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

**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.**
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. CSI reacts with alkenes to give chlorosulfonyl beta-lactams that are readily reduced to beta-lactams. This reaction sequence provides a synthetic route to beta-lactam antibiotics. 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. Moriconi suggests that some 1,2-disubstituted olefins retain stereochemistry through fast collapse of the dipolar intermediate. Ab initio calculations show that [2 + 2] cycloadditions between alkenes and isocyanates can react via a concerted transition state with zwitterionic character. 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. Calculations also support a concerted process for the cycloaddition of isocyanates with aldehydes. 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; 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 step-wise pathway is raised significantly by the vinyl fluorine atom through its strong inductive effect. 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 stereochernistry 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. 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-fluorolactams (1), (2), 3-fluorohex-3-enes (3) (E) and (3) (Z), and the dialkylsubstituted 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 13C NMR three bond coupling with fluorine ($J_{CF} = 3-$)
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. 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 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 $[\pi^*(s) + \pi^*(a)]$ process. A six electron process, involving the lone pair on nitrogen represented as $\omega^2 [\pi^*(s) + \pi^*(s) + \omega^2(s)]$, would allow for a concerted cyclization where the alkene carbon atoms and the O=C=O 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]

5 or 6 + CSI $\xrightarrow{\text{concentrated}}$ 13

(c1) and (d1) 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.

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(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 vigeux column to give enriched 1-fluorocyclohexlenes 1, 2 and 4 containing various amounts of 1,1-difluorocyclohexanes. Acyclic fluoroalkenes 3E, 3Z, 5E, 5Z, 6E, 6Z 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°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. 19F 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°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 (19F 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 Available: Spectral data to characterize the products, X-Ray data for 12 and quantum chemical data are available on line at http://pubs.acs.org.

REFERENCES:

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Supporting Information

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

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S1
Quantum Chemical Calculated Data for CSI and Vinyl Fluoride

Structure 1. Stepwise Transition State
Structure 2. Intermediate in Stepwise Pathway
Structure 3. Concerted Transition State
Structure 4. Reaction Product
Localized calculated Molecular Orbitals of the Concerted Transition State

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$_3$) $\delta$ = 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$_3$) $\delta$ = -112.8 (m). $^{13}$C NMR 100.6 MHz (CDCl$_3$). $\delta$ = 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$_7$H$_{10}$N$_3$FSCl 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$_3$) $\delta$ = 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 $\delta$ = -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 $\delta$ = 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, $J$ = 248 Hz); 161.7 (d, $J$ = 6 Hz). 8 cis $\delta$ = 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$_3$FSCl 298.067996; found 298.068000.

9E: Isolated (50%) by column chromatography as described above. $^1$H NMR 400 MHz (CDCl$_3$) $\delta$ = 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$_3$) $\delta$ = -119.4 (ddd, $J$ = 30.5, 13.7 and 9.2 Hz). $^{13}$C NMR 100.6 MHz (CDCl$_3$). 9E trans $\delta$ = 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$_7$H$_{12}$NO$_3$FSCl 244.0210; found 244.0202.

9Z: Isolated (50%) by column chromatography as described above. $^1$H NMR 400 MHz (CDCl$_3$) $\delta$ = 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$_3$) $\delta$ = -137.3 (dt, $J$ = 27.5 and 6.9 Hz). $^{13}$C NMR 100.6 MHz (CDCl$_3$) $\delta$ = 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$_7$H$_{10}$NO$_3$FSCl 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$_6$D$_6$) $\delta =$ [**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$_3$) $\delta =$ -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$_6$H$_6$) assignments supported by DEPT and HSQC experiments. **10 cis** $\delta =$ 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**: $\delta =$ 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$_9$H$_{12}$NO$_3$FSCl 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$_3$) $\delta =$ 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$_3$) $\delta =$ -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$_3$). $\delta =$ 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 mixture 1831 cm$^{-1}$. Exact mass, negative ion ESI [M$^-$-H] calcd. for C$_{11}$H$_{18}$NO$_3$FSCl 298.0680; found 298.0716.

