Supporting Information

The Phenylselenyl Radical and Its Reaction with Molecular Oxygen

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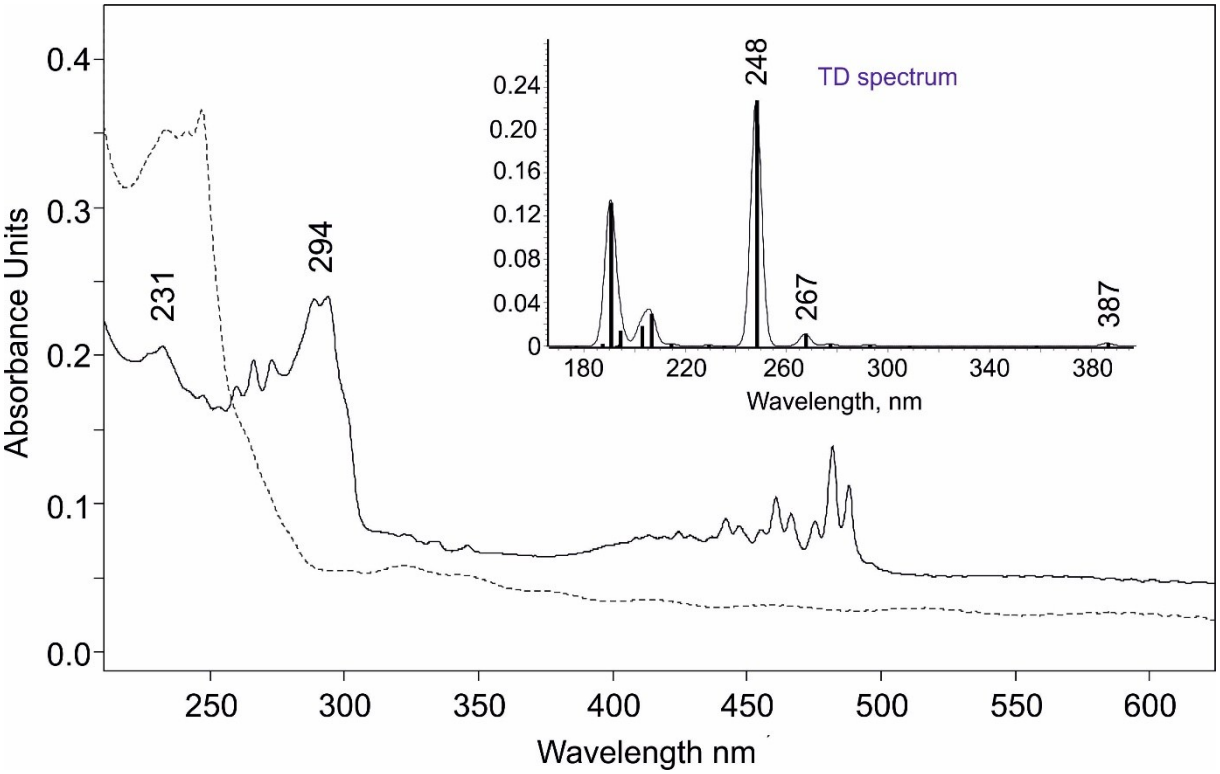

Figure S1. Solid line: UV/Vis spectrum of pyrolysis of **1** at 850 °C, isolated at 10 K in Ar, indicative for **1**. Dashed line: UV/Vis spectrum of **2** at 10 K, Ar. Inset: Computed [TD-B3LYP/cc-pVTZ] electronic transition for **1**.

