Supporting Information:
Computational Design of Intrinsic Molecular Rectifiers based on Asymmetric Functionalization of N-phenylbenzamide

Wendu Ding.[a,b] Matthieu Koepf,[b] Christopher Koenigsmann,[b] Arunabh Batra,[c] Latha Venkataraman,[c,*] Christian F. A. Negre,[a,b,*] Gary W. Brudvig,[a,b,*] Robert H. Crabtree.[a,b,*] Charles A. Schmuttenmaer,[a,b,*] and Victor S. Batista[a,b,*]

[a]*Department of Chemistry, Yale University, P.O. Box 208107, New Haven, CT 06520-8107*
[b]*Yale Energy Sciences Institute, Yale University, P.O. Box 27394, West Haven, CT 06516-7394*
[c]*Department of Applied Physics and Applied Mathematics, Columbia University, New York, NY 10027*

*E-mail: lv2117@columbia.edu, christian.negre@yale.edu, gary.brudvig@yale.edu, robert.crabtree@yale.edu, charles.schmuttenmaer@yale.edu, victor.batista@yale.edu

Current Address
Christian F. A. Negre: Theoretical Division, Los Alamos National Laboratory, Los Alamos, New Mexico 87545, United States

Table of Contents:

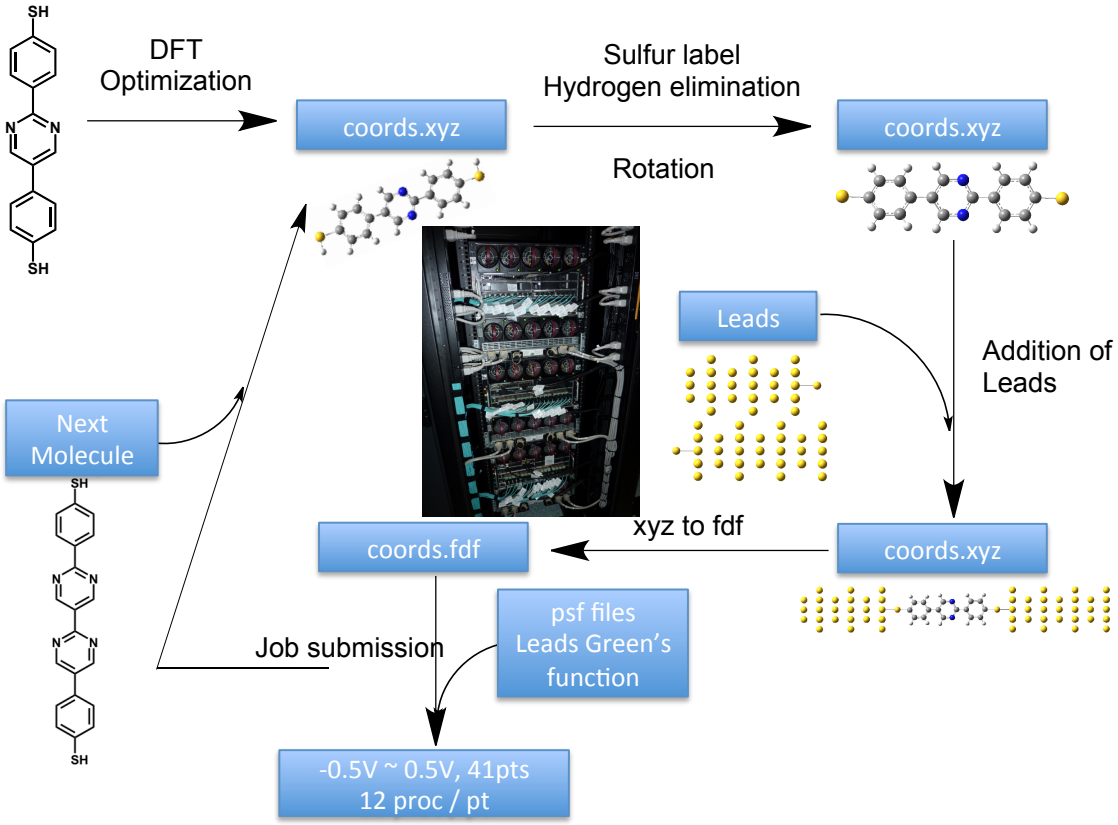


Figure S1. Flow chart of computational screening procedure.

