Electronic Supplementary information

Structural relationships between *o*-, *m*- and *p*-tolyl substituted R_3EI_2 (E = As, P) and $[(R_3P)AuX)]$ (E = As, P; X = Cl, Br, I).

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FULL CHARACTERISING DATA FOR COMPOUNDS

LIGANDS

(*o*-$CH_3C_6H_4)_3As$: Yield = 2.719g (84.7%). ^{1}H NMR ($CDCl_3$): 2.47 [s, 9H, CH_3], 7.20 [m, 3H, Ar], 7.28 [m, 3H, Ar], 7.36 [m, 3H, Ar], 7.45 [m, 3H, Ar]. $^{13}C\{^1H\}$ NMR ($CDCl_3$): 21.6 [s, CH_3], 129.8 [s, C_m], 130.5 [s, C_p], 132.0 [s, C_o], 133.9 [s, C_m], 136.8 [s, C_i], 148.2 [s, $C_{o(quat)}$].

(*p*-$CH_3C_6H_4)_3As$: Yield = 2.652g (90.4%). ^{1}H NMR ($CDCl_3$): 2.21 [s, 9H], 7.01 [d, ^3J(HH) = 8.0 Hz, 4H], 7.12 [d, ^3J(HH) = 8.0 Hz, 4H]. $^{13}C\{^1H\}$ NMR ($CDCl_3$): 21.4 [s, CH_3], 129.6 [s, C_m], 133.8 [s, C_o], 136.6 [s, C_i], 138.3 [s, C_p].

DI-IODIDE ADDUCTS

(*o*-$CH_3C_6H_4)_3AsI_2$, 1a. Yield = 47.8%. Orange solid. Calculated for $C_{21}H_{21}AsI_2$: C, 41.9; H, 3.5; I, 42.2; Found: C, 42.1; H, 3.2; I, 42.0. ^{1}H NMR ($CDCl_3$): 2.36 [s, 9H, CH_3], 6.90 [dd, *J*(HH) = 7.6, 1.4 Hz, 3H, Ar], 7.11 [t, *J*(HH) = 7.2 Hz, 3H, Ar], 7.25 [d, *J*(HH) = 7.2 Hz, 3H, Ar], 7.34 [td, *J*(HH) = 7.6, 1.4 Hz, 3H, Ar]. $^{13}C\{^1H\}$ NMR ($CDCl_3$): 22.6 [s, CH_3], 127.0 [s], 130.4 [s, C_i], 131.1 [s], 131.6 [s], 133.0 [s], 142.5 [s, $C_{o(quat)}$].

(*m*-$CH_3C_6H_4)_3PI_2$, 1c. Yield = 72.6%. Yellow solid. Calculated for $C_{21}H_{21}PI_2$: C, 45.2; H, 3.8; P, 5.6; I, 45.5; Found: C, 45.1; H, 3.6; P, 5.6; I, 45.2. ^{1}H NMR ($CDCl_3$): 2.41 [s, 9H, CH_3], 7.20–7.52 [m, 12H, Ar]. $^{13}C\{^1H\}$ NMR ($CDCl_3$): 21.6 [s, CH_3], 122.2 [d, C_i, ^1J(PC) = 62.5 Hz], 129.4 [d, C_m, ^3J(PC) = 13.7 Hz], 129.8 [d, C_o, ^2J(PC) = 13.7 Hz], 132.7 [d, C_o, ^2J(PC) = 11.0 Hz], 135.5 [d, C_p, ^4J(PC) = 2.9 Hz], 139.6 [d, C_m, ^3J(PC) = 13.1 Hz]. $^{31}P\{^1H\}$ NMR ($CDCl_3$): –13.1 [s, br]. Raman (cm^{-1}): 3052, 2908, 1590, 1573, 1218, 1174, 1097, 1086, 994, 852, 781, 700, 675, 547, 524, 454, 412, 369, 358, 258, 151.

(*p*-$CH_3C_6H_4)_3AsI_2$, 1d. Yield = 37.8%. Orange solid. Calculated for $C_{21}H_{21}AsI_2$: C, 41.9; H, 3.5; I, 42.2; Found: C, 41.5; H, 3.6; I, 42.6. ^{1}H NMR ($CDCl_3$): 2.35 [s, 9H, CH_3], 7.24 [d, *J*(HH) = 8.3 Hz, 6H, Ar], 7.27 [d, *J*(HH) = 8.3 Hz, 6H, Ar]. $^{13}C\{^1H\}$ NMR ($CDCl_3$): 21.5 [s, CH_3], 125.2 [s, C_i], 130.8 [s], 132.3 [s], 143.2 [s, C_p].

(*p*-$CH_3C_6H_4)_3PI_2$, 1e. Yield = 55.4%. Yellow solid. Calculated for $C_{21}H_{21}PI_2$: C, 45.2; H, 3.8; P, 5.6; I, 45.5; Found: C, 45.6; H, 3.3; P, 5.6; I, 45.1. ^{1}H NMR ($CDCl_3$): 2.44 [s, 9H, CH_3], 7.33-7.41 [m, 12H, Ar]. $^{13}C\{^1H\}$ NMR ($CDCl_3$): 21.9 [s, CH_3], 118.6 [d, C_i, ^1J(PC) = 71.2 Hz], 130.9 [d, C_o, ^2J(PC) = 13.8 Hz], 133.5 [d, C_m, ^3J(PC) = 10.8 Hz], 146.5 [d, C_p, ^4J(PC) = 3.6 Hz]. $^{31}P\{^1H\}$ NMR ($CDCl_3$): –6.7 [s, br]. Raman (cm^{-1}): 3049, 2916, 1593, 1561, 1493, 1396, 1375, 1309, 1213, 1186, 1093, 1018, 808, 702, 650, 611, 513, 457, 428, 395, 355, 295, 224, 160.

GOLD COMPLEX

[{(*o*-$CH_3C_6H_4)_3As$}AuCl], 2. Yield = 79.2%. White solid. Calculated for $C_{21}H_{21}AsAuCl$: C, 43.4; H, 3.7; Cl, 6.1; Found: C, 43.3; H, 3.8; Cl, 6.1. ^{1}H NMR ($CDCl_3$): 2.56 [s, 9H, CH_3], 6.90 [d, *J*(HH) = 7.3 Hz, 3H, Ar], 7.13 [t, *J*(HH) = 7.3 Hz, 3H, Ar], 7.29 [d, *J*(HH) = 7.3 Hz, 3H, Ar], 7.39 [t, *J*(HH) = 7.3 Hz, 3H, Ar]. $^{13}C\{^1H\}$ NMR ($CDCl_3$): 22.1 [s, CH_3], 126.1 [s], 127.0 [s, C_i], 130.6 [s], 131.1 [s], 131.7 [s], 141.3 [s, $C_{o(quat)}$]. Raman (cm^{-1}): 3058, 2966, 2937, 2907, 1589, 1566, 1448, 1427, 1381, 1280, 1203, 1163, 1128, 1057, 1041, 798, 656, 544, 415, 322, 264, 216, 193, 173, 121.

