Cluster halogenation of adamantane and its derivatives with bromine and iodine monochloride

Andrey V. Shernyukov, George E. Salnikov, Vyacheslav I. Krasnov and Alexander M. Genaev*

Supporting Information

Contents

Page

^{1}H NMR spectra of the reaction mixtures for the halogenation reactions 2

AdH + Br_2 2

AdH + ICl 2

AdCl + ICl 3

AdBr + ICl 3

AdCl + Br_2 4

AdOH + Br_2 4

AdOH + ICl 5

Quantum chemical calculations 6

AdH-Br_2, TS1 and AdBr-HBr (Fig. 2 in main text) 6

AdH-2Br_2, TS2, $Ad^+Br_3^-$-HBr, TS2' and AdBr-HBr-Br_2 (Fig. 2 in main text) 7

AdH-3Br_2, TS3, $Ad^+Br_5^-$-HBr, TS3' and AdBr-HBr-2Br_2 (Fig. 2 in main text) 10

AdH+ClI(2.8), TS(34.4) and AdCl+HI (Fig. 5 in main text) 13

AdH+ClI(1.5) and TS(36.5) (Fig. 5 in main text) 15

AdH+ICl(0.4), TS(35.3), Intermediate and AdI+HCl (Fig. 5 in main text) 16

AdH+ClI+ICl(-1.6), TS(8.0), Intermediate(-13.0) and AdCl+I_2+HCl(-25.2) (Fig. 6 in main text) 19

AdH+ClI+ClI(3.7), TS(22.4), Intermediate(11.1) and AdCl+HI+ClI(-6.3) (Fig. 6 in main text) 21

AdH+ICl+ICl(3.4), TS(17.7), Intermediate(9.3) and AdI+HCl+ICl(-12.8) (Fig. 6 in main text) 23

AdH+ICl+ClI(4.3), TS(33.6), Intermediate(12.8) and AdI+HCl+ClI(-6.2) (Fig. 6 in main text) 26

AdH+3ICl, TS(a-d) (Fig. 7 in main text) 28

AdH+3ICl, TS(e-h) (Fig. 7 in main text) 31

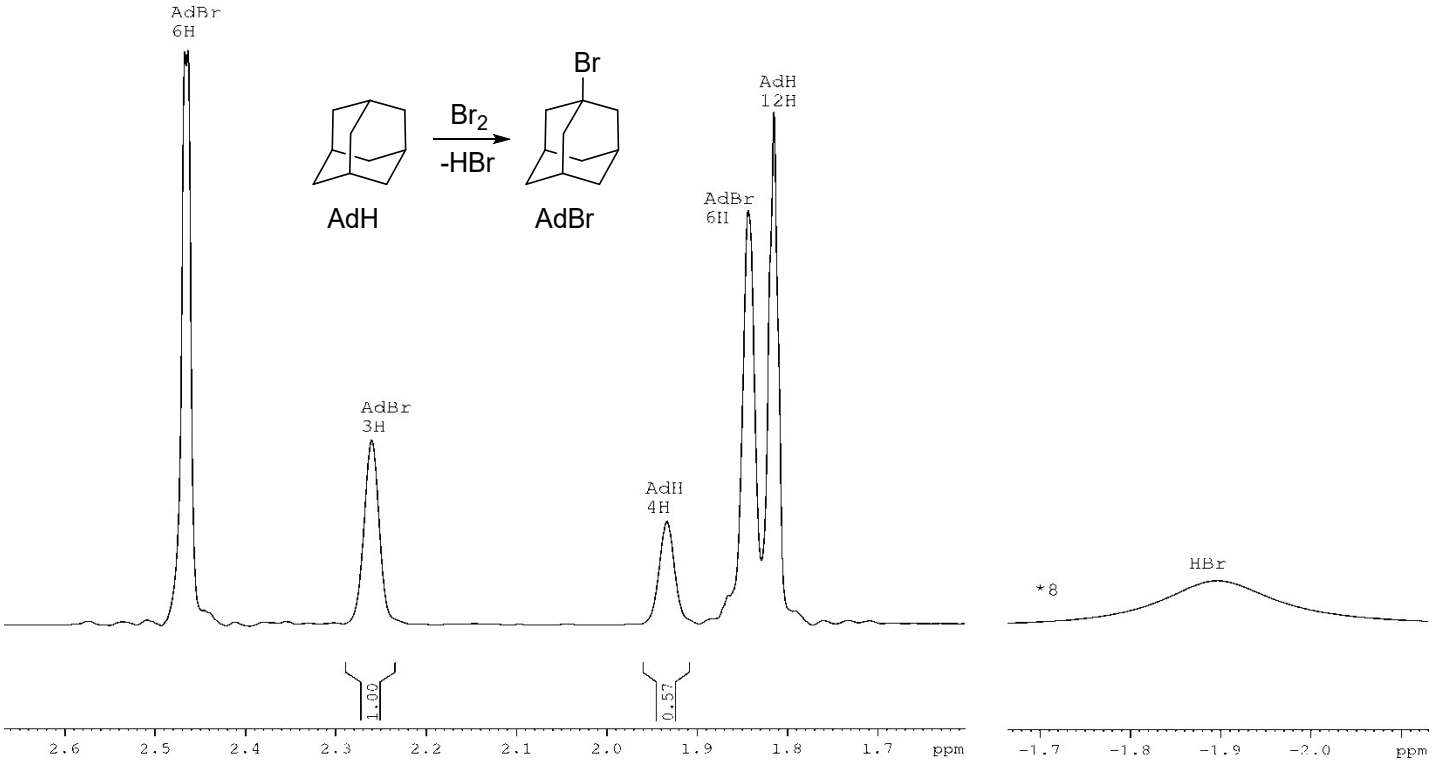
AdBr-ICl, TS(17.7), Intermediate(2.2), TS(3.8), Intermediate(2.1), TS(15.8), AdCl-BrI (Fig. 10 in main text) 33

^{1}H NMR spectra of the reaction mixtures for the halogenation reactions

The integrals on the spectra show the signals from which the kinetic data were taken

