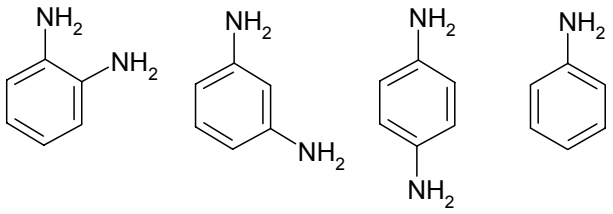
Supplementary Material (ESI) for Chemical Communications


**Supplementary information**:

**1.1** Full list of compounds




**1** **2** **3** **4**

| Name | Abbr. |
|---|---|
| $[1]^{2+}\cdot 2(BF_4)$ | 1a |
| $[1]^{2+}\cdot 2Br$ | 1b |
| $[1]^{2+}\cdot 2Cl$ | 1c |
| $[1]^{2+}\cdot 2(CF_3CO_2)$ | 1d |
| $[1]^{2+}\cdot 2(H_2PO_4)$ | 1e |
| $[1]^{2+}\cdot 2(NO_3)$ | 1f |
| $[1]^{2+}\cdot SiF_6$ | 1g |
| $[1]^{2+}_4\cdot 3(SO_4)\cdot 2(HSO_4)$ | 1h |
| $[2]^{2+}\cdot 2BF_4$ | 2a |
| $[2]^{2+}\cdot 2Br$ | 2b |
| $[2]^{2+}_2\cdot HPO_4\cdot 2(H_2PO_4)$ | 2c |
| $[2]^{2+}\cdot 2(HSO_4)$ | 2d |
| $[2]^{2+}\cdot 2(NO_3)$ | 2e |
| $[2]^{2+}\cdot SiF_6$ (previously thought to be $PF_6$ salt) | 2f |
| $[2]^{2+}\cdot SiF_6$ | 2g |
| $[2]^{1+}.Cl$ | 2h |
| $[3]^{2+}\cdot 2Br$ | 3a |
| $[3]^{2+}\cdot 2Cl$ | 3b |
| $[3]^{2+}\cdot 2(F_3CCO_2)$ | 3c |
| $[3]^{2+}\cdot SiF_6$ | 3d |
| $[3]^{2+}\cdot SO_4$ | 3e |
| $[4]^{2+}\cdot BF_4$ | 4a |
| $[4]^{2+}\cdot Br$ | 4b |
| $[4]^{2+}\cdot Cl$ | 4c |
| $[4]^{2+}\cdot (F_3CCO_2)$ | 4d |
| $[4]^{2+}\cdot H_2PO_4$ | 4e |
| $[4]^{2+}\cdot HSO_4$ | 4f |
| $[4]^{2+}\cdot NO_3$ | 4g |
| $[4]^{2+}\cdot 0.5(SiF_6)$ | 4h |

**1.2** Experimental procedures

Samples were prepared by recrystallising the relevant amine from an acid solution.

The resulting crystals were mounted on a thin glass fibre using silicon grease and cooled on the diffractometer to 100 K using an Oxford Cryostream low temperature attachment. Approximate unit cell dimensions were determined by the Nonius Collect program[1] from 5 index frames of width $2^o$ in $\phi$ using a Nonius $^{Kappa}$CCD diffractometer, with a detector to crystal distance of 30 mm. The Collect program was then used to calculate a data collection strategy to 99.5 % completeness for $\theta = 27.5^o$ using a combination of $2^o$ $\phi$ and $\omega$ scans of 10 - 120 s $deg^{-1}$ exposure time (depending on crystal quality). Crystals were indexed using the DENZO-SMN package[2] and positional data were refined along with diffractometer constants to give the final unit cell parameters. Integration and scaling (DENZO-SMN, Scalepack[2]) resulted in unique data sets corrected for Lorentz and polarisation effects and for the effects of crystal decay and absorption by a combination of averaging of equivalent reflections and an overall volume and scaling correction. Structures were solved using SHELXS-97[3] and developed *via* alternating least squares cycles and difference Fourier synthesis (SHELXL-97[3]) with the aid of the program X-Seed.[4] In general all non-hydrogen atoms were modelled anisotropically, while hydrogen atoms are assigned an isotropic thermal parameter 1.2 times that of the parent atom (1.5 for terminal atoms) and allowed to ride. Individual refinement details can be found in the _refine_special_details section of the individual cif files.

1. R. Hooft, 'Collect', Nonius B.V., Delft, 1998.
2. Z. Otwinowski and W. Minor, in *Methods in Enzymology*, **276**, 1997, *pp* 307 - 326. C. W. Carter and R. M. Sweet (Eds.), Academic Press, New York.
3. G. M. Sheldrick, 'SHELXL-97', University of Göttingen, 1997.
4. L. J. Barbour, *J. Supramol. Chem.*, 2001, **1**, 189..

