SUPPORTING INFORMATION

A New Synthesis of Difluorodiazirine and the Absolute Reactivity of Difluorocarbene

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Contents	**Page**

Preparation of difluorodiazirine (4). A 25-mL flask with a tall neck bearing a side exit tube, and fitted with a pressure-equalized addition funnel and a magnetic stirring bar, was charged with a suspension of 3.0 g (71 mmol) of anhydrous LiF (Acros, used as supplied) and 1.8 g (8.0 mmol) of 15-crown-5 (Aldrich, used as supplied) in 8 mL of HMPA (Aldrich: 100 g of HMPA were dried over a mixture of 5 g of 4A molecular sieves and 10 g of 13X molecular sieves for at least a week before use.[1]) The side exit tube was connected to the inlet of a trap that contained 1.5 mL of pentane. The trap was fitted with stopcocks at both inlet and outlet, and was cooled by liquid nitrogen. Then, 200 mg of 2,4-dinitrophenoxyfluorodiazirine,[2] dissolved in 5 mL of dry HMPA was transferred to the addition funnel. The trap outlet was connected to a vacuum manifold and the reaction train was evacuated to 1 Torr. The reaction flask was heated to 55 $^{\circ}$C in an oil bath. When the temperature reached 55 $^{\circ}$C, the diazirine solution was added slowly (15 min) to the stirred reaction mixture. Bubbling was observed in the reaction mixture, and its color changed from pale yellow to dark red. After completion of the addition, the reaction was continued for 20 minutes until no further effervescence was observed. Then, heating and stirring were discontinued, the outlet stopcock of the trap was closed, and nitrogen was admitted to the reaction system via the addition funnel until the systemic pressure reached atmospheric pressure. The inlet stopcock of the trap was closed and the trap was disconnected from the reaction train. An additional 1 mL of pentane was added to the trap via the stopcock, and the trap was then removed from the liquid nitrogen coolant with both stopcocks open. The contents of the trap melted as the trap warmed, and the contents were transferred to a storage flask while they were still cold.

We obtained 2.5 mL of a pentane solution of difluorodiazirine (DFD) with $A_{356} = 1.0$. The UV spectrum of DFD appears below in Figure S-1. DFD pentane solutions could be stored in the freezer or, for better preservation, in a Dewar flask over Dry Ice.

The contents of the reaction flask were analyzed by GC to obtain the ratio of 2,4-dinitrophenol (partner of DFD) to 2,4-dinitrofluorobenzene (partner of diazirinone). This ratio was found to be 3:1. Table S-1, below, summarizes the ratios obtained with LiF, KF, or NaF as fluoride sources in various DFD preparations.

(1) The quality of the HMPA is critical. "Poor" quality HMPA significantly reduces the yield of DFD and raises the baseline at 300 nm. This HMPA is characterized by UV absorption at 308 nm. "Good" quality HMPA displays a maximum at 270 nm and minimal absorption at 300 nm or higher.

(2) Experimental details for the preparation of 2,4-dinitrophenoxyfluorodiazirine from *N*-methanesulfonyloxy-*O*-phenylisourea are given in Moss, R.A.; Tian, J., Sauers, R.R.: Skalit, C.; Krogh-Jerspersen, K. *Org. Lett*. **2007**, *9*, 4053, and its Supporting Information. A "complete" reaction scheme for the preparation of DFD appears below in Scheme S-1.

Scheme S-1. Synthesis of Difluorodiazirine
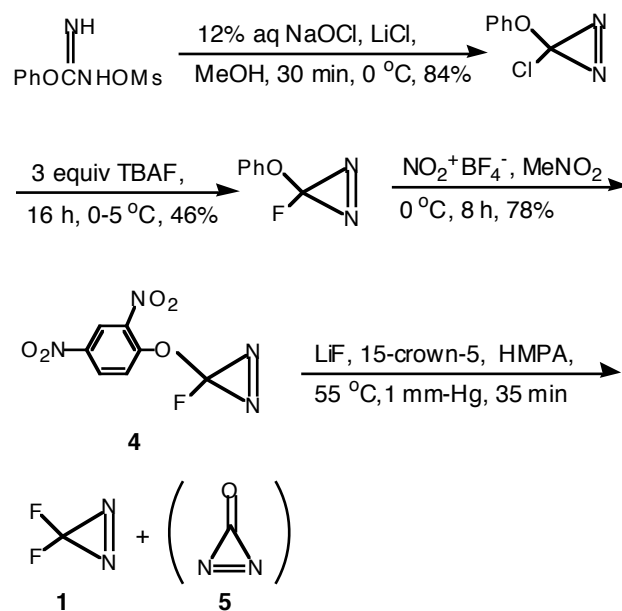
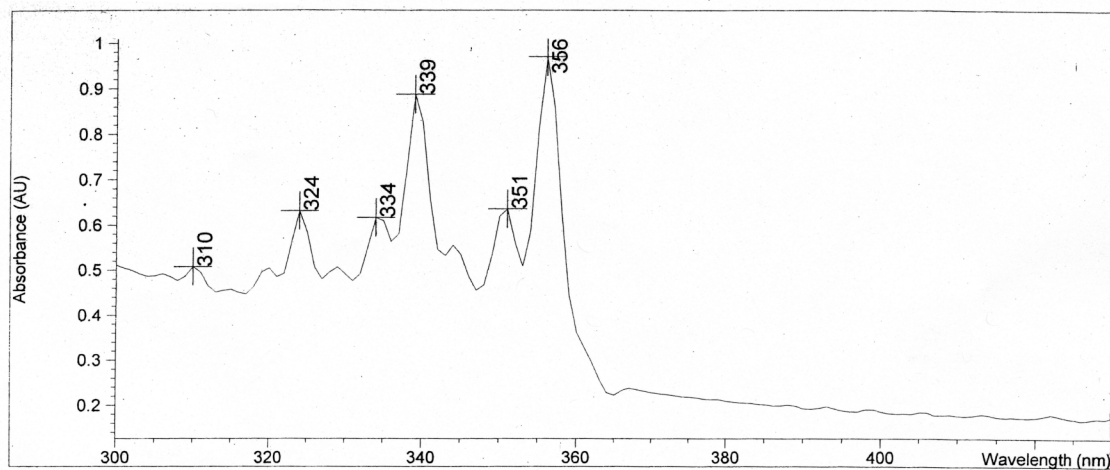(This Scheme also appears in the Communication, designated Scheme 1.)

Figure S-1. UV spectrum of difluorodiazirine in pentane.

