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SELECTIVE INTRAMOLECULAR OXYSELENENYLATION OF OLEFINIC ALCOHOLS AND CARBOXYLIC ACIDS BY USING ORGANIC CYANOSELENIDES IN THE PRESENCE OF METAL TRIFLATES

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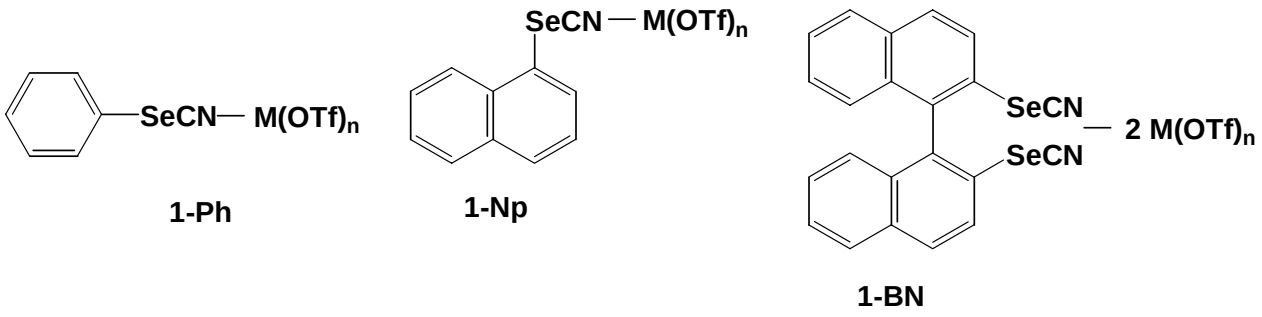
Abstract – The reagent, ArSeCN—$M(OTf)_n$, is prepared from equimolar amounts of an aromatic selenocyanate and metal trifluoromethanesulfonate. It reacts with unsaturated alcohols and carboxylic acids to give cyclic ethers and lactones, respectively. Depending on conditions, reactions of *trans*-2-allylcyclohexanol with the reagent selectively afford *exo*-cyclized tetrahydrofuran or *endo*-cyclized tetrahydropyran. The mechanism of *exo/endo* selection is discussed based on molecular dynamics studies.

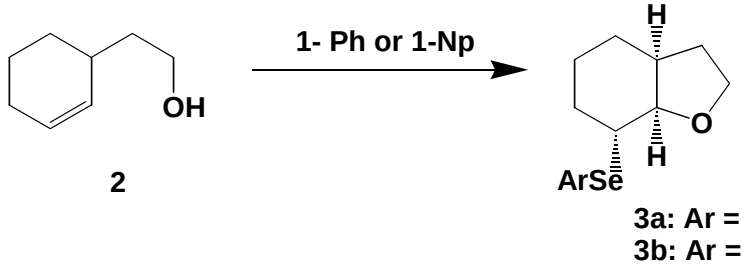
INTRODUCTION

Intramolecular oxyselenenylation of unsaturated alcohols and carboxylic acids is one of the most important organic transformations using electrophilic organoselenium compounds, and various reagents have been developed for this purpose.[1–3] Among those organoselenium electrophiles, benzeneselenenyl triflate (PhSeOTf)[4] prepared *in situ* from PhSeCl and AgOTf is the most reactive and performs the cyclization with high regio- and stereoselectivities, because triflate anion is inert toward cationic intermediates.[5–9] Since preparation of an organoselenenyl chloride or bromide (RSeCl or RSeBr) is usually carried out by chlorination or bromination of the corresponding diselenide obtained by a reaction of Grignard reagent with Se, it is difficult to prepare the reagent (RSeOTf) with sensitive functional groups and chirality on the subsituent (R). This is the major limitation of organoselenenyl triflate in the reagent design. Recently, we have reported that a novel reagent, which was obtained from a reaction of benzeneselenocyanate with copper triflate in toluene, carried out oxyselenenylation of unsaturated alcohols to yield cyclic ethers in high yields.[10] In this paper we would like to describe the scope and limitations of the new organoselenium electrophile based on the coupling of aromatic selenocyanates and metal triflates.

RESULTS AND DISCUSSION

Reactions of benzeneselenocyanate and 1-naphthaleneselenocyanate with equimolar amounts of a metal triflate ($M(OTf)_n$) in toluene at 50 °C gave the reagents ($ArSeCN—M(OTf)_n$: **1-Ph** and **1-Np** (Ar = 1-naphthyl) as brown suspensions. Cyclizations of unsaturated substrates (**2**, **4**, and **5**) by **1-Ph** or **1-Np** were carried out in various conditions (solvent, temperature, and metal). The results are summarized in Table 1. Toluene was the best solvent, and tetrahydrofuran derivatives (**3a**, **3b**, **6**, **7a**, and **7b**) were obtained in high to moderate yields, when reactions were carried out in toluene at 50 °C. The reagents (**1-Ph** and **1-Np**) containing Cu, Ni, and Ag triflates are effective for the cyclizations, but **1-Ph** with Pd triflate[11] is not suitable for activation of selenocyanates (entry 7 in Table 1). Since insoluble dark tar precipitated from the reaction mixture, yields of the products (**3b**, **7a**, and **7b**) were moderate to poor in the reactions using **1-Ph** or **1-Np** with $Ni(OTf)_2$ (entries 10, 14, and 17). Formation of other products, such as *endo*-cyclized 6-membered ring heterocycles, nitriles resulting from attack of cyanide ions, and heterocyclic compounds without the SeAr group resulting from cyclization mediated by acid, were not observed in crude reaction mixtures.





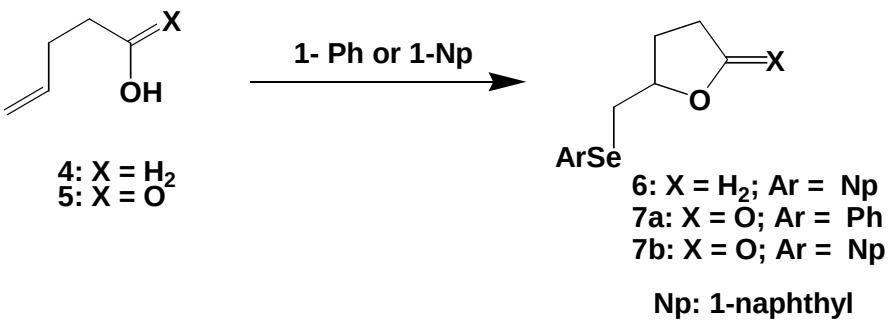
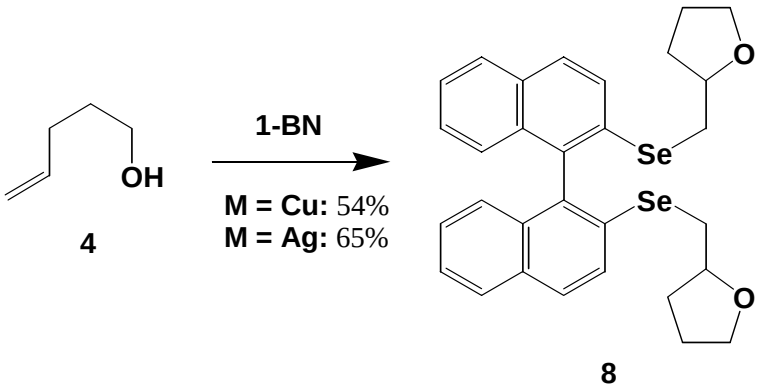


Table 1. Cyclization of Unsaturated Compounds by 1-Ph or 1-Np.

