Supporting Information

Rearrangement of 3-Membered 1,1,2-Trifluorobromonium and Iodonium Ions and Comparison of Trifluorochloronium to Fluorocarbenium Ions.

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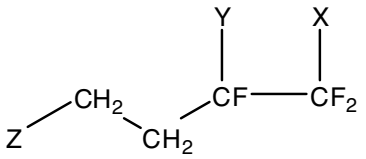
TABLE S1

Mass Spectral Data and Characterization of Products



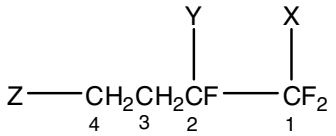
Structure			Mass Spectrum Fragments m/e (rel. intensity) (EI Unless Noted)			
Z	Y	X	$[CH_2Z]^{+\bullet}$	$[CF_2X]^{+\bullet}$	Other	**Exact Mass/Characterization**
Cl	**8** Cl	Cl	49, 51 (39, 15)	85, 87 (26, 8)	M^+–$[CF_2Cl]$ 129, 131 (79, 48); $[C_3H_3ClF]^{+\bullet}$ 93, 95 (100, 59).	MS and NMR data identical to commercial sample.
Cl	**9** Br	Br	49, 51 (22, 9)	129, 131 (17, 13)	M^+–Br 227, 225, 223, (14, 58, 45). PCI, CH_4, 302, 304, 306, 308, (0.4, 2, 3,1) M+1–[HF] 283, 285, 287, 289 (10, 21, 15, 3) M+1–[HBr] 223, 225, 227 (80, 100, 25)	Calcd. for $C_4H_4Br_2ClF_3$ 301.83201 found 301.83307
Cl	**10** Cl	Br	49, 51 (47, 21)	129, 131 (76, 41)	M^+–[Br] 179, 181, 183 (41, 29, 5); $[C_2H_3F_2]^{+\bullet}$ 65(100). PCI,CH_4 M^+–[HF] 239, 241, 243, 245, (11, 19, 8, 1); M+1–[HCl] 223, 225, 227 (78, 100, 24)	Both regioisomers converted to known compounds **16** and **17** by S_N2 conversion of **10** and **11** with bromide ion. Independent synthesis confirmed by GC/MS.
Cl	**11** Br	Cl	49, 51 (40, 16)	85, 87 (22, 7)	M^+258, 260, 262 (2, 3, 1); M^+–Br 179, 181, 183 (65, 41, 7); M^+–BrCl 143, 145, (83, 29); $[C_2H_3F_2]^{+\bullet}$ 65 (100). PCICH_4 M+1 258, 260, 262, 264, (4, 6, 3, 1); M+1–[HF] 239, 241, 243, 245, (15, 25, 11, 2); M+1–[HCl] 223, 225, 227 (80, 100, 25).	
Cl	**12** Br	I	49, 51 (34, 17)	177 (5)	M^+350, 352, 354, (8, 11, 2); M^+–[I] 223, 225, 227 (61, 82, 20); M^+–[HBrI] 143, 145 (100, 33).	calcd. for $C_4H_4BrClIF_3$ 353.8132. found on a 60:40 mixture of both regioisomers 353.8143.
Cl	**13** I	Br	49, 51 (15, 7)	129, 131 (18, 11)	M^+–[I] 223, 225, 227 (52, 72, 17); M^+–[HBrI] 143, 145 (100, 33).	

Cl	**23** Cl	I	49, 51 (37, 17)	M^+–[CF_2I] 129, 131, 133 (84, 51, 9)	M^+–HI 178, 180, 182 (9, 5, 0.6); M^+–HClI 143, 145 (32, 10); [C_3H_3ClF]$^{+\bullet}$ 93, 95 (100, 58). PCI, CH_4 M^+ 306, 308, 310 (4, 2, 0.5)	calcd. for $C_4H_4Cl_2F_3I$ 305.86869 found 305.86869. Converted to known compound **18**.
Br	**14** Cl	Cl	93, 95 (100, 72)	85, 87 (57, 20)	M^+ 258, 260, 262, 264, (6, 11, 5, 07). M^+–Br 179, 181, 183 (40, 27, 4)	calcd. for $C_4H_4BrCl_2F_3$ 157.8828 found 257.8814. See *J. Org. Chem.*, **2003**, *68*, 3932, bp 64-5º at 35 Torr. See prep. scale synthesis below.
Br	**15** Br	Br	93, 95 (40, 73)	129, 131 (23, 32)	M^+ 346, 348, 350, 352, (4, 10, 11, 4); M^+–Br 267, 269, 271 (44, 82, 43); [$C_4H_3F_3$]$^{+\bullet}$ 108 (100)	calcd. for $C_4H_4Br_3F_3$ 345.7815 found 345.7818. See *J. Org. Chem.*, **2003**, *68*, 3932. bp 84-5º at 25 Torr.
Br	**16** Cl	Br	93, 95 (60, 52)	129, 131 (15, 12)	M^+ 302, 304, 306, 308 (12, 27, 19, 4); M^+–Br 223, 225, 227 (78, 100, 68); M^+–HBrCl 187, 189 (23, 22); M^+–[CF_2Br] 173, 175, 177 (16, 20, 5).	calcd. for $C_4H_4Br_2ClF$ 301.8320 found 321.8311 on a 2:1 **16/17** mixture of both regioisomers. See *J. Org. Chem.*, **2003**, *68*, 3932. See below for the independent synthesis of (**16**).
Br	**17** Br	Cl		85, 87 (17, 7)	M^+ 302, 304, 306, 308 (36, 81, 56, 11); M^+–Br 223, 225, 227 (66, 84, 21); M^+–HBrCl 187, 189 (27, 26).	
Br	**18** Cl	I	93, 95 (48, 62)	177 (12)	M^+ 350, 352, 354 (0.1, 0.1, 0.0); M^+–I 223, 225, 227 (38, 57, 11); M^+–HBrI 143, 145 (100, 32).	Reported in *J. Org. Chem.*, **2003**, *68*, 3932.
Br	**19** I	Cl	93, 95 (54, 64)	85, 87 (20, 7)	M^+ 350, 352, 354 (16, 20, 5); M^+–I 223, 225, 227 (24, 29, 7); M^+–HBrI 143, 145 (100, 30).	Reported in *J. Org. Chem.*, **2003**, *68*, 3932.
Br	**20** Br	I	93, 95 and 95[$C_3H_2F_3$]$^{+\bullet}$ (16, 41)	177 (7)	M^+ 394, 396, 398 (1, 3, 1); M^+–I 267, 269, 271 (45, 90, 50); M^+–HBrI 187, 189 (95, 100); [$C_4H_3F_3$]$^{+\bullet}$ 108 (53).	Exact mass on a 10:90 mixture of **20**:**21** calcd. for $C_4H_4F_3{}^{79}Br^{81}BrI$ 395.7656; found 395.7654. The internal reference interfered with the $C_4H_4F_3{}^{79}Br_2I$ peak.
Br	**21** I	Br	93, 95 and 95[$C_3H_2F_3$]$^{+\bullet}$ (17, 48)	129, 131 (7, 8)	M^+ 394, 396, 398 (10, 19, 9); M^+–I 267, 269, 271 (50, 100, 51); M^+–HBrI 187, 189 (99, 98); [$C_4H_3F_3$]$^{+\bullet}$ 108 (77).	

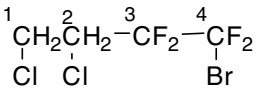
I	**22** Cl	Cl	141 (47)	85, 87 (78, 27)	M^+ 306, 308, 310 (86, 57, 10); M^+–I 179, 181, 183 (100, 66, 11); M^+–HClI 143, 145 (90, 30).	calcd. for $C_4H_4Cl_2F_3I$ 305.86869 found 305.8685. See Supporting Information below for conversion to 4-bromo-1,2-dichloro-1,1,2-trifluorobutane (**14**).
I	**24** Br	Br	141 (36)	129, 131 (28, 26)	M^+ 394, 396, 398 (13, 25, 12); M^+–I 267, 269, 271 (30, 57, 29); M^+–IBr 187, 189 (80, 79); $[I]^{+\bullet}$ 127 (93); M^+–H2BrI 108 (100); $[C_3H_4F]^+$ 59 (52).	Independent Synthesis from reaction of Lithium Iodide with 1,2,4-tribromo-1,1,2-trifluorobutane(**15**). Also, the 4-iodoproduct **24** was converted back to **15**, a known characterized compound (*J. Org. Chem.*, **2003**, *68*, 3932).
I	**25** Br	I	141 (29)	177 (8)	M^+ 442, 444 (7, 6); M^+–I 315, 317 (90, 87); M^+–HBrI 235 (25); M^+–HI_2 187, 189 (39, 39); M^+–2I 188 (7); M^+–Br2I 109 (100); M^+–HBr2I 108 (87); $[C_3H_2F_3]^{+\bullet}$ 95 (23).	Attempted isolation by preparative GC or column chromatography led to decomposition. Peaks were well resolved on the GC/MS. NMR for **26** are from a crude reaction mixture. See Table S2.
I	**26** I	Br	141 (15)	129, 131 (6, 6)	M^+ 442, 444 (22, 21); M^+–I 315, 317 (100, 97); $[2I]^+$ 254 (26); M^+–HBrI 235 (19); M^+–H2I 187, 189 (18, 17); M^+–Br2I 109 (27); M^+–HBr2I 108 (32); $[C_3H_2F_3]^{+\bullet}$ 95 (24).	
Br	**27** I	I	93, 95 and 95$[C_3H_2F_3]^{+\bullet}$ (8, 59)	177 (8)	M^+ 442, 444 (1, 1); M^+–I 315, 317 (35, 34); M^+–$[BrI_2]$ 109 (100); M^+–$[HBrI_2]$ 108 (67).	Minor Product (2%). Attempted isolation by preparative GC or column chromatography led decomposition
$BrCF_2CF_2CH(Cl)-CH_2Cl$ **7**			$[CF_2Br]^{+\bullet}$ 129, 131 (30, 38)	$[CH_2Cl]^{+\bullet}$ 49, 51 (51, 48)	M^+–[HCl] 240, 242, 244 (3, 11, 7); M^+–[Br] 197, 199, 201 (49, 32, 5); M^+–[HBrCl] 161, 163 (55, 18); 67, 69 (100, 49). PCI, CH_4 M+1–[HCl] 241, 243, 245 (81, 100, 24); M+1–[HBr] 197, 199, 201 (3, 17, 27)	calcd. for M^+–[Br] $C_4H_3Cl_2F_4$ 196.95406; found 196.95479

TABLE S2

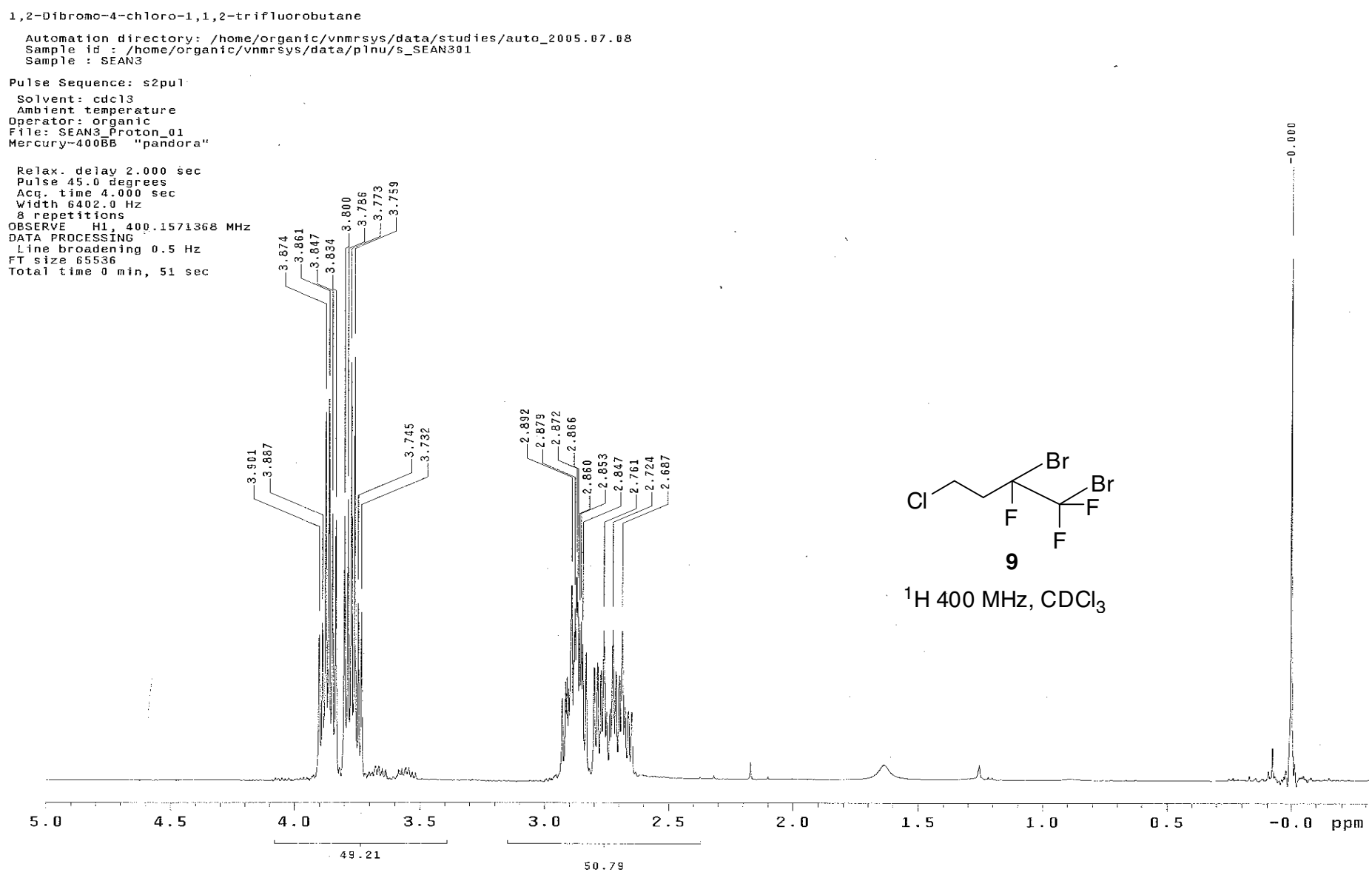
NMR[1] DATA IN $CDCl_3$[a]



