Supporting Information
On the Population of Triplet States of 2-Seleno-Thymine

Danillo Valverde,† Sebastian Mai,* ,‡, Adalberto Vasconcelos Sanches de Araújo,§ Sylvio Canuto,† Leticia González, Antonio Carlos Borin*,§

† *Institute of Physics, University of São Paulo, São Paulo, SP, 05508-090, Brazil*

‡ *Photonics Institute, Vienna University of Technology, Vienna, Austria*

Institute of Theoretical Chemistry, Faculty of Chemistry, University of Vienna, Vienna, Austria

Email: sebastian.mai@univie.ac.at

§ Department of Fundamental Chemistry, Institute of Chemistry, University of São Paulo

Avenida Professor Lineu Prestes, 748, São Paulo, SP, CEP 05508-000, Brazil

Email: ancborin@iq.usp.br

Table of Contents

I. Spin-orbit Couplings

Spin-orbit couplings were performed at the MS-CASPT2 within the atomic mean-field (AMFI) approximation. The effective spin-orbit couplings reported in the main text are given by:

$$\langle \Psi_S | H_{eff}^{S0} | \Psi_T \rangle = \sqrt{\frac{1}{3}\sum_i \langle \Psi_S | H_i^{S0} | \Psi_T \rangle^2} \quad (i = x,y,z)$$

where, Ψ_S and Ψ_T are the perturbatively modified electronic wavefunctions of the corresponding singlet and triplet states and H_i^{S0}, $i = (x, y, z)$, are the components of the spin-orbit operators.

II. Comparison among different active spaces and atomic basis set

Table S1: Vertical excitations energies of 2SeThy in gas phase computed with the MS(4,3)-CASPT2(14,11) level using two different basis sets. The relativistic effects via Douglas-Kroll-Hess formalism were incorporated in the calculation with the ANO-RCC-VDZP basis set. These calculations were performed in the ground-state optimized structure at the MP2/ANO-RCC-VDZP level.

Nature	cc-pVDZ		ANO-RCC-VDZP	
	ΔE	Osc. Str.	ΔE	Osc. Str.
S1 1(nSeπ5*)	3.48	0.000	3.44	0.000
S2 1(πSeπ5*)/1(πSeπ6*)	3.96	0.549	3.94	0.544
S3 1(πSeπ6*)	4.29	0.161	4.28	0.156
T1 3(πSeπ5*)/3(πSeπ6*)	2.97	—	2.97	—
T2 3(nSeπ5*)	3.44	—	3.43	—
T3 3(πSeπ6*)	3.62	—	3.64	—

Table S2: Bond lengths (A) for the ground state of 2SeThy in gas-phase computed at the MP2 level using two different basis set. The relativistic effects via Douglas-Kroll-Hess formalism were incorporated in the calculation with the ANO-RCC-VDZP basis set.

Bond Length	cc-pVDZ	ANO-RCC-VDZP
r(N1C2)	1.373	1.368
r(C2N3)	1.373	1.369
r(N3C4)	1.413	1.409
r(C4C5)	1.468	1.459
r(C5C6)	1.365	1.358
r(N1C6)	1.380	1.378
r(C2Se)	1.802	1.812
r(C4O)	1.225	1.228

Table S3: Vertical excitation energies of 2SeThy in gas phase computed with the MS(4,3)-CASPT2/cc-pVDZ level using three different active space. These calculations were performed in the ground-state optimized structure obtained at the MS(4)-CASPT2(12,9)/cc-pVDZ level.

