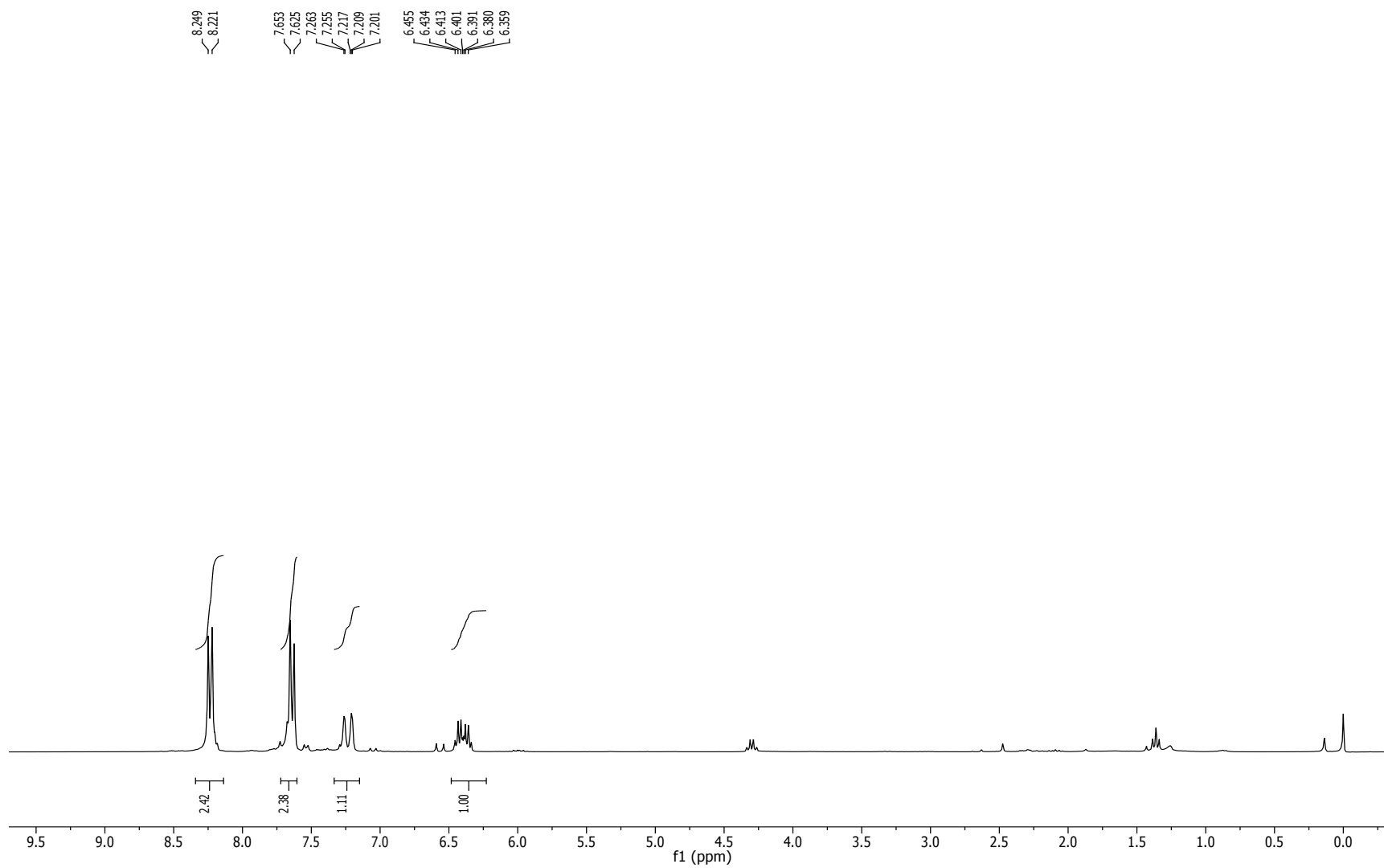
^1H NMR Spectrum of (*E*)-1-methoxy-4-(3,3,3-trifluoroprop-1-en-1-yl)benzene (**3d**)



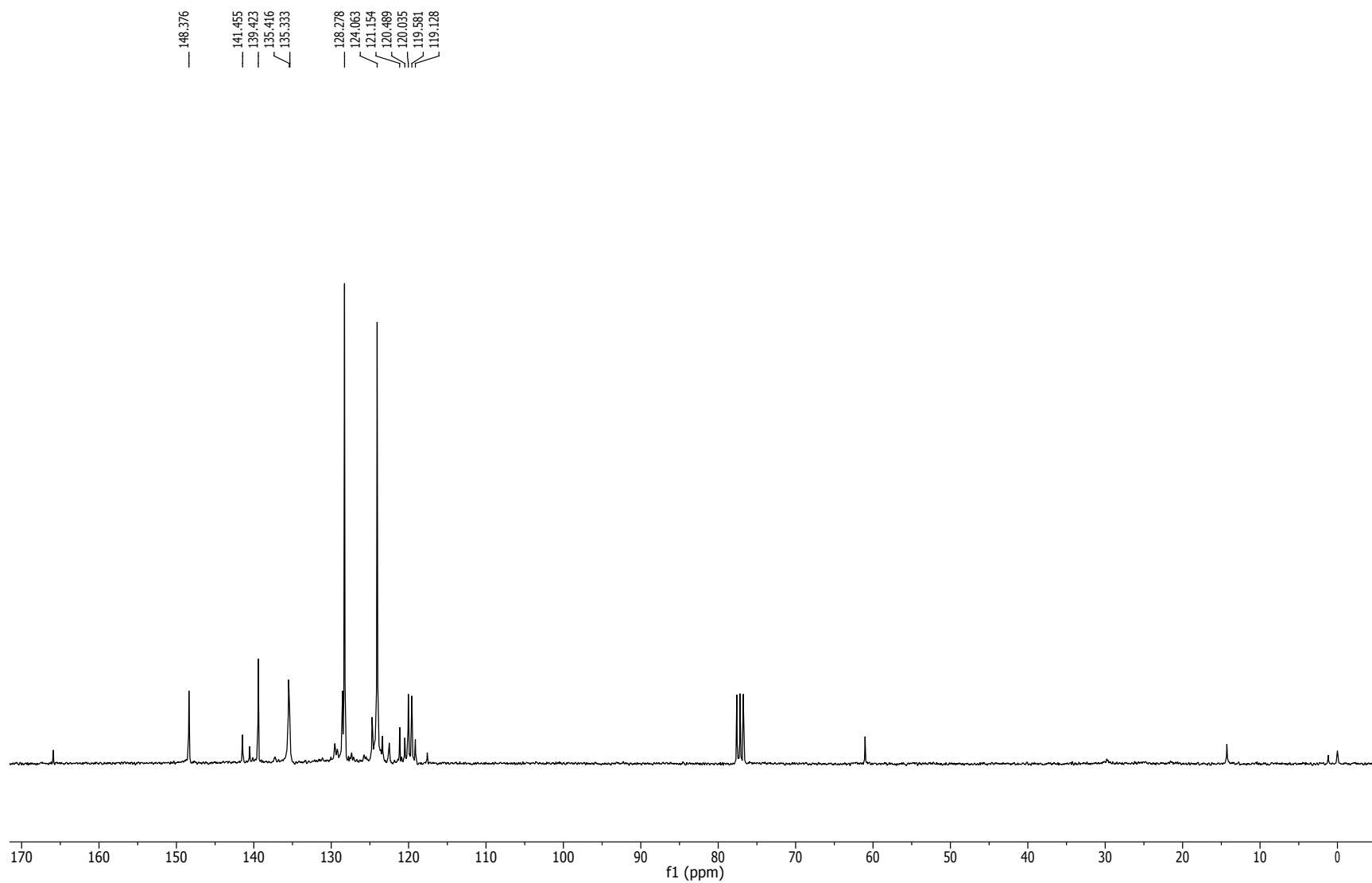
^{13}C NMR Spectrum of (*E*)-1-methoxy-4-(3,3,3-trifluoroprop-1-en-1-yl)benzene (**3d**)



