SUPPORTING INFORMATION

Cyclizations of 5-Hexenyl, 6-Heptenyl, 7-Octenyl and 8-Nonenyl Radicals - the Kinetic and Regiochemical Impact of Fluorine and Oxygen Substituents

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Tables of Raw Kinetic Data

Table 1. Competition data for the reaction of 2-methoxyl-1,1,2,2-tetrafluoroethyl radical with 2,3,4,5,6-pentafluorostyrene and $(TMS)_3SiH$ at 298K

$[C_6F_5CH{=}CH_2]$	$[(TMS)_3SiH]/[C_6F_5CH{=}CH_2]$	$[CF_2H]/[CH_2CF_2]$	Yield(%)
0.33	0.65	1.18	98
0.28	0.85	1.47	99
0.26	0.98	1.87	97
0.23	1.14	2.08	96
0.20	1.34	2.38	96
0.18	1.60	2.77	95

Slope = 1.69 $\pm$ 0.10 $r^2 = 0.988$ $k_H = (5.2 \pm 0.6) \times 10^7 M^{-1}s^{-1}$

Table 2. Kinetic data for the competition between Et_3SiH and Et_3SiD in reaction with n-C_4F_9I.

$[C_4F_9I]$	$[Et_3SiD]$	$[Et_3SiH]$ / $[Et_3SiD]$	$[C_4F_9H]$ / $[C_4F_9D]$	Yield, (%)
0.038	0.823	0.682	3.49	96
0.038	0.952	0.455	2.54	98
0.038	1.090	0.314	2.07	98
0.038	0.610	1.292	5.94	98
0.038	0.704	1.038	5.02	98
0.038	0.883	0.614	3.21	98

Slope = 4.04 (±0.13)
Intercept = 0.75 (±0.11)
$r^2 = 0.999$

1,1,2,2-Tetrafluoro-2-allyloxyeth-1-yl radical 1. The competition kinetic study was carried out by using tris(trimethylsilyl)silane [k_H = (5.2 ± 0.6) × $10^7 M^{-1}s^{-1}$] as a hydrogen-transfer reagent. Ratios of $H(CF_2)_2OCH_2CH{=}CH_2$/3-Methyl-4,4,5,5-tetrafluoro-1-oxacyclopentane were determined by the integration of the $-CF_2H$ and $-CHCF_2-$ (signals at δ -136.85 and -127.14 respectively) in the ^{19}F NMR.

Table 3. Competition data for the reaction of 1,1,2,2-tetrafluoro-2-iodoethyl allyl ether with $(TMS)_3SiH$ at 298 K

[Iodide]	$[(TMS)_3SiH]$	$[-CF_2H]/[CHCF_2]$	Yield(%)
0.029	0.18	0.25	98
0.029	0.24	0.35	97
0.029	0.30	0.42	98
0.029	0.37	0.50	99
0.029	0.43	0.60	96
0.029	0.49	0.69	98

Slope = 1.38 ± 0.04 $r^2 = 0.996$ $k_c = (3.8 \pm 0.4) \times 10^7 s^{-1}$

1,1,2,2-Tetrafluorohept-6-en-1-yl radical 2. In this competition study, $(TMS)_3SiH$ [k_H = (1.8 ± 0.1) × $10^7 M^{-1}s^{-1}$] was used as a hydrogen transfer reagent. Ratios of $H(CF_2)_2(CH_2)_3CH{=}CH_2$/1-Methyl-2,2,3,3-tetrafluorocyclohexane were determined by the integration of the $-CF_2H$ and $-CHCF_2-$ (signals at δ -137.0 and -120.27 respectively) in the ^{19}F NMR.

Table 4. Competition Data for the *exo*-cyclization of 1,1,2,2-Tetrafluorohept-6-en-1-yl radical at 298K

[Iodide]	$(TMS)_3SiH$	$[-CF_2H]/[CHCF_2]$	Yield(%)
0.016	0.12	0.05	96
0.016	0.15	0.09	97
0.016	0.18	0.13	96
0.016	0.21	0.16	97
0.016	0.24	0.20	95
0.016	0.27	0.24	96

Slope = 1.25 ± 0.02 $r^2 = 0.999$ $k_{exo} = (1.44 \pm 0.09) \times 10^7 s^{-1}$

Ratios of $H(CF_2)_2(CH_2)_3CH{=}CH_2$/1,1,2,2-tetrafluorocycloheptane were determined by the integration of the $-CF_2H$ and $-CH_2CF_2-$ (signals at δ -137.0 and -110.80 respectively) in the ^{19}F NMR.

Table 5. Competition Data for the *endo*-cyclization of 1,1,2,2-Tetrafluorohept-6-en-1-yl radical at 298K

[Iodide]	$(TMS)_3SiH$	$[-CF_2H]/[CHCF_2]$	Yield(%)
0.016	0.12	0.21	96
0.016	0.15	0.72	97
0.016	0.18	1.48	96
0.016	0.21	2.15	97
0.016	0.24	2.73	95
0.016	0.27	3.43	96

Slope = 21.7 ± 0.5 $r^2 = 0.998$ $k_{endo} = (8.3 \pm 0.5) \times 10^5 s^{-1}$

1,1,2,2,3,3,4,4-Octafluorohept-6-en-1-yl radical 3. The competition kinetic study was done by using tris(trimethylsilyl)silane [$k_H = (5.1 \pm 0.5.) \times 10^7 M^{-1}s^{-1}$] as a hydrogen transfer reagent. Ratios of $HCF_2(CF_2)_3CH_2CH{=}CH_2$/1-Methyl-2,2,3,3,4,4,5,5-octafluorocyclohexane were determined by the integration of the $-CF_2H$ and $-CHCF_2-$ (signals at δ -137.47 and -143.86 respectively) in the ^{19}F NMR.

Table 6. Competition Data for the reaction of 4,4,5,5,6,6,7,7-octafluoro-7-iodo-1-heptene with $(TMS)_3SiH$ at 298K

[Iodide]	$[(TMS)_3SiH]$	$[-CF_2H]/[CHCF_2]$	Yield(%)
0.022	0.18	0.45	97
0.022	0.24	0.61	98
0.022	0.30	0.76	98
0.022	0.37	0.92	98
0.022	0.43	1.09	97
0.022	0.49	1.25	99

Slope = 2.56 ± 0.08 $r^2 = 0.999$ $k_{endo} = (1.99 \pm 0.2) \times 10^7 s^{-1}$

1,1,2,2,3,3-Hexafluoro-3-allyloxyprop-1-yl radical 4 Procedure for the determination of rate of cyclization using Et_3SiH as reducing reagent. 10 % Bis(tributyltin) was used as a catalyst in this reaction, otherwise the procedure was the same. Et_3SiH was used as a hydrogen transfer reagent [$k_H = (5.0 \pm 0.4) \times 10^5 M^{-1}s^{-1}$]. Ratios of products were determined by the integration of the $-CF_2H$ and $-CHCF_2-$ (signals at δ -138.02 and -145.09 respectively) in the ^{19}F NMR..

Table 7. Competition Data for the reaction of 1,1,2,2,3,3-hexafluoro-3-iodopropyl allyl ether with Et_3SiH in the presence of bistributyltin (10%) at 298 K

[Iodide]	[Et_3SiH]	[3]/[4] × 10^{-2}	Yield (%)
0.025	0.122	4.81	92
0.025	0.146	5.67	90
0.025	0.170	6.96	91
0.025	0.193	7.84	92
0.025	0.217	8.96	91
0.025	0.240	9.46	92

Slope = 0.41 $\pm$0.02 $r^2 = 0.999$ $k_{exo} = (1.21 \pm 0.12) \times 10^6 s^{-1}$

1,1,2,2-Tetrafluoro-4-vinyloxybut-1-yl radical 5. In this competition study, Bu_3SnH [$k_H = (9.2 \pm 0.8) \times 10^7 M^{-1}s^{-1}$] was used as a hydrogen transfer reagent. Ratios of $H(CF_2)_2CH_2CH_2OCH{=}CH_2$/2-methyl-3,3,4,4-tetrafluoro-1-oxacyclohexane were determined by the integration of the $-CF_2H$ and $-CHCF_2-$ (signals at δ -137.63 and -120.46 respectively) in the ^{19}F NMR.

Table 8. Competition Data for the *exo*-cyclization of 1,1,2,2-tetrafluoro-4-(vinyloxyl)but-1-yl radical at 298K

[Iodide]	Bu_3SnH	[$-CF_2H$]/[$CHCF_2$]	Yield(%)
0.016	0.143	1.32	97
0.016	0.180	1.63	96
0.016	0.218	2.08	98
0.016	0.257	2.38	98
0.016	0.297	2.84	98
0.016	0.337	3.19	99

Slope = 9.77 $\pm$0.23 $r^2 = 0.998$ $k_{exo} = (9.4 \pm 0.9) \times 10^6 s^{-1}$

Ratio of $H(CF_2)_2CH_2CH_2OCH{=}CH_2$/4,4,5,5-Tetrafluoro-1-oxacycloheptane were determined by the integration of the $-CF_2H$ and $-CH_2CF_2-$ (signals at δ -137.63 and -111.81 respectively) in the ^{19}F NMR.

Table 9. Competition Data for the *endo* -cyclization of 1,1,2,2-tetrafluoro-4-(vinyloxyl)but-1-yl radical at 298K

[Iodide]	Bu_3SnH	[$-CF_2H$]/[$CHCF_2$]	Yield(%)
0.016	0.143	3.60	97
0.016	0.180	4.51	96
0.016	0.218	5.82	98

0.016	0.257	6.54	98
0.016	0.297	7.75	98
0.016	0.337	8.88	99

Slope = 27.1 $\pm$ 0.8 r^2 = 0.997 k_{endo} = $(3.4 \pm 0.3) \times 10^6 s^{-1}$

1,1,2,2-Tetrafluorooct-7-en-1-yl radical 6. In this competition study, t-$BuMe_2SiD$ [k_H = $(5.5 \pm 1.3) \times 10^4 M^{-1}s^{-1}$] was used as a hydrogen transfer reagent. Ratios of $H(CF_2)_2(CH_2)_4CH{=}CH_2$/1,1,2,2-tetrafluorocyclooctane were determined by the integration of the -CF_2D and -CH_2CF_2- (signals at δ -137.47 and -116.54 respectively) in the ^{19}F NMR.

Table 10. Competition data for the *endo*-cyclization of 1,1,2,2-Tetrafluorooct-7-en-1-yl radical at 298K

[Iodide]	$(TMS)_3SiH$	[-CF_2H]/[$CHCF_2$]	Yield(%)
0.015	0.26	0.77	95
0.015	0.37	1.18	97
0.015	0.49	1.37	97
0.015	0.60	1.69	94
0.015	0.72	2.11	95
0.015	0.81	2.37	96

Slope = 2.84 $\pm$ 0.14 r^2 = 0.991 k_{endo} = $(2.0 \pm 0.5) \times 10^4 s^{-1}$

3-Butenyl 1,1,2,2-tetrafluoropropionate 1-yl radical 7. In this competition study, Et_3SiD [k_H = $(1.2 \pm 0.1) \times 10^5 M^{-1}s^{-1}$] was used as a hydrogen transfer reagent. Ratios of $H(CF_2)_2COO(CH_2)_2CH{=}CH_2$/1,1,2,2-tetrafluoroheptanolactone were determined by the integration of the -CF_2D and -CF_2COO- (signals at δ -140.41 and -122.24 respectively) in the ^{19}F NMR.

Table 11. Competition data for the *endo*-cyclization of 3-Butenyl 1,1,2,2-tetrafluoropropionate 1-yl radical at 298K

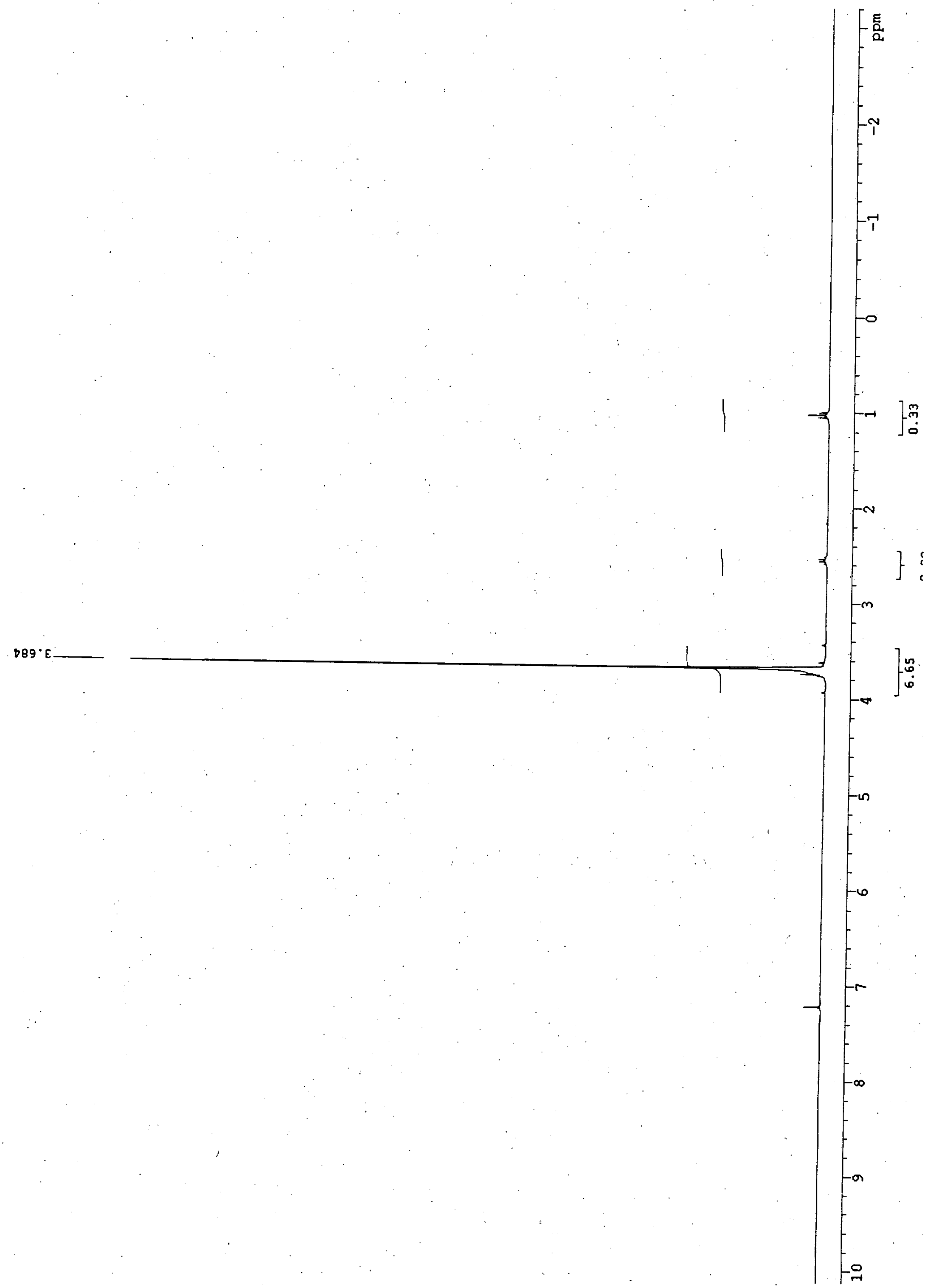
[Iodide]	Et_3SiD	[-CF_2H]/[$CHCF_2$]	Yield(%)
0.01	0.26	0.91	94
0.01	0.39	1.31	92
0.01	0.52	1.86	95
0.01	0.65	2.14	94
0.01	0.78	2.52	96
0.01	0.92	3.14	96

Slope = 3.28 $\pm$ 0.15 r^2 = 0.992 k_{endo} = $(3.6 \pm 0.3) \times 10^4 s^{-1}$

1,1,2,2-Tetrafluoro-6-vinyloxyhex-1-yl radical 14. No cyclization compound was observed even using the slow proton transfer reagent: t-$BuMe_2SiH$. $H(CF_2)_2(CH_2)_4OCH{=}CH_2$ was the only product based on ^{19}F NMR. So the *exo* and *endo*-cyclization rate was estimated to be less than 1.3×10^3 s^{-1}