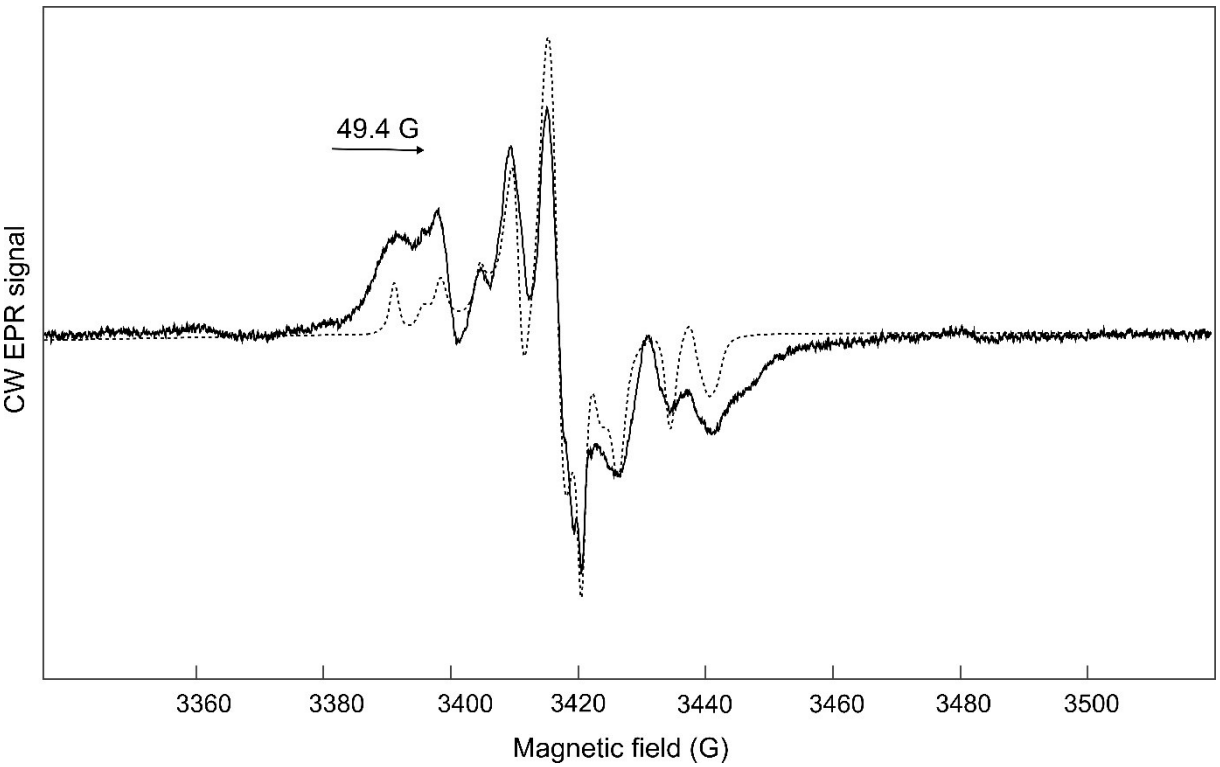

Figure S2. Solid line: EPR spectrum produced by λ = 254 nm irradiation of **2** for 30 minutes, matrix-isolated in argon at 4 K. Dashed line: simulated spectrum proposing a best fit to the experimental spectrum. The fitting were done in accordance with the reference mentioned in the main text.

