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Manuscript Title: $(Me_3Si)_3SiH$- Mediated Intermolecular Radical Perfluoroalkylation Reactions of Olefins in Water

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Experimental Section

General Methods. The internal standard method was used for quantitative GC analysis using authentic samples, and one of the following capillary columns was employed: HP-1 (5 m X 0.53 mm i.d.) or HP-1 (30m X 0.32 mm i.d.). Oven program: starting at 50 °C for 5 min, followed by an increase of 5 °C/min up to 250 °C. NMR spectra were recorded at 400 MHz (for ^{1}H) or 100.6 MHz (for ^{13}C) in $CDCl_3$ as deuterated solvent and referenced with the residual solvent peak at 7.26 ppm in the ^{1}H NMR spectra and 77.0 ppm ($CDCl_3$) in the ^{13}C NMR spectra. Hydrogen multiplicity (CH, CH_2, CH_3) information was obtained from carbon DEPT-135 experiments for compounds **1c**, **7a**, **7d**, and **8d**. Some NMR spectral data connectivity were confirmed by ^{1}H-^{13}C HSQC and HMBC 2-D experiments. Reduced pressure distillation employed a bulb-to-bulb destillation apparatus with four glass bulbs. When necessary, compounds were isolated by flash chromatography performed on silica gel. High-resolution mass spectrometry measurements were performed with a resolution of 1-5ppm.

Water was obtained from a milli-pore system, and extraction and chromatographic solvents were HPLC-grade. Products from Tables 1, 2, 3, and 4 were characterized by standard spectroscopic techniques and compared with spectral data from the literature when available.

Materials. Perfluoroalkyl iodides and bromides were commercially available and used as received from the supplier. Alkene substrates were also commercially available and used as received from the supplier, exept for styrene, 4-methylstyrene, acrylonitrile, crotonaldehyde, methyl acrylate, and vinyl methyl ketone which were previously distilled and stored over molecular sieves (4 Å) prior to use.

Methods of Radical Initiation in Water. Study of the Reaction Stoichiometry

Initiation by Thermal Decomposition of an Azo Compound

The water-insoluble radical initiator 1,1´-azobis(cyclohexanecarbonitrile) (ACCN; half-life of 2.33 h at 100 ºC) has been found to give the best performance for both hydrophobic and hydrophilic substrates in our initial studies and this trend has been confirmed by the present results.

A preliminary set of experiments were conducted in order to adjust the right stoichiometry of the radical addition reactions of R_f• radicals to alkenes so as to favor the radical addition product over the reduction product in water (as in products **3** and **2**, equation 2). For this preliminary experiment, we used 1-hexene as the alkene, and *n*-$C_6F_{13}I$, as the source of R_f• radicals. Reduction product *n*-$C_6F_{13}H$ and addition product C_6F_{13}-C_6H_{13} were both obtained under different reaction conditions (by incremental amounts of $(Me_3Si)_3SiH$, and keeping alkene and *n*-$C_6F_{13}I$ concentrations constant), under thermal initiation. The most favorable reaction conditions are obtained by using a molar ratio of *alkene* : *$(Me_3Si)_3SiH$* : *R_fI* equal to 25:2.5:5 and this ratio was chosen as optimal.

The procedure is the following: In a 5 mL conical vial, provided with a conical stir bar, a heterogeneous aqueous (5 mL) mixture of the alkene (20-25 x 10^{-5} mol), $(Me_3Si)_3SiH$ (2.5 x 10^{-5} mol), the perfluoroalkyl halide (5 x 10^{-5} mol) and ACCN (1.5 x 10^{-5} mol) is flushed with Ar for ten minutes before heating at 70 ºC for 2-4 hours or otherwise indicated. After the reaction time elapsed, addition of pentane and extraction, the organic-phase is analyzed. Perfluoroalkylated products are isolated and purified by distillation under reduced pressure using a short path distillation apparatus, and characterized by standard spectroscopic techniques. The purity of products is checked by gas chromatography, and in some cases re-distilled or silica-gel chromatographed.

Dioxygen Initiation

A balloon filled with pure oxygen connected to the vessel where no apparent bubbling resulted, allowed dioxygen to be introduced, in the reaction vessel, up to its solubility limits in water.

The dioxygen-initiated radical-induced reactions of alkenes with perfluoroalkyl halides in Ar-degassed water is carried out by adding subsequently $(Me_3Si)_3SiH$ (2.5×10^{-5} moles), the alkene ($20\text{-}25\times10^{-5}$ moles), and the perfluoroalkyl halide[i] (5×10^{-5} moles) in a conical vial provided with a conical stir bar, filled with 5 mL of milliQ water previously deoxygenated with an stream of Ar for 10 min. The vessel is tight-sealed, connected with a balloon filled with 99.99 % dioxygen, and vigorously stirred at 20 ºC (36 h). As a slight positive oxygen-pressure is exerted on the reaction vessel, air does not leak in the system.

The mechanism for the unusual reaction of $(Me_3Si)_3SiH$ with oxygen has been investigated before[iia] and applied successfully in water.

Spectroscopic characterization of known compounds 1a-6a, 1b, 1c, 1d-6d, 8d, 9d, 1e-4e, 6e, 9e.

These compounds were characterized from comparison of their ^1H and ^{13}C NMR data with those found in the literature (references of compounds throughtout the manuscript).

Spectral Data of Unknown Compounds: 7a, 8a, 1c, 7d, 5e, 7e, 8e:

Spectroscopic characterization of unknown compounds 7,8-a; **1c**; **7-d**; **5,7,8-e** :

7a (4,4,5,5,6,6,7,7,8,8,9,9,9-tridecafluoro-3-methylnonanal): yellowish oil. GC/MS EI, *m/z* (%): 390 (32), 375 (21), 373 (12), 362 (29), 320 (39), 273 (100). EI-HRMS anal. calc. for $C_{10}H_7F_{13}O$: 390.0289. Found: 390.0296. Elemental analyses: Found: C (30.05%), H

(1.71%), O (4.21%). Calcd. For $C_{11}H_7F_{13}O$: C (30.79%), H (1.81%), F (63.31%), O (4.10%). FT-IR (ν, cm^{-1}): 1795 (C=O), 1204, 1140. ^1H NMR δ_H ppm (400.13 MHz, $CDCl_3$): 1.34 (d, 3H, Me), 2.69 (complex m, 3 H, CH & CH_2), 9.51 (s, 1 H, CHO). ^{13}C NMR δ $^{13}_C$ ppm (100.6 MHz, $CDCl_3$): 11.3, 39.7, 43.0, 100-130 (^{13}C-^{19}F coupling from $(CF_2)_6$), 203.4.

8a (methyl 4,4,5,5,6,6,7,7,8,8,9,9,9-tridecafluorononanoate): colorless oil. GC/MS EI, *m/z* (%): 406 (2), 391 (15), 373 (11), 354 (21), 347 (25), 319 (100), 87 (67). EI-HRMS anal. calc. for $C_{10}H_7F_{13}O_2$: 406.0238. Found: 406.0240. Elemental analyses. Found: C (29.54), H (1.75%), O (7.81%). Calcd. for $C_9H_5F_{13}O_2$: C (29.57%), H (1.74%), F (60.81%), O (7.88%). FT-IR (ν, cm^{-1}): 1800 (C=O), 1527, 1302, 1209, 1143. ^1H NMR δ_H ppm (400.13 MHz, $CDCl_3$): 2.24 (complex m, 2 H, *CH_2*-R_f), 2.61 (complex m, 2 H, *CH_2*-COOMe), 3.62 (s, 3 H, CH_3). ^{13}C NMR δ $^{13}_C$ ppm (100.6 MHz, $CDCl_3$): 26.2 (br. s, **C**H_2-COOMe), 27.5 (m, **C**H_2-R_f), 51.0, 100-130 (^{13}C-^{19}F coupling from $(CF_2)_6$), 176.0 (**C**O).

1c (1,1,2,2,3,3,4,4-octafluoro-1-iododecane): pinkish oil. GC/MS EI, *m/z* (%): 413 (10), 412 (4), 335 (58), 327 (43), 285 (100), 185 (45). EI-HRMS anal. calc. for $C_{10}H_{13}F_8I$: 411.9934. Found: 411.9940. Elemental analyses. Found: C (29.24%), H (3.92%). Calcd. for $C_{10}H_{13}F_8I$: C (29.14%), H (3.81%), F (36.86%), I (30.79%). ^1H NMR δ_H ppm (400.13 MHz, $CDCl_3$): 0.79 (t, 3 H, J = 7 Hz, *CH_3*), 1.32 (complex m, 2 H, *CH_2*-CH_3), 1.39 (complex m, 2 H), 1.60 (complex m, 1 H, *CH*-HR_f), 1.90 (complex m, 1 H, *CH*-HR_f). ^{13}C NMR δ $^{13}_C$ ppm (100.6 MHz, $CDCl_3$): 13.9, 20.6, 22.1, 28.9, 30.3, 31.7, 80-120 (^{13}C-^{19}F coupling from $(CF_2)_4$).

7d (4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptadecafluoro-3-methylundecanal): yellowish oil. GC/MS EI, *m/z* (%): 490 (12), 471 (23), 462 (100), 420 (100), 371 (55), 271

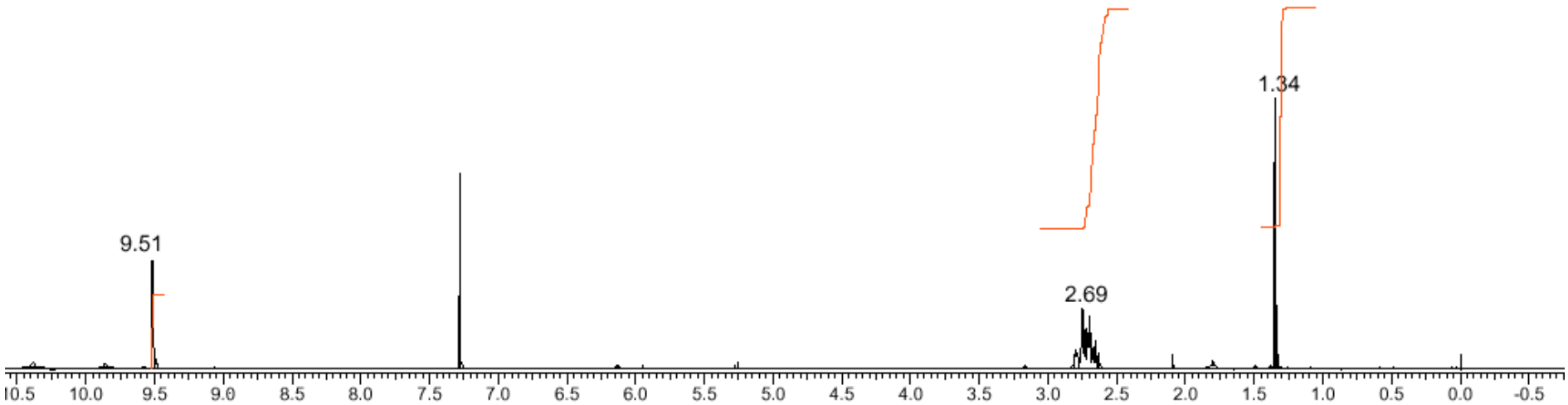
(87). EI-HRMS anal. calc. for $C_{12}H_7F_{17}O$: 490.0225. Found: 490.0220. Elemental analyses . Found: C (29.10 %), H (1.49 %), O (3.33 %) Calcd. For $C_{12}H_7F_{17}O$: C (29.40 %), H (1.44 %), F (65.89 %), O (3.26 %). FT-IR (ν, $cm^{-}1$): 1798 (C=O), 1689, 1209, 1145. ^1H NMR δ_H ppm (400.13 MHz, $CDCl_3$): 1.30 (t, 3 H, J = 6.7 Hz, CH_3), 2.80 (complex m, 3 H, *CH*-R_f & *CH_2*-CHO), 9.61 (s, *CHO*). ^{13}C NMR $\delta\ ^{13}_C$ ppm (100.6 MHz, $CDCl_3$): 12.0, 40.3, 41.6, 100-135 (^{13}C-^{19}F coupling from $(CF_2)_8$), 200.5 (CHO).

5e (1-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,12-henicosafluorododecyl)-4-methylbenzene): colorless oil. GC/MS EI*, m/z* (%): 638 (5), 623 (41), 619 (21), 519 (100), 419 (23), 319 (33), 92 (54), 77 (51), 65 (11). EI-HRMS anal. calc. for $C_{19}H_{11}F_{21}$: 638.0525. Found: 638.0534. Elemental analyses. Found: C (35.55 %), H (1.88 %). Calcd. for $C_{19}H_{11}F_{21}$: C (35.75 %), H (1.74 %), F (62.51 %). ^1H NMR δ_H ppm (400.13 MHz, $CDCl_3$): 2.07 (s, 3 H, *CH_3*-Ph), 2.40 (complex m, 2 H, *CH_2*), 2.96 (complex m, 2 H, *CH_2*-R_f), 7.01 (m, 2 H, Ph), 7.23 (m, 2 H, Ph). ^{13}C NMR $\delta\ ^{13}_C$ ppm (100.6 MHz, $CDCl_3$): 21.1, 27.0, 33.1, 100-120 (^{13}C-^{19}F coupling from $(CF_2)_{10}$), 128.45, 128.11, 135.11, 137.51.

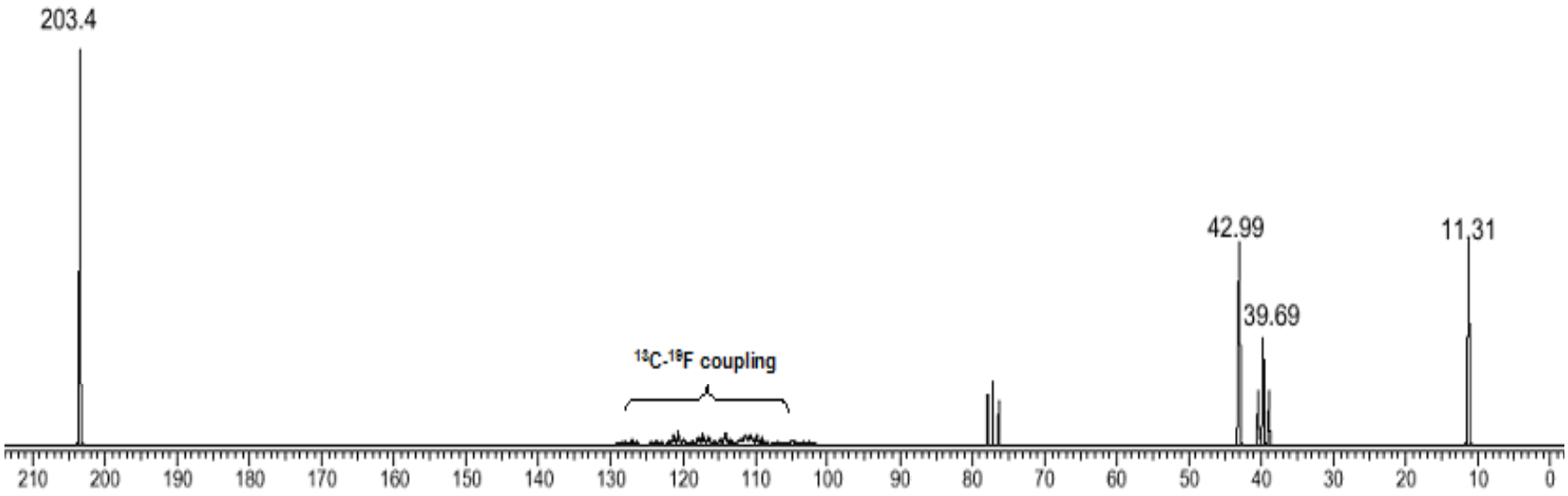
7e (4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,13,13,13-henicosafluoro-3-methyltridecanal): yellowish oil. GC/MS EI*, m/z* (%): 590 (5), 575 (32), 571 (12), 562 (59), 519 (55), 471 (100). EI-HRMS anal. calc. for $C_{14}H_7F_{21}O$: 590.0162. Found: 590.0156. Elemental analyses. Found: C (27.29 %), H (1.29 %), O (2.65 %). Calcd. for $C_{14}H_7F_{21}O$: C (28.49 %), H (1.20 %), F (67.60 %), O (2.71 %). FT-IR (ν, $cm^{-}1$): 1800 (C=O), 1206, 1143. ^1H NMR δ_H ppm (400.13 MHz, $CDCl_3$): 1.33 (d, 3 H, J = 7 Hz, *CH_3*), 2.65 (complex m, 3 H, *CH*-R_f & *CH_2*-CHO), 9.11 (s, *CHO*). ^{13}C NMR $\delta\ ^{13}_C$ ppm (100.6 MHz, $CDCl_3$): 11.2, 40.4, 44.5, 95-135 (^{13}C-^{19}F coupling from $(CF_2)_{10}$), 200.21 (*CHO*).

8e (methyl 4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,13,13,13-henicosafluorotridecanoate): colorless oil. GC/MS EI, *m/z* (%): 606 (5), 591 (35), 587 (13), 578 (54), 575 (12), 519 (51), 487 (100), 387 (21). EI-HRMS anal. calc. for $C_{14}H_7F_{21}O_2$: 606.0111. Found: 606.0103. Elemental analyses. Found: C (26.94 %), H (1.07 %), O (5.39 %). Calcd. for $C_{14}H_7F_{21}O_2$: C (27.74 %), H (1.16 %), F (65,82 %), O (5.28 %). FT-IR (ν, $cm^{-}1$): 1798 (C=O), 1717, 1446, 1209, 1143. ^{1}H NMR δ_H ppm (400.13 MHz, $CDCl_3$): 2.15 (complex m, 2 H, CH_2-R_f), 2.55 (complex m, 2 H, CH_2-COOMe), 3.56 (s, 3 H, CH_3-COO). ^{13}C NMR $\delta\ ^{13}_C$ ppm (100.6 MHz, $CDCl_3$): 26.2, 27.2, 52.6, 100-130 (^{13}C-^{19}F coupling from $(CF_2)_{10}$), 176.55.

