Supporting Informations

Generation and Reactivity of the Vinyl Telluryl Radical

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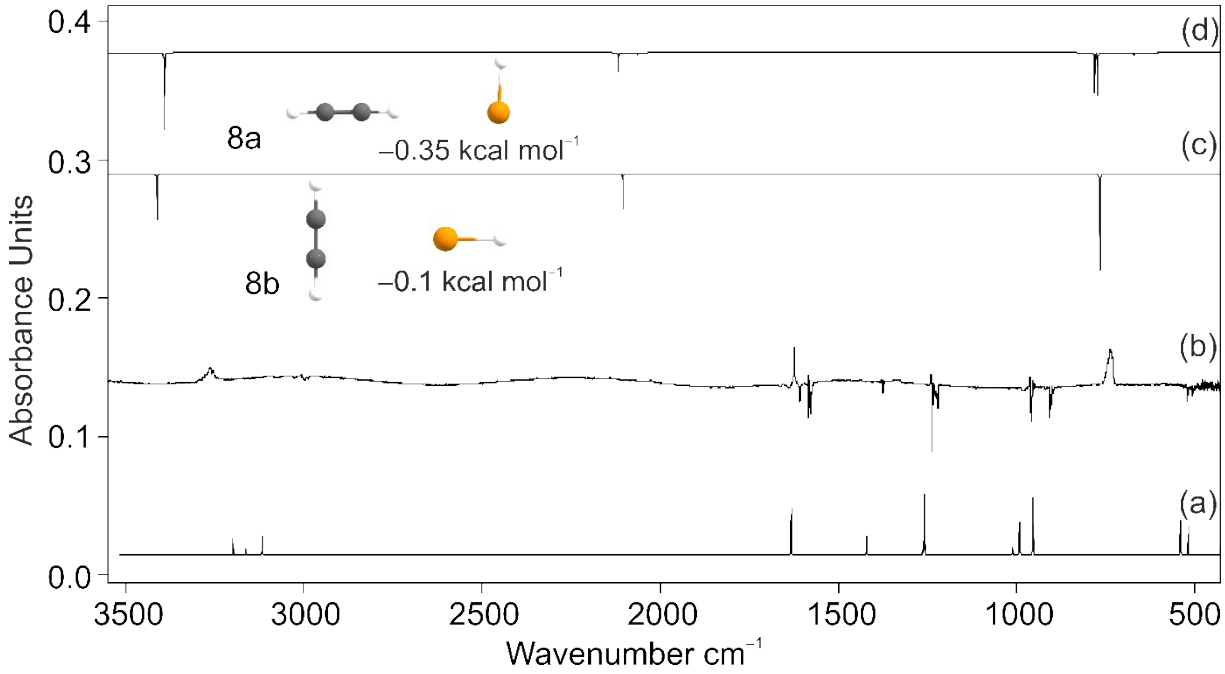


Figure S1. IR spectra showing the photochemistry of **6**. (a) IR spectrum of **5** computed at UB3LYP/def2-QZVPP (unscaled). (b) IR difference spectra showing the photochemistry of **5** after irradiation with λ = 365 nm in argon at 10 K. Downward bands assigned to **6** disappear while upward bands assigned to **8** appear after 15 min irradiation time. (c) IR spectrum of **8a** computed at UB3LYP/def2-QZVPP (unscaled). (d) IR spectrum of **8b** computed at UB3LYP/def2-QZVPP (unscaled).

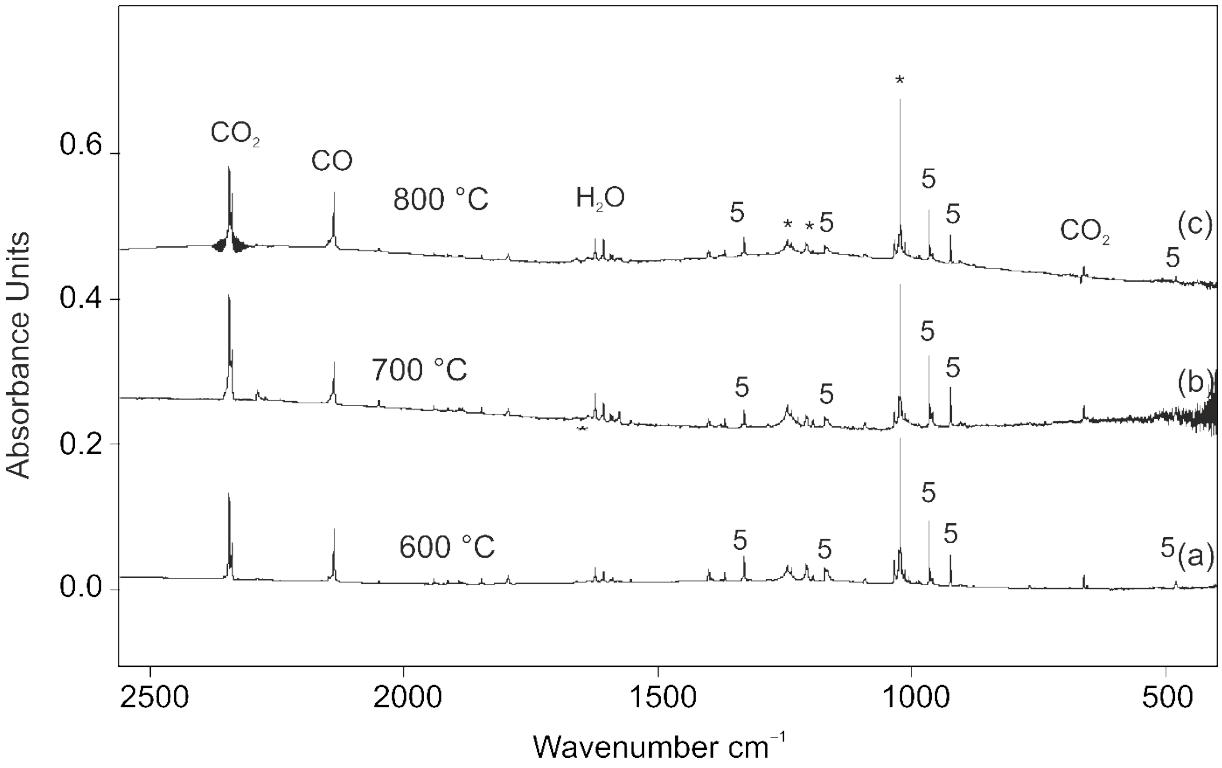


Figure S2. IR spectrum of a matrix containing the FVP products of **6** at different temperatures Bands due to unassigned products are marked (*).

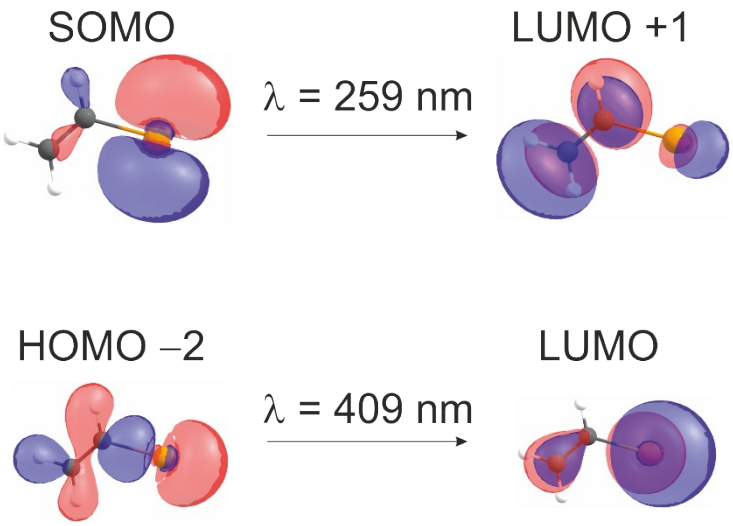


Figure S3. UV/Vis transitions of **5**.

