Electronic Supplementary Information

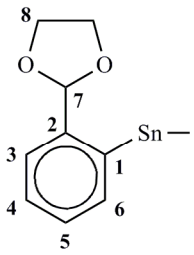
Di(imino)aryltin(IV) dichlorides as tectons for heterometallic coordination compounds

Ioana Barbul,[a] Richard A. Varga,*[a] Kieran C. Molloy[b] and Cristian Silvestru*[a]

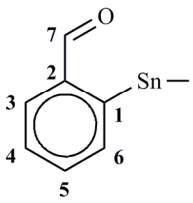
[a] *Departamentul de Chimie, Centrul de Chimie Supramoleculară Organică şi Organometalică (CCSOOM), Facultatea de Chimie şi Inginerie Chimică, Universitatea Babeş-Bolyai, RO-400028, Cluj-Napoca, Romania. E-mail: cristian.silvestru@ubbcluj.ro; richy@chem.ubbcluj.ro; Fax: (+40) 264-590818; Tel: (+40) 264-593833*
[b] *Department of Chemistry, University of Bath, Claveron Down, Bath BA2 7AY, UK. E-mail: k.c.molloy@bath.ac.uk; Fax: (+44) 1225-386231; Tel: (+44) 1225-386382*

Electronic Supplementary Material (ESI) for Dalton Transactions

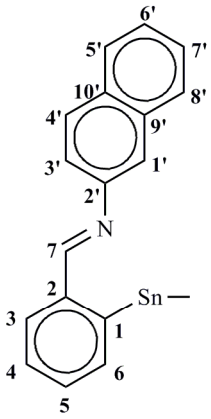
Numbering schemes for NMR resonance assignments



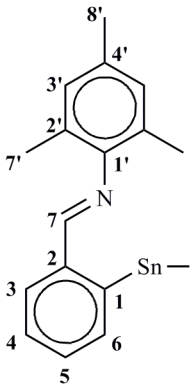
(**1**)



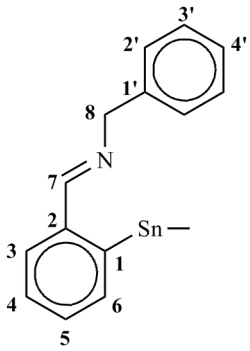
(**2**)



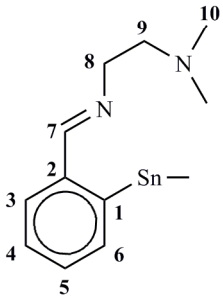
(**3**)



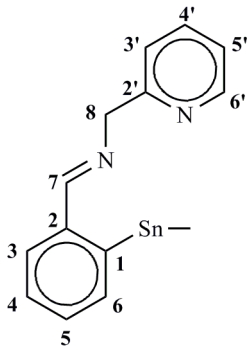
(**4**)



(**5**)



(**6**)



(**7**)

[2-{$(CH_2O)_2CH$}C_6H_4]$_2SnCl_2$ (1)

- the crystal contains a 1:1 mixture of Δ-[$pS_{O(1)}pS_{O(3)}$]-[$S_{C(7)}R_{C(16)}$]-**1** and Λ-[$pR_{O(1)}pR_{O(3)}$]-[$R_{C(7)}S_{C(16)}$]-**1** isomers

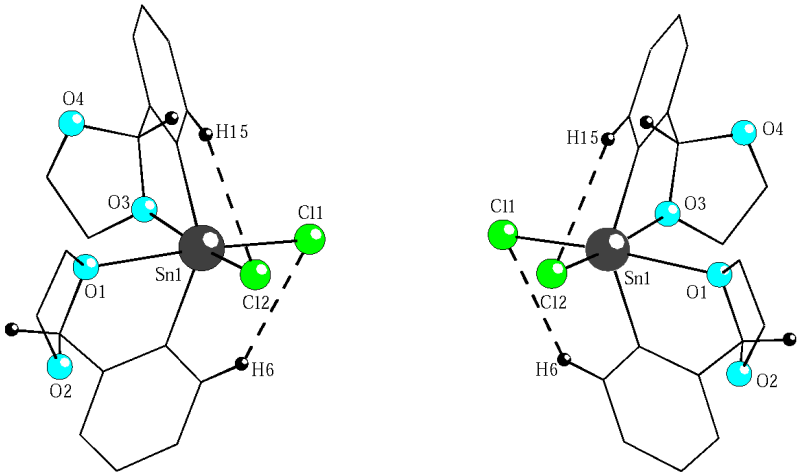


Figure S1. Molecular structure of Δ-[$pS_{O(1)}pS_{O(3)}$]-[$S_{C(7)}R_{C(16)}$]-**1** isomer (*left*) and Λ-[$pR_{O(1)}pR_{O(3)}$]-[$R_{C(7)}S_{C(16)}$]-**1** isomer (*right*) in the crystal of **1**, showing the intramolecular chlorine-hydrogen contacts (only methine hydrogens and hydrogen atoms involved in intramolecular contacts are shown).

- intramolecular distance Cl(1)···H(6)$_{aryl}$ 2.85 Å ∑r_{vdW}(Cl,H) 3.01 Å
  Cl(2)···H(15)$_{aryl}$ 2.88 Å

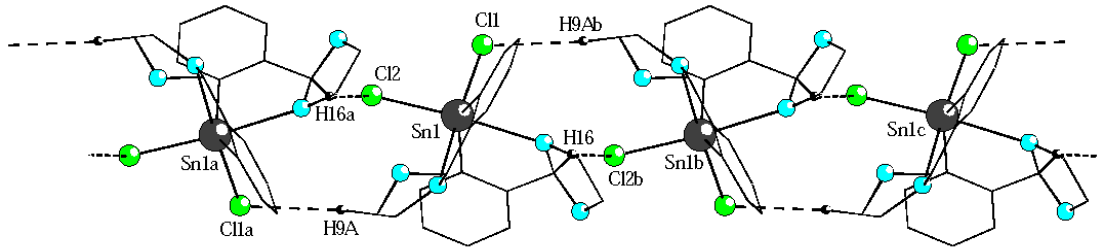


Figure S2. View along *a* axis of a chain polymer based on intermolecular chlorine-hydrogen contacts between alternating Δ-[$pS_{O(1)}pS_{O(3)}$]-[$S_{C(7)}R_{C(16)}$]-**1** and Λ-[$pR_{O(1)}pR_{O(3)}$]-[$R_{C(7)}S_{C(16)}$]-**1** isomers in the crystal of **1** (only hydrogen atoms involved in C–H···Cl contacts are shown) [symmetry equivalent atoms (*0.5+x, 1.5–y, 0.5+z*), (*–0.5+x, 1.5–y, –0.5+z*) and (*–1+x, y, –1+z*) are given by "a", "b" and "c", respectively].

- intermolecular distance Cl(1)···H(9Ab)$_{methylene}$ 2.77 Å ∑r_{vdW}(Cl,H) 3.01 Å
  Cl(2)···H(16a)$_{methine}$ 2.90 Å

