

***NEW STEREOSELECTIVE SYNTHESIS OF POLYFLUORINATED
exo-NORBORNENES.***

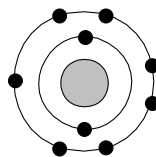
Viacheslav Petrov

*^a DuPont Central Research and Development
Experimental Station, PO Box 0328 Wilmington DE 19880*

**7th ALL-RUSSIAN CONFERENCE
“FLUORINE CHEMISTRY”**

**On the occasion of 100th anniversary of
Professor
Ivan Ludvigovich KNUNYANTS**

**June 5-9, 2006
MOSCOW, Russia**



June 6, 2006



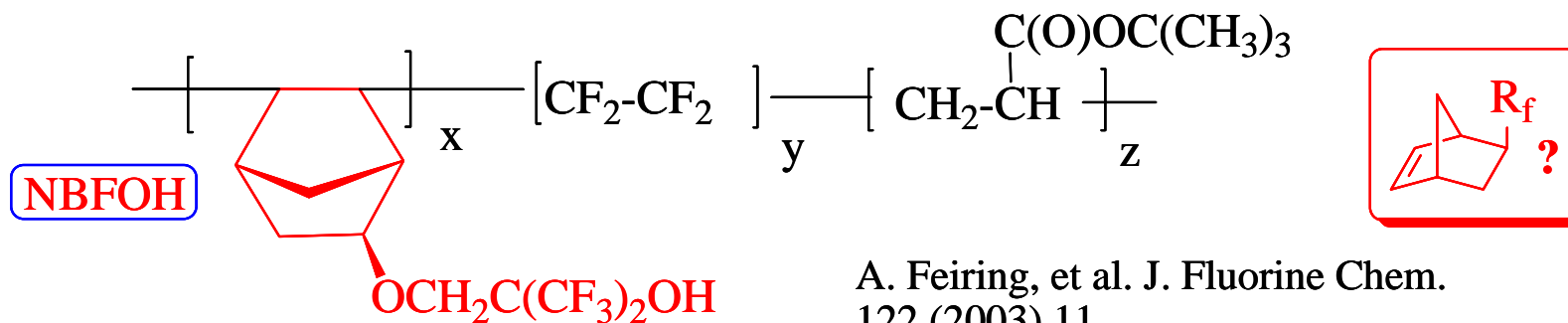
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NEW STEREOSELECTIVE SYNTHESIS OF POLYFLUORINATED exo-NORBORNENES.

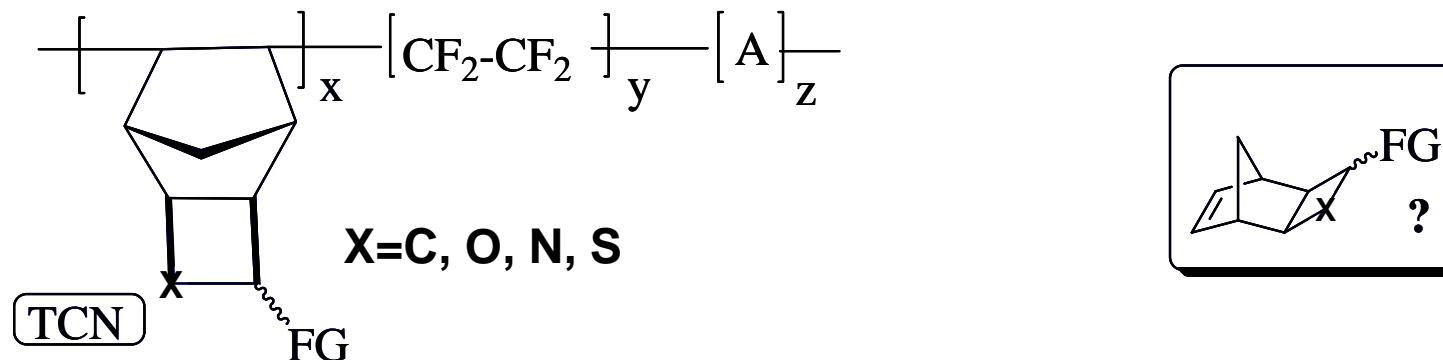
- 1. Norbornene Based Synthesis of *exo*-4-Fluoroalkylnorborn-1-
enes.**
- 2. Quadricyclane Based *exo*- Selective Synthesis of Functional
Fluorinated TriCycloNonene (TCN) Monomers.**
- 3. Quadricyclane Based Synthesis of Oxa-, Aza- and Thia-
Norbornencyclobutanes.**
- 4. Chemical of Transformations of Polyfluorinated
Tricyclononenes.**
- 5. Conclusion.**

DuPont Photoresist Polymer Platforms.

NBFOH platform:



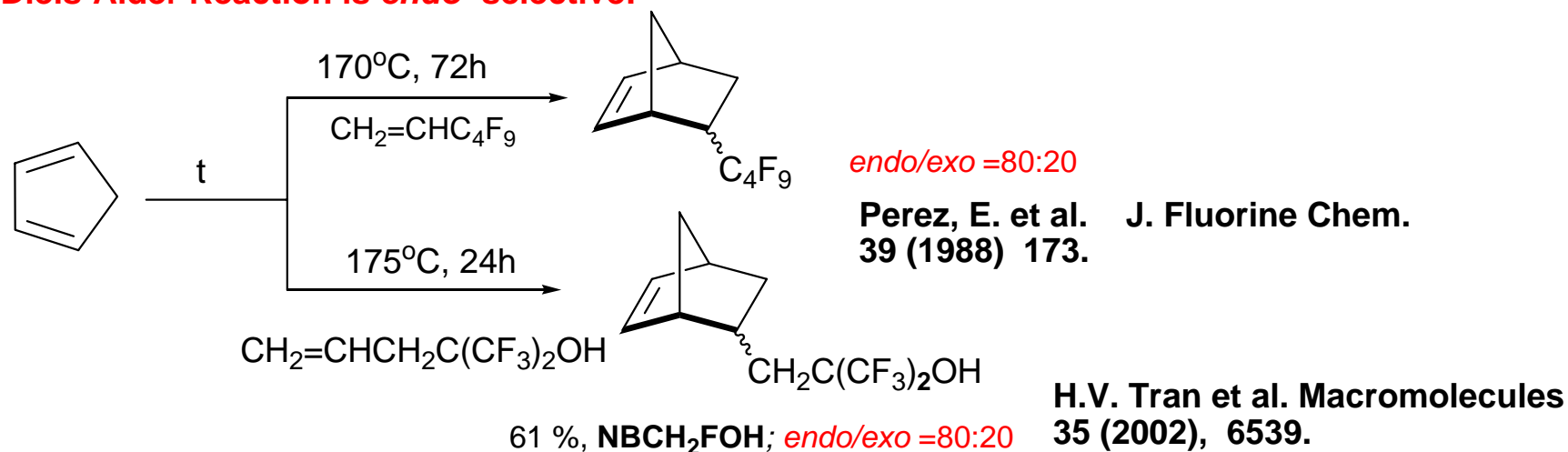
TCN platform:



1. Practical Synthesis of 4-Fluoroalkylnorborn-1-enes.

Endo-/Exo- Selectivity: Diels-Alder vs. Radical Addition.

Diels-Alder Reaction is *endo*- selective:



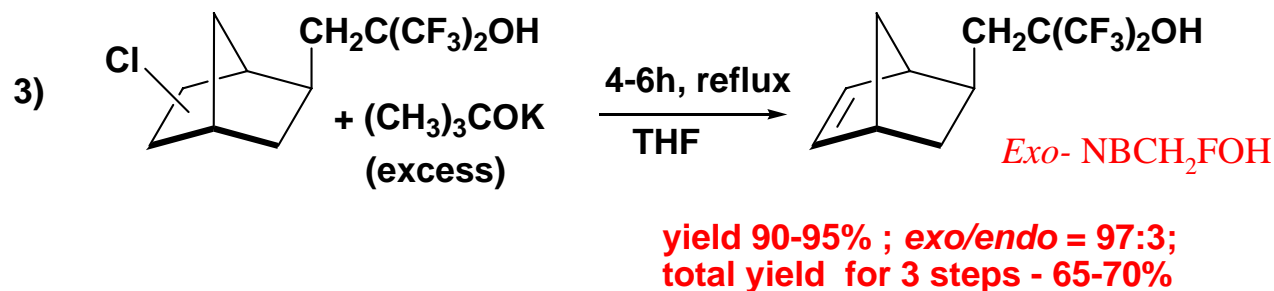
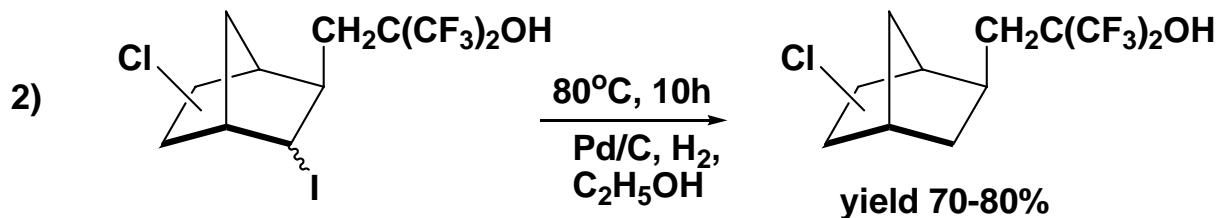
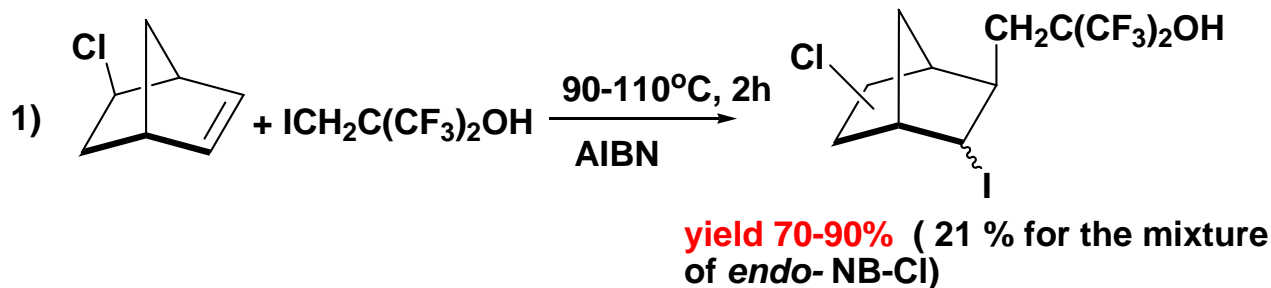
Radical Addition to NB is *exo*- selective (!)



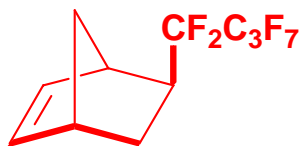
N. O. Brace. J. Org. Chem. 27 (1962), 3027.