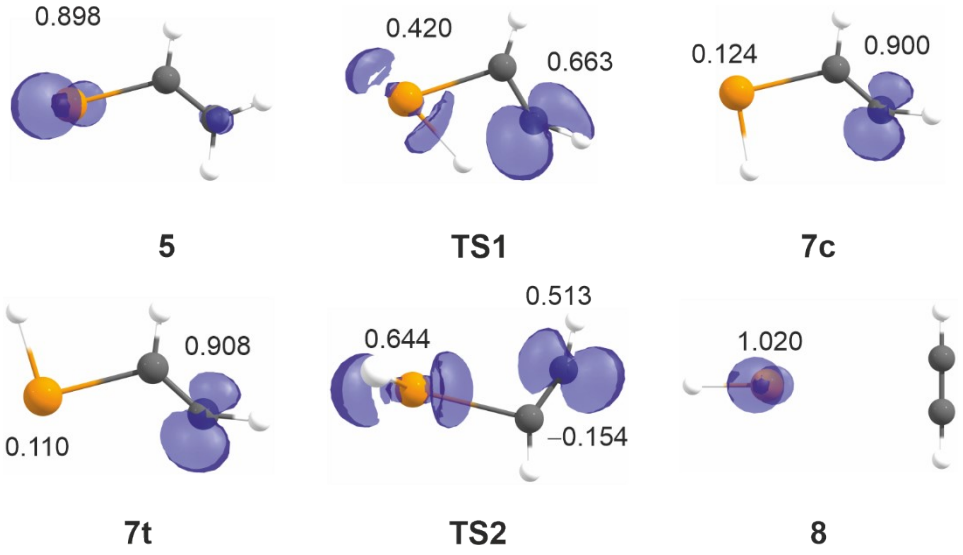


Figure S4. Computed spin densities of radicals at UB3LYP/def2-QZVPP level of theory.

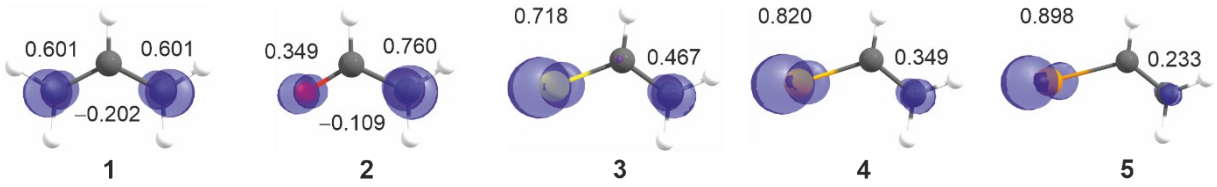


Figure S5. Computed spin densities of vinyl radicals **1** – **5** at UB3LYP/def2QZVPP level of theory.

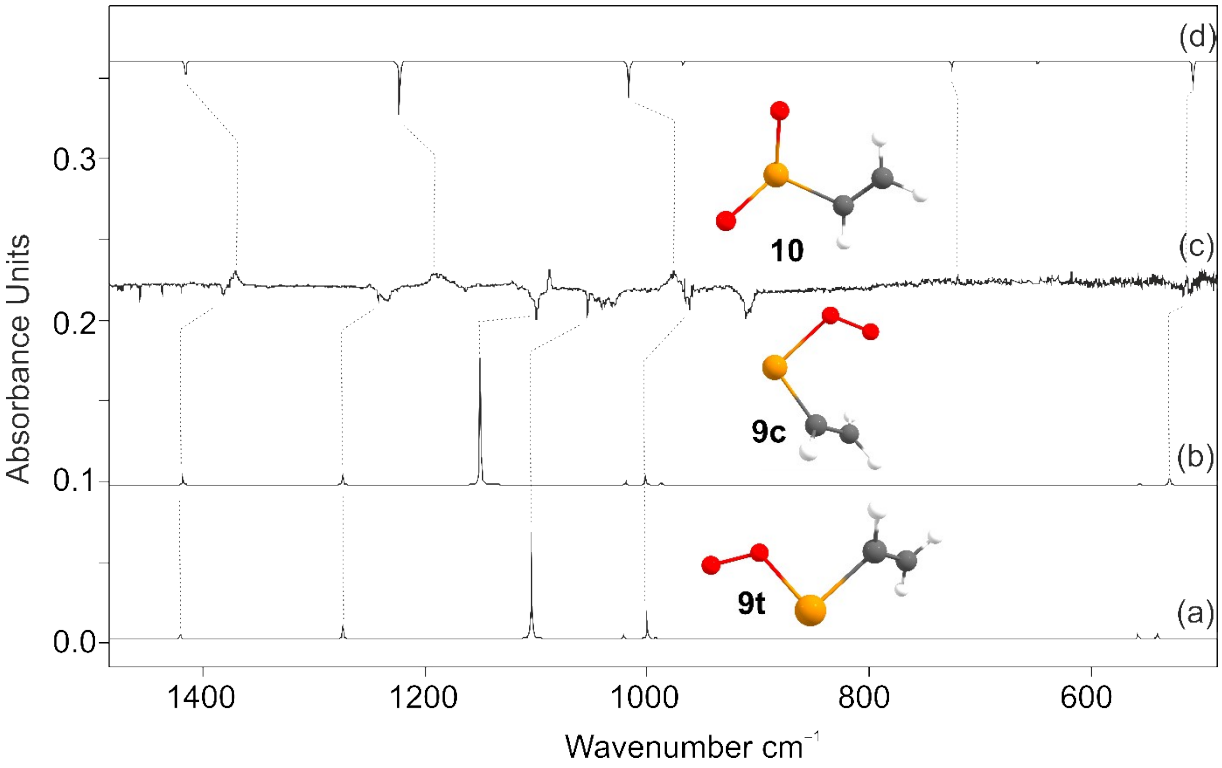


Figure S6. (a) IR spectrum of $^{18}O_2$-**9t** computed at UB3LYP/def2-QZVPP (unscaled). b) IR spectrum of $^{18}O_2$-**9c** computed at UB3LYP/def2-QZVPP (unscaled). (c) IR difference spectra showing the photochemistry of $^{18}O_2$-**9c** and $^{18}O_2$-**9t** after irradiation at λ = 523 nm in argon at 10 K. Downward bands assigned to $^{18}O_2$-**9c** and $^{18}O_2$-**9t** disappear while upward bands assigned to $^{18}O_2$-**10** appear after 5 min of irradiation time. (d) IR spectrum of $^{18}O_2$-**10** computed at UB3LYP/def2-QZVPP (unscaled).

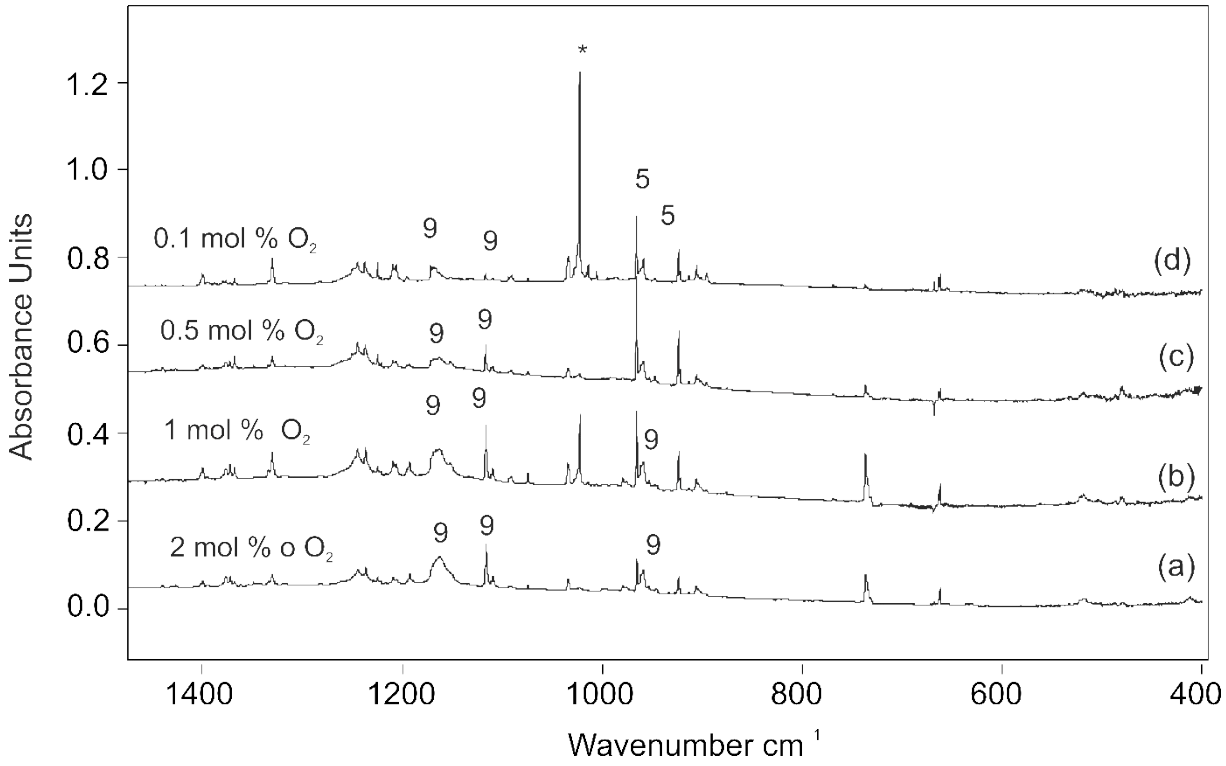


Figure S7. IR spectrum of a matrix containing the FVP products of 6 in the presence of different concertation of O_2. (a) 2 mol %. (b) 1 mol %. (c) 0.5 mol %. (d) 0.1 mol %.

