Electronic Supplementary Material (ESI) for Dalton Transactions

Electronic Supplementary Information

Diorganodiselenides and zinc(II) organoselenolates containing (imino)aryl groups of type 2-(RN=CH)C_6H_4

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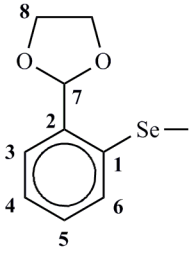
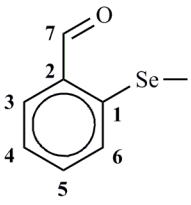
Numbering schemes for NMR resonance assignments



(**2**)



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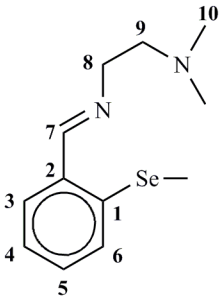

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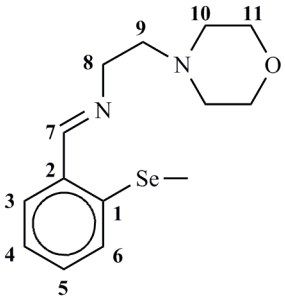

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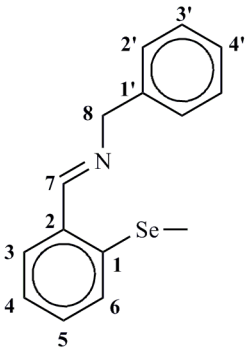
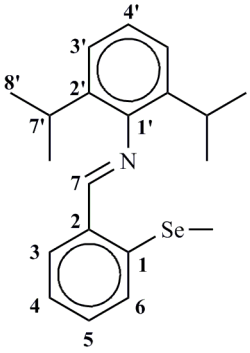
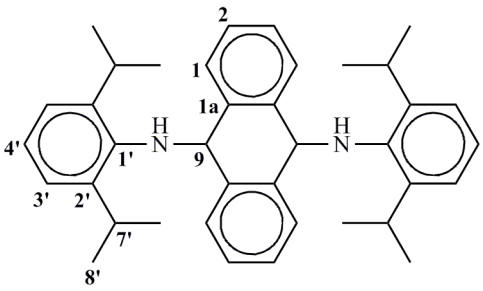


(**6**, **9** or **11**)



(**7** or **10**)



(**8**)

NMR studies

^{1}H NMR was used to monitor the reaction between aldehyde [2-{(O)CH}C_6H_4]$_2$$Se_2$ (**3**) and 2,6-diisopropylaniline until condensation was achieved. Figure S1 shows the ^{1}H NMR spectra of the products of this reaction after 24 h of refluxing in toluene using a Dean-Stark trap (up) and after two hours of refluxing in acetonitrile (down). When this reaction was carried out the presence of the characteristic resonance for the –C*H*O proton of the aldehyde (δ 10.16 ppm) and the resonace at δ 3.77 ppm corresponding to the –NH_2 protons of the 2,6-diisopropylaniline show that no reaction took place. When the reaction was carried out in acetonitrile the absence of the signals corresponding to the protons of the –C*H*O and the –NH_2 groups, respectively, indicates full conversion of the starting materials to the desired imine **7** with a characteristic –C*H*=N- resonance at δ 8.52 ppm.

