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Modular chiral selenium-containing oxazolines: synthesis and application in the palladium-catalyzed asymmetric allylic alkylation

Antonio L. Braga,* Diogo S. Lüdtke, Jasquer A. Sehnem and Eduardo E. Alberto

Departamento de Química, Universidade Federal de Santa Maria, 97105-900 Santa Maria, RS, Brazil

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Abstract—A new series of modular chiral selenium-containing oxazolines has been synthesized from inexpensive and commercially available L-serine and L-aspartic acid. These new compounds were evaluated as chiral ligands in the palladium-catalyzed asymmetric allylic alkylation reaction, furnishing the product in high enantiomeric excess, using Cs_2CO_3/CH_2Cl_2 as the base/solvent system.

1. Introduction

The preparation of new and efficient enantiopure ligands providing a chiral environment to metals for asymmetric catalysis is currently one of the major challenges in synthetic organic chemistry. Among the transition metal-catalyzed reactions known to form carbon–carbon and carbon-heteroatom bonds, the palladium-catalyzed allylic substitution stands out as one of the most valuable synthetic tools available.[1] The development of effective chiral ligands for this process has grown steadily over the past few years since several new catalysts have been successfully employed for asymmetric induction in this reaction. Among the wide variety of catalysts designed, hetero-bidentate ligands play an important role once they capitalize upon the difference in electronic character of the two donor atoms to exert a stereoelectronic bias upon intermediate π-allyl complexes. Stereoelectronically, the palladium-allyl terminus opposite to the more powerful acceptor atom will be longer; hence, more susceptible to cleavage as a result of nucleophilic attack.[2]

In this context, chiral bidentate ligands, equipped with an oxazoline framework and a soft donor heteroatom, have been the subject of research of many groups. The pioneering chiral phosphine-oxazolines developed by Pfaltz,[3] Helmchen,[4] and Williams[5] are by far the most widely studied[6] and have served as inspiration for the design of many other heterobidentate *P*,*N* ligands with an oxazoline backbone.[7,8] Some of these ligands are shown in Figure 1 and all of them have been successfully employed in the enantioselective allylation reaction.

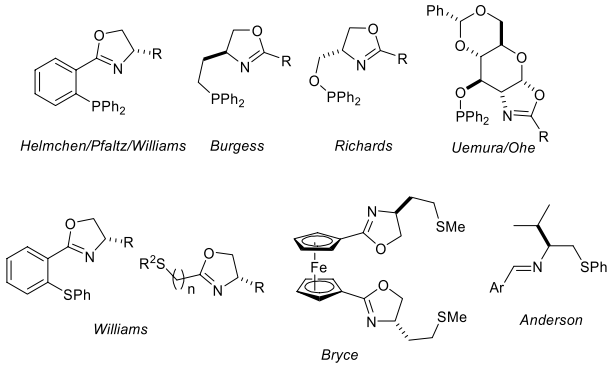

Figure 1. Oxazoline ligands for palladium-catalyzed allylic alkylations.

Mixed *S*,*N*-ligands have also been extensively studied in palladium-catalyzed allylic substitutions. Various sulfur-containing oxazolines were reported to act as chiral catalysts in this reaction.[9] Ferrocenyl-oxazolines incorporating a thioether moiety were applied to such a process as well.[10] A series of sulfur-imine mixed donors, derived from amino acids has also been described to induct high degrees of enantioselectivity in the allylation reaction.[11] Our group has recently published the synthesis of cysteine and methionine-derived *N*,*S*-ligands and its application to asymmetric allylations.[12]

On the other hand, chiral organoselenium compounds have

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* Corresponding author. Tel.: +55 55 3220 8761; fax: +55 55 3220 8998; e-mail: albraga@quimica.ufsm.br

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attracted much attention of organic chemists over the last decade, and are now a very important tool for stereoselective transformations.[13] These compounds have found use in the stereoselective ring opening of epoxides,[14] anti-stereoselectivity and Markownikoff regioselectivity in the electrophilic selenenylation of alkenes.[15] Most importantly, chiral diselenides have been employed as useful ligands in various asymmetric transformations such as asymmetric hydrosilylation of acetophenone,[16] enantioselective diethylzinc addition to aldehydes,[17,18] and 1,4 addition of Grignard reagents to enones.[19]

In the course of our current interest in chiral organoselenium mediated asymmetric transformations,[18,19] and as only few examples of chiral ligands containing a selenium atom coordinated to palladium have been described,[20] we decided to prepare a new class of chiral oxazoline ligands **1** and **2** (Fig. 2) with an organoselenium moiety as a soft donor, starting from an easily available and inexpensive chiral pool. These chiral selenium-containing oxazolines had their efficiency examined as catalysts in the enantioselective palladium-catalyzed allylic alkylation reaction.

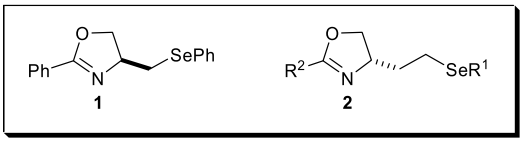
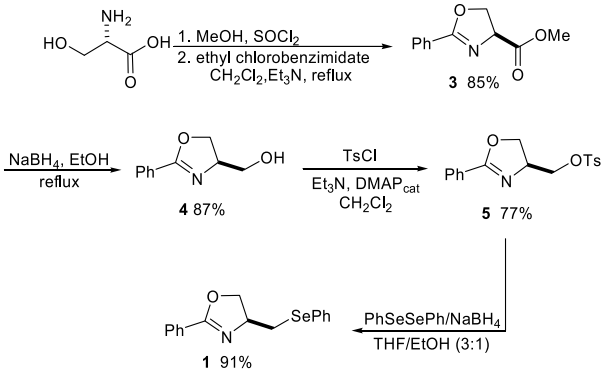


Figure 2. Selenium-containing oxazolines **1** and **2**.

