Table S1. Comparison of experimental and calculated values for structural parameters of IMeAuCl complex.

?	Experimental*	Calculated
Au–Cl (Å)	2.288 (3)	2.34
Au–C (Å)	1.979 (11)	2.02
C–N	1.35 (2)	1.36
N–C	1.36 (2)	1.39
C–Au–Cl (º)	178.8 (2)	180
N–C–N	105.8 (10)	104.7
N–Au–C	126.2 (5)	127.6

Table S2. Assessment of various levels of theory for the reaction of a water molecule with IMeAuCl. Values reported in kcal/mol.

Methods	R->P		R->TS	
	ΔH	ΔG	ΔH	ΔG
B3LYP / LACV3P**++	7.2	1.3	16.8	23.0
CAM-B3LYP / LACV3P**++	4.2	-1.7	13.3	19.5
M06-2X / LACV3P**++	2.6	-3.3	8.2	14.5
wB97X / LACV3P**++	4.5	-1.4	11.2	17.4
MP2 / LACV3P**++	10.1	4.2	15.0	21.2
MP2 / aug-cc-pVTZ	9.9	4.0	14.2	20.4

vibrational corrections and solvation energies always calculated with B3LYP/LACVP** and B3LYP/LACV3P**++, respectively

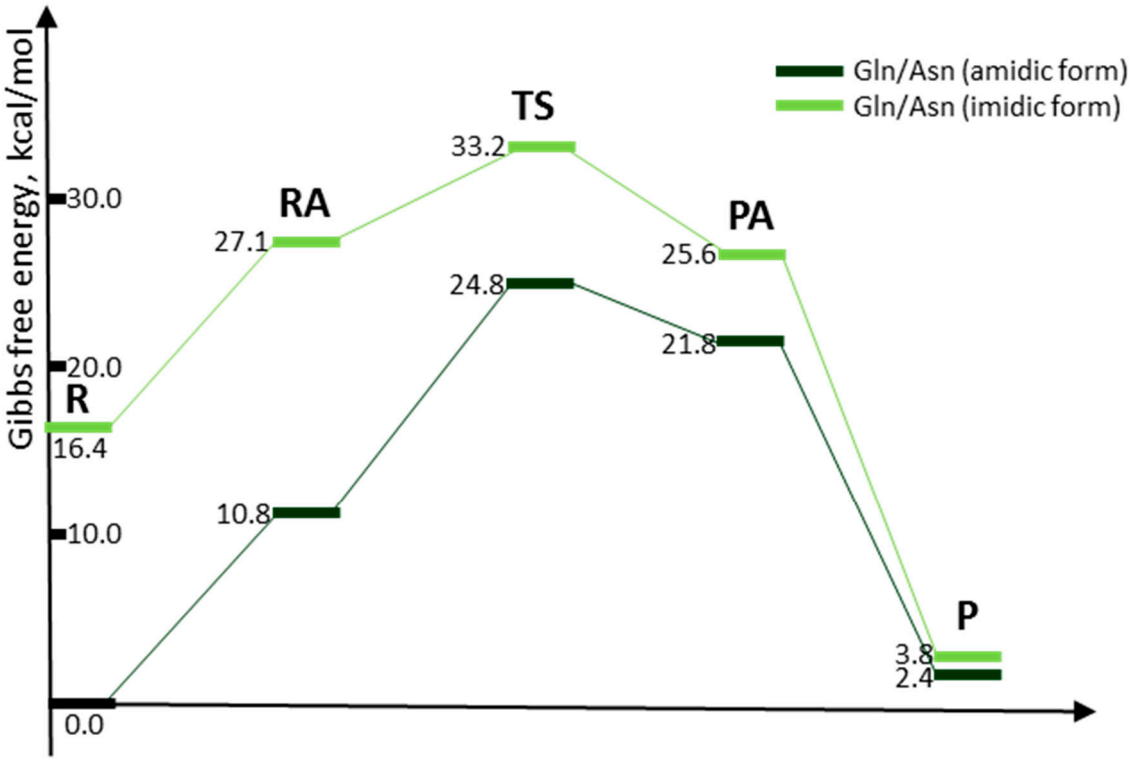

Figure S1. Reaction profiles for the Cl substitution by the amidic and imidic forms of glutamine / asparagine. Values in kcal/mol are calculated at the B3LYP/LACV3P**++//B3LYP/LACVP** level. R, P, TS, RA, and PA stand for reactant, product, transition state, reactant-adduct, and product-adduct, respectively.

