

## Ligand-driven formation of halogen bonds involving Au(I) complexes

Ferdinand Groenewald, Jan Dillen and Catharine Esterhuysen

*Department of Chemistry and Polymer Science, Stellenbosch University, Private Bag X1, Matieland, Stellenbosch, 7602, South Africa; ce@sun.ac.za*

### S1. Optimised coordinates and relevant properties of Au<sup>-</sup> adducts (energies in a.u. and frequencies in cm<sup>-1</sup>)

#### Au<sup>-</sup>.ICH<sub>3</sub>

B3LYP/aug-cc-pVTZ-pp

Energy: -471.5840878

Low Frequencies:

73.2018            87.6059            89.1945

Optimised Coordinates:

|    |           |           |           |
|----|-----------|-----------|-----------|
| 79 | -1.877427 | 0.000537  | -0.000052 |
| 6  | 3.390018  | 0.001976  | -0.000337 |
| 1  | 3.717780  | -0.583189 | -0.854694 |
| 1  | 3.717671  | -0.445235 | 0.933702  |
| 1  | 3.717440  | 1.034565  | -0.080011 |
| 53 | 1.085266  | 0.001420  | -0.000281 |

TPSS/aug-cc-pVTZ-pp

Energy: -471.3037054

Low Frequencies:

90.3903            93.7359            95.6291

Optimised Coordinates:

|    |           |           |           |
|----|-----------|-----------|-----------|
| 79 | -1.792838 | -0.001498 | -0.000614 |
| 6  | 3.384853  | 0.002085  | -0.000305 |
| 1  | 3.706385  | -0.587264 | -0.860285 |
| 1  | 3.707336  | -0.448390 | 0.939517  |
| 1  | 3.709339  | 1.040496  | -0.080602 |
| 53 | 1.035674  | 0.004646  | 0.000615  |

MP2/cc-pVTZ-pp

Energy: -470.2070992

Low Frequencies:

86.6666            100.4839            100.4956

Optimised Coordinates:

|    |           |           |           |
|----|-----------|-----------|-----------|
| 79 | -1.744982 | 0.000619  | -0.000109 |
| 6  | 3.343221  | 0.001968  | -0.000324 |
| 1  | 3.689703  | -0.580634 | -0.850905 |

|    |          |           |           |
|----|----------|-----------|-----------|
| 1  | 3.689742 | -0.443267 | 0.929543  |
| 1  | 3.689305 | 1.030020  | -0.079649 |
| 53 | 1.083759 | 0.001367  | -0.000229 |

MP2/aug-cc-pVTZ-pp

Energy: -470.2463922

Low Frequencies:

|         |          |          |
|---------|----------|----------|
| 96.1891 | 101.4562 | 101.4566 |
|---------|----------|----------|

Optimised Coordinates:

|    |           |           |           |
|----|-----------|-----------|-----------|
| 79 | -1.711293 | 0.000631  | -0.000112 |
| 6  | 3.344833  | 0.001955  | -0.000323 |
| 1  | 3.683758  | -0.582667 | -0.853907 |
| 1  | 3.683797  | -0.444816 | 0.932822  |
| 1  | 3.683367  | 1.033613  | -0.079926 |
| 53 | 1.066285  | 0.001358  | -0.000228 |

**Au<sup>-</sup>.BrCH<sub>3</sub>**

B3LYP/aug-cc-pVTZ-pp

Energy: -2749.9960093

Low Frequencies:

|         |         |         |
|---------|---------|---------|
| 47.5696 | 82.8397 | 84.0070 |
|---------|---------|---------|

Optimised Coordinates:

|    |           |           |           |
|----|-----------|-----------|-----------|
| 79 | -1.807507 | 0.000323  | -0.000163 |
| 6  | 3.317971  | 0.001990  | -0.000279 |
| 1  | 3.652126  | -0.581664 | -0.852649 |
| 1  | 3.652290  | -0.443973 | 0.931308  |
| 1  | 3.651716  | 1.032063  | -0.079815 |
| 35 | 1.284153  | 0.001335  | -0.000075 |

TPSS/aug-cc-pVTZ-pp

Energy: -2749.7984915

Low Frequencies:

|         |         |         |
|---------|---------|---------|
| 82.5011 | 96.5678 | 97.3468 |
|---------|---------|---------|

Optimised Coordinates:

|    |           |           |           |
|----|-----------|-----------|-----------|
| 79 | -1.600449 | 0.000941  | 0.000653  |
| 6  | 3.301637  | 0.001954  | -0.000393 |
| 1  | 3.622219  | -0.586707 | -0.859871 |
| 1  | 3.621014  | -0.447888 | 0.939640  |
| 1  | 3.620551  | 1.041144  | -0.080367 |
| 35 | 1.185778  | 0.000631  | -0.001334 |

MP2/cc-pVTZ-pp

Energy: -2748.0118814

Low Frequencies:

48.8756            92.2191            92.2191

Optimised Coordinates:

|    |           |           |           |
|----|-----------|-----------|-----------|
| 79 | -1.736678 | 0.000346  | -0.000079 |
| 6  | 3.280015  | 0.002006  | -0.000328 |
| 1  | 3.633571  | -0.578330 | -0.847702 |
| 1  | 3.633615  | -0.441483 | 0.926019  |
| 1  | 3.633079  | 1.026181  | -0.079354 |
| 35 | 1.307147  | 0.001353  | -0.000229 |

MP2/aug-cc-pVTZ-pp

Energy: -2748.0463797

Low Frequencies:

52.9217            98.4905            98.4906

Optimised Coordinates:

|    |           |           |           |
|----|-----------|-----------|-----------|
| 79 | -1.674885 | 0.000365  | -0.000080 |
| 6  | 3.273003  | 0.002004  | -0.000328 |
| 1  | 3.621179  | -0.579935 | -0.850040 |
| 1  | 3.621223  | -0.442711 | 0.928575  |
| 1  | 3.620686  | 1.029003  | -0.079572 |
| 35 | 1.289542  | 0.001348  | -0.000229 |

**Au<sup>-</sup>.ClCH<sub>3</sub>**

B3LYP/aug-cc-pVTZ-pp

Energy: -135.8315614

Low Frequencies:

11.4266            46.4911            47.6974

Optimised Coordinates:

|    |           |           |           |
|----|-----------|-----------|-----------|
| 79 | -2.408858 | 0.000812  | -0.000004 |
| 6  | 3.381743  | 0.001992  | -0.000331 |
| 1  | 3.732883  | -0.578688 | -0.848651 |
| 1  | 3.732716  | -0.441709 | 0.927081  |
| 1  | 3.731133  | 1.027569  | -0.079449 |
| 17 | 1.581131  | 0.000098  | -0.000318 |

TPSS/aug-cc-pVTZ-pp

Energy: -635.9169400

Low Frequencies:

42.0253            93.4677            94.2205

Optimised Coordinates:

|    |           |          |           |
|----|-----------|----------|-----------|
| 79 | -1.676371 | 0.000066 | -0.000183 |
|----|-----------|----------|-----------|

|    |          |           |           |
|----|----------|-----------|-----------|
| 6  | 3.252165 | 0.001989  | -0.000317 |
| 1  | 3.593156 | -0.583562 | -0.855145 |
| 1  | 3.593510 | -0.445485 | 0.934100  |
| 1  | 3.593640 | 1.034891  | -0.080038 |
| 17 | 1.394648 | 0.002176  | -0.000089 |

MP2/cc-pVTZ-pp

Energy: -635.0240350

Low Frequencies:

|         |         |         |
|---------|---------|---------|
| 33.5593 | 61.8320 | 61.8321 |
|---------|---------|---------|

Optimised Coordinates:

|    |           |           |           |
|----|-----------|-----------|-----------|
| 79 | -2.063805 | 0.000244  | -0.000065 |
| 6  | 3.301510  | 0.002012  | -0.000328 |
| 1  | 3.663140  | -0.576533 | -0.845089 |
| 1  | 3.663182  | -0.440107 | 0.923163  |
| 1  | 3.662651  | 1.023032  | -0.079112 |
| 17 | 1.524069  | 0.001426  | -0.000241 |

MP2/aug-cc-pVTZ-pp

Energy: -635.0531231

Low Frequencies:

|         |         |         |
|---------|---------|---------|
| 41.9316 | 69.3849 | 69.3859 |
|---------|---------|---------|

Optimised Coordinates:

|    |           |           |           |
|----|-----------|-----------|-----------|
| 79 | -1.940061 | 0.000300  | -0.000074 |
| 6  | 3.280110  | 0.002001  | -0.000327 |
| 1  | 3.637602  | -0.577851 | -0.846992 |
| 1  | 3.637644  | -0.441117 | 0.925248  |
| 1  | 3.637118  | 1.025320  | -0.079287 |
| 17 | 1.498335  | 0.001421  | -0.000240 |

**Au<sup>-</sup>.ICF<sub>3</sub>**

B3LYP/aug-cc-pVTZ-pp

Energy: -633.5556912

Low Frequencies:

|         |         |          |
|---------|---------|----------|
| 52.1101 | 52.9245 | 101.7314 |
|---------|---------|----------|

Optimised Coordinates:

|    |           |           |           |
|----|-----------|-----------|-----------|
| 79 | -1.886316 | 0.001057  | -0.001122 |
| 6  | 3.278715  | 0.001938  | -0.000036 |
| 9  | 3.818098  | -0.706625 | -1.035021 |
| 9  | 3.819948  | -0.539629 | 1.130604  |
| 9  | 3.818597  | 1.252340  | -0.096984 |
| 53 | 0.901704  | 0.000993  | 0.000887  |

TPSS/aug-cc-pVTZ-pp

Energy: -769.1910874

Low Frequencies:

51.6263            52.4041            116.2693

Optimised Coordinates:

|    |           |           |           |
|----|-----------|-----------|-----------|
| 79 | -1.856133 | 0.001531  | 0.000016  |
| 6  | 3.273297  | 0.001502  | -0.000355 |
| 9  | 3.827288  | -0.712058 | -1.042886 |
| 9  | 3.826921  | -0.543705 | 1.139561  |
| 9  | 3.825318  | 1.262001  | -0.097508 |
| 53 | 0.854054  | 0.000803  | -0.000500 |

MP2/cc-pVTZ-pp

Energy: -767.6274061

Low Frequencies:

59.6769            59.6777            108.0066

Optimised Coordinates:

|    |           |           |           |
|----|-----------|-----------|-----------|
| 79 | -1.759425 | 0.000882  | -0.000171 |
| 6  | 3.238393  | 0.001868  | -0.000305 |
| 9  | 3.764055  | -0.702964 | -1.029383 |
| 9  | 3.764075  | -0.536764 | 1.124704  |
| 9  | 3.763721  | 1.245625  | -0.096273 |
| 53 | 0.979926  | 0.001426  | -0.000244 |

MP2/aug-cc-pVTZ-pp

Energy: -767.6952546

Low Frequencies:

59.2936            59.2938            117.5208

Optimised Coordinates:

|    |           |           |           |
|----|-----------|-----------|-----------|
| 79 | -1.739778 | 0.000892  | -0.000173 |
| 6  | 3.233141  | 0.001863  | -0.000303 |
| 9  | 3.765136  | -0.703715 | -1.030475 |
| 9  | 3.765161  | -0.537338 | 1.125898  |
| 9  | 3.764782  | 1.246950  | -0.096375 |
| 53 | 0.962303  | 0.001420  | -0.000244 |

**Au<sup>-</sup>.BrCF<sub>3</sub>**

B3LYP/aug-cc-pVTZ-pp

Energy: -2911.9874013

Low Frequencies:

61.9355            62.0376            83.9799

Optimised Coordinates:

|    |           |           |           |
|----|-----------|-----------|-----------|
| 79 | -1.663395 | 0.000855  | -0.000526 |
| 6  | 3.191965  | 0.001859  | -0.000177 |
| 9  | 3.710314  | -0.705893 | -1.033580 |
| 9  | 3.711181  | -0.538943 | 1.129164  |
| 9  | 3.710323  | 1.250741  | -0.096651 |
| 35 | 1.090358  | 0.001454  | 0.000096  |

TPSS/aug-cc-pVTZ-pp

Energy: -3047.6845002

Low Frequencies:

|         |         |          |
|---------|---------|----------|
| 62.0838 | 63.1638 | 116.5945 |
|---------|---------|----------|

Optimised Coordinates:

|    |           |           |           |
|----|-----------|-----------|-----------|
| 79 | -1.616250 | 0.002439  | 0.000397  |
| 6  | 3.193116  | 0.001249  | -0.000719 |
| 9  | 3.731583  | -0.711586 | -1.042214 |
| 9  | 3.729826  | -0.543251 | 1.138913  |
| 9  | 3.727633  | 1.261426  | -0.097326 |
| 35 | 0.984839  | -0.000204 | -0.000725 |

MP2/cc-pVTZ-pp

Energy: -3045.4341104

Low Frequencies:

|         |         |         |
|---------|---------|---------|
| 69.4559 | 69.4563 | 82.5048 |
|---------|---------|---------|

Optimised Coordinates:

|    |           |           |           |
|----|-----------|-----------|-----------|
| 79 | -1.557072 | 0.000925  | -0.000196 |
| 6  | 3.158414  | 0.001845  | -0.000297 |
| 9  | 3.671044  | -0.702568 | -1.028786 |
| 9  | 3.671066  | -0.536473 | 1.124061  |
| 9  | 3.670652  | 1.244900  | -0.096205 |
| 35 | 1.136642  | 0.001445  | -0.000253 |

MP2/aug-cc-pVTZ-pp

Energy: -3045.4977006

Low Frequencies:

|         |         |          |
|---------|---------|----------|
| 70.7930 | 70.7931 | 106.5905 |
|---------|---------|----------|

Optimised Coordinates:

|    |           |           |           |
|----|-----------|-----------|-----------|
| 79 | -1.515909 | 0.000923  | -0.000194 |
| 6  | 3.153952  | 0.001850  | -0.000299 |
| 9  | 3.674572  | -0.703857 | -1.030669 |
| 9  | 3.674587  | -0.537458 | 1.126119  |
| 9  | 3.674206  | 1.247176  | -0.096381 |
| 35 | 1.089338  | 0.001440  | -0.000253 |

**Au<sup>-</sup>.ClCF<sub>3</sub>**

B3LYP/aug-cc-pVTZ-pp

Energy: -798.0044112

Low Frequencies:

50.1289            64.8304            65.2626

Optimised Coordinates:

|    |           |           |           |
|----|-----------|-----------|-----------|
| 79 | -1.822641 | -0.000177 | -0.000415 |
| 6  | 3.026366  | 0.000047  | 0.000057  |
| 9  | 3.527216  | -0.986059 | -0.768900 |
| 9  | 3.529109  | -0.172750 | 1.237676  |
| 9  | 3.528211  | 1.158432  | -0.469850 |
| 17 | 1.229093  | 0.000407  | 0.001079  |

TPSS/aug-cc-pVTZ-pp

Energy: -933.7998845

Low Frequencies:

78.2529            78.9157            87.5807

Optimised Coordinates:

|    |           |           |           |
|----|-----------|-----------|-----------|
| 79 | -1.578221 | -0.000491 | 0.000372  |
| 6  | 2.995410  | 0.000106  | -0.000172 |
| 9  | 3.511619  | -0.994984 | -0.775731 |
| 9  | 3.512130  | -0.174354 | 1.249095  |
| 9  | 3.513085  | 1.168835  | -0.473965 |
| 17 | 1.063330  | 0.000789  | 0.000049  |

MP2/cc-pVTZ-pp

Energy: -932.4466459

Low Frequencies:

52.4719            61.5764            61.5827

Optimised Coordinates:

|    |           |           |           |
|----|-----------|-----------|-----------|
| 79 | -1.828948 | 0.000493  | 0.000293  |
| 6  | 3.018990  | -0.000119 | -0.000130 |
| 9  | 3.517764  | -0.980813 | -0.764782 |
| 9  | 3.517863  | -0.171767 | 1.231492  |
| 9  | 3.517275  | 1.152541  | -0.467303 |
| 17 | 1.274409  | -0.000434 | 0.000079  |

MP2/aug-cc-pVTZ-pp

Energy: -932.5019841

Low Frequencies:

58.8706            69.9230            69.9235

Optimised Coordinates:

|    |           |           |           |
|----|-----------|-----------|-----------|
| 79 | -1.726443 | 0.000204  | 0.000326  |
| 6  | 2.995972  | -0.000061 | -0.000140 |
| 9  | 3.501640  | -0.982461 | -0.766019 |
| 9  | 3.501847  | -0.172098 | 1.233502  |
| 9  | 3.501696  | 1.154356  | -0.468053 |
| 17 | 1.242642  | -0.000040 | 0.000033  |