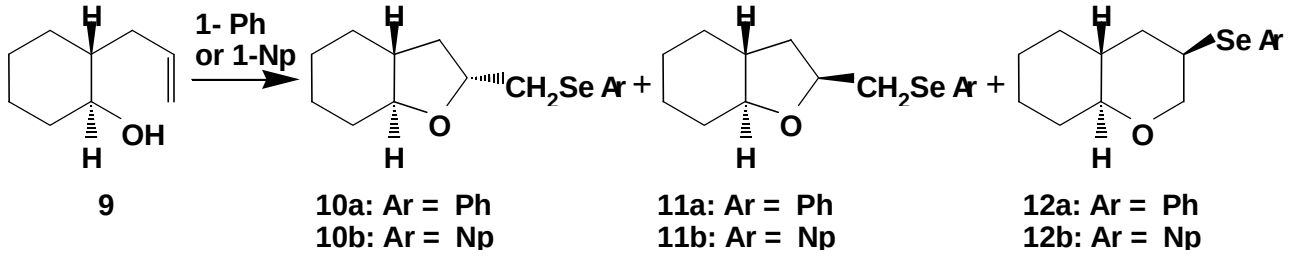
		Conditions					product	
entry	substrate	reagent	$M(OTf)_n$	Solvent	temp/°C	time/h	no.	yield/%[a)]
1	**2**	**1-Ph**	$Cu(OTf)_2$	CH_3CN	80	1	--	0
2	**2**	**1-Ph**	$Cu(OTf)_2$	CH_2Cl_2	40	1	--	0
3	**2**	**1-Ph**	$Cu(OTf)_2$	Toluene	25	10	**3a**	39
4	**2**	**1-Ph**	$Cu(OTf)_2$	Toluene	50	1	**3a**	88
5	**2**	**1-Ph**	AgOTf	Toluene	50	1	**3a**	87
6	**2**	**1-Ph**	$Ni(OTf)_2$	Toluene	50	1	**3a**	92
7	**2**	**1-Ph**	$Pd(OTf)_2$	Toluene	50	1	--	0
8	**2**	**1-Np**	$Cu(OTf)_2$	Toluene	50	1	**3b**	92
9	**2**	**1-Np**	AgOTf	Toluene	50	1	**3b**	84
10	**2**	**1-Np**	$Ni(OTf)_2$	Toluene	50	1	**3b**	57
11	**4**	**1-Np**	$Cu(OTf)_2$	Toluene	50	1	**6**	67
12	**5**	**1-Ph**	$Cu(OTf)_2$	Toluene	50	1	**7a**	75
13	**5**	**1-Ph**	AgOTf	Toluene	50	1	**7a**	79
14	**5**	**1-Ph**	$Ni(OTf)_2$	Toluene	50	1	**7a**	40
15	**5**	**1-Np**	$Cu(OTf)_2$	Toluene	50	1	**7b**	87
16	**5**	**1-Np**	AgOTf	Toluene	50	1	**7b**	89
17	**5**	**1-Np**	$Ni(OTf)_2$	Toluene	50	1	**7b**	18

[a)] Isolated yields by SiO_2 flush columun chromatography.

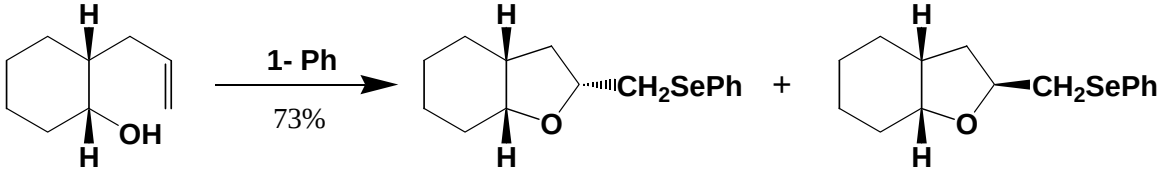
1,1'-Binaphthyl-2,2'-diselenocyanate, which was synthesized from 2,2'-diamino-1,1'-binaphthyl *via* bis(diazonium) ion and a potent compound for chiral recognission,[12–19] was activated by 2 equivalents of $Cu(OTf)_2$ or AgOTf to give the reagent (**1-BN**). The reaction of (±)-**1-BN** with **4** in the same conditions gave the bis(tetrahydrofuran) derivative (**8**) in 54% (M = Cu) and 65% yields (M = Ag). Since 4 peaks which were assignable to each carbon atom were observed in the ^{13}C NMR spectrum of **8**, the product was a mixture of possibly 3 diastereomers.[20] For example, signals of carbon atoms at the 1- and 1'-position (1-C and 1'-C, respectively) of 1,1'-binaphthyl skeleton appeared at δ = 137.15, 137.29, 137.53, and 137.63 ppm.



Cyclization of *trans*-2-allylcyclohexanol (**9**) by **1-Ph** or **1-Np** in toluene at 50 °C for 1 h afforded a mixture of tetrahydrofuran derivatives (**10a**, **10b**, **11a** and **11b**) and tetrahydropyran (**12a** and **12b**). Each product was isolated by preparative HPLC using a normal phase silica gel column. The yields and selectivities of the cyclic products are shown in Table 2. Here, the *endo*-cyclized **12a** and **12b** formed predominantly over 5-membered ring ethers in cases of reagents (**1-Ph** and **1-Np**) with Ni or Cu, respectively (entries 1, 3, and 4). In the cases of the reagents with Ag (entries 2 and 5), the *exo*-cyclized **10a**, **10b**, **11a** and **11b** were obtained as major products. Reactions of benzeneselenenyl triflate (PhSeOTf) with **9** selectively gave a mixture of 5-membered ring ethers (**10a** and **11a**) at -78 °C and the 6-membered ring ether (**12a**) at 0 °C (entries 9 and 10). Addition of base (pyridine) to the reaction mixture increased the formation of *exo*-cyclized products (entries 7 and 11). The selectivity of *endo*-cyclization increased in the presence of acid (TfOH) (entry 8). On the contrary, cyclization of *cis*-2-allylcyclohexanol (**13**) by **1-Ph** (M = Cu) exclusively afforded the *exo*-cyclized tetrahydrofurans (**14**) in 73% yield.[10]



9 **10a: Ar = Ph** **10b: Ar = Np** **11a: Ar = Ph** **11b: Ar = Np** **12a: Ar = Ph** **12b: Ar = Np**