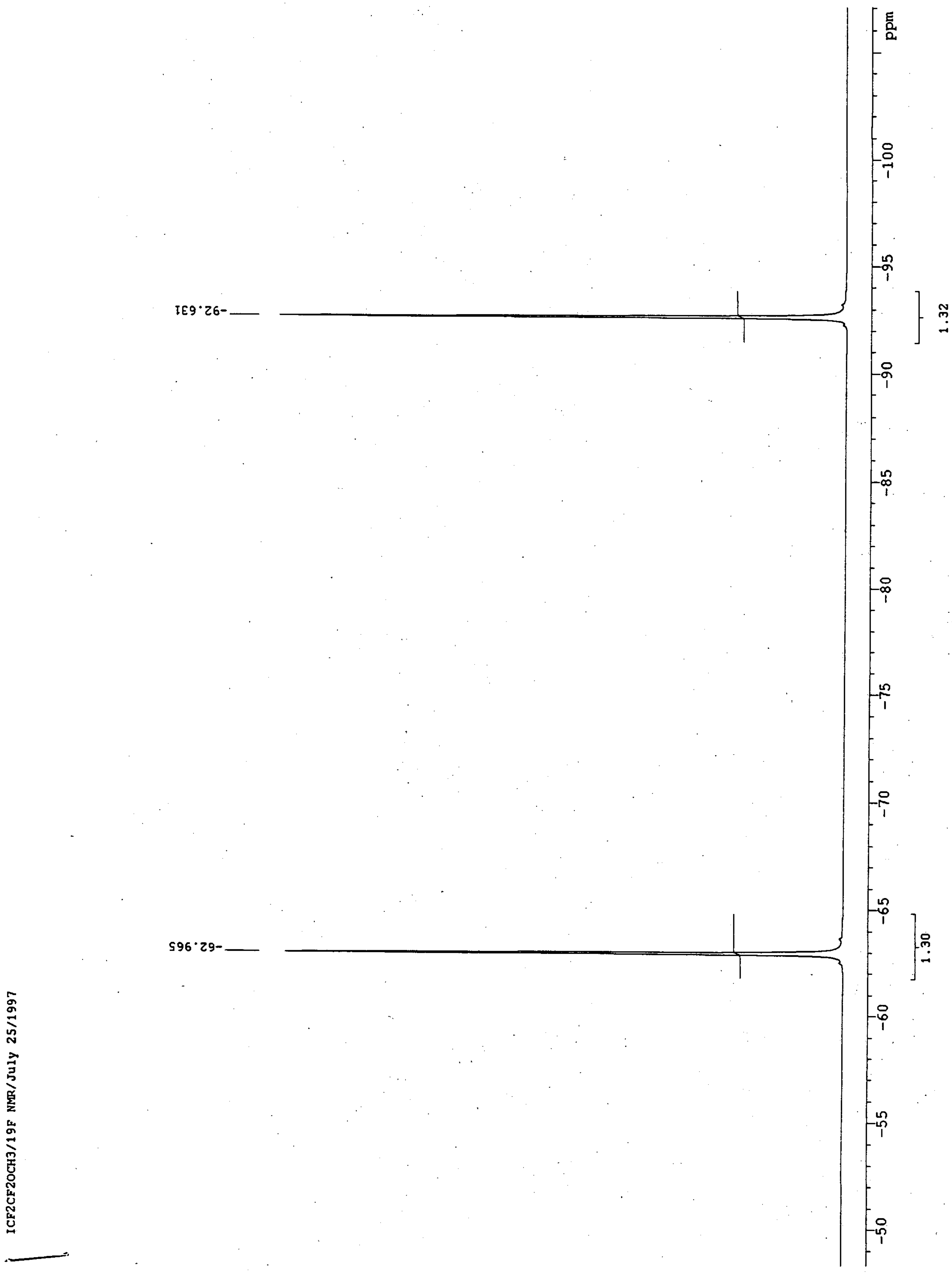
1,1,2,2-Tetrafluoro-4-cyclopropane-but-1-yl radical 15. The radical did not proceed intramolecular attack to cyclopropane. We only observe the reduction product by using t-BuMea$_2$SiH as the reducing reagent. So the cyclization rate was estimated to be less than $1.1\times 10^3 s^{-1}$

 S-7



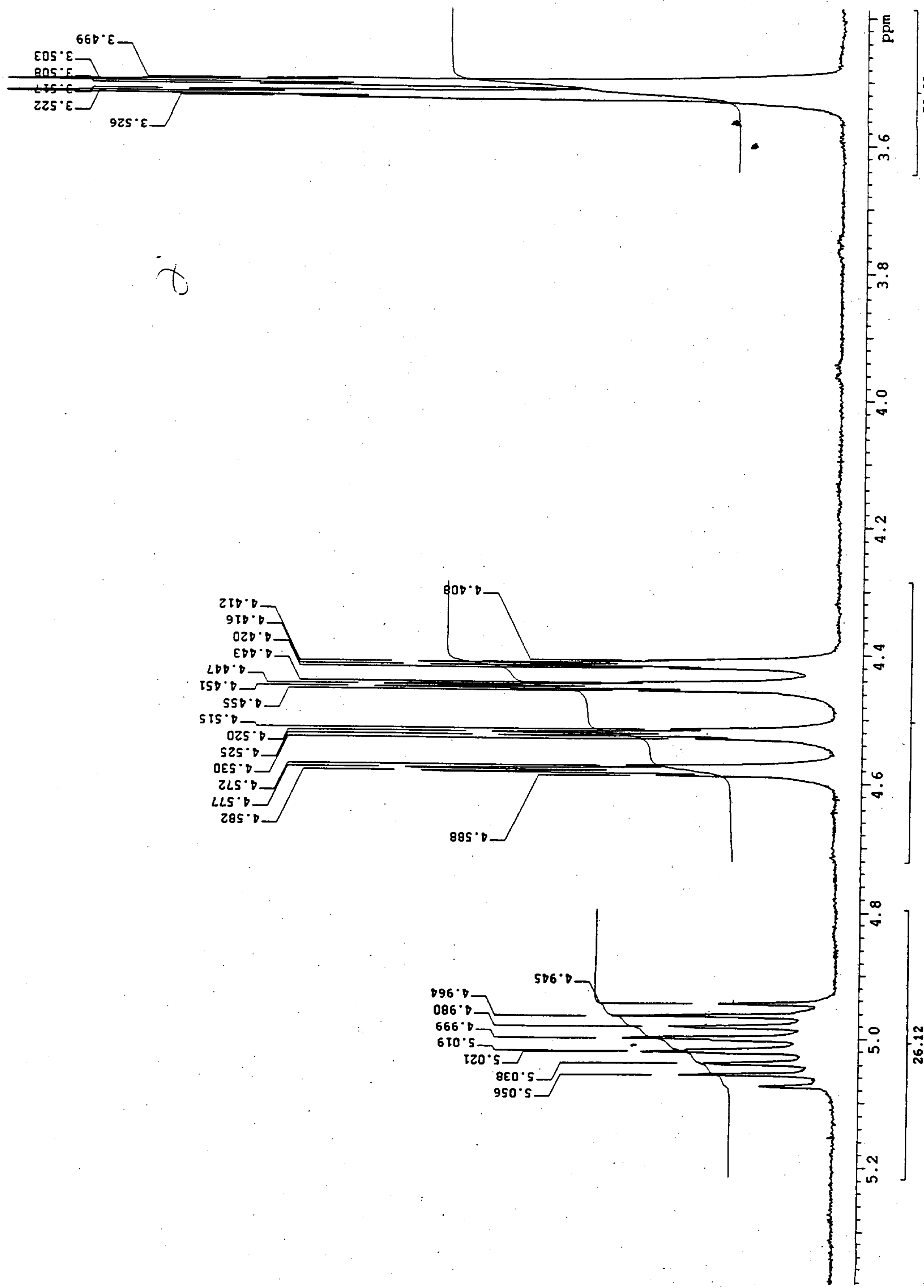
^{1}H NMR: 1.1.2.2-Tetrafluoro-2-iodoethyl methyl ether

 S-8



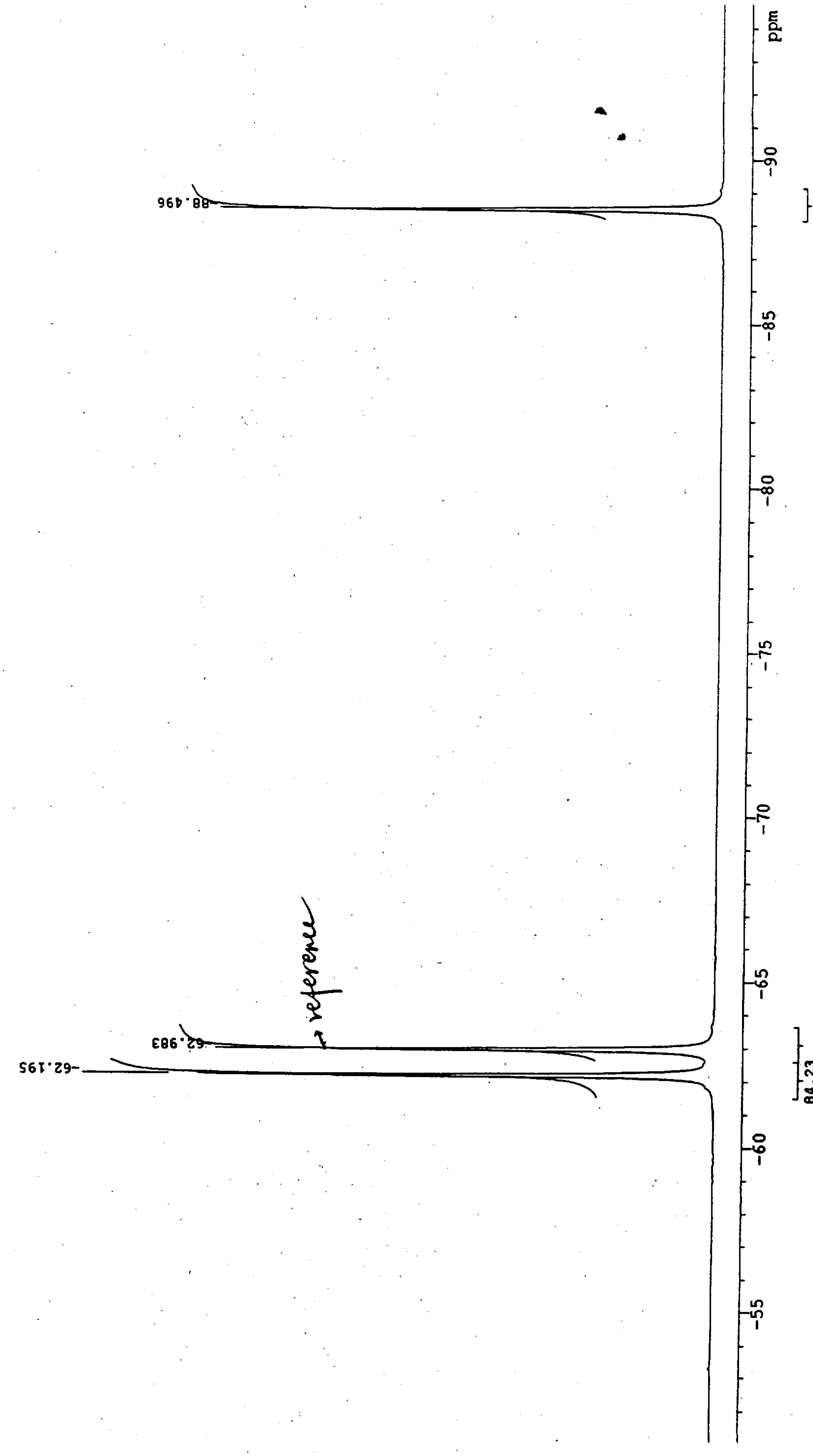
^{19}F NMR: 1.1.2.2-Tetrafluoro-2-iodoethyl methyl ether

5-9

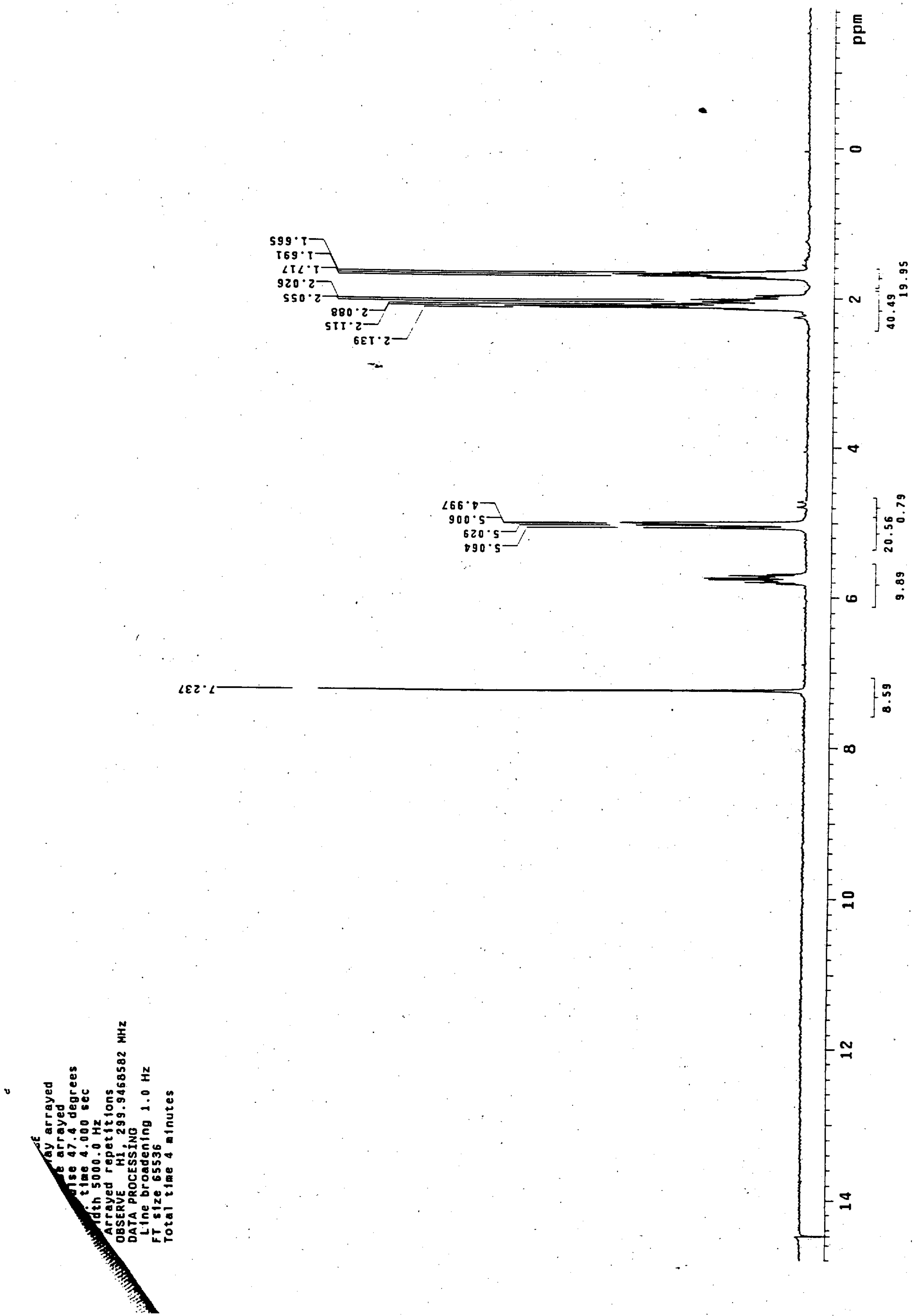


^{1}H NMR: 1,1,2,2-Tetrafluoro-2-iodoethyl allyl ether (Precursor to radical 1)

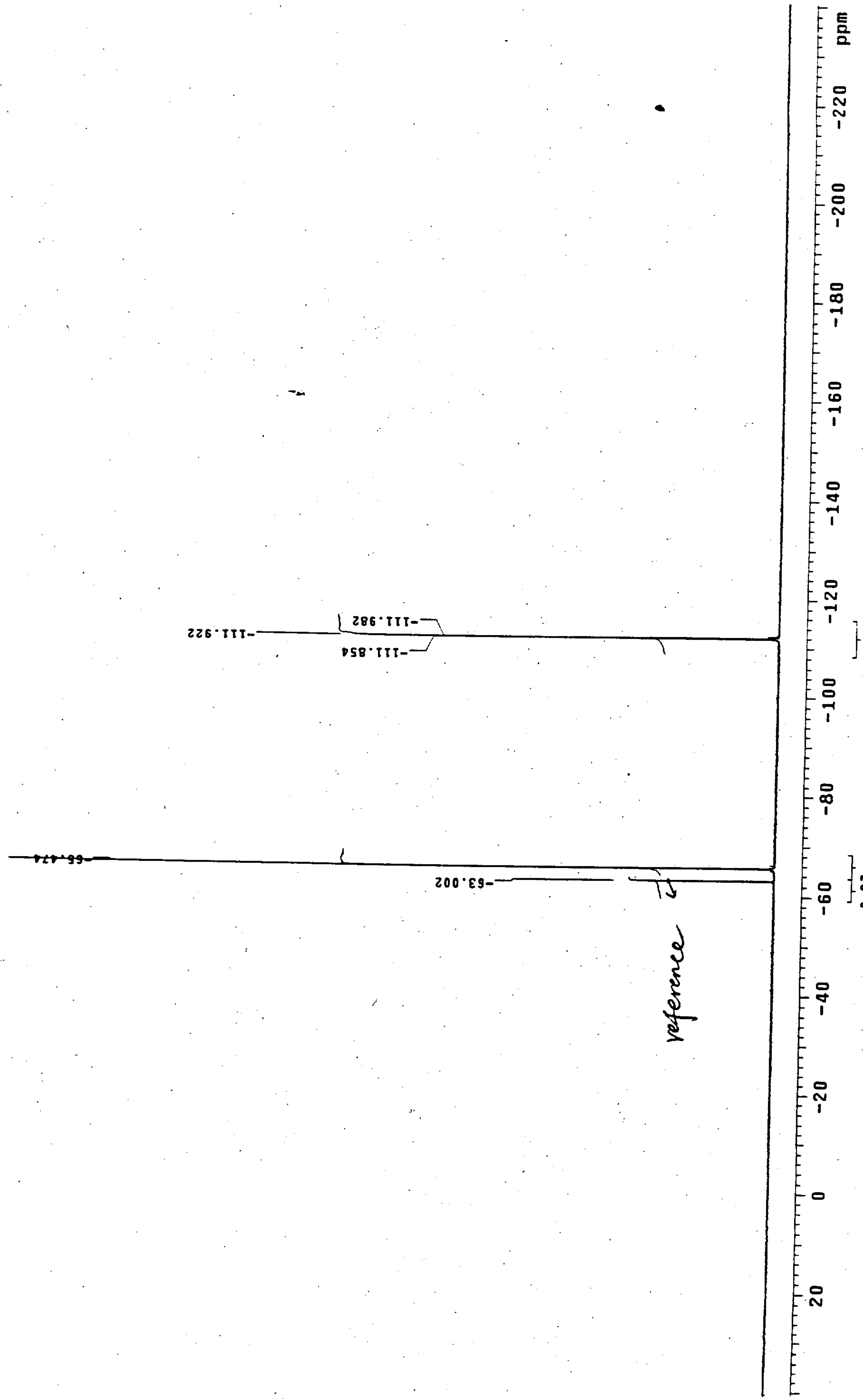
S - 10



^{19}F NMR: 1,1,2,2-Tetrafluoro-2-iodoethyl allyl ether (Precursor to radical 1)