### **Au<sup>-</sup>.I<sub>2</sub>**

B3LYP/aug-cc-pVTZ-pp

Energy: -727.5476765

Low Frequencies:

|         |         |         |
|---------|---------|---------|
| 37.9204 | 50.0443 | 51.3156 |
|---------|---------|---------|

Optimised Coordinates:

|    |           |           |           |
|----|-----------|-----------|-----------|
| 79 | 0.451483  | -0.653276 | -0.532488 |
| 6  | -0.456722 | -2.140041 | -1.738673 |
| 1  | 0.296208  | -2.544542 | -2.427444 |
| 1  | -0.849925 | -2.969776 | -1.146251 |
| 1  | -1.278330 | -1.739043 | -2.337400 |
| 6  | 1.528713  | 0.800286  | 0.570552  |
| 1  | 1.100997  | 1.800085  | 0.462956  |
| 1  | 1.564256  | 0.565836  | 1.637281  |
| 1  | 2.560593  | 0.832685  | 0.197646  |
| 53 | -1.895104 | -0.177651 | 0.888797  |
| 53 | -4.398336 | 0.331386  | 2.404730  |

TPSSTPSS/aug-cc-pVTZ-pp

Energy: -727.0575603

Low Frequencies:

|         |         |         |
|---------|---------|---------|
| 22.0112 | 47.3611 | 50.6621 |
|---------|---------|---------|

Optimised Coordinates:

|    |           |           |           |
|----|-----------|-----------|-----------|
| 79 | 0.440064  | -0.652904 | -0.528620 |
| 6  | -0.458783 | -2.138439 | -1.737139 |
| 1  | 0.302761  | -2.546898 | -2.422347 |
| 1  | -0.859243 | -2.970503 | -1.144250 |
| 1  | -1.278539 | -1.736122 | -2.345990 |
| 6  | 1.513240  | 0.798905  | 0.574123  |
| 1  | 1.085361  | 1.803364  | 0.464352  |
| 1  | 1.548273  | 0.564457  | 1.645520  |
| 1  | 2.549730  | 0.827939  | 0.198507  |
| 53 | -1.858323 | -0.177930 | 0.877345  |
| 53 | -4.360708 | 0.334081  | 2.398205  |

MP2/cc-pVTZ-pp

Energy: -725.3344724

Low Frequencies:

42.5549            54.8259            57.7037

Optimised Coordinates:

|    |           |           |           |
|----|-----------|-----------|-----------|
| 79 | 0.457497  | -0.654069 | -0.535045 |
| 6  | -0.449417 | -2.100861 | -1.698983 |
| 1  | 0.268839  | -2.516741 | -2.415100 |
| 1  | -0.832588 | -2.928262 | -1.096536 |
| 1  | -1.289811 | -1.697865 | -2.269674 |
| 6  | 1.490515  | 0.767139  | 0.552835  |
| 1  | 1.050202  | 1.761745  | 0.446828  |
| 1  | 1.507739  | 0.531319  | 1.619815  |
| 1  | 2.529835  | 0.826126  | 0.209312  |
| 53 | -1.838963 | -0.187966 | 0.850035  |
| 53 | -4.270016 | 0.305385  | 2.316221  |

MP2/aug-cc-pVTZ-pp

Energy: -725.3814239

Low Frequencies:

38.7691            53.9962            56.6174

Optimised Coordinates:

|    |           |           |           |
|----|-----------|-----------|-----------|
| 79 | 0.455144  | -0.653581 | -0.533592 |
| 6  | -0.452011 | -2.101054 | -1.698142 |
| 1  | 0.272666  | -2.511945 | -2.411817 |
| 1  | -0.832916 | -2.925473 | -1.088778 |
| 1  | -1.291994 | -1.690811 | -2.265778 |
| 6  | 1.488868  | 0.768207  | 0.554626  |
| 1  | 1.042571  | 1.760518  | 0.444096  |
| 1  | 1.501808  | 0.525830  | 1.621007  |
| 1  | 2.527290  | 0.821249  | 0.205074  |
| 53 | -1.823460 | -0.191154 | 0.840561  |
| 53 | -4.264133 | 0.304164  | 2.312451  |

**Table S1** – The  $E_{\text{INT}}$  values in kcal/mol, the  $\text{Au}\cdots\text{X-CH}_3$  distances (Å), the  $\text{Au}\cdots\text{X-CH}_3$  angles ( $^\circ$ ), the  $\text{X-CH}_3$  bond elongation (Å) indicated as  $\Delta R(\text{X-CH}_3)$  for the optimised X-bonded adducts to the  $\text{Au}^-$  ion at the B3LYP, TPSS, MP2\* and MP2 levels of theory. The ratio of the  $\text{Au}\cdots\text{X}$  distances with respect to the sum of the vdW radii is included as  $(\text{Au}\cdots\text{X})/\Sigma_{\text{vdW}}$ .

| Method  | X-bond donor      | $E_{\text{INT}}$<br>(kcal/mol) | $\text{Au}\cdots\text{XCH}_3$<br>(Å) | $(\text{Au}\cdots\text{X})/\Sigma_{\text{vdW}}$ | $\text{Au}\cdots\text{X-CH}_3$<br>(deg) | $\Delta R(\text{X-CH}_3)$<br>(Å) |
|---------|-------------------|--------------------------------|--------------------------------------|-------------------------------------------------|-----------------------------------------|----------------------------------|
| B3LYP   | ICH <sub>3</sub>  | -12.38                         | 2.963                                | 0.814                                           | 180.0                                   | 0.140                            |
| TPSS    |                   | -19.75                         | 2.829                                | 0.777                                           | 179.8                                   | 0.184                            |
| MP2*    |                   | -16.13                         | 2.829                                | 0.777                                           | 180.0                                   | 0.135                            |
| MP2     |                   | -20.06                         | 2.778                                | 0.763                                           | 180.0                                   | 0.156                            |
| CCSD(T) |                   | -10.99                         |                                      |                                                 |                                         |                                  |
| B3LYP   | BrCH <sub>3</sub> | -2.67                          | 3.092                                | 0.881                                           | 180.0                                   | 0.074                            |
| TPSS    |                   | -9.52                          | 2.786                                | 0.794                                           | 179.9                                   | 0.154                            |
| MP2*    |                   | -3.70                          | 3.044                                | 0.867                                           | 180.0                                   | 0.047                            |
| MP2     |                   | -5.64                          | 2.964                                | 0.845                                           | 180.0                                   | 0.058                            |
| CCSD(T) |                   | -1.65                          |                                      |                                                 |                                         |                                  |
| B3LYP   | ClCH <sub>3</sub> | 2.29                           | 3.990                                | 1.170                                           | 179.9                                   | -0.001                           |
| TPSS    |                   | 0.49                           | 3.071                                | 0.901                                           | 180.0                                   | 0.052                            |
| MP2*    |                   | 1.19                           | 3.588                                | 1.052                                           | 180.0                                   | -0.001                           |
| MP2     |                   | 0.10                           | 3.438                                | 1.008                                           | 180.0                                   | 0.002                            |
| CCSD(T) |                   | 1.45                           |                                      |                                                 |                                         |                                  |
| B3LYP   | ICF <sub>3</sub>  | -36.76                         | 2.788                                | 0.766                                           | 179.9                                   | 0.212                            |
| TPSS    |                   | -46.15                         | 2.710                                | 0.745                                           | 180.0                                   | 0.240                            |
| MP2*    |                   | -33.27                         | 2.739                                | 0.753                                           | 180.0                                   | 0.121                            |
| MP2     |                   | -39.73                         | 2.702                                | 0.742                                           | 180.0                                   | 0.141                            |
| CCSD(T) |                   | -29.45                         |                                      |                                                 |                                         |                                  |
| B3LYP   | BrCF <sub>3</sub> | -22.65                         | 2.754                                | 0.785                                           | 180.0                                   | 0.152                            |
| TPSS    |                   | -36.09                         | 2.601                                | 0.741                                           | 179.9                                   | 0.255                            |
| MP2*    |                   | -20.70                         | 2.694                                | 0.767                                           | 180.0                                   | 0.104                            |
| MP2     |                   | -28.32                         | 2.605                                | 0.742                                           | 180.0                                   | 0.153                            |
| CCSD(T) |                   | -17.16                         |                                      |                                                 |                                         |                                  |
| B3LYP   | ClCF <sub>3</sub> | -8.59                          | 3.05                                 | 0.895                                           | 180.0                                   | 0.022                            |
| TPSS    |                   | -18.63                         | 2.64                                 | 0.775                                           | 180.0                                   | 0.153                            |
| MP2*    |                   | -9.00                          | 3.10                                 | 0.910                                           | 180.0                                   | -0.010                           |
| MP2     |                   | -12.00                         | 2.97                                 | 0.871                                           | 180.0                                   | 0.002                            |
| CCSD(T) |                   | -8.08                          |                                      |                                                 |                                         |                                  |

## S2. Optimised coordinates and relevant properties of adducts with anionic complexes 1–7 (energies in a.u. and frequencies in cm<sup>-1</sup>)

### 1.ICF<sub>3</sub>

B3LYP/aug-cc-pVTZ-pp

Energy: -849.2851635

Low Frequencies:

12.0747            44.4683            49.1120

Optimised Coordinates:

|    |           |           |           |
|----|-----------|-----------|-----------|
| 79 | 0.935136  | 0.145495  | 0.133570  |
| 6  | 0.757577  | -1.344993 | -1.362428 |
| 1  | 1.724858  | -1.504081 | -1.855790 |
| 1  | 0.438542  | -2.308837 | -0.951583 |
| 1  | 0.036977  | -1.067834 | -2.139391 |
| 6  | 1.227869  | 1.648018  | 1.598683  |
| 1  | 0.602770  | 2.529162  | 1.418205  |
| 1  | 1.003789  | 1.291588  | 2.609786  |
| 1  | 2.273120  | 1.982377  | 1.594242  |
| 6  | -4.123807 | -0.389772 | 1.443317  |
| 9  | -4.459480 | -1.680694 | 1.680789  |
| 9  | -4.959472 | 0.046654  | 0.470229  |
| 9  | -4.453119 | 0.299080  | 2.562542  |
| 53 | -1.968439 | -0.155115 | 0.890020  |

TPSSTPSS/aug-cc-pVTZ-pp

Energy: -849.0466579

Low Frequencies:

15.6662            41.2020            43.9800

Optimised Coordinates:

|    |           |           |           |
|----|-----------|-----------|-----------|
| 79 | 0.897110  | 0.144406  | 0.142657  |
| 6  | 0.729819  | -1.342403 | -1.352086 |
| 1  | 1.712166  | -1.518468 | -1.820740 |
| 1  | 0.381402  | -2.303577 | -0.947465 |
| 1  | 0.031996  | -1.051128 | -2.150620 |
| 6  | 1.204517  | 1.645780  | 1.599565  |
| 1  | 0.591388  | 2.539018  | 1.410914  |
| 1  | 0.970122  | 1.296430  | 2.615474  |
| 1  | 2.260255  | 1.963705  | 1.595697  |
| 6  | -4.080481 | -0.390500 | 1.434278  |
| 9  | -4.424709 | -1.694132 | 1.669929  |
| 9  | -4.932178 | 0.051585  | 0.458074  |
| 9  | -4.421243 | 0.297043  | 2.567779  |

53            -1.883842   -0.146711   0.868734

MP2/ cc-pVTZ-pp

Energy: -847.2553067

Low Frequencies:

0.3705            46.9148            48.7251

Optimised Coordinates:

|    |           |           |           |
|----|-----------|-----------|-----------|
| 79 | 0.920945  | 0.140651  | 0.136460  |
| 6  | 0.727223  | -1.311871 | -1.313274 |
| 1  | 1.673139  | -1.483579 | -1.839799 |
| 1  | 0.416036  | -2.274756 | -0.894718 |
| 1  | -0.015371 | -1.042426 | -2.071648 |
| 6  | 1.172310  | 1.599213  | 1.571207  |
| 1  | 0.520518  | 2.462660  | 1.401510  |
| 1  | 0.952115  | 1.230564  | 2.578569  |
| 1  | 2.201921  | 1.974883  | 1.586906  |
| 6  | -4.029631 | -0.373575 | 1.419547  |
| 9  | -4.366163 | -1.655839 | 1.658095  |
| 9  | -4.856919 | 0.064073  | 0.450778  |
| 9  | -4.347018 | 0.316461  | 2.531868  |
| 53 | -1.932784 | -0.155413 | 0.876690  |

MP2/aug-cc-pVTZ-pp

Energy: -847.3329937

Low Frequencies:

0.3458            47.1887            49.6646

Optimised Coordinates:

|    |           |           |           |
|----|-----------|-----------|-----------|
| 79 | 0.905243  | 0.141790  | 0.139498  |
| 6  | 0.739121  | -1.377068 | -1.245098 |
| 1  | 1.694503  | -1.553308 | -1.754281 |
| 1  | 0.437537  | -2.320920 | -0.777308 |
| 1  | -0.004962 | -1.144007 | -2.014948 |
| 6  | 1.132240  | 1.667205  | 1.508145  |
| 1  | 0.466883  | 2.509946  | 1.289654  |
| 1  | 0.909379  | 1.333510  | 2.527763  |
| 1  | 2.159889  | 2.050624  | 1.505178  |
| 6  | -4.001272 | -0.376337 | 1.414190  |
| 9  | -4.483302 | -1.605950 | 1.134169  |
| 9  | -4.798428 | 0.498484  | 0.764333  |
| 9  | -4.218189 | -0.177858 | 2.731898  |
| 53 | -1.902321 | -0.155063 | 0.868998  |

**1.BrCF<sub>3</sub>**

B3LYP/aug-cc-pVTZ-pp

Energy: -3127.702105

Low Frequencies:

16.7771            41.6539            47.9895

Optimised Coordinates:

|    |           |           |           |
|----|-----------|-----------|-----------|
| 79 | 0.835442  | -0.115295 | 0.374095  |
| 6  | 0.555671  | -1.602890 | -1.108380 |
| 1  | 1.519563  | -1.963367 | -1.490134 |
| 1  | 0.015110  | -2.474884 | -0.721359 |
| 1  | -0.011782 | -1.226576 | -1.967947 |
| 6  | 1.180833  | 1.367155  | 1.847883  |
| 1  | 0.728816  | 2.329355  | 1.578997  |
| 1  | 0.773310  | 1.081016  | 2.824833  |
| 1  | 2.255735  | 1.542112  | 1.984777  |
| 6  | -4.134780 | 0.301113  | 1.044933  |
| 9  | -4.669793 | -0.829295 | 1.545719  |
| 9  | -4.778704 | 0.562813  | -0.108940 |
| 9  | -4.443917 | 1.294243  | 1.900709  |
| 35 | -2.187975 | 0.137296  | 0.780053  |

TPSSTPSS/aug-cc-pVTZ-pp

Energy: -3127.54581

Low Frequencies:

21.1748            39.0914            49.5279

Optimised Coordinates:

|    |           |           |           |
|----|-----------|-----------|-----------|
| 79 | 0.853913  | -0.053265 | 0.307340  |
| 6  | 0.637203  | -1.544057 | -1.175576 |
| 1  | 1.620522  | -1.861306 | -1.560643 |
| 1  | 0.133129  | -2.443177 | -0.789329 |
| 1  | 0.050247  | -1.187497 | -2.036123 |
| 6  | 1.169374  | 1.436967  | 1.772784  |
| 1  | 0.650206  | 2.375958  | 1.526146  |
| 1  | 0.815767  | 1.122518  | 2.766750  |
| 1  | 2.242266  | 1.673064  | 1.867988  |
| 6  | -3.957718 | -0.008515 | 1.112648  |
| 9  | -4.442993 | -1.249971 | 1.386906  |
| 9  | -4.654112 | 0.453113  | 0.038369  |
| 9  | -4.298111 | 0.783023  | 2.165931  |
| 35 | -1.962907 | -0.025046 | 0.779416  |

MP2/ cc-pVTZ-pp

Energy: -3125.069464

Low Frequencies:

0.3498            27.0251            47.5347

Optimised Coordinates:

|    |           |           |           |
|----|-----------|-----------|-----------|
| 79 | 0.932465  | -0.088782 | 0.335937  |
| 6  | 0.665567  | -1.482588 | -1.156646 |
| 1  | 1.615663  | -1.795052 | -1.605827 |
| 1  | 0.176790  | -2.392805 | -0.790395 |
| 1  | 0.042600  | -1.100145 | -1.973464 |
| 6  | 1.203002  | 1.304928  | 1.827949  |
| 1  | 0.688074  | 2.248123  | 1.611709  |
| 1  | 0.822563  | 0.955563  | 2.794766  |
| 1  | 2.260873  | 1.551442  | 1.977016  |
| 6  | -3.966050 | 0.065860  | 1.067338  |
| 9  | -4.465421 | -1.145089 | 1.350100  |
| 9  | -4.616541 | 0.515997  | -0.014330 |
| 9  | -4.293613 | 0.872591  | 2.085815  |
| 35 | -2.066909 | 0.006274  | 0.784251  |

MP2/aug-cc-pVTZ-pp

Energy: -3125.143337

Low Frequencies:

0.8354            29.6307            49.9653

Optimised Coordinates:

|    |           |           |           |
|----|-----------|-----------|-----------|
| 79 | 0.883786  | -0.001190 | 0.246849  |
| 6  | 0.631502  | -1.465180 | -1.180310 |
| 1  | 1.580957  | -1.733393 | -1.660179 |
| 1  | 0.215502  | -2.383955 | -0.749260 |
| 1  | -0.053170 | -1.143192 | -1.974392 |
| 6  | 1.140917  | 1.462975  | 1.672965  |
| 1  | 0.556620  | 2.361748  | 1.441003  |
| 1  | 0.825459  | 1.121242  | 2.666292  |
| 1  | 2.190693  | 1.771166  | 1.754637  |
| 6  | -3.904356 | -0.106578 | 1.204614  |
| 9  | -4.347096 | -1.357067 | 1.415082  |
| 9  | -4.629645 | 0.398685  | 0.193242  |
| 9  | -4.214735 | 0.605657  | 2.300104  |
| 35 | -2.019243 | -0.064833 | 0.827890  |

**1.CICF<sub>3</sub>**

B3LYP/aug-cc-pVTZ-pp

Energy: -1013.703902

Low Frequencies:

13.3013            26.3991            29.9364

Optimised Coordinates:

|    |           |           |           |
|----|-----------|-----------|-----------|
| 79 | 0.704188  | 0.580157  | 0.326379  |
| 6  | 0.473986  | -0.944405 | -1.126744 |
| 1  | 1.400183  | -1.098928 | -1.695627 |
| 1  | 0.211007  | -1.909291 | -0.674637 |
| 1  | -0.312543 | -0.705800 | -1.854125 |
| 6  | 0.958125  | 2.108932  | 1.770989  |
| 1  | 0.278471  | 2.953699  | 1.600385  |
| 1  | 0.772717  | 1.748981  | 2.791090  |
| 1  | 1.979566  | 2.511070  | 1.753907  |
| 6  | -4.009403 | -0.166502 | 1.889574  |
| 9  | -4.278473 | -1.474376 | 2.039201  |
| 9  | -4.904361 | 0.327468  | 1.017597  |
| 9  | -4.238549 | 0.425155  | 3.073746  |
| 17 | -2.356026 | 0.097131  | 1.341027  |

TPSSTPSS/aug-cc-pVTZ-pp

Energy: -1013.669593

Low Frequencies:

22.7283            39.8769            45.0880

Optimised Coordinates:

|    |           |           |           |
|----|-----------|-----------|-----------|
| 79 | 0.669557  | 0.321208  | 0.687425  |
| 6  | 0.428608  | -1.164941 | -0.794415 |
| 1  | 1.402187  | -1.509739 | -1.181560 |
| 1  | -0.097435 | -2.054164 | -0.410324 |
| 1  | -0.149109 | -0.798547 | -1.658851 |
| 6  | 0.959251  | 1.806607  | 2.161040  |
| 1  | 0.464655  | 2.755666  | 1.896638  |
| 1  | 0.563366  | 1.501355  | 3.143460  |
| 1  | 2.029997  | 2.031014  | 2.301873  |
| 6  | -4.063918 | 0.418389  | 1.402541  |
| 9  | -4.603482 | -0.825546 | 1.368123  |
| 9  | -4.702182 | 1.153849  | 0.458081  |
| 9  | -4.384245 | 0.955361  | 2.606091  |
| 17 | -2.296211 | 0.384570  | 1.136200  |

MP2/ cc-pVTZ-pp

Energy: -1012.088

Low Frequencies:

0.9717            22.3080            26.3578

Optimised Coordinates:

|    |           |           |           |
|----|-----------|-----------|-----------|
| 79 | 0.732879  | 0.189358  | 0.602460  |
| 6  | 0.666978  | -1.298102 | -0.819098 |
| 1  | 1.666172  | -1.576826 | -1.175126 |
| 1  | 0.204187  | -2.216997 | -0.439578 |
| 1  | 0.092101  | -1.002562 | -1.704969 |
| 6  | 0.796516  | 1.677898  | 2.025091  |
| 1  | 0.245220  | 2.574796  | 1.717284  |
| 1  | 0.364818  | 1.361029  | 2.982330  |
| 1  | 1.822517  | 2.001216  | 2.238273  |
| 6  | -4.125120 | 0.657211  | 1.547235  |
| 9  | -4.779101 | -0.459323 | 1.211705  |
| 9  | -4.668958 | 1.660483  | 0.851016  |
| 9  | -4.373820 | 0.889700  | 2.839749  |
| 17 | -2.423341 | 0.517268  | 1.239954  |

MP2/aug-cc-pVTZ-pp

Energy: -1012.156026

Low Frequencies:

|        |         |         |
|--------|---------|---------|
| 0.8015 | 21.8553 | 36.4174 |
|--------|---------|---------|

Optimised Coordinates:

|    |           |           |           |
|----|-----------|-----------|-----------|
| 79 | 0.698140  | 0.203456  | 0.619245  |
| 6  | 0.603068  | -1.285855 | -0.799366 |
| 1  | 1.599949  | -1.566538 | -1.162576 |
| 1  | 0.137048  | -2.197321 | -0.404236 |
| 1  | 0.017103  | -0.979093 | -1.674941 |
| 6  | 0.788189  | 1.693728  | 2.039027  |
| 1  | 0.240073  | 2.591289  | 1.724909  |
| 1  | 0.356899  | 1.373563  | 2.996200  |
| 1  | 1.821903  | 2.002500  | 2.239766  |
| 6  | -4.057004 | 0.631601  | 1.516376  |
| 9  | -4.710610 | -0.484770 | 1.167019  |
| 9  | -4.605042 | 1.641725  | 0.827178  |
| 9  | -4.316355 | 0.851215  | 2.812334  |
| 17 | -2.352313 | 0.499646  | 1.215391  |

**1.ICH<sub>3</sub>**

B3LYP/aug-cc-pVTZ-pp

Energy: -551.4320537

Low Frequencies:

|         |         |         |
|---------|---------|---------|
| 25.6722 | 36.6890 | 38.2591 |
|---------|---------|---------|

Optimised Coordinates:

|    |           |           |           |
|----|-----------|-----------|-----------|
| 79 | 1.150444  | 0.049080  | 0.043889  |
| 6  | 0.829209  | -1.631130 | -1.207910 |
| 1  | 1.739771  | -1.884110 | -1.766930 |
| 1  | 0.542441  | -2.521741 | -0.635879 |
| 1  | 0.036502  | -1.451641 | -1.944049 |
| 6  | 1.547136  | 1.731566  | 1.270498  |
| 1  | 0.883774  | 2.574197  | 1.041646  |
| 1  | 1.422100  | 1.502703  | 2.335726  |
| 1  | 2.578023  | 2.083758  | 1.133349  |
| 6  | -4.061800 | -0.117025 | 1.757943  |
| 1  | -4.332936 | -1.156263 | 1.911892  |
| 1  | -4.680120 | 0.332663  | 0.988004  |
| 1  | -4.132070 | 0.442127  | 2.685176  |
| 53 | -1.965329 | -0.050846 | 1.074653  |

TPSSTPSS/aug-cc-pVTZ-pp

Energy: -551.1674207

Low Frequencies:

|         |         |         |
|---------|---------|---------|
| 24.0209 | 38.3956 | 41.3036 |
|---------|---------|---------|

Optimised Coordinates:

|    |           |           |           |
|----|-----------|-----------|-----------|
| 79 | 1.073708  | 0.045511  | 0.069436  |
| 6  | 0.770814  | -1.624550 | -1.191701 |
| 1  | 1.691283  | -1.865552 | -1.749964 |
| 1  | 0.487985  | -2.525455 | -0.625221 |
| 1  | -0.023066 | -1.446324 | -1.933518 |
| 6  | 1.486386  | 1.719296  | 1.293919  |
| 1  | 0.825847  | 2.570937  | 1.068925  |
| 1  | 1.364831  | 1.489453  | 2.363969  |
| 1  | 2.524437  | 2.063786  | 1.149935  |
| 6  | -3.965788 | -0.111886 | 1.726385  |
| 1  | -4.218066 | -1.152625 | 1.927874  |
| 1  | -4.586965 | 0.295513  | 0.929081  |
| 1  | -4.038070 | 0.493045  | 2.629950  |
| 53 | -1.836191 | -0.047814 | 1.028937  |

MP2/cc-pVTZ-pp

Energy: -549.8412558

Low Frequencies:

|        |         |         |
|--------|---------|---------|
| 1.7344 | 40.1861 | 58.5276 |
|--------|---------|---------|

Optimised Coordinates:

|    |          |           |           |
|----|----------|-----------|-----------|
| 79 | 1.114960 | 0.048468  | 0.051793  |
| 6  | 0.778018 | -1.577974 | -1.166409 |

|    |           |           |           |
|----|-----------|-----------|-----------|
| 1  | 1.676164  | -1.867279 | -1.725448 |
| 1  | 0.460793  | -2.460034 | -0.598618 |
| 1  | -0.006560 | -1.383633 | -1.906483 |
| 6  | 1.474587  | 1.675660  | 1.262546  |
| 1  | 0.830410  | 2.526291  | 1.012530  |
| 1  | 1.298040  | 1.449830  | 2.320319  |
| 1  | 2.510061  | 2.028172  | 1.182456  |
| 6  | -3.927155 | -0.113813 | 1.721318  |
| 1  | -4.133084 | -1.103501 | 2.116417  |
| 1  | -4.580746 | 0.095256  | 0.880417  |
| 1  | -4.064043 | 0.633942  | 2.495950  |
| 53 | -1.874301 | -0.048052 | 1.041219  |

MP2/aug-cc-pVTZ-pp

Energy: -549.8923144

Low Frequencies:

|        |         |         |
|--------|---------|---------|
| 3.0581 | 41.9427 | 64.2119 |
|--------|---------|---------|

Optimised Coordinates:

|    |           |           |           |
|----|-----------|-----------|-----------|
| 79 | 1.096677  | 0.047975  | 0.057937  |
| 6  | 0.763847  | -1.588258 | -1.149626 |
| 1  | 1.667291  | -1.873427 | -1.703684 |
| 1  | 0.448640  | -2.462399 | -0.567157 |
| 1  | -0.023301 | -1.391931 | -1.887583 |
| 6  | 1.453223  | 1.684980  | 1.257725  |
| 1  | 0.802208  | 2.527508  | 0.994935  |
| 1  | 1.274057  | 1.456939  | 2.315386  |
| 1  | 2.490163  | 2.033623  | 1.169883  |
| 6  | -3.898856 | -0.113173 | 1.711835  |
| 1  | -4.131589 | -1.133394 | 2.001576  |
| 1  | -4.540418 | 0.205356  | 0.895785  |
| 1  | -4.001751 | 0.556578  | 2.560219  |
| 53 | -1.843049 | -0.047046 | 1.030777  |

### 1.BrCH<sub>3</sub>

B3LYP/aug-cc-pVTZ-pp

Energy: -2829.850197

Low Frequencies:

|         |         |         |
|---------|---------|---------|
| 22.2369 | 23.0004 | 30.6564 |
|---------|---------|---------|

Optimised Coordinates:

|    |          |           |           |
|----|----------|-----------|-----------|
| 79 | 1.183420 | -0.065358 | 0.047852  |
| 6  | 0.544924 | -0.308664 | -1.958289 |

|    |           |           |           |
|----|-----------|-----------|-----------|
| 1  | 1.396870  | -0.347518 | -2.650322 |
| 1  | -0.025306 | -1.236176 | -2.097454 |
| 1  | -0.099568 | 0.516668  | -2.287111 |
| 6  | 1.852806  | 0.177595  | 2.043950  |
| 1  | 1.478121  | -0.616491 | 2.702565  |
| 1  | 2.949109  | 0.157552  | 2.106797  |
| 1  | 1.523251  | 1.132477  | 2.473398  |
| 6  | -4.029241 | 0.104629  | 1.719661  |
| 1  | -4.589929 | -0.648829 | 1.176197  |
| 1  | -4.421385 | 1.094957  | 1.512545  |
| 1  | -4.049349 | -0.098593 | 2.785363  |
| 35 | -2.156577 | 0.041085  | 1.112857  |

TPSSTPSS/aug-cc-pVTZ-pp

Energy: -2829.667992

Low Frequencies:

|         |         |         |
|---------|---------|---------|
| 19.9525 | 36.7845 | 40.9831 |
|---------|---------|---------|

Optimised Coordinates:

|    |           |           |           |
|----|-----------|-----------|-----------|
| 79 | 1.051504  | -0.065189 | 0.086228  |
| 6  | 0.434209  | -0.297175 | -1.921322 |
| 1  | 1.298346  | -0.371565 | -2.603544 |
| 1  | -0.170450 | -1.207509 | -2.065266 |
| 1  | -0.177418 | 0.552572  | -2.266100 |
| 6  | 1.729542  | 0.166465  | 2.074211  |
| 1  | 1.358737  | -0.634985 | 2.733888  |
| 1  | 2.831424  | 0.147923  | 2.130655  |
| 1  | 1.399573  | 1.122112  | 2.513559  |
| 6  | -3.829537 | 0.105096  | 1.663382  |
| 1  | -4.372339 | -0.703354 | 1.174605  |
| 1  | -4.237636 | 1.075057  | 1.381211  |
| 1  | -3.832828 | -0.020093 | 2.745639  |
| 35 | -1.925984 | 0.033981  | 1.040861  |

MP2/ cc-pVTZ-pp

Energy: -2827.653569

Low Frequencies:

|         |         |         |
|---------|---------|---------|
| 14.8183 | 24.6350 | 40.3056 |
|---------|---------|---------|

Optimised Coordinates:

|    |           |           |           |
|----|-----------|-----------|-----------|
| 79 | 1.132935  | -0.068318 | 0.071340  |
| 6  | 0.519702  | -0.198344 | -1.889920 |
| 1  | 1.361787  | -0.259060 | -2.590444 |
| 1  | -0.102238 | -1.083580 | -2.070145 |

|    |           |           |           |
|----|-----------|-----------|-----------|
| 1  | -0.078767 | 0.669100  | -2.193724 |
| 6  | 1.732281  | 0.062056  | 2.036876  |
| 1  | 1.352354  | -0.771224 | 2.640375  |
| 1  | 2.824003  | 0.054972  | 2.144781  |
| 1  | 1.375853  | 0.981483  | 2.517015  |
| 6  | -3.870533 | 0.104883  | 1.618029  |
| 1  | -4.453679 | -0.570532 | 1.000850  |
| 1  | -4.239262 | 1.119227  | 1.507235  |
| 1  | -3.928659 | -0.198960 | 2.657973  |
| 35 | -2.022462 | 0.041945  | 1.046518  |

MP2/aug-cc-pVTZ-pp

Energy: -2827.701427

Low Frequencies:

|        |         |         |
|--------|---------|---------|
| 4.2505 | 17.8836 | 38.8607 |
|--------|---------|---------|

Optimised Coordinates:

|    |           |           |           |
|----|-----------|-----------|-----------|
| 79 | 1.102336  | -0.062548 | 0.079716  |
| 6  | 0.487429  | -0.198605 | -1.881220 |
| 1  | 1.334497  | -0.255505 | -2.577199 |
| 1  | -0.129995 | -1.090255 | -2.049387 |
| 1  | -0.115848 | 0.669550  | -2.175951 |
| 6  | 1.700515  | 0.073933  | 2.045818  |
| 1  | 1.319286  | -0.764635 | 2.642479  |
| 1  | 2.793672  | 0.072290  | 2.146566  |
| 1  | 1.333529  | 0.995209  | 2.516010  |
| 6  | -3.815964 | 0.094089  | 1.603297  |
| 1  | -4.371571 | -0.663646 | 1.059952  |
| 1  | -4.214998 | 1.080083  | 1.387245  |
| 1  | -3.854831 | -0.102296 | 2.670071  |
| 35 | -1.964632 | 0.035850  | 1.029265  |

