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Silver-mediated intramolecular P–C coupling

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1. Synthetic procedures

All reactions and manipulations were carried out (while protected from light) under an atmosphere of dry argon using standard Schlenk techniques. Dry, oxygen-free solvents were employed. Solution ^{1}H and ^{31}P NMR spectra were recorded on Bruker Avance 300 spectrometer at 298 K. Chemical shifts (δ) are expressed with a positive sign, in parts per million. ^{1}H chemical shifts reported are referenced internally to residual protio (^{1}H) solvent, while ^{31}P, chemical shifts are relative to 85% H_3PO_4. The following abbreviations and their combination are used: br, broad; s, singlet; d, doublet; t, triplet; m, multiplet; sept, septuplet. The synthesis and characterization of **3a** was previously reported [S1]. 1-Iodo-8-diisopropylphosphinonaphthalene **1** was prepared according to the reported procedure [S2]. All other reagents were used as received from commercial suppliers.

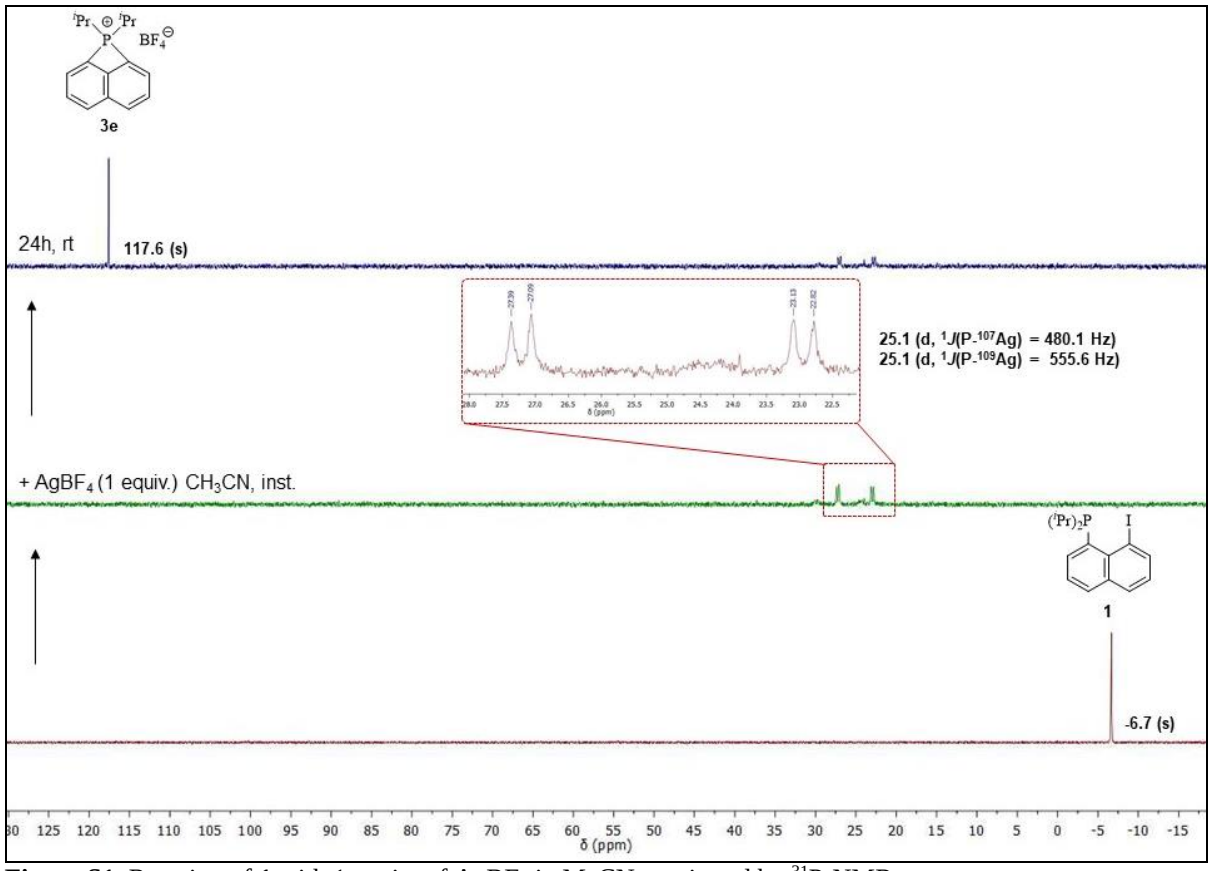
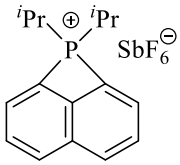


Figure S1. Reaction of **1** with 1 equiv. of $AgBF_4$ in MeCN monitored by ^{31}P-NMR.

1,1-Diisopropyl-1*H*-naphtho[1,8-*bc*]phosphetium hexafluoroantimonate 3b



3b

(8-Iodo-1-naphthyl)(diisopropyl)phosphine **1** (50 mg, 0.135 mmol) and $AgSbF_6$ (46 mg, 0.135 mmol, 1 equiv.) were stirred in MeCN at 85 °C for 30 min. ^{31}P NMR monitoring revealed complete conversion of **1** to **3b** (δ 116.1 ppm). The mixture was filtered, concentrated under vacuum and dried overnight to give the product **3b** as a pale yellow solid (60 mg, 92%). **^{1}H NMR** (300 MHz, CD_2Cl_2): δ 8.22 (dd, J_{HH} = 8.3, 3.8 Hz, 2H, H_{Ar}), 8.00-7.88 (m, 4H, H_{Ar}), 3.33 (sept d, $^{2}J_{HP}$ = 7.3 Hz, $^{3}J_{HH}$ = 7.1 Hz, 2H, CH*i*Pr), 1.43 (dd, $^{3}J_{PH}$ = 20.1 Hz, $^{3}J_{HH}$ = 7.4 Hz, 12H, CH_3*i*Pr); **^{31}P{^{1}H} NMR** (121 MHz, CD_2Cl_2): δ 116.1. The ^{1}H and ^{31}P NMR data match those of the previously described phosphonium diiodocuprate **3a**.