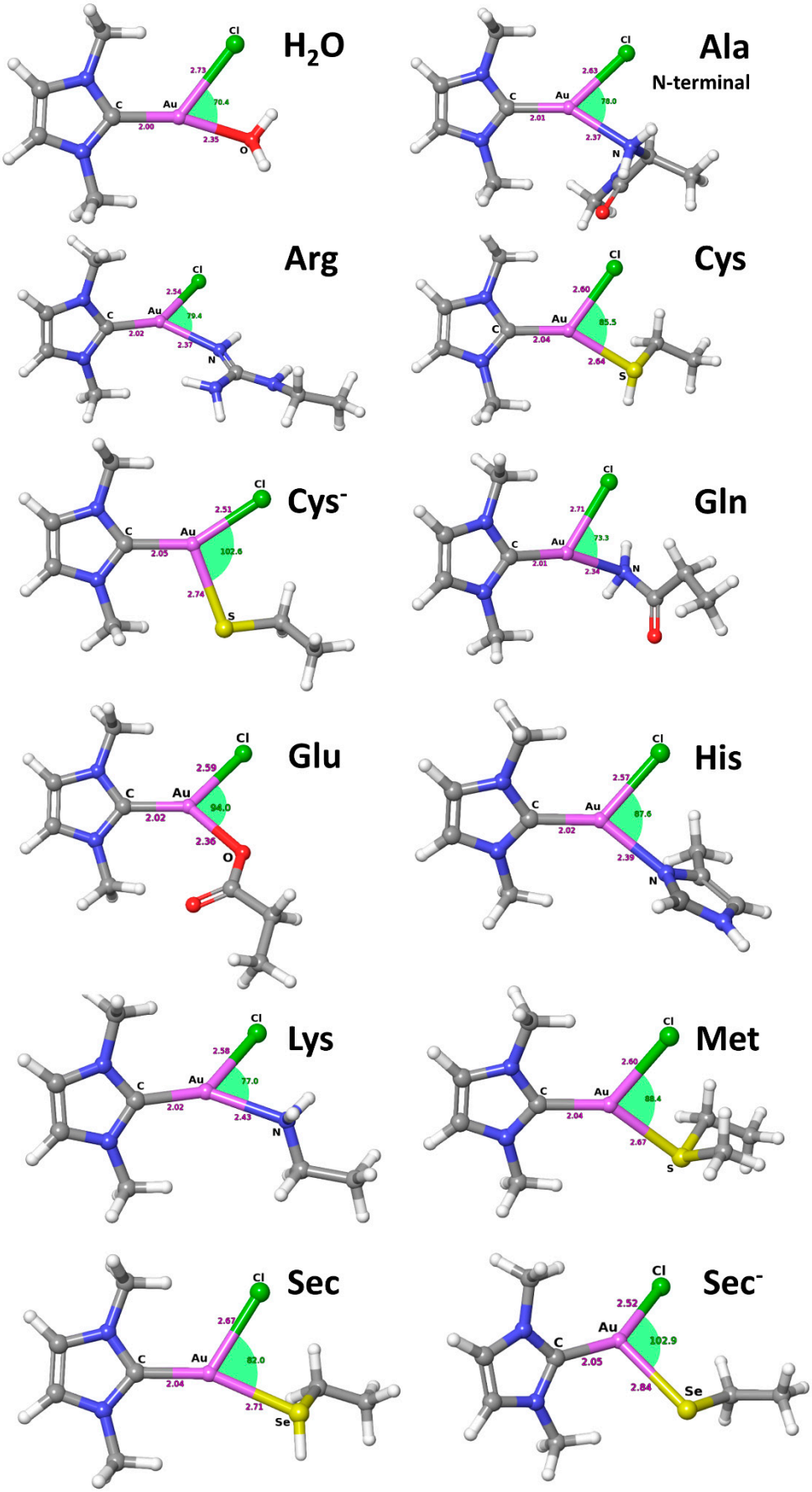

Figure S2. Transition states for various nucleophiles. All distances in angstroms, all angles in degrees.