## 2.I<sub>2</sub>

B3LYP/aug-cc-pVTZ-pp

Energy: -1403.097770

Low Frequencies:

20.7486            26.0922            29.0342

Optimised Coordinates:

|    |           |           |           |
|----|-----------|-----------|-----------|
| 79 | 1.289191  | 0.049302  | -0.060737 |
| 6  | 0.896506  | -1.615027 | -1.270949 |
| 9  | -0.071758 | -1.452021 | -2.227165 |
| 9  | 2.024966  | -1.969460 | -1.991566 |
| 9  | 0.545124  | -2.766210 | -0.615117 |
| 6  | 1.897858  | 1.707053  | 1.066016  |
| 9  | 3.236386  | 1.983258  | 0.840978  |
| 9  | 1.262506  | 2.889556  | 0.787555  |
| 9  | 1.808710  | 1.578393  | 2.427354  |
| 53 | -1.432413 | 0.104326  | 1.024547  |
| 53 | -4.078829 | 0.149114  | 2.088280  |

## 2.ICF<sub>3</sub>

B3LYP/aug-cc-pVTZ-pp

Energy: -1445.026756

Low Frequencies:

12.0725            14.0029            17.0088

Optimised Coordinates:

|    |           |           |           |
|----|-----------|-----------|-----------|
| 79 | 1.016389  | 0.049535  | 0.086146  |
| 6  | 0.717723  | -1.613444 | -1.141848 |
| 9  | -0.246053 | -1.470147 | -2.117545 |
| 9  | 1.850100  | -1.972715 | -1.851524 |
| 9  | 0.358945  | -2.775472 | -0.491614 |
| 6  | 1.425553  | 1.714248  | 1.278855  |
| 9  | 2.730652  | 2.158541  | 1.159809  |
| 9  | 0.673350  | 2.838595  | 1.011403  |
| 9  | 1.267942  | 1.526830  | 2.636016  |
| 6  | -4.179793 | -0.128907 | 1.799940  |
| 9  | -4.622696 | -1.395226 | 1.915747  |
| 9  | -5.007833 | 0.501698  | 0.945426  |
| 9  | -4.337137 | 0.454453  | 3.003176  |
| 53 | -2.103161 | -0.052518 | 1.122831  |

## 2.ICH<sub>3</sub>

B3LYP/aug-cc-pVTZ-pp

Energy: -1147.181737

Low Frequencies:

6.8493            13.1520            17.2338

Optimised Coordinates:

|    |           |           |           |
|----|-----------|-----------|-----------|
| 79 | 1.316685  | 0.060941  | -0.009832 |
| 6  | 0.982305  | -1.594828 | -1.232877 |
| 9  | 0.010252  | -1.433306 | -2.202512 |
| 9  | 2.093738  | -1.995492 | -1.957895 |
| 9  | 0.596015  | -2.749261 | -0.577280 |
| 6  | 1.713642  | 1.717321  | 1.193149  |
| 9  | 3.001207  | 2.214364  | 1.065703  |
| 9  | 0.919795  | 2.825202  | 0.961655  |
| 9  | 1.585915  | 1.506967  | 2.553852  |
| 6  | -4.352406 | -0.138686 | 1.848902  |
| 1  | -4.619553 | -1.181798 | 1.972737  |
| 1  | -4.962810 | 0.330307  | 1.085791  |
| 1  | -4.425868 | 0.396167  | 2.788816  |
| 53 | -2.285880 | -0.054118 | 1.192582  |

MP2/aug-cc-pVTZ-pp

Energy: -1144.810450

Low Frequencies:

3.5145            16.6613            17.2291

Optimised Coordinates:

|    |           |           |           |
|----|-----------|-----------|-----------|
| 79 | 1.166542  | 0.099910  | 0.074241  |
| 6  | 0.864079  | -1.503340 | -1.130832 |
| 9  | -0.099969 | -1.338674 | -2.097943 |
| 9  | 1.977159  | -1.886571 | -1.849144 |
| 9  | 0.484243  | -2.658639 | -0.488374 |
| 6  | 1.517570  | 1.705122  | 1.263498  |
| 9  | 2.807605  | 2.187458  | 1.193111  |
| 9  | 0.746614  | 2.813008  | 0.998885  |
| 9  | 1.328161  | 1.492763  | 2.609150  |
| 6  | -4.042418 | -0.101504 | 1.772750  |
| 1  | -4.150101 | -0.949855 | 2.439909  |
| 1  | -4.679279 | -0.216486 | 0.902369  |
| 1  | -4.265128 | 0.824536  | 2.291600  |
| 53 | -2.011534 | -0.025971 | 1.110185  |

**2.BrCF<sub>3</sub>**

B3LYP/aug-cc-pVTZ-pp

Energy: -3723.449740834103

Low Frequencies:

3.6877            11.3584            12.1205

Optimised Coordinates:

|    |           |           |           |
|----|-----------|-----------|-----------|
| 79 | 1.001808  | 0.047986  | 0.092507  |
| 6  | 0.672663  | -1.613653 | -1.124485 |
| 9  | -0.301517 | -1.456050 | -2.092110 |
| 9  | 1.783382  | -2.014055 | -1.846806 |
| 9  | 0.287759  | -2.763935 | -0.461772 |
| 6  | 1.381301  | 1.709919  | 1.294155  |
| 9  | 2.667272  | 2.208995  | 1.180969  |
| 9  | 0.585023  | 2.812395  | 1.047731  |
| 9  | 1.234867  | 1.501759  | 2.652767  |
| 6  | -4.086418 | -0.124282 | 1.765949  |
| 9  | -4.516558 | -1.388460 | 1.884018  |
| 9  | -4.901525 | 0.501378  | 0.904668  |
| 9  | -4.232374 | 0.465100  | 2.961021  |
| 35 | -2.243430 | -0.059113 | 1.166320  |

## 2.CICF<sub>3</sub>

B3LYP/aug-cc-pVTZ-pp

Energy: -1609.455596100921

Low Frequencies:

8.8976            11.3577            12.2873

Optimised Coordinates:

|    |           |           |           |
|----|-----------|-----------|-----------|
| 79 | 0.830928  | 0.592685  | 0.292158  |
| 6  | 0.594409  | -0.909541 | -1.133018 |
| 6  | 1.082860  | 2.096469  | 1.713021  |
| 9  | 0.337266  | -2.169420 | -0.621157 |
| 9  | -0.439117 | -0.711854 | -2.032003 |
| 9  | 1.693980  | -1.113326 | -1.948535 |
| 9  | 2.288298  | 2.772171  | 1.634044  |
| 9  | 1.037488  | 1.675045  | 3.030403  |
| 9  | 0.142963  | 3.111591  | 1.669021  |
| 6  | -4.239604 | -0.179978 | 1.933940  |
| 9  | -4.501414 | -1.485428 | 2.076166  |
| 9  | -5.116256 | 0.317758  | 1.052515  |
| 9  | -4.467574 | 0.411616  | 3.113184  |
| 17 | -2.587160 | 0.081458  | 1.401221  |

## 3.I<sub>2</sub>

B3LYP/aug-cc-pVTZ-pp

Energy: -996.752327

Low Frequencies:

23.9966            28.3183            37.2872

Optimised Coordinates:

|    |           |           |           |
|----|-----------|-----------|-----------|
| 79 | 1.704430  | -6.359567 | 0.083757  |
| 7  | 0.423142  | -6.181179 | 1.656792  |
| 7  | 3.416741  | -6.439395 | -1.015166 |
| 6  | -0.427867 | -5.012371 | 1.716133  |
| 1  | 0.121747  | -4.120248 | 1.414356  |
| 1  | -1.324702 | -5.087370 | 1.078387  |
| 1  | -0.782138 | -4.853574 | 2.747257  |
| 6  | -0.297137 | -7.359889 | 2.087555  |
| 1  | -1.183719 | -7.584585 | 1.470950  |
| 1  | 0.351873  | -8.235984 | 2.069124  |
| 1  | -0.652831 | -7.229540 | 3.122137  |
| 6  | 3.809295  | -7.714322 | -1.575876 |
| 1  | 3.637085  | -8.519095 | -0.860562 |
| 1  | 3.274283  | -7.970309 | -2.505946 |
| 1  | 4.884074  | -7.707208 | -1.818083 |
| 6  | 3.678676  | -5.367659 | -1.951617 |
| 1  | 4.753075  | -5.329024 | -2.192650 |
| 1  | 3.140969  | -5.476474 | -2.908614 |
| 1  | 3.401245  | -4.404725 | -1.521787 |
| 53 | -0.127832 | -6.776964 | -1.921514 |
| 53 | -2.183907 | -7.245313 | -4.169987 |

### 3.ICF<sub>3</sub>

B3LYP/aug-cc-pVTZ-pp

Energy: -1038.632553

Low Frequencies:

10.3103            29.4422            31.7997

Optimised Coordinates:

|    |           |           |           |
|----|-----------|-----------|-----------|
| 79 | 1.652271  | -6.388813 | 0.033286  |
| 7  | 0.281071  | -6.209169 | 1.541501  |
| 7  | 3.307756  | -6.487766 | -1.164352 |
| 6  | -0.611615 | -5.075320 | 1.510915  |
| 1  | -0.071910 | -4.166727 | 1.238348  |
| 1  | -1.457288 | -5.182670 | 0.803384  |
| 1  | -1.060479 | -4.909172 | 2.506202  |
| 6  | -0.426475 | -7.397916 | 1.953344  |
| 1  | -1.256752 | -7.688386 | 1.279734  |
| 1  | 0.253869  | -8.248926 | 2.017683  |
| 1  | -0.874805 | -7.254968 | 2.952449  |
| 6  | 3.673047  | -7.775298 | -1.704753 |

|    |           |           |           |
|----|-----------|-----------|-----------|
| 1  | 3.576096  | -8.553598 | -0.945778 |
| 1  | 3.069019  | -8.088804 | -2.579073 |
| 1  | 4.724762  | -7.769686 | -2.041898 |
| 6  | 3.488199  | -5.453921 | -2.155140 |
| 1  | 4.538561  | -5.422176 | -2.495012 |
| 1  | 2.871557  | -5.585586 | -3.066087 |
| 1  | 3.248617  | -4.474123 | -1.738322 |
| 53 | -0.339060 | -6.946949 | -2.121053 |
| 6  | -1.853195 | -7.374196 | -3.747433 |
| 9  | -2.207962 | -6.259230 | -4.432128 |
| 9  | -1.392441 | -8.254674 | -4.669197 |
| 9  | -3.002796 | -7.902011 | -3.260991 |

#### 4.I<sub>2</sub>

B3LYP/aug-cc-pVTZ-pp

Energy: -1648.103049176609

Low Frequencies:

|         |         |         |
|---------|---------|---------|
| 34.6939 | 42.4037 | 43.0094 |
|---------|---------|---------|

Optimised Coordinates:

|    |           |           |           |
|----|-----------|-----------|-----------|
| 79 | 0.012787  | 0.214160  | -0.291121 |
| 17 | -1.049653 | -1.830797 | -0.178005 |
| 17 | 1.054786  | 2.234882  | -0.691983 |
| 53 | 0.218226  | 0.472132  | 2.626668  |
| 53 | 0.409264  | 0.719143  | 5.457485  |

MP2/aug-cc-pVTZ-pp

Energy: -1644.911879147108

Low Frequencies:

|         |         |         |
|---------|---------|---------|
| 41.6864 | 50.2627 | 51.8036 |
|---------|---------|---------|

Optimised Coordinates:

|    |           |           |           |
|----|-----------|-----------|-----------|
| 79 | 0.014917  | 0.200891  | -0.194123 |
| 17 | -1.013520 | -1.780053 | -0.078386 |
| 17 | 1.025501  | 2.159041  | -0.567735 |
| 53 | 0.207713  | 0.447044  | 2.590692  |
| 53 | 0.401349  | 0.694269  | 5.387625  |

#### 4.ICF<sub>3</sub>

B3LYP/aug-cc-pVTZ-pp

Energy: -1690.032594329337

Low Frequencies:

|         |         |         |
|---------|---------|---------|
| 13.0499 | 24.7111 | 34.9860 |
|---------|---------|---------|

Optimised Coordinates:

|    |           |           |           |
|----|-----------|-----------|-----------|
| 79 | 0.021843  | 0.209946  | -0.543082 |
| 17 | -1.014077 | -1.845960 | -0.332349 |
| 17 | 1.053800  | 2.256869  | -0.845701 |
| 53 | 0.111991  | 0.401037  | 2.756463  |
| 6  | 0.212666  | 0.583103  | 4.928868  |
| 9  | -0.705536 | -0.189629 | 5.541941  |
| 9  | 1.417021  | 0.215242  | 5.408765  |
| 9  | -0.003507 | 1.847781  | 5.340041  |

MP2/aug-cc-pVTZ-pp

Energy: -1687.251044

Low Frequencies:

|        |         |         |
|--------|---------|---------|
| 1.6810 | 26.0121 | 35.1247 |
|--------|---------|---------|

Optimised Coordinates:

|    |           |           |           |
|----|-----------|-----------|-----------|
| 79 | 0.013497  | 0.196155  | -0.441704 |
| 17 | -1.133386 | -1.718443 | -0.278869 |
| 17 | 1.158481  | 2.107102  | -0.653337 |
| 53 | 0.133436  | 0.429310  | 2.721551  |
| 6  | 0.215720  | 0.588591  | 4.850791  |
| 9  | -0.486327 | -0.382928 | 5.458352  |
| 9  | 1.474693  | 0.504652  | 5.313773  |
| 9  | -0.281911 | 1.757881  | 5.288320  |

#### 4.BrCF<sub>3</sub>

B3LYP/aug-cc-pVTZ-pp

Energy: -3968.455100807475

Low Frequencies:

|         |         |         |
|---------|---------|---------|
| 13.3497 | 19.8561 | 31.0646 |
|---------|---------|---------|

Optimised Coordinates:

|   |    |   |           |           |           |
|---|----|---|-----------|-----------|-----------|
| 1 | 79 | 0 | 0.031970  | 0.228568  | -0.508795 |
| 2 | 17 | 0 | -0.998846 | -1.824023 | -0.220890 |
| 3 | 17 | 0 | 1.061425  | 2.277451  | -0.825014 |
| 4 | 35 | 0 | 0.101863  | 0.384997  | 2.929604  |
| 5 | 6  | 0 | 0.204742  | 0.568341  | 4.854242  |
| 6 | 9  | 0 | -0.711441 | -0.194616 | 5.469716  |
| 7 | 9  | 0 | 1.409505  | 0.201510  | 5.317205  |
| 8 | 9  | 0 | -0.005014 | 1.836160  | 5.238878  |

#### 5.I<sub>2</sub>

B3LYP/aug-cc-pVTZ-pp

Energy: -1319.268132

Low Frequencies:

19.0898            27.3716            39.9415

Optimised Coordinates:

|    |           |          |           |
|----|-----------|----------|-----------|
| 79 | -0.101029 | 0.000000 | 0.000000  |
| 53 | 0.145677  | 0.000000 | 2.604056  |
| 53 | 0.145677  | 0.000000 | -2.604056 |
| 53 | -3.071600 | 0.000000 | 0.000000  |
| 53 | -5.918725 | 0.000000 | 0.000000  |

MP2/aug-cc-pVTZ-pp

Energy: -1315.271005

Low Frequencies:

28.2175            31.9360            46.2223

Optimised Coordinates:

|    |           |          |           |
|----|-----------|----------|-----------|
| 79 | -0.146406 | 0.000000 | 0.000000  |
| 53 | 0.054903  | 0.000000 | 2.508622  |
| 53 | 0.054903  | 0.000000 | -2.508622 |
| 53 | -2.975293 | 0.000000 | 0.000000  |
| 53 | -5.788107 | 0.000000 | 0.000000  |

## 6.I<sub>2</sub>

B3LYP/aug-cc-pVTZ-pp

Energy: -879.250326

Low Frequencies:

40.4145            50.0489            60.9001

Optimised Coordinates:

|    |           |           |           |
|----|-----------|-----------|-----------|
| 79 | -0.058527 | 0.057296  | -0.337570 |
| 8  | 0.767366  | 1.835405  | -0.710663 |
| 1  | 0.492619  | 2.455808  | -0.028945 |
| 8  | -0.902747 | -1.748520 | -0.286278 |
| 1  | -0.571173 | -2.227070 | 0.479355  |
| 53 | 0.099971  | 0.316681  | 2.431388  |
| 53 | 0.269252  | 0.595385  | 5.375796  |

