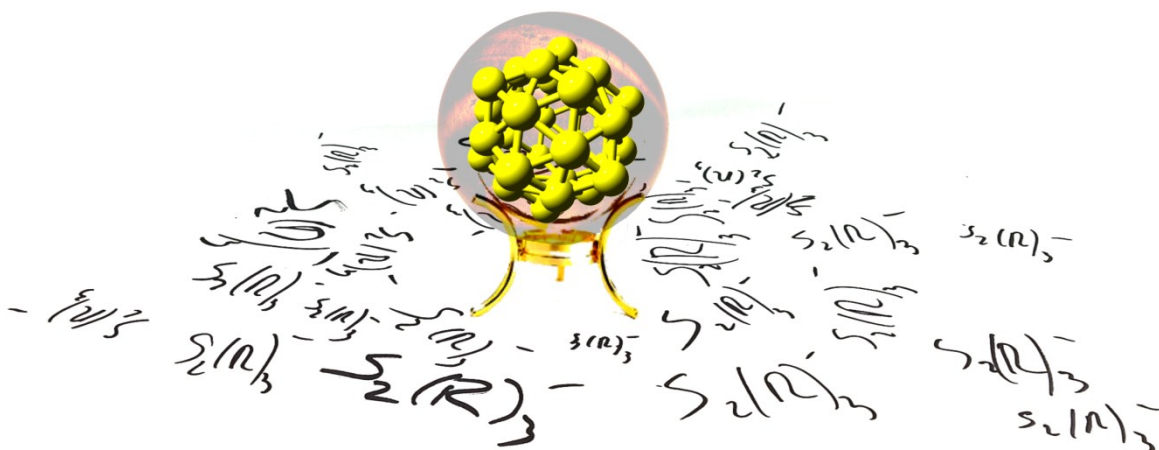


Thiolate-protected golden fullerenes. A 32-*ve*  
Core Involving a Hollow Au<sub>32</sub> cage

Markus Rauhalahti, Alvaro Muñoz-Castro and Dage Sundholm



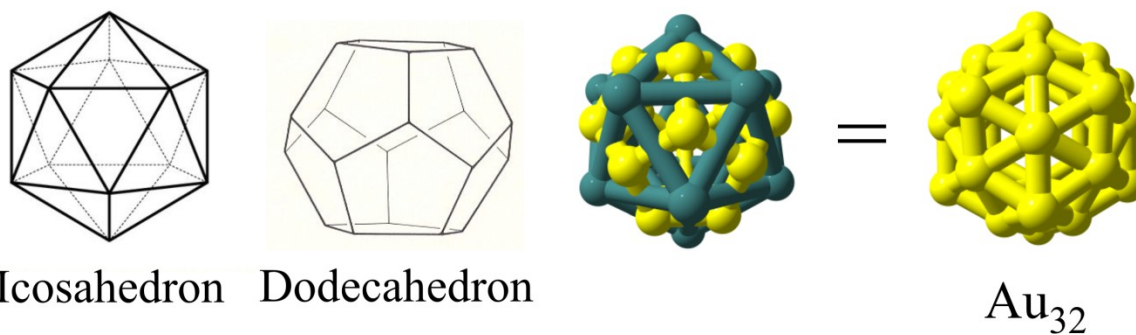
**Figure S1.** Icosahedron and Dodecahedral motifs in Au<sub>32</sub> golden fullerene.

**Figure S2.** Comparison between the absorption spectrum obtained at the PBE and LB94 functionals for  $[\text{Au}_{25}(\text{SMe})_{18}]^-$ .

