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Synthesis and characterization of a novel chiral azomethine diselenide

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Abstract

The first chiral diselenide **9** having an *ortho*-azomethine functional group has been synthesized by the reaction of bis(*o*-formyl-phenyl) diselenide with the chiral amine *R*(+)-(1-phenylethylamine). The chiral diselenide **9** was further characterized by derivatizing it into the corresponding selenenyl halides. The derivatives are characterized by single crystal X-ray diffraction studies. In the solid state, the bromide derivative **11** shows the strongest Se···N intramolecular interaction. The chiral azomethine diselenide **9** has been further reduced to afford the diselenide **13**. The monoselenide analogues of **9** and **13** have also been synthesized.
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Keywords: Chiral azomthine diselenide; Se···N interaction; Selenenyl halide; Tridentate and tetradentate ligand
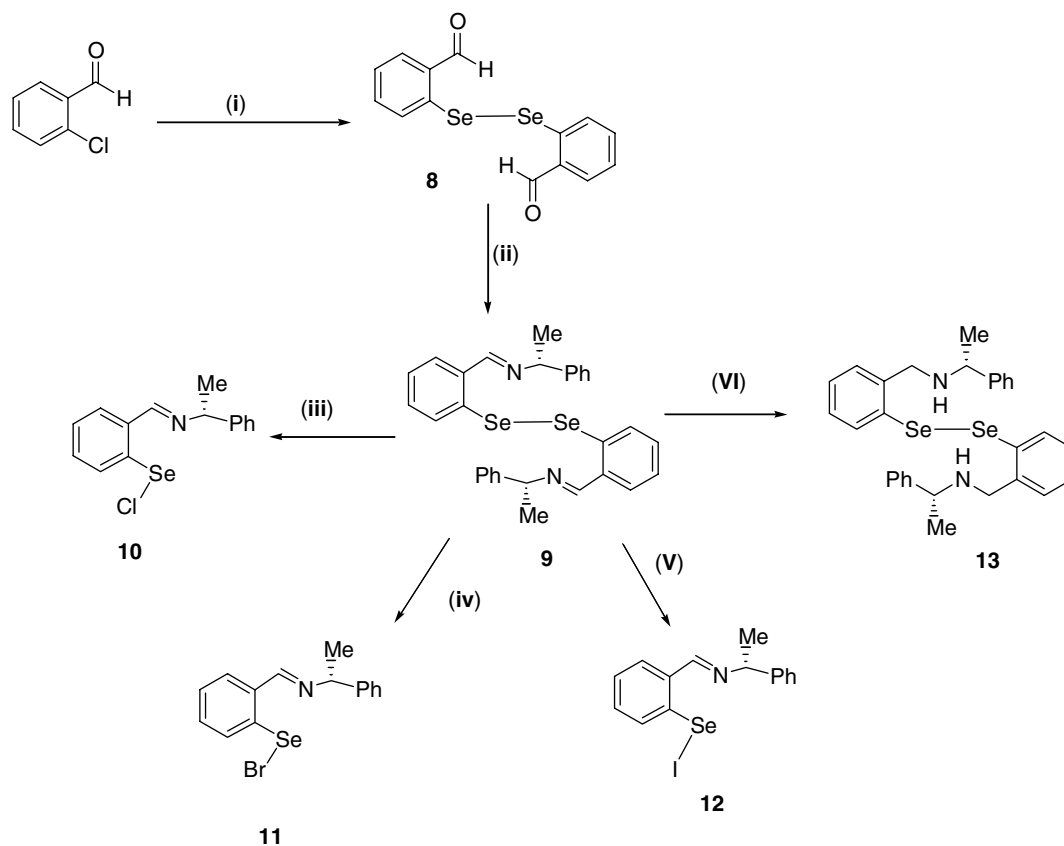
1. Introduction

