Electronic Supplementary Information for

Theoretical Spectroscopic Studies on Chemical and Electronic Structures of Selenocysteine and Pyrrolysine

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Table S1. The relative electronic energies (ΔE), relative Gibbs free energies (ΔG) (in kcal mol^{-1}) and the equilibrium distributions (Dis) of the most stable conformers of Sec in its canonical (U_{c1}-U_{c10}), deprotonated (U_{d1}-U_{d5}) and protonated (U_{p1}-U_{p5}) forms at 298 and 498 K, calculated by the CBS-QB3 method. The previous conformational results (cn, dsn pn, n=1,2,3…) in Ref. 29 were also calculated at the same level and given for comparison.

Conf.	Ref. 29	ΔE	298K		498K	
			ΔG	Dis	ΔG	Dis
U_{c1}	c1	0.00	0.00	24.41	0.00	9.56
U_{c2}	c2	1.11	0.21	17.00	-0.44	14.91
U_{c3}		1.17	0.09	20.82	-0.68	19.06
U_{c4}	c4	1.42	1.01	4.41	0.73	4.58
U_{c5}		1.43	1.18	3.31	1.01	3.46
U_{c6}	c5	1.63	0.76	6.71	0.11	8.52
U_{c7}		1.69	0.99	4.59	0.46	6.01
U_{c8}	c6	1.84	0.93	5.08	0.26	7.34
U_{c9}		2.04	1.00	4.50	0.26	7.35
U_{c10}		2.29	1.80	1.16	1.46	2.19
U_{d1}	ds1	0.00	0.00	49.59	0.00	39.13
U_{d2}	ds2	0.31	0.24	32.79	0.20	32.08
U_{d3}		0.97	0.95	10.00	0.92	15.44
U_{d4}	ds3	1.08	1.11	7.55	1.13	12.48
U_{d5}	ds5	3.83	3.90	0.07	3.95	0.72
U_{p1}	p1	0.00	0.00	54.30	0.00	36.29
U_{p2}	p2	0.68	0.50	23.52	0.36	25.12
U_{p3}	p3	1.02	0.77	14.69	0.60	19.75
U_{p4}	p4	1.58	1.21	6.98	0.96	13.74
U_{p5}	p5	3.19	3.07	0.30	2.97	1.80

Table S2. The relative electronic energies (ΔE), relative Gibbs free energies (ΔG) (in kcal mol^{-1}) and the equilibrium distributions (Dis) of the most stable conformers of Pyl in its canonical (O_{c1}- O_{c10}), deprotonated (O_{d1}-O_{d5}) and two protonated (O_{pb1}-O_{pb5} and O_{ps1}-O_{ps5}) forms at 298 and 498 K, calculated at the DSD-PBEP86-D3(BJ)/aug-cc-pVTZ level with zero-point correction at the B3LYP/6-311++G(d, p) level. The previous results in Ref. 30 (cn, dn, p_Bn, p_Sn, n=1,2,3…) were also calculated at the same level and given for comparison.

Conf.	Ref. 30	ΔE	298 K		498 K	
			ΔG	Dis	ΔG	Dis
O_{c1}	c1	0.00	0.00	33.53	0.00	21.12
O_{c2}	c2	0.07	0.13	26.99	0.12	18.71
O_{c3}		0.83	1.18	4.60	1.15	6.59
O_{c4}		0.91	1.24	4.14	1.22	6.15
O_{c5}	c11	0.92	1.28	3.85	1.25	5.96
O_{c6}		0.93	1.05	5.70	1.04	7.38
O_{c7}		1.02	1.08	5.45	1.06	7.20
O_{c8}	c3	1.04	1.12	5.06	1.12	6.77
O_{c9}	c14	1.26	1.11	5.15	1.02	7.53
O_{c10}	c26	1.38	1.96	1.21	1.94	2.97
O_{d1}	d1	0.00	0.00	52.18	0.00	33.85
O_{d2}	d2	0.08	0.26	33.91	0.24	26.68
O_{d3}		1.20	2.06	1.61	2.01	4.42
O_{d4}	d4	1.38	1.65	3.22	1.63	6.52
O_{d5}		1.38	2.34	0.99	2.30	3.29
O_{pb1}	p_B2	0.00	0.00	41.41	0.00	32.62
O_{pb2}	p_B1	0.06	0.07	36.91	0.07	30.44
O_{pb3}	p_B6	0.86	0.77	11.34	0.78	14.84
O_{pb4}	p_B5	1.09	1.20	5.48	1.12	10.49
O_{pb5}		1.20	1.32	4.44	1.28	8.92
O_{ps1}	p_S1	0.00	0.00	58.25	0.00	42.16
O_{ps2}	p_S2	0.37	0.43	28.21	0.42	27.58
O_{ps3}	p_S3	1.22	1.28	6.69	1.26	11.77
O_{ps4}	p_S6	1.62	1.46	4.94	1.42	10.02
O_{ps5}		2.52	2.46	0.92	2.41	3.67

Table S3. Cartesian coordinates (Å) of the most stable conformers of Sec, Pyl and ions showed in Figure 2 and 3.

	U_{c1}		
H	2.44843000	0.78552500	-1.02503100
O	2.58976300	-0.18169500	-0.92039300
C	1.74071400	-0.55394000	0.04162400
O	1.59346700	-1.69485800	0.39268100
C	0.99385400	0.63318800	0.69488400
H	1.59417300	0.87904300	1.58093900
N	1.05106500	1.79116200	-0.20343900
H	1.01987700	2.66723000	0.30467100
H	0.26231900	1.76685900	-0.84785900
C	-0.39316500	0.21201600	1.19024900
H	-0.32141700	-0.69204600	1.78997000
H	-0.84384500	1.00407200	1.78978700
Se	-1.70454600	-0.12638900	-0.25949900
H	-1.07669700	-1.38675400	-0.68427400
	U_{c2}		
H	2.27500900	-2.15043500	0.04975300
O	1.72898700	-1.53215100	0.55891600
C	1.77174200	-0.34412000	-0.09385200
O	2.38951200	-0.18497900	-1.11340300
C	0.99796800	0.75663600	0.64478200
H	1.60425700	0.97328600	1.53704700
N	0.86529000	1.98336800	-0.11921300
H	1.77099100	2.24988300	-0.49279300
H	0.27205200	1.80156200	-0.92604500
C	-0.36148800	0.28182200	1.16822900
H	-0.26142100	-0.57899000	1.82339200
H	-0.82970500	1.09980600	1.71430800
Se	-1.68250600	-0.18289900	-0.24115200
H	-1.08034300	-1.48911100	-0.55105500
	U_{c3}		
H	2.28377100	-2.14718600	-0.02313400
O	1.75933600	-1.53947500	0.52005400
C	1.76940700	-0.34147800	-0.11259800
O	2.35693800	-0.15350300	-1.14494100
C	0.99660100	0.73319700	0.66541100
H	1.60377100	0.93356500	1.55973300
N	0.85431100	1.98096400	-0.06548300

