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Electronic Supplementary Information

Spectroscopic Characterization and Photochemistry of the Vinylsulfinyl Radical

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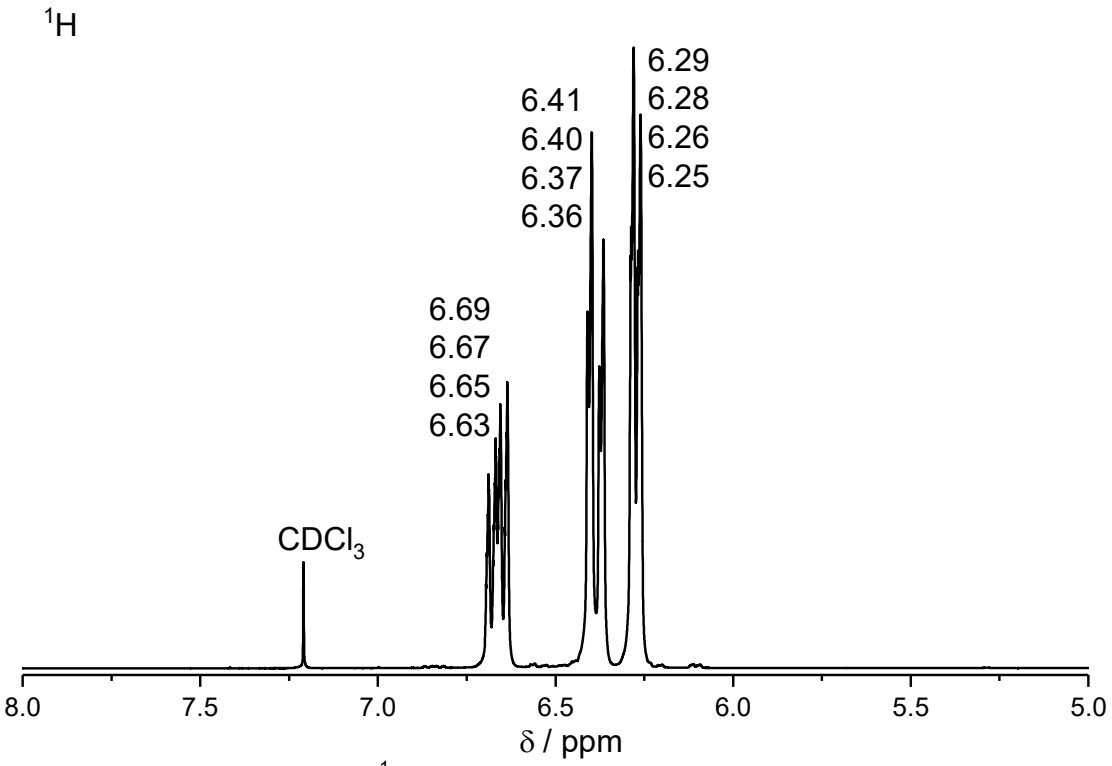

Figure S1. ^{1}H NMR of CH_2=C(H)S(O)CF_3 in $CDCl_3$.