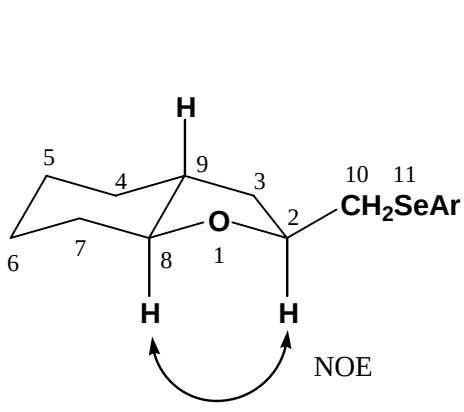
13 **14: mixture of two isomers**

Structures of products (**10a** – **12b**) were determined as illustrated by 1-D and 2-D ^{1}H NMR studies. NOE Correlations between hydrogen atoms on 2- and 8-positions (2-H–8-H NOEs) were observed on NOESY spectra of **10a** and **10b**. Therefore, these two protons existed on a *cis* position. On the other hand, since 2-H–9-H NOEs were detected on **11a** and **11b**, these hydrogens occupied the *cis* location. The signal on 3-H of **12a** appeared at δ = 3.35 ppm as a dddd type signal (like a triple of triplet shape) with coupling constants of J = 3.91, 3.91, 11.70, and 11.70 Hz. The smaller and larger J values are assignable to couplings of H_{ax}—H_{eq} and H_{ax}—H_{ax}, respectively. In the spectrum of **12b**, 3-H also appears at 3.40 ppm with J = 11.71 Hz (H_{ax}—H_{ax}). In addition, 3-H–10-H NOEs are observed on NOESY spectra of **12a** and **12b**. Thus, the structures of **12a** and **12b**, in which SeAr groups occupied equatorial positions, were confirmed.

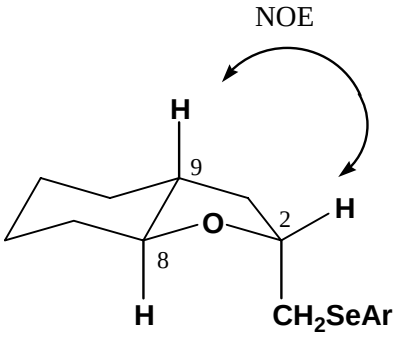
Table 2. Selectivities on the Cyclization of 9 by 1-Ph or 1-Np.[a)]

	conditions			% yield of product[b)]			selectivity	
entry	reagent	M	additive	**10a** or **10b**	**11a** or **11b**	**12a** or **12b**	(**10** + **11**)/**12**[c)]	**10**/**11**
1	**1-Ph**	Cu	none	5	12	60	22:78	29:71
2	**1-Ph**	Ag	none	14	48	19	77:23	23:77
3	**1-Ph**	Ni	none	2	10	71	14:86	17:83
4	**1-Np**	Cu	none	13	4	65	21:79	76:24
5	**1-Np**	Ag	none	10	39	40	55:45	20:80
6	**1-Np**	Ni	none	0	0	0	--	--
7	**1-Ph**	Ni	C_5H_5N	32	51	0	100:0	39:61
8	**1-Ph**	Ni	TfOH	0	4	46	8:92	0:100
9[d)]	PhSeOTf	--	none[e)]	5[f)]	--	84	5:95	--
10[d)]	PhSeOTf	--	none[g)]	79[f)]	--	8	91:9	--
11[d)]	PhSeOTf	--	C_5H_5N[e)]	45[f)]	--	0	100:0	--

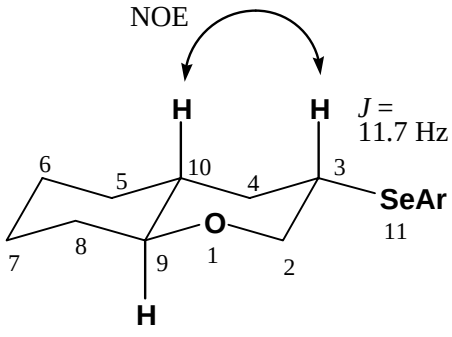
[a)]Unless otherwise stated, reactions were carried out in toluene at 50 °C for 1 h. [b)]Isolated yields by preparative HPLC. [c)]Selectivities for *exo*/*endo* cyclization. [d)]The reaction was carried out in CH_2Cl_2 using PhSeOTf prepared from PhSeCl and AgOTf, see ref. 4 — 8. [e)]At 0 °C. [f)]A mixture of **10a** and **10b**. [g)]At –78 °C.



10a: Ar = Ph (E = 15.745 kcal/mol)
10b: Ar = Np



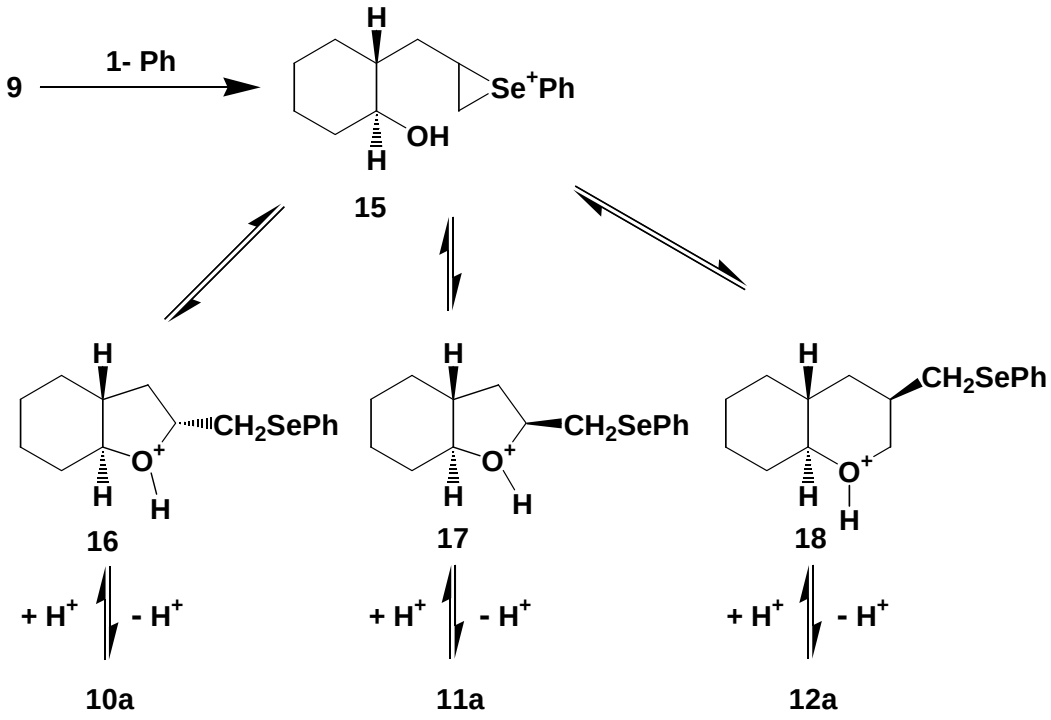
11a: Ar = Ph
(E = 15.730 kcal/mol)
11b: Ar = Np