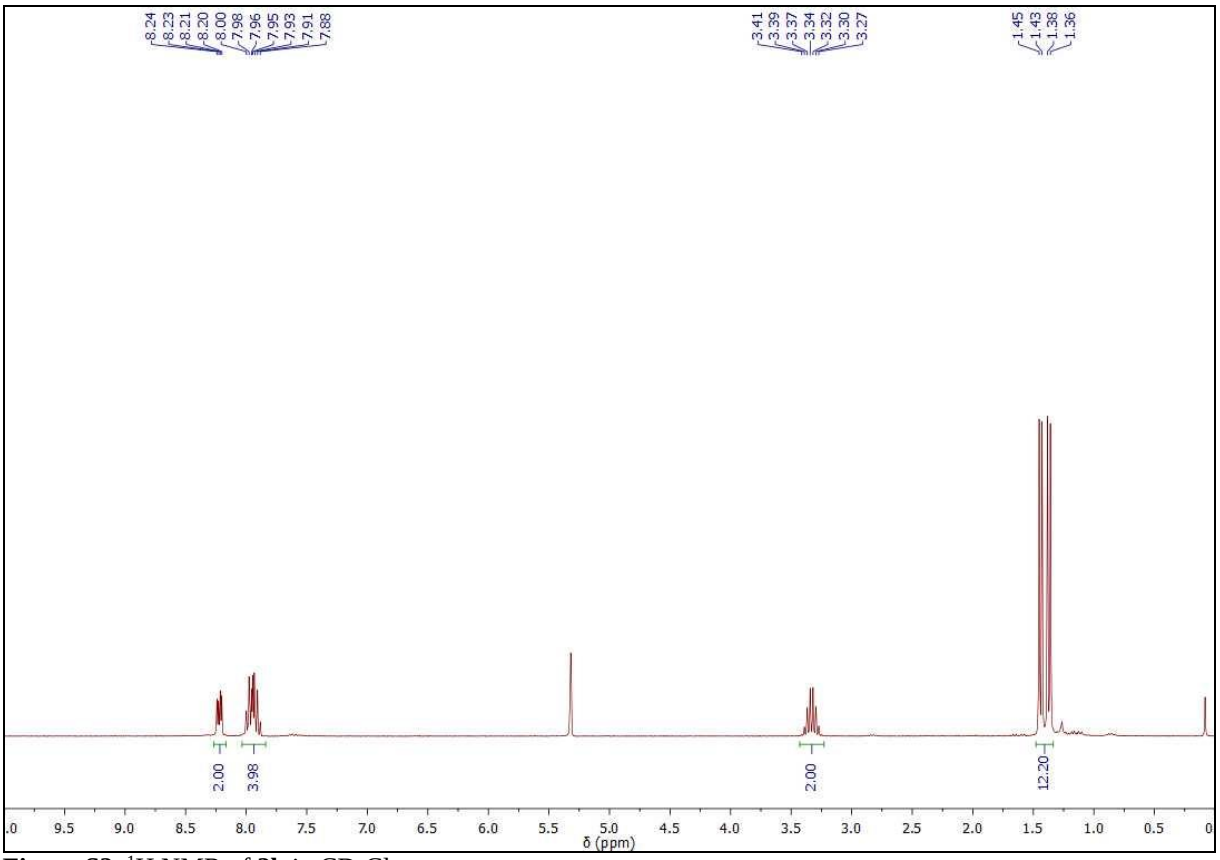


Figure S2. ^{1}H NMR of **3b** in CD_2Cl_2.

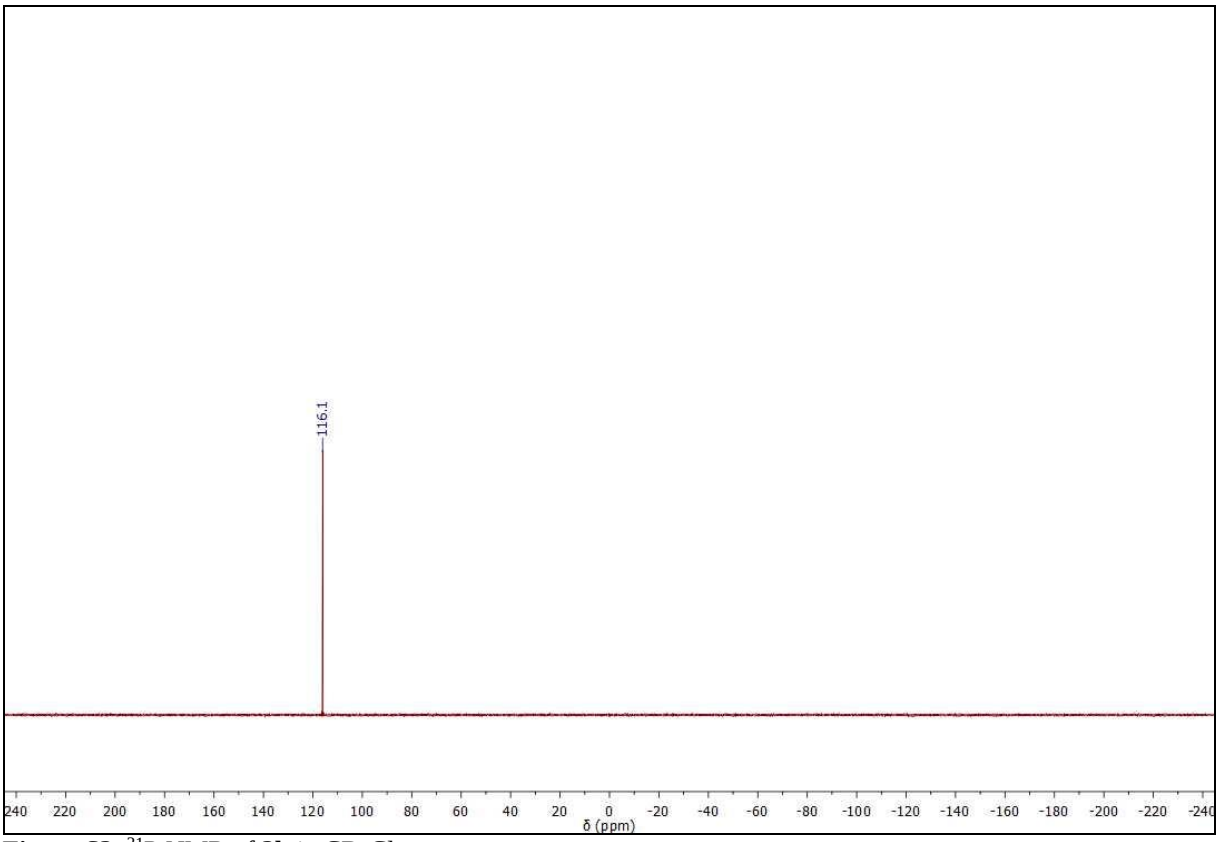


Figure S3. ^{31}P NMR of **3b** in CD_2Cl_2.