**12**: Yield (65%) by $^{19}$F NMR with 4-fluoroanisole as internal standard. $^1$H NMR 400 MHz (CDCl$_3$) $\delta =$ 3.62-3.85 (m, 2H); 7.51 (m, 3H); 7.61 (m, 2H). $^{19}$F NMR 376 MHz (CDCl$_3$) $\delta =$ -129.0 (t, $J =$ 10.5 Hz). $^{13}$C NMR 100.6 MHz (CDCl$_3$). $\delta =$ 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$^{-1}$. 

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Automation directory: /home/organic/vnmrsys/data/studies/auto_2008.06.18_01
Sample id: /home/organic/vnmrsys/data/plnu/s.DO429_C01
Sample: DO429_C

Pulse Sequence: s2pul
Solvent: d2o
Ambient temperature
Operator: plnu
File: DO429_C_Carbon_01
Mercury-400BB "pandora.scst.sandiego.edu"

Relax. delay 5.000 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 25154.8 Hz
128 repetitions
OBSERVE C13, 100.6108270 MHz
DECouple, Hi, 400.1091051 MHz
Pover 41 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 85536
Total time 1 hr, 49 min, 30 sec

$^{13}$C 100.6 MHz
in CDCl$_3$
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Solvent: d2o
Ambient temperature
Operator: plnu
File: DNN12_F_Fluorine_01
Hermeneut=436000 "pandora.scsc.ucsd.edu"

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Pulse 35.0 degrees
Acq. time 0.670 sec
Width 93339.6 Hz
10 repetitions
OBSERVE F1, 376.5246668 MHz
DATA PROCESSING
Line broadening 0.9 Hz
Quartz apodization 0.462 sec
FT size 131072
Total time 0 min, 53 sec

19F 376 MHz in CDCl3
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Sample: D00129_H

Pulse Sequence: s2pul
Solvent: cdcl3
Ambient temperature
Operator: plnu
File: D00129_H_Proton_01
Mercury=400B5 "pandora.scst.sandiego.edu"

Relax. delay 2.008 sec
Pulse 45.0 degrees
Acq. line 1.396 sec
Width 5402.0 Hz
8 repetitions
Observe: H1, 400.1571242 MHz
Data Processing
Line broadening 0.5 Hz
FT size 65536
Total time 0 min, 33 sec

\[ \text{\textsuperscript{1}H 400 MHz in CDCl}_3 \]
H: 400 MHz

8 cis/trans

3H 400 MHz

in CDCl3
Automation directory: /home/organic/vnmrsys/data/studies/auto_2007.06.21
Sample id : /home/organic/vnmrsys/data/plnu/s_K033-F01
Sample : K033-F

Pulse Sequence: s2pul
Solvent: acetone
Temp. 29.6 C / 293.1 K
Operator: organic
File: K033-F_Fluorine_01
Mercury-400B "pandora"

Relax. delay 1.000 sec
Pulse 68.7 degrees
Acq. time 0.649 sec
Width 100.0 kHz
64 repetitions
OBSERVE F19, 376.524831 MHz
DATA PROCESSING
Line broadening 0.9 Hz
Gaus apodization 0.452 sec
FT size 131072
Total time 2 min, 13 sec

8 cis/trans
$^{19}$F 376 MHz
in CDCl$_3$
Automation directory: /home/organic/vmsys/data/studies/auto_2007.06.21
Sample id: topstudy
Sample: KS33-FH

Pulse Sequence: s2pul
Solvent: cdc13
Temp. 26.0 C / 293.1 K
Operator: pla
Mercury-400B "pandora"

Relax. delay 2.000 sec
Pulse 45.0 degrees
Acq. time 1.360 sec
Width 24158.6 Hz
1024 repetitions
OBSERVE C13, 100.6139508 MHz
DECOUPLE N1, 000.1591567 MHz
Power 41 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Lb line broadening 0.5 Hz
FT size 65536
Total time 1 hr, 1 min, 2 sec

8 cis/ trans
\(^{13}\)C 100.6 MHz
in CDCl\(_3\)
Automated directory: /home/organic/vmrssys/data/studies/auto_2007.07.10
Sample Id: tmgstudy
Sample: KN-4pH

Pulse Sequence: s2pul
Solvent: cdcl3
Temp. 25.0 C / 293.1 K
Operator: pnum

Mercury-400BB "pandora"