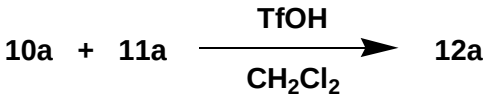


12a: Ar = Ph
(E = 12.084 kcal/mol)
12b: Ar = Np

As we have already mentioned, oxyselenenylation proceeds *via* the 3-membered ring seleniranium intermediate (**15**).[9, 21—24] Following intramolecular S_N2 attack of the OH group to a cationic carbon of **15** affords oxisonium ions (**16**—**18**). Finally, products are obtained after deprotonation from **16**—**18**. It seems that the reaction is reversible in the presence of acidic hydrogens and gives an equilibrium mixture of **10a**—**12a** and **15**—**18**. Indeed, when a mixture of **10a** and **11a** was treated with 1 equivalent of trifluoromethanesulfonic acid in CH_2Cl_2 at 0 °C, isomerization to **12a** occurred in 18%

conversion. Usually, in comparison to 5-*exo*- and 6-*endo*-cyclization modes, the former proceeds faster to give predominantly 5-membered ring ethers. Therefore, **10a** and **11a**, which were supposed to be kinetically controlled products, were obtained as major products in reactions at -78 °C or in the presence of pyridine which could quench the equilibrium. On the other hand, **12a** was probably more stable than 5-membered ring isomers and was yielded mainly as a thermodynamic product in reactions at higher temperatures. Presence of excess hydrogen ion in the reaction mixture especially accelerated the isomerization of **10a** and **11a** to **12a**. Reagents **1-Ph** and **1-Np** with AgOTf produced more basic conditions than those with Cu or Ni and resulted in increased yields of 5-membered ring ethers.





18%

In order to confirm the mechanistic speculation, total energies of products (**10a**, **11a**, and **12a**) and the β-isomer of **12a**, whose PhSe group is located on the axial position, were calculated by using MM+® molecular mechanic method. Energies obtained for the most stable conformations of **10a**, **11a**, **12a**, and the β-isomer are 15.745, 15.730, 12.084, and 16.972 kcal/mol, respectively. The thermodynamic product (**12a**) is *ca.* 3.7 kcal/mol more stable than kinetic products (**10a** and **11a**). The energy difference between **10a** and **11a** is very small, but **11a** is mainly obtained *ca.* 3:1 selectivity. This phenomena could be explained by a difference in the stabilities of these compounds in reaction

conditions. For example, no **10a** was left in the forcing conditions (entry 8 of Table 2), and more **10a** existed in the presence of pyridine (entry 7). On the contrary, in the cases of products obtained from the *cis*-isomer (**13**) energies of 5-membered ring ethers (**14**) are 16.053 and 18.237 kcal/mol. These are about 1.7 kcal/mol higher than the energies of isomeric 6-membered ring ethers (15.677 kcal/mol and 14.352 kcal/mol) which were not produced in the reaction. Thus, depending on kinetically and thermodynamically controlled conditions, intramolecular oxyselenenylation of **9** produces different products. However, reaction of other starting materials (**2**, **4**, **5**, and **13**) affords the same product, regardless of the reaction conditions, because stability of the 5-*exo*-cyclized product might be very similar to the 6-*endo*-cyclized product.

ACKNOWLEDGMENT

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EXPERIMENTAL

1-Naphthaleneselenocyanate: Brown solids. R_f = 0.16 (hexane/ethyl acetate = 95:5); mp 69 – 70 °C; IR (KBr): ν/cm^{-1} = 2148; ^{1}H NMR ($CDCl_3$): δ/ppm = 7.43 – 7.47 (m, 1H, Ar), 7.59 – 7.69 (m, 2H, Ar), 7.88 – 8.02 (m, 3H, Ar), 8.16 – 8.21 (m, 1H, Ar); ^{13}C NMR ($CDCl_3$): δ/ppm = 101.02 (SeCN), 120.60 (CH of Ar), 120.16 (CH of Ar), 126.60 (CH of Ar), 127.18 (CH of Ph), 128.19 (CH of Ph), 129.03 (CH of Ph), 131.72 (CH of Ph), 133.19 (C of Ph), 134.49 (C of Ph), 134.60 (C of Ph).

1,1'-Binaphthyl-2,2'-diselenocyanate: Orange solids. R_f = 0.18 (hexane/ethyl acetate = 10:1); mp 154 – 155 °C (Lit., [10] 153 – 156 °C); IR (KBr): ν/cm^{-1} = 2153; ^{1}H NMR ($CDCl_3$): δ/ppm = 7.04 – 7.06 (m, 2H, Ar), 7.39 – 7.43 (m, 2H, Ar), 7.58 – 7.62 (m, 2H, Ar), 8.01 – 8.12 (m, 6H, Ar); ^{13}C NMR ($CDCl_3$): δ/ppm = 100.91 (SeCN), 124.68 (C of Ar), 124.70 (CH of Ar), 127.03 (CH of Ar), 127.73 (CH of Ar), 128.71 (CH of Ar), 128.82 (CH of Ar), 131.98 (CH of Ar), 132.42 (C of Ar), 133.22 (C of Ar), 134.01 (C of Ar).

*Reaction of **1-Ph** with **2**; A Typical Example*: Under Ar atmosphere, a mixture of $Cu(OTf)_2$ (0.36 g, 1.00 mmol) and PhSeCN (0.18 g, 1.00 mmol) in dry toluene (2 mL) was stirred at 50 °C for 1 h. To the resulting suspension was added a solution of **2** (0.11 g, 0.90 mmol) in toluene (1 mL). After 1 h stirring, to this was added sat. $NaHCO_3$ solution, and the organic components were extracted with ether (25 mL x 3). The extracts were dried over $MgSO_4$, and the residue was subjected to column chromatography on silica gel (hexane:ethyl acetate = 95:5). Pure **3a** (0.22 g, 88% yield) was obtained as pale yellow oil. TLC: R_f = 0.24 (hexane:ethyl acetate = 95:5); IR (neat): ν/cm^{-1} = 2930, 2876, 1580, 1478, 1437, 1163, 1069, 1022, 739, 693; ^{1}H NMR ($CDCl_3$): δ/ppm = 1.35 – 1.75 (m, 6H, 3-H, 4-H_2, 5-H_2 and 6-H), 1.91 – 2.03 (m, 2H, 3-H and 6-H), 2.34 – 2.41 (m,1H, 9-H_{ax}), 3.51 (ddd, *J* = 4.88, 4.88, 5.37 Hz, 1H, CH_{eq}– Se), 3.86 (ddd, *J* = 5.36, 8.78, 8.78 Hz, 1H, 2-H), 3.91 (dd, J = 4.88, 4.88 Hz, 1H, 8-H_{eq}), 4.00 (ddd, *J* = 6.83, 8.78, 8.78 Hz, 1H, 2-H), 7.25 – 7.28 (m, 3H, Ph), 7.54 – 7.58 (m, 2H, Ph);

^{13}C NMR ($CDCl_3$): δ/ppm = 21.31 (C-5), 26.51 (C-4), 28.37 (C-6), 30.14 (C-3), 36.14 (C-9), 43.97 (CH–Se), 66.37 (CH_2–O), 80.55 (CH–O), 127.32 (CH of Ph), 128.97 (CH of Ph), 129.35 (C of Ph), 134.24 (CH of Ph). Anal. Calcd for $C_{14}H_{18}OSe$: C, 59.79; H, 6.45. Found: C, 59.72; H, 6.65.

