Reaction of Chlorosulfonyl Isocyanate with Fluorosubstituted Alkenes Evidence of a Concerted Pathway

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Reaction of Chlorosulfonyl Isocyanate (CSI) with Fluorosubstituted Alkenes: Evidence of a Concerted Pathway for Reaction of CSI with Fluorosubstituted Alkenes (PREPRINT)

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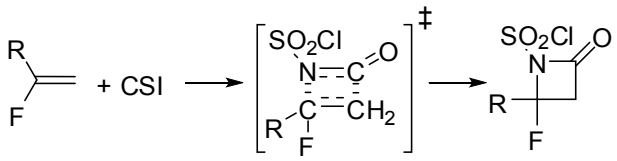
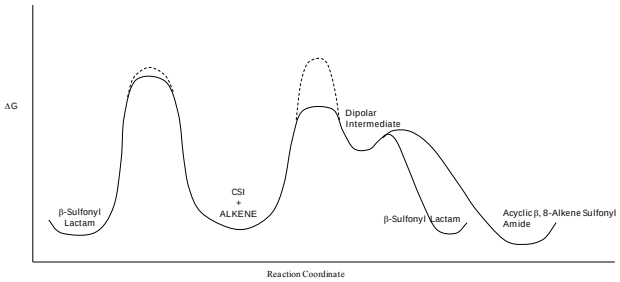


Abstract: Concerted reactions are indicated for the electrophilic addition of chlorosulfonyl isocyanate with monofluoroalkenes. A vinyl fluorine atom on an alkene raises the energy of a step-wise transition state more than the energy of the competing concerted pathway. This energy shift induces CSI to react with monofluoroalkenes by a one-step process. The low reactivity of CSI with monofluoroalkenes, stereospecific reactions, the absence of 2:1 uracil products with neat fluoroalkenes and quantum chemical calculations support a concerted pathway.

Introduction: Chlorosulfonyl isocyanate (CSI) is the most reactive and versatile isocyanate.[1] CSI reacts with alkenes to give chlorosulfonyl *beta*-lactams that are readily reduced to beta-lactams.[2,3] This reaction sequence provides a synthetic route to beta-lactam antibiotics.[4] Fluorine in *beta*-lactam antibiotics have the fluorine atom attached to the periphery of the compound while the *beta*-lactam ring, the location which interacts with Penicillin binding proteins and *beta*-lactamases, remains unchanged. We demonstrate here a method to synthesize this new class of compounds with the fluorine located on the *beta*-lactam ring.

Reactions of CSI with hydrocarbon alkenes are reported to proceed through an open-ion dipolar intermediate.[1,3,5] Moriconi suggests that some 1,2-disubsituted olefins retain stereochemistry through fast collapse of the dipolar intermediate.[3,5] *Ab* initio calculations show that [2 + 2] cycloadditions between alkenes and isocyanates can react via a concerted transition state with zwitterionic character.[6] These calculations also found that electron-donating groups on the alkene, or electron-withdrawing groups on the isocyanate, lower the activation energy and induce the nature of the reaction to become more synchronous.[6] Calculations also support a concerted process for the cycloaddition of isocyanates with aldehydes.[7] Quantum chemical calculations and photoelectron spectral data show that substituting a hydrogen with a fluorine atom on the pi-bond of an alkene does not significantly alter the molecular energy of the pi-bond;[8] and therefore, the HOMO and LUMO orbital energies for a concerted pathway should not be altered either. On the other hand, the energy for a dipolar stepwise pathway is raised significantly by the vinyl fluorine atom through its strong inductive effect.[9] This perturbation of the Free Energy profile is described in Figure 1 where the fluorine atom raises the transition state energy significantly for the step-wise process, but it only increases the energy of the concerted pathway by a modest amount. In Figure 1 the solid line represents the energy profile for hydrocarbon alkenes while the dashed line describes the pathway for monofluoroalkenes. Therefore, alkenes with a vinyl fluorine atom may allow a concerted process to compete with or completely dominate the step-wise pathway. Both concerted and step-wise pathways might be realized for reactions of CSI with appropriately substituted fluoroalkenes. The product stereochemistry and perhaps even the regiochemistry might be influenced by changing from an open-ion dipolar intermediate compared to a one-step concerted pathway.

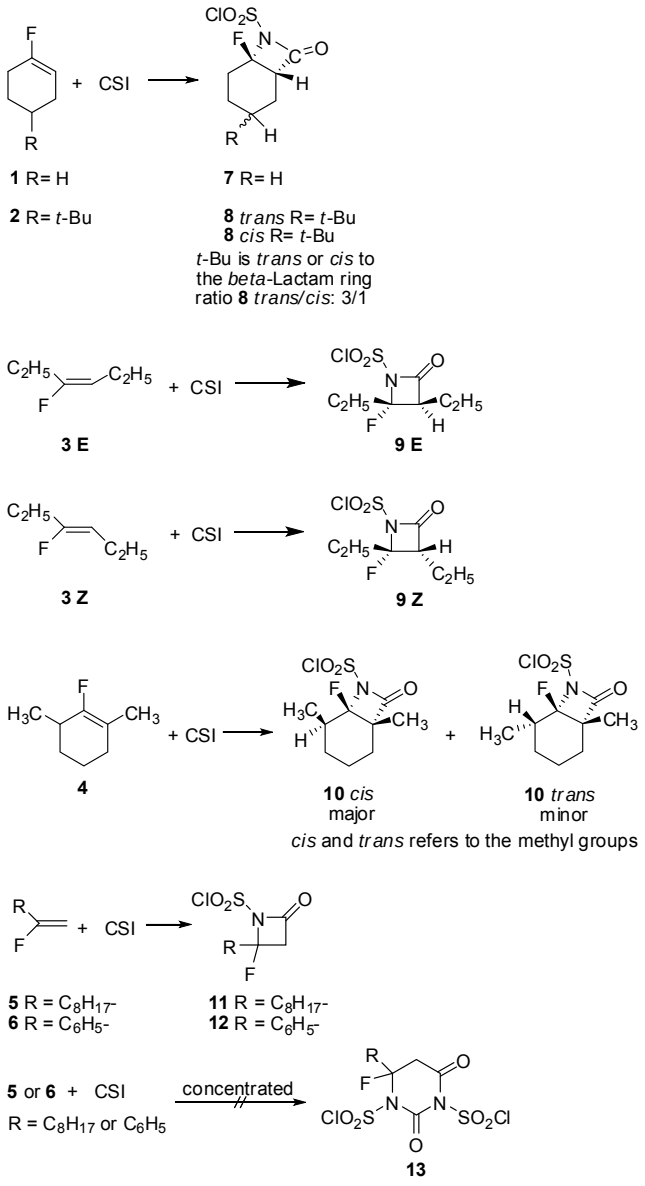
Figure 1
Free Energy Diagram for Reaction of Chlorosulfonyl Isocyanate (CSI) with Hydrocarbon Alkenes and Fluorocarbon Alkenes



Results and Discussion: CSI is a sluggish electrophile and it reacts poorly in solution with alkenes that contain an electron-withdrawing vinyl fluorine[10]. We found that neat reactions of CSI with these less reactive fluoroalkenes proceed smoothly and in good yield. Neat reactions of CSI with these monofluoroalkenes allow for the synthesis of beta-fluorolactams under "Green Chemistry" conditions. Thus, dialkylsubstituted monofluoroalkenes like the 1-fluorocyclohexenes (**1**), (**2**), 3-fluorohex-3-enes **3** (**E**) and **3** (**Z**), and the trialkylsubstituted fluorocyclohexene (**4**) react with CSI to give the chlorosulfonyl *beta*-fluorolactams (**7**), **8** *cis/trans*, **9**(**E**), **9**(**Z**), and **10** *cis/trans*, respectively (Scheme 1). A stereospecific reaction of CSI with **3** (**E**) and **3** (**Z**) is consistent with a concerted process for this series of fluoroalkenes. Product regiochemistry was confirmed by the carbonyl ^{13}C NMR three bond coupling with fluorine (J_{C-F} = 3-

6 Hz). The nitrogen of the *beta*-lactams is bonded to the carbon with the fluorine since the developing positive charge in the concerted transition state prefers to be on the carbon stabilized by back-bond resonance from fluorine.

Scheme 1
(Concerted)

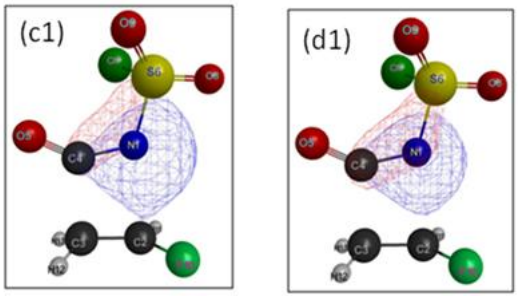


The regiochemistry of the *beta*-sulfonyl fluorolactam products did not change when a third alkyl group was incorporated in fluoroalkene **4** as indicated by the three bond fluorine to carbonyl coupling of 3 Hz in the *beta*-lactams (**10** *cis/trans***)**. Assignment of the carbons from **10** *cis* and **10** ***trans*** were apparent from the magnitude of the carbon-fluorine coupling and from DEPT and HSQC experiments. The ***cis/trans*** stereochemistry of **10** was assigned using a 1-dimension ROESY experiment. Irradiating the upfield methyl adjacent to the carbonyl of the major isomer enhanced the methyl on the methine carbon. Irradiating the upfield methyl of the minor isomer enhanced the methine hydrogen on the minor isomer. Irradiating the methine hydrogen's of each isomer separately confirmed the experiments irradiating the methyl groups above.

Products from 2-fluorodec-1-ene (**5**) and 2-fluoro-2-phenylethene (**6**) decomposed at elevated temperatures. The *beta*-sulfonyl fluorolactams (**11** and **12**) were formed with **5** or **6** and CSI in methylene chloride at room temperature (Scheme 1). At high concentrations of **5** or **6**, approaching the reaction conditions used for fluoroalkenes **1**, **2**, **3** (**E**), **3** (**Z**) and **4**, uracil products **13** were not formed. At these high concentrations we would expect capture of a dipolar intermediate by a second molecule of CSI to give uracil products like those reported for the reaction of CSI with hydrocarbon alkenes that can support stable dipolar intermediates.[1a,2a,11] Thus we suggest that fluoroalkenes **1** through **6** react by a concerted pathway.

Quantum chemical calculations at the MP2/6-311G(d,p) level of theory[12a-e,13] also support our claim of a one-step process for reaction of CSI with fluoroalkenes as described in Figure 1. Transition states for the concerted pathway and a portion of the stepwise pathway were calculated for reaction of CSI with vinyl fluoride (Supporting Information). Intrinsic reaction coordinate calculations were performed to trace the minimum energy paths connecting the transition states to the corresponding local minima; i.e., reactants and products. The step-wise transition state, which is 60.9 kcal/mol above separated CSI + fluoroethene reactants, was found to be 26.6 kcal/mol higher in energy than the concerted transition state (34.3 kcal/mol above reactants.) The concerted transition state is not orthogonal as reported for ketene cycloadditions where the orbitals mix by a $[\pi^2(s) + \pi^2(a)]$ process[14] A six electron process, involving the lone pair on nitrogen represented as ω^2 $[\pi^2(s) + \pi^2(s) + \omega^2(s)]$, would allow for a concerted cyclization where the alkene carbon atoms and the O=C=N- moiety of CSI are in the same plane. Calculated localized molecular orbitals of the cyclic 2+2 transition state for the cycloaddition of CSI to vinyl fluoride show significant mixing between the C-N pi bond in CSI and the nitrogen lone pair electrons (Figure 2).

Figure 2



(c1) are the electrons of the C-N pi bond. (d1) the lone pair electrons of the nitrogen atom.

Our data support a concerted reaction of CSI with these less reactive fluoroalkenes because:

(1) Reactions with **3** (**E**) and **3** (**Z**) are stereospecific.

(2) Neat reactions of CSI with **1**, **2**, **3** (**E**), **3** (**Z**) **4**, **5**, and **6** do not give uracil products.

(3) A concerted pathway is supported by quantum chemical calculations.

We are investigating the parameters that seem to influence a change of mechanism for reactions of fluoroalkenes with CSI.

Experimental Section: Diethylaminosulfur trifluoride was added to cyclohexanones in methylene chloride to give mixtures of 1,1-difluorocyclohexanes and 1-fluorocyclohexenes. After water work-up, the methylene chloride was removed by distillation and the mixture was distilled through a vigreux column to give enriched 1-fluorocyclohexenes **1**, **2** and **4** containing various amounts of 1,1-difluorocyclohexanes. Acyclic fluoroalkenes **3E**[15], **3Z**[15] and **5**[15], **6**[16] were prepared as described in the literature. The products were isolated by chromatography (column or preparative thin layer), or in one case by crystallization. The following procedure is representative.

To 156 mg (1.00 mmol) 4-*tert*-butyl-1-fluorocyclohexene (**4**) in a small round bottom flask was added 155 mg, 96 microliter (1.10 mmol) chlorosulfonyl isocyanate (CSI). The stirred mixture was heated to 65-70^{o} C for one hour and then cooled. Methylene chloride (2-3 mL) was added, followed by dropwise addition of ice water. The organic layer was separated and the aqueous layer extracted with methylene chloride. The combined organic extractions were washed with 2 % aqueous sodium bicarbonate, dried over anhyd. magnesium sulfate and concentrated. ^{19}F NMR analysis on the crude mixture showed **8** *cis*/*trans* to be formed in a ratio of 1.0/3.0, respectively. Column chromatography (10 g silica gel) of the crude mixture with hexanes/chloroform gave a 194 mg, 65%, of pure **8** *cis*/**8** *trans* in a ratio of 1.0/2.6 respectively. Reactions of fluoroalkenes **1**, **2**, **3E**, **3Z** with CSI were done similarly. Spectral and exact mass data are listed in the **Supporting Information** section.