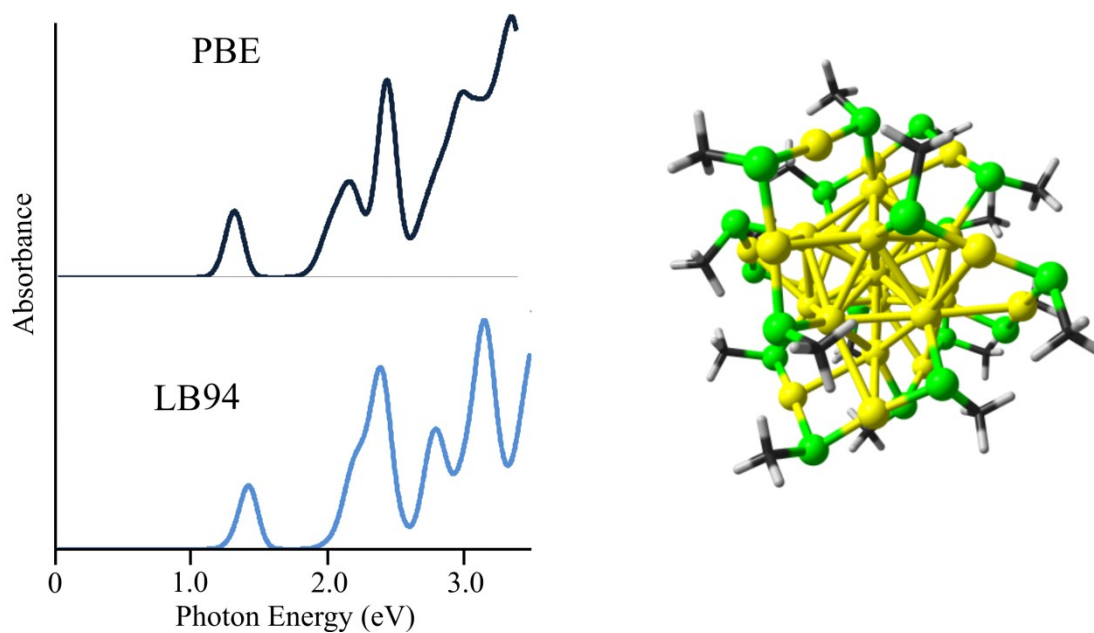
**Figure S3.** Comparison of the geometrical structure between the compact and hollow isomers of  $[\text{Au}_{32}@\text{Au}_{12}(\text{SMe})_{18}]^{6-}$ .

**Figure S4.** Comparison of the electronic structure between the compact and hollow isomers of  $[\text{Au}_{32}@\text{Au}_{12}(\text{SMe})_{18}]^{6-}$ .

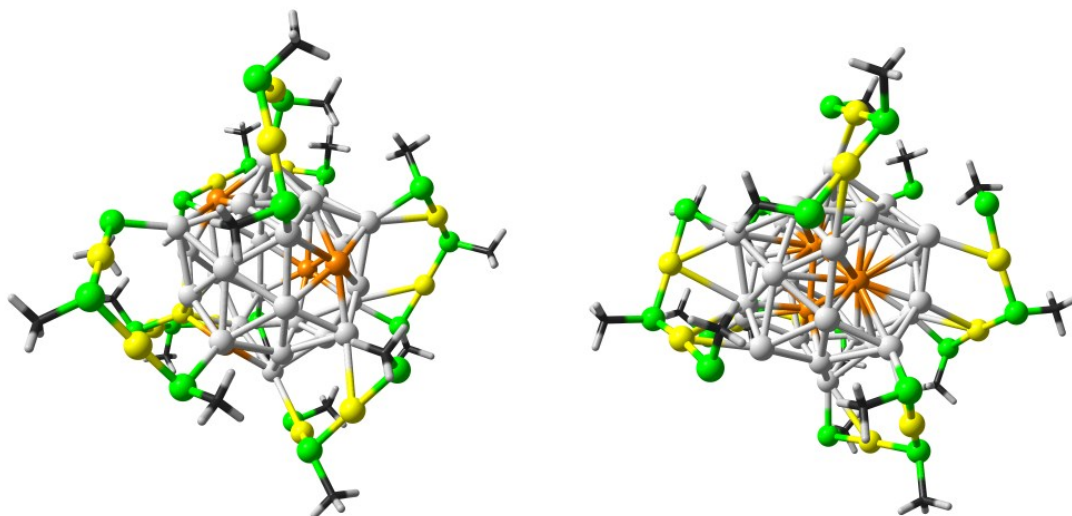
**Table S1.** Coordinates of the optimized structures for hollow and compact isomers of  $[\text{Au}_{32}@\text{Au}_{12}(\text{SMe})_{18}]^{6-}$ .