H	1.77371100	2.34407100	-0.29718400
H	0.40807600	1.78679200	-0.95884600
C	-0.35605900	0.22985200	1.17976400
H	-0.23530800	-0.68292800	1.75942300
H	-0.81779000	0.99391100	1.80090000
Se	-1.65703700	-0.24768300	-0.24259400
H	-2.04704900	1.14063400	-0.53067200
	U_{c6}		
H	3.15564800	-0.98853100	-1.00083600
O	2.72094300	-0.16232500	-0.74088800
C	1.71425000	-0.50282300	0.09766200
O	1.48153600	-1.64675200	0.39756800
C	0.97660200	0.73229600	0.63636100
H	1.56578200	1.03519600	1.51543600
N	0.90817700	1.88252400	-0.25495900
H	1.83544300	2.12465000	-0.58650400
H	0.35136100	1.63971500	-1.07074700
C	-0.40948700	0.35243300	1.15623900
H	-0.35637400	-0.47460400	1.85884900
H	-0.85618300	1.21827600	1.64235600
Se	-1.71179200	-0.15433900	-0.25661900
H	-1.16002300	-1.50364500	-0.44379200
	U_{d1}		
H	0.13519900	-1.27085700	-0.39914600
O	1.12570000	-1.49069700	-0.37043500
C	1.81718600	-0.44809900	0.08937900
O	3.02196700	-0.51516700	0.24428200
C	1.05853200	0.87311600	0.34188100
H	1.72726600	1.43589300	1.00470600
N	0.89828800	1.64981000	-0.90199100
H	1.71998400	1.53051700	-1.48794800
H	0.09659100	1.24750500	-1.39369600
C	-0.30633000	0.72423700	1.02988900
H	-0.18230700	0.18538100	1.97252900
H	-0.67299400	1.72803300	1.25532200
Se	-1.69733600	-0.21334600	-0.07045600
	U_{d2}		
H	0.21355900	-1.40493200	-0.04792400
O	-0.74487500	-1.74923900	0.03247300
C	-1.60491200	-0.74184400	-0.01594000
O	-2.79856500	-0.92190800	0.14808000

C	-1.04376600	0.66193800	-0.34794500
H	-0.77178900	0.62520000	-1.41095800
N	-2.07725100	1.70187100	-0.17409000
H	-2.97362500	1.24169000	-0.32954000
H	-2.09253900	1.94629000	0.81501600
C	0.23068000	1.03544300	0.42546700
H	0.44324400	2.08355100	0.20723800
H	0.03926200	0.95007300	1.50180400
Se	1.83935700	-0.05055900	-0.03914500
	U_{d3}		
H	0.21869300	-1.39124000	-0.01942800
O	-0.74190000	-1.73599800	0.05848100
C	-1.60701300	-0.73784000	-0.01819100
O	-2.80596400	-0.93024800	0.07980600
C	-1.03834700	0.66963100	-0.28801500
H	-0.75126100	0.65458600	-1.35276500
N	-2.10123200	1.65213100	-0.00571300
H	-2.05627600	2.40175700	-0.68726400
H	-2.99257800	1.17449700	-0.11677200
C	0.23946600	1.00537200	0.50205000
H	0.45103800	2.06540300	0.34553100
H	0.05077200	0.86513100	1.56982600
Se	1.84136800	-0.04788400	-0.05825000
	U_{d4}		
H	0.19476600	-1.21839300	-0.55204200
O	1.18216200	-1.42535800	-0.51588200
C	1.84682000	-0.41478800	0.05155300
O	3.01723900	-0.52103700	0.34811600
C	1.05504100	0.88416700	0.28932400
H	1.72746700	1.49037000	0.90522300
N	0.89741100	1.57751900	-1.00601700
H	0.09311700	1.12980200	-1.45685900
H	0.57527300	2.52217400	-0.80076700
C	-0.27318300	0.66634500	1.05013200
H	-0.09365400	0.08191000	1.95794200
H	-0.65085900	1.64706800	1.35730600
Se	-1.69103700	-0.23349300	-0.04037100
	U_{p1}		
H	2.62953700	-2.00917100	-0.25893000
O	2.00903000	-1.52635000	0.31360100
C	1.86336900	-0.28831900	-0.12706200

O	2.37874500	0.19637000	-1.10186800
C	0.94970800	0.53882900	0.79266600
H	1.52709500	0.77840900	1.69051800
N	0.71334500	1.82398100	0.03879100
H	0.65787400	2.64773900	0.64004100
H	-0.18090100	1.71060700	-0.48667400
H	1.47738200	1.92472100	-0.65159300
C	-0.37160200	-0.13579000	1.19180800
H	-0.16810200	-1.14616700	1.53758000
H	-0.84800000	0.41080000	2.00662400
Se	-1.73025200	-0.17583900	-0.25009000
H	-1.01078600	-1.15478500	-1.08438900
	U_{p2}		
H	3.59503200	-1.46816200	-0.02734300
O	2.70615000	-1.31848800	0.33834200
C	2.26929500	-0.12166400	-0.01539600
O	2.84865600	0.69881700	-0.67976000
C	0.84229400	0.12123600	0.49368100
H	0.76756200	-0.10968000	1.55613100
N	0.59452600	1.59863100	0.31631300
H	0.90660100	2.14519200	1.12223100
H	-0.42677100	1.74250100	0.18130200
H	1.14021900	1.91921000	-0.49936700
C	-0.18327400	-0.70038500	-0.31148400
H	0.00376900	-0.61457100	-1.38387400
H	-0.09279300	-1.74838400	-0.03520800
Se	-2.05646400	-0.09979600	-0.08036600
H	-2.14385900	-0.50121300	1.33492400
	U_{p3}		
H	2.57122100	-2.03775800	-0.25978900
O	1.96435400	-1.53957600	0.31428000
C	1.85046900	-0.29780400	-0.12366300
O	2.38280000	0.17929900	-1.09298900
C	0.94992900	0.54956400	0.79347300
H	1.53712300	0.79253500	1.68388000
N	0.72497000	1.82687300	0.02471100
H	0.66326800	2.65715700	0.61608000
H	-0.16235500	1.70615700	-0.51022500
H	1.49678000	1.91810300	-0.65859800
C	-0.37424400	-0.10602600	1.21225700
H	-0.16598400	-1.11229000	1.56776200
H	-0.84681200	0.45134300	2.01869800

Se	-1.67189000	-0.23012600	-0.29463300
H	-2.65792300	0.66873700	0.32401800
	U_{p4}		
H	-3.59704800	-1.46635600	0.02007300
O	-2.70560200	-1.31735500	-0.33950900
C	-2.27052200	-0.12059700	0.01651300
O	-2.85350300	0.70068700	0.67667000
C	-0.84098200	0.12186800	-0.48392200
H	-0.76012700	-0.11074100	-1.54586400
N	-0.59325800	1.59898200	-0.31122600
H	0.42984800	1.74083100	-0.18847200
H	-1.13051700	1.92251200	0.50824000
H	-0.91232900	2.14332800	-1.11607100
C	0.17739700	-0.70035200	0.32996100
H	-0.01134600	-0.61741500	1.39979100
H	0.08127900	-1.74548500	0.04397200
Se	2.05360800	-0.12374100	-0.00595700
H	2.30785100	0.27547000	1.38685100
	O_{c1}		
H	0.18640600	-1.70792900	-0.32785400
O	1.18714700	-1.79779800	-0.40995100
C	1.77744700	-1.15534000	0.59405100
O	1.19137600	-0.80410600	1.60482400
C	3.25346400	-0.84295000	0.33975200
C	3.41083400	0.15159100	-0.83855200
N	4.08670600	-2.02065100	0.08406000
C	2.31743400	1.22388700	-0.98134400
C	2.13170100	2.18419700	0.20980700
C	0.68884000	2.70118600	0.33762900
N	-0.23193600	1.62231300	0.69690300
C	-1.30126800	1.25727200	-0.05138600
C	-1.99301000	-0.04729700	0.41407100
C	-3.53283400	-0.01533500	0.19897600
C	-3.71817300	-0.84709100	-1.09547100
C	-2.39658500	-1.54933400	-1.21618900
N	-1.48005100	-1.16303800	-0.42090600
H	3.61195400	-0.38315500	1.26282800
H	4.40189800	0.60664800	-0.74636100
H	3.42502600	-0.43588600	-1.76246400
H	3.72902800	-2.54110400	-0.71152000
H	4.09198800	-2.64632300	0.88337300
H	1.36890500	0.71989000	-1.18613700
H	2.53062500	1.81032600	-1.88097200