**1.3** Crystal data footnotes

Crystal data for 1a: $C_6H_{10}B_2F_8N_2$, $M$ = 283.78, colourless prism, 0.50 × 0.20 × 0.10 mm$^3$, monoclinic, space group $P2_1/c$ (No. 14), $a$ = 11.180(2), $b$ = 7.1600(14), $c$ = 13.983(3) Å, $\beta$ = 91.27(3)°, $V$ = 1119.1(4) Å$^3$, $Z$ = 4, $D_c$ = 1.684 g/cm$^3$, $F_{000}$ = 568, kappaccd, MoKα radiation, λ = 0.71070 Å, $T$ = 100(2)K, $2\theta_{max}$ = 55.0º, 7843 reflections collected, 2567 unique ($R_{int}$ = 0.0318). Final *GooF* = 1.011, *R1* = 0.0285, *wR2* = 0.0739, *R* indices based on 2250 reflections with I >2sigma(I) (refinement on $F^2$), 166 parameters, 0 restraints. Lp and absorption corrections applied, $\mu$ = 0.193 mm$^{-1}$.

Crystal data for 1b: $C_6H_{10}Br_2N_2$, $M$ = 269.98, 0.50 × 0.25 × 0.10 mm$^3$, monoclinic, space group $P2_1/c$ (No. 14), $a$ = 13.5054(10), $b$ = 7.4498(10), $c$ = 9.418(8) Å, $\beta$ = 110.351(6)°, $V$ = 888.5(8) Å$^3$, $Z$ = 4, $D_c$ = 2.018 g/cm$^3$, $F_{000}$ = 520, Kappa CCD, MoKα radiation, λ = 0.71073 Å, $T$ = 100(2)K, $2\theta_{max}$ = 52.0º, 1983 reflections collected, 1064 unique ($R_{int}$ = 0.0521). Final *GooF* = 1.222, *R1* = 0.1014, *wR2* = 0.2528, *R* indices based on 1007 reflections with I >2sigma(I) (refinement on $F^2$), 68 parameters, 0 restraints. Lp and absorption corrections applied, $\mu$ = 9.056 mm$^{-1}$.
Platon suggests missed symmetry however no suitable higher symmetry structure could be found. The large residual electron density peak may be unrefined solvent/water but attempts to model this failed. Some atoms have been refined isotropically as refining them anisotropically leads to non-positive-definites. Although the maximum shift/error and R1 and wR2 are large for this compound (due to reasons above), the relative structure of the compound is not in doubt.

Crystal data for 1c: $C_6H_{10}Cl_2N_2$, $M$ = 181.06, 1.00 × 0.50 × 0.20 mm$^3$, monoclinic, space group $C2/c$ (No. 15), $a$ = 7.3184(6), $b$ = 14.5495(9), $c$ = 7.8594(6) Å, $\beta$ = 94.794(5)°, $V$ = 833.93(11) Å$^3$, $Z$ = 4, $D_c$ = 1.442 g/cm$^3$, $F_{000}$ = 376, Kappa CCD, MoKα radiation, λ = 0.71070 Å, $T$ = 100(2)K, $2\theta_{max}$ = 51.9º, 2797 reflections collected, 814 unique ($R_{int}$ = 0.0313). Final *GooF* = 1.192, *R1* = 0.0237, *wR2* = 0.0565, *R* indices based on 746 reflections with I >2sigma(I) (refinement on $F^2$), 46 parameters, 0 restraints. Lp and absorption corrections applied, $\mu$ = 0.705 mm$^{-1}$.

Crystal data for 1d: $C_{10}H_{10}F_6N_2O_4$, $M$ = 336.20, 0.30 × 0.15 × 0.10 mm$^3$, monoclinic, space group $C2/c$ (No. 15), $a$ = 25.649(3), $b$ = 8.6558(9), $c$ = 11.7964(13) Å, $\beta$ = 102.093(6)°, $V$ = 2560.9(5) Å$^3$, $Z$ = 8, $D_c$ = 1.744 g/cm$^3$, $F_{000}$ = 1360, KAppa CCD, MoKα radiation, λ = 0.71070 Å, $T$ = 100(2)K, $2\theta_{max}$ = 55.0º, 6459 reflections collected, 2815 unique ($R_{int}$ = 0.0569). Final *GooF* = 1.087, *R1* = 0.0495, *wR2* = 0.0891, *R* indices based on 2213 reflections with I >2sigma(I) (refinement on $F^2$), 224 parameters, 0 restraints. Lp and absorption corrections applied, $\mu$ = 0.187 mm$^{-1}$.

Crystal data for 1e: $C_6H_{14}N_2O_8P_2$, $M$ = 304.13, 0.40 × 0.30 × 0.25 mm$^3$, triclinic, space group $P$-1 (No. 2), $a$ = 6.6630(2), $b$ = 9.8070(6), $c$ = 10.1060(6) Å, $\alpha$ = 66.947(3), $\beta$ = 73.474(4), $\gamma$ = 73.262(4)°, $V$ = 570.74(5) Å$^3$, $Z$ = 2, $D_c$ = 1.770 g/cm$^3$, $F_{000}$ = 316, Kappa CCD, MoKα radiation, λ = 0.71070 Å, $T$ = 100(2)K, $2\theta_{max}$ = 55.0º, 4490 reflections collected, 2620 unique ($R_{int}$ = 0.0307). Final *GooF* = 1.056, *R1* = 0.0340, *wR2* = 0.0751, *R* indices based on 2324 reflections with I >2sigma(I) (refinement on $F^2$), 204 parameters, 0 restraints. Lp and absorption corrections applied, $\mu$ = 0.419 mm$^{-1}$.