Relax. delay 1.000 sec
Pulse 45.6 degrees
Acq. time 1.938 sec
Width 4002.0 Hz
8 repetitions

OBsERVE H1, 400.15/1342 MHz
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 0 min, 25 sec

\( ^1H \) 400 MHz

in CDCl3
Automation directory: /home/organic/vnmrsys/data/studies/auto_2007.07.12
Sample id: teststudy
Sample: K9-45.0
Pulse Sequence: zg-pul
Solvent: cdc13
Temp. 26.0°C / 293.1 K
Operator: phil
Mercury-40000 "pandora"

Relax. delay 2.000 sec
Pulse 45.0 Degrees
Acq. time 1.300 sec
Width 24156.6 Hz
17152 repetitions
OBSERVE C13, 100.6185968 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 94 hr, 14 min, 36 sec

This page is Distribution A: approved for public release; distribution unlimited.
$\text{ClO}_2\text{S}$

$\text{N}$

$\text{CH}_2\text{CH}_3$

$\text{H}_2\text{C}$

$\text{H}$

$\text{CH}_3$

$\text{g Z}$

$^1\text{H}$ $400 \ \text{MHz}$

in $\text{CDCl}_3$
Pulse Sequence: s2pu
Solvent: d2o
Ambient temperature
Operator: plnu
File: PM27_C_Carbon_61
Mercury-600B - pandora.scst.sandiego.edu

Relax. delay 5.008 sec
Pulse 45.0 degrees
Acq. time 1.306 sec
Width 74152.6 Hz
64 repetitions
OBSERVE C13, 100.6135812 MHz
DECOUPLE H2, 600.1801851 MHz
Power 41 dB
continuously on
VALT=16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
F1 size 65536
Total time 1 hr, 46 min, 34 sec

9 Z
$^{13}$C 100.6 MHz
in CDCl$_3$
1H 600 MHz in C6D6

10 cis/trans

S16

This page is Distribution A: approved for public release; distribution unlimited.
10 cis/trans
$^{19}\text{F}$ 376 MHz
in CDCl$_3$

10 cis/trans
$^{19}\text{F}$ 56.5 MHz
in CDCl$_3$
Sample: DFS_H
Sample ID: /home/organic/vnarsys/data/plmu/s_DFS_H01
File: /home/organic/vnarsys/data/plmu/s_DFS_H01/data/DFS_H_Proton_01.fid

Pulse Sequence: s2pul
Solvent: cdcl3
Ambient temperature
Operator: plmu
File: DFS_H_Proton_01

Mercury-400BB "pandora"

Relax. delay 2.000 sec
Pulse 45.0 degrees
Acq. time 1.398 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
1H 400 MHz
in CDCl3

This page is Distribution A: approved for public release; distribution unlimited.
Sample: DFG_4_15_F
Sample ID: /home/organic/vnmrsys/data/plnu/s_DFG_4_15_F#1
File: /home/organic/vnmrsys/data/plnu/s_DFG_4_15_F#1/data/DFG_4_15_F_Fluorine_01.fid

Pulse Sequence: s2pu
Solvent: cdc13
Ambient temperature
Operator: plnu
File: DFG_4_15_F_Fluorine_01
Mercury-4006b "pandora"

Relax. delay 1.860 sec
Pulse 30.0 degrees
Acq. time 0.710 sec
Width 90896.1 Hz
16 repetitions
Observe FID, 376.5240564 Hz
DATA PROCESSING
Line broadening 0.9 Hz
Gauss apodization 0.462 sec
FT size 131072
Total time 6 min, 55 sec

19F 376 MHz
in CDCl3

S21

This page is Distribution A: approved for public release; distribution unlimited.
Sample: DF0_4_15_C
Sample ID: /home/organic/vnmrsys/data/plnu/s_DF0_4_15_C01
File: /home/organic/vnmrsys/data/plnu/s_DF0_4_15_C01/data/DF0_4_15_C_Carbon_01.fid

Pulse Sequence: z2pul
Solvent: cdcl3
Ambient temperature
Operator: plnu
File: DF0_4_15_C_Carbon_01
Mercury-400BH "pandora"

