

**The distance between minima of electron density and electrostatic potential  
as a measure of halogen bond strength**

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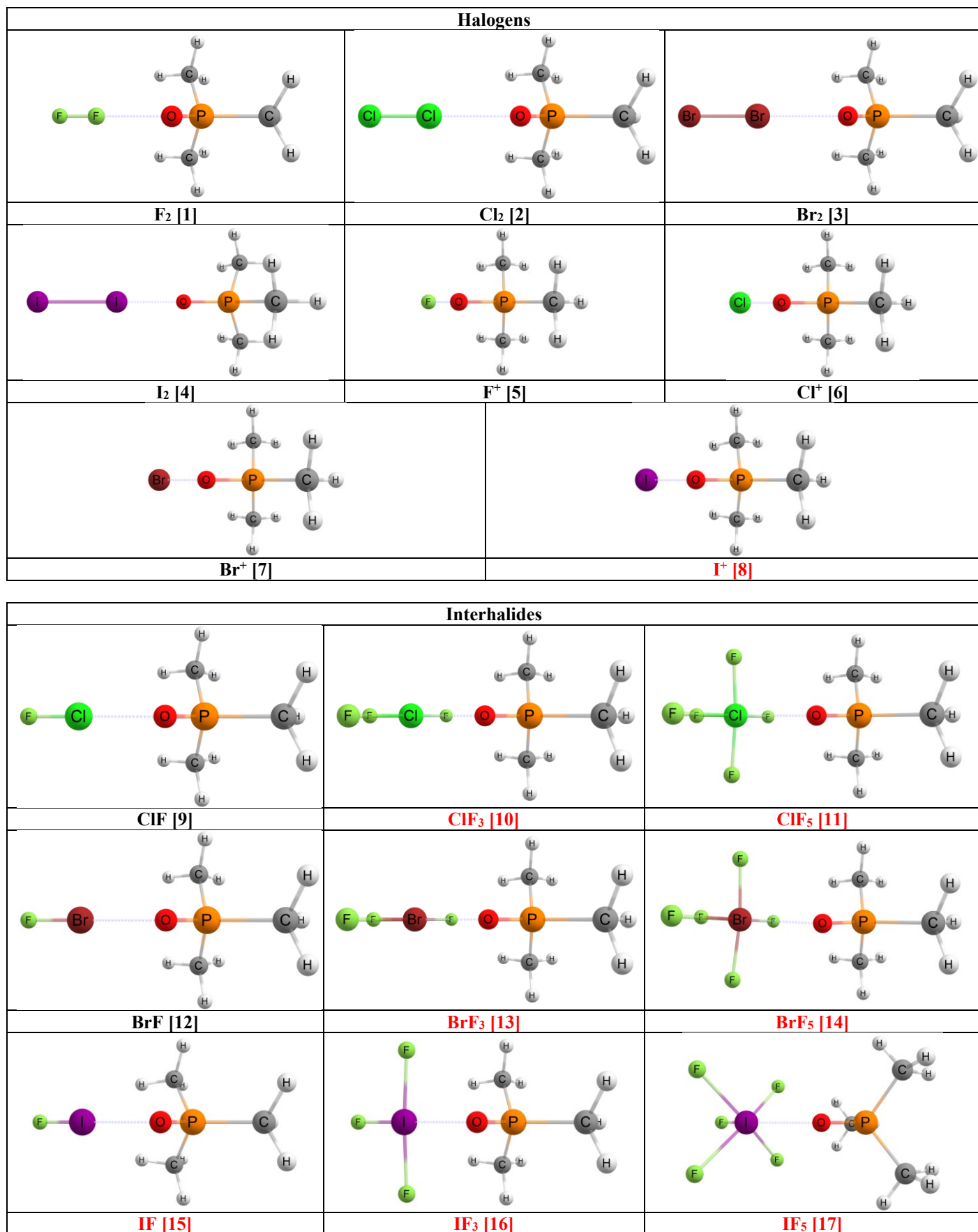
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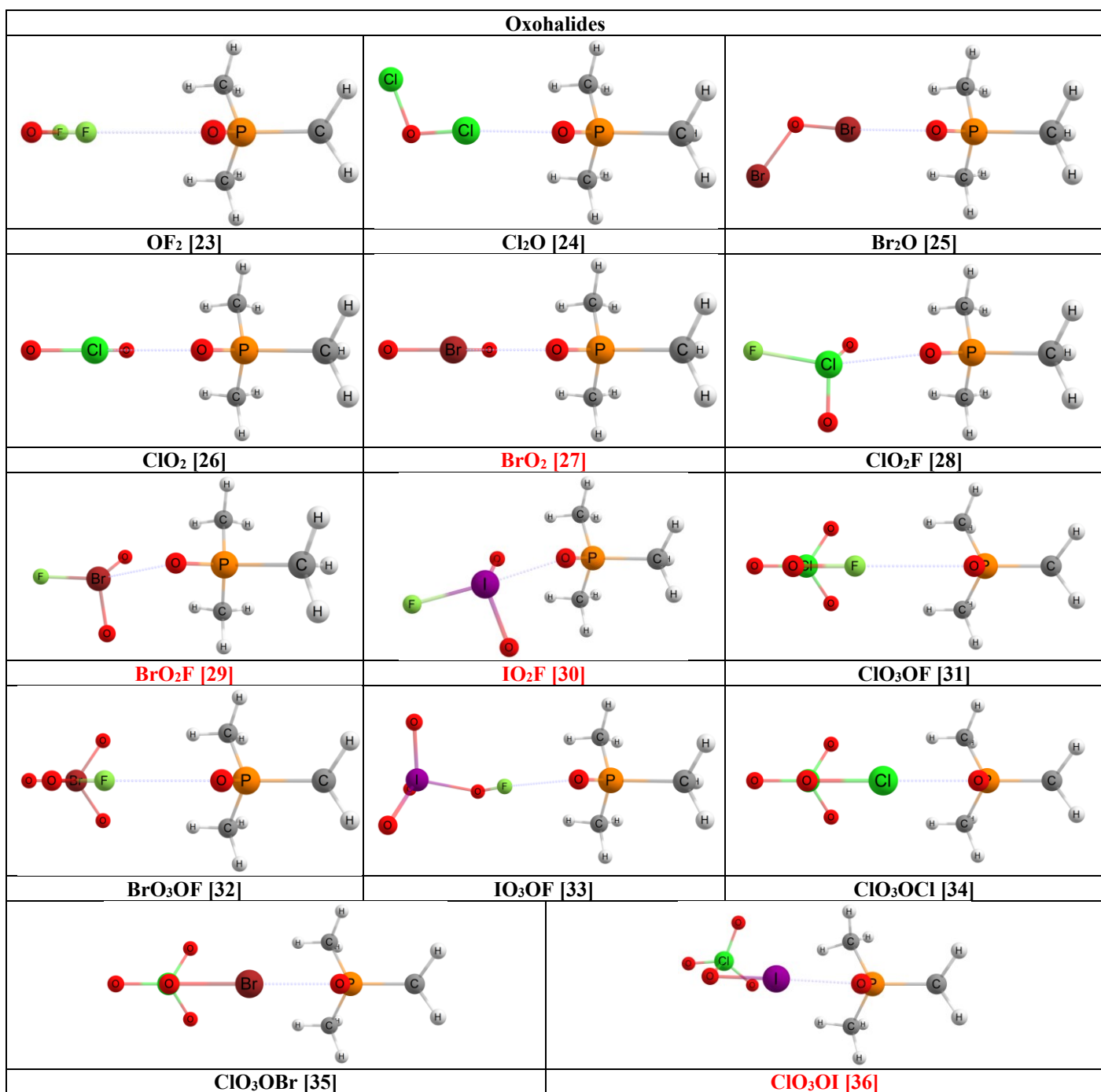
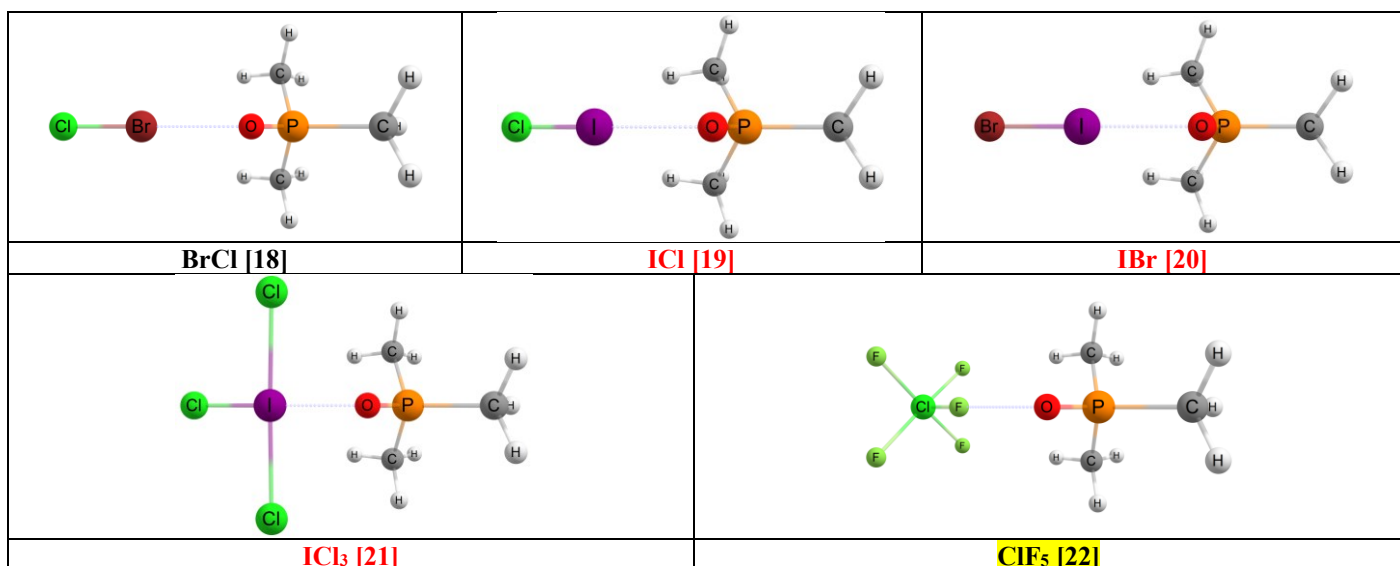
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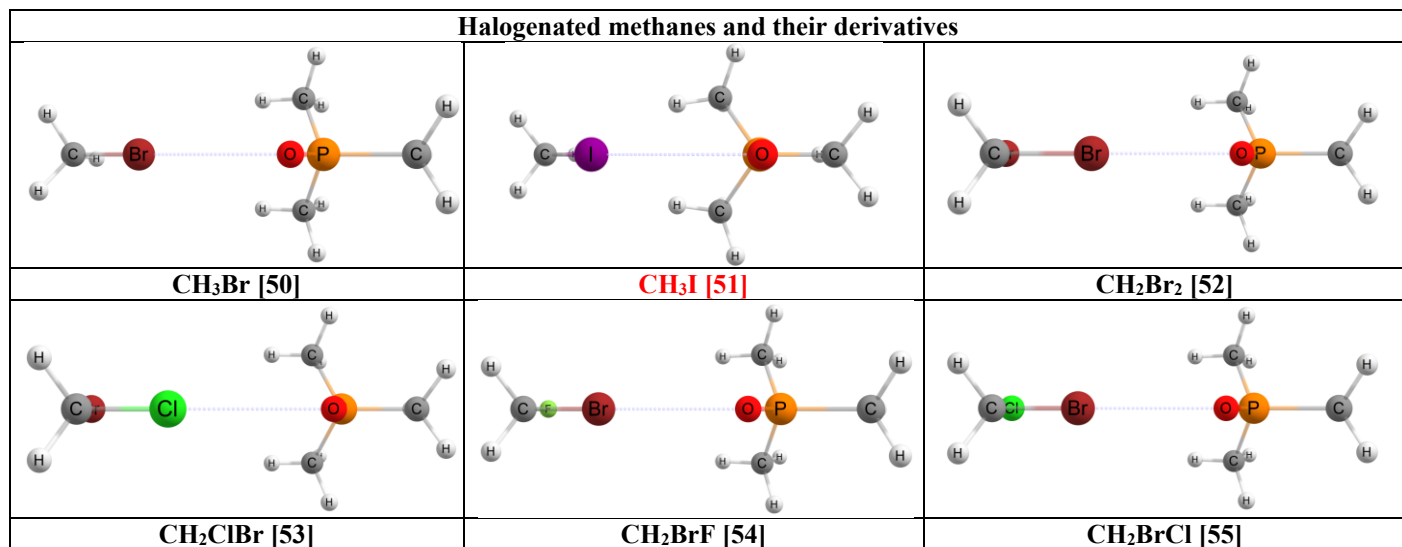
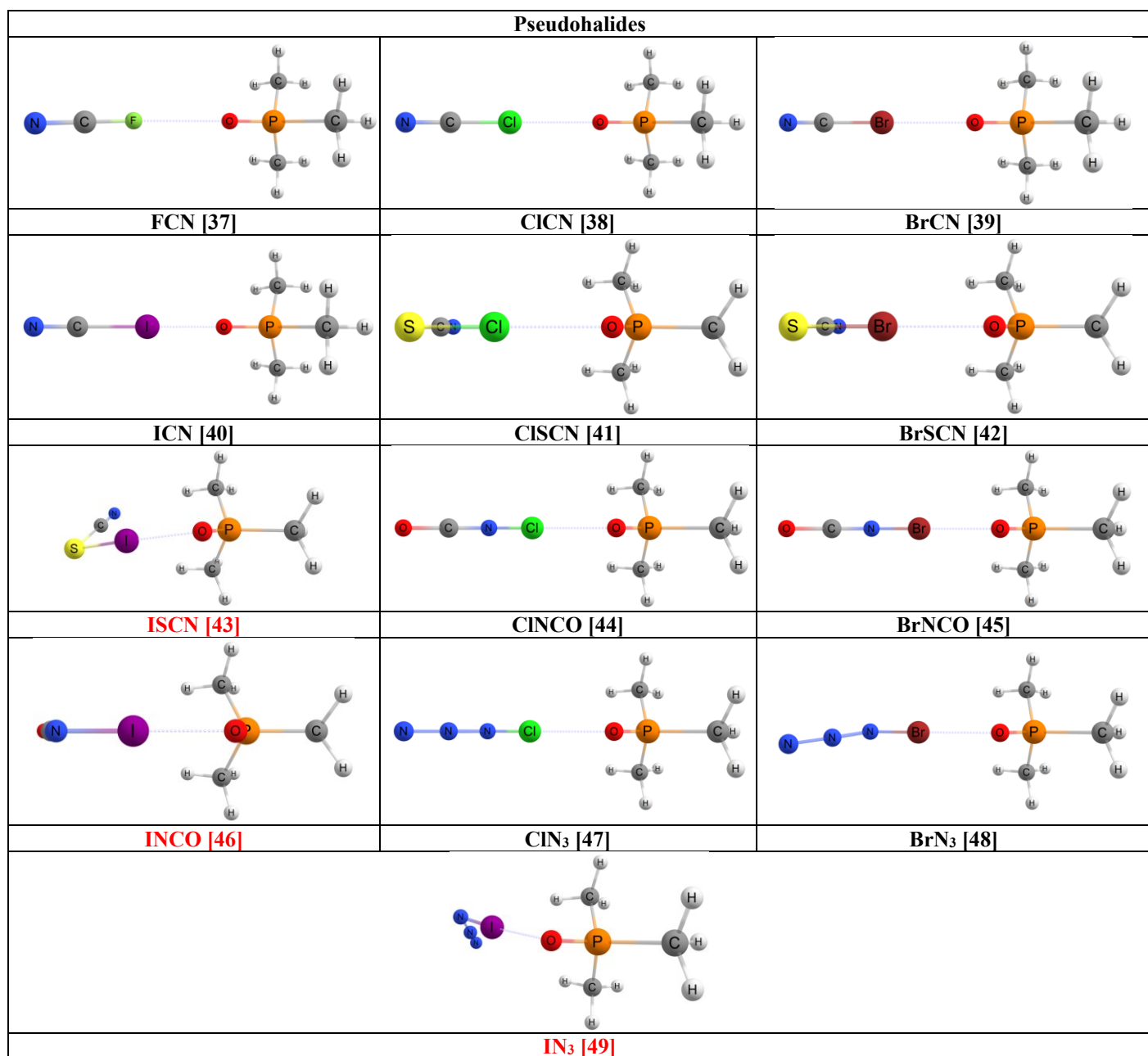
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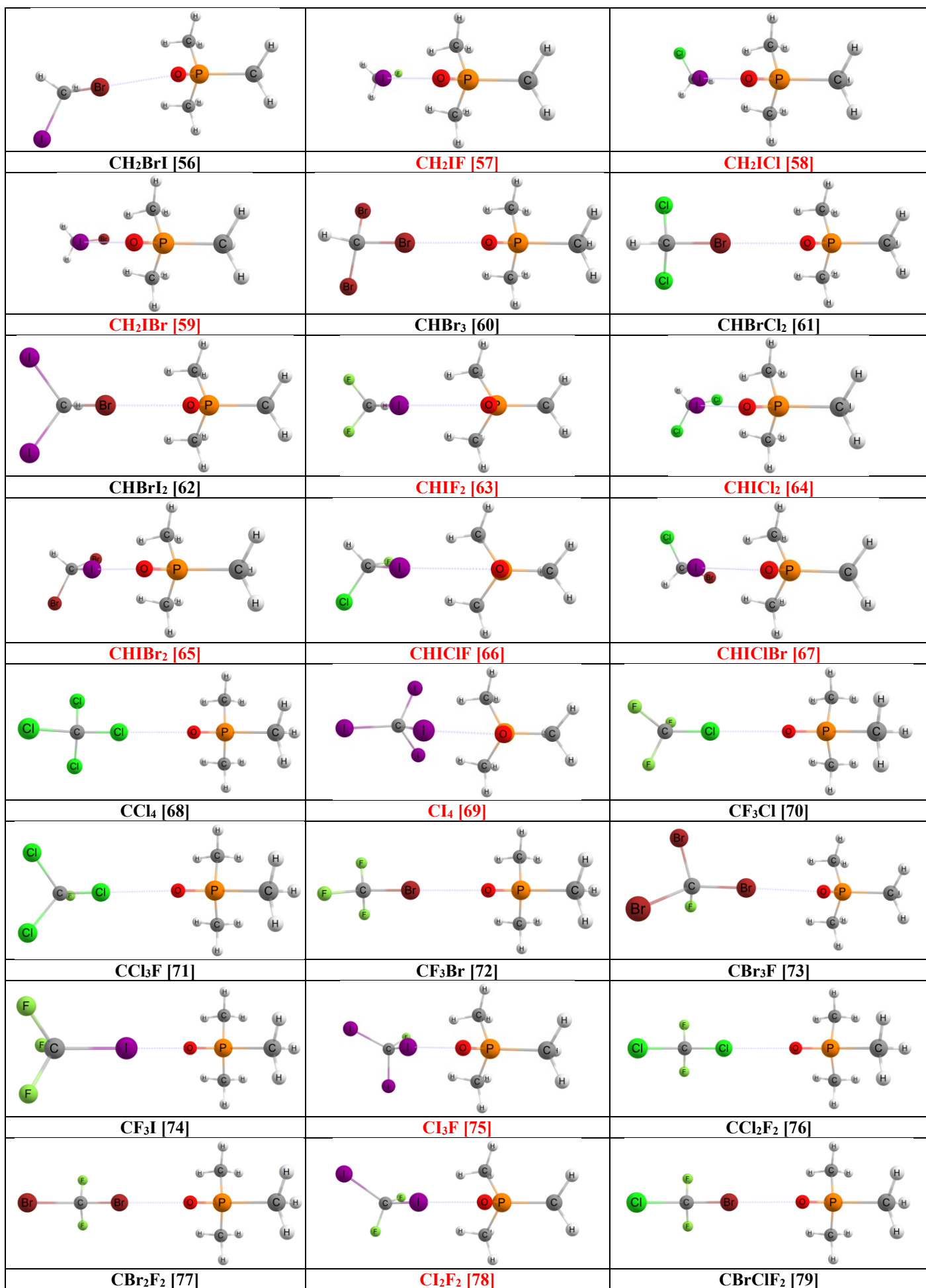
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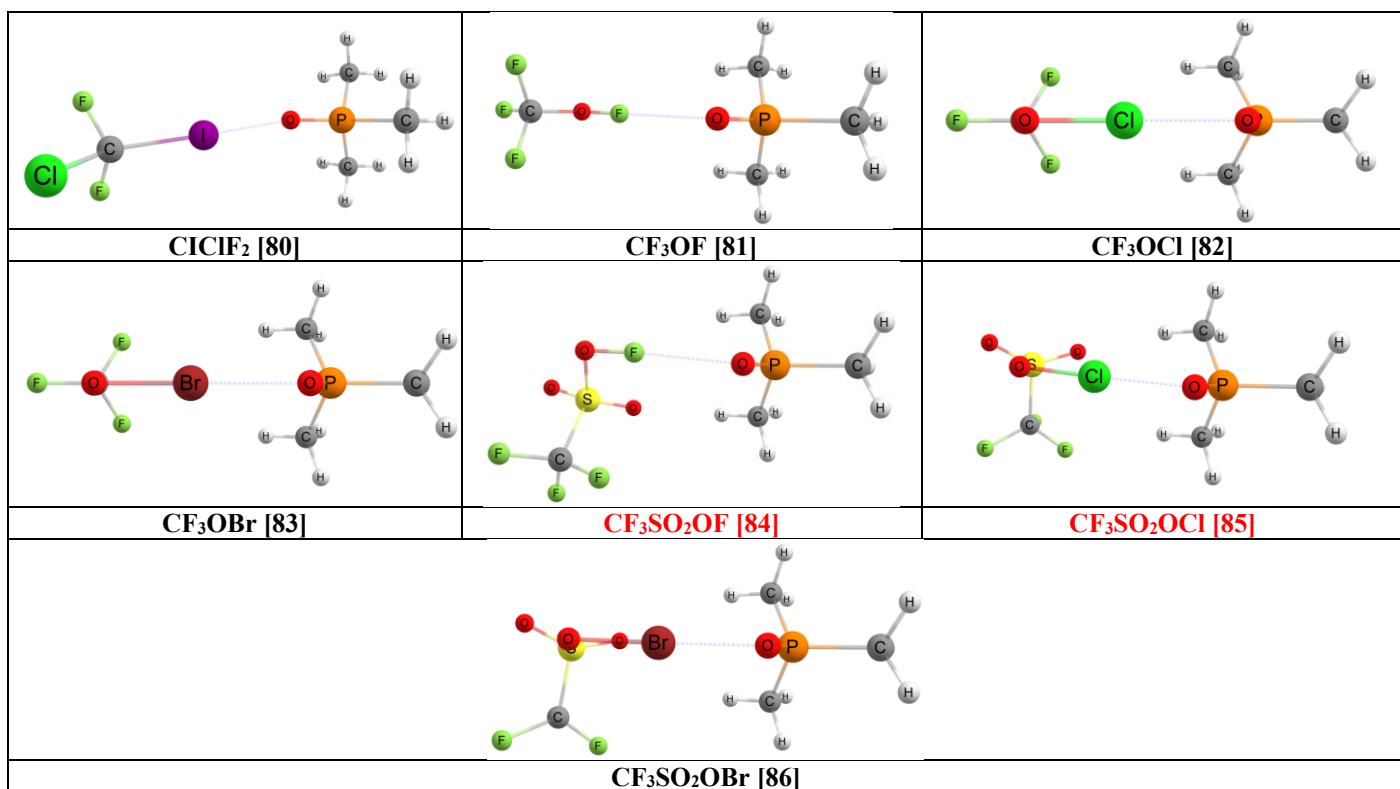
**Figure S1.** Calculated (B3LYP/jorge-ATZP, vacuum) optimized structures of 145 intermolecular 1:1 complexes formed by Me<sub>3</sub>PO with halogen-donating molecules. The complexes with additional Y...H (Y = N, O, F, Cl, Br or I; H are protons of methyl groups) contacts shorter than the sum of Bondi's van der Waals radii of corresponding atoms are marked in red color.



