

# Supporting Information

## Pentafluorophenylhalocarbenes

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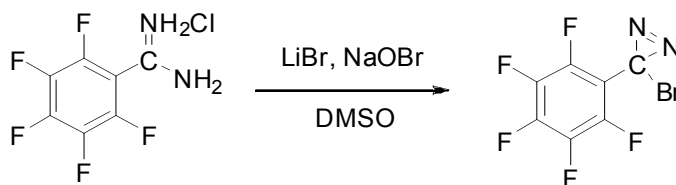
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## 1. Preparation of 3-bromo-3-pentafluorophenyldiazirine (4c).



The method of Graham<sup>9</sup> was used to prepare this diazirine. LiBr (11 g) and 6.0 g (24 mmol) of pentafluorobenzamidine hydrochloride<sup>8</sup> were stirred in 105 mL DMSO until most of the LiBr had dissolved. Then 100 mL of pentane was added. A fresh solution of NaOBr (0.235 mol) was prepared by the slow addition of 24 mL of bromine to a stirred and cooled (0 °C) solution of 25 g of NaOH and 155 g of NaBr in 360 mL of water. The cool hypobromite solution was slowly added to the reaction mixture at 0 °C. After addition, stirring was continued for another 2 h at room temperature. The pentane layer was separated and saved, while the aqueous phase was extracted with 4x50 mL of pentane. The pentane phases were combined, dried over MgSO<sub>4</sub>, concentrated in vacuum to about 5 ml and purified over a short column of silica gel using pentane as eluent. The yield of **4c** was 3.4 g, 12 mmol, 50%. The diazirine was characterized by IR, UV, <sup>19</sup>F NMR, and <sup>13</sup>C NMR spectra; Figures S-1 – S-4. Purity (>95%) was demonstrated by TLC.

**Figure S-1:** IR spectrum of **4c**.

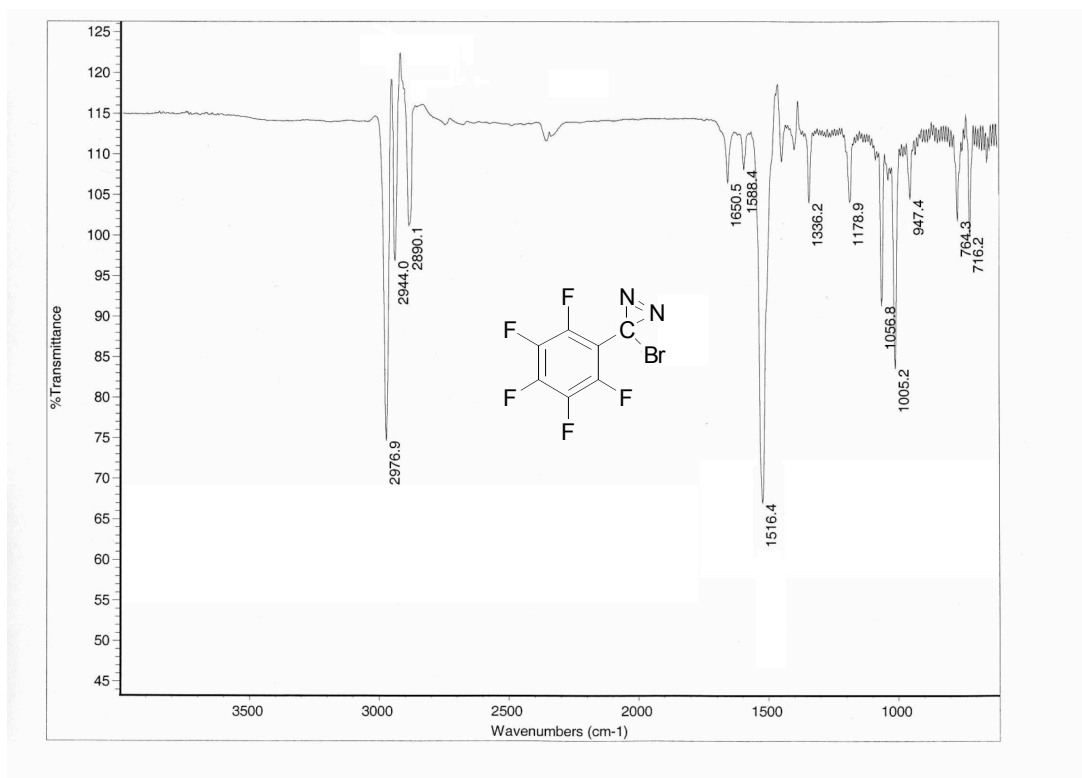
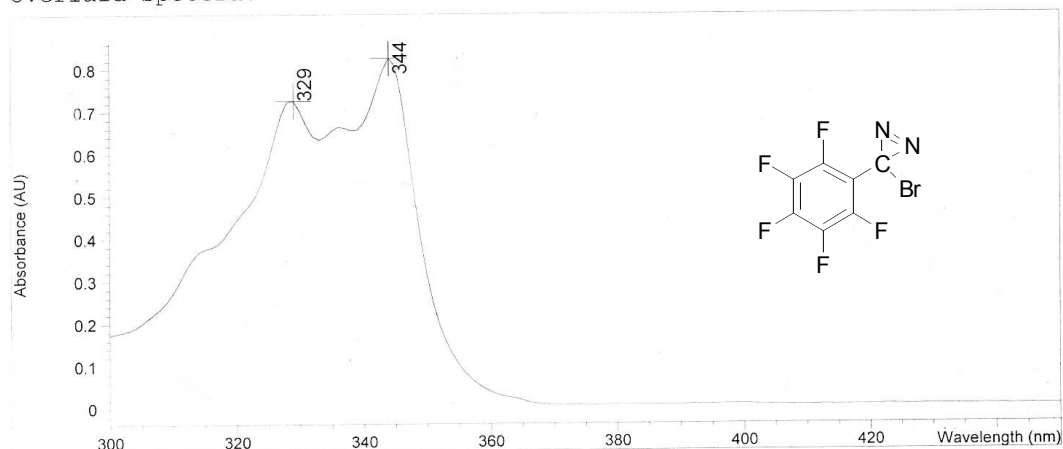


Figure S-2: UV spectrum of 4c.

Overlaid Spectra:



#	Name	Peaks (nm)	Abs (AU)
1		344.0	0.82589
1		329.0	0.7253

Figure S-3: <sup>19</sup>F NMR spectrum of 4c.

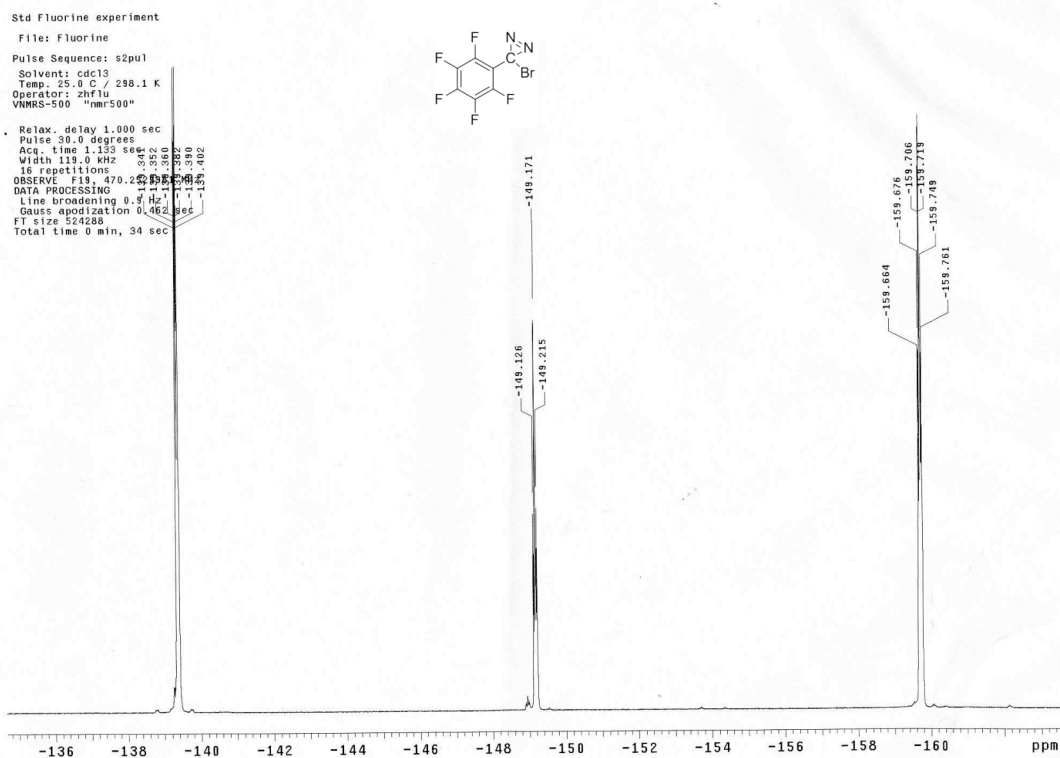
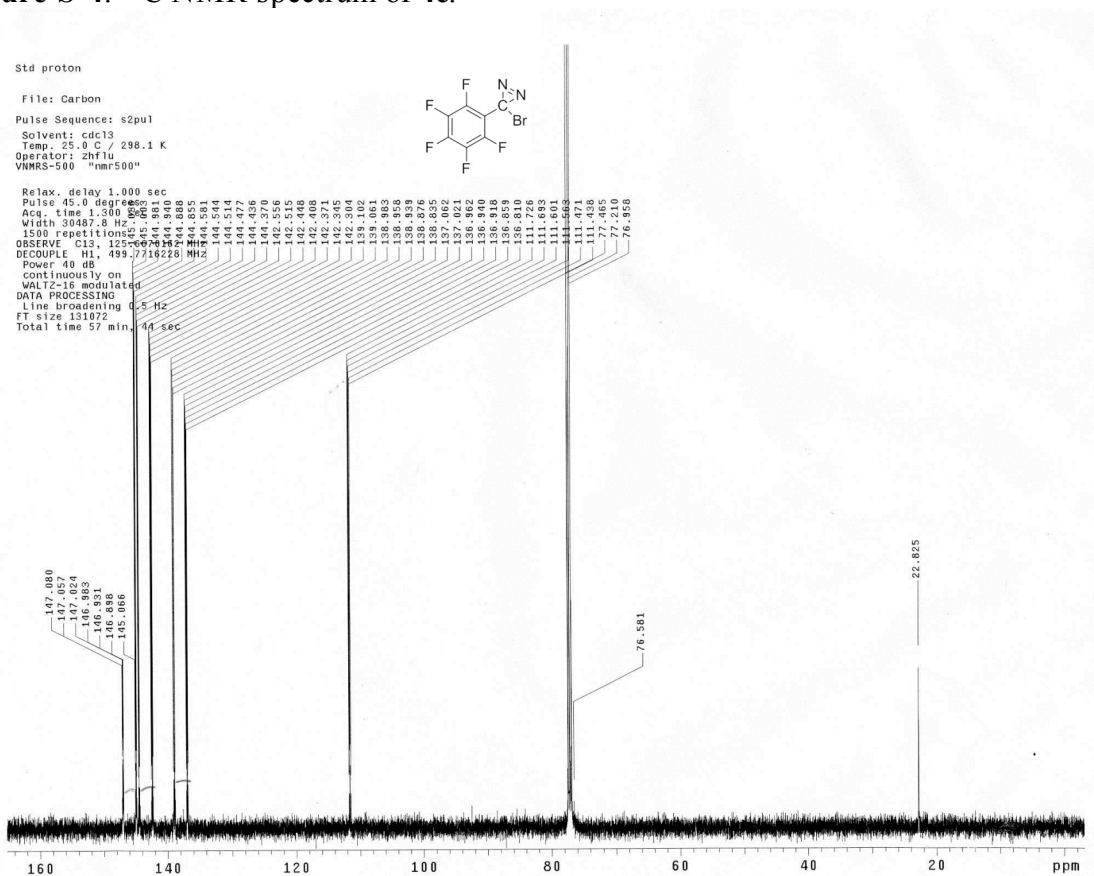
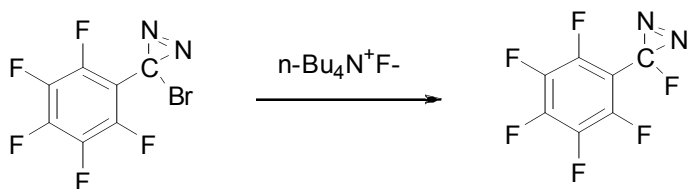


Figure S-4:  $^{13}\text{C}$  NMR spectrum of **4c**.



