SUPPORTING INFORMATION

Activation Parameters for Additions to Alkenes of Arylchlorocarbenes with Enhanced Electrophilicity

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Additions to TME

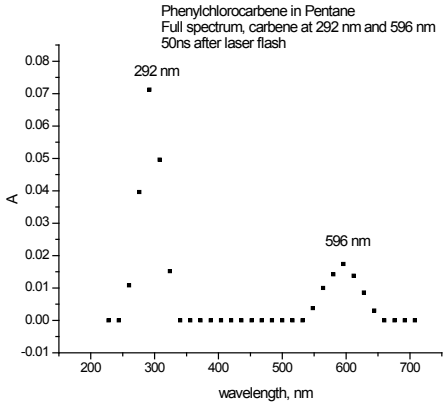

Figure S-1. LFP UV-vis spectrum of phenylchlorocarbene in pentane; carbene absorptions at 292 nm and 596 nm.

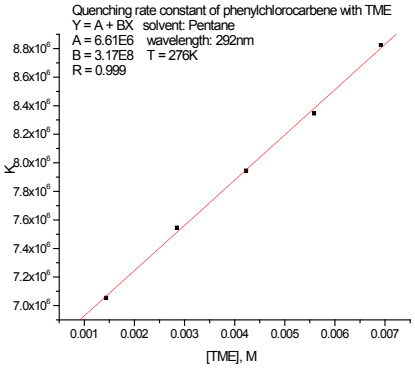

Figure S-2. Rate constant for addition of PhCCl to TME at 276 K: k = 3.17 exp 8 M^{-1} s^{-1}, r = 0.999.

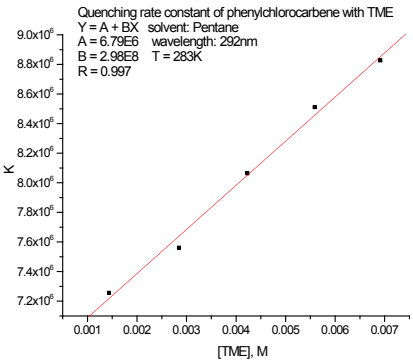

Figure S-3. Rate constant for addition of PhCCl to TME at 283 K: k = 2.98 exp 8 M^{-1} s^{-1}, r = 0.997.

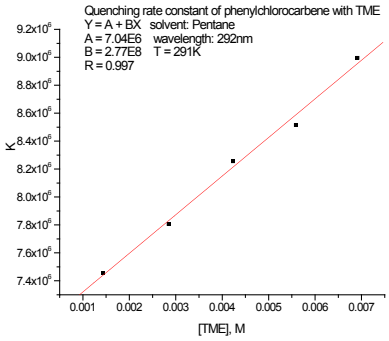

Figure S-4. Rate constant for addition of PhCCl to TME at 291 K: k = 2.77 exp 8 M^{-1} s^{-1}, r = 0.997.

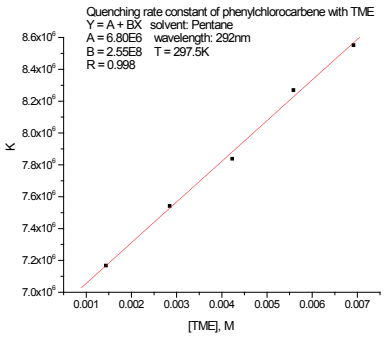

Figure S-5. Rate constant for addition of PhCCl to TME at 297.5 K: k = 2.55 exp 8 M^{-1} s^{-1}, r = 0.998.

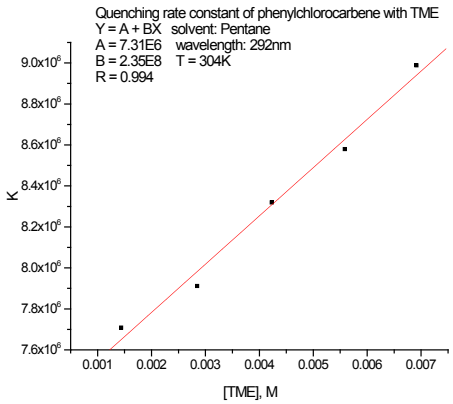

Figure S-6. Rate constant for addition of PhCCl of to TME at 304 K: k = 2.35 exp 8 M^{-1} s^{-1}, r = 0.994.

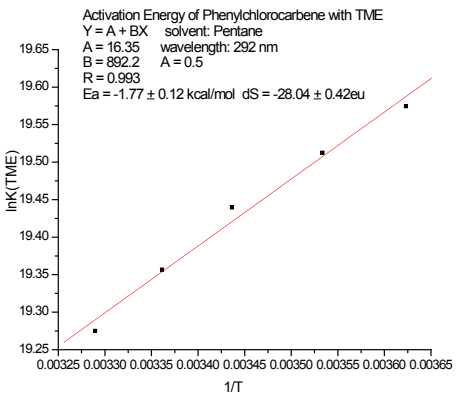

Figure S-7. Activation energy for addition PhCCl to TME: E_a = -1.77 ± 0.12 kcal/mol, log A = 7.1 s^{-1}, $\Delta S^{\ddagger}$ = -28.0 ± 0.4 e.u., r = 0.993.

Additions to cyclohexene

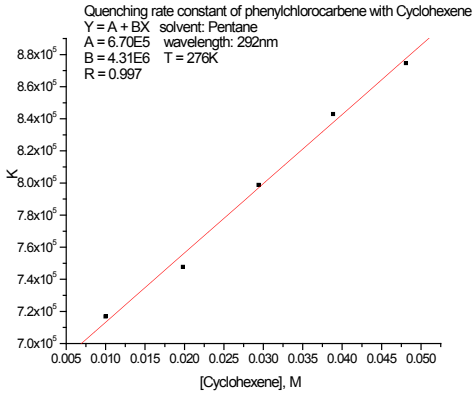

Figure S-8. Rate constant for addition of PhCCl to cyclohexene at 276 K: k = 4.31 exp 6 M^{-1} s^{-1}, r = 0.997.

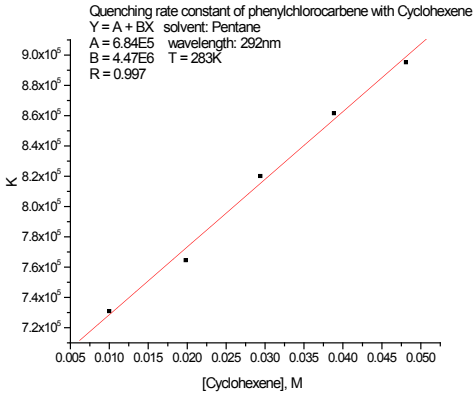

Figure S-9. Rate constant for addition of PhCCl to cyclohexene at 283 K: k = 4.47 exp 6 M^{-1} s^{-1}, r = 0.997.

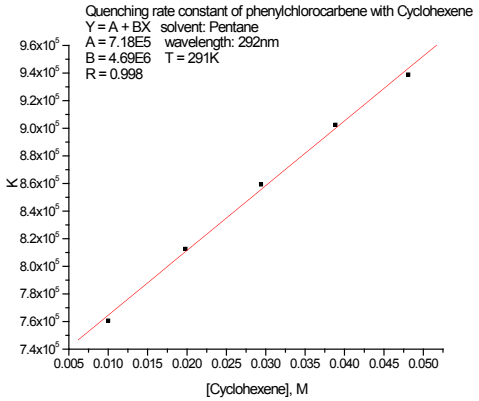

Figure S-10. Rate constant for addition of PhCCl to cyclohexene at 291 K: k = 4.69 exp 6 M^{-1} s^{-1}, r = 0.998.

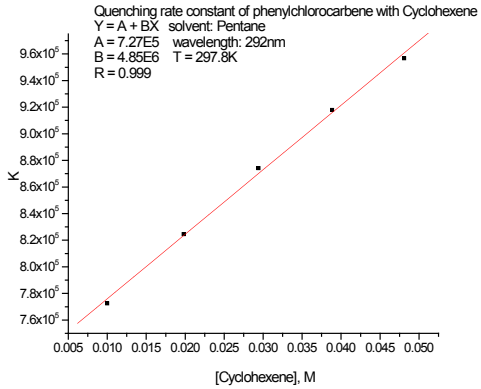

Figure S-11. Rate constant for addition of PhCCl to cyclohexene at 298 K: k = 4.85 exp 6 M^{-1} s^{-1},

$r = 0.999$.

