Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Effect of total charge on the electronic structure of thiolate-protected X@Ag_{12} superatoms (X = Ag, Au)

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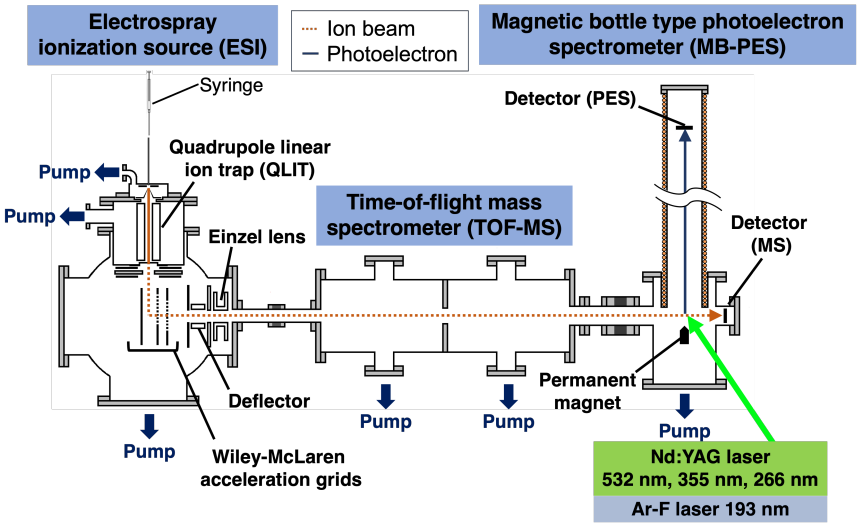

Figure S1. Schematic illustration of home-built apparatus consisting of an electrospray ionization (ESI) source, a quadrupole ion guide, a time-of-flight mass spectrometer (TOF-MS), and a magnetic bottle type photoelectron spectrometer (MB-PES). Brown and blue arrows indicate the trajectories of the cluster ions and photoelectrons, respectively.

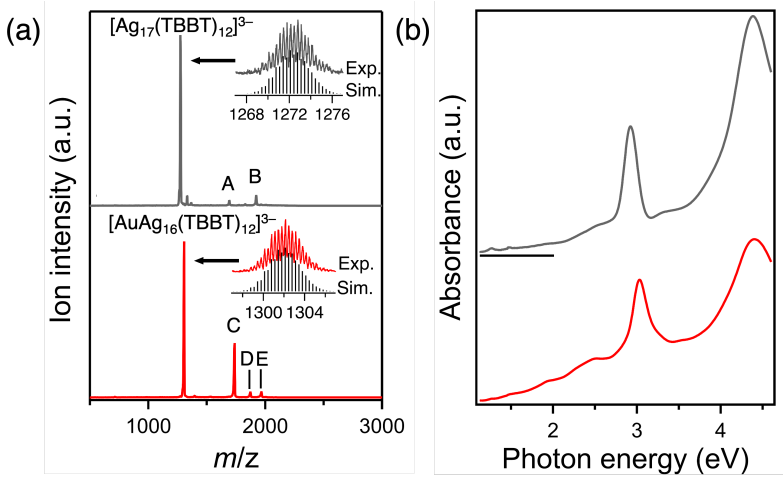

Figure S2. (a) ESI-MS spectra and (b) UV-visible absorption spectra of $\mathbf{3}^{3-}$ (gray) and $\mathbf{4}^{3-}$ (red). Small peaks A–E in panel (a) are assigned to $[Ag_{16}(TBBT)_{10}]^{2-}$, $Na^+[Ag_{17}(TBBT)_{12}]^{3-}$, $[AuAg_{15}(TBBT)_{10}]^{2-}$, $[AuAg_{16}(TBBT)_{11}]^{2-}$, and $Na^+[AuAg_{16}(TBBT)_{12}]^{3-}$, respectively. The insets in panel (a) compare the experimental and theoretical isotope patterns of the main peaks.