Crystal data for 1f: $C_6H_{10}N_4O_6$, $M$ = 234.18, × × mm$^3$, monoclinic, space group $P2_1/c$ (No. 14), $a$ = 12.6849(14), $b$ = 7.9519(6), $c$ = 10.3950(10) Å, $\beta$ = 105.817(5)°, $V$ = 1008.83(17) Å$^3$, $Z$ = 4, $D_c$ = 1.542 g/cm$^3$, $F_{000}$ = 488, Kappa CCD, MoKα radiation, λ = 0.71070 Å, $T$ = 100(2)K, $2\theta_{max}$ = 49.9º, 5968 reflections collected, 1768 unique ($R_{int}$ = 0.0835). Final *GooF* = 1.866, *R1* = 0.1472, *wR2* = 0.4231, *R* indices based on 1405 reflections with I >2sigma(I) (refinement on $F^2$), 147 parameters, 0 restraints. Lp and absorption corrections applied, $\mu$ = 0.138 mm$^{-1}$.
The large R1 and wR2 values may be due to unresolved twinning in the data. The connectivity of the structure is unaffected by this.

Crystal data for 1g: $C_6H_{10}F_6N_2Si$, $M$ = 252.25, 0.80 × 0.20 × 0.20 mm$^3$, monoclinic, space group $P2/n$ (No. 13), $a$ = 5.5242(2), $b$ = 11.1775(8), $c$ = 7.6086(5) Å, $\beta$ = 90.75(3)°, $V$ = 469.77(5) Å$^3$, $Z$ = 2, $D_c$ = 1.783 g/cm$^3$, $F_{000}$ = 256, MoKα radiation, λ = 0.71070 Å, $T$ = 100(2)K, $2\theta_{max}$ = 55.0º, 1922 reflections collected, 1001 unique ($R_{int}$ = 0.0245). Final *GooF* = 1.063, *R1* = 0.0369, *wR2* = 0.0943, *R* indices

based on 924 reflections with I >2sigma(I) (refinement on $F^2$), 82 parameters, 0 restraints. Lp and absorption corrections applied, $\mu = 0.312$ mm$^{-1}$.

The structure can be refined in Pmmn (as suggested by Platon) but R1 = 0.0759. In the monoclinic solution the anion is slightly offset compared to the cation, giving beta = 90.8 (>>90 for an otherwise precise structure). In Pmmn (with beta forced to be 90) the molecule is on a mirror and the offset manifests itself in elongated ellipsoids and the large R1 value. Therefore while the anion fits the Pmmn space group the cation does not therefore we believe the lower symmetry solution is the correct one.

Crystal data for 1h: $C_{24}H_{25}N_8O_{24}S_5$, $M = 969.82$, $0.50 \times 0.20 \times 0.10$ mm$^3$, monoclinic, space group $P2_1$ (No. 4), $a = 7.5897(15)$, $b = 27.591(6)$, $c = 19.190(4)$ Å, $\beta = 91.58(3)°$, $V = 4016.9(14)$ Å$^3$, $Z = 4$, $D_c = 1.604$ g/cm$^3$, $F_{000} = 1988$, Kappa CCD, MoKα radiation, $\lambda = 0.71070$ Å, $T = 100(2)$K, $2\theta_{max} = 52.0°$, 23828 reflections collected, 14446 unique ($R_{int} = 0.0867$). Final *GooF* = 1.027, *R1* = 0.0729, *wR2* = 0.1363, *R* indices based on 8507 reflections with I >2sigma(I) (refinement on $F^2$), 1101 parameters, 1 restraint. Lp and absorption corrections applied, $\mu = 0.387$ mm$^{-1}$. Absolute structure parameter = 0.29(8) (Flack, H. D. *Acta Cryst*. **1983**, *A39*, 876-881). We were unable to locate hydrogen atoms on SO4, HSO4 and H2O groups so formula deduced on a charge balance basis

Crystal data for 2a: $C_6H_{10}B_2F_8N_2$, $M = 283.78$, $0.30 \times 0.20 \times 0.10$ mm$^3$, triclinic, space group *P*-1 (No. 2), $a = 7.2396(13)$, $b = 8.8215(16)$, $c = 9.4429(16)$ Å, $\alpha = 73.712(11)$, $\beta = 74.877(9)$, $\gamma = 76.677(9)°$, $V = 550.70(17)$ Å$^3$, $Z = 2$, $D_c = 1.711$ g/cm$^3$, $F_{000} = 284$, Kappa CCD, MoKα radiation, $\lambda = 0.71070$ Å, $T = 100(2)$K, $2\theta_{max} = 55.0°$, 4105 reflections collected, 2518 unique ($R_{int} = 0.0730$). Final *GooF* = 1.005, *R1* = 0.0619, *wR2* = 0.1097, *R* indices based on 1352 reflections with I >2sigma(I) (refinement on $F^2$), 166 parameters, 0 restraints. Lp and absorption corrections applied, $\mu = 0.196$ mm$^{-1}$.

Crystal data for 2b: $C_6H_{10}Br_2N_2$, $M = 269.98$, $0.50 \times 0.20 \times 0.10$ mm$^3$, monoclinic, space group $P2_1/c$ (No. 14), $a = 8.3858(17)$, $b = 8.1422(16)$, $c = 13.592(3)$ Å, $\beta = 92.82(3)°$, $V = 926.9(3)$ Å$^3$, $Z = 4$, $D_c = 1.935$ g/cm$^3$, $F_{000} = 520$, Kappa CCD, MoKα radiation, $\lambda = 0.71070$ Å, $T = 100(2)$K, $2\theta_{max} = 52.0°$, 3417 reflections collected, 1784 unique ($R_{int} = 0.1037$). Final *GooF* = 1.162, *R1* = 0.0822, *wR2* = 0.2037, *R* indices based on 1534 reflections with I >2sigma(I) (refinement on $F^2$), 93 parameters, 0 restraints. Lp and absorption corrections applied, $\mu = 8.680$ mm$^{-1}$. Largest residual electron density peaks are close to the bromines.