Table S-1. Product Ratios for Various Difluorodiazirine Preparations[a]

Reagent	2,4-Dinitrophenol:2,4-Dinitrofluorobenzene[b]
NaF/18-crown-6	1:2
NaF/15-crown-5	1:5
KF	1:13.5
CsF/18-crown-6[c]	d
LiF/12-crown-4	1:2.7
LiF/15-crown-5	3:1
LiF/18-crown-6	1.1:1

[a] The reactions were performed as described above, unless otherwise indicated. [b] Analyzed by GC (detector not calibrated): column: 30 m x 0.53 mm x 1.5 μm (film thickness) 5% phenyl-methylsiloxane; temperature: 50 °C for 3 min, programmed to 260 °C at 30 °C/min. [c] The reaction was carried out at ambient temperature. [d] Only 2,4-dinitrofluorobenzene formed in this case.
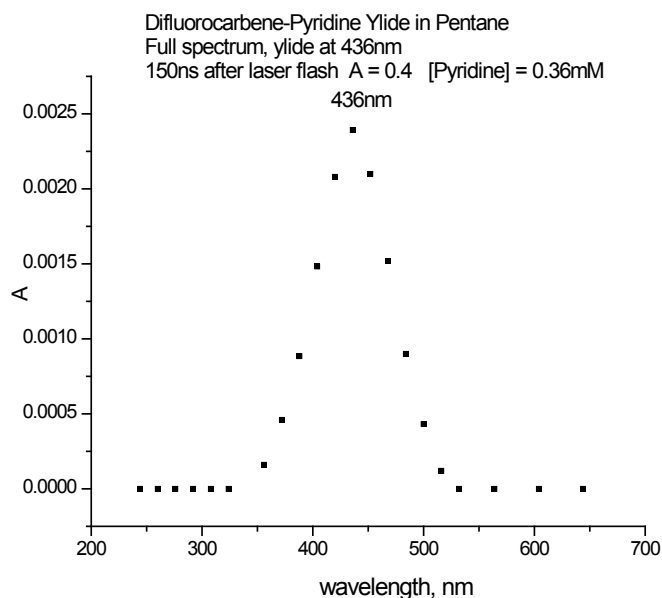

Spectra of Difluorocarbene Ylides

Difluorocarbene-Pyridine Ylide in Pentane
Full spectrum, ylide at 436nm
150ns after laser flash A = 0.4 [Pyridine] = 0.36mM

Figure S-2. LFP-UV spectrum of difluorocarbene-pyridine ylide (**8**) in pentane; λ_{max} at 436 nm.
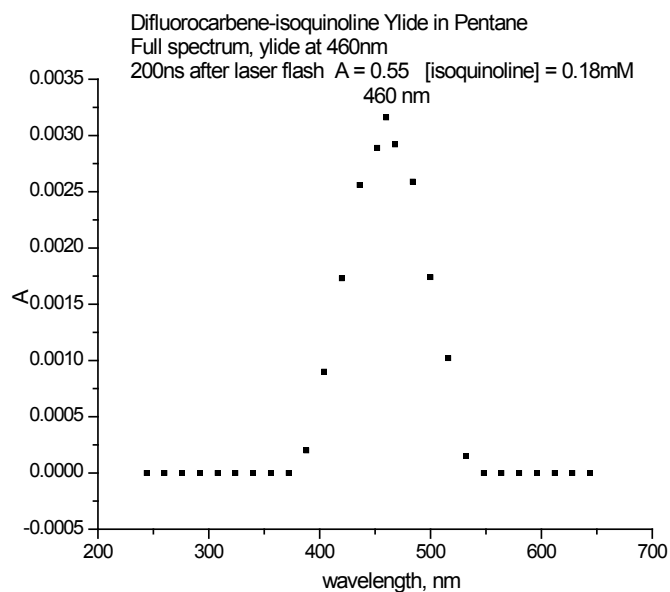
Figure S-3. LFP-UV spectrum of difluorocarbene-isoquinoline ylide (**9**) in pentane; λ_{max} at 460 nm.
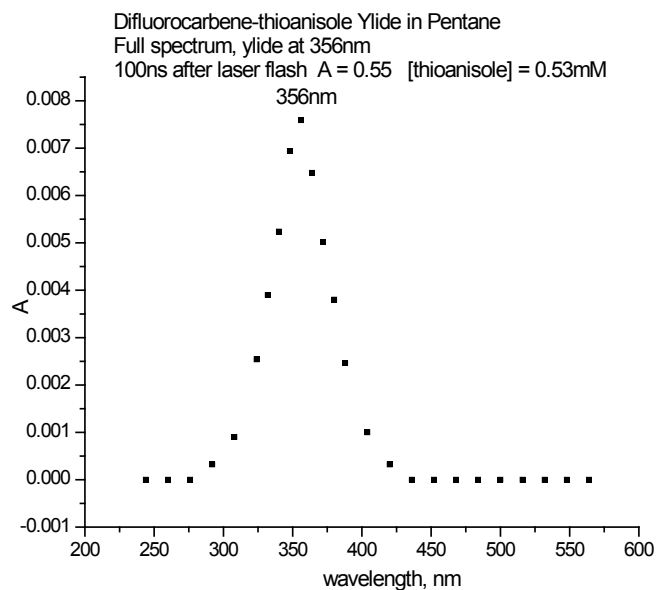

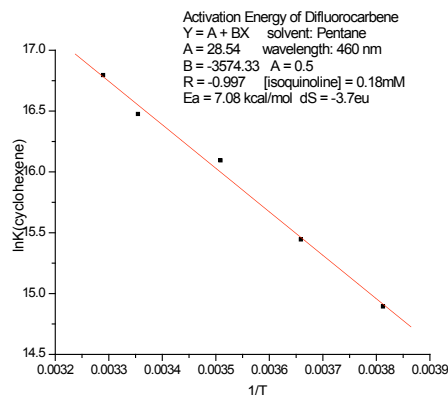**Figure S-4**. LFP-UV spectrum of difluorocarbene-thioanisole ylide (**10**) in pentane; λ_{max} at 356 nm.

Figure S-5. Activation energy for addition of CF$_2$ to cyclohexene: Ea = 7.08 kcal/mol, A = 2.48 exp 12 M^{-1}s^{-1}, R = -0.997.

Figure S-8. Rate constant for addition of CF$_2$ to cyclohexene at 285 K: k = 9.77 exp 6 M^{-1}s^{-1}, R = 0.999.

Figure S-6. Rate constant for addition of CF$_2$ to cyclohexene at 262.3 K: k = 2.94 exp 6 M^{-1}s^{-1}, R = 0.998.

Figure S-9. Rate constant for addition of CF$_2$ to cyclohexene at 298.1 K: k = 1.43 exp 7 M^{-1}s^{-1}, R = 0.998.

Figure S-7. Rate constant for addition of CF$_2$ to cyclohexene at 273.3 K: k = 5.10 exp 6 M^{-1}s^{-1}, R = 0.998.

Figure S-10. Rate constant for addition of CF$_2$ to cyclohexene at 304 K: k = 1.97 exp 7 M^{-1}s^{-1}, R = 0.999.

