

**Table S1.** Crystallographic data for structures of the **A1.1** type (trigonal space group  $R\bar{3}$ ,  $Z = 18$ ).

|   | <b><i>α</i>-Br~CF<sub>3</sub></b>   | <b><i>α</i>-Br~I</b>  | <b><i>α</i>-Br~Br</b>  | <b>Cl~Br</b>   |
|---|---|---|--|--|
| Formula                                   | C <sub>13</sub> H <sub>9</sub> BrF <sub>3</sub> N <sub>2</sub> O <sub>2</sub> S | C <sub>12</sub> H <sub>9</sub> BrIN <sub>2</sub> O <sub>2</sub> S | C <sub>12</sub> H <sub>9</sub> Br <sub>2</sub> N <sub>2</sub> O <sub>2</sub> S | C <sub>12</sub> H <sub>9</sub> ClBrN <sub>2</sub> O <sub>2</sub> S |
| Formula weight                            | 380.18  | 438.07  | 391.08   | 346.62   |
| Temperature (K)                           | 293   | 120   | 120  | 120  |
| a (Å)                                     | 28.0220(6)  | 28.134(4)   | 27.3197(11)  | 27.045(4)  |
| c (Å)                                     | 9.5386(3)   | 9.0240(18)  | 9.2582(6)  | 9.1556(10)   |
| V (Å <sup>3</sup> )                       | 6486.5(3)   | 6185.8(18)  | 5984.2(5)  | 5799.5(13)   |
| D <sub>calc</sub> (g/cm <sup>3</sup> )    | 1.752   | 2.117   | 1.953  | 1.786  |
| μ(Mo-K <sub>α</sub> ) (mm <sup>-1</sup> ) | 3.032   | 5.380   | 6.244  | 3.550  |
| Reflections collected                     | 14120   | 5868  | 3490   | 6040   |
| Independent                               | 2552 (0.0504)   | 2401 (0.1199)   | 1962 (0.1862)  | 2049 (0.1049)  |
| reflections (R <sub>int</sub> )           |   |   |  |  |
| Parameters                                | 231   | 176   | 166  | 176  |
| R <sub>i</sub> [I > 2σ(I)] <sup>c</sup>   | 0.0401  | 0.0600  | 0.0864   | 0.0494   |
| wR <sub>2</sub> (all data) <sup>c</sup>   | 0.1118  | 0.1796  | 0.2064   | 0.1134   |
| Crystal                                   | colourless block  | colourless block  | colourless block   | colourless plate   |
| Crystal size (mm)                         | 0.30 × 0.22 × 0.17  | 0.20 × 0.20 × 0.10  | 0.40 × 0.20 × 0.10   | 0.5 × 0.15 × 0.15  |

  

|   | <b>Cl~CF<sub>3</sub></b>  | <b>Cl~Cl</b>   | <b>Cl~I</b>   | <b>CN~CF<sub>3</sub></b>  |
|---|---|--|---|---|
| Formula                                   | C <sub>13</sub> H <sub>9</sub> ClF <sub>3</sub> N <sub>2</sub> O <sub>2</sub> S | C <sub>12</sub> H <sub>9</sub> Cl <sub>2</sub> N <sub>2</sub> O <sub>2</sub> S | C <sub>12</sub> H <sub>9</sub> ClIN <sub>2</sub> O <sub>2</sub> S | C <sub>14</sub> H <sub>9</sub> F <sub>3</sub> N <sub>2</sub> O <sub>2</sub> S |
| Formula weight                            | 335.72  | 302.16   | 393.61  | 326.29  |
| Temperature (K)                           | 293   | 120  | 120   | 120   |
| a (Å)                                     | 27.805(3)   | 26.5773(11)  | 27.812(4)   | 27.6017(8)  |
| c (Å)                                     | 9.4583(12)  | 9.3206(4)  | 9.0055(18)  | 9.4505(3)   |
| V (Å <sup>3</sup> )                       | 6332.8(12)  | 5701.6(4)  | 6032.6(17)  | 6235.3(3)   |
| D <sub>calc</sub> (g/cm <sup>3</sup> )    | 1.585   | 1.584  | 1.950   | 1.564   |
| μ(Mo-K <sub>α</sub> ) (mm <sup>-1</sup> ) | 0.456   | 0.668  | 2.736   | 0.276   |
| Reflections collected                     | 9157  | 5243   | 8871  | 9968  |
| Independent                               | 2745 (0.1465)   | 2451 (0.1531)  | 2603 (0.0523)   | 2439 (0.0675)   |
| reflections (R <sub>int</sub> )           |   |  |   |   |
| Parameters                                | 257   | 175  | 173   | 268   |
| R <sub>i</sub> [I > 2σ(I)] <sup>c</sup>   | 0.0556  | 0.0565   | 0.0255  | 0.0668  |
| wR <sub>2</sub> (all data) <sup>c</sup>   | 0.1390  | 0.1292   | 0.0580  | 0.1699  |
| Crystal                                   | colourless block  | colourless block   | colourless block  | colourless block  |
| Crystal size (mm)                         | 0.30 × 0.30 × 0.20  | 0.15 × 0.15 × 0.05   | 0.25 × 0.20 × 0.10  | 0.20 × 0.10 × 0.07  |

