- SUPPLEMENTARY INFORMATION -

Nature and Strength of Chalcogen–π Bonds

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Benchmark Data

Table S1 Chalcogen bond energies Δ*E* (in kcal mol^{-1}) computed with DFT and CC.[a]

Complex	DFT	CC	Error Δ (DFT-CC)
F_2O•••ac	-1.3	0.2	-1.5
F_2S•••ac	-4.3	-2.2	-2.1
F_2Te•••ac	-9.4	-5.7	-3.7
F_2Se•••ac	-7.5	-3.7	-3.8
Cl_2Se•••ac	-5.3	-2.7	-2.6
Br_2Se•••ac	-5.0	-2.5	-2.5
I_2Se•••ac	-4.3	-2.1	-2.2
F_2Se•••et	-9.1	-4.2	-4.9
F_2Se•••2but	-11.3	-6.4	-4.9
Average error			-3.1

[a] Computed with correction for basis-set superposition error. DFT = ZORA-BLYP-D3(BJ)/QZ4Pae//ZORA-BLYP-D3(BJ)/TZ2Psc. CC = DLPNO-CCSD(T)/aug-cc-pV5Z-DK, aug-cc-pVQZ-DK.

Table S2. Chalcogen bond energies ΔE (in kcal mol^{-1}) computed with DFT and CC.[a]

Complex	DFT	CC	Error Δ (DFT-CC)
F_2O•••ac	-1.3	0.1	-1.4
F_2S•••ac	-4.3	-2.3	-2.0
F_2Te•••ac	-9.4	-8.4	-1.0
F_2Se•••ac	-7.5	-4.6	-2.9
Cl_2Se•••ac	-5.4	-3.4	-2.0
Br_2Se•••ac	-5.1	-3.5	-1.4
I_2Se•••ac	-4.4	-3.8	-0.6
F_2Se•••et	-9.1	-5.6	-3.5
F_2Se•••2but	-11.4	-7.9	-3.5
Average error			-2.0

[a] Computed without correction for basis-set superposition error. DFT = ZORA-BLYP-D3(BJ)/QZ4Pae//ZORA-BLYP-D3(BJ)/TZ2Psc. CC = DLPNO-CCSD(T)/aug-cc-pV5Z-DK, aug-cc-pVQZ-DK.

Orbitals

Table S3 HOMO-LUMO energy gap Δε (in eV), overlap S, and $S^2/\Delta\varepsilon$ for the chalcogen-π complexes.[a]

Complex	**Δε**	**S**	**$(S^2/\Delta\varepsilon)\cdot10^3$**	Complex	**Δε**	**S**	**$(S^2/\Delta\varepsilon)\cdot10^3$**
F_2O•••ac	1.84	0.06	1.95	F_2Se•••ac	3.03	0.17	9.54
Cl_2O•••ac	2.01	0.06	1.79	Cl_2Se•••ac	2.91	0.14	6.74
Br_2O•••ac	1.97	0.07	2.49	Br_2Se•••ac	2.75	0.13	6.14
I_2O•••ac	2.14	0.07	2.29	I_2Se•••ac	2.71	0.09	2.99
F_2O•••et	1.24	0.07	3.95	F_2Se•••et	2.39	0.19	15.09
Cl_2O•••et	1.51	0.07	3.24	Cl_2Se•••et	2.40	0.15	9.37
Br_2O•••et	1.46	0.08	4.37	Br_2Se•••et	2.25	0.14	8.73
I_2O•••et	1.66	0.08	3.85	I_2Se•••et	2.22	0.13	7.60
F_2O•••2but	0.19	0.07	25.93	F_2Se•••2but	1.63	0.17	17.78
Cl_2O•••2but	0.58	0.06	6.17	Cl_2Se•••2but	1.55	0.12	9.29
Br_2O•••2but	0.57	0.07	8.55	Br_2Se•••2but	1.41	0.11	8.59
I_2O•••2but	0.83	0.07	5.91	I_2Se•••2but	1.40	0.08	4.58
F_2S•••ac	3.58	0.13	4.72	F_2Te•••ac	2.89	0.20	13.83
Cl_2S•••ac	3.14	0.10	3.18	Cl_2Te•••ac	3.11	0.18	10.42
Br_2S•••ac	2.84	0.10	3.52	Br_2Te•••ac	2.99	0.14	6.56
I_2S•••ac	2.74	0.08	2.33	I_2Te•••ac	2.92	0.12	4.93
F_2S•••et	3.00	0.16	8.52	F_2Te•••et	2.27	0.22	21.30
Cl_2S•••et	2.67	0.11	4.53	Cl_2Te•••et	2.57	0.20	15.57
Br_2S•••et	2.39	0.11	5.07	Br_2Te•••et	2.49	0.16	10.29
I_2S•••et	2.28	0.10	4.39	I_2Te•••et	2.44	0.13	6.94
F_2S•••2but	2.09	0.14	9.40	F_2Te•••2but	1.55	0.18	20.96
Cl_2S•••2but	1.77	0.09	4.58	Cl_2Te•••2but	1.75	0.16	14.65
Br_2S•••2but	1.49	0.08	4.30	Br_2Te•••2but	1.66	0.12	8.66
I_2S•••2but	1.42	0.08	4.50	I_2Te•••2but	1.62	0.09	5.01

[a] Computed at ZORA-BLYP-D3(BJ)/QZ4Pae//ZORA-BLYP-D3(BJ)/TZ2Psc.