CSI (1.10 mmol) was added to fluoroalkenes **5** or **6** (1.00 mmol) in 0.2 to 4 mL methylene chloride at 0^{o} C. The mixture was allowed to warm to room temperature and then stirred for four hours. Work-up was accomplished as described above for the reactions with **5** and **6**. Product **11** was obtained 90% pure (^{19}F NMR) by preparative TLC while product **12** was isolated by crystallization from ether. Crystals from **12** decomposed in several minutes at room temperature, but were sufficiently stable in solution to obtain spectral data. Wet crystals of **12** were kept cold during transportation for X-Ray analysis at low temperature.

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Supporting Information Avaliable: Spectral data to characterize the products, X-Ray data for **12** and quantum chemical data are available on line at http://pubs.acs.org.

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Supporting Information

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Table of Contents

Tabulated ^{1}H, ^{19}F, and ^{13}C NMR, Infrared, Exact Mass and Isolated Yield Data

7: Isolated (50%) by column chromatography on silica gel with hexanes/methylene chloride. ^{1}H NMR 400 MHz ($CDCl_3$) δ = 1.59-1.72 (m, 3H); 1.81-1.99 (m, 2H); 2.01-2.21 (m, 2H); 2.69-2.80 (m, 1H); 3.52-3.63 (m, 1H). ^{19}F NMR 376 MHz ($CDCl_3$) δ = -112.8 (m). ^{13}C NMR 100.6 MHz ($CDCl_3$). δ = 15.5 (d, *J* = 8 Hz); 16.0 (s); 18.4 (s); 24.7 (d, *J* = 25 Hz); 53.5 (d, *J* = 21 Hz); 102.9 (d, *J* = 248 Hz); 160.1 (d, *J* = 4 Hz). IR (KBr) neat 1832 cm^{-1}. Exact mass $[MH]^+$ calcd. for $C_7H_{10}N)_3FSCl$ 242.00539; found 242.00470.

8 *trans*/*cis***:** Isolated (65%) as a 2.6/1.0 ratio *trans*/*cis* by column chromatography as described above. ^{1}H NMR 400 MHz ($CDCl_3$) δ = 0.89 (s, 9H); 1.20-2.30 (m, 6H); [*trans* 2.55-2.75 (m) and *cis* 2.78-2.90 (m), 1H]; [*cis* 3.50 (m) and *trans* 3.67 (dm, *J* = 13 Hz), 1H]. ^{19}F NMR 376 MHz ($CDCl_3$) *trans* δ = -117.7 (m) and *cis* -114.1 (m), ratio 3/1, respectively on the crude reaction mixture. ^{13}C NMR 100.6 MHz ($CDCl_3$) **8** *trans* δ = 19.2 (d, *J* = 8 Hz); 21.6 (s); 26.4 (d, *J* = 26 Hz); 26.7 (s); 33.2 (s); 40.0 (s); 57.5 (d, *J* = 21 Hz); 105.2 (d, *J* = 248 Hz); 161.7 (d, *J* = 6 Hz). **8** *cis* δ = 21.2 (d, *J* = 9 Hz); 22.9 (s); 26.9 (s); 29.4 (d, *J* = 26 Hz); 32.9 (s); 43.2 (s); 55.5 (d, *J* =22 Hz); 105.1 (d, *J* = 246 Hz); 162.9 (d, *J* = 4 Hz). IR (KBr) neat mixture *trans* 1826 cm^{-1} *cis* 1838 cm^{-1}. Exact mass $[MH]^+$ calcd. for $C_{11}H_{18}NO_3FSCl$ 298.067996; found 298.068000.

9E: Isolated (50%) by column chromatography as described above. ^{1}H NMR 400 MHz ($CDCl_3$) δ = 1.18 (t, *J* = 7.4 Hz, 6H); 1.65-1.98 (m, 2H); 2.03-2.23 (m, 1H); 2.54-2.68 (m, 1H); 3.42-3.52 (m, 1H). ^{19}F NMR 376 MHz ($CDCl_3$) δ = -119.4 (ddd, *J* = 30.5, 13.7 and 9.2 Hz). ^{13}C NMR 100.6 MHz ($CDCl_3$) δ = 7.6 (d, *J* = 4 Hz); 11.6 (s); 18.5 (d, *J* = 2 Hz); 24.7 (d, *J* = 28 Hz; 63.1 (d, *J* = 24 Hz); 108.2 (d, *J* = 247 Hz); 162.2 (d, *J* = 5 Hz). IR (KBr) neat 1830 cm^{-1}. Exact mass $[MH]^+$ calcd. for $C_7H_{12}NO_3FSCl$ 244.0210; found 244.0202.

9Z: Isolated (55%) by column chromatography as described above. ^{1}H NMR 400 MHz ($CDCl_3$) δ = 1.11 (t, *J* = 7.6 Hz, 3H); 1.14 (t, *J* = 7.4 Hz, 3H); 1.78-1.99 (m, 2H); 2.10-2.29 (m, 1H); 2.47-2.60 (m, 1H); 3.36-3.43 (m, 1H). ^{19}F NMR 376 MHz ($CDCl_3$) δ = -137.3 (dt, *J* = 27.5 and 6.9 Hz). ^{13}C NMR 100.6 MHz ($CDCl_3$) δ = 7.8 (d, *J* = 4 Hz); 11.7 (s); 17.7 (d, *J* = 5 Hz); 27.5 (d, *J* = 28 Hz); 60.2 (d, *J* = 22 Hz); 107.6 (d, *J* = 249 Hz); 162.4 (d, *J* = 1.5 Hz). IR (KBr) neat 1833 cm^{-1}. Exact mass, negative ion ESI $[M^+-H]$ calcd. for $C_7H_{10}NO_3FSCl$ 242.0054; found 242.0051.

10 *cis*/*trans***:** *cis* and *trans* refers to the two methyl groups on the cyclohexane ring. Isolated (48%) by column chromatography as described above. ^{1}H NMR 600 MHz (C_6D_6) δ = [*cis* 1.15 (dd, *J* = 7.0 and 1.8 Hz) and *trans* 1.26 (d, *J* = 7.0 Hz, 3H)]; [*trans* 1.30 (d, *J* = 2.9 Hz) and *cis 1.33 (d, J* = 2.9 Hz, 3H); *cis* and *trans* 1.43-1.62 (m, 2H); *cis* and *trans* 1.62-1.73 (m, 2H); *cis* and *trans* 1.80-1.96 (m, 2H); [*cis* 2.26 (m) and *trans* 2.78 (m), 1H]. ^{19}F NMR 376 MHz ($CDCl_3$) *trans* δ = -135.3 (s); *cis* -138.6 (brd. s), ratio of 1.0/1.1, respectively on the crude reaction mixture. ^{13}C NMR 150.8 MHz (C_6H_6) assignments supported by DEPT and HSQC experiments. **10** *cis* δ = 15.2 (CH_3, d, *J* = 8.4 Hz); 16.1 (CH_3, d, *J* = 7.9 Hz); 16.0 (CH_2, s); 26.0 (CH_2, d, *J* = 4.5 Hz); 28.7 (CH_2, s); 31.5 (CH, d, *J* = 24.7 Hz); 59.9 (C adj. to the carbonyl, d, *J* = 20.2 Hz); 108.7 (d, *J* = 256.4 Hz); 166.3 (d, *J* = 2.8 Hz). **10** *trans***:** δ = 14.4 (CH_3, d, *J* = 9.0 Hz); 14.7 (CH_3, d, *J* = 2.8 Hz); 17.1 (CH_2, s); 25.6 (CH_2, d, *J* = 7.3 Hz); 28.8 (CH_2, s); 32.4 (CH, d, *J* = 24.1 Hz); 61.8 (C adj. to the carbonyl, d, *J* = 18.0 Hz); 111.2 (d, *J* = 256.4 Hz); 166.7 (d, *J* = 2.8 Hz). IR (KBr) neat mixture 1834 cm^{-1}. Exact mass, negative ion ESI [M^+-H] calcd. for $C_9H_{12}NO_3FSCl$ 268.0210; found 268.0212.

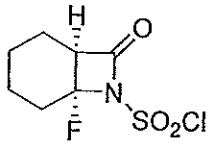
11: Decomposition produced 8% side products during purification by preparative thin layer chromatography on silica gel with chloroform/methanol (95:5). Isolated in 33% yield. ^{1}H NMR 400 MHz ($CDCl_3$) δ = 0.89 (t, *J* = 7.0 Hz, 3H); 1.29 (m, 10H); 1.38-1.62 (m, 2H); 2.06-2.26 (m, 1H); 2.44-2.56 (m, 1H); 3.33-3.48 (m, 2H). ^{19}F NMR 376 MHz ($CDCl_3$) δ = -120.9 (m). The 8% impurity around -131 to -132 ppm is from decomposition during purification by TLC. ^{13}C NMR 100.6 MHz ($CDCl_3$). δ = 14.0 (s); 22.5 (s); 23.5 (s); 23.7 (s); 29.0 (s); 29.1 (d, *J* = 14.0 Hz); 31.7 (s); 48.9 (d, *J* = 25.1 Hz); 76.8 (d, *J* = 4.8 Hz); 105.7 (d, *J* = 246.1 Hz); 158.6 (d, *J* = 3.0 Hz). IR (KBr) neat 1831 cm^{-1}. Exact mass, negative ion ESI [M^+-H] calcd. for $C_{11}H_{18}NO_3FSCl$ 298.0680; found 298.0716.

12: Yield (65%) by ^{19}F NMR with 4-fluoroanisole as internal standard. ^{1}H NMR 400 MHz ($CDCl_3$) δ = 3.62-3.85 (m, 2H); 7.51 (m, 3H); 7.61 (m, 2H). ^{19}F NMR 376 MHz ($CDCl_3$) δ = -129.0 (t, *J* = 10.5 Hz). ^{13}C NMR 100.6 MHz ($CDCl_3$). δ = 53.4 (d, *J* = 25 Hz); 103.7 (d, *J* = 246 Hz); 125.2 (d, *J* = 8 Hz); 129.2 (s); 130.9 (s); 132.0 (d, *J* = 29 Hz); 158.9 (d, *J* = 2 Hz). IR (KBr) neat 1834 cm^{-1}.

Automation directory: /home/organic/vnmrsys/data/studies/auto_2008.06.13_01
Sample id : /home/organic/vnmrsys/data/plnu/s_DMH29_C01
Sample : DMH29_C

Pulse Sequence: s2pul
Solvent: d2o
Ambient temperature
Operator: plnu
File: DMH29_C_Carbon_01
Mercury-400BB "pandora.scst.sandiego.edu"

Relax. delay 5.000 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 24154.6 Hz
128 repetitions
OBSERVE C13, 100.6198270 MHz
DECOUPLE H1, 400.1601851 MHz
Power 41 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 1 hr, 49 min, 38 sec



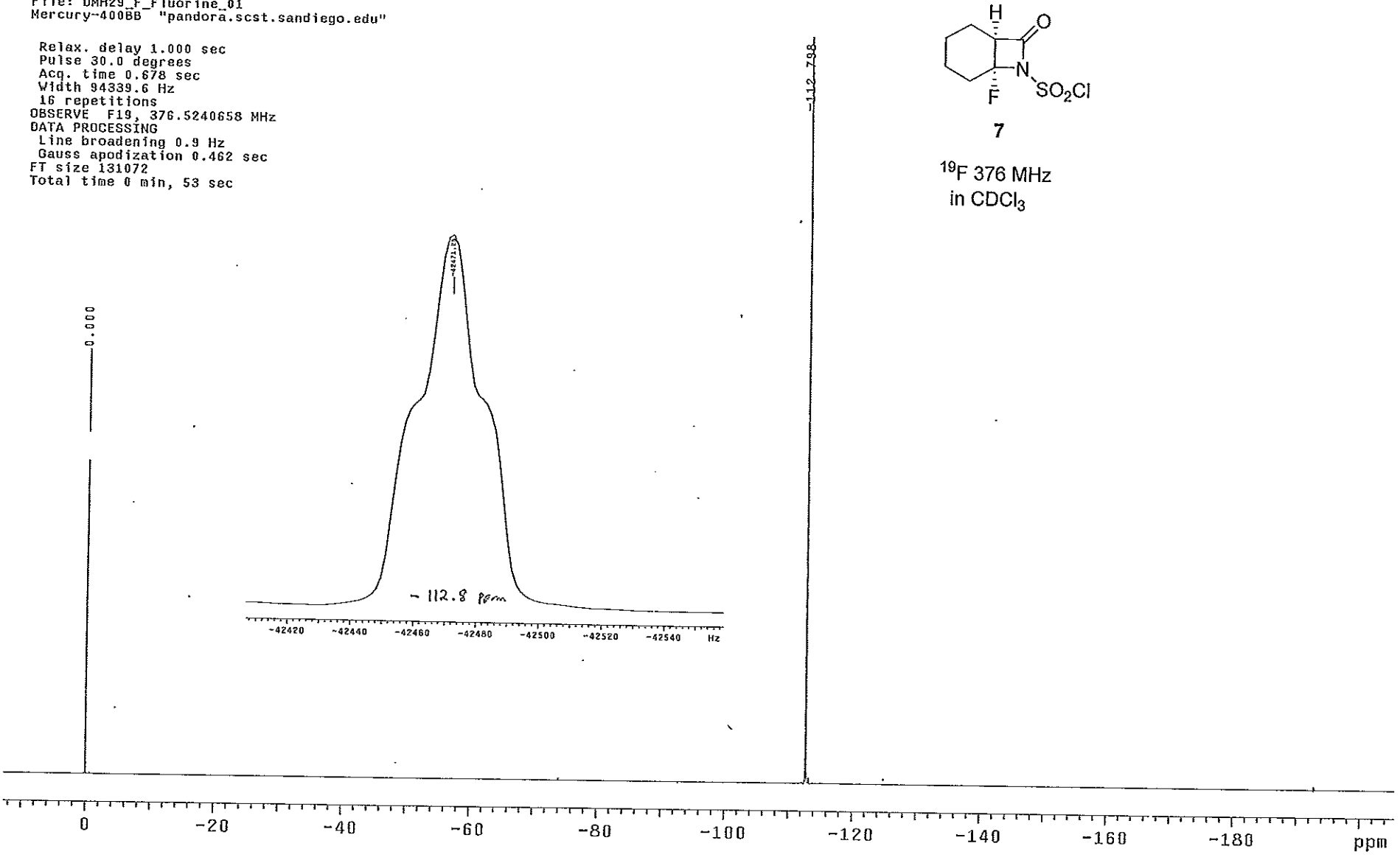
7

^{13}C 100.6 MHz
in $CDCl_3$

Automation directory: /home/organic/vnmrsys/data/studies/auto_2008.06.13_01
Sample id : /home/organic/vnmrsys/data/plnu/s_DMH29_F01
Sample : DMH29_F