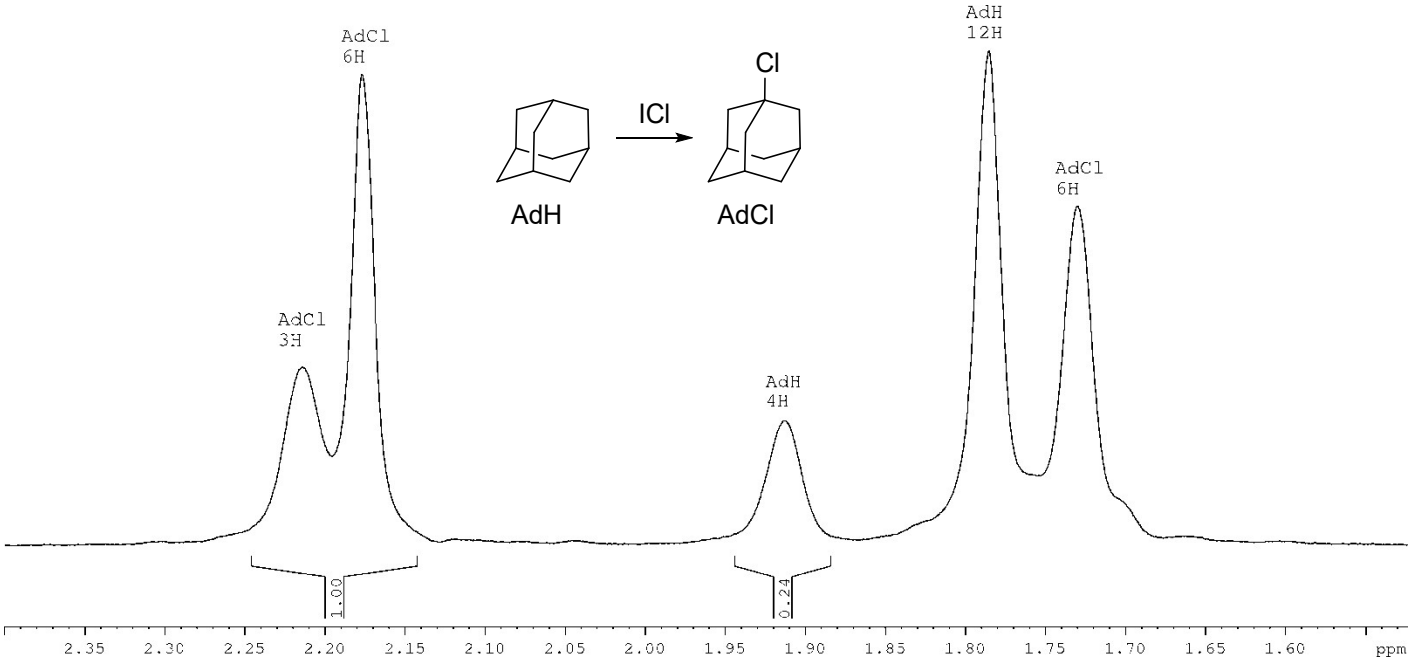
AdH + Br_2

600 MHz, 22 mg AdH + 0.3 ml Br_2 + 0.1 ml CCl_4 + 0.1 ml CD_2Cl_2 after 7.7 h at 0 °C



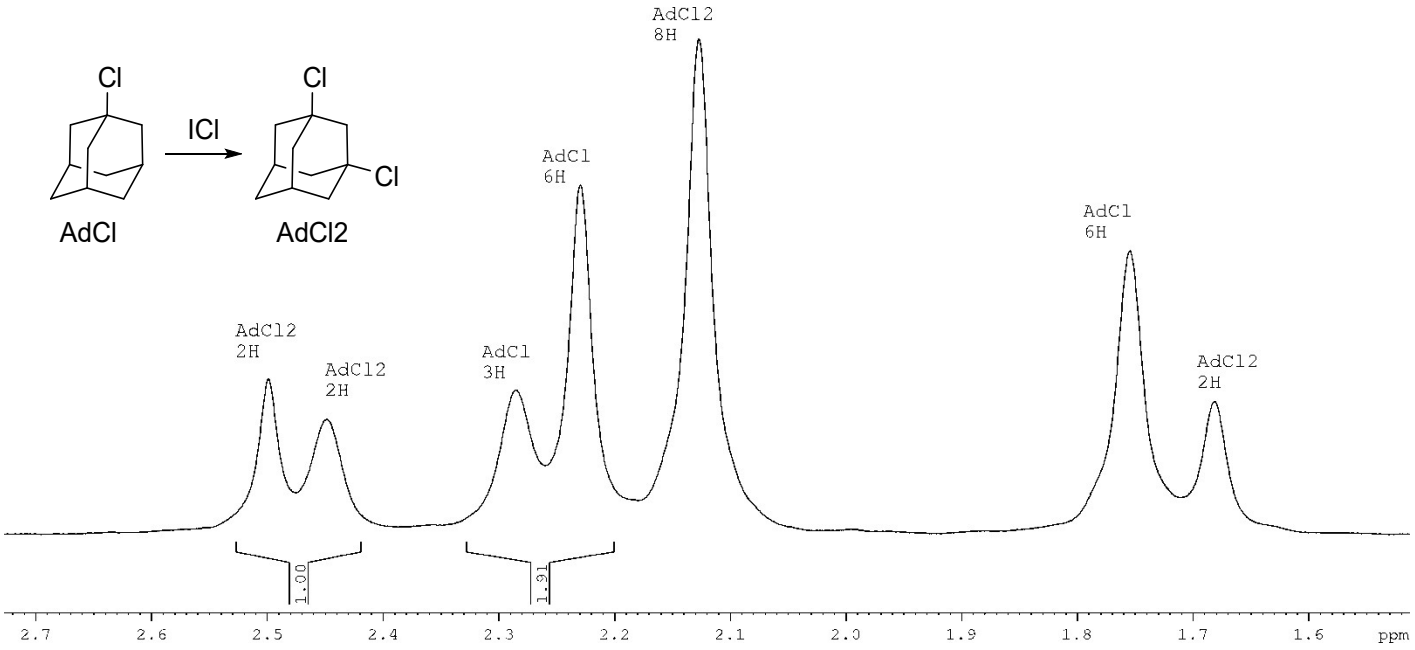
AdH + ICl

500 MHz, 5.2 mg AdH, 0.03 ml (97 mg) ICl, 0.37 ml CCl_4, 0.1 ml CD_2Cl_2 after 18 min at 20 °C



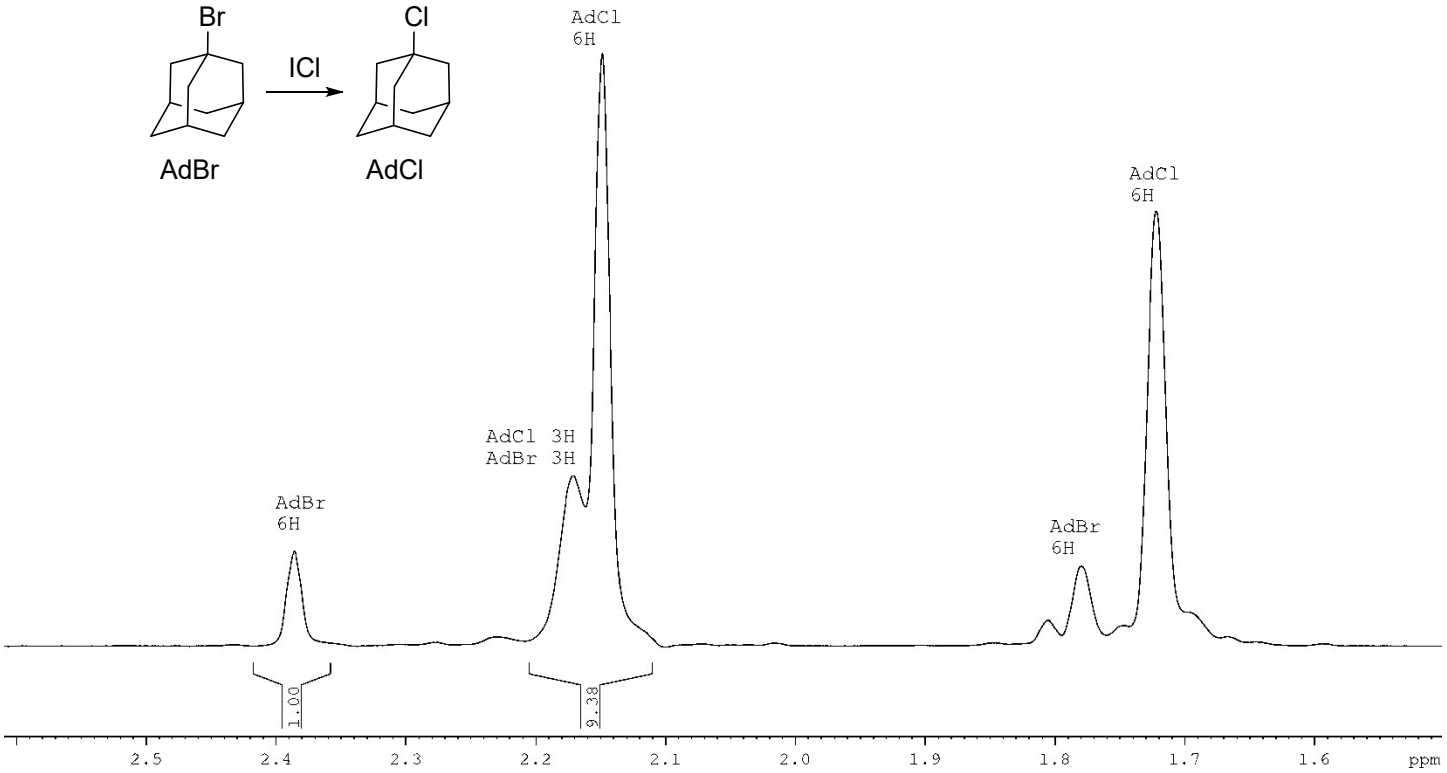
AdCl + ICl

500 MHz, 14 mg AdH, 0.2 ml (627 mg) ICl, 0.2 ml CCl_4, 0.1 ml CD_2Cl_2 after 1.8 h at 20 °C



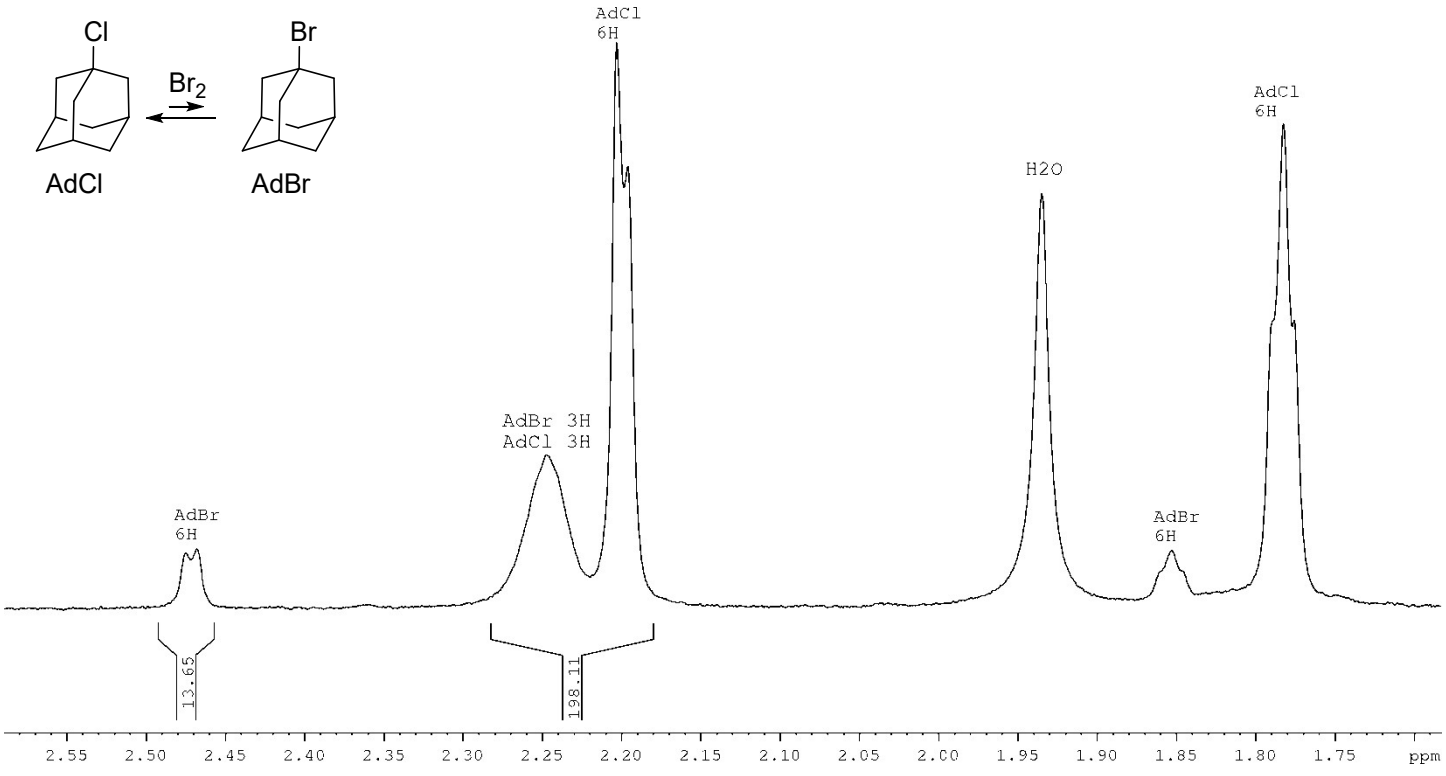
AdBr + ICl

500 MHz, 15.6 mg AdBr, 0.003 ml (11.9 mg) ICl, 0.4 ml CCl_4, 0.1 ml CD_2Cl_2 after 1 min at 20 °C



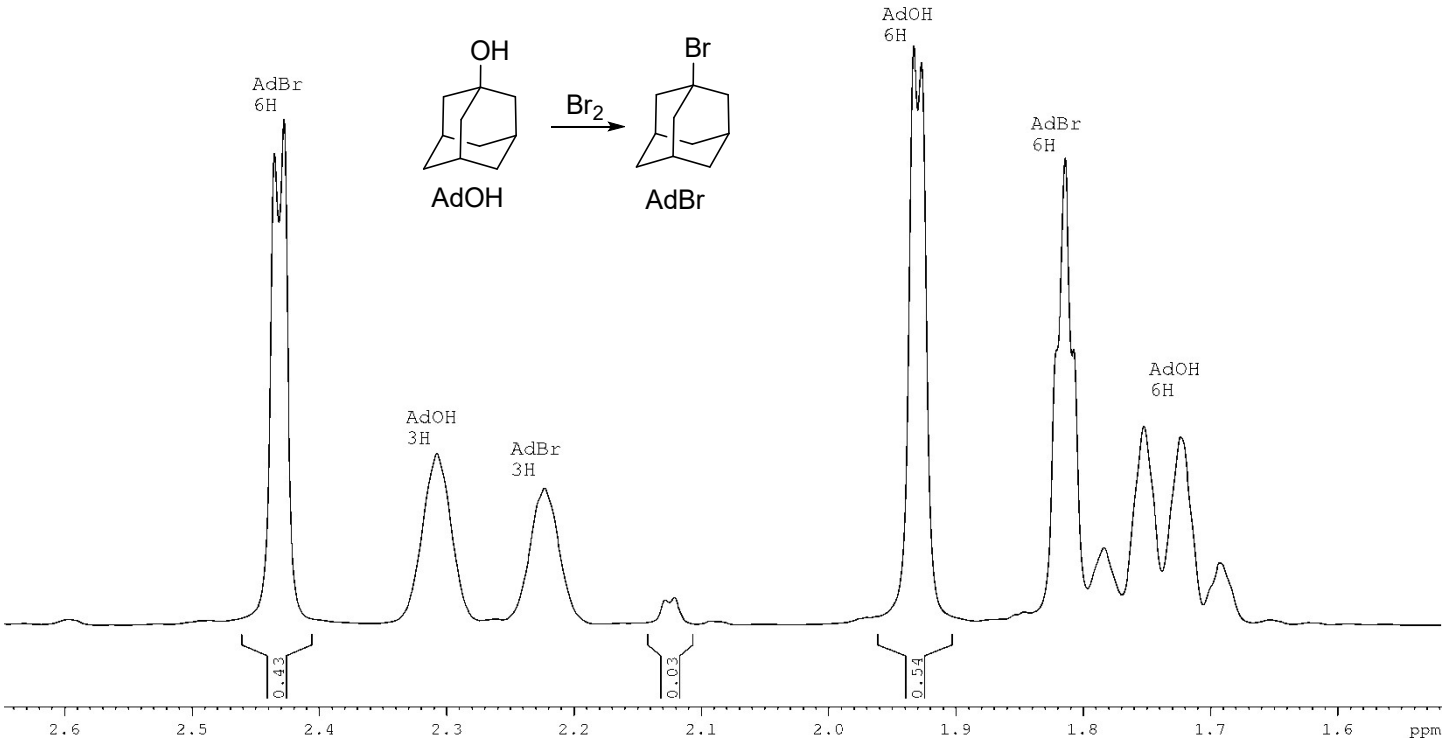
AdCl + Br_2

500 MHz, 0.6 mg AdCl, 0.4 ml Br_2, 0.1 ml CD_2Cl_2 after 27 h at 20 °C (equilibrium mixture)



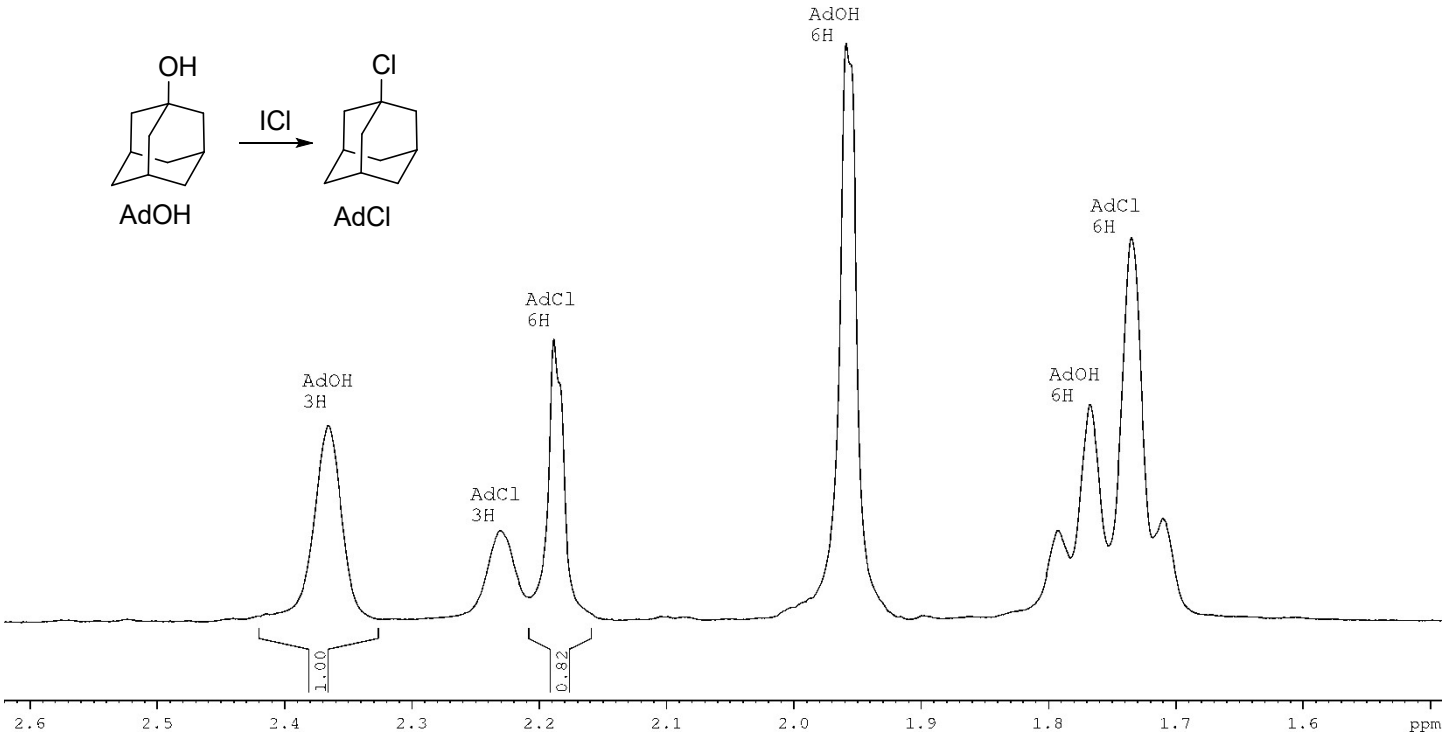
AdOH + Br_2

400 MHz, 13 mg AdOH, 0.4 ml Br_2, 0.1 ml CD_2Cl_2 after 39 h at 20 °C



AdOH + ICl

400 MHz, 13 mg AdOH, 0.05 ml (164 mg) ICl,0.35 ml CCl_4, 0.1 ml CD_2Cl_2 after 16 h at 20 °C



Quantum chemical calculations

See also http://limor1.nioch.nsc.ru/quant/bromination/adamantane/

Structures are in XMol xyz format. Energies are in a.u., Gibbs energy G in kcal/mol