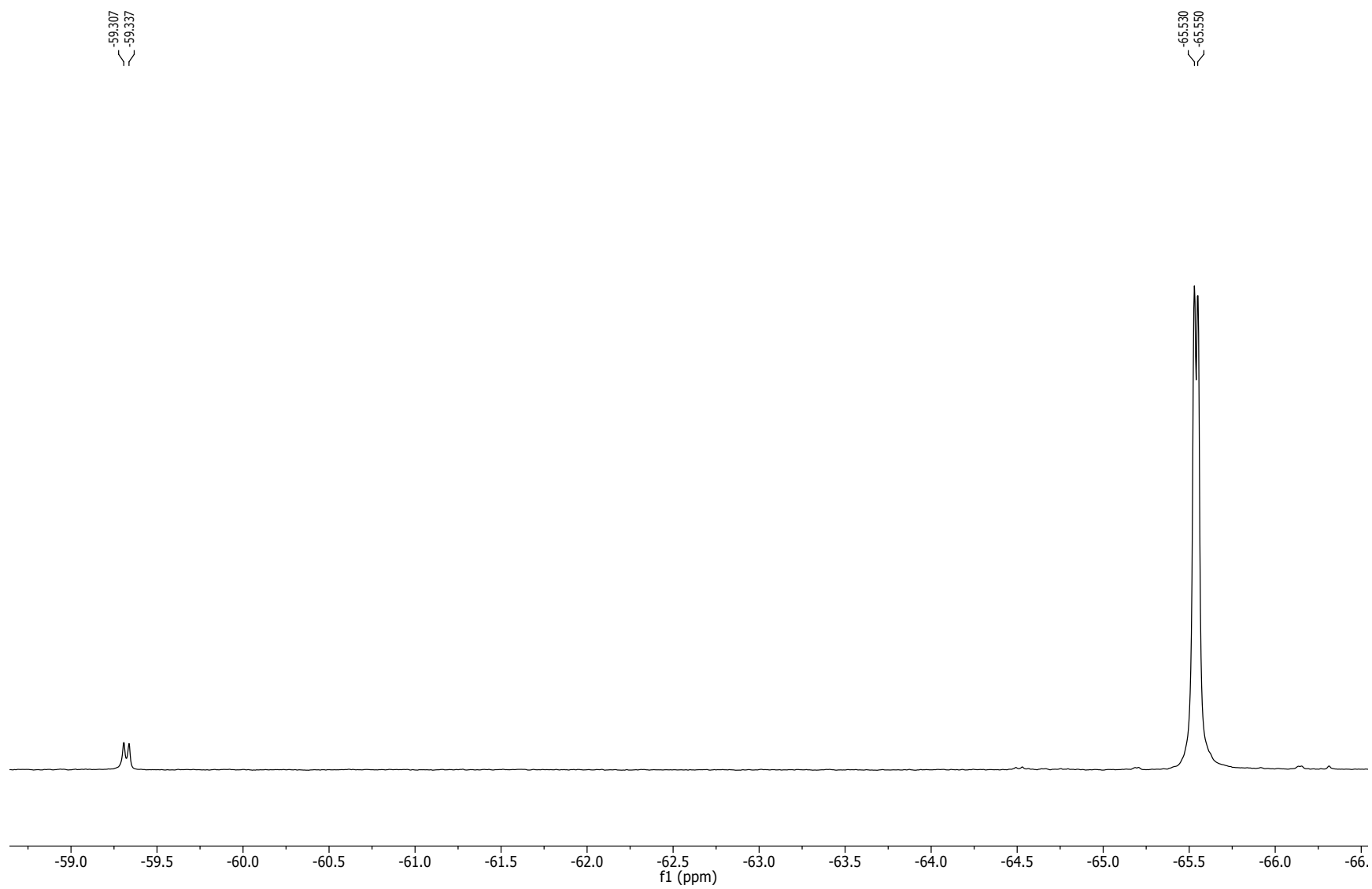
^{19}F NMR Spectrum of (*E*)-1-methoxy-4-(3,3,3-trifluoroprop-1-en-1-yl)benzene (**3d**)



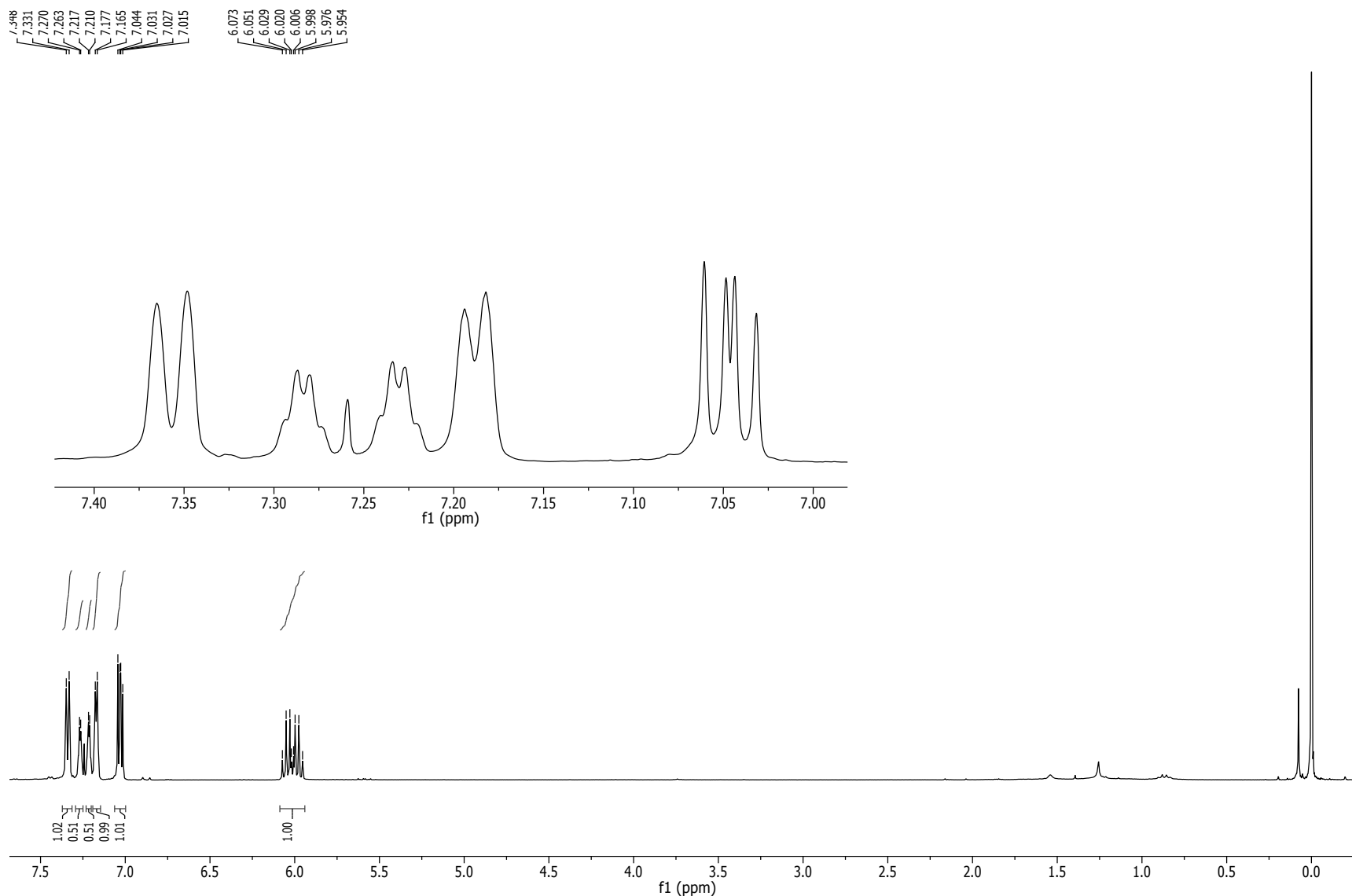
^1H NMR Spectrum of (*E*)-1-nitro-4-(3,3,3-trifluoroprop-1-en-1-yl)benzene (**3e**)