Structures

Table S4 Geometries of the stationary points for the unsaturated substrates. [a]

2-butyne

E = -1.99297282 Ha

C	2.418473000	-0.375988000	-0.605218000
C	2.418473000	-0.375988000	0.605218000
C	2.418492000	-0.375903000	-2.068288000
H	3.441539000	-0.388912000	-2.466318000
H	1.895662000	-1.255326000	-2.466403000
H	1.918271000	0.516629000	-2.466253000
C	2.418492000	-0.375903000	2.068288000
H	1.895662000	-1.255326000	2.466403000
H	3.441539000	-0.388912000	2.466318000
H	1.918271000	0.516629000	2.466253000

Ethylene

E= -1.13133289 Ha

C	-1.840613000	-0.753021000	0.006481000
C	-1.840613000	-0.753021000	1.339518000
H	-1.840613000	0.172802000	-0.565823000
H	-1.840613000	-1.678843000	-0.565823000
H	-1.840613000	0.172802000	1.911822000
H	-1.840613000	-1.678843000	1.911822000

Acetylene

E = -0.8130827 Ha

C	-0.021270000	-0.267224000	-0.934497000
C	-0.021270000	-0.267224000	0.270179000
H	-0.021270000	-0.267224000	1.337050000
H	-0.021270000	-0.267224000	-2.001368000

[a] Computed at ZORA-BLYP-D3(BJ)/QZ4Pae//ZORA-BLYP-D3(BJ)/TZ2Psc

Table S5 Geometries of the stationary points for oxygen complexes. [a]

F_2O

E= -0.30075091 Ha

O	0.474869000	-0.010511000	0.000000000
F	0.773739000	1.404232000	0.000000000
F	1.767463000	-0.658595000	0.000000000

F_2O•••ac

E = -1.11870501 Ha

O	0.467249000	-0.008720000	0.000000000
F	0.770940000	1.412267000	0.000000000
F	1.776685000	-0.668137000	0.000000000
C	-2.423048000	-0.336116000	0.602620000
C	-2.423048000	-0.336116000	-0.602620000
H	-2.422664000	-0.335024000	1.669996000
H	-2.422664000	-0.335024000	-1.669996000

F_2O•••et

E= -1.43967342 Ha

O	0.501507000	-0.062737000	0.000000000
F	0.778102000	1.367139000	0.000000000
F	1.834099000	-0.706590000	0.000000000
C	-2.320230000	-0.198067000	0.668414000
H	-2.342884000	-1.123604000	1.239858000
H	-2.296693000	0.727473000	1.239545000
C	-2.320230000	-0.198067000	-0.668414000
H	-2.296693000	0.727473000	-1.239545000
H	-2.342884000	-1.123604000	-1.239858000

F_2O•••2but

E= -2.31137570 Ha

O	-0.573739000	0.147912000	0.000000000
C	1.922369000	-0.174002000	-0.607699000
C	1.922369000	-0.174002000	0.607699000
F	-0.806750000	1.600215000	0.000000000
F	-1.966072000	-0.496630000	0.000000000
C	1.931354000	-0.165013000	-2.064999000
H	2.959806000	-0.176235000	-2.448717000
H	1.409195000	-1.041476000	-2.468304000
H	1.435083000	0.733792000	-2.451864000
C	1.931354000	-0.165013000	2.064999000
H	1.409195000	-1.041476000	2.468304000
H	2.959806000	-0.176235000	2.448717000
H	1.435083000	0.733792000	2.451864000

Cl_2O

E=-0.26463878 Ha

O	0.413107000	-0.041533000	0.000000000
Cl	0.651878000	1.694741000	0.000000000
Cl	1.920502000	-0.935605000	0.000000000

Cl_2O•••ac

E= -1.08226418 Ha

O	0.458498000	-0.058004000	0.000000000
Cl	0.668375000	1.686159000	0.000000000
Cl	1.992381000	-0.926570000	0.000000000
C	-2.570276000	-0.326580000	0.602344000
C	-2.570276000	-0.326580000	-0.602344000
H	-2.562985000	-0.325707000	1.669332000
H	-2.562985000	-0.325707000	-1.669332000