## 2. Preparation of 3-fluoro-3-pentafluorophenyldiazirine (**4b**).



A solution of 12 g (38 mmol) of  $n\text{-Bu}_4\text{N}^+\text{F}^-$  trihydrate in 8 mL of acetonitrile was added slowly to a magnetically stirred solution of 3.0 g (10.5 mmol) of 3-bromo-3-pentafluorophenyldiazirine in 2 mL of acetonitrile at 0 °C. After addition, stirring was continued for another hour at less than 10.0 °C. Then, 20 mL of water was added and the mixture was extracted with 4 x 25 mL of pentane. The combined pentane extracts were dried ( $\text{MgSO}_4$ ), filtered, concentrated, and purified through a short column of silica gel using pentane as eluent. The yield of diazirine **4b** was 0.7 g (3.1 mmol), 30%.

The diazirine was characterized by IR, UV,  $^{19}\text{F}$  NMR, and  $^{13}\text{C}$  NMR spectra; Figures S-5 – S-8. Purity (>95%) was demonstrated by TLC.

Figure S-5: IR spectrum of diazirine **4b**.

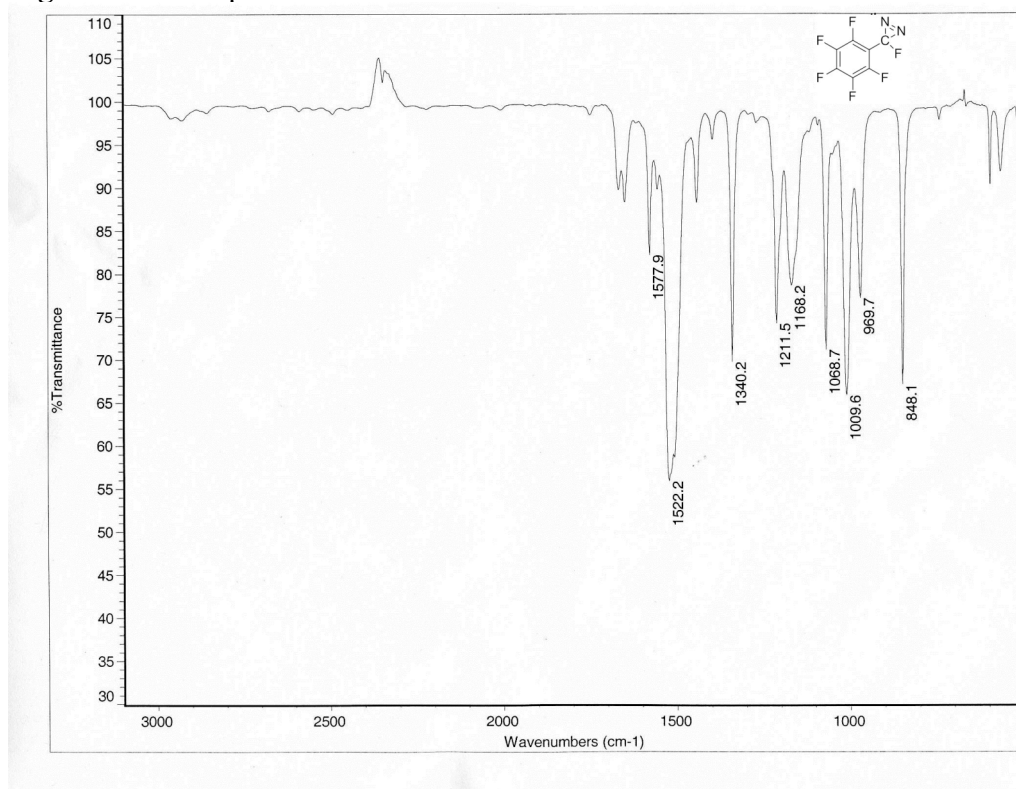
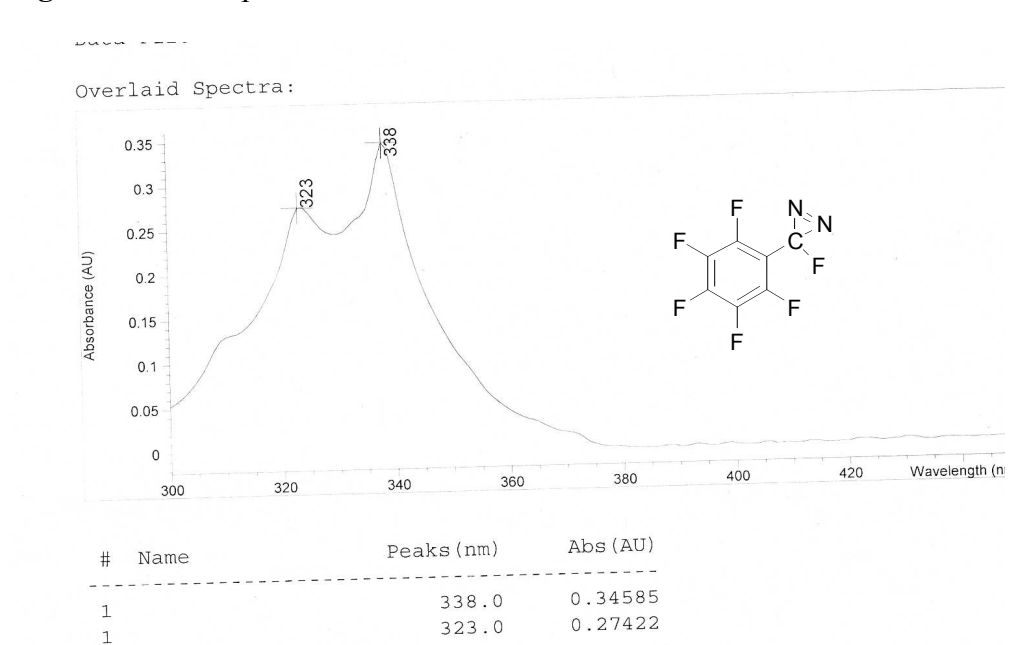


Figure S-6: UV spectrum of diazirine **4b**.

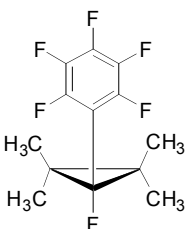




### 3. Preparation of Products 7-F – 11-F.

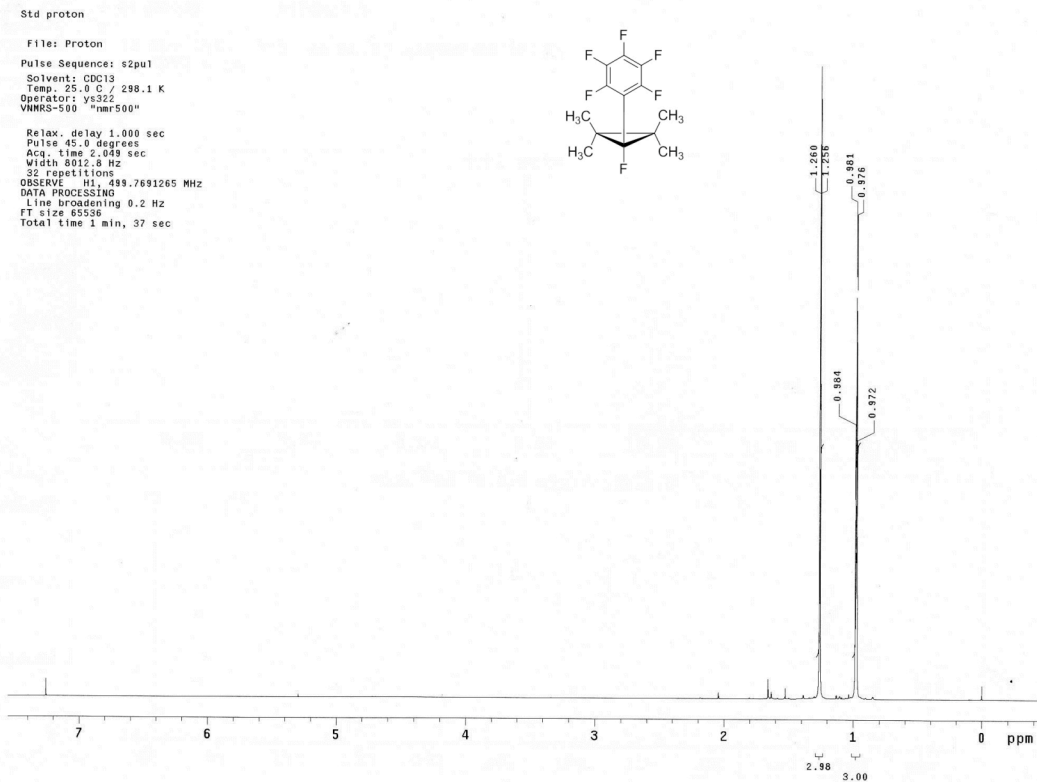
3-Fluoro-3-pentafluorophenyldiazirine **4b** (0.15 g, 0.66 mmol) was mixed with 13 mmol of an alkene and 5 mL of pentane (or with excess adamantane in benzene in the case of **11-F**) and photolyzed for 18 h in a Pyrex tube with the light from a 200 W, focused Osram XE mercury lamp at room temperature. Excess alkene and pentane were removed, and the product was purified by chromatography over a short column of silica gel using pentane as eluent. Product purity was assured by TLC and GC. Products were characterized by  $^1\text{H}$ ,  $^{19}\text{F}$ , and  $^{13}\text{C}$  NMR spectra and by GC-MS. Purity was (>95%) by GC and TLC. Spectra follow in Figures S-9 – S-26.

#### Cyclopropane 7-F:



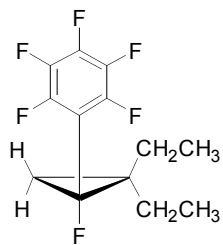
Mass spectrum:  $\text{M}^+$  at  $m/e$  282.