Products			Nuclei that Resonate on Carbons:			
Z	Y	X	C_1 (ppm)	C_2 (ppm)	C_3 (ppm)	C_4 (ppm)
Cl	**8** Cl	Cl	^{19}F = –67.9 (m, 2F) ^{13}C = 125.2 (td, J = 299 and 32 Hz)	^{19}F = –120.7 (m, 1F) ^{13}C = 109.1 (dt, J = 257 and 32 Hz)	^{1}H = 3.72–3.89 (m, 2H) ^{13}C = 39.5 (d, J = 21 Hz)	^{1}H = 2.58–2.90 (m, 2H) ^{13}C = 36.6 (d, J = 4 Hz)
Cl	**9** Br	Br	^{19}F = –58.4 (dd, J = 170.9 and 15.3 Hz, 1F); –59.9 (dd, J = 170.9 and 15.3 Hz, 1F). ^{13}C = 119.1 (td, J = 310 and 33Hz)	^{19}F = –117.3 (m, 1F) ^{13}C = 104.5 (dt, J = 266 and 29 Hz)	^{1}H = 3.76 (m, 1H); 3.86 (m, 1H) ^{13}C = 41.3 (d, J = 20 Hz)	^{1}H = 2.64–2.94 (m, 2H) ^{13}C = 37.9 (d, J = 4 Hz)
Cl	**12** Br	I	^{19}F = –51.5 (brdd, J = 169 Hz, 1F) –56.8 (dd, J = 169 and 29 Hz, 1F) ^{13}C = 118.2 (dd, J = 309 and 32 Hz); 121.4 (dd, J = 309 and 32 Hz).	^{19}F = –117.5 (m, 1F) ^{13}C = 85.8 (ddd, J = 266, 32 and 32 Hz)	^{1}H = 3.75 (m, 1H) 3.82 (m, 1H) ^{13}C = 44.3 (d, J = 19 Hz)	^{1}H = 2.62–2.79 (m, 2H) ^{13}C = 40.7 (d, J = 3 Hz)
Cl	**13** I	Br	^{19}F = –58.2 (dd, J = 170.9 and 15.3 Hz, 1F); –58.7 (dd, J = 170.9 and 15.3 Hz, 1F). ^{13}C = 120.7 (dd, J = 310 and 33 Hz) 117.5 (dd, J = 310 and 34 Hz)	^{19}F = –117.3 (m, 1F) ^{13}C = 104.3 (ddd, J = 266, 31 and 28 Hz)	^{1}H = 3.77 (m, 1H); 3.85 (m, 1H). ^{13}C = 41.3 (d, J = 19 Hz)	^{1}H = 2.64–2.94 (m, 2H) ^{13}C = 37.8 (d, J = 4 Hz)
Cl	**23** Cl	I	^{19}F = –67.9 (m, 2F) ^{13}C = 125.3 (td, J = 299 and 33 Hz)	^{19}F = –120.7 (m, 1F) ^{13}C = 109.1 (dt, J = 257 and 32 Hz)	^{1}H = 3.65–3.90 (m, 2H) ^{13}C = 39.5 (d, J = 21 Hz)	^{1}H = 2.25–2.90 (m, 2H) ^{13}C = 36.6 (d, J = 4 Hz)
Br	**16** Cl	Br	^{19}F = –61.9 (m, 2F) ^{13}C = 119.2 (td, J = 310 and 33 Hz)	^{19}F = –112.0 (m, 1F) ^{13}C = 109.6 (dt, J = 257 and 30 Hz)	^{1}H = 2.80–2.99 (m, 2H); ^{13}C = 39.6 (d, J = 21 Hz)	^{1}H = 3.56 (m, 2H) ^{13}C = 22.5 (d, J = 4 Hz)
Br	**17** Br	Cl	^{19}F = –64.9 (dd, J = 169 and 13 Hz, 1F); –65.9 (dd, J = 169 and 12 Hz, 1F) ^{13}C = 119.5 (td, J = 312 and 35 Hz)	^{19}F = –118.6 (m, 1F) ^{13}C = 110.4 (dt, J = 257 and 30 Hz)	^{13}C = 40.1 (d, J = 20 Hz) ^{1}H = 2.63 (m, 2H)	^{13}C = 23.8 (d, J = 4 Hz) ^{1}H = 3.63 (m, 2H)
Br	**21** I	Br	^{19}F (56.4 MHz) = –51.0 (dd, J = 170 and 19 Hz, 1F); –57.1 (dd, J = 170 and 22 Hz, 1F ^{13}C (100 MHz) = 118.3 (dd, J = 309 and 32 Hz); 121.4 (dd, J = 309 and 32 Hz)	^{19}F (56.4 MHz) = –117.7 (m, 1F) ^{13}C (100 MHz) = 88.5 (ddd, J = 265, 32 and 27 Hz)	^{1}H = 3.48–3.58 (m, 1H) 3.61–3.72 (m, 1H) ^{13}C = 44.9 (d, J = 20 Hz)	^{1}H = 2.66–2.88 (m, 2H) ^{13}C = 26.7 (d, J = 3 Hz)

Products			Nuclei that Resonate on Carbons:			
Z	Y	X	C_1 (ppm)	C_2 (ppm)	C_3 (ppm)	C_4 (ppm)
I	**22** Cl	Cl	^{19}F = –67.5 (m, 2F) ^{13}C = 125.0 (td, J = 299 and33 Hz)	^{19}F = –121.4 (m, 1F) ^{13}C = 110.6 (dt, J = 257 and 32 Hz).	^{1}H = 3.28 (m, 1H); 3.29 (m, 1H). ^{13}C = 41.4 (d, J = 21 Hz)	^{1}H = 2.65–2.98 (m, 2H) ^{13}C = –8.6 (d, J = 4 Hz)
I	**24** Br	Br	^{19}F = –57.8 (dd, J = 171 and 15 Hz, 1F); –59.6 (dd, J = 171 and 15 Hz, 1F). ^{13}C = 117.7 (dd, J = 310 and 33 Hz); 120.7 (dd, J = 310 and 33 Hz)	^{19}F = –117.9 (m, 1F). ^{13}C = 106.1 (ddd, J = 267, 31 and 28 Hz)	^{1}H = 3.29 (m, 1H); 3.37 (m, 1H) ^{13}C = 43.5 (d, J = 21 Hz)	^{1}H = 2.70–3.05 (m, 2H) ^{13}C = –6.6 (d, J = 4 Hz)
I	**26** I	Br	^{19}F = –56.3 (t, J = 12 Hz, 1F); –56.7 (t, J = 18 Hz, 1F) ^{13}C = 118.0 (dd, J = 292 and 33 Hz) 121.3 (dd, J = 292 and 32 Hz).	^{19}F = 118.0 (m, 1F). ^{13}C = 90.6 (ddd, J = 267, 46 and 27 Hz)	^{1}H = 3.22–3.34 (m, 1H); 3.36–3.47 (m, 1H) ^{13}C = 46.5 (d, J = 19 Hz)	^{1}H = 2.62–2.76 (m, 2H) ^{13}C = –3.5 (brd. s)
NMR on crude reaction mixture. Attempted Purification led to decomposition.						
 **7**			^{1}H (60 MHz) 3.48–4.38 (m, 3H); 4.38–4.90 (m, 1H).		^{19}F (376 MHz)–115.4 (dm, J = 267 Hz, 1F); –110.1 (d, J = 276 Hz, 1F). ^{13}C (100 MHz) 113.8 (tt, J = 262 and 13 Hz)	^{19}F (376 MHz) –62.0 (dd, J = 180 and 7 Hz, 1F); –62.8 (d, J = 180 Hz, 1F). ^{13}C (100 MHz) 116.7 (tt, J = 313 and 39 Hz)
			^{13}C (100 MHz) 42.9 (s)	^{13}C (100 MHz) 57.0 (dd, J = 28 and 24 Hz)		

[a]Proton at 400 MHz, ^{19}F at 346 MHz and ^{13}C at 100 MHz unless noted.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3.861
3.847
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3.800
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3.773
3.759
3.745
3.732
2.892
2.879
2.872
2.866
2.860
2.853
2.847
2.761
2.724
2.687
0.000
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
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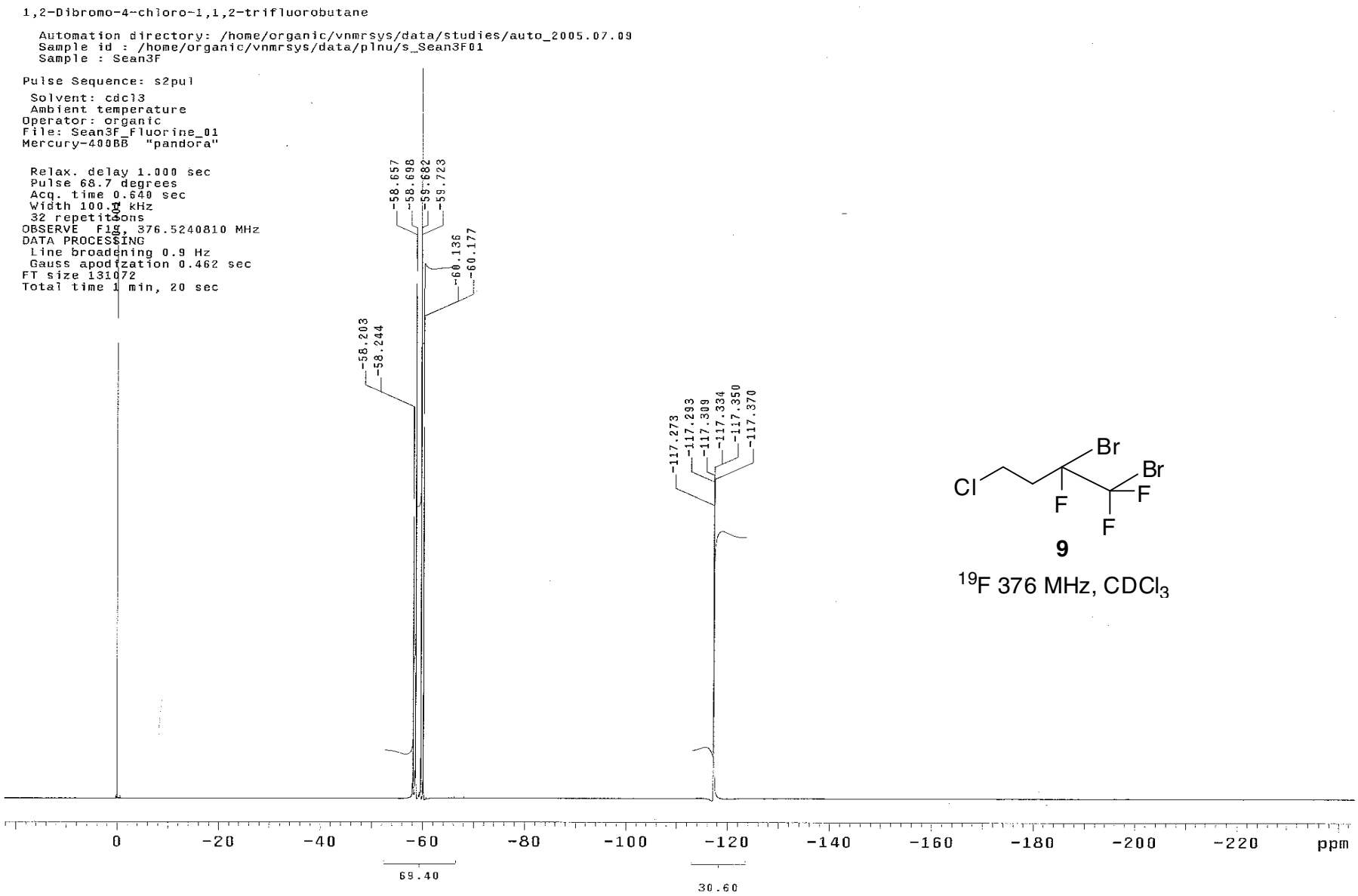
Cl
Br
Br
F
F
F
9
1H 400 MHz, CDCl3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Ambient temperature
Operator: organic
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32 repetitions
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Line broadening 0.9 Hz
Gauss apodization 0.462 sec
FT size 131072
Total time 1 min, 20 sec
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-58.682
-59.723
-60.136
-60.177
-58.203
-58.244
-117.273
-117.293
-117.309
-117.334
-117.350
-117.370
0
-20
-40
-60
-80
-100
-120
-140
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Br
Br
Cl
F
F
F
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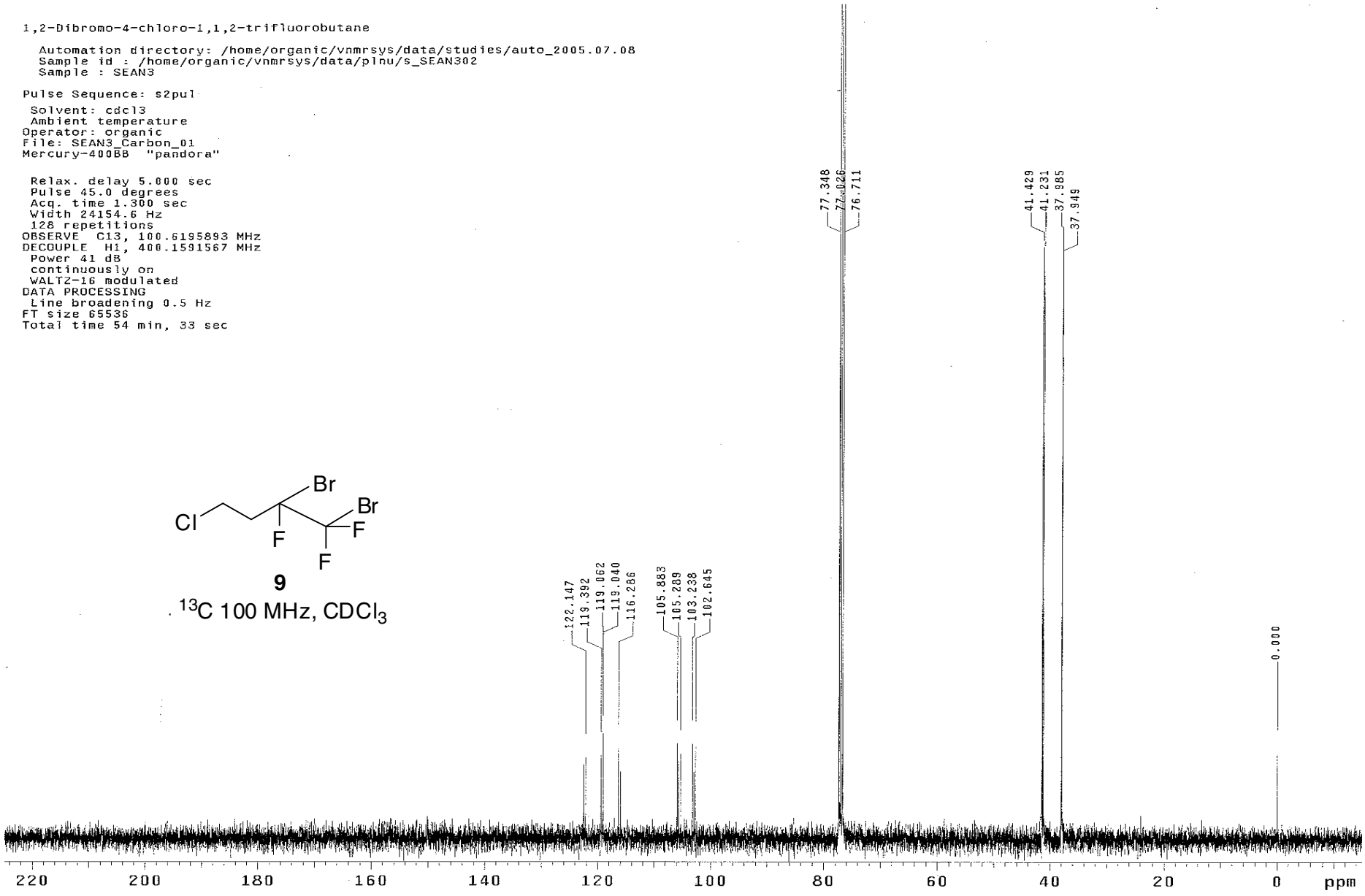
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Ambient temperature
Operator: organic
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Power 41 dB
continuously on
WALTZ-16 modulated
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Cl
Br
Br
F
F
F
9
13C 100 MHz, CDCl3
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77.026
76.711
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37.949
122.147
119.392
119.062
119.040
116.286
105.883
105.289
103.238
102.645
0.000
220
200
180
160
140
120
100
80
60
40
20
0
ppm