Cl_2O•••et

E= -1.40355594 Ha

O	0.484296000	-0.062965000	0.000000000
Cl	0.625139000	1.695380000	0.000000000
Cl	2.058949000	-0.872114000	0.000000000
C	-2.401713000	-0.384280000	0.667928000
H	-2.394376000	-1.309924000	1.239365000
H	-2.401416000	0.541624000	1.238582000
C	-2.401713000	-0.384280000	-0.667928000
H	-2.401416000	0.541624000	-1.238582000
H	-2.394376000	-1.309924000	-1.239365000

Cl_2O•••2but

E=-2.27442399 Ha

O	-0.646368000	0.157894000	0.000000000
Cl	-0.732505000	1.923907000	0.000000000
Cl	-2.266204000	-0.617110000	0.000000000
C	2.030055000	-0.291037000	-0.606410000
C	2.030055000	-0.291037000	0.606410000
C	2.011936000	-0.277858000	-2.064133000
H	3.025590000	-0.377185000	-2.473876000
H	1.405737000	-1.103262000	-2.458157000
H	1.586044000	0.661199000	-2.440117000
C	2.011936000	-0.277858000	2.064133000
H	1.405737000	-1.103262000	2.458157000
H	3.025590000	-0.377185000	2.473876000
H	1.586044000	0.661199000	2.440117000

Br_2O

E=-0.24862694 Ha

O	0.424678000	-0.078557000	0.000000000
Br	0.611646000	1.807521000	0.000000000
Br	2.055964000	-1.043767000	0.000000000

Br_2O•••ac

E= -1.06666675 Ha

O	0.411790000	-0.064429000	0.000000000
Br	0.624906000	1.824886000	0.000000000
Br	2.041678000	-1.049363000	0.000000000
C	-2.559411000	-0.371003000	0.602445000
C	-2.559411000	-0.371003000	-0.602445000
H	-2.549909000	-0.369648000	1.669343000
H	-2.549909000	-0.369648000	-1.669343000

Br_2O•••et

E= -1.38836178 Ha

O	0.425718000	-0.054668000	0.000000000
Br	0.586723000	1.849837000	0.000000000
Br	2.090530000	-0.998951000	0.000000000
C	-2.349204000	-0.466844000	0.668589000
H	-2.259565000	-1.388212000	1.239481000
H	-2.428986000	0.455741000	1.238636000
C	-2.349204000	-0.466844000	-0.668589000
H	-2.428986000	0.455741000	-1.238636000
H	-2.259565000	-1.388212000	-1.239481000

Br_2O•••2but

E= -2.25971276 Ha

O	-0.594832000	0.165155000	0.000000000
Br	-0.692575000	2.079324000	0.000000000
Br	-2.304029000	-0.741095000	0.000000000
C	2.011678000	-0.339760000	-0.606836000
C	2.011678000	-0.339760000	0.606836000
C	1.993715000	-0.325445000	-2.063935000
H	2.997777000	-0.495613000	-2.473959000
H	1.330306000	-1.106369000	-2.456062000
H	1.633689000	0.641199000	-2.438510000
C	1.993715000	-0.325445000	2.063935000
H	1.330306000	-1.106369000	2.456062000
H	2.997777000	-0.495613000	2.473959000
H	1.633689000	0.641199000	2.438510000

I_2O

E= -0.24538325 Ha

O	0.396113000	-0.074066000	0.000000000
I	0.552732000	1.973942000	0.000000000
I	2.115828000	-1.197205000	0.000000000

I_2O•••ac

E=-1.06364869 Ha

O	0.396968000	-0.080547000	0.000000000
I	0.552884000	1.972672000	0.000000000
I	2.125416000	-1.197231000	0.000000000
C	-2.607648000	-0.360683000	0.602358000
C	-2.607648000	-0.360683000	-0.602358000
H	-2.595579000	-0.359465000	1.669100000
H	-2.595579000	-0.359465000	-1.669100000

I_2O•••et

E=-1.38540746 Ha

O	0.412790000	-0.076212000	0.000000000
I	0.511817000	1.988680000	0.000000000
I	2.181484000	-1.139933000	0.000000000
C	-2.414607000	-0.444956000	0.668273000
H	-2.253541000	-1.356426000	1.239117000
H	-2.564038000	0.468979000	1.238354000
C	-2.414607000	-0.444956000	-0.668273000
H	-2.564038000	0.468979000	-1.238354000
H	-2.253541000	-1.356426000	-1.239117000

I_2O•••2but

E=-2.25673036 Ha

O	-0.610639000	0.108331000	0.000000000
I	-0.599612000	2.177518000	0.000000000
I	-2.440791000	-0.866778000	0.000000000
C	2.124115000	-0.258664000	-0.606284000
C	2.124115000	-0.258664000	0.606284000
C	2.097952000	-0.243973000	-2.063576000
H	3.096500000	-0.426234000	-2.481663000
H	1.421339000	-1.015728000	-2.451289000
H	1.747026000	0.727147000	-2.436042000
C	2.097952000	-0.243973000	2.063576000
H	1.421339000	-1.015728000	2.451289000
H	3.096500000	-0.426234000	2.481663000
H	1.747026000	0.727147000	2.436042000

