Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Protonation of Nitriles: Isolation and Characterization of Alkyl- and Arylnitrilium Ions

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Experimental Details

General

Caution! Anhydrous HF can cause severe burns and contact with the skin must be avoided. AsF_5 and SbF_5 are corrosive and highly poisonous and should only be handled in a well ventilated fume hood. Appropriate safety precautions should be taken when working with these materials.

***Materials and apparatus**:* All reactions were carried out in either Teflon-FEP ampules or NMR tubes that were closed by stainless steel valves. Volatile materials were handled in grease-less Pyrex glass or stainless steel/Teflon-FEP vacuum lines.[1] Reaction vessels and the stainless steel vacuum line were passivated with ClF_3 prior to use. Non-volatile materials were handled in the dry nitrogen atmosphere of a glove box. HF (Galaxy Chemicals) was dried by storage over BiF_5.[2] AsF_5 was prepared from AsF_3 and F_2.[3-5] SbF_5 (Ozark Mahoning) was triple distilled before use. Acetonitrile, propionitrile, butyronitrile, and benzonitrile (all Aldrich) were dried over molecular sieves and freshly distilled prior to use. Toluidine and dicyanobenzene (both Alrich) were used as received.

The NMR spectra were recorded at 298 K on Bruker AMX-500, Varian NMRS-600, or Varian NMRS-500 spectrometers. Spectra were externally referenced to neat nitromethane for ^{14}N NMR spectra, neat tetramethylsilane for ^{1}H and ^{13}C NMR spectra, and to 80% $CFCl_3$ in chloroform-d for ^{19}F NMR spectra. Raman spectra were recorded directly in the Teflon reactors or in a 5mm J. Young nmr tube in the range 4000–80 cm^{-1} on Bruker Equinox 55 FT-RA or Vertex 70/RAM II spectrophotometer, using Nd-YAG lasers at 1064 nm. Infrared spectra were recorded in the range 4000-400 cm^{-1} on Bruker Alpha, Bruker Vertex 70, or Bruker Tensor FT-IR spectrometers using KBr pellets.

Crystal Structure determinations

The single-crystal X-ray diffraction data were collected on a Bruker SMART APEX DUO 3-circle platform diffractometer, equipped with an APEX II CCD, using Mo Kα radiation (TRIUMPH curved-crystal monochromator) from a fine-focus tube. The diffractometer was equipped with an Oxford Cryosystems Cryostream 700 apparatus for low-temperature data collection. The frames were integrated using the SAINT algorithm to give the *hkl* files corrected for Lp/decay.[6] The absorption correction was performed using the SADABS program.[7, 8] The structures were solved by the direct method and refined on F^2 using the Bruker SHELXTL Software Package and ShelXle.[9-13] All non-hydrogen atoms were refined anisotropically. ORTEP drawings were prepared using the ORTEP-3 for Windows V2.02 program.[14] Further crystallographic details can be obtained from the Cambridge Crystallographic Data Centre (CCDC, 12 Union Road, Cambridge CB21EZ, UK (Fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk) on quoting the deposition no. CCDC 1469645-1469652.

Preparation of [RCNH][AsF_6] (R = CH_3, C_2H_5, C_3H_7, C_6H_5, o-$CH_3C_6H_4$)

Anhydrous HF (2.0 mL) and AsF_5 (3.50 mmol) were condensed into a Teflon-FEP ampule containing a frozen sample of the corresponding nitrile (3.00 mmol) at -196 ˚C. The mixture was allowed to warm to ambient temperature and the colorless solution stirred for 30 min. The volatile compounds were removed *in vacuo*, first at -64 ˚C, then at ambient temperature, leaving behind a colourless solid. Single crystals were grown from HF solution by slow evaporation of the solvent *in vacuo* at -30 °C.

[CH_3CNH][AsF_6] (687 mg; weight expected for 3.00 mmol: 693 mg).

Raman (200 mW): $\tilde{\upsilon}$ (rel. Intensity) = 3039 (1.1), 3003 (1.5), 2945 (5.1), 2293 (0.9), 1744 (0.8), 1415 (1.3), 1361 (1.9), 1052 (0.5), 916 (0.5), 884 (3.4), 791 (0.7), 732 (0.8), 682 (10.0), 624 (0.8), 572 (1.5), 534 (1.5), 430 (0.8), 371 (5.0) cm^{-1}; IR (KBr): $\tilde{\upsilon}$ = 2950 (w), 2345 (w), 2324 (w), 2293 (w), 2258 (vw), 1743 (m), 1706 (m), 1672 (m), 1558 (vw), 1534 (m), 1419 (m), 1404 (m sh), 1375 (vw), 1363 (vw), 1343 (vw), 1301 (vw), 1196 (w), 1151 (m), 1037 (m), 927 (m), 881 (vw), 701 (vs), 674 (s sh), 544 (w), 510 (vw) cm^{-1}. ^{1}H NMR (HF, unlocked, 25˚C) δ = 2.54 ppm (s, C***H***$_3$), 10.44 ppm (t, $^{1}J(^{1}H^{14}N)$ = 95.0 Hz, CN***H***); ^{13}C NMR (HF, unlocked, 25˚C) δ = 8.2 ppm (s, ***C***H$_3$), 117.7 ppm (t, $^{1}J(^{13}C^{14}N)$ = 42.7 Hz, ***C***NH); ^{14}N NMR (HF, unlocked, 25˚C) δ = -241.1 ppm (d, $^{1}J(^{1}H^{14}N)$ = 95.7 Hz).

[C_2H_5CNH][AsF_6] (731 mg; weight expected for 3.00 mmol: 735 mg).
Raman (200 mW): $\tilde{\upsilon}$ (rel. Intensity) = 3022 (2.4), 2967 (5.4), 2943 (4.9), 2898 (2.7), 2262 (6.4), 1467 (4.5), 1411 (3.8), 1076 (4.1), 989 (4.2), 837 (3.2), 693 (10.0), 680 (8.8), 672 (10.0), 586 (3.9), 557 (4.6), 373 (7.9), 225 (5.6) cm^{-1}; IR (KBr): $\tilde{\upsilon}$ = 2975 (m), 2943 (vw), 2884 (vw), 2326 (w), 2250 (w), 1743 (vw), 1725 (vw), 1572 (w sh), 1548 (m), 1536 (w sh), 1467 (w), 1389 (w), 1343 (vw), 1327 (vw), 1278 (vw), 1255 (w), 1155 (m), 1087 (m), 1040 (vw), 874 (vw), 745 (s sh), 702 (vs), 562 (vw) cm^{-1}.
^{1}H NMR (HF, unlocked, 25˚C) δ = 1.24 ppm (t, $^{3}J(^{1}H^{1}H)$ = 7.8 Hz, C***H***$_3$), 2.80 ppm (q, $^{3}J(^{1}H^{1}H)$ = 7.8 Hz, C***H***$_2$), 10.58 ppm (t, $^{1}J(^{1}H^{14}N)$ = 94.5 Hz, CN***H***); ^{13}C NMR (HF, unlocked, 25˚C) δ = 9.1 ppm (s, ***C***H$_3$), 18.2 ppm (s, ***C***H$_2$), 111.0 ppm (t, $^{1}J(^{13}C^{14}N)$ = 44.8 Hz, ***C***NH); ^{14}N NMR (HF, unlocked, 25˚C) δ = -241.0 ppm (d, $^{1}J(^{1}H^{14}N)$ = 96.0 Hz).

[C_3H_7CNH][AsF_6] (775 mg; weight expected for 3.00 mmol: 777 mg).
Raman (200 mW): $\tilde{\upsilon}$ (rel. Intensity) = 2952 (5.8), 2929 (6.9), 2890 (4.5), 2257 (7.2), 1276 (5.9), 1091 (6.0), 869 (5.5), 694 (10.0), 671 (8.7), 572 (5.5), 540 (7.4), 369 (8.3), 194 (6.2), 140 (7.3) cm^{-1}; IR (KBr): $\tilde{\upsilon}$ = 2973 (w), 2940 (vw), 2884 (vw), 2354 (vw), 2326 (w), 2256 (vw), 1558 (m), 1541 (m), 1458 (w), 1251 (vw), 1152 (w), 1088 (w), 873 (vw), 743 (s sh), 701 (vs), 551 (w) cm^{-1}.
^{1}H NMR (HF, unlocked, 25˚C) δ = 0.75 ppm (t, $^{3}J(^{1}H^{1}H)$ = 8.0 Hz, C***H***$_3$), 1.59 ppm (tq, $^{3}J(^{1}H^{1}H)$ = 8.0 Hz, $^{3}J(^{1}H^{1}H)$ = 7.3 Hz, CH_3C***H***$_2$), 2.67 ppm (t, $^{3}J(^{1}H^{1}H)$ = 7.3 Hz, C***H***$_2$CNH), 10.34 ppm (t, $^{1}J(^{1}H^{14}N)$ = 94.5 Hz, CN***H***); ^{13}C NMR (HF, unlocked, 25˚C) δ = 10.8 ppm (s, ***C***H$_3$), 16.6 ppm (s, CH_3***C***H$_2$), 16.8 ppm (s, ***C***H$_2$CNH), 110.4 ppm (t, $^{1}J(^{13}C^{14}N)$ = 45.1 Hz, ***C***NH); ^{14}N NMR (HF, unlocked, 25˚C) δ = -240.5 ppm (d, $^{1}J(^{1}H^{14}N)$ = 94.6 Hz).

[C_6H_5CNH][AsF_6] (877 mg; weight expected for 3.00 mmol: 879 mg).
Raman (200 mW): $\tilde{\upsilon}$ (rel. Intensity) = 3092 (0.9), 2230 (4.5), 1592 (8.2), 1200 (1.9), 1173 (3.6), 1025 (1.6), 1000 (10.0), 774 (1.2), 761 (1.5), 694 (2.7), 669 (1.6), 625 (1.9), 553 (1.4), 538 (1.1), 468 (1.3), 387 (1.6), 364 (1.4), 183 (2.3) cm^{-1}; IR (KBr): $\tilde{\upsilon}$ = 3111 (vw), 3066 (vw), 2925 (vw), 2299 (m), 2264 (vw), 2229 (w), 1624 (m), 1591 (s), 1561 (m), 1495 (vw), 1474 (vw), 1450 (m), 1419 (vw), 1396 (vw), 1359 (m), 1339 (vw), 1307 (w), 1285 (vw), 1256 (vw), 1230 (vw), 1199 (w), 1174 (m), 1106 (vw), 1071 (vw), 1025 (w), 999 (w), 947 (vw), 830 (vw), 748 (s sh), 701 (vs), 656 (s sh), 552 (m), 533 (w), 467 (m) cm^{-1}.
^{1}H NMR (HF, unlocked, 25˚C) δ = 7.1 – 7.8 ppm (m, C_6***H***$_5$), 11.48 ppm (t, $^{1}J(^{1}H^{14}N)$ = 94.6 Hz, CN***H***); ^{13}C NMR (HF, unlocked, 25˚C) δ = 108.6 ppm (t, $^{1}J(^{13}C^{14}N)$ = 45.0 Hz, ***C***NH), 130.3 ppm, 133.1 ppm, 140.2 ppm, 150.1 ppm (***C***$_6$H$_5$); ^{14}N NMR (HF, unlocked, 25˚C) δ = -230.7 ppm (d, $^{1}J(^{1}H^{14}N)$ = 95.3 Hz, C***N***H).

[*o*-$CH_3C_6H_4CNH$][AsF_6] (916 mg; weight expected for 3.00 mmol: 921 mg).
Raman (200 mW): $\tilde{\upsilon}$ (rel. Intensity) = 3083 (1.2), 2936 (1.6), 2230 (10.0), 1597 (9.9), 1573 (2.2), 1483 (1.8), 1216 (6.7), 1192 (2.8), 1173 (3.9), 1112 (1.5), 1048 (7.0), 724 (8.7), 687 (6.4), 546 (3.3), 463 (1.9), 459 (2.0), 364 (1.9), 234 (1.8), 178 (4.2), 157 (3.2) cm^{-1}; IR (KBr): $\tilde{\upsilon}$ = 3110 (vw), 3075 (vw), 2923 (w), 2298 (m), 2230 (w), 1621 (s), 1590 (s), 1563 (s), 1523 (w), 1496 (w), 1474 (m), 1450 (w), 1420 (vw), 1394 (vw), 1357 (m), 1307 (m), 1280 (m), 1193 (m), 1106 (w), 1025 (w), 999 (m), 895 (vw), 838 (vw), 748 (s sh), 702 (vs), 648 (m sh), 553 (w), 481 (vw), 467 (w) cm^{-1}.
^1H NMR (HF, unlocked, 25˚C) δ = 2.58 ppm (s, C***H***$_3$), 7.4 – 8.1 ppm (m, C_6***H***$_4$), 10.90 ppm (t, $^1J(^1H^{14}N)$ = 93.4 Hz, CN***H***); ^{13}C NMR (HF, unlocked, 25˚C) δ = 18.4 ppm (s, ***C***H_3), 109.3 ppm (t, $^1J(^{13}C^{14}N)$ = 41.0 Hz, ***C***NH), 127.6 ppm, 131.6 ppm, 136.0, 139.8 ppm, 148.6 ppm (***C***$_6H_5$); ^{14}N NMR (HF, unlocked, 25˚C) δ = -219 ppm (s, broad, C***N***H).

Preparation of $[(CH_3)_2NCH_2CNH][AsF_6]_2$ and $[C_6H_4(CNH)_2][AsF_6]_2$

Anhydrous HF (2.0 mL) and AsF_5 (6.50 mmol) were condensed into a Teflon-FEP ampule containing a frozen sample of the corresponding nitrile (3.00 mmol) at -196 ˚C. The mixture was allowed to warm to ambient temperature and the colorless solution stirred for 30 min. The volatile compounds were removed *in vacuo*, first at -64 ˚C, then at ambient temperature, leaving behind a colourless solid. Single crystals were grown from HF solution by slow evaporation of the solvent *in vacuo* at -30 °C.

$[(CH_3)_2NCH_2CNH][AsF_6]_2$ (1.387 g; weight expected for 3.00 mmol: 1.392 g).
Raman (200 mW): $\tilde{\upsilon}$ (rel. Intensity) = 3059 (2.0), 2989 (4.4), 2964 (2.6), 2252 (1.0), 822 (2.7), 791 (1.4), 733 (5.2), 702 (2.8), 682 (10.0), 537 (3.7), 386 (2.8), 214 (1.1) cm^{-1}; IR (KBr): $\tilde{\upsilon}$ =2978 (vw), 2940 (w), 2879 (vw), 2326 (w), 2256 (m), 1541 (w), 1523 (w), 1471 (w), 1419 (vw), 1407 (w), 1329 (vw), 1307 (vw), 1255 (w), 1240 (w), 1135 (vw), 1091 (vw), 1067 (vw), 1011 (vw), 959 (w), 846 (vw), 814 (m sh), 744 (s sh), 701 (vs), 671 (s sh), 583 (vw), 545 (m) cm^{-1}.
^1H NMR (HF, unlocked, 25˚C) δ = 3.12 ppm (s, C***H***$_3$), 4.70 ppm (s, C***H***$_2$), 10.7 ppm (t, $^1J(^1H^{14}N)$ = 96.0 Hz, CN***H***); ^{13}C NMR (HF, unlocked, 25˚C) δ = 46.4 ppm (s, ***C***H_3), 54.9 ppm (s, ***C***H_2), 108.0 ppm (t, $^1J(^{13}C^{14}N)$ = 45.6 Hz, ***C***NH); ^{14}N NMR (HF, unlocked, 25˚C) δ = -222.0 ppm (d, $^1J(^1H^{14}N)$ = 96 Hz, C***N***H), -346.7 ppm (d, $^1J(^1H^{14}N)$ = 63 Hz, $(CH_3)_2$***N***H).

$[C_6H_4(CNH)_2][AsF_6]_2$ (1.517 g; weight expected for 3.00 mmol: 1.524 g).
Raman (200 mW): $\tilde{\upsilon}$ (rel. Intensity) = 3105 (0.4), 3087 (0.4), 2223 (2.2), 1602 (10.0), 1317 (1.1), 1167 (6.9), 819 (3.1), 694 (3.4), 664 (1.7), 655 (1.5), 589 (1.4), 566 (1.7), 526 (2.2), 378 (1.7), 364 (1.8), 209 (1.9) cm^{-1}; IR (KBr): $\tilde{\upsilon}$ = 3122 (vw), 3098 (w), 3054 (w), 2998 (vw), 2369 (vw), 2353 (vw), 2319 (w), 2233 (m), 1504 (w), 1403 (w), 1278 (w), 1255 (w), 1201 (w), 1181 (vw), 1125 (vw), 1021 (vw), 986 (vw), 845 (m), 743 (s sh), 702 (svs), 562 (m), 531 (vw) cm^{-1}.
^1H NMR (HF, unlocked, 25˚C) δ = 7.0 ppm (s, C_6***H***$_4$), 10.8 ppm (s, broad, CN***H***); ^{13}C NMR (HF, unlocked, 25˚C) δ = 111.9 ppm (s, broad, ***C***NH), 126.0 ppm, 136.8 ppm (***C***$_6H_4$); ^{14}N NMR (HF, unlocked, 25˚C) δ = -223 ppm (s, broad, C***N***H).

Preparation of $[RCNH][SbF_6]$ (R = CH_3, C_2H_5, C_3H_7, C_6H_5, o-$CH_3C_6H_4$)

Anhydrous HF (2.0 mL) was condensed into a Teflon-FEP ampule containing a frozen sample of SbF_5 (3.00 mmol) at -196˚C. The mixture was allowed to warm to ambient temperature to form a clear colourless solution. The solution was cooled to about -50˚C and, under a stream of dry nitrogen using an 18 gauge FEP tubing, transferred into a second Teflon-FEP ampule containing a frozen sample of the corresponding nitrile (3.00 mmol) at -196˚C. The mixture was allowed to warm to ambient temperature and, after 30 min, the volatile compounds removed *in vacuo*, first at -64˚C, then at ambient temperature, leaving behind a colourless crystalline solid.

$[CH_3CNH][SbF_6]$ (830 mg; weight expected for 3.00 mmol: 833 mg).
$[C_2H_5CNH][SbF_6]$ (874 mg; weight expected for 3.00 mmol: 875 mg).
$[C_3H_7CNH][SbF_6]$ (913 mg; weight expected for 3.00 mmol: 917 mg).
$[C_6H_5CNH][SbF_6]$ (1.009 g; weight expected for 3.00 mmol: 1.019 g).