H	2.80160500	3.04505000	0.11325900
H	2.40342100	1.69523300	1.15103700
H	0.33208100	3.12872000	-0.60105800
H	0.63999700	3.48649100	1.09942700
H	0.09294400	0.95624100	1.38843900
O	-1.71355100	1.87370800	-1.02482500
C	-4.28730300	-0.61384500	1.39060800
H	-1.72317900	-0.25533600	1.45244400
H	-3.85671400	1.01205300	0.03346300
H	-4.55234500	-1.55469700	-1.04207100
H	-3.88217500	-0.21867900	-1.97689000
H	-2.19925400	-2.34434100	-1.93311100
H	-5.36587600	-0.61492000	1.20889400
H	-4.10432900	-0.03767400	2.30204200
H	-3.97811700	-1.64704500	1.58072900

O_{c2}

H	-0.24076400	-1.64344300	-0.85458200
O	-1.19360700	-1.55718600	-1.15178000
C	-1.97000000	-1.34586100	-0.08897200
O	-1.59018800	-1.50041100	1.05842200
C	-3.35949200	-0.80195000	-0.42845900
C	-3.36958200	0.70013100	-0.06147800
N	-4.43716100	-1.48458500	0.28651500
C	-2.33635400	1.56292000	-0.82514000
C	-1.57504300	2.59491800	0.02348600
C	-0.67395300	2.01462400	1.13236900
N	0.23336400	0.95695900	0.68660800
C	1.34131700	1.19519000	-0.04970600
C	2.15356500	-0.03100300	-0.48704700
C	3.49988400	-0.15767100	0.29346000
C	3.65396000	-1.68962200	0.45027500
C	2.26369300	-2.18360500	0.16308000
N	1.45915400	-1.32881400	-0.33062100
H	-3.52685600	-0.91931300	-1.50186800
H	-4.38514600	1.06235000	-0.23728300
H	-3.20355900	0.76403700	1.01938800
H	-4.23516300	-1.49489200	1.28278500
H	-4.51321600	-2.45225200	-0.01123800
H	-2.84418300	2.09583400	-1.63464800
H	-1.60221800	0.92247200	-1.32058800
H	-2.27984300	3.28369900	0.50550300
H	-0.95151800	3.19945100	-0.64063700
H	-1.27417900	1.58390300	1.93612600

H	-0.07996100	2.82487200	1.56187200
H	-0.01982500	0.00047200	0.89887200
O	1.73603000	2.31528500	-0.35351700
C	4.67726400	0.55064800	-0.37270900
H	2.34152200	0.11334300	-1.55698600
H	3.34857400	0.27272900	1.28895300
H	4.34919000	-2.11292000	-0.28750500
H	4.01247500	-2.00142800	1.43497400
H	1.94076100	-3.20956500	0.33041600
H	5.58859200	0.44227700	0.22245900
H	4.46638900	1.61559700	-0.48689800
H	4.87199300	0.13403900	-1.36657900
	O_{d1}		
O	-1.02391600	-0.89300900	-1.33647000
C	-1.77166400	-1.44015400	-0.49047300
O	-1.55189400	-2.49470500	0.13148600
C	-3.12650700	-0.73204800	-0.21310100
C	-2.96488600	0.78469400	-0.19364100
N	-3.80507800	-1.21516300	0.98682700
C	-1.99934500	1.28608100	0.88667400
C	-1.28104500	2.59229100	0.55075200
C	-0.38333600	2.52289400	-0.68780400
N	0.53849400	1.41067900	-0.68763200
C	1.75708600	1.49247400	-0.14367200
C	2.59030600	0.21622300	-0.16876200
C	2.12018700	-0.82391200	0.89489900
C	1.75939200	-2.06058400	0.05108300
C	2.11223800	-1.61738500	-1.33191400
N	2.55731900	-0.44270000	-1.47174000
H	-3.76211300	-0.98181900	-1.06519800
H	-2.59950200	1.07005100	-1.17326700
H	-3.94320000	1.24856800	-0.06169400
H	-3.35182000	-0.81655000	1.79534400
H	-3.59430300	-2.20104600	1.04986000
H	-1.24070000	0.52743400	1.06919500
H	-2.52978100	1.41807100	1.83029700
H	-0.66673900	2.88760800	1.40007800
H	-2.00818300	3.39264700	0.39398600
H	0.19347700	3.43967500	-0.76078000
H	-0.98723700	2.43594400	-1.58630200
H	0.18358500	0.52392800	-1.03614600
O	2.19861000	2.50619000	0.38814700
C	3.19035300	-1.09284300	1.94390400

H	3.60581900	0.54910400	0.02933500
H	1.22915200	-0.45800100	1.39768200
H	2.34327800	-2.93875800	0.33465500
H	0.70540000	-2.33163400	0.10180600
H	1.99129100	-2.25918200	-2.19402100
H	2.85299300	-1.83621500	2.66403500
H	3.44322100	-0.18506200	2.48785700
H	4.10112700	-1.46867400	1.47811700

O_{d2}

O	-1.04118800	-0.74742700	-1.08634800
C	-1.89954200	-1.18215300	-0.28058800
O	-1.78324000	-2.14806800	0.49514900
C	-3.22996700	-0.40004500	-0.21734200
C	-3.18090900	0.64778300	0.90441700
N	-4.39360400	-1.25594700	0.00887600
C	-1.88828600	1.45352400	1.00166300
C	-1.54685300	2.28796100	-0.23314600
C	-0.07055100	2.65383000	-0.31133700
N	0.73729300	1.46955500	-0.51693600
C	2.02512800	1.42535800	-0.16444600
C	2.72982200	0.08256400	-0.32070400
C	2.38870600	-0.89522000	0.84645900
C	1.65586100	-2.04892600	0.13733600
C	1.81592600	-1.68823600	-1.30492900
N	2.38743300	-0.59176700	-1.56876100
H	-3.36241200	0.10059700	-1.17285100
H	-4.04147200	1.30789100	0.78671100
H	-3.32532300	0.11843000	1.84615400
H	-4.11717200	-1.92152300	0.71830800
H	-4.55490400	-1.80896100	-0.81886100
H	-1.06961600	0.76662100	1.20029700
H	-1.94669800	2.11225200	1.87016000
H	-2.13375800	3.20746000	-0.23737900
H	-1.80766700	1.73789900	-1.13278700
H	0.26397700	3.14210900	0.60126300
H	0.09604300	3.36291800	-1.12403500
H	0.27173700	0.63938900	-0.87258700
O	2.62711200	2.37890100	0.31952200
C	3.64028500	-1.34583000	1.58793300
H	3.78818100	0.32883000	-0.32954100
H	1.72246200	-0.41057400	1.55490700
H	2.10772000	-3.01945600	0.35018700
H	0.59634300	-2.11865500	0.37837000