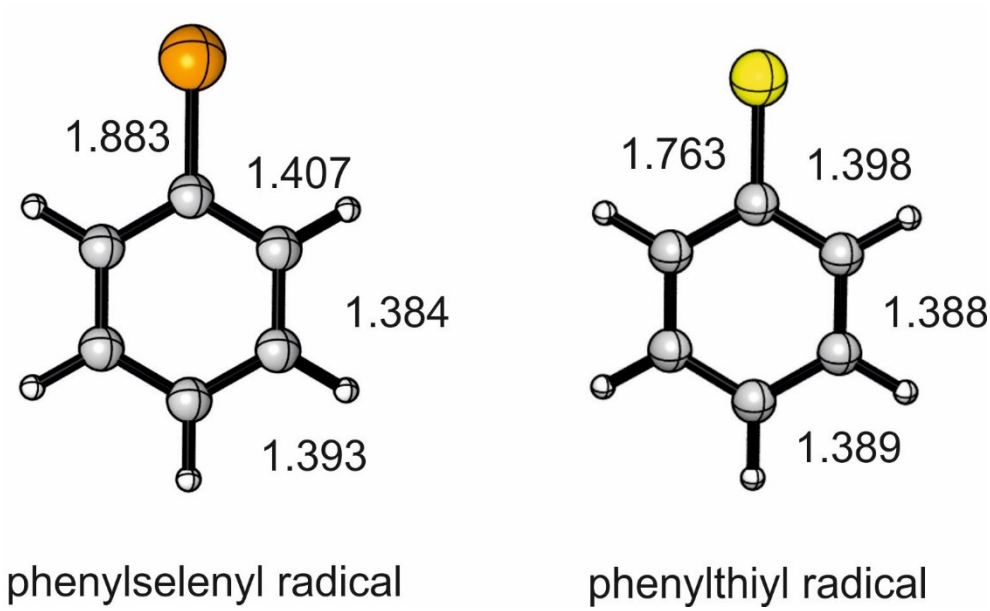

Figure S3. UB3LYP/cc-pVTZ bond lengths (Å) of phenylselenyl radical (**1**) and phenylthiyl radical (**5**).

