Supporting Information

Photochemistry of Furyl- and Thienyldiazomethanes: Spectroscopic Characterization of Triplet 3-Thienylcarbene

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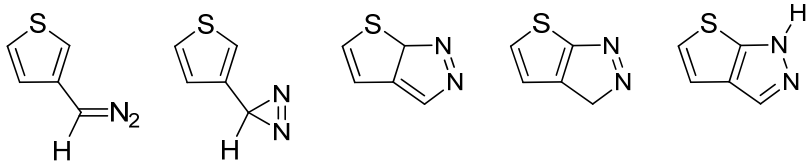
Matrix Isolation Spectroscopy. The matrix isolation apparatus and technique has been described previously.[1,2] Irradiation was carried out with an ILC Technology LX300UV 300 W high-pressure xenon arc lamp, and wavelength selection was achieved with cut-off filters ($\lambda >$ 613 nm, Corning 2-58; $\lambda >$ 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 3-075; $\lambda >$ 330 nm, Corning 3-28; $\lambda >$ 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). IR spectra were recorded on a Nicolet Nexus™ 870 FT-IR spectrometer equipped with a DTGS detector at a resolution of 2 cm^{-1}. UV/vis spectra were recorded with a Varian Cary 5000 UV/vis/NIR spectrophotometer utilizing a spectral bandwidth of 1.0 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. Zero-field splitting parameters were determined by a best fit of the observed spectrum to the spin Hamiltonian (assuming $g_x = g_y = g_z = g_e$).[3]

EPR Experiments in Organic Glasses. The diazo compound was prepared by thermolysis of the tosylhydrazone sodium salt in the usual manner. The diazo compound was rinsed from the cold finger with 3-methylpentane. The UV/vis spectrum of the solution was measured in order to determine the concentration of diazo compound. Solutions for EPR measurement were prepared by diluting the stock solution to ca. 1-5 mM. The solution was introduced into a quartz EPR sample tube, purged with Ar, subjected to four freeze-pump-thaw cycles, and the tube was flame-sealed under vacuum. Under a wide variety of photolysis conditions, irradiation of 3-thienyldiazomethane (**1**) afforded an extremely weak EPR spectrum in which only the strongest Z_1 transition of triplet 3-thienylcarbene (**13**) was observable at 4.2 K.

Photochemistry derived from (3-thienyl)diazomethane (1).

Efforts at elucidating the photochemistry of 1*H*-2-thiabicyclo[3.1.0]hexa-3,5-diene (**12**) were attempted by using a monochromator to irradiate at various wavelengths between 350 and 250 nm. Irradiation was carried out in incremental 20 nm steps from 350 to 250 nm. The experiment was begun with broad-band irradiation ($\lambda > 534$ nm) of 3-thienyldiazomethane (**1**) to give a mixture of triplet 3-thienylcarbene (**13**), 1*H*-2-thiabicyclo[3.1.0]hexa-3,5-diene (**12**)**,** and (*s*-*Z*)-α-thial methylenecyclopropene (**9**), and residual **1**. The matrix was then selectively irradiated at $\lambda = 467$ nm with a monochromator to drive away carbene **13**. After this photochemical transformation was complete, irradiation of a matrix containing **1**, **12**, and **9** at $\lambda =$ 350 nm was begun. Interestingly, irradiation at this wavelength causes **1**, **13** and (*s*-*E*) **9** to grow into the matrix while **12** and (*s*-*Z*) **9** disappear (Figure S7). The growth of (*s*-*E*) **9** was to be expected, as a decrease in (*s*-*Z*) **9** and the corresponding growth of (*s*-*E*) **9** is observed upon broadband irradiation of the matrix at similar wavelengths. The growth of **1**, however, was surprising to us, and we considered the possibility that the minor product in the matrix was not **12**, but rather resulted from a rearrangement of diazo compound **1** to give an alternate structure such as (3-thienyl)diazirine (**34**), 6a*H*-thieno[2,3-c]pyrazole (**35**), or H shift products of 6a*H*-thieno[2,3-c]pyrazole (**36** and **37**) (Scheme S1).

Scheme S1. Suspected products from an intramolecular photochemical reaction of (3-thienyl)diazomethane (**1**) and their computed relative energies.[a]



1	**34**	**35**	**36**	**37**
17.1	*29.5*	*33.3*	*16.2*	*0.0*

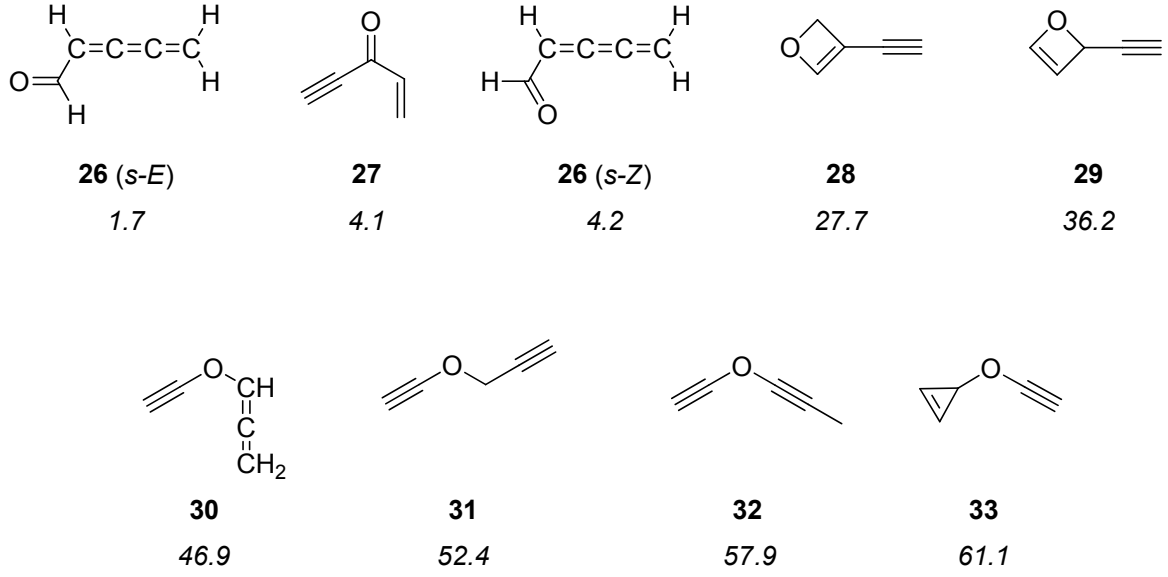
[a] Energy (kcal/mol; ZPVE included). B3LYP/6-31G* level of theory.

The computed spectra of these compounds display poor agreement with the experimentally observed bands. The irradiation conditions were repeated to verify these results and the spectra was reproduced. Further irradiation became markedly more complicated due to the number of species present in the matrix and was not helpful in providing evidence to support a positive identification of the compound of interest (currently assigned as **12**). We are left then, in agreement with Albers and Sander,[4] tentatively assigning **12** to 1*H*-2-thiabicyclo[3.1.0]hexa-3,5-diene. It is conceivable that **12** photochemically reverts back to carbene **13**, which in an excited state could react with nitrogen in the matrix to regenerate the starting material **1**.

Photochemistry derived from (3-furyl)diazomethane (3).

An unidentified intermediate (**U**, 3429 m, 1636 m, 1476 m cm^{-1}, Figure S16), likely a C_5H_4O isomer, was observed during the photolysis of (3-furyl)diazomethane (**3**). In addition to the structures depicted in Scheme 3 of the manuscript, we also considered the structures depicted in Scheme S2, but none of the computed IR spectra shows a good correlation with the experimentally observed bands of intermediate **U**.

Scheme S2. Additional C_5H_4O isomers considered as possible photoproducts from (3-furyl)diazomethane (**3**).



26 (*s-E*) *1.7* | **27** *4.1* | **26** (*s-Z*) *4.2* | **28** *27.7* | **29** *36.2*

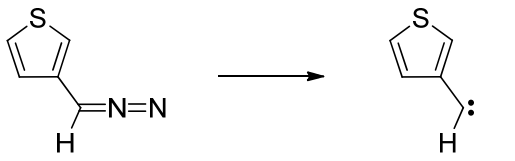
30 *46.9* | **31** *52.4* | **32** *57.9* | **33** *61.1*

Computed Electronic Absorption Spectrum of 3-Thienyldiazomethane (1).

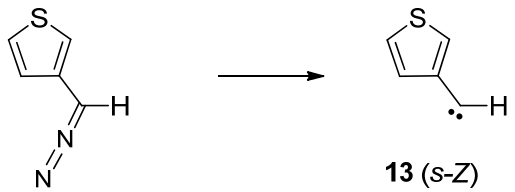
EPR experiments on triplet 3-thienylcarbene (**13**) reveal a wavelength dependence in the photolysis of 3-thienyldiazomethane (**1**) (Figure 1 and S8). Knowing that the conformational isomers of singlet arylhalocarbenes exhibit distinct differences in their electronic absorption spectra,[5-9] we wondered if the same might be true for the conformers of 3-thienyldiazomethane (**1**). TD-DFT calculations suggest that this is not the case for the visible absorption (Table S.1), which is the region of the spectrum where the wavelength dependence was observed. The only notable difference between the computed absorption spectra of the conformers of **1** involves the oscillator strength of the UV absorption near 245 nm. The computed transitions exhibit modest agreement with the experimental spectrum of 3-thienyldiazomethane (**1**).

It is worth noting that, because of a change in the priority of the substituents involved in naming the compounds, the (*s-Z*) conformer of diazo compound **1** correlates with the (*s-E*) conformer of carbene **13**, and vice versa (Scheme S3).

Scheme S3. Conformational isomers of Diazo Compounds and Carbenes.



1 (*s-Z*) **13** (*s-E*)



1 (*s-E*) **13** (*s-Z*)

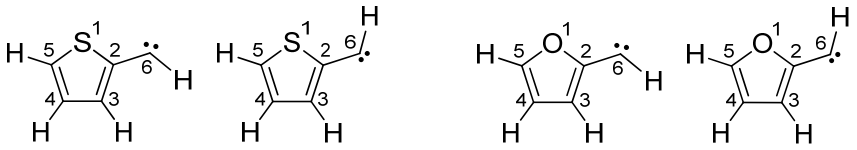
Table S.1. Computed Electronic Absorption Spectra of Diazo Compounds.[a]

(*s*-*Z*)-3-thienyl diazomethane (**1**)		(*s*-*E*)-3-thienyl diazomethane (**1**)		3-thienyl diazomethane (**1**) (expt; N_2, 10 K)	phenyl diazomethane		phenyl diazomethane (expt)
λ_{max}	*f*	λ_{max}	*f*	λ_{max}	λ_{max}	*f*	λ_{max}
519.5	0.0001	520.0	0.0001	494 [b]	508.9	0.0000	490 [c,d]
312.0	0.0001	314.5	0.0000		305.3	0.0001	
289.1	0.1450	291.0	0.0004	302 sh	285.2	0.0440	
285.8	0.0032	283.9	0.1368	289	283.8	0.0001	
282.4	0.0008	279.5	0.0006		276.9	0.0018	
267.4	0.0001	266.8	0.0009		272.2	0.3992	275 [c,e]
261.0	0.0002	264.3	0.0703	256	256.8	0.0152	
258.9	0.0315	263.8	0.0052		254.4	0.0006	
248.0	0.0063	250.0	0.0002	232 sh	252.9	0.0044	
245.3	0.0533	246.0	0.2087	227	247.0	0.0013	
237.7	0.0011	238.7	0.0003		234.4	0.0008	
235.8	0.0008	233.8	0.0000		230.2	0.0004	
231.7	0.0003	231.3	0.0006		226.2	0.0001	
228.1	0.0000	227.8	0.0004		223.4	0.0894	229 [e]
227.8	0.0030	227.0	0.0065		218.6	0.0006	

[a] (TD)M06/aug-cc-pVTZ // B3LYP/6-31G*; λ_{max} (nm), *f* = oscillator strength. Fifteen lowest-energy singlet excitations reported. [b] in CH_3CN. [c] reference 10. [d] reference 11. [e] reference 12.

Table S.2. Natural Spin Densities for Triplet 2-Thienylcarbene (**11**)

and Triplet 2-Furylcarbene (**22**).[a]



	2-thienylcarbene (**11**)		2-furylcarbene (**22**)	
Atom	(*s*-*E*)-**11**	(*s*-*Z*)-**11**	(*s*-*E*)-**22**	(*s*-*Z*)-**22**
1	+0.098	+0.146	+0.056	+0.078
2	–0.203	–0.215	–0.174	–0.176
3	+0.393	+0.377	+0.390	+0.372
4	–0.119	–0.124	–0.097	–0.103
5	+0.314	+0.322	+0.283	+0.291
6	+1.55	+1.53	+1.58	+1.58

[a] NBO spin densities at B3LYP/6-31G*.

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Complete citation to reference 69:

Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. *Gaussian 09; Revision B.1*, 2009.

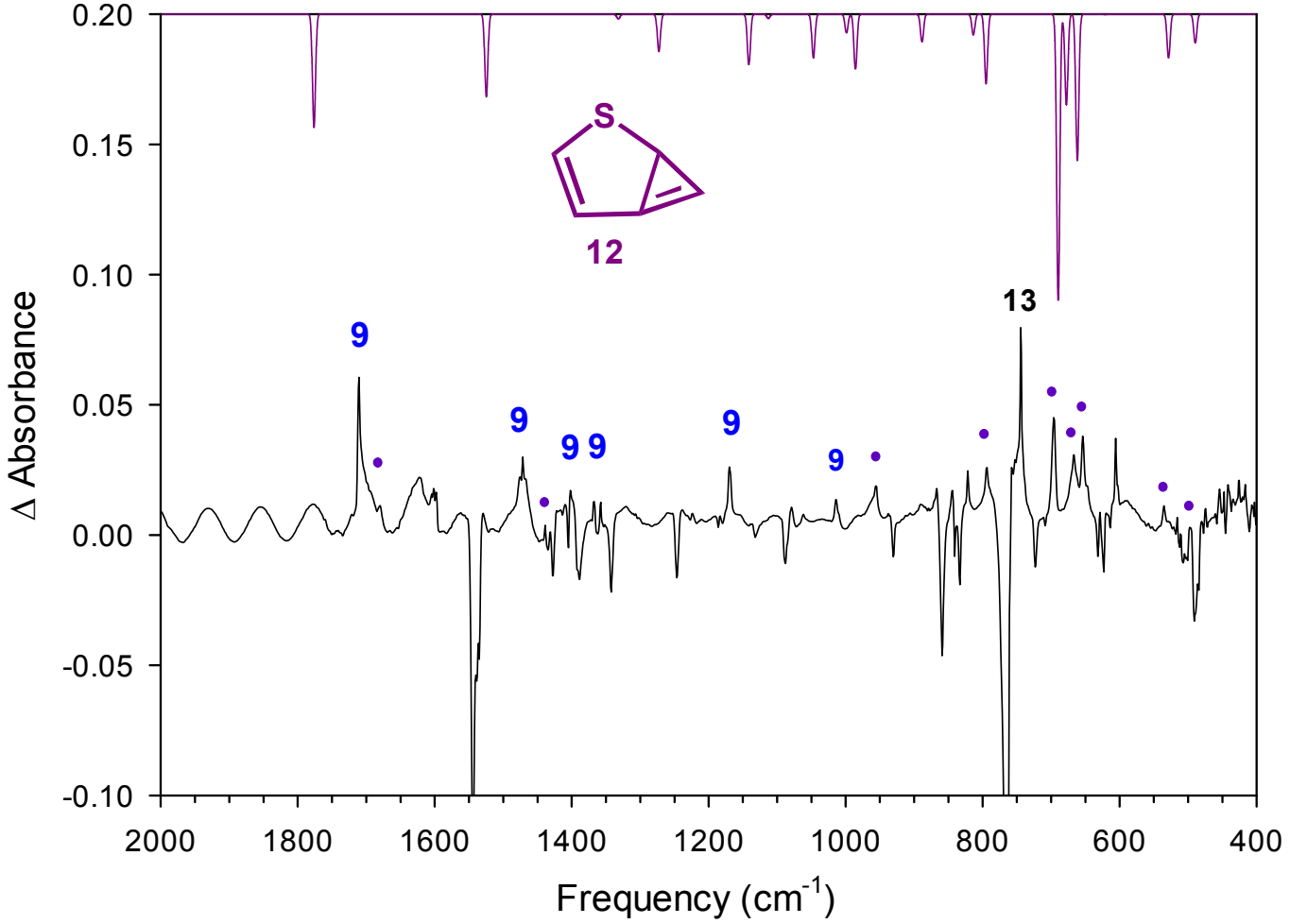

Figure S1. IR subtraction spectrum showing spectral changes observed upon irradiation (λ > 534 nm, 18 h) of 3-thienyldiazomethane (**1**) (N_2, 10 K). The spectrum shows the disappearance of **1** and the growth of bands attributed to 1*H*-2-thiabicyclo[3.1.0]hexa-3,5-diene (**12**) (marked with purple •). The B3LYP/6-31G* calculated IR frequencies of **12** can be seen on top of spectrum. (*s*-*Z*)-α-thial methylenecyclopropene (**9**) and (*s*-*Z*) and (*s*-*E*) 3-thienylcarbene (**13**) are also present in the matrix and labeled accordingly.

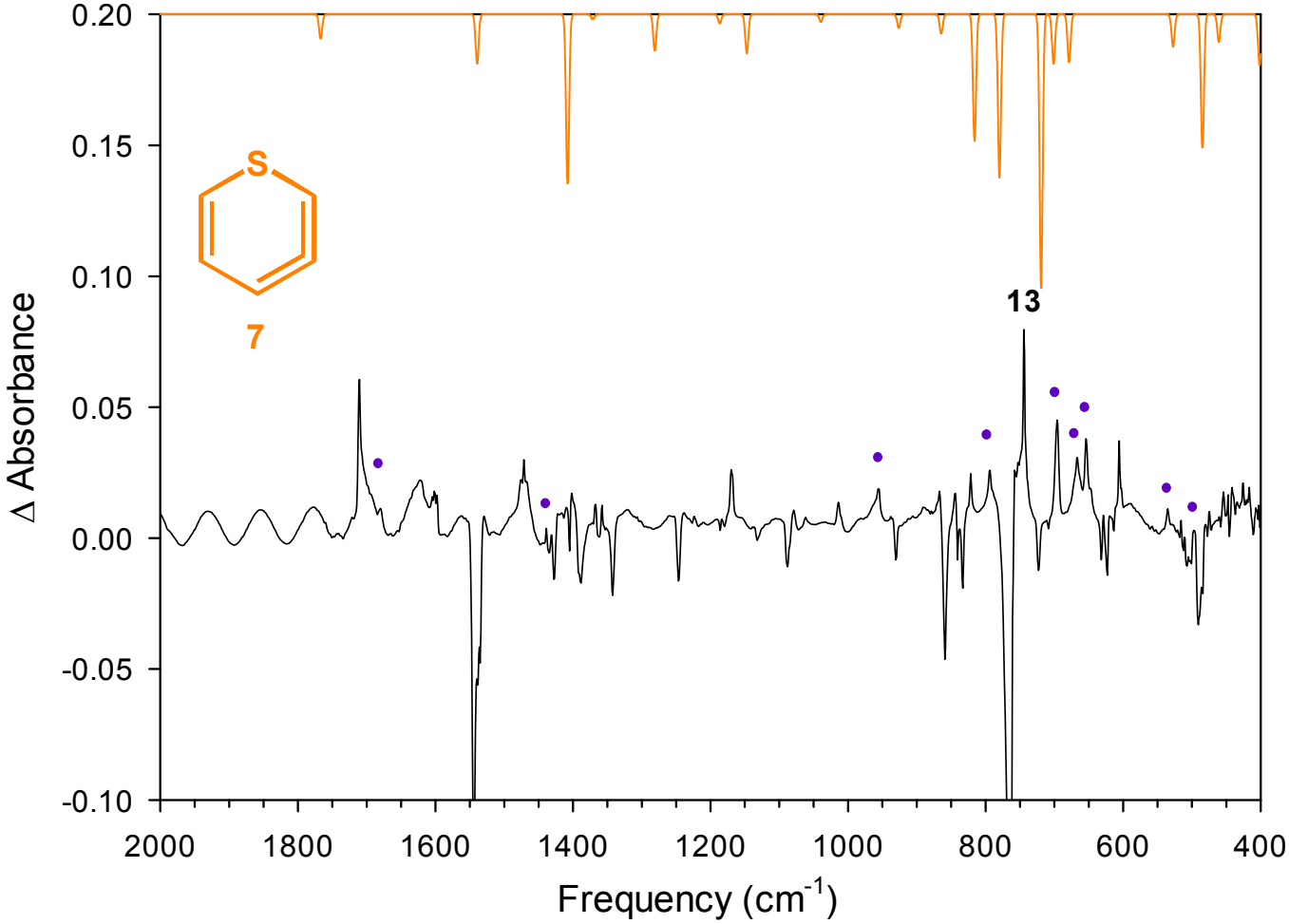

Figure S2. IR subtraction spectrum showing spectral changes observed upon irradiation (λ > 534 nm, 18 h) of 3-thienyldiazomethane (**1**) (N_2, 10 K). The spectrum shows the disappearance of **1** and the growth of bands attributed to 1*H*-2-thiabicyclo[3.1.0]hexa-3,5-diene (**12**) (marked with purple •). The B3LYP/6-31G* calculated IR frequencies of thiabicyclohexa-2,3,5-triene (**7**), another low lying isomer on the C_5H_4S potential energy surface can be seen on top of spectrum. The purpose of this spectrum is to illustrate that the experimentally observed bands assigned to **12** do not match up with **7**.

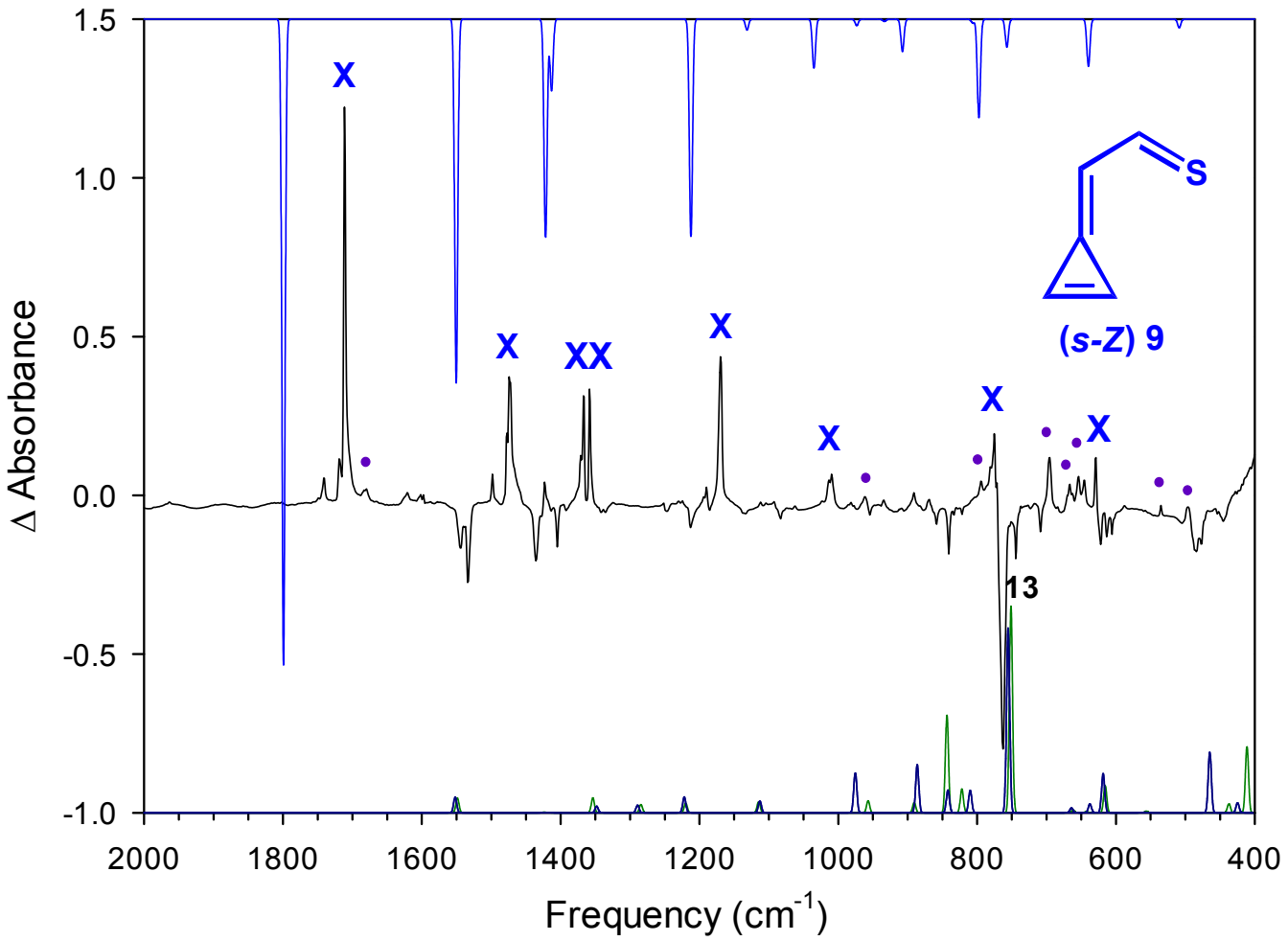

Figure S3. IR subtraction spectrum showing spectral changes observed upon irradiation (λ > 444 nm,15 h) of a mixture of 3-thienyldiazomethane (**1**), 1*H*-2-thiabicyclo[3.1.0]hexa-3,5-diene (**12**), (*s*-*Z*)-α-thial methylenecyclopropene **9**), and 3-thienyl carbene rotamers (**13**) (N_2, 10 K). The spectrum shows the disappearance of **1** and **13** and the growth of **9** (marked with blue **X**) and **12** (marked with purple •). B3LYP/6-31G* calculated IR frequencies for **13** are seen on the bottom of the spectrum, and the major band for **13** is labeled. Calculated IR frequencies for **9** are seen along the top of the spectrum.

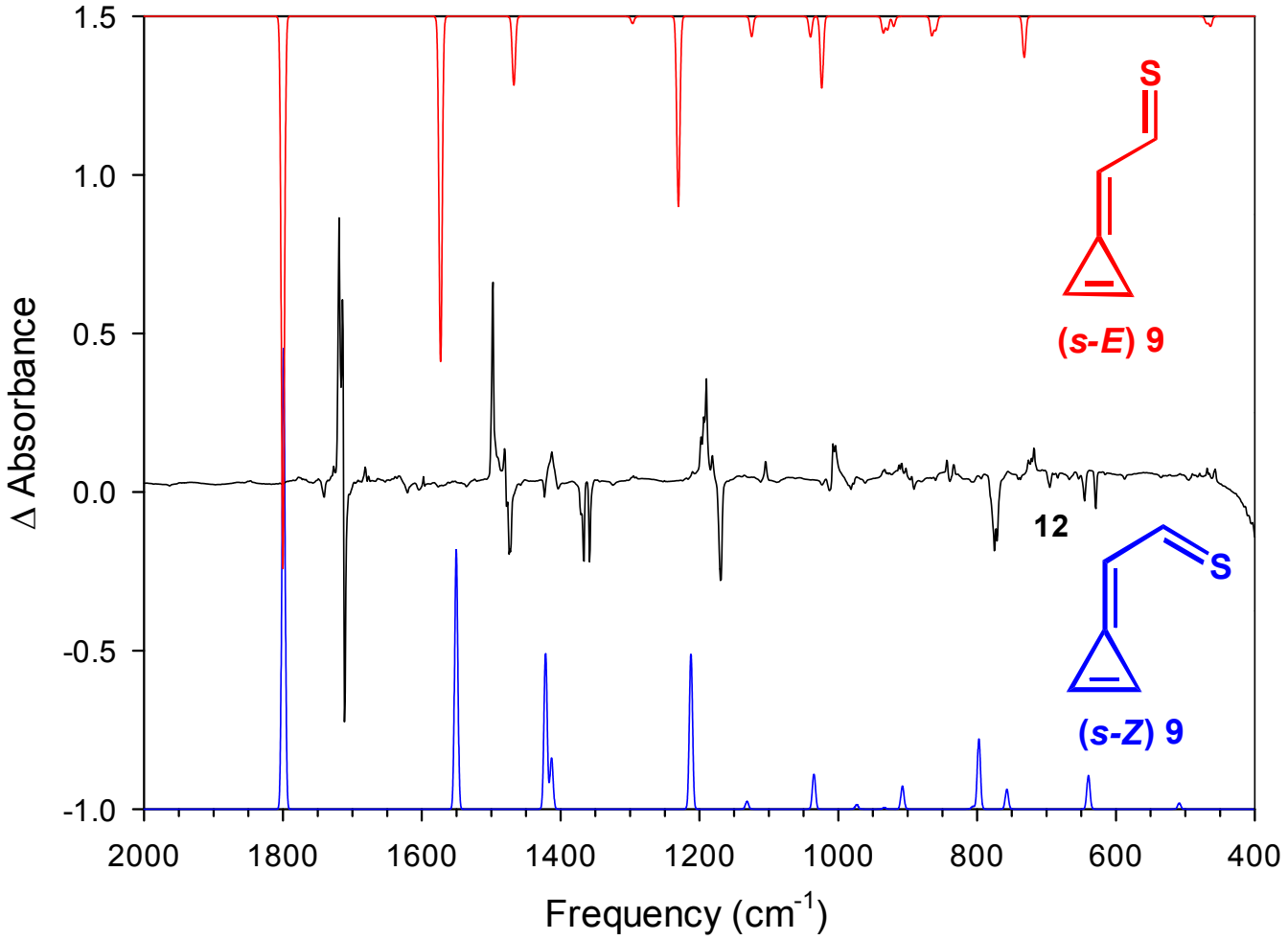

Figure S4. IR subtraction spectrum showing spectral changes observed upon irradiation (λ > 363 nm, 18 h) of a mixture of a minor amount of 1*H*-2-thiabicyclo[3.1.0]hexa-3,5-diene (**12**) and (s-Z)-α-thial methylenecyclopropene (**9**) (N_2, 10 K). The spectrum shows the disappearance of **12**, a decrease in the amount of (*s*-*Z*) **9**, and the growth of (*s*-*E*)-α-thial methylenecyclopropene (**9**).