A. Feiring, J. Org. Chem. 50 (1985), 3269.

1. Pactical Synthesis of 4-Fluoroalkylnorborn-1-enes.



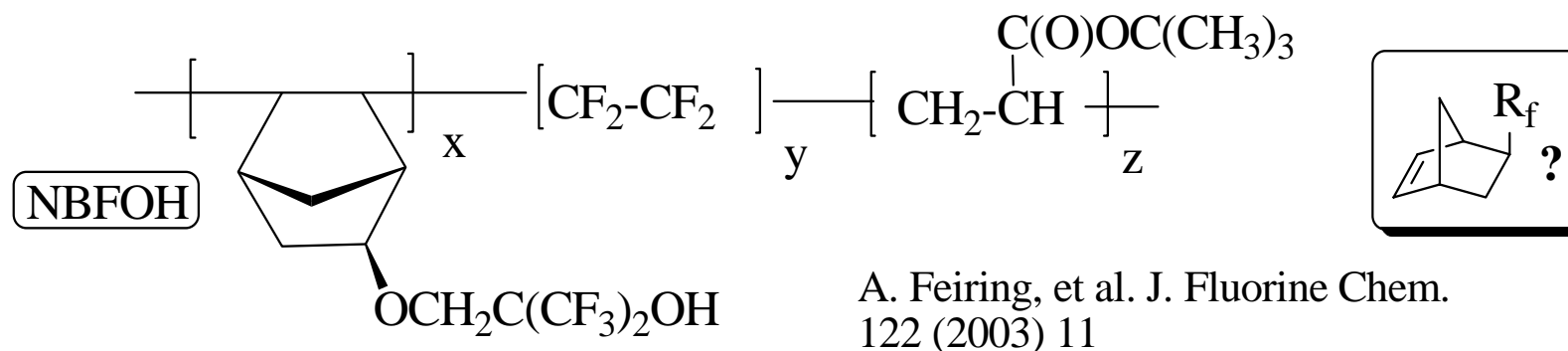
Using similar sequence



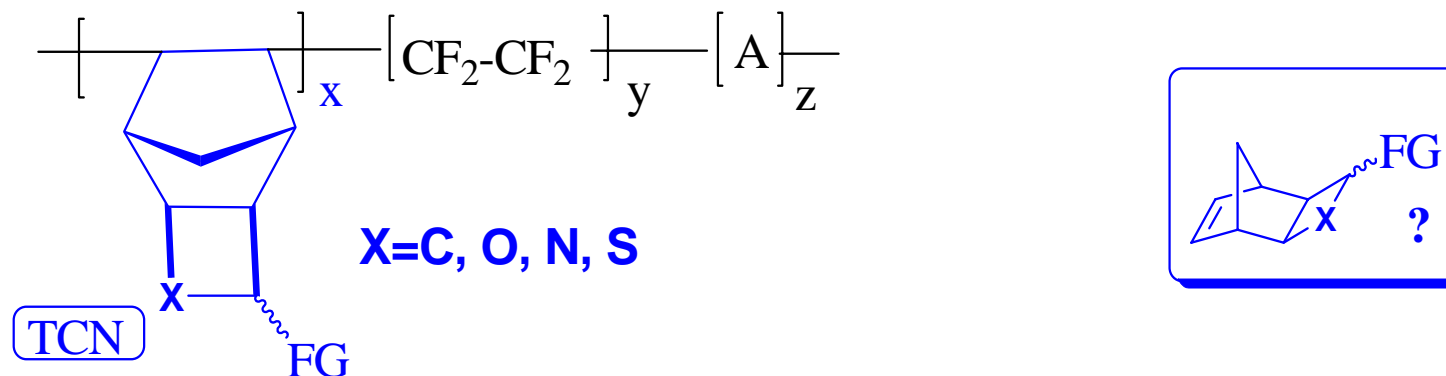
was prepared in ~45% yield (*exo-endo* = 98:2)

DuPont Photoresist Polymer Platforms.

NBFOH platform:

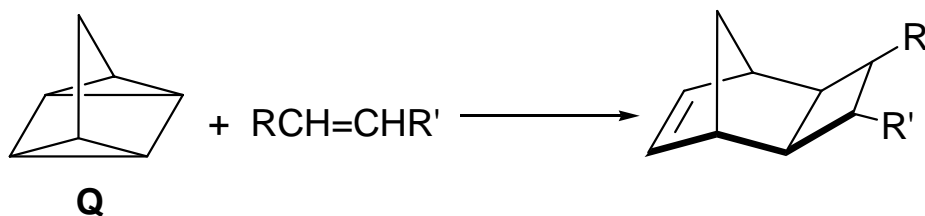


TCN platform:



2. Quadricyclane Based Exo- Selective Synthesis of Fluorinated TriCycloNonene (TCN) Monomers.

Quadricyclane - $[2\sigma+2\sigma+2\pi]$ Cycloaddition Reactions with activated olefins:

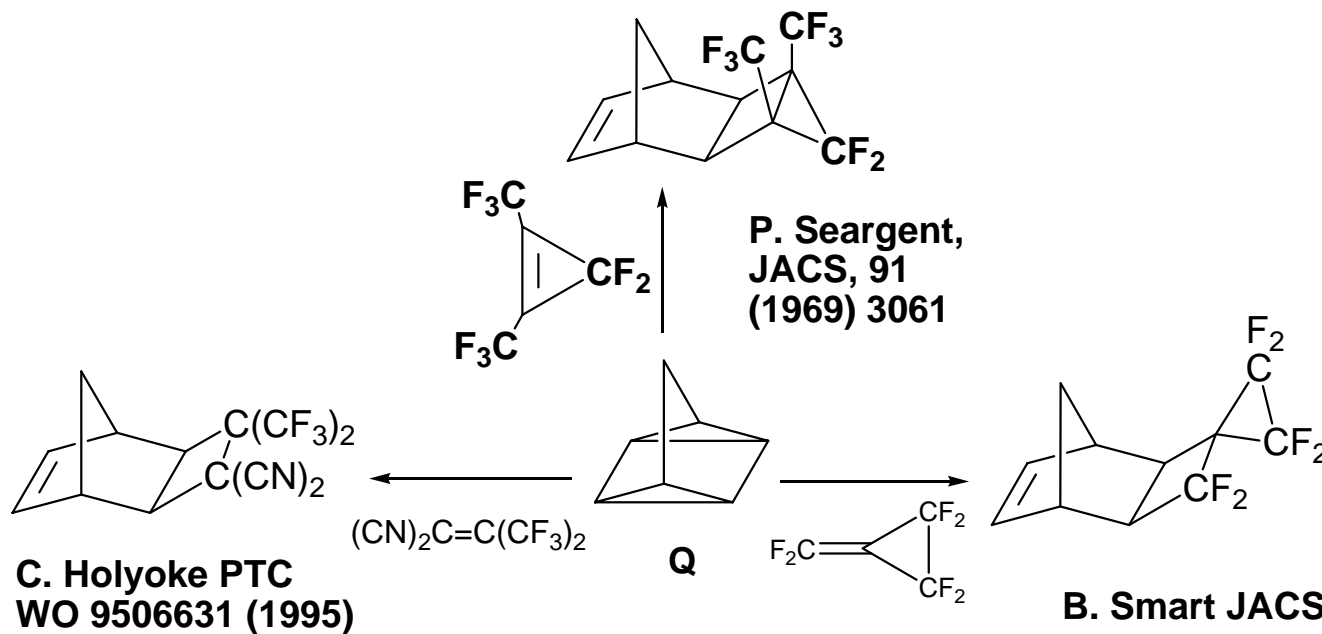


C.D. Smith JACS 88 (1966) 4273.

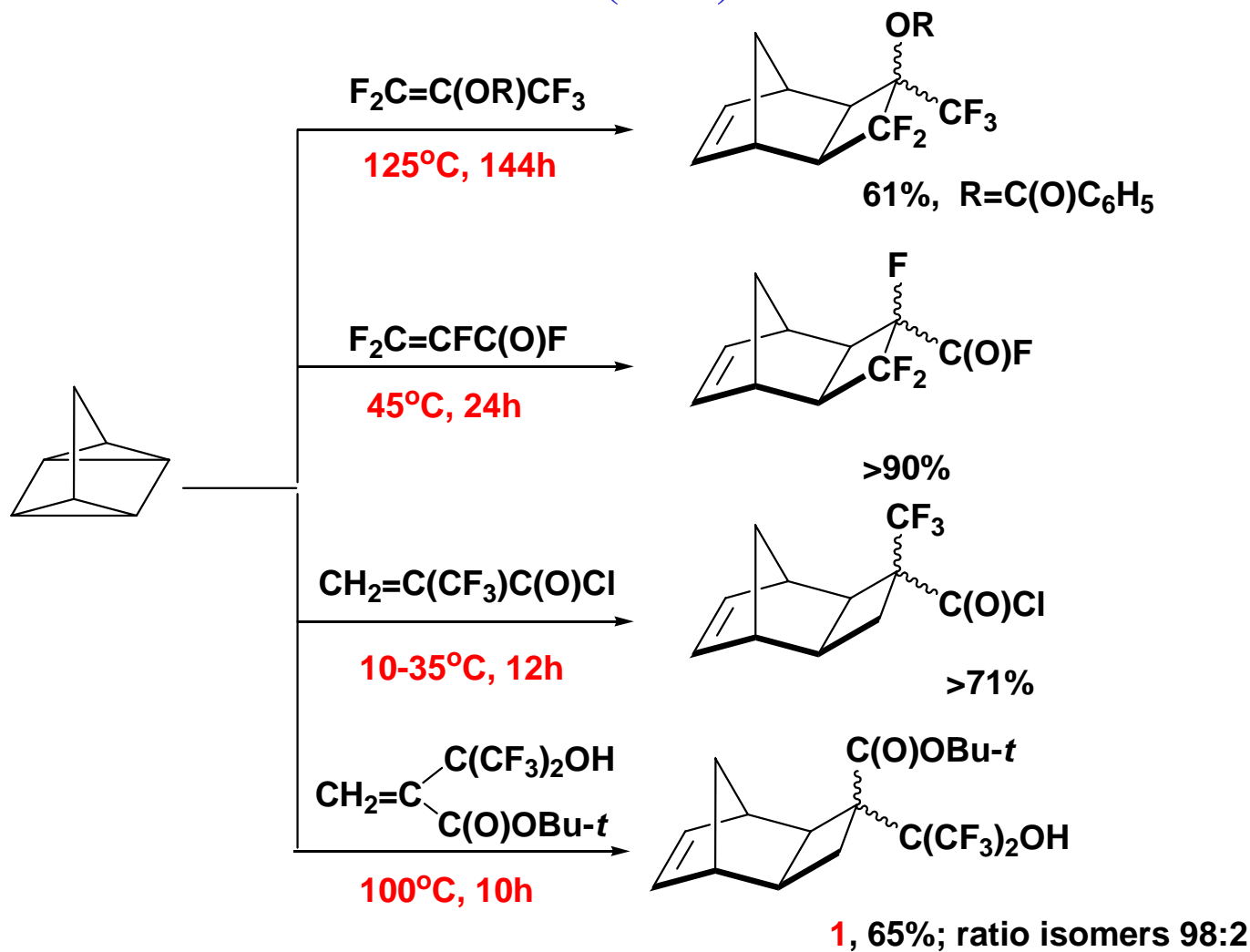
I. Tabushi et al. JACS 94 (1972) 787.

V. Petrov, N. Vasil'ev Current Organic Synthesis, v.3, 2006, pp. 215-259

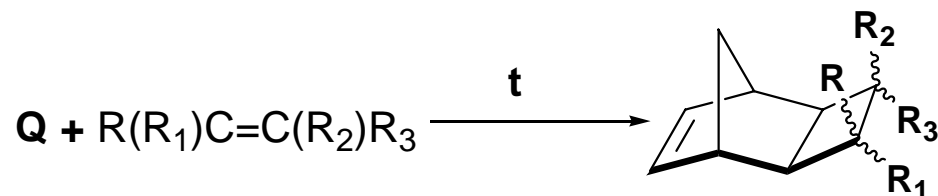
Cycloaddition to Fluoroolefins:



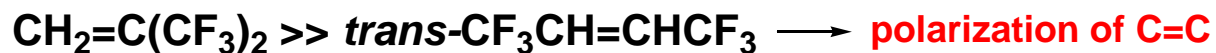
2.1. Synthesis of Functional Fluorinated TCN-Monomers (X=C).