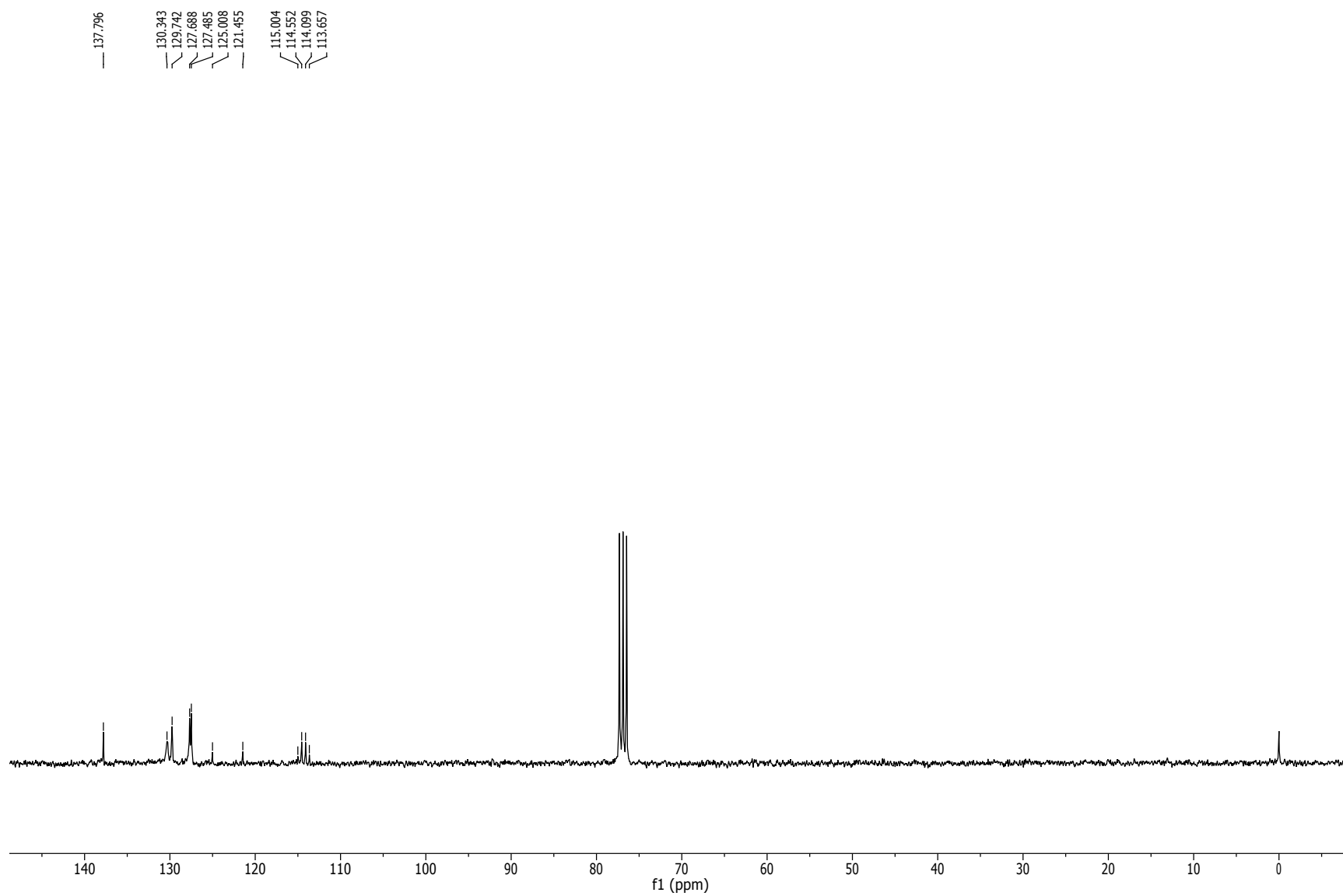
^{13}C NMR Spectrum of (*E*)-1-nitro-4-(3,3,3-trifluoroprop-1-en-1-yl)benzene (3e)



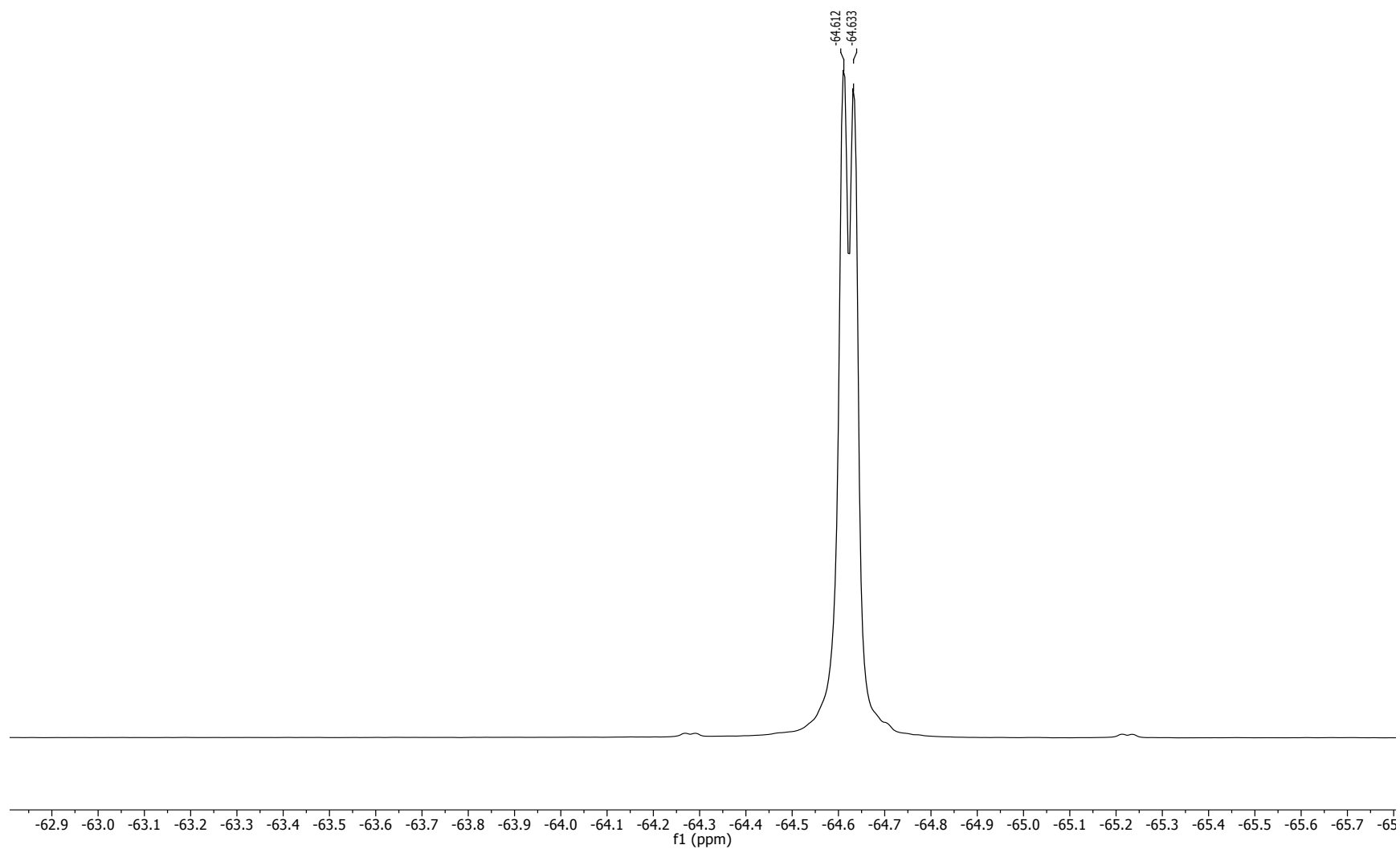
^{19}F NMR Spectrum of (*E*)-1-nitro-4-(3,3,3-trifluoroprop-1-en-1-yl)benzene (**3e**)



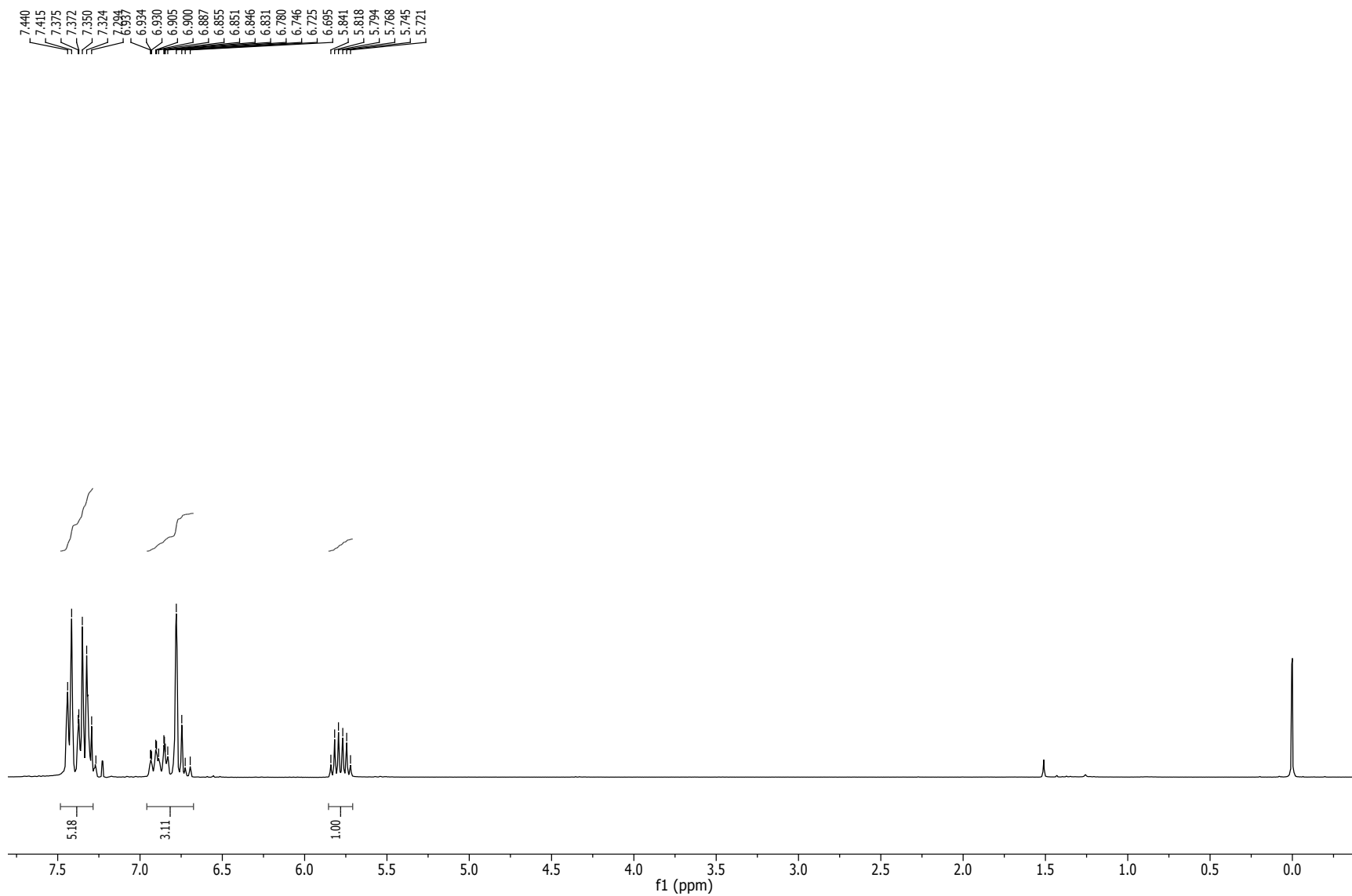
^1H NMR Spectrum of *(E)*-2-(3,3,3-trifluoroprop-1-en-1-yl)thiophene (**3f**)