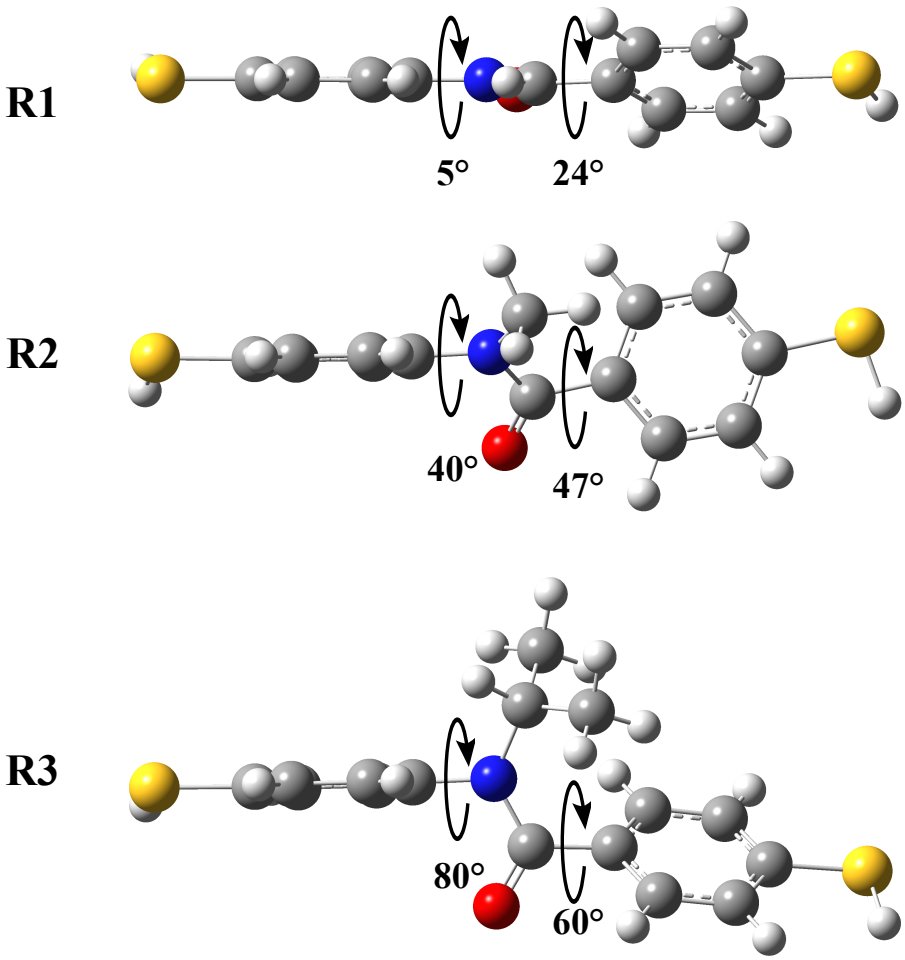
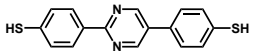
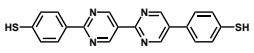
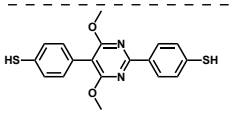
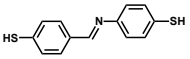
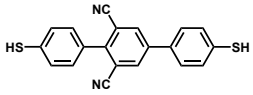
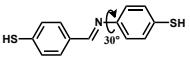
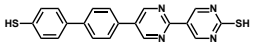
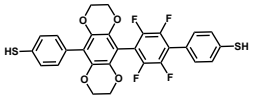
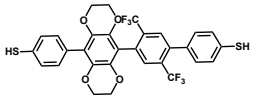
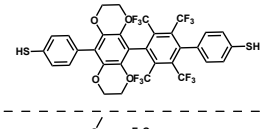
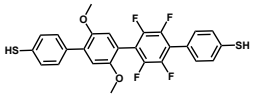
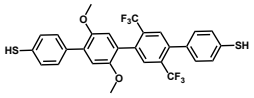
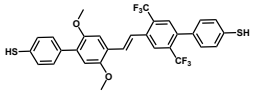
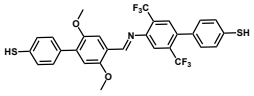
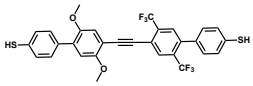
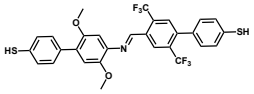
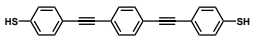
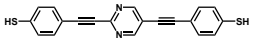
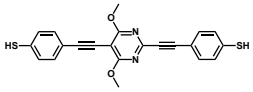
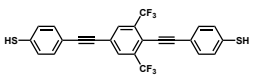
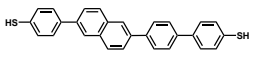
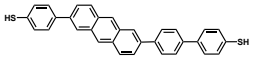
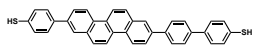
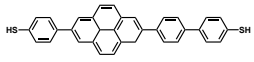
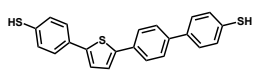
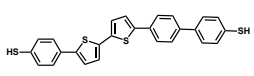
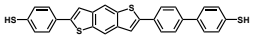
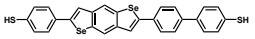
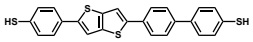
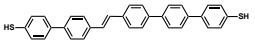
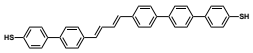
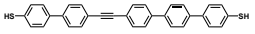
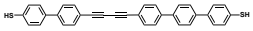
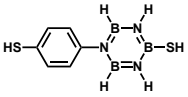
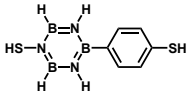
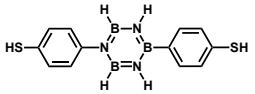
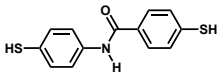
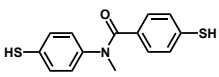
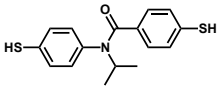
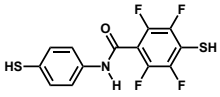
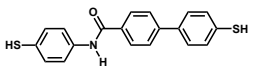