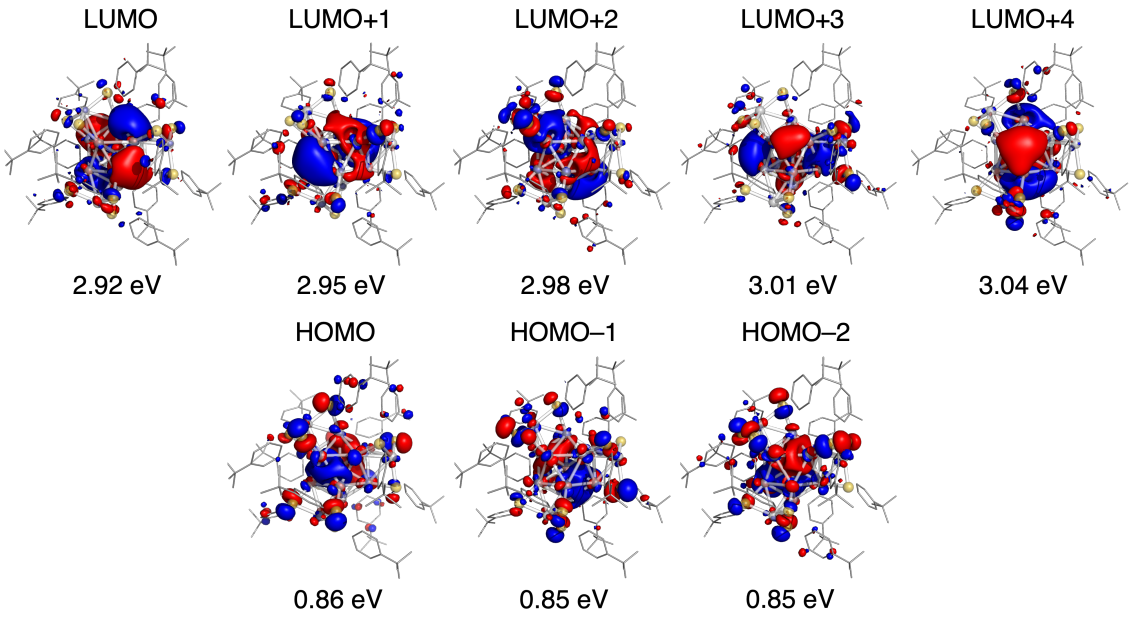

Figure S3. Frontier orbitals of $\mathbf{3}^{3-}$. All orbitals were depicted at 0.02 level.

Table S1. Atomic coordinates for optical structure of $\mathbf{3}^{3-}$.

	x	**y**	**z**
Ag	6.512	5.125	9.97
Ag	5.051	4.134	7.714
Ag	2.437	2.931	8.441
Ag	2.597	5.736	7.407
Ag	3.611	5.076	10.135
Ag	2.57	7.672	9.574
Ag	4.939	7.374	11.134
Ag	7.738	6.834	12.059
Ag	7.285	7.902	9.366
Ag	6.305	8.621	6.813
Ag	4.901	9.469	9.149
Ag	3.39	8.423	6.836
Ag	2.172	10.478	8.58
Ag	4.826	6.271	5.688
Ag	7.272	5.837	7.297
Ag	7.456	7.12	4.568
S	5.888	8.064	13.287
S	7.87	4.352	11.871
S	4.049	11.701	9.693
S	9.255	8.359	10.746
S	4.372	1.843	7.18
S	5.562	6.068	3.336
S	7.693	9.57	4.997
S	0.562	9.058	9.899