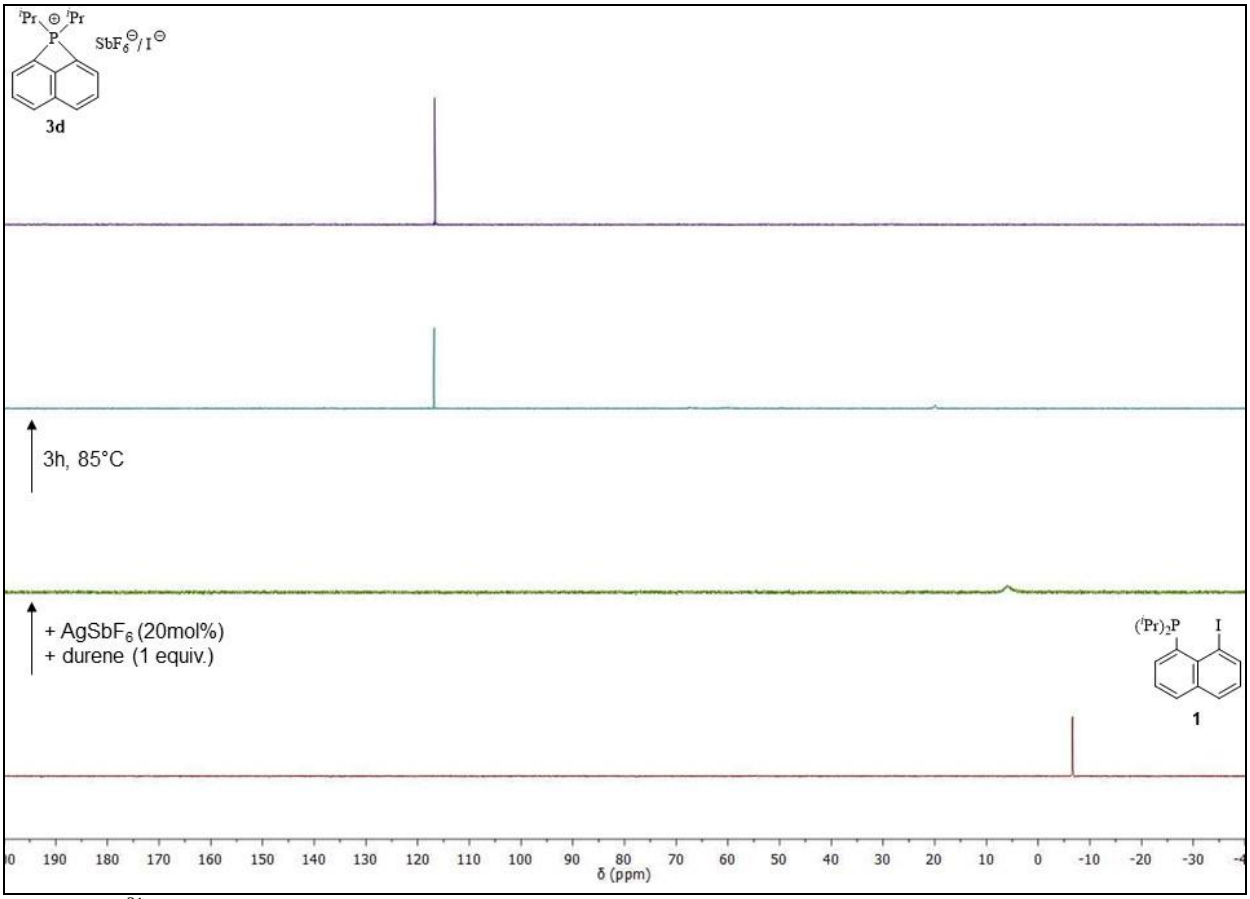


Figure S4. ^{31}P NMR monitoring of transformation of **1** in the presence of $AgSbF_6$ (20 mol%) and durene (internal standard, 1 equiv.) in CD_3CN at 85°C.

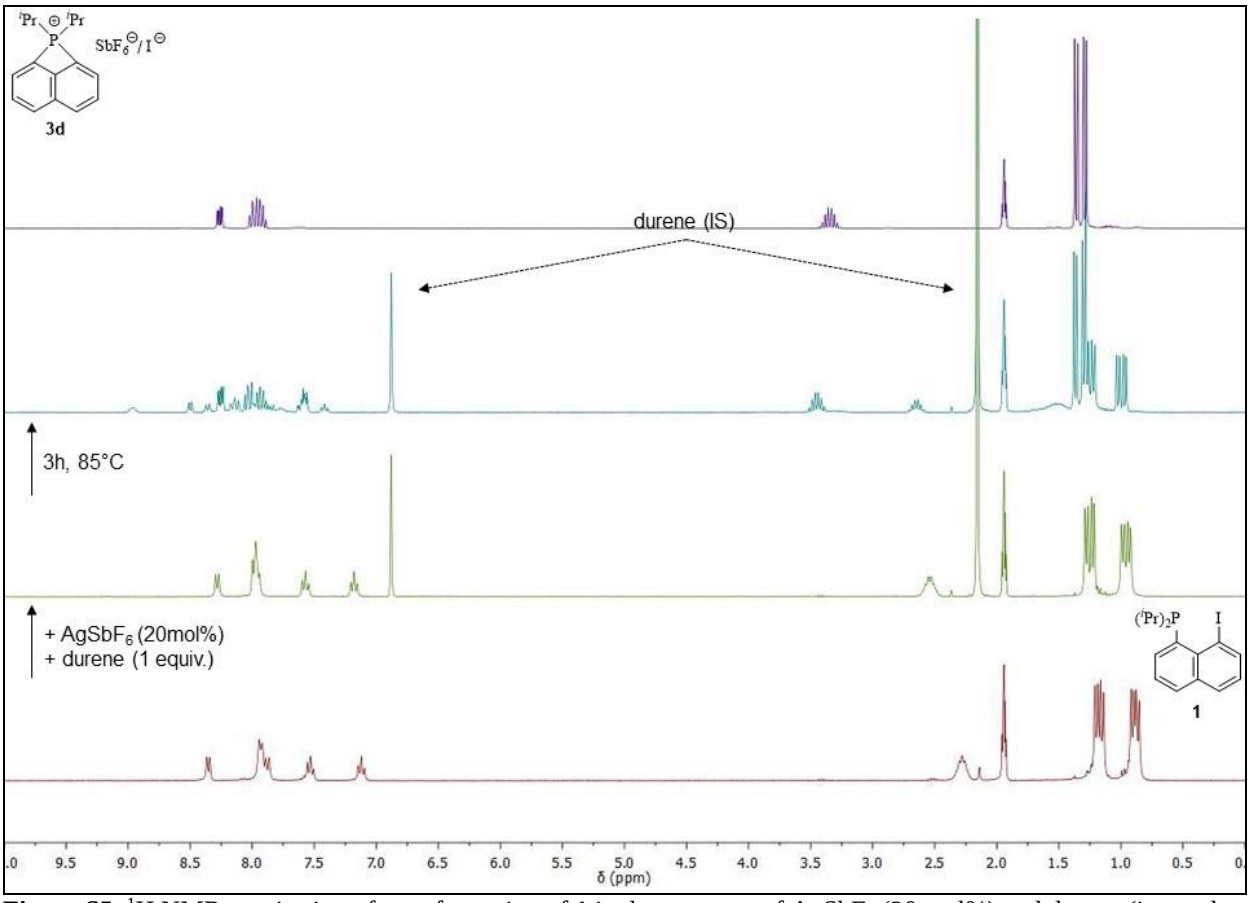


Figure S5. ^{1}H NMR monitoring of transformation of **1** in the presence of $AgSbF_6$ (20 mol%) and durene (internal standard, 1 equiv.) in CD_3CN at 85°C.

2. Computational details

All calculations were performed using the Gaussian 09 package [S3] and the B3PW91 [S4] hybrid functional on the real silver and gold systems, in solvent (chloroform, MeCN) by means of the universal Solvation Model based on solute electron Density (SMD) [S5]. The silver and gold atoms were described with the relativistic electron core potential SDD and associated basis set, augmented by a set of f-orbital polarization functions [S6]. The halogen atom (I) was also described with the relativistic electron core potential SDD and associated basis set [S6]. The 6-31G** basis set was employed for all other atoms (C, H, P). All stationary points involved were fully optimized in solvent. Frequency calculations were undertaken to confirm the nature of the stationary points, yielding one imaginary frequency for transition states (TS), corresponding to the expected process, and all of them positive for *minima*. The connectivity of the transition states and their adjacent *minima* was confirmed by intrinsic reaction coordinate (IRC) calculations [S7]. All structures have been plotted with Chemcraft software [S8].

The reaction of **1** with AgI was compared with that investigated previously with CuI [S9]. Calculations were also carried out for the reaction of **1** with AuI at the same level of theory to enable comparison.

