Supporting Information

Singlet Vinylcarbenes: Spectroscopy and Photochemistry

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Experimental

NMR spectra were determined on a General Electric QE 300 spectrometer. Chemical shifts are reported in ppm relative to TMS. IR spectra were recorded on a Perkin Elmer System 2000 FT-IR spectrometer with 1 cm^{-1} resolution. UV/vis spectra were obtained on a modified Perkin Elmer Lambda 4C UV/VIS spectrophotometer.

Synthesis of Precursors

General procedure for the synthesis of amidines.[1] A 2M solution of Me_3Al in toluene (25 ml, 50 mmol) was slowly added to a magnetically stirred suspension of 2.9 g (54 mmol) of NH_4Cl in 20 ml of dry toluene (distilled from CaH_2) at 5°C under a N_2 atmosphere. After the addition, the mixture was warmed to 25°C and stirred for 2 h until gas evolution (CH_4) had ceased. Then, 4.83 g (30 mmol) of carbonitrile in 10 ml of dry toluene was added and the solution was heated to 80°C for 18 h under N_2. The reaction mixture was slowly poured into a slurry of 15 g of silica gel in 50 ml of $CHCl_3$ and stirred for 1 h. The silica gel was filtered and washed with MeOH. The filtrate and wash were combined and solvent was removed in vacuo. The residual solid was amidine usually pure enough to be further used without additional purification.

Acrylamidine: Yield 65%. ^{1}H NMR (DMSO-d_6) δ 9.3 (broad s, ca. 1.5 H), 8.9(broad s, ca. 1.5 H), 6.61 (d, 1 H, *J*=17.6 Hz), 6.36 (dd, 1 H, *J*=17.6, 11.0 Hz), 6.06 (d, 11.0 Hz).

1-Methacrylamidine: Yield 98%. ^{1}H NMR (DMSO-d_6) δ 9.03 (broad, 3 H), 5.89 (s, 1 H), 5.67 (s, 1 H); 1.97 (s, 3 H).

1-Cyclopenteneamidine: Yield 21%. ^{1}H NMR (DMSO-d_6) δ 8.95 (broad s, 3 H), 3.44 (s, 1 H), 2.80-1.80 (m, 6 H).

General procedure for the synthesis of diazirines:[2] 30 mL of commercial "pool chlorine" (PURECHLOR, Sierra Chemical Co., 12% hypochlorite) was added dropwise to a cooled (0° C) magnetically stirred solution containing 1.5 g (10 mmol) of amidine and 3 g (50 mmol) of NaCl in 30 mL of dimethyl sulfoxide. The receiving solution was contained in a 250-mL, round-bottom, three-neck flask. When addition was completed the reaction vessel was connected to a series of traps and evacuated to 4 mm Hg by a vacuum pump at room temperature. The forming diazirine was carried out of the generating flask, through a U-trap filled with NaOH pellets, then through an empty trap cooled to –20 °C, and was finally condensed in a trap cooled with liquid nitrogen. The reaction was completed in 45 min. The obtained product could be purified by trap-to-trap distillation, if needed.

Vinylchlorodiazirine (1): ^{1}H NMR ($CDCl_3$) δ 5.51-5.42 (m, 2H), 5.31 (dd, 1 H, *J*=15.6, *J*=1.5 Hz); IR (N_2, 9K) 1640 (w), 1582 (m), 1578 (m), 1420 (m), 1413 (w), 1183 (m), 1174 (m), 1065 (m), 1031 (m), 980 (m), 932(s), 855 (w), 678 (w), 662 (m), 589 (m) cm^{-1}; UV/vis (N_2, 9K) λmax 385, 373, 364, 356, 326, 281, 259 nm. When working with this compound as a neat liquid, it is advisable not to let it warm up higher than –10° C. Quick carbonization at higher temperatures occurred in some experiments.

2-Propenylchlorodiazirine (5): ^{1}H NMR ($CDCl_3$) δ 5.20 (s, 1 H), 5.07 (s, 1 H), 1.61 (s, 3 H); IR (N_2, 8K)1646 (w), 1584 (m), 1570 (w), 1461 (m), 1436 (m), 1382 (m), 1298 (m), 1029 (s), 978 (s), 959 (m), 904 (s), 894 (m), 856 (w), 597 (m), 546 (w) cm^{-1}; UV/vis (N_2, 9K) λmax 392, 386, 380, 370, 352, 340, 312, 284 nm.

1-Cyclopentenylchlorodiazirine (11): ^{1}H NMR ($CDCl_3$) δ 5.77 (s, 1 H), 2.80-1.80 (m, 6 H); IR (N_2, 10K) 1574 (s), 1477 (w), 1449 (w), 1340 (w), 1211 (w), 1140 (w), 1043 (w), 1016 (w), 1009 (w), 934 (m), 915 (m), 901 (w), 894 (w), 855 (w), 827 (w), 780 (m), 727 (w), 536 (m) cm^{-1}; UV/vis (N_2, 10K) λmax 407, 394, 384, 363, 342, 313, 284, 252 nm.