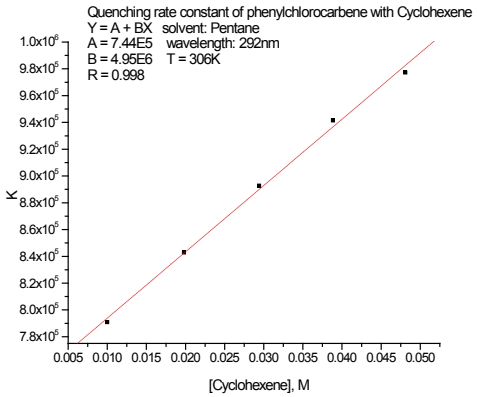

Figure S-12. Rate constant for addition of PhCCl to cyclohexene at 306 K: $k = 4.95$ exp 6 M^{-1} s^{-1}, r = 0.998

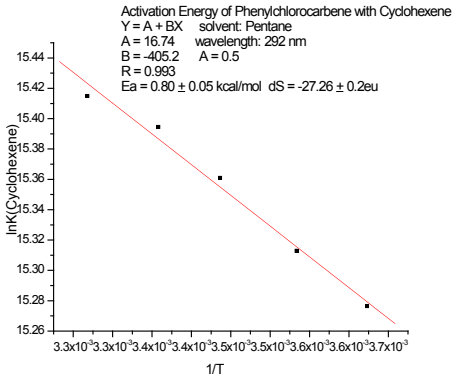

Figure S-13. Activation energy for addition of PhCCl to cyclohexene: $E_a = -0.80 \pm 0.05$ kcal/mol, log $A = 7.3$ s^{-1}, $\Delta S^{\ddagger} = -27.3 \pm 0.2$ e.u., $r = 0.993$.

Additions to 1-hexene

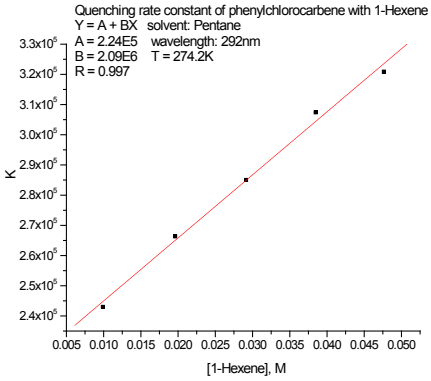

Figure S-14. Rate constant for addition of PhCCl to 1-hexene at 274 K: $k = 2.09$ exp 6 M^{-1} s^{-1}, $r = 0.997$.

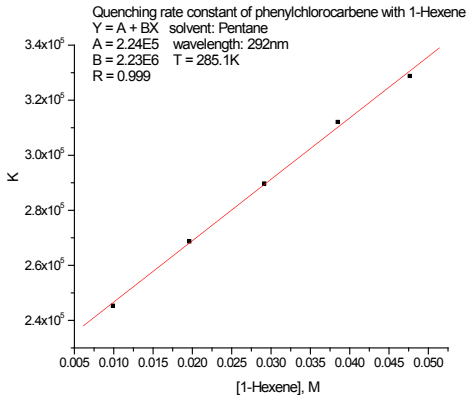

Figure S-15. Rate constant for addition of PhCCl to 1-hexene at 285 K: $k = 2.23$ exp 6 M^{-1} s^{-1}, $r = 0.999$.

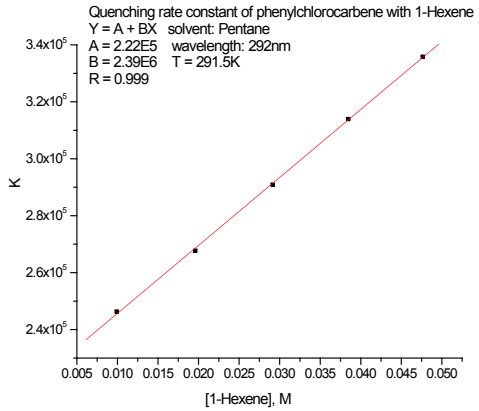

Figure S-16. Rate constant for addition of PhCCl to 1-hexene at 291.5 K: $k = 2.39$ exp 6 M^{-1} s^{-1}, $r = 0.999$.

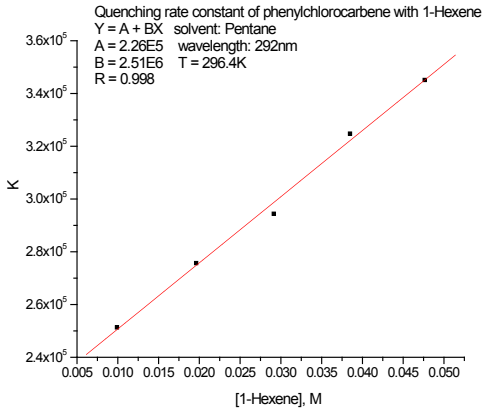

Figure S-17. Rate constant for addition of PhCCl to 1-hexene at 296 K: $k = 2.51$ exp 6 M^{-1} s^{-1}, $r = 0.998$.

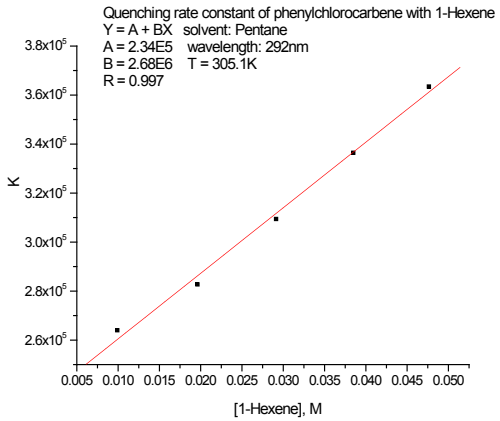

Figure S-18. Rate constant for addition of PhCCl to 1-hexene at 305 K: k = 2.68 exp 6 M^{-1} s^{-1}, r = 0.997.

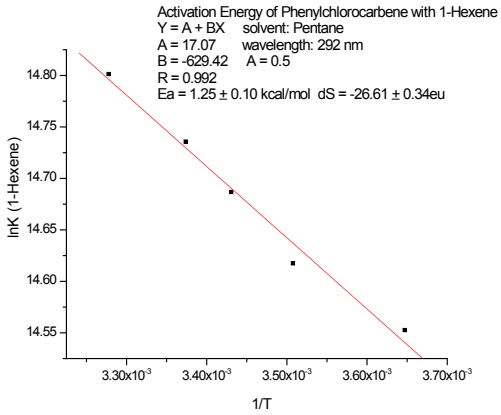

Figure S-19. Activation energy for addition of PhCCl to 1-hexene: E_a = 1.25 ± 0.10 kcal/mol, log A = 7.41 s^{-1}, $\Delta S^{\ddagger}$ = -26.6 ± 0.3 e.u., r = 0.992.

2. Pentafluorophenylchlorocarbene (F_5-PhCCl)

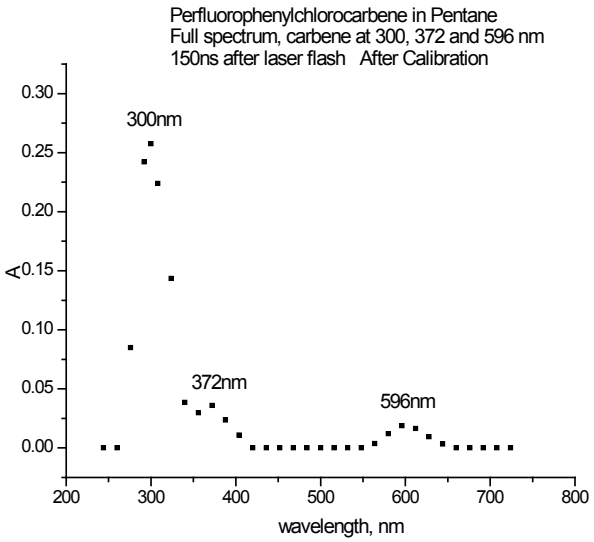

Figure S-20. Calibrated LFP UV-vis spectrum of pentafluorophenylchlorocarbene in pentane; carbene signals at 300 nm, 372 nm, and 596 nm.

Additions to tetramethylethylene

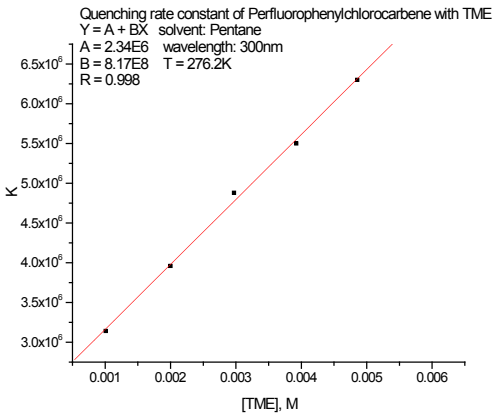

Figure S-21. Rate constant for addition of F_5-PhCCl to TME at 276 K: k = 8.17 exp 8 M^{-1} s^{-1}, r = 0.998.

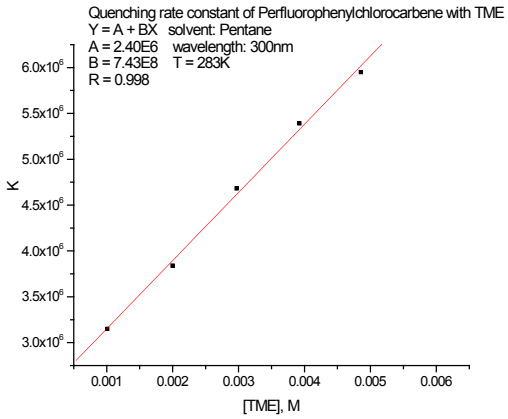

Figure S-22. Rate constant for addition of F_5-PhCCl to TME at 283 K: k = 7.43 exp 8 M^{-1} s^{-1}, r = 0.998.

