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Electrophilic organic selenium reagents—protonated seleninic acids as precursors for unsymmetrical aromatic selenides

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ABSTRACT

Arylselenylations of methylbenzenes, methoxybenzenes and thiophene were smoothly achieved with selenenium ions generated by comproportionation of 1:1 mixtures of *p*-toluenesulfonic acid salts of seleninic acids and the corresponding diselenides. A series of *p*-toluenesulfonic salts of seleninic acids were prepared by hydrogen peroxide oxidation of the corresponding diselenides in the presence of *p*-toluenesulfonic acid. Novel 2-(organylseleno)thiophenes were obtained by heating the protonated seleninic acids with a 50-fold excess of thiophene in glacial acetic acid.

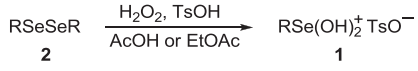
1. Introduction

In 1959 Pitombo[1] was the first to apply electrophilic organic selenium reagents (RSe^+) for preparations of unsymmetrical selenides. Since then a large variety of methods for generation of these reactive transient organic selenenium species have been developed,[2] but the attention has been mostly focused on phenylselenylations. Amongst the reagents for generation of the synthon phenylselenenium ion ($PhSe^+$) are included *N*-phenylselenophthalimide,[3] (phenylseleno)-dimethylsulfonium tetrafluoroborate,[4] benzeneselenenyl chloride/silver hexafluorophosphate,[5] diphenyl diselenide/*m*-nitrobenzenesulfonyl peroxide,[6] and diphenyl diselenide/ammonium peroxydisulfate.[7] Henriksen[8] found that benzeneseleninic acid/diphenyl diselenide/*p*-toluenesulfonic acid effectively generated the phenylselenenium ion. The stable non-hygroscopic salt dihydroxy phenylselenonium *p*-toluenesulfonate was prepared in high yield and purity directly from diphenyl diselenide.[9] The arylsulfonate salts of benzeneseleninic acid were found to constitute an excellent reagent for phenylselenylation[10] when mixed with diphenyl diselenide and as a specific oxidant viz. in the oxidation of phenanthrene to 9,10-phenanthrenequinone.[11] In view of the interest in the introduction of selenium containing functionalities as tools for selective chemical transformations and for modification of material properties we have investigated the scope of direct oxidation of diselenides **2** into dihydroxy arylselenonium *p*-toluenesulfonates **1** and the application of these salts in the synthesis of unsymmetrical diarylselenides with specific substitution patterns. These findings are presented in this paper.

2. Results and discussion

2.1. Protonated salts of seleninic acids

p-Toluenesulfonic acid salts of seleninic acids, dihydroxy arylselenonium *p*-toluenesulfonates **1**, were readily prepared by the hydrogen peroxide oxidation of the corresponding diselenides **2** in acetic acid or in ethyl acetate in the presence of a stoichiometric amount of *p*-toluenesulfonic acid (Scheme 1).



Scheme 1.

The yields of the pure isolated recrystallised salts from the reaction above were in all cases above 75%. The diselenides utilized needed no purification before use, since triselenides and higher polyselenides, which usually contaminate crude diselenides, lose the excess selenium as soluble inorganic Se(IV) species during the oxidation process. The reaction proceeded rapidly as a titration at room temperature and its completion was marked by the disappearance of the yellow

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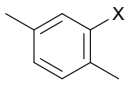
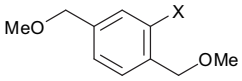
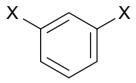
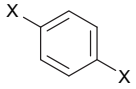
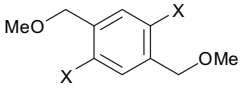
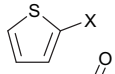
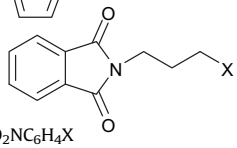
Table 1
p-Toluenesulfonic acid salts of seleninic acids

Salt ($X = Se(OH)_2^+TsO^-$)	Route to precursor diselenide **2**	Solvent for prep. of **1**	Yield[a] (%)
1a 4-MeC_6H_4X	A	AcOH	83
1b 4-$(C_7H_{15})C_6H_4X$	B	EtOAc	43
1c 4-$BrC6H_4X$	A	AcOH	47
1d 4-ClC_6H_4X	A	AcOH	58
1e 	B	EtOAc	53
1f 	B	EtOAc	68
1g 	E	EtOAc	51
1h 	E	EtOAc	19(63)[b]
1i 	E	EtOAc	60[b]
1j 	C	EtOAc	74
1k 	D	AcOH	26
1l 3-$O_2NC_6H_4X$	F	AcOH	88[c]
1m 4-$O_2NC_6H_4X$	G	AcOH	72[c]

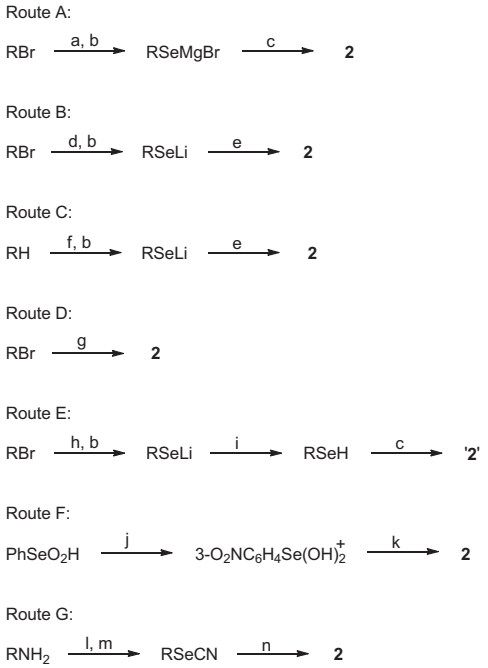
2 $\xrightarrow{H_2O_2,\ TsOH}$ **1**.

[a] Recrystallised analytically pure prod.
[b] Of crude product, sufficiently pure for preparative use.
[c] Isolated yield from the di (nitrophenyl) diselenide.

diselenide colour. A list of isolated salts is presented in Table 1. All these salts were found shelf-stable.

Seven different methods were used to prepare diselenide precursors **2** from available starting materials (Scheme 2). In route B arylbromides were metallated with *tert*-butyllithium and reacted with elemental selenium in order to generate lithium selenolates, which were smoothly oxidized into **2** with aqueous potassium hexacyanoferrate(III). However, when arylselenolates were prepared from Grignard reagents the hexacyanoferrate(III) ion produced a somewhat cumbersome precipitate with magnesium arylselenolates and iron(III)chloride was instead used as the oxidant in route A. 2-Thienyllithium was easily generated by treatment of thiophene with *n*-butyllithium (route C) and further reacted as described in route B. On reacting dilithiobenzene derivatives with selenium (route D) the initially formed bis-selenolate was treated with acid in order to obtain the corresponding free bis-selenol, which was oxidized directly into **1**. This procedure was used in the preparations of the diseleninic acid derivatives, **1g**, **1h** and **1i** to bypass the formation of insoluble polyphenylene diselenides. Dihydroxy alkylselenonium *p*-toluenesulfonates[12] were obtained from dialkyl diselenides prepared by reacting alkylbromides with sodium polyselenide (route E).

The diselenides used for preparation of *ortho*- and *para*-nitrobenzeneseleninic acid derivatives were prepared from arylselenocyanates treated with sulfuric acid and air (route G). The precursor diselenide for the *meta* derivative **1l** was prepared by nitration of benzeneseleninic acid followed by reduction with hydrazine (route F). In one case, the tosylate salt of the seleninic acid could not be



Scheme 2. Reagents and conditions: (a) Mg, Et_2O; (b) Se_8; (c) H_2O_2 (35% aq); (d) *t*-BuLi, THF; (e) $K_3[Fe(CN)_6]$, H_2O; (f) *n*-BuLi, THF, −78 °C; (g) Se_8, NaOMe, N_2H_4, DMSO; (h) *t*-BuLi, THF, −78 °C then rt; (i) HCl (0.5 M aq); (j) HNO_3 (concd); (k) N_2H_2, H_2O; (l) $NaNO_2$, H_2SO_4 (2 M aq); (m) KSeCN, NaOAc; (n) H_2SO_4, (80% aq), O_2, 60 °C, 48 h.

prepared. Un-protonated 2-nitrobenzeneseleninic acid[13] precipitated during the hydrogen peroxide oxidation of di(*ortho*-nitrophenyl) diselenide in the presence of *p*-toluenesulfonic acid monohydrate under standard conditions and the *p*-toluenesulfonic acid salt of this seleninic acid was not isolated. Attempted synthesis of donorsubstituted benzeneseleninic acid derivatives, viz. dihydroxy *p*-methoxyphenylselenonium *p*-toluenesulfonate and dihydroxy *p*-(dimethylamino)phenylselenonium *p*-toluenesulfonate, failed due to extensive decompositions during oxidation of diselenides. The routes to diselenide precursors **2** are outlined in Scheme 2.

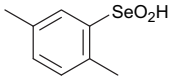
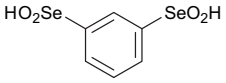
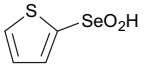
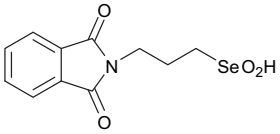
The free seleninic acids, **3**, were easily prepared from **1** by the addition of 1 equiv of sodium hydrogencarbonate to a concentrated aqueous solution of **1** (Scheme 3) in accord with our previously described method since the salts are acidic ($pK_a \approx -0.8$)[14] compared to free seleninic acids ($pK_a \approx -4.6$). This procedure was demonstrated by the preparation of the new seleninic acids **3a**–**d** (Table 2) and the yields of isolated compounds were only limited by their solubility in water.

1 $\xrightarrow{NaHCO_3,\ H_2O}$ $RSeO_2H$ **3**

Scheme 3.

The preparations of seleninic acids via the dihydroxy selenonium salts is an excellent method because seleninic acids tend to become over-oxidized during the oxidation with hydrogen peroxide in absence of *p*-toluenesulfonic acid. In the presence of this acid the oxidation was instantaneous and could be performed as a colourimetric titration (yellow to colourless). Any risks of accidential isolation of potentially explosive[15] peroxoseleninic acids were avoided using this oxidation procedure because these species were readily soluble and cleaved into oxygen and the corresponding organylseleninic acid under the reaction conditions.