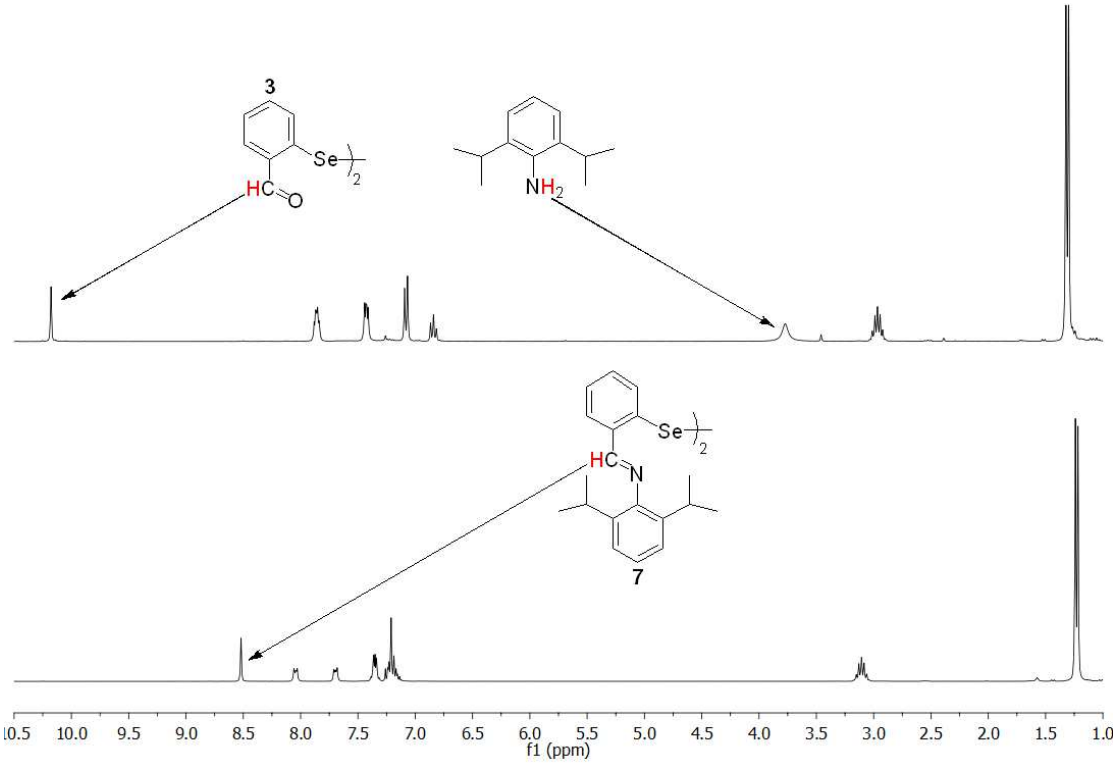


Figure S1. ^{1}H NMR ($CDCl_3$, 300 MHz, r.t.) spectra of the reaction products of **3** with 2,6-diisopropylaniline in toluene, using a Dean-Stark trap, in the presence of TosOH (up), and in acetonitrile, without catalyst (down).

[2-(PhCH$_2$NCH)C$_6$H$_4$]$_2$Se$_2$ (6)

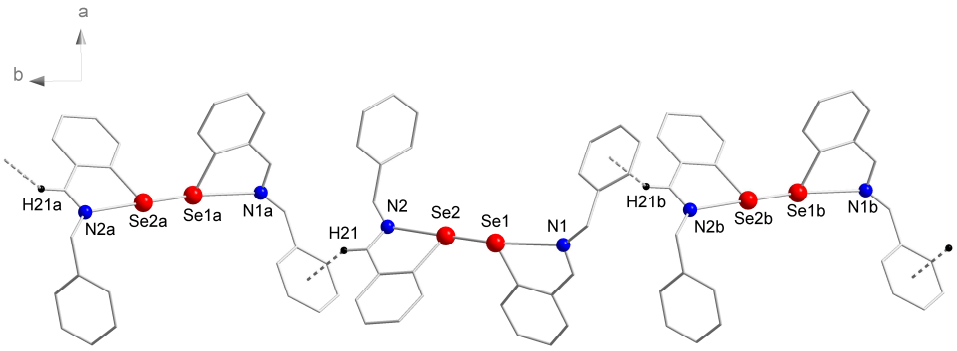


Figure S2. View of a chain polymer based on C–H$_{aryl}$···π (Ph$_{centroid}$) contacts between molecules in the crystal of **6** (only hydrogen atoms involved in intermolecular contacts are shown) [symmetry equivalent atoms (1 – *x*, 0.5 + *y*, 1.5 – *z*) and (1 – *x*, –0.5 + *y*, 1.5 – *z*) are given by "a" and "b", respectively].

- intermolecular distance C(21)–H(21)···Ph$_{centroid}$ 2.96 Å

- no further contacts between parallel chains.

9,10-(2',6'-$^{i}Pr_2C_6H_3NH)_2C_{14}H_{10}$ (8)