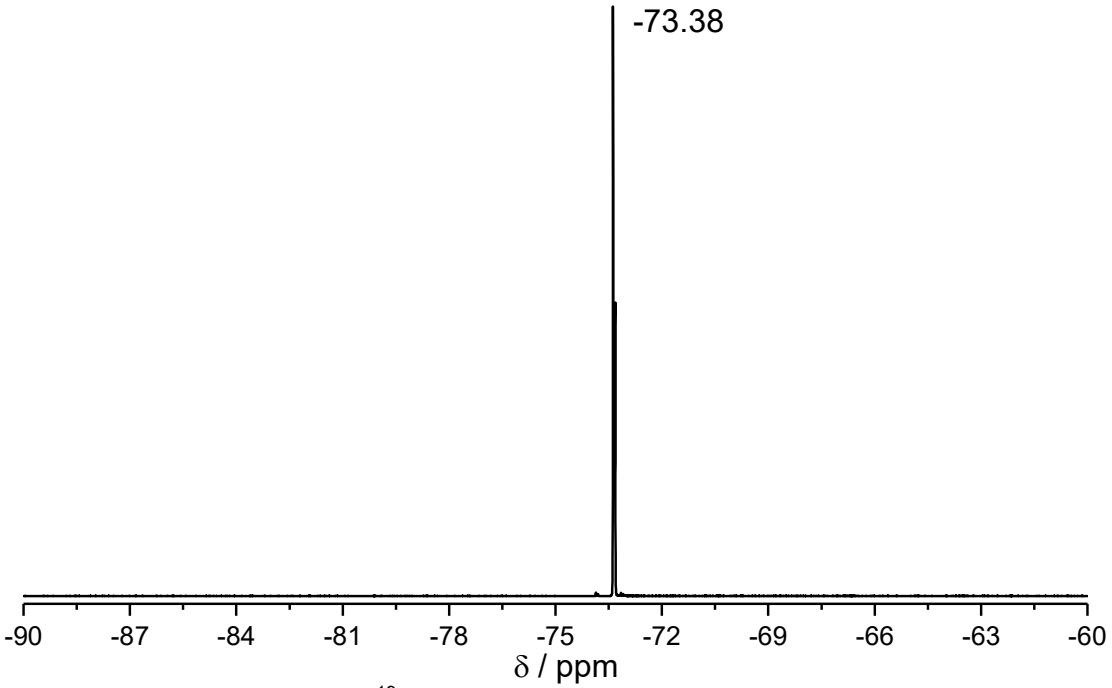

Figure S2. ^{19}F NMR of CH_2=C(H)S(O)CF_3 in $CDCl_3$.

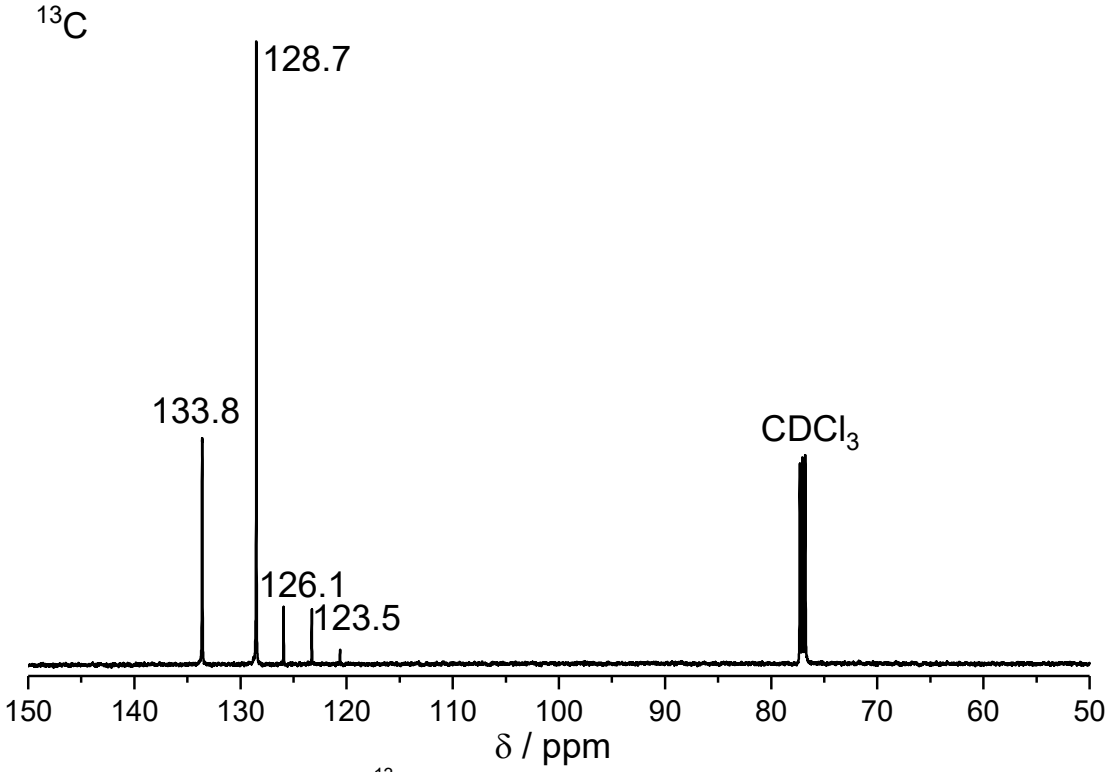

Figure S3. ^{13}C NMR of $CH_2=C(H)S(O)CF_3$ in $CDCl_3$.