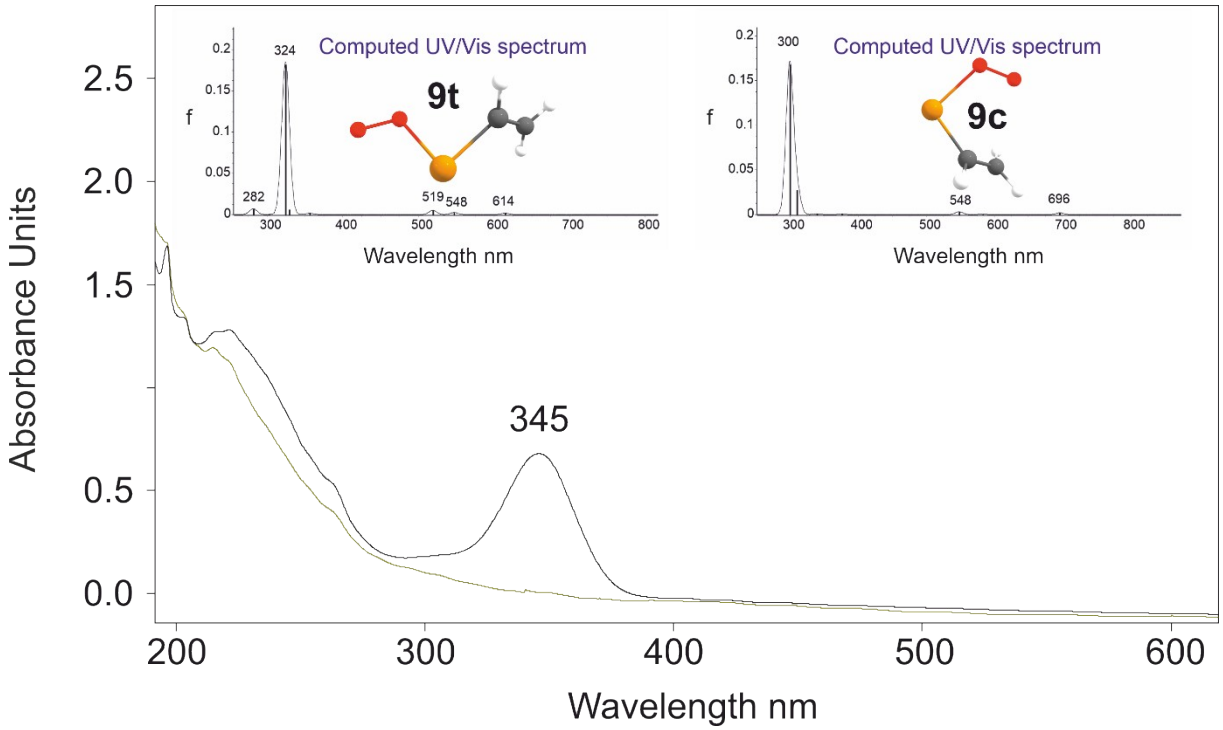


Figure S8. Solid line: UV/Vis spectrum of **9** isolated at 10 K in Ar. Green line: the photochemistry of **9** after irradiation with λ = 365 nm in argon at 10 K. Inset left: computed [TD-UB3LYP/def2-QZVPP] electronic transitions for **9t**. Inset right: computed [TD-UB3LYP/def2-QZVPP] electronic transitions of **9c**.

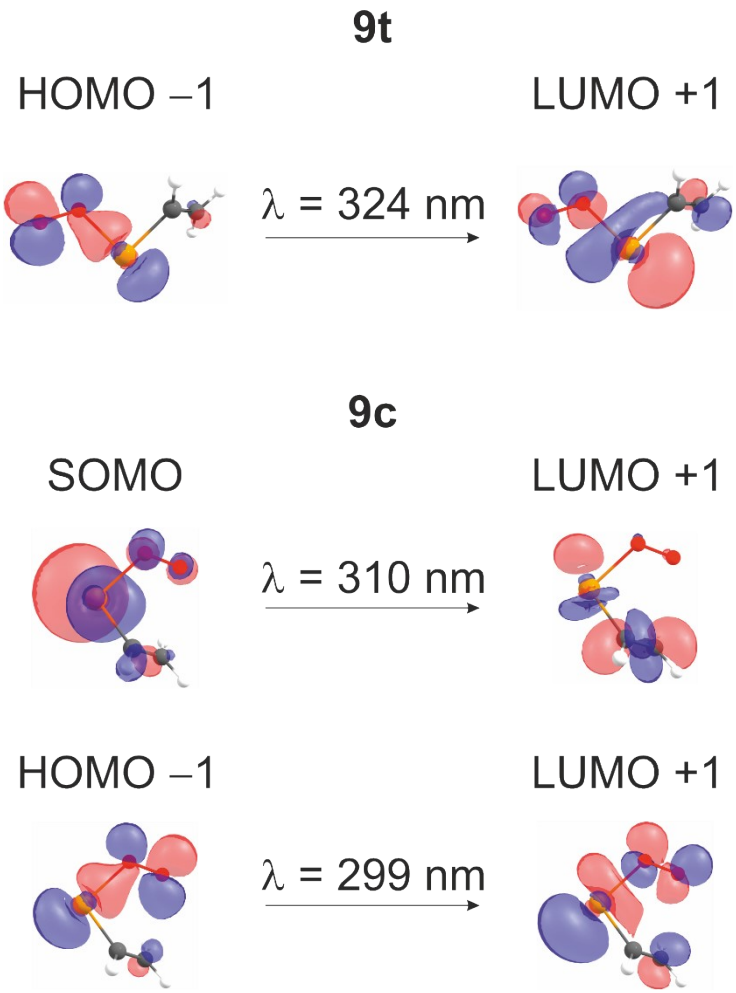


Figure S9. UV/Vis transitions of **9**, computed at UB3LYP/def2-QZVPP level of theory.

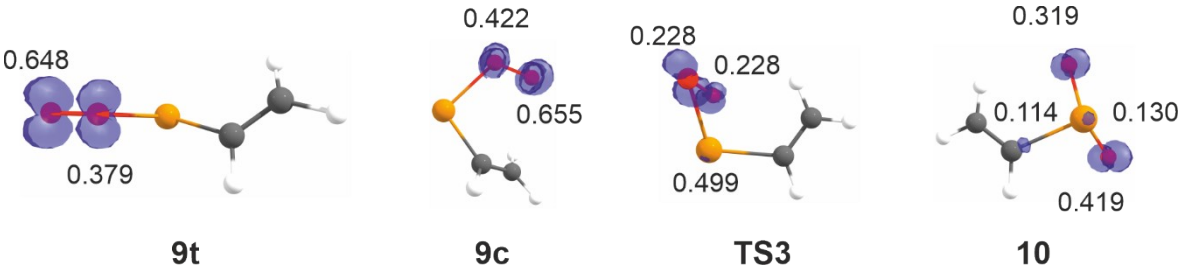


Figure S10. Computed spin density of **9**, **10** and **TS3** at UB3LYP/def2QZVPP level of theory.

Table S1. Experimental (Ar matrix, 10 K) and computed IR frequencies of **5**, band origins in cm^{-1}, computed intensities (km mol^{-1}) in parentheses.

Mode	Computed[a]	Ar, 10 K[b]	Sym.	Assignment (approx.)
12	3207 (3.4)	3036 (w)	*A'*	asym. CH_2 str.
11	3157 (10.3)	2995 (w)	*A'*	C–H str.
10	3113 (11)	2988 (w)	*A'*	sym. CH_2 str.
9	1581 (1.3)	1553 (w)	*A'*	C=C str.
8	1398 (12.1)	1368 (m)	*A'*	CH_2 bend
7	1280 (18.1)	1245 (m)	*A'*	C–H bend
6	1015 (2.5)	-	*A'*	CH_2 rock
5	996 (36.4)	965 (s)	*A''*	C–H o.o.p. bend
4	983 (12.8)	923 (s)	*A''*	CH_2 o.o.p. bend
3	545 (4.4)	480 (m)	*A'*	C–Te str.
2	413 (5.9)	-	*A''*	CH_2 o.o.p. bend
1	298(1.5)	-	*A'*	CCTe bend

[a] UB3LYP/def2-QZVPP, harmonic approximation, unscaled frequencies, intensities (in parentheses) in km mol^{-1}. [b] Experiment: argon matrix, 10 K.; approximate relative intensities (v. w: very weak, w: weak, s: strong).

Table S2. Experimental (Ar matrix, 10 K) and computed IR frequencies of **8**, band origins in cm^{-1}, computed intensities (km mol^{-1}) in parentheses.