2-Bromo-4-chloro-1,1,2-trifluoro-1-iodobutane

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Ambient temperature
Operator: organic
File: SEAN1_Proton_01
Mercury-400BB "pandora"

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Pulse 45.0 degrees
Acq. time 4.000 sec
Width 6402.0 Hz
8 repetitions
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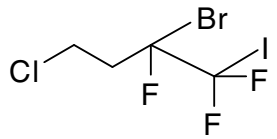
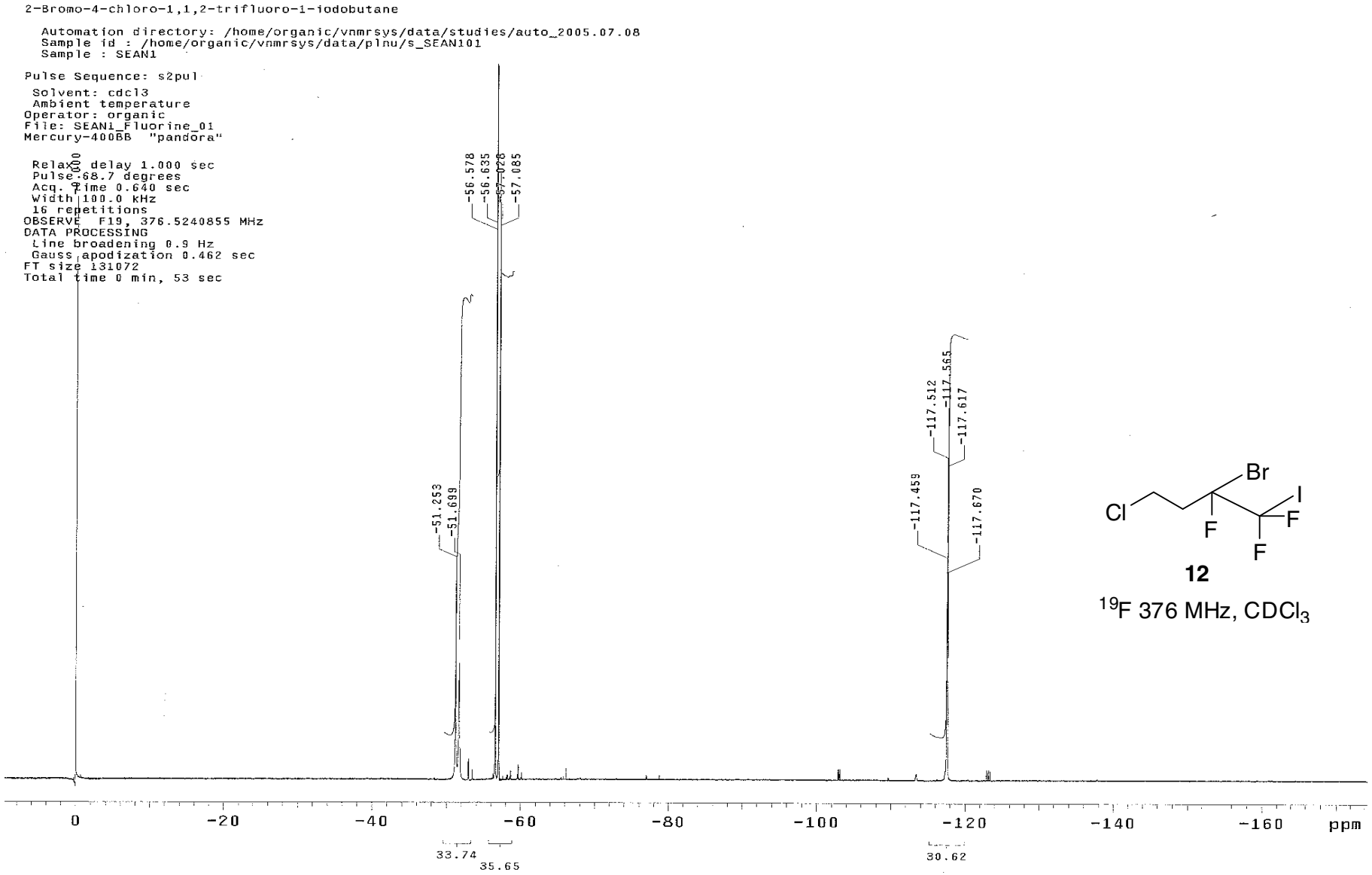


12

^{1}H 400 MHz, $CDCl_3$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Solvent: cdcl3
Ambient temperature
Operator: organic
File: SEAN1_Fluorine_01
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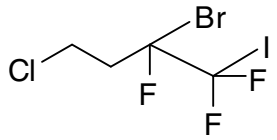
Relax. delay 1.000 sec
Pulse 68.7 degrees
Acq. time 0.640 sec
Width 100.0 kHz
16 repetitions
OBSERVE F19, 376.5240855 MHz
DATA PROCESSING
Line broadening 0.9 Hz
Gauss apodization 0.462 sec
FT size 131072
Total time 0 min, 53 sec
-56.578
-56.635
-57.028
-57.085
-51.253
-51.699
-117.459
-117.512
-117.565
-117.617
-117.670
0
-20
-40
-60
-80
-100
-120
-140
-160
ppm
33.74
35.65
30.62
Br
Cl
I
F
F
F
12
19F 376 MHz, CDCl3

2-Bromo-4-chloro-1,1,2-trifluoro-1-iodobutane

Automation directory: /home/organic/vnmrsys/data/studies/auto_2005.07.08
Sample id : /home/organic/vnmrsys/data/plnu/s_SEAN101
Sample : SEAN1

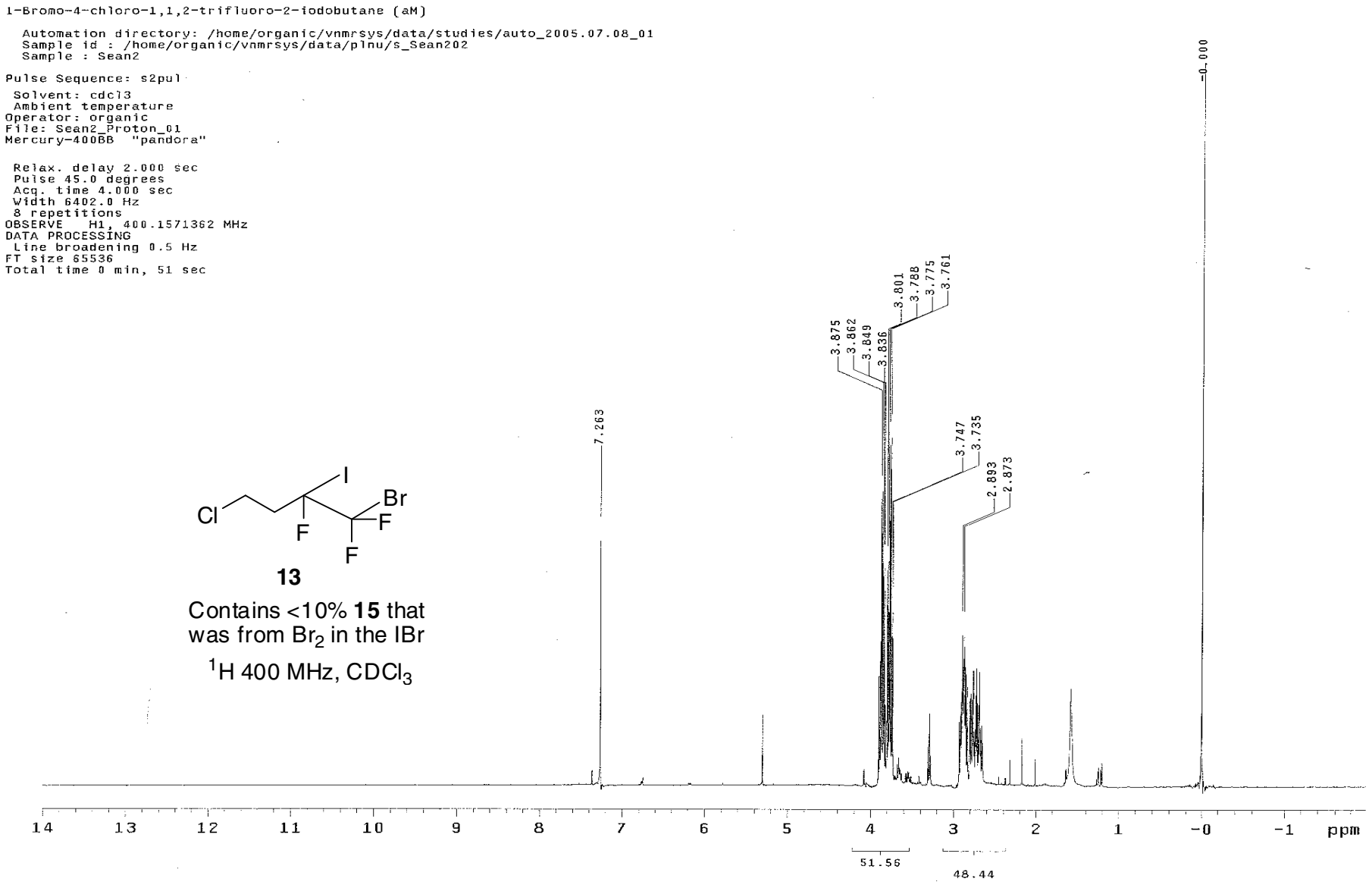
Pulse Sequence: s2pul
Solvent: cdcl3
Ambient temperature
Operator: organic
File: SEAN1_Carbon_01
Mercury-400BB "pandora"

Relax. delay 5.000 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 24154.6 Hz
256 repetitions
OBSERVE C13, 100.6195916 MHz
DECOUPLE H1, 400.1591567 MHz
Power 41 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 27 min, 16 sec



12

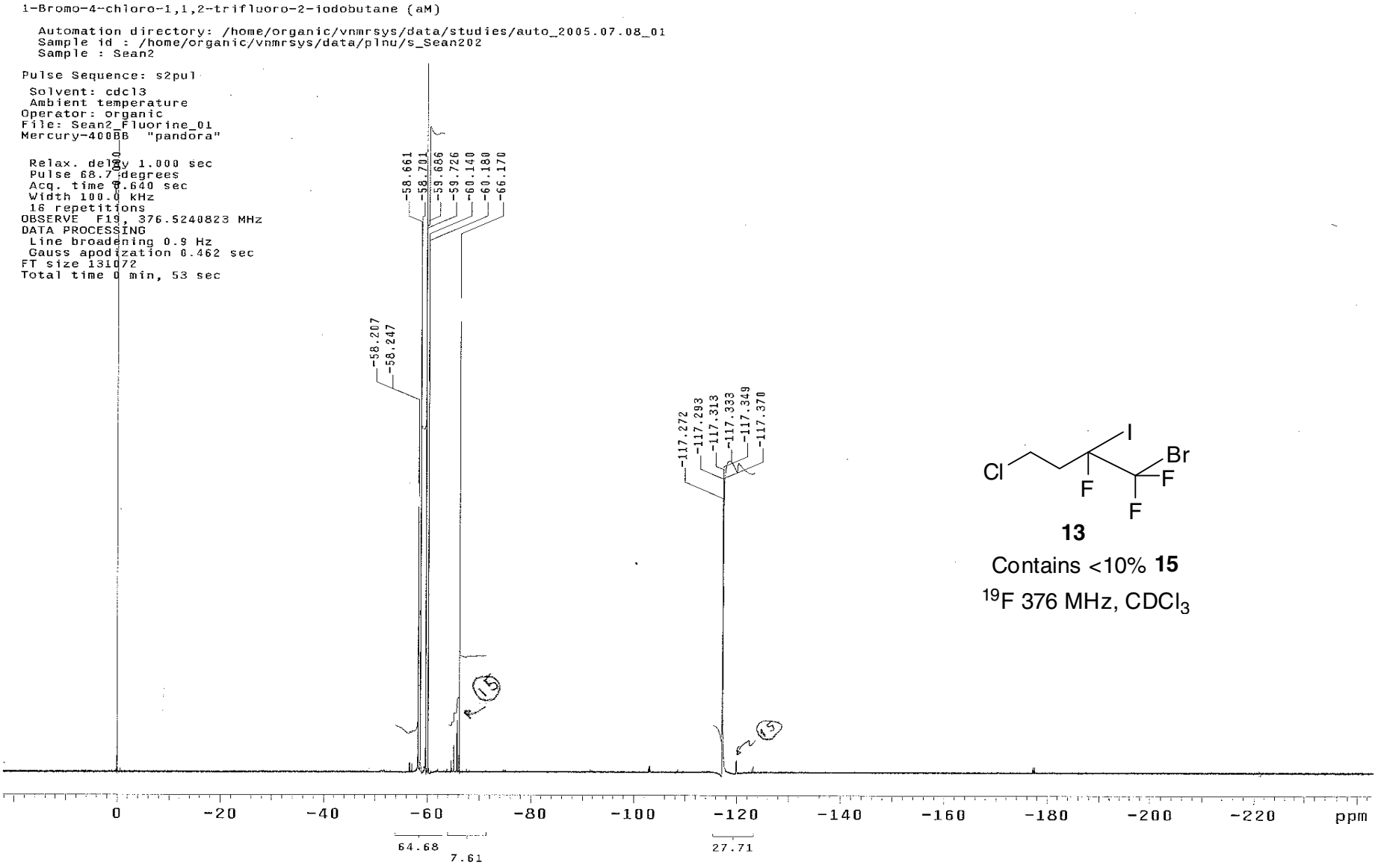
^{13}C 100 MHz, $CDCl_3$



13

Contains <10% **15** that was from Br_2 in the IBr

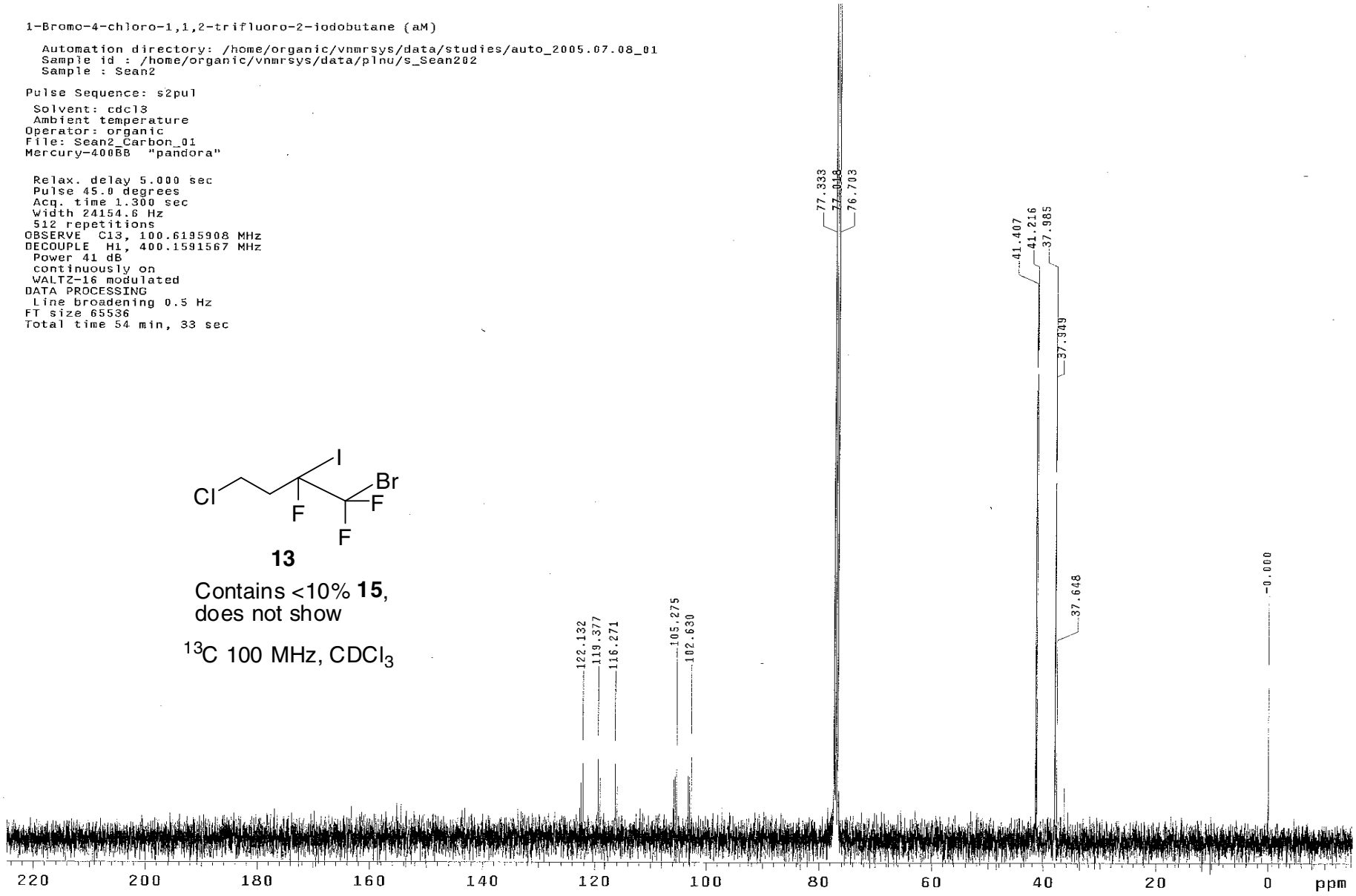
^{1}H 400 MHz, $CDCl_3$



13

Contains <10% **15**

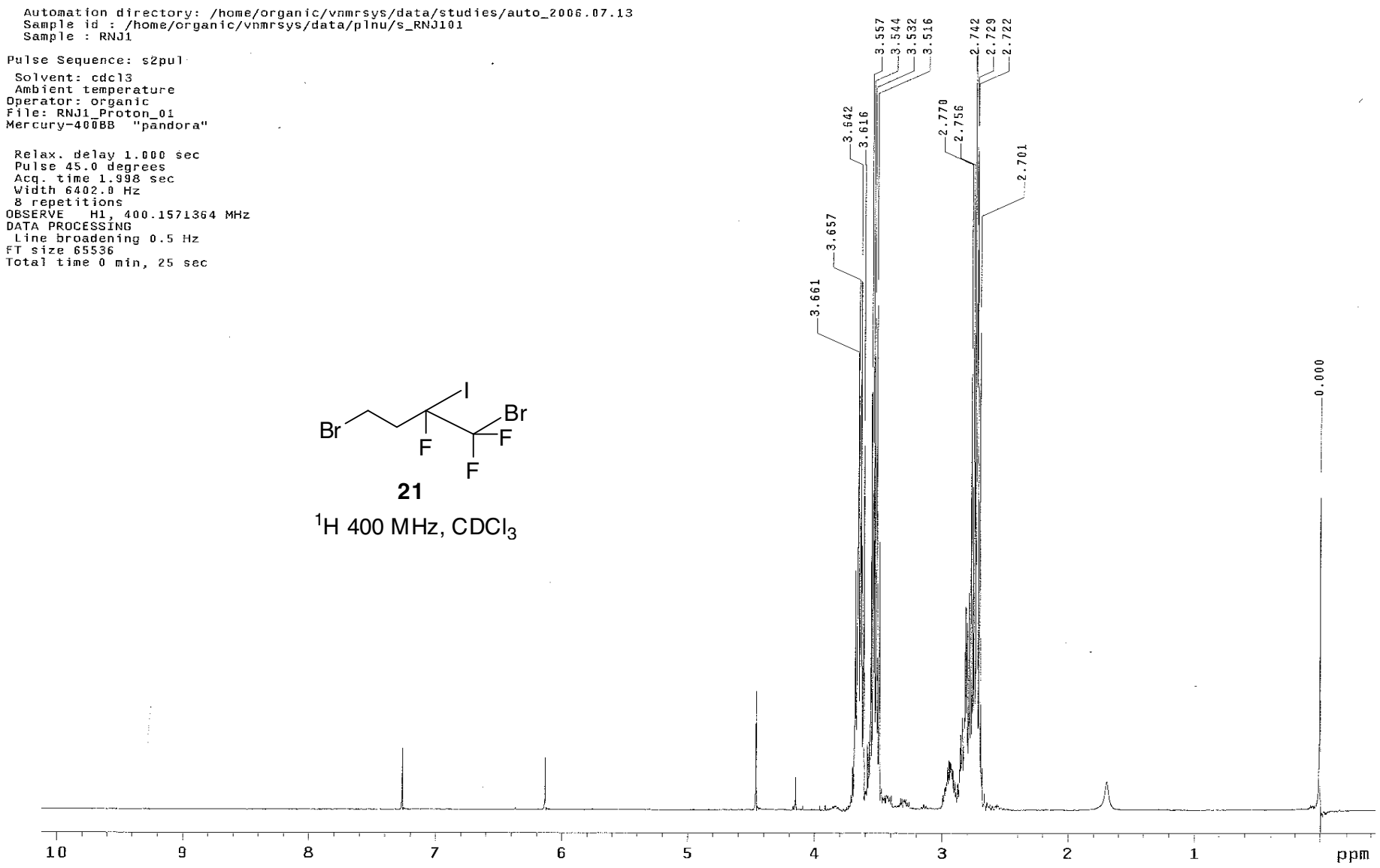
^{19}F 376 MHz, $CDCl_3$



13

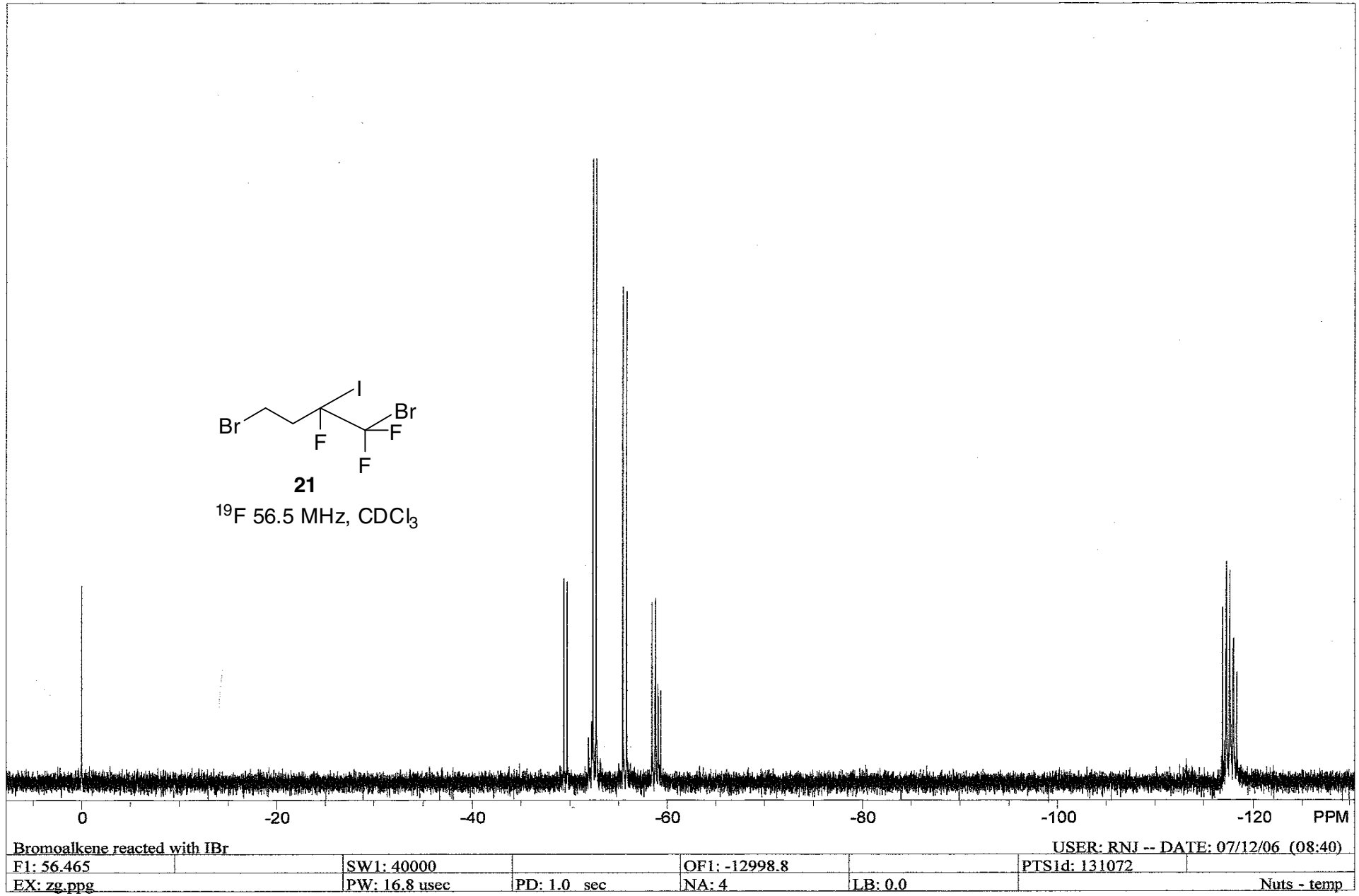
Contains <10% **15**, does not show

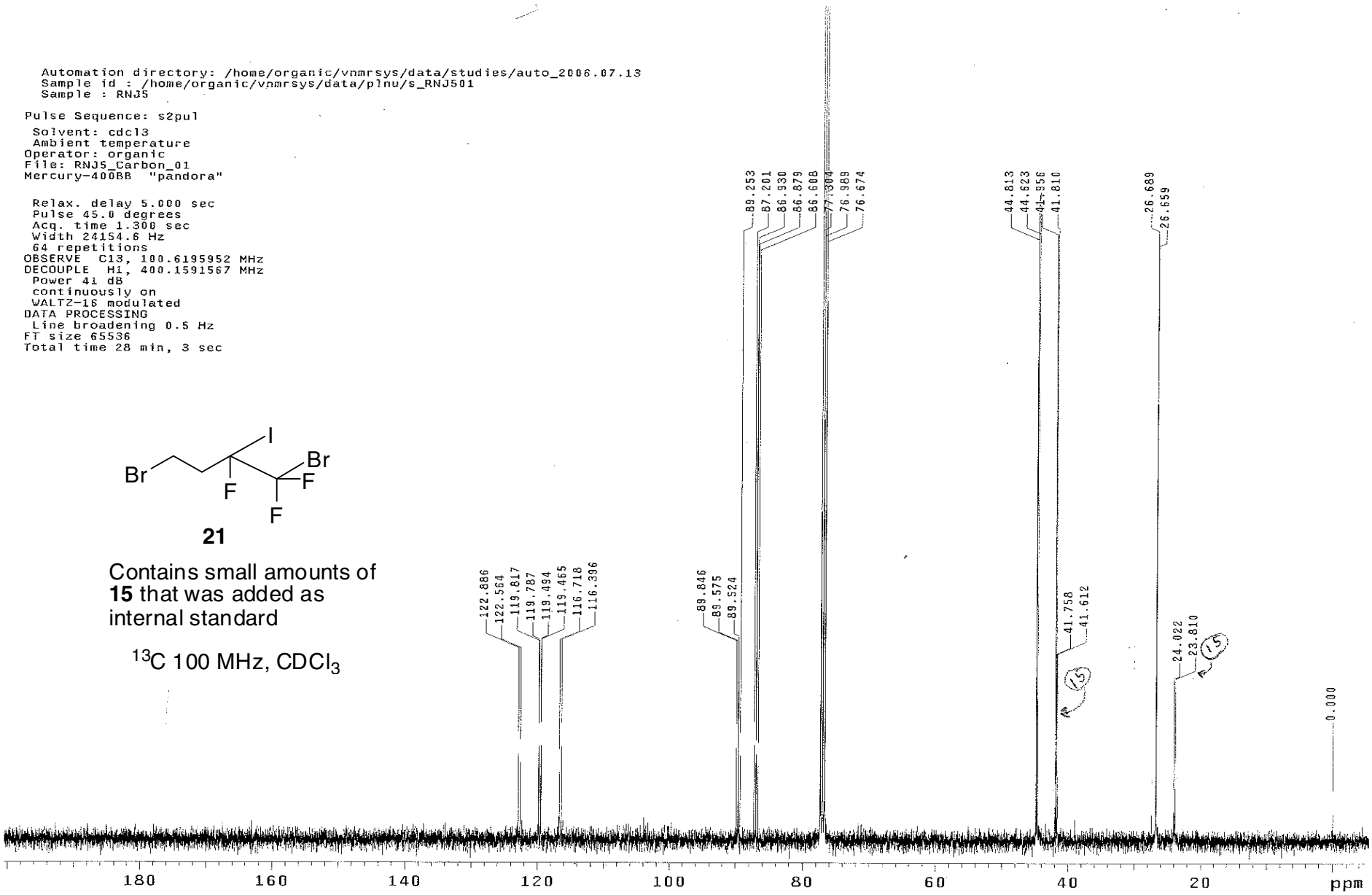
^{13}C 100 MHz, $CDCl_3$



21

^{1}H 400 MHz, $CDCl_3$

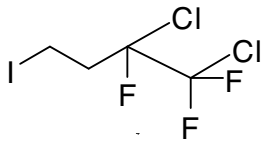

I
Br
Br
F
F
F
21
19F 56.5 MHz, CDCl3
0
-20
-40
-60
-80
-100
-120
PPM
Bromoalkene reacted with IBr
USER: RNJ -- DATE: 07/12/06 (08:40)
F1: 56.465
SW1: 40000
OF1: -12998.8
PTS1d: 131072
EX: zg.ppg
PW: 16.8 usec
PD: 1.0 sec
NA: 4
LB: 0.0
Nuts - temp


Automation directory: /home/organic/vnmrsys/data/studies/auto_2006.07.13
Sample id : /home/organic/vnmrsys/data/plnu/s_RNJ501
Sample : RNJ5
Pulse Sequence: s2pul
Solvent: cdcl3
Ambient temperature
Operator: organic
File: RNJ5_Carbon_01
Mercury-400BB "pandora"
Relax. delay 5.000 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 24154.6 Hz
64 repetitions
OBSERVE C13, 100.6195952 MHz
DECOUPLE H1, 400.1591567 MHz
Power 41 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 28 min, 3 sec
Br
I
Br
F
F
F
21
Contains small amounts of 15 that was added as internal standard
13C 100 MHz, CDCl3
122.886
122.564
119.817
119.787
119.494
119.465
116.718
116.396
89.846
89.575
89.524
89.253
87.201
86.930
86.879
86.608
77.304
76.989
76.674
44.813
44.623
41.956
41.810
41.758
41.612
26.689
26.659
24.022
23.810
0.000
180
160
140
120
100
80
60
40
20
ppm

Automation directory: /home/organic/vnmrsys/data/studies/auto_2005.06.16_01
Sample id : /home/organic/vnmrsys/data/plnu/s_sony201
Sample : sony2

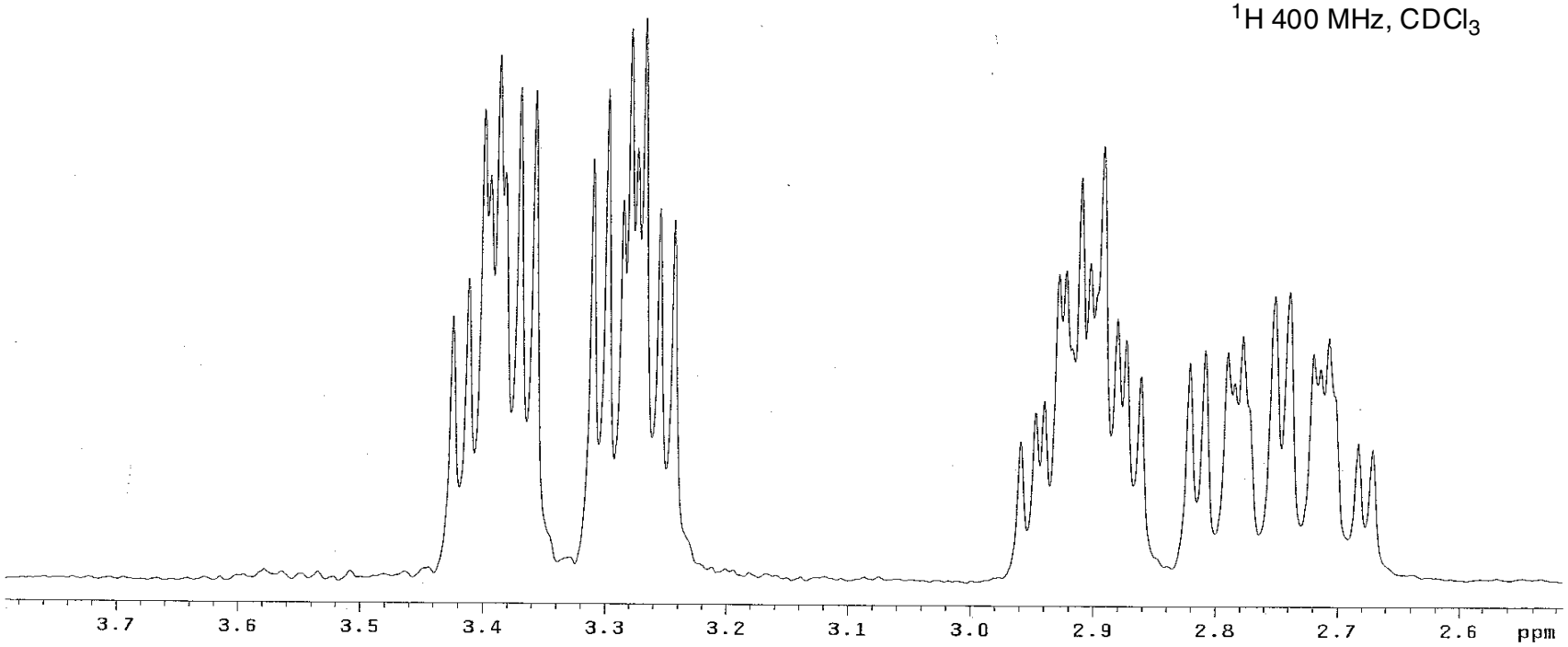
Pulse Sequence: s2pul
Solvent: cdcl3
Ambient temperature
Operator: organic
File: sony2_Proton_01
Mercury-400BB "pandora"

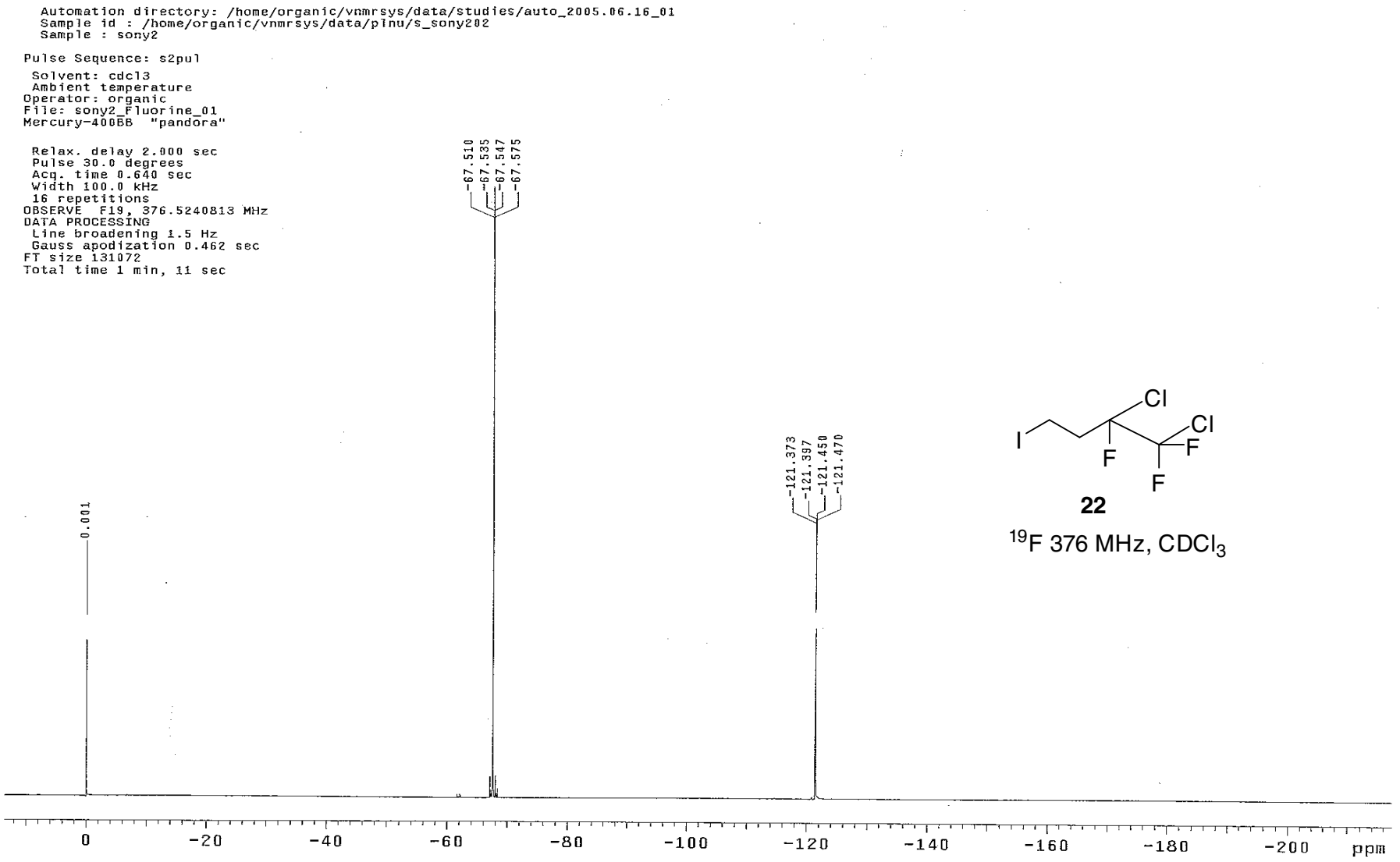
Relax. delay 2.000 sec
Pulse 45.0 degrees
Acq. time 4.000 sec
Width 6402.0 Hz
8 repetitions
OBSERVE H1, 400.1571350 MHz
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 0 min, 51 sec



