Chapter 2
New Selenium Electrophiles and Their Reactivity

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2.1 Introduction

The functionalisation of activated carbon-carbon double bonds with electrophilic organoselenium compounds has been successfully applied in various cases [1–3]. Several research groups including ours have investigated stereoselective reactions of alkenes with chiral selenium electrophiles [4–22]. A range of optically active diselenides has been synthesised and the selenium electrophiles generated from these diselenides can add to alkenes with high selectivities. A variety of nucleophiles have been used to open the seleniranium intermediates 1 and the addition products 2 have been used in different subsequent reactions (Scheme 2.1).

![Scheme 2.1 Selenenylation of alkenes](image)

2.2 Generation and Reactivity of Selenium Electrophiles

Phenylselenenylation chloride and phenylselenenylation bromide are commercially available and can be easily produced from diphenyl diselenide by treatment with sulfuryl chloride or chlorine in hexane and with bromine in tetrahydrofuran, respectively.
Other selenium electrophiles can be easily prepared from the corresponding diselenides employing the same strategy. In order to avoid the incorporation of the halide anions as nucleophiles during the selenenylation reaction which could, due to the reversibility, lead to a potential decrease in stereoselectivity it is possible to exchange the halide ion in situ. Silver salts such as triflate [23–25], hexafluorophosphate [26], hexafluoroantimonate [26], or toluenesulfonate [27, 28] can be employed for this purpose. The selenium electrophiles can also be generated by oxidation with ammonium peroxodisulfate [29, 30]. Phenylselenyl sulfate is a very efficient reagent and can be generated via this route. Other reagents like KNO₃ [29–31], CuSO₄ [29, 30], Ce(NH₄)₂(NO₂)₆ [29, 30, 32], Mn(OAc)₃ [33], [bis(trifluoroacetoxy)iodo]benzene [34] and (diacetoxyiodo)benzene [35] were also successfully employed to generate selenium electrophiles by oxidation from the corresponding diselenides. A third possibility is the generation of the phenylselenyl cation via photosensitised single electron transfer from the diselenide to 1,4-dicyanonephthalene [36, 37]. However, the synthesis of the selenium electrophiles is strongly depending on the reaction requirements. Very efficient and broadly applicable are the triflate and the sulfate counterions, which generally produce clean reactions. The preparation of the sulfate is easier than the generation of the triflate, but is has the drawback that it cannot be employed at temperatures below $-30^\circ$C.

The most important use of electrophilic phenylselenyl reagents is the functionalisation of carbon-carbon double and triple bonds. The selenium moiety in the addition products 2 can be used for further useful transformations as shown in Scheme 2.2.

\[ \text{Scheme 2.2 Deselenenylation strategies} \]

The arylseleno group can be functionalised in several ways. Treatment with tin hydrides leads to the homolytic cleavage of the carbon-selenium bond, and the generated carbon radicals can be used for subsequent radical reactions. The oxidation of the arylseleno moiety to the selenoxides leads to elimination products via the well known selenoxide elimination mechanism. Further oxidation to the selenone
results in the generation of a good leaving group, which can be substituted by a variety of nucleophiles X as shown in Scheme 2.2. Likewise, the treatment with another equivalent of the selenium electrophile generates a selenonium ion which can be substituted by a nucleophile as well.

The addition of optically active selenenylating reagents to carbon-carbon double bonds leads to a mixture of two diastereomers. In some cases, these diastereomers can be separated and the subsequent deselenenylation leads to enantiomerically pure products. Asymmetric oxyselenenylation reactions with an external nucleophile (e.g., methanol) are often employed to test the efficiency of a new chiral selenium electrophile. The stereospecific anti-addition of an organoseleneno-group and an oxygen nucleophile are used for the preparation of simple as well as complex molecules.

Wirth and co-workers investigated the methoxyselenenylation of styrene in detail and established the stereochemical course of the reaction [38–40]. The stereochemistry determining step is the formation of seleniranium intermediates 1 during the attack of the alkene onto the selenium electrophile [41, 42].

Recent advances with selenenylation reactions include an asymmetric azido selenenylation reaction by Tiecco et al. (Scheme 2.3), which allows further transformations into aziridines and triazoles [43]. It is remarkable that his reaction occurs with a very high level of facial selectivity and with “Markovnikov” orientation. The sulfur atom in the chiral side chain in electrophile 3 seems to play an important role in this reaction.