[a] Computed at ZORA-BLYP-D3(BJ)/QZ4Pae//ZORA-BLYP-D3(BJ)/TZ2Psc

Table S6 Geometries of the stationary points for sulfur complexes. [a]

F_2S

E= -0.37754084 Ha

S	0.241423000	0.289180000	0.000000000
F	0.118137000	-1.346483000	0.000000000
F	1.874929000	0.438459000	0.000000000

F_2S•••ac

E = -1.20031061 Ha

S	0.448300000	-0.324400000	0.000000000
F	0.465700000	1.322000000	0.000000000
F	2.092700000	-0.554100000	0.000000000
C	-2.418100000	-0.162700000	0.603600000
C	-2.418100000	-0.162700000	-0.603600000
H	-2.433700000	-0.156200000	1.670900000
H	-2.433700000	-0.156200000	-1.670900000

F_2S•••et

E = -1.52187844 Ha

S	0.462500000	-0.375100000	0.000000000
F	0.493800000	1.275000000	0.000000000
F	2.116400000	-0.585200000	0.000000000
C	-2.295100000	-0.039900000	0.671000000
H	-2.471500000	-0.948400000	1.242600000
H	-2.138900000	0.872000000	1.242100000
C	-2.295100000	-0.039900000	-0.671000000
H	-2.138900000	0.872000000	-1.242100000
H	-2.471500000	-0.948400000	-1.242600000

F_2S•••2but

E = -2.39375124 Ha

S	-0.693800000	-0.178500000	0.000000000
F	-0.659300000	1.475200000	0.000000000
F	-2.371000000	-0.304500000	0.000000000
C	2.008700000	-0.102600000	-0.608100000
C	2.008700000	-0.102600000	0.608100000
C	2.085400000	-0.090800000	-2.068500000
H	3.131500000	-0.053000000	-2.397900000
H	1.624800000	-0.989100000	-2.496400000
H	1.565800000	0.782400000	-2.480400000
C	2.085400000	-0.090800000	2.068500000
H	1.624800000	-0.989100000	2.496400000
H	3.131500000	-0.053000000	2.397900000
H	1.565800000	0.782400000	2.480400000

Cl_2S

E = -0.26514050 Ha

S	0.188960000	-0.486495000	0.000000000
Cl	0.142198000	1.588921000	0.000000000
Cl	2.206636000	-0.974875000	0.000000000

Cl_2S•••ac

E = -1.08618590 Ha

S	0.172700000	-0.493200000	0.000000000
Cl	0.149700000	1.589100000	0.000000000
Cl	2.214000000	-0.969000000	0.000000000
C	-2.918800000	-0.620200000	0.602900000
C	-2.918800000	-0.620200000	-0.602900000
H	-2.919000000	-0.616500000	1.669900000
H	-2.919000000	-0.616500000	-1.669900000

Cl_2S•••et

E = -1.40774031 Ha

S	0.409500000	-0.367100000	0.000000000
Cl	0.470900000	1.718200000	0.000000000
Cl	2.439800000	-0.908400000	0.000000000
C	-2.610700000	-0.198400000	0.668800000
H	-2.770100000	-1.110500000	1.240200000
H	-2.455400000	0.714100000	1.239500000
C	-2.610700000	-0.198400000	-0.668800000
H	-2.455400000	0.714100000	-1.239500000
H	-2.770100000	-1.110500000	-1.240200000

Cl_2S•••2but

E = -2.28002547 Ha

S	-0.644300000	-0.173000000	0.000000000
Cl	-0.603800000	1.915500000	0.000000000
Cl	-2.724900000	-0.605800000	0.000000000
C	2.212000000	-0.202800000	-0.607100000
C	2.212000000	-0.202800000	0.607100000
C	2.228600000	-0.179700000	-2.068000000
H	3.256300000	-0.112900000	-2.446200000
H	1.771700000	-1.085900000	-2.483700000
H	1.668400000	0.683400000	-2.448600000
C	2.228600000	-0.179700000	2.068000000
H	1.771700000	-1.085900000	2.483700000
H	3.256300000	-0.112900000	2.446200000
H	1.668400000	0.683400000	2.448600000

Br_2S

E = -0.23463753 Ha

S	0.273248000	-0.395957000	0.000000000
Br	0.221818000	1.848629000	0.000000000
Br	2.443631000	-0.970689000	0.000000000

Br_2S•••ac

E = -1.05566517 Ha

S	0.254000000	-0.403700000	0.000000000
Br	0.226300000	1.848100000	0.000000000
Br	2.447000000	-0.967000000	0.000000000
C	-2.852700000	-0.648700000	0.602900000
C	-2.852700000	-0.648700000	-0.602900000
H	-2.852800000	-0.645600000	1.669800000
H	-2.852800000	-0.645600000	-1.669800000