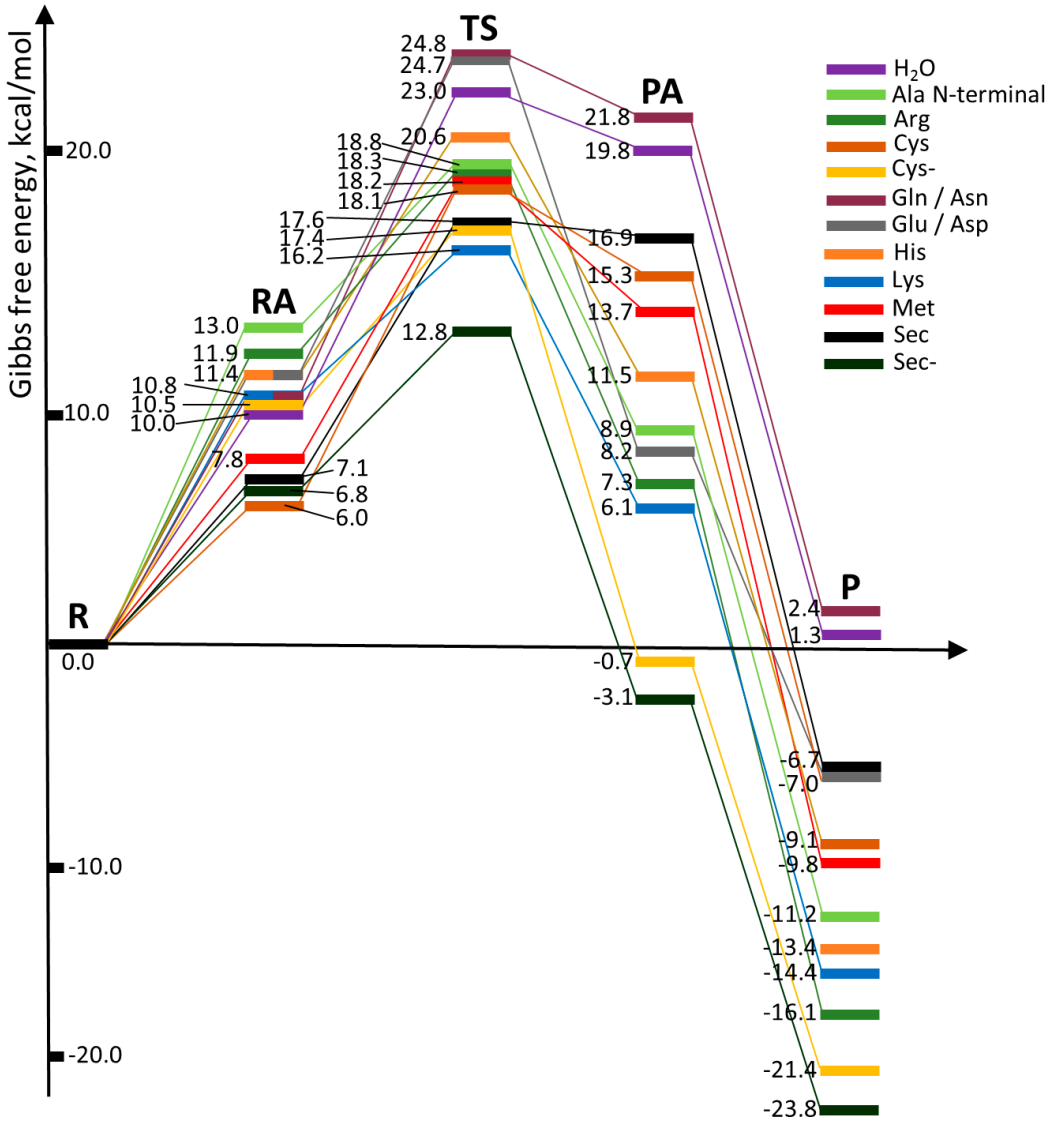

Figure S3. Reaction profiles for IMeAuCl interacting with various nucleophiles. Values in kcal/mol are calculated at the B3LYP/LACV3P**++//B3LYP/LACVP** level. R, P, TS, RA, and PA stand for reactant, product, transition state, reactant-adduct, and product-adduct, respectively.

Transition States for:

Dissociation of Cl

Au	-0.014904	0.002348	0.011039
Cl	3.724822	0.047590	0.010883
C	-2.018369	-0.022896	0.011196
N	-2.822041	-1.112841	-0.049385
C	-4.153142	-0.728909	-0.028317
C	-4.171158	0.626415	0.047864
N	-2.850798	1.045413	0.072154

H	-4.958343	-1.445286	-0.068999
H	-4.995037	1.321348	0.086860
C	-2.372074	-2.502888	-0.128262
H	-2.749109	-3.063077	0.730776
H	-2.734000	-2.957441	-1.053562
H	-1.282744	-2.519053	-0.119929
C	-2.438651	2.446956	0.153857
H	-2.827019	2.997235	-0.706376
H	-2.816204	2.891267	1.077913
H	-1.350196	2.492171	0.149973