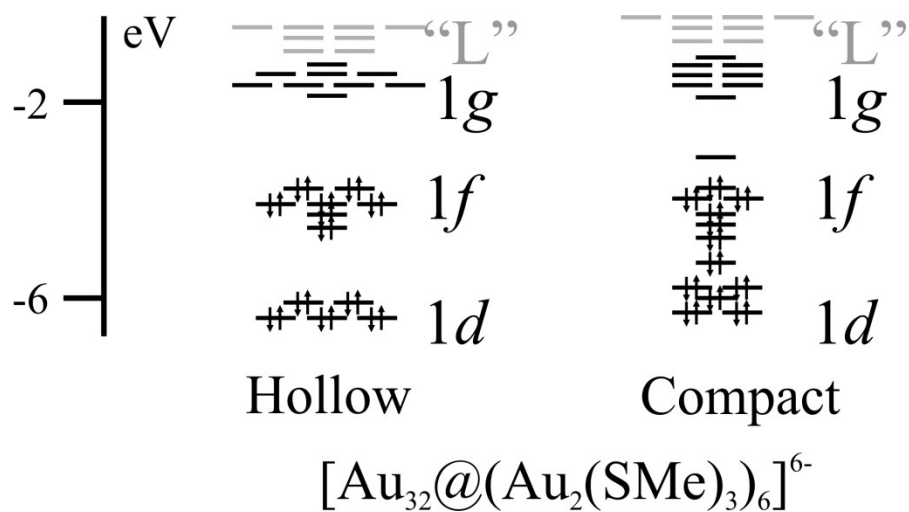
**Figure S1.** Icosahedron and Dodecahedral motifs in Au<sub>32</sub> golden fullerene.



**Figure S2.** Comparison between the absorption spectrum obtained at the PBE and LB94 functionals for [Au<sub>25</sub>(SMe)<sub>18</sub>]<sup>−</sup>.



**Figure S3.** Comparison of the geometrical structure between the compact and hollow isomers of  $[\text{Au}_{32}@\text{Au}_{12}(\text{SMe})_{18}]^{6-}$ . Orange, denote atoms that are shifted towards the center. Grey, denote atoms that remain in the initial  $\text{Au}_{32}$  contour.



**Figure S4.** Comparison of the electronic structure between the compact and hollow isomers of  $[\text{Au}_{32}@\text{Au}_{12}(\text{SMe})_{18}]^{6-}$ .

**Table S1.** Coordinates of the optimized structures for hollow and compact isomers of  $[\text{Au}_{32}@\text{Au}_{12}(\text{SMe})_{18}]^{6-}$ . Values in Angstrom.