Preparation of $[RCNH][Sb_2F_{11}]$ (R = CH_3, C_2H_5, C_3H_7, C_6H_5)

Anhydrous HF (2.5 mL) was condensed into a Teflon-FEP ampule containing a frozen sample of SbF5 (4.00 mmol) at -196˚C. The mixture was allowed to warm to ambient temperature to form a clear colourless solution. The solution was cooled to about -50˚C and, under a stream of dry nitrogen using an 18 gauge FEP tubing, transferred into a second Teflon-FEP ampule containing a frozen sample of the corresponding nitrile (2.00 mmol) at -196˚C. The mixture was allowed to warm to ambient temperature and, after 30 min, the volatile compounds removed *in vacuo*, first at -64˚C, then at ambient temperature, leaving behind a colourless crystalline solid.

$[CH_3CNH][Sb_2F_{11}]$ (0.981 g; weight expected for 2.00 mmol: 0.989 g).
Raman (200 mW): $\tilde{\upsilon}$ (rel. Intensity) = 2944 (3.7), 2305 (4.4), 1743 (1.4), 1739 (1.3), 1358 (2.0), 1284 (1.2), 914 (0.7), 679 (10.0), 670 (5.3), 663 (4.4), 657 (6.1), 625 (1.7), 608 (1.2), 604 (1.2), 543 (0.5), 530 (0.9), 386 (1.1), 294 (3.7), 229 (2.7), 127 (2.1); IR (KBr): $\tilde{\upsilon}$ = 2944 (w), 2339 (w), 2311 (w), 2290 (vw), 2254 (w), 1742 (w), 1701 (m), 1663 (m), 1607 (vw), 1530 (m), 1419 (m), 1361 (m), 1298 (vw), 1255 (w), 1194 (vw), 1181 (vw), 1154 (vw), 1035 (m), 919 (w), 695 (s sh), 664 (vs), 545 (w), 495 (w) cm^{-1}.
^{1}H NMR (HF, unlocked, 25˚C) δ = 2.53 ppm (s, C***H***$_3$), 10.40 ppm (t, $^{1}J(^{1}H^{14}N)$ = 94.6 Hz, CN***H***); ^{13}C NMR (HF, unlocked, 25˚C) δ = 8.1 ppm (s, ***C***H_3), 117.7 ppm (t, $^{1}J(^{13}C^{14}N)$ = 43.2 Hz, ***C***NH); ^{14}N NMR (HF, unlocked, 25˚C) δ = -239.2 ppm (d, $^{1}J(^{1}H^{14}N)$ = 94.9 Hz).
$[C_2H_5NH][Sb_2F_{11}]$ (1.013 g; weight expected for 2.00 mmol: 1.017 g).
$[C_3H_5NH][Sb_2F_{11}]$ (1.038 g; weight expected for 2.00 mmol: 1.045 g).
$[C_6H_5CNH][Sb_2F_{11}]$ (1.107 g; weight expected for 2.00 mmol: 1.113 g).

Crystallographic Details

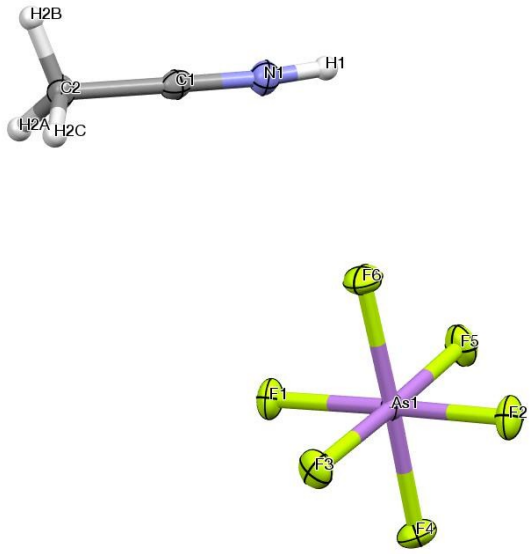

Figure S1. The crystal structure of $CH_3CNHAsF_6$.

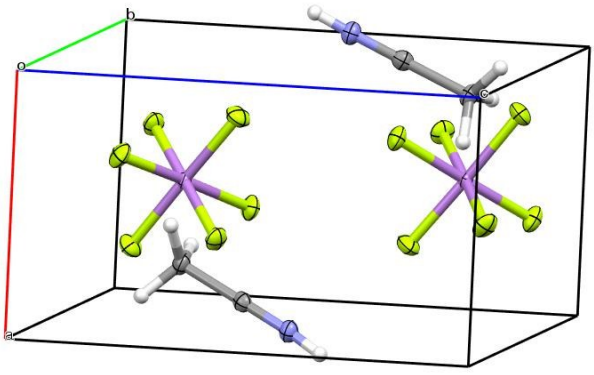

Figure S2. The unit cell in the crystal structure of $CH_3CNHAsF_6$.

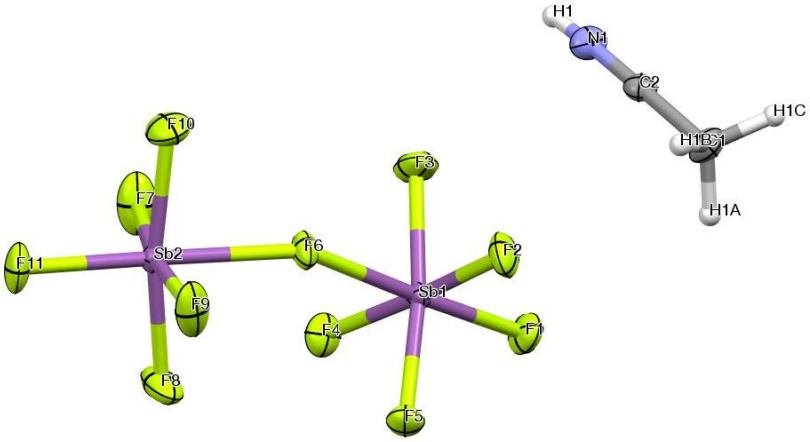

Figure S3. The crystal structure of $CH_3CNHSb_2F_{11}$.

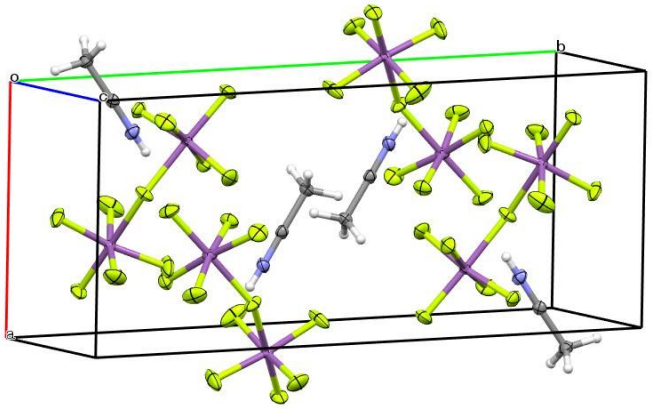

Figure S4. The unit cell in the crystal structure of $CH_3CNHSb_2F_{11}$.

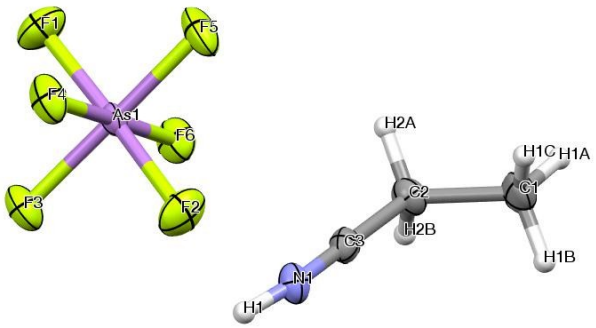

Figure S5. The crystal structure of $C_2H_5CNHAsF_6$.

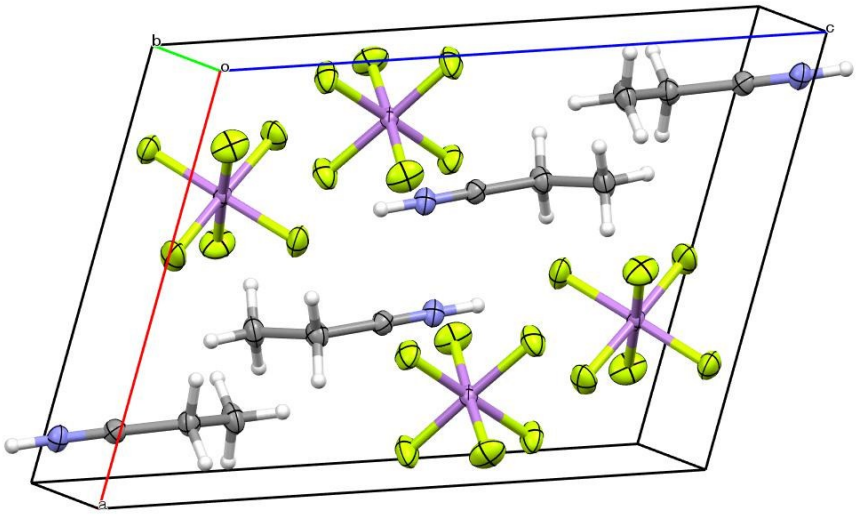

Figure S6. The unit cell in the crystal structure of $C_2H_5CNHAsF_6$.

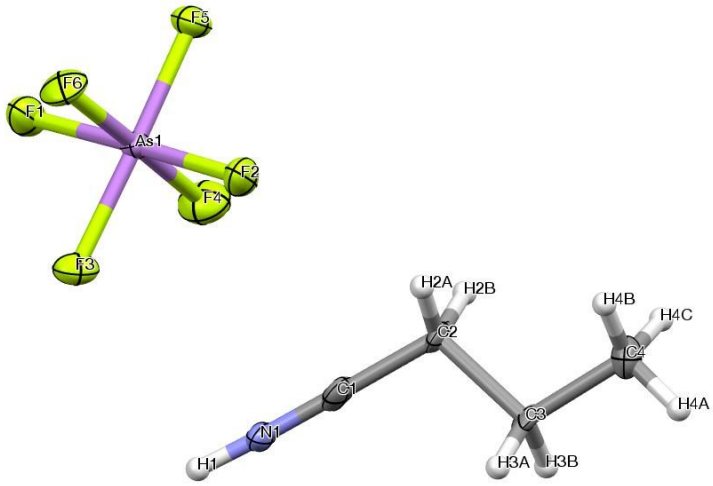

Figure S7. The crystal structure of $C_3H_7CNHAsF_6$.

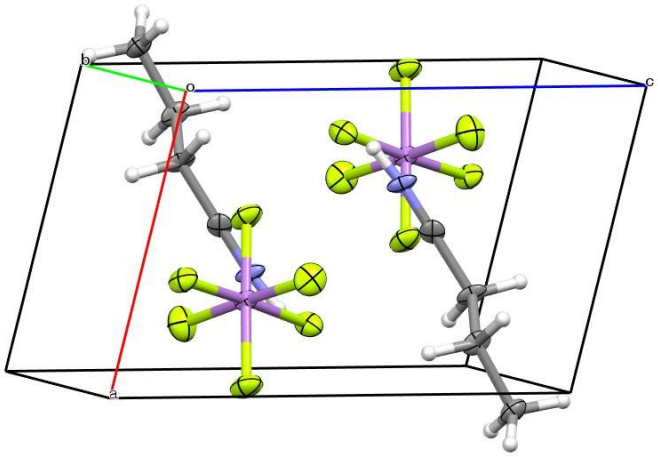

Figure S8. The unit cell in the crystal structure of $C_3H_7CNHAsF_6$.

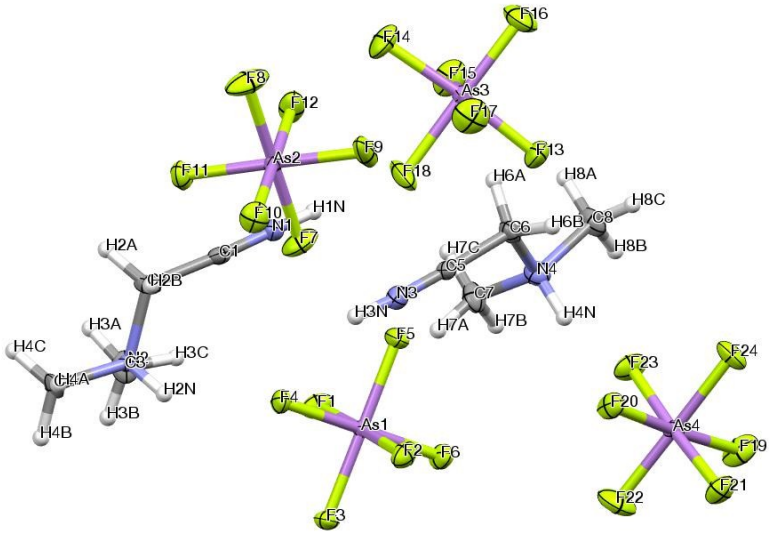

Figure S9. The crystal structure of $(CH_3)_2NCH_2CNH(AsF_6)_2$.

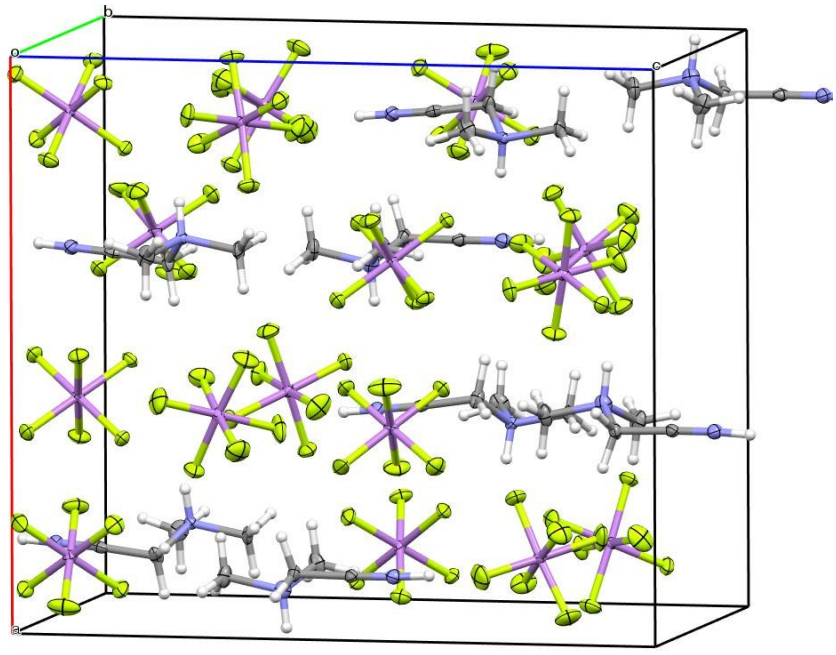

Figure S10. The unit cell in the crystal structure of $(CH_3)_2NCH_2CNH(AsF_6)_2$.

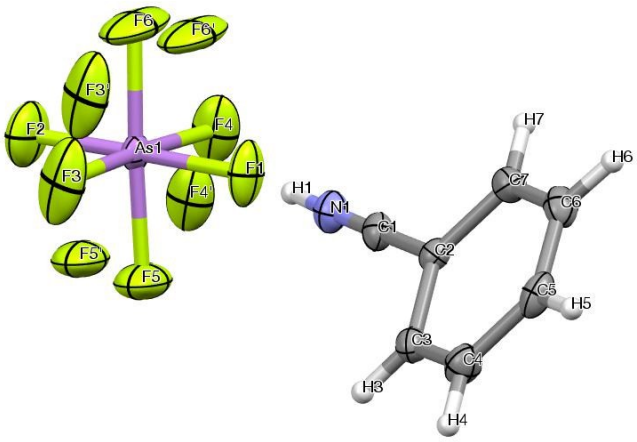

Figure S11. The crystal structure of $C_6H_5CNHAsF_6$.

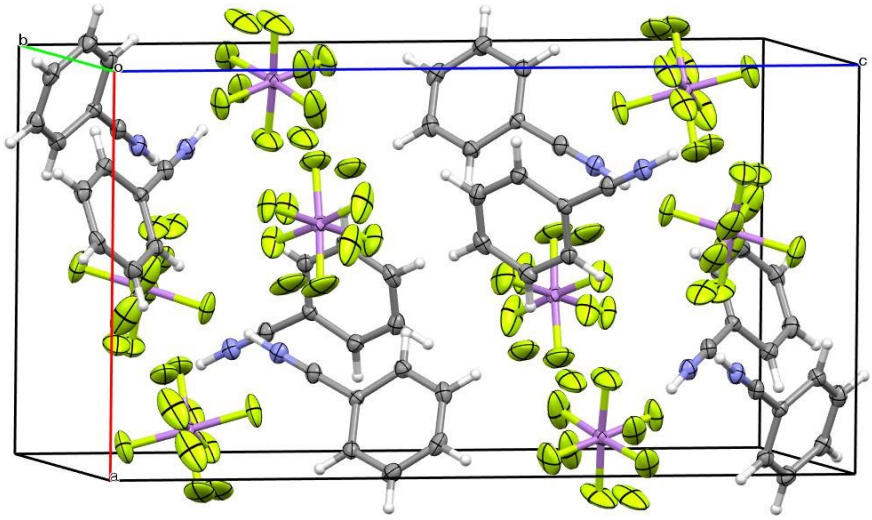

Figure S12. The unit cell in the crystal structure of $C_6H_5CNHAsF_6$.

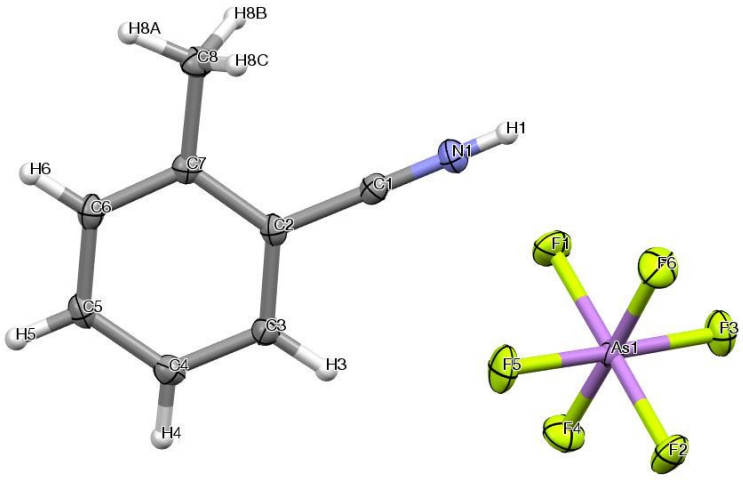

Figure S13. The crystal structure of *o*-$CH_3C_6H_4CNHAsF_6$.