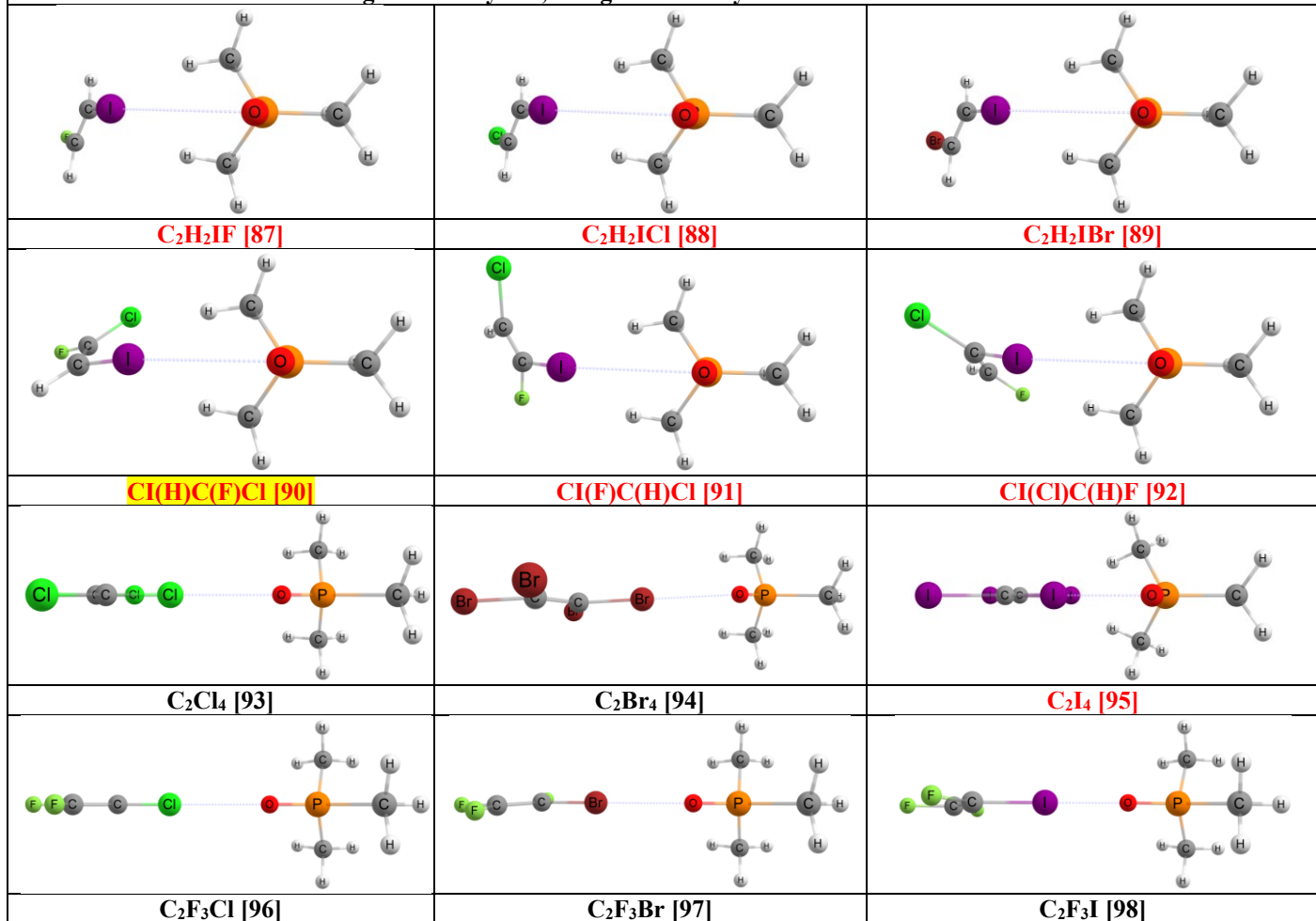




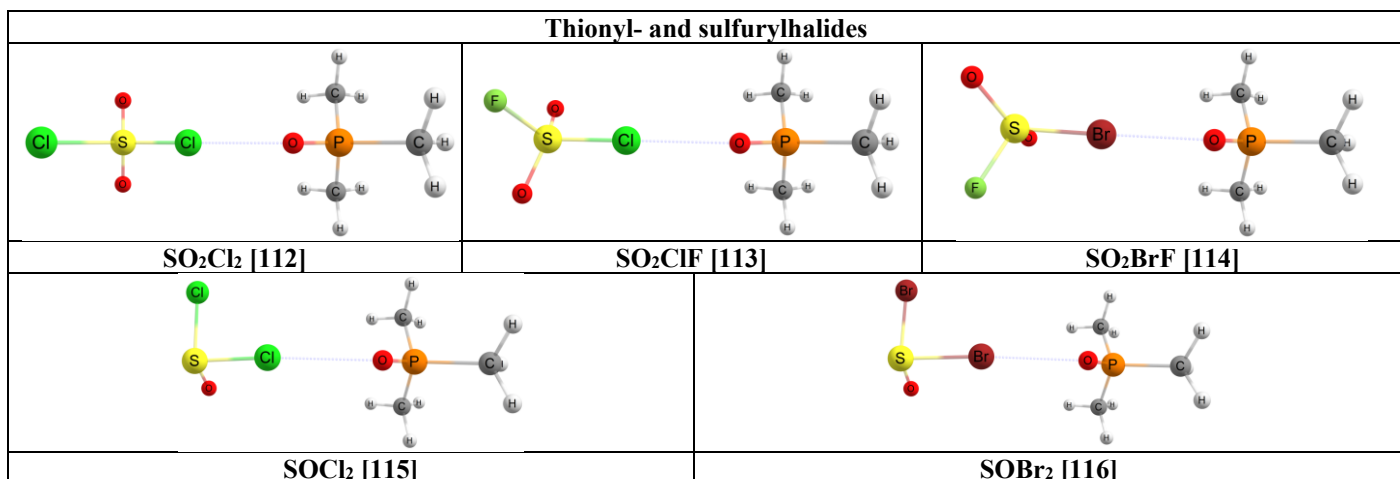
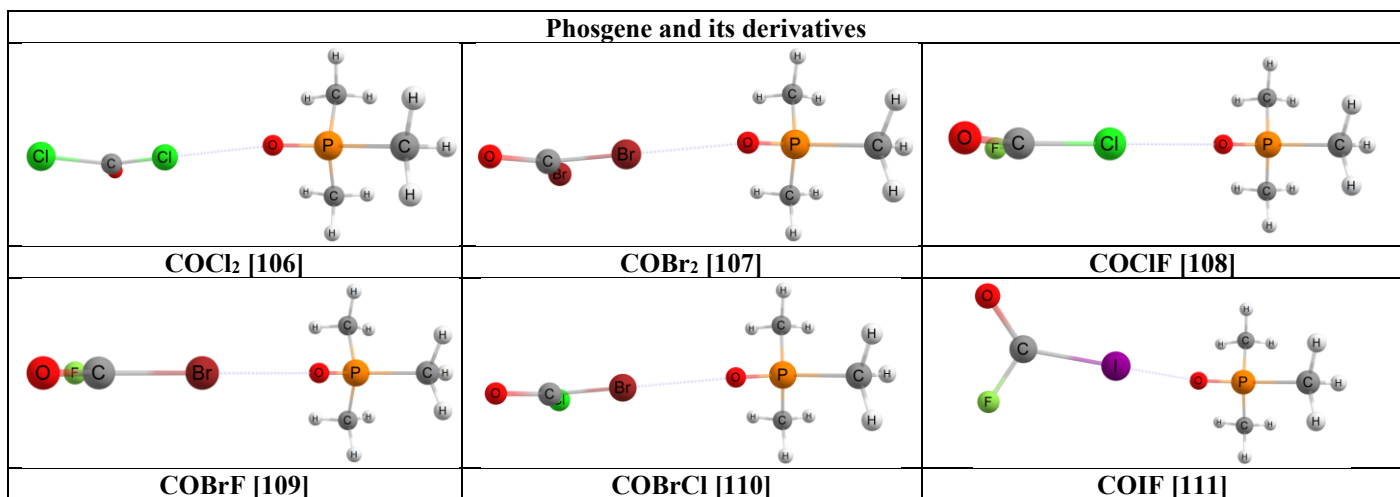
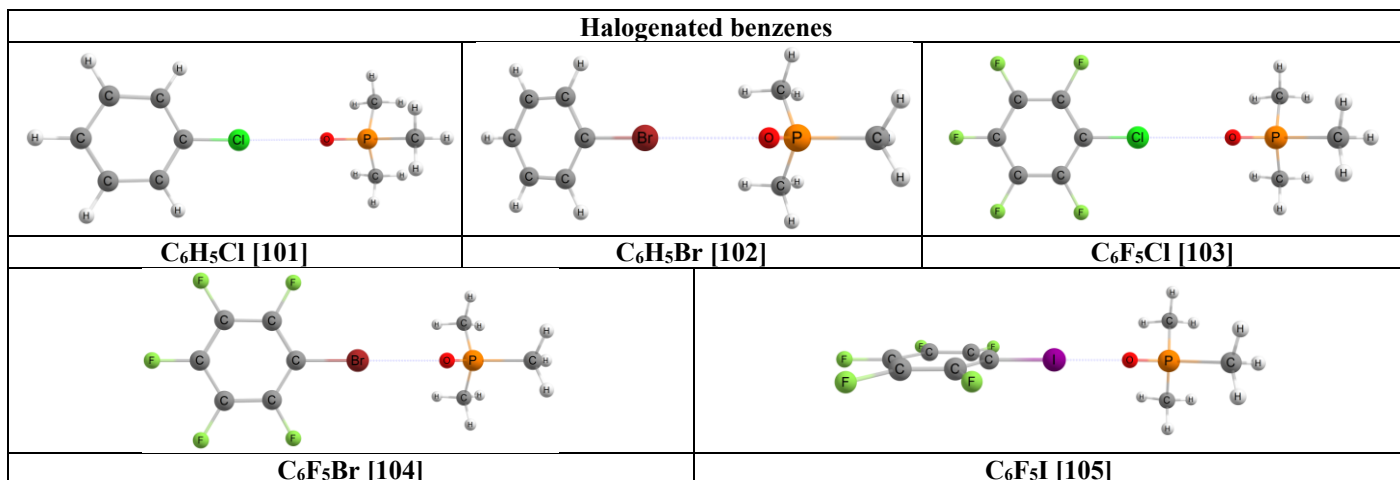
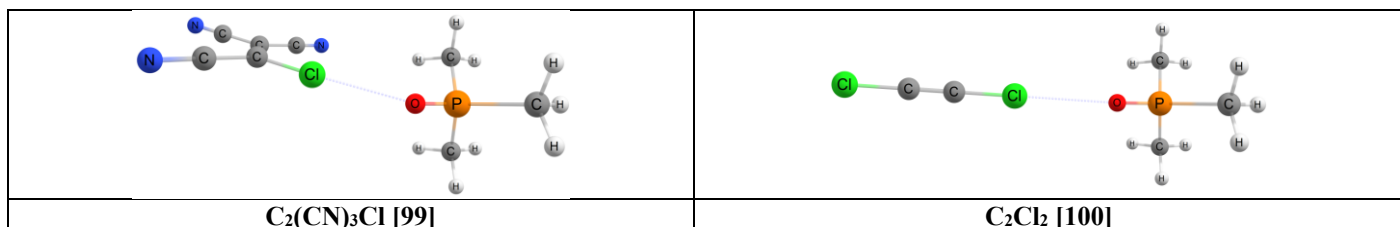