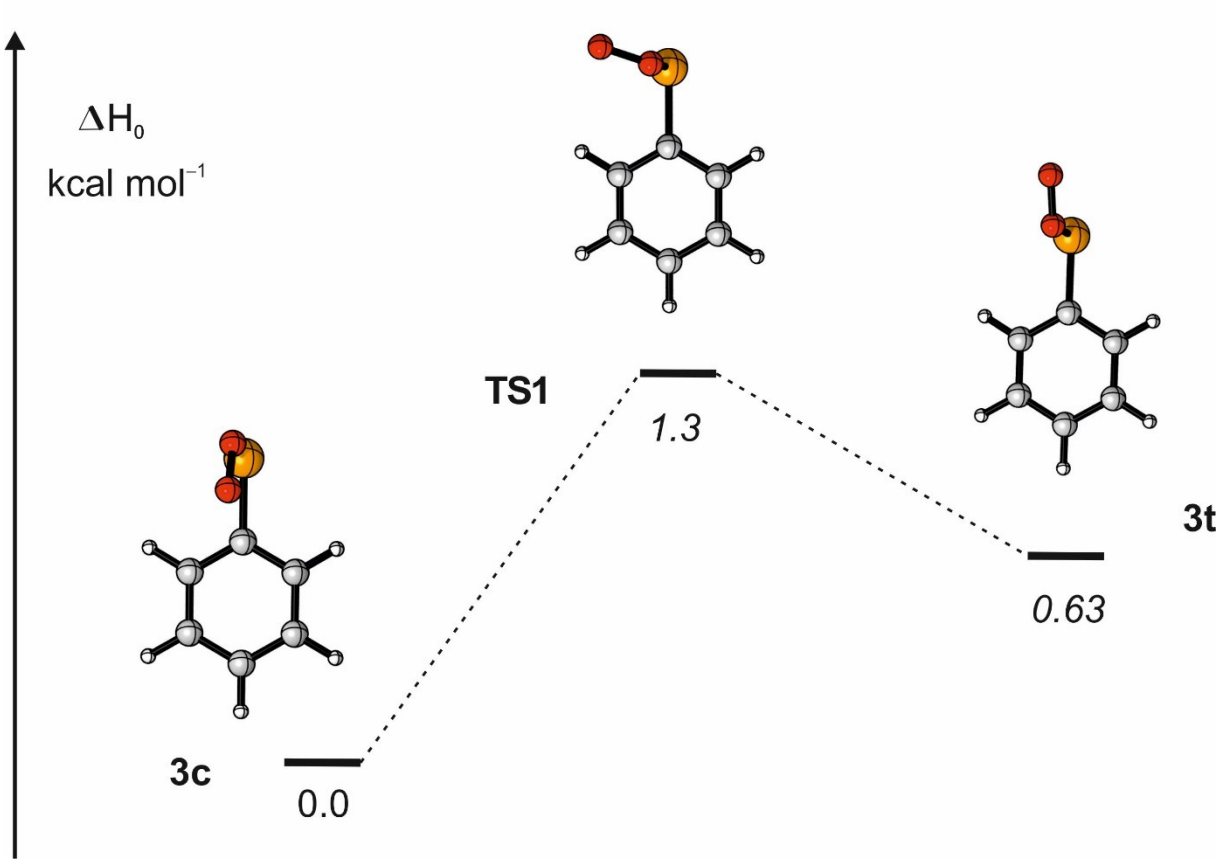

Figure S4. Theoretical isomerization pathway between two isomers of phenylselenyl peroxy radical (**3c** and **3t**). Stationary points and transition state were computed by use UB3LYP/cc-pVTZ method.

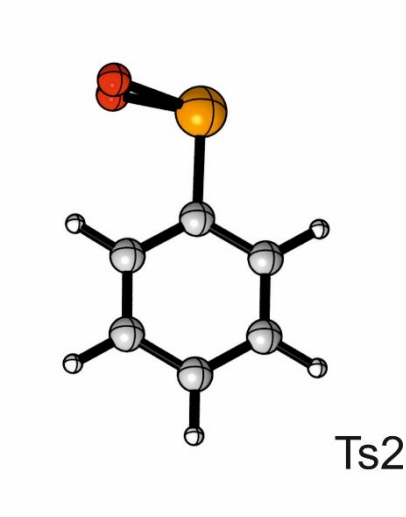

Figure S5. TS2 calculated at the UB3LYP/cc-pVTZ level of theory.

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

Mode	Computed[a]	Ar, 10 K[b]	Symm.	Assignment (approx.)
25	1603 (25)	1565 (m)	a_1	C=C str
24	1590 (0.4)	-	b_2	C=C str
23	1494 (0.7)	-	a_1	C–H def
22	1467 (13)	1435 (m)	b_2	C–H def
21	1347 (7)	1321 (w)	b_2	C–H def
20	1308 (0)	-	b_2	C=C str + CH def
19	1204 (3)	1175 (w)	a_1	C–H def
18	1183 (0.5)	-	b_2	C–H def
17	1098 (3)	1083 (w)	b_2	ring distortion
16	1069 (13)	1052 (s)	a_1	C–Se str + ring distortion
15	1041 (0)	1022 (w)	a_1	ring distortion
14	1017 (0)	-	b_1	C–H o.o.p. def
13	1014 (4)	995 (m)	a_1	ring distortion
12	998 (0)	-	a_2	C–H o.o.p. def
11	950 (1.4)	-	b_1	C–H o.o.p. def
10	856 (0)	-	a_2	C–H o.o.p. def
9	767 (37)	741 (s)	b_1	C–H o.o.p. def
8	698 (36)	678 (s)	b_1	C–H o.o.p. def.
7	694 (0.2)	-	a_1	C–Se str. + ring distortion
6	625(0)	-	b_2	ring distortion
5	460 (4)	445 (m)	b_1	ring breathing
4	390 (0)	-	a_2	ring breathing
3	317 (3)	-	a_1	ring breathing

[a] UB3LYP/cc-pVTZ, unharmonic approximation, unscaled frequencies, intensities (in parentheses) in km mol^{-1}. [b] Experiment: argon matrix, 10 K.; approximate relative intensities (w: weak, m: medium, s: strong).

Table S2. Experimental (Ar matrix, 10 K) and computed IR frequencies of **3g** and $^{18}O_2$-**3g**, band origins in cm^{-1}, computed intensities (km mol^{-1}) in parentheses.