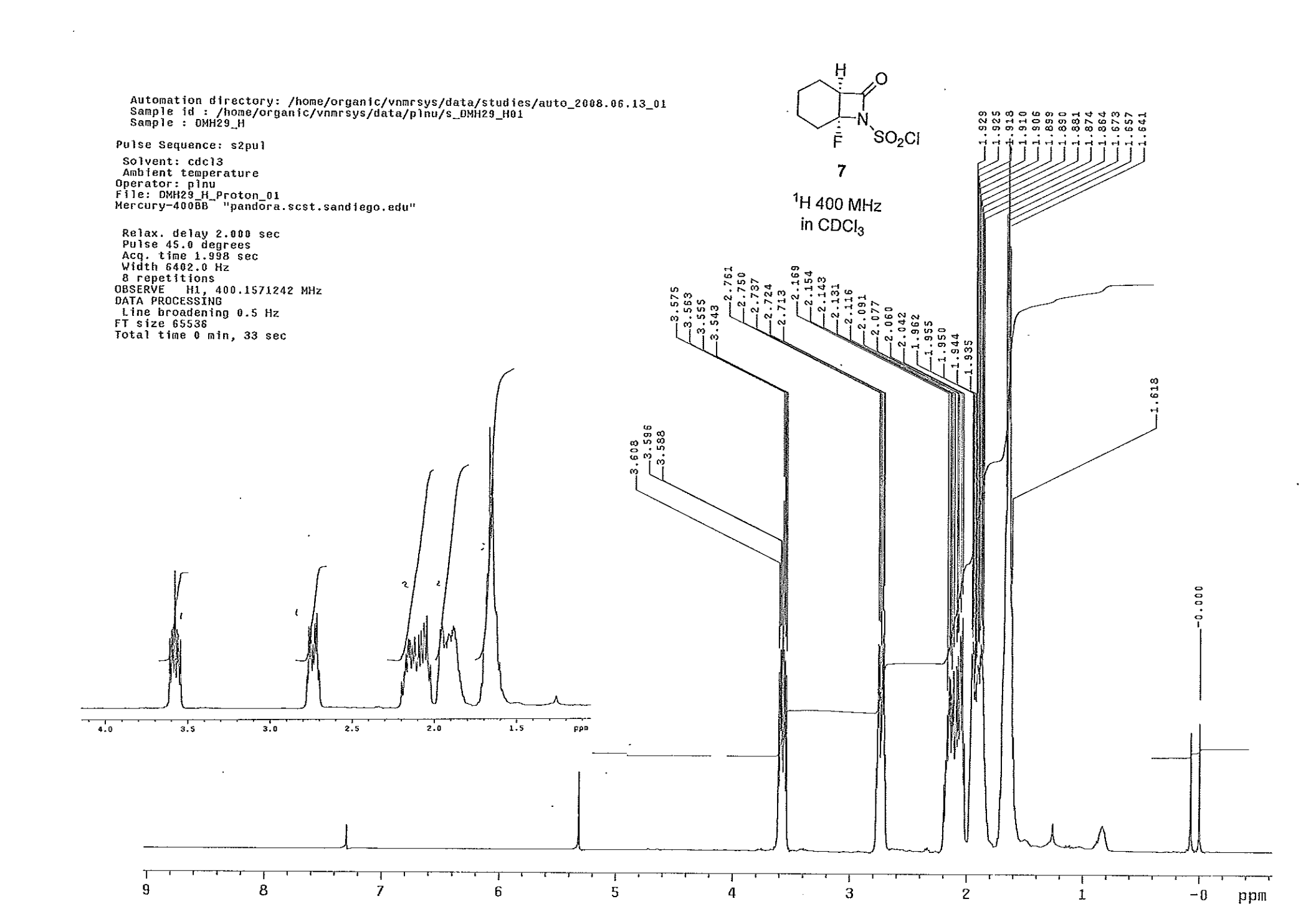
Pulse Sequence: s2pul
Solvent: d2o
Ambient temperature
Operator: plnu
File: DMH29_F_Fluorine_01
Mercury-400BB "pandora.scst.sandiego.edu"

Relax. delay 1.000 sec
Pulse 30.0 degrees
Acq. time 0.678 sec
Width 94339.6 Hz
16 repetitions
OBSERVE F19, 376.5240658 MHz
DATA PROCESSING
Line broadening 0.9 Hz
Gauss apodization 0.462 sec
FT size 131072
Total time 0 min, 53 sec



7

^{19}F 376 MHz
in $CDCl_3$

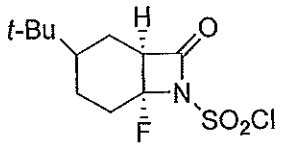


Automation directory: /home/organic/vnmrsys/data/studies/auto_2007.06.21
Sample id : /home/organic/vnmrsys/data/plnu/s_KD33_H01
Sample : KD33_H

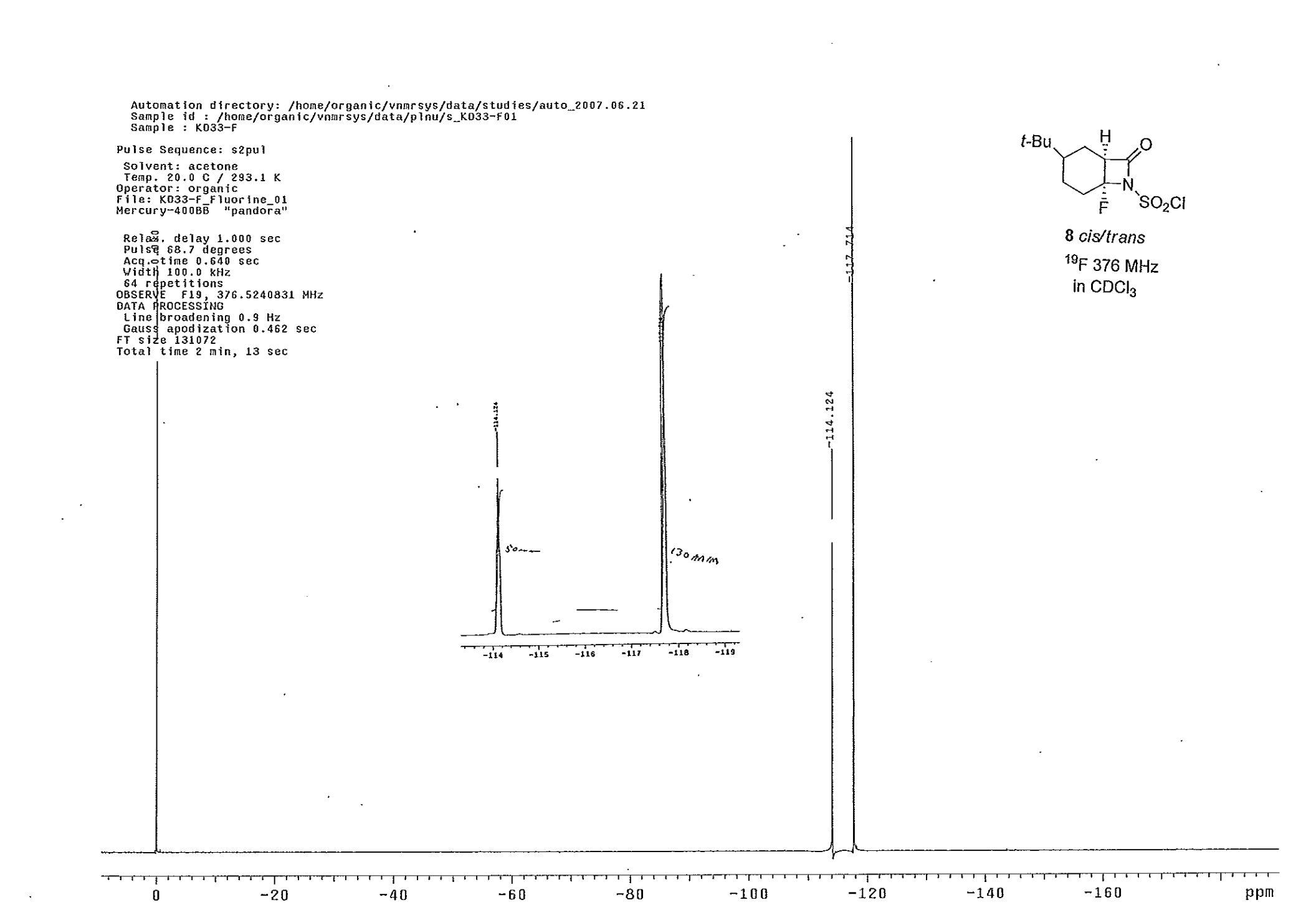
Pulse Sequence: s2pul
Solvent: cdcl3
Temp. 20.0 C / 293.1 K
Operator: organic
File: KD33_H_Proton_01
Mercury-400BB "pandora"

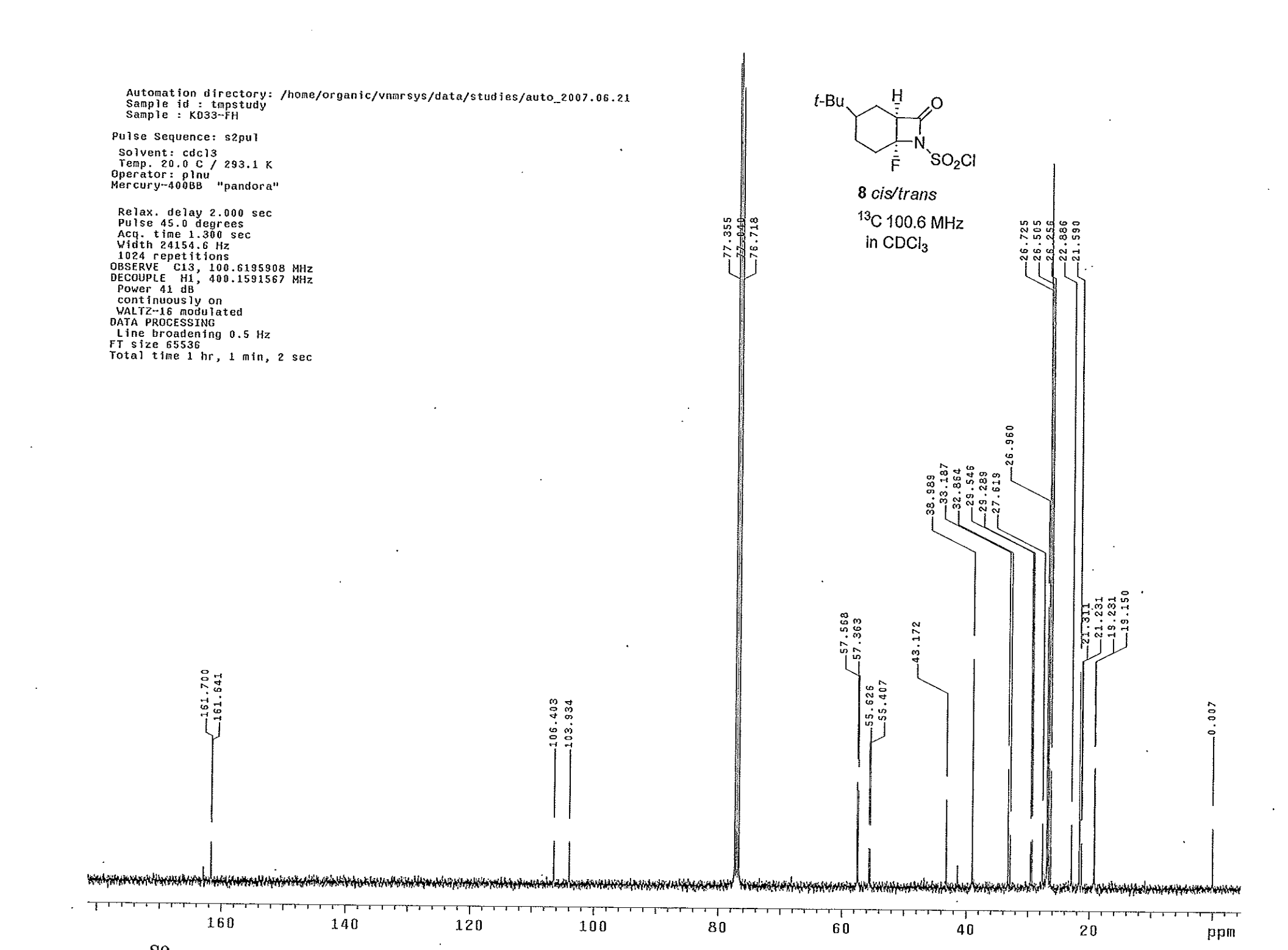
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.998 sec
Width 6402.0 Hz
8 repetitions
OBSERVE H1, 400.1571327 MHz
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 0 min, 25 sec

^1H 400 MHz δ = 0,89 (s, 9H), 1,20 - 2,30 (m, 6H), 2,55 - 2,75 (m, 1H), [3,50 (m) and 3,67 (dm, J = 12,9 Hz) 1H, ratio 1:3 respectively].