FULL TORSION ANGLE AND CONE ANGLE DATA FOR TOLYL–SUBSTITUTED R_3EI_2 and [$(R_3E)AuX$] COMPOUNDS

Adduct / complex	I/Au–P/As–C_i–C_o Torsion angles (°)	Conformation of Ar_3P fragment	Cone angle (°)[a]
o-tolyl$_3$PI$_2$ **1b**	50.0(4), 53.6(4), 54.6(4)	*exo*$_3$ – close to ideal propeller	192.2
(*m*-tolyl$_3$PI$_2$ **1c**	32.4(14) *endo*, 44.9(16) *endo*, 71.0(13) *exo*	*exo*$_1$ – staggered orientation	154.5
p-tolyl$_3$PI$_2$ **1e**	22.8(14), 68.9(12), 28.4(13)	Staggered – two upright, one flat	145.0
Ph_3PI_2	38.4(10), 56.8(10), 45.2(11)	Staggered propeller	147.2
[(Ph_3P)AuCl]	38.8, 29.9, 58.2[b]	Staggered propeller	150.3
[(Ph_3P)AuBr]	-39.8(16), -33.5(14), -57.6(16)	Staggered propeller	149.8
[(Ph_3P)AuI]	-59.4(14), -42(2), -34.6(15)	Staggered propeller	147.8
[(*o*-tolyl$_3$P)AuCl] **Ia** (monoclinic)	-47.3(9), -45.6(8), -51.6(9)	*exo*$_3$ – close to ideal propeller	197.4
[(*o*-tolyl$_3$P)AuCl] **I** (orthorhombic)	-48.4(12), -58.4(12), -41.8(14) (molecule 1)	*exo*$_3$ – somewhat staggered	191.3
	51.3(12), 45.5(13), 50.5(12) (molecule 2)	*exo*$_3$ – close to ideal propeller	194.5
[(*o*-tolyl$_3$P)AuBr] **II**	-47.2(17), -56.5(16), -41.0(16) (molecule 1)	*exo*$_3$ – somewhat staggered	196.2
	-44.5(18), -48.2(17), -49.7(14) (molecule 2)	*exo*$_3$ – close to ideal propeller	195.9
[(*o*-toly$_3$P)AuI] **III**	-45.1(11), -54.6(10), -43.7(10) (molecule 1)	*exo*$_3$ – somewhat staggered	195.8
	-44.4(12), -50.6(11), -51.1(10) (molecule 2)	*exo*$_3$ – close to ideal propeller	192.6
[(*m*-tolyl$_3$P)AuCl] **IV**	-27.2(8) *endo*, -45.5(7) *endo*, -68.5(7) *exo*	*exo*$_1$ – staggered orientation	154.4
[(*p*-tolyl$_3$P)AuCl] **V** (monoclinic)	23.2(13), 42.1(14), 45.7(14) (molecule 1)	Staggered – one more upright than others	154.0
	-22.4(17), -32.3(17), -52.9(14) (molecule 2)	Staggered – more even distribution	153.4
[(*p*-tolyl$_3$P)AuCl] **Va** (orthorhombic)	37.8(15), 66.8(15), 33.9(16)	Staggered – one flat	145.1
[(*p*-tolyl$_3$P)AuBr] **VI**	23(3), 44(4), 40(2) (molecule 1)	Staggered – one more upright than others	151.9
	-32(3), -56(4), -17(4) (molecule 2)	Staggered – more even distribution	152.2
[(*p*-tolyl$_3$P)AuI] **VII**	23.2(13), 42.1(14), 45.7(14)(molecule 1)	Staggered – one more upright than others	151.5
	-22.4(17), -52.9(14), -32.3(17)(molecule 2)	Staggered – more even distribution	152.8
o-tolyl$_3$AsI$_2$ **1a**	-55.4(8), -47.7(9), -51.2(11)	*exo*$_3$ – close to ideal propeller	174.7
p-tolyl$_3$AsI$_2$ **1d**	-18.6(12), -26.9(11), -68.8(11)	Staggered – two upright, one flat	140.6
Ph_3AsI_2 (orthorhombic)	48.1(7), 7.7(6), 49.8(7)	Two rings propeller like, one upright	145.1
Ph_3AsI_2 (monoclinic)	-41.8(1), -62.0(1), -53.2(1)	Staggered propeller	139.9
Ph_3AsI_2 (cubic)	53.6(13)	Perfect propeller due to symmetry	141.3
Ph_3AsI_2.toluene solvate	-45.5(7)	Perfect propeller due to symmetry	142.7
[(Ph_3As)AuCl] (polymorph 1)	59(2), 30(2), 40(3)	Staggered propeller	146.6
[(Ph_3As)AuCl] (polymorph 2)	46.1(10), 31.2(12), 10.0(10)	Two rings propeller like, one upright	151.5
[(Ph_3As)AuBr]	-32.8, -43.3, -60.4[b]	Staggered propeller	N/A[c]
[(*o*-tolyl$_3$As)AuCl] **2**	45.9(12), 52.3(12), 52.1(12) (molecule 1)	*exo*$_3$ – close to ideal propeller	196.2
	-37.9(12), -48.2(13), -59.2(13) (molecule 2)	*exo*$_3$ – somewhat staggered	194.6

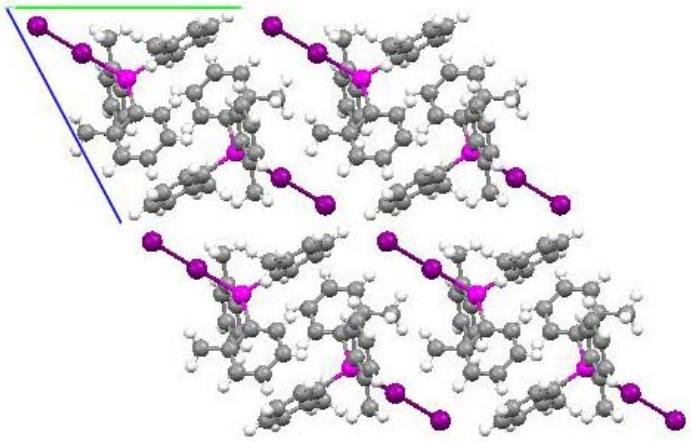
[a]All cone angles are calculated from the crystal structure of the adduct or complex

[b]No esd values given in the CIF file

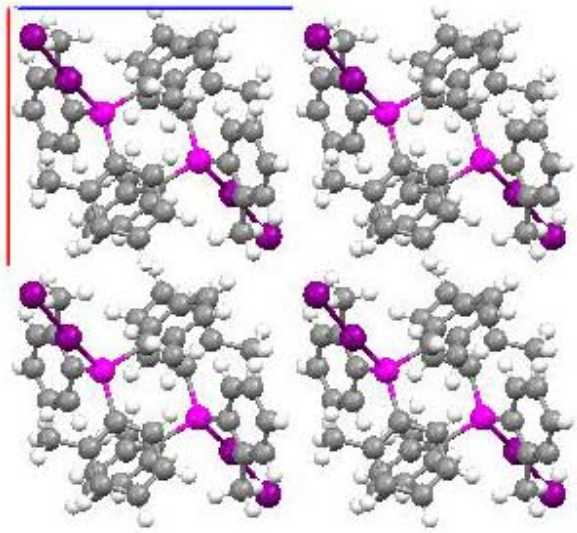
[c]No protons in CIF file to calculate accurate crystallographic cone angle