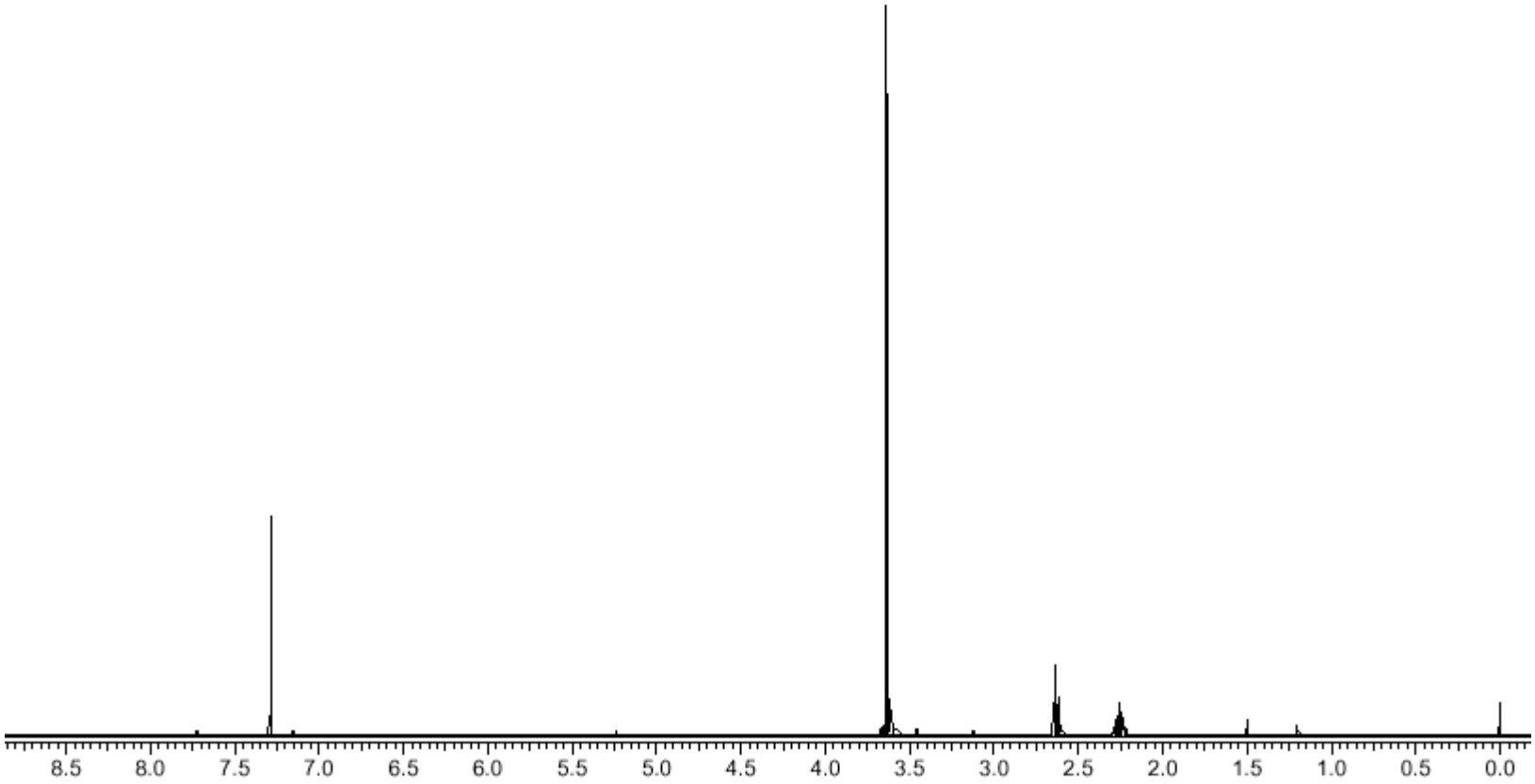
^{1}H NMR spectrum of Compound **7a** (4,4,5,5,6,6,7,7,8,8,9,9,9-tridecafluoro-3-methylnonanal) in $CDCl_3$



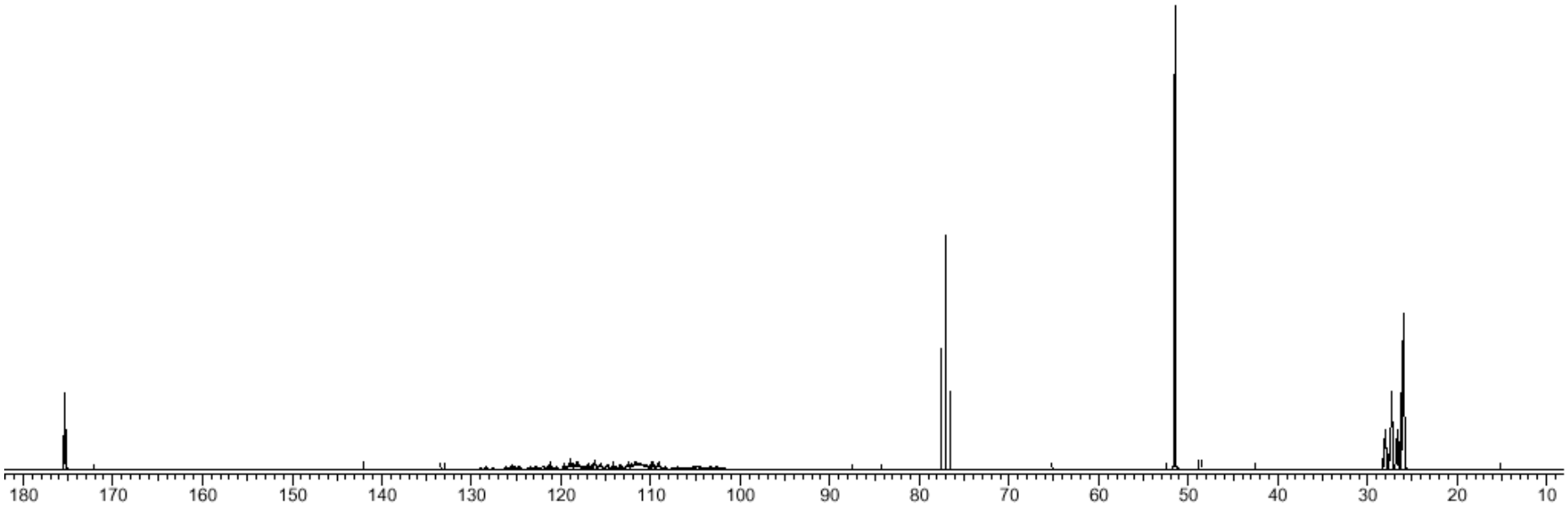
^{13}C NMR spectrum of Compound **7a** (4,4,5,5,6,6,7,7,8,8,9,9,9-tridecafluoro-3-methylnonanal) in $CDCl_3$



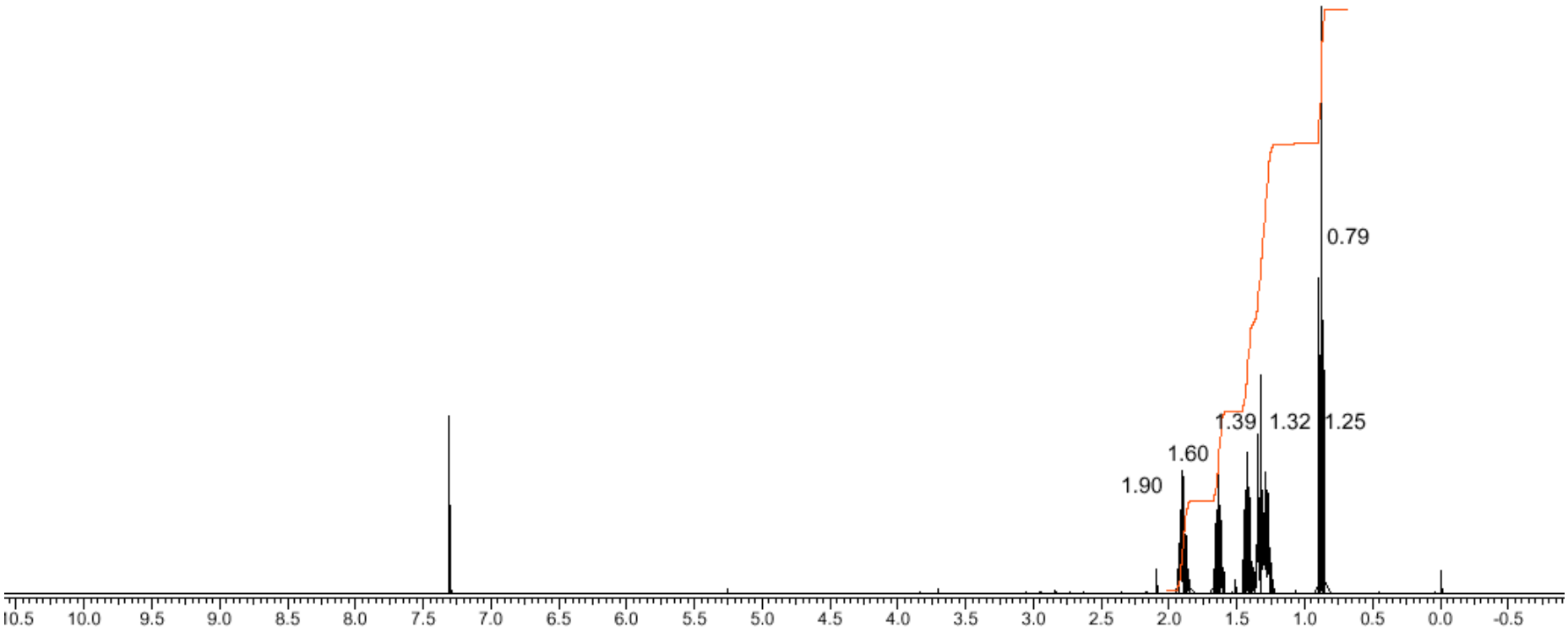
^{1}H NMR spectrum of Compound **8a** (methyl 4,4,5,5,6,6,7,7,8,8,9,9,9-tridecafluorononanoate) in $CDCl_3$



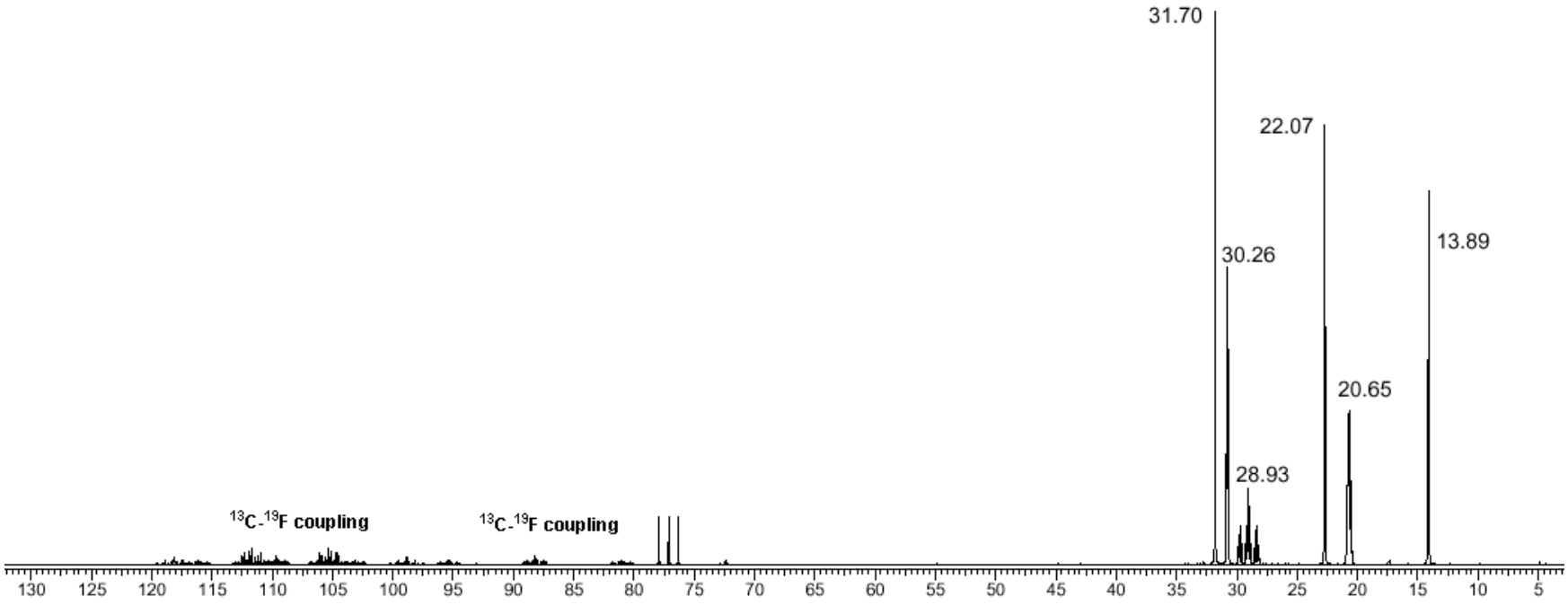
^{13}C NMR spectrum of Compound **8a** (methyl 4,4,5,5,6,6,7,7,8,8,9,9,9-tridecafluorononanoate) in $CDCl_3$



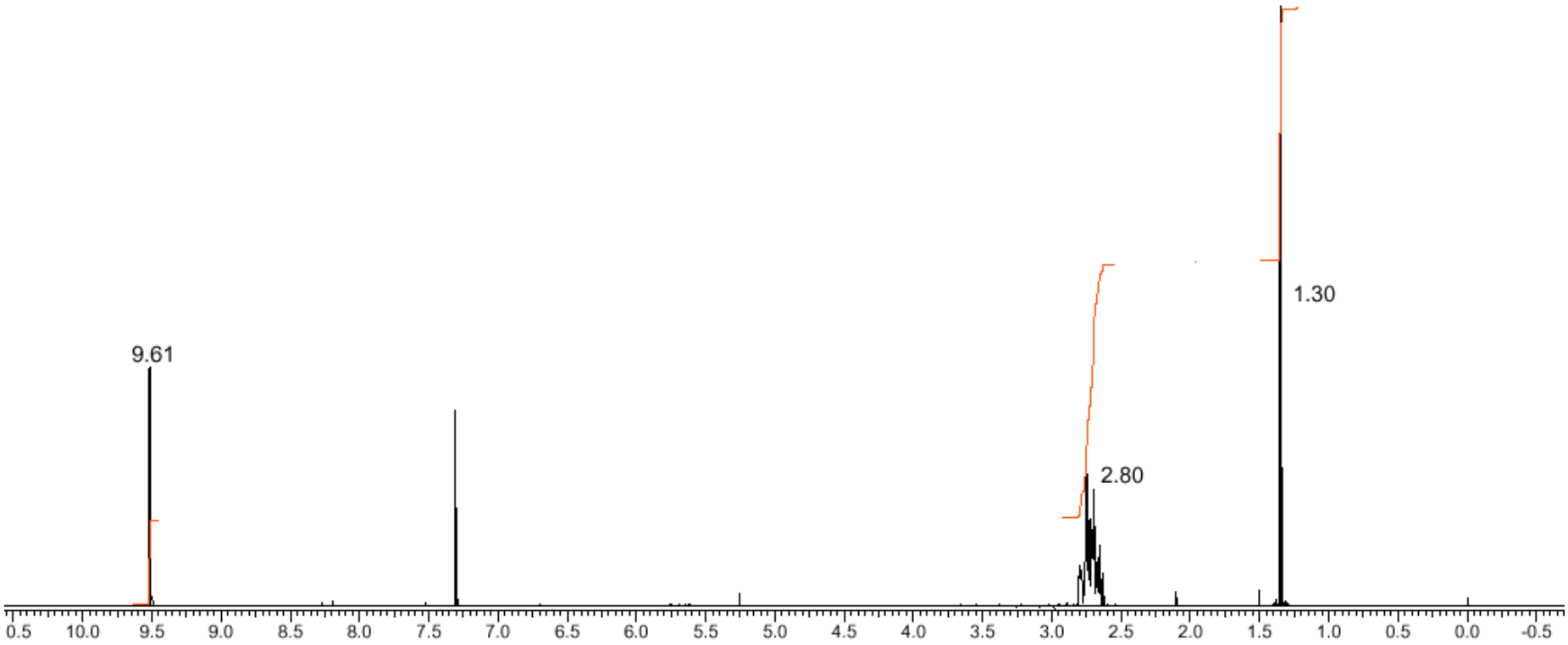
^{1}H NMR spectrum of Compound **1c,** 1,1,2,2,3,3,4,4-octafluoro-1-iododecane, in $CDCl_3$



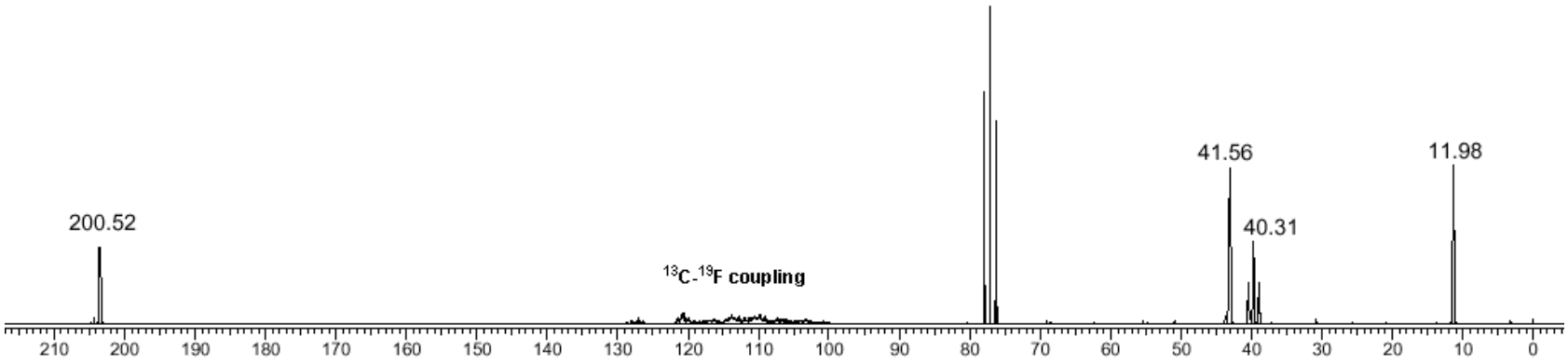
^{13}C NMR spectrum of Compound **1c,** 1,1,2,2,3,3,4,4-octafluoro-1-iododecane, in $CDCl_3$