8 *cis/trans*
^1H 400 MHz
in $CDCl_3$

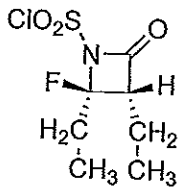




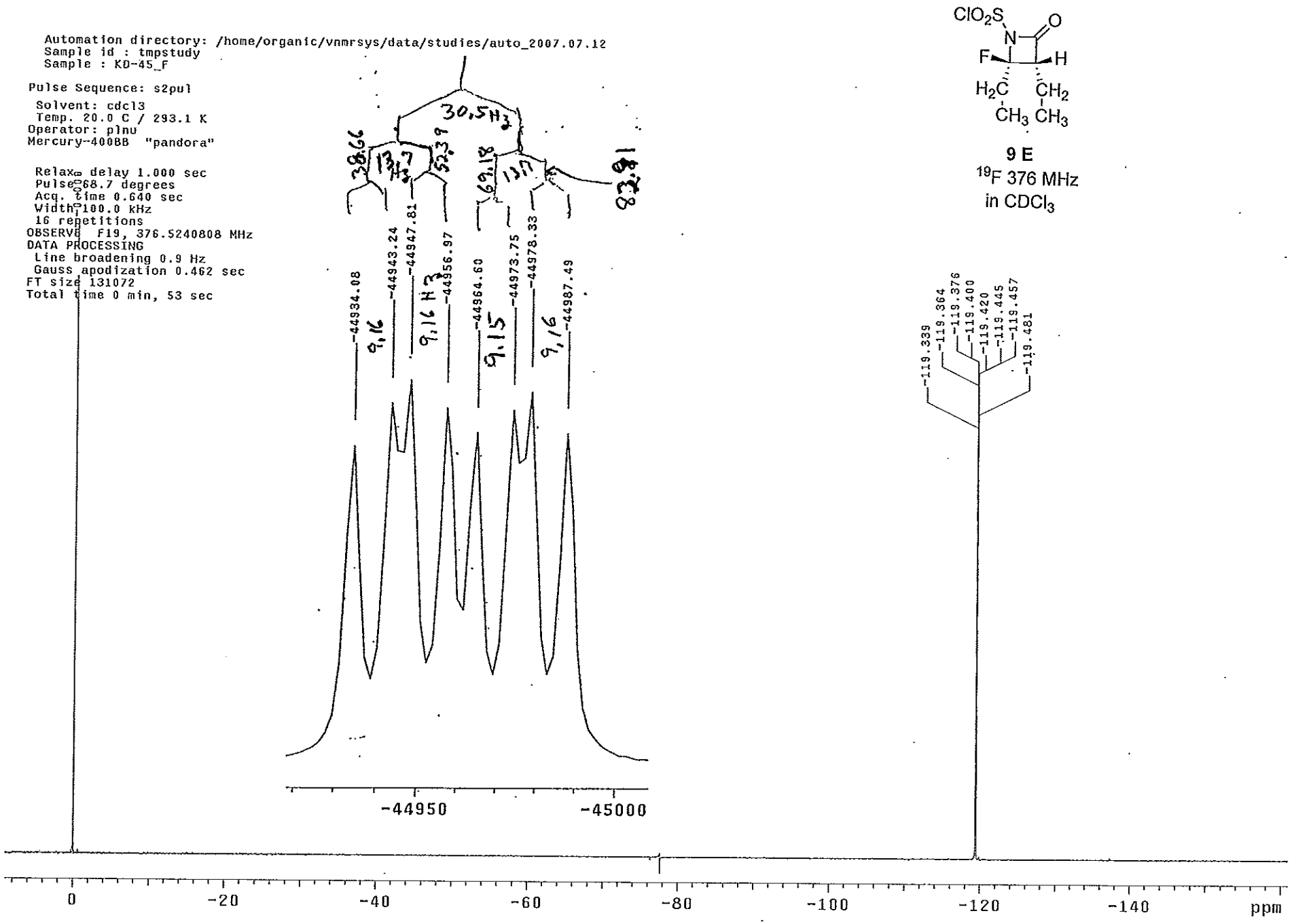
Automation directory: /home/organic/vnmrsys/data/studies/auto_2007.07.12
Sample id : tmpstudy
Sample : KD-45_H

Pulse Sequence: s2pul
Solvent: cdcl3
Temp. 20.0 C / 293.1 K
Operator: plnu
Mercury-400BB "pandora"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.998 sec
Width 6402.0 Hz
8 repetitions
OBSERVE H1, 400.1571342 MHz
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 0 min, 25 sec