Matrix Isolation Experiments

General descriptions of the low temperature apparatus and matrix isolation techniques have been published previously.[3] Deposition mixtures were prepared in a 2.5-L glass manifold evacuated to 10^{-6} Torr (MKS Instruments Inc., HPS Division, SensaVac Series 941 Cold Cathode Ionization Vacuum Gauge System). Diazirine was released into the manifold and measured using a MKS Instruments Inc., PDR-C-2C differential pressure gauge. The inert medium, argon or nitrogen, was then added to the manifold as monitored by the MKS differential pressure gauge. Typical inert gas to diazirine ratios were 600-800:1 for nitrogen and 400-500:1 for argon. The flow rate to the cold finger was controlled by a variable leak valve and measured by the MKS differential preassure gauge. Standard experiments consisted of 100-150 Torr for nitrogen or 50-60 Torr for argon deposited at 2 Torr/min for transparent matrices of sufficient concentration for analysis, onto a 2.5-cm CsI window at 21 K for nitrogen or 23 K for argon. The window temperatures were measured using a 0.07% iron-doped gold vs chromel thermocouple imbedded in the cold-tip adjacent to the window holder, and connected to a Scientific Instruments, Inc. temperature indicator/controller. This unit operated a 25-W resistive heater which allowed for thermal regulation of the cryostat at preset temperatures. After completion of deposition, the window was cooled to 8 K. Monochromatic irradiation of the matrix medium was provided by Photon Technologies Inc. 01-001 Series monochromator with a HBO 100-W Hg lamp. Broad-band irradiation was accomplished using a high-pressure 300-W high-pressure Xe lamp.

Vinylchlorocarbene (2): IR (N_2, 9K) (*s*-E): 1574 (m), 1403 (w), 1389 (s), 1287 (w), 1158 (m), 1016 (m), 982 (m), 969 (m), and 741 (m) cm^{-1}; (*s*-cisoid): 1527 (m), 1394 (m), 1110 (m), 993 (m), 926 (m), 753 (m), and 617 (m) cm^{-1}; UV/vis (N_2, 9K) broad 550-850 nm (λmax 690 nm).

Propenylchlorocarbene (6): IR (N_2, 8K) 1311(m), 1012 (m), 996 (w), 844 (m), 742 (w) cm^{-1}; UV/vis (N_2, 9K) broad 550-850 nm (λmax 690 nm).

Cyclopentenylchlorocarbene (12): IR (N_2, 10K) 1563 (w); 1549 (s), 1500 (w), 1416 (m), 1370 (vw), 1355 (m), 1300 (m), 1293 (m), 1260 (m), 1252 (sh), 1236 (m), 1185 (m), 1179 (m), 1170 (w), 1124 (vw), 1033 (w), 953 (m), 934 (vw), 899 (w), 882 (w) 816 (w), 741 (s) cm^{-1}; UV/vis (N_2, 10K) broad 550-850 nm (λmax 660 nm).

Computational Details

All structures were fully optimized by analytical gradient methods using the Gaussian98 and Gaussian03 suites and density functional (DFT) calculations at the 6-31G(d) level, the exchange potentials of Becke[4] and the correlation functional of Lee, Yang and Parr.[5] Activation energies were corrected for zero-point energy differences (ZPVE) (unscaled). Vibrational analyses established the nature of all stationary points as either energy minima (no imaginary frequencies) or 1st order saddle points (one imaginary frequency). B3LYP/6-31+G** level of theory was used for IR and TD calculations (on geometries optimized with that basis set).

Scott and Radom[6] recommend a general scaling factor of 0.9614 for vibrational frequencies calculated at the B3LYP/6-31G* level. We find a slightly higher factor of 0.97 gives generally better agreement between frequencies calculated with the 6-31+G** basis set and experiment.

Gaussian 98, Revision A.9, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, Jr., R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, A. G. Baboul, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, C. Gonzalez, M. Head-Gordon, E. S. Replogle, and J. A. Pople, Gaussian, Inc., Pittsburgh PA, 1998.

Gaussian 03, Revision B.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford,

J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz,
I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham,
C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill,
B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople,
Gaussian, Inc., Pittsburgh PA, 2003.