2. Results and discussion

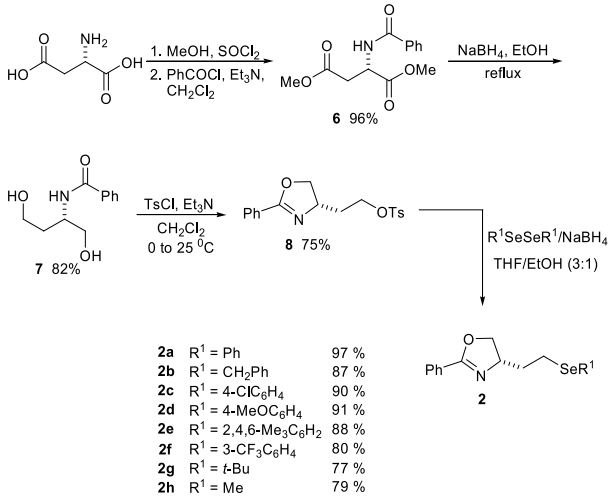
Ligands **1** and **2** were synthesized starting from natural amino acids L-serine and L-aspartic acid, respectively. Oxazolinyl selenide **1** was prepared by the sequence shown in Scheme 1. First, esterification of L-serine with $SOCl_2$/MeOH, followed by cyclization of the resulting ester with ethyl chlorobenzimidate resulted in the corresponding oxazolinyl ester **3** in 85% yield for the two steps.[21] The ester was further reduced to the alcohol **4**, which was treated with TsCl in dichloromethane affording the tosylate **5** in good yield.[22] Thus the desired oxazolinyl selenide was obtained by nucleophilic displacement with PhSeSePh/$NaBH_4$ in a 3:1 mixture of THF/ethanol as solvents.



Scheme 1. Synthesis of ligand **1**.

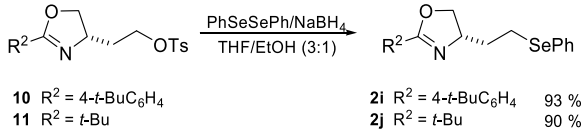
Ligand **2a** was obtained by esterification of both carboxyl groups of aspartic acid, followed by acylation at nitrogen with benzoyl chloride. The diester **6** was cleanly reduced to the diol **7**[23] which was treated, without further purification, with TsCl in dichloromethane using triethylamine as base. The ditosylated intermediate immediately cyclizes to the entropically favored oxazoline **8**.[7c] The organoselenium functionalization took place again by nucleophilic displacement of the tosylate leaving group by a phenyl selenide anion generated by reduction of PhSeSePh with $NaBH_4$ in a 3:1 mixture of THF and ethanol.

Ligands **2b–h** were prepared in a similar way as **2a** by nucleophilic displacement of tosylate leaving group with the selenide anion generated by reaction of the corresponding diorganoyl diselenide with $NaBH_4$ in THF/EtOH. The desired oxazolinyl selenides were obtained with yields ranging from 77 to 97% (Scheme 2).



Scheme 2. Synthesis of ligands **2a–h**.

Structural variations at R^2 positions were also introduced. Thus, we prepared tosylates **10** and **11** in a similar way to **8**, and they were further submitted to substitution with phenylselenolate anion to afford oxazolinyl selenide **2i** and **2j** (Scheme 3).



Scheme 3. Synthesis of ligands **2i–j**.

One of the major advantages of the strategy developed is its modular construction and, thus, modifications in the structure of the catalysts can be easily introduced. This characteristic is important for the fine-tuning of the catalytic activity and for a deeper understanding of the steric and electronic effects in the reaction outcome (Fig. 3). Moreover, it is interesting to point out that, for the first time, an organoselenium group is attached to a sp^3 carbon in a ligand designed for palladium-catalyzed allylic alkylations. This structural feature is highly interesting, since it facilitates the

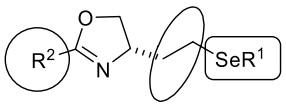


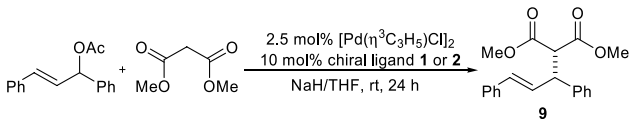
Figure 3. Modular construction of chiral selenium-containing oxazolines.

introduction of the selenium atom into the framework of the molecule thus permiting a highly flexible strategy for steric and electronic modifications at R^1 position.

With this set of ligands in hand, we turned our attention to investigate their potential in the palladium-catalyzed asymmetric allylic alkylation.

We studied the alkylation reaction of racemic 1,3-diphenyl-2-propenyl acetate with sodium dimethyl malonate, using the chiral selenium-containing oxazolines **1** and **2** as chiral ligands (10 mol%) in the presence of $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ (2.5 mol%) in THF as solvent. The results of these studies are summarized in Table 1.

Table 1.