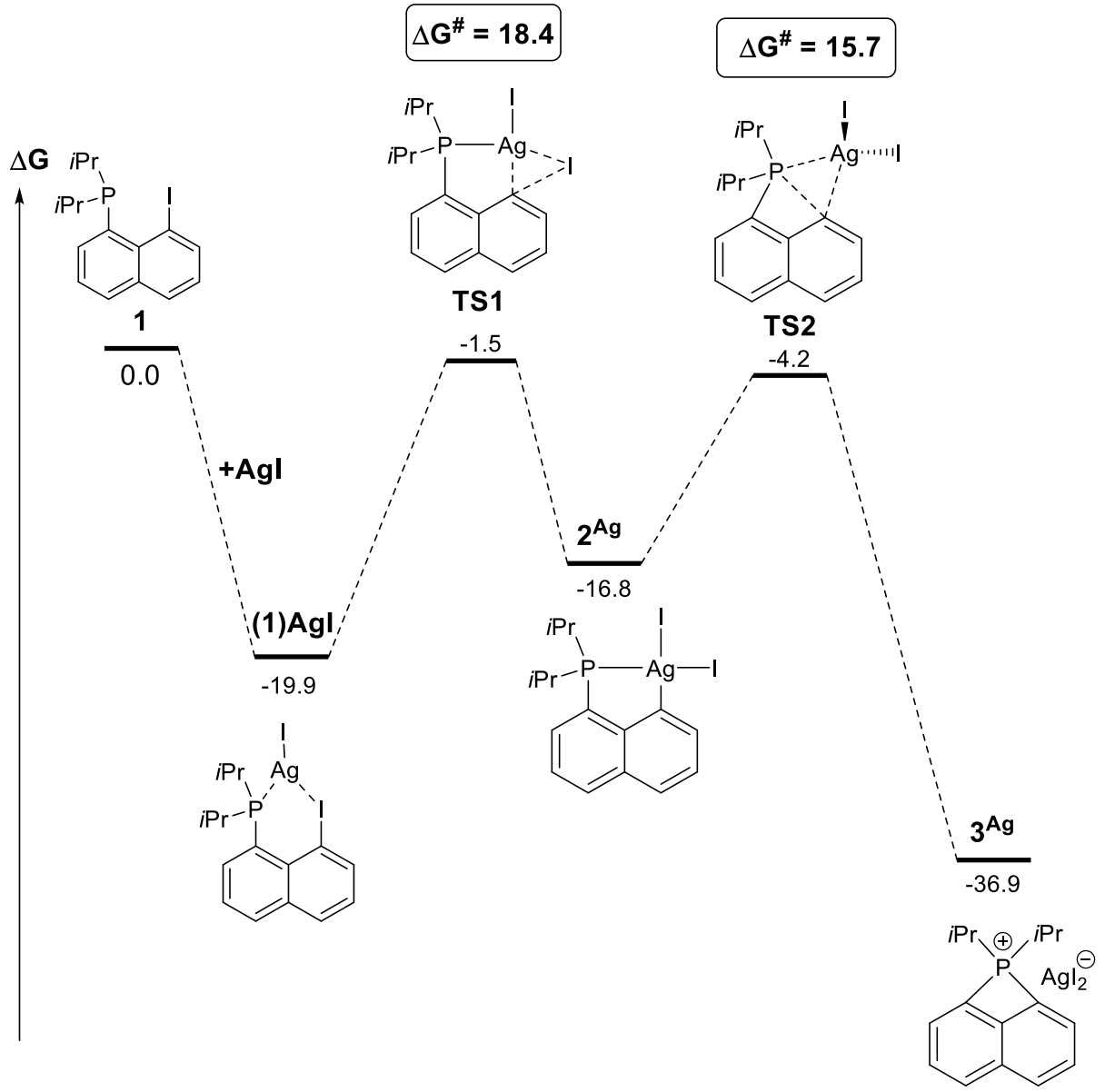


Figure S6 Energy profile, **1** + **AgI**, computed in MeCN solution for the C–I oxidative addition / P–C reductive elimination sequence. Free energies ΔG in kcal mol^{-1}, computed at SMD(MeCN)-B3PW91/SDD+f(Ag), SDD(I),6-31G**(other atoms) level of theory.

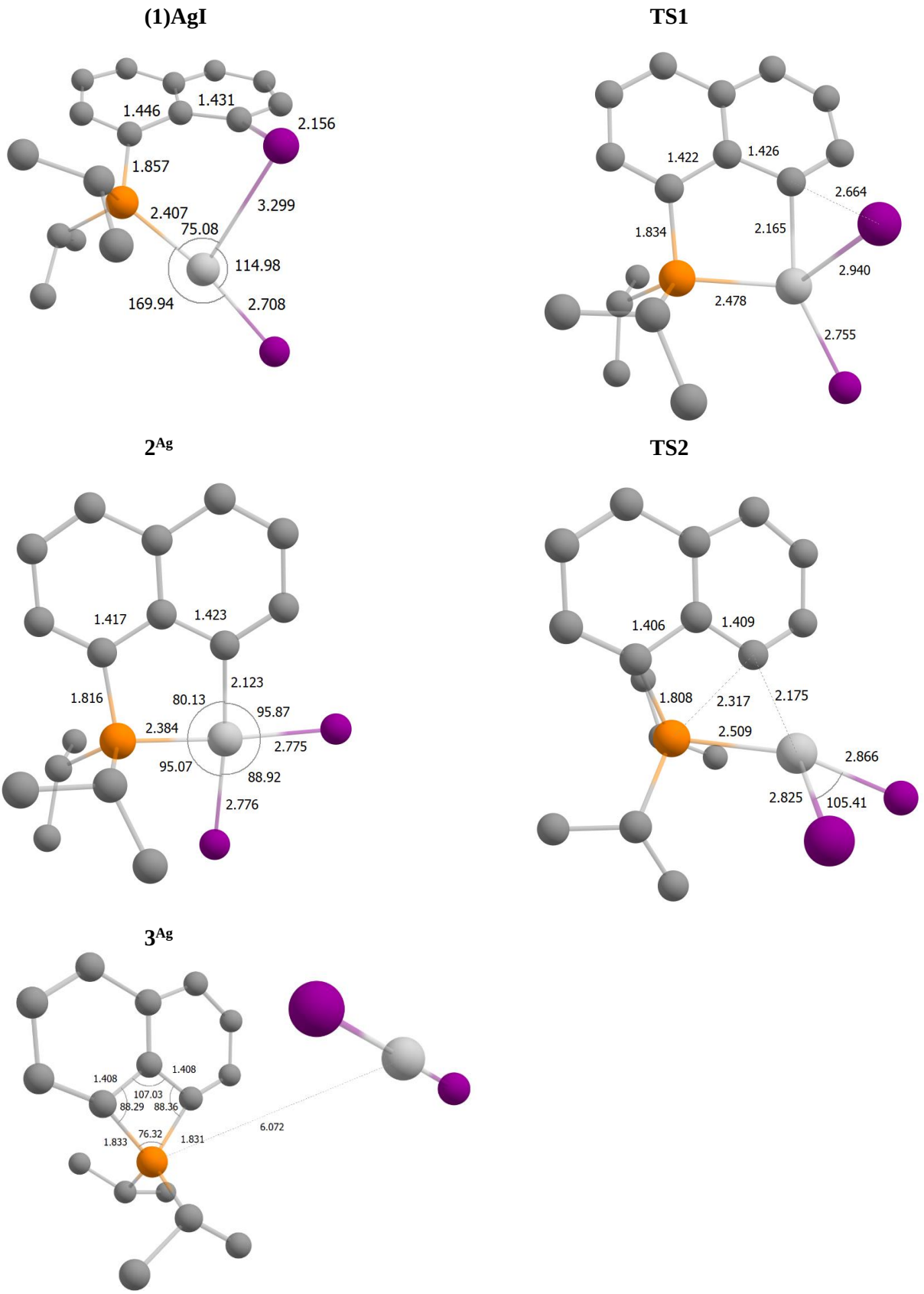


Figure S7 Reaction **1** + AgI in MeCN solvent. Main geometrical parameters for **TS1**, **TS2** and complexes **(1)AgI**, $\mathbf{2^{Ag}}$ and $\mathbf{3^{Ag}}$ (distances in Å and bond angles in °) optimized at SMD(CH_3CN)-B3PW91/SDD+f(Ag), I(SDD), 6-31G** (other atoms) level of theory. Hydrogens have been omitted for clarity.