Hollow  $[\text{Au}_{32}@\text{Au}_{12}(\text{SMe})_{18}]^{6-}$

|    |              |              |              |
|----|--------------|--------------|--------------|
| Au | 2.650848000  | 1.723800000  | 3.789411000  |
| Au | 3.995239000  | 2.889273000  | -0.768047000 |
| Au | -0.215696000 | 4.700160000  | 1.090970000  |
| Au | 4.495617000  | -1.772241000 | 0.919876000  |
| Au | -2.111698000 | -1.407150000 | -3.703832000 |
| Au | 0.718851000  | -4.433204000 | -0.946616000 |
| Au | 2.804696000  | -0.937147000 | -3.786424000 |
| Au | -1.454471000 | 3.390399000  | -1.141171000 |
| Au | -2.116697000 | 1.284499000  | -2.781274000 |
| Au | 0.218742000  | 0.203024000  | -3.793834000 |
| Au | 2.344527000  | 1.654595000  | -2.802205000 |
| Au | 1.288565000  | 3.628025000  | -1.178418000 |
| Au | -2.229490000 | 2.732564000  | 1.404742000  |
| Au | -3.360371000 | 0.233142000  | 1.360749000  |
| Au | -3.312159000 | -0.685072000 | -1.225468000 |
| Au | 0.016996000  | 2.601313000  | 2.995735000  |
| Au | 2.198053000  | 3.157411000  | 1.380244000  |
| Au | -1.737421000 | -2.946334000 | -1.310266000 |
| Au | 0.465508000  | -2.380107000 | -2.884124000 |
| Au | 2.749668000  | -2.501378000 | -1.306488000 |
| Au | 3.906692000  | -0.011033000 | -1.269769000 |
| Au | 3.793598000  | 0.916489000  | 1.311100000  |
| Au | -1.795905000 | -1.427429000 | 2.920740000  |
| Au | -0.798648000 | -3.375740000 | 1.244457000  |
| Au | 1.939843000  | -3.117533000 | 1.258464000  |
| Au | 2.601090000  | -0.992941000 | 2.903409000  |
| Au | 0.282998000  | 0.036143000  | 3.964091000  |
| Au | 0.584620000  | -2.842261000 | 3.710045000  |
| Au | -3.492437000 | -2.595721000 | 0.955395000  |
| Au | -2.367525000 | 1.254298000  | 3.820963000  |
| Au | -4.027677000 | 2.034544000  | -0.696931000 |
| Au | -0.031292000 | 3.034272000  | -3.631009000 |
| S  | -0.212266000 | 4.858794000  | -5.497689000 |
| S  | 0.555743000  | -4.263498000 | 5.884980000  |
| S  | -3.473940000 | 1.335346000  | 6.184721000  |
| S  | 3.308536000  | 2.590349000  | 6.158902000  |
| S  | 6.138085000  | 3.690395000  | -1.992887000 |
| S  | 4.594410000  | -2.135714000 | -5.279760000 |
| S  | -3.582000000 | -2.099445000 | -5.741505000 |
| S  | -5.826441000 | 3.457428000  | -1.893733000 |
| S  | 0.139375000  | 7.260972000  | 1.225026000  |
| S  | 6.201250000  | -3.730231000 | 1.063926000  |
| S  | -5.809906000 | -3.697745000 | 1.274815000  |
| S  | 0.486525000  | -7.140122000 | -1.272893000 |
| Au | -6.564044000 | -2.345412000 | 3.016455000  |
| Au | -5.364440000 | 0.150921000  | 5.517235000  |
| S  | -7.314284000 | -0.934569000 | 4.752508000  |
| Au | -5.596333000 | -1.073596000 | -5.189524000 |
| Au | -6.703779000 | 1.794043000  | -3.259150000 |
| S  | -7.587892000 | 0.027283000  | -4.549949000 |
| Au | 2.865305000  | -3.721692000 | -5.313963000 |
| Au | 0.832345000  | -6.188876000 | -3.386452000 |
| S  | 1.128229000  | -5.290004000 | -5.538825000 |
| Au | 3.013042000  | 4.839083000  | 5.629062000  |
| Au | 1.480969000  | 7.215241000  | 3.130135000  |
| S  | 2.839600000  | 7.127141000  | 5.058994000  |
| Au | 5.698206000  | -4.080719000 | 3.312313000  |
| Au | 2.879656000  | -4.317684000 | 5.759484000  |

