

Supporting Information

Hammett Analyses of Halocarbene – Halocarbanion Equilibria

Lei Wang, Robert A. Moss,* and Karsten Krogh-Jespersen*

*Department of Chemistry and Chemical Biology
Rutgers, The State University of New Jersey
New Brunswick, New Jersey 08903*

E-mail: moss@rutchem.rutgers.edu; krogh@rutchem.rutgers.edu

Contents

1. Calibration of the LFP Spectra; Figures S-1 – S-5	S2
2. Determination of Equilibrium Constants; Figures S-6 – S-35	S4
3. Determination of Rate Constants k_f ; Figures S-36 – S-40	S19
4. Hammett Correlations; Figures S-41 – S-51	S22
5. Computational Details	S28
6. Table S-1. Computed Thermodynamic Parameters	S30
7. Optimized geometries, absolute energies, electronic excitation energies and oscillator strengths of <i>p</i> -X-PhCCl and <i>p</i> -X-PhCCl ₂ ⁻ , X = H, Cl, CF ₃ and F; <i>m</i> -Cl-PhCCl and <i>m</i> -Cl-PhCCl ₂ ⁻ ; and Cl ⁻ .	S31

1. Calibration of the LFP Spectra. A solution of phenylchlorodiazirine in DCE ($A = 0.5$) was positioned in the sample cell in the path of the xenon lamp monitoring beam. Apparent intensities were determined at each wavelength scanning from 244 – 804 nm. The intensity measured at each wavelength was divided by the maximum observed intensity to obtain a relative intensity or sensitivity, which takes account of wavelength-dependent variations in the xenon lamp emission, sample absorptivity, and detector sensitivity. A plot of the relative sensitivity vs wavelength (cf. Figure S-1) then afforded a calibration curve, which was used to calibrate the observed signals of PhCCl and PhCCl₂ in the LFP experiments: i.e., the intensities of the “raw” LFP absorptions were divided by the corresponding relative sensitivities at each wavelength to give the calibrated spectrum.

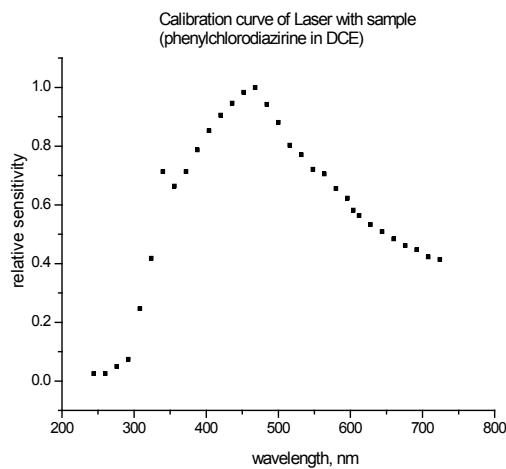


Figure S-1. Calibration curve with phenylchlorodiazirine in DCE, relative sensitivity vs wavelength (nm).

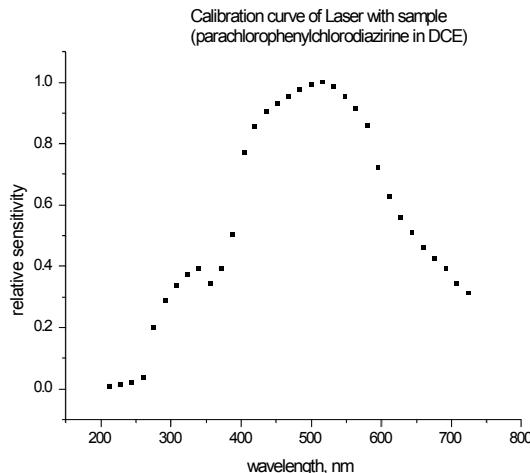


Figure S-2. Calibration curve with *p*-chlorophenylchlorodiazirine in DCE, relative sensitivity vs wavelength (nm).

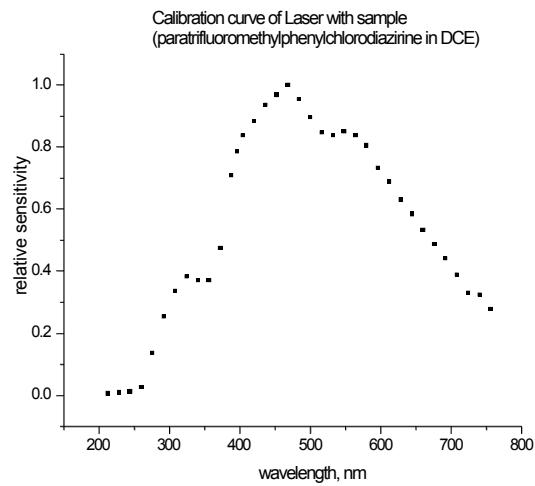


Figure S-3. Calibration curve with *p*-trifluoromethylphenylchlorodiazirine in DCE, relative sensitivity vs wavelength (nm).

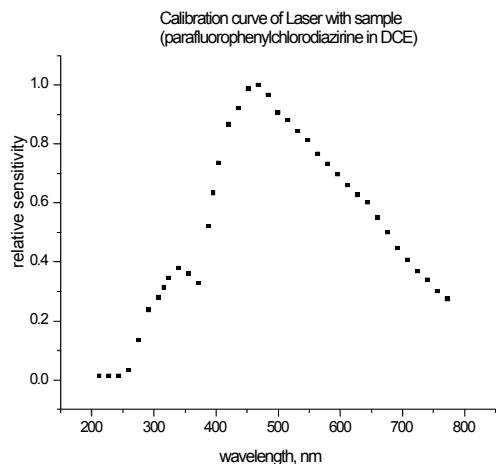


Figure S-4. Calibration curve with *p*-fluorophenylchlorodiazirine in DCE, relative sensitivity vs wavelength (nm).

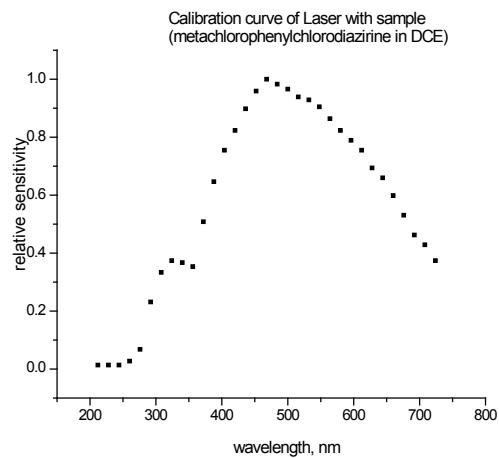


Figure S-5. Calibration curve with *m*-chlorophenylchlorodiazirine in DCE, relative sensitivity vs wavelength (nm).

2. Determination of Equilibrium Constants.

A. 1a/1b (H) [From reference 2]

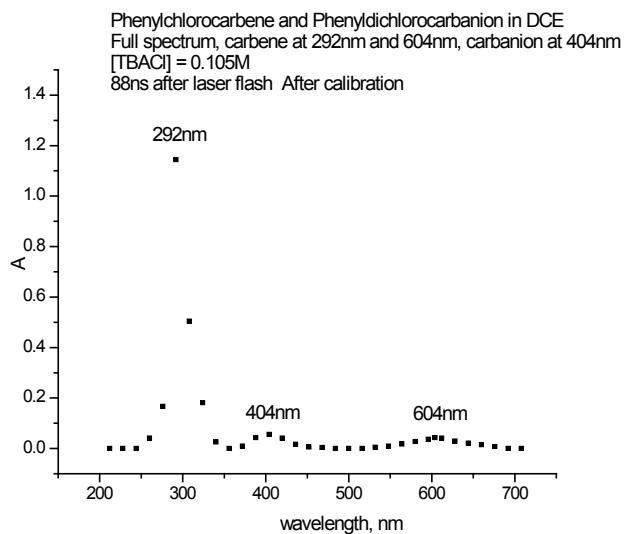


Figure S-6. UV-vis spectrum acquired 88 ns after LFP of phenylchlorodiazirine with 0.105 M TBACl in DCE, after calibration. Absorptions of PhCCl are at 292 nm and 604 nm; absorption of PhCCl₂⁻ is at 404 nm.

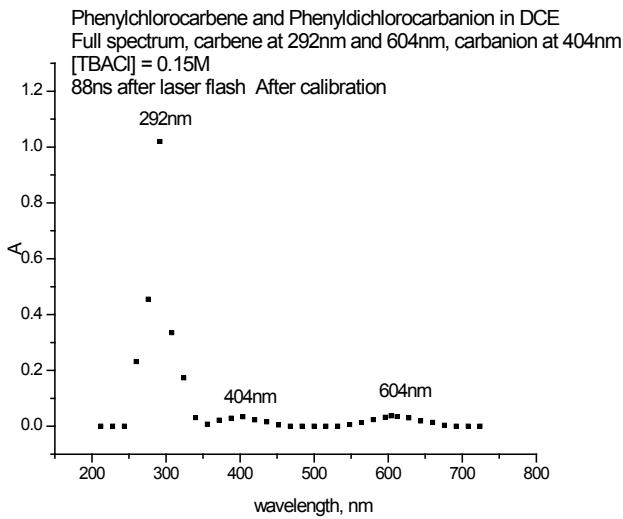


Figure S-7. UV-vis spectrum acquired 88 ns after LFP of phenylchlorodiazirine with 0.15 M TBACl in DCE, after calibration. Absorptions of PhCCl are at 292 nm and 604 nm; absorption of PhCCl_2^- is at 404 nm.

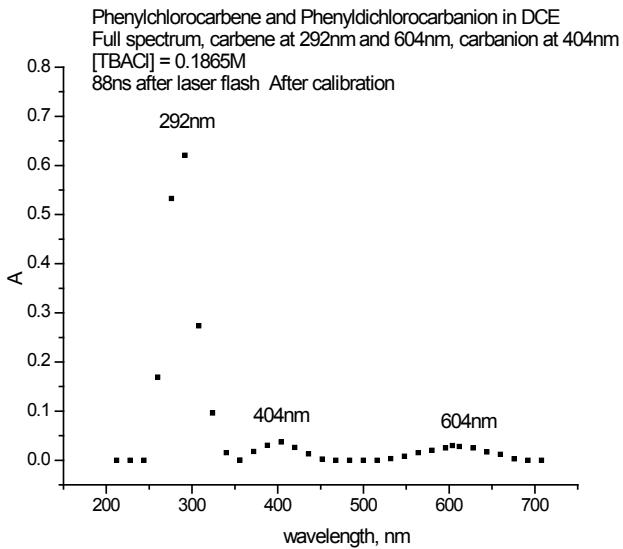


Figure S-8. UV-vis spectrum acquired 88 ns after LFP of phenylchlorodiazirine with 0.1865 M TBACl in DCE, after calibration. Absorptions of PhCCl are at 292 nm and 604 nm; absorption of PhCCl_2^- is at 404 nm.

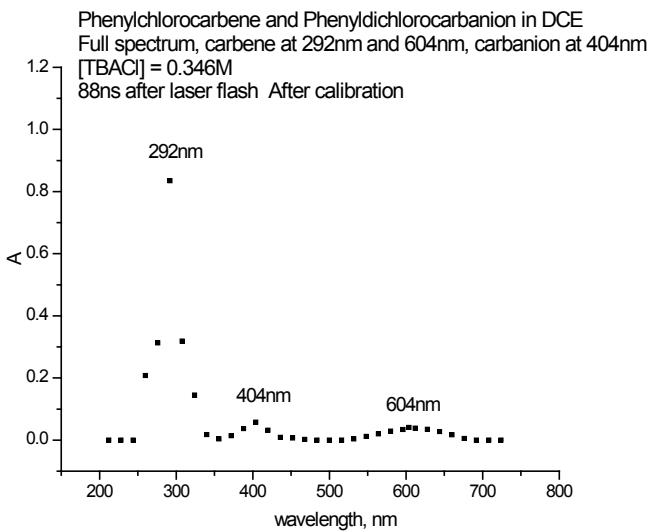


Figure S-9. UV-vis spectrum acquired 88 ns after LFP of phenylchlorodiazirine with 0.346 M TBACl in DCE, after calibration. Absorptions of PhCCl are at 292 nm and 604 nm; absorption of PhCCl_2^- is at 404 nm.

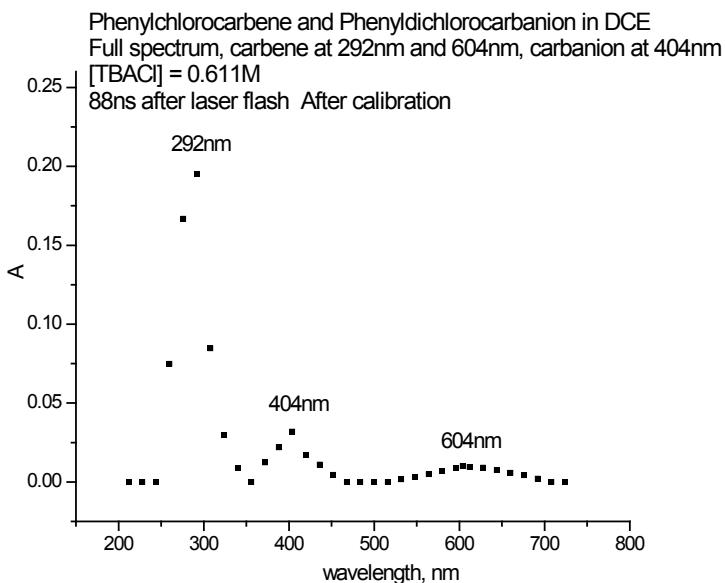


Figure S-10. UV-vis spectrum acquired 88 ns after LFP of phenylchlorodiazirine with 0.611 M TBACl in DCE, after calibration. Absorptions of PhCCl are at 292 nm and 604 nm; absorption of PhCCl_2^- is at 404 nm.