22

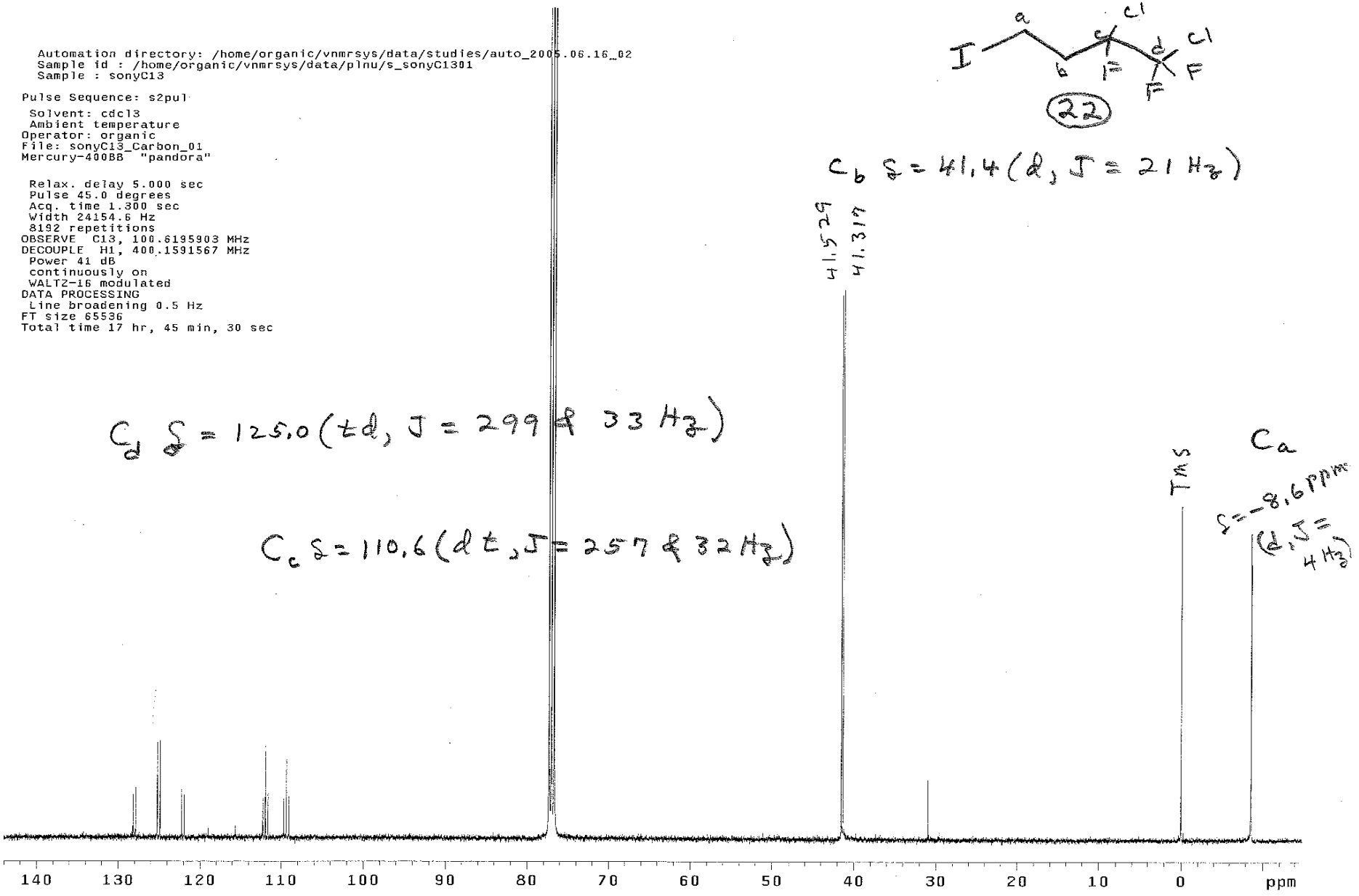
^{1}H 400 MHz, $CDCl_3$

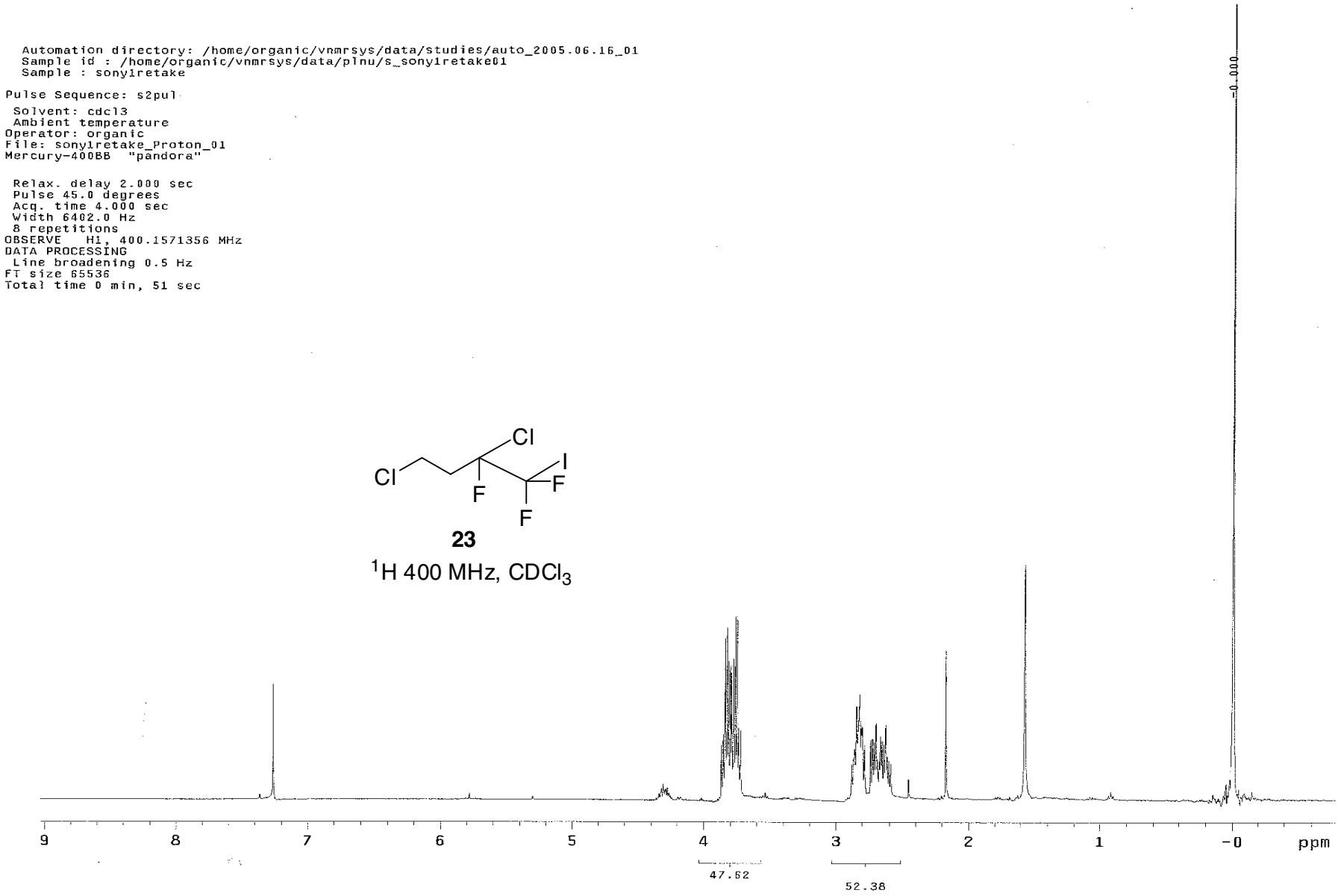


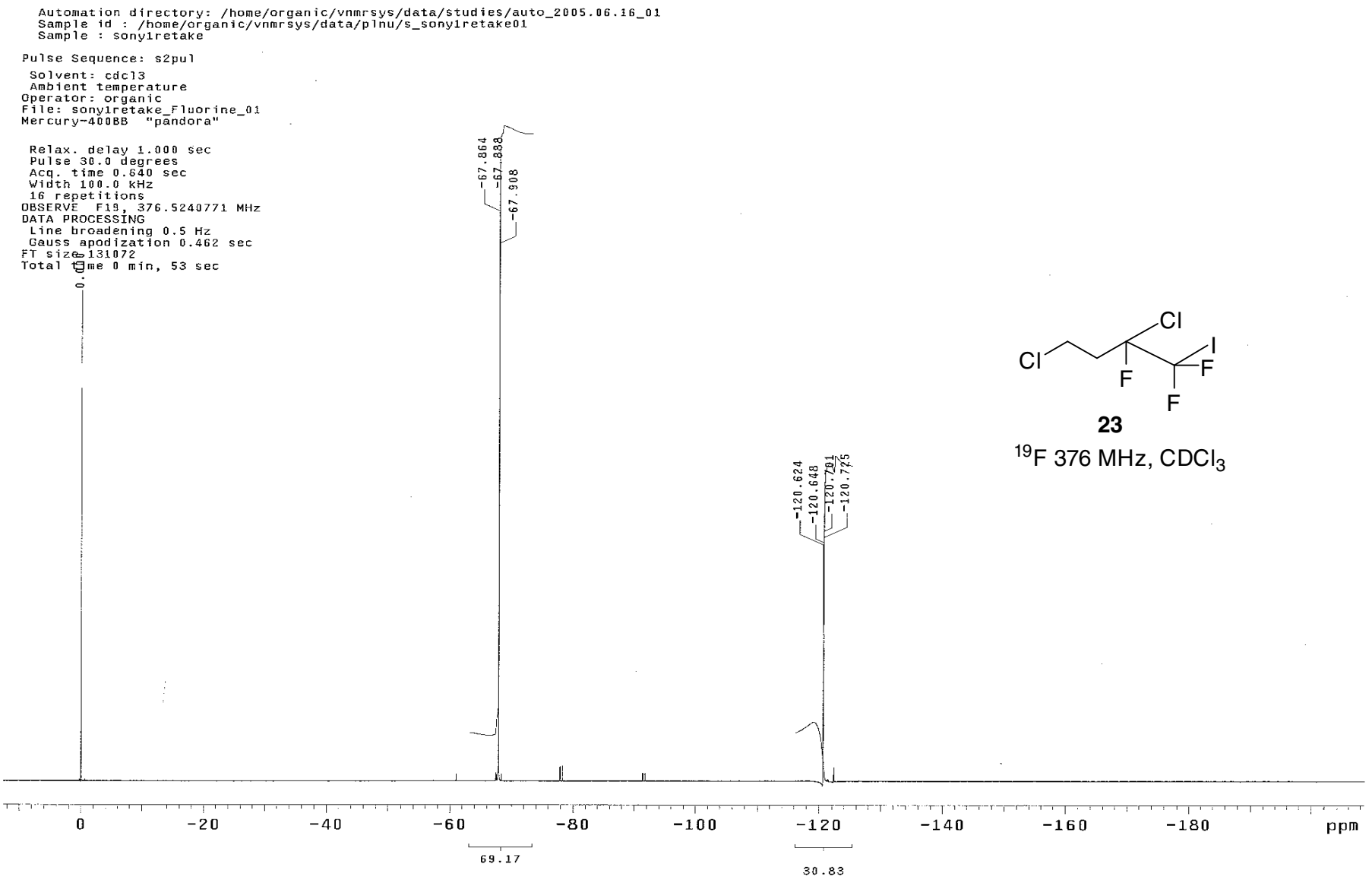


22

^{19}F 376 MHz, $CDCl_3$

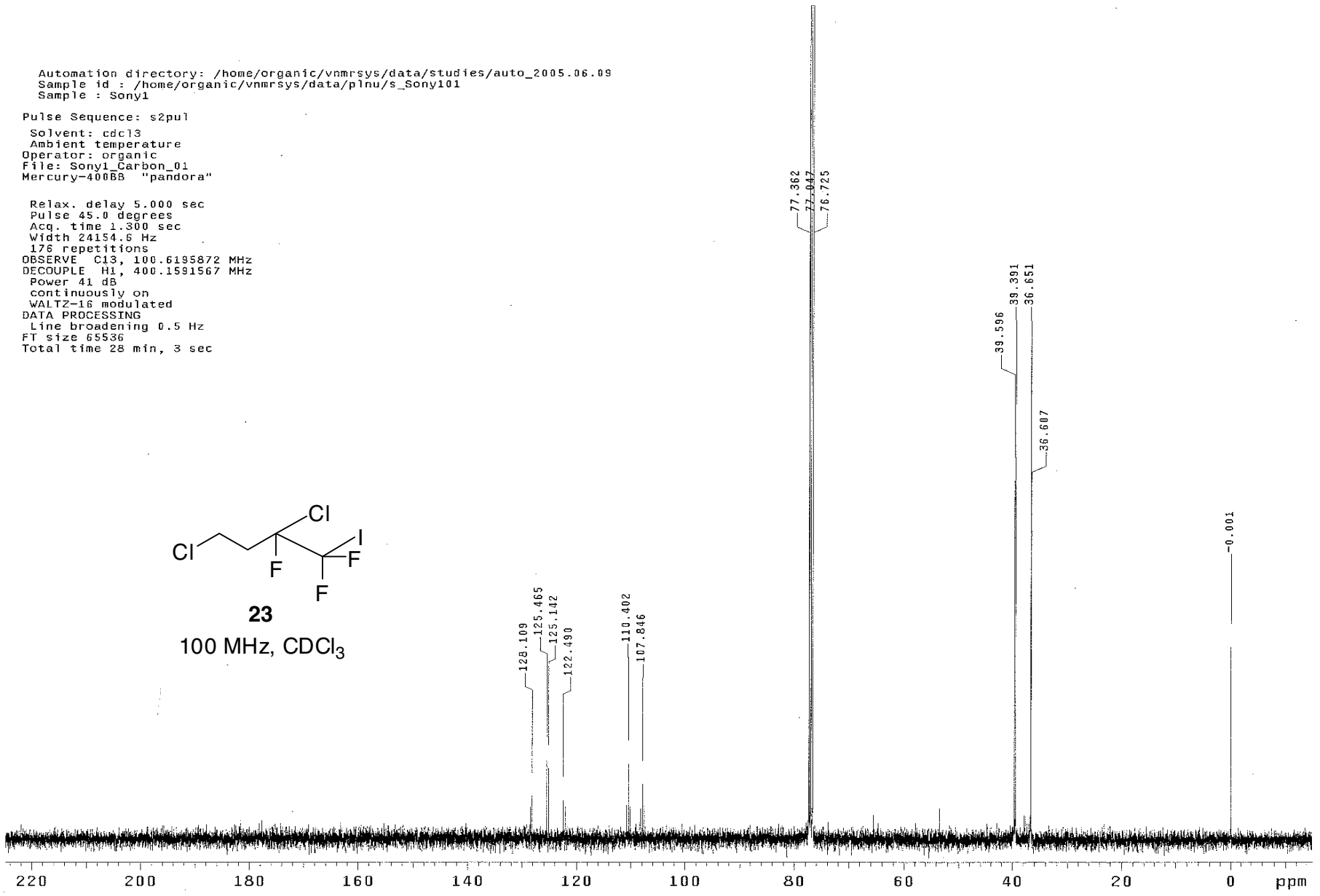

Automation directory: /home/organic/vnmrsys/data/studies/auto_2005.06.16_02
Sample id : /home/organic/vnmrsys/data/plnu/s_sonyC1301
Sample : sonyC13
Pulse Sequence: s2pul
Solvent: cdcl3
Ambient temperature
Operator: organic
File: sonyC13_Carbon_01
Mercury-400BB "pandora"
Relax. delay 5.000 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 24154.6 Hz
8192 repetitions
OBSERVE C13, 100.6195903 MHz
DECOUPLE H1, 400.1591567 MHz
Power 41 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 17 hr, 45 min, 30 sec
I
a
b
c
d
Cl
Cl
F
F
22
C_b δ = 41.4 (d, J = 21 Hz)
41.529
41.317
C_d δ = 125.0 (td, J = 299 & 33 Hz)
C_c δ = 110.6 (dt, J = 257 & 32 Hz)
TMS
C_a
δ = -8.6 ppm
(d, J = 4 Hz)
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