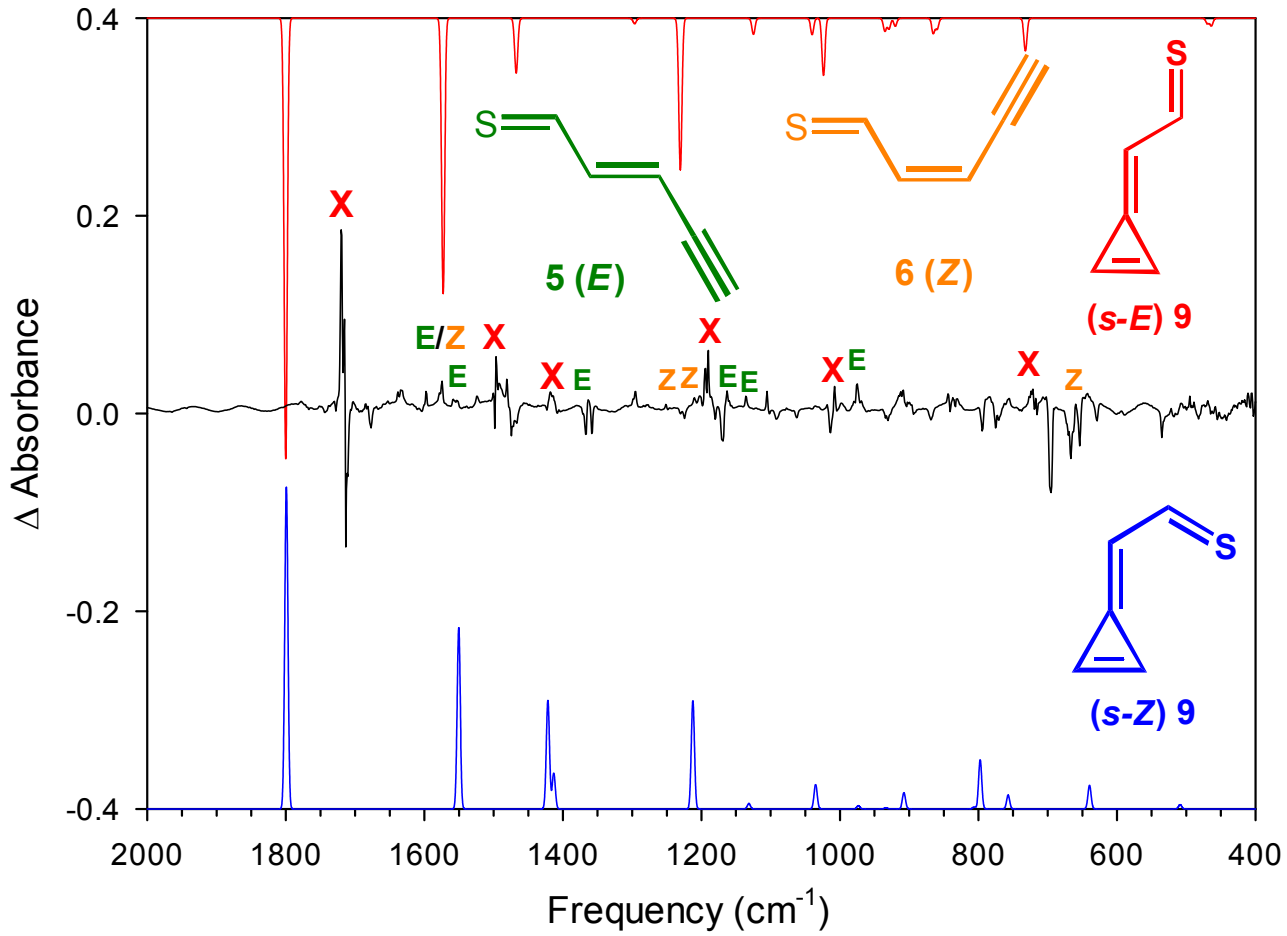

Figure S5. IR subtraction spectrum showing spectral changes observed upon irradiation (λ > 330 nm, 27 h) of a mixture of (*s*-*Z*)- and (*s*-*E*)-α-thial methylenecyclopropene (**9**) (N_2, 10 K). The spectrum shows further decrease in the amount of (*s*-*Z*)-**9** and the growth of (*s*-*E*)-**9** as the major product (marked with red X's). Minor products *E*-pent-2-en-4-ynethial (**5**) and *Z*-pent-2-en-4-ynethial (**6**) are also observed and are labeled accordingly with *E* or *Z*.

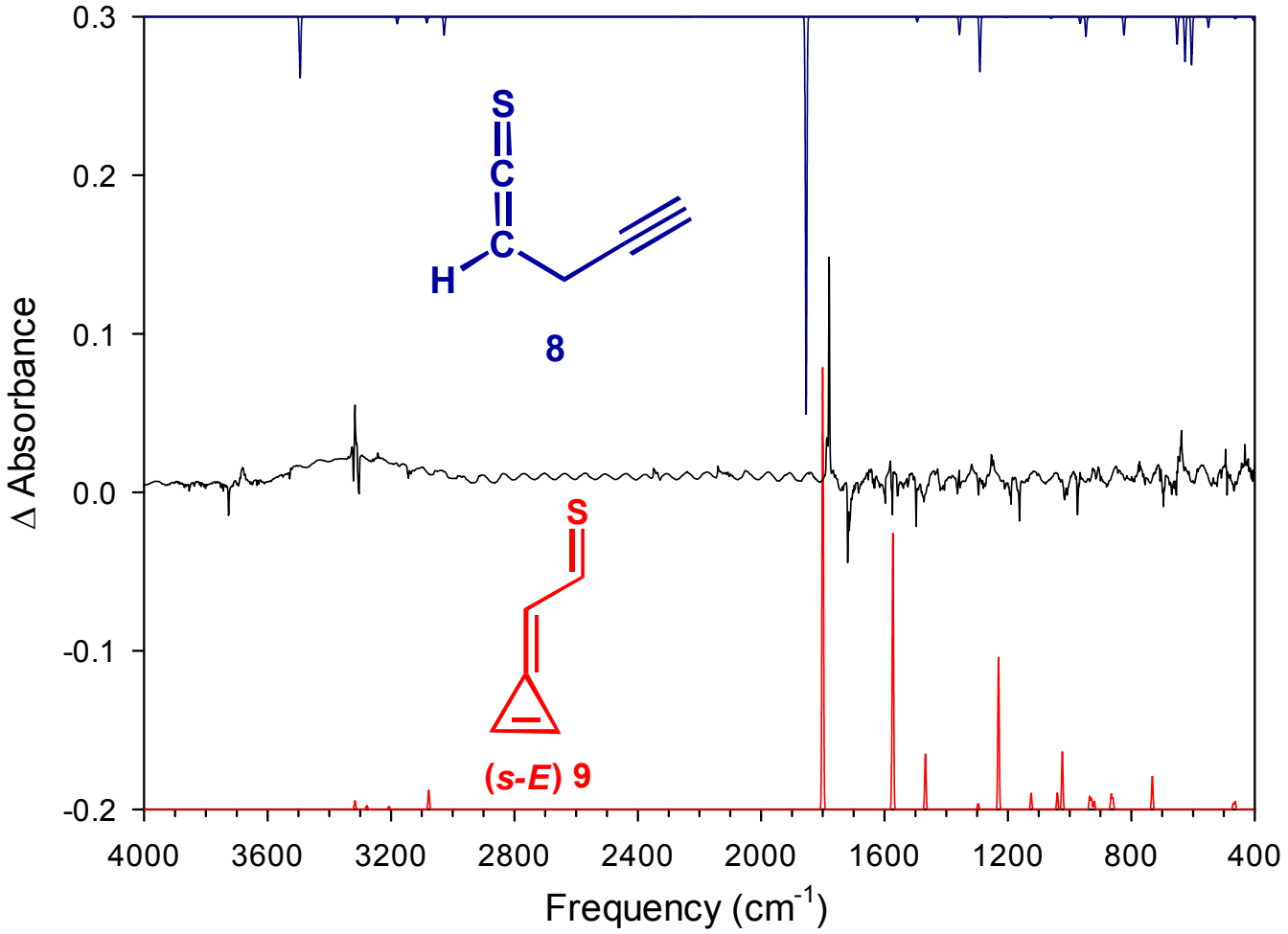

Figure S6. IR subtraction spectrum showing spectral changes observed upon irradiation (λ > 280 nm, 24 h) of a mixture of (*s*-*Z*)- and (*s*-*E*)-α-thial methylenecyclopropene (**9**), and minor amounts of *E*-pent-2-en-4-ynethial (**5**) and *Z*-pent-2-en-4-ynethial (**6**) (N_2, 10 K). The spectrum shows decreases in **5**, **6**, and **9** (major) and the growth of propargylthioketene (**8**).

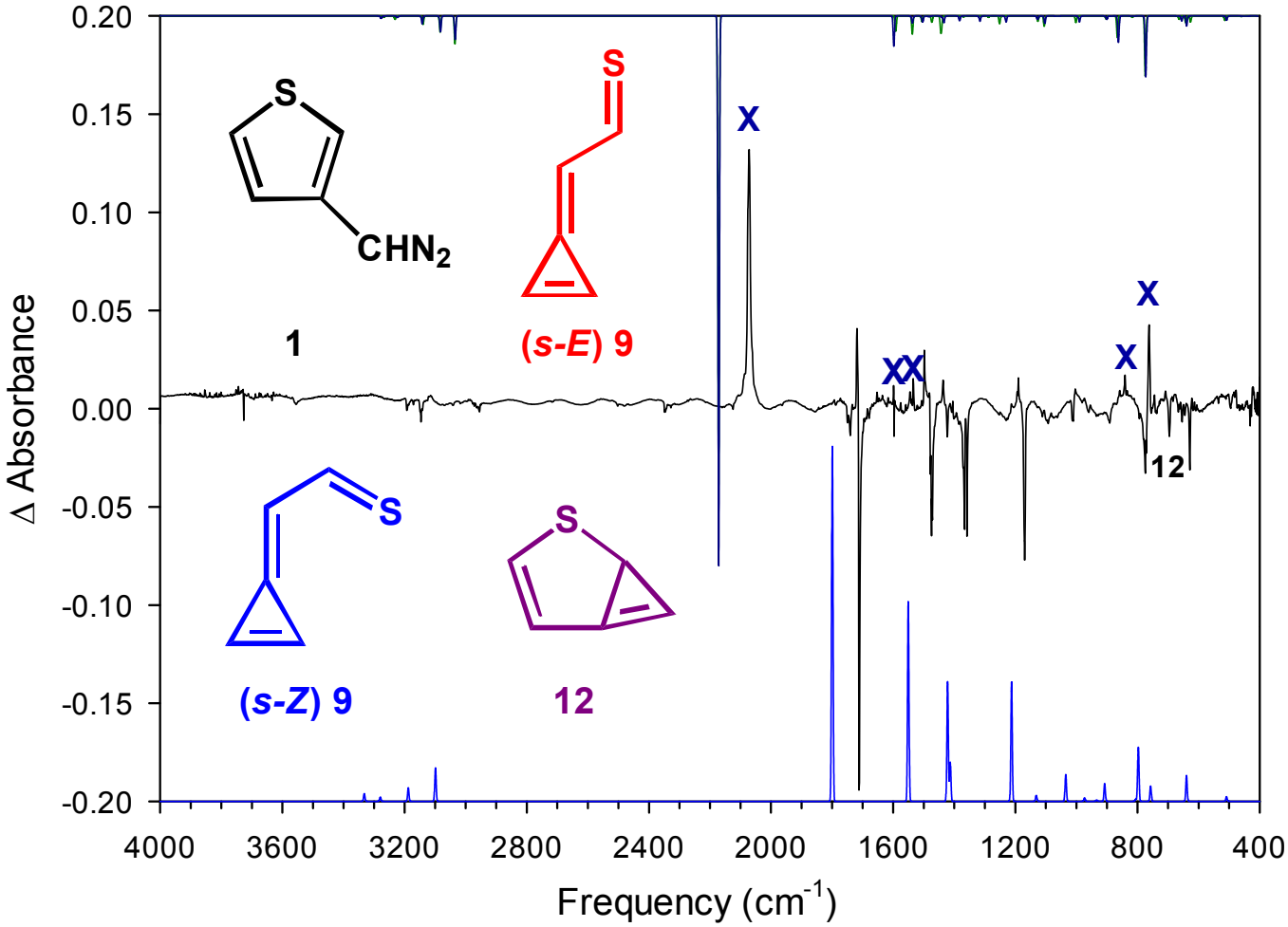

Figure S7. IR subtraction spectrum showing spectral changes observed upon irradiation with a monochromator (λ = 350 nm, 5.5 h) of a mixture of 3-thienyldiazomethane (**1**), 3-thienylcarbene (**13**), 1*H*-2-thiabicyclo[3.1.0]hexa-3,5-diene (**12**), (*s*-*Z*)- and (*s*-*E*)-α-thial methylenecyclopropene (**9**) (N_2, 10 K). The spectrum shows the growth **1** (marked by blue **X**), a minor amount of **13** (unmarked because of small amount), and (*s*-*E*)-**9**. A decrease in the amount of **12** and (*s*-*Z*)-**9** is observed. The B3LYP/6-31G* calculated IR frequencies of **1** are seen at the top of spectrum. The calculated spectrum of (*s*-*Z*)-**9** is seen along the bottom of the spectrum.

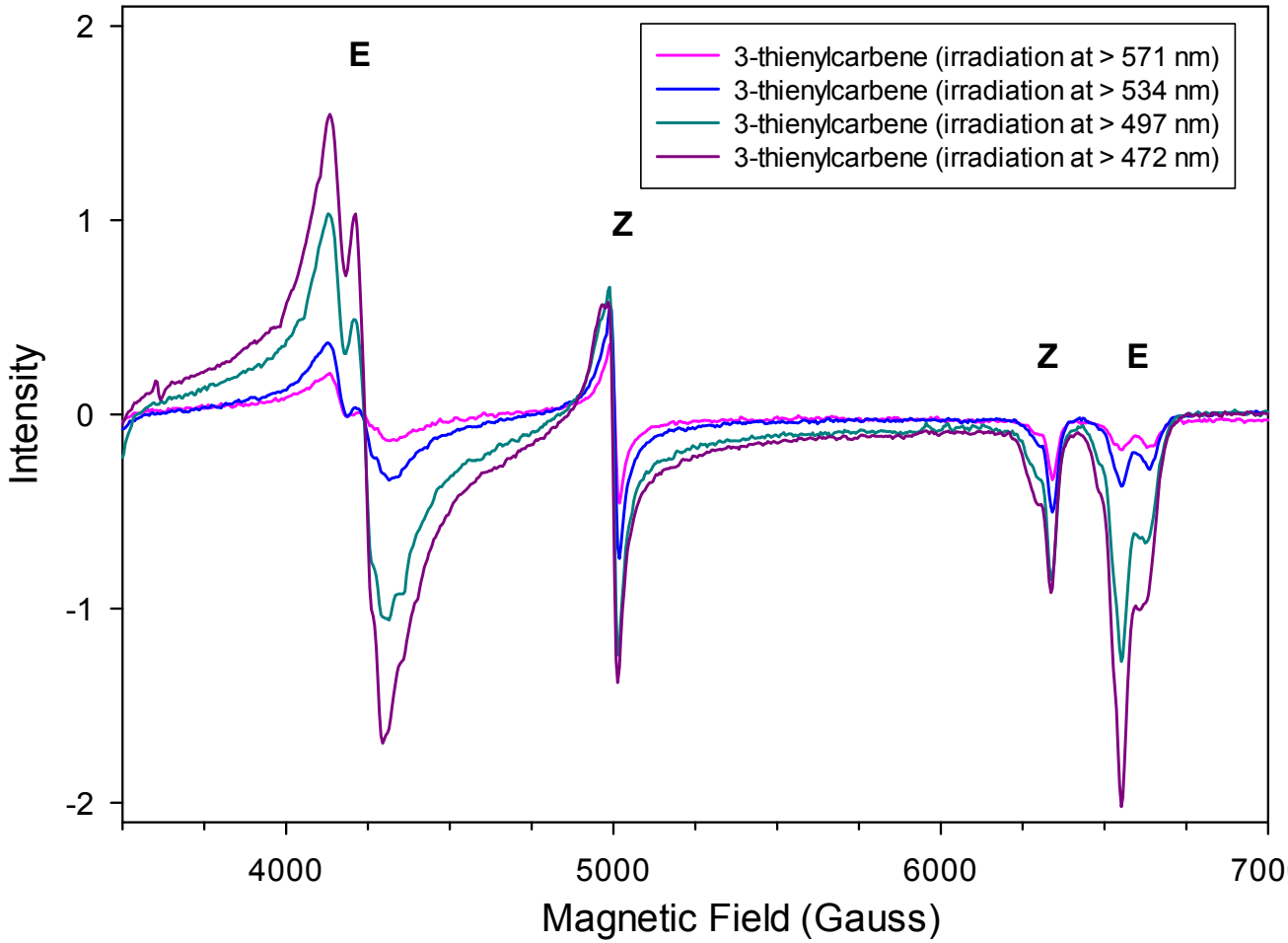

Figure S8. EPR spectra of *s*-*Z* and *s*-*E* 3-thienylcarbene (**13**) illustrating the wavelength dependence in the photolysis of 3-thienyldiazomethane (**1**) (Ar, 15 K). The *s*-*Z* conformer is formed in greater proportion upon irradiation at $\lambda > 571$ nm, while the *s*-*E* conformer becomes the major photoproduct upon shorter-wavelength irradiation ($\lambda > 534$, > 497, > 472 nm). Both rotamers decrease in intensity upon irradiation at > 444 nm (not shown).

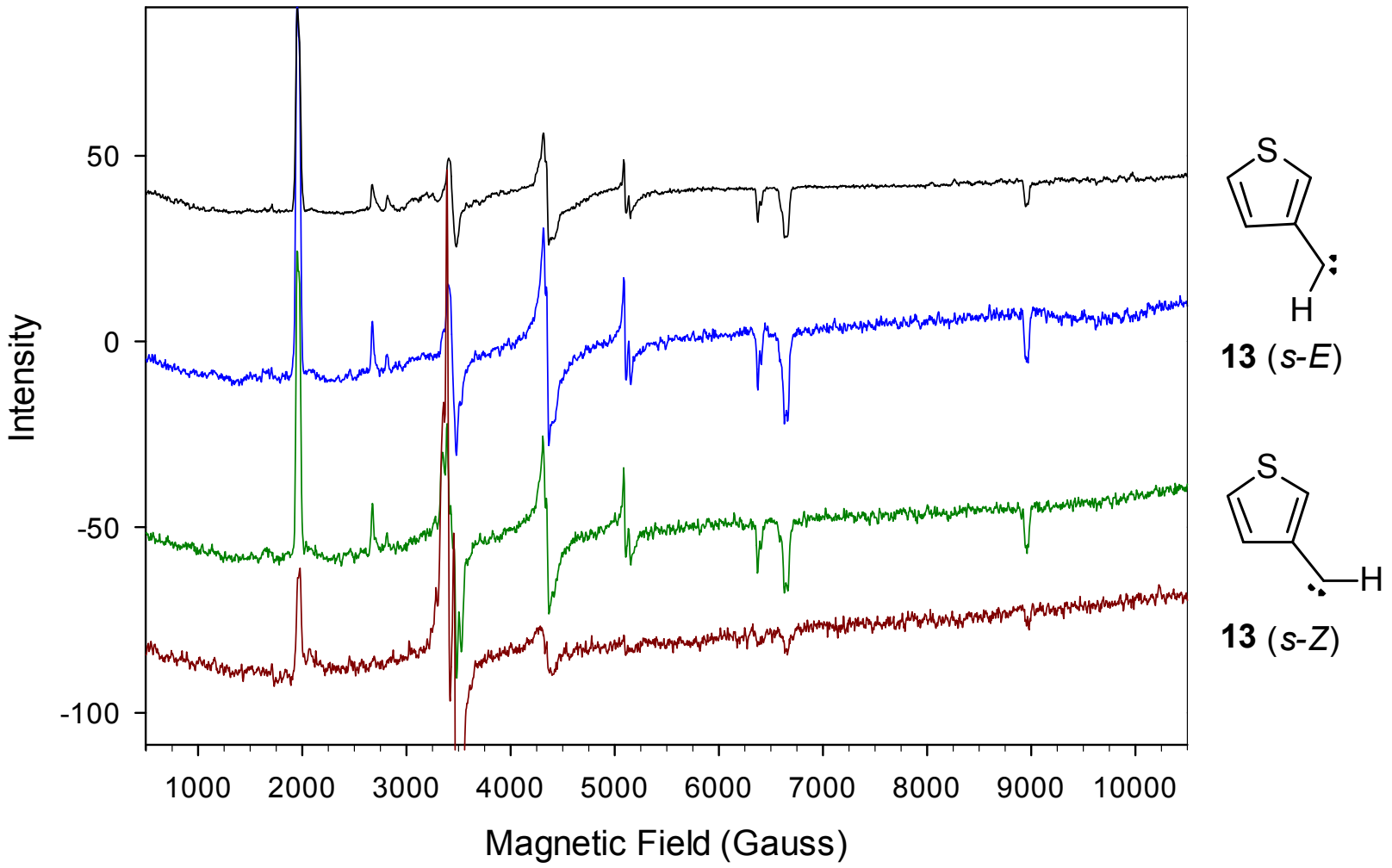

Figure S9. EPR spectra of 3-thienylcarbene rotamers (*s*-*Z* **13** and *s*-*E* **13**) upon formation and being annealed (N_2, 15 K). Top (black): 3-thienylcarbene (**13**) after irradiation ($\lambda > 472$ nm, 17 h) (Receiver Gain = 1.25×10^4). Second from top (blue): **13** after being annealed to 24 K (Receiver Gain = 1.00×10^5). Second from bottom (green): **13** after being annealed to 29 K (Receiver Gain = 1.00×10^5). Bottom (dark red): **13** after being annealed to 35 K (Receiver Gain = 1.00×10^5).

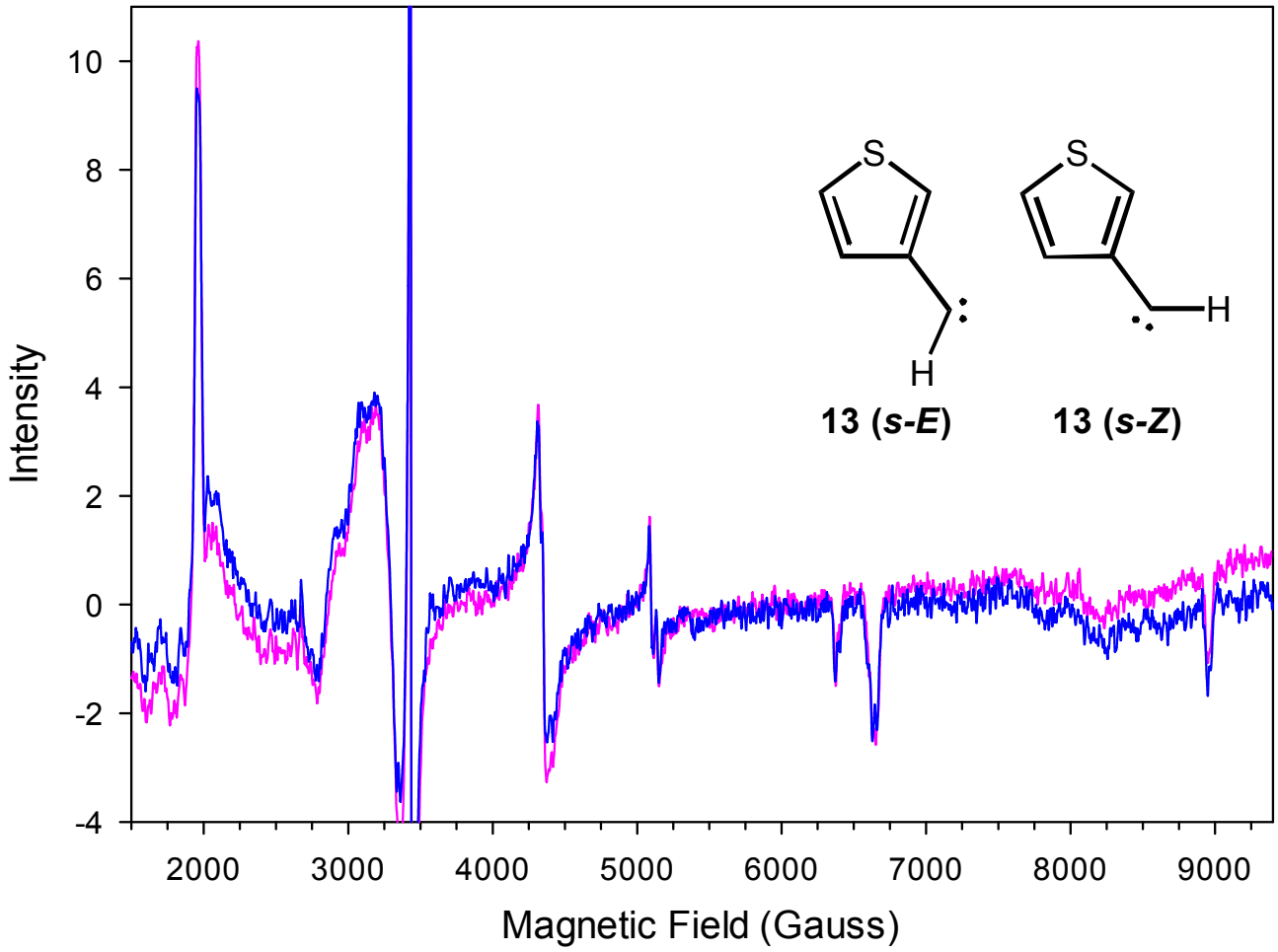

Figure S10. Pink: EPR spectrum of *s*-*Z* and *s*-*E* 3-thienylcarbene (**13**) formed upon irradiation of (3-thienyl)diazomethane (λ > 472 nm, 26 h; Ar, 15 K). Blue: EPR spectrum of *s*-*Z* and *s*-*E* 3-thienylcarbene (**13**) after standing in the dark for 46 h. Spectra are on the same scale.