AdH-Br_2, TS1 and AdBr-HBr (Fig. 2 in main text)

```
28
 Energy -5537.69018717
C    0.72565552   0.48665630   0.00000000
C    2.17801163   0.00000000   0.00000000
C    0.00055953  -0.00084795   1.25784452
C   -0.00055953   0.00084795  -1.25784452
C    2.17932680  -1.54327685  -0.00182885
C   -0.00054746  -1.54466201   1.25614447
C    0.00104477  -1.54231859  -1.25980252
C    1.45172791  -2.05216174   1.25456181
C   -0.72509222  -2.05045590  -0.00289300
C    1.45230510  -2.05073303  -1.25864747
Br   0.74957964   3.74251949  -0.01173605
H    2.71131903   0.38156127  -0.88561371
H    2.70456469   0.37841807   0.89136948
H    0.50786119   0.37525762   2.16041634
H   -1.03367967   0.37940120   1.27494007
H   -1.03690412   0.37570773  -1.26979277
H    0.50189742   0.38282485  -2.16125788
H    3.22118187  -1.90324613  -0.00101807
H   -0.52264996  -1.90569766   2.15700354
H   -0.51890096  -1.90268555  -2.16231071
H    1.97362121  -1.70173671   2.16015329
H    1.46604867  -3.15473300   1.27830308
H   -1.77097896  -1.69922653  -0.00411379
H   -0.75333572  -3.15314669  -0.00534490
H    1.97552515  -1.70483552  -2.16565126
H    1.46413731  -3.15336570  -1.27760543
H    0.72546231   1.61347278   0.00080849
Br   0.78102192   6.10625128  -0.02826064
28
 Energy -5537.64439305
C    0.71951876   0.31737856   0.00000000
C    2.16498270   0.00000000   0.00000000
C    0.00088173  -0.00056475   1.25270817
C   -0.00088173   0.00056475  -1.25270817
C    2.17478184  -1.58153807  -0.00242683
C    0.00376675  -1.58689516   1.25368933
C    0.00262525  -1.58511345  -1.25680510
C    1.45648845  -2.07819652   1.25784644
C   -0.72846125  -2.07741261  -0.00195756
C    1.45578348  -2.07569031  -1.26369766
Br   1.10735923   3.10135020  -0.02761113
H    2.67716513   0.37176755  -0.89614070
H    2.67559689   0.36986174   0.89758689
H    0.52296378   0.36859330   2.14474403
H   -1.03785766   0.35417340   1.25377692
H   -1.03978344   0.35644537  -1.25261142
H    0.52170943   0.37049528  -2.14430978
```

```
H    3.22937345  -1.89555503  -0.00343223
H   -0.52204976  -1.90592408   2.16638376
H   -0.52466965  -1.90270486  -2.16902254
H    1.97843985  -1.72535210   2.16066377
H    1.47299952  -3.17917133   1.28541537
H   -1.77091796  -1.72276707  -0.00033115
H   -0.76354033  -3.17822484  -0.00228631
H    1.97529569  -1.72036403  -2.16771707
H    1.47342085  -3.17656830  -1.29302677
H   -0.15615500   2.32903110   0.01264694
Br   3.13827591   5.20877503  -0.10357255
28
 Energy -5537.72002120
C    0.72529407   0.46611167   0.00000000
C    2.17684596   0.00000000   0.00000000
C    0.00116793  -0.00141345   1.25683519
C   -0.00116793   0.00141345  -1.25683519
C    2.17621882  -1.54734877  -0.00238719
C    0.00197690  -1.54851670   1.25365756
C    0.00075211  -1.54572684  -1.25705359
C    1.45265748  -2.05730363   1.25410510
C   -0.72590589  -2.05498874  -0.00202530
C    1.45177354  -2.05340717  -1.26052554
Br   0.74021258   2.50678261   0.00304603
H    2.69908827   0.38414123  -0.88912721
H    2.69702671   0.38054193   0.89224768
H    0.51313812   0.38006340   2.15330558
H   -1.03188155   0.37653847   1.26669451
H   -1.03527245   0.37781374  -1.26300363
H    0.50572393   0.38388193  -2.15512633
H    3.22113416  -1.89606360  -0.00305166
H   -0.52005076  -1.89747509   2.15848258
H   -0.52197967  -1.89423620  -2.16187162
H    1.97501267  -1.70834734   2.15972966
H    1.46446754  -3.15914509   1.27207159
H   -1.77125832  -1.70513114  -0.00211699
H   -0.74982791  -3.15643373  -0.00191993
H    1.97489597  -1.70271813  -2.16533456
H    1.46523075  -3.15527666  -1.28155143
H   -1.54293929   2.64842439  -0.01749992
Br  -3.01132045   2.57274188  -0.03922299
```

AdH-2Br_2, TS2, $Ad^+Br_3^-$-HBr, TS2' and AdBr-HBr-Br_2 (Fig. 2 in main text)

```
30
 Energy -10685.23705937
C    0.72657916   0.47391242   0.00000000
C    2.17905421   0.00000000   0.00000000
C    0.00010643  -0.00147029   1.25841963
C   -0.00010643   0.00147029  -1.25841963
C    2.17772101  -1.54633055  -0.00286979
C   -0.00082370  -1.54860907   1.25275254
C    0.00067367  -1.54461494  -1.26131620
C    1.45044442  -2.05512095   1.25250491
C   -0.72602453  -2.05246702  -0.00530522
```

```
C    1.45272532  -2.04904286  -1.26150636
Br   0.83553551   3.60911471  -0.18852154
H    2.70836764   0.37672181  -0.88952549
H    2.70731334   0.37576648   0.89034956
H    0.50956867   0.37211746   2.16069644
H   -1.03367608   0.37775765   1.27472933
H   -1.03455393   0.37884784  -1.26899453
H    0.50501276   0.38167293  -2.16034340
H    3.22058565  -1.90222082  -0.00242664
H   -0.52332904  -1.90453908   2.15525113
H   -0.51982517  -1.89871205  -2.16559896
H    1.97213128  -1.70744267   2.15967351
H    1.46164947  -3.15770741   1.27271345
H   -1.77187152  -1.70382585  -0.00576554
H   -0.75298122  -3.15521087  -0.00523503
H    1.97537323  -1.69580977  -2.16571923
H    1.46751751  -3.15155530  -1.28738153
H    0.72271909   1.61662860   0.00283971
Br   0.98389521   5.99419695  -0.43453218
Br  -0.97090305   7.11864804   1.37935082
Br  -2.54186067   8.16667257   2.83387419
30
 Energy -10685.22454042
C    0.72783664   0.30465846   0.00000000
C    2.17517898   0.00000000   0.00000000
C   -0.00060699   0.00762283   1.24794722
C    0.00060699  -0.00762283  -1.24794722
C    2.16648925  -1.59536648   0.01126496
C   -0.00986540  -1.58480936   1.25452230
C   -0.00017870  -1.59702542  -1.24889189
C    1.44221340  -2.07080562   1.27389348
C   -0.73933931  -2.07631997   0.00261993
C    1.45157446  -2.08416367  -1.25094930
Br  -0.08692107   3.16542960   0.01695841
H    2.68874301   0.34765560  -0.90492749
H    2.69017335   0.36061524   0.89881173
H    0.52234418   0.36624709   2.14343548
H   -1.03607779   0.37473552   1.23724585
H   -1.03448879   0.35416251  -1.22805380
H    0.51602292   0.35691310  -2.14551591
H    3.22280427  -1.90373794   0.01623015
H   -0.54735493  -1.88087637   2.16735326
H   -0.52517446  -1.90689467  -2.16488254
H    1.95967143  -1.70531812   2.17469675
H    1.46315783  -3.17157520   1.31500016
H   -1.77829009  -1.71505668   0.00380492
H   -0.77807199  -3.17768047   0.00900219
H    1.97878708  -1.73186406  -2.15163328
H    1.46914387  -3.18538859  -1.27887152
H    0.84737888   1.96116318  -0.00706681
Br  -2.63227977   4.71168424   0.27677855
Br  -3.46912158   2.23014420   0.69516579
Br  -4.11321121  -0.19063959   1.08158517
30
```

Energy -10685.24327496
C 0.71139810 0.26014951 0.00000000
C 2.15428846 0.00000000 0.00000000
C -0.00011169 -0.00225732 1.24959082
C 0.00011169 0.00225732 -1.24959082
C 2.15543214 -1.60304579 -0.00042735
C -0.01467308 -1.60287115 1.25096583
C -0.01440945 -1.60241385 -1.24920577
C 1.43629218 -2.09212025 1.26032283
C -0.75552703 -2.07655968 0.00070547
C 1.43539515 -2.09140020 -1.26031354
Br 0.59581155 3.14318452 0.06860262
H 2.66320453 0.35266794 -0.90510412
H 2.66351357 0.35530730 0.90344866
H 0.53999829 0.34954975 2.13654845
H -1.03343620 0.36493103 1.24800295
H -1.03698184 0.35732289 -1.25013144
H 0.54453947 0.34733510 -2.13640854
H 3.21410261 -1.90208627 -0.00042227
H -0.54534968 -1.89698426 2.16826292
H -0.55410776 -1.88896497 -2.16312146
H 1.95802575 -1.74204393 2.16412910
H 1.45412249 -3.19324595 1.28524254
H -1.78905551 -1.70141402 -0.01006908
H -0.81481839 -3.17671339 -0.00074128
H 1.95556640 -1.73937883 -2.16477318
H 1.45319689 -3.19227361 -1.28802076
H 1.86550630 3.25378014 -0.61100279
Br -2.47424008 2.90513303 1.67833821
Br -3.30945037 1.15431005 -0.06816565
Br -3.92812371 -0.64900914 -1.80988057
30
Energy -10685.22474834
C 0.71690291 0.28672146 0.00000000
C 2.16284922 0.00000000 0.00000000
C -0.00274516 -0.01852938 1.24726727
C 0.00274516 0.01852938 -1.24726727
C 2.16564951 -1.59404503 -0.02024598
C -0.01402410 -1.61255886 1.22371516
C 0.00534167 -1.58169156 -1.27628169
C 1.43961693 -2.09899345 1.23220387
C -0.74236190 -2.07825031 -0.03664949
C 1.45585845 -2.06779134 -1.29141441
Br 0.63676158 3.00510834 0.04915217
H 2.67297830 0.37157674 -0.89728394
H 2.67620732 0.34103309 0.90878051
H 0.53029457 0.32121151 2.14499656
H -1.03341228 0.35773779 1.25358732
H -1.04903828 0.32849949 -1.24037753
H 0.50916990 0.39174302 -2.13314056
H 3.22328400 -1.89774048 -0.01617682
H -0.54548910 -1.93072571 2.13265542
H -0.53288625 -1.84995880 -2.20005767
H 1.95227922 -1.75272537 2.13929809

```
H    1.46056288  -3.19822448   1.25062367
H   -1.77687988  -1.70042868  -0.05622103
H   -0.79375056  -3.17903079  -0.05028767
H    1.97880613  -1.69607296  -2.18650983
H    1.47840147  -3.16828620  -1.33621369
H    1.96561521   2.94666872   0.59103273
Br  -2.40280878   4.78517529  -0.35753391
Br  -2.96987053   2.36410184  -1.01642953
Br  -3.58772113  -0.08584190  -1.72256701
30
 Energy -10685.27227568
C    0.72298686   0.45974946   0.00000000
C    2.17482446   0.00000000   0.00000000
C    0.00102239  -0.00081783   1.25855608
C   -0.00102239   0.00081783  -1.25855608
C    2.17203274  -1.54834692  -0.00337063
C   -0.00083794  -1.54857888   1.25397339
C   -0.00173746  -1.54667728  -1.25634155
C    1.44866360  -2.05749741   1.25383528
C   -0.72903949  -2.05409882  -0.00137531
C    1.44826649  -2.05416519  -1.26141844
Br   0.75180820   2.51497524  -0.00247106
H    2.69856950   0.38080955  -0.88955914
H    2.69674410   0.37670715   0.89243402
H    0.51628858   0.37608818   2.15482538
H   -1.03305039   0.37421927   1.27110886
H   -1.03292215   0.38104554  -1.26812124
H    0.51237465   0.38088473  -2.15478876
H    3.21740594  -1.89575462  -0.00299626
H   -0.52506961  -1.89440477   2.15856940
H   -0.52773709  -1.89111690  -2.16070841
H    1.97337329  -1.71072904   2.15924495
H    1.46009714  -3.15915520   1.27303126
H   -1.77504617  -1.70723592  -0.00382962
H   -0.75162123  -3.15574670  -0.00162076
H    1.97061615  -1.70206704  -2.16607680
H    1.46221018  -3.15573467  -1.28502205
H   -1.10803553   2.99247798   0.90678626
Br  -2.43048959   3.32849405   1.53804883
Br  -3.65106496   1.15817670  -0.02502862
Br  -4.49269047  -0.64830814  -1.33029887
```