Table S1 Selected bond distances (Å) and angles (°) for compound **8**

C(1)-C(2)	1.393(3)	C(7)-C(8)	1.395(3)
C(2)-C(3)	1.386(3)	C(8)-C(9)	1.382(4)
C(3)-C(4)	1.369(4)	C(9)-C(10)	1.379(4)
C(4)-C(5)	1.375(4)	C(10)-C(11)	1.379(4)
C(5)-C(6)	1.371(4)	C(11)-C(12)	1.372(4)
C(1)-C(6)	1.383(4)	C(7)-C(12)	1.378(4)
C(1)-C(13)	1.506(3)	C(7)-C(13)	1.507(3)
C(2)-C(14)	1.500(3)	C(8)-C(14)	1.507(3)
N(1)-C(13)	1.489(3)	N(2)-C(14)	1.498(3)
N(1)-C(15)	1.425(3)	N(2)-C(27)	1.445(3)
N(1)-H(1)	0.858(17)	N(2)-H(2)	0.850(17)
C(15)-C(16)	1.397(3)	C(27)-C(28)	1.409(4)
C(16)-C(17)	1.386(4)	C(28)-C(29)	1.383(4)
C(17)-C(18)	1.376(4)	C(29)-C(30)	1.359(4)
C(18)-C(19)	1.366(4)	C(30)-C(31)	1.371(4)
C(19)-C(20)	1.384(4)	C(31)-C(32)	1.385(4)
C(15)-C(20)	1.407(3)	C(27)-C(32)	1.396(4)
C(16)-C(21)	1.521(3)	C(28)-C(33)	1.509(4)
C(21)-C(22)	1.523(4)	C(33)-C(34)	1.513(4)
C(21)-C(23)	1.518(4)	C(33)-C(35)	1.522(4)
C(20)-C(24)	1.516(4)	C(32)-C(36)	1.513(4)
C(24)-C(25)	1.523(4)	C(36)-C(37)	1.514(4)
C(24)-C(26)	1.531(4)	C(36)-C(38)	1.522(4)
C(3)-C(2)-C(1)	119.2(2)	C(9)-C(8)-C(7)	119.4(2)
C(4)-C(3)-C(2)	121.2(3)	C(10)-C(9)-C(8)	120.9(3)
C(3)-C(4)-C(5)	119.4(3)	C(9)-C(10)-C(11)	119.3(3)
C(6)-C(5)-C(4)	120.2(3)	C(12)-C(11)-C(10)	120.4(3)
C(5)-C(6)-C(1)	121.1(3)	C(11)-C(12)-C(7)	120.8(3)
C(6)-C(1)-C(2)	118.8(2)	C(12)-C(7)-C(8)	119.3(2)
C(2)-C(1)-C(13)	120.0(2)	C(8)-C(7)-C(13)	119.7(2)
C(6)-C(1)-C(13)	121.2(2)	C(12)-C(7)-C(13)	121.0(2)
C(1)-C(2)-C(14)	119.5(2)	C(7)-C(8)-C(14)	119.5(2)
C(3)-C(2)-C(14)	121.3(2)	C(9)-C(8)-C(14)	121.2(2)
C(1)-C(13)-C(7)	111.6(2)	C(2)-C(14)-C(8)	111.19(19)
N(1)-C(13)-C(1)	109.11(19)	N(2)-C(14)-C(2)	110.93(19)
N(1)-C(13)-C(7)	113.6(2)	N(2)-C(14)-C(8)	107.88(19)
C(16)-C(15)-N(1)	121.6(2)	C(28)-C(27)-N(2)	120.4(2)
C(20)-C(15)-N(1)	118.2(2)	C(32)-C(27)-N(2)	118.7(2)
C(17)-C(16)-C(15)	118.4(2)	C(29)-C(28)-C(27)	117.6(3)

C(18)-C(17)-C(16)	121.6(3)	C(30)-C(29)-C(28)	122.4(3)
C(19)-C(18)-C(17)	119.5(3)	C(29)-C(30)-C(31)	119.3(3)
C(18)-C(19)-C(20)	121.4(3)	C(30)-C(31)-C(32)	121.8(3)
C(19)-C(20)-C(15)	118.7(2)	C(31)-C(32)-C(27)	118.1(3)
C(16)-C(15)-C(20)	120.2(2)	C(32)-C(27)-C(28)	120.8(2)
C(15)-C(16)-C(21)	123.2(2)	C(27)-C(28)-C(33)	122.7(2)
C(17)-C(16)-C(21)	118.3(2)	C(29)-C(28)-C(33)	119.7(2)
C(15)-C(20)-C(24)	122.6(2)	C(27)-C(32)-C(36)	121.8(2)
C(19)-C(20)-C(24)	118.6(2)	C(31)-C(32)-C(36)	120.0(3)
C(16)-C(21)-C(22)	111.0(2)	C(28)-C(33)-C(34)	112.0(3)
C(23)-C(21)-C(16)	112.3(2)	C(28)-C(33)-C(35)	111.6(3)
C(23)-C(21)-C(22)	110.7(2)	C(34)-C(33)-C(35)	109.4(3)
C(20)-C(24)-C(25)	112.5(3)	C(32)-C(36)-C(37)	110.4(3)
C(20)-C(24)-C(26)	111.1(2)	C(32)-C(36)-C(38)	114.0(3)
C(25)-C(24)-C(26)	109.9(3)	C(37)-C(36)-C(38)	110.4(3)
C(15)-N(1)-C(13)	116.58(19)	C(27)-N(2)-C(14)	115.94(19)
C(13)-N(1)-H(1)	108(2)	C(14)-N(2)-H(2)	103(2)
C(15)-N(1)-H(1)	112(2)	C(27)-N(2)-H(2)	112(2)

