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Enantioselective Allylation of Selected *ortho*-Substituted Benzaldehydes: A Comparative Study

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We report a systematic study of the allylation of *ortho*-substituted benzaldehydes under catalysis of a Lewis base (*N*,*N*-dioxide), a Lewis acid (Keck allylation), and a Brønsted acid. *ortho*-Halobenzaldehydes were used as the aldehydic substrates, and special attention was paid to *ortho*-vinyl and alkynyl benzaldehydes, which might serve as interesting synthons for the preparation of more complex chiral compounds. Similar enantioselectivities were achieved under catalytic conditions. In the case of *ortho*-halobenzaldehydes, Lewis base catalysis proved to be more efficient, and the highest asymmetric induction for allylation of *ortho*-fluorobenzaldehyde reached 82 % *ee*, which is comparable to other used catalytic conditions. In cases of *ortho*-vinylbenzaldehyde, the Keck allylation provided the product in 88 % *ee*. An enantioenriched homoallylic alcohol was used as the starting material for the synthesis of a sertraline intermediate.

Introduction

Secondary chiral homoallylic alcohols are important synthetic building blocks that have been conveniently used in the syntheses of various natural compounds and pharmaceutically active substances. Out of numerous examples, those of Fluoxetine,[1] goniothalamin,[2] argentinolactone,[3] diospongine,[4] epicalyxin F,[5] dodonein,[6] HMG-CoA reductase inhibitor FR901512,[7] and papulacandine D[8] can be highlighted. Although there are several possible synthetic approaches to chiral secondary homoallylic alcohols, probably the most straightforward and at the same time most flexible strategy is based on allylation of aldehydes with a suitable allylic reagent in the presence of a chiral catalytic system.[9]

Among these methods, the use of a Lewis-base-catalyzed enantioselective allylation of aldehydes constitutes a vast area for exploratory research. This methodology has evolved over the last decade into a mature synthetic procedure that is complimentary to other allylation reactions such as those based on catalysis by Lewis acids or transition metals. Out of the plethora of various Lewis base catalysts, those having the pyridine oxide activating moiety situated within a chiral environment constitute a distinct class of highly active catalysts that are capable of high asymmetric induction, usually under mild reaction conditions. Various types of *N*-oxide-based catalyst have been developed by Nakajima,[10] Hayashi,[11] Kočovský,[12] and others.[13] Our group has also developed a series of bis(tetrahydroisoquinoline) based *N*,*N*-dioxides that were suitable for highly enantioselective allylation of aryl and α,β-unsaturated aldehydes (up to 99% *ee*) with a low loading of catalyst (1 mol-%).[14]

The *N*-oxide-catalyzed enantioselective allylation has been carried out predominantly with *para*- and, to a lesser extent, *meta*-substituted benzaldehydes. Surprisingly little attention has been paid to the systematic allylation of *ortho*-substituted benzaldehydes, and only individual examples have been occasionally reported.[10a,11b,11c,12d,12e,14a,14d,14f,15–17] In this respect, it is worth noting that other studies using *S*-oxide,[18] *P*-oxide,[19] alcohols,[20] Brønsted acids,[21] Ti,[22] In,[23] Sn,[24] Cr,[25] Rh,[26] Pd,[27] Bi,[28] and Ag[29] chiral catalytic systems have also been used only superficially to address allylations of *ortho*-substituted benzaldehydes. Allylations of *ortho*-fluoro-, -chloro-, -bromo-, -iodo-, -methyl-, -methoxy, -cyano, and -nitro-benzaldehydes have been reported so far. In general, but not always, a lower asymmetric induction in comparison with the *para* and *meta*-substituted derivatives has been observed. As far as enantioselective allylation of *ortho*-alkenyl- or alkynylbenzaldehydes is concerned, to our knowledge, no systematic study has been undertaken, but allylations of such compounds under racemic conditions have been reported. These include allylation of *ortho*-vinylbenzaldehyde by using a Ag-catalyzed process[30] and allylations of *ortho*-alkynylbenzaldehydes with allylmagnesium halides.[31] A lone example of an enantioselective methallylation of a substituted *ortho*-vinylbenzaldehyde was carried out during the total synthesis of HMG-CoA reductase inhibitor FR901512.[7] Recently, while working on this project, an interesting and synthetically valuable report

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was published dealing with concomitant asymmetric allylation followed by ring-closing metathesis yielding cyclic benzo-fused homoallylic alcohols with *ee* values up to 99%.[32]

From a synthetic point of view, this lack of interest in broader screening is surprising, because chiral homoallylic alcohols bearing an *ortho*-substituted benzene ring could be valuable intermediates for the synthesis of interesting substances with high or at least reasonable asymmetric induction. One such molecule is the recently synthesized analogue[33] of spinosine A, possessing the dihydronaphthalene skeleton **1**, as a substitute for the naturally occurring substance with the tricyclo[7.3.0.0^{2,6}]dodecane framework (Figure 1). Another molecule is sertraline **2**, which is an antidepressant.[34]

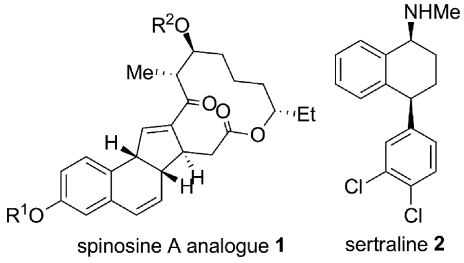
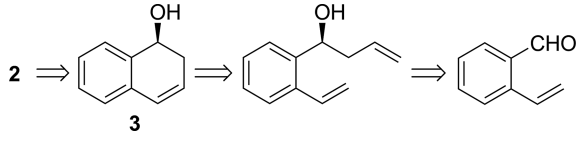


Figure 1. Spinosine A analogue **1** and sertraline **2**.

We originally envisioned that enