Electronic Supplementary Information

for

Hypervalent Diorganoantimony(III) Fluorides *via* Diorganoantimony(III) Cations – A General Method of Synthesis

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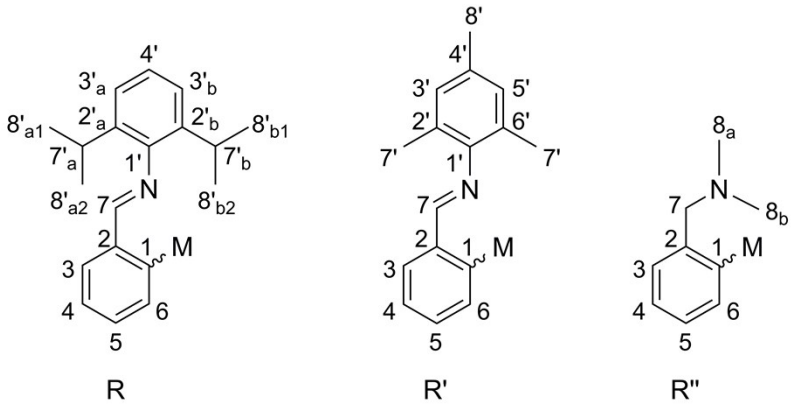

Scheme S1. Numbering scheme for NMR assignments.

[{2-(2′,6′-^{i}Pr$_2$C$_6$H$_3$N=CH)C$_6$H$_4$}$_2$Sb]$^+$[PF$_6$]$^-$·2CH$_2$Cl$_2$ (1·2CH$_2$Cl$_2$)

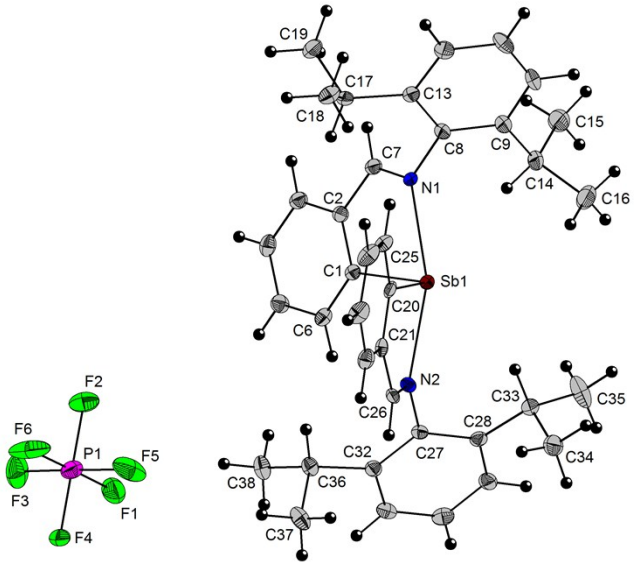

Figure S1. Structure of **1**·2CH$_2$Cl$_2$ showing the atom numbering scheme in the (Λ_{Sb})-cation. Displacement ellipsoids are depicted at the 30% probability level. Solvent molecules are omitted for clarity.

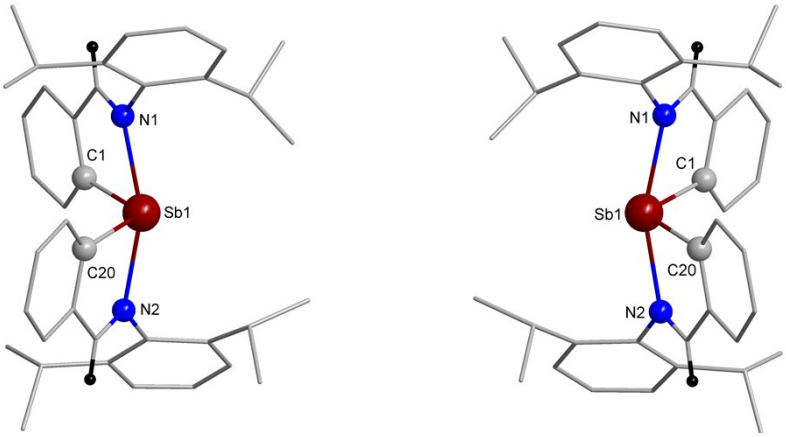

Figure S2. Structure of (Λ_{Sb})-cation (*left*) and (Δ_{Sb})-cation (*right*) in the crystal of **1**·2CH$_2$Cl$_2$.

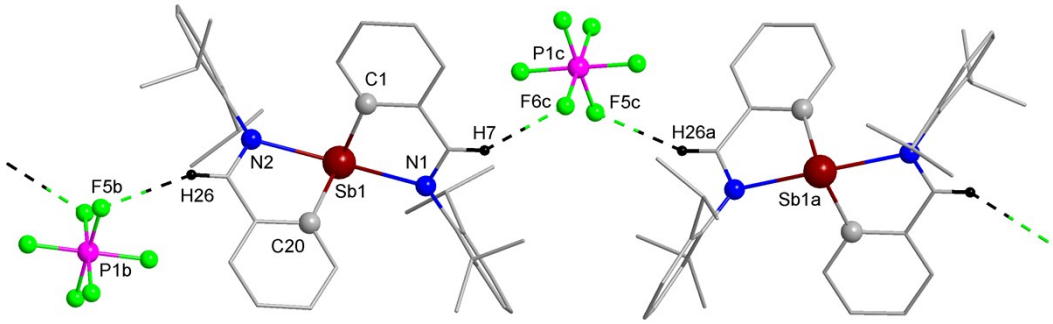

Figure S3. View of the chain polymer in the crystal of **1**·2CH$_2$Cl$_2$ based on F···H$_{imine}$ contacts between (Λ_{Sb})-cations and anions (only hydrogen atoms involved in cation-anion contacts are shown) [symmetry equivalent atoms (*–x, –0.5+y, 0.5–z*), (*–x, 1–y, 1–z*) and (*x, 0.5–y, –0.5+z*) are given by "a", "b" and "c", respectively].

