Supporting Information

Spectroscopy and Photochemistry of

Triplet Methylpentadiynylidene (Me−C≡C−C̈−C≡C−H)

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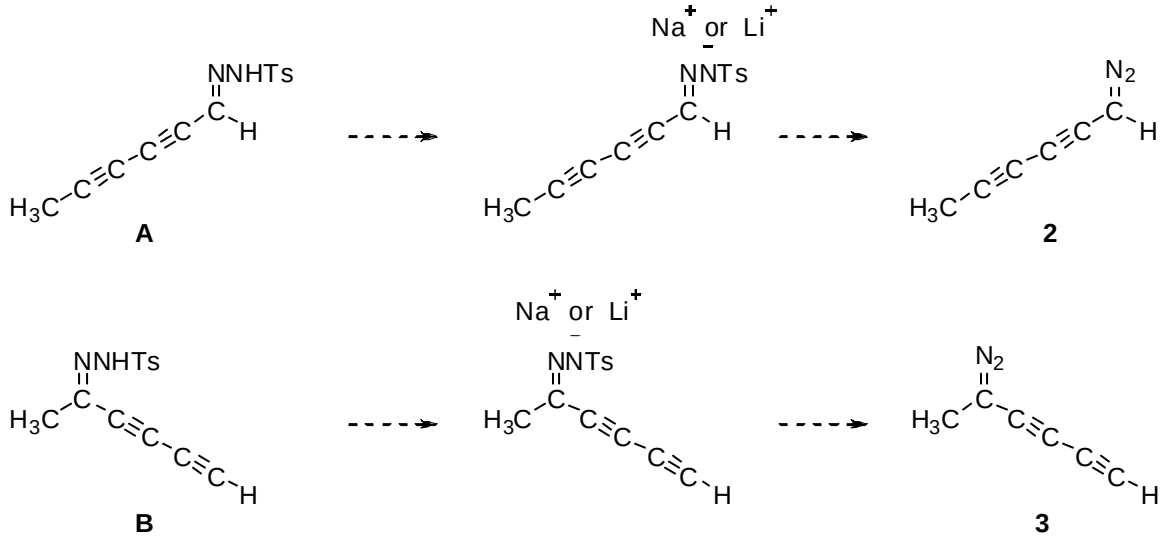
Matrix-Isolation Spectroscopy. Irradiation was carried out with an ILC Technology LX300UV 300 W high-pressure xenon arc lamp, and wavelength selection was achieved with cut-off filters ($\lambda > 613$ nm, Corning 2-58; $\lambda > 534$ nm, Corning 3-66; $\lambda > 497$ nm, Corning 3-69; $\lambda > 472$ nm, Corning 3-71; $\lambda > 444$ nm, Corning 3-72; $\lambda > 399$ nm, Corning 3-74; $\lambda > 363$ nm, Corning 3-75; $\lambda > 328$ nm, Schott WG 345; $\lambda > 300$ nm, Schott WG 320; $\lambda > 280$ nm, Pyrex; $\lambda > 261$ nm; Corning 0-53; $\lambda > 237$ nm, Corning 0-56) or a Spectral Energy GM 252 monochromator (bandpass of 20 nm). All IR spectra were recorded on a Nicolet Nexus 870 FT-IR spectrometer with a DTGS detector: mid-IR experiments (400-4000 cm^{-1}) employed KBr outer windows and a spectral resolution of 2 cm^{-1}; far-IR (200-600 cm^{-1}) scans were performed using CsI outer windows and a resolution of 4 cm^{-1}. UV-vis spectra were recorded with a Varian Cary 5000 UV/vis/NIR spectrophotometer utilizing a spectral bandwidth of 2.0 nm. EPR spectra were obtained on a Bruker ESP 300 spectrometer with a Bruker ER 042 MRH E microwave bridge and an EIP Model 625A microwave frequency counter.



Hexa-2,4-diynal Tosylhydrazone (A) and Hexa-3,5-diyn-2-one Tosylhydrazone (B). The syntheses of tosylhydrazone precursors to diazo compounds **2** and **3** are described elsewhere.[1]

1-Diazo-hexa-2,4-diyne (2) from sodium salt of tosylhydrazone A. To an oven-dried 50 mL round-bottom flask with 14/20 joint, a stir bar and 104.0 mg (0.400 mmol) *anti*-tosylhydrazone **A** were added. The solid was dissolved by adding 5 mL CH_2Cl_2 (dried over CaH_2, distilled), and the flask was outfitted with a stopper with N_2 bleed-in and bleed-out

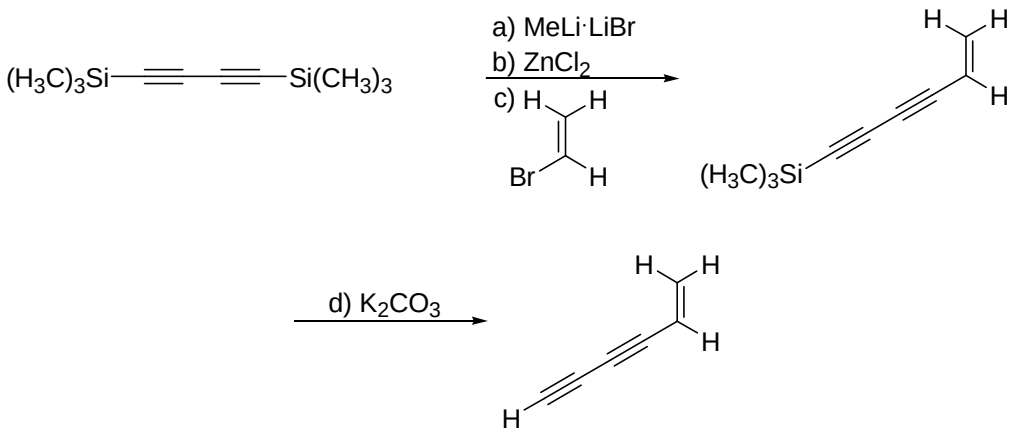
needles. To this mixture, 16.4 mg NaH (1.03 eq. 60 % in mineral oil) was added, the bleed-out needle was removed, and the mixture was stirred for 4.1 h. Meanwhile, a deposition tube modified with a side valve, a connecting U-tube, and a terminating round-bottom flask were flame dried, assembled, and evacuated. The side valve was closed, and the U-tube and terminating round-bottom flask were vented to N_2. After stirring, the stir bar was quickly removed from the sample flask, and the terminating round-bottom flask at the end of the U-tube was immediately replaced with the sample flask. The sample flask was subsequently cooled to −60 °C and evacuated. The sample was pumped under roughing pump vacuum (0.3 mmHg) for 15-20 min, until the solvent layer was no longer visible, and a yellow-white solid remained on the walls of the flask. Once the solvent layer had been removed, the sample was pumped at room temperature for 0.5-1.0 h, and an oil bath was preheated to 75 °C. The deposition tube was immersed in liquid N_2, and thermolysis of the salt was initiated by raising the oil bath to the sample. Within 2 min, the sample turned black, and diazo compound **2** began to appear as an orange solid in the side valve of the deposition tube shortly thereafter. Diazo collection proceeded for 1.1 h. The deposition tube was sealed and transferred to the matrix isolation apparatus. The sample was pumped under diffusion pump vacuum until the pressure fell below 1 × 10^{-6} mmHg, first at 77 K, then at −78 °C. One freeze-pump-thaw cycle was performed at −41 °C, after which the spectroscopic window was cooled to 30 K. Diazo compound **2** was warmed to −24 °C and co-deposited with argon for 2.9 h at an argon deposition rate of 0.8 mmHg/min. During deposition, diazo compound **2** showed visible signs of decomposition in the deposition tube. The IR spectrum, obtained after cooling the matrix to 10 K, revealed a maximum diazo absorbance of 1.3 absorbance units (infrared band at 2076 cm^{-1}). A large amount of matrix-isolated water was evident in the infrared spectrum, leading us to consider an alternate route.

1-Diazo-hexa-2,4-diyne (2) from lithium salt of tosylhydrazone A. In an oven-dried 25 mL round-bottom flask with 14/20 joint, a stir bar and 29.1 mg (0.112 mmol) *anti*-tosylhydrazone **A** were added. The solid was dissolved by adding 6 mL Et_2O (dried over CaH_2, distilled) with stirring, and the flask was outfitted with a stopper with N_2 bleed-in and bleed-out needles. After purging the sample with N_2 for 20 min, the bleed-out needle was removed and the sample was cooled to −78 °C. Addition of 60 μL 2.3 M *n*-BuLi (in hexanes) resulted in the sample turning a red-orange color, which faded upon warming to reveal a white solid. Meanwhile, an oven-dried glass deposition adaptor was attached to a vacuum line and flushed

with N_2. Once the sample reached room temperature, the stir bar was then quickly removed from the sample flask, and the sample flask immediately attached to the deposition adaptor. After momentary evacuation, the sample flask was cooled to −78 °C. The sample was pumped under roughing pump vacuum (0.1 torr) for 20 min at −78 °C, followed by 30 min at room temperature. Afterward, the sample was vented to N_2, transferred to the matrix-isolation apparatus, and pumped under diffusion pump vacuum at −15 °C until the final pressure dropped below 1×10^{-6} mmHg. Pumping was continued at room temperature, during which time the sample turned blue. After the pressure fell below 1×10^{-6} mmHg, the spectroscopic window was cooled to 11 K. Diazo compound **2** was deposited by thermolysis of the lithium tosylhydrazide salt for 30 min at 76 °C concomitant with N_2 deposition at a rate of 1.1 mmHg/min. This method resulted in a larger amount of diazo deposited and a much cleaner IR spectrum than the previous procedure.

2-Diazo-hexa-3,5-diyne (3) from lithium salt of tosylhydrazone B. The procedure for generation of diazo compound **3** is similar to that of **2**. In an oven-dried 50 mL round-bottom flask with 14/20 joint, a stir bar and 33.0 mg (0.127 mmol) *anti*- tosylhydrazone **B** were added. A portion of the solid was dissolved by adding 6 mL Et_2O (dried over CaH_2, distilled) with stirring, and the flask was outfitted with a stopper with N_2 bleed-in and bleed-out needles. The remaining solid appeared as a brown suspension throughout the procedure. After purging the sample with N_2 for 20 min, the bleed-out needle was removed, and the sample was cooled to −78 °C. Addition of 60 μL 2.29 M *n*-BuLi (in hexanes) resulted in the sample turning slightly lighter in color, followed by darkening with warming. Meanwhile, an oven-dried glass deposition adaptor was attached to a vacuum line and flushed with N_2. Once the sample reached room temperature, the stir bar was then quickly removed from the sample flask, and the sample flask immediately attached to the deposition adaptor. After momentary evacuation, the sample flask was cooled to −78 °C. The sample was pumped under roughing pump vacuum for 2 min at −78 °C, followed by 0.5 h at room temperature. Afterwards, the sample was vented to N_2, transferred to the matrix-isolation apparatus, and pumped under diffusion pump vacuum at room temperature until the final pressure dropped below 1×10^{-6} mmHg. Afterward, the spectroscopic window was cooled to 21 K. Diazo compound **3** was deposited by thermolysis of the lithium tosylhydrazide salt for 30 min at 80 °C concomitant with N_2 deposition at a rate of 1.3 mmHg/min. Finally, the spectroscopic window was cooled to 10 K at which temperature all spectroscopy and irradiation took place.

Scheme S1. Synthesis of authentic sample of hex-1-ene-3,5-diyne.



6-(Trimethylsilyl)-hex-1-ene-3,5-diyne. In a flame-dried 100 mL round-bottom flask 0.500 g (2.57 mmol) bis(trimethylsilyl)butadiyne was dissolved in 25 mL dry THF. To this solution 1.71 mL 1.5 M MeLi·LiBr was added dropwise via syringe, and the resultant mixture was stirred for 3.5 h at RT. Afterwards, this mixture was added to a mixture of 0.350 g $ZnCl_2$ in 5 mL dry THF precooled to −30°C. After slowly warming the resultant mixture to 0 °C, 0.212 mL vinyl bromide and 0.173 g $Pd(PPh_3)_4$ were added, and this reaction mixture was stirred for 14 h at RT. This final mixture was extracted with ether, washed sequentially with sat. aq. NH_4Cl and sat. aq. $NaHCO_3$, dried over $MgSO_4$, and concentrated to reveal an oily solid, which was purified by flash chromatography (pentane, $R_f = 0.67$). 0.119 g colorless oil was isolated (31 % yield). ^{1}H NMR δ 5.81 (d, J = 7.2 Hz, 1H), 5.81 (d, J = 6.3 Hz, 1H), 5.65 (dd, J = 6.9, 6.3 Hz, 1H), 0.21 (s, 9H). ^{13}C NMR δ 131.0, 116.1, 90.8, 87.9, 75.7, 75.0.

Hex-1-ene-3,5-diyne (6). 6-(Trimethylsilyl)-hex-1-ene-3,5-diyne (7.7 mg, 0.052 mmol) was drawn up into a Pasteur pipet by capillary action, and subsequently was flushed into a small round-bottom flask using 5 mL MeOH. To this solution 11.1 mg of K_2CO_3 was added, and the mixture was stirred for 45 min at RT. The resultant mixture was extracted with decane, washed with water, and dried over $MgSO_4$. The solution of **6** in decane was microfiltered into a deposition tube, from which **6** was deposited at −63 °C (chloroform/N_2) for matrix-isolation purposes.