Figure S-11. Activation energy for addition of CF_2 to cyclohexene: Ea = 6.79 kcal/mol, A = 1.52 exp 12 $M^{-1}s^{-1}$, R = -0.998.
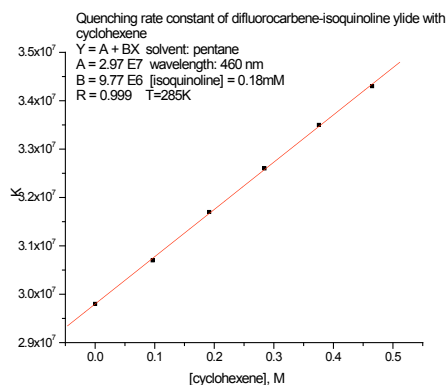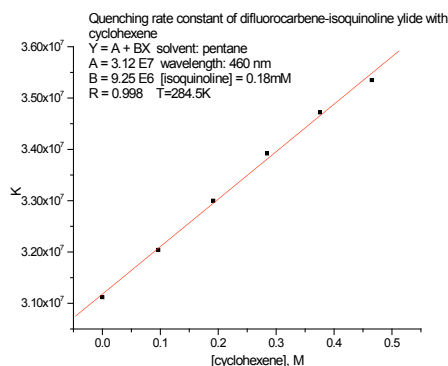

Figure S-14. Rate constant for addition of CF_2 to cyclohexene at 284.5 K: k = 9.25 exp 6 $M^{-1}s^{-1}$, R = 0.998.
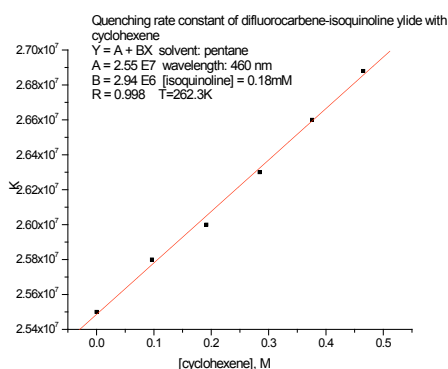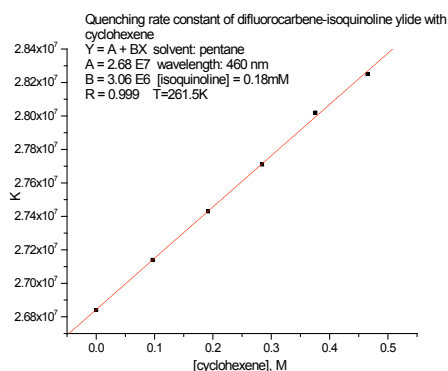

Figure S-12. Rate constant for addition of CF_2 to cyclohexene at 261.5 K: k = 3.06 exp 6 $M^{-1}s^{-1}$, R = 0.999.
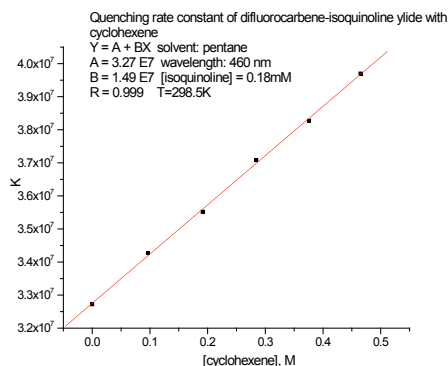
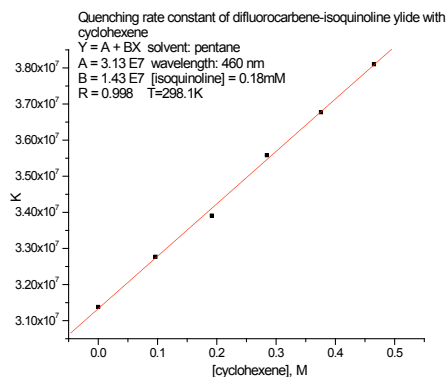**Figure S-15**. Rate constant for addition of CF_2 to cyclohexene at 298.5 K: k = 1.49 exp 7 $M^{-1}s^{-1}$, R = 0.999.
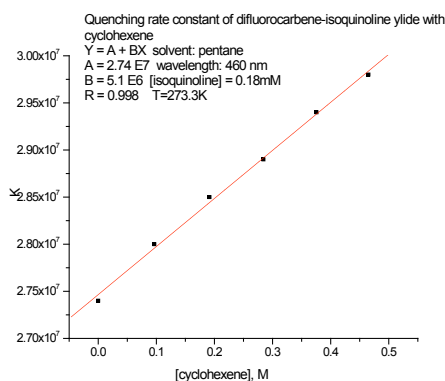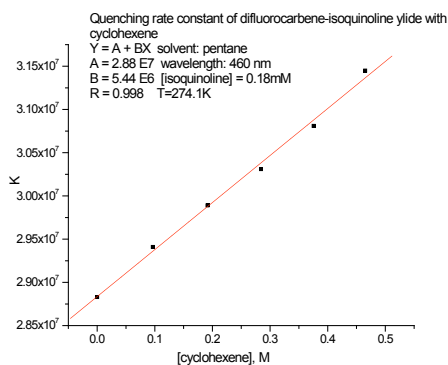

Figure S-13. Rate constant for addition of CF_2 to cyclohexene at 274.1 K: k = 5.44 exp 6 $M^{-1}s^{-1}$, R = 0.998.
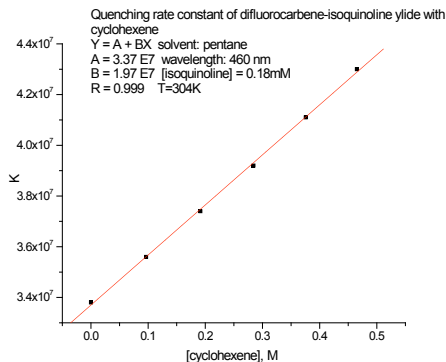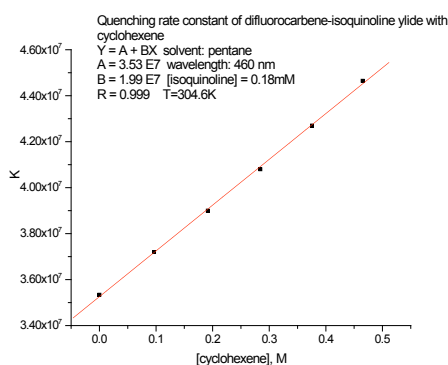