-	cation-anion distance	F(5b)···H(26)$_{imine}$	2.48 Å	$\sum r_{vdW}$(F,H) 2.55 Å
		F(6c)···H(7)$_{imine}$	2.38 Å	

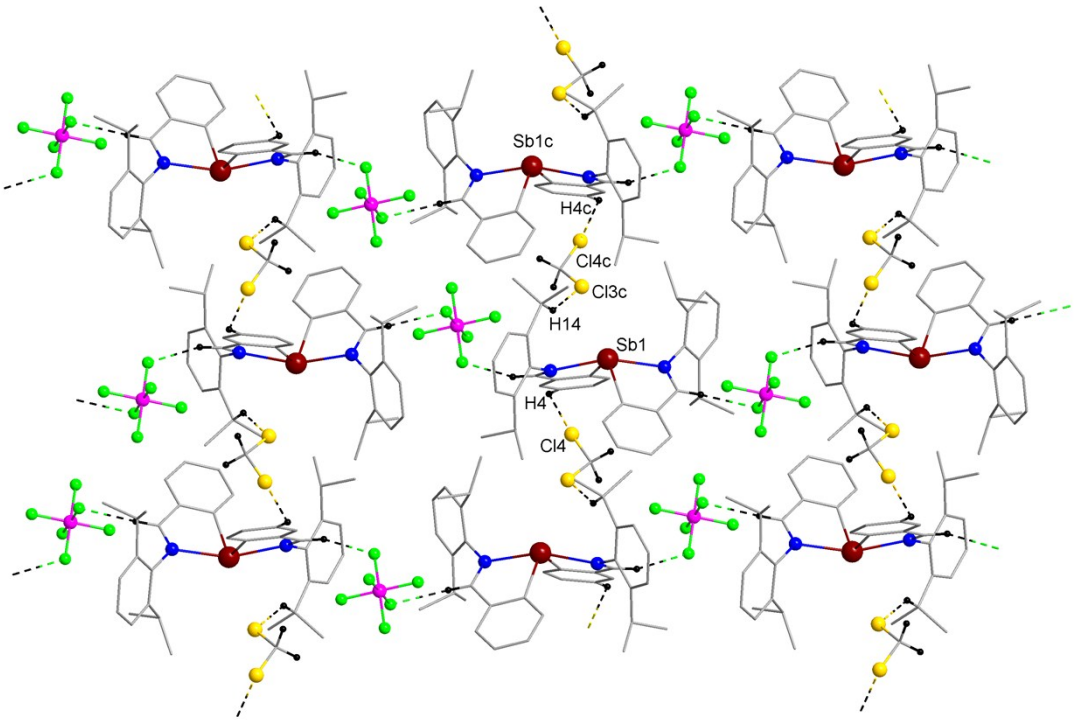

Figure S4. View of the layer in the crystal of **1**·2CH_2Cl_2 based on Cl···H contacts establish by the solvent molecules between parallel chains built from (Λ_{Sb})- and (Δ_{Sb})- cations, respectively, and anions (only hydrogen atoms involved in chlorine-hydrogen and cation-anion contacts are shown) [symmetry equivalent atoms (*x, 0.5–y, –0.5+z*) are given by "c"].

- cation-solvent contacts Cl(3c)···$H(14)_{methine}$ 2.85 Å; Cl(4c)···$H(4c)_{aryl}$ 2.87 Å; $\sum r_{vdW}$(Cl,H) 3.01 Å

- no further contacts between parallel layers.

[{2-(2′,4′,6′-$Me_3C_6H_2N$=CH)C_6H_4}$_2$Sb]$^+$[PF_6]$^-$·2$CHCl_3$ (3·2$CHCl_3$)

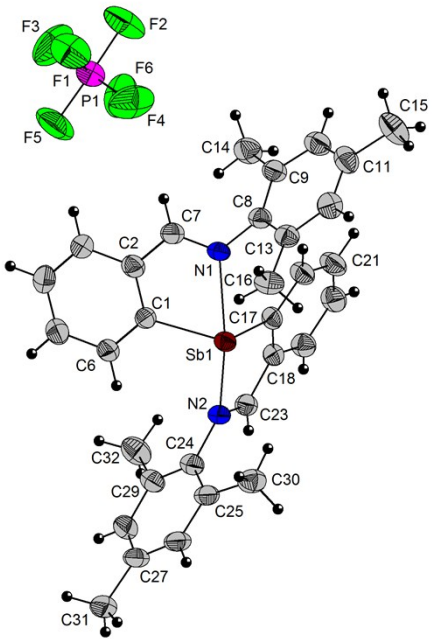

Figure S5. Structure of **3**·2$CHCl_3$ showing the atom numbering scheme in the (Λ_{Sb})-cation. Displacement ellipsoids are depicted at the 25% probability level. Solvent molecules are omitted for clarity.

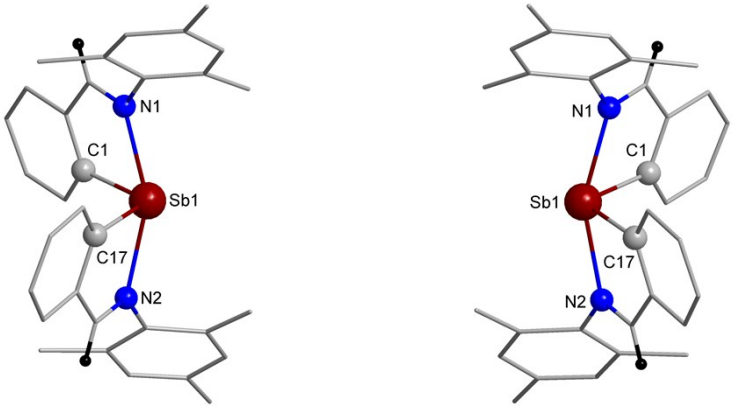

Figure S6. Structure of (Λ_{Sb})-cation (*left*) and (Δ_{Sb})-cation (*right*) in the crystal of **3**·2$CHCl_3$.

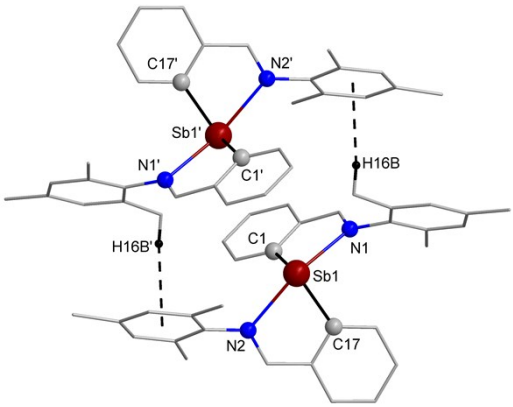

Figure S7. View of the dinuclear association of (Λ_{Sb})- and (Δ_{Sb})-cations based on C–$H_{methyl}\cdots\pi$ ($Ar_{centroid}$) contacts in the crystal of **3**·2$CHCl_3$ (only hydrogen atoms involved in cation-cation contacts are shown) [symmetry equivalent atoms (*1–x, –y, 1–z*) are given by "prime"].