	$C_6H_5Se^{16}O^{16}O$		$C_6H_5Se^{18}O^{18}O$		Assignment
Mode	Computed[a]	Ar, 10 K[b]	Computed[a]	Ar, 10 K[b]	(approx.)
31	1618 (7)	-	1618 (7)	-	C=C str
30	1611 (0.2)	-	1611 (0.2)	-	C=C str
29	1507 (2)	1479	1507 (2)	1479	C–H def
28	1474 (13)	1440	1474 (13)	1440	C–H def
27	1349 (7)	1332	1349 (7)	1332	C–H def
26	1318 (0.5)	1284	1318 (0.5)	1281	C=C str +CH def
25	1247 (247)	1220	1176 (222)	1152	O–O str
24	1205 (5)	1194	1206 (2)	1187	C–H def
23	1187 (0.4)	1158	1187 (0.4)	1161?	C–H def
22	1099 (3)	1074	1099 (3)	1073	C–H def
21	1087 (10)	1065	1087 (10)	1065	C–Se str
20	1043 (1)	1023	1043 (1)	-	ring distortion
19	1021 (1)	-	1021 (1)	-	C–H o.o.p. def
18	1020 (2)	-	1020 (2)	-	C–H o.o.p. def
17	996 (0)	-	996 (0)	-	C–H o.o.p. def
16	953 (0)	-	953 (0)	-	C–H o.o.p. def
15	861 (0.3)	-	861 (0)	-	C–H o.o.p. def
14	765 (34)	742	765 (34)	742	C–H o.o. p. def + ring distortion
13	704 (28)	687	704 (27)	687	C–H o.o. p. def + ring distortion
12	694 (1)	-	694 (1)	-	C–S str +ring distortion
11	629 (0)	-	629 (0)	-	ring distortion
10	515 (33)	529?	499 (33)	-	ring distortion + Se–O str
9	450 (3)	-	439 (7)	-	ring breathing
8	413 (0)		413 (0)	-	ring breathing

[a]UB3LYP/cc-pVTZ, unharmonic 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. Experimental (Ar matrix, 10 K) and computed IR frequencies of **4** and $^{18}O_2$-**4**, band origins in cm^{-1}, computed intensities (km mol^{-1}) in parentheses.

	$C_6H_5Se(^{16}O)^{16}O$		$C_6H_5Se(^{18}O)^{18}O$		Assignment
Mode	Computed	Ar, 10 K	Computed	Ar, 10 K	(approx.)
31	1624 (2)	-	1624 (2)	-	C=C str
30	1609 (0.7)	-	1609 (0.7)	-	C=C str
29	1507 (8)	1487	1507 (8)	1486	C–H def
28	1479 (10)	1447	1479 (10)	1447	C–H def
27	1348 (5)	-	1348 (5)	-	C–H def
26	1328 (1)	-	1328 (1)	-	C=C str + CH def
25	1200 (3)	1188	1200 (3)	1185	C–H def
24	1187 (0)	-	1187 (0)	-	C–H def
23	1098 (6)	-	1098 (6)	-	C–H o.o.p. def
22	1064 (9)	-	1064 (9)	-	ring distortion
21	1032 (0.3)	-	1032 (0.3)	-	ring distortion
20	1022 (1)	-	1022 (1)	-	C–H o.o.p. def
19	1012 (4)	-	1012 (4)	-	ring distortion
18	998 (0.4)	993	998 (0.4)	993	C–H o.o.p. def
17	950 (2)	-	950 (1)	-	C–H o.o.p. def
16	867 (17)	-	828 (17)	-	OSO asym. str
15	859 (2)		860 (0)		C–H o.o.p. def
14	851 (28)	860	806 (27)	821	OSO symm. str
13	759 (54)	738	759 (53)	738	C–H o.o.p. def
12	701 (20)	678	701 (20)	678	C–H o.o.p. def
11	670 (0)	-	670 (0)	-	ring distortion
10	623 (0)	-	623 (0)	-	ring distortion
9	469 (12)	-	469 (11)	-	ring breathing
8	410 (0)	-	410 (0)	-	ring breathing

[a]UB3LYP/cc-pVTZ, unharmonic 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).