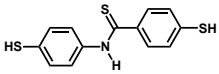
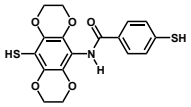
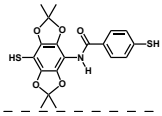
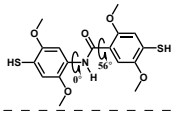
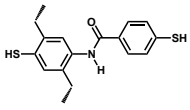
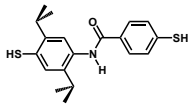
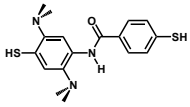
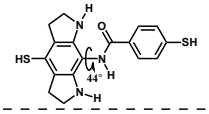
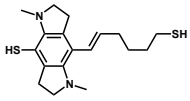
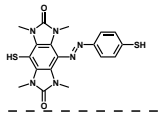
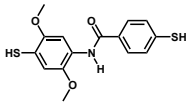
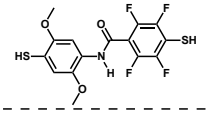
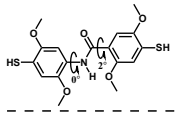
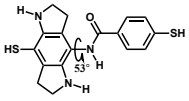
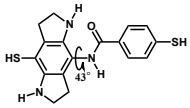
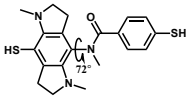
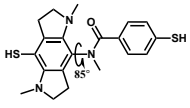
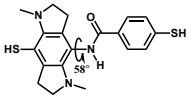
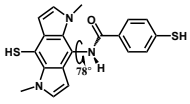
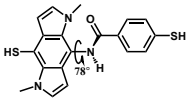
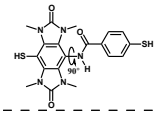
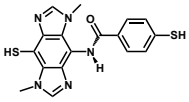
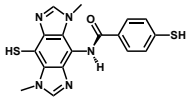
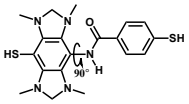
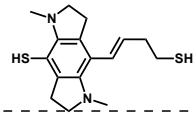
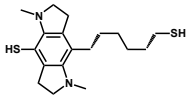
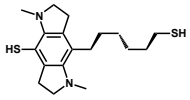
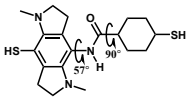
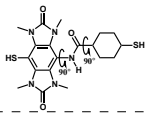
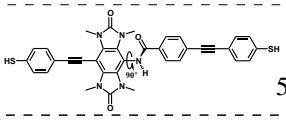
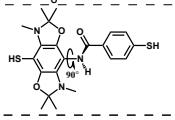
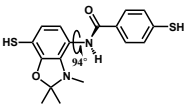
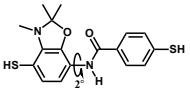
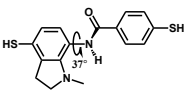
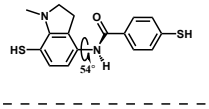
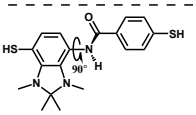
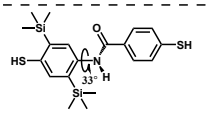
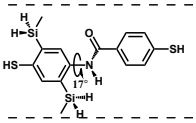
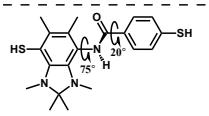
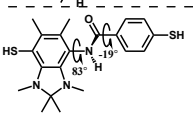
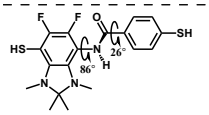