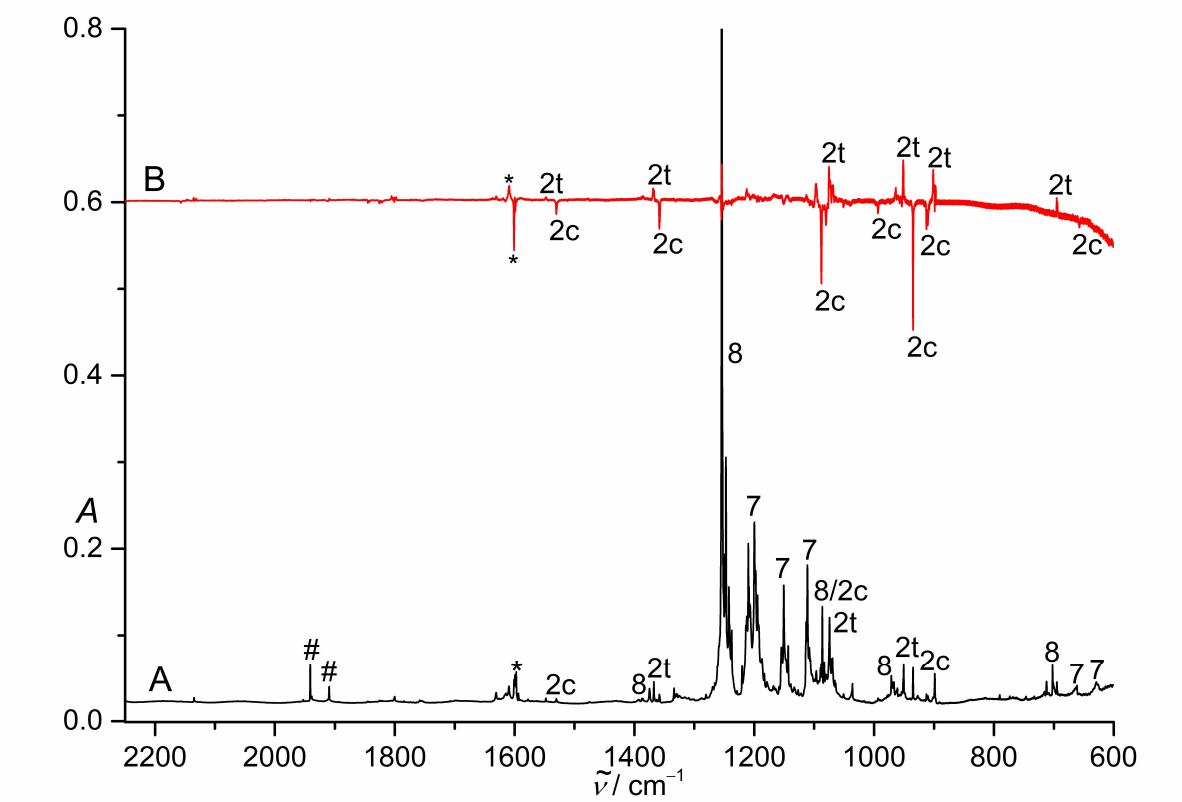

Figure S4. (A) IR spectrum of the high-vacuum flash pyrolysis (HVFP, 800 K) products of CH_2=C(H)S(O)CF_3 (**7**) in solid Ne (**7** : Ne = 1:1000, 150 min deposition) at 2.8 K; (B) IR difference spectrum reflecting the conversion of *cis*-CH_2=C(H)SO• (**2c**) to *trans*-CH_2=C(H)SO• (**2t**) upon irradiation with an UV-light LED (365 nm, 10 min). The IR bands of •CF_3 (**8**), CF_2O (#), and H_2O (*) are also labeled.