The increasing usefulness of catalytic and stoichiometric asymmetric synthesis has been demonstrated for the synthesis of optically active compounds [1], particularly, biologically active chiral compounds [2]. In this regard, the chiral selenium compounds have drawn considerable attention and have become standard reagents for organic synthesis [3]. A variety of chiral electrophilic selenenylating reagents in asymmetric reactions, such as methoxyselenenylation, hydroxyselenenylation, aminoselenenylation and selenocyclization, have been investigated extensively over the past few years [4]. A common characteristic of all these reagents described in the literature is the close proximity of a heteroatom (heteroatom = N, O, S) to the selenium. The intramolecular nonbonding interactions between selenium and the heteroatom facilitate
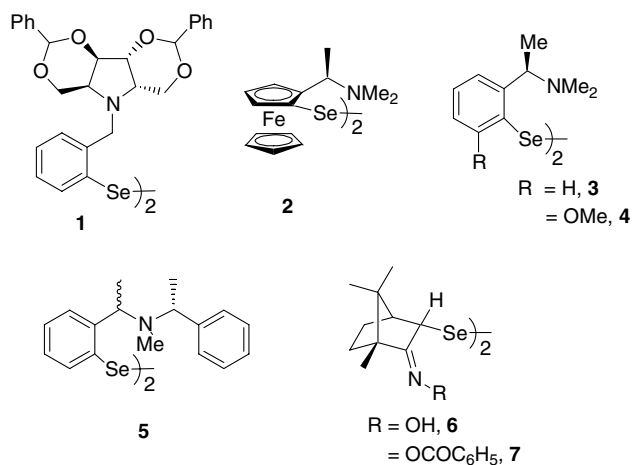
the chiral center to approach the reaction center during the addition of the selenenylating agent to the alkene moiety. This results in asymmetric induction. The Se···heteroatom interactions in such cases, therefore, not only dictate the molecular structure of the active selenium reagent so that the reaction proceeds through a relatively confined transition state but also increase or decrease the electrophilic reactivity of the selenium compounds depending upon the nature of the heteroatom and substituents on the heteroatom [5].

Although, a number of chiral diselenides (**1**–**7**) with nitrogen as heteroatom in close proximity to selenium are known [4f,6], there is no report on a chiral Schiff base diselenide. In continuation of our work on intramolecularly coordinated organochalcogens [7], we report here the synthesis and characterization of a chiral Schiff base diselenide and related reduced Schiff base tetradentate and tridentate ligands incorporating Se and N as donor atoms and the corresponding selenenyl halide derivatives Scheme 1.

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(i) Na, Se, THF, HMPA   (ii) (R)-(+)-1-phenylethylamine, benzene, Aceticacid

(iii) SO₂Cl₂, CH₂Cl₂   (iv) Br₂, CH₂Cl₂   (V) I₂, CH₂Cl₂   (VI) NaBH₄, MeOH

Scheme 1.

R = OH, 6
= OCOC₆H₅, 7

2. Results and discussion

The precursor bis(o-formylphenyl) diselenide (8) was prepared by reacting *ortho*-chlorobenzaldehyde with sodium diselenide. Sodium diselenide was synthesized in situ by refluxing a mixture of sodium and selenium in THF in the presence of catalytic amount of naphthalene. Syper et al. [8] have reported the synthesis of the diselenide 8 using the lithium diselenide route and characterized it by mp, IR and ¹H NMR spectroscopy. They have separated the pure diselenide from the crude product by using column chromatography. In the present case, the pure diselenide has been separated from the product mixture by washing the crude product with ether, followed by recrystallization from chloroform/ether (1:1) solution. The optically active tetradentate azomethine diselenide 9 was obtained by the reaction of bis(o-formylphenyl) diselenide with (R)-(+)-1-phenylethylamine in the presence of a catalytic amount of acetic acid for the enhancement of the reaction rate. The preparative procedure involved separation of water formed from the reaction by using a Dean-Stark trap. The unreacted amine was removed from the reaction mixture by washing the product several times with water. The Schiff base diselenide 9 was obtained as an orange liquid. The diselenide 9 was further characterized by derivatising it into the corresponding selenenyl

halide derivatives. The compounds **10**, **11** and **12** were obtained as crystalline solids in good yields by reacting **9** with stoichiometric amounts of sulfuryl chloride, bromine and iodine, respectively. Reduction of the Schiff base diselenide **9** has been carried out using $NaBH_4$ to generate compound **13** which would produce more stable selenium compound for organic synthesis than the parent Schiff base ligand **9**. The monoselenide analogue **15** (Scheme 2) has also been synthesized by the reaction of bis(o-formylphenyl) selenide [9] with (R)-(+)-1-phenylethylamine following a similar procedure used for the preparation of the corresponding diselenide. Reduction of the Schiff base monoselenide (**15**) with sodium borohydride afforded the amine compound **16**.

