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Synthesis and Catalytic Application of Chiral 1,1′-Bi-2-naphthol- and Biphenanthrol-Based Pincer Complexes: Selective Allylation of Sulfonimines with Allyl Stannane and Allyl Trifluoroborate

Juhanes Aydin, K. Senthil Kumar, Mahmoud J. Sayah, Olov A. Wallner, and Kálmán J. Szabó*

Department of Organic Chemistry, Arrhenius Laboratory, Stockholm University, SE-106 91, Stockholm, Sweden

kalman@organ.su.se

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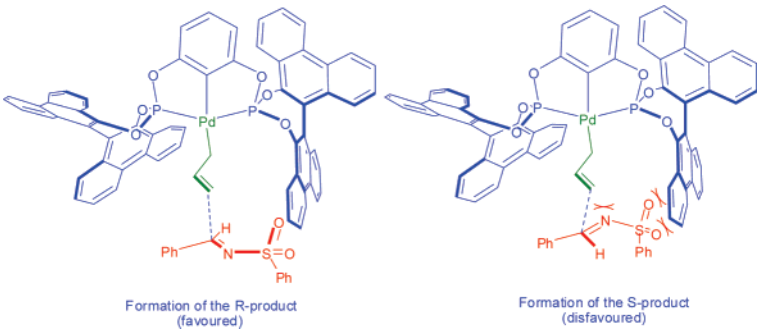

New easily accessible 1,1′-bi-2-naphthol- (BINOL-) and biphenanthrol-based chiral pincer complex catalysts were prepared for selective (up to 85% enantiomeric excess) allylation of sulfonimines. The chiral pincer complexes were prepared by a flexible modular approach allowing an efficient tuning of the selectivity of the catalysts. By employment of the different enantiomeric forms of the catalysts, both enantiomers of the homoallylic amines could be selectively obtained. Both allyl stannanes and allyl trifluoroborates can be employed as allyl sources in the reactions. The biphenanthrol-based complexes gave higher selectivity than the substituted BINOL-based analogues, probably because of the well-shaped chiral pocket generated by employment of the biphenanthrol complexes. The enantioselective allylation of sulfonimines presented in this study has important implications for the mechanism given for the pincer complex-catalyzed allylation reactions, confirming that this process takes place without involvement of palladium(0) species.

1. Introduction

Development of catalytic asymmetric allylation reactions is a challenging task in organic synthesis, as in these processes the stereogenic carbon is created via enantioselective carbon−carbon or carbon−heteroatom bond formation.[1−3] Palladium catalysis offers a versatile tool for enantioselective introduction of the allylic moiety into nucleophilic[1,3,4] and electrophilic[5−7] substrates. Although asymmetric allylic alkylation of nucleophiles is a very useful and well-established method,[1,3,4] application of electrophiles,[5−11] including aldehydes[8−10] and imines,[5−7] has received considerable current attention. Development of new methods for selective allylation of imines is particularly important, as these substrates are more difficult to allylate than aldehydes, and therefore relatively few efficient enantioselective

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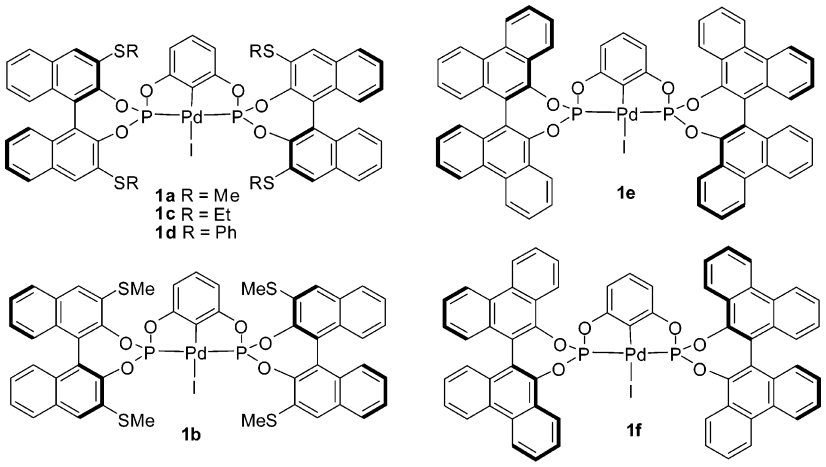

FIGURE 1. Chiral pincer complexes employed for allylation of sulfonimines.

processes are available.[12−14] As asymmetric allylation of imines leads to formation of chiral homoallyl amines, which are important motifs in bioactive natural products and pharmaceuticals,[12] a large effort has been devoted recently to devise new synthetically useful versions of these reactions.[5−7,15−21] Considering the needs of versatile chiral homoallyl amines, full control of the selectivity and possibilities for facile deprotection of the amines are important requirements in method development of the new catalytic processes.

There have been two major strategies for palladium-catalyzed enantioselective allylation of imines. Yamamoto and coworkers[5,6] employed chiral allyl−palladium complexes for the asymmetric induction. In these transformations the imine substrates could be allylated with allyl stannanes via bis(allyl)-palladium intermediates.[22−25] Although this excellent method found many applications for enantioselective synthesis of homoallyl amines, the complex reactivity of bis(allyl)palladium complexes imposes limitations on the synthetic scope of the reaction.[26−28] One problem is that allyl−allyl coupling may occur prior to the allylation of the imine electrophile,[26] which leads to allylation of the chiral allylic ligand and accordingly to loss of the chiral information. The allyl−allyl coupling is particularly dominant in the presence of high phosphine concentrations,[26,29] and therefore use of chiral phosphines as auxiliaries in allylation reactions via bis(allyl)palladium complexes is strongly limited. A further problem arises from the fact that bis(allyl)palladium complexes undergo facile isomerization processes altering the hapticity of the allyl moieties,[23,24,27,28] and therefore either allyl group can be transferred to the electrophile. For example, allylation of a chiral ligand may lead to loss of the enantioselectivity of the catalyst.

We have shown that the above side reactions can be avoided by the use of so-called "pincer complex"[30−35] catalysts.[36−38] By use of pincer complex (such as **1**) catalysis, the electrophilic allylation reactions can be carried out without formation of bis-(allyl)palladium intermediates. Furthermore, in pincer complex-catalyzed reactions, phosphine-based ligands can be used for chiral induction, which allows an efficient fine-tuning of the selectivity of the catalyst. In consideration of these features, the second strategy for palladium-catalyzed asymmetric allylation of imines is based on application of chiral pincer complexes (such as **1**) with allylstannanes (**2**) as reagents (cf. eq 1).[7] In a previous publication,[7] we have shown that 1,1′-bi-2-naphthol- (BINOL-) based chiral pincer complexes are potentially useful catalysts for allylation of sulfonimines. Unfortunately, the synthetically easily accessible pincer complexes gave poor enantioselectivity (20% ee), while the synthesis of more selective (up to 59% ee) catalysts could be only be achieved with poor yield (18%). We have now found that the enantioselectivity of the allylation can be considerably enhanced by application of thioalkyl/aryl substituents (**1a**−**d**) in the γ-position of the BINOL ligands or employment of biphenanthrol-based complexes (**1e,f**). We were also able to prepare both enantiomers of the thiomethyl- (**1a,b**) and biphenanthrol-based complexes (**1e,f**) to study the possibilities for full control of the enantioselectivity in the allylation processes (Figure 1).

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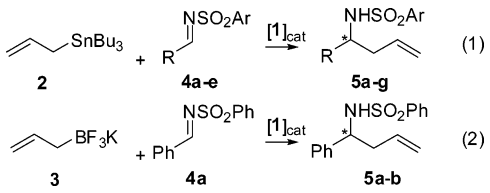
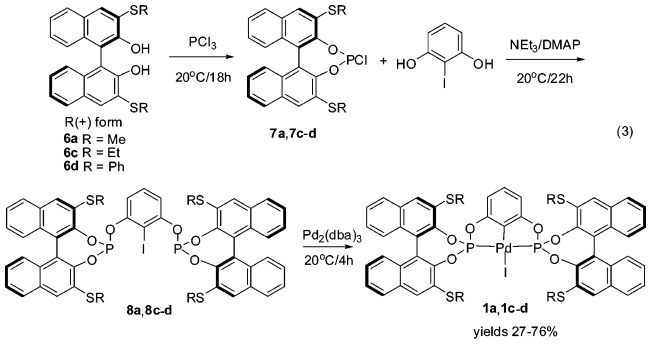
Furthermore, we employed allyl trifluoroborate (**3**) as an alternative allyl source to allyl stannanes in the substitution reactions. Our studies are focused on allylation of sulfonimines, as these reactions afford homoallylic sulfonamines, which can easily be deprotected, affording homoallyl amines. Exploration of palladium-catalyzed asymmetric allylation of sulfonimines is particularly important, as these species cannot be selectively allylated via chiral bis(allyl)palladium complexes.[6]

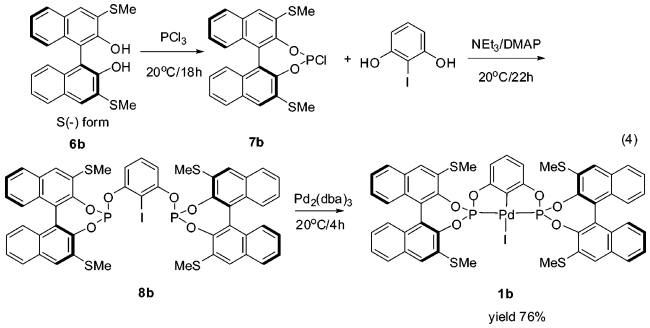


2. Results and Discussion

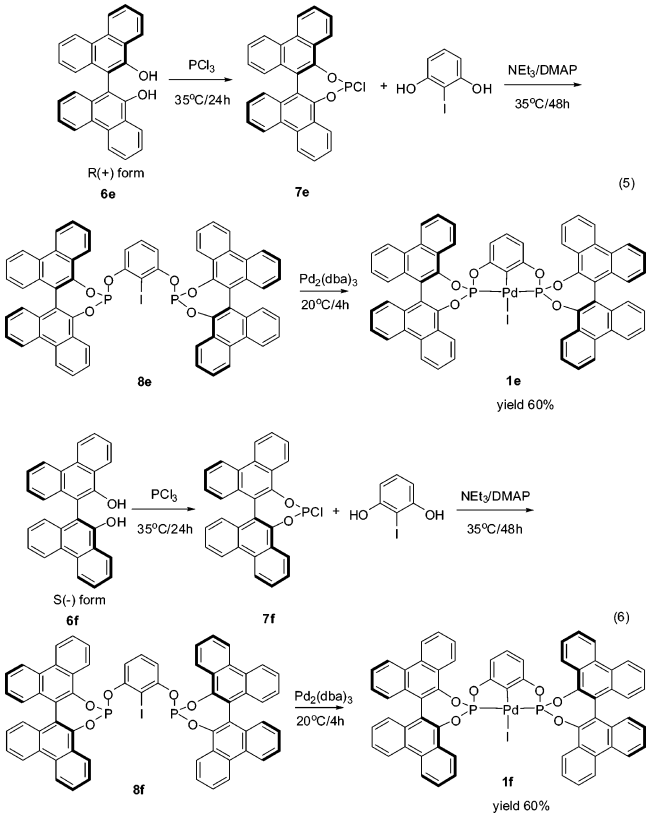
Synthesis of Chiral Pincer Complexes 1a−f. Complexes **1a−f** could be obtained by a flexible modular approach (eqs 3−6) starting from optically pure BINOL (**6a−d**) or biphenanthrol derivatives (**6e,f**). In the first step **6a−f** are converted to the corresponding phosphochloridates **7a−f**, which were coupled with iodoresorcinol to obtain proligands **8a−f**. These proligands are usually very sensitive to hydrolysis, and therefore their purification is difficult. For example, purification by column chromatography leads to extensive loss of the proligands. However, we have found that the crude product of **8** could be metalated under mild conditions (20 °C, 4 h) with $Pd_2(dba)_3$ via facile oxidative addition of the carbon−iodine bond to palladium(0). The obtained yields are usually high (60−76%) except for the synthesis of ethyl sulfide **1c** (27%). The mild reaction conditions (20−35 °C/4 h) ensure that the BINOL moieties do not undergo racemization in the applied procedure. In our experience, raising the reaction temperature over 60 °C in any of the reaction steps leads to a certain degree of racemization, decreasing the optical purity of pincer complex **1**.



The above procedure is based on our previously published[7] (web online August 2005) synthetic strategy devised for the first preparation of BINOL-based chiral pincer complexes (analogues of **1a−d**). It should be mentioned that, independently from us, Bedford and co-workers[39] have developed a similar synthetic scheme for synthesis of the parent BINOL-based complex using resorcinol instead of iodoresorcinol for coupling with the phosphochloridate component (such as **7**). This strategy requires that the palladation step be carried out by carbon−hydrogen bond activation instead of the above-described oxidative addition (**8** → **1**). As this carbon−hydrogen bond activation applied by Bedford and co-workers[39] requires harsh conditions (150 °C/$\mu\nu$, 1 h, or 83 °C/6 days) in the final step of the synthesis of the chiral pincer complexes, we employed our own strategy allowing the synthesis of **1a−f** under mild conditions.



As it appears from eqs 3−6, synthesis of the chiral pincer complexes by the above sequence is flexible and highly modular. Thus, starting from *R*-BINOL derivative[40,41] **6a** (eq 3), chiral pincer complex **1a** was obtained ($[\alpha]_D = -544°$), while its enantiomer **1b** ($[\alpha]_D = +542°$) can be prepared from *S*-BINOL derivative[40] **6b** (eq 4). Similarly, both enantiomers **1e** ($[\alpha]_D = -588°$) and **1f** ($[\alpha]_D = +586°$) can be prepared from optically pure biphenanthrol derivatives **6e** (*R*-form) and **6f** (*S*-form), respectively (eqs 5 and 6) by slight modification of the reaction conditions applied for preparation of **1a−d**. Accordingly, by use of the above procedure a great variety of chiral pincer complexes can be prepared by choosing the appropriate BINOL or biphenanthrol derivatives.



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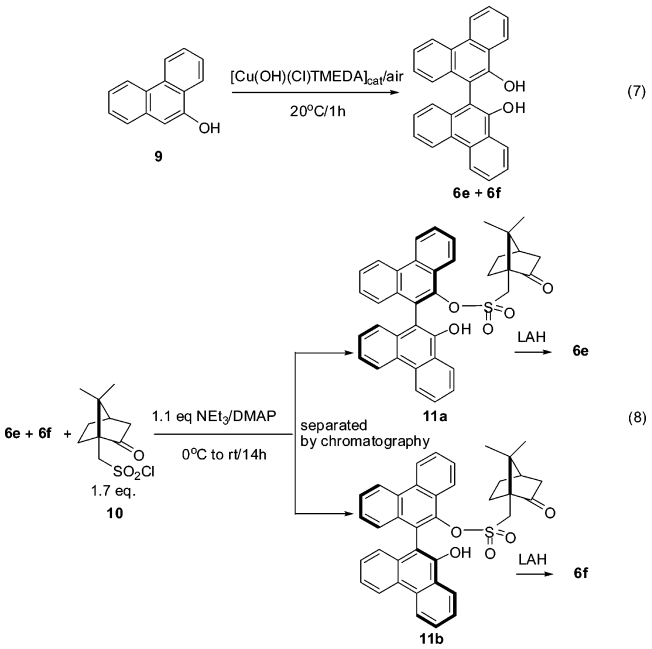
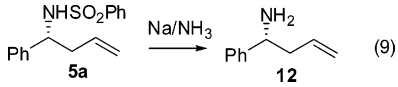
The optically pure thioalkyl/aryl BINOL derivatives **6a**−**d** could be obtained by the procedure of Woodward and Snieckus and their co-workers.[40,41] Although there are literature procedures available for resolvation of bisphenanthrol,[42] in our hands these procedures were not suitable for preparation of **6e** and **6f** in sufficiently high optical purity and amounts required for synthesis of **1e** and **1f**. Therefore, we devised a new method for resolvation of bisphenanthrol. The racemic biphenanthrol was obtained from **9** by a slightly modified procedure of Hashimoto and co-workers (eq 7).[43] The racemic mixture of **6e** and **6f** was reacted with 1.7 equiv of (1*S*)-(+)-10-camphorsulfonyl chloride (**10**) in the presence of 1.1 equiv of NEt_3 to give diastereomeric monoesters **11a** and **11b** (eq 8). These monoesters could easily be separated by silica chromatography in high yields (43% for each diastereomer). Optically pure **6e** and **6f** were obtained from **11a** and **11b** by reduction with lithium aluminum hydride. Hydrolysis with a strong base (such as NaOH) could not be used for deprotection of **11a,b** because of substantial racemization of the products. Diesters of **6e** and **6f** may also be obtained by use of an excess of **10** and NEt_3; however, these diesters could not be efficiently separated by chromatography or crystallization.



Catalytic Allylation of Sulfonimines with Chiral Pincer Complexes. The allylation reactions with allylstannane **2** and benzenesulfonyl imine **4a** could be carried out under mild conditions (6−20 °C) in dry DMF or DMSO without additives (eq 1, Table 1). Application of *R*-BINOL-based thiomethyl catalyst (5 mol %) **1a** in DMF provided encouraging levels of enantioselectivity, affording homoallyl amine **5a** with 73% ee (Table 1, entry 1). The yield of this reaction (49%) could be improved by use of DMSO as solvent (57%); however the enantioselectivity in this reaction (entry 2) is slightly decreased (71%). The reaction product (**5a**) was reduced with sodium in ammonia, providing (1*R*)-1-phenyl-3-butenylamine[44,45] (**12**) in 67% yield (without racemization), showing that the major enantiomer, **5a**, has the *R* configuration (eq 9). The allylation reaction was also carried out with the *S*-BINOL analogue of **1a** (**1b**). The major product (74% ee) of this reaction was the *S*-enantiomer **5b** (entry 3). As the availability of *R*- and *S*-BINOL precursors for preparation (see above) of **1a** and **1b** are similar, the enantioselectivity of the presented reaction can be fully controlled by the choice of the appropriate pincer complex catalyst. The allylstannane reagent (**2**) could be successfully replaced (eq 2) with potassium trifluoro(allyl)borate (**3**),[46] which reacted readily[38,47] with **4a**, providing homoallyl amine **5a** or **5b** in good yield (eq 2), however, with somewhat lower enantioselectivity than **2** (Table 1, entries 6 and 7). Similarly to allylstannane (**2**), the reaction of **3** catalyzed with *R*-BINOL derivative **1a** gave predominantly *R*-product **5a**, while with *S*-BINOL derivative **1b** the main product had *S*-configuration (**5b**).

We have also studied the effects of the bulkiness of the R substituent in **1** on the selectivity of the allylation process. It was found that as one goes from methyl substituent (**1a**) to ethyl substituent (**1c**) the enantioselectivity is slightly decreased (cf. Table 1, entries 1 and 4), while thiophenyl derivative **1d** proved to be a relatively unselective catalyst (48% ee; entry 5). This trend suggests that the enantioselectivity of **1a** cannot be simply increased by replacement of the thiomethyl functionality with more bulky substituents. We have also attempted the enantioselective allylation of a bulky sulfonimine **4b** (entry 8); however, this reaction proceeds much more slowly and with lower selectivity (48% ee) than the corresponding process with **4a**.



Cinnamyl derivative **4c** displayed high reactivity in the allylation reaction, providing the corresponding allyl amine derivative with 59% ee. The reactivity of the imine component can also be increased by nitro substitution of the aromatic ring. Accordingly, **4d** could be allylated with high yield (85%) and only slightly lower selectivity (66% ee) than **4a**.

As indicated above, the enantioselectivity (71−74% ee) obtained by **1a** and **1b** cannot be improved by simple increase of the steric bulk of the thio alkyl substituent. On the basis of our DFT modeling studies[47] for pincer complex-catalyzed allylation of sulfonimines, we reasoned that substitution of the δ-position or simultaneous substitution of both the γ- and δ-positions of the BINOL system would increase the selectivity of the allylation reaction. In this respect, replacement of the BINOL units with biphenanthrol moieties (such as in **1e,f**) appeared to be an attractive approach. Indeed, we have found that the enantioselectivity of the allylation reaction can be increased up to 85% ee by employment of biphenanthrol

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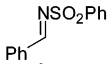
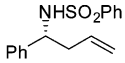
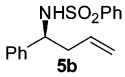
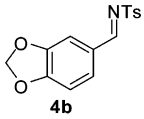
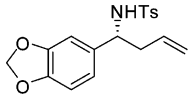
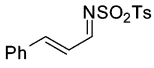
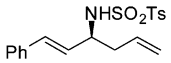
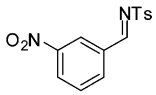
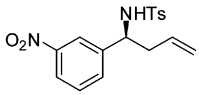
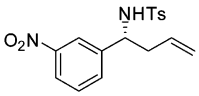
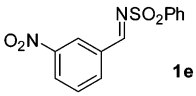
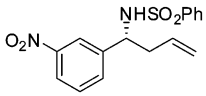
TABLE 1. Allylation of Sulfonimines in the Presence of Chiral Pincer Complexes 1a−f[a]

Entry	Allyl	Imine	Cat.	Temp./time[b]	Solvent	Product	ee[%]	Yield[c]
1	**2**	 **4a**	**1a**	6/66	DMF	 **5a**	73	49
2	**2**	**4a**	**1a**	20/94	DMSO	**5a**	71	57
3	**2**	**4a**	**1b**	20/94	DMSO	 **5b**	74	53
4	**2**	**4a**	**1c**	20/94	DMSO	**5a**	67	44
5	**2**	**4a**	**1d**	20/94	DMF	**5a**	48	70
6	**3**	**4a**	**1a**	20/96	DMSO	**5a**	60	66
7	**3**	**4a**	**1b**	20/96	DMSO	**5b**	54	68
8	**2**	 **4b**	**1a**	20/116	DMF/THF[e]	 **5c**	48	55
9	**2**	 **4c**	**1b**	6/66	DMF	 **5d**	59	53
10	**2**	 **4d**	**1b**	20/68	DMF	 **5e**	66	85
11	**2**	**4d**	**1e**	20/94	DMF	 **5f**	85	71
12	**2**	 **4e**	**1e**	20/68	DMF	 **5g**	82	78
13	**2**	**4a**	**1f**	20/91	DMF	**5b**	83	28
14	**2**	**4a**	**1f**[d]	20/91	DMF	**5b**	80	50