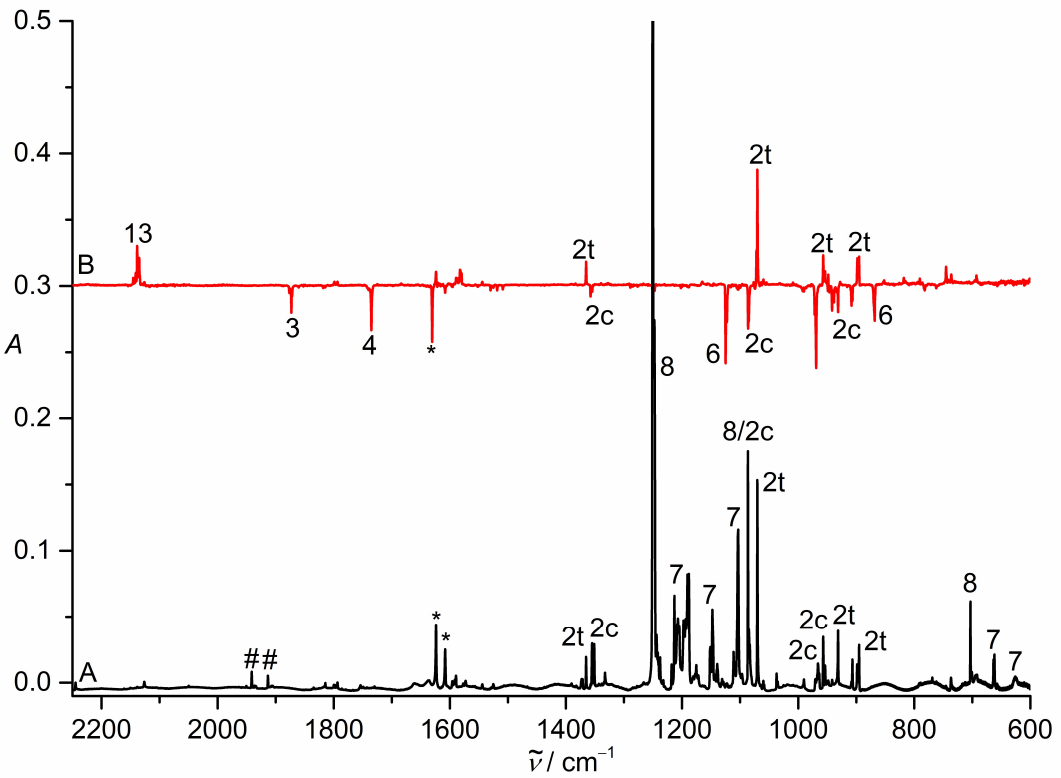

Figure S5. (A) IR spectrum of the high-vacuum flash pyrolysis (HVFP, 800 K) products of CH_2=C(H)S(O)CF_3 (**7**) in solid Ar (**7** : Ar = 1:1000, 150 min deposition) at 10.0 K; (B) IR difference spectrum reflecting the conversion of *cis*-CH_2=C(H)SO• (**2c**) to *trans*-CH_2=C(H)SO• (**2t**) upon irradiation with an UV-light LED (365 nm, 10 min). The IR bands of CH_3SCO• (**3**), •$CH_2SC(O)H$ (**4**), $CH_3C(O)S$• (**6**), CH_2=C(H)S(O)CF_3 (**7**), •CF_3 (**8**), CH_3S•···CO (**9**), CO (**13**), CF_2O (#), and H_2O (*) are also labeled.