|    |              |              |              |
|----|--------------|--------------|--------------|
| S  | 5.231926000  | -4.349933000 | 5.607315000  |
| Au | 1.833306000  | 5.881947000  | -5.071704000 |
| Au | 5.063570000  | 5.246113000  | -3.348722000 |
| S  | 3.922630000  | 6.885620000  | -4.607533000 |
| C  | 5.220055000  | -5.036988000 | 0.191436000  |
| H  | 5.649451000  | -6.030237000 | 0.390973000  |
| H  | 4.167862000  | -4.993880000 | 0.501666000  |
| H  | 5.267805000  | -4.807627000 | -0.881965000 |
| C  | 5.666952000  | -6.122024000 | 5.942510000  |
| H  | 5.372640000  | -6.362179000 | 6.974508000  |
| H  | 5.143550000  | -6.787613000 | 5.247984000  |
| H  | 6.753093000  | -6.242204000 | 5.818398000  |
| C  | 0.191707000  | -2.961290000 | 7.148060000  |
| H  | -0.898095000 | -2.822140000 | 7.149997000  |
| H  | 0.533470000  | -3.279300000 | 8.146689000  |
| H  | 0.663569000  | -2.013497000 | 6.862128000  |
| C  | 1.747013000  | 2.121190000  | 7.044775000  |
| H  | 0.870753000  | 2.385202000  | 6.440576000  |
| H  | 1.770469000  | 1.028474000  | 7.159544000  |
| H  | 1.708355000  | 2.606419000  | 8.029274000  |
| C  | 1.753748000  | 7.804901000  | 6.397851000  |
| H  | 0.814990000  | 7.248221000  | 6.456233000  |
| H  | 2.292130000  | 7.716308000  | 7.348705000  |
| H  | 1.546538000  | 8.861284000  | 6.174834000  |
| C  | 1.344661000  | 7.464132000  | -0.166243000 |
| H  | 2.086200000  | 6.652558000  | -0.147553000 |
| H  | 0.767654000  | 7.382151000  | -1.098637000 |
| H  | 1.834273000  | 8.446208000  | -0.109158000 |
| C  | -1.447932000 | 6.002451000  | -4.728776000 |
| H  | -1.456715000 | 6.972005000  | -5.252653000 |
| H  | -2.426817000 | 5.514098000  | -4.821051000 |
| H  | -1.231572000 | 6.144335000  | -3.666623000 |
| C  | 4.791244000  | 6.874135000  | -6.245748000 |
| H  | 5.817726000  | 7.244286000  | -6.096104000 |
| H  | 4.823955000  | 5.859064000  | -6.661864000 |
| H  | 4.242340000  | 7.535336000  | -6.933489000 |
| C  | 6.383416000  | 2.225503000  | -3.100138000 |
| H  | 6.714043000  | 1.400604000  | -2.452049000 |
| H  | 5.432499000  | 1.931945000  | -3.567497000 |
| H  | 7.147061000  | 2.448700000  | -3.859226000 |
| C  | -4.692602000 | 4.395380000  | -3.016612000 |
| H  | -5.273389000 | 4.945942000  | -3.769722000 |
| H  | -4.131009000 | 5.090497000  | -2.377715000 |
| H  | -3.975001000 | 3.711538000  | -3.488503000 |
| C  | -8.185140000 | 0.862112000  | -6.096016000 |
| H  | -7.390398000 | 1.470938000  | -6.538917000 |
| H  | -8.500050000 | 0.090055000  | -6.812109000 |
| H  | -9.037515000 | 1.505806000  | -5.832562000 |
| C  | -3.853720000 | -3.895968000 | -5.383198000 |
| H  | -2.883138000 | -4.389718000 | -5.526728000 |
| H  | -4.169393000 | -4.037408000 | -4.342435000 |
| H  | -4.600573000 | -4.318647000 | -6.072476000 |
| C  | -6.698103000 | -3.028484000 | -0.208577000 |
| H  | -6.312559000 | -3.576939000 | -1.077943000 |
| H  | -7.779166000 | -3.187487000 | -0.107660000 |
| H  | -6.475242000 | -1.967400000 | -0.344905000 |
| C  | -7.754437000 | -2.090771000 | 6.133134000  |
| H  | -8.609832000 | -2.703378000 | 5.811962000  |
| H  | -6.908754000 | -2.742215000 | 6.381027000  |
| H  | -8.026178000 | -1.489553000 | 7.013723000  |
| C  | -2.419507000 | 0.064106000  | 7.022748000  |
| H  | -2.876255000 | -0.245257000 | 7.979531000  |
| H  | -2.266131000 | -0.798508000 | 6.370140000  |