The FT IR spectra of all the compounds were recorded and are quite informative about the presence of the (–C=O, –C=N) functional groups and intramolecular coordination. The carbonyl stretching frequency of the bis(o-formylphenyl) diselenide (**8**) was observed at 1692 cm^{-1}. The peak at 1692 cm^{-1} was split and indicates a significantly different environment for the two C=O groups. In case of the chiral Schiff base diselenide **9**, the carbonyl stretching frequency was absent and a new peak at 1641 cm^{-1} for $v_{C=N}$ was observed. In compounds **10–12**, the $v_{C=N}$ stretching frequency appeared at ~1640–1650 cm^{-1} as weak broad multiplet indicating the strong coordination of N to Se, thus enhancing the delocalization of the double bond in the five membered ring formed by the coordination. In compound **13**, as expected, the $v_{C=N}$ stretching frequency was absent. For the chiral azomethine monoselenide **15**, the C=N stretching frequency appeared at 1641 cm^{-1} whereas in the case of **16**, it was absent, which confirmed the complete reduction of the azomethine moiety to the corresponding amine.

The peak at 10.2 ppm in the ^{1}H NMR spectrum of **8** indicates the presence of the formyl group. For the Schiff base diselenide **9** and for the related selenenyl halide derivatives **10–12**, the azomethine protons were observed in the region 8.5–9 ppm as sharp singlets. The peaks for the azomethine protons of selenenyl halides are slightly downfield shifted compared to the parent Schiff base.

As expected in the case of **13**, there is absence of the peak corresponding to the azomethine proton. Also, there is an upfield shift of the CH and CH$_3$ protons, which reflects relatively weaker Se···N interaction in **13** compared to that in **9**. The presence of NH peak at 2 ppm was confirmed by a D$_2$O exchange experiment. For **15**, the azomethine peak is observed at 8.63, whereas in case of **16** the azomethine peak is absent.

The ^{77}Se NMR spectra for all the compounds were recorded in CDCl$_3$ solution. There is a small downfield shift for diselenide **9** (478 ppm) compared to the precursor diselenide **8** (468 ppm). This probably is due to the presence of a stronger Se···N nonbonded interaction compared to Se···O interaction in the latter case. Similarly, in the case of **15** (402 ppm), there is a downfield shift compared to formyl monoselenide **14** (393 ppm) [9]. The downfield shift for compound **9** compared to its reduced analogue **13** (426 ppm) indicates that sp^2 nitrogen atoms have stronger Se···N nonbonded interaction. This is also observed in the case of **16** (341 ppm). In the case of the selenenyl halides **10–12**, a large deshielding in ^{77}Se chemical shift is observed with respect to the diselenide **9** and the magnitude of the downfield shift is according to the electronegativity of the halide atoms attached to the selenium atom.

The electrospray ionization mass spectra (ESI-MS) of all the compounds, except **11**, do not show the molecular ion peak. For the chloro and iodo derivatives (**10** and **12**, respectively) the highest peak is at M − X at $m/e = 288$. In all cases the base peak is at $m/e = 184$, which corresponds to C$_7$H$_6$NSe.

The optical rotation values are given with the analytical data. The optical purity of a representative compound **9** was determined by recording the ^{1}H NMR spectra in presence of different mole ratios of the chiral shift reagent tris[3-(heptafluropropyl)hydroxymethylene-(+)-camphorato]europium(III) [Eu(tfc)$_3$] in CDCl$_3$ from 1:0.25 to 1:1.25 ratio. There was no change in the resonances of the compound indicating the optical purity of the compound.
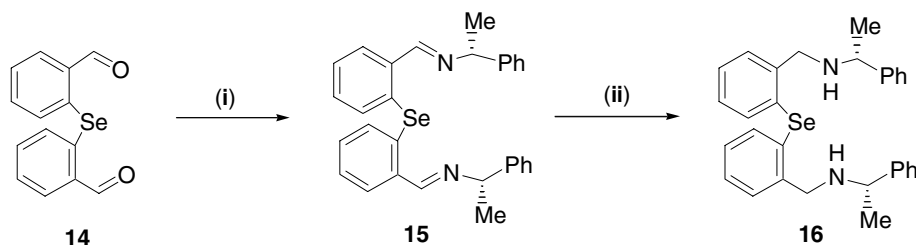
Scheme 2.