Nature	(5π, nSe,3 π*)		(5π, nSe, σ, σ*, 3 π*)		(5π, nSe, nO, σ, σ*, 3π*)	
	ΔE	Osc. Str.	ΔE	Osc. Str.	ΔE	Osc. Str.
S1 1(nSeπ5*)	3.44	0.000	3.44	0.000	3.32	0.000
S2 1(πSeπ5*)/1(πSeπ6*)	3.83	0.564	3.87	0.582	3.79	0.234
S3 1(πSeπ6*)	4.30	0.078	4.14	0.065	4.21	0.238
T1 3(πSeπ5*)/3(πSeπ6*)	2.99	—	3.02	—	2.84	—
T2 3(nSeπ5*)	3.02	—	3.49	—	3.32	—
T3 3(πSeπ6*)	3.62	—	3.67	—	3.52	—

III. Optimized Geometries (Ångstrom)

```
15
  (S0)min
C  -1.17711378  +0.86011068  +0.00053813
N  +0.08620112  +1.39862830  +0.02680022
C  +1.24595970  +0.64513216  +0.01383940
C  +1.21975739  -0.72221745  +0.00389444
C  -0.08211507  -1.39326435  +0.01237425
N  -1.18762155  -0.51075243  +0.03375482
C  +2.44863066  -1.58566069  -0.01181058
O  -0.25987768  -2.60558291  -0.00150477
Se -2.68118967  +1.88861138  -0.06915882
H  +0.12459170  +2.41429930  -0.00033179
H  +2.17643494  +1.21927073  +0.00914255
H  -2.10759183  -0.95363926  +0.01516993
H  +2.45014127  -2.23588418  -0.90169273
H  +2.46265726  -2.24925354  +0.86815053
H  +3.36487057  -0.97518273  -0.01339659
```

```
15
  (S1)min
C  -1.19176884  +0.89336104  +0.24358017
N  +0.09560811  +1.42728127  +0.24267093
C  +1.23088775  +0.66021808  +0.11703288
C  +1.19238147  -0.70343990  -0.00160678
C  -0.11349266  -1.37477124  +0.08682847
N  -1.20312767  -0.50687870  +0.24235102
C  +2.41293425  -1.56458165  -0.15639075
O  -0.27783370  -2.59125398  +0.07242229
Se -2.50051445  +1.67140110  -1.03360562
H  +0.18555753  +2.43665298  +0.26951244
H  +2.17280689  +1.21711480  +0.12976917
H  -2.09847560  -0.97588788  +0.36878561
H  +2.48496513  -2.29294428  +0.66828173
H  +3.32961878  -0.95379464  -0.17287547
H  +2.36418804  -2.14786200  -1.09098714
```

```
15
  (S2)min boat
C  -1.13108985  +0.89348078  +0.08447154
N  +0.13927241  +1.41009722  +0.03739265
C  +1.28705960  +0.64505424  +0.03107102
C  +1.23862036  -0.72314261  +0.01710220
C  -0.07528281  -1.37889634  -0.00805223
N  -1.15990447  -0.47843424  +0.01229054
C  +2.45367906  -1.60356307  +0.00155133
O  -0.26198376  -2.58917269  -0.04155715
Se -2.34104072  +1.79983231  -1.39604370
H  +0.20234565  +2.42408846  -0.00191587
H  +2.22754424  +1.20295164   0.04374580
H  -2.08374141  -0.91195287  -0.01056262
H  +2.45704079  -2.23545548  -0.90184270
H  +2.44543150  -2.28690107   0.86675343
H  +3.37944955  -1.00841696   0.02445184
```

```
15
  (S2)min pyramid
C  -1.13108985  +0.89348078  +0.08447154
N  +0.13927241  +1.41009722  +0.03739265
C  +1.28705960  +0.64505424  +0.03107102
C  +1.23862036  -0.72314261  +0.01710220
C  -0.07528281  -1.37889634  -0.00805223
N  -1.15990447  -0.47843424  +0.01229054
C  +2.45367906  -1.60356307  +0.00155133
O  -0.26198376  -2.58917269  -0.04155715
Se -2.34104072  +1.79983231  -1.39604370
H  +0.20234565  +2.42408846  -0.00191587
H  +2.22754424  +1.20295164  +0.04374580
H  -2.08374141  -0.91195287  -0.01056262
H  +2.45704079  -2.23545548  -0.90184270
H  +2.44543150  -2.28690107  +0.86675343
H  +3.37944955  -1.00841696  +0.02445184
```

```
   15
    (T1)min
   C   -1.30608013   +0.83604045   +0.34835704
   N   +0.02619457   +1.38431485   +0.30976453