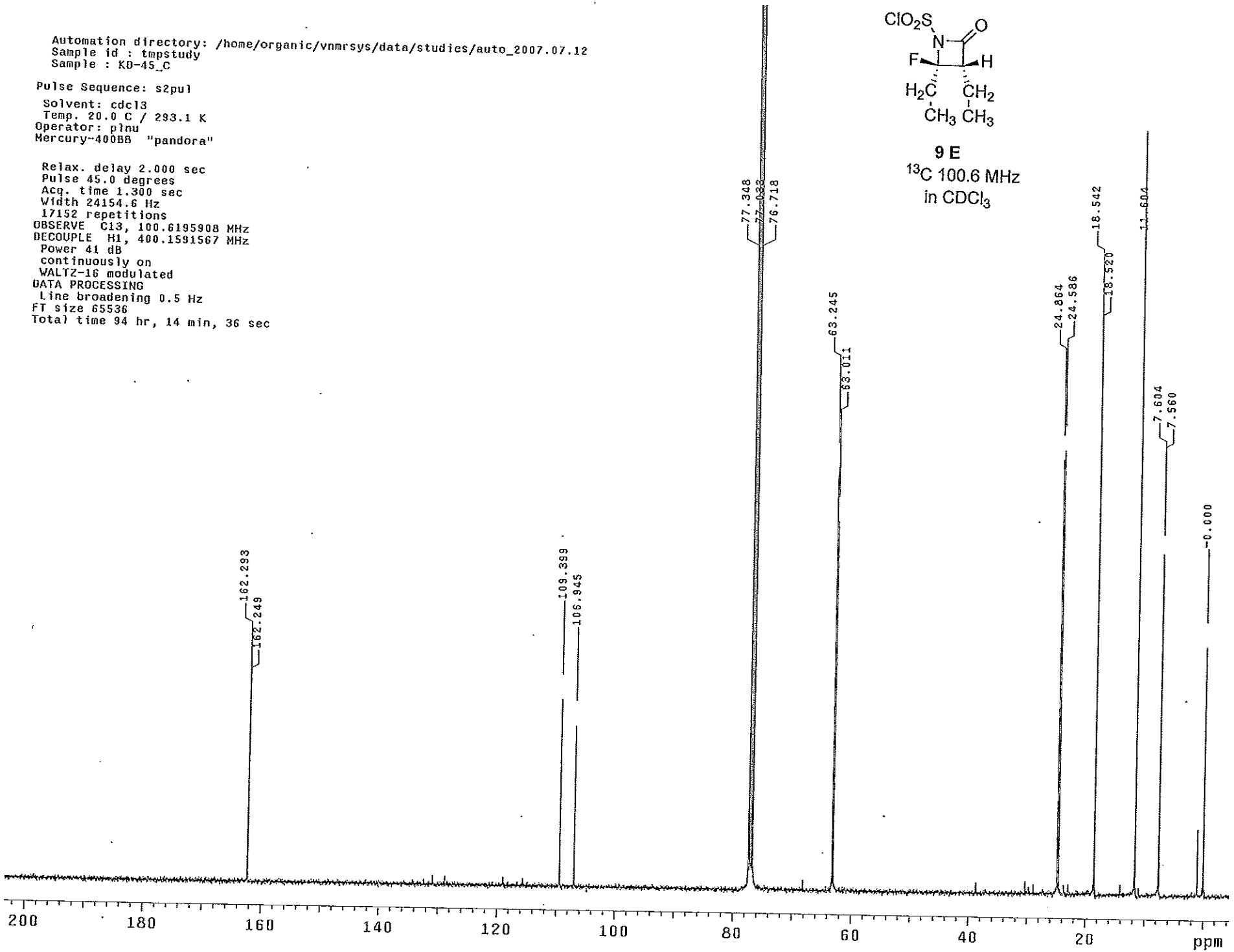
9 E
^{1}H 400 MHz
in $CDCl_3$

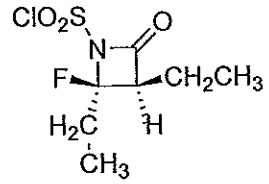


9 E

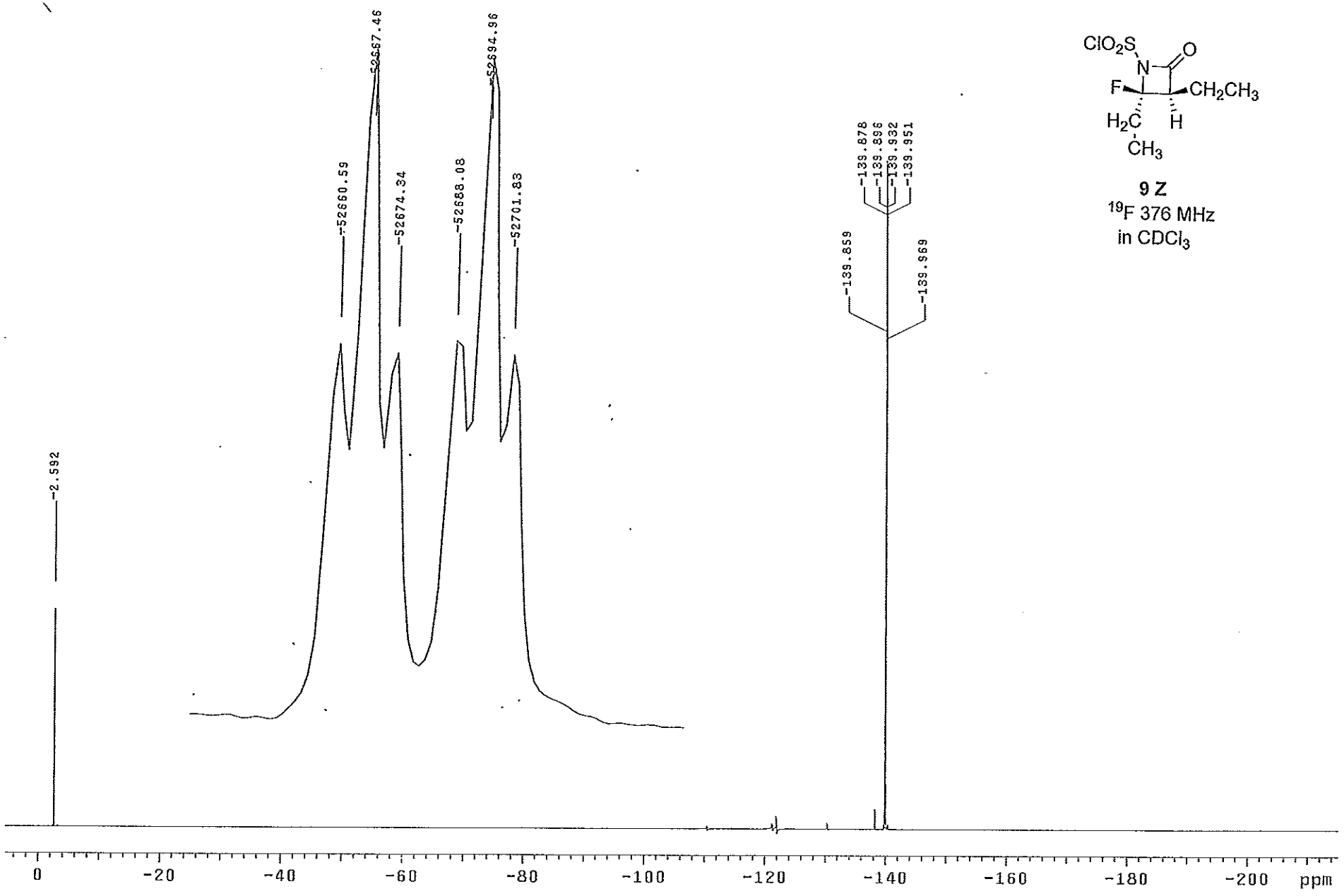
^{19}F 376 MHz

in $CDCl_3$





9 Z
^{1}H 400 MHz
in $CDCl_3$

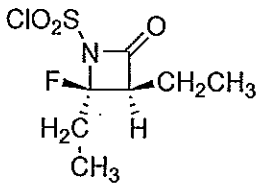


9 Z
^{19}F 376 MHz
in $CDCl_3$

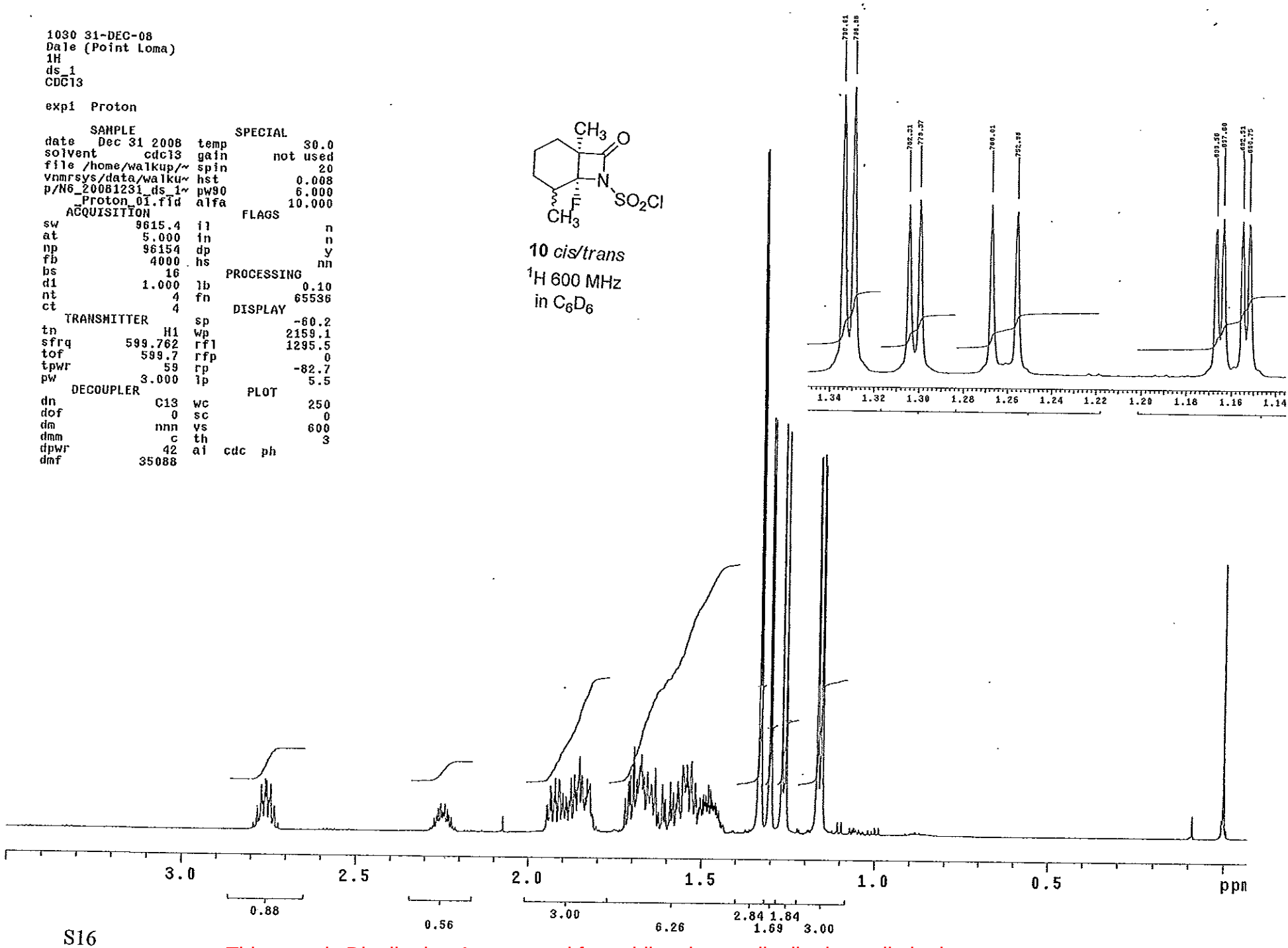
Automation directory: /home/organic/vnmrsys/data/studies/auto_2008.06.05
Sample id : /home/organic/vnmrsys/data/plnu/s_DMH27_C01
Sample : DMH27_C

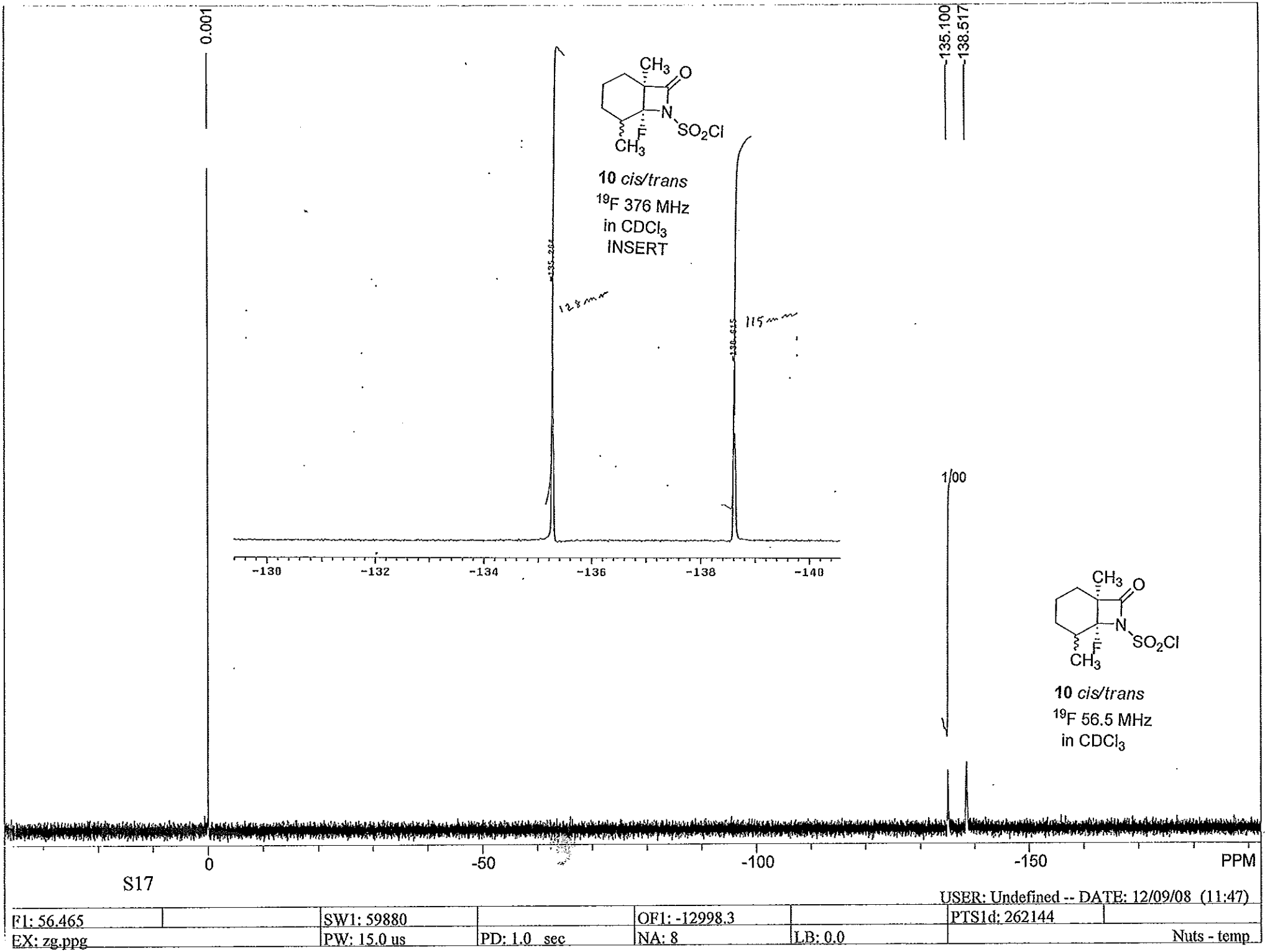
Pulse Sequence: s2pul
Solvent: d2o
Ambient temperature
Operator: plnu
File: DMH27_C_Carbon_01
Mercury-400BB "pandora.scst.sandiego.edu"

Relax. delay 5.000 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 24154.6 Hz
64 repetitions
OBSERVE C13, 100.6195812 MHz
DECOUPLE H1, 400.1601851 MHz
Power 41 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 1 hr, 46 min, 34 sec



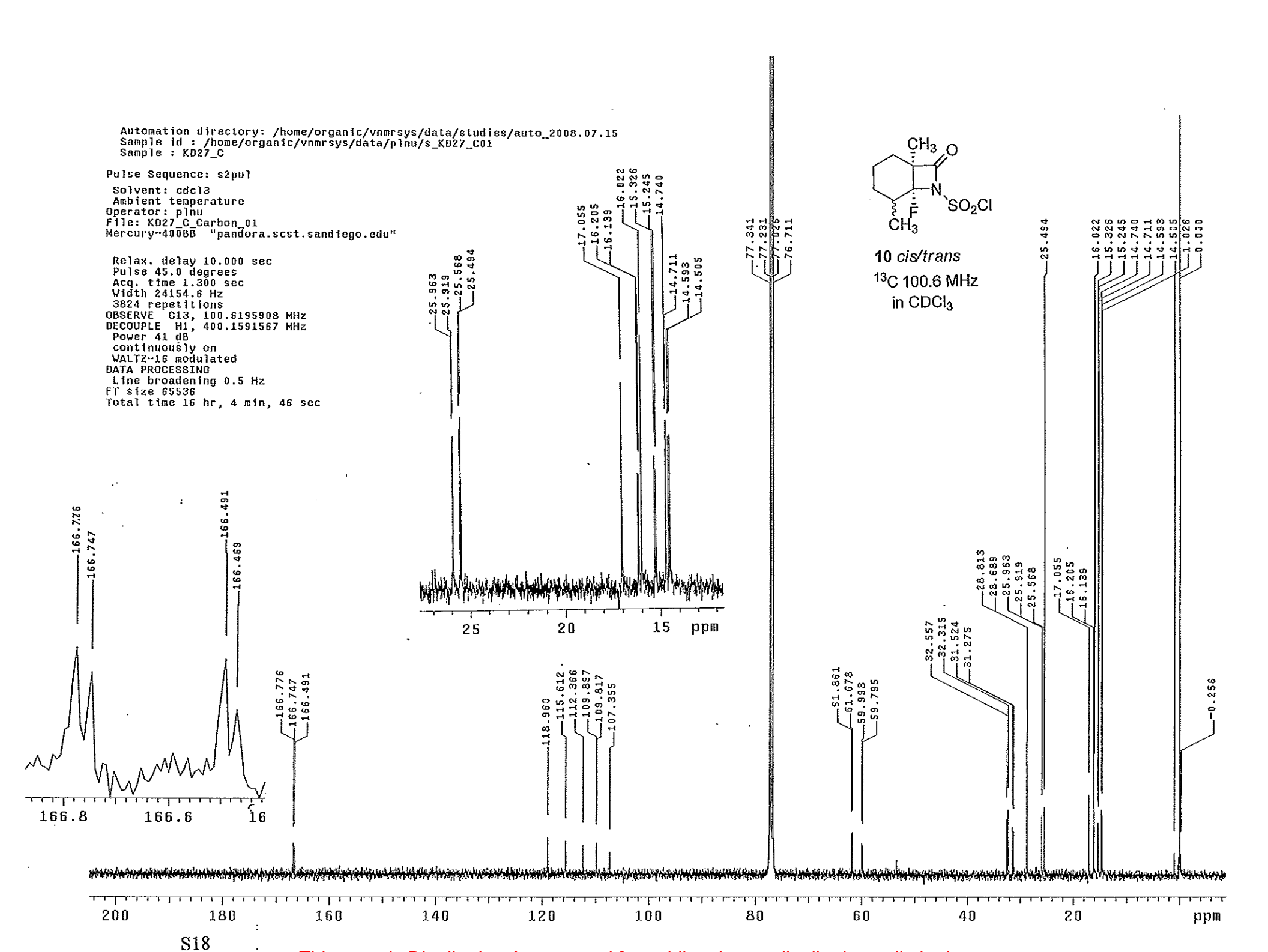
9 Z
^{13}C 100.6 MHz
in $CDCl_3$

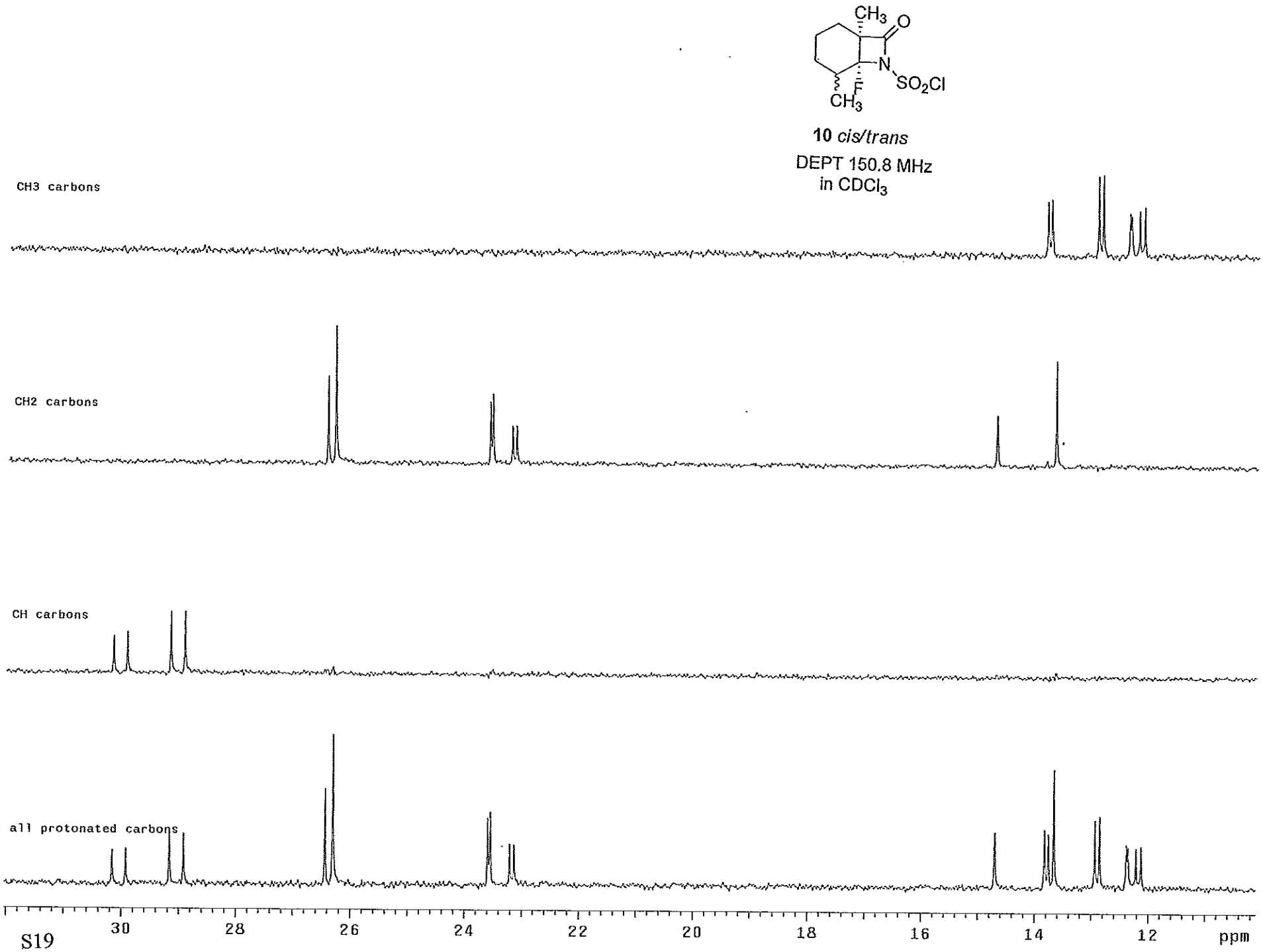




USER: Undefined -- DATE: 12/09/08 (11:47)