![Scheme 2.3 Asymmetric azido-selenenylation by Tiecco et al.](image)

2.3 Reactivity of Sulfoxide-Containing Selenium Electrophiles

We recently reported the synthesis of (t-butylsulfanyl)phenyl diselenide 4 and 2-(t-butylsulfanyl)-6-methoxy phenyl diselenide 5 by lithiation of the corresponding aryl sulfoxides and treatment with elemental selenium, followed by an oxidative work-up [44]. The diselenides were used for methoxyselenenylation to establish their ability to influence the stereochemical outcome of these reactions (Scheme 2.4). As already stated, there is a broad choice of methods and reagents available to generate the selenium electrophiles from the diselenides. With respect to the nature of the chiral centre of the diselenides, a sulfoxide moiety, the generation of the electrophiles with bromine was preferred over the oxidative methods.
Because of the good results which, according to literature, were obtained with triflates as counterions, silver triflate was used for the halogen exchange reaction.

A typical procedure proceeds by generation of the selenenyl bromide from the diselenide with bromine, the exchange of the bromide with the less nucleophilic triflate, and the addition of the selenenyl cation to the carbon-carbon double bond in the presence of a nucleophile leading to product formation (Scheme 2.5). The diastereomeric ratio (d.r.) of the products was determined by NMR. Initial reactions were screened with 2-chlorostyrene as substrate in different solvents.

The highest diastereomeric ratios with triflate 6 were found using dichloromethane (11:1) or chloroform (7:1) (Table 2.1). These solvents also proved to give the best yields (up to 48%). When the reactions were carried out in polar ethers like tetrahydrofurane and cyclopentyl methyl ether (CPME), the selectivities dropped to 4:1. However, in diethyl ether the selectivity was slightly higher (5:1),
which could be caused by the difference in the solvation of the diselenide. The diastereomeric ratio in a 4:1 mixture of diethyl ether and dichloromethane was again observed as 5:1, presumably because of the high excess of the more polar solvent. The reaction was not carried out in unpolar solvents such as hexane or toluene, as the diselenide is insoluble in these solvents. It is assumed that the selectivities are a synergetic effect of the coordination of the oxygen from sulfoxide to the selenium and the bulky $t$-butyl group. The coordination of the oxygen would be stronger in less polar solvents and would force therefore the chiral centre closer to the reaction site.

Interestingly, the colour of the selenium electrophile with the triflate 6 is depending on the solvent (Fig. 2.1) and can be used as an indicator for the progress of the reaction. This is not the case with 7 which always gives yellow mixtures.

![Fig. 2.1](image)

**Fig. 2.1** Colour of 7 (orange in all solvents) and 6 in THF: purple, CPME: red, CH$_2$Cl$_2$: green

Surprisingly, triflate 7 was less reactive and much less selective under the same reaction conditions (Table 2.2). The highest diastereomeric ratio was observed in tetrahydrofuran (3:1), but with low yield (18%). In chloroform and cyclopentylmethyl ether (CPME) the yields were higher but the diasteromeric ratio decreased to 2:1 and 1:1, respectively. Obviously, triflate 7 shows a slightly better selectivity in polar solvents than in unpolar solvents, compared to triflate 6, where the reactivity is inverse. It could not yet be established why the reaction shows some selectivity in tetrahydrofuran but not in solvents of similar polarity such as diethyl ether and cyclopentylmethyl ether.

The reason for the low yields obtained with both selenenylating reagents could not be determined. Besides the products, it was generally possible to re-isolate most of the diselenide and 2-chlorostyrene with a variable amount of byproducts.
which were not characterised. It is possible that the diselenides are not completely converted to the corresponding selenenyl bromides in the first step of the one-pot procedure. Oxidative reagents for the generation of the selenium electrophiles were ruled out due to the nature of the auxiliary and the alternative generation of the corresponding selenenyl chlorides with SO$_2$Cl$_2$ failed. The silver triflate was suspected as a possible cause for the low yields, but could be ruled out as a test reaction with commercially available selenenyl chloride showed yields of 80%. Most of the styrene derivatives were used without further purification, which could have been responsible for the low yields as well. However, when freshly distilled styrene derivatives were used it was not possible to observe significant higher yields (increase by 2–3%). To keep all experiments comparable, it was decided to continue to generate the selenenylationing reagents with bromine. The reactivity of selenenyltriflate $^6$ towards different substrates was investigated employing methanol as standard nucleophile (Scheme 2.6).