   C   +1.17264912   +0.65875338   +0.10630608
   C   +1.15939256   -0.69228719   -0.00028726
   C   -0.13753571   -1.40396877   +0.13830287
   N   -1.23559230   -0.57553807   +0.32644136
   C   +2.39428849   -1.52428513   -0.19423614
   O   -0.23901555   -2.62811352   +0.12689116
   Se  -1.92817824   +1.82025560   -1.33021815
   H   +0.07383021   +2.39433550   +0.41557915
   H   +2.10039977   +1.24345116   +0.04436284
   H   -2.11725282   -1.07437196   +0.42755593
   H   +2.33128177   -2.10132560   -1.12920825
   H   +2.49810598   -2.25536338   +0.62127134
   H   +3.29124733   -0.88728234   -0.22511351


   15
    (T2)min
   C   -1.19736100   +0.87785663   +0.26880995
   N   +0.07963049   +1.40901233   +0.28579444
   C   +1.22530907    0.65611309   +0.13190136
   C   +1.19365989   -0.70468162   +0.01327759
   C   -0.10962103   -1.37895779   +0.11314948
   N   -1.19679226   -0.50666477   +0.29728831
   C   +2.41295920   -1.56110245   -0.17054088
   O   -0.27750185   -2.59330958   +0.08106545
   Se  -2.44152232   +1.70921010   -1.16812012
   H   +0.15821001   +2.42031431   +0.30237292
   H   +2.16122326   +1.22284981   +0.12640616
   H   -2.09846325   -0.97650330   +0.36499277
   H   +2.35314883   -2.12551401   -1.11568690
   H   +2.49200587   -2.30442064   +0.63965286
   H   +3.32885013   -0.94958712   -0.18459441


   15
    (S1/S2_boat)CI
   C   -1.09715606   +0.81880221   +0.00025916
   N   +0.06998750   +1.39029421   -0.14909434
   C   +1.28978892   +0.64436578   -0.25875800
   C   +1.18611345   -0.75893047   -0.03389232
   C   -0.04519493   -1.40799651   +0.09512821
   N   -1.18170354   -0.48020530   +0.10890083
   C   +2.44281740   -1.58585047   -0.01597845
   O   -0.35893250   -2.58343352   +0.21764488
   Se  -2.69709016   +1.87937488   +0.04442344
   H   +0.08305404   +2.37783104   -0.29811659
   H   +2.16040981   +1.20947620   +0.04518654
   H   -2.07566555   -0.90513402   +0.26189688
   H   +2.21799346   -2.59613517   +0.31844530
   H   +3.19041049   -1.15620522   +0.65855292
   H   +2.89890272   -1.65163864   -1.00882947
```

```
   15
    (S1/S2_pyramid)CI
   C   -1.18891547   +0.82786730   +0.38125186
   N   +0.06504003   +1.36746551   +0.34354606
   C   +1.22275853   +0.62923049   +0.21269997
   C   +1.19574996   -0.72954220   +0.03548153
   C   -0.11162795   -1.39808391   -0.03512550
   N   -1.20363707   -0.51523505   +0.12600371
   C   +2.44120239   -1.56418903   -0.11780612
   O   -0.30165257   -2.59389914   -0.21487637
   Se  -2.43979836   +1.89603992   -1.01459478
   H   +0.10571590   +2.38201156   +0.41298467
   H    2.15479121   +1.19956974   +0.26250929
   H   -2.12562029   -0.95104039   +0.06880587
   H   +3.09187075   -1.48174726   +0.76845614
   H   +3.02492866   -1.25649847   -1.00118700
   H   +2.15292930   -2.61733409   -0.24238035


   15
    (T1/T2)CI
   C   -1.20310092   +0.86474880   +0.17436161
   N   +0.05614802   +1.39591568   +0.43037149
   C   +1.21665098   +0.67646357   +0.16225480
   C   +1.18511637   -0.68330580   +0.05393534
   C   -0.09721497   -1.35944034   +0.33248439
   N   -1.21491855   -0.51069819   +0.35122154