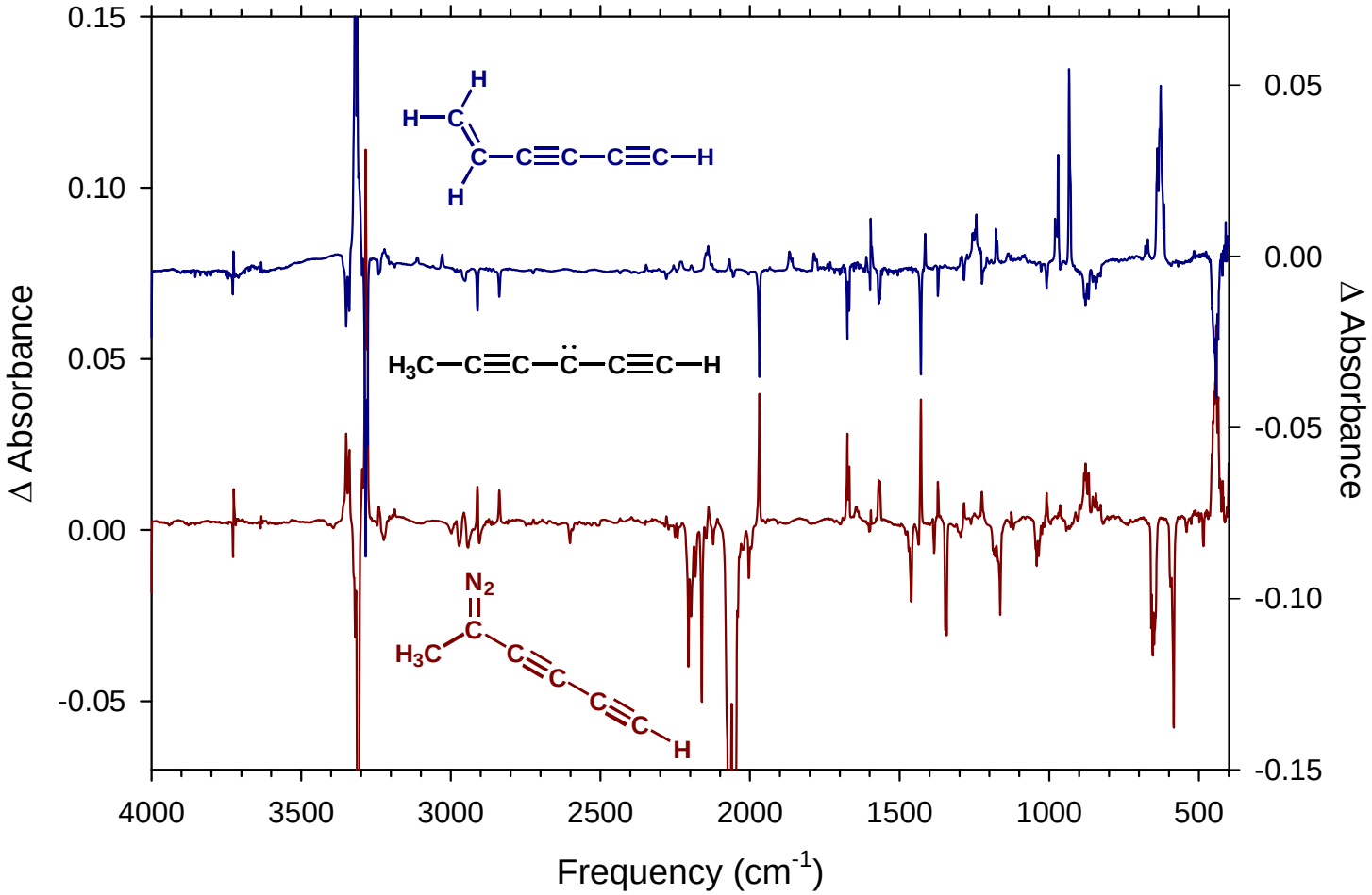


Figure S1. IR subtraction spectra showing generation and photochemistry of MeC_5H (**1**). Bottom: difference IR showing disappearance of diazo compound **3** with growth of triplet MeC_5H (**1**) ($\lambda > 497$ nm, 80 min, N_2, 10 K). Top: difference IR showing photolysis of triplet MeC_5H (**1**) to yield enediyne **6** ($\lambda > 363$ nm, 14.3 h; $\lambda > 444$ nm, 2 h; N_2, 10 K).

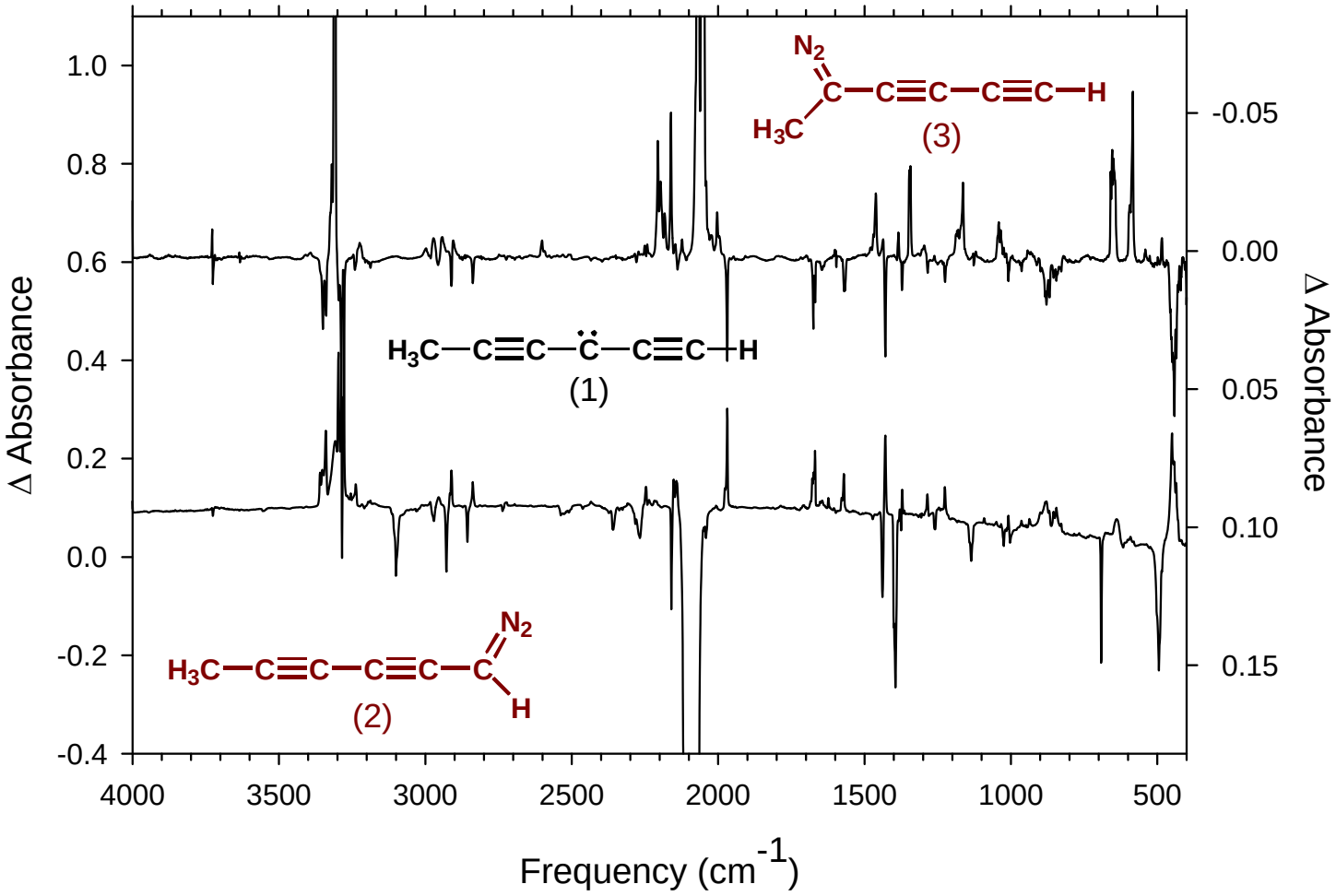


Figure S2. Comparison of the spectra of MeC_5H (**1**) as generated from diazo compounds **2** and **3**. Top: difference IR showing disappearance of diazo **3** with growth of carbene **1** ($\lambda > 497$ nm, 80 min, N_2, 10 K). Bottom: difference IR showing disappearance of diazo **2** with growth of carbene **1** ($\lambda > 497$ nm, 3 h, N_2, 10 K). The top spectrum is inverted to facilitate comparison of carbene bands.

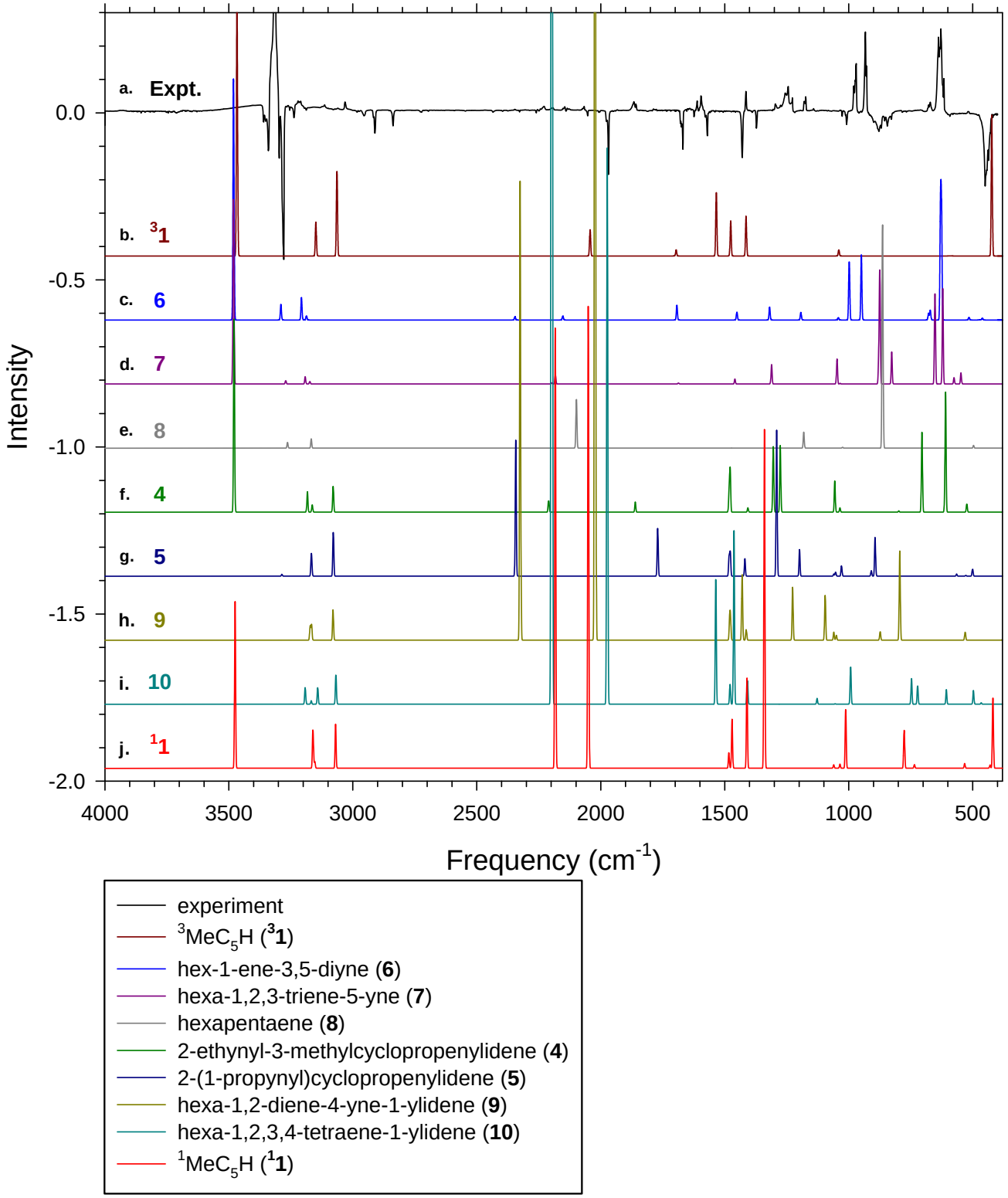


Figure S3. (a) Experimental IR subtraction spectrum showing disappearance of triplet MeC_5H (**1**) and the appearance of photoproduct upon irradiation ($\lambda > 399$ nm, 21.2 h). (b-j) Comparison with computed harmonic vibrational frequencies and IR intensities of various C_6H_4 isomers (CCSD/cc-pVDZ).

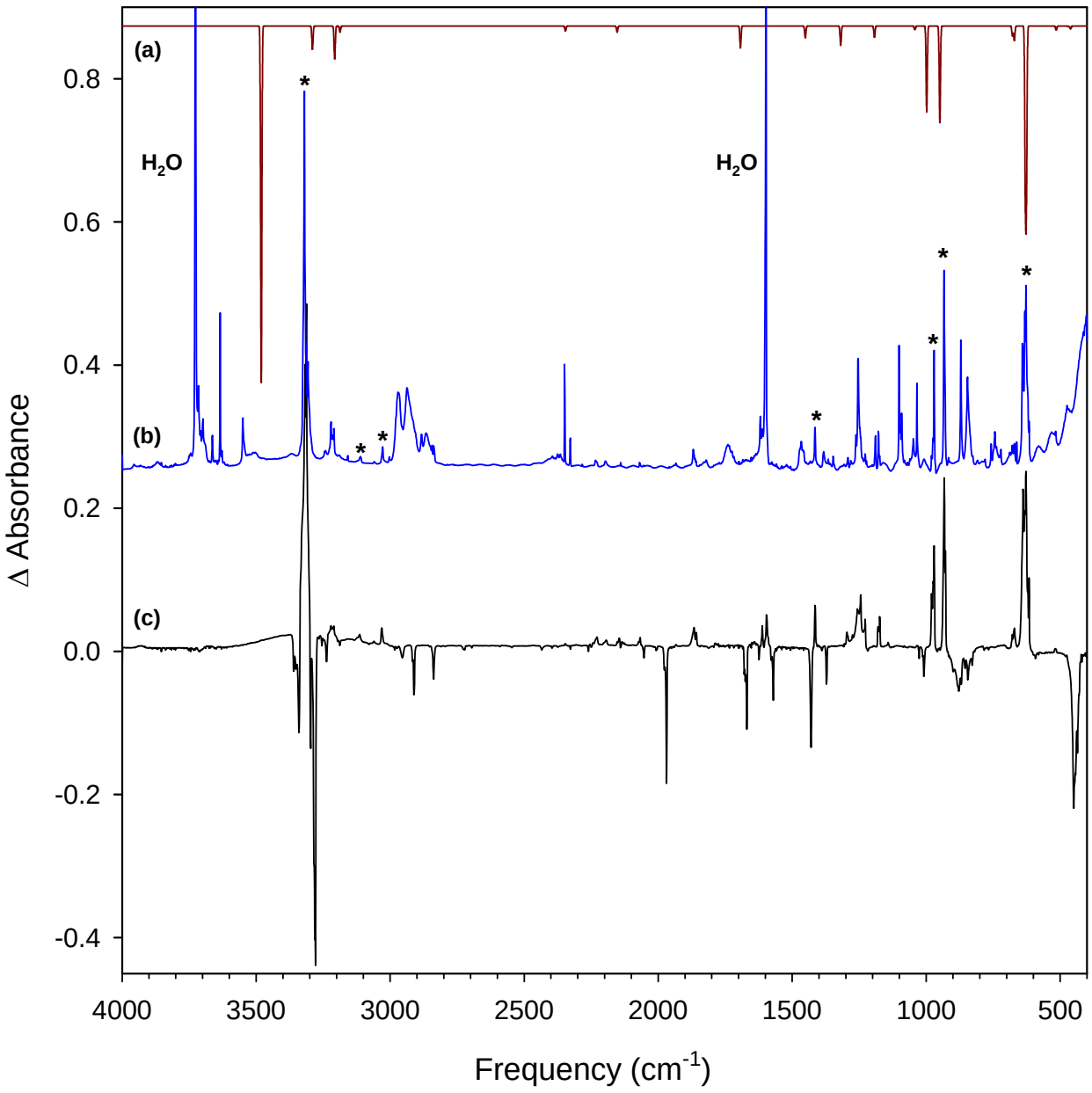


Figure S4. (a) Computed harmonic vibrational frequencies and IR intensities (CCSD/cc-pVDZ) for hex-1-en-3,5-diyne (**6**). (b) IR spectrum of an authentic sample of hex-1-ene-3,5-diyne (**6**) (N_2, 10 K). Bands assigned to **6** are marked with an asterisk (*). The sample is contaminated with H_2O and other impurities. (c) Experimental IR subtraction spectrum showing disappearance of triplet MeC_5H (**1**) and the appearance of hex-1-ene-3,5-diyne (**6**) upon irradiation ($\lambda > 399$ nm, 21.2 h).