Vinyl(chloro)carbene (2 - *E*)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.986741	-0.759253	-0.907113
2	1	0	-3.033494	-0.471056	-0.962320
3	1	0	-1.681052	-1.676612	-1.402757
4	6	0	-1.067609	-0.016907	-0.247236
5	1	0	-1.354916	0.908354	0.257340
6	6	0	0.283837	-0.540013	-0.268717
7	17	0	1.334855	0.537432	0.626243

Zero-point correction= 0.046374 (Hartree/Particle)
Thermal correction to Energy= 0.051013
Thermal correction to Enthalpy= 0.051957
Thermal correction to Gibbs Free Energy= 0.018802
Sum of electronic and zero-point Energies= -576.151371
Sum of electronic and thermal Energies= -576.146732
Sum of electronic and thermal Enthalpies= -576.145788
Sum of electronic and thermal Free Energies= -576.178942

Vinyl(chloro)carbene (2 - *Z*)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.698776	-0.747959	-0.097160
2	1	0	-2.766249	-0.948282	-0.077753
3	1	0	-1.036992	-1.596988	-0.239914
4	6	0	-1.223465	0.519490	-0.045184
5	1	0	-1.930339	1.347830	0.014372
6	6	0	0.118615	0.930060	-0.392671
7	17	0	1.326784	-0.177183	0.206670

Zero-point correction= 0.046234 (Hartree/Particle)

Thermal correction to Energy= 0.050742
Thermal correction to Enthalpy= 0.051686
Thermal correction to Gibbs Free Energy= 0.018853
Sum of electronic and zero-point Energies= -576.143938
Sum of electronic and thermal Energies= -576.139431
Sum of electronic and thermal Enthalpies= -576.138487
Sum of electronic and thermal Free Energies= -576.171320

Vinyl(chloro)carbene (2 - E)Triplet

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.168060	-0.827366	-0.695089
2	1	0	-3.209788	-0.537679	-0.623775
3	1	0	-1.928459	-1.747865	-1.216329
4	6	0	-1.180627	-0.039099	-0.134914
5	1	0	-1.472793	0.880974	0.379681
6	6	0	0.170582	-0.322013	-0.174489
7	17	0	1.510569	0.502084	0.440434

Zero-point correction= 0.045313 (Hartree/Particle)
Thermal correction to Energy= 0.050006
Thermal correction to Enthalpy= 0.050950
Thermal correction to Gibbs Free Energy= 0.016985
Sum of electronic and zero-point Energies= -576.147075
Sum of electronic and thermal Energies= -576.142382
Sum of electronic and thermal Enthalpies= -576.141438
Sum of electronic and thermal Free Energies= -576.175403
S**2 before annihilation 2.0362, after 2.0003

1-Chlorocyclopropene (3)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.380639	-0.564430	-0.797239
2	6	0	-1.194754	-0.696581	0.726430
3	6	0	-0.243395	-0.129075	0.059749
4	1	0	-1.276972	-1.451638	-1.427726
5	1	0	-2.081452	0.178153	-1.188182
6	1	0	-1.637551	-1.049554	1.643009
7	17	0	1.288747	0.627268	0.061133

Zero-point correction= 0.047600 (Hartree/Particle)
Thermal correction to Energy= 0.051767
Thermal correction to Enthalpy= 0.052711
Thermal correction to Gibbs Free Energy= 0.020654
Sum of electronic and zero-point Energies= -576.178421
Sum of electronic and thermal Energies= -576.174255
Sum of electronic and thermal Enthalpies= -576.173311
Sum of electronic and thermal Free Energies= -576.205368

Transition state for E-vinylchlorocarbene (2) to 1-chlorocyclopropene (3)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.004717	-0.027936	-0.132709
2	1	0	-2.657958	0.417364	0.622419
3	1	0	-2.285530	-0.999156	-0.509761
4	6	0	-0.902677	0.692459	-0.621345
5	1	0	-0.743987	1.769281	-0.632823
6	6	0	-0.120602	-0.388604	-0.394670
7	17	0	1.403261	-0.167236	0.436030

Zero-point correction= 0.045297 (Hartree/Particle)
Thermal correction to Energy= 0.049402
Thermal correction to Enthalpy= 0.050346
Thermal correction to Gibbs Free Energy= 0.018328
Sum of electronic and zero-point Energies= -576.131791
Sum of electronic and thermal Energies= -576.127687
Sum of electronic and thermal Enthalpies= -576.126742
Sum of electronic and thermal Free Energies= -576.158761
Low frequencies --- -534.7701 -4.2708 -0.0037 -0.0029 0.0028 5.8050
Low frequencies --- 8.7809 235.5983 369.4841

1-Chloropropa-1,2-diene (4)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.343462	-0.307707	0.000100
2	1	0	-2.865971	-0.527450	-0.928612
3	1	0	-2.864611	-0.527500	0.929637
4	6	0	-1.137314	0.199322	-0.000273
5	6	0	0.060107	0.717476	0.000185

6	1	0	0.257970	1.783024	0.000514
7	17	0	1.529213	-0.257801	-0.000095

Zero-point correction= 0.047052 (Hartree/Particle)
Thermal correction to Energy= 0.051531
Thermal correction to Enthalpy= 0.052475
Thermal correction to Gibbs Free Energy= 0.019719
Sum of electronic and zero-point Energies= -576.215166
Sum of electronic and thermal Energies= -576.210687
Sum of electronic and thermal Enthalpies= -576.209743
Sum of electronic and thermal Free Energies= -576.242500