[a] In a typical reaction, 5 mol % catalyst **1 was employed.** [b] Reaction temperature in degrees Celsius; time in hours. [c] Isolated yield. [d] 10 mol % catalyst was employed. [e] A 1:1 mixture of DMF/THF was employed.

complexes **1e,f**. Accordingly, nitro-substituted imine **4d** reacted (Table 1, entry 11) with **2** in the presence of 5 mol % **1e** in high yield (71%) and selectivity (85% ee). The yield could be increased by using phenylsulfonyl derivative **4e**, affording **5g** (78%) at the cost of a slight decrease in selectivity (82% ee). The parent sulfonimine **4a** also reacted with about as high selectivity as **4d**. Thus, the allylation reaction with **2** in the presence of **1f** provided **5b** with 83% ee (entry 13). Similarly to the thiomethyl complexes, the *R*-biphenanthrol-based complex **1e** provides the homoallylamine products (**5f,g**) with *R*-selectivity, while **1f**, containing *S*-biphenanthrol moieties, induces *S*-configuration at the stereogenic carbon of the product **5b**. On the other hand, the higher selectivity of **1e,f** is accompanied by lower catalytic activity than BINOL derivatives **1a,b**. This is reflected (cf. entries 3 and 13) by the relatively low yield obtained for allylation of **4a** with **1f** (28%) compared to **1b** (53%). The yield can be improved either by increasing the catalyst loading to 10 mol % (entry 14) or by employment of activated sulfonimines, such as **4d** and **4e** (entries 11 and 12).

3. Mechanistic Aspects

Model for Mechanism of Enantioselection. The above experimental results (Table 1) clearly show that, by use of **2** or **3** as reagents, the *R*-BINOL-based catalyst (**1a**) provides mainly *R*-homoallylamine **5a**, while changing the configuration of the BINOL ligand (**1b**) leads to reversal of the enantioselectivity, resulting in *S*-homoallylamine **5b**. Although the exact mechanism of the enantioselection is not perfectly understood yet, on the basis of previous DFT studies[47] on the (achiral) pincer complex-catalyzed allylation of sulfonimines, at least a qualitative model can be constructed.

According to this model (Figure 2), the electrophilic carbon of sulfonimine **4a** interacts with the γ-position of the η^1-allyl moiety. Formation of the *R*-form **5a** is supposed to proceed via TS as shown in panel a, in which the sulfonimine functionality points away from the *R*-BINOL-based complex. On the other hand, in the TS structure for formation of the *S*-enantiomer **5b**, the sulfonimine group points in the opposite direction, experiencing repulsive steric interactions with the thiomethyl group

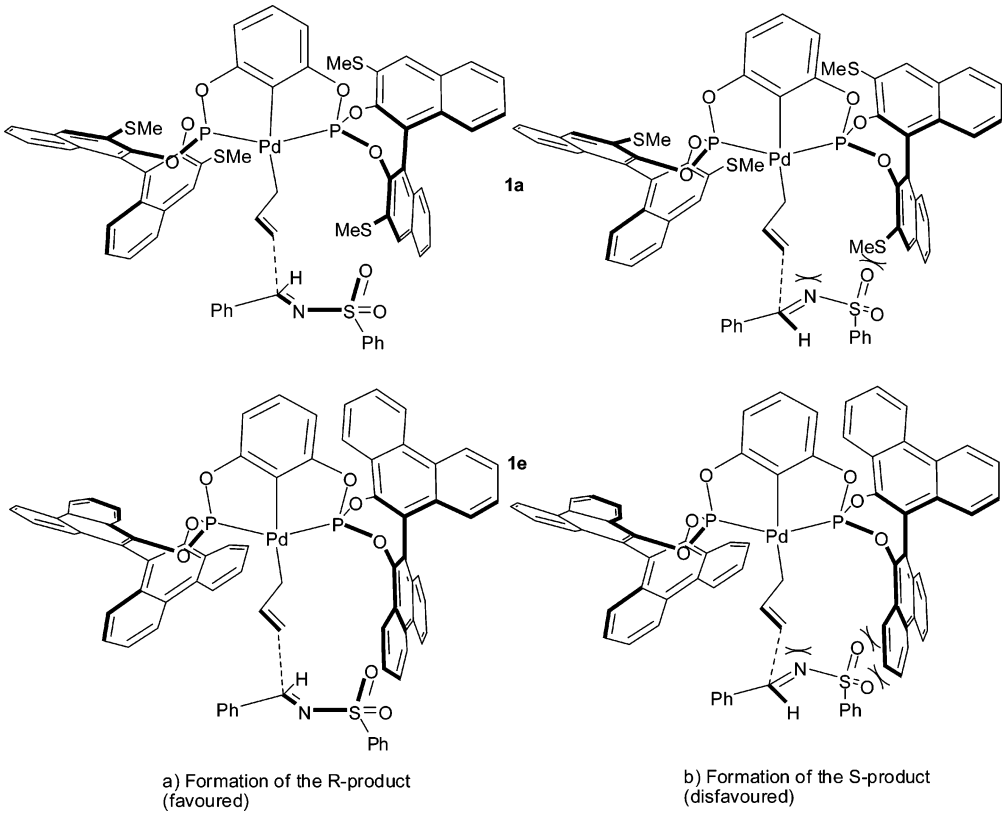
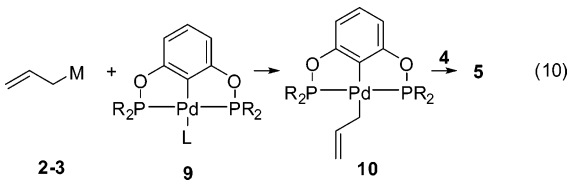


FIGURE 2. Supposed mechanism of the enantioselection in allylation of sulfonimine **4a** with *R*-BINOL-based catalyst **1a** and biphenanthrol derivative **1e**. (a) formation of **5a**; (b) formation of **5b**.

of the binaphthyl ligands. This interaction is thermodynamically destabilizing, and therefore formation of the *S*-form **5b** is disfavored. Replacement of the BINOL moieties with biphenanthrol units is expected to increase the selectivity of the catalyst by increasing the destabilizing interactions with the sulfonimine functionality in the type of TS structures shown in panel b.

Implications of This Study for the Mechanism of Pincer Complex-Catalyzed Allylations. The present study further confirms the mechanistic description given for the pincer complex-catalyzed allylation reactions (eq 10).[36,37,48] According to this mechanism, the applied pincer complex (**9**) undergoes transmetalation with the employed allylmetal reagent to give η^1-allyl palladium complex **10**. Because of the η^1-coordination of the allyl moiety and the electron-supplying feature of the pincer ligand, complex **10** is able to efficiently allylate electrophiles (such as **5a** and **5b**) under catalytic conditions. We have shown that complex **10** can be generated from pincer complex **9** (R = Ph[49]) and allyl stannane **2**[37] or allyl boronate **3**.[47] According to this mechanistic picture, the palladium atom does not undergo redox reactions under the catalytic transformation, and the enantioselectivity of the process is determined by the reaction of the η^1-allyl moiety of **10** with the electrophilic substrate. Considering the enantioselectivity (up to 85%) achieved in the above study, a possible palladium(0)-catalyzed process can be ruled out. Recently, it was shown[50,51] that catalytically active palladium(0) can be generated from pincer complexes; however, this process involves decomposition of the pincer complex, which for the presented transformations (eqs 1 and 2) would involve a complete loss of the enantioselectivity of the catalyst. On the contrary, complexes **1a**−**f** displayed excellent stability under the allylation reactions, and the unchanged catalyst could be detected in the final reaction mixture of the process. This high stability suggests that highly durable, easily recyclable catalysts may be obtained by immobilization of **1a**−**f**.