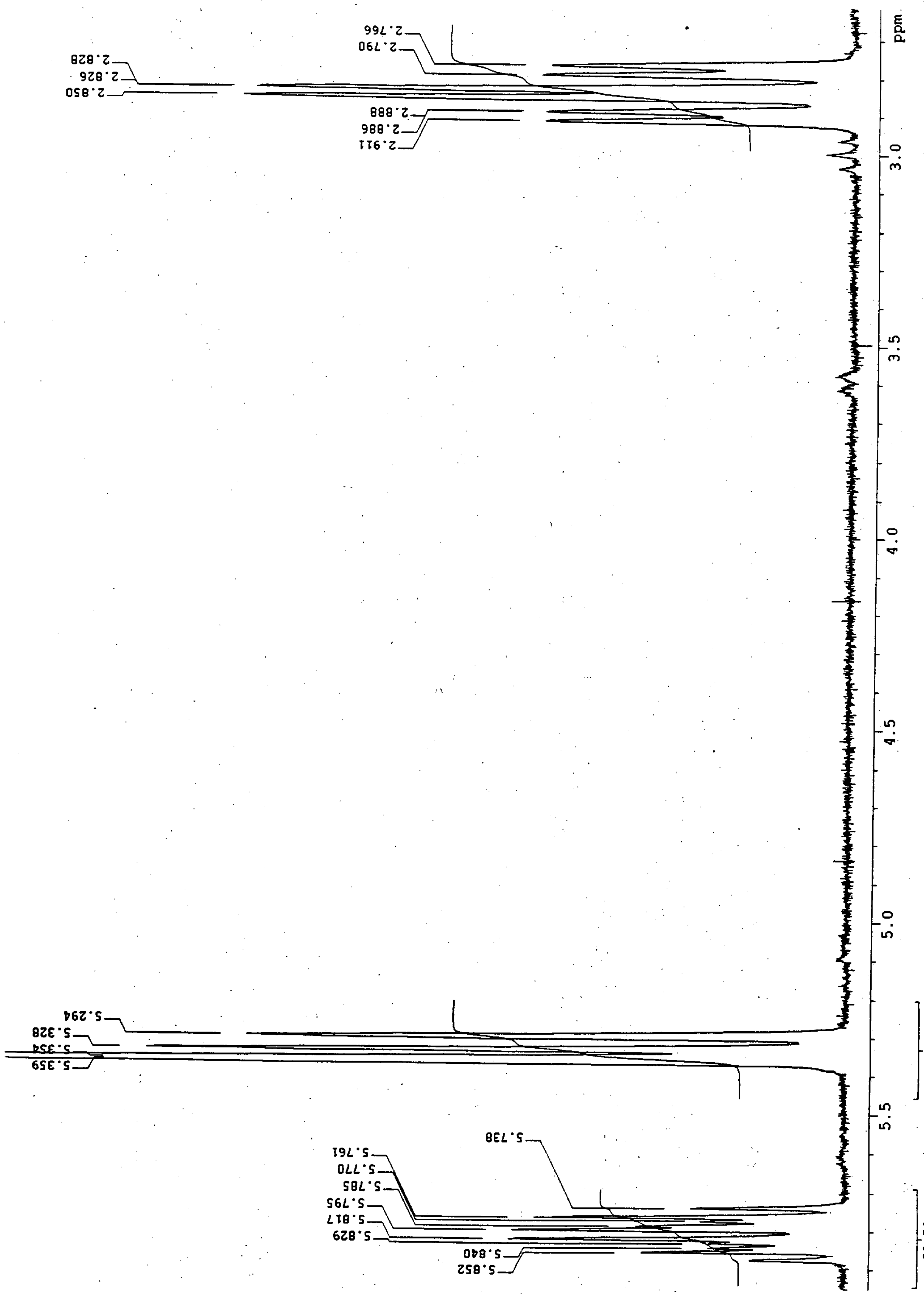


^{1}H NMR: 6,6,7,7-Tetrafluoro-7-bromoheptene (Precursor to radical 2)



^{19}F NMR: 6,6,7,7-Tetrafluoro-7-bromoheptene (Precursor to radical 2)

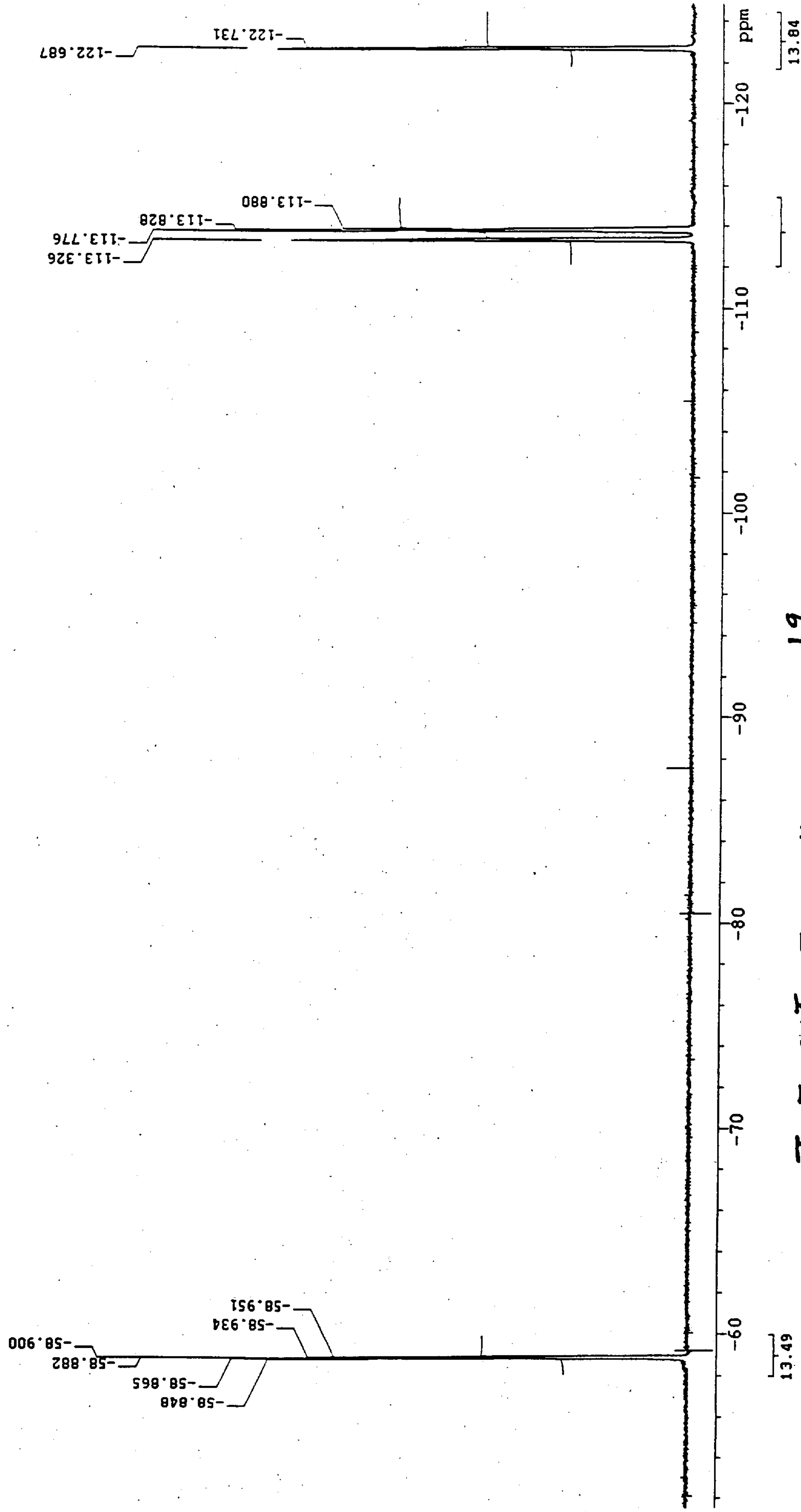
S-13



^{1}HNMR: $ICF_2CF_2CF_2CF_2CH_2CH=CH_2$

^{1}H NMR: 4,4,5,5,6,6,7,7-Octafluoro-7-iodo-1-heptene (Precursor to radical 3)

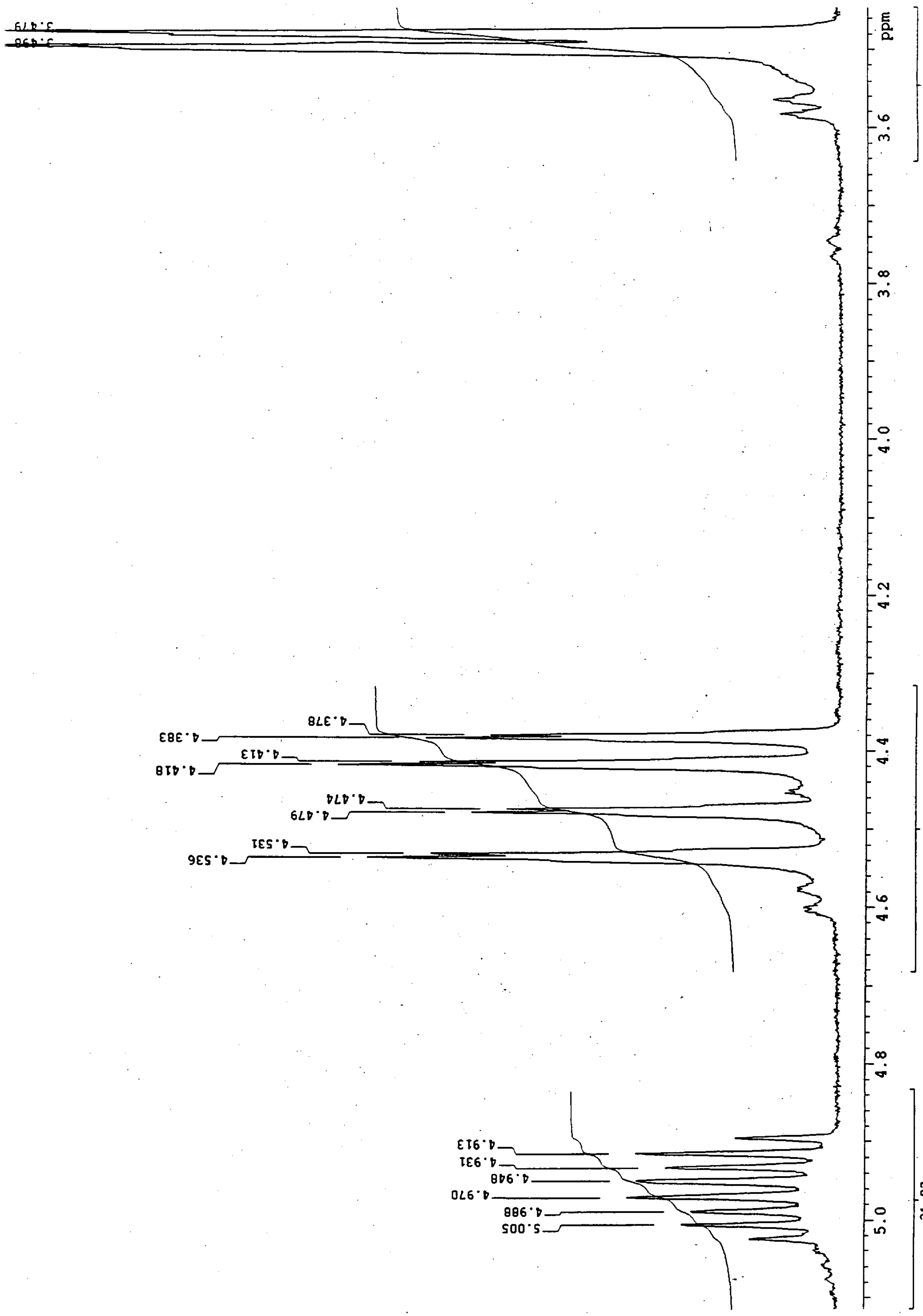
S-14



$ICF_2CF_2CF_2CF_2CH_2CH=CH_2$ ^{19}F

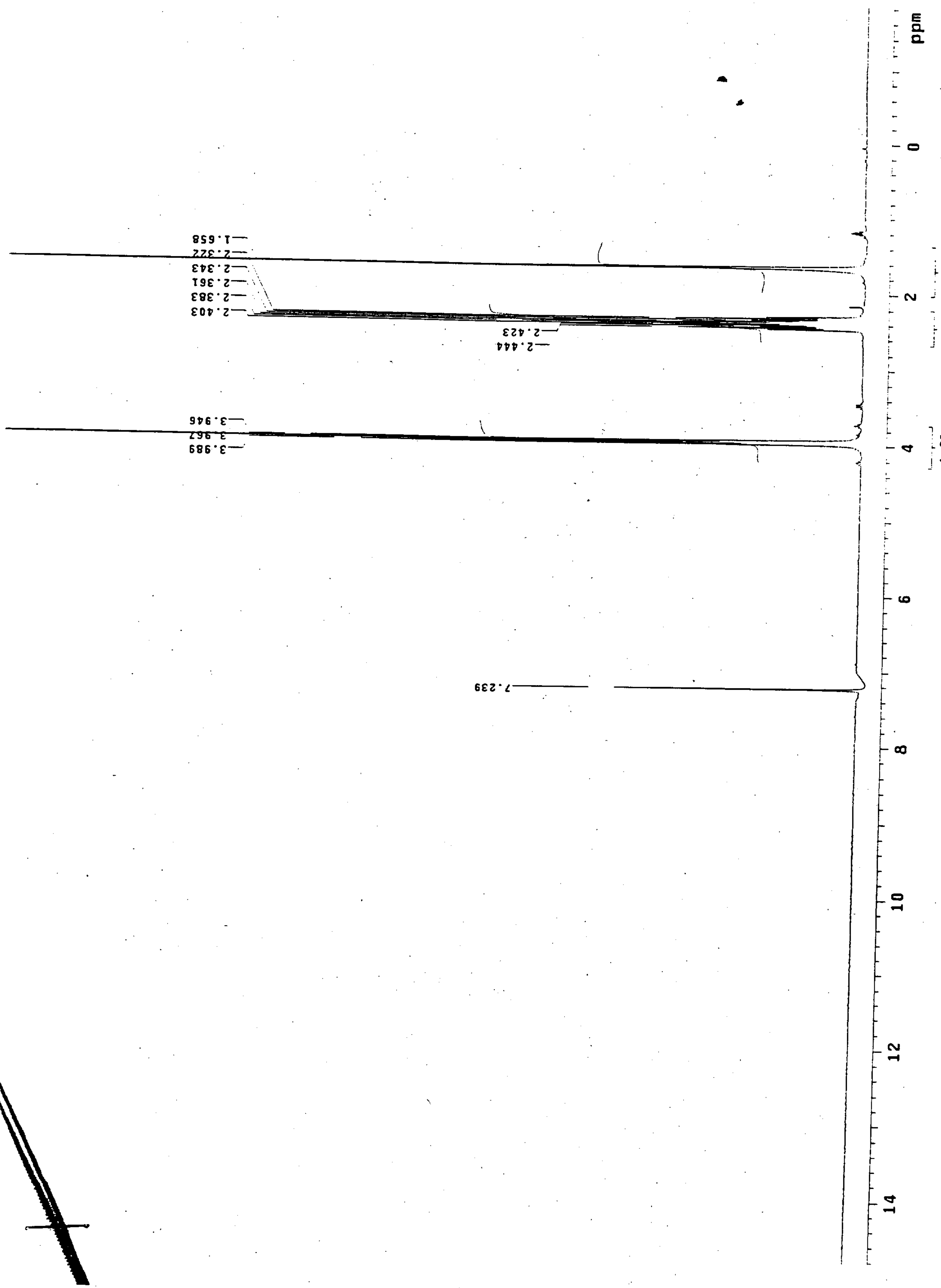
^{19}F NMR: 4,4,5,5,6,6,7,7-Octafluoro-7-iodo-1-heptene (Precursor to radical 3)

S – 15



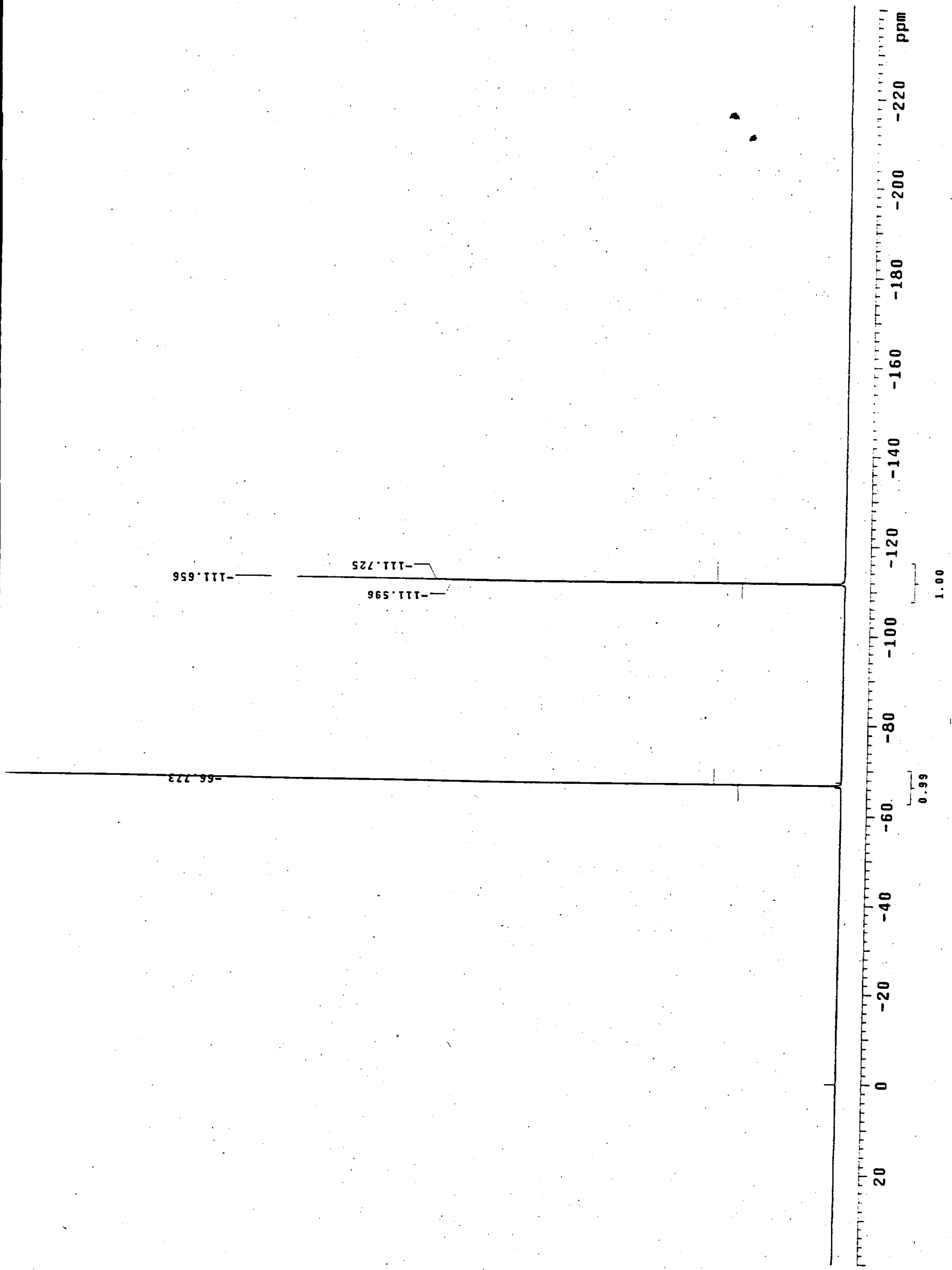
^{1}H NMR: 1,1,2,2,3,3-Hexafluoro-3-iodopropyl allyl ether (Precursor to radical 4)