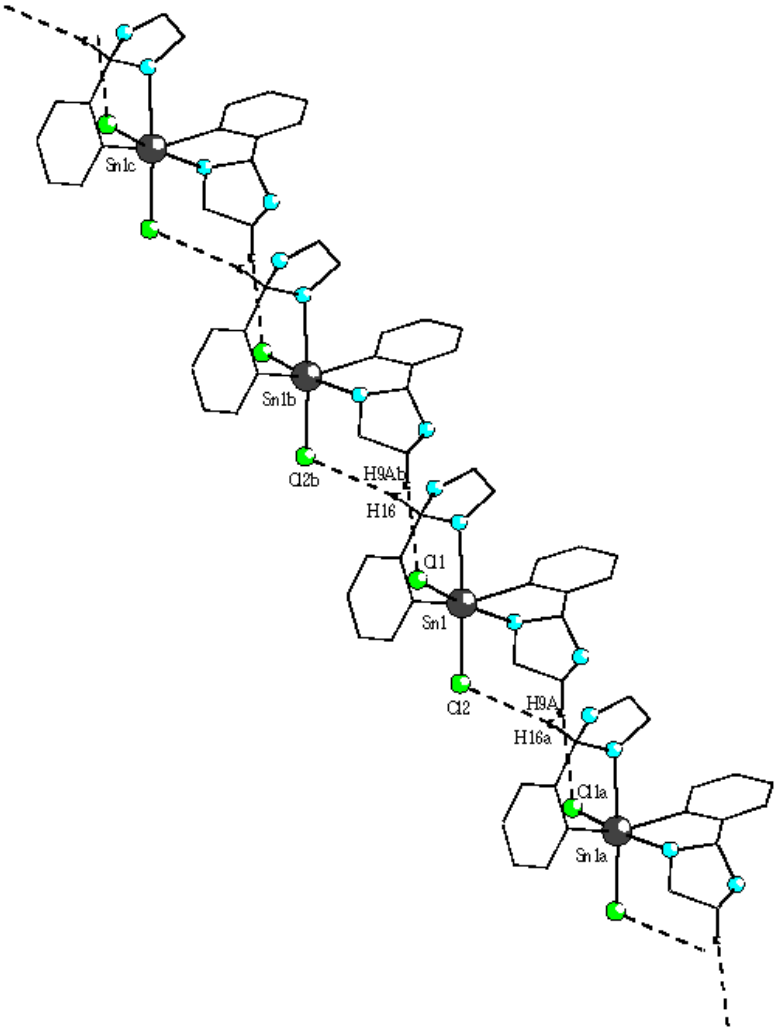


Figure S3. View along *b* axis of a chain polymer based on intermolecular chlorine-hydrogen contacts between alternating Δ-[$pS_{O(1)}pS_{O(3)}$]-[$S_{C(7)}R_{C(16)}$]-**1** and Λ-[$pR_{O(1)}pR_{O(3)}$]-[$R_{C(7)}S_{C(16)}$]-**1** isomers in the crystal of **1** (only hydrogen atoms involved in C–H···Cl contacts are shown) [symmetry equivalent atoms (*0.5+x*, *1.5–y*, *0.5+z*), (*–0.5+x*, *1.5–y*, *–0.5+z*) and (*–1+x*, *y*, *–1+z*) are given by "a", "b" and "c", respectively].

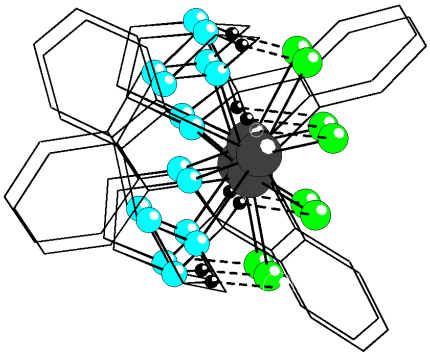


Figure S4. View along a chain polymer in the crystal of **1** (only hydrogen atoms involved in C–H···Cl contacts are shown).

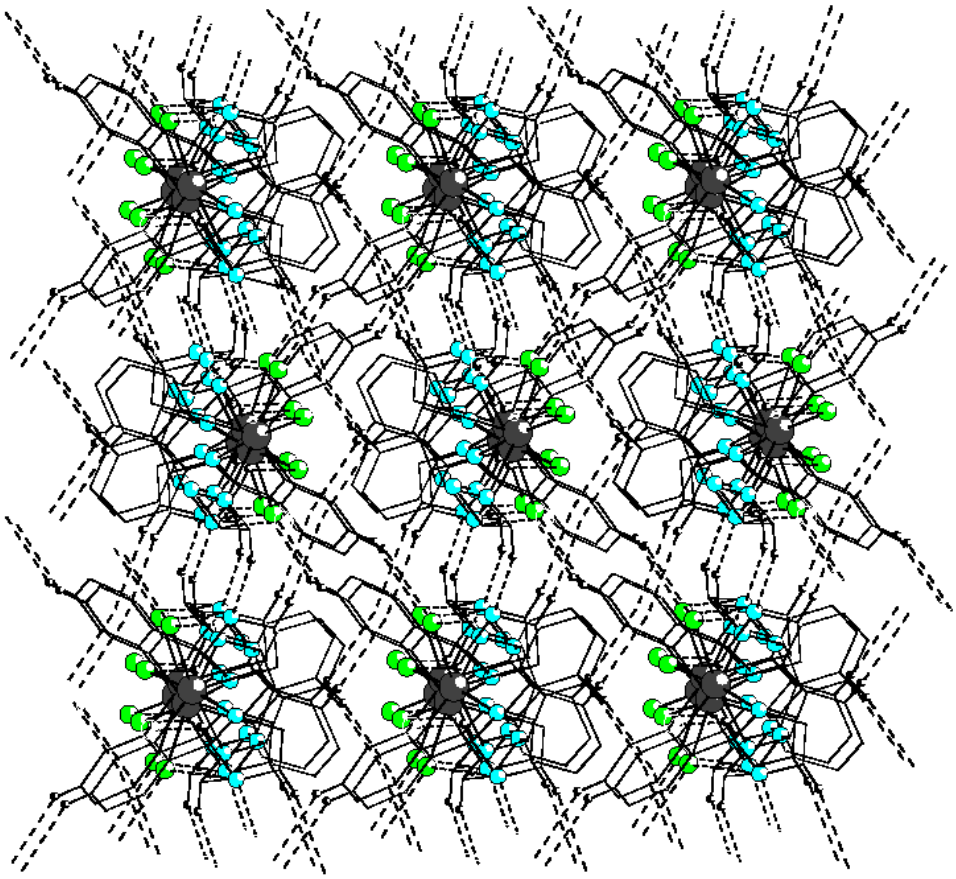


Figure S5. View of the 3D architecture in the crystal of **1**, based on chlorine-hydrogen, oxygen-hydrogen and C–H···π ($Ph_{centroid}$) contacts between parallel chain polymers (only hydrogen atoms involved in such contacts are shown) [symmetry equivalent atoms (*–0.5–x, 0.5+y, 0.5–z*), (*–x, 1–y, –z*), (*–1+x, y, z*) and (*–x, 1–y, –z*) are given by "d", "e", "f" and "g", respectively].

- inter-chain distance

  $Cl(1)\cdots H(14d)_{aryl}$ 2.94 Å $\sum r_{vdW}(Cl,H)$ 3.01 Å

  $O(4)\cdots H(8Ae)_{methine}$ 2.53 Å $\sum r_{vdW}(O,H)$ 2.60 Å

  $C(3f)–H(3f)_{aryl}\cdots Ph_{centroid}\{C(10)\text{-}C(15)\}$ 2.98 Å, γ = 4.7°

  $C(18g)–H(18Bg)_{methine}\cdots Ph_{centroid}\{C(10)\text{-}C(15)\}$ 2.83 Å, γ = 16.8°

[2-(O=CH)C$_6$H$_4$]$_2$SnCl$_2$ (2)

- the crystal contains a 1:1 mixture of Δ-**2** and Λ-**2** isomers

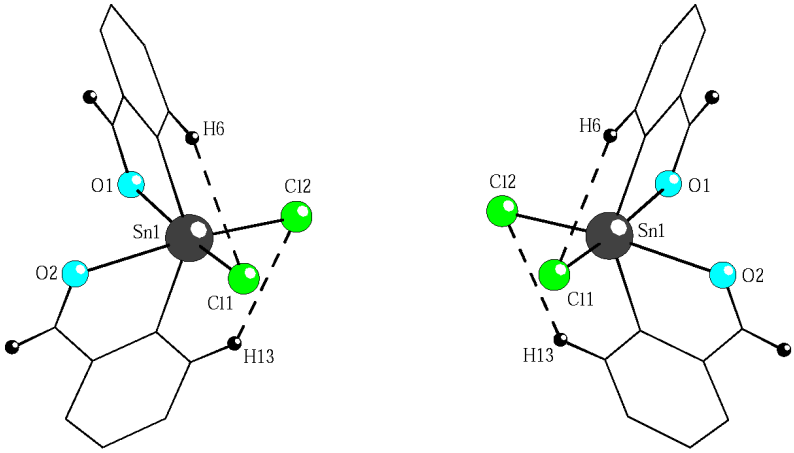


Figure S6. Molecular structure of Δ-**2** isomer (*left*) and Λ-**2** isomer (*right*) in the crystal of **2**, showing the intramolecular chlorine-hydrogen contacts (only carbonyl hydrogens and hydrogen atoms involved in intramolecular contacts are shown).

- intramolecular distance Cl(1)···H(6)$_{aryl}$ 2.87 Å Cl(2)···H(13)$_{aryl}$ 2.84 Å $\sum r_{vdW}$(Cl,H) 3.01 Å

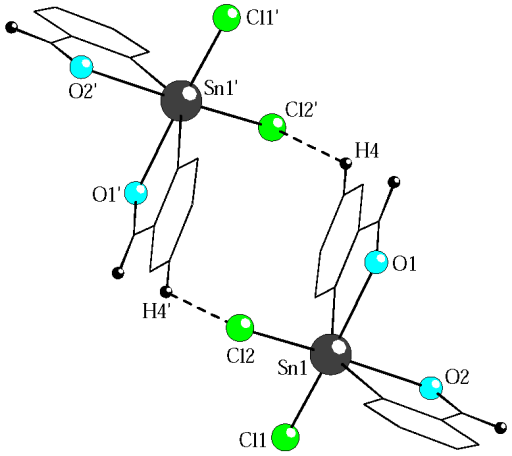


Figure S7. View along *a* axis of a dimer association of Δ-**2** and Λ-**2** isomers based on intermolecular chlorine-hydrogen contacts in the crystal of **2** (only carbonyl hydrogens and hydrogen atoms involved in intermolecular contacts are shown) [symmetry equivalent atoms (*–x, 1–y, 2–z*) are given by "prime"].