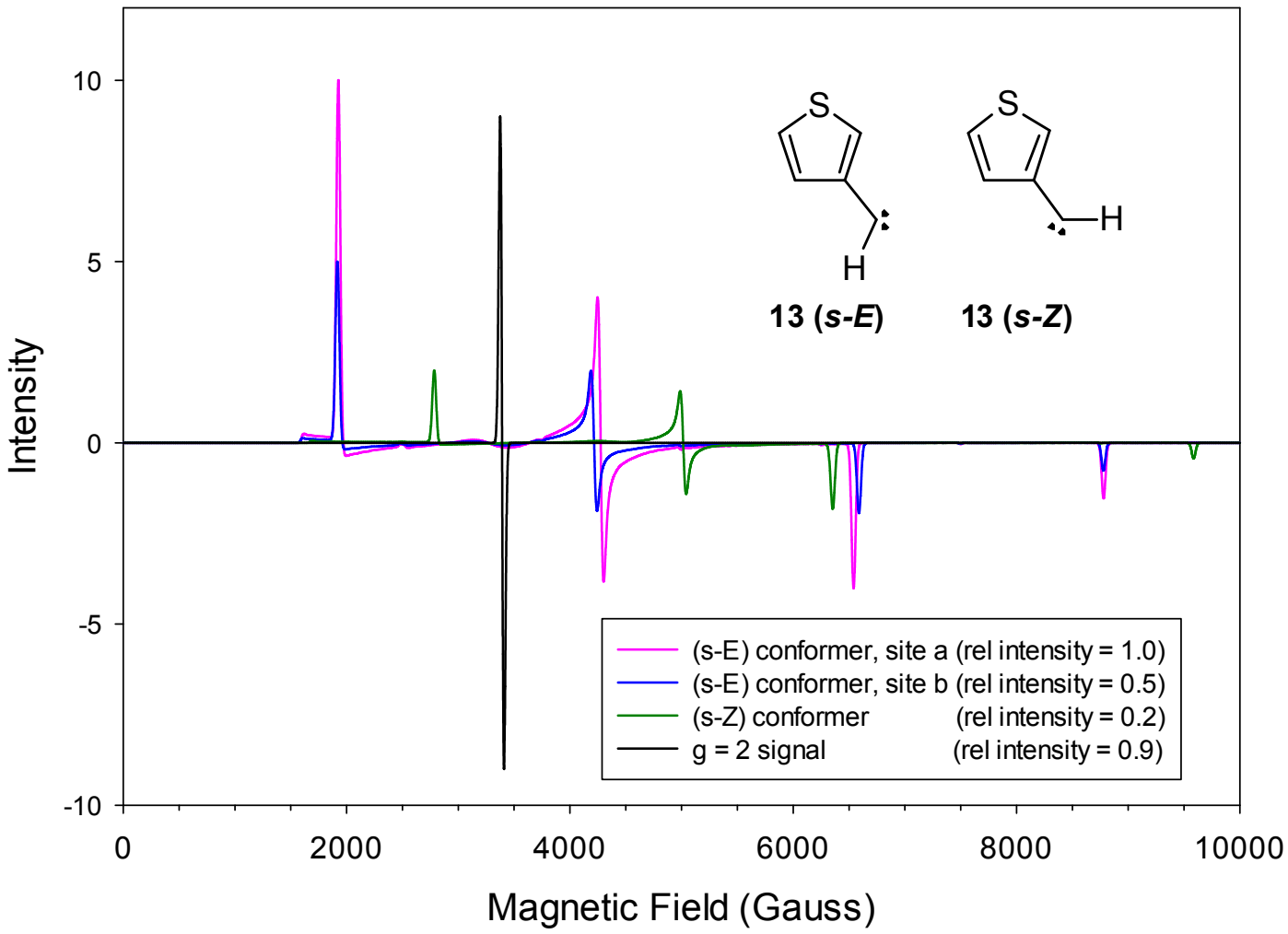

Figure S10a. Simulated EPR spectrum of triplet 3-thienylcarbene (**13**) using data from XSophe. Individual components and relative intensities are given in the figure legend.

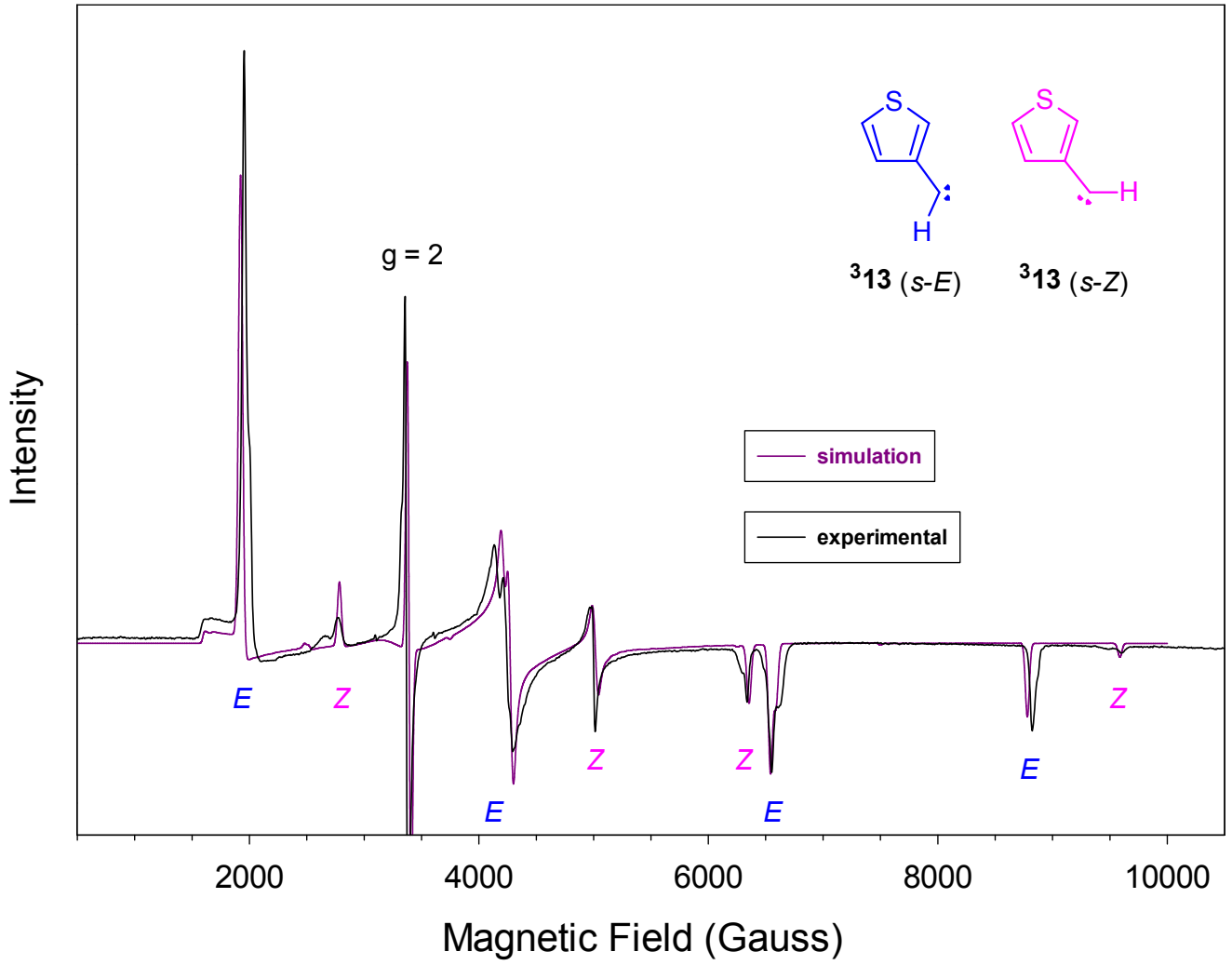

Figure S10b. Overlay of experimental and simulated EPR spectra of triplet 3-thienylcarbene (**13**). This figure represents a direct overlay of the spectral data depicted in Figure 5 of the manuscript.

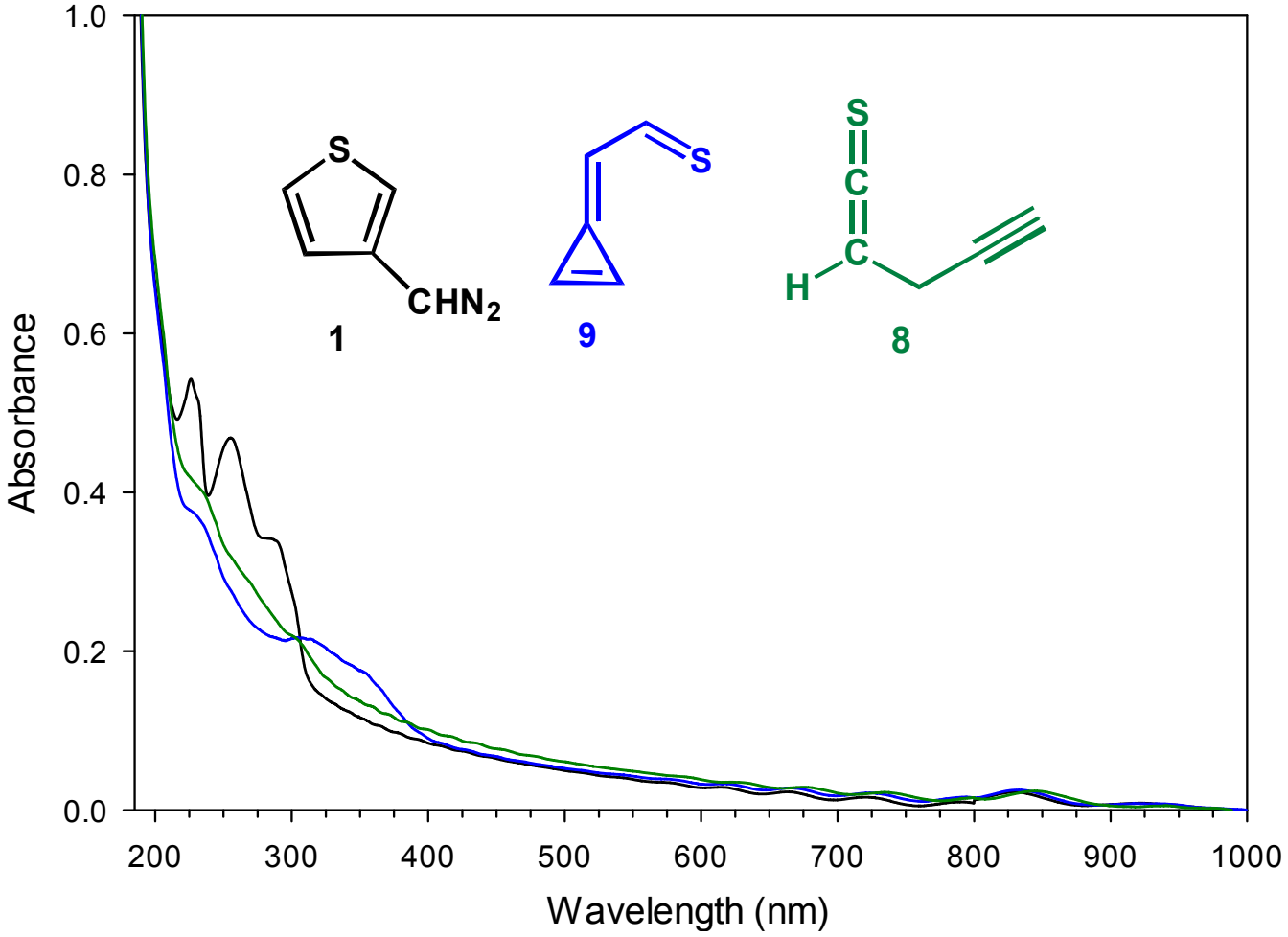

Figure S11. UV/vis spectra. **Black:** 3-thienyldiazomethane (**1**) (prior to irradiation; N_2, 10 K). **Blue:** (*s*-*Z*)-α-thial methylenecyclopropene (**9**) (λ > 497 nm, 15 h; N_2, 10 K). **Green:** propargyl thioketene (**8**) (λ > 280 nm, 24 h; N_2, 10 K).

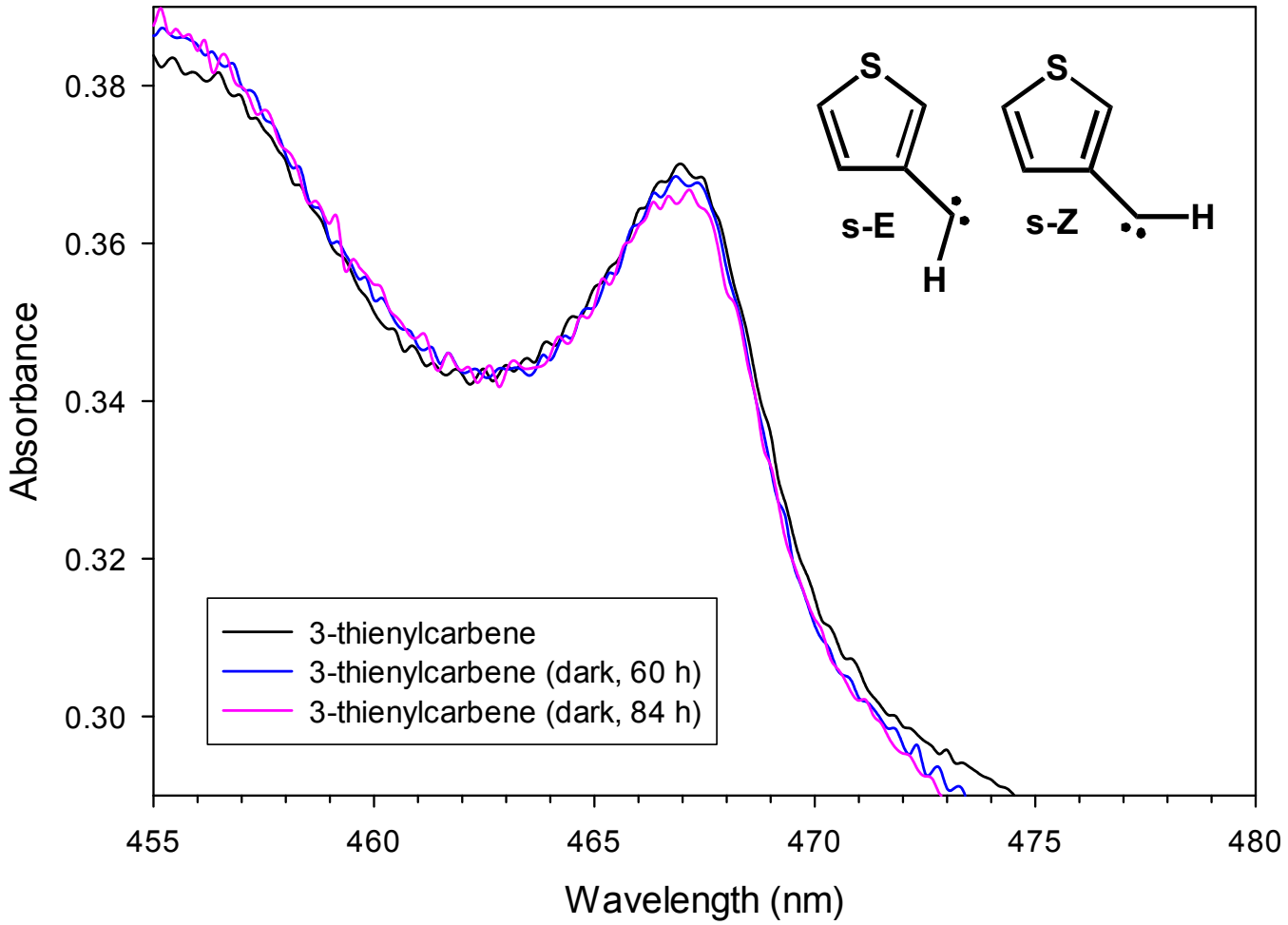

Figure S12. Visible spectra. **Black:** *s-Z* and *s-E* triplet 3-thienylcarbene (**13**) after irradiation of 3-thienyldiazomethane (**1**) ($\lambda > 472$ nm, 26 h; Ar, 15 K). **Blue:** spectrum obtained after standing in the dark for 60 h. **Pink:** spectrum obtained after standing in the dark for 84 h. Spectra are on the same scale.

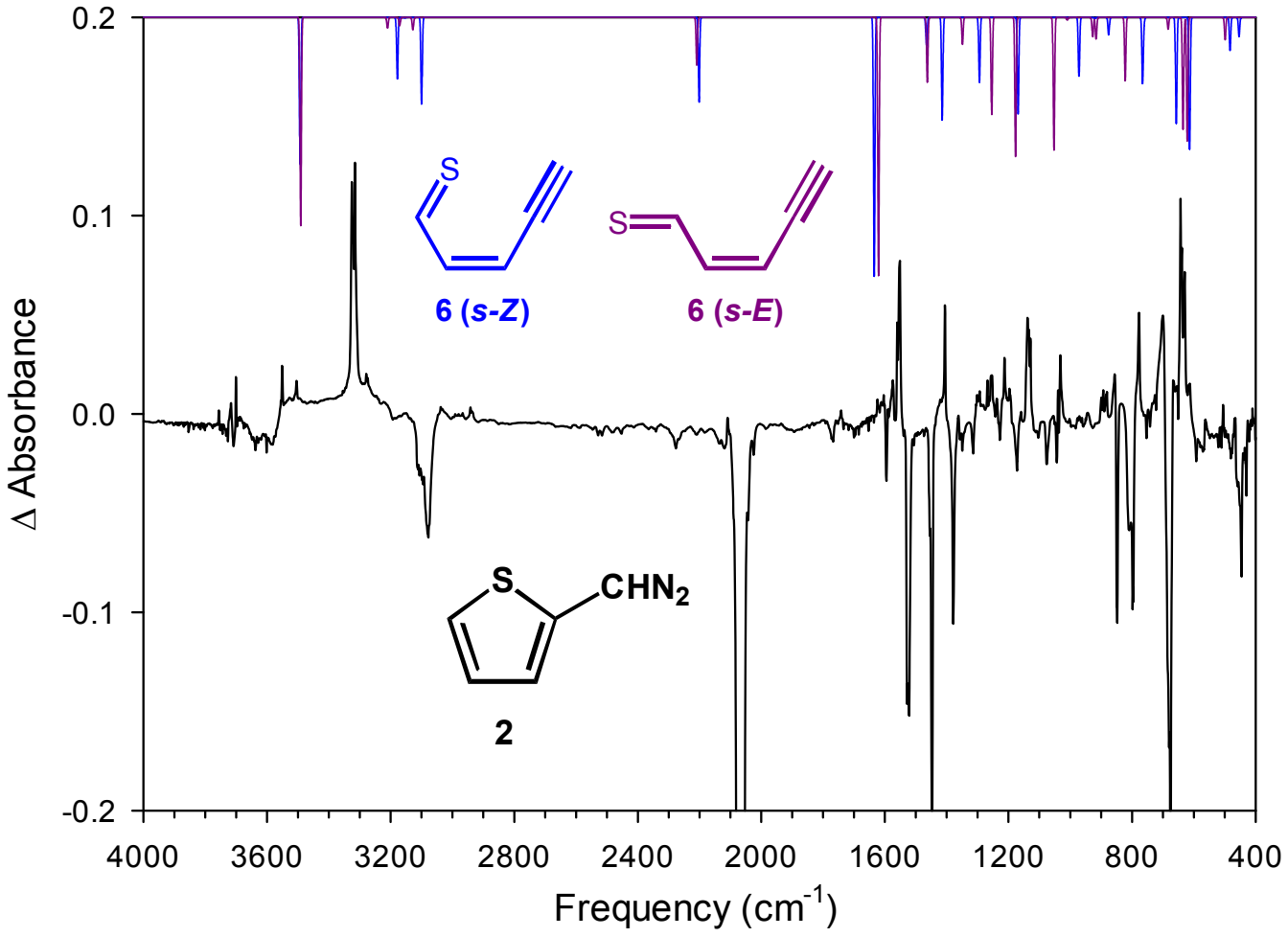

Figure S13. IR subtraction spectrum showing spectral changes observed upon irradiation (λ > 534 nm, 22 h) of (2-thienyl) diazomethane (**2**) (Ar, 10 K). The spectrum shows the disappearance of **2** and the growth of (*s*-*Z*) and (*s*-*E*)-Z-pent-2-en-4-ynethial (**6**).

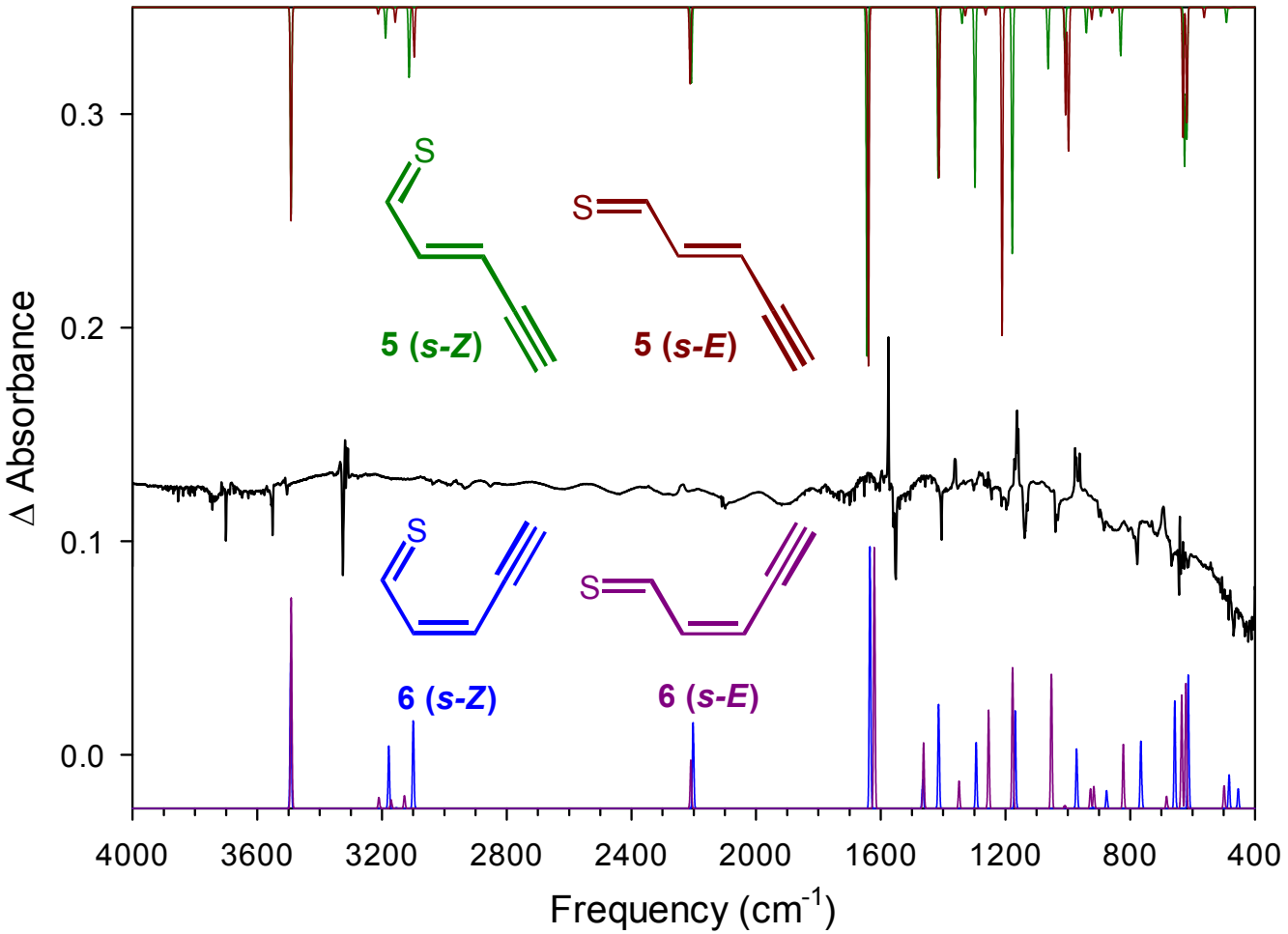

Figure S14. IR subtraction spectrum showing spectral changes observed upon irradiation of the matrix shown in Figure S13 (λ > 363 nm, 20 h) of (*s*-*Z*) and (*s*-*E*)-*Z*-pent-2-en-4-ynethial (**6**) (Ar, 10 K). The spectrum shows the disappearance of **6** and the growth of (*s*-*E*)-*E*-pent-2-en-4-ynethial (**5**). The calculated spectrum of (*s*-*Z*)-*E*-pent-2-en-4-ynethial is also shown (green) for comparison purposes.

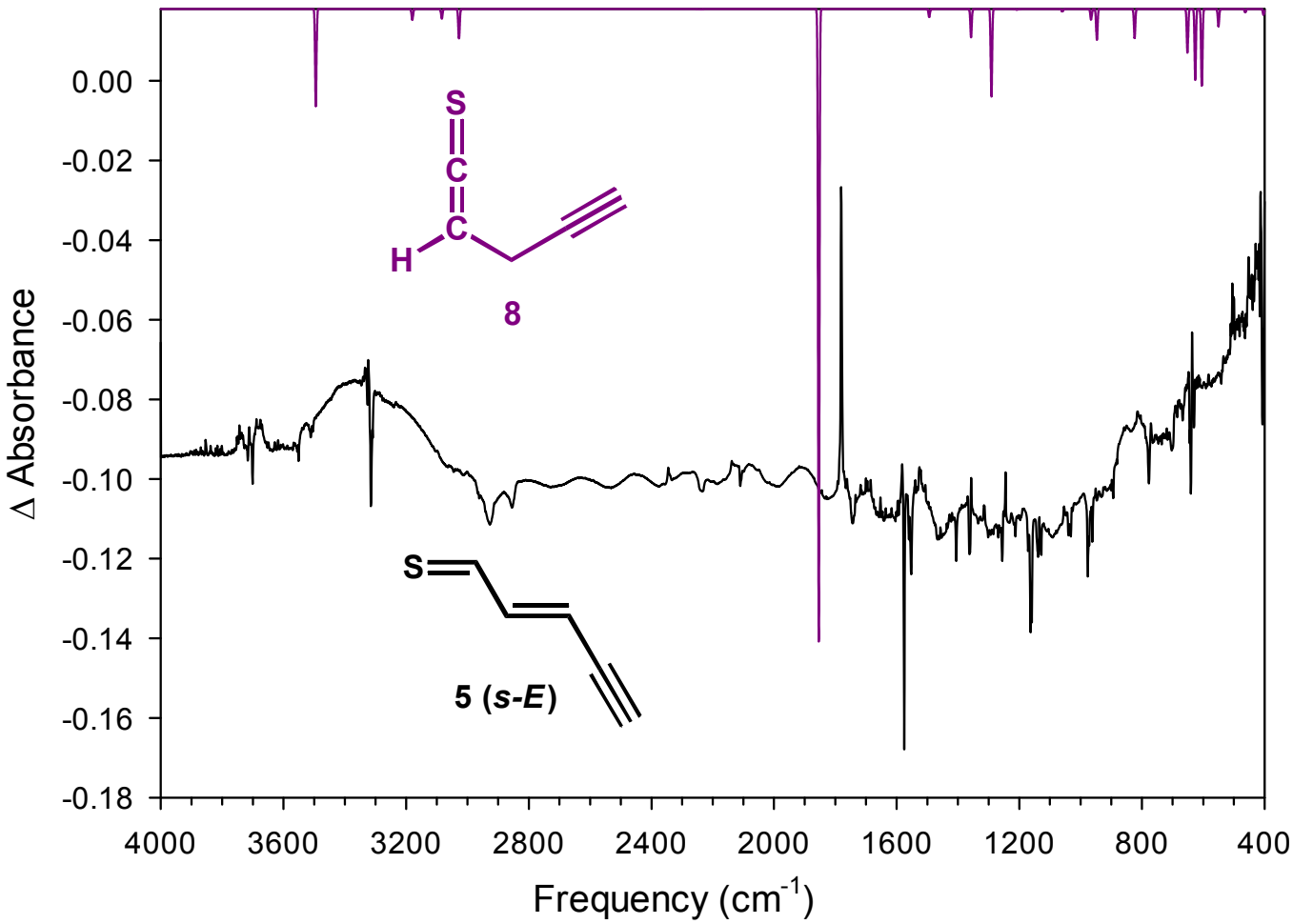

Figure S15. IR subtraction spectrum showing spectral changes observed upon irradiation of the matrix shown in Figure S14 (λ > 237 nm, 4 h) of *E*-pent-2-en-4-ynethial (**5**) (Ar, 10 K). The spectrum shows the disappearance of (*s*-*E*)-**5** and the growth of propargyl thioketene (**8**).