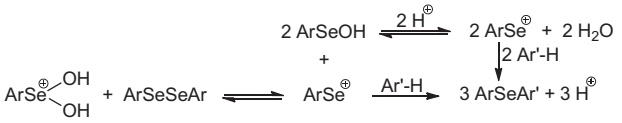
Table 2
Representative novel organylseleninic acids

Seleninic acid	Yield[a] (%)
 **3a**	57
 **3b**	69
 **3c**	64
 **3d**	71

[a] Recrystallised analytically pure product.

2.2. Protonated seleninic acids and diselenides generating reactive arylselenenium ions

The comproportionation reaction between salts **1** and the corresponding diselenides **2** generated selenenium species sufficiently reactive to attack methoxybenzenes, mesitylene and thiophene affording unsymmetrical aryl selenides by a traditional electrophilic aromatic substitution pattern. Comproportionation between a dihydroxy arylselenonium ion and a diaryl diselenide forms one arylselenenium ion and two arylselenenic acids. Essentially, upon protonation the poor electrophile arylselenenic acid is in equilibrium with the arylselenenium ion[8] and over-all 3 equiv of arene can be reacted with 3 equiv of arylselenenium ions in electrophilic aromatic substitution generating 3 equiv of diaryl selenide (Scheme 4).

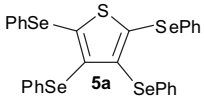
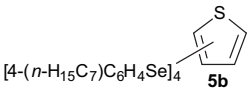
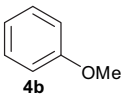
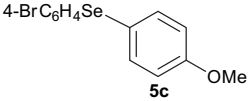
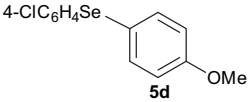
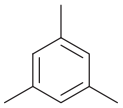
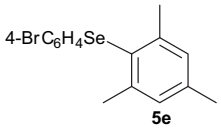
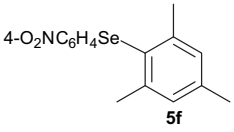


Scheme 4.

The produced selenenium species ranged from 4-(*n*-heptyl)phenylselenenium to 2-nitrophenylselenenium *p*-toluenesulfonates. Representative unsymmetrical selenides are presented in Table 3.

The presented method for the preparation of selenides was restricted to arylselenenium species. Attempts to generate and react aliphatic selenenium ions in a similar fashion to arenes failed using standard protonated seleninic acid/diselenide conditions and GC–MS analysis of product compositions showed alkenes and side-products from multiple pericyclic reactions. In the case of benzenediseleninic acids, e.g., **1g**, **1h** and **1i**, selenenium ion formation was complicated because of the polymeric nature of the corresponding sparsely soluble 'diselenide' counterpart[16] and arylselenylation could not be observed even upon heating in the presence of large amounts of chlorinated solvents. Thiophene **4a** was rapidly attacked by arylselenenium ions and only the tetrakis-selenylated products **5a** and **5b** were obtained easily in high purity because thiophene underwent over-reaction due to its high reactivity of too high reactivity against all positions in thiophene. Anisole **4b** and mesitylene **4c** were mono-substituted by arylselenenium ions affording viz. the diarylselenides **5b**–**f** (Table 3). Although reaction of anisole led to mixtures of *ortho*- and *para*-selenylated products (in a 1:4 ratio by GC–MS), the *para*-selenylated products were readily obtained by simple recrystallisation.

Table 3
Electrophilic aromatic substitution with 1:1 mixtures of dihydroxy arylselenonium *p*-toluenesulfonates and the corresponding diaryl diselenides

Substrate	$ArSe^+$ equivalents	Product	Conditions	Yield[a] (%)
 **4a**	4	 **5a**	MeOH reflux, 20 h	91
4a	4	 **5b**	MeOH/$CHCl_3$ reflux, 20 h	63
 **4b**	1	 **5c**	MeOH reflux, 8 h	64
4b	1	 **5d**	MeOH reflux, 8 h	74
 **4c**	1	 **5e**	AcOH reflux, 1 h	67
4c	1	 **5f**	AcOH reflux, 1 h	53

1 + **2** + 3ArH → 3ArSeAr′
[a] Recrystallised analytically pure product.

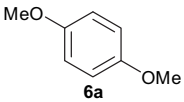
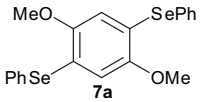
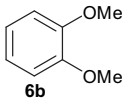
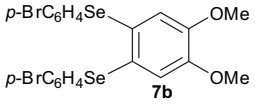
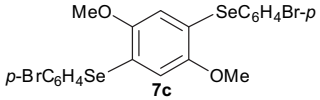
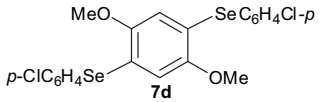
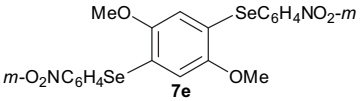
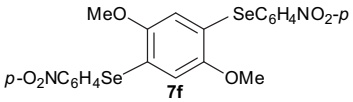
Arylselenylations utilizing arylselenenium tosylates are restricted to activated arenes. Benzene, chlorobenzene and benzonitrile remained non-reactive despite prolonged heating. Arylselenylation of amines, such as *N*,*N*-dimethylaniline, *N*-methylpyrrole and methoxypyridines failed due to undefined oxidation reactions.

Arylselenium ions are transient species with low or no shelf stability. In contrast to arylselenenium ions generated from ArSeCl or ArSeBr the precursors for arylselenium tosylates, namely **1** and **2**, are highly stable towards water and air. In our hands phenylselenylations using PhSeOTs preceeded much cleaner and in higher yields compared to PhSeCl or PhSeBr. Furthermore, when using the latter reagents the counter ions are not inert and arylselenylations using these reagents also produced chlorinated or brominated by-products, respectively.

2.3. Electrophilic aromatic substitution patterns in reactions between arylselenenium ions and dimethoxybenzenes

Hydroquinone dimethyl ether **6a** and veratrole **6b** underwent double-substitution with phenyl- and halophenyl-selenenium ions (Table 4). More interestingly, the *o*/*p*-activating effect of an initially introduced arylseleno group induced a second arylselenenium

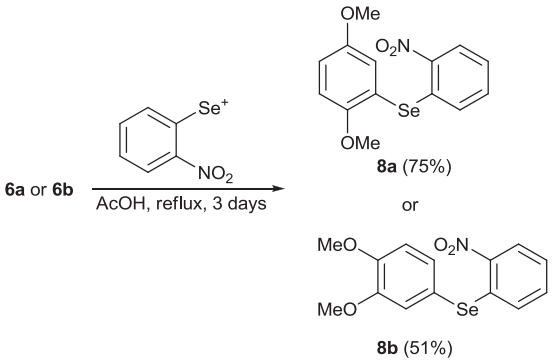
Table 4
Electrophilic bis-arylselenylations with 2 equiv of arylselenenium tosylates

Substrate	Product	Conditions	Yield[a] (%)
 **6a**	 **7a**	MeOH reflux, 8 h	84
 **6b**	 **7b**	MeOH reflux, 8 h	59
6a	 **7c**	MeOH reflux, 3 days	81
6a	 **7d**	MeOH reflux, 3 days	67
6a	 **7e**	MeOH reflux, 3 days	58
6a	 **7f**	MeOH reflux, 3 days	61

[a] Of recryst anal. pure prod.

attack to occur. Phenyl- and chlorophenyl-selenylations of **6a** were also performed by treating these arylselenenium tosylates with a 20-fold excess of **6a** and **6b** followed by GC–MS examination of quenched samples showing that *no mono-selenylated products* were detectable, but only bis-substituted products 2,5-bis(phenylseleno) hydroquinone dimethyl ether **7a** and 2,5-bis(4-chlorophenylseleno) hydroquinone dimethyl ether **7d** appeared in reaction mixtures. The X-ray structure of **7d** was recently published by our group.[17]

An identical investigation was initiated with the 2-nitrophenylselenenium ion. In this case a lack of activation was observed after introduction of one arylselenyl group. Even prolonged heating with a limiting amount of **6a** or **6b** did not force 2-(2-nitrophenylseleno)hydroquinone dimethyl ether **8a** or 4-(2-nitrophenylseleno)veratrole **8b** to undergo substitution with a second selenenium ion (Scheme 5).

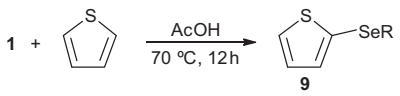


Scheme 5.

Since *m*- and *p*-nitrophenylselenenium ions cleanly gave bis-selenylated products (**7e** and **7f**) uncontaminated with mono-selenylated products the lack of *o*/*p*-activation from the 2-nitrophenylseleno group in **8a** and **8b** can only be explained by the presence of the *o*-nitro group. The resulting polarization with positive charge on Se caused the observed deactivating effect. A strong through-space interaction between a nitro group O-atom and the Se-atom of an *o*-arylseleno substituent on a benzene ring was evidenced by crystallographic investigations of our two previously prepared selenides 2-nitrophenyl phenyl selenide and 1,3-dinitro-4,6-bis(phenylseleno)benzene.[18] The structures revealed non-bonded Se–O distances of 2.65–2.68 Å, significantly shorter than the sum of Van der Waals radii (3.42 Å).

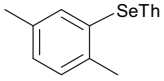
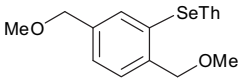
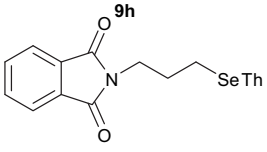
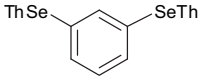
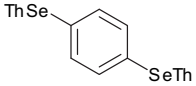
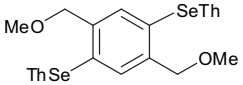
2.3.1. 2-Thienyl selenides. Under comproportionation conditions between salt **1** and diselenide **2** only tetrakis-selenylations of thiophene were controllable and viz. mono-selenylations seemed impossible due to over-arylselenylation. However, a new synthesis of 2-thienyl selenides **9** directly from **1** without using diselenides for generation of selenenium species was found. By heating **1** with a 50-fold excess of thiophene in glacial acetic acid (Scheme 6) mono-selenylated products **9** were smoothly isolated (Table 5) in high purity without any diselenide contamination.