S-16



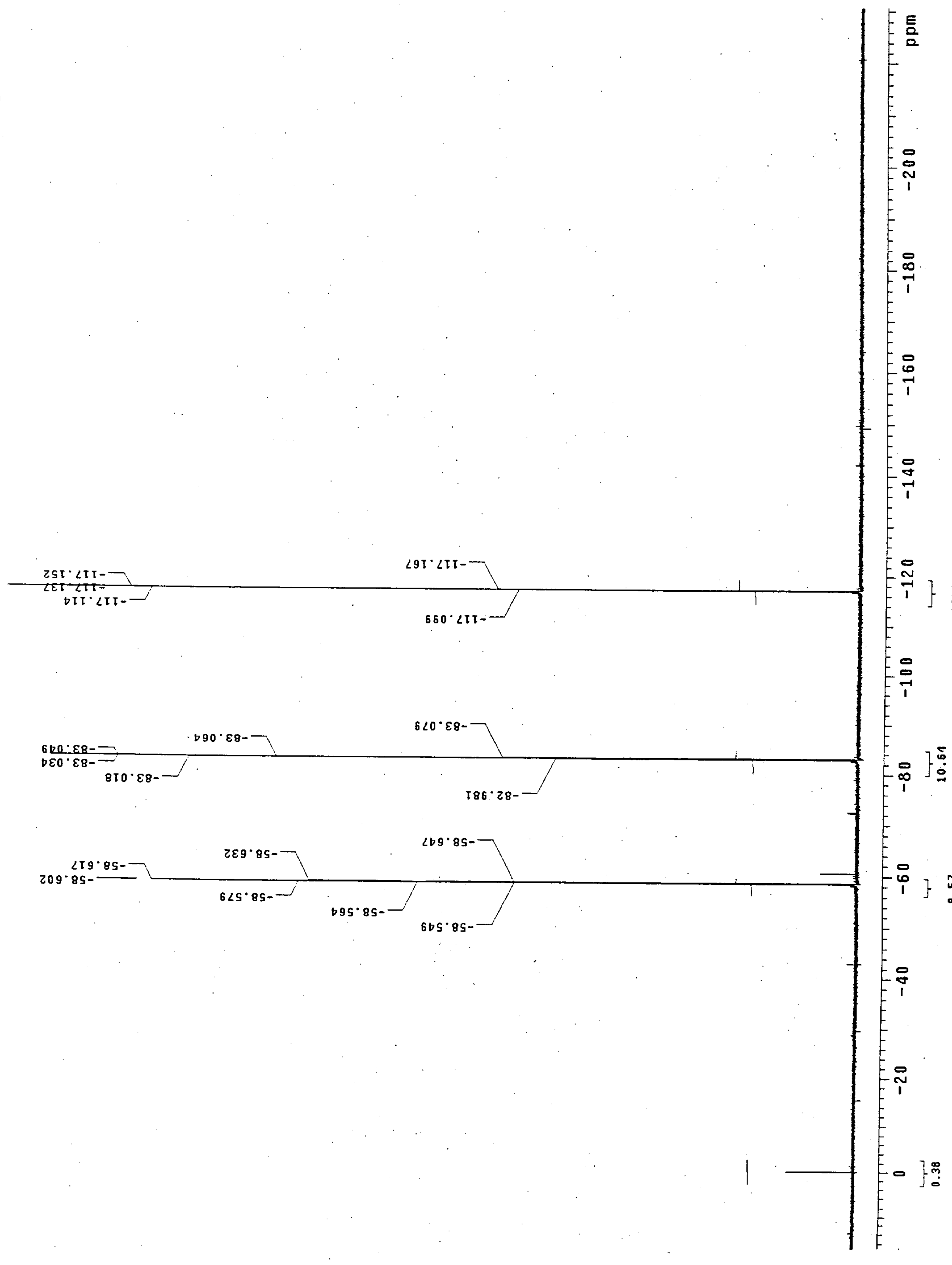
^1H NMR: 3,3,4,4-Tetrafluoro-4-bromobutanol

S-17



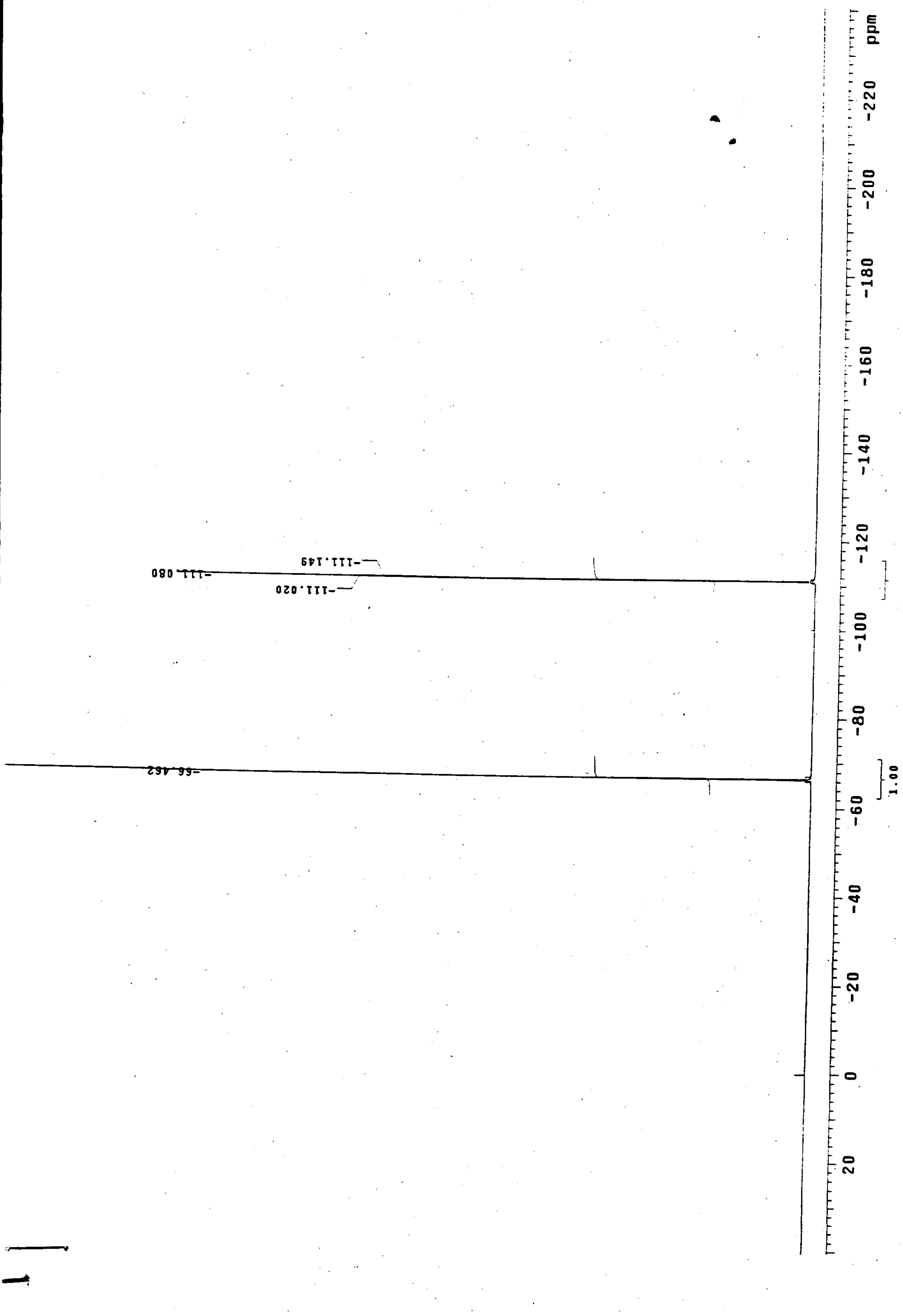
^{19}F NMR: 3,3,4,4-Tetrafluoro-4-bromobutanol

S-18



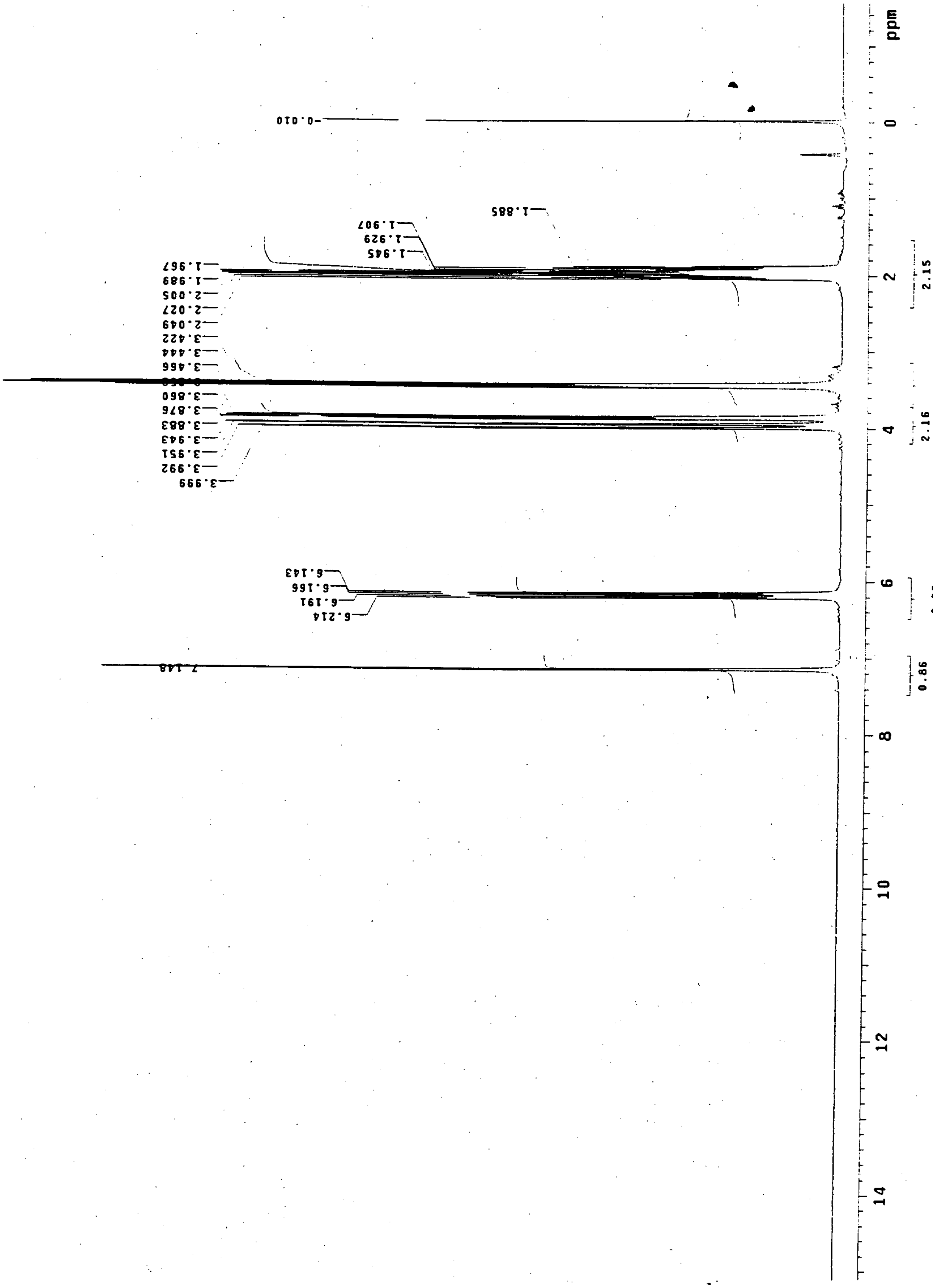
^{19}F NMR: 1,1,2,2,3,3-Hexafluoro-3-iodopropyl allyl ether (Precursor to radical 4)

S-19

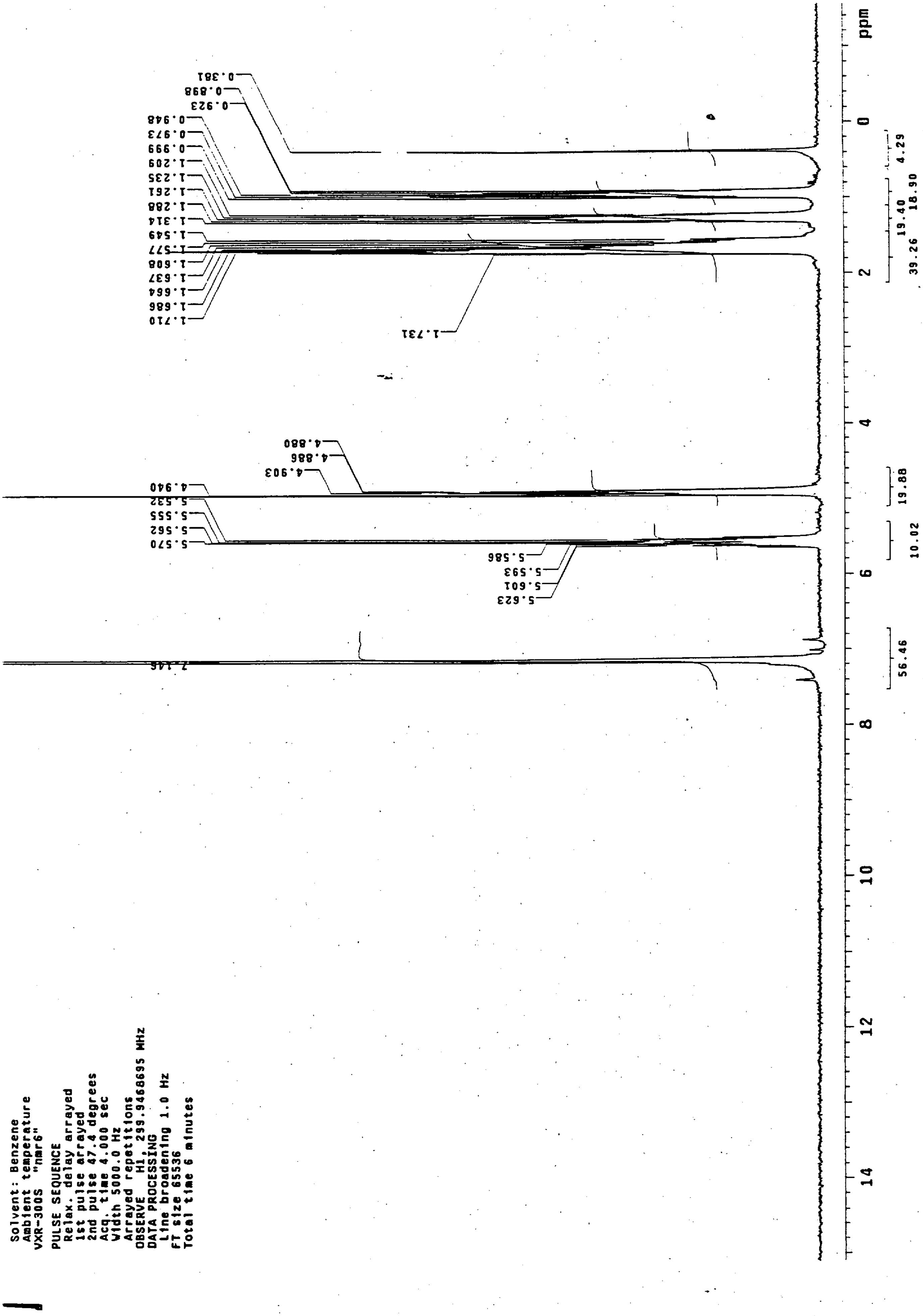


^{1}H NMR: 3,3,4,4-Tetrafluoro-4-bromobutyl vinyl ether (Precursor to radical 5)

 S-20



^{19}F NMR: 3,3,4,4-Tetrafluoro-4-bromobutyl vinyl ether (Precursor to radical 5)



^{1}H NMR: 7,7,8,8-Tetrafluoro-8-bromooctene (Precursor to radical 6)