Table 2.2 Selectivities of the methoxyselenenylation of 2-chlorostyrene with 7 in different solvents

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent</th>
<th>Yield [%]</th>
<th>$d.r.$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>THF</td>
<td>18</td>
<td>3:1</td>
</tr>
<tr>
<td>2</td>
<td>CPME$^b$</td>
<td>30</td>
<td>1:1</td>
</tr>
<tr>
<td>3</td>
<td>Et$_2$O</td>
<td>10</td>
<td>1:1</td>
</tr>
<tr>
<td>4</td>
<td>CH$_3$CN</td>
<td>23</td>
<td>1:1</td>
</tr>
<tr>
<td>5</td>
<td>CH$_2$Cl$_2$</td>
<td>20</td>
<td>1:1</td>
</tr>
<tr>
<td>6</td>
<td>CHCl$_3^c$</td>
<td>40</td>
<td>2:1</td>
</tr>
</tbody>
</table>

$^a$Determined from NMR spectra of crude products.$^b$CPME: cyclopentylmethyl ether.$^c$Reaction performed at –50°C

(10–30%) which were not characterised. It is possible that the diselenides are not completely converted to the corresponding selenenyl bromides in the first step of the one-pot procedure. Oxidative reagents for the generation of the selenium electrophiles were ruled out due to the nature of the auxiliary and the alternative generation of the corresponding selenenyl chlorides with SO$_2$Cl$_2$ failed. The silver triflate was suspected as a possible cause for the low yields, but could be ruled out as a test reaction with commercially available selenenyl chloride showed yields of 80%. Most of the styrene derivatives were used without further purification, which could have been responsible for the low yields as well. However, when freshly distilled styrene derivatives were used it was not possible to observe significant higher yields (increase by 2–3%). To keep all experiments comparable, it was decided to continue to generate the selenenylationing reagents with bromine. The reactivity of selenenyltriflate $^6$ towards different substrates was investigated employing methanol as standard nucleophile (Scheme 2.6).

![Scheme 2.6](image)

Scheme 2.6 Methoxyselenenylation of different styrenes with methanol as nucleophile

The monosubstituted double bonds of styrene and 2-vinylnaphthalene (Table 2.3, Entries 1 and 2) showed reasonable selectivities with diastereomeric ratios of 5:1, although they were performed in THF.

A chlorine substituent in the 2-position of the aromatic system (Entry 2) enhanced the selectivity considerably (11:1) and led to 9c in 41% yield. Generally, the use of sterically more hindered alkenes led to lower yields (Entries 2–6) between 30% and 41%. However, β-substitution on the styrene enhanced the selectivity (Entries 5 and 6) to 11:1 and 9:1, respectively. The slightly electron deficient double bonds of methyl cinnamate and 3-nitrostyrene were not reactive
### Table 2.3 Reaction of rac-4 with different styrene derivatives

<table>
<thead>
<tr>
<th>Entry</th>
<th>Alkene</th>
<th>Solvent</th>
<th>Yield [%]</th>
<th>d.r.(^a)</th>
<th>Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>THF</td>
<td>52</td>
<td>5:1</td>
<td></td>
<td><img src="9a.png" alt="Image" /></td>
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<tr>
<td>2</td>
<td>THF</td>
<td>32</td>
<td>5:1</td>
<td></td>
<td><img src="9b.png" alt="Image" /></td>
</tr>
<tr>
<td>3</td>
<td>(\text{CH}_2\text{Cl}_2)</td>
<td>41</td>
<td>11:1</td>
<td></td>
<td><img src="9c.png" alt="Image" /></td>
</tr>
<tr>
<td>4</td>
<td>(\text{CH}_2\text{Cl}_2)</td>
<td>38</td>
<td>4:1</td>
<td></td>
<td><img src="9d.png" alt="Image" /></td>
</tr>
<tr>
<td>5</td>
<td>(\text{CH}_2\text{Cl}_2)</td>
<td>30</td>
<td>11:1</td>
<td></td>
<td><img src="9e.png" alt="Image" /></td>
</tr>
<tr>
<td>6</td>
<td>(\text{CH}_2\text{Cl}_2)</td>
<td>30</td>
<td>9:1</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(continued)
enough under the conditions of the methoxyselenenylation reaction. The diastereomeric ratios obtained using the enantiomerically enriched (S)-6 and the racemic selenenyltriflate rac-6 are identical (5:1). Whereas the optical rotation obtained for 9a was $[\alpha]_D^{20} = 0$ when using rac-6, the value for 9a was $[\alpha]_D^{20} = -128$ when (S)-6 was used, but the absolute stereochemistry was not determined.