Figure S-9:  $^1\text{H}$  NMR spectrum of 7-F,



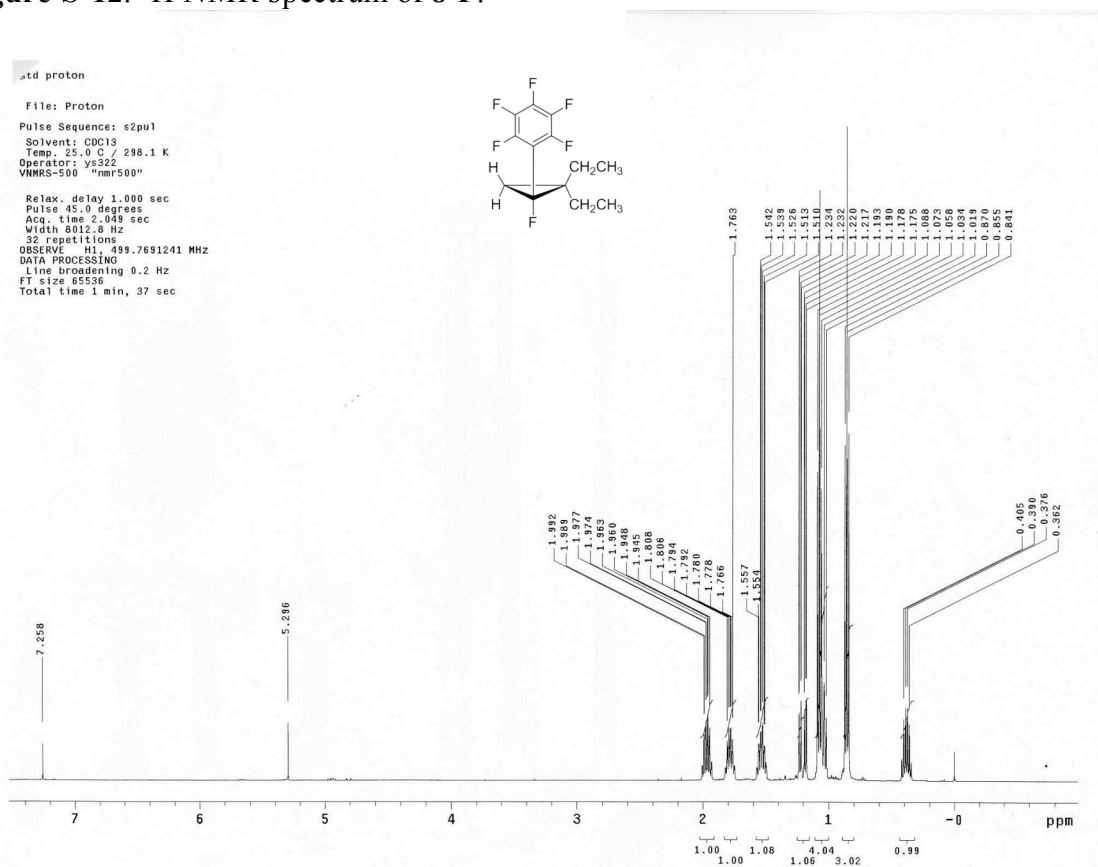


**Cyclopropane 8-F:**



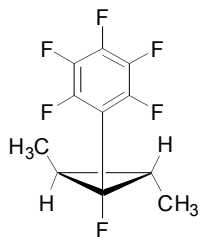
Mass spectrum:  $M^+$  at  $m/e$  282.

**Figure S-12.**  $^1H$  NMR spectrum of **8-F**.



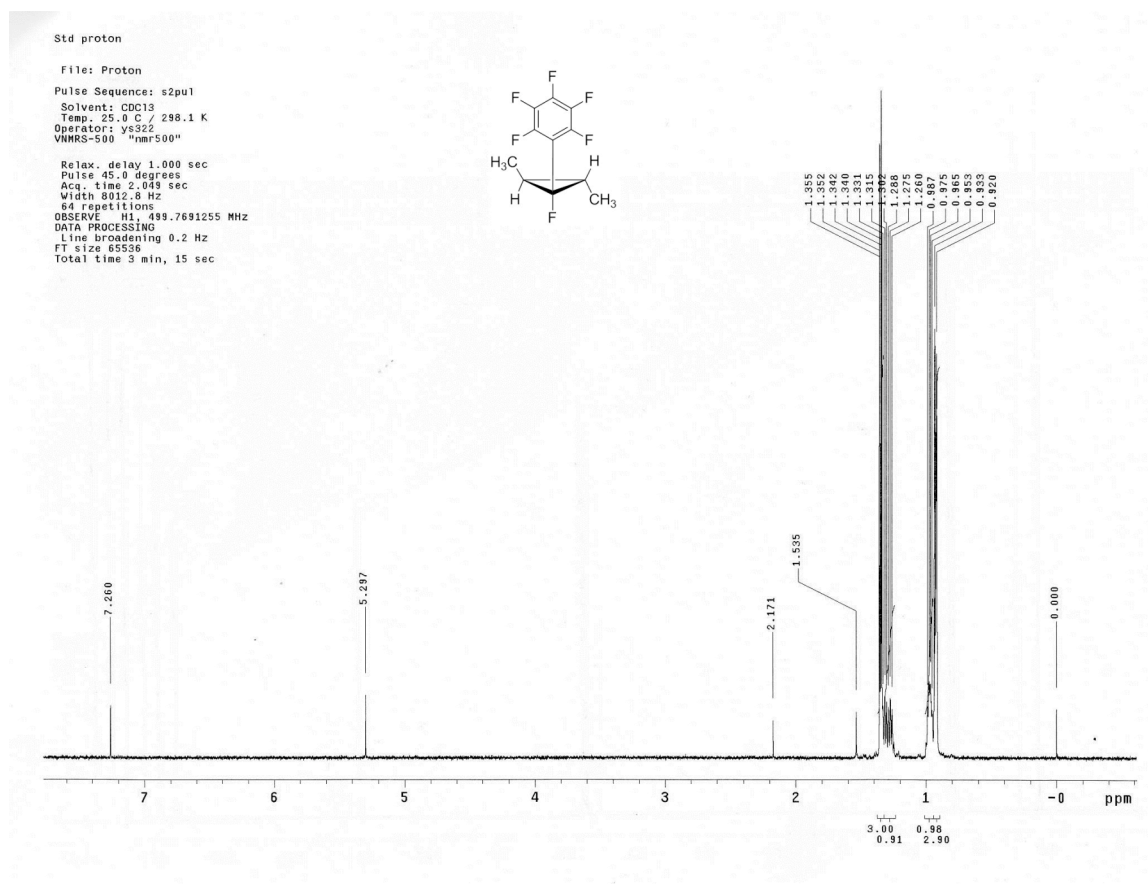


# Cyclopropane 9-F:



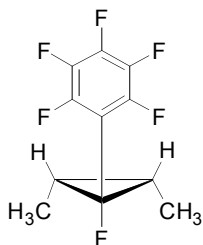
Mass spectrum:  $M^+$  at  $m/e$  254.

Figure S-15:  $^1\text{H}$  NMR spectrum of 9-F.



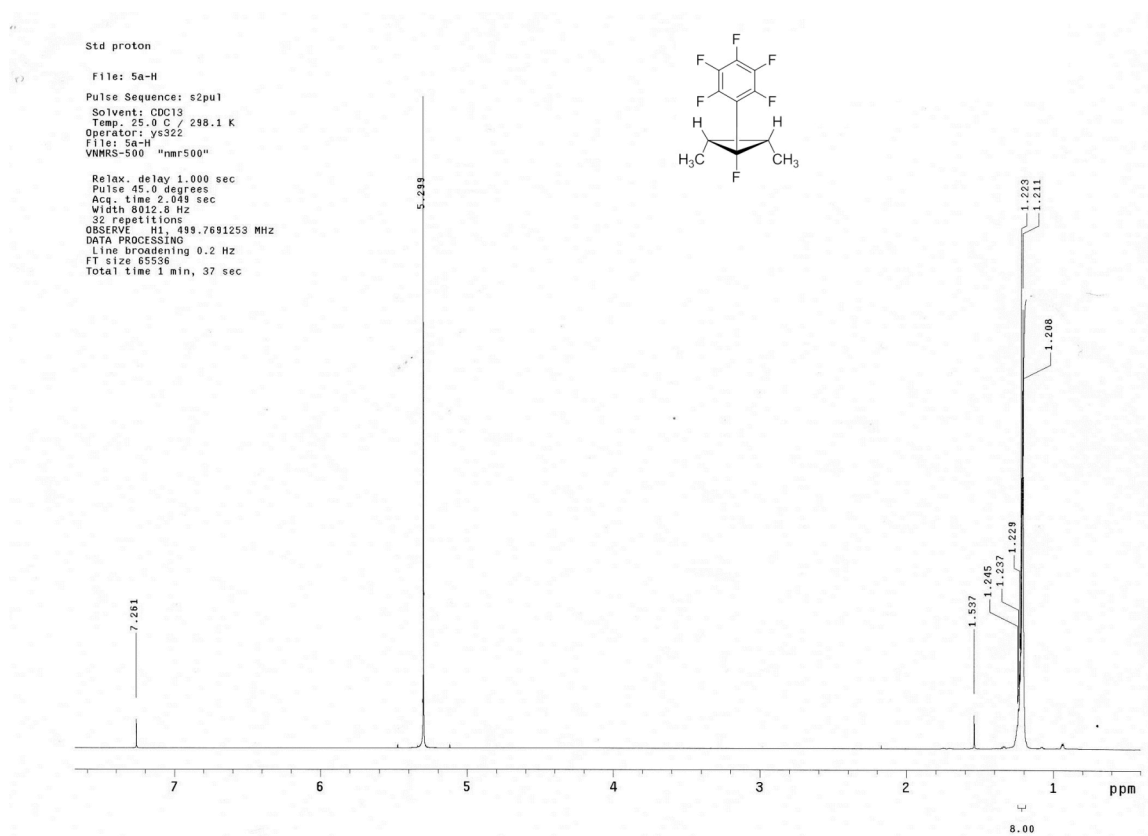


Cyclopropane 10-F (*syn*-F):



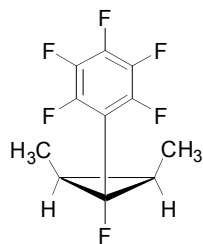
Mass spectrum:  $M^+$  at  $m/e$  254.

Figure S-18:  $^1\text{H}$  NMR spectrum of 10-F (*syn*-F).





**Cyclopropane 10-F (*anti*-F):**



**Mass spectrum: M<sup>+</sup> at *m/e* 254.**

**Figure S-21: <sup>1</sup>H NMR spectrum of 10-F (*anti*-F).**

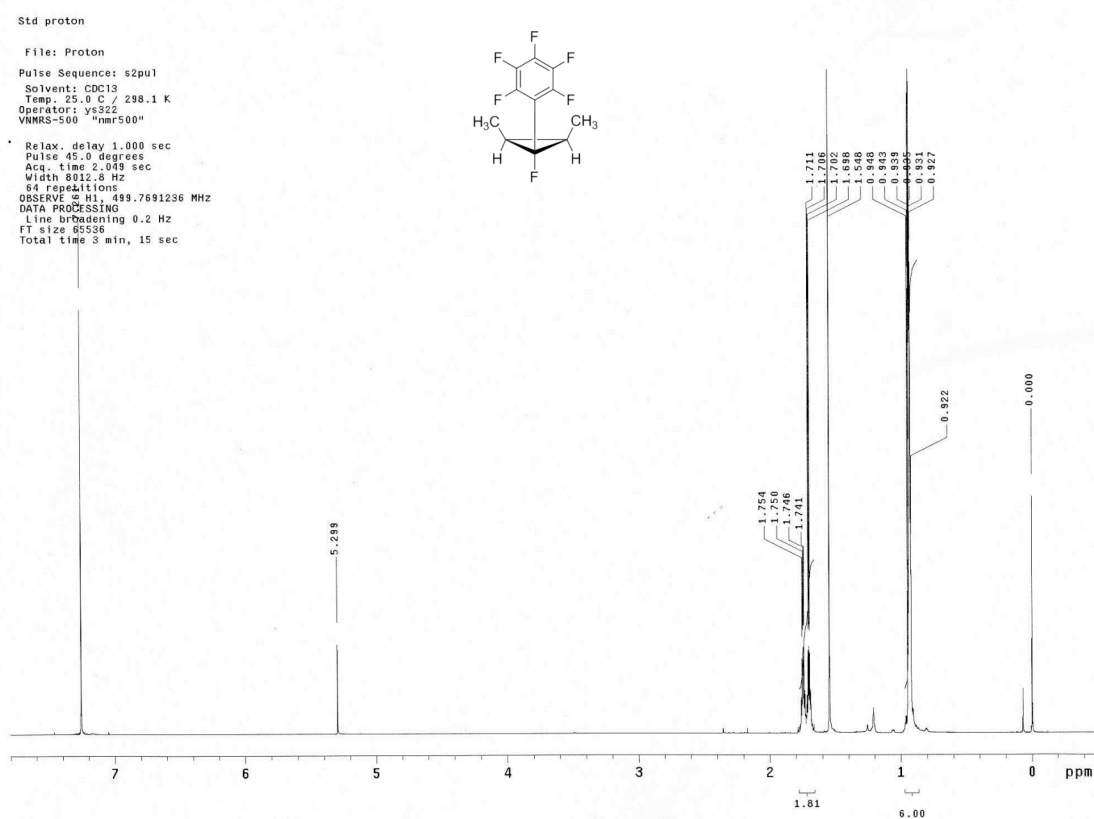


Figure S-22:  $^{19}\text{F}$  NMR spectrum of 10-F (*anti*-F).