Table S1. Calculated anharmonic frequencies of CH_2=C(H)SO• isomers at B3LYP/6 311++G(3df,3pd) level.

trans-CH_3SCO•	*cis*-CH_3SCO•	*trans*-•$CH_2SC(O)H$	*cis*-•$CH_2SC(O)H$
3016 (3)	3008 (3)	3136 (0.1)	3138 (2)
3006 (3)	2995 (3)	3026 (2)	3026 (0.8)
2956 (16)	2941 (9)	2775 (49)	2812 (51)
1844 (401)	1822 (308)	1744 (431)	1717 (328)
1438 (13)	1437 (4)	1378 (0.2)	1356 (4)
1433 (6)	1414 (7)	1319 (12)	1327 (6)
1328 (2)	1308 (5)	934 (15)	931 (7)
972 (6)	942 (2)	904 (2)	881 (3)
965 (3)	941 (13)	812 (5)	807 (2)
688 (1)	642 (2)	732 (105)	709 (116)
562 (66)	557 (54)	510 (150)	513 (49)

trans-CH_3CSO•	*cis*-CH_3CSO•	*trans*-•$CH_2C(O)SH$	*cis*-•$CH_2C(O)SH$
2911 (2)	2923 (2)	3118 (1)	3120 (1)
2895 (5)	2906 (3)	3022 (1)	3023 (0.3)
2864 (5)	2864 (0.2)	2552 (1)	2685 (2)
1416 (9)	1407 (9)	1597 (150)	1611 (163)
1400 (10)	1396 (11)	1424 (8)	1422 (12)
1359 (1)	1350 (6)	1154 (115)	1144 (100)
1330 (4)	1339 (0.5)	1015 (12)	1002 (10)
1102 (176)	1046 (135)	878 (4)	870 (8)
991 (1)	992 (0)	745 (27)	746 (27)
971 (1)	966 (2)	611 (20)	605 (66)
722 (7)	703 (8)	534 (1)	534 (1)

trans-CH_3OCS•	*cis*-CH_3OCS•	$CH_3C(O)S$•	CH_3S•···CO
3014 (8)	3033 (8)	3133 (2)	2913 (106)
2996 (12)	3007 (10)	3105 (1)	2886 (12)
2960 (43)	2967 (16)	3039 (0.2)	2886 (12)
1462 (425)	1464 (156)	1682 (119)	2198 (81)
1454 (1159)	1443 (4)	1466 (13)	1478 (97)
1447 (219)	1440 (12)	1458 (20)	1301 (38)
1339 (458)	1331 (321)	1388 (24)	1297 (20)
1169 (5)	1147 (0.2)	1153 (102)	
1140 (1)	1116 (1)	1027 (1)	
996 (68)	903 (0.6)	933 (66)	
878 (6)	788 (26)	632 (33)	
465 (19)	602 (3)	500 (1)	

Table S2. TD-DFT B3LYP/6-311++G(3df,3pd) calculated vertical transitions (> 190 nm) of CH_2=C(H)SO• isomers.

trans-CH_2=C(H)SO•		*cis*-CH_2=C(H)SO•		*trans*-•CH_2C(O)SH		*cis*-•CH_2C(O)SH	
Energy (nm)	oscillator strength	Energy (nm)	oscillator strength	Energy (nm)	oscillator strength	Energy (nm)	oscillator strength
540	0.0007	520	0.0006	710	0.0001	694	0.0001
389	0.0112	368	0.0065	515	0.0154	522	0.0139
269	0.1082	282	0.1622	237	0.0001	265	0.0006
265	0.0003	275	0.0009	235	0.0032	237	0.0001
235	0.0006	232	0.0002	226	0.0002	235	0.0024
228	0.0001	229	0.0148	221	0.001	220	0.0017
225	0.0538	228	0.0002	218	0.0005	215	0.0194
217	0.004	214	0.0019	211	0.0356	211	0.0178
213	0.0173	213	0.0013			209	0.0007

trans-CH_3SCO•		*cis*-CH_3SCO•		*trans*-•CH_2SC(O)H		*cis*-•CH_2SC(O)H	
Energy (nm)	oscillator strength	Energy (nm)	oscillator strength	Energy (nm)	oscillator strength	Energy (nm)	oscillator strength
445	0.0005	424	0.001	378	0.0273	412	0.0211
387	0.0007	364	0.0005	361	0.0001	305	0.0026
279	0.0177	284	0.0003	307	0.0041	283	0.0001
265	0.0007	259	0.0012	270	0.0803	275	0.0025
249	0.0044	240	0.0045	234	0.0048	260	0.1035
229	0.0284	235	0.0066	231	0.0001	241	0.0005
227	0.0011	218	0.002	226	0.0045	233	0.0022
214	0.0262	207	0.0112	218	0.008	222	0.0041
212	0.0146						