Transition state for E-vinylchlorocarbene (2) to chloroallene (4)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.340023	-0.138289	0.115905
2	1	0	-3.026188	0.680396	-0.060561
3	1	0	-2.725605	-1.152417	0.108017
4	6	0	-1.047552	0.062208	0.334763
5	1	0	-0.563668	1.158224	0.686529
6	6	0	0.226144	0.011582	0.782005
7	17	0	1.487297	-0.017601	-0.478237

Zero-point correction= 0.041469 (Hartree/Particle)
Thermal correction to Energy= 0.045934
Thermal correction to Enthalpy= 0.046878
Thermal correction to Gibbs Free Energy= 0.014176
Sum of electronic and zero-point Energies= -576.120057
Sum of electronic and thermal Energies= -576.115592
Sum of electronic and thermal Enthalpies= -576.114648
Sum of electronic and thermal Free Energies= -576.147350

Low frequencies --- -886.3705 -8.4383 -0.0267 -0.0030 0.0121 7.0187
Low frequencies --- 10.0872 181.1620 385.1491

Transition state for E-vinylchlorocarbene (2 – E) to Z-vinylchlorocarbene (2 –Z)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z

1	6	0	-2.135037	0.047454	-0.067486
2	1	0	-2.996179	0.683785	0.101031
3	1	0	-2.267314	-1.021454	0.067174
4	6	0	-0.957107	0.573462	-0.435451
5	1	0	-0.860959	1.653529	-0.603038
6	6	0	0.253705	-0.120831	-0.832445
7	17	0	1.362064	-0.253904	0.496890

Zero-point correction= 0.044664 (Hartree/Particle)
Thermal correction to Energy= 0.048827
Thermal correction to Enthalpy= 0.049772
Thermal correction to Gibbs Free Energy= 0.017537
Sum of electronic and zero-point Energies= -576.136520
Sum of electronic and thermal Energies= -576.132356
Sum of electronic and thermal Enthalpies= -576.131412
Sum of electronic and thermal Free Energies= -576.163646
Low frequencies --- -270.4558 -15.4852 -0.0057 -0.0034 0.0041 4.5310
Low frequencies --- 11.2893 228.1166 362.2608

1-Methylvinyl(chloro)carbene (6 - E)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.575075	-1.213215	-0.975591
2	1	0	-2.656051	-1.112543	-1.049423
3	1	0	-1.105241	-2.063677	-1.459270
4	6	0	-0.807071	-0.315347	-0.304030
5	6	0	-1.391573	0.891128	0.392491
6	1	0	-2.478130	0.926179	0.276158
7	1	0	-1.156202	0.875925	1.461638
8	1	0	-0.968076	1.816861	-0.010370
9	6	0	0.600147	-0.702161	-0.372105
10	17	0	1.612067	0.446754	0.490393

Zero-point correction= 0.074550 (Hartree/Particle)
Thermal correction to Energy= 0.080500
Thermal correction to Enthalpy= 0.081444
Thermal correction to Gibbs Free Energy= 0.044706
Sum of electronic and zero-point Energies= -615.444579
Sum of electronic and thermal Energies= -615.438629
Sum of electronic and thermal Enthalpies= -615.437685
Sum of electronic and thermal Free Energies= -615.474423

1-Methylvinyl(chloro)carbene (6 - Z)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.532747	-0.386342	-0.525625
2	1	0	-2.605618	-0.216042	-0.566683
3	1	0	-1.146079	-1.235601	-1.078763
4	6	0	-0.709323	0.489948	0.104153
5	6	0	-1.230480	1.697008	0.856866
6	1	0	-2.323852	1.708269	0.871628
7	1	0	-0.874593	1.683915	1.893120
8	1	0	-0.864447	2.622238	0.401875
9	6	0	0.719511	0.507630	-0.153090
10	17	0	1.431343	-1.083073	-0.189118

Zero-point correction= 0.074046 (Hartree/Particle)
Thermal correction to Energy= 0.080098
Thermal correction to Enthalpy= 0.081043
Thermal correction to Gibbs Free Energy= 0.044233
Sum of electronic and zero-point Energies= -615.438710
Sum of electronic and thermal Energies= -615.432658
Sum of electronic and thermal Enthalpies= -615.431714
Sum of electronic and thermal Free Energies= -615.468523

1-Chloro-2-methylcyclopropene (7)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.599807	1.486662	-0.000009
2	1	0	-0.699038	2.077732	-0.916498
3	1	0	-0.699157	2.078231	0.916114
4	6	0	0.222907	0.248208	-0.000013
5	6	0	-1.048944	0.009605	0.000238
6	6	0	-2.238130	-0.866216	-0.000081
7	1	0	-2.860039	-0.673791	0.882477
8	1	0	-2.860472	-0.672371	-0.881959
9	1	0	-1.950765	-1.921908	-0.000813
10	17	0	1.826666	-0.362203	-0.000008

Zero-point correction= 0.075896 (Hartree/Particle)
Thermal correction to Energy= 0.081681

