SUPPORTING INFORMATION

Ultrafast UV-Vis and Infrared Spectroscopic Observation of a Singlet Vinylcarbene and the Intramolecular Cyclopropenation Reaction

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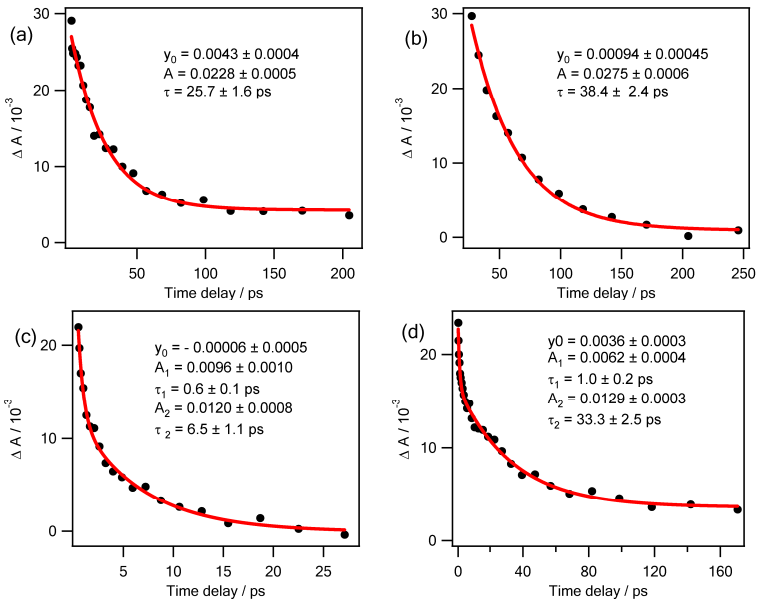
Ultrafast IR pump-probe absorption measurements were performed using the home-built spectrometer at the Ohio State University. Solution concentrations were adjusted to absorption of unity in a 1 mm cell. Sample solutions were excited in a stainless steel flow cell equipped with 2 mm thick BaF_2 windows. After passing the sample reference and probe beam were spectrally dispersed with a polychromator and independently imaged on a liquid-nitrogen cooled HgCdTe detector (2 x 32 pixels). The pump pulse energy was about 4 μJ at the sample position. The entire set of pump-probe delay positions (cycle) is repeated at least three times, to observe data reproducibility from cycle to cycle. To avoid rotational diffusion effects, the angle between polarizations of the pump beam and the probe beam was set to the magic angle (54.7°). Kinetic traces are analyzed by fitting to a sum of exponential terms. All experiments were performed at room temperature.

Ground state geometry optimizations were carried out using Becke's three-parameter hybrid exchange functional with the Lee-Yang-Parr correlation functional (B3LYP) [1-4] as implemented in Gaussian 03.[5] Vibrational frequency analyses were performed to verify that the stationary points obtained corresponded to energy minima. Frequencies were scaled by 0.9614.[6] The absolute energies of optimized structures are in Hartrees. The electronic spectra were computed using Time-Dependent B3LYP (TD-B3LYP) methodology with *Gaussian 03* at the B3LYP/6-311+G(d,p)//B3LYP/6-31G(d) level. All calculations were performed at The Ohio Supercomputer Center.



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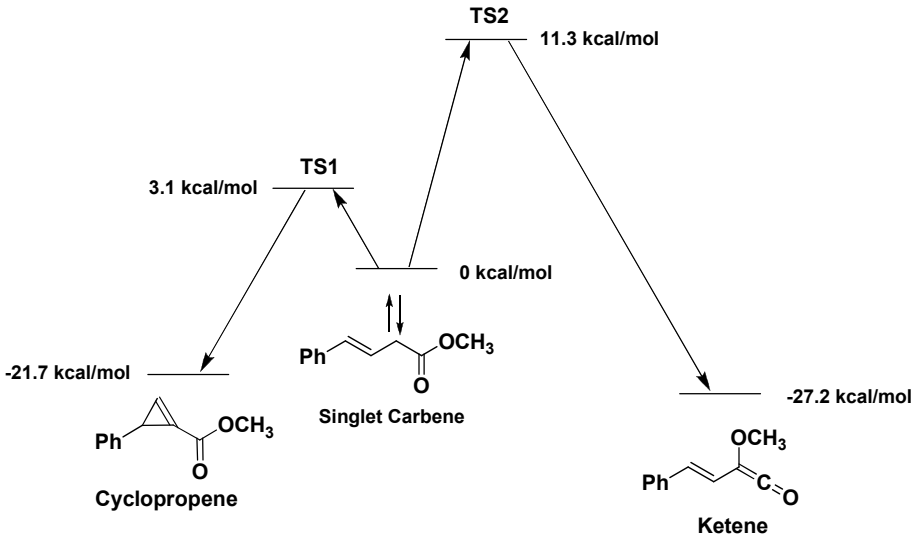