2.2 Cycloaddition of Quadricyclane to Fluoroolefins.



R	R ₁	R ₂	R ₃	Temp. (°C)	Time(h)	Yield (%)
F	F	F	F	110	72	10
CF ₃	F	F	F	110	48	22
CF ₃	F	CF ₃	F	110	48	30
CF ₃	CF ₃	H	H	100	16	63
CF ₃	H	CF ₃	H	110	72	<1
CF ₃	CF ₃	C ₂ F ₅	F	90	12	56



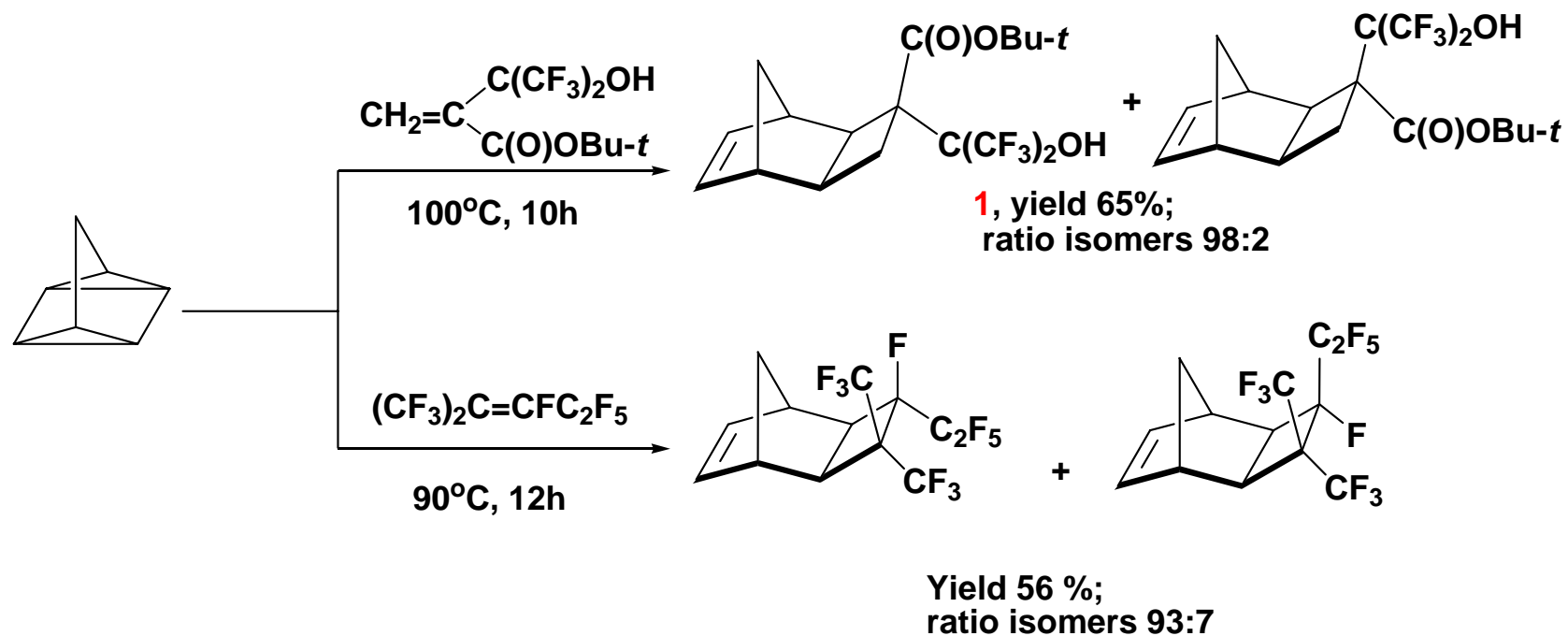
V. Petrov, F. Davidson, P. Krusic, A. Marchione, W. Marshall
J. Fluorine Chem. 126 (2005) 601-610.

2.4 Relative Reactivities of Fluoroolefins in the $[_p2+_s2+_s2]$ Cycloaddition to Quadricyclane at 109 °C.

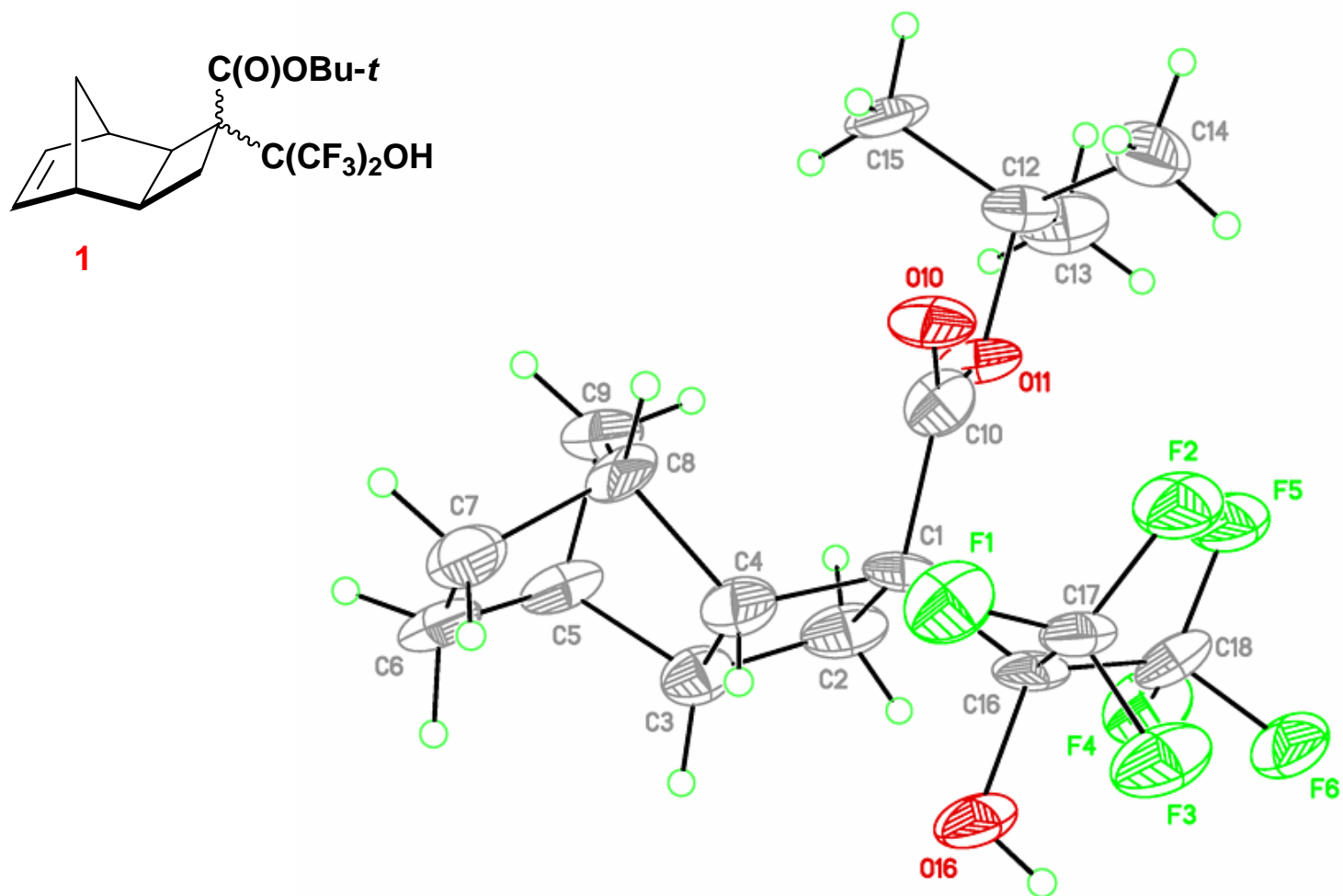
Fluoroolefin	Pseudo first-order Rate (h^{-1})	Relative Reactivity	
$\text{CF}_3\text{CF}=\text{CF}_2$ HFP	0.021	1	Reactivity towards Q: $(\text{CF}_3)_2\text{C}=\text{CFC}_2\text{F}_5 \gg (\text{CF}_3)_2\text{C}=\text{C}(\text{CF}_3)_2$
<i>cis</i> - $\text{CF}_3\text{CF}=\text{CFCF}_3$	0.026	1.2	$>\text{CF}_3\text{CF}=\text{CFCF}_3 > \text{CF}_3\text{CF}=\text{CF}_2 > \text{CF}_2=\text{CF}_2$
<i>trans</i> - $\text{CF}_3\text{CF}=\text{CFCF}_3$	0.039	1.9	Calculated LUMO (MINDO): $(\text{CF}_3)_2\text{C}=\text{C}(\text{CF}_3)_2 > (\text{CF}_3)_2\text{C}=\text{CFCF}_3 >$
$(\text{CF}_3)_2\text{C}=\text{C}(\text{CF}_3)_2$	0.085	4.0	$>\text{CF}_3\text{CF}=\text{CFCF}_3 > \text{CF}_3\text{CF}=\text{CF}_2 > \text{CF}_2=\text{CF}_2$
$(\text{CF}_3)_2\text{C}=\text{CH}_2$	0.27	13	LUMO of $\text{CF}_2=\text{CF}_2$ is ~ 2 eV higher compared to LUMO of $(\text{CF}_3)_2\text{C}=\text{C}(\text{CF}_3)_2$
$(\text{CF}_3)_2\text{C}=\text{CHCH}=\text{CH}_2$	0.6	29	
$(\text{CF}_3)_2\text{C}=\text{CF}-\text{CF}_2\text{CF}_3$ HFP dimer	2.9	138	I.N. Rozhkov, Yu. A. Borisov Izv. AN USSR. Ser Khim. 1992, 1334 -1340

* TFE ~ 0.3 - 0.5

2.5 Effect of Substituent.

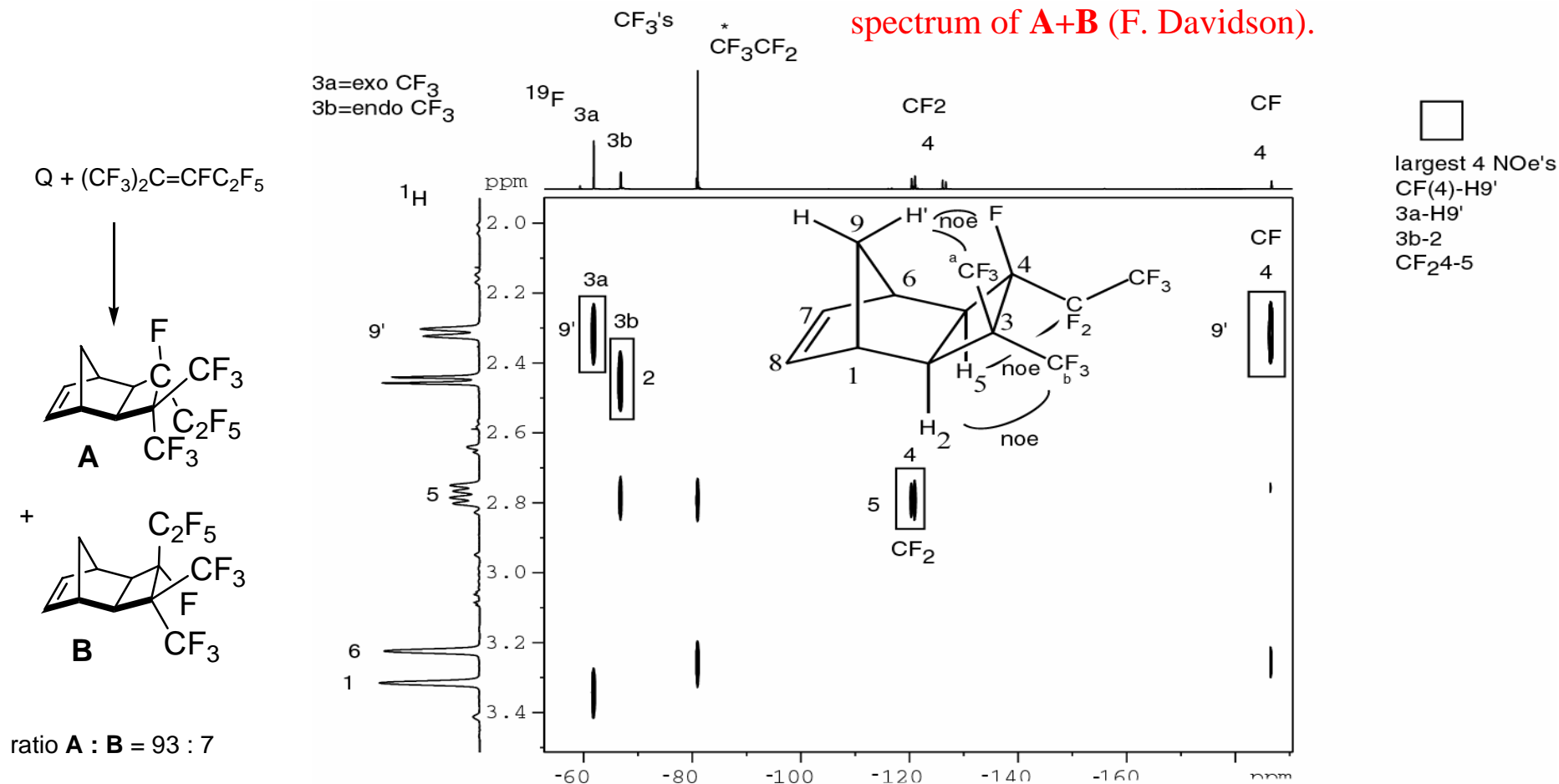


2.6.a Structure of Bifunctional Monomer 1. (W. Marshall, DuPont, CCAS).