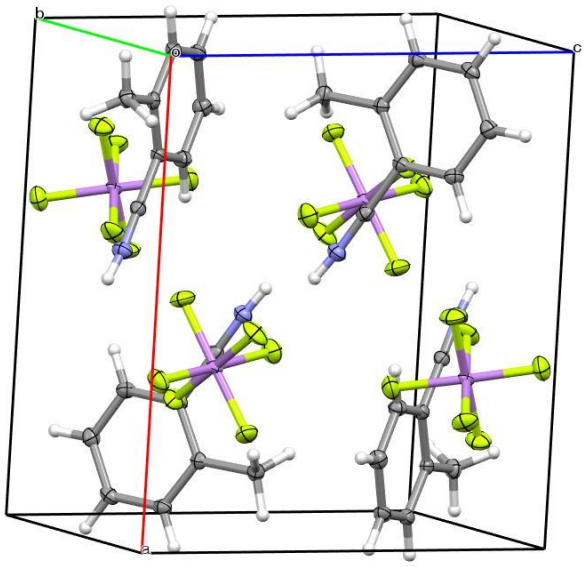

Figure S14. The unit cell in the crystal structure of *o*-$CH_3C_6H_4CNHAsF_6$.

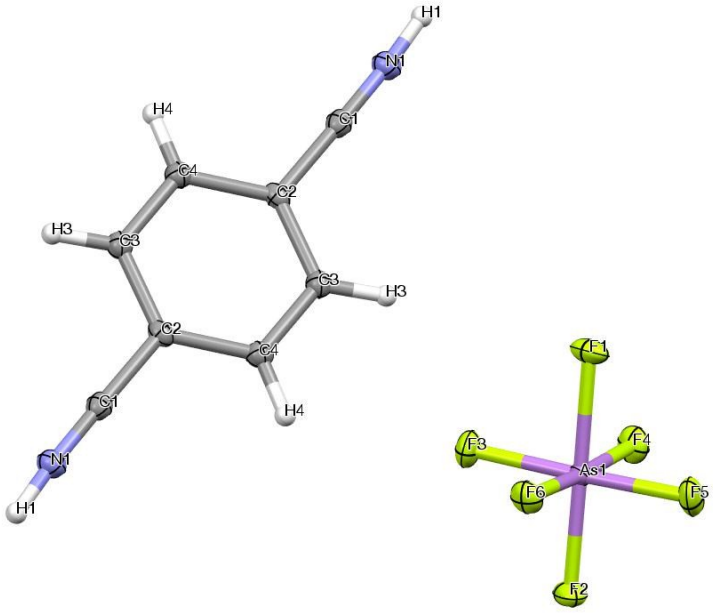

Figure S15. The crystal structure of $C_6H_4(CNH)_2(AsF_6)_2$.

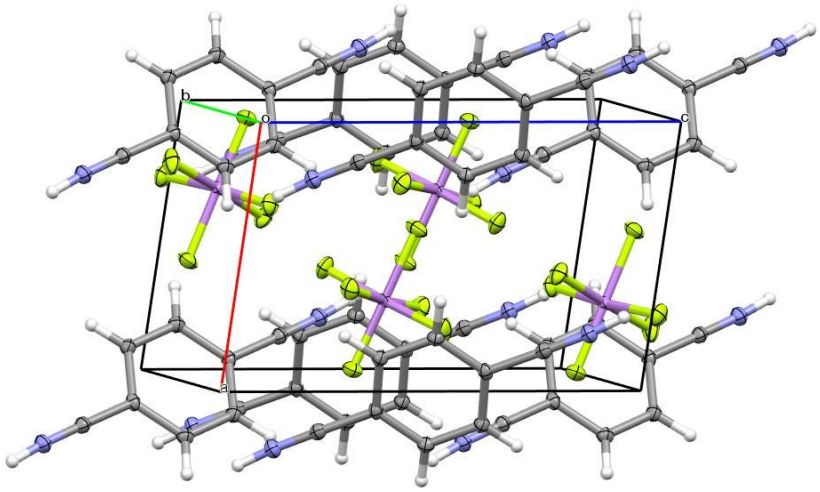

Figure S16. The unit cell in the crystal structure of $C_6H_4(CNH)_2(AsF_6)_2$.

Table S1. Sample and crystal data for $MeCNHAsF_6$.

Identification code	MeCNHAsF6	
Chemical formula	$C_2H_4AsF_6N$	
Formula weight	230.98 g/mol	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	monoclinic	
Space group	P 1 21 1	
Unit cell dimensions	a = 5.2169(6) Å	α = 90°
	b = 6.5905(7) Å	β = 92.267(2)°
	c = 9.3342(10) Å	γ = 90°
Volume	320.68(6) $Å^3$	
Z	2	
Density (calculated)	2.392 g/cm^3	
Absorption coefficient	5.347 mm^{-1}	
F(000)	220	

Table S2. Data collection and structure refinement for $MeCNHAsF_6$.

Diffractometer	Bruker APEX DUO
Radiation source	fine-focus tube, MoKα
Theta range for data collection	2.18 to 30.52°
Index ranges	-7<=h<=7, -9<=k<=9, -13<=l<=13
Reflections collected	6612
Independent reflections	1927 [R(int) = 0.0268]
Coverage of independent reflections	99.2%
Absorption correction	multi-scan
Structure solution technique	direct methods
Structure solution program	SHELXTL XT 2013/1 (Bruker AXS, 2014)
Refinement method	Full-matrix least-squares on F^2
Refinement program	SHELXTL XL 2014/7 (Bruker AXS, 2014)
Function minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	1927 / 1 / 95
Goodness-of-fit on F^2	1.122
Δ/σ_{max}	0.001
Final R indices	1908 data; I>2σ(I) R1 = 0.0169, wR2 = 0.0426
	all data R1 = 0.0173, wR2 = 0.0427
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0234P)^2+0.0179P]$ where $P=(F_o^2+2F_c^2)/3$
Absolute structure parameter	0.5(0)
Largest diff. peak and hole	0.243 and -1.040 eÅ^{-3}
R.M.S. deviation from mean	0.112 eÅ^{-3}

Table S3. Atomic coordinates and equivalent isotropic atomic displacement parameters (Å^2) for $MeCNHAsF_6$.

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x/a	y/b	z/c	U(eq)
C1	0.9815(4)	0.4792(5)	0.7187(3)	0.0146(5)
C2	0.1020(4)	0.5079(7)	0.8599(2)	0.0170(4)
N1	0.8871(4)	0.4570(4)	0.6102(2)	0.0168(5)
F1	0.6534(6)	0.3328(4)	0.3679(4)	0.0188(6)
F2	0.3121(5)	0.6685(4)	0.1451(4)	0.0197(5)
F3	0.6083(6)	0.6986(4)	0.3544(4)	0.0197(5)
F4	0.7340(2)	0.5058(8)	0.14466(14)	0.0207(3)
F5	0.3573(6)	0.2959(4)	0.1612(4)	0.0204(6)
F6	0.2275(3)	0.4858(8)	0.36802(16)	0.0213(5)
As1	0.47792(3)	0.50056(15)	0.25471(2)	0.01045(7)

Table S4. Bond lengths (Å) for $MeCNHAsF_6$.

C1-N1	1.119(3)	C1-C2	1.449(3)
C2-H2A	0.98	C2-H2B	0.98
C2-H2C	0.98	N1-H1	0.79(3)
F1-As1	1.761(3)	F2-As1	1.718(3)
F3-As1	1.727(3)	F4-As1	1.7174(12)
F5-As1	1.713(3)	F6-As1	1.7158(13)

Table S5. Bond angles (°) for $MeCNHAsF_6$.

N1-C1-C2	179.6(2)	C1-C2-H2A	109.5
C1-C2-H2B	109.5	H2A-C2-H2B	109.5
C1-C2-H2C	109.5	H2A-C2-H2C	109.5
H2B-C2-H2C	109.5	C1-N1-H1	175.(2)
F5-As1-F6	89.77(18)	F5-As1-F4	89.43(18)
F6-As1-F4	177.5(3)	F5-As1-F2	92.15(9)
F6-As1-F2	91.49(16)	F4-As1-F2	90.91(15)
F5-As1-F3	177.14(19)	F6-As1-F3	90.21(18)
F4-As1-F3	90.46(18)	F2-As1-F3	90.72(19)
F5-As1-F1	89.03(17)	F6-As1-F1	89.14(16)
F4-As1-F1	88.48(17)	F2-As1-F1	178.66(17)
F3-As1-F1	88.10(9)		

Table S6. Anisotropic atomic displacement parameters (Å^2) for $MeCNHAsF_6$.

The anisotropic atomic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C1	0.0154(8)	0.0122(16)	0.0164(9)	0.0026(12)	0.0019(7)	0.0008(10)
C2	0.0198(8)	0.0180(10)	0.0130(9)	0.0018(15)	-0.0032(7)	-0.0019(18)
N1	0.0196(9)	0.0168(15)	0.0139(9)	0.0000(7)	-0.0011(7)	-0.0008(7)
F1	0.0220(11)	0.0196(11)	0.0144(11)	0.0026(8)	-0.0040(8)	0.0040(8)
F2	0.0239(12)	0.0197(11)	0.0151(9)	0.0004(8)	-0.0042(9)	0.0067(9)
F3	0.0236(12)	0.0174(10)	0.0177(10)	-0.0065(8)	-0.0021(9)	-0.0034(8)
F4	0.0192(5)	0.0256(8)	0.0179(6)	0.0029(15)	0.0076(5)	-0.0026(15)
F5	0.0239(11)	0.0165(11)	0.0202(13)	-0.0046(9)	-0.0068(8)	-0.0034(8)
F6	0.0165(5)	0.0275(14)	0.0205(6)	0.0030(12)	0.0072(5)	0.0002(11)
As1	0.01088(10)	0.01240(10)	0.00799(11)	-0.00047(13)	-0.00059(6)	-0.0008(2)

Table S7. Hydrogen atomic coordinates and isotropic atomic displacement parameters (Å^2) for $MeCNHAsF_6$.

	x/a	y/b	z/c	U(eq)
H2A	0.2600	0.4277	0.8680	0.026
H2B	-0.0156	0.4635	0.9330	0.026
H2C	0.1429	0.6518	0.8741	0.026
H1	-0.186(6)	0.432(5)	0.536(3)	0.02

Table S8. Sample and crystal data for $MeCNHSb_2F_{11}$.

Identification code	C2H4F11NSb2	
Chemical formula	$C_2H_4F_{11}NSb_2$	
Formula weight	494.56 g/mol	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal size	0.043 x 0.102 x 0.191 mm	
Crystal habit	clear colourless plateplate	
Crystal system	monoclinic	
Space group	P 1 21/n 1	
Unit cell dimensions	a = 7.7010(15) Å	α = 90°
	b = 16.831(3) Å	β = 98.287(3)°
	c = 8.4837(17) Å	γ = 90°
Volume	1088.1(4) $Å^3$	
Z	4	
Density (calculated)	3.019 g/cm^3	
Absorption coefficient	5.092 mm^{-1}	
F(000)	896	

Table S9. Data collection and structure refinement for $MeCNHSb_2F_{11}$.

Diffractometer	Bruker APEX DUO
Radiation source	fine-focus tube, MoKα
Theta range for data collection	2.42 to 30.51°
Reflections collected	3267
Coverage of independent reflections	98.9%
Absorption correction	multi-scan
Max. and min. transmission	0.8110 and 0.4430
Structure solution technique	direct methods
Structure solution program	SHELXTL XT 2013/1 (Bruker AXS, 2014)
Refinement method	Full-matrix least-squares on F^2
Refinement program	SHELXTL XL 2014/7 (Bruker AXS, 2014)
Function minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	3267 / 0 / 150
Goodness-of-fit on F^2	1.108
Δ/σ_{max}	0.001
Final R indices	2985 data; I>2σ(I) R1 = 0.0183, wR2 = 0.0369
	all data R1 = 0.0229, wR2 = 0.0382
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0119P)^2+1.3064P]$ where $P=(F_o^2+2F_c^2)/3$
Largest diff. peak and hole	0.626 and -0.727 eÅ^{-3}
R.M.S. deviation from mean	0.111 eÅ^{-3}

Table S10. Atomic coordinates and equivalent isotropic atomic displacement parameters (Å^2) for $MeCNHSb_2F_{11}$.

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x/a	y/b	z/c	U(eq)
C1	0.4083(3)	0.41311(15)	0.8111(3)	0.0217(5)
C2	0.5673(3)	0.36625(14)	0.8275(3)	0.0171(4)
N1	0.6910(3)	0.33073(13)	0.8396(3)	0.0203(4)
F1	0.5068(2)	0.23917(10)	0.3402(2)	0.0306(4)
F2	0.5967(2)	0.37794(11)	0.49167(19)	0.0308(4)
F3	0.8265(2)	0.26078(11)	0.5079(2)	0.0349(4)
F4	0.7952(2)	0.25772(9)	0.19739(19)	0.0259(3)
F5	0.5748(2)	0.37602(9)	0.18066(18)	0.0238(3)
F6	0.88586(19)	0.39243(9)	0.35863(17)	0.0225(3)
F7	0.1825(2)	0.33498(10)	0.2804(3)	0.0397(4)
F8	0.9564(3)	0.40582(13)	0.06564(19)	0.0449(5)
F9	0.9705(2)	0.53258(10)	0.2465(2)	0.0364(4)
F10	0.1927(2)	0.46040(12)	0.4592(2)	0.0357(4)
F11	0.2711(2)	0.47639(9)	0.1557(2)	0.0287(3)
Sb1	0.68729(2)	0.31401(2)	0.34517(2)	0.01491(4)
Sb2	0.08931(2)	0.43661(2)	0.25424(2)	0.01419(4)

Table S11. Bond lengths (Å) for $MeCNHSb_2F_{11}$.

C1-C2	1.446(3)	C1-H1A	0.98
C1-H1B	0.98	C1-H1C	0.98
C2-N1	1.117(3)	N1-H1	0.74(3)
F1-Sb1	1.8718(15)	F2-Sb1	1.8545(16)
F3-Sb1	1.8524(15)	F4-Sb1	1.8603(15)
F5-Sb1	1.8544(14)	F6-Sb1	2.0107(14)
F6-Sb2	2.0474(14)	F7-Sb2	1.8559(17)
F8-Sb2	1.8449(17)	F9-Sb2	1.8530(16)
F10-Sb2	1.8485(16)	F11-Sb2	1.8562(14)

Table S12. Bond angles (°) for $MeCNHSb_2F_{11}$.

C2-C1-H1A	109.5	C2-C1-H1B	109.5
H1A-C1-H1B	109.5	C2-C1-H1C	109.5
H1A-C1-H1C	109.5	H1B-C1-H1C	109.5
N1-C2-C1	179.3(3)	C2-N1-H1	177.(3)
Sb1-F6-Sb2	146.82(8)	F3-Sb1-F5	172.08(7)
F3-Sb1-F2	90.83(8)	F5-Sb1-F2	89.88(8)
F3-Sb1-F4	89.37(8)	F5-Sb1-F4	89.14(7)
F2-Sb1-F4	174.24(7)	F3-Sb1-F1	92.26(7)
F5-Sb1-F1	95.57(7)	F2-Sb1-F1	93.19(8)
F4-Sb1-F1	92.55(7)	F3-Sb1-F6	85.49(7)
F5-Sb1-F6	86.68(7)	F2-Sb1-F6	86.42(7)
F4-Sb1-F6	87.86(6)	F1-Sb1-F6	177.71(7)
F8-Sb2-F10	170.49(8)	F8-Sb2-F9	90.27(10)
F10-Sb2-F9	89.32(9)	F8-Sb2-F7	90.08(10)
F10-Sb2-F7	88.87(9)	F9-Sb2-F7	171.17(8)
F8-Sb2-F11	94.06(8)	F10-Sb2-F11	95.44(8)
F9-Sb2-F11	94.03(7)	F7-Sb2-F11	94.75(7)
F8-Sb2-F6	84.82(7)	F10-Sb2-F6	85.67(7)
F9-Sb2-F6	85.83(7)	F7-Sb2-F6	85.41(7)
F11-Sb2-F6	178.88(7)		

Table S13. Anisotropic atomic displacement parameters ($Å^2$) for $MeCNHSb_2F_{11}$.

The anisotropic atomic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C1	0.0165(11)	0.0178(11)	0.0298(12)	-0.0027(9)	0.0003(9)	0.0031(9)
C2	0.0192(11)	0.0166(11)	0.0147(10)	-0.0026(8)	0.0000(8)	-0.0011(8)
N1	0.0218(10)	0.0172(10)	0.0214(10)	-0.0039(8)	0.0009(8)	0.0036(8)
F1	0.0205(7)	0.0320(9)	0.0386(9)	0.0091(7)	0.0017(6)	-0.0116(7)
F2	0.0299(8)	0.0400(10)	0.0264(8)	-0.0055(7)	0.0170(7)	-0.0038(7)
F3	0.0272(8)	0.0415(10)	0.0323(9)	0.0216(8)	-0.0081(7)	-0.0022(7)
F4	0.0261(8)	0.0195(7)	0.0333(8)	-0.0041(6)	0.0090(6)	0.0023(6)
F5	0.0236(7)	0.0246(8)	0.0223(7)	0.0084(6)	0.0004(6)	0.0051(6)
F6	0.0209(7)	0.0265(8)	0.0217(7)	-0.0030(6)	0.0089(6)	-0.0101(6)
F7	0.0411(10)	0.0153(8)	0.0688(13)	0.0062(8)	0.0284(9)	0.0073(7)
F8	0.0466(11)	0.0714(14)	0.0161(7)	-0.0040(8)	0.0026(7)	-0.0298(10)
F9	0.0316(9)	0.0258(8)	0.0571(11)	0.0178(8)	0.0241(8)	0.0165(7)
F10	0.0304(9)	0.0470(11)	0.0266(8)	-0.0043(7)	-0.0068(7)	-0.0111(8)
F11	0.0205(7)	0.0239(8)	0.0459(10)	0.0048(7)	0.0189(7)	-0.0014(6)
Sb1	0.01181(7)	0.01702(7)	0.01603(7)	0.00467(5)	0.00247(5)	-0.00083(5)
Sb2	0.01212(7)	0.01372(7)	0.01727(7)	0.00105(5)	0.00394(5)	-0.00056(5)

Table S14. Hydrogen atomic coordinates and isotropic atomic displacement parameters ($Å^2$) for $MeCNHSb_2F_{11}$.

	x/a	y/b	z/c	U(eq)
H1A	0.3364	0.4009	0.7090	0.032
H1B	0.4385	0.4697	0.8148	0.032
H1C	0.3423	0.4005	0.8984	0.032
H1	0.771(4)	0.3064(19)	0.843(4)	0.024

Table S15. Sample and crystal data for $EtCNHAsF_6$.