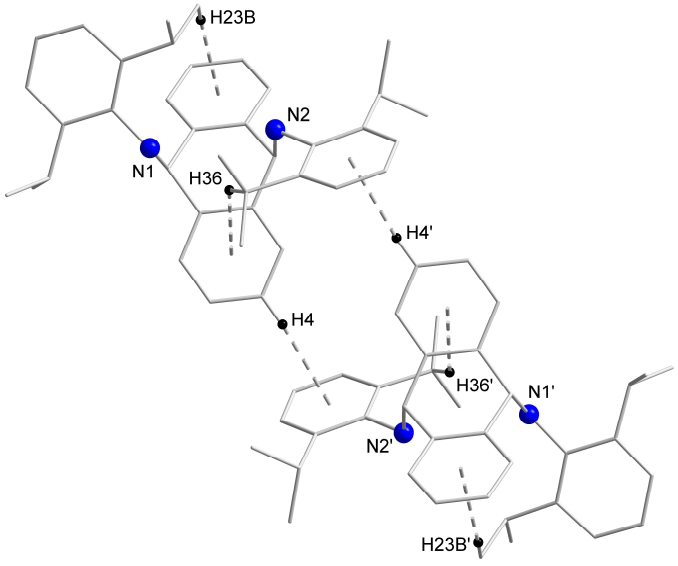


Figure S3. View of a dimer based on C–$H_{aryl}\cdots\pi$ ($Ph_{centroid}$) contacts between molecules in the crystal of **8** (only hydrogen atoms involved in intra- and intermolecular contacts are shown) [symmetry equivalent atoms (1 – *x*, 1 – *y*, 1 – *z*) are given by "prime"].

-	intramolecular distance	C(23)–H(23B)···$Ph_{centroid}$	2.86 Å
		C(36)–H(36)···$Ph_{centroid}$	3.00 Å
-	intermolecular distance	C(4)–H(4)···$Ph_{centroid}$	2.86 Å

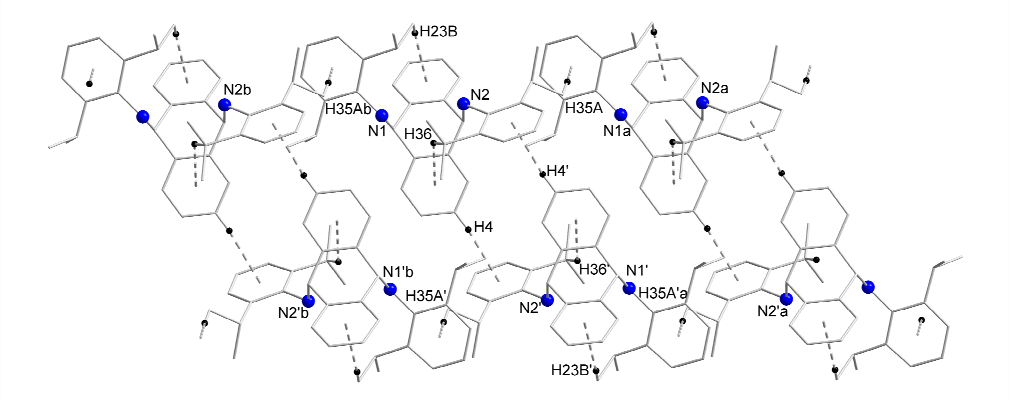


Figure S4. View of a ribbon-like polymer of dimers based on C–$H_{methyl}\cdots\pi$ ($Ph_{centroid}$) contacts in the crystal of **8** (only hydrogen atoms involved in intra- and intermolecular contacts are shown) [symmetry equivalent atoms (–1 + *x*, *y*, *z*), (1 + *x*, *y*, *z*), (1 – *x*, 1 – *y*, 1 – *z*), (–*x*, 1 – *y*, 1 – *z*) and (0.5 – *x*, 0.5 + *y*, 0.5 – *z*) are given by "a", "b", "prime", "a prime" and "b prime", respectively].