2.6.b Structure of Cycloadducts: *exo*- Orientation of Cyclobutane Ring in Polyfluorinated TriCycloNonenes (TCN's).

Phase-sensitive ^1H - ^{19}F HOESY NMR spectrum of **A+B** (F. Davidson).



V. Petrov, F. Davidson, P. Krusic, A. Marchione, W. Marshall

J. Fluorine Chem. 126 (2005) 601-610

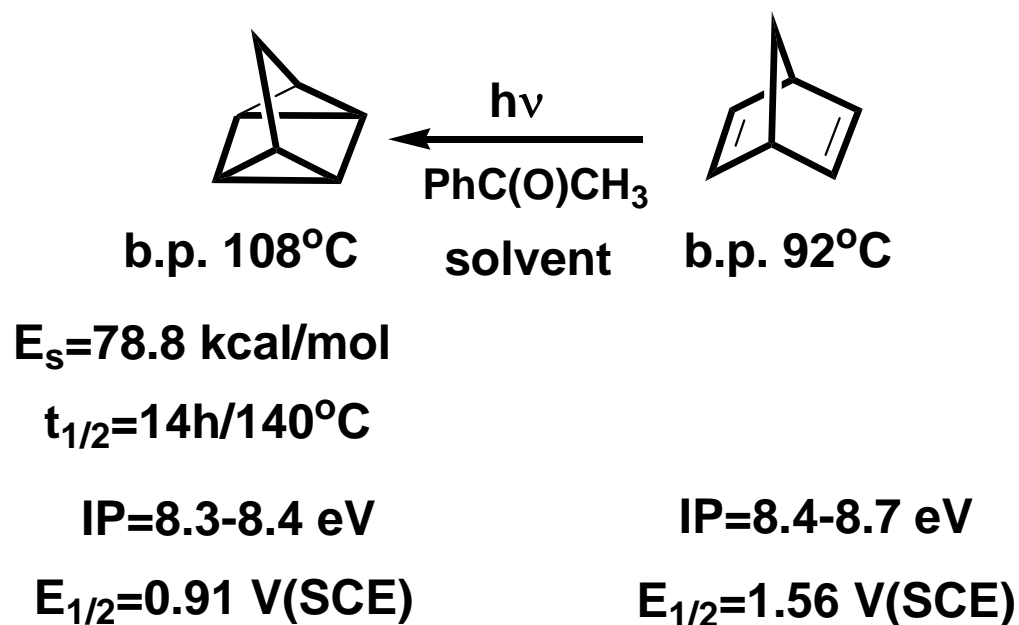
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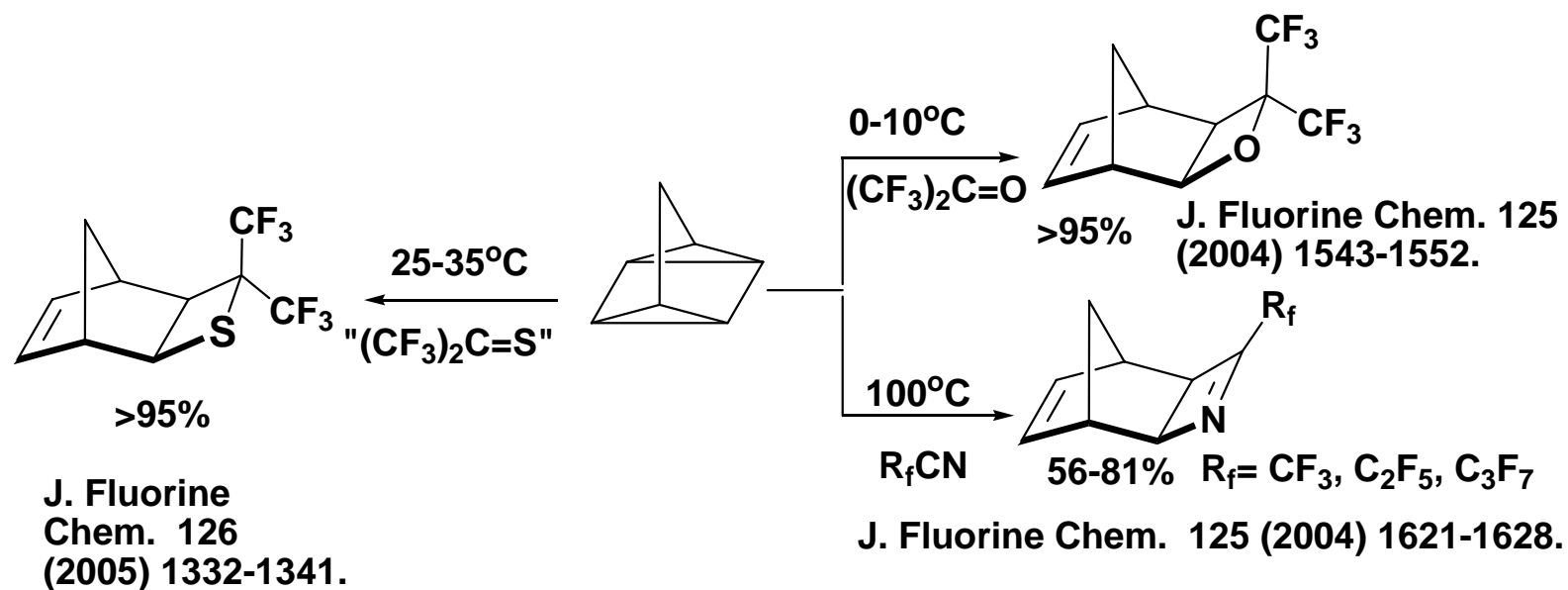
3. Quadricyclane Reactions with Polyfluorinated Carbonyl, Nitrogen and Sulfur Containing Substrates.

Quadricyclane - Preparation and Properties



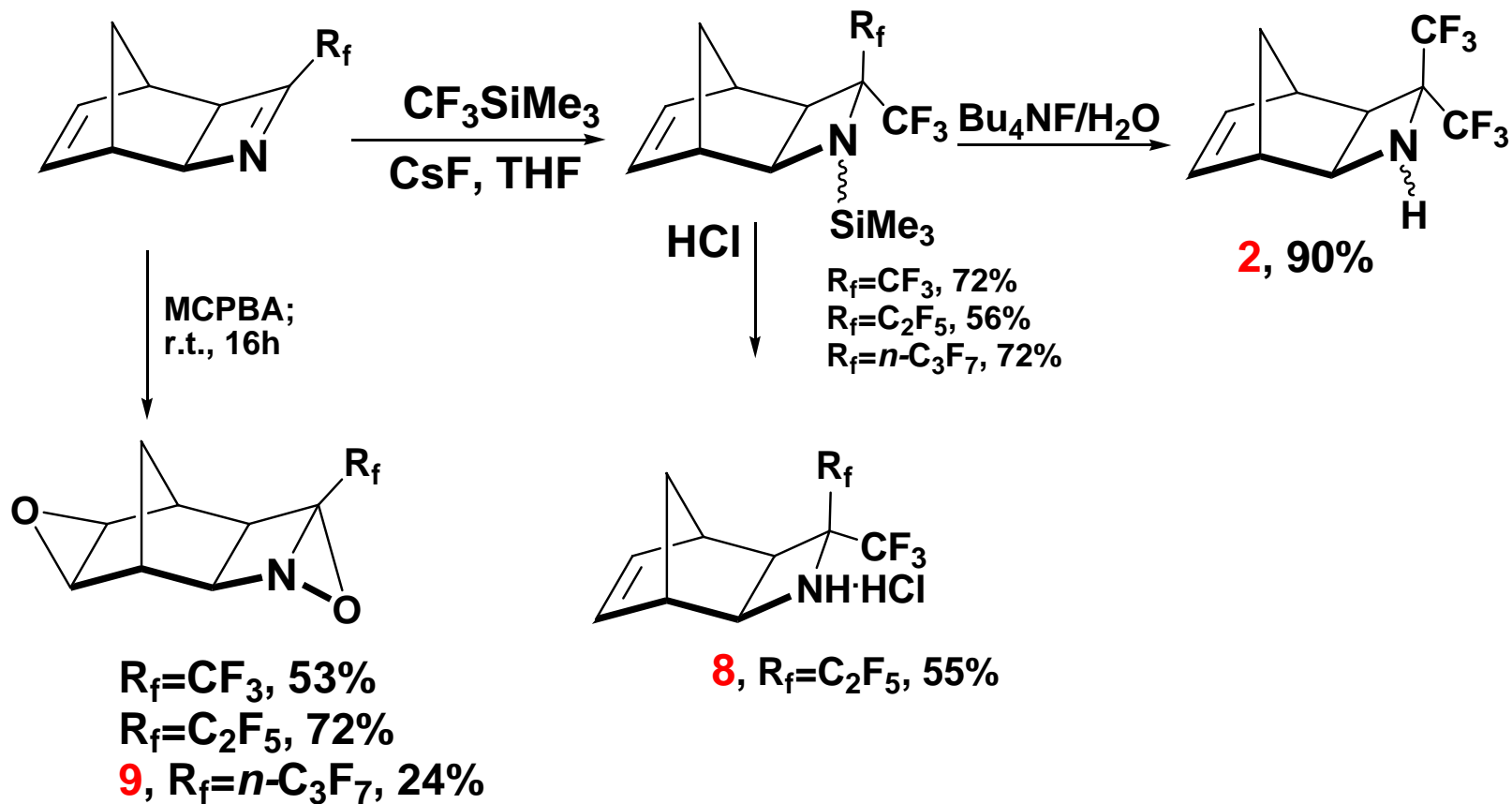
Preparation: Dauben, W., Cargill, R. Tetrahedron, 1961, 15, 197;
Smith, C. Org. Synthesis, 1971, 51, 962

3. Quadricyclane Reactions with Polyfluorinated Carbonyl, Nitrogen and Sulfur Containing Substrates. Preparation of "Hetero-TCN" (X=O, N, S).

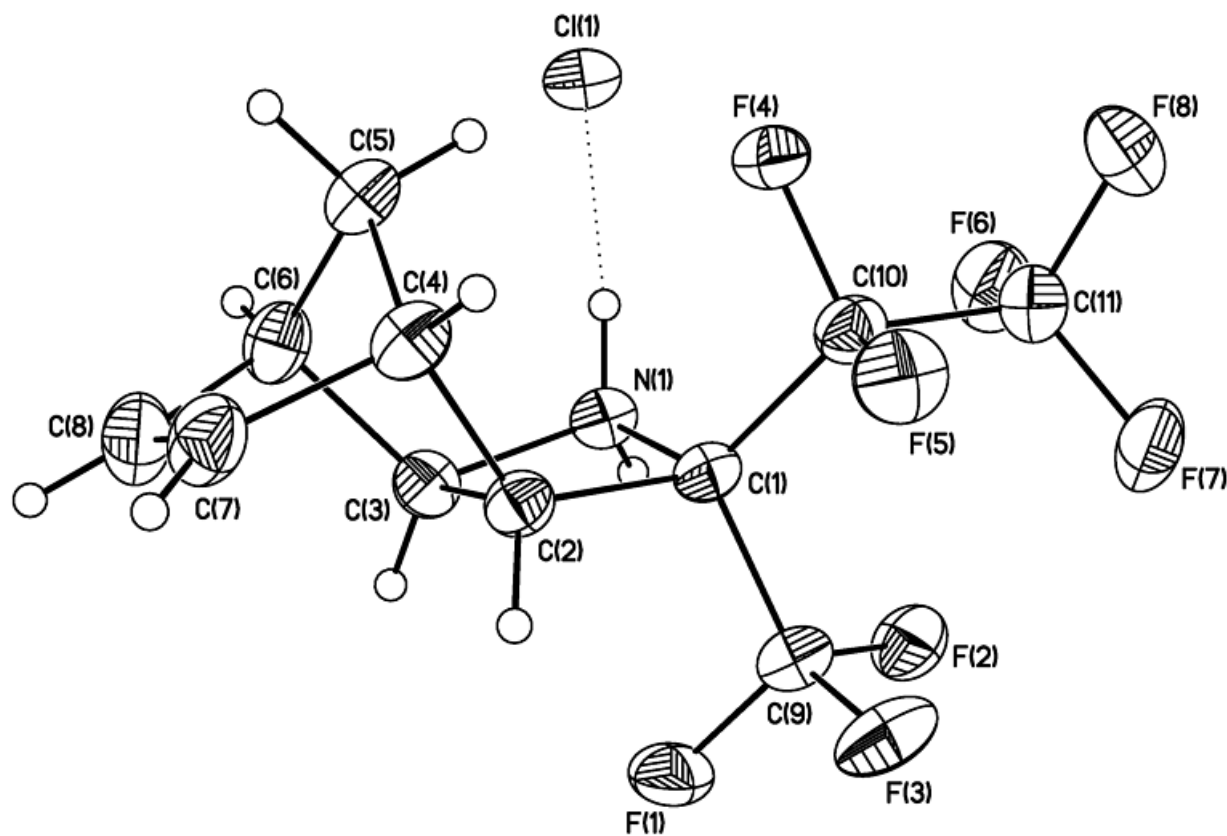
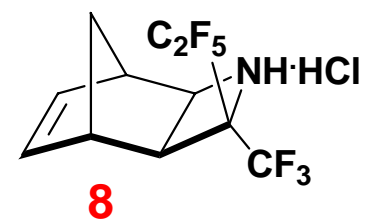