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Ambient temperature
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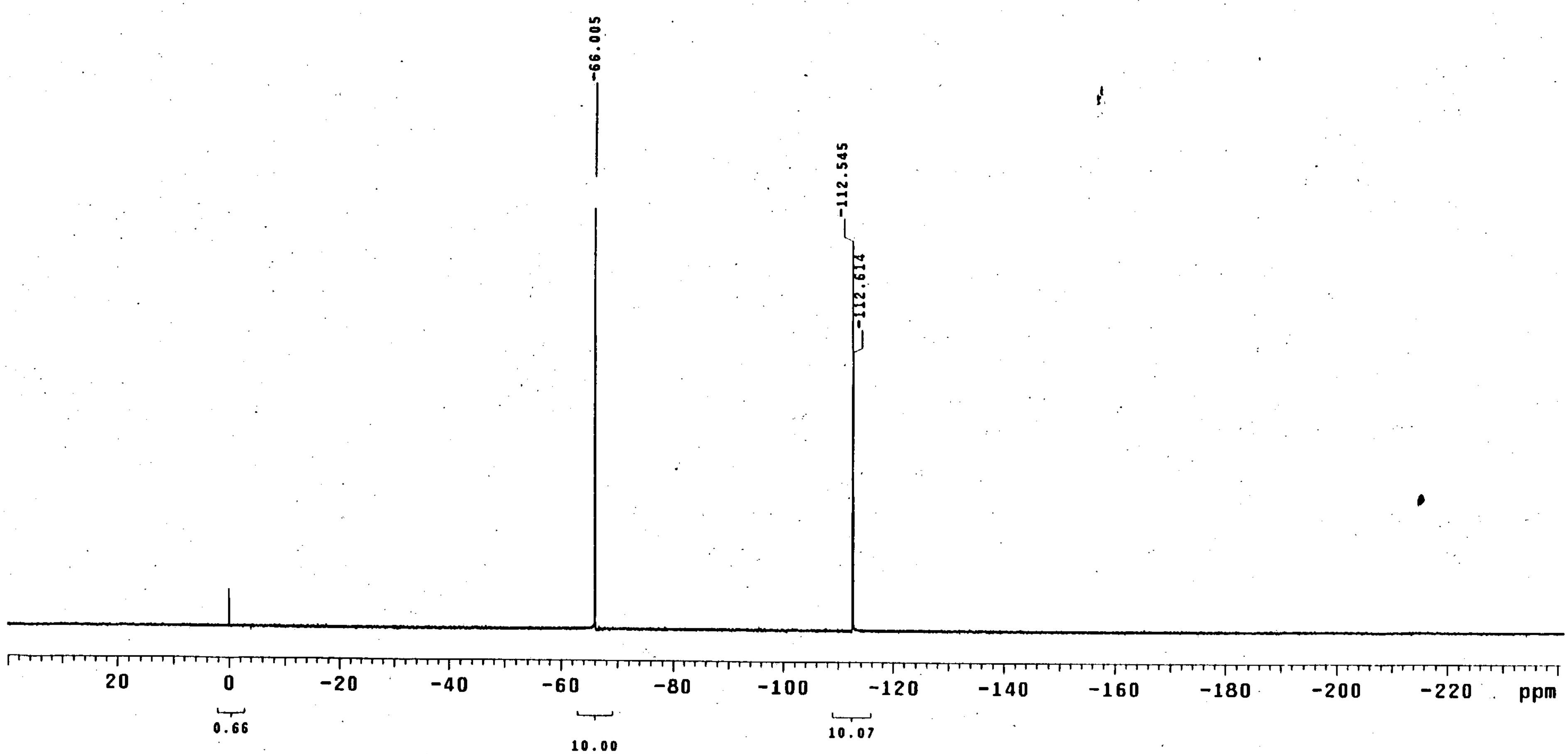
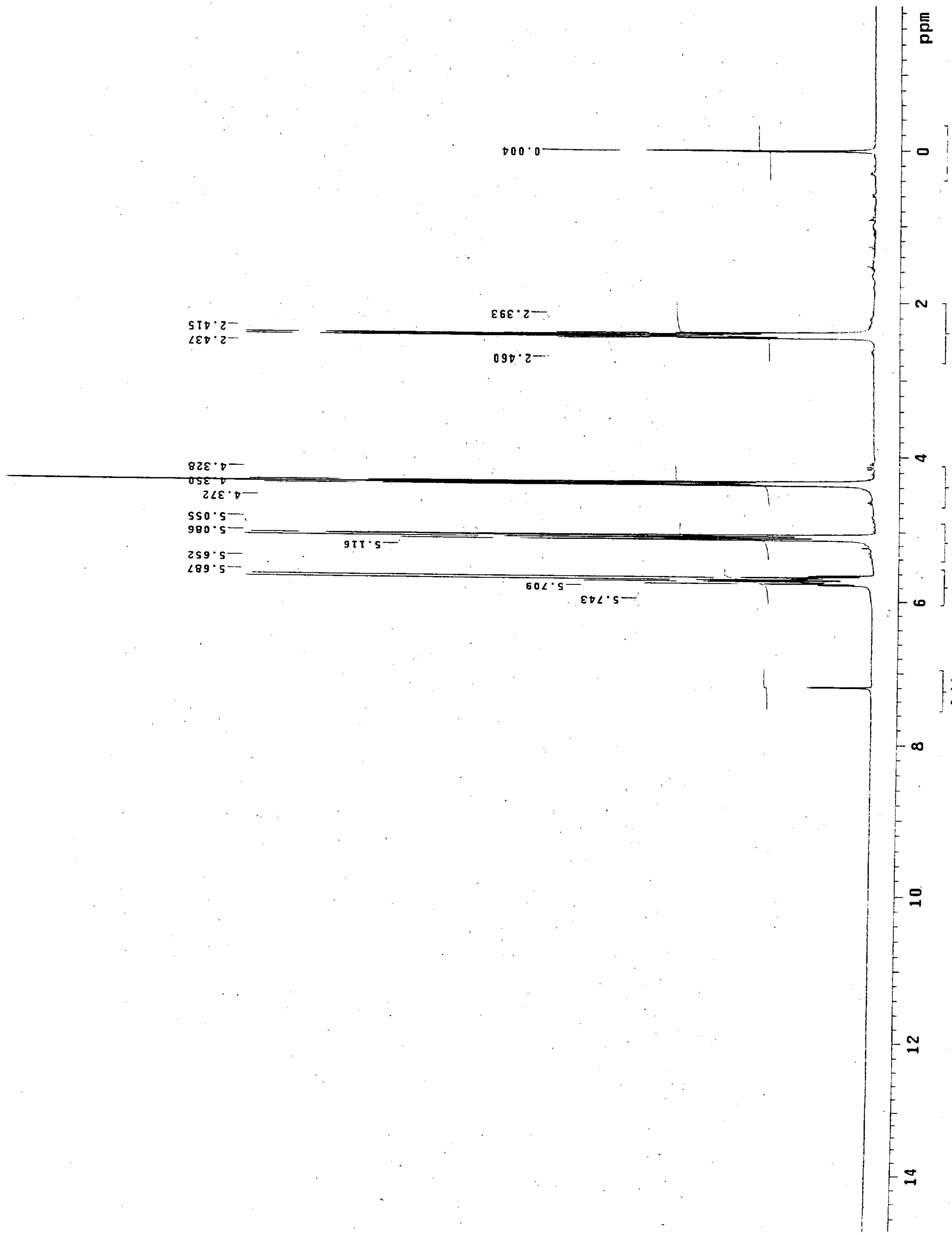
1st pulse arrayed
2nd pulse 51.4 degrees
Acq. time 0.300 sec
Width 79365.1 Hz
Arrayed repetitions
OBSERVE F19, 282.2321644 MHz
DATA PROCESSING
Line broadening 2.0 Hz
FT size 65536
Total time 2 minutes



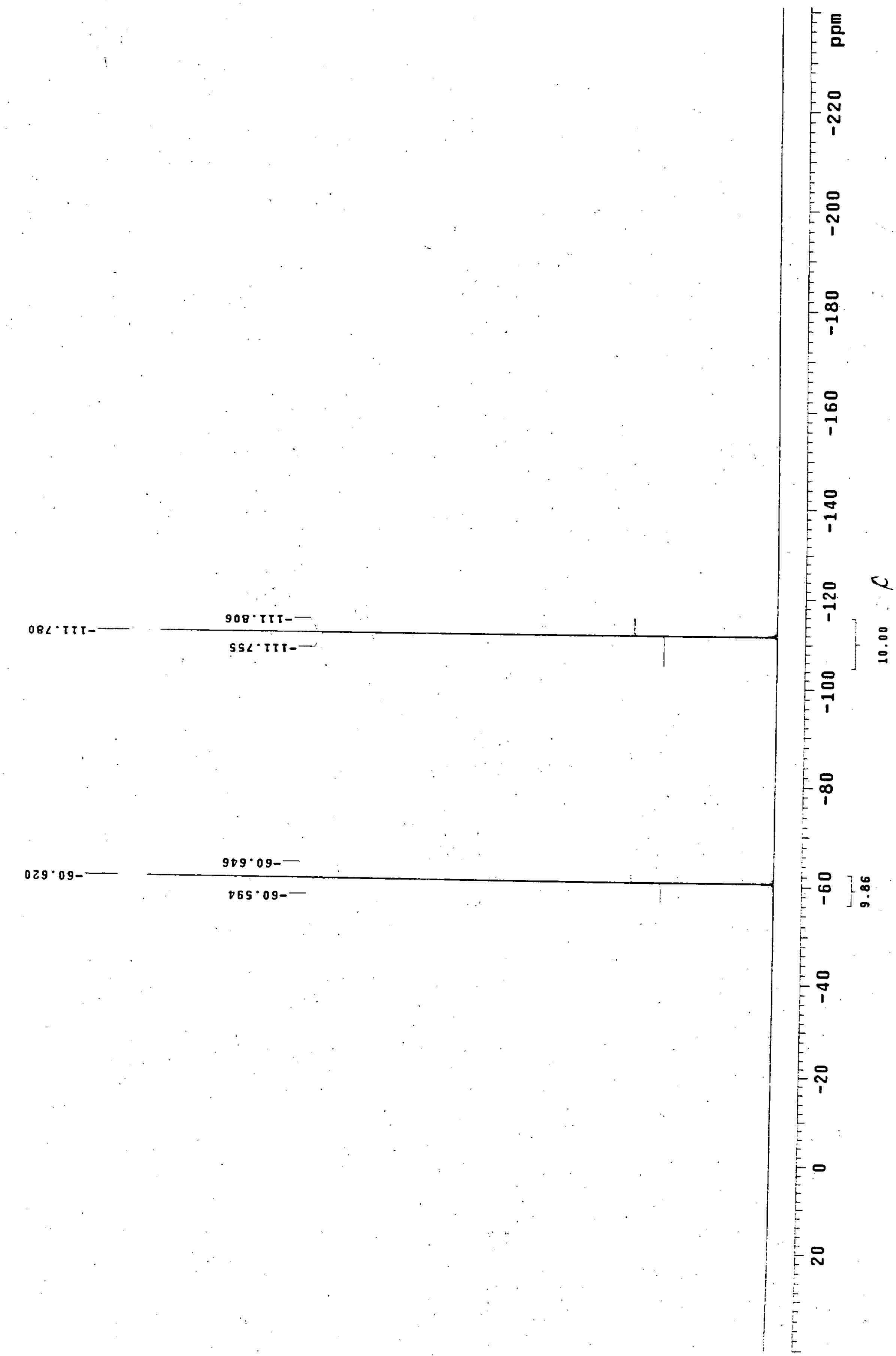
^{19}F NMR: 7,7,8,8-Tetrafluoro-8-bromooctene (Precursor to radical 6)

S-23



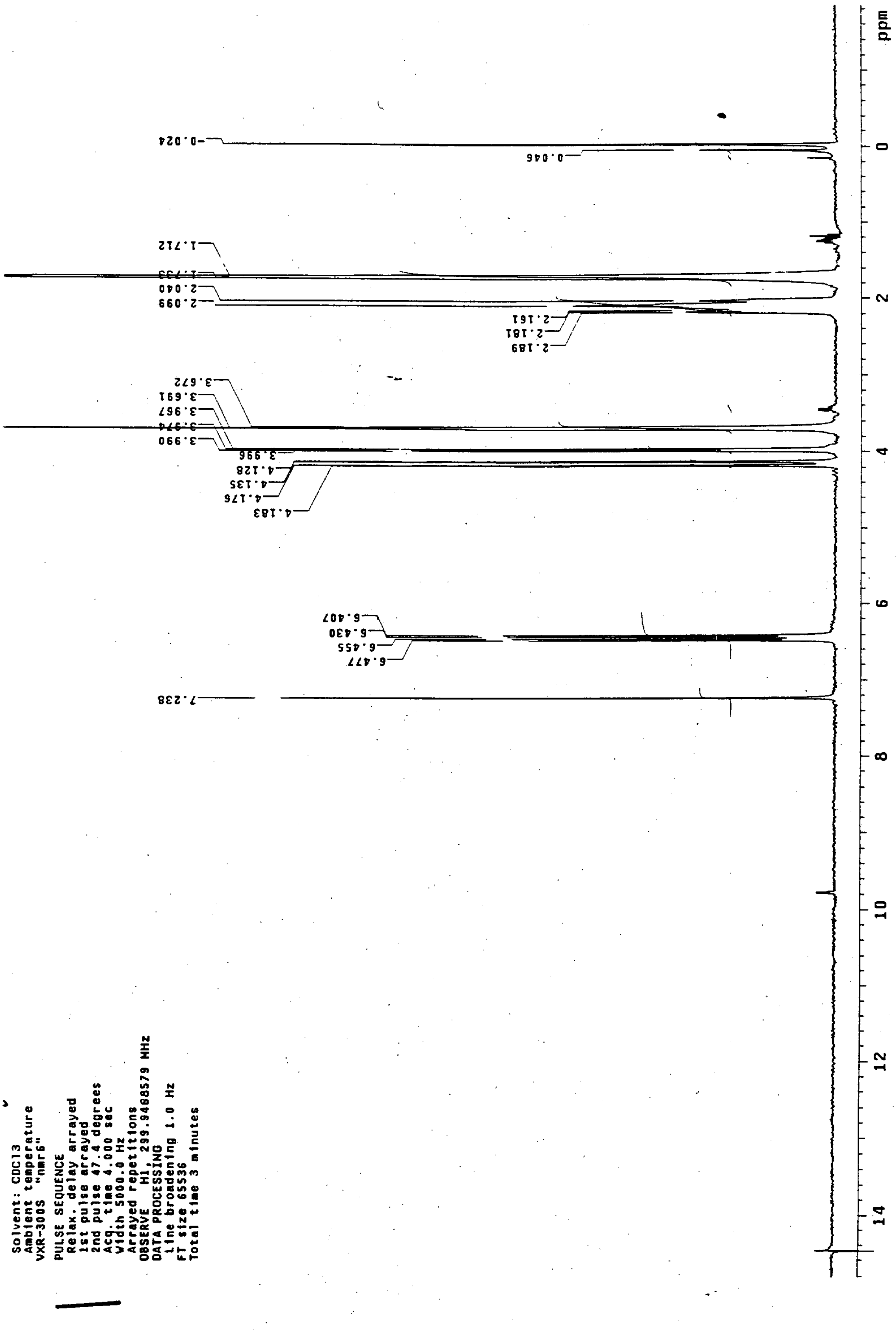
^{1}H NMR: 3-Butenyl 3-iodo-2,2,3,3-tetrafluoropropionate (Precursor to radical 7)

s-24



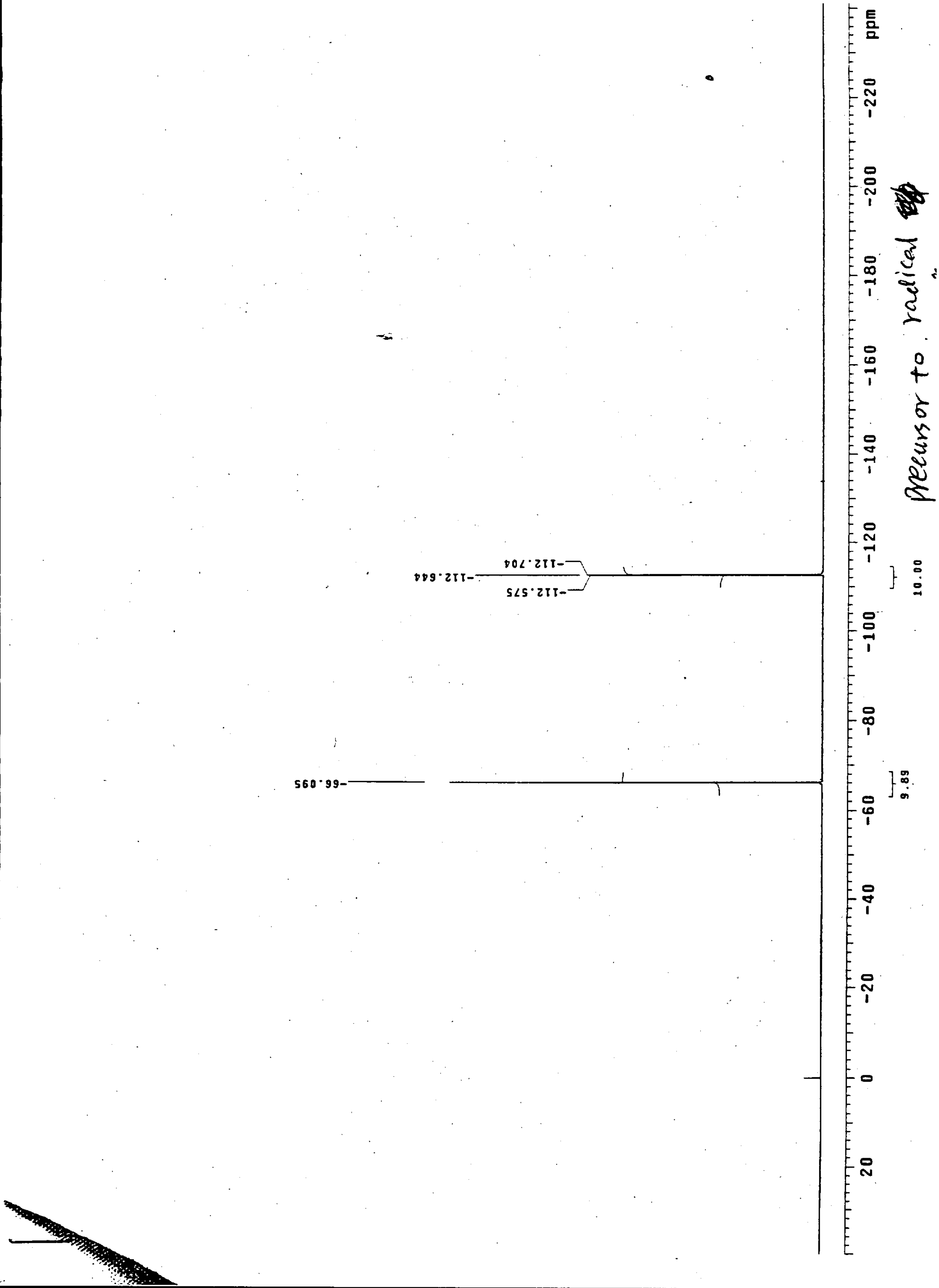
^{19}F NMR: 3-Butenyl 3-iodo-2,2,3,3-tetrafluoropropionate (Precursor to radical 7)