AdH-3Br_2, TS3, $Ad^+Br_5^-$-HBr, TS3' and AdBr-HBr-2Br_2 (Fig. 2 in main text)

```
32
 Energy -15832.79332964
C    0.72844883   0.45533326   0.00000000
C    2.18329469   0.00000000   0.00000000
C    0.00155734  -0.00042974   1.25727072
C   -0.00155734   0.00042974  -1.25727072
C    2.17835357  -1.55124456  -0.00119678
C    0.00298800  -1.54909335   1.25748677
C    0.00077148  -1.55058621  -1.25697399
C    1.45341979  -2.05414908   1.25636541
C   -0.72452966  -2.05186788   0.00098342
```

```
C    1.45340512  -2.05160615  -1.25980192
Br   0.32737323   3.46741529   0.27764616
H    2.71269887   0.37673980  -0.88878825
H    2.70603169   0.37381977   0.89427372
H    0.50503924   0.37949890   2.15962801
H   -1.03387559   0.37123852   1.26738359
H   -1.03633813   0.37493112  -1.25905953
H    0.50091351   0.38094468  -2.15984839
H    3.22282207  -1.90245792  -0.00176717
H   -0.52343793  -1.89669432   2.16040247
H   -0.52260486  -1.90078108  -2.16104844
H    1.97949023  -1.70905678   2.16190050
H    1.46485421  -3.15635142   1.27540783
H   -1.76821466  -1.69859321   0.00543807
H   -0.75498202  -3.15406169   0.00144454
H    1.97595507  -1.69839491  -2.16394931
H    1.46901376  -3.15367716  -1.28663800
H    0.74425651   1.61761168  -0.00323562
Br  -0.30760589   5.78068301   0.74965410
Br  -2.56919452   5.02396852   2.21651024
Br  -4.47539084   4.17173927   3.43637024
Br  -4.01893506   1.35588427   2.98628602
Br  -3.64466673  -0.98084225   2.61727411
32
 Energy -15832.78838217
C    0.72449130   0.31319673   0.00000000
C    2.17420453   0.00000000   0.00000000
C    0.00035078   0.00722707   1.25072719
C   -0.00035078  -0.00722707  -1.25072719
C    2.17165186  -1.59318473   0.00146285
C    0.00088338  -1.58746519   1.25146945
C    0.00100841  -1.59559118  -1.25207144
C    1.45203698  -2.07231334   1.26459992
C   -0.73167844  -2.07604408   0.00139507
C    1.45437268  -2.07746056  -1.26098105
Br   0.26466963   3.27553433  -0.31396903
H    2.68847939   0.35695279  -0.90146865
H    2.68875244   0.35805114   0.90108653
H    0.51989666   0.36697079   2.14739754
H   -1.03981455   0.35602663   1.24559091
H   -1.03669232   0.35427152  -1.24325644
H    0.52025619   0.35578170  -2.14581531
H    3.22893314  -1.89907611   0.00165322
H   -0.53814686  -1.88290011   2.16373236
H   -0.52862089  -1.90410279  -2.16549611
H    1.97496008  -1.71460469   2.16495769
H    1.46841997  -3.17388270   1.30100425
H   -1.77184319  -1.71935977   0.00470053
H   -0.77256982  -3.17764194   0.00785376
H    1.97567100  -1.71633210  -2.16098092
H    1.47786360  -3.17807579  -1.29716592
H    0.79417002   1.87107935   0.01811943
Br  -1.38886202   5.55715510  -1.22402492
Br  -3.03582952   3.67205385  -1.71848321
```

```
Br  -4.56789305   1.61922459  -2.12249122
Br  -4.05048984   0.27122745   0.19673107
Br  -3.60757071  -0.94173473   2.30665679
32
 Energy -15832.81459997
C    0.72597165   0.40074723   0.00000000
C    2.17722860   0.00000000   0.00000000
C   -0.00385716   0.00118942   1.25643008
C    0.00385716  -0.00118942  -1.25643008
C    2.17379424  -1.56041484   0.00493590
C    0.00018653  -1.55881930   1.25806437
C    0.00328450  -1.56179316  -1.24831279
C    1.45177561  -2.05847905   1.26541065
C   -0.72996638  -2.06004447   0.00379523
C    1.45246162  -2.06663795  -1.25234936
Br   0.72395496   2.60701228   0.06875397
H    2.69088347   0.37500527  -0.89667369
H    2.69731635   0.37564349   0.89230843
H    0.50919711   0.37586304   2.15342990
H   -1.03838631   0.37232933   1.25426306
H   -1.02832389   0.37276334  -1.26444666
H    0.52600716   0.36010055  -2.15353010
H    3.22301416  -1.89395445   0.00636534
H   -0.52686622  -1.89071841   2.16566651
H   -0.52199033  -1.89153347  -2.15733778
H    1.97270469  -1.70358912   2.16885899
H    1.46785746  -3.15969425   1.29283958
H   -1.77029239  -1.69917306   0.00154846
H   -0.76243740  -3.16143224   0.00366871
H    1.97602658  -1.72188926  -2.15859794
H    1.46143560  -3.16830818  -1.26869432
H    0.49817829   2.88046467  -1.50400712
Br   2.41482329   1.98559419  -3.72933619
Br   0.24915935   3.19077652  -3.28909728
Br  -2.00985856   4.39638211  -2.60239597
Br  -3.12437236   2.31775579  -1.14781055
Br  -4.02891982   0.45101953   0.14826185
32
 Energy -15832.81327462
C    0.71938569   0.27817672   0.00000000
C    2.16237763   0.00000000   0.00000000
C   -0.00458223   0.00320892   1.24852906
C    0.00458223  -0.00320892  -1.24852906
C    2.16382158  -1.59663377  -0.00025515
C   -0.00946231  -1.59459229   1.25036633
C   -0.00306304  -1.59946725  -1.25157816
C    1.44249270  -2.08368138   1.26095755
C   -0.74486044  -2.07866328  -0.00223413
C    1.44782562  -2.08692264  -1.26224818
Br   0.72070527   3.02578767   0.01173045
H    2.66502111   0.36361641  -0.90521437
H    2.67314415   0.35714220   0.90203876
H    0.52452541   0.35676645   2.14169804
H   -1.04167096   0.36208668   1.23412865
```

```
H   -1.03006256   0.35794164  -1.24761376
H    0.53689629   0.34891183  -2.14075553
H    3.22122588  -1.90027447   0.00195277
H   -0.54052453  -1.89596055   2.16525000
H   -0.53292478  -1.89341760  -2.16927787
H    1.96185235  -1.72669080   2.16326314
H    1.45984380  -3.18459025   1.29258616
H   -1.77947005  -1.70369861  -0.00644585
H   -0.79464303  -3.17914017   0.00142961
H    1.96698377  -1.72813677  -2.16396613
H    1.46732876  -3.18815731  -1.29163084
H    1.04495107   2.98498873  -1.41195445
Br   2.60560839   2.13741054  -3.36561596
Br   0.18404284   2.77831658  -3.79779524
Br  -2.36654371   3.38082208  -4.04880325
Br  -3.16593784   2.01421473  -1.84600301
Br  -3.79505616   0.71188116   0.17247856
32
 Energy -15832.82417009
C    0.72631754   0.45402104   0.00000000
C    2.17766567   0.00000000   0.00000000
C   -0.00152322   0.00169184   1.25697876
C    0.00152322  -0.00169184  -1.25697876
C    2.17325801  -1.54954112   0.00124228
C   -0.00044923  -1.54766380   1.25689824
C   -0.00009860  -1.55010873  -1.25219349
C    1.45003294  -2.05403590   1.26026385
C   -0.72904416  -2.05481377   0.00209925
C    1.44874500  -2.05914317  -1.25479252
Br   0.71788921   2.52004637   0.03788926
H    2.69848735   0.37656195  -0.89353207
H    2.70185367   0.38083759   0.88900300
H    0.50896088   0.38026736   2.15488541
H   -1.03488458   0.37877798   1.26062431
H   -1.02821809   0.38046037  -1.27218301
H    0.51224323   0.36938071  -2.15818306
H    3.21855431  -1.89621487   0.00168023
H   -0.52589380  -1.89130524   2.16178421
H   -0.52480624  -1.89256374  -2.15788798
H    1.97345994  -1.70230363   2.16415173
H    1.46398262  -3.15561946   1.28359865
H   -1.77266770  -1.70230709   0.00287242
H   -0.75592824  -3.15647996   0.00295193
H    1.97177336  -1.71335253  -2.16181201
H    1.46053460  -3.16103668  -1.27124628
H    1.40338597   2.82830164  -1.81003977
Br   1.81407771   3.04867206  -3.27875549
Br  -0.92549141   2.70364292  -3.85453095
Br  -3.29467540   2.33615401  -4.16390361
Br  -3.81224161   1.23188833  -1.54494787
Br  -4.14152928   0.32786782   0.64686101
```

AdH+ClI(2.8), TS(34.4) and AdCl+HI (Fig. 5 in main text)

```
28
```

Energy -1148.071991265083 G(298.15) 120.62

C	-0.37609900	0.99780600	0.22929700
C	-1.54561900	0.11394400	-0.23825700
C	0.67705300	1.10279300	-0.88762700
C	0.26193700	0.39316700	1.49218700
C	-1.01468200	-1.29809300	-0.56669400
C	1.21008400	-0.30833200	-1.21666200
C	0.79454400	-1.01861800	1.16543900
C	0.04219100	-1.19884800	-1.68415900
C	1.84898600	-0.91982000	0.04565600
C	-0.37277000	-1.90820900	0.69475700
Cl	-1.56243400	4.14289500	0.98433100
H	-2.31610600	0.05465600	0.55149400
H	-2.02255900	0.55645000	-1.13134400
H	0.22999200	1.55855900	-1.78946200
H	1.50806700	1.75600100	-0.56573300
H	1.08737700	1.03686600	1.84598100
H	-0.48428100	0.33768500	2.30518300
H	-1.85257700	-1.93561900	-0.90296900
H	1.96700500	-0.23633400	-2.01885100
H	1.25360900	-1.45583600	2.07082700
H	-0.41286100	-0.77667200	-2.59879100
H	0.41578300	-2.20712000	-1.94086900
H	2.69831800	-0.29621500	0.37974000
H	2.25130000	-1.92367300	-0.18347100
H	-1.12741900	-1.99802800	1.49743200
H	-0.00590100	-2.92782500	0.47604300
H	-0.76047600	2.01760400	0.46615600
I	-2.39246300	6.34081700	1.52036800

28

Energy -1148.018751532390 G(298.15) 118.87

C	-0.32414800	0.90419600	0.27681500
C	-1.55186200	0.17958400	-0.17208900
C	0.66359700	1.16972200	-0.81304300
C	0.29000200	0.33704000	1.52324200
C	-1.04412900	-1.24494200	-0.59702900
C	1.18087400	-0.25054300	-1.24063600
C	0.80657500	-1.08906000	1.10548000
C	-0.01484300	-1.08698800	-1.73063300
C	1.83760400	-0.92908500	-0.02536800
C	-0.39010400	-1.92495200	0.61891700
Cl	-1.27371300	3.31140600	0.70561200
H	-2.29545900	0.08219900	0.63603200
H	-2.02847400	0.67636200	-1.03217900
H	0.19583200	1.67028300	-1.67576200
H	1.51074000	1.78358100	-0.46520500
H	1.14405300	0.93803400	1.88093600
H	-0.44402300	0.22797600	2.34048200
H	-1.91167200	-1.83359200	-0.94497400
H	1.91832400	-0.12178500	-2.05290000
H	1.27290500	-1.56066500	1.98902600
H	-0.48373700	-0.60464600	-2.60657100
H	0.33502100	-2.08233900	-2.05842000
H	2.69963600	-0.33374800	0.32498800

```
H    2.22733100  -1.92121500  -0.31555000
H   -1.12802700  -2.04530000   1.43210100
H   -0.04713900  -2.93784900   0.34174200
H   -0.69503200   2.59290100   1.63268000
I   -2.45013300   6.09342500   0.92230600
28
 Energy -1148.092042723480  G(298.15) 121.02
C    0.06865900   0.99016600   0.71914500
C   -1.37012000   0.56971000   0.41594000
C    0.87718000   1.13083200  -0.57131100
C    0.73463500  -0.00887700   1.66712900
C   -1.33171100  -0.81000100  -0.28359600
C    0.91344200  -0.24933600  -1.27008100
C    0.77196900  -1.38857400   0.96783900
C   -0.52516200  -0.69690800  -1.59113400
C    1.58116100  -1.27797100  -0.33821600
C   -0.66616300  -1.83918000   0.64926100
Cl   0.03284100   2.65333600   1.58287500
H   -1.94815600   0.51234200   1.35363900
H   -1.85275200   1.31698400  -0.23620600
H    0.41015100   1.88219800  -1.23005700
H    1.89928900   1.47261000  -0.33637100
H    1.75618200   0.32948000   1.90938200
H    0.16352600  -0.06829800   2.60895500
H   -2.36784800  -1.12021500  -0.50738300
H    1.49467800  -0.15560300  -2.20457600
H    1.25197100  -2.11558600   1.64700300
H   -1.00532700   0.02896700  -2.27138900
H   -0.50950200  -1.67219000  -2.10982700
H    2.61974700  -0.97251100  -0.11701000
H    1.62875200  -2.26304400  -0.83599000
H   -1.24881300  -1.93866100   1.58281500
H   -0.65091800  -2.83228600   0.16563100
H   -0.98925200   3.87542900  -0.04951700
I   -1.73845900   4.64718700  -1.31694800
```

AdH+ClI(1.5) and TS(36.5) (Fig. 5 in main text)

```
28
 Energy -1148.072127879994  G(298.15) 119.46
C   -1.13105700   0.46151300  -0.79854400
C   -1.13947300  -0.96891700  -1.37329800
C    0.22980200   1.12391200  -1.09261200
C   -1.35143300   0.40230800   0.72628800
C   -0.01305200  -1.79609400  -0.72221400
C    1.35865200   0.30000300  -0.44145900
C   -0.22560600  -0.42294300   1.38094800
C    1.34599100  -1.13031800  -1.01682300
C    1.13420300   0.23953300   1.08266800
C   -0.23546300  -1.85199100   0.80240500
Cl  -0.88010900   4.75303100   1.12572000
H   -2.11782200  -1.44735100  -1.18278700
H   -0.99925300  -0.93692600  -2.46950900
H    0.39090100   1.18729600  -2.18458800
H    0.23861700   2.15670700  -0.69898600
```

```
H   -1.36430600   1.42521900   1.14482600
H   -2.33284400  -0.05577200   0.94851400
H   -0.02026400  -2.82146500  -1.13521600
H    2.33372200   0.77576600  -0.65351100
H   -0.38515000  -0.46493200   2.47403900
H    1.52341600  -1.10049600  -2.10766900
H    2.16311000  -1.72544600  -0.56894900
H    1.15936400   1.25934400   1.50913800
H    1.94787000  -0.33607500   1.56167700
H   -1.20029800  -2.34350900   1.02560300
H    0.55773900  -2.45801300   1.27782800
H   -1.93909100   1.05336000  -1.26622200
I    0.95183600   4.72225800   2.65273400
28
 Energy -1148.015082852297  G(298.15) 118.61
C   -0.68591200   0.84378500  -0.26741700
C   -1.32413900  -0.11260200  -1.21565400
C    0.70840700   1.24445200  -0.62182300
C   -0.88221900   0.52195000   1.17763500
C   -0.49177400  -1.44425200  -1.01471500
C    1.54255700  -0.08183600  -0.42193000
C   -0.05269000  -0.80650200   1.38244400
C    0.97963400  -1.16214200  -1.35944700
C    1.41823900  -0.51905900   1.04544300
C   -0.62098200  -1.88934300   0.45110100
Cl  -1.78663500   3.57598700  -0.14364400
H   -2.38194100  -0.30428500  -0.97392200
H   -1.24098700   0.21411500  -2.26468300
H    0.79392000   1.57623400  -1.66913700
H    1.08893700   2.03510200   0.04645400
H   -0.48830800   1.31852000   1.83095000
H   -1.93987400   0.33462500   1.42368700
H   -0.91230600  -2.20782500  -1.69320500
H    2.59388000   0.14519600  -0.67300400
H   -0.15876000  -1.10540000   2.44035900
H    1.07234900  -0.84222200  -2.41230200
H    1.56784800  -2.09158800  -1.25301200
H    1.81445100   0.26693200   1.71140200
H    2.02475900  -1.42687100   1.21703700
H   -1.67790800  -2.09192300   0.69873700
H   -0.06923800  -2.83532900   0.59902800
H   -1.39381800   2.25300300  -0.32735700
I    0.50251000   4.59127800   2.28697700
```