Relax delay 5.000 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 24154.6 Hz
256 repetitions
OBSERVE C13, 100.6155874 MHz
DECOUPL. H1, 400.1661564 MHz
Power 36 dB
continuously on
VALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 28 min, 4 sec

ClO2S
N
F

C6H17

11
13C 100.6 MHz
in CDCl3

This page is Distribution A: approved for public release; distribution unlimited.
Sample: DFS
Sample ID: s_20090721_02
File: rssearc/s_20090721_02/data/DFS_01.fid

Pulse Sequence: s2pol
Solvent: cdc13
Ambient temperature
Operator: rssearc
File: DFS_01
Mercury-400BB “pandora”

Relax. delay 1.000 sec
Pulse: 45.0 degrees
Acq. time 1.996 sec
Width 6492.0 Hz
6 repetitions
OBSERVE H1, 400.1571405 MHz
DATA PROCESSING
FT size 32760
Total time 0 min, 26 sec

1H 400 MHz
in CDCl3 Contains trace Ether from Crystallization

This page is Distribution A: approved for public release; distribution unlimited.
$^{19}$F NMR spectrum of Compound 12 in CDCl$_3$. The spectrum was recorded at 376 MHz.
Sample: DFS
Sample ID: c_00000721_01
File: research/s_00000721_01/data/DFS_01.fld

Pulse Sequence: s2pol
Solvent: cdcl3
Ambient temperature
Operators: researc
File: DFS_01
Mercury-S080B "pandora"

Relax. delay 5.000 sec
Pulse 45.0 degrees
Acq. time 1.000 sec
Width 24554.6 Hz
240 repetitions
OBSERVE C13, 100.6150524 MHz
DECOUPLE H1, 100.6150564 MHz
Power 49 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 9 hr, 8 min, 7 sec

\[ \text{ClO}_2S \]
\[ \text{Ph} \]

$^{13}$C 100.6 MHz
In CDCl$_3$

This page is Distribution A: approved for public release; distribution unlimited.
Table 1. Crystal data and structure refinement for plnu05.

<table>
<thead>
<tr>
<th>Identification code</th>
<th>plnu05</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>C9 H7 Cl F N O3 S</td>
</tr>
<tr>
<td>Formula weight</td>
<td>263.67</td>
</tr>
<tr>
<td>Temperature</td>
<td>120(2) K</td>
</tr>
<tr>
<td>Wavelength</td>
<td>1.54178 Å</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P2(1)/n</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
<td>a = 13.4185(5) Å, b = 5.6716(3) Å, c = 13.7167(6) Å, α = 90°, β = 98.008(3)°, γ = 90°.</td>
</tr>
<tr>
<td>Volume</td>
<td>1033.72(8) Å³</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
</tr>
<tr>
<td>Density (calculated)</td>
<td>1.694 Mg/m³</td>
</tr>
<tr>
<td>Absorption coefficient</td>
<td>5.265 mm⁻¹</td>
</tr>
<tr>
<td>F(000)</td>
<td>536</td>
</tr>
<tr>
<td>Crystal size</td>
<td>0.25 x 0.17 x 0.11 mm³</td>
</tr>
<tr>
<td>Crystal color, habit</td>
<td>Colorless Rod</td>
</tr>
<tr>
<td>Theta range for data collection</td>
<td>4.97 to 65.54°.</td>
</tr>
<tr>
<td>Index ranges</td>
<td>-14&lt;=h&lt;=15, -6&lt;=k&lt;=6, -15&lt;=l&lt;=16</td>
</tr>
<tr>
<td>Reflections collected</td>
<td>5633</td>
</tr>
<tr>
<td>Independent reflections</td>
<td>1710 [R(int) = 0.0248]</td>
</tr>
<tr>
<td>Completeness to theta = 65.00°</td>
<td>96.9 %</td>
</tr>
<tr>
<td>Absorption correction</td>
<td>Multi-scan</td>
</tr>
<tr>
<td>Max. and min. transmission</td>
<td>0.5951 and 0.3528</td>
</tr>
<tr>
<td>Refinement method</td>
<td>Full-matrix least-squares on F²</td>
</tr>
<tr>
<td>Data / restraints / parameters</td>
<td>1710 / 0 / 146</td>
</tr>
<tr>
<td>Goodness-of-fit on F²</td>
<td>1.042</td>
</tr>
<tr>
<td>Final R indices [I&gt;2sigma(I)]</td>
<td>R1 = 0.0287, wR2 = 0.0731</td>
</tr>
<tr>
<td>R indices (all data)</td>
<td>R1 = 0.0319, wR2 = 0.0748</td>
</tr>
<tr>
<td>Extinction coefficient</td>
<td>0.0010(3)</td>
</tr>
<tr>
<td>Largest diff. peak and hole</td>
<td>0.261 and -0.312 e.Å⁻³</td>
</tr>
</tbody>
</table>