Table S1 Comparison of aryl ring torsion angles, conformations and crystallographic cone angles in linear R_3EX_2 (E = P, As) adducts and in related linear [$(R_3E)AuX$] gold(I) complexes

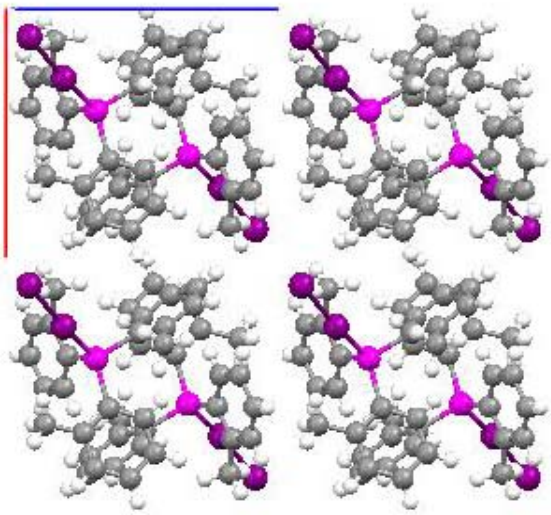
Packing diagrams based on 8 unit cells viewed down *a*, *b* and *c* axes for **1a–e** and **I–VII**.