(10)

4. Conclusions

Easily accessible chiral BINOL- and biphenanthrol-based pincer complexes readily catalyze the allylation of sulfonimines up to 85% ee. So far, this is the highest enantioselectivity achieved in pincer complex-catalyzed allylation reactions[39,52,53] and also in palladium-catalyzed[6] allylation of sulfonimines. Both allyl stannanes and allyl trifluoroborates can be employed as allyl sources in these processes. The enantioselectivity of the transformation can be reversed by changing the configuration of the BINOL or biphenanthrol ligands, and thus full control

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of the enantioselectivity can be achieved. The enantioselection is assumed to take place in the TS of the electrophilic attack of the η^1-allyl moiety coordinated to the chiral complex. The chiral cavity of the biphenanthrol-based complex is better shaped than that of the BINOL-based complexes, leading to higher selectivity in the allylation process.

5. Experimental Section

All experiments were conducted under argon atmosphere employing standard manifold techniques. All solvents used in the reactions were freshly distilled prior to use. NMR spectra were recorded in $CDCl_3$ on Varian or Bruker spectrometers with ^1H at 300 or 400 MHz and ^{13}C at 75.4 or 100.5 MHz with $CDCl_3$ ($\delta[^1H] = 7.26$, $\delta[^{13}C] = 77.0$) as internal standard. ^{31}P was recorded at 161.9 or 121.4 MHz with H_3PO_4 as external standard. HPLC chromatograms were obtained by use of Acquity Ultra Performance LC and Daicel Chiracel OD-H or AD-H columns with the parameters given in each description. Optical rotations were measured at 20 °C. Mass spectrometry data were obtained with a Bruker MicrOTOF spectrometer (ESI) and a Bruker Biflex III instrument (MALDI-TOF) with 2′,4′,6′-trihydroxyacetophenone (THAP) as matrix. For column chromatography, Merck silica gel 60 (230−400 mesh) was used.

Synthesis of Racemic 10-(10-Hydroxy-1,4-dihydro-9-phenanthrenyl)-5,8-dihydro-9-phenanthrenol (6e and 6f). A slightly modified procedure by Hashimoto and co-workers[43] was applied. In an open beaker (300 mL), freshly purified 5,8-dihydro-9-phenanthrenol **9** (0.32 g, 1.65 mmol) was dissolved in CH_2Cl_2 (11 mL). To this solution CuCl(OH)·TMEDA (0.0038 g, 0.0165 mmol) was added and this reaction mixture was stirred for 10 min. Thereafter, another portion of CuCl(OH)·TMEDA (0.0038 g, 0.0165 mmol) was added and the stirring was continued for a further 50 min. Then the reaction mixture was filtered through a thin pad of silica, which was washed with CH_2Cl_2. The solvent was removed and the crude product was purified by column chromatography with pentane/EtOAc 10:1 as eluent to obtain a racemic mixture of **6e** and **6f** in 88% yield. ^1H NMR (400 MHz, $CDCl_3$) δ 8.82 (d, J = 8.5 Hz, 2H), 8.76 (d, J = 8.5 Hz, 2H), 8.48 (d, J = 8.5 Hz, 2H), 7.83 (t, J = 7.6 Hz, 2H), 7.74 (t, J = 7.6 Hz, 2H), 7.55 (t, J = 7.6 Hz, 2H), 7.37 (t, J = 7.6 Hz, 2H), 7.28 (d, J = 8.5 Hz, 2H), 5.58 (s, 2H). ^{13}C NMR (100.5 MHz, $CDCl_3$) δ 149.4, 132, 131.7, 128.2, 127.7, 127.1, 126.9, 125.1, 124.9, 124.8, 123.5, 122.9, 122.7, 107.1. HRMS *m*/*z* 387.1373 (calcd $[M + H]^+$ for $C_{28}H_{19}O_2$ 387.1380).

Synthesis of Mono[(1*S*)-camphor-10-sulfonates] of 10-(10-Hydroxy-1,4-dihydro-9-phenanthrenyl)-5,8-dihydro-9-phenanthrenol (11a and 11b). Racemic biphenanthrol (**6e** and **6f**) (0.145 g, 0.38 mmol), (1*S*)-(+)-10-camphorsulfonyl chloride **10** (0.116 g, 0.46 mmol), and DMAP (0.007 g, 0.057 mmol) were dissolved in CH_2Cl_2 (6 mL). Then freshly distilled triethylamine (0.006 mL, 0.42 mmol) was added dropwise at 0 °C in 10 min. The resultingsolution was stirred first at 0 °C for 1 h and then at rt for 14 h. Thereafter, another portion of (1*S*)-(+)-10-camphorsulfonyl chloride (0.050 g, 0.2 mmol) in CH_2Cl_2 (1 mL) was added and the stirring continued for an additional hour. Subsequently, water (2 mL) was added and the aqueous layer was extracted with CH_2Cl_2 (3 × 2 mL) and the collected organic layers were washed with water (2 × 5 mL). The CH_2Cl_2 solution was dried and evaporated and the residue was purified by column chromatography with pure CH_2Cl_2 to separate the diastereomeric mixture, yielding 43% yield of each diastereomer **11a** and **11b**. Spectral data for **11a**: ^1H NMR (400 MHz, $CDCl_3$) δ 8.82 (m, 3H), 8.73 (d, J = 8 Hz, 1H), 8.6 (d, J = 8 Hz, 1H), 8.55 (d, J = 8 Hz, 1H), 7.82 (m, 3H), 7.71 (m, 2H), 7.53 (m, 2H), 7.42 (t, J = 8 Hz, 1H), 7.36 (t, J = 8 Hz, 1H), 7.26 (d, J = 8 Hz, 1H), 5.81 (s, 1H), 2.72 (d, J = 14.9 Hz, 1H), 2.14 (m, 2H), 1.75 (m, 4H), 1.4 (m, 1H), 1.18 (m, 1H), 0.36 (s, 3H), 0.15 (s, 3H). ^{13}C NMR (100.5 MHz, $CDCl_3$) δ 212.8, 148.3, 145.4, 132.1, 131.6, 130.9, 129.9, 128.4, 128, 127.9, 127.8, 127.6, 127.4, 127.1, 126.9, 126.6, 125.7, 125.3, 124.8, 124.4, 123.9, 123, 122.96, 122.7, 122.65, 122.5, 111.5, 57.6, 50.1, 47.2, 42.9, 42.1, 26.5, 25.5, 18.6, 18.5. HRMS *m*/*z* 623.1862 (calcd $[M + Na]^+$ for $C_{38}H_{32}NaSO_5$ 323.1863). Spectral data for **11b**: ^1H NMR (400 MHz, $CDCl_3$) δ 8.83 (q, J = 8 Hz, 3H), 8.74 (d, J = 8 Hz, 1H), 8.63 (d, J = 8 Hz, 1H), 8.53 (d, J = 8 Hz, 1H), 7.82 (m, 3H), 7.7 (t, J = 7.5 Hz, 2H), 7.56 (m, 2H), 7.43 (m 3H), 7.31 (d, J = 8.4 Hz, 1H), 5.71 (s, 1H), 2.93 (d, J = 14.8 Hz, 1H), 2.05 (m, 2H), 1.79 (m, 4H), 1.46 (dddd, J = 4.6 Hz, 1H), 1.24 (m, 1H), 0.35 (s, 3H), 0.09 (s, 3H). ^{13}C NMR (100.5 MHz, $CDCl_3$) δ 213, 148.1, 145.3, 132.1, 131.7, 131.4, 130.6, 129.9, 128.5, 128.1, 127.95, 127.9, 127.7, 127.5, 126.8, 126.4, 125.3, 124.9, 124.5, 123.9, 123.1, 122.9, 122.7, 122.63, 122.6, 111.6, 57.2, 49.1, 47.2, 42.5, 42.1, 26.6, 24.8, 18.4, 18.3. HRMS *m*/*z* 623.1863 (calcd $[M + Na]^+$ for $C_{38}H_{32}NaO_5S$ 323.1863).