|  | <b>CN~I</b>   | <b>CN~Br</b>   | <b>CN~Cl</b>   | <b><math>\alpha</math>-CN~Me</b>                                |
|--|---|--|--|---|
| Formula  | C <sub>13</sub> H <sub>9</sub> IN <sub>2</sub> O <sub>2</sub> S | C <sub>13</sub> H <sub>9</sub> BrN <sub>2</sub> O <sub>2</sub> S | C <sub>13</sub> H <sub>9</sub> ClN <sub>2</sub> O <sub>2</sub> S | C <sub>14</sub> H <sub>12</sub> N <sub>2</sub> O <sub>2</sub> S |
| Formula weight                                   | 384.18  | 337.19   | 292.73   | 272.32  |
| Temperature (K)                                  | 120   | 120  | 120  | 120   |
| a (Å)  | 27.4867(7)  | 27.0722(8)   | 26.8055(15)  | 26.9964(6)  |
| c (Å)  | 9.3972(7)   | 9.4838(8)  | 9.5489(6)  | 9.5869(5)   |
| V (Å <sup>3</sup> )                              | 6148.6(5)   | 6019.5(6)  | 5942.0(6)  | 6050.9(4)   |
| D <sub>calc</sub> (g/cm <sup>3</sup> )           | 1.868   | 1.674  | 1.473  | 1.345   |
| $\mu$ (Mo-K $\alpha$ ) (mm <sup>-1</sup> )       | 2.495   | 3.227  | 0.445  | 0.239   |
| Reflections collected                            | 6654  | 7964   | 6911   | 11791   |
| Independent                                      | 2357 (0.1036)   | 2569 (0.1110)  | 2482 (0.0987)  | 2632 (0.1020)   |
| reflections (R <sub>int</sub> )                  |   |  |  |   |
| Parameters                                       | 176   | 184  | 184  | 192   |
| R <sub>1</sub> [I > 2 $\sigma$ (I)] <sup>c</sup> | 0.0488  | 0.0470   | 0.0435   | 0.0428  |
| wR <sub>2</sub> (all data) <sup>c</sup>          | 0.1292  | 0.1133   | 0.1205   | 0.1082  |
| Crystal  | colourless block  | colourless block   | colourless block   | colourless block  |
| Crystal size (mm)                                | 0.35 × 0.10 × 0.10  | 0.25 × 0.12 × 0.10   | 0.20 × 0.15 × 0.15   | 0.20 × 0.15 × 0.14  |

|  | <b>F~CF<sub>3</sub></b>   | <b>F~I</b>   | <b>F~Br</b>   | <b>F~Cl</b>   |
|--|---|--|---|---|
| Formula  | C <sub>13</sub> H <sub>9</sub> F <sub>4</sub> N <sub>2</sub> O <sub>2</sub> S | C <sub>12</sub> H <sub>9</sub> FIN <sub>2</sub> O <sub>2</sub> S | C <sub>12</sub> H <sub>9</sub> FBrN <sub>2</sub> O <sub>2</sub> S | C <sub>12</sub> H <sub>9</sub> FCIN <sub>2</sub> O <sub>2</sub> S |
| Formula weight                                   | 319.27  | 377.16   | 330.17  | 285.71  |
| Temperature (K)                                  | 293   | 120  | 120   | 120   |
| a (Å)  | 27.4403(4)  | 27.3131(5)   | 26.5333(4)  | 25.9241(8)  |
| c (Å)  | 9.5034(3)   | 9.1331(2)  | 9.2014(3)   | 9.3533(5)   |
| V (Å <sup>3</sup> )                              | 6197.1(2)   | 5900.5(2)  | 5610.1(2)   | 5443.8(4)   |
| D <sub>calc</sub> (g/cm <sup>3</sup> )           | 1.540   | 1.911  | 1.759   | 1.569   |
| $\mu$ (Mo-K $\alpha$ ) (mm <sup>-1</sup> )       | 0.284   | 2.606  | 3.469   | 0.493   |
| Reflections collected                            | 13733   | 14479  | 12683   | 5545  |
| Independent                                      | 2654 (0.0573)   | 2564 (0.0360)  | 2449 (0.0541)   | 2048 (0.1149)   |
| reflections (R <sub>int</sub> )                  |   |  |   |   |
| Parameters                                       | 249   | 176  | 176   | 175   |
| R <sub>1</sub> [I > 2 $\sigma$ (I)] <sup>c</sup> | 0.0468  | 0.0317   | 0.0313  | 0.0559  |
| wR <sub>2</sub> (all data) <sup>c</sup>          | 0.1396  | 0.0834   | 0.0808  | 0.1541  |
| Crystal  | colourless block  | colourless block   | colourless block  | colourless block  |
| Crystal size (mm)                                | 0.35 × 0.20 × 0.15  | 0.40 × 0.30 × 0.20   | 0.30 × 0.20 × 0.10  | 0.20 × 0.15 × 0.15  |