(**i**) (R)-(+)-1-phenylethylamine , benzene, Acetic acid
(**ii**) $NaBH_4$, EtOH
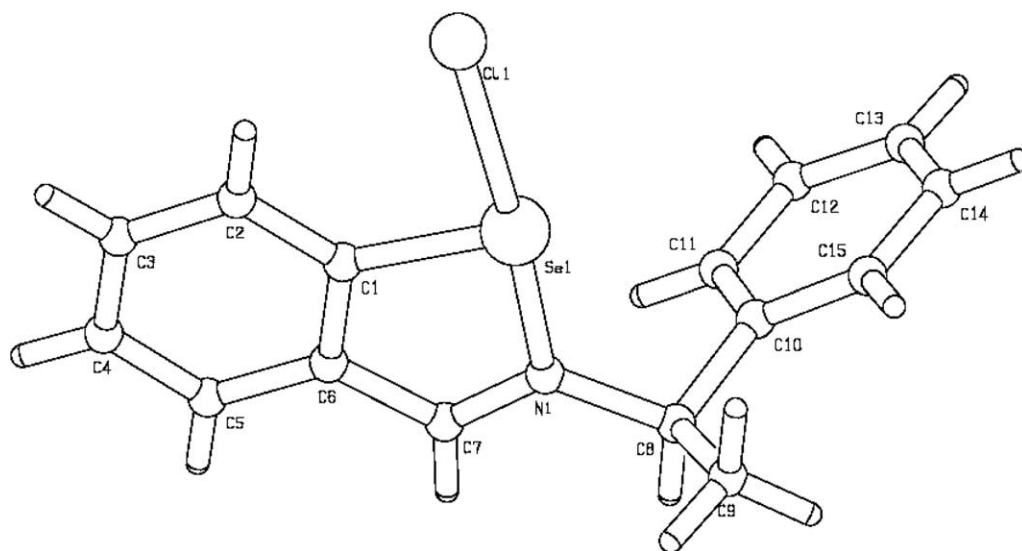
Fig. 1. PLUTON view of the compound **10**.

Table 1
Significant bond lengths (Å) and bond angles (°) for **10**, **11** and **12**

	10	**11**	**12**
Se(1)-C(1)	1.889(3)	1.891(3)	1.900(3)
N(1)–C(7)	1.275(4)	1.274(5)	1.284(4)
N(1)–C(8)	1.487(4)	1.495(5)	1.475(5)
Se(1)–X(1)	2.6097(9)	2.7767(5)	2.9868(4)
Se(1)–N(1)	1.951(3)	1.943(3)	1.960(3)
C(1)–Se(1)–N(1)	83.14(12)	83.21(14)	83.45(13)
C(1)–Se(1)–X (1)	92.91(10)	93.93(11)	95.87(9)
N(1)–Se(1)–X(1)	176.04(7)	177.14(9)	178.46(8)
C(7)–N(1)–Se(1)	114.6(2)	114.9(2)	114.0(2)
C(8)–N(1)–Se(1)	121.0(2)	121.0(3)	119.2(2)
C(2)–C(1)–Se(1)	127.6(2)	127.5(3)	128.0(2)
C(6)–C(1)–Se(1)	112.26(19)	112.3(2)	110.9(3)

The single crystal structures of **10**, **11** and **12** have been determined. These are isostructural and therefore, the crystal structure of only **10** is discussed in detail. Only the salient features of **11** and **12** are compared with **10**. The PLUTON view of compound **10** is shown in Fig. 1. The significant bond lengths and bond angles of **10**, **11** and **12** are given in Table 1. The geometry around Se is T shaped due to the strong Se···N nonbonded interaction. In compound **10**, the strongest Se···N interaction (1.951(3) Å) is observed compared to other selenenyl chlorides reported in the literature [7]. The Se···N distance is close to the sum of the covalent radii of Se and N (1.80 Å). The Se–Cl bond length [2.6097(9) Å] is much longer compared to the sum of the covalent radii (2.16 Å). This value is longer than the Se–Cl distance reported for 2-(4,4-dimethyl-2-phenyloxazolinyl)benzeneselenenyl chloride (2.482(8) Å) [7a]. The Se–Cl bond is longer by 0.128 Å than the reported longest *trans* Se–Cl bond distance [10a]. The almost linear alignment of N···Se–Cl [N(1)–Se–Cl:

176.04(7)°] allows an effective orbital interaction between the nitrogen lone pair and σ* orbital of the Se–Cl bond and also easy availability of lone pair of sp² nitrogen atom towards coordination leads to elongation of the *trans* Se–Cl bond and stronger Se···N interaction.

In compound **11**, the Se···N distance [1.943(3) Å] is the shortest compared to the distances reported for any selenenyl derivatives. This Se···N distance is much closer to the sum of the single bond covalent radii of Se (1.16 Å) and N (0.75 Å). The Se–Br bond distance [2.7767(5) Å] is greater than the reported value for (*R*)-(4-ethyl)-2-phenyloxazoline [2.661(2) Å] [10a] and bis [3-(4,5-dihydro-4,4-dimethyl-1,3-oxazol-2-yl)-4-(3,5-dimethylphenyl)-2-naphthyl] selenium bromide [2.6485(7) Å] [7d,10b]. The Se···N–Br angle [177.14(9)°] is close to a linear arrangement. In selenenyl iodide **12** the Se···N nonbonding distance [1.960(3) Å] is smaller than the reported Se···N distances for other selenenyl iodide compounds [7]. There is no intermolecular interaction between the molecules in the packing diagram of **10**, **11** and **12**.

3. Experimental

3.1. General methods

Air-sensitive reactions were carried out under an inert atmosphere. Solvents were purified and dried by standard procedures and were freshly distilled prior to use. All chemicals used, *o*-chlorobenzaldehyde (sd fine), sodium (sd fine), *R*-(+)-(1-phenylethylamine) (Fluka) and the chiral shift reagent tris[3-(heptafluropropyl)hydroxy-methylene-(+)-camphorato]europium(III) (Merck), were reagent grade and were used as received. Melting points

were recorded in capillary tubes and are uncorrected. The elemental analyses were performed on Carlo-Erba model 1106 and Eager 300 EA1112 elemental analyzers. The IR spectra were recorded as KBr pellets on a Thermo Nicolet Avatar 320 FTIR spectrometer. ^{1}H and ^{13}C NMR spectra were obtained at 400 MHz in CDCl$_3$ on Varian spectrometer. ^{77}Se NMR spectra were obtained at 95.34 MHz on a Bruker 500 spectrometer. Chemical shifts are cited with respect to SiMe$_4$ (^{1}H and ^{13}C) and Me$_2$Se (^{77}Se) as external standard. The enantiomeric purity of **9** was determined by the integration of the signals in the ^{1}H NMR signal using the chiral shift reagent tris[3-(heptafluropropyl)hydroxymethylene-(+)-camphorato] europium(III) [Eu(tfc)$_3$]. ESI-MS mass spectra were recorded at room temperature on a Q-Tof micro (YA-105) micromass. Optical rotations were measured by a JASCO Model DIP 370 digital polarimeter.

3.2. Synthesis of bis(o-formylphenyl) diselenide (**8**) [8]

Sodium diselenide (50 mmol) was prepared from selenium and sodium in the presence of catalytic amount of naphthalene in dry THF (50 mL). *o*-Chlorobenzaldehyde (7.02 g, 50 mmol) and HMPA (20 mL) were added to this solution. After stirring for 12 h at room temperature the reaction mixture was refluxed for 6 h. The mixture was allowed to cool slowly at room temperature. The solvent was evaporated and the resulting product was washed with water to remove HMPA. The solid obtained after washing with water, was filtered, dried and washed with ether several times to separate the monoselenide and other side products. The diselenide was obtained as a pure yellow solid and was recrystallized from CHCl$_3$/ether (1:1) mixture. Yield: 2.5 g, 30%; m.p. 172 °C (m.p. 172 °C) [8] (Anal. calc. for C$_{14}$H$_{10}$Se$_2$O$_2$: C, 45.65; H, 2.7. Found: C, 45.2; H, 2.78.) IR (KBr): 1692, 1665 cm^{-1} (C=O) ^{1}H NMR (CDCl$_3$): 10.2 (s, –CHO, 2H), 7.86–7.26 (m, Ar–H, 12H), ^{13}C NMR (CDCl$_3$): 193 (aldehydic carbon), 136, 135, 134.7, 134.5, 131, 126.5 (aromatic carbons), ^{77}Se NMR (CDCl$_3$): 468 ppm.