Crystal data for 2c: $C_{12}H_{25}N_4O_{12}P_3$, $M = 510.27$, $0.50 \times 0.20 \times 0.10$ mm$^3$, triclinic, space group *P*-1 (No. 2), $a = 10.9056(6)$, $b = 13.2510(4)$, $c = 15.7992(8)$ Å, $\alpha = 113.296(3)$, $\beta = 99.154(3)$, $\gamma = 95.774(3)°$, $V = 2036.36(16)$ Å$^3$, $Z = 4$, $D_c = 1.664$ g/cm$^3$, $F_{000} = 1064$, Kappa CCD, MoKα radiation, $\lambda = 0.71070$ Å, $T = 100(2)$K, $2\theta_{max} = 55.0°$, 16581 reflections collected, 9285 unique ($R_{int} = 0.0865$). Final *GooF* = 1.004, *R1* = 0.0604, *wR2* = 0.1100, *R* indices based on 5912 reflections with I >2sigma(I) (refinement on $F^2$), 568 parameters, 0 restraints. Lp and absorption corrections applied, $\mu = 0.364$ mm$^{-1}$.

Crystal data for 2d: $C_6H_{12}N_2O_8S_2$, $M = 304.30$, $0.50 \times 0.20 \times 0.10$ mm$^3$, triclinic, space group *P*-1 (No. 2), $a = 7.1298(9)$, $b = 8.8359(8)$, $c = 10.3489(14)$ Å, $\alpha = 65.177(8)$, $\beta = 87.006(8)$, $\gamma = 77.515(8)°$, $V = 577.19(12)$ Å$^3$, $Z = 2$, $D_c = 1.751$ g/cm$^3$, $F_{000} = 316$, Kappa CCD, MoKα radiation, $\lambda = 0.71070$ Å, $T = 100(2)$K, $2\theta_{max} = 55.0°$, 4537 reflections collected, 2640 unique ($R_{int} = 0.0667$). Final *GooF* = 1.038, *R1* = 0.0567, *wR2* = 0.1474, *R* indices based on 2264 reflections with I >2sigma(I) (refinement on $F^2$), 168 parameters, 0 restraints. Lp and absorption corrections applied, $\mu = 0.499$ mm$^{-1}$.

Crystal data for 2e: $C_6H_{12}N_4O_7$, $M = 252.20$, $0.50 \times 0.20 \times 0.10$ mm$^3$, monoclinic, space group $P2_1/c$ (No. 14), $a = 10.677(2)$, $b = 6.8471(18)$, $c = 15.621(3)$ Å, $\beta = 108.610(10)°$, $V = 1082.2(4)$ Å$^3$, $Z = 4$, $D_c = 1.548$ g/cm$^3$, $F_{000} = 528$, Kappa CCD, MoKα radiation, $\lambda = 0.71070$ Å, $T = 100(2)$K, $2\theta_{max} = 52.0°$, 5985 reflections collected, 2124 unique ($R_{int} = 0.1332$). Final *GooF* = 1.041, *R1* = 0.0660, *wR2* = 0.1069, *R* indices based on 1211 reflections with I >2sigma(I) (refinement on $F^2$), 165 parameters, 0 restraints. Lp and absorption corrections applied, $\mu = 0.141$ mm$^{-1}$.

Crystal data for 2f: $C_6H_{12}F_6N_2OSi$, $M$ = 270.27, 0.50 × 0.20 × 0.10 mm$^3$, monoclinic, space group $P2_1$ (No. 4), $a$ = 8.9269(11), $b$ = 6.0679(10), $c$ = 10.4425(15) Å, $\beta$ = 113.210(9)°, $V$ = 519.86(13) Å$^3$, $Z$ = 2, $D_c$ = 1.727 g/cm$^3$, $F_{000}$ = 276, Kappa CCD, MoKα radiation, λ = 0.71070 Å, $T$ = 100(2)K, $2\theta_{max}$ = 50.0º, 3030 reflections collected, 1798 unique ($R_{int}$ = 0.0402). Final *GooF* = 1.033, *R1* = 0.0419, *wR2* = 0.1201, *R* indices based on 1736 reflections with I >2sigma(I) (refinement on $F^2$), 156 parameters, 3 restraints. Lp and absorption corrections applied, $\mu$ = 0.295 mm$^{-1}$. Absolute structure parameter = -0.04(19) (Flack, H. D. *Acta Cryst*. **1983**, *A39*, 876-881). This compound was originally assigned as the $PF_6$ salt but further refinement showed that it was in fact the $SiF_6$ salt, isomorphous with 2g. R values from refinement as $PF_6$ were: *R1* = 0.0436, *wR2*= 0.1253.