Mode	Computed[a]		Computed[a]		Experimental[b]	Assignment (approx.)
	8a	**8b**	acetylene	HTe•	Ar, 10 K	
12	3498 (1.6)	3509 (0.2)	3511 (0.0)		3283 (s)	sym. C–H str.
11	3391 (206)	3411 (90)	3413 (89)		-	asym. C–H str
10	2118 (36)	2104 (72)		2120 (41)	2065 (w)	Te–H str.
9	2063 (4.4)	2064 (1.4)	2067 (0.0)		-	C≡C str.
8	781 (76)	767 (120)	764 (99)		739 (s)	HCCH wagging
7	773 (83)	767 (87)	764 (99)		736 (s)	HCCH wagging
6	673 (4.7)	666 (0.2)	663 (0)		667 (w)	CC–H bend
5	670 (2.6)	665 (0.0)	663 (0)		662 (w)	CC–H bend

[a] UB3LYP/def2-QZVPP, harmonic approximation, unscaled frequencies, intensities (in parentheses) in km mol^{-1}. [b] Experiment: argon matrix, 10 K.; approximate relative intensities (v. w: very weak, w: weak, s: strong).

Table S3. Computed BDEs.

X	BDE_{Dimer} [kcal mol^{-1}]	$BDE_{Hydrogen}$ [kcal mol^{-1}]	Homodesmic equitation [kcal mol^{-1}]	Spin density[a]
Te	40.9	65.4	17.3	0.898
Se	41.1	71.7	11.0	0.820
S	41.9	77.0	5.7	0.718
O	–16.0	80.5	2.2	0.348
CH_2	47.6	82.7	0.0	0.500

Table S4. Experimental (Ar matrix, 10 K) and computed IR frequencies of **9c** and **9t** and $^{18}O_2$-**9c** and $^{18}O_2$-**9t**, band origins in cm^{-1}, computed intensities (km mol^{-1}) in parentheses.

Mode	$C_2H_3Te^{16}O^{16}O$			$C_2H_3Te^{18}O^{18}O$			Assignment (approx.)
	Computed[a]		Ar, 10 K[b]	Computed[a]		Ar, 10 K[b]	
	9c	**9t**		^{18}O-**9c**	^{18}O-**9t**		
18	3217 (1.8)	3206 (2.3)	-	3217 (1.8)	3208 (2.3)	-	asym. CH_2 str.
17	3170 (6.9)	3166 (4.8)	-	3170 (6.9)	3166 (4.8)	-	C–H str.
16	3120 (6.5)	3119 (6.1)	2995 (w)	3120 (6.2)	3119 (6.1)	-	sym. CH_2 str.
15	1619 (0.2)	1628 (1.9)	1582 (w)	1619 (0.2)	1628 (1.9)	-	C=C str.
14	1418 (13.1)	1420 (10.6)	1376 (w)	1418 (13.4)	1420 (10.6)	1382 (w)	CH_2 bend
13	1274 (18.7)	1274 (24.6)	1236 (m)	1274 (20.4)	1274 (25.8)	1235 (m)	C–H bend
12	1220 (280)	1171 (217)	1165c (s) 1115t (s)	1050 (249)	1104 (194)	1100c (s) 1053t (s)	O–O str.
11	1020 (7.0)	1021 (9.6)	998 (w)	1019 (6.9)	1021 (9.2)	-	CH_2 bend
10	1002 (17.4)	1000 (39.0)	960 (m)	1002 (16.9)	1000 (37.5)	962 (s)	CH_2 o.o.p. bend
9	988 (7.6)	992 (4.0)		988 (7.2)	992 (4.0)	-	CH o.o.p. bend
8	558 (3.7)	561 (10.2)	545c (w)	557 (3.2)	559 (9.7)	-	C–Te str.
7	532 (20.4)	542 (8.2)	530t (w) 517c (w)	530 (18.1)	541 (9.8)	517 (w)	CCTe bend
6	445 (13.9)	465 (12.1)		422 (14.1)	443 (10.1)	-	TeOO bend
5	291 (1.6)	287 (1.9)		290 (1.6)	286 (1.9)	-	CCH bend
4	228 (3.3)	223 (1.5)		218 (3.1)	213 (1.4)	-	Te–O str.

[a] UB3LYP/def2-QZVPP, harmonic approximation, unscaled frequencies, intensities (in parentheses) in km mol^{-1}. [b] Experiment: argon matrix, 10 K.; approximate relative intensities (v. w: very weak, w: weak, s: strong).

Table S5. Experimental (Ar matrix, 10 K) and computed IR frequencies of **10** and $^{18}O_2$-**10**, band origins in cm^{-1}, computed intensities (km mol^{-1}) in parentheses.

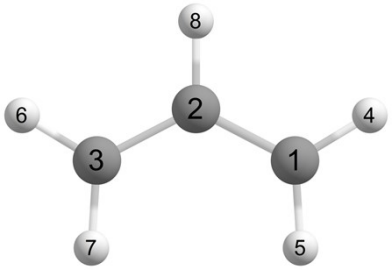
Mode	$C_2H_3Te(^{16}O)^{16}O$		$C_2H_3Te(^{18}O)^{18}O$		Assignment (approx.)
	Computed	Ar, 10 K	Computed	Ar, 10 K	
18	3206 (0.5)	-	3206 (0.5)	-	asym. CH_2 str.
17	3180 (1.9)	-	3180 (1.9)	-	C–H str.
16	3117 (2.0)	-	3117 (2.0)	-	sym. CH_2 str.
15	1636 (5.2)	1590 (m)	1636 (5.2)	-	C=C str.
14	1418 (18.0)	1370 (m)	1416 (18.0)	1370 (s)	CH_2 bend
13	1223 (54.5)	1191 (s)	1223 (54.5)	1191 (s)	C–H bend
12	1017 (45.8)	975 (m)	1017 (45.8)	976 (s)	CH_2 o.o.p. bend
11	979 (0.6)	-	979 (0.6)	-	CH_2 bend/ CH bend
10	968 (5.5)	947 (w)	968 (5.4)	-	CH o.o.p. bend
9	767 (9.1)	737 (w)	726 (8.4)	721 (w)	OTeO sym. str.
8	682 (4.0)	-	649 (3.9)	-	OTeO asym. str.
7	509 (22.4)	495 (w)	509 (21.9)	496 (w)	CH_2/CH o.o.p. bend
6	484 (3.9)	-	484 (3.9)	-	C–Te str.
5	300 (6.4)	-	299 (5.6)	-	CCTe bend
4	237 (20.4)	-	225 (18.1)	-	OSO bend

[a] UB3LYP/def2-QZVPP, harmonic approximation, unscaled frequencies, intensities (in parentheses) in km mol^{-1}. [b] Experiment: argon matrix, 10 K.; approximate relative intensities (v. w: very weak, w: weak, s: strong).

Natural resonance theory (NRT) analysis

We performed the natural resonance theory (NRT) analysis using the NBO7 program package. The computations are done at UB3LYP/def2-QZVPP, UM06-2X/def2-QZVPP, and UMP2/def2-QZVPP level of theories.[1, 2] The following outputs for radicals **1** – **5** for alpha electrons.

Allyl radical **1**



UB3LYP/def2-QZVPP

```
$NRTSTRA
   STR        ! Wgt=43.11%; rhoNL=0.26195; D(0)=0.04044
     LONE 1 1 END
     BOND S 1 2 S 1 4 S 1 5 D 2 3 S 2 8 S 3 6 S 3 7 END
   END
   STR        ! Wgt=43.11%; rhoNL=0.26195; D(0)=0.04044
     LONE 3 1 END
     BOND D 1 2 S 1 4 S 1 5 S 2 3 S 2 8 S 3 6 S 3 7 END
   END
   STR        ! Wgt=1.62%; rhoNL=1.14018; D(0)=0.08430
     LONE 1 2 END
     BOND S 1 4 S 1 5 T 2 3 S 2 8 S 3 7 END
   END
   STR        ! Wgt=1.62%; rhoNL=1.14018; D(0)=0.08430
     LONE 3 2 END
     BOND T 1 2 S 1 5 S 2 8 S 3 6 S 3 7 END
   END
   STR        ! Wgt=1.00%; rhoNL=1.18745; D(0)=0.08603
     LONE 1 1 5 1 END
     BOND D 1 2 S 1 4 D 2 3 S 3 6 S 3 7 END
   END
   STR        ! Wgt=1.00%; rhoNL=1.18745; D(0)=0.08603
     LONE 1 1 7 1 END
     BOND S 1 2 S 1 4 S 1 5 T 2 3 S 3 6 END
   END
   STR        ! Wgt=1.00%; rhoNL=1.18745; D(0)=0.08603
     LONE 3 1 5 1 END
     BOND T 1 2 S 1 4 S 2 3 S 3 6 S 3 7 END
   END
   STR        ! Wgt=1.00%; rhoNL=1.18745; D(0)=0.08603
     LONE 3 1 7 1 END
     BOND D 1 2 S 1 4 S 1 5 D 2 3 S 3 6 END
   END
 $END
```