The generation of selenenium species must involve reduction of the salts **1**. Since **1** remained unreacted in acetic acid at 70 °C,



Scheme 6.

Table 5
2-Thienyl selenides prepared from **1** and **4a** (Scheme 6)

Thienyl aryl selenide (Th=2-thienyl)	Yield (%)
PhSeTh **9a**	82
4-(n-$H_{15}C_7$)C_6H_4SePh **9b**	86
p-BrC_6H_4SeTh **9c**	66
p-ClC_6H_4SeTh **9d**	73
o-$O_2NC_6H_4$SeTh **9e**	48[a]
ThSeTh **9f**	43
 **9g**	71
 **9h**	41
 **9i**	43
 **9j**	67
 **9k**	63
 **9l**	36

[a] o-Nitrophenylseleneium tosylate prepared from a (1:1) mixture of o-nitrobenzeneseleninic acid and p-toluenesulfonic acid.

thiophene must serve as the reducing agent. Organylselenenium species (RSe^+) were slowly generated in situ and trapped by the large excess of thiophene forming **9**. After 12 h the dihydroxy phenylselenonium ion was completely absent according to TLC and hydrazine reduction of the aqueous phases gave only negative test for diselenides. The dichloromethane/pentane extracts could smoothly be filtered through silica to provide almost pure **9a** contaminated with only a few percent of the easily removable corresponding bis-selenylated product 2,5-bis(organylseleno)thiophene.

In the preparation of aryl 2-thienyl selenides **9** an obvious advantage using this method was the complete absence of diselenides. The consumption-rate of these selenenium ions was high enough (50 equiv of thiophene) to avoid the formation of diselenides by disproportionation of the RSe^+ species. Diselenides were neither formed nor needed in the reactions since selenenium ions were slowly generated in situ by reduction of **1**. In the only reported[19] electrophilic approaches to 2-thienyl selenides the selenenium species were obtained by in situ oxidation of the corresponding diselenides by ammonium peroxydisulfate. Using this method some diselenide remained after the reaction and a purification procedure involving removal of residual diselenide by borohydride reduction had to be applied. The compounds **9j**, **9k** and **9l** seemed impossible to prepare via any diselenide oxidation techniques since the precursor 'diselenides' in these cases were polyphenylene diselenides with very low solubility in organic solvents. This class of compounds, bis-(thienylseleno) benzene derivatives, were to the best of our knowledge unreported till now.

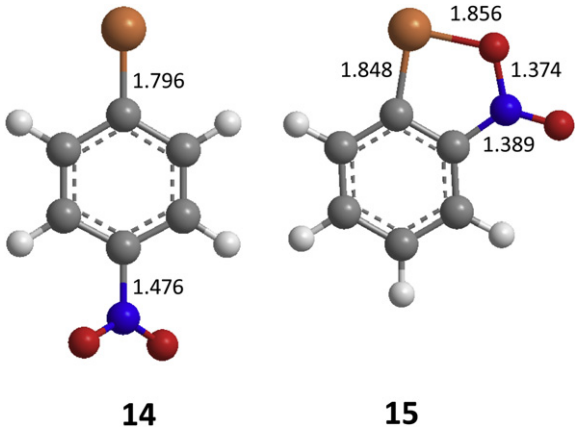


Fig. 1. Calculated geometries (B3LYP/6-31G(d)) with selected optimized bond lengths (Å). The bond formation between the o-nitro group and the selenium atom is evident.

2.4. Computations on nitroarylselenenium ions

The structure of the electrophile is the key to understand the formation of the bis-substituted product **7f** when the electrophile is the arylselenium ion p-NO_2–C_6H_4–Se^+ **10**, in contrast to specific formations of the mono-substituted products **8a** and **8b** when the reacting electrophile is the arylselenium ion o-NO_2–C_6H_4–Se^+ **11**. The calculated geometries are shown (Fig. 1). It can be seen that the nitro group gives rise to an intrinsic stabilization when located in the *ortho* position. Thus, the *para* isomer **10** is found to lie 37.2 kcal mol^{-1} higher in energy at the B3LYP/6-31G(d) level compared to the *ortho* isomer **11**. This value is 34.8 kcal mol^{-1} at the G2(MP2)//B3LYP level. The reaction energy for double electrophilic substitution using the *para*-nitrophenylselenenium ion **10** in formation of the bis-selenylated product is 294.5 kcal mol^{-1}, whereas the bis-selenylation with the *ortho*-nitrophenylselenenium ion **11** requires a significantly higher energy of 378.8 kcal mol^{-1}. The difference between the two heats of reaction is 84.2 kcal mol^{-1}, which is essentially twice the difference in energy of the *ortho*- and *para*-substituted electrophiles (74.4 kcal mol^{-1}). This suggests that the principal source of the higher energy requirement for the formation of the bis-selenylated product in the case of selenylation with **11** is the intramolecular stabilization of the nitro group. At the very accurate G2(MP2)//B3LYP level twice energy difference is similar at 69.6 kcal mol^{-1}. We expect the substitution reaction to be just as selective for other electrophiles possessing an *ortho* group that intramolecularly can stabilize the Se^+-center.

3. Conclusion

In conclusion, diarylselenides could easily be prepared by electrophilic aromatic arylselenylations between an activated arene and an arylselenenium ion generated by comproportionation of a diselenide and the tosylate salt of its corresponding seleninic acid. Synthesis of 2-thienyl selenides directly from any protonated seleninic acid and thiophene seems of unlimited scope.

4. Experimental

4.1. Computational methods

Geometries were calculated at the B3LYP/6-31G(d) level of theory and the calculation of the vibrational frequencies verified that they represent equilibrium structures (zero imaginary frequencies). The 0 K energy (E_{0K}) of the each of the reactants and products was then calculated as the sum of electronic energy and the zero point vibrational energy (ZPVE) scaled by 0.9806 as suggested by Radom and Scott.[20] The heat of reaction is obtained as:

$$\Delta_r E_{0K} = E_{0K}(\text{product}) - E_{0K}(HO - C_6H_4 - OCH_3) - 2E_{0K}\left(NO_2 - C_6H_4 - Se^+\right)$$

To arrive at a more accurate measure for the energy difference of the *ortho* and the *para* isomer of the electrophile (NO_2–C_6H_4–Se^+) we employed the composite G2(MP2)//B3LYP method, which is known to be accurate within chemical accuracy (2.0 kcal mol^{-1}).[21] All calculations were carried out with the GAUSSIAN03 suite of programs.[22]

4.2. Preparation of diselenides (2)

4.2.1. Route A, Scheme 1. Di(4-methylphenyl) diselenide **2a**,[23] di(4-bromophenyl) diselenide **2c**,[24] and di(4-chlorophenyl) diselenide **2d**[25] were prepared from 4-bromotoluene, 4-bromochlorobenzene and 1,4-dibromobenzene, respectively, in exact analogy with our earlier described procedure for the syntheses of diphenyl diselenide.[26] Etheral solutions of 4-methylphenylselenomagnesium bromide and 4-chlorophenylselenomagnesium bromide were prepared from selenium (0.45 mol) by the method of Ref. [27]

4-Bromophenylmagnesium bromide was generated from 1,4-dibromobenzene (106 g, 0.45 mol) and magnesium (10.9 g, 0.45 mol) in ether (250 mL) immersed in an ultrasound bath at 25 °C. Vigorous metallation began after 15 min and shortly thereafter the bath temperature was elevated above 40 °C to maintain steady reflux.

4.2.2. Route B, Scheme 1. A solution of arylhalide (0.03 mol) in THF (100 mL) was cooled in a dry ice/acetone bath while *tert*-butyllithium (1.5 M in hexane, 40 mL, 0.06 mol) was added dropwise under nitrogen during a 10 min period. The reaction mixture was stirred under nitrogen for one hour at −78 °C. Selenium (2.37 g, 30 mmol) was added in one portion and the reaction mixture was stirred at room temperature for 45 min. An aqueous solution (50 mL) of potassium hexacyanoferrate(III) (10.0 g, 0.03 mol) was added slowly and stirring was continued for 1 h at room temperature. The phases were separated and the aqueous phase was further extracted with ether (3×40 mL). The combined etheral phases were filtered through aluminium oxide (15 g) by means of ether and evaporation of the solvent gave the diselenide in a satisfactory quality for production of salts **1**.

4.2.3. Route C, Scheme 1. 2-Thienyllithium was prepared by dropwise addition of *n*-butyllithium (2.0 M in hexane, 15 mL, 0.03 mol) to a mixture of thiophene (2.52 g, 0.03 mol) and THF (100 mL) at −78 °C, reacted with selenium (2.37 g, 30 mmol) and worked up as described above.

4.2.4. Route D, Scheme 1. A solution of sodium diselenide was prepared in the following manner: to a stirred solution of sodium methoxide (3.38 g. 0.063 mol) and 95% hydrazine (0.5 g, 0.016 mol) in DMSO (80 mL) was added selenium (9.87 g, 0.125 mol) in small portions during a 5 min period under vigorous stirring. After stirring at room temperature for 30 min under nitrogen alkylbromide (0.05 mol) was added. The resulting black reaction mixture was stirred at room temperature under nitrogen for 30 min, diluted with water (400 mL) and extracted with ether (4×50 mL). The combined etheral phases were washed with water (2×30 mL) and dried (sodium sulfate). Filtration and evaporation gave the crude dialkyl diselenide.

4.3. *p*-Toluenesulfonic acid salts of seleninic acids (1a–f, j,k)

p-Toluenesulfonic acid monohydrate (2 equiv) per diselenide equivalent (estimated from the weight of crude precursor diselenide) in glacial acetic acid (400 mL, route A; 40 mL, route D) or ethyl acetate (50 mL, route B and C) as indicated in Table 1 were added to the crude diselenide and the resulting solution was titrated dropwise (yellow to colourless) with 35% aqueous hydrogen peroxide whilst the reaction temperature was kept at 30 °C by cooling in an ice-bath. The salts were filtered off, recrystallised and dried (vacuum oven, 70 °C, 0.75 mmHg).