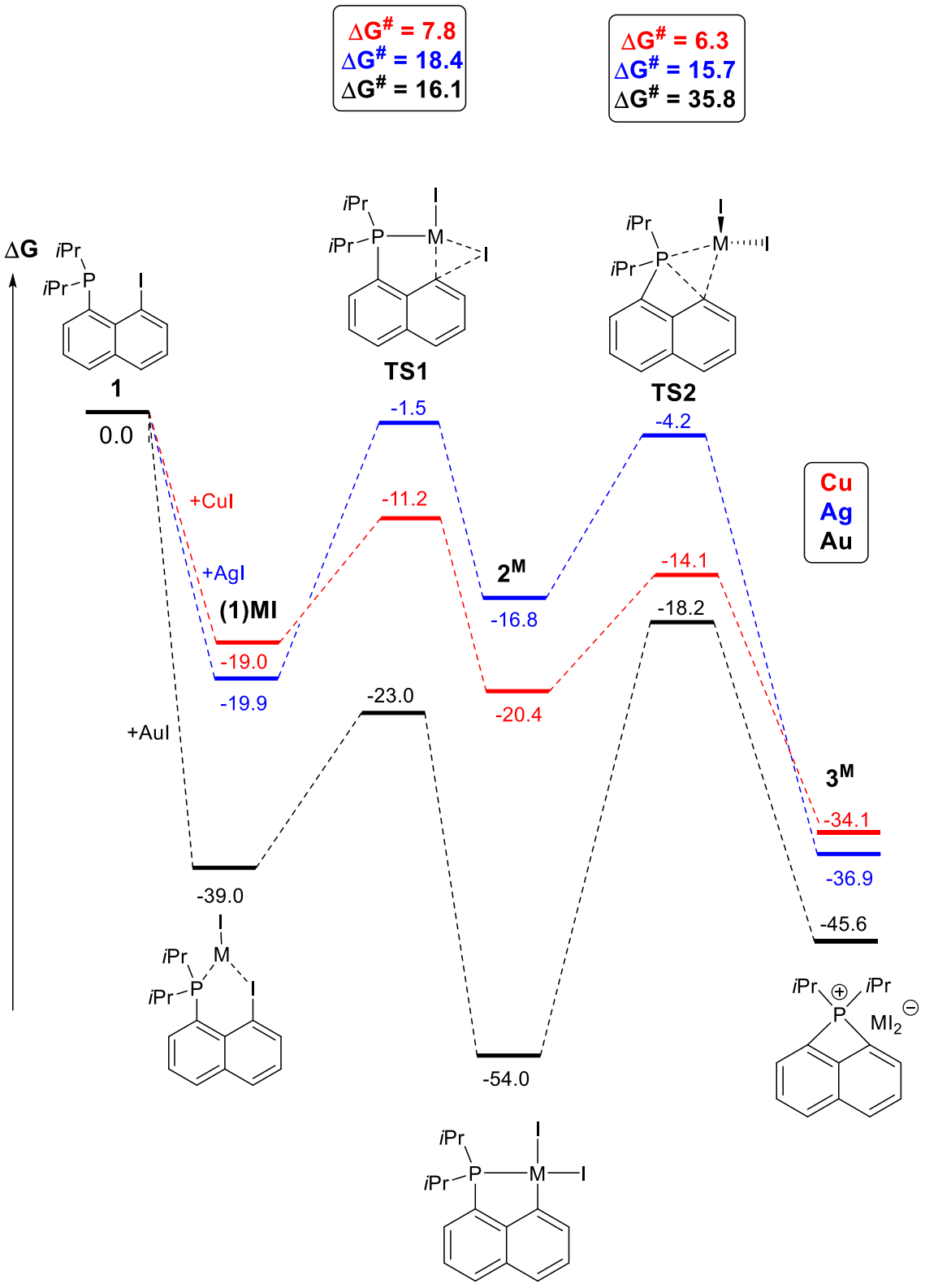


Figure S8 Comparison between the energy profiles **1** + **AgI**, **1** + **CuI** [S9] and **1** + **AuI**, computed in MeCN solution for the C–I oxidative addition / P–C reductive elimination sequence. Free energies ΔG, in kcal mol^{-1}, computed at SMD(MeCN)-B3PW91/SDD+f(Cu,Ag,Au), SDD(I),6-31G**(other atoms) level of theory.

Z-matrices and energies in a.u.

1

15	-1.512829000	-0.042872000	-0.393180000
6	-2.152518000	-0.853908000	1.198341000
1	-1.221476000	-1.058185000	1.741975000
6	1.908228000	-0.157827000	-0.238307000
6	1.173458000	1.025467000	0.094065000
6	3.254620000	-0.140355000	-0.538382000
6	-0.255913000	1.174184000	0.271037000
6	1.994516000	2.205654000	0.269481000
6	3.996141000	1.054445000	-0.472874000
1	3.764735000	-1.063423000	-0.792293000
6	-0.731872000	2.377153000	0.771465000
6	1.427747000	3.410123000	0.760617000
6	3.378926000	2.196025000	-0.034221000
1	5.053048000	1.043981000	-0.721888000
6	0.093239000	3.484657000	1.052004000
1	-1.798467000	2.504959000	0.919111000
1	2.083259000	4.265763000	0.900356000
1	3.938284000	3.118909000	0.094585000
1	-0.343457000	4.396502000	1.449263000
6	-2.904679000	1.085494000	-0.976336000
1	-3.268084000	1.723426000	-0.162157000
6	-2.804455000	-2.206241000	0.889949000
1	-2.151527000	-2.840619000	0.281132000
1	-3.018326000	-2.742605000	1.822842000
1	-3.752552000	-2.094524000	0.354373000
6	-3.040791000	0.008693000	2.092627000
1	-3.987019000	0.267182000	1.605685000
1	-3.288208000	-0.540518000	3.010169000
1	-2.546390000	0.937071000	2.393346000
6	-4.077142000	0.222046000	-1.454886000
1	-3.763139000	-0.500535000	-2.217888000
1	-4.547660000	-0.332149000	-0.638316000
1	-4.848159000	0.860700000	-1.903180000
6	-2.405130000	1.970714000	-2.121684000
1	-2.035004000	1.364869000	-2.957785000
1	-3.225947000	2.591130000	-2.501765000
1	-1.598445000	2.641491000	-1.811927000
53	1.134353000	-2.170534000	-0.081987000

Sum of electronic and zero-point Energies= -973.981935
Sum of electronic and thermal Free Energies= -974.030034

Silver profile

AgI

53	0.000000000	0.000000000	1.270940000
47	0.000000000	0.000000000	-1.433188000

Sum of electronic and zero-point Energies= -158.559889
Sum of electronic and thermal Free Energies= -158.586267