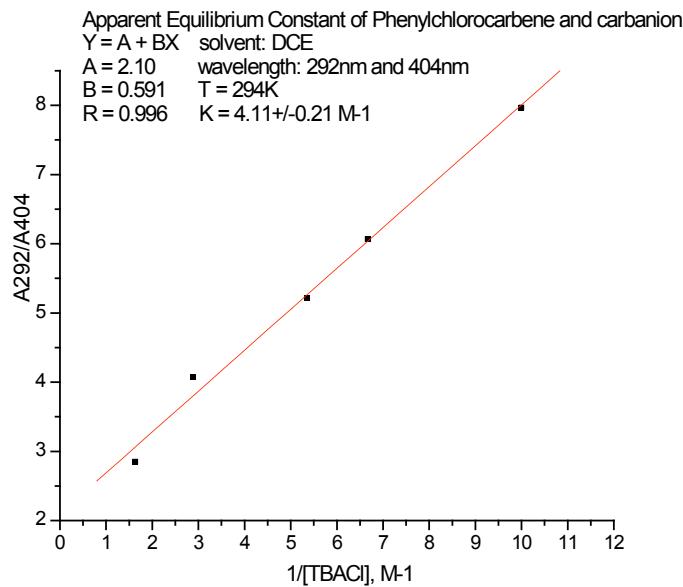


Figure S-11. Calibrated absorption intensities of PhCCl at 292 nm relative to PhCCl₂⁻ at 404 nm vs 1/[TBACl] in DCE solution at 294 K. The slope of the correlation line is 0.591 M ($r = 0.996$), leading to $K = 4.11 (\pm 0.21) M^{-1}$.

B. 1b/2b (*p*-Cl)

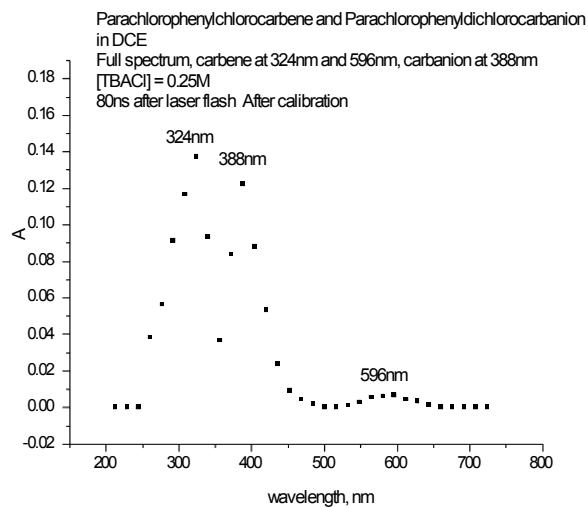


Figure S-12. UV-vis spectrum acquired 80 ns after LFP of *p*-chlorophenylchlorodiazirine with 0.25 M TBACl in DCE, after calibration. Absorptions of *p*-Cl-PhCCl are at 324 nm and 596 nm; absorption of *p*-Cl-PhCCl₂⁻ is at 388 nm.

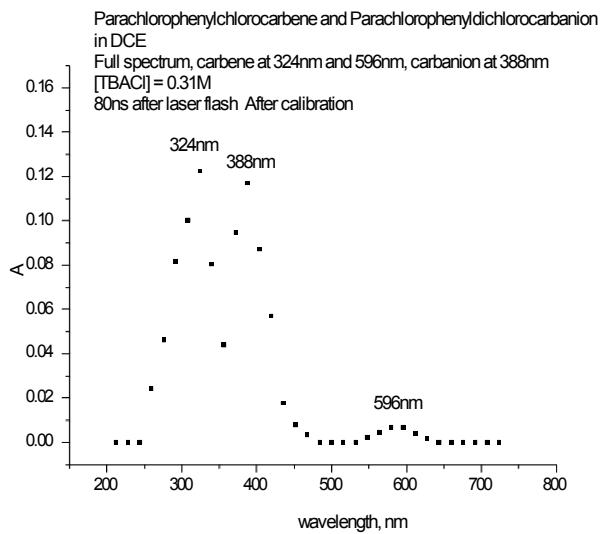


Figure S-13. UV-vis spectrum acquired 80 ns after LFP of *p*-chlorophenylchlorodiazirine with 0.31 M TBACl in DCE, after calibration. Absorptions of *p*-Cl-PhCCl are at 324 nm and 596 nm; absorption of *p*-Cl-PhCCl₂⁻ is at 388 nm.

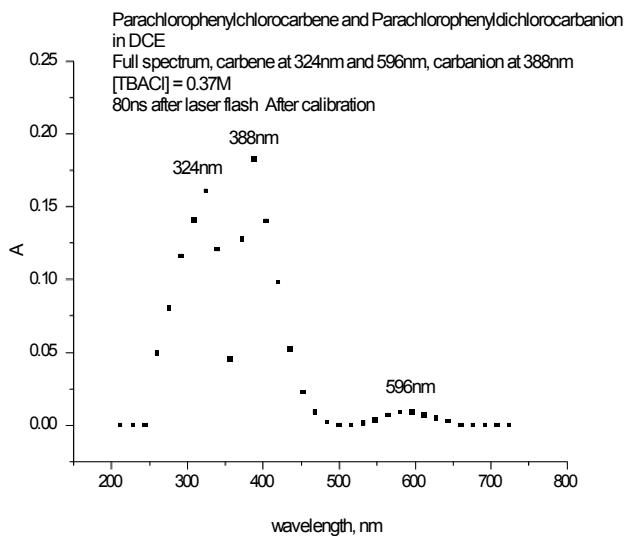


Figure S-14. UV-vis spectrum acquired 80 ns after LFP of *p*-chlorophenylchlorodiazirine with 0.37 M TBACl in DCE, after calibration. Absorptions of *p*-Cl-PhCCl are at 324 nm and 596 nm; absorption of *p*-Cl-PhCCl₂⁻ is at 388 nm.

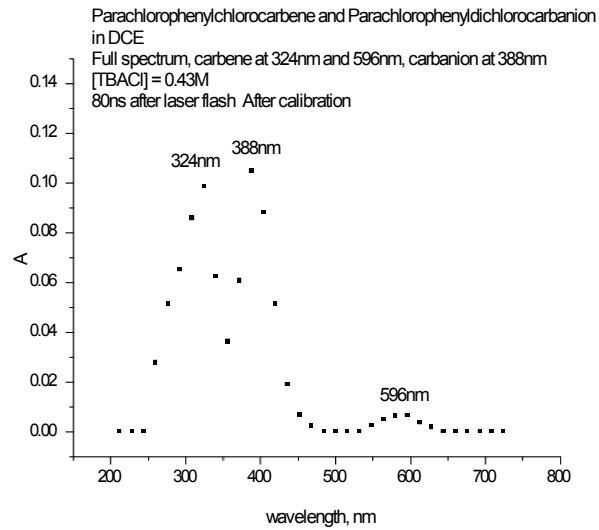


Figure S-15. UV-vis spectrum acquired 80 ns after LFP of *p*-chlorophenylchlorodiazirine with 0.43 M TBACl in DCE, after calibration. Absorptions of *p*-Cl-PhCCl are at 324 nm and 596 nm; absorption of *p*-Cl-PhCCl₂⁻ is at 388 nm.

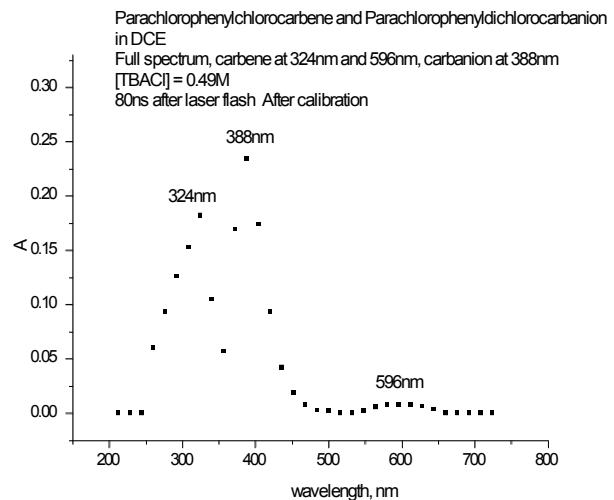


Figure S-16. UV-vis spectrum acquired 80 ns after LFP of *p*-chlorophenylchlorodiazirine with 0.49 M TBACl in DCE, after calibration. Absorptions of *p*-Cl-PhCCl are at 324 nm and 596 nm; absorption of *p*-Cl-PhCCl₂⁻ is at 388 nm.

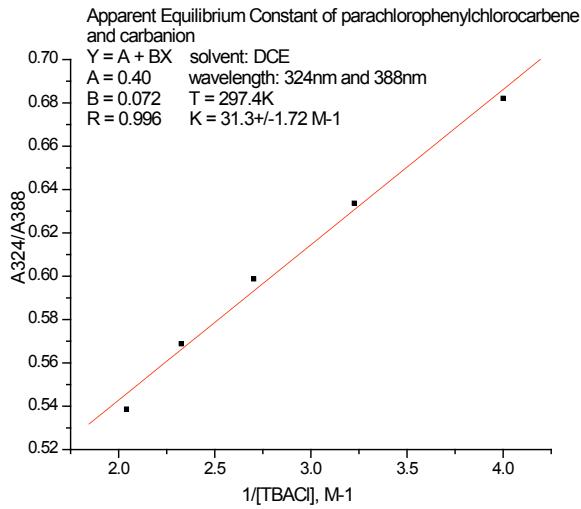


Figure S-17. Calibrated absorption intensities of *p*-Cl-PhCCl at 324 nm relative to *p*-Cl-PhCCl⁻ at 388 nm vs 1/[TBACl] in DCE solution at 297 K. The slope of the correlation line is 0.072 M ($r = 0.996$), leading to $K = 31.3 (\pm 1.72) M^{-1}$.

C. 1c/2c (*p*-CF₃)

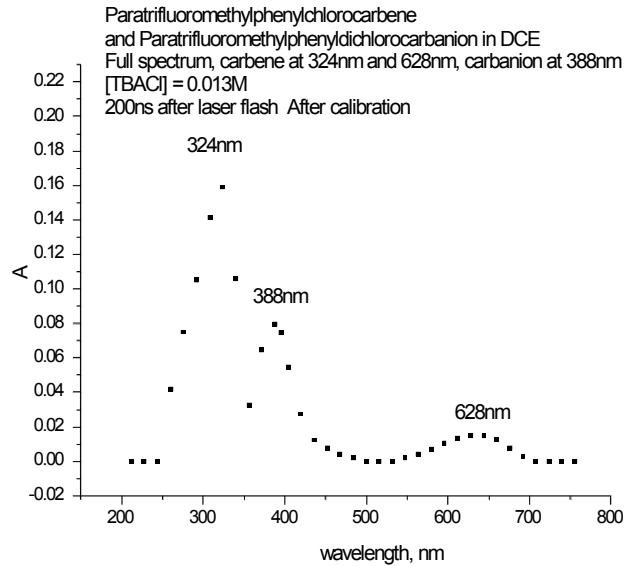


Figure S-18. UV-vis spectrum acquired 200 ns after LFP of *p*-trifluoromethylphenylchlorodiazirine with 0.013 M TBACl in DCE, after calibration. Absorptions of *p*-CF₃-PhCCl are at 324 nm and 628 nm; absorption of *p*-CF₃-PhCCl⁻ is at 388 nm.

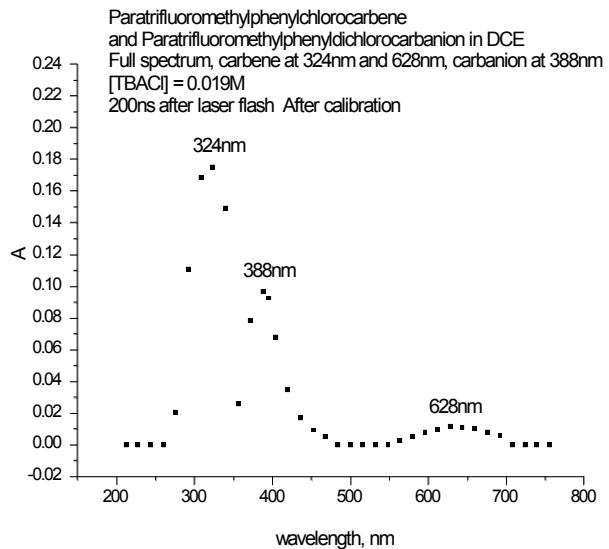


Figure S-19. UV-vis spectrum acquired 200 ns after LFP of *p*-trifluoromethylphenylchlorodiazirine with 0.019 M TBACl in DCE, after calibration. Absorptions of *p*-CF₃-PhCCl are at 324 nm and 628 nm; absorption of *p*-CF₃-PhCCl₂⁻ is at 388 nm.

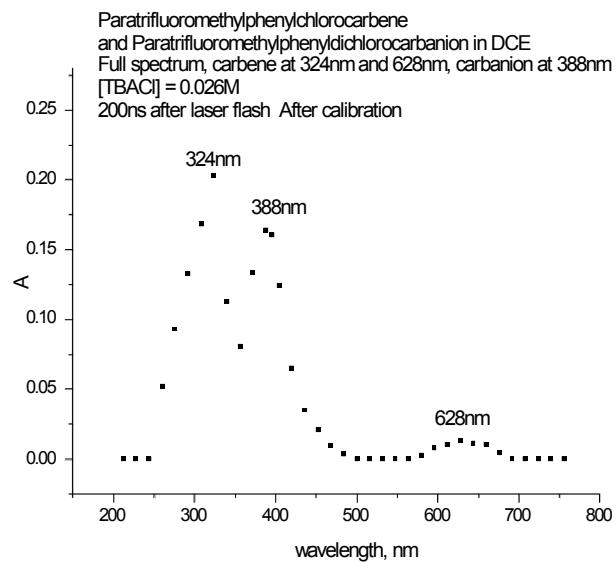


Figure S-20. UV-vis spectrum acquired 200 ns after LFP of *p*-trifluoromethylphenylchlorodiazirine with 0.026 M TBACl in DCE, after calibration. Absorptions of *p*-CF₃-PhCCl are at 324 nm and 628 nm; absorption of *p*-CF₃-PhCCl₂⁻ is at 388 nm.