Geometric Structures and Electronic energies

1: Phenylselenyl radical – $^2B_1$ (C_{2v} point group)

0 2

6	0.000000000	0.000000000	-2.848507000
6	0.000000000	1.207544000	-2.153029000
6	0.000000000	-1.207544000	-2.153029000
1	0.000000000	2.143997000	-2.694401000
1	0.000000000	-2.143997000	-2.694401000
6	0.000000000	1.211751000	-0.768310000
6	0.000000000	-1.211751000	-0.768310000
1	0.000000000	2.143850000	-0.221493000
1	0.000000000	-2.143850000	-0.221493000
6	0.000000000	0.000000000	-0.053150000
1	0.000000000	0.000000000	-3.930242000
34	0.000000000	0.000000000	1.830236000

E[UB3LYP] = -2633.3368026
ZPVE[UB3LYP] = 0.090040

3c: Phenylselenyl peroxy radical –$^2A''$ (C_s point group)

0 2

6	-0.420947000	2.417988000	1.206710000
6	-0.422254000	3.110441000	0.000000000
6	-0.420947000	2.417988000	-1.206710000
6	-0.420947000	1.030309000	-1.210766000
6	-0.427242000	0.331042000	0.000000000
6	-0.420947000	1.030309000	1.210766000
8	1.625844000	-1.776192000	0.000000000
8	2.299121000	-0.709096000	0.000000000
1	-0.416728000	0.484336000	2.143101000
1	-0.417058000	2.958874000	2.143295000
1	-0.422179000	4.192279000	0.000000000
1	-0.417058000	2.958874000	-2.143295000
1	-0.416728000	0.484336000	-2.143101000
34	-0.415007000	-1.565437000	0.000000000

E[UB3LYP] = -2783.7190516
ZPVE[UB3LYP] = 0.095383

3t: Phenylselenyl peroxy radical –$^2A''$ (C_s point group)

0 2

6	0.384139000	3.306622000	0.000000000
6	0.383822000	2.613615000	1.206265000
6	0.383822000	1.225296000	1.210430000
6	0.383784000	0.526939000	0.000000000
6	0.383822000	1.225296000	-1.210430000
6	0.383822000	2.613615000	-1.206265000
1	0.384884000	4.388394000	0.000000000
1	0.382798000	3.153956000	2.143190000
1	0.382442000	0.679809000	2.143199000
1	0.382442000	0.679809000	-2.143199000
1	0.382798000	3.153956000	-2.143190000
34	0.391850000	-1.380890000	0.000000000
8	-1.595955000	-1.538130000	0.000000000
8	-2.036235000	-2.733618000	0.000000000

E[UB3LYP] = -2783.717955
ZPVE[UB3LYP] = 0.095309

TS1: (C_1 point group)

0 2

6	-2.682003000	-0.765830000	0.802105000
6	-3.245719000	0.370263000	0.230933000
6	-2.467942000	1.223262000	-0.545916000
6	-1.124744000	0.942321000	-0.755673000
6	-0.556042000	-0.197384000	-0.180531000
6	-1.338310000	-1.052216000	0.599970000
8	1.976164000	0.462461000	1.071226000
8	2.587037000	1.544838000	0.773035000
1	-0.892113000	-1.930933000	1.043098000
1	-3.287599000	-1.427739000	1.406271000
1	-4.292614000	0.591095000	0.390578000
1	-2.907763000	2.106272000	-0.989456000
1	-0.514422000	1.599139000	-1.358806000
34	1.290513000	-0.591727000	-0.475033000

E[UB3LYP] = -2783.7167054
ZPVE[UB3LYP] = 0.095117

4: Phenylselenonyl radical $-{}^2A'$ (C_s point group)

0 2

6	-0.119542000	3.259134000	0.000000000
6	-0.117059000	2.568982000	1.208036000
6	-0.117059000	1.178467000	1.218101000
6	-0.108405000	0.516212000	0.000000000
6	-0.117059000	1.178467000	-1.218101000
6	-0.117059000	2.568982000	-1.208036000