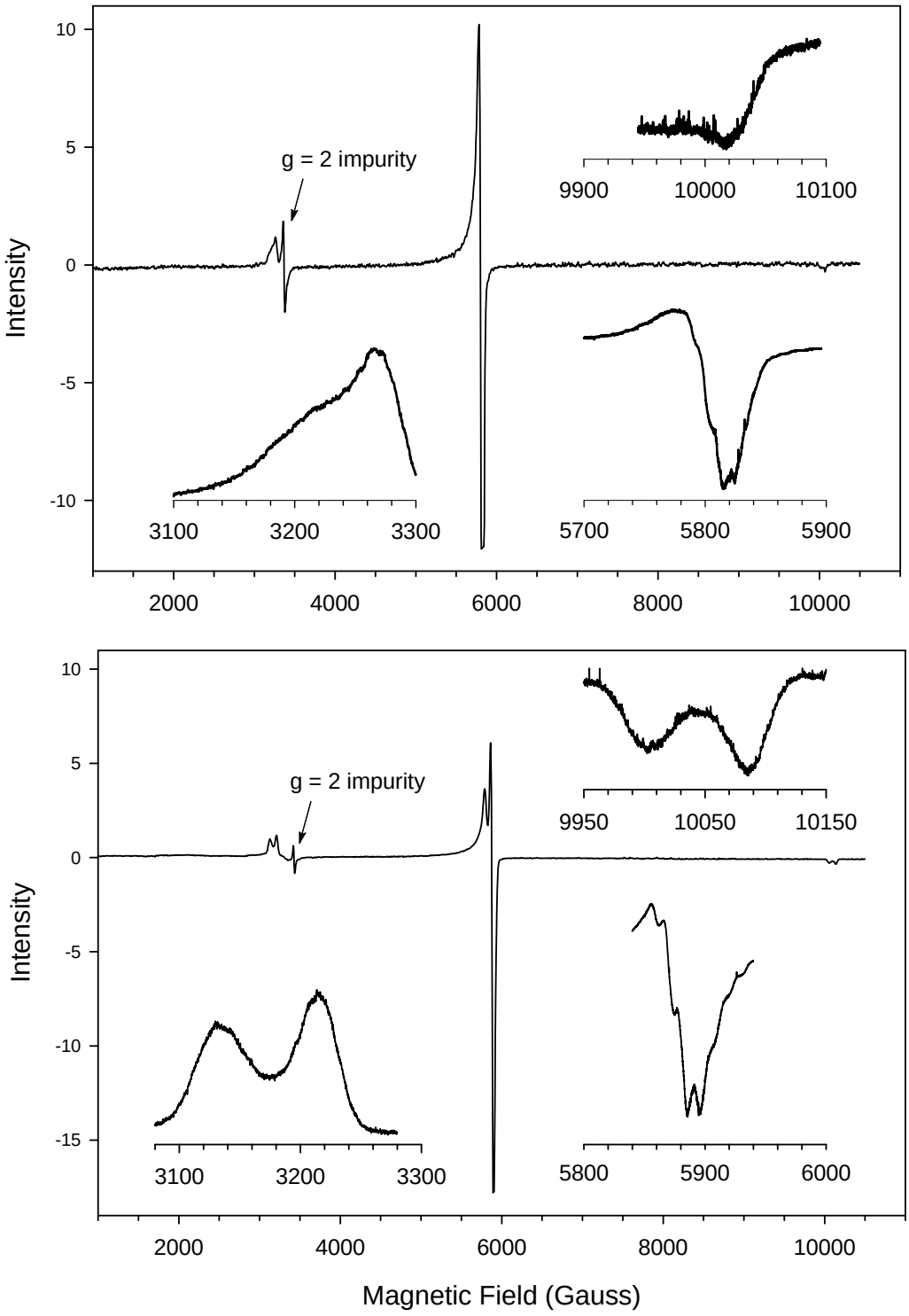


Figure S5. Top: EPR spectrum of triplet MeC_5H (**1**) obtained upon irradiation ($\lambda > 497$ nm, 16 h) of 1-diazo-hexa-2,4-diyne (**2**) (N_2, 15 K). Bottom: EPR spectrum of triplet MeC_5H (**1**), obtained upon irradiation ($\lambda > 472$ nm, 19.4 h) of 2-diazo-hexa-3,5-diyne (**3**) (N_2, 15 K).

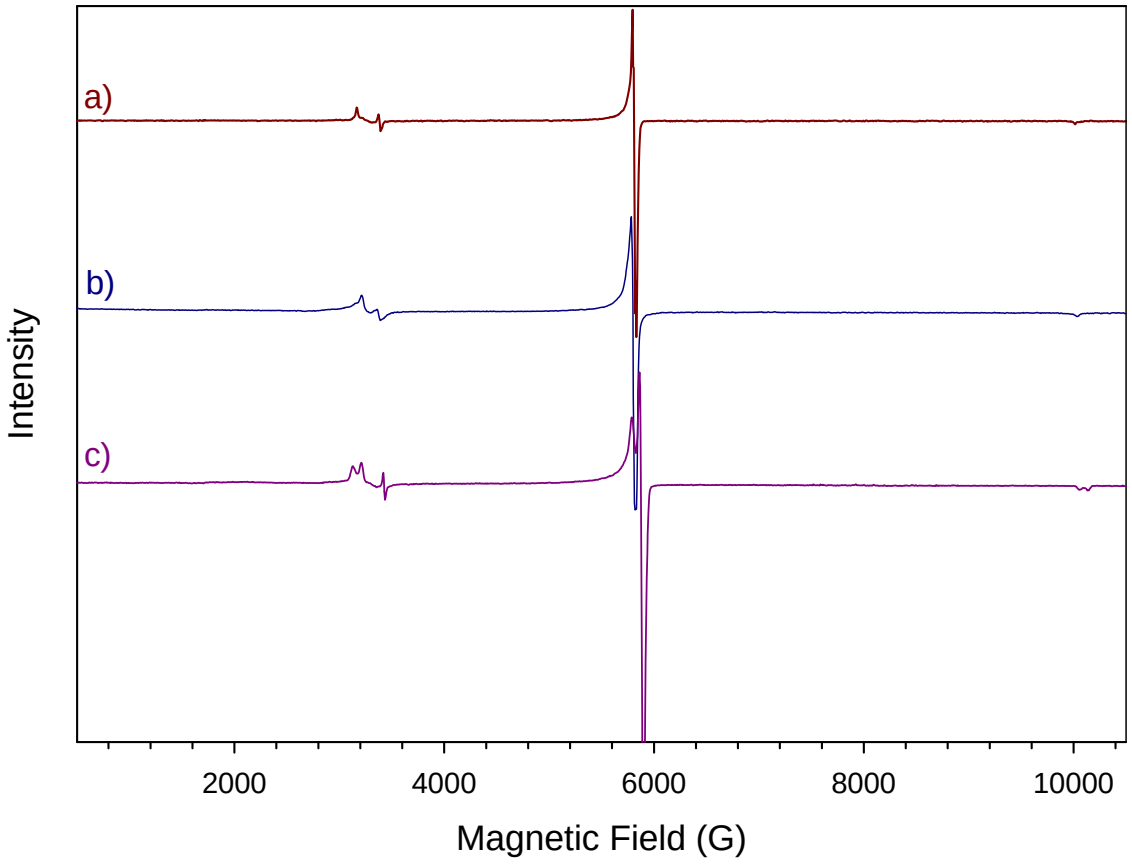


Figure S6. Comparison of the full sweep EPR spectra of HC_5H and MeC_5H (**1**). a) EPR spectrum of HC_5H generated by photolysis of 1-diazo-2,4-pentadiyne, (Ar, 15 K, $\lambda > 444$ nm);[2] b) EPR spectrum of **1** generated by photolysis of diazo **2** (Ar, 15 K, $\lambda > 497$ nm); c) EPR spectrum of **1** generated by photolysis of diazo **3** (N_2, 16 K, $\lambda > 472$ nm).

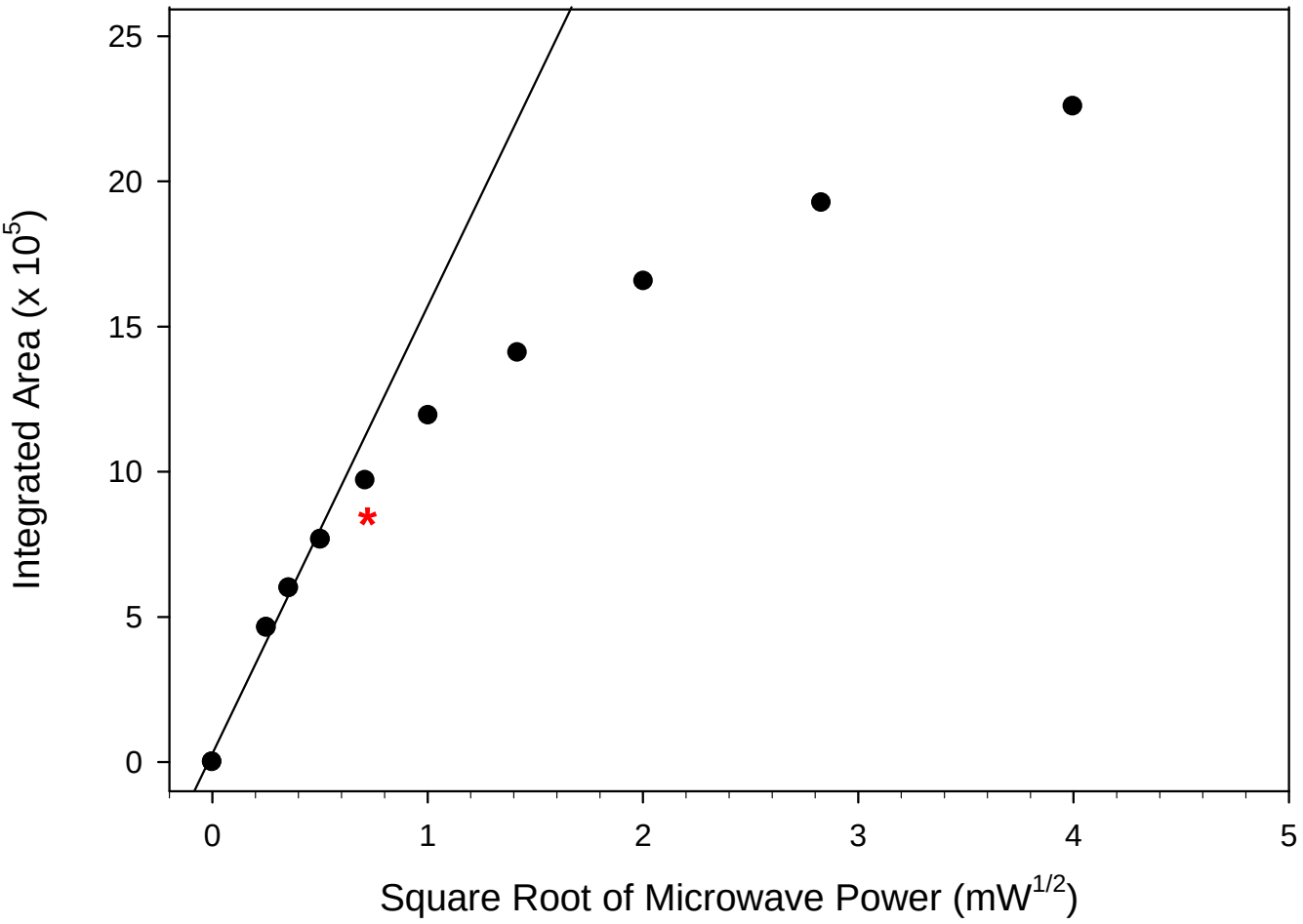


Figure S7. Plot of peak area vs. square root of microwave power for the XY_2 transition of triplet MeC_5H (**1**) in MCH-d_{14} at 4.3 K. Peak area was evaluated by double integration of the EPR signal for the XY_2 transition.

The microwave power used for all successive measurements was 0.51 mW (denoted by asterisk). Subsequent measurement of the temperature dependence of the EPR signal (Figure S8) suggests that this power level was too high, resulting in saturation of the signal at low temperatures and subsequent deviation from Curie Law behavior. Consistent with that hypothesis, this plot reveals that the power level used in the Curie Law measurements (0.51 mW) falls outside the range of linear signal response.

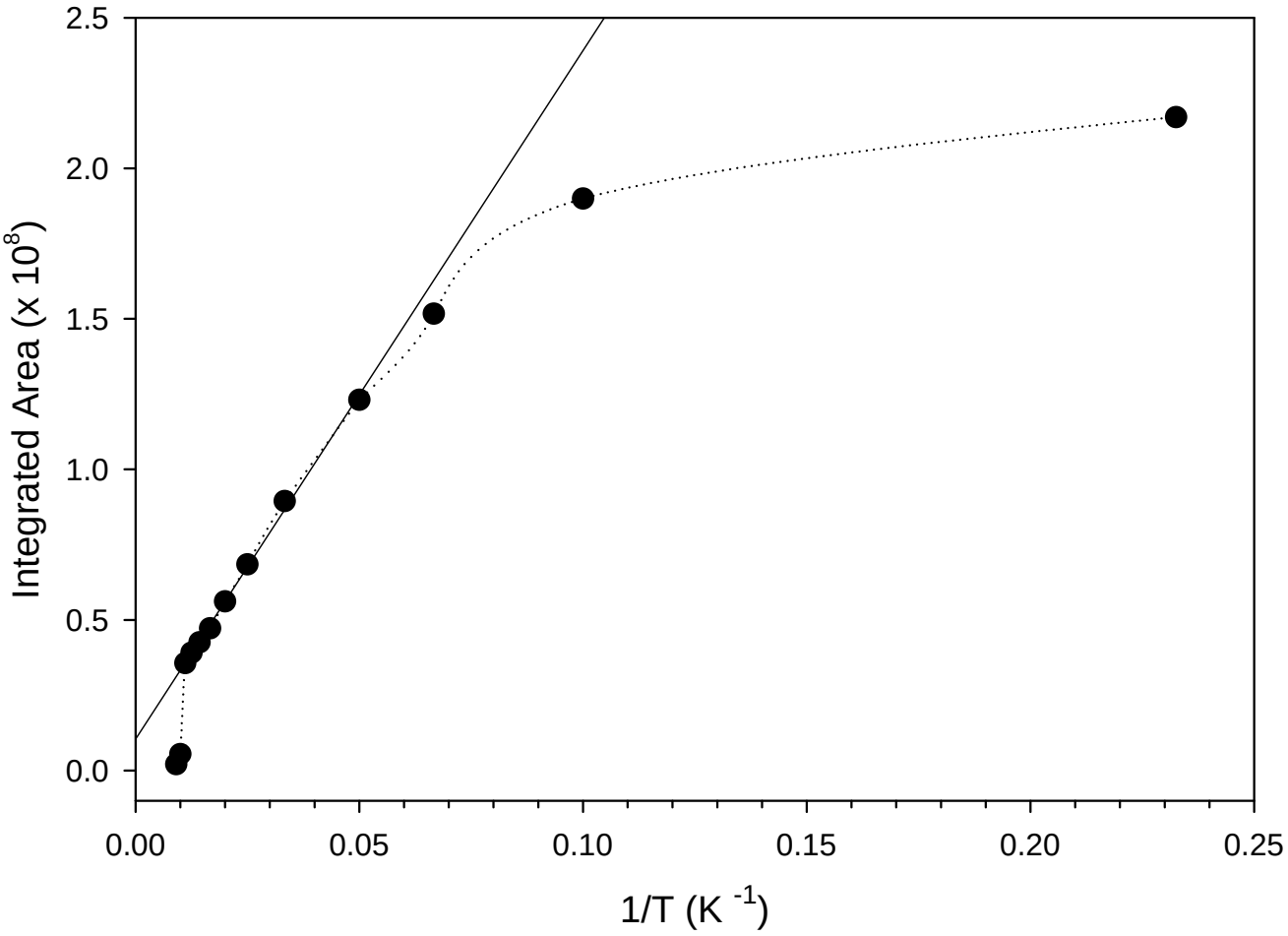


Figure S8. Curie Law plot for triplet MeC_5H (**1**) in MCH-d_{14} over the temperature range 4.3-110 K. The doubly-integrated area of the XY_2 transition is plotted.