AdH+ICl(0.4), TS(35.3), Intermediate and AdI+HCl (Fig. 5 in main text)

```
28
 Energy -1148.077233106013  G(298.15) 121.56
C   -0.44291900   0.95655600   0.22147400
C   -1.55098200  -0.00559900  -0.23142900
C    0.58960500   1.14654100  -0.89941700
C    0.23917600   0.42504700   1.49070200
C   -0.91254200  -1.37614600  -0.55136900
C    1.22699600  -0.22466100  -1.21901600
C    0.87668600  -0.94572200   1.16982100
```

```
C    0.12817100  -1.20424500  -1.67479900
C    1.91607300  -0.77408100   0.04512500
C   -0.22224600  -1.92454800   0.71258200
I   -1.87945100   4.00216200   0.95085300
H   -2.30956700  -0.11572200   0.56365900
H   -2.06188400   0.39402200  -1.12531700
H    0.10309900   1.55918600  -1.80095900
H    1.36819700   1.86353200  -0.58404100
H    1.01370600   1.13385900   1.83339400
H   -0.49905900   0.31978100   2.30535900
H   -1.70283500  -2.07561200  -0.87843400
H    1.97195400  -0.09791400  -2.02511100
H    1.37029100  -1.33631300   2.07788700
H   -0.36144400  -0.82542700  -2.59027500
H    0.57649800  -2.18264400  -1.92575900
H    2.71636800  -0.08492900   0.37056100
H    2.39314300  -1.74555000  -0.17825900
H   -0.96466000  -2.06426100   1.51925100
H    0.21979200  -2.91501000   0.50075900
H   -0.90923100   1.95905700   0.45557800
Cl  -2.89293500   6.13863800   1.46718000
28
 Energy -1148.018939444842  G(298.15) 119.89
C   -0.22599000   1.00010400   0.27083300
C   -1.50759600   0.30587800  -0.13004800
C    0.74632400   1.12690500  -0.87280900
C    0.38991300   0.40653900   1.51134300
C   -1.11000600  -1.15640600  -0.51147300
C    1.14562000  -0.33738100  -1.25735500
C    0.78966400  -1.05826300   1.12960100
C   -0.11180000  -1.11487800  -1.68080100
C    1.79498800  -1.01327100  -0.03585100
C   -0.46834600  -1.83686300   0.70954900
I   -1.25806400   3.44736700   0.83426400
H   -2.23180100   0.29125300   0.69981600
H   -1.97816800   0.80136100  -0.99398000
H    0.28749600   1.63283700  -1.73779800
H    1.64914600   1.68787400  -0.58082600
H    1.28920000   0.96067900   1.82640600
H   -0.32434200   0.39677200   2.35080900
H   -2.02771000  -1.69354500  -0.81088800
H    1.86538500  -0.28713700  -2.09385500
H    1.25268300  -1.52801300   2.01579200
H   -0.57661600  -0.63770100  -2.56173800
H    0.16527700  -2.14260900  -1.97659800
H    2.70455400  -0.46381800   0.26608100
H    2.10840600  -2.03935200  -0.29874100
H   -1.18894300  -1.87758600   1.54557200
H   -0.19890300  -2.87922900   0.46178800
H    0.37598100   2.92418600   0.96174600
Cl  -3.35635300   5.08429800   0.95916200
28
 Energy -1148.047211967483  G(298.15) 122.75
C   -0.18773500   1.08120500   0.37861600
```

```
C   -1.53871400   0.44238700   0.12455600
C    0.65309000   1.17419000  -0.87922600
C    0.55559600   0.42208200   1.52105100
C   -1.25905500  -1.01577500  -0.33836100
C    0.92566400  -0.28626900  -1.33893500
C    0.83276900  -1.04389500   1.05718800
C   -0.41230500  -0.99041200  -1.62235400
C    1.68687100  -1.02565800  -0.22340600
C   -0.50299100  -1.75690400   0.77947700
I   -0.65682900   3.32218400   0.98795700
H   -2.14365500   0.43022400   1.04698900
H   -2.07969500   1.01245800  -0.65019500
H    0.10581400   1.74240500  -1.65090400
H    1.60942400   1.68347700  -0.67174700
H    1.51016200   0.93340100   1.73020800
H   -0.04833200   0.41299900   2.44386800
H   -2.22893800  -1.50687500  -0.53280100
H    1.53745300  -0.24915800  -2.25762900
H    1.37655300  -1.55744100   1.87012200
H   -0.95612400  -0.46032500  -2.42322700
H   -0.22874000  -2.02175500  -1.97344900
H    2.65499700  -0.52978900  -0.02976800
H    1.90830400  -2.06149200  -0.53699100
H   -1.11671600  -1.78943400   1.69757900
H   -0.31048100  -2.80236300   0.47900700
H    0.15314100   2.92458700   2.46776200
Cl  -1.83952800   3.51594700  -1.45538700
28
 Energy -1148.097922995699  G(298.15) 121.74
C   -1.07404400   0.52747200   0.27570400
C   -1.63012400  -0.83462900  -0.13437800
C   -0.36339100   1.20564900  -0.89400800
C   -0.14816000   0.40180700   1.48406000
C   -0.43135500  -1.73008400  -0.54557600
C    0.83317800   0.30611600  -1.30326900
C    1.04790400  -0.49590100   1.06930100
C    0.31109100  -1.07882900  -1.72674900
C    1.79261000   0.15939500  -0.10811900
C    0.52623900  -1.88241200   0.65038500
I   -2.83928600   1.83400600   0.87709700
H   -2.17826700  -1.29514000   0.70461300
H   -2.33069900  -0.72595200  -0.97925600
H   -1.05501600   1.32814300  -1.74414100
H   -0.00214900   2.20476000  -0.59933600
H    0.21476000   1.39469800   1.79713600
H   -0.68591800  -0.05031000   2.33404800
H   -0.82211500  -2.71930200  -0.84460000
H    1.35589100   0.78738200  -2.14916000
H    1.72561000  -0.59362200   1.93621700
H   -0.36622400  -0.98115900  -2.59425200
H    1.15401900  -1.72026700  -2.04096800
H    2.17911100   1.14963000   0.19161700
H    2.66155100  -0.45935600  -0.39592300
H    0.00404000  -2.36406500   1.49665600
```

```
H    1.37258500  -2.53654100   0.37376900
H   -1.15213300   3.69397500   1.35088700
Cl  -0.09970800   4.47453400   1.51824600
```

AdH+ClI+ICl(-1.6), TS(8.0), Intermediate(-13.0) and AdCl+I_2+HCl(-25.2) (Fig. 6 in main text)

```
30
 Energy -1905.814460746882  G(298.15) 113.65
C   -1.00322800   0.41951000  -0.17390000
C   -0.54073300   1.88384500  -0.32742700
C   -0.57770600  -0.10304400   1.21132400
C   -0.34564300  -0.43906500  -1.27152200
C    0.99289500   1.95944100  -0.19421900
C    0.95570500  -0.03387000   1.34803700
C    1.18841100  -0.36876100  -1.13962400
C    1.41319900   1.43096900   1.19120900
C    1.60800300  -0.89382300   0.24759100
C    1.64576300   1.09626200  -1.29163500
H   -2.10333800   0.37214700  -0.27065300
H   -0.85628800   2.27606600  -1.31132000
H   -1.02024100   2.51289900   0.44450600
H   -1.05904500   0.49405200   2.00722600
H   -0.91738900  -1.14952300   1.34466500
H   -0.68189000  -1.49042200  -1.18569200
H   -0.65831600  -0.08143800  -2.26947100
H    1.32152900   3.00912000  -0.30471300
H    1.25729500  -0.41120600   2.34208100
H    1.65714100  -0.98636800  -1.92720500
H    0.96425500   2.05400400   1.98625200
H    2.51078300   1.49629100   1.30495600
H    1.30120600  -1.95030300   0.36101900
H    2.70852700  -0.86267300   0.34669600
H    1.36475700   1.47781600  -2.29026900
H    2.74691600   1.15707400  -1.21628500
Cl  -5.35628500  -0.04087100  -0.56276400
I   -4.49045300  -2.28459400  -0.07218900
I   -2.18577700  -4.07875600   0.63216600
Cl  -1.84005300  -6.46477700   1.04116200
30
 Energy -1905.799492567934  G(298.15) 113.90
C   -0.80513600   0.62254200  -0.04136800
C   -0.27627000   1.99777500   0.06079600
C   -0.67039500  -0.22273900   1.14968200
C   -0.62424100  -0.05664600  -1.33834200
C    1.29959200   1.71924100   0.06760000
C    0.90701300  -0.51643900   1.15329200
C    0.94599100  -0.33236200  -1.34873700
C    1.63243000   0.83136800   1.27550500
C    1.27972200  -1.22831000  -0.15130800
C    1.67214100   1.01810600  -1.24747100
H   -2.73441000   0.91087000  -0.08571100
H   -0.52388800   2.62996800  -0.80572100
H   -0.55478200   2.50404100   0.99760900
H   -0.93221000   0.29751900   2.08391300
H   -1.20809700  -1.18466000   1.07101200
```

```
H   -1.16389500  -1.01611100  -1.38670700
H   -0.88554100   0.57931200  -2.19825600
H    1.79400000   2.70324200   0.14786000
H    1.09619700  -1.16866100   2.02156600
H    1.17706500  -0.83741600  -2.30244400
H    1.35695000   1.34060500   2.21551700
H    2.72287600   0.65888000   1.31310900
H    0.75314200  -2.19628100  -0.20676900
H    2.36269700  -1.44969600  -0.14729700
H    1.42172000   1.66100400  -2.10953800
H    2.76366200   0.85262900  -1.27839400
Cl  -3.88742200   0.25859500  -0.18835600
I   -5.60366300  -2.68963000  -0.29538200
I   -2.87678500  -3.52917400   0.44218700
Cl  -0.43846500  -4.15757400   1.13215400
30
 Energy -1905.835086344822  G(298.15) 115.18
C   -0.48293100  -0.91886300   0.00082300
C   -1.24707300   0.13338700  -0.75452000
C   -0.00058700  -0.43883100   1.34986400
C    0.60407200  -1.56233200  -0.82747700
C   -0.20576300   1.26586500  -1.05161400
C    1.03844100   0.68745000   1.05167600
C    1.64236600  -0.43227500  -1.11559300
C    0.33773100   1.81734500   0.27753900
C    2.19173600   0.10545000   0.21672900
C    0.94638800   0.69601500  -1.89589500
H   -3.43542800   1.97386300   3.38505000
H   -1.65708400  -0.25561500  -1.70006700
H   -2.07929600   0.54198800  -0.16047700
H   -0.83606500  -0.03009300   1.94096000
H    0.47287700  -1.26155100   1.90941300
H    1.07761300  -2.39068000  -0.27652500
H    0.20009400  -1.94695400  -1.77819500
H   -0.73372400   2.05993500  -1.60856900
H    1.41895600   1.06226000   2.01841800
H    2.45921300  -0.86899600  -1.71697300
H   -0.48749600   2.23700100   0.87945000
H    1.04975700   2.63817100   0.07852300
H    2.69335400  -0.70421400   0.77503300
H    2.94763500   0.88725700   0.02251200
H    0.56196400   0.31417200  -2.85812300
H    1.67058700   1.49702900  -2.12857400
Cl  -3.75616400   1.16461100   2.42739100
I   -4.40868300  -1.57445800  -0.64149800
I   -2.01462100  -2.76384900   0.53749500
Cl   0.03213000  -3.93308800   1.64322200
30
 Energy -1905.855296733595  G(298.15) 115.74
C   -0.06438300  -1.11471300  -0.14344900
C   -0.52608800  -0.13953200  -1.22237400
C   -0.31815500  -0.55681300   1.25396900
C    1.40938200  -1.47730900  -0.32993900
C    0.30397900   1.15951300  -1.07057400
```

```
C    0.51307900   0.74247400   1.40054100
C    2.23845700  -0.17717900  -0.18004100
C    0.06614400   1.75536100   0.32963600
C    2.00742700   0.41746500   1.22161300
C    1.79817500   0.83502200  -1.25377800
H   -4.08515700   0.05018800   0.62977900
H   -0.37477800  -0.58138000  -2.22142700
H   -1.60018700   0.08019500  -1.10320500
H   -1.38915000  -0.33539200   1.39147200
H   -0.01681300  -1.29588500   2.01500000
H    1.71495800  -2.21806200   0.42780900
H    1.56571000  -1.92158200  -1.32710900
H   -0.02439500   1.87493900  -1.84497900
H    0.33420500   1.15763300   2.40789800
H    3.30584500  -0.42821200  -0.31286500
H   -1.00239400   1.99835900   0.46305200
H    0.63636400   2.69495700   0.43951100
H    2.33830400  -0.29667900   1.99709600
H    2.61014300   1.33499400   1.34372400
H    1.97834200   0.42212400  -2.26269300
H    2.39727200   1.75884400  -1.16679600
Cl  -3.98708200   1.19340000   1.26508400
I   -6.77010200  -1.95998000  -1.10404400
I   -4.02289400  -2.24211500  -0.71520700
Cl  -1.03620600  -2.73063400  -0.32770300
```