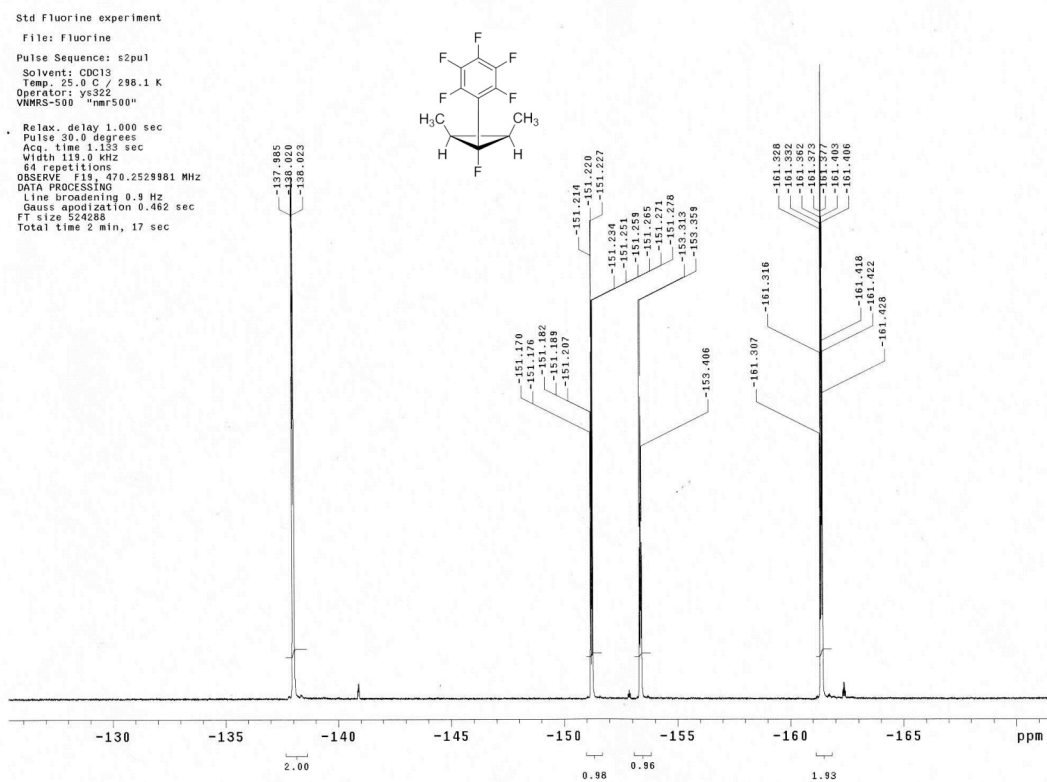
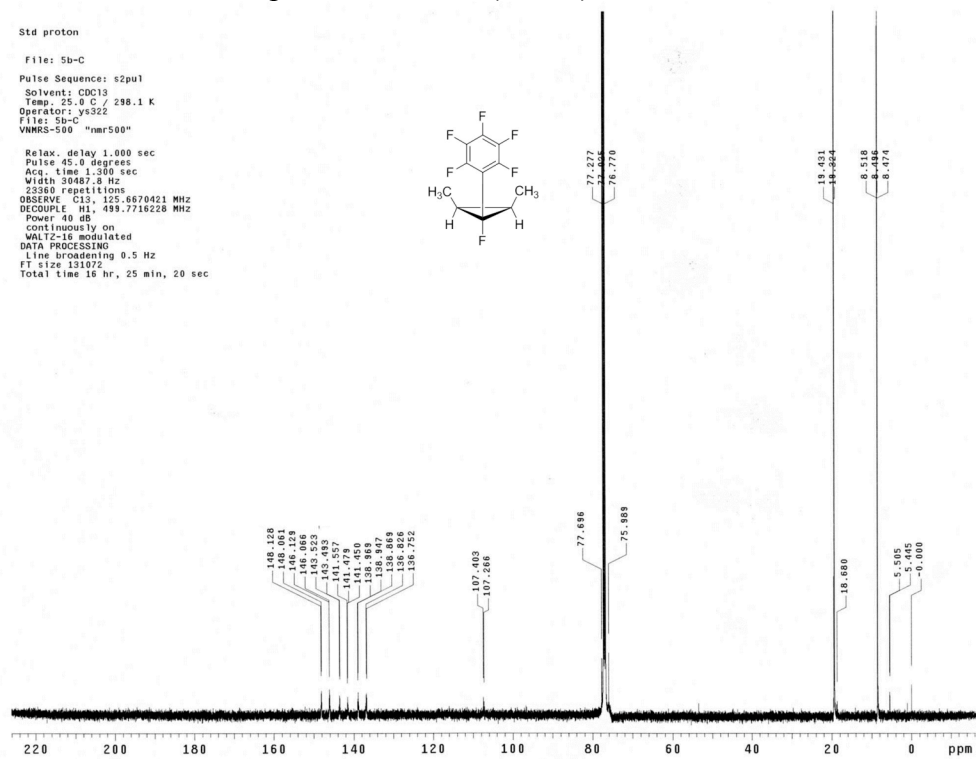
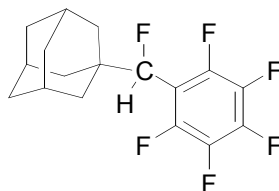


Figure S-23:  $^{13}\text{C}$  NMR spectrum of 10-F (*anti*-F).



Adamantane insertion product 11-F:



Mass Spectrum (MALDI-TOF): Calcd for  $C_{17}H_{15}F_6$  ( $M^+-1$ ) 333.12; found 333.13.

Figure S-24:  $^1H$  NMR spectrum of 11-F.

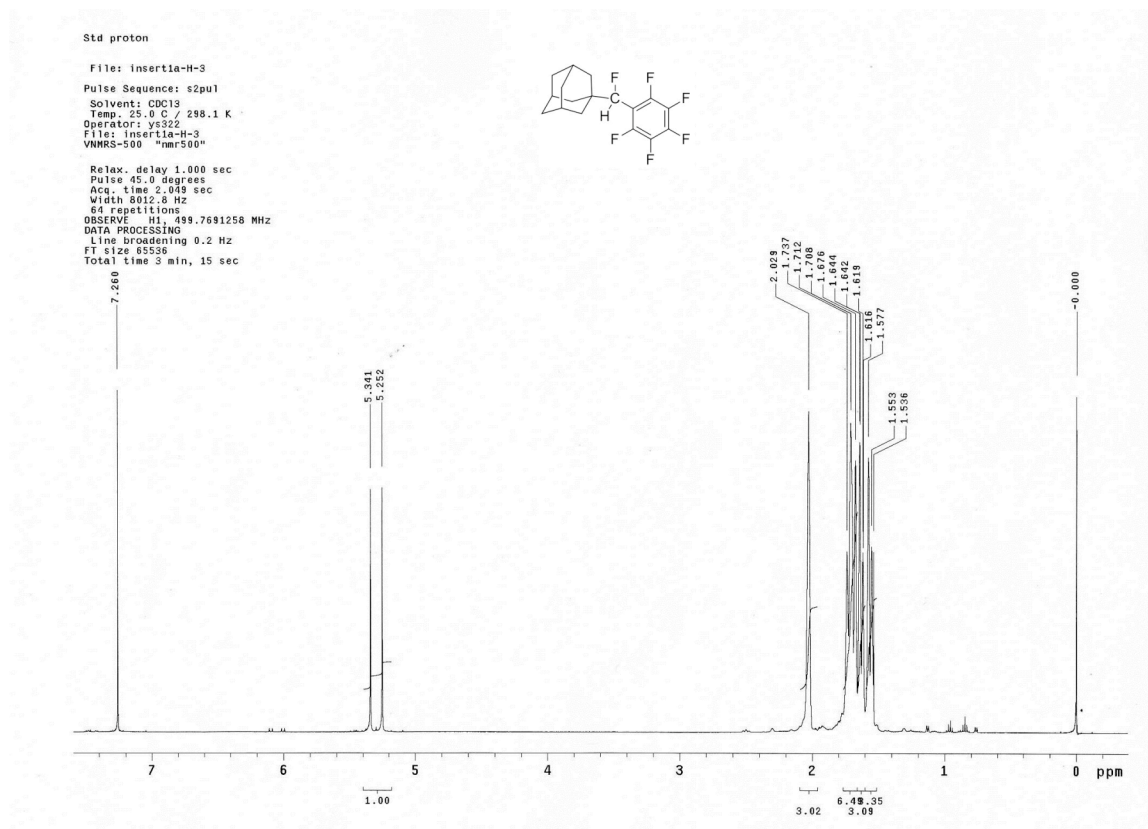


Figure S-25: <sup>19</sup>F NMR spectrum of 11-F.