S-25



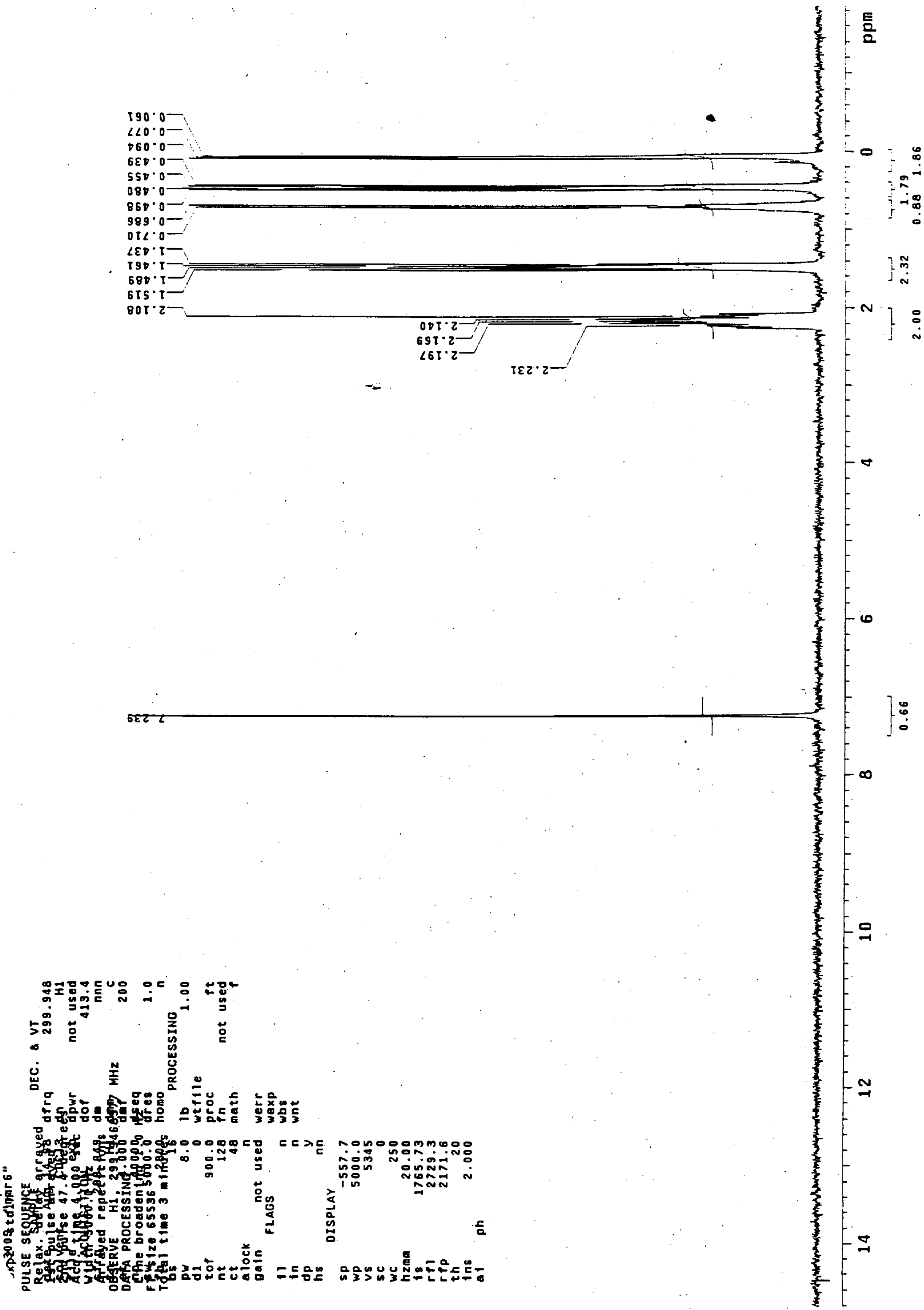
^{1}H NMR: 5,5,6,6-Tetrafluoro-6-bromohexyl vinyl ether (Precursor to radical 8)

S-26



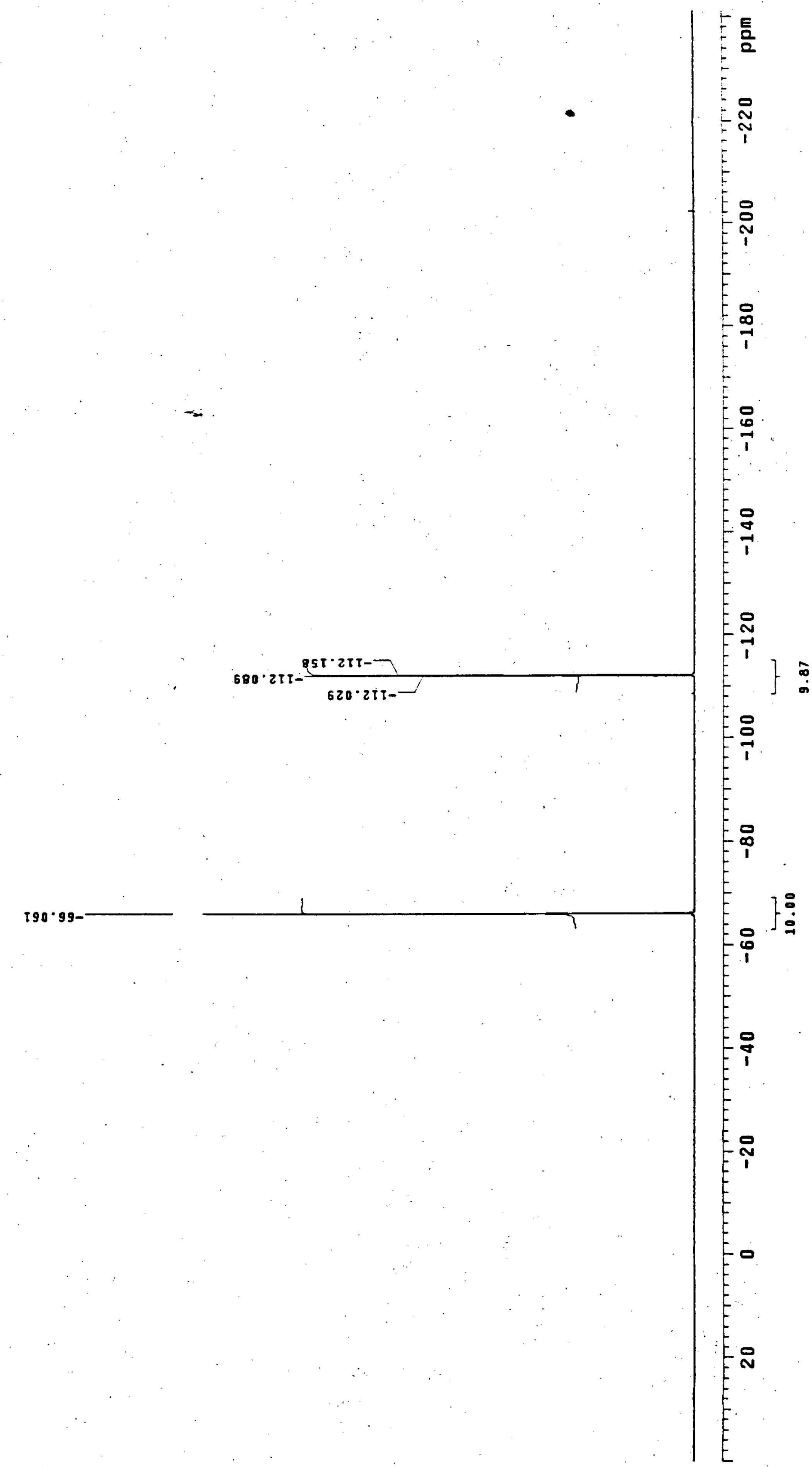
^{19}F NMR: 5,5,6,6-Tetrafluoro-6-bromohexyl vinyl ether (Precursor to radical 8)

S-27

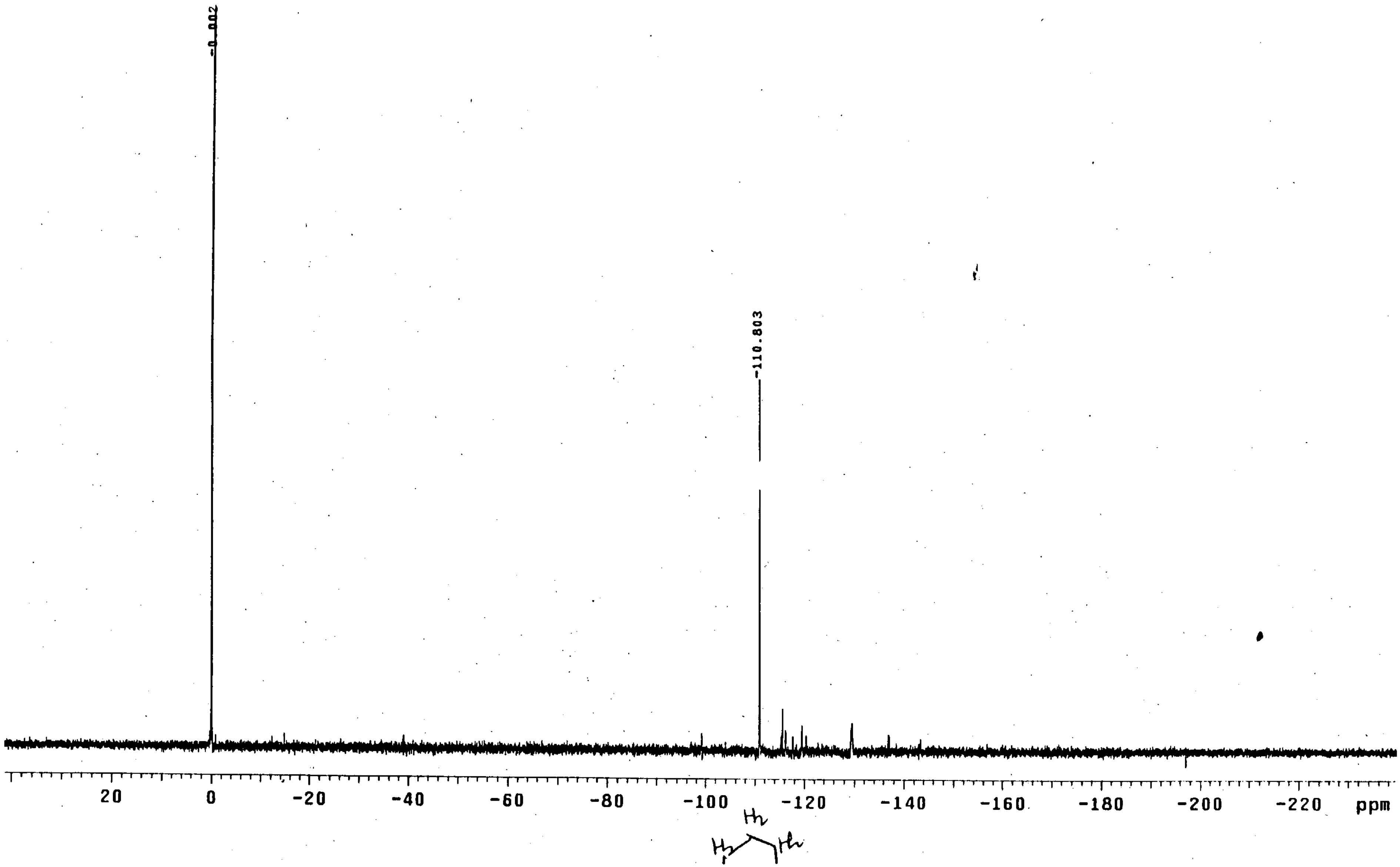


^{1}H NMR: 3,3,4,4-Tetrafluoro-4-bromobutylcyclopropane (Precursor to radical 15)

 S-28



^{19}F NMR: 3,3,4,4-Tetrafluoro-4-bromobutylcyclopropane (Precursor to radical 15)



^{19}F NMR: 1,1,2,2-Tetrafluorocycloheptane (13)

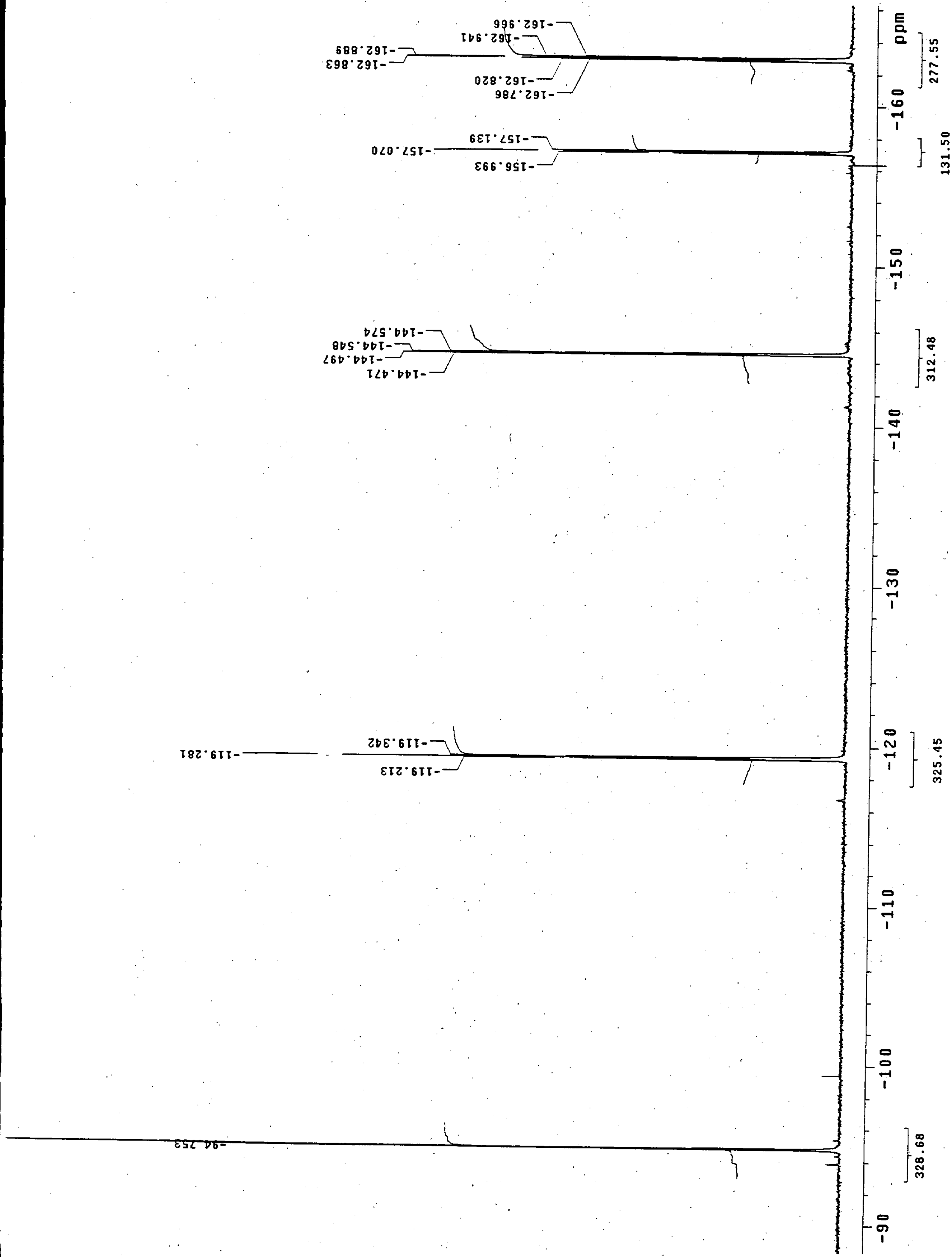
S-40

0.26

0.26

^{1}H NMR: 1,1,2,2-Tetrafluoro-4-(2,3,4,5,6-pentafluorophenyl)butyl methyl ether

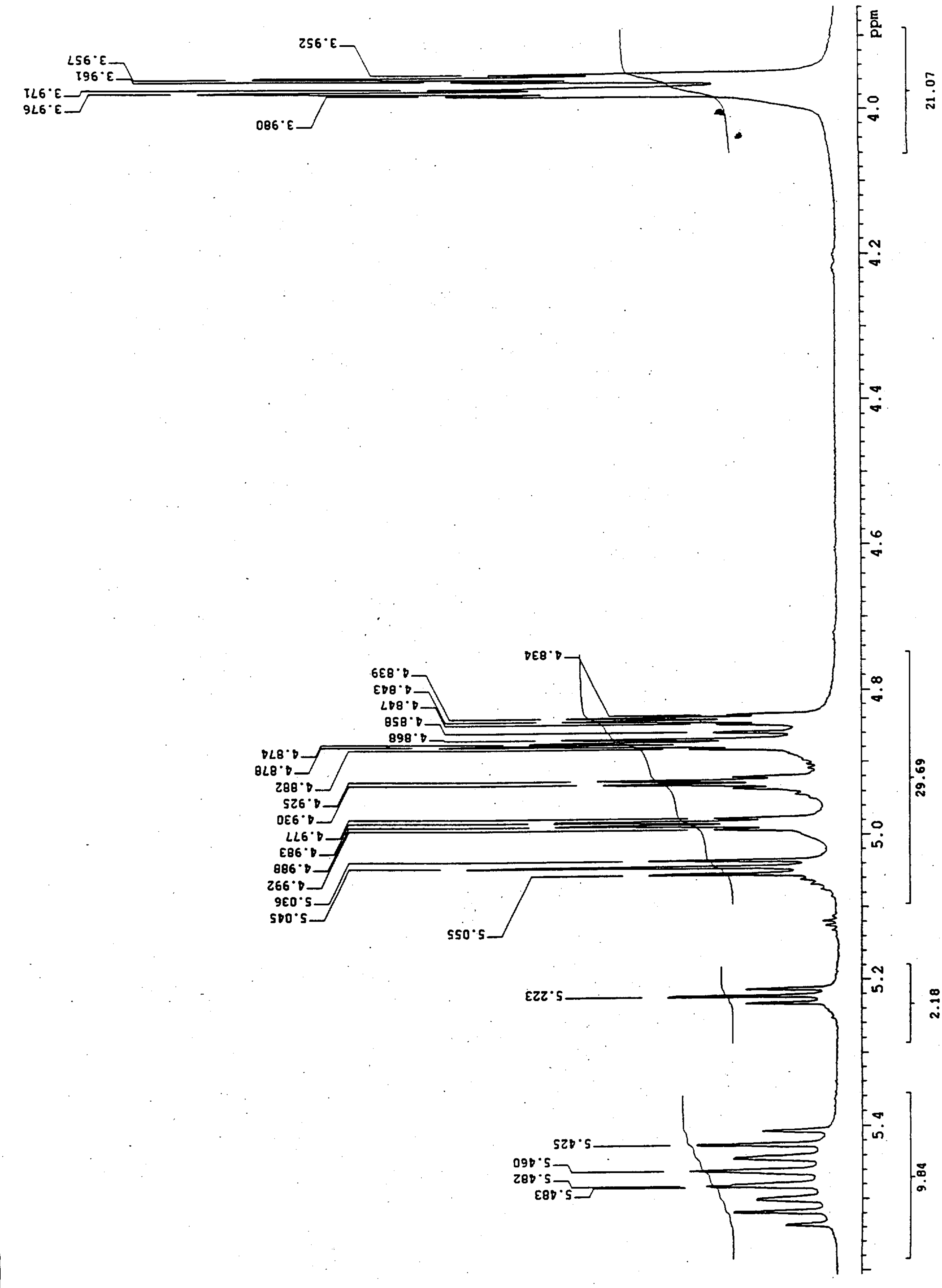
S-29



^{19}F NMR: 1,1,2,2-Tetrafluoro-4-(2,3,4,5,6-pentafluorophenyl)butyl methyl ether