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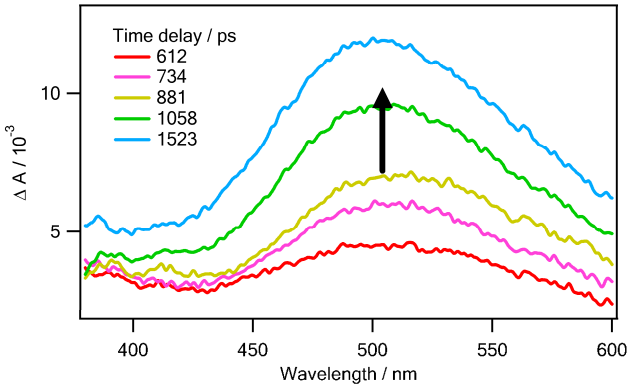


Figure S3. Ultrafast UV-Vis Spectroscopic Studies on bleached $PhCHCHCN_2CO_2CH_3$ solution in acetonitrile.
A bleached solution of $PhCHCHCN_2CO_2CH_3$ in acetonitrile (A = 1.0 at 310 nm in 1mm cuvetee) was prepared by photolysis with 308 nm laser pulses for a few minutes until the absorbance at 310 nm decreased to 0.1. Ultrafast UV-vis spectroscopy studies was carried out on this bleached solution under the same condition of fresh solutions.

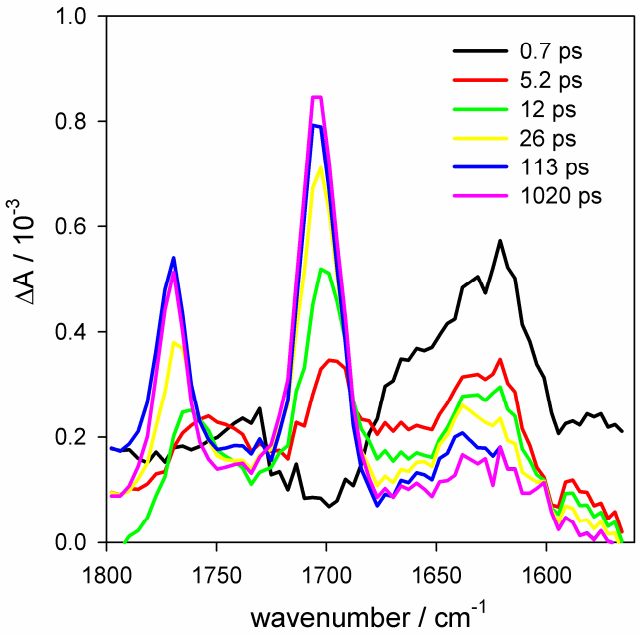
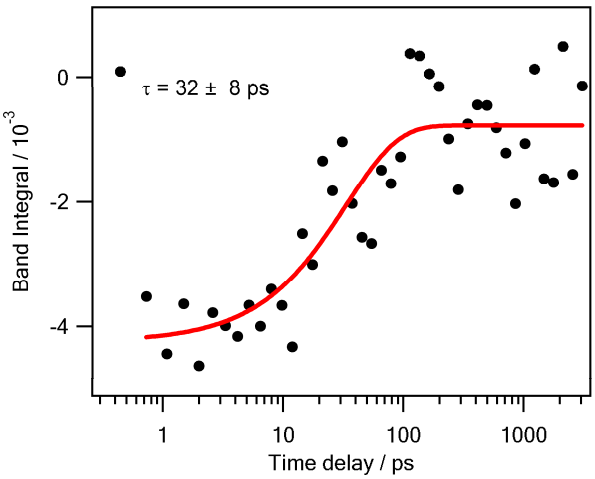