Automation directory: /home/organic/vnmrsys/data/studies/auto_2005.06.16_01
Sample id : /home/organic/vnmrsys/data/plnu/s_sony1retake01
Sample : sony1retake
Pulse Sequence: s2pul
Solvent: cdcl3
Ambient temperature
Operator: organic
File: sony1retake_Proton_01
Mercury-400BB "pandora"
Relax. delay 2.000 sec
Pulse 45.0 degrees
Acq. time 4.000 sec
Width 6402.0 Hz
8 repetitions
OBSERVE H1, 400.1571356 MHz
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 0 min, 51 sec
Cl
Cl
I
F
F
F
23
1H 400 MHz, CDCl3
-0.000
9
8
7
6
5
4
3
2
1
-0
ppm
47.62
52.38



23

^{19}F 376 MHz, $CDCl_3$

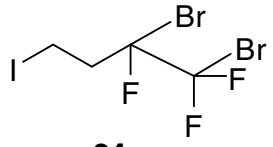

Automation directory: /home/organic/vnmrsys/data/studies/auto_2005.06.09
Sample id : /home/organic/vnmrsys/data/plnu/s_Sony101
Sample : Sony1
Pulse Sequence: s2pul
Solvent: cdcl3
Ambient temperature
Operator: organic
File: Sony1_Carbon_01
Mercury-400BB "pandora"
Relax. delay 5.000 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 24154.6 Hz
176 repetitions
OBSERVE C13, 100.6195872 MHz
DECOUPLE H1, 400.1591567 MHz
Power 41 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 28 min, 3 sec
77.362
77.047
76.725
39.596
39.391
36.651
36.607
-0.001
128.109
125.465
125.142
122.490
110.402
107.846
Cl
Cl
F
F
F
I
23
100 MHz, CDCl3
220
200
180
160
140
120
100
80
60
40
20
0
ppm

1,2-Dibromo-1,1,2-trifluoro-4-iodobutane

Automation directory: /home/organic/vnmrsys/data/studies/auto_2005.07.08
Sample id : /home/organic/vnmrsys/data/plnu/s_SONY301
Sample : SONY3

Pulse Sequence: s2pul
Solvent: cdcl3
Ambient temperature
Operator: organic
File: SONY3_Proton_01
Mercury-400BB "pandora"

Relax. delay 2.000 sec
Pulse 45.0 degrees
Acq. time 4.000 sec
Width 6402.0 Hz
8 repetitions
OBSERVE H1, 400.1571350 MHz
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 0 min, 51 sec



24

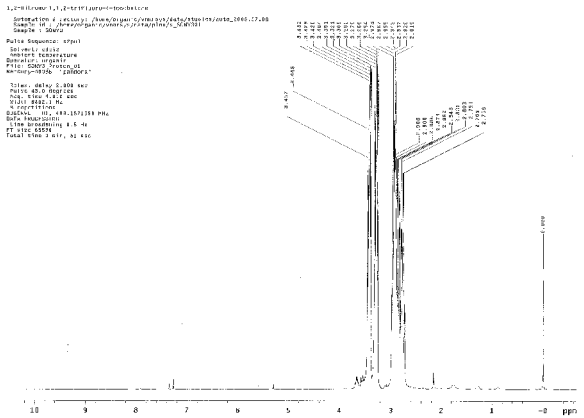
^{1}H 400 MHz, $CDCl_3$

1,2-Dibromo-1,1,2-trifluoro-4-iodobutane

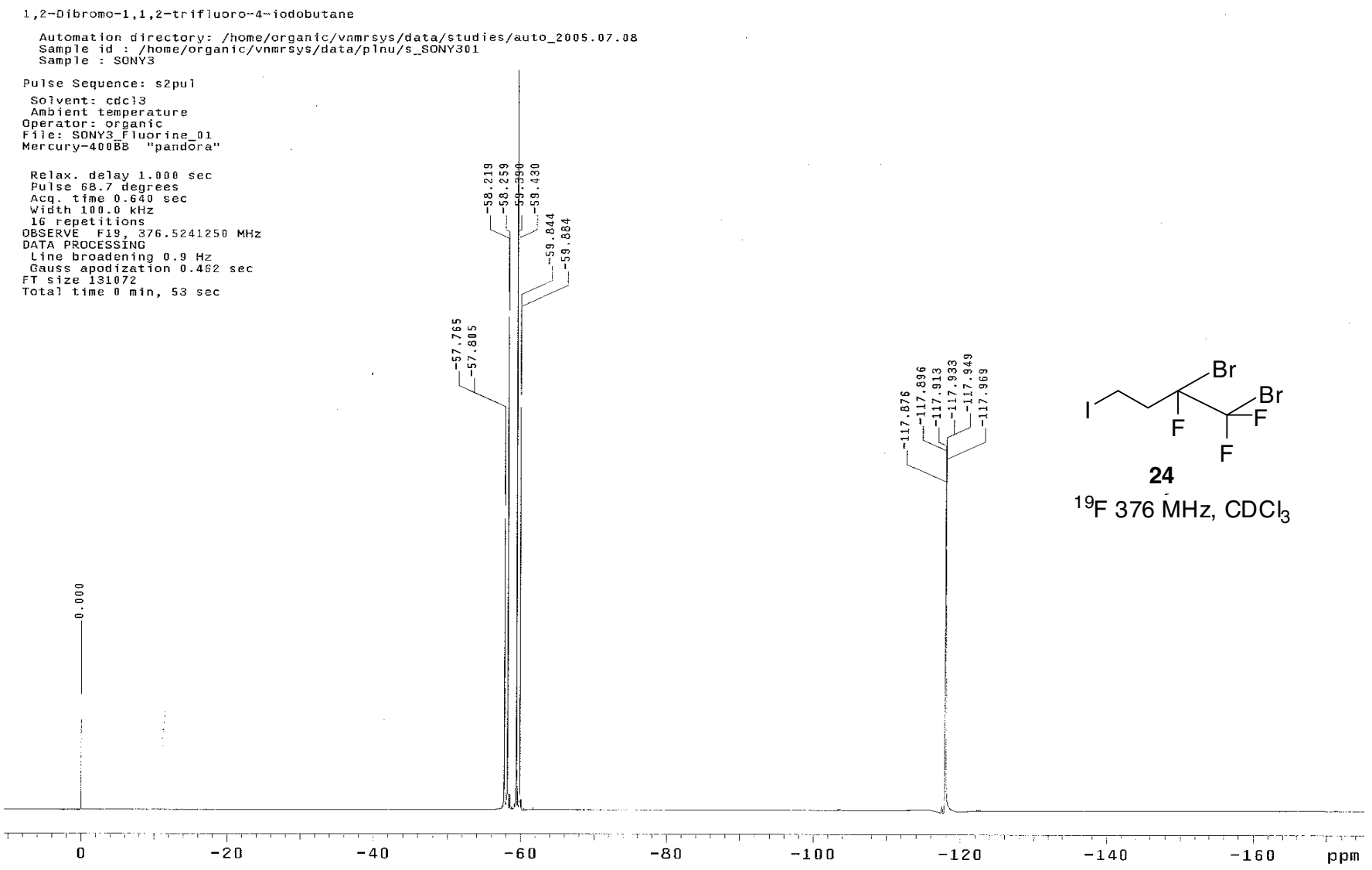
Automation directory: /home/organic/vnmrsys/data/studies/auto_2005.07.08
Sample id : /home/organic/vnmrsys/data/plnu/s_SONY301
Sample : SONY3

Pulse Sequence: s2pul
Solvent: cdcl3
Ambient temperature
Operator: organic
File: SONY3_Proton_01
Mercury-400BB "pandora"

Relax. delay 2.000 sec
Pulse 45.0 degrees
Acq. time 4.000 sec
Width 6402.0 Hz
8 repetitions
OBSERVE H1, 400.1571350 MHz
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 0 min, 51 sec



24



24

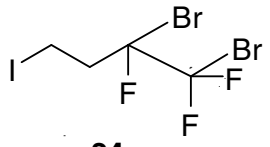
^{19}F 376 MHz, $CDCl_3$

1,2-Dibromo-1,1,2-trifluoro-4-iodobutane

Automation directory: /home/organic/vnmrsys/data/studies/auto_2005.07.08
Sample id : /home/organic/vnmrsys/data/plnu/s_SONY301
Sample : SONY3

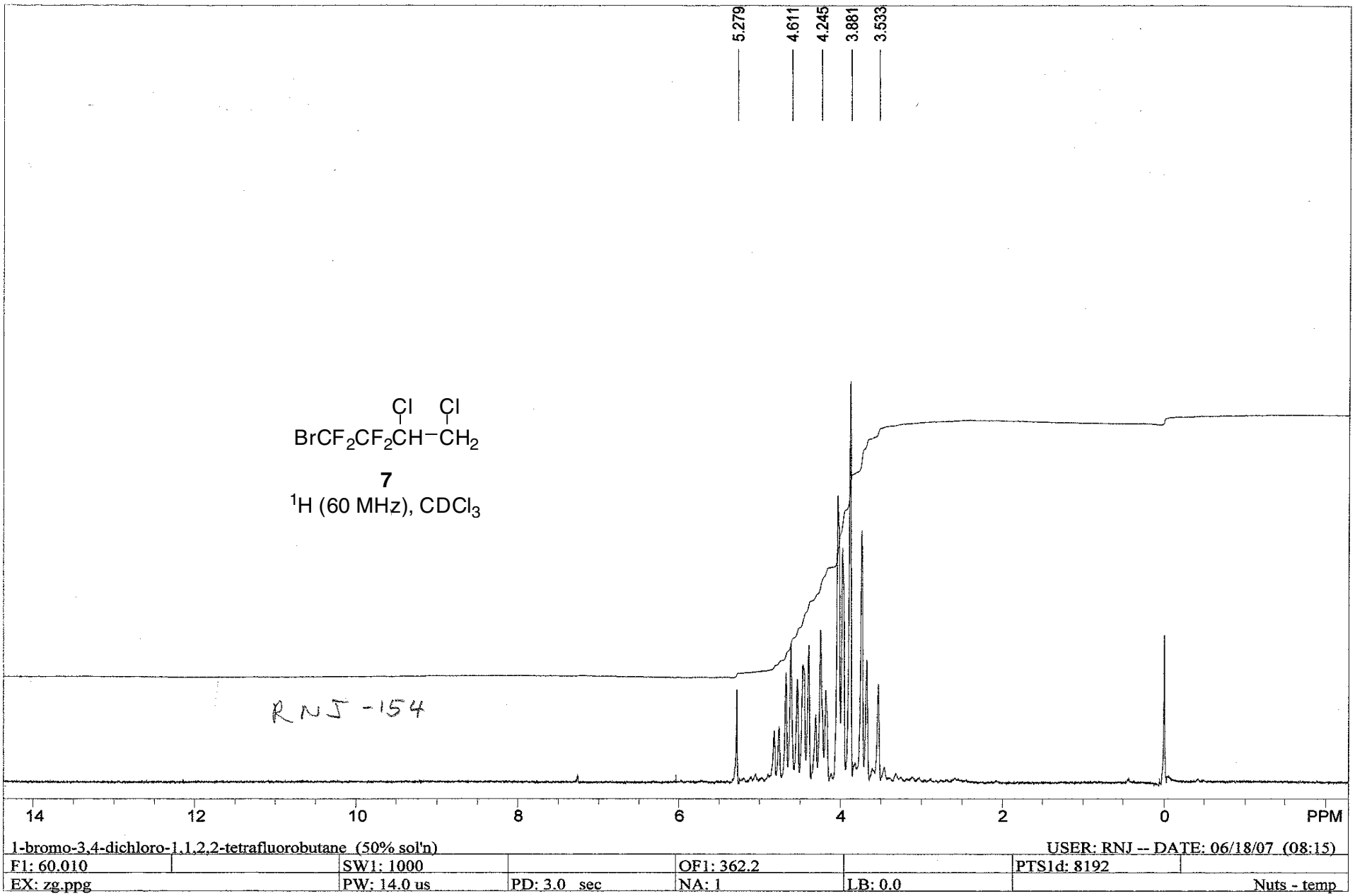
Pulse Sequence: s2pul
Solvent: cdcl3
Ambient temperature
Operator: organic
File: SONY3_Carbon_01
Mercury-400BB "pandora"

Relax. delay 5.000 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 24154.6 Hz
192 repetitions
OBSERVE C13, 100.6195683 MHz
DECOUPLE H1, 400.1591567 MHz
Power 41 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 27 min, 16 sec