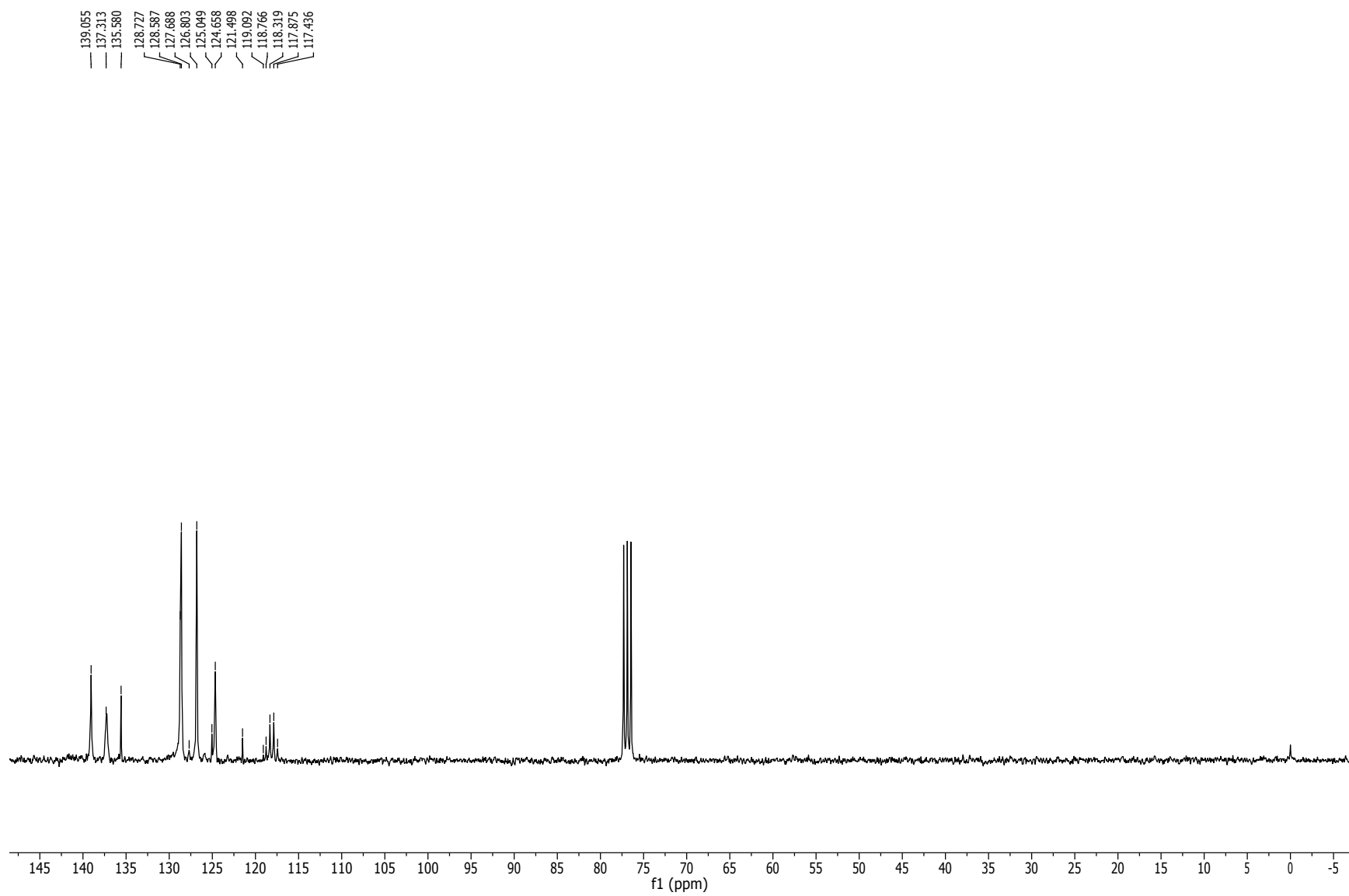
^{13}C NMR Spectrum of (*E*)-2-(3,3,3-trifluoroprop-1-en-1-yl)thiophene (**3f**)



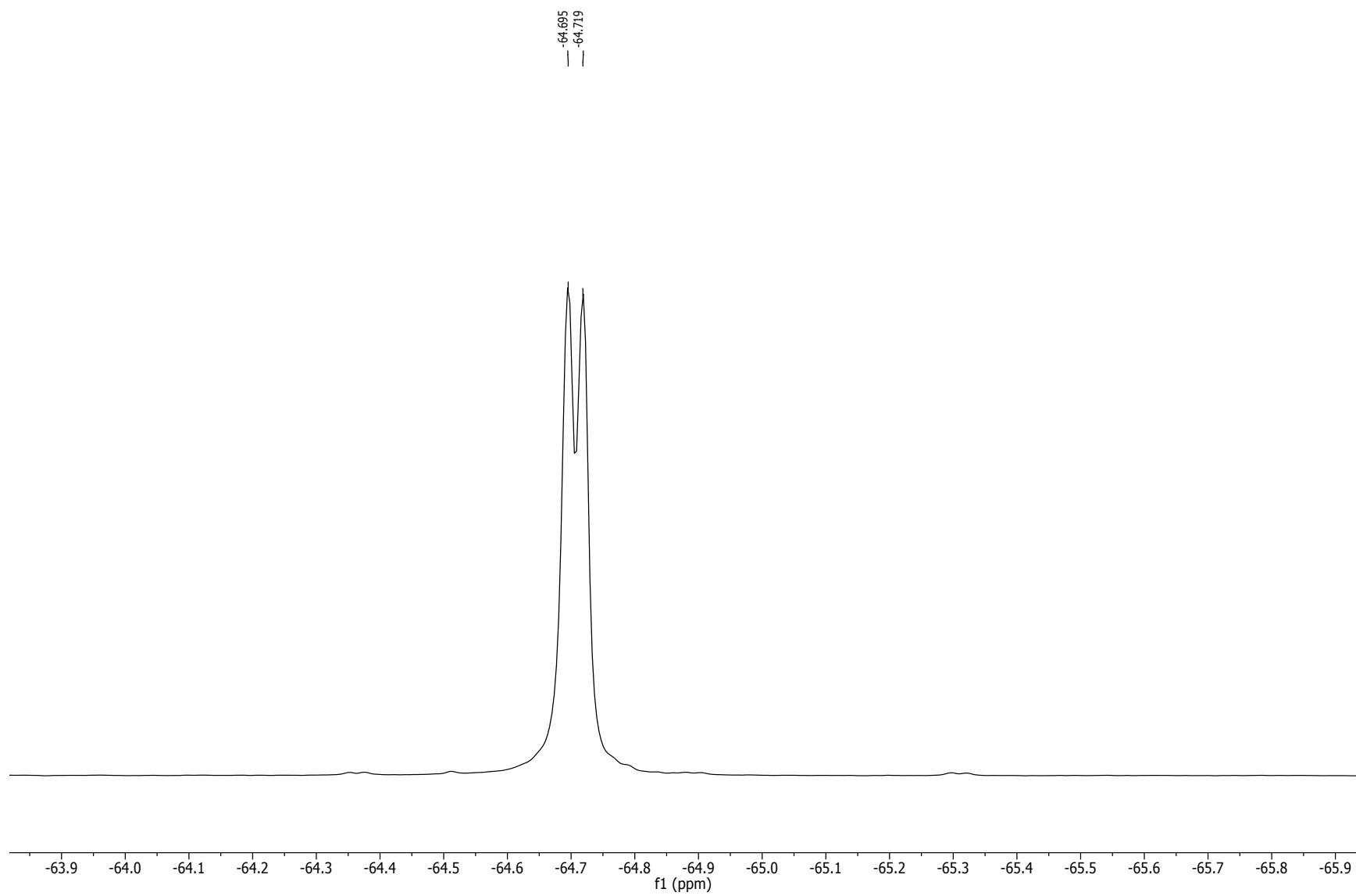
^{19}F NMR Spectrum of (*E*)-2-(3,3,3-trifluoroprop-1-en-1-yl)thiophene (**3f**)