Figure S4. Transient spectra produced by ultrafast photolysis (270 nm) of $PhCH{=}CHCN_2CO_2CH_3$ in chloroform. Transient spectra at selected time delays after subtracting the bleaching band of precursor.



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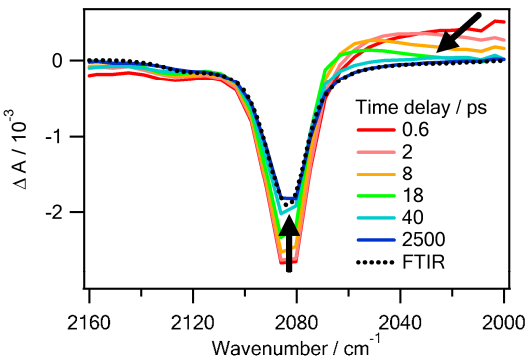


Figure S6. Transient spectra produced upon 270 nm photolysis of $PhCH{=}CHCN_2CO_2CH_3$ in chloroform. The dotted curve is the FTIR spectra of $PhCH{=}CHCN_2CO_2CH_3$.

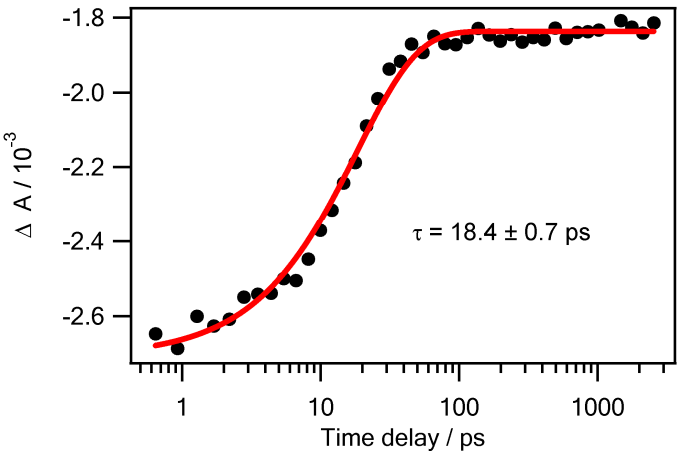


Figure S7. Transient spectra produced by ultrafast photolysis (270 nm) of $PhCH{=}CHCN_2CO_2CH_3$ in chloroform. The kinetic traces of the diazo stretching band 2095 cm^{-1} (peak of the negative band) by fitting into an exponential function.

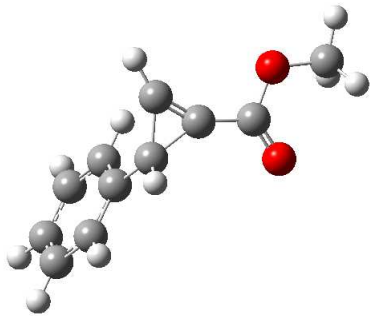
Table S1. TD B3LYP/6-311+G(d,p) // B3LYP/6-31G calculations (vertical transition and oscillator strength *f*) on the singlet carbene ^{1}PhCH=CHCCO$_2$CH$_3$ (^{1}2), triplet carbene ^{3}PhCH=CHCCO$_2$CH$_3$ (^{3}2), and the cyclopropene product (3).