Thermal correction to Enthalpy= 0.082625
Thermal correction to Gibbs Free Energy= 0.046286
Sum of electronic and zero-point Energies= -615.478989
Sum of electronic and thermal Energies= -615.473204
Sum of electronic and thermal Enthalpies= -615.472260
Sum of electronic and thermal Free Energies= -615.508599

3-Chloro-3-methylbuta1-1,2-diene (8)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.458216	-0.441356	0.000242
2	1	0	-3.001498	-0.611264	-0.927564
3	1	0	-3.000001	-0.610736	0.929040
4	6	0	-1.207695	-0.054425	-0.000686
5	6	0	0.036245	0.346531	-0.000132
6	6	0	0.522685	1.767984	0.000088
7	1	0	1.137365	1.963915	-0.885167
8	1	0	-0.327893	2.454211	0.000790
9	1	0	1.138190	1.963288	0.884944
10	17	0	1.335042	-0.874813	0.000052

Zero-point correction= 0.075231 (Hartree/Particle)
Thermal correction to Energy= 0.081119
Thermal correction to Enthalpy= 0.082063
Thermal correction to Gibbs Free Energy= 0.045708
Sum of electronic and zero-point Energies= -615.511307
Sum of electronic and thermal Energies= -615.505419
Sum of electronic and thermal Enthalpies= -615.504475
Sum of electronic and thermal Free Energies= -615.540830

Bicyclocyclopropene 13

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.296852	-0.633222	0.804696
2	6	0	0.360609	0.899822	0.819962
3	6	0	1.378463	1.228750	-0.294258
4	6	0	1.863195	-0.155682	-0.841965

5	6	0	1.478673	-1.285246	0.192061
6	1	0	0.413204	1.470257	1.748008
7	1	0	0.967679	1.845601	-1.101111
8	1	0	2.209653	1.790085	0.147497
9	1	0	1.358039	-0.382170	-1.785694
10	1	0	2.940356	-0.157069	-1.034994
11	1	0	1.265764	-2.237166	-0.302776
12	1	0	2.277772	-1.443735	0.923645
13	6	0	-0.796706	0.019377	0.523948
14	17	0	-2.289352	-0.078153	-0.342426

Zero-point correction= 0.112557 (Hartree/Particle)
Thermal correction to Energy= 0.118964
Thermal correction to Enthalpy= 0.119908
Thermal correction to Gibbs Free Energy= 0.081404
Sum of electronic and zero-point Energies= -692.839761
Sum of electronic and thermal Energies= -692.833354
Sum of electronic and thermal Enthalpies= -692.832409
Sum of electronic and thermal Free Energies= -692.870914

1-Chlorocyclohexa-1,2-diene (14)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.122675	-0.058566	-0.519645
2	6	0	1.501013	-1.288524	0.143859
3	6	0	0.183980	-1.249593	0.311856
4	6	0	-0.606905	-0.190405	0.395631
5	6	0	0.122168	1.082056	0.776511
6	6	0	1.248779	1.221402	-0.303288
7	1	0	2.154983	-2.038446	0.583702
8	1	0	3.112249	0.072182	-0.061968
9	1	0	2.303477	-0.208275	-1.590590
10	1	0	-0.530816	1.958924	0.761131
11	1	0	0.551151	0.995005	1.779223
12	1	0	0.763651	1.497419	-1.245195
13	1	0	1.902212	2.057034	-0.027383
14	17	0	-2.216892	-0.084239	-0.295792

Zero-point correction= 0.112043 (Hartree/Particle)
Thermal correction to Energy= 0.118604
Thermal correction to Enthalpy= 0.119548
Thermal correction to Gibbs Free Energy= 0.080956

Sum of electronic and zero-point Energies= -692.856509
Sum of electronic and thermal Energies= -692.849948
Sum of electronic and thermal Enthalpies= -692.849004
Sum of electronic and thermal Free Energies= -692.887596

1-Cyclopentene(chloro)carbene (12 - Z)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.386836	0.854651	-1.530490
2	6	0	-0.250814	0.089625	-0.217592
3	6	0	1.063061	-0.005640	0.137997
4	6	0	1.978449	0.624122	-0.868632
5	6	0	1.058411	0.892249	-2.090577
6	1	0	-1.102306	0.379668	-2.207395
7	1	0	-0.766131	1.864011	-1.321963
8	1	0	1.414818	-0.515692	1.029355
9	1	0	2.382573	1.556822	-0.441358
10	1	0	2.848778	0.000272	-1.104787
11	1	0	1.294422	1.833345	-2.594940
12	1	0	1.189668	0.088207	-2.822773
13	6	0	-1.360670	-0.642110	0.329300
14	17	0	-1.168907	-0.946119	2.053166

Zero-point correction= 0.110699 (Hartree/Particle)
Thermal correction to Energy= 0.117632
Thermal correction to Enthalpy= 0.118576
Thermal correction to Gibbs Free Energy= 0.078906
Sum of electronic and zero-point Energies= -692.831103
Sum of electronic and thermal Energies= -692.824170
Sum of electronic and thermal Enthalpies= -692.823226