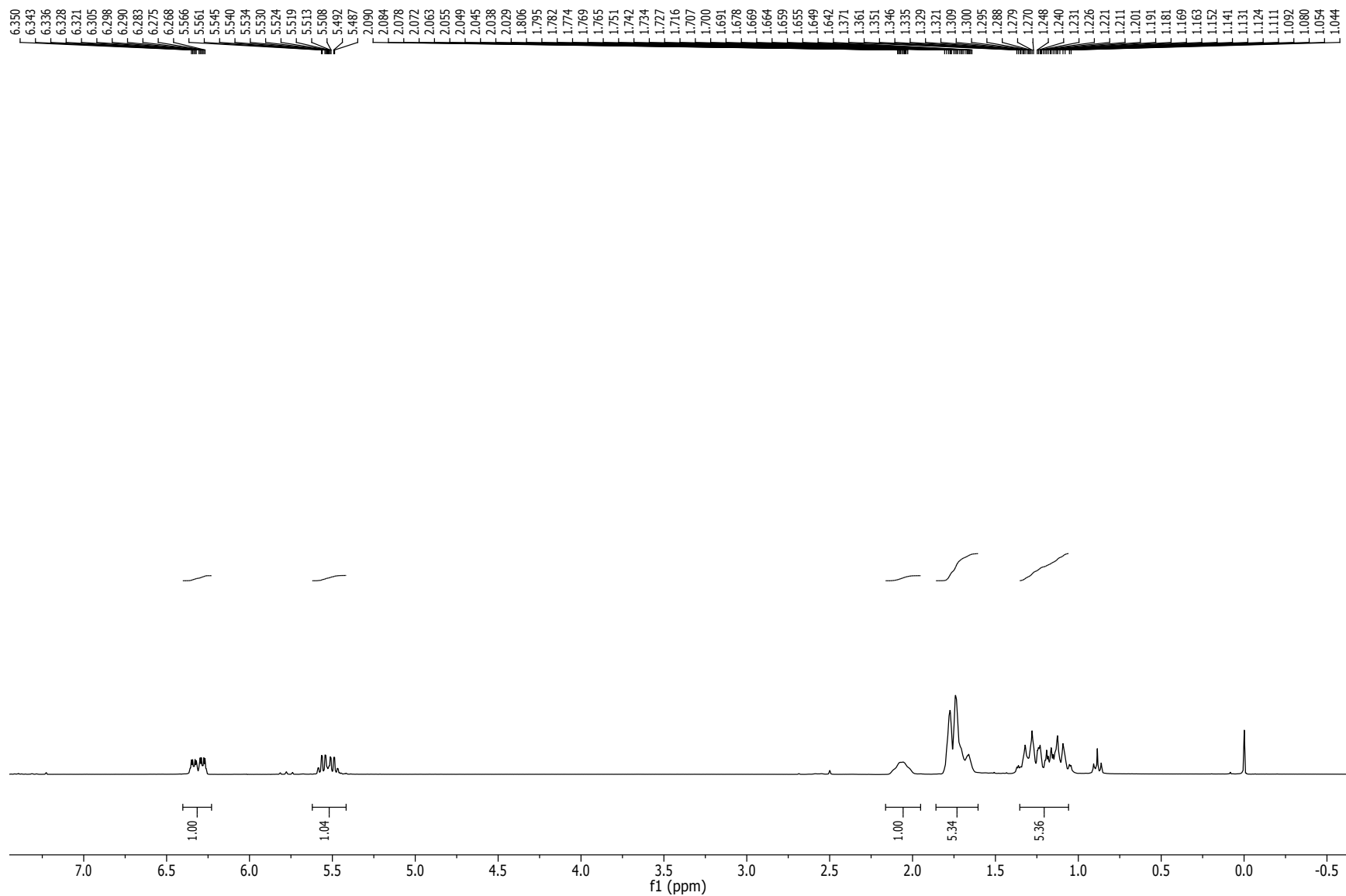
¹H NMR Spectrum of ((1*E*,3*E*)-5,5,5-trifluoropenta-1,3-dien-1-yl)benzene (**3g**)



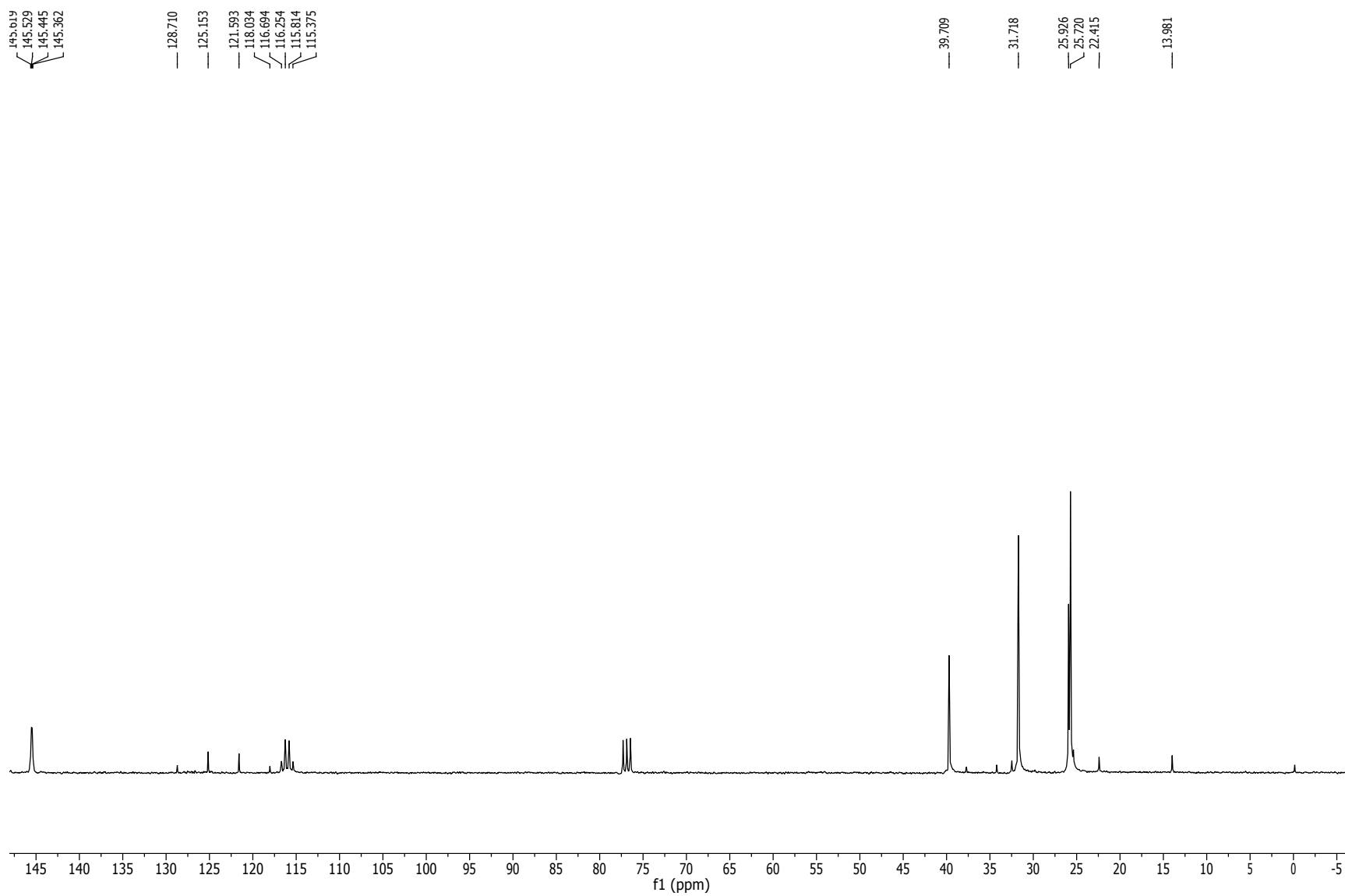
^{13}C NMR Spectrum of ((1*E*,3*E*)-5,5,5-trifluoropenta-1,3-dien-1-yl)benzene (**3g**)