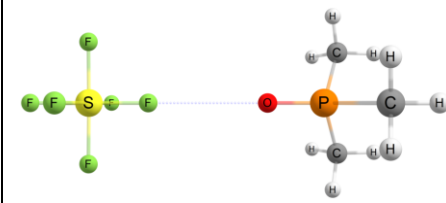
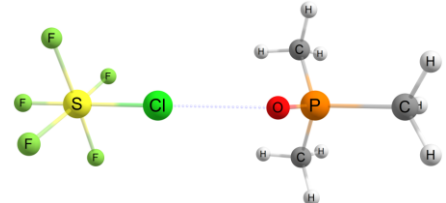
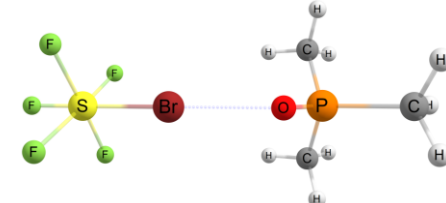
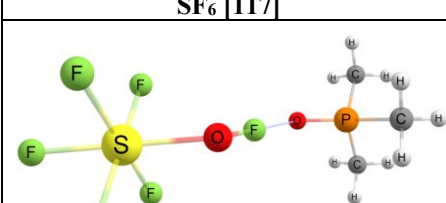
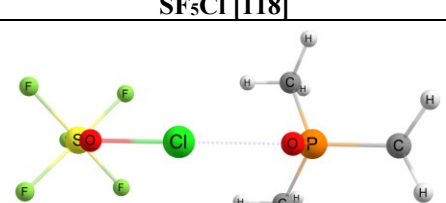
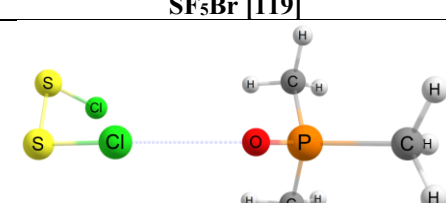
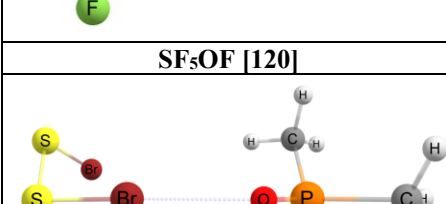
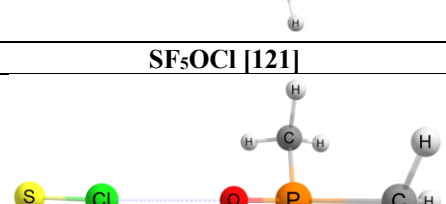
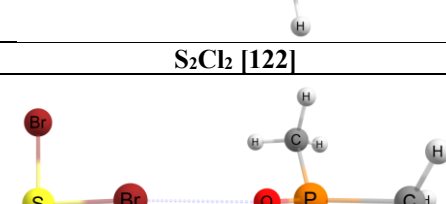
### Halogenated ethylene, halogenated acetylene and their derivatives



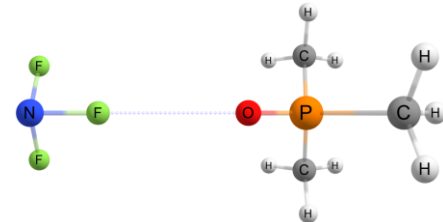
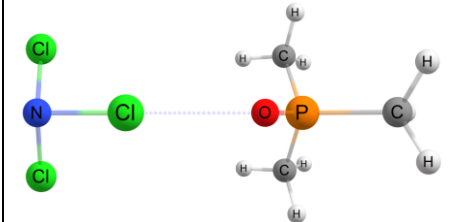
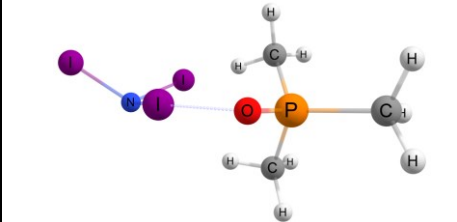
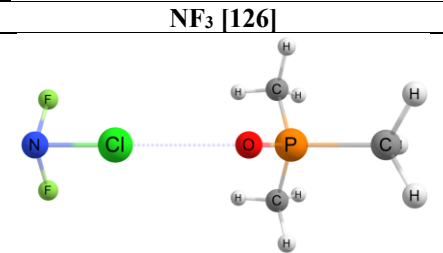
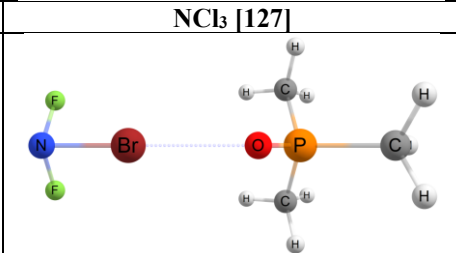
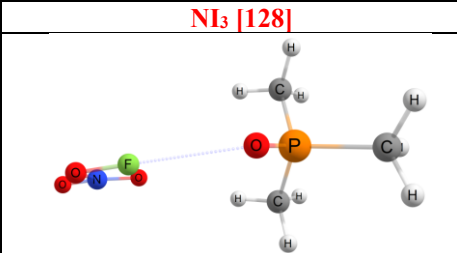
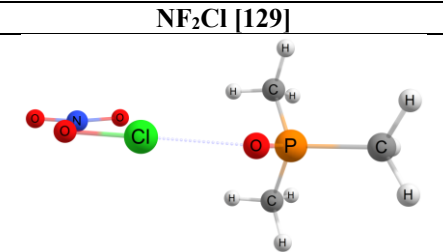
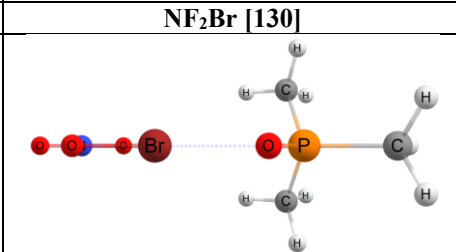
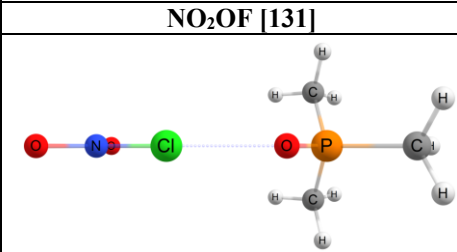
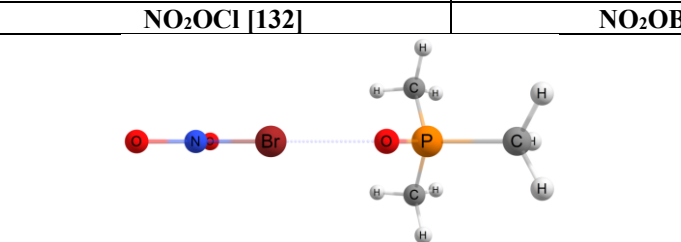
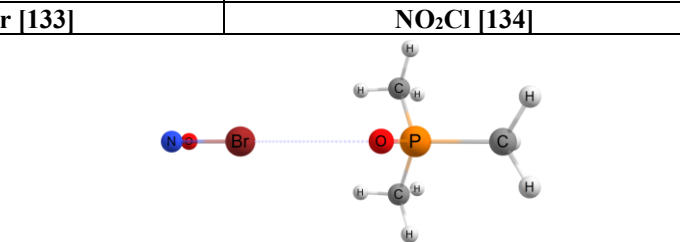




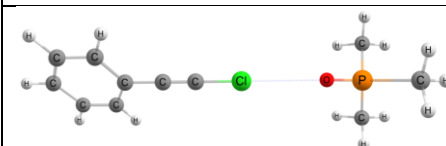
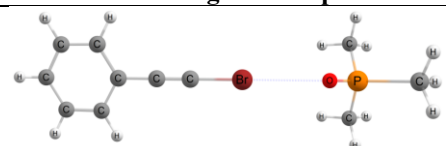
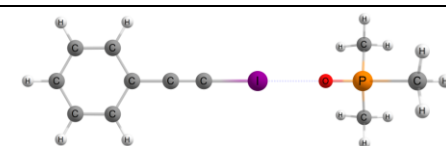
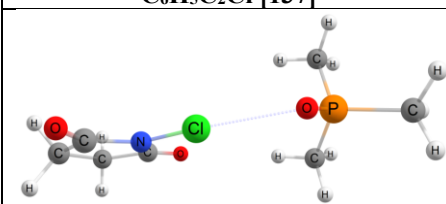
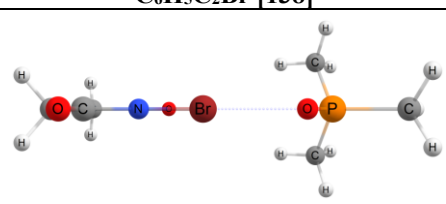
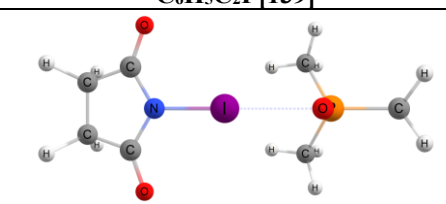
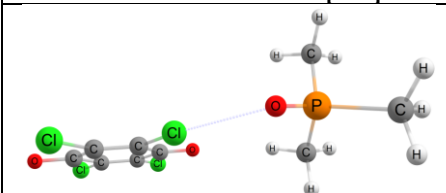
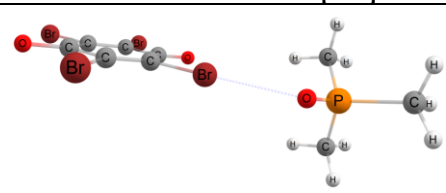
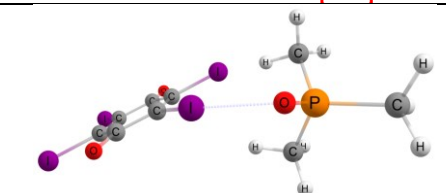
### Sulfur halides and sulfur hypohalites

|  |  |   |
|--|--|---|
|  |  |  |
| <b>SF<sub>6</sub> [117]</b>  | <b>SF<sub>5</sub>Cl [118]</b>  | <b>SF<sub>5</sub>Br [119]</b>   |
|  |  |  |
| <b>SF<sub>5</sub>OF [120]</b>  | <b>SF<sub>5</sub>OCl [121]</b>   | <b>S<sub>2</sub>Cl<sub>2</sub> [122]</b>  |
|  |  |  |
| <b>S<sub>2</sub>Br<sub>2</sub> [123]</b>   | <b>SCl<sub>2</sub> [124]</b>   | <b>SBr<sub>2</sub> [125]</b>  |

### Halogenated nitrogen-containing inorganic compounds

|   |  |   |
|---|--|---|
|  |  |  |
| <b>NF<sub>3</sub> [126]</b>   | <b>NCl<sub>3</sub> [127]</b>   | <b>NI<sub>3</sub> [128]</b>   |
|  |  |  |
| <b>NF<sub>2</sub>Cl [129]</b>   | <b>NF<sub>2</sub>Br [130]</b>  | <b>NO<sub>2</sub>OF [131]</b>   |
|  |  |  |
| <b>NO<sub>2</sub>OCl [132]</b>  | <b>NO<sub>2</sub>OBr [133]</b>   | <b>NO<sub>2</sub>Cl [134]</b>   |
|  |  |   |
| <b>NO<sub>2</sub>Br [135]</b>   | <b>NOBr [136]</b>  |   |



| Assorted organic compounds   |  |   |
|--|--|---|
|  |  |  |
| <b>C<sub>6</sub>H<sub>5</sub>C<sub>2</sub>Cl [137]</b>                           | <b>C<sub>6</sub>H<sub>5</sub>C<sub>2</sub>Br [138]</b>                             | <b>C<sub>6</sub>H<sub>5</sub>C<sub>2</sub>I [139]</b>                               |
|  |  |  |
| <b>N-Chlorosuccinimide [140]</b>   | <b>N-Bromosuccinimide [141]</b>  | <b>N-Iodosuccinimide [142]</b>  |
|  |  |  |
| <b>Tetrachloro-1,4-benzoquinone [143]</b>  | <b>Tetrabromo-1,4-benzoquinone [144]</b>   | <b>Tetraiodo-1,4-benzoquinone [145]</b>   |

**Table S1.** Results of DFT calculation (B3LYP/jorge-ATZP, vacuum) of 145 intermolecular 1:1 complexes formed by Me<sub>3</sub>PO with halogen-donating molecules: optimized halogen bond lengths  $R$  and normalized (by the sum of van der Waals radii of oxygen and halogen) halogen bond lengths  $R_{\text{norm}}$ , valence bond angles  $\alpha(\text{R}-\text{X}\cdots\text{O})$  and  $\beta(\text{X}\cdots\text{O}-\text{P})$ , <sup>31</sup>P NMR chemical shifts  $\Delta\delta^{31}\text{P}$ , complexation enthalpies  $\Delta H$  and Gibbs energies  $\Delta G$ . The complexes with additional Y $\cdots$ H (Y = N, O, F, Cl, Br or I; H are protons of methyl groups) contacts shorter than the sum of Bondi's van der Waals radii of corresponding atoms are marked in red color. In ambiguous cases the halogen atoms which participate in halogen bond formation are highlighted in bold.