Figure S2. Dihedral angles between phenylene rings and amide bond in **R1**, **R2**, and **R3**.

Table S1. Collective data for all molecules screened in Fig. 4 on conductance (G) and rectification ratio (RR).

Label	Molecule	RR G (G_0)	Label	Molecule	RR G (G_0)
1		1.06 7.5×10^{-3}	2		1.12 1.8×10^{-3}
3		1.26 1.1×10^{-2}	4		1.07 3.3×10^{-2}
5		1.01 1.9×10^{-3}	6		1.27 2.8×10^{-2}
7		1.42 5.8×10^{-4}	8		1.38 4.0×10^{-4}
9		1.40 2.1×10^{-4}	10		1.52 2.1×10^{-5}
11		1.19 4.4×10^{-4}	12		1.39 3.3×10^{-4}
13		1.30 8.4×10^{-4}	14		1.09 3.8×10^{-4}
15		1.11 8.3×10^{-4}	16		1.41 8.2×10^{-4}
17		1.04 9.1×10^{-3}	18		1.01 4.4×10^{-3}
19		1.25 8.3×10^{-3}	20		1.03 4.3×10^{-3}
21		1.04 9.2×10^{-4}	22		1.06 6.2×10^{-4}
23		1.01 1.7×10^{-4}	24		1.00 2.8×10^{-4}
25		1.18 6.1×10^{-3}	26		1.25 3.7×10^{-3}

27		1.08 1.3×10^{-3}	28		1.13 2.0×10^{-3}
29		1.13 4.4×10^{-3}	30		1.10 4.9×10^{-4}
31		1.13 4.3×10^{-4}	32		1.04 3.4×10^{-4}
33		1.19 1.7×10^{-4}	34		1.58 4.8×10^{-3}
35		1.55 1.9×10^{-2}	36		1.28 1.6×10^{-3}
37		1.65 9.9×10^{-3}	38		1.64 5.5×10^{-3}
39		1.19 1.9×10^{-3}	40		1.82 2.6×10^{-3}
41		1.46 2.3×10^{-3}	42		1.30 5.4×10^{-3}
43		1.97 7.9×10^{-3}	44		1.91 4.5×10^{-3}
45		2.16 1.4×10^{-2}	46		1.78 1.0×10^{-2}
47		1.80 1.1×10^{-2}	48		1.88 1.2×10^{-2}
49		1.33 7.8×10^{-3}	50		2.18 1.5×10^{-3}
51		1.26 4.0×10^{-2}	52		3.06 2.0×10^{-2}
53		3.29 4.0×10^{-3}	54		3.08 4.2×10^{-2}