3.3. Synthesis of bis[o-(R)-(methylbenzyliminomethinyl)-phenyl] diselenide (**9**)

Bis(*o*-formylphenyl) diselenide **8** (1 g, 2.7 mmol) was refluxed azeotropically in benzene (200 mL), with (*R*)-(+)-1-phenylethylamine (0.66 g, 5.4 mmol) and two drops of acetic acid, using a Dean-Stark trap till the completion of the reaction (by IR). The mixture was washed with water (3 × 100 mL) to remove the unreacted amine. The remaining water from the organic layer was removed azeotropically and finally benzene was evaporated under vacuum to give a yellow viscous liquid of the Schiff base **9**. Yield: 1.07 g, 68%; IR(neat): 1641 cm^{-1} (C=N stretching), [α]^{25} = −250.28 (c = 3.5,

C$_6$H$_6$), ^{1}H NMR (CDCl$_3$): 8.55 (s, CH=N, 2H), 7.87–7.14 (m, aromatic protons, 18H), 4.68 (q, CHPh, 2H), 1.68 (d, Me, 6H), ^{13}C NMR (CDCl$_3$): 159.51 (imine carbon), 144.73, 134.68, 133.31, 131.90, 130.31, 128.50, 128.29, 126.90, 126.80, 125.61 (aromatic carbons), 70.22 (CHPh), 26.54 (Me), ^{77}Se NMR (CDCl$_3$): 478 ppm.

3.4. Synthesis of bis[o-(R)-(methylbenzyliminomethinyl)-phenyl] selenenyl chloride (**10**)

To a solution of diselenide **9** (0.2 g, 0.34 mmol) in dichloromethane (25 mL), SO$_2$Cl$_2$ (0.045 g, 0.34 mmol) in dichloromethane (25 mL) was added drop wise at 0 °C for 1 h. The reaction mixture was stirred for 6 h at room temperature. Then the solvent was completely evaporated under vacuum. The viscous product so obtained was triturated with pentane to give a white solid and the solid was recrystallized from CHCl$_3$/pentane (1:1) mixture. Yield: 0.1 g, 88%; (Anal. calc. for C$_{15}$H$_{15}$NSeCl: C, 55.67; H, 4.67; N, 4.32. Found: C, 54.98; H, 4.20; N, 3.8.) IR(neat): 1641 cm^{-1} (C=N stretching), [α]^{25} = −4.34 (c = 1.15, CH$_2$Cl$_2$) MS *m/z* 288 (M$^+$ − Cl), 183 (C$_7$H$_6$NSe), ^{1}H NMR (CDCl$_3$): 9.04 (s, CH=N, 1H), 9.04–7.26 (m, aromatic protons, 9H), 5.59 (q, CHPh, 1H), 2.02 (d, Me, 3H), ^{13}C NMR (CDCl$_3$): 156.52 (imine carbon), 151.68, 139.42, 132.17, 132.07, 129.67, 129.52, 129.44, 126.90, 129.38, 126.78 (aromatic carbons), 64.18 (CHPh), 23.21 (Me), ^{77}Se NMR (CDCl$_3$): 1004 ppm.