H_2O

Au	0.042778	0.139011	2.322318
C	-4.096982	0.258619	1.688258
C	-3.999555	1.353552	2.484588
N	-2.662293	1.481810	2.824207
C	-1.924691	0.491538	2.252979
N	-2.819329	-0.257193	1.553772
H	-4.751629	2.043675	2.832832
Cl	1.429172	-1.673958	0.830343
H	-4.952293	-0.193782	1.211906
C	-2.129677	2.549225	3.663176
H	-2.664315	2.575224	4.616295
H	-1.074355	2.343123	3.840824
H	-2.233977	3.514509	3.159618
C	-2.498303	-1.459633	0.780031
H	-2.920728	-1.365845	-0.223260
H	-1.413834	-1.564916	0.711337
H	-2.918021	-2.340442	1.273387
O	2.319329	0.211462	2.905190
H	2.457041	-0.563190	2.298311
H	2.696454	0.960963	2.422905

Alanine N-terminal

Au	0.0683062008	0.0599121847	2.1900937165
C	-4.1202480450	0.3703300155	1.7902220698
C	-3.9144553361	1.4342416631	2.6084713703
N	-2.5515170090	1.4929304076	2.8530034874
C	-1.8987943702	0.4882791862	2.2040473367
N	-2.8795157037	-0.1991723246	1.5556738861