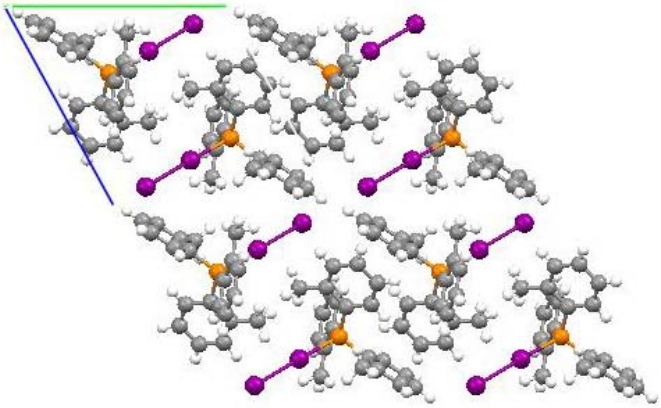
View down *a* axis for **1a**



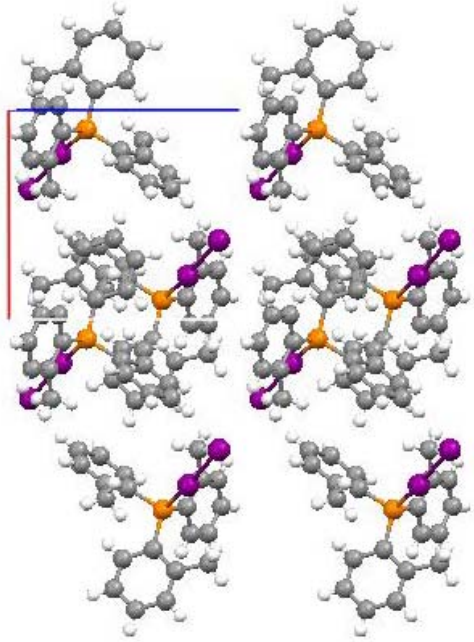
View down *b* axis for **1a**



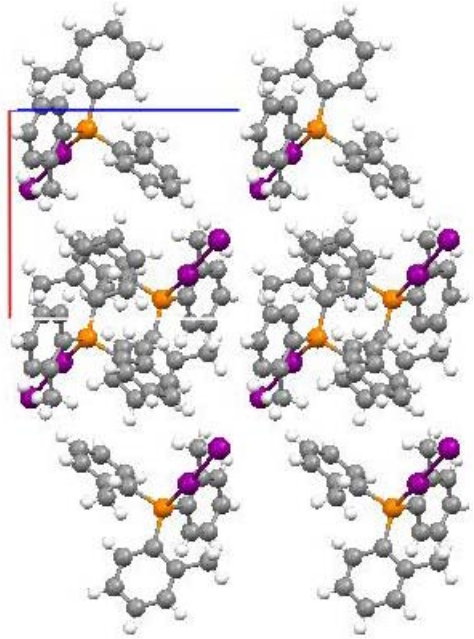
View down *c* axis for **1a**



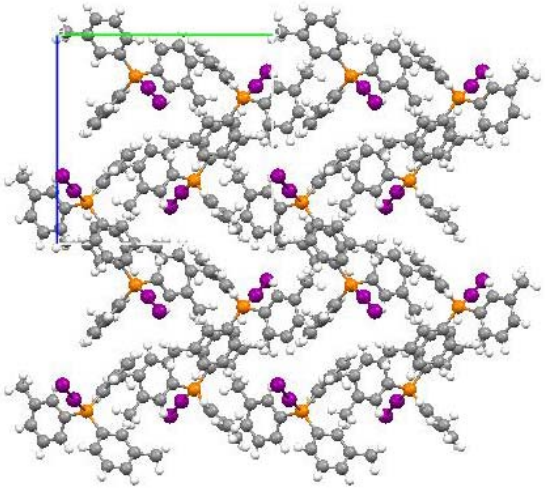
View down *a* axis for **1b**



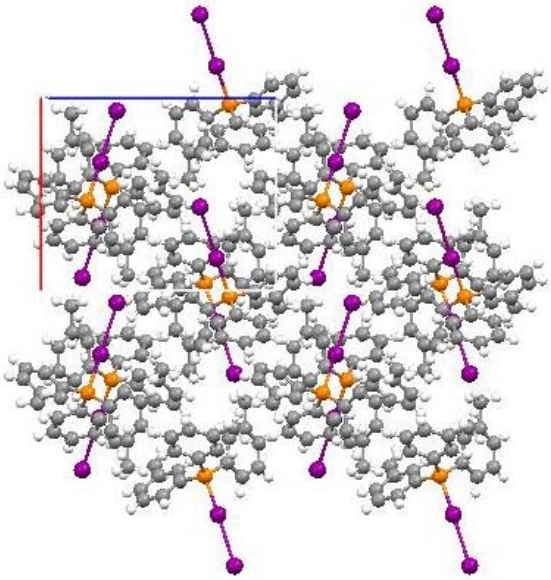
View down *b* axis for **1b**



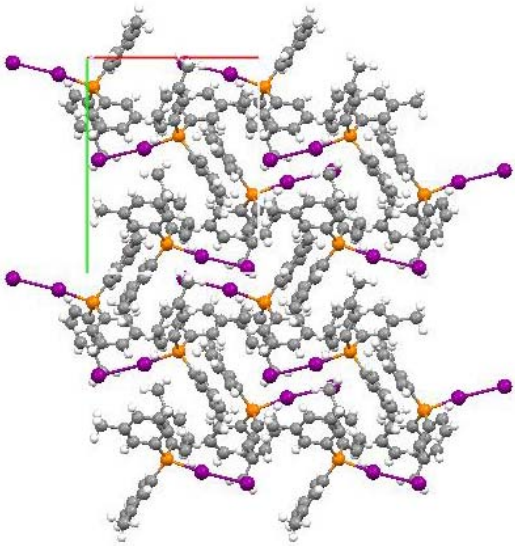
View down *c* axis for **1b**



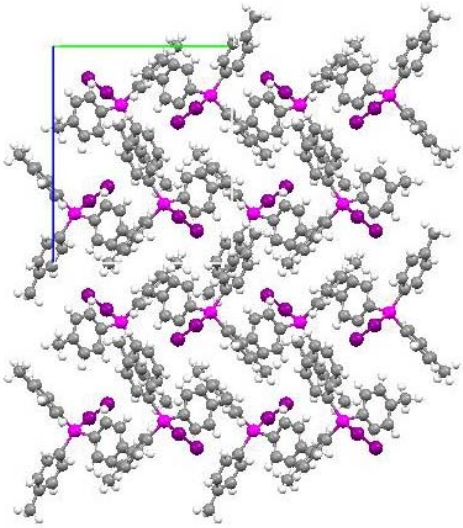
View down *a* axis for **1c**



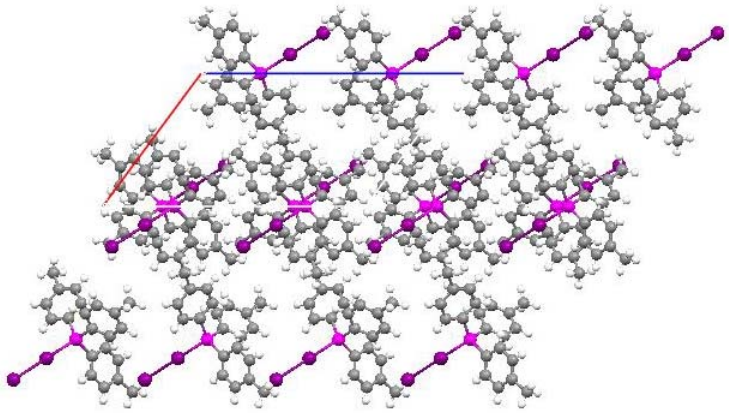
View down *b* axis for **1a**



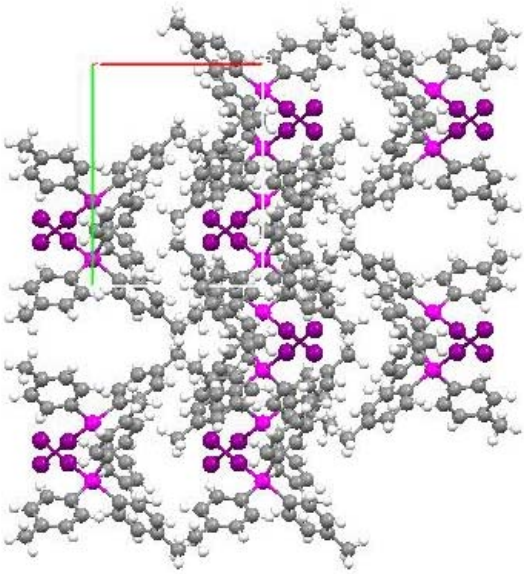