(+)-10-(10-Hydroxy-1,4-dihydro-9-phenanthrenyl)-5,8-dihydro-9-phenanthrenol (6e). To lithium aluminum hydride (0.16 g, 4.2 mmol) in THF (2 mL) was added monoester **11a** (0.51 g, 0.848 mmol) in THF (4 mL) dropwise at 0 °C in 30 min. Then this reaction mixture was stirred for 19 h at 60 °C. Thereafter, water (0.16 mL), 15% aqueous NaOH (0.16 mL), and once again water (0.48 mL) were added in this order.[54] Then ether (5 mL) was added, and the precipitate was filtered and washed with ether (5 mL). To the ether phase was added water (2 mL), and the pH of the mixture was adjusted to about 6 by HCl (1 M) at 0 °C. Subsequently, the ether phase was separated and the water phase was extracted with ether (2 × 10 mL). The organic phases were collected, and after evaporation the crude product was purified by chromatography (pentane/EtOAc, 20:1) affording 90% yield with 99.5% ee. The ^1H NMR and ^{13}C NMR data are in accordance with the above-described values obtained for racemic biphenanthrol (**6e** and **6f**). $[\alpha]_D = +68°$ (c = 0.16, THF). HPLC (OD-H, hexane/*i*-PrOH 65:35, flow rate 0.8 mL/min) minor enantiomer t_R = 12.24 min, major enantiomer t_R = 15.60 min.

(−)-10-(10-Hydroxy-1,4-dihydro-9-phenanthrenyl)-5,8-dihydro-9-phenanthrenol (6f). The above procedure with monoester **11b** afforded **6f** in 90% yield with 99.5% ee. The ^1H NMR and ^{13}C NMR data are in accordance with the above-described values obtained for racemic biphenanthrol (**6e** and **6f**). $[\alpha]_D = -68°$ (c = 0.16, THF).[42] HPLC (OD-H, hexane/*i*-PrOH 65:35, flow rate 0.8 mL/min) major enantiomer t_R = 12.24 min, minor enantiomer t_R = 15.60 min.

General Procedure for Synthesis of BINOL-Based Complexes 1a-f. The corresponding BINOL derivative (**6a**−**f**) (0.528 mmol, azeotropically dried with toluene) was stirred in freshly distilled PCl_3 (1.11 mL, 12.7 mmol) at 20 °C for 18 h. Then the excess PCl_3 was distilled under atmospheric pressure, and even traces of PCl_3 were removed by coevaporation with 2 × 3 mL toluene, affording a yellow oil of **7a**−**f**. The crude oil was dissolved in toluene (5.0 mL), and then this solution was added to a mixture of iodoresorcinol (0.062 g, 0.264 mmol) and DMAP (0.008 mg, 0.066 mmol) in toluene (1.0 mL). Subsequently, NEt_3 (0.073 mL, 0.528 mmol) was added dropwise to this solution and the reaction mixture was stirred for 22 h at 20 °C. Thereafter, the obtained suspension was filtered through a thin pad of Celite, washed with toluene (70 mL) and concentrated to give proligand **8a**−**f**. Thereafter, **8a**−**f** was dissolved in toluene (5.0 mL) and this solution was added to $Pd_2(dba)_3$ (0.088 g, 0.096 mmol) in toluene (1.0 mL). This reaction mixture was stirred for 4 h at 20 °C. The crude reaction mixture was thereafter subjected to silica gel chromatography with CH_2Cl_2/pentane 2:1 as eluent, affording the corresponding pincer complex as a yellow solid.

Synthesis of Complexes 1a and 1b. These complexes were prepared from **6a** or **6b** by the above general procedure, yielding 0.169 g (76%) of **1a** or **1b**. Spectral data for **1a**: ^1H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, J = 8.0 Hz, 2H), 7.79 (d, J = 8.0 Hz, 2H), 7.75 (s, 2H), 7.61 (s, 2H), 7.47 (t, J = 7.6 Hz, 2H), 7.41

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(t, J = 7.6 Hz, 2H), 7.15−7.34 (m, 9H), 6.83 (d, J = 8.0 Hz, 2H), 2.62 (s, 6H), 2.50 (s, 6H). ^{13}C NMR (100.5 MHz, $CDCl_3$) δ 156.7, 156.5, 145.0, 144.97, 143.6, 133.1, 132.7, 132.3, 132.0, 131.7, 129.91, 129.85, 127.4, 127.22, 127.16, 126.9, 126.3, 126.2, 126.1, 125.6, 125.4, 125.1, 122.5, 122.4, 108.2, 108.1, 15.07, 14.99. ^{31}P NMR (121.4 MHz, $CDCl_3$) δ 150.2. MALDI-TOF MS for **1a**: ($M^+ - I^-$) 1028.043, $C_{50}H_{35}O_6P_2PdS_4$. Optical rotation data for **1a**: $[\alpha]_D = -544°$ (c = 0.67, $CHCl_3$). Spectral data for **1b**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, J = 8.0 Hz, 2H), 7.79 (d, J = 8.0 Hz, 2H), 7.76 (s, 2H), 7.60 (s, 2H), 7.48 (t, J = 7.6 Hz, 2H), 7.42 (t, J = 7.6 Hz, 2H), 7.17−7.34 (m, 9H), 6.82 (d, J = 8.0 Hz, 2H), 2.63 (s, 6H), 2.50 (s, 6H). ^{13}C NMR (100.5 MHz, $CDCl_3$) δ 156.6, 156.5, 156.4, 145.0, 143.6, 133.1, 132.7, 132.3, 132.0, 131.7, 129.91, 129.85, 127.4, 127.22, 127.16, 126.9, 126.3, 126.2, 126.1, 125.6, 125.4, 125.1, 122.5, 122.4, 108.2, 108.1, 108.0, 15.07, 14.99. ^{31}P NMR (161.9 MHz, $CDCl_3$) δ 150.2. MALDI-TOF MS for **1b**: ($M^+ - I^-$) 1028.112, $C_{50}H_{35}O_6P_2PdS_4$. Optical rotation data for **1b**: $[\alpha]_D = +542°$ (c = 0.59, $CHCl_3$).

Synthesis of Complex 1c. This complex was prepared from **6c** by the above general procedure, yielding 63 mg (27%) of **1c**. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.84−7.93 (m, 4H), 7.79 (d, J = 8.0 Hz, 2H), 7.72 (s, 2H), 7.37−7.54 (m, 4H), 7.14−7.36 (m, 9H), 6.81 (d, J = 8.0 Hz, 2H), 2.93−3.24 (m, 8H), 1.42 (t, J = 7.3 Hz, 6H), 1.34 (t, J = 7.3 Hz, 6H). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 156.9 156.7, 145.7, 144.0, 132.3, 132.2, 131.9, 130.5, 130.3, 130.0, 129.9, 128.1, 127.8, 127.6, 127.3, 127.0, 126.3, 126.1, 125.9, 125.5, 122.9, 122.8, 108.0, 26.7, 26.5, 13.9, 13.5. ^{31}P NMR (121.4 MHz, $CDCl_3$) δ 150.6. MALDI-TOF MS for **1c**: ($M^+ - I^-$) 1084.059, $C_{54}H_{43}O_6P_2PdS_4$. Optical rotation data for **1c**: $[\alpha]_D = -517°$ (c = 0.87, $CHCl_3$).