MP2/aug-cc-pVTZ-pp

Energy: -876.842206

Low Frequencies:

47.8731            53.5116            69.1565

Optimised Coordinates:

|    |           |           |           |
|----|-----------|-----------|-----------|
| 79 | -0.062665 | 0.059552  | -0.332706 |
| 8  | 0.676835  | 1.837620  | -0.705829 |
| 1  | 0.556986  | 2.380398  | 0.084543  |
| 8  | -0.820861 | -1.748828 | -0.282649 |

|    |           |           |          |
|----|-----------|-----------|----------|
| 1  | -0.605603 | -2.136914 | 0.575671 |
| 53 | 0.092841  | 0.311693  | 2.354509 |
| 53 | 0.259226  | 0.581461  | 5.229542 |

### 6.ICF<sub>3</sub>

B3LYP/aug-cc-pVTZ-pp

Energy: -921.168503

Low Frequencies:

|         |         |         |
|---------|---------|---------|
| 38.4593 | 41.5368 | 48.1238 |
|---------|---------|---------|

Optimised Coordinates:

|    |           |           |           |
|----|-----------|-----------|-----------|
| 79 | -0.053875 | 0.056840  | -0.374530 |
| 8  | 0.843418  | 1.826951  | -0.688011 |
| 1  | 0.437860  | 2.469064  | -0.098320 |
| 8  | -0.958603 | -1.732267 | -0.272411 |
| 1  | -0.524518 | -2.242773 | 0.416971  |
| 53 | 0.057752  | 0.299127  | 2.648962  |
| 6  | 0.147590  | 0.474830  | 4.874533  |
| 9  | 1.151167  | -0.259901 | 5.408157  |
| 9  | -0.992010 | 0.056001  | 5.472199  |
| 9  | 0.347147  | 1.749310  | 5.283314  |

MP2/aug-cc-pVTZ-pp

Energy: -919.168675

Low Frequencies:

|        |         |         |
|--------|---------|---------|
| 1.0422 | 33.5283 | 47.1721 |
|--------|---------|---------|

Optimised Coordinates:

|    |           |           |           |
|----|-----------|-----------|-----------|
| 79 | -0.060961 | 0.055578  | -0.320814 |
| 8  | 1.031366  | 1.666172  | -0.601004 |
| 1  | 0.729794  | 2.325557  | 0.035732  |
| 8  | -1.160460 | -1.572578 | -0.244264 |
| 1  | -0.816485 | -2.111661 | 0.478379  |
| 53 | 0.059307  | 0.298939  | 2.625216  |
| 6  | 0.147924  | 0.477920  | 4.790818  |
| 9  | 1.217400  | -0.154627 | 5.314919  |
| 9  | -0.937664 | -0.045430 | 5.395593  |
| 9  | 0.227831  | 1.761632  | 5.196292  |

### 6.ICH<sub>3</sub>

B3LYP/aug-cc-pVTZ-pp

Energy: -623.317041

Low Frequencies:

|         |         |         |
|---------|---------|---------|
| 24.8982 | 44.7162 | 46.7530 |
|---------|---------|---------|

Optimised Coordinates:

|    |           |           |           |
|----|-----------|-----------|-----------|
| 79 | -0.064087 | 0.051716  | -0.496807 |
| 8  | 0.833608  | 1.829763  | -0.814540 |
| 1  | 0.517210  | 2.423472  | -0.127581 |
| 8  | -0.971029 | -1.742215 | -0.346496 |
| 1  | -0.571908 | -2.190944 | 0.404369  |
| 53 | 0.060738  | 0.313265  | 2.799348  |
| 6  | 0.149796  | 0.479056  | 4.994294  |
| 1  | 1.018150  | -0.073480 | 5.337069  |
| 1  | -0.763196 | 0.055884  | 5.399678  |
| 1  | 0.235421  | 1.530067  | 5.248731  |

MP2/aug-cc-pVTZ-pp

Energy: -621.729909

Low Frequencies:

|        |         |         |
|--------|---------|---------|
| 8.7168 | 33.0405 | 49.4193 |
|--------|---------|---------|

Optimised Coordinates:

|    |           |           |           |
|----|-----------|-----------|-----------|
| 79 | -0.050363 | 0.044950  | -0.419047 |
| 8  | 0.706926  | 1.844828  | -0.686700 |
| 1  | 0.334934  | 2.396071  | 0.012432  |
| 8  | -0.806225 | -1.772481 | -0.318154 |
| 1  | -0.471616 | -2.154964 | 0.502074  |
| 53 | 0.072396  | 0.309409  | 2.735097  |
| 6  | 0.150502  | 0.480661  | 4.885793  |
| 1  | 0.767054  | -0.325364 | 5.271116  |
| 1  | -0.860615 | 0.404596  | 5.273296  |
| 1  | 0.583497  | 1.443764  | 5.137282  |

## 6.BrCF<sub>3</sub>

B3LYP/aug-cc-pVTZ-pp

Energy: -3199.585509

Low Frequencies:

|         |         |         |
|---------|---------|---------|
| 33.5373 | 38.9150 | 41.5416 |
|---------|---------|---------|

Optimised Coordinates:

|    |           |           |           |
|----|-----------|-----------|-----------|
| 79 | -0.196879 | 0.109497  | -0.923419 |
| 8  | 0.120263  | 2.078070  | -1.220344 |
| 1  | 0.985072  | 2.149309  | -1.635569 |
| 8  | -0.520912 | -1.854122 | -0.595655 |
| 1  | -1.338192 | -2.068871 | -1.055300 |
| 6  | 0.230874  | 0.578448  | 4.148660  |
| 9  | 0.105384  | 1.858912  | 4.543208  |
| 9  | -0.706734 | -0.129303 | 4.805442  |

|    |          |          |          |
|----|----------|----------|----------|
| 9  | 1.428677 | 0.147275 | 4.585754 |
| 35 | 0.056985 | 0.392783 | 2.213069 |

### 6.CICF<sub>3</sub>

B3LYP/aug-cc-pVTZ-pp

Energy: -1085.588814

Low Frequencies:

|         |         |         |
|---------|---------|---------|
| 29.0204 | 37.5942 | 38.7498 |
|---------|---------|---------|

Optimised Coordinates:

|    |           |           |           |
|----|-----------|-----------|-----------|
| 79 | -0.136953 | 0.150226  | -0.913258 |
| 8  | 0.189356  | 2.119924  | -1.212401 |
| 1  | 0.836166  | 2.174531  | -1.922242 |
| 8  | -0.449427 | -1.808604 | -0.533897 |
| 1  | -1.297982 | -2.021983 | -0.933348 |
| 6  | 0.211616  | 0.539541  | 4.166775  |
| 17 | 0.078914  | 0.349209  | 2.428158  |
| 9  | 0.167533  | 1.832146  | 4.528043  |
| 9  | -0.786668 | -0.088244 | 4.810338  |
| 9  | 1.366002  | 0.034445  | 4.632124  |

### 7.I<sub>2</sub>

B3LYP/aug-cc-pVTZ-pp

Energy: -913.332981

Low Frequencies:

|         |         |         |
|---------|---------|---------|
| 31.6862 | 36.0237 | 40.0380 |
|---------|---------|---------|

Optimised Coordinates:

|    |          |           |          |
|----|----------|-----------|----------|
| 79 | 3.648005 | -0.748982 | 0.626871 |
| 6  | 3.368767 | -2.711313 | 0.324857 |
| 7  | 3.201265 | -3.833809 | 0.093230 |
| 6  | 3.909851 | 1.232582  | 0.784962 |
| 7  | 4.053462 | 2.381327  | 0.819177 |
| 53 | 4.018183 | -1.147348 | 3.626595 |
| 53 | 4.355878 | -1.512307 | 6.382341 |

MP2/aug-cc-pVTZ-pp

Energy: -910.806854

Low Frequencies:

|         |         |         |
|---------|---------|---------|
| 36.3101 | 38.8292 | 46.3986 |
|---------|---------|---------|

Optimised Coordinates:

|    |          |           |          |
|----|----------|-----------|----------|
| 79 | 3.648711 | -0.752137 | 0.658231 |
| 6  | 3.378059 | -2.670885 | 0.380453 |

|    |          |           |          |
|----|----------|-----------|----------|
| 7  | 3.210138 | -3.819702 | 0.172811 |
| 6  | 3.905777 | 1.181005  | 0.828187 |
| 7  | 4.055308 | 2.349307  | 0.889875 |
| 53 | 4.007324 | -1.132123 | 3.504139 |
| 53 | 4.350095 | -1.495315 | 6.224337 |

### 7.ICF<sub>3</sub>

B3LYP/aug-cc-pVTZ-pp

Energy: -955.266164

Low Frequencies:

|        |         |         |
|--------|---------|---------|
| 9.6098 | 18.7330 | 28.7847 |
|--------|---------|---------|

Optimised Coordinates:

|    |          |           |           |
|----|----------|-----------|-----------|
| 79 | 5.048082 | -2.428580 | 0.809491  |
| 6  | 4.703501 | -4.285776 | 1.477789  |
| 7  | 4.510626 | -5.368273 | 1.844407  |
| 6  | 5.406697 | -0.589747 | 0.098851  |
| 7  | 5.620738 | 0.464764  | -0.331952 |
| 53 | 4.000410 | -1.111633 | 3.801148  |
| 6  | 3.316796 | -0.271876 | 5.686369  |
| 9  | 3.473441 | 1.062652  | 5.721639  |
| 9  | 2.013369 | -0.525055 | 5.897730  |
| 9  | 3.995303 | -0.779480 | 6.730285  |

MP2/aug-cc-pVTZ-pp

Energy: -953.149699

Low Frequencies:

|        |         |         |
|--------|---------|---------|
| 0.6713 | 17.7961 | 30.4393 |
|--------|---------|---------|

Optimised Coordinates:

|    |          |           |           |
|----|----------|-----------|-----------|
| 79 | 5.017048 | -2.386003 | 0.898645  |
| 6  | 4.666060 | -4.193464 | 1.560446  |
| 7  | 4.456983 | -5.286616 | 1.952210  |
| 6  | 5.374171 | -0.586215 | 0.219491  |
| 7  | 5.592156 | 0.495811  | -0.197497 |
| 53 | 4.016748 | -1.142350 | 3.715219  |
| 6  | 3.356957 | -0.325941 | 5.571974  |
| 9  | 3.474533 | 1.009490  | 5.599592  |
| 9  | 2.068693 | -0.612776 | 5.810670  |
| 9  | 4.065617 | -0.804942 | 6.605005  |

### 7.ICH<sub>3</sub>

B3LYP/aug-cc-pVTZ-pp

Energy: -657.423147

Low Frequencies:

9.2124            13.1296            29.1855

Optimised Coordinates:

|    |          |           |           |
|----|----------|-----------|-----------|
| 79 | 5.124913 | -2.517010 | 0.596459  |
| 6  | 4.729663 | -4.365479 | 1.261723  |
| 7  | 4.506021 | -5.441541 | 1.631891  |
| 6  | 5.529583 | -0.680777 | -0.096687 |
| 7  | 5.768589 | 0.375098  | -0.512559 |
| 53 | 3.902784 | -0.994884 | 4.103196  |
| 6  | 3.211287 | -0.149061 | 5.973071  |
| 1  | 3.179178 | 0.928042  | 5.858459  |
| 1  | 2.224401 | -0.549706 | 6.172915  |
| 1  | 3.912543 | -0.437687 | 6.747288  |

MP2/aug-cc-pVTZ-pp

Energy: -655.717698

Low Frequencies:

2.7198            12.1413            37.4915

Optimised Coordinates:

|    |          |           |           |
|----|----------|-----------|-----------|
| 79 | 5.031779 | -2.404682 | 0.862084  |
| 6  | 4.639448 | -4.210272 | 1.506069  |
| 7  | 4.406872 | -5.304283 | 1.882876  |
| 6  | 5.431690 | -0.608421 | 0.196756  |
| 7  | 5.676864 | 0.469807  | -0.215711 |
| 53 | 3.971680 | -1.095607 | 3.842508  |
| 6  | 3.311111 | -0.268005 | 5.694743  |
| 1  | 3.243163 | 0.808120  | 5.579964  |
| 1  | 2.340671 | -0.692002 | 5.927874  |
| 1  | 4.035682 | -0.527658 | 6.458594  |

**7.BrCF<sub>3</sub>**

B3LYP/aug-cc-pVTZ-pp

Energy: -3233.690307

Low Frequencies:

9.5134            12.5025            22.4516

Optimised Coordinates:

|    |          |           |           |
|----|----------|-----------|-----------|
| 79 | 5.040323 | -2.426452 | 0.830780  |
| 6  | 4.686476 | -4.281472 | 1.500230  |
| 7  | 4.484444 | -5.358440 | 1.879284  |
| 6  | 5.398880 | -0.577540 | 0.147382  |
| 7  | 5.609358 | 0.488701  | -0.256587 |
| 35 | 3.950344 | -1.039286 | 3.928933  |

|   |          |           |          |
|---|----------|-----------|----------|
| 6 | 3.343772 | -0.298478 | 5.610706 |
| 9 | 3.473029 | 1.034019  | 5.628400 |
| 9 | 2.053678 | -0.584966 | 5.828203 |
| 9 | 4.048659 | -0.789090 | 6.638428 |

**Table S2** - The  $E_{\text{INT}}$  values (kcal/mol),  $\text{Au}\cdots\text{X}$  distances (Å), the  $\text{Au}\cdots\text{X}-\text{C}$  angles ( $^{\circ}$ ), the X-C bond lengths (Å) and the X-C bond length elongation shown as  $\Delta R(\text{X}-\text{C})$  (Å), at four different levels of theory for the optimised geometries of **1** with X-bond donors.

| Method  | X-bond donor      | $E_{\text{INT}}$ (kcal/mol) | $\text{Au}\cdots\text{X}$ (Å) | $\text{Au}\cdots\text{X}-\text{C}$ (deg) | X-C (Å) | $\Delta R(\text{X}-\text{C})$ (Å) |
|---------|-------------------|-----------------------------|-------------------------------|------------------------------------------|---------|-----------------------------------|
| B3LYP   | ICH <sub>3</sub>  | -3.71                       | 3.283                         | 179.7                                    | 2.206   | 0.041                             |
| TPSS    |                   | -7.81                       | 3.065                         | 179.8                                    | 2.242   | 0.076                             |
| MP2*    |                   | -6.74                       | 3.150                         | 180.0                                    | 2.164   | 0.039                             |
| MP2     |                   | -8.44                       | 3.098                         | 180.0                                    | 2.167   | 0.044                             |
| CCSD(T) |                   | -5.60                       |                               |                                          |         |                                   |
| B3LYP   | BrCH <sub>3</sub> | 0.79                        | 3.507                         | 179.7                                    | 1.970   | 0.010                             |
| TPSS    |                   | -1.17                       | 3.128                         | 179.7                                    | 1.970   | 0.008                             |
| MP2*    |                   | -1.24                       | 3.304                         | 180.0                                    | 1.935   | 0.010                             |
| MP2     |                   | -2.49                       | 3.212                         | 180.0                                    | 1.939   | 0.014                             |
| CCSD(T) |                   | -1.13                       |                               |                                          |         |                                   |
| B3LYP   | ICF <sub>3</sub>  | -18.05                      | 3.016                         | 179.6                                    | 2.24    | 0.063                             |
| TPSS    |                   | -24.80                      | 2.889                         | 179.6                                    | 2.28    | 0.102                             |
| MP2*    |                   | -19.11                      | 2.963                         | 180.0                                    | 2.18    | 0.040                             |
| MP2     |                   | -22.12                      | 2.916                         | 180.0                                    | 2.18    | 0.050                             |
| CCSD(T) |                   | -18.05                      |                               |                                          |         |                                   |
| B3LYP   | BrCF <sub>3</sub> | -9.92                       | 3.061                         | 179.9                                    | 1.97    | 0.022                             |
| TPSS    |                   | -15.01                      | 2.856                         | 179.9                                    | 2.02    | 0.069                             |
| MP2*    |                   | -10.83                      | 3.034                         | 180.0                                    | 1.92    | 0.003                             |
| MP2     |                   | -13.13                      | 2.961                         | 180.0                                    | 1.92    | 0.012                             |
| CCSD(T) |                   | -10.70                      |                               |                                          |         |                                   |
| B3LYP   | ClCF <sub>3</sub> | -5.42                       | 3.260                         | 179.9                                    | 1.76    | -0.014                            |
| TPSS    |                   | -7.32                       | 3.000                         | 179.9                                    | 1.79    | 0.009                             |
| MP2*    |                   | -6.75                       | 3.237                         | 178.3                                    | 1.73    | -0.019                            |
| MP2     |                   | -8.48                       | 3.122                         | 178.5                                    | 1.74    | -0.015                            |
| CCSD(T) |                   | -7.20                       |                               |                                          |         |                                   |