Figure S-16. Rate constant for addition of CF_2 to cyclohexene at 304.6 K: k = 1.99 exp 7 $M^{-1}s^{-1}$, R = 0.999.
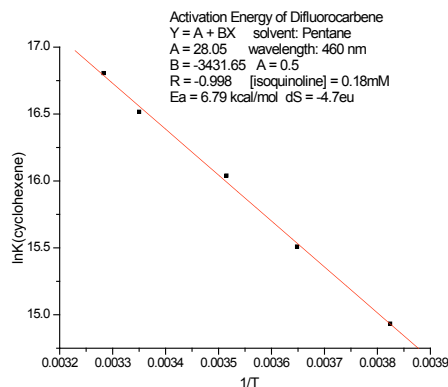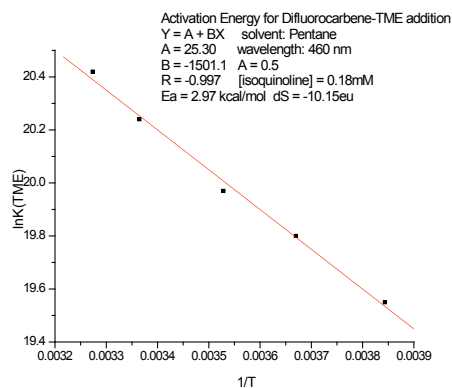
Figure S-17. Activation energy for addition of CF_2 to TME: Ea = 2.97 kcal/mol, A = 9.72 exp 10 $M^{-1}s^{-1}$, R = -0.997.
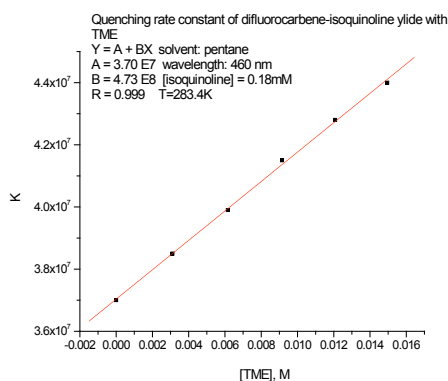
Figure S-20. Rate constant for addition of CF_2 to TME at 283.4 K: k = 4.73 exp 8 $M^{-1}s^{-1}$, R = 0.999.
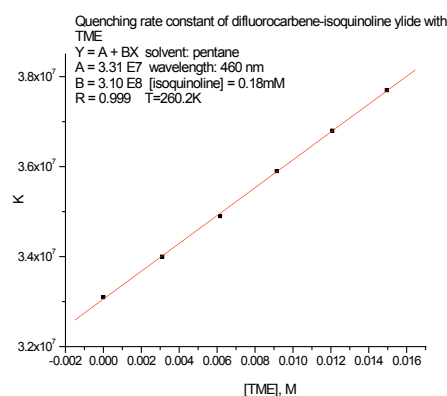
Figure S-18. Rate constant for addition of CF_2 to TME at 260.2 K: k = 3.10 exp 8 $M^{-1}s^{-1}$, R = 0.999.
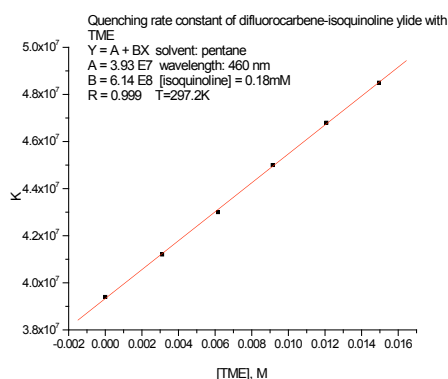
Figure S-21. Rate constant for addition of CF_2 to TME at 297.2 K: k = 6.14 exp 8 $M^{-1}s^{-1}$, R = 0.999.
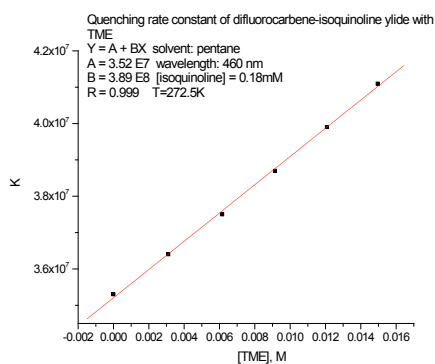
Figure S-19. Rate constant for addition of CF_2 to TME at 272.5 K: k = 3.89 exp 8 $M^{-1}s^{-1}$, R = 0.999.
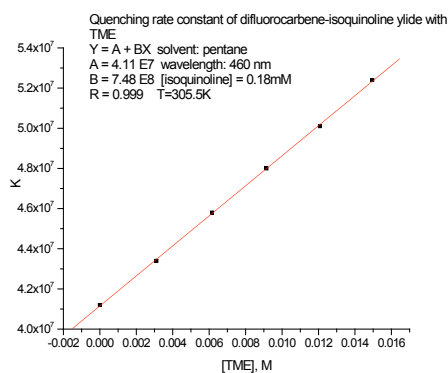
Figure S-22. Rate Constant for addition of CF_2 to TME at 305.5 K: k = 7.48 exp 8 $M^{-1}s^{-1}$, R = 0.999.

Activation Energy for Difluorocarbene-TME addition
Y = A + BX   solvent: Pentane
A = 25.49   wavelength: 460 nm
B = -1547.7   A = 0.5
R = -0.998   [isoquinoline] = 0.18mM
Ea = 3.06 kcal/mol dS = -9.77eu
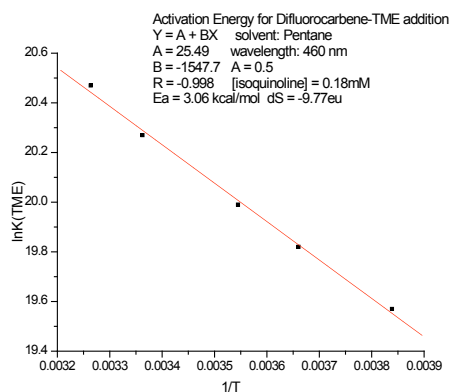
Figure S-23. Activation energy for addition of CF_2 to TME; Ea = 3.06 kcal/mol, A = 1.18 exp 11 $M^{-1}s^{-1}$, R = -0.998.

Quenching rate constant of difluorocarbene-isoquinoline ylide with TME
Y = A + BX solvent: pentane
A = 3.78 E7 wavelength: 460 nm
B = 4.80 E8 [isoquinoline] = 0.18mM
R = 0.999   T=282.1K
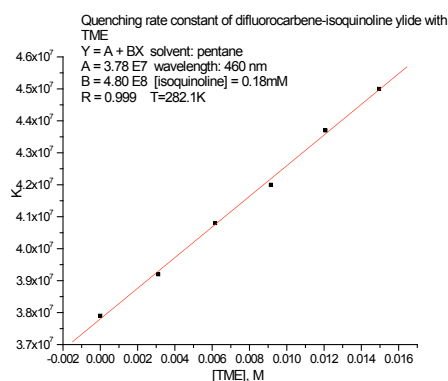
Figure S-26. Rate constant for addition of CF_2 to TME at 282.1 K: k = 4.80 exp 8 $M^{-1}s^{-1}$, R = 0.999.

Quenching rate constant of difluorocarbene-isoquinoline ylide with TME
Y = A + BX solvent: pentane
A = 3.41 E7 wavelength: 460 nm
B = 3.16 E8 [isoquinoline] = 0.18mM
R = 0.998   T=260.5K
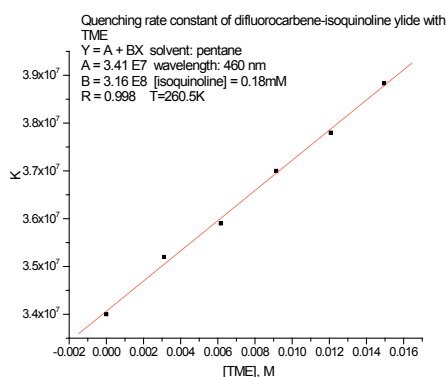
Figure S-24. Rate constant for addition of CF_2 to TME at 260.5 K: k = 3.16 exp 8 $M^{-1}s^{-1}$, R = 0.998.