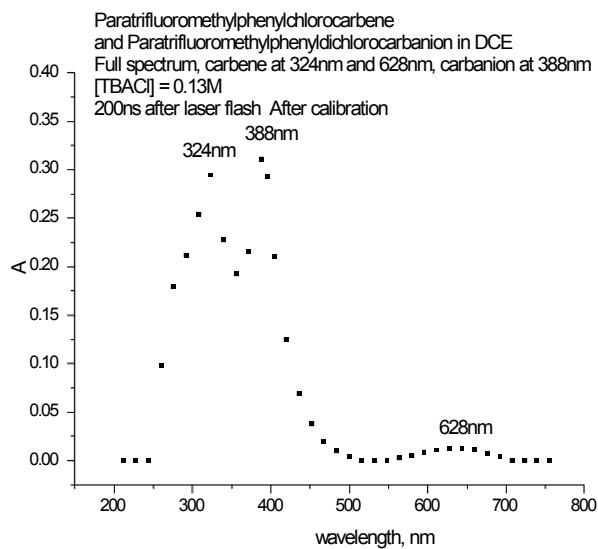


Figure S-21. UV-vis spectrum acquired 200 ns after LFP of *p*-trifluoromethylphenylchlorodiazirine with 0.13 M TBACl in DCE, after calibration. Absorptions of *p*-CF₃-PhCCl are at 324 nm and 628 nm; absorption of *p*-CF₃-PhCCl⁻ is at 388 nm.

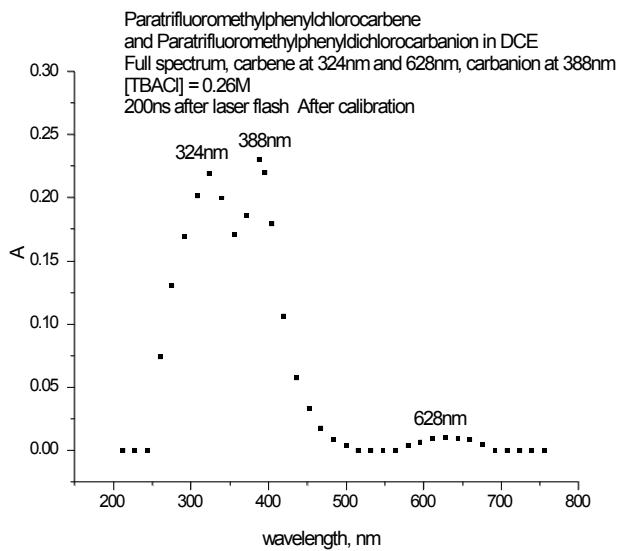


Figure S-22. UV-vis spectrum acquired 200 ns after LFP of *p*-trifluoromethylphenylchlorodiazirine with 0.26 M TBACl in DCE, after calibration. Absorptions of *p*-CF₃-PhCCl are at 324 nm and 628 nm; absorption of *p*-CF₃-PhCCl⁻ is at 388 nm.

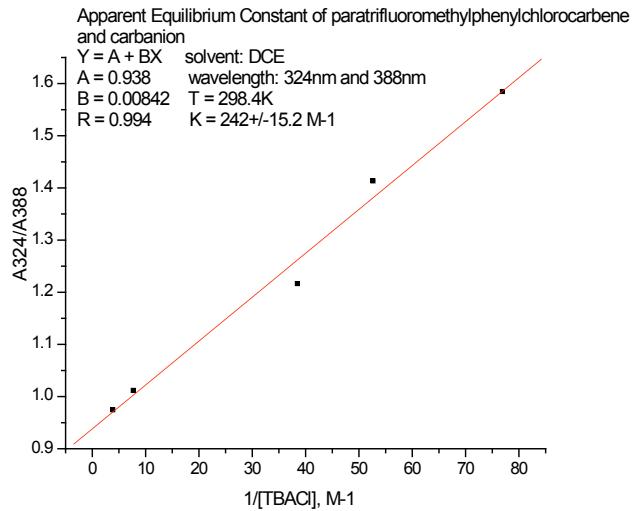


Figure S-23. Calibrated absorption intensities of *p*-CF₃-PhCCl at 324 nm relative to *p*-CF₃-PhCCl₂⁻ at 388 nm vs 1/[TBACl] in DCE solution at 298 K. The slope of the correlation line is 0.00842 M ($r = 0.994$), leading to $K = 242 (\pm 15.2)$ M⁻¹.

D. 1d/2d (*p*-F)

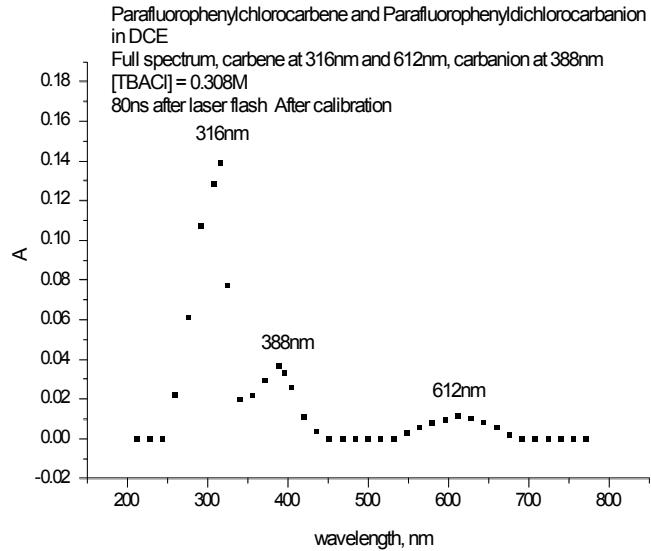


Figure S-24. UV-vis spectrum acquired 80 ns after LFP of *p*-fluorophenylchlorodiazirine with 0.308 M TBACl in DCE, after calibration. Absorptions of *p*-F-PhCCl are at 316 nm and 612 nm; absorption of *p*-F-PhCCl₂⁻ is at 388 nm.

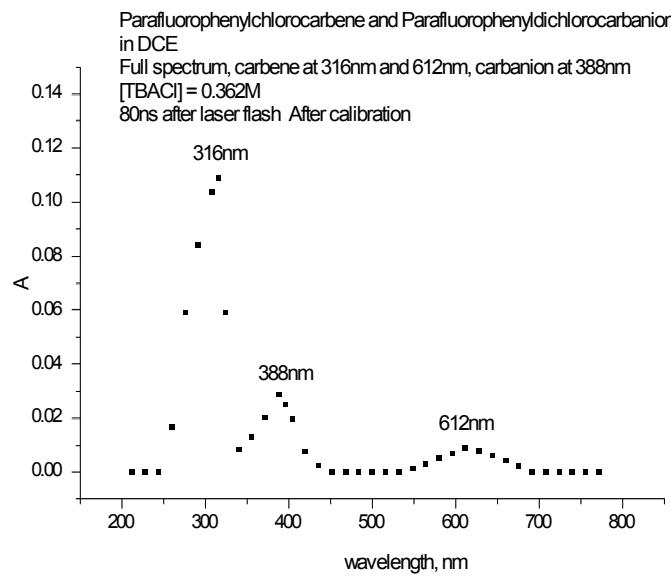


Figure S-25. UV-vis spectrum acquired 80 ns after LFP of *p*-fluorophenylchlorodiazirine with 0.362 M TBACl in DCE, after calibration. Absorptions of *p*-F-PhCCl are at 316 nm and 612 nm; absorption of *p*-F-PhCCl₂⁻ is at 388 nm.

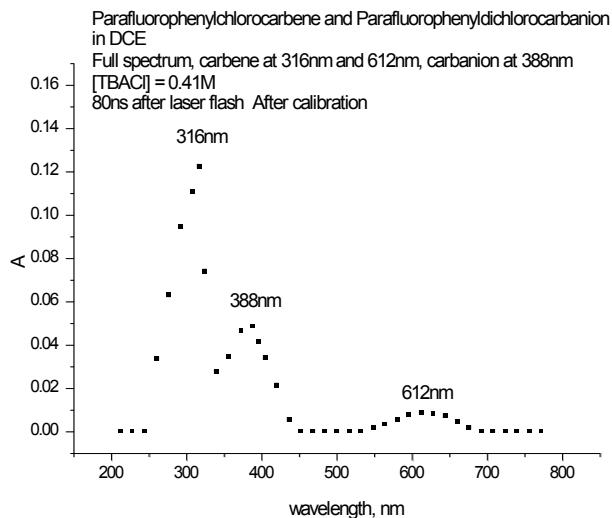


Figure S-26. UV-vis spectrum acquired 80 ns after LFP of *p*-fluorophenylchlorodiazirine with 0.41 M TBACl in DCE, after calibration. Absorptions of *p*-F-PhCCl are at 316 nm and 612 nm; absorption of *p*-F-PhCCl₂⁻ is at 388 nm.

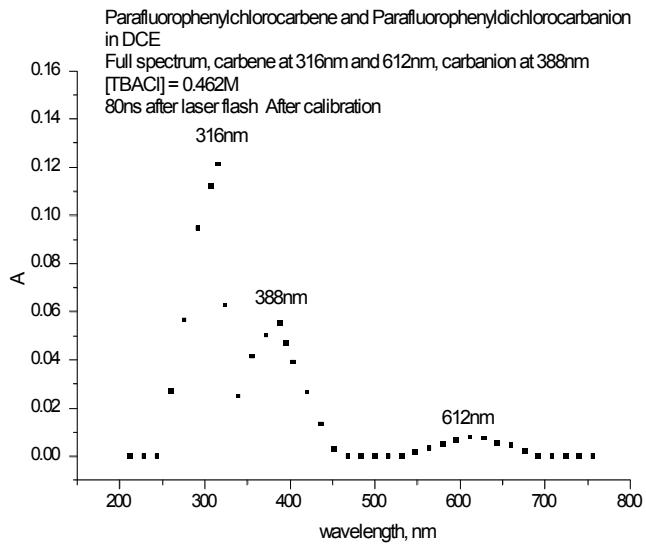


Figure S-27. UV-vis spectrum acquired 80 ns after LFP of *p*-fluorophenylchlorodiazirine with 0.462 M TBACl in DCE, after calibration. Absorptions of *p*-F-PhCCl are at 316 nm and 612 nm; absorption of *p*-F-PhCCl₂⁻ is at 388 nm.

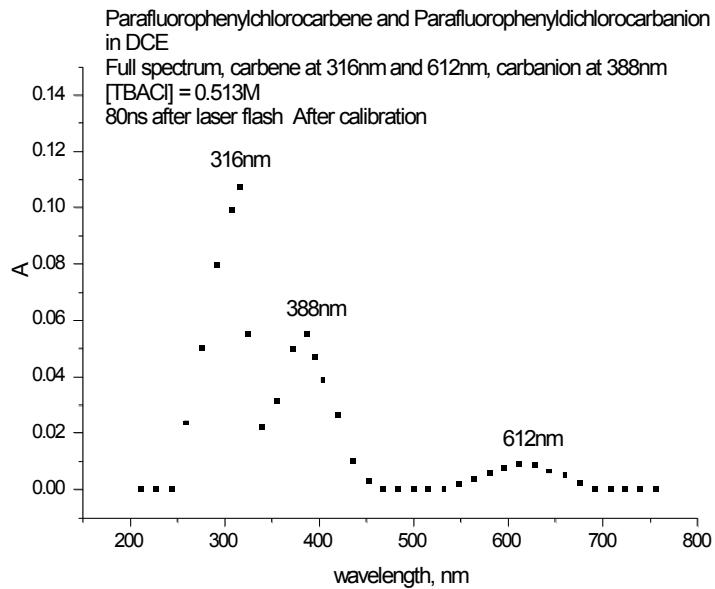


Figure S-28. UV-vis spectrum acquired 80 ns after LFP of *p*-fluorophenylchlorodiazirine with 0.513 M TBACl in DCE, after calibration. Absorptions of *p*-F-PhCCl are at 316 nm and 612 nm; absorption of *p*-F-PhCCl₂⁻ is at 388 nm.

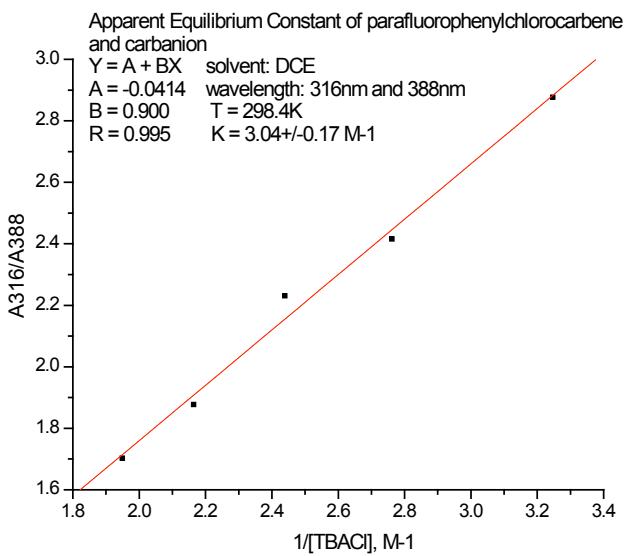


Figure S-29. Calibrated absorption intensities of *p*-F-PhCCl at 316 nm relative to *p*-F-PhCCl⁻ at 388 nm vs 1/[TBACl] in DCE solution at 298 K. The slope of the correlation line is 0.900 M ($r = 0.994$), leading to $K = 3.04 (\pm 0.17) M^{-1}$.