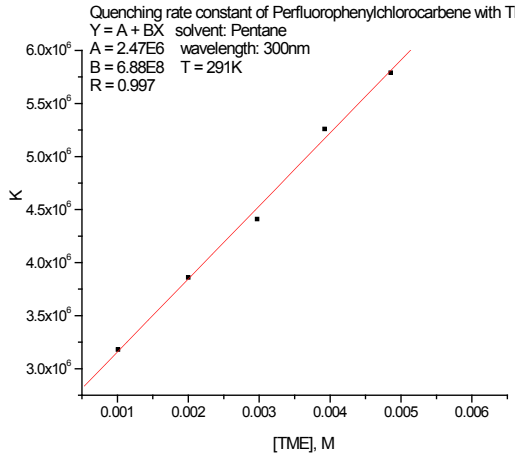

Figure S-23. Rate constant for addition of F_5-PhCCl to TME at 291 K: k = 6.88 exp 8 M^{-1} s^{-1}, r = 0.997.

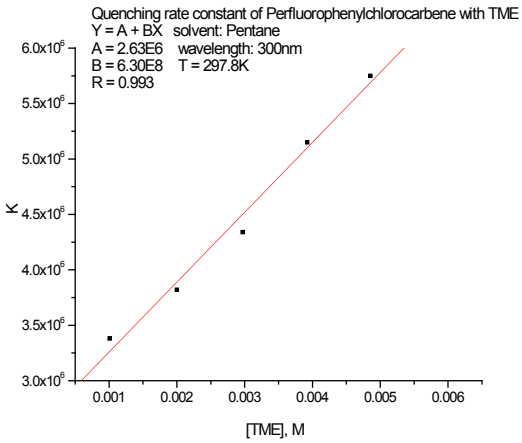

Figure S-24. Rate constant for addition of F_5-PhCCl to TME at 298 K: k = 6.30 exp 8 M^{-1} s^{-1}, r = 0.993.

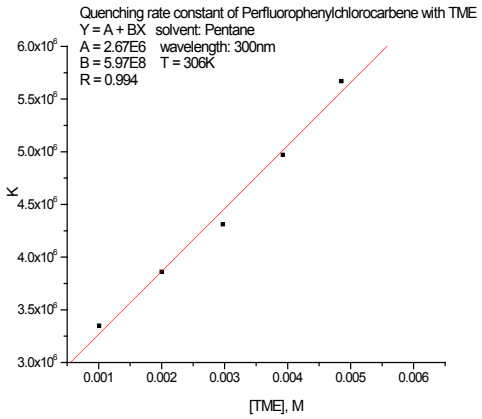

Figure S-25. Rate constant for addition of F_5-PhCCl to TME at 306 K: k = 5.97 exp 8 M^{-1} s^{-1}, r = 0.994.

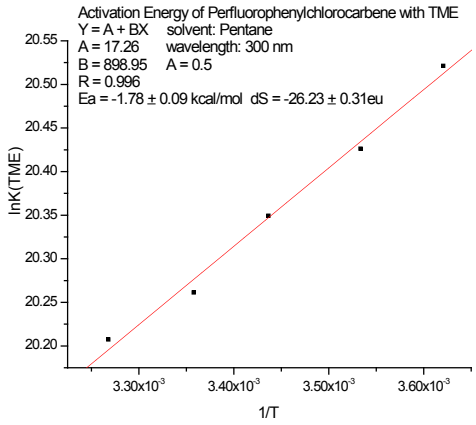

Figure S-26. Activation energy for addition of F_5-PhCCl to TME: E_a = -1.78 ± 0.09 kcal/mol, log A = 7.49 s^{-1}, $\Delta S^{\ddagger}$ = -26 ± 0.3 e.u., r = 0.996.

Additions to cyclohexene

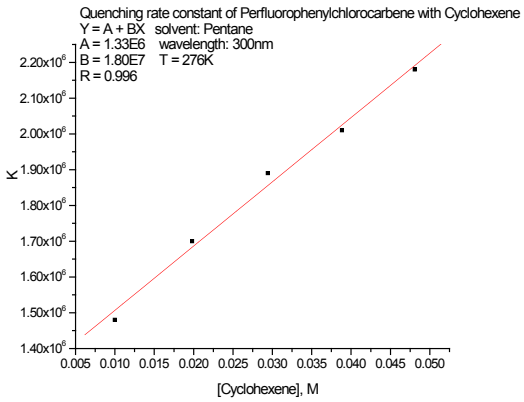

Figure S-27. Rate constant for addition of F_5-PhCCl to cyclohexene at 276 K: k = 1.80 exp 7 M^{-1} s^{-1}, r = 0.996.

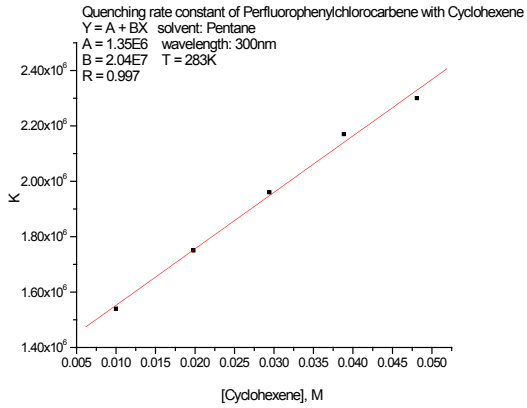

Figure S-28. Rate constant for addition of F_5-PhCCl to cyclohexene at 283 K: k = 2.04 exp 7 M^{-1} s^{-1}, r = 0.997.

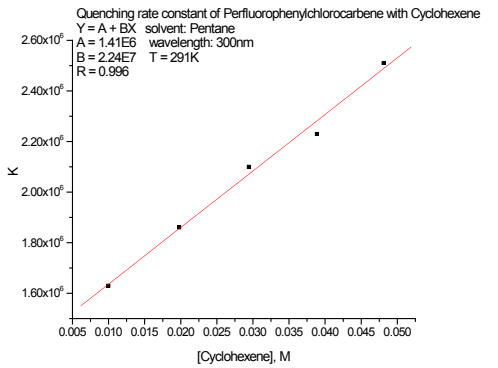

Figure S-29. Rate constant for addition of F_5-PhCCl to cyclohexene at 291 K: k = 2.24 exp 7 M^{-1} s^{-1}, r = 0.996.

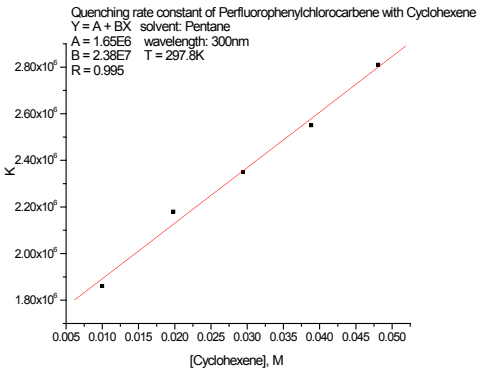

Figure S-30. Rate constant for addition of F_5-PhCCl to cyclohexene at 298 K: k = 2.38 exp 7 M^{-1} s^{-1}, r = 0.995.

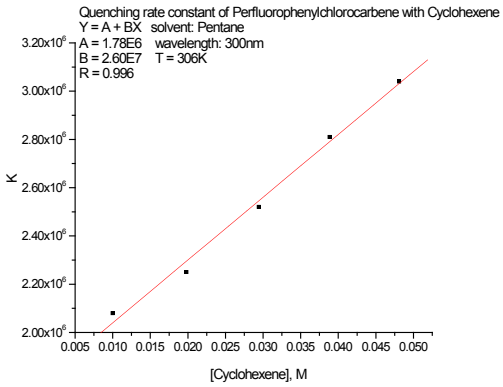

Figure S-31. Rate constant for addition of F_5-PhCCl to cyclohexene at 306 K: k = 2.60 exp 7 M^{-1} s^{-1}, r = 0.996.

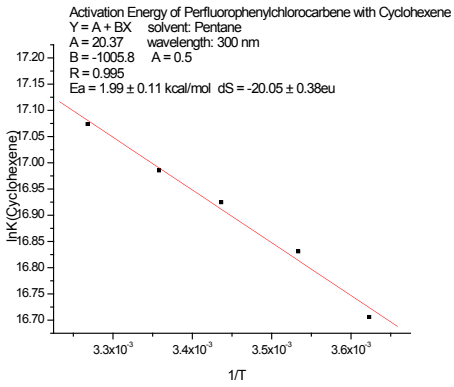

Figure S-32. Activation energy for addition of F_5-PhCCl to cyclohexene: E_a = 1.99 ± 0.11 kcal/mol, log A = 8.84 s^{-1}, $\Delta S^{\ddagger}$ = -20 ± 0.4 e.u., r = 0.995.

Additions to 1-hexene

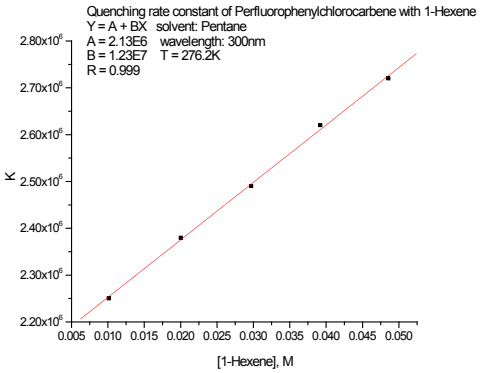

Figure S-33. Rate constant for addition of F_5-PhCCl to 1-hexene at 276 K: k = 1.23 exp 7 M^{-1} s^{-1}, r = 0.999.