Identification code	EtCNHAsF6	
Chemical formula	$C_3H_6AsF_6N$	
Formula weight	245.01	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal size	0.243 x 0.264 x 0.278 mm	
Crystal habit	clear pale yellow prism	
Crystal system	monoclinic	
Space group	P 1 21/n 1	
Unit cell dimensions	a = 8.6760(10) Å	α = 90°
	b = 7.8918(9) Å	β = 108.7610(17)°
	c = 11.7685(14) Å	γ = 90°
Volume	762.97(15) $Å^3$	
Z	4	
Density (calculated)	2.133 g/cm^3	
Absorption coefficient	4.502 mm^{-1}	
F(000)	472	

Table S16. Data collection and structure refinement for $EtCNHAsF_6$.

Diffractometer	Bruker APEX DUO
Radiation source	fine-focus tube, MoKα
Theta range for data collection	2.56 to 30.59°
Index ranges	-12<=h<=12, -11<=k<=11, -16<=l<=16
Reflections collected	17027
Independent reflections	2325 [R(int) = 0.0386]
Coverage of independent reflections	99.1%
Absorption correction	multi-scan
Max. and min. transmission	0.4080 and 0.3680
Structure solution technique	direct methods
Structure solution program	SHELXTL XT 2013/6 (Sheldrick, 2013)
Refinement method	Full-matrix least-squares on F^2
Refinement program	SHELXTL XLMP 2014/1 (Bruker AXS, 2013)
Function minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	2325 / 1 / 105
Goodness-of-fit on F^2	1.124
Δ/σ_{max}	0.001
Final R indices	1985 data; I>2σ(I) R1 = 0.0395, wR2 = 0.0992
	all data R1 = 0.0488, wR2 = 0.1042
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0596P)^2+0.8354P]$ where $P=(F_o^2+2F_c^2)/3$
Largest diff. peak and hole	2.218 and -0.721 eÅ^{-3}
R.M.S. deviation from mean	0.169 eÅ^{-3}

Table S17. Atomic coordinates and equivalent isotropic atomic displacement parameters (Å^2) for $EtCNHAsF_6$.

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x/a	y/b	z/c	U(eq)
As1	0.19050(3)	0.77854(4)	0.40384(2)	0.01716(11)
C1	0.3316(5)	0.1970(5)	0.7213(3)	0.0311(7)
C2	0.3259(4)	0.3378(4)	0.6318(3)	0.0248(6)
C3	0.3385(4)	0.2740(4)	0.5190(3)	0.0208(6)
F1	0.0663(3)	0.9532(3)	0.3676(2)	0.0388(5)
F2	0.3156(3)	0.6055(3)	0.4353(2)	0.0377(5)
F3	0.3159(2)	0.8702(3)	0.33315(17)	0.0320(4)
F4	0.0787(3)	0.6860(3)	0.26728(17)	0.0318(5)
F5	0.0639(3)	0.6847(3)	0.46961(19)	0.0379(5)
F6	0.3019(2)	0.8712(3)	0.53698(16)	0.0303(4)
N1	0.3502(4)	0.2278(3)	0.4326(2)	0.0233(5)

Table S18. Bond lengths (Å) for $EtCNHAsF_6$.

As1-F5	1.703(2)	As1-F2	1.709(2)
As1-F1	1.716(2)	As1-F6	1.7174(18)
As1-F3	1.7263(19)	As1-F4	1.7477(19)
C1-C2	1.521(5)	C1-H1A	0.98
C1-H1B	0.98	C1-H1C	0.98
C2-C3	1.456(4)	C2-H2A	0.99
C2-H2B	0.99	C3-N1	1.115(4)
N1-H1	0.881(19)		

Table S19. Bond angles (°) for $EtCNHAsF_6$.

F5-As1-F2	90.66(12)	F5-As1-F1	90.97(12)
F2-As1-F1	178.00(11)	F5-As1-F6	91.51(10)
F2-As1-F6	90.61(11)	F1-As1-F6	90.50(11)
F5-As1-F3	178.22(10)	F2-As1-F3	89.11(11)
F1-As1-F3	89.23(11)	F6-As1-F3	90.25(10)
F5-As1-F4	89.31(10)	F2-As1-F4	89.50(11)
F1-As1-F4	89.36(11)	F6-As1-F4	179.17(10)
F3-As1-F4	88.92(10)	C2-C1-H1A	109.5
C2-C1-H1B	109.5	H1A-C1-H1B	109.5
C2-C1-H1C	109.5	H1A-C1-H1C	109.5
H1B-C1-H1C	109.5	C3-C2-C1	112.5(3)
C3-C2-H2A	109.1	C1-C2-H2A	109.1
C3-C2-H2B	109.1	C1-C2-H2B	109.1
H2A-C2-H2B	107.8	N1-C3-C2	178.6(3)
C3-N1-H1	168.(3)		

Table S20. Anisotropic atomic displacement parameters (Å^2) for EtCNHAsF$_6$.

The anisotropic atomic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
As1	0.01983(16)	0.01939(17)	0.01242(15)	0.00089(9)	0.00542(11)	-0.00197(10)
C1	0.0388(18)	0.036(2)	0.0223(15)	0.0037(13)	0.0159(14)	0.0035(14)
C2	0.0287(15)	0.0261(15)	0.0211(13)	-0.0034(12)	0.0101(11)	-0.0016(12)
C3	0.0225(13)	0.0189(13)	0.0204(13)	0.0035(10)	0.0060(11)	-0.0014(10)
F1	0.0350(11)	0.0307(11)	0.0453(12)	0.0010(9)	0.0055(9)	0.0121(9)
F2	0.0400(11)	0.0175(9)	0.0503(13)	0.0030(9)	0.0072(10)	0.0052(9)
F3	0.0376(10)	0.0337(11)	0.0294(10)	-0.0001(8)	0.0175(9)	-0.0112(9)
F4	0.0395(11)	0.0358(12)	0.0191(9)	-0.0060(8)	0.0080(8)	-0.0124(9)
F5	0.0401(12)	0.0510(14)	0.0257(10)	0.0023(9)	0.0150(9)	-0.0181(10)
F6	0.0328(10)	0.0351(11)	0.0202(9)	-0.0058(7)	0.0046(7)	-0.0066(8)
N1	0.0288(13)	0.0223(12)	0.0185(11)	-0.0002(9)	0.0070(10)	-0.0038(10)

Table S21. Hydrogen atomic coordinates and isotropic atomic displacement parameters (Å^2) for EtCNHAsF$_6$.

	x/a	y/b	z/c	U(eq)
H1A	0.3203	0.2459	0.7948	0.047
H1B	0.4358	0.1372	0.7405	0.047
H1C	0.2423	0.1173	0.6863	0.047
H2A	0.2224	0.4009	0.6155	0.03
H2B	0.4163	0.4180	0.6675	0.03
H1	0.361(7)	0.215(6)	0.361(3)	0.057(16)

Table S22. Sample and crystal data for $PrCNHAsF_6$.

Identification code	PrCNHAsF6	
Chemical formula	$C_4H_8AsF_6N$	
Formula weight	259.03 g/mol	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal size	0.009 x 0.010 x 0.105 mm	
Crystal habit	clear colourless needle	
Crystal system	triclinic	
Space group	P -1	
Unit cell dimensions	a = 6.0657(3) Å	α = 94.120(4)°
	b = 8.0332(4) Å	β = 105.177(4)°
	c = 8.9481(5) Å	γ = 94.836(4)°
Volume	417.30(4) $Å^3$	
Z	2	
Density (calculated)	2.061 g/cm^3	
Absorption coefficient	6.142 mm^{-1}	
F(000)	252	

Table S23. Data collection and structure refinement for $PrCNHAsF_6$.

Diffractometer	Bruker APEX DUO
Radiation source	IuS microsource, CuKα
Theta range for data collection	5.15 to 68.31°
Reflections collected	1473
Coverage of independent reflections	97.4%
Absorption correction	multi-scan
Max. and min. transmission	0.9470 and 0.5650
Structure solution technique	direct methods
Structure solution program	SHELXTL XT 2014/4 (Bruker AXS, 2014)
Refinement method	Full-matrix least-squares on F^2
Refinement program	SHELXTL XL 2014/7 (Bruker AXS, 2014)
Function minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	1473 / 0 / 114
Goodness-of-fit on F^2	1.063
Final R indices	1284 data; I>2σ(I) R1 = 0.0600, wR2 = 0.1512
	all data R1 = 0.0704, wR2 = 0.1601
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0870P)^2+2.2221P]$ where $P=(F_o^2+2F_c^2)/3$
Largest diff. peak and hole	0.977 and -1.120 eÅ^{-3}
R.M.S. deviation from mean	0.199 eÅ^{-3}

Table S24. Atomic coordinates and equivalent isotropic atomic displacement parameters (Å^2) for $PrCNHAsF_6$.

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x/a	y/b	z/c	U(eq)
C1	0.4951(13)	0.2894(9)	0.6824(8)	0.0201(16)
C2	0.7053(12)	0.3182(10)	0.8095(9)	0.0203(17)
C3	0.8491(13)	0.1692(9)	0.8092(9)	0.0207(16)
C4	0.0759(13)	0.2086(11)	0.9355(9)	0.0246(17)
N1	0.3345(10)	0.2687(8)	0.5849(8)	0.0200(14)
F1	0.9860(7)	0.1943(7)	0.3383(5)	0.0313(11)
F2	0.4443(8)	0.3290(6)	0.2795(5)	0.0293(11)
F3	0.8014(7)	0.3766(6)	0.4843(5)	0.0242(10)
F4	0.7997(9)	0.4274(6)	0.2203(6)	0.0363(12)
F5	0.6309(7)	0.1441(6)	0.1310(5)	0.0261(10)
F6	0.6288(9)	0.0927(6)	0.3943(6)	0.0318(11)
As1	0.71005(13)	0.26065(10)	0.30650(8)	0.0157(3)

Table S25. Bond lengths (Å) for $PrCNHAsF_6$.

C1-N1	1.115(10)	C1-C2	1.459(10)
C2-C3	1.540(10)	C2-H2A	0.99
C2-H2B	0.99	C3-C4	1.527(10)
C3-H3A	0.99	C3-H3B	0.99
C4-H4A	0.98	C4-H4B	0.98
C4-H4C	0.98	N1-H1	0.88(9)
F1-As1	1.758(4)	F2-As1	1.709(4)
F3-As1	1.716(4)	F4-As1	1.712(5)
F5-As1	1.700(4)	F6-As1	1.710(5)

Table S26. Bond angles (°) for $PrCNHAsF_6$.

N1-C1-C2	179.4(9)	C1-C2-C3	110.4(6)
C1-C2-H2A	109.6	C3-C2-H2A	109.6
C1-C2-H2B	109.6	C3-C2-H2B	109.6
H2A-C2-H2B	108.1	C4-C3-C2	109.2(6)
C4-C3-H3A	109.8	C2-C3-H3A	109.8
C4-C3-H3B	109.8	C2-C3-H3B	109.8
H3A-C3-H3B	108.3	C3-C4-H4A	109.5
C3-C4-H4B	109.5	H4A-C4-H4B	109.5
C3-C4-H4C	109.5	H4A-C4-H4C	109.5
H4B-C4-H4C	109.5	C1-N1-H1	173.(6)
F5-As1-F2	92.2(2)	F5-As1-F6	90.6(2)
F2-As1-F6	91.0(2)	F5-As1-F4	89.6(2)
F2-As1-F4	90.7(3)	F6-As1-F4	178.3(3)
F5-As1-F3	177.6(2)	F2-As1-F3	90.1(2)
F6-As1-F3	89.7(2)	F4-As1-F3	90.0(2)
F5-As1-F1	89.2(2)	F2-As1-F1	178.5(2)
F6-As1-F1	89.3(2)	F4-As1-F1	89.0(3)
F3-As1-F1	88.5(2)		

Table S27. Anisotropic atomic displacement parameters ($Å^2$) for $PrCNHAsF_6$.

The anisotropic atomic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C1	0.023(4)	0.017(4)	0.024(4)	0.003(3)	0.009(3)	0.013(3)
C2	0.017(3)	0.011(4)	0.029(4)	0.002(3)	-0.002(3)	0.009(3)
C3	0.023(4)	0.007(4)	0.028(4)	0.004(3)	-0.001(3)	0.005(3)
C4	0.022(4)	0.026(5)	0.024(4)	0.006(3)	0.000(3)	0.008(3)
N1	0.015(3)	0.014(3)	0.026(3)	-0.003(3)	-0.003(3)	0.006(3)
F1	0.023(2)	0.038(3)	0.030(2)	-0.008(2)	0.0009(18)	0.013(2)
F2	0.026(2)	0.030(3)	0.029(2)	-0.003(2)	-0.0004(18)	0.014(2)
F3	0.024(2)	0.020(3)	0.028(2)	-0.0052(19)	0.0083(18)	-0.0028(19)
F4	0.048(3)	0.025(3)	0.038(3)	0.005(2)	0.016(2)	-0.002(2)
F5	0.024(2)	0.025(3)	0.024(2)	-0.008(2)	0.0011(18)	0.003(2)
F6	0.040(3)	0.012(2)	0.041(3)	0.004(2)	0.008(2)	-0.002(2)
As1	0.0160(4)	0.0122(4)	0.0170(4)	-0.0014(3)	0.0015(3)	0.0024(3)

Table S28. Hydrogen atomic coordinates and isotropic atomic displacement parameters ($Å^2$) for $PrCNHAsF_6$.

	x/a	y/b	z/c	U(eq)
H2A	0.6660	0.3326	0.9100	0.024
H2B	0.7964	0.4224	0.7981	0.024
H3A	0.7635	0.0664	0.8289	0.025
H3B	0.8796	0.1492	0.7063	0.025
H4A	1.1773	0.1221	0.9257	0.037
H4B	1.0462	0.2105	1.0381	0.037
H4C	1.1497	0.3184	0.9239	0.037
H1	0.218(15)	0.260(11)	0.502(10)	0.024

Table S29. Sample and crystal data for $C_4H_{10}As_2F_{12}N_2$.

Identification code	DiNH2acetonitrileH	
Chemical formula	$C_4H_{10}As_2F_{12}N_2$	
Formula weight	463.98 g/mol	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	orthorhombic	
Space group	P c a 21	
Unit cell dimensions	a = 14.703(4) Å	α = 90°
	b = 10.260(3) Å	β = 90°
	c = 16.759(4) Å	γ = 90°
Volume	2528.1(11) $Å^3$	
Z	8	
Density (calculated)	2.438 g/cm^3	
Absorption coefficient	5.426 mm^{-1}	
F(000)	1776	

Table S30. Data collection and structure refinement for $C_4H_{10}As_2F_{12}N_2$.

Diffractometer	Bruker APEX DUO
Radiation source	fine-focus tube, MoKα
Theta range for data collection	1.99 to 30.48°
Index ranges	-20<=h<=20, -14<=k<=14, -23<=l<=23
Reflections collected	59685
Independent reflections	7636 [R(int) = 0.0557]
Coverage of independent reflections	99.4%
Absorption correction	multi-scan
Structure solution technique	direct methods
Structure solution program	SHELXTL XT 2013/1 (Bruker AXS, 2014)
Refinement method	Full-matrix least-squares on F^2
Refinement program	SHELXTL XL 2014/7 (Bruker AXS, 2014)
Function minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	7636 / 5 / 378
Goodness-of-fit on F^2	1.032
Δ/σ_{max}	0.001
Final R indices	6795 data; I>2σ(I) R1 = 0.0263, wR2 = 0.0547
	all data R1 = 0.0331, wR2 = 0.0568
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0178P)^2+2.3671P]$ where $P=(F_o^2+2F_c^2)/3$
Absolute structure parameter	0.5(0)
Largest diff. peak and hole	0.718 and -0.596 eÅ^{-3}
R.M.S. deviation from mean	0.102 eÅ^{-3}

Table S31. Atomic coordinates and equivalent isotropic atomic displacement parameters (Å^2) for $C_4H_{10}As_2F_{12}N_2$.

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x/a	y/b	z/c	U(eq)
C1	0.1219(3)	0.5777(5)	0.5751(3)	0.0156(10)
C2	0.1079(3)	0.5684(5)	0.6612(3)	0.0176(9)
N1	0.1288(2)	0.5868(5)	0.5082(3)	0.0169(9)
N2	0.1583(2)	0.4580(3)	0.6990(2)	0.0114(6)
C3	0.1344(3)	0.3288(5)	0.6616(4)	0.0237(12)
C4	0.1384(3)	0.4591(5)	0.7874(3)	0.0193(9)
C5	0.3817(3)	0.0879(5)	0.5401(3)	0.0147(10)
C6	0.3796(3)	0.0920(5)	0.4525(3)	0.0179(10)
N3	0.3815(3)	0.0879(5)	0.6065(3)	0.0173(9)
N4	0.4170(3)	0.9742(4)	0.4168(2)	0.0212(8)
C7	0.3789(3)	0.8495(5)	0.4526(4)	0.0233(11)
C8	0.3951(4)	0.9758(5)	0.3275(3)	0.0231(9)
As1	0.37446(3)	0.46335(5)	0.52521(3)	0.01211(10)
F1	0.29677(17)	0.3398(3)	0.50909(19)	0.0244(6)
F2	0.45301(17)	0.5835(3)	0.54379(17)	0.0221(6)
F3	0.43147(16)	0.3625(3)	0.59112(17)	0.0192(5)
F4	0.30669(17)	0.5204(3)	0.60191(16)	0.0187(6)
F5	0.31727(18)	0.5626(3)	0.45951(17)	0.0224(6)
F6	0.44051(19)	0.4032(3)	0.44872(17)	0.0241(6)
As2	0.13285(3)	0.95935(5)	0.58442(3)	0.01398(11)
F7	0.20995(18)	0.8352(3)	0.5749(2)	0.0317(8)
F8	0.05395(19)	0.0807(3)	0.5923(2)	0.0383(9)
F9	0.1957(2)	0.0515(4)	0.5194(2)	0.0410(9)
F10	0.19359(19)	0.0222(3)	0.66268(18)	0.0253(6)
F11	0.07069(19)	0.8635(3)	0.64891(17)	0.0240(6)
F12	0.07017(19)	0.8970(3)	0.50564(17)	0.0296(7)
As3	0.13102(3)	0.75023(4)	0.28460(3)	0.01421(11)

F13	0.23158(19)	0.7049(3)	0.24068(19)	0.0309(7)
F14	0.03210(19)	0.7875(3)	0.3338(2)	0.0340(8)
F15	0.0777(2)	0.6208(3)	0.24041(19)	0.0328(7)
F16	0.1033(2)	0.8488(3)	0.2066(2)	0.0367(8)
F17	0.1846(2)	0.8749(3)	0.3332(2)	0.0376(8)
F18	0.1614(2)	0.6484(3)	0.36453(19)	0.0371(8)
As4	0.62392(3)	0.74491(4)	0.32252(3)	0.01263(11)
F19	0.66891(19)	0.6583(3)	0.24418(19)	0.0327(8)
F20	0.57880(18)	0.8396(3)	0.39626(16)	0.0246(6)
F21	0.73026(17)	0.8076(3)	0.34183(18)	0.0250(7)
F22	0.6420(2)	0.6203(3)	0.3870(2)	0.0367(8)
F23	0.51719(18)	0.6889(3)	0.29910(19)	0.0270(7)
F24	0.6047(2)	0.8769(3)	0.25729(17)	0.0274(6)

Table S32. Bond lengths (Å) for $C_4H_{10}As_2F_{12}N_2$.