View down *c* axis for **1c**



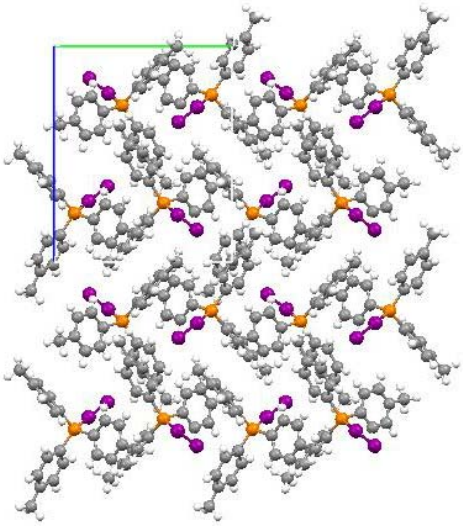
View down *a* axis for **1d**



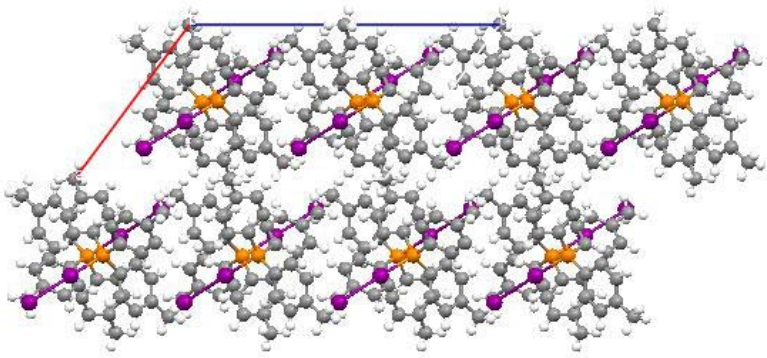
View down *b* axis for **1d**



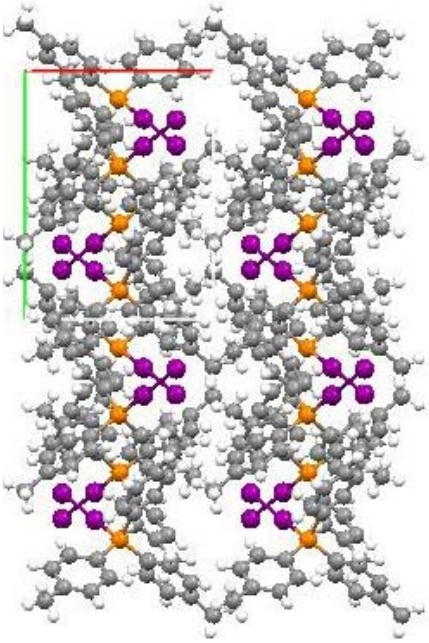
View down *c* axis for **1d**



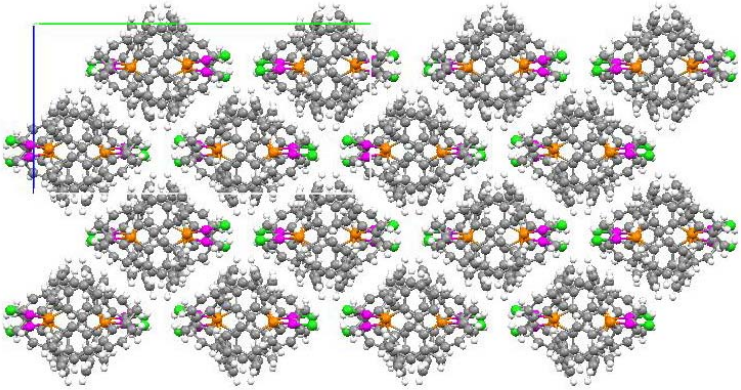
View down *a* axis for **1e**



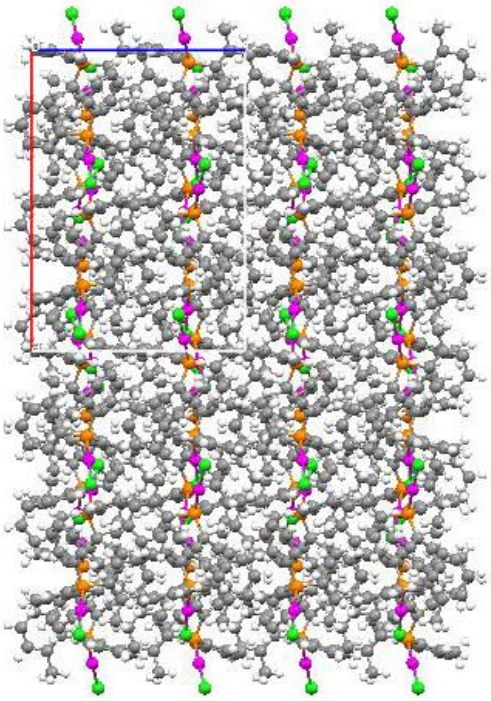
View down *b* axis for **1e**



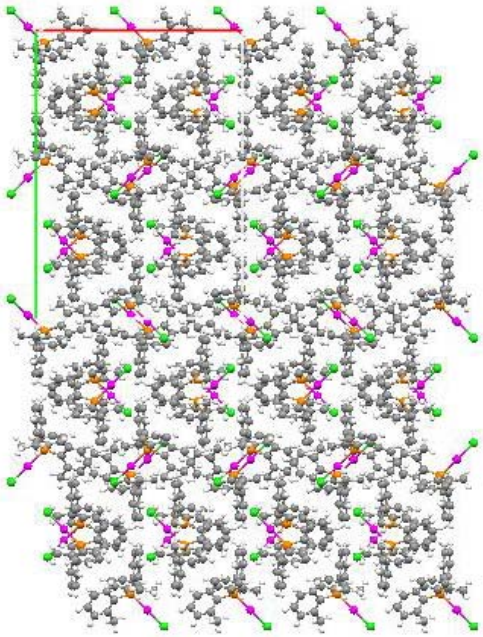
View down *c* axis for **1e**



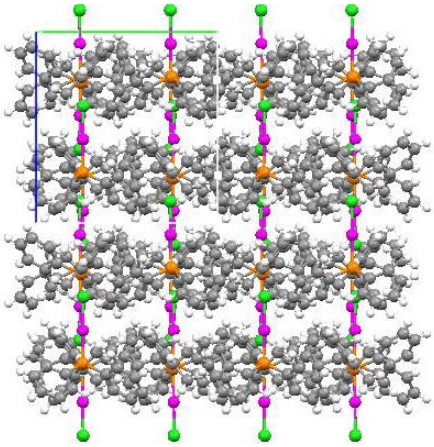
View down *a* axis for **I**



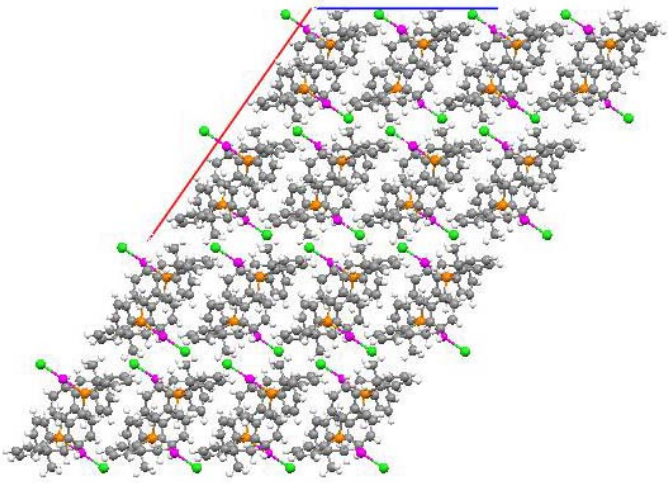
View down *b* axis for **I**



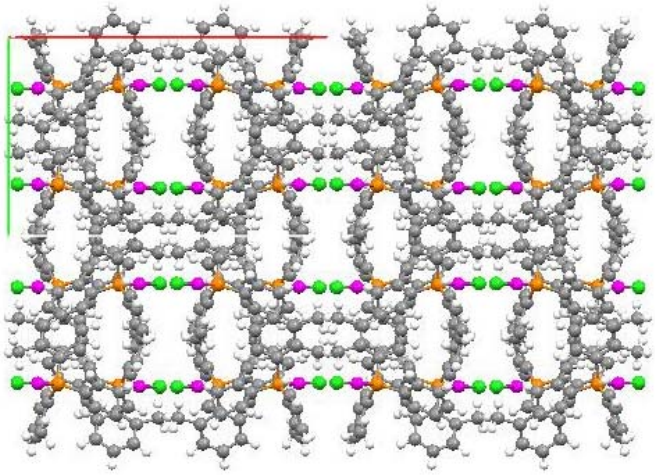