Br_2S•••et

E = -1.37745878 Ha

S	0.301500000	-0.415400000	0.000000000
Br	0.335100000	1.839000000	0.000000000
Br	2.488000000	-1.019200000	0.000000000
C	-2.713000000	-0.359500000	0.669000000
H	-2.827000000	-1.278200000	1.240500000
H	-2.599000000	0.559300000	1.239400000
C	-2.713000000	-0.359500000	-0.669000000
H	-2.599000000	0.559300000	-1.239400000
H	-2.827000000	-1.278200000	-1.240500000

Br_2S•••2but

E = -2.24994313 Ha

S	-0.544900000	-0.208400000	0.000000000
Br	-0.485500000	2.049500000	0.000000000
Br	-2.781200000	-0.720700000	0.000000000
C	2.315700000	-0.323200000	-0.607300000
C	2.315700000	-0.323200000	0.607300000
C	2.334000000	-0.301000000	-2.067900000
H	3.362000000	-0.229100000	-2.444500000
H	1.882400000	-1.209800000	-2.483600000
H	1.769700000	0.559100000	-2.449100000
C	2.334000000	-0.301000000	2.067900000
H	1.882400000	-1.209800000	2.483600000
H	3.362000000	-0.229100000	2.444500000
H	1.769700000	0.559100000	2.449100000

I_2S

E = -0.21167251 Ha

S	0.224145000	-0.455154000	0.000000000
I	0.126750000	1.993448000	0.000000000
I	2.589656000	-1.095043000	0.000000000

I_2S•••ac

E = -1.03229559 Ha

S	0.208300000	-0.462300000	0.000000000
I	0.129200000	1.993200000	0.000000000
I	2.591300000	-1.093000000	0.000000000
C	-2.939800000	-0.634800000	0.602600000
C	-2.939800000	-0.634800000	-0.602600000
H	-2.936300000	-0.630400000	1.669800000
H	-2.936300000	-0.630400000	-1.669800000

I_2S•••et

E = -1.35412334 Ha

S	0.223700000	-0.489000000	0.000000000
I	0.192400000	1.973100000	0.000000000
I	2.602300000	-1.158100000	0.000000000
C	-2.859700000	-0.476500000	0.668600000
H	-2.978400000	-1.394500000	1.240400000
H	-2.740900000	0.442000000	1.238400000
C	-2.859700000	-0.476500000	-0.668600000
H	-2.740900000	0.442000000	-1.238400000
H	-2.978400000	-1.394500000	-1.240400000

I_2S•••2but

E = -2.22663862 Ha

S	-0.468300000	-0.298000000	0.000000000
I	-0.327400000	2.159600000	0.000000000
I	-2.903300000	-0.840400000	0.000000000
C	2.418500000	-0.394600000	-0.607300000
C	2.418500000	-0.394600000	0.607300000
C	2.418900000	-0.363200000	-2.067500000
H	3.443100000	-0.365500000	-2.460500000
H	1.892600000	-1.231600000	-2.481800000
H	1.914800000	0.540600000	-2.433200000
C	2.418900000	-0.363200000	2.067500000
H	1.892600000	-1.231600000	2.481800000
H	3.443100000	-0.365500000	2.460500000
H	1.914800000	0.540600000	2.433200000

[a] Computed at ZORA-BLYP-D3(BJ)/QZ4Pae//ZORA-BLYP-D3(BJ)/TZ2Psc

Table S7 Geometries of the stationary points for selenium complexes. [a]

F_2Se

E = -0.36081381 Ha

Se	0.206812000	0.320676000	0.000000000
F	0.111500000	-1.463448000	0.000000000
F	1.989002000	0.447251000	0.000000000

F_2Se•••ac

E = -1.18867680 Ha

Se	0.403300000	-0.361900000	0.000000000
F	0.453000000	1.432200000	0.000000000
F	2.211700000	-0.559600000	0.000000000
C	-2.280400000	-0.161800000	0.605900000
C	-2.280400000	-0.161800000	-0.605900000
H	-2.335800000	-0.144800000	1.672500000
H	-2.335800000	-0.144800000	-1.672500000

F_2Se•••et

E = -1.51164808 Ha

Se	0.399800000	-0.409800000	0.000000000
F	0.466300000	1.387600000	0.000000000
F	2.224800000	-0.566900000	0.000000000
C	-2.168300000	-0.030400000	0.677300000
H	-2.389500000	-0.929800000	1.247100000
H	-2.008900000	0.881300000	1.246400000
C	-2.168300000	-0.030400000	-0.677300000
H	-2.008900000	0.881300000	-1.246400000
H	-2.389500000	-0.929800000	-1.247100000