|  | <b><math>\alpha</math>-F~F</b>  | <b>Me~CF<sub>3</sub></b>   | <b>Me~I</b>  | <b>Me~Br</b>  |
|--|---|--|--|---|
| Formula  | C <sub>12</sub> H <sub>9</sub> F <sub>2</sub> N <sub>2</sub> O <sub>2</sub> S | C <sub>14</sub> H <sub>12</sub> F <sub>3</sub> N <sub>2</sub> O <sub>2</sub> S | C <sub>13</sub> H <sub>12</sub> IN <sub>2</sub> O <sub>2</sub> S | C <sub>13</sub> H <sub>12</sub> BrN <sub>2</sub> O <sub>2</sub> S |
| Formula weight                                   | 269.26  | 315.31   | 373.20   | 326.21  |
| Temperature (K)                                  | 120   | 293  | 120  | 120   |
| a (Å)  | 24.9922(5)  | 27.7243(7)   | 27.7443(14)  | 27.1912(10)   |
| c (Å)  | 9.5804(4)   | 9.8101(5)  | 9.3639(9)  | 9.4503(7)   |
| V (Å <sup>3</sup> )                              | 5182.3(3)   | 6530.2(4)  | 6242.2(7)  | 6051.1(5)   |
| D <sub>calc</sub> (g/cm <sup>3</sup> )           | 1.553   | 1.443  | 1.787  | 1.611   |
| $\mu$ (Mo-K $\alpha$ ) (mm <sup>-1</sup> )       | 0.300   | 0.259  | 2.452  | 3.205   |
| Reflections collected                            | 5887  | 11133  | 6287   | 6656  |
| Independent                                      | 2157 (0.0645)   | 2548 (0.0632)  | 2338 (0.0954)  | 2334 (0.1132)   |
| reflections (R <sub>int</sub> )                  |   |  |  |   |
| Parameters                                       | 176   | 222  | 166  | 177   |
| R <sub>1</sub> [I > 2 $\sigma$ (I)] <sup>c</sup> | 0.0395  | 0.0554   | 0.0449   | 0.0436  |
| wR <sub>2</sub> (all data) <sup>c</sup>          | 0.0992  | 0.1527   | 0.1192   | 0.0985  |
| Crystal  | colourless block  | colourless block   | colourless block   | colourless block  |
| Crystal size (mm)                                | 0.20 × 0.15 × 0.15  | 0.20 × 0.12 × 0.10   | 0.15 × 0.05 × 0.05   | 0.20 × 0.20 × 0.10  |