| №                    | Halogen donor        | $R$ , Å | $R_{\text{norm}}$ | $\alpha(\text{R}-\text{X}\cdots\text{O})$ , ° | $\beta(\text{X}\cdots\text{O}-\text{P})$ , ° | $\Delta\delta^{31}\text{P}$ , ppm | $\Delta H$ , kJ/mol | $\Delta G$ , kJ/mol |
|----------------------|----------------------|---------|-------------------|---|--|-----------------------------------|---------------------|---------------------|
| <b>Halogens</b>      |                      |         |                   |   |  |                                   |                     |                     |
| 1                    | F <sub>2</sub>       | 2.259   | 0.755             | 179.5   | 103.2  | 12.25                             | -9.32               | 22.75               |
| 2                    | Cl <sub>2</sub>      | 2.514   | 0.769             | 179.6   | 116.5  | 13.59                             | -17.74              | 14.43               |
| 3                    | Br <sub>2</sub>      | 2.528   | 0.750             | 179.8   | 119.0  | 17.48                             | -27.38              | 6.04                |
| 4                    | I <sub>2</sub>       | 2.229   | 0.637             | 180.0   | 179.9  | 1.01                              | -136.59             | -103.20             |
| 5                    | F <sup>+</sup>       | 1.431   | 0.479             | –   | 106.3  | 120.78                            | -1348.96            | -1315.91            |
| 6                    | Cl <sup>+</sup>      | 1.718   | 0.525             | –   | 116.7  | 115.44                            | -788.55             | -755.61             |
| 7                    | Br <sup>+</sup>      | 1.857   | 0.551             | –   | 119.7  | 110.09                            | -655.60             | -622.88             |
| 8                    | I <sup>+</sup>       | 1.951   | 0.557             | –   | 113.6  | 106.16                            | -722.03             | -686.70             |
| <b>Interhalides</b>  |                      |         |                   |   |  |                                   |                     |                     |
| 9                    | ClF                  | 2.287   | 0.699             | 180.0   | 115.0  | 22.91                             | -40.17              | -1.93               |
| 10                   | ClF <sub>3</sub>     | 2.264   | 0.692             | 179.3   | 122.9  | 27.70                             | -52.88              | -9.21               |
| 11                   | ClF <sub>5</sub>     | 2.494   | 0.763             | 177.5   | 125.7  | 18.59                             | -35.59              | 0.14                |
| 12                   | BrF                  | 2.331   | 0.692             | 180.0   | 118.3  | 25.58                             | -55.32              | -16.50              |
| 13                   | BrF <sub>3</sub>     | 2.298   | 0.682             | 177.5   | 124.6  | 30.67                             | -70.44              | -26.30              |
| 14                   | BrF <sub>5</sub>     | 2.525   | 0.749             | 171.4   | 129.4  | 21.03                             | -49.88              | -14.42              |
| 15                   | IF                   | 2.252   | 0.644             | 172.8   | 105.8  | 49.39                             | -186.49             | -135.94             |
| 16                   | IF <sub>3</sub>      | 2.171   | 0.620             | 178.2   | 109.8  | 48.87                             | -178.16             | -128.81             |
| 17                   | IF <sub>5</sub>      | 2.347   | 0.671             | 151.7   | 137.5  | 24.12                             | -107.67             | -64.58              |
| 18                   | BrCl                 | 2.469   | 0.733             | 179.8   | 119.1  | 19.50                             | -33.32              | 2.81                |
| 19                   | ICl                  | 2.309   | 0.660             | 172.5   | 104.8  | 43.77                             | -154.34             | -104.66             |
| 20                   | IBr                  | 2.321   | 0.663             | 173.7   | 104.6  | 42.89                             | -149.38             | -100.92             |
| 21                   | ICl <sub>3</sub>     | 2.207   | 0.631             | 174.5   | 111.8  | 46.38                             | -158.89             | -108.35             |
| 22                   | ClF <sub>5</sub>     | 2.480   | 0.829             | 175.8   | 109.4  | 8.00                              | -5.31               | 24.19               |
| <b>Oxohalides</b>    |                      |         |                   |   |  |                                   |                     |                     |
| 23                   | OF <sub>2</sub>      | 2.840   | 0.950             | 178.7   | 114.3  | 0.94                              | 2.53                | 20.98               |
| 24                   | Cl <sub>2</sub> O    | 2.450   | 0.749             | 176.2   | 117.1  | 15.33                             | -21.55              | 14.37               |
| 25                   | Br <sub>2</sub> O    | 2.446   | 0.726             | 176.0   | 119.4  | 19.16                             | -34.60              | 3.90                |
| 26                   | ClO <sub>2</sub>     | 2.817   | 0.862             | 154.9   | 124.4  | 7.76                              | -20.10              | 14.04               |
| 27                   | BrO <sub>2</sub>     | 2.721   | 0.807             | 161.4   | 124.1  | 12.40                             | -34.13              | 5.25                |
| 28                   | ClO <sub>2</sub> F   | 2.619   | 0.801             | 151.5   | 128.8  | 11.72                             | -29.79              | 3.12                |
| 29                   | BrO <sub>2</sub> F   | 2.474   | 0.734             | 159.3   | 123.5  | 22.06                             | -52.11              | -9.92               |
| 30                   | IO <sub>2</sub> F    | 2.146   | 0.613             | 176.6   | 121.0  | 39.97                             | -191.53             | -137.80             |
| 31                   | ClO <sub>3</sub> OF  | 2.722   | 0.910             | 176.7   | 119.5  | 2.53                              | 0.96                | 26.74               |
| 32                   | BrO <sub>3</sub> OF  | 2.661   | 0.890             | 173.8   | 119.7  | 3.17                              | -1.27               | 28.57               |
| 33                   | IO <sub>3</sub> OF   | 2.512   | 0.840             | 173.1   | 101.7  | 3.79                              | -12.70              | 22.49               |
| 34                   | ClO <sub>3</sub> OCl | 2.249   | 0.688             | 178.1   | 114.5  | 27.49                             | -35.81              | 5.45                |
| 35                   | ClO <sub>3</sub> OBr | 2.238   | 0.664             | 178.1   | 116.8  | 35.63                             | -60.43              | -18.07              |
| 36                   | ClO <sub>3</sub> OI  | 2.175   | 0.622             | 175.2   | 103.1  | 45.90                             | -192.85             | -143.24             |
| <b>Pseudohalides</b> |                      |         |                   |   |  |                                   |                     |                     |
| 37                   | FCN                  | 2.860   | 0.957             | 176.4   | 179.7  | 1.86                              | -4.05               | 8.61                |
| 38                   | ClCN                 | 2.773   | 0.848             | 180.0   | 179.9  | 4.21                              | -17.92              | 4.53                |
| 39                   | BrCN                 | 2.729   | 0.810             | 179.9   | 161.1  | 5.16                              | -24.30              | -5.95               |
| 40                   | ICN                  | 2.328   | 0.665             | 180.0   | 180.0  | 2.40                              | -99.07              | -63.81              |
| 41                   | ClSCN                | 2.695   | 0.824             | 179.9   | 123.1  | 7.87                              | -11.58              | 18.12               |
| 42                   | BrSCN                | 2.587   | 0.768             | 179.9   | 122.0  | 14.71                             | -24.53              | 9.50                |
| 43                   | ISCN                 | 2.318   | 0.662             | 173.5   | 106.5  | 37.70                             | -138.97             | -86.99              |
| 44                   | CINCO                | 2.594   | 0.793             | 178.0   | 120.7  | 8.06                              | -14.42              | 16.23               |
| 45                   | BrNCO                | 2.505   | 0.743             | 178.1   | 121.7  | 14.72                             | -29.61              | 4.19                |
| 46                   | INCO                 | 2.269   | 0.648             | 177.0   | 105.5  | 30.90                             | -140.43             | -94.88              |
| 47                   | CIN <sub>3</sub>     | 2.647   | 0.809             | 177.0   | 119.6  | 7.14                              | -10.71              | 18.68               |
| 48                   | BrN <sub>3</sub>     | 2.556   | 0.759             | 177.5   | 121.5  | 15.83                             | -23.93              | 7.77                |
| 49                   | IN <sub>3</sub>      | 2.333   | 0.666             | 175.9   | 108.2  | 40.48                             | -135.69             | -81.95              |

| Halogenated methanes and their derivatives                        |                                     |       |       |       |       |       |         |         |
|---|-------------------------------------|-------|-------|-------|-------|-------|---------|---------|
| 50  | CH <sub>3</sub> Br                  | 3.258 | 0.967 | 176.3 | 111.5 | 1.99  | 2.76    | 23.34   |
| 51  | CH <sub>3</sub> I                   | 3.429 | 0.980 | 162.8 | 83.7  | 8.48  | -87.51  | -43.93  |
| 52  | CH <sub>2</sub> Br <sub>2</sub>     | 3.005 | 0.892 | 178.4 | 121.5 | 3.30  | -3.59   | 23.39   |
| 53  | CH <sub>2</sub> ClBr                | 3.155 | 0.965 | 176.2 | 112.8 | 1.42  | 1.11    | 25.26   |
| 54  | CH <sub>2</sub> BrF                 | 3.093 | 0.918 | 176.0 | 118.9 | 3.69  | -1.56   | 24.65   |
| 55  | CH <sub>2</sub> BrCl                | 3.018 | 0.896 | 178.0 | 121.3 | 3.36  | -3.10   | 23.61   |
| 56  | CH <sub>2</sub> BrI                 | 2.962 | 0.879 | 174.1 | 112.8 | 4.68  | -8.95   | 24.26   |
| 57  | CH <sub>2</sub> IF                  | 3.375 | 0.964 | 160.9 | 84.7  | 9.61  | -90.49  | -47.50  |
| 58  | CH <sub>2</sub> ICl                 | 3.330 | 0.952 | 164.7 | 85.7  | 9.70  | -87.07  | -40.96  |
| 59  | CH <sub>2</sub> IBr                 | 3.333 | 0.952 | 161.7 | 85.4  | 9.69  | -90.48  | -48.11  |
| 60  | CHBr <sub>3</sub>                   | 2.878 | 0.854 | 179.5 | 128.8 | 3.44  | -8.13   | 19.56   |
| 61  | CHBrCl <sub>2</sub>                 | 2.892 | 0.858 | 179.7 | 128.3 | 6.34  | -7.60   | 19.42   |
| 62  | CHBrI <sub>2</sub>                  | 2.830 | 0.840 | 173.1 | 109.6 | 6.15  | -19.99  | 15.58   |
| 63  | CHIF <sub>2</sub>                   | 3.285 | 0.939 | 167.3 | 86.3  | 10.27 | -89.36  | -47.78  |
| 64  | CHICl <sub>2</sub>                  | 3.250 | 0.929 | 163.4 | 87.1  | 11.81 | -87.14  | -41.56  |
| 65  | CHIBr <sub>2</sub>                  | 2.617 | 0.748 | 173.0 | 99.6  | 24.49 | -91.40  | -43.16  |
| 66  | CHICIF                              | 3.267 | 0.934 | 162.7 | 86.7  | 11.08 | -90.79  | -45.63  |
| 67  | CHIClBr                             | 3.247 | 0.928 | 162.5 | 87.1  | 12.33 | -90.49  | -44.31  |
| 68  | CCl <sub>4</sub>                    | 2.880 | 0.881 | 179.6 | 144.6 | 3.09  | -4.63   | 22.03   |
| 69  | Cl <sub>4</sub>                     | 2.507 | 0.716 | 147.6 | 91.3  | 13.68 | -225.91 | -169.64 |
| 70  | CF <sub>3</sub> Cl                  | 2.919 | 0.893 | 179.9 | 163.3 | 0.61  | -5.20   | 18.24   |
| 71  | CCl <sub>3</sub> F                  | 2.895 | 0.885 | 178.6 | 149.8 | 2.31  | -4.84   | 19.33   |
| 72  | CF <sub>3</sub> Br                  | 2.857 | 0.848 | 179.7 | 143.7 | 4.56  | -11.14  | 16.54   |
| 73  | CBr <sub>3</sub> F                  | 2.807 | 0.833 | 178.0 | 133.7 | 6.66  | -11.70  | 16.11   |
| 74  | CF <sub>3</sub> I                   | 2.348 | 0.671 | 180.0 | 179.7 | 2.50  | -74.10  | -44.13  |
| 75  | Cl <sub>3</sub> F                   | 2.515 | 0.719 | 164.0 | 100.3 | 27.79 | -135.69 | -85.15  |
| 76  | CCl <sub>2</sub> F <sub>2</sub>     | 2.907 | 0.889 | 179.0 | 157.4 | 1.11  | -4.98   | 17.08   |
| 77  | CBr <sub>2</sub> F <sub>2</sub>     | 2.833 | 0.841 | 178.0 | 136.7 | 5.96  | -11.31  | 16.55   |
| 78  | Cl <sub>2</sub> F <sub>2</sub>      | 2.530 | 0.723 | 170.3 | 101.1 | 26.05 | -114.78 | -64.60  |
| 79  | CBrClF <sub>2</sub>                 | 2.837 | 0.842 | 178.5 | 138.6 | 4.80  | -11.15  | 17.14   |
| 80  | ClCIF <sub>2</sub>                  | 2.345 | 0.670 | 177.2 | 168.7 | 2.31  | -73.69  | -41.35  |
| 81  | CF <sub>3</sub> OF                  | 2.770 | 0.927 | 179.7 | 111.5 | 0.95  | 2.33    | 23.87   |
| 82  | CF <sub>3</sub> OCl                 | 2.320 | 0.709 | 178.2 | 116.0 | 21.00 | -32.33  | 5.41    |
| 83  | CF <sub>3</sub> OBr                 | 2.311 | 0.686 | 178.0 | 118.4 | 27.41 | -53.10  | -14.08  |
| 84  | CF <sub>3</sub> SO <sub>2</sub> OF  | 2.601 | 0.870 | 176.5 | 111.6 | 4.52  | -2.54   | 29.10   |
| 85  | CF <sub>3</sub> SO <sub>2</sub> OCl | 2.118 | 0.648 | 178.7 | 111.3 | 39.14 | -49.66  | -5.38   |
| 86  | CF <sub>3</sub> SO <sub>2</sub> OBr | 2.183 | 0.648 | 179.0 | 115.3 | 41.48 | -73.18  | -30.84  |
| Halogenated ethylene, halogenated acetylene and their derivatives |                                     |       |       |       |       |       |         |         |
| 87  | C <sub>2</sub> H <sub>2</sub> IF    | 3.470 | 0.991 | 152.1 | 83.7  | 7.48  | -90.39  | -48.46  |
| 88  | C <sub>2</sub> H <sub>2</sub> ICl   | 3.464 | 0.990 | 152.0 | 83.9  | 8.50  | -88.90  | -47.06  |
| 89  | C <sub>2</sub> H <sub>2</sub> IBr   | 3.452 | 0.986 | 152.6 | 84.1  | 9.03  | -89.55  | -47.23  |
| 90  | Cl(H)C(F)Cl                         | 3.291 | 0.940 | 167.9 | 86.3  | 11.10 | -86.20  | -40.70  |
| 91  | Cl(F)C(H)Cl                         | 3.307 | 0.945 | 159.4 | 86.6  | 9.24  | -89.45  | -44.86  |
| 92  | Cl(Cl)C(H)Cl                        | 3.284 | 0.938 | 162.7 | 86.5  | 11.51 | -86.34  | -41.07  |
| 93  | C <sub>2</sub> Cl <sub>4</sub>      | 2.943 | 0.900 | 179.5 | 152.5 | 2.16  | -3.07   | 22.20   |
| 94  | C <sub>2</sub> Br <sub>4</sub>      | 2.861 | 0.849 | 178.5 | 135.9 | 4.57  | -9.48   | 17.53   |
| 95  | C <sub>2</sub> I <sub>4</sub>       | 2.470 | 0.706 | 168.0 | 94.6  | 16.87 | -204.58 | -143.54 |
| 96  | C <sub>2</sub> F <sub>3</sub> Cl    | 2.942 | 0.900 | 178.9 | 157.4 | 0.34  | -4.44   | 19.70   |
| 97  | C <sub>2</sub> F <sub>3</sub> Br    | 2.877 | 0.854 | 178.8 | 146.8 | 4.08  | -10.71  | 15.23   |
| 98  | C <sub>2</sub> F <sub>3</sub> I     | 2.373 | 0.678 | 179.1 | 178.4 | 0.46  | -65.54  | -33.23  |
| 99  | C <sub>2</sub> (CN) <sub>3</sub> Cl | 2.744 | 0.839 | 174.4 | 138.8 | 6.59  | -18.37  | 12.28   |
| 100   | C <sub>2</sub> Cl <sub>2</sub>      | 2.906 | 0.889 | 179.9 | 164.7 | 2.15  | -6.97   | 14.92   |
| Halogenated benzenes  |                                     |       |       |       |       |       |         |         |
| 101   | C <sub>6</sub> H <sub>5</sub> Cl    | 3.472 | 1.062 | 171.1 | 103.9 | -0.02 | 4.31    | 24.70   |
| 102   | C <sub>6</sub> H <sub>5</sub> Br    | 3.141 | 0.932 | 176.1 | 118.8 | 2.16  | 0.71    | 25.31   |
| 103   | C <sub>6</sub> F <sub>5</sub> Cl    | 2.941 | 0.899 | 179.7 | 165.5 | -0.96 | -3.66   | 14.86   |
| 104   | C <sub>6</sub> F <sub>5</sub> Br    | 2.866 | 0.850 | 179.7 | 147.0 | 3.90  | -10.28  | 14.78   |
| 105   | C <sub>6</sub> F <sub>5</sub> I     | 2.390 | 0.683 | 179.0 | 165.6 | 1.02  | -58.38  | -24.02  |
| Phosgene and its derivatives                                      |                                     |       |       |       |       |       |         |         |
| 106   | COCl <sub>2</sub>                   | 2.916 | 0.892 | 177.7 | 150.5 | 2.85  | -5.54   | 17.65   |
| 107   | COBr <sub>2</sub>                   | 2.846 | 0.844 | 178.9 | 144.0 | 3.47  | -10.85  | 15.60   |
| 108   | COClF                               | 2.908 | 0.889 | 179.3 | 179.7 | 2.98  | -7.03   | 13.65   |
| 109   | COBrF                               | 2.867 | 0.851 | 178.8 | 164.4 | 2.11  | -12.44  | 8.91    |
| 110   | COBrCl                              | 2.862 | 0.849 | 178.7 | 149.9 | 4.17  | -10.64  | 13.32   |
| 111   | COIF                                | 2.356 | 0.673 | 179.6 | 172.2 | 1.04  | -75.57  | -44.27  |
| Thionyl- and sulfonylhalides                                      |                                     |       |       |       |       |       |         |         |