S	0.728	4.168	7.099
S	2.498	3.055	10.943
S	1.993	10.273	6.043
S	9.042	5.487	5.64
C	5.239	6.946	14.497
C	4.739	7.484	15.661
H	4.759	8.427	15.774
C	4.216	6.722	16.660999
H	3.934	7.138	17.466
C	4.095	5.408	16.534
C	4.531	4.802	15.36
H	4.395	3.871	15.226
C	5.221	5.618	14.301
H	5.621	5.216	13.541
C	3.536	4.519	17.671
C	3.08	3.143	17.257
H	2.328	2.863	17.822001
H	3.818	2.506	17.360001
H	2.795	3.16	16.318001
C	4.69	4.394	18.636999
H	4.344	4.242	19.541
H	5.216	5.221	18.627001
H	5.257	3.641	18.372999
C	2.393	5.241	18.349001
H	1.813	5.646	17.671
H	2.749	5.943	18.934999
H	1.875	4.604	18.884001
C	9.342	3.865	11.024
C	9.842	2.596	11.089
H	9.316	1.974	11.579
C	10.968	2.115	10.565
H	11.214	1.212	10.719
C	11.788	2.942	9.784
C	11.309	4.202	9.63
H	11.735	4.754	8.983
C	10.211	4.774	10.36
H	10.073	5.714	10.397
C	13.122	2.432	9.192
C	13.489	0.983	9.503
H	13.727	0.903	10.452
H	14.258	0.716	8.952
H	12.729	0.402	9.308
C	14.258	3.31	9.671
H	13.955	4.236	9.743
H	15.007	3.262	9.034
H	14.568	2.999	10.551

C	13.027	2.571	7.685
H	13.791	2.149	7.26
H	12.988	3.522	7.445
H	12.196	2.135	7.373
C	4.924	12.662	8.555
C	5.606	13.767	9.027
H	5.593	13.996	9.949
C	6.319	14.545	8.099
H	6.796	15.287	8.449
C	6.406	14.344	6.695
C	5.742	13.206	6.305
H	5.734	12.994	5.38
C	5.093	12.362	7.151
H	4.742	11.55	6.808
C	7.244	15.199	5.723
C	7.688	16.533001	6.322
H	7.703	17.218	5.623
H	8.585	16.437	6.705
H	7.06	16.799	7.027
C	8.496	14.455	5.284
H	8.244	13.597	4.887
H	9.075	14.302	6.062
H	8.98	14.993	4.62
C	6.442	15.525	4.452
H	7.011	16.018	3.825
H	5.665	16.073999	4.688
H	6.137	14.693	4.034
C	9.011	9.995	11.318
C	10.116	10.864	11.548
H	11.004	10.544	11.418
C	9.924	12.071	11.928
H	10.704	12.606	12.014
C	8.801	12.662	12.212
C	7.644	11.858	12.038
H	6.785	12.19	12.271
C	7.791	10.624	11.534
H	7.003	10.142	11.312
C	8.685	14.16	12.558
C	7.247	14.568	12.86
H	7.178	15.545	12.849
H	6.99	14.231	13.743
H	6.652	14.191	12.181
C	9.521	14.395	13.781
H	10.304	14.939	13.544
H	9.819	13.535	14.144
H	8.988	14.868	14.455

C	5.37	0.827	8.195
C	5.778	-0.399	7.712
H	5.436	-0.719	6.887
C	6.678	-1.161	8.425
H	7.001	-1.954	8.01
C	7.165	-0.864	9.719
C	6.678	0.306	10.199
H	6.919	0.58	11.075
C	5.811	1.144	9.425
H	5.529	1.968	9.801
C	8.091	-1.804	10.517
C	7.516	-3.208	10.493
H	7.144	-3.395	9.603
H	6.806	-3.282	11.164
H	8.224	-3.856	10.692
C	9.283	-1.77	9.548
H	9.729	-2.642	9.551
H	9.914	-1.079	9.832
H	8.962	-1.569	8.644
C	8.657	-1.566	11.918
H	7.926	-1.586	12.572
H	9.096	-0.691	11.945
H	9.306	-2.265	12.13
C	6.611	10.394	3.911
C	7.052	11.414	3.147
H	7.985	11.578	3.12
C	6.224	12.238	2.394
H	6.598	12.903	1.829
C	4.78	12.079	2.476
C	4.308	11.046	3.199
H	3.377	10.864	3.199
C	5.185	10.216	3.969
H	4.818	9.539	4.527
C	3.826	12.954	1.647
C	4.516	13.965	0.753
H	4.983	13.501	0.031
H	5.159	14.48	1.284
H	3.847	14.574	0.373
C	2.957	13.69	2.637
H	2.872	13.158	3.455
H	2.067	13.832	2.25
H	3.362	14.554	2.849
C	3.003	12.025	0.818
H	2.264	12.521	0.408
H	2.641	11.312	1.387
H	3.562	11.629	0.116