|  | <b>Me~Cl</b>  | <b><math>\alpha</math>-MeO~I</b>                                 | <b>(Cl~Cl)<sub>0.80</sub> · (Cl~F)<sub>0.20</sub></b>                                 | <b>Cl~CCH</b>   |
|--|---|--|---|---|
| Formula  | C <sub>13</sub> H <sub>12</sub> ClN <sub>2</sub> O <sub>2</sub> S | C <sub>13</sub> H <sub>12</sub> IN <sub>2</sub> O <sub>3</sub> S | C <sub>12</sub> H <sub>9</sub> Cl <sub>1.80</sub> F <sub>0.20</sub> NO <sub>2</sub> S | C <sub>14</sub> H <sub>10</sub> ClN <sub>2</sub> O <sub>2</sub> S |
| Formula weight                                   | 281.75  | 389.20   | 298.87  | 291.74  |
| Temperature (K)                                  | 120   | 120  | 120   | 120   |
| a (Å)  | 26.7454(4)  | 27.3759(8)   | 26.4119(8)  | 27.3848(15)   |
| c (Å)  | 9.5265(3)   | 9.9002(4)  | 9.3936(5)   | 9.2241(7)   |
| V (Å <sup>3</sup> )                              | 5901.5(2)   | 6425.6(4)  | 5674.9(4)   | 5990.6(6)   |
| D <sub>calc</sub> (g/cm <sup>3</sup> )           | 1.427   | 1.810  | 1.574   | 1.456   |
| $\mu$ (Mo-K $\alpha$ ) (mm <sup>-1</sup> )       | 0.443   | 2.391  | 0.631   | 0.439   |
| Reflections collected                            | 13967   | 30339  | 5704  | 4127  |
| Independent                                      | 2577 (0.0501)   | 2769 (0.1397)  | 2455 (0.0876)   | 2006 (0.0913)   |
| reflections (R <sub>int</sub> )                  |   |  |   |   |
| Parameters                                       | 179   | 176  | 187   | 180   |
| R <sub>1</sub> [I > 2 $\sigma$ (I)] <sup>c</sup> | 0.0372  | 0.0536   | 0.0481  | 0.0716  |
| wR <sub>2</sub> (all data) <sup>c</sup>          | 0.1027  | 0.1286   | 0.1259  | 0.1756  |
| Crystal  | colourless block  | colourless block   | colourless block  | colourless block  |
| Crystal size (mm)                                | 0.25 × 0.20 × 0.20  | 0.20 × 0.20 × 0.10   | 0.25 × 0.20 × 0.20  | 0.25 × 0.20 × 0.20  |

**Table S2** Geometrical parameters (Å and °) of the N–H···S=O hydrogen bond in isostructures of the **A1.1** type.

| Structure  | N–H       | H···O     | N···O     | NHO       |
|--|-----------|-----------|-----------|-----------|
| $\alpha$ -Br~CF <sub>3</sub>                     | 0.90(2)   | 1.99(2)   | 2.892(4)  | 175(4)    |
| $\alpha$ -Br~I                                   | 0.92(7)   | 1.96(7)   | 2.864(9)  | 168(9)    |
| $\alpha$ -Br~Br                                  | 0.901(10) | 1.96(4)   | 2.846(12) | 166(12)   |
| Cl~Br  | 0.893(15) | 1.975(19) | 2.860(6)  | 171(6)    |
| Cl~CF <sub>3</sub>                               | 0.92(2)   | 1.97(2)   | 2.885(4)  | 169(3)    |
| Cl~Cl  | 0.891(10) | 1.976(12) | 2.860(3)  | 171(3)    |
| Cl~I   | 0.895(8)  | 1.967(10) | 2.855(3)  | 171(3)    |
| CN~CF <sub>3</sub>                               | 0.898(9)  | 2.005(13) | 2.895(4)  | 170(4)    |
| CN~I   | 0.895(8)  | 1.999(7)  | 2.877(6)  | 167(4)    |
| CN~Br  | 0.899(8)  | 2.039(13) | 2.920(3)  | 166(4)    |
| CN~Cl  | 0.898(8)  | 2.048(11) | 2.926(2)  | 165(2)    |
| $\alpha$ -CN~Me                                  | 0.896(8)  | 2.047(9)  | 2.932(2)  | 169(2)    |
| F~CF <sub>3</sub>                                | 0.893(12) | 1.996(13) | 2.878(3)  | 169(3)    |
| F~I  | 0.889(10) | 1.975(16) | 2.845(4)  | 166(5)    |
| F~Br   | 0.87(3)   | 1.98(3)   | 2.843(3)  | 169(3)    |
| F~Cl   | 0.90(4)   | 1.95(4)   | 2.844(3)  | 170(4)    |
| $\alpha$ -F~F                                    | 0.91(2)   | 2.00(3)   | 2.882(2)  | 164(2)    |
| Me~CF <sub>3</sub>                               | 0.892(12) | 1.987(13) | 2.874(3)  | 173(3)    |
| Me~I   | 0.90(6)   | 1.96(6)   | 2.852(5)  | 170(5)    |
| Me~Br  | 0.887(10) | 1.976(12) | 2.853(4)  | 170(3)    |
| Me~Cl  | 0.893(8)  | 1.982(9)  | 2.865(2)  | 169.8(19) |
| $\alpha$ -MeO~I                                  | 0.898(10) | 1.98(2)   | 2.855(6)  | 166(6)    |
| (Cl~Cl) <sub>0.80</sub> · (Cl~F) <sub>0.20</sub> | 0.894(10) | 1.988(12) | 2.867(3)  | 167(3)    |
| Cl~CCH   | 0.898(8)  | 1.985(10) | 2.882(5)  | 177(5)    |