Synthesis of Complex 1d. This complex was prepared from **6d** by the above general procedure, yielding 0.167 g (62%) of **1d**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, J = 8.3 Hz, 4H), 7.58−7.64 (m, 8H), 7.52 (br d, J = 7.0 Hz, 4H), 7.29−7.45 (m, 15H), 7.15−7.25 (m, 10H), 6.76 (d, J = 8.0 Hz, 2H). ^{13}C NMR (100.5 MHz, $CDCl_3$) δ 156.6, 156.4, 156.3, 145.3, 144.3, 133.8, 133.6, 132.6, 132.22, 132.16, 131.9, 131.5, 131.1, 131.0, 130.7, 130.6, 130.1, 130.0, 129.6, 129.2, 128.4, 128.1, 127.9, 127.6, 127.2, 127.1, 126.2, 126.1, 123.1, 122.9, 108.2, 108.1, 108.0. ^{31}P NMR (161.9 MHz, $CDCl_3$) δ 151.0. MALDI-TOF MS for **1d**: ($M^+ - I^-$) 1276.042, $C_{70}H_{43}O_6P_2PdS_4$. Optical rotation data for **1d**: $[\alpha]_D = -342°$ (c = 1.08, $CHCl_3$).

Synthesis of Complexes 1e and 1f. These complexes were prepared from **6e** or **6f** by the above general procedure except that the first (**6e,f** → **7e,f**) and the second (**7e,f** → **8e,f**) steps were run for 24 and 48 h, respectively, at 35 °C, yielding 60% **1e** or **1f**. These complexes were purified by using CH_2Cl_2/pentane (1:1) as eluent. Spectral data for **1e**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.82 (m, 4H), 8.69 (m, 4H), 8.44 (m, 2H), 8.26 (d, J = 8.2 Hz, 2H), 7.82 (t, J = 7.5 Hz, 2H), 7.65 (m, 10H), 7.34 (m, 9H), 6.66 (d, J = 7.9 Hz, 2H). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 156.4, 156.3, 156.1, 144.6, 144.3, 131.9, 131.7, 130.65, 130.5, 129.3, 129.1, 128.3, 127.5, 127.4, 126.8, 126.7, 126.5, 126.2, 124.1, 123.1, 123.04, 123.0, 122.7, 122.5, 120.8, 119.95, 108.4, 108.3, 108.2. ^{31}P NMR (121.4 MHz, $CDCl_3$) δ 153.3. MALDI-TOF MS for **1e**: ($M^+ - I^-$) 1043.194, $C_{62}H_{35}O_6P_2Pd$. Optical rotation data for **1e**: $[\alpha]_D = +586°$ (c = 0.91, $CHCl_3$). Spectral data for **1f**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.82 (m, 4H), 8.69 (m, 4H), 8.44 (m, 2H), 8.26 (d, J = 8.2 Hz, 2H), 7.82 (t, J = 7.5 Hz, 2H), 7.66 (m, 8H), 7.58 (t, J = 7.5 Hz, 2H), 7.45 (d, J = 8.2 Hz, 2H), 7.41 (d, J = 8.2 Hz, 2H), 7.28 (m, 5H), 6.66 (d, J = 7.9 Hz, 2H). ^{13}C NMR (100.5 MHz, $CDCl_3$) δ 156.4, 156.3, 156.2, 144.6, 144.3, 131.9, 131.7, 130.7, 130.5, 129.3, 129.1, 128.3, 127.5, 127.4, 126.8, 126.7, 126.5, 126.2, 124.1, 123.1, 123.04, 123.0, 122.7, 122.5, 120.8, 119.9, 108.4, 108.3, 108.2. ^{31}P NMR (161.9 MHz, $CDCl_3$) δ 153.4. MALDI-TOF MS for **1f**: ($M^+ - I^-$) 1043.333, $C_{62}H_{35}O_6P_2Pd$. Optical rotation data for **1f**: $[\alpha]_D = -588°$ (c = 0.55, $CHCl_3$).

General Procedure for Palladium Pincer Complex-Catalyzed Allylation of Imines 4a−e. Tributylallylstannane 2 (0.062 mL, 0.20 mmol) or potassium trifluoroallylborate **3** (0.0296 g, 0.20 mmol) was added to a mixture of sulfonimine **4a−e** (0.10 mmol) and the corresponding catalyst **1a−f** (0.005 mmol, 5.0 mol %) in 1.0 mL of solvent. The reaction mixture was then stirred for the allotted times and temperatures (Table 1). The crude product was purified by silica gel chromatography (pentane/ethyl acetate 9:2) affording the corresponding homoallylic amine **5a−g**. The enantiomeric excess was determined by chiral-phase HPLC (Daicel Chiracel OD-H and AD-H columns).

***N*1-(1-Phenyl-3-butenyl)-1-benzenesulfonamide (5a).** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, J = 7.7 Hz, 2H), 7.45 (t, J = 7.7 Hz, 1H), 7.33 (t, J = 7.7 Hz, 2H), 7.15 (m, 3H), 7.06 (m, 2H) 5.52 (m, 1H), 5.06 (br d, J = 12.9 Hz, 3H), 4.42 (q, J = 6.9 Hz, 1H), 2.47 (br s, 2H). ^{13}C NMR (100.5 MHz, $CDCl_3$) δ 140.4, 140.1, 133.0, 132.3, 128.7, 128.4, 127.4, 127.1, 126.5, 119.3, 57.2, 41.9. HRMS m/z 310.0875 (calcd [M + Na]$^+$ for $C_{16}H_{17}NaNO_2S$ 310.0872). $[\alpha]_D = +47°$ (c = 0.27, $CHCl_3$) corresponding to 73% ee. The enantiomeric excess of **5a** was determined by chiral-phase HPLC (Daicel Chiracel OD-H, hexane/*i*PrOH 95:5, flow rate 1.0 mL/min): major enantiomer t_r = 13.1 min, minor enantiomer t_r = 18.0 min.

***N*1-(1-Phenyl-3-butenyl)-1-benzenesulfonamide (5b).** The above general procedure was employed except that **2** was added slowly (in 24 h) to the reaction mixture, when **1f** was employed as catalyst (Table 1, entries 13 and 14). The NMR and HRMS data are identical to those for **5a**. $[\alpha]_D = -52°$ (c = 0.21, $CHCl_3$) corresponding to 83% ee. The enantiomeric excess of **5b** was determined by chiral-phase HPLC (Daicel Chiracel OD-H, hexane/*i*PrOH 95:5, flow rate 1.0 mL/min): minor enantiomer t_r = 13.1 min, major enantiomer t_r = 18.0 min.