*4.3.1. Dihydroxy p-methylphenylselenonium p-toluenesulfonate **1a** (diselenide prepared via route A).* Yield 140 g (83%). Recrystallised from glacial acetic acid as colourless needles; mp 155–158 °C (dec). $C_{14}H_{16}O_5SSe$: found C 44.71% H 4.17% S 9.06%; calcd C 44.81% H 4.30% S 8.54%. ^{1}H NMR (DMSO-d_6) δ: 2.29 (3H, s), 2.38 (3H, s), 7.14 (2H, d, *J* 8.0 Hz), 7.43 (2H, d, *J* 8.0 Hz), 7.51 (2H, d, *J* 8.0 Hz), 7.77 (2H, d, *J* 8.0 Hz), 10.23 (2H, br s) ppm. ^{13}C NMR (DMSO-d_6) δ: 20.49, 22.01, 126.43, 127.11, 129.34, 137.97, 135.73, 139.19, 140.27, 145.04 ppm. ^{77}Se NMR[28] (DMSO-d_6) δ: 1150 ppm.

*4.3.2. Dihydroxy p-(4-n-heptyl)phenylselenonium p-toluenesulfonate **1b** (diselenide prepared via route B).* Yield 5.95 g (43%). Recrystallised from ethyl acetate as colourless needles; mp 122–124 °C (dec). $C_{20}H_{28}O_5SSe$: found C 52.50% H 6.25% S 7.14%; calcd C 52.28% H 6.14% S 6.98%. ^{1}H NMR (DMSO-d_6) δ: 0.83–0.87 (3H, t, *J* 6.8 Hz), 1.24–1.27 (8H, m), 1.56–1.61 (2H, m), 2.29 (3H, s), 2.63–2.66 (2H, t, *J* 7.6 Hz), 5.07 (2H, br s), 7.12 (2H, d, *J* 7.1 Hz), 7.42 (2H, d, *J* 7.9 Hz), 7.48 (2H, d, *J* 7.9 Hz), 7.75 (2H, d) ppm. ^{13}C NMR (DMSO-d_6) δ: 13.56, 20.45, 22.81, 29.35, 31.53, 32.06, 35.90, 38.98, 125.91, 126.60, 126.90, 128.77, 129.62, 140.09, 142.20, 144.91 ppm. ^{77}Se NMR (DMSO-d_6) δ: 1163 ppm.

*4.3.3. Dihydroxy p-bromophenylselenonium p-toluenesulfonate **1c** (diselenide prepared via route A).* Yield 92.3 g (47%). Recrystallised from glacial acetic acid as a white solid; mp 163–165 °C (dec). $C_{13}H_{13}BrO_5SSe$: found C 35.59% H 2.94%; calcd C 35.47% H 2.98%. ^{1}H NMR (DMSO-d_6) δ: 2.30 (3H, s), 7.16 (2H, d, *J* 8.4 Hz), 7.54 (2H, d), 7.83 (4H, s), 8.09 (2H, br s) ppm. ^{13}C NMR (DMSO-d_6) δ: 20.40, 124.91, 126.78, 129.89, 130.53, 133.33, 134.98, 141.01, 145.27 ppm. ^{77}Se NMR (DMSO-d_6) δ: 1164 ppm.

*4.3.4. Dihydroxy p-chlorophenylselenonium p-toluenesulfonate **1d** (diselenide prepared via route A).* Yield 104 g (58%). Recrystallised from glacial acetic acid as colourless needles; mp 160–161 °C (dec). $C_{13}H_{13}ClO_5SSe$: found C 39.27% H 3.37% Cl 9.33%; calcd C 39.46% H 3.31% Cl 8.96%. ^{1}H NMR (DMSO-d_6) δ: 2.28 (3H, s), 7.14–7.16 (2H, m), 7.53–7.55 (2H, m), 7.66–7.68 (2H, m), 7.89–7.91 (2H, m), 11.06 (2H, br s) ppm. ^{13}C NMR (DMSO-d_6) δ: 20.41, 127.06, 130.68, 130.89, 131.10, 134.38, 135.43, 140.23, 145.45 ppm. ^{77}Se NMR (DMSO-d_6) δ: 1162 ppm.

*4.3.5. Dihydroxy 2,5-dimethylphenylselenonium p-toluenesulfonate **1e** (diselenide prepared via route B).* Yield 6.21 g (53%). Recrystallised from ethyl acetate as colourless needles; mp 124–125 °C (dec). $C_{15}H_{18}O_5SSe$: found C 46.30% H 4.49% S 8.23%; calcd C 46.28% H 4.66% S 8.23%. ^{1}H NMR (DMSO-d_6) δ: 2.29 (3H, s), 2.35 (3H, s), 2.46 (3H, s), 7.17 (2H, d, *J* 7.1 Hz), 7.25 (1H, d, *J* 7.7 Hz), 7.32 (1H, d, *J*

7.7 Hz), 7.56 (2H, d, *J* 7.1 Hz), 7.75 (1H, s), 11.38 (2H, br s) ppm. ^{13}C NMR (DMSO-d_6) δ: 20.00, 20.33, 23.72, 126.56, 127.91, 128.49, 128.66, 130.21, 131.40, 136.35, 136.57, 140.09, 145.20 ppm. ^{77}Se NMR (DMSO-d_6) δ: 1130 ppm.

4.3.6. Dihydroxy 2,5-bis(methoxymethyl)phenylselenonium p-toluenesulfonate ***1f*** *(diselenide prepared via route B).* Yield 9.16 g (68%). Recrystallised from ethyl acetate as colourless plates; mp 110–111 °C (dec). $C_{11}H_{12}O_5S_2Se$: found C 45.45% H 4.94% S 7.34%; calcd C 45.44% H 4.93% S 7.13%. ^{1}H NMR (DMSO-d_6) δ: 2.29 (3H, s), 3.32 (3H, s), 3.41 (3H, s), 4.50 (2H, s), 4.77 (2H, s), 7.15 (2H, d, *J* 7.9 Hz), 7.45 (1H, d, *J* 7.8 Hz), 7.53–7.56 (3H, m), 8.04 (1H, s), 9.82 (2H, br s) ppm. ^{13}C NMR (DMSO-d_6) δ: 20.38, 57.42, 58.74, 73.55, 76.13, 125.40, 120.10, 127.62, 128.24, 129.92, 130.44, 135.61, 137.17, 140.39, 145.08 ppm. ^{77}Se NMR (DMSO-d_6) δ: 1127 ppm.

4.3.7. Dihydroxy 2-thienylselenonium p-toluenesulfonate ***1j*** *(diselenide prepared via route C).* Yield 8.19 g (74%). Recrystallised from ethyl acetate as colourless needles; mp 114–115 °C (dec). $C_{11}H_{12}O_5S_2Se$: found C 35.91% H 3.30% S 17.44%; calcd C 35.97% H 3.29% S 17.46%. ^{1}H NMR (DMSO-d_6) δ: 2.30 (3H, s), 7.12–7.30 (3H, several peaks), 7.55 (2H, d, *J* 8.2 Hz), 7.73 (1H, d, *J* 3.7 Hz), 8.08 (1H, d, *J* 4.6 Hz), 10.40 (2H, br s) ppm. ^{13}C NMR (DMSO-d_6) δ: 20.39, 125.70, 125.91, 126.29, 126.64, 128.03, 130.12, 140.10, 144.85 ppm. ^{77}Se NMR (DMSO-d_6) δ: 1164 ppm.

4.3.8. Dihydroxy 3-(N-phthalimido)propylselenonium p-toluenesulfonate ***1k*** *(diselenide prepared via route D).* Yield 6.07 g (26%). Recrystallised from glacial acetic acid as a white solid; mp 129–130 °C. $C_{18}H_{19}NO_7SSe$: found C 45.78% H 4.03% N 2.93% S 7.10%; calcd C 45.77% H 4.05% N 2.97% S 6.79%. ^{1}H NMR (DMSO-d_6) δ: 2.06–2.13 (2H, m), 2.29 (3H, s), 3.14–3.18 (2H, m), 3.68–3.72 (2H, s), 5.02 (2H, br s), 7.12 (2H, d, *J* 8.0 Hz), 7.48 (2H, d), 7.82–7.89 (4H, m) ppm. ^{13}C NMR (DMSO-d_6) δ: 20.48, 21.99, 36.25, 48.63, 123.07, 125.86, 130.05, 132.11, 134.24, 140.18, 145.12, 168.56 ppm. ^{77}Se NMR (DMSO-d_6) δ: 1199 ppm.

4.4. Benzenediseleninic acid dihydrotosylates (1g–i) via route E

A solution of dibromobenzene (3.54 g, 0.015 mol) in THF (100 mL) was cooled in a dry ice/acetone bath whilst *tert*-butyllithium (1.5 M in hexane, 40 mL, 0.06 mol) was added dropwise under nitrogen during a 10 min period. The reaction mixture was stirred at room temperature for 1 h. After cooling in a dry ice/acetone bath selenium (2.37 g, 0.03 mol) was added in one portion. The reaction mixture was stirred at room temperature for 1 h.[29] The reaction mixture was poured into hydrochloric acid (0.5 M, 130 mL) and extracted with ether (3×40 mL). The combined etheral phases were dried (Na_2SO_4), filtered and evaporated. A solution of *p*-toluenesulfonic acid monohydrate (5.71 g, 0.03 mol) in ethyl acetate (100 mL) was added. Oxidation with 35% aqueous hydrogen peroxide was performed to a sharp end point (yellow to colourless) upon cooling in an ice bath. The di-salt precipitated as a white solid during the oxidation procedure.

4.4.1. 1,3-Benzenediseleninic acid dihydrotosylate ***1g****.* Yield 4.90 g (51%). Recrystallised from acetic acid as a white solid; mp 159–160 °C. $C_{20}H_{22}O_{10}S_2Se_2$: found C 37.07% H 3.46% S 10.04%; calcd C 37.28% H 3.44% S 9.95%. ^{1}H NMR (DMSO-d_6) δ: 2.30 (6H, s), 7.17 (4H, d, *J* 7.9 Hz), 7.55 (4H, d, *J* 7.9 Hz), 7.79–7.85 (1H, t, *J* 7.7 Hz), 8.10 (2H, d, *J* 7.7 Hz), 8.46 (1H, s), 11.29 (4H, s) ppm. ^{13}C NMR (DMSO-d_6) δ: 20.59, 125.94, 128.96, 129.12, 130.79, 131.62, 141.04, 141.96, 145.10 ppm. ^{77}Se NMR (DMSO-d_6) δ: 1166 ppm.