- inter-dimers distance C(35)–H(35A)···$Ph_{centroid}$ 2.84 Å

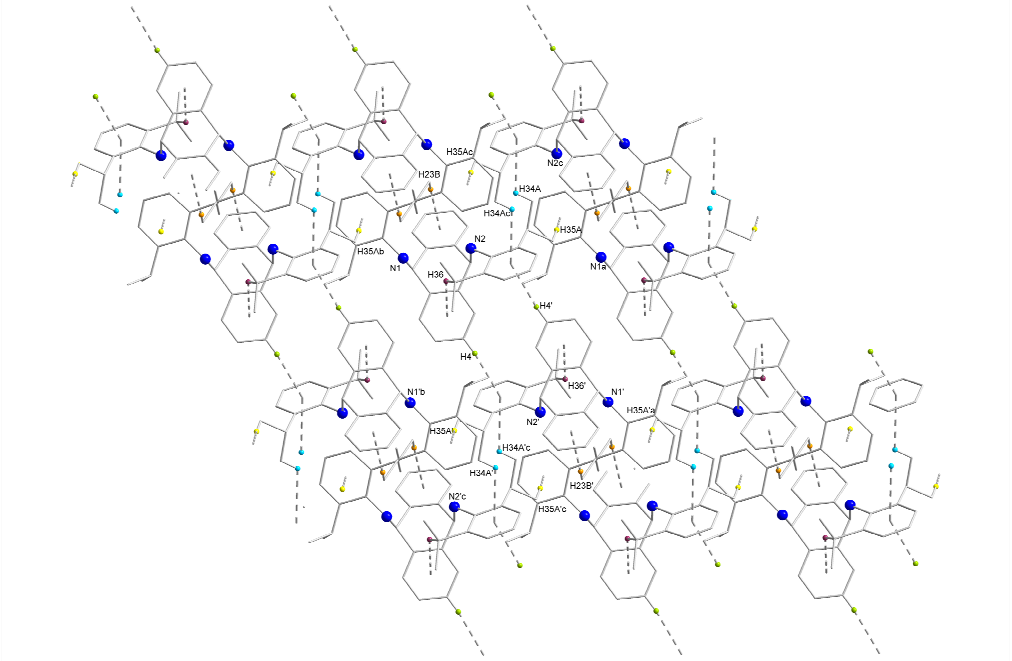


Figure S5. View of a layer with inter-chains C–$H_{methyl}\cdots\pi$ ($Ph_{centroid}$) contacts between alternating chain polymers in the crystal of **8** (only hydrogen atoms involved in intermolecular contacts are shown) [symmetry equivalent atoms (*x*, –1 + *y*, *z*), (0.5 – *x*, –0.5 + *y*, 0.5 – *z*), (0.5 – *x*, 0.5 + *y*, 0.5 – *z*) and (0.5 – *x*, 0.5 + *y*, 0.5 – *z*) are given by ''a'', ''b'', ''c'' and ''d'', respectively].

- inter-chains distance C(34)–H(34A)···$Ph_{centroid}$ 2.84 Å

[2-(PhCH$_2$N=CH)C$_6$H$_4$Se]$_2$Zn (11)

- the crystal contains a 1:1 mixture of Λ_{Zn}-($R_{Zn(N1)}$,$R_{Zn(N2)}$) and Δ_{Zn}-($S_{Zn(N1)}$,$S_{Zn(N2)}$) isomers

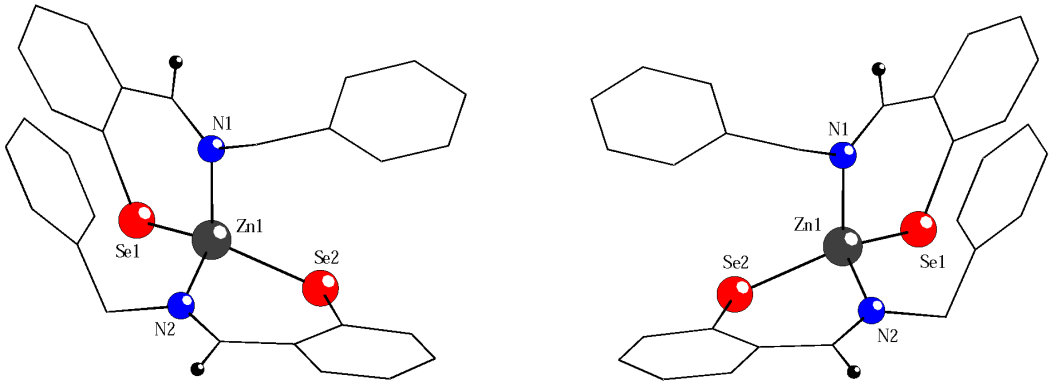


Figure S6. Molecular structure of Λ_{Zn}-($R_{Zn(N1)}$,$R_{Zn(N2)}$)-**11** isomer (*left*) and Δ_{Zn}-($S_{Zn(N1)}$,$S_{Zn(N2)}$)-**11** isomer (*right*) in the crystal of **11** (only *imine* hydrogen atoms are shown).