Quenching rate constant of difluorocarbene-isoquinoline ylide with TME
Y = A + BX solvent: pentane
A = 4.02 E7 wavelength: 460 nm
B = 6.35 E8 [isoquinoline] = 0.18mM
R = 0.999   T=297.4K
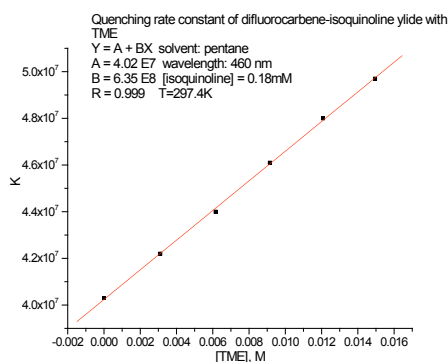
Figure S- 27. Rate constant for addition of CF_2 to TME at 297.4 K: k = 6.35 exp 8 $M^{-1}s^{-1}$, R = 0.999.

Quenching rate constant of difluorocarbene-isoquinoline ylide with TME
Y = A + BX solvent: pentane
A = 3.61 E7 wavelength: 460 nm
B = 4.06 E8 [isoquinoline] = 0.18mM
R = 0.999   T=273.2K
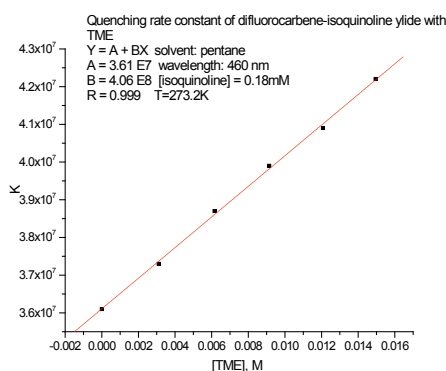
Figure S-25. Rate constant for addition of CF_2 to TME at 273.2 K: k = 4.06 exp 8 $M^{-1}s^{-1}$, R = 0.999.

Quenching rate constant of difluorocarbene-isoquinoline ylide with TME
Y = A + BX solvent: pentane
A = 4.21 E7 wavelength: 460 nm
B = 7.76 E8 [isoquinoline] = 0.18mM
R = 0.998   T=306.4K
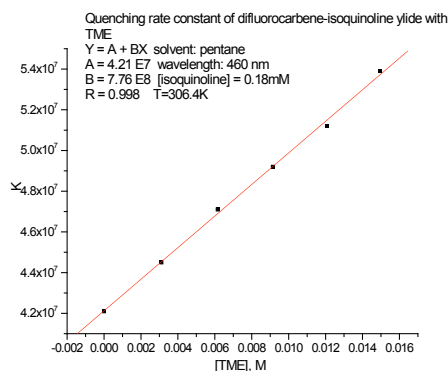
Figure S-28. Rate constant for addition of CF_2 to TME at 306.4 K: k = 7.76 exp 8 $M^{-1}s^{-1}$, R = 0.998.

Additional rate constant determinations

Quenching rate constant of difluorocarbene-isoquinoline ylide with TME
Y = A + BX   solvent: pentane
A = 3.88 E7   wavelength: 460 nm
B = 6.80 E8   [isoquinoline] = 0.18mM
R = 0.998
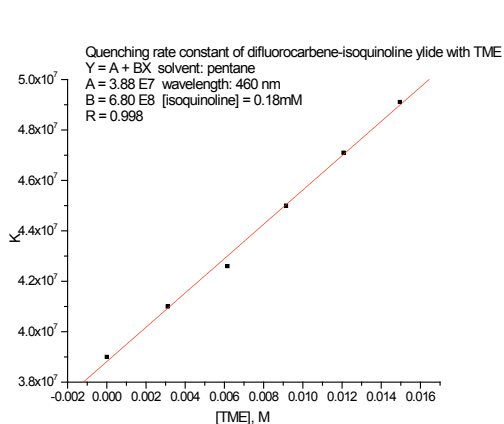
Figure S-29. Rate constant for addition of CF_2 to TME at 297 K: k = 6.80 exp 8 $M^{-1}s^{-1}$, R = 0.998.

Quenching rate constant of difluorocarbene-isoquinoline ylide with 2-methyl-2-butylene
Y = A + BX   solvent: pentane
A = 3.86 E7   wavelength: 460 nm
B = 1.28 E8   [isoquinoline] = 0.18mM
R = 0.998   T=297K
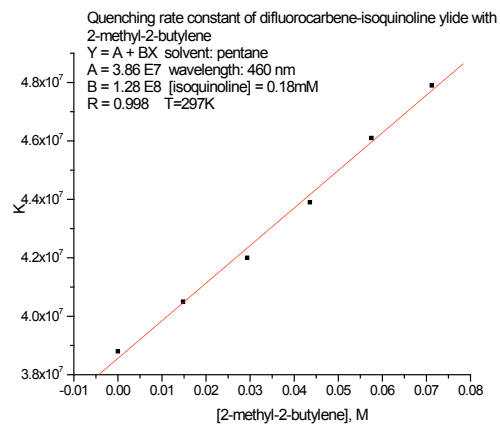
Figure S-30. Rate constant for addition of CF_2 to 2-methyl-2-butene at 297 K: k = 1.28 exp 8 $M^{-1}s^{-1}$, R = 0.998.

Quenching rate constant of difluorocarbene-isoquinoline ylide with cyclohexene
Y = A + BX   solvent: pentane
A = 3.17 E7   wavelength: 460 nm
B = 1.45 E7   [isoquinoline] = 0.18mM
R = 0.998   T=297K
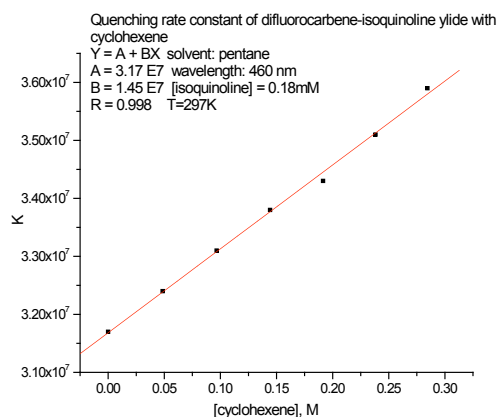
Figure S-31. Rate constant for addition of CF_2 to cyclohexene at 297 K: k = 1.45 exp 7 $M^{-1}s^{-1}$, R = 0.998.

Quenching rate constant of difluorocarbene-isoquinoline ylide with 1-hexene
Y = A + BX   solvent: pentane
A = 1.64 E7   wavelength: 460 nm
B = 2.1 E6   [isoquinoline] = 0.18mM
R = 0.998   T=297K

Figure S-32. Rate constant for addition of CF_2 to 1-hexene at 297 K: k = 2.10 exp 6 $M^{-1}s^{-1}$, R = 0.998.