H	1.45252700	-2.32006800	-2.10293300
H	3.39310500	-2.05237200	2.37851400
H	4.15480200	-0.49956300	2.03840200
H	4.33507800	-1.83701800	0.90697400

O_{pb1}

H	-4.56508400	-2.03240000	-1.38112500
O	-4.19343300	-1.24753700	-0.94597900
C	-3.10760200	-1.60465300	-0.25615800
C	-2.50810600	-0.41537700	0.49437200
C	-2.15073200	0.79395100	-0.38838800
C	-2.00755500	2.11147600	0.40562400
C	-1.21029000	3.21134500	-0.32793400
C	0.30422300	3.21670500	-0.05849800
N	1.01543300	2.01863500	-0.52440000
C	1.21128800	0.92733700	0.24130000
C	1.90938100	-0.25904800	-0.42127500
C	3.34130400	-0.55484400	0.10282700
C	3.38699600	-2.09967600	0.01126400
C	1.92932300	-2.45371100	0.05622600
N	1.11809000	-1.48877900	-0.14601800
O	-2.65601600	-2.71906400	-0.19407100
H	-3.23408500	-0.11207300	1.25543500
N	-1.29360400	-0.93675500	1.20700000
H	-0.56006600	-1.31707800	0.53824800
H	-0.77619200	-0.19040300	1.70033700
H	-1.53564200	-1.68884300	1.85355300
H	-1.24190000	0.55876800	-0.94818500
H	-2.94332000	0.90612900	-1.13015200
H	-1.53537500	1.93490200	1.37637100
H	-3.01463300	2.48146200	0.61865000
H	-1.57939900	4.18905100	-0.00406300
H	-1.39978700	3.16219700	-1.40645000
H	0.49413100	3.30768500	1.01203900
H	0.76053000	4.07761800	-0.55088400
H	1.36540400	2.00894600	-1.47138300
O	0.80748100	0.84584400	1.40563900
H	1.92501600	-0.12249200	-1.51033800
H	3.36060600	-0.28152200	1.16281400
C	4.45927800	0.17839600	-0.63394700
H	5.43499200	-0.09261200	-0.22443800
H	4.35873100	1.26277400	-0.53637800
H	4.46466400	-0.07044500	-1.69974200
H	3.82026500	-2.44499300	-0.93722300

H	3.95894700	-2.57523900	0.81140100
H	1.55345100	-3.45849800	0.23824300

O_{pb2}

H	-5.19268200	-1.34358400	-0.84293600
O	-4.68648400	-0.91505400	-0.13298400
C	-3.41241100	-1.30143000	-0.20700400
C	-2.57143400	-0.64145900	0.88469200
C	-2.44334100	0.88711500	0.72331300
C	-1.92401000	1.35449000	-0.64862900
C	-1.34764600	2.78117500	-0.65347400
C	-0.01593700	2.96272600	0.10284900
N	1.02366300	2.03307100	-0.35163600
C	1.24577000	0.84615000	0.23437800
C	2.19472200	-0.12048500	-0.45832700
C	3.53570200	-0.36540500	0.28960600
C	3.78387400	-1.86151800	-0.01791100
C	2.39631800	-2.34347400	-0.33764100
N	1.51938100	-1.44184100	-0.55251100
O	-2.95615300	-2.06019000	-1.02385000
H	-3.02804100	-0.85423700	1.85303600
N	-1.22318200	-1.31653400	0.86483500
H	-0.96224600	-1.60993700	-0.08785900
H	-0.44490600	-0.67496800	1.18735500
H	-1.22070500	-2.16284700	1.43475600
H	-3.43265600	1.30953800	0.91373200
H	-1.79068800	1.23551100	1.52653700
H	-2.74032000	1.31064300	-1.37566200
H	-1.15914400	0.66985100	-1.03119800
H	-2.07031500	3.48397300	-0.22470300
H	-1.20717900	3.08903000	-1.69460000
H	-0.13540900	2.80653100	1.17418300
H	0.35100400	3.98042600	-0.04096800
H	1.50236000	2.23435600	-1.21818700
O	0.66848900	0.51457100	1.28470700
H	2.38663100	0.22051700	-1.48371200
H	3.33347400	-0.27178500	1.36151100
C	4.66895600	0.58132400	-0.09881100
H	5.58223300	0.33806300	0.44898400
H	4.42087200	1.62081900	0.13338200
H	4.89430500	0.51446900	-1.16770600
H	4.43359000	-2.00084200	-0.89233300
H	4.24247100	-2.41203200	0.80699900
H	2.12813000	-3.39623800	-0.40665700

	O_{pb3}		
H	5.37521600	-0.61488600	-0.49432500
O	4.46775900	-0.56156200	-0.83728900
C	3.62225200	-0.99446800	0.09957900
O	3.93298000	-1.37661600	1.19853100
C	2.17993500	-0.99774900	-0.40633600
C	1.69998000	0.30405200	-1.07216600
N	1.30707100	-1.38313500	0.75290000
C	1.97444700	1.60746600	-0.29174500
C	1.04711600	2.77280900	-0.70299000
C	-0.25850100	2.90767800	0.09932800
N	-1.20561100	1.78841400	-0.03685100
C	-1.18838100	0.72050100	0.77895800
C	-2.18952300	-0.41967300	0.54926000
C	-3.43780400	-0.23516900	-0.34555700
C	-3.61724700	-1.65976600	-0.92546400
C	-2.23000100	-2.22048100	-0.80114500
N	-1.43852600	-1.57678700	-0.03412200
H	2.10713200	-1.81190700	-1.13381000
H	2.18466600	0.35985400	-2.04953600
H	0.63276200	0.18481500	-1.27364000
H	1.05476900	-0.56888700	1.34376000
H	0.36218800	-1.72036900	0.42767700
H	3.01170300	1.89966600	-0.47244800
H	1.88116700	1.45428800	0.78692000
H	0.82444600	2.71737600	-1.77488400
H	1.58291300	3.71574400	-0.55837800
H	-0.78496600	3.81033200	-0.21642600
H	-0.03318700	3.00875400	1.16218700
H	-1.93426700	1.86032400	-0.73046400
O	-0.34359100	0.58614000	1.67080800
C	-4.65922800	0.33577100	0.37419200
H	-2.49172200	-0.72005000	1.55964400
H	-3.18281800	0.41467500	-1.19262100
H	-4.30659700	-2.26319200	-0.31946700
H	-3.99634600	-1.68224300	-1.94946600
H	-1.89761700	-3.12785700	-1.30112700
H	-5.50909700	0.42058000	-0.30662200
H	-4.45968100	1.33204300	0.77763000
H	-4.95917700	-0.30734000	1.20630800
H	1.78252300	-2.07069100	1.34371500