singlet carbene (^{1}2)		triplet carbene (^{1}2)		cyclopropene (3)	
λ / nm	*f*	λ / nm	*f*	λ / nm	*f*
899.74	0.0416	457.34	0.0001	327.28	0.0251
377.56	0.1220	391.7	0.0028	281.64	0.0064
337.64	0.0057	359.5	0.0009	267.6	0.0014
327.64	0.0186	358.7	0.0002	239.14	0.0171
317.48	0.0008	341.77	0.5761	236.36	0.1987
310.29	0.4164	318.8	0.1518	217.84	0.1262
297.34	0.2051	313.69	0.0183	209.17	0.0002
247.97	0.0075	305.83	0.0001	207.74	0.0003
239.37	0.0119	301.35	0.0598	199.62	0.0434
235.41	0.0126	292.66	0	199.1	0.0011
232.78	0.0101	290.44	0.0111	198.27	0.01
228.54	0.0059	282.9	0.0362	196.74	0.004
224.15	0.0147	262.4	0.0003	195.94	0.0093
222.05	0.0188	256.64	0.0409	192.49	0.0154
219.08	0.0195	255.11	0	192.2	0.0585

Table S2. Summary of lifetimes (given in ps) obtained by ultrafast UV-Vis (310 nm) and IR (270 nm) transient absorption on PhCH=CHCN$_2$CO$_2$CH$_3$.

Solvents	Ultrafast UV-Vis Singlet carbene	Ultrafast IR Cyclopropene
ACN	25.7 ± 1.6	
MeOH	38.4 ± 2.4	
CHCl3	33.3 ± 2.5	32 ± 8
Cyclohexane	6.5 ± 1.1	

Table S3. Optimized structure of the cyclopropene (3) at the B3LYP/6-31G(d) level of theory.



Energy = -575.553055878

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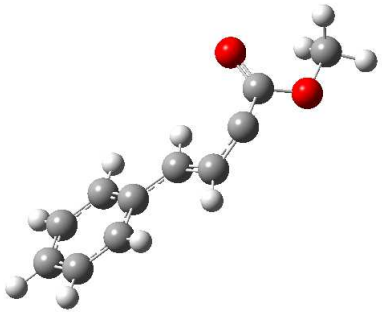
C	-1.514867000	-0.682470000	-0.766484000
C	-2.678035000	-1.450281000	-0.732064000
C	-3.774605000	-1.035270000	0.026939000
H	-4.542312000	0.487731000	1.347607000
H	-2.475358000	1.847711000	1.282966000
H	-0.667230000	-1.017026000	-1.359092000
H	-2.727895000	-2.376626000	-1.298811000
H	-4.680486000	-1.634876000	0.053974000
C	-0.192603000	1.370295000	-0.063032000
C	0.714145000	1.434952000	-1.274091000
H	0.809841000	1.754482000	-2.302065000
C	1.190113000	0.795064000	-0.248006000
C	2.251932000	-0.000900000	0.376650000
O	2.200182000	-0.466315000	1.495146000
O	3.304739000	-0.139552000	-0.460948000
C	4.405014000	-0.896859000	0.070213000
H	5.156283000	-0.911390000	-0.719716000
H	4.801507000	-0.419003000	0.970216000
H	4.087506000	-1.913073000	0.319036000
H	-0.291381000	2.272474000	0.547632000

Frequency (cm^{-1})	IR intensity (km/mol)	Frequency (cm^{-1})	IR intensity (km/mol)	Frequency (cm^{-1})	IR intensity (km/mol)
26	0.8	784	11.1	1317	0.5
31	0.6	795	11.9	1360	0.6
47	0.3	828	0.0	1433	6.8
122	2.0	871	17.9	1447	7.9
136	1.4	892	0.2	1454	6.2
144	2.2	929	0.0	1465	10.0
168	0.8	949	2.9	1487	12.4
232	1.9	955	0.1	1581	1.0
286	11.3	977	0.8	1601	8.4
324	11.4	1012	19.8	1723	176.5
354	1.2	1020	9.8	1776	187.4
402	0.0	1033	12.3	2956	34.1
453	2.1	1070	5.8	2967	38.1
529	5.9	1119	124.7	3027	19.8
552	1.8	1137	1.0	3051	8.7
598	2.5	1146	0.3	3057	0.6
612	0.5	1167	1.2	3061	17.8
677	59.7	1171	2.0	3067	11.0
687	20.1	1197	254.1	3074	42.3
746	17.2	1237	272.3	3085	24.5
768	4.2	1275	3.4	3161	0.4

Table S4. Optimized structure of the singlet carbene ^{1}PhCH=CHCCO$_2$CH$_3$ (^{1}2) at the B3LYP/6-31G(d) level of theory.