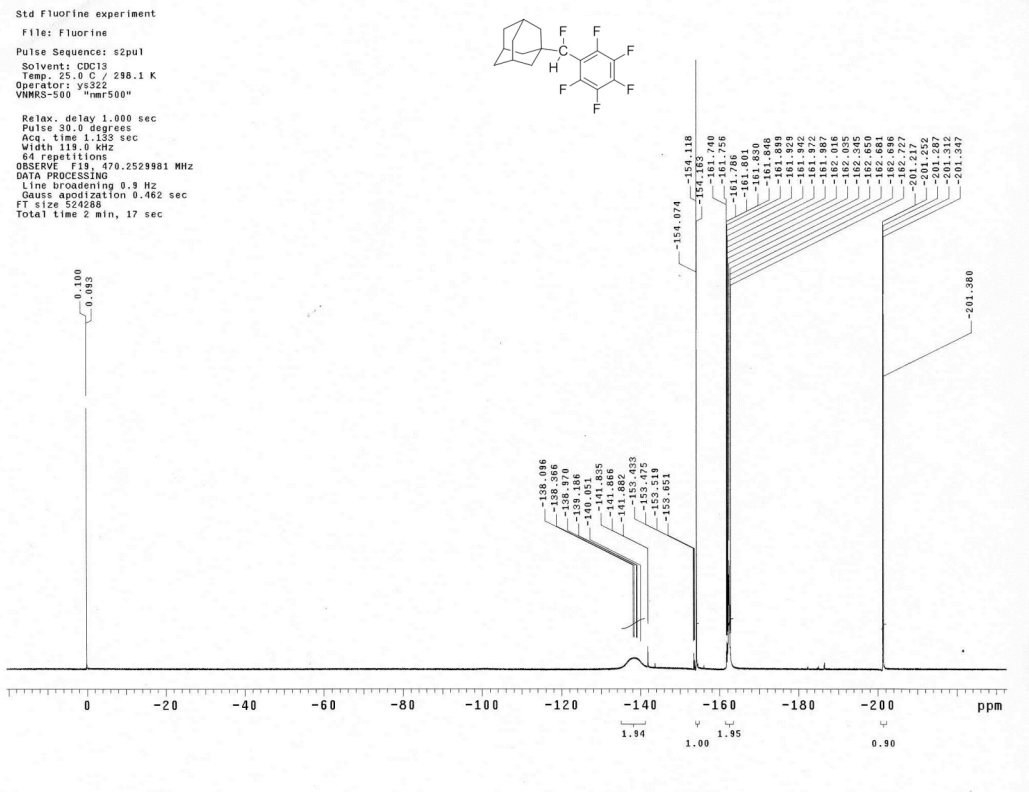
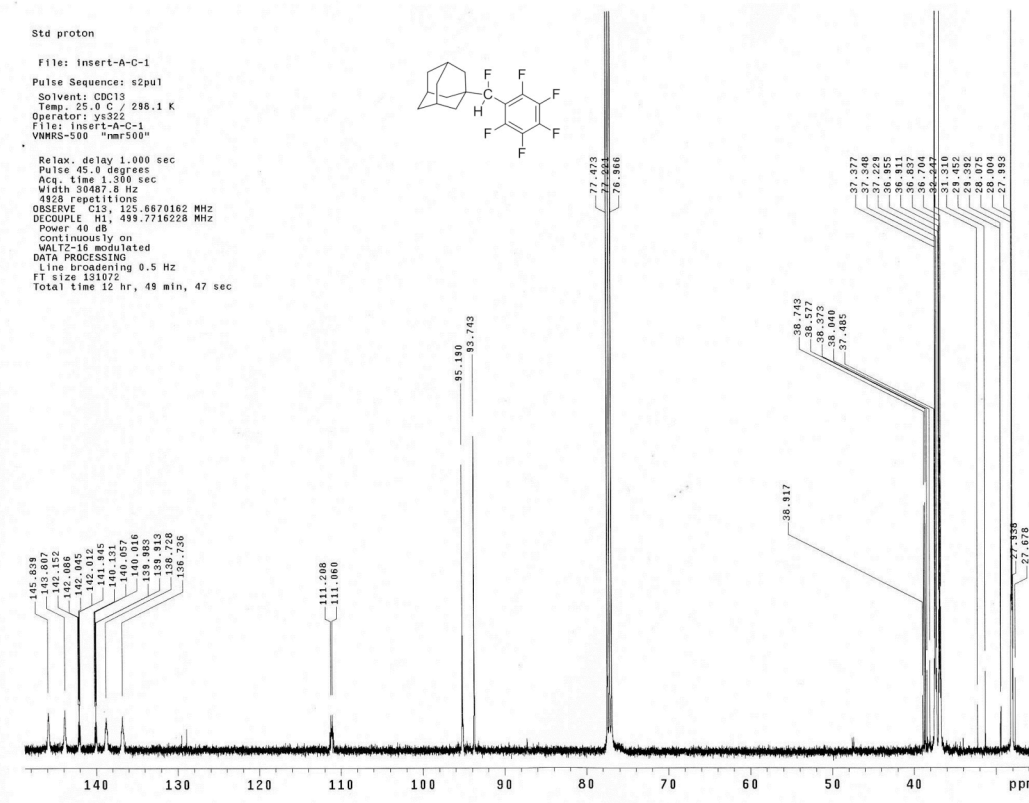


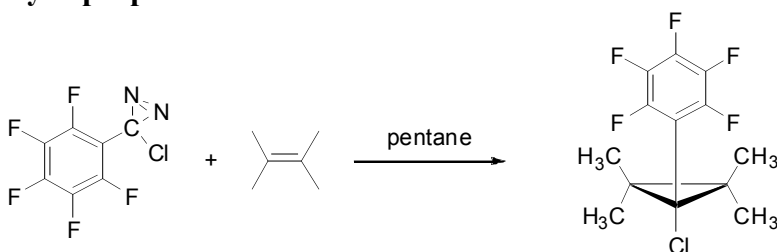
Figure S-26: <sup>13</sup>C NMR spectrum of 11-F.



#### 4. Preparation of products 7-Cl – 11-Cl.

A solution of pentafluorophenylchlorodiazirine<sup>8</sup> (0.485 g, 2.0 mmol) and alkene (10 mmol) in 5 mL of pentane (or of excess adamantane in 10 mL of benzene) was photolyzed for 18 h in a Pyrex tube with the light from a 200 W, focused Osram XE mercury lamp at room temperature. After irradiation, excess alkenes and solvent were evaporated, and the residue was purified by column chromatograph using pentane as eluent. Purity was (>95%) by GC and TLC. Spectra follow in Figures S-27 – S-41.

#### Cyclopropane 7-Cl:



**Mass Spectrum:** M<sup>+</sup> at *m/e* 298, 300.

**Figure S- 27.** <sup>1</sup>H NMR spectrum of 7-Cl.

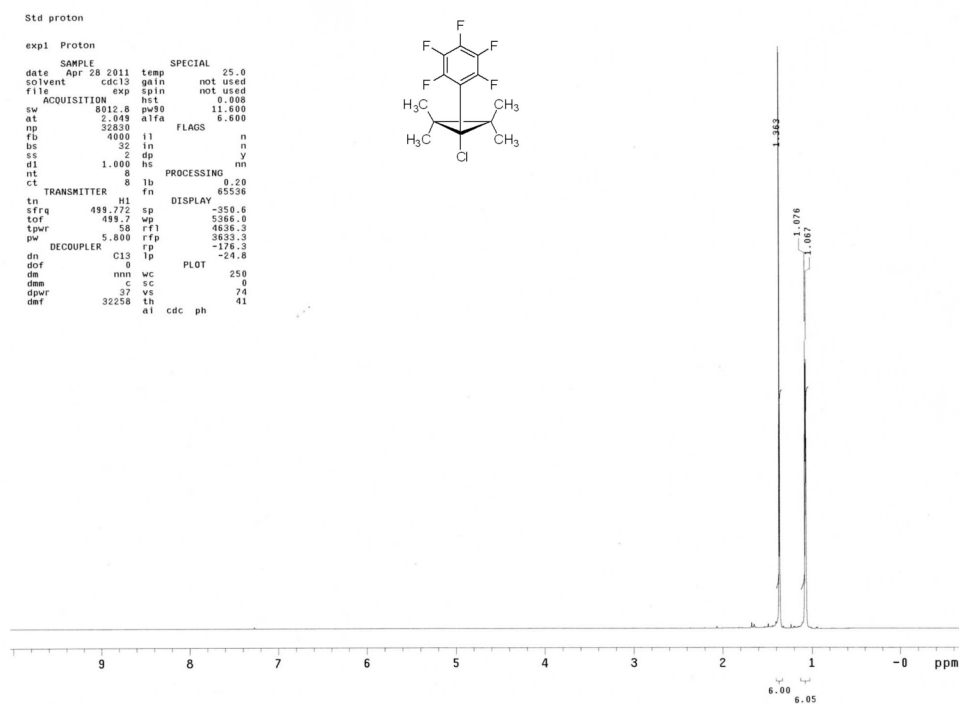


Figure S-28. <sup>19</sup>F NMR spectrum of 7-Cl.

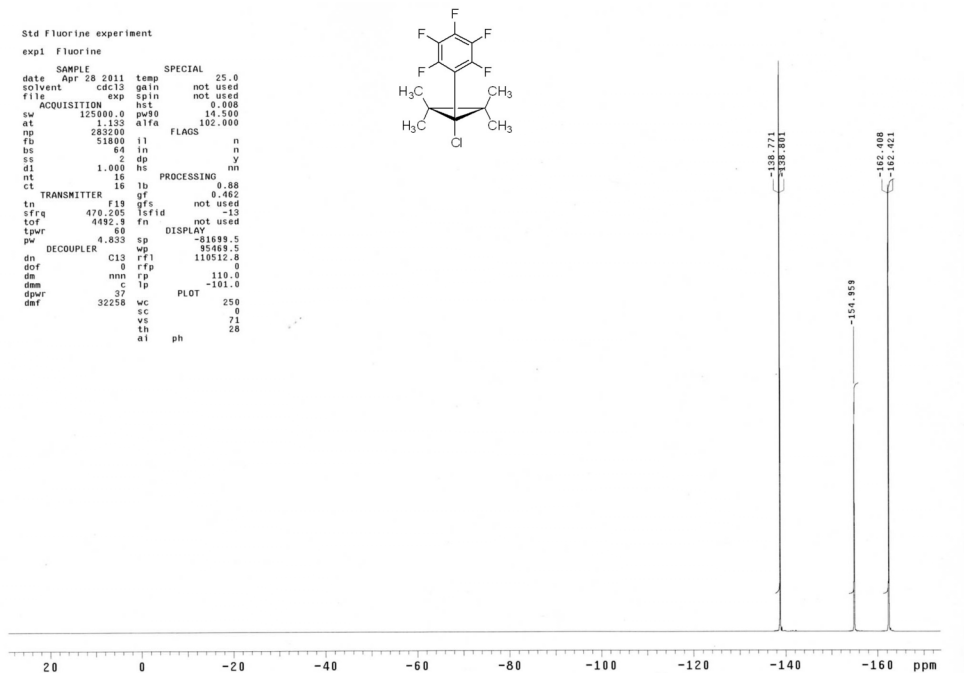
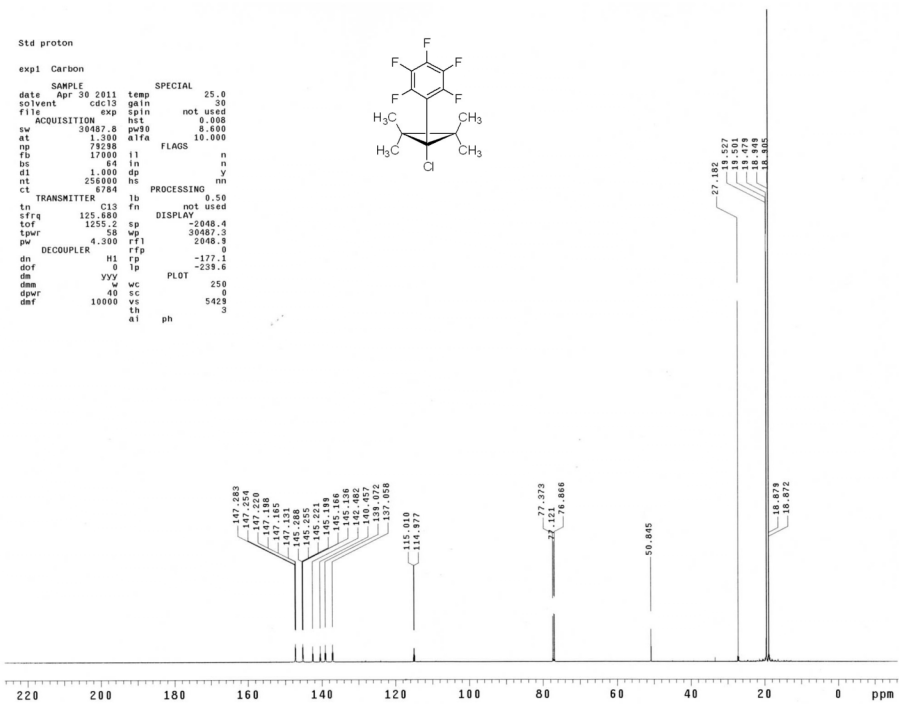


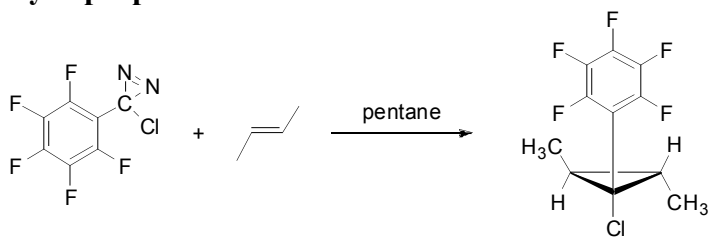
Figure S-29. <sup>13</sup>C NMR spectrum of 7-Cl.