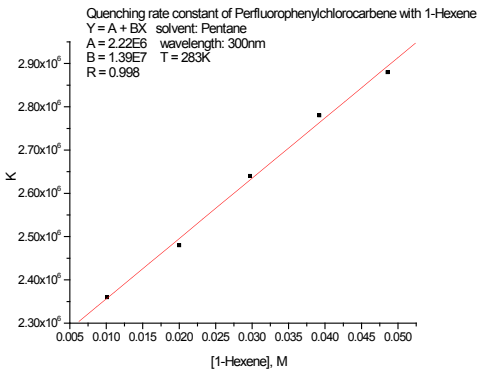

Figure S-34. Rate constant for addition of F_5-PhCCl to 1-hexene at 283 K: k = 1.39 exp 7 M^{-1} s^{-1}, r = 0.998.

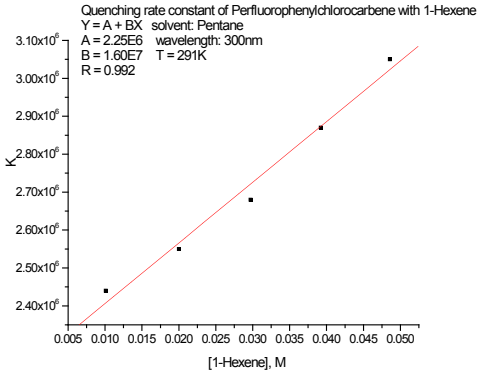

Figure S-35. Rate constant for addition of F_5-PhCCl to 1-hexene at 291 K: k = 1.60 exp 7 M^{-1} s^{-1}, r = 0.992.

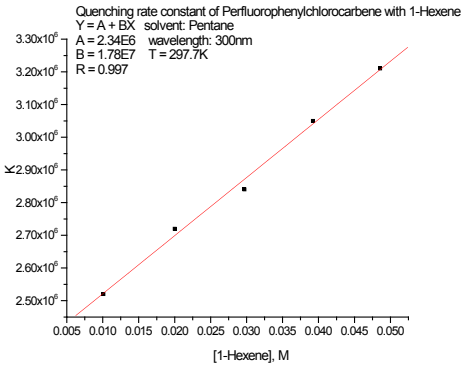

Figure S-36. Rate constant for addition of F_5-PhCCl to 1-hexene at 298 K: k = 1.78 exp 7 M^{-1} s^{-1}, r = 0.997.

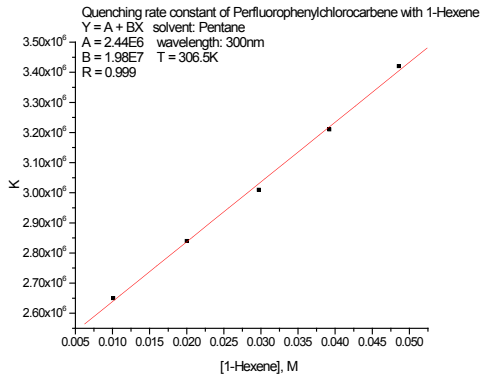

Figure S-37. Rate constant for addition of F_5-PhCCl to 1-hexene at 306.5 K: k = 1.98 exp 7 M^{-1} s^{-1}, r = 0.999.

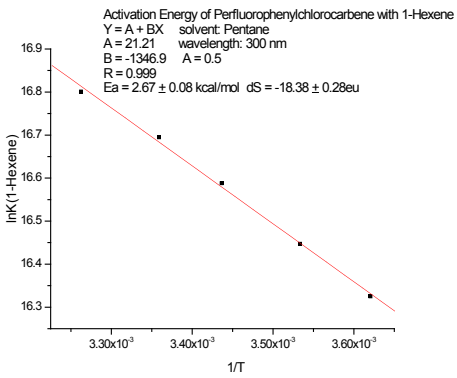

Figure S-38. Activation energy for addition of F_5-PhCCl to 1-hexene: E_a = 2.67 ± 0.08 kcal/mol, log A = 9.21 s^{-1}, $\Delta S^{\ddagger}$ = -18 ± 0.3 e.u., r = 0.999.

3. 3,5-Dinitrophenylchlorocarbene (3,5-DN-PhCCl)

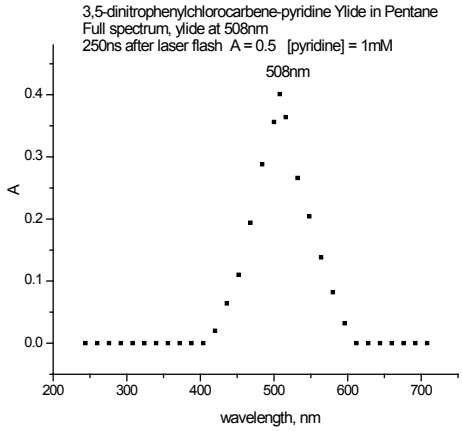

Figure S-39. LFP-UV-vis spectrum of pyridinium ylide of 3,5-DN-PhCCl in pentane. Ylide absorption at 508 nm.

Additions to tetramethylethylene

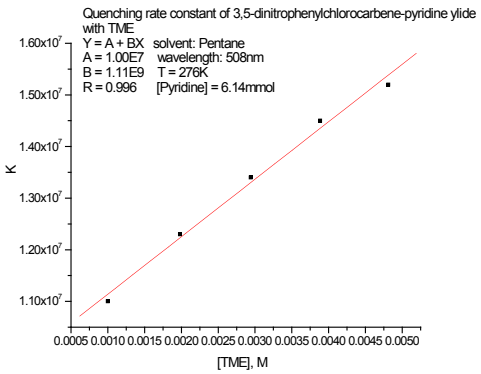

Figure S-40. Rate constant for addition of 3,5-DN-PhCCl to TME at 276 K: k = 1.11 exp 9 M^{-1} s^{-1}, r = 0.996.

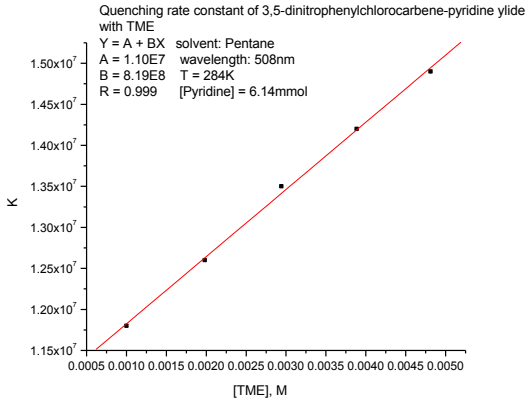

Figure S-41. Rate constant for addition of 3,5-DN-PhCCl to TME at 284 K: k = 8.19 exp 8 M^{-1} s^{-1}, r = 0.999.

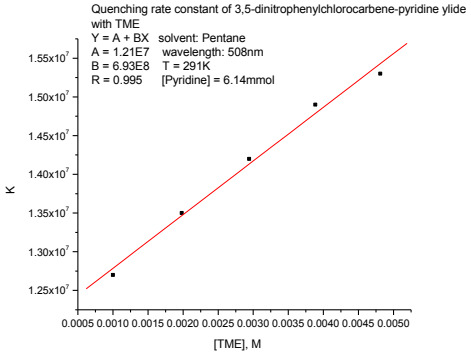

Figure S-42. Rate constant for addition of 3,5-DN-PhCCl to TME at 291 K: k = 6.93 exp 8 M^{-1} s^{-1}, r = 0.995.

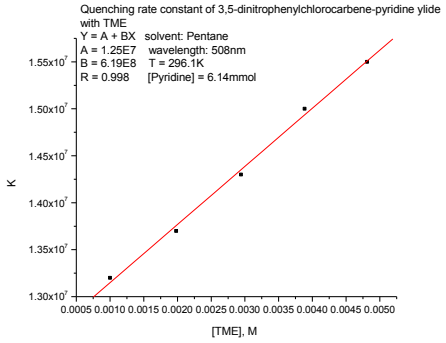

Figure S-43. Rate constant for addition of 3,5-DN-PhCCl to TME at 296 K: k = 6.19 exp 8 M^{-1} s^{-1}, r = 0.998.

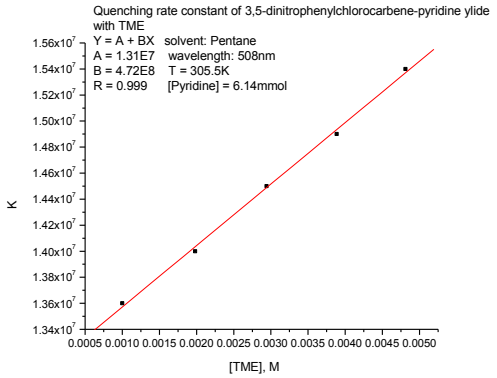

Figure S-44. Rate constant for addition of 3,5-DN-PhCCl to TME at 305.5 K: k = 4.72 exp 8 M^{-1} s^{-1}, r = 0.999.