F_2Se•••2but

E = -2.38348276 Ha

Se	-0.651700000	-0.237100000	0.000000000
F	-0.612000000	1.565000000	0.000000000
F	-2.486900000	-0.312900000	0.000000000
C	1.967700000	-0.116000000	-0.609900000
C	1.967700000	-0.116000000	0.609900000
C	2.112900000	-0.071300000	-2.064100000
H	3.173000000	0.019900000	-2.335500000
H	1.714000000	-0.978500000	-2.532600000
H	1.574900000	0.788700000	-2.480100000
C	2.112900000	-0.071300000	2.064100000
H	1.714000000	-0.978500000	2.532600000
H	3.173000000	0.019900000	2.335500000
H	1.574900000	0.788700000	2.480100000

Cl_2Se

E = -0.25373249 Ha

Se	0.127323000	0.399685000	0.000000000
Cl	-0.083025000	-1.804943000	0.000000000
Cl	2.327743000	0.650181000	0.000000000

Cl_2Se•••ac

E = -1.07817812 Ha

Se	0.338200000	-0.354500000	0.000000000
Cl	0.438400000	1.865900000	0.000000000
Cl	2.514100000	-0.897400000	0.000000000
C	-2.613200000	-0.347700000	0.603800000
C	-2.613200000	-0.347700000	-0.603800000
H	-2.631000000	-0.340600000	1.671500000
H	-2.631000000	-0.340600000	-1.671500000

Cl_2Se•••et

E = -1.40064794 Ha

Se	0.358200000	-0.405600000	0.000000000
Cl	0.461300000	1.820200000	0.000000000
Cl	2.550700000	-0.934200000	0.000000000
C	-2.499000000	-0.197700000	0.671700000
H	-2.653100000	-1.110700000	1.242600000
H	-2.366500000	0.718500000	1.241500000
C	-2.499000000	-0.197700000	-0.671700000
H	-2.366500000	0.718500000	-1.241500000
H	-2.653100000	-1.110700000	-1.242600000

Cl_2Se•••2but

E = -2.27336893 Ha

Se	-0.619400000	-0.225300000	0.000000000
Cl	-0.583800000	2.004200000	0.000000000
Cl	-2.855800000	-0.611100000	0.000000000
C	2.180700000	-0.221200000	-0.608000000
C	2.180700000	-0.221200000	0.608000000
C	2.257100000	-0.182600000	-2.065800000
H	3.302700000	-0.109600000	-2.392400000
H	1.821700000	-1.084700000	-2.512100000
H	1.713500000	0.685200000	-2.459100000
C	2.257100000	-0.182600000	2.065800000
H	1.821700000	-1.084700000	2.512100000
H	3.302700000	-0.109600000	2.392400000
H	1.713500000	0.685200000	2.459100000

Br_2Se

E = -0.22461022 Ha

Se	0.049581000	0.478311000	0.000000000
Br	-0.208830000	-1.883183000	0.000000000
Br	2.406299000	0.777179000	0.000000000

$Br_2Se•••ac$

E = -1.04855899 Ha

Se	0.242700000	-0.408800000	0.000000000
Br	0.301700000	1.972300000	0.000000000
Br	2.566400000	-1.003900000	0.000000000
C	-2.740200000	-0.517700000	0.603600000
C	-2.740200000	-0.517700000	-0.603600000
H	-2.754700000	-0.511600000	1.671300000
H	-2.754700000	-0.511600000	-1.671300000

$Br_2Se•••et$

E = -1.37110606 Ha

Se	0.263600000	-0.455500000	0.000000000
Br	0.329100000	1.932000000	0.000000000
Br	2.601100000	-1.046700000	0.000000000
C	-2.629300000	-0.361100000	0.671500000
H	-2.742000000	-1.280100000	1.242600000
H	-2.534600000	0.560000000	1.241100000
C	-2.629300000	-0.361100000	-0.671500000
H	-2.534600000	0.560000000	-1.241100000
H	-2.742000000	-1.280100000	-1.242600000

$Br_2Se•••2but$

E = -2.24393846 Ha

Se	-0.543700000	-0.258900000	0.000000000
Br	-0.462400000	2.128500000	0.000000000
Br	-2.928500000	-0.701700000	0.000000000
C	2.278400000	-0.334400000	-0.607900000
C	2.278400000	-0.334400000	0.607900000
C	2.348500000	-0.297600000	-2.065700000
H	3.393200000	-0.239400000	-2.397800000
H	1.898200000	-1.193700000	-2.509300000
H	1.815000000	0.577800000	-2.456400000
C	2.348500000	-0.297600000	2.065700000
H	1.898200000	-1.193700000	2.509300000
H	3.393200000	-0.239400000	2.397800000
H	1.815000000	0.577800000	2.456400000

I_2Se

E = -0.20068295 Ha

Se	0.181444000	-0.475156000	0.000000000
I	0.151863000	2.100747000	0.000000000
I	2.669537000	-1.142694000	0.000000000

$I_2Se•••ac$

E = -1.02352248 Ha

Se	0.160800000	-0.484600000	0.000000000
I	0.158700000	2.101300000	0.000000000
I	2.675700000	-1.137300000	0.000000000
C	-2.906800000	-0.632000000	0.603300000
C	-2.906800000	-0.632000000	-0.603300000
H	-2.914500000	-0.626000000	1.670800000
H	-2.914500000	-0.626000000	-1.670800000