UM06-2X/def2-QZVPP

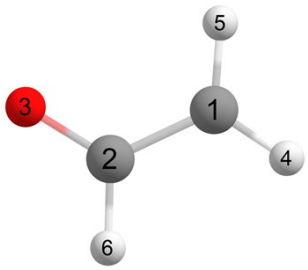
```
$NRTSTRA
   STR        ! Wgt=44.77%; rhoNL=0.18787; D(0)=0.03426
     LONE 1 1 END
```

```
     BOND S 1 2 S 1 4 S 1 5 D 2 3 S 2 8 S 3 6 S 3 7 END
   END
   STR         ! Wgt=44.77%; rhoNL=0.18787; D(0)=0.03426
     LONE 3 1 END
     BOND D 1 2 S 1 4 S 1 5 S 2 3 S 2 8 S 3 6 S 3 7 END
   END
   STR         ! Wgt=1.93%; rhoNL=1.05478; D(0)=0.08109
     LONE 1 2 END
     BOND S 1 4 S 1 5 T 2 3 S 2 8 S 3 7 END
   END
   STR         ! Wgt=1.93%; rhoNL=1.05478; D(0)=0.08109
     LONE 3 2 END
     BOND T 1 2 S 1 5 S 2 8 S 3 6 S 3 7 END
   END
 $END
```

UHF/def2-QZVPP

```
$NRTSTRA
   STR         ! Wgt=44.17%; rhoNL=0.18787; D(0)=0.03403
     LONE 3 1 END
     BOND D 1 2 S 1 4 S 1 5 S 2 3 S 2 8 S 3 6 S 3 7 END
   END
   STR         ! Wgt=44.17%; rhoNL=0.18787; D(0)=0.03403
     LONE 1 1 END
     BOND S 1 2 S 1 4 S 1 5 D 2 3 S 2 8 S 3 6 S 3 7 END
   END
   STR         ! Wgt=1.23%; rhoNL=1.05478; D(0)=0.08098
     LONE 3 2 END
     BOND T 1 2 S 1 5 S 2 8 S 3 6 S 3 7 END
   END
   STR         ! Wgt=1.23%; rhoNL=1.05478; D(0)=0.08098
     LONE 1 2 END
     BOND S 1 4 S 1 5 T 2 3 S 2 8 S 3 7 END
   END
 $END
```

Vinoxy radical **2**



UB3LYP/def2-QZVPP

```
$NRTSTRA
   STR         ! Wgt=43.51%; rhoNL=0.25793; D(0)=0.04450
     LONE 3 3 END
     BOND D 1 2 S 1 4 S 1 5 S 2 3 S 2 6 END
   END
   STR         ! Wgt=39.11%; rhoNL=0.27802; D(0)=0.04620
     LONE 1 1 3 2 END
     BOND S 1 2 S 1 4 S 1 5 D 2 3 S 2 6 END
   END
   STR         ! Wgt=6.94%; rhoNL=0.78336; D(0)=0.07750
     LONE 1 2 3 1 END
     BOND S 1 4 S 1 5 T 2 3 S 2 6 END
   END
   STR         ! Wgt=5.88%; rhoNL=0.79894; D(0)=0.07827
     LONE 3 2 6 1 END
     BOND D 1 2 S 1 4 S 1 5 D 2 3 END
```

```
   END
   STR        ! Wgt=1.95%; rhoNL=1.20529; D(0)=0.09612
     LONE 3 3 5 1 END
     BOND T 1 2 S 1 4 S 2 3 END
   END
   STR        ! Wgt=1.49%; rhoNL=0.81903; D(0)=0.07925
     LONE 1 1 3 1 6 1 END
     BOND S 1 2 S 1 4 S 1 5 T 2 3 END
   END
   STR        ! Wgt=1.12%; rhoNL=0.99391; D(0)=0.08729
     LONE 3 4 END
     BOND T 1 2 S 1 5 S 2 6 END
   END
 $END
```

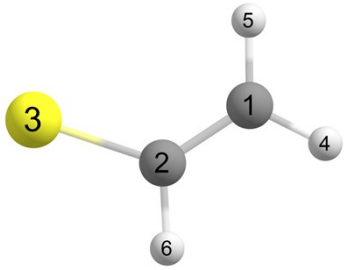
UM06-2X/def2-QZVPP

```
$NRTSTRA
   STR        ! Wgt=48.66%; rhoNL=0.25497; D(0)=0.04425
     LONE 3 3 END
     BOND D 1 2 S 1 4 S 1 5 S 2 3 S 2 6 END
   END
   STR        ! Wgt=34.54%; rhoNL=0.26629; D(0)=0.04521
     LONE 1 1 3 2 END
     BOND S 1 2 S 1 4 S 1 5 D 2 3 S 2 6 END
   END
   STR        ! Wgt=7.05%; rhoNL=0.81832; D(0)=0.07921
     LONE 1 1 3 1 6 1 END
     BOND S 1 2 S 1 4 S 1 5 T 2 3 END
   END
   STR        ! Wgt=7.02%; rhoNL=0.77223; D(0)=0.07695
     LONE 1 2 3 1 END
     BOND S 1 4 S 1 5 T 2 3 S 2 6 END
   END
   STR        ! Wgt=1.81%; rhoNL=1.20630; D(0)=0.09616
     LONE 3 3 5 1 END
     BOND T 1 2 S 1 4 S 2 3 END
   END
 $END
```

UHF/def2-QZVPP

```
$NRTSTRA
   STR        ! Wgt=48.30%; rhoNL=0.16453; D(0)=0.03541
     LONE 3 3 END
     BOND D 1 2 S 1 4 S 1 5 S 2 3 S 2 6 END
   END
   STR        ! Wgt=41.89%; rhoNL=0.20315; D(0)=0.03936
     LONE 1 1 3 2 END
     BOND S 1 2 S 1 4 S 1 5 D 2 3 S 2 6 END
   END
   STR        ! Wgt=7.04%; rhoNL=0.71678; D(0)=0.07406
     LONE 3 2 6 1 END
     BOND D 1 2 S 1 4 S 1 5 D 2 3 END
   END
   STR        ! Wgt=1.32%; rhoNL=1.12738; D(0)=0.09289
     LONE 3 3 5 1 END
     BOND T 1 2 S 1 4 S 2 3 END
   END
 $END
```

Vinylthiyl radical **3**



UB3LYP/def2-QZVPP

```
$NRTSTRA
   STR         ! Wgt=66.59%; rhoNL=0.15950; D(0)=0.03399
     LONE 3 3 END
     BOND D 1 2 S 1 4 S 1 5 S 2 3 S 2 6 END
   END
   STR         ! Wgt=23.22%; rhoNL=0.41770; D(0)=0.05512
     LONE 1 1 3 2 END
     BOND S 1 2 S 1 4 S 1 5 D 2 3 S 2 6 END
   END
   STR         ! Wgt=3.03%; rhoNL=1.08065; D(0)=0.08875
     LONE 3 3 6 1 END
     BOND T 1 2 S 1 4 S 2 3 END
   END
   STR         ! Wgt=2.65%; rhoNL=1.05739; D(0)=0.08780
     LONE 3 4 END
     BOND T 1 2 S 1 5 S 2 6 END
   END
   STR         ! Wgt=2.25%; rhoNL=1.08503; D(0)=0.08893
     LONE 3 3 5 1 END
     BOND T 1 2 S 1 4 S 2 3 END
   END
   STR         ! Wgt=2.25%; rhoNL=1.10541; D(0)=0.08977
     LONE 3 3 4 1 END
     BOND T 1 2 S 1 5 S 2 6 END
   END
 $END
```

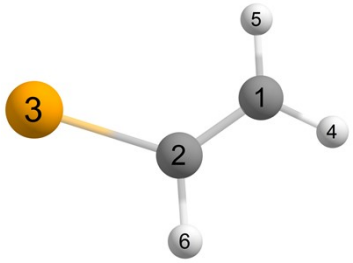
UM06-2X/def2-QZVPP

```
$NRTSTRA
   STR         ! Wgt=68.72%; rhoNL=0.14888; D(0)=0.03284
     LONE 3 3 END
     BOND D 1 2 S 1 4 S 1 5 S 2 3 S 2 6 END
   END
   STR         ! Wgt=21.34%; rhoNL=0.42654; D(0)=0.05572
     LONE 1 1 3 2 END
     BOND S 1 2 S 1 4 S 1 5 D 2 3 S 2 6 END
   END
   STR         ! Wgt=2.71%; rhoNL=1.07353; D(0)=0.08846
     LONE 3 3 6 1 END
     BOND T 1 2 S 1 4 S 2 3 END
   END
   STR         ! Wgt=2.43%; rhoNL=1.04764; D(0)=0.08739
     LONE 3 4 END
     BOND T 1 2 S 1 5 S 2 6 END
   END
   STR         ! Wgt=2.21%; rhoNL=1.07743; D(0)=0.08862
     LONE 3 3 5 1 END
     BOND T 1 2 S 1 4 S 2 3 END
   END
   STR         ! Wgt=2.18%; rhoNL=1.09761; D(0)=0.08945
     LONE 3 3 4 1 END
     BOND T 1 2 S 1 5 S 2 6 END
   END
 $END
```