C1-N1	1.129(8)	C1-C2	1.461(8)
C2-N2	1.494(6)	C2-H2A	0.99
C2-H2B	0.99	N1-H1N	0.86(3)
N2-C3	1.508(6)	N2-C4	1.511(6)
N2-H2N	0.89(2)	C3-H3A	0.98
C3-H3B	0.98	C3-H3C	0.98
C4-H4A	0.98	C4-H4B	0.98
C4-H4C	0.98	C5-N3	1.112(7)
C5-C6	1.470(7)	C6-N4	1.457(6)
C6-H6A	0.99	C6-H6B	0.99
N3-H3N	0.94(3)	N4-C7	1.520(6)
N4-C8	1.530(6)	N4-H4N	0.95(3)
C7-H7A	0.98	C7-H7B	0.98
C7-H7C	0.98	C8-H8A	0.98
C8-H8B	0.98	C8-H8C	0.98
As1-F2	1.718(3)	As1-F5	1.719(3)
As1-F6	1.723(3)	As1-F1	1.728(3)
As1-F4	1.729(3)	As1-F3	1.730(3)
As2-F8	1.707(3)	As2-F7	1.712(3)
As2-F10	1.713(3)	As2-F9	1.714(3)
As2-F11	1.723(3)	As2-F12	1.733(3)
As3-F16	1.702(3)	As3-F17	1.708(3)
As3-F15	1.711(3)	As3-F14	1.715(3)
As3-F13	1.716(3)	As3-F18	1.757(3)
As4-F22	1.696(3)	As4-F20	1.706(3)
As4-F23	1.717(3)	As4-F19	1.718(3)
As4-F21	1.721(3)	As4-F24	1.763(3)

Table S33. Bond angles (°) for $C_4H_{10}As_2F_{12}N_2$.

N1-C1-C2	176.9(5)	C1-C2-N2	113.5(4)
C1-C2-H2A	108.9	N2-C2-H2A	108.9
C1-C2-H2B	108.9	N2-C2-H2B	108.9
H2A-C2-H2B	107.7	C1-N1-H1N	178.(4)
C2-N2-C3	112.0(4)	C2-N2-C4	108.3(3)
C3-N2-C4	111.7(4)	C2-N2-H2N	107.(3)
C3-N2-H2N	110.(3)	C4-N2-H2N	107.(3)
N2-C3-H3A	109.5	N2-C3-H3B	109.5
H3A-C3-H3B	109.5	N2-C3-H3C	109.5
H3A-C3-H3C	109.5	H3B-C3-H3C	109.5
N2-C4-H4A	109.5	N2-C4-H4B	109.5
H4A-C4-H4B	109.5	N2-C4-H4C	109.5
H4A-C4-H4C	109.5	H4B-C4-H4C	109.5
N3-C5-C6	177.8(6)	N4-C6-C5	112.2(4)
N4-C6-H6A	109.2	C5-C6-H6A	109.2
N4-C6-H6B	109.2	C5-C6-H6B	109.2
H6A-C6-H6B	107.9	C5-N3-H3N	175.(4)
C6-N4-C7	113.4(4)	C6-N4-C8	108.2(4)
C7-N4-C8	108.5(4)	C6-N4-H4N	109.(3)
C7-N4-H4N	109.(3)	C8-N4-H4N	108.(3)
N4-C7-H7A	109.5	N4-C7-H7B	109.5
H7A-C7-H7B	109.5	N4-C7-H7C	109.5
H7A-C7-H7C	109.5	H7B-C7-H7C	109.5
N4-C8-H8A	109.5	N4-C8-H8B	109.5
H8A-C8-H8B	109.5	N4-C8-H8C	109.5
H8A-C8-H8C	109.5	H8B-C8-H8C	109.5
F2-As1-F5	91.14(14)	F2-As1-F6	90.74(14)

F5-As1-F6	90.66(14)	F2-As1-F1	178.18(14)
F5-As1-F1	90.65(14)	F6-As1-F1	89.62(14)
F2-As1-F4	90.55(13)	F5-As1-F4	89.64(13)
F6-As1-F4	178.67(14)	F1-As1-F4	89.07(13)
F2-As1-F3	89.29(13)	F5-As1-F3	179.57(14)
F6-As1-F3	89.29(13)	F1-As1-F3	88.92(13)
F4-As1-F3	90.41(13)	F8-As2-F7	178.44(15)
F8-As2-F10	91.15(16)	F7-As2-F10	90.34(15)
F8-As2-F9	90.76(17)	F7-As2-F9	89.68(17)
F10-As2-F9	89.89(15)	F8-As2-F11	90.42(15)
F7-As2-F11	89.13(15)	F10-As2-F11	90.64(14)
F9-As2-F11	178.70(18)	F8-As2-F12	88.12(16)
F7-As2-F12	90.38(16)	F10-As2-F12	179.24(15)
F9-As2-F12	90.34(16)	F11-As2-F12	89.14(14)
F16-As3-F17	91.79(17)	F16-As3-F15	91.11(17)
F17-As3-F15	177.04(17)	F16-As3-F14	91.93(17)
F17-As3-F14	89.72(16)	F15-As3-F14	89.57(15)
F16-As3-F13	92.15(16)	F17-As3-F13	90.57(16)
F15-As3-F13	89.93(16)	F14-As3-F13	175.90(16)
F16-As3-F18	179.08(17)	F17-As3-F18	87.99(17)
F15-As3-F18	89.12(17)	F14-As3-F18	88.97(16)
F13-As3-F18	86.95(15)	F22-As4-F20	91.62(17)
F22-As4-F23	92.12(15)	F20-As4-F23	90.03(14)
F22-As4-F19	92.10(17)	F20-As4-F19	176.26(16)
F23-As4-F19	90.24(14)	F22-As4-F21	91.11(15)
F20-As4-F21	90.25(13)	F23-As4-F21	176.75(15)
F19-As4-F21	89.27(14)	F22-As4-F24	178.70(16)
F20-As4-F24	87.12(14)	F23-As4-F24	88.22(14)

F19-As4-F24	89.15(16)	F21-As4-F24	88.56(14)

Table S34. Torsion angles (°) for $C_4H_{10}As_2F_{12}N_2$.

C1-C2-N2-C3	-56.5(5)	C1-C2-N2-C4	179.9(4)
C5-C6-N4-C7	48.6(5)	C5-C6-N4-C8	169.1(4)

Table S35. Anisotropic atomic displacement parameters (Å^2) for $C_4H_{10}As_2F_{12}N_2$.

The anisotropic atomic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C1	0.0098(19)	0.015(2)	0.022(3)	0.0023(19)	-0.0030(17)	0.0007(14)
C2	0.024(2)	0.016(2)	0.013(2)	-0.0031(17)	-0.0037(18)	0.0088(18)
N1	0.0146(19)	0.021(2)	0.015(2)	0.0018(17)	-0.0001(14)	0.0008(14)
N2	0.0115(15)	0.0117(16)	0.0109(16)	0.0002(12)	-0.0013(12)	0.0006(12)
C3	0.033(3)	0.012(2)	0.026(3)	-0.0044(19)	0.005(2)	-0.0031(18)
C4	0.024(2)	0.025(2)	0.008(2)	0.0030(17)	-0.0009(17)	0.0015(17)
C5	0.0114(18)	0.016(2)	0.016(3)	0.0040(18)	-0.0008(16)	0.0008(16)
C6	0.020(2)	0.021(2)	0.012(2)	0.0019(17)	-0.0026(17)	-0.0004(17)
N3	0.0151(19)	0.019(2)	0.018(2)	-0.0014(17)	0.0011(14)	-0.0005(14)
N4	0.024(2)	0.0185(19)	0.021(2)	0.0001(15)	-0.0007(16)	0.0011(15)
C7	0.033(3)	0.015(2)	0.022(3)	0.0026(19)	0.006(2)	-0.0004(19)
C8	0.035(2)	0.021(2)	0.013(2)	-0.0041(18)	-0.002(2)	0.0034(19)
As1	0.0106(2)	0.0155(2)	0.0102(2)	-0.00017(17)	-0.00037(15)	0.00188(15)
F1	0.0170(12)	0.0230(14)	0.0331(17)	-0.0057(12)	-0.0061(11)	-0.0027(10)
F2	0.0170(12)	0.0205(13)	0.0287(16)	-0.0002(11)	0.0024(11)	-0.0028(10)
F3	0.0158(11)	0.0216(13)	0.0202(13)	0.0064(11)	-0.0044(11)	0.0022(10)
F4	0.0161(12)	0.0262(14)	0.0138(13)	-0.0002(11)	0.0031(10)	0.0026(10)
F5	0.0213(13)	0.0280(15)	0.0178(14)	0.0079(11)	-0.0003(11)	0.0075(11)
F6	0.0206(13)	0.0350(17)	0.0165(14)	-0.0040(12)	0.0021(11)	0.0078(12)
As2	0.0109(2)	0.0165(2)	0.0145(3)	0.00085(19)	0.00064(17)	-0.00181(15)
F7	0.0199(13)	0.0319(16)	0.043(2)	-0.0132(15)	0.0013(13)	0.0078(11)
F8	0.0214(14)	0.0169(14)	0.077(3)	-0.0021(17)	-0.0055(16)	0.0050(11)
F9	0.0213(15)	0.069(2)	0.0331(19)	0.0317(17)	-0.0071(14)	-0.0198(15)
F10	0.0255(15)	0.0272(15)	0.0234(15)	-0.0085(12)	-0.0036(12)	-0.0070(12)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
F11	0.0216(13)	0.0285(16)	0.0218(15)	0.0073(12)	0.0013(11)	-0.0080(11)
F12	0.0204(14)	0.051(2)	0.0177(15)	-0.0040(13)	-0.0021(11)	-0.0111(13)
As3	0.0126(2)	0.0158(2)	0.0143(3)	0.00325(17)	0.00111(19)	0.00143(15)
F13	0.0176(13)	0.0468(18)	0.0283(17)	0.0043(14)	0.0070(12)	0.0072(13)
F14	0.0219(14)	0.0367(16)	0.043(2)	-0.0073(15)	0.0125(14)	0.0062(12)
F15	0.0295(16)	0.0271(16)	0.0416(19)	-0.0114(14)	0.0040(14)	-0.0062(13)
F16	0.0466(19)	0.0326(18)	0.0310(18)	0.0150(14)	-0.0059(15)	0.0082(15)
F17	0.0354(16)	0.0372(17)	0.040(2)	-0.0084(15)	-0.0074(15)	-0.0098(14)
F18	0.052(2)	0.0387(18)	0.0203(15)	0.0156(14)	0.0071(15)	0.0151(16)
As4	0.0126(2)	0.0135(2)	0.0118(3)	-0.00129(17)	-0.00186(19)	0.00001(14)
F19	0.0249(15)	0.0430(19)	0.0303(17)	-0.0239(15)	-0.0020(13)	0.0075(13)
F20	0.0216(13)	0.0354(17)	0.0169(14)	-0.0094(12)	-0.0008(11)	0.0070(12)
F21	0.0149(13)	0.0308(15)	0.0292(17)	-0.0090(13)	-0.0029(11)	-0.0050(11)
F22	0.047(2)	0.0255(17)	0.0376(19)	0.0150(14)	-0.0151(15)	-0.0007(14)
F23	0.0155(13)	0.0274(15)	0.038(2)	-0.0056(14)	-0.0060(11)	-0.0055(10)
F24	0.0394(16)	0.0262(15)	0.0165(14)	0.0079(11)	-0.0057(12)	-0.0002(13)

Table S36. Hydrogen atomic coordinates and isotropic atomic displacement parameters (Å^2) for $C_4H_{10}As_2F_{12}N_2$.

	x/a	y/b	z/c	U(eq)
H2A	0.0421	0.5577	0.6719	0.021
H2B	0.1276	0.6510	0.6864	0.021
H1N	0.134(3)	0.591(6)	0.4572(16)	0.02
H2N	0.2175(18)	0.475(4)	0.693(3)	0.014
H3A	0.0684	0.3163	0.6633	0.035
H3B	0.1643	0.2584	0.6911	0.035
H3C	0.1550	0.3278	0.6059	0.035
H4A	0.1567	0.5431	0.8101	0.029
H4B	0.1726	0.3889	0.8135	0.029
H4C	0.0732	0.4458	0.7961	0.029
H6A	0.3159	1.1033	0.4345	0.022
H6B	0.4148	1.1683	0.4338	0.022
H3N	0.378(3)	1.095(6)	0.6623(16)	0.021
H4N	0.4815(18)	0.975(5)	0.423(3)	0.025
H7A	0.3921	0.8473	0.5099	0.035
H7B	0.4071	0.7741	0.4266	0.035
H7C	0.3129	0.8467	0.4443	0.035
H8A	0.3292	0.9694	0.3200	0.035
H8B	0.4250	0.9019	0.3014	0.035
H8C	0.4172	1.0574	0.3040	0.035

Table S37. Sample and crystal data for $PhCNHAsF_6$.

Identification code	PhCNHAsF6	
Chemical formula	$C_7H_6AsF_6N$	
Formula weight	293.05 g/mol	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	orthorhombic	
Space group	P b c a	
Unit cell dimensions	a = 10.3956(10) Å	α = 90°
	b = 9.5385(9) Å	β = 90°
	c = 19.5358(19) Å	γ = 90°
Volume	1937.1(3) $Å^3$	
Z	8	
Density (calculated)	2.010 g/cm^3	
Absorption coefficient	3.565 mm^{-1}	
F(000)	1136	

Table S38. Data collection and structure refinement for $PhCNHAsF_6$.

Diffractometer	Bruker APEX DUO
Radiation source	fine-focus tube, MoKα
Theta range for data collection	2.09 to 30.53°
Reflections collected	2954
Coverage of independent reflections	99.8%
Absorption correction	multi-scan
Structure solution technique	direct methods
Structure solution program	SHELXTL XT 2013/1 (Bruker AXS, 2014)
Refinement method	Full-matrix least-squares on F^2
Refinement program	SHELXTL XL 2014/7 (Bruker AXS, 2014)
Function minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	2954 / 6 / 152
Goodness-of-fit on F^2	1.123
Final R indices	2160 data; I>2σ(I) R1 = 0.0606, wR2 = 0.1092
	all data R1 = 0.0966, wR2 = 0.1187
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0182P)^2+14.0236P]$ where $P=(F_o^2+2F_c^2)/3$
Largest diff. peak and hole	1.127 and -1.222 eÅ^{-3}
R.M.S. deviation from mean	0.135 eÅ^{-3}

Table S39. Atomic coordinates and equivalent isotropic atomic displacement parameters ($Å^2$) for $PhCNHAsF_6$.

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x/a	y/b	z/c	U(eq)
C1	0.7836(5)	0.6166(5)	0.3508(2)	0.0229(10)
C2	0.8383(4)	0.5167(5)	0.3963(2)	0.0174(9)
C3	0.9616(5)	0.4681(5)	0.3831(2)	0.0228(9)
C4	0.0121(5)	0.3649(6)	0.4249(2)	0.0279(11)
C5	0.9396(5)	0.3147(5)	0.4796(2)	0.0261(11)
C6	0.8184(5)	0.3659(5)	0.4934(2)	0.0260(10)
C7	0.7650(5)	0.4681(5)	0.4515(2)	0.0237(9)
N1	0.7385(4)	0.6937(5)	0.3139(2)	0.0252(9)
As1	0.59179(4)	0.96071(5)	0.16329(2)	0.01965(12)
F1	0.6411(4)	0.8940(3)	0.24233(15)	0.0431(9)
F2	0.5460(4)	0.0262(4)	0.08567(17)	0.0559(10)
F3	0.6517(7)	0.8192(6)	0.1246(3)	0.074(2)
F4	0.5380(6)	0.1073(6)	0.2065(3)	0.0532(15)
F5	0.7405(5)	0.0396(7)	0.1597(3)	0.0652(17)
F6	0.4444(5)	0.8907(8)	0.1703(3)	0.070(2)
F3'	0.551(2)	0.7832(17)	0.1446(9)	0.074(2)
F4'	0.6194(16)	0.1214(15)	0.1870(8)	0.0532(15)
F5'	0.7292(13)	0.932(2)	0.1263(8)	0.0652(17)
F6'	0.4450(15)	0.964(2)	0.2036(10)	0.070(2)

Table S40. Bond lengths (Å) for $PhCNHAsF_6$.

C1-N1	1.132(6)	C1-C2	1.422(6)
C2-C3	1.387(6)	C2-C7	1.399(6)
C3-C4	1.383(7)	C3-H3	0.95
C4-C5	1.392(7)	C4-H4	0.95
C5-C6	1.378(7)	C5-H5	0.95
C6-C7	1.389(7)	C6-H6	0.95
C7-H7	0.95	N1-H1	0.99(6)
As1-F5'	1.624(14)	As1-F4'	1.626(15)
As1-F3	1.668(5)	As1-F6	1.677(5)
As1-F2	1.708(3)	As1-F6'	1.718(16)
As1-F5	1.721(5)	As1-F4	1.726(5)
As1-F1	1.747(3)	As1-F3'	1.783(16)

Table S41. Bond angles (°) for $PhCNHAsF_6$.