$CH_3C(O)S$•		CH_3S•···CO	
Energy (nm)	oscillator strength	Energy (nm)	oscillator strength
870	0.0060	326	0.002
284	0.0011	275	0.0006
268	0.0001	257	0.0007
258	0.0033	244	0.0003
219	0.0691	228	0.0043
198	0.0012	216	0.0022
		213	0.0013

Calculated atomic coordinates (in Angstroms) and energies (in Hartree) for the isomers of CH_2=C(H)SO• and the transition states with the B3LYP/6-311++G(3df,3pd) method.

***trans*-CH_2=C(H)SO• (2t)**

C	1.32715100	-1.60645400	0.00000000
H	1.39001200	-2.68529900	0.00000000
H	2.26133300	-1.05910100	0.00000000
C	0.14354200	-0.98574700	0.00000000
H	-0.80494600	-1.51046700	0.00000000
S	0.00000000	0.75453600	0.00000000
O	-1.45881900	1.09193700	0.00000000

Zero-point correction= 0.045252 (Hartree/Particle)
Thermal correction to Energy= 0.050049
Thermal correction to Enthalpy= 0.050993
Thermal correction to Gibbs Free Energy= 0.016934
Sum of electronic and zero-point Energies= -551.417021
Sum of electronic and thermal Energies= -551.412224
Sum of electronic and thermal Enthalpies= -551.411280
Sum of electronic and thermal Free Energies= -551.445340

***cis*-CH_2=C(H)SO• (2c)**

C	-1.76847300	0.50693800	-0.00000600
H	-2.84342400	0.39576900	-0.00001400
H	-1.35729500	1.50718200	0.00001600
C	-0.96494100	-0.56135900	-0.00002200
H	-1.33467100	-1.58102200	0.00018800
S	0.77519200	-0.47795300	-0.00001100
O	1.19160100	0.95648000	0.00001800

Zero-point correction= 0.045544 (Hartree/Particle)
Thermal correction to Energy= 0.050132
Thermal correction to Enthalpy= 0.051077
Thermal correction to Gibbs Free Energy= 0.017510
Sum of electronic and zero-point Energies= -551.418327
Sum of electronic and thermal Energies= -551.413739
Sum of electronic and thermal Enthalpies= -551.412794
Sum of electronic and thermal Free Energies= -551.446361

***trans*-•CH_2C(O)SH (5t)**

C	1.30438400	-1.05095900	-0.00004200
H	0.85025600	-2.03056900	0.00056300
H	2.37984400	-0.95329500	-0.00017300
S	-1.27022300	-0.17998200	-0.00003400
H	-1.61103900	1.11823700	0.00034800
C	0.51323400	0.14774000	-0.00002200
O	0.97485000	1.27058100	0.00002400

Zero-point correction= 0.042431 (Hartree/Particle)
Thermal correction to Energy= 0.047256
Thermal correction to Enthalpy= 0.048200
Thermal correction to Gibbs Free Energy= 0.014297
Sum of electronic and zero-point Energies= -551.427692
Sum of electronic and thermal Energies= -551.422866
Sum of electronic and thermal Enthalpies= -551.421922
Sum of electronic and thermal Free Energies= -551.455826

***cis*-•CH_2C(O)SH (5c)**

C	-1.28545200	1.07419200	-0.00001200
H	-0.83482300	2.05388000	-0.00003800
H	-2.36173500	0.97843500	-0.00007300
S	1.29235700	-0.00112000	-0.00000700
H	1.38089200	1.33808500	-0.00010500