|  |   |       |       |       |       |       |         |         |
|--|---|-------|-------|-------|-------|-------|---------|---------|
| 112  | SO <sub>2</sub> Cl <sub>2</sub>                 | 2.711 | 0.829 | 177.4 | 135.1 | 6.05  | -12.67  | 14.96   |
| 113  | SO <sub>2</sub> ClF                             | 2.732 | 0.836 | 178.9 | 144.5 | 6.39  | -13.89  | 12.59   |
| 114  | SO <sub>2</sub> BrF                             | 2.626 | 0.779 | 178.5 | 130.6 | 13.40 | -24.85  | 3.59    |
| 115  | SOCl <sub>2</sub>                               | 2.933 | 0.897 | 176.3 | 128.5 | 2.61  | -2.81   | 20.30   |
| 116  | SOBr <sub>2</sub>                               | 2.837 | 0.842 | 176.5 | 127.2 | 7.43  | -9.13   | 18.89   |
| <b>Sulfur halides and sulfur hypohalites</b>               |   |       |       |       |       |       |         |         |
| 117  | SF <sub>6</sub>                                 | 3.089 | 1.033 | 176.3 | 177.1 | -1.30 | 3.95    | 13.83   |
| 118  | SF <sub>5</sub> Cl                              | 2.644 | 0.808 | 179.4 | 124.4 | 9.77  | -13.02  | 12.83   |
| 119  | SF <sub>5</sub> Br                              | 2.513 | 0.746 | 179.4 | 121.3 | 19.74 | -28.64  | 3.53    |
| 120  | SF <sub>5</sub> OF                              | 2.758 | 0.922 | 179.7 | 125.0 | 1.53  | 2.25    | 19.04   |
| 121  | SF <sub>5</sub> OCl                             | 2.227 | 0.681 | 176.8 | 114.3 | 28.41 | -38.09  | 2.33    |
| 122  | S <sub>2</sub> Cl <sub>2</sub>                  | 2.932 | 0.897 | 177.9 | 120.7 | 4.13  | -0.98   | 23.14   |
| 123  | S <sub>2</sub> Br <sub>2</sub>                  | 2.800 | 0.831 | 178.6 | 123.2 | 8.25  | -8.65   | 20.28   |
| 124  | SCl <sub>2</sub>                                | 2.876 | 0.879 | 177.9 | 126.6 | 2.69  | -3.69   | 20.75   |
| 125  | SBr <sub>2</sub>                                | 2.758 | 0.818 | 177.2 | 125.0 | 7.03  | -12.38  | 18.53   |
| <b>Halogenated nitrogen-containing inorganic compounds</b> |   |       |       |       |       |       |         |         |
| 126  | NF <sub>3</sub>                                 | 3.041 | 1.017 | 173.7 | 147.5 | 0.43  | 3.88    | 20.33   |
| 127  | NCl <sub>3</sub>                                | 2.639 | 0.807 | 176.0 | 123.0 | 9.23  | -11.37  | 17.09   |
| 128  | NI <sub>3</sub>                                 | 2.330 | 0.666 | 158.0 | 97.8  | 36.98 | -209.85 | -154.85 |
| 129  | NF <sub>2</sub> Cl                              | 2.651 | 0.811 | 178.1 | 125.4 | 8.99  | -13.63  | 15.76   |
| 130  | NF <sub>2</sub> Br                              | 2.591 | 0.769 | 178.2 | 123.6 | 14.51 | -24.21  | 9.00    |
| 131  | NO <sub>2</sub> OF                              | 2.843 | 0.951 | 178.8 | 115.2 | 1.75  | 3.15    | 27.77   |
| 132  | NO <sub>2</sub> OCl                             | 2.360 | 0.722 | 177.7 | 116.1 | 19.41 | -27.01  | 10.63   |
| 133  | NO <sub>2</sub> OBr                             | 2.324 | 0.690 | 177.1 | 118.0 | 27.24 | -48.17  | -9.23   |
| 134  | NO <sub>2</sub> Cl                              | 2.639 | 0.807 | 179.0 | 121.1 | 10.20 | -10.49  | 19.75   |
| 135  | NO <sub>2</sub> Br                              | 2.574 | 0.764 | 179.3 | 121.8 | 16.01 | -22.09  | 11.97   |
| 136  | NOBr  | 3.285 | 0.975 | 178.5 | 113.1 | 1.21  | 4.32    | 26.50   |
| <b>Assorted organic compounds</b>                          |   |       |       |       |       |       |         |         |
| 137  | C <sub>6</sub> H <sub>5</sub> C <sub>2</sub> Cl | 2.937 | 0.898 | 179.6 | 157.8 | 0.10  | -3.77   | 18.58   |
| 138  | C <sub>6</sub> H <sub>5</sub> C <sub>2</sub> Br | 2.872 | 0.852 | 179.1 | 142.7 | 4.34  | -10.22  | 13.24   |
| 139  | C <sub>6</sub> H <sub>5</sub> C <sub>2</sub> I  | 2.405 | 0.687 | 179.0 | 164.8 | -1.78 | -58.41  | -20.00  |
| 140  | N-Chlorosuccinimide                             | 2.686 | 0.821 | 171.3 | 115.3 | 6.89  | -11.50  | 22.73   |
| 141  | N-Bromosuccinimide                              | 2.574 | 0.764 | 176.2 | 119.3 | 14.65 | -23.63  | 7.76    |
| 142  | N-Iodosuccinimide                               | 2.328 | 0.665 | 175.0 | 104.5 | 27.39 | -108.57 | -61.35  |
| 143  | Tetrachloro-1,4-benzoquinone                    | 2.961 | 0.906 | 167.6 | 117.3 | 3.58  | -6.16   | 25.07   |
| 144  | Tetrabromo-1,4-benzoquinone                     | 2.866 | 0.850 | 175.4 | 125.3 | 5.42  | -11.62  | 17.24   |
| 145  | Tetraiodo-1,4-benzoquinone                      | 2.642 | 0.755 | 162.5 | 98.8  | 20.98 | -138.62 | -85.11  |

**Table S2.** Results of the electron density QTAIM analysis of the X...O (X = F, Cl, Br and I) halogen bond for 145 intermolecular 1:1 complexes formed by Me<sub>3</sub>PO with halogen-donating molecules: distances from oxygen atom to minima positions of electron density  $d(ED_{\min})$  and molecular electrostatic potential  $d(ESP_{\min})$  along the bond path and the distance between them  $\Delta d$ , molecular electrostatic potential  $ESP(r_{\text{BCP}})$ , electron density  $\rho(r_{\text{BCP}})$ , Laplacian of electron density  $\nabla^2\rho(r_{\text{BCP}})$ , local electron potential  $V(r_{\text{BCP}})$  and kinetic  $G(r_{\text{BCP}})$  energy densities and total electron energy density  $K(r_{\text{BCP}})$  at critical point of type (3; -1). The complexes with additional Y...H (Y = N, O, F, Cl, Br or I; H are protons of methyl groups) contacts shorter than the sum of Bondi's van der Waals radii of corresponding atoms are marked in red color. In ambiguous cases the halogen atoms which participate in halogen bond formation are highlighted in bold.

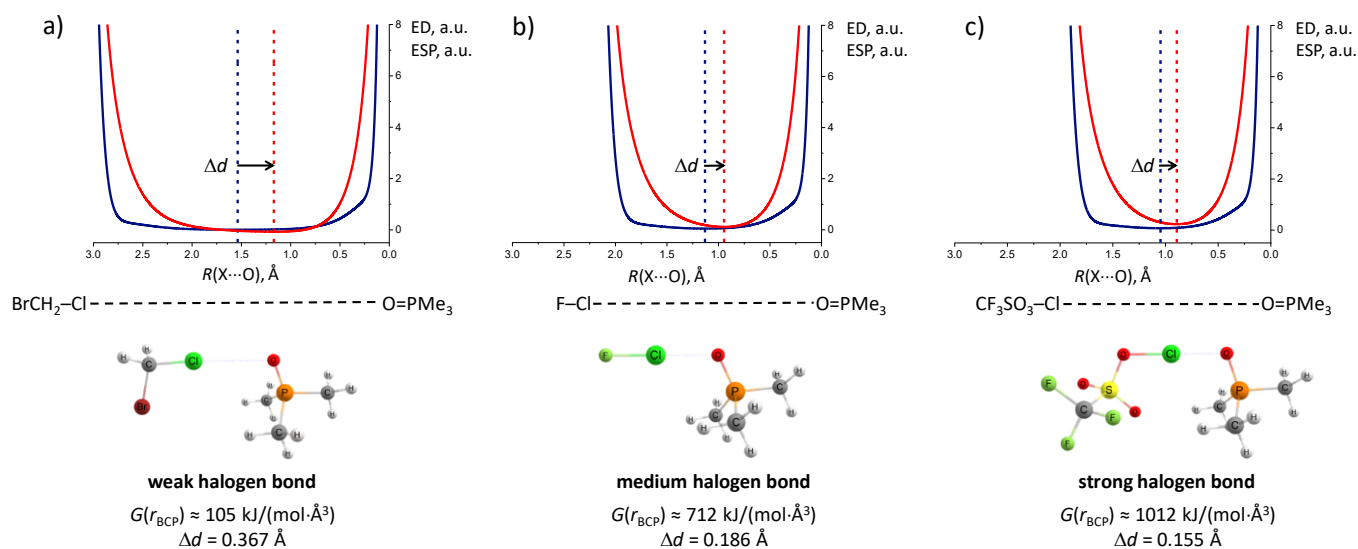
| №                    | Halogen donor            | $d(ED_{\min})$ ,<br>Å | $d(ESP_{\min})$ ,<br>Å | $\Delta d$ ,<br>Å | $ESP(r_{\text{BCP}})$ ,<br>kJ/mol | $\rho(r_{\text{BCP}})$ ,<br>e/Å <sup>3</sup> | $\nabla^2\rho(r_{\text{BCP}})$ ,<br>e/Å <sup>5</sup> | $V(r_{\text{BCP}})$ ,<br>kJ/(mol·Å <sup>3</sup> ) | $G(r_{\text{BCP}})$ ,<br>kJ/(mol·Å <sup>3</sup> ) | $K(r_{\text{BCP}})$ ,<br>kJ/(mol·Å <sup>3</sup> ) |
|----------------------|--------------------------|-----------------------|------------------------|-------------------|-----------------------------------|--|--|---|---|---|
| <b>Halogens</b>      |                          |                       |                        |                   |                                   |  |  |   |   |   |
| 1                    | F <sub>2</sub>           | 1.1922                | 1.0652                 | 0.1270            | 31.65                             | 0.210  | 3.357  | -496.91   | 556.99  | 60.08   |
| 2                    | Cl <sub>2</sub>          | 1.2293                | 1.0203                 | 0.2090            | 202.55                            | 0.200  | 2.493  | -417.65   | 437.92  | 20.27   |
| 3                    | Br <sub>2</sub>          | 1.2139                | 0.9935                 | 0.2204            | 331.49                            | 0.226  | 2.499  | -471.45   | 465.39  | -6.06   |
| 4                    | I <sub>2</sub>           | <b>1.0380</b>         | <b>0.8546</b>          | 0.1834            | 1042.55                           | 0.484  | 4.511  | -1584.60  | 1206.91   | -377.69   |
| 5                    | F <sup>+</sup>           | 0.6919                | 0.7255                 | -0.0336           | 2603.91                           | 1.868  | 6.991  | -7070.22  | 4177.59   | -2892.63  |
| 6                    | Cl <sup>+</sup>          | 0.8819                | 0.7504                 | 0.1315            | 2687.61                           | 1.310  | -1.676   | -4489.13  | 2090.57   | -2398.57  |
| 7                    | Br <sup>+</sup>          | 0.9464                | 0.7747                 | 0.1717            | 2584.57                           | 1.016  | 1.942  | -3538.27  | 1947.58   | -1590.69  |
| 8                    | <b>I<sup>+</sup></b>     | <b>0.9811</b>         | <b>0.7700</b>          | <b>0.2111</b>     | <b>2883.26</b>                    | <b>0.934</b>                                 | <b>6.760</b>   | <b>-3633.30</b>                                   | <b>2437.88</b>                                    | <b>-1195.41</b>                                   |
| <b>Interhalides</b>  |                          |                       |                        |                   |                                   |  |  |   |   |   |
| 9                    | ClF                      | 1.1314                | 0.9459                 | 0.1855            | 484.53                            | 0.328  | 3.567  | -768.06   | 711.81  | -56.26  |
| 10                   | <b>ClF<sub>3</sub></b>   | <b>1.0967</b>         | <b>0.9332</b>          | <b>0.1635</b>     | <b>540.38</b>                     | <b>0.374</b>                                 | <b>3.834</b>   | <b>-857.95</b>                                    | <b>781.28</b>                                     | <b>-76.67</b>                                     |
| 11                   | <b>ClF<sub>5</sub></b>   | <b>1.1798</b>         | <b>1.0033</b>          | <b>0.1765</b>     | <b>261.13</b>                     | <b>0.242</b>                                 | <b>2.809</b>   | <b>-519.15</b>                                    | <b>517.70</b>                                     | <b>-1.45</b>                                      |
| 12                   | BrF                      | 1.1401                | 0.9282                 | 0.2119            | 645.51                            | 0.335  | 3.346  | <b>-801.15</b>                                    | 708.04  | <b>-93.11</b>                                     |
| 13                   | <b>BrF<sub>3</sub></b>   | <b>1.1025</b>         | <b>0.9118</b>          | <b>0.1908</b>     | <b>727.39</b>                     | <b>0.390</b>                                 | <b>3.522</b>   | <b>-918.58</b>                                    | <b>783.01</b>                                     | <b>-135.57</b>                                    |
| 14                   | <b>BrF<sub>5</sub></b>   | <b>1.1719</b>         | <b>0.9763</b>          | <b>0.1955</b>     | <b>394.33</b>                     | <b>0.259</b>                                 | <b>2.792</b>   | <b>-563.84</b>                                    | <b>538.50</b>                                     | <b>-25.34</b>                                     |
| 15                   | <b>IF</b>                | <b>1.0729</b>         | <b>0.8671</b>          | <b>0.2059</b>     | <b>1101.11</b>                    | <b>0.516</b>                                 | <b>3.021</b>   | <b>-1572.25</b>                                   | <b>1063.74</b>                                    | <b>-508.51</b>                                    |
| 16                   | <b>IF<sub>3</sub></b>    | <b>1.0319</b>         | <b>0.8350</b>          | <b>0.1969</b>     | <b>1375.57</b>                    | <b>0.628</b>                                 | <b>2.993</b>   | <b>-1993.46</b>                                   | <b>1271.81</b>                                    | <b>-721.65</b>                                    |
| 17                   | <b>IF<sub>5</sub></b>    | <b>1.0634</b>         | <b>0.8829</b>          | <b>0.1805</b>     | <b>860.91</b>                     | <b>0.442</b>                                 | <b>4.041</b>   | <b>-1257.84</b>                                   | <b>1000.31</b>                                    | <b>-257.52</b>                                    |
| 18                   | BrCl                     | 1.1912                | 0.9740                 | 0.2172            | 414.65                            | 0.254  | 2.745  | -551.56   | 528.08  | -23.48  |
| 19                   | <b>ICl</b>               | <b>1.0832</b>         | <b>0.8866</b>          | <b>0.1966</b>     | <b>921.33</b>                     | <b>0.468</b>                                 | <b>3.174</b>   | <b>-1372.75</b>                                   | <b>978.10</b>                                     | <b>-394.65</b>                                    |
| 20                   | <b>IBr</b>               | <b>1.0856</b>         | <b>0.8914</b>          | <b>0.1942</b>     | <b>886.40</b>                     | <b>0.460</b>                                 | <b>3.131</b>   | <b>-1338.27</b>                                   | <b>956.88</b>                                     | <b>-381.39</b>                                    |
| 21                   | <b>ICl<sub>3</sub></b>   | <b>1.0377</b>         | <b>0.8483</b>          | <b>0.1895</b>     | <b>1244.32</b>                    | <b>0.591</b>                                 | <b>3.069</b>   | <b>-1821.25</b>                                   | <b>1192.65</b>                                    | <b>-628.60</b>                                    |
| 22                   | <b>ClF<sub>3</sub></b>   | 1.3079                | 1.1248                 | 0.1831            | -58.27                            | 0.123  | 2.076  | -260.68   | 321.11  | 60.43   |
| <b>Oxohalides</b>    |                          |                       |                        |                   |                                   |  |  |   |   |   |
| 23                   | OF <sub>2</sub>          | 1.5166                | 1.1917                 | 0.3249            | -140.35                           | 0.049  | 0.884  | -86.67  | 124.55  | 37.88   |
| 24                   | Cl <sub>2</sub> O        | 1.2028                | 0.9970                 | <b>0.2059</b>     | 278.33                            | 0.228  | 2.780  | -497.00   | 503.94  | 6.94  |
| 25                   | Br <sub>2</sub> O        | 1.1846                | 0.9647                 | 0.2199            | 455.27                            | 0.263  | 2.850  | -586.37   | 555.13  | -31.24  |
| 26                   | ClO <sub>2</sub>         | 1.3566                | 1.0777                 | 0.2789            | 73.15                             | 0.106  | <b>1.492</b>   | -201.14   | 237.64  | 36.50   |
| 27                   | <b>BrO<sub>2</sub></b>   | <b>1.2875</b>         | <b>1.0256</b>          | <b>0.2619</b>     | <b>231.72</b>                     | <b>0.154</b>                                 | <b>1.923</b>   | <b>-305.24</b>                                    | <b>329.36</b>                                     | <b>24.12</b>                                      |
| 28                   | ClO <sub>2</sub> F       | 1.2597                | 1.0242                 | 0.2355            | 217.68                            | 0.168  | 2.117  | -338.65   | 363.88  | 25.24   |
| 29                   | <b>BrO<sub>2</sub>F</b>  | <b>1.1769</b>         | <b>0.9560</b>          | <b>0.2209</b>     | <b>506.81</b>                     | <b>0.272</b>                                 | <b>2.742</b>   | <b>-573.72</b>                                    | <b>538.85</b>                                     | <b>-34.87</b>                                     |
| 30                   | <b>IO<sub>2</sub>F</b>   | <b>1.0353</b>         | <b>0.8186</b>          | <b>0.2167</b>     | <b>1548.64</b>                    | <b>0.647</b>                                 | <b>2.420</b>   | <b>-2014.64</b>                                   | <b>1229.71</b>                                    | <b>-784.93</b>                                    |
| 31                   | ClO <sub>3</sub> OF      | 1.4478                | 1.1690                 | 0.2789            | -128.57                           | 0.064  | 1.168  | <b>-121.14</b>                                    | 167.94  | 46.79   |
| 32                   | BrO <sub>3</sub> OF      | 1.4134                | 1.1565                 | 0.2569            | -115.47                           | 0.074  | 1.353  | -145.84   | 197.26  | 51.42   |
| 33                   | IO <sub>3</sub> OF       | 1.3356                | 1.1364                 | 0.1992            | -53.24                            | 0.114  | 1.961  | -242.18   | 301.32  | 59.14   |
| 34                   | ClO <sub>3</sub> OCl     | 1.1086                | 0.9340                 | 0.1746            | 559.19                            | 0.367  | 3.752  | -862.16   | 775.87  | -86.29  |
| 35                   | ClO <sub>3</sub> OBr     | 1.0959                | 0.8996                 | 0.1963            | 849.97                            | 0.423  | 3.625  | -1052.05  | 859.21  | -192.85   |
| 36                   | <b>ClO<sub>3</sub>OI</b> | <b>1.0510</b>         | <b>0.8425</b>          | <b>0.2085</b>     | <b>1399.74</b>                    | <b>0.605</b>                                 | <b>2.774</b>   | <b>-1938.50</b>                                   | <b>1224.16</b>                                    | <b>-714.34</b>                                    |
| <b>Pseudohalides</b> |                          |                       |                        |                   |                                   |  |  |   |   |   |
| 37                   | FCN                      | 1.4963                | 1.1999                 | 0.2963            | -153.20                           | 0.041  | 0.829  | -77.36  | 114.90  | 37.54   |
| 38                   | ClCN                     | 1.3372                | 1.0777                 | <b>0.2596</b>     | 75.48                             | 0.098  | 1.565  | -196.88   | 242.27  | 45.39   |
| 39                   | BrCN                     | 1.2952                | 1.0367                 | 0.2585            | 201.75                            | 0.129  | 1.855  | -263.44   | 302.18  | 38.74   |
| 40                   | ICN                      | 1.0658                | 0.8861                 | 0.1797            | 793.00                            | 0.390  | 4.820  | -1229.55  | 1057.76   | -171.79   |
| 41                   | CISCN                    | 1.3084                | 1.0676                 | 0.2408            | 78.46                             | 0.134  | 1.808  | -257.79   | 295.01  | 37.22   |
| 42                   | BrSCN                    | 1.2375                | 1.0078                 | 0.2297            | 285.20                            | 0.199  | 2.286  | -404.35   | 412.27  | 7.93  |
| 43                   | <b>ISCN</b>              | <b>1.0803</b>         | <b>0.8893</b>          | <b>0.1910</b>     | <b>887.40</b>                     | <b>0.461</b>                                 | <b>3.344</b>   | <b>-1349.97</b>                                   | <b>982.35</b>                                     | <b>-367.62</b>                                    |
| 44                   | CINCO                    | 1.2721                | 1.0359                 | <b>0.2363</b>     | 162.82                            | 0.161  | 2.174  | -332.88   | 366.20  | 33.32   |
| 45                   | BrNCO                    | 1.2116                | 0.9803                 | 0.2313            | 392.03                            | 0.228  | 2.630  | -496.33   | 489.86  | -6.47   |
| 46                   | <b>INCO</b>              | <b>1.0721</b>         | <b>0.8718</b>          | <b>0.2003</b>     | <b>1029.31</b>                    | <b>0.493</b>                                 | <b>3.410</b>   | <b>-1519.01</b>                                   | <b>1072.93</b>                                    | <b>-446.08</b>                                    |
| 47                   | CIN <sub>3</sub>         | 1.2936                | 1.0533                 | 0.2403            | 112.07                            | 0.146  | 1.962  | -290.80   | 325.68  | 34.88   |