$I_2Se•••et$

E = -1.34599555 Ha

Se	0.183500000	-0.527100000	0.000000000
I	0.189500000	2.065800000	0.000000000
I	2.707800000	-1.181700000	0.000000000
C	-2.800600000	-0.486100000	0.670500000
H	-2.903700000	-1.406000000	1.241900000
H	-2.707900000	0.435600000	1.239600000
C	-2.800600000	-0.486100000	-0.670500000
H	-2.707900000	0.435600000	-1.239600000
H	-2.903700000	-1.406000000	-1.241900000

$I_2Se•••2but$

E = -2.21881472 Ha

Se	-0.477900000	-0.324600000	0.000000000
I	-0.323700000	2.261000000	0.000000000
I	-3.052800000	-0.821000000	0.000000000
C	2.420100000	-0.424300000	-0.607400000
C	2.420100000	-0.424300000	0.607400000
C	2.467600000	-0.385900000	-2.065400000
H	3.506200000	-0.330700000	-2.416600000
H	2.006300000	-1.279400000	-2.503100000
H	1.930600000	0.492200000	-2.445900000
C	2.467600000	-0.385900000	2.065400000
H	2.006300000	-1.279400000	2.503100000
H	3.506200000	-0.330700000	2.416600000
H	1.930600000	0.492200000	2.445900000

[a] Computed at ZORA-BLYP-D3(BJ)/QZ4Pae//ZORA-BLYP-D3(BJ)/TZ2Psc

Table S8 Geometries of the stationary points for tellurium complexes. [a]

F_2Te

E = -0.36908760 Ha

Te	0.192762000	0.333544000	0.000000000
F	0.114787000	-1.608497000	0.000000000
F	2.133078000	0.446787000	0.000000000

F_2Te•••ac

E = -1.19998570 Ha

Te	0.423300000	-0.404900000	0.000000000
F	0.418800000	1.545500000	0.000000000
F	2.398400000	-0.441000000	0.000000000
C	-2.325800000	-0.083700000	0.607500000
C	-2.325800000	-0.083700000	-0.607500000
H	-2.414400000	-0.056500000	1.671800000
H	-2.414400000	-0.056500000	-1.671800000

F_2Te•••et

E = -1.52411312 Ha

Te	0.416000000	-0.453500000	0.000000000
F	0.433400000	1.500700000	0.000000000
F	2.399300000	-0.435700000	0.000000000
C	-2.225900000	0.067800000	0.680600000
H	-2.509900000	-0.814000000	1.250000000
H	-2.027200000	0.973400000	1.247000000
C	-2.225900000	0.067800000	-0.680600000
H	-2.027200000	0.973400000	-1.247000000
H	-2.509900000	-0.814000000	-1.250000000

F_2Te•••2but

E = -2.39476081 Ha

Te	-0.678500000	-0.292400000	0.000000000
F	-0.562800000	1.661800000	0.000000000
F	-2.662100000	-0.182200000	0.000000000
C	2.053100000	-0.072300000	-0.610900000
C	2.053100000	-0.072300000	0.610900000
C	2.237700000	-0.011900000	-2.061500000
H	3.304200000	0.101200000	-2.298500000
H	1.868800000	-0.920800000	-2.549900000
H	1.696600000	0.842500000	-2.484300000
C	2.237700000	-0.011900000	2.061500000
H	1.868800000	-0.920800000	2.549900000
H	3.304200000	0.101200000	2.298500000
H	1.696600000	0.842500000	2.484300000

Cl_2Te

E = -0.25351206 Ha

Te	0.117323000	0.407479000	0.000000000
Cl	-0.068756000	-1.971774000	0.000000000
Cl	2.492121000	0.643859000	0.000000000

Cl_2Te•••ac

E = -1.08029858 Ha

Te	0.338900000	-0.423900000	0.000000000
Cl	0.422200000	1.971600000	0.000000000
Cl	2.724400000	-0.831000000	0.000000000
C	-2.664800000	-0.183900000	0.604500000
C	-2.664800000	-0.183900000	-0.604500000
H	-2.696700000	-0.170700000	1.672000000
H	-2.696700000	-0.170700000	-1.672000000

Cl_2Te•••et

E = -1.40348349 Ha

Te	0.354800000	-0.477900000	0.000000000
Cl	0.444600000	1.923300000	0.000000000
Cl	2.758900000	-0.849600000	0.000000000
C	-2.534800000	-0.043000000	0.673800000
H	-2.765700000	-0.939500000	1.244700000
H	-2.341700000	0.862900000	1.242500000
C	-2.534800000	-0.043000000	-0.673800000
H	-2.341700000	0.862900000	-1.242500000
H	-2.765700000	-0.939500000	-1.244700000