F1: 56.465		SW1: 59880		OF1: -12998.3		PTS1d: 262144	
EX: zg.ppg		PW: 15.0 us	PD: 1.0 sec	NA: 8	LB: 0.0		Nuts - temp

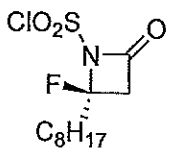




Sample: DFS_H
Sample ID: /home/organic/vnmrsys/data/plnu/s_DFS_H01
File: /home/organic/vnmrsys/data/plnu/s_DFS_H01/data/DFS_H_Proton_01.fid

Pulse Sequence: s2pul
Solvent: cdcl3
Ambient temperature
Operator: plnu
File: DFS_H_Proton_01
Mercury-400BB "pandora"

Relax. delay 2.000 sec
Pulse 45.0 degrees
Acq. time 1.998 sec
Width 6402.0 Hz
8 repetitions
OBSERVE H1, 400.1571270 MHz
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 0 min, 34 sec

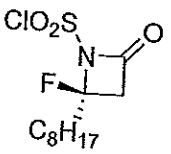


11
^{1}H 400 MHz
in $CDCl_3$

Sample: DFS_4_15_F
Sample ID: /home/organic/vnmrsys/data/plnu/s_DFS_4_15_F01
File: /home/organic/vnmrsys/data/plnu/s_DFS_4_15_F01/data/DFS_4_15_F_Fluorine_01.fid

Pulse Sequence: s2pul
 Solvent: cdcl3
 Ambient temperature
Operator: plnu
File: DFS_4_15_F_Fluorine_01
Mercury-400BB "pandora"

 Relax. delay 1.000 sec
 Pulse 30.0 degrees
 Acq. time 0.710 sec
 Width 90090.1 Hz
 16 repetitions
OBSERVE F19, 376.5240564 MHz
DATA PROCESSING
 Line broadening 0.9 Hz
 Gauss apodization 0.462 sec
FT size 131072
Total time 0 min, 55 sec

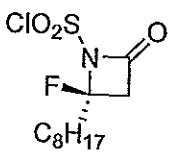


11
^{19}F 376 MHz
in $CDCl_3$

Sample: DFS_4_15_C
Sample ID: /home/organic/vnmrsys/data/plnu/s_DFS_4_15_C01
File: /home/organic/vnmrsys/data/plnu/s_DFS_4_15_C01/data/DFS_4_15_C_Carbon_01.fid

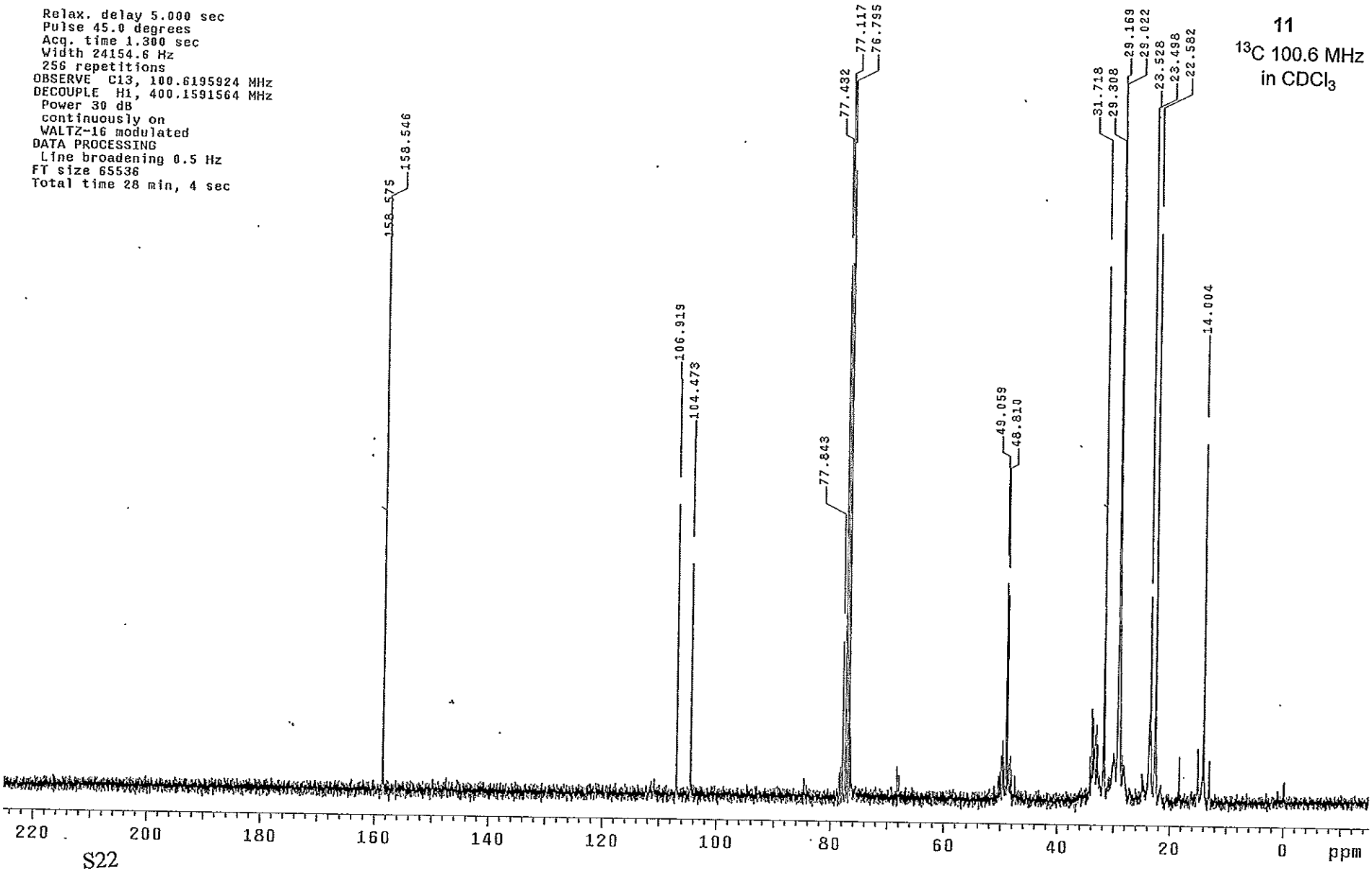
Pulse Sequence: s2pul
Solvent: cdcl3
Ambient temperature
Operator: plnu
File: DFS_4_15_C_Carbon_01
Mercury-400BB "pandora"

Relax. delay 5.000 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 24154.6 Hz
256 repetitions
OBSERVE C13, 100.6195924 MHz
DECOUPLE H1, 400.1591564 MHz
Power 30 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 28 min, 4 sec



11

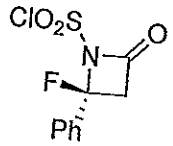
^{13}C 100.6 MHz in $CDCl_3$



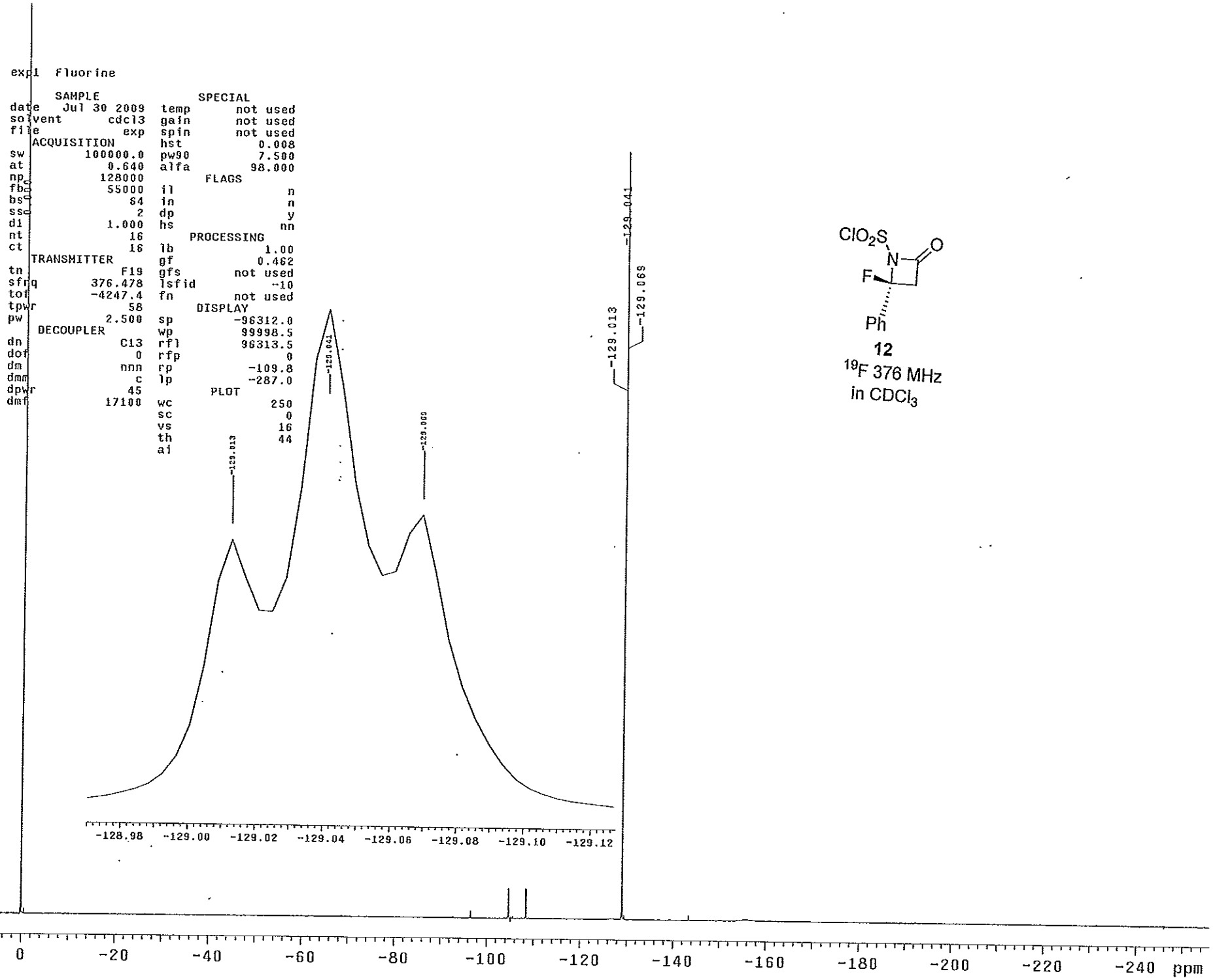
Sample: DFS
Sample ID: s_20090721_02
File:.researc/s_20090721_02/data/DFS_01.fid

Pulse Sequence: s2pul
 Solvent: cdcl3
 Ambient temperature
Operator: researc
File: DFS_01
Mercury-400BB "pandora"

 Relax. delay 1.000 sec
 Pulse 45.0 degrees
 Acq. time 1.998 sec
 Width 6402.0 Hz
 8 repetitions
OBSERVE   H1, 400.1571405 MHz
DATA PROCESSING
FT size 32768
Total time 0 min, 26 sec