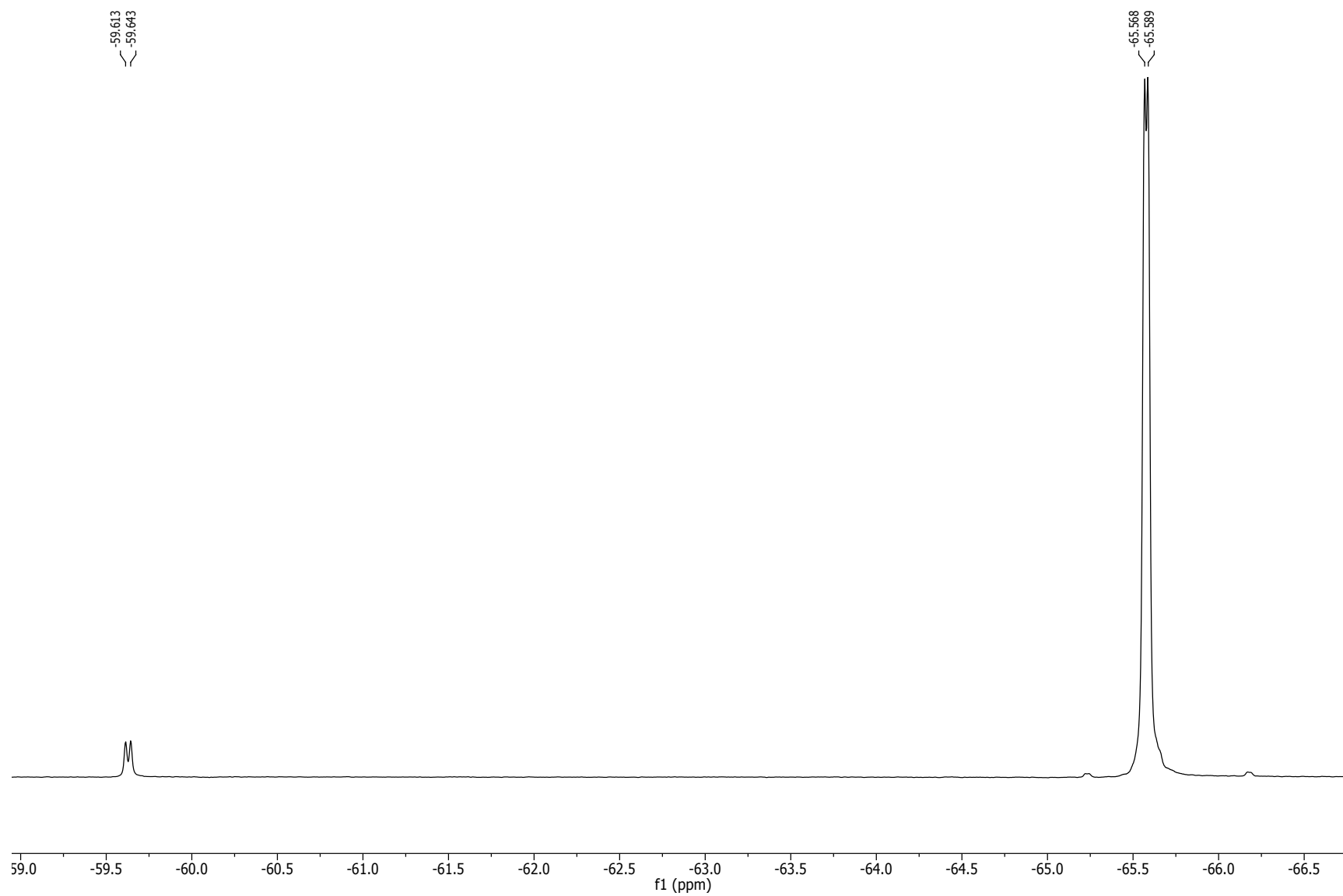
^{19}F NMR Spectrum of ((1*E*,3*E*)-5,5,5-trifluoropenta-1,3-dien-1-yl)benzene (**3g**)



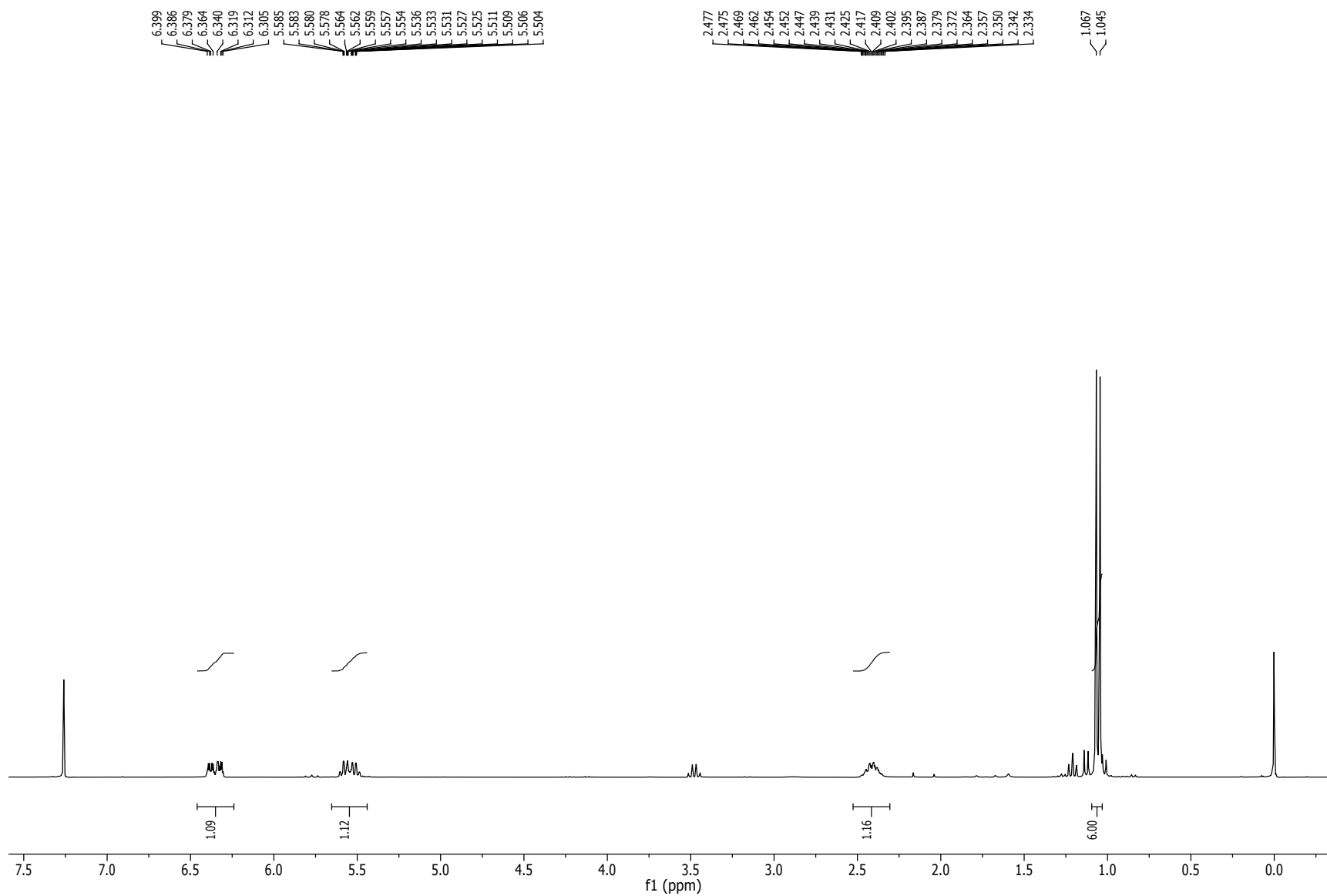
¹H NMR Spectrum of (*E*)-(3,3,3-trifluoroprop-1-en-1-yl)cyclohexane (**3h**)



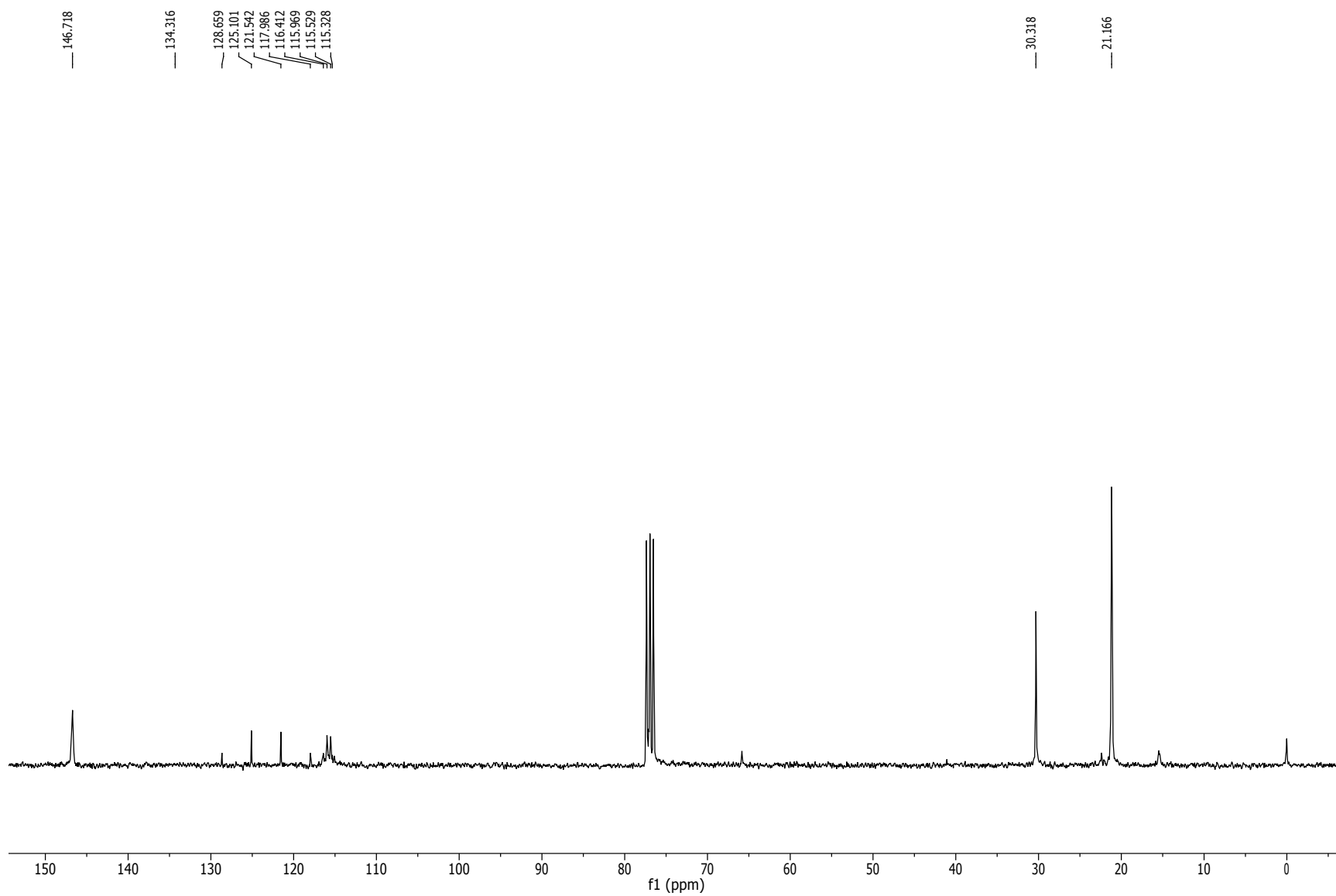
^{13}C NMR Spectrum of (*E*)-(3,3,3-trifluoroprop-1-en-1-yl)cyclohexane (**3h**)