4.4.2. 1,4-Benzenediseleninic acid dihydrotosylate ***1h***[30]*.* Yield 6.11 g (63%). Upon recrystallisation from water/acetic acid (1:2) the yield of pure isolated product was (19%). White solid; mp 155–158 °C (dec). $C_{20}H_{22}O_{10}S_2Se_2$: calcd C, 37.28; H, 3.44. Found C, 37.16; H, 3.51. ^{1}H NMR (DMSO-d_6) δ: 2.30 (6H, s), 7.15 (4H, d, *J* 8.0 Hz), 7.52 (4H, d), 8.08 (4H, s), 9.10 (4H, br s) ppm. ^{13}C NMR (DMSO-d_6) δ: 20.43, 125.76, 127.83, 127.98, 132.56, 140.80, 144.84 ppm. ^{77}Se NMR (DMSO-d_6) δ: 1176 ppm.

4.4.3. 1,4-Bis(methoxymethyl)-2,5-benzenediseleninic acid dihydrotosylate ***1i***[31]*.* Yield (≈60%). White solid; mp 165–166 °C. $C_{24}H_{30}O_{12}S_2Se_2$: found C 39.90% H 4.15%; calcd C 39.35% H 4.13%. ^{1}H NMR (DMSO-d_6) δ: 2.29 (6H, s), 3.40 (6H, s), 4.85 (4H, s), 7.15 (4H, d, *J* 8.0 Hz), 7.51 (4H, d, *J* 8.0 Hz), 8.09 (2H, s), 10.5 (4H, br s) ppm. ^{13}C NMR (DMSO-d_6) δ: 20.06, 57.95, 72.91, 124.82, 125.45, 125.90, 128.40, 140.38, 141.75, 144.08 ppm. ^{77}Se NMR (DMSO-d_6) δ: 1127 ppm.

4.5. Dihydroxy 3-nitrophenylselenonium *p*-toluenesulfonate (1l) via route F

Benzeneseleninic acid (9.45 g, 50 mmol) was added to a mixture of concentrated nitric acid (15 mL) and concentrated sulfuric acid (15 mL). After stirring for two hours at 100 °C the reaction mixture was poured into water (200 mL) and reduction to the diselenide was performed by dropwise addition of hydrazine hydrate at such a rate that forming could be controlled. Extraction with ether (3×50 mL), filtration through alumina (neutral, 6 g) by means of ether and evaporation of the solvent. Recrystallisation from toluene/hexane (1:3) gave bis(*m*-nitrophenyl) diselenide (71%) as yellow prisms; mp 76–77 °C (lit.[32] mp 81 °C). $C_{12}H_8N_2O_4Se_2$: found C 36.03% H 3.00% N 6.84%; calcd C 35.84% H 2.01% N 6.97%. Mass spectrum (EI; *m*/*z*, relative intensity): 404 (M^+, 70), 324 (8), 236 (10), 202 (59), 156 (100). ^{77}Se NMR (DMSO-d_6) δ: 464 ppm.

A slurry of bis(*m*-nitrophenyl) diselenide (4.02 g, 10 mmol) and *p*-toluenesulfonic acid monohydrate (3.80 g, 20 mmol) in glacial acetic acid (50 mL) cooled in an ice bath was dropwise oxidized with 35% aqueous hydrogen peroxide until the yellow diselenide colour had disappeared. The product was filtered off. Upon recrystallisation from glacial acetic acid and drying (vacuum oven, 70 °C, 1 mmHg) **1l** (6.37 g, 78%) was obtained as a white solid; mp 157–158 °C (dec). $C_{13}H_{13}NO_7SSe$: found C 38.48% H 3.00% N 3.37%; calcd C 38.43% H 3.23% N 3.45%. ^{1}H NMR (DMSO-d_6) δ: 2.15 (3H, s), 7.15 (2H, d, *J* 7.3 Hz), 7.40 (2H, d, *J* 7.3 Hz), 7.72 (1H, m), 8.17 (1H, d, *J* 8.0 Hz), 8.27 (1H, d, *J* 8.2 Hz), 8.56 (1H, s), 11.69 (2H, br s) ppm. ^{13}C NMR (DMSO-d_6) δ: 20.55, 123.34, 125.58, 126.29, 126.18, 130.34, 132.66, 138.29, 140.49, 146.12, 149.14 ppm. ^{77}Se NMR (DMSO-d_6) δ: 1151 ppm.

4.6. Route G. Dihydroxy 4-nitrophenylselenonium *p*-toluenesulfonate 1m

A slurry of 4-nitroaniline (13.8 g, 0.1 mol) in sulfuric acid (2 M, 0.12L) cooled in an ice bath was diazotised by adding sodium nitrite (10.4 g, 0.15 mol) in small portions over 30 min at approximately 3 °C. After neutrallisation with sodium acetate (16.5 g, 0.2 mol) the resulting slurry was poured on solid sodium selenocyanate (15.8 g, 0.11 mol) placed in a 1L Erlenmeyer flask. The vigorously foaming solution was stirred manually for 10 min and then magnetically for one hour. A brown mass was filtered off, boiled with active coal in methanol (150 mL) for one hour and filtered into water (300 ml). *p*-Nitrophenylselenocyanate (≈50% yield) was filtered off and stirred in sulfuric acid (80% aq, 250 mL) at 60 °C for 48 h in an open flask. Filtration and drying gave di(*p*-nitrophenyl) diselenide[33] (17% yield) as a yellow gum. *p*-Toluenesulfonic acid monohydrate (1.90 g, 10 mmol) in glacial acetic acid (25 mL) was added and cooling in an ice-bath was maintained during dropwise oxidation with 35% aqueous hydrogen peroxide until the yellow diselenide colour had disappeared. The product was filtered off. Upon recrystallisation

from glacial acetic acid and drying (vacuum oven, 70 °C, 1 mmHg) **1m** (2.91 g, 7% from nitroaniline) was obtained as a white solid; mp 139–141 °C (dec). $C_{13}H_{13}NO_7SSe$: found C 38.42% H 3.05% N 3.36%; calcd C 38.43% H 3.23% N 3.45%. ^{13}C NMR (DMSO-d_6) δ: 20.63, 120.59, 126.38, 130.49, 133.74, 137.91, 140.82, 145.96, 149.05 ppm. ^{77}Se NMR (DMSO-d_6) δ: 1158 ppm.

4.7. Seleninic acids (3), Scheme 2; general procedure

To a boiling solution of salt **1** (8 mmol) in water (10 mL) was added sodium hydrogencarbonate (0.67 g, 8 mmol) in small portions and upon cooling the product crystallised. The free seleninic acids were purified by recrystallisation from water and dried in a vacuum oven (70 °C, 1 mmHg).

*4.7.1. 2,5-Dimethylbenzeneseleninic acid (**3a**).* Yield 0.99 g (57%). Long white needles; mp 138–140 °C (dec). $C_8H_{10}O_2Se$: found C 44.09% H 4.59%; calcd C 44.25% H 4.64%. ^1H NMR (DMSO-d_6) δ: 2.35 (3H, s), 2.43 (3H, s), 7.20 (1H, d, *J* 7.7 Hz), 7.27 (1H, d, *J* 7.7 Hz), 7.74 (1H, s), 9.09 (1H, br s) ppm. ^{13}C NMR (DMSO-d_6) δ: 21.09, 23.97, 128.14, 129.41, 129.89, 130.41, 135.76, 136.51 ppm. ^{77}Se NMR (DMSO-d_6) δ: 1157 ppm.

*4.7.2. 1,3-Benzenediseleninic acid (**3b**).* Yield 1.65 g (69%)White solid; 178–182 °C (not well defined; anhydride formation). $C_6H_6O_4Se_2$: calcd C, 24.02; H, 2.02. Found C, 24.18; H, 1.94. ^1H NMR (DMSO-d_6) δ: 7.75–7.80 (1H, t, *J* 7.4 Hz), 7.99 (2H, d, *J* 7.4 Hz), 8.29 (1H, s), 8.64 (2H, br s) ppm. ^{13}C NMR (DMSO-d_6) δ: 129.17, 129.81, 129.97, 136.23 ppm. ^{77}Se NMR (DMSO-d_6) δ: 1178 ppm.

*4.7.3. 2-Thiopheneseleninic acid (**3c**).* Yield 1.00 g (64%). White solid; decomposed above 100 °C without a defined melting point. $C_4H_4O_2SSe$: found C 24.51% H 2.03% S 16.48%; calcd C 24.63% H 2.07% S 16.43%. ^1H NMR (DMSO-d_6) δ: 4.2 (1H, br s), 7.23 (1H, dd, *J* 4.9, 3.7 Hz), 7.61 (1H, dd, *J* 3.7, 1.2 Hz), 7.93 (1H, dd, *J* 4.9, 1.2 Hz) ppm. ^{13}C NMR (DMSO-d_6) δ: 127.14, 127.72, 128.44, 129.37 ppm. ^{77}Se NMR (DMSO-d_6) δ: 1180 ppm.

*4.7.4. 3-(N-Phthalimido)propaneseleninic acid (**3d**).* Yield 1.71 g (71%). White flakes; mp[34] 140–142 °C (dec). $C_{11}H_{11}NO_4Se$: found C 44.39% H 3.71% N 4.74%; calcd C 44.02% H 3.69% N 4.67%. ^1H NMR (DMSO-d_6) δ: 2.01–2.05 (2H, m), 2.79 (2H, t, *J* 7.6 Hz), 3.66 (2H, t, *J* 6.7 Hz), 7.25 (1H, br s), 7.70–7.85 (4H, m) ppm. ^{13}C NMR (DMSO-d_6) δ: 20.27, 37.10, 52.86, 122.99, 131.65, 134.34, 167.93 ppm. ^{77}Se NMR (D_2O) δ: 1216 ppm.