#	Ligand	R^1	R^2	Yield (%)[a]	ee (%)[b]
1	**1**	—	—	71	23
2	**2a**	Ph	Ph	99	85
3	**2b**	CH_2Ph	Ph	93	79
4	**2c**	4-ClPh	Ph	85	63
5	**2d**	4-MeOPh	Ph	81	75
6	**2e**	2,4,6-Me_3Ph	Ph	67	6[c]
7	**2f**	3-CF_3Ph	Ph	83	54
8	**2g**	*t*-Bu	Ph	91	37
9	**2h**	Me	Ph	89	70
10	**2i**	Ph	4-*t*-BuPh	68	58
11	**2j**	Ph	*t*-Bu	63	5

[a] Isolated yields.
[b] Determined by HPLC with a Daicel Chiralcel OD column, hexane/isopropanol 99:1; 0.5 mL/min; 254 nm.
[c] The opposite enantiomer was obtained.

Ligand **1** furnished quite disappointing results, once the alkylation product was obtained with poor enantioselectivity. On the other hand, ligands of type **2** performed much more successfully.

Ligand **2a** has proven to be more efficient than **1**, giving the alkylated product in 85% ee (Table 1, entry 2). We could observe that the nature of the group attached to the selenium atom plays an important role in the enantioselection event. The catalyst **2b** with a benzyl substituent at selenium was tested, but no increase in the ee could be achieved (entry 3). Since the best result was obtained using catalyst **2a**, which has R^1=Ph, we attempted to test ligands with several different substituents at the aromatic ring of the organoselenium moiety. Ligands with electron-withdrawing groups like chlorine (**2c**) and trifluormethyl (**2f**) at the selenium donor were also evaluated. Unfortunately, a decrease in the enantioselectivity was observed together with diminished yields. A plausible explanation for this account is that the presence of the electron-withdrawing group reduces the ability of the selenium to coordinate to palladium, which would account for the lowering in the yields of **9** (see entries 4 and 7). When catalyst **2d** bearing an electron-donating group was employed, an ee of 75% was obtained (entry 5).

Steric effects seem to be crucial in our catalytic system. The increase of the bulk around selenium causes a negative effect in the enantioselectivity of the reaction. This can be easily evidenced by a dramatic decrease in the ee by using ligand **2g**, which has an *t*-Bu substituent directly attached to selenium (entry 6). A more pronounced effect can be seen when the highly encumbered ligand **2e** was employed. A poor yield of **9** was achieved and interestingly the opposite enantiomer was formed with a very low enantioselectivity of only 6% (entry 6).

The influence of the sterics at the oxazoline ring was also evaluated. When the phenyl group in **2a** was replaced by bulkier ones such as in the case of **2i** and **2j**, a decrease in the ee was detected (entries 10 and 11). **2i** gave an ee of 58% and in the case of ligand **2j** an essentially racemic product was obtained (5% ee, entry 11).

All ligands furnished the alkylated product with the (*R*) configuration as the major product, except for ligand **2e**, which furnished a slight excess of the opposite enantiomer. The stereochemistry of **9** was assigned by comparison of the sign of optical rotation with literature data.[7b]

A plausible explanation for such a high difference in the level of enantioselection showed between **1** and **2a** can be found in the difference of the bite angle of the chiral ligand. It is known that as the length of the tether in bidentate ligands is increased, the bite angle can be increased as well.[9b,24] This increase places the chiral environment of the ligand closer to the allyl system and it may result in greater asymmetric induction. So, as ligand **2a** has a longer side chain, it coordinates to palladium in a greater bite angle. This behavior results in closer proximity of the oxazoline moiety to the allyl unit and, hence, greater enantioselectivity should be observed in comparison with ligand **1** (Fig. 4).

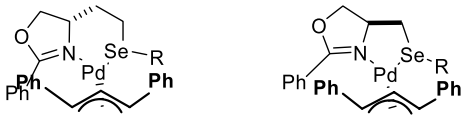


Figure 4. Effect of the bite angle.

Attempts to study the loading of the catalyst used were also performed. As depicted in the Figure 5, quantities of 15, 10, 5, and 2.5 mol% of chiral ligand **2a** were employed in the asymmetric allylic alkylation. The best results were obtained by using 10 mol% of **2a** and 2.5 mol% of the palladium source. This amount corresponds to a 2:1 ratio of ligand to palladium. Changing this ratio to 1:1, by lowering the amount of **2a** to 5 mol%, a decrease of the ee to 78% was observed. Moreover, a dramatic decrease in the ee was verified when 2.5 mol% of the ligand was used.

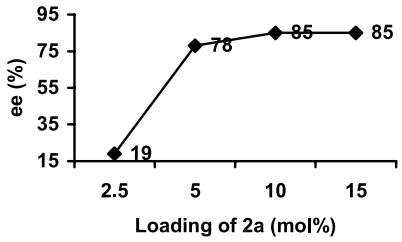
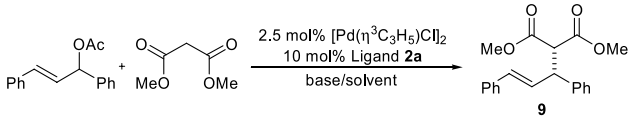


Figure 5. Variation in the amount of **2a** in the presence of 2.5 mol% of $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$.

The results obtained with ligand **2a** encouraged us to continue our search to find out some improvements in the reaction conditions using this catalyst. The results of these studies are summarized in Table 2.