4. Chemical Transformations of Polyfluorinated Tricyclonones.

4.1 Reactions of *exo*-3-Aza-tricyclo[4.2.1.0^{2,5}]non-3,7-dienes.



Structure of Cycloadduct 8 (W. Marshall, DuPont CCAS)

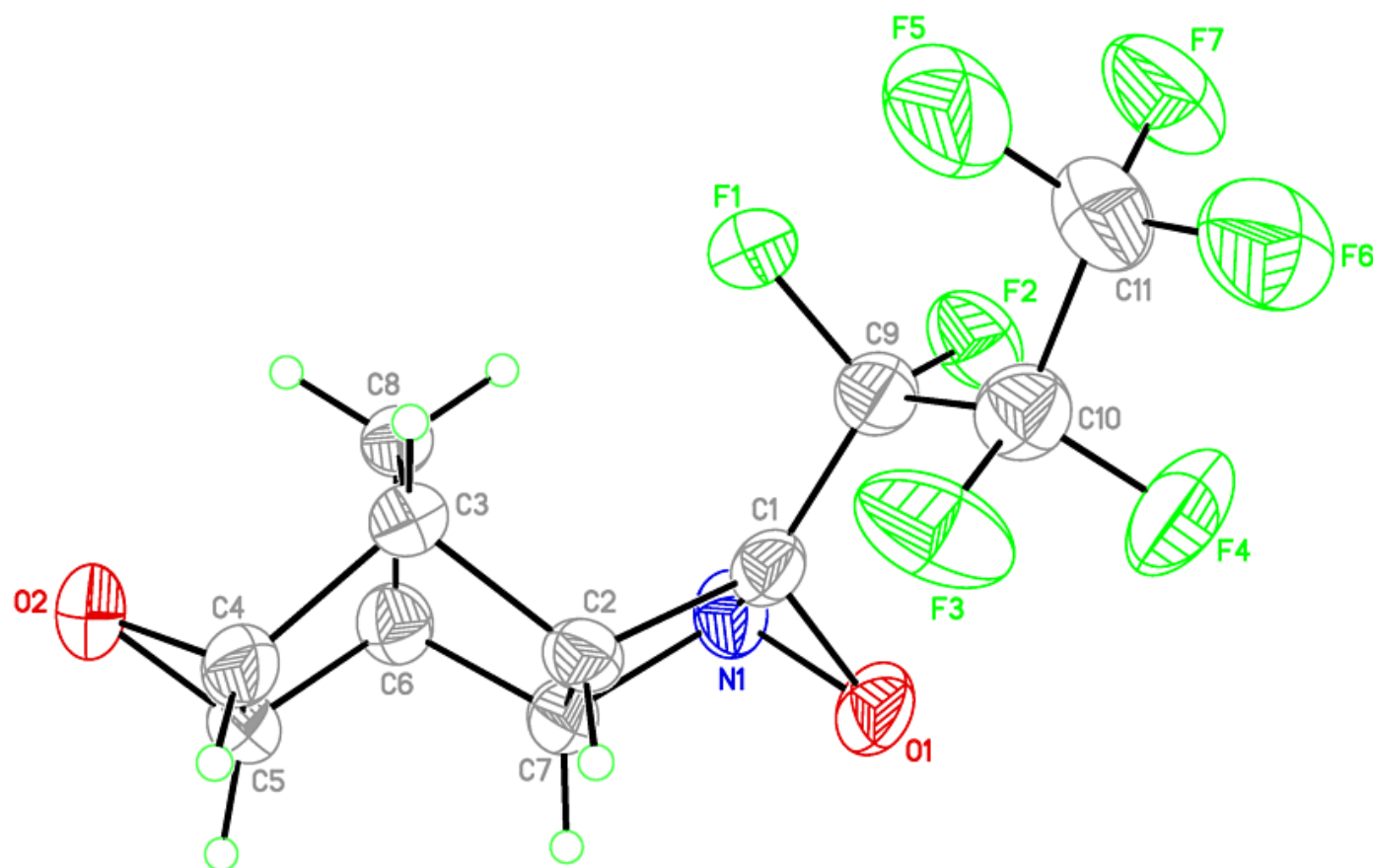


June 6, 2006

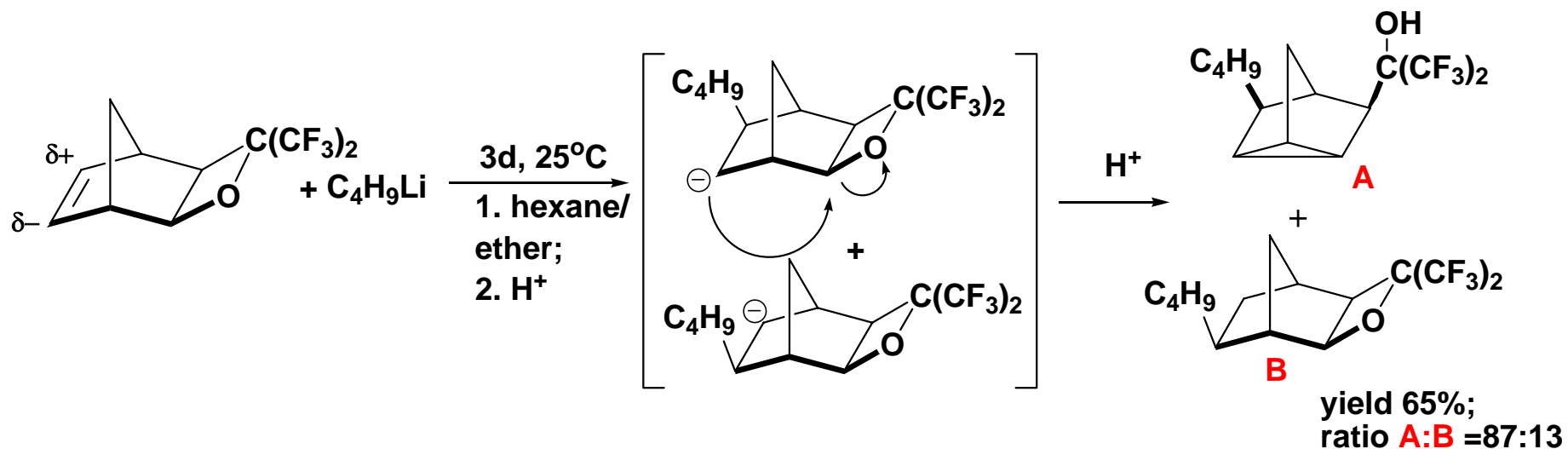


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Structure of Oxaziridine 9 (W. Marshall, DuPont CCAS)

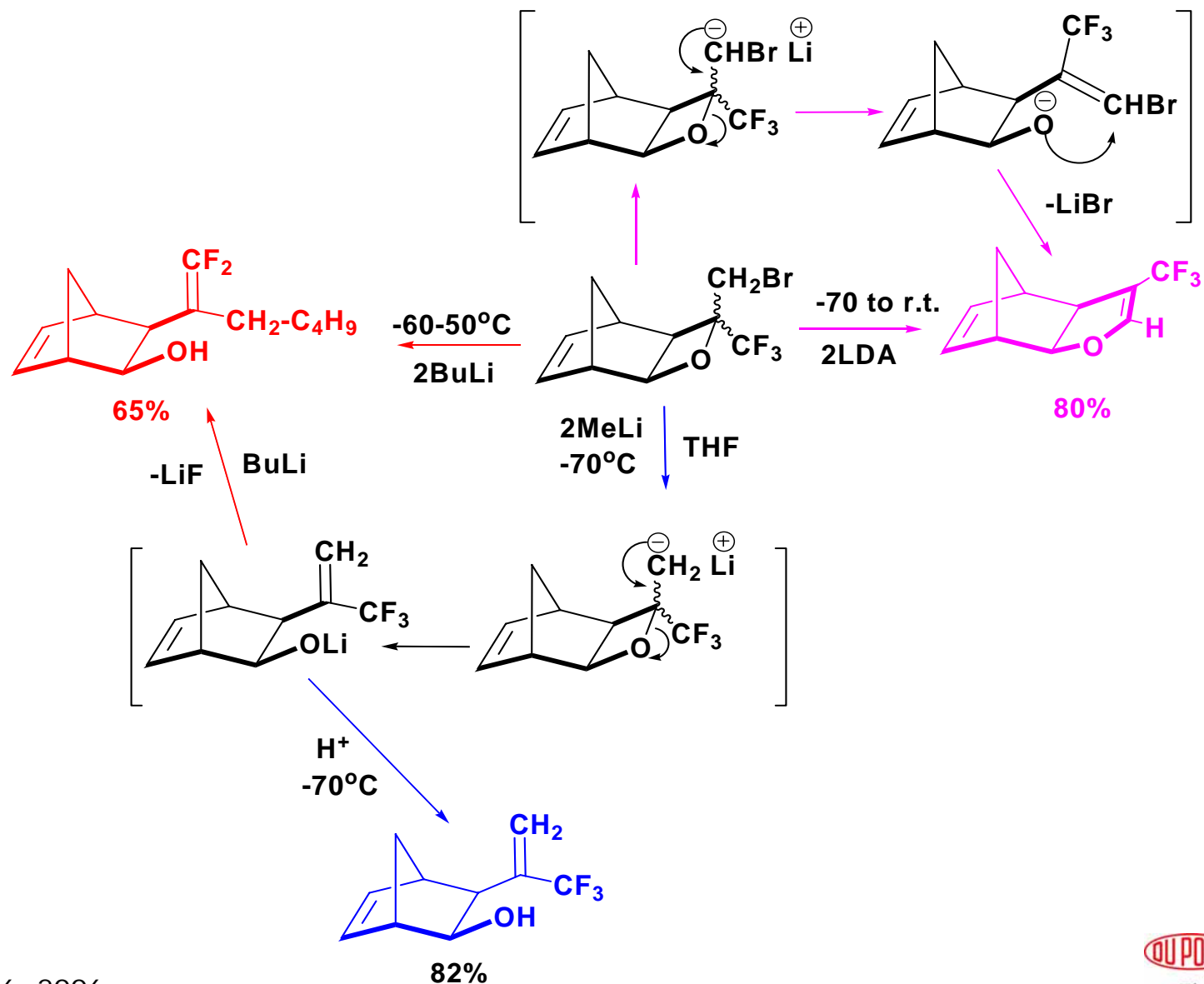


4.2 *Exo*-Selective Ring Opening Reactions of Norbornene-Oxetanes.