C	-0.51286400	-0.13747000	0.00012800
O	-1.00901800	-1.24660200	-0.00004700

Zero-point correction= 0.042343 (Hartree/Particle)
Thermal correction to Energy= 0.047224
Thermal correction to Enthalpy= 0.048168
Thermal correction to Gibbs Free Energy= 0.014147
Sum of electronic and zero-point Energies= -551.425312
Sum of electronic and thermal Energies= -551.420432
Sum of electronic and thermal Enthalpies= -551.419487
Sum of electronic and thermal Free Energies= -551.453508

***trans*-$CH_3SCO•$ (3t)**

C	-1.74260400	0.59095900	-0.00000600
H	-2.67036000	0.02345300	-0.00113900
H	-1.69410100	1.20508900	0.89382500
H	-1.69271300	1.20638600	-0.89286400
S	-0.40719500	-0.64344000	0.00000600
C	0.98913500	0.44810700	0.00006300
O	2.13663800	0.20321400	-0.00003400

Zero-point correction= 0.045054 (Hartree/Particle)
Thermal correction to Energy= 0.050338
Thermal correction to Enthalpy= 0.051282
Thermal correction to Gibbs Free Energy= 0.015928
Sum of electronic and zero-point Energies= -551.431308
Sum of electronic and thermal Energies= -551.426024
Sum of electronic and thermal Enthalpies= -551.425080
Sum of electronic and thermal Free Energies= -551.460433

***cis*-$CH_3SCO•$ (3c)**

C	1.60374200	0.03570200	0.00000000
H	2.37274700	0.80495000	0.00000000
H	1.69209300	-0.57667700	0.89233600
H	1.69209300	-0.57667700	-0.89233600
S	0.00000000	0.92018100	0.00000000
C	-1.17002600	-0.37246500	0.00000000
O	-1.04490400	-1.54424000	0.00000000

Zero-point correction= 0.044905 (Hartree/Particle)
Thermal correction to Energy= 0.050165
Thermal correction to Enthalpy= 0.051109
Thermal correction to Gibbs Free Energy= 0.015661
Sum of electronic and zero-point Energies= -551.429378
Sum of electronic and thermal Energies= -551.424118
Sum of electronic and thermal Enthalpies= -551.423173
Sum of electronic and thermal Free Energies= -551.458621

***trans*-•$CH_2SC(O)H$ (4t)**

C	1.76790400	0.54455000	0.00003100
H	1.57174000	1.60582600	-0.00168800
H	2.77612500	0.16737500	0.00140100
S	0.49783500	-0.59247400	-0.00007700
H	-0.69925600	1.52922400	0.00092900
C	-0.94972000	0.45319700	0.00008300
O	-2.06538400	0.02383400	-0.00001100

Zero-point correction= 0.042633 (Hartree/Particle)
Thermal correction to Energy= 0.048095
Thermal correction to Enthalpy= 0.049039
Thermal correction to Gibbs Free Energy= 0.013759
Sum of electronic and zero-point Energies= -551.416344
Sum of electronic and thermal Energies= -551.410882
Sum of electronic and thermal Enthalpies= -551.409937

Sum of electronic and thermal Free Energies= -551.445218

***cis*-•$CH_2SC(O)H$ (4c)**

C	-1.28545200	1.07419200	-0.00001200
H	-0.83482300	2.05388000	-0.00003800
H	-2.36173500	0.97843500	-0.00007300
S	1.29235700	-0.00112000	-0.00000700
H	1.38089200	1.33808500	-0.00010500
C	-0.51286400	-0.13747000	0.00012800
O	-1.00901800	-1.24660200	-0.00004700

Zero-point correction= 0.042343 (Hartree/Particle)
Thermal correction to Energy= 0.047224
Thermal correction to Enthalpy= 0.048168
Thermal correction to Gibbs Free Energy= 0.014147
Sum of electronic and zero-point Energies= -551.425312
Sum of electronic and thermal Energies= -551.420432
Sum of electronic and thermal Enthalpies= -551.419487
Sum of electronic and thermal Free Energies= -551.453508

$CH_3C(O)S$• (6)

C	1.45278000	-0.85177400	-0.00001100
H	1.34268600	-1.48590500	-0.88030500
H	2.43450100	-0.38271000	-0.00145400
H	1.34441900	-1.48381200	0.88201900
C	0.39010600	0.20522300	-0.00007000
O	0.59746300	1.39844600	0.00001700
S	-1.30991400	-0.24724000	0.00000500