Energy = -575.517499674

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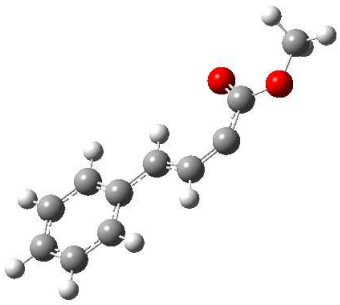
C	-1.614840000	0.000458000	-0.010898000
C	-2.482766000	-1.115359000	-0.004945000
C	-3.859441000	-0.939895000	-0.062643000
C	-4.405989000	0.347675000	-0.114855000
H	-3.985673000	2.464631000	-0.134005000
H	-1.530523000	2.158958000	-0.033668000
H	-2.072837000	-2.117656000	0.064673000
H	-4.513851000	-1.806982000	-0.055437000
H	-5.483827000	0.478832000	-0.152365000
C	-0.173862000	-0.113540000	-0.032539000
H	0.375428000	0.815914000	0.107225000
C	0.573763000	-1.278615000	-0.092174000
H	0.064693000	-2.230868000	-0.253571000
C	1.890616000	-1.294259000	0.354760000
C	2.790557000	-0.176050000	0.343434000
O	2.793514000	0.679508000	1.224208000
O	3.700657000	-0.235608000	-0.660788000
C	4.733860000	0.760556000	-0.606184000
H	5.388685000	0.544557000	-1.451249000
H	4.313745000	1.766254000	-0.698536000
H	5.288456000	0.693695000	0.333818000

Frequency (cm^{-1})	IR intensity (km/mol)	Frequency (cm^{-1})	IR intensity (km/mol)	Frequency (cm^{-1})	IR intensity (km/mol)
38	1.2	819	0.5	1323	10.8
43	3.8	820	54.7	1389	188.9
59	0.1	827	4.6	1431	38.4
95	4.9	876	13.2	1442	47.4
106	0.8	903	8.0	1454	4.5
121	2.9	937	3.2	1469	7.7
149	4.9	954	36.8	1482	3.3
183	3.1	968	6.9	1498	57.9
255	18.5	975	8.4	1565	2.2
299	9.9	996	16.0	1591	12.4
386	20.6	1015	0.1	1641	181.4
398	1.6	1074	4.8	2952	52.5
407	47.5	1135	6.4	3006	16.6
485	81.9	1150	1.2	3021	22.8
505	137.9	1159	427.0	3054	23.3
573	44.0	1167	144.3	3060	3.3
606	0.0	1173	429.9	3066	4.6
614	5.5	1200	152.4	3072	0.2
670	23.7	1263	4.0	3081	13.7
733	43.4	1287	10.6	3090	25.1
748	24.0	1314	77.8	3097	15.1

Table S5. Optimized structure of the triplet carbene ^{3}PhCH=CHCCOCH$_3$ (^{3}2) at the B3LYP/6-31G(d) level of theory.



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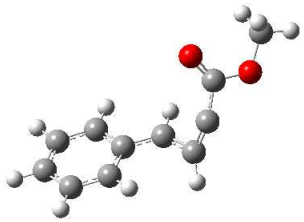
C	2.539338000	-1.138574000	0.000184000
C	3.926116000	-1.061807000	0.000171000
C	4.568705000	0.181992000	0.000008000
H	4.294592000	2.322947000	-0.000285000
H	1.825570000	2.192698000	-0.000278000
H	2.064088000	-2.114832000	0.000289000
H	4.514216000	-1.975699000	0.000276000
H	5.653767000	0.235973000	-0.000006000
C	0.302841000	0.029415000	0.000025000
H	-0.193024000	0.995831000	0.000355000
C	-0.524596000	-1.100491000	-0.000248000
H	-0.060202000	-2.087694000	-0.000470000
C	-1.893990000	-1.079551000	-0.000148000
C	-2.898380000	-0.038510000	0.000028000
O	-2.646659000	1.159936000	0.000278000
O	-4.154059000	-0.537556000	-0.000121000
C	-5.201766000	0.443939000	0.000030000
H	-6.132263000	-0.124437000	-0.000136000
H	-5.138834000	1.076718000	0.889846000
H	-5.138743000	1.077092000	-0.889513000