Quenching rate constant of difluorocarbene-isoquinoline ylide with 1-hexene
Y = A + BX   solvent: pentane
A = 1.57 E7   wavelength: 460 nm
B = 2.71 E6   [isoquinoline] = 0.18mM
R = 0.998   T=297K

Quenching rate constant of difluorocarbene-isoquinoline ylide with 1-hexene
Y = A + BX   solvent: pentane
A = 1.58 E7   wavelength: 460 nm
B = 2.27 E6   [isoquinoline] = 0.18mM
R = 0.998   T=297K
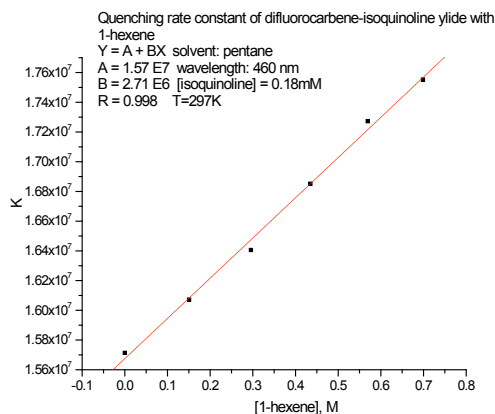
Figure S-33. Rate constant for addition of CF_2 to 1-hexene at 297 K: $k = 2.71$ exp 6 $M^{-1}s^{-1}$, $R = 0.998$.
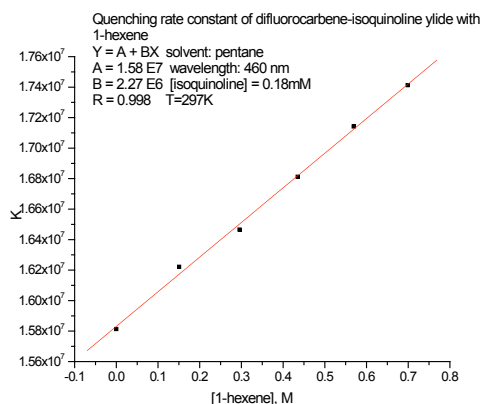
Figure S-34. Rate constant for addition of CF_2 to 1-hexene at 297 K: $k = 2.27$ exp 6 $M^{-1}s^{-1}$, $R = 0.998$.

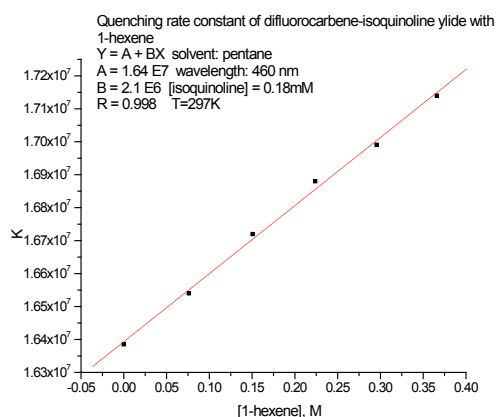## Computational details

Electronic structure calculations, based on density functional theory (DFT), were carried out with the Gaussian 03 suite[1] of programs. We employed both the PBE and B3LYP exchange and correlation functionals[2,3] with 6-311+G(d) basis sets.[4] The PBE functionals were used in ground state geometry optimizations (PBEPBE/6-311+G(d)), whereas excited state properties (transition energies (λ) and oscillator strengths (f)) were calculated at the optimized ground state geometries using time-dependent density functional theory and the B3LYP functionals (TD-B3LYP/6-311+G(d)//PBEPBE/6-311+G(d)).[5] General solvent effects were incorporated with the polarizable conductor self-consistent reaction field model (CPCM).[6] Solute molecular cavities were generated using explicit hydrogen atoms and Pauling atomic radii. The hydrocarbon solvent used experimentally (pentane) was simulated with heptane parameters.

(1) Gaussian 03, Revision C.02. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, Jr., J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.;

Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; 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.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; and Pople, J. A.; Gaussian, Inc., Wallingford CT, 2004.

(2) Perdew, J.P.; Burke, K.; Ernzerhof, M. *Phys. Rev. Lett*. **1996**, *77*, 3865.

(3) Becke, A.D. *J. Chem. Phys.* **1993**, *98*, 5648; Lee, C.; Yang, W.; Parr, R.G. *Phys. Rev. B*. **1988**, *37*, 785.

(4) Ditchfield, R.; Hehre, W.J.; Pople, J.A. *J. Chem. Phys.* **1971**, *54*, 721. Hariharan, P.C.; Pople, J.A. *Mol. Phys.* **1974**, *27*, 209. Krishnan, R.; Binkley, J.S.; Seeger, R.; Pople, J.A. *J. Chem. Phys.* **1980**, *72*, 650. McLean, A.D.; Chandler, G.S. *J. Chem. Phys.* **1980**, *72*, 5639. Clark, T.; Chandrasekhar, J.; Spitznagel, G.W.; Schleyer, P.v.R. *J. Comp. Chem.* **1983**, *4*, 294.

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

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

Optimized ground state cartesian geometries (Å), absolute energies (a.u.), and excited state transition energies and intensities.

PBEPBE/6-311+G(d) geometry optimization data for CF$_2$
C,0,-0.4967270355,0.,-0.3512390552
F,0,-0.4378742798,0.,0.9704868003
F,0,0.7690256368,0.,-0.7363274301

SCF Done: E(RPBE-PBE) = -237.544581731   A.U. after   1 cycles

Zero-point correction=   0.006419 (Hartree/Particle)
Thermal correction to Energy=   0.009445
Thermal correction to Enthalpy=   0.010390
Thermal correction to Gibbs Free Energy=   -0.017032
Sum of electronic and zero-point Energies=   -237.538163
Sum of electronic and thermal Energies=   -237.535136
Sum of electronic and thermal Enthalpies=   -237.534192
Sum of electronic and thermal Free Energies=   -237.561614

TD-B3LYP/6-311+G(d)//PBEPBE/6-311+G(d), excited state data, CF$_2$ in vacuum
 Excited State   1: Singlet-B1   4.7091 eV 263.29 nm f=0.0344
     12 -> 13   0.61517
Excited State 2: Singlet-A2   7.7300 eV 160.39 nm f=0.0000
     11 -> 13   0.70111
Excited State 3: Singlet-A1   8.7174 eV 142.23 nm f=0.0383
     12 -> 14   0.68401
     12 -> 16   -0.11434

TD-B3LYP/6-311+G(d)//PBEPBE/6-311+G(d), excited state data, CPCM: CF$_2$ in heptane solvent
Excited State 1: Singlet-B1   4.6284 eV 267.88 nm f=0.0431
     12 -> 13   0.63200
Excited State 2: Singlet-A2   7.8028 eV 158.90 nm f=0.0000
     11 -> 13   0.70139
Excited State 3: Singlet-A1   8.6687 eV 143.03 nm f=0.0585
     12 -> 14   0.67788
     12 -> 16   -0.16492

PBEPBE/6-311+G(d) geometry optimization data for pyridine (C$_5$H$_5$N)
C,0,-1.1419440583,0.0520198395,0.4600399661
C,0,-1.1904302152,0.0254282003,1.859181448
C,0,0.0154401917,0.0000552446,2.5666785219
C,0,1.2129790637,0.0019946294,1.844702181
C,0,1.1481883101,0.0296927106,0.4462592326
N,0,-0.0009834306,0.0550449207,-0.2505972432
H,0,-2.0682365279,0.072151596,-0.1262730587
H,0,-2.1528710931,0.0244033284,2.378022112
H,0,2.1813835701,-0.0178623082,2.3519386996
H,0,2.0675573841,0.0318358723,-0.1511831587
H,0,0.0218271273,-0.0216824926,3.6603699464