|   |                                     |        |        |        |         |       |       |          |         |         |
|---|-------------------------------------|--------|--------|--------|---------|-------|-------|----------|---------|---------|
| 48  | BrN <sub>3</sub>                    | 1.2303 | 0.9975 | 0.2328 | 319.03  | 0.208 | 2.402 | -434.44  | 437.95  | 3.51    |
| 49  | IN <sub>3</sub>                     | 1.0906 | 0.8933 | 0.1974 | 864.18  | 0.443 | 3.341 | -1286.73 | 950.39  | -336.34 |
| Halogenated methanes and their derivatives                        |                                     |        |        |        |         |       |       |          |         |         |
| 50  | CH <sub>3</sub> Br                  | 1.5547 | 1.1698 | 0.3850 | -80.25  | 0.050 | 0.658 | -70.00   | 95.49   | 25.49   |
| 51  | CH <sub>3</sub> I                   | 1.6108 | 1.2491 | 0.3617 | 58.87   | 0.060 | 0.727 | -86.45   | 110.07  | 23.62   |
| 52  | CH <sub>2</sub> Br <sub>2</sub>     | 1.4293 | 1.1142 | 0.3151 | -6.59   | 0.081 | 1.085 | -131.85  | 165.64  | 33.79   |
| 53  | CH <sub>2</sub> ClBr                | 1.5375 | 1.1708 | 0.3667 | -89.30  | 0.051 | 0.726 | -76.92   | 105.16  | 28.23   |
| 54  | CH <sub>2</sub> BrF                 | 1.4693 | 1.1343 | 0.3350 | -40.89  | 0.069 | 0.915 | -105.84  | 137.00  | 31.16   |
| 55  | CH <sub>2</sub> BrCl                | 1.4349 | 1.1171 | 0.3178 | -13.39  | 0.079 | 1.057 | -127.49  | 160.92  | 33.43   |
| 56  | CH <sub>3</sub> BrI                 | 1.4116 | 1.1081 | 0.3035 | 18.18   | 0.092 | 1.189 | -154.13  | 186.33  | 32.20   |
| 57  | CH <sub>2</sub> IF                  | 1.5711 | 1.2079 | 0.3633 | 69.05   | 0.067 | 0.787 | -97.83   | 121.23  | 23.40   |
| 58  | CH <sub>2</sub> ICl                 | 1.5489 | 1.1883 | 0.3606 | 82.82   | 0.071 | 0.832 | -107.06  | 130.00  | 22.93   |
| 59  | CH <sub>2</sub> IBr                 | 1.5468 | 1.1904 | 0.3564 | 75.49   | 0.072 | 0.839 | -108.00  | 131.11  | 23.11   |
| 60  | CHBr <sub>3</sub>                   | 1.3682 | 1.0816 | 0.2866 | 58.71   | 0.103 | 1.383 | -182.51  | 218.37  | 35.87   |
| 61  | CHBrCl <sub>2</sub>                 | 1.3745 | 1.0851 | 0.2895 | 50.34   | 0.100 | 1.345 | -175.93  | 211.55  | 35.62   |
| 62  | CHBrI <sub>2</sub>                  | 1.3521 | 1.0764 | 0.2757 | 98.57   | 0.123 | 1.520 | -223.27  | 251.35  | 28.08   |
| 63  | CHIF <sub>2</sub>                   | 1.5217 | 1.1690 | 0.3527 | 98.88   | 0.077 | 0.894 | -119.94  | 142.16  | 22.21   |
| 64  | CHICl <sub>2</sub>                  | 1.5029 | 1.1584 | 0.3445 | 101.35  | 0.083 | 0.942 | -129.91  | 151.57  | 21.66   |
| 65  | CHIBr <sub>2</sub>                  | 1.1967 | 0.9845 | 0.2122 | 379.36  | 0.257 | 2.783 | -640.37  | 575.94  | -64.43  |
| 66  | CHIClF                              | 1.5121 | 1.1642 | 0.3479 | 98.38   | 0.080 | 0.920 | -124.61  | 146.85  | 22.24   |
| 67  | CHIClBr                             | 1.5005 | 1.1584 | 0.3421 | 100.44  | 0.083 | 0.950 | -131.28  | 152.95  | 21.67   |
| 68  | CCl <sub>4</sub>                    | 1.3912 | 1.1086 | 0.2826 | -15.84  | 0.082 | 1.250 | -148.93  | 189.37  | 40.44   |
| 69  | Cl <sub>4</sub>                     | 1.1401 | 0.9589 | 0.1812 | 488.98  | 0.335 | 3.431 | -918.10  | 774.34  | -143.76 |
| 70  | CF <sub>3</sub> Cl                  | 1.4026 | 1.1195 | 0.2831 | -31.86  | 0.073 | 1.151 | -132.36  | 171.93  | 39.57   |
| 71  | CCl <sub>3</sub> F                  | 1.3994 | 1.1129 | 0.2866 | -19.41  | 0.078 | 1.201 | -140.98  | 180.86  | 39.89   |
| 72  | CF <sub>3</sub> Br                  | 1.3528 | 1.0748 | 0.2781 | 74.88   | 0.103 | 1.437 | -189.26  | 226.68  | 37.42   |
| 73  | CBr <sub>3</sub> F                  | 1.3343 | 1.0629 | 0.2715 | 105.14  | 0.118 | 1.577 | -219.44  | 254.63  | 35.19   |
| 74  | CF <sub>3</sub> I                   | 1.0695 | 0.8951 | 0.1744 | 702.12  | 0.377 | 4.724 | -1168.39 | 1018.30 | -150.09 |
| 75  | Cl <sub>3</sub> F                   | 1.1518 | 0.9538 | 0.1979 | 502.20  | 0.316 | 3.192 | -835.62  | 711.20  | -124.42 |
| 76  | CCl <sub>2</sub> F <sub>2</sub>     | 1.3989 | 1.1163 | 0.2826 | -27.67  | 0.075 | 1.179 | -137.05  | 176.92  | 39.87   |
| 77  | CBr <sub>2</sub> F <sub>2</sub>     | 1.3446 | 1.0692 | 0.2754 | 89.15   | 0.111 | 1.502 | -203.96  | 240.04  | 36.08   |
| 78  | Cl <sub>2</sub> F <sub>2</sub>      | 1.1592 | 0.9576 | 0.2016 | 485.92  | 0.304 | 3.153 | -799.21  | 689.41  | -109.80 |
| 79  | CBrClF <sub>2</sub>                 | 1.3460 | 1.0703 | 0.2757 | 85.71   | 0.109 | 1.489 | -200.80  | 237.25  | 36.44   |
| 80  | ClCIF <sub>2</sub>                  | 1.0700 | 0.8938 | 0.1762 | 715.48  | 0.381 | 4.610 | -1177.68 | 1012.50 | -165.18 |
| 81  | CF <sub>3</sub> OF                  | 1.4788 | 1.1843 | 0.2945 | -133.38 | 0.059 | 1.050 | -107.10  | 150.01  | 42.91   |
| 82  | CF <sub>3</sub> OCl                 | 1.1436 | 0.9562 | 0.1873 | 445.89  | 0.308 | 3.407 | -706.02  | 666.08  | -39.94  |
| 83  | CF <sub>3</sub> OBr                 | 1.1287 | 0.9224 | 0.2064 | 690.48  | 0.355 | 3.392 | -849.35  | 736.43  | -112.92 |
| 84  | CF <sub>3</sub> SO <sub>2</sub> OF  | 1.3827 | 1.1502 | 0.2326 | -102.12 | 0.089 | 1.563 | -177.49  | 232.39  | 54.90   |
| 85  | CF <sub>3</sub> SO <sub>2</sub> OCl | 1.0472 | 0.8925 | 0.1548 | 800.81  | 0.503 | 4.244 | -1244.82 | 1012.43 | -232.40 |
| 86  | CF <sub>3</sub> SO <sub>2</sub> OBr | 1.0740 | 0.8824 | 0.1916 | 977.86  | 0.480 | 3.737 | -1233.70 | 960.27  | -273.43 |
| Halogenated ethylene, halogenated acetylene and their derivatives |                                     |        |        |        |         |       |       |          |         |         |
| 87  | C <sub>2</sub> H <sub>2</sub> IF    | 1.6304 | 1.2666 | 0.3638 | 72.15   | 0.057 | 0.692 | -79.25   | 103.19  | 23.94   |
| 88  | C <sub>2</sub> H <sub>2</sub> ICl   | 1.6243 | 1.2579 | 0.3665 | 71.54   | 0.058 | 0.696 | -80.13   | 104.00  | 23.87   |
| 89  | C <sub>2</sub> H <sub>2</sub> IBr   | 1.6153 | 1.2483 | 0.3670 | 70.81   | 0.059 | 0.707 | -82.34   | 106.14  | 23.80   |
| 90  | Cl(H)C(F)Cl                         | 1.5312 | 1.1690 | 0.3622 | 102.30  | 0.075 | 0.885 | -116.47  | 139.53  | 23.07   |
| 91  | Cl(F)C(H)Cl                         | 1.5328 | 1.1745 | 0.3583 | 93.31   | 0.074 | 0.865 | -113.43  | 136.24  | 22.81   |
| 92  | Cl(Cl)C(H)F                         | 1.5235 | 1.1679 | 0.3556 | 99.30   | 0.077 | 0.896 | -119.81  | 142.25  | 22.43   |
| 93  | C <sub>2</sub> Cl <sub>4</sub>      | 1.4177 | 1.1245 | 0.2932 | -44.04  | 0.070 | 1.100 | -124.54  | 163.29  | 38.75   |
| 94  | C <sub>2</sub> Br <sub>4</sub>      | 1.3587 | 1.0758 | 0.2829 | 72.27   | 0.104 | 1.432 | -188.97  | 226.04  | 37.08   |
| 95  | C <sub>2</sub> I <sub>4</sub>       | 1.1343 | 0.9414 | 0.1929 | 560.35  | 0.345 | 3.537 | -971.15  | 810.59  | -160.56 |
| 96  | C <sub>2</sub> F <sub>3</sub> Cl    | 1.4161 | 1.1245 | 0.2916 | -41.07  | 0.069 | 1.101 | -124.32  | 163.35  | 39.03   |
| 97  | C <sub>2</sub> F <sub>3</sub> Br    | 1.3621 | 1.0793 | 0.2829 | 65.29   | 0.097 | 1.389 | -178.45  | 216.85  | 38.41   |
| 98  | C <sub>2</sub> F <sub>3</sub> I     | 1.0782 | 0.9030 | 0.1752 | 647.47  | 0.356 | 4.652 | -1094.20 | 974.67  | -119.53 |
| 99  | C <sub>2</sub> (CN) <sub>3</sub> Cl | 1.3288 | 1.0692 | 0.2596 | 91.68   | 0.113 | 1.669 | -223.20  | 264.95  | 41.75   |
| 100   | C <sub>2</sub> Cl <sub>2</sub>      | 1.3999 | 1.1147 | 0.2852 | -21.75  | 0.073 | 1.187 | -136.02  | 177.07  | 41.06   |
| Halogenated benzenes  |                                     |        |        |        |         |       |       |          |         |         |
| 101   | C <sub>6</sub> H <sub>5</sub> Cl    | 1.7063 | 1.2221 | 0.4842 | -108.39 | 0.028 | 0.379 | -35.86   | 52.74   | 16.88   |
| 102   | C <sub>6</sub> H <sub>5</sub> Br    | 1.4931 | 1.1441 | 0.3490 | -56.41  | 0.062 | 0.831 | -93.52   | 123.14  | 29.62   |
| 103   | C <sub>6</sub> F <sub>5</sub> Cl    | 1.4137 | 1.1256 | 0.2881 | -43.85  | 0.069 | 1.099 | -123.95  | 162.93  | 38.98   |
| 104   | C <sub>6</sub> F <sub>5</sub> Br    | 1.3573 | 1.0769 | 0.2805 | 70.80   | 0.099 | 1.415 | -183.36  | 221.69  | 38.33   |
| 105   | C <sub>6</sub> F <sub>5</sub> I     | 1.0869 | 0.9089 | 0.1781 | 620.75  | 0.346 | 4.419 | -1042.77 | 927.47  | -115.30 |
| Phosgene and its derivatives                                      |                                     |        |        |        |         |       |       |          |         |         |
| 106   | COCl <sub>2</sub>                   | 1.4023 | 1.1174 | 0.2850 | -27.22  | 0.076 | 1.167 | -136.40  | 175.48  | 39.08   |
| 107   | COBr <sub>2</sub>                   | 1.3449 | 1.0724 | 0.2725 | 83.65   | 0.107 | 1.469 | -197.71  | 233.82  | 36.12   |
| 108   | COCIF                               | 1.3939 | 1.1166 | 0.2773 | -20.83  | 0.075 | 1.181 | -137.35  | 177.18  | 39.82   |
| 109   | COBrF                               | 1.3499 | 1.0777 | 0.2723 | 74.31   | 0.098 | 1.411 | -183.01  | 221.20  | 38.19   |
| 110   | COBrCl                              | 1.3507 | 1.0766 | 0.2741 | 73.30   | 0.102 | 1.423 | -187.84  | 224.68  | 36.84   |