55		5.57 1.2×10^{-2}	56		8.35 3.1×10^{-2}
57		7.16 6.6×10^{-3}	58		6.72 2.4×10^{-3}
59		7.20 7.8×10^{-3}	60		5.41 1.6×10^{-2}
61		4.96 1.6×10^{-2}	62		1.48 2.7×10^{-4}
63		3.83 6.6×10^{-3}	64		4.22 1.6×10^{-2}
65		12.66 6.2×10^{-5}	66		2.12 1.0×10^{-2}
67		6.21 1.6×10^{-5}	68		1.04 7.5×10^{-5}
69		1.73 6.4×10^{-5}	70		3.28 1.4×10^{-5}
71		1.28 5.8×10^{-6}	72		16.67 9.1×10^{-5}
73		1.82 1.8×10^{-4}	74		4.73 1.4×10^{-2}
75		1.88 7.8×10^{-3}	76		5.96 4.8×10^{-3}
77		7.38 1.6×10^{-4}	78		1.38 4.4×10^{-3}
79		1.35 6.5×10^{-3}	80		1.21 4.6×10^{-4}
81		1.17 8.0×10^{-5}	82		7.53 3.9×10^{-4}

Sample input for lead calculation in TranSIESTA:

```
SystemName                AU TRANS
SystemLabel               Auleads

PAO.BasisType             split
PAO.SplitNorm             0.15

%block ChemicalSpeciesLabel
  1   79 Au
%endblock ChemicalSpeciesLabel

%block    PAO.BasisSizes
  Au       DZ
%endblock PAO.BasisSizes

PAO.EnergyShift     0.01 eV

LatticeConstant         1.00 Ang

%block LatticeVectors
 30.000   0.000   0.000   1
  0.000  30.000   0.000   1
  0.000   0.000   9.4224   1
%endblock LatticeVectors

AtomicCoordinatesFormat  Ang
NumberOfAtoms               20
NumberOfSpecies             1
%block AtomicCoordinatesAndAtomicSpecies
   -0.83280000   -1.44250000    0.00000000   1  Au   1
    1.66560000    0.00000000    0.00000000   1  Au   2
   -0.83280000    1.44250000    0.00000000   1  Au   3
    0.00000000   -2.88500000    2.35560000   1  Au   4
   -2.49850000   -1.44250000    2.35560000   1  Au   5
    2.49850000   -1.44250000    2.35560000   1  Au   6
    0.00000000    0.00000000    2.35560000   1  Au   7
   -2.49850000    1.44250000    2.35560000   1  Au   8
    2.49850000    1.44250000    2.35560000   1  Au   9
    0.00000000    2.88500000    2.35560000   1  Au  10
   -0.83280000   -1.44250000    4.71120000   1  Au  11
    1.66560000    0.00000000    4.71120000   1  Au  12
   -0.83280000    1.44250000    4.71120000   1  Au  13
    0.00000000   -2.88500000    7.06680000   1  Au  14
   -2.49850000   -1.44250000    7.06680000   1  Au  15
    2.49850000   -1.44250000    7.06680000   1  Au  16
    0.00000000    0.00000000    7.06680000   1  Au  17
   -2.49850000    1.44250000    7.06680000   1  Au  18
    2.49850000    1.44250000    7.06680000   1  Au  19
    0.00000000    2.88500000    7.06680000   1  Au  20
%endblock AtomicCoordinatesAndAtomicSpecies

%block kgrid_Monkhorst_Pack
  1   0   0    0.0
  0   1   0    0.0
```

```
 0   0  50    0.0
%endblock kgrid_Monkhorst_Pack

BandLinesScale         ReciprocalLatticeVectors

xc.functional              GGA
xc.authors                 PBE

SpinPolarized              F
FixSpin                    F
TotalSpin                  0.0
NonCollinearSpin           F

SolutionMethod             diagon
MeshCutoff                 200. Ry
ElectronicTemperature      300 K
MaxSCFIterations           10000
DM.MixingWeight            0.1
DM.NumberPulay             5
DM.MixSCF1                 F
DM.PulayOnFile             F
DM.Tolerance               5.0E-5
DM.UseSaveDM               F

WriteCoorXmol              F
SaveElectrostaticPotential T
SaveHS                     F
SaveRho                    F
SaveDeltaRho               F
WriteDenchar               F

WriteEigenvalues           F

WriteMullikenPop           0

BulkTransport              T
BulkLeads                  LR
```