N1-C1-C2	178.4(5)	C3-C2-C7	122.4(4)
C3-C2-C1	118.5(4)	C7-C2-C1	119.1(4)
C4-C3-C2	118.6(4)	C4-C3-H3	120.7
C2-C3-H3	120.7	C3-C4-C5	119.5(5)
C3-C4-H4	120.2	C5-C4-H4	120.2
C6-C5-C4	121.6(5)	C6-C5-H5	119.2
C4-C5-H5	119.2	C5-C6-C7	119.9(4)
C5-C6-H6	120.0	C7-C6-H6	120.0
C6-C7-C2	118.0(4)	C6-C7-H7	121.0
C2-C7-H7	121.0	C1-N1-H1	178.(3)
F5'-As1-F4'	97.5(9)	F3-As1-F6	93.2(4)
F5'-As1-F2	84.9(6)	F4'-As1-F2	87.6(6)
F3-As1-F2	89.9(2)	F6-As1-F2	87.9(2)
F5'-As1-F6'	171.3(10)	F4'-As1-F6'	90.5(8)
F2-As1-F6'	98.8(6)	F3-As1-F5	90.0(4)
F6-As1-F5	176.6(4)	F2-As1-F5	93.1(2)
F3-As1-F4	176.5(3)	F6-As1-F4	89.2(3)
F2-As1-F4	92.7(2)	F5-As1-F4	87.5(3)
F5'-As1-F1	94.2(6)	F4'-As1-F1	92.3(6)
F3-As1-F1	89.8(2)	F6-As1-F1	92.9(2)
F2-As1-F1	179.11(19)	F6'-As1-F1	82.1(6)
F5-As1-F1	86.1(2)	F4-As1-F1	87.6(2)
F5'-As1-F3'	87.5(9)	F4'-As1-F3'	174.3(9)
F2-As1-F3'	95.7(6)	F6'-As1-F3'	84.3(9)
F1-As1-F3'	84.5(6)		

Table S42. Torsion angles (°) for $PhCNHAsF_6$.

C7-C2-C3-C4	2.0(7)	C1-C2-C3-C4	-176.2(4)
C2-C3-C4-C5	-1.2(7)	C3-C4-C5-C6	-0.4(7)
C4-C5-C6-C7	1.4(7)	C5-C6-C7-C2	-0.6(7)
C3-C2-C7-C6	-1.0(7)	C1-C2-C7-C6	177.2(4)

Table S43. Anisotropic atomic displacement parameters ($Å^2$) for $PhCNHAsF_6$.

The anisotropic atomic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C1	0.027(2)	0.023(2)	0.018(2)	-0.0026(17)	-0.0015(18)	-0.001(2)
C2	0.019(2)	0.016(2)	0.0178(19)	-0.0011(16)	-0.0033(17)	-0.0001(17)
C3	0.024(2)	0.026(2)	0.0186(19)	0.0014(19)	-0.0008(18)	-0.003(2)
C4	0.027(3)	0.030(3)	0.027(2)	-0.003(2)	-0.005(2)	0.006(2)
C5	0.036(3)	0.020(2)	0.023(2)	-0.0006(18)	-0.011(2)	0.002(2)
C6	0.034(3)	0.024(2)	0.020(2)	0.0016(18)	0.002(2)	-0.005(2)
C7	0.022(2)	0.027(2)	0.021(2)	-0.002(2)	0.0015(18)	0.000(2)
N1	0.030(2)	0.023(2)	0.0231(17)	-0.0015(16)	-0.0017(18)	0.0031(18)
As1	0.0206(2)	0.0222(2)	0.01615(19)	0.0015(2)	-0.0029(2)	0.0037(2)
F1	0.072(2)	0.0355(17)	0.0219(15)	0.0056(13)	-0.0127(16)	0.0168(18)
F2	0.071(3)	0.067(3)	0.0303(17)	0.0152(18)	-0.0171(17)	0.008(2)
F3	0.111(6)	0.055(4)	0.054(3)	-0.032(3)	-0.027(4)	0.051(4)
F4	0.065(4)	0.049(3)	0.045(3)	-0.014(2)	-0.011(3)	0.040(3)
F5	0.033(2)	0.107(5)	0.055(3)	0.015(3)	-0.003(2)	-0.031(3)
F6	0.039(2)	0.090(5)	0.080(5)	0.029(4)	-0.019(3)	-0.043(3)
F3'	0.111(6)	0.055(4)	0.054(3)	-0.032(3)	-0.027(4)	0.051(4)
F4'	0.065(4)	0.049(3)	0.045(3)	-0.014(2)	-0.011(3)	0.040(3)
F5'	0.033(2)	0.107(5)	0.055(3)	0.015(3)	-0.003(2)	-0.031(3)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
F6'	0.039(2)	0.090(5)	0.080(5)	0.029(4)	-0.019(3)	-0.043(3)

Table S44. Hydrogen atomic coordinates and isotropic atomic displacement parameters ($Å^2$) for $PhCNHAsF_6$.

	x/a	y/b	z/c	U(eq)
H3	1.0103	0.5050	0.3461	0.027
H4	1.0957	0.3286	0.4164	0.034
H5	0.9744	0.2433	0.5080	0.031
H6	0.7715	0.3315	0.5316	0.031
H7	0.6812	0.5040	0.4600	0.028
H1	0.697(5)	0.763(6)	0.283(3)	0.03

Table S45. Sample and crystal data for $C_8H_8AsF_6N$.

Identification code	TolHAsF6	
Chemical formula	$C_8H_8AsF_6N$	
Formula weight	307.07 g/mol	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal size	0.176 x 0.201 x 0.320 mm	
Crystal habit	clear colourless prism	
Crystal system	monoclinic	
Space group	P 1 21/c 1	
Unit cell dimensions	a = 11.1940(9) Å	α = 90°
	b = 9.7842(8) Å	β = 92.4450(10)°
	c = 9.5122(8) Å	γ = 90°
Volume	1040.87(15) $Å^3$	
Z	4	
Density (calculated)	1.960 g/cm^3	
Absorption coefficient	3.322 mm^{-1}	
F(000)	600	

Table S46. Data collection and structure refinement for $C_8H_8AsF_6N$.

Diffractometer	Bruker APEX DUO
Radiation source	fine-focus tube, MoKα
Theta range for data collection	1.82 to 30.68°
Index ranges	-16<=h<=16, -13<=k<=13, -13<=l<=13
Reflections collected	25393
Independent reflections	3197 [R(int) = 0.0307]
Coverage of independent reflections	99.1%
Absorption correction	multi-scan
Structure solution technique	direct methods
Structure solution program	SHELXTL XT 2013/1 (Bruker AXS, 2014)
Refinement method	Full-matrix least-squares on F^2
Refinement program	SHELXTL XL 2014/7 (Bruker AXS, 2014)
Function minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	3197 / 0 / 149
Goodness-of-fit on F^2	1.060
Δ/σ_{max}	0.001
Final R indices	2871 data; I>2σ(I) R1 = 0.0184, wR2 = 0.0439
	all data R1 = 0.0226, wR2 = 0.0453
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0205P)^2+0.3924P]$ where $P=(F_o^2+2F_c^2)/3$
Largest diff. peak and hole	0.388 and -0.327 eÅ^{-3}
R.M.S. deviation from mean	0.060 eÅ^{-3}

Table S47. Atomic coordinates and equivalent isotropic atomic displacement parameters (Å^2) for $C_8H_8AsF_6N$.

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x/a	y/b	z/c	U(eq)
C1	0.33356(11)	0.34452(12)	0.05843(12)	0.0157(2)
C2	0.23082(11)	0.40164(12)	0.12073(13)	0.0149(2)
C3	0.24799(11)	0.50905(13)	0.21759(13)	0.0170(2)
C4	0.14849(11)	0.56471(13)	0.27804(13)	0.0183(2)
C5	0.03551(11)	0.51400(13)	0.24122(13)	0.0176(2)
C6	0.01977(11)	0.40816(13)	0.14446(13)	0.0166(2)
C7	0.11713(11)	0.34845(12)	0.08149(12)	0.0144(2)
C8	0.10201(12)	0.23469(13)	0.97672(13)	0.0183(2)
N1	0.41460(10)	0.29880(12)	0.00960(12)	0.0195(2)
As1	0.66121(2)	0.43454(2)	0.30257(2)	0.01374(4)
F1	0.58239(8)	0.28683(9)	0.34798(10)	0.02906(19)
F2	0.73694(7)	0.58031(8)	0.25681(9)	0.02596(18)
F3	0.79135(7)	0.36170(9)	0.36721(9)	0.02676(18)
F4	0.63618(8)	0.50116(9)	0.46507(8)	0.02729(18)
F5	0.52967(7)	0.50472(10)	0.23709(10)	0.03015(19)
F6	0.68313(8)	0.36385(10)	0.14078(8)	0.02920(19)

Table S48. Bond lengths (Å) for $C_8H_8AsF_6N$.

C1-N1	1.1291(17)	C1-C2	1.4298(16)
C2-C3	1.4054(17)	C2-C7	1.4103(16)
C3-C4	1.3864(17)	C3-H3	0.95
C4-C5	1.3895(18)	C4-H4	0.95
C5-C6	1.3917(18)	C5-H5	0.95
C6-C7	1.3942(17)	C6-H6	0.95
C7-C8	1.4988(17)	C8-H8A	0.98
C8-H8B	0.98	C8-H8C	0.98
N1-H1	0.789(17)	As1-F4	1.7117(8)
As1-F3	1.7122(8)	As1-F6	1.7144(8)
As1-F5	1.7173(8)	As1-F2	1.7244(8)
As1-F1	1.7569(8)		

Table S49. Bond angles (°) for $C_8H_8AsF_6N$.

N1-C1-C2	179.64(15)	C3-C2-C7	123.10(11)
C3-C2-C1	118.30(11)	C7-C2-C1	118.60(11)
C4-C3-C2	118.41(11)	C4-C3-H3	120.8
C2-C3-H3	120.8	C3-C4-C5	119.60(12)
C3-C4-H4	120.2	C5-C4-H4	120.2
C4-C5-C6	121.37(11)	C4-C5-H5	119.3
C6-C5-H5	119.3	C5-C6-C7	121.11(12)
C5-C6-H6	119.4	C7-C6-H6	119.4
C6-C7-C2	116.41(11)	C6-C7-C8	121.92(11)
C2-C7-C8	121.67(11)	C7-C8-H8A	109.5
C7-C8-H8B	109.5	H8A-C8-H8B	109.5
C7-C8-H8C	109.5	H8A-C8-H8C	109.5
H8B-C8-H8C	109.5	C1-N1-H1	174.1(13)
F4-As1-F3	90.22(4)	F4-As1-F6	178.21(4)
F3-As1-F6	90.13(4)	F4-As1-F5	90.25(4)
F3-As1-F5	178.97(4)	F6-As1-F5	89.37(4)
F4-As1-F2	90.81(4)	F3-As1-F2	90.86(4)
F6-As1-F2	90.94(4)	F5-As1-F2	90.05(4)
F4-As1-F1	89.31(4)	F3-As1-F1	89.87(4)
F6-As1-F1	88.94(4)	F5-As1-F1	89.21(5)
F2-As1-F1	179.26(4)		

Table S50. Torsion angles (°) for $C_8H_8AsF_6N$.

C7-C2-C3-C4	0.42(18)	C1-C2-C3-C4	179.93(11)
C2-C3-C4-C5	-0.34(18)	C3-C4-C5-C6	-0.06(19)
C4-C5-C6-C7	0.42(19)	C5-C6-C7-C2	-0.34(17)
C5-C6-C7-C8	-179.80(11)	C3-C2-C7-C6	-0.08(18)
C1-C2-C7-C6	-179.59(11)	C3-C2-C7-C8	179.38(11)
C1-C2-C7-C8	-0.13(17)		

Table S51. Anisotropic atomic displacement parameters (Å^2) for $C_8H_8AsF_6N$.

The anisotropic atomic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C1	0.0153(5)	0.0161(5)	0.0155(5)	0.0017(4)	-0.0009(4)	-0.0014(4)
C2	0.0131(5)	0.0166(5)	0.0151(5)	0.0024(4)	0.0023(4)	0.0014(4)
C3	0.0147(5)	0.0170(6)	0.0192(6)	0.0004(5)	0.0009(4)	-0.0010(4)
C4	0.0205(6)	0.0154(5)	0.0191(6)	-0.0006(5)	0.0022(5)	0.0013(5)
C5	0.0162(5)	0.0183(6)	0.0187(6)	0.0030(5)	0.0048(4)	0.0042(4)
C6	0.0133(5)	0.0202(6)	0.0162(5)	0.0044(4)	0.0016(4)	0.0003(4)
C7	0.0155(5)	0.0149(5)	0.0127(5)	0.0033(4)	0.0008(4)	0.0001(4)
C8	0.0206(6)	0.0188(6)	0.0155(5)	-0.0010(5)	0.0005(4)	-0.0017(5)
N1	0.0167(5)	0.0213(5)	0.0207(5)	-0.0020(4)	0.0039(4)	0.0017(4)
As1	0.01083(6)	0.01556(6)	0.01498(6)	0.00050(5)	0.00227(4)	-0.00219(4)
F1	0.0303(4)	0.0220(4)	0.0361(5)	-0.0006(4)	0.0156(4)	-0.0112(3)
F2	0.0228(4)	0.0229(4)	0.0320(4)	0.0081(3)	-0.0003(3)	-0.0092(3)
F3	0.0188(4)	0.0308(4)	0.0307(4)	0.0071(4)	0.0007(3)	0.0068(3)
F4	0.0331(4)	0.0287(4)	0.0204(4)	-0.0064(3)	0.0055(3)	0.0015(4)
F5	0.0143(4)	0.0392(5)	0.0365(5)	0.0039(4)	-0.0048(3)	0.0031(3)
F6	0.0315(5)	0.0375(5)	0.0192(4)	-0.0070(4)	0.0076(3)	-0.0041(4)

Table S52. Hydrogen atomic coordinates and isotropic atomic displacement parameters (Å^2) for $C_8H_8AsF_6N$.

	x/a	y/b	z/c	U(eq)
H3	0.3259	0.5427	0.2411	0.02
H4	0.1575	0.6371	0.3442	0.022
H5	-0.0324	0.5524	0.2830	0.021
H6	-0.0586	0.3761	0.1209	0.02
H8A	0.0167	0.2150	-0.0396	0.027
H8B	0.1430	0.1528	0.0133	0.027
H8C	0.1364	0.2620	-0.1120	0.027
H1	0.4686(15)	0.2698(18)	-0.0321(18)	0.023

Table S53. Sample and crystal data for $C_8H_6As_2F_{12}N_2$.

Identification code	Dicyanobenzene	
Chemical formula	$C_8H_6As_2F_{12}N_2$	
Formula weight	507.99 g/mol	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal size	0.065 x 0.141 x 0.269 mm	
Crystal habit	clear colourless rod	
Crystal system	monoclinic	
Space group	P 1 21/c 1	
Unit cell dimensions	a = 6.1068(5) Å	α = 90°
	b = 12.0339(10) Å	β = 98.3970(10)°
	c = 9.5336(8) Å	γ = 90°
Volume	693.10(10) $Å^3$	
Z	2	
Density (calculated)	2.434 g/cm^3	
Absorption coefficient	4.961 mm^{-1}	
F(000)	484	

Table S54. Data collection and structure refinement for $C_8H_6As_2F_{12}N_2$.

Diffractometer	Bruker APEX DUO
Radiation source	fine-focus tube, MoKα
Theta range for data collection	2.74 to 30.51°
Index ranges	-8<=h<=8, -17<=k<=17, -13<=l<=13
Reflections collected	13844
Independent reflections	2116 [R(int) = 0.0217]
Coverage of independent reflections	99.9%
Absorption correction	multi-scan
Max. and min. transmission	0.7390 and 0.3490
Structure solution technique	direct methods
Structure solution program	SHELXTL XT 2013/1 (Bruker AXS, 2014)
Refinement method	Full-matrix least-squares on F^2
Refinement program	SHELXTL XL 2014/7 (Bruker AXS, 2014)
Function minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	2116 / 0 / 112
Goodness-of-fit on F^2	1.072
Δ/σ_{max}	0.001
Final R indices	1958 data; I>2σ(I) R1 = 0.0145, wR2 = 0.0355
	all data R1 = 0.0171, wR2 = 0.0363
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0162P)^2+0.2971P]$ where $P=(F_o^2+2F_c^2)/3$
Largest diff. peak and hole	0.476 and -0.323 eÅ^{-3}
R.M.S. deviation from mean	0.060 eÅ^{-3}

Table S55. Atomic coordinates and equivalent isotropic atomic displacement parameters (Å^2) for $C_8H_6As_2F_{12}N_2$.

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x/a	y/b	z/c	U(eq)
C1	0.84317(19)	0.59048(10)	0.23655(12)	0.0150(2)
C2	0.92383(19)	0.54421(9)	0.11485(12)	0.0135(2)
C3	0.12466(19)	0.48689(10)	0.13571(12)	0.0148(2)
C4	0.20306(19)	0.44215(10)	0.01861(12)	0.0151(2)
N1	0.77712(18)	0.62615(9)	0.33111(11)	0.0178(2)
As1	0.68887(2)	0.31457(2)	0.41911(2)	0.01170(4)
F1	0.42102(13)	0.29715(7)	0.46720(9)	0.02271(17)
F2	0.94651(13)	0.33234(8)	0.37160(9)	0.02534(18)
F3	0.57326(13)	0.39898(7)	0.28259(8)	0.02144(16)
F4	0.72493(13)	0.42804(6)	0.53002(8)	0.02191(16)
F5	0.79476(14)	0.22925(7)	0.55548(8)	0.02509(17)
F6	0.63581(13)	0.20098(6)	0.31078(8)	0.01990(15)

Table S56. Bond lengths (Å) for $C_8H_6As_2F_{12}N_2$.

C1-N1	1.1250(16)	C1-C2	1.4373(16)
C2-C3	1.3958(16)	C2-C4	1.3994(16)
C3-C4	1.3863(16)	C3-H3	0.95
C4-C2	1.3994(16)	C4-H4	0.95
N1-H1	0.886(17)	As1-F5	1.7080(8)
As1-F2	1.7130(8)	As1-F6	1.7153(7)
As1-F3	1.7193(7)	As1-F4	1.7214(7)
As1-F1	1.7745(8)		

Table S57. Bond angles (°) for $C_8H_6As_2F_{12}N_2$.