1-Cyclopentene(chloro)carbene (12 - E)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.138843	-0.133652	-1.185032
2	6	0	0.162493	-0.071791	0.339235
3	6	0	1.359858	-0.526065	0.812454
4	6	0	2.291973	-0.936108	-0.283208
5	6	0	1.369993	-1.012388	-1.530299
6	1	0	-0.798962	-0.544935	-1.568919
7	1	0	0.227905	0.879560	-1.598185
8	1	0	1.603700	-0.546759	1.870486

9	1	0	3.074082	-0.167520	-0.392346
10	1	0	2.820202	-1.871166	-0.061423
11	1	0	1.875903	-0.694457	-2.445849
12	1	0	1.051083	-2.049791	-1.677808
13	6	0	-0.770574	0.401010	1.323688
14	17	0	-2.186437	1.098178	0.530178

Zero-point correction= 0.111104 (Hartree/Particle)
Thermal correction to Energy= 0.117906
Thermal correction to Enthalpy= 0.118850
Thermal correction to Gibbs Free Energy= 0.079371
Sum of electronic and zero-point Energies= -692.838433
Sum of electronic and thermal Energies= -692.831631
Sum of electronic and thermal Enthalpies= -692.830687
Sum of electronic and thermal Free Energies= -692.870167

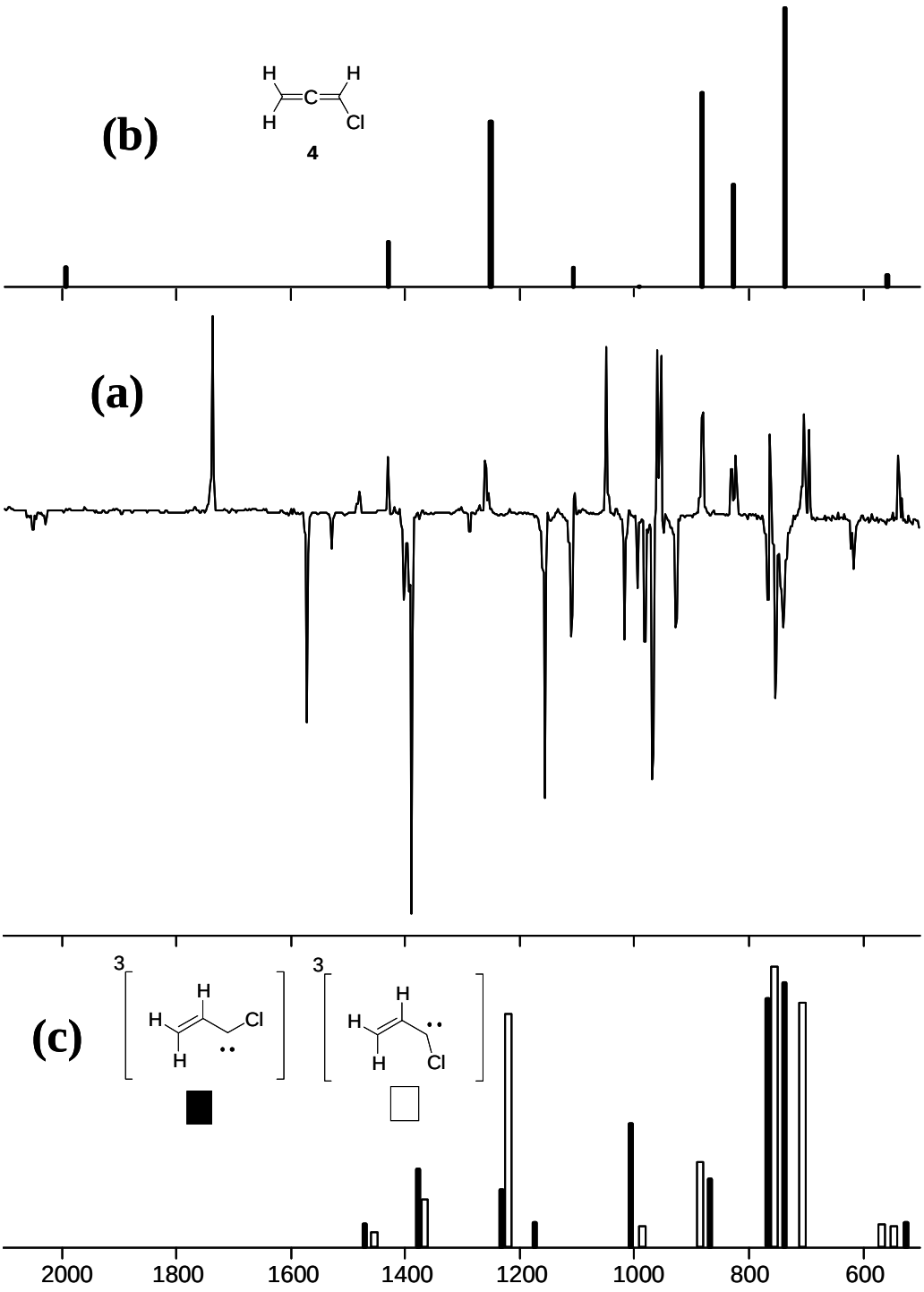