Frequency (cm^{-1})	IR intensity (km/mol)	Frequency (cm^{-1})	IR intensity (km/mol)	Frequency (cm^{-1})	IR intensity (km/mol)
36	1.8	808	0.3	1318	0.8
41	0.2	826	2.7	1403	146.6
64	0.6	835	0.9	1427	7.3
88	0.3	861	9.7	1446	157.6
127	0.5	877	7.2	1454	5.9
155	3.0	895	28.7	1457	7.4
158	1.1	928	0.3	1466	4.1
220	4.2	956	0.4	1483	13.0
252	0.6	969	0.4	1557	2.1
323	1.0	991	15.6	1579	5.5
324	30.9	1014	0.3	1653	103.8
395	0.0	1070	5.2	2953	43.4
397	2.0	1137	0.8	3018	5.7
486	3.6	1146	1.2	3023	23.2
502	3.0	1157	84.9	3058	23.9
606	0.1	1165	23.7	3060	4.5
613	1.3	1175	19.2	3066	0.3
668	20.9	1200	530.6	3075	11.4
678	5.4	1219	179.4	3083	31.1
708	24.5	1260	149.9	3086	5.2
738	24.0	1302	104.6	3090	22.5

Table S6. Optimized transition state for the formation of cyclopropene from singlet carbene at the B3LYP/6-31G(d) level of theory.



Energy = -575.512797

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C	1.510124000	0.053940000	-0.355106000
C	2.260700000	1.056992000	0.298722000
C	3.585070000	0.829474000	0.653617000
C	4.188087000	-0.402034000	0.376496000
H	3.916827000	-2.373333000	-0.460374000
H	1.556934000	-1.976349000	-1.095924000
H	1.788589000	2.003041000	0.545262000
H	4.149386000	1.608537000	1.158632000
H	5.221572000	-0.577617000	0.661857000
C	0.162494000	0.276744000	-0.819716000
C	-0.568767000	1.491239000	-0.692014000
H	-0.167863000	2.499853000	-0.800726000
C	-1.626921000	1.126509000	0.029511000
C	-2.529383000	0.071926000	0.367895000
O	-2.377964000	-0.734543000	1.274087000
O	-3.658690000	0.151925000	-0.396727000
C	-4.709307000	-0.743771000	-0.006903000
H	-5.543420000	-0.519066000	-0.673116000
H	-4.398282000	-1.785912000	-0.124241000
H	-4.996415000	-0.578030000	1.035426000
H	-0.368045000	-0.586381000	-1.209680000

Frequency (cm^{-1})	IR intensity (km/mol)	Frequency (cm^{-1})	IR intensity (km/mol)	Frequency (cm^{-1})	IR intensity (km/mol)
-123	40.1	818	9.0	1374	3.1
42	2.2	833	23.7	1454	28.9
53	1.4	852	39.9	1487	7.0
76	7.4	855	8.6	1511	12.4
109	2.3	884	21.4	1511	2.3
124	0.4	932	3.5	1527	14.5
140	4.7	972	0.0	1540	1.9
151	0.8	1002	0.0	1626	1.1
240	2.8	1013	1.0	1651	0.2
312	11.3	1038	13.2	1687	109.7
396	9.1	1054	0.4	1757	435.3
415	0.1	1116	2.6	3069	55.7
430	26.2	1181	9.4	3131	32.0
549	22.8	1193	321.7	3140	22.7
559	93.4	1195	16.2	3174	25.4
567	0.7	1207	568.1	3186	2.9
631	1.8	1213	57.6	3192	0.1
631	3.4	1220	268.4	3202	11.6
699	17.9	1275	5.3	3209	15.3
710	57.1	1296	109.1	3211	24.9
769	24.5	1358	23.8	3218	15.5

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