N1-C1-C2	179.02(13)	C3-C2-C4	123.09(10)
C3-C2-C1	118.29(10)	C4-C2-C1	118.62(10)
C4-C3-C2	118.48(10)	C4-C3-H3	120.8
C2-C3-H3	120.8	C3-C4-C2	118.43(11)
C3-C4-H4	120.8	C2-C4-H4	120.8
C1-N1-H1	175.0(11)	F5-As1-F2	90.92(4)
F5-As1-F6	89.80(4)	F2-As1-F6	92.31(4)
F5-As1-F3	178.02(4)	F2-As1-F3	91.01(4)
F6-As1-F3	89.68(4)	F5-As1-F4	90.52(4)
F2-As1-F4	91.34(4)	F6-As1-F4	176.33(4)
F3-As1-F4	89.88(4)	F5-As1-F1	89.61(4)
F2-As1-F1	179.47(4)	F6-As1-F1	87.78(4)
F3-As1-F1	88.47(4)	F4-As1-F1	88.57(4)

Table S58. Torsion angles (°) for $C_8H_6As_2F_{12}N_2$.

C4-C2-C3-C4	0.5(2)	C1-C2-C3-C4	-179.99(11)
C2-C3-C4-C2	-0.52(19)		

Table S59. Anisotropic atomic displacement parameters (Å²) for $C_8H_6As_2F_{12}N_2$.

The anisotropic atomic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C1	0.0139(5)	0.0152(5)	0.0156(5)	0.0007(4)	0.0009(4)	-0.0008(4)
C2	0.0156(5)	0.0126(5)	0.0128(5)	-0.0014(4)	0.0039(4)	-0.0020(4)
C3	0.0153(5)	0.0155(5)	0.0133(5)	0.0001(4)	0.0014(4)	-0.0003(4)
C4	0.0145(5)	0.0150(5)	0.0156(5)	0.0001(4)	0.0022(4)	0.0006(4)
N1	0.0172(5)	0.0202(5)	0.0164(5)	-0.0024(4)	0.0043(4)	0.0008(4)
As1	0.01129(6)	0.01389(6)	0.01009(6)	-0.00030(4)	0.00215(4)	0.00146(4)
F1	0.0167(4)	0.0282(4)	0.0255(4)	-0.0069(3)	0.0107(3)	-0.0029(3)
F2	0.0133(3)	0.0423(5)	0.0212(4)	-0.0011(3)	0.0053(3)	-0.0029(3)
F3	0.0252(4)	0.0205(4)	0.0167(3)	0.0037(3)	-0.0031(3)	0.0045(3)
F4	0.0268(4)	0.0193(4)	0.0187(3)	-0.0065(3)	0.0002(3)	-0.0009(3)
F5	0.0352(5)	0.0259(4)	0.0140(3)	0.0054(3)	0.0028(3)	0.0113(3)
F6	0.0246(4)	0.0175(4)	0.0180(4)	-0.0058(3)	0.0045(3)	0.0016(3)

Table S60. Hydrogen atomic coordinates and isotropic atomic displacement parameters (Å^2) for $C_8H_6As_2F_{12}N_2$.

	x/a	y/b	z/c	U(eq)
H3	0.2058	0.4787	0.2280	0.018
H4	0.3397	0.4031	0.0287	0.018
H1	-0.286(3)	0.6514(15)	0.4027(17)	0.021

Spectroscopy

Table S61. Comparison of the ν(CN) stretching frequencies for the nitrilium ions and free nitriles.

	ν(CN) [cm^{-1}][a]	
Compound	Nitrilium ion $[RCNH]^+$	Free nitrile
$[CH_3CNH][Sb_2F_{11}]$	2305	2253
$[C_2H_5CNH][AsF_6]$	2262	2247
$[C_3H_7CNH][AsF_6]$	2257	2250
$[Me_2HNCH_2CNH][AsF_6]_2$	2252	2231
$[PhCNH][AsF_6]$	2230	2230
$[o\text{-}MeC_6H_4CNH][AsF_6]$	2230	2227
$[p\text{-}C_6H_4(CNH)_2][AsF_6]_2$	2223	2230

a: In the Raman spectrum.

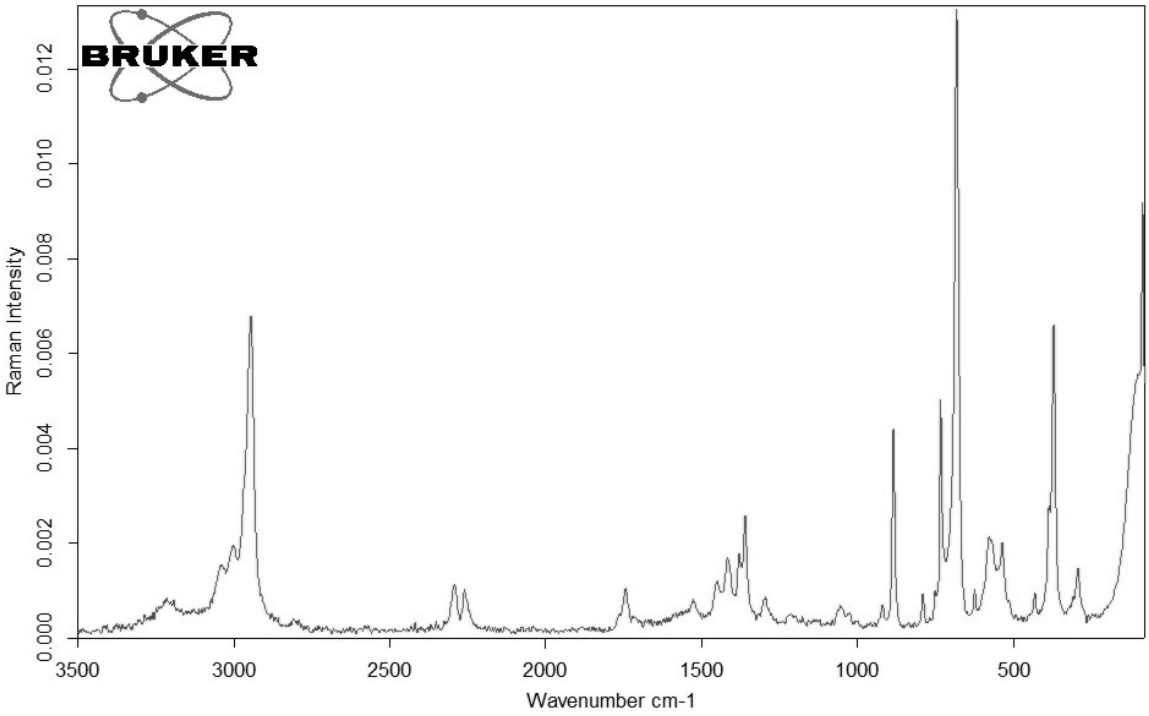

Figure S17. Raman spectrum of $[CH_3CNH][AsF_6]$.

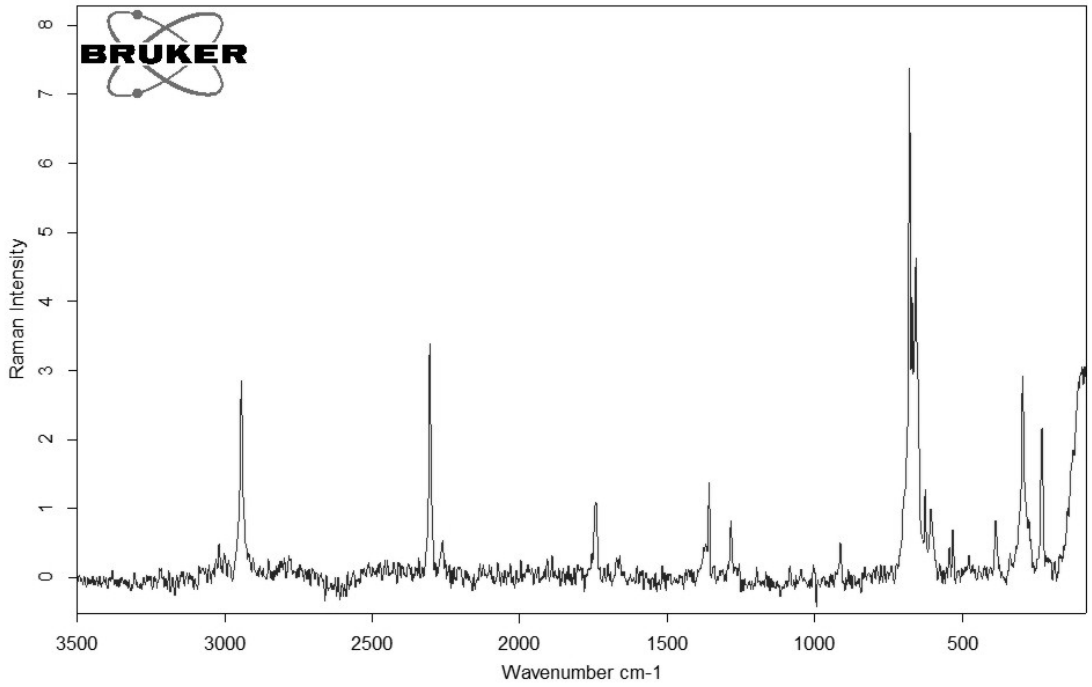

Figure S18. Raman spectrum of $[CH_3CNH][Sb_2F_{11}]$.

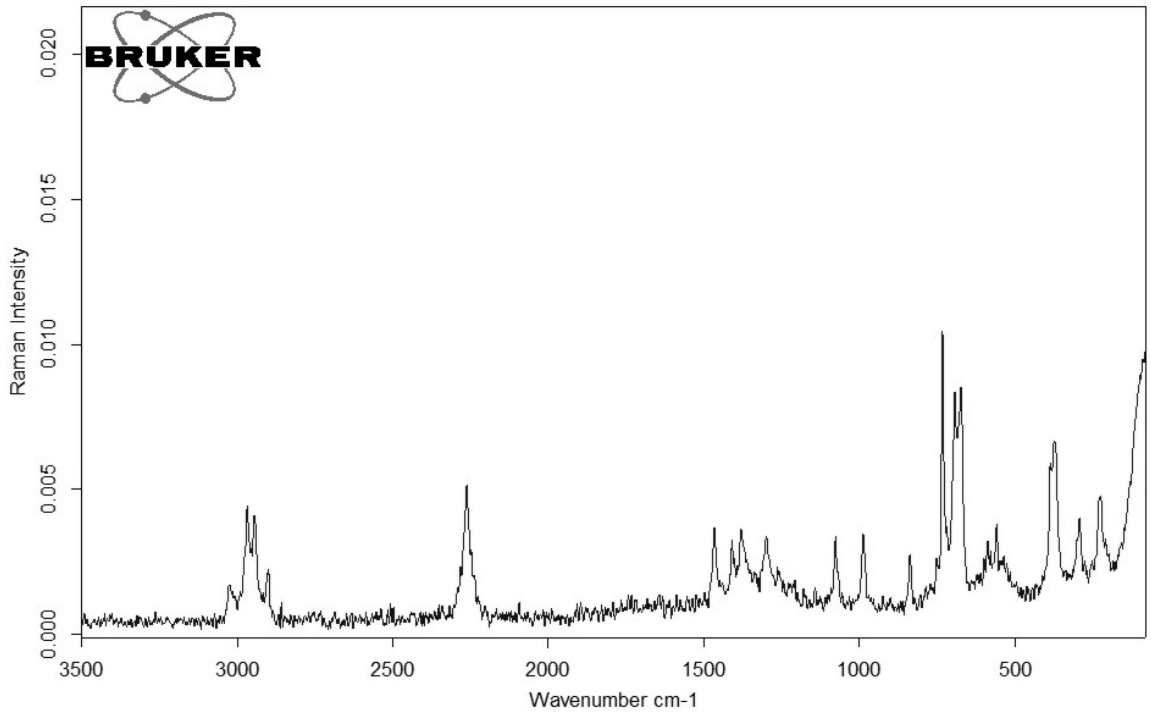

Figure S19. Raman spectrum of $[C_2H_5CNH][AsF_6]$.

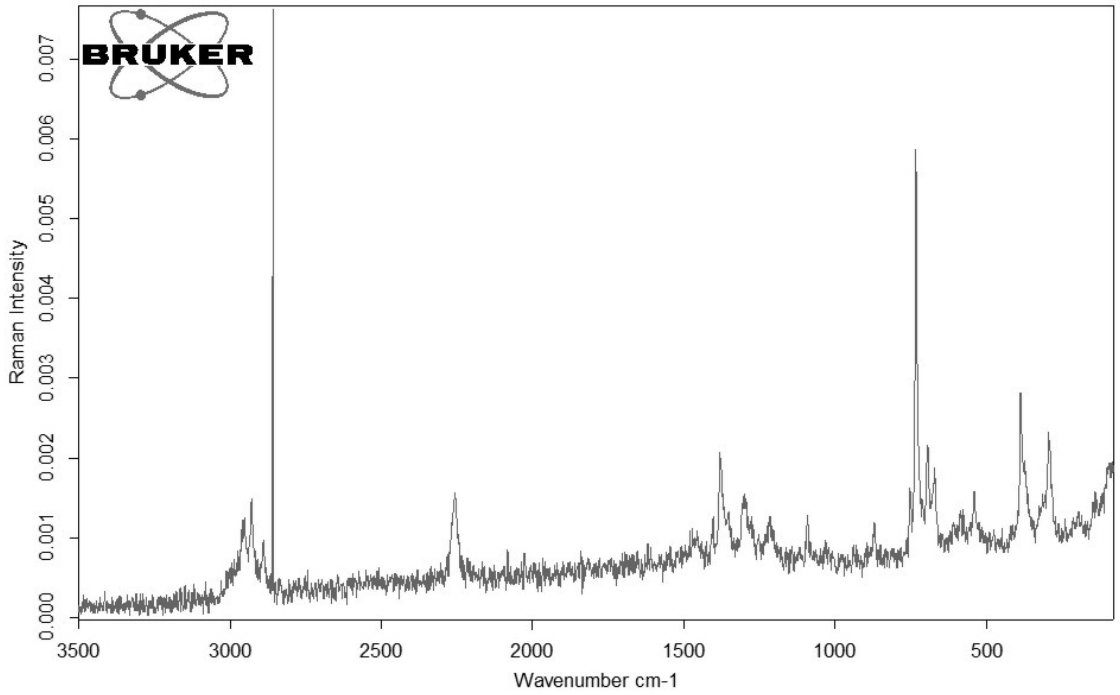

Figure S20. Raman spectrum of $[C_3H_7CNH][AsF_6]$.

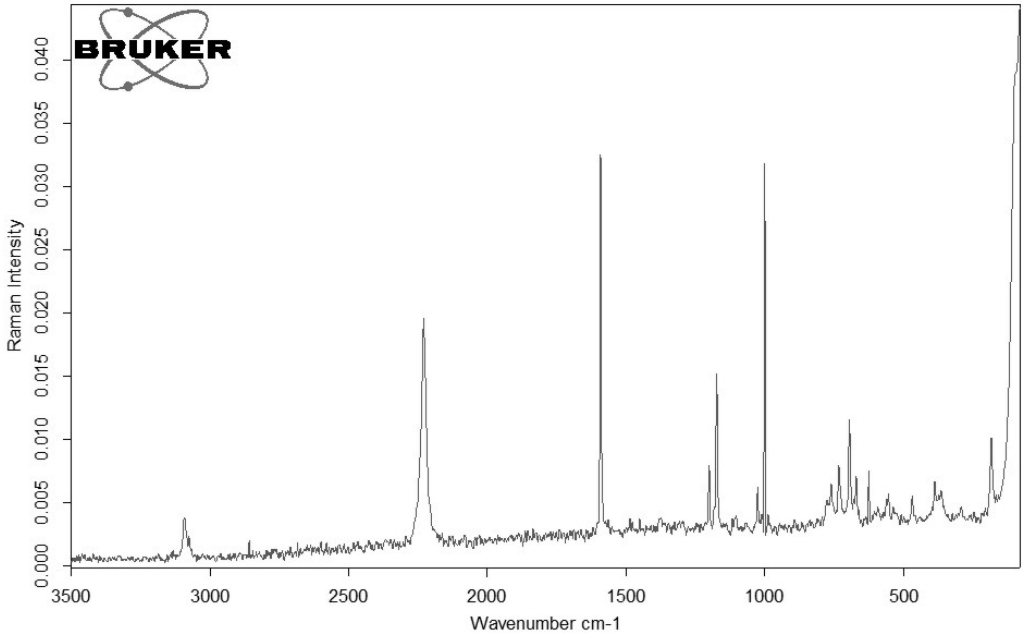

Figure S21. Raman spectrum of $[PhCNH][AsF_6]$.

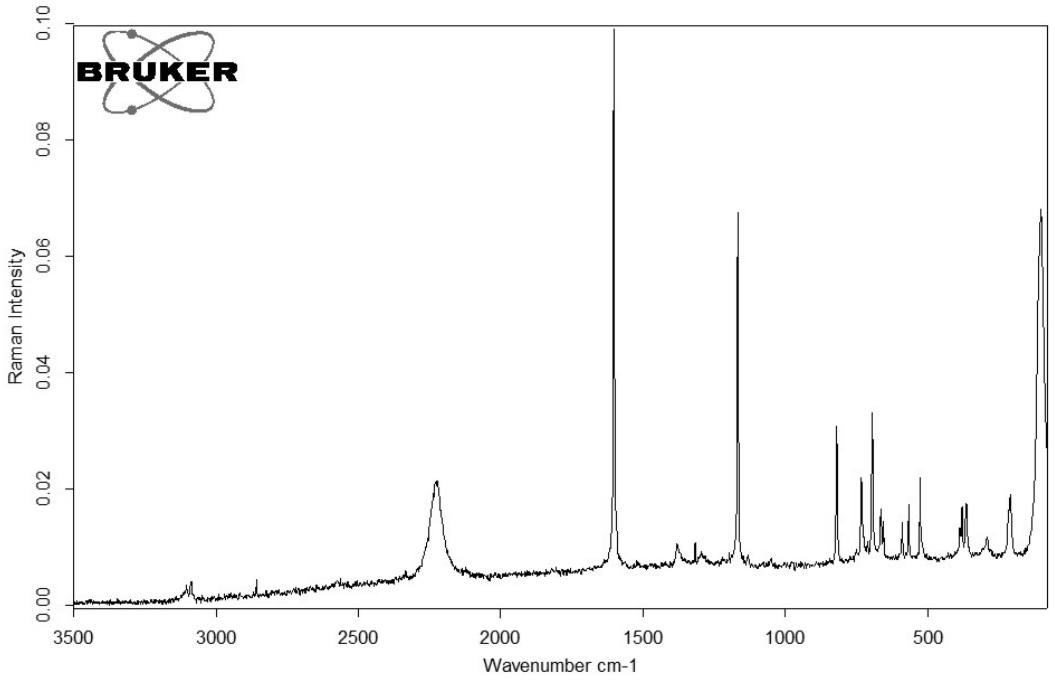

Figure S22. Raman spectrum of [*p*-$C_6H_4(CNH)_2$][AsF_6]$_2$.