- intermolecular distance Cl(2)···H(4')$_{aryl}$ 2.93 Å $\sum r_{vdW}$(Cl,H) 3.01 Å

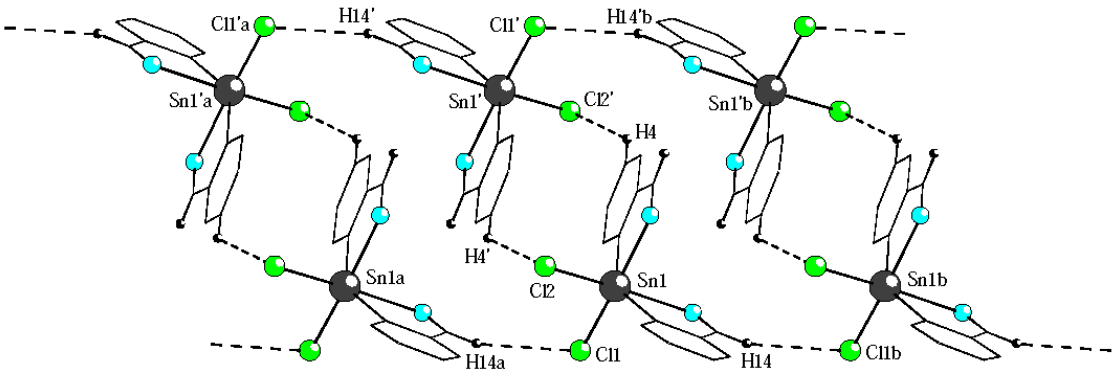


Figure S8. View along *a* axis of a ribbon-like polymer of dimers based on inter-dimer chlorine-hydrogen contacts in the crystal of **2** (only hydrogen atoms involved in intermolecular contacts are shown) [symmetry equivalent atoms (*–x, 1–y, 2–z*), (*x, y, 1+z*), (*–x, 1–y, 3–z*), (*x, y, –1+z*) and (*–x, 1–y, 1–z*) are given by "prime", "a", "prime a", "b" and "prime b", respectively].

- inter-dimer distance $Cl(1)\cdots H(14a)_{carbonyl}$ 2.95 Å $\sum r_{vdW}(Cl,H)$ 3.01 Å

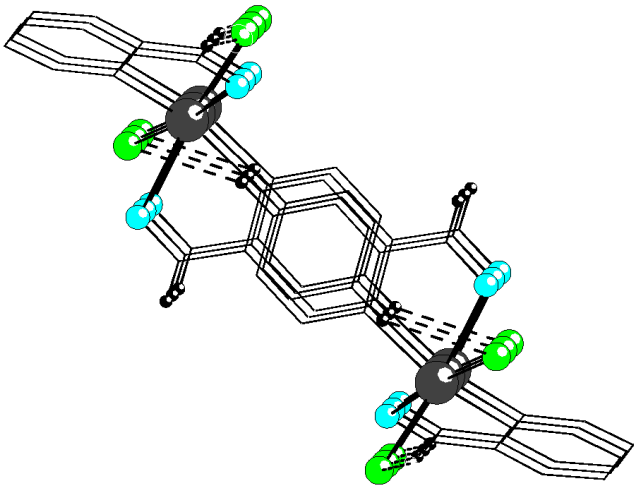


Figure S9. View along *c* axis of a ribbon-like polymer of dimers based on inter-dimer chlorine-hydrogen contacts in the crystal of **2** (only hydrogen atoms involved in intermolecular contacts are shown).

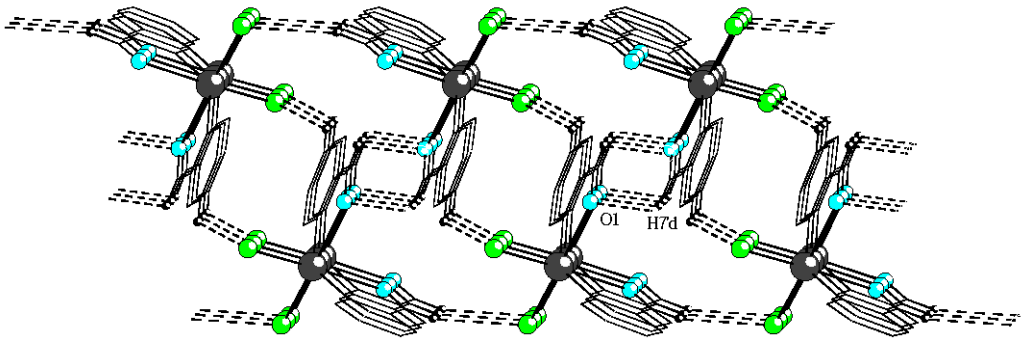


Figure S10. View along *a* axis of a layer based on inter-chain oxygen-hydrogen contacts in the crystal of **2** (only hydrogen atoms involved in intermolecular contacts are shown) [symmetry equivalent atoms (*1–x*, *1–y*, *1–z*) are given by "prime d"].

- inter-chain distance $O(1)\cdots H(7'd)_{carbonyl}$ 2.53 Å $\sum r_{vdW}(O,H)$ 2.60 Å
- no further contacts between parallel layers.

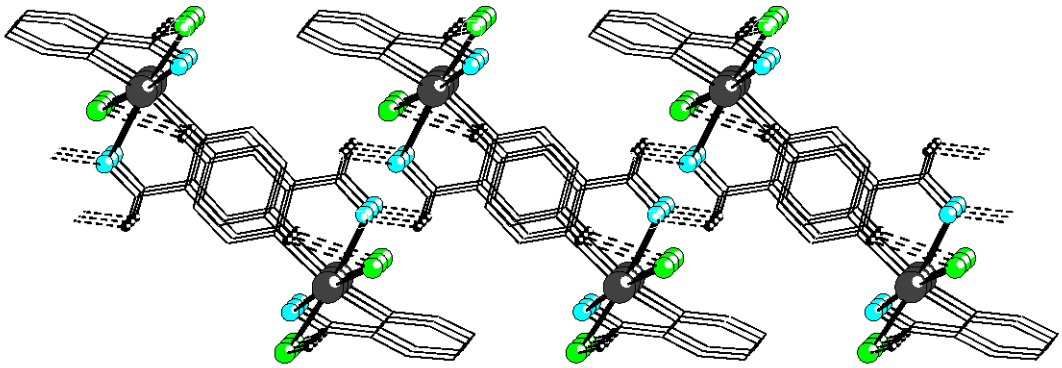


Figure S11. View along *c* axis of a layer based on inter-chain oxygen-hydrogen contacts in the crystal of **2** (only hydrogen atoms involved in intermolecular contacts are shown).

[2-(2′,4′,6′-$Me_3C_6H_2N$=CH)C_6H_4]$_2SnCl_2$ (4)

- the crystal contains a 1:1 mixture of Δ-**4** and Λ-**4** isomers

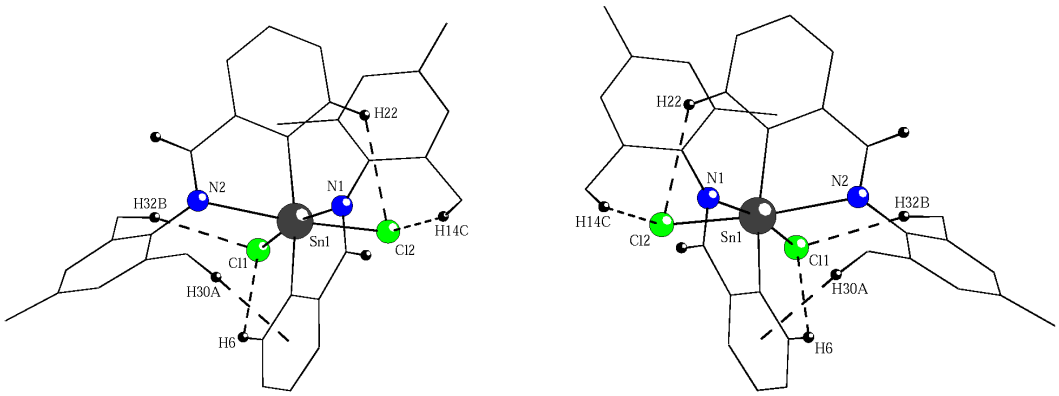


Figure S12. Molecular structure of Δ-**4** isomer (*left*) and Λ-**4** isomer (*right*) in the crystal of **4**, showing the intramolecular chlorine-hydrogen and C–H···π ($Ph_{centroid}$) contacts (only imine hydrogens and hydrogen atoms involved in intramolecular contacts are shown).