E. 1e/2e (*m*-Cl)

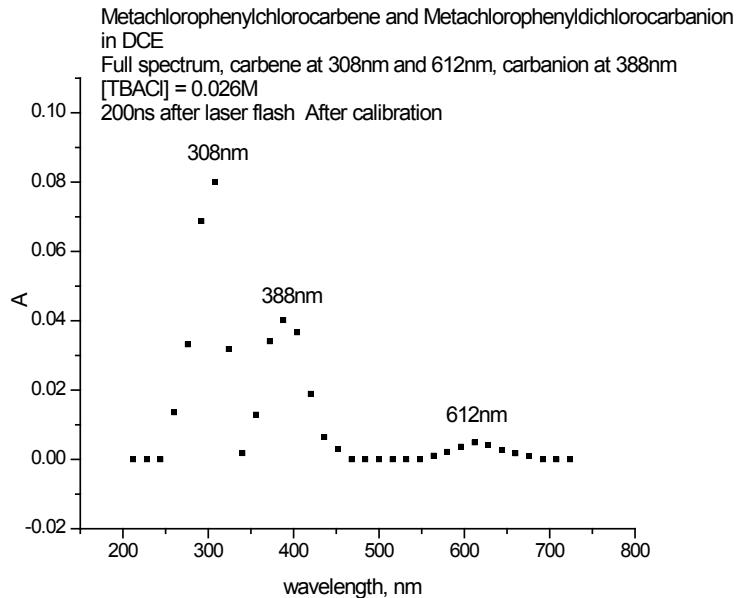


Figure S-30. UV-vis spectrum acquired 200 ns after LFP of *m*-chlorophenylchlorodiazirine with 0.026 M TBACl in DCE, after calibration. Absorptions of *m*-Cl-PhCCl are at 308 nm and 612 nm; absorption of *m*-Cl-PhCCl⁻ is at 388 nm.

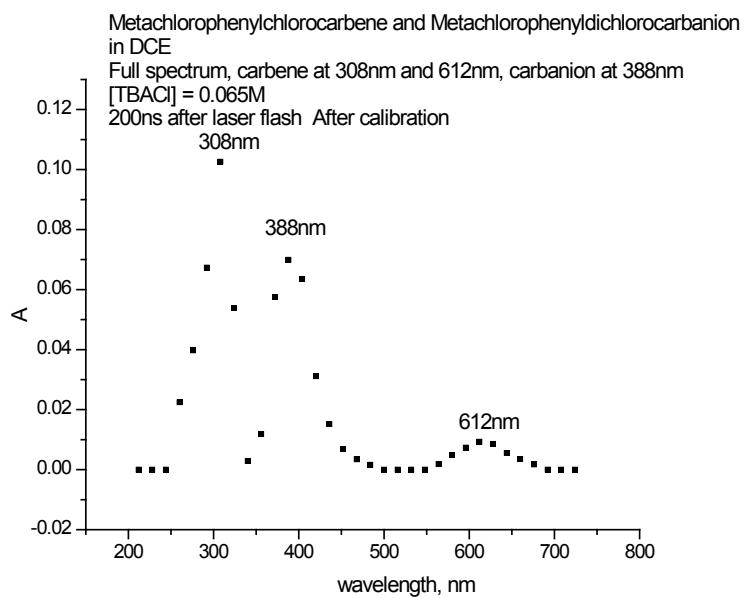


Figure S-31. UV-vis spectrum acquired 200 ns after LFP of *m*-chlorophenylchlorodiazirine with 0.065 M TBACl in DCE, after calibration. Absorptions of *m*-Cl-PhCCl are at 308 nm and 612 nm; absorption of *m*-Cl-PhCCl₂⁻ is at 388 nm.

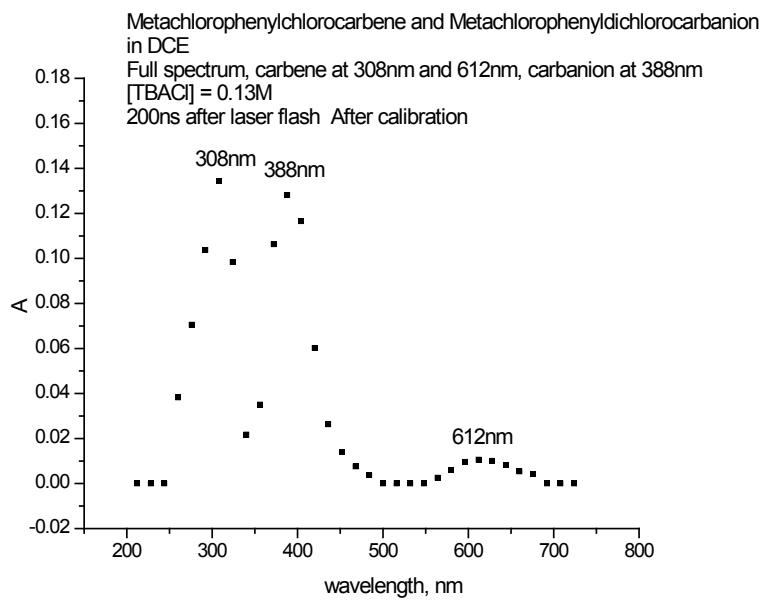


Figure S-32. UV-vis spectrum acquired 200 ns after LFP of *m*-chlorophenylchlorodiazirine with 0.13 M TBACl in DCE, after calibration. Absorptions of *m*-Cl-PhCCl are at 308 nm and 612 nm; absorption of *m*-Cl-PhCCl₂⁻ is at 388 nm.

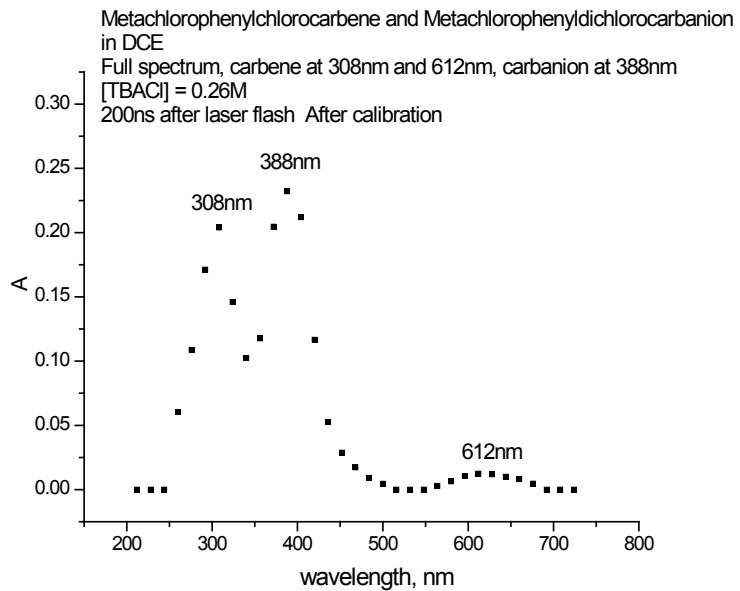


Figure S-33. UV-vis spectrum acquired 200 ns after LFP of *m*-chlorophenylchlorodiazirine with 0.26 M TBACl in DCE, after calibration. Absorptions of *m*-Cl-PhCCl are at 308 nm and 612 nm; absorption of *m*-Cl-PhCCl₂⁻ is at 388 nm.

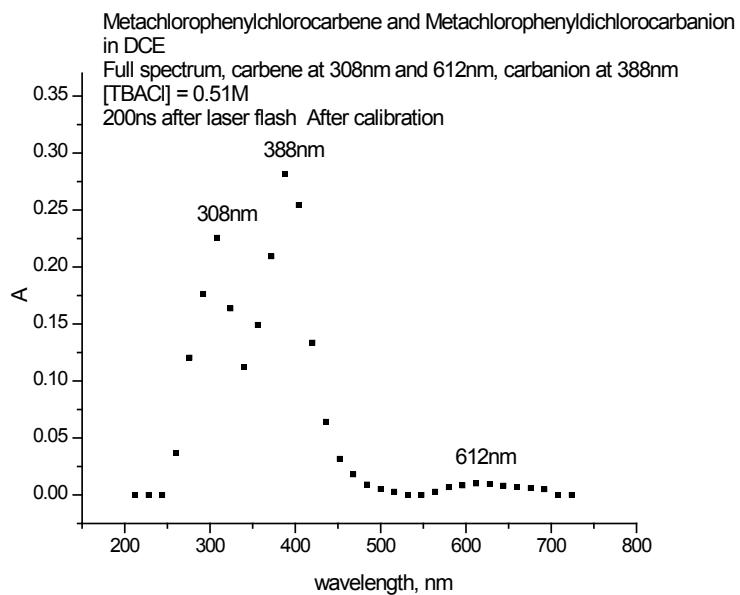


Figure S-34. UV-vis spectrum acquired 200 ns after LFP of *m*-chlorophenylchlorodiazirine with 0.51 M TBACl in DCE, after calibration. Absorptions of *m*-Cl-PhCCl are at 308 nm and 612 nm; absorption of *m*-Cl-PhCCl₂⁻ is at 388 nm.

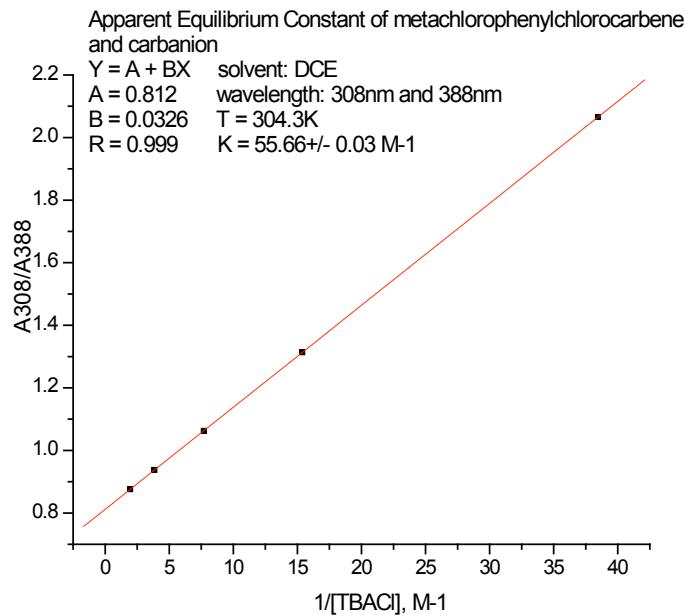


Figure S-35. Calibrated absorption intensities of *m*-Cl-PhCCl at 308 nm relative to *m*-Cl-PhCCl₂⁻ at 388 nm vs 1/[TBACl] in DCE solution at 304 K. The slope of the correlation line is 0.0326 M ($r = 0.999$), leading to $K = 55.7 (\pm 0.03) M^{-1}$.

3. Determination of Rate Constants k_f

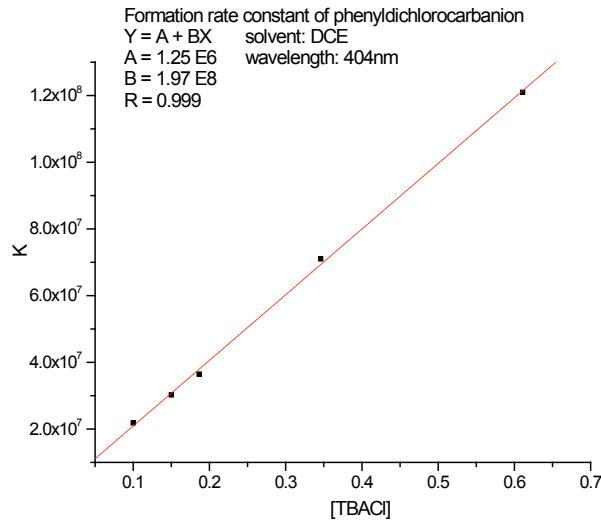


Figure S-36. Formation of PhCCl₂⁻ (**2a**) at 404 nm in DCE. Apparent rate constant (s^{-1}) for rise of **2a** vs [TBACl] (M). Slope = $k_f = 1.97 \times 10^8 M^{-1} s^{-1}$ ($r = 0.999$).

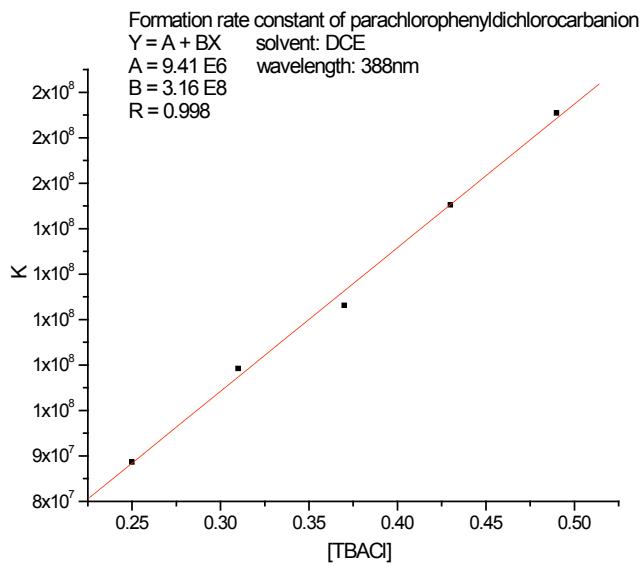


Figure S-37. Formation of *p*-Cl-PhCCl₂⁻ (**2b**) at 388 nm in DCE.
 Apparent rate constant (s⁻¹) for rise of **2b** vs [TBACl]
 (M). Slope = $k_f = 3.16 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ ($r = 0.998$).