|   |              |              |              |
|---|--------------|--------------|--------------|
| H | -1.444512000 | 0.536877000  | 7.200900000  |
| C | -1.357970000 | -7.241049000 | -1.111598000 |
| H | -1.810714000 | -6.259086000 | -1.313474000 |
| H | -1.769810000 | -8.004093000 | -1.792601000 |
| H | -1.573264000 | -7.514794000 | -0.067601000 |
| C | 1.876597000  | -6.672004000 | -6.535007000 |
| H | 2.799557000  | -7.040350000 | -6.066205000 |
| H | 1.141657000  | -7.491779000 | -6.598285000 |
| H | 2.101031000  | -6.286959000 | -7.541546000 |
| C | 5.735630000  | -2.715668000 | -3.940917000 |
| H | 5.158056000  | -2.921620000 | -3.021397000 |
| H | 6.285379000  | -3.611742000 | -4.266518000 |
| H | 6.436308000  | -1.892982000 | -3.735402000 |

Compact [Au<sub>32</sub>@Au<sub>12</sub>(SMe)<sub>18</sub>]<sup>6-</sup>

|    |              |              |              |
|----|--------------|--------------|--------------|
| Au | 2.731600000  | 1.415600000  | 3.893400000  |
| Au | 3.886800000  | 2.680500000  | -0.647600000 |
| Au | -0.359300000 | 4.131500000  | 1.238800000  |
| Au | 4.447500000  | -1.690700000 | 0.892500000  |
| Au | -1.991100000 | -1.544100000 | -3.689200000 |
| Au | 0.972100000  | -4.507700000 | -0.970000000 |
| Au | 3.039600000  | -1.126900000 | -3.773700000 |
| Au | -1.513100000 | 3.127400000  | -1.090300000 |
| Au | -2.065900000 | 1.151100000  | -2.930200000 |
| Au | 0.113400000  | 0.095600000  | -1.489500000 |
| Au | 2.247200000  | 1.335000000  | -2.855300000 |
| Au | 1.237700000  | 3.153700000  | -0.960900000 |
| Au | -0.750800000 | 1.277700000  | 0.931600000  |
| Au | -3.248000000 | 0.039400000  | 1.501400000  |
| Au | -3.052900000 | -0.774000000 | -1.154000000 |
| Au | 0.139600000  | 2.388700000  | 3.341400000  |
| Au | 2.305900000  | 3.078100000  | 1.660300000  |
| Au | -1.440700000 | -2.960900000 | -1.186100000 |
| Au | 0.572300000  | -2.276900000 | -2.989300000 |
| Au | 2.745100000  | -2.499300000 | -1.252100000 |
| Au | 4.057900000  | -0.085300000 | -1.314500000 |
| Au | 2.074200000  | 0.455400000  | 0.671800000  |
| Au | -1.640800000 | -1.745600000 | 2.955100000  |
| Au | 0.054100000  | -1.490800000 | 0.751100000  |
| Au | 2.073000000  | -3.382800000 | 1.340700000  |
| Au | 2.652000000  | -1.162300000 | 2.919800000  |
| Au | 0.370500000  | -0.241800000 | 4.165500000  |
| Au | 0.730900000  | -3.022000000 | 3.774900000  |
| Au | -3.221100000 | -2.772100000 | 0.921900000  |
| Au | -2.184300000 | 0.945300000  | 3.883500000  |
| Au | -3.936800000 | 1.730600000  | -0.613800000 |
| Au | 0.025700000  | 2.893300000  | -3.510500000 |
| S  | -0.166200000 | 4.588600000  | -5.444400000 |
| S  | 0.517800000  | -4.778200000 | 5.741700000  |
| S  | -3.318300000 | 1.256400000  | 6.408800000  |
| S  | 3.413900000  | 2.297200000  | 6.317300000  |
| S  | 6.202300000  | 3.285800000  | -1.452000000 |
| S  | 4.794000000  | -2.511100000 | -5.219100000 |
| S  | -3.491500000 | -2.043000000 | -5.659900000 |
| S  | -5.494400000 | 3.602500000  | -1.278800000 |
| S  | -0.373000000 | 6.686800000  | 1.144600000  |
| S  | 6.359600000  | -3.477000000 | 1.053000000  |
| S  | -5.517000000 | -3.915300000 | 0.992500000  |
| S  | -0.176100000 | -6.666200000 | -1.520700000 |
| Au | -5.933600000 | -1.916600000 | 2.165900000  |