AdH+ClI+ClI(3.7), TS(22.4), Intermediate(11.1) and AdCl+HI+ClI(-6.3) (Fig. 6 in main text)

```
30
 Energy -1905.805550373911  G(298.15) 113.38
C   -1.01975000   0.39931100  -0.19545300
C   -0.59090200   1.83976800  -0.54720400
C   -0.56716400   0.07016400   1.23955300
C   -0.35937100  -0.58271800  -1.18132700
C    0.94265800   1.96006300  -0.44800700
C    0.96609400   0.18605100   1.34222000
C    1.17426600  -0.46806000  -1.08293500
C    1.39152400   1.62612400   0.98796700
C    1.62181100  -0.79875600   0.35439800
C    1.59939400   0.97316400  -1.43276400
H   -2.11974200   0.31464600  -0.26701500
H   -0.92612300   2.09363500  -1.56935700
H   -1.07313600   2.55567500   0.14311000
H   -1.04966400   0.75932500   1.95647600
H   -0.88562800  -0.95466500   1.51106500
H   -0.67430100  -1.61874400  -0.95140200
H   -0.69176600  -0.36506100  -2.21276700
H    1.24824600   2.99231300  -0.70025900
H    1.28846700  -0.05167200   2.37236600
H    1.64573600  -1.17443900  -1.79031200
H    0.93962000   2.33942400   1.70131400
H    2.48895300   1.72698600   1.07507400
H    1.33525800  -1.83591900   0.60953800
H    2.72278500  -0.73575300   0.43190100
H    1.29777600   1.21475900  -2.46838500
```

```
H    2.70001100   1.06396100  -1.38273800
Cl  -6.00045700  -1.00065800  -0.23443900
I   -4.23772100  -2.56275700   0.33194400
Cl  -1.71931400  -3.80623200   0.87792700
I   -1.44756100  -6.15993500   1.52950800
30
 Energy -1905.776250886801  G(298.15) 113.74
C   -0.80402900   0.60817900  -0.11143200
C   -0.29174900   1.98263100   0.06171900
C   -0.70662500  -0.28137200   1.04938200
C   -0.57960400  -0.01353900  -1.42954200
C    1.28581500   1.71984200   0.10928600
C    0.87426100  -0.55550800   1.09358000
C    0.99395800  -0.27521700  -1.39700900
C    1.58724900   0.78862300   1.29234700
C    1.29441000  -1.21422700  -0.22408800
C    1.70720000   1.07399400  -1.21911600
H   -2.80827900   1.04082600  -0.20572500
H   -0.51626300   2.64645800  -0.78715500
H   -0.60584600   2.44782600   1.00824300
H   -1.00396100   0.20092400   1.99256600
H   -1.23518900  -1.24161400   0.92241600
H   -1.10935000  -0.97136200  -1.53604900
H   -0.81623700   0.65573100  -2.27072300
H    1.76579000   2.70503700   0.24283300
H    1.03350400  -1.24402900   1.94003800
H    1.25996300  -0.74095500  -2.36152500
H    1.27746700   1.25865800   2.24186100
H    2.67724200   0.62214600   1.35853100
H    0.77389700  -2.18119200  -0.33508500
H    2.37668400  -1.43595700  -0.19430900
H    1.48091100   1.74853300  -2.06343600
H    2.80016500   0.91613400  -1.21985600
Cl  -3.79080300   0.14541200  -0.20315500
I   -5.46788700  -2.61994800   0.04464300
Cl  -2.93206500  -3.43505000   0.74007300
I   -0.52062800  -4.35098600   1.46068900
30
 Energy -1905.791796009956  G(298.15) 112.13
C   -0.65166400   0.83217300   0.30361300
C    0.28456500   1.95886900   0.41704000
C   -0.50851500  -0.25913100   1.24698900
C   -1.14632400   0.51755500  -1.03314300
C    1.60224700   1.28389500  -0.20613100
C    0.81636500  -0.95456500   0.61575500
C    0.15706800  -0.17058300  -1.66988300
C    1.95916300   0.06482800   0.65636000
C    0.49977200  -1.39199800  -0.81521100
C    1.29460000   0.86220200  -1.65095600
H   -3.64711000   2.76712200   1.81020500
H    0.00418400   2.82688100  -0.19771200
H    0.49154000   2.26048100   1.45438600
H   -0.27227500   0.05566600   2.27320900
H   -1.31426500  -1.00844700   1.21732200
```

```
H   -1.97225000  -0.22282700  -1.02818200
H   -1.39619400   1.41232500  -1.62301900
H    2.39502000   2.05158100  -0.17567600
H    0.99671400  -1.83605400   1.26648800
H   -0.11128900  -0.45717100  -2.70110100
H    2.17256600   0.37230800   1.69472400
H    2.88031100  -0.40424400   0.26817100
H   -0.32969400  -2.11792900  -0.80539100
H    1.37776300  -1.91166100  -1.23841400
H    1.03202600   1.74350700  -2.26186100
H    2.19982300   0.41934600  -2.10199700
Cl  -3.67487400   1.56478900   1.32903000
I   -3.80863500  -2.24594500  -0.31188900
Cl  -1.76036900  -3.53225700   1.01562000
I    0.42973300  -4.48071500   2.25165400
30
 Energy -1905.823994849053  G(298.15) 114.97
C   -1.09119700   0.61876900  -0.04322500
C   -0.49284200   2.01981000  -0.16857100
C   -0.62307600  -0.06237300   1.24056100
C   -0.75542900  -0.22904400  -1.26864200
C    1.04696100   1.87656200  -0.23974400
C    0.91773100  -0.20436100   1.16591400
C    0.78530100  -0.36959900  -1.33997800
C    1.55607900   1.19149500   1.04259200
C    1.29329000  -1.05816300  -0.05964500
C    1.42241700   1.02657900  -1.46814300
H   -0.87660000   2.51355000  -1.07717300
H   -0.78339500   2.63166900   0.70192400
H   -0.91177200   0.54503000   2.11473900
H   -1.09059300  -1.05563000   1.34014500
H   -1.22214300  -1.22437500  -1.18250800
H   -1.14248100   0.25606300  -2.18050600
H    1.48905400   2.88480300  -0.32983000
H    1.26601900  -0.70140400   2.08837000
H    1.03941900  -0.98232400  -2.22295500
H    1.30521100   1.80543100   1.92642300
H    2.65652500   1.10149900   1.00857000
H    0.85388100  -2.06665800   0.03314300
H    2.38992700  -1.18153700  -0.10938900
H    1.07505000   1.52141300  -2.39312400
H    2.52076500   0.93369100  -1.53962200
Cl  -2.96734300   0.83114700   0.04237100
H   -3.70648300  -1.14942500  -0.08706900
I   -4.36922800  -2.69428800  -0.21984200
Cl  -1.80506100  -3.92229600   1.08983500
I    0.22001200  -4.85603300   2.13538100
```

AdH+ICl+ICl(3.4), TS(17.7), Intermediate(9.3) and AdI+HCl+ICl(-12.8) (Fig. 6 in main text)

```
30
 Energy -1905.812569327197  G(298.15) 117.46
C   -0.52177200  -0.10334300  -0.04307200
C   -1.01536900   1.26230200   0.44664200
C    0.51935000  -0.68267100   0.92055000
```

```
C    0.04921700   0.00181200  -1.46125200
C    0.19662300   2.22541600   0.48434100
C    1.72906800   0.28309800   0.95763600
C    1.25981600   0.96654900  -1.42085700
C    1.26070100   1.66632200   1.44762200
C    2.32413800   0.40775900  -0.45767600
C    0.79144600   2.34982900  -0.93107100
H   -1.41874700  -0.81556900  -0.07149800
H   -1.79253500   1.65650600  -0.23114600
H   -1.46068900   1.17271300   1.45280200
H    0.08950900  -0.79199500   1.93146200
H    0.84195900  -1.68293200   0.58293400
H    0.36676100  -0.99161500  -1.82308800
H   -0.71756300   0.38390500  -2.15757200
H   -0.14538900   3.21520300   0.83619700
H    2.48834800  -0.12288900   1.64972700
H    1.68185400   1.05157700  -2.43822400
H    0.84522900   1.58728300   2.46838800
H    2.12098800   2.35780200   1.49912300
H    2.67553800  -0.57860800  -0.81038500
H    3.20211900   1.07835800  -0.43825800
H    0.03758100   2.76342200  -1.62499700
H    1.64380900   3.05283300  -0.91990900
I   -3.10380700  -2.23302300  -0.11369300
Cl  -5.03095700  -3.81973100  -0.16532700
I   -4.49233400  -6.61752600   0.11365200
Cl  -4.42489000  -9.04278400   0.31695100
30
 Energy -1905.786001777623  G(298.15) 115.07
C   -0.84476500   0.58267500  -0.00213200
C   -0.31564000   1.97404300  -0.00237300
C   -0.62903300  -0.18165500   1.24899100
C   -0.62514000  -0.18388700  -1.25122200
C    1.25570000   1.74498700   0.00025700
C    0.94136900  -0.40937600   1.25493500
C    0.94527500  -0.41151300  -1.25189400
C    1.63655500   0.96042800   1.26485600
C    1.32402100  -1.21042300   0.00282900
C    1.64035000   0.95835400  -1.26194500
H   -2.63057500   1.27672000  -0.00591600
H   -0.59836200   2.53719300  -0.90508300
H   -0.60193400   2.53861800   0.89834100
H   -0.92048500   0.38520600   2.14650000
H   -1.13733400  -1.15921600   1.23370500
H   -1.13345100  -1.16143700  -1.23567600
H   -0.91390600   0.38130900  -2.15064400
H    1.72360000   2.74513900   0.00001800
H    1.17472400  -0.97898700   2.17071200
H    1.18153800  -0.98261400  -2.16598600
H    1.35837500   1.53032900   2.16875600
H    2.73171700   0.82160500   1.29648800
H    0.81960600  -2.19265000   0.00292200
H    2.41249100  -1.40021300   0.00468000
H    1.36470200   1.52679300  -2.16756800
```

```
H    2.73562300   0.81962000  -1.29025300
I   -3.85349100   0.07674900  -0.00607100
Cl  -5.40758900  -2.43458100  -0.00480300
I   -2.99438400  -3.59396900   0.00103300
Cl  -0.63955600  -4.55924500   0.00654400
30
 Energy -1905.803346657334  G(298.15) 117.58
C   -0.89844400   0.16908000  -0.00132600
C   -0.66001800   1.66236600  -0.00276500
C   -0.40978800  -0.50514700   1.25820900
C   -0.40663700  -0.50811500  -1.25802600
C    0.89356000   1.84073800  -0.00100100
C    1.14390600  -0.31913000   1.25667800
C    1.14705300  -0.32209200  -1.25301900
C    1.47496800   1.18239400   1.26202400
C    1.72788500  -0.99170400   0.00334700
C    1.47819800   1.17940000  -1.26096200
H   -3.41658600   1.53942900  -0.00627000
H   -1.08443900   2.13965700  -0.90175700
H   -1.08670700   2.14172500   0.89404600
H   -0.83969400  -0.03628300   2.15834200
H   -0.64502900  -1.58217100   1.25407400
H   -0.64187100  -1.58513200  -1.25187800
H   -0.83423900  -0.04139600  -2.16036800
H    1.10574100   2.92475200  -0.00205900
H    1.53588200  -0.80401500   2.16771700
H    1.54132400  -0.80903600  -2.16196300
H    1.06420700   1.66413500   2.16747000
H    2.56967300   1.32631600   1.28613300
H    1.48241700  -2.06694800   0.00432800
H    2.82826700  -0.89527200   0.00461000
H    1.07010300   1.65914600  -2.16865900
H    2.57299900   1.32309900  -1.28235000
I   -3.33396200  -0.14123000  -0.00407700
Cl  -5.60308700  -2.62323500  -0.00434400
I   -3.14660900  -3.45090700  -0.00009600
Cl  -0.62907600  -4.07042600   0.00394300
30
 Energy -1905.835871163298  G(298.15) 115.95
C   -1.04489600   0.57532100  -0.08160000
C   -0.53253500   2.01206700  -0.04907000
C   -0.70769400  -0.16334900   1.20783500
C   -0.52736700  -0.17156400  -1.30501700
C    1.01563100   1.94987500   0.06192000
C    0.84217300  -0.22127800   1.31557900
C    1.02160700  -0.22914100  -1.19007900
C    1.40408400   1.21070100   1.35536000
C    1.41111700  -0.97376400   0.09969000
C    1.58391700   1.20324200  -1.15853200
H   -0.82505800   2.54943700  -0.96665900
H   -0.95256600   2.55423200   0.81459500
H   -1.12937300   0.36487900   2.07905000
H   -1.11843300  -1.18613700   1.18973900
H   -0.93779200  -1.19409200  -1.33935500
```

```
H   -0.82037000   0.35105900  -2.23071100
H    1.40129500   2.98485700   0.08647400
H    1.10118000  -0.75692600   2.24604800
H    1.41074500  -0.77066000  -2.07044400
H    1.01093900   1.75159600   2.23503300
H    2.50385000   1.18124300   1.45505400
H    1.03026600  -2.00977800   0.07514400
H    2.51146400  -1.03417500   0.17850300
H    1.31979800   1.73831600  -2.08853100
H    2.68665300   1.17375200  -1.10084400
I   -3.33431000   0.71475200  -0.24691100
H   -4.07985800  -1.55549800  -0.20894200
Cl  -4.59797700  -2.80329600  -0.19402500
I   -1.93658100  -4.13161100  -0.11795600
Cl   0.29009200  -5.11406000  -0.05134800
```