- cation-cation distance C(16)–H(16B)$_{methyl}\cdots$Ar$_{centroid}${C(24')-C(29')} 2.85 Å (γ = 3.8°)

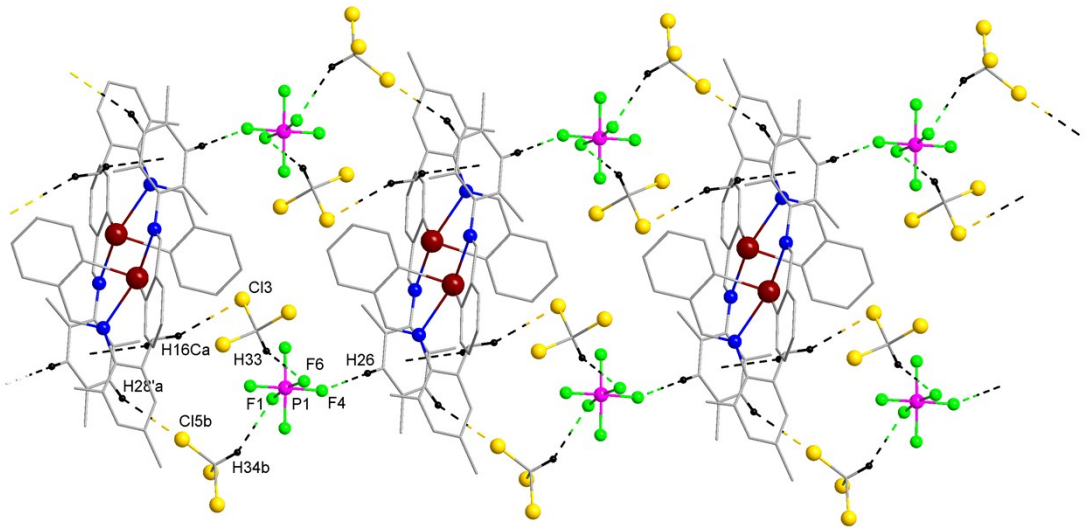

Figure S8. View of the chain polymer built from dimers of cations connected through anions and solvent molecules in the crystal of **3**·2CHCl$_3$ (only hydrogen atoms involved in cation-anion, cation-solvent and anion-solvent contacts are shown) [symmetry equivalent atoms (*–1+x, y, z*), (*–x, –y, 1–z*) and (*–1+x, y, z*) are given by "a", "prime a" and "b", respectively].

-	cation-anion distance	F(4)···H(26)$_{aryl}$	2.46 Å	$\sum r_{vdW}$(F,H) 2.55 Å
-	anion-solvent distance	F(1)···H(34b)$_{solvent}$	2.44 Å	
		F(6)···H(33)$_{solvent}$	2.49 Å	
-	cation-solvent distance	Cl(3)···H(16Ca)$_{methyl}$	2.94 Å	$\sum r_{vdW}$(Cl,H) 3.01 Å
		Cl(5b)···H(28'a)$_{aryl}$	2.97 Å	

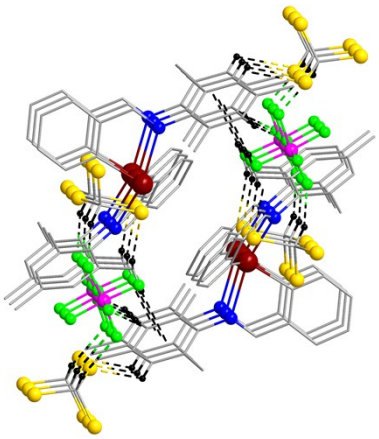

Figure S9. View along axis *a* of the chain polymer built from dimers of cations connected through anions and solvent molecules in the crystal of **3**·2CHCl$_3$.

- no further contacts between parallel chains.

[2-(2′,6′-^{i}Pr$_2$C$_6$H$_3$N=CH)C$_6$H$_4$]$_2$SbF (5)

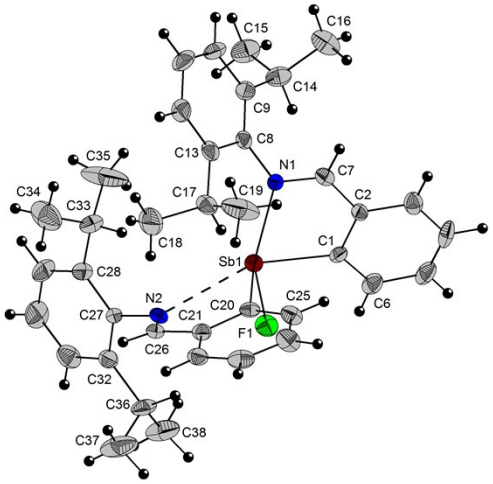

Figure S10. Structure of (C_{Sb})-**5**, showing the atom numbering scheme. Displacement ellipsoids are depicted at the 25% probability level.

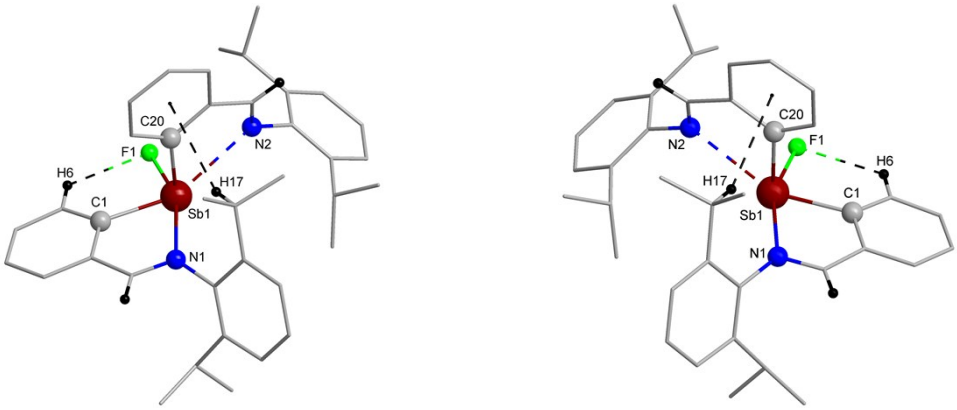

Figure S11. Molecular structure of (C_{Sb})-**5** isomer (*left*) and (A_{Sb})-**5** isomer (*right*) in the crystal of **5**, showing the intramolecular F···H and C–H$_{methine}$···π (Ar$_{centroid}$) contacts (only imine hydrogen atoms and hydrogen atoms involved in intramolecular contacts are shown).