Crystal data for 2g: $C_6H_{12}F_6N_2OSi$, $M$ = 270.27, 0.20 × 0.10 × 0.10 mm$^3$, monoclinic, space group $P2_1$ (No. 4), $a$ = 8.9265(18), $b$ = 6.0639(12), $c$ = 10.440(2) Å, $\beta$ = 113.15(3)°, $V$ = 519.59(18) Å$^3$, $Z$ = 2, $D_c$ = 1.727 g/cm$^3$, $F_{000}$ = 276, Kappa CCD, MoKα radiation, λ = 0.71070 Å, $T$ = 100(2)K, $2\theta_{max}$ = 52.0º, 3125 reflections collected, 1960 unique ($R_{int}$ = 0.0463). Final *GooF* = 1.053, *R1* = 0.0440, *wR2* = 0.0999, *R* indices based on 1756 reflections with I >2sigma(I) (refinement on $F^2$), 154 parameters, 1 restraint. Lp and absorption corrections applied, $\mu$ = 0.295 mm$^{-1}$. Absolute structure parameter = -0.1(2) (Flack, H. D. *Acta Cryst*. **1983**, *A39*, 876-881).

Crystal data for 2h: $C_6H_9ClN_2$, $M$ = 144.60, 0.30 × 0.20 × 0.10 mm$^3$, orthorhombic, space group $P2_12_12_1$ (No. 19), $a$ = 5.7025(11), $b$ = 8.5328(17), $c$ = 14.781(3) Å, $V$ = 719.2(2) Å$^3$, $Z$ = 4, $D_c$ = 1.335 g/cm$^3$, $F_{000}$ = 304, Kappa CCD, MoKα radiation, λ = 0.71070 Å, $T$ = 100(2)K, $2\theta_{max}$ = 52.0º, 4119 reflections collected, 1408 unique ($R_{int}$ = 0.0585). Final *GooF* = 1.060, *R1* = 0.0352, *wR2* = 0.0675, *R* indices based on 1229 reflections with I >2sigma(I) (refinement on $F^2$), 118 parameters, 0 restraints. Lp and absorption corrections applied, $\mu$ = 0.440 mm$^{-1}$. Absolute structure parameter = 0.01(9) (Flack, H. D. *Acta Cryst*. **1983**, *A39*, 876-881).

Crystal data for 3a: $C_6H_{10}Br_2N_2$, $M$ = 269.98, orange block, 0.50 × 0.20 × 0.10 mm$^3$, triclinic, space group *P*-1 (No. 2), $a$ = 4.4488(5), $b$ = 6.089(5), $c$ = 8.701(6) Å, $\alpha$ = 103.616(4), $\beta$ = 104.616(5), $\gamma$ = 101.392(5)°, $V$ = 213.2(2) Å$^3$, $Z$ = 1, $D_c$ = 2.102 g/cm$^3$, $F_{000}$ = 130, Kappa CCD, MoKα radiation, λ = 0.71070 Å, $T$ = 100(2)K, $2\theta_{max}$ = 52.0º, 1357 reflections collected, 824 unique ($R_{int}$ = 0.0943). Final *GooF* = 1.134, *R1* = 0.0364, *wR2* = 0.0901, *R* indices based on 806 reflections with I >2sigma(I) (refinement on $F^2$), 47 parameters, 0 restraints. Lp and absorption corrections applied, $\mu$ = 9.433 mm$^{-1}$.

Crystal data for 3b: $C_6H_{10}Cl_2N_2$, $M$ = 181.06, colourless plate, 0.50 × 0.20 × 0.10 mm$^3$, triclinic, space group *P*-1 (No. 2), $a$ = 4.2850(2), $b$ = 5.8053(15), $c$ = 8.6259(6) Å, $\alpha$ = 71.035(4), $\beta$ = 76.868(5), $\gamma$ = 79.631(5)°, $V$ = 196.30(5) Å$^3$, $Z$ = 1, $D_c$ = 1.532 g/cm$^3$, $F_{000}$ = 94, Kappa CCD, MoKα radiation, λ = 0.71070 Å, $T$ = 100(2)K, $2\theta_{max}$ = 55.0º, 1501 reflections collected, 875 unique ($R_{int}$ = 0.0358). Final *GooF* = 1.062, *R1* = 0.0209, *wR2* = 0.0658, *R* indices based on 843 reflections with I >2sigma(I) (refinement on $F^2$), 47 parameters, 0 restraints. Lp and absorption corrections applied, $\mu$ = 0.749 mm$^{-1}$.

Crystal data for 3c: $C_{10}H_{10}F_6N_2O_4$, $M$ = 336.20, 0.40 × 0.20 × 0.10 mm$^3$, monoclinic, space group $P2_1/c$ (No. 14), $a$ = 5.9661(5), $b$ = 16.0900(14), $c$ = 7.2186(5) Å, $\beta$ = 101.075(5)°, $V$ = 680.04(9) Å$^3$, $Z$ = 2, $D_c$ = 1.642 g/cm$^3$, $F_{000}$ = 340, Kappa CCD, MoKα radiation, λ = 0.71070 Å, $T$ = 100(2)K, $2\theta_{max}$ = 55.0º, 5611 reflections collected, 1544 unique ($R_{int}$ = 0.0714). Final *GooF* = 1.134, *R1* = 0.0825, *wR2* = 0.2111, *R* indices based on 1293 reflections with I >2sigma(I) (refinement on $F^2$), 113 parameters, 0 restraints. Lp and absorption corrections applied, $\mu$ = 0.176 mm$^{-1}$. R1 possibly high due to twinning.