This page is Distribution A: approved for public release; distribution unlimited.
Table 2. Atomic coordinates (x $10^4$) and equivalent isotropic displacement parameters (Å$^2$ $10^3$) for plnu05. U(eq) is defined as one third of the trace of the orthogonalized $U^0$ tensor.

<table>
<thead>
<tr>
<th></th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>U(eq)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(1)</td>
<td>4343(1)</td>
<td>3211(3)</td>
<td>6656(1)</td>
<td>22(1)</td>
</tr>
<tr>
<td>C(2)</td>
<td>3613(1)</td>
<td>5327(4)</td>
<td>6491(2)</td>
<td>27(1)</td>
</tr>
<tr>
<td>C(3)</td>
<td>3488(1)</td>
<td>5188(4)</td>
<td>7570(2)</td>
<td>24(1)</td>
</tr>
<tr>
<td>C(4)</td>
<td>5422(1)</td>
<td>3414(3)</td>
<td>6474(1)</td>
<td>19(1)</td>
</tr>
<tr>
<td>C(5)</td>
<td>5857(1)</td>
<td>1624(3)</td>
<td>5987(1)</td>
<td>22(1)</td>
</tr>
<tr>
<td>C(6)</td>
<td>6844(1)</td>
<td>1838(3)</td>
<td>5806(1)</td>
<td>24(1)</td>
</tr>
<tr>
<td>C(7)</td>
<td>7399(1)</td>
<td>3811(4)</td>
<td>6112(1)</td>
<td>24(1)</td>
</tr>
<tr>
<td>C(8)</td>
<td>6970(2)</td>
<td>5586(4)</td>
<td>6610(2)</td>
<td>25(1)</td>
</tr>
<tr>
<td>C(9)</td>
<td>5983(1)</td>
<td>5391(4)</td>
<td>6790(1)</td>
<td>24(1)</td>
</tr>
<tr>
<td>Cl(1)</td>
<td>5793(1)</td>
<td>3521(1)</td>
<td>9275(1)</td>
<td>27(1)</td>
</tr>
<tr>
<td>F(1)</td>
<td>3920(1)</td>
<td>1210(2)</td>
<td>6204(1)</td>
<td>30(1)</td>
</tr>
<tr>
<td>N(1)</td>
<td>4163(1)</td>
<td>3233(3)</td>
<td>7699(1)</td>
<td>21(1)</td>
</tr>
<tr>
<td>O(1)</td>
<td>3060(1)</td>
<td>6206(3)</td>
<td>8141(1)</td>
<td>33(1)</td>
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<tr>
<td>O(2)</td>
<td>3915(1)</td>
<td>1555(2)</td>
<td>9306(1)</td>
<td>28(1)</td>
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<tr>
<td>O(3)</td>
<td>5020(1)</td>
<td>-445(2)</td>
<td>8254(1)</td>
<td>26(1)</td>
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<tr>
<td>S(1)</td>
<td>4620(1)</td>
<td>1614(1)</td>
<td>8632(1)</td>
<td>20(1)</td>
</tr>
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</table>
Table 3. Bond lengths [Å] and angles [°] for plnu05.