|    |              |              |              |
|----|--------------|--------------|--------------|
| Au | -4.888000000 | 0.529700000  | 4.813700000  |
| S  | -6.600500000 | 0.028400000  | 3.297300000  |
| Au | -5.290600000 | -1.116600000 | -4.477900000 |
| Au | -6.329000000 | 1.687300000  | -2.371300000 |
| S  | -7.162900000 | -0.274100000 | -3.325000000 |
| Au | 2.774600000  | -3.715700000 | -5.365800000 |
| Au | 0.333200000  | -5.764100000 | -3.646200000 |
| S  | 0.780000000  | -4.900600000 | -5.777000000 |
| Au | 3.310700000  | 4.235200000  | 4.996200000  |
| Au | 1.540000000  | 6.353700000  | 2.468000000  |
| S  | 3.487500000  | 6.232300000  | 3.779600000  |
| Au | 5.505200000  | -3.395600000 | 3.237600000  |
| Au | 2.757400000  | -4.039400000 | 5.637300000  |
| S  | 4.972900000  | -3.270700000 | 5.521000000  |
| Au | 1.641800000  | 5.524400000  | -4.280700000 |
| Au | 4.801300000  | 4.922700000  | -2.389200000 |
| S  | 3.403300000  | 6.613500000  | -3.168800000 |
| C  | 5.556200000  | -4.935200000 | 0.239400000  |
| H  | 5.893900000  | -5.861400000 | 0.714000000  |
| H  | 4.465600000  | -4.831900000 | 0.299700000  |
| H  | 5.865100000  | -4.927000000 | -0.815500000 |
| C  | 6.042100000  | -4.522700000 | 6.379800000  |
| H  | 5.775300000  | -4.507200000 | 7.444000000  |
| H  | 5.894100000  | -5.525500000 | 5.963100000  |
| H  | 7.086100000  | -4.207000000 | 6.253300000  |
| C  | -0.254600000 | -3.751300000 | 7.076800000  |
| H  | -1.338600000 | -3.929500000 | 7.021700000  |
| H  | 0.127000000  | -4.061500000 | 8.053500000  |
| H  | -0.056700000 | -2.681200000 | 6.901800000  |
| C  | 1.748300000  | 2.136600000  | 7.108500000  |
| H  | 0.971600000  | 2.133200000  | 6.319900000  |
| H  | 1.735500000  | 1.165200000  | 7.639400000  |
| H  | 1.580100000  | 2.962800000  | 7.831600000  |
| C  | 3.355800000  | 7.607500000  | 5.021400000  |
| H  | 2.432400000  | 7.515100000  | 5.590600000  |
| H  | 4.222100000  | 7.541900000  | 5.692700000  |
| H  | 3.371900000  | 8.554500000  | 4.472000000  |
| C  | 0.226500000  | 7.035400000  | -0.568600000 |
| H  | 1.058300000  | 6.368100000  | -0.822700000 |
| H  | -0.612000000 | 6.830200000  | -1.252100000 |
| H  | 0.533100000  | 8.087300000  | -0.642400000 |
| C  | -1.613700000 | 5.667100000  | -5.033000000 |
| H  | -1.473200000 | 6.660200000  | -5.475200000 |
| H  | -2.503300000 | 5.189900000  | -5.463700000 |
| H  | -1.727100000 | 5.743800000  | -3.947200000 |
| C  | 4.347100000  | 7.545900000  | -4.465600000 |