AdH+ICl+ClI(4.3), TS(33.6), Intermediate(12.8) and AdI+HCl+ClI(-6.2) (Fig. 6 in main text)

```
30
 Energy -1905.808193903161  G(298.15) 115.64
C   -0.90283800   0.16985600  -0.00268800
C   -0.62414700   1.67871700  -0.00069800
C   -0.32671400  -0.48604800   1.25882800
C   -0.32210600  -0.48384000  -1.26326600
C    0.90896600   1.88855900   0.00222600
C    1.20535200  -0.27401600   1.26024600
C    1.20990300  -0.27178700  -1.25862600
C    1.51074800   1.23615000   1.26164900
C    1.81044500  -0.92411100   0.00130200
C    1.51512500   1.23839900  -1.25625300
H   -2.02927400   0.01535600  -0.00511300
H   -1.06970200   2.15351300  -0.89278200
H   -1.07306200   2.15185800   0.89054300
H   -0.77238000  -0.03399900   2.16265100
H   -0.56524000  -1.56333100   1.26984900
H   -0.56062900  -1.56109100  -1.27695500
H   -0.76439800  -0.03020100  -2.16794700
H    1.12254900   2.97266100   0.00355100
H    1.63155600  -0.74318100   2.16514900
H    1.63950900  -0.73934100  -2.16276300
H    1.09250400   1.70718300   2.16968600
H    2.60345900   1.39976700   1.28348800
H    1.60514700  -2.00977100   0.00006000
H    2.90843900  -0.79847400   0.00343700
H    1.10009700   1.71088300  -2.16500400
H    2.60790300   1.40213500  -1.27393200
I   -4.26670600  -0.40927500  -0.00120600
Cl  -6.66446100  -0.75588400   0.00246300
Cl  -2.90617800  -3.27879100   0.00112200
I   -1.62386600  -5.36189400  -0.00901800
30
 Energy -1905.760235753715  G(298.15) 114.86
C   -0.84979700   0.48210500  -0.00355200
C   -0.37326500   1.90207700  -0.00082400
C   -0.56355500  -0.26967400   1.25080800
```

```
C   -0.55604600  -0.26744400  -1.25746900
C    1.19947400   1.77631300   0.00386400
C    1.01271200  -0.39175200   1.25653200
C    1.02026100  -0.38953200  -1.25378500
C    1.62920200   1.01512600   1.26772000
C    1.44841800  -1.16414300   0.00199100
C    1.63679600   1.01737200  -1.25873700
H   -2.67140100   1.35459200  -0.01177900
H   -0.69238500   2.45048100  -0.90094600
H   -0.69801900   2.44879100   0.89830500
H   -0.89508700   0.27368800   2.14897500
H   -1.00794400  -1.27597800   1.24130200
H   -1.00040000  -1.27379000  -1.25260100
H   -0.88198000   0.27750600  -2.15673400
H    1.60976400   2.80152100   0.00598500
H    1.28666500  -0.94745400   2.17004400
H    1.29990500  -0.94354700  -2.16661700
H    1.31671000   1.56649300   2.17202300
H    2.73065300   0.94024400   1.29984200
H    0.99878700  -2.17248900  -0.00014700
H    2.54582200  -1.29135700   0.00515100
H    1.32975900   1.57036600  -2.16391800
H    2.73840900   0.94245500  -1.28440700
I   -3.69817000  -0.01617000  -0.01027200
Cl  -5.53008200  -2.15028400  -0.00840400
Cl  -3.30583400  -3.52112300  -0.00001900
I   -1.07937300  -4.74439200   0.00766900
30
 Energy -1905.772773876536  G(298.15) 116.96
C   -0.87652600   0.14942900  -0.00142200
C   -0.63476900   1.64762800  -0.00277300
C   -0.36191800  -0.51563700   1.26035200
C   -0.35829300  -0.51848300  -1.26020500
C    0.91378600   1.83943400  -0.00076300
C    1.18461000  -0.31876600   1.25849800
C    1.18822600  -0.32161200  -1.25434000
C    1.50433900   1.18602900   1.26129600
C    1.77534900  -0.98482300   0.00367900
C    1.50797000   1.18317200  -1.25963000
H   -3.42035700   1.43146100  -0.00649500
H   -1.06412500   2.12278700  -0.90108000
H   -1.06670100   2.12482600   0.89321700
H   -0.79754800  -0.05114100   2.16068200
H   -0.59769300  -1.59338300   1.26646800
H   -0.59405900  -1.59624000  -1.26458600
H   -0.79132100  -0.05600400  -2.16282600
H    1.12078200   2.92451900  -0.00169300
H    1.58750900  -0.79746300   2.16829600
H    1.59373300  -0.80237800  -2.16188600
H    1.09137400   1.66364400   2.16793000
H    2.59787400   1.33927700   1.28301400
H    1.54386300  -2.06407600   0.00456600
H    2.87502500  -0.88063600   0.00514200
H    1.09763400   1.65872900  -2.16853500
```

```
H    2.60156500   1.33637300  -1.27854100
I   -3.26369000  -0.22872800  -0.00442500
Cl  -5.71169300  -2.15435100  -0.00587100
Cl  -3.50406400  -3.28586300  -0.00142600
I   -1.14088200  -4.43772500   0.00335800
30
 Energy -1905.826124312380  G(298.15) 116.39
C   -0.94023800   0.84646600  -0.00406600
C   -0.10096800   2.12282500  -0.00449000
C   -0.69160700   0.02328600   1.25720600
C   -0.68520100   0.01825700  -1.26075900
C    1.39323400   1.70532800   0.00010400
C    0.80547000  -0.38897800   1.25951800
C    0.81185600  -0.39400900  -1.25385600
C    1.68525100   0.87423700   1.26280400
C    1.10533900  -1.22936400   0.00526600
C    1.69164400   0.86920300  -1.25776500
I   -3.12616900   1.49410500  -0.01093000
H   -0.32316600   2.72948300  -0.89837500
H   -0.32768600   2.73303000   0.88583800
H   -0.92396700   0.61681500   2.15699600
H   -1.32890700  -0.87625600   1.26462900
H   -1.32252500  -0.88127100  -1.26783400
H   -0.91298400   0.60820100  -2.16407200
H    2.01023100   2.62184000  -0.00017100
H    0.99786300  -0.98658700   2.16839800
H    1.00884400  -0.99526000  -2.15934100
H    1.48610300   1.47589900   2.16794400
H    2.75252000   0.58984300   1.28787000
H    0.49108000  -2.14668500   0.00552800
H    2.16429400  -1.54477600   0.00858400
H    1.49708000   1.46723100  -2.16630400
H    2.75902700   0.58473400  -1.27630000
H   -4.18625900  -0.77532000  -0.00331800
Cl  -4.80176100  -1.95245200   0.00085400
Cl  -2.40490200  -3.81260200  -0.00150700
I   -0.58349400  -5.39722500  -0.00245000
```

AdH+3ICl, TS(a-d) (Fig. 7 in main text)

```
32
 Energy -2663.551738843684  G(298.15) 111.19
C   -0.66062200   0.48944100   0.32697500
C   -0.68536600   1.93627300   0.00827100
C    0.05443000   0.10534200   1.55617000
C   -0.52193800  -0.42379600  -0.82121700
C    0.82679000   2.19861000  -0.42331900
C    1.57908400   0.36965500   1.12496400
C    0.99598300  -0.16905200  -1.25408000
C    1.73366400   1.85260200   0.76619900
C    1.90053600  -0.53048700  -0.07211000
C    1.14617600   1.31075800  -1.63472200
H   -2.35155500   0.25219400   0.74417400
H   -1.35219400   2.17775900  -0.83276100
H   -0.92814700   2.56602100   0.87754600
```

```
H   -0.18332600   0.74840000   2.41705800
H   -0.03495100  -0.96125100   1.81950300
H   -0.64075200  -1.48672000  -0.55014100
H   -1.18537600  -0.16341400  -1.65940300
H    0.90174300   3.26880300  -0.68398300
H    2.18945700   0.09294100   2.00143100
H    1.18614200  -0.82853000  -2.11815800
H    1.49276400   2.49189700   1.63333300
H    2.78593600   2.05797100   0.50001400
H    1.77897900  -1.58820200   0.21608500
H    2.95854300  -0.39255500  -0.36052600
H    0.48515800   1.56363400  -2.48172500
H    2.18159900   1.50208500  -1.96849900
Cl  -3.65813300  -0.04864200   0.61892500
I   -6.34466700  -1.76187900  -0.19251700
I   -4.28668600  -3.64392100  -0.85298200
Cl  -2.15659500  -5.28335400  -1.36569400
I   -0.41050000  -4.33690100   0.48198100
Cl   1.20382400  -3.36568400   2.17920800
32
 Energy -2663.536707926814  G(298.15) 110.33
C   -0.59221000   0.44306900   0.33388400
C   -0.69753700   1.88142700   0.01457200
C    0.12456800   0.09275500   1.56555500
C   -0.43399900  -0.46754500  -0.80791900
C    0.80513100   2.20788000  -0.42463700
C    1.64110400   0.42007100   1.12718800
C    1.07529000  -0.15340600  -1.24592000
C    1.72945300   1.90666300   0.76317900
C    1.99432100  -0.47444000  -0.06417900
C    1.15973100   1.32988900  -1.63313000
H   -2.36535900   0.08921400   0.83529300
H   -1.37574900   2.08838300  -0.82608800
H   -0.96181000   2.50331500   0.88282600
H   -0.13498600   0.73331200   2.42166300
H    0.08852400  -0.97803900   1.83099400
H   -0.51133600  -1.53417400  -0.53457000
H   -1.10803500  -0.22992800  -1.64381700
H    0.82908200   3.27930600  -0.68916300
H    2.25983000   0.17175900   2.00616200
H    1.28742200  -0.80870200  -2.10784500
H    1.46447800   2.53819600   1.62884000
H    2.77074700   2.15658200   0.49206500
H    1.90785800  -1.53383600   0.23306700
H    3.04632600  -0.30015800  -0.35461300
H    0.48652000   1.54996000  -2.47955100
H    2.18494300   1.56532900  -1.96998900
Cl  -3.64172200  -0.20678400   0.60139700
I   -6.43037800  -1.77144800  -0.22466200
Cl  -4.65008700  -3.54518200  -0.85933500
I   -2.58409400  -5.35007900  -1.45490200
I   -0.56366300  -4.29726600   0.47250700
Cl   1.19563500  -3.30612200   2.11112900
32
```

Energy -2663.532185840383 G(298.15) 110.13

C	-0.90427200	0.70898900	0.04862200
C	-0.52858600	2.14237100	0.09633200
C	-0.41350700	-0.13038400	1.15789600
C	-0.87968600	0.07875000	-1.28943100
C	1.03561700	2.07849000	-0.21484600
C	1.15462100	-0.19632500	0.84983600
C	0.67997900	0.01019100	-1.60419700
C	1.70987900	1.23333200	0.87479300
C	1.35123100	-0.84483100	-0.52408700
C	1.23214400	1.44359800	-1.59914800
H	-2.56552300	0.73316300	0.35001100
H	-1.02610700	2.74531700	-0.67857800
H	-0.68095300	2.59609200	1.08742400
H	-0.56078900	0.32729800	2.14783700
H	-0.81516700	-1.15604300	1.14314300
H	-1.29789900	-0.94148000	-1.28256200
H	-1.37702700	0.69105400	-2.05729100
H	1.40414700	3.11927000	-0.20012200
H	1.59122400	-0.81927200	1.64973000
H	0.78324600	-0.45329800	-2.60031000
H	1.55951500	1.69141500	1.86784200
H	2.80003600	1.20695600	0.69791600
H	0.94213900	-1.86853600	-0.52590800
H	2.43241700	-0.92871900	-0.73712600
H	0.73862200	2.05349900	-2.37598800
H	2.30907300	1.42453700	-1.84384800
Cl	-3.81379000	0.19411600	0.40218600
I	-5.72934600	-2.43211200	0.16350800
I	-3.05519600	-3.51672500	-0.20270000
Cl	-0.56004700	-4.35944300	-0.54073700
Cl	0.66294300	-3.74444300	1.82042100
I	1.82106200	-3.08682400	3.91938300

32

Energy -2663.516496895100 G(298.15) 109.52

C	-0.79433500	0.59878700	0.17188600
C	-0.58681900	2.06053000	0.06883000
C	-0.20859100	-0.06761400	1.34083300
C	-0.76369700	-0.15414800	-1.09620300
C	0.96520800	2.13705700	-0.30159000
C	1.35693000	0.00762600	0.96860800
C	0.78853400	-0.08354600	-1.47141200
C	1.75743400	1.48036100	0.83743900
C	1.57911800	-0.75141200	-0.34214300
C	1.18352900	1.39202900	-1.62631500
H	-2.54694400	0.55016200	0.57134500
H	-1.17364600	2.52373800	-0.73837800
H	-0.75653000	2.59025100	1.01822000
H	-0.36613400	0.47171800	2.28626400
H	-0.48118600	-1.12953200	1.43896500
H	-1.06468600	-1.20680700	-0.98269500
H	-1.34900600	0.32632600	-1.89401600
H	1.21480900	3.20781200	-0.40165100
H	1.86496000	-0.50009500	1.80959100

```
 H    0.90457500  -0.63125500  -2.42221800
 H    1.58858100   2.01792000   1.78657800
 H    2.83854700   1.54798600   0.62079100
 H    1.28248900  -1.80610100  -0.21958900
 H    2.65636500  -0.74545600  -0.58833700
 H    0.60267400   1.86778900  -2.43552900
 H    2.24762600   1.46030100  -1.91418700
 Cl  -3.78065800   0.03706600   0.45687500
 I   -6.01926100  -2.22786600  -0.18679300
 Cl  -3.71277000  -3.43994700  -0.56240800
 I   -1.23867100  -4.59453600  -0.93123800
 Cl   0.26898500  -3.81966800   1.35587300
 I    1.74257000  -3.11947600   3.38260400
```

AdH+3ICl, TS(e-h) (Fig. 7 in main text)

```
32
  Energy -2663.539690089339  G(298.15) 110.50
 C   -0.65571200   0.55104200   0.33250900
 C   -0.62309900   1.99673800   0.01400700
 C    0.03179200   0.13800000   1.56508300
 C   -0.54856000  -0.36755700  -0.81332400
 C    0.90007100   2.20000900  -0.40881700
 C    1.56774800   0.34446800   1.14303500
 C    0.98074700  -0.16947900  -1.23694100
 C    1.78541100   1.82018400   0.78673600
 C    1.86619000  -0.56601000  -0.05205900
 C    1.19355700   1.30199500  -1.61892400
 H   -2.50228300   0.71291900   1.06549900
 H   -1.27726600   2.26278300  -0.82920500
 H   -0.84177200   2.63548200   0.88287400
 H   -0.18583300   0.78900800   2.42479000
 H   -0.10365100  -0.92460800   1.82316900
 H   -0.71007500  -1.42324700  -0.54258000
 H   -1.19534700  -0.08223900  -1.65513100
 H    1.01504600   3.26693300  -0.66753900
 H    2.15844500   0.04321300   2.02483300
 H    1.14705400  -0.83705500  -2.09946300
 H    1.56398200   2.46906100   1.65195500
 H    2.84646500   1.98301600   0.52740200
 H    1.70396400  -1.61867700   0.23442300
 H    2.93002500  -0.46578600  -0.33321300
 H    0.54888100   1.58101900  -2.47026500
 H    2.23787300   1.45226600  -1.94499200
 I   -3.85375700  -0.15978700   0.56271500
 Cl  -6.07243100  -2.00601800  -0.47815500
 I   -4.26399800  -3.73698500  -1.00819600
 Cl  -2.22303200  -5.40333600  -1.43862600
 I   -0.49042900  -4.39868500   0.42035500
 Cl   1.06999900  -3.38866700   2.13804500
 32
  Energy -2663.520210349516  G(298.15) 109.76
 C   -0.89356600   0.74774900   0.06230000
 C   -0.47849000   2.17373600   0.11881800
 C   -0.41324600  -0.10803100   1.16390500
```

```
C   -0.87705300   0.12966700  -1.28267800
C    1.07928800   2.08435200  -0.19309600
C    1.14951500  -0.19725900   0.85284600
C    0.67869800   0.03916500  -1.59776800
C    1.74041000   1.21795400   0.88787000
C    1.33651000  -0.83934100  -0.52675500
C    1.26537500   1.45850800  -1.58300700
H   -2.68099000   1.24047300   0.46081300
H   -0.96681700   2.79169200  -0.64993900
H   -0.62242800   2.62169200   1.11367200
H   -0.55574800   0.34416400   2.15660200
H   -0.83408400  -1.12459000   1.14180100
H   -1.30953800  -0.88279900  -1.28535300
H   -1.36815700   0.75497400  -2.04341500
H    1.46607800   3.11818800  -0.16940200
H    1.57665000  -0.83512200   1.64677100
H    0.77147700  -0.41742400  -2.59806300
H    1.60222200   1.67169100   1.88471800
H    2.82880400   1.16842700   0.70720600
H    0.90926700  -1.85564700  -0.53390300
H    2.41529200  -0.94279400  -0.74057300
H    0.78544700   2.08525600  -2.35494300
H    2.34164100   1.41728700  -1.82653000
I   -3.91261300   0.05975700   0.45311700
Cl  -5.49769400  -2.48349200   0.25542000
I   -3.19311300  -3.63959200  -0.16316300
Cl  -0.84605900  -4.65941500  -0.58242200
Cl   0.58314000  -3.92073400   1.62455200
I    1.91978400  -3.21849000   3.60059800
32
 Energy -2663.517984245028  G(298.15) 110.46
C   -0.61879400   0.47006700   0.31995000
C   -0.67387400   1.91170500  -0.01088700
C    0.08646300   0.11155200   1.56102800
C   -0.43804500  -0.44727300  -0.81980800
C    0.83738400   2.20698300  -0.41992700
C    1.60805300   0.40990100   1.15277900
C    1.07931200  -0.15854800  -1.22717800
C    1.73555900   1.89378900   0.78556400
C    1.97586800  -0.49120300  -0.03046700
C    1.20291100   1.32072600  -1.61933700
H   -2.46021100   0.53630500   1.28177400
H   -1.33558700   2.12865100  -0.86197900
H   -0.94369700   2.54073100   0.85028100
H   -0.17904600   0.75491300   2.41315400
H    0.01379200  -0.95635500   1.82594800
H   -0.54226100  -1.50821100  -0.54313600
H   -1.09133800  -0.20574200  -1.66977000
H    0.88750000   3.27692700  -0.68668400
H    2.20872300   0.15632400   2.04284100
H    1.29740300  -0.81940000  -2.08341100
H    1.46560100   2.53342100   1.64389700
H    2.78611300   2.12234700   0.53306600
H    1.86881900  -1.54935300   0.26380500
```

```
H    3.03466200  -0.32994300  -0.30179200
H    0.55097700   1.55052600  -2.47982000
H    2.23919200   1.53576200  -1.93465700
I   -3.72375200  -0.30411500   0.55451300
Cl  -6.04574800  -1.81908100  -0.58530900
Cl  -4.53484500  -3.59713400  -1.03604200
I   -2.71851600  -5.50031800  -1.43997200
I   -0.65408300  -4.39518100   0.45626000
Cl   1.08146700  -3.37877400   2.06531400
32
 Energy -2663.498704847052  G(298.15) 109.57
C   -0.83782000   0.64679100   0.07557700
C   -0.55113700   2.10672800   0.03003800
C   -0.31944500  -0.07226800   1.25384400
C   -0.71546100  -0.06297000  -1.21928200
C    1.01338900   2.14976400  -0.23153900
C    1.25599700  -0.02690100   0.99122700
C    0.85244900  -0.02226600  -1.48323000
C    1.71376100   1.43518300   0.93316000
C    1.55254000  -0.74915000  -0.32838200
C    1.30586400   1.44264400  -1.56309400
H   -2.73207900   1.22286300   0.52973000
H   -1.07293400   2.61429000  -0.79543400
H   -0.77088900   2.61267700   0.98244700
H   -0.53831400   0.43764000   2.20343100
H   -0.63618300  -1.12415400   1.30068800
H   -1.04879900  -1.10872700  -1.16100300
H   -1.23784200   0.45404400  -2.03766700
H    1.30136800   3.21455900  -0.27841000
H    1.70978400  -0.57137200   1.83877600
H    1.02270900  -0.54132400  -2.44219000
H    1.49825900   1.94907100   1.88620800
H    2.80792900   1.47408300   0.78843200
H    1.22399400  -1.79998600  -0.26381500
H    2.64320900  -0.76280400  -0.50198300
H    0.79670300   1.96188900  -2.39380000
H    2.38906500   1.48460200  -1.77363100
I   -3.81479000  -0.07136500   0.36630600
Cl  -5.73275400  -2.25977500   0.08056100
Cl  -3.74485300  -3.62387800  -0.33825900
I   -1.56989700  -4.98069900  -0.77539300
Cl   0.26789300  -4.05748900   1.26643000
I    1.96828100  -3.37170200   3.06025800
```