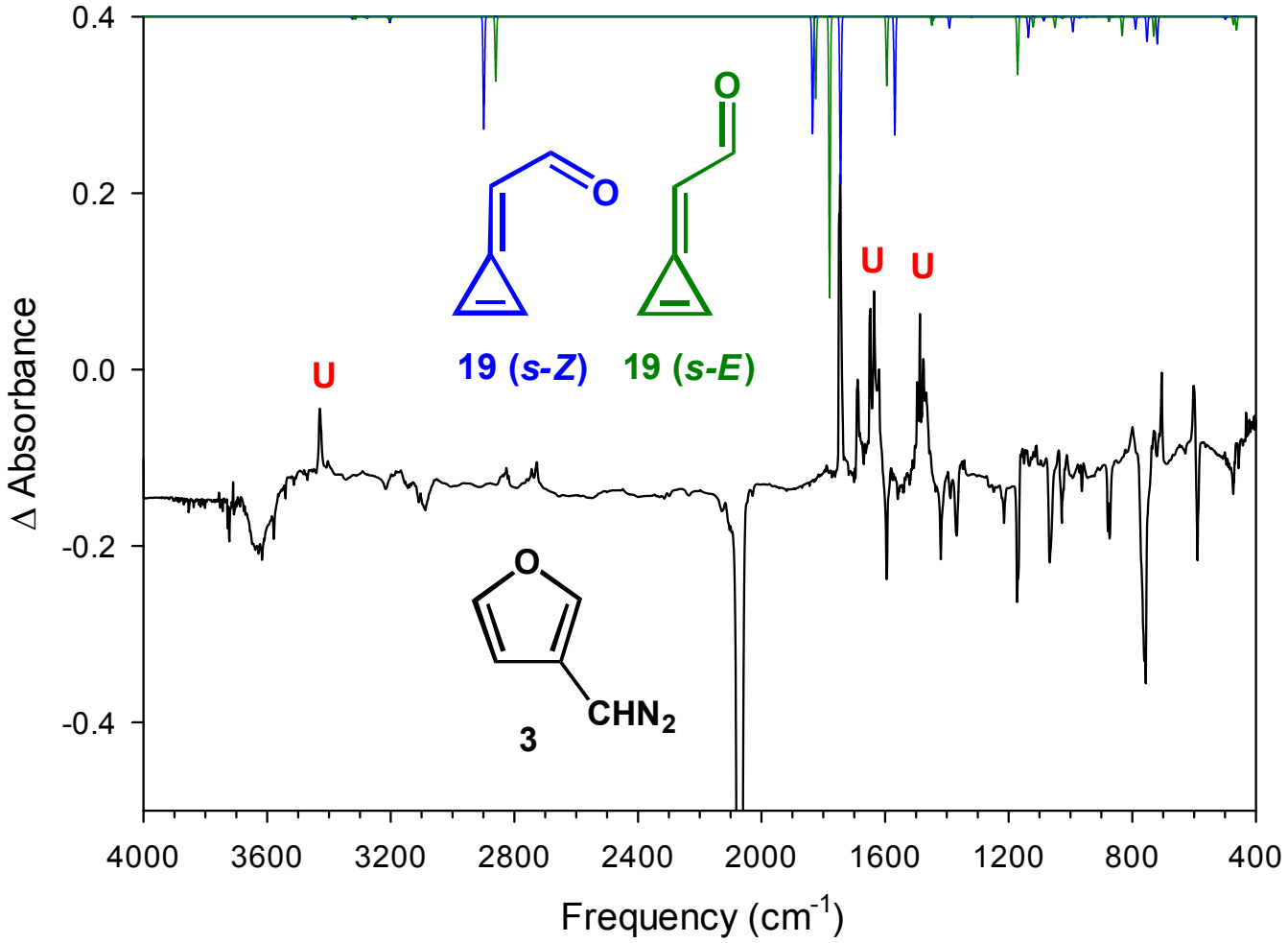

Figure S16. IR subtraction spectrum showing spectral changes observed upon irradiation (λ > 472 nm, 19 h) of (3-furyl) diazomethane (**3**) (Ar, 10 K). The spectrum shows the disappearance of **3** and the growth of the growth of (*s*-*Z*) and (*s*-*E*)-(α-formyl)methylenecyclopropene (**19**) and an unknown species (**U**).

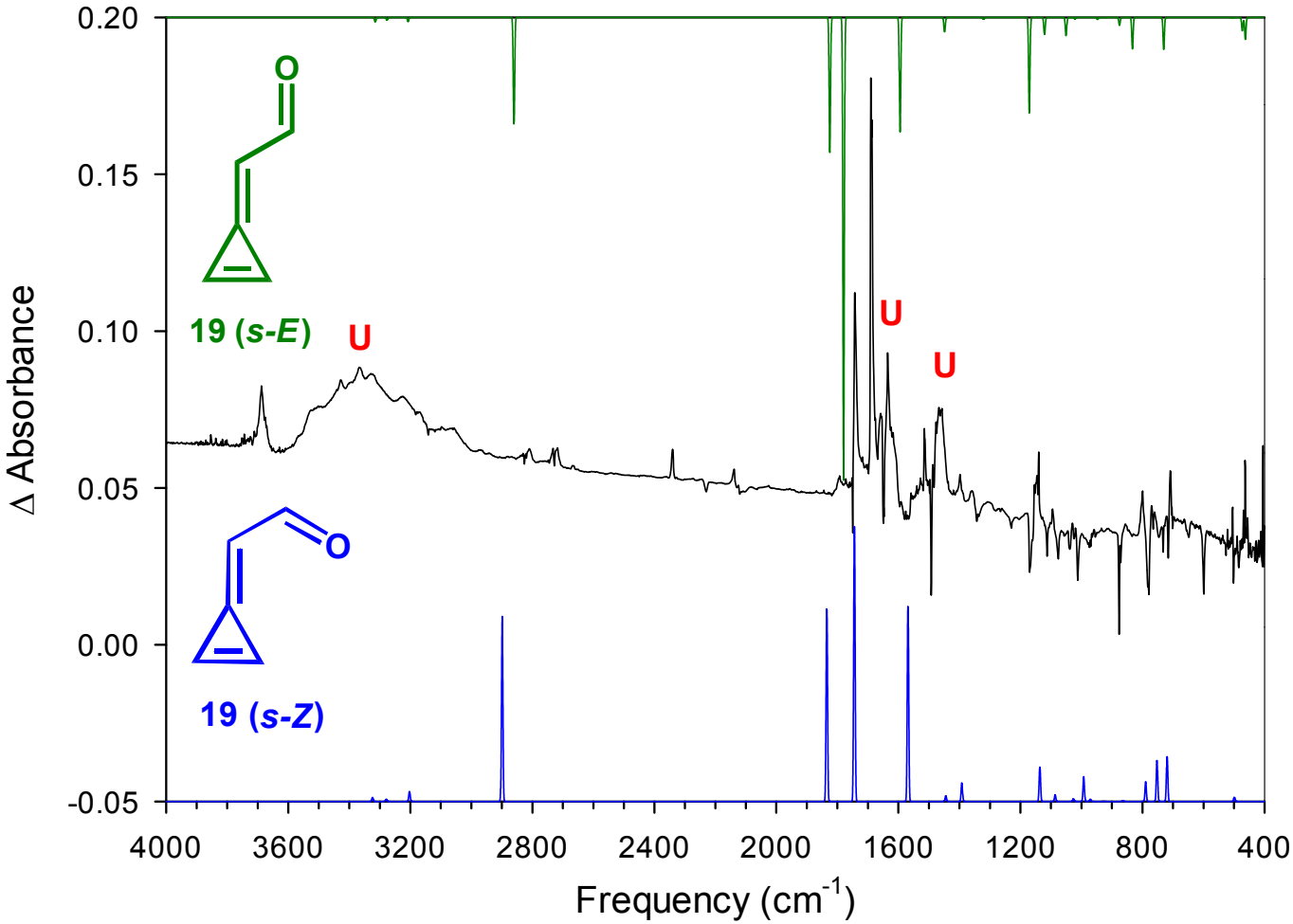

Figure S17. IR subtraction spectrum showing spectral changes observed upon irradiation (λ > 399 nm, 10 h) of mixture of (*s*-*Z*) and (*s*-*E*)-(α-formyl)methylenecyclopropene (**19**) and an unknown species (**U**) (Ar, 10 K). The spectrum shows the disappearance of (*s*-*Z*)-**19** and the growth of (*s*-*E*)-**19** and **U**.

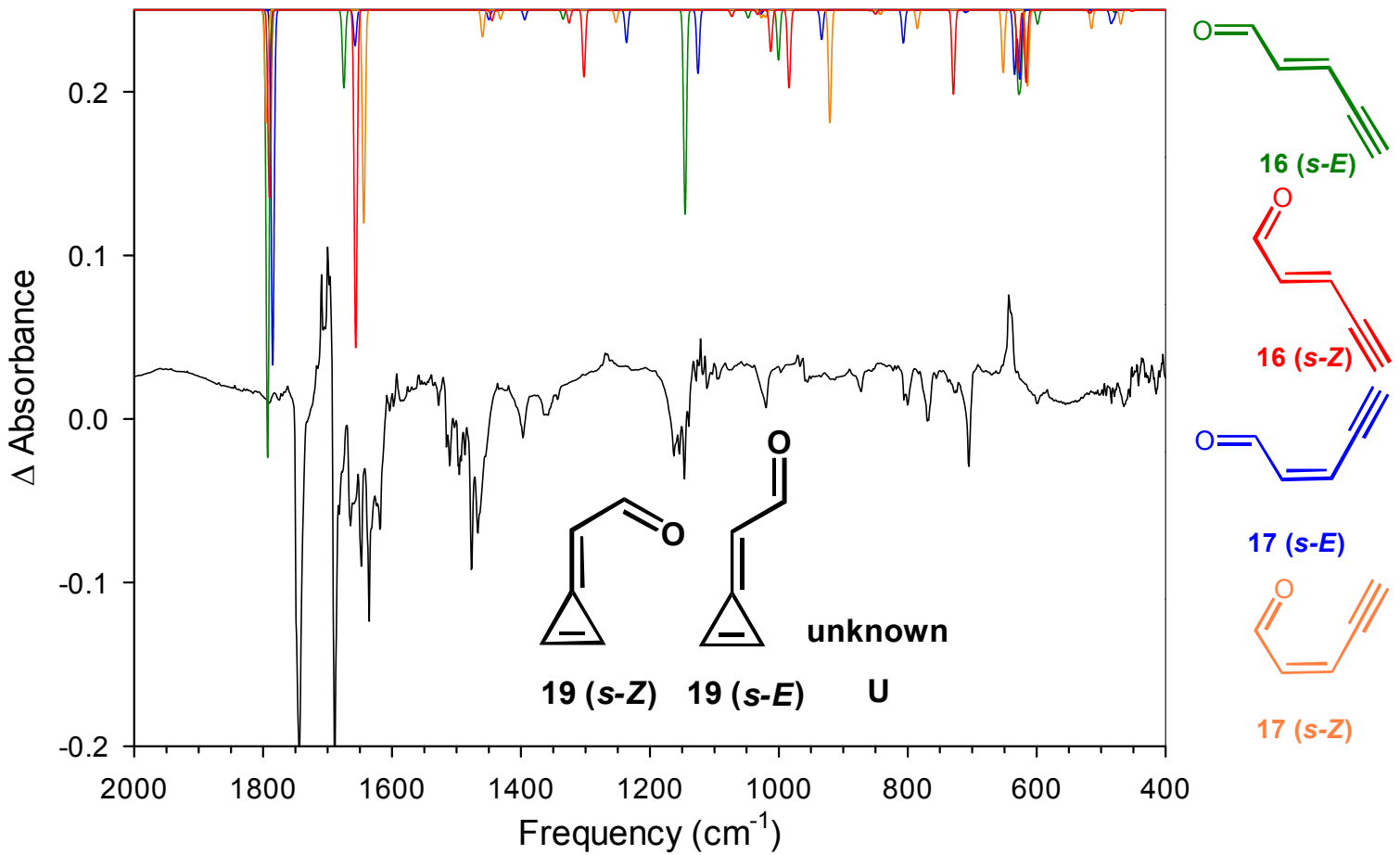

Figure S18. IR subtraction spectrum showing spectral changes observed upon irradiation (λ > 330 nm, 20 h) of mixture of (*s*-*Z*) and (*s*-*E*)-(α-formyl)methylenecyclopropene (**19**), and an unknown species (**U**) (Ar, 10 K). The spectrum shows the disappearance of **19** and the growth of *E*-pent-2-en-4-ynal (**16**) and *Z*-pent-2-en-4-ynal (**17**). Calculated spectra for (*s*-*Z*) and (*s*-*E*) rotamers of **16** and **17** are seen at the top of the spectrum. Experimental IR stretches are best matched with the (*s*-*E*) rotamers of **16** and **17**.

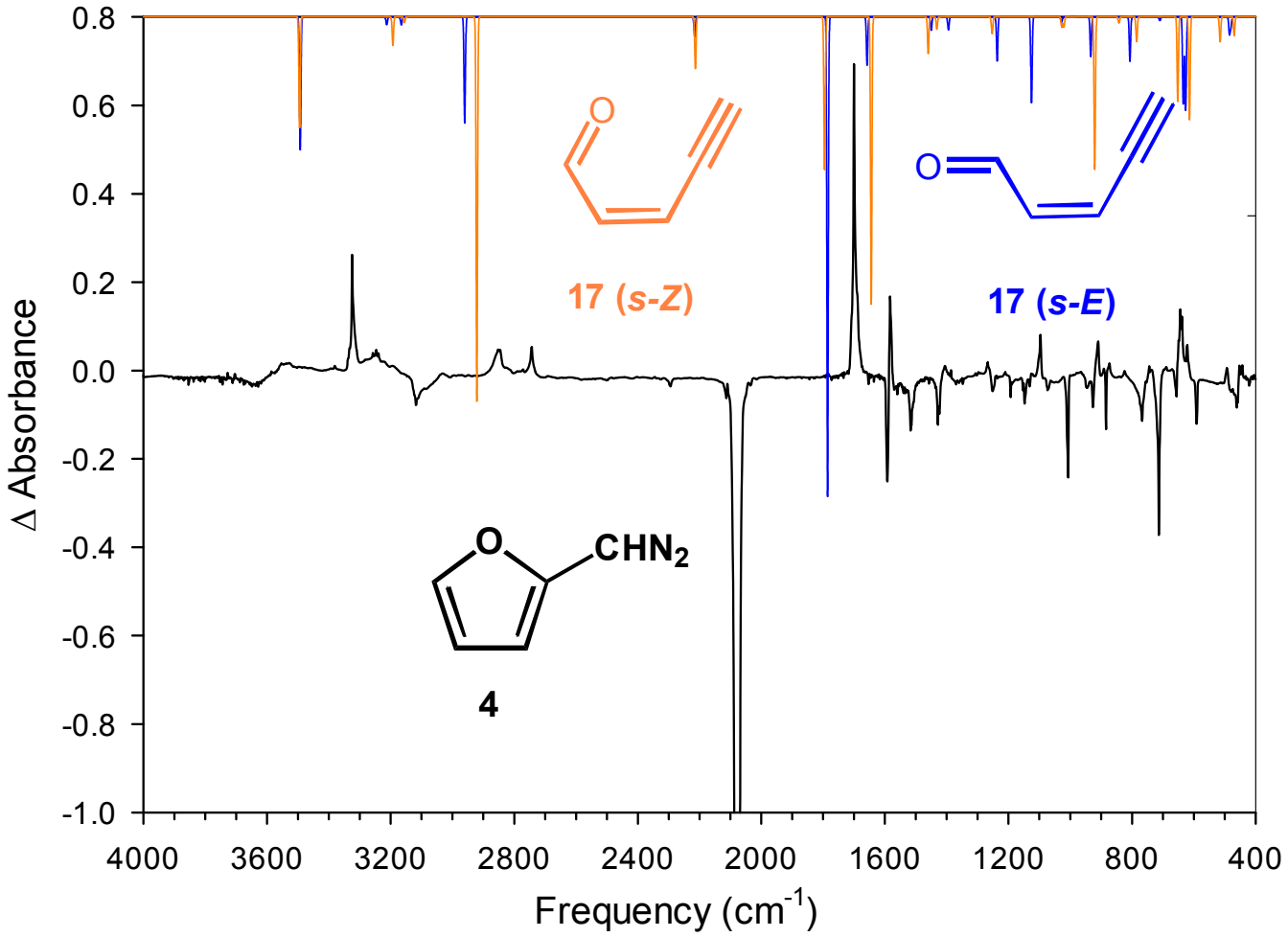

Figure S19. IR subtraction spectrum showing spectral changes observed upon irradiation (λ > 613 nm, 22 h) of (2-furyl) diazomethane (**4**) (Ar, 10 K). The spectrum shows the disappearance of **4** and the growth of (*s*-*E*)-Z-pent-2-en-4-ynal (**17**). B3LYP/6-31G* calculated IR frequencies of (*s*-*Z*) and (*s*-*E*)-**17** can be seen at the top of the spectrum.

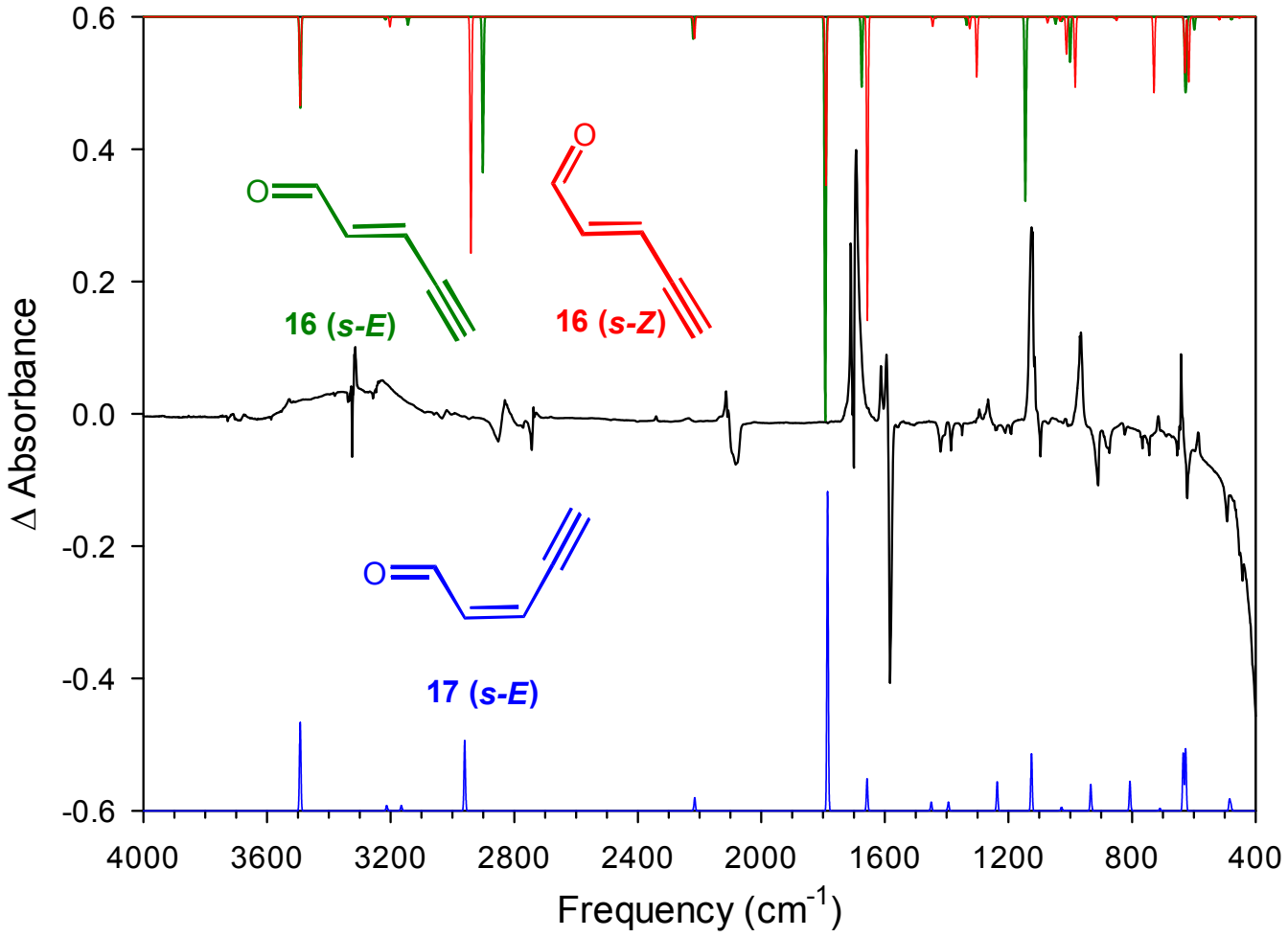

Figure S20. IR subtraction spectrum showing spectral changes observed upon irradiation (λ > 444 nm, 24 h) of *Z*-pent-2-en-4-ynal (**17**). The spectrum shows the disappearance of (*s*-*E*)-**17** and the growth of (*s*-*E*)-*E*-pent-2-en-4-ynal (**16**).

Table S.3 B3LYP/6-31G* Uncorrected Energies (Hartree), Zero Point Vibrational Energies (kcal/mol), and Cartesian Coordinates (Å)

(*s*-*Z*)-3-thienyldiazomethane (1)

E = -700.553741306
ZPVE = 50.87070

S	-2.07625	0.015839	-0.71449
C	-2.01168	0.010835	1.017988
C	-0.72651	0.000994	1.474384
C	0.2497	-0.00278	0.41695
C	-0.34599	0.004504	-0.82519
C	1.676788	-0.01312	0.703399
N	2.570433	-0.01664	-0.24027
N	3.337686	-0.01955	-1.09372
H	-2.92471	0.015441	1.597788
H	-0.4637	-0.00355	2.527155
H	2.064017	-0.01839	1.714264
H	0.133652	0.003836	-1.79458

Table S.4 B3LYP/6-31G* Uncorrected Energies (Hartree), Zero Point Vibrational Energies (kcal/mol), and Cartesian Coordinates (Å)

(*s*-*E*)-3-thienyldiazomethane (1)

E = -700.554121914
ZPVE = 50.90832

S	-1.94906	0.043913	-1.36711
C	-1.91142	-0.14688	0.356599
C	-0.63722	-0.12972	0.841763
C	0.354857	0.040962	-0.18753
C	-0.21951	0.148491	-1.43462
C	1.790615	0.095862	0.036428
H	-2.83247	-0.26065	0.912116
H	-0.39914	-0.23413	1.894957
H	0.280298	0.282753	-2.38427
H	2.501598	0.226066	-0.76969
N	2.305117	-0.00795	1.225572
N	2.747848	-0.10191	2.28082

Table S.5 B3LYP/6-31G* Uncorrected Energies (Hartree), Zero Point Vibrational Energies (kcal/mol), and Cartesian Coordinates (Å)

(*s*-*Z*)-2-thienyldiazomethane (2)

E = -700.553197517
ZPVE = 50.77410

S	-1.20807	0.003383	0.270744
C	-1.10131	0.020685	2.009413
C	0.197652	0.024149	2.431026
C	1.136306	0.012901	1.358315
C	0.539743	0.000835	0.115407
C	1.219403	-0.01227	-1.15944
N	0.592726	-0.02328	-2.29948
N	0.034095	-0.03296	-3.30239
H	2.30094	-0.01348	-1.21924
H	2.212635	0.013639	1.494053
H	0.483562	0.034433	3.47743
H	-2.0066	0.027106	2.600538

Table S.6 B3LYP/6-31G* Uncorrected Energies (Hartree), Zero Point Vibrational Energies (kcal/mol), and Cartesian Coordinates (Å)

(*s*-*E*)-2-thienyldiazomethane (2)

E = -700.553077536
ZPVE = 50.80675

S	-1.7554	-0.00733	0.05404
C	-1.58888	0.015937	1.786132
C	-0.27445	0.026804	2.158748
C	0.626437	0.016599	1.053807
C	-0.01604	-0.0022	-0.16555
C	0.524087	-0.01706	-1.50808
N	1.808351	-0.01427	-1.71813
N	2.944439	-0.01089	-1.879
H	-0.09548	-0.03166	-2.39557
H	1.706433	0.022878	1.155702
H	0.050067	0.041722	3.193808
H	-2.47118	0.02001	2.411016

Table S.7 B3LYP/6-31G* Uncorrected Energies (Hartree), Zero Point Vibrational Energies (kcal/mol), and Cartesian Coordinates (Å)

(*s*-*Z*)-3-furyldiazomethane (3)

E = -377.570395709
ZPVE = 52.91204

O	-2.13693	0.01059	-0.47614
C	-2.22163	0.010872	0.881173
C	-0.98311	0.00478	1.439803
C	-0.04248	0.000278	0.345544
C	-0.80763	0.004146	-0.79204
C	1.401916	-0.00677	0.495305
N	2.203138	-0.01093	-0.52791
N	2.892966	-0.01451	-1.44571
H	-3.22037	0.01578	1.290342
H	-0.74749	0.003518	2.49518
H	1.88174	-0.00891	1.465457
H	-0.57353	0.003098	-1.8452

Table S.8 B3LYP/6-31G* Uncorrected Energies (Hartree), Zero Point Vibrational Energies (kcal/mol), and Cartesian Coordinates (Å)

(*s*-*E*)-3-furyldiazomethane (3)

E = -377.571292646
ZPVE = 52.96146

O	-2.08686	0.012437	-1.18277
C	-2.15829	0.174879	0.166226
C	-0.91919	0.150471	0.722502
C	0.009192	-0.04332	-0.36585
C	-0.7634	-0.11931	-1.49489
C	1.455101	-0.14047	-0.30561
N	2.096715	-0.05532	0.821095
N	2.65318	0.021388	1.822836
H	-3.15075	0.29387	0.573487
H	-0.67935	0.255519	1.771588
H	2.07041	-0.28726	-1.18438
H	-0.53515	-0.25765	-2.54029

Table S.9 B3LYP/6-31G* Uncorrected Energies (Hartree), Zero Point Vibrational Energies (kcal/mol), and Cartesian Coordinates (Å)

(*s*-*Z*)-2-furyldiazomethane (4)

E = -377.574344875
ZPVE = 52.85073

O	-0.87271	0.002739	0.476679
C	-0.96234	0.001086	1.845738
C	0.279339	-0.00227	2.398681
C	1.211423	-0.00417	1.310427
C	0.457809	-0.00133	0.164201
C	0.821376	-0.00179	-1.2302
N	-0.07307	0.001506	-2.17534
N	-0.86376	0.004454	-3.00571
H	1.855477	-0.00498	-1.54737
H	2.290683	-0.00746	1.369116
H	0.512189	-0.00388	3.454527
H	-1.96451	0.003482	2.244562

Table S.10 B3LYP/6-31G* Uncorrected Energies (Hartree), Zero Point Vibrational Energies (kcal/mol), and Cartesian Coordinates (Å)

(*s*-*E*)-2-furyldiazomethane (4)

E = -377.573818739
ZPVE = 52.79835

O	0.954121	0.293333	-1.25779
C	1.026666	1.659096	-1.33543
C	0.285215	2.227249	-0.34732
C	-0.29174	1.15103	0.401221
C	0.146978	-0.00445	-0.19441
C	-0.04588	-1.41497	0.041724
N	-0.78777	-1.84766	1.01698
N	-1.44572	-2.21645	1.882081
H	0.420455	-2.1636	-0.58497
H	-0.94166	1.225632	1.261683
H	0.158896	3.28565	-0.1661
H	1.636321	2.046749	-2.13644

Table S.11 B3LYP/6-31G* Uncorrected Energies (Hartree), Zero Point Vibrational Energies (kcal/mol), and Cartesian Coordinates (Å)

(*s*-*Z*)-*E*-pent-2-en-4-ynethial (5)

E = -591.019126029
ZPVE = 43.29916

C	-0.996467	-0.090462	3.392487
H	-1.265453	-0.184432	4.420477
C	-0.683956	0.002428	2.224432
C	-0.340779	0.152396	0.864375
H	-0.643804	1.073228	0.365847
C	0.340356	-0.776447	0.143930
H	0.649177	-1.700231	0.628339
C	0.694236	-0.624844	-1.253638
S	0.371084	0.644384	-2.248739
H	1.242395	-1.477140	-1.664353

Table S.12 B3LYP/6-31G* Uncorrected Energies (Hartree), Zero Point Vibrational Energies (kcal/mol), and Cartesian Coordinates (Å)

(*s*-*E*)-*E*-pent-2-en-4-ynethial (5)

E = -591.022652707
ZPVE = 43.37235

S	-1.254499	-0.002629	-2.355870
C	-1.090475	-0.012578	-0.721709
C	0.160911	0.002761	-0.010727
C	0.205531	-0.007036	1.348734
C	1.395365	0.006895	2.109512
C	2.398453	0.018325	2.790000
H	3.290649	0.028653	3.374801
H	-0.730885	-0.026975	1.907215
H	1.077322	0.022560	-0.594179
H	-1.983815	-0.032376	-0.088782

Table S.13 B3LYP/6-31G* Uncorrected Energies (Hartree), Zero Point Vibrational Energies (kcal/mol), and Cartesian Coordinates (Å)

(*s*-*Z*)-*Z*-pent-2-en-4-ynethial (6)