(1)AgI

6	4.388456000	0.852752000	-1.624145000
6	4.373990000	-0.474493000	-1.956159000
6	3.366393000	-1.337903000	-1.452558000
6	2.350023000	-0.831521000	-0.557361000
6	3.314961000	1.382173000	-0.880519000
6	3.396224000	-2.702676000	-1.833632000
6	2.487353000	-3.595175000	-1.327729000

1	4.165286000	-3.023321000	-2.531052000
1	5.174621000	1.512101000	-1.979274000
1	5.136547000	-0.899297000	-2.603550000
1	3.285733000	2.457487000	-0.746779000
1	2.494153000	-4.638370000	-1.628563000
6	1.584738000	-3.163462000	-0.336910000
1	0.948738000	-3.893176000	0.152898000
6	1.544698000	-1.841942000	0.057349000
53	0.418665000	-1.548701000	1.872506000
6	2.279488000	0.603050000	-0.386980000
6	1.119767000	2.119804000	1.904495000
1	1.579838000	1.233119000	2.355817000
6	0.720152000	3.040835000	-0.960693000
1	1.644529000	3.613170000	-0.824199000
15	0.766290000	1.534799000	0.152789000
47	-1.314498000	0.370300000	-0.175498000
53	-3.762767000	-0.579478000	-0.834988000
6	-0.458364000	3.936213000	-0.566835000
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1	-0.346403000	4.363214000	0.432734000
1	-0.528790000	4.769440000	-1.275588000
6	0.594784000	2.612630000	-2.424303000
1	1.437803000	2.002803000	-2.760283000
1	-0.326432000	2.039213000	-2.584757000
1	0.549353000	3.502380000	-3.062659000
6	-0.170317000	2.417232000	2.672944000
1	-0.867463000	1.573417000	2.636136000
1	0.068344000	2.610923000	3.725247000
1	-0.686808000	3.300376000	2.285194000
6	2.119707000	3.273337000	1.988433000
1	2.337414000	3.483137000	3.042231000
1	3.068837000	3.035145000	1.499701000
1	1.724396000	4.192951000	1.545726000

Sum of electronic and zero-point Energies= -1132.591298
Sum of electronic and thermal Free Energies= -1132.648024

TS1-Ag

6	0.974535000	-2.489307000	-1.274782000
6	1.074714000	-1.299752000	-0.588243000
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6	3.389528000	-1.038778000	-1.286969000
6	3.275619000	-2.272078000	-1.984214000
6	2.078350000	-2.941435000	-2.040284000
1	0.091418000	-3.112306000	-1.191659000
6	2.298637000	0.855103000	-0.148383000
6	4.591297000	-0.288831000	-1.306188000
1	4.152787000	-2.665795000	-2.490188000
1	1.982146000	-3.868757000	-2.597117000
6	4.652065000	0.967090000	-0.746359000
6	3.490054000	1.559021000	-0.210814000
1	5.458208000	-0.714235000	-1.804974000
1	5.578915000	1.532424000	-0.768760000
1	3.533067000	2.591573000	0.121138000
53	0.072255000	-2.059640000	1.760016000
6	0.706948000	1.911658000	2.139344000
1	1.143340000	0.975008000	2.508744000
6	0.675785000	3.249233000	-0.619843000
1	1.564404000	3.803918000	-0.290979000
47	-0.799778000	-0.237288000	-0.376145000
53	-3.495835000	0.003712000	-0.889199000
15	0.693282000	1.624585000	0.290716000

6	-0.575409000	4.063257000	-0.281236000
1	-0.580395000	4.979302000	-0.882815000
1	-1.490478000	3.507594000	-0.515059000
1	-0.609885000	4.358980000	0.770128000
6	0.769356000	2.992976000	-2.126181000
1	1.671329000	2.439544000	-2.403131000
1	-0.101610000	2.432789000	-2.485685000
1	0.790849000	3.951931000	-2.655980000
6	-0.711833000	2.022047000	2.704908000
1	-1.328708000	1.164097000	2.419640000
1	-0.661916000	2.051184000	3.799336000
1	-1.218129000	2.932763000	2.372436000
6	1.598323000	3.074231000	2.579263000
1	1.616480000	3.115150000	3.674705000
1	2.630345000	2.958536000	2.237074000
1	1.220289000	4.036001000	2.219166000

Sum of electronic and zero-point Energies= -1132.562486
Sum of electronic and thermal Free Energies= -1132.618760

2^{Ag}

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6	3.522837000	-2.076068000	-0.270480000
6	2.441583000	-1.143950000	-0.153336000
6	3.943557000	0.672930000	-0.776431000
6	3.292978000	-3.437612000	0.045338000
6	2.053492000	-3.844536000	0.474920000
1	4.112184000	-4.145998000	-0.044903000
1	5.959099000	0.091732000	-1.300685000
1	5.596285000	-2.309020000	-0.829951000
1	4.141840000	1.727058000	-0.942066000
1	1.876860000	-4.883704000	0.739510000
6	0.971394000	-2.930455000	0.559765000
1	0.006393000	-3.303114000	0.880877000
6	1.146521000	-1.613114000	0.203434000
53	-2.473938000	1.651751000	-0.229842000
6	2.698846000	0.232299000	-0.370615000
6	1.615460000	1.704670000	1.916520000
1	1.896748000	0.720135000	2.313273000
6	1.361052000	2.765237000	-0.998878000
1	2.433071000	3.010285000	-0.966185000
15	1.308183000	1.289410000	0.125980000
47	-0.492008000	-0.272154000	0.047813000
53	-2.455460000	-2.230994000	-0.030997000
6	0.588622000	3.997399000	-0.532991000
1	0.885616000	4.323772000	0.465981000
1	0.804892000	4.816876000	-1.227549000
1	-0.489303000	3.824396000	-0.537870000
6	0.998812000	2.351442000	-2.426919000
1	-0.065230000	2.109386000	-2.508884000
1	1.209087000	3.187459000	-3.102369000
1	1.579319000	1.490105000	-2.770947000
6	0.356803000	2.171418000	2.647637000
1	0.598425000	2.303590000	3.707971000
1	-0.014617000	3.126698000	2.266836000
1	-0.447063000	1.433255000	2.574302000
6	2.798263000	2.659915000	2.097415000
1	2.572282000	3.665100000	1.731032000
1	3.017515000	2.736431000	3.168187000
1	3.702838000	2.300073000	1.599308000

Sum of electronic and zero-point Energies= -1132.587360

Sum of electronic and thermal Free Energies= -1132.643097

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6	-3.323301000	-0.831730000	-1.907194000
6	-2.425878000	-0.420644000	-0.896085000
6	-3.906992000	1.296444000	-0.066470000
6	-2.944604000	-1.967727000	-2.668039000
6	-1.783513000	-2.652049000	-2.365812000
1	-3.586280000	-2.315227000	-3.472864000
1	-5.697566000	1.534236000	-1.247671000
1	-5.222314000	-0.296818000	-2.810665000
1	-4.192110000	2.064395000	0.643752000
1	-1.517700000	-3.536773000	-2.937617000
6	-0.898902000	-2.249011000	-1.323623000
1	-0.007670000	-2.831797000	-1.116920000
6	-1.205969000	-1.084323000	-0.656701000
53	2.947666000	-1.753434000	0.168589000
6	-2.729495000	0.589269000	0.033762000
6	-0.755101000	1.802960000	2.072556000
1	-0.478537000	2.464705000	1.244057000
6	-1.826138000	-1.002440000	2.480531000
1	-1.984247000	-0.404326000	3.387092000
15	-1.389336000	0.278957000	1.207248000
47	0.660269000	-0.066655000	-0.197200000
53	1.687350000	2.406000000	-1.097516000
6	-0.642196000	-1.947222000	2.709077000
1	0.283943000	-1.417685000	2.946762000
1	-0.880235000	-2.602564000	3.553444000
1	-0.467429000	-2.572413000	1.828415000
6	-3.111310000	-1.759740000	2.154640000
1	-3.324627000	-2.440445000	2.985459000
1	-3.968491000	-1.092146000	2.036638000
1	-3.007761000	-2.364864000	1.249129000
6	0.470418000	1.529517000	2.942201000
1	0.813300000	2.481670000	3.360074000
1	0.232676000	0.863519000	3.777099000
1	1.296512000	1.097148000	2.369319000
6	-1.900122000	2.436167000	2.874740000
1	-2.762625000	2.695425000	2.257666000
1	-2.230976000	1.799886000	3.700702000
1	-1.514113000	3.366452000	3.307377000