Cl_2Te•••2but

E = -2.27589722 Ha

Te	-0.629800000	-0.315100000	0.000000000
Cl	-0.543500000	2.087500000	0.000000000
Cl	-3.062300000	-0.518800000	0.000000000
C	2.265900000	-0.138400000	-0.608600000
C	2.265900000	-0.138400000	0.608600000
C	2.371800000	-0.085300000	-2.065100000
H	3.422700000	0.021800000	-2.364800000
H	1.973400000	-0.995100000	-2.529200000
H	1.811900000	0.770100000	-2.462300000
C	2.371800000	-0.085300000	2.065100000
H	1.973400000	-0.995100000	2.529200000
H	3.422700000	0.021800000	2.364800000
H	1.811900000	0.770100000	2.462300000

Br_2Te

E = -0.22222590 Ha

Te	0.026712000	0.497913000	0.000000000
Br	-0.212513000	-2.040307000	0.000000000
Br	2.559568000	0.788336000	0.000000000

Br_2Te•••ac

E = -1.04814302 Ha

Te	0.225200000	-0.489900000	0.000000000
Br	0.302000000	2.066200000	0.000000000
Br	2.755400000	-0.981500000	0.000000000
C	-2.830900000	-0.312600000	0.604200000
C	-2.830900000	-0.312600000	-0.604200000
H	-2.856400000	-0.301400000	1.671800000
H	-2.856400000	-0.301400000	-1.671800000

Br_2Te•••et

E = -1.37120309 Ha

Te	0.243300000	-0.543800000	0.000000000
Br	0.325100000	2.018800000	0.000000000
Br	2.791300000	-1.007200000	0.000000000
C	-2.703600000	-0.164500000	0.673000000
H	-2.915400000	-1.065700000	1.244000000
H	-2.522200000	0.743900000	1.241600000
C	-2.703600000	-0.164500000	-0.673000000
H	-2.522200000	0.743900000	-1.241600000
H	-2.915400000	-1.065700000	-1.244000000

Br_2Te•••2but

E = -2.24385961 Ha

Te	0.011500000	-0.562700000	0.000000000
Br	-0.596100000	1.928400000	0.000000000
Br	2.600500000	-0.335200000	0.000000000
C	-2.895800000	-0.991800000	0.608300000
C	-2.895800000	-0.991800000	-0.608300000
C	-2.995300000	-0.962000000	2.065400000
H	-4.042900000	-1.064700000	2.376900000
H	-2.420300000	-1.775700000	2.522600000
H	-2.610700000	-0.013300000	2.459100000
C	-2.995300000	-0.962000000	-2.065400000
H	-2.420300000	-1.775700000	-2.522600000
H	-4.042900000	-1.064700000	-2.376900000
H	-2.610700000	-0.013300000	-2.459100000

I_2Te

E = -0.19435102 Ha

Te	-0.070910000	0.596828000	0.000000000
I	-0.349688000	-2.149737000	0.000000000
I	2.670499000	0.922413000	0.000000000

I_2Te•••ac

E = -1.01887095 Ha

Te	0.120900000	-0.562700000	0.000000000
I	0.168500000	2.207300000	0.000000000
I	2.845700000	-1.143600000	0.000000000
C	-3.031900000	-0.429600000	0.603600000
C	-3.031900000	-0.429600000	-0.603600000
H	-3.047800000	-0.420200000	1.671200000
H	-3.047800000	-0.420200000	-1.671200000

I_2Te•••et

E = -1.34172275 Ha

Te	0.141700000	-0.613600000	0.000000000
I	0.191600000	2.163000000	0.000000000
I	2.881400000	-1.176200000	0.000000000
C	-2.904200000	-0.279800000	0.671600000
H	-3.102700000	-1.183700000	1.243100000
H	-2.725100000	0.629400000	1.240000000
C	-2.904200000	-0.279800000	-0.671600000
H	-2.725100000	0.629400000	-1.240000000
H	-3.102700000	-1.183700000	-1.243100000

I_2Te•••2but

E = -2.21458402 Ha

Te	-0.513800000	-0.395300000	0.011800000
I	-0.243200000	2.366600000	-0.032100000
I	-3.309800000	-0.644000000	0.009200000
C	2.496800000	-0.342800000	-0.582900000
C	2.492900000	-0.432000000	0.629100000
C	2.567800000	-0.184200000	-2.032600000
H	3.612000000	-0.084000000	-2.356200000
H	2.129200000	-1.044900000	-2.551400000
H	2.023200000	0.714700000	-2.347700000
C	2.562600000	-0.497900000	2.086200000
H	2.112500000	-1.422300000	2.467600000
H	3.607600000	-0.463200000	2.421000000
H	2.029500000	0.348000000	2.537600000

[a] Computed at ZORA-BLYP-D3(BJ)/QZ4Pae//ZORA-BLYP-D3(BJ)/TZ2Psc