12
^{1}H 400 MHz
in $CDCl_3$ Contains
trace Ether from
Crystallization



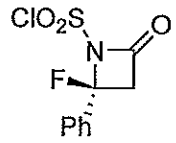
12

^{19}F 376 MHz in $CDCl_3$

Sample: DFS
Sample ID: s_20090721_01
File: researc/s_20090721_01/data/DFS_01.fid

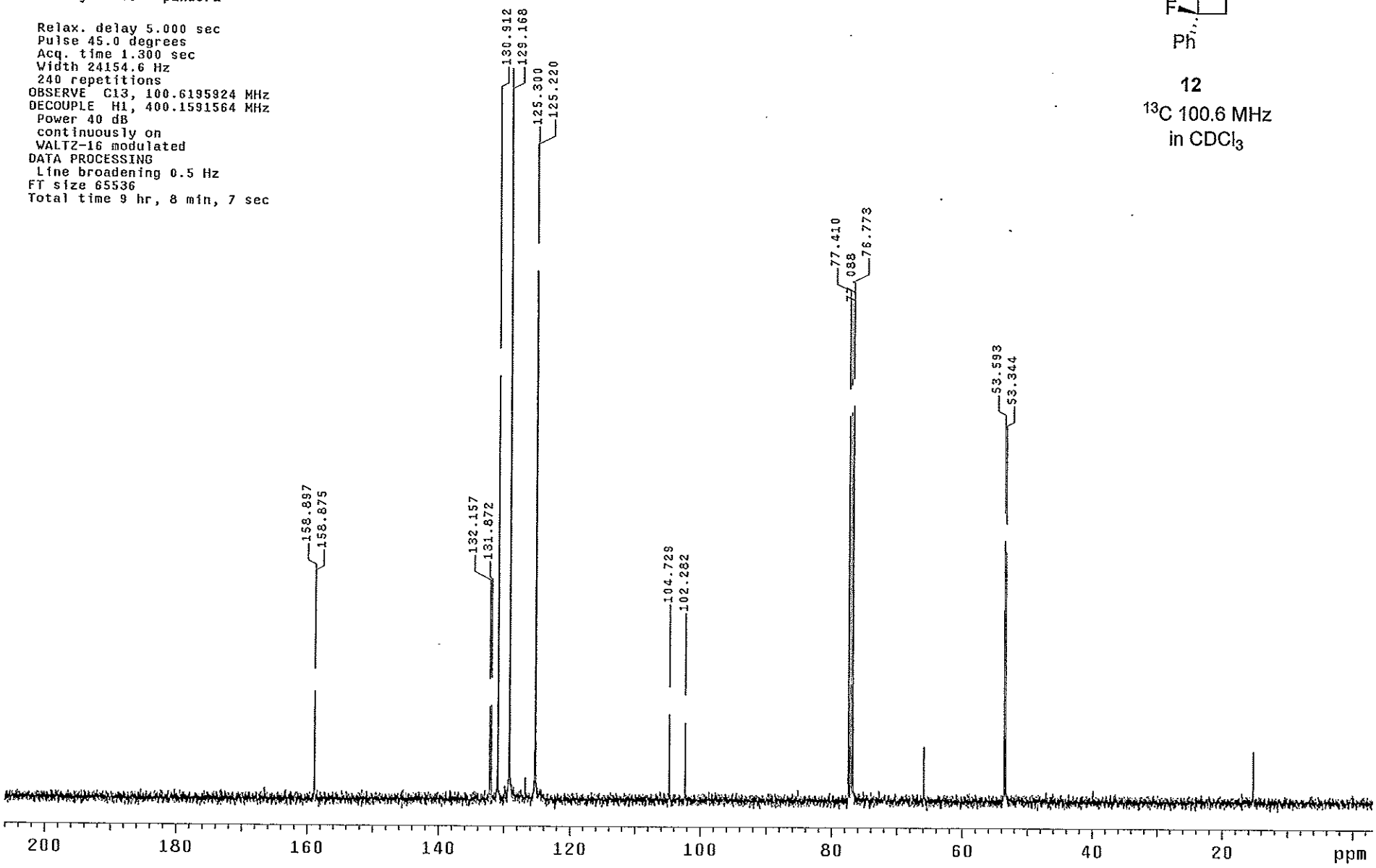
Pulse Sequence: s2pul
Solvent: cdcl3
Ambient temperature
Operator: researc
File: DFS_01
Mercury-400BB "pandora"

Relax. delay 5.000 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 24154.6 Hz
240 repetitions
OBSERVE C13, 100.6195924 MHz
DECOUPLE H1, 400.1591564 MHz
Power 40 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 9 hr, 8 min, 7 sec



12

^{13}C 100.6 MHz
in $CDCl_3$



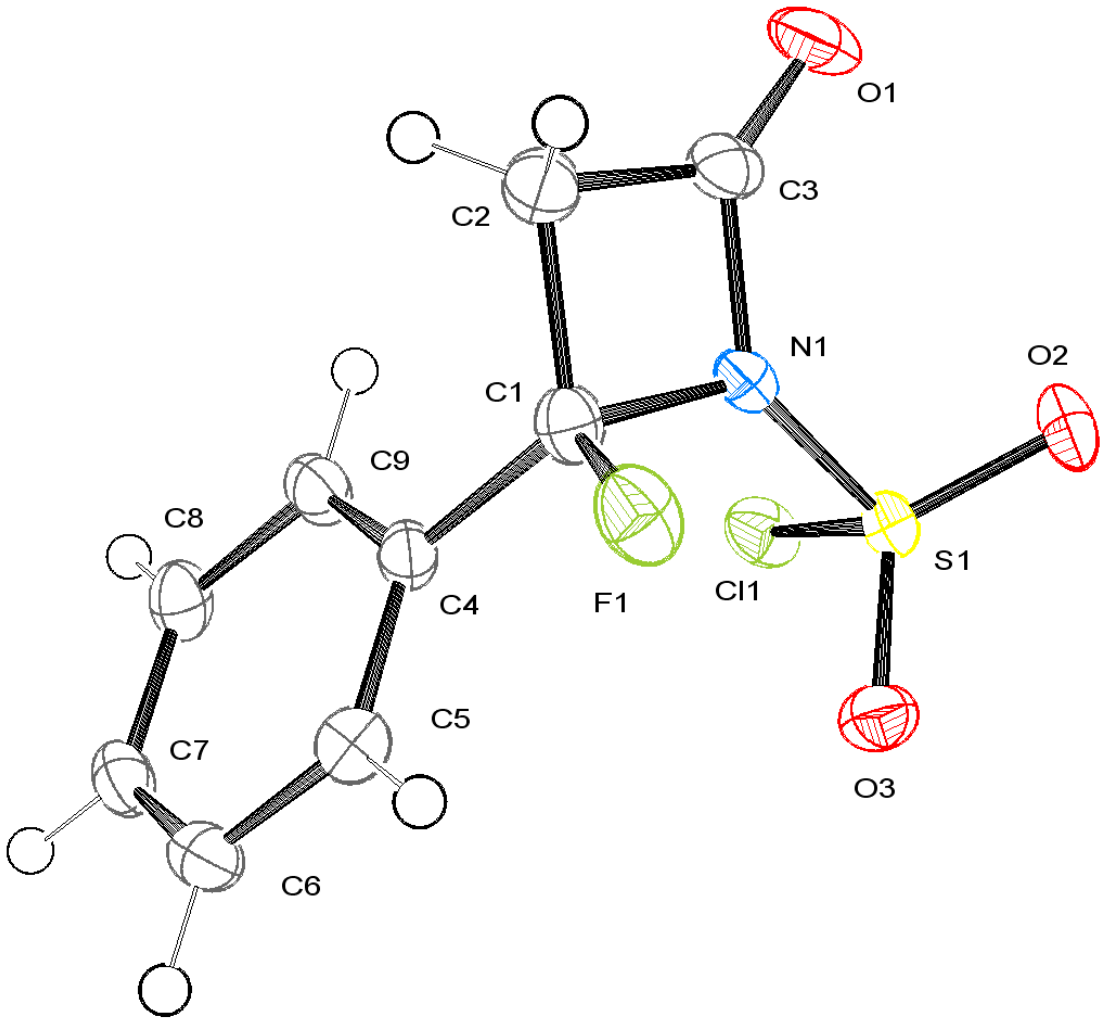


Table 1. Crystal data and structure refinement for plnu05.

Identification code	plnu05	
Empirical formula	C9 H7 Cl F N O3 S	
Formula weight	263.67	
Temperature	120(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 13.4185(5) Å	α= 90°.
	b = 5.6716(3) Å	β= 98.008(3)°.
	c = 13.7167(6) Å	γ = 90°.
Volume	1033.72(8) $Å^3$	
Z	4	
Density (calculated)	1.694 Mg/m^3	
Absorption coefficient	5.265 mm^{-1}	
F(000)	536	
Crystal size	0.25 x 0.17 x 0.11 mm^3	
Crystal color, habit	Colorless Rod	
Theta range for data collection	4.97 to 65.54°.	
Index ranges	-14<=h<=15, -6<=k<=6, -15<=l<=16	
Reflections collected	5633	
Independent reflections	1710 [R(int) = 0.0248]	
Completeness to theta = 65.00°	96.9 %	
Absorption correction	Multi-scan	
Max. and min. transmission	0.5951 and 0.3528	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	1710 / 0 / 146	
Goodness-of-fit on F^2	1.042	
Final R indices [I>2sigma(I)]	R1 = 0.0287, wR2 = 0.0731	
R indices (all data)	R1 = 0.0319, wR2 = 0.0748	
Extinction coefficient	0.0010(3)	
Largest diff. peak and hole	0.261 and -0.312 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for plnu05. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	4343(1)	3211(3)	6656(1)	22(1)
C(2)	3613(1)	5327(4)	6491(2)	27(1)
C(3)	3488(1)	5188(4)	7570(2)	24(1)
C(4)	5422(1)	3414(3)	6474(1)	19(1)
C(5)	5857(1)	1624(3)	5987(1)	22(1)
C(6)	6844(1)	1838(3)	5806(1)	24(1)
C(7)	7399(1)	3811(4)	6112(1)	24(1)
C(8)	6970(2)	5586(4)	6610(2)	25(1)
C(9)	5983(1)	5391(4)	6790(1)	24(1)
Cl(1)	5793(1)	3521(1)	9275(1)	27(1)
F(1)	3920(1)	1210(2)	6204(1)	30(1)
N(1)	4163(1)	3233(3)	7699(1)	21(1)
O(1)	3060(1)	6206(3)	8141(1)	33(1)
O(2)	3915(1)	1555(2)	9306(1)	28(1)
O(3)	5020(1)	-445(2)	8254(1)	26(1)
S(1)	4620(1)	1614(1)	8632(1)	20(1)

Table 3. Bond lengths [Å] and angles [°] for plnu05.

C(1)-F(1)	1.378(2)	C(3)-C(2)-H(2B)	113.9
C(1)-N(1)	1.483(2)	C(1)-C(2)-H(2B)	113.9
C(1)-C(4)	1.508(3)	H(2A)-C(2)-H(2B)	111.1
C(1)-C(2)	1.547(3)	O(1)-C(3)-N(1)	130.84(19)
C(2)-C(3)	1.514(3)	O(1)-C(3)-C(2)	138.70(19)
C(2)-H(2A)	0.9900	N(1)-C(3)-C(2)	90.43(14)
C(2)-H(2B)	0.9900	C(9)-C(4)-C(5)	119.77(17)
C(3)-O(1)	1.185(2)	C(9)-C(4)-C(1)	120.10(16)
C(3)-N(1)	1.427(2)	C(5)-C(4)-C(1)	120.13(17)
C(4)-C(9)	1.386(3)	C(4)-C(5)-C(6)	119.89(18)
C(4)-C(5)	1.387(3)	C(4)-C(5)-H(5)	120.1
C(5)-C(6)	1.388(3)	C(6)-C(5)-H(5)	120.1
C(5)-H(5)	0.9500	C(7)-C(6)-C(5)	120.39(18)
C(6)-C(7)	1.377(3)	C(7)-C(6)-H(6)	119.8
C(6)-H(6)	0.9500	C(5)-C(6)-H(6)	119.8
C(7)-C(8)	1.386(3)	C(6)-C(7)-C(8)	119.77(17)
C(7)-H(7)	0.9500	C(6)-C(7)-H(7)	120.1
C(8)-C(9)	1.386(3)	C(8)-C(7)-H(7)	120.1
C(8)-H(8)	0.9500	C(9)-C(8)-C(7)	120.22(19)
C(9)-H(9)	0.9500	C(9)-C(8)-H(8)	119.9
Cl(1)-S(1)	2.0087(6)	C(7)-C(8)-H(8)	119.9
N(1)-S(1)	1.6247(16)	C(8)-C(9)-C(4)	119.96(18)
O(2)-S(1)	1.4128(14)	C(8)-C(9)-H(9)	120.0
O(3)-S(1)	1.4137(14)	C(4)-C(9)-H(9)	120.0
		C(3)-N(1)-C(1)	94.16(14)
F(1)-C(1)-N(1)	109.23(15)	C(3)-N(1)-S(1)	134.47(13)
F(1)-C(1)-C(4)	109.44(15)	C(1)-N(1)-S(1)	131.35(13)
N(1)-C(1)-C(4)	116.66(16)	O(2)-S(1)-O(3)	122.92(9)
F(1)-C(1)-C(2)	111.11(16)	O(2)-S(1)-N(1)	108.39(8)
N(1)-C(1)-C(2)	87.13(14)	O(3)-S(1)-N(1)	107.40(8)
C(4)-C(1)-C(2)	121.36(16)	O(2)-S(1)-Cl(1)	106.32(6)
C(3)-C(2)-C(1)	88.28(15)	O(3)-S(1)-Cl(1)	106.94(6)
C(3)-C(2)-H(2A)	113.9	N(1)-S(1)-Cl(1)	103.18(6)
C(1)-C(2)-H(2A)	113.9		

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for plnu05. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