*4.7.5. 2,3,4,5-Tetrakis(phenylseleno)thiophene (**5a**).* A solution of thiophene **4a** (2.10 g, 25 mmol), dihydroxy phenylselenonium *p*-toluenesulfonate (12.64 g, 35 mmol) and diphenyl diselenide (10.30 g, 33 mmol) in methanol (100 mL) was heated at reflux for 20 h. During the reaction the product formed as a white precipitate. After cooling (0 °C) the motherliquor was decanted. The precipitate was washed with cold methanol, filtered off, recrystallised from toluene/hexane (1:3, 400 mL) and dried (vacuum oven, 70 °C, 1 mmHg) affording **5a** (16.09 g, 91%) as large faintly yellow cubic crystals; mp 116–117 °C (lit.[35] mp 105–108 °C). $C_{28}H_{20}SSe_4$: found C, 47.96; H, 2.86; S, 4.68; calcd C, 47.75; H, 2.86; S, 4.55. ^1H NMR ($CDCl_3$) δ: 7.06–7.10 (4H, m), 7.15–7.18 (6H, m), 7.20–7.27 (6H, m), 7.43–7.46 (4H, m) ppm. ^{13}C NMR ($CDCl_3$) δ: 126.44, 128.32, 128.93, 129.15, 129.92, 130.46, 132.19, 133.47, 134.88, 138.76 ppm. ^{77}Se NMR ($CDCl_3$) δ: 360, 415.

*4.7.6. 2,3,4,5-Tetrakis(4-n-heptylphenylseleno)thiophene (**5b**).* A solution of thiophene **4a** (0.084 g, 1 mmol), dihydroxy 4-*n*-heptylphenylselenonium *p*-toluenesulfonate **1b** (0.643 g, 1.4 mmol) and di(4-*n*-heptylphenyl) diselenide (0.661 g, 1.3 mmol) in methanol/chloroform (1:1, 10 mL) was heated at reflux for 20 h. The reaction mixture was diluted with water (70 mL), extracted with dichloromethane/pentane (1:2, 4×20 mL) and the solvent was evaporated in vacuo. Column chromatography (silica gel; dichloromethane/pentane, 1:2, R_f=0.70) afforded the tetrakis-selenylated product **5b** (0.695 g, 63%) as a colourless oil after removal of traces of diselenide with pentane. $C_{56}H_{76}SSe_4$: found C 61.25% H 7.11% S 3.19%; calcd C 61.31% H 6.98% S 2.92%. Mass spectrum (FAB$^+$, *m*/*z*): 1099 (M^+). ^1H NMR ($CDCl_3$) δ: 0.85–0.90 (12H, m), 1.27–1.28 (32H, m), 1.52–1.54 (8H, m), 2.47–2.55 (8H, m), 6.91 (4H, d, *J* 8.2 Hz), 7.05 (4H, d, *J* 8.3 Hz), 7.12 (4H, d, *J* 8.3 Hz), 7.36 (4H, d, *J* 8.2 Hz) ppm. ^{13}C NMR ($CDCl_3$) δ: 13.74, 13.86, 22.45, 22.67, 30.02, 30.19, 31.14, 31.39, 32.28, 32.42, 33.20, 33.78, 36.67, 37.01, 125.11, 126.70, 127.22, 128.12, 128.99, 129.86, 131.42, 132.95, 133.82, 137.81 ppm. ^{77}Se NMR ($CDCl_3$) δ: 367, 426 ppm.

4.8. Halophenylselenylations of anisole

A stirred suspension of anisole **4b** (3.24 g, 30 mmol), dihydroxy *p*-halophenylselenonium *p*-toluenesulfonate (10.2 mmol) and bis (*p*-halophenyl) diselenide (9.9 mmol) in methanol (60 mL) was heated at reflux d for 8 h. The clear reaction mixture was diluted with water (200 mL) and extracted with dichloromethane/pentane (1:4, 3×35 mL). The combined organic phases were filtered through silica gel 60 (10 g) by means of dichloromethane/pentane (1:4). Evaporation in vacuo gave white crystalline residues.

*4.8.1. 4-(p-Bromophenylseleno)anisole **5c**.* Yield 6.52 g (64%). Recrystallised from hexane as a white solid; mp 68–69 °C (lit.[36] mp 69–70 °C). $C_{13}H_{11}BrOSe$: found C 45.56% H 3.16%; calcd C 45.64% H 3.24%. Mass spectrum (EI; *m*/*z*, relative intensity): 342 (M^+, 58), 299 (8), 262 (100). ^1H NMR ($CDCl_3$) δ: 3.80 (3H, s), 6.86 (2H, d, *J* 8.8 Hz), 7.16 (2H, d, *J* 8.4 Hz), 7.16 (2H, d, *J* 8.4 Hz), 7.49 (2H, d) ppm. ^{13}C NMR ($CDCl_3$) δ: 55.13, 114.60, 118.88, 128.83, 129.01, 130.17, 132.19, 135.91, 159.68 ppm. ^{77}Se NMR ($CDCl_3$) δ: 408 ppm.

*4.8.2. 4-(p-Chlorophenylseleno)anisole **5d**.* Yield 6.59 g (74%). Recrystallised from pentane as white flakes; mp 63–64 °C (lit.[37] oil). $C_{13}H_{11}ClOSe$: found C 52.13% H 3.75%; calcd C 52.46% H 3.72%. Mass spectrum (EI; *m*/*z*, relative intensity): 298 (M^+, 38), 255 (6), 218 (100), 203 (40). ^1H NMR ($CDCl_3$) δ: 3.81 (3H, s), 6.86 (2H, d, *J* 9 Hz), 7.20–7.25 (4H, m), 7.50 (2H, d) ppm. ^{13}C NMR ($CDCl_3$) δ: 55.41, 115.28, 119.50, 129.23, 131.63, 132.03, 132.46, 136.66, 159.91 ppm. ^{77}Se NMR ($CDCl_3$) δ: 408 ppm.

4.9. Typical procedure; 2-(*p*-bromophenylseleno)mesitylene (5e)

A stirred suspension of mesitylene **4c** (10 mL), dihydroxy 4-bromophenylselenonium *p*-toluenesulfonate (**1c**) (1.50 g, 3.4 mmol) and bis(4-bromophenyl) diselenide (1.55 g, 3.3 mmol) in glacial acetic acid (15 mL) was heated at reflux for 1 h. The light-yellow reaction mixture was diluted with water (100 mL) and extracted with dichloromethane/pentane (1:4, 3×25 mL). The combined organic phases were filtered through silica gel 60 (6 g) by means of dichloromethane/pentane (1:4) and volatile organic compounds were evaporated in vacuo. The light-yellow crystalline residue was recrystallised from hexane and dried (vacuum oven, 45 °C) to afford **5e** (2.39 g, 67%) as small cubic crystals; mp 97–98 °C. $C_{15}H_{15}BrSe$: found C 50.93% H 4.24%; calcd C 50.87% H 4.27%. Mass spectrum (EI; *m*/*z*, relative intensity): 354 (M^+, 100), 274 (27), 260 (10), 195 (33). ^1H NMR ($CDCl_3$) δ: 2.30 (3H, s), 2.41 (6H, s), 6.91 (2H, d, *J* 8.3 Hz), 6.99 (2H, s), 7.24 (2H, d) ppm. ^{13}C NMR ($CDCl_3$) δ: 20.07, 22.91, 124.22, 128.23, 128.37, 129.19, 131.99, 134.17, 135.27, 146.02 ppm. ^{77}Se NMR ($CDCl_3$) δ: 300 ppm.

4.9.1. 2-(o-Nitrophenylseleno)mesitylene ***5f***. Yield 1.71 g (53%). Recrystallisation from hexane gave a yellow solid; mp 133–34 °C. $C_{15}H_{15}NO_2Se$: found C 56.18% H 4.70% N 4.32%; calcd C 56.26% H 4.72% N 4.37%. Mass spectrum (EI; *m*/*z*, relative intensity): 321 (M^+, 100), 291 (5), 273 (23), 259 (18). ^{1}H NMR ($CDCl_3$) δ: 2.35 (3H, s), 2.40 (6H, s), 6.91–6.83 (1H, m), 7.06 (2H, s), 7.24–7.28 (2H, m), 8.32–8.36 (1H, s) ppm. ^{13}C NMR ($CDCl_3$) δ: 20.17, 23.04, 122.74, 127.56, 128.00, 129.05, 135.09, 136.36, 143.42, 149.14 ppm. ^{77}Se NMR ($CDCl_3$) δ: 377 ppm.

4.10. Bis-arylselenylations of dimethoxybenzenes; general procedure

Hydroquinone dimethyl ether **4a** or veratrole **4b** (3 mmol) was heated at reflux in methanol (15 mL) for the times indicated in Table 3 in the presence of **1** (2 mmol) and the corresponding diselenide 2 (2 mmol). During the reactions the bis-selenylated products precipitated as white solids that were filtered off and washed with methanol.

4.10.1. 2,5-Bis(phenylseleno)hydroquinone dimethyl ether ***7a***. Yield 1.13 g (84%). Recrystallised from chloroform as large white prisms; mp 175–177 °C. $C_{20}H_{18}O_2Se_2$: found C 53.62% H 3.82%; calcd C 53.59% H 4.05%. Mass spectrum (EI; *m*/*z*, relative intensity): 450 (M^+, 24), 278 (36), 250 (28), 199 (100). ^{1}H NMR ($CDCl_3$) δ: 3.58 (6H, s), 6.54 (2H, s), 7.28–7.54 (10H, m) ppm. ^{13}C NMR ($CDCl_3$) δ: 56.51, 114.11, 120.53, 128.03, 128.29, 129.42, 134.72, 151.68 ppm. ^{77}Se NMR ($CDCl_3$) δ: 374 ppm.

*4.10.2. 4,5-Bis(p-bromophenylseleno)veratrole (****7b****).* Yield 1.08 g (59%). Recrystallised from ethyl acetate as a white solid; mp 121–122 °C. $C_{20}H_{16}Br_2O_2Se_2$: found C 39.86% H 2.60%; calcd C 39.64% H 2.66%. Mass spectrum (EI; *m*/*z*, relative intensity): 606 (M^+, 100), 528 (14), 291 (53). ^{1}H NMR ($CDCl_3$) δ: 3.72 (6H, s), 6.85 (2H, s), 7.26 (4H, d, *J* 8.4 Hz), 7.39 (2H, d) ppm. ^{13}C NMR ($CDCl_3$) δ: 56.20, 108.51, 122.93, 124.63, 128.75, 133.43, 134.03, 135.11 ppm. ^{77}Se NMR ($CDCl_3$) δ: 427 ppm.