H	-4.6086853166	2.1409990012	3.0357470135
Cl	1.4974357093	-2.0841163137	1.6733697855
H	-5.0282346768	-0.0294604346	1.3665504450
C	-1.9119315306	2.5197010013	3.6718509976
H	-2.4256868895	2.5948139079	4.6342499597
H	-0.8695138983	2.2463467187	3.8357188139
H	-1.9547123947	3.4877868370	3.1636470865
C	-2.6568831260	-1.3770193583	0.7190804637
H	-2.8167983091	-1.1278951583	-0.3339228871
H	-1.6290190647	-1.7148007363	0.8616068607
H	-3.3479235624	-2.1707920522	1.0141554069
C	1.9686190702	0.9684690613	4.9879328838
C	2.7952867372	0.3188599737	3.8726041376
N	2.2768338964	0.8301232335	2.5929971925
C	4.2896688996	0.6155101459	4.0854367549
H	2.6306550810	-0.7635974089	3.8475532982
H	2.3359859346	1.8460730670	2.5802755192
H	2.7993788494	0.4275609773	1.8184684879
H	4.8806879305	0.1661944176	3.2816551354
H	4.4727963147	1.6949297119	4.0976366716
H	4.6412449694	0.1995100723	5.0361245329
N	1.6968160051	0.1565104541	6.0450643911
O	1.6295871279	2.1505980307	4.9285120513
C	0.9598169878	0.6047828466	7.2137518421
H	1.9164271578	-0.8249677388	5.9566188351
H	1.5336236300	0.4353404252	8.1321024611
H	0.7824310212	1.6743423057	7.0954983928
H	-0.0034380799	0.0888236364	7.3002611512

Arginine

Au	-0.2098533167	-0.1312548723	2.2164225906
C	-4.0425179985	0.5762535440	0.5821909913
C	-4.4014857461	0.4540070801	1.8838836809
N	-3.2343421024	0.2251076364	2.5991435370
C	-2.1491519602	0.1928786226	1.7708173792
N	-2.6670725643	0.4098324159	0.5279794977
H	-5.3692666370	0.5019113154	2.3576337536
Cl	1.7688442121	-1.5729103150	1.5346846745
H	-4.6362377238	0.7616579669	-0.2988456178
C	-3.1893056426	0.0007885772	4.0373538036
H	-3.6466629351	-0.9600838249	4.2919019525

H	-2.1438435208	-0.0103778986	4.3463787809
H	-3.7216759591	0.8027931003	4.5575826777
C	-1.8761581752	0.4689939799	-0.6973383229
H	-1.6728859406	1.5073843810	-0.9763239334
H	-0.9322583595	-0.0494421072	-0.5235788386
H	-2.4231790243	-0.0243033005	-1.5044666693
N	2.7736945587	2.1302109385	5.0521974739
C	1.6384937244	1.8113772650	4.3288085516
N	1.4703643278	0.7202667446	3.6605090443
N	0.6329687863	2.7644048683	4.3572445144
H	2.2945885973	0.1397243593	3.5211669488
H	3.5264210997	1.4703243476	4.9033394111
C	3.2202158097	3.5132008006	5.2529091064
H	-0.2121211955	2.4221541503	3.9161906306
H	0.4768489451	3.2160042719	5.2486056599
C	4.5618310071	3.5267198349	5.9799197230
H	3.2975164689	4.0508526434	4.2969689842
H	2.4792344275	4.0481513467	5.8582889329
H	4.8899192623	4.5548629245	6.1555655474
H	4.4884114357	3.0175583806	6.9455945782
H	5.3374178170	3.0280181589	5.3874663776

Cysteine

Au	-0.1787508576	0.1085659420	2.3017229792
C	-4.0038510136	-0.4539075367	0.5885199713
C	-4.4081368706	0.1427456419	1.7388191715
N	-3.2624685137	0.4061696827	2.4729294382
C	-2.1500950927	-0.0123255005	1.8065312722
N	-2.6227229110	-0.5389345382	0.6434570011
H	-5.3936600429	0.4031836553	2.0917705846
Cl	1.8235668574	-0.3315698333	0.6984858337
H	-4.5704810090	-0.8209434111	-0.2528376538
C	-3.2600951522	1.0611976804	3.7743119439
H	-3.9337848775	0.5373334570	4.4577754513
H	-2.2423219355	1.0293596006	4.1620150344
H	-3.5798457977	2.1023989377	3.6776677514
C	-1.7976817633	-1.1331219228	-0.4110803992
H	-2.1085435077	-0.7309881624	-1.3786096466
H	-0.7490346671	-0.8876158527	-0.2288356983
H	-1.9207389130	-2.2201684374	-0.4129889216
C	3.9467283851	-0.8174237346	4.9993359637