Figure S-1. (a) Difference of IR spectra taken before (displaying carbene **2** as "down bands", generated by 385 nm irradiation of diazirine **1**) and after 1 h at 578 nm irradiation in N_2 at 8 K (displaying products as "up bands"). Spectra are plotted in arbitrary absorbance units. (b) B3LYP/6-31+G** calculated IR spectrum for chloroallene **4**. (c) B3LYP/6-31+G** calculated IR spectrum for *triplet* **2**: *s*-E filled bars, *s*-cisoid open bars. All calculated frequencies are scaled by 0.97 factor.

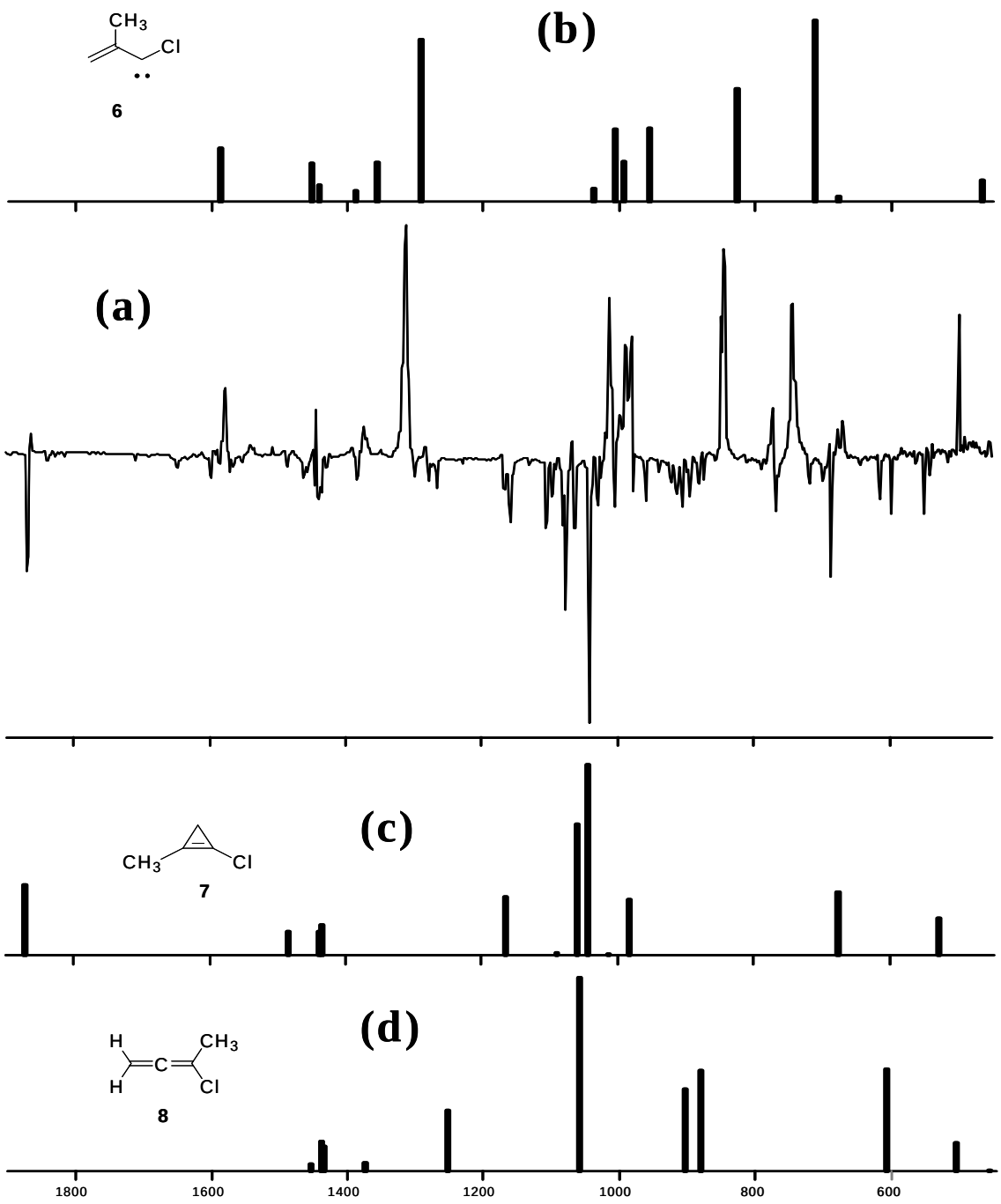

Figure S-2. (a) Difference of IR spectra taken before (displaying carbene **6** as "up bands", generated by 385 nm irradiation of diazirine **5**) and after 2 h at 578 nm irradiation in N_2 at 8 K (displaying product **7** as "down bands"). Spectra are plotted in arbitrary absorbance units. (b) B3LYP/6-31+G** calculated IR spectrum for carbene **6**. (c) B3LYP/6-31+G** calculated IR spectrum for methylchlorocyclopropene **7**. (d) B3LYP/6-31+G** calculated IR spectrum for chloromethylallene **8**. All calculated frequencies are scaled by 0.97 factor.