- intramolecular distance

Cl(1)···H(6)$_{aryl}$ 2.93 Å	$\sum r_{vdW}$(Cl,H) 3.01 Å
Cl(1)···H(32B)$_{methyl}$ 2.70 Å	
Cl(2)···H(22)$_{aryl}$ 2.96 Å	
Cl(2)···H(14C)$_{methyl}$ 2.72 Å	
C(30)–H(30A)$_{methyl}$···$Ph_{centroid}${C(1)-C(6)} 2.71 Å	
γ = 19.1°	

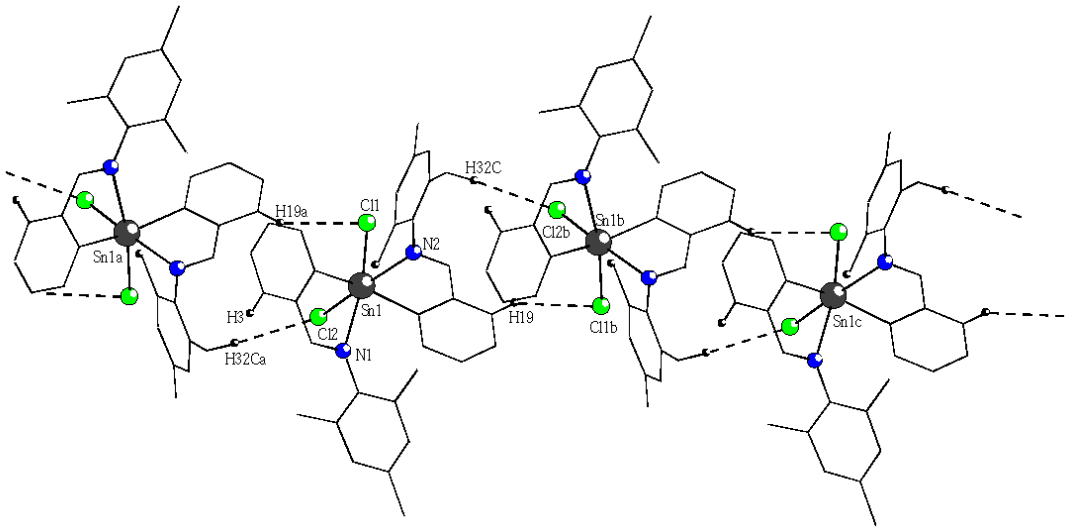


Figure S13. View of a chain polymer of alternating Δ-**4** and Λ-**4** isomers based on intermolecular chlorine-hydrogen contacts in the crystal of **4** (only hydrogen atoms involved in intermolecular contacts are shown) [symmetry equivalent atoms (*x, 0.5–y, 0.5+z*), (*x, 0.5–y, –0.5+z*) and (*x, y, –1+z*) are given by "a", "b" and "c", respectively].

- intermolecular distance

Cl(1)···H(19a)$_{aryl}$ 2.89 Å	$\sum r_{vdW}$(Cl,H) 3.01 Å
Cl(2)···H(32Ca)$_{methyl}$ 2.93 Å	

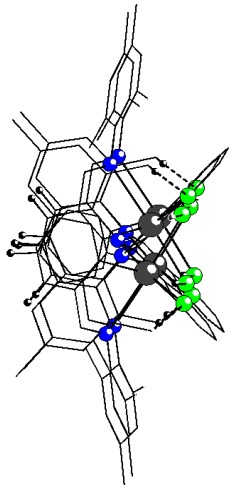


Figure S14. View along *c* axis of a chain polymer of alternating Δ-**4** and Λ-**4** isomers in the crystal of **4**.

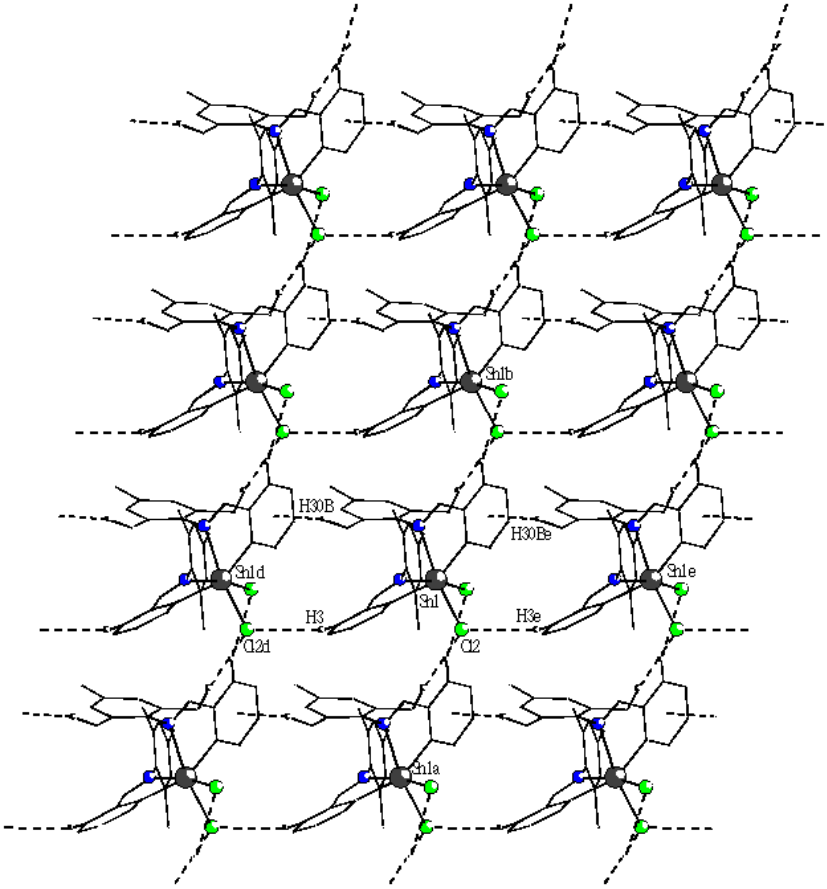


Figure S15. View along *b* axis of a layer based on inter-chain chlorine-hydrogen and C–H···π ($Ph_{centroid}$) contacts in the crystal of **4** (only hydrogen atoms involved in intermolecular contacts are shown) [symmetry equivalent atoms (*–1+x*, *y*, *z*) and (*1+x*, *y*, *z*) are given by "d" and "e", respectively].

- inter-chain distance $Cl(2)\cdots H(3e)_{aryl}$ 2.91 Å $\sum r_{vdW}(Cl,H)$ 3.01 Å
  $C(30)–H(30B)_{methyl}\cdots Ph_{centroid}\{C(17d)\text{-}C(22d)\}$ 2.92 Å
  γ = 10.0°

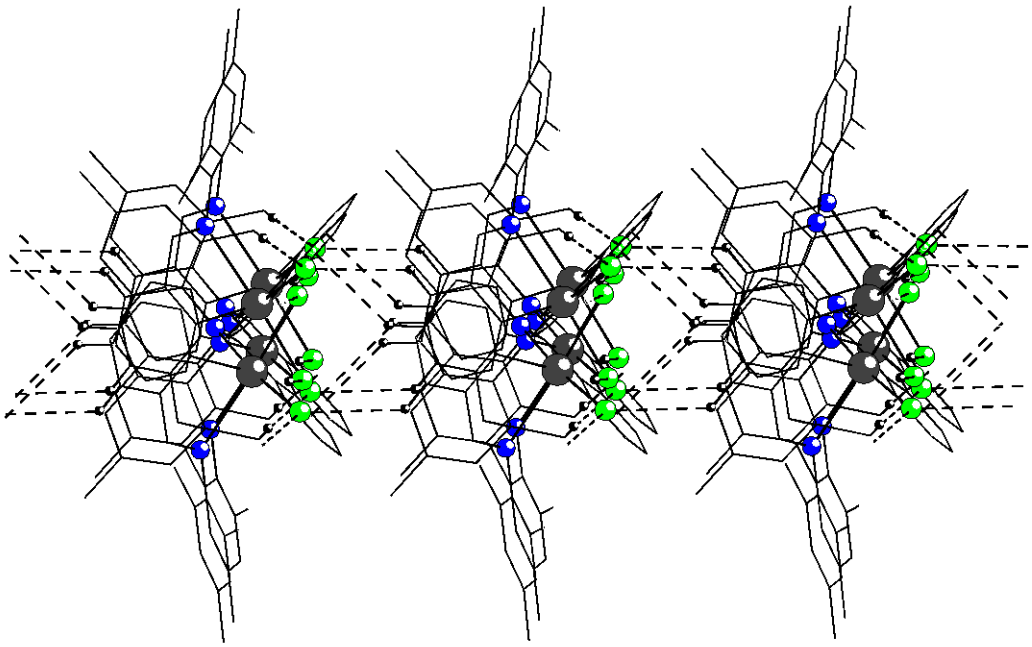


Figure S16. View along *c* axis of a layer based on inter-chain chlorine-hydrogen and C–H$\cdot\cdot\pi$ ($Ph_{centroid}$) contacts in the crystal of **4** (only hydrogen atoms involved in intermolecular contacts are shown).

- no further contacts between parallel layers.