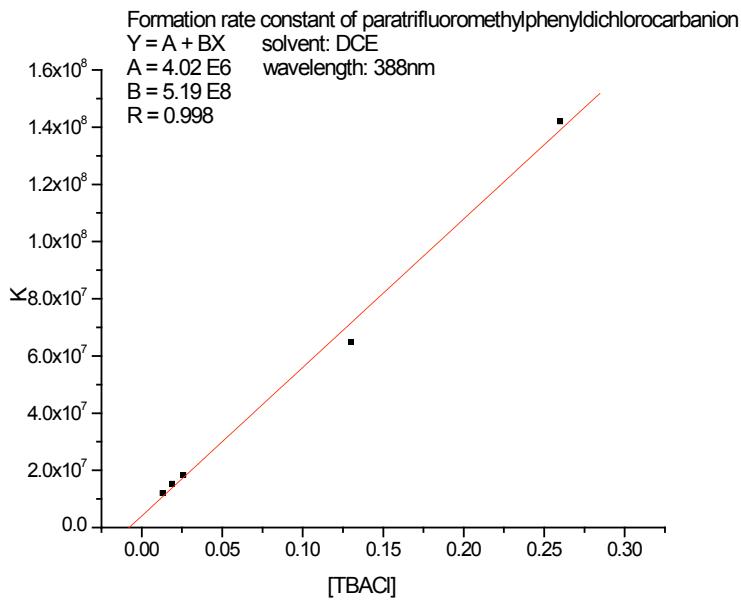


Figure S-38. Formation of *p*-CF₃-PhCCl₂⁻ (**2c**) at 388 nm in DCE.
 Apparent rate constant (s⁻¹) for rise of **2c** vs [TBACl]
 (M). Slope = $k_f = 5.19 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ ($r = 0.998$).

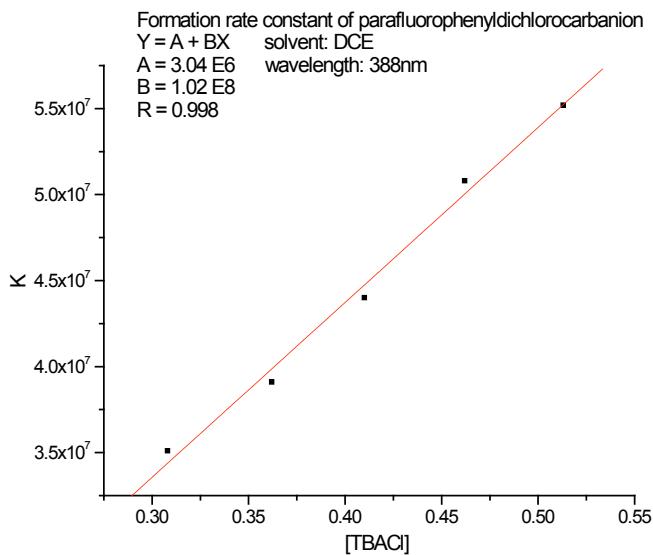


Figure S-39. Formation of *p*-F-PhCCl₂⁻ (**2d**) at 388 nm in DCE; Apparent rate constant (s⁻¹) for rise of **2d** vs [TBACl] (M). Slope = $k_f = 1.02 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ ($r = 0.998$).

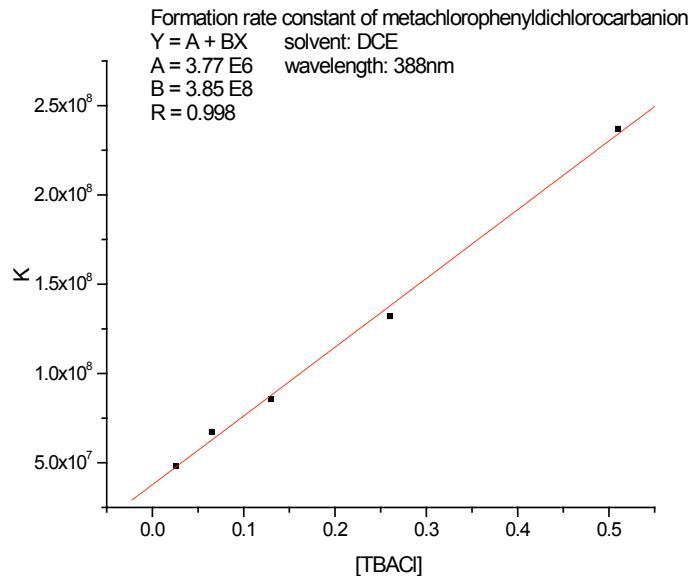


Figure S-40. Formation of *m*-Cl-PhCCl₂⁻ (**2e**) at 388 nm in DCE. Apparent rate constant (s⁻¹) for rise of **2e** vs [TBACl] (M). Slope = $k_f = 3.85 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ ($r = 0.998$).

4. Hammett Correlations

A. K_{exp}

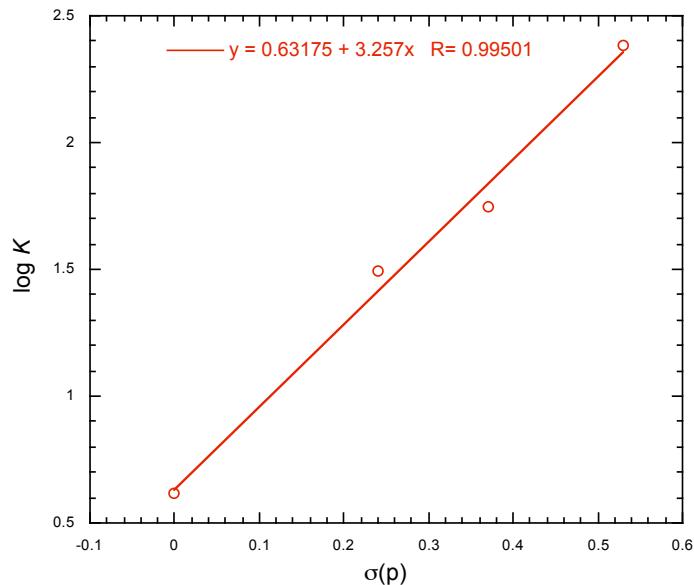


Figure S-41. Hammett correlation of $\log K_{\text{exp}}$ vs σ_p (σ_m for *m*-Cl), omitting X = *p*-F; $\rho = +3.26$, $r = 0.995$.

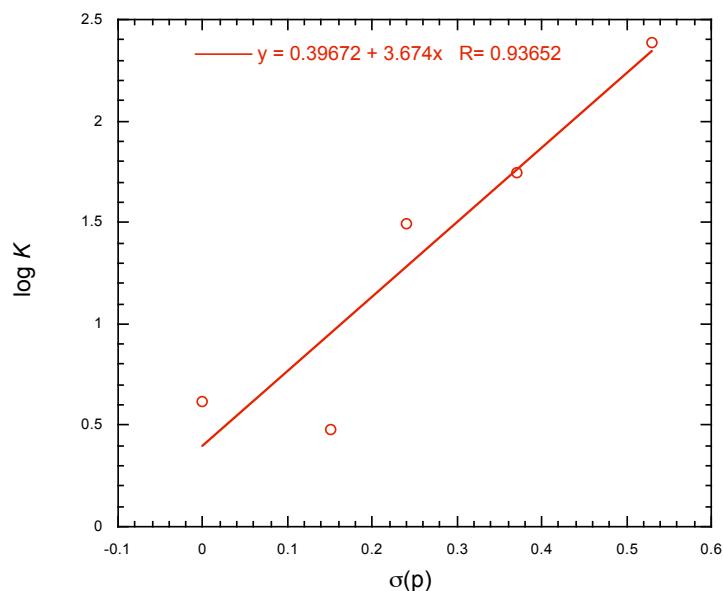


Figure S-42. Hammett correlation of $\log K_{\text{exp}}$ vs σ_p (σ_m for *m*-Cl); $\rho = +3.67$, $r = 0.937$.

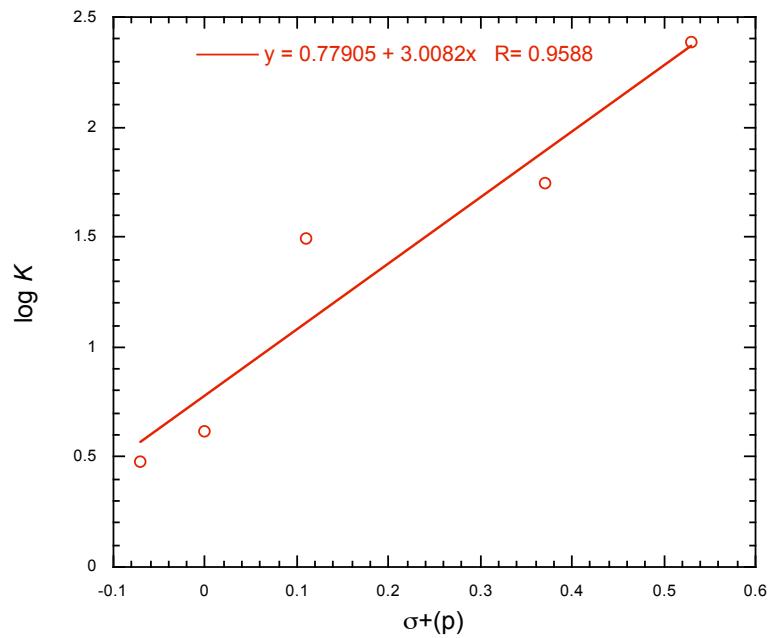


Figure S-43. Hammett correlation of $\log K_{\text{exp}}$ vs σ_p^+ (σ_m for *m*-Cl); $\rho = +3.01$, $r = 0.959$.

B. K_{calc}

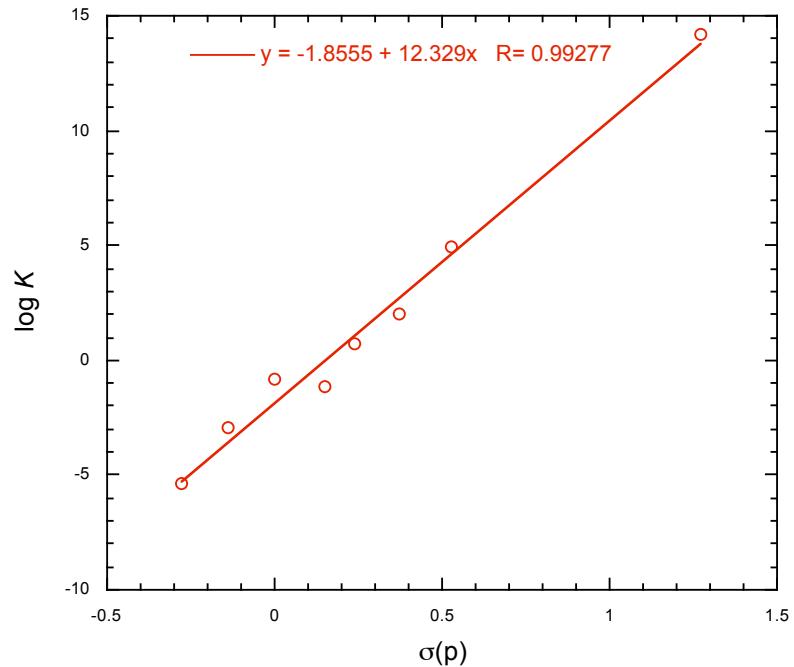


Figure S-44. Hammett correlation of $\log K_{\text{calc}}$ vs σ_p (σ_m for *m*-Cl); $\rho = +12.3$, $r = 0.993$.

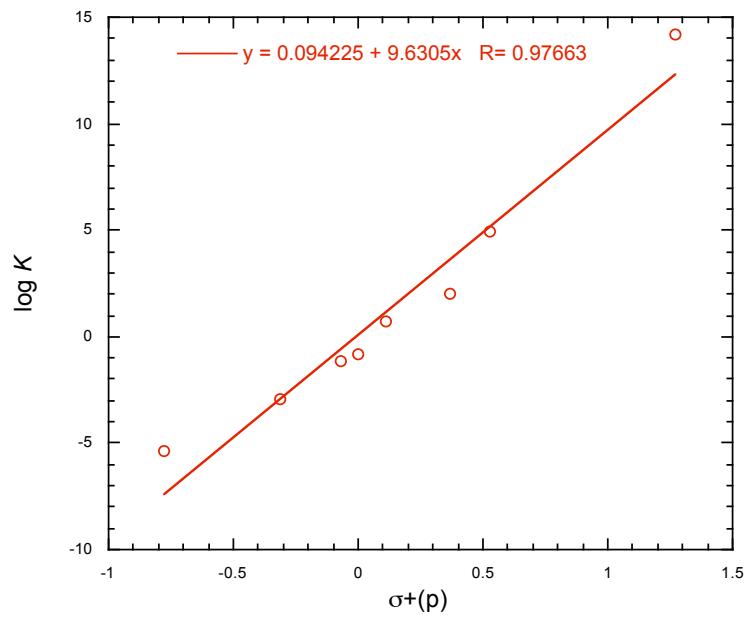


Figure S-45. Hammett correlation of $\log K_{\text{calc}}$ vs σ_p^+ (σ_m for *m*-Cl); $\rho = +9.6$, $r = 0.977$.