AdBr-ICl, TS(17.7), Intermediate(2.2), TS(3.8), Intermediate(2.1), TS(15.8), AdCl-BrI (Fig. 10 in main text)

```
28
 Energy -3721.09282239
C   -0.91609400   0.57368600   0.84454400
C   -1.24430500   0.56870000  -0.63954200
C    0.58486300   0.58808800   1.08642900
C   -1.58517000  -0.58704200   1.56716300
C   -0.66313100  -0.73663900  -1.23531500
C    1.16088500  -0.71853900   0.48805500
```

```
C   -1.00685900  -1.89308500   0.96689500
C    0.85821800  -0.76388700  -1.01753900
C    0.51353200  -1.92389600   1.18850800
C   -1.31430100  -1.94158400  -0.53773500
I   -0.28912500   4.37771300   0.15066700
H   -2.33391500   0.60421900  -0.79022600
H   -0.80107800   1.44615200  -1.13379400
H    1.04365200   1.46284800   0.60146300
H    0.79796700   0.64152100   2.16459000
H   -1.37675000  -0.54076000   2.64718000
H   -2.67633400  -0.55370700   1.42397800
H   -0.89053500  -0.75490700  -2.31262700
H    2.24945400  -0.72367200   0.65471900
H   -1.48122800  -2.74537600   1.47831300
H    1.32895500   0.09328000  -1.52554600
H    1.28475100  -1.67861300  -1.45987300
H    0.74005000  -1.90058100   2.26705200
H    0.93182700  -2.86070600   0.78673400
H   -2.40429300  -1.93012600  -0.70245400
H   -0.92781300  -2.87932300  -0.96813300
Cl   0.87979000   6.10274700  -1.10932200
Br  -1.70608700   2.29404700   1.66384400
28
 Energy -3721.06109751
C    0.13607000  -1.53744500   0.05188100
C   -0.67096800  -1.61195300  -1.16231700
C    1.56706000  -1.29080900  -0.11432200
C   -0.26535800  -2.38194100   1.17589500
C   -0.20868100  -3.04917200  -1.71229200
C    2.03970000  -2.72720900  -0.65965200
C    0.20024100  -3.81891800   0.63561300
C    1.29894500  -3.00478200  -1.96961700
C    1.71072700  -3.78281000   0.39690500
C   -0.55913000  -4.10573600  -0.66224500
I    0.04459000   1.93789500  -0.06655400
H   -1.74889900  -1.63018100  -0.96836400
H   -0.41209600  -0.84579700  -1.90091400
H    1.79729600  -0.53115400  -0.86896300
H    2.08686500  -1.07800700   0.82671100
H    0.27027100  -2.15426700   2.10433700
H   -1.34686100  -2.39430000   1.34250400
H   -0.77249800  -3.20382300  -2.64376600
H    3.12389400  -2.63869400  -0.82036200
H   -0.06549800  -4.53778000   1.42443900
H    1.53903600  -2.23537600  -2.71859700
H    1.63114300  -3.97066800  -2.38147000
H    2.24473900  -3.56909200   1.33522600
H    2.05406100  -4.77091900   0.05146300
H   -1.64385500  -4.11969400  -0.47783100
H   -0.28256100  -5.10383000  -1.03760000
Cl   1.90075300   2.87226900  -1.53695300
Br  -1.87609600   0.67512500   1.47948800
28
 Energy -3721.08578127
```

```
C    0.48605800  -0.92678500  -0.33063500
C   -0.66219100  -1.38815900  -1.19523800
C    1.81375300  -1.03149000  -1.02957000
C    0.49716900  -1.56793900   1.03522500
C   -0.43818800  -2.91117500  -1.42922300
C    2.03822000  -2.55904500  -1.26971600
C    0.71636900  -3.09017200   0.79110900
C    0.90489500  -3.11016000  -2.14586700
C    2.06188500  -3.29045600   0.07972900
C   -0.42882800  -3.63408600  -0.07473600
I    0.06820000   1.41120900   0.07488800
H   -1.62814400  -1.22395000  -0.69705100
H   -0.66519300  -0.86025800  -2.15914300
H    1.81139400  -0.50222500  -1.99153500
H    2.63090800  -0.62713100  -0.41676300
H    1.31471600  -1.16847900   1.65241900
H   -0.45589800  -1.40777700   1.55815900
H   -1.26602400  -3.28135500  -2.05381100
H    3.00650600  -2.66797000  -1.78296300
H    0.72291400  -3.58957300   1.77212800
H    0.89426900  -2.59847300  -3.12087700
H    1.07270700  -4.18145300  -2.34219600
H    2.88416400  -2.90784000   0.70597700
H    2.24640200  -4.36490000  -0.08153300
H   -1.39327300  -3.48895900   0.43944600
H   -0.30063900  -4.71727300  -0.22901200
Cl   2.19554400   2.18071600  -1.06153000
Br  -2.23125400   0.75252300   1.30778000
28
 Energy -3721.08332820
C    0.48864500  -0.96351500  -0.32493000
C   -0.31290100  -1.30569800  -1.55657700
C    1.97465700  -1.07175800  -0.53538700
C    0.03100600  -1.70457600   0.90181500
C   -0.03480000  -2.81085300  -1.84238600
C    2.24921400  -2.58052900  -0.82935100
C    0.30431400  -3.21340200   0.61026500
C    1.46935800  -3.00326600  -2.08251200
C    1.80598300  -3.41878900   0.37596700
C   -0.48783800  -3.64154600  -0.63318000
I    0.02464600   1.38801400   0.05861700
H   -1.38758500  -1.14947400  -1.38425700
H    0.00165500  -0.69475600  -2.41465000
H    2.31292200  -0.46227300  -1.38306600
H    2.52854600  -0.75979300   0.36213700
H    0.59199700  -1.38812400   1.79301800
H   -1.03912000  -1.55574500   1.09316200
H   -0.60624400  -3.09710600  -2.73923800
H    3.33182800  -2.68955900  -0.99822300
H   -0.03003900  -3.78359800   1.49094400
H    1.79559700  -2.40886500  -2.95100900
H    1.68029300  -4.05925500  -2.31393900
H    2.37721500  -3.12937900   1.27243600
H    2.01260100  -4.48497700   0.18873100
```

```
H   -1.56816700  -3.50761900  -0.46140000
H   -0.32127000  -4.71295900  -0.83073300
Cl   1.92216800   2.08598300  -1.48064800
Br  -2.10286100   0.87777000   1.61231900
28
 Energy -3721.08605864
C    0.43471600  -0.96289300  -0.36742400
C    0.15386600  -1.19744000  -1.83255100
C    1.89594300  -1.10017100  -0.01270300
C   -0.45750700  -1.77505500   0.52982300
C    0.53133000  -2.68313200  -2.10720800
C    2.26551500  -2.58662700  -0.29698800
C   -0.08312000  -3.26666800   0.25133300
C    2.01624300  -2.89507700  -1.78049100
C    1.39726500  -3.49122500   0.58749800
C   -0.34026900  -3.58851100  -1.22701100
I   -0.07734300   1.36431400  -0.01495000
H   -0.90936600  -1.03572600  -2.06140900
H    0.76011500  -0.53300900  -2.46335600
H    2.51768600  -0.43514900  -0.62719000
H    2.06665800  -0.86996400   1.04886500
H   -0.29089300  -1.54313200   1.59049400
H   -1.52024400  -1.61268200   0.30387900
H    0.34273100  -2.88601100  -3.17297500
H    3.33118700  -2.71903500  -0.05299800
H   -0.72173900  -3.88944400   0.89609300
H    2.63991300  -2.24299800  -2.41241900
H    2.30475900  -3.93592300  -1.99938700
H    1.58318000  -3.27312800   1.65161500
H    1.66107300  -4.54790000   0.41868600
H   -1.40552300  -3.44209600  -1.46798700
H   -0.10228000  -4.64647400  -1.42433100
Cl   1.74109300   1.91343900  -1.71022500
Br  -2.02527300   0.93949800   1.77514400
28
 Energy -3721.06415895
C    0.79787000  -1.36134800  -1.03831200
C    0.98069400  -1.65831500  -2.45797900
C    1.99215700  -1.33704800  -0.20015400
C   -0.44085900  -1.83045400  -0.41845100
C    1.28536000  -3.23100400  -2.38619500
C    2.30594000  -2.91093600  -0.12080100
C   -0.13812300  -3.40592000  -0.33779700
C    2.54584700  -3.43144700  -1.54026400
C    1.10787400  -3.60879000   0.52765900
C    0.07947300  -3.93206400  -1.75758300
I   -0.25901100   1.66816900   0.20885400
H    0.07753600  -1.49348700  -3.05598500
H    1.83981500  -1.14439500  -2.89946500
H    2.83852300  -0.82015800  -0.66431500
H    1.80490500  -0.95829300   0.81053500
H   -0.60026900  -1.44572100   0.59437100
H   -1.32802000  -1.67288500  -1.04140500
H    1.44322300  -3.55465700  -3.42553000
```

```
H    3.20963800  -3.00170700   0.49915600
H   -1.02816200  -3.85370900   0.12750500
H    3.40175500  -2.91372400  -1.99862200
H    2.80011400  -4.50229600  -1.50188600
H    0.93818900  -3.21904800   1.54245600
H    1.31703300  -4.68591900   0.62636200
H   -0.82169700  -3.76962700  -2.36828400
H    0.25641700  -5.01899800  -1.72484100
Cl   1.22055100   1.60444200  -1.96689100
Br  -1.75265300   1.48011800   2.43738600
28
 Energy -3721.09804327
C    1.18851400  -1.36166200  -1.63302800
C    1.93187000  -1.87024900  -2.86483600
C    2.03459400  -1.53398800  -0.37691400
C   -0.16290400  -2.05180500  -1.48952900
C    2.18738200  -3.38243000  -2.66806900
C    2.28914300  -3.04561100  -0.18342000
C    0.09473200  -3.56226400  -1.29180900
C    3.03839800  -3.59793700  -1.40640400
C    0.94269200  -3.77135600  -0.02624500
C    0.84259600  -4.11133600  -2.51749300
I   -0.56929500   1.40929500   0.42779600
H    1.32653500  -1.70070900  -3.76783100
H    2.88391000  -1.33157600  -2.98309300
H    2.98686500  -0.99310500  -0.48439200
H    1.50483100  -1.12122500   0.49530200
H   -0.70850500  -1.63854700  -0.62759400
H   -0.77002300  -1.87829300  -2.39047700
H    2.72236000  -3.76148400  -3.55320700
H    2.89683400  -3.18214500   0.72474900
H   -0.87642100  -4.06966300  -1.18407900
H    4.01354300  -3.09607400  -1.51391000
H    3.23754000  -4.67306500  -1.26897900
H    0.40732900  -3.38245500   0.85543600
H    1.11151300  -4.84739000   0.14047200
H    0.23388000  -3.97106200  -3.42612600
H    1.01408200  -5.19375900  -2.40283100
Cl   0.89278400   0.47062800  -1.90177000
Br  -1.85742100   2.30685500   2.45406600
```