Zero-point correction= 0.046025 (Hartree/Particle)
Thermal correction to Energy= 0.051026
Thermal correction to Enthalpy= 0.051970
Thermal correction to Gibbs Free Energy= 0.016010
Sum of electronic and zero-point Energies= -551.441214
Sum of electronic and thermal Energies= -551.436212
Sum of electronic and thermal Enthalpies= -551.435268
Sum of electronic and thermal Free Energies= -551.471228

CH_3S•···CO (9)

C	-1.38627300	1.07440900	0.00006100
H	-1.67537800	1.61846000	0.89702000
H	-0.29646300	0.97687400	-0.00035800
H	-1.67604600	1.61880700	-0.89647200
C	2.59086400	0.15666400	-0.00032600
O	3.63753400	-0.25261000	0.00019000
S	-2.04249600	-0.59873200	-0.00000800

Zero-point correction= 0.041102 (Hartree/Particle)
Thermal correction to Energy= 0.048521
Thermal correction to Enthalpy= 0.049466
Thermal correction to Gibbs Free Energy= 0.003939
Sum of electronic and zero-point Energies= -551.424776
Sum of electronic and thermal Energies= -551.417357
Sum of electronic and thermal Enthalpies= -551.416412
Sum of electronic and thermal Free Energies= -551.461939

CH_3S•···OC (9)

C	1.36402200	1.10594800	0.02728900
H	1.58826700	1.40701400	1.05499000
H	2.09662700	1.57917600	-0.62367500
H	0.35631900	1.43916100	-0.21113000
S	1.50476000	-0.68553200	-0.02034700
O	-2.45763900	0.45078200	-0.07447700

C	-2.77339900	-0.61646300	0.08957400

Zero-point correction= 0.041000 (Hartree/Particle)
Thermal correction to Energy= 0.048477
Thermal correction to Enthalpy= 0.049421
Thermal correction to Gibbs Free Energy= 0.003921
Sum of electronic and zero-point Energies= -551.424577
Sum of electronic and thermal Energies= -551.417100
Sum of electronic and thermal Enthalpies= -551.416156
Sum of electronic and thermal Free Energies= -551.461656

***trans*-$CH_3CSO•$ (10t)**

C	-2.18913400	-0.07056700	0.00003200
H	-2.66464500	-0.50445800	-0.88248000
H	-2.66493300	-0.50260300	0.88317200
H	-2.39378700	1.00578300	-0.00147000
C	-0.75464500	-0.34620900	0.00009600
S	0.65110900	0.38176700	0.00003100
O	1.87103600	-0.45079300	-0.00005900

Zero-point correction= 0.044568 (Hartree/Particle)
Thermal correction to Energy= 0.049767
Thermal correction to Enthalpy= 0.050711
Thermal correction to Gibbs Free Energy= 0.015811
Sum of electronic and zero-point Energies= -551.362344
Sum of electronic and thermal Energies= -551.357145
Sum of electronic and thermal Enthalpies= -551.356201
Sum of electronic and thermal Free Energies= -551.391101

***cis*-$CH_3CSO•$ (10c)**

C	-2.04561800	0.28805500	0.00001500
H	-2.64254600	0.05414200	-0.88418700
H	-2.64242500	0.05421800	0.88431800
H	-1.84177200	1.36466600	-0.00007000
C	-0.79372200	-0.45571400	-0.00004800
S	0.79107500	-0.46713800	0.00001200
O	1.43819800	0.87589200	-0.00000700

Zero-point correction= 0.044529 (Hartree/Particle)
Thermal correction to Energy= 0.049752
Thermal correction to Enthalpy= 0.050696
Thermal correction to Gibbs Free Energy= 0.015143
Sum of electronic and zero-point Energies= -551.363280
Sum of electronic and thermal Energies= -551.358057
Sum of electronic and thermal Enthalpies= -551.357112
Sum of electronic and thermal Free Energies= -551.392666