C. k_f

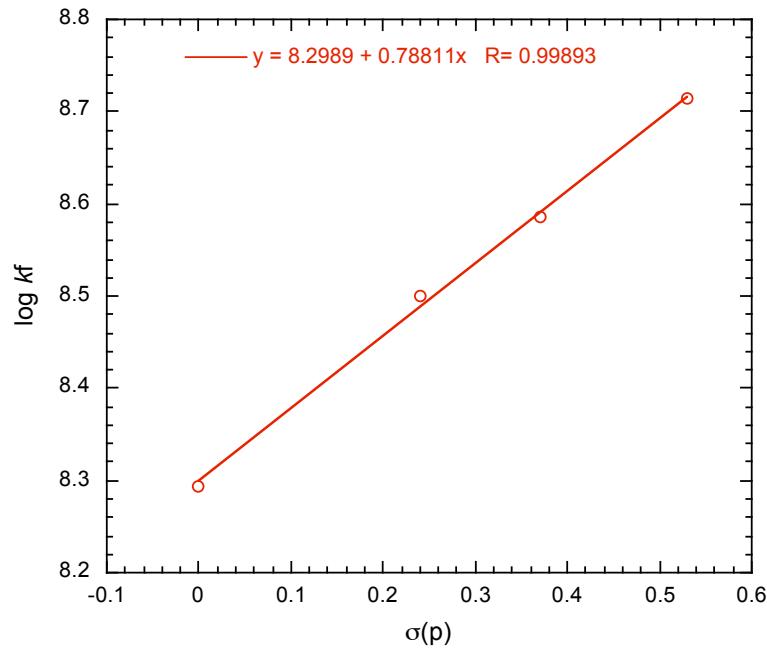


Figure S-46. Hammett correlation of $\log k_f$ vs σ_p (σ_m for *m*-Cl), omitting $X = p\text{-F}$; $\rho = +0.79$, $r = 0.999$.

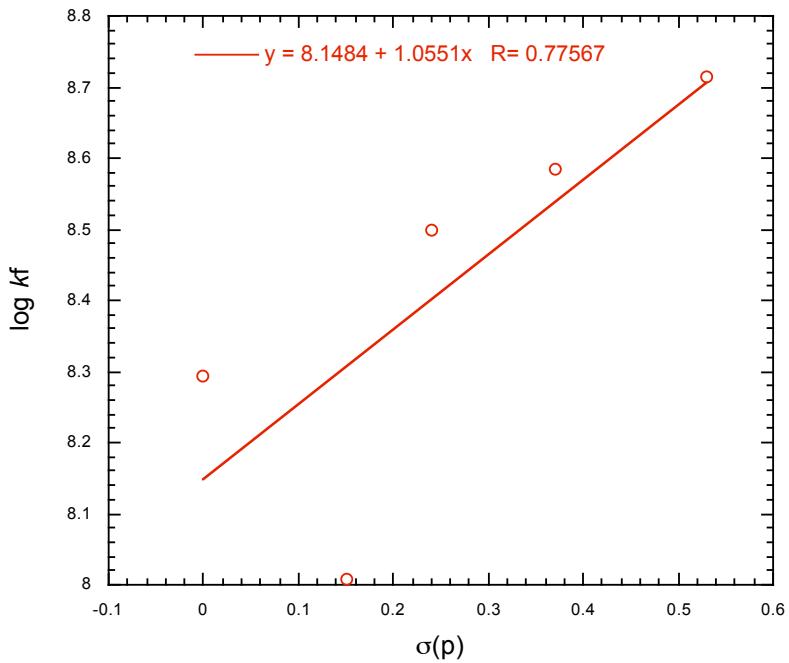


Figure S-47. Hammett correlation of $\log k_f$ vs σ_p (σ_m for *m*-Cl); $\rho = +1.06$, $r = 0.776$.

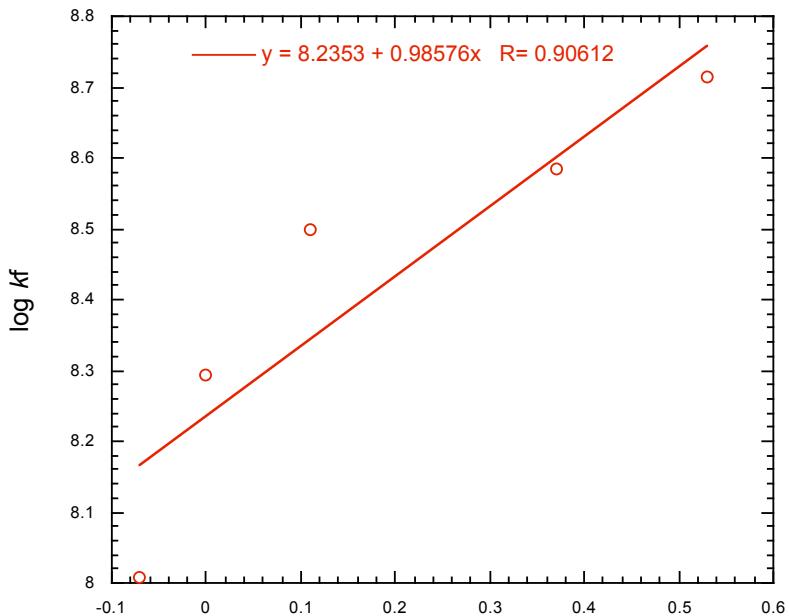


Figure S-48. Hammett correlation of $\log k_f$ vs σ_p^+ (σ_m for *m*-Cl); $\rho = +0.99$, $r = 0.906$.

D. k_b

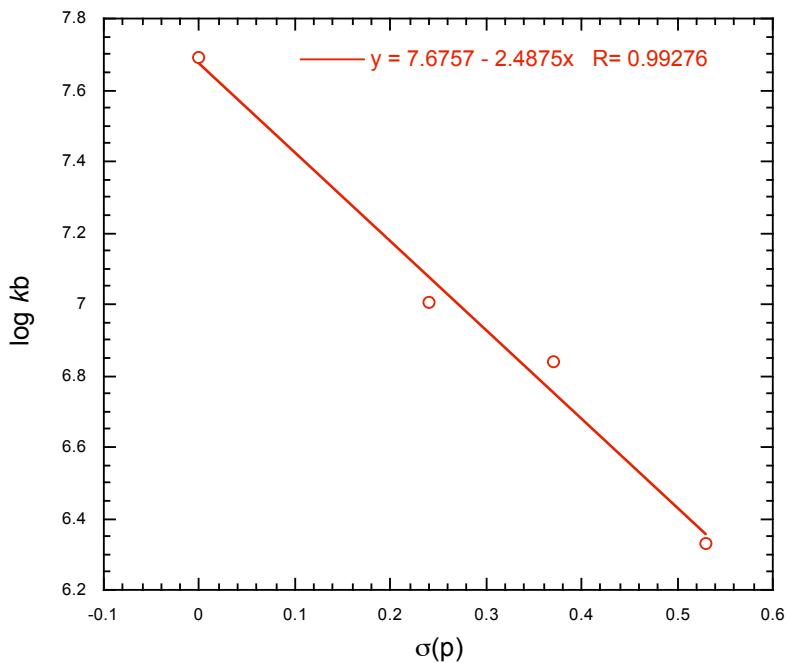


Figure S-49. Hammett correlation of $\log k_b$ vs σ_p
(σ_m for *m*-Cl), omitting X = *p*-F; $\rho = -2.49$, $r = 0.993$.

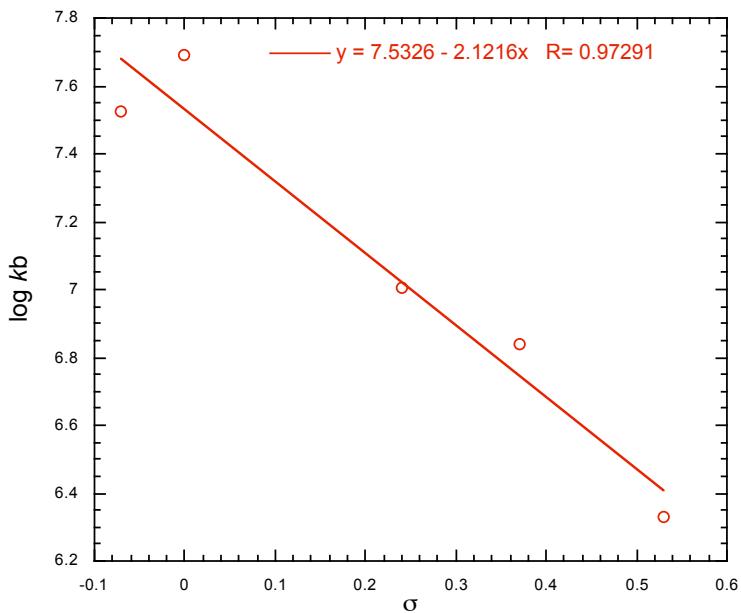


Figure S-50. Hammett correlation of $\log k_b$ vs σ_p ,
 σ_p^+ for *p*-F (σ_m for *m*-Cl); $\rho = -2.12$, $r = 0.973$.

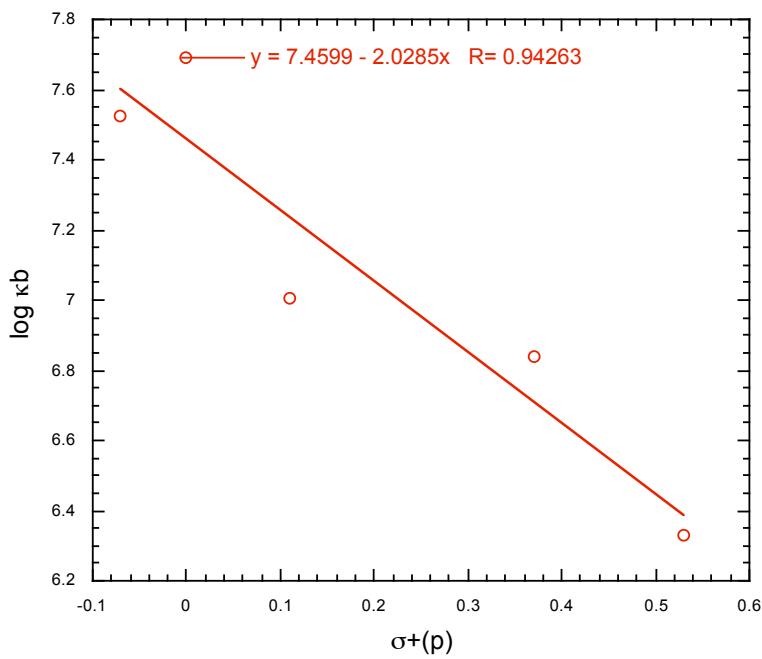


Figure S-51. Hammett correlation of $\log k_b$ vs σ_p^+
(σ_m for *m*-Cl); $\rho = -2.03$, $r = 0.943$.

5. Computational details

Electronic structure calculations, based on density functional theory (DFT), were carried out with the Gaussian 09 suite of programs.¹ We employed the long-range and empirically dispersion-corrected wB97XD exchange and correlation functionals² with 6-311+G(d) basis sets³ in geometry optimizations of chloro-carbene and chloro-carbanion structures (wB97XD/6-311+G(d)). The polarizable conductor self-consistent reaction field model (CPCM) was used to incorporate general solvent effects into the calculations; G09 default parameters were applied for the solvent used in the present set of experiments, dichloroethane (DCE).⁴ It was found beneficial to increase the integration grid size (integral=ultrafine) and use more stringent geometry optimization cut-offs (opt=tight).⁵ The stationary points located on the potential energy surfaces were characterized further by normal mode analysis. The (unscaled) vibrational frequencies formed the basis for the calculation of vibrational zero-point energy (ZPE) corrections. Standard thermodynamic corrections (based on the harmonic oscillator/rigid rotor approximations and ideal gas behavior) were made to convert from purely electronic energies to enthalpies (H ; ΔZPE included and $T = 298$ K) and free energies (G ; $T = 298$ K, $P = 1$ atm).⁶ Equilibrium constants were computed at $T = 298$ K from reaction free energies for carbanion formation corrected to a reference state corresponding to a 1.0 M concentration for each species participating in the reaction. This ‘2 species going to 1’ adjustment was accomplished by simply subtracting 1.89 kcal/mol from the reaction Gibbs free energy changes computed at $P = 1$ atm by Gaussian 09. Computed thermodynamic parameters for carbanion formation (eq 2 in the text) are collected in Table S-1 below.

Calculations of electronically excited state properties (transition wavelengths (λ) and oscillator strengths (f)) were performed at the optimized ground state geometries using the time-dependent DFT formalism⁷ and the B3LYP exchange-correlation functionals⁸ (TD-B3LYP/6-311+G(d)//wB97XD/6-311+G(d)). Again, the CPCM model CPCM was used to incorporate the general solvent effects exerted by DCE into the calculations.⁴ The character of a particular electronic transition was assigned by consideration of the largest transition amplitude(s) for the excitation and by visualization of the contributing MOs.

Values for transition energies and oscillator strengths derived from excited state calculations with the wB97XD functionals parallel those obtained with the B3LYP functionals.

References.

- (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) wB97XD reference Grimme, S. *J. Comp. Chem.* **2006**, 27, 1787.
- (3) (a) Raghavachari, K., Binkley, J. S., Seeger, R.; Pople, J. A.. *J. Chem. Phys.* **1980**, 72, 650-654. (b) McLean, A.D.; Chandler, G..S. *J. Chem. Phys.* **1980**, 72, 5639. (c) Clark, T.; Chandrasekhar, J.; Spitznagel, G.. W.; Schleyer, P.v.R. *J. Comp. Chem.* **1983**, 4, 294.
- (4) Barone, V.; Cossi, M. *J. Phys. Chem. A* **1998**, 102, 1995.
- (5) ÅE. Frisch, M. J. Frisch, F. R. Clemente, G. W. Trucks, *Gaussian 09 User's Reference*, pp.147.
- (6) McQuarrie, D. A. *Statistical Thermodynamics*; Harper and Row: New York, 1973.
- (7) Casida, M. E.; Jamorski, C.; Casida, K. C.; Salahub, D. R. *J. Chem. Phys.* **1998**, 108, 4439.
- (8) Becke, A.D. *J. Chem. Phys.* **1993**, 98, 5648; Lee, C.; Yang, W.; Parr, R.G. *Phys. Rev. B.* **1988**, 37, 785.