Table 2. Effect of the base/solvent system in the asymmetric allylic alkylation



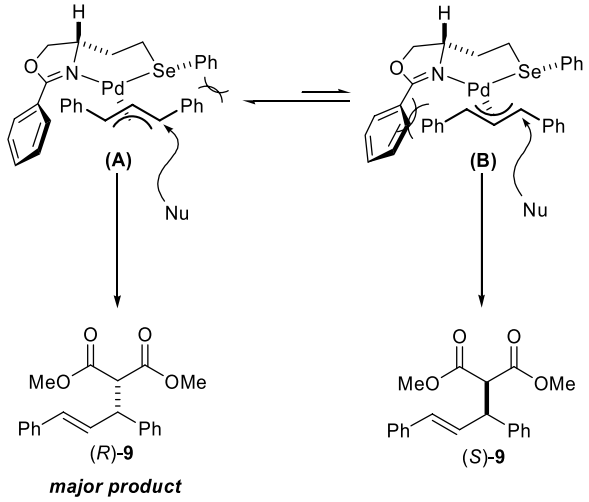
Entry	Base	Solvent	Time (h)	Yield (%)[a]	ee (%)[b]
1[c]	BSA/KOAc	CH_2Cl_2	24	71	23
2	BSA/KOAc	CH_2Cl_2	24	97	81
3[d]	BSA/KOAc	CH_2Cl_2	24	93	79
4	BSA/KOAc	CH_3CN	24	95	79
5	BSA/KOAc	Toluene	24	63	66
6	NaH	THF	24	99	85
7[d]	NaH	THF	24	96	85
8	Cs_2CO_3	CH_2Cl_2	2	99	85
9[d]	Cs_2CO_3	CH_2Cl_2	10	99	91
10	Cs_2CO_3	Toluene	24	49	32

[a] Isolated yields.
[b] Determined by HPLC with a Daicel Chiralcel OD column, hexane/isopropanol 99:1; 0.5 mL/min; 254 nm.
[c] Reaction carried out using **1** as ligand.
[d] Reaction was carried out at 0 °C.

We examined the effect of another base/solvent system and results are depicted in Table 2. Changing the base from NaH to *N*,*O*-bis(trimethylsilyl)acetamide (BSA) and the solvent from THF to dichloromethane, a decrease in the ee was observed (entries 2 and 3). Another change to a more polar solvent, acetonitrile, and to the apolar toluene, did not result in any improvement (see entries 4 and 5). When using acetonitrile the ee of the product did not change significantly. With toluene, however, the enantioselectivity decreased to 66% ee.

On the other hand, employing cesium carbonate as base and performing the reaction in dichloromethane, the reaction proceeded smoothly and the product was isolated in 85% of enantiomeric excess and full conversion after only 2 h at room temperature (entry 8). The use of these conditions gave the same ee of product **9** when compared to the NaH/THF system; however, the reaction goes to completion in much reduced reaction time. On decreasing the temperature to 0 °C, the reaction took 10 h to completion and, to our delight the ee of **9** increased to 91% (entry 9). Again, reducing the polarity of the solvent proved to negatively influence the reaction outcome, since a dramatic drop in the ee was observed when toluene was used instead of dichloromethane (compare entries 9 and 10).

In order to propose a plausible explanation of the stereoselectivity observed, a schematic reaction pathway is shown in Scheme 4.[25]



Scheme 4. Plausible reaction pathways for the asymmetric allylic alkylation.

Taking into analogy the previous work of Anderson where he proposes that the attack of the nucleophile occurs trans to a nitrogen donor,[11b] which is the contrary of that expected for a nitrogen–sulfur chelate complex, we assumed that our system behaves in a similar way, that is, the nucleophile attacks preferentially at the allylic position trans to the Pd–N bond in the π-allylpalladium complex.

Since (*R*)-**9** is the major product of the alkylation reaction of racemic 1,3-diphenyl-2-propenyl acetate with dimethyl malonate, the reaction appears to proceed preferentially via the intermediate (**A**) in the equilibrium depicted in Scheme 4.

The steric repulsion in the intermediate (**A**) between a phenyl terminus of the allylic substrate arranged in a 'W' orientation and the selenophenyl group seems to be smaller than the repulsion of the phenyl ring attached to the 2-position of the oxazoline ring and the phenyl moiety in structure (**B**), which is disposed in a 'M' orientation.

These disfavoring steric interactions, which are present in intermediate (**B**) would lead to a predominance of the intermediate (**A**) in the equilibrium and explain the stereoselectivity observed in favor of (*R*)-**9** (Scheme 4).

3. Conclusions

In summary, we have described herein a new class of chiral selenium-containing oxazoline chiral ligands, which were prepared in a concise and flexible synthetic route in good yields. This flexibility permits the preparation of a wide range of compounds with varied steric and electronic combination of substituents. This feature confers to this

class of compounds a modular character allowing the synthesis of small libraries of new chiral selenium compounds.

Additionally, these compounds were systematically screened as chiral ligands in the asymmetric palladium-catalyzed allylic alkylation of racemic 1,3-diphenyl-2-propenyl acetate with dimethyl malonate. We were able to identify among the set of ligands prepared, a catalyst that can effectively promote the allylic alkylation reaction in high ee. This approach demonstrates the importance of the easy access to modification in the structure of the chiral ligand in order to readily identify an efficient ligand for a given catalytic setup through a correct combination of structural and electronic properties of the catalyst and refinement of reaction conditions.