E = -591.013697909
ZPVE = 43.41683

C	-1.781609	1.613933	-1.781609
H	-2.831713	1.773040	1.098856
C	-0.607969	1.352791	0.838403
C	0.789485	1.193918	0.739941
H	1.369461	1.978407	1.226134
C	1.496328	0.203814	0.126315
H	2.579841	0.293089	0.181644
C	1.018189	-0.956570	-0.592842
S	-0.527122	-1.431979	-0.887480
H	1.829815	-1.580194	-0.979338

Table S.14 B3LYP/6-31G* Uncorrected Energies (Hartree), Zero Point Vibrational Energies (kcal/mol), and Cartesian Coordinates (Å)

(*s*-*E*)-*Z*-pent-2-en-4-ynethial (6)

E = -591.021458570
ZPVE = 43.51655

S	-0.054650	0.027762	-2.450383
C	-0.150679	0.007590	-0.810735
C	0.983258	0.010905	0.077967
C	0.884919	-0.006034	1.436059
C	-0.319996	-0.029116	2.178572
C	-1.323368	-0.049029	2.858371
H	-2.215427	-0.066511	3.443274
H	1.803586	-0.001791	2.021156
H	1.970133	0.028030	-0.376245
H	-1.128700	-0.009818	-0.323466

Table S.15 B3LYP/6-31G* Uncorrected Energies (Hartree), Zero Point Vibrational Energies (kcal/mol), and Cartesian Coordinates (Å)

4-thiacyclohexa-1,2,5-triene (7)

E = -591.011046449
ZPVE = 44.46642

C	-1.317088	0.395131	-0.839503
C	-1.215232	0.097976	0.484653
S	0.256927	-0.387857	1.316351
C	1.433311	0.164147	0.106397
C	1.024983	0.137162	-1.165962
C	-0.204243	0.061865	-1.711579
H	2.328625	0.640947	0.494453
H	-0.401292	-0.358501	-2.696876
H	-2.088639	0.072131	1.130161
H	-2.279922	0.713444	-1.233390

Table S.16 B3LYP/6-31G* Uncorrected Energies (Hartree), Zero Point Vibrational Energies (kcal/mol), and Cartesian Coordinates (Å)

propargyl thioketene (8)

E = -591.004477685
ZPVE = 42.96739

C	2.175379	0.986530	-2.435036
C	1.734175	0.920018	-1.313336
C	1.185851	0.854391	0.043815
C	-0.333728	0.720887	0.051348
C	-0.970803	-0.275047	0.617427
S	-1.718493	-1.471537	1.306976
H	2.565157	1.035736	-3.426401
H	-0.914325	1.491015	-0.453047
H	1.467700	1.763396	0.594766
H	1.632119	0.013769	0.587756

Table S.17 B3LYP/6-31G* Uncorrected Energies (Hartree), Zero Point Vibrational Energies (kcal/mol), and Cartesian Coordinates (Å)

(s-*Z*)-α-thial methylenecyclopropene (9)

E = -591.000463018
ZPVE = 43.70925

C	-1.245447	-0.712609	0.355189
C	-0.045466	-0.579653	1.117434
C	1.036313	0.109970	0.667977
C	2.355626	0.624596	0.770949
C	1.669701	0.886257	-0.338233
S	-1.592611	-0.106376	-1.151500
H	3.268601	0.730805	1.340737
H	1.604727	1.346551	-1.312030
H	0.004926	-1.048802	2.096473
H	-2.020845	-1.297918	0.858916

Table S.18 B3LYP/6-31G* Uncorrected Energies (Hartree), Zero Point Vibrational Energies (kcal/mol), and Cartesian Coordinates (Å)

(s-*E*)-α-thial methylenecyclopropene (9)

E = -591.000292033
ZPVE = 43.60790

C	-0.719099	0.025677	-2.452066
C	-0.597864	0.003970	-0.803898
C	0.608423	0.008094	-0.043757
C	0.587840	-0.011254	1.312738
C	1.226481	-0.021368	2.588760
S	-0.099428	-0.037342	2.566109
H	2.138148	-0.018335	3.169064
H	-1.029838	-0.056510	3.115525
H	1.561015	0.027135	-0.564810
H	-1.516453	-0.015728	-0.206434

Table S.19 B3LYP/6-31G* Uncorrected Energies (Hartree), Zero Point Vibrational Energies (kcal/mol), and Cartesian Coordinates (Å)

4-thiacyclohexa-2,5-dienylidene (triplet) (10)

E = -590.988208
ZPVE = 43.7022

C	0.000000	1.374198	0.267267
C	0.000000	1.251424	-1.098883
C	0.000000	0.000000	-1.719587
C	0.000000	-1.251424	-1.098883
C	0.000000	-1.374198	0.267267
H	0.000000	-2.162246	-1.695591
H	0.000000	-2.336798	0.767253
S	0.000000	0.000000	1.384599
H	0.000000	2.162246	-1.695591
H	0.000000	2.336798	0.767253

Table S.20 B3LYP/6-31G* Uncorrected Energies (Hartree), Zero Point Vibrational Energies (kcal/mol), and Cartesian Coordinates (Å)

4-thiacyclohexa-2,5-dienylidene (singlet) (10)

E = -590.993805
ZPVE = 44.1904

C	0.000000	1.333144	0.296508
C	0.000000	1.205648	-1.071672
C	0.000000	0.000000	-1.853743
C	0.000000	-1.205648	-1.071672
C	0.000000	-1.333144	0.296508
H	0.000000	-2.157543	-1.610882
H	0.000000	-2.294663	0.806294
S	0.000000	0.000000	1.377100
H	0.000000	2.157543	-1.610882
H	0.000000	2.294663	0.806294

Table S.21 B3LYP/6-31G* Uncorrected Energies (Hartree), Zero Point Vibrational Energies (kcal/mol), and Cartesian Coordinates (Å)

(*s*-*Z*)-2-thienyl carbene (triplet) (11)

E = -590.991165600
ZPVE = 42.79053

C	-1.509330	0.004531	-0.452290
C	-1.421630	0.004177	0.923238
C	-0.101756	0.000204	1.406855
C	0.884654	-0.002683	0.388788
C	2.237789	-0.006705	0.503868
S	0.055785	-0.000071	-1.214753
H	3.097744	-0.009290	-0.149197
H	0.169953	-0.000690	2.455833
H	-2.294597	0.006753	1.567539
H	-2.404026	0.007218	-1.060878

Table S.22 B3LYP/6-31G* Uncorrected Energies (Hartree), Zero Point Vibrational Energies (kcal/mol), and Cartesian Coordinates (Å)

(*s*-*Z*)-2-thienyl carbene (singlet) (11)

E = -590.990451033
ZPVE = 43.38796

C	-1.465527	0.006505	-0.530525
C	-1.450800	0.005978	0.859166
C	-0.151978	0.000197	1.377029
C	0.888397	-0.003978	0.426669
C	2.242463	-0.009924	0.721593
S	0.086905	0.000035	-1.228691
H	2.847291	-0.012227	-0.204200
H	0.095668	-0.001225	2.432556
H	-2.353915	0.009678	1.458738
H	-2.354857	0.010553	-1.151631

Table S.23 CCSD/cc-pVTZ Uncorrected Energies (Hartree), Zero Point Vibrational Energies (kcal/mol), and Cartesian Coordinates (Å)

(*s*-*Z*)-2-thienyl carbene (triplet) (11)

E = -590.1204072
ZPVE = 43.1902

S	0.00000000	0.00000000	0.00000000
C	0.00000000	0.00000000	1.72958016
C	1.26854928	0.00000000	2.25037638
C	2.27514010	0.00000000	1.26639166
C	1.77172264	0.00000000	-0.04832951
H	-0.93186721	0.00000000	2.26828124
H	1.46805547	0.00000000	3.31071878
H	3.33386164	0.00000000	1.47001539
C	2.46781358	0.00000000	-1.22438561
H	2.22203627	0.00000000	-2.27189881

Table S.24 CCSD/cc-pVTZ Uncorrected Energies (Hartree), Zero Point Vibrational Energies (kcal/mol), and Cartesian Coordinates (Å)

(*s*-*Z*)-2-thienyl carbene (singlet) (11)

E = -590.118175
ZPVE = 43.9838

S	0.00000000	0.00000000	0.00000000
C	0.00000000	0.00000000	1.69545971
C	1.27372857	0.00000000	2.23636199
C	2.26042222	0.00000000	1.24394197
C	1.76642692	0.00000000	-0.06475263
H	-0.92558569	0.00000000	2.24896229
H	1.46508134	0.00000000	3.29733791
H	3.32486294	0.00000000	1.42043902
C	2.56296869	0.00000000	-1.22125773
H	1.90295610	0.00000000	-2.10572111

Table S.25 B3LYP/6-31G* Uncorrected Energies (Hartree), Zero Point Vibrational Energies (kcal/mol), and Cartesian Coordinates (Å)

(*s*-*E*)-2-thienyl carbene (triplet) (11)

E = -590.989918677
ZPVE = 42.77867

C	-1.469404	0.010213	-0.578724
C	-1.477478	0.004520	0.799288
C	-0.192641	-0.004485	1.370875
C	0.856407	-0.006119	0.412680
C	2.203758	-0.013972	0.602340
S	0.144164	0.004073	-1.228795
H	2.873577	-0.020718	1.450489
H	0.007867	-0.009821	2.436031
H	-2.392258	0.006981	1.383029
H	-2.319654	0.017447	-1.247581

Table S.26 B3LYP/6-31G* Uncorrected Energies (Hartree), Zero Point Vibrational Energies (kcal/mol), and Cartesian Coordinates (Å)

(*s*-*E*)-2-thienyl carbene (singlet) (11)

E = -590.987685382
ZPVE = 43.44608

C	-1.452976	0.009825	-0.558454
C	-1.462709	0.003910	0.833715
C	-0.170729	-0.005013	1.367862
C	0.867001	-0.005944	0.412525
C	2.263412	-0.013477	0.480967
S	0.116216	0.004406	-1.214383
H	2.529177	-0.018870	1.559248
H	0.049842	-0.010595	2.430839
H	-2.375303	0.006106	1.419580
H	-2.327167	0.017059	-1.199233

Table S.27 CCSD/cc-pVTZ Uncorrected Energies (Hartree), Zero Point Vibrational Energies (kcal/mol), and Cartesian Coordinates (Å)

(*s*-*E*)-2-thienyl carbene (triplet) (11)

E = -590.1193378
ZPVE = 43.167

S	0.00000000	0.00000000	0.00000000
C	0.00000000	0.00000000	1.72888219
C	1.26805256	0.00000000	2.25002611
C	2.27370359	0.00000000	1.26398469
C	1.76148423	0.00000000	-0.05015265
H	-0.93143031	0.00000000	2.26807986
H	1.46910636	0.00000000	3.31016934
H	3.33283734	0.00000000	1.46712995
C	2.45144211	0.00000000	-1.23260092
H	3.49416343	0.00000000	-1.50050938

Table S.28 CCSD/cc-pVTZ Uncorrected Energies (Hartree), Zero Point Vibrational Energies (kcal/mol), and Cartesian Coordinates (Å)

(*s*-*E*)-2-thienyl carbene (singlet) (11)

E = -590.1167887
ZPVE = 43.9689

S	0.00000000	0.00000000	0.00000000
C	0.00000000	0.00000000	1.69192547
C	1.27627033	0.00000000	2.23384088
C	2.25895267	0.00000000	1.23991869
C	1.75119292	0.00000000	-0.06636238
H	-0.92463665	0.00000000	2.24644457
H	1.46924446	0.00000000	3.29476977
H	3.32241248	0.00000000	1.42825655
C	2.37566048	0.00000000	-1.32815855
H	3.46238124	0.00000000	-1.12768245

Table S.29 B3LYP/6-31G* Uncorrected Energies (Hartree), Zero Point Vibrational Energies (kcal/mol), and Cartesian Coordinates (Å)

2-thiabicyclo[3.1.0]hexa-3,5-diene (12)

E = -590.989255448
ZPVE = 44.11613

S	-1.061637	0.372671	-0.782874
C	-0.824509	0.728174	0.933207
C	0.252763	0.172246	1.549855
C	1.024813	-0.522570	0.551657
C	0.335023	-0.870530	-0.729227
C	1.755996	-0.483780	-0.541682
H	-1.464643	1.477482	1.388066
H	2.641524	-0.082046	-1.013781
H	0.546311	0.370331	2.573122
H	-0.001518	-1.869751	-1.004271

Table S.30 B3LYP/6-31G* Uncorrected Energies (Hartree), Zero Point Vibrational Energies (kcal/mol), and Cartesian Coordinates (Å)

(*s*-*Z*)-3-thienyl carbene (triplet) (13)

E = -590.983919116
ZPVE = 43.00741

C	-1.278238	0.001949	-0.734658
C	-1.191399	-0.004441	0.618478
C	0.177790	-0.005126	1.113388
C	1.086677	0.001089	0.039340
C	0.524589	-0.011098	2.456610
S	0.292811	0.007576	-1.500189
H	-2.171970	0.003747	-1.344550
H	-2.050043	-0.008664	1.280164
H	1.454301	-0.012607	3.010194
H	2.166232	0.002071	0.098266

Table S.31 B3LYP/6-31G* Uncorrected Energies (Hartree), Zero Point Vibrational Energies (kcal/mol), and Cartesian Coordinates (Å)

(*s*-*Z*)-3-thienyl carbene (singlet) (13)

E = -590.976821079
ZPVE = 43.28164

C	-1.184279	0.001811	-0.893148
C	-1.260903	-0.004820	0.460533
C	0.031548	-0.005307	1.123791
C	1.062416	0.001384	0.172206
C	0.181002	-0.011795	2.545528
S	0.486463	0.007875	-1.435908
H	-1.978483	0.003672	-1.627533
H	-2.185739	-0.009443	1.025585
H	1.275700	-0.010490	2.748592
H	2.126405	0.002627	0.374417

Table S.32 CCSD/cc-pVTZ Uncorrected Energies (Hartree), Zero Point Vibrational Energies (kcal/mol), and Cartesian Coordinates (Å)

(*s*-*Z*)-3-thienyl carbene (triplet) (13)

E = -590.1157646
ZPVE = 43.4472

S	0.00000000	0.00000000	0.00000000
C	0.00000000	0.00000000	1.73404154
C	1.24790302	0.00000000	2.25078588
C	2.28445421	0.00000000	1.23521334
C	1.72016380	0.00000000	-0.04059993
H	-0.93304108	0.00000000	2.27105435
H	1.46361013	0.00000000	3.30751158
C	3.65028968	0.00000000	1.50847703
H	2.24622803	0.00000000	-0.97942479
H	4.53958910	0.00000000	0.89988341

Table S.33 CCSD/cc-pVTZ Uncorrected Energies (Hartree), Zero Point Vibrational Energies (kcal/mol), and Cartesian Coordinates (Å)

(*s*-*Z*)-3-thienyl carbene (singlet) (13)

E = -590.1094858
ZPVE = 43.7883

S	0.00000000	0.00000000	0.00000000
C	0.00000000	0.00000000	1.74094967
C	1.26049372	0.00000000	2.23552145
C	2.27877566	0.00000000	1.20967095
C	1.69643684	0.00000000	-0.05403604
H	-0.93568084	0.00000000	2.27253218
H	1.50652001	0.00000000	3.28545128
C	3.68492366	0.00000000	1.48305202
H	2.21988994	0.00000000	-0.99624452
H	4.18872820	0.00000000	0.49777241

Table S.34 B3LYP/6-31G* Uncorrected Energies (Hartree), Zero Point Vibrational Energies (kcal/mol), and Cartesian Coordinates (Å)

(*s*-*E*)-3-thienyl carbene (triplet) (13)

E = -590.983510731
ZPVE = 42.92266

C	-1.217547	0.002415	-0.794979
C	-1.189588	-0.005101	0.560841
C	0.162142	-0.005708	1.113369
C	1.111277	0.000664	0.078722
C	0.459289	-0.012014	2.468669
S	0.384136	0.008693	-1.491687
H	-2.084699	0.004689	-1.442166
H	-2.077780	-0.009827	1.182847
H	-0.123983	-0.017322	3.379905
H	2.186850	0.001821	0.186676

Table S.35 B3LYP/6-31G* Uncorrected Energies (Hartree), Zero Point Vibrational Energies (kcal/mol), and Cartesian Coordinates (Å)

(*s*-*E*)-3-thienyl carbene (singlet) (13)

E = -590.977504416
ZPVE = 43.30839

C	-0.784873	0.002175	-1.249901
C	-1.205794	-0.004605	0.569751
C	0.146397	-0.005528	1.113106
C	1.083097	0.001156	0.070027
C	0.631152	-0.011388	2.455567
S	0.366904	0.008030	-1.476506
H	-2.106903	0.004208	-1.445498
H	-2.089167	-0.009002	1.199684
H	-0.260719	-0.016588	3.122639
H	2.156619	0.002034	0.205811

Table S.36 CCSD/cc-pVTZ Uncorrected Energies (Hartree), Zero Point Vibrational Energies (kcal/mol), and Cartesian Coordinates (Å)

(*s*-*E*)-3-thienyl carbene (triplet) (13)

E = -590.1153869
ZPVE = 43.3765

S	0.00000000	0.00000000	0.00000000
C	0.00000000	0.00000000	1.73328855
C	1.24821244	0.00000000	2.25004256
C	2.28557377	0.00000000	1.22975426
C	1.71899716	0.00000000	-0.04167027
H	-0.93250327	0.00000000	2.27131601
H	1.46182409	0.00000000	3.30750711
C	3.65221888	0.00000000	1.50132362
H	2.24656581	0.00000000	-0.97938130
H	4.23477212	0.00000000	2.40768084

Table S.37 CCSD/cc-pVTZ Uncorrected Energies (Hartree), Zero Point Vibrational Energies (kcal/mol), and Cartesian Coordinates (Å)

(*s*-*E*)-3-thienyl carbene (singlet) (13)

E = -590.1101821
ZPVE = 43.787

S	0.00000000	0.00000000	0.00000000
C	0.00000000	0.00000000	1.74217342
C	1.26015170	0.00000000	2.23683976
C	2.27978253	0.00000000	1.20653402
C	1.69423050	0.00000000	-0.05446200
H	-0.93534461	0.00000000	2.27485481
H	1.49133977	0.00000000	3.29111050
C	3.70622124	0.00000000	1.30593513
H	2.23557037	0.00000000	-0.98565696
H	3.95209108	0.00000000	2.38520589

Table S.38 B3LYP/6-31G* Uncorrected Energies (Hartree), Zero Point Vibrational Energies (kcal/mol), and Cartesian Coordinates (Å)

2-ethynylcyclopropanethione (14)

E = -590.983060512
ZPVE = 43.05633

C	0.237091	0.519188	-0.498136
C	-0.044515	0.425117	0.966005
C	1.378668	0.689005	0.398982
S	-0.345211	0.412887	-1.990025
C	1.791954	1.686017	0.545147
C	2.108446	-0.117542	0.452521
H	-0.532300	1.298881	1.401358
H	-0.385491	-0.837414	1.564427
H	-0.672268	-1.901257	2.059863
H	-0.925621	-2.841385	2.494522

Table S.39 B3LYP/6-31G* Uncorrected Energies (Hartree), Zero Point Vibrational Energies (kcal/mol), and Cartesian Coordinates (Å)

4-thiabicyclo[3.1.0]hexa-2,5-diene (15)

E = -590.979013030
ZPVE = 44.13261

S	-1.198730	-0.484549	-0.592656
C	-0.838419	-0.121413	1.137695
C	0.440649	0.175221	1.437326
C	1.378685	0.038278	0.273847
C	0.454330	-0.029423	-0.919330
C	1.289973	0.976075	-0.916295
H	-1.673342	-0.181993	1.827150
H	0.759911	0.354271	2.460533
H	1.501252	1.970980	-1.284037
H	2.240559	-0.622907	0.399386

Table S.40 B3LYP/6-31G* Uncorrected Energies (Hartree), Zero Point Vibrational Energies (kcal/mol), and Cartesian Coordinates (Å)

(*s*-*Z*)-*E*-pent-2-en-4-ynal (16)

E = -268.057404604
ZPVE = 44.63198

C	0.156966	-0.000027	-0.511425
C	0.060600	-0.000015	0.836097
H	0.946733	0.000123	1.465580
C	-1.260606	-0.000171	1.496026
H	-0.771322	-0.000152	-1.083140
C	1.372548	0.000141	-1.234802
C	2.396870	0.000280	-1.881823
H	3.303971	0.000404	-2.443069
H	-1.232576	-0.000197	2.605966
O	-2.325635	-0.000179	0.903778

Table S.41 B3LYP/6-31G* Uncorrected Energies (Hartree), Zero Point Vibrational Energies (kcal/mol), and Cartesian Coordinates (Å)

(*s*-*E*)-*E*-pent-2-en-4-ynal (16)

E = -268.058742846
ZPVE = 44.57668

O	-1.444613	-0.004027	-2.477961
C	-1.342252	-0.012490	-1.265720
C	-0.062020	0.003534	-0.545609
C	-0.036019	-0.007413	0.804648
C	1.138515	0.006191	1.595425
C	2.124212	0.017270	2.299045
H	3.003070	0.027340	2.903630
H	-0.984243	-0.028343	1.345150
H	0.847219	0.024245	-1.139841
H	-2.243758	-0.033571	-0.611979

Table S.42 B3LYP/6-31G* Uncorrected Energies (Hartree), Zero Point Vibrational Energies (kcal/mol), and Cartesian Coordinates (Å)

(*s*-*Z*)-*Z*-pent-2-en-4-ynal (17)

E = -268.052691689
ZPVE = 44.64611

C	1.088595	-0.000927	-0.590814
C	1.148288	-0.002874	0.761571
H	2.126859	-0.004675	1.236017
C	-0.017776	-0.002491	1.664539
H	0.242232	-0.005102	2.745443
H	2.030066	-0.001137	-1.140427
C	-0.075492	0.002003	-1.395765
C	-0.993338	0.004568	-2.186604
H	-1.845222	0.006806	-2.828371
O	-1.181949	0.000304	1.308722

Table S.43 B3LYP/6-31G* Uncorrected Energies (Hartree), Zero Point Vibrational Energies (kcal/mol), and Cartesian Coordinates (Å)

(*s*-*E*)-*Z*-pent-2-en-4-ynal (17)

E = -268.056898484
ZPVE = 44.72311

O	-0.055028	0.031129	-2.583313
C	-0.169430	0.014875	-1.370552
C	0.982830	0.017102	-0.455757
C	0.874780	-0.000738	0.891994
C	-0.338488	-0.024012	1.630402
C	-1.335844	-0.044128	2.317399
H	-2.226852	-0.061762	2.903802
H	1.786208	0.002580	1.489006
H	1.964135	0.034312	-0.921849
H	-1.166351	-0.002753	-0.885374

Table S.44 B3LYP/6-31G* Uncorrected Energies (Hartree), Zero Point Vibrational Energies (kcal/mol), and Cartesian Coordinates (Å)

propargyl ketene (18)

E = -268.046614903
ZPVE = 44.40468

C	1.779707	0.644491	-2.159384
C	1.340551	0.602028	-1.035675
C	0.802266	0.567267	0.328518
C	-0.712199	0.406438	0.365619
C	-1.304031	-0.640234	0.900130
O	-1.826653	-1.569554	1.389538
H	2.162525	0.673816	-3.154193
H	-1.345235	1.156137	-0.097324
H	1.081563	1.493647	0.850046
H	1.276614	-0.247102	0.889926

Table S.45 B3LYP/6-31G* Uncorrected Energies (Hartree), Zero Point Vibrational Energies (kcal/mol), and Cartesian Coordinates (Å)

(*s*-*Z*)-(α-formyl)methylenecyclopropene (19)

E = -268.036073667
ZPVE = 44.90026

O	-1.752300	-0.125702	-1.028875
C	-1.581152	-0.670587	0.055671
C	-0.359170	-0.623552	0.844910
C	0.705859	0.066556	0.386327
C	2.036854	0.579281	0.430876
C	1.292993	0.877488	-0.626770
H	2.980434	0.665849	0.951531
H	1.185380	1.373536	-1.579664
H	-0.316727	-1.145062	1.796276
H	-2.402992	-1.263823	0.516765

Table S.46 B3LYP/6-31G* Uncorrected Energies (Hartree), Zero Point Vibrational Energies (kcal/mol), and Cartesian Coordinates (Å)

(*s*-*E*)-(α-formyl)methylenecyclopropene (19)

E = -268.035619450
ZPVE = 44.79678

O	-0.836396	0.027631	-2.570317
C	-0.757831	0.010660	-1.351411
C	0.478824	0.014484	-0.589225
C	0.456562	-0.005592	0.757640
C	1.084054	-0.016872	2.043557
C	-0.239309	-0.032485	2.011302
H	1.991572	-0.014467	2.630237
H	-1.172960	-0.051834	2.555168
H	1.421106	0.033870	-1.128597
H	-1.682358	-0.009785	-0.725443

Table S.47 B3LYP/6-31G* Uncorrected Energies (Hartree), Zero Point Vibrational Energies (kcal/mol), and Cartesian Coordinates (Å)

4-oxacyclohexa-1,2,4-triene (20)

E = -268.027820635
ZPVE = 46.75153

C	-1.254420	-0.205270	-0.488901
C	-0.978686	0.034622	0.829875
O	0.265992	0.211431	1.289089
C	1.300453	-0.055858	1.300453
C	1.130201	-0.044127	-0.948408
C	-0.181467	0.012226	-1.399559
H	2.205480	-0.250129	0.962855
H	-0.421745	0.306473	-2.423364
H	-1.722954	0.166176	1.607053
H	-2.285205	-0.363518	-0.793818

Table S.48 B3LYP/6-31G* Uncorrected Energies (Hartree), Zero Point Vibrational Energies (kcal/mol), and Cartesian Coordinates (Å)

2-ethynylcyclopropanone (21)

E = -268.019201813
ZPVE = 44.25621

C	-0.020317	0.731036	-0.862479
C	0.031367	0.413642	0.602984
C	-0.824039	1.201437	-0.366001
O	-1.817533	-1.149532	-0.095687
H	-1.393637	2.013387	-1.393637
H	-0.461622	1.396074	-1.373770
H	0.066398	0.689871	1.650052
C	1.432075	-0.034538	0.154209
C	2.514623	-0.403383	-0.236430
H	3.468719	-0.731884	-0.580843

Table S.49 B3LYP/6-31G* Uncorrected Energies (Hartree), Zero Point Vibrational Energies (kcal/mol), and Cartesian Coordinates (Å)

(*s*-*Z*)-2-furyl carbene (triplet) (22)

E = -268.00865915
ZPVE = 44.77567

C	-1.246033	0.006198	-0.762920
C	-1.434452	0.009205	0.594750
C	-0.149452	0.002709	1.181953
C	0.786277	-0.004442	0.129362
C	2.151373	-0.012409	0.109698
O	0.079402	-0.002120	-1.077226
H	2.931132	-0.018060	-0.635733
H	0.099825	0.002937	2.233338
H	-2.387484	0.015543	1.105812
H	-1.924967	0.008977	-1.602670

Table S.50 B3LYP/6-31G* Uncorrected Energies (Hartree), Zero Point Vibrational Energies (kcal/mol), and Cartesian Coordinates (Å)

(*s*-*Z*)-2-furyl carbene (singlet) (22)

E = -268.014547
ZPVE = 45.49315

C	-0.565548	-1.336945	0.000000
C	0.821539	-1.312713	0.000000
C	1.164911	0.042351	0.000000
C	0.000000	0.826765	0.000000
C	-0.149348	2.193971	0.000000
O	-1.097841	-0.132105	0.000000
H	-1.224257	2.449447	0.000000
H	2.155840	0.475545	0.000000
H	1.474955	-2.173680	0.000000
H	-1.253136	-2.175045	0.000000

Table S.51 B3LYP/6-31G* Uncorrected Energies (Hartree), Zero Point Vibrational Energies (kcal/mol), and Cartesian Coordinates (Å)

(*s*-*E*)-2-furyl carbene (triplet) (22)

E = -268.008539619
ZPVE = 44.85671

C	-1.214680	0.009688	-0.840757
C	-1.454666	0.006082	0.508552
C	-0.191998	-0.002240	1.143226
C	0.781303	-0.004983	0.120501
C	2.147633	-0.012353	0.140558
O	0.002673	0.002673	-1.103516
H	2.900307	-0.018300	0.913647
H	0.016960	-0.006260	2.203482
H	-2.426012	0.009762	0.984210
H	-1.860863	0.016261	-1.705684

Table S.52 B3LYP/6-31G* Uncorrected Energies (Hartree), Zero Point Vibrational Energies (kcal/mol), and Cartesian Coordinates (Å)

(*s*-*E*)-2-furyl carbene (singlet) (22)