4.10.3. 2,5-Bis(p-bromophenylseleno)hydroquinone dimethyl ether ***7c***. Yield 1.47 g (81%). Recrystallised from toluene as a white solid; mp 203–205 °C. $C_{20}H_{16}Br_2O_2Se_2$: found C 39.51% H 2.71%; calcd C 39.64% H 2.66%. Mass spectrum (EI; *m*/*z*, relative intensity): 607 (M^+, 100), 528 (10), 432 (8), 328 (18), 277 (45). ^{1}H NMR ($CDCl_3$) δ: 3.63 (6H, s), 6.60 (4H, s), 7.38 (4H, d, *J* 8.7 Hz), 7.44 (4H, d) ppm. ^{13}C NMR ($CDCl_3$) δ: 56.27, 114.32, 120.71, 123.65, 129.70, 135.10, 137.85, 152.34 ppm. ^{77}Se NMR ($CDCl_3$) δ: 372 ppm.

4.10.4. 2,5-Bis(p-chlorophenylseleno)hydroquinone dimethyl ether ***7d***. Yield 1.04 g (67%). Recrystallised from toluene as colourless crystals; mp 193–94 °C. $C_{20}H_{16}Cl_2O_2Se_2$: found C 46.62% H 3.17%; calcd C 46.45% H 3.12%. Mass spectrum (EI; *m*/*z*, relative intensity): 518 (M^+, 100), 468 (10), 388 (5), 233 (55). ^{1}H NMR ($CDCl_3$) δ: 3.63 (6H, s), 6.58 (2H, s), 7.23–7.52 (8H, m) ppm. ^{13}C NMR ($CDCl_3$) δ: 56.32, 114.46, 120.97, 127.44, 127.99, 131.05, 136.83, 152.51 ppm. ^{77}Se NMR ($CDCl_3$) δ: 371 ppm. X-ray crystals were grown by crystallisation from an under-saturated toluene solution.[17]

4.10.5. 2,5-Bis(m-nitrophenylseleno)hydroquinone dimethyl ether ***7e***. Yield 0.94 g (58%). Recrystallised from toluene as dark orange crystals; mp 215–216 °C. $C_{20}H_{16}N_2O_6Se_2$: found C 44.57% H 2.93% N 5.29%; calcd C 44.63% H 3.00% N 5.20%. Mass spectrum (EI; *m*/*z*, relative intensity): 540 (M^+, 100; only negligible fragmentation). Not sufficiently soluble in NMR-solvents.

4.10.6. 2,5-Bis(p-nitrophenylseleno)hydroquinone dimethyl ether ***7f***. Yield 0.99 g (61%). Recrystallised from toluene as yellow prisms; mp 166–167 °C. $C_{20}H_{16}N_2O_6Se_2$: found C 44.61% H 2.84% N 5.20%; calcd C 44.63% H 3.00% N 5.20%. Mass spectrum (EI; *m*/*z*, relative intensity): 540 (M^+, 100), 508 (8), 476 (4), 404 (17). ^{13}C NMR (DMSO-d_6) δ: 55.65, 117.94, 118.17, 124.02, 124.10, 130.42, 130.84, 141.02, 145.94, 152.46 ppm. ^{13}C NMR ($CDCl_3$) δ: 56.52, 114.92, 121.39, 121.82, 133.11, 136.19, 146.28, 153.50 ppm. ^{77}Se NMR (DMSO-d_6) δ: 278 ppm.

4.10.7. 2-(o-Nitrophenylseleno)hydroquinone dimethyl ether ***8a***. A stirred suspension of **6a** (0.82 g, 6 mmol), 2-nitrobenzeneseleninic acid (0.47 g, 2 mmol), di(*o*-nitrophenyl diselenide)[37] (0.80 g, 2 mmol) and *p*-toluenesulfonic acid (0.38 g, 2 mmol) in glacial acetic acid (15 mL) was heated at reflux for 3 days.[38] The light-yellow reaction mixture was diluted with water (50 mL) and extracted with ether (3×25 mL). The etheral phases were filtered through aluminium oxide (6 g) by means of ether and evaporated. The crystalline residue was recrystallised from hexane and dried (vacuum oven, 45 °C) giving the nitrophenyl selenide (1.52 g, 75%) as a yellow solid; mp 133–134 °C. $C_{14}H_{13}NO_4Se$: found C 49.74% H 3.61% N 4.13%; calcd C 49.72% H 3.87% N 4.14%. Mass spectrum (EI; *m*/*z*, relative intensity): 339 (M^+, 100), 309 (18), 264 (19), 219 (42), 207 (64), 186 (93). ^{1}H NMR (DMSO-d_6) δ: 3.70 (3H, s), 3.75 (3H, s), 6.96 (1H, d, *J* 8.2 Hz), 7.14–7.17 (2H, several peaks), 7.26 (1H, s), 7.42–7.47 (1H, m), 7.53–7.58 (1H, m), 8.34 (1H, d, *J* 8.2 Hz) ppm. ^{13}C NMR (DMSO-d_6) δ: 56.01, 56.71, 104.62, 112.45, 117.45, 123.78, 125.61, 126.05, 130.09, 130.38, 133.49, 145.88, 153.98, 154.64 ppm. ^{77}Se NMR (DMSO-d_6) δ: 420 ppm.

4.10.8. 4-(o-Nitrophenylseleno)veratrole ***8b*** *(identical procedure refluxing* ***6b*** *for 24 h).* Yield 1.03 g (51%). Recrystallised from ethanol as a yellow solid; mp 150–151 °C. $C_{14}H_{13}NO_4Se$: found C 49.80% H 3.68% N 4.24%; calcd C 49.72% H 3.87% N 4.14%. Mass spectrum (EI; *m*/*z*, relative intensity): 339 (M^+, 87), 309 (15), 294 (10), 281 (9), 247 (11), 219 (37), 207 (58), 186 (80), 153 (100). ^{1}H NMR (DMSO-d_6) δ: 3.76 (3H, s), 3.83 (3H, s), 7.00 (1H, d, *J* 8.2 Hz), 7.10 (1H, d, *J* 8.2 Hz), 7.24–7.29 (2H, several peaks), 7.40–7.45 (1H, m), 7.54–7.59 (1H, m), 8.33 (1H, d, *J* 8.2 Hz) ppm. ^{13}C NMR (DMSO-d_6) δ: 55.91, 56.50, 105.18, 114.69, 122.16, 123.27, 124.25, 128.01, 131.03, 132.70, 133.41, 144.82, 150.75, 151.61 ppm. ^{77}Se NMR (DMSO-d_6) δ: 474 ppm.

4.11. 2-Thienyl selenides (9), Scheme 6; general procedure

A stirred solution of salt **1** (0.005 mol) in a mixture of **4a** (21.0 g, 0.25 mol)[39] and glacial acetic acid (50 mL) was heated for 12 h at 70 °C. The dark-purple reaction mixture was poured into water (150 mL) and extracted with pentane (3×35 mL). The combined organic phases were washed with water (15 mL) and the solvent evaporated in vacuo. The residue was filtered through silica gel 60 (15 g) with pentane and the solvent evaporated. Additional dichloromethane/pentane (1:1) was needed to wash out the products **9e**, **9h**, **9i** and **9l**.

4.11.1. Phenyl 2-thienyl selenide ***9a***[40]. Yield 0.98 g (82%). Bulb-to-bulb distillation (air-bath 110 °C, 1 mmHg) gave the product[41] as a colourless oil. Purity >98%. Mass spectrum (EI; *m*/*z*, relative intensity): 240 (M^+, 34), 160 (100), 128 (7), 115 (20). ^{1}H NMR ($CDCl_3$) δ: 6.99 (1H, dd, *J* 5.3, 3.4 Hz), 7.16–7.25 (4H, m), 7.28–7.36 (3H, m) ppm. ^{13}C NMR ($CDCl_3$) δ: 122.36, 128.12, 128.77, 129.52, 130.56, 131.93, 133.04, 136.69 ppm. ^{77}Se NMR ($CDCl_3$) δ: 249 ppm.

4.11.2. p-(4′-n-Heptyl)phenyl 2-thienyl selenide ***9b***. Yield 1.45 g (86%). Bulb-to-bulb (air-bath 180 °C, 1 mmHg) gave the product as a colourless oil. Purity >98% (GC–MS). $C_{17}H_{22}SSe$: found C 60.33% H 6.51% S 9.83%; calcd C 60.52% H 6.57% S 9.50%. Mass spectrum (EI; *m*/*z*, relative intensity): 338 (M^+, 20), 258 (33), 173 (100). ^{1}H NMR ($CDCl_3$) δ: 0.84–0.89 (3H, m), 1.26–1.39 (8H, m), 1.52–1.57 (2H, m),

2.52 (2H, t, *J* 7.7 Hz), 6.97–7.06 (3H, m), 7.25–7.30 (2H, m), 7.38 (1H, dd, *J* 5.3, 1.1 Hz), 7.45 (1H, dd, *J* 5.3, 1.8 Hz) ppm. ^{13}C NMR ($CDCl_3$) δ: 13.68, 22.38, 29.57, 30.06, 31.48, 36.22, 36.40, 122.01, 126.41, 127.77, 129.88, 130.99, 132.01, 132.19, 138.91 ppm. ^{77}Se NMR ($CDCl_3$) δ: 316 ppm.

4.11.3. p-Bromophenyl 2-thienyl selenide ***9c***. Yield 1.05 g (66%). Recrystallised from pentane; faintly yellow solid; mp 50–51 °C. $C_{10}H_7BrSSe$: found C 37.34% H 2.01% S 9.92%; calcd 37.76% H 2.22% S 10.08%. Purity >98% (GC–MS). Mass spectrum (EI; *m*/*z*, relative intensity): 318 (M^+, 35), 238 (100), 195 (5). ^{1}H NMR ($CDCl_3$) δ: 7.03 (1H, dd, *J* 5.3, 3.5 Hz), 7.16 (2H, d, *J* 8.6 Hz), 7.28–7.33 (3H, m), 7.45 (1H, dd, *J* 5.3, 1.1 Hz) ppm. ^{13}C NMR ($CDCl_3$) δ: 120.82, 122.45, 128.53, 131.49, 132.19, 132.45, 132.87, 137.22 ppm. ^{77}Se NMR ($CDCl_3$) δ: 319 ppm.