We also believe that this modular approach, which permits ready access of a range of new chiral selenium compounds, may have significant importance in the design of new Se, N-ligand systems for application in asymmetric catalysis.

4. Experimental

4.1. General procedures

Melting Points are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded at 400 and 100 MHz, respectively, with tetramethylsilane as internal standard. High-resolution mass spectra were recorded on a Bruker BioApex 70e FT-ICR (Bruker Daltonics, Billerica, USA) instrument in ESI-mode. Column chromatography was performed using Merck Silica Gel (230–400 mesh) following the methods described by Still.[26] Thin-layer chromatography (TLC) was performed using Merck Silica Gel GF_{254}, 0.25 mm thickness. For visualization, TLC plates were either placed under ultraviolet light, or stained with iodine vapor, or acidic vanillin. THF was dried over sodium benzophenone ketyl and distilled prior to use. Dichloromethane and acetonitrile were distilled from phosphorus pentoxide. All other solvents were used as purchased unless otherwise noted. Racemic 1,3-diphenyl-3-acetoxyprop-1-ene was prepared according to literature procedure.[27] Compounds **3**,[21] **6** and **7**[7c] were prepared by the procedures described in the cited references.

4.1.1. (*R*)-(2-phenyl-4,5-dihydrooxazol-4-yl)methanol 4.[28] Under an argon atmosphere, sodium borohydride (0.760 g, 20 mmol) was added, at 0 °C, to a solution of oxazolinyl ester **3** (1.025 g, 5 mmol) in dry ethanol (20 mL). The reaction was then stirred for 12 h under reflux and after this time, cooled to room temperature, diluted with CH_2Cl_2 (30 mL) and washed with saturated $NaCl_{(aq)}$ (20 mL). The organic layer was dried with $MgSO_4$, filtered and the solvent removed under vacuum. Alcohol **4** was used without further purification. Yield 87%; $[\alpha]_D^{20}$ +35 (*c* 0.42, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz): δ=7.81–7.79 (m, 2H), 7.43–7.26 (m, 3H), 4.44–4.30 (m, 3H), 3.93 (dd, J^1=11.6 Hz, J^2=4.0 Hz, 1H), 3.63 (dd, J^1=11.6 Hz, J^2=4 Hz, 1H), 2.89 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ=165.45, 131.38, 128.24, 128.14, 126.95, 69.17, 68.00, 63.60; HRMS *m/z* calcd for $C_{10}H_{11}O_2N+Na^+$ 200.0682, found 200.0683.

4.1.2. (*S*)-(2-phenyl-4,5-dihydrooxazol-4-yl)methyl 4-methylbenzenesulfonate 5.[29] Under an argon atmosphere, TsCl (0.420 g, 2.2 mmol) was added in one portion, at 0 °C, to a solution of alcohol **4** (0.354 g, 2 mmol) in dichloromethane (5 mL) and Et_3N (0.6 mL, 4 mmol) in the presence of a catalytic amount of DMAP (25 mg, 10 mol%). The mixture was then stirred for 24 h at room temperature diluted with CH_2Cl_2 (30 mL) and washed with saturated $NaCl_{(aq)}$ (20 mL). The organic layer was dried with $MgSO_4$, filtered and the solvent evaporated. The crude product was purified by flash chromatography eluting with a mixture of hexanes–ethyl acetate (80/20). Yield: 77%; $[\alpha]_D^{24}$ +56.6 (*c* 1.0, EtOH); ^{1}H NMR ($CDCl_3$, 400 MHz): δ=7.86–7.79 (m, 2H), 7.77–7.69 (m, 2H), 7.49–7.20 (m, 5H), 4.55–4.38 (m, 2H), 4.33–4.19 (m, 2H), 4.05–3.96 (m, 1H), 2.39 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ=166.0, 145.0, 132.5, 131.8, 129.9, 128.4, 128.3, 128.0, 127.0, 70.8, 69.8, 65.1, 21.7.

4.1.3. (*S*)-2-(2-phenyl-4,5-dihydrooxazol-4-yl)ethyl 4-methylbenzenesulfonate 8.[7c] Under an argon atmosphere, TsCl (2.88 g, 15 mmol) was added in one portion to a solution of diol **7** (1.045 g, 5 mmol) in dichloromethane (50 mL) and Et_3N (4.2 mL, 30 mmol) at 0 °C. The mixture was then stirred for 24 h and slowly warmed to 25 °C. The reaction mixture was diluted with CH_2Cl_2 (50 mL) and washed with 1 M $HCl_{(aq)}$ (20 mL), saturated $NaHCO_{3(aq)}$ (20 mL) and saturated $NaCl_{(aq)}$ (20 mL). The organic layer was dried with $MgSO_4$, filtered, and concentrated. The crude product was purified by flash chromatography eluting with a mixture of hexanes–ethyl acetate (70/30). Yield: 75%; $[\alpha]_D^{24}$ −59 (*c* 2.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz): δ=7.86 (d, J=8.4 Hz, 2H), 7.79 (d, J=8.4 Hz, 2H), 7.46–7.30 (m, 5H), 4.48–4.44 (m, 1H), 4.35–4.23 (m, 3H), 4.04–4.00 (m, 1H), 2.42 (s, 3H), 2.03–1.97 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ=164.01, 144.75, 132.76, 131.37, 129.78, 128.29, 128.22, 128.15, 127.83, 72.28, 67.88, 63.34, 34.98, 21.54.