[2-(PhCH$_2$N=CH)C$_6$H$_4$]$_2$SnCl$_2$ (5)

- the crystal contains a 1:1 mixture of Δ-**5** and Λ-**5** isomers

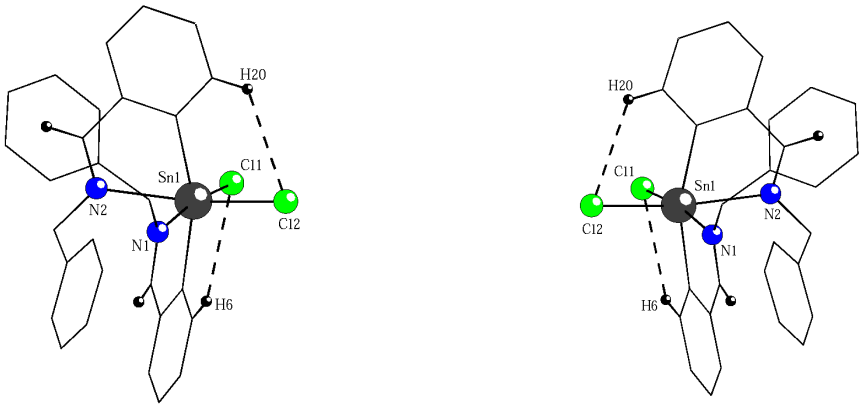


Figure S17. Molecular structure of Δ-**5** isomer (*left*) and Λ-**5** isomer (*right*) in the crystal of **5**, showing the intramolecular chlorine-hydrogen contacts (only imine hydrogens and hydrogen atoms involved in intramolecular contacts are shown).

- intramolecular distance Cl(1)···H(6)$_{aryl}$ 2.90 Å $\sum r_{vdW}$(Cl,H) 3.01 Å
  Cl(2)···H(20)$_{aryl}$ 2.86 Å

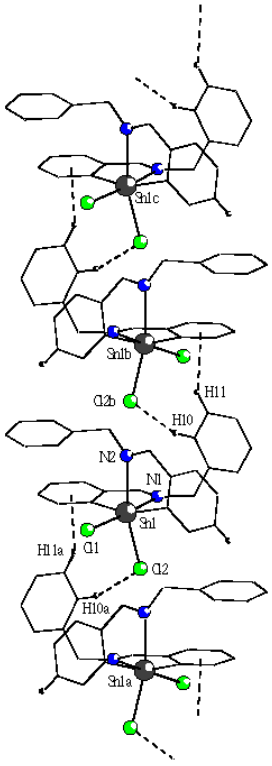


Figure S18. View along *a* axis of a *zig-zag* chain polymer of Λ-**5** isomers based on intermolecular chlorine-hydrogen and C–H···π (Ph$_{centroid}$) contacts in the crystal of **5** (only hydrogen atoms involved in intermolecular contacts are shown) [symmetry equivalent atoms (*0.5–x, –0.5+y, 1.5–z*), (*0.5–x, 0.5+y, 1.5–z*) and (*x, 1+y, z*) are given by "a", "b" and "c", respectively].

- intermolecular distance Cl(2)···H(10a)$_{aryl}$ 2.95 Å $\sum r_{vdW}$(Cl,H) 3.01 Å
  C(11)–H(11)$_{aryl}$···Ph$_{centroid}${C(1b)-C(6b)} 2.75 Å
  γ = 7.5°

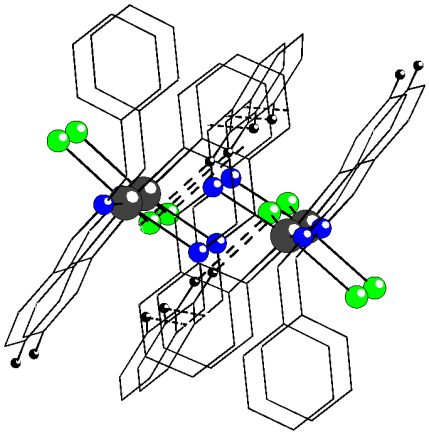


Figure S19. View along *b* axis of a *zig-zag* chain polymer of Λ-**5** isomers based on intermolecular chlorine-hydrogen contacts in the crystal of **5** (only hydrogen atoms involved in intermolecular contacts are shown).

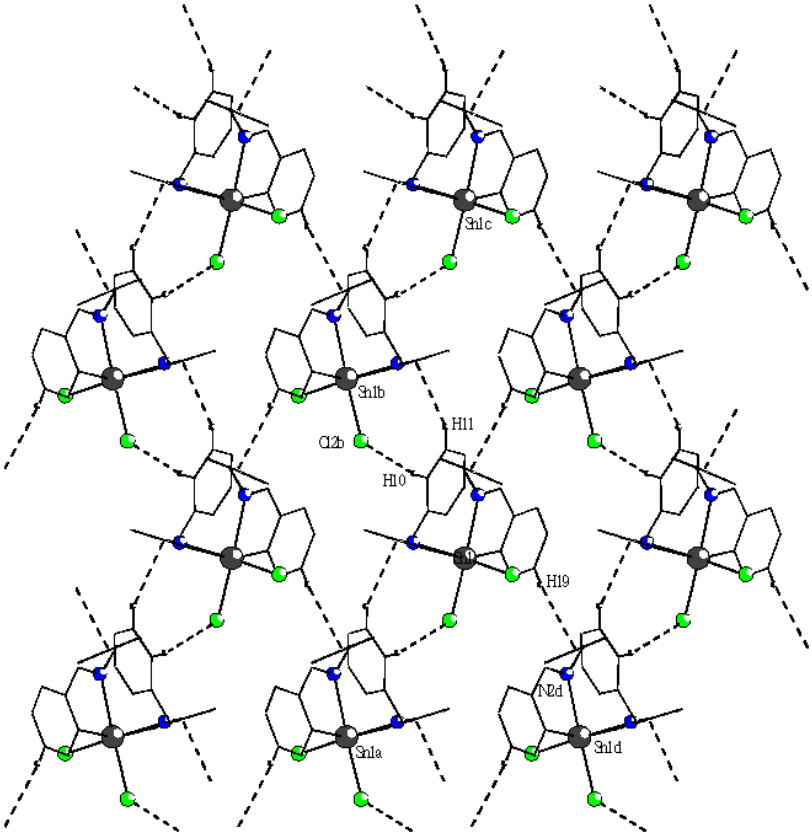


Figure S20. View along *c* axis of a layer based on C–H···π ($Ph_{centroid}$) contacts between alternating chains of Δ-**5** and Λ-**5** isomers, respectively, in the crystal of **5** (only hydrogen atoms involved in intermolecular contacts are shown) [symmetry equivalent atoms (*0.5–x, –0.5+y, 1.5–z*), (*0.5–x, 0.5+y, 1.5–z*), (*x, 1+y, z*) and (*1.5–x, –0.5+y, 1.5–z*) are given by "a", "b", "c" and "d", respectively].

- inter-chain distance $C(19)–H(19)_{aryl}\cdots Ph_{centroid}\{C(23d)\text{-}C(28d)\}$ 2.76 Å
  γ = 6.6°

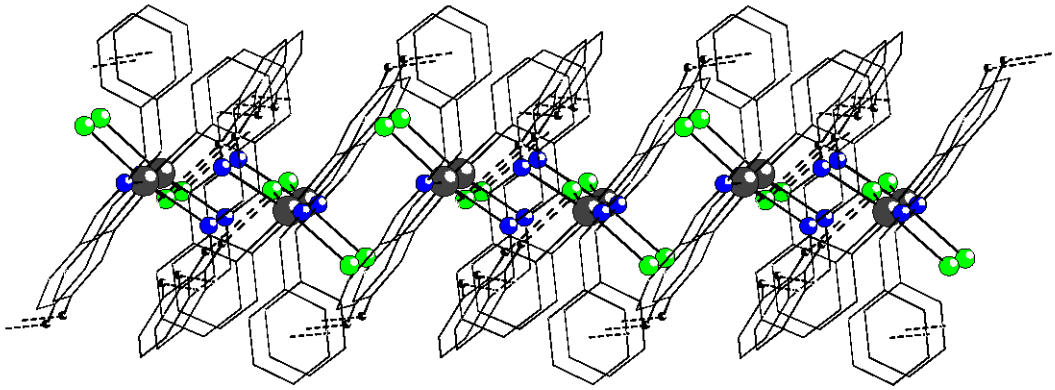


Figure S21. View along *b* axis of a layer based on C–H···π ($Ph_{centroid}$) contacts between alternating chains of Δ-**5** and Λ-**5** isomers, respectively, in the crystal of **5** (only hydrogen atoms involved in intermolecular contacts are shown).

- no further contacts between parallel layers.