	O_{ps1}		
H	-2.36758200	-2.67886900	0.81928300
O	-1.53017300	-2.60139500	0.28083500
C	-1.75234100	-1.57838300	-0.51886300
C	-3.09704300	-0.86430300	-0.29209900
C	-2.84628500	0.56043300	0.26531400
C	-2.35171400	1.56060900	-0.79140400
C	-1.86176100	2.90470700	-0.23053800
C	-0.59901000	2.83882400	0.64710700
N	0.50767700	2.12604600	-0.00270400
C	0.96770800	0.93576800	0.43634800
C	2.04906300	0.26368400	-0.44441200
C	3.44306900	0.16770700	0.25145300
C	3.46946800	-1.28257100	0.81626700
C	2.35109500	-1.95522500	0.11258700
N	1.64680900	-1.14998300	-0.58847200
O	-0.92438600	-1.21583000	-1.34360000
H	-3.58843800	-0.78597100	-1.26669600
N	-3.87898900	-1.69188100	0.64308500
H	-4.64136600	-2.18156500	0.18815400
H	-4.26407100	-1.15325800	1.41050400
H	-3.79582000	0.91769500	0.67851800
H	-2.14253600	0.48864000	1.10105000
H	-3.16829700	1.75995200	-1.49316800
H	-1.55570900	1.10308200	-1.38197800
H	-2.64626400	3.38422300	0.36530800
H	-1.67415100	3.57883400	-1.07375700
H	-0.78481300	2.31899000	1.58583100
H	-0.26958300	3.85106400	0.89457300
H	0.84952400	2.48372600	-0.88312900
O	0.59894700	0.36939200	1.45386700
H	2.10637500	0.71535400	-1.43691000
H	3.48647800	0.88317300	1.07287300
C	4.59276200	0.43561700	-0.72440600
H	5.55556200	0.33273200	-0.21886400
H	4.53868600	1.45038500	-1.12595300
H	4.57886500	-0.26314600	-1.56677300
H	4.41819000	-1.80243000	0.65115400
H	3.26937200	-1.32825300	1.89317100
H	2.09486500	-3.00884300	0.16265700
H	0.72706300	-1.39332800	-1.03214800

	O_{ps2}		
H	-2.56365200	-2.59333900	0.98219300
O	-1.71255800	-2.58895100	0.45936000
C	-1.85213000	-1.58440500	-0.37604000
O	-0.98566700	-1.29882500	-1.19359700
C	-3.15996800	-0.78703600	-0.21658900
C	-2.84850500	0.66014300	0.24220200
N	-3.99713900	-1.51140000	0.75617800
C	-2.28979600	1.55873200	-0.87234100
C	-1.75122100	2.91684500	-0.39727000
C	-0.50399400	2.85985200	0.50287000
N	0.59266500	2.07839000	-0.08123400
C	0.96398400	0.87161600	0.39881600
C	2.06489500	0.13679700	-0.39247800
C	3.39761400	-0.03671400	0.39374300
C	3.77153500	-1.52787800	0.16080000
C	2.49549800	-2.13416000	-0.29804100
N	1.61368800	-1.26026100	-0.59824900
H	-3.63601600	-0.75555000	-1.20148000
H	-3.78607700	1.09009800	0.61099900
H	-2.16029200	0.61414700	1.09222000
H	-4.80664700	-1.94701900	0.32916800
H	-4.31982000	-0.91634300	1.51065200
H	-3.08333600	1.74234400	-1.60438400
H	-1.50378300	1.02648700	-1.41111300
H	-2.52266300	3.46739600	0.15267700
H	-1.52423000	3.52361200	-1.28097200
H	-0.72297800	2.40254400	1.46668500
H	-0.14421700	3.87339700	0.69641600
H	1.00725100	2.40923500	-0.94055700
O	0.49664300	0.33634300	1.39177000
C	4.48528200	0.96114000	0.00250100
H	2.22602600	0.57835100	-1.38144500
H	3.15663400	0.07713400	1.45359300
H	4.52474600	-1.66070500	-0.62847600
H	4.16154000	-2.03235000	1.04809800
H	2.28040800	-3.19301500	-0.40457900
H	5.38989000	0.79337300	0.59080800
H	4.16318600	1.98831100	0.18959500
H	4.74981700	0.87216600	-1.05546200
H	0.62319700	-1.46550700	-0.90080700

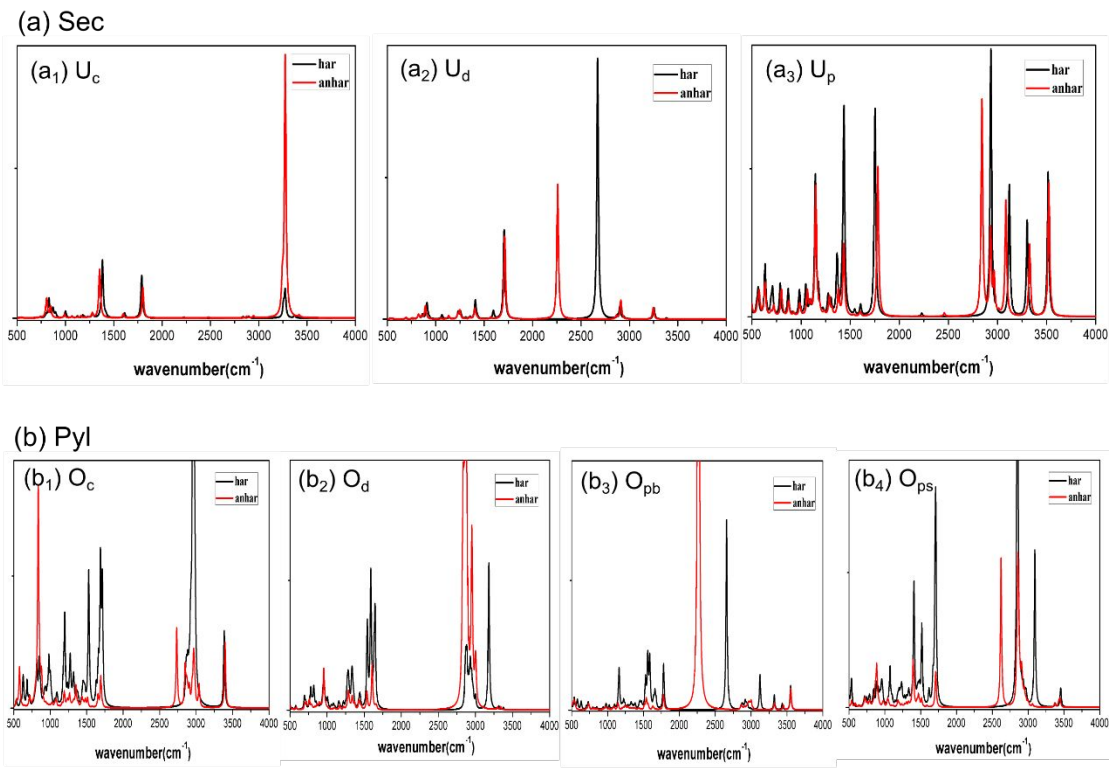

Figure S1. The computed IR spectra of representative conformer of the different forms (canonical, deprotonated and protonated) of (a) Sec and (b) Pyl in anharmonic motion (red) and the calibrated harmonic motion (black, scaled) at the B3LYP/6-311++G (d, p) level. A Lorentzian profile with a FWHM of 20 cm^{-1} is used to convolute the calculated spectra.

Table S4. Scaling factors simulated according to the IR spectral comparisons between the anharmonic and harmonic frequency calculations of Sec and Pyl (see **Figure S1**).