4.1.4. (*S*)-2-(2-*tert*-butyl-phenyl-4,5-dihydrooxazol-4-yl) ethyl 4-methylbenzenesulfonate 10. This compound was prepared in the same method used for **8**, starting from (*S*)-2-*tert*-butyl-benzoylamino-1,4-butanediol (0.795 g, 3 mmol). Yield 55%; $[\alpha]_D^{20}$ −56 (*c* 0.6, CH_2Cl_2); ^{1}H NMR ($CDCl_3$, 400 MHz): δ=7.80 (d, J=8.4 Hz, 4H), 7.40 (d, J=8.4 Hz, 2H), 7.31 (d, J=8.4 Hz, 2H), 4.47–4.42 (m, 1H), 4.33–4.23 (m, 3H), 4.03–3.99 (m, 1H), 2.42 (s, 3H), 2.01–1.96 (m, 2H), 1.30 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ=164.11, 154.91, 144.67, 133.02, 129.78, 128.05, 127.85, 125.19, 124.60, 72.22, 67.91, 63.36, 35.07, 34.87, 31.08, 21.52; HRMS *m/z* calcd for $C_{22}H_{27}O_4NS+H^+$ 402.1729, found 402.1733.

4.1.5. (*S*)-2-(2-*tert*-butyl-4,5-dihydrooxazol-4-yl)ethyl 4-methylbenzenesulfonate 11.[30] This compound was prepared in the same method used for **8**, starting from (*S*)-2-trimethyl-acetylamino-1,4-butanediol (0.567 g, 3 mmol). Yield 62%; $[\alpha]_D^{20}$ −54 (*c* 0.6, CH_2Cl_2); ^{1}H NMR ($CDCl_3$, 400 MHz): δ=7.78 (d, J=8.4 Hz, 2H), 7.34 (d, J=8.4 Hz, 2H), 4.26–4.07 (m, 4H), 3.85–3.81 (m, 1H), 2.44 (s, 3H), 1.89–1.86 (m, 2H), 1.16 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ=174.32, 144.62, 132.44, 129.75, 128.74,

71.94, 67.72, 62.69, 34.89, 32.93, 27.17, 21.39; HRMS *m/z* calcd for $C_{16}H_{24}O_4NS+H^+$ 326.1416, found 326.1420.

4.2. General procedure for the synthesis of ligands 1 and 2

Under an argon atmosphere, sodium borohydride was added to a solution of the diorganoil diselenide (0.55 mmol) in THF (4 mL). Ethanol (2 mL) was then dropwise added and the clear solution formed was stirred at room temperature for 10 min. After this time a THF (1 mL) solution of the appropriate oxazolinyl tosylate (1 mmol) was added dropwise. After stirring for 24 h at room temperature, the reaction mixture was quenched with aqueous saturated NH_4Cl (10 mL) and extracted with CH_2Cl_2 (3×15 mL). The combined organic layers were dried with $MgSO_4$, filtered, and concentrated. The crude product was purified by flash chromatography first eluting with hexanes and then with a mixture of hexanes–ethyl acetate (80/20).

4.2.1. (*S*)-2-phenyl-4-(phenylselanylmethyl)-4,5-dihydrooxazole 1. Yield: 91%; $[\alpha]_D^{20}$ −15 (*c* 0.5, CH_2Cl_2); ^1H NMR ($CDCl_3$, 400 MHz): δ=7.90 (d, *J*=7.2 Hz, 2H), 7.56–7.53 (m, 8H), 4.53–4.46 (m, 2H), 4.25–4.22 (m, 1H), 3.42–3.38 (m, 1H), 2.95–2.89 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ=164.66, 133.02, 131.47, 129.15, 128.29, 128.29, 128.27, 127.48, 127.28, 72.53, 66.58, 32.73; HRMS *m/z* calcd for $C_{16}H_{15}ONSe+H^+$ 318.0392, found 318.0391.

4.2.2. (*S*)-2-phenyl-4-(2-(phenylselanyl)ethyl)-4,5-dihydrooxazole 2a. Yield: 97%; $[\alpha]_D^{20}$ −57 (*c* 0.55, CH_2Cl_2); ^1H NMR ($CDCl_3$, 400 MHz): δ=7.93 (d, *J*=7.16 Hz, 2H), 7.52–7.37 (m, 5H), 7.26–7.20 (m, 3H), 4.48–4.37 (m, 2H), 4.02–3.98 (m, 1H), 3.14–2.99 (m, 2H), 2.10–2.01 (m, 1H), 2.00–1.94 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ=165.88, 132.48, 131.24, 130.04, 129.14, 128.21, 128.17, 127.99, 126.74, 72.12, 66.46, 36.45, 24.04; HRMS *m/z* calcd for $C_{17}H_{17}ONSe+Na^+$ 354.0366, found 354.0367.

4.2.3. (*S*)-4-(2-(benzylselanyl)ethyl)-2-phenyl-4,5-dihydrooxazole 2b. Yield: 87%; $[\alpha]_D^{20}$ −58 (*c* 0.5, CH_2Cl_2); ^1H NMR ($CDCl_3$, 400 MHz): δ=7.93 (d, *J*=7.2 Hz, 2H), 7.45–7.36 (m, 3H), 7.29–7.17 (m, 5H), 4.42–4.38 (m, 1H), 4.33–4.29 (m, 1H), 3.96–3.92 (m, 1H), 3.78 (s, 2H), 2.62–2.59 (m, 2H), 2.04–1.95 (m, 1H), 1.90–1.81 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ=163.33, 139.07, 131.02, 128.59, 128.19, 128.01, 127.91, 127.50, 126.39, 71.87, 66.30, 36.38, 26.79, 19.56; HRMS *m/z* calcd for $C_{18}H_{19}ONSe+Na^+$ 368.0563, found 368.0526.