3.5. Synthesis of bis[o-(R)-(methylbenzyliminomethinyl)-phenyl] selenenyl bromide (**11**)

The procedure followed was the same as that used for the preparation of compound **10**, except the addition of Br$_2$ in place of SO$_2$Cl$_2$. Yield: (0.12 g, 96%); (Anal. calc. for C$_{15}$H$_{15}$NSeBr: C, 48.94; H, 3.84; N, 3.81. Found: C, 46.03; H, 3.02; N, 3.06.); IR(neat): 1641 cm^{-1} (C=N stretching); [α]^{25} = −6.38 (c = 0.47, CH$_2$Cl$_2$); ESI-MS: *m/z* 367 (M$^+$), 288 (M$^+$ − Cl), 183 (C$_7$H$_6$NSe); ^{1}H NMR (CDCl$_3$, 400 MHz): 8.89 (s, CH=N, 1H), 9.08–7.26 (m, aromatic protons, 9H), 5.58 (q, CHPh, 1H), 2.00 (d, Me, 3H); ^{13}C NMR (CDCl$_3$,): 156.23 (imine carbon), 149.91, 139.24, 132.13, 132.06, 130.36, 129.81, 129.39, 129.30, 129.38, 126.90 (aromatic carbons), 64.20 (CHPh), 23.14 (Me), ^{77}Se NMR (CDCl$_3$,): 1006 ppm.

3.6. Synthesis of bis[o-(R)-(methylbenzyliminomethinyl)-phenyl] selenenyl iodide (**12**)

The procedure followed was the same as that used for the preparation of compound **10**, except the use of an iodine solution in place of SO$_2$Cl$_2$. Yield: 0.13 g, 90%; (Anal. calc. for C$_{15}$H$_{15}$NSeI: C, 43.51; H, 3.4; N, 3.38.

Found: C, 42.7; H, 2.89; N, 2.97.) IR(neat): 1641 cm^{-1} (C=N stretching), $[\alpha]^{25} = -4.34$ ($c = 1.15$, CH$_2$Cl$_2$), MS m/z 288 (M$^+$ − I), 183 (C$_7$H$_6$NSe), ^{1}H NMR (CDCl$_3$): 8.73 (s, CH=N, 1H), 8.95–7.26 (m, aromatic protons, 9H), 5.37 (q, CHPh, 1H), 2.03 (d, Me, 3H), ^{13}C NMR (CDCl$_3$): 155.17 (imine carbon), 146.68, 139.30, 133.22, 132.45, 132.02, 129.95, 129.46, 129.30, 127.08, 126.96 (aromatic carbons), 64.03 (CHPh), 23.33 (Me), ^{77}Se NMR (CDCl$_3$): 988 ppm.

3.7. Synthesis of bis[o-(R)-(methylbenzylamino-methinyl)phenyl] diselenide (13)

To the Schiff base diselenide **9** (0.8 g, 14 mmol) in ethanol under nitrogen, solid NaBH$_4$ (excess) was added in small portions. The reaction mixture was stirred for 4 h and then refluxed for 1 h. Excess ethanol was removed under vacuum. To the residue water (50 mL) was added and the product was extracted with chloroform. Removal of the solvent afforded viscous yellow oil. Yield: 0.6 g, 74%; IR(neat): 1451, 1491 cm^{-1}; $[\alpha]^{25} = -5.99$ ($c = 1$, CH$_2$Cl$_2$), MS m/z 286 (M$^+$/2), 183 (C$_7$H$_6$NSe), ^{1}H NMR (CDCl$_3$): 7.76–7.1 (m, aromatic protons, 18H), 3.69–3.81 (m, CHPh, CH$_2$Ph, 6H), 1.40 (d, $J = 6.5$ Hz, Me, 6H), ^{13}C NMR (CDCl$_3$): 144.5, 139.77, 132.98, 131.96, 129.38, 128.06, 126.96, 126.55, 126.44, (aromatic carbons), 57.64 (CH$_2$Ar), 52.36 (CHPh), 23.96 (Me), ^{77}Se NMR (CDCl$_3$): 426 ppm.