   C   +2.36381919   -1.54569854   -0.29134368
   O   -0.21195133   -2.56207221   +0.54266684
   Se  -2.14787194   +1.54107467   -1.47946904
   H   +0.12007453   +2.40578342   +0.38959670
   H   +2.13074046   +1.28194127   +0.07342740
   H   -2.10728251   -0.99564804   +0.38735417
   H   +2.41048569   -1.74320103   -1.37559719
   H   +2.28267778   -2.50952813   +0.22981430
   H   +3.30036224   -1.06172013   +0.00469031


   15
    (S2_boat/T2)ISC
   C   -1.11872479   +0.83912464   -0.01666059
   N   +0.08002648   +1.39586150   +0.13119161
   C   +1.27736158   +0.64385365   +0.29338372
   C   +1.19324147   -0.76311092   +0.03514737
   C   -0.04905148   -1.43578134   -0.10637800
   N   -1.21547085   -0.50073275   -0.04634504
   C   +2.45190467   -1.58531920   -0.00360990
   O   -0.33838600   -2.62641945   -0.28923854
   Se  -2.70303812   +1.92253234   -0.07609590
   H   +0.10289244   +2.40852187   +0.22503357
   H   +2.19107286   +1.21930435   +0.12085167
   H   -2.12140320   -0.92527547   -0.24460132
   H   +2.20110258   -2.62902613   -0.24325005
   H   +2.97410444   -1.56443921   +0.97079073
   H   +3.15810295   -1.20447889   -0.76445032
```

```
15
  (S0/S1)CI
C  -1.27535093  +0.83098481  +0.50875643
N  +0.03645215  +1.37851237  +0.30321895
C  +1.17947282  +0.63369077  +0.18297685
C  +1.17815467  -0.71936819  +0.02181729
C  -0.13137559  -1.39762283  +0.04848304
N  -1.22706638  -0.54028562  +0.16548907
C  +2.42756680  -1.54300916  -0.15977683
O  -0.28691451  -2.61175087  -0.06213955
Se -2.17836523  +1.90898643  -1.30934063
H  +0.11739957  +2.36910168  +0.51273493
H  +2.10535431  +1.21986524  +0.17648372
H  -2.11058900  -1.04121189  +0.22784084
H  +2.19670547  -2.44176918  -0.75703347
H  +2.84077230  -1.88725657   0.80967136
H  +3.21151858  -0.96425197  -0.68341300


  15
  (S1/T2)ISC
C  -1.19176884  +0.89336104  +0.24358017
N  +0.09560811  +1.42728127  +0.24267093
C  +1.23088775  +0.66021808  +0.11703288
C  +1.19238147  -0.70343990  -0.00160678
C  -0.11349266  -1.37477124  +0.08682847
N  -1.20312767  -0.50687870  +0.24235102
C  +2.41293425  -1.56458165  -0.15639075
O  -0.27783370  -2.59125398  +0.07242229
Se -2.50051445  +1.67140110  -1.03360562
H  +0.18555753  +2.43665298  +0.26951244
H  +2.17280689  +1.21711480  +0.12976917
H  -2.09847560  -0.97588788  +0.36878561
H  +2.48496513  -2.29294428  +0.66828173
H  +3.32961878  -0.95379464  -0.17287547
H  +2.36418804  -2.14786200  -1.09098714


  15
  (S0/T1)ISC
C  -1.30608013  +0.83604045  +0.34835704
N  +0.02619457  +1.38431485  +0.30976453
C  +1.17264912  +0.65875338  +0.10630608
C  +1.15939256  -0.69228719  -0.00028726
C  -0.13753571  -1.40396877  +0.13830287
N  -1.23559230  -0.57553807  +0.32644136
C  +2.39428849  -1.52428513  -0.19423614
O  -0.23901555  -2.62811352  +0.12689116
Se -1.92817824  +1.82025560  -1.33021815
H  +0.07383021  +2.39433550  +0.41557915
H   2.10039977  +1.24345116  +0.04436284
H  -2.11725282  -1.07437196  +0.42755593
H  +2.33128177  -2.10132560  -1.12920825
H  +2.49810598  -2.25536338  +0.62127134
H  +3.29124733  -0.88728234  -0.22511351
```