Sec	**neu**	**depro**	**pro**
500-2000 cm^{-1}	0.977	0.977	0.965
2000-4000 cm^{-1}	0.940	0.955	0.945

Pyl	**neu**	**depro**	**pb**	**ps**
500-2000 cm^{-1}	0.980	0.970	0.980	0.975
2000-4000 cm^{-1}	0.950	0.960	0.950	0.958

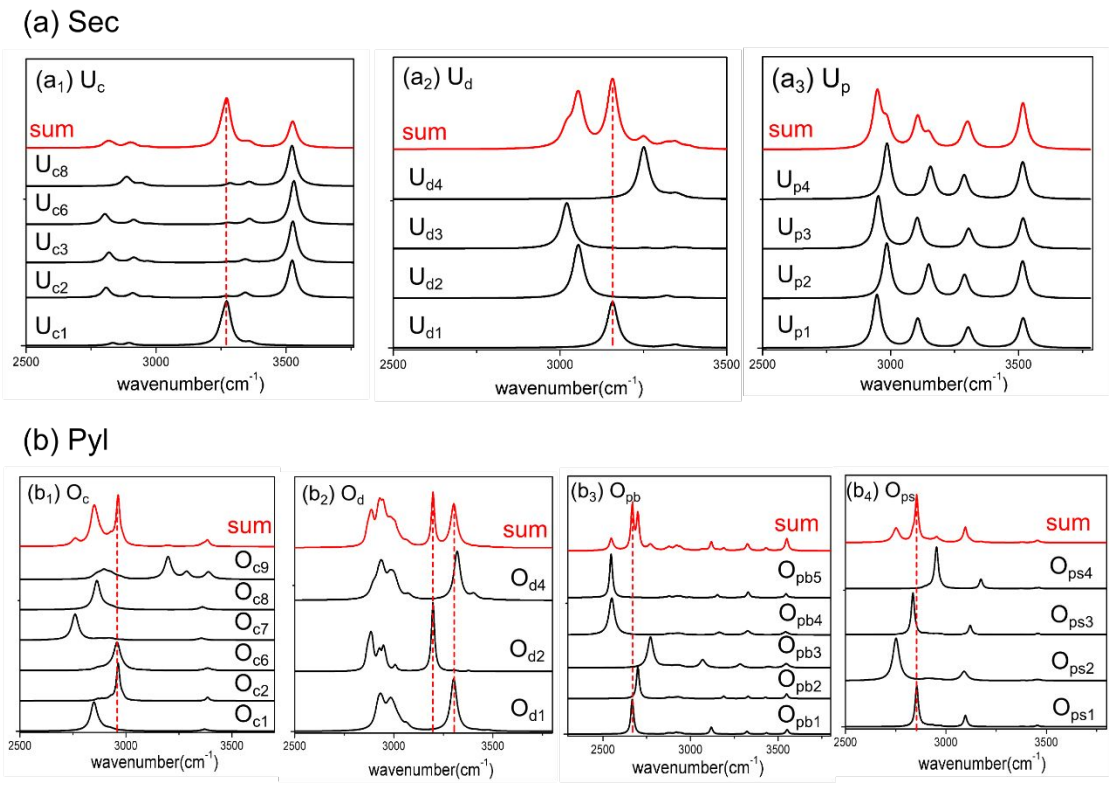

Figure S2. Simulated IR spectra (2500-4000 cm^{-1}) of the dominant conformers of (a) Sec and (b) Pyl in their canonical, deprotonated and protonated forms calculated at the B3LYP/6-311++G (d, p) level of theory, as well as their summation (sum) calculated using the percentage abundance at 298 K listed in Table S1 and S2. A Lorentzian profile with a FWHM of 20 cm^{-1} is used to convolute the calculated spectra.

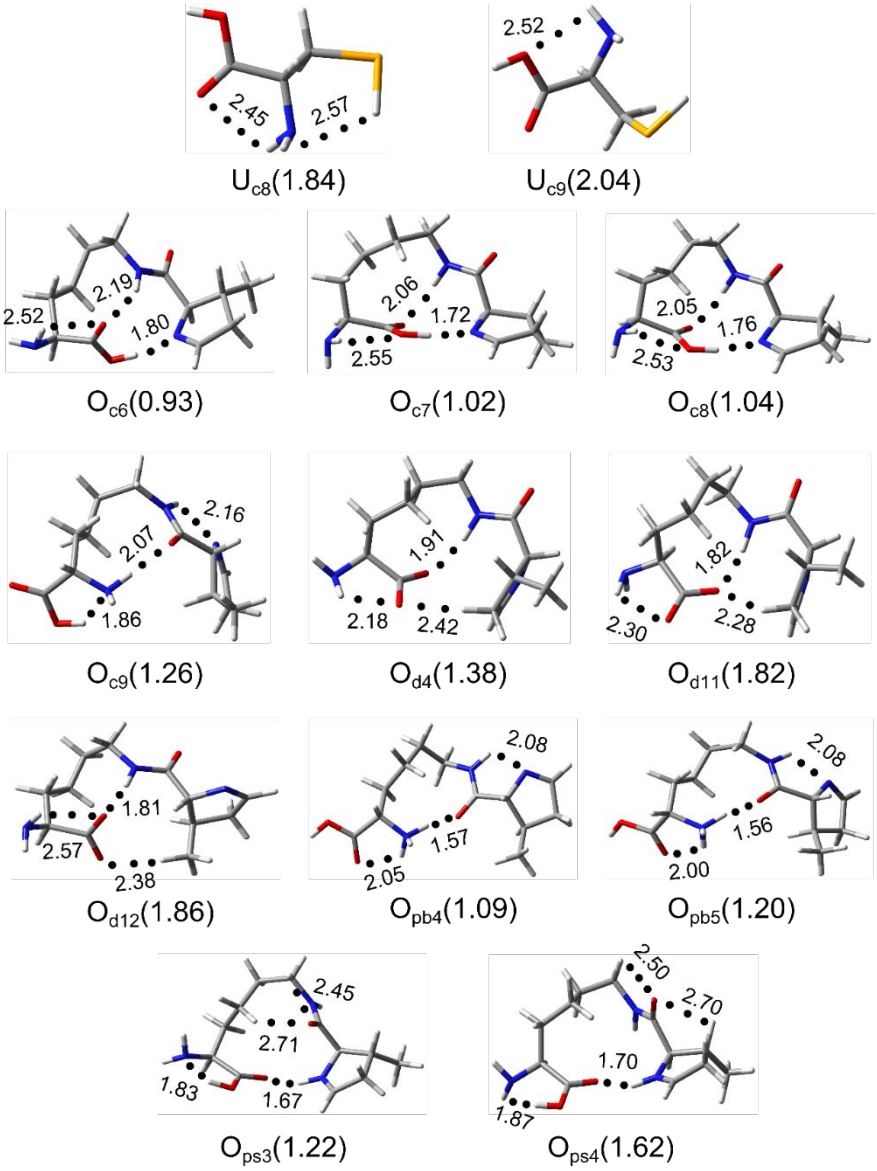

Figure S3. Geometric structures of the most stable conformers of Sec and Pyl in their canonical, deprotonated and protonated forms and their relative energies comparing with the global minimum of each form. The intramolecular interactions (HBs) are depicted by dotted lines in Å.