C	2.7742775358	-0.8928173415	4.0283836711
S	1.6596441059	0.5801464135	4.1328038584
H	4.5462007967	0.0805761458	4.8267610092
H	3.0831888555	-0.8863882845	2.9801426945
H	2.1646419007	-1.7855555496	4.1828227214
H	1.0617235510	0.2630224092	5.3013346049
H	3.6150284672	-0.8108612039	6.0432540850
H	4.5937434982	-1.6911793169	4.8600428765

Glutamic Acid

Au	-0.099885	-0.222925	2.281731
C	-3.941199	0.677610	0.734397
C	-4.111801	1.160510	1.991952
N	-2.921774	0.950911	2.669387
C	-2.000666	0.337922	1.871143
N	-2.651399	0.173281	0.677346
H	-4.963937	1.630858	2.457789
Cl	1.436988	-2.046044	1.278953
H	-4.611433	0.654095	-0.110869
C	-2.689792	1.305293	4.068821
H	-2.991247	0.477565	4.719984
H	-1.623208	1.531509	4.221619
H	-3.293707	2.186127	4.307893
C	-2.052279	-0.442133	-0.499396
H	-1.794927	0.318853	-1.244017
H	-1.143480	-0.961634	-0.184951
H	-2.757321	-1.154080	-0.939991
C	2.504797	2.075529	5.347528
C	1.288734	1.573974	4.524448
O	1.566860	0.619284	3.729592
O	0.190637	2.144539	4.715030
H	3.257035	2.435509	4.633499
C	2.165515	3.160628	6.369845
H	1.705746	4.023044	5.878005
H	1.437405	2.792539	7.100092
H	2.958678	1.203365	5.833980
H	3.057871	3.501368	6.913010

Glutamine

Au	-0.228586	0.098253	2.412592

C	-3.931282	-0.344101	0.470222
C	-4.218372	0.782450	1.171690
N	-3.083797	1.098026	1.901157
C	-2.096401	0.190381	1.670132
N	-2.629592	-0.694292	0.785230
H	-5.115995	1.378839	1.214924
Cl	1.610078	-1.809041	1.832366
H	-4.531111	-0.920335	-0.216571
C	-2.977681	2.248430	2.791910
H	-3.723967	2.177411	3.587663
H	-1.977988	2.248949	3.225889
H	-3.131678	3.173127	2.229542
C	-1.938218	-1.860471	0.228505
H	-1.914283	-1.783777	-0.861560
H	-0.917825	-1.894163	0.615529
H	-2.466573	-2.772381	0.518601
C	3.196994	1.743653	2.112842
C	2.283078	1.851374	3.321655
N	1.685355	0.629784	3.719503
O	2.048103	2.881945	3.921399
H	2.150111	-0.238581	3.425311
H	2.816154	0.967985	1.438631
C	3.397659	3.084217	1.406397
H	2.459675	3.441806	0.970109
H	3.746254	3.845705	2.108470
H	1.388416	0.644166	4.690760
H	4.158869	1.360516	2.484151
H	4.131282	2.985809	0.601206

Histidine

Au	-0.1782903518	-0.0538610309	2.1241990553
C	-4.1455486783	0.2819852259	0.7298998648
C	-4.3833276206	0.5751243420	2.0333319332
N	-3.1570157104	0.5354866119	2.6795425022
C	-2.1560029106	0.2170335372	1.8099030752
N	-2.7832453969	0.0608992232	0.6102435074
H	-5.3026503688	0.8004178265	2.5505173593
Cl	1.5426743083	-1.4901718661	0.8680104719
H	-4.8174450236	0.2122001331	-0.1109762113
C	-2.9727049993	0.7711149034	4.1046571520
H	-3.3668440148	-0.0665582457	4.6873368156