4.2.4. (S)-4-(2-(4-chlorophenylselanyl)ethyl)-2-phenyl-4,5-dihydrooxazole 2c. Yield: 90%; $[\alpha]_D^{20}$ −48 (*c* 0.55, CH_2Cl_2); ^1H NMR ($CDCl_3$, 400 MHz): δ=7.93 (d, *J*=7.2 Hz, 2H), 7.47–7.40 (m, 5H), 7.22 (d, *J*=8.4 Hz, 2H), 4.50–4.45 (m, 1H), 4.40–3.37 (m, 1H), 4.02–3.98 (m, 1H), 3.11–3.01 (m, 2H), 2.05–1.95 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ=163.73, 133.76, 132.93, 131.27, 129.11, 128.23, 128.21, 128.15, 127.56, 72.06, 66.36, 36.36, 24.08; HRMS *m/z* calcd for $C_{17}H_{16}ONSeCl+H^+$ 366.0154, found 366.0163.

4.2.5. (S)-4-(2-(4-methoxyphenylselanyl)ethyl)-2-phenyl-4,5-dihydrooxazole 2d. Yield: 91%; $[\alpha]_D^{20}$ −48 (*c* 0.55, CH_2Cl_2); ^1H NMR ($CDCl_3$, 400 MHz): δ=7.92 (d, *J*=7.2 Hz, 2H), 7.49–7.39 (m, 5H), 6.81 (d, *J*=8.8 Hz, 2H), 4.47–4.35 (m, 2H), 4.00–3.96 (m, 1H), 3.78 (s, 3H), 3.02–2.91 (m, 2H), 2.07–1.99 (m, 1H), 1.96–1.89 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ=163.60, 159.21, 135.47, 131.19, 128.17, 128.13, 127.64, 119.60, 114.71, 72.09, 66.44, 55.12, 36.47, 25.10; HRMS *m/z* calcd for $C_{18}H_{19}O_2NSe+H^+$ 362.0648, found 362.0653.

4.2.6. (S)-4-(2-(mesitylselanyl)ethyl)-2-phenyl-4,5-dihydrooxazole 2e. Yield: 88%; $[\alpha]_D^{20}$ −35 (*c* 0.5, CH_2Cl_2); ^1H NMR ($CDCl_3$, 400 MHz): δ=7.91 (d, *J*=8.0 Hz, 2H), 7.47–7.36 (m, 3H), 6.91 (s, 2H), 4.46–4.44 (m, 1H), 4.36–4.32 (m, 1H), 3.99–3.95 (m, 1H), 2.82–2.77 (m, 2H), 2.53 (s, 6H), 2.25 (s, 3H), 1.98–1.86 (s, 1H), 1.84–1.83 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ=163.54, 142.95, 137.91, 131.15, 128.40, 128.37, 128.34, 127.65, 127.31, 72.04, 66.69, 36.65, 24.42, 24.62, 20.80; HRMS *m/z* calcd for $C_{20}H_{23}ONSe+H^+$ 374.1011, found 374.1017.

4.2.7. (*S*)-2-phenyl-4-(2-(3-(trifluoromethyl)phenylselanyl)-ethyl)-4,5-dihydrooxazole 2f. Yield: 80%; $[\alpha]_D^{20}$ −59 (*c* 0.5, CH_2Cl_2); ^1H NMR ($CDCl_3$, 400 MHz): δ=7.93 (d, *J*=7.2 Hz, 2H), 7.74 (s, 1H), 7.46 (d, *J*=7.2 Hz, 1H), 7.42–7.35 (m, 5H), 4.51–4.49 (m, 1H), 4.47–4.41 (m, 1H), 4.03–4.00 (m, 1H), 3.19–3.16 (m, 1H), 3.13–3.11 (m, 1H), 2.05–1.99 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ=163.89, 135.17, 131.59, 131.34, 131.32 (q, *J*=32.1 Hz), 129.26, 128.55, 128.51, 128.26, 128.22, 127.58, 123.43 (q, *J*=3.8 Hz), 72.11, 66.36, 36.37, 23.92; HRMS *m/z* calcd for $C_{18}H_{16}ONSe+H^+$ 400.0442, found 400.0421.

4.2.8. (*S*)-4-(2-(*tert*-butylselanyl)ethyl)-2-phenyl-4,5-dihydrooxazole 2g. Yield: 77%; $[\alpha]_D^{20}$ −75 (*c* 0.5, CH_2Cl_2); ^1H NMR ($CDCl_3$, 400 MHz): δ=7.94 (d, *J*=7.12 Hz, 2H), 7.47–7.38 (m, 3H), 4.53–4.49 (m, 1H), 4.39–4.36 (m, 1H), 4.07–4.03 (m, 1H), 2.79–2.71 (m, 2H), 2.08–2.04 (m, 1H), 1.97–1.94 (m, 1H), 1.46 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ=163.63, 131.19, 128.20, 128.19, 127.74, 72.25, 66.95, 38.86, 37.09, 32.46, 17.91; HRMS *m/z* calcd for $C_{15}H_{21}ONSe+Na^+$ 334.0672, found 334.0680.