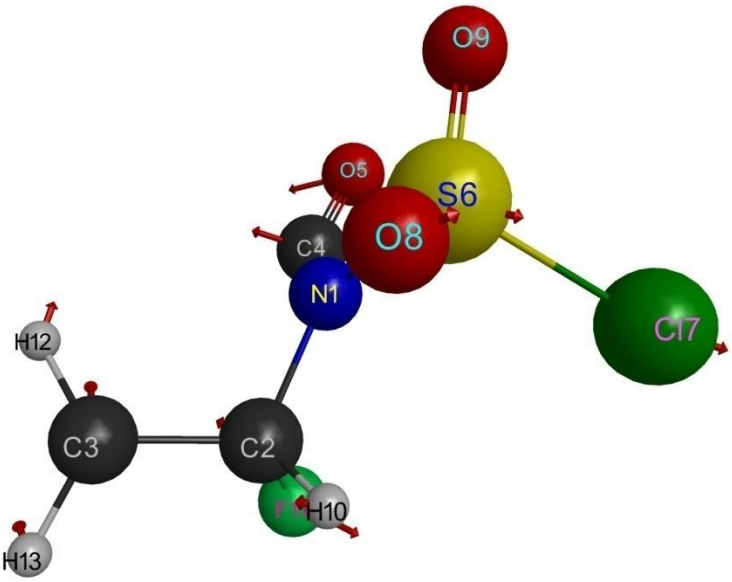
	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	21(1)	23(1)	22(1)	-1(1)	4(1)	-4(1)
C(2)	20(1)	30(1)	31(1)	7(1)	3(1)	2(1)
C(3)	15(1)	22(1)	35(1)	0(1)	4(1)	0(1)
C(4)	19(1)	22(1)	18(1)	3(1)	5(1)	0(1)
C(5)	22(1)	22(1)	21(1)	0(1)	0(1)	-2(1)
C(6)	22(1)	27(1)	24(1)	-1(1)	5(1)	4(1)
C(7)	18(1)	32(1)	22(1)	4(1)	6(1)	0(1)
C(8)	25(1)	25(1)	26(1)	-1(1)	7(1)	-8(1)
C(9)	26(1)	23(1)	25(1)	-3(1)	10(1)	-1(1)
Cl(1)	18(1)	30(1)	34(1)	-5(1)	2(1)	-3(1)
F(1)	24(1)	32(1)	33(1)	-8(1)	7(1)	-9(1)
N(1)	18(1)	24(1)	22(1)	1(1)	8(1)	3(1)
O(1)	23(1)	34(1)	44(1)	-6(1)	11(1)	8(1)
O(2)	22(1)	38(1)	25(1)	2(1)	10(1)	-4(1)
O(3)	26(1)	20(1)	32(1)	0(1)	4(1)	2(1)
S(1)	16(1)	21(1)	22(1)	1(1)	6(1)	-1(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^{-3}) for plnu05.

	x	y	z	U(eq)
H(2A)	3932	6804	6305	32
H(2B)	2989	4990	6037	32
H(5)	5478	255	5778	27
H(6)	7140	617	5468	29
H(7)	8074	3955	5982	29
H(8)	7354	6941	6828	30
H(9)	5690	6612	7131	29

Quantum Chemical Data for CSI and Vinyl Fluoride

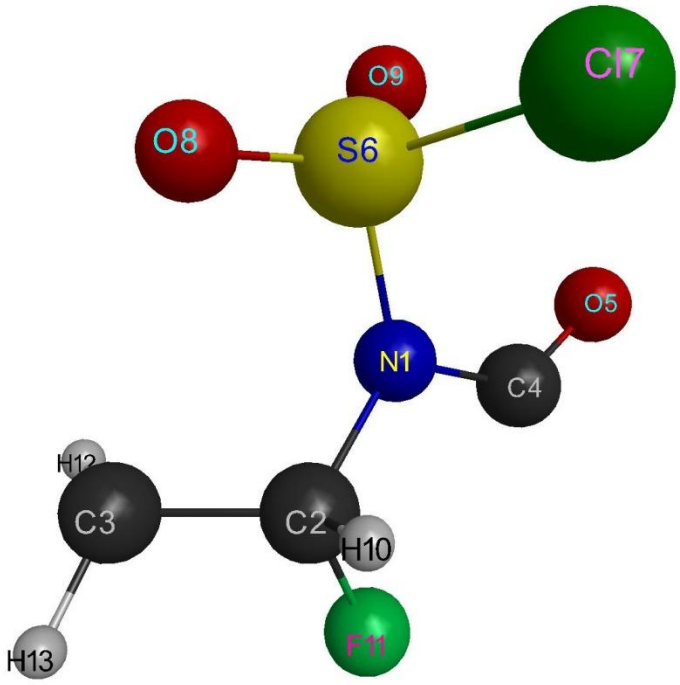
Structure 1. Stepwise transition state geometry and normal mode corresponding to the single imaginary frequency of 119.2i cm^{-1}.



Cartesian coordinates (in angstroms)

N	0.665493	0.418156	-0.179637
C	1.506227	0.451207	1.051268
C	2.816076	-0.226468	0.891209
C	0.878744	1.350863	-1.139308
O	0.301163	1.700881	-2.119813
S	-0.653670	-0.675017	-0.220016
CL	-2.049923	0.370244	0.897448
O	-0.248118	-1.814620	0.556094
O	-1.125028	-0.729734	-1.571876
H	0.910104	-0.008886	1.843423
F	1.634490	1.793043	1.371460
H	3.222614	-0.339300	-0.111212
H	3.495338	-0.174672	1.737348

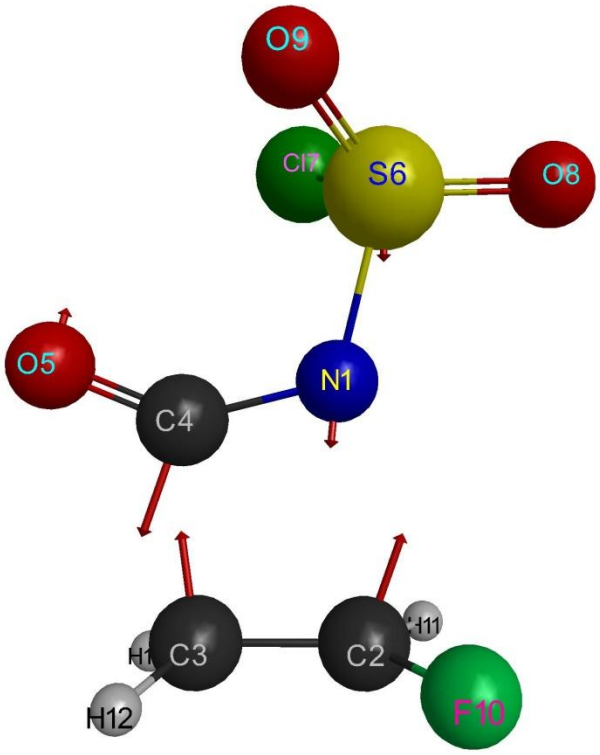
Structure 2. Local reactive intermediate in stepwise mechanism



Cartesian coordinates (in angstroms)

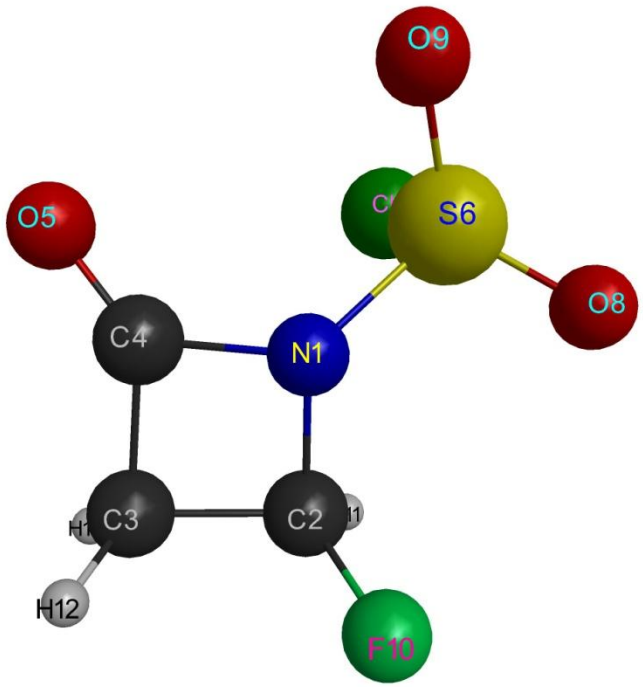
N	0.643432	0.535411	-0.128092
C	1.528550	0.597228	1.110207
C	2.360275	-0.631964	1.415735
C	0.472412	1.663876	-0.893380
O	-0.311075	1.901562	-1.765771
S	-0.525950	-0.674258	-0.221505
CL	-2.146779	0.312321	0.624224
O	-0.119179	-1.688164	0.708468
O	-0.838309	-0.902352	-1.599683
H	0.881375	0.873960	1.947915
F	2.357640	1.655669	0.844106
H	2.822503	-1.098021	0.544829
H	3.026637	-0.442723	2.257462

Structure 3. Concerted transition state geometry and normal mode corresponding to the single imaginary frequency of 599.6i cm^{-1}.




```
Cartesian coordinates (in angstroms)
N        0.457119   -0.170217    0.154261
C        2.473411   -0.391100    0.971303
C        2.745437    0.713232    0.177182
C        1.045789    0.835911   -0.493058
O        0.846808    1.714573   -1.258577
S       -1.132957   -0.515751   -0.228693
CL      -2.121174    1.133346    0.627833
O       -1.477952   -1.660921    0.568354
O       -1.383246   -0.451139   -1.645827
F        2.772563   -1.587991    0.563583
H        2.093155   -0.356071    1.985310
H        3.361003    0.549561   -0.701659
H        2.847900    1.663904    0.690610
```

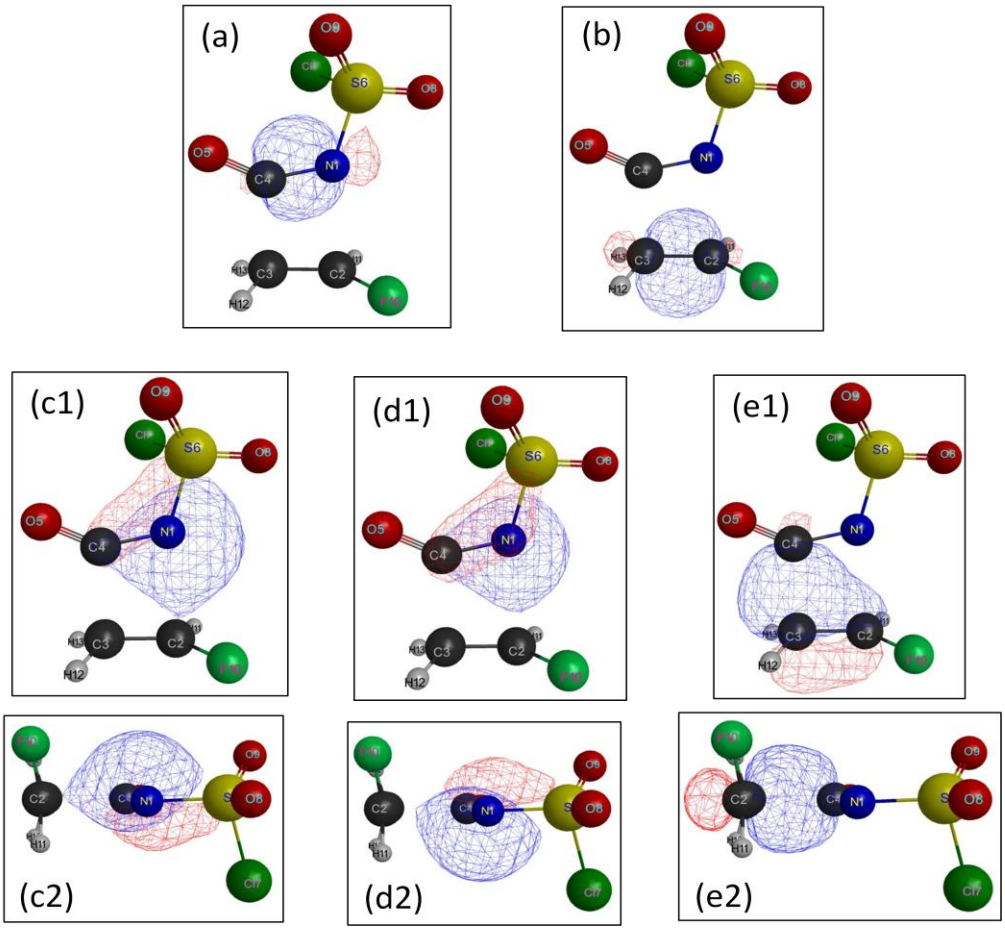
Structure 4. Reaction product local minimum



Cartesian coordinates (in angstroms)

N	0.618167	-0.137219	-0.240307
C	1.569329	-0.303473	0.858611
C	2.443394	0.792026	0.219812
C	1.293181	1.024826	-0.763196
O	0.976592	1.825037	-1.586651
S	-0.986867	-0.565398	-0.260045
CL	-1.794172	0.986050	0.886519
O	-1.109205	-1.760749	0.524399
O	-1.475615	-0.399241	-1.595299
F	2.130019	-1.539889	0.892142
H	1.144927	-0.082138	1.840211
H	3.339505	0.382031	-0.248867
H	2.681197	1.654629	0.843558

Localized molecular orbitals of the cyclic 2+2 transition state,5a-e2.



5a-e. RHF/6-311G(d,p) energy localized molecular orbitals at the concerted transition state.
(a) C-N sigma bond; (b) C-C sigma bond, (c1,c2) two views of the C-N pi bond; (d1,d2) two views of the N atom lone pair; (e1,e2) two views of the vinyl pi bond.

Stationary point	E(MP2/6-311G(d,p)[a]	Zero-point energy[b]	Relative energy[c]
CSI + CH2=CHF	-1352.507608	0.067482	0.0
Stepwise reactive intermediate	-1352.422724	0.073312	56.9
Stepwise TS	**-1352.412566**	**0.069565**	**60.9**
Concerted TS	**-1352.461899**	**0.069305**	**29.8**
Product	-1352.540651	0.073210	-17.1

[a] In hartrees.
[b] In hartrees, scaled by 0.9748
[c] In kcal/mol, including scaled zero point energies.