*Compound (**3b**)*: Brown oil. TLC: R_f = 0.12 (hexane:ethyl acetate = 97:3); IR (neat): ν/cm^{-1} = 2932, 2876, 1588, 1501, 1453, 1379, 1163, 1069, 1020, 963, 797, 772; UV (ether): λ_{max}/nm (ε) = 276 sh (7400), 284 (8100), 308 sh (6400); ^{1}H NMR ($CDCl_3$): δ/ppm = 1.33 – 1.48 (m, 2H, 4-H and 5-H), 1.54 – 1.73 (m, 4H, 3-H, 4-H, 5-H and 6-H), 1.88 – 1.98 (m, 2H, 3-H and 6-H), 2.38 – 2.46 (m,1H, 9-H$_{ax}$), 3.54 (ddd, *J* = 4.88, 4.88, 5.37 Hz, 1H, CH$_{eq}$– Se), 3.83 (ddd, *J* = 5.36, 8.78, 8.78 Hz, 1H, 2-H), 3.93 (dd, J = 4.88, 4.88 Hz, 1H, 8-H$_{eq}$), 3.98 (ddd, *J* = 7.81, 8.78, 8.78 Hz, 1H, 2-H), 7.35 – 7.39 (m, 1H, Ar), 7.47 – 7.58 (m, 2H, Ar), 7.80 – 7.88 (m, 3H, Ar), 8.49 – 8.51 (m, 1H, Ar); ^{13}C NMR ($CDCl_3$): δ/ppm = 21.29 (C-5), 26.53 (C-4), 28.38 (C-6), 30.99 (C-3), 36.23 (C-9), 44.17 (CH–Se), 66.35 (CH_2 – O), 80.64 (CH–O), 125.69 (CH of Ar), 126.12 (CH of Ar), 126.65 (CH of Ar), 128.21 (CH of Ar), 128.52 (CH of Ar), 128.81 (C of Ar), 128.86 (CH of Ar), 134.00 (C of Ar), 134.48 (CH of Ar), 135.06 (C of Ar). Anal. Calcd for $C_{18}H_{20}OSe$: C, 65.25; H, 6.08. Found: C, 65.25; H, 6.04.

*Compound (**6**)*: Brown oil. TLC: R_f = 0.39 (hexane:ethyl acetate = 10:1); IR (neat): ν/cm^{-1} = 2973, 2866, 1561, 1503, 1379, 1096, 1057, 961, 797, 772; UV (ether): λ_{max}/nm (ε) = 276 sh (9800), 284 (11000), 307 (11700); ^{1}H NMR ($CDCl_3$): δ/ppm = 1.59 – 1.67 (m, 1H, 3-H), 1.83 – 1.95 (m, 2H, 4-H_2), 2.01 – 2.09 (m, 1H, 3-H), 3.00 (dd, *J* = 6.83, 12.20 Hz, 1H, CH–Se), 3.16 (dd, *J* = 5.86, 12.20 Hz, 1H, CH–Se), 3.73 – 3.78 (m, 1H, 5-H), 3.89 – 3.94 (m, 1H, 5-H), 4.04 – 4.11 (m, 1H, 2-H), 7.34 – 7.38 (m, 1H, Ar), 7.48 – 7.58 (m, 2H, Ar), 7.77 – 7.84 (m, 3H, Ar), 8.39 – 8.41 (m, 1H, Ar); ^{13}C NMR ($CDCl_3$): δ/ppm = 25.95 (C-4), 31.55 (C-3), 33.30 (CH_2–Se), 68.34 (CH_2–O), 78.35 (CH–O), 125.75 (CH of Ar), 126.17 (CH of Ar), 126.60 (CH of Ar), 127.62 (CH of Ar), 128.30 (CH of Ar), 128.60 (CH of Ar), 129.49 (C of Ar), 132.35 (CH of Ar), 133.97 (C of Ar), 134.24 (C of Ar). Anal. Calcd for $C_{15}H_{16}OSe$: C, 61.86; H, 5.54. Found: C, 61.90; H, 5.46.

*Compound (**7a**)*: Pale yellow oil. TLC: R_f = 0.05 (hexane:ethyl acetate = 10:1); IR (neat): ν/cm^{-1} = 1771, 1167; ^{1}H NMR ($CDCl_3$): δ/ppm = 1.91 – 2.00 (m, 1H, 3-H), 2.37 – 2.44 (m, 1H, 3-H), 2.45 – 2.63 (m, 2H, 2-H_2), 3.01 (dd, *J* = 7.81 and 13.17 Hz, 1H, CH–Se), 3.29 (dd, J = 4.88 and 13.17 Hz, 1H, CH–Se), 4.62 – 4.69 (m, 1H, 4-H), 7.28 – 7.30 (m, 3H, Ph), 7.54 – 7.56 (m, 2H, Ph); ^{13}C NMR ($CDCl_3$): δ/ppm = 27.32 (C-3), 28.38 (C-2), 31.87 (CH_2–Se), 78.94 (CH–O), 127.20 (CH of Ph), 128.82 (C of Ph), 129.01 (CH of Ph), 132.72 (CH of Ph), 175.95 (C=O). Anal. Calcd for $C_{11}H_{12}O_2Se$: C, 51.78; H, 4,74. Found: C, 51.78; H, 4.82

*Compound (**7b**)*: Brown oil. TLC: R_f = 0.15 (hexane:ethyl acetate = 4:1); IR (neat): ν/cm^{-1} = 1774, 1171; UV (ether): λ_{max}/nm (ε) = 276 sh (9400), 284 (10500), 302 (11100); ^{1}H NMR ($CDCl_3$): δ/ppm = 1.89 – 2.00 (m, 1H, 3-H), 2.34 – 2.42 (m, 1H, 3-H), 2.44 – 2.60 (m, 2H, 2-H_2), 3.02 (dd, *J* = 8.30 and 12.68 Hz, 1H, CH–Se), 3.30 (dd, *J* = 4.88 and 12.68 Hz, 1H, CH–Se), 4.55–4.62 (m, 1H, 4-H), 7.38-7.41 (m, 1H, Ar), 7.51–7.61 (m, 2H, Ar), 7.83–7.88 (m, 3H, Ar), 8.39–8.42 (m, 1H, Ar); ^{13}C NMR ($CDCl_3$): δ/ppm = 27.71 (C-3), 28.75 (C-2), 31.97 (CH_2–Se), 79.44 (CH–O), 125.80 (CH of Ar), 126.44 (CH of Ar), 127.07 (CH of Ar), 127.52 (CH of Ar), 127.91 (C of Ar), 128.82 (CH of Ar), 129.32 (CH of Ar), 133.69 (CH of Ar), 134.12 (C of Ar), 134.34 (C of Ar), 176.45 (C=O). Anal. Calcd for

$C_{15}H_{14}O_2Se$: C, 59.02; H, 4.62. Found: C, 59.18; H, 4.50.