[2-($Me_2NCH_2CH_2N$=CH)C_6H_4]$_2SnCl_2$ (6)

- the crystal contains a 1:1 mixture of Δ-**6** and Λ-**6** isomers

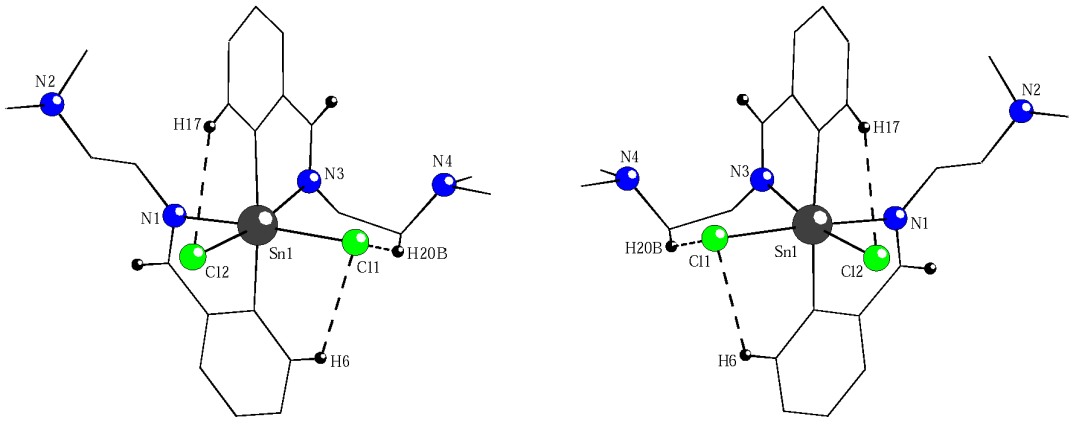


Figure S22. Molecular structure of Δ-**6** isomer (*left*) and Λ-**6** isomer (*right*) in the crystal of **6**, showing the intramolecular chlorine-hydrogen contacts (only imine hydrogens and hydrogen atoms involved in intramolecular contacts are shown).

- intramolecular distance Cl(1)···H(6)$_{aryl}$ 2.97 Å ∑r_{vdW}(Cl,H) 3.01 Å
  Cl(1)···H(20B)$_{methylene}$ 2.90 Å
  Cl(2)···H(17)$_{aryl}$ 2.93 Å

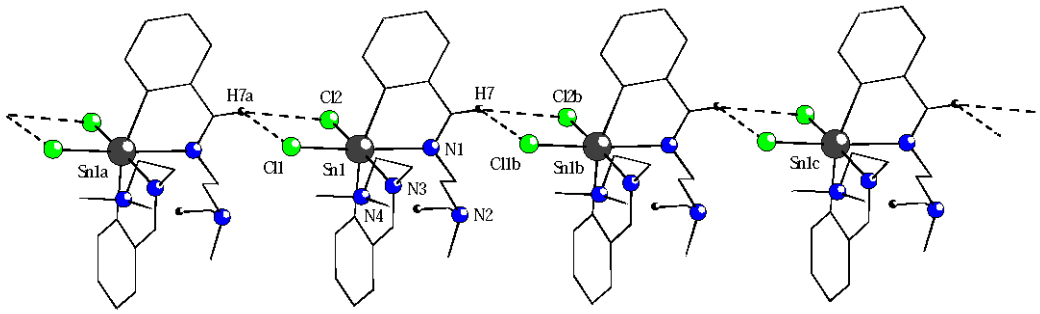


Figure S23. View along *b* axis of a chain polymer of Λ-**6** isomers based on intermolecular chlorine-hydrogen contacts in the crystal of **6** (only hydrogen atoms involved in intermolecular contacts are shown) [symmetry equivalent atoms (*–1+x, y, z*), (*1+x, y, z*) and (*2+x, y, z*) are given by "a", "b" and "c", respectively].

- intermolecular distance Cl(1)···H(7a)$_{imine}$ 2.92 Å ∑r_{vdW}(Cl,H) 3.01 Å
  Cl(2)···H(7a)$_{imine}$ 2.95 Å

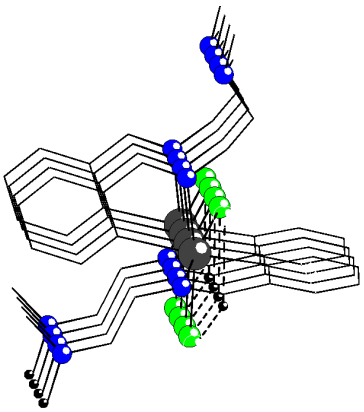


Figure S24. View along *a* axis of a chain polymer of Λ-**6** isomers based on intermolecular chlorine-hydrogen contacts in the crystal of **6** (only hydrogen atoms involved in intermolecular contacts are shown).

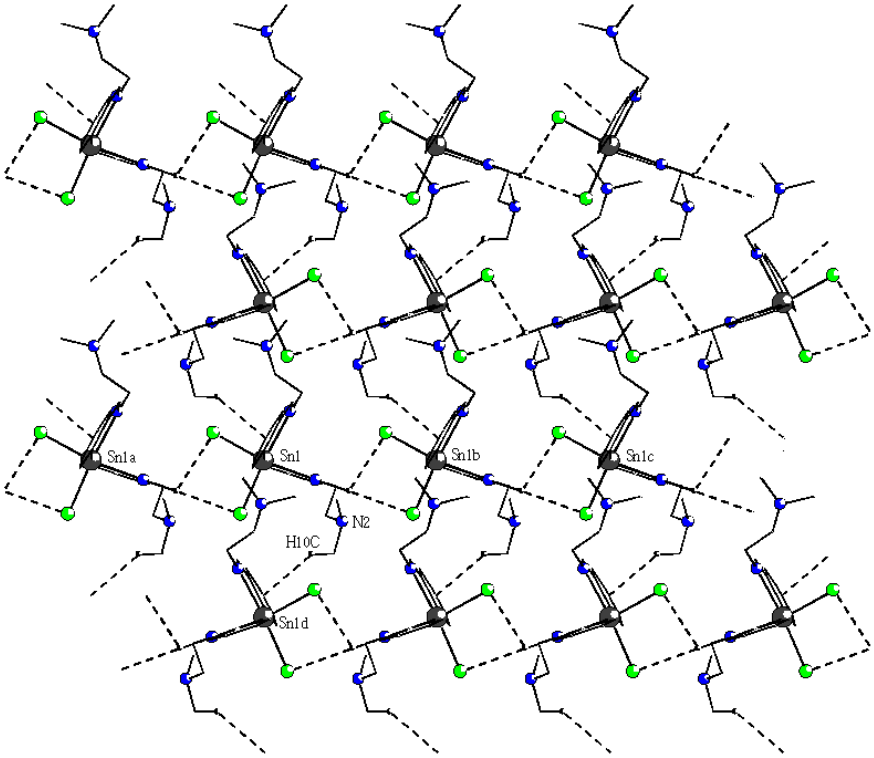


Figure S25. View along *c* axis of a wave-like layer based on C–H···π ($Ph_{centroid}$) contacts between parallel chains of Λ-**6** isomers in the crystal of **6** (only hydrogen atoms involved in intermolecular contacts are shown) [symmetry equivalent atoms (*–1+x, y, z*), (*1+x, y, z*), (*2+x, y, z*) and (*0.5+x, –0.5+y, 0.5–z*) are given by "a", "b", "c" and "d", respectively].

- inter-chain distance $C(10)–H(10C)_{methyl}\cdots Ph_{centroid}$ {C(12d)-C(17d)} 2.82 Å
  γ = 12.3°

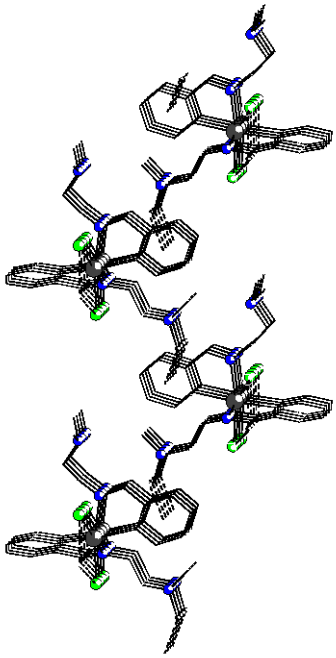


Figure S26. View along *b* axis of a wave-like layer based on C–H···π ($Ph_{centroid}$) contacts between parallel chains of Λ-**6** isomers in the crystal of **6** (only hydrogen atoms involved in intermolecular contacts are shown).

- no further contacts between parallel layers of Δ-**6** and Λ-**6** isomers, respectively.