The abrupt deviation from linearity at high temperature is due to chemical reaction of the carbene. Loss of the EPR signal is irreversible; the signal is not recoverable upon re-cooling the sample. (See Figure S9)

The deviation from linearity at low temperature is presumably due to saturation of the signal as a result of using excessive microwave power. (See Figure S7)

Curie Law behavior is demonstrated by the linear region of the plot (ca. 15-100 K), and establishes that the triplet state of MeC_5H (**1**) is either the ground state of the molecule, or that it lies within several cal/mol of the ground state. This conclusion agrees with the prediction of quantum chemical calculations.

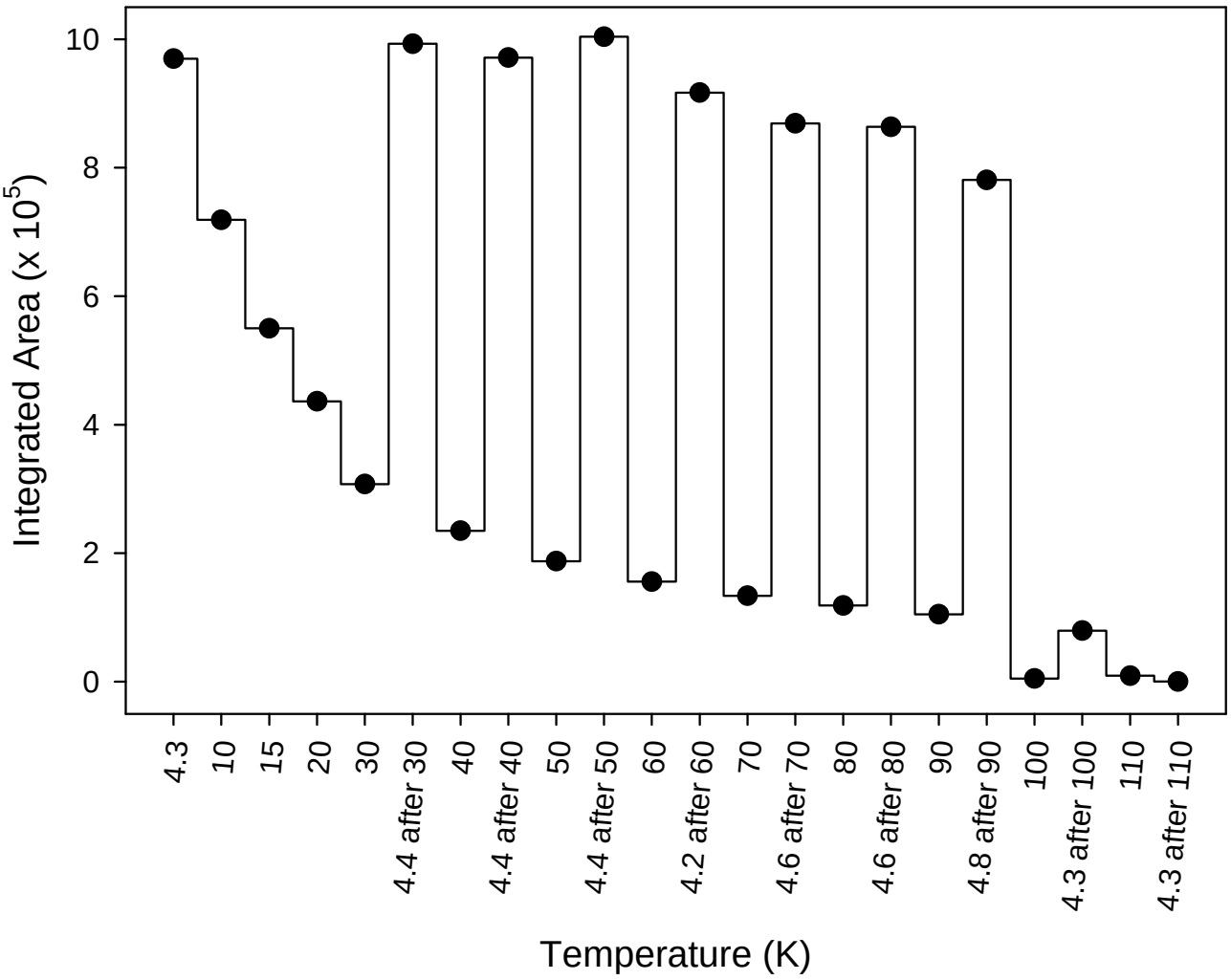
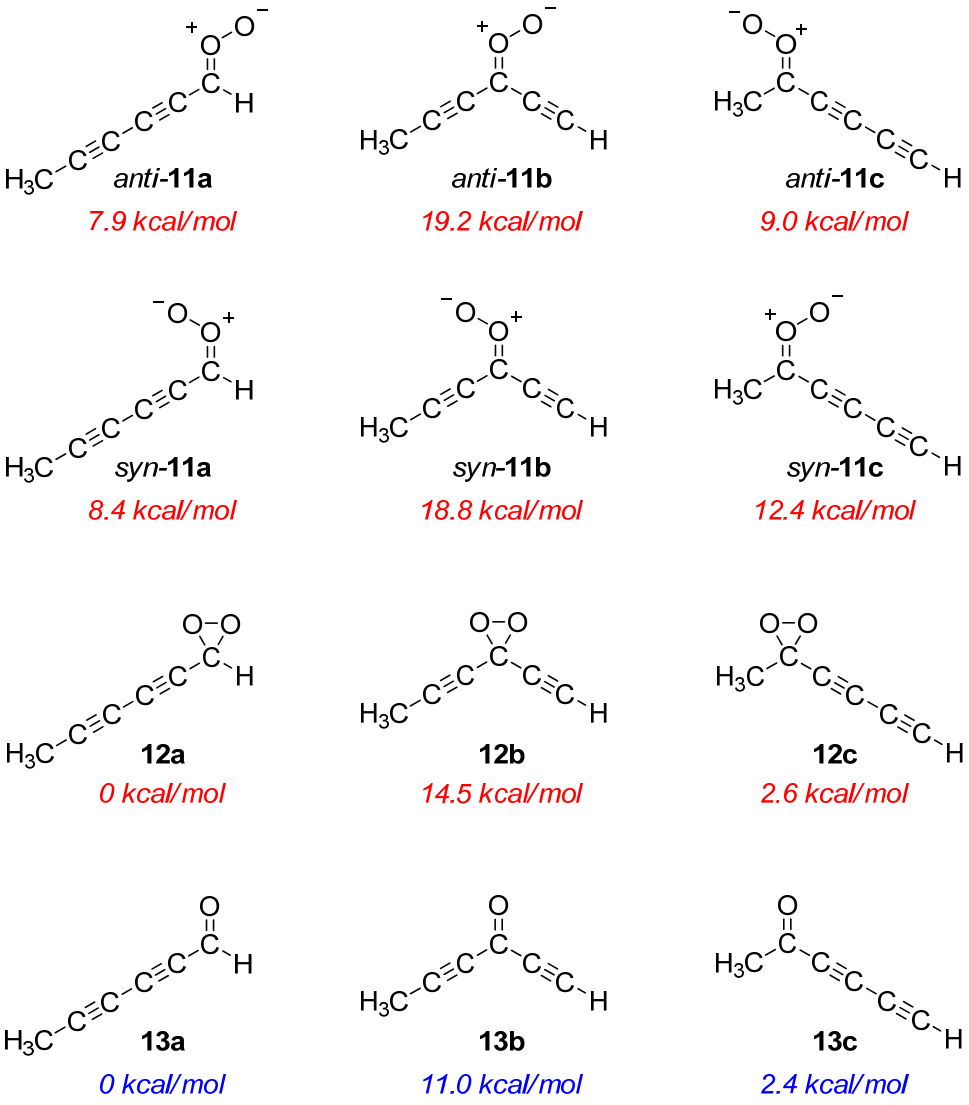


Figure S9. EPR signal intensity for triplet MeC_5H (**1**) in MCH-d_{14} as a function of annealing. This plot shows the doubly-integrated area of the XY_2 transition of **1** as a function of temperature at each successive step of warming / recooling. The majority of the signal intensity is lost, irreversibly, upon warming to 100 K.

Oxygen-trapping Experiments.

Considerable computational effort was devoted to identifying the isomers of oxygen-trapping products (**11**, **12**, and **13**) observed in the matrix. In light of previous oxygen-trapping studies with HC_5H,[2] we anticipated that trapping would occur regioselectively at the central carbon in MeC_5H. The differences in the computed spectra for the isomers of each series of photoproducts, however, are subtle and do not permit unequivocal, quantitative assignments.

Scheme S2. Computed Relative Energies (BLYP/6-31G*).



Irradiation of carbonyl *O*-oxide(s) **11** ($\lambda > 613$ nm) produces a significant amount of carbon monoxide and/or other species exhibiting IR absorptions near 2140 cm^{-1} (Figure S12). We were concerned that acyl radicals, which might exhibit IR absorptions in this region, could be formed upon photolysis of **11** or **13**. The computed IR spectrum for the doublet radical MeC_5O is shown in Figure S15. The spectrum indeed contains a vibrational mode near 2100 cm^{-1}, but it also includes a mode of substantially greater intensity at higher frequency (2300 cm^{-1}). The interpretation of these data turns on the expected accuracy of the computed harmonic vibrational frequencies. If the intense feature at 2300 cm^{-1} does not require scaling, the feature is incompatible with the experimental spectrum. If the intense feature, however, is not suitably modeled with the B3LYP/6-31G* calculation, and the true vibrational frequency is lower by 5-10% (as is commonly the case for cumulenes), then alkynyl acyl radicals such as MeC_5O are highly plausible structures to account for the experimental cluster of bands near 2100 cm^{-1}. This matter is a peripheral point with respect to the current investigation, and has not been pursued further.

Attempts were made to photolyze the dioxirane(s) **12** that had been formed under the $\lambda = 450$ nm conditions (Figures S13 and S14). Broadband irradiation at shorter wavelengths is known to convert dioxiranes to esters.[3-5] After irradiation at $\lambda > 399$ nm (20.3 h), it was clear that dioxirane bands were diminishing (Figure S14), but the interpretation of the spectrum was problematic for several reasons. First, each isomer of dioxirane may give rise to two possible structural isomers of ester, each of which can exist in the form of two distinct rotamers under our conditions. Thus, even if trapping occurred only at the central carbon, then four isomeric esters could be formed. A second problem was that even when the concentration of O_2 in the matrix was 0.81 % (twice the concentration used in the HC_5H study), not all of carbene **1** was consumed upon the initial annealing of the matrix. Therefore the photochemistry of the dioxirane is further obscured by the $\lambda > 399$ nm photolysis of **1** remaining in the matrix.

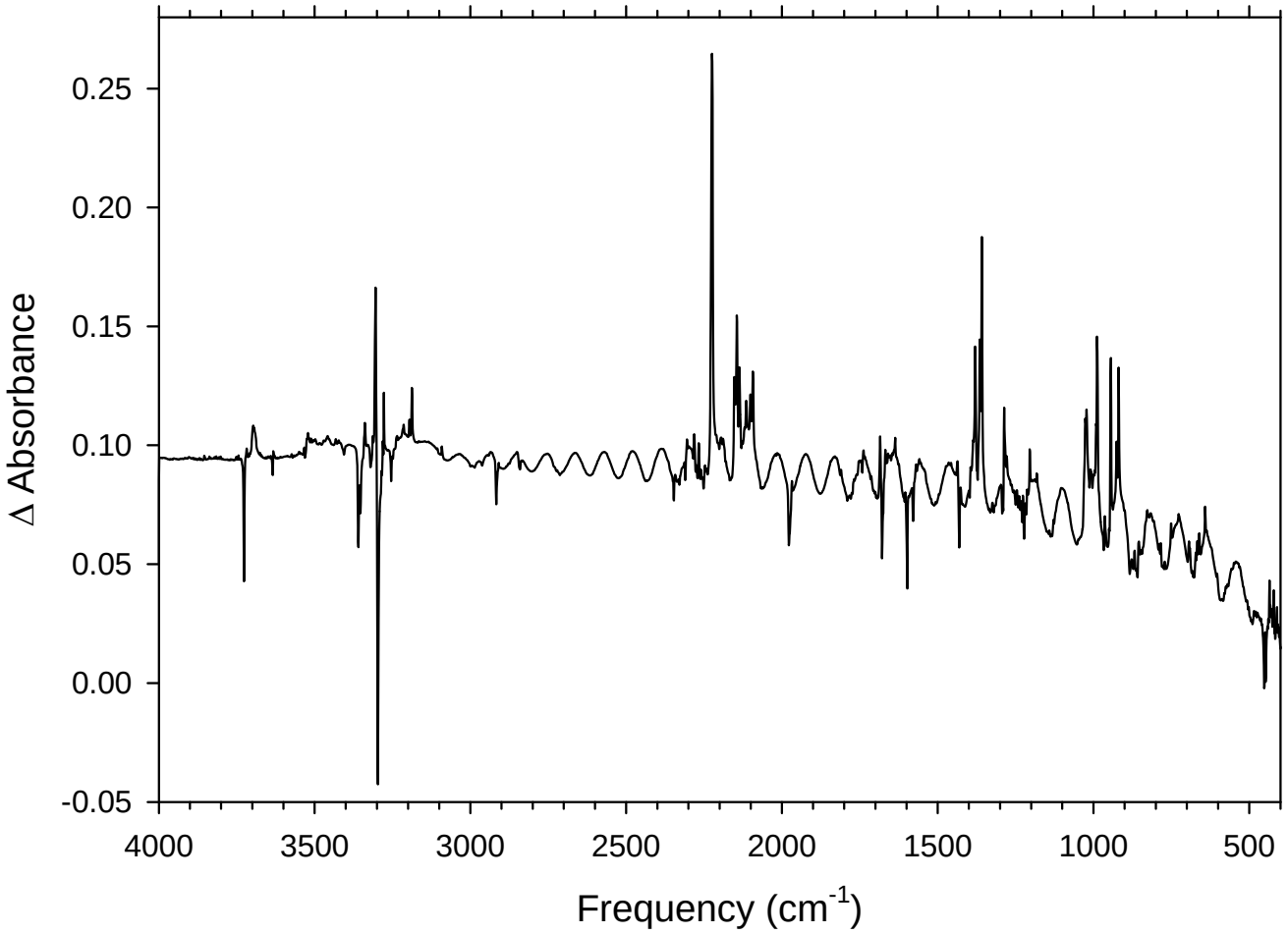


Figure S10. Oxygen trapping of MeC_5H (**1**): difference IR spectrum obtained after annealing an N_2 matrix containing **1** and 0.81% O_2 (warmed to 35 K, 10 min; re-cooled to 9 K). Spectrum shows the decrease of triplet MeC_5H (**1**) and the appearance of carbonyl-*O*-oxide(s) **11**.