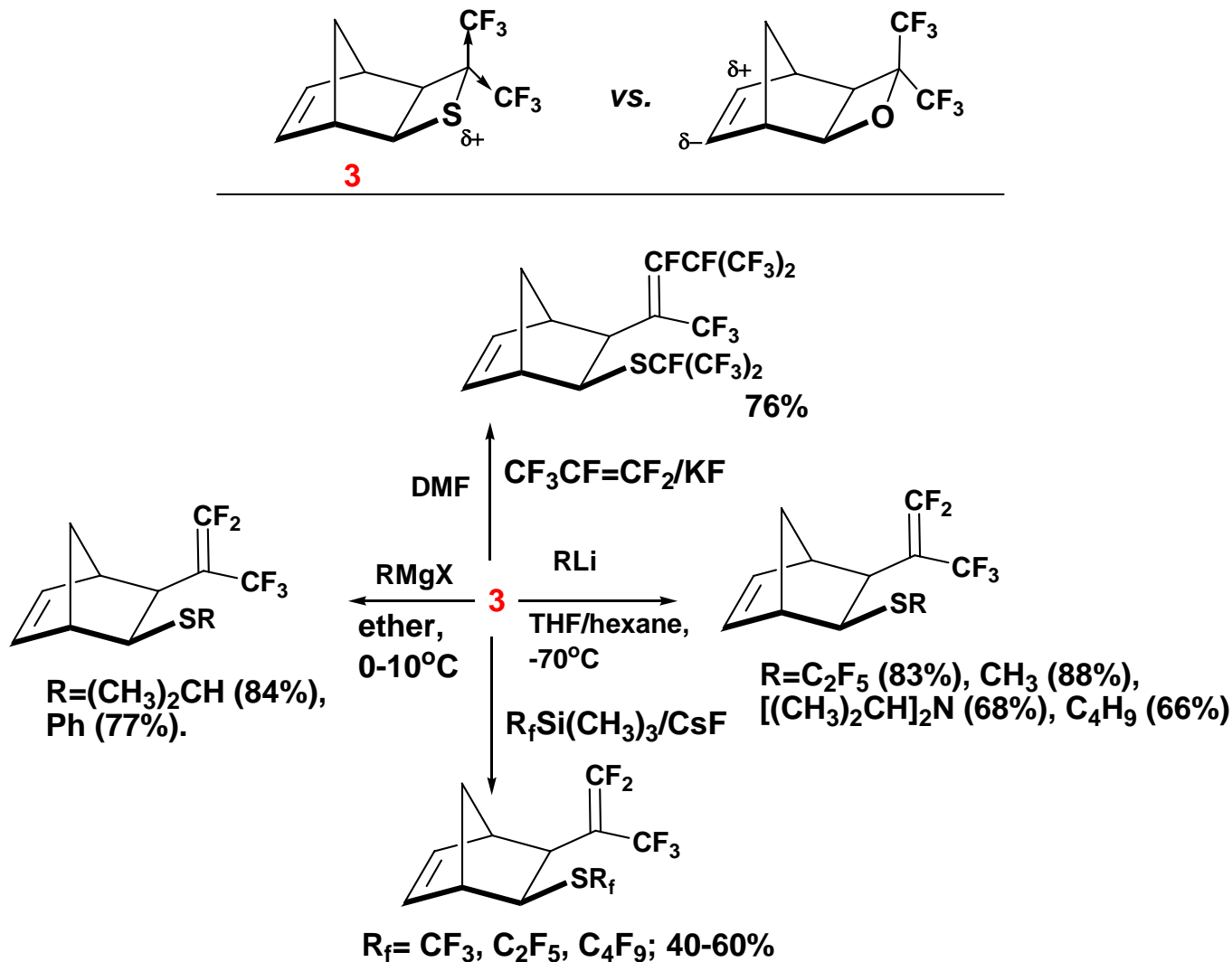


V. Petrov, F. Davidson, B. Smart J. Fluorine Chem.
125, 2004, 1543-1552

4.2 *Exo*-Selective Ring Opening Reactions of Norbornene-Oxetanes.



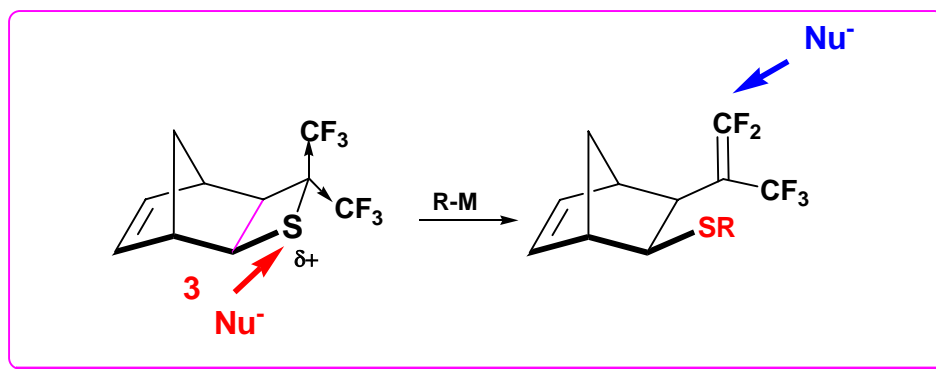
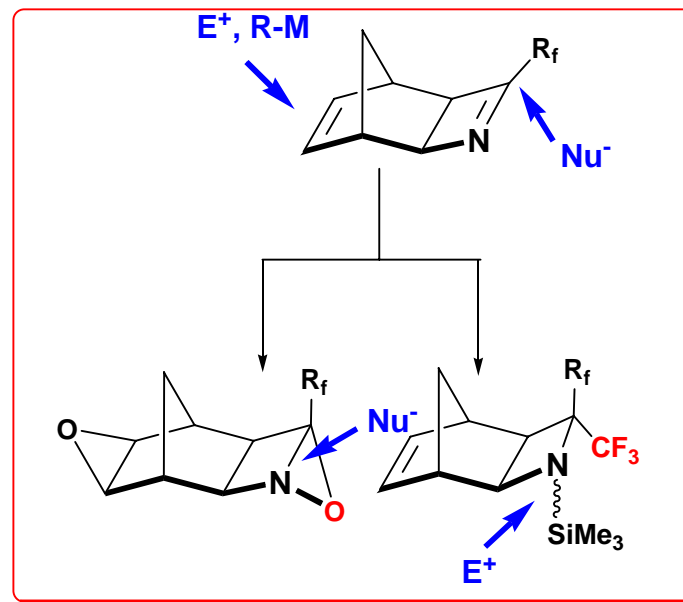
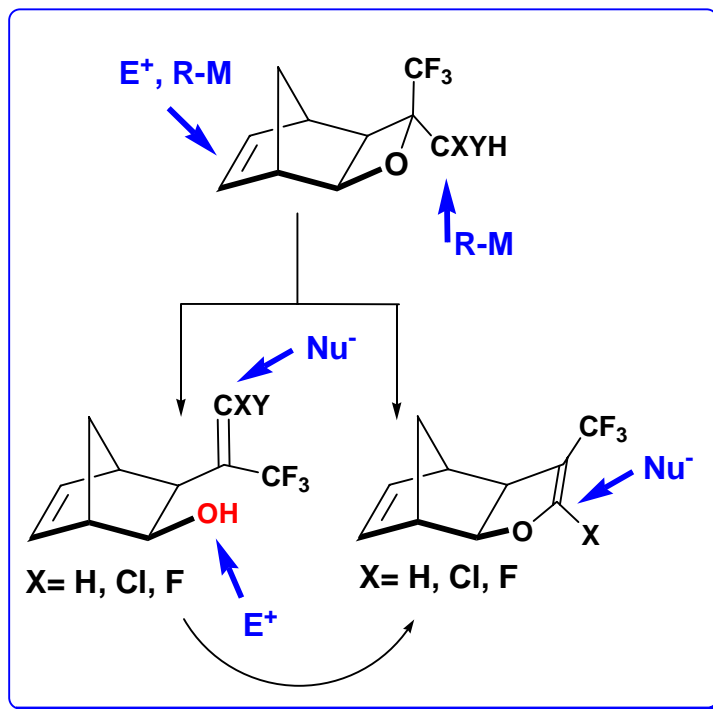
4.3 *Exo*-Selective Ring Opening Reactions of Norbornene-Thietane (3).



V. Petrov, Mendelevov Communications, accepted for publication

5. Conclusion:

Polyfluorinated Tricyclononene Derivatives Are Valuable Starting Materials for Stereoselective Synthesis of Substituted *exo*-Norbornenes.



Acknowledgement

DuPont Analytical

Fredric Davidson (2D HOESY NMR experiments)

Paul Krusic
Alex Marchione (kinetic measurements, high temp. NMR)

Will Marshall (single crystal X-ray diffraction)

DuPont CRD

Andy Feiring

Kurt Adams

157/193 nm Photoresist Team

Vlad Grushin

Robert Smith Jr.

NOE Experiment Data (F. Davidson, DuPont CCAS)

Nucleus= H1
Probe= 5mm CPQUAD
submitter= Petrov, Slava
sample=# 109691-42-2 in CDCl3
run by fred davidson 8/9/05
file=v9_149_1H_Petrov_Noesy_overnight
lms#564374 Job#194625
experiment: 1H 2D Noesy experiment
Temperature: 30 oC
comment: analyzed 8/10/05

2D H1 Noesy for sample 109691-42-2 in CDCl3

Bridge-head show only one coupling indicating a exo endo config.
compound is a norbornene containing -SCF3 and a -C(CF3)=CF2

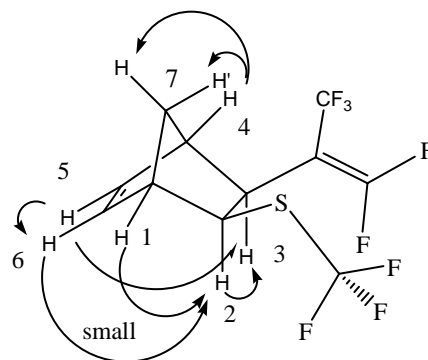
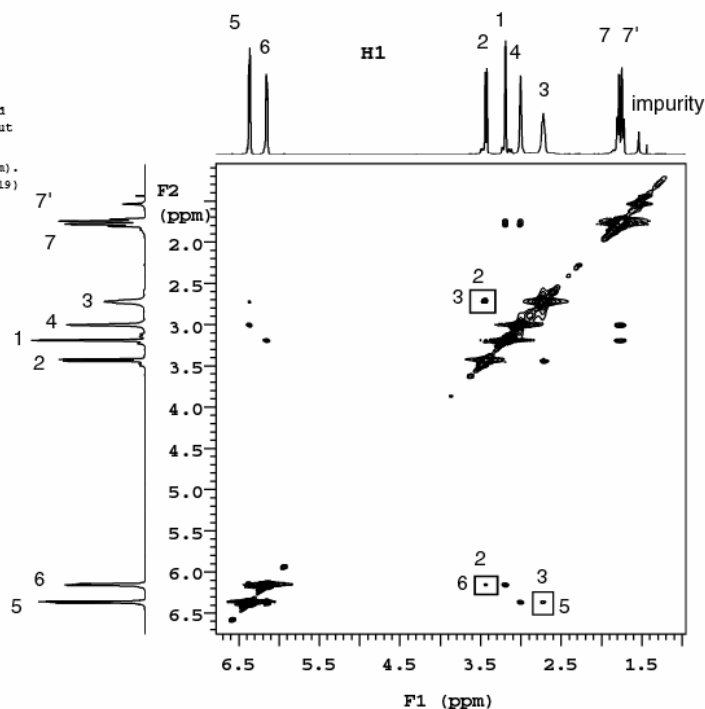
1)The noesy spectrum shows an NOE between the methine protons bound to the carbon bearing the S(3.4ppm) and the -C(CF3)=CF2(2.7ppm), but does not show any Noe between the bridge CH2(approx 1.8ppm) and these protons.
2)The bridge CH2's show noe's to the bridge methine(3.01 and 3.2ppm).
3)The upfield olefin(3.16ppm) shows Noe's to the bridge methine(3.19) and the CH-S(3.4, small Noe).

4) The downfield olefin show noe's to the bridge methine(3.0) and the Methine bearing the -CF=CF2(2.7,small Noe).

Conclusion:

Since the protons whose carbons bear the Sulfur and the -CF=CF2 group show Noe's to themselves but not to the bridge head methylene, one would have to conclude that the substituents are cis-exo, and the protons are cis-endo.