UHF/def2-QZVPP

```
$NRTSTRA
   STR         ! Wgt=70.43%; rhoNL=0.11163; D(0)=0.02840
     LONE 3 3 END
     BOND D 1 2 S 1 4 S 1 5 S 2 3 S 2 6 END
   END
   STR         ! Wgt=20.80%; rhoNL=0.29765; D(0)=0.04652
     LONE 1 1 3 2 END
     BOND S 1 2 S 1 4 S 1 5 D 2 3 S 2 6 END
   END
   STR         ! Wgt=2.60%; rhoNL=1.03219; D(0)=0.08674
     LONE 3 3 6 1 END
     BOND T 1 2 S 1 4 S 2 3 END
   END
   STR         ! Wgt=2.19%; rhoNL=1.00936; D(0)=0.08578
     LONE 3 4 END
     BOND T 1 2 S 1 5 S 2 6 END
   END
   STR         ! Wgt=1.96%; rhoNL=1.05574; D(0)=0.08772
     LONE 3 3 5 1 END
     BOND T 1 2 S 1 4 S 2 3 END
   END
   STR         ! Wgt=1.85%; rhoNL=1.07057; D(0)=0.08835
     LONE 3 3 4 1 END
     BOND T 1 2 S 1 5 S 2 6 END
   END
 $END
```

Vinylselenyl radical **4**



UB3LYP/def2-QZVPP

```
$NRTSTRA
   STR         ! Wgt=72.48%; rhoNL=0.12589; D(0)=0.02918
     LONE 3 3 END
     BOND D 1 2 S 1 4 S 1 5 S 2 3 S 2 6 END
   END
   STR         ! Wgt=16.18%; rhoNL=0.45760; D(0)=0.05581
     LONE 1 1 3 2 END
     BOND S 1 2 S 1 4 S 1 5 D 2 3 S 2 6 END
   END
   STR         ! Wgt=3.20%; rhoNL=1.02051; D(0)=0.08340
     LONE 3 4 END
     BOND T 1 2 S 1 5 S 2 6 END
   END
   STR         ! Wgt=2.93%; rhoNL=1.04802; D(0)=0.08452
     LONE 3 3 6 1 END
     BOND T 1 2 S 1 4 S 2 3 END
   END
   STR         ! Wgt=2.79%; rhoNL=1.05206; D(0)=0.08468
     LONE 3 3 4 1 END
     BOND T 1 2 S 1 5 S 2 6 END
   END
   STR         ! Wgt=2.41%; rhoNL=1.05029; D(0)=0.08461
     LONE 3 3 5 1 END
     BOND T 1 2 S 1 4 S 2 3 END
   END
```

```
 $END
```

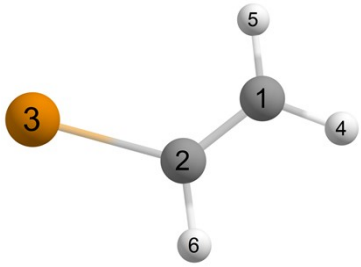
UM06-2X/def2-QZVPP

```
$NRTSTRA
   STR        ! Wgt=75.71%; rhoNL=0.11309; D(0)=0.02764
     LONE 3 3 END
     BOND D 1 2 S 1 4 S 1 5 S 2 3 S 2 6 END
   END
   STR        ! Wgt=13.35%; rhoNL=0.48039; D(0)=0.05718
     LONE 1 1 3 2 END
     BOND S 1 2 S 1 4 S 1 5 D 2 3 S 2 6 END
   END
   STR        ! Wgt=3.07%; rhoNL=1.00751; D(0)=0.08287
     LONE 3 4 END
     BOND T 1 2 S 1 5 S 2 6 END
   END
   STR        ! Wgt=2.76%; rhoNL=1.03960; D(0)=0.08418
     LONE 3 3 6 1 END
     BOND T 1 2 S 1 4 S 2 3 END
   END
   STR        ! Wgt=2.68%; rhoNL=1.04417; D(0)=0.08437
     LONE 3 3 4 1 END
     BOND T 1 2 S 1 5 S 2 6 END
   END
   STR        ! Wgt=2.31%; rhoNL=1.04016; D(0)=0.08420
     LONE 3 3 5 1 END
     BOND T 1 2 S 1 4 S 2 3 END
   END
 $END
```

UHF/def2-QZVPP

```
$NRTSTRA
   STR        ! Wgt=75.90%; rhoNL=0.09120; D(0)=0.02484
     LONE 3 3 END
     BOND D 1 2 S 1 4 S 1 5 S 2 3 S 2 6 END
   END
   STR        ! Wgt=14.32%; rhoNL=0.32788; D(0)=0.04724
     LONE 1 1 3 2 END
     BOND S 1 2 S 1 4 S 1 5 D 2 3 S 2 6 END
   END
   STR        ! Wgt=2.75%; rhoNL=0.98685; D(0)=0.08203
     LONE 3 4 END
     BOND T 1 2 S 1 5 S 2 6 END
   END
   STR        ! Wgt=2.61%; rhoNL=1.01337; D(0)=0.08312
     LONE 3 3 6 1 END
     BOND T 1 2 S 1 4 S 2 3 END
   END
   STR        ! Wgt=2.35%; rhoNL=1.03473; D(0)=0.08399
     LONE 3 3 4 1 END
     BOND T 1 2 S 1 5 S 2 6 END
   END
   STR        ! Wgt=2.07%; rhoNL=1.03396; D(0)=0.08396
     LONE 3 3 5 1 END
     BOND T 1 2 S 1 4 S 2 3 END
   END
 $END
```

Vinyltelluryl radical **5**



UB3LYP/def2-QZVPP

```
$NRTSTRA
   STR         ! Wgt=76.86%; rhoNL=0.10180; D(0)=0.02655
     LONE 3 3 END
     BOND D 1 2 S 1 4 S 1 5 S 2 3 S 2 6 END
   END
   STR         ! Wgt=10.35%; rhoNL=0.50113; D(0)=0.05913
     LONE 1 1 3 2 END
     BOND S 1 2 S 1 4 S 1 5 D 2 3 S 2 6 END
   END
   STR         ! Wgt=3.76%; rhoNL=0.99728; D(0)=0.08346
     LONE 3 4 END
     BOND T 1 2 S 1 5 S 2 6 END
   END
   STR         ! Wgt=3.42%; rhoNL=0.99683; D(0)=0.08344
     LONE 3 3 4 1 END
     BOND T 1 2 S 1 5 S 2 6 END
   END
   STR         ! Wgt=2.92%; rhoNL=1.02109; D(0)=0.08445
     LONE 3 3 6 1 END
     BOND T 1 2 S 1 4 S 2 3 END
   END
   STR         ! Wgt=2.69%; rhoNL=1.02263; D(0)=0.08451
     LONE 3 3 5 1 END
     BOND T 1 2 S 1 4 S 2 3 END
   END
 $END
```

UM06-2X/def2-QZVPP

```
$NRTSTRA
   STR         ! Wgt=79.42%; rhoNL=0.09148; D(0)=0.02515
     LONE 3 3 END
     BOND D 1 2 S 1 4 S 1 5 S 2 3 S 2 6 END
   END
   STR         ! Wgt=8.23%; rhoNL=0.51973; D(0)=0.06022
     LONE 1 1 3 2 END
     BOND S 1 2 S 1 4 S 1 5 D 2 3 S 2 6 END
   END
   STR         ! Wgt=3.69%; rhoNL=0.98512; D(0)=0.08295
     LONE 3 4 END
     BOND T 1 2 S 1 5 S 2 6 END
   END
   STR         ! Wgt=3.28%; rhoNL=0.99489; D(0)=0.08336
     LONE 3 3 4 1 END
     BOND T 1 2 S 1 5 S 2 6 END
   END
   STR         ! Wgt=2.82%; rhoNL=1.01503; D(0)=0.08420
     LONE 3 3 6 1 END
     BOND T 1 2 S 1 4 S 2 3 END
   END
   STR         ! Wgt=2.57%; rhoNL=1.01548; D(0)=0.08421
     LONE 3 3 5 1 END
     BOND T 1 2 S 1 4 S 2 3 END
   END
 $END
```