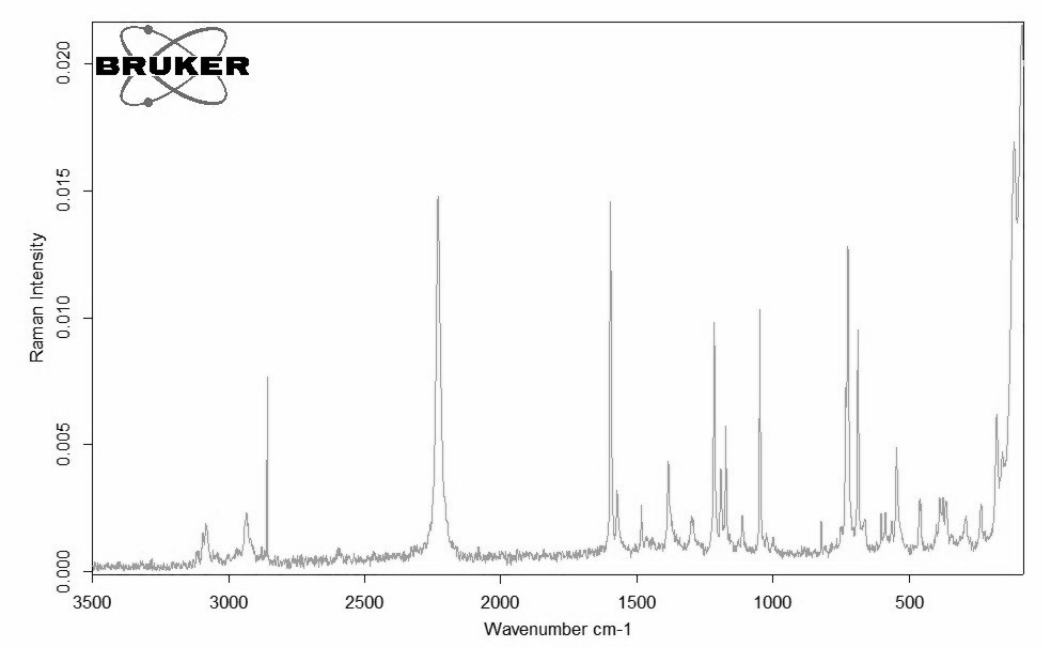

Figure S22. Raman spectrum of [*o*-$CH_3C_6H_4CNH$][AsF_6].

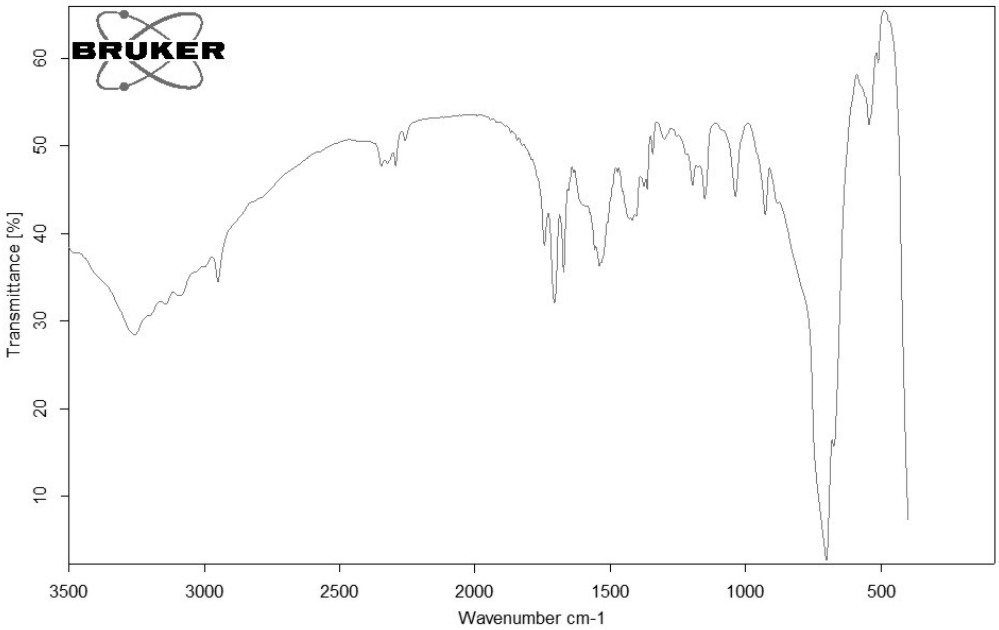

Figure S23. IR spectrum of $[CH_3CNH][AsF_6]$.

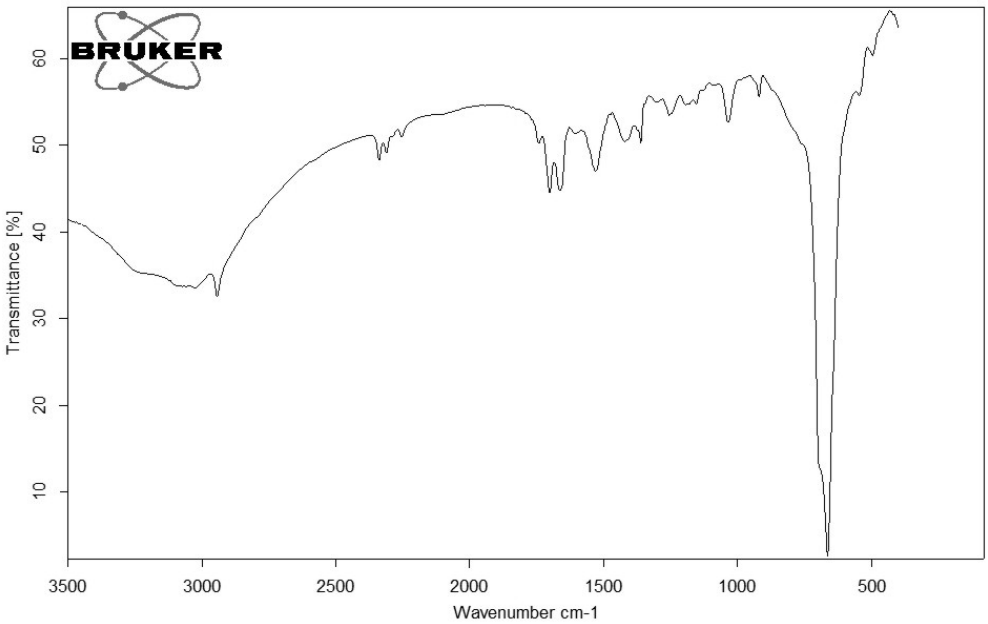

Figure S24. IR spectrum of $[CH_3CNH][Sb_2F_{11}]$.

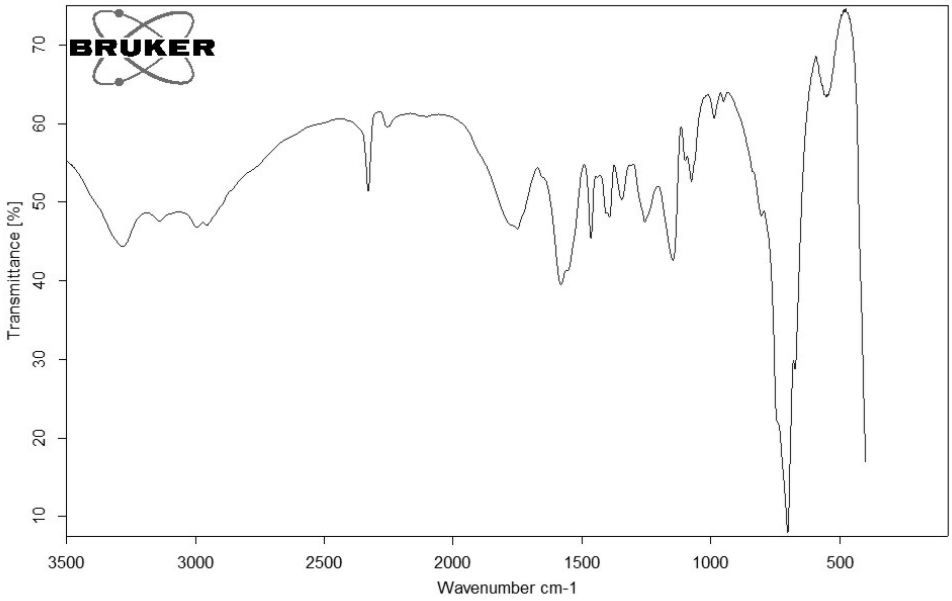

Figure S25. IR spectrum of $[C_2H_5CNH][AsF_6]$.

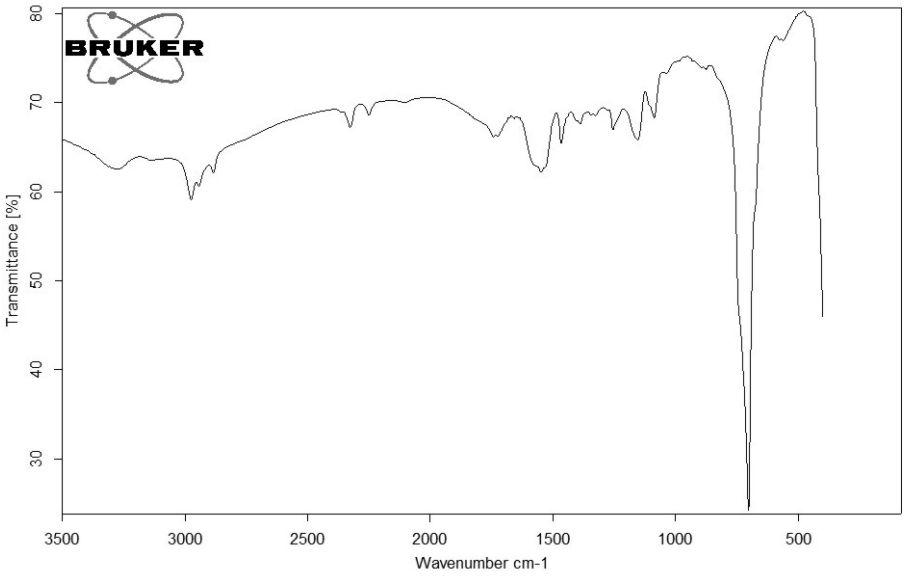

Figure S26. IR spectrum of $[C_3H_7CNH][AsF_6]$.

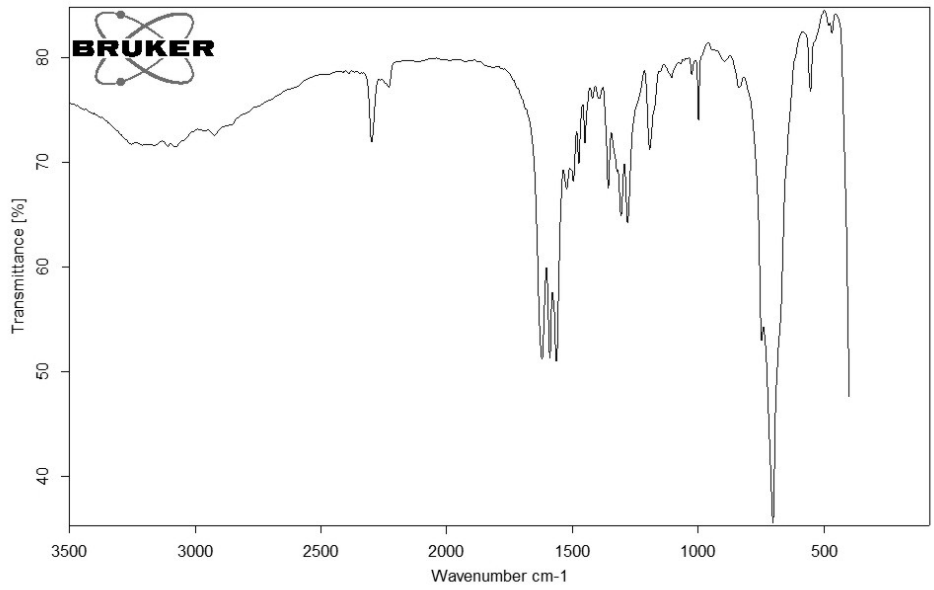

Figure S27. IR spectrum of [PhCNH][AsF_6].

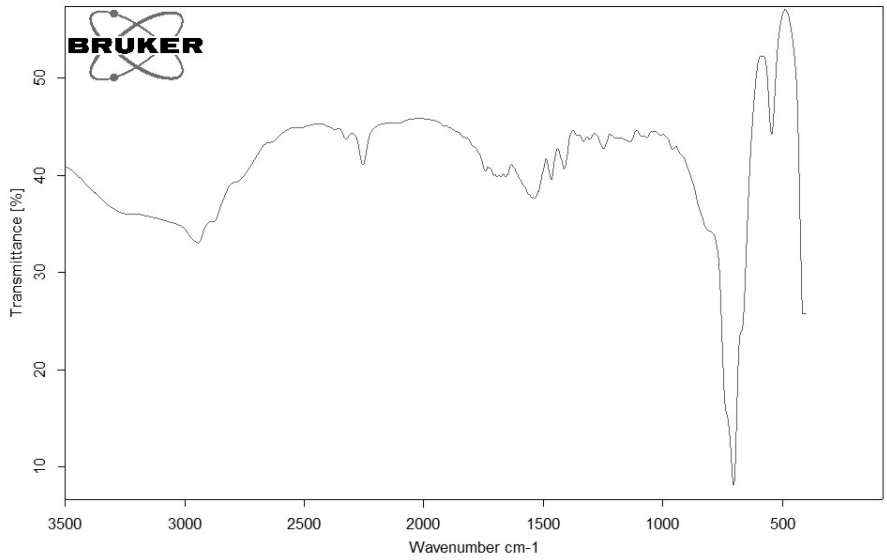

Figure S28. IR spectrum of [Me_2HNCH_2CNH][AsF_6]$_2$.

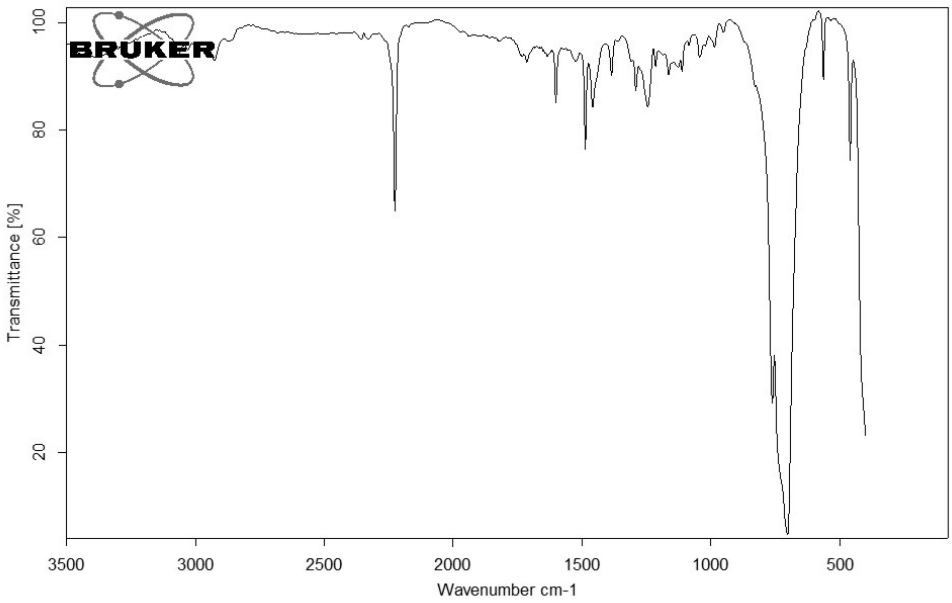

Figure S29. IR spectrum of [*o*-$CH_3C_6H_4CNH$][AsF_6].

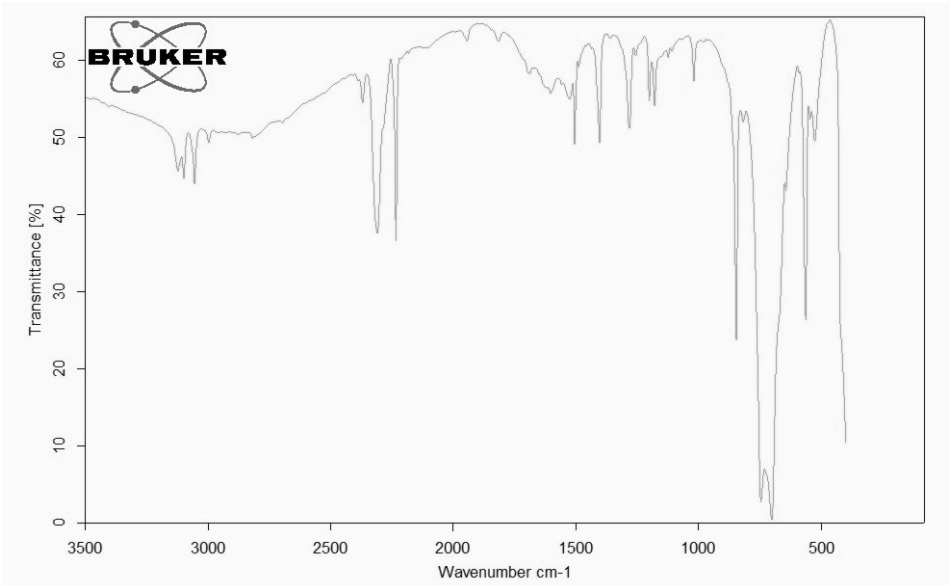

Figure S30. IR spectrum of [*p*-$C_6H_4(CNH)_2$][AsF_6]$_2$.

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