Sample input for transport calculation in TranSIESTA:

```
SystemName      Transport
SystemLabel     amide1

SolutionMethod             transiesta

LatticeConstant       1.0000 Ang
%block LatticeVectors
   30.000    0.000    0.00000
    0.000   30.000    0.00000
  0.00000   0.00000  45.74497
%endblock LatticeVectors

PAO.BasisType split
```

```
PAO.SplitNorm 0.15
%block    PAO.BasisSizes
   Au  DZ
   S   DZ
   C   DZ
   H   DZ
   N   DZ
   O   DZ
%endblock  PAO.BasisSizes
PAO.EnergyShift 0.01 eV

%block kgrid_Monkhorst_Pack
   1   0   0    0.0
   0   1   0    0.0
   0   0   1    0.0
%endblock kgrid_Monkhorst_Pack
BandLinesScale         ReciprocalLatticeVectors

XC.functional        GGA
XC.authors           PBE
MeshCutoff  200.0 Ry

ElectronicTemperature          300 K
MaxSCFIterations              30000
DM.MixingWeight                0.02
DM.NumberPulay                 4
DM.Tolerance                  1.0D-5
DM.UseSaveDM                   T

TS.HSFileLeft   AuLeads.TSHS
TS.NumUsedAtomsLeft    20
TS.HSFileRight  AuLeads.TSHS
TS.NumUsedAtomsRight   20

TS.TBT.NPoints        1000
TS.TBT.Emin          -1.0 eV
TS.TBT.Emax           1.0 eV
TS.TBT.OutputRegionData False
TS.BiasContour.NumPoints 100
TS.ComplexContour.Emin  -20.0 Ry
TS.ComplexContour.NumCircle 100
TS.ComplexContour.NumLine  20
TS.ComplexContour.NumPoles 10
TS.BiasContour.Eta 10D-4  Ry
TS.Voltage 0.000  eV

%block ChemicalSpeciesLabel
        1         79 Au
        2         16 S
        3          6 C
        4          1 H
        5          7 N
        6          8 O
%endblock ChemicalSpeciesLabel

AtomicCoordinatesFormat  Ang
```

```
NumberOfAtoms          93
NumberOfSpecies         6
%block AtomicCoordinatesAndAtomicSpecies
  -0.83280000   -1.44250000    0.00000000   1  Au   1
   1.66560000    0.00000000    0.00000000   1  Au   2
  -0.83280000    1.44250000    0.00000000   1  Au   3
   0.00000000   -2.88500000    2.35560000   1  Au   4
  -2.49850000   -1.44250000    2.35560000   1  Au   5
   2.49850000   -1.44250000    2.35560000   1  Au   6
   0.00000000    0.00000000    2.35560000   1  Au   7
  -2.49850000    1.44250000    2.35560000   1  Au   8
   2.49850000    1.44250000    2.35560000   1  Au   9
   0.00000000    2.88500000    2.35560000   1  Au  10
  -0.83280000   -1.44250000    4.71120000   1  Au  11
   1.66560000    0.00000000    4.71120000   1  Au  12
  -0.83280000    1.44250000    4.71120000   1  Au  13
   0.00000000   -2.88500000    7.06680000   1  Au  14
  -2.49850000   -1.44250000    7.06680000   1  Au  15
   2.49850000   -1.44250000    7.06680000   1  Au  16
   0.00000000    0.00000000    7.06680000   1  Au  17
  -2.49850000    1.44250000    7.06680000   1  Au  18
   2.49850000    1.44250000    7.06680000   1  Au  19
   0.00000000    2.88500000    7.06680000   1  Au  20
  -0.83280000   -1.44250000    9.42240000   1  Au  21
   1.66560000    0.00000000    9.42240000   1  Au  22
  -0.83280000    1.44250000    9.42240000   1  Au  23
   0.00000000   -2.88500000   11.77800000   1  Au  24
  -2.49850000   -1.44250000   11.77800000   1  Au  25
   2.49850000   -1.44250000   11.77800000   1  Au  26
   0.00000000    0.00000000   11.77800000   1  Au  27
  -2.49850000    1.44250000   11.77800000   1  Au  28
   2.49850000    1.44250000   11.77800000   1  Au  29
   0.00000000    2.88500000   11.77800000   1  Au  30