The same investigation was performed with selenenyl triflate 7. The solvent screening had already shown that 7 was much less selective than 6 using 2-chlorostyrene as substrate. As this observation could only be due to the substrate two other styrenes were tested (Scheme 2.7). Unsubstituted styrene lead to a diastereomeric ratio of 2:1 with 24% yield and trans-β-methylstyrene to a product ratio of 1:1 in 22% yield. No further investigations using diselenide 5 were undertaken.

In a last series of reactions, the influence of the nature of the nucleophile on the diastereoselectivity was investigated, employing triflate 6 in the selenenylation reaction with 2-chlorostyrene as substrate.

The reaction was performed with several oxygen, nitrogen and sulfur nucleophiles. Table 2.4 presents the results obtained with different oxygen nucleophiles. The yields with small nucleophiles such as methanol, ethanol and i-propanol are comparable and better than that obtained with t-butanol, which is lower due to its steric bulkiness. The diastereomeric ratios are decreasing from methanol to ethanol and i-propanol to t-butanol. The nucleophilicity of these alcohols can be influenced by several properties [45], of which: (a) the solvation energy of the nucleophile;
(b) the bond strength of the new Nu-C bond formed; (c) the electronegativity of the attacking atom; (d) the polarisability of the attacking atom; and (e) the steric bulk of the nucleophile are most important.

The first characteristic expresses that a strong solvation leads to an increase in the activation energy, as the solvation shell of the anionic nucleophile needs to be disrupted. The second suggests that if the newly formed bond is very stable, the transition state in a $S_N2$ reaction shows a higher stability as well. This leads overall to a decrease in the activation energy. The third point takes into account that a strongly electronegative nucleophilic centre is less reactive because the electrons, which are necessary for the bond formation, are more tightly bound to the nucleus. This observation is closely related to the fourth statement, the polarisability of the electron shell. Finally, a more sterically hindered nucleophile is less reactive than an unhindered centre, because it can not necessarily avoid the non-bonded repulsions in a transition state.

Taking these points into account, it can be assumed that the most important influence in the above attempted selenenylation reactions is the steric bulk which increases from methanol to ethanol and $i$-propanol to $t$-butanol. However, the selectivity obtained with benzyl alcohol (3.5:1, Table 2.4, Entry 5) can not be explained by the steric bulk involved. In this case it should be expected that the diastereoselectivity would be better than 6:1 (as for $t$-butanol). If the rate of the epimerisation of the three membered ring systems is higher than that of the nucleophilic attack of the alcohol, this would lead to a decrease in diastereoselectivity. Hence it can be assumed that another of the mentioned properties, concerning the nucleophilicity of benzyl alcohol, gains more influence. Using benzoic acid as nucleophile (Table 2.4, Entry 6) led only to traces of the product, which was not isolated.

It was also attempted to use thiophenol and several nitrogen nucleophiles such as $n$-butyl amine, benzyl amine, $N$-methylbenzyl amine, sodium azide and trimethylsilyl azide in different solvents. However, the only successful reaction occurred with trimethylsilyl azide ($\text{TMSN}_3$) as nucleophile in dichloromethane as solvent (Table 2.4, Entry 7), which resulted in 35% yield and in a diastereomeric ratio of 6:1. Employing other nitrogen or sulfur nucleophiles resulted either in the recovery of starting material or led to complex reaction mixtures.

Table 2.4 Selenenylation using diselenide 4 with 2-chlorostyrene and different nucleophiles

<table>
<thead>
<tr>
<th>Entry</th>
<th>Nucleophile (NuH)</th>
<th>Product</th>
<th>Yield [%]</th>
<th>$d.r.$(^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>MeOH</td>
<td>9c</td>
<td>41</td>
<td>11:1</td>
</tr>
<tr>
<td>2</td>
<td>EtOH</td>
<td>9g</td>
<td>47</td>
<td>8:1</td>
</tr>
<tr>
<td>3</td>
<td>$i$-PrOH</td>
<td>9h</td>
<td>47</td>
<td>8:1</td>
</tr>
<tr>
<td>4</td>
<td>$t$-BuOH</td>
<td>9i</td>
<td>30</td>
<td>6:1</td>
</tr>
<tr>
<td>5</td>
<td>BnOH</td>
<td>9j</td>
<td>30</td>
<td>3.5:1</td>
</tr>
<tr>
<td>6</td>
<td>PhCO$_2$H</td>
<td>–</td>
<td>Traces</td>
<td>–</td>
</tr>
<tr>
<td>7</td>
<td>TMSN$_3$</td>
<td>9k</td>
<td>35</td>
<td>6:1</td>
</tr>
</tbody>
</table>