View down *c* axis for **I**



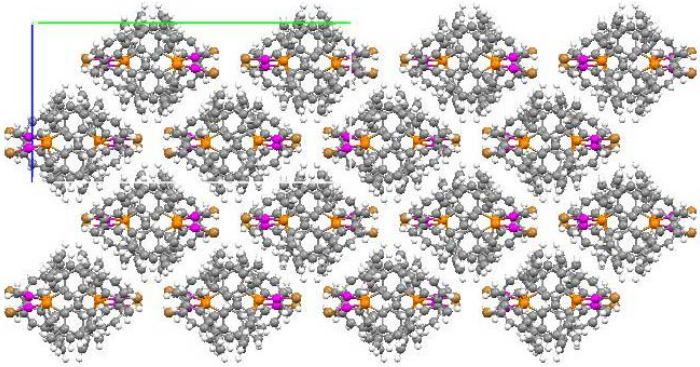
View down *a* axis for **Ia**



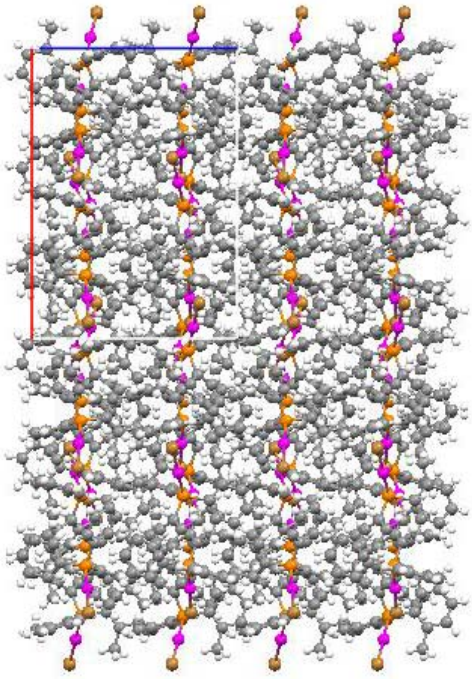
View down *b* axis for **Ia**



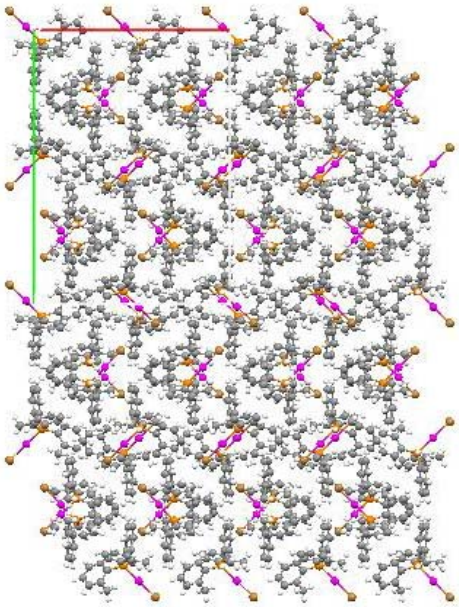
View down *c* axis for **Ia**



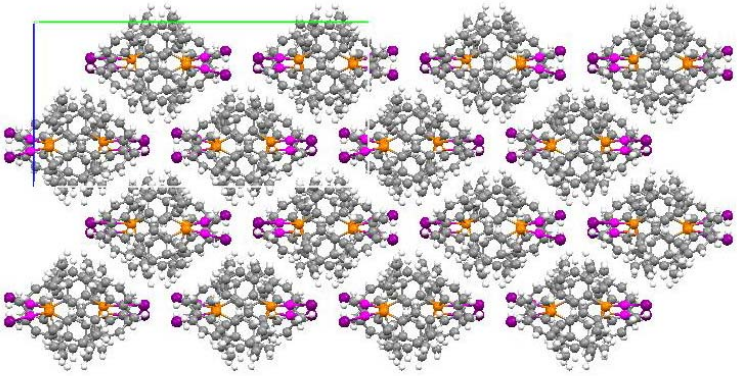
View down *a* axis for **II**



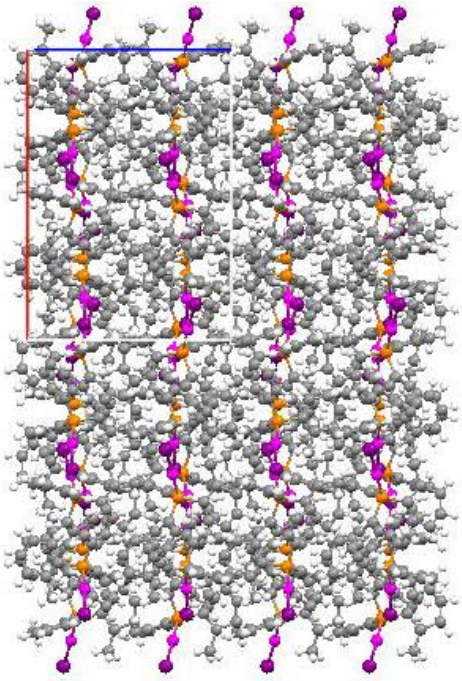
View down *a* axis for **II**



View down *c* axis for **II**



View down *a* axis for **III**



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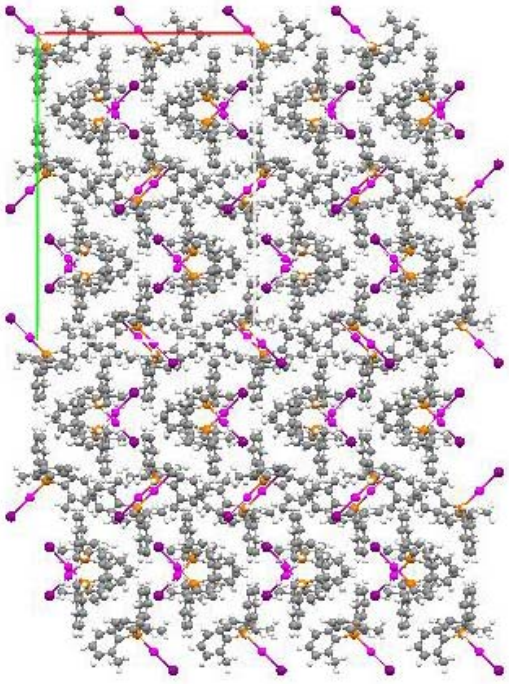
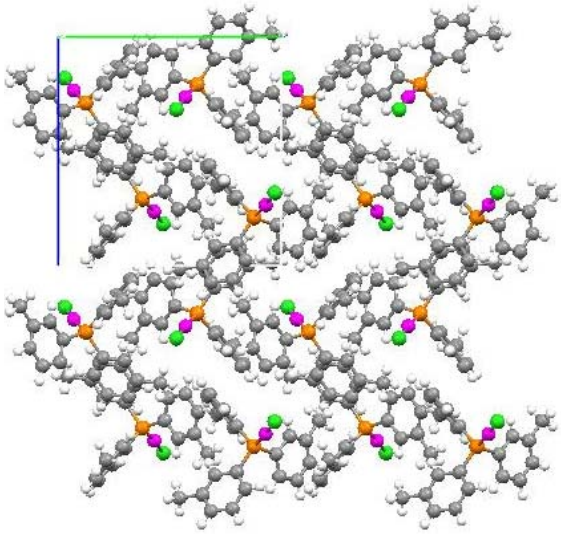
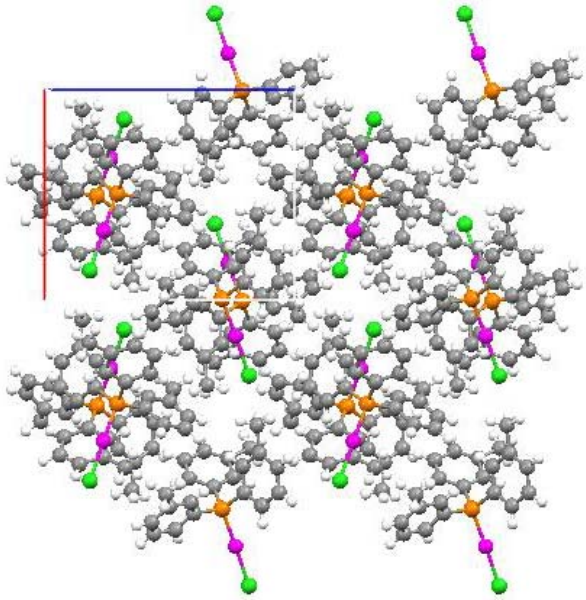