|   |              |              |              |
|---|--------------|--------------|--------------|
| H | 5.206200000  | 8.016100000  | -3.969000000 |
| H | 4.684000000  | 6.881800000  | -5.266800000 |
| H | 3.677900000  | 8.319800000  | -4.864600000 |
| C | 6.616500000  | 2.128000000  | -2.841800000 |
| H | 7.175600000  | 1.290200000  | -2.408300000 |
| H | 5.695800000  | 1.750000000  | -3.301500000 |
| H | 7.237300000  | 2.654700000  | -3.574700000 |
| C | -4.633400000 | 4.573800000  | -2.605100000 |
| H | -5.382300000 | 5.108400000  | -3.201500000 |
| H | -3.968600000 | 5.290000000  | -2.107600000 |
| H | -4.038900000 | 3.900200000  | -3.228000000 |
| C | -8.369600000 | 0.231300000  | -4.642500000 |
| H | -7.912000000 | 0.930600000  | -5.347400000 |
| H | -8.687500000 | -0.683600000 | -5.159800000 |
| H | -9.227000000 | 0.697500000  | -4.141600000 |
| C | -3.749100000 | -3.877300000 | -5.605500000 |
| H | -2.824500000 | -4.341500000 | -5.973400000 |
| H | -3.939100000 | -4.205300000 | -4.578300000 |
| H | -4.587800000 | -4.145100000 | -6.259100000 |
| C | -6.239600000 | -3.637600000 | -0.692500000 |
| H | -5.873800000 | -4.452700000 | -1.328600000 |
| H | -7.330400000 | -3.666500000 | -0.627900000 |
| H | -5.901000000 | -2.678700000 | -1.097900000 |
| C | -8.090800000 | -0.435500000 | 4.306100000  |
| H | -8.890300000 | -0.736300000 | 3.613700000  |
| H | -7.861800000 | -1.258000000 | 4.992200000  |
| H | -8.396000000 | 0.459600000  | 4.860900000  |
| C | -2.530300000 | -0.261600000 | 7.116000000  |
| H | -3.269500000 | -0.847300000 | 7.704400000  |
| H | -2.108800000 | -0.868100000 | 6.295300000  |
| H | -1.711300000 | 0.082400000  | 7.781800000  |
| C | -2.007200000 | -6.450100000 | -1.322400000 |
| H | -2.276200000 | -5.391100000 | -1.470000000 |
| H | -2.524400000 | -7.096200000 | -2.044000000 |
| H | -2.256900000 | -6.748200000 | -0.293900000 |
| C | 1.250700000  | -6.345900000 | -6.843000000 |
| H | 2.084200000  | -6.916300000 | -6.403000000 |
| H | 0.371300000  | -6.996300000 | -6.959300000 |
| H | 1.541400000  | -5.963100000 | -7.825600000 |
| C | 5.752500000  | -3.233100000 | -3.811700000 |
| H | 5.121100000  | -3.279100000 | -2.914600000 |
| H | 6.123900000  | -4.228700000 | -4.087300000 |
| H | 6.597800000  | -2.557700000 | -3.626200000 |