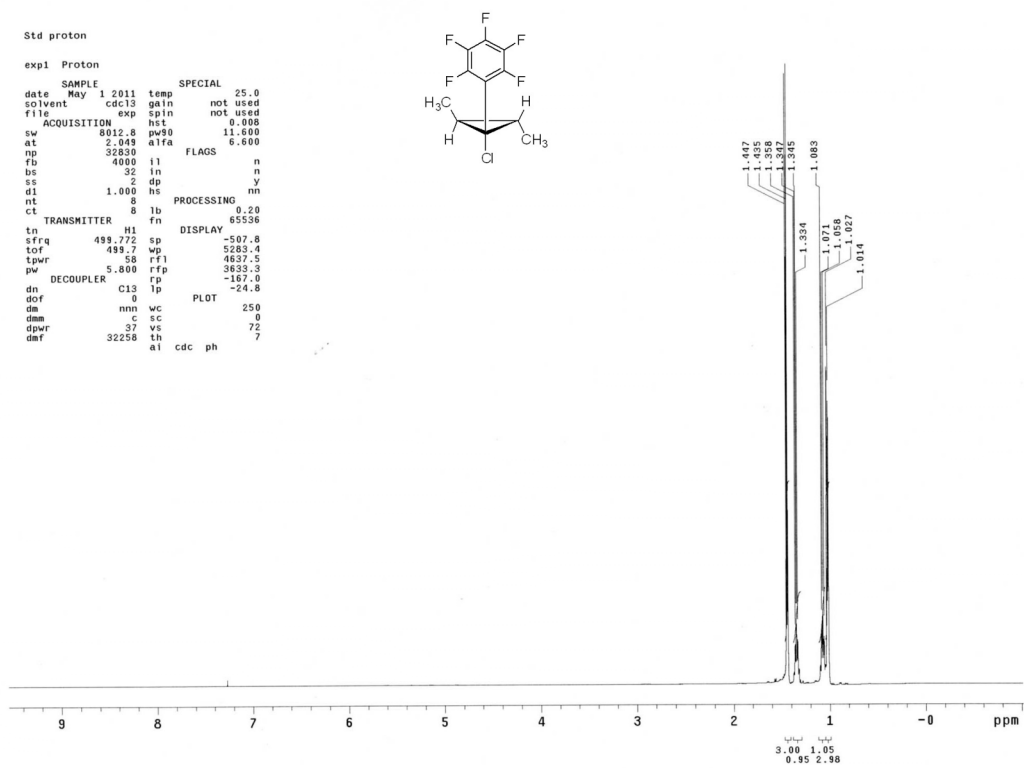


### Cyclopropane 9-Cl:



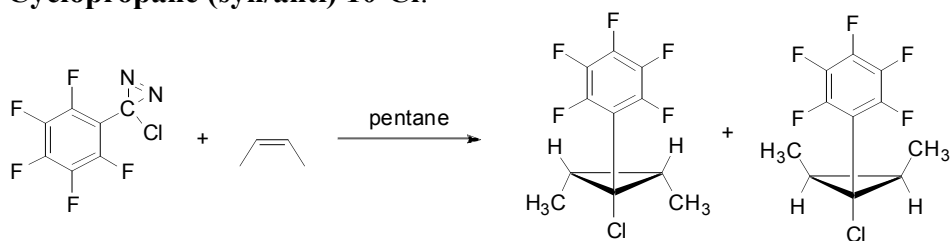
Mass spectrum:  $M^+$  at  $m/e$  270,272.

Figure 33:  $^1\text{H}$  NMR spectrum of 9-Cl.



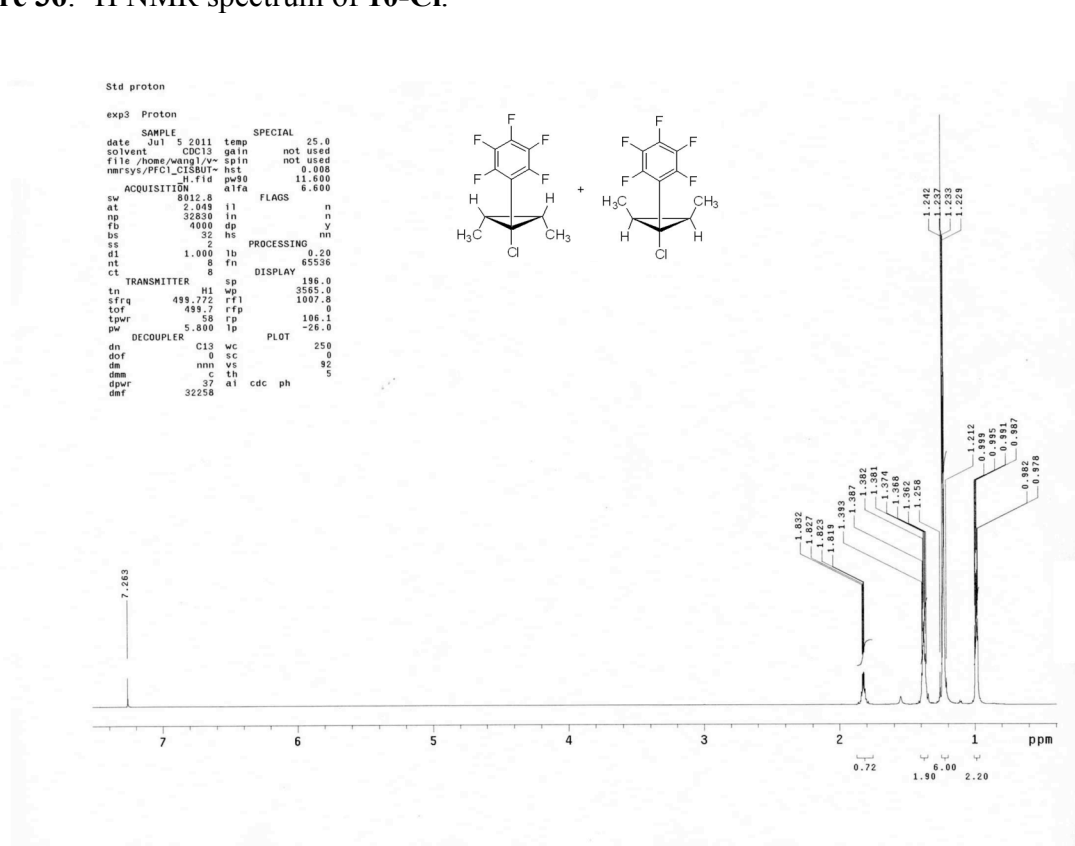


**Cyclopropane (syn/anti) 10-Cl:**



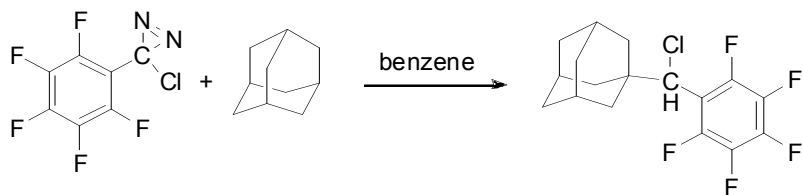
**Mass spectrum:  $M^+$  at  $m/e$  270, 272.**

**Figure 36:  $^1\text{H}$  NMR spectrum of 10-Cl.**



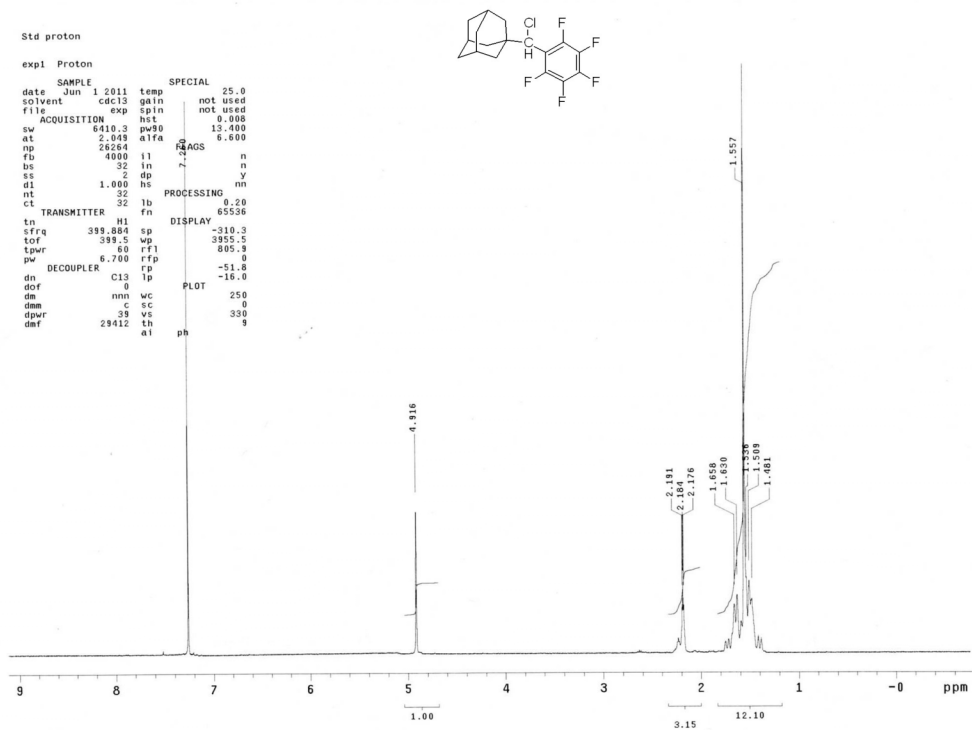


### Adamantane Insertion Product 11-Cl:



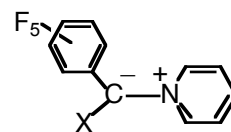
Mass spectrum:  $M^+$  at  $m/e$  350, 352.

Figure 39: <sup>1</sup>H NMR spectrum of 11-Cl.

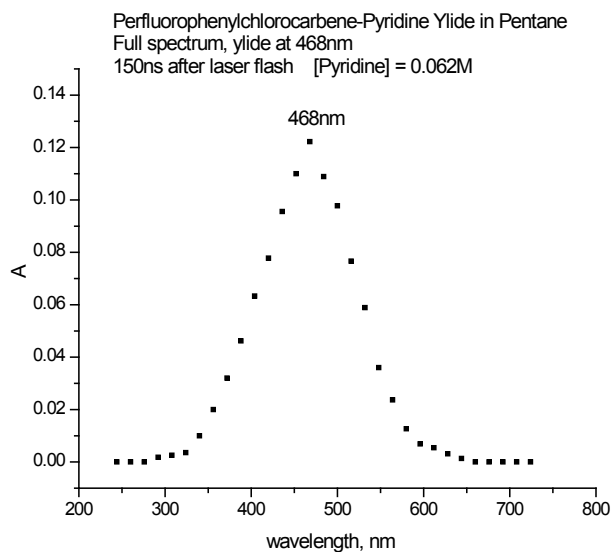




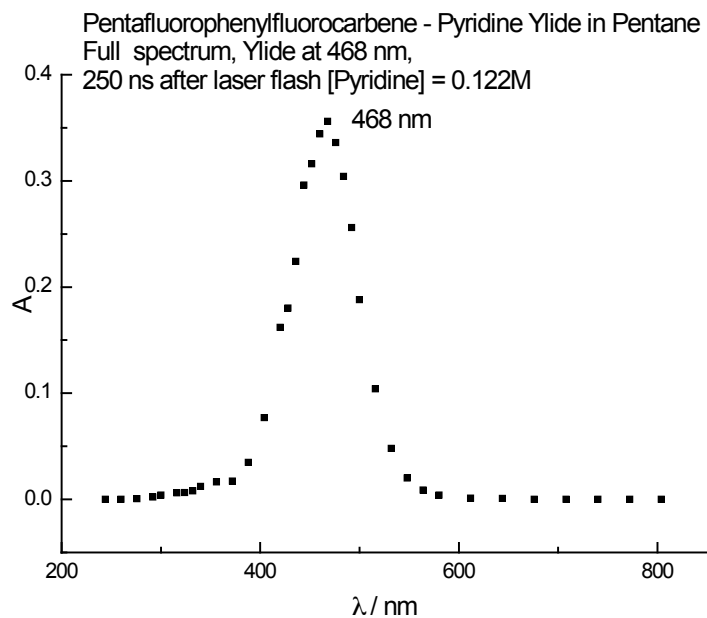
## 5. UV-vis Spectra of Ylides **6a** and **6b**.