Crystal data for 3d: $C_6H_{10}F_6N_2Si$, $M$ = 252.25, 1.00 × 0.50 × 0.20 mm$^3$, triclinic, space group *P*-1 (No. 2), $a$ = 5.5834(11), $b$ = 9.4219(19), $c$ = 9.6386(19) Å, $\alpha$ = 80.826(7), $\beta$ = 89.959(6), $\gamma$ = 73.219(6)°, $V$ = 478.70(16) Å$^3$, $Z$ = 2, $D_c$ = 1.750 g/cm$^3$, $F_{000}$ = 256, Kappa CCD, MoKα radiation, λ = 0.71070 Å, $T$ = 100(2)K, $2\theta_{max}$ = 50.0º, 3157 reflections collected, 1681 unique ($R_{int}$ = 0.0538). Final *GooF* = 1.040, *R1* = 0.0676, *wR2* = 0.1670, *R* indices based on 1259 reflections with I >2sigma(I) (refinement on $F^2$), 139 parameters, 0 restraints. Lp and absorption corrections applied, $\mu$ = 0.306 mm$^{-1}$. Platon suggests C2/c as an alternative space group however it was not possible to refine the structure in this space group

Crystal data for 3e: $C_6H_{10}N_2O_4S$, $M$ = 206.22, 0.50 × 0.20 × 0.10 mm$^3$, orthorhombic, space group $P2_12_12_1$ (No. 19), $a$ = 6.6270(13), $b$ = 7.3642(15), $c$ = 18.130(4) Å, $V$ = 884.8(3) Å$^3$, $Z$ = 4, $D_c$ = 1.548 g/cm$^3$, $F_{000}$ = 432, Kappa CCD, MoKα radiation, λ = 0.71070 Å, $T$ = 100(2)K, $2\theta_{max}$ = 52.0º, 5658 reflections collected, 1727 unique ($R_{int}$ = 0.0614). Final *GooF* = 1.045, *R1* = 0.0375, *wR2* = 0.0821, *R* indices based on 1508 reflections with I >2sigma(I) (refinement on $F^2$), 159 parameters, 0 restraints. Lp and absorption corrections applied, $\mu$ = 0.351 mm$^{-1}$. Absolute structure parameter = 0.19(13) (Flack, H. D. *Acta Cryst*. **1983**, *A39*, 876-881).

Crystal data for 4a: $C_6H_8BF_4N$, $M$ = 180.94, 0.50 × 0.20 × 0.10 mm$^3$, monoclinic, space group $P2_1$ (No. 4), $a$ = 7.3752(16), $b$ = 5.7860(9), $c$ = 9.3866(19) Å, $\beta$ = 97.620(11)°, $V$ = 397.02(13) Å$^3$, $Z$ = 2, $D_c$ = 1.514 g/cm$^3$, $F_{000}$ = 184, Kappa CCD, MoKα radiation, λ = 0.71070 Å, $T$ = 100(2)K, $2\theta_{max}$ = 52.7º, 2751 reflections collected, 1543 unique ($R_{int}$ = 0.0566). Final *GooF* = 1.061, *R1* = 0.0671, *wR2* = 0.1786, *R* indices based on 1303 reflections with I >2sigma(I) (refinement on $F^2$), 111 parameters, 1 restraint. Lp and absorption corrections applied, $\mu$ = 0.154 mm$^{-1}$. Absolute structure parameter = -0.5(17) (Flack, H. D. *Acta Cryst*. **1983**, *A39*, 876-881).

Crystal data for 4b: $C_6H_8BrN$, $M$ = 174.04, × × mm$^3$, monoclinic, space group $P2_1/m$ (No. 11), $a$ = 6.8425(14), $b$ = 5.9749(12), $c$ = 8.4158(17) Å, $\beta$ = 91.35(3)°, $V$ = 343.97(12) Å$^3$, $Z$ = 2, $D_c$ = 1.680 g/cm$^3$, $F_{000}$ = 172, Kappa CCD, MoKα radiation, λ = 0.71073 Å, $T$ = 173(2)K, $2\theta_{max}$ = 56.6º, 2241 reflections collected, 894 unique ($R_{int}$ = 0.0958). Final *GooF* = 1.104, *R1* = 0.0763, *wR2* = 0.1983, *R* indices based on 823 reflections with I >2sigma(I) (refinement on $F^2$), 64 parameters, 0 restraints. Lp and absorption corrections applied, $\mu$ = 5.869 mm$^{-1}$.

Crystal data for 4c: $C_6H_8ClN$, $M$ = 129.58, colourless prism, 0.50 × 0.20 × 0.10 mm$^3$, monoclinic, space group *Cc* (No. 9), $a$ = 15.760(3), $b$ = 5.3285(10), $c$ = 8.3932(11) Å, $\beta$ = 101.102(11)°, $V$ = 691.6(2) Å$^3$, $Z$ = 4, $D_c$ = 1.244 g/cm$^3$, $F_{000}$ = 272, Kappa CCD, MoKα radiation, λ = 0.71070 Å, $T$ = 100(2)K, $2\theta_{max}$ = 55.0º, 2122 reflections collected, 1486 unique ($R_{int}$ = 0.0294). Final *GooF* = 1.056, *R1* = 0.0351, *wR2* = 0.0774, *R* indices based on 1375 reflections with I >2sigma(I) (refinement on $F^2$), 74 parameters, 2 restraints. Lp and absorption corrections applied, $\mu$ = 0.446 mm$^{-1}$. Absolute structure parameter = 0.06(9) (Flack, H. D. *Acta Cryst*. **1983**, *A39*, 876-881). Checks showed an 87% fit in C2/c. The aryl groups obey this symmetry but the ammonium groups (which form ordered polar stacks in Cc) do not, therefore we believe that Cc is the correct space group.