- intramolecular distance	F(1)···H(6)$_{aryl}$	2.40 Å	$\sum r_{vdW}$(F,H) 2.55 Å
	C(17)–H(17)$_{methine}$···Ar$_{centroid}${C(20)-C(25)}		2.77 Å (γ = 22.1°)

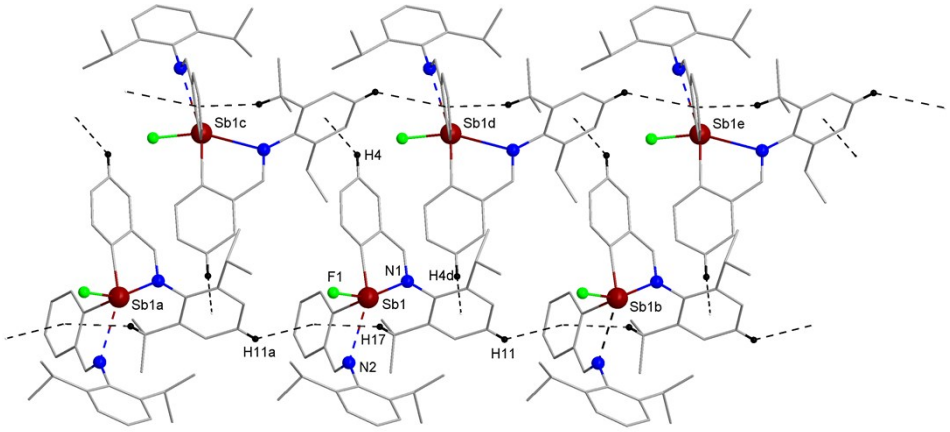

Figure S12. View of a ribbon-like polymer of (C_{Sb})-**5** isomers based on C–H···π (Ar$_{centroid}$) contacts in the crystal of **5** (only hydrogen atoms involved in C–H···π contacts are shown) [symmetry equivalent atoms (*x, y, 1+z*), (*x, y, –1+z*), (*1–x, –y, 0.5+z*), (*1–x, –y, –0.5+z*) and (*1–x, –y, –1.5+z*) are given by "a", "b", "c", "d" and "e", respectively].

- intermolecular distance	C(11a)–H(11a)$_{aryl}$···Ar$_{centroid}${C(20)-C(25)}		2.96 Å (γ = 19.4°)
	C(4)–H(4)$_{aryl}$···Ar$_{centroid}${C(8c)-C(13c)}		2.82 Å (γ = 9.4°)

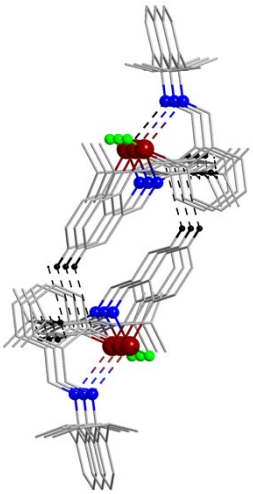

Figure S13. View along axis *c* of the ribbon-like polymer of (C_{Sb})-**5** isomers in the crystal of **5**.

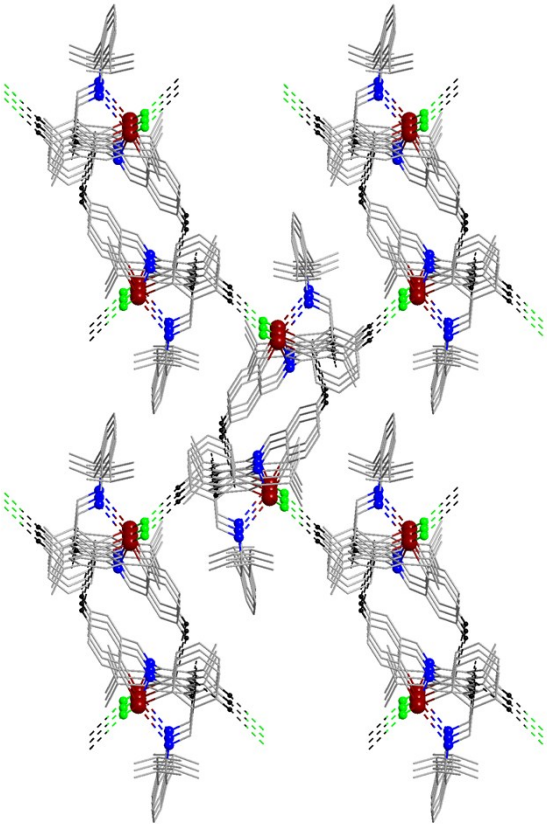

Figure S14. View along axis *c* showing the F···H contacts between parallel ribbon-like polymers of (C_{Sb})-**5** isomers (the central one) and four neighboring polymers of (A_{Sb})-**5** isomers in the crystal of **5** [symmetry equivalent atoms (*–0.5+x, 0.5–y, z*) are given by "f"].

- inter-chain distance F(1)···H(22f)$_{aryl}$ 2.54 Å $\sum r_{vdW}$(F,H) 2.55 Å

[2-(2′,6′-^{i}Pr$_2$C$_6$H$_3$N=CH)C$_6$H$_4$]PhSbF (6)

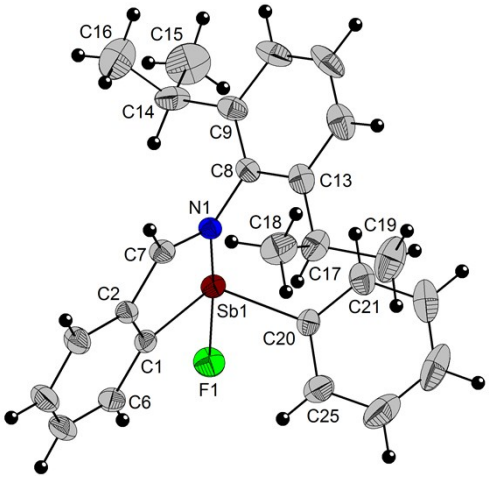

Figure S15. Structure of (C_{Sb})-**6**, showing the atom numbering scheme. Displacement ellipsoids are depicted at the 25% probability level.