Sum of electronic and zero-point Energies= -1132.565294

Sum of electronic and thermal Free Energies= -1132.623126

3^{Ag}

6	3.482020000	3.022742000	1.277386000
6	2.787804000	2.504705000	2.363760000
6	2.379563000	1.141981000	2.371266000
6	2.749855000	0.437296000	1.220979000
6	3.835611000	2.268599000	0.117060000
6	1.666138000	0.356518000	3.318889000
6	1.392085000	-0.980664000	3.057840000
1	1.330525000	0.796861000	4.253916000
1	3.776491000	4.068178000	1.306514000
1	2.558302000	3.150097000	3.207259000
1	4.376728000	2.741118000	-0.695977000
1	0.846072000	-1.548989000	3.805752000
6	1.782264000	-1.661690000	1.864553000
1	1.529230000	-2.707415000	1.725390000
6	2.475744000	-0.915996000	0.943890000

53	-3.487131000	-2.288664000	0.371504000
6	3.452551000	0.950702000	0.114128000
6	2.205905000	-0.704274000	-2.134968000
1	1.345318000	-0.123910000	-1.778184000
6	4.869480000	-1.654337000	-0.913945000
1	5.076590000	-1.564742000	-1.987690000
15	3.313524000	-0.700580000	-0.670381000
47	-2.663505000	0.227014000	-0.138368000
53	-1.838553000	2.736730000	-0.675793000
6	4.649446000	-3.128770000	-0.551756000
1	3.834708000	-3.589225000	-1.115914000
1	5.567370000	-3.680301000	-0.778856000
1	4.441433000	-3.243544000	0.516465000
6	6.021391000	-1.036063000	-0.118682000
1	6.925967000	-1.623820000	-0.304998000
1	6.220196000	-0.003480000	-0.417087000
1	5.824202000	-1.057646000	0.957929000
6	1.742422000	-2.111132000	-2.518184000
1	0.989805000	-2.024033000	-3.308556000
1	2.567309000	-2.714676000	-2.907660000
1	1.284044000	-2.639218000	-1.676974000
6	2.870862000	0.040413000	-3.297006000
1	3.170908000	1.054924000	-3.018748000
1	3.748659000	-0.496274000	-3.669972000
1	2.150435000	0.117449000	-4.117558000

Sum of electronic and zero-point Energies= -1132.610900
Sum of electronic and thermal Free Energies= -1132.675120

Gold profile

AuI

53	0.000000000	0.000000000	-1.564215000
79	0.000000000	0.000000000	1.049410000

Sum of electronic and zero-point Energies= -147.313884
Sum of electronic and thermal Free Energies= -147.340887

(1)AuI

6	4.438876000	0.786849000	-1.603367000
6	4.373016000	-0.524348000	-1.989653000
6	3.346008000	-1.374316000	-1.502246000
6	2.368226000	-0.871762000	-0.565402000
6	3.386355000	1.325209000	-0.835849000
6	3.319088000	-2.724143000	-1.933881000
6	2.395622000	-3.604428000	-1.432000000
1	4.056740000	-3.044051000	-2.664646000
1	5.243532000	1.432667000	-1.941152000
1	5.110515000	-0.947623000	-2.666364000
1	3.387715000	2.397125000	-0.673169000
1	2.356847000	-4.634712000	-1.772279000
6	1.547704000	-3.185031000	-0.388271000
1	0.915302000	-3.915163000	0.105452000
6	1.564084000	-1.878615000	0.055158000
53	0.583410000	-1.616039000	1.954178000
6	2.333426000	0.558755000	-0.360054000
6	1.151372000	2.056875000	1.949605000
1	1.614254000	1.163319000	2.382075000
6	0.832271000	3.045162000	-0.905127000
1	1.762978000	3.593707000	-0.722343000
15	0.842034000	1.520369000	0.178490000
53	-3.487514000	-0.733289000	-0.776992000
6	-0.342214000	3.951568000	-0.523292000

1 -1.298951000 3.425886000 -0.624909000
1 -0.265763000 4.334200000 0.497319000
1 -0.358777000 4.813803000 -1.199674000
6 0.747515000 2.660399000 -2.383606000
1 1.590686000 2.046797000 -2.711283000
1 -0.177698000 2.109425000 -2.589853000
1 0.739487000 3.571395000 -2.992643000
6 -0.148996000 2.326150000 2.709522000
1 -0.834574000 1.474968000 2.648311000
1 0.081165000 2.501594000 3.766772000
1 -0.671234000 3.210901000 2.333777000
6 2.145895000 3.212741000 2.070457000
1 2.362708000 3.381900000 3.131408000
1 3.095683000 2.996537000 1.572828000
1 1.744948000 4.146089000 1.663756000
79 -1.138204000 0.418782000 -0.212450000
Sum of electronic and zero-point Energies= -1121.376631
Sum of electronic and thermal Free Energies= -1121.433142

TS1-Au
6 0.007833000 -2.610900000 -0.911098000
6 0.580459000 -1.476235000 -0.367272000
6 1.913764000 -1.077020000 -0.708222000
6 2.697511000 -1.990565000 -1.482464000
6 2.093941000 -3.162904000 -2.012649000
6 0.763218000 -3.423843000 -1.788971000
1 -0.986801000 -2.923320000 -0.614235000
6 2.447340000 0.204953000 -0.401891000
6 4.046674000 -1.654840000 -1.761579000
1 2.698595000 -3.837117000 -2.612674000
1 0.291552000 -4.303839000 -2.216739000
6 4.581420000 -0.455563000 -1.348587000
6 3.764122000 0.500640000 -0.710485000
1 4.645177000 -2.355736000 -2.337799000
1 5.616228000 -0.212082000 -1.570131000
1 4.167696000 1.487904000 -0.507399000
53 0.088866000 -1.699640000 2.113413000
6 1.571013000 1.914856000 1.904330000
1 1.795506000 0.936031000 2.345379000
6 1.503959000 2.920746000 -0.988480000
1 2.546347000 3.226131000 -0.826649000
53 -3.454505000 0.147603000 -0.725535000
15 1.229123000 1.460810000 0.127657000
6 0.574951000 4.081343000 -0.625536000
1 0.730054000 4.898136000 -1.339087000
1 -0.477811000 3.782526000 -0.684539000
1 0.767871000 4.473802000 0.375629000
6 1.318875000 2.504551000 -2.449119000
1 2.000015000 1.702334000 -2.746182000
1 0.291192000 2.171042000 -2.634333000
1 1.514739000 3.366913000 -3.095862000
6 0.331549000 2.474301000 2.607457000
1 -0.526847000 1.803408000 2.504542000
1 0.547791000 2.585285000 3.675959000
1 0.046572000 3.457735000 2.222801000
6 2.795099000 2.818283000 2.067479000
1 2.991419000 2.956970000 3.136768000
1 3.693236000 2.382741000 1.620761000
1 2.634020000 3.808084000 1.629475000
79 -0.772088000 0.272558000 -0.227032000
Sum of electronic and zero-point Energies= -1121.351081