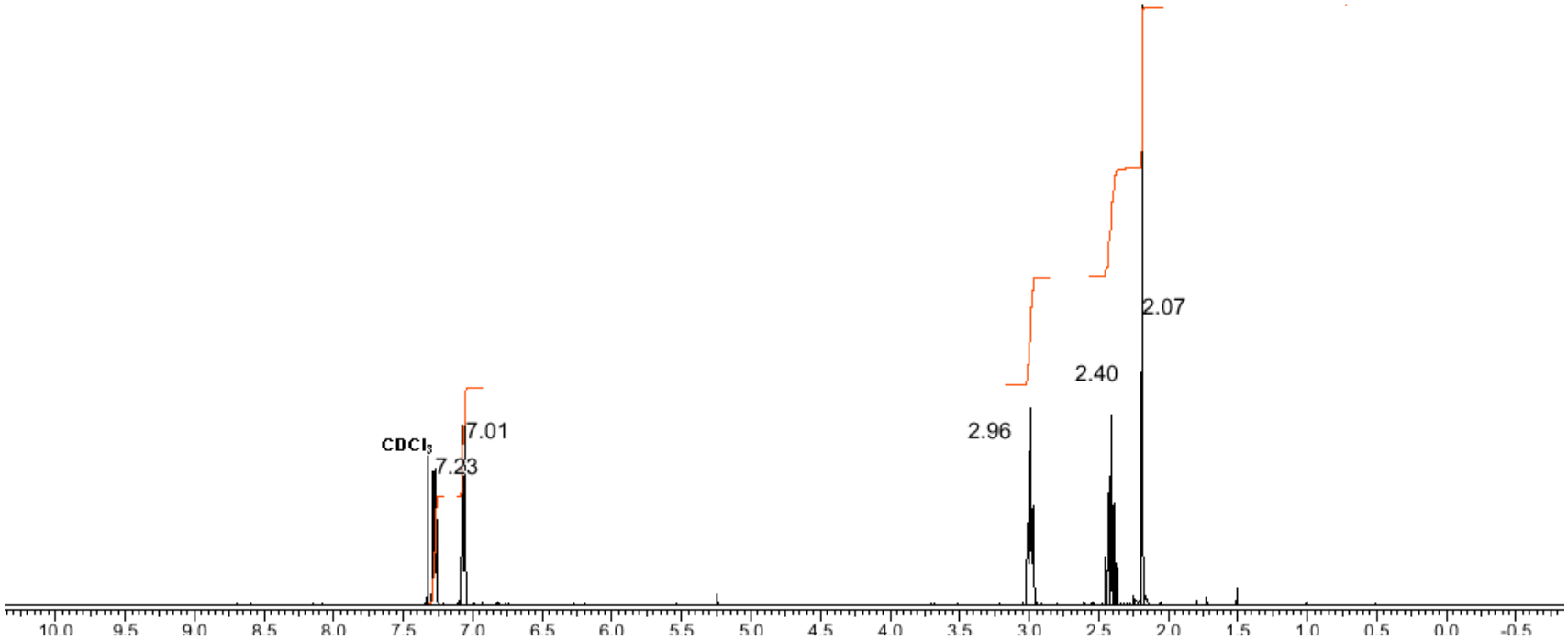
^{1}H NMR spectrum of Compound **7d,** 4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptadecafluoro-3-methylundecanal, in $CDCl_3$



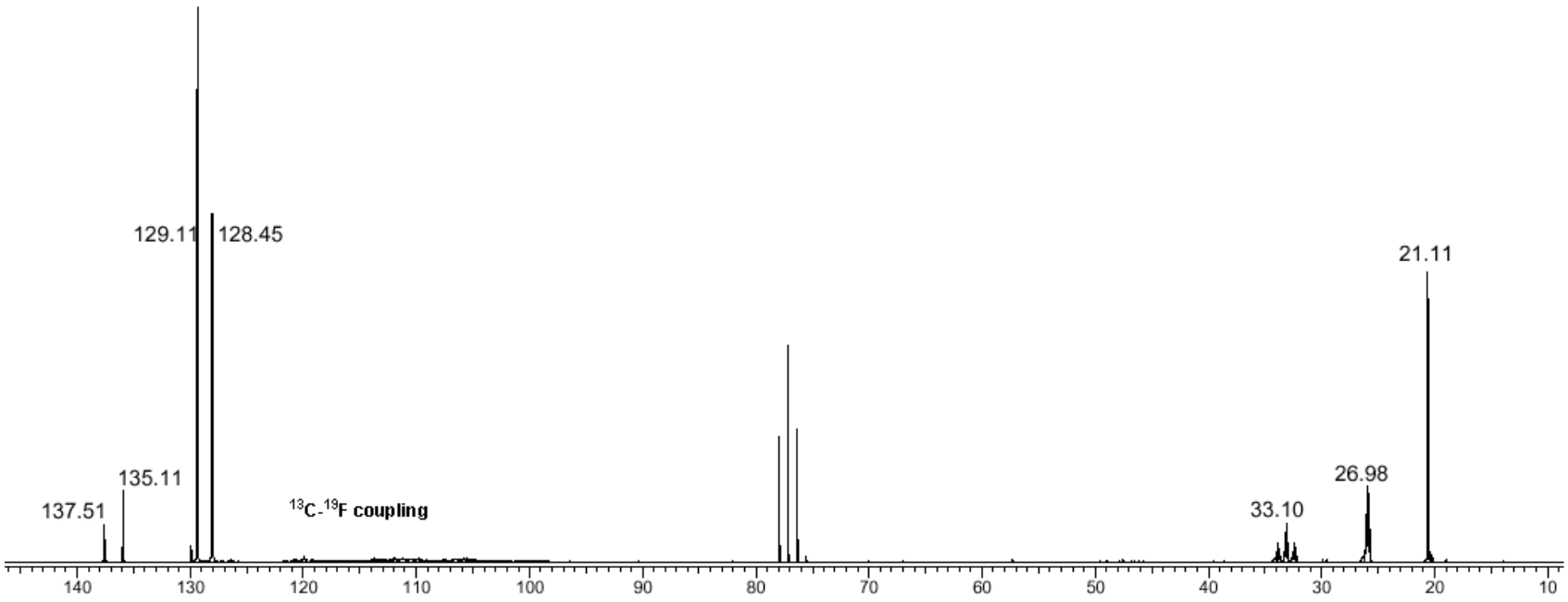
^{13}C NMR spectrum of Compound **7d,** 4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptadecafluoro-3-methylundecanal, in $CDCl_3$



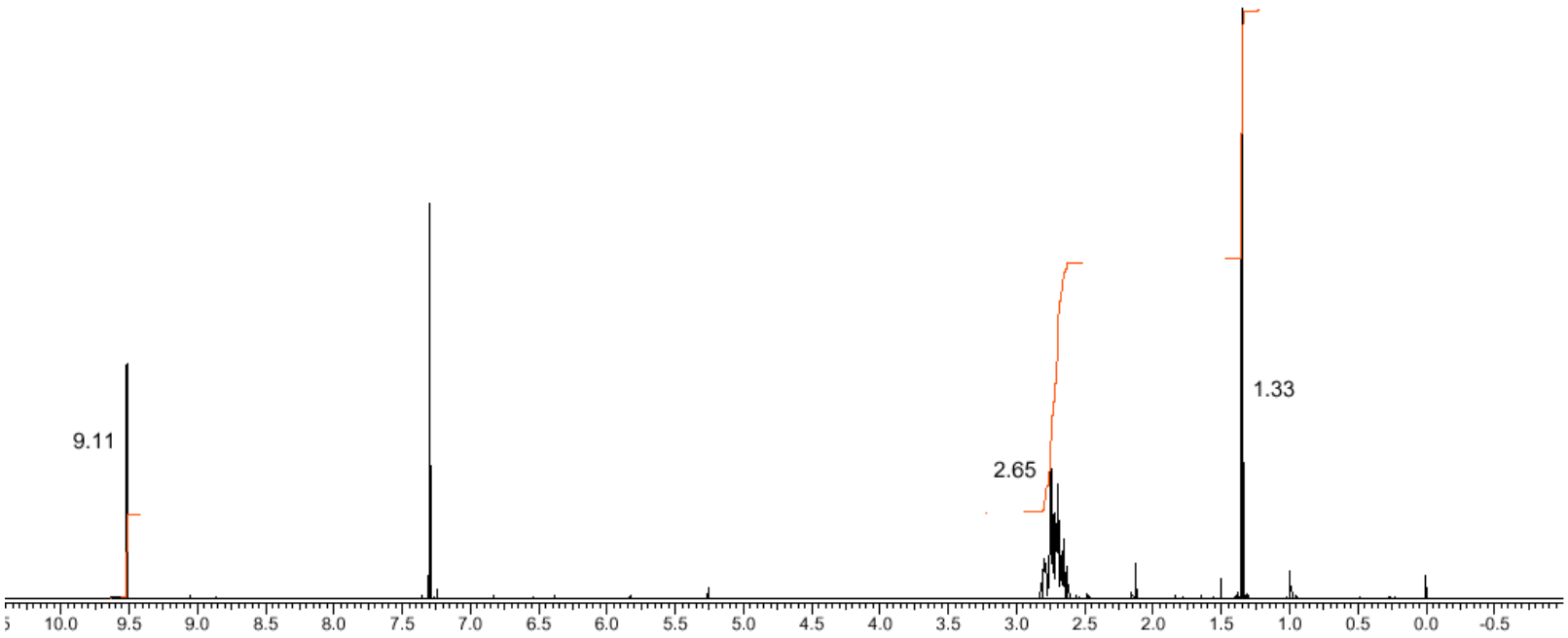
[1]H NMR spectrum of Compound **5e,** 1-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,12-henicosafluorododecyl)-4-methylbenzene, in $CDCl_3$



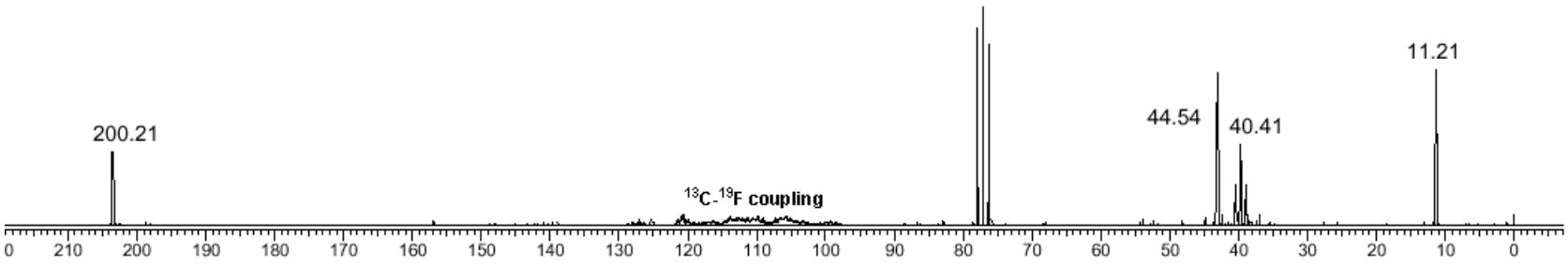
^{13}C NMR spectrum of Compound **5e,** 1-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,12-henicosafluorododecyl)-4-methylbenzene, in $CDCl_3$



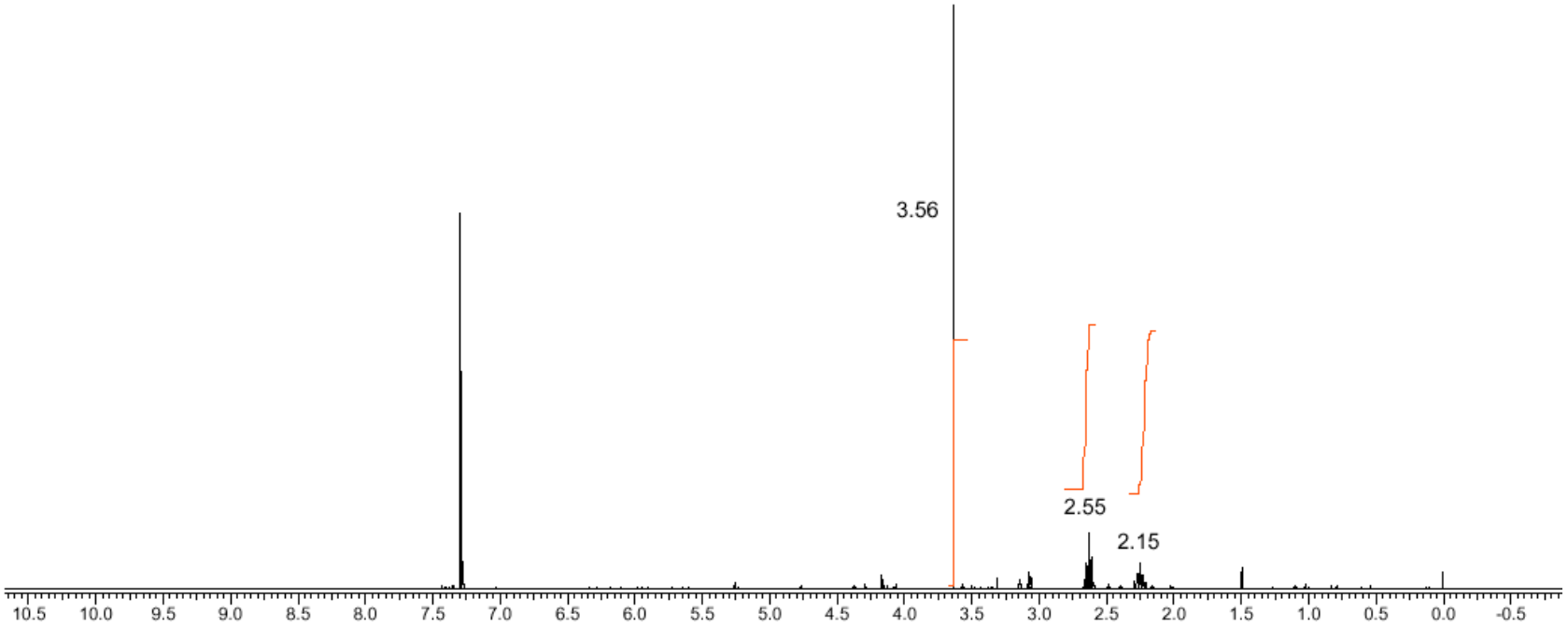
^{1}H NMR spectrum of Compound **7e,** 4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,13,13,13-henicosafluoro-3-methyltridecanal, in $CDCl_3$



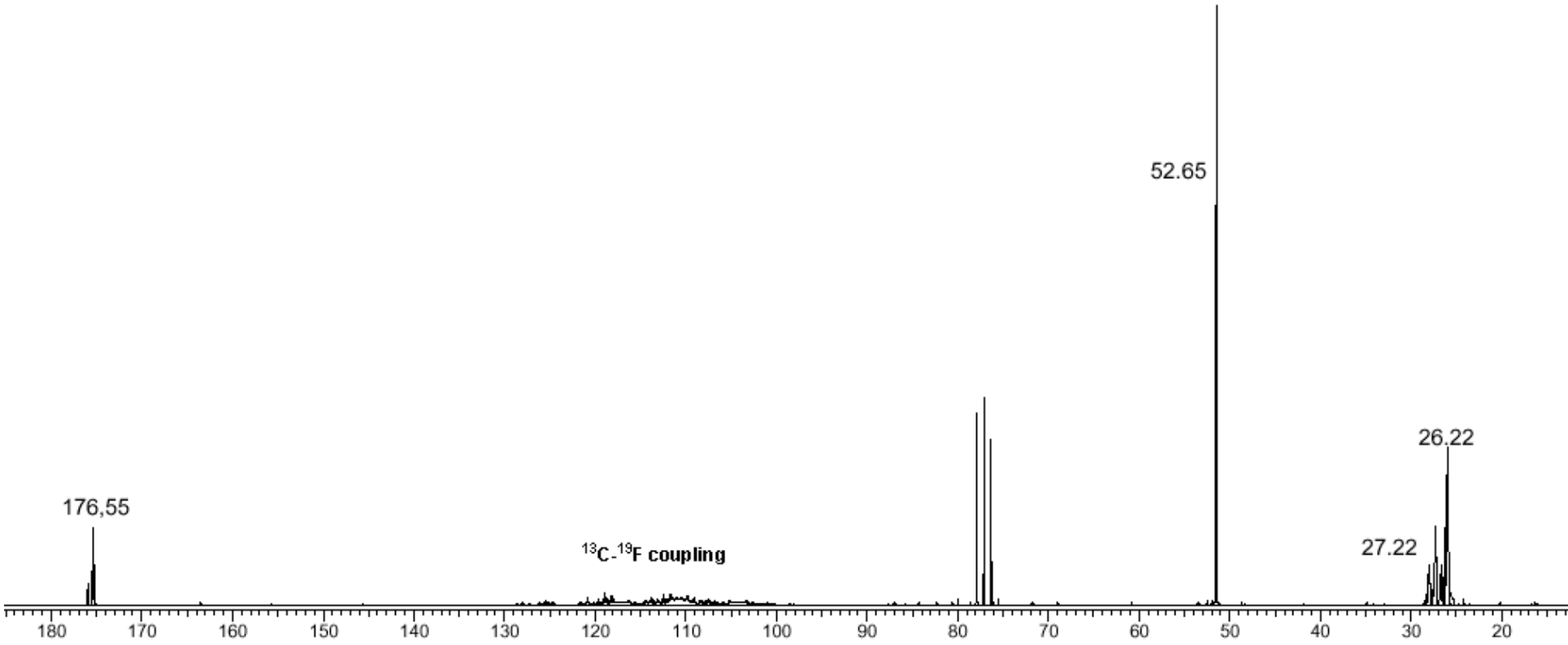
^{13}C NMR spectrum of Compound **7e,** 4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,13,13,13-henicosafluoro-3-methyltridecanal, in $CDCl_3$