<table>
<thead>
<tr>
<th>Bond</th>
<th>Length/角度</th>
<th>Bond</th>
<th>Length/角度</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(1)-F(1)</td>
<td>1.378(2)</td>
<td>C(3)-C(2)-H(2B)</td>
<td>113.9</td>
</tr>
<tr>
<td>C(1)-N(1)</td>
<td>1.483(2)</td>
<td>C(1)-C(2)-H(2B)</td>
<td>113.9</td>
</tr>
<tr>
<td>C(1)-C(4)</td>
<td>1.508(3)</td>
<td>H(2A)-C(2)-H(2B)</td>
<td>111.1</td>
</tr>
<tr>
<td>C(1)-C(2)</td>
<td>1.547(3)</td>
<td>O(1)-C(3)-N(1)</td>
<td>130.84(19)</td>
</tr>
<tr>
<td>C(2)-C(3)</td>
<td>1.514(3)</td>
<td>O(1)-C(3)-C(2)</td>
<td>138.70(19)</td>
</tr>
<tr>
<td>C(2)-H(2A)</td>
<td>0.9900</td>
<td>N(1)-C(3)-C(2)</td>
<td>90.43(14)</td>
</tr>
<tr>
<td>C(2)-H(2B)</td>
<td>0.9900</td>
<td>C(9)-C(4)-C(5)</td>
<td>119.77(17)</td>
</tr>
<tr>
<td>C(3)-O(1)</td>
<td>1.185(2)</td>
<td>C(9)-C(4)-C(1)</td>
<td>120.10(16)</td>
</tr>
<tr>
<td>C(3)-N(1)</td>
<td>1.427(2)</td>
<td>C(5)-C(4)-C(1)</td>
<td>120.13(17)</td>
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<tr>
<td>C(4)-C(9)</td>
<td>1.386(3)</td>
<td>C(4)-C(5)-C(6)</td>
<td>119.89(18)</td>
</tr>
<tr>
<td>C(4)-C(5)</td>
<td>1.387(3)</td>
<td>C(4)-C(5)-H(5)</td>
<td>120.1</td>
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<tr>
<td>C(5)-C(6)</td>
<td>1.388(3)</td>
<td>C(6)-C(5)-H(5)</td>
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<tr>
<td>C(5)-H(5)</td>
<td>0.9500</td>
<td>C(7)-C(6)-C(5)</td>
<td>120.39(18)</td>
</tr>
<tr>
<td>C(6)-C(7)</td>
<td>1.377(3)</td>
<td>C(7)-C(6)-H(6)</td>
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<tr>
<td>C(6)-H(6)</td>
<td>0.9500</td>
<td>C(5)-C(6)-H(6)</td>
<td>119.8</td>
</tr>
<tr>
<td>C(7)-C(8)</td>
<td>1.386(3)</td>
<td>C(6)-C(7)-C(8)</td>
<td>119.77(17)</td>
</tr>
<tr>
<td>C(7)-H(7)</td>
<td>0.9500</td>
<td>C(6)-C(7)-H(7)</td>
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</tr>
<tr>
<td>C(8)-C(9)</td>
<td>1.386(3)</td>
<td>C(8)-C(7)-H(7)</td>
<td>120.1</td>
</tr>
<tr>
<td>C(8)-H(8)</td>
<td>0.9500</td>
<td>C(9)-C(8)-C(7)</td>
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</tr>
<tr>
<td>C(9)-H(9)</td>
<td>0.9500</td>
<td>C(9)-C(8)-H(8)</td>
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<tr>
<td>Cl(1)-S(1)</td>
<td>2.0087(6)</td>
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<td>119.9</td>
</tr>
<tr>
<td>N(1)-S(1)</td>
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<tr>
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<td>F(1)-C(1)-N(1)</td>
<td>109.23(15)</td>
<td>C(3)-N(1)-S(1)</td>
<td>134.47(13)</td>
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<tr>
<td>F(1)-C(1)-C(4)</td>
<td>109.44(15)</td>
<td>C(1)-N(1)-S(1)</td>
<td>131.35(13)</td>
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<td>N(1)-C(1)-C(4)</td>
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<td>122.92(9)</td>
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<td>F(1)-C(1)-C(2)</td>
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<td>O(2)-S(1)-N(1)</td>
<td>108.39(8)</td>
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<tr>
<td>N(1)-C(1)-C(2)</td>
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<td>107.40(8)</td>
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<td>C(4)-C(1)-C(2)</td>
<td>121.36(16)</td>
<td>O(2)-S(1)-Cl(1)</td>
<td>106.32(6)</td>
</tr>
<tr>
<td>C(3)-C(2)-C(1)</td>
<td>88.28(15)</td>
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<td>106.94(6)</td>
</tr>
<tr>
<td>C(3)-C(2)-H(2A)</td>
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<td>N(1)-S(1)-Cl(1)</td>
<td>103.18(6)</td>
</tr>
<tr>
<td>C(1)-C(2)-H(2A)</td>
<td>113.9</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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Table 4. Anisotropic displacement parameters (Å² x 10³) for plnu05. The anisotropic displacement factor exponent takes the form: -2π²[h² a²U₁₁ + ... + 2 h k a* b* U₁₂]