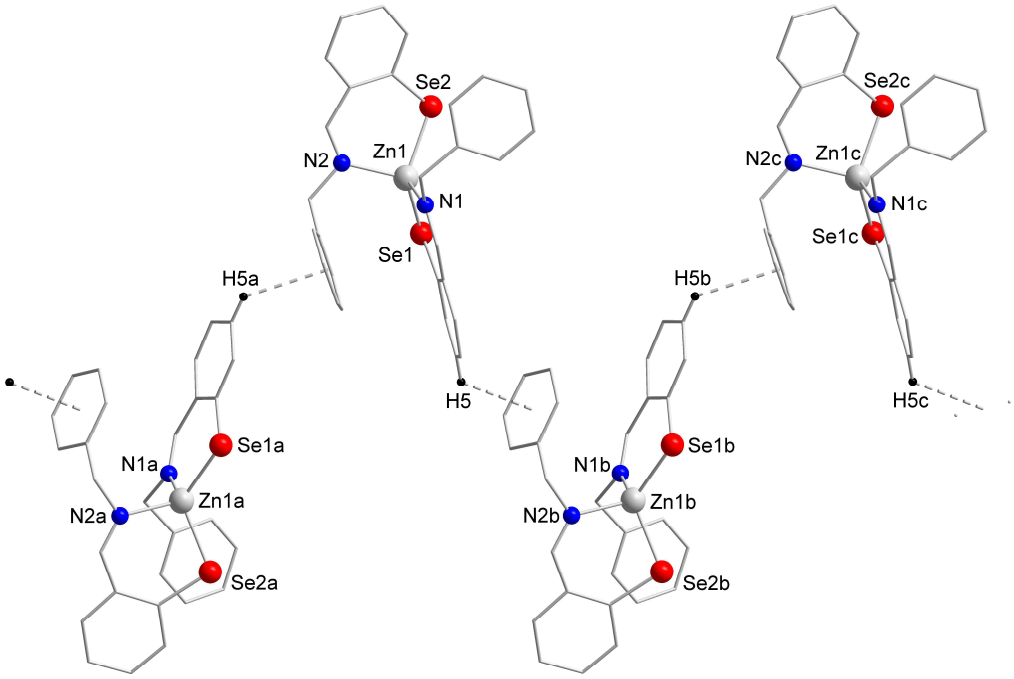


Figure S7. View of a chain polymer based on C–H$_{aryl}$···π (Ph$_{centroid}$) contacts between Λ_{Zn}-($R_{Zn(N1)}$,$R_{Zn(N2)}$)-**11** isomers in the crystal of **11** (only hydrogen atoms involved in intermolecular contacts are shown) [symmetry equivalent atoms (1.5 – *x*, 0.5 + *y*, 0.5 – *z*), (1.5 – *x*, –0.5 + *y*, 0.5 – *z*) and (*x*, –1 + *y*, *z*) are given by "a", "b" and "c", respectively].

- intermolecular distance C(5)–H(5)···Ph$_{centroid}$ 2.73 Å

- no further contacts between parallel chains.

[2-(2',6'-^{i}Pr$_2$C$_6$H$_3$N=CH)C$_6$H$_4$Se]$_2$Zn (12)

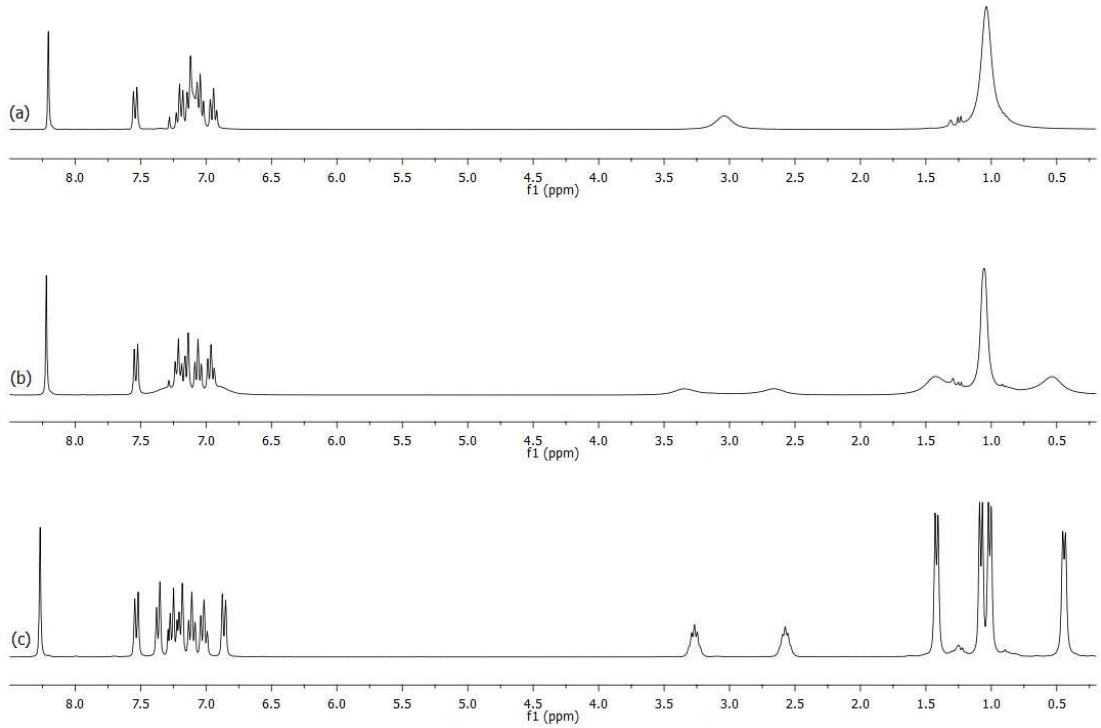


Figure S8. Comparison of the ^{1}H NMR ($CDCl_3$, 300 MHz) spectra of compound **12** at (a) +50 °C, (b) +20 °C and (c) -40 °C.