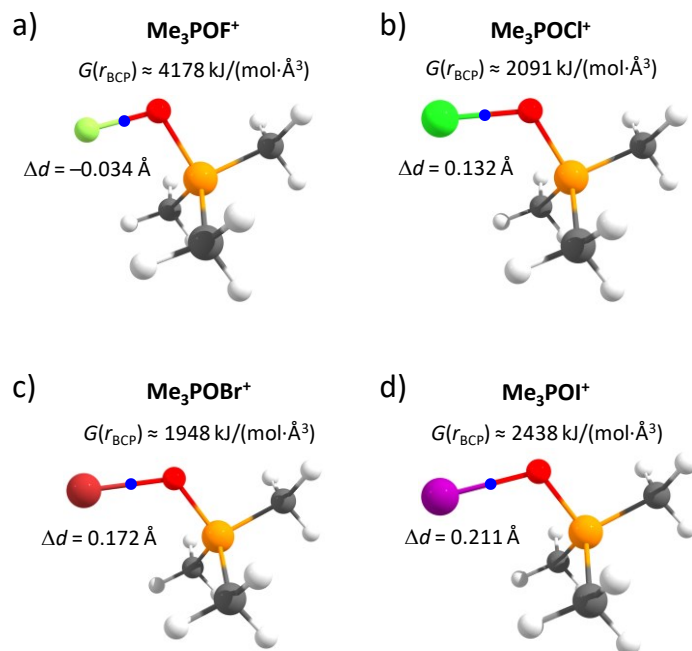


|  |   |        |        |        |         |       |       |          |         |         |
|--|---|--------|--------|--------|---------|-------|-------|----------|---------|---------|
| 111  | COIF  | 1.0713 | 0.8972 | 0.1741 | 694.09  | 0.373 | 4.694 | -1153.58 | 1008.19 | -145.39 |
| <b>Thionyl- and sulfurylhalides</b>                        |   |        |        |        |         |       |       |          |         |         |
| 112  | SO <sub>2</sub> Cl <sub>2</sub>                 | 1.3095 | 1.0679 | 0.2416 | 78.56   | 0.127 | 1.760 | -244.98  | 284.28  | 39.30   |
| 113  | SO <sub>2</sub> ClF                             | 1.3179 | 1.0705 | 0.2474 | 74.72   | 0.117 | 1.692 | -228.08  | 269.53  | 41.46   |
| 114  | SO <sub>2</sub> BrF                             | 1.2515 | 1.0147 | 0.2368 | 264.24  | 0.180 | 2.163 | -361.62  | 379.63  | 18.02   |
| 115  | SOCl <sub>2</sub>                               | 1.4111 | 1.1266 | 0.2844 | -48.46  | 0.081 | 1.139 | -137.22  | 173.25  | 36.03   |
| 116  | SOBr <sub>2</sub>                               | 1.3399 | 1.0766 | 0.2633 | 70.93   | 0.119 | 1.480 | -210.60  | 241.35  | 30.75   |
| <b>Sulfur halides and sulfur hypohalites</b>               |   |        |        |        |         |       |       |          |         |         |
| 117  | SF <sub>6</sub>                                 | 1.6153 | 1.2383 | 0.3770 | -199.13 | 0.024 | 0.462 | -39.29   | 62.15   | 22.85   |
| 118  | SF <sub>5</sub> Cl                              | 1.2835 | 1.0533 | 0.2302 | 114.47  | 0.150 | 1.987 | -296.16  | 330.74  | 34.57   |
| 119  | SF <sub>5</sub> Br                              | 1.2047 | 0.9872 | 0.2175 | 368.31  | 0.234 | 2.561 | -492.04  | 481.41  | -10.63  |
| 120  | SF <sub>5</sub> OF                              | 1.4648 | 1.1790 | 0.2858 | -146.09 | 0.057 | 1.059 | -105.99  | 150.31  | 44.32   |
| 121  | SF <sub>5</sub> OCl                             | 1.0996 | 0.9271 | 0.1725 | 591.53  | 0.384 | 3.847 | -912.82  | 809.94  | -102.88 |
| 122  | S <sub>2</sub> Cl <sub>2</sub>                  | 1.4182 | 1.1290 | 0.2892 | -49.20  | 0.082 | 1.137 | -137.85  | 173.43  | 35.59   |
| 123  | S <sub>2</sub> Br <sub>2</sub>                  | 1.3285 | 1.0676 | 0.2609 | 92.50   | 0.128 | 1.581 | -231.27  | 260.95  | 29.69   |
| 124  | SCL <sub>2</sub>                                | 1.3917 | 1.1121 | 0.2797 | -22.26  | 0.089 | 1.273 | -157.24  | 195.63  | 38.39   |
| 125  | SBr <sub>2</sub>                                | 1.3118 | 1.0541 | 0.2577 | 128.61  | 0.137 | 1.716 | -256.31  | 285.87  | 29.57   |
| <b>Halogenated nitrogen-containing inorganic compounds</b> |   |        |        |        |         |       |       |          |         |         |
| 126  | NF <sub>3</sub>                                 | 1.6042 | 1.2216 | 0.3826 | -185.73 | 0.028 | 0.525 | -45.04   | 70.74   | 25.69   |
| 127  | NCl <sub>3</sub>                                | 1.2878 | 1.0491 | 0.2387 | 121.25  | 0.148 | 1.992 | -297.03  | 331.59  | 34.57   |
| 128  | NI <sub>3</sub>                                 | 1.0835 | 0.8967 | 0.1868 | 845.52  | 0.459 | 3.375 | -1348.87 | 984.59  | -364.27 |
| 129  | NF <sub>2</sub> Cl                              | 1.2917 | 1.0510 | 0.2408 | 119.32  | 0.144 | 1.947 | -288.01  | 322.96  | 34.95   |
| 130  | NF <sub>2</sub> Br                              | 1.2425 | 1.0065 | 0.2360 | 284.80  | 0.194 | 2.263 | -397.60  | 406.78  | 9.18    |
| 131  | NO <sub>2</sub> OF                              | 1.5177 | 1.1928 | 0.3249 | -144.32 | 0.049 | 0.877 | -85.77   | 123.50  | 37.72   |
| 132  | NO <sub>2</sub> OCl                             | 1.1613 | 0.9684 | 0.1929 | 396.79  | 0.282 | 3.215 | -636.61  | 613.74  | -22.87  |
| 133  | NO <sub>2</sub> OBr                             | 1.1330 | 0.9266 | 0.2064 | 668.17  | 0.347 | 3.341 | -822.83  | 718.46  | -104.37 |
| 134  | NO <sub>2</sub> Cl                              | 1.2822 | 1.0536 | 0.2286 | 109.37  | 0.154 | 1.978 | -301.79  | 332.64  | 30.85   |
| 135  | NO <sub>2</sub> Br                              | 1.2314 | 1.0046 | 0.2268 | 292.81  | 0.206 | 2.313 | -420.34  | 422.76  | 2.42    |
| 136  | NOBr  | 1.5431 | 1.1811 | 0.3620 | -108.86 | 0.053 | 0.632 | -70.11   | 93.17   | 23.05   |
| <b>Assorted organic compounds</b>                          |   |        |        |        |         |       |       |          |         |         |
| 137  | C <sub>6</sub> H <sub>5</sub> C <sub>2</sub> Cl | 1.4158 | 1.1224 | 0.2934 | -39.71  | 0.069 | 1.115 | -125.41  | 165.16  | 39.75   |
| 138  | C <sub>6</sub> H <sub>5</sub> C <sub>2</sub> Br | 1.3642 | 1.0771 | 0.2871 | 69.77   | 0.098 | 1.408 | -180.61  | 219.69  | 39.08   |
| 139  | C <sub>6</sub> H <sub>5</sub> C <sub>2</sub> I  | 1.0930 | 0.9134 | 0.1797 | 586.46  | 0.334 | 4.372 | -1002.87 | 903.22  | -99.65  |
| 140  | N-Chlorosuccinimide                             | 1.3163 | 1.0613 | 0.2551 | 92.08   | 0.135 | 1.837 | -265.10  | 301.41  | 36.31   |
| 141  | N-Bromosuccinimide                              | 1.2420 | 0.9996 | 0.2424 | 304.57  | 0.199 | 2.354 | -416.55  | 424.61  | 8.06    |
| 142  | N-Iodosuccinimide                               | 1.0893 | 0.8914 | 0.1979 | 846.28  | 0.438 | 3.579 | -1305.86 | 981.80  | -324.05 |
| 143  | Tetrachloro-1,4-benzoquinone                    | 1.4378 | 1.1285 | 0.3093 | -33.40  | 0.076 | 1.090 | -129.48  | 164.91  | 35.43   |
| 144  | Tetrabromo-1,4-benzoquinone                     | 1.3640 | 1.0774 | 0.2866 | 76.96   | 0.107 | 1.426 | -191.73  | 226.88  | 35.16   |
| 145  | Tetraiodo-1,4-benzoquinone                      | 1.2036 | 0.9933 | 0.2104 | 342.75  | 0.246 | 2.791 | -612.50  | 562.71  | -49.80  |

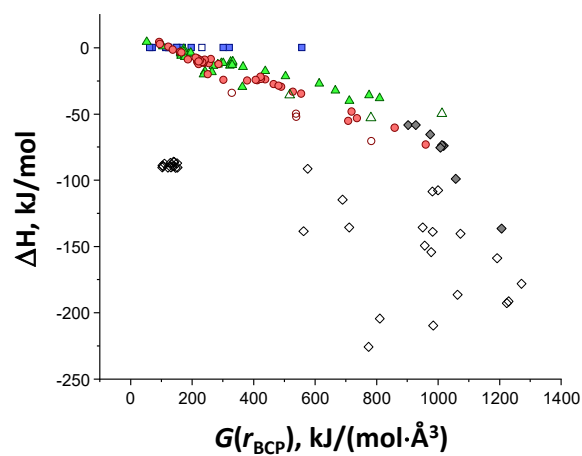
**Figure S2.** ED and ESP profiles along the halogen bond path (blue and red curves, respectively, where minima positions are indicated by vertical dashed lines) for (a) weak, (b) medium and (c) strong R–Cl⋯OPMe<sub>3</sub> complexes (complexes [53], [9] and [85], respectively; see Figure S1). The values of  $\Delta d$  and  $G(r_{\text{BCP}})$  for the Cl⋯O bonds are given at the bottom of the figure.



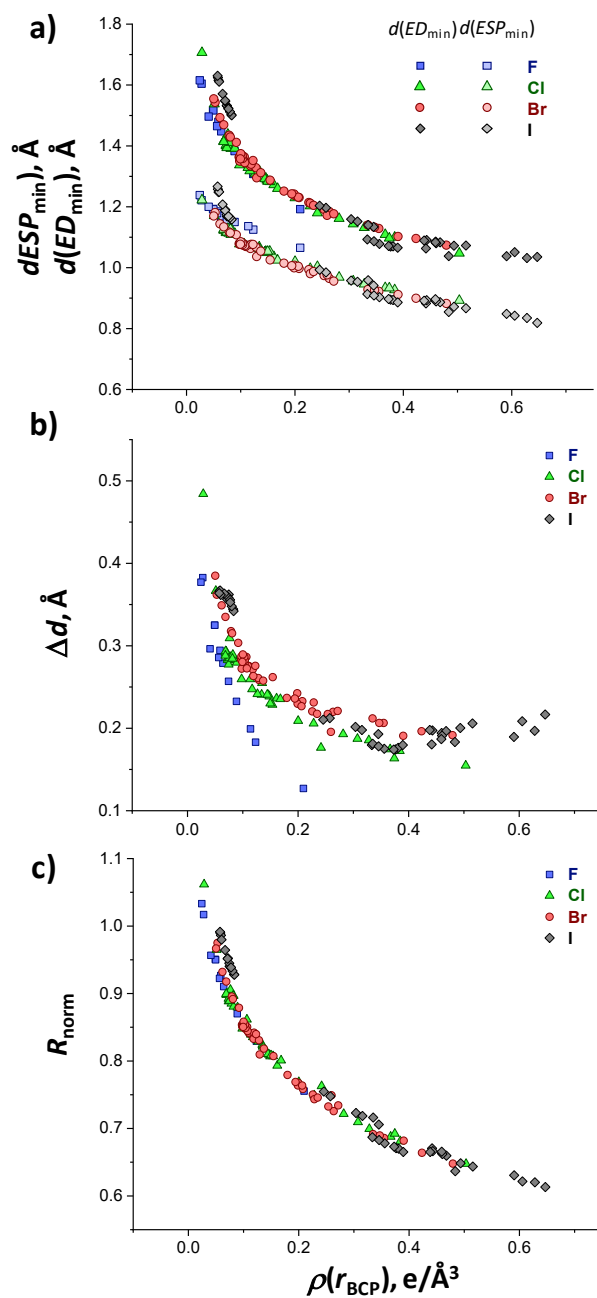
**Figure S3.** Optimized structures of (a)  $\text{Me}_3\text{POF}^+$ , (b)  $\text{Me}_3\text{POCl}^+$ , (c)  $\text{Me}_3\text{POBr}^+$  and (d)  $\text{Me}_3\text{POI}^+$  complexes. Blue dot marks the position of the  $\text{X}\cdots\text{O}$  bond critical point. The values of  $G(r_{\text{BCP}})$  and  $\Delta d$  for the  $\text{X}\cdots\text{O}$  bonds are given.