\(^a\)Determined from NMR spectra of crude products
2.4 Chiral Counteranions in Selenenylation Reactions

Most selenium electrophiles are generated in situ by treating the corresponding diselenides with chlorine, sulfuryl chloride or bromine. Addition reactions with these reagents can be problematic as the halide anions compete with other external nucleophiles or during cyclisation reactions, which can lead to undesired side products and to a decrease in selectivity. Halide anions can be replaced with less nucleophilic anions such as triflate, sulfate, perchorlate, tetrafluoroborane or hexafluorophosphate by treating the selenium electrophile with the appropriate silver salt as shown for silver triflate in Scheme 2.8.

The effect of the counteranion on the course of these reactions was investigated by Tomoda et al. [16], Tiecco and co-workers [46], and Khokhar and Wirth [47]. On the basis of these results it was suggested that a decrease in the nucleophilicity of the counteranion, i.e., an increase in the electrophilicity of the selenium reagent, produces an enhancement of the diastereomeric excess in these reactions. These examples have shown that the counterion can have a strong influence on the selectivities of selenenylation reactions. Therefore it seemed to be viable to combine these observations with the concept of the “Asymmetric Counteranion Directed Catalysis” (ACDC). This is a relatively new development which emerged in the field of organocatalysis [48]. Reactions proceeding via anionic intermediates have been successfully influenced by chiral cationic counterions. The combination of chiral ions with enantiopure counterions can lead to two ion pairs with different stabilities and different chemical and physical properties. One ion pair can be formed preferentially if it is more stable. This concept has already been used for racemic resolutions as well as for synthesis. It is well known that high levels of asymmetric induction can be achieved using chiral cations and achiral anions. Recently, it has also been shown that this concept works also for cationic intermediates and transition states with chiral counteranions. For a long time, only cationic counterions were used and able to control the stereoselective outcome of reactions and to produce chiral products as single enantiomers. However, in recent years several independent reports in the field of enantioselective organocatalysis could show that chiral anions are also able to influence the selectivity of a reaction.

In 2003, Lacour published a review highlighting the synthesis and reactions of chiral counteranions [49]. Beside natural compounds such as chiral carboxylic acids 10 and sulfonic acids 11, which possess a rather large number of potential conformations, tetrahedral borate 12, a number of chiral metallo-organic complexes 13, and phosphate anions 14 have been investigated as shown in Fig. 2.2.
Toste and co-workers reported in 2007 the first highly successful application of the metal-ACDC catalysis concept in a gold(I) catalysed heteroatom cyclisations of allenes [50]. High enantioselectivities with up to 99% enantiomeric excess were observed in hydroaminations and hydroalkoxylations of allene derivatives. In 2006, Komanduri and Kirsche had already described a Rh-catalysed reductive coupling of 1,3-enynes with heterocyclic aromatic carbonyl compounds using chiral bisphosphine ligands [51]. The group of List reported the first application of the chiral counteranion strategy in the Pd-catalysed asymmetric allylic alkylation [52] and a manganese(III)-catalysed epoxidation of alkenes [53]. The same group has shown that chiral phosphoric acids together with secondary amines can modulate the enantioselective transfer hydrogenation of \( \alpha,\beta \)-unsaturated aldehydes with an enantiomeric excess of up to 98% [54]. The catalytic concept of ACDC was also successfully applied for the iminium-catalysed enantioselective epoxidation of \( \alpha,\beta \)-unsaturated aldehydes [55] for the enantioselective synthesis of \( \beta \)-alkoxyamines and for the desymmetrisation of meso-episulfonium ions [56].

The counteranion effects on the enantioselectivity of selenenylation and the synthesis and use of chiral counter anions using the ACDC concept seemed to be a promising tool to enhance the diastereoselectivity of selenenylation reactions. Several silver salts (Fig. 2.3) were synthesised as chiral anionic reagents for the selenenylation reactions of alkenes.

BINOL derivatives have proven to be effective in several asymmetric counteranion mediated reactions. A tool to enhance the rigidity of the backbone is the introduction of large substituents at 3,3'-positions or 6,6'-positions on the BINOL scaffold. In this case the synthetic efforts were concentrated on the 3,3'-positions. Precursors for the silver salts of phosphoric acids 15 and 16 are commercially available which can be prepared easily [49]. Additionally, the silver salt of camphorsulfonic acid 18 [57] and the prolin derivative 19 were synthesised from camphor.
and proline. Both starting materials are cheap and especially proline derivatives have already proven to be successful organocatalysts.