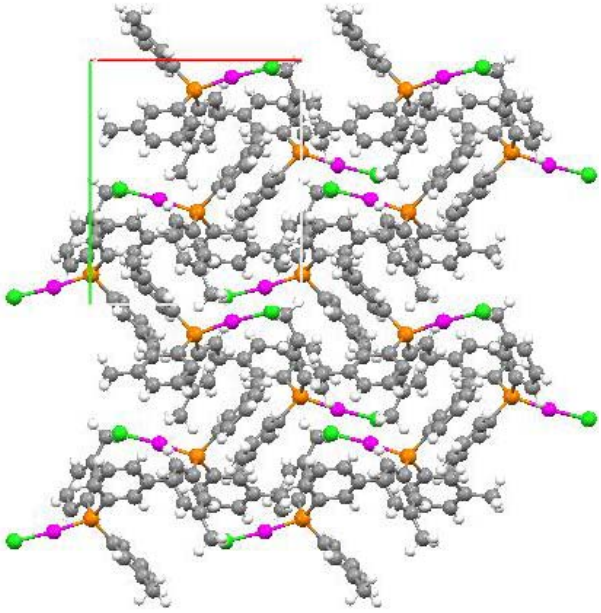
View down *c* axis for **III**



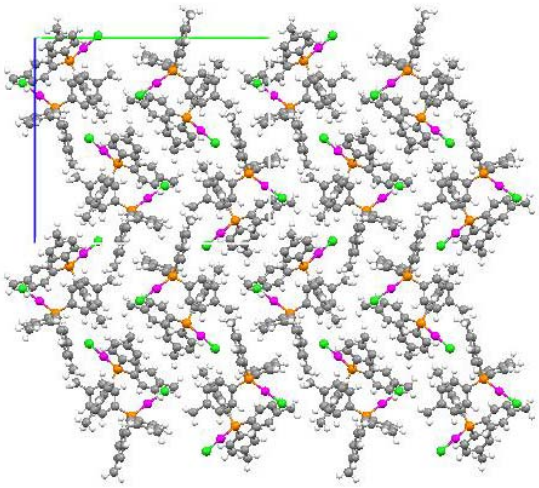
View down *a* axis for **IV**



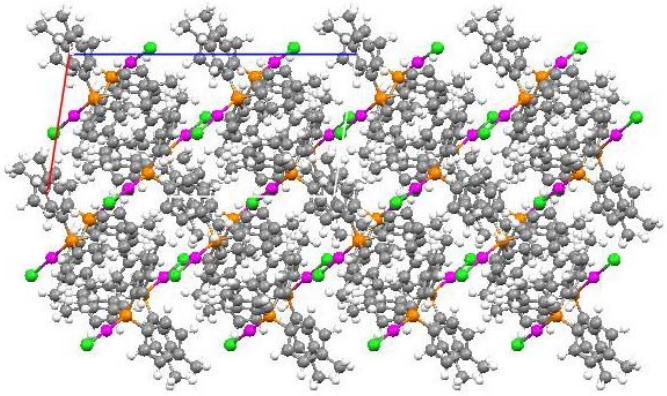
View down *b* axis for **IV**



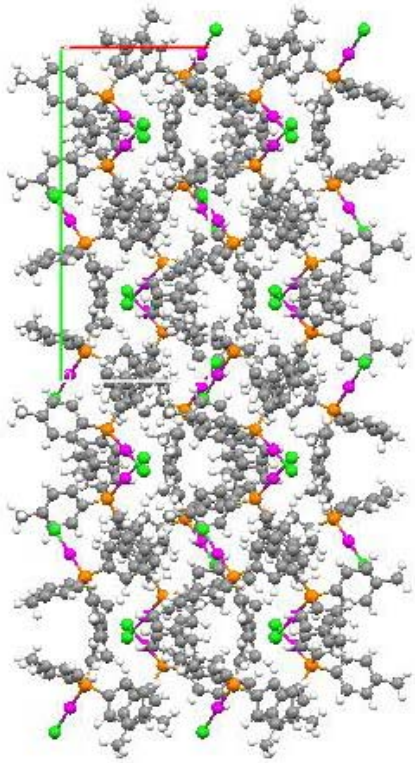
View down *c* axis for **IV**



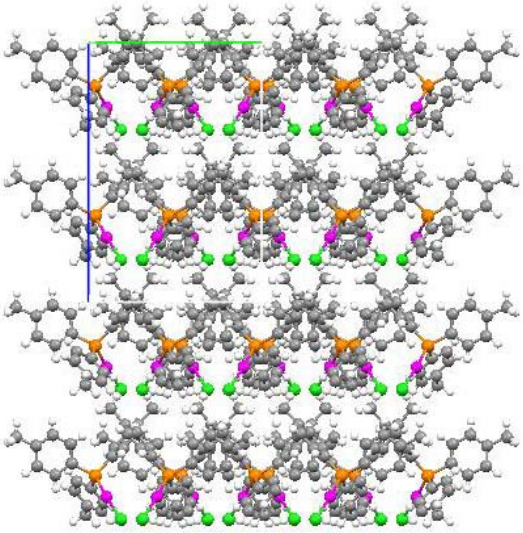
View down *a* axis for **V**



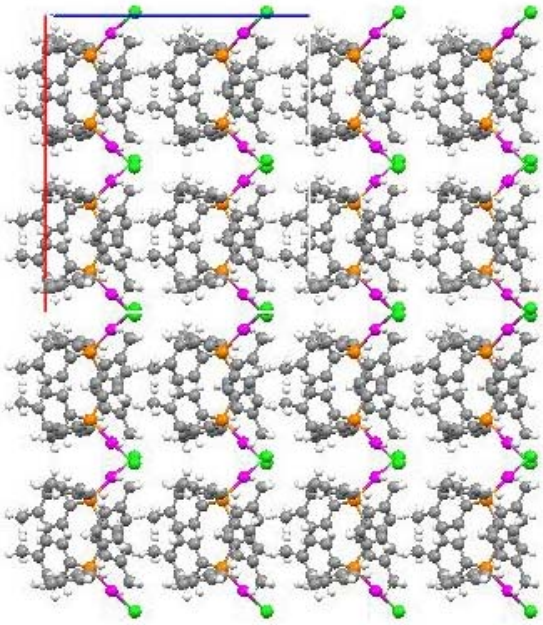
View down *a* axis for **V**



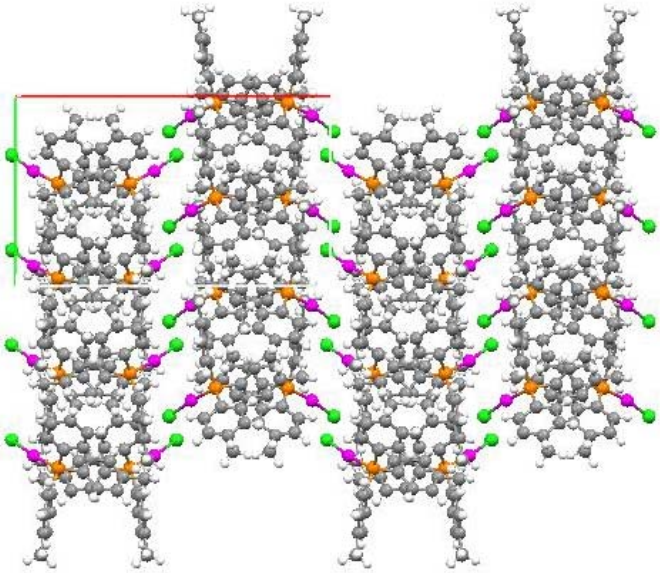
View down *c* axis for **V**