Pulse Sequence: noesy
Solvent: CDCl3
Temp. 30.0 C / 303.1 K
INNOVA-400 "fred400"
PULSE SEQUENCE: noesy
Relax. delay 1.500 sec
Mixing 0.600 sec
Acq. time 0.250 sec
Width 4344.5 Hz
2D Width 4344.5 Hz
48 repetitions
2 x 256 increments
OBSERVE H1, 399.9437186 MHz
DATA PROCESSING
Gauss apodization 0.064 sec
F1 DATA PROCESSING
Line broadening 3.9 Hz
Gauss apodization 0.037 sec
Recall time 19 min, 57 sec



Noe's between	distance in angstroms
H2/H3(large Noe)	2.33
H7,H7'/H1,H4(large)	2.65
H7/H7'(large)	1.8
H5,H7and , H6,H7(small)	3.08

No Noe's between	
H2/H7' or H3/H7'	3.8

distances based on model from Chem Draw 3D.

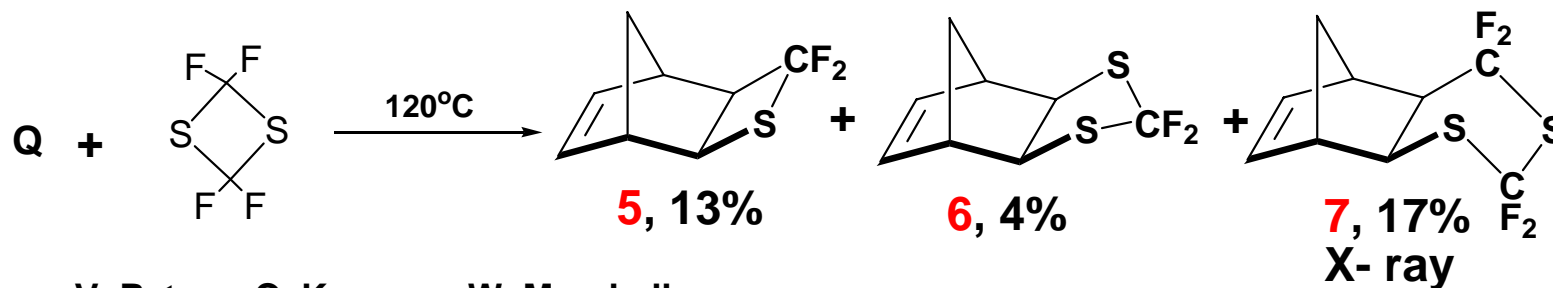
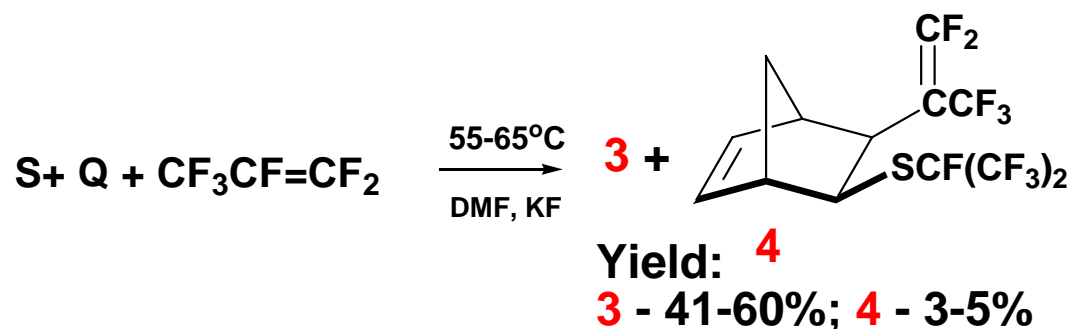
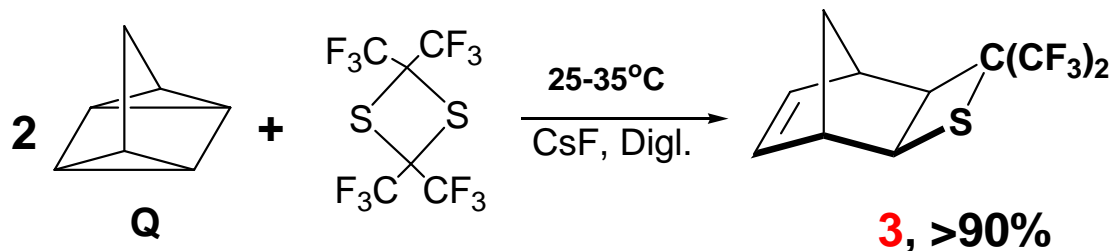
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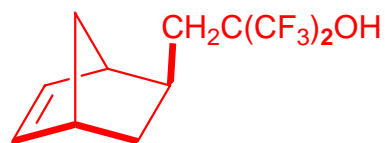
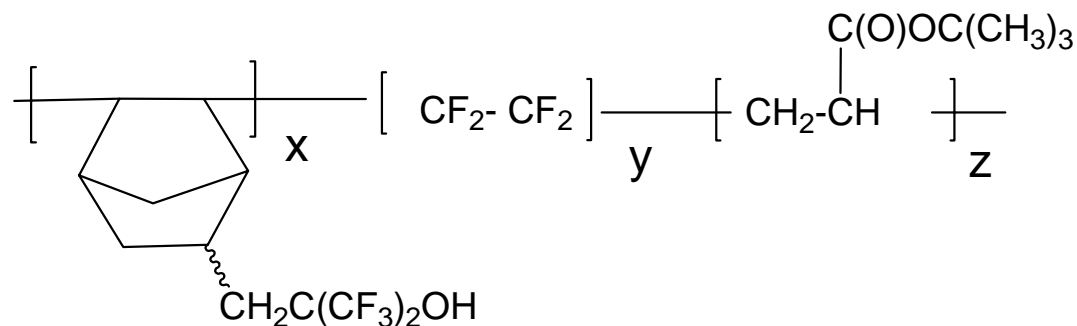
4.3 Fluorinated Sulfur Containing Compounds.

Synthesis of *exo*-3-Thiatricyclo[4.2.1.0^{2,5}]non-7-enes.

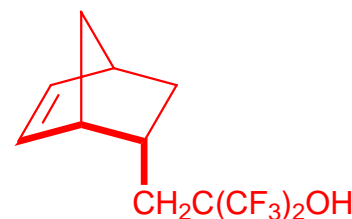


V. Petrov, C. Krespan, W. Marshall
 J. Fluorine Chem. 126 (2005)1332-1341

1. Pactical Synthesis of 4-Fluoroalkylnorborn-1-enes.
***Exo-* Effect in Preparation of TFE/NBCH₂FOH/t-BuAcrylate**
Terpolymer (A.Feiring).