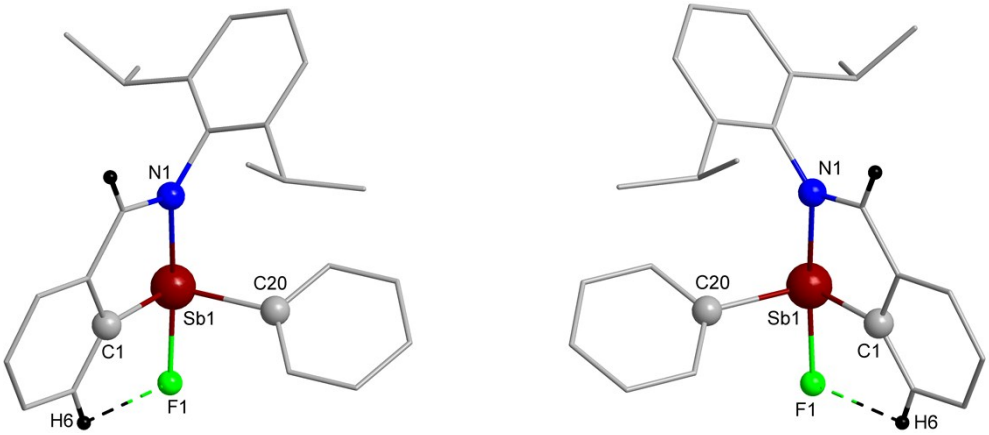

Figure S16. Molecular structure of (C_{Sb})-**6** isomer (*left*) and (A_{Sb})-**6** isomer (*right*) in the crystal of **6**, showing the intramolecular fluorine-hydrogen contact (only imine hydrogen atom and the hydrogen atom involved in the intramolecular contacts are shown).

- intramolecular distance F(1)···H(6)$_{aryl}$ 2.48 Å $\sum r_{vdW}$(F,H) 2.55 Å

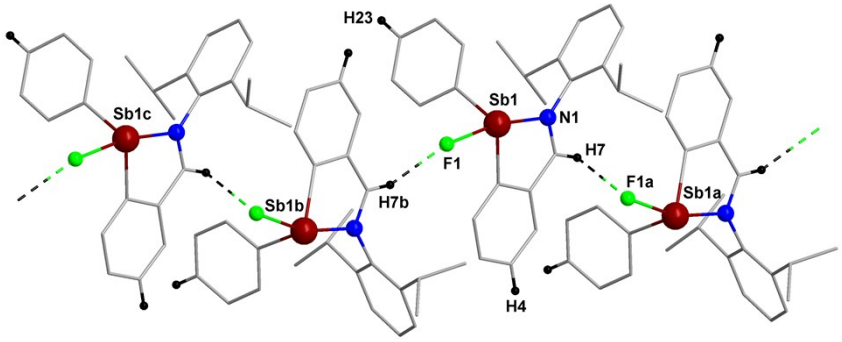

Figure S17. View of the chain polymer of alternating (C_{Sb})-**6** and (A_{Sb})-**6** isomers based on F···H$_{imine}$ contacts in the crystal of **6** (only hydrogen atoms involved in intermolecular contacts are shown) [symmetry equivalent atoms (*x, 1–y, 0.5+z*), (*x, 1–y, –0.5+z*) and (*x, y, –1+z*) are given by "a", "b" and "c", respectively].

- intermolecular distance F(1)···H(7b)$_{imine}$ 2.31 Å $\sum r_{vdW}$(F,H) 2.55 Å

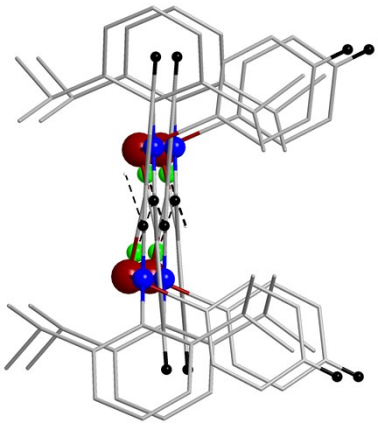

Figure S18. View along axis *c* of the chain polymer of alternating (C_{Sb})-**6** and (A_{Sb})-**6** isomers based on F···H_{imine} contacts in the crystal of **6**.

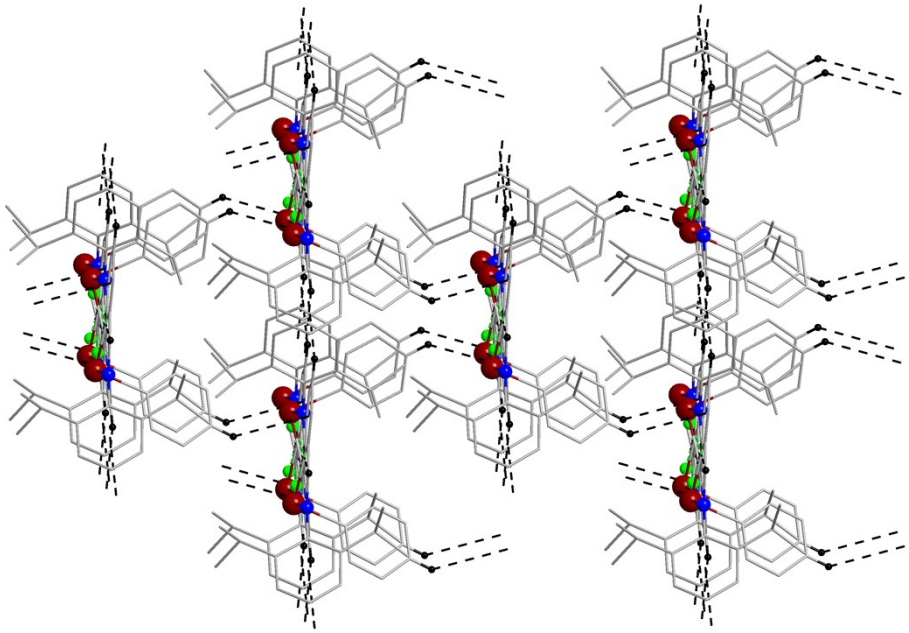

Figure S19. View along axis *c* of the 3D architecture based on C–H···π ($Ar_{centroid}$) contacts between parallel chain polymers in the crystal of **6** [symmetry equivalent atoms (*0.5+x, 1.5–y, –0.5+z*), (*–0.5+x, 0.5+y, –1+z*) and (*–0.5+x, 0.5–y, –1.5+z*) are given by "d", "e" and "f", respectively].