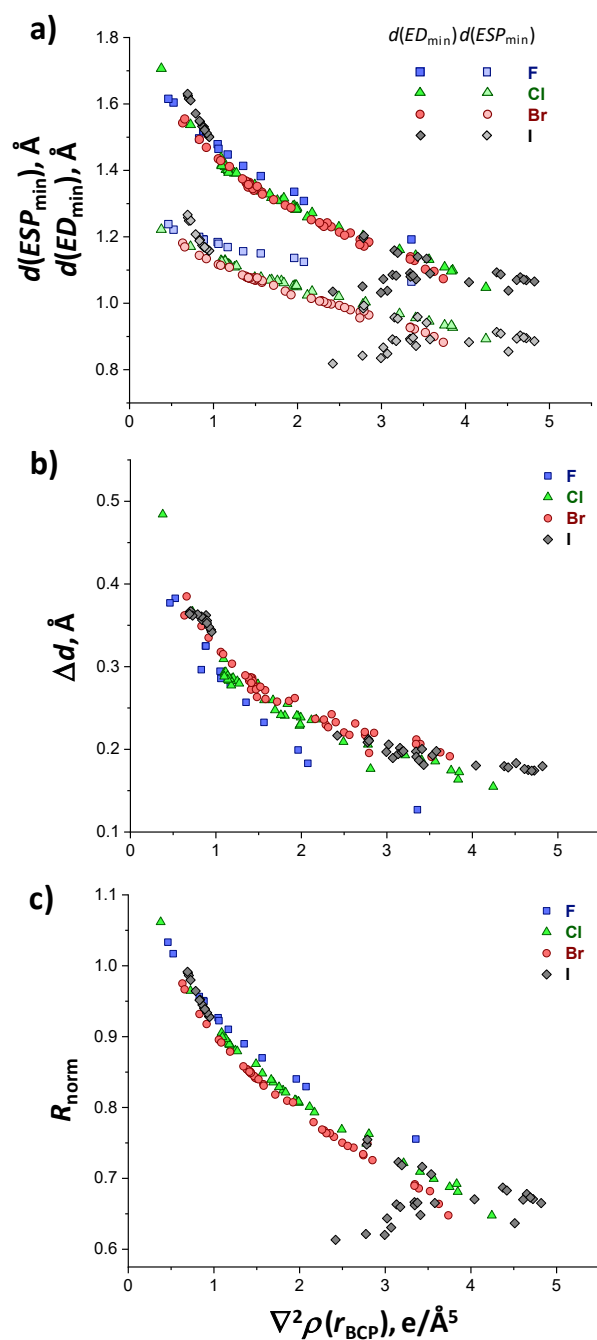
**Figure S4.** Complexation enthalpy  $\Delta H$  as a function of  $G(r_{\text{BCP}})$  at critical point of type (3; -1) of 145 intermolecular 1:1 complexes formed by  $\text{Me}_3\text{PO}$  with halogen-donating molecules. Open symbols correspond to complex with the presence of additional non-covalent interactions, filled symbols – without such interactions (halogen bond only).



**Figure S5.** (a) Distances from oxygen atom to minima of electron density  $d(ED_{\min})$  and molecular electrostatic potential  $d(ESP_{\min})$  along the  $X\cdots O$  ( $X = F, Cl, Br$  and  $I$ ) bond path; (b) distances between ED and ESP minima  $\Delta d$ ; (c) normalized  $X\cdots O$  ( $X = F, Cl, Br$  and  $I$ ) distances  $R_{\text{norm}}$  as a function of electron density  $\rho(r_{\text{BCP}})$  at critical point of type (3; -1) of 145 intermolecular 1:1 complexes formed by  $\text{Me}_3\text{PO}$  with halogen-donating molecules.

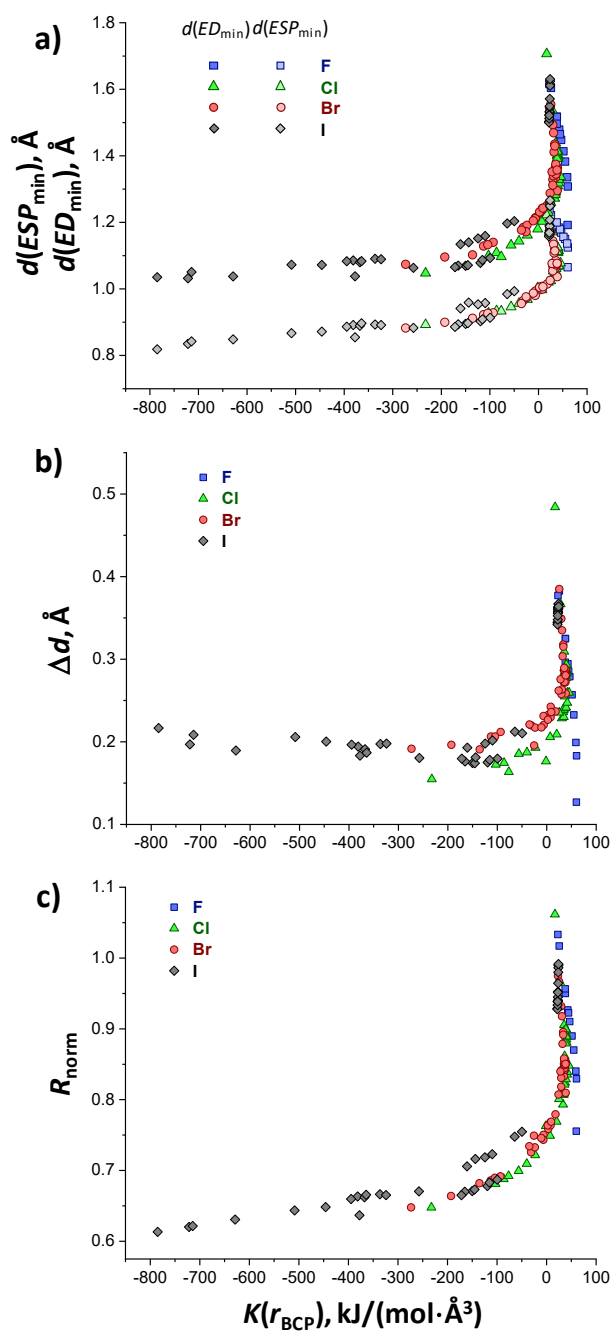


**Figure S6.** (a) Distances from oxygen atom to minima of electron density  $d(ED_{\min})$  and molecular electrostatic potential  $d(ESP_{\min})$  along the  $X\cdots O$  ( $X = F, Cl, Br$  and  $I$ ) bond path; (b) distances between ED and ESP minima  $\Delta d$ ; (c) normalized  $X\cdots O$  ( $X = F, Cl, Br$  and  $I$ ) distances  $R_{\text{norm}}$  as a function of Laplacian of electron density  $\nabla^2\rho(r_{\text{BCP}})$  at critical point of type (3; -1) of 145 intermolecular 1:1 complexes formed by  $\text{Me}_3\text{PO}$  with halogen-donating molecules.

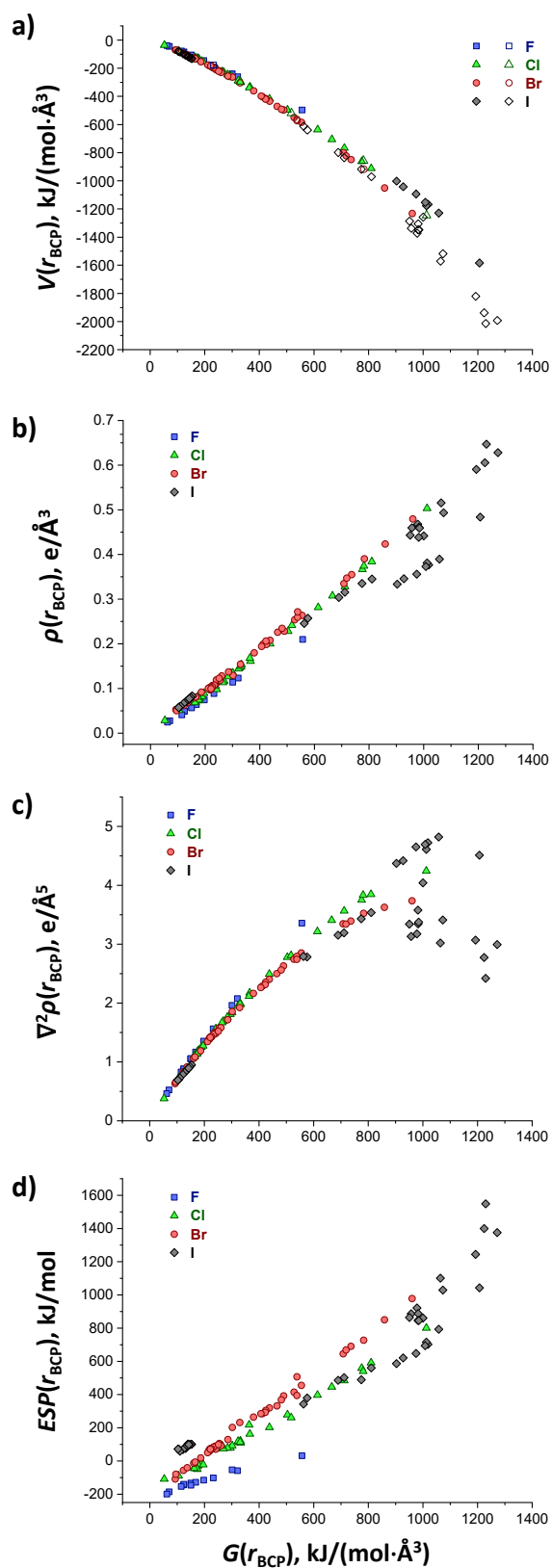




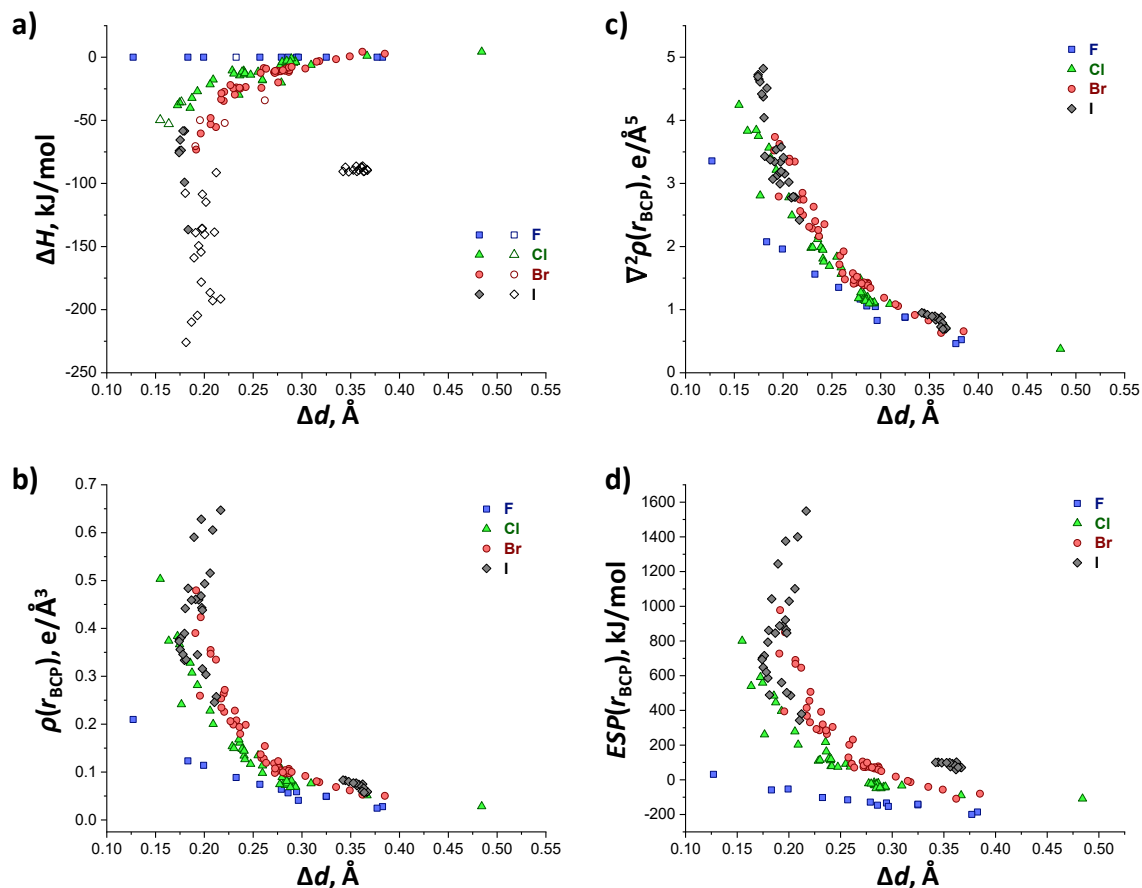
**Figure S7.** (a) Distances from oxygen atom to minima of electron density  $d(ED_{\min})$  and molecular electrostatic potential  $d(ESP_{\min})$  along the  $X\cdots O$  ( $X = F, Cl, Br$  and  $I$ ) bond path; (b) distances between ED and ESP minima  $\Delta d$ ; (c) normalized  $X\cdots O$  ( $X = F, Cl, Br$  and  $I$ ) distances  $R_{\text{norm}}$  as a function of total electron energy density  $K(r_{\text{BCP}})$  at critical point of type (3; -1) of 145 intermolecular 1:1 complexes formed by  $\text{Me}_3\text{PO}$  with halogen-donating molecules.



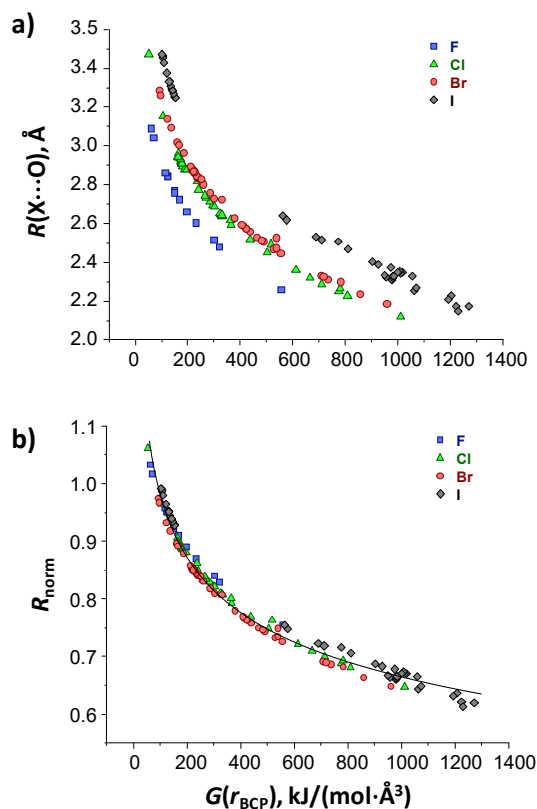
**Figure S8.** (a) Local electron potential energy density  $V(r_{\text{BCP}})$ , (b) electron density  $\rho(r_{\text{BCP}})$ , (c) Laplacian of electron density  $\nabla^2\rho(r_{\text{BCP}})$ , (d) molecular electrostatic potential  $ESP(r_{\text{BCP}})$  at the X...O (X = F, Cl, Br and I) bond critical point of type (3; -1) as a function of local electron kinetic energy density  $G(r_{\text{BCP}})$  of 145 intermolecular 1:1 complexes formed by Me<sub>3</sub>PO with halogen-donating molecules.



**Figure S9.** (a) Complexation enthalpy  $\Delta H$ , (b) electron density  $\rho(r_{\text{BCP}})$ , (c) Laplacian of electron density  $\nabla^2\rho(r_{\text{BCP}})$ , (d) molecular electrostatic potential  $ESP(r_{\text{BCP}})$  at the X...O (X = F, Cl, Br and I) bond critical point of type (3; -1) as a function of distance between ED and ESP minima  $\Delta d$  of 145 intermolecular 1:1 complexes formed by Me<sub>3</sub>PO with halogen-donating molecules. Open symbols correspond to complex with the presence of additional non-covalent interactions, filled symbols – without such interactions (halogen bond only).



**Figure S10.** (a) Absolute,  $R(X\cdots O)$ , and (b) normalized,  $R_{\text{norm}}$ , values of  $X\cdots O$  ( $X = \text{F}, \text{Cl}, \text{Br}$  and  $\text{I}$ ) distances as a function of local electron kinetic energy density  $G(r_{\text{BCP}})$  at critical point of type (3; -1) of 145 intermolecular 1:1 complexes formed by  $\text{Me}_3\text{PO}$  with halogen-donating molecules. The solid curve was obtained as described below the figure.



The  $R_{\text{norm}}$  values fall predictably with the increase of  $G(r_{\text{BCP}})$ , making the terms “halogen bond strength” and “halogen bond shortness” virtually interchangeable. By losing some precision and gaining some generality, one could propose the following halogen-independent fitting curve for the whole set of data points in Figure S10:

$$R_{\text{norm}} = -0.784 \cdot \ln(0.062 \cdot \ln G(r_{\text{BCP}}))$$

This functional dependence is clearly lacking a physical meaning, but it described the data points fairly and thus might appear to be useful.

**Figure S11.** (a) Complexation enthalpy  $\Delta H$  and (b) local electron kinetic energy density  $G(r_{\text{BCP}})$  at the  $\text{X}\cdots\text{O}$  ( $\text{X} = \text{F}, \text{Cl}, \text{Br}$  and  $\text{I}$ ) bond critical point of type (3; -1) as a function of the change of the  $^{31}\text{P}$  NMR chemical shift upon complexation  $\Delta\delta^{31}\text{P}$  of 145 intermolecular 1:1 complexes formed by  $\text{Me}_3\text{PO}$  with halogen-donating molecules. Open symbols correspond to complex with the presence of additional non-covalent interactions, filled symbols – without such interactions (halogen bond only).