E = -268.01185094
ZPVE = 45.65862

C	-1.207228	0.009035	-0.812943
C	-1.440022	0.005010	0.555561
C	-0.169550	-0.002955	1.137201
C	0.808024	-0.004150	0.124348
C	2.186953	-0.011808	0.029362
O	0.075345	0.003807	-1.107128
H	2.567326	-0.016986	1.069306
H	0.063642	-0.007556	2.194277
H	-2.406320	0.007854	1.040629
H	-1.896469	0.015447	-1.648357

Table S.53 B3LYP/6-31G* Uncorrected Energies (Hartree), Zero Point Vibrational Energies (kcal/mol), and Cartesian Coordinates (Å)

(*s*-*Z*)-3-furyl carbene (triplet) (23)

E = -268.001020802
ZPVE = 44.99565

C	-1.036030	0.004390	-1.081642
C	-1.143781	-0.003692	0.265436
C	0.215305	-0.004382	0.798886
C	1.027569	0.004049	-0.339200
C	0.597914	-0.011644	2.131635
O	0.276203	0.009258	-1.475616
H	-1.759332	0.007668	-1.883165
H	-2.054030	-0.008785	0.847621
H	1.539831	-0.012767	2.663197
H	2.098042	0.007491	-0.473412

Table S.54 B3LYP/6-31G* Uncorrected Energies (Hartree), Zero Point Vibrational Energies (kcal/mol), and Cartesian Coordinates (Å)

(*s*-*Z*)-3-furyl carbene (singlet) (23)

E = -267.995922135
ZPVE = 45.39890

C	-1.021673	0.004496	-1.103651
C	-1.156569	-0.003378	0.237156
C	0.188531	-0.004262	0.806280
C	1.022202	0.003569	-0.311788
C	0.531374	-0.011537	2.188280
O	0.330373	0.008829	-1.448128
H	-1.697130	0.008103	-1.944654
H	-2.074035	-0.008240	0.808173
H	1.644683	-0.009820	2.230142
H	2.100304	0.005997	-0.406303

Table S.55 B3LYP/6-31G* Uncorrected Energies (Hartree), Zero Point Vibrational Energies (kcal/mol), and Cartesian Coordinates (Å)

(*s*-*E*)-3-furyl carbene (triplet) (23)

E = -268.001170103
ZPVE = 44.94363

C	-0.945160	0.004741	-1.142625
C	-1.125904	-0.003285	0.196824
C	0.207915	-0.004068	0.801064
C	1.075453	0.003629	-0.291512
C	0.535461	-0.011264	2.148773
O	0.385149	0.009018	-1.465758
H	-1.625475	0.008204	-1.981208
H	-2.067306	-0.008197	0.727453
H	-0.026377	-0.017419	3.072533
H	2.151374	0.006748	-0.367864

Table S.56 B3LYP/6-31G* Uncorrected Energies (Hartree), Zero Point Vibrational Energies (kcal/mol), and Cartesian Coordinates (Å)

(*s*-*E*)-3-furyl carbene (singlet) (23)

E = -267.998171927
ZPVE = 45.49664

C	-0.987125	0.004396	-1.127338
C	-1.152744	-0.003439	0.209610
C	0.186319	-0.004031	0.807084
C	1.038895	0.003679	-0.295452
C	0.713521	-0.010382	2.125747
O	0.371964	0.008624	-1.444788
H	-1.645198	0.007949	-1.982644
H	-2.092818	-0.008290	0.744075
H	-0.149604	-0.016207	2.827669
H	2.118706	0.006215	-0.348698

Table S.57 B3LYP/6-31G* Uncorrected Energies (Hartree), Zero Point Vibrational Energies (kcal/mol), and Cartesian Coordinates (Å)

2-oxabicyclo[3.1.0]hexa-3,5-diene (24)

E = -267.998433618
ZPVE = 45.89506

C	-1.087760	0.044759	-0.837655
C	-1.267621	0.315502	0.486506
C	0.070807	0.172344	1.008495
C	1.040178	0.250385	-0.111914
O	0.185476	-0.098106	-1.276880
C	1.136186	-0.613068	1.070103
H	-1.849901	-0.170194	-1.578339
H	-2.210134	0.399487	1.007189
H	1.524890	-1.531180	1.491061
H	1.700588	1.067205	-0.398082

Table S.58 B3LYP/6-31G* Uncorrected Energies (Hartree), Zero Point Vibrational Energies (kcal/mol), and Cartesian Coordinates (Å)

4-oxabicyclo[3.1.0]hexa-2,5-diene (25)

E = -267.980564699
ZPVE = 45.85743

O	-1.228878	-0.141102	-0.523793
C	-1.030672	-0.338301	0.846856
C	0.256853	-0.326566	1.251870
C	1.114397	-0.248120	0.023552
C	0.060066	0.069266	-0.947033
C	0.972780	1.010890	-0.917336
H	-1.951943	-0.504020	1.388176
H	0.574153	-0.512504	2.270757
H	1.032340	2.092050	-0.895158
H	1.935930	-0.949732	-0.120883

Table S.59 B3LYP/6-31G* Uncorrected Energies (Hartree), Zero Point Vibrational Energies (kcal/mol), and Cartesian Coordinates (Å)

(*s*-*E*)-penta-2,3,4-trienal (26)

E = -268.056021576
ZPVE = 44.54690

O	-0.867958	0.000000	-2.801218
C	-0.810471	0.000000	-1.585887
C	0.459182	0.000000	-0.834036
C	0.481151	0.000000	0.493749
H	-1.726181	0.000000	-0.958424
H	1.375914	0.000000	-1.421860
C	0.468819	0.000000	1.761419
C	0.463278	0.000000	3.080048
H	-0.466316	0.000000	3.645509
H	1.388494	0.000000	3.652760

Table S.60 B3LYP/6-31G* Uncorrected Energies (Hartree), Zero Point Vibrational Energies (kcal/mol), and Cartesian Coordinates (Å)

(*s*-*Z*)-penta-2,3,4-trienal (26)

E = -268.051997686
ZPVE = 44.56577

O	-2.092817	0.000000	-0.842680
C	-1.956487	0.000000	0.365324
C	-0.659528	0.000000	1.080885
C	0.510906	0.000000	0.452908
H	-2.839482	0.000000	1.040208
H	-0.698130	0.000000	2.170221
C	1.621235	0.000000	-0.155699
C	2.773873	0.000000	-0.796749
H	2.816849	0.000000	-1.884023
H	3.723311	0.000000	-0.264983

Table S.61 B3LYP/6-31G* Uncorrected Energies (Hartree), Zero Point Vibrational Energies (kcal/mol), and Cartesian Coordinates (Å)

(*s*-*E*)-pent-1-en-4-yn-3-one (27)

E = -268.052183662
ZPVE = 44.51333

H	1.262562	0.000000	-3.038760
C	1.281003	0.000000	-1.953167
H	2.249262	0.000000	-1.460465
C	0.157551	0.000000	-1.228341
H	-0.825511	0.000000	-1.692509
C	0.207852	0.000000	0.207852
O	1.251410	0.000000	0.899120
C	-1.085105	0.000000	0.934310
C	-2.160955	0.000000	1.487229
H	-3.099677	0.000000	1.995329

Table S.62 B3LYP/6-31G* Uncorrected Energies (Hartree), Zero Point Vibrational Energies (kcal/mol), and Cartesian Coordinates (Å)

1-ethynyl-3-oxacyclobutene (28)

E = -268.016013
ZPVE = 45.468047

C	0.000000	0.133189	0.000000
C	-0.471121	-1.315130	0.000000
O	0.951534	-1.716607	0.000000
C	1.253728	-0.372390	0.000000
H	-0.967253	-1.679995	0.902857
H	2.282051	-0.028459	0.000000
H	-0.967253	-1.679995	-0.902857
C	-0.628340	1.385780	0.000000
C	-1.198992	2.455317	0.000000
H	-1.691460	3.400711	0.000000

Table S.63 B3LYP/6-31G* Uncorrected Energies (Hartree), Zero Point Vibrational Energies (kcal/mol), and Cartesian Coordinates (Å)

4-ethynyl-3-oxacyclobutene (29)

E = -268.001778290
ZPVE = 45.06897

C	-0.113225	0.598765	-1.301578
C	-0.270887	0.490163	0.209685
O	1.222070	0.497618	0.293586
C	1.206529	0.608236	-1.089702
H	-0.638564	1.395575	0.704433
H	2.135550	0.686224	-1.643559
H	-0.795606	0.637603	-2.135442
C	-0.863427	-0.706725	0.776895
C	-1.396626	-1.681384	1.249272
H	-1.852118	-2.554677	1.658437

Table S.64 B3LYP/6-31G* Uncorrected Energies (Hartree), Zero Point Vibrational Energies (kcal/mol), and Cartesian Coordinates (Å)

allenyl ethynyl ether (30)

E = -267.982337428
ZPVE = 43.57935

H	2.030607	3.028296	-0.120754
C	1.109817	2.720515	0.373811
H	0.525858	3.509121	0.525858
C	0.723794	1.473260	0.393276
C	0.357298	0.220983	0.445585
H	0.640745	-0.472783	1.230699
O	-0.463252	-0.332506	-0.554883
C	-0.779718	-1.595841	-0.419317
C	-1.096146	-2.756403	-0.334735
H	-1.381464	-3.779663	-0.269990

Table S.65 B3LYP/6-31G* Uncorrected Energies (Hartree), Zero Point Vibrational Energies (kcal/mol), and Cartesian Coordinates (Å)

ethynyl prop-2-ynyl ether (31)

E = -267.973904028
ZPVE = 43.73710

H	0.797020	-0.028395	-3.878277
C	0.727896	-0.019707	-2.816369
C	0.682883	-0.009633	-1.610216
O	0.650539	0.001423	-0.302566
C	-0.700572	-0.002980	0.248515
H	-1.219945	-0.898925	-0.112636
H	-1.232362	0.878904	-0.128825
C	-0.620721	0.010836	1.700391
C	-0.589358	0.022278	2.905759
H	-0.549784	0.032262	3.971783

Table S.66 B3LYP/6-31G* Uncorrected Energies (Hartree), Zero Point Vibrational Energies (kcal/mol), and Cartesian Coordinates (Å)

ethynyl prop-1-ynyl ether (32)

E = -267.965254406
ZPVE = 43.81419

H	-0.071017	-1.814521	-3.480357
C	-0.037875	-1.617041	-2.434640
C	-0.000789	-1.382317	-1.255550
O	0.044007	-1.225618	0.057883
C	0.020445	0.017615	0.534955
C	0.004085	1.101464	1.058338
C	-0.018728	2.424962	1.677468
H	0.992903	2.776019	1.913138
H	-0.595172	2.413411	2.609979
H	-0.481596	3.161939	1.010756

Table S.67 B3LYP/6-31G* Uncorrected Energies (Hartree), Zero Point Vibrational Energies (kcal/mol), and Cartesian Coordinates (Å)

3-cyclopropenyl ethynyl ether (33)

E = -267.959912743
ZPVE = 43.65893

C	-1.175074	0.117694	-1.182711
C	-1.484185	0.763383	-0.088721
C	-0.132242	0.989255	-0.621250
O	1.066683	0.449400	0.036141
H	0.217361	1.916366	-1.069664
H	-2.198581	0.983142	0.691395
H	-1.449600	-0.581372	-1.959357
C	0.945365	-0.682758	0.670103
C	0.860510	-1.731073	1.264881
H	0.811116	-2.652345	1.794692

Table S.68 B3LYP/6-31G* Uncorrected Energies (Hartree), Zero Point Vibrational Energies (kcal/mol), and Cartesian Coordinates (Å)

(3-thienyl)diazirine (34)

E = -700.534882342
ZPVE = 51.21966

S	-1.88398	0.019251	-1.30028
C	-1.86037	-0.38169	0.387456
C	-0.59996	-0.31053	0.906835
C	0.383095	0.075492	-0.06683
C	-0.17361	0.285881	-1.30494
C	1.819141	0.232444	0.20838
N	2.27096	0.615634	1.570392
N	2.454555	-0.56703	1.286873
H	-2.77756	-0.64601	0.896115
H	-0.36858	-0.52331	1.944229
H	0.329267	0.582318	-2.21585
H	2.472153	0.529123	-0.60631

Table S.69 B3LYP/6-31G* Uncorrected Energies (Hartree), Zero Point Vibrational Energies (kcal/mol), and Cartesian Coordinates (Å)

6a*H*-thieno[2,3-c]pyrazole (35)

E = -700.530124494
ZPVE = 51.98501

S	-0.12669	0.059281	0.026258
C	0.04403	-0.04414	1.787298
C	1.294206	0.131997	2.284805
C	2.24836	0.347349	1.2284
C	1.597165	0.7293	-0.05952
C	3.530134	0.075735	0.884867
N	3.683564	0.168798	-0.52783
N	2.589086	0.450119	-1.11107
H	-0.84685	-0.25788	2.368307
H	1.540729	0.025492	3.334949
H	1.47047	1.821419	-0.1271
H	4.377555	-0.22955	1.483418

Table S.70 B3LYP/6-31G* Uncorrected Energies (Hartree), Zero Point Vibrational Energies (kcal/mol), and Cartesian Coordinates (Å)

3*H*-thieno[2,3-c]pyrazole (36)

E = -700.557835098
ZPVE = 52.27689

S	-1.70357	-0.06202	-0.57054
C	-1.69707	0.280714	1.142922
C	-0.43492	0.350363	1.68405
C	0.559616	0.122494	0.697681
C	0.027162	-0.1101	-0.54595
N	2.153405	-0.26462	-0.99267
H	-2.64126	0.412267	1.655754
H	-0.25155	0.554667	2.732918
C	2.02924	0.032395	0.472356
H	2.587937	0.956241	0.668629
H	2.534891	-0.77609	1.015337
N	1.007003	-0.33681	-1.5288

Table S.71 B3LYP/6-31G* Uncorrected Energies (Hartree), Zero Point Vibrational Energies (kcal/mol), and Cartesian Coordinates (Å)

1*H*-thieno[2,3-c]pyrazole (37)

E = -700.585329634
ZPVE = 53.37376

S	-0.02131	0.139258	0.009655
C	0.059692	0.007772	1.777128
C	1.327359	0.033361	2.270068
C	2.308615	0.1622	1.228296
C	1.714699	0.229448	-0.03299
C	3.699445	0.25356	0.9524
N	3.935486	0.365752	-0.35159
N	2.706885	0.349903	-0.94641
H	-0.87025	-0.08058	2.322967
H	1.55001	-0.03656	3.328881
H	4.53525	0.243487	1.639569
H	2.650634	0.424469	-1.94992

Table S.72 B3LYP/6-31G* (unscaled) Computed Vibrational Frequencies and Intensities

(*s*-*Z*)-3-thienyldiazomethane (1)

Frequency (cm^{-1})	Intensity (Km/mol)	Symmetry
67.9948	0.6952	A″
115.1815	1.3535	A′
243.4098	7.5597	A″
334.367	2.454	A′
441.8484	3.5564	A″
462.7147	0.0363	A′
501.742	33.0661	A″
518.8187	2.9114	A″
620.9694	6.7952	A′
640.6707	3.6921	A″
665.6771	0.3828	A″
717.4506	9.8269	A′
774.5411	86.5153	A″
845.1619	21.8562	A′
880.9808	4.8958	A′
884.2482	0.8031	A″
975.2918	2.6311	A′
1120.69	5.3865	A′
1168.734	2.9248	A′
1231.921	4.7109	A′
1248.395	9.0477	A′
1380.264	0.9202	A′
1462.126	22.8486	A′
1491.213	19.2361	A′
1595.96	17.9079	A′
2192.98	648.0729	A′
3219.813	5.6485	A′
3240.45	4.3451	A′
3267.048	1.6796	A′
3273.904	0.8701	A′

Table S.73 B3LYP/6-31G* (unscaled) Computed Vibrational Frequencies and Intensities

(*s*-*E*)-3-thienyldiazomethane (1)

Frequency (cm^{-1})	Intensity (Km/mol)	Symmetry
68.2344	1.2956	A″
124.7495	3.0647	A′
236.7713	6.5194	A″
328.3994	1.5697	A′
446.3139	1.5169	A″
453.2039	0.075	A′
512.4703	2.9643	A″
515.7405	33.3387	A″
637.1866	2.5489	A′
643.5547	2.5313	A″
668.709	0	A″
736.6116	8.5787	A′
775.8217	90.4222	A″
833.4447	5.4728	A′
864.9622	21.3979	A′
887.9528	0.351	A″
948.0424	4.3855	A′
1123.189	5.4359	A′
1172.032	2.3461	A′
1226.495	2.544	A′
1281.193	9.9472	A′
1403.813	13.3034	A′
1430.589	6.0949	A′
1492.699	1.2137	A′
1603.769	31.7335	A′
2191.371	706.7952	A′
3223.512	1.887	A′
3238.904	3.9907	A′
3267.568	2.2943	A′
3273.589	0.5409	A′

Table S.74 B3LYP/6-31G* (unscaled) Computed Vibrational Frequencies and Intensities

(*s*-*Z*)-2-thienyldiazomethane (2)

Frequency (cm^{-1})	Intensity (Km/mol)	Symmetry
61.5525	0.4324	A″
114.9224	1.5774	A′
232.0754	4.6913	A′
320.3136	1.5365	A″
442.0645	11.6018	A′
462.5427	0.0749	A″
496.7696	14.0781	A′
543.8082	5.7719	A″
581.287	11.7111	A″
654.1297	0.8339	A″
672.7584	9.1493	A′
683.6408	56.9655	A′
753.8615	3.9393	A″
809.3561	20.4494	A′
859.3568	7.3098	A″
902.1479	0.1619	A′
1074.522	3.5267	A′
1113.854	2.9485	A′
1174.511	1.3543	A′
1246.443	0.0405	A′
1260.62	7.7564	A′
1362.92	0.9245	A′
1446.08	0.8146	A′
1512.818	29.5981	A′
1587.891	38.508	A′
2188.473	722.5566	A′
3216.336	10.2289	A′
3230.525	10.0659	A′
3234.881	2.4761	A′
3276.541	0.445	A′

Table S.75 B3LYP/6-31G* (unscaled) Computed Vibrational Frequencies and Intensities

(*s*-*E*)-2-thienyldiazomethane (2)

Frequency (cm^{-1})	Intensity (Km/mol)	Symmetry
51.2505	1.7536	A″
121.444	2.1919	A′
230.6631	5.9085	A″
302.0054	1.3669	A′
455.3316	0.4133	A′
471.5209	23.3246	A″
493.2055	5.188	A″
528.3816	14.3764	A″
575.4642	10.5605	A″
596.6012	2.0548	A′
682.7846	47.1987	A″
740.0267	1.3275	A′
806.6708	16.7025	A″
822.0989	18.5787	A′
854.7316	21.1042	A′
902.9899	0.0407	A′
1061.796	7.6103	A″
1104.787	4.1004	A′
1138.437	4.3303	A′
1222.348	4.7235	A′
1281.227	2.5325	A′
1400.309	0.0648	A′
1444.138	22.9093	A′
1506.891	28.6863	A′
1585.674	23.5275	A′
2191.352	747.6351	A′
3217.355	8.3076	A′
3230.922	5.0639	A′
3242.866	6.4851	A′
3276.558	0.9239	A′

Table S.76 B3LYP/6-31G* (unscaled) Computed Vibrational Frequencies and Intensities

(*s*-*Z*)-3-furyldiazomethane (3)

Frequency (cm^{-1})	Intensity (Km/mol)	Symmetry
59.3634	0.8037	A″
120.2299	1.4573	A′
283.2808	7.9281	A″
339.8381	2.5308	A′
490.624	33.5189	A″
496.5291	0.1551	A′
515.7408	5.5347	A″
609.5514	9.1838	A″
643.212	0.5736	A″
701.7831	0.6946	A″
761.6543	65.3438	A″
766.6645	30.6482	A′
835.9544	4.7888	A″
890.6266	20.3563	A′
1000.103	1.2522	A′
1065.616	21.9174	A′
1104.642	19.6156	A′
1202.397	2.1485	A′
1220.24	31.7613	A′
1249.713	17.1404	A′
1288.383	5.3728	A′
1397.657	0.6282	A′
1467.877	28.719	A′
1556.188	9.5135	A′
1637.264	7.945	A′
2193.18	570.7618	A′
3242.779	5.1859	A′
3266.039	1.5935	A′
3300.284	1.6675	A′
3305.091	0.5694	A′

Table S.77 B3LYP/6-31G* (unscaled) Computed Vibrational Frequencies and Intensities

(*s*-*E*)-3-furyldiazomethane (3)

Frequency (cm^{-1})	Intensity (Km/mol)	Symmetry
72.4341	1.7422	A″
123.8016	3.2081	A′
270.527	7.1273	A″
340.3996	1.4817	A′
500.8832	0.31	A′
509.7103	7.6095	A″
515.5509	31.9401	A″
608.867	10.274	A″
643.2145	0.5804	A″
705.9543	1.9367	A″
758.9425	10.8418	A′
764.4992	66.3674	A″
839.0708	3.3673	A″
888.786	30.3699	A′
982.1826	5.5697	A′
1067.875	18.0401	A′
1102.404	27.5327	A′
1208.482	9.1488	A′
1219.656	24.1074	A′
1261.307	1.0033	A′
1300.322	4.2796	A′
1409.967	17.6207	A′
1447.709	7.8772	A′
1554.963	1.8325	A′
1646.114	13.2472	A′
2193.915	624.7275	A′
3237.677	3.9354	A′
3267.15	0.5494	A′
3299.705	1.8306	A′
3305.011	0.224	A′

Table S.78 B3LYP/6-31G* (unscaled) Computed Vibrational Frequencies and Intensities

(*s*-*Z*)-2-furyldiazomethane (4)

Frequency (cm^{-1})	Intensity (Km/mol)	Symmetry
72.3094	0.0565	A″
122.3977	1.351	A′
250.9248	8.4059	A″
347.6685	2.7145	A′
491.4539	3.0899	A″
505.0006	1.0656	A′
506.0435	30.019	A″
603.5326	5.7695	A″
671.3991	16.7524	A″
713.5283	26.0695	A″
774.6244	8.3681	A′
778.77	39.2023	A″
857.3926	0.0997	A″
899.4584	7.7351	A′
949.9972	13.0447	A′
1042.259	18.4323	A′
1106.112	0.3689	A′
1182.4	4.046	A′
1198.707	1.5697	A′
1245.643	0.421	A′
1292.512	8.8606	A′
1409.988	0.0131	A′
1436.39	3.7479	A′
1564.267	20.9292	A′
1638.349	65.0334	A′
2201.824	735.8133	A′
3254.257	5.0751	A′
3265.268	7.4192	A′
3277.267	1.1023	A′
3309.883	0.275	A′

Table S.79 B3LYP/6-31G* (unscaled) Computed Vibrational Frequencies and Intensities

(*s*-*E*)-2-furyldiazomethane (4)

Frequency (cm^{-1})	Intensity (Km/mol)	Symmetry
56.9148	1.4249	A″
124.8033	2.4959	A′
258.7831	11.466	A″
350.1311	2.1281	A′
488.6428	11.2276	A″
498.9758	0.9367	A′
500.6121	28.6373	A″
603.4963	3.3106	A″
670.2043	17.3448	A″
714.096	23.0989	A″
766.3146	15.5013	A′
777.2369	31.691	A″
857.1539	0.3028	A″
899.577	4.9867	A′
970.0631	6.4009	A′
1040.204	25.6445	A′
1112.56	9.0079	A′
1165.095	3.173	A′
1210.119	0.0152	A′
1229.868	7.374	A′
1275.198	0.349	A′
1406.712	4.4653	A′
1476.085	23.8639	A′
1551.21	17.6665	A′
1629.159	34.9201	A′
2197.736	721.4159	A′
3251.789	7.8303	A′
3264.888	6.9082	A′
3276.539	0.5917	A′
3308.817	0.3374	A′

Table S.80 B3LYP/6-31G* (unscaled) Computed Vibrational Frequencies and Intensities

(*s*-*Z*)-*E*-pent-2-en-4-ynethial (5)

Frequency (cm^{-1})	Intensity (Km/mol)	Symmetry
113.4619	0.0695	A″
129.9601	0.5332	A′
209.5252	4.6920	A″
238.7765	1.6417	A′
453.5988	0.2093	A″
491.3680	5.6945	A′
618.3954	48.8150	A′
624.9773	41.4990	A″
626.5890	21.2564	A′
830.5196	18.1436	A″
893.9276	3.4002	A′
940.7766	9.5219	A″
1009.2095	17.0070	A″
1063.4628	23.0222	A′
1178.1559	92.2518	A′
1297.9323	67.4517	A′
1339.5577	6.0182	A′
1416.1371	63.8249	A′
1644.1315	130.5609	A′
2207.4167	28.2867	A′
3113.1178	26.2082	A′
3166.5137	0.3702	A′
3188.7021	11.4620	A′
3491.9872	77.4926	A′

Table S.81 B3LYP/6-31G* (unscaled) Computed Vibrational Frequencies and Intensities

(*s*-*E*)-*E*-pent-2-en-4-ynethial (5)

Frequency (cm^{-1})	Intensity (Km/mol)	Symmetry
119.9506	0.0037	A″
121.5038	1.7361	A′
221.0709	3.1216	A″
303.3371	5.6185	A′
389.0593	0.4820	A′
481.4243	0.3356	A″
562.7597	3.8055	A′
618.3334	43.0838	A″
630.4640	48.7332	A′
857.3707	2.0734	A″
923.1258	4.5381	A″
997.8385	53.7718	A′
1007.4915	40.2870	A″
1079.0621	0.3563	A′
1210.7960	122.8575	A′
1263.5040	2.8110	A′
1328.9197	3.0635	A′
1413.5206	63.7720	A′
1639.5495	134.2853	A′
2211.4309	28.6808	A′
3096.9096	18.6736	A′
3157.7164	5.6104	A′
3212.3500	2.5273	A′
3491.9089	79.9740	A′

Table S.82 B3LYP/6-31G* (unscaled) Computed Vibrational Frequencies and Intensities

(*s*-*Z*)-*Z*-pent-2-en-4-ynethial (6)

Frequency (cm^{-1})	Intensity (Km/mol)	Symmetry
89.8786	2.1706	A″
130.3166	1.0425	A′
232.6436	0.2480	A′
307.6903	0.7308	A″
453.6725	7.3173	A′
482.8862	12.5251	A″
613.7152	49.8211	A′
656.9285	40.1386	A″
762.9269	4.0650	A′
766.0970	23.3718	A″
875.6077	6.6331	A′
919.7187	0.3341	A″
971.7686	22.2245	A′
1002.4086	0.0001	A″
1168.8603	36.5243	A′
1293.9497	24.6557	A″
1414.3513	38.8276	A′
1465.1306	10.7272	A′
1634.4097	97.9164	A′
2201.7281	32.0999	A′
3099.9723	32.7816	A′
3154.3279	0.2032	A′
3178.4863	23.2403	A′
3493.0391	55.6347	A′

Table S.83 B3LYP/6-31G* (unscaled) Computed Vibrational Frequencies and Intensities

(*s*-*E*)-*Z*-pent-2-en-4-ynethial (6)

Frequency (cm^{-1})	Intensity (Km/mol)	Symmetry
119.0970	0.6960	A′
131.5279	0.9965	A″
271.2126	0.7273	A″
295.5563	8.3691	A′
383.3593	0.8871	A′
498.7992	8.4511	A″
621.3576	46.7021	A″
634.8250	42.3143	A′
683.2353	4.4973	A′
822.0271	23.9330	A″
916.4752	8.1759	A″
927.3896	7.2893	A′
1009.5280	0.9909	A″
1052.7528	50.1993	A′
1177.1601	52.6203	A′
1254.1288	36.6719	A′
1348.8011	10.1599	A′
1462.7122	24.4400	A′
1620.6126	97.5833	A′
2209.1829	17.9576	A′
3128.1780	4.6967	A′
3170.9944	3.1582	A′
3210.1232	4.0062	A′
3491.2258	78.6710	A′

Table S.84 B3LYP/6-31G* (unscaled) Computed Vibrational Frequencies and Intensities

4-thiacyclohexa-1,2,5-triene (7)

Frequency (cm^{-1})	Intensity (Km/mol)	Symmetry
247.4932	23.1487	A
401.6391	13.0244	A
460.8204	7.0565	A
484.7846	33.9136	A
527.4042	8.2922	A
678.6087	12.1999	A
701.1234	12.6085	A
719.2167	69.6481	A
779.8097	41.5891	A
816.0627	32.1764	A
864.5795	4.9097	A
926.2950	3.5085	A
1039.5061	1.9353	A
1147.1519	9.9364	A
1186.4460	2.3453	A
1281.1095	9.2474	A
1371.3954	1.2743	A
1407.9035	43.0420	A
1539.4797	12.5549	A
1767.0630	6.1463	A
3160.8330	20.6219	A
3181.8226	14.3791	A
3198.0943	12.7714	A
3216.0695	3.6599	A