^{1}H NMR spectrum of Compound **8e,** methyl 4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,13,13,13-henicosafluorotridecanoate, in $CDCl_3$

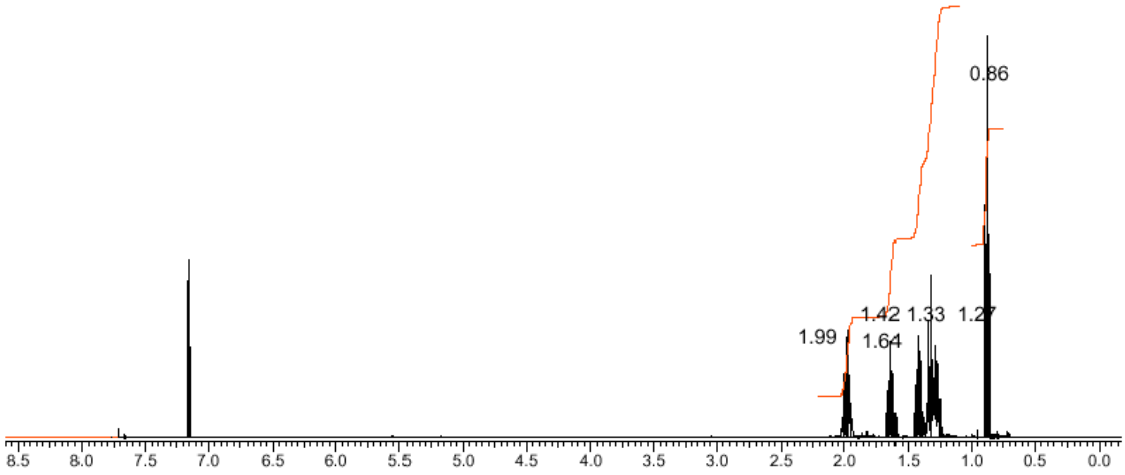


^{13}C NMR spectrum of Compound **8e,** methyl 4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,13,13,13-henicosafluorotridecanoate in $CDCl_3$

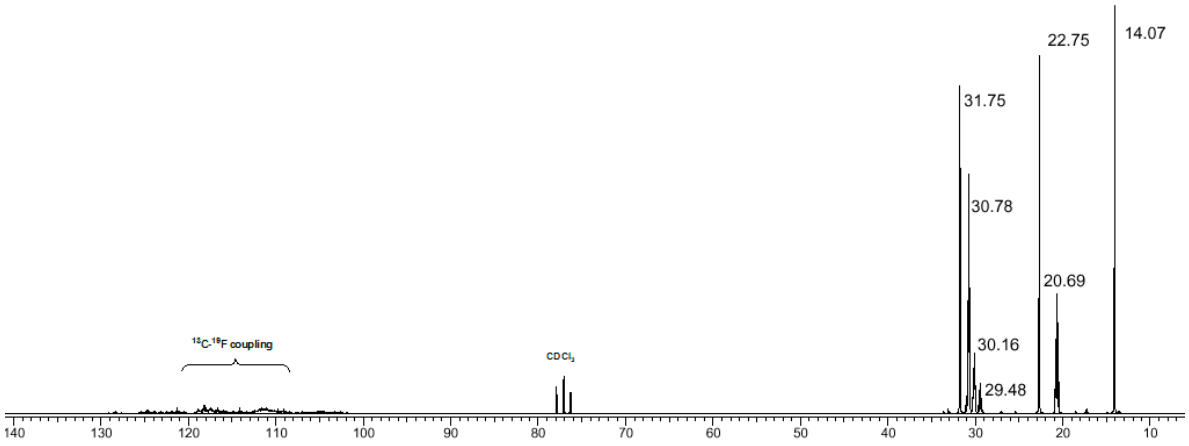


SPECTRAL CHARACTERIZATION OF KNOWN COMPOUNDS: 1a-6a, 1b, 1c, 1d, 1e, 2d-6d, 8d, 9d, 1e-4e. 6e.

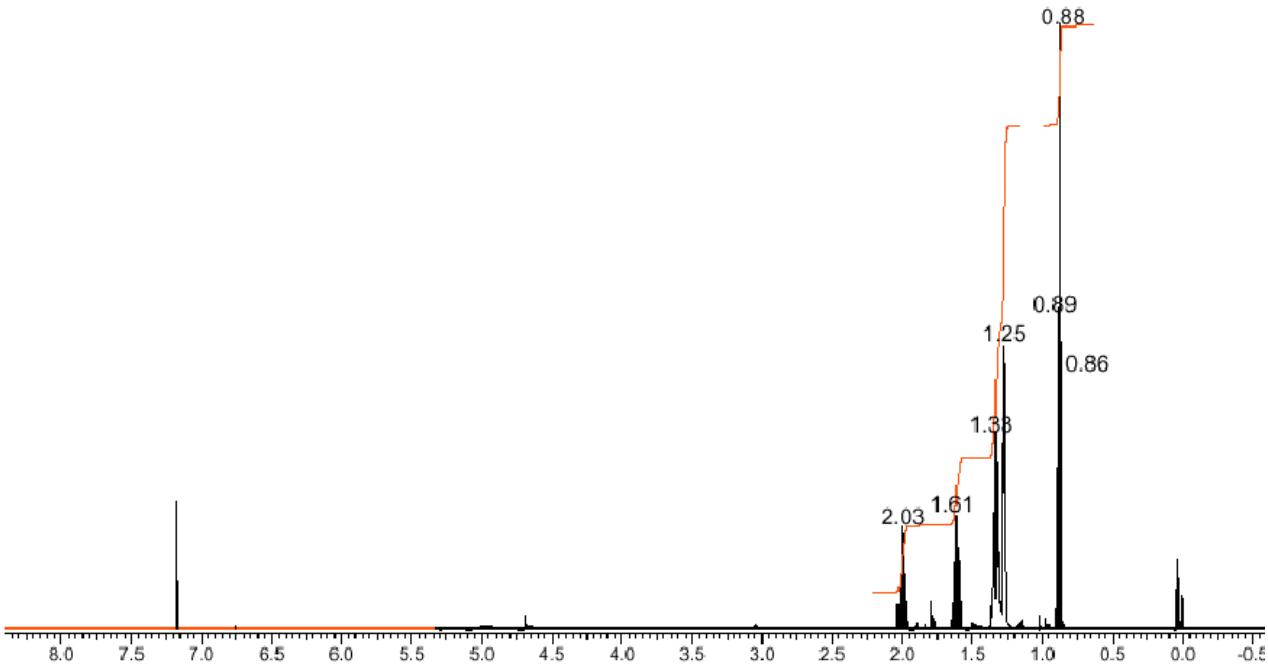
^{1}H NMR spectrum of Compound **1a** (1,1,1,2,2,3,3,4,4,5,5,6,6-tridecafluorododecane) in $CDCl_3$



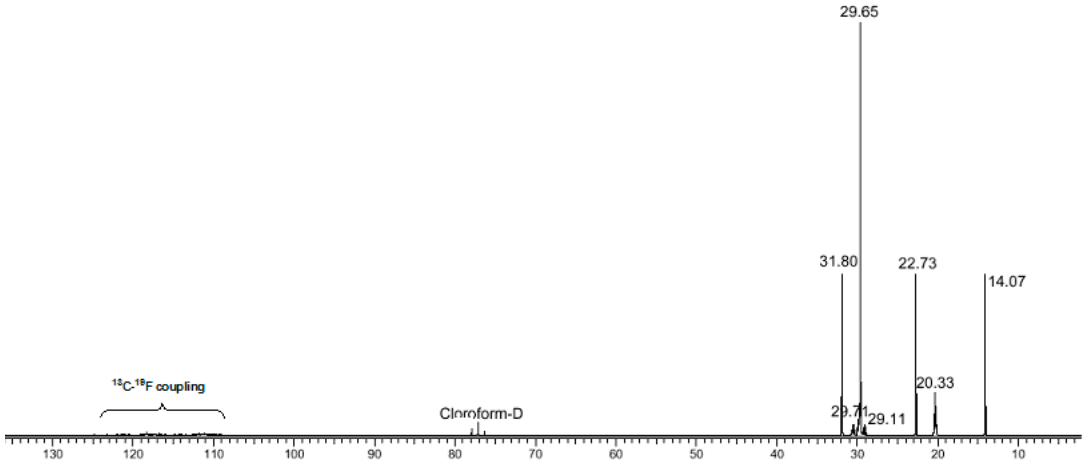
^{13}C NMR spectrum of Compound **1a** (1,1,1,2,2,3,3,4,4,5,5,6,6-tridecafluorododecane) in $CDCl_3$



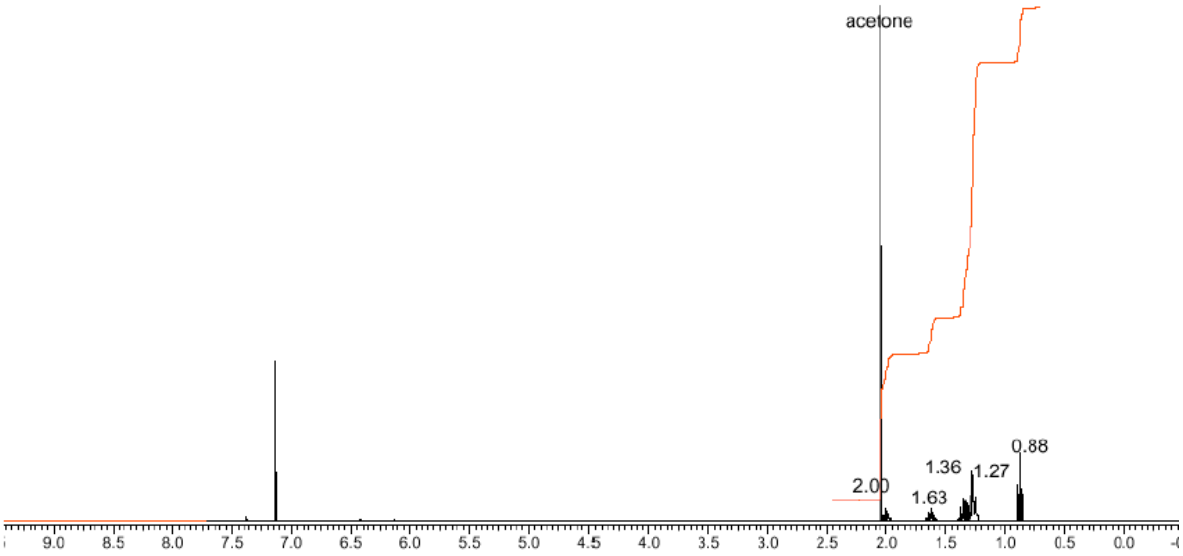
^{1}H NMR spectrum of Compound **2a** (1,1,1,2,2,3,3,4,4,5,5,6,6-tridecafluorotetradecane) in $CDCl_3$



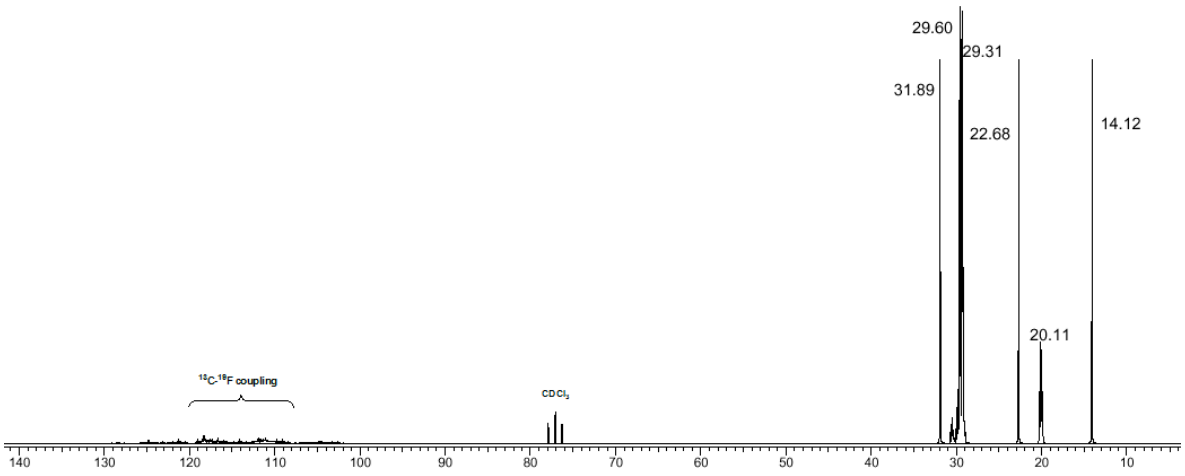
^{13}C NMR spectrum of Compound **2a** (1,1,1,2,2,3,3,4,4,5,5,6,6-tridecafluorotetradecane) in $CDCl_3$



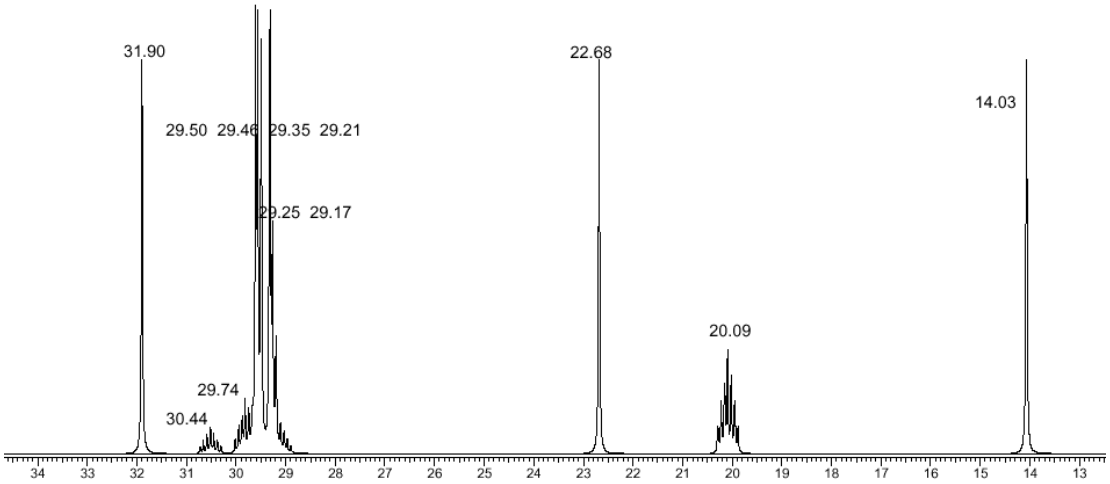
^{1}H NMR spectrum of Compound **3a** (1,1,1,2,2,3,3,4,4,5,5,6,6-tridecafluorohexadecane) in $CDCl_3$



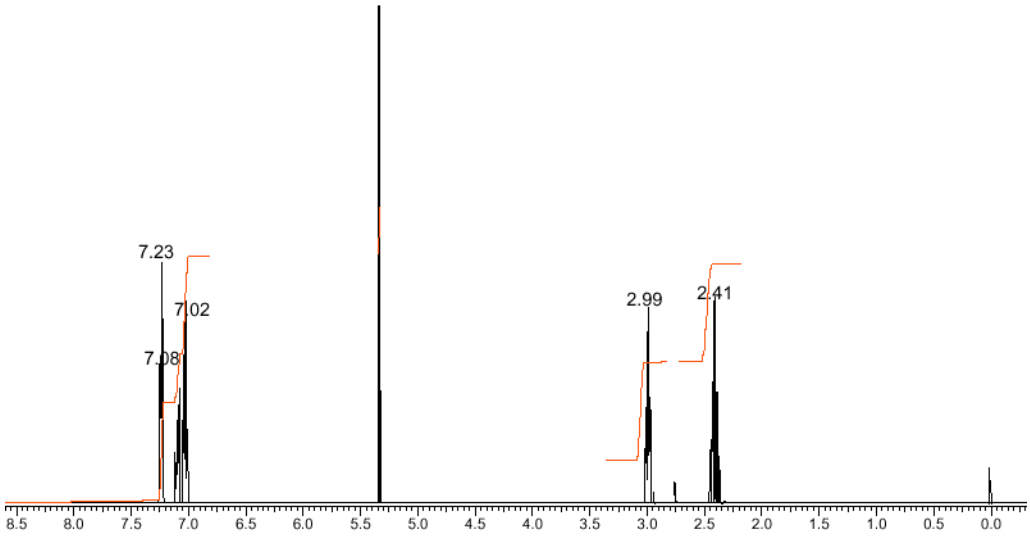
^{13}C NMR spectrum of Compound **3a** (1,1,1,2,2,3,3,4,4,5,5,6,6-tridecafluorohexadecane) in $CDCl_3$