-	inter-chain distance	C(23)–$H(23)_{aryl}$···$Ar_{centroid}${C(1d)-C(6d)}	2.96 Å (γ = 22.0°)
		C(4e)–$H(4e)_{aryl}$···$Ar_{centroid}${C(8f)-C(13f)}	3.07 Å (γ = 14.8°)

[2-(Me$_2$NCH$_2$)C$_6$H$_4$]$_2$SbF (7)

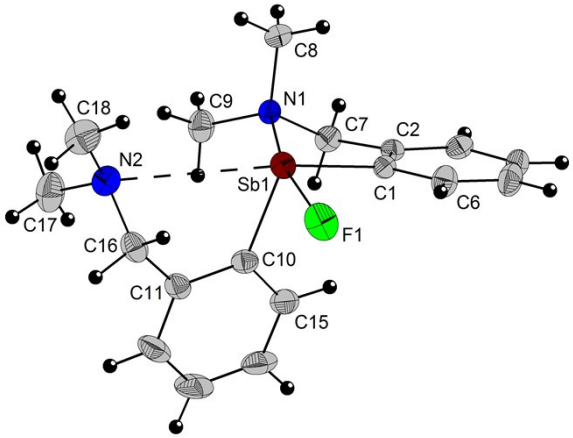

Figure S20. Structure of (A_{Sb})(pS_{N1},pS_{N2})-**7**, showing the atom numbering scheme. Displacement ellipsoids are depicted at the 25% probability level.

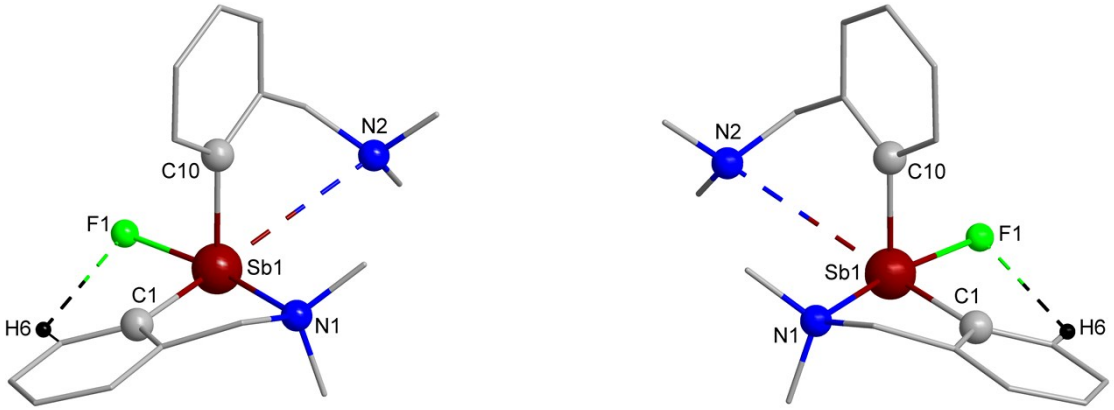

Figure S21. Molecular structure of (C_{Sb})(pR_{N1},pR_{N2})-**7** isomer (*left*) and (A_{Sb})(pS_{N1},pS_{N2})-**7** isomer (*right*) in the crystal of **7**, showing the intramolecular fluorine-hydrogen contact (only the hydrogen atom involved in the intramolecular contact is shown).

- intramolecular distance F(1)···H(6)$_{aryl}$ 2.48 Å $\sum r_{vdW}$(F,H) 2.55 Å

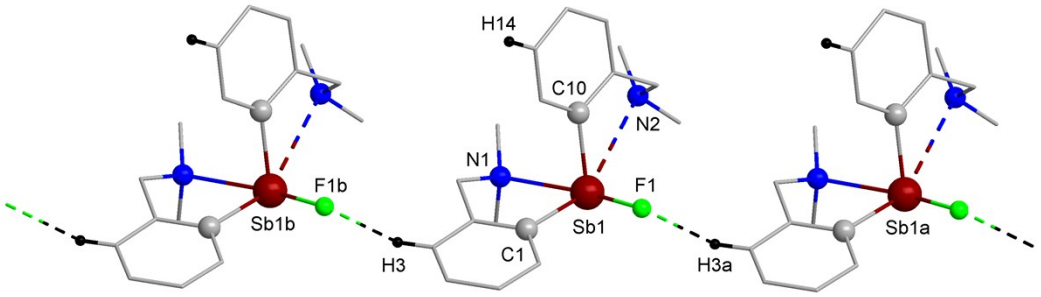

Figure S22. View of the chain polymer of (A_{Sb})(pS_{N1},pS_{N2})-**7** isomers based on F···H$_{aryl}$ contacts in the crystal of **7** (only hydrogen atoms involved in intermolecular contacts are shown) [symmetry equivalent atoms (*x, 1+y, z*) and (*x, –1+y, z*) are given by "a" and "b", respectively].

- intermolecular distance F(1)···H(3a)$_{aryl}$ 2.49 Å $\sum r_{vdW}$(F,H) 2.55 Å

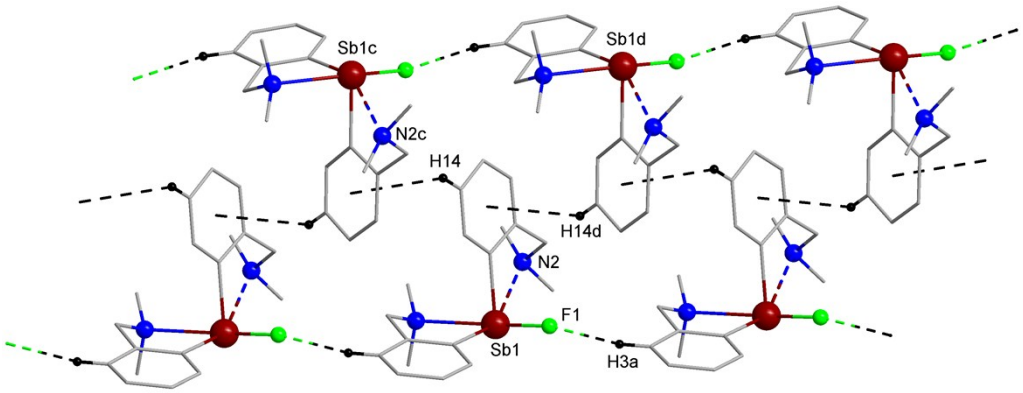

Figure S23. View of a pair of chain polymers of (A_{Sb})(pS_{N1},pS_{N2})-**7** isomers with inter-chain C–H···π ($Ar_{centroid}$) contacts in the crystal of **7** (only hydrogen atoms involved in intermolecular contacts are shown) [symmetry equivalent atoms (*0.5–x, –0.5+y, 0.5–z*) and (*0.5–x, 0.5+y, 0.5–z*) are given by "c" and "d", respectively].