Ideally, the use of an unsubstituted selenenyl halide like phenylselenenyl bromide together with a chiral counteranion would form a new chiral selenenylation reagent to achieve a stereoselective reaction pathway during a selenenylation reaction. To test this hypothesis phenylselenenyl bromide was generated from diselenide and the chiral silver salts were added either neat or as a methanolic solution (Scheme 2.9). In principle, this approach leads to the formation of the envisioned chiral reagents and could, when reacting with styrene, lead to enantiomeric enriched products.

Initially, phenyl selenenyl bromide was used together with the silver salt (S)-15. Three different solvents, diethylether, dichloromethane and toluene, were investigated. It was expected that the selectivity, if any could be observed, would increase from the more to the less polar solvents.

The low solubility of the silver salts in some solvents was a problem for this reaction. It was improved when the reaction was carried out in dichloromethane, but the selectivities observed by HPLC analysis were extremely small as shown in Table 2.5.

With further investigations using different silver salts it could be established if the encountered low enantiomeric excesses were generic for these reactions or if the properties of the chosen silver salt (S)-15 were insufficient to positively influence the stereochemical course of the methoxyselenenylation. (S)-16 was used under
identical reaction conditions as mentioned above. It was possible to obtain 1% e.e. using dichloromethane and toluene as solvents. However, this is again within the error limit of the HPLC system. In diethylether, the product was racemic.

To exclude the possibility that the use of styrene or methanol has major effects (S)-15 was tested in a cyclisation reaction of acid 23 as shown in Scheme 2.10.

![Scheme 2.10 Selenocyclisation with phenylselenenyl derivative 24](image)

The seleneny compound 24 was again obtained from diphenyl diselenide 19 with bromine and (S)-15 in dichloromethane at −78°C. The selenocyclisation was carried out at room temperature by addition of (E)-4-phenylbut-3-enoic acid 23. The product 25 was obtained in 26% yield after 4 h. According to HPLC analysis the chiral counteranion again did not show any influence in the stereochemical outcome of the reaction, the product 25 was obtained as a racemate.

As it was not possible to obtain and isolate a silver salt from acid (S)-18, a different approach was used to investigate its ability to influence the stereochemical outcome of these reactions. The chiral anion was generated in situ when the phenylselenyl bromide 20 was treated with silver(I) carbonate which led to the precipitation of silver bromide. The carbonate counteranion could be easily exchanged with N-benzoylproline (S)-18 due to the higher acidity of the carboxylic acid (Scheme 2.11).

![Table 2.5 Methoxyselenenylation reaction with phenylselenenyl bromide, styrene and different silver salts](image)

<table>
<thead>
<tr>
<th>Silver salt</th>
<th>Solvent</th>
<th>Yield [%]</th>
<th>e.e. [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>(S)-15</td>
<td>Diethylether</td>
<td>21</td>
<td>0</td>
</tr>
<tr>
<td>(S)-15</td>
<td>Dichloromethane</td>
<td>53</td>
<td>3</td>
</tr>
<tr>
<td>(S)-15</td>
<td>Toluene</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>(S)-16</td>
<td>Diethylether</td>
<td>10</td>
<td>0</td>
</tr>
<tr>
<td>(S)-16</td>
<td>Dichloromethane</td>
<td>48</td>
<td>1</td>
</tr>
<tr>
<td>(S)-16</td>
<td>Toluene</td>
<td>24</td>
<td>1</td>
</tr>
<tr>
<td>(S)-18</td>
<td>Acetonitrile</td>
<td>18</td>
<td>0</td>
</tr>
</tbody>
</table>

* Determined by HPLC.
This methoxyselenenylation has again been performed in different solvents (tetrahydrofurane, toluene, cyclopentylmethyl ether, toluene/cyclopentylmethyl ether 19:1, chlorobenzene). The obtained enantiomeric excesses in all reactions are only 3% or below.

In conclusion, two new diselenides were synthesised with a sulfoxide moiety as a side chain. One of these diselenides shows, depending on the solvent, good diastereoselectivities in the methoxyselenenylation of activated alkenes. Investigations towards stereoselective methoxyselenenylations using chiral counteranions have, however, been unsuccessful.

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