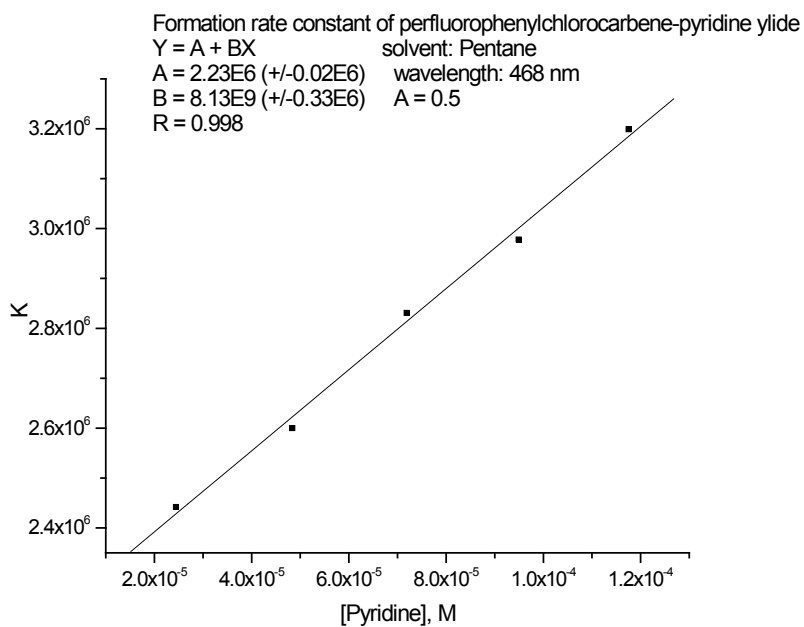
**Figure 42.** UV-vis LFP spectrum of Ylide **6a** (X = Cl):



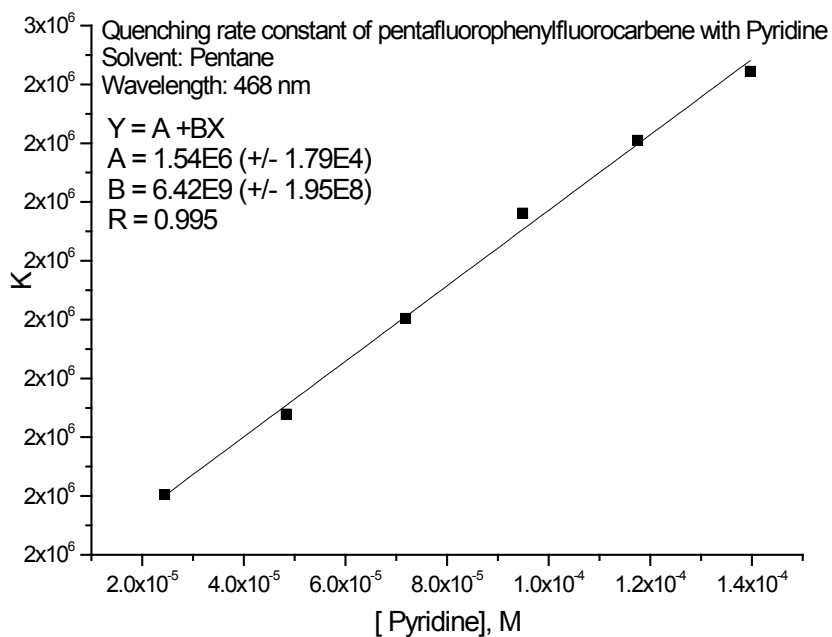
**Figure 43:** UV-vis LFP spectrum of Ylide **6b** (X = F):



**Figure 44:** Formation of ylide **6a** from PFPCl and pyridine:  $k_f = 8.1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ .

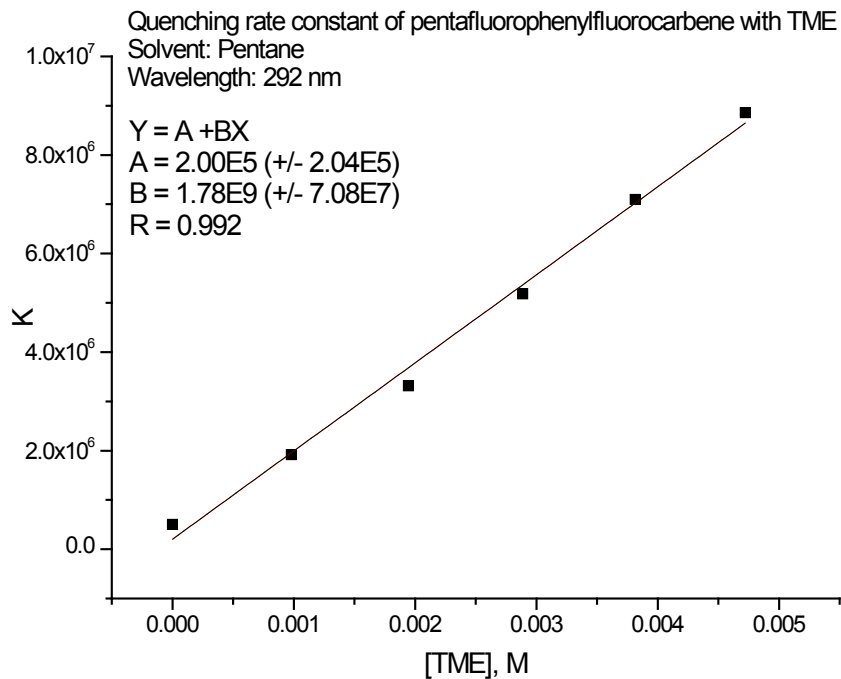


**Figure 45:** Formation of ylide **6b** from PFPCl and pyridine:  $k_f = 6.4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ .

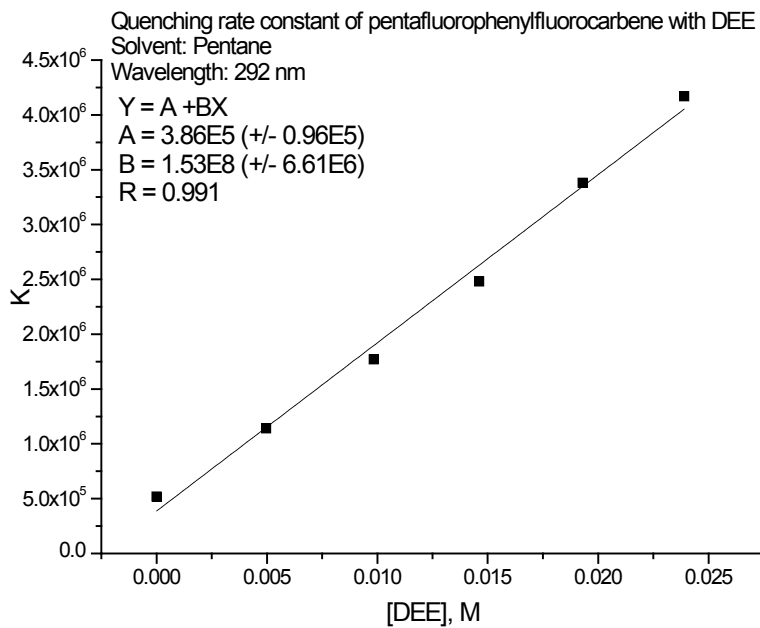


## 6. Kinetics of Carbene Addition Reactions.

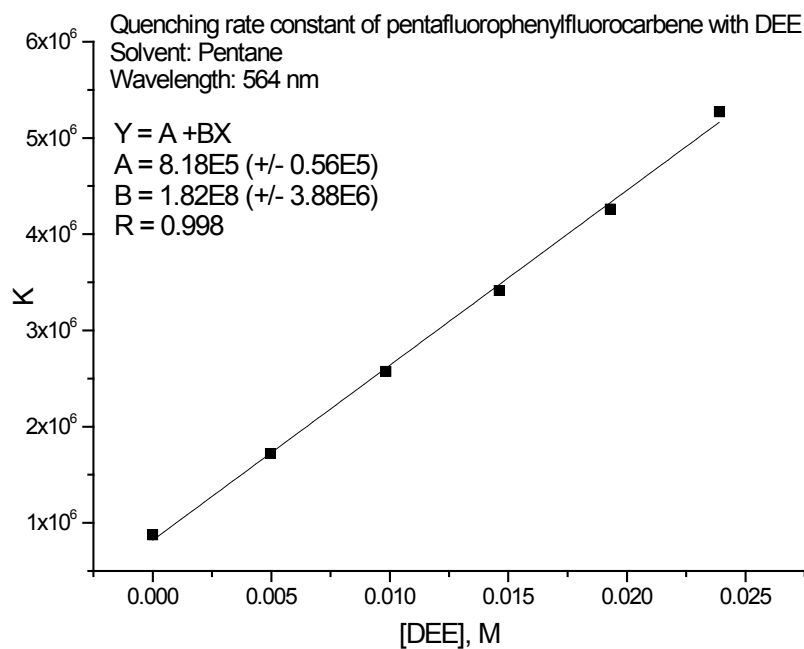
**Figure S-46:** Addition of PFPCF to tetramethylethylene.



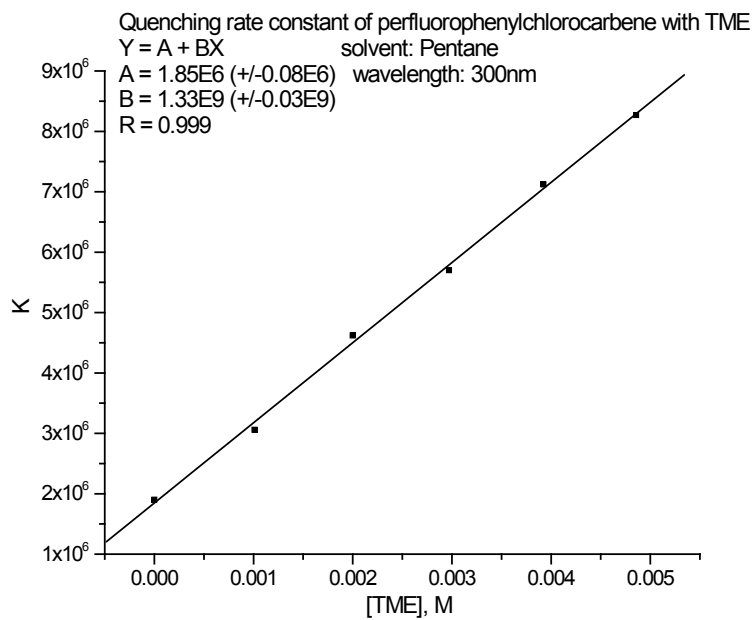
**Figure S-47:** Addition of PFPCF to 2-ethyl-1-butene (monitored at 292 nm).