C	0.649	9.471	11.579
C	-0.528	9.361	12.411
H	-1.341	9.032	12.044
C	-0.467	9.723	13.695
H	-1.285	9.735	14.178
C	0.703	10.094	14.408
C	1.841	10.21	13.616
H	2.652	10.482	14.031
C	1.846	9.947	12.233
H	2.641	10.083	11.729
C	0.708	10.462	15.904
C	-0.426	9.862	16.709
H	-1.282	10.171	16.349001
H	-0.344	10.14	17.643999
H	-0.382	8.882	16.653999
C	2.018	10.006	16.497
H	2.277	9.149	16.099001
H	1.918	9.899	17.466
H	2.711	10.675	16.312
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H	0.839	12.362	15.127
H	1.259	12.291	16.667999
H	-0.285	12.229	16.257
C	0.99	3.755	5.322
C	-0.115	3.723	4.551
H	-0.957	3.981	4.904
C	0.003	3.279	3.127
H	-0.764	3.248	2.565
C	1.19	2.928	2.658
C	2.203	3.052	3.425
H	3.064	2.956	3.034
C	2.146	3.321	4.798
H	2.913	3.202	5.346
C	1.357	2.458	1.199
C	2.162	3.483	0.438
H	2.013	3.367	-0.524
H	3.113	3.364	0.64
H	1.882	4.383	0.705
C	2.103	1.141	1.199
H	1.862	0.629	0.397
H	1.867	0.629	2
H	3.07	1.314	1.192
C	0.018	2.274	0.538
H	-0.38	3.151	0.353
H	-0.574	1.767	1.134
H	0.133	1.784	-0.305

C	0.926	3.664	11.514
C	0.167	4.601	10.764
H	0.472	4.924	9.925
C	-1.046	5.034	11.301
H	-1.508	5.742	10.87
C	-1.623	4.451	12.479
C	-0.823	3.556	13.161
H	-1.118	3.211	13.997
C	0.397	3.146	12.654
H	0.885	2.475	13.12
C	-2.98	4.961	13.014
C	-2.941	6.447	13.257
H	-2.395	6.878	12.568
H	-2.552	6.623	14.14
H	-3.852	6.807	13.226
C	-4.031	4.672	11.945
H	-4.695	4.046	12.301
H	-3.598	4.278	11.161
H	-4.472	5.507	11.692
C	-3.4	4.259	14.284
H	-3.721	3.358	14.072
H	-4.121	4.765	14.716
H	-2.636	4.199	14.894
C	0.459	9.477	5.661
C	-0.1	8.415	6.295
H	0.328	8.101	7.082
C	-1.249	7.758	5.887
H	-1.592	7.005	6.356
C	-1.905	8.296	4.685
C	-1.441	9.262	4.192
H	-1.936	9.636	3.473
C	-0.282	9.919	4.517
H	0.023	10.649	3.993
C	-3.223	7.69	4.175
C	-2.975	6.195	4.099
H	-3.459	5.824	3.329
H	-3.305	5.771	4.921
H	-2.021	6.025	4
C	-3.641	8.163	2.781
H	-2.998	7.806	2.12
H	-3.616	9.143	2.753
H	-4.531	7.84	2.575
C	-4.359	7.954	5.123
H	-4.388	8.905	5.346
H	-4.236	7.427	5.942
H	-5.208	7.696	4.699