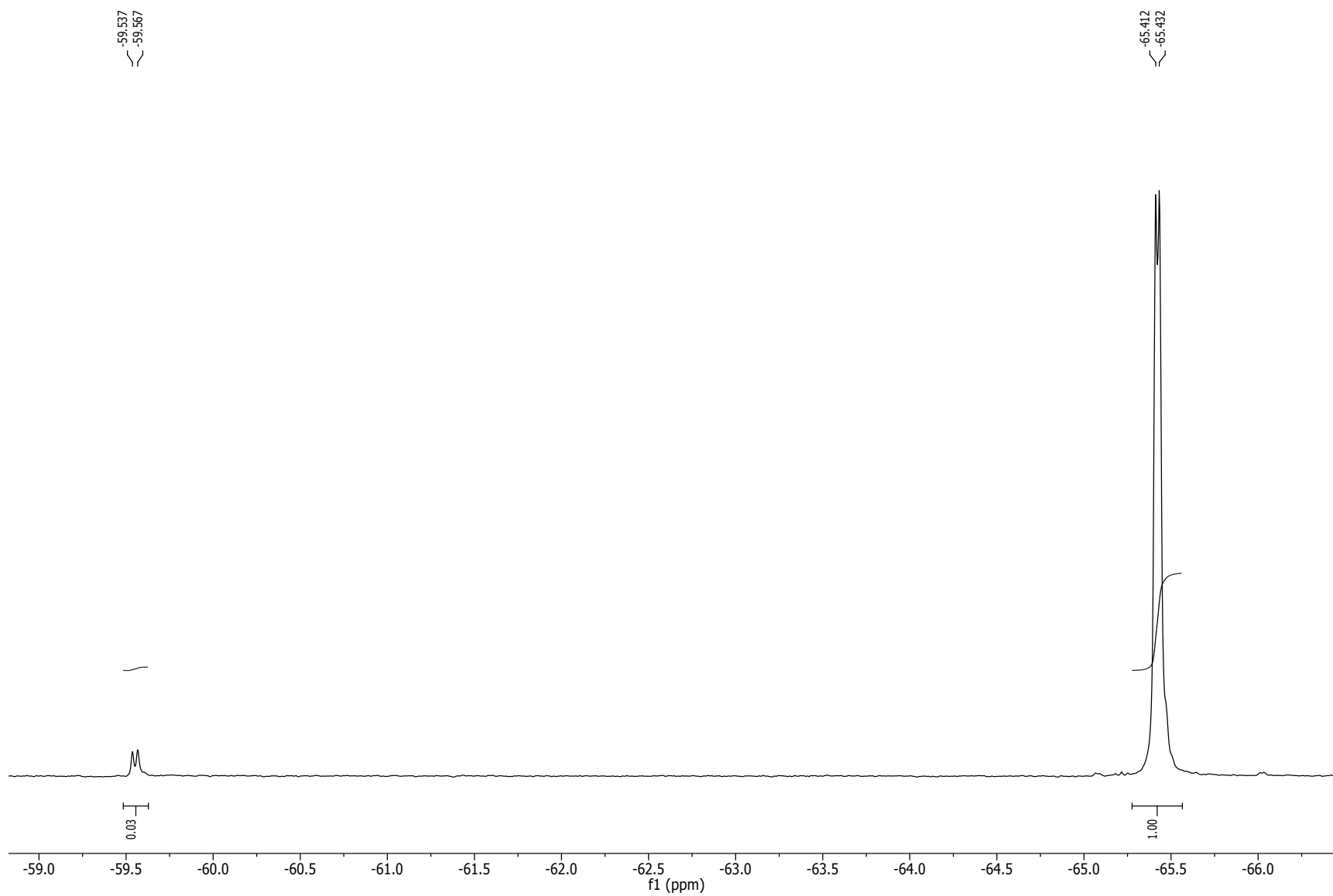
^{19}F NMR Spectrum of *(E)*-(3,3,3-trifluoroprop-1-en-1-yl)cyclohexane (**3h**)



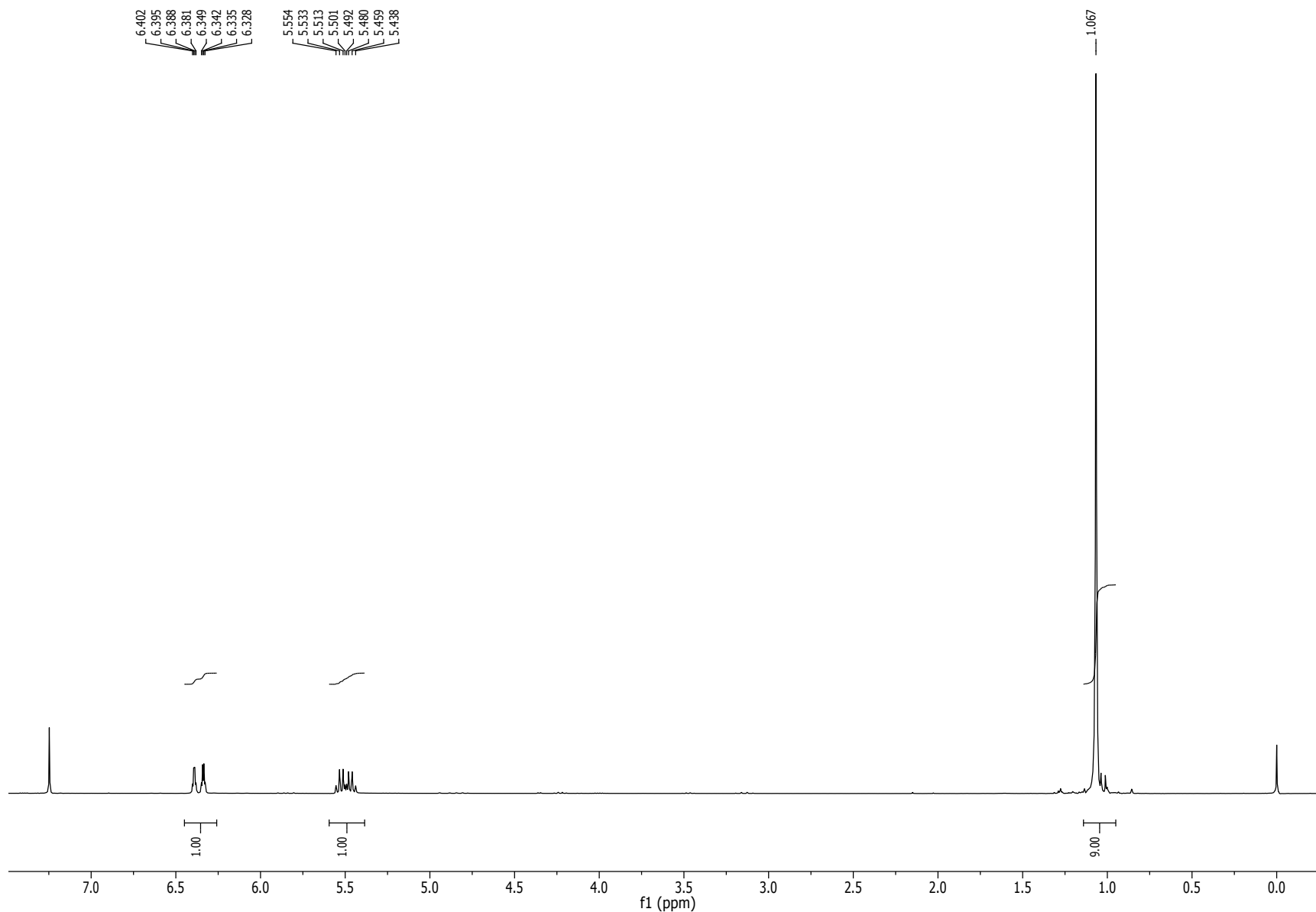
^1H NMR Spectrum of (*E*)-1,1,1-trifluoro-4-methylpent-2-ene (**3i**)