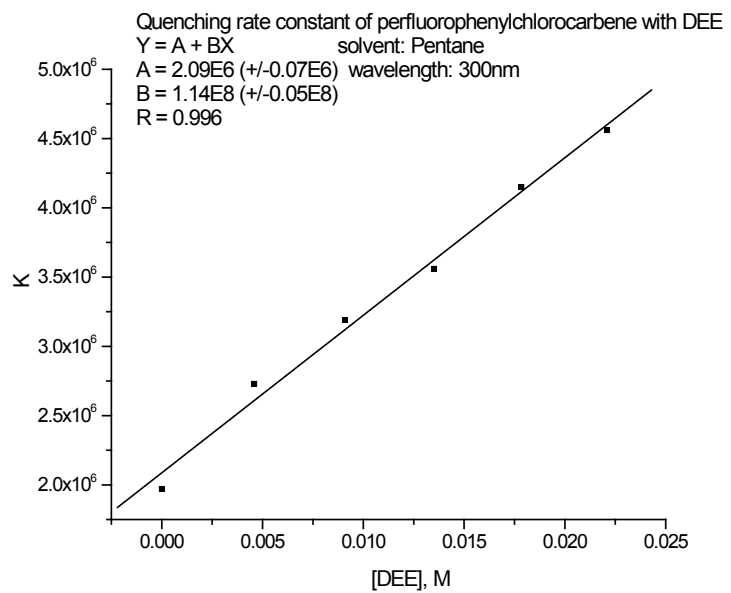
**Figure S-48:** Addition of PFPCF to 2-ethyl-1-butene (monitored at 564 nm).



**Figure S-49:** Addition of PFPCCl to tetramethylethylene.



**Figure S-50.** Addition of PFPCCl to 2-ethyl-1-butene.



## 7. Computational Details.

Electronic structure calculations were carried out using methodologies implemented in the Gaussian09 suite of programs.<sup>1</sup> Ground state geometry optimizations of F<sub>5</sub>PhCF were carried out at the DFT level using the dispersion-corrected B97D<sup>2</sup> and the hybrid B3LYP<sup>3</sup> exchange-correlation functionals and 6-311+G(d)<sup>4</sup> basis sets (B97D/6-311+G(d); B3LYP/6-311+G(d)). Stationary points were characterized by normal mode analysis, and the (unscaled) vibrational frequencies formed the basis for the calculation of vibrational zero-point energy (ZPE) corrections. Standard thermodynamic corrections (based on harmonic oscillator/rigid rotor approximations and ideal gas behavior) were then applied to convert from purely electronic energies (*E*) to (standard) enthalpies (*H*; T = 298.15 K) and free energies (*G*; T = 298.15 K, P = 1 atm).<sup>5</sup>

Carbene singlet-triplet energy separations were evaluated at the CCSD(T)<sup>6</sup> levels of theory with 6-311+G(d) basis sets. The electronic to free energy corrections obtained at the B3LYP level were applied to the electronic energies obtained in the CCSD(T) calculations to arrive at approximate CCSD(T) free energies.

Excited state calculations (transition wavelengths ( $\lambda$ ) and oscillator strengths (*f*)) at optimized ground state geometries utilized the time-dependent DFT formalism<sup>7</sup> and the B3LYP functionals (TD-B3LYP/6-311+G(d)//B97D/6-311+G(d)). General solvent effects were incorporated with the polarizable conductor self-consistent reaction field model (CPCM)<sup>8</sup> and default parameters for n-pentane provided in Gaussian 09. Assignment of a particular electronic transition ( $\pi \rightarrow p$ ,  $\pi \rightarrow \pi^*$  or  $\sigma \rightarrow p$ ) was based on inspection of the largest transition amplitudes for the excitation and by visualization of the contributing MOs.

(1) Gaussian 09, Revision A.02, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.;

Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; and Fox, D. J., Gaussian, Inc., Wallingford CT, 2009.

(2) Grimme, S. *J. Comp. Chem.* **2006**, *27*, 1787.

(3) (a) Becke, A.D. *J. Chem. Phys.* **1993**, *98*, 5468. (b) Lee, C.; Yang, W.; Parr, R.G. *Phys. Rev. B* **1988**, *37*, 785.

(4) (a) Hehre, W.J.; Ditchfield, R.; Pople, J.A. *J. Chem. Phys.* **1972**, *56*, 2257. (b) Clark, T.; Chandrasekhar, J.; Spitznagel, G.W.; Schleyer, P.v.R. *J. Comp. Chem.* **1983**, *4*, 294.

(5) McQuarrie, D.A. *Statistical Thermodynamics*; Harper and Row: New York, 1973.

(6) Pople, J. A.; Head-Gordon, M.; Raghavachari, K. *J. Chem. Phys.* **1987**, *87*, 5968.

(7) Casida, M.E.; Jamorski, C.; Casida, K.C.; Salahub, D.R. *J. Chem. Phys.* **1998**, *108*, 4439.

(8) Barone, V.; Cossi, M. *J. Phys. Chem. A* **1998**, *102*, 1995.

## 8. B3LYP/6-311+G(d) Optimized Geometries and Absolute Energies of Singlet and Triplet F<sub>5</sub>PhCF.

-----  
F5PhCF, singlet, Cs symmetry  
-----

Charge = 0 Multiplicity = 1  
C,0,-1.4423317234,-0.9540440789,0.  
F,0,-2.3172628836,0.0444611666,0.  
C,0,-0.0823090189,-0.3961460518,0.  
C,0,0.3016191803,0.9655037145,0.  
C,0,0.9595039649,-1.3513635054,0.  
C,0,1.6314359702,1.3487231829,0.  
C,0,2.2958185722,-0.9791923341,0.  
C,0,2.6273248959,0.3718369699,0.  
F,0,-0.6078133276,1.9342752158,0.  
F,0,1.976620151,2.6366080146,0.  
F,0,3.9006151698,0.7359482573,0.  
F,0,3.262671741,-1.8962161604,0.  
F,0,0.6908782981,-2.648370951,0.

SCF Done: E(RB3LYP) = -865.883269230 A.U. after 1 cycles

Zero-point correction=	0.054695 (Hartree/Particle)
Thermal correction to Energy=	0.065526
Thermal correction to Enthalpy=	0.066471
Thermal correction to Gibbs Free Energy=	0.017670
Sum of electronic and zero-point Energies=	-865.828574
Sum of electronic and thermal Energies=	-865.817743
Sum of electronic and thermal Enthalpies=	-865.816799
Sum of electronic and thermal Free Energies=	-865.865599

Iteration Nr. 12

\*\*\*\*\*

DD1Dir will call FoFDir 2 times, MxPair= 630  
NAB= 630 NAA= 0 NBB= 0 NumPrc= 8.  
DE(Corr)= -2.1451268 E(CORR)= -863.91252418 Delta=-2.70D-06  
NORM(A)= 0.12740559D+01  
Largest amplitude= 7.25D-02  
Time for triples= 1819394.63 seconds.  
T4(CCSD)= -0.90925340D-01  
T5(CCSD)= 0.62002103D-02  
CCSD(T)= -0.86399724931D+03

-----  
F5PhCF, triplet, Cs symmetry  
-----

Charge = 0 Multiplicity = 3  
C,0,-1.3890921228,-0.928825521,0.  
F,0,-2.3587058446,-0.0531282775,0.  
C,0,-0.0150069888,-0.678226508,0.  
C,0,0.559962261,0.6220569629,0.  
C,0,0.8937121781,-1.7692578069,0.  
C,0,1.9291675788,0.8092625003,0.  
C,0,2.2601631456,-1.5830278631,0.  
C,0,2.7885331535,-0.2899324678,0.  
F,0,-0.2381617694,1.6956989217,0.  
F,0,2.4386249534,2.043240913,0.  
F,0,4.1085055427,-0.1081161399,0.  
F,0,3.0862303122,-2.6316889282,0.  
F,0,0.4034846605,-3.0142697457,0.

SCF Done: E(UB3LYP) = -865.865295268 A.U. after 1 cycles

Zero-point correction=	0.054445 (Hartree/Particle)
Thermal correction to Energy=	0.065350
Thermal correction to Enthalpy=	0.066294
Thermal correction to Gibbs Free Energy=	0.016491
Sum of electronic and zero-point Energies=	-865.810850
Sum of electronic and thermal Energies=	-865.799945
Sum of electronic and thermal Enthalpies=	-865.799001
Sum of electronic and thermal Free Energies=	-865.848804

D1Dir will call FoFDir 3 times, MxPair= 1214  
NAB= 1224 NAA= 630 NBB= 561 NumPrc= 8.  
DE(Corr)= -2.0999073 E(CORR)= -863.89293355 Delta=-5.71D-06  
NORM(A)= 0.13029919D+01

Dominant configurations:

\*\*\*\*\*

Spin Case	I	J	A	B	Value
AA	48	56			0.137869D+00

Largest amplitude= 1.38D-01  
Time for triples= 2962065.00 seconds.  
T4(CCSD)= -0.85967918D-01  
T5(CCSD)= 0.66151954D-02  
CCSD(T)= -0.86397228628D+03

**9. B97D/6-311+G(d) Optimized Geometry and Absolute Energies of Singlet F<sub>5</sub>PhCF; TD-B3LYP/6-311+G(d)//B97D/6-311+G(d) Electronic Excitation Energies and Oscillator Strengths of Singlet F<sub>5</sub>PhCF.**

-----  
 F5PhCF, singlet, Cs symmetry  
 -----

Charge = 0 Multiplicity = 1  
 C,0,-1.4591670261,-0.9691495484,0.  
 F,0,-2.3574312125,0.0261780926,0.  
 C,0,-0.0935117844,-0.3937284131,0.  
 C,0,0.3005746144,0.9764396851,0.  
 C,0,0.9568400499,-1.3570212426,0.  
 C,0,1.6395745862,1.3618635261,0.  
 C,0,2.3033251755,-0.9849495558,0.  
 C,0,2.640337297,0.3752633043,0.  
 F,0,-0.6113110033,1.953068108,0.  
 F,0,1.9923973345,2.6547294845,0.  
 F,0,3.9209599752,0.7375803482,0.  
 F,0,3.2742179515,-1.9066306552,0.  
 F,0,0.6899650322,-2.6616196936,0.

SCF Done: E(RB97D) = -865.396168560 A.U. after 1 cycles

Zero-point correction=	0.052775 (Hartree/Particle)
Thermal correction to Energy=	0.063851
Thermal correction to Enthalpy=	0.064795
Thermal correction to Gibbs Free Energy=	0.015331
Sum of electronic and zero-point Energies=	-865.343394
Sum of electronic and thermal Energies=	-865.332318
Sum of electronic and thermal Enthalpies=	-865.331374
Sum of electronic and thermal Free Energies=	-865.380837

Excitation energies and oscillator strengths:

Excited State 1: Singlet-A" 1.9946 eV 621.61 nm f=0.0045 <S\*\*2>=0.000  
 48 -> 49 0.70986

Excited State 2: Singlet-A' 3.6247 eV 342.06 nm f=0.0506 <S\*\*2>=0.000  
 46 -> 50 0.10645  
 47 -> 49 0.69872

Excited State 3: Singlet-A' 4.5709 eV 271.25 nm f=0.2870 <S\*\*2>=0.000  
 46 -> 49 0.67285  
 47 -> 50 -0.10006  
 48 -> 51 -0.17693