***N*1-[1-(1,3-Benzodioxol-5-yl)-3-butenyl]-4-methyl-1-benzenesulfonamide (5c).** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, J = 8.1 Hz, 2H), 7.16 (d, J = 8.1 Hz, 2H), 6.56 (m, 3H), 5.87 (dd, J = 1.3 and 9.5 Hz, 2H), 5.51 (m, 1H) 5.03 (m, 3H), 4.27 (q, J = 6.7 Hz, 1H), 2.43 (m, 5H). ^{13}C NMR (100.5 MHz, $CDCl_3$) δ 147.6, 146.8, 143.0, 137.5, 134.3, 133.1, 129.2, 127.2, 120.2, 119.2, 107.9, 106.9, 101.0, 57.0, 41.8, 21.4. HRMS m/z 386.0928 (calcd [M + Na]$^+$ for $C_{18}H_{19}NaNO_4S$ 368.0927). $[\alpha]_D = +29°$ (c = 0.16, $CHCl_3$) corresponding to 48% ee. The enantiomeric excess of **5c** was determined by chiral-phase HPLC (Daicel Chiracel OD-H, hexane/*i*PrOH 95:5, flow rate 1.0 mL/min): major enantiomer t_r = 24.1 min, minor enantiomer t_r = 31.7 min.

***N*1-1-[(*E*)-2-Phenyl-1-ethenyl]-3-butenyl-4-methyl-1-benzenesulfonamide (5d).** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, J = 8.0 Hz, 2H), 7.24 (m, 5H), 7.14 (d, J = 8.0 Hz, 2H), 6.3 (d, J = 15.9 Hz, 1H), 5.81 (dd, J = 7.0 Hz, 1H), 5.65 (m, 1H), 5.1 (m, 2H), 4.62 (d, J = 7.2 Hz, 1H), 4.04 (m, 1H), 2.33 (br s, 5 H). ^{13}C NMR (100.5 MHz, $CDCl_3$) δ 143.3, 138.0, 136.2, 132.7, 131.6, 129.5, 128.4, 128.3, 127.7, 127.3, 126.4, 119.5, 55.1, 40.2, 21.4. HRMS m/z 350.1181 (calcd [M + Na]$^+$ for $C_{19}H_{21}NaNO_2S$ 350.1185). $[\alpha]_D = -35°$ (c = 0.26, $CHCl_3$) corresponding to 59% ee. The enantiomeric excess of **5d** was determined by chiral-phase HPLC (Daicel Chiracel OD-H, hexane/*i*PrOH 95:5, flow rate 1.0 mL/min): major enantiomer t_r = 23.9 min, minor enantiomer t_r = 26.5 min.

***N*1-[1-(3-Nitrophenyl)-3-butenyl]-4-methyl-1-benzenesulfonamide (5e).** ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, J = 7.9 Hz, 1H), 7.84 (s, 1H), 7.52 (d, J = 7.8 Hz, 3H), 7.39 (t, J = 7.9 Hz, 1H), 7.13 (d, J = 7.1 Hz, 2H), 5.5 (m, 1H), 5.1 (m, 3H), 4.49 (q, J = 6.3 Hz, 1H), 2.44 (t, J = 7 Hz, 2H), 2.35 (s, 3H). ^{13}C NMR (100.5 MHz, $CDCl_3$) δ 148.1, 143.7, 142.6, 137.0, 133.0, 131.9, 129.5, 129.3, 127.1, 122.4, 121.7, 120.6, 56.3, 41.7, 21.4. HRMS m/z 369.0871 (calcd [M + Na]$^+$ for $C_{17}H_{18}NaN_2O_4S$ 369.0879). $[\alpha]_D = -67°$ (c = 1.15, $CHCl_3$) corresponding to 66% ee. The enantiomeric excess of **5e** was determined by chiral-phase HPLC (Daicel Chiracel AD-H, hexane/*i*PrOH 95:5, flow rate 1.2 mL/min): minor enantiomer t_r = 28.7 min, major enantiomer t_r = 33.5 min.

***N*1-[1-(3-Nitrophenyl)-3-butenyl]-4-methyl-1-benzenesulfonamide (5f).** The above general procedure was employed except that

2 was added slowly (in 24 h) to the reaction mixture, when **1e** was employed as catalyst (Table 1, entry 11). The NMR and HRMS data are identical to those for **5e**. $[\alpha]_D = +97°$ ($c = 0.67$, $CHCl_3$) corresponding to 85% ee. The enantiomeric excess of **5f** was determined by chiral-phase HPLC (Daicel Chiracel AD-H, hexane/*i*PrOH 95:5, flow rate 1.2 mL/min): major enantiomer $t_r = 29.1$ min, minor enantiomer $t_r = 34.2$ min.

***N*1-[1-(3-Nitrophenyl)-3-butenyl]-1-benzenesulfonamide (5g).** The above general procedure was employed except that **2** was added slowly (in 24 h) to the reaction mixture, when **1e** was employed as catalyst (Table 1, entry 12). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, $J = 8.1$ Hz, 1H), 7.88 (s, 1H), 7.66 (d, $J = 8.1$ Hz, 2H), 7.43 (m, 5H), 5.49 (m, 1H) 5.12 (m, 3H), 4.52 (q, $J = 6.7$ Hz, 1H), 2.45 (t, $J = 6.7$ Hz, 2H). ^{13}C NMR (100.5 MHz, $CDCl_3$) δ 148.1, 142.5, 140.0, 132.9, 132.7, 131.9, 129.4, 128.9, 127.0, 122.5, 121.6, 120.6, 56.4, 41.7. HRMS *m*/*z* 355.0721 (calcd $[M + Na]^+$ for $C_{16}H_{16}NaN_2O_4S$ 355.0723). $[\alpha]_D = +88°$ ($c = 0.85$, $CHCl_3$) corresponding to 82% ee. The enantiomeric excess of **5g** was determined by chiral-phase HPLC (Daicel Chiracel AD-H, hexane/*i*PrOH 95:5, flow rate 1.2 mL/min): major enantiomer $t_r = 32.3$ min, minor enantiomer $t_r = 35.8$ min.

(1*R*)-1-Phenyl-3-butenylamine (12). Ammonia (5 mL) was condensed into a flask containing sodium (0.052 g, 2.28 mmol) at −78 °C. Subsequently, **5a** (0.077 g, 0.268 mmol, 67% ee) in THF (1.3 mL) was added, and the reaction mixture was stirred for 75 min. Thereafter, water was added in small portions until the gas evolution ceased. The crude mixture was then extracted with CH_2Cl_2 (3×10 mL) and the organic layer was dried over $MgSO_4$ and concentrated, followed by purification by silica-gel chromatography (CH_2Cl_2/MeOH 4:2), affording 0.026 g (65%) of **12** with 66% ee. The ee was determined by chiral-phase HPLC (Daicel Chiracel OD-H, hexane/*i*PrOH 95:5 with 0.1% ethanolamine as additive in *i*PrOH, flow rate 0.4 mL/min): *R* enantiomer $t_r = 16.2$ min, *S* enantiomer $t_r = 20.4$ min. The absolute configuration of **12** was assigned on the basis of literature data[44,45] available for (1*R*)-1-phenyl-3-butenylamine. $[\alpha]_D = +29°$ ($c = 0.99$, $CHCl_3$) corresponding to 66% ee. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.3 (m, 5H), 5.75 (m, 1H), 5.11 (m, 2H), 4.0 (m, 1H), 2.42 (m, 2H) 2.08 (br s, 2H). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 145.4, 135.2, 128.4, 127.0, 126.3, 117.7, 55.3, 43.9. HRMS *m*/*z* 148.1122 (calcd $[M + H]^+$ for $C_{10}H_{14}N$ 148.1121).

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Supporting Information Available: ^{1}H/^{13}C NMR spectra of the prepared homoallyl amines as well as the NMR spectra (^{1}H, ^{13}C, and ^{31}P) for chiral pincer complexes **1a**−**f**. This material is available free of charge via the Internet at http://pubs.acs.org.

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