   0.00000000    0.00000000   14.09800000   2  S   31
  -0.01554000    0.15204000   15.88056000   3  C   32
  -0.35248000    2.28263000   15.97585000   4  H   33
   0.32584000   -1.96516000   16.15479000   4  H   34
  -0.20245000    1.36918000   16.54396000   3  C   35
   0.18218000   -1.00598000   16.64292000   3  C   36
  -0.19870000    1.44411000   17.93531000   3  C   37
   0.19189000   -0.93833000   18.03046000   3  C   38
  -0.33928000    2.39042000   18.43713000   4  H   39
   0.34506000   -1.84915000   18.60507000   4  H   40
   0.00133000    0.28259000   18.69564000   3  C   41
   0.00901000    0.26270000   20.10544000   5  N   42
   0.19840000   -0.63971000   20.51516000   4  H   43
  -0.14605000    2.49478000   20.62852000   6  O   44
  -0.07904000    1.32173000   20.98319000   3  C   45
  -0.82336000   -1.08106000   22.26360000   4  H   46
  -0.07005000    0.94617000   22.43672000   3  C   47
  -0.45711000   -0.30718000   22.93260000   3  C   48
   0.59032000    2.91171000   22.96562000   4  H   49
   0.31815000    1.93491000   23.35032000   3  C   50
  -0.43404000   -0.57375000   24.29801000   3  C   51
  -0.75060000   -1.54640000   24.66218000   4  H   52
   0.35404000    1.67511000   24.71478000   3  C   53
```

```
-0.01921000    0.41412000   25.20177000   3  C   54
 0.67048000    2.45521000   25.40064000   4  H   55
 0.00000000    0.00000000   26.93577000   2  S   56
 0.00000000   -2.88500000   29.25577000   1  Au  57
-2.49850000   -1.44250000   29.25577000   1  Au  58
 2.49850000   -1.44250000   29.25577000   1  Au  59
 0.00000000    0.00000000   29.25577000   1  Au  60
-2.49850000    1.44250000   29.25577000   1  Au  61
 2.49850000    1.44250000   29.25577000   1  Au  62
 0.00000000    2.88500000   29.25577000   1  Au  63
-0.83280000   -1.44250000   31.61137000   1  Au  64
 1.66560000    0.00000000   31.61137000   1  Au  65
-0.83280000    1.44250000   31.61137000   1  Au  66
 0.00000000   -2.88500000   33.96697000   1  Au  67
-2.49850000   -1.44250000   33.96697000   1  Au  68
 2.49850000   -1.44250000   33.96697000   1  Au  69
 0.00000000    0.00000000   33.96697000   1  Au  70
-2.49850000    1.44250000   33.96697000   1  Au  71
 2.49850000    1.44250000   33.96697000   1  Au  72
 0.00000000    2.88500000   33.96697000   1  Au  73
-0.83280000   -1.44250000   36.32257000   1  Au  74
 1.66560000    0.00000000   36.32257000   1  Au  75
-0.83280000    1.44250000   36.32257000   1  Au  76
 0.00000000   -2.88500000   38.67817000   1  Au  77
-2.49850000   -1.44250000   38.67817000   1  Au  78
 2.49850000   -1.44250000   38.67817000   1  Au  79
 0.00000000    0.00000000   38.67817000   1  Au  80
-2.49850000    1.44250000   38.67817000   1  Au  81
 2.49850000    1.44250000   38.67817000   1  Au  82
 0.00000000    2.88500000   38.67817000   1  Au  83
-0.83280000   -1.44250000   41.03377000   1  Au  84
 1.66560000    0.00000000   41.03377000   1  Au  85
-0.83280000    1.44250000   41.03377000   1  Au  86
 0.00000000   -2.88500000   43.38937000   1  Au  87
-2.49850000   -1.44250000   43.38937000   1  Au  88
 2.49850000   -1.44250000   43.38937000   1  Au  89
 0.00000000    0.00000000   43.38937000   1  Au  90
-2.49850000    1.44250000   43.38937000   1  Au  91
 2.49850000    1.44250000   43.38937000   1  Au  92
 0.00000000    2.88500000   43.38937000   1  Au  93
%endblock AtomicCoordinatesAndAtomicSpecies
```