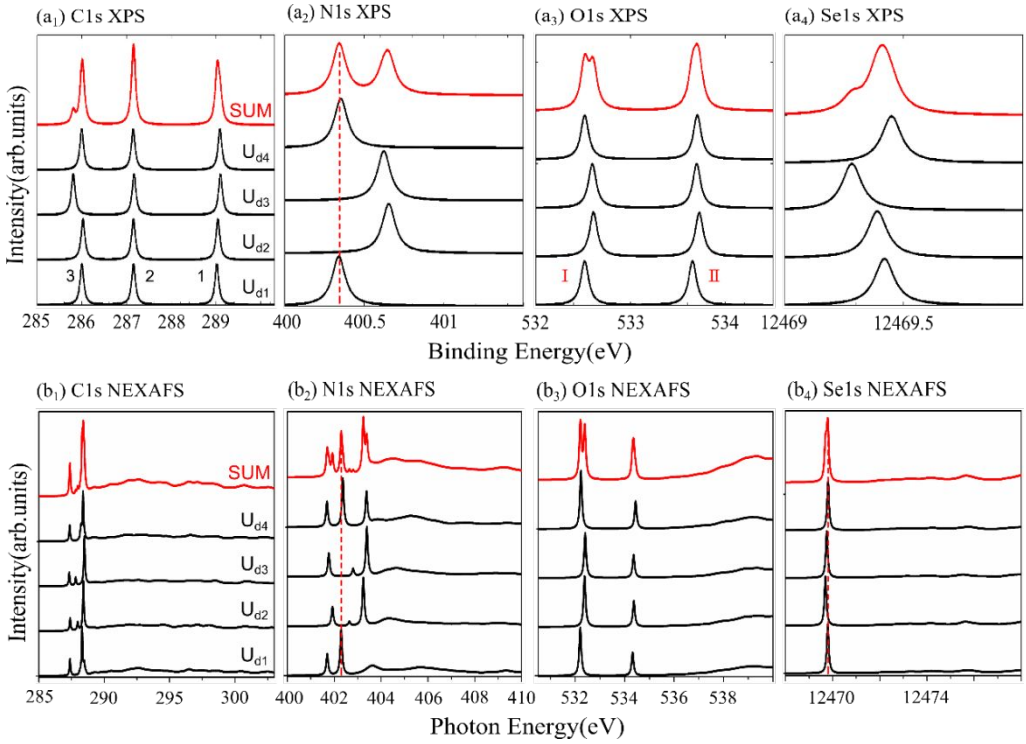

Figure S4. Calculated (a_1) C1s, (a_2) N1s, (a_3) O1s and (a_4) Se1s XPS spectra and (b_1) C1s, (b_2) N1s, (b_3) O1s and (b_4) Se1s NEXAFS spectra of the four low-energy conformers of Sec in its deprotonated form, as well as the averaged spectra (SUM, plotted in red) at 498 K, computed according to their equilibrium distributions.

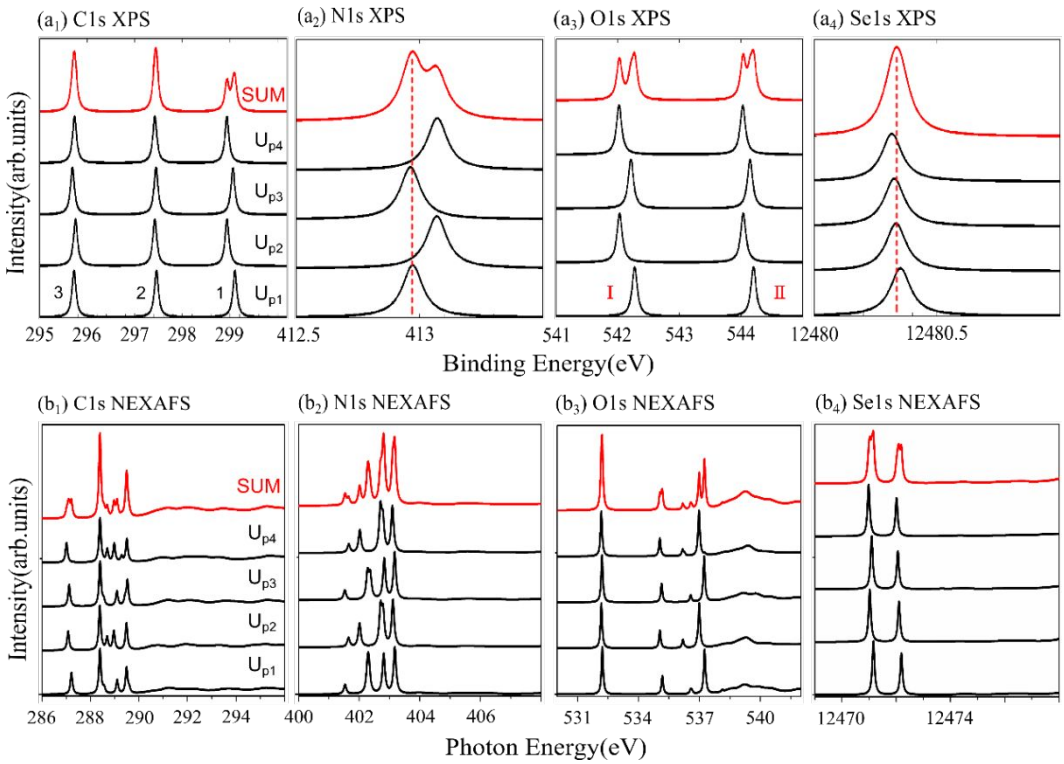

Figure S5. Calculated (a_1) C1s, (a_2) N1s, (a_3) O1s and (a_4) Se1s XPS spectra and (b_1) C1s, (b_2) N1s, (b_3) O1s and (b_4) Se1s NEXAFS spectra of the four low-energy conformers of Sec in its protonated form, as well as the averaged spectra (SUM, plotted in red) at 498 K, computed according to their equilibrium distributions.