**S3. Optimised coordinates and relevant properties of adducts of neutral complexes 8-12 with X-bond donors (energies in a.u. and frequencies in cm<sup>-1</sup>)**

**8.I<sub>2</sub>**

B3LYP/aug-cc-pVTZ-pp

Energy: -954.356050

Low Frequencies:

29.0557            37.1141            45.3343

Optimised Coordinates:

|    |           |           |          |
|----|-----------|-----------|----------|
| 6  | 2.491233  | -1.712760 | 2.312795 |
| 7  | 1.247465  | -2.235442 | 2.237660 |
| 7  | 2.265998  | -0.411289 | 2.579289 |
| 6  | 0.919241  | -0.118661 | 2.670481 |
| 6  | 0.265903  | -1.282313 | 2.452595 |
| 1  | -0.783447 | -1.508627 | 2.432474 |
| 1  | 0.548607  | 0.867602  | 2.877254 |
| 1  | 3.029785  | 0.241521  | 2.692606 |
| 1  | 1.077107  | -3.207145 | 2.046599 |
| 79 | 4.393601  | -2.582758 | 2.094507 |
| 1  | 5.852481  | -3.214881 | 1.935687 |
| 53 | 6.928576  | 2.468414  | 3.083049 |
| 53 | 5.971867  | -0.135851 | 2.563158 |

MP2/aug-cc-pVTZ-pp

Energy: -951.701617

Low Frequencies:

32.3011            39.0540            49.6669

Optimised Coordinates:

|    |           |           |          |
|----|-----------|-----------|----------|
| 6  | 2.535933  | -1.703764 | 2.315849 |
| 7  | 1.286475  | -2.221430 | 2.236828 |
| 7  | 2.307649  | -0.400416 | 2.586251 |
| 6  | 0.971608  | -0.103190 | 2.675104 |
| 6  | 0.309753  | -1.277163 | 2.449913 |
| 1  | -0.740772 | -1.500826 | 2.426585 |
| 1  | 0.601113  | 0.883390  | 2.883973 |
| 1  | 3.083084  | 0.244691  | 2.701277 |
| 1  | 1.120565  | -3.195438 | 2.041879 |
| 79 | 4.367182  | -2.557042 | 2.103210 |
| 1  | 5.793861  | -3.195212 | 1.942967 |
| 53 | 6.746265  | 2.386907  | 3.060224 |
| 53 | 5.825701  | -0.192697 | 2.554091 |

**8.ICF<sub>3</sub>**

B3LYP/aug-cc-pVTZ-pp

Energy: -996.285667

Low Frequencies:

16.2893            24.1606            32.2558

Optimised Coordinates:

|    |           |           |          |
|----|-----------|-----------|----------|
| 6  | 2.368744  | -1.787583 | 2.331414 |
| 7  | 1.127840  | -2.307505 | 2.195503 |
| 7  | 2.130260  | -0.471576 | 2.516647 |
| 6  | 0.780612  | -0.171505 | 2.498275 |
| 6  | 0.138739  | -1.343205 | 2.293213 |
| 1  | -0.907948 | -1.567743 | 2.210893 |
| 1  | 0.401088  | 0.824299  | 2.629157 |
| 1  | 2.880805  | 0.188936  | 2.649870 |
| 1  | 0.968936  | -3.287675 | 2.041485 |
| 79 | 4.234664  | -2.723332 | 2.281658 |
| 1  | 5.679938  | -3.419701 | 2.249302 |
| 53 | 5.966376  | -0.020522 | 2.755820 |
| 6  | 6.733978  | 2.013897  | 3.084290 |
| 9  | 7.339658  | 2.116084  | 4.273151 |
| 9  | 5.735320  | 2.912094  | 3.055523 |
| 9  | 7.617620  | 2.355477  | 2.139535 |

### 8.ICH<sub>3</sub>

B3LYP/aug-cc-pVTZ-pp

Energy: -698.447707

Low Frequencies:

25.1963            29.1581            41.8293

Optimised Coordinates:

|    |           |           |          |
|----|-----------|-----------|----------|
| 6  | 2.385698  | -1.872285 | 2.284517 |
| 7  | 1.106921  | -2.308735 | 2.203000 |
| 7  | 2.241819  | -0.557833 | 2.559810 |
| 6  | 0.915103  | -0.178686 | 2.648952 |
| 6  | 0.188474  | -1.295714 | 2.421303 |
| 1  | -0.873495 | -1.452088 | 2.396707 |
| 1  | 0.606720  | 0.827615  | 2.861412 |
| 1  | 3.044397  | 0.044952  | 2.679608 |
| 1  | 0.880023  | -3.266979 | 2.003817 |
| 79 | 4.162862  | -2.929201 | 2.051037 |
| 1  | 5.542745  | -3.734641 | 1.873358 |
| 53 | 5.943077  | 0.165906  | 2.677518 |
| 6  | 6.657392  | 2.180014  | 3.079168 |
| 1  | 6.362398  | 2.439195  | 4.088604 |

|   |          |          |          |
|---|----------|----------|----------|
| 1 | 7.735569 | 2.159729 | 2.977345 |
| 1 | 6.206040 | 2.842190 | 2.350543 |

### 8.BrCF<sub>3</sub>

B3LYP/aug-cc-pVTZ-pp

Energy: -3274.709188

Low Frequencies:

|         |         |         |
|---------|---------|---------|
| 15.8417 | 23.0395 | 33.1095 |
|---------|---------|---------|

Optimised Coordinates:

|    |           |           |          |
|----|-----------|-----------|----------|
| 6  | 2.474268  | -1.605753 | 2.364161 |
| 7  | 1.200019  | -2.043671 | 2.242523 |
| 7  | 2.321061  | -0.276010 | 2.551283 |
| 6  | 0.992553  | 0.109972  | 2.547658 |
| 6  | 0.275452  | -1.018382 | 2.350488 |
| 1  | -0.784323 | -1.175387 | 2.279916 |
| 1  | 0.678418  | 1.127837  | 2.682076 |
| 1  | 3.111197  | 0.336131  | 2.676428 |
| 1  | 0.978736  | -3.011947 | 2.090395 |
| 79 | 4.258446  | -2.676322 | 2.289314 |
| 1  | 5.647139  | -3.482435 | 2.234576 |
| 6  | 6.689128  | 1.965588  | 3.090005 |
| 9  | 7.551183  | 2.318062  | 2.138508 |
| 9  | 5.670197  | 2.833700  | 3.075987 |
| 9  | 7.298922  | 2.057751  | 4.270327 |
| 35 | 6.031832  | 0.144975  | 2.789972 |

### 9.I<sub>2</sub>

B3LYP/aug-cc-pVTZ-pp

Energy: -591.6295938

Low Frequencies:

|         |         |         |
|---------|---------|---------|
| 30.1752 | 32.5602 | 43.3784 |
|---------|---------|---------|

Optimised Coordinates:

|    |           |           |          |
|----|-----------|-----------|----------|
| 6  | 2.417668  | -1.698814 | 2.257338 |
| 7  | 1.189563  | -2.265509 | 2.251593 |
| 7  | 2.156597  | -0.398574 | 2.497117 |
| 6  | 0.805279  | -0.149819 | 2.638862 |
| 6  | 0.184818  | -1.340756 | 2.482429 |
| 1  | -0.855795 | -1.603216 | 2.514362 |
| 1  | 0.409198  | 0.828898  | 2.834068 |
| 1  | 2.901633  | 0.282561  | 2.557815 |
| 1  | 1.046150  | -3.247619 | 2.095408 |
| 79 | 4.300051  | -2.566836 | 1.970869 |

|    |          |           |          |
|----|----------|-----------|----------|
| 6  | 6.124813 | -3.497229 | 1.676505 |
| 1  | 6.782897 | -3.392162 | 2.539043 |
| 1  | 5.926520 | -4.561871 | 1.521280 |
| 1  | 6.643002 | -3.112108 | 0.798242 |
| 53 | 6.703421 | 2.636246  | 2.677293 |
| 53 | 5.751853 | 0.003538  | 2.300170 |

TPSSTPSS/aug-cc-pVTZ-pp

Energy: - 591.2177281

Low Frequencies:

31.7387 34.7230 45.1193

Optimised Coordinates:

|    |           |           |          |
|----|-----------|-----------|----------|
| 6  | 2.426835  | -1.713531 | 2.255231 |
| 7  | 1.181370  | -2.263590 | 2.245740 |
| 7  | 2.176945  | -0.404751 | 2.503669 |
| 6  | 0.826999  | -0.136564 | 2.645688 |
| 6  | 0.186429  | -1.324294 | 2.481175 |
| 1  | -0.860702 | -1.577098 | 2.509977 |
| 1  | 0.446239  | 0.851298  | 2.846429 |
| 1  | 2.943487  | 0.264260  | 2.565844 |
| 1  | 1.020756  | -3.247085 | 2.083077 |
| 79 | 4.310225  | -2.564085 | 1.971893 |
| 6  | 6.139831  | -3.477742 | 1.681047 |
| 1  | 6.797855  | -3.364996 | 2.547689 |
| 1  | 5.936553  | -4.546987 | 1.529740 |
| 1  | 6.654564  | -3.089797 | 0.797061 |
| 53 | 6.613375  | 2.588193  | 2.661263 |
| 53 | 5.686907  | -0.076500 | 2.286873 |

MP2/cc-pVTZ-pp

Energy: -589.7443186

Low Frequencies:

33.0995 34.4654 48.9322

Optimised Coordinates:

|   |           |           |          |
|---|-----------|-----------|----------|
| 6 | 2.458240  | -1.700294 | 2.253681 |
| 7 | 1.226667  | -2.266663 | 2.248977 |
| 7 | 2.187809  | -0.398643 | 2.494526 |
| 6 | 0.846233  | -0.150759 | 2.636094 |
| 6 | 0.223338  | -1.355340 | 2.477984 |
| 1 | -0.816539 | -1.620007 | 2.510233 |
| 1 | 0.446479  | 0.826236  | 2.831463 |

|    |          |           |          |
|----|----------|-----------|----------|
| 1  | 2.937448 | 0.280316  | 2.554073 |
| 1  | 1.091094 | -3.251203 | 2.092041 |
| 79 | 4.277816 | -2.540471 | 1.976200 |
| 6  | 6.069099 | -3.439850 | 1.690853 |
| 1  | 6.721379 | -3.334417 | 2.557669 |
| 1  | 5.893327 | -4.505705 | 1.523725 |
| 1  | 6.592172 | -3.040914 | 0.821829 |
| 53 | 6.652529 | 2.495195  | 2.653878 |
| 53 | 5.680578 | -0.080749 | 2.289171 |

MP2/aug-cc-pVTZ-pp

Energy: -589.7648

Low Frequencies:

32.8819 36.4311 49.0840

Optimised Coordinates:

|    |           |           |          |
|----|-----------|-----------|----------|
| 6  | 2.459584  | -1.703985 | 2.252986 |
| 7  | 1.225793  | -2.266585 | 2.249152 |
| 7  | 2.195000  | -0.400949 | 2.493535 |
| 6  | 0.854166  | -0.147940 | 2.635922 |
| 6  | 0.225897  | -1.350712 | 2.478623 |
| 1  | -0.815776 | -1.611556 | 2.511694 |
| 1  | 0.458113  | 0.831449  | 2.831355 |
| 1  | 2.949988  | 0.274660  | 2.552056 |
| 1  | 1.086738  | -3.251542 | 2.092481 |
| 79 | 4.279458  | -2.541090 | 1.976025 |
| 6  | 6.073422  | -3.435562 | 1.691259 |
| 1  | 6.721838  | -3.326649 | 2.561661 |
| 1  | 5.892092  | -4.501539 | 1.523996 |
| 1  | 6.592681  | -3.031574 | 0.821162 |
| 53 | 6.623031  | 2.488700  | 2.654881 |
| 53 | 5.665643  | -0.108394 | 2.285608 |

### 9.ICF<sub>3</sub>

B3LYP/aug-cc-pVTZ-pp

Energy: -1035.616298

Low Frequencies:

18.9820 27.1102 31.0870

Optimised Coordinates:

|   |          |           |          |
|---|----------|-----------|----------|
| 6 | 1.650587 | -1.823106 | 2.169582 |
| 7 | 0.454112 | -2.455219 | 2.201396 |
| 7 | 1.314266 | -0.527283 | 2.350196 |

|    |           |           |          |
|----|-----------|-----------|----------|
| 6  | -0.049908 | -0.349188 | 2.491464 |
| 6  | -0.600779 | -1.579584 | 2.396580 |
| 1  | -1.624569 | -1.898659 | 2.449688 |
| 1  | -0.501207 | 0.613106  | 2.643674 |
| 1  | 2.011071  | 0.201546  | 2.375655 |
| 1  | 0.369984  | -3.450594 | 2.093476 |
| 79 | 3.543359  | -2.630769 | 1.907763 |
| 6  | 5.415187  | -3.472662 | 1.641976 |
| 1  | 6.069031  | -3.292412 | 2.497865 |
| 1  | 5.315556  | -4.554842 | 1.521570 |
| 1  | 5.913430  | -3.083624 | 0.751465 |
| 53 | 5.001504  | 0.292281  | 2.179942 |
| 6  | 5.623318  | 2.387713  | 2.421551 |
| 9  | 4.575257  | 3.159377  | 2.752077 |
| 9  | 6.542096  | 2.510296  | 3.385673 |
| 9  | 6.145216  | 2.870983  | 1.288402 |

### 9.BrCF<sub>3</sub>

B3LYP/aug-cc-pVTZ-pp

Energy: -3314.040206

Low Frequencies:

|         |         |         |
|---------|---------|---------|
| 18.3309 | 22.8996 | 26.5497 |
|---------|---------|---------|

Optimised Coordinates:

|    |           |           |          |
|----|-----------|-----------|----------|
| 6  | 1.512036  | -2.151940 | 2.135090 |
| 7  | 0.296670  | -2.748296 | 2.158600 |
| 7  | 1.211478  | -0.847768 | 2.329723 |
| 6  | -0.148039 | -0.631979 | 2.470978 |
| 6  | -0.733172 | -1.844985 | 2.361811 |
| 1  | -1.765875 | -2.134807 | 2.409891 |
| 1  | -0.572453 | 0.340893  | 2.632948 |
| 1  | 1.925745  | -0.138567 | 2.363295 |
| 1  | 0.185884  | -3.739718 | 2.039191 |
| 79 | 3.373112  | -3.009502 | 1.867839 |
| 6  | 5.232811  | -3.875115 | 1.598408 |
| 1  | 5.891126  | -3.688437 | 2.450412 |
| 1  | 5.139196  | -4.958324 | 1.483954 |
| 1  | 5.728930  | -3.489809 | 0.704210 |
| 6  | 5.337063  | 1.919780  | 2.420608 |
| 9  | 4.268937  | 2.662050  | 2.733134 |
| 9  | 6.230999  | 2.039394  | 3.399808 |
| 9  | 5.868430  | 2.403426  | 1.299328 |
| 35 | 4.815095  | 0.045566  | 2.186545 |

**10.I<sub>2</sub>**

B3LYP/aug-cc-pVTZ-pp

Energy: -1414.046451

Low Frequencies:

26.0224            34.3676            38.9314

Optimised Coordinates:

|    |           |           |          |
|----|-----------|-----------|----------|
| 6  | 2.509351  | -1.713869 | 2.315519 |
| 7  | 1.261644  | -2.228273 | 2.237395 |
| 7  | 2.300483  | -0.410149 | 2.584081 |
| 6  | 0.955691  | -0.107827 | 2.673521 |
| 6  | 0.291708  | -1.264561 | 2.452990 |
| 1  | -0.759543 | -1.481072 | 2.431065 |
| 1  | 0.594639  | 0.881604  | 2.881400 |
| 1  | 3.071640  | 0.234243  | 2.698307 |
| 1  | 1.085364  | -3.198597 | 2.043817 |
| 79 | 4.272663  | -2.644236 | 2.086881 |
| 17 | 6.267661  | -3.728286 | 1.818350 |
| 53 | 6.807255  | 2.584557  | 3.101049 |
| 53 | 5.936873  | 0.008639  | 2.593745 |

MP2/aug-cc-pVTZ-pp

Energy: -1410.883239

Low Frequencies:

29.6408            36.2439            40.9759

Optimised Coordinates:

|    |           |           |          |
|----|-----------|-----------|----------|
| 6  | 2.549323  | -1.689988 | 2.317860 |
| 7  | 1.303369  | -2.217131 | 2.236878 |
| 7  | 2.318542  | -0.387277 | 2.588694 |
| 6  | 0.979607  | -0.099536 | 2.676029 |
| 6  | 0.323999  | -1.275988 | 2.449902 |
| 1  | -0.725235 | -1.504989 | 2.425573 |
| 1  | 0.604659  | 0.885187  | 2.885037 |
| 1  | 3.089848  | 0.261779  | 2.704700 |
| 1  | 1.146249  | -3.192721 | 2.041102 |
| 79 | 4.258355  | -2.586954 | 2.098268 |
| 17 | 6.200734  | -3.648252 | 1.840148 |
| 53 | 6.737305  | 2.453187  | 3.074055 |
| 53 | 5.808672  | -0.065146 | 2.579874 |

**10.ICF<sub>3</sub>**

B3LYP/aug-cc-pVTZ-pp

Energy: -1455.980905

Low Frequencies:

11.8101            14.1338            21.7379

Optimised Coordinates:

|    |          |           |          |
|----|----------|-----------|----------|
| 6  | 2.505763 | -2.005448 | 3.667774 |
| 7  | 1.325060 | -2.595682 | 3.960382 |
| 7  | 2.167353 | -0.716044 | 3.449383 |
| 6  | 0.809919 | -0.501110 | 3.600387 |
| 6  | 0.272109 | -1.697298 | 3.925844 |
| 1  | 0.742817 | -1.980806 | 4.130717 |
| 1  | 0.354250 | 0.461626  | 3.466225 |
| 1  | 2.855137 | -0.019569 | 3.206997 |
| 1  | 1.250010 | -3.574676 | 4.174383 |
| 79 | 4.338292 | -2.787751 | 3.559326 |
| 17 | 6.478584 | -3.589915 | 3.402013 |
| 53 | 5.974795 | 0.265071  | 2.764833 |
| 6  | 6.090537 | 2.403646  | 2.358441 |
| 9  | 6.766106 | 3.039306  | 3.318825 |
| 9  | 6.698265 | 2.639528  | 1.193698 |
| 9  | 4.859622 | 2.937047  | 2.297825 |

#### 10.BrCF<sub>3</sub>

B3LYP/aug-cc-pVTZ-pp

Energy: -3734.406161

Low Frequencies:

15.0560            17.5343            23.1274

Optimised Coordinates:

|    |           |           |          |
|----|-----------|-----------|----------|
| 6  | 2.315584  | -1.411030 | 3.517563 |
| 7  | 1.037760  | -1.803993 | 3.724154 |
| 7  | 2.202754  | -0.081120 | 3.303994 |
| 6  | 0.890189  | 0.349312  | 3.374476 |
| 6  | 0.147400  | -0.747083 | 3.642034 |
| 1  | -0.911005 | -0.864465 | 3.777702 |
| 1  | 0.604774  | 1.374300  | 3.231621 |
| 1  | 3.005141  | 0.498650  | 3.116716 |
| 1  | 0.793374  | -2.760106 | 3.913812 |
| 79 | 3.985962  | -2.500156 | 3.520306 |
| 17 | 5.935134  | -3.699371 | 3.511506 |
| 35 | 5.927339  | 0.490908  | 2.750435 |
| 6  | 6.318881  | 2.363724  | 2.366804 |
| 9  | 7.125354  | 2.872034  | 3.293596 |
| 9  | 6.902382  | 2.485471  | 1.178536 |

9 5.186510 3.076548 2.355850

### 11.I<sub>2</sub>

B3LYP/aug-cc-pVTZ-pp

Energy: -823.975351

Low Frequencies:

36.9894 40.4414 43.1531

Optimised Coordinates:

|    |           |           |           |
|----|-----------|-----------|-----------|
| 79 | -0.015603 | 0.055721  | 0.108530  |
| 6  | -0.110585 | 0.040219  | 2.145884  |
| 7  | 0.022589  | 0.077189  | -2.100903 |
| 1  | 0.450215  | 0.874914  | 2.563362  |
| 1  | -1.159809 | 0.132895  | 2.433087  |
| 1  | 0.288240  | -0.892580 | 2.541425  |
| 1  | 0.986258  | -0.042079 | -2.399827 |
| 1  | -0.527303 | -0.673366 | -2.504629 |
| 1  | -0.316905 | 0.954017  | -2.481305 |
| 53 | 2.950268  | -0.163771 | 0.050479  |
| 53 | 5.722636  | -0.363159 | -0.356103 |

MP2/aug-cc-pVTZ-pp

Energy: -821.600003

Low Frequencies:

Optimised Coordinates:

|    |           |           |           |
|----|-----------|-----------|-----------|
| 79 | -0.002862 | 0.064246  | 0.084308  |
| 6  | -0.049769 | 0.048388  | 2.075198  |
| 7  | 0.033358  | 0.082555  | -2.045492 |
| 1  | 0.522304  | 0.886292  | 2.472510  |
| 1  | -1.089966 | 0.135162  | 2.395568  |
| 1  | 0.369149  | -0.883180 | 2.454574  |
| 1  | 1.008954  | 0.001532  | -2.324869 |
| 1  | -0.473182 | -0.692583 | -2.461835 |
| 1  | -0.332525 | 0.941408  | -2.444579 |
| 53 | 2.775908  | -0.175011 | 0.066494  |
| 53 | 5.528630  | -0.408811 | -0.271877 |

### 12.I<sub>2</sub>

B3LYP/aug-cc-pVTZ-pp

Energy: -1110.565385

Low Frequencies:

32.0941 37.5885 47.6049

Optimised Coordinates:

|    |           |           |           |
|----|-----------|-----------|-----------|
| 79 | 0.350429  | -0.925194 | -0.780479 |
| 6  | -0.632094 | -2.359898 | -1.904190 |
| 1  | 0.086928  | -2.770299 | -2.615652 |
| 1  | -1.004338 | -3.161921 | -1.269021 |
| 1  | -1.465073 | -1.920721 | -2.450597 |
| 15 | 1.532710  | 0.703042  | 0.471653  |
| 1  | 1.070084  | 2.033075  | 0.433101  |
| 1  | 1.607167  | 0.536008  | 1.868414  |
| 1  | 2.898069  | 0.940229  | 0.207538  |
| 53 | -2.239255 | -0.411639 | 0.772976  |
| 53 | -4.352987 | 0.358248  | 2.408770  |

**S4. Optimised coordinates and relevant properties of adducts of cationic complexes 13 and 14 with I<sub>2</sub> (energies in a.u. and frequencies in cm<sup>-1</sup>)**

**13.I<sub>2</sub> (end on)**

B3LYP/aug-cc-pVTZ-pp

Energy: -840.427772

Low Frequencies:

7.4257            9.7003            32.2876

Optimised Coordinates:

|    |           |           |           |
|----|-----------|-----------|-----------|
| 79 | -0.117463 | -0.000623 | -0.000084 |
| 7  | -0.110882 | -0.002215 | 2.072465  |
| 7  | -0.110497 | 0.001007  | -2.072633 |
| 1  | 0.844014  | -0.002329 | 2.426062  |
| 1  | -0.578465 | 0.817885  | 2.451288  |
| 1  | -0.578207 | -0.823034 | 2.450045  |
| 1  | 0.844467  | 0.001141  | -2.426045 |
| 1  | -0.578016 | -0.819066 | -2.451590 |
| 1  | -0.577739 | 0.821853  | -2.450259 |
| 53 | 3.269353  | 0.001701  | 0.000103  |
| 53 | 5.983436  | 0.003681  | 0.000650  |

MP2/aug-cc-pVTZ-pp

Energy: -838.037629

Low Frequencies:

Optimised Coordinates:

|    |           |           |           |
|----|-----------|-----------|-----------|
| 79 | -0.075952 | -0.000554 | -0.000047 |
| 7  | -0.054446 | -0.002157 | 2.010536  |
| 7  | -0.054117 | 0.001090  | -2.010627 |
| 1  | 0.908409  | -0.001727 | 2.346950  |
| 1  | -0.514266 | 0.817578  | 2.402373  |
| 1  | -0.513208 | -0.822958 | 2.401362  |
| 1  | 0.908797  | 0.001543  | -2.346877 |
| 1  | -0.513147 | -0.819024 | -2.402589 |

|    |           |          |           |
|----|-----------|----------|-----------|
| 1  | -0.513534 | 0.821512 | -2.401483 |
| 53 | 3.015001  | 0.001505 | 0.000146  |
| 53 | 5.696463  | 0.003192 | 0.000256  |

#### 14.I<sub>2</sub> (end on)

B3LYP/aug-cc-pVTZ-pp

Energy: -591.6320203

Low Frequencies:

9.7107 12.0838 18.6384

Optimised Coordinates:

|    |           |           |           |
|----|-----------|-----------|-----------|
| 79 | 0.134222  | 0.177088  | -0.007952 |
| 15 | 0.064653  | 0.182324  | 2.328959  |
| 53 | 4.036062  | 0.479905  | 0.049366  |
| 15 | 0.109670  | 0.189536  | -2.345623 |
| 1  | 0.162349  | 1.440053  | 2.946078  |
| 1  | -1.097291 | -0.339420 | 2.920741  |
| 1  | 1.075908  | -0.542318 | 2.979401  |
| 1  | 0.173463  | 1.452381  | -2.956744 |
| 1  | 1.158549  | -0.495539 | -2.979136 |
| 1  | -1.021045 | -0.371567 | -2.961370 |
| 53 | 3.493460  | -2.172443 | 0.026281  |

TPSSTPSS/aug-cc-pVTZ-pp

Energy: -591.2214522

Low Frequencies:

6.6375 14.0288 24.4186

Optimised Coordinates:

|    |           |           |           |
|----|-----------|-----------|-----------|
| 79 | -0.052261 | 0.158334  | 0.002032  |
| 15 | -0.038556 | 0.198780  | 2.330909  |
| 53 | 3.049336  | -0.384944 | -0.007889 |
| 15 | -0.069248 | 0.126004  | -2.326908 |
| 1  | 0.833840  | 1.135017  | 2.911807  |
| 1  | -1.260086 | 0.488919  | 2.965995  |
| 1  | 0.346645  | -1.001327 | 2.952397  |
| 1  | 0.796003  | 1.042155  | -2.948899 |
| 1  | 0.306197  | -1.093618 | -2.915515 |
| 1  | -1.298985 | 0.397839  | -2.954242 |
| 53 | 5.677116  | -1.067159 | -0.009688 |

MP2/cc-pVTZ-pp

Energy: -1410.4175474

Low Frequencies:

Could not be determined owing to computational constraints

Optimised Coordinates:

|    |           |           |           |
|----|-----------|-----------|-----------|
| 79 | -0.112484 | 0.183143  | 0.002595  |
| 15 | -0.028455 | 0.204374  | 2.280843  |
| 53 | 2.943020  | -0.463338 | -0.006453 |
| 15 | -0.057007 | 0.132326  | -2.276066 |
| 1  | 0.858298  | 1.143049  | 2.814576  |
| 1  | -1.217438 | 0.467842  | 2.967026  |
| 1  | 0.405658  | -0.995024 | 2.851195  |
| 1  | 0.822646  | 1.053630  | -2.850281 |
| 1  | 0.370372  | -1.084521 | -2.813598 |
| 1  | -1.254588 | 0.373999  | -2.955283 |
| 53 | 5.559979  | -1.015481 | -0.014553 |

MP2/aug-cc-pVTZ-pp

Energy: -1410.458238

Low Frequencies:

Could not be determined owing to computational constraints

Optimised Coordinates:

|    |           |           |           |
|----|-----------|-----------|-----------|
| 79 | -0.092699 | 0.178954  | 0.002484  |
| 15 | -0.024200 | 0.203456  | 2.279468  |
| 53 | 2.929195  | -0.459893 | -0.006613 |
| 15 | -0.052796 | 0.131450  | -2.274741 |
| 1  | 0.857824  | 1.144158  | 2.818173  |
| 1  | -1.220189 | 0.468019  | 2.953661  |
| 1  | 0.405166  | -0.995583 | 2.854827  |
| 1  | 0.821881  | 1.054799  | -2.853963 |
| 1  | 0.369929  | -1.085107 | -2.817295 |
| 1  | -1.257317 | 0.374415  | -2.941825 |
| 53 | 5.553206  | -1.014668 | -0.014175 |

### 13.I<sub>2</sub> (side on)

MP2/aug-cc-pVTZ-pp

Energy: -838.041125

Low Frequencies:

18.1052            22.2537            30.5909

Optimised Coordinates:

|    |           |           |          |
|----|-----------|-----------|----------|
| 79 | 0.009618  | 0.001830  | 0.071697 |
| 7  | -0.181785 | -0.095290 | 2.071529 |

|    |           |           |           |
|----|-----------|-----------|-----------|
| 7  | 0.207953  | 0.090880  | -1.929411 |
| 1  | 0.669781  | 0.213800  | 2.535603  |
| 1  | -0.941442 | 0.490547  | 2.411373  |
| 1  | -0.370678 | -1.044427 | 2.386598  |
| 1  | 1.085276  | -0.354752 | -2.197682 |
| 1  | -0.544242 | -0.380302 | -2.427165 |
| 1  | 0.238687  | 1.051751  | -2.263243 |
| 53 | 3.282550  | 1.342861  | -0.028781 |
| 53 | 3.344281  | -1.281945 | -0.503806 |

#### 14.I<sub>2</sub> (side on)

B3LYP/aug-cc-pVTZ-pp

Energy: -591.6320261

Low Frequencies:

11.4204 13.2986 14.0088

Optimised Coordinates:

|    |          |           |           |
|----|----------|-----------|-----------|
| 79 | 2.633568 | -0.963318 | -0.297114 |
| 15 | 1.339626 | -2.626077 | -1.310245 |
| 1  | 0.289342 | -3.157265 | -0.543934 |
| 1  | 2.024739 | -3.786726 | -1.704717 |
| 1  | 0.681208 | -2.258089 | -2.494356 |
| 15 | 3.900191 | 0.669484  | 0.795965  |
| 1  | 5.263132 | 0.379204  | 0.969736  |
| 1  | 3.506432 | 0.998142  | 2.103417  |
| 1  | 3.946282 | 1.929461  | 0.178446  |
| 53 | 4.248824 | -0.030124 | -3.701190 |
| 53 | 2.043077 | 1.535877  | -3.583818 |

TPSSTPSS/aug-cc-pVTZ-pp

Energy: -591.2215711

Low Frequencies:

16.3223 19.0053 26.7170

Optimised Coordinates:

|    |          |           |           |
|----|----------|-----------|-----------|
| 79 | 2.689032 | -0.913222 | -0.446883 |
| 15 | 1.414225 | -2.614336 | -1.377278 |
| 1  | 0.195998 | -2.900212 | -0.734714 |
| 1  | 2.013762 | -3.885990 | -1.420945 |
| 1  | 1.002306 | -2.446212 | -2.710939 |
| 15 | 3.946472 | 0.657477  | 0.708884  |
| 1  | 5.170195 | 0.206318  | 1.235992  |
| 1  | 3.341698 | 1.222810  | 1.846062  |

|    |          |          |           |
|----|----------|----------|-----------|
| 1  | 4.345555 | 1.802726 | -0.002472 |
| 53 | 3.991486 | 0.088386 | -3.658134 |
| 53 | 1.765692 | 1.472824 | -3.027383 |