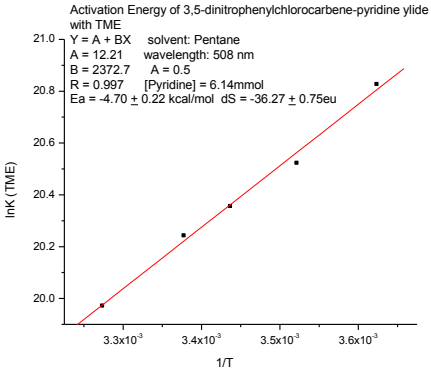

Figure S-45. Activation energy, addition of 3,5-DN-PhCCl to TME: E_a = -4.70 ± 0.22 kcal/mol, log A = 5.30 s^{-1}, $\Delta S^{\ddagger}$ = -36 ± 0.8 e.u., r = 0.997.

Additions to cyclohexene

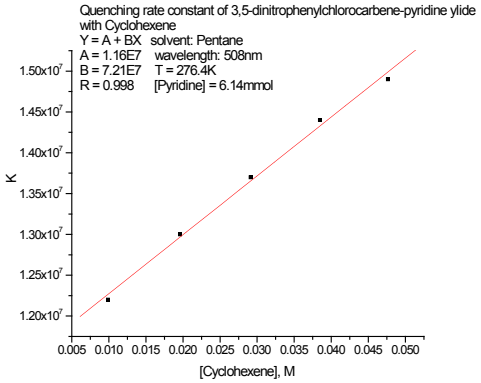

Figure S-46. Rate constant for addition of 3,5-DN-PhCCl to cyclohexene at 276 K: k = 7.21 exp 7 M^{-1} s^{-1}, r = 0.998.

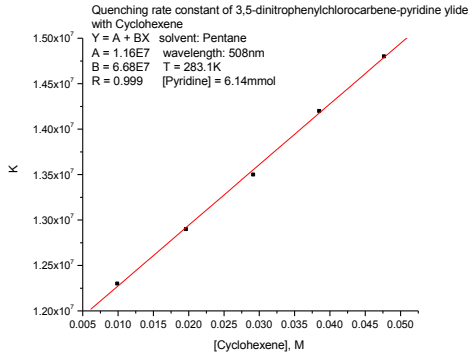

Figure S-47. Rate constant for addition of 3,5-DN-PhCCl to cyclohex. at 283 K: k = 6.68 exp 7 M^{-1} s^{-1}, r = 0.999.

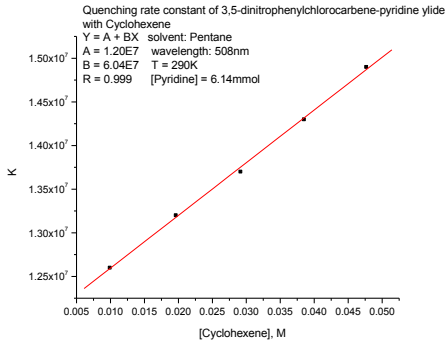

Figure S-48. Rate constant for addition of 3,5-DN-PhCCl to cyclohex. at 290 K: k = 6.04 exp 7 M^{-1} s^{-1}, r = 0.999.

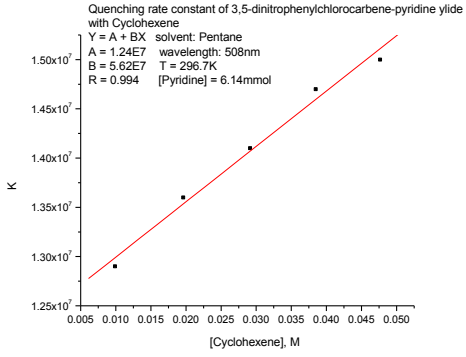

Figure S-49. Rate constant for addition of 3,5-DN-PhCCl to cyclohex. at 297 K: k = 5.62 exp 7 M^{-1} s^{-1}, r = 0.994.

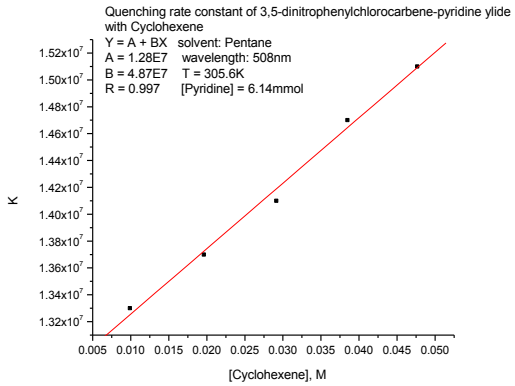

Figure S-50. Rate constant for addition of 3,5-DN-PhCCl to cyclohex. at 306 K: k = 4.87 exp 7 M^{-1} s^{-1}, r = 0.997.

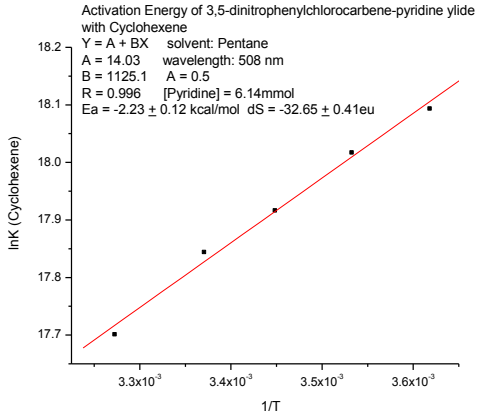

Figure S-51. Activation energy, addition of 3,5-DN-PhCCl to cyclohex.: E_a = -2.23 ± 0.12 kcal/mol, log A = 6.09 s^{-1}, $\Delta S^{\ddagger}$ = -33 ± 0.4 e.u., r = 0.996.

Additions to 1-hexene

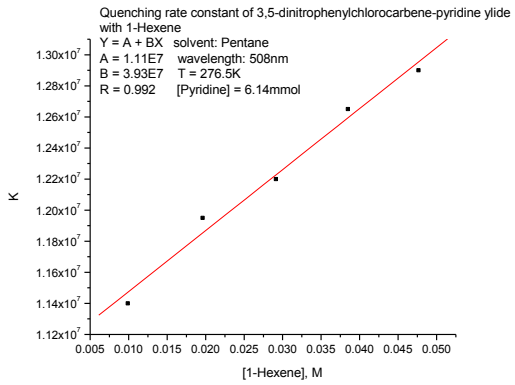

Figure S-52. Rate constant for addition of 3,5-DN-PhCCl to 1-hexene at 276.5 K: k = 3.93 exp 7 M^{-1} s^{-1}, r = 0.992.

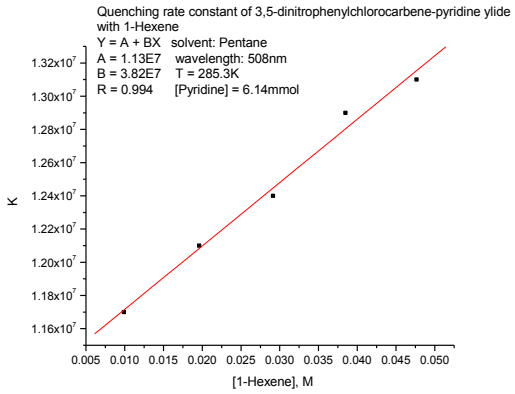

Figure S-53. Rate constant for addition of 3,5-DN-PhCCl to 1-hexene at 285 K: k = 3.82 exp 7 M^{-1} s^{-1}, r = 0.994.

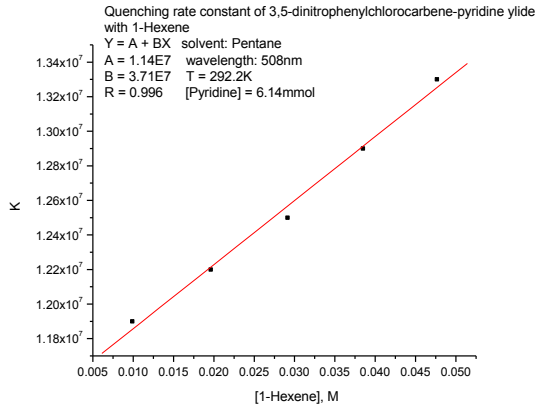

Figure S-54. Rate constant for addition of 3,5-DN-PhCCl to 1-hexene at 292 K: k = 3.71 exp 7 M^{-1} s^{-1}, r = 0.996.

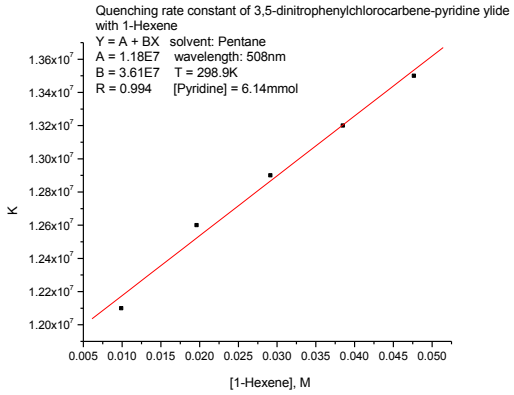

Figure S-55. Rate constant for addition of 3,5-DN-PhCC to 1-hexene at 299 K: k = 3.61 exp 7 M^{-1} s^{-1}, r = 0.994.