Table S-1. Computed Thermodynamic Parameters for Carbanion Formation; Eq 2 in Text.^a

X	ΔE	ΔH^b	ΔG^b	$\Delta\Delta G$	ΔG_{corr}^c	K	K_{rel}
<i>p</i> -NO ₂	-27.34	-26.98	-17.43	-20.44	-19.32	1.46E+14	9.69E+14
<i>p</i> -CF ₃	-13.22	-13.23	-4.85	-7.86	-6.74	8.76E+04	5.81E+05
<i>m</i> -Cl	-9.40	-9.32	-0.88	-3.89	-2.77	1.08E+02	7.16E+02
<i>p</i> -Cl	-7.63	-7.43	0.94	-2.07	-0.95	5.00E+00	3.32E+00
<i>p</i> -H	-5.37	-5.30	3.02	0.00	1.12	1.51E-01	1.00E+00
<i>p</i> -Me	-2.73	-2.58	5.90	2.88	4.00	1.16E-03	7.71E-03
<i>p</i> -OMe ^c	1.19	1.26	9.22	6.21	7.33	4.24E-06	2.81E-05

^a Units are kcal/mol for ΔE , ΔH , ΔG , $\Delta\Delta G$, and ΔG_{corr} ; M⁻¹ for K. ^bThe reference state for ΔH and ΔG is T = 298 K and P = 1 atm. ^cThe reference state for ΔG_{corr} is T = 298 K and a molar concentration of 1.0 M; $\Delta G_{corr} = \Delta G - 1.89$ kcal/mol

7. wB97XD/6-311+G(d) Optimized geometries and absolute energies; TD-B3LYP/6-311+G(d) electronic excitation energies and oscillator strengths; CPCM solvation model with dichloroethane parameters applied throughout.

Cl⁻ and p-X-PhCCl , X = H, Cl, CF₃, and F

Cl-minus

Charge = -1 Multiplicity = 1

Cl

SCF Done: E(RwB97XD) = -460.384183796 A.U. after 9 cycles

Sum of electronic and zero-point Energies=	-460.384184
Sum of electronic and thermal Energies=	-460.382768
Sum of electronic and thermal Enthalpies=	-460.381823
Sum of electronic and thermal Free Energies=	-460.399207

p-H-PhCCl

Charge = 0 Multiplicity = 1

C,0,0.4233930116,-0.4412518673,0.5545671652
C,0,0.8416407305,-1.7912513909,0.2734517367
C,0,2.1584141986,-2.0658850577,0.6998501511
C,0,0.1040517893,-2.8208888403,-0.3557903972
C,0,2.7225146694,-3.3175575659,0.5084349523
H,0,2.7196861251,-1.2730756966,1.1817434409
C,0,0.6690036385,-4.0652320886,-0.5444536046
H,0,-0.9089163102,-2.6329992634,-0.6915230269
C,0,1.9762717083,-4.3128995994,-0.112891807
H,0,3.7346524494,-3.5189333226,0.8393928571
H,0,0.1019450586,-4.853111381,-1.0269925152
H,0,2.411652322,-5.2948298953,-0.2658644604
Cl,0,-1.2038643686,-0.1075084888,0.0257649444

SCF Done: E(RwB97XD) = -729.816403046 A.U. after 1 cycles

Sum of electronic and zero-point Energies=	-729.720772
Sum of electronic and thermal Energies=	-729.714208
Sum of electronic and thermal Enthalpies=	-729.713264
Sum of electronic and thermal Free Energies=	-729.752394

Excitation energies and oscillator strengths:

*Excited State 1: Singlet-A 1.7372 eV 713.68 nm f=0.0024 <S**2>=0.000*
32 -> 33 0.71021

*Excited State 2: Singlet-A 3.7198 eV 333.30 nm f=0.0324 <S**2>=0.000*
31 -> 33 0.69848

*Excited State 3: Singlet-A 4.2609 eV 290.98 nm f=0.4770 <S**2>=0.000*
30 -> 33 0.69325

*Excited State 4: Singlet-A 4.5206 eV 274.26 nm f=0.0005 <S**2>=0.000*
32 -> 34 0.70526

*Excited State 5: Singlet-A 4.9203 eV 251.98 nm f=0.0002 <S**2>=0.000*
29 -> 33 0.69928

p-Cl-PhCCl

Charge = 0 Multiplicity = 1
C,0,1.3949119116,-0.9710832968,0.
C,0,0.0841256553,-0.3718600852,0.
C,0,-0.9629050438,-1.3159765715,0.
C,0,-0.2482613073,1.0019058002,0.
C,0,-2.2893930783,-0.9208942774,0.
H,0,-0.7096670046,-2.3699921523,0.
C,0,-1.5646175,1.4075658372,0.
H,0,0.5347691225,1.7505136322,0.
C,0,-2.5725924252,0.4393267779,0.
H,0,-3.0899461926,-1.6497915781,0.
H,0,-1.822624131,2.459335178,0.
Cl,0,2.678476999,0.2034344706,0.
Cl,0,-4.2301812656,0.9583198852,0.

SCF Done: E(RwB97XD) = -1189.42464967 A.U. after 1 cycles

Sum of electronic and zero-point Energies= -1189.338678
Sum of electronic and thermal Energies= -1189.330957
Sum of electronic and thermal Enthalpies= -1189.330013
Sum of electronic and thermal Free Energies= -1189.372470

Excitation energies and oscillator strengths:

*Excited State 1: Singlet-A" 1.7165 eV 722.29 nm f=0.0023 <S**2>=0.000*
40 -> 41 0.70993

*Excited State 2: Singlet-A' 3.8579 eV 321.38 nm f=0.0990 <S**2>=0.000*
38 -> 41 0.59702
39 -> 41 0.36204

*Excited State 3: Singlet-A' 3.9950 eV 310.35 nm f=0.5454 <S**2>=0.000*
38 -> 41 -0.35569
39 -> 41 0.59793

*Excited State 4: Singlet-A" 4.3249 eV 286.67 nm f=0.0003 <S**2>=0.000*
40 -> 42 0.70604

*Excited State 5: Singlet-A" 4.8767 eV 254.24 nm f=0.0001 <S**2>=0.000*
36 -> 41 0.48203
37 -> 41 -0.50574

p-CF₃-PhCCl

Charge = 0 Multiplicity = 1
C,0,1.4051533522,-0.9665864519,-0.0035349231
C,0,0.0813864236,-0.3707895329,-0.0002138943
C,0,-0.9531971462,-1.3211255423,0.0232295397
C,0,-0.2535594104,1.0000894743,-0.0171891856
C,0,-2.2849882905,-0.9290742561,0.0298216531
H,0,-0.6925925529,-2.3729356534,0.0364265554
C,0,-1.574393003,1.3931476494,-0.0104380323
H,0,0.5260545451,1.7516702889,-0.0350956336
C,0,-2.5840451158,0.4251214392,0.014484122
H,0,-3.0729115318,-1.6707667983,0.0492981985
H,0,-1.8279676304,2.4467703707,-0.0217275103
Cl,0,2.6741360148,0.2101963262,-0.0285949101
C,0,-4.0186037523,0.8920974507,-0.0012844714
F,0,-4.2441433461,1.8212904197,0.9432093679
F,0,-4.331632042,1.4551269582,-1.1831078
F,0,-4.8895880943,-0.1028465224,0.2047169685

SCF Done: E(RwB97XD) = -1066.87292579 A.U. after 1 cycles

Sum of electronic and zero-point Energies= -1066.772973
 Sum of electronic and thermal Energies= -1066.762761
 Sum of electronic and thermal Enthalpies= -1066.761817
 Sum of electronic and thermal Free Energies= -1066.811808

Excitation energies and oscillator strengths:

*Excited State 1: Singlet-A 1.5984 eV 775.67 nm f=0.0020 <S**2>=0.000*
 48 -> 49 0.71037

*Excited State 2: Singlet-A 3.7349 eV 331.96 nm f=0.0365 <S**2>=0.000*
 46 -> 50 0.10708
 47 -> 49 0.69787

*Excited State 3: Singlet-A 4.2997 eV 288.35 nm f=0.5254 <S**2>=0.000*
 46 -> 49 0.69567

*Excited State 4: Singlet-A 4.3616 eV 284.26 nm f=0.0007 <S**2>=0.000*
 48 -> 50 0.70518

*Excited State 5: Singlet-A 4.8278 eV 256.82 nm f=0.0000 <S**2>=0.000*
 45 -> 49 0.68108
 48 -> 51 0.17439

p-F-PhCl

Charge = 0 Multiplicity = 1
 C,0,0.4205903142,-0.4496843571,0.5698824548
 C,0,0.8406401135,-1.792022503,0.2736952708
 C,0,2.1602942817,-2.0709919882,0.6924239693
 C,0,0.103857942,-2.8183165784,-0.3650704964
 C,0,2.7332270658,-3.3130775523,0.4901703952
 H,0,2.723708652,-1.2846864726,1.1813954359
 C,0,0.6610699441,-4.0594784837,-0.5731400716
 H,0,-0.9103555593,-2.6319727407,-0.6965000041
 C,0,1.9665277267,-4.2792735644,-0.1396636891
 H,0,3.7438133868,-3.5389081033,0.8066603782
 H,0,0.1143470179,-4.8579282645,-1.0597680927
 F,0,2.5018514657,-5.4844753737,-0.3439441473
 Cl,0,-1.2091273428,-0.114608488,0.0495480699

SCF Done: E(RwB97XD) = -829.061109412 A.U. after 1 cycles

Sum of electronic and zero-point Energies=	-828.973935
Sum of electronic and thermal Energies=	-828.966560
Sum of electronic and thermal Enthalpies=	-828.965616
Sum of electronic and thermal Free Energies=	-829.006822

Excitation energies and oscillator strengths:

Excited State 1: Singlet-A 1.7814 eV 696.01 nm f=0.0024 <S**2>=0.000
 36 -> 37 0.71005

Excited State 2: Singlet-A 3.9795 eV 311.56 nm f=0.0373 <S**2>=0.000
 34 -> 37 0.63217
 35 -> 37 -0.29311
 35 -> 38 0.10980

Excited State 3: Singlet-A 4.2291 eV 293.17 nm f=0.4874 <S**2>=0.000
 34 -> 37 0.28545
 35 -> 37 0.63165

Excited State 4: Singlet-A 4.3000 eV 288.33 nm f=0.0003 <S**2>=0.000
 36 -> 38 0.70621

Excited State 5: Singlet-A 4.9765 eV 249.14 nm f=0.0002 <S**2>=0.000
 33 -> 37 0.69921

m-X-PhCCl, X = Cl

mCl-PhCCl, Cl's 'cis'

Charge = 0 Multiplicity = 1
 C,0,-1.8835881085,-0.0649432366,0.5204504737
 C,0,-0.4561672777,0.0768458926,0.3326559669
 C,0,0.2838424742,1.2765796188,0.2449453388
 C,0,0.2195260607,-1.1534209156,0.2326499934
 C,0,1.646749109,1.2144606999,0.0639490648
 H,0,-0.2115014517,2.2366839986,0.3187556897
 C,0,1.5944953356,-1.194085801,0.0502360549
 H,0,-0.3581611471,-2.0677622292,0.3013151004
 C,0,2.3124842872,-0.0100349584,-0.0346917756
 H,0,2.1120333881,-2.1425698795,-0.0264182738
 Cl,0,-2.7077588,1.4569857588,0.6425934606
 Cl,0,2.5743957855,2.691828217,-0.0462286602

H,0,3.3867328346,-0.0282315354,-0.1770879236

SCF Done: E(RwB97XD) = -1189.42273294 A.U. after 2 cycles

Sum of electronic and zero-point Energies= -1189.336840
Sum of electronic and thermal Energies= -1189.329107
Sum of electronic and thermal Enthalpies= -1189.328163
Sum of electronic and thermal Free Energies= -1189.370711

Excitation energies and oscillator strengths:

*Excited State 1: Singlet-A 1.6859 eV 735.43 nm f=0.0022 <S**2>=0.000*
40 -> 41 0.71044

*Excited State 2: Singlet-A 3.4243 eV 362.07 nm f=0.0432 <S**2>=0.000*
38 -> 41 0.11883
39 -> 41 0.69089

*Excited State 3: Singlet-A 4.1914 eV 295.81 nm f=0.3880 <S**2>=0.000*
38 -> 41 0.68731
39 -> 41 -0.11658

*Excited State 4: Singlet-A 4.4215 eV 280.41 nm f=0.0001 <S**2>=0.000*
40 -> 42 0.70562

*Excited State 5: Singlet-A 4.8327 eV 256.55 nm f=0.0000 <S**2>=0.000*
35 -> 41 -0.30837
37 -> 41 0.63186

p-X-PhCCl₂⁻, X = H, Cl, CF₃, and F.

p-H-PhCCl₂(-)

Charge = -1 Multiplicity = 1
C,0,-1.4345311315,-0.9468581527,-0.4362011872
C,0,-0.0766239018,-0.4687827994,-0.1425716925
C,0,1.0237075184,-1.3530242104,-0.0804258154
C,0,0.2278141212,0.9097496949,-0.0839167289
C,0,2.3288735737,-0.889073285,0.014302961
H,0,0.8523750879,-2.4224899999,-0.1157184051
C,0,1.5359437852,1.365274729,0.0108249207
H,0,-0.5752617953,1.636370267,-0.1219806329
C,0,2.6054032224,0.474888782,0.0601120485
H,0,3.1413824754,-1.6091322152,0.0588915055
H,0,1.7187333453,2.4355467757,0.0526512434
H,0,3.6263472596,0.8341089461,0.1378373829
Cl,0,-2.7047637457,0.1628282601,0.3225362423
Cl,0,-1.7311117248,-2.6053057822,0.3267980379

SCF Done: E(RwB97XD) = -1190.20914667 A.U. after 1 cycles

Sum of electronic and zero-point Energies= -1190.112537
Sum of electronic and thermal Energies= -1190.104482
Sum of electronic and thermal Enthalpies= -1190.103537
Sum of electronic and thermal Free Energies= -1190.146796