<table>
<thead>
<tr>
<th></th>
<th>U₁₁</th>
<th>U₂₂</th>
<th>U₃₃</th>
<th>U₁₂</th>
<th>U₁₃</th>
<th>U₁₂</th>
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</thead>
<tbody>
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<td>23(1)</td>
<td>22(1)</td>
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<td>4(1)</td>
<td>-4(1)</td>
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<tr>
<td>C(2)</td>
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<td>30(1)</td>
<td>31(1)</td>
<td>7(1)</td>
<td>3(1)</td>
<td>2(1)</td>
</tr>
<tr>
<td>C(3)</td>
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<td>22(1)</td>
<td>35(1)</td>
<td>0(1)</td>
<td>4(1)</td>
<td>0(1)</td>
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<td>C(4)</td>
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<td>18(1)</td>
<td>3(1)</td>
<td>5(1)</td>
<td>0(1)</td>
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<td>-8(1)</td>
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<td>25(1)</td>
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<td>10(1)</td>
<td>-1(1)</td>
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<tr>
<td>Cl(1)</td>
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<td>30(1)</td>
<td>34(1)</td>
<td>-5(1)</td>
<td>2(1)</td>
<td>-3(1)</td>
</tr>
<tr>
<td>F(1)</td>
<td>24(1)</td>
<td>32(1)</td>
<td>33(1)</td>
<td>-8(1)</td>
<td>7(1)</td>
<td>-9(1)</td>
</tr>
<tr>
<td>N(1)</td>
<td>18(1)</td>
<td>24(1)</td>
<td>22(1)</td>
<td>1(1)</td>
<td>8(1)</td>
<td>3(1)</td>
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<tr>
<td>O(1)</td>
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<td>34(1)</td>
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<td>11(1)</td>
<td>8(1)</td>
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<tr>
<td>O(3)</td>
<td>26(1)</td>
<td>20(1)</td>
<td>32(1)</td>
<td>0(1)</td>
<td>4(1)</td>
<td>2(1)</td>
</tr>
<tr>
<td>S(1)</td>
<td>16(1)</td>
<td>21(1)</td>
<td>22(1)</td>
<td>1(1)</td>
<td>6(1)</td>
<td>-1(1)</td>
</tr>
</tbody>
</table>
Table 5. Hydrogen coordinates ($x \times 10^4$) and isotropic displacement parameters ($\AA^2 \times 10^3$) for plnu05.

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

<p>| | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>N</td>
<td>0.665493</td>
<td>0.418156</td>
<td>-0.179637</td>
</tr>
<tr>
<td>C</td>
<td>1.506227</td>
<td>0.451207</td>
<td>1.051268</td>
</tr>
<tr>
<td>C</td>
<td>2.816076</td>
<td>-0.226468</td>
<td>0.891209</td>
</tr>
<tr>
<td>C</td>
<td>0.878744</td>
<td>1.350863</td>
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<tr>
<td>O</td>
<td>0.301163</td>
<td>1.700881</td>
<td>-2.119813</td>
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<tr>
<td>S</td>
<td>-0.653670</td>
<td>-0.675017</td>
<td>-0.220016</td>
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<tr>
<td>CL</td>
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<td>0.370244</td>
<td>0.897448</td>
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<tr>
<td>O</td>
<td>-2.481118</td>
<td>1.814620</td>
<td>0.556094</td>
</tr>
<tr>
<td>O</td>
<td>-1.125028</td>
<td>-0.729734</td>
<td>-1.571876</td>
</tr>
<tr>
<td>H</td>
<td>0.910104</td>
<td>-0.008866</td>
<td>1.843423</td>
</tr>
<tr>
<td>F</td>
<td>1.634490</td>
<td>1.793043</td>
<td>1.371460</td>
</tr>
<tr>
<td>H</td>
<td>3.222614</td>
<td>-0.339300</td>
<td>-0.111212</td>
</tr>
<tr>
<td>H</td>
<td>3.495338</td>
<td>-0.174672</td>
<td>1.737348</td>
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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)