- inter-chain distance C(14)–$H(14)_{aryl}$···$Ar_{centroid}${C(10c)-C(15c)} 3.09 Å (γ = 13.3°)

- no further contacts between parallel pair of chains built from (C_{Sb})(pR_{N1},pR_{N2})-**7** and (A_{Sb})(pS_{N1},pS_{N2})-**7** isomers, respectively, developed along axis *b*

[2-(Me_2NCH_2)C_6H_4]PhSbF (8)

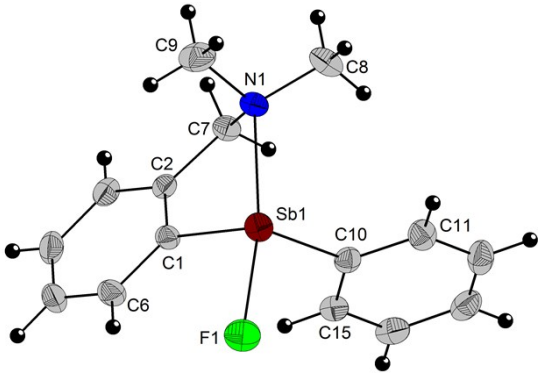

Figure S24. Structure of (A_{Sb})(pR_{N1})-**8**, showing the atom numbering scheme. Displacement ellipsoids are depicted at the 25% probability level.

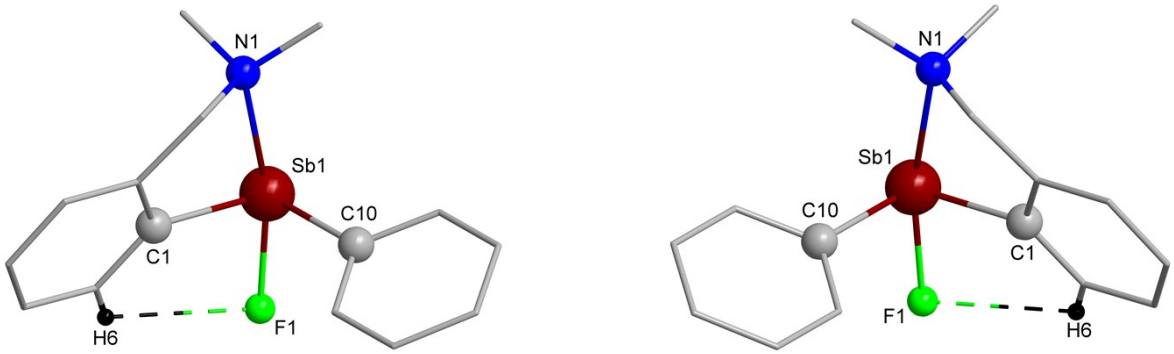

Figure S25. Molecular structure of (C_{Sb})(pS_{N1})-**8** isomer (*left*) and (A_{Sb})(pR_{N1})-**8** isomer (*right*) in the crystal of **8**, showing the intramolecular fluorine-hydrogen contact (only the hydrogen atom involved in the intramolecular contact is shown).

- intramolecular distance F(1)···H(6)$_{aryl}$ 2.53 Å $\sum r_{vdW}$(F,H) 2.55 Å

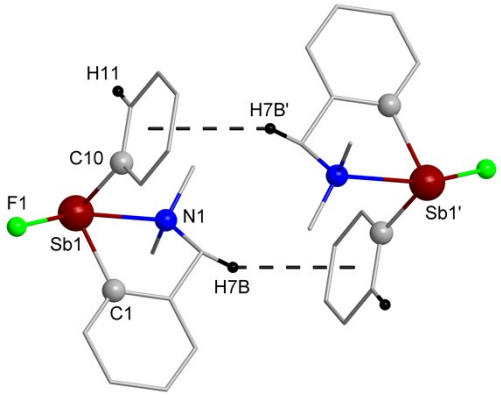

Figure S26. View of the dimer association of (C_{Sb})(pS_{N1})-**8** and (A_{Sb})(pR_{N1})-**8** isomers based on C–$H_{methylene}$···π ($Ar_{centroid}$) contacts in the crystal of **8** (only hydrogen atoms involved in intermolecular contacts are shown) [symmetry equivalent atoms (*1–x, –y, 2–z*) are given by "prime"].

- intermolecular distance C(7)–H(7B)$_{methylene}$···$Ar_{centroid}${C(10')-C(15')} 2.99 Å (γ = 17.7°)

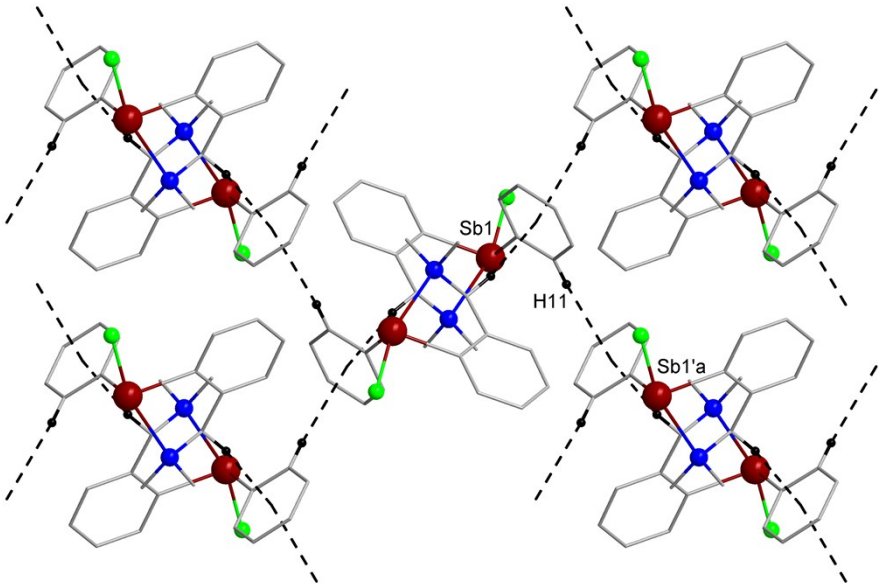

Figure S27. View along axis *a* of a fragment of the layer of dimers based on C–$H_{aryl}\cdots\pi$ ($Ar_{centroid}$) contacts in the crystal of **8** (only hydrogen atoms involved in intermolecular contacts are shown) [symmetry equivalent atoms (*0.5–x, –0.5+y, 1.5–z*) are given by "prime a"].