4.11.4. p-Chlorophenyl 2-thienyl selenide ***9d***. Yield 1.00 g (73%). Bulb-to-bulb (air-bath 130 °C, 1 mmHg) gave the product as a colourless oil. Purity >98% (GC–MS). $C_{10}H_7ClSSe$: found C 43.63% H 2.61% S 11.31%; calcd 43.89% H 2.58% S 11.72%. Purity >98% (GC–MS). Mass spectrum (EI; *m*/*z*, relative intensity): 274 (M^+, 26), 238 (3), 194 (100). ^{1}H NMR ($CDCl_3$) δ: 6.99–7.03 (1H, m), 7.16 (2H, d, *J* 7.6 Hz), 7.23 (2H, d, *J* 7.6 Hz), 7.30 (1H, d, *J* 2.2 Hz), 7.42–7.49 (1H, m) ppm. ^{13}C NMR ($CDCl_3$) δ: 123.11, 126.20, 129.78, 132.26, 132.81, 133.19, 133.50, 137.84 ppm. ^{77}Se NMR ($CDCl_3$) δ: 305 ppm.

4.11.5. o-Nitrophenyl 2-thienyl selenide ***9e***. Yield 0.68 g (48%). Recrystallised from pentane; yellow needles; mp 58–59 °C. $C_{10}H_7NO_2SSe$: found C 42.32% H 2.41% N 4.83% S 11.29%; calcd 42.26% H 2.48% N 4.93% S 11.28%. Mass spectrum (EI; *m*/*z*, relative intensity): 285 (M^+, 46), 238 (17), 185 (100). ^{1}H NMR ($CDCl_3$) δ: 7.05 (1H, d, *J* 8.0 Hz), 7.17–7.21 (1H, m), 7.26–7.43 (3H, m), 7.65 (1H, d, *J* 5.25 Hz), 8.31 (1H, d, *J* 8.0 Hz) ppm. ^{13}C NMR ($CDCl_3$) δ: 123.73, 127.86, 129.17, 130.39, 131.37, 132.88, 135.17, 137.28, 146.34, 150.56 ppm. ^{77}Se NMR ($CDCl_3$) δ: 384 ppm.

4.11.6. 2,2′-Dithienyl selenide ***9f***[42]. Yield 0.53 g (43%). Upon bulb-to-bulb distillation (air-bath 175 °C, 6.8 mmHg) the product was obtained as a light-yellow oil. Purity >98% (GC–MS). Mass spectrum (EI; *m*/*z*, relative intensity): 246 (M^+, 26), 201 (6), 166 (100). ^{1}H NMR ($CDCl_3$) δ: 6.94 (2H, dd, *J* 5.3, 3.6 Hz), 7.26 (2H, dd, *J* 3.6, 1.2 Hz), 7.35 (2H, dd, *J* 5.3, 1.2 Hz) ppm. ^{13}C NMR ($CDCl_3$) δ: 122.66, 127.33, 130.78, 133.85 ppm. ^{77}Se NMR ($CDCl_3$) δ: 249 ppm.

4.11.7. 2,5-Dimethylphenyl 2-thienyl selenide ***9g***. Yield 0.95 g (71%). Bulb-to-bulb (air-bath 190 °C, 0.6 mmHg) gave the product as a colourless oil. Purity >98% (GC–MS). $C_{12}H_{12}SSe$: found C 53.96% H 4.52%; calcd 53.96% H 4.53%. Purity >98% (GC–MS). Mass spectrum (EI; *m*/*z*, relative intensity): 268 (M^+, 61), 253 (3), 238 (2), 188 (81), 174 (47), 155 (18), 143 (11), 103 (42), 91 (22), 77 (100). ^{1}H NMR ($CDCl_3$) δ: 2.19 (3H, s), 2.38 (3H, s), 6.90–6.93 (2H, several peaks), 7.02–7.08 (2H, several peaks), 7.29 (1H, dd, *J* 3.6, 1.2 Hz), 7.47 (1H, dd, *J* 5.2, 1.2 Hz) ppm. ^{13}C NMR ($CDCl_3$) δ: 20.09, 22.49, 122.47, 126.10, 127.13, 127.91, 129.52, 130.92, 132.25, 132.72, 136.81, 138.29 ppm. ^{77}Se NMR ($CDCl_3$) δ: 278 ppm.

4.11.8. 2,5-Bis(methoxymethyl)phenyl 2-thienyl selenide ***9h***. Yield 0.67 g (41%). Bulb-to-bulb (air-bath 200 °C, 2 mmHg) gave the product as a colourless oil. Purity >98% (GC–MS). $C_{14}H_{16}O_2SSe$: found C 51.54% H 4.94%; calcd 51.38% H 4.93%. Purity >98% (GC–MS). Mass spectrum (EI; *m*/*z*, relative intensity): 328 (M^+, 73), 295 (47), 244 (82), 184 (26), 171 (30), 119 (30), 91 (96), 45 (100). ^{1}H NMR (DMSO-d_6) δ: 3.17 (3H, s), 3.29 (3H, s), 4.26 (2H, s), 4.50 (2H, s), 7.03 (1H, d, *J* 1.4 Hz), 7.13–7.18 (2H, several peaks), 7.34 (1H, d, *J* 7.7 Hz), 7.44 (1H, dd, *J* 3.6, 1.1 Hz), 7.47 (1H, dd, *J* 5.2, 1.1 Hz) ppm. ^{13}C NMR ($CDCl_3$) δ: 58.66, 59.32, 73.76, 74.91, 122.08, 125.19, 126.24, 126.45, 127.52, 132.16, 132.83, 134.13, 136.23, 137.60 ppm. ^{77}Se NMR (DMSO-d_6) δ: 280 ppm.

4.11.9. 3-(N-Phthalimido)propyl 2-thienyl selenide ***9i***. Yield 0.76 g (43%). Recrystallised from pentane to give colourless needles; mp 61–62 °C. $C_{15}H_{13}NO_2SSe$: found C 51.38% H 3.81% N 3.85% S 8.97%; calcd C 51.43% H 3.74% N 4.00% S 9.15%. Mass spectrum (FAB +, *m*/*z*): 351 (M^+) [^{80}Se]. ^{1}H NMR ($CDCl_3$) δ: 1.95–2.11 (2H, t, *J* 7.0 Hz), 2.70–2.86 (2H, t, *J* 7.0 Hz), 3.72–3.87 (2H, t, *J* 7.0 Hz), 6.90–7.00 (1H, m), 7.19–7.37 (2H, m), 7.64–7.84 (4H, m) ppm. ^{13}C NMR ($CDCl_3$) δ: 24.86, 32.49, 39.13, 120.94, 123.01, 127.46, 131.21, 132.74, 133.69, 133.98, 167.03 ppm. ^{77}Se NMR ($CDCl_3$) δ: 218 ppm.

4.11.10. m-Bis(2-thienylseleno)benzene ***9j***. Yield 1.35 g (67%). Upon bulb-to-bulb distillation (air-bath 235 °C, 1 mmHg) the product was obtained as a light-yellow oil [purity >98% (GC–MS)], which crystallised into white crystals at room temperature; mp 63–65 °C. $C_{14}H_{10}S_2Se_2$: found C 42.31% H 2.59%; calcd 42.01% H 2.52%. Mass spectrum (EI; *m*/*z*, relative intensity): 402 (M^+, 38), 322 (3), 242 (100). ^{1}H NMR (DMSO-d_6) δ: 7.07 (1H, s), 7.11–7.14 (2H, m), 7.16–7.20 (3H, several peaks), 7.33–7.34 (2H, m), 7.79 (2H, d, *J* 5.2 Hz) ppm. ^{13}C NMR ($CDCl_3$) δ: 124.10, 125.82, 128.55, 128.82, 132.62, 133.87, 134.48, 138.18 ppm. ^{77}Se NMR (DMSO-d_6) δ: 310 ppm.

4.11.11. p-Bis(2-thienylseleno)benzene ***9k***. Yield 1.27 g (63%). Upon bulb-to-bulb distillation (air-bath 235 °C, 1 mmHg) the product was obtained as a light-yellow oil [purity >98% (GC–MS)], which crystallised into white crystals at room temperature; mp 80–81 °C. $C_{14}H_{10}S_2Se_2$: found C 42.39% H 2.52%; calcd 42.01% H 2.52%. Mass spectrum (EI; *m*/*z*, relative intensity): 402 (M^+, 23), 322 (5), 281 (3), 242 (100). ^{1}H NMR (DMSO-d_6) δ: 7.11 (2H, m), 7.21 (4H, s), 7.39 (2H, d, *J* 3.6 Hz), 7.75 (2H, d, *J* 5.5 Hz) ppm. ^{13}C NMR ($CDCl_3$) δ: 123.74, 128.58, 131.27, 132.15, 133.35, 133.80 ppm. ^{77}Se NMR (DMSO-d_6) δ: 306 ppm.

4.11.12. 2,5-Bis(methoxymethyl)-1,4-bis(2-thienylseleno)benzene ***9l***. Yield 0.88 g (36%). Recrystallised from heptane[43] affording **9l** as colourless plates, mp 118–119 °C. $C_{18}H_{18}O_2S_2Se_2$: found C 44.14% H 3.63%; calcd C 44.27% H 3.71%. Mass spectrum (EI; *m*/*z*, relative intensity): 490 (M^+, 76), 457 (8), 406 (24), 322 (12), 279 (13), 247 (22), 171 (63), 127 (100). ^{1}H NMR (DMSO-d_6) δ: 3.06 (6H, s), 4.23 (4H, s), 6.95 (2H, s), 7.15 (2H, dd, *J* 5.2, 3.4 Hz), 7.43 (2H, d, *J* 3.4 Hz), 7.80 (2H, d, *J* 5.2 Hz) ppm. ^{13}C NMR ($CDCl_3$) δ: 57.89, 74.15, 122.99, 128.44, 130.22, 130.71, 132.22, 133.03, 137.39 ppm. ^{77}Se NMR (DMSO-d_6) δ: 381 ppm.

Supplementary data

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.tet.2011.02.004.

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