3.8. Synthesis of bis[o-(R)-(methylbenzylimino-methinyl)phenyl] selenide (15)

Bis(o-formylphenyl)selenide **7** was refluxed azeotropically in benzene (200 mL), with (R)-(+)-1-phenylethylamine and two drops of acetic acid, using a Dean-Stark trap till the completion of the reaction (by IR). The resulting reaction mixture was washed with water (3 × 100 mL) to remove the unreacted amine. The remaining water from the organic layer was removed azeotropically and finally benzene was evaporated under vaccum to give a viscous yellow oil of the Schiff base. Yield: 80% IR(neat): 1641 cm^{-1}(C=N stretching), $[\alpha]^{25} = 42.826$ ($c = 4.6$, CHCl$_3$) ^{1}H NMR (CD$_3$Cl): 8.63 (CH=N, 2H), 7.07–7.82 (m, C$_6$H$_5$, C$_6$H$_4$, 18H), 4.47(q, CHPh, 2H), 1.53 (d, Me, 6H), ^{13}C NMR (CDCl$_3$): 160 (imine carbon), 145, 136.63, 134.07, 130.87, 130.40, 128.53, 127.42, 126.91, 126.86 (aromatic carbon atoms), 70.16 (CHPh), 25.95 (Me), ^{77}Se NMR (CDCl$_3$): 402 ppm.

3.9. Synthesis of bis[o-(R)-(methylbenzylamino-methinyl)phenyl] selenide (16)

The compound was prepared as an yellow oil by the reduction of the bis[o-(R)-(methylbenzyliminomethi-

nyl)phenyl]selenide **15** with NaBH$_4$ in methanol following the procedure used for **13**. Yield: 65% IR(neat): 1585, 1451 cm^{-1}, $[\alpha]^{25} = 9.4285$($c = 3.5$, C$_6$H$_6$) ^{1}H NMR (CD$_3$Cl): 7.31–7.05(m, 18H), 3.70(m, 8H), 1.74(2H, NH), 1.29(d, 6H), ^{13}C NMR (CDCl$_3$): 145.29, 141.72, 134.29, 132.48, 129.87, 128.43, 128.00, 127.57, 126.93, 126.72 (aromatic carbons), 57.81 (CH$_2$), 52.37 (CH), 24.57 (Me), ^{77}Se NMR (CDCl$_3$): 341 ppm.

4. X-ray structure determination

The diffraction measurements were performed on a STOE (Darmstadt, Germany) IPDS imaging plate single crystal diffractometer at room temperature with graphite-monochromated Mo Kα radiation ($\lambda = 0.7107$ Å). The structures were solved by direct methods and full-matrix least-squares refinement on F^2 (program SHELXL-97) [11]. Hydrogen atoms were localized by geometrical means. A riding model was chosen for refinement. The isotropic thermal parameters of the H atoms were fixed at 1.5 times (CH$_3$ groups) or 1.2 times U_{eq} (Ar–H) of the corresponding C atom. Some details of the data collection and refinement are given in Table 2.

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre; CCDC Nos. 254801–254803 for compounds **10**, **11** and **12**, respectively. Copies of this information may be obtained free of the charge

Table 2
Crystal data and structure refinement of **10**, **11** and **12**

	10	11	12
Empirical formula	C$_{15}$H$_{14}$ClNSe	C$_{15}$H$_{14}$BrNSe	C$_{15}$H$_{14}$INSe
F_w	322.68	367.14	414.13
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic
Space group	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$
Unit cell dimensions			
a (Å)	10.9277(7)	11.1543(7)	10.0377(7)
b (Å)	11.1710(8)	11.1669(8)	11.6427(9)
c (Å)	11.3708(10)	11.5569(10)	12.8939(11)
α (°)	90	90	90
β (°)	90	90	90
γ (°)	90	90	90
V (Å^3)	1388.07(18)	1439.52(19)	1506.9(2)
Z	4	4	4
Temperature (K)	293(2)	293(2)	293(2)
Absorption coefficient (mm^{-1})	2.878	5.366	4.524
Observed reflections [$I > 2\sigma$]	2944	2978	3077
Final $R(F)$ [$I > 2\sigma$][a]	0.0270	0.0257	0.0183
$wR(F^2)$ indices [$I > 2\sigma$]	0.0563	0.0460	0.0380

[a] Definition: $R(F_0) = \sum ||F_o| - |F_c||/\Sigma |F_o|$ and $wR(F_o^2) = \left\{ \sum w (F_o^2 - F_c^2)^2] / \sum [w(F_c^2)^2] \right\}^{1/2}$.

from The Director, CCDC, 12 Union Road, Cambridge, CB2 1 EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk. or http://www.ccdc.cam.ac.uk).

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