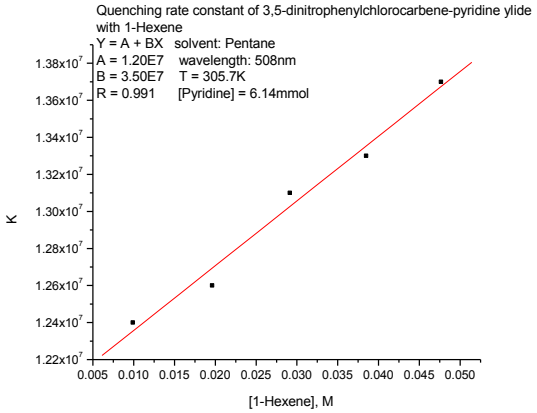

Figure S-56. Rate constant for addition of 3,5-DN-PhCCl to 1-hexene at 306 K: $k = 3.50 \exp 7$ M^{-1} s^{-1}, $r = 0.991$

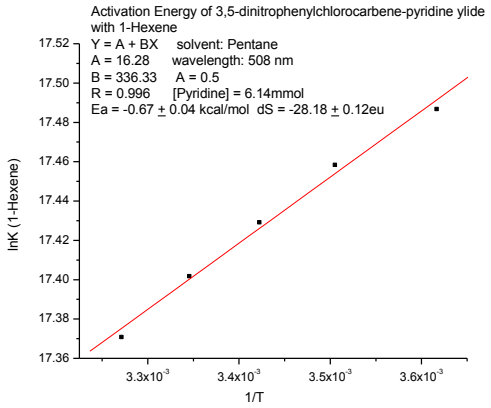

Figure S-57. Activation energy, addition of 3,5-DN-PhCCl to 1-hexene: $E_a = -0.67 \pm 0.04$ kcal/mol, $\log A = 7.07$ s^{-1}, $\Delta S^{\ddagger} = -28 \pm 0.4$ e.u., $r = 0.996$.

4. NMR Spectra

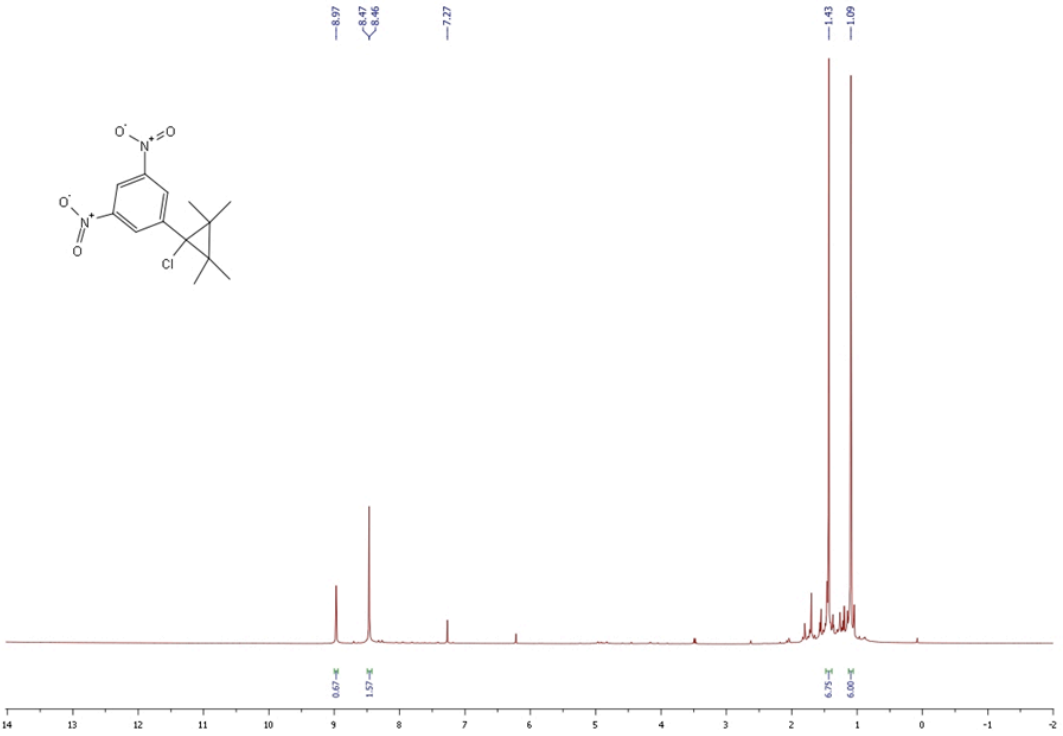

Figure S-58. ^{1}H NMR spectrum of 1-chloro-1-(3,5-dinitrophenyl)-2,2,3,3-tetramethylcyclopropane.

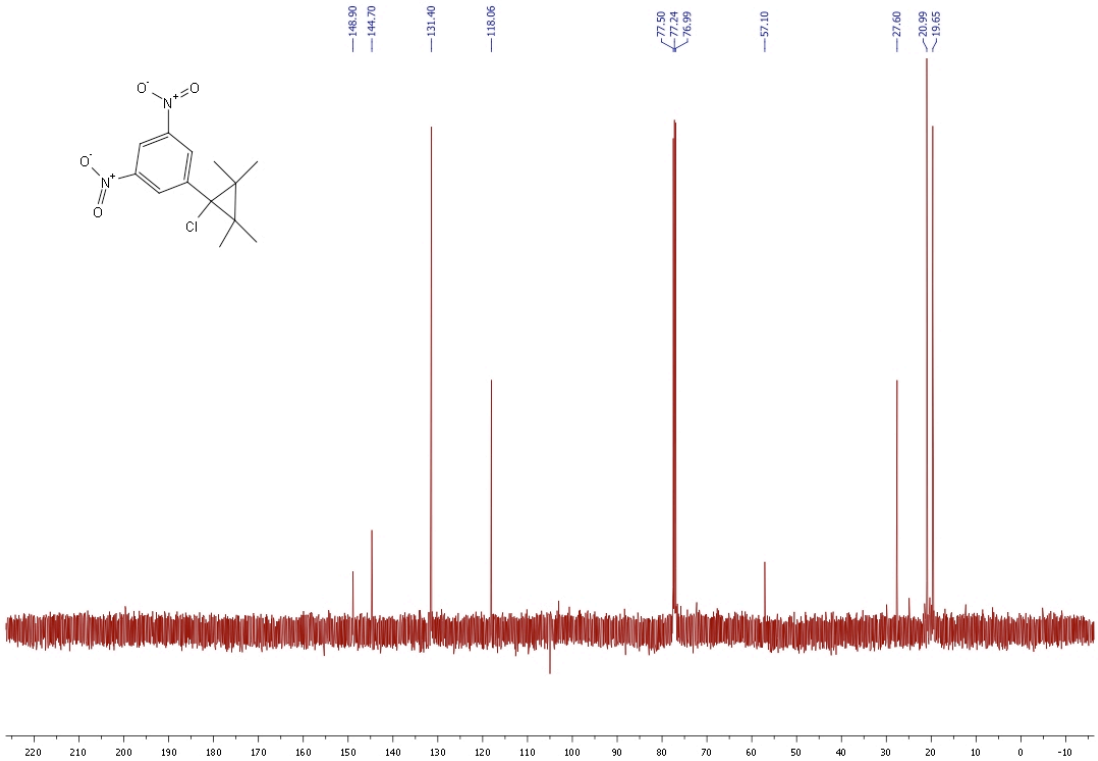

Figure S-59. ^{13}C NMR spectrum of 1-chloro-1-(3,5-dinitrophenyl)-2,2,3,3-tetramethylcyclopropane.

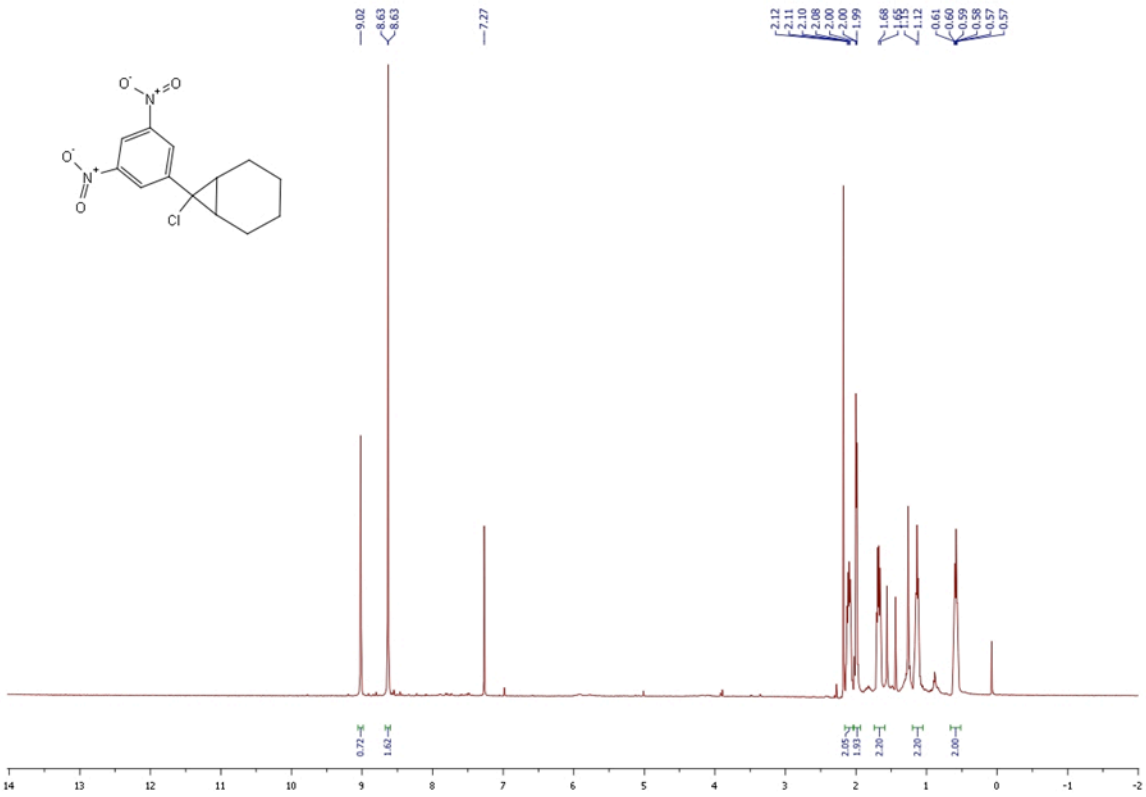

Figure S-60. ^{1}H NMR spectrum of *exo*- or *endo*-7-chloro-7-(3,5-dinitrophenyl)norcarane.