Crystal data for 4d: $C_8H_8F_3NO_2$, $M$ = 207.15, 1.00 × 0.50 × 0.10 mm$^3$, monoclinic, space group $P2_1/n$ (No. 14), $a$ = 10.334(2), $b$ = 8.8820(18), $c$ = 19.973(4) Å, $\beta$ = 98.07(3)°, $V$ = 1815.1(6) Å$^3$, $Z$ = 8, $D_c$ = 1.516 g/cm$^3$, $F_{000}$ = 848, Kappa CCD, MoKα radiation, λ = 0.71070 Å, $T$ = 100(2)K, $2\theta_{max}$ = 52.0º, 10454 reflections collected, 3551 unique ($R_{int}$ = 0.0500). Final *GooF* = 1.039, *R1* = 0.0422, *wR2* = 0.0914, *R* indices based on 2876 reflections with I >2sigma(I) (refinement on $F^2$), 254 parameters, 0 restraints. Lp and absorption corrections applied, $\mu$ = 0.148 mm$^{-1}$.

Crystal data for 4e: $C_6H_{12}NO_5P$, $M$ = 209.14, 0.40 × 0.30 × 0.20 mm$^3$, monoclinic, space group $P2_1/n$ (No. 14), $a$ = 9.6419(19), $b$ = 21.039(4), $c$ = 10.100(2) Å, $\beta$ = 110.639(3)°, $V$ = 1917.3(7) Å$^3$, $Z$ = 8, $D_c$ = 1.449 g/cm$^3$, $F_{000}$ = 880, Kappa CCD, MoKα radiation, λ = 0.71070 Å, $T$ = 100(2)K, $2\theta_{max}$ = 50.0º, 10584 reflections collected, 3314 unique ($R_{int}$ = 0.0876). Final *GooF* = 1.061, *R1* = 0.1229, *wR2* = 0.2944, *R* indices based on 2199 reflections with I >2sigma(I) (refinement on $F^2$), 204 parameters, 0 restraints. Lp and absorption corrections applied, $\mu$ = 0.279 mm$^{-1}$. Due to poor data quality and disorder, the carbon atoms were refined isotropically. The maximum shift/error is also slightly large but could not be reduced by further refinement and is probably an artefact of the disorder/poor data quality. Although the residuals are high the connectivity of the structure is not in doubt.

Crystal data for 4f: $C_6H_9NO_4S$, $M$ = 191.20, 1.00 × 0.50 × 0.20 mm$^3$, orthorhombic, space group $Pca2_1$ (No. 29), $a$ = 14.2459(7), $b$ = 9.1043(6), $c$ = 12.6132(9) Å, $V$ = 1635.92(18) Å$^3$, $Z$ = 8, $D_c$ = 1.553 g/cm$^3$, $F_{000}$ = 800, Kappa CCD, MoKα radiation, λ = 0.71073 Å, $T$ = 100(2)K, $2\theta_{max}$ = 55.0º, 7565 reflections collected, 3063 unique ($R_{int}$ = 0.0401). Final *GooF* = 1.051, *R1* = 0.0316, *wR2* = 0.0774, *R* indices based on 2846 reflections with I >2sigma(I) (refinement on $F^2$), 241 parameters, 1 restraint. Lp

and absorption corrections applied, $\mu = 0.370$ mm$^{-1}$. Absolute structure parameter = 0.03(9) (Flack, H. D. *Acta Cryst*. **1983**, *A39*, 876-881). Platon checks show that there may be some additional symmetry but this is thought to be pseudosymmetry.

Crystal data for 4g: $C_6H_8N_2O_3$, $M = 156.14$, not known × not known × not known mm$^3$, orthorhombic, space group *Pcab* (No. 61), $a = 9.1787(3)$, $b = 9.9711(4)$, $c = 16.0278(4)$ Å, $V = 1466.89(8)$ Å$^3$, $Z = 8$, $D_c = 1.414$ g/cm$^3$, $F_{000} = 656$, Kappa CCD, MoKα radiation, $\lambda = 0.71070$ Å, $T = 100(2)$K, $2\theta_{max} = 52.0°$, 2621 reflections collected, 1415 unique ($R_{int} = 0.0148$). Final *GooF* = 1.119, *R1* = 0.0332, *wR2* = 0.0895, *R* indices based on 1315 reflections with I >2sigma(I) (refinement on $F^2$), 113 parameters, 0 restraints. Lp and absorption corrections applied, $\mu = 0.115$ mm$^{-1}$.