C	10.442	6.337	6.322
C	11.717	5.796	6.205
H	11.84	4.966	5.76
C	12.809	6.47	6.74
H	13.681	6.099	6.658
C	12.624	7.685	7.387
C	11.35	8.225	7.503
H	11.224	9.058	7.949
C	10.257	7.552	6.969
H	9.386	7.923	7.048
C	13.763	8.319	8.181
C	15.053	8.22	7.411
H	15.076	7.376	6.918
H	15.809	8.254	8.034
H	15.114	8.97	6.781
C	13.394	9.78	8.473
H	12.483	9.822	8.832
H	13.442	10.301	7.644
H	14.022	10.151	9.13
C	13.899	7.617	9.531
H	14.219	6.691	9.39
H	13.009	7.569	9.966
H	14.514	8.092	10.106
C	6.042	4.426	2.983
C	5.878	3.916	1.702
H	5.654	4.496	0.983
C	6.042	2.554	1.469
H	5.931	2.206	0.592
C	6.367	1.705	2.521
C	6.531	2.217	3.801
H	6.755	1.637	4.521
C	6.367	3.576	4.034
H	6.478	3.927	4.911
C	6.872	0.246	2.586
C	6.949	-0.765	3.729
H	7.28	-1.608	3.397
H	6.052	-0.875	4.11
H	7.549	-0.411	4.425
C	5.847	-0.227	1.596
H	5.236	0.512	1.377
H	5.329	-0.963	1.986
H	6.288	-0.535	0.781
C	8.232	0.283	1.918
H	8.442	1.184	1.61
H	8.224	-0.326	1.123
H	8.924	-0.031	2.531

C	9.1993	15.0382	11.4023
H	9.9593	14.5109	10.8644
H	8.3897	15.2687	10.7418
H	9.6064	15.9454	11.7975
Ag	4.944	6.799	8.416

Table S2. Atomic coordinates for optimized structure of **4**$^{3-}$.

	x	**y**	**z**
Au	4.944	6.799	8.416
Ag	6.512	5.125	9.97
Ag	5.051	4.134	7.714
Ag	2.437	2.931	8.441
Ag	2.597	5.736	7.407
Ag	3.611	5.076	10.135
Ag	2.57	7.672	9.574
Ag	4.939	7.374	11.134
Ag	7.738	6.834	12.059
Ag	7.285	7.902	9.366
Ag	6.305	8.621	6.813
Ag	4.901	9.469	9.149
Ag	3.39	8.423	6.836
Ag	2.172	10.478	8.58
Ag	4.826	6.271	5.688
Ag	7.272	5.837	7.297
Ag	7.456	7.12	4.568
S	5.888	8.064	13.287
S	7.87	4.352	11.871
S	4.049	11.701	9.693
S	9.255	8.359	10.746
S	4.372	1.843	7.18
S	5.562	6.068	3.336
S	7.693	9.57	4.997
S	0.562	9.058	9.899
S	0.728	4.168	7.099
S	2.498	3.055	10.943
S	1.993	10.273	6.043
S	9.042	5.487	5.64
C	5.239	6.946	14.497
C	4.739	7.484	15.661
H	4.759	8.427	15.774
C	4.216	6.722	16.660999
H	3.934	7.138	17.466
C	4.095	5.408	16.534
C	4.531	4.802	15.36
H	4.395	3.871	15.226
C	5.221	5.618	14.301

H	5.621	5.216	13.541
C	3.536	4.519	17.671
C	3.08	3.143	17.257
H	2.328	2.863	17.822001
H	3.818	2.506	17.360001
H	2.795	3.16	16.318001
C	4.69	4.394	18.636999
H	4.344	4.242	19.541
H	5.216	5.221	18.627001
H	5.257	3.641	18.372999
C	2.393	5.241	18.349001
H	1.813	5.646	17.671
H	2.749	5.943	18.934999
H	1.875	4.604	18.884001
C	9.342	3.865	11.024
C	9.842	2.596	11.089
H	9.316	1.974	11.579
C	10.968	2.115	10.565
H	11.214	1.212	10.719
C	11.788	2.942	9.784
C	11.309	4.202	9.63
H	11.735	4.754	8.983
C	10.211	4.774	10.36
H	10.073	5.714	10.397
C	13.122	2.432	9.192
C	13.489	0.983	9.503
H	13.727	0.903	10.452
H	14.258	0.716	8.952
H	12.729	0.402	9.308
C	14.258	3.31	9.671
H	13.955	4.236	9.743
H	15.007	3.262	9.034
H	14.568	2.999	10.551
C	13.027	2.571	7.685
H	13.791	2.149	7.26
H	12.988	3.522	7.445
H	12.196	2.135	7.373
C	4.924	12.662	8.555
C	5.606	13.767	9.027
H	5.593	13.996	9.949
C	6.319	14.545	8.099
H	6.796	15.287	8.449
C	6.406	14.344	6.695
C	5.742	13.206	6.305
H	5.734	12.994	5.38
C	5.093	12.362	7.151