Exo-endo: 97:3



Exo-endo: 15:85

Yield of polymer (g): 29.5

8.5

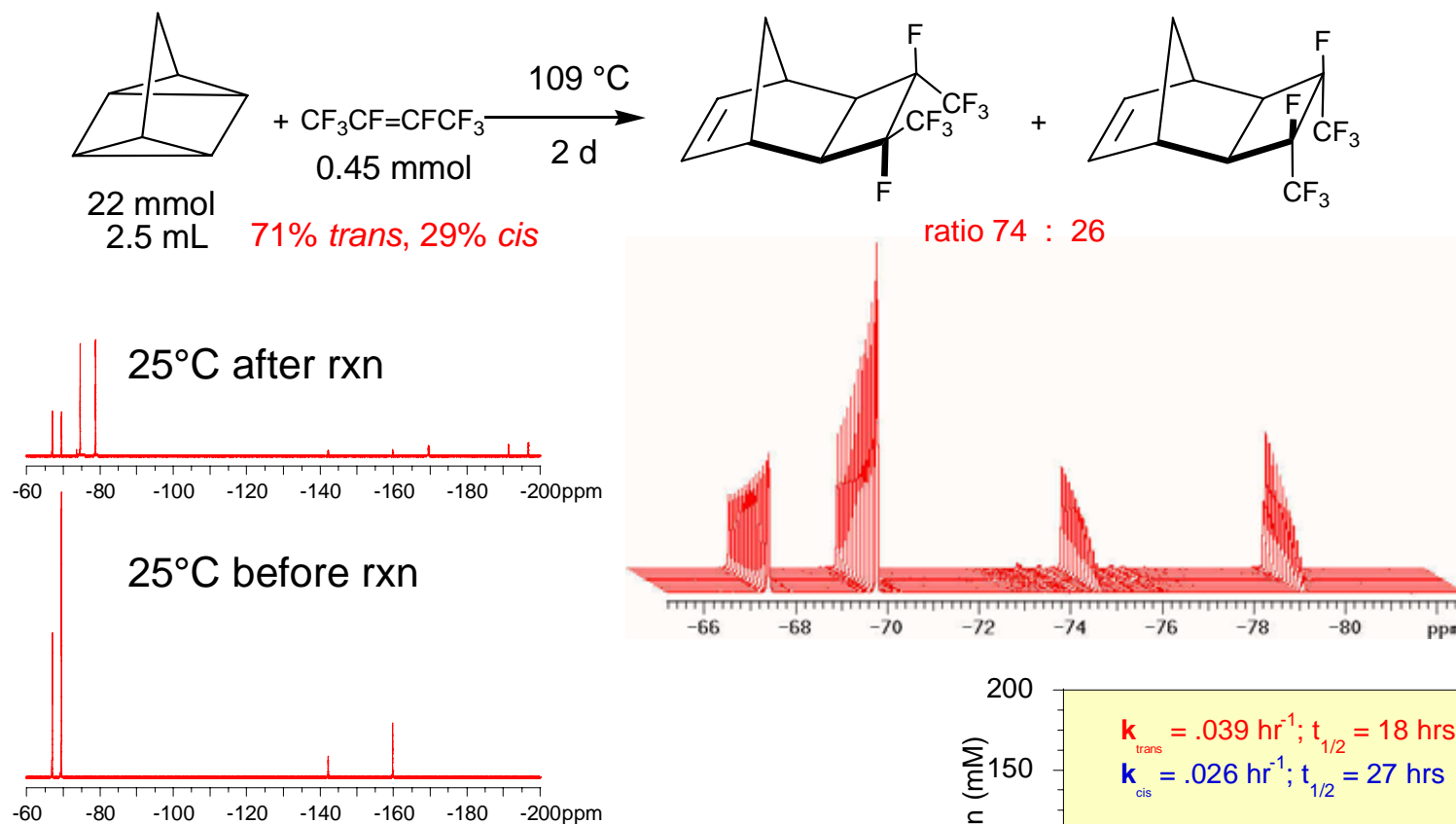
M_n: 6200

5800

M_w: 8100

7000

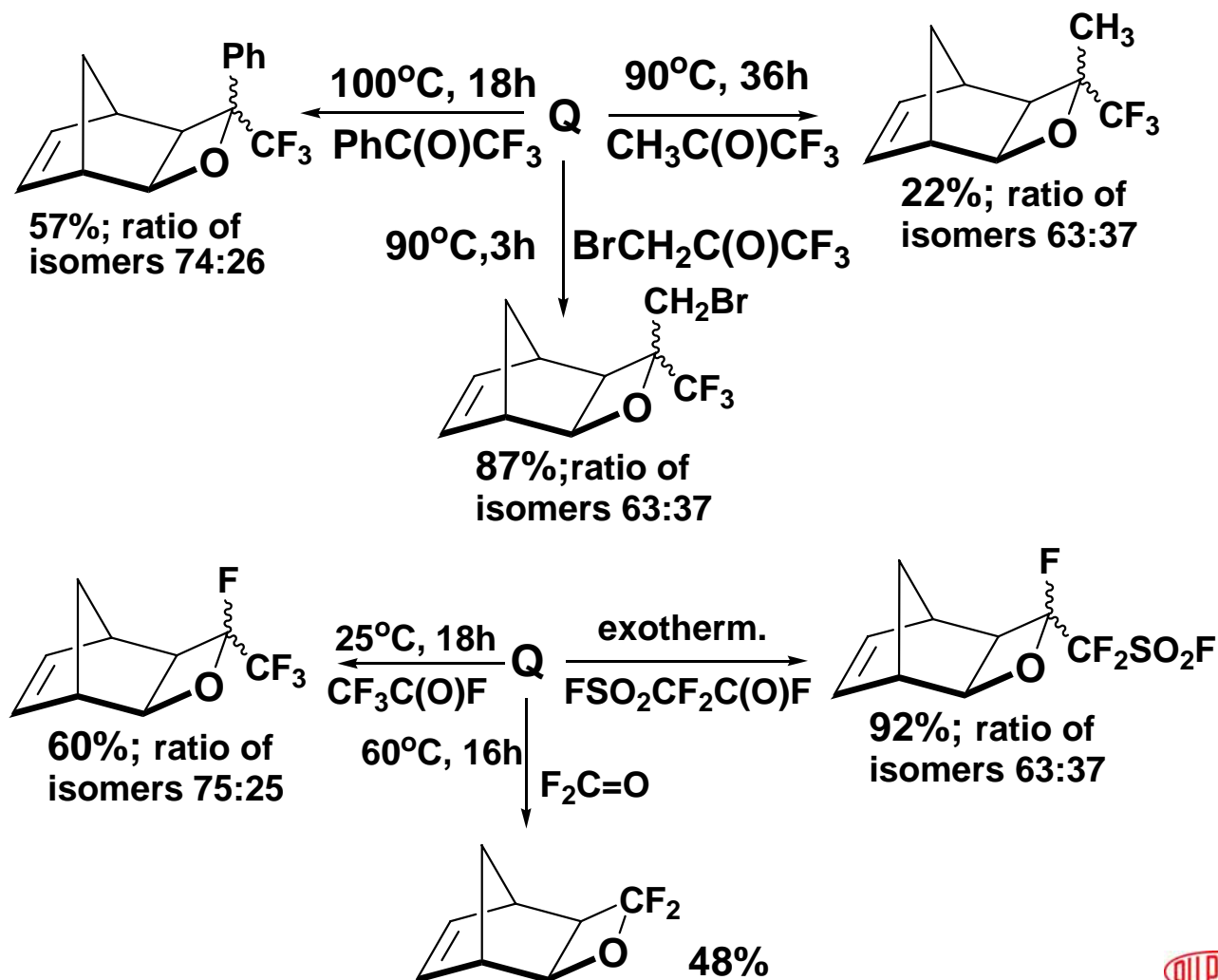
2.3 Kinetic NMR: Pseudo First-Order Reaction of Quadricyclane with $\text{CF}_3\text{CF}=\text{CFCF}_3$ (P. Krusic, A. Marchione).



- Adducts are formed at the same rate at which their corresponding starting reagents disappear. Therefore, the addition is stereospecific.
- 4% isomerization of quadricyclane to norbornadiene occurred during the acquisition.

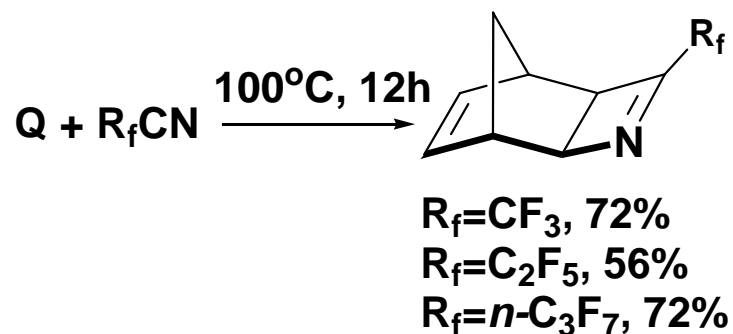
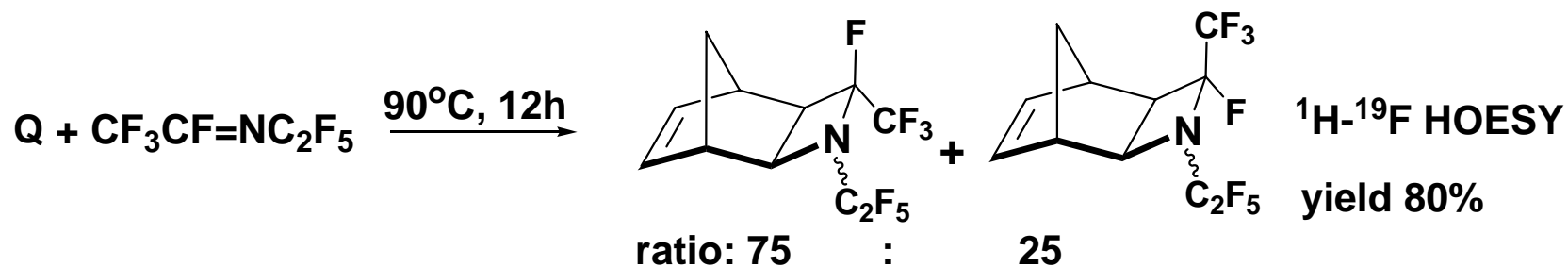
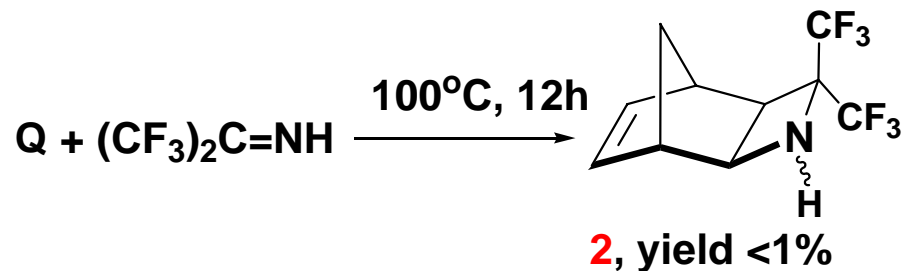
3.1 Fluorinated Carbonyl Compounds.

Synthesis of *exo*-3-Oxa-tricyclo[4.2.1.0^{2,5}]non-7-enes



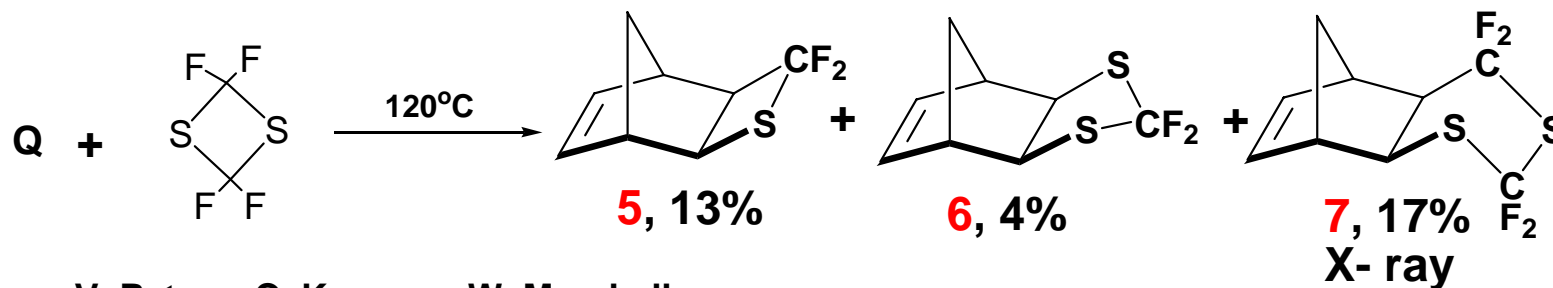
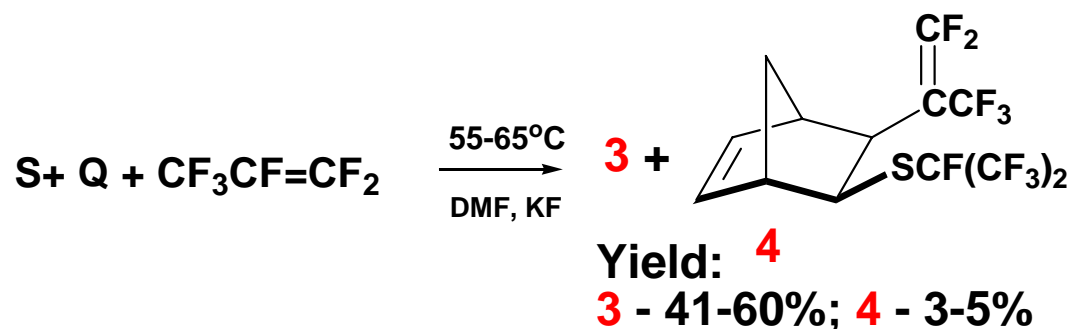
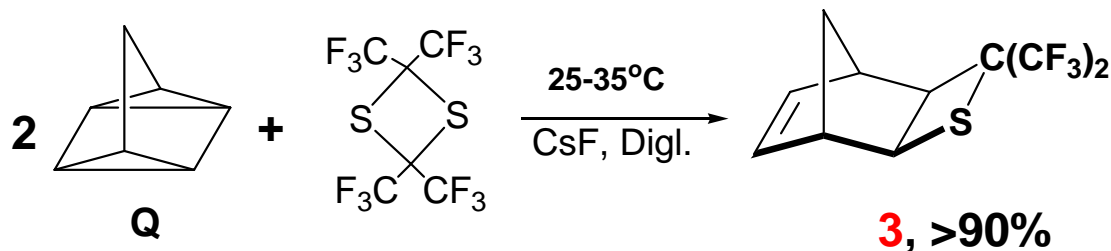
3.2 Fluorinated Nitrogen Containing Compounds.

Synthesis of *exo*-3-Aza-tricyclo[4.2.1.0^{2,5}]non-3,7-dienes



3.3 Fluorinated Sulfur Containing Compounds.

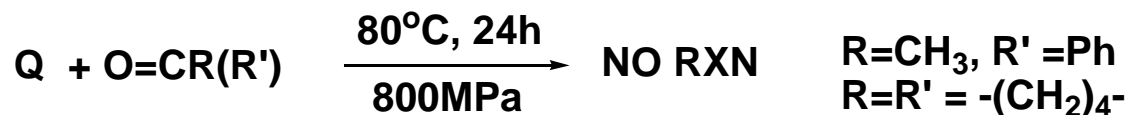
Synthesis of *exo*-3-Thiatricyclo[4.2.1.0^{2,5}]non-7-enes.



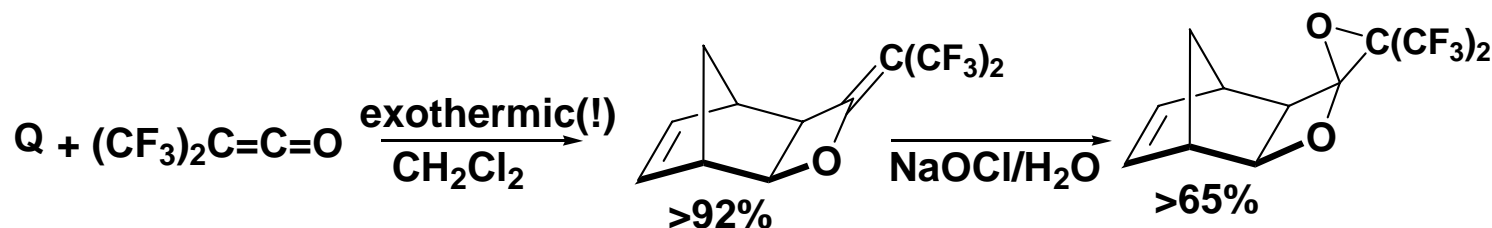
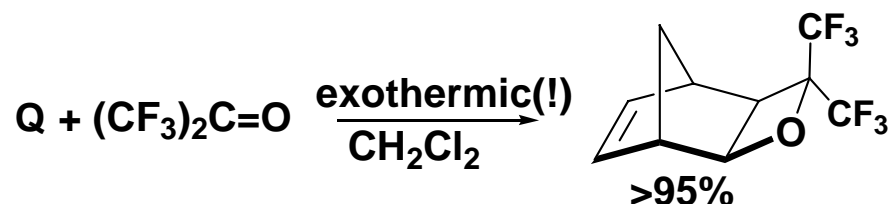
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3.1 Fluorinated Carbonyl Compounds.

Synthesis of *exo*-3-Oxa-tricyclo[4.2.1.0^{2,5}]non-7-enes



G., Jenner et al. Chem. Comm. 1983, 221



PCT Int. Appl. (to DuPont Co.) WO 2004/014960

V. Petrov, F. Davidson, B. Smart J. Fluorine Chem. 125, 2004, 1543-1552