Table S.85 B3LYP/6-31G* (unscaled) Computed Vibrational Frequencies and Intensities

propargyl thioketene (8)

Frequency (cm^{-1})	Intensity (Km/mol)	Symmetry
46.4027	0.2898	A
152.1138	0.1636	A
197.9184	0.6962	A
332.1916	2.2120	A
403.5622	3.7307	A
463.1063	1.9995	A
550.3167	10.8165	A
604.6812	48.6021	A
626.1152	44.8356	A
651.5315	27.7815	A
823.9461	18.2129	A
947.1696	19.5565	A
965.8906	6.5005	A
1059.6143	1.4786	A
1207.4163	0.4836	A
1290.9242	55.6585	A
1357.2021	18.2251	A
1493.8699	5.1053	A
1853.9544	398.9808	A
2241.7639	0.1758	A
3027.9453	18.1239	A
3084.0111	5.8203	A
3179.8179	7.6738	A
3494.6626	60.3348	A

Table S.86 B3LYP/6-31G* (unscaled) Computed Vibrational Frequencies and Intensities

(*s*-*Z*)-α-thial methylenecyclopropene (9)

Frequency (cm^{-1})	Intensity (Km/mol)	Symmetry
129.5721	3.7294	A′
148.0544	1.0367	A″
247.4935	9.8051	A″
334.7602	0.3736	A′
508.8217	5.3639	A″
639.6986	29.7384	A′
757.1140	17.6312	A″
797.4082	62.0034	A′
806.0586	2.4993	A″
907.5507	20.4238	A′
928.7995	0.0206	A″
933.5975	1.4645	A″
973.3675	4.0430	A′
1035.0499	30.7528	A′
1131.4944	6.8191	A′
1212.4920	136.8468	A′
1413.2696	45.0903	A′
1421.8994	137.2799	A′
1550.5023	229.0089	A′
1799.3744	406.9012	A′
3099.0361	38.4754	A′
3188.0784	15.5984	A′
3279.5207	4.7207	A′
3332.0464	8.9792	A′

Table S.87 B3LYP/6-31G* (unscaled) Computed Vibrational Frequencies and Intensities

(*s*-*E*)-α-thial methylenecyclopropene (9)

Frequency (cm^{-1})	Intensity (Km/mol)	Symmetry
118.1890	0.0700	A″
142.1994	0.0871	A′
283.1040	2.1594	A″
350.3533	6.4049	A′
463.6324	9.6171	A″
469.4910	6.9309	A′
732.1181	41.4395	A″
859.5871	13.5639	A″
865.2882	18.9020	A′
920.1508	10.0260	A″
929.0043	13.3951	A″
935.1766	16.4156	A′
1023.7360	72.2054	A′
1040.0664	20.7261	A′
1124.7751	20.3880	A′
1230.5468	191.6680	A′
1296.5497	7.1558	A′
1467.5649	69.4352	A′
1573.0652	348.2824	A′
1800.2869	557.2771	A′
3077.8390	24.3687	A′
3206.2680	3.3427	A′
3278.3670	4.4177	A′
3316.8080	10.4195	A′

Table S.88 B3LYP/6-31G* (unscaled) Computed Vibrational Frequencies and Intensities

4-thiacyclohexa-2,5-dienylidene (triplet) (10)

Frequency (cm^{-1})	Intensity (Km/mol)	Symmetry
144.1251	7.5001	B1
359.2745	0.0000	A2
440.8691	2.6367	A1
515.8622	39.5622	B1
538.3881	0.4052	B2
663.6756	0.0000	A2
682.4337	9.1395	A1
689.1932	49.8622	B1
737.9576	0.0015	B2
900.0327	1.6531	B1
902.0157	0.7272	A1
912.3045	0.0000	A2
976.7184	11.2770	A1
1148.1954	7.8178	B2
1192.6933	0.1673	A1
1257.3035	43.1047	B2
1353.5471	2.0660	B2
1403.6466	0.4580	A1
1429.0412	0.0513	B2
1537.2398	0.0168	A1
3169.0973	9.8611	B2
3170.5543	2.2931	A1
3222.9428	0.6162	A1
3223.0129	4.4386	B2

Table S.89 B3LYP/6-31G* (unscaled) Computed Vibrational Frequencies and Intensities

4-thiacyclohexa-2,5-dienylidene (singlet) (10)

Frequency (cm^{-1})	Intensity (Km/mol)	Symmetry
132.7398	23.0410	B1
198.6640	0.0000	A2
461.7588	4.7197	A1
520.8193	4.2635	B1
567.7926	0.3136	B2
736.9938	23.5377	A1
745.2104	29.7440	B1
795.7296	0.0000	A2
810.4740	2.4001	B2
898.4520	1.3163	A1
981.4225	0.3104	A1
985.4722	0.0000	A2
994.2722	0.9534	B1
1143.0010	0.2523	B2
1228.1877	10.0049	A1
1335.8336	0.1375	B2
1403.5048	1.3821	B2
1429.9689	7.3029	A1
1459.0924	2.5861	B2
1510.6393	42.5923	A1
3100.8511	66.6766	B2
3103.1646	6.7913	A1
3182.1225	1.0344	A1
3185.3162	16.9256	B2

Table S.90 B3LYP/6-31G* (unscaled) Computed Vibrational Frequencies and Intensities

(*s*-*Z*)-2-thienyl carbene (triplet) (11)

Frequency (cm^{-1})	Intensity (Km/mol)	Symmetry
316.5488	1.5614	A″
316.5488	4.0862	A′
445.3312	27.1973	A″
469.9115	21.2356	A″
541.3309	0.0942	A′
567.0699	0.2381	A″
616.3511	1.7204	A′
665.2321	47.7807	A″
737.8128	4.9278	A′
770.0327	12.3142	A″
825.2680	19.6047	A′
856.8486	24.2974	A′
906.1707	0.3353	A″
1076.2463	4.7195	A′
1106.2570	3.9419	A′
1167.1874	14.4231	A′
1305.6986	3.5426	A′
1388.6117	2.4407	A′
1429.8178	1.2706	A′
1502.7392	5.8233	A′
3220.5441	5.7219	A′
3241.5605	3.8123	A′
3266.0516	1.3643	A′
3293.6811	1.4745	A′

Table S.91 B3LYP/6-31G* (unscaled) Computed Vibrational Frequencies and Intensities

(*s*-*Z*)-2-thienyl carbene (singlet) (11)

Frequency (cm^{-1})	Intensity (Km/mol)	Symmetry
207.3744	0.2558	A″
311.4328	11.4749	A′
377.4984	13.2334	A″
519.2452	14.9018	A′
550.8419	0.4830	A″
563.7090	1.3012	A′
678.4411	678.4411	A″
764.1951	764.1951	A′
792.1635	792.1635	A″
882.0084	882.0084	A′
906.9368	906.9368	A″
962.7151	962.7151	A″
1036.1229	1036.1229	A′
1069.0584	1069.0584	A′
1111.4208	1111.4208	A′
1162.7304	36.5675	A′
1313.5615	16.4147	A′
1398.3658	88.5173	A′
1472.0547	61.7295	A′
1548.2557	44.7907	A′
3000.6408	96.5967	A′
3228.1613	0.6329	A′
3241.7119	1.9977	A′
3251.6763	2.1462	A′

Table S.92 CCSD/cc-pVTZ (unscaled) Computed Vibrational Frequencies and Intensities

(*s*-*Z*)-2-thienyl carbene (triplet) (11)

Frequency (cm^{-1})	Intensity (Km/mol)	Symmetry
221.3541	2.0971	A"
317.4751	2.472	A'
472.6379	1.3954	A"
481.449	40.0569	A"
547.8369	0.017	A'
572.7244	1.6391	A"
671.7829	1.8324	A'
696.0119	60.0742	A"
751.5079	3.3614	A'
800.7288	11.6682	A"
850.3227	11.2152	A'
873.7626	22.0313	A'
926.6199	0.7524	A"
1069.5794	2.1261	A'
1106.8333	3.112	A'
1202.0997	14.4147	A'
1307.508	5.0891	A'
1336.8968	2.0957	A'
1424.8357	2.713	A'
1517.114	3.0655	A'
3239.5566	3.035	A'
3258.1141	1.5051	A'
3279.6246	1.416	A'
3285.6548	1.5976	A'

Table S.93 CCSD/cc-pVTZ (unscaled) Computed Vibrational Frequencies and Intensities

(*s*-*Z*)-2-thienyl carbene (singlet) (11)

Frequency (cm^{-1})	Intensity (Km/mol)	Symmetry
212.3067	0.1371	A"
323.8503	7.2728	A'
414.4724	15.5979	A"
563.9221	0.2107	A"
574.4751	3.0932	A'
666.4761	10.0451	A'
673.8652	12.8811	A"
770.8974	5.5254	A'
796.2943	87.1228	A"
889.6467	31.4826	A'
923.6027	0.4922	A"
978.8093	1.1324	A"
1061.4314	43.6353	A'
1095.7343	2.8837	A'
1113.3491	8.9153	A'
1226.0312	1.8816	A'
1310.8983	36.3312	A'
1385.7939	208.3565	A'
1463.4538	58.3526	A'
1559.3321	66.0987	A'
2991.0898	73.6756	A'
3244.9759	0.5159	A'
3257.6918	0.1462	A'
3268.7358	0.9064	A'

Table S.94 B3LYP/6-31G* (unscaled) Computed Vibrational Frequencies and Intensities

(*s*-*E*)-2-thienyl carbene (triplet) (11)

Frequency (cm^{-1})	Intensity (Km/mol)	Symmetry
221.0622	0.8541	A″
318.1642	2.3337	A′
422.4918	26.1967	A″
496.2700	1.4929	A″
551.2696	0.3875	A′
565.7129	0.0059	A″
606.2826	7.4542	A′
666.1551	60.9509	A″
735.2658	3.3006	A′
759.7439	17.4776	A″
848.7283	15.6982	A′
860.6903	20.6393	A′
902.4638	0.3101	A″
1080.6544	3.3910	A′
1107.2466	3.1960	A′
1169.5270	2.7287	A′
1304.7931	3.3091	A′
1379.7566	4.3825	A′
1425.8801	1.3981	A′
1496.2238	6.0276	A′
3217.9159	5.5371	A′
3237.9314	5.8051	A′
3268.8858	1.2862	A′
3280.9970	1.7172	A′

Table S.95 B3LYP/6-31G* (unscaled) Computed Vibrational Frequencies and Intensities

(*s*-*E*)-2-thienyl carbene (singlet) (11)

Frequency (cm^{-1})	Intensity (Km/mol)	Symmetry
212.2615	4.4798	A″
322.9003	6.8612	A′
382.2628	22.2833	A″
557.8655	24.7571	A″
573.4436	2.1794	A′
619.1107	7.7638	A′
656.4700	24.7508	A′
755.8438	3.6963	A′
775.8639	34.9585	A″
888.4902	22.8314	A′
897.2212	1.7960	A″
952.2453	0.3299	A″
1019.8118	18.8553	A′
1099.6760	22.7661	A′
1115.5050	14.8857	A′
1226.4940	7.8393	A′
1309.7834	22.5603	A′
1368.0635	94.7470	A′
1470.2844	50.2940	A′
1530.1176	24.8875	A′
2950.9513	124.1566	A′
3219.6077	1.9728	A′
3234.3427	4.2945	A′
3252.3611	1.4719	A′

Table S.96 CCSD/cc-pVTZ (unscaled) Computed Vibrational Frequencies and Intensities

(*s*-*E*)-2-thienyl carbene (triplet) (11)

Frequency (cm^{-1})	Intensity (Km/mol)	Symmetry
227.8632	1.2252	A"
318.4351	2.6373	A'
443.3949	25.4583	A"
506.8472	1.8271	A"
555.0675	0.227	A'
570.0468	0.569	A"
652.4392	5.548	A'
697.2255	70.7629	A"
750.4378	2.3227	A'
791.2244	15.1957	A"
865.2881	13.4012	A'
889.8573	14.7389	A'
922.4388	0.7718	A"
1072.4772	2.6001	A'
1107.8788	3.118	A'
1197.437	3.579	A'
1308.6599	4.1452	A'
1333.2854	6.0493	A'
1422.4506	2.5026	A'
1512.8406	3.5513	A'
3237.4528	3.2021	A'
3254.4694	2.662	A'
3277.2482	1.88	A'
3281.0038	1.3188	A'

Table S.97 CCSD/cc-pVTZ (unscaled) Computed Vibrational Frequencies and Intensities

(*s*-*E*)-2-thienyl carbene (singlet) (11)

Frequency (cm^{-1})	Intensity (Km/mol)	Symmetry
214.1141	3.6496	A"
324.2148	6.8595	A'
421.9359	17.1741	A"
560.9453	31.0831	A"
578.5733	1.7944	A'
665.6466	28.949	A"
691.2529	4.9288	A'
766.9046	6.3076	A'
790.3233	45.2846	A"
897.5405	37.0796	A'
916.7778	4.0901	A"
966.5625	0.4894	A"
1058.2013	5.297	A'
1101.2101	43.2672	A'
1113.7807	23.1358	A'
1262.2311	23.4255	A'
1313.0967	38.1073	A'
1364.4314	220.9169	A'
1466.8165	53.0407	A'
1549.582	52.7949	A'
2976.2711	89.8395	A'
3236.7837	0.7131	A'
3251.8515	1.3835	A'
3267.7154	0.7645	A'

Table S.98 B3LYP/6-31G* (unscaled) Computed Vibrational Frequencies and Intensities

2-thiabicyclo[3.1.0]hexa-3,5-diene (12)

Frequency (cm^{-1})	Intensity (Km/mol)	Symmetry
288.4450	5.1232	A
328.0444	2.4098	A
489.5940	7.3413	A
528.5782	11.1556	A
620.8399	0.0842	A
661.7199	37.4769	A
677.6008	23.1284	A
689.6169	73.2052	A
794.9829	17.8243	A
813.5686	5.3080	A
888.4722	7.0667	A
985.6982	13.9957	A
998.7725	4.7365	A
1047.0441	11.1798	A
1112.7496	1.0918	A
1141.2439	12.8832	A
1272.8739	9.5953	A
1331.9973	1.2254	A
1524.7865	21.1318	A
1776.3356	28.9732	A
3133.2911	32.5063	A
3227.0272	0.5068	A
3251.2479	4.0529	A
3275.1449	0.3753	A

Table S.99 B3LYP/6-31G* (unscaled) Computed Vibrational Frequencies and Intensities

(*s*-*Z*)-3-thienyl carbene (triplet) (13)

Frequency (cm^{-1})	Intensity (Km/mol)	Symmetry
230.2856	2.8102	A″
332.9358	5.2268	A′
424.8469	3.7521	A″
464.7577	22.9057	A′
558.3848	0.2322	A′
618.3891	15.0062	A″
637.2126	3.2917	A″
664.0452	1.8485	A′
755.3259	69.7490	A″
810.0020	8.5495	A′
841.9969	8.6248	A′
886.2660	18.2022	A′
899.2907	0.1709	A″
975.4522	15.0728	A′
1112.8602	4.4187	A′
1221.9962	5.9258	A′
1289.3100	2.8476	A′
1348.1937	2.4775	A′
1419.6152	0.0459	A′
1551.8065	5.9277	A′
3233.3796	2.3103	A′
3264.4344	1.8267	A′
3270.0802	1.1249	A′
3273.2543	1.7141	A′

Table S.100 B3LYP/6-31G* (unscaled) Computed Vibrational Frequencies and Intensities

(*s*-*Z*)-3-thienyl carbene (singlet) (13)

Frequency (cm^{-1})	Intensity (Km/mol)	Symmetry
144.0879	19.4556	A″
362.9422	10.1430	A′
388.0851	14.4198	A″
559.9900	2.4644	A′
584.6080	20.5627	A″
632.2876	28.5065	A″
662.4395	0.2993	A′
722.2213	5.1535	A″
806.7412	1.9645	A′
823.0643	61.0665	A″
888.3153	42.3332	A′
933.6567	0.8227	A″
961.5001	1.1772	A′
1104.9649	14.9100	A′
1116.4781	21.2112	A′
1219.9507	13.1133	A′
1272.5976	63.9307	A′
1402.8998	27.4016	A′
1437.5696	106.9324	A′
1546.2689	13.6591	A′
2922.0172	138.4670	A′
3243.5535	0.6321	A′
3263.9619	1.3179	A′
3275.7428	0.8887	A′

Table S.101 CCSD/cc-pVTZ (unscaled) Computed Vibrational Frequencies and Intensities

(*s*-*Z*)-3-thienyl carbene (triplet) (13)

Frequency (cm^{-1})	Intensity (Km/mol)	Symmetry
235.3709	3.0888	A"
334.5247	4.9067	A'
434.3221	6.4414	A"
476.7988	18.0179	A"
565.2696	0.1529	A'
626.2352	15.1979	A"
673.1558	1.1725	A'
684.8437	3.366	A"
780.2331	70.7374	A"
833.0116	10.4657	A'
858.8637	8.1745	A'
902.4998	10.5506	A'
933.5874	0.0555	A"
987.1748	12.2723	A'
1110.9139	3.6535	A'
1222.1019	3.4673	A'
1286.3188	3.693	A'
1380.5828	4.8959	A'
1423.0909	0.4454	A'
1571.4291	6.8802	A'
3248.1656	0.9645	A'
3265.1588	0.3891	A'
3277.5372	0.6528	A'
3280.6259	1.3911	A'

Table S.102 CCSD/cc-pVTZ (unscaled) Computed Vibrational Frequencies and Intensities

(*s*-*Z*)-3-thienyl carbene (singlet) (13)

Frequency (cm^{-1})	Intensity (Km/mol)	Symmetry
173.2718	15.4985	A"
363.0906	13.5752	A'
405.5744	19.1486	A"
565.2993	4.3719	A'
588.2931	25.2927	A"
631.9141	34.5473	A"
674.9791	2.5239	A'
746.4618	9.6746	A"
831.9761	4.1341	A'
849.6883	57.5203	A"
908.7085	42.6943	A'
950.9422	0.8466	A"
972.169	0.3961	A'
1107.7167	13.6072	A'
1124.5858	24.136	A'
1233.1251	21.5553	A'
1280.8466	94.4411	A'
1439.4544	21.2349	A'
1456.5178	186.1406	A'
1557.2204	46.3792	A'
2957.6457	95.1939	A'
3255.5259	1.2804	A'
3270.4853	2.1538	A'
3284.8737	0.3869	A'

Table S.103 B3LYP/6-31G* (unscaled) Computed Vibrational Frequencies and Intensities

(*s*-*E*)-3-thienyl carbene (triplet) (13)

Frequency (cm^{-1})	Intensity (Km/mol)	Symmetry
229.8101	0.8370	A″
331.9465	0.7930	A′
410.8722	25.0543	A″
437.3061	3.2842	A″
556.2456	0.6577	A′
615.6011	10.2787	A″
642.7157	0.4713	A″
661.7021	0.9120	A′
751.0335	78.1174	A″
822.3692	8.9274	A′
843.3596	36.9560	A′
890.4561	3.6215	A′
891.6614	0.1986	A″
956.9979	4.5144	A′
1114.5889	4.1435	A′
1220.0644	3.6349	A′
1284.6886	3.0712	A′
1353.8378	5.6938	A′
1423.4396	0.2916	A′
1548.4560	5.6303	A′
3228.0574	3.4317	A′
3264.8925	2.6215	A′
3268.0110	1.4553	A′
3276.7229	1.3771	A′

Table S.104 B3LYP/6-31G* (unscaled) Computed Vibrational Frequencies and Intensities

(*s*-*E*)-3-thienyl carbene (singlet) (13)

Frequency (cm^{-1})	Intensity (Km/mol)	Symmetry
182.9407	0.0395	A″
354.6757	9.9085	A′
391.4328	22.5641	A″
565.9100	2.0179	A′
577.4740	27.8792	A″
636.3785	0.7619	A″
654.4438	2.1454	A′
722.5307	22.0043	A″
803.0433	1.6801	A′
849.5372	56.6115	A″
892.7329	48.6351	A′
920.3262	0.8105	A″
959.3598	6.7322	A′
1098.2640	1.7404	A′
1114.7693	8.1600	A′
1209.7266	15.5958	A′
1271.4795	43.4238	A′
1396.8120	1.2913	A′
1446.8240	134.4207	A′
1548.9581	19.1897	A′
2921.1716	144.1146	A′
3227.2383	1.3762	A′
3268.7398	1.1843	A′
3279.8893	4.8018	A′

Table S.105 CCSD/cc-pVTZ (unscaled) Computed Vibrational Frequencies and Intensities

(*s*-*E*)-3-thienyl carbene (triplet) (13)

Frequency (cm^{-1})	Intensity (Km/mol)	Symmetry
234.5973	1.6152	A"
334.131	0.7034	A'
426.1609	25.2401	A"
447.826	0.6607	A"
562.8277	0.4627	A'
622.4599	13.7079	A"
671.0272	0.6627	A'
689.4085	0.0922	A"
777.1296	77.537	A"
842.5105	15.069	A'
862.8557	23.0059	A'
908.0348	2.0181	A'
927.2128	0.0443	A"
968.0389	4.726	A'
1112.0735	3.7861	A'
1221.4077	2.3989	A'
1281.4432	3.5418	A'
1386.3272	6.1221	A'
1426.6971	0.9257	A'
1568.4304	6.9173	A'
3243.717	1.5683	A'
3267.296	1.499	A'
3278.7094	0.3721	A'
3282.0464	1.744	A'

Table S.106 CCSD/cc-pVTZ (unscaled) Computed Vibrational Frequencies and Intensities

(*s*-*E*)-3-thienyl carbene (singlet) (13)

Frequency (cm^{-1})	Intensity (Km/mol)	Symmetry
192.1676	0.0296	A"
355.9647	8.4185	A'
408.6436	19.7686	A"
568.9531	4.9646	A'
577.7256	30.968	A"
638.1522	1.0058	A"
668.1496	5.6529	A'
744.6824	26.9329	A"
830.2523	2.0544	A'
874.5624	54.2404	A"
909.2113	53.3167	A'
939.3064	0.5914	A"
972.4137	5.0539	A'
1110.8894	1.2063	A'
1113.372	12.495	A'
1223.658	24.9687	A'
1283.7225	79.7315	A'
1431.2672	2.7276	A'
1465.7064	195.5607	A'
1558.1581	54.9221	A'
2956.5676	103.1564	A'
3242.5994	0.7693	A'
3280.1471	0.6654	A'
3283.2391	6.1921	A'

Table S.107 B3LYP/6-31G* (unscaled) Computed Vibrational Frequencies and Intensities

2-ethynylcyclopropanethione (14)

Frequency (cm^{-1})	Intensity (Km/mol)	Symmetry
97.7477	0.3097	A
197.1614	1.0186	A
305.5630	2.1012	A
336.4695	1.1782	A
486.0304	3.8697	A
521.0215	0.5027	A
581.6420	39.8244	A
640.4928	17.7266	A
643.7578	44.5728	A
777.3970	2.4094	A
845.8627	7.8936	A
945.8408	35.8659	A
1020.8839	9.5491	A
1050.1037	2.7201	A
1089.4792	2.2814	A
1110.7083	2.3368	A
1322.3515	17.6559	A
1430.8667	12.8438	A
1512.3123	105.7016	A
2239.7044	8.8600	A
3127.9513	0.2314	A
3129.1300	4.5308	A
3210.2488	0.7549	A
3495.6150	72.6217	A

Table S.108 B3LYP/6-31G* (unscaled) Computed Vibrational Frequencies and Intensities

4-thiabicyclo[3.1.0]hexa-2,5-diene (15)

Frequency (cm^{-1})	Intensity (Km/mol)	Symmetry
267.7921	5.3174	A
330.6983	6.1987	A
505.6039	5.7910	A
545.4197	2.4363	A
604.6023	15.1090	A
626.4690	33.7196	A
703.4525	28.6051	A
728.8625	43.6012	A
806.9800	30.7263	A
810.8157	8.8798	A
904.7869	2.4901	A
961.4174	2.7801	A
1004.5923	1.8446	A
1036.9201	20.0388	A
1114.6529	5.3037	A
1146.7939	0.8737	A
1302.9820	4.6975	A
1340.4968	5.6335	A
1588.5295	9.7375	A
1735.9352	29.4007	A
3091.4112	56.2736	A
3200.7944	6.7057	A
3243.1264	3.8712	A
3268.0711	1.1603	A

Table S.109 B3LYP/6-31G* (unscaled) Computed Vibrational Frequencies and Intensities

(*s*-*Z*)-*E*-pent-2-en-4-ynal (16)

Frequency (cm^{-1})	Intensity (Km/mol)	Symmetry
140.0421	0.1208	A″
146.4983	1.8962	A′
224.2771	9.2594	A″
271.2857	6.3504	A′
451.9460	0.9043	A″
517.6884	2.0939	A′
616.5676	49.1881	A′
628.7955	42.1807	A″
729.1429	57.2711	A′
850.1561	2.7060	A″
984.0504	52.9424	A′
1012.4862	28.1649	A″
1032.7158	3.061	A″
1073.2936	4.3842	A′
1302.5823	45.3873	A′
1325.4820	8.7816	A′
1445.1690	7.1146	A′
1656.5550	229.3551	A′
1790.4961	127.2157	A′
2216.8698	16.2175	A′
2940.3429	178.4587	A′
3169.1836	0.0529	A′
3202.2933	7.5349	A′
3492.6068	67.0650	A′

Table S.110 B3LYP/6-31G* (unscaled) Computed Vibrational Frequencies and Intensities

(*s*-*E*)-*E*-pent-2-en-4-ynal (16)

Frequency (cm^{-1})	Intensity (Km/mol)	Symmetry
126.2381	0.9190	A″
138.7480	2.9319	A′
232.4875	8.2971	A″
323.5595	12.8641	A′
476.1565	0.0243	A″
478.0668	1.8233	A′
598.5769	9.4822	A′
624.4967	42.2101	A″
628.7080	47.6258	A′
857.7822	0.5969	A″
1000.5995	33.9012	A″
1028.4981	3.0892	A″
1047.4066	5.2321	A′
1145.5134	138.7691	A′
1262.7693	0.4024	A′
1334.9790	6.1120	A′
1436.2679	0.6909	A′
1674.9334	52.9233	A′
1793.1451	303.9245	A′
2219.9754	16.5428	A′
2900.7039	117.6071	A′
3144.2873	5.8488	A′
3216.2585	1.8512	A′
3491.6830	68.8304	A′

Table S.111 B3LYP/6-31G* (unscaled) Computed Vibrational Frequencies and Intensities

(*s*-*Z*)-*Z*-pent-2-en-4-ynal (17)

Frequency (cm^{-1})	Intensity (Km/mol)	Symmetry
120.2705	8.8031	A″
142.1430	3.6717	A′
267.4848	1.7523	A′
298.2561	0.0211	A″
469.5454	9.4160	A″
515.0672	12.5448	A′
614.1571	51.5521	A′
652.0249	42.4449	A″
785.1828	12.4465	A″
842.4305	2.9959	A′
920.7101	76.5299	A′
993.3496	0.0481	A″
1020.4132	5.0019	A′
1027.2601	5.1858	A″
1252.8438	8.4405	A′
1431.8652	6.1727	A′
1459.7740	18.2928	A′
1644.0015	144.4513	A′
1795.0842	76.5903	A′
2213.8061	25.9430	A′
2921.1204	193.2650	A′
3155.8329	2.8196	A′
3193.0249	14.3286	A′
3494.7580	55.6365	A′

Table S.112 B3LYP/6-31G* (unscaled) Computed Vibrational Frequencies and Intensities

(*s*-*E*)-*Z*-pent-2-en-4-ynal (17)

Frequency (cm^{-1})	Intensity (Km/mol)	Symmetry
135.9469	1.6544	A′
153.4572	6.1021	A″
267.0435	1.3114	A″
317.2154	12.2995	A′
480.1791	4.9391	A′
484.8071	8.4698	A″
626.4132	46.7011	A″
634.2116	43.6891	A′
709.9447	1.7825	A′
806.7349	22.3611	A″
933.5544	19.9797	A′
1009.5120	0.2373	A″
1028.3629	2.5254	A″
1125.4295	43.0638	A′
1236.5934	22.0665	A′
1394.3473	6.5193	A′
1449.9965	6.5841	A′
1657.5144	24.2745	A′
1785.3771	241.1509	A′
2216.0511	9.9396	A′
2960.3515	53.2327	A′
3165.5829	4.0445	A′
3212.7588	3.8731	A′
3492.8776	66.7394	A′