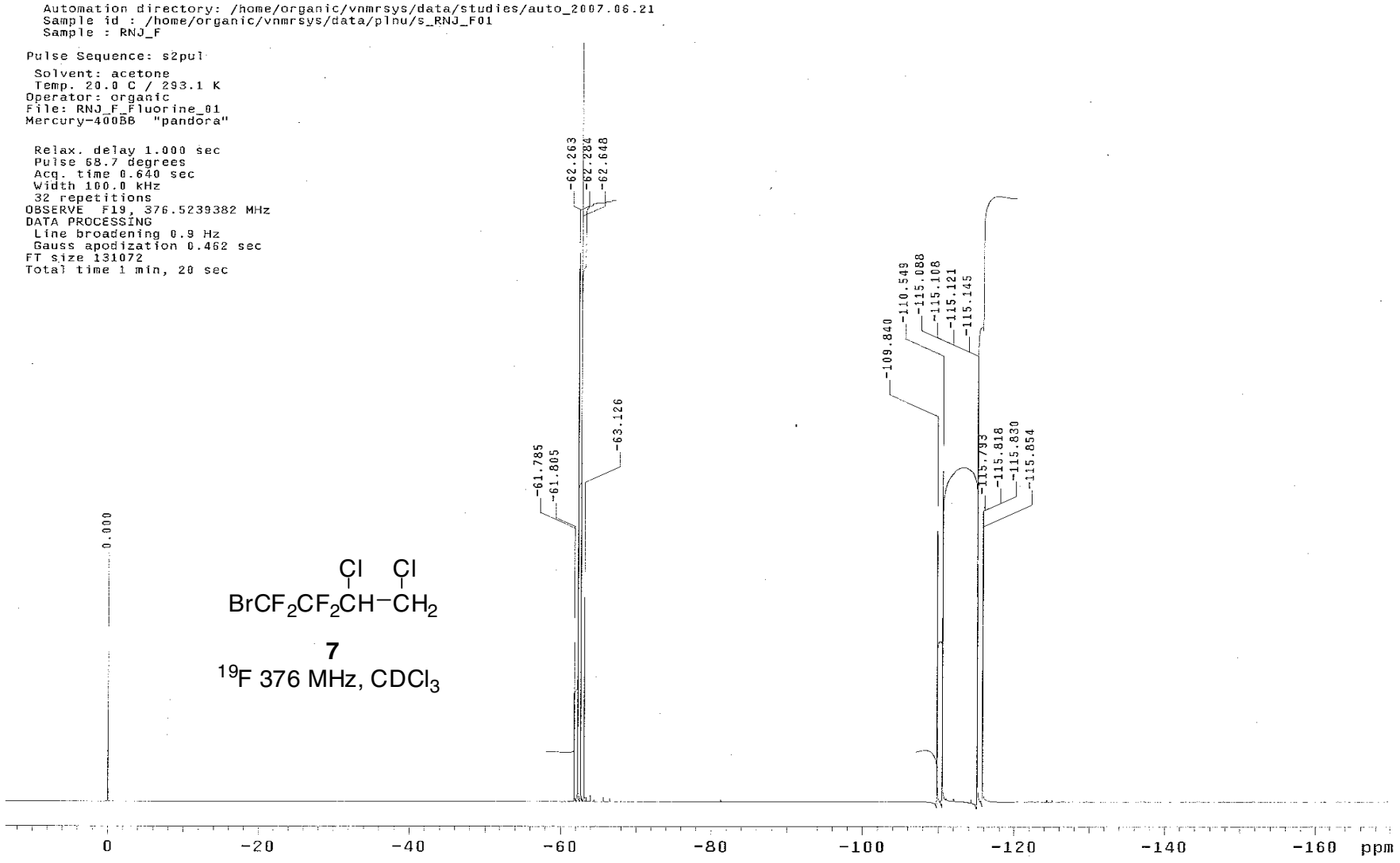


24

^{13}C 100 MHz, $CDCl_3$

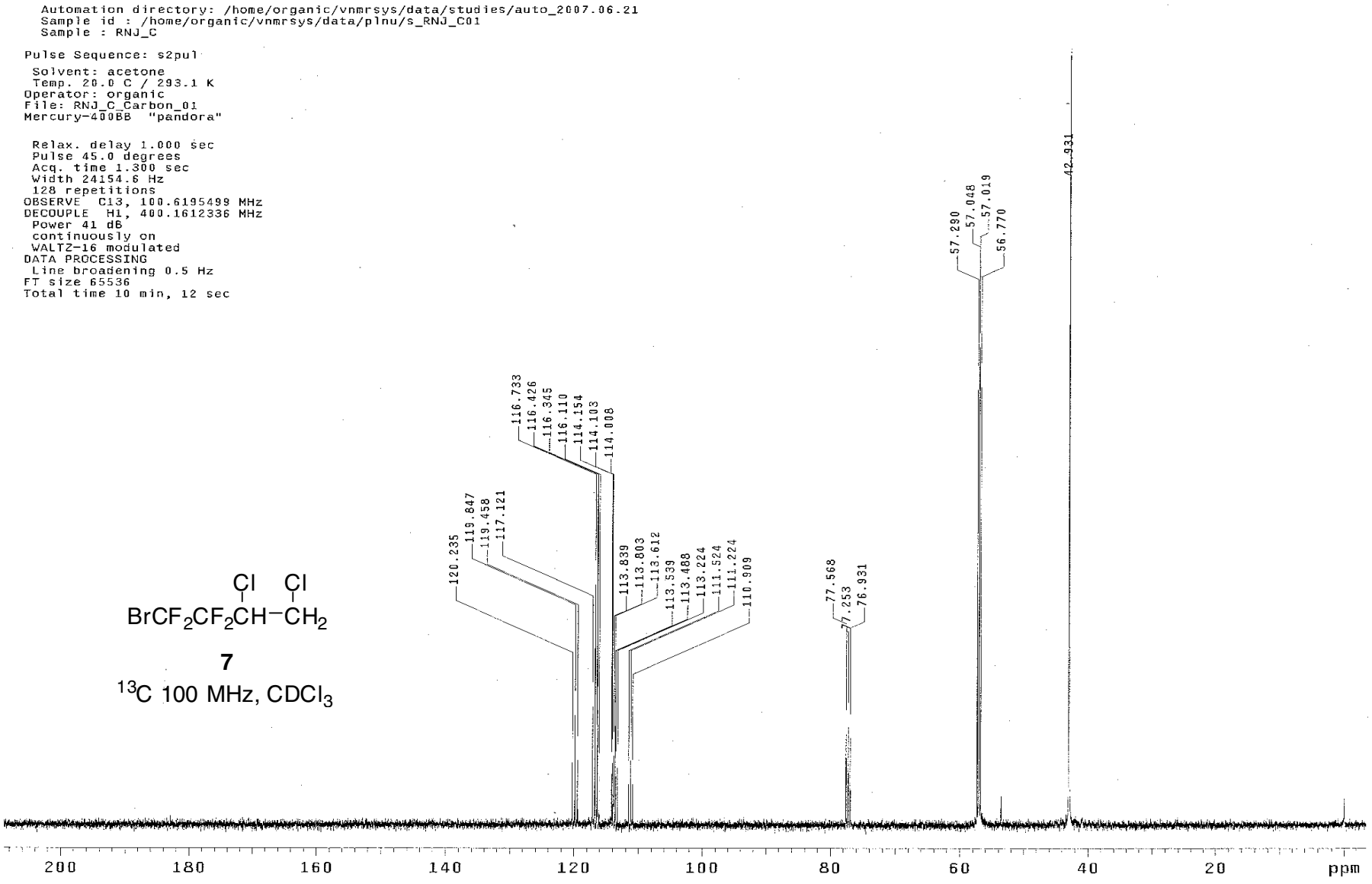

5.279
4.611
4.245
3.881
3.533
Cl Cl
BrCF2CF2CH−CH2
7
1H (60 MHz), CDCl3
RNJ -154
14
12
10
8
6
4
2
0
PPM
1-bromo-3,4-dichloro-1,1,2,2-tetrafluorobutane (50% sol'n)
USER: RNJ -- DATE: 06/18/07 (08:15)
F1: 60.010
SW1: 1000
OF1: 362.2
PTS1d: 8192
EX: zg.ppg
PW: 14.0 us
PD: 3.0 sec
NA: 1
LB: 0.0
Nuts - temp

RNJ 154



7

^{19}F 376 MHz, $CDCl_3$



$BrCF_2CF_2\underset{Cl}{CH}-\underset{Cl}{CH_2}$

7

^{13}C 100 MHz, $CDCl_3$

5. Product Characterization

Compound **8** was commercially available and **16** was characterized in the literature.[2,3] We identified **14**, **15**, **18** and **19** in an earlier paper.[1]

(a) *Converting Products* **24**, **22**, **14**, **10** *and* **11** by *S_N2 Reactions*.

Some products were converted to known compounds by S_N2 reactions replacing the number 4-halogen substituent. The following reaction is representative.

To 394 mg (1.00 mmol) **24** in 1.0 mL dry DMSO was added 462 mg (3.00 mmol) tetramethylammonium bromide (TMABr). The mixture was heated to 90ºC for four hours and **15**[1] was formed in 35 percent yield by GC with **14** as internal standard.

Similarly (**compound → product**, nucleophile, solvent, temperature, time, percent yield).

14 → 8, tetramethylammonium chloride, DMSO, 25º, 2 hours, 68% by GC with **15** as internal standard.

22 → 14, TMABr, DMSO, 90º, 5 hours, converted 10% of **22** into **14** as determined by GC with **15** as internal standard. Similarly **23** was converted to **18**.

A 1.0:2.7 mixture of **10**:**11**, TMABr, DMSO, 25º, 4 days, 20% of **10** and **11** were converted to a mixture of **16** and **17** as determined by GC with **14** as internal standard.

All products were confirmed by GC/MS

(b) *Independent Synthesis. S_N2 Conversion of Known Compounds **14** and **15** to **22** and **24**.*

To 130 mg (0.50 mmol) **14**[1] in 0.5 mL dry acetone was added 204 mg (1.5 mmol) lithium iodide. The mixture was refluxed for 20 hours and **22** was formed in 90 percent yield by GC with **15** as internal standard.

Similarly, 346 mg (1.00 mmol) **15**[1] with 462 mg (3.00) mmol) lithium iodide in 1.0 mL acetone refluxed overnight gave **24** in 100 percent yield by GC with **14** as internal standard.

(b) *Independent Synthesis of 1,4-Dibromo-2-chloro-1,1,2-trifluorobutane* (**16**).

To 2.23g (0.010 mol) 4-bromo-3-chloro-3,4,4-trifluorobutene-1 was added dropwise 10.0 mL 1.0M boron-tetrahydrofuran complex. The mixture was stirred for 1 hour at room temperature. Aqueous sodium hydroxide (6.0 mL of 3.0 M) was slowly added to the stirred mixture followed by 6.0 mL 30% hydrogen peroxide. The reaction mixture was heated to 45-50º for 1 hour, then extracted with methylene chloride, dried over anhyd. magnesium sulfate and concentrated. Distillation (bp 60-62º at 40 Torr.) gave 0.50g (20%) 4-bromo-3-chloro-3,4,4-trifluorobutan-1-ol.

To 120 mg (0.50 mmol) the alcohol in 0.10 mL benzene and 20 microliter pyridine was added 36 mg (0.133 mmol) phosphorous tribromide. The reaction was stirred at room temperature for 2 days. 1,4-Dibromo-2-chloro-1,1,2-trifluorobutane (**16**) was formed in 85% yield as determined by gas chromatography with **15** as internal standard. The GC/MS data were identical to data we obtained for **16** from reaction BrCl with alkene **2**. Literature NMR data[3] are consistent with our spectra.

6. Preparative Scale Reactions to Synthesize 1-Bromo-3,4-dichloro-1,1,2,2-tetrafluorobutane (7).

(a) The ionic reaction of Cl_2 with alkene **6**, was very slow. Compound **7** was prepared by a free-radical reaction as follows. To 5.13g (0.0248 mol) alkene **6** at 0ºC in 3.0 mL methylene chloride and illumination with a 300 watt sun lamp was slowly bubbled Cl_2 gas. The reaction was followed by GC and the solvent removed under vacuum when completed. Distillation gave 2.33g (0.0084 mol) 34% **7** bp 89-90º at 100 Torr. See Tables S1 and S2 for characterization.

Preparative Scale Reactions for Pure Internal Standards. Synthesis of:

(b) *4-Bromo-1,2-dichloro-1,1,2-trifluorobutane* **(14).** Chlorine gas was slowly bubbled into 4.92g (0.0260 mol) alkene **2** at 0ºC in 3.0 mL methylene chloride until the alkene was consumed. Distillation gave 3.80g (0.0146 mol) **14** in 56 percent yield that was 98 percent pure by GC (bp 64-5º at 35 Torr.) Spectral data were identical to those we reported ealier.[1]

(c) *Synthesis of 1,2,4-Tribromo-1,1,2-trifluorobutane* (**15**). Bromine 4.16g (0.0260 mol) in 3.0 ml methylene chloride was added slowly to 4.92g (0.0260 mol) alkene **2** in 2.0 ml methylene chloride at room temperature. Distillation gave 7.30g (0.0210 mol) **15** in 81 percent yield that was 98-99 percent pure by GC (bp 84-5º at 23 Torr.). Spectral data were identical to our data reported earlier.[1]

7. Reactions of 2-Fluorooct-1-ene

(a) *Hydrolysis***.** To 0.85 mL 70% perchloric acid and 0.35 mL formic acid in a 10 mL round bottom flask fitted with a reflux condenser was added 110 mg (1.00 mmol) 2-fluorooct-1-ene. The stirred mixture was refluxed vigorously for 10 minutes and then allowed to cool. Water (1.0 mL) was added followed by extraction with 0.8 mL deuterochloroform containing 0.1 mmol anisol as internal standard. The organic extract was washed with aqueous sodium bicarbonate, dried over anhyd. magnesium sulfate. 2-Octanone, confirmed by GC/MS with a commercial sample, was obtained in 25 percent yield by NMR analysis.

(b) *1-Chloromethyl-4-fluoro-1,4-diazoniabicyclo [2,2,2] octane bis(tetrafluoroborate), [F-TEDA-BF_4].* To 0.9 mL acetonitrile and 0.1 mL water in an apparatus as described above in (a) was added 110 mg (1.00 mmol) 2-fluorooct-1-ene and 354 mg (1.0 mmol) F-TEDA-BF_4. The stirred mixture was heated to 60ºC for 18 hours. Aqueous work-up above gave a 10 percent yield of 1-fluoro-2-octanone with spectral data similar to that reported in the literature.[4]

8. Reference:

1. Shellhamer, D.F.; Allen, J.L.; Allen, R.D.; Gleason, D.C.; O'Neil Schlosser, C.; Powers, B.J.; Probst, J.W.; Rhodes, M.C.; Ryan, A.J.; Titterington, P.K.; Vaughan, G.G. and Heasley, V.L.; *J. Org. Chem.*, **2003**, *68*, 3932.

2. Tarrant, P. and Gillman, E.G.; *J. Am. Chem. Soc.*, **1954**, *76*, 5423.

3. Hinton, J.F.; Jaques, L.W.; *J. Mag. Res.*, **1975**, *17*, 95.

4. Prakash, G.K.S.; Hu, J. and Olah, G.A.; J. Fluorine Chem., 2001, 112, 357. Tomoya, K.; Asai, M.; Lin, T.J. and Takashi; *ibid.*, **1978**, *35*, 477.