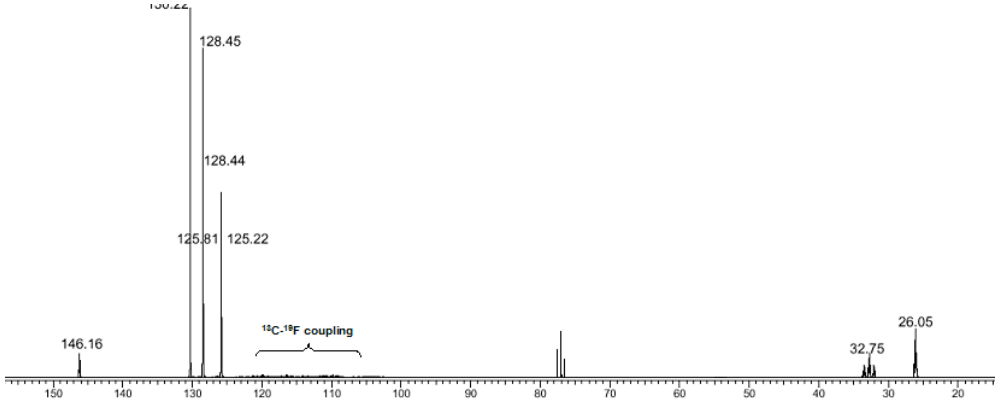
^{13}C NMR spectrum of Compound **3a** (1,1,1,2,2,3,3,4,4,5,5,6,6-tridecafluorohexadecane) in $CDCl_3$ (enlargement area 10-40 ppm)



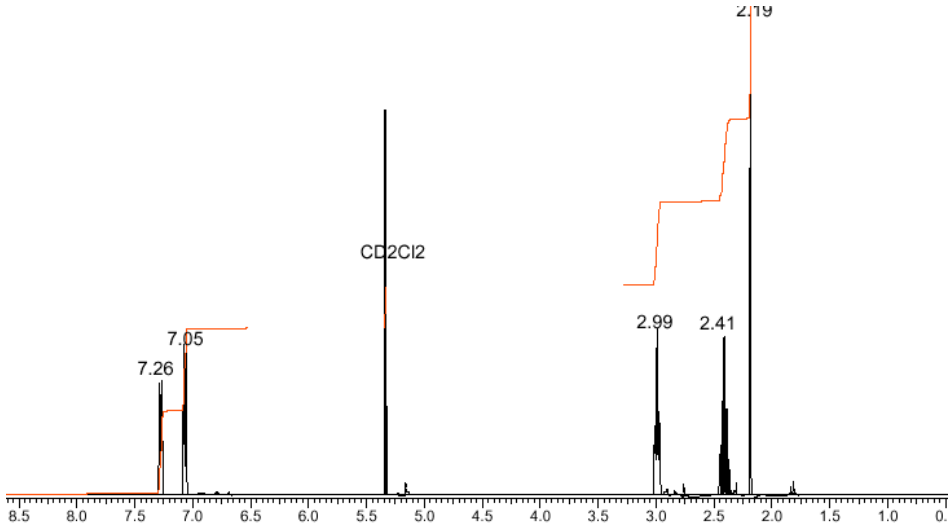
^{1}H NMR spectrum of Compound **4a** ((3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)benzene) in CD_2Cl_2



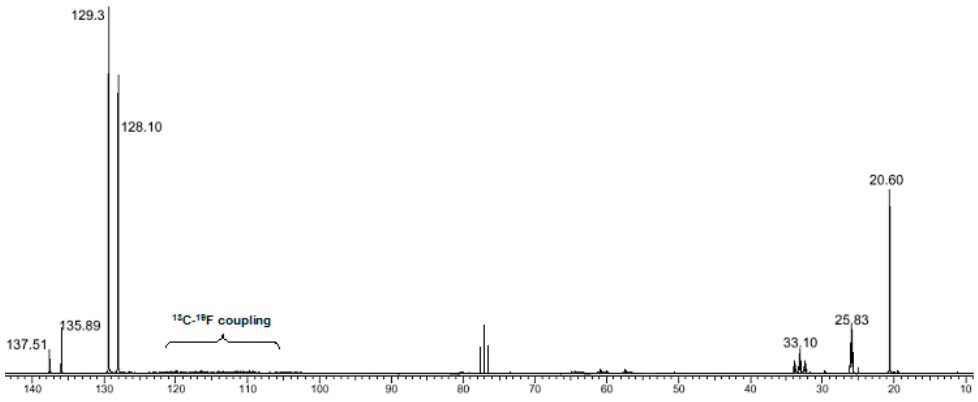
^{13}C NMR spectrum of Compound **4a** ((3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)benzene) in $CDCl_3$



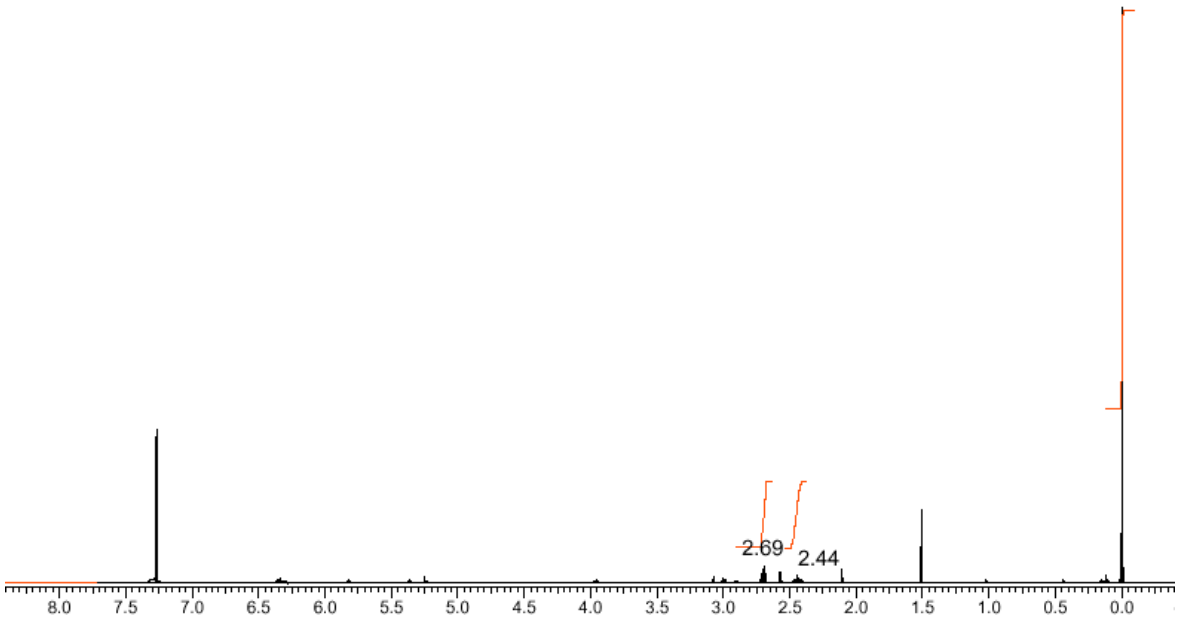
^{1}H NMR spectrum of Compound **5a** (1-methyl-4-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)benzene) in CD_2Cl_2



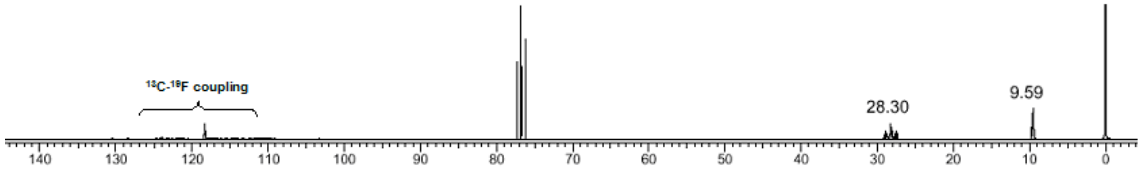
^{13}C NMR spectrum of Compound **5a** (1-methyl-4-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)benzene) in $CDCl_3$



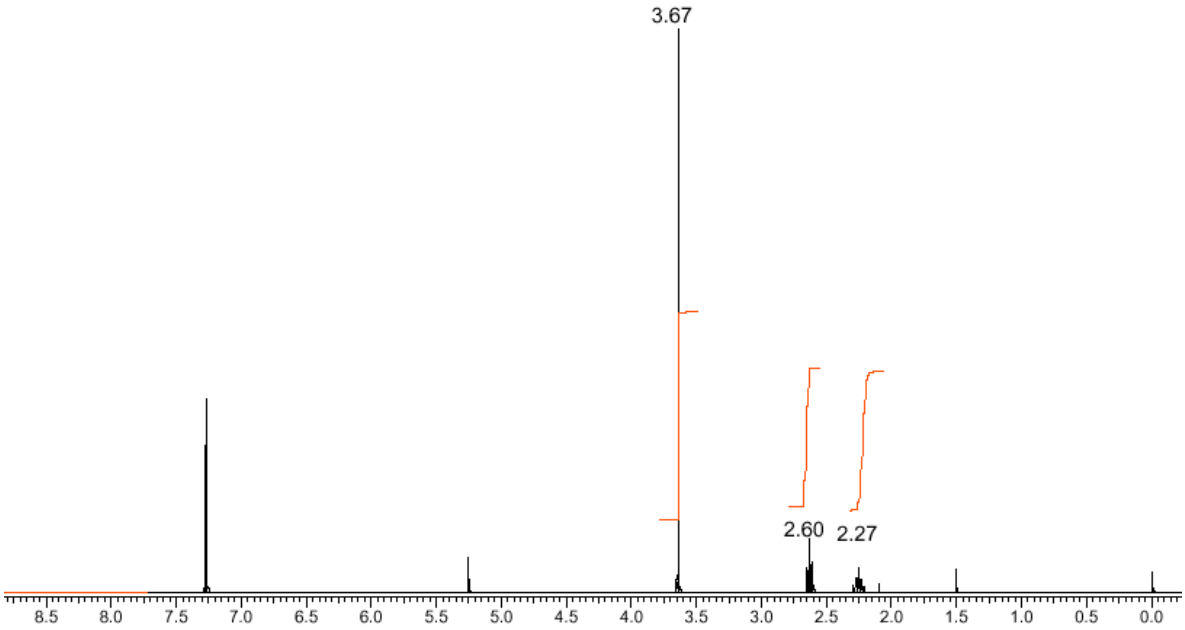
^{1}H NMR spectrum of Compound **6a** ((4,4,5,5,6,6,7,7,8,8,9,9,9-tridecafluorononanenitrile) in $CDCl_3$



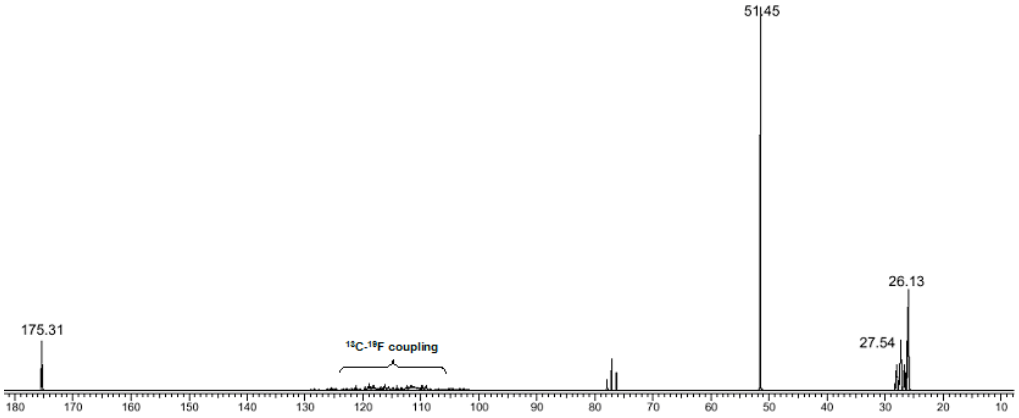
^{13}C NMR spectrum of Compound **6a** (4,4,5,5,6,6,7,7,8,8,9,9,9-tridecafluorononanenitrile) in $CDCl_3$



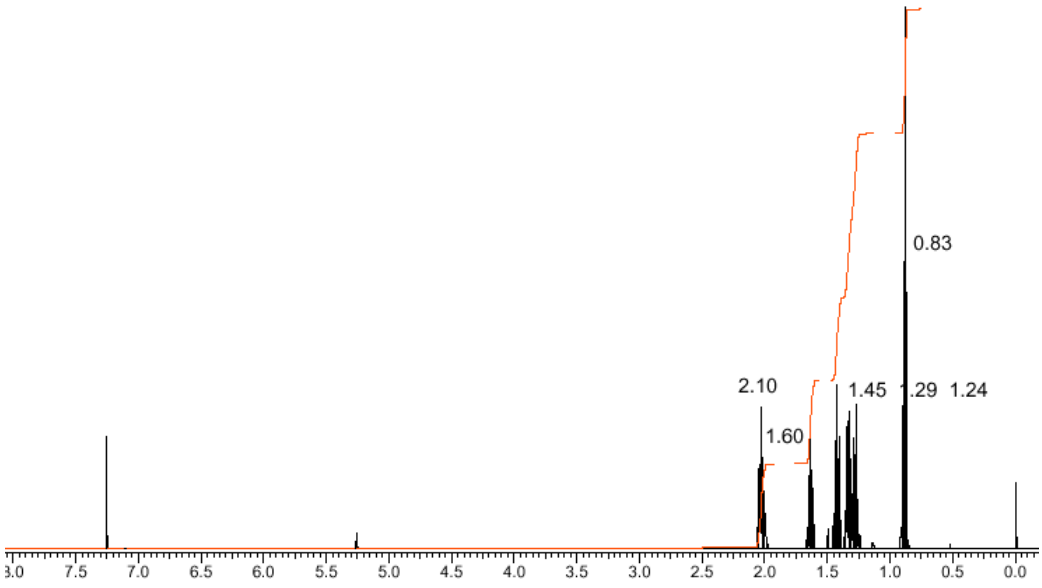
^{1}H NMR spectrum of Compound **9a** (5,5,6,6,7,7,8,8,9,9,9,10,10,10-tridecafluoro-2-decanone) in $CDCl_3$



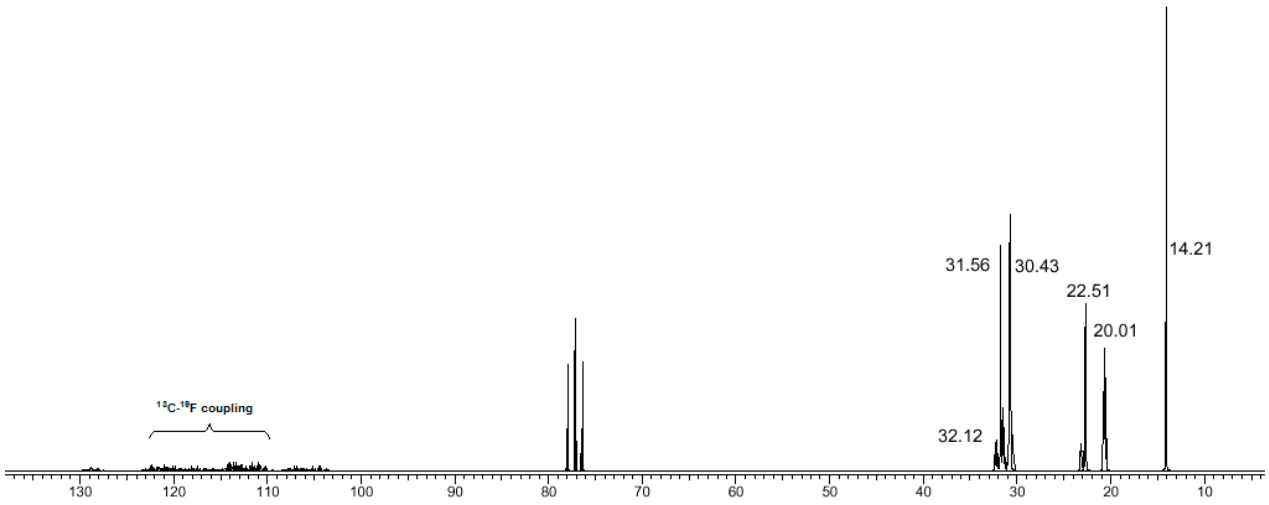
^{13}C NMR spectrum of Compound **9a** (5,5,6,6,7,7,8,8,9,9,9,10,10,10-tridecafluoro-2-decanone) in $CDCl_3$



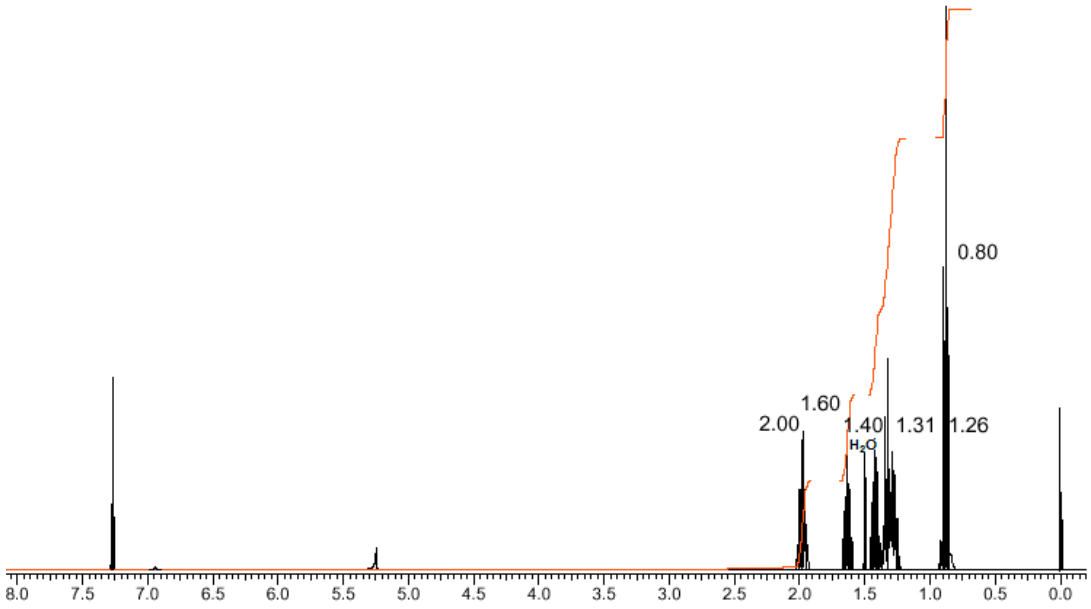
^{1}H NMR spectrum of Compound **1b,** 1,1,1,2,2,3,3,4,4-nonafluorodecane, in $CDCl_3$