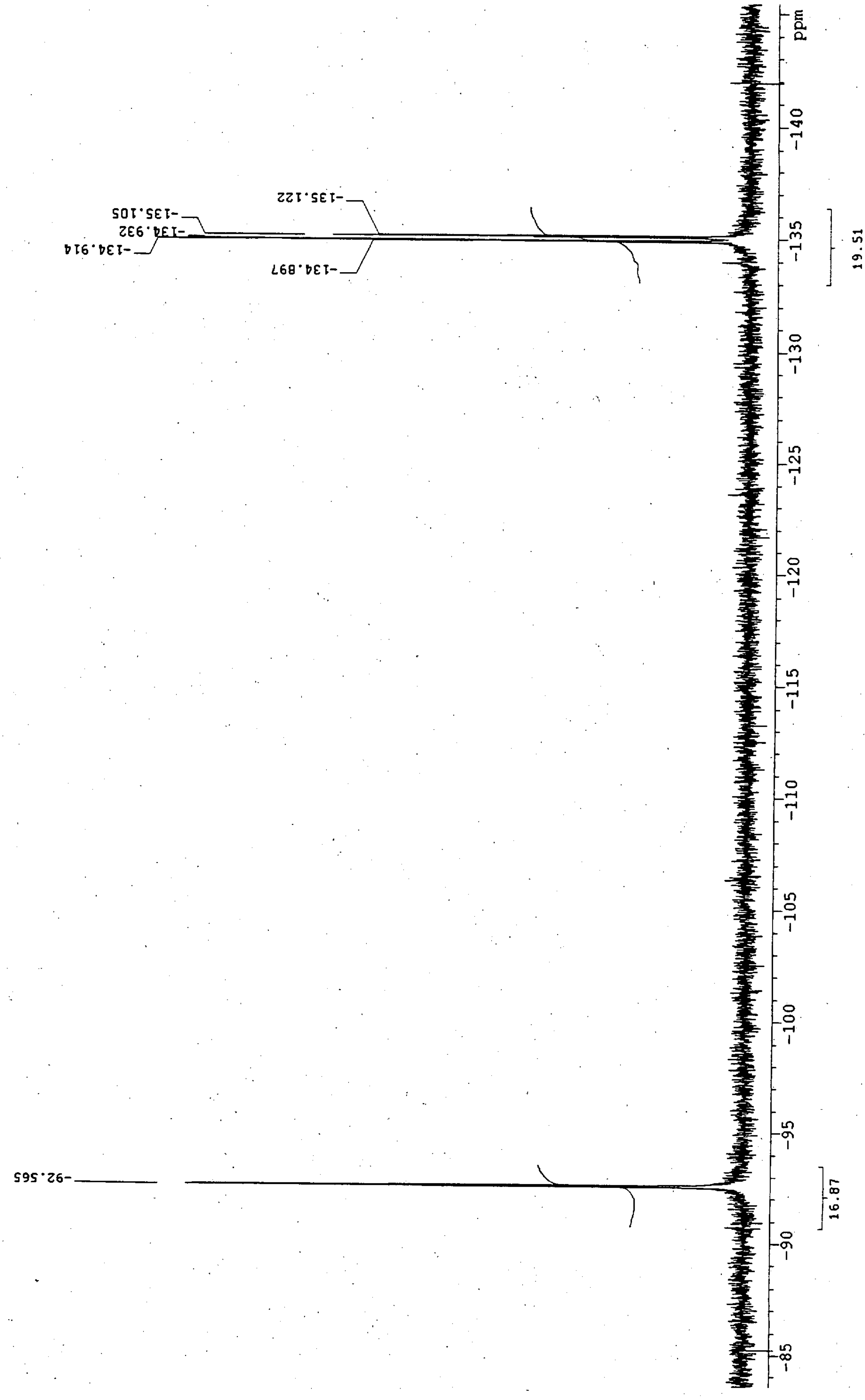
s-30

S-31



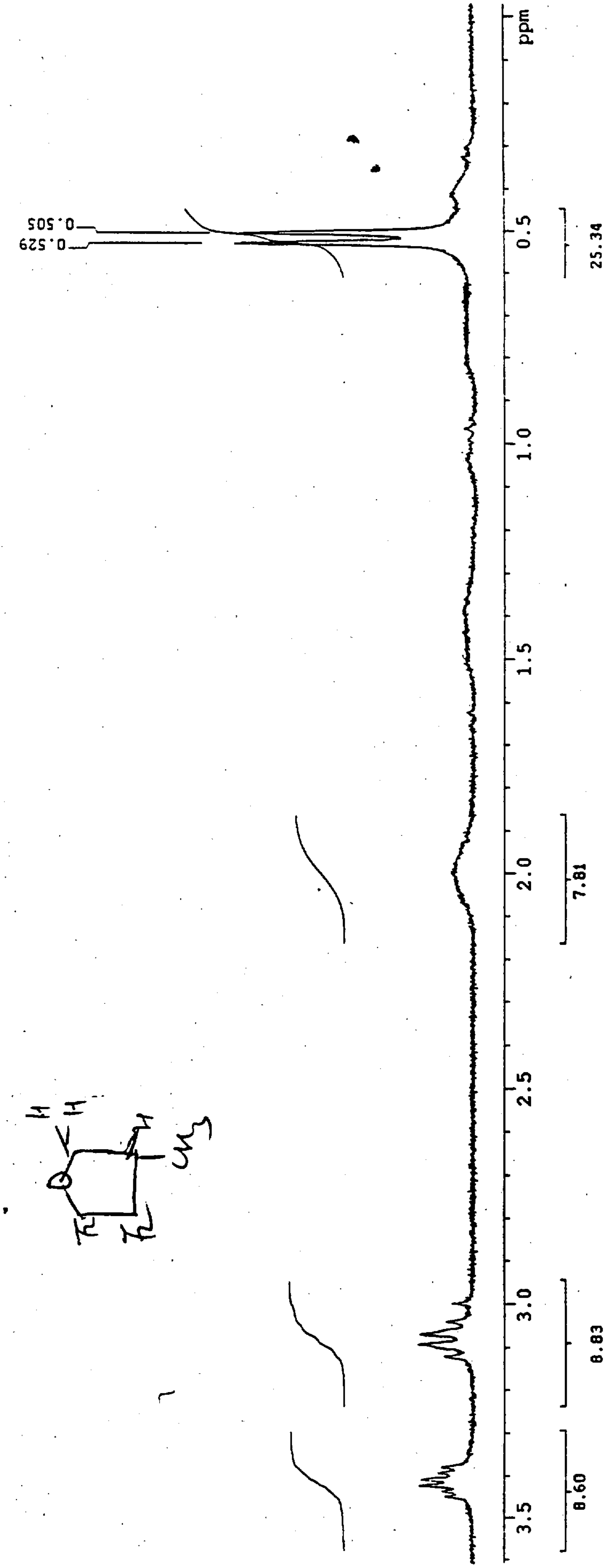
^{1}H NMR: 1,1,2,2-Tetrafluoroethyl allyl ether

s-32



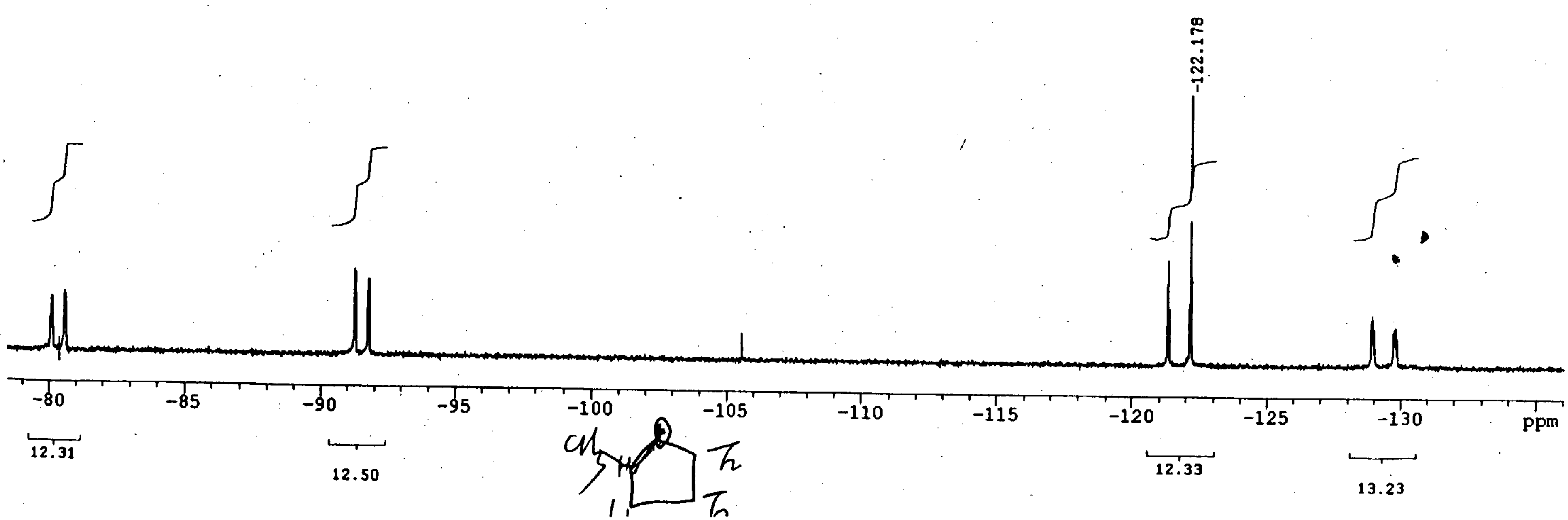
^{19}F NMR: 1,1,2,2-Tetrafluoroethyl allyl ether

S-33



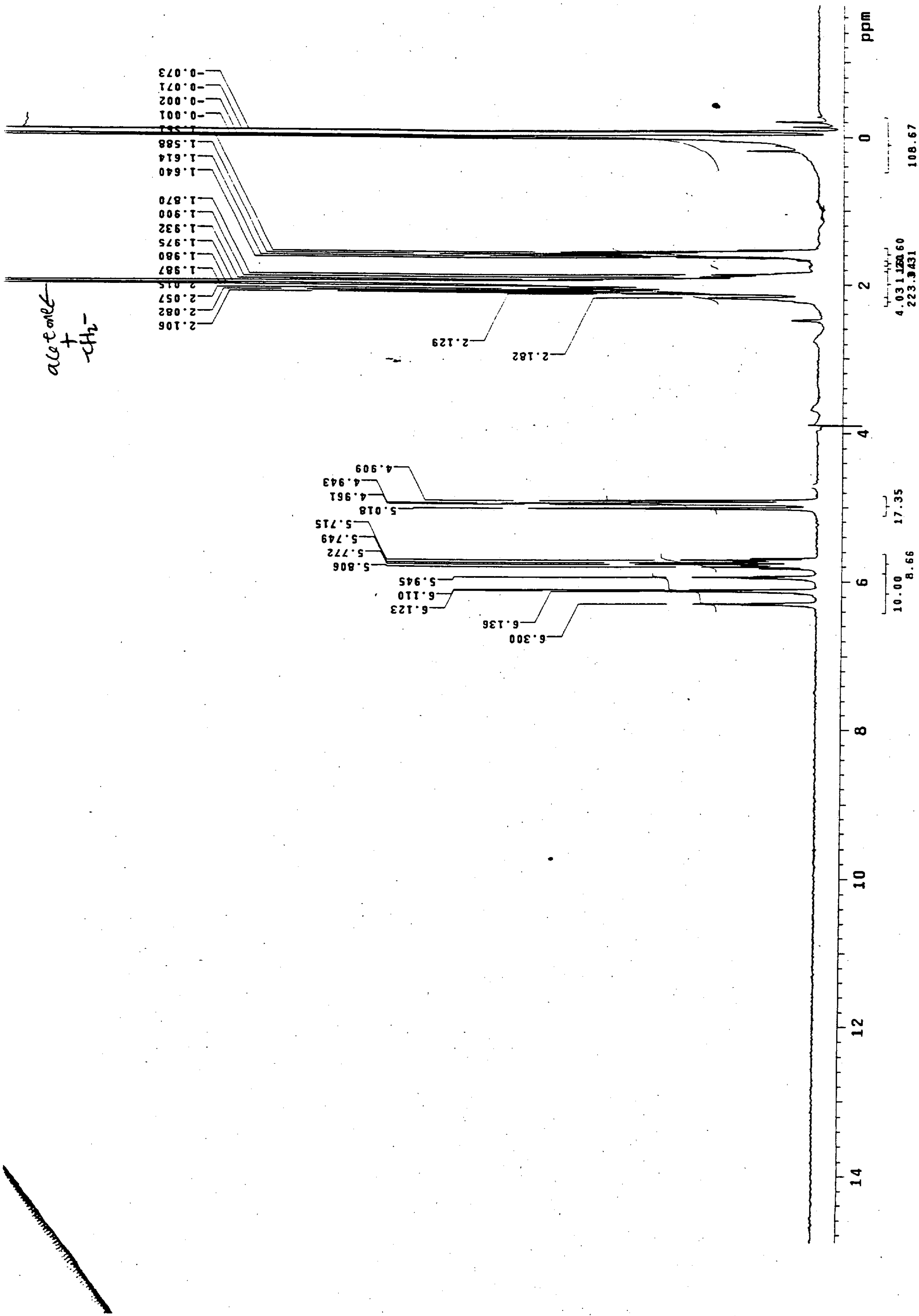
^{1}H NMR: 3-Methyl-4,4,5,5-tetrafluoro-1-oxacyclopentane

OBSERVE F19
FREQUENCY 282.202 MHz
SPECTRAL WIDTH 80000.0 Hz
ACQUISITION TIME 0.300 sec
RELAXATION DELAY 4.000 sec
PULSE WIDTH 5.0 usec
AMBIENT TEMPERATURE
NO. REPETITIONS 256
DOUBLE PRECISION ACQUISITION
DATA PROCESSING
LINE BROADENING 0.3 Hz
FT SIZE 65536
TOTAL ACQUISITION TIME 18 minutes