1	-0.121113000	4.340694000	0.000000000
1	-0.110768000	3.110368000	2.144192000
1	-0.099308000	0.622427000	2.144662000
1	-0.099308000	0.622427000	-2.144662000
1	-0.110768000	3.110368000	-2.144192000
8	0.581176000	-1.883311000	1.413192000
8	0.581176000	-1.883311000	-1.413192000
34	-0.134719000	-1.449846000	0.000000000

E[UB3LYP] = -2783.7577906
ZPVE[UB3LYP] = 0.095876

TS2: (C_1 point group)

0 2

6	3.234491000	0.311066000	-0.000006000
6	2.340480000	1.379101000	-0.000011000
6	0.971850000	1.150993000	-0.000008000
6	0.510756000	-0.162495000	0.000000000
6	1.393493000	-1.241401000	0.000006000
6	2.760388000	-0.996859000	0.000003000
1	4.299530000	0.498525000	-0.000008000
1	2.711517000	2.395130000	-0.000017000
1	0.264137000	1.967344000	-0.000012000
1	1.024684000	-2.259671000	0.000012000
1	3.453347000	-1.827169000	0.000007000
8	-2.038071000	0.921593000	0.840672000
8	-2.038073000	0.921580000	-0.840680000
34	-1.365082000	-0.534176000	0.000005000

E[UB3LYP] = -2783.6736454
ZPVE[UB3LYP] = 0.092851

5: Phenylthiyl radical $-^2B_1$ (C_{2v} point group)

0 2

C	0.000000000	0.000000000	-2.240288000
C	0.000000000	1.199543000	-1.538236000
C	0.000000000	1.208332000	-0.149665000
C	0.000000000	0.000000000	0.553509000
C	0.000000000	-1.208332000	-0.149665000
C	0.000000000	-1.199543000	-1.538236000
H	0.000000000	0.000000000	-3.321376000
H	0.000000000	2.141147000	-2.071299000
H	0.000000000	2.148472000	0.384708000
H	0.000000000	-2.148472000	0.384708000
H	0.000000000	-2.141147000	-2.071299000
S	0.000000000	0.000000000	2.316878000

E[UB3LYP] = -629.9104751
ZPVE[UB3LYP] = 0.090403

Phenoxyl radical $-^2B_1$ (C_{2v} point group)

0 2

6	0.000000000	1.235386000	0.288290000
6	0.000000000	0.000000000	1.044849000
6	0.000000000	-1.235386000	0.288290000
6	0.000000000	-1.220432000	-1.082957000
6	0.000000000	0.000000000	-1.778060000
6	0.000000000	1.220432000	-1.082957000
1	0.000000000	2.157661000	0.852771000
1	0.000000000	-2.157661000	0.852771000
1	0.000000000	-2.148900000	-1.638778000
1	0.000000000	0.000000000	-2.859644000
1	0.000000000	2.148900000	-1.638778000
8	0.000000000	0.000000000	2.295866000

E[UB3LYP] = -306.93913
ZPVE[UB3LYP] = 0.091419

Phenylaminyl radical $-^2A''$ (C_s point group)

0 2

6	0.000000000	1.017249000	0.000000000
6	1.226611000	0.283554000	0.000000000
6	1.228133000	-1.092751000	0.000000000
6	0.021446000	-1.801727000	0.000000000
6	-1.196606000	-1.112678000	0.000000000
6	-1.216024000	0.264006000	0.000000000
1	2.145545000	0.852874000	0.000000000
1	2.166177000	-1.631833000	0.000000000
1	0.029405000	-2.883120000	0.000000000
1	-2.126096000	-1.666671000	0.000000000
1	-2.156749000	0.800937000	0.000000000
7	0.063378000	2.349595000	0.000000000
1	-0.883288000	2.734731000	0.000000000

E[UB3LYP] = -286.955134
ZPVE[UB3LYP] = 0.103686

Oxygen: ($D_{\infty h}$ point group)

O	0.000000000	0.000000000	0.602914000
O	0.000000000	0.000000000	-0.602914000

E[UB3LYP] = -150.38094430
ZPVE[UB3LYP] = 0.003710