H	4.742	11.55	6.808
C	7.244	15.199	5.723
C	7.688	16.533001	6.322
H	7.703	17.218	5.623
H	8.585	16.437	6.705
H	7.06	16.799	7.027
C	8.496	14.455	5.284
H	8.244	13.597	4.887
H	9.075	14.302	6.062
H	8.98	14.993	4.62
C	6.442	15.525	4.452
H	7.011	16.018	3.825
H	5.665	16.073999	4.688
H	6.137	14.693	4.034
C	9.011	9.995	11.318
C	10.116	10.864	11.548
H	11.004	10.544	11.418
C	9.924	12.071	11.928
H	10.704	12.606	12.014
C	8.801	12.662	12.212
C	7.644	11.858	12.038
H	6.785	12.19	12.271
C	7.791	10.624	11.534
H	7.003	10.142	11.312
C	8.685	14.16	12.558
C	7.247	14.568	12.86
H	7.178	15.545	12.849
H	6.99	14.231	13.743
H	6.652	14.191	12.181
C	9.521	14.395	13.781
H	10.304	14.939	13.544
H	9.819	13.535	14.144
H	8.988	14.868	14.455
C	5.37	0.827	8.195
C	5.778	-0.399	7.712
H	5.436	-0.719	6.887
C	6.678	-1.161	8.425
H	7.001	-1.954	8.01
C	7.165	-0.864	9.719
C	6.678	0.306	10.199
H	6.919	0.58	11.075
C	5.811	1.144	9.425
H	5.529	1.968	9.801
C	8.091	-1.804	10.517
C	7.516	-3.208	10.493
H	7.144	-3.395	9.603

H	6.806	-3.282	11.164
H	8.224	-3.856	10.692
C	9.283	-1.77	9.548
H	9.729	-2.642	9.551
H	9.914	-1.079	9.832
H	8.962	-1.569	8.644
C	8.657	-1.566	11.918
H	7.926	-1.586	12.572
H	9.096	-0.691	11.945
H	9.306	-2.265	12.13
C	6.611	10.394	3.911
C	7.052	11.414	3.147
H	7.985	11.578	3.12
C	6.224	12.238	2.394
H	6.598	12.903	1.829
C	4.78	12.079	2.476
C	4.308	11.046	3.199
H	3.377	10.864	3.199
C	5.185	10.216	3.969
H	4.818	9.539	4.527
C	3.826	12.954	1.647
C	4.516	13.965	0.753
H	4.983	13.501	0.031
H	5.159	14.48	1.284
H	3.847	14.574	0.373
C	2.957	13.69	2.637
H	2.872	13.158	3.455
H	2.067	13.832	2.25
H	3.362	14.554	2.849
C	3.003	12.025	0.818
H	2.264	12.521	0.408
H	2.641	11.312	1.387
H	3.562	11.629	0.116
C	0.649	9.471	11.579
C	-0.528	9.361	12.411
H	-1.341	9.032	12.044
C	-0.467	9.723	13.695
H	-1.285	9.735	14.178
C	0.703	10.094	14.408
C	1.841	10.21	13.616
H	2.652	10.482	14.031
C	1.846	9.947	12.233
H	2.641	10.083	11.729
C	0.708	10.462	15.904
C	-0.426	9.862	16.709
H	-1.282	10.171	16.349001

