Supporting Information:

[$AsCl_3$([9]aneS_3)]: Addition of a CH_2Cl_2 solution (5 cm^3) of [9]aneS_3 (0.045 g, 0.25 mmol) to a CH_2Cl_2 solution (5 cm^3) of $AsCl_3$ (0.045 g, 0.25 mmol) produced a clear pale yellow solution. Concentration of the solution *in vacuo* produced a yellow solid which was filtered, washed with CH_2Cl_2 and dried *in vacuo*. Yield 54%. Calculated for $C_6H_{12}AsCl_3S_3$: C, 19.9; H, 3.3%. Found: C, 20.3; H, 3.5%. ^{1}H NMR: δ 3.1 (*s*, CH_2). IR/cm^{-1}: 418 br (As-Cl).

[$AsBr_3$([9]aneS_3)]: Procedure as above, giving a bright yellow crystalline solid. Yield 83%. Calculated for $C_6H_{12}AsBr_3S_3$: C, 14.6; H, 2.4%. Found: C, 15.0; H, 2.5%. ^{1}H NMR: δ 3.1 (*s*, CH_2). IR/cm^{-1}: 284 br (As-Br).

[AsI_3([9]aneS_3)]: Procedure as above but using thf in place of CH_2Cl_2. Yellow/orange solid. Yield 62%. Calculated for $C_6H_{12}AsI_3S_3$: C, 11.3; H, 1.9%. Found: C, 11.4; H, 2.1%. ^{1}H NMR: δ 3.1 (*s*, CH_2).

[$AsCl_3$([14]aneS_4)]: Method as above using CH_2Cl_2. White solid. Yield 77%. Calculated for $C_{10}H_{20}AsCl_3S_4$: C, 24.2; H, 4.1%. Found: C, 23.9; H, 4.3%. ^{1}H NMR: δ 1.94 (*quintet*, 4H, $CH_2CH_2CH_2$), 2.67 (*t*, 8H, SCH_2), 2.78, (*s*, 8H, SCH_2). IR/cm^{-1}: 409, 390 (As-Cl)

[$AsCl_3$([8]aneSe_2)]: Method as above, giving a deep red gum which was triturated with hexane to give a waxy red solid. Yield 45%. Calculated for $C_6H_{12}AsCl_3Se_2$: C, 17.0; H, 2.9. Found: C, 16.9; H, 3.0. ^{1}H NMR: δ 2.24 (*m*, $CH_2CH_2CH_2$, 4H), 2.88 (*m*, $SeCH_2$, 8H). IR/cm^{-1}: 402, 392 (As-Cl).

[$AsBr_3$([8]aneSe_2)]: Method as above. Burgandy solid. Yield 55%. Calculated for $C_6H_{12}AsBr_3Se_2$: C, 12.9; H, 2.2%. Found: C, 12.8; H, 2.2. IR/cm^{-1}: 297, 282 (As-Br).

[AsI_3([8]aneSe_2)]: Method as above, but using thf in place of CH_2Cl_2. Burgandy powder. Yield 77%. Calculated for $C_6H_{12}AsI_3Se_2$: C, 10.3; H, 1.7. Found: C, 10.0; H, 1.9%.

[($AsCl_3$)$_2$([16]aneSe_4)]: Method as above using CH_2Cl_2. Pale yellow solid. Yield 92%. Calculated for $C_{12}H_{24}As_2Cl_6Se_4$: C, 17.0; H, 3.1. Found: C, 16.7; H, 3.2. ^{1}H NMR: δ 2.07

(*quin*, $CH_2CH_2CH_2$, 8H), 2.70 (*t*, $SeCH_2$, 16H). IR/cm^{-1}: 401 br (As-Cl).

[$(AsBr_3)_2$([16]aneSe_4)]: Method as above. Yellow solid. Yield 71%. Calculated for $C_{12}H_{24}As_2Br_6Se_4$: C, 12.9; H, 2.2%. Found: C, 13.5; H, 2.3%. ^{1}H NMR: δ 2.07 (*quin*, $CH_2CH_2CH_2$, 8H), 2.70 (*t*, $SeCH_2$, 16H). IR/cm^{-1}: 298, 281, 268 (As-Br).

[$(AsBr_3)_2$([24]aneSe_6)]: Method as above. Bright yellow solid. Yield 95%. Calculated for $C_{18}H_{36}As_2Br_6Se_6$: C, 15.9; H, 2.7%. Found: C, 15.6; H, 2.6%. ^{1}H NMR: δ 2.04 (*quin.*, 12H, $CH_2CH_2CH_2$), 2.70 (*t*, $SeCH_2$, 24H). IR/cm^{-1}: 297, 260 (As-Br).

[$AsBr_3${$MeS(CH_2)_2SMe$}]: Method as above. Yellow solid. Yield 84%. Calculated for $C_4H_{10}AsBr_3S_2$: C, 11.0; H, 2.3%. Found: C, 10.9; H, 2.3%. ^{1}H NMR: δ 2.16 (*s*, 6H, Me), 2.74 (s, 4H, CH_2). IR/cm^{-1}: 298, 281, 261 (As-Br).