*Compound (**8**)*: Pale yellow solids. mp 95 – 97 °C; TLC: R_f = 0.23 (hexane:ethyl acetate = 4:1); IR (neat): ν/cm^{-1} = 2969, 2863, 1580, 1501, 1101, 1053, 941, 804, 747; ^{1}H NMR ($CDCl_3$): δ/ppm = 1.33 – 2.00 (m, 8H, 3-H_2, 4-H_2, 3'-H_2 and 4'-H_2), 2.79 – 2.89 (m, 2H, CH–Se and C'H–Se), 3.13–3.20 (m, 2H, CH–Se and C'H–Se), 3.64 – 3.71 (m, 2H, 5-H and5'-H), 3.77 – 3.85 (m, 2H, 5-H and 5'-H), 3.94 – 4.07 (m, 2H, 2-H and 2'-H), 6.99 – 7.04 (m, 2H, Ar), 7.20 – 7.25 (m, 2H, Ar), 7.39 – 7.43 (m, 2H, Ar), 7.74 - 7.78 (m, 2H, Ar), 7.87 – 7.90 (m, 4H, Ar); ^{13}C NMR ($CDCl_3$): δ/ppm = 25.74 and 25.79 (C-4), 31.37 and 31.41 (C-3), 31.50 (CH_2–Se), 68.33 (CH_2–O), 78.31, 78.34 and 78.41 (CH–O), 125.49, 125.78 and 125.80 (CH of Ar), 125.76, 125.78 and 125.80 (C of Ar), 126.68, 126.70, 126.79 and 126.82 (CH of Ar), 127.51 and 127.61 (CH of Ar), 127.93 and 128.00 (CH of Ar), 128.09 and 128.11 (CH of Ar), 128.63, 128.66 and 128.68 (CH of Ar), 130.71, 131.01 and 131.22 (CH of Ar), 132.13, 132.17 and 132.19 (C of Ar), 132.76, 132.78, 132.92 and 132.95 (C of Ar), 137.15, 137.29, 137.53 and 137.63 (C of Ar). Anal. Calcd for $C_{30}H_{30}OSe$: C, 62.07; H, 5.21. Found: C, 62.09; H, 5.13.

*Compound (**10a**)*: Colorless oil. TLC: R_f = 0.11 (hexane:ethyl acetate = 97:3); HPLC: (column: Inertsil-SIL 4.6 i.d. x 250 mm; eluant: 3% ethyl acetate in hexane) v_R = 11.0 mL; IR (neat): ν/cm^{-1} = 2932, 2855, 1580, 1478, 1449, 1061, 974, 880, 737, 691; ^{1}H NMR ($CDCl_3$): δ/ppm = 1.06 (dddd, *J* = 3.41, 12.20, 12.20 and 12.20 Hz, 1H, 4-H), 1.15 – 1.35 (m, 3H, 5-H, 6-H and 7-H), 1.43 (ddddd, *J* = 3.41, 7.32, 9.27, 10.73 and 12.20 Hz, 1H, 9-H_{ax}), 1.66 – 1.70 (m, 1H, 6-H), 1.70 (ddd, *J* = 9.27, 12.20 and 12.20 Hz, 1H, 3-H), 1.78 – 1.83 (m, 1H, 5-H), 1.87 (ddd, *J* = 2.93, 7.32 and 12.20 Hz, 1H, 3-H), 1.89 – 1.93 (m, 1H, 4-H), 2.07 – 2.12 (m, 1H, 7-H), 2.96 (dd, *J* = 7.81 and 12.20 Hz, 1H, CH–Se), 3.06 (ddd, *J* = 3.90, 10.73 and 10.73 Hz, 1H, 8-H_{ax}), 3.13 (dd, *J* = 4.88 and 12.20 Hz, 1H, CH–Se), 4.23 (dddd, *J* = 2.93, 4.88, 7.81 and 12.20 Hz, 1H, 2-H), 7.21 – 7.27 (m, 3H, Ph), 7.50 – 7.53 (m, 2H, Ph); ^{13}C NMR ($CDCl_3$): δ/ppm = 24.26 (C-5), 25.80 (C-6), 29.03 (C-4), 31.34 (C-7), 34.05 (CH_2– Se), 36.36 (C-3), 44.26 (C-9), 77.21 (CH–O), 84.29 (CH–O), 126.73 (CH of Ph), 129.01 (CH of Ph), 130.37 (C of Ph), 132.39 (CH of Ph). Anal. Calcd for $C_{15}H_{20}OSe$: C, 61.01; H, 6.83. Found: C, 60.10; H, 6.79.

*Compound (**11a**)*: Colorless oil. TLC: R_f = 0.11 (hexane:ethyl acetate = 97:3); HPLC: v_R = 12.3 mL; IR (neat): ν/cm^{-1} = 2930, 2857, 1578, 1478, 1437, 1068, 976, 868, 735, 691; ^{1}H NMR ($CDCl_3$): δ/ppm = 1.01 – 1.36 (m, 5H, 3-H, 4-H, 5-H, 6-H and 7-H), 1.40 – 1.51 (m, 1H, 9-H_{ax}), 1.70 – 1.72 (m, 1H, 6-H), 1.79 – 1.82 (m, 1H, 5-H), 1.89 – 1.92 (m, 1H, 4-H), 2.07 – 2.08 (m, 1H, 7-H), 2.23 (ddd, *J* = 5.85, 5.85 and 11.70 Hz, 1H, 3-H), 3.00 (dd, *J* = 7.32 and 12.20 Hz, 1H, CH–Se), 3.19 – 3.23 (m, 1H, 8-H_{ax}), 3.23 (dd, *J* = 5.38 and 12.20 Hz, 1H, CH–Se), 4.23 – 4.30 (m, 1H, 2-H), 7.21 – 7.27 (m, 3H, Ph), 7.51 – 7.53 (m, 2H, Ph); ^{13}C NMR ($CDCl_3$): δ/ppm = 24.30 (C-5), 25.66 (C-6), 28.95 (C-4), 31.41 (C-7), 34.18 (CH_2–Se), 38.35 (C-3), 46.53 (C-9), 77.44 (CH–O), 82.86 (CH–O), 126.77 (CH of Ph), 129.02 (CH of Ph), 130.28 (C of Ph), 132.48 (CH of Ph). Anal. Calcd for $C_{15}H_{20}OSe$: C, 61.01; H, 6.83. Found: C, 60.92; H, 6.86.