MP2/cc-pVTZ-pp

Energy: -589.747150

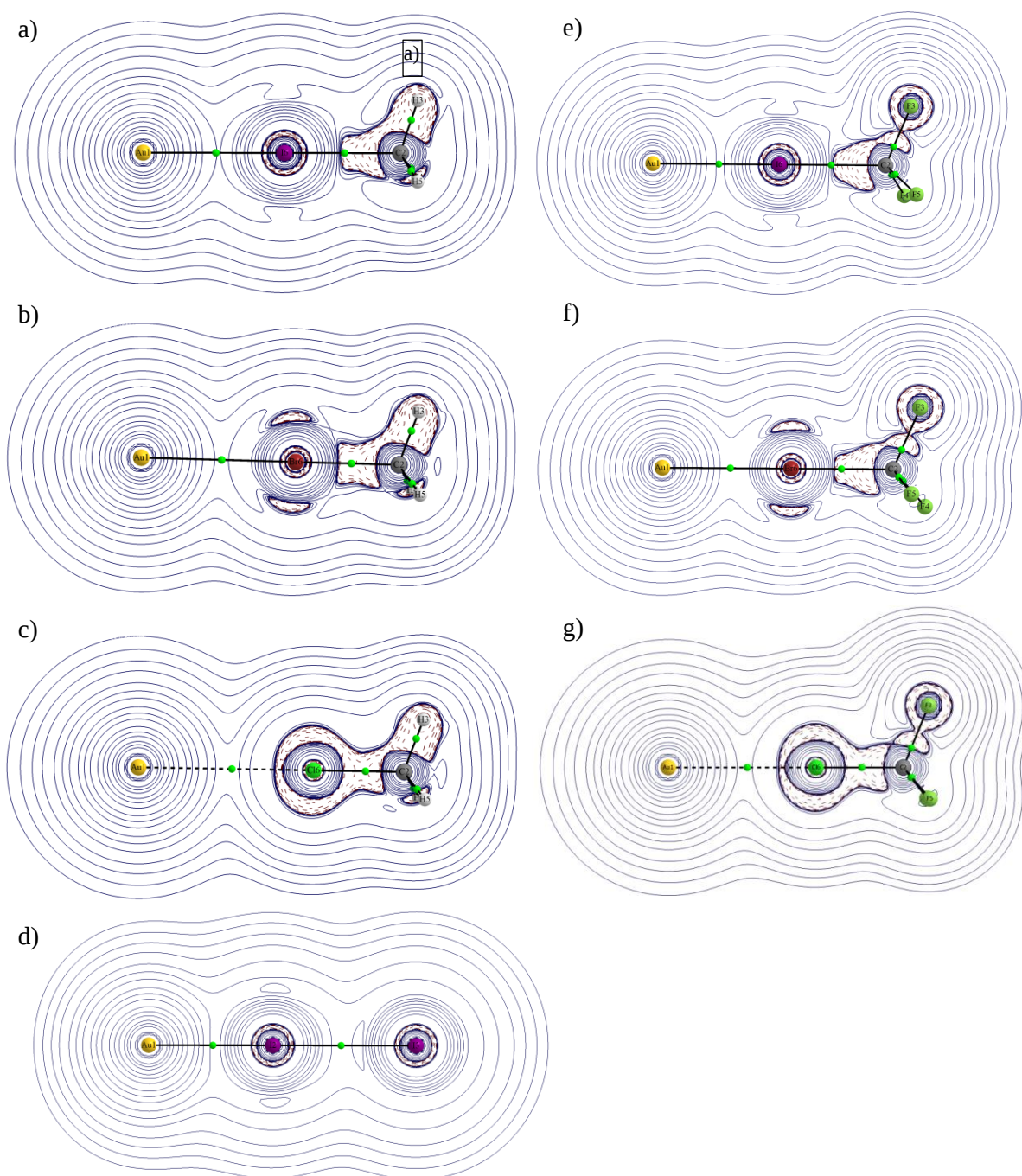
Low Frequencies:

17.1202 24.1305 33.0389

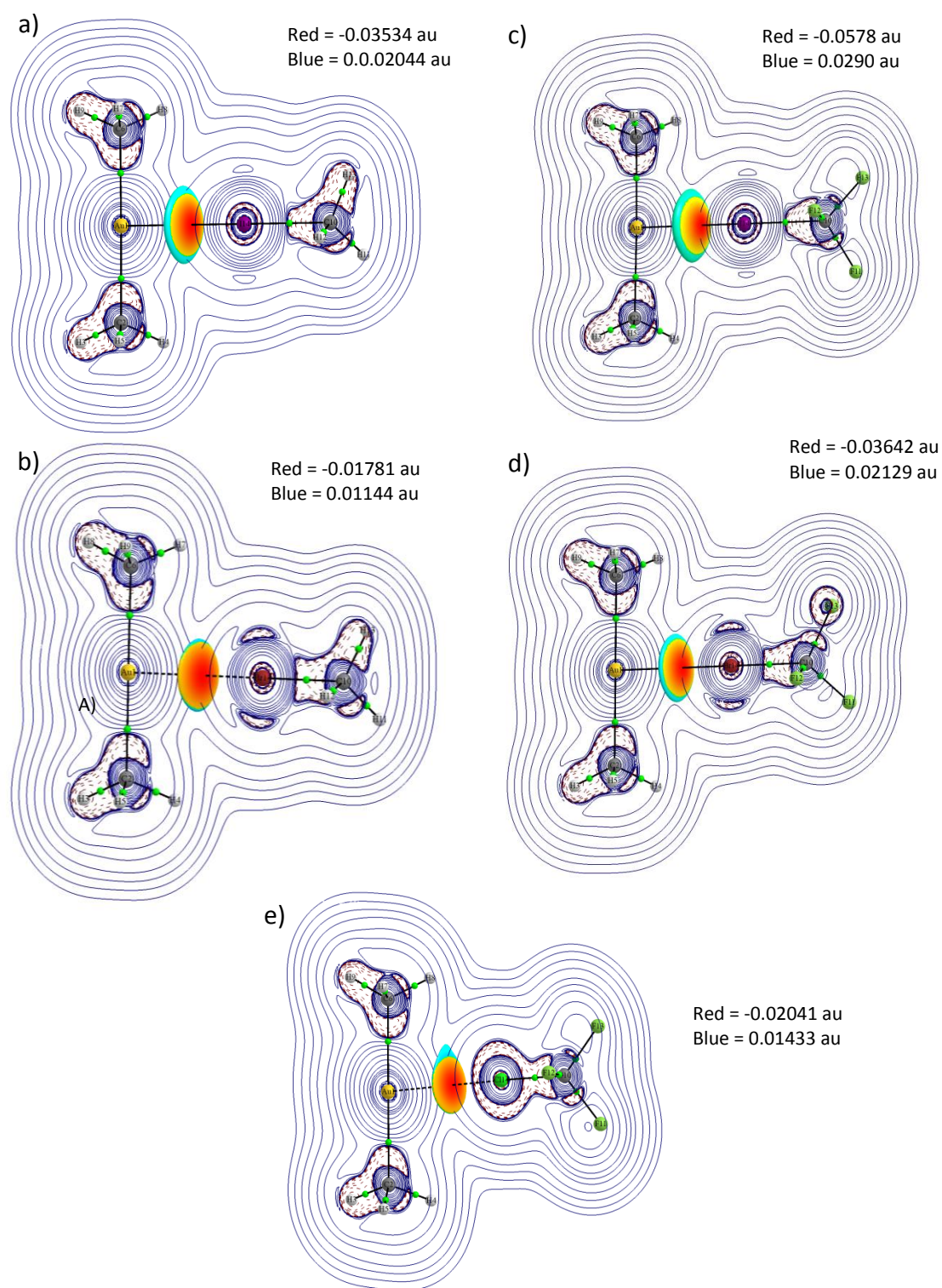
Optimised Coordinates:

|    |          |           |           |
|----|----------|-----------|-----------|
| 79 | 2.693924 | -0.945307 | -0.404111 |
| 15 | 1.459515 | -2.595605 | -1.374987 |
| 1  | 0.459836 | -3.167367 | -0.583602 |
| 1  | 2.178378 | -3.715288 | -1.801676 |
| 1  | 0.760653 | -2.229321 | -2.528210 |
| 15 | 3.922953 | 0.636053  | 0.681551  |
| 1  | 4.844371 | 0.166369  | 1.621204  |
| 1  | 3.189818 | 1.566419  | 1.422806  |
| 1  | 4.710835 | 1.453728  | -0.132827 |
| 53 | 3.835345 | -0.006791 | -3.657003 |
| 53 | 1.820793 | 1.527679  | -2.830955 |

## S5. AIM and NCI results for adducts with Au<sup>-</sup> and anionic complex 1



**Figure S1.** Molecular graphs with the two-dimensional contour plot of  $\nabla^2(\rho)$  for the optimised geometries of the Au<sup>-</sup> ion X-bonded to XCH<sub>3</sub> [X = a) I, b) Br, c) Cl] and d) I<sub>2</sub> on the left and XCF<sub>3</sub> [X = e) I, f) Br, g) Cl] on the right at the MP2/aug-cc-pVTZ-pp level of theory. Atomic interaction lines are indicated by solid (covalent bond) and dotted (noncovalent interactions) black lines, with the BCPs represented by green spheres.



**Figure S2.** Molecular graphs and two-dimensional contour plots of  $\nabla^2(\rho)$  with the NCI plots included of adducts of a)  $\text{ICH}_3$  b)  $\text{BrCH}_3$  and c)  $\text{ICF}_3$ , d)  $\text{BrCF}_3$  and e)  $\text{ClCF}_3$  with **1** at the MP2/aug-cc-pVTZ-pp level of theory. The red (minimum) regions indicate a stabilising interaction with blue (maximum) regions indicating repulsion.

## S6. Energy Decomposition Analysis (EDA) results for Au<sup>-</sup> adducts

**Table S3** – EDA results (kcal/mol) at the BP86-D3/def2-TZVP level of theory for Au<sup>-</sup> adducts with X-bond donors.

|                                        | <b>Total<br/>Bonding<br/>Energy</b> | <b>Electrostatic<br/>Interaction</b> | <b>Total Pauli<br/>Repulsion</b> | <b>Total<br/>Orbital<br/>Interactions</b> | <b>Dispersion<br/>Energy</b> |
|----------------------------------------|-------------------------------------|--------------------------------------|----------------------------------|-------------------------------------------|------------------------------|
| <b>Au<sup>-</sup>.ICF<sub>3</sub></b>  | -32.08                              | -89<br>(60.5)                        | 114.82                           | -57<br>(39.1)                             | -0.63<br>(0.4)               |
| <b>Au<sup>-</sup>.BrCF<sub>3</sub></b> | -26.17                              | -68<br>(55.8)                        | 94.95                            | -53<br>(43.6)                             | -0.72<br>(0.6)               |
| <b>Au<sup>-</sup>.ClCF<sub>3</sub></b> | -12.38                              | -23<br>(55.5)                        | 29.2                             | -17<br>(41.7)                             | -1.16<br>(2.8)               |
| <b>Au<sup>-</sup>.ICH<sub>3</sub></b>  | -14.98                              | -68<br>(60.9)                        | 96.58                            | -43<br>(38.5)                             | -0.7<br>(0.6)                |
| <b>Au<sup>-</sup>.BrCH<sub>3</sub></b> | -7.65                               | -24<br>(51.0)                        | 38.48                            | -21<br>(46.2)                             | -1.29<br>(2.8)               |
| <b>Au<sup>-</sup>.ClCH<sub>3</sub></b> | -0.97                               | -1.8<br>(17.8)                       | 9.09                             | -6.4<br>(63.5)                            | -1.88<br>(18.7)              |
| <b>Au<sup>-</sup>.I<sub>2</sub></b>    | -60.12                              | -118<br>(54.3)                       | 157.99                           | -99<br>(45.4)                             | -0.67<br>(0.3)               |
| <b>AuI.I<sup>-</sup></b>               | -56.29                              | -53<br>(33.3)                        | 102.25                           | -105<br>(66.4)                            | -0.55<br>(0.3)               |

## S7. Energy Decomposition Analysis (EDA) results for adducts with anionic complexes 1-7

**Table S4** – EDA results (kcal/mol) at the BP86-D3/def2-TZVP level of theory for adducts of anionic complexes with X-bond donors.

|                           | <b>Total<br/>Bonding<br/>Energy</b> | <b>Electrostatic<br/>Interaction</b> | <b>Total Pauli<br/>Repulsion</b> | <b>Total<br/>Orbital<br/>Interactions</b> | <b>Dispersion<br/>Energy</b> |
|---------------------------|-------------------------------------|--------------------------------------|----------------------------------|-------------------------------------------|------------------------------|
| <b>1.ICF<sub>3</sub></b>  | -21.05                              | -42<br>(55.6)                        | 55.04                            | -30<br>(39.6)                             | -3.7<br>(4.9)                |
| <b>1.BrCF<sub>3</sub></b> | -15.68                              | -24<br>(51.0)                        | 30.86                            | -19<br>(41.5)                             | -3.49<br>(7.5)               |
| <b>1.ClCF<sub>3</sub></b> | -9.62                               | -12<br>(49.3)                        | 15.31                            | -9.7<br>(38.9)                            | -2.94<br>(11.8)              |
| <b>1.ICH<sub>3</sub></b>  | -8.28                               | -21<br>(50.0)                        | 34.24                            | -17<br>(40.9)                             | -3.85<br>(9.1)               |
| <b>1.BrCH<sub>3</sub></b> | -4.85                               | -7<br>(34.1)                         | 15.59                            | -9.8<br>(47.8)                            | -3.71<br>(18.1)              |
| <b>1.I<sub>2</sub></b>    | -40.42                              | -68<br>(50.1)                        | 96.04                            | -64<br>(47.2)                             | -3.73<br>(2.7)               |
| <b>2.I<sub>2</sub></b>    | -25.44                              | -29.3<br>(42.6)                      | 43.33                            | -35.74<br>(52.0)                          | -3.73<br>(5.4)               |
| <b>3.I<sub>2</sub></b>    | -60.69                              | -61.61<br>(42.4)                     | 84.77                            | -78.07<br>(53.7)                          | -5.78<br>(4.0)               |

|             |        |                  |       |                  |                |
|-------------|--------|------------------|-------|------------------|----------------|
| <b>4.I2</b> | -23.88 | -27.24<br>(42.6) | 40.04 | -33.69<br>(52.7) | -2.99<br>(4.7) |
| <b>5.I2</b> | -21.13 | -38.85<br>(47.9) | 60.01 | -38.87<br>(47.9) | -3.42<br>(4.2) |
| <b>6.I2</b> | -43.93 | -55.98<br>(47.0) | 75.11 | -60.25<br>(50.6) | -2.81<br>(2.4) |
| <b>7.I2</b> | -16.95 | -18.34<br>(40.5) | 28.32 | -23.53<br>(52.0) | -3.41<br>(7.5) |

#### S8. Energy Decomposition Analysis (EDA) results for adducts with neutral complexes 8-12

**Table S5** – EDA results (kcal/mol) at the BP86-D3/def2-TZVP level of theory for adducts of neutral complexes with X-bond donors.

|              | <b>Total Bonding Energy</b> | <b>Electrostatic Interaction</b> | <b>Total Pauli Repulsion</b> | <b>Total Orbital Interactions</b> | <b>Dispersion Energy</b> |
|--------------|-----------------------------|----------------------------------|------------------------------|-----------------------------------|--------------------------|
| <b>8.I2</b>  | -20.98                      | -31.99<br>(47.9)                 | 45.79                        | -31<br>(46.4)                     | -3.78<br>(5.7)           |
| <b>9.I2</b>  | -22                         | -30.78<br>(46.3)                 | 44.54                        | -30.96<br>(46.5)                  | -4.8<br>(7.2)            |
| <b>10.I2</b> | -14.8                       | -16.44<br>(41.6)                 | 24.71                        | -18.3<br>(46.3)                   | -4.77<br>(12.1)          |
| <b>11.I2</b> | -12.61                      | -8.6<br>(20.0)                   | 30.3                         | -30.6<br>(71.2)                   | -3.8<br>(8.9)            |
| <b>12.I2</b> | -14.36                      | -19.65<br>(44.3)                 | 30.03                        | -20.47<br>(46.1)                  | -4.26<br>(9.6)           |

#### S9. Energy Decomposition Analysis (EDA) results for adducts with cationic complexes 13-14

**Table S6** – EDA results (kcal/mol) at the BP86-D3/def2-TZVP level of theory for adducts of cationic complexes with X-bond donors.

|                | <b>Total Bonding Energy</b> | <b>Electrostatic Interaction</b> | <b>Total Pauli Repulsion</b> | <b>Total Orbital Interactions</b> | <b>Dispersion Energy</b> |
|----------------|-----------------------------|----------------------------------|------------------------------|-----------------------------------|--------------------------|
| <b>13.I2</b>   | -6.26                       | -11.66<br>(37.5)                 | 24.81                        | -15.28<br>(49.2)                  | -4.13<br>(13.3)          |
| <b>14.I2</b>   | -5.69                       | -10.98<br>(35.2)                 | 25.52                        | -15.41<br>(49.4)                  | -4.82<br>(15.4)          |
| <b>13.I2_s</b> | -9.7                        | -11.2<br>(39.4)                  | 18.74                        | -8.44<br>(29.7)                   | -8.82<br>(31.0)          |
| <b>14.I2_s</b> | -11.39                      | -3.9<br>(23.2)                   | -5.43                        | -4.42<br>(26.3)                   | -8.5<br>(50.5)           |