H	-0.344	10.14	17.643999
H	-0.382	8.882	16.653999
C	2.018	10.006	16.497
H	2.277	9.149	16.099001
H	1.918	9.899	17.466
H	2.711	10.675	16.312
C	0.623	11.969	15.997
H	0.839	12.362	15.127
H	1.259	12.291	16.667999
H	-0.285	12.229	16.257
C	0.99	3.755	5.322
C	-0.115	3.723	4.551
H	-0.957	3.981	4.904
C	0.003	3.279	3.127
H	-0.764	3.248	2.565
C	1.19	2.928	2.658
C	2.203	3.052	3.425
H	3.064	2.956	3.034
C	2.146	3.321	4.798
H	2.913	3.202	5.346
C	1.357	2.458	1.199
C	2.162	3.483	0.438
H	2.013	3.367	-0.524
H	3.113	3.364	0.64
H	1.882	4.383	0.705
C	2.103	1.141	1.199
H	1.862	0.629	0.397
H	1.867	0.629	2
H	3.07	1.314	1.192
C	0.018	2.274	0.538
H	-0.38	3.151	0.353
H	-0.574	1.767	1.134
H	0.133	1.784	-0.305
C	0.926	3.664	11.514
C	0.167	4.601	10.764
H	0.472	4.924	9.925
C	-1.046	5.034	11.301
H	-1.508	5.742	10.87
C	-1.623	4.451	12.479
C	-0.823	3.556	13.161
H	-1.118	3.211	13.997
C	0.397	3.146	12.654
H	0.885	2.475	13.12
C	-2.98	4.961	13.014
C	-2.941	6.447	13.257
H	-2.395	6.878	12.568

H	-2.552	6.623	14.14
H	-3.852	6.807	13.226
C	-4.031	4.672	11.945
H	-4.695	4.046	12.301
H	-3.598	4.278	11.161
H	-4.472	5.507	11.692
C	-3.4	4.259	14.284
H	-3.721	3.358	14.072
H	-4.121	4.765	14.716
H	-2.636	4.199	14.894
C	0.459	9.477	5.661
C	-0.1	8.415	6.295
H	0.328	8.101	7.082
C	-1.249	7.758	5.887
H	-1.592	7.005	6.356
C	-1.905	8.296	4.685
C	-1.441	9.262	4.192
H	-1.936	9.636	3.473
C	-0.282	9.919	4.517
H	0.023	10.649	3.993
C	-3.223	7.69	4.175
C	-2.975	6.195	4.099
H	-3.459	5.824	3.329
H	-3.305	5.771	4.921
H	-2.021	6.025	4
C	-3.641	8.163	2.781
H	-2.998	7.806	2.12
H	-3.616	9.143	2.753
H	-4.531	7.84	2.575
C	-4.359	7.954	5.123
H	-4.388	8.905	5.346
H	-4.236	7.427	5.942
H	-5.208	7.696	4.699
C	10.442	6.337	6.322
C	11.717	5.796	6.205
H	11.84	4.966	5.76
C	12.809	6.47	6.74
H	13.681	6.099	6.658
C	12.624	7.685	7.387
C	11.35	8.225	7.503
H	11.224	9.058	7.949
C	10.257	7.552	6.969
H	9.386	7.923	7.048
C	13.763	8.319	8.181
C	15.053	8.22	7.411
H	15.076	7.376	6.918

H	15.809	8.254	8.034
H	15.114	8.97	6.781
C	13.394	9.78	8.473
H	12.483	9.822	8.832
H	13.442	10.301	7.644
H	14.022	10.151	9.13
C	13.899	7.617	9.531
H	14.219	6.691	9.39
H	13.009	7.569	9.966
H	14.514	8.092	10.106
C	6.042	4.426	2.983
C	5.878	3.916	1.702
H	5.654	4.496	0.983
C	6.042	2.554	1.469
H	5.931	2.206	0.592
C	6.367	1.705	2.521
C	6.531	2.217	3.801
H	6.755	1.637	4.521
C	6.367	3.576	4.034
H	6.478	3.927	4.911
C	6.872	0.246	2.586
C	6.949	-0.765	3.729
H	7.28	-1.608	3.397
H	6.052	-0.875	4.11
H	7.549	-0.411	4.425
C	5.847	-0.227	1.596
H	5.236	0.512	1.377
H	5.329	-0.963	1.986
H	6.288	-0.535	0.781
C	8.232	0.283	1.918
H	8.442	1.184	1.61
H	8.224	-0.326	1.123
H	8.924	-0.031	2.531
C	9.1993	15.0382	11.4023
H	9.9593	14.5109	10.8644
H	8.3897	15.2687	10.7418
H	9.6064	15.9454	11.7975