H	-1.9031258851	0.8690856493	4.2925885307
H	-3.4869089714	1.6901904726	4.3985651893
C	-2.1069252188	-0.2787866889	-0.6417971874
H	-1.9525954765	0.6197646310	-1.2473433074
H	-1.1392241687	-0.7270493549	-0.4076953920
H	-2.7202091956	-0.9917614530	-1.1984410384
N	1.6310838007	0.7750854877	3.4533502338
C	2.5785113212	0.0706133004	4.1776046396
C	3.5625104096	0.9414591634	4.5730871680
N	3.2035376996	2.1822128247	4.0764601631
C	2.0326541878	2.0304875298	3.4077144408
H	1.5220593021	2.8393145680	2.9066004930
H	3.7264953466	3.0386664121	4.1722956402
H	4.4653789905	0.7915706333	5.1440139453
C	2.4609016372	-1.3989433746	4.4125017061
H	3.3203143677	-1.7712248848	4.9776565210
H	1.5498683295	-1.6344549890	4.9754930262
H	2.4012528027	-1.9204735573	3.4511267383

Lysine

Au	-0.1550946211	-0.0805414437	2.1661259303
C	-4.0675438633	0.5090818921	0.7041006388
C	-4.3536562003	0.5219515952	2.0298958637
N	-3.1494018850	0.3595274911	2.6988193347
C	-2.1146919855	0.2365747805	1.8194702181
N	-2.6981112978	0.3286186829	0.5909810162
H	-5.2932572767	0.6254888617	2.5492488388
Cl	1.7429338631	-1.5212185478	1.1879421301
H	-4.7086585395	0.6099676642	-0.1572704135
C	-3.0217083571	0.2864835212	4.1478246011
H	-3.3828918148	-0.6771578972	4.5192583772
H	-1.9669524750	0.3957641150	4.3999855585
H	-3.5969197336	1.0928324653	4.6102847654
C	-1.9787094563	0.2617532982	-0.6787967146
H	-1.8123084716	1.2663011838	-1.0794042777
H	-1.0171854632	-0.2244967276	-0.5083786221
H	-2.5629863378	-0.3227169351	-1.3936700656
C	3.1790407836	0.9751496147	5.5136039798
C	1.8155504946	0.6375628257	4.9042853321
N	1.7880452480	0.6441031864	3.4323958577
H	1.4925164519	-0.3569934546	5.2297280555

H	1.0593986251	1.3479043638	5.2582437539
H	2.0889211056	1.5453506299	3.0674799157
H	2.4034287793	-0.0664544906	3.0286099458
H	3.5064356213	1.9790959870	5.2185666470
H	3.1362116413	0.9462001785	6.6083423969
H	3.9429825854	0.2616548293	5.1868143737

Methionine

Au	-0.1425441801	0.1069984109	2.1692002469
C	-4.1036732638	-0.3710111034	0.7439390166
C	-4.4072943437	0.0382489565	2.0018171282
N	-3.2019512242	0.2597691938	2.6492622184
C	-2.1501491791	-0.0038947150	1.8244217613
N	-2.7219667720	-0.3924436536	0.6514712661
H	-5.3597123542	0.1875513908	2.4857171084
Cl	1.7989275027	-0.5510568397	0.5763874489
H	-4.7411212720	-0.6438055095	-0.0822344002
C	-3.0876213101	0.7061802483	4.0322483232
H	-3.4982868075	-0.0484015528	4.7092642207
H	-2.0300412085	0.8544117493	4.2502073420
H	-3.6268677676	1.6478489788	4.1679223291
C	-1.9901803717	-0.7729678666	-0.5576452180
H	-2.1990861792	-0.0563033926	-1.3565281609
H	-0.9199774249	-0.7735012530	-0.3399282743
H	-2.3011709481	-1.7723219474	-0.8737582034
C	3.9384047682	-0.6274184471	4.9119439171
C	2.6783251636	-0.7384388847	4.0567456921
S	1.6864972155	0.8130423062	3.9840093223
H	1.9846636079	-1.4753562495	4.4725736444
C	2.7767014323	1.8889504419	2.9839711903
H	2.2407157417	2.8296334649	2.8442031901
H	3.7097052257	2.0839190590	3.5160710375
H	2.9507387110	1.4150473905	2.0154902799
H	2.8853777712	-1.0254116602	3.0217002907
H	4.4509957209	-1.5955880793	4.9367818300
H	3.7043109429	-0.3383700932	5.9410272647
H	4.6434791653	0.1025041112	4.5042911988