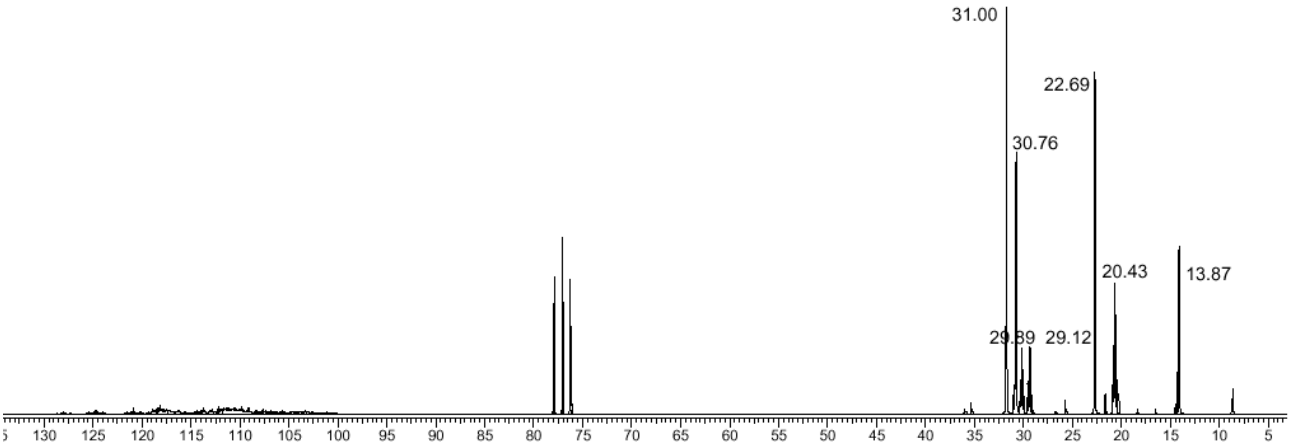
^{13}C NMR spectrum of Compound **1b,** 1,1,1,2,2,3,3,4,4-nonafluorodecane, in $CDCl_3$



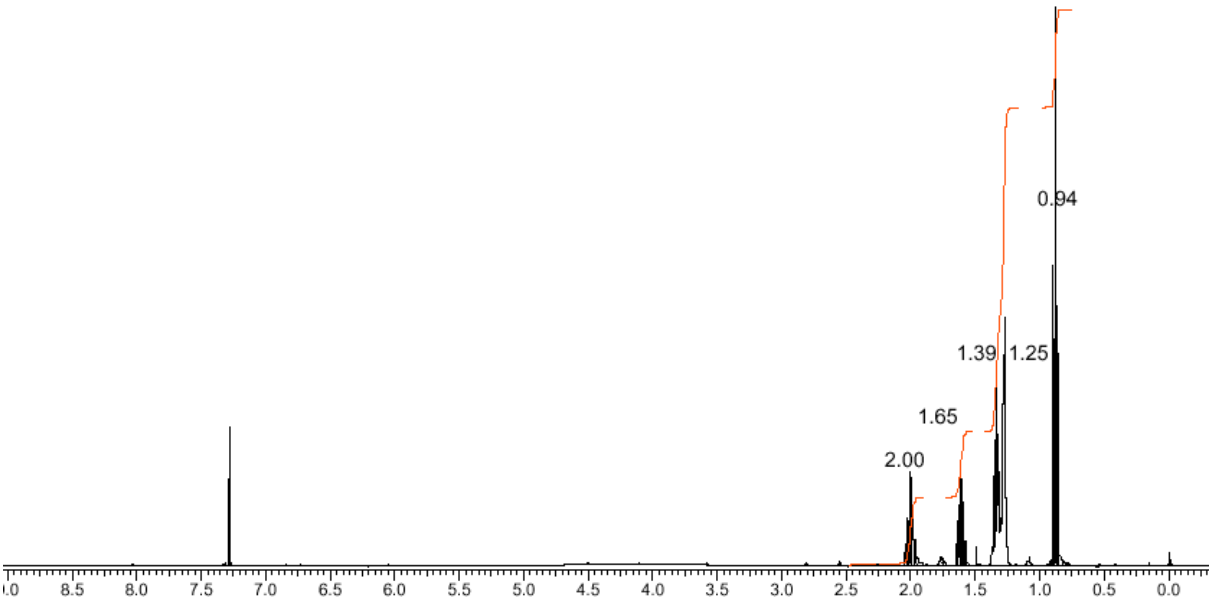
^{1}H NMR spectrum of Compound **1d,** 1,1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8-heptadecafluorotetradecane, in $CDCl_3$



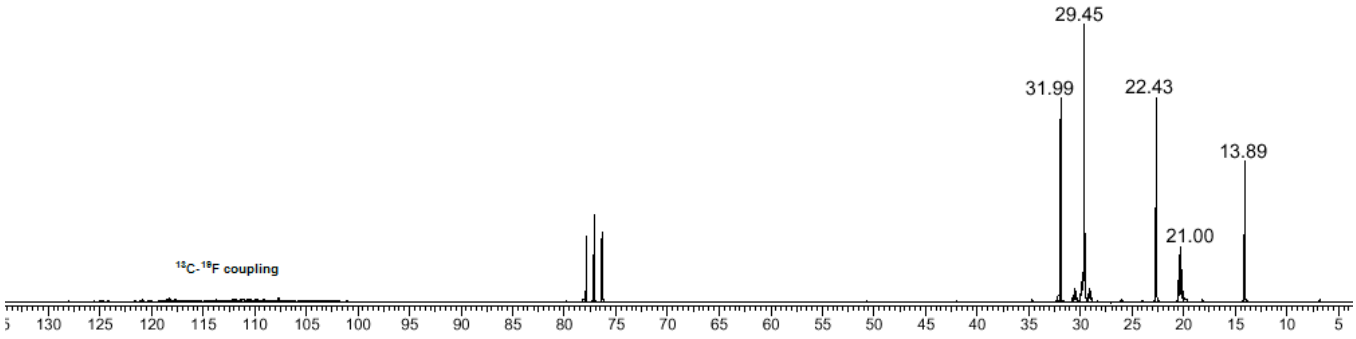
^{13}C NMR spectrum of Compound **1d,** 1,1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8-heptadecafluorotetradecane, in $CDCl_3$



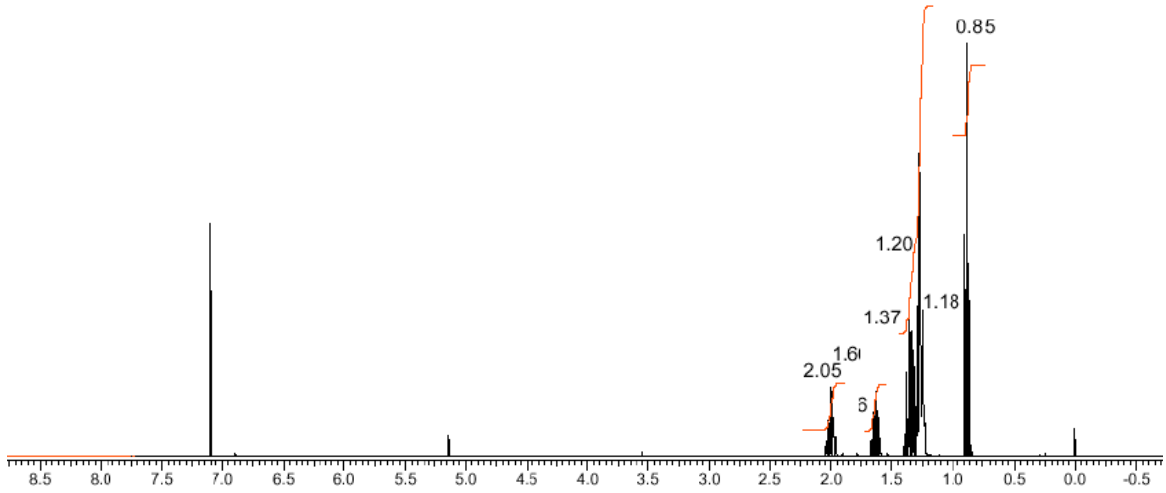
^{1}H NMR spectrum of Compound **2d,** 1,1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8-heptadecafluorohexadecane , in $CDCl_3$



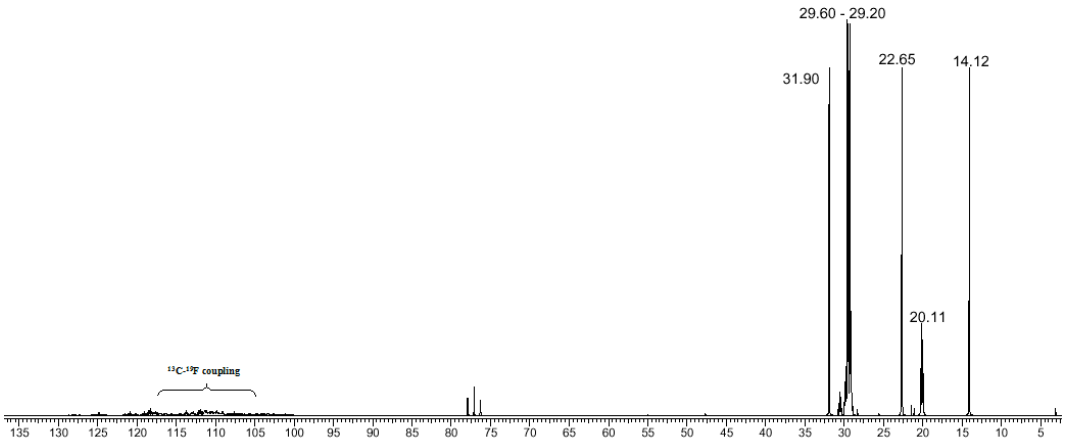
^{13}C NMR spectrum of Compound **2d,** 1,1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8-heptadecafluorohexadecane , in $CDCl_3$



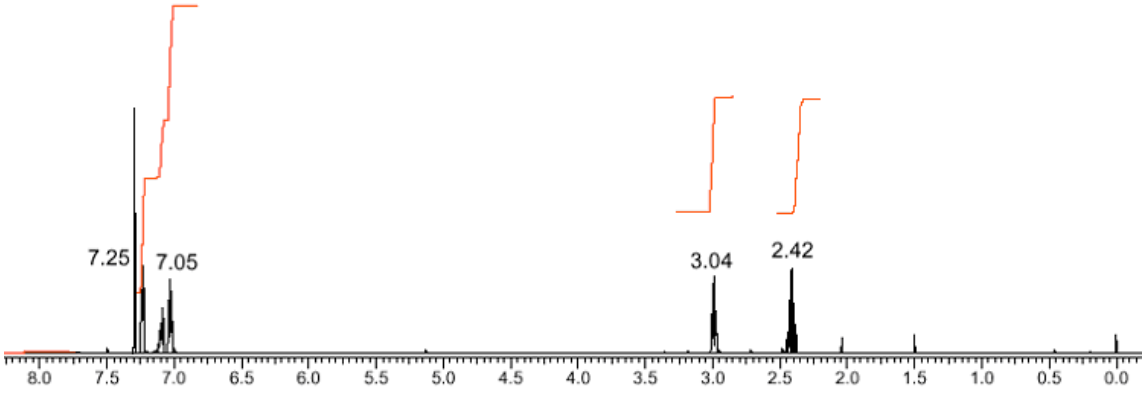
^{1}H NMR spectrum of Compound **3d,** (1,1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8-heptadecafluorooctadecane), in $CDCl_3$



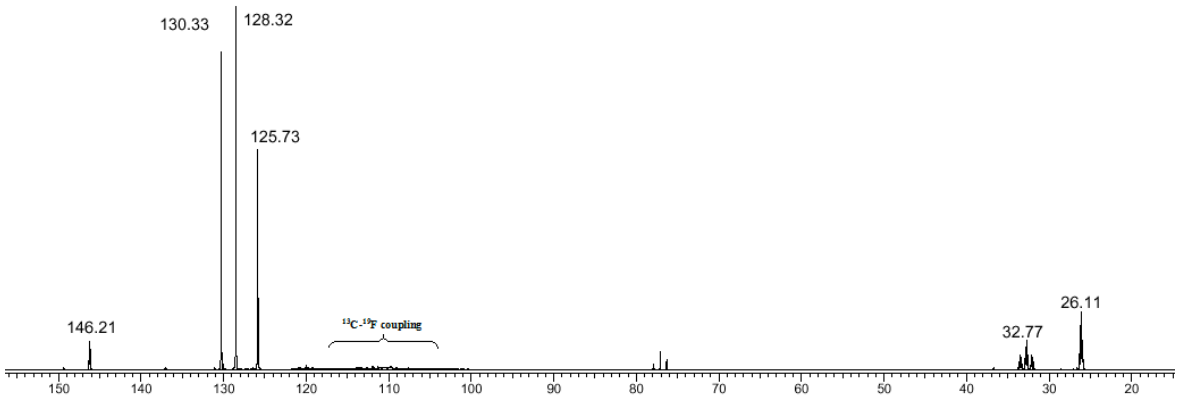
^{13}C NMR spectrum of Compound **3d,** (1,1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8-heptadecafluorooctadecane), in $CDCl_3$



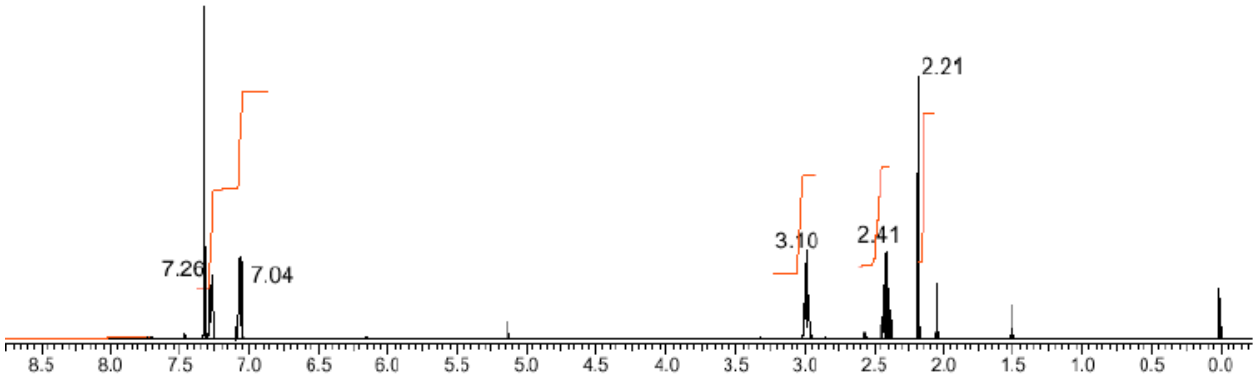
^{1}H NMR spectrum of Compound **4d,** (3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl)benzene, in $CDCl_3$



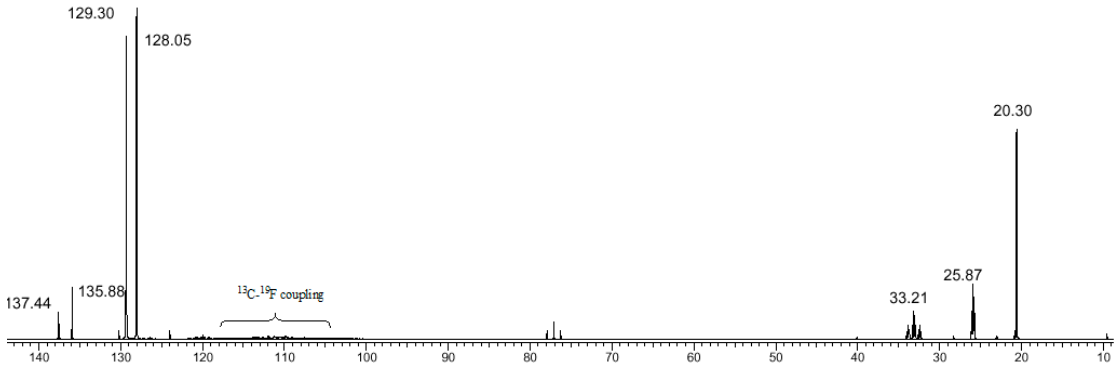
^{13}C NMR spectrum of Compound **4d,** (3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl)benzene, in $CDCl_3$



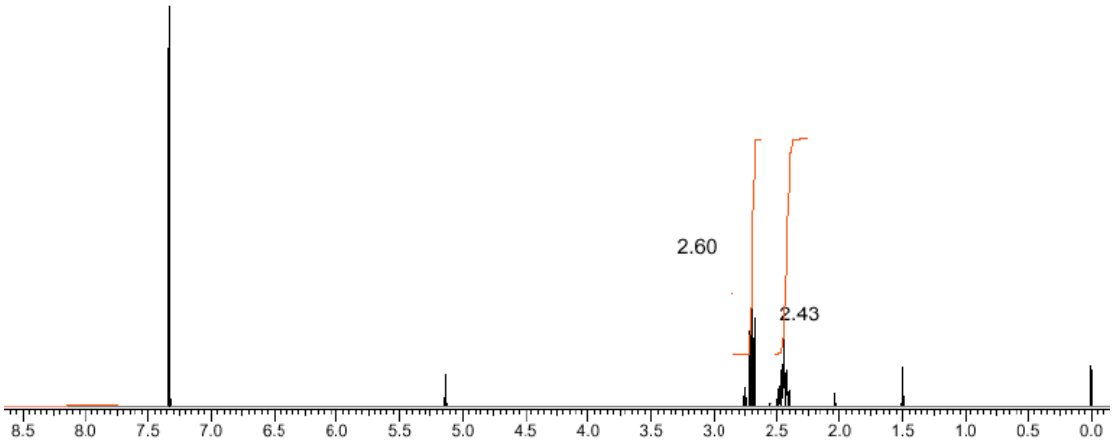
^{1}H NMR spectrum of Compound **5d,** 1-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl)-4-methylbenzene, in $CDCl_3$