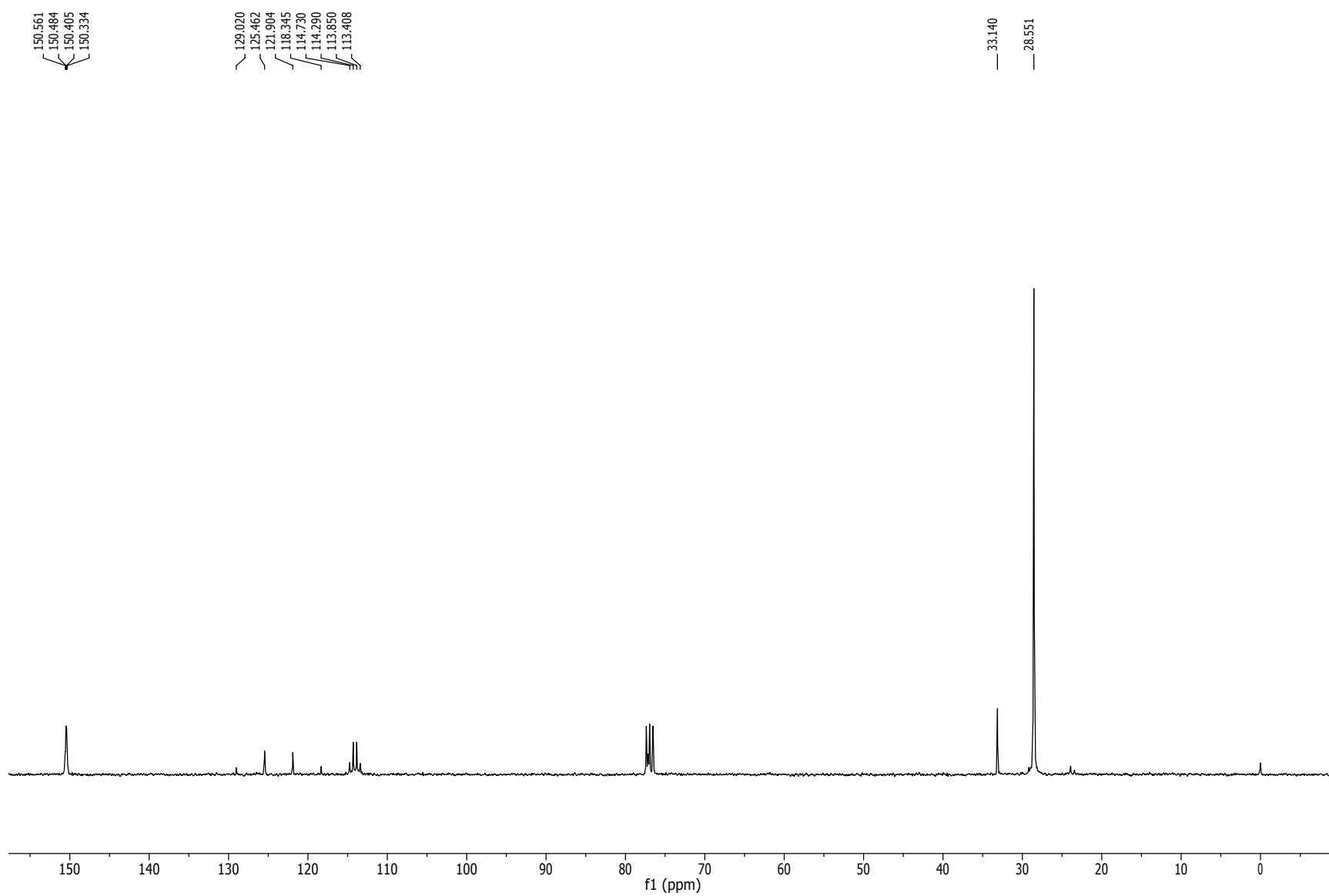
^{13}C NMR Spectrum of (*E*)-1,1,1-trifluoro-4-methylpent-2-ene (**3i**)



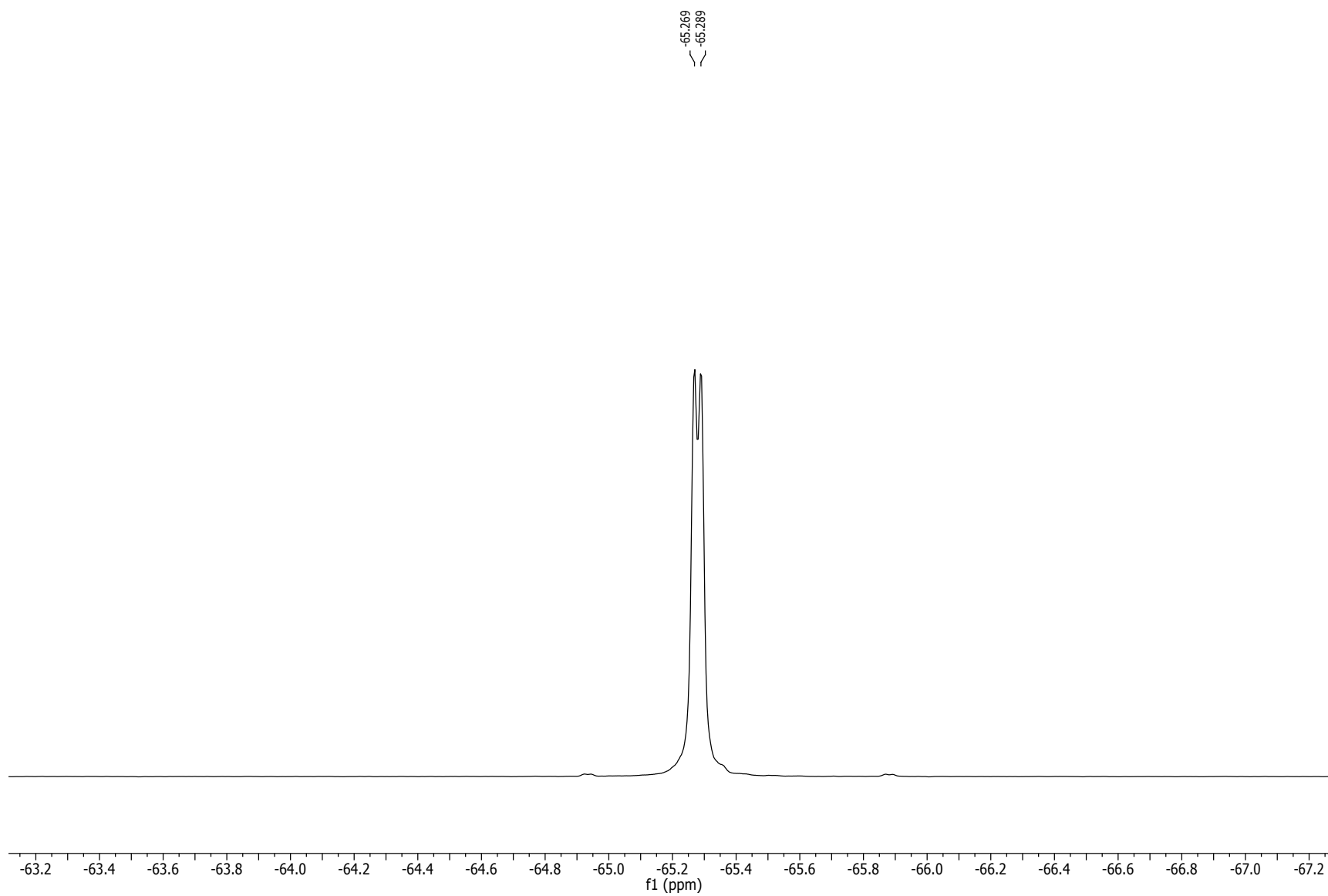
¹⁹F NMR Spectrum of (*E*)-1,1,1-trifluoro-4-methylpent-2-ene (**3i**)



^1H NMR Spectrum of (*E*)-1,1,1-trifluoro-4,4-dimethylpent-2-ene (**3j**)



^{13}C NMR Spectrum of (*E*)-1,1,1-trifluoro-4,4-dimethylpent-2-ene (**3j**)



^{19}F NMR Spectrum of (*E*)-1,1,1-trifluoro-4,4-dimethylpent-2-ene (**3j**)