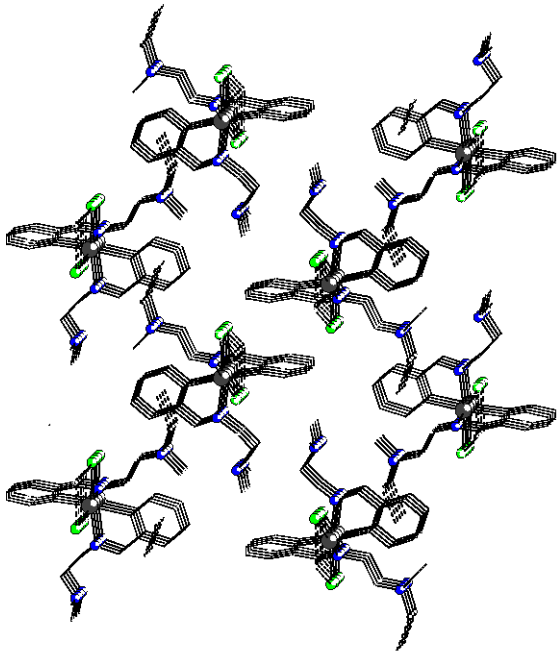


Figure S27. View along *b* axis of parallel wave-like layers of Δ-**6** and Λ-**6** isomers, respectively, in the crystal of **6** (only hydrogen atoms involved in intermolecular contacts are shown).

[2-(2′-PyCH$_2$N=CH)C$_6$H$_4$]$_2$SnCl$_2$ (7)

- the crystal contains a 1:1 mixture of Δ-**7** and Λ-**7** isomers

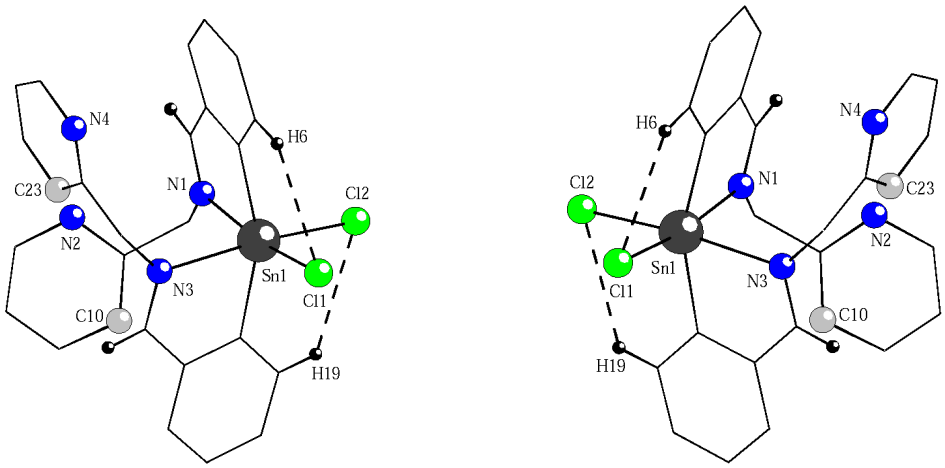


Figure S28. Molecular structure of Δ-**7** isomer (*left*) and Δ-**7** isomer (*right*) in the crystal of **6**, showing the intramolecular chlorine-hydrogen contacts (only imine hydrogens and hydrogen atoms involved in intramolecular contacts are shown). The occupancy degree is: 0.93 for N2 (0.07 for C10B) / 0.93 for C10 (0.07 for N2B) and 0.74 for N4 (0.26 for C23B) / 0.74 for C23 (0.26 for N4B).

- intramolecular distance Cl(1)···H(6)$_{aryl}$ 2.85 Å Cl(2)···H(19)$_{aryl}$ 2.92 Å $\sum r_{vdW}$(Cl,H) 3.01 Å

$[Cl_2Pd\{2\text{-}(2'\text{-}PyCH_2N{=}CH)C_6H_4\}_2SnCl_2]\cdot CH_3CN$ ($8\cdot CH_3CN$)

- the crystal contains a 1:1 mixture of Δ-**8** and Λ-**8** isomers

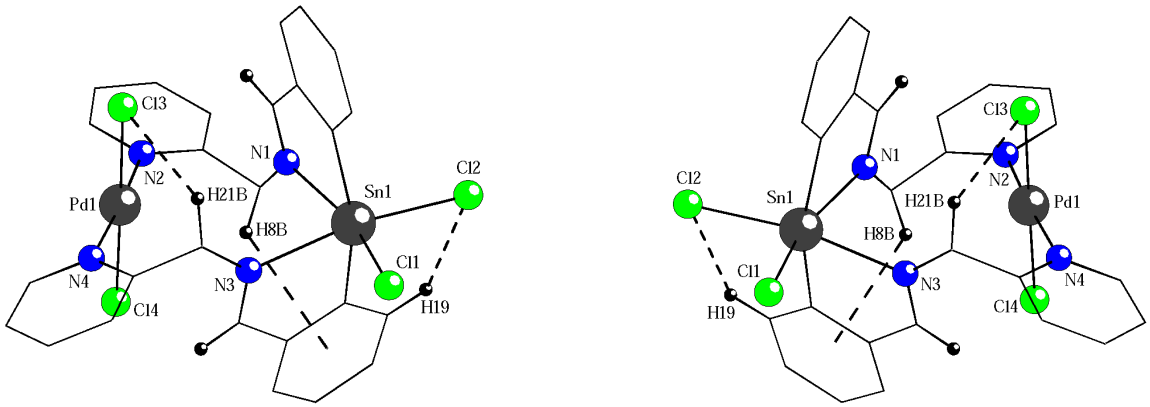


Figure S29. Molecular structure of Δ-**8** isomer (*left*) and Λ-**8** isomer (*right*) in the crystal of $\mathbf{8}\cdot CH_3CN$, showing the intramolecular chlorine-hydrogen and C–H···π ($Ph_{centroid}$) contacts (only imine hydrogens and hydrogen atoms involved in intramolecular contacts are shown; the solvent molecule is omitted).

- intramolecular distance $Cl(2)\cdots H(19)_{aryl}$ 2.81 Å $\sum r_{vdW}(Cl,H)$ 3.01 Å
  $Cl(3)\cdots H(21B)_{methylene}$ 2.74 Å
  $C(8)\text{–}H(8B)_{methylene}\cdots Ph_{centroid}\{C(14)\text{-}C(19)\}$ 2.97 Å
  γ = 25.5°

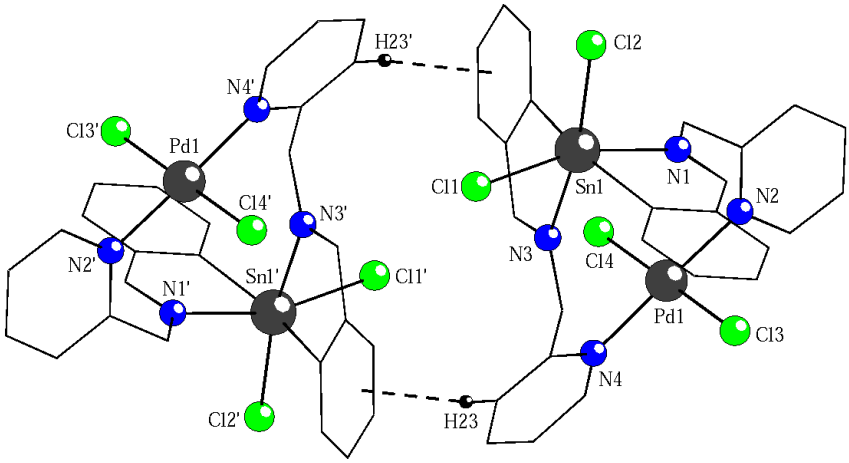


Figure S30. View along *a* axis of a dimer association of Δ-**8** and Λ-**8** isomers based on intermolecular C–H···π ($Ph_{centroid}$) contacts in the crystal of $\mathbf{8}\cdot CH_3CN$ (only hydrogen atoms involved in intermolecular contacts are shown) [symmetry equivalent atoms (*1–x, 1–y, 1–z*) are given by "prime"].

- intermolecular distance $C(23)\text{–}H(23)_{aryl}\cdots Ph_{centroid}\{C(14')\text{-}C(19')\}$ 2.61 Å
  γ = 2.8°