*Compound (**12a**)*: Colorless oil. TLC: R_f = 0.17 (hexane:ethyl acetate = 97:3); HPLC: v_R = 9.2 mL; IR (neat): ν/cm^{-1} = 2928, 2857, 1578, 1478, 1449, 1078, 995, 866, 737; ^{1}H NMR ($CDCl_3$): δ/ppm = 0.94 – 1.03 (m, 1H, 5-H), 1.15 – 1.33 (m, 4H, 4-H_{eq}, 6-H, 7-H and 8-H), 1.35 – 1.38 (m, 1H, 10-H_{ax}), 1.57 – 1.65 (m, 2H, 5-H and 7-H), 1.75 – 1.78 (m,1H, 6-H), 1.85 – 1.88 (m,1H, 8-H), 2.11 (ddd, *J* = 2.93,

11.70 and 11.70 Hz, 1H, 4-H$_{ax}$), 2.87 (ddd, *J* = 3.91, 9.76, 9.76 Hz, 1H, 9-H$_{ax}$), 3.35 (dddd, *J* = 3.91, 3.91, 11.70 and 11.70 Hz, 1H, CH$_{ax}$–Se), 3.42 (dd, *J* = 11.70 and 11.70 Hz, 1H, 2-H$_{ax}$), 4.05 (dd, *J* = 3.91 and 11.70 Hz, 1H, 2-H$_{eq}$), 7.23 – 7.28 (m, 3H, Ph), 7.53 – 7.55 (m, 2H, Ph); ^{13}C NMR ($CDCl_3$): δ/ppm = 24.86 (C-6), 25.49 (C-7), 31.52 (C-5), 32.20 (C-8), 37.95 (C-4), 39.70 (CH–Se), 43.63 (C-10), 72.94 (CH$_2$–O), 81.50 (CH–O), 127.60 (CH of Ph), 127.79 (C of Ph), 128.98 (CH of Ph), 134.65 (CH of Ph). Anal. Calcd for $C_{15}H_{20}OSe$: C, 61.01; H, 6.83. Found: C, 60.82; H, 6.89.

*Compound (**10b**)*: Orange oil. TLC: R_f = 0.15 (hexane:ethyl acetate = 97:3); HPLC: (column : Inertsil-SIL 4.6 i.d. x 250 mm; eluant: 5% ethyl acetate in hexane) v_R = 8.5 mL; IR (neat): ν/cm^{-1} = 2932, 2856, 1502, 1449, 1373, 1061, 974, 796, 770; UV (ether): λ_{max}/nm (ε) = 276 sh (10400), 285 (11800), 303 sh (9900); ^{1}H NMR ($CDCl_3$): δ/ppm = 1.00 – 1.35 (m, 5H, 3-H, 4-H, 5-H, 6-H and 7-H), 1.38 – 1.49 (m, 1H, 9-H$_{ax}$), 1.67 –1.69 (m, 1H, 6-H), 1.77 – 1.80 (m, 1H, 5-H), 1.86 – 1.89 (m, 1H, 4-H), 2.06 – 2.07 (m, 1H, 7-H), 2.20 (ddd, *J* = 5.85, 5.85 and 11.70 Hz, 1H, 3-H), 3.04 (dd, *J* = 7.32 and 12.20 Hz, 1H, CH–Se), 3.22 – 3.26 (m, 1H, 8-H$_{ax}$), 3.27 (dd, *J* = 5.38 and 12.20 Hz, 1H, CH–Se), 4.20 – 4.27 (m, 1H, 2-H), 7.35 – 7.39 (m, 1H, Ar), 7.51 – 7.60 (m, 2H, Ar), 7.84 – 7.89 (m, 3H, Ar), 8.46 – 8.49 (m, 1H, Ar); ^{13}C NMR ($CDCl_3$): δ/ppm = 24.28 (C-5), 25.65 (C-6), 28.94 (C-4), 31.15 (C-7), 34.15 (CH$_2$–Se), 38.30 (C-3), 46.49 (C-9), 77.43 (CH–O), 82.83 (CH–O), 125.54 (CH of Ar), 126.15 (CH of Ar), 126.71 (CH of Ar), 127.29 (C of Ar), 128.20 (CH of Ar), 128.52 (CH of Ar), 129.15 (CH of Ar), 134.10 (C of Ar), 134.76 (CH of Ar), 135.12 (C of Ar). Anal. Calcd for $C_{19}H_{22}OSe$: C, 66.08; H, 6.42. Found: C, 66.13; H, 6.44.

*Compound **11b***: Orange oil. TLC: R_f = 0.15 (hexane:ethyl acetate = 97:3); HPLC: v_R = 8.0 mL; IR (neat): ν/cm^{-1} = 2932, 2856, 1502, 1449, 1373, 1061, 974, 796, 770; UV (ether): λ_{max}/nm (ε) = 276 sh (10200), 284 (11600), 307 sh (9800); ^{1}H NMR ($CDCl_3$): δ/ppm = 1.06 (dddd, *J* = 3.41, 12.20, 12.20 and 12.20 Hz, 1H, 4-H), 1.12 – 1.33 (m, 3H, 5-H, 6-H and 7-H), 1.41 (ddddd, *J* = 3.41, 7.32, 9.27, 10.25 and 12.20 Hz, 1H, 9-H$_{ax}$), 1.64 – 1.68 (m, 1H, 6-H), 1.66 (ddd, *J* = 9.27, 12.20 and 12.20 Hz, 1H, 3-H), 1.74 – 1.79 (m, 1H, 5-H), 1.83 (ddd, *J* = 2.93, 7.32 and 12.20 Hz, 1H, 3-H), 1.85 – 1.89 (m, 1H, 4-H), 2.06 – 2.10 (m, 1H, 7-H), 2.97 (dd, *J* = 7.81 and 12.20 Hz, 1H, CH–Se), 3.04 (ddd, *J* = 3.90, 10.25 and 10.25 Hz, 1H, 8-H$_{ax}$), 3.16 (dd, *J* = 4.88 and 12.20 Hz, 1H, CH–Se), 4.20 (dddd, *J* = 2.93, 4.88, 7.81 and 12.20 Hz, 1H, 2-H), 7.34 – 7.39 (m, 1H, Ar), 7.48 – 7.57 (m, 2H, Ar), 7.76 – 7.83 (m, 3H, Ar), 8.38 – 8.40 (m, 1H, Ar); ^{13}C NMR ($CDCl_3$): δ/ppm = 24.27 (C-5), 25.81 (C-6), 29.04 (C-4), 31.37 (C-7), 34.34 (CH$_2$–Se), 36.41 (C-3), 44.28 (C-9), 77.22 (CH–O), 84.27 (CH–O), 125.770 (CH of Ar), 126.16 (CH of Ar), 126.57 (CH of Ar), 127.62 (C of Ar), 128.22 (CH of Ar), 128.61 (CH of Ar), 129.54 (CH of Ar), 132.20 (C of Ar), 134.00 (CH of Ar), 134.25 (C of Ar). Anal. Calcd for $C_{19}H_{22}OSe$: C, 66.08; H, 6.42. Found: C, 66.07; H, 6.48.