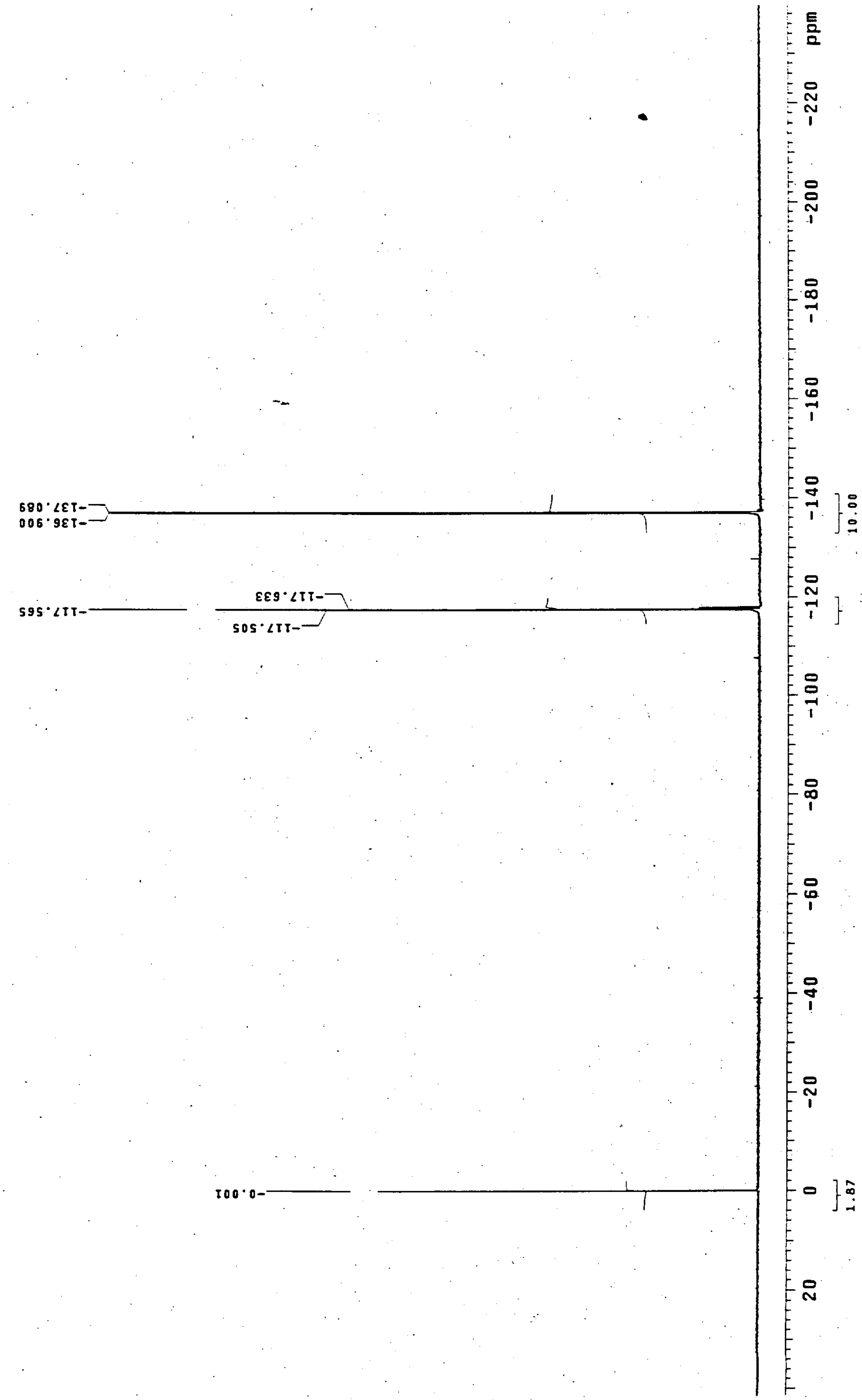
^{19}F NMR: 3-Methyl-4,4,5,5-tetrafluoro-1-oxacyclopentane

S-35



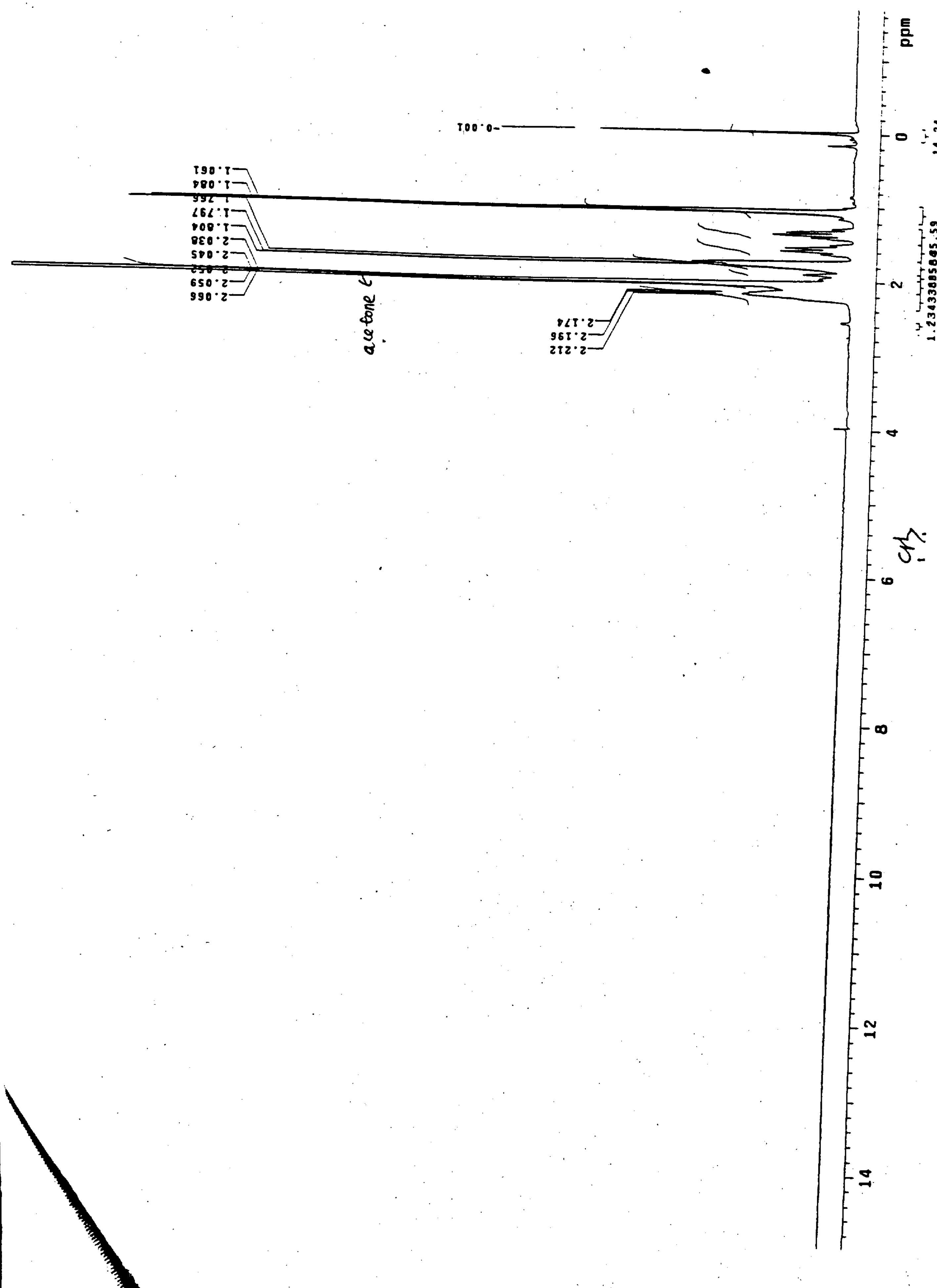
^{1}H NMR: 6,6,7,7-Tetrafluoroheptene (9)

S-36



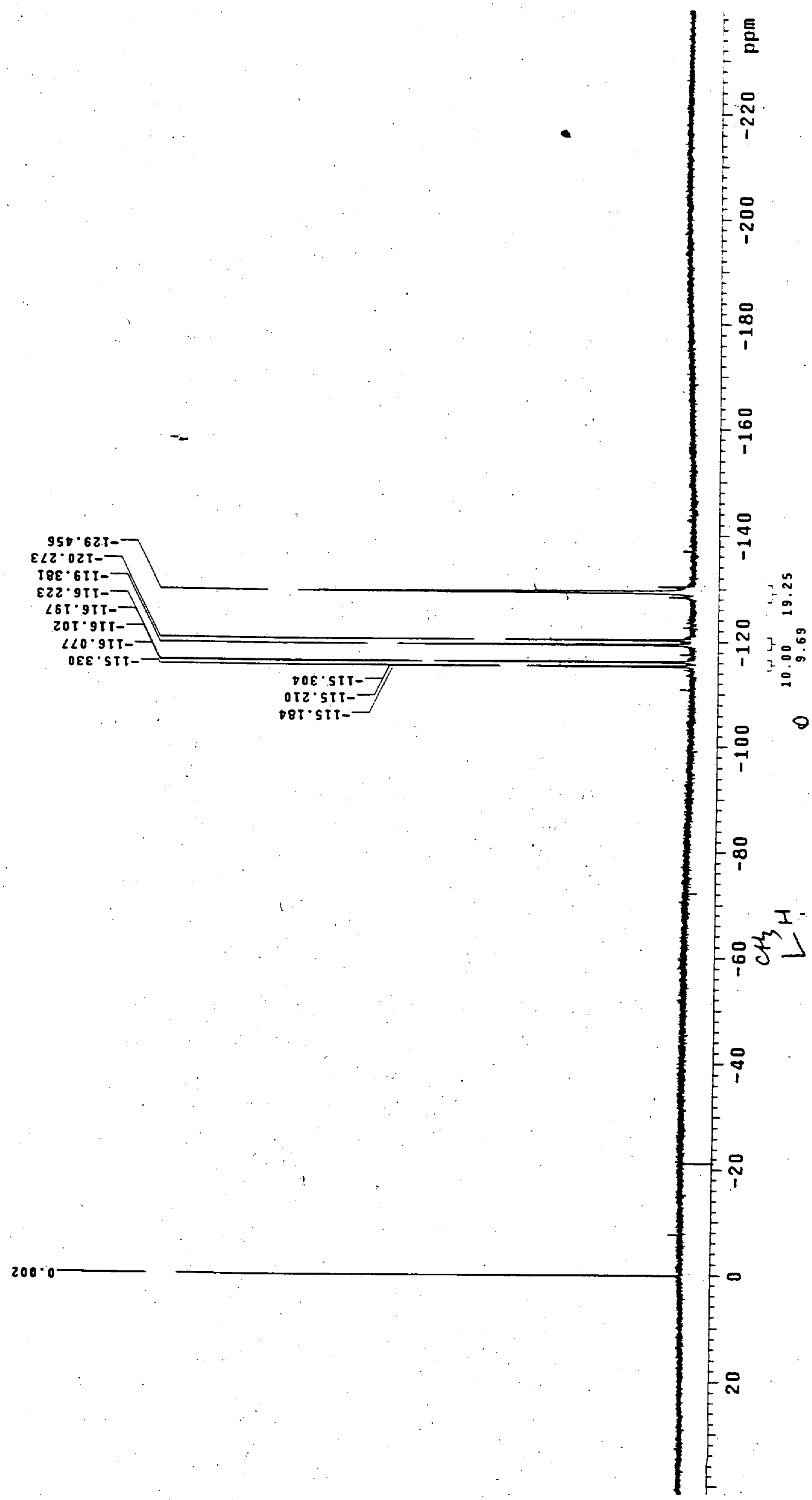
^{19}F NMR: 6,6,7,7-Tetrafluoroheptene (9)

 S-37



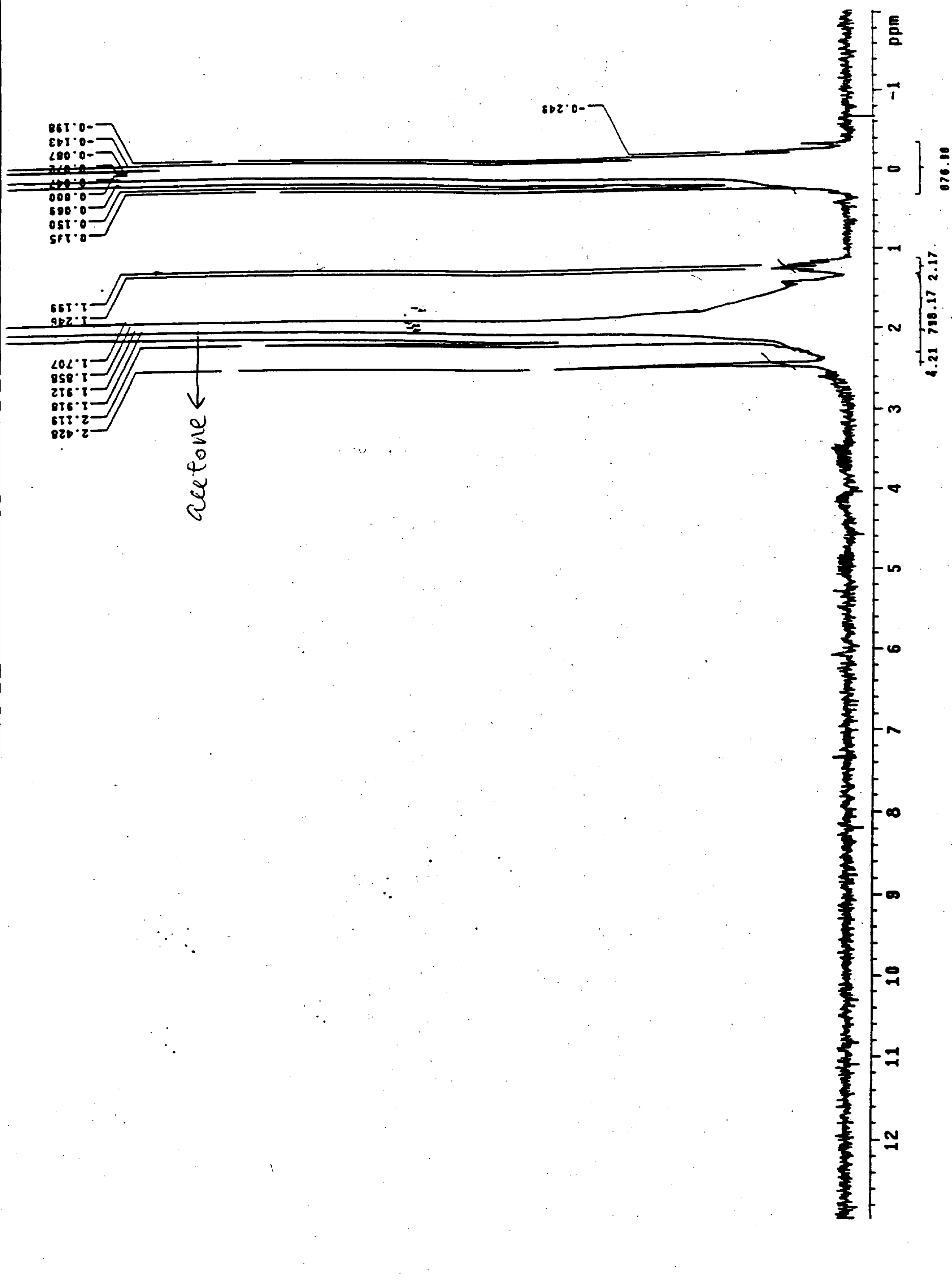
^{1}H NMR: 1-Methyl-2,2,3,3-tetrafluorocyclohexane (11)

S-38



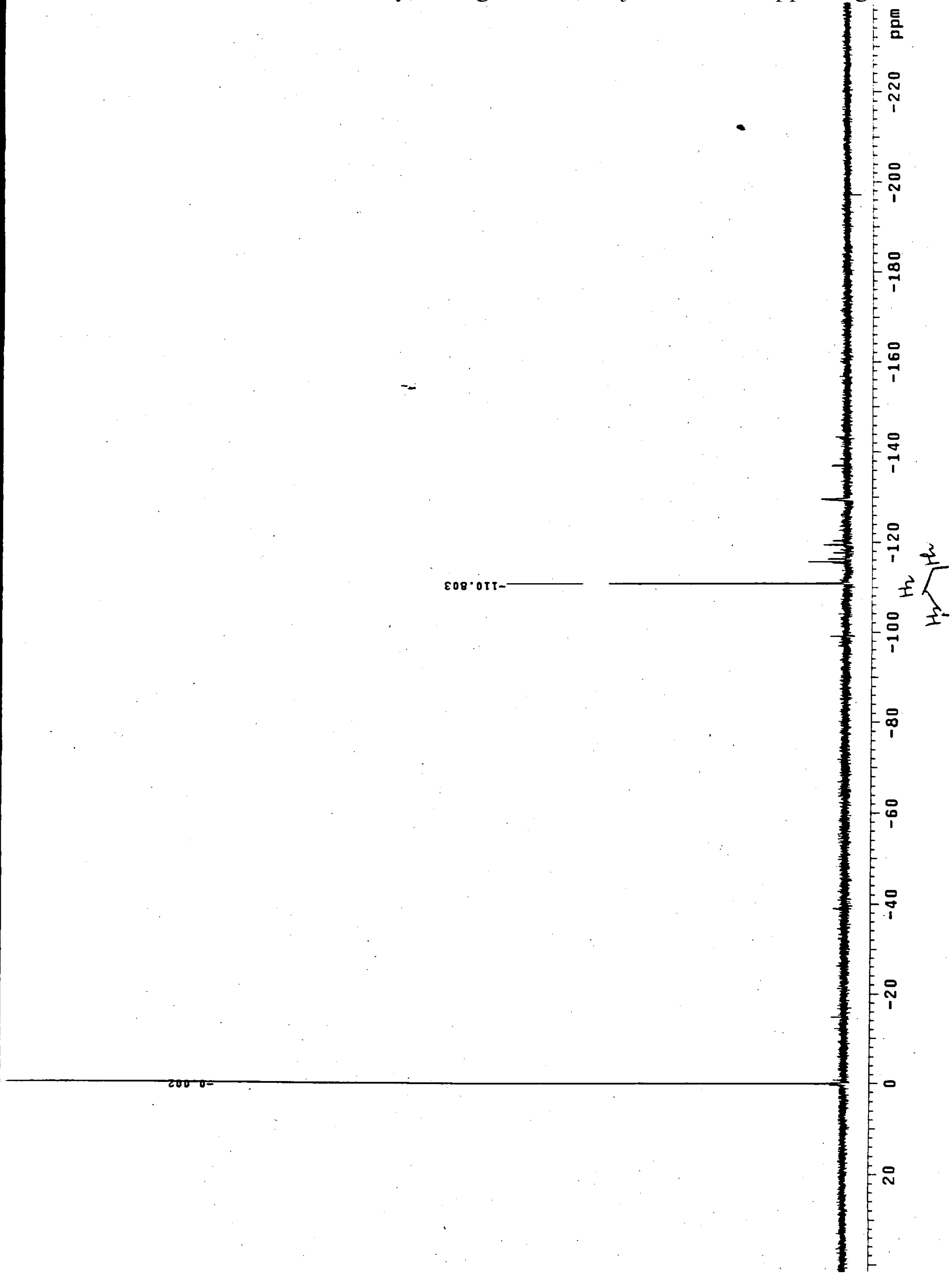
^{19}F NMR: 1-Methyl-2,2,3,3-tetrafluorocyclohexane (11)

S-39



^1H NMR: 1,1,2,2-Tetrafluorocycloheptane (13)

S-40



^{19}F NMR: 1,1,2,2-Tetrafluorocycloheptane (13)