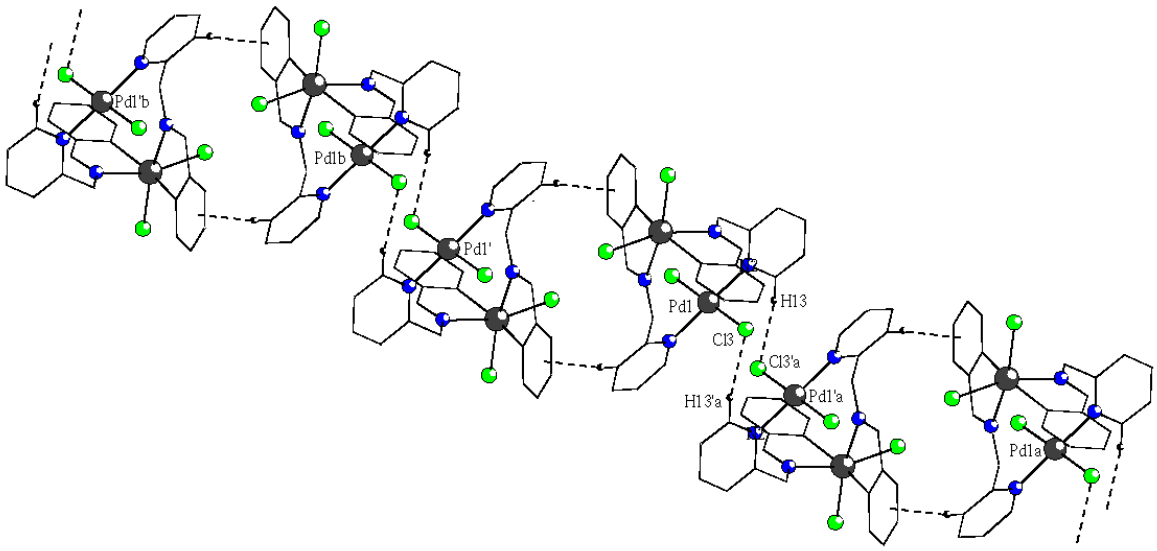


Figure S31. View along *a* axis of a ribbon-like polymer of dimers based on inter-dimer chlorine-hydrogen interactions in the crystal of **8**·CH_3CN (only hydrogen atoms involved in intermolecular contacts are shown) [symmetry equivalent atoms (*1–x, 1–y, 1–z*), (*–1+x, –1+y, –1+z*), (*–x, –y, –z*), (*1+x, 1+y, 1+z*) and (*2–x, 2–y, 2–z*) are given by "prime", "a", "prime a", "b" and "prime b", respectively].

- inter-dimer distance Cl(3)···H(13'a)$_{aryl}$ 2.65 Å $\sum r_{vdW}$(Cl,H) 3.01 Å

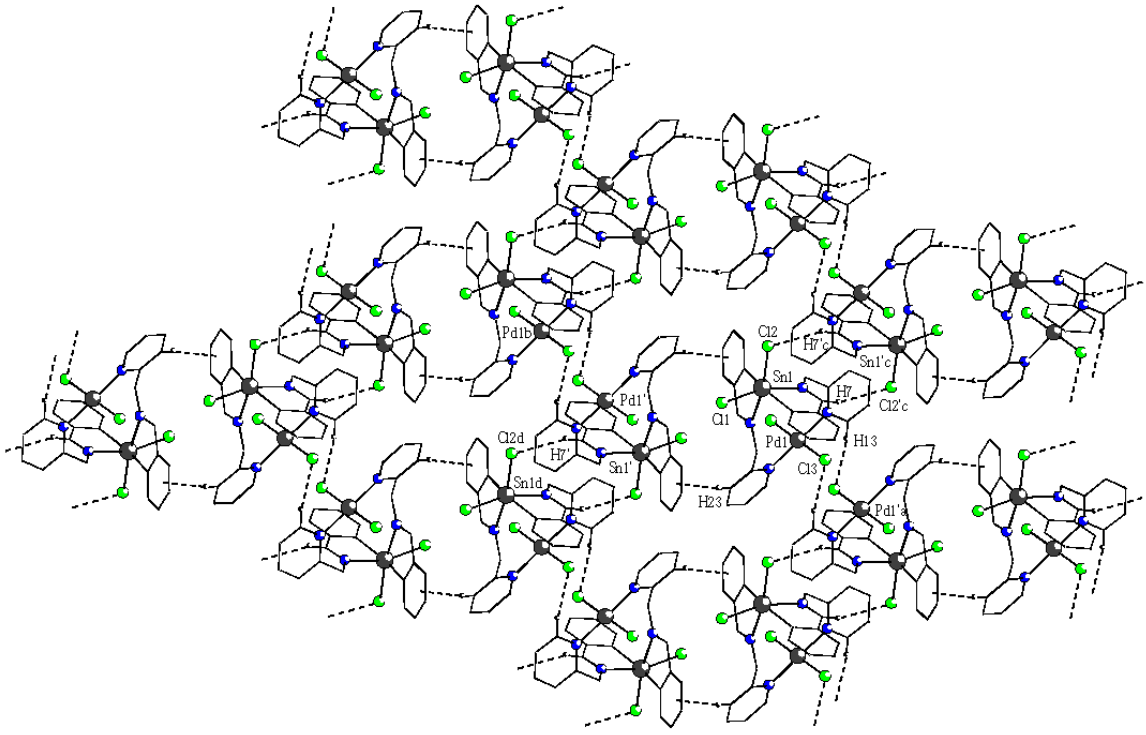


Figure S32. View along *a* axis of a layer based on inter-chain chlorine-hydrogen interactions in the crystal of **8**·CH_3CN (only hydrogen atoms involved in intermolecular contacts are shown) [symmetry equivalent atoms (*1–x, 1–y, 1–z*), (*–x, –y, –z*), (*1+x, 1+y, 1+z*), (*1–x, 1–y, –z*) and (*x, y, 1+z*) are given by "prime", "prime a", "b", "prime c" and "d", respectively].

- inter-chain distance Cl(2)···H(7'c)$_{imine}$ 2.75 Å $\sum r_{vdW}$(Cl,H) 3.01 Å

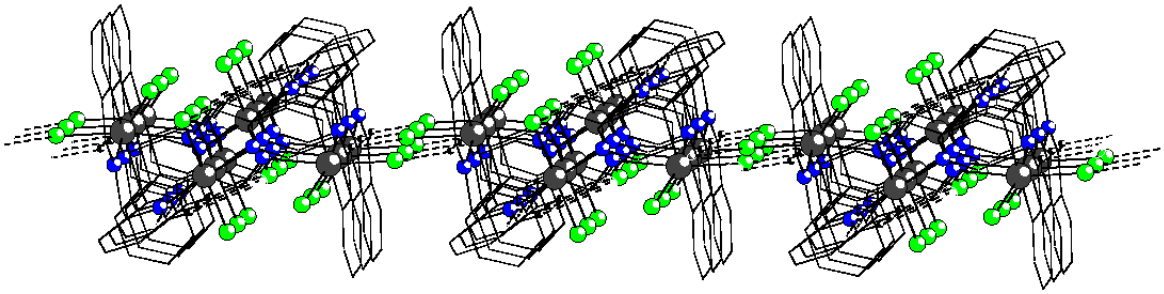


Figure S33. View along chain polymers of a layer based on inter-chain chlorine-hydrogen interactions in the crystal of **8**·CH_3CN (only hydrogen atoms involved in intermolecular contacts are shown).

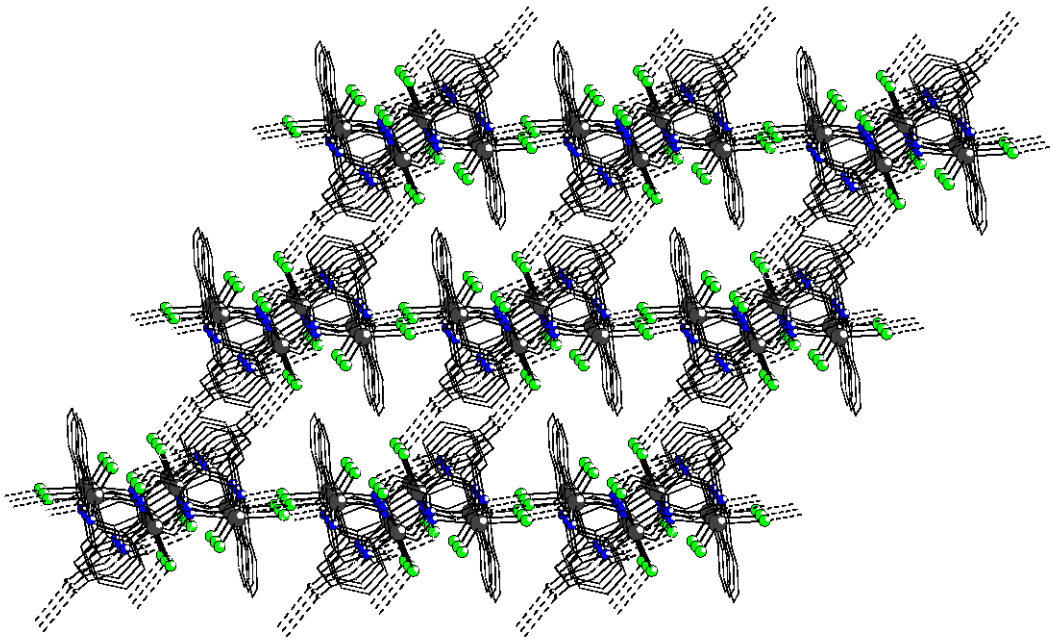


Figure S34. View of the 3D architecture in the crystal of **8**·CH_3CN, based on chlorine-hydrogen contacts between parallel layers (only hydrogen atoms involved in intermolecular contacts are shown) [symmetry equivalent atoms (*–x, 1–y, –z*) are given by "prime e"].

- inter-layer distance Cl(4)···H(11'e)$_{aryl}$ 2.83 Å $\sum r_{vdW}$(Cl,H) 3.01 Å