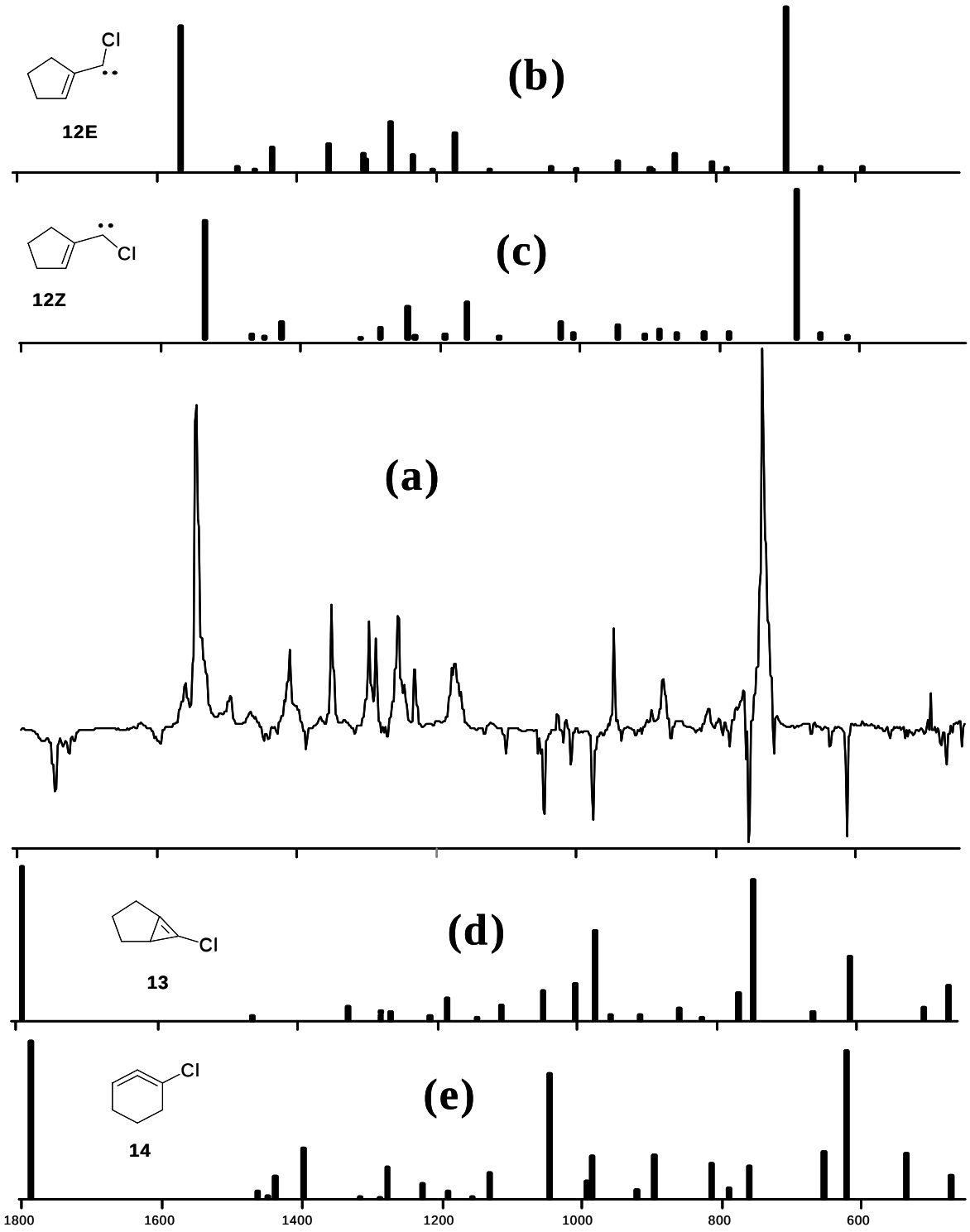

Figure S-3. (a) Difference of IR spectra taken before (displaying carbene **12** as "up bands", generated by 385 nm irradiation of diazirine **11**) and after 3.5 h at 600 nm irradiation in N_2 at 10 K (displaying product **13** as "down bands"). Spectra are plotted in arbitrary absorbance units. (b) B3LYP/6-31+G** calculated IR spectrum for s-E carbene **12**. (c) B3LYP/6-31+G** calculated IR spectrum for s-Z carbene **12**. (d) B3LYP/6-31+G** calculated IR spectrum for bicyclopropene **13**. (e) B3LYP/6-31+G** calculated IR spectrum for allene **14**. All calculated frequencies are scaled by 0.97 factor.

References for Supporting Information

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