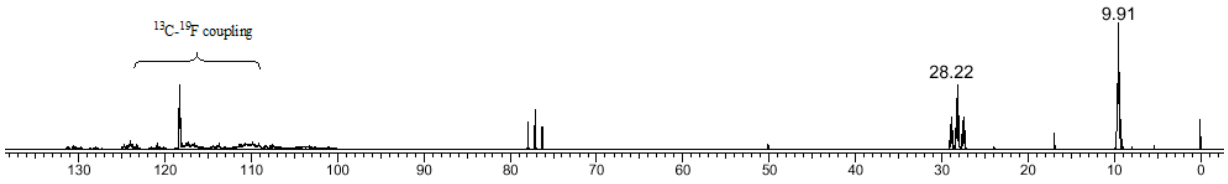
^{13}C NMR spectrum of Compound **5d,** 1-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl)-4-methylbenzene, in $CDCl_3$



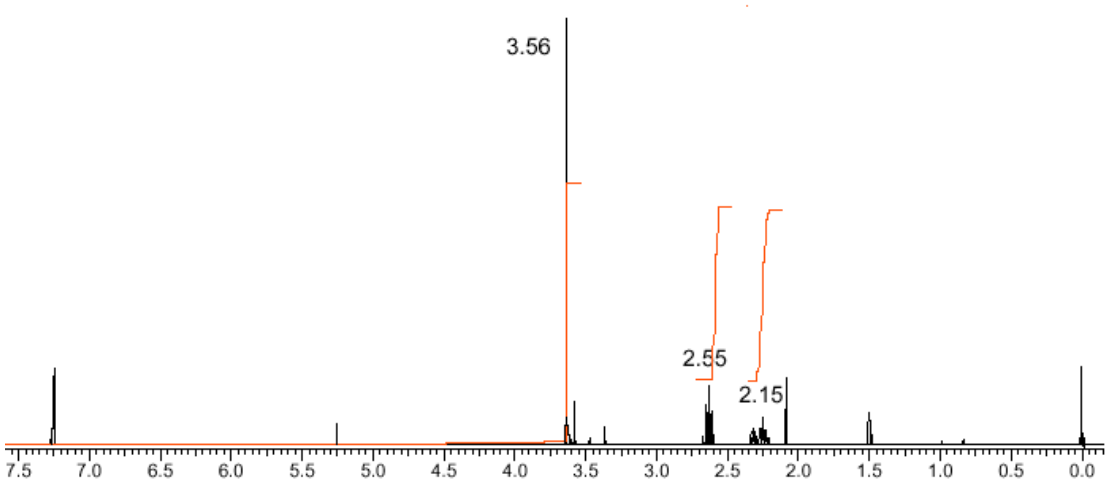
^{1}H NMR spectrum of Compound **6d,** 4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptadecafluoroundecanenitrile, in $CDCl_3$



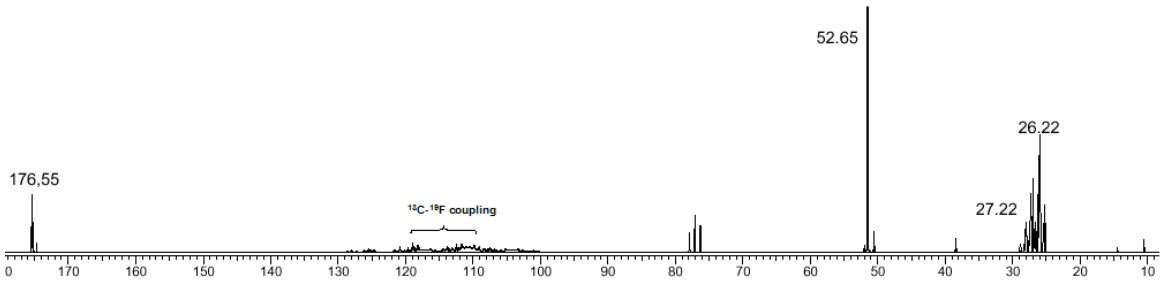
^{13}C NMR spectrum of Compound **6d,** 4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptadecafluoroundecanenitrile, in $CDCl_3$



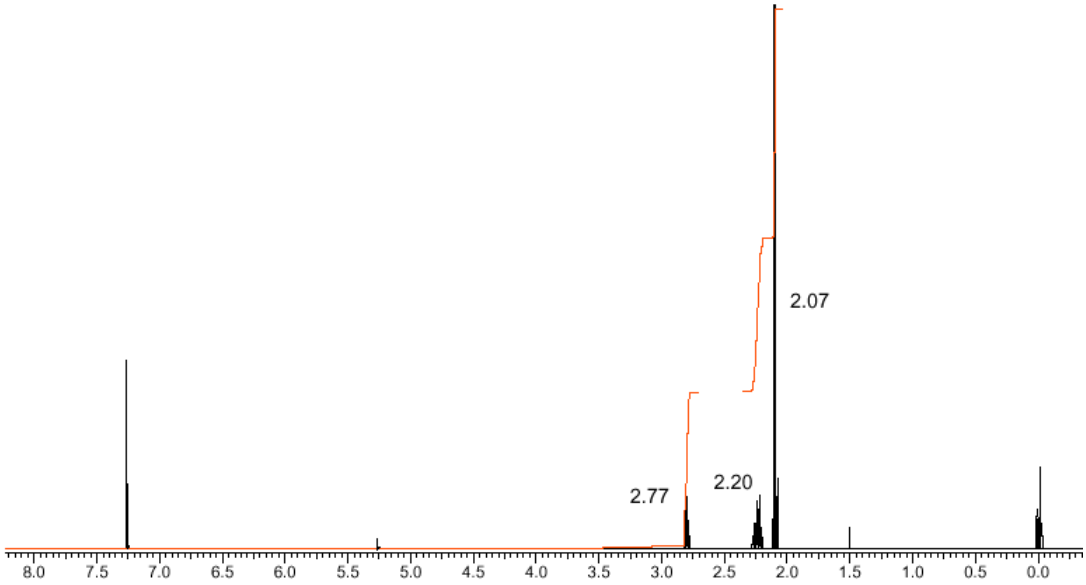
^{1}H NMR spectrum of Compound **8d,** methyl 4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptadecafluoroundecanoate, in $CDCl_3$



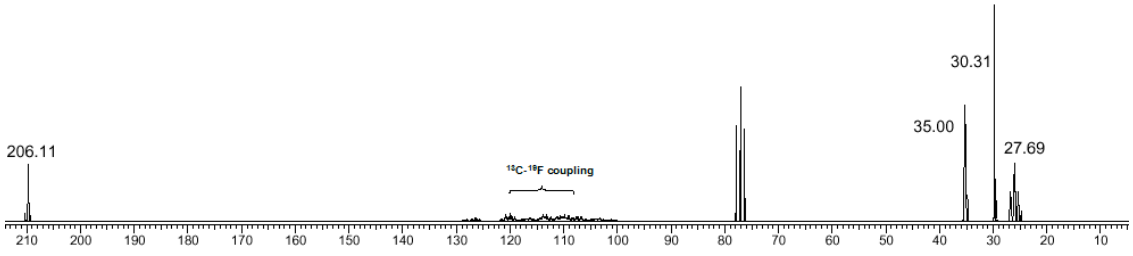
^{13}C NMR spectrum of Compound **8d,** methyl 4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptadecafluoroundecanoate, in $CDCl_3$



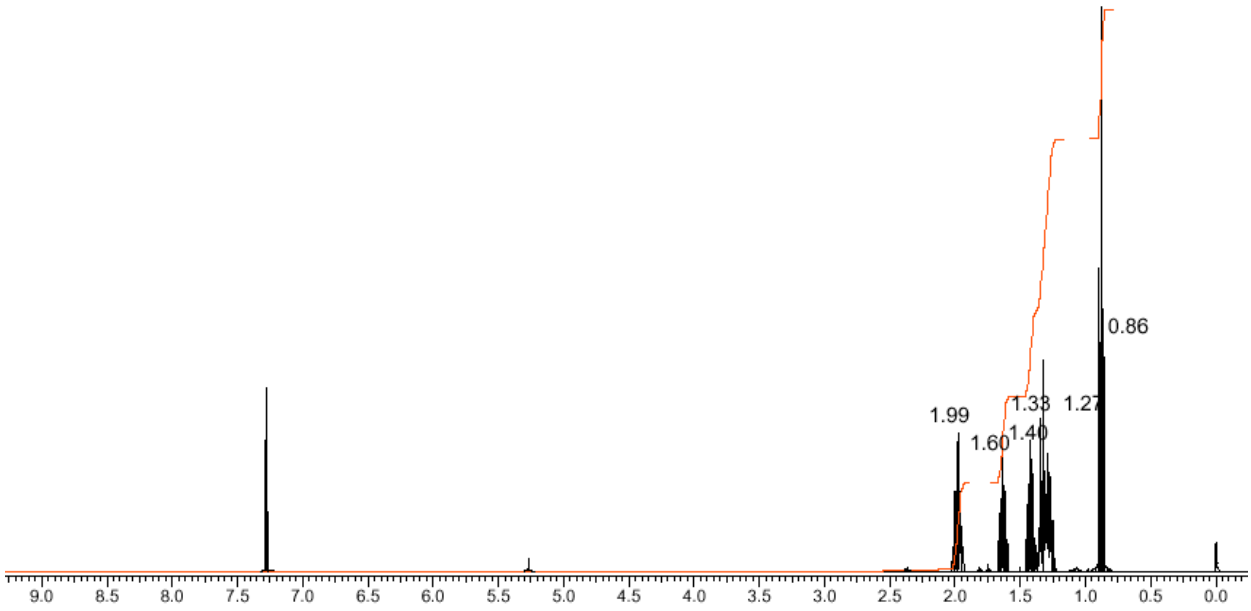
^{1}H NMR spectrum of Compound **9d,** 5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,12-heptadecafluorododecan-2-one, in $CDCl_3$



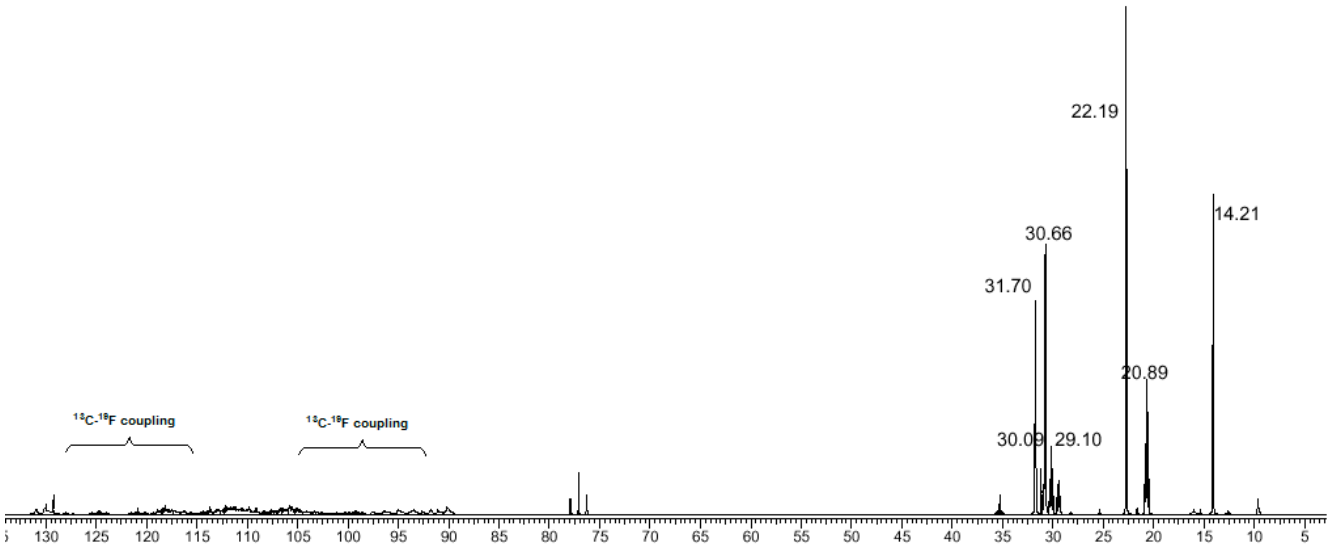
^{13}C NMR spectrum of Compound **9d,** 5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,12-heptadecafluorododecan-2-one, in $CDCl_3$



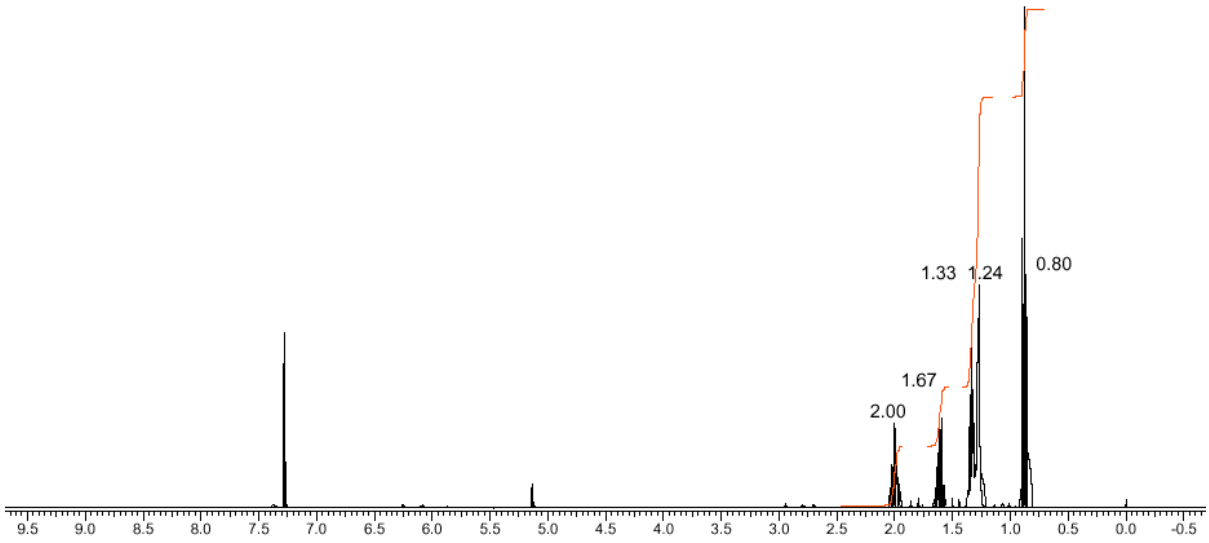
^{1}H NMR spectrum of Compound **1e,** 1,1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10-henicosafluorohexadecane, in $CDCl_3$



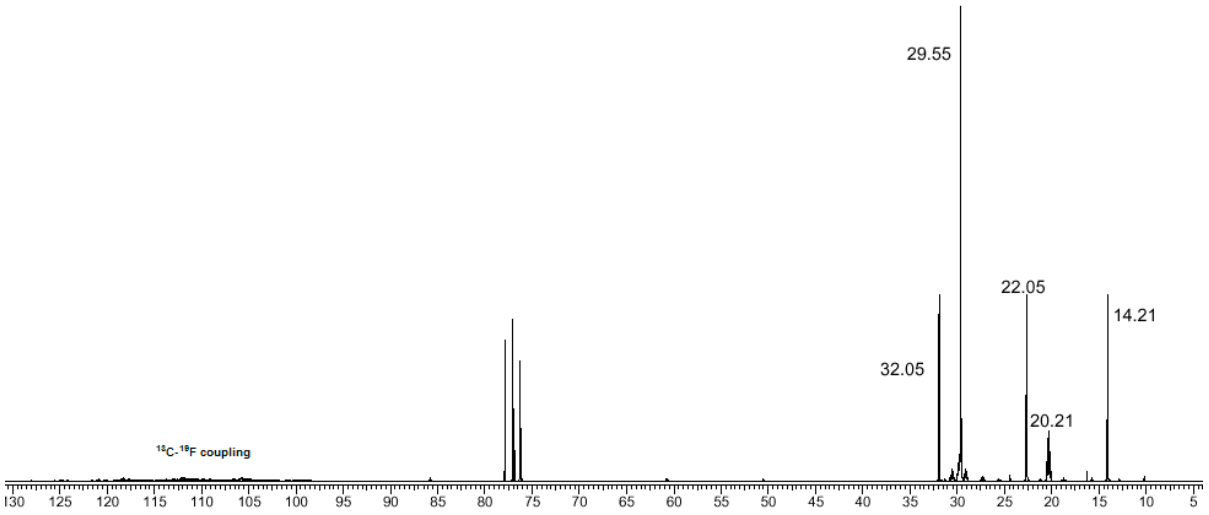
^{13}C NMR spectrum of Compound **1e,** 1,1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10-henicosafluorohexadecane, in $CDCl_3$