Table S.113 B3LYP/6-31G* (unscaled) Computed Vibrational Frequencies and Intensities

propargyl ketene (18)

Frequency (cm^{-1})	Intensity (Km/mol)	Symmetry
53.2345	0.7321	A
179.5269	1.1953	A
212.7502	2.6663	A
333.5144	2.1207	A
469.5441	14.4606	A
520.2441	4.0194	A
579.1460	41.1375	A
604.0994	48.4077	A
620.0565	37.4139	A
640.3155	20.8690	A
895.4473	6.1617	A
958.2668	6.0746	A
1033.3068	14.9841	A
1156.6894	1.7458	A
1239.0005	4.1715	A
1342.2090	39.6794	A
1437.5749	5.7483	A
1496.2695	4.2126	A
2228.7130	662.5854	A
2241.9015	24.9702	A
3030.7101	20.3332	A
3074.4988	8.9207	A
3219.1862	8.6421	A
3495.3174	55.8752	A

Table S.114 B3LYP/6-31G* (unscaled) Computed Vibrational Frequencies and Intensities

(*s*-*Z*)-(α-formyl)methylenecyclopropene (19)

Frequency (cm^{-1})	Intensity (Km/mol)	Symmetry
136.8213	8.1545	A′
180.2756	3.6383	A″
246.8634	14.3640	A″
392.1039	2.1273	A′
498.9675	4.8649	A″
719.3387	51.5021	A′
752.4857	47.0178	A″
789.6789	22.8471	A″
864.0791	0.8649	A′
926.6929	0.3477	A″
971.0256	2.6297	A′
992.5756	28.5340	A′
1026.3594	3.1327	A″
1086.3757	7.7068	A′
1136.3259	39.5112	A′
1392.0914	21.3319	A′
1444.6763	6.6258	A′
1568.5299	223.9695	A′
1744.1227	315.4390	A′
1834.5703	220.8581	A′
2898.9783	212.4197	A′
3202.7774	11.4735	A′
3278.6264	2.6719	A′
3323.8406	4.7007	A′

Table S.115 B3LYP/6-31G* (unscaled) Computed Vibrational Frequencies and Intensities

(*s*-*E*)-(α-formyl)methylenecyclopropene (19)

Frequency (cm^{-1})	Intensity (Km/mol)	Symmetry
146.1791	0.3891	A″
160.5009	0.7763	A′
289.3906	4.0399	A″
462.9068	25.0986	A′
472.7502	15.0159	A″
504.8372	0.4857	A′
730.5565	36.6097	A′
832.9059	35.9903	A″
875.3525	8.9669	A″
921.9663	0.2336	A′
947.1219	2.2653	A″
1021.2407	1.7506	A′
1050.5802	20.7167	A″
1121.1117	19.2963	A′
1170.9502	109.7027	A′
1320.9771	1.8806	A′
1448.6383	16.3587	A′
1594.5773	131.0810	A′
1779.5883	531.1781	A′
1824.6984	154.9566	A′
2860.3484	122.0688	A′
3207.1659	4.5146	A′
3276.5067	3.0018	A′
3314.9490	4.9691	A′

Table S.116 B3LYP/6-31G* (unscaled) Computed Vibrational Frequencies and Intensities

4-oxa-cyclohexa-1,2,4-triene (20)

Frequency (cm^{-1})	Intensity (Km/mol)	Symmetry
248.9299	48.2386	A
406.6117	6.5075	A
559.1819	27.8678	A
605.0359	23.3726	A
658.7406	22.2755	A
784.8191	22.8614	A
830.2104	15.3764	A
899.5470	19.9317	A
920.4787	20.5335	A
939.4773	20.4667	A
1001.2944	27.2957	A
1063.4409	3.5709	A
1075.7982	6.2206	A
1197.3030	22.5968	A
1251.6667	5.2670	A
1369.9190	5.3480	A
1455.1897	7.8989	A
1464.9349	36.2807	A
1513.1290	63.3784	A
1659.7514	95.4252	A
3131.0151	36.0057	A
3199.8172	13.0120	A
3221.2075	20.6224	A
3245.6705	4.0732	A

Table S.117 B3LYP/6-31G* (unscaled) Computed Vibrational Frequencies and Intensities

2-ethynylcyclopropanone (21)

Frequency (cm^{-1})	Intensity (Km/mol)	Symmetry
118.2940	2.4019	A
193.9604	1.0401	A
349.5135	4.7454	A
415.7740	0.5049	A
491.8777	6.3414	A
559.8702	22.2428	A
579.3170	30.4424	A
644.4178	43.7529	A
699.2489	6.4151	A
804.0236	22.0010	A
831.4665	10.2700	A
970.2859	125.2053	A
1056.3484	20.5733	A
1076.2142	9.8706	A
1098.3476	6.1566	A
1109.8581	5.7188	A
1333.8925	1.3511	A
1440.5205	6.9172	A
1959.3309	322.7898	A
2237.1948	8.9872	A
3134.4296	3.7286	A
3135.3155	3.2077	A
3222.6278	0.5927	A
3495.5387	71.0680	A

Table S.118 B3LYP/6-31G* (unscaled) Computed Vibrational Frequencies and Intensities

(*s*-*Z*)-2-furyl carbene (triplet) (22)

Frequency (cm^{-1})	Intensity (Km/mol)	Symmetry
250.8064	2.4684	A″
353.7840	4.6285	A′
393.7740	50.8312	A″
574.9451	5.9102	A″
649.4992	0.1996	A″
704.4588	2.5517	A′
707.4175	34.0121	A″
751.5593	22.7070	A″
829.2771	16.4733	A′
864.4375	1.5940	A″
887.0370	6.8136	A′
902.8122	16.6826	A′
1042.6724	18.7904	A′
1122.9069	4.0823	A′
1183.2791	23.8907	A′
1199.1987	14.2740	A′
1328.7676	6.2954	A′
1411.3550	1.4725	A′
1463.3999	3.0982	A′
1550.1465	6.9466	A′
3264.3045	2.7171	A′
3280.0413	0.8495	A′
3297.0073	0.9598	A′
3308.1484	2.3686	A′

Table S.119 B3LYP/6-31G* (unscaled) Computed Vibrational Frequencies and Intensities

(*s-Z*)-2-furyl carbene (singlet) (22)

Frequency (cm^{-1})	Intensity (Km/mol)	Symmetry
227.2654	0.3118	A"
375.1207	13.0064	A'
483.7331	1.1038	A"
629.0945	5.5878	A"
645.4633	8.2596	A'
745.3974	13.1390	A'
794.7456	2.7285	A"
814.0636	78.7819	A"
894.8558	15.7301	A'
919.3408	0.9139	A"
949.1199	2.2238	A"
1016.3512	30.6832	A'
1063.3078	5.9274	A'
1122.4535	24.8743	A'
1142.0766	2.0772	A'
1237.7969	26.1104	A'
1359.6187	14.5566	A'
1460.0156	158.4865	A'
1496.8366	13.6779	A'
1613.5297	63.5868	A'
3023.7744	72.2026	A'
3246.9002	3.2706	A'
3274.3439	0.8905	A'
3287.6714	0.7742	A'

Table S.120 B3LYP/6-31G* (unscaled) Computed Vibrational Frequencies and Intensities

(*s*-*E*)-2-furyl carbene (triplet) (22)

Frequency (cm^{-1})	Intensity (Km/mol)	Symmetry
255.5985	4.1001	A″
362.5039	4.5723	A′
415.8359	28.6552	A″
577.4798	7.7708	A″
655.2127	0.0481	A″
710.4745	1.4475	A′
710.7934	42.7340	A″
741.2464	24.7221	A″
804.6540	23.5612	A′
860.3853	1.5121	A″
887.4626	6.4402	A′
939.1879	15.1278	A′
1044.0301	21.1842	A′
1126.0918	3.6914	A′
1190.4175	18.6569	A′
1211.3437	11.6238	A′
1330.1588	6.3714	A′
1415.8119	1.4542	A′
1447.0539	2.5990	A′
1547.3601	8.8295	A′
3262.1185	2.8009	A′
3278.3058	2.5990	A′
3299.5668	8.8295	A′
3304.6283	2.8009	A′

Table S.121 B3LYP/6-31G* (unscaled) Computed Vibrational Frequencies and Intensities

(*s*-*E*)-2-furyl carbene (singlet) (22)

Frequency (cm^{-1})	Intensity (Km/mol)	Symmetry
209.4108	6.2055	A″
402.5419	6.7976	A′
496.8343	51.2663	A″
644.2936	0.0951	A″
706.7343	3.7559	A′
778.3044	7.6397	A″
793.6735	17.4552	A′
802.3143	40.1115	A″
894.9587	13.8230	A′
914.1238	0.4505	A″
935.6967	0.7982	A″
1019.4621	22.3307	A′
1076.4437	49.0444	A′
1137.2593	3.0767	A′
1194.1875	22.5314	A′
1238.0298	15.6712	A′
1360.0333	15.9717	A′
1450.6927	162.8699	A′
1485.9295	4.5141	A′
1598.0842	43.3995	A′
2994.8455	91.9093	A′
3257.6721	0.3398	A′
3265.6963	1.6596	A′
3281.4441	1.6777	A′

Table S.122 B3LYP/6-31G* (unscaled) Computed Vibrational Frequencies and Intensities

(*s*-*Z*)-3-furyl carbene (triplet) (23)

Frequency (cm^{-1})	Intensity (Km/mol)	Symmetry
272.4610	4.3693	A″
337.7293	5.9415	A′
428.6168	29.5463	A″
577.5824	11.6350	A″
613.5692	10.3667	A″
663.6617	5.3279	A″
692.2183	1.8025	A′
764.5913	48.8508	A″
852.9238	1.5578	A″
853.5562	1.5297	A′
878.4461	27.8103	A′
992.7920	6.4094	A′
1055.5830	28.0826	A′
1111.6178	12.5731	A′
1207.0684	39.4959	A′
1250.5499	4.7002	A′
1339.9183	0.9642	A′
1356.7244	9.3020	A′
1483.8085	8.5754	A′
1591.4407	9.0902	A′
3269.0373	2.7983	A′
3275.7900	0.5302	A′
3300.3820	1.7569	A′
3304.8487	0.4371	A′

Table S.123 B3LYP/6-31G* (unscaled) Computed Vibrational Frequencies and Intensities

(*s-Z*)-3-furyl carbene (singlet) (23)

Frequency (cm^{-1})	Intensity (Km/mol)	Symmetry
171.9752	19.9192	A″
355.8628	15.8110	A′
462.3785	48.0999	A″
642.0724	10.6500	A″
681.1990	1.5497	A″
687.9483	5.3648	A′
761.1125	23.9133	A″
866.6188	17.7558	A′
868.2995	17.8963	A″
897.9915	6.7453	A″
985.2046	8.2998	A′
999.9655	6.3014	A′
1105.9919	4.0279	A′
1124.7083	24.1882	A′
1199.7729	145.7700	A′
1271.9939	0.7536	A′
1367.9329	5.7886	A′
1401.9734	5.1642	A′
1524.3782	138.0744	A′
1589.3271	2.3966	A′
2913.6583	133.8775	A′
3278.5076	0.6044	A′
3282.6166	0.8365	A′
3315.4997	0.5115	A′

Table S.124 B3LYP/6-31G* (unscaled) Computed Vibrational Frequencies and Intensities

(*s*-*E*)-3-furyl carbene (triplet) (23)

Frequency (cm^{-1})	Intensity (Km/mol)	Symmetry
278.8254	0.2919	A″
336.6509	0.4229	A′
380.9679	28.9464	A″
580.9075	12.7767	A″
610.5475	5.9562	A″
671.8706	5.3637	A″
696.3092	1.8621	A′
759.0373	55.4163	A″
844.8439	1.2696	A″
857.3213	33.9331	A′
879.4840	7.3233	A′
980.7396	1.1579	A′
1056.6246	30.5447	A′
1113.0200	11.8473	A′
1210.5773	29.6645	A′
1252.1322	8.5963	A′
1336.1129	5.8893	A′
1353.8050	5.8103	A′
1496.0955	12.7749	A′
1589.6684	8.2298	A′
3272.2165	2.8297	A′
3274.4279	1.3287	A′
3299.7735	2.1918	A′
3306.5650	0.0119	A′

Table S.125 B3LYP/6-31G* (unscaled) Computed Vibrational Frequencies and Intensities

(*s*-*E*)-3-furyl carbene (singlet) (23)

Frequency (cm^{-1})	Intensity (Km/mol)	Symmetry
207.1103	0.0147	A″
350.2188	7.5088	A′
476.9788	15.3098	A″
639.2899	14.4615	A″
688.6728	4.8387	A′
699.7608	29.0011	A″
760.8670	50.3192	A″
865.0109	19.5512	A′
880.1838	0.0068	A″
890.7635	12.9683	A″
982.6692	9.3569	A′
999.5582	9.2558	A′
1095.9764	10.0679	A′
1127.7180	5.8386	A′
1199.2723	123.0707	A′
1260.3807	2.9913	A′
1371.5866	7.2094	A′
1389.6145	5.1084	A′
1538.0856	149.5905	A′
1592.0706	3.8642	A′
2934.5228	125.0698	A′
3271.6684	0.3513	A′
3295.1556	0.9949	A′
3308.2299	1.3775	A′

Table S.126 B3LYP/6-31G* (unscaled) Computed Vibrational Frequencies and Intensities

2-oxabicyclo[3.1.0]hexa-3,5-diene (24)

Frequency (cm^{-1})	Intensity (Km/mol)	Symmetry
318.2112	8.1687	A
412.5504	7.5841	A
531.5536	14.5501	A
660.5663	38.7793	A
691.0475	34.8198	A
755.1214	1.2951	A
773.5956	91.3513	A
822.6357	43.0682	A
837.7598	4.3420	A
893.8253	4.5480	A
989.5356	5.0603	A
999.8441	4.9892	A
1066.0503	2.8851	A
1083.4689	27.9670	A
1147.0900	3.4644	A
1197.0171	29.0645	A
1310.6128	7.5832	A
1373.3564	3.5091	A
1561.0755	53.2297	A
1738.5660	36.8913	A
3155.7085	40.2948	A
3245.6127	1.7165	A
3255.8748	1.7620	A
3283.3830	5.0194	A

Table S.127 B3LYP/6-31G* (unscaled) Computed Vibrational Frequencies and Intensities

4-oxabicyclo[3.1.0]hexa-2,5-diene (25)

Frequency (cm^{-1})	Intensity (Km/mol)	Symmetry
299.9406	5.8598	A
351.0738	62.0938	A
537.1570	9.1042	A
635.4606	39.2655	A
747.7441	27.3076	A
770.9878	24.4220	A
802.5328	18.4349	A
848.7503	12.2183	A
882.1933	18.0170	A
928.0299	36.5749	A
975.3585	14.4543	A
1000.4389	42.6129	A
1025.3728	17.6140	A
1036.9804	5.9799	A
1160.3671	13.7365	A
1178.9378	7.0788	A
1295.1351	6.3230	A
1349.7956	5.2435	A
1595.7989	24.1955	A
1742.6551	93.0955	A
3136.1499	38.1804	A
3244.2705	4.8265	A
3247.1434	1.8845	A
3285.4659	2.5205	A

Table S.128 B3LYP/6-31G* (unscaled) Computed Vibrational Frequencies and Intensities

(*s*-*Z*)-penta-2,3,4-trienal (26)

Frequency (cm^{-1})	Intensity (Km/mol)	Symmetry
101.5660	4.0447	A′
152.0528	10.3354	A″
267.2152	0.0931	A″
279.2958	2.9970	A′
412.1453	2.8860	A′
453.5928	1.4142	A″
643.0065	1.5682	A″
733.7557	53.3868	A′
847.0247	15.5231	A″
874.3865	3.0627	A′
910.0444	43.8710	A″
1023.1604	3.7007	A″
1043.9750	1043.9750	A′
1046.7968	1046.7968	A′
1043.9750	1329.7361	A′
1440.7792	16.8161	A′
1473.3356	17.2048	A′
1680.6887	116.8208	A′
1790.0970	134.8376	A′
2211.4510	46.0476	A′
2926.1892	220.6286	A′
3149.3387	1.1020	A′
3158.7282	9.9606	A′
3225.8452	1.8487	A′

Table S.129 B3LYP/6-31G* (unscaled) Computed Vibrational Frequencies and Intensities

(*s*-*E*)-penta-2,3,4-trienal (26)

Frequency (cm^{-1})	Intensity (Km/mol)	Symmetry
109.7651	0.4984	A′
119.2197	4.0026	A″
269.8093	6.3067	A″
308.5272	9.4261	A′
452.3181	26.6358	A′
495.4880	2.8964	A″
517.4076	0.4497	A′
623.2963	0.1494	A″
873.9906	19.6719	A″
904.5470	45.4524	A″
959.3689	1.1824	A′
1015.6132	1.6290	A″
1044.7972	0.7771	A′
1119.6195	141.5806	A′
1279.2943	0.1343	A′
1421.3334	2.2438	A′
1474.3456	1.9843	A′
1687.2202	30.5462	A′
1779.8731	330.7272	A′
2209.3391	23.8023	A′
2942.5095	88.1665	A′
3149.9669	0.9912	A′
3177.3620	1.7024	A′
3225.9991	1.7521	A′

Table S.130 B3LYP/6-31G* (unscaled) Computed Vibrational Frequencies and Intensities

(*s*-*E*)-pent-1-en-4-yn-3-one (27)

Frequency (cm^{-1})	Intensity (Km/mol)	Symmetry
94.1312	0.4532	A″
151.9578	2.9999	A′
263.4129	0.4532	A″
299.4949	6.0858	A′
510.1140	0.5265	A′
519.8281	6.0858	A″
594.4999	4.0105	A′
623.6813	48.7276	A′
670.0306	27.9763	A″
783.3988	2.0461	A′
813.5353	30.6722	A″
1000.2521	12.9588	A″
1028.5886	27.6403	A″
1087.7786	3.3913	A′
1137.1371	248.9918	A′
1332.6184	3.0883	A′
1449.9833	69.1188	A′
1683.3864	84.3484	A′
1751.9426	104.2145	A′
2212.9267	78.7533	A′
3175.8091	5.3028	A′
3198.0060	6.5413	A′
3267.2070	2.8284	A′
3487.8040	44.4006	A′

Table S.131 B3LYP/6-31G* (unscaled) Computed Vibrational Frequencies and Intensities

1-ethynyl-3-oxacyclobutene (28)

Frequency (cm^{-1})	Intensity (Km/mol)	Symmetry
184.2333	0.3917	A'
186.8109	0.2472	A"
434.1234	26.8476	A"
493.9701	56.7157	A"
528.9462	6.9423	A'
537.4421	3.0110	A"
625.3355	0.5693	A'
647.3739	41.4139	A'
869.4109	9.3420	A"
891.8286	33.1472	A'
979.6936	53.9326	A'
1017.5406	5.7056	A"
1076.7982	115.8402	A'
1117.8398	3.7344	A"
1202.5518	6.3455	A'
1250.2253	14.4330	A'
1340.0727	48.5890	A'
1512.6511	0.1523	A'
1677.2678	27.3533	A'
2221.8396	16.7904	A'
3097.6750	24.8261	A'
3162.9272	16.2266	A"
3252.4264	6.2511	A'
3496.5332	84.7839	A'

Table S.132 B3LYP/6-31G* (unscaled) Computed Vibrational Frequencies and Intensities

4-ethynyl-3-oxacyclobutene (29)

Frequency (cm^{-1})	Intensity (Km/mol)	Symmetry
170.0676	3.0628	A
189.3397	2.6957	A
383.8833	4.5503	A
503.5885	6.4126	A
577.3276	10.3432	A
604.6351	46.5555	A
658.4244	36.5690	A
679.0304	39.4659	A
658.4244	45.8372	A
884.9699	6.8463	A
914.0398	37.4121	A
948.7142	3.6463	A
1040.9180	80.3903	A
1062.5058	20.0064	A
1172.1779	12.6956	A
1186.6629	5.9555	A
1306.2888	15.0250	A
1354.0428	28.5289	A
1647.2004	19.4152	A
2242.1288	3.3973	A
3088.3746	14.8574	A
3246.7948	10.6404	A
3314.0969	2.3386	A
3494.6787	57.2626	A

Table S.133 B3LYP/6-31G* (unscaled) Computed Vibrational Frequencies and Intensities

allenyl ethynyl ether (30)

Frequency (cm^{-1})	Intensity (Km/mol)	Symmetry
36.5970	0.1494	A″
130.9412	0.3866	A′
242.0982	0.2275	A″
309.8126	5.1223	A″
397.7315	25.2113	A″
517.0980	33.7940	A″
538.4420	3.2387	A′
560.9143	0.8834	A′
610.6236	0.0018	A″
634.2227	46.9326	A′
862.4654	16.8975	A″
927.5205	37.4873	A′
980.3638	90.2571	A′
1041.9412	0.1511	A″
1125.4529	66.8376	A′
1217.4502	267.3235	A′
1387.2070	97.7180	A′
1512.1191	41.1860	A′
2092.1397	47.7512	A′
2293.0356	253.9879	A′
3134.4451	13.2419	A′
3202.8869	4.3770	A″
3214.3815	6.4472	A′
3514.3095	123.6772	A′

Table S.134 B3LYP/6-31G* (unscaled) Computed Vibrational Frequencies and Intensities

ethynyl prop-2-ynyl ether (31)

Frequency (cm^{-1})	Intensity (Km/mol)	Symmetry
52.0705	0.2909	A″
127.6538	0.1612	A′
228.8140	1.9224	A′
332.2239	4.7107	A″
404.0525	29.9391	A″
497.3133	1.3522	A′
524.7495	26.9599	A″
539.4418	2.5877	A′
602.6135	51.3744	A″
628.5964	45.5111	A′
675.0857	38.6300	A′
937.6435	71.1976	A′
995.7516	16.3934	A′
1028.3151	1.9013	A″
1142.0233	224.5609	A′
1257.5950	2.1650	A″
1412.8869	83.9140	A′
1519.6080	1.8956	A′
2254.9936	19.8844	A′
2286.1976	152.7229	A′
3048.8314	16.5231	A′
3089.7796	15.0399	A″
3493.6885	58.0406	A′
3514.6172	98.2137	A′

Table S.135 B3LYP/6-31G* (unscaled) Computed Vibrational Frequencies and Intensities

ethynyl prop-1-ynyl ether (32)

Frequency (cm^{-1})	Intensity (Km/mol)	Symmetry
14.3132	0.1437	A
94.0539	1.1198	A
225.0077	1.9727	A
261.3240	2.2709	A
370.5199	0.3663	A
380.7692	2.9104	A
389.3649	9.6729	A
537.6380	40.7245	A
541.6252	0.1312	A
623.4015	47.5236	A
755.0028	4.7988	A
1039.9591	39.7180	A
1072.7128	4.0198	A
1075.2056	2.5737	A
1298.6292	204.7286	A
1448.7811	0.2789	A
1507.9484	6.4400	A
1511.3199	5.9081	A
2300.3913	205.0706	A
2429.8571	101.1048	A
3044.2991	28.8322	A
3105.6670	12.3432	A
3108.3546	10.9109	A
3512.3237	113.1782	A

Table S.136 B3LYP/6-31G* (unscaled) Computed Vibrational Frequencies and Intensities

3-cyclopropenyl ethynyl ether (33)

Frequency (cm^{-1})	Intensity (Km/mol)	Symmetry
33.8054	1.1429	A″
146.6279	1.3364	A′
389.4523	27.9199	A″
393.6370	7.3393	A′
427.5257	12.6923	A″
521.8962	19.1276	A″
585.8935	30.7133	A′
616.3897	27.4467	A′
723.7522	16.5804	A′
810.3721	177.6873	A′
880.0576	13.8749	A″
897.0395	1.9057	A″
944.6464	4.4094	A′
1063.3535	0.2187	A″
1095.1086	31.1132	A″
1118.5769	215.4399	A′
1230.9305	63.6170	A′
1395.3817	13.0893	A′
1711.6367	1711.6367	A′
2277.6945	2277.6945	A′
3176.1842	3176.1842	A′
3271.4572	3271.4572	A″
3312.7290	3312.7290	A′
3515.7186	3515.7186	A′

Table S.137 B3LYP/6-31G* (unscaled) Computed Vibrational Frequencies and Intensities

(3-thienyl)diazirine (34)

Frequency (cm^{-1})	Intensity (Km/mol)	Symmetry
70.8257	2.0157	A
173.4147	1.1082	A
181.2356	3.2427	A
381.381	0.4702	A
413.1713	0.3488	A
473.4441	0.1013	A
623.9542	2.8911	A
661.7858	15.8855	A
683.6524	0.461	A
700.8897	6.8471	A
788.2523	70.0383	A
829.524	6.1809	A
838.2792	0.1285	A
864.8269	19.275	A
895.9402	0.1544	A
940.0085	0.1459	A
1022.516	15.4933	A
1076.968	18.3512	A
1124.423	4.3806	A
1209.302	2.0435	A
1283.128	10.583	A
1374.061	1.2808	A
1442.942	0.7098	A
1478.471	6.0957	A
1598.544	4.1818	A
1725.593	80.793	A
3196.93	16.1864	A
3235.217	0.7262	A
3265.97	0.8283	A
3274.022	0.4813	A

Table S.138 B3LYP/6-31G* (unscaled) Computed Vibrational Frequencies and Intensities

6a*H*-thieno[2,3-c]pyrazole (35)

Frequency (cm^{-1})	Intensity (Km/mol)	Symmetry
172.4527	1.0932	A
222.3073	1.6106	A
330.3839	2.6176	A
477.2338	1.3077	A
498.2226	0.6028	A
587.6961	2.979	A
629.0628	15.6564	A
698.3896	12.5787	A
730.051	42.1873	A
773.8213	14.166	A
804.9231	8.8745	A
850.5765	35.1725	A
914.8893	7.0608	A
920.583	7.1356	A
972.0091	1.2647	A
993.3452	5.765	A
999.0702	6.4864	A
1121.427	2.074	A
1150.675	6.4007	A
1178.019	20.8616	A
1244.983	12.2076	A
1308.828	9.5803	A
1343.425	2.2514	A
1453.294	59.7512	A
1559.038	22.982	A
1646.576	23.4173	A
3034.022	5.1725	A
3228.1	0.458	A
3245.878	3.5153	A
3274.762	2.6236	A

Table S.139 B3LYP/6-31G* (unscaled) Computed Vibrational Frequencies and Intensities

3*H*-thieno[2,3-c]pyrazole (36)

Frequency (cm^{-1})	Intensity (Km/mol)	Symmetry
203.727	0.3664	A
236.4425	7.9875	A
373.796	1.6715	A
430.1503	1.0184	A
505.8612	1.2369	A
559.9985	0.0299	A
582.2192	1.4836	A
652.6558	11.4461	A
730.0153	33.9826	A
733.6763	6.0987	A
837.0326	5.7712	A
844.1791	10.9835	A
882.9476	2.3892	A
922.1495	0.9051	A
959.2657	37.1501	A
1040.288	9.2716	A
1132.493	5.4277	A
1141.856	2.9477	A
1211.301	29.5041	A
1225.872	11.8924	A
1289.437	9.9906	A
1413.415	34.6129	A
1435.716	20.0318	A
1482.73	21.4653	A
1513.77	11.6983	A
1561.656	1.8531	A
3066.772	1.8386	A
3103.614	1.6844	A
3231.525	4.0116	A
3263.655	1.0492	A

Table S.140 B3LYP/6-31G* (unscaled) Computed Vibrational Frequencies and Intensities

1*H*-thieno[2,3-c]pyrazole (37)

Frequency (cm^{-1})	Intensity (Km/mol)	Symmetry
209.7183	0.0031	A″
262.0235	0.0043	A″
385.3046	67.9332	A′
392.8737	2.549	A′
498.819	13.134	A″
549.4503	0.0112	A″
592.8861	0.1352	A′
638.8059	0.6337	A″
676.1856	60.4756	A″
730.2446	10.0355	A′
742.5057	13.6368	A″
835.3389	17.2918	A′
860.7895	14.0636	A″
887.0491	5.7503	A′
965.1463	40.8967	A″
1072.243	3.5198	A′
1088.52	11.4095	A″
1138.42	5.6422	A′
1240.569	3.057	A′
1307.396	2.5175	A′
1315.562	0.052	A′
1411.764	23.3756	A′
1443.583	12.3056	A′
1498.762	16.1824	A′
1563.856	14.0227	A′
1583.467	23.4015	A′
3231.229	3.9703	A′
3264.277	6.5793	A′
3268.801	1.7548	A′
3679.895	81.8305	A′