4.2.9. (*S*)-4-(2-(methylselanyl)ethyl)-2-phenyl-4,5-dihydrooxazole 2h. Yield: 79%; $[\alpha]_D^{20}$ −82 (*c* 0.55, CH_2Cl_2); ^1H NMR ($CDCl_3$, 400 MHz): δ=7.94 (d, *J*=7.2 Hz, 2H), 7.47–7.38 (m, 3H), 4.53–4.49 (m, 1H), 4.42–4.38 (m, 1H), 4.07–4.03 (m, 1H), 2.72–2.67 (m, 2H), 2.07–1.95 (m, 5H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ=163.68, 131.24, 128.22, 128.18, 127.69, 72.18, 66.52, 36.42, 21.20, 4.05; HRMS *m/z* calcd for $C_{12}H_{15}ONSe+H^+$ 270.0386, found 270.0397.

4.2.10. (S)-2-(4-*tert*-butylphenyl)-4-(2-(phenylselanyl) ethyl)-4,5-dihydrooxazole 2i. Yield: 93%; $[\alpha]_D^{20}$ −51 (*c* 0.55, CH_2Cl_2); ^1H NMR ($CDCl_3$, 400 MHz): δ=7.85 (d, *J*=8.4 Hz, 2H), 7.50 (d, *J*=7.2 Hz, 2H), 7.41 (d, *J*=8.4 Hz, 2H), 7.26–7.23 (m, 3H), 4.47–4.39 (m, 2H), 4.01–3.98 (m, 1H), 3.10–3.01 (m, 2H), 2.06–2.04 (m, 1H), 1.98–1.96 (m, 1H), 1.32 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ=163.69, 154.68, 132.42, 130.08, 128.98, 127.98, 126.71, 125.17, 124.81, 71.97, 66.42, 36.48, 34.83, 31.08, 23.68; HRMS *m/z* calcd for $C_{21}H_{25}ONSe+H^+$ 388.1168, found 388.1179.

4.2.11. (S)-2-*tert*-butyl-4-(2-(phenylselanyl)ethyl)-4,5-dihydrooxazole 2j. Yield: 90%; $[\alpha]_D^{20}$ −26 (*c* 0.55, CH_2Cl_2); ^1H NMR ($CDCl_3$, 400 MHz): δ=7.48 (d, *J*= 7.6 Hz, 2H), 7.27–7.21 (m, 3H), 4.26–4.21 (m, 1H), 4.16–4.13 (m, 1H), 3.84–3.80 (m, 1H), 3.01–2.97 (m, 1H), 2.95–2.91 (m, 1H), 1.94–1.88 (m, 2H), 1.20 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ=174.11, 132.29, 130.16, 129.00, 126.70, 71.90, 65.85, 36.53, 33.13, 27.78, 23.33; HRMS *m/z* calcd for $C_{15}H_{21}ONSe+H^+$312.0869, found 312.0866.

4.3. General procedure for the asymmetric allylic alkylation with NaH/THF

A THF (1 mL) solution of $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ (10 mg, 2.5 mol%), catalyst (10 mol%) was stirred for 30 min under an argon atmosphere and then 1,3-diphenyl-2-propenyl acetate (252 mg, 1.0 mmol) was added. The mixture was stirred for 10 min and a solution of sodium dimethyl malonate, prepared from dimethyl malonate (264 mg, 2.0 mmol) and sodium hydride (36 mg, 1.5 mmol) in THF (3 mL), was added at room temperature. The reaction mixture was then stirred for 24 h at room temperature. After this time, saturated $NH_4Cl_{(aq)}$ was added and the aqueous solution was extracted with CH_2Cl_2 (3× 15 mL). The combined organic layers were dried with $MgSO_4$, the solvent was evaporated and the crude product was purified by flash chromatography eluting with hexane–ethyl acetate (98/2). Enantiomeric excess was determined by chiral HPLC (Chiralcel OD column, 0.5 mL/min, hexane/2-propanol 99:1, 254 nm). The optical rotation of the product was compared with literature data to assign the absolute configuration (*R*).

4.4. General procedure for the asymmetric allylic alkylation with Cs_2CO_3/CH_2Cl_2

A solution of $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ (10 mg, 2.5 mol%), catalyst (10 mol%) in dichloromethane (2.5 mL) was stirred for 1 h under an argon atmosphere, at room temperature, and then cooled to 0 °C, when 1,3-diphenyl-2-propenyl acetate (126 mg, 0.5 mmol) was added. The mixture was stirred for 10 min at this temperature and dimethyl malonate (173 mg, 1.5 mmol), and cesium carbonate (489 mg, 1.5 mmol) were sequentially added. The reaction mixture was then stirred for 10 h at 0 °C. After this time, saturated $NH_4Cl_{(aq)}$ was added and the aqueous solution was extracted with CH_2Cl_2 (3×15 mL). The combined organic layers were dried with $MgSO_4$, the solvent was evaporated and the crude product was purified by flash chromatography eluting with hexane–ethyl acetate (98/2). Enantiomeric excess was determined by chiral HPLC (Chiralcel OD column, 0.5 mL/min, hexane/2-propanol 99:1, 254 nm). The optical rotation of the product was compared with literature data to assign the absolute configuration (*R*).

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