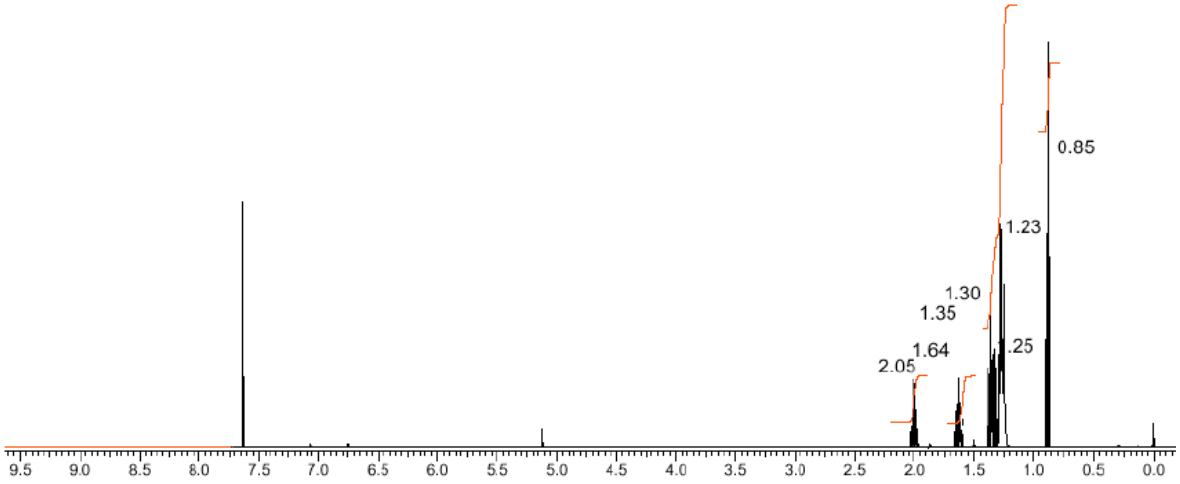
^{1}H NMR spectrum of Compound **2e,** 1,1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10-henicosafluorooctadecane, in $CDCl_3$



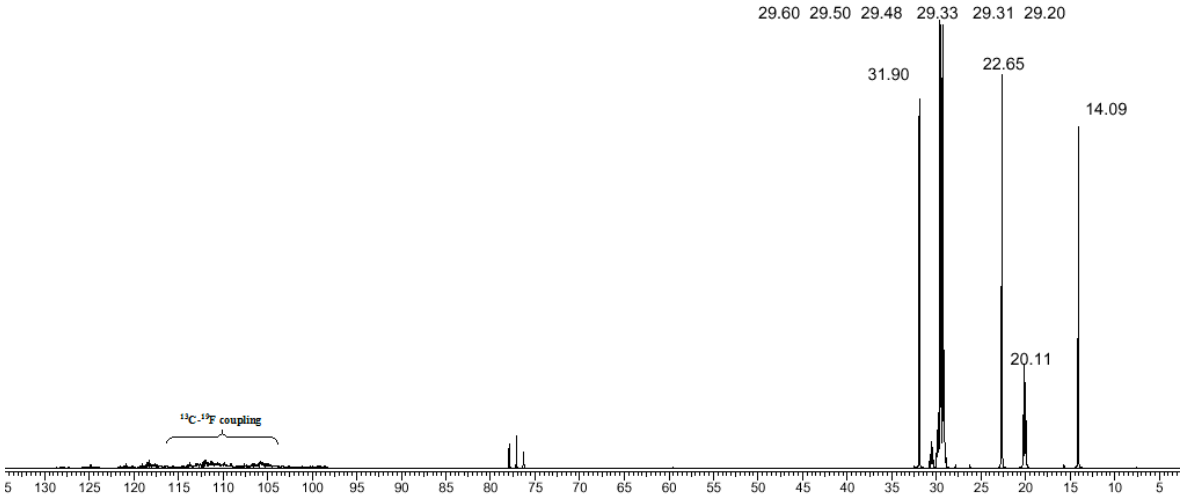
^{13}C NMR spectrum of Compound **2e,** 1,1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10-henicosafluorooctadecane, in $CDCl_3$



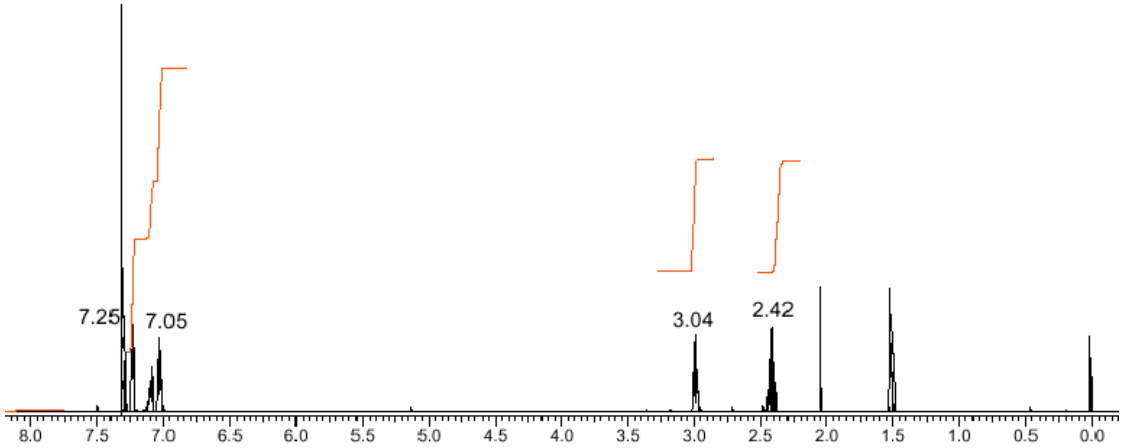
^{1}H NMR spectrum of Compound **3e,** (1,1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10-henicosafluoroicosane), in $CDCl_3$



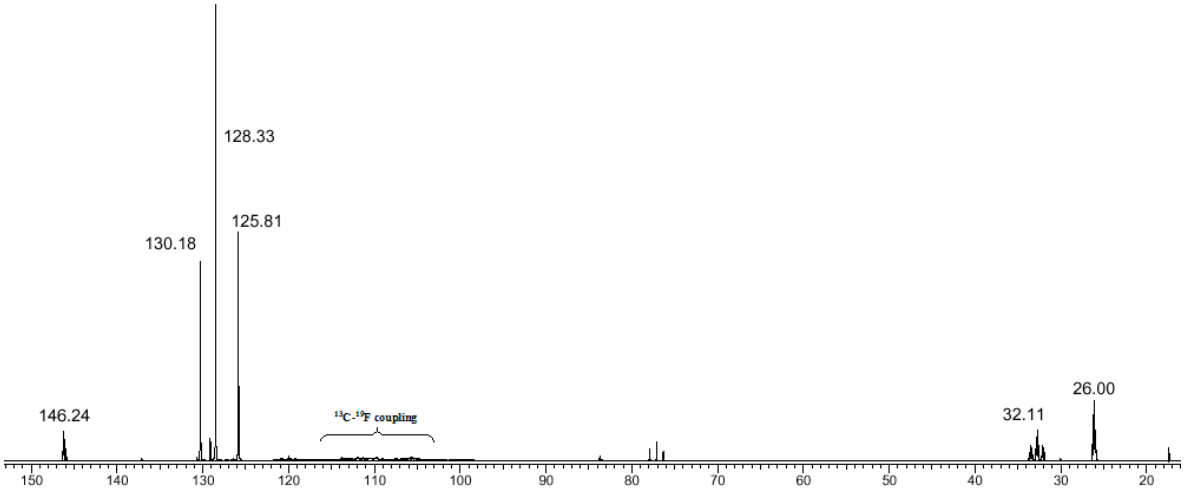
^{13}C NMR spectrum of Compound **3e,** (1,1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10-henicosafluoroicosane), in $CDCl_3$



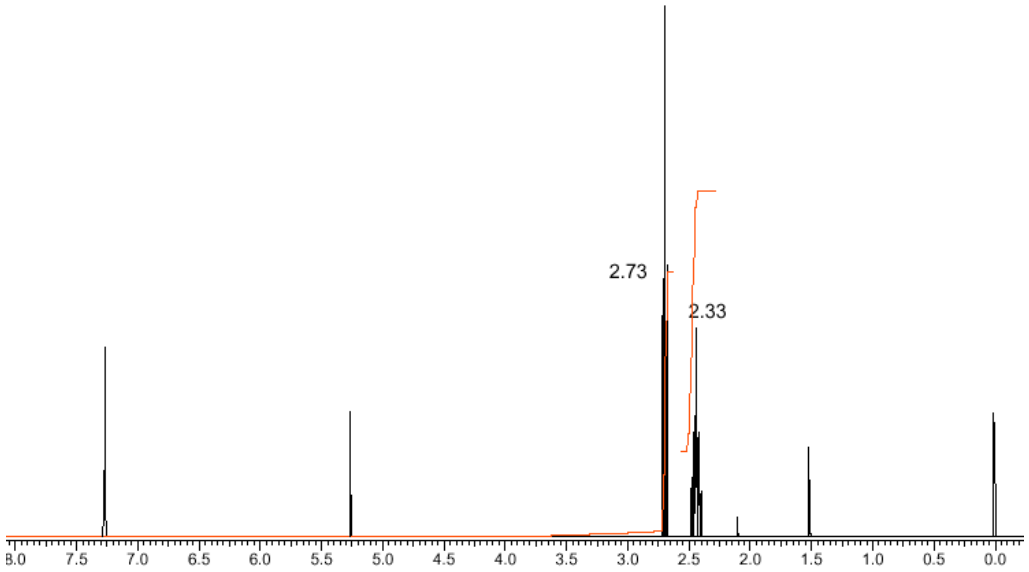
^{1}H NMR spectrum of Compound **4e,** (3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,12-henicosafluorododecyl)benzene, in $CDCl_3$



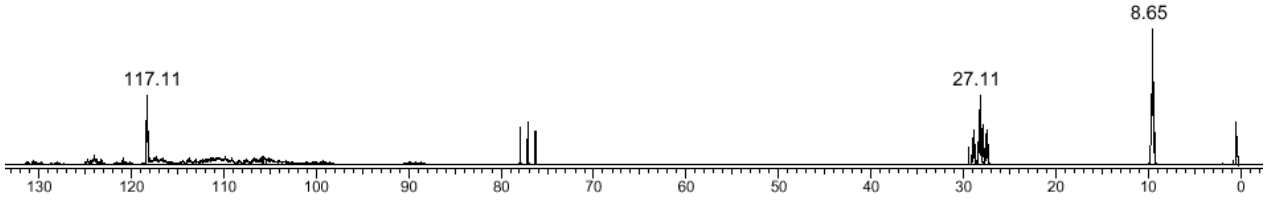
^{13}C NMR spectrum of Compound **4e,** (3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,12-henicosafluorododecyl)benzene, in $CDCl_3$



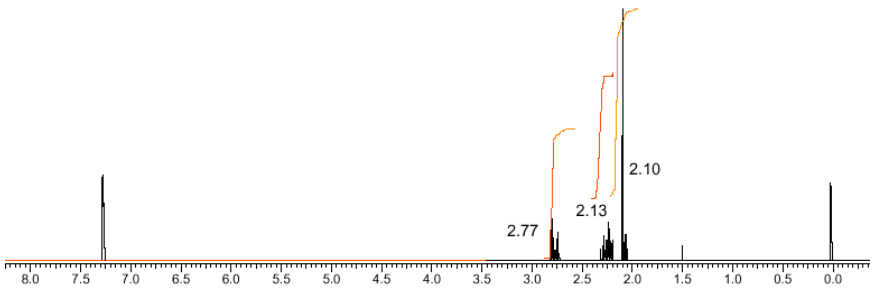
^{1}H NMR spectrum of Compound **6e,** 4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,13,13,13-henicosafluorotridecanenitrile, in $CDCl_3$



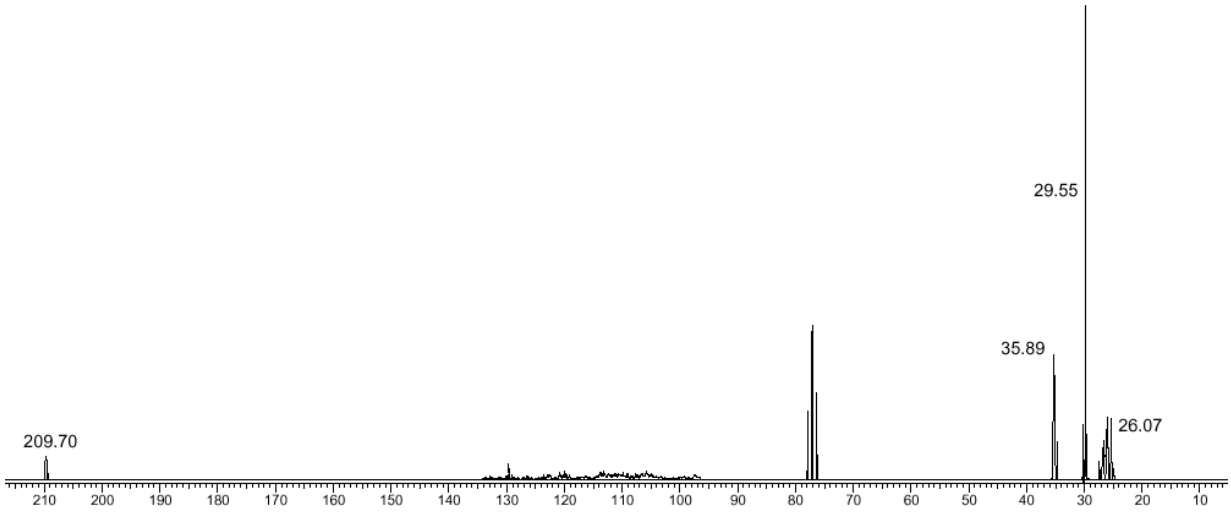
^{13}C NMR spectrum of Compound **6e,** 4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,13,13,13-henicosafluorotridecanenitrile, in $CDCl_3$



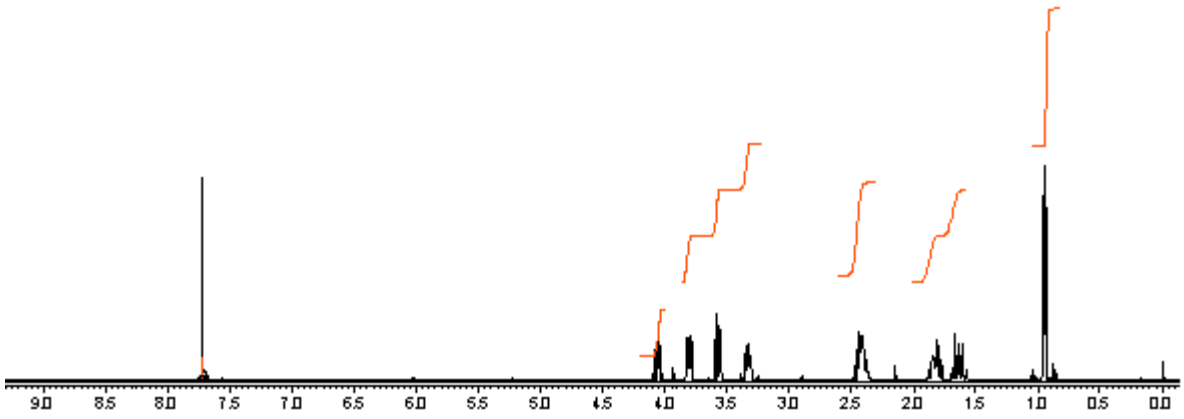
^{1}H NMR spectrum of Compound **9e,** 5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,13,13,14,14,14-henicosafluorotetradecan-2-one, in $CDCl_3$



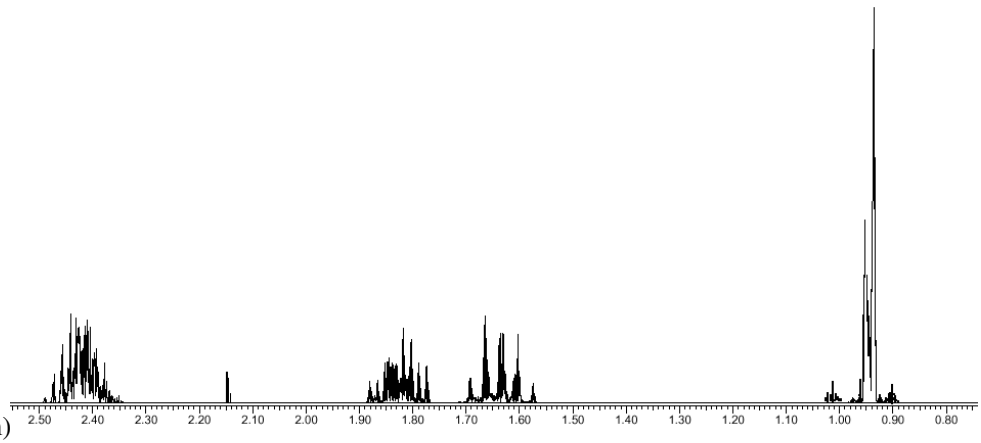
^{13}C NMR spectrum of Compound **9e,** 5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,13,13,14,14,14-henicosafluorotetradecan-2-one, in $CDCl_3$



^{1}H NMR spectrum of Compound **10a,** *cis* and *trans*-3-methyl-4-(2,2,3,3,4,4,5,5,6,6,7,7,7-tridecafluoroheptyl)tetrahydrofuran in $CDCl_3$



^{1}H NMR spectrum of Compound **10a,** *cis* and *trans*-3-methyl-4-(2,2,3,3,4,4,5,5,6,6,7,7,7-tridecafluoroheptyl)tetrahydrofuran in $CDCl_3$ (expansion 0.8-2.5



ppm)

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[i] $\frac{[3]}{[2]} = \frac{k_{add}\,[1\text{-hexene}]}{K_H\,[(Me_3Si)_3SiH]}$ where k_{add} is the rate constant for of addition of perfluorinated radical to 1-hexene, k_H is the rate constant for H atom abstraction from the silane, and 2 and 3 the reduced perfluorinated alkane, and the addition product, respectively, shown in eq 2.

[ii] (a) Zaborovskiy, A. B.; Lutsyk, D. S.; Prystansky, R. E.; Kopylets, V. I.; Timokhin, V. I.; Chatgilialoglu, C. *J.Organomet.Chem.* **2004**; *689,* 2912-2919.