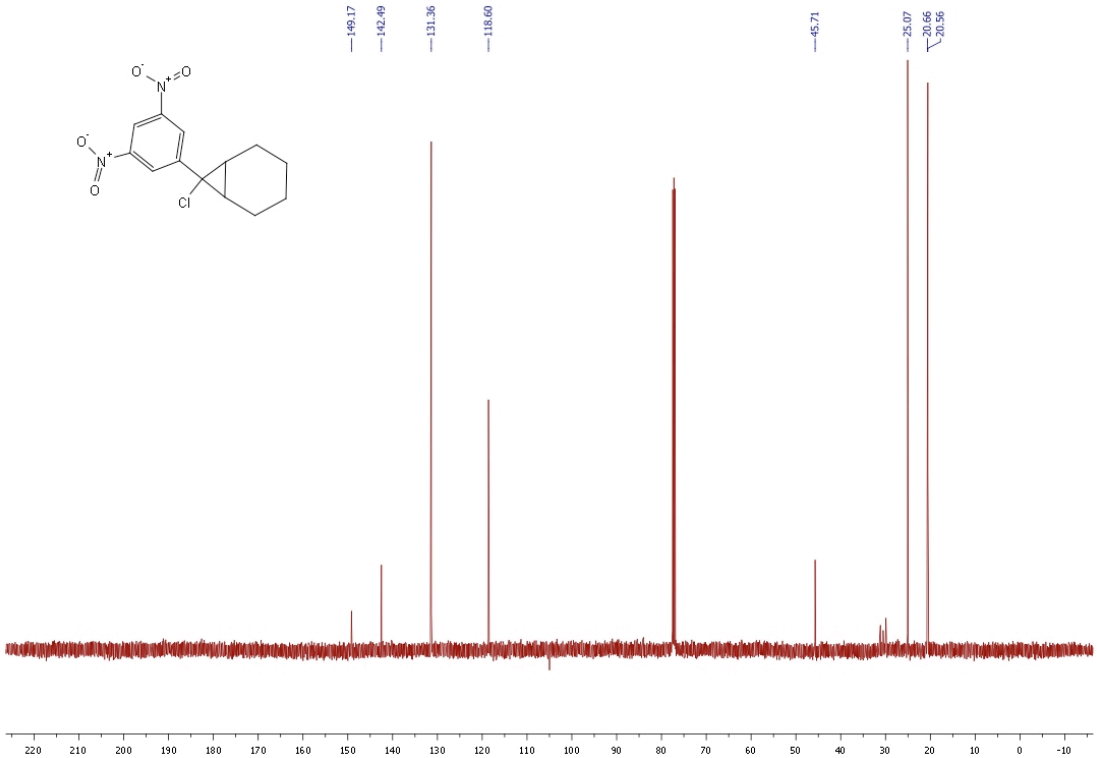

Figure S-61. ^{13}C NMR spectrum of *exo*- or *endo*-7-chloro-7-(3,5-dinitrophenyl)norcarane.

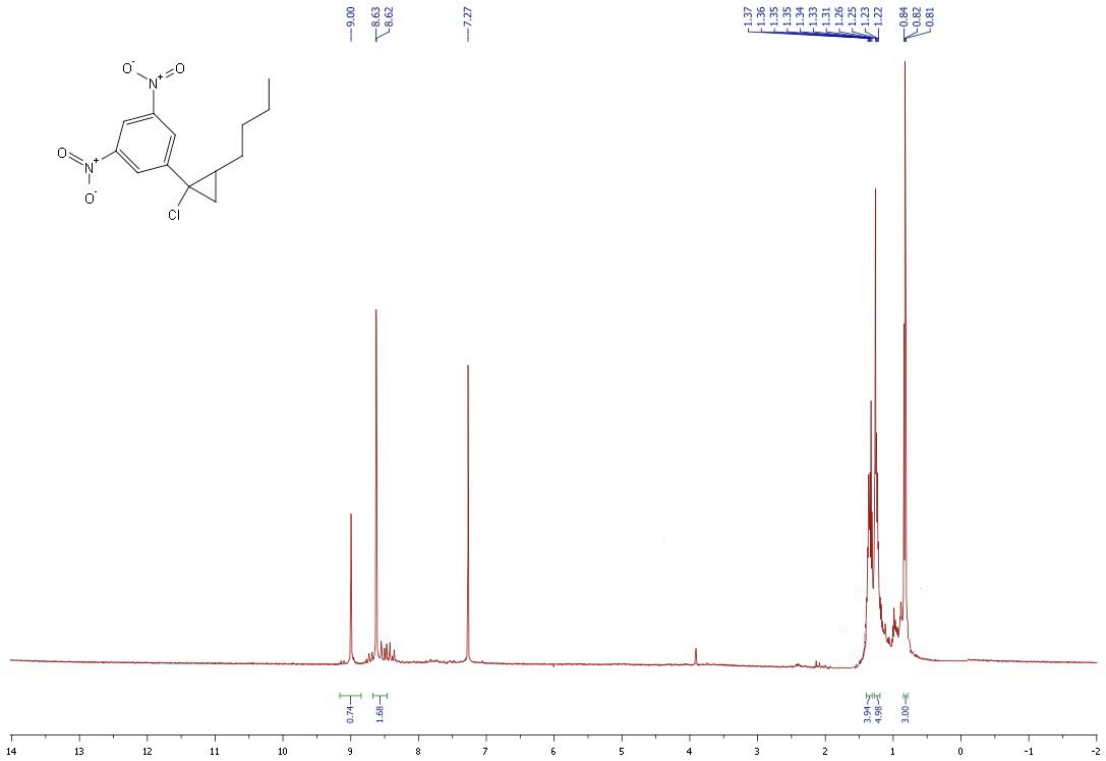

Figure S-62. ^{1}H NMR spectrum of *cis- or trans*-1-chloro-1-(3,5-dinitrophenyl)-2-butylcyclopropane.

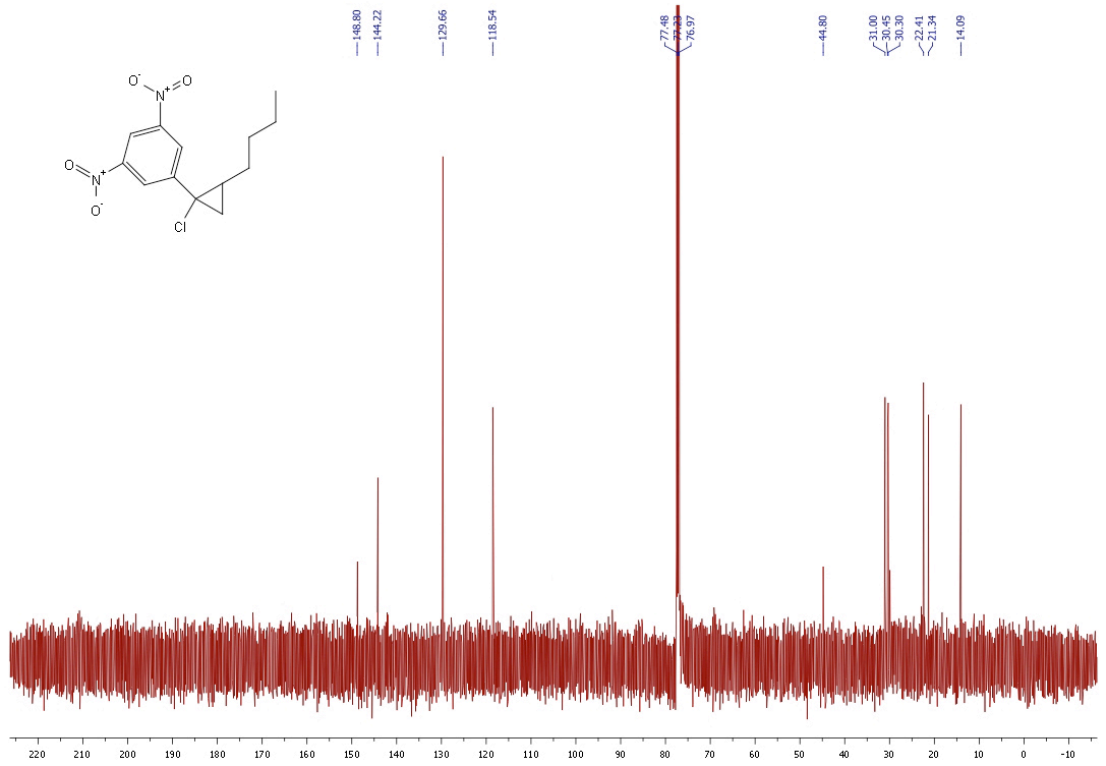

Figure S-63. ^{13}C NMR spectrum of *cis- or trans*-1-chloro-1-(3,5-dinitrophenyl)-2-butylcyclopropane.