UHF/def2-QZVPP

```
$NRTSTRA
   STR        ! Wgt=80.03%; rhoNL=0.07720; D(0)=0.02311
     LONE 3 3 END
     BOND D 1 2 S 1 4 S 1 5 S 2 3 S 2 6 END
   END
   STR        ! Wgt=8.82%; rhoNL=0.37259; D(0)=0.05098
     LONE 1 1 3 2 END
     BOND S 1 2 S 1 4 S 1 5 D 2 3 S 2 6 END
   END
   STR        ! Wgt=3.29%; rhoNL=0.97782; D(0)=0.08265
     LONE 3 4 END
     BOND T 1 2 S 1 5 S 2 6 END
   END
   STR        ! Wgt=2.97%; rhoNL=0.99458; D(0)=0.08335
     LONE 3 3 4 1 END
     BOND T 1 2 S 1 5 S 2 6 END
   END
   STR        ! Wgt=2.60%; rhoNL=0.99769; D(0)=0.08348
     LONE 3 3 6 1 END
     BOND T 1 2 S 1 4 S 2 3 END
   END
   STR        ! Wgt=2.29%; rhoNL=1.01627; D(0)=0.08426
     LONE 3 3 5 1 END
     BOND T 1 2 S 1 4 S 2 3 END
   END
 $END
```

Geometric structures and electronic energies

All geometries were optimized and characterized as minima by means of analytic harmonic vibrational frequency computations at the UB3LYP/def2-QZVPP[3, 4] level of theory. The grid size was defined with 99 radial shells and 590 angular points and convergence criteria was set with the keyword "tight". All computations were performed with the Gaussian16 program package.[5]

Tellurium containing compounds

Vinyltelluryl radical **5** – ^{2}A´´ (C_s)

6	-0.448781000	-2.415437000	0.000000000
6	0.472538000	-1.448058000	0.000000000
52	0.000000000	0.587284000	0.000000000
1	-0.159701000	-3.460633000	0.000000000
1	-1.508131000	-2.198278000	0.000000000
1	1.525290000	-1.698907000	0.000000000

E(UB3LYP) = –346.080281
ZVPE(UB3LYP) = 0.040987

TS1 – ^{2}A (C_s)

52	-0.533017000	-0.014693000	0.000011000
6	1.502070000	0.662277000	-0.000057000
6	2.166806000	-0.453807000	-0.000025000
1	1.831541000	1.692081000	-0.000108000
1	3.178025000	-0.830506000	-0.000030000
1	0.694057000	-1.348361000	0.000048000

E(UB3LYP) = –345.991797
ZVPE(UB3LYP) = 0.032540

TeH-radical **7t** – ^{2}A´ (C_s)

6	0.385216000	-2.486933000	0.000000000
6	-0.479826000	-1.533049000	0.000000000
52	0.000000000	0.558853000	0.000000000
1	0.489326000	-3.556212000	0.000000000
1	-1.559041000	-1.675777000	0.000000000
1	1.637380000	0.291522000	0.000000000

E(UB3LYP) = –346.017178
ZVPE(UB3LYP) = 0.033476

TeH-radical **7c** - ^{2}A´ (C_s)

6	0.385117000	-2.487232000	0.000000000
6	-0.480018000	-1.533392000	0.000000000
52	0.000000000	0.558932000	0.000000000
1	0.490896000	-3.556312000	0.000000000
1	-1.559262000	-1.676099000	0.000000000
1	1.637773000	0.291705000	0.000000000

E(UB3LYP) = –346.017182
ZVPE(UB3LYP) = 0.033472

TS2 – ^{2}A

6	-2.552513000	-0.408454000	-0.019952000
6	-1.827940000	0.593530000	0.023961000
52	0.584917000	-0.020606000	-0.031491000
1	-2.825411000	-1.436536000	-0.080927000
1	-1.829932000	1.661342000	0.084495000
1	0.522401000	-0.263744000	1.609884000

E(UB3LYP) = –346.019511
ZVPE(UB3LYP) = 0.032358

Acetylene – TeH-complex **8** – C_{2v} ($^2B_1$)

52	0.000000000	0.000000000	0.793213000
1	0.000000000	0.000000000	2.458713000
6	0.000000000	0.597932000	-3.121687000
1	0.000000000	1.659550000	-3.122782000
6	0.000000000	-0.597932000	-3.121687000
1	0.000000000	-1.659550000	-3.122782000

E(UB3LYP) = –346.028053
ZVPE(UB3LYP) = 0.032380

Vinyltelluryl peroxy radical trans **9t** – C_1 (^{2}A)

6	1.586490000	0.745267000	0.445795000
6	2.650643000	0.838237000	-0.343519000
8	-1.381497000	1.102162000	-0.062909000
8	-2.629105000	0.794024000	-0.099964000
1	2.715346000	0.324993000	-1.293159000
52	-0.021021000	-0.532761000	0.012408000
1	3.505028000	1.439019000	-0.053526000
1	1.534743000	1.269048000	1.390805000

E(UB3LYP) = –496.476210
ZVPE(UB3LYP) = 0.046236

Vinyltelluryl peroxy radical cis **9c** – C_1 (^{2}A)

6	0.883534000	-1.317840000	0.477081000
6	1.955597000	-1.400300000	-0.305494000
8	0.381029000	1.739382000	0.176782000
8	1.635416000	1.692224000	-0.012648000
1	1.990746000	-0.955799000	-1.289485000
52	-0.747473000	-0.125129000	-0.048934000
1	2.847333000	-1.918508000	0.029332000
1	0.864173000	-1.762973000	1.462147000

E(UB3LYP) = – 496.476460
ZVPE(UB3LYP) = 0.046514

Vinyltelluroyl radical **10** – C_1 (^{2}A)

8	-0.157031000	1.682805000	0.503263000
52	-0.391755000	0.033695000	-0.226263000
6	1.570207000	-0.806361000	-0.041370000
6	2.594934000	-0.012489000	0.210069000
8	-1.380782000	-1.132492000	0.778588000
1	2.477080000	1.057852000	0.319810000
1	3.592272000	-0.418500000	0.334385000
1	1.613585000	-1.880902000	-0.155498000

E(UB3LYP) = –496.510072
ZVPE(UB3LYP) = 0.045917

TeH-radical – $C_{\infty v}$

52	0.000000000	0.000000000	0.031356000
1	0.000000000	0.000000000	-1.630494000

E(UB3LYP) = –268.684061
ZVPE(UB3LYP) = 0.004831

Acetylene – D_{16h}

6	0.000000000	0.000000000	0.597705000
1	0.000000000	0.000000000	1.659080000
6	0.000000000	0.000000000	-0.597705000
1	0.000000000	0.000000000	-1.659080000

E(B3LYP) = –77.34823
ZVPE(B3LYP) = 0.0026997

Selenium containing compounds

Divinylditelluride **6** – ^{1}A

6	3.502041000	0.969866000	0.933597000
6	2.228436000	0.629717000	1.072645000
52	1.209802000	-0.625777000	-0.302610000
52	-1.209802000	0.625775000	-0.302612000
6	-2.228436000	-0.629713000	1.072648000
6	-3.502040000	-0.969862000	0.933602000
1	4.005311000	1.555740000	1.693562000
1	4.093250000	0.683635000	0.073560000
1	1.645311000	0.935506000	1.931149000
1	-1.645311000	-0.935498000	1.931154000
1	-4.093249000	-0.683636000	0.073564000
1	-4.005310000	-1.555734000	1.693569000

E(B3LYP) = –692.225680
ZVPE(B3LYP) = 0.083686

Vinyltellurol cis – C_s (^{1}A')

6	0.299408000	-2.492872000	0.000000000
6	-0.519368000	-1.450599000	0.000000000
52	0.000000000	0.593264000	0.000000000
1	-0.097264000	-3.500517000	0.000000000
1	1.376296000	-2.395366000	0.000000000
1	-1.593575000	-1.588273000	0.000000000
1	1.634302000	0.295232000	0.000000000

E(B3LYP) = –346.686679
ZVPE(B3LYP) = 0.047955

Vinyltellurol trans – ^{1}A'

6	-2.471456000	0.303380000	0.048725000
6	-1.452705000	-0.538815000	-0.046414000
52	0.574866000	0.059361000	-0.011253000
1	-3.490323000	-0.051240000	-0.046159000
1	-2.343333000	1.363870000	0.220973000
1	-1.608604000	-1.595795000	-0.213570000
1	1.094199000	-1.390980000	0.610048000