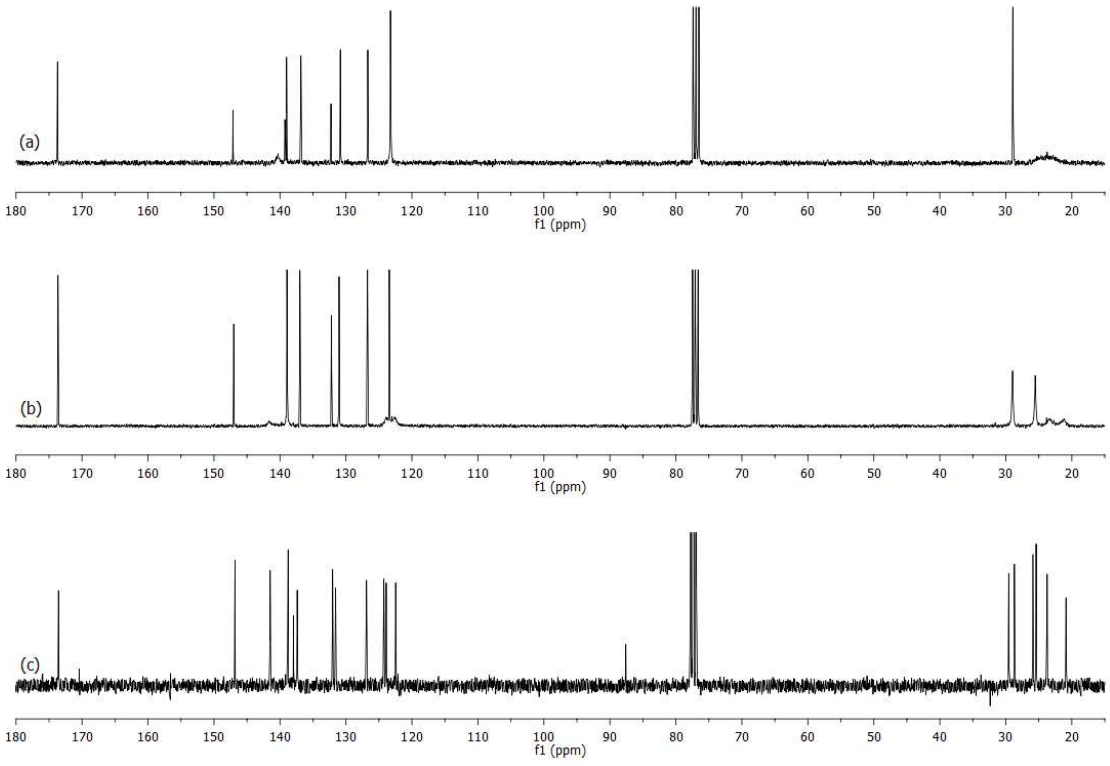


Figure S9. Comparison of the ^{13}C NMR ($CDCl_3$, 300 MHz) spectra of compound **12** at (a) +50 °C, (b) +20 °C and (c) -40 °C.

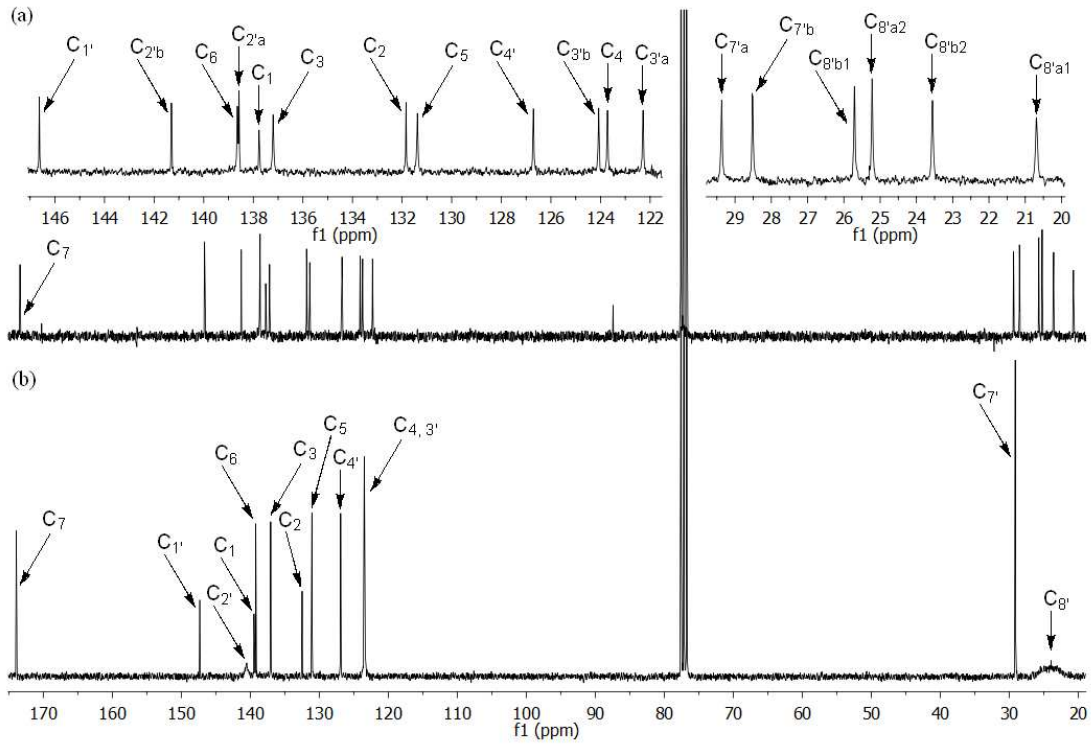


Figure S10. Assignments of the ^{13}C resonances in the spectra ($CDCl_3$, 300 MHz) of compound **12** at (a) -40 °C, and (b) +50 °C.