5. MP2/cc-pVTZ Optimized geometries and absolute energies for the lowest singlet and triplet states of PhCCl, F_5-PhCCl, and 3,5-DN-PhCCl. CCSD(T)/cc-pVTZ//MP2/cc-pVTZ absolute energies.

PhCCl, singlet, MP2/cc-pVTZ
---
0 1
C,0,-2.2910946343,-0.9096259023,0.
C,0,-0.9637076771,-1.3201508904,0.
C,0,0.0801408418,-0.3739997621,0.
C,0,-0.2371188043,0.9991749511,0.
C,0,-1.5620825288,1.403092713,0.
C,0,-2.5882696243,0.4519402987,0.
H,0,-0.6907621014,-2.3664575632,0.
H,0,0.5606213752,1.7281423639,0.
H,0,-3.6199490877,0.777915151,0.
C,0,1.3969205246,-0.9904637545,0.
H,0,-1.8073788092,2.4561341659,0.
H,0,-3.088769048,-1.6389371979,0.
Cl,0,2.6526508334,0.1838219767,0.

Zero-point correction= 0.095170 (Hartree/Particle)
Thermal correction to Energy= 0.101847
Thermal correction to Enthalpy= 0.102791
Thermal correction to Gibbs Free Energy= 0.063254
Sum of electronic and zero-point Energies= -728.658780
Sum of electronic and thermal Energies= -728.652103
Sum of electronic and thermal Enthalpies= -728.651158
Sum of electronic and thermal Free Energies= -728.690696

CCSD(T)= -0.72886521400D+03
T1 Diagnostic = 0.01467442
Largest amplitude= 7.55D-02

PhCCl, triplet, MP2/cc-pVTZ
---
0 3
C,0,-1.4143329938,-0.7127111798,0.0000002618
C,0,-0.2924596209,-1.4828077016,0.0000001016
C,0,0.9699246353,-0.8873624493,0.0000000192
C,0,1.0558591787,0.5041876639,0.0000001232
C,0,-0.0795322928,1.2602744253,0.0000002958
C,0,-1.3206738779,0.6643164721,0.0000003428
H,0,-0.3662894076,-2.560512138,0.0000000268
H,0,2.0278487487,0.9748778236,0.0000000763
H,0,-2.2146569603,1.269827407,0.0000004631
C,0,2.1255268875,-1.7052127931,-0.0000001379

Cl,0,3.7382486119,-1.2774529794,-0.0000002503
H,0,0.0005238874,2.3379811336,0.0000003658
H,0,-2.3855865762,-1.1862338242,0.0000003031

Zero-point correction= 0.097865 (Hartree/Particle)
Thermal correction to Energy= 0.104206
Thermal correction to Enthalpy= 0.105150
Thermal correction to Gibbs Free Energy= 0.065417
Sum of electronic and zero-point Energies= -728.609500
Sum of electronic and thermal Energies= -728.603160
Sum of electronic and thermal Enthalpies= -728.602216
Sum of electronic and thermal Free Energies= -728.641949

CCSD(T)= -0.72884798801D+03
T1 Diagnostic = 0.03494237
Largest amplitude= 1.40D-01

F5-PhCCl, singlet, MP2/cc-pVTZ
---
0 1
C,0,-1.6368019599,-0.8991512699,0.
C,0,-0.3302691325,-1.3622645705,0.
C,0,0.784438259,-0.4850729292,0.
C,0,0.4904831665,0.9005372865,0.
C,0,-0.8115365844,1.3705546277,0.
C,0,-1.8737470094,0.4700430624,0.
C,0,2.0521463994,-1.1932489038,0.
Cl,0,3.4153683739,-0.1803118916,0.
F,0,1.4469207095,1.8161504437,0.
F,0,-1.0633231219,2.6726754766,0.
F,0,-3.1143258146,0.9237557717,0.
F,0,-2.660240577,-1.741354728,0.
F,0,-0.1635408986,-2.6710343256,0.

Zero-point correction= 0.054488 (Hartree/Particle)
Thermal correction to Energy= 0.065600
Thermal correction to Enthalpy= 0.066544
Thermal correction to Gibbs Free Energy= 0.016214
Sum of electronic and zero-point Energies= -1224.297784
Sum of electronic and thermal Energies= -1224.286672
Sum of electronic and thermal Enthalpies= -1224.285728
Sum of electronic and thermal Free Energies= -1224.336058

CCSD(T)= -0.12244795695D+04
T1 Diagnostic = 0.01501720
Largest amplitude= 7.54D-02

F5-PhCCl, triplet, MP2/cc-pVTZ
---
0 3

C	-1.61248	-0.92325	0.
C	-0.32006	-1.33001	0.
C	0.73983	-0.42482	0.
C	0.40979	0.92668	0.
C	-0.88504	1.34339	0.
C	-1.9019	0.42249	0.
C	2.05574	-0.93597	0.
Cl	3.54312	-0.21331	0.
F	1.36995	1.84642	0.
F	-1.17539	2.64023	0.
F	-3.16303	0.82673	0.
F	-2.60544	-1.80608	0.
F	-0.05051	-2.63138	0.

Zero-point correction= 0.056587 (Hartree/Particle)
Thermal correction to Energy= 0.067181
Thermal correction to Enthalpy= 0.068125
Thermal correction to Gibbs Free Energy= 0.018288
Sum of electronic and zero-point Energies= -1224.253385
Sum of electronic and thermal Energies= -1224.242790
Sum of electronic and thermal Enthalpies= -1224.241846
Sum of electronic and thermal Free Energies= -1224.291683

CCSD(T)= -0.12244679204D+04
T1 Diagnostic = 0.02776907
Largest amplitude= 1.35D-01

3,5-DN-PhCCl, singlet, MP2/cc-pVTZ
---
0 1
C,0,-1.43400506,-0.62014219,0.
C,0,-0.36893103,-1.50484015,0.
C,0,0.93829795,-0.99531711,0.
C,0,1.1474239,0.3936149,0.
C,0,0.04730488,1.22626486,0.
C,0,-1.25953611,0.75366982,0.
H,0,-0.527322,-2.57268916,0.
H,0,2.14170189,0.81347993,0.
H,0,-2.10091713,1.42802079,0.
N,0,0.25842483,2.69027387,0.
N,0,-2.81246105,-1.15163223,0.
O,0,-2.93638101,-2.37084224,0.

O,0,-0.7435382,3.39680484,0.
C,0,1.96340198,-2.05330507,0.
Cl,0,3.53207196,-1.40361502,0.
O,0,1.41909282,3.08419891,0.
O,0,-3.72469507,-0.33235126,0.

Zero-point correction= 0.099740 (Hartree/Particle)
Thermal correction to Energy= 0.111763
Thermal correction to Enthalpy= 0.112707
Thermal correction to Gibbs Free Energy= 0.057089
Sum of electronic and zero-point Energies= -1137.077105
Sum of electronic and thermal Energies= -1137.065081
Sum of electronic and thermal Enthalpies= -1137.064137
Sum of electronic and thermal Free Energies= -1137.119756

CCSD(T)= -0.11373184105D+04
T1 Diagnostic = 0.02025759
Largest amplitude= 5.61D-02

3,5-DN-PhCCl, triplet, MP2/cc-pVTZ
---
0 3
C,0,-1.388762,-0.696672,0.
C,0,-0.285335,-1.482674,0.
C,0,0.976731,-0.890854,0.
C,0,1.058171,0.498897,0.
C,0,-0.08631,1.231914,0.
C,0,-1.333151,0.673373,0.
H,0,-0.395486,-2.556232,0.
H,0,2.012517,1.002384,0.
H,0,-2.225339,1.276851,0.
N,0,0.024575,2.708399,0.
N,0,-2.718089,-1.34725,0.
O,0,-2.743589,-2.572836,-0.
O,0,-1.020779,3.346916,-0.
C,0,2.132635,-1.70826,0.
Cl,0,3.734745,-1.281438,0.
O,0,1.153838,3.185735,0.
O,0,-3.698422,-0.612433,0.

Zero-point correction= 0.102718 (Hartree/Particle)
Thermal correction to Energy= 0.114181
Thermal correction to Enthalpy= 0.115125
Thermal correction to Gibbs Free Energy= 0.061535
Sum of electronic and zero-point Energies= -1137.032651
Sum of electronic and thermal Energies= -1137.021188
Sum of electronic and thermal Enthalpies= -1137.020244
Sum of electronic and thermal Free Energies= -1137.073834

CCSD(T)= -0.11373052797D+04
T1 Diagnostic = 0.03070135
Largest amplitude= 1.26D-01