SCF Done: E(RPBE-PBE) = -248.023283559   A.U. after   1 cycles

Zero-point correction=   0.086054 (Hartree/Particle)
Thermal correction to Energy=   0.090476
Thermal correction to Enthalpy=   0.091420
Thermal correction to Gibbs Free Energy=   0.058569
Sum of electronic and zero-point Energies=   -247.937229
Sum of electronic and thermal Energies=   -247.932807
Sum of electronic and thermal Enthalpies=   -247.931863
Sum of electronic and thermal Free Energies=   -247.964715

TD-B3LYP/6-311+G(d)//PBEPBE/6-311+G(d), excited state data, CPCM: pyridine (C_5H_5N) in heptane holvent

Excited State   1: Singlet-A   4.9354 eV 251.22 nm f=0.0062
    20 -> 22   0.68675
Excited State   2: Singlet-A   5.3088 eV 233.54 nm f=0.0000
    20 -> 23   0.70465
Excited State   3: Singlet-A   5.3699 eV 230.89 nm f=0.0838
    19 -> 23   0.32887
    21 -> 22   0.62232
Excited State   4: Singlet-A   6.1127 eV 202.83 nm f=0.0349
    19 -> 22   -0.37504
    21 -> 23   0.55759

PBEPBE/6-311+G(d) geometry optimization data for isoquinoline (C_9H_7N)
C,0,-0.7002310227,0.0118292639,-0.6513703308
C,0,-0.7398731633,0.059631584,0.7723359505
C,0,0.5132426194,0.0778127419,1.4712030775
C,0,1.6950483043,0.0468841786,0.6830494572
C,0,1.592757682,0.0017419184,-0.69412192
H,0,-2.9058626203,0.0753512436,0.9661509596
H,0,-1.6470661218,-0.0025835839,-1.2086557395

C,0,-1.9547479689,0.0894654056,1.5082039082
C,0,0.5053132391,0.1253186526,2.8925197476
H,0,2.6772309085,0.0588599768,1.1658679675
H,0,2.4912480629,-0.0226148907,-1.3198390761
C,0,-0.692575204,0.1534020594,3.5833630636
C,0,-1.9312384637,0.1355119097,2.8898285083
H,0,1.4580527961,0.1393305305,3.4310872916
H,0,-0.6897771583,0.1899231081,4.6765896737

H,0,-2.8669651716,0.1584060898,3.4552920817
N,0,0.4081964568,-0.016510494,-1.3736750522

SCF Done: E(RPBE-PBE) = -401.504943495   A.U. after   2 cycles

Zero-point correction=   0.131547 (Hartree/Particle)
Thermal correction to Energy=   0.138509
Thermal correction to Enthalpy=   0.139454
Thermal correction to Gibbs Free Energy=   0.100178
Sum of electronic and zero-point Energies=   -401.373397
Sum of electronic and thermal Energies=   -401.366434
Sum of electronic and thermal Enthalpies=   -401.365490
Sum of electronic and thermal Free Energies=   -401.404765

TD-B3LYP/6-311+G(d)//PBEPBE/6-311+G(d), Excited State Data, CPCM:
isoquinoline (C_9H_7N) in heptane solvent
Excited State   1: Singlet-A   4.1506 eV 298.72 nm f=0.1048
     32 -> 35   0.10982
     32 -> 36   0.15788
     34 -> 35   0.63374
     34 -> 36   -0.14136
Excited State   2: Singlet-A   4.4624 eV 277.84 nm f=0.0019
     33 -> 35   0.68842
Excited State   3: Singlet-A   4.5478 eV 272.63 nm f=0.0248
     32 -> 35   -0.44342
     34 -> 35   0.15594
     34 -> 36   0.52620
Excited State   4: Singlet-A   5.2312 eV 237.01 nm f=0.0016
     33 -> 36   0.69363

PBEPBE/6-311+G(d) Geometry Optimization Data for thioanisole (C_7H_8S)
C,0,1.2896422828,-0.7138650119,-1.1102425822
C,0,2.5373788894,-1.1938893215,-0.7101301165
C,0,3.2077701487,-0.6171533065,0.3779064483
C,0,2.6105789318,0.4471739405,1.0593683596

C,0,1.3581959973,0.9378423723,0.667018549
C,0,0.6861562113,0.3597192243,-0.4236317848
H,0,0.7753453314,-1.1716417217,-1.9609758369
H,0,2.9899006692,-2.0276265663,-1.2550007395
H,0,4.185086324,-0.9952945318,0.6890647382

H,0,3.1200712968,0.9087666351,1.9105913358
H,0,0.9171919081,1.7703676678,1.218939855
S,0,-0.9048895448,0.8880830481,-1.0214622592
C,0,-1.3429802761,2.2560279059,0.0925605786
H,0,-2.3256055119,2.6082515537,-0.2495186251
H,0,-1.4351505543,1.9216685365,1.1357246109
H,0,-0.6285691039,3.0884125754,0.0202554688

SCF Done: E(RPBE-PBE) = -669.281787524   A.U. after   1 cycles

Zero-point correction=   0.125460 (Hartree/Particle)
Thermal correction to Energy=   0.133291
Thermal correction to Enthalpy=   0.134235
Thermal correction to Gibbs Free Energy= 0.092412
Sum of electronic and zero-point Energies=   -669.156328
Sum of electronic and thermal Energies=   -669.148497
Sum of electronic and thermal Enthalpies=   -669.147552
Sum of electronic and thermal Free Energies=   -669.189375

TD-B3LYP/6-311+G(d)//PBEPBE/6-311+G(d), excited state data, CPCM: thioanisole in heptane solvent

Excited State   1: Singlet-A   4.5755 eV 270.97 nm f=0.0317
     32 -> 34   -0.10890
     32 -> 35   0.19616
     33 -> 34   0.62702
     33 -> 35   0.22297
Excited State   2: Singlet-A   4.8785 eV 254.14 nm f=0.3382
     32 -> 34   -0.13296
     33 -> 34   -0.22869
     33 -> 35   0.61593
Excited State   3: Singlet-A   4.9680 eV 249.57 nm f=0.0002
     33 -> 36   0.65720
     33 -> 37   -0.20209
Excited State   4: Singlet-A   5.2894 eV 234.40 nm f=0.0052
     33 -> 36   0.22603
     33 -> 37   0.64263
     33 -> 39   0.11641

PBEPBE/6-311+G(d) geometry optimization data for CF$_2$:pyridine ylide
C,0,-1.1868698139,0.047882808,0.4719382349
C,0,-1.187594969,0.0242724876,1.8535997933
C,0,0.0156399902,0.0138491102,2.5755258015

C,0,1.2102176753,0.0008190619,1.8390825617
C,0,1.1932685666,0.0247136418,0.4577249198
N,0,-0.0006184202,0.0927007009,-0.2401084375
H,0,-2.0918114656,0.0640781093,-0.130968264
H,0,-2.1529574702,-0.0016025487,2.3641913876
H,0,2.1809108076,-0.0440243474,2.3381159484
H,0,2.0908359221,0.0235007024,-0.1563017879
C,0,-0.0059832424,0.376302305,-1.6323669948
H,0,0.021889499,0.0068918149,3.6663384893
F,0,-1.1275596465,-0.1899610496,-2.2040717676
F,0,1.0968254697,-0.2127928531,-2.217444078