Excitation energies and oscillator strengths:

Excited State 1: Singlet-A 3.1567 eV 392.76 nm f=0.1961 <S**2>=0.000
41 -> 42 0.68546
41 -> 45 0.12331

Excited State 2: Singlet-A 3.3849 eV 366.29 nm f=0.0038 <S**2>=0.000
41 -> 43 0.70118

Excited State 3: Singlet-A 3.8200 eV 324.57 nm f=0.0214 <S**2>=0.000
41 -> 44 0.43192
41 -> 45 0.54642

Excited State 4: Singlet-A 4.0739 eV 304.34 nm f=0.0831 <S**2>=0.000
41 -> 44 0.55397
41 -> 45 -0.41524

Excited State 5: Singlet-A 4.1786 eV 296.71 nm f=0.0780 <S**2>=0.000
41 -> 46 0.63012

41 -> 48 0.29551

Excited State 6: Singlet-A 4.5120 eV 274.79 nm f=0.0006 <S**2>=0.000
41 -> 46 -0.31211
41 -> 48 0.61578
41 -> 52 -0.13070

Excited State 7: Singlet-A 4.5126 eV 274.75 nm f=0.0623 <S**2>=0.000
41 -> 47 0.68289

Excited State 8: Singlet-A 4.8801 eV 254.06 nm f=0.0628 <S**2>=0.000
41 -> 47 -0.10504
41 -> 49 0.63933
41 -> 50 0.26264

p-Cl-PhCCl₂(-)

Charge = -1 Multiplicity = 1

C,0,-1.1011715212,-0.0000033857,0.5711751468
C,0,0.3150760548,-0.0000081386,0.2105415283
C,0,1.0572732192,1.1990372626,0.107767465
C,0,1.057282451,-1.1990494526,0.107774396
C,0,2.4338719891,1.2023024799,-0.0610187751
H,0,0.5482768517,2.1530796175,0.170353301
C,0,2.4338815708,-1.2023043875,-0.0610104702
H,0,0.5482962593,-2.153095892,0.1703674385
C,0,3.1211991003,0.0000014796,-0.1438443964
H,0,2.966020415,2.144689617,-0.1347716341
H,0,2.9660377196,-2.1446876847,-0.1347568647
Cl,0,-1.9746333115,-1.465996369,-0.114698134
Cl,0,-1.9745935289,1.4660236162,-0.1146731735
Cl,0,4.8692473707,0.0000077171,-0.3643776378

SCF Done: E(RwB97XD) = -1649.82098776 A.U. after 2 cycles

Sum of electronic and zero-point Energies= -1649.733890
Sum of electronic and thermal Energies= -1649.724616
Sum of electronic and thermal Enthalpies= -1649.723671
Sum of electronic and thermal Free Energies= -1649.770178

Excitation energies and oscillator strengths:

Excited State 1: Singlet-A 3.1343 eV 395.57 nm f=0.2421 <S**2>=0.000
49 -> 50 -0.68241
49 -> 54 -0.13453

Excited State 2: Singlet-A 3.1794 eV 389.96 nm f=0.0049 <S**2>=0.000
49 -> 51 0.70269

Excited State 3: Singlet-A 3.8025 eV 326.06 nm f=0.0171 <S**2>=0.000
49 -> 52 -0.38019
49 -> 53 0.10257
49 -> 54 0.56674
49 -> 56 -0.11468

Excited State 4: Singlet-A 4.0083 eV 309.31 nm f=0.0834 <S**2>=0.000
49 -> 50 -0.10081
49 -> 52 0.38382
49 -> 53 -0.47523
49 -> 54 0.30258
49 -> 56 -0.13836

Excited State 5: Singlet-A 4.0781 eV 304.02 nm f=0.0297 <S**2>=0.000
49 -> 52 0.44617
49 -> 53 0.50275
49 -> 54 0.19196

Excited State 6: Singlet-A 4.1828 eV 296.42 nm f=0.0686 <S**2>=0.000
49 -> 55 0.64018
49 -> 57 0.27595

Excited State 7: Singlet-A 4.4897 eV 276.15 nm f=0.0382 <S**2>=0.000
49 -> 54 0.16016
49 -> 56 0.67211

Excited State 8: Singlet-A 4.5355 eV 273.36 nm f=0.0009 <S**2>=0.000
49 -> 55 0.29188
49 -> 57 -0.62394
49 -> 62 0.13659

p-CF₃-PhCCl₂(-)

Charge = -1 Multiplicity = 1
C,0,-1.0864969544,-0.0000004169,0.4642192218

C,0,0.3058586106,-0.0000000469,0.1824122736
 C,0,1.0605005226,1.2072753102,0.0886013741
 C,0,1.0605019503,-1.2072749416,0.0886060206
 C,0,2.4325191311,1.2003848299,-0.0459773726
 H,0,0.5494060382,2.1609342818,0.1378558041
 C,0,2.4325204764,-1.2003833421,-0.0459726996
 H,0,0.5494085577,-2.1609343121,0.1378641221
 C,0,3.1478099778,0.0000010869,-0.1050320418
 H,0,2.9571896604,2.1486461281,-0.1088092334
 H,0,2.9571921524,-2.1486442881,-0.1088008993
 Cl,0,-1.9993383655,-1.4630271655,-0.0480569224
 Cl,0,-1.9993402587,1.4630232923,-0.0480622084
 C,0,4.612487351,0.0000008415,-0.3232854138
 F,0,5.2264611476,-1.0835099498,0.2035217344
 F,0,4.9650341381,-0.0000106778,-1.6428586811
 F,0,5.2264587544,1.0835219481,0.2035026916

SCF Done: E(RwB97XD) = -1527.27816955 A.U. after 2 cycles

Sum of electronic and zero-point Energies= -1527.177540
 Sum of electronic and thermal Energies= -1527.165675
 Sum of electronic and thermal Enthalpies= -1527.164731
 Sum of electronic and thermal Free Energies= -1527.218741

Excitation energies and oscillator strengths:

Excited State 1: Singlet-A 3.1220 eV 397.13 nm f=0.2570 <S**2>=0.000

57 -> 58	0.66874
57 -> 60	0.14828
57 -> 61	0.15501

Excited State 2: Singlet-A 3.2193 eV 385.13 nm f=0.0096 <S**2>=0.000

57 -> 59	0.70342
----------	---------

Excited State 3: Singlet-A 3.8381 eV 323.03 nm f=0.0116 <S**2>=0.000

57 -> 60	-0.30524
57 -> 61	0.50238
57 -> 63	-0.38509

Excited State 4: Singlet-A 3.9685 eV 312.42 nm f=0.1900 <S**2>=0.000

57 -> 58	-0.17650
57 -> 60	0.61414
57 -> 61	0.19702
57 -> 63	-0.20333

Excited State 5: Singlet-A 4.1473 eV 298.95 nm f=0.0410 <S**2>=0.000
 57 -> 62 -0.63430
 57 -> 64 0.29095

Excited State 6: Singlet-A 4.3685 eV 283.81 nm f=0.0672 <S**2>=0.000
 57 -> 61 0.41994
 57 -> 63 0.53927
 57 -> 65 -0.11592

Excited State 7: Singlet-A 4.4250 eV 280.19 nm f=0.0012 <S**2>=0.000
 57 -> 62 0.30584
 57 -> 64 0.61134
 57 -> 69 -0.15304

Excited State 8: Singlet-A 4.7113 eV 263.16 nm f=0.0864 <S**2>=0.000
 57 -> 65 0.61268
 57 -> 66 -0.29098
 57 -> 68 0.14829

Excited State 9: Singlet-A 4.8240 eV 257.01 nm f=0.0235 <S**2>=0.000
 57 -> 65 -0.30189
 57 -> 66 -0.61916

p-F-PhCCl₂(-)

Charge = -1 Multiplicity = 1
 C,0,-1.4401264698,-0.9477058817,-0.4432740768
 C,0,-0.0784193774,-0.4677168029,-0.1444328822
 C,0,1.0205863601,-1.3509307994,-0.0849527039
 C,0,0.223751737,0.9094178518,-0.0844240313
 C,0,2.329563831,-0.895423949,0.0094763644
 H,0,0.8530372778,-2.4202881246,-0.1217104145
 C,0,1.529016242,1.3754516227,0.0100076714
 H,0,-0.5773800981,1.6373039318,-0.120755629
 C,0,2.5659798146,0.4644535071,0.0543546722
 H,0,3.157600678,-1.5947905753,0.0541872082
 H,0,1.7354265804,2.4394611981,0.0551352537
 F,0,3.8475860452,0.9162407055,0.151318081
 Cl,0,-2.7022644195,0.1639039501,0.3343600962
 Cl,0,-1.7260701113,-2.6052756242,0.3338502706

SCF Done: E(RwB97XD) = -1289.45322027 A.U. after 1 cycles

Sum of electronic and zero-point Energies= -1289.364921

Sum of electronic and thermal Energies= -1289.356016
 Sum of electronic and thermal Enthalpies= -1289.355072
 Sum of electronic and thermal Free Energies= -1289.400488

Excitation energies and oscillator strengths:

Excited State 1: Singlet-A 3.1846 eV 389.33 nm f=0.0053 <S**2>=0.000
 45 -> 47 0.70253

Excited State 2: Singlet-A 3.1917 eV 388.46 nm f=0.1776 <S**2>=0.000
 45 -> 46 0.68355
 45 -> 49 0.14258

Excited State 3: Singlet-A 3.8452 eV 322.44 nm f=0.0293 <S**2>=0.000
 45 -> 46 -0.10509
 45 -> 48 -0.42670
 45 -> 49 0.53751
 45 -> 51 -0.11456

Excited State 4: Singlet-A 4.1827 eV 296.42 nm f=0.0796 <S**2>=0.000
 45 -> 50 0.63616
 45 -> 52 0.28386

Excited State 5: Singlet-A 4.1924 eV 295.73 nm f=0.0869 <S**2>=0.000
 45 -> 48 0.55786
 45 -> 49 0.40743

Excited State 6: Singlet-A 4.4617 eV 277.88 nm f=0.0296 <S**2>=0.000
 45 -> 49 0.13299
 45 -> 51 0.68295

Excited State 7: Singlet-A 4.5463 eV 272.71 nm f=0.0004 <S**2>=0.000
 45 -> 50 -0.30017
 45 -> 52 0.62162
 45 -> 57 -0.13406

Excited State 8: Singlet-A 4.7543 eV 260.78 nm f=0.0156 <S**2>=0.000
 45 -> 53 0.69552

m-X-PhCCl₂⁻, X = Cl

m-Cl-PhCCl₂(-)

Charge = -1 Multiplicity = 1

C,0,-1.9330379772,-0.0023257815,0.5420741917
 C,0,-0.5078977216,-0.0016789063,0.2454369292
 C,0,0.2302616817,1.2029376514,0.1669522122
 C,0,0.240494911,-1.2021390576,0.1749739225
 C,0,1.6086412229,1.1749052752,0.0593753962
 H,0,-0.2780044665,2.1576669326,0.2011955986
 C,0,1.6207208245,-1.1924096447,0.0641902834
 H,0,-0.2732172636,-2.1545836958,0.2190396126
 C,0,2.3421505897,-0.0010008756,0.0067628051
 H,0,2.1540476522,-2.1370589541,0.0155723451
 Cl,0,-2.7874593947,-1.454440117,-0.1775638647
 Cl,0,-2.784453336,1.4742989241,-0.1285278531
 Cl,0,2.4706995033,2.713194559,-0.0277807009
 H,0,3.4214504144,0.0091776604,-0.0813920178

SCF Done: E(RwB97XD) = -1649.82190198 A.U. after 1 cycles

Sum of electronic and zero-point Energies= -1649.735062
 Sum of electronic and thermal Energies= -1649.725765
 Sum of electronic and thermal Enthalpies= -1649.724821
 Sum of electronic and thermal Free Energies= -1649.771319

Excitation energies and oscillator strengths:

*Excited State 1: Singlet-A 3.1526 eV 393.28 nm f=0.2139 <S**2>=0.000*
 49 -> 50 0.68182
 49 -> 54 -0.12186

*Excited State 2: Singlet-A 3.2328 eV 383.51 nm f=0.0080 <S**2>=0.000*
 49 -> 51 0.70233

*Excited State 3: Singlet-A 3.8171 eV 324.81 nm f=0.0237 <S**2>=0.000*
 49 -> 52 0.47669
 49 -> 53 -0.23720
 49 -> 54 0.42599
 49 -> 56 -0.13900

*Excited State 4: Singlet-A 3.9558 eV 313.42 nm f=0.0340 <S**2>=0.000*
 49 -> 52 0.19421
 49 -> 53 0.63973
 49 -> 54 0.16938
 49 -> 57 0.11717

*Excited State 5: Singlet-A 4.1022 eV 302.24 nm f=0.0806 <S**2>=0.000*
 49 -> 52 -0.45907
 49 -> 54 0.48279

49 -> 55 0.11455
49 -> 56 -0.11693
49 -> 57 0.10028

Excited State 6: Singlet-A 4.3174 eV 287.18 nm f=0.0529 <S**2>=0.000

49 -> 52 0.12997
49 -> 53 -0.10611
49 -> 55 0.62693
49 -> 56 0.17372
49 -> 57 0.18763

Excited State 7: Singlet-A 4.5405 eV 273.06 nm f=0.0589 <S**2>=0.000

49 -> 54 0.18457
49 -> 55 -0.10092
49 -> 56 0.62874
49 -> 57 -0.18345

Excited State 8: Singlet-A 4.5648 eV 271.61 nm f=0.0080 <S**2>=0.000

49 -> 53 -0.10860
49 -> 55 -0.26242
49 -> 56 0.13944
49 -> 57 0.61483

Excited State 9: Singlet-A 4.8385 eV 256.25 nm f=0.0822 <S**2>=0.000

49 -> 58 0.67741
49 -> 59 -0.14491