<table>
<thead>
<tr>
<th>Atom</th>
<th>X</th>
<th>Y</th>
<th>Z</th>
</tr>
</thead>
<tbody>
<tr>
<td>N</td>
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<td>0.154261</td>
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<tr>
<td>C</td>
<td>2.473411</td>
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<td>0.971303</td>
</tr>
<tr>
<td>C</td>
<td>2.745437</td>
<td>0.713232</td>
<td>0.177182</td>
</tr>
<tr>
<td>C</td>
<td>1.045789</td>
<td>0.835911</td>
<td>-0.493058</td>
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<tr>
<td>O</td>
<td>0.846808</td>
<td>1.714573</td>
<td>-1.258577</td>
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<tr>
<td>S</td>
<td>-1.132957</td>
<td>-0.515751</td>
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<tr>
<td>CL</td>
<td>-2.121174</td>
<td>1.133346</td>
<td>0.627833</td>
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<tr>
<td>O</td>
<td>-1.477952</td>
<td>-1.660921</td>
<td>0.568354</td>
</tr>
<tr>
<td>O</td>
<td>-1.383246</td>
<td>-0.451139</td>
<td>-1.645827</td>
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<tr>
<td>F</td>
<td>2.772563</td>
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<tr>
<td>H</td>
<td>2.093155</td>
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<td>H</td>
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<tr>
<td>H</td>
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<td>1.663904</td>
<td>0.690610</td>
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</table>

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Structure 4. Reaction product local minimum

Cartesian coordinates (in angstroms)

<table>
<thead>
<tr>
<th>Atom</th>
<th>X</th>
<th>Y</th>
<th>Z</th>
</tr>
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<tbody>
<tr>
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<tr>
<td>C</td>
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<tr>
<td>C</td>
<td>2.443394</td>
<td>0.792026</td>
<td>0.219812</td>
</tr>
<tr>
<td>C</td>
<td>1.293181</td>
<td>1.024826</td>
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<tr>
<td>O</td>
<td>0.976592</td>
<td>1.825037</td>
<td>-1.586651</td>
</tr>
<tr>
<td>S</td>
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<td>-0.565398</td>
<td>-0.260045</td>
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<tr>
<td>CL</td>
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<td>0.886519</td>
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<tr>
<td>O</td>
<td>-1.109205</td>
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<td>0.524399</td>
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<tr>
<td>O</td>
<td>-1.475615</td>
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<td>-1.595299</td>
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<tr>
<td>F</td>
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<td>0.892142</td>
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<tr>
<td>H</td>
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<tr>
<td>H</td>
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<tr>
<td>H</td>
<td>2.681197</td>
<td>1.654629</td>
<td>0.843558</td>
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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.

<table>
<thead>
<tr>
<th>Stationary point</th>
<th>E(MP2/6-311G(d,p))</th>
<th>Zero-point energy</th>
<th>Relative energy</th>
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<tbody>
<tr>
<td>CSI + CH2=CHF</td>
<td>-1352.507608</td>
<td>0.067482</td>
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<tr>
<td>Stepwise reactive</td>
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<tr>
<td>intermediate</td>
<td>-1352.422724</td>
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<td>56.9</td>
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<tr>
<td>Stepwise TS</td>
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<td>0.069565</td>
<td>60.9</td>
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<tr>
<td>Concerted TS</td>
<td>-1352.461899</td>
<td>0.069305</td>
<td>29.8</td>
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<tr>
<td>Product</td>
<td>-1352.540651</td>
<td>0.073210</td>
<td>-17.1</td>
</tr>
</tbody>
</table>

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