- the crystal contains a 1:1 mixture of Λ_{Zn}-($R_{Zn(N1)}$,$R_{Zn(N1a)}$) and Δ_{Zn}-($S_{Zn(N1)}$,$S_{Zn(N1a)}$) isomers

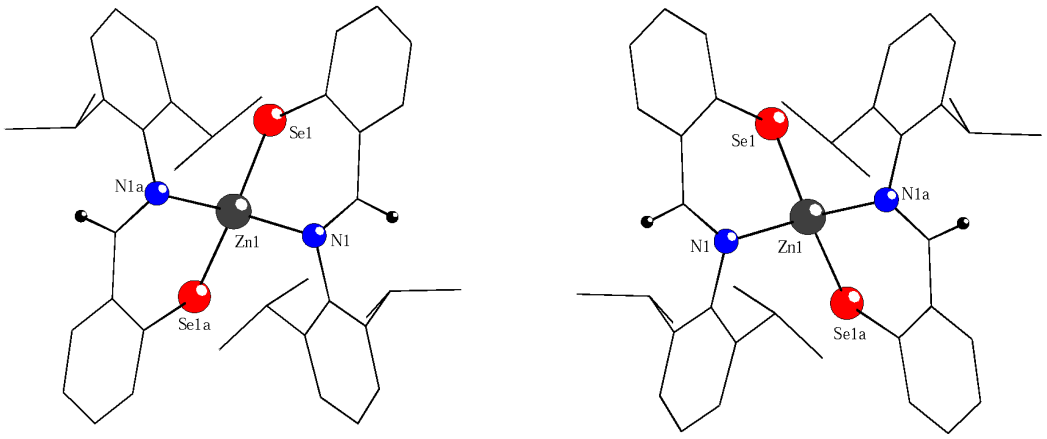


Figure S11. Molecular structure of Λ_{Zn}-($R_{Zn(N1)}$,$R_{Zn(N1a)}$)-**12** isomer (*left*) and Δ_{Zn}-($S_{Zn(N1)}$,$S_{Zn(N1a)}$)-**12** isomer (*right*) in the crystal of **12** (only *imine* hydrogen atoms are shown).

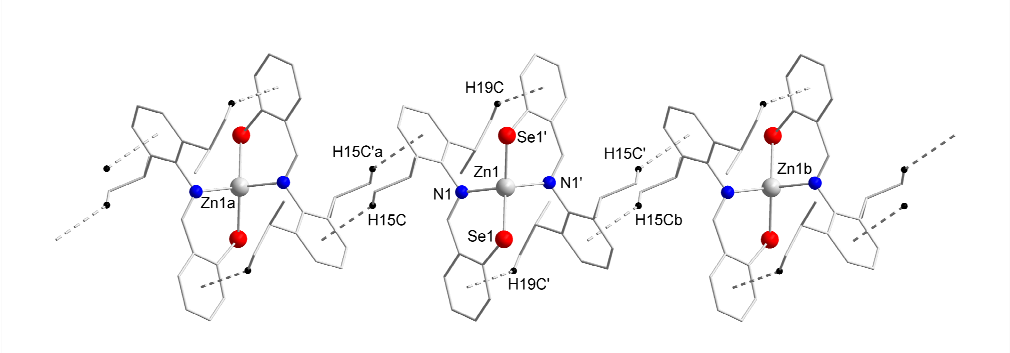


Figure S12. View of a chain polymer based on C–H_{aryl}···π ($Ph_{centroid}$) contacts between alternating Λ_{Zn}-($R_{Zn(N1)}$,$R_{Zn(N1a)}$)-**12** and Δ_{Zn}-($S_{Zn(N1)}$,$S_{Zn(N1a)}$)-**12** isomers in the crystal of **12** (only hydrogen atoms involved in intra- and intermolecular contacts are shown) [symmetry equivalent atoms (–0.5 – *x*, 0.5 – *y*, –*z*) and (0.5 – *x*, 0.5 – *y*, 1 – *z*) are given by "a" and "b", respectively].

- intramolecular distance C(19)–H(19C)···$Ph_{centroid}$ 2.93 Å
- intermolecular distance C(15)–H(15C)···$Ph_{centroid}$ 2.92 Å

- no further contacts between parallel chains.