Crystal data for 4h: $C_{12}H_{20}F_6N_2O_2Si$, $M = 366.39$, colourless prism, 0.50 × 0.20 × 0.10 mm$^3$, monoclinic, space group $P2_1/c$ (No. 14), $a = 9.2142(6)$, $b = 5.8046(3)$, $c = 14.4759(11)$ Å, $\beta = 92.110(3)°$, $V = 773.71(9)$ Å$^3$, $Z = 2$, $D_c = 1.573$ g/cm$^3$, $F_{000} = 380$, kappaccd, MoKα radiation, $\lambda = 0.71070$ Å, $T = 100(2)$K, $2\theta_{max} = 54.9°$, 5710 reflections collected, 1768 unique ($R_{int} = 0.0369$). Final *GooF* = 1.039, *R1* = 0.0320, *wR2* = 0.0725, *R* indices based on 1526 reflections with I >2sigma(I) (refinement on $F^2$), 116 parameters, 0 restraints. Lp and absorption corrections applied, $\mu = 0.226$ mm$^{-1}$.

**1.5** Hydrogen bond table for **2c**

| D | H | A | D-H | H···A | D···A | D-H···A | symop |
|---|---|---|---|---|---|---|---|
| N1 | H1A | O17 | 0.91 | 1.87 | 2.728(4) | 156 | 1-x, 1-y, -z |
| N1 | H1B | O17 | 0.91 | 1.9 | 2.751(3) | 155 | -1+x, -1+y, z |
| N1 | H1C | O5 | 0.91 | 1.85 | 2.750(4) | 171 | 1-x,-y,-z |
| N2 | H2A | O22 | 0.91 | 1.93 | 2.777(3) | 155 | x,-1+y,-1+z |
| N2 | H2B | O1 | 0.91 | 1.97 | 2.840(4) | 160 | |
| N2 | H2B | O4 | 0.91 | 2.47 | 3.180(4) | 135 | |
| N2 | H2C | O10 | 0.91 | 1.91 | 2.779(4) | 158 | 1-x, 1-y, -z |
| N3 | H3A | O6 | 0.91 | 1.95 | 2.826(4) | 162 | 2-x,1-y,-z |
| N3 | H3B | O16 | 0.91 | 1.77 | 2.680(4) | 178 | x,y,-1+z |
| N3 | H3C | O6 | 0.91 | 1.91 | 2.795(3) | 164 | x,y,-1+z |
| O3 | H3O | O5 | 0.99 | 1.79 | 2.544(3) | 130 | |
| N4 | H4A | O2 | 0.91 | 1.77 | 2.685(3) | 176 | |
| N4 | H4B | O3 | 0.91 | 1.99 | 2.895(4) | 170 | 2-x,1-y,-z |
| N4 | H4C | O11 | 0.91 | 2.57 | 3.028(3) | 112 | 2-x,1-y,-z |
| N4 | H4C | O20 | 0.91 | 2.05 | 2.930(4) | 161 | 2-x,1-y,-z |
| O4 | H4O | O9 | 0.91 | 1.59 | 2.459(3) | 159 | |
| N5 | H5A | O9 | 0.91 | 1.87 | 2.778(4) | 174 | 1-x, 1-y, -z |
| N5 | H5B | O10 | 0.91 | 2.05 | 2.914(3) | 157 | |
| N5 | H5C | O2 | 0.91 | 1.82 | 2.723(4) | 173 | |
| N6 | H6A | O14 | 0.91 | 2.04 | 2.904(4) | 159 | 1-x, 1-y, -z |
| N6 | H6A | O16 | 0.91 | 2.53 | 3.229(3) | 133 | 1-x, 1-y, -z |
| N6 | H6B | O16 | 0.91 | 1.81 | 2.716(3) | 177 | x,y,-1+z |
| N6 | H6C | O24 | 0.91 | 1.8 | 2.691(4) | 167 | x,y,-1+z |
| N7 | H7A | O22 | 0.91 | 1.76 | 2.654(3) | 168 | 1-x,2-y,1-z |
| N7 | H7B | O21 | 0.91 | 1.97 | 2.843(3) | 161 | |
| N7 | H7C | O12 | 0.91 | 1.84 | 2.698(3) | 157 | |
| O7 | H7O | O13 | 0.81 | 1.8 | 2.591(3) | 167 | |
| N8 | H8A | O6 | 0.91 | 1.93 | 2.842(4) | 175 | x,1+y,z |
| N8 | H8B | O18 | 0.91 | 1.72 | 2.621(3) | 173 | |
| N8 | H8C | O15 | 0.91 | 1.86 | 2.774(3) | 178 | 2-x,2-y,1-z |
| O8 | H8O | O24 | 0.97 | 1.6 | 2.562(3) | 167 | 1-x,1-y,1-z |
| O11 | H11O | O13 | 0.91 | 1.82 | 2.726(3) | 170 | |
| O14 | H14O | O12 | 1.01 | 1.6 | 2.591(3) | 166 | |
| O19 | H19O | O1 | 0.94 | 1.68 | 2.537(3) | 150 | 2-x,1-y,-z |
| O20 | H20O | O10 | 0.96 | 1.7 | 2.638(3) | 163 | |
| C4 | H4 | O4 | 0.95 | 2.51 | 3.198(4) | 130 | |
| C6 | H6 | O23 | 0.95 | 2.43 | 3.187(4) | 137 | 1-x,1-y,1-z |
| C14 | H14 | O9 | 0.95 | 2.56 | 3.287(4) | 134 | 1-x, 1-y, -z |
| C17 | H17 | O5 | 0.95 | 2.58 | 3.340(4) | 137 | 2-x,1-y,-z |
| C18 | H18 | O20 | 0.95 | 2.55 | 3.438(4) | 157 | |