See Figure S11 for comparison of experimental and computed IR spectra of carbonyl-*O*-oxide(s) **11**.

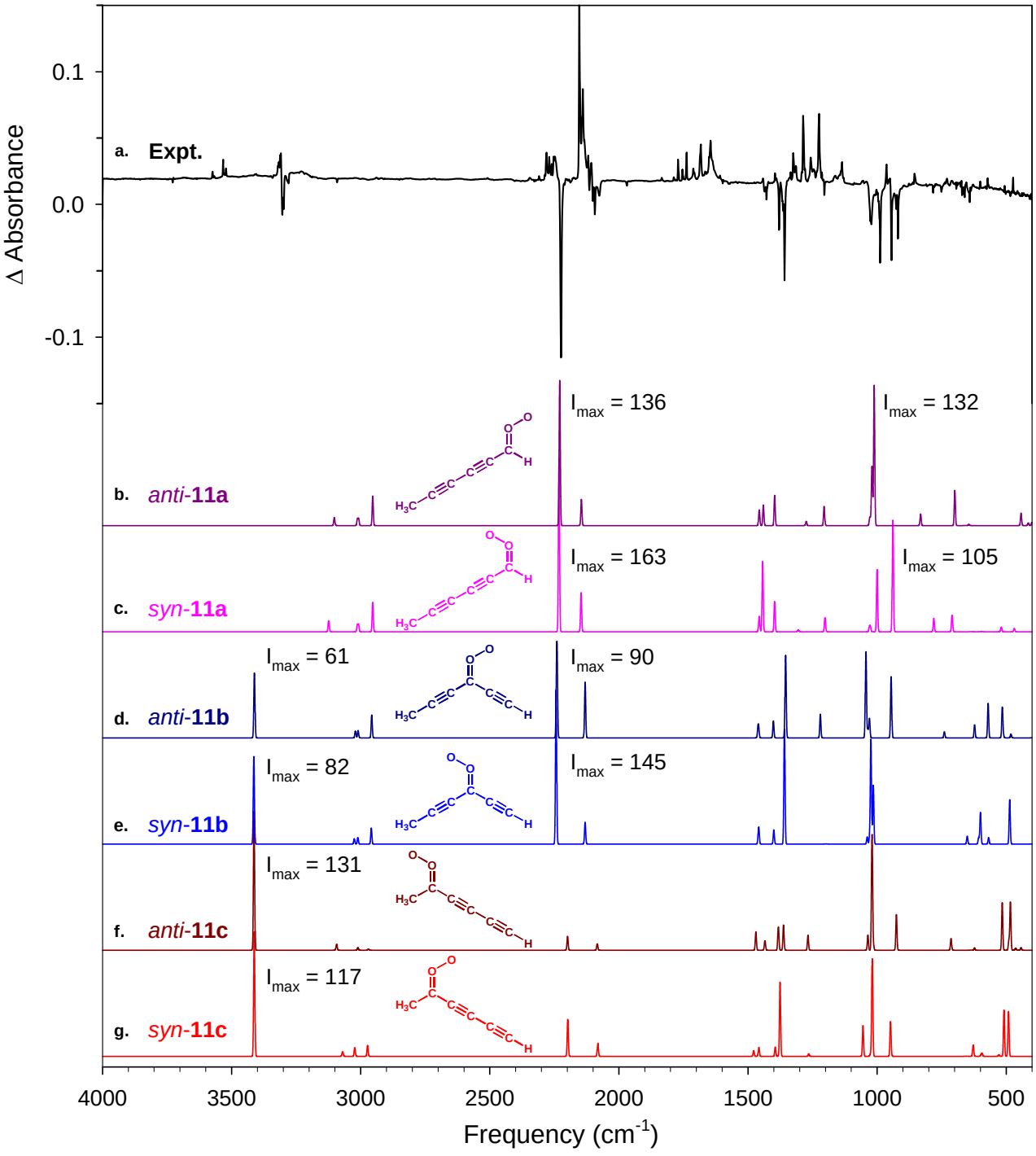


Figure S11. Oxygen trapping of MeC_5H (**1**): (a) difference IR spectrum shows disappearance of carbonyl-*O*-oxide(s) upon photolysis ($\lambda > 613$ nm, 0.7 h, N_2, 9 K). (b-g) The experimental spectrum is compared with computed spectra (BLYP/6-31G*) of carbonyl-*O*-oxide structures (**11**).

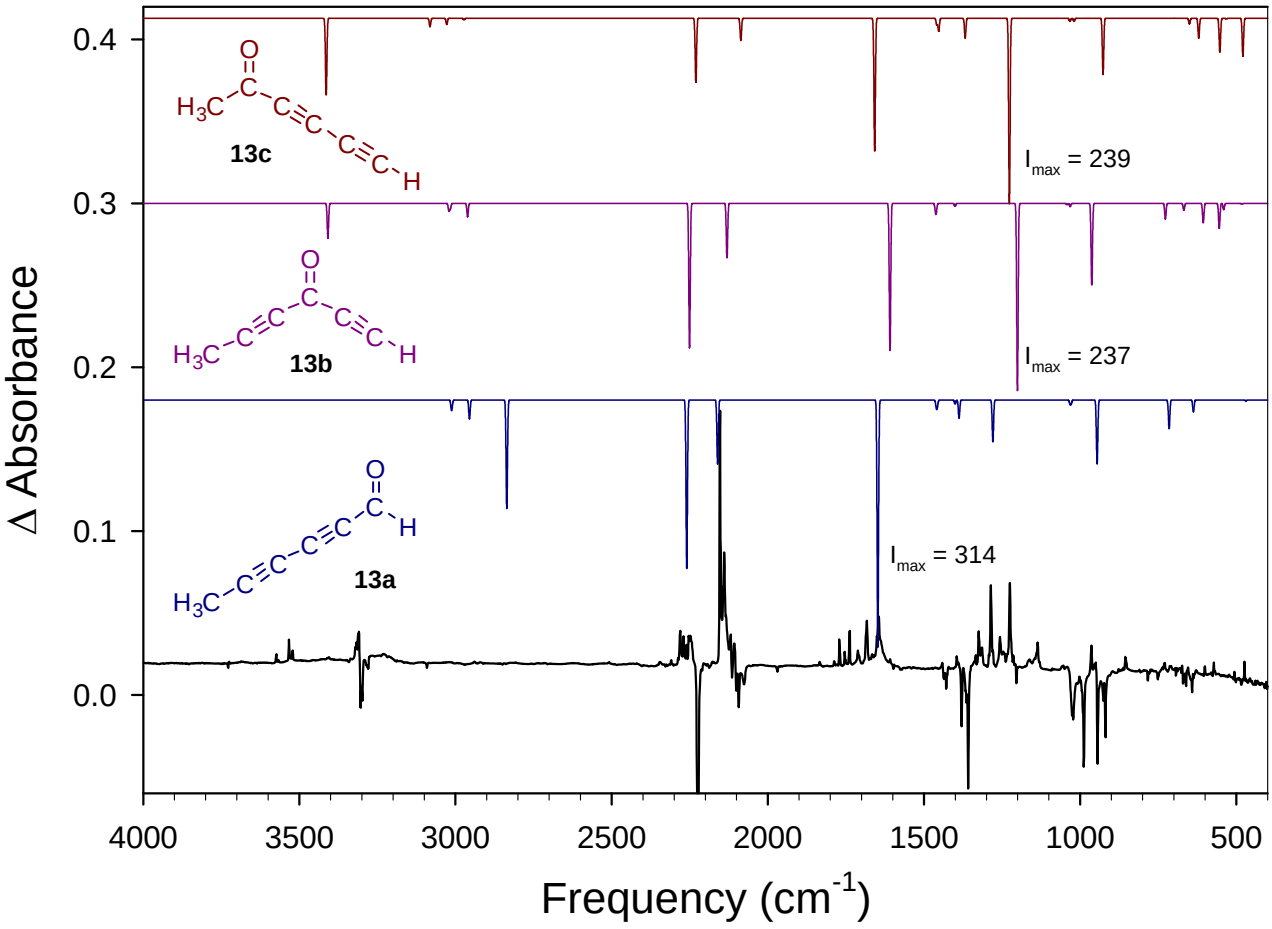


Figure S12. Oxygen trapping of MeC_5H (**1**): the difference IR spectrum shows photolysis of carbonyl-*O*-oxide(s) ($\lambda > 613$ nm, 0.7 h, N_2, 9 K). The experimental spectrum is compared with computed spectra (BLYP/6-31G*) of anticipated carbonyl-containing photoproducts (**13**).

The experimental spectrum is the same as depicted in Figure S11.

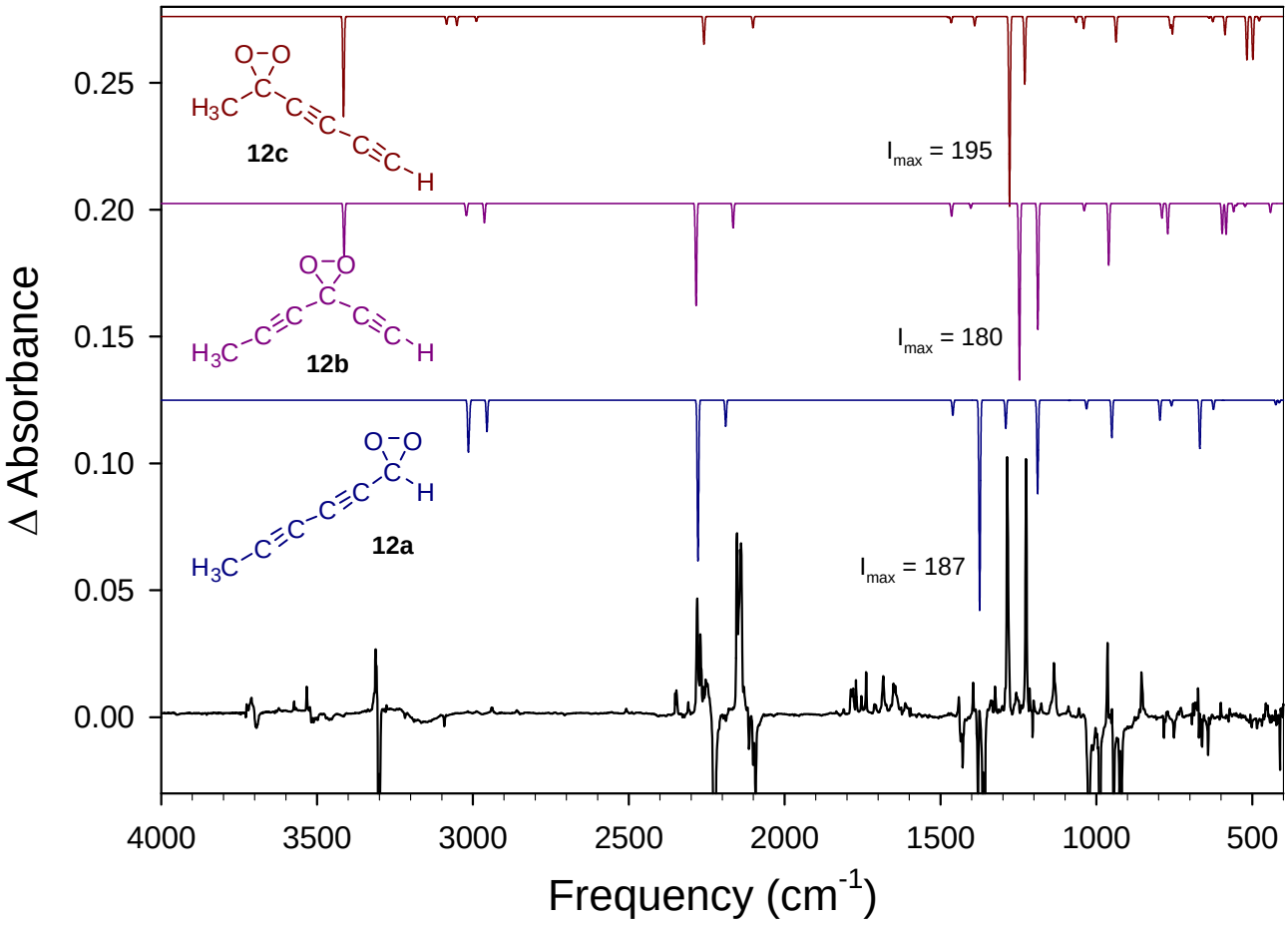


Figure S13. Oxygen trapping of MeC_5H (**1**): the difference IR spectrum shows photolysis of carbonyl-*O*-oxide(s) (λ = 450 ± 10 nm, 0.7 h, N_2, 9 K). The experimental spectrum is compared with computed spectra (BLYP/6-31G*) of anticipated dioxirane photoproducts (**12**).