Selenocysteine

Au	-0.182328	0.148844	2.390135

C	-3.862560	-0.647062	0.454023
C	-4.339475	-0.526681	1.718954
N	-3.249885	-0.248941	2.528558
C	-2.102116	-0.194522	1.796369
N	-2.494893	-0.442542	0.517889
H	-5.341678	-0.612719	2.108211
Cl	1.848635	0.040880	0.661616
H	-4.369863	-0.856456	-0.474460
C	-3.336037	-0.050461	3.969610
H	-3.686223	-0.964943	4.457311
H	-2.338454	0.198457	4.331843
H	-4.025070	0.768502	4.195453
C	-1.611482	-0.484032	-0.650536
H	-1.889630	0.310871	-1.347976
H	-0.576341	-0.342060	-0.329630
H	-1.711025	-1.453744	-1.145044
C	4.213560	-0.857126	4.723438
C	2.951164	-0.886130	3.878136
Se	1.813006	0.772762	4.114309
H	4.831737	0.014022	4.489701
H	3.136365	-0.868645	2.802081
H	2.304298	-1.734507	4.106833
H	1.294524	0.392058	5.451015
H	3.994446	-0.845693	5.796225
H	4.805328	-1.756641	4.514638

Selenolate

Au	0.177958	-0.244728	2.019334
C	-3.917562	0.513564	1.024715
C	-4.042674	0.292375	2.357742
N	-2.777227	-0.010542	2.835852
C	-1.848089	0.000926	1.831688
N	-2.576795	0.328167	0.718349
H	-4.909170	0.326553	3.000097
Cl	2.250092	-1.342118	1.103151
H	-4.651661	0.787845	0.282926
C	-2.473743	-0.337170	4.225683
H	-2.635079	-1.404649	4.412379
H	-1.424846	-0.087896	4.428092
H	-3.127734	0.247515	4.879347
C	-2.003229	0.466903	-0.610081

H	-1.910099	1.522153	-0.888677
H	-1.009847	0.013758	-0.587586
H	-2.634813	-0.045958	-1.343080
C	4.037529	1.041595	4.933217
C	2.887625	0.091552	4.612044
Se	1.133059	1.064561	4.345563
H	4.184106	1.757283	4.117546
H	3.078272	-0.459649	3.689212
H	2.749155	-0.630435	5.423401
H	3.838396	1.618369	5.844872
H	4.981648	0.492149	5.078895

Thiolate

Au	-0.001452	-0.135580	1.894538
C	-4.213869	0.114031	1.151142
C	-4.211546	0.313765	2.494487
N	-2.889221	0.266636	2.905216
C	-2.046869	0.043916	1.853669
N	-2.889159	-0.047818	0.775957
H	-5.024735	0.481226	3.183729
Cl	2.090664	-0.561888	0.580413
H	-5.029300	0.068724	0.445511
C	-2.442119	0.468209	4.282174
H	-3.266496	0.216834	4.955961
H	-1.568518	-0.159781	4.482195
H	-2.145199	1.509036	4.436898
C	-2.440234	-0.290916	-0.586678
H	-2.727071	0.543064	-1.236283
H	-1.351226	-0.380344	-0.557436
H	-2.879033	-1.217499	-0.972380
C	3.673505	0.570068	4.996609
C	2.689440	-0.438884	4.399526
S	0.943776	0.155205	4.447284
H	3.637195	1.511070	4.437650
H	2.951402	-0.642436	3.356837
H	2.760758	-1.386736	4.949868
H	3.422608	0.797441	6.039880
H	4.707624	0.192220	4.968187