Sum of electronic and thermal Free Energies= -1121.407528

2^{Au}

6	-5.067406000	0.221901000	-0.796259000
6	-4.855349000	1.561944000	-0.569693000
6	-3.572505000	2.052090000	-0.212748000
6	-2.481644000	1.128657000	-0.126013000
6	-4.010191000	-0.702162000	-0.645283000
6	-3.338586000	3.422125000	0.060393000
6	-2.081422000	3.843506000	0.416562000
1	-4.166602000	4.122870000	-0.006062000
1	-6.053576000	-0.138627000	-1.073127000
1	-5.673848000	2.271594000	-0.660927000
1	-4.212726000	-1.759575000	-0.783764000
1	-1.897670000	4.889309000	0.647961000
6	-0.993874000	2.936622000	0.466490000
1	-0.017447000	3.325995000	0.726509000
6	-1.165457000	1.601663000	0.164122000
53	2.434100000	-1.646524000	-0.183093000
6	-2.747024000	-0.253276000	-0.311163000
6	-1.616761000	-1.855251000	1.859976000
1	-1.881987000	-0.896398000	2.325304000
6	-1.375211000	-2.708370000	-1.133959000
1	-2.446335000	-2.954876000	-1.138718000
15	-1.337348000	-1.320805000	0.097768000
53	2.405885000	2.174351000	-0.021394000
6	-0.608799000	-3.974800000	-0.757744000
1	-0.913000000	-4.374816000	0.211911000
1	-0.823909000	-4.737287000	-1.514701000
1	0.469598000	-3.806077000	-0.743797000
6	-0.992844000	-2.181122000	-2.518896000
1	0.069812000	-1.923176000	-2.561367000
1	-1.183019000	-2.963688000	-3.261045000
1	-1.577069000	-1.300597000	-2.803331000
6	-0.358712000	-2.387481000	2.545554000
1	-0.594351000	-2.583270000	3.597354000
1	-0.010601000	-3.322979000	2.099757000
1	0.458178000	-1.662099000	2.510317000
6	-2.806684000	-2.808932000	1.996096000
1	-2.601164000	-3.785767000	1.549413000
1	-3.001790000	-2.964178000	3.062815000
1	-3.718775000	-2.404299000	1.549571000
79	0.401926000	0.245855000	0.038135000

Sum of electronic and zero-point Energies= -1121.402010

Sum of electronic and thermal Free Energies= -1121.456925

TS2-Au

6	-4.723554000	1.111319000	0.703910000
6	-4.532588000	1.500382000	-0.612866000
6	-3.377031000	1.084277000	-1.326950000
6	-2.440688000	0.360208000	-0.569749000
6	-3.820480000	0.260721000	1.398641000
6	-3.073850000	1.219898000	-2.708393000
6	-1.974151000	0.570854000	-3.246379000
1	-3.735811000	1.787731000	-3.356339000
1	-5.625297000	1.429962000	1.218811000
1	-5.287681000	2.101200000	-1.112402000
1	-4.069123000	-0.097692000	2.391675000
1	-1.789592000	0.643204000	-4.314486000
6	-1.070205000	-0.207029000	-2.471671000
1	-0.249380000	-0.724288000	-2.957059000
6	-1.255082000	-0.213795000	-1.094008000

53	3.313322000	-0.794640000	-0.556016000
6	-2.666981000	-0.096782000	0.737230000
6	-0.396404000	-1.459557000	2.311603000
1	0.068408000	-0.479142000	2.463815000
6	-1.831477000	-2.987351000	0.134335000
1	-1.895086000	-3.545392000	1.076929000
15	-1.297879000	-1.295260000	0.679081000
53	0.723860000	2.758047000	0.871383000
6	-0.746514000	-3.611009000	-0.751126000
1	0.243269000	-3.597751000	-0.288073000
1	-1.012902000	-4.655648000	-0.942350000
1	-0.685999000	-3.094333000	-1.713713000
6	-3.198445000	-2.990880000	-0.545450000
1	-3.449820000	-4.025258000	-0.802520000
1	-3.985454000	-2.603701000	0.106344000
1	-3.190789000	-2.411198000	-1.473664000
6	0.673046000	-2.547218000	2.321948000
1	1.179846000	-2.514743000	3.292171000
1	0.239140000	-3.545006000	2.207102000
1	1.426423000	-2.393488000	1.545086000
6	-1.462031000	-1.682569000	3.393828000
1	-2.147022000	-0.837160000	3.486339000
1	-2.039200000	-2.597799000	3.228031000
1	-0.937953000	-1.790053000	4.350122000
79	0.731901000	0.081646000	-0.270328000

Sum of electronic and zero-point Energies= -1121.340596
Sum of electronic and thermal Free Energies= -1121.399854

3^{Au}

6	-5.563064000	-2.230643000	1.629207000
6	-4.652175000	-1.976693000	2.646954000
6	-3.598648000	-1.041197000	2.450884000
6	-3.603879000	-0.445013000	1.185398000
6	-5.528143000	-1.604702000	0.346116000
6	-2.541113000	-0.593306000	3.290242000
6	-1.630390000	0.349333000	2.828945000
1	-2.438453000	-0.984899000	4.298659000
1	-6.353772000	-2.952275000	1.815082000
1	-4.751191000	-2.499869000	3.594198000
1	-6.271943000	-1.854930000	-0.403048000
1	-0.836791000	0.668879000	3.498740000
6	-1.667621000	0.930386000	1.524662000
1	-0.919546000	1.658768000	1.230505000
6	-2.685724000	0.509046000	0.705738000
53	2.821115000	2.471292000	0.509325000
6	-4.519519000	-0.695807000	0.145387000
6	-2.696968000	-0.308348000	-2.282627000
1	-2.203127000	-1.157572000	-1.793482000
6	-4.431709000	2.055716000	-1.374161000
1	-4.638346000	1.929036000	-2.444379000
15	-3.584926000	0.493819000	-0.890084000
53	2.290185000	-2.692406000	-0.537892000
6	-3.487837000	3.247864000	-1.170368000
1	-2.539191000	3.133902000	-1.700991000
1	-3.980086000	4.147727000	-1.552652000
1	-3.275975000	3.401887000	-0.107919000
6	-5.750095000	2.227429000	-0.617075000
1	-5.586690000	2.299455000	0.462893000
1	-6.222330000	3.157996000	-0.948035000
1	-6.444581000	1.406018000	-0.811664000
6	-1.637932000	0.605052000	-2.904140000

1	-1.077825000	0.028077000	-3.647021000
1	-2.094201000	1.457572000	-3.416086000
1	-0.926348000	0.978654000	-2.162149000
6	-3.706044000	-0.832756000	-3.309053000
1	-4.435425000	-1.512705000	-2.859324000
1	-4.243020000	-0.015605000	-3.800725000
1	-3.160553000	-1.386785000	-4.079739000
79	2.550374000	-0.111009000	-0.011193000

Sum of electronic and zero-point Energies= -1121.381226
Sum of electronic and thermal Free Energies= -1121.443628

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