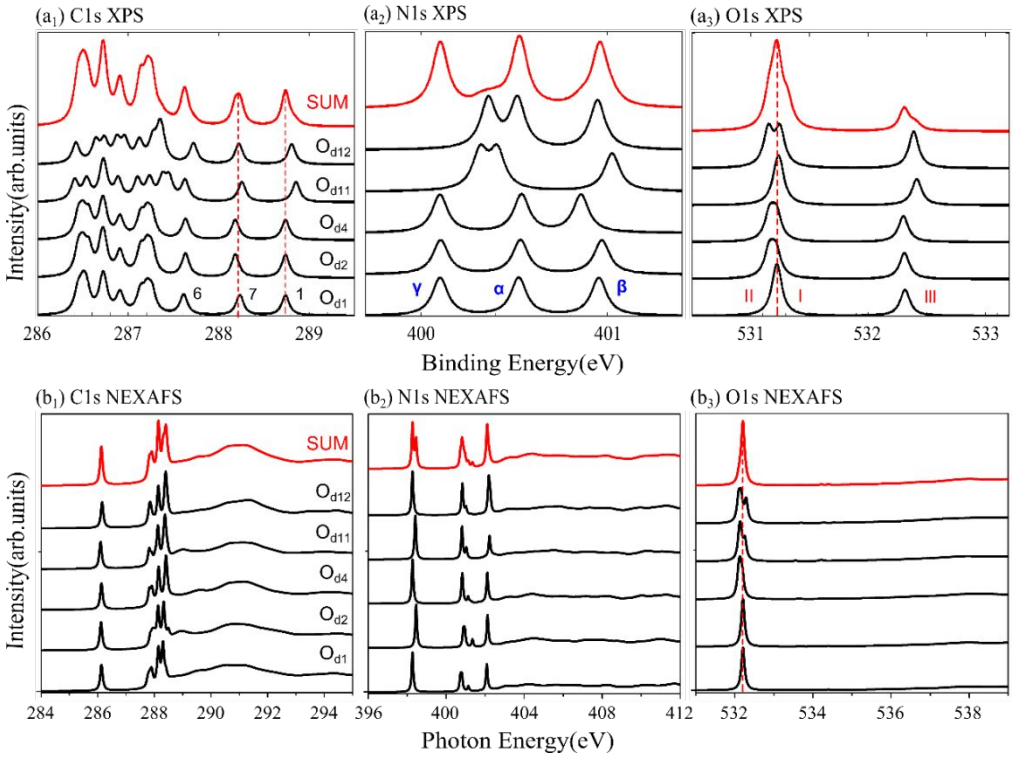

Figure S6. Calculated (a_1) C1s, (a_2) N1s and (a_3) O1s XPS spectra and (b_1) C1s, (b_2) N1s and (b_3) O1s NEXAFS spectra of the five low-energy conformers of Pyl in its deprotonated form, as well as the averaged spectra (SUM, plotted in red) at 498 K, computed according to their equilibrium distributions.

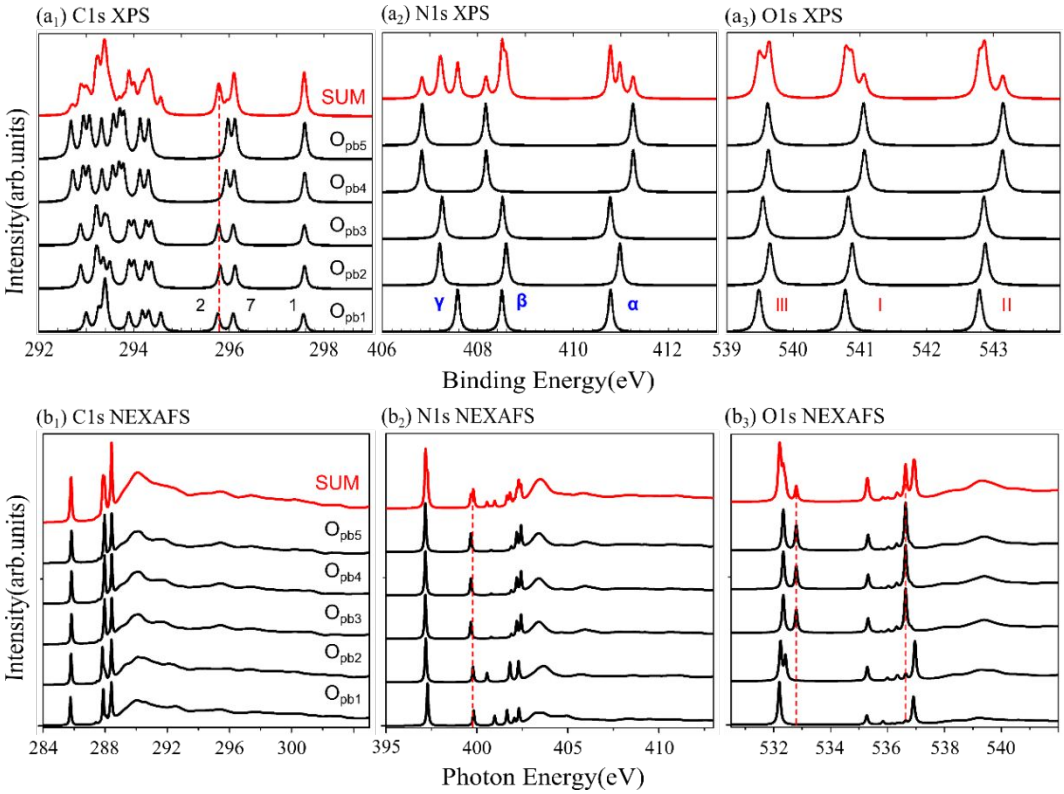

Figure S7. Calculated (a_1) C1s, (a_2) N1s and (a_3) O1s XPS spectra and (b_1) C1s, (b_2) N1s and (b_3) O1s NEXAFS spectra of the five low-energy conformers of Pyl in its O_{pb} form, as well as the averaged spectra (SUM, plotted in red) at 498 K, computed according to their equilibrium distributions.

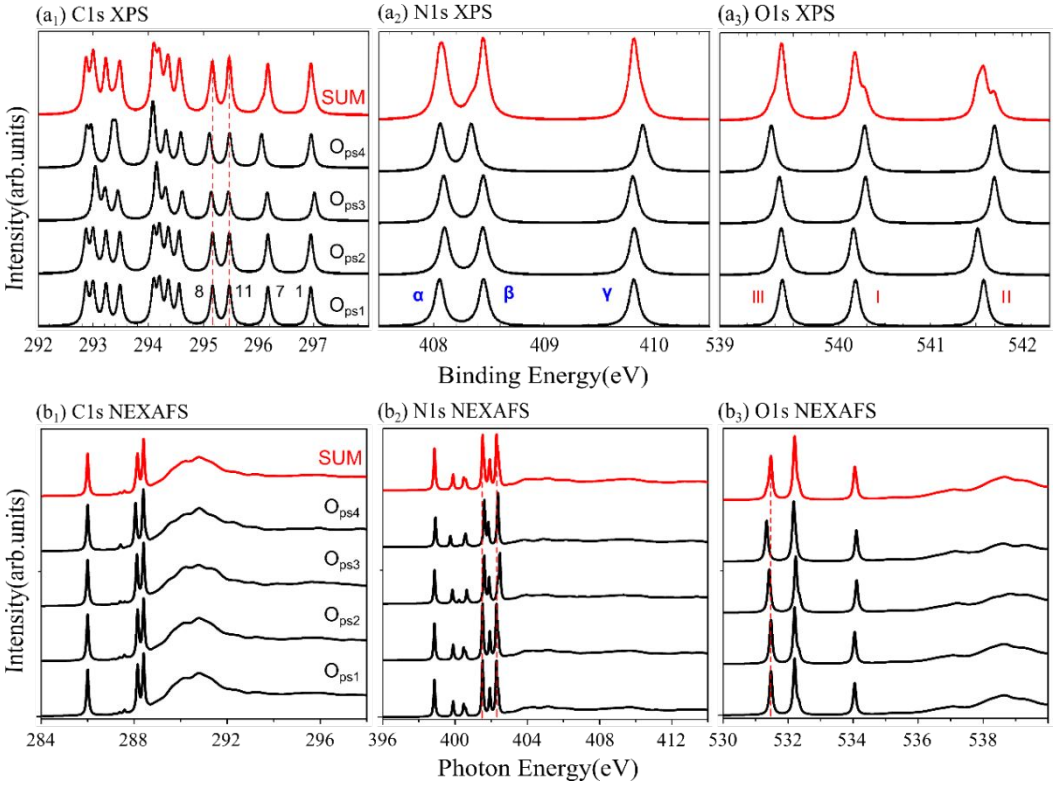

Figure S8. Calculated (a_1) C1s, (a_2) N1s and (a_3) O1s XPS spectra and (b_1) C1s, (b_2) N1s and (b_3) O1s NEXAFS spectra of the four low-energy conformers of Pyl in its O_{ps} form, as well as the averaged spectra (SUM, plotted in red) at 498 K, computed according to their equilibrium distributions.