- intermolecular distance C(11)–$H(11)_{aryl}\cdots Ar_{centroid}${C(10'a)-C(15'a)} 3.02 Å (γ = 13.7°)

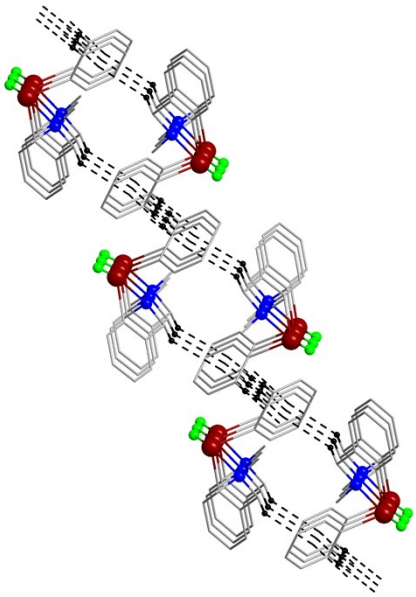

Figure S28. View along axis *b* of a fragment of the layer of dimers based on C–$H_{aryl}\cdots\pi$ ($Ar_{centroid}$) contacts in the crystal of **8** (only hydrogen atoms involved in intermolecular contacts are shown).

- no further contacts between parallel layers

Table S1. Crystallographic Data and Details of Data Collection and Structure Refinement Parameters for Compounds **1**·2CH_2Cl_2 and **3**·2$CHCl_3$

	1·2CH_2Cl_2	**3**·2$CHCl_3$
chemical formula	$C_{40}H_{48}Cl_4F_6N_2PSb$	$C_{34}H_{34}Cl_6F_6N_2PSb$
fw (g mol^{-1})	965.32	950.05
cryst size [mm]	0.04x0.10x0.12	0.10x0.18x0.22
cryst syst	monoclinic	triclinic
space group	$P2_1/c$	P-1
a (Å)	10.3364(4)	12.2715(12)
b (Å)	24.8372(7)	12.4401(9)
c (Å)	16.7958(5)	15.1691(10)
α (deg)	90	80.778(6)
β (deg)	98.284(3)	71.653(8)
γ (deg)	90	70.246(8)
V (Å^3)	4267.0(2)	2064.9(3)
Z	4	2
ρ_{calcd} (g cm^{-3})	1.503	1.528
μ (MoKα) (mm^{-1})	0.992	
μ (CuKα) (mm^{-1})		9.708
Absorption correction	Multi-scan[1]	Multi-scan[1]
F(000)	1960	948
T (K)	110	293
θ min / max (deg)	2.9 / 25.0	3.1 / 62.1
Reflns collected	19369	11151
Reflns independent	7483	6479
Reflns observed	4640	5226
R_{int}	0.052	0.070
No. parameters	516	589
Goodness-of-fit on F^2	0.84	0.97
final R indices [$I > 2\sigma(I)$]		
R_1	0.0375	0.0611
wR_2	0.0742	0.1489
R indices (all data)		
R_1	0.0721	0.0698
wR_2	0.0784	0.1521
$\Delta\rho_{min}$ and $\Delta\rho_{max}$ (e Å^{-3})	−0.56 and 0.82	−0.80 and 0.88

(1) Sheldrick, G. M. *SADABS, Program for area detector adsorption correction*; University of Göttingen: Göttingen, Germany, 1996.

Table S2. Crystallographic Data and Details of Data Collection and Structure Refinement Parameters for Compounds **5-8**

	5	**6**	**7**	**8**
chemical formula	$C_{38}H_{44}FN_2Sb$	$C_{25}H_{27}FNSb$	$C_{18}H_{24}FN_2Sb$	$C_{15}H_{17}FNSb$
fw (g mol^{-1})	669.50	482.23	409.14	352.05
cryst size [mm]	0.26x0.29x0.32	0.25x0.29x0.32	0.22x0.26x0.30	0.29x0.29x0.45
cryst syst	orthorhombic	monoclinic	monoclinic	monoclinic
space group	*Pna*2$_1$	*Cc*	*P*2$_1$/*n*	*P*2$_1$/*n*
a (Å)	14.847(11)	15.136(2)	9.1371(8)	11.3139(8)
b (Å)	21.755(16)	10.038(2)	8.0760(7)	8.1198(6)
c (Å)	10.693(8)	15.178(3)	24.949(2)	15.8500(12)
α (deg)	90	90	90	90
β (deg)	90	100.706(4)	95.549(2)	101.487(1)
γ (deg)	90	90	90	90
V (Å^3)	3454(4)	2265.9(7)	1832.4(3)	1426.92(18)
Z	4	4	4	4
ρ_{calcd} (g cm^{-3})	1.288	1.414	1.483	1.639
μ (MoKα) (mm^{-1})	0.831	1.235	1.513	1.927
Absorption correction	Multi-scan[1]	Multi-scan[1]	Multi-scan[1]	Multi-scan[1]
F(000)	1384	976	824	696
T (K)	297	297	297	297
θ min / max (deg)	1.7 / 25.0	2.5 / 25.0	1.6 / 25.0	2.0 / 25.0
Reflns collected	21151	10576	16818	13223
Reflns independent	6049	3944	3223	2516
Reflns observed	5253	3879	2982	2387
R_{int}	0.050	0.023	0.034	0.026
No. parameters	387	257	203	165
Goodness-of-fit on F^2	1.08	1.08	1.25	1.15
final *R* indices [$I > 2\sigma(I)$]				
R_1	0.0476	0.0215	0.0630	0.0281
wR_2	0.1028	0.0499	0.1085	0.0633
R indices (all data)				
R_1	0.0577	0.0220	0.0698	0.0302
wR_2	0.1078	0.0501	0.1115	0.0645
Flack	0.017(15)	−0.006(18)	-	-
$\Delta\rho_{min}$ and $\Delta\rho_{max}$ (e Å^{-3})	−0.80 and 1.09	−0.34 and 0.56	−0.55 and 0.84	−0.56 and 0.51

(1) Sheldrick, G. M. *SADABS, Program for area detector adsorption correction*; University of Göttingen: Göttingen, Germany, 1996.