*Compound (**12b**)*: Orange oil. TLC: R_f = 0.23 (hexane:ethyl acetate = 97:3); HPLC: v_R = 6.5 mL; IR (neat): ν/cm^{-1} = 2928, 2957, 1501, 1449, 1373, 1078, 995, 796, 771; UV (ether): λ_{max}/nm (ε) = 276 sh (11500), 285 (12700), 306 sh (10200); ^{1}H NMR ($CDCl_3$): δ/ppm = 0.92 – 1.01 (m, 1H, 5-H), 1.12 – 1.38 (m, 5H, 4-H, 6-H, 7-H, 8-H and 10-H$_{ax}$), 1.55 – 1.63 (m, 2H, 5-H and 7-H), 1.73 – 1.76 (m,1H, 6-H), 1.81 – 1.84 (m,1H, 8-H), 2.12 – 2.15 (m, 1H, 4-H), 2.86 (ddd, *J* = 3.91, 10.25 and 10.25 Hz, 1H, 9-H$_{ax}$), 3.40 (dddd, *J* = 3.91, 3.91, 11.71 and 11.71 Hz, 1H, CH$_{ax}$–Se), 3.45 (dd, *J* = 11.71, 11.71 Hz,

1H, 2-H_{ax}), 3.97 (dd, *J* = 3.91 and 11.71 Hz, 1H, 2-H_{eq}), 7.34 – 7.38 (m, 1H, Ar), 7.49 – 7.58 (m, 2H, Ar), 7.81 – 7.87 (m, 3H, Ar), 8.44 – 8.46 (m, 1H, Ar); ^{13}C NMR ($CDCl_3$): δ/ppm = 24.84 (C-6), 25.47 (C-7), 31.51 (C-5), 32.17 (C-8), 38.07 (C-4), 40.06 (CH–Se), 43.62(C-10), 73.02(CH_2–O), 81.52(CH–O), 125.60 (CH of Ar), 126.18 (CH of Ar), 126.73 (CH of Ar), 127.31 (C of Ar), 128.17 (CH of Ar), 128.55 (CH of Ar), 129.13 (CH of Ar), 134.00 (C of Ar), 134.77 (CH of Ar), 135.08 (C of Ar). Anal. Calcd for $C_{19}H_{22}OSe$: C, 66.08; H, 6.42. Found: C, 66.08; H, 6.45.

Molecular Dynamics Calculation: MM+® Calculations were carried out on a HyperChem® program running on Windows95®. Default parameters were used for torsions, stretches and bends. Optimized structures of **10a** and **11a** were obtained by using automatic structural optimization starting from 144 initial conformers which were generated manually every 30 ° rotation around 2-C—CH_2Se and CH_2-Se bonds. Optimization of 12 initial rotermers around the 3-C—Se bond (30 °) of **12a** was performed in the same way. Atom coordinates of the most stable structures of **10a**—**12a** are shown Table 3, where hydrogen atoms are omitted.

Table 3. Atomic Coordinates of the Optimized Structures of 10a—12a.

10a
atom number-element symbol (x/Å, y/Å, z/Å)
1-O (-0.585, 0.347, -0.744); 2-C (-0.328, 1.720, -0.502); 3-C (-1.655, 2.360, -0.032); 4-C (-3.984, 1.177, 0.361); 5-C (-4.516, -0.245, 0.625); 6-C (-3.953, -1.282, -0.368); 7-C(-2.414, -1.260, -0.435); 8-C (-1.978, 0.173, -0.739); 9-C (-2.457, 1.120, 0.357); 10-C (0.786, 1.847, 0.548); 11-Se (2.471, 0.997, 0.004); 1'-C[a] (1.784, -0.771, 0.107); 2'-C[a] (1.321, -1.292, 1.320); 3'-C[a] (0.792, -2.583, 1.376); 4'-C[a] (0.728, -3.365, 0.222); 5'-C[a] (1.204, -2.857, -0.987); 6'-C[a] (1.735, -1.566, -1.043)
11a
atom number-element symbol (x/Å, y/Å, z/Å)
1-O (-0.635, 0.262, 0.587); 2-C (-0.388, 1.642, 0.379); 3-C (-1.705, 2.278 , -0.121); 4-C (-4.046, 1.108, -0.467); 5-C (-4.778, -0.160, 0.014); 6-C (-3.916, -1.430, -0.129); 7-C(-2.540, -1.288, 0.548); 8-C (-1.872, -0.032, -0.009); 9-C (-2.717, 1.205, 0.280); 10-C (0.780, 1.840, -0.597); 11-Se (2.468, 1.069, 0.04576); 1'-C[a] (1.861, -0.727, -0.064); 2'-C[a] (1.790, -1.509, 1.093); 3'-C[a] (1.315, -2.821, 1.031); 4'-C[a] (0.915, -3.363, -0.191); 5'-C[a] (1.000, -2.593, -1.352); 6'-C[a] (1.476, -1.282, -1.290)
12a
atom number-element symbol (x/Å, y/Å, z/Å)
1-O (2.467, -1.517, -0.820); 2-C (1.226, -1.977, -0.323); 3-C (0.187, -0.846, -0.351); 4-C (0.703, 0.346, 0.471); 5-C (2.712, 1.889, 0.762); 6-C (4.103, 2.251, 0.219); 7-C(5.027, 1.025, 0.203); 8-C (4.399, -0.126, -0.597); 9-C (3.018, -0.483, -0.032); 10-C (2.092, 0.742, -0.051); 11-Se (-1.534, -1.514, 0.337); 1'-C[a] (-2.442, 0.118, 0.001); 2'-C[a] (-2.664, 0.554, -1.310); 3'-C[a] (-3.326, 1.760, -1.548); 4'-C[a] (-3.776, 2.535, -0.477); 5'-C[a] (-3.565, 2.099, 0.831); 6'-C[a] (-2.903, 0.893, 1.070)

[a] Carbon atoms on the benzene ring, and these atomic numbering is consistent with monosubstituted benzene.

2D NMR studies: NOESY Observations were performed on a JEOL A-400 spectrometer (400 MHz for ^{1}H and 100 MHz for ^{13}C), and default parameters were employed. Signal assignments and coupling constants were confirmed by using H—H and C—H COSY spectra.

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20. Three diastereomers with *R*-***R***-*R*, *R*-***R***-*S*, and *S*-***R***-*S* relative configurations, in which the center sign, bold, means chirality of 1,1'-binaphthyl and both sides mean asymmetric carbons on the tetrahydrofuran. The two carbon atoms on 1- and 1'-posisions of 1,1'-binapthyl are identical in the *R*-***R***-*R* and *S*-***R***-*S* isomers, but not in *R*-***R***-*S*. Thus, 4 signals are detectable in the mixture of those diastereomers.
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