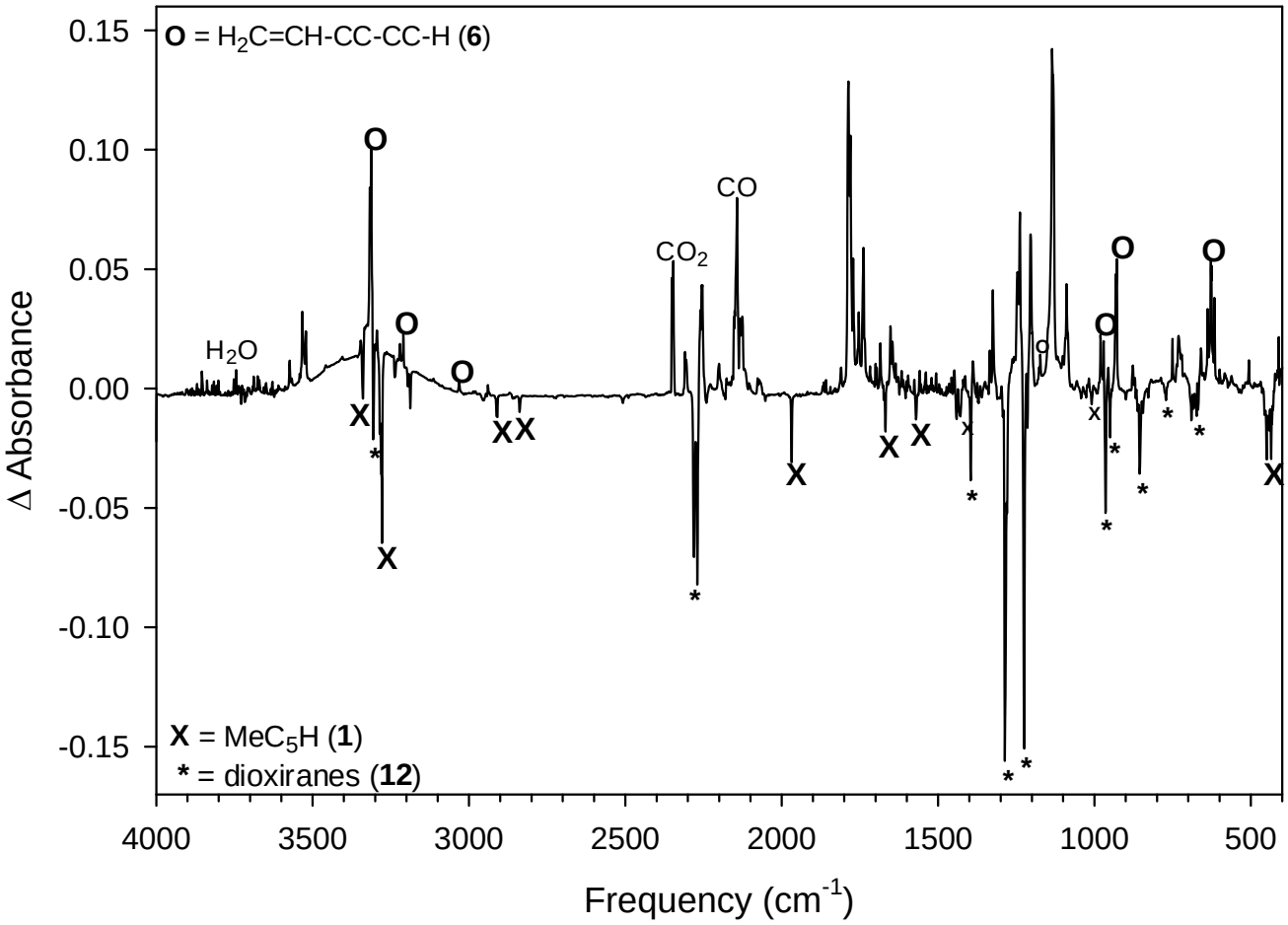


Figure S14. Oxygen trapping of MeC_5H (**1**): the difference IR spectrum shows photolysis of dioxirane(s) (λ = 399 nm, 11.2 h, N_2, 9 K). Unmarked peaks growing in presumably belong to ester(s).

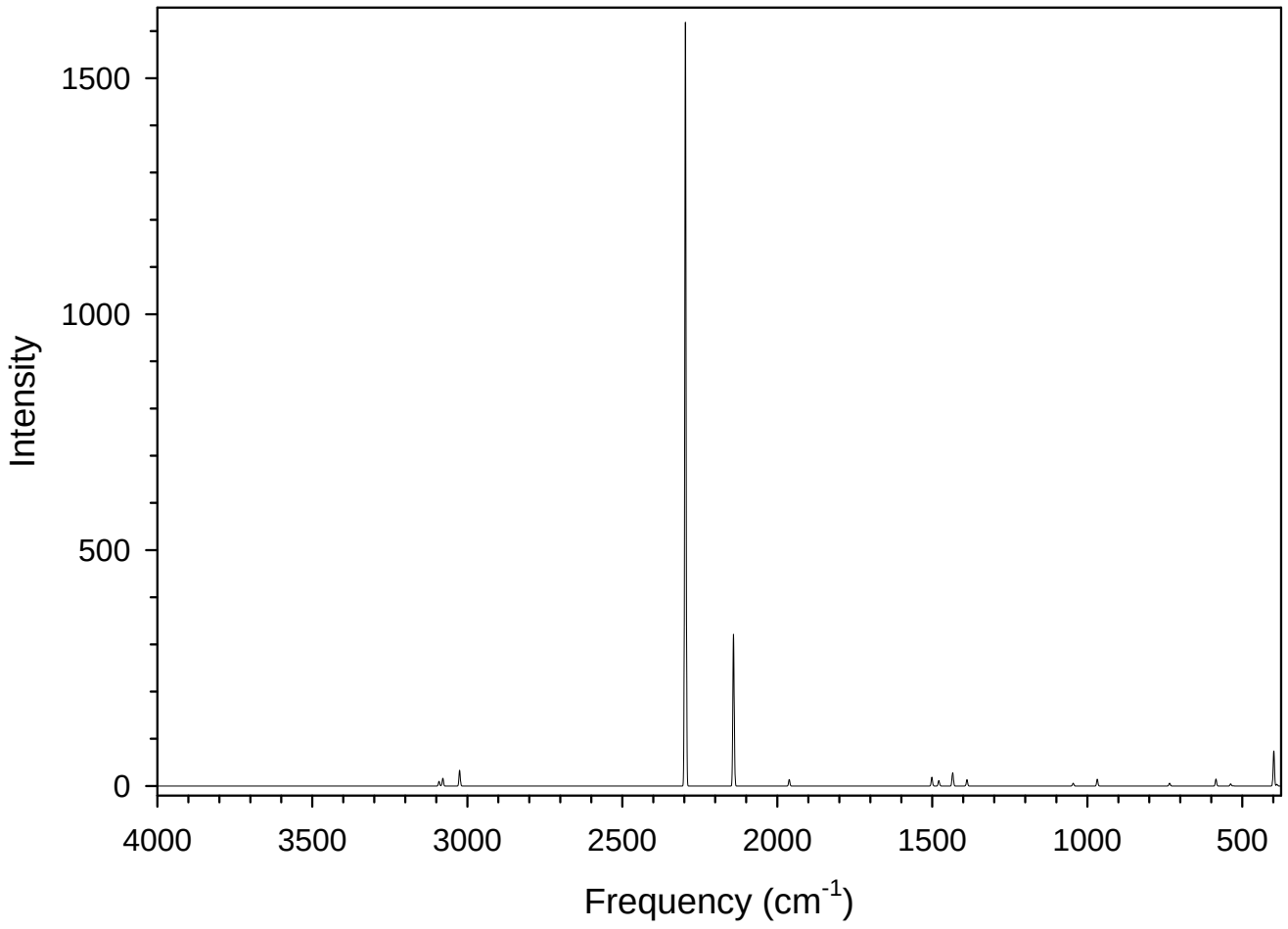


Figure S15. Computed IR spectrum (B3LYP/6-31G*) for doublet radical MeC_5O.

Table S1. Experimental electronic absorption maxima.

Wavelength (nm)	Frequency (cm^{-1})
triplet MeC_5H (^{3}1)	
421.3	23736
411.7	24290
402.7	24832
391.3	25556
382.5	26144
374.6	26695
366.0	27322
357.2	27996
350.4	28539
hex-1-ene-3,5-diyne (6)	
273.5	36563
269.9	37051
263.7	37922
258.4	38700
250.6	39904
244.9	40833
233.0	42918
222.2	45005
carbene dimer(s)	
322.5	31008
308.6	32404
302.1	33102
290.2	34459
283.9	35224
271.6	36819
265.9	37608
257.4	38850

Table S2. Experimental vibrational frequencies

triplet MeC_5H (^{3}1)	
Frequency (cm^{-1})	Relative intensity
381	5
435,448	94
827, 843, 854, 867, 878, 899	57
1008	6
1027	1
1373	5
1431	21
1569, 1578	10
1622	1
1668, 1675, 1678	16
1969, 1977	22
2051	2
2838	6
2910	10
2953	4
3237	5
3254	1
3278, 3297	100
3339,3351,3359	32

hex-1-ene-3,5-diyne (6)	
Frequency (cm^{-1})	Relative intensity
616, 628, 638	64
671, 680	4
928, 932	25
970, 980	17
1173, 1180	4
1227, 1244, 1258, 1276	19
1295	1
1414	4
1611	2
1858, 1866	5
2067	1
2197	1
2228	1
3031	2
3114	2
3210, 3214, 3221	4
3312, 3317	100

Table S2. Experimental vibrational frequencies (*continued*)

1-diazo-hexa-2,4-diyne (2)		2-diazo-hexa-3,5-diyne (3)	
Frequency (cm^{-1})	Relative intensity	Frequency (cm^{-1})	Relative intensity
364	44	485	2
493	100	581	24
615	3	647, 655, 660	35
691	26	1031, 1043	4
999	4	1164, 1185	19
1024	6	1346	17
1133	22	1385	2
1259	6	1461	24
1371	1	2003	10
1393	91	2053	770 [a]
1438	24	2068	296 [a]
1472	2	2160, 2188, 2195, 2205	69
2076	2469 [a]	2600	5
2101, 2114	694 [a]	2942	7
2160	19	2965	8
2269, 2283	36	3222	16
2354	9	3307	100
2507, 2537	16		
2736	1		
2856	10		
2927	20		
2969	8		
3099	48		

[a] Approximate intensities: Absorbance scale was expanded to facilitate observation of weaker bands.

Table S2. Experimental vibrational frequencies (*continued*)

carbonyl *O*-oxides 11	
Frequency (cm^{-1})	Relative intensity
641	4
664, 669, 671	4
751	3
785	3
919, 927	21
945	23
987	29
1021, 1026	37
1201	2
1355, 1365	47
1379	14
1426, 1435	10
2092, 2102	23
2115	5
2222	100
3089	1
3296, 3306	23

dioxiranes 12	
Frequency (cm^{-1})	Relative intensity
473	9
575	6
1160	9
1246, 1258	55
1312, 1324	52
1645	100
1682	48
1712	15
1738	21
1754	9
1771	15
2248	55

carbonyl compounds 13	
Frequency (cm^{-1})	Relative intensity
855	20
965	17
1136	29
1224	79
1285	100
1395	8
1441	5
1780, 1789	15
2267, 2281	67
2859	2
2939	3

Table S3. Computed harmonic vibrational frequencies (unscaled) and IR intensities

triplet MeC_5H (1) CCSD/cc-pVDZ		**singlet MeC_5H (1b)** CCSD/cc-pVDZ	
Frequency (cm^{-1})	Intensity (km/mol)	Frequency (cm^{-1})	Intensity (km/mol)
58.3664	5.3901	30.5119*i*	0.2511
58.3671	5.3901	92.8882	4.4756
186.7187	0.4940	180.9112	0.9960
186.7188	0.4941	190.0903	1.8573
287.4555	11.0028	304.2810	0.0189
287.4556	11.0028	350.3674	39.2845
354.3579	5.6123	418.3580	27.4016
354.3579	5.6121	430.1209	1.3203
422.7602	27.4728	532.4430	1.8611
422.7605	27.4730	735.1159	1.4045
589.6656	0.0157	776.1983	14.8035
1039.7706	1.1555	1012.1449	22.9491
1039.7710	1.1555	1035.4544	1.6321
1040.5739	0.0060	1060.5557	1.3547
1414.4707	15.5498	1340.0665	132.2862
1475.8878	6.8669	1410.4647	35.2151
1475.8880	6.8669	1470.5549	19.1915
1534.2619	24.7116	1483.3402	6.0779
1695.8917	2.3780	2050.3898	180.3028
2043.3534	10.2980	2183.4460	171.8974
3064.0699	32.9555	3069.4514	17.2272
3148.7922	6.6203	3153.3147	2.6293
3148.7922	6.6203	3160.6997	14.9701
3466.7245	103.1270	3474.9194	65.0910

Table S3. Computed harmonic vibrational frequencies (unscaled) and IR intensities (*continued*)

singlet MeC_5H (1a) CCSD/cc-pVDZ		**singlet MeC_5H (1a')** CCSD/cc-pVDZ	
Frequency (cm^{-1})	Intensity (km/mol)	Frequency (cm^{-1})	Intensity (km/mol)
135.1295*i*	8.0647	183.3357*i*	0.6220
88.8854	5.7317	88.7603	5.5516
126.2138	0.6567	127.4281	0.5604
183.5964	8.4409	188.5300	9.0538
303.4401	4.8902	303.7051	3.8076
400.6930	11.0980	400.8923	11.9362
515.9101	11.5020	504.5863	4.8274
522.8499	36.2964	520.7028	41.6200
581.8002	2.5729	580.7579	2.1808
658.9004	3.2861	660.4496	1.4707
718.4635	26.8057	717.3227	25.2976
930.3524	0.1036	765.5042	6.6007
992.5216	20.6757	998.4093	51.9917
1068.6279	11.1484	1089.3446	6.7511
1329.8356	81.1583	1330.5932	21.5025
1351.7487	5.3255	1352.1006	31.4307
1463.0330	11.5434	1467.6544	3.9054
1478.4267	16.8536	1484.9047	8.0371
2005.8836	53.2454	2000.0138	43.3809
2163.6748	8.4758	2161.8654	5.7127
3037.1219	17.6451	3033.0872	5.7246
3120.5552	0.8178	3104.1748	3.7796
3133.1540	31.8190	3167.9081	37.0354
3477.5661	111.4978	3477.6966	111.6698

Table S3. Computed harmonic vibrational frequencies (unscaled) and IR intensities (*continued*)

2-ethynyl-3-methylcyclopropenylidene (4) CCSD/cc-pVDZ		**2-(1-propynyl)cyclopropenylidene (5)** CCSD/cc-pVDZ	
Frequency (cm^{-1})	Intensity (km/mol)	Frequency (cm^{-1})	Intensity (km/mol)
12.3258*i*	1.6474	6.2578	4.6309
133.9326	2.7582	126.6626	4.7623
205.0900	0.7662	134.2705	0.6219
321.5452	0.5892	296.5340	4.8936
365.3023	4.0764	352.4617	2.3243
523.7642	3.1890	500.4686	2.7156
609.4685	45.8888	527.8349	0.3124
612.0067	2.0353	565.0190	0.8332
688.9166	0.0435	893.5903	15.1483
704.5544	31.3716	909.0287	2.0730
798.1442	0.4658	1029.0460	4.0063
1035.5499	1.7005	1052.8115	1.5619
1056.2764	12.1774	1060.2295	0.8426
1275.9239	26.0019	1198.3453	10.3726
1304.0980	25.5891	1290.6125	57.0268
1406.6207	1.7367	1418.8153	6.8137
1478.1819	16.3871	1477.7713	8.8772
1482.4052	7.8070	1482.2761	7.2163
1860.7867	3.9540	1770.4517	18.6289
2210.1572	4.4353	2342.7353	53.0874
3079.3570	10.0750	3078.6338	17.0666
3163.6998	2.8523	3165.5439	3.8931
3183.2452	7.9775	3167.7583	6.2339
3478.8687	75.3205	3286.1746	0.7036