SCF Done: E(RPBE-PBE) = -485.594964624   A.U. after   1 cycles

Zero-point correction=   0.096616 (Hartree/Particle)
Thermal correction to Energy=   0.104056
Thermal correction to Enthalpy=   0.105000
Thermal correction to Gibbs Free Energy=   0.064457
Sum of electronic and zero-point Energies=   -485.498349
Sum of electronic and thermal Energies=   -485.490909
Sum of electronic and thermal Enthalpies=   -485.489965
Sum of electronic and thermal Free Energies=   -485.530507

TD-B3LYP/6-311+G(d)//PBEPBE/6-311+G(d), excited state data, CPCM:
CF_2:pyridine ylide in heptane solvent
 Excited State   1: Singlet-A   2.9411 eV 421.56 nm f=0.3283
      33 -> 34   0.58665
Excited State   2: Singlet-A   3.1422 eV 394.57 nm f=0.0103
      32 -> 34   -0.12428
      33 -> 35   0.68725
Excited State   3: Singlet-A   4.5952 eV 269.81 nm f=0.0174
      33 -> 36   0.69942
Excited State   4: Singlet-A   5.0843 eV 243.86 nm f=0.0035
      32 -> 34   -0.11252
      33 -> 37   0.68692
      33 -> 40   -0.11735
Excited State   5: Singlet-A   5.2984 eV 234.00 nm f=0.1526
      31 -> 35   -0.18245
      32 -> 34   0.63301
      33 -> 37   0.12936

PBEPBE/6-311+G(d) geometry optimization data for CF₂:isoquinoline ylide
C,0,-0.7430587934,-0.0028882821,-0.6433241671
C,0,-0.7474406093,0.0677615781,0.7624309437
C,0,0.5028300819,0.083942131,1.4720142917
C,0,1.6913274401,0.0345434944,0.6801832551
C,0,1.6398084598,0.0085896388,-0.6809962511
H,0,-2.9161154141,0.0765780578,0.9781470043
H,0,-1.6600651362,-0.0278085392,-1.2288888216
C,0,-1.9601596492,0.0918515103,1.5098701987
C,0,0.5037738671,0.1344180492,2.8832624151
H,0,2.6713569721,0.0140354495,1.1639610557
H,0,2.5191369535,-0.0048841497,-1.3213025424
C,0,-0.6926846863,0.1592277763,3.5881534281
C,0,-1.9262039564,0.1345207792,2.8929815745
H,0,1.4604471761,0.1485084751,3.4148449988
H,0,-0.6850878315,0.1940751276,4.6805449621
H,0,-2.8631243096,0.152333314,3.4566974124
N,0,0.4180126099,0.0169552838,-1.3607501895
C,0,0.439117203,0.2434043041,-2.7690264388
F,0,-0.7493161811,-0.1994873331,-3.3067389862
F,0,1.4497058673,-0.5120405112,-3.3368219296

SCF Done: E(RPBE-PBE) = -639.078490637   A.U. after   2 cycles

Zero-point correction=   0.142070 (Hartree/Particle)
Thermal correction to Energy=   0.152183
Thermal correction to Enthalpy=   0.153127
Thermal correction to Gibbs Free Energy=   0.106264
Sum of electronic and zero-point Energies=   -638.936420
Sum of electronic and thermal Energies=   -638.926308
Sum of electronic and thermal Enthalpies=   -638.925364
Sum of electronic and thermal Free Energies=   -638.972227

TD-B3LYP/6-311+G(d)//PBEPBE/6-311+G(d), excited state data, CPCM:
CF₂:isoquinoline ylide in heptane solvent
Excited State   1: Singlet-A   2.5957 eV 477.64 nm f=0.2123
      46 -> 47   0.53029
      46 -> 48   -0.35188
Excited State   2: Singlet-A   2.9142 eV 425.44 nm f=0.2681
      46 -> 47   0.26647
      46 -> 48   0.58693
Excited State   3: Singlet-A   4.0146 eV 308.83 nm f=0.1072
      44 -> 48   0.12524
      45 -> 47   0.65749

Excited State   4:   Singlet-A   4.1006 eV 302.35 nm f=0.0027
   46 -> 49   0.68873
Excited State   5:   Singlet-A   4.6305 eV 267.75 nm f=0.0060
   46 -> 50   0.68233
   46 -> 52   -0.13448

The isoquinoline-CF_2 ylide has an intense transition computed at 478 nm and a second transition at 425 nm of similar intensity. Together, they should yield a strong (broad) absorption around 450 nm. The overall intensity should be ~(0.212 + 0.268) ~ 0.48.

PBEPBE/6-311+G(d) Geometry Optimization Data for CF_2:thioanisole ylide
C,0,-1.0667449118,-1.0778281341,1.3785048171
C,0,-0.9426295027,-0.9056652084,2.7596968291
C,0,0.2329866052,-0.37227472,3.3032928403
C,0,1.2815286943,-0.0004999908,2.4544091357
C,0,1.1639509805,-0.1538589605,1.068293629
C,0,-0.0100404906,-0.7041233509,0.5295446556
H,0,-1.9783168234,-1.5106199156,0.9565034985
H,0,-1.7671383289,-1.2009288976,3.4146677486
H,0,0.3305022175,-0.2462948313,4.3848969871
H,0,2.1992768986,0.4254705874,2.8698892963
H,0,1.9769812683,0.1683112204,0.4150913727
S,0,-0.2787526356,-0.8884828025,-1.2235874969
C,0,1.4006063335,-1.0852859646,-1.8896736353
H,0,1.2787949597,-1.4125582969,-2.9309815011
H,0,1.9275554654,-0.1207753,-1.8735971558
H,0,1.9468721366,-1.8539248611,-1.3278426834
C,0,-0.0220799525,1.6638717328,-1.6644560505
F,0,-0.5455967576,1.7920476338,-2.9055257967
F,0,-0.9743979268,2.1836226677,-0.8687965297

SCF Done: E(RPBE-PBE) = -906.835193726   A.U. after   2 cycles

Zero-point correction=   0.133361 (Hartree/Particle)
Thermal correction to Energy=   0.145612
Thermal correction to Enthalpy=   0.146556
Thermal correction to Gibbs Free Energy=   0.092286
Sum of electronic and zero-point Energies=   -906.701833
Sum of electronic and thermal Energies=   -906.689582
Sum of electronic and thermal Enthalpies=   -906.688638
Sum of electronic and thermal Free Energies=   -906.742907

TD-B3LYP/6-311+G(d)//PBEPBE/6-311+G(d), excited state data, CPCM: CF$_2$:thioanisole ylide in heptane solvent

Excited State   1:   Singlet-A   3.7778 eV 328.19 nm f=0.3266
    45 -> 46   0.63662

Excited State   2:   Singlet-A   4.6252 eV 268.06 nm f=0.0007
    44 -> 46   0.56609
    45 -> 47   -0.31758
    45 -> 48   -0.25635

Excited State   3:   Singlet-A   4.7660 eV 260.14 nm f=0.0297
    43 -> 46   0.44743
    44 -> 46   0.25900
    45 -> 47   0.42411