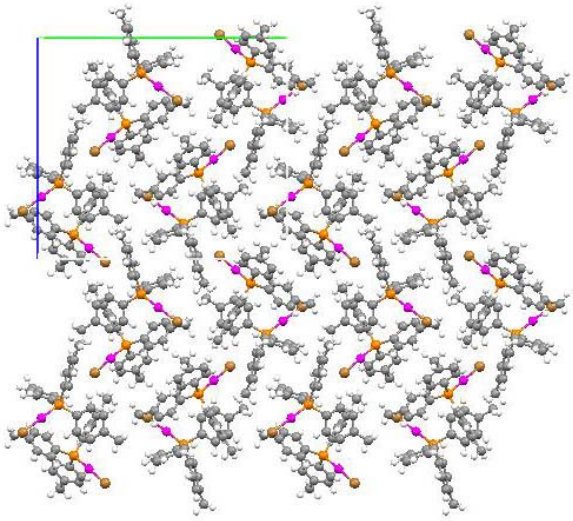
View down *a* axis for **Va**



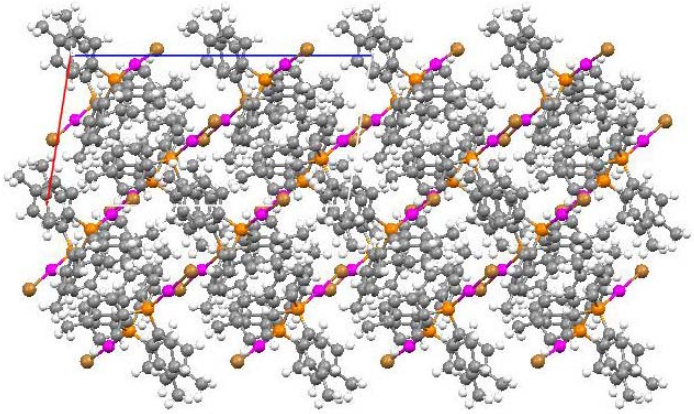
View down *b* axis for **Va**



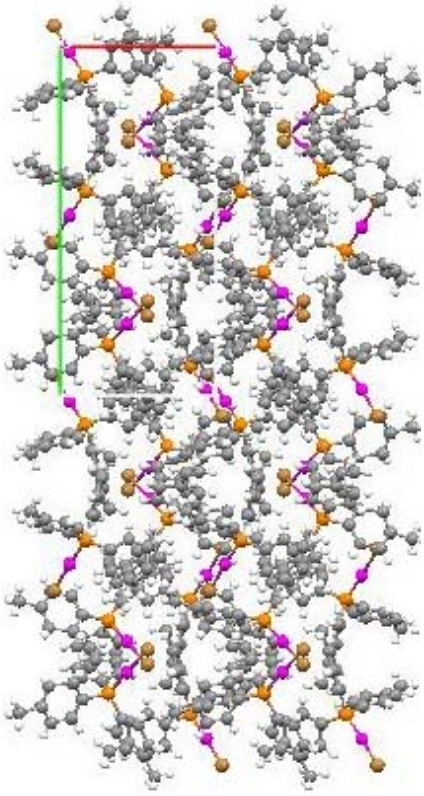
View down *c* axis for **Va**



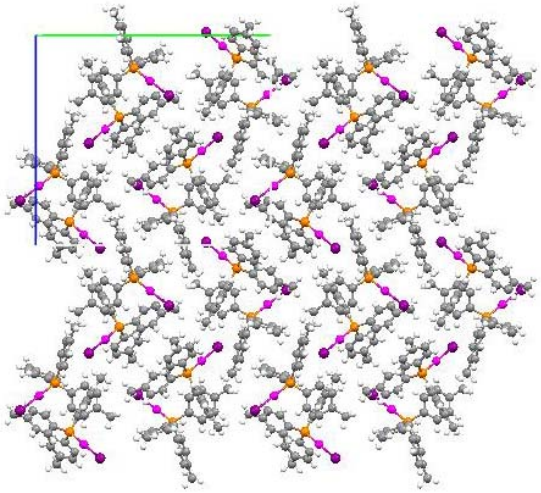
View down *a* axis for **VI**



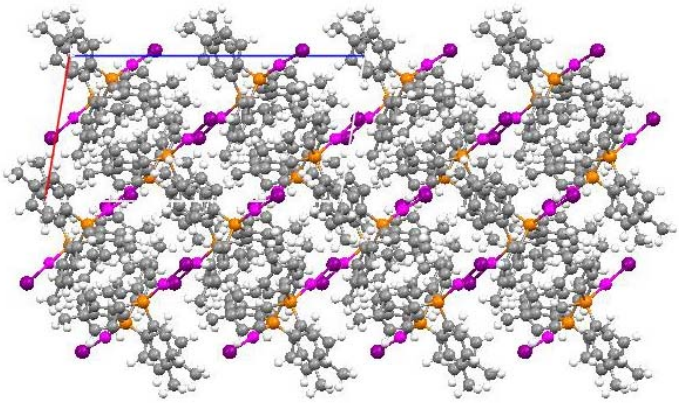
View down *b* axis for **VI**



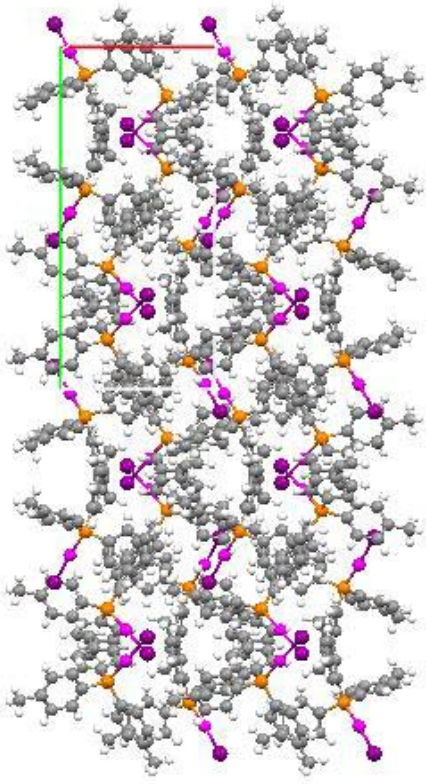
View down *c* axis for **VI**



View down *a* axis for **VII**



View down *b* axis for **VII**



View down *c* axis for **VII**