Table S3. Computed harmonic vibrational frequencies (unscaled) and IR intensities (*continued*)

hex-1-ene-3,5-diyne (6) CCSD/cc-pVDZ		**hex-1,2,3-triene-5-yne (7)** CCSD/cc-pVDZ		**hexapentaene (8)** CCSD/cc-pVDZ	
Frequency (cm^{-1})	Intensity (km/mol)	Frequency (cm^{-1})	Intensity (km/mol)	Frequency (cm^{-1})	Intensity (km/mol)
105.6048	2.4121	93.7372	0.9835	105.7501	2.9770
139.2687	4.2136	203.7111	4.4374	108.5162	2.7629
239.8050	0.7294	251.3462	2.2903	247.7494	0.0000
309.9194	0.1648	301.6540	3.5805	251.5045	0.0000
461.1862	0.7084	328.3195	1.5915	311.8221	2.5102
469.4331	0.1474	513.6511	0.0068	418.8679	0.0000
515.2170	1.0056	547.1817	4.3517	492.9290	0.0000
625.6914	41.9424	575.2494	2.5333	496.6082	1.0570
630.0557	39.9135	620.7914	37.2973	624.3736	0.0000
670.6670	3.8644	652.0495	35.2151	636.6395	0.0000
677.8835	2.6480	826.4461	12.5143	863.1556	0.0000
949.0966	25.5449	874.8090	43.1517	863.5197	87.1285
997.8371	22.6595	878.7976	8.0230	1024.8148	0.2850
1042.2840	0.9364	1034.8208	0.2748	1026.2986	0.0000
1193.1292	2.9560	1047.2225	9.7970	1181.3830	6.2446
1319.1495	5.1027	1311.2555	7.6423	1436.7794	0.0000
1451.0515	3.0913	1458.9439	1.9945	1482.0864	0.0018
1692.5399	5.7712	1686.8206	0.3911	1710.2624	0.0000
2152.6679	1.5993	2183.0717	3.3327	2098.3142	18.9813
2346.4843	1.3043	2199.1256	0.5240	2201.8768	0.0000
3186.8820	1.6032	3173.4823	1.0036	3167.3405	0.0000
3207.0316	8.7227	3192.0878	2.8836	3167.6788	3.6073
3290.3912	6.1149	3270.6377	1.3466	3263.2331	2.2296
3481.4615	94.0533	3481.2040	72.1079	3263.2391	0.0000

Table S3. Computed harmonic vibrational frequencies (unscaled) and IR intensities (*continued*)

hexa-1,2-diene-4-yne-1-ylidene (9) CCSD/cc-pVDZ		**hexa-1,2,3,4-tetraene-1-ylidene (10)** CCSD/cc-pVDZ	
Frequency (cm^{-1})	Intensity (km/mol)	Frequency (cm^{-1})	Intensity (km/mol)
17.2826	1.2728	95.5402	0.5568
91.4789	3.8109	113.9555	0.8063
189.1818	11.1678	164.2438	2.6543
224.3163	1.9465	213.1675	2.2811
227.4796	3.8710	282.2023	5.8677
339.7725	1.0390	465.7184	0.5748
383.4564	0.1028	496.9716	5.3544
530.4202	3.1500	606.2045	5.7102
794.1526	34.8363	722.0177	7.1277
873.2505	3.3369	746.7885	10.0636
1050.1063	1.9406	992.2572	14.5107
1060.0703	3.1967	1054.7686	0.1628
1095.1229	17.4928	1127.6602	2.3026
1226.1000	20.6748	1285.4911	0.0241
1413.2827	4.1171	1408.5729	9.1915
1429.8256	25.6391	1462.7707	67.7934
1476.9111	7.7299	1478.6154	7.7784
1479.9735	7.5303	1535.9798	48.6752
2023.1071	767.8448	1973.8710	217.1532
2325.0813	179.2472	2197.8242	1136.2158
3079.7418	11.8916	3068.1073	11.3544
3166.2132	3.1946	3141.5624	6.4736
3166.2613	2.9024	3167.8315	1.3825
3171.8230	5.6275	3192.0288	6.5355

Table S3. Computed harmonic vibrational frequencies (unscaled) and IR intensities (*continued*)

1-diazo-hexa-2,4-diyne (2) BLYP/6-31G*		**2-diazo-hexa-3,5-diyne (3)** BLYP/6-31G*	
Frequency (cm^{-1})	Intensity (km/mol)	Frequency (cm^{-1})	Intensity (km/mol)
42.3404	0.2108	67.4480	0.7681
60.9907	0.9464	81.6361	0.0164
145.9376	2.8121	109.7009	1.9167
182.2210	9.3782	195.3292	2.7314
279.2189	0.2375	245.8151	0.1874
293.6427	0.5001	246.6556	0.1790
367.2538	4.2427	363.7864	54.3166
418.3713	11.5112	419.1495	0.0411
469.5112	3.3006	432.5458	0.7018
472.3847	1.1602	472.7460	7.8066
513.3338	24.0447	522.4973	2.8643
640.2374	0.3746	527.1653	41.9726
669.9875	1.5125	632.1313	2.4754
687.4739	9.9244	644.5476	0.6635
964.3186	0.9949	646.2087	10.2298
1030.9846	3.2930	916.1743	2.2512
1037.4056	3.0016	1029.7732	0.6516
1127.5709	1.6418	1033.3385	11.9282
1280.0916	4.4630	1233.8167	0.3083
1398.3635	27.2370	1353.0162	4.9050
1413.6095	15.5298	1399.5366	6.3672
1461.2478	5.9386	1466.4951	5.9523
1465.5178	6.6963	1491.0715	13.6921
2104.3940	723.0350	2078.2519	298.3753
2164.5984	8.7527	2092.9473	371.4856
2247.0151	4.9936	2214.6314	13.5210
2946.4503	61.0813	2972.0853	35.6952
2997.5550	13.9269	3026.6752	15.6673
3001.7499	12.0645	3058.6410	10.5545
3110.6056	11.3259	3417.8381	124.1007

Table S3. Computed harmonic vibrational frequencies (unscaled) and IR intensities (*continued*)

anti-11a BLYP/6-31G*		**syn-11a** BLYP/6-31G*		**12a** BLYP/6-31G*		**13a** BLYP/6-31G*	
Frequency (cm^{-1})	Intensity (km/mol)	Frequency (cm^{-1})	Intensity (km/mol)	Frequency (cm^{-1})	Intensity (km/mol)	Frequency (cm^{-1})	Intensity (km/mol)
-16.1813	0.7125	-21.2967	0.3802	-17.5728	0.2085	-16.7595	1.7623
60.7913	0.9137	58.3214	3.4265	62.9416	1.4998	74.0771	2.2503
82.0079	2.0725	90.6220	4.4660	70.9074	1.8440	95.4662	5.1910
163.3427	4.9146	142.9936	2.1918	147.7318	1.2212	175.0770	5.2309
168.4200	3.9008	212.2404	0.6990	171.9097	4.1690	220.0267	0.0935
284.1508	0.0181	269.6525	1.7097	317.6504	2.3914	320.7682	1.9778
316.4363	1.6765	340.0527	3.6404	320.6288	1.7349	373.2479	2.0683
400.5080	2.6363	344.7922	0.4907	413.1273	2.5793	469.3399	1.1933
414.8767	2.2560	468.8902	2.9664	424.1781	4.2595	637.3649	14.9469
442.7551	11.6941	519.2717	4.3090	592.8003	0.3807	715.0524	36.5123
644.8337	1.1381	596.4596	0.3673	624.2937	8.3288	719.6866	0.4746
657.7582	0.0168	634.2895	0.0393	668.0708	43.0151	945.7464	81.2455
699.1292	33.0418	709.7751	15.5243	758.8006	5.1062	968.5050	0.1589
831.6759	10.8002	780.5119	12.5894	795.9513	17.9978	1029.1743	5.2093
1011.4387	132.0862	939.0014	105.0053	950.2557	33.5831	1032.8391	3.7455
1019.9881	55.6623	1000.0951	58.3762	1031.1999	3.8990	1279.4412	53.4008
1026.3788	4.4464	1026.2520	4.6393	1031.9569	4.1701	1387.7114	23.2489
1028.9574	5.0880	1030.0694	3.9216	1086.9064	0.5507	1400.4588	5.0249
1205.2431	18.0289	1201.9254	13.1917	1188.3189	83.2336	1457.3053	7.4023
1274.6582	3.9143	1305.4876	1.6848	1290.5930	25.3764	1460.5462	8.2589
1396.9716	28.3462	1397.1095	28.4330	1374.2518	187.2018	1647.8432	314.3075
1440.4290	19.3906	1443.2627	65.9356	1402.0653	0.1808	2160.8104	81.3664
1456.2037	7.8018	1456.3045	7.5050	1459.9207	7.0791	2259.6808	214.5358
1457.2773	7.3815	1457.4443	7.4695	1460.9592	6.9075	2835.8967	138.1831
2145.2247	24.5452	2146.3469	36.5193	2189.0754	23.2483	2955.4464	24.4904
2229.3847	136.6737	2232.2001	163.6555	2278.0030	143.1984	3011.6478	7.0901
2953.4842	27.7577	2953.5455	27.6968	2955.0400	28.1667	3013.4723	7.6330
3008.0287	6.2618	3008.3269	6.5619	3011.0674	7.8246		
3012.9180	6.1298	3013.1778	6.2912	3012.0281	7.2659		
3102.2899	7.5136	3124.1997	10.1475	3014.9347	40.9364		

Table S3. Computed harmonic vibrational frequencies (unscaled) and IR intensities (*continued*)

anti-11b BLYP/6-31G*		**syn-11b** BLYP/6-31G*		**12b** BLYP/6-31G*		**13b** BLYP/6-31G*	
Frequency (cm^{-1})	Intensity (km/mol)	Frequency (cm^{-1})	Intensity (km/mol)	Frequency (cm^{-1})	Intensity (km/mol)	Frequency (cm^{-1})	Intensity (km/mol)
24.7403	0.0695	25.4055	0.0134	-21.1753	0.0152	-19.4839	0.3880
79.0324	2.5348	68.6599	3.5341	79.6888	2.1882	78.8455	3.0714
113.5718	0.1486	134.9132	0.5650	120.3113	0.8749	133.9542	0.2770
154.4745	0.8811	158.2548	1.2043	186.4761	0.5211	191.1690	1.1014
247.1125	3.4734	193.3128	1.4516	205.8786	0.0209	254.0783	0.1726
271.7403	0.2765	260.2334	2.6946	304.4247	5.9853	306.3780	5.8901
277.8092	7.6269	326.9078	0.6525	308.7010	1.4180	366.0951	1.4905
339.3169	1.1191	339.6797	3.2558	420.2341	0.0027	481.9833	0.9934
395.9086	0.1141	399.1419	0.0446	441.3337	9.0129	540.5989	8.0877
481.6625	3.4647	486.5525	41.6014	522.7867	2.9916	554.5060	31.8845
510.7755	1.8494	489.7600	0.3542	551.5259	2.3409	605.8869	24.8338
515.2926	28.6838	568.2043	6.0412	559.4858	8.3455	668.0968	9.1321
570.1108	32.5642	600.0325	29.7294	583.6899	31.4757	727.1810	19.7682
622.6600	12.1683	606.7244	5.5890	596.2557	30.4740	962.8284	103.4722
739.4340	5.6133	651.1472	7.4655	770.8784	31.0637	1032.0854	4.1843
945.6762	57.6242	1014.8253	55.2153	789.6708	14.8764	1042.1083	1.5206
1029.6000	18.3361	1023.9135	98.2222	960.2260	62.9192	1200.8795	237.8008
1035.9508	7.8608	1028.8491	6.9781	1038.2367	3.3826	1400.7825	3.8929
1043.4145	81.1538	1038.5487	6.6963	1039.4740	4.3037	1460.8006	9.8009
1220.0641	22.2247	1198.2329	0.1597	1187.5395	128.0856	1463.3914	6.7518
1354.4625	77.5437	1358.8545	108.0135	1246.7843	179.7268	1608.8663	186.9116
1401.8687	15.8008	1400.1419	13.3279	1402.7695	4.8830	2130.8871	69.2829
1458.9999	7.5428	1458.0145	8.9813	1463.4956	7.1327	2250.7234	183.7002
1461.4147	7.6836	1459.3065	7.7582	1465.2107	6.9743	2961.4349	16.9201
2130.9363	52.2569	2131.0002	20.5582	2165.2826	24.7830	3016.5045	6.2845
2240.1006	90.9737	2243.2403	145.1050	2284.0386	103.7063	3021.2498	9.2594
2957.4823	21.3785	2959.0337	14.9260	2963.1974	19.7197	3408.6880	44.3885
3010.3575	6.9585	3011.2124	6.0334	3019.3204	7.8652		
3020.5562	6.1300	3024.7645	4.9944	3022.5180	7.8778		
3411.6517	61.1778	3413.7122	82.3460	3413.3701	53.4691		

Table S3. Computed harmonic vibrational frequencies (unscaled) and IR intensities (*continued*)

anti-11c BLYP/6-31G*		**syn-11c** BLYP/6-31G*		**12c** BLYP/6-31G*		**13c** BLYP/6-31G*	
Frequency (cm^{-1})	Intensity (km/mol)	Frequency (cm^{-1})	Intensity (km/mol)	Frequency (cm^{-1})	Intensity (km/mol)	Frequency (cm^{-1})	Intensity (km/mol)
72.9279	1.4557	63.2333	2.9175	78.7733	2.2373	79.9430	3.4402
92.6850	0.0832	106.5465	0.4717	91.8769	0.3894	96.4832	0.0041
168.2409	0.2548	122.2021	0.5249	190.4908	0.1786	111.5662	0.4970
231.9989	3.9206	206.8638	3.2821	233.0432	2.5199	240.6246	3.2676
239.0318	4.5939	244.6548	1.1648	258.7830	1.1523	299.6600	1.0592
294.3502	6.7532	244.9324	1.6212	342.7438	6.4858	373.2628	2.9484
359.8285	0.0851	304.7153	0.6347	355.8678	0.0418	478.9576	48.9066
442.7008	2.3364	387.4199	3.8062	477.6322	4.4215	532.0797	0.8596
463.4439	1.9720	491.1283	42.2518	493.9410	0.0014	552.7356	43.8223
483.8762	45.1482	508.5341	43.6171	497.9931	44.3725	561.8536	0.2650
489.8238	8.9393	528.2591	1.4770	517.0726	44.6087	620.4259	25.6560
515.5464	44.5463	593.5146	2.6103	587.2170	18.7730	650.2424	7.1016
622.9129	2.0762	597.3212	1.3080	626.2405	5.4275	706.5828	0.0003
635.2208	0.0257	628.1290	10.5340	638.0931	1.6133	926.6309	72.4635
713.6538	10.9826	654.7455	0.0195	755.8344	17.6899	1019.6248	3.9965
925.3690	33.3863	947.9303	32.7848	762.8905	11.7024	1032.8915	4.0985
1013.8259	3.3414	1018.9621	91.8220	936.9156	26.5378	1226.6457	239.5248
1019.6069	108.5785	1026.0331	2.1305	1040.4660	12.2888	1368.1036	25.4434
1035.8272	14.1952	1054.6004	28.8666	1065.1649	6.0835	1452.8043	16.4586
1267.8061	14.1407	1264.6447	2.2582	1229.4468	69.7047	1459.1796	8.4407
1362.4112	23.6734	1376.0945	69.8704	1278.4901	195.6094	1657.9387	171.3396
1382.5959	21.8425	1394.5770	8.5578	1390.2069	9.6391	2086.5959	28.7835
1434.4452	8.8570	1458.0818	8.3159	1465.6615	6.3876	2230.4337	82.4595
1469.5896	17.0211	1478.0198	5.3311	1474.8791	1.1912	2972.5412	1.8421
2083.8725	5.9502	2081.6878	12.0076	2101.4102	11.6888	3028.1989	8.0345
2198.8588	13.1225	2198.0195	34.7999	2258.8554	28.8389	3081.7404	11.0397
2970.1573	1.0792	2973.4297	10.1532	2988.9497	4.8835	3414.1561	98.9596
3011.0326	2.4409	3023.0088	8.1987	3051.5808	9.3268		
3093.4947	5.6259	3070.1809	4.3308	3084.6928	8.0363		
3413.0485	131.0889	3412.2059	117.4662	3415.0254	102.9493		