E(B3LYP) = –346.686919
ZVPE(B3LYP) = 0.047855

Divinyldiselenide – ^{1}A

6	-3.378798000	-0.527677000	0.690010000
6	-2.070032000	-0.390849000	0.849538000
34	-0.989294000	0.637522000	-0.358810000
34	0.989295000	-0.637524000	-0.358807000
6	2.070030000	0.390846000	0.849544000
6	3.378794000	0.527691000	0.690006000
1	-3.972068000	-1.044265000	1.433048000
1	-3.903396000	-0.129893000	-0.168184000
1	-1.540307000	-0.802913000	1.697335000
1	1.540308000	0.802893000	1.697352000
1	3.903387000	0.129924000	-0.168198000
1	3.972064000	1.044275000	1.433046000

E(B3LYP) = –4959.268946
ZVPE(B3LYP) = 0.084976

Vinylselenyl-radical – C_s (^{2}A′′)

6	-0.444407000	-2.062620000	0.000000000
6	0.464450000	-1.071018000	0.000000000
34	0.000000000	0.737227000	0.000000000
1	-0.136099000	-3.101129000	0.000000000
1	-1.505104000	-1.854170000	0.000000000
1	1.520945000	-1.308586000	0.000000000

E(UB3LYP) = –2479.601737

Sulphur containing compounds

Divinyldisulphide – ^{1}A

6	3.255479000	0.446190000	-0.167504000
6	1.936299000	0.583858000	-0.223141000
16	0.835576000	-0.524299000	0.606355000
16	-0.835583000	-0.524301000	-0.606359000
6	-1.936293000	0.583882000	0.223118000
6	-3.255472000	0.446184000	0.167536000
1	3.903033000	1.187560000	-0.613759000
1	3.727093000	-0.390552000	0.329339000
1	1.462582000	1.411431000	-0.734289000
1	-1.462575000	1.411496000	0.734199000
1	-3.727086000	-0.390597000	-0.329240000
1	-3.903026000	1.187569000	0.613767000

E(B3LYP) = –952.448367
ZVPE(B3LYP) = 0.086893

Vinylthiyl-radical – C_s (^{2}A′′)

6	1.341918000	0.925254000	0.000000000
6	0.000000000	0.710060000	0.000000000
16	-0.698187000	-0.837930000	0.000000000
1	1.746911000	1.929071000	0.000000000
1	2.035525000	0.096277000	0.000000000
1	-0.662957000	1.569658000	0.000000000

E(UB3LYP) = – 476.190806
ZVPE(UB3LYP) = 0.041554

ZVPE(UB3LYP) = 0.041234

Vinylselenol cis – C_s (^{1}A′)

6	0.303590000	-2.153520000	0.000000000
6	-0.494741000	-1.095523000	0.000000000
34	0.000000000	0.747504000	0.000000000
1	-0.115296000	-3.150641000	0.000000000
1	1.381798000	-2.073969000	0.000000000
1	-1.571421000	-1.204876000	0.000000000
1	1.451829000	0.508624000	0.000000000

E(B3LYP) = –2480.218334
ZVPE(B3LYP) = 0.049504

Vinylselenol trans – ^{1}A’

6	-2.140727000	0.280959000	0.023666000
6	-1.091830000	-0.527772000	-0.018618000
34	0.720253000	0.090161000	-0.009554000
1	-3.142817000	-0.121242000	-0.033353000
1	-2.048143000	1.355037000	0.111488000
1	-1.202345000	-1.599151000	-0.103156000
1	1.300061000	-1.219223000	0.319579000

E(B3LYP) = –2480.218384
ZVPE(B3LYP) = 0.049253

Vinylthiol cis – C_s (^{1}A)

6	1.280051000	1.111358000	0.000000000
6	0.000000000	0.758775000	0.000000000
16	-0.688004000	-0.858290000	0.000000000
1	1.556361000	2.155784000	0.000000000
1	2.083248000	0.387421000	0.000000000
1	-0.779873000	1.510017000	0.000000000
1	0.468017000	-1.541381000	0.000000000

E(B3LYP) = –476.815868
ZVPE(B3LYP) = 0.051092

Vinylthiol trans – ^{1}A’

6	1.682231000	-0.246972000	0.006023000
6	0.579616000	0.492225000	-0.004022000
16	-1.050406000	-0.182579000	-0.005610000
1	2.653707000	0.224597000	-0.009947000
1	1.657127000	-1.327917000	0.027941000
1	0.631231000	1.571577000	-0.025243000
1	-1.706646000	0.981489000	0.084998000

E(B3LYP) = –476.815817
ZVPE(B3LYP) = 0.050680

Oxygen containing compounds

Divinylperoxide – C_s (^{1}A)

6	-2.872674000	-0.063449000	0.181255000
6	-1.670422000	0.259592000	-0.270933000
8	-0.573684000	-0.462505000	0.103851000
8	0.573683000	0.462504000	0.103850000
6	1.670422000	-0.259594000	-0.270931000
6	2.872674000	0.063451000	0.181255000
1	-3.742528000	0.432797000	-0.218624000
1	-3.011798000	-0.842365000	0.915777000
1	-1.469491000	1.042394000	-0.989896000
1	1.469492000	-1.042399000	-0.989890000
1	3.011798000	0.842371000	0.915773000
1	3.742529000	-0.432795000	-0.218624000

E(B3LYP) = –306.389562
ZVPE(B3LYP) = 0.091597

Vinyloxy-radical – C_s (^{2}A'')

6	1.054450000	-0.524092000	0.000000000
6	0.000000000	0.426362000	0.000000000
8	-1.190281000	0.110486000	0.000000000
1	2.088326000	-0.209733000	0.000000000
1	0.819331000	-1.578818000	0.000000000
1	0.287891000	1.491043000	0.000000000

E(UB3LYP) = –153.207558
ZVPE(UB3LYP) = 0.042368

Ethenol cis – C_s (^{1}A')

6	1.211028000	-0.101558000	0.000000000
6	0.000000000	0.440990000	0.000000000
8	-1.189929000	-0.217171000	0.000000000
1	2.084064000	0.530884000	0.000000000
1	1.364378000	-1.172957000	0.000000000
1	-0.158800000	1.510484000	0.000000000
1	-1.036376000	-1.167635000	0.000000000

E(B3LYP) = –153.838240
ZVPE(B3LYP) = 0.056435

Ethenol trans – C_s (^{1}A')

6	1.234280000	-0.067107000	0.000000000
6	0.000000000	0.413318000	0.000000000
8	-1.100509000	-0.396436000	0.000000000
1	2.071643000	0.611521000	0.000000000
1	1.427972000	-1.129698000	0.000000000
1	-0.202257000	1.478218000	0.000000000
1	-1.898963000	0.134180000	0.000000000

E(B3LYP) = –153.836573
ZVPE(B3LYP) = 0.056153

“Carbon” containing compounds

1,5-Hexadien – C_2 (^{1}A)

6	0.433895000	2.840471000	0.586269000
6	0.420711000	1.885268000	-0.334242000
6	-0.420711000	0.646506000	-0.285642000
1	-1.061213000	0.664528000	0.597626000
6	0.420711000	-0.646506000	-0.285642000
1	-1.084743000	0.626680000	-1.156097000
1	1.061213000	-0.664528000	0.597626000
1	1.084743000	-0.626680000	-1.156097000
6	-0.420711000	-1.885268000	-0.334242000
6	-0.433895000	-2.840471000	0.586269000
1	1.069372000	3.710150000	0.492790000
1	-0.194673000	2.787966000	1.466745000
1	1.071076000	1.981667000	-1.199378000
1	-1.071076000	-1.981667000	-1.199378000
1	0.194673000	-2.787966000	1.466745000
1	-1.069372000	-3.710150000	0.492790000

E(B3LYP) = – 234.584703
ZVPE(B3LYP) = 0.141474

Vinyl-radical – C_{2v} ($^2A_2$)

6	0.000000000	1.224087000	-0.195404000
6	0.000000000	0.000000000	0.440952000
6	0.000000000	-1.224087000	-0.195404000
1	0.000000000	2.148703000	0.361375000
1	0.000000000	1.292099000	-1.274837000
1	0.000000000	-2.148703000	0.361375000
1	0.000000000	-1.292099000	-1.274837000
1	0.000000000	0.000000000	1.526055000

E(UB3LYP) = –117.254404
ZVPE(UB3LYP) = 0.065990

Propene - C_s (^{1}A’)

6	1.287368000	0.151984000	0.000000000
6	0.000000000	0.471819000	0.000000000
6	-1.133794000	-0.504900000	0.000000000
1	2.059537000	0.908607000	0.000000000
1	1.615404000	-0.880286000	0.000000000
1	-1.771835000	-0.364809000	0.875622000
1	-0.775836000	-1.533761000	0.000000000
1	-0.276878000	1.521645000	0.000000000
1	-1.771835000	-0.364809000	-0.875622000

E(B3LYP) = – 117.888629
ZVPE(B3LYP) = 0.079389

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