Table S4. Cartesian coordinates (Å) and uncorrected energies (a.u.)

triplet MeC_5H (1)			
E (CCSD/cc-pVDZ) = -230.149331098200			
H	0.000000	0.000000	0.000000
C	0.000000	0.000000	1.076610
C	0.000000	0.000000	2.333006
C	0.000000	0.000000	3.661946
C	0.000000	0.000000	4.994036
C	0.000000	0.000000	6.247787
C	0.000000	0.000000	7.719050
H	1.032317	0.000000	8.109049
H	-0.516158	0.894012	8.109049
H	-0.516158	-0.894012	8.109049

singlet MeC_5H (1b)			
E (CCSD/cc-pVDZ) = -230.124442665837			
H	3.879059	1.214838	0.000000
C	2.985508	0.613377	0.000000
C	1.916467	-0.010365	0.000000
C	0.820810	-0.881814	0.000000
C	-0.461618	-0.343656	0.000000
C	-1.661552	-0.029046	0.000000
C	-3.062476	0.411759	0.000000
H	-3.767904	-0.435002	0.000000
H	-3.253395	1.037381	0.888925
H	-3.253395	1.037381	-0.888925

singlet MeC_5H (1a)			
E (CCSD/cc-pVDZ) = -230.116544161973			
H	4.313232	0.307668	0.000000
C	3.241995	0.194296	0.000000
C	2.021323	0.042854	0.000000
C	0.653489	-0.112115	0.000000
C	-0.591178	-0.257726	0.000000
C	-1.921597	-0.589142	0.000000
C	-2.944963	0.508415	0.000000
H	-2.574112	1.549720	0.000000
H	-3.602580	0.341872	0.874606
H	-3.602580	0.341872	-0.874606

singlet MeC_5H (1a')			
E (CCSD/cc-pVDZ) = -230.116380203202			
H	4.307940	0.306426	0.000000
C	3.236581	0.194499	0.000000
C	2.015929	0.042083	0.000000
C	0.648188	-0.112926	0.000000
C	-0.596974	-0.255817	0.000000
C	-1.923635	-0.600830	0.000000
C	-2.940442	0.503012	0.000000
H	-3.974645	0.128103	0.000000
H	-2.784051	1.151892	0.885150
H	-2.784051	1.151892	-0.885150

2-ethynyl-3-methylcyclopropenylidene (4)			
E (CCSD/cc-pVDZ) = -230.154570462613			
H	3.729350	0.798528	0.000000
C	2.702954	0.471180	0.000000
C	1.537988	0.095352	0.000000
C	0.189135	-0.348509	0.000000
C	-1.126781	-0.062922	0.000000
C	-0.748694	-1.451200	0.000000
C	-2.230741	0.934378	0.000000
H	-1.858661	1.970262	0.000000
H	-2.863429	0.769085	-0.888313
H	-2.863429	0.769085	0.888313

2-(1-propynyl)cyclopropenylidene (5)			
E (CCSD/cc-pVDZ) = -230.153540184682			
H	-2.767442	1.602071	0.000000
C	-2.239838	0.647422	0.000000
C	-1.066046	-0.010317	0.000000
C	-2.295819	-0.786650	0.000000
C	0.349089	0.011745	0.000000
C	1.573951	0.006645	0.000000
C	3.046458	-0.000934	0.000000
H	3.448619	1.025089	0.000000
H	3.423193	-0.527197	-0.892529
H	3.423193	-0.527197	0.892529

Table S4. Cartesian coordinates (Å) and uncorrected energies (a.u.) (*continued*)

hex-1-ene-3,5-diyne (6)			
E (CCSD/cc-pVDZ) = -230.212052097041			
H	-8.128091	0.612154	0.000000
C	-6.108577	0.361675	0.000000
C	-3.809739	0.076551	0.000000
C	-1.195415	-0.247702	0.000000
C	1.107482	-0.533329	0.000000
C	3.813242	-0.868923	0.000000
C	5.463302	1.080306	0.000000
H	4.500499	-2.823578	0.000000
H	4.814114	3.044390	0.000000
H	7.501965	0.731864	0.000000

hexa-1,2,3-triene-5-yne (7)			
E (CCSD/cc-pVDZ) = -230.191967326144			
H	0.893379	1.942752	0.000000
C	0.719817	0.859377	0.000000
C	1.880527	0.002603	0.000000
C	2.892611	-0.686845	0.000000
H	3.770828	-1.309982	0.000000
C	-0.536542	0.393269	0.000000
C	-1.749698	-0.029188	0.000000
C	-3.004729	-0.479723	0.000000
H	-3.216361	-1.554412	0.000000
H	-3.852851	0.213258	0.000000

hexapentaene (8)			
E (CCSD/cc-pVDZ) = -230.18558593957			
H	-3.838494	0.939445	0.000000
C	-3.274393	0.000000	0.000000
C	-1.941898	0.000000	0.000000
C	-0.652247	0.000000	0.000000
C	0.652247	0.000000	0.000000
C	1.941898	0.000000	0.000000
C	3.274393	0.000000	0.000000
H	3.838494	0.939445	0.000000
H	3.838494	-0.939445	0.000000
H	-3.838494	-0.939445	0.000000

hexa-1,2-diene-4-yne-1-ylidene (9)			
E (CCSD/cc-pVDZ) = -230.131379918549			
H	1.062337	1.897791	0.000000
C	0.902493	0.809050	0.000000
C	1.971920	-0.015887	0.000000
C	3.027812	-0.781391	0.000000
C	-0.457528	0.361792	0.000000
C	-1.636292	0.023714	0.000000
C	-3.039956	-0.420150	0.000000
H	-3.725490	0.442293	0.000000
H	-3.243312	-1.033869	0.893034
H	-3.243312	-1.033869	-0.893034

hexa-1,2,3,4-tetraene-1-ylidene (10)			
E (CCSD/cc-pVDZ) = -230.126492316128			
H	-2.197451	1.556475	0.000000
C	-1.831288	0.518995	0.000000
C	-0.509262	0.319484	0.000000
C	0.760782	0.136072	0.000000
C	2.063114	-0.058671	0.000000
C	3.352135	-0.252153	0.000000
C	-2.860805	-0.580860	0.000000
H	-2.389397	-1.574726	0.000000
H	-3.509221	-0.484222	-0.889326
H	-3.509221	-0.484222	0.889326

Table S4. Cartesian coordinates (Å) and uncorrected energies (a.u.) (*continued*)

1-diazo-hexa-2,4-diyne (2)			
E (BLYP/6-31G*) = -340.271167904			
H	0.000077	0.070631	-0.032837
C	-0.000338	0.004439	1.058359
N	-0.000089	1.176692	1.681117
N	0.000147	2.199795	2.223266
C	-0.000126	-1.198383	1.777253
C	0.000037	-2.271004	2.394104
C	0.000176	-3.450973	3.068658
C	0.000417	-4.519931	3.679677
C	0.000014	-5.788986	4.403594
H	0.891869	-5.890787	5.048918
H	-0.892132	-5.890347	5.048586
H	-0.000052	-6.644768	3.703974

2-diazo-hexa-3,5-diyne (3)			
E (BLYP/6-31G*) = -340.261358178			
C	0.022584	0.038544	-0.087467
C	-0.036757	-0.029413	1.436975
N	-0.119337	1.115540	2.106271
N	-0.191489	2.119742	2.681482
C	-0.009043	-1.223753	2.175619
C	0.015477	-2.298486	2.788375
C	0.043822	-3.480425	3.459985
C	0.070118	-4.547975	4.067059
H	0.090695	-5.479902	4.596158
H	0.952194	-0.424284	-0.459994
H	-0.830855	-0.499920	-0.533505
H	-0.007407	1.083422	-0.433299

Table S4. Cartesian coordinates (Å) and uncorrected energies (a.u.) (*continued*)

	***anti*-11a**		
	E (BLYP/6-31G*) = -381.130629298		
C	-0.091689	-0.003078	0.088968
C	0.013841	0.006242	1.543613
C	0.099618	0.008249	2.773368
C	0.196227	0.012387	4.122339
C	0.285314	0.015694	5.361075
C	0.337633	0.023192	6.744313
H	-0.537784	0.027573	7.403101
H	-0.120072	1.024553	-0.316991
H	0.769462	-0.520536	-0.370704
H	-1.010955	-0.519104	-0.241751
O	1.512556	0.024696	7.353960
O	1.495850	0.032131	8.718708

	***syn*-11a**		
	E (BLYP/6-31G*) = -381.129904262		
O	-0.249136	0.000248	0.116350
O	-0.052665	0.000764	1.465791
C	1.192607	0.000610	1.914759
H	1.228140	0.001031	3.007774
C	2.316999	-0.000143	1.106545
C	3.369511	-0.000812	0.448388
C	4.510648	-0.001535	-0.277759
C	5.549576	-0.002588	-0.940939
C	6.777040	-0.001378	-1.728682
H	6.631400	-0.513367	-2.696776
H	7.110027	1.030500	-1.943368
H	7.597711	-0.513329	-1.194773

	***anti*-11b**		
	E (BLYP/6-31G*) = -381.112610618		
C	-0.403936	-0.008170	0.331204
C	0.117869	0.008855	1.695260
C	0.559500	0.018039	2.840172
C	1.034625	0.029634	4.165806
C	0.182622	0.012315	5.292689
C	-0.621812	-0.002729	6.213597
H	-1.301960	-0.017519	7.043446
H	-0.574570	1.016397	-0.046626
H	0.301557	-0.505426	-0.357626
H	-1.365719	-0.548521	0.279829
O	2.366711	0.058471	4.315846
O	2.855112	0.070655	5.586402

	***syn*-11b**		
	E (BLYP/6-31G*) = -381.113356535		
H	-0.187389	0.038427	0.048719
C	-0.120234	0.020774	1.119289
C	-0.043114	-0.009576	2.339731
C	0.043916	-0.005467	3.750351
O	0.149410	-1.214660	4.323093
O	0.236191	-1.257139	5.680245
C	0.023938	1.169380	4.522339
C	0.001283	2.220189	5.155415
C	-0.021840	3.458671	5.927190
H	0.856851	4.087405	5.695493
H	-0.924505	4.053667	5.699328
H	-0.014509	3.250400	7.011063

	***anti*-11c**		
	E (BLYP/6-31G*) = -381.128895010		
H	-0.001188	-0.027067	0.009531
C	-0.000940	-0.020722	1.082193
C	-0.000662	-0.012760	2.310475
C	-0.000359	-0.004592	3.666561
C	-0.000125	0.011990	4.905518
C	0.000181	0.046416	6.299799
O	-0.001597	-1.138299	6.908733
O	-0.001521	-1.110882	8.279375
C	0.002528	1.281385	7.140504
H	-0.876742	1.265159	7.809746
H	0.880153	1.260216	7.811685
H	0.005535	2.186229	6.518735

	***syn*-11c**		
	E (BLYP/6-31G*) = -381.123586256		
C	-0.259817	0.001834	0.440285
C	0.786378	-0.018465	1.525793
C	0.500827	0.005804	2.891153
C	0.137188	0.030179	4.075117
C	-0.242221	0.056092	5.376923
C	-0.588071	0.079520	6.555195
H	-0.883455	0.099737	7.586192
H	-0.879422	0.912937	0.507056
H	0.231269	-0.025672	-0.543951
H	-0.936247	-0.865986	0.528471
O	2.037601	-0.061851	1.087955
O	3.045970	-0.082128	2.009812

Table S4. Cartesian coordinates (Å) and uncorrected energies (a.u.) (*continued*)

	12a		
	E (BLYP/6-31G*) = -381.143259650		
H	-0.066089	0.006746	-0.007248
C	-0.024581	-0.000319	1.093604
C	1.298307	-0.017065	1.670447
C	2.447845	-0.007016	2.108951
C	3.719966	-0.004382	2.595080
C	4.866981	-0.001290	3.036466
C	6.230374	0.002338	3.559464
H	6.236488	0.002727	4.664173
H	6.790568	-0.887875	3.221182
H	6.785986	0.895187	3.220577
O	-1.052962	-0.763019	1.719897
O	-1.038166	0.773970	1.729224

	13a		
	E (BLYP/6-31G*) = -306.037567518		
O	-0.032562	0.004608	1.455622
C	1.104213	-0.000983	1.935892
H	1.267855	-0.007473	3.042302
C	2.312754	0.000041	1.148731
C	3.345241	0.001012	0.470649
C	4.486213	0.002102	-0.267429
C	5.518231	0.003069	-0.936887
C	6.743505	0.002422	-1.729890
H	6.594808	0.509275	-2.700100
H	7.075488	-1.030311	-1.940592
H	7.566114	0.516238	-1.200988

	12b		
	E (BLYP/6-31G*) = -381.120110126		
C	-0.022445	0.632367	0.000322
C	1.191873	1.434571	0.000432
C	2.177403	2.149596	-0.000641
C	-1.267331	1.374564	0.000257
C	-2.292343	2.037835	-0.001828
C	-3.529100	2.819330	-0.000264
H	3.059879	2.759908	0.000100
H	-4.416920	2.163205	-0.000015
H	-3.589552	3.469417	-0.890884
H	-3.587760	3.467863	0.891609
O	0.019271	-0.581432	0.767057
O	0.019453	-0.581600	-0.766145

	13b		
	E (BLYP/6-31G*) = -306.020062596		
C	-0.023871	0.621637	-0.000092
C	1.206371	1.406470	-0.000125
C	2.246342	2.046516	-0.000166
C	-1.249310	1.397810	0.000549
C	-2.298785	2.029433	0.000726
C	-3.554411	2.777943	0.001097
H	3.167366	2.597608	-0.000204
H	-4.199839	2.465448	0.841187
H	-4.118316	2.598451	-0.931698
H	-3.381389	3.864653	0.089262
O	-0.009862	-0.618763	-0.000537

	12c		
	E (BLYP/6-31G*) = -381.139185307		
H	0.061351	-0.000002	-0.085230
C	0.054585	0.000000	0.987253
C	0.044438	0.000000	2.212526
C	0.033899	0.000001	3.576635
C	0.027504	0.000001	4.805626
C	-0.046139	0.000000	6.257459
C	-1.435104	0.000000	6.875636
H	-1.338032	-0.000004	7.970673
H	-1.995893	0.892394	6.552486
H	-1.995895	-0.892392	6.552481
O	0.951398	-0.768198	6.934163
O	0.951397	0.768200	6.934163

	13c		
	E (BLYP/6-31G*) = -306.033732929		
H	0.256622	0.008962	0.037772
C	0.173608	0.002756	1.107127
C	0.079388	-0.000585	2.329607
C	-0.024830	-0.003900	3.687577
C	-0.115576	0.005102	4.917470
C	-0.243593	-0.050246	6.368353
O	-0.579156	-1.099623	6.927350
C	0.057512	1.242429	7.123072
H	-0.070781	1.073949	8.201939
H	1.089119	1.577081	6.915073
H	-0.617051	2.049392	6.786431

Complete citation for Aces II Mainz-Austin-Budapest version.[6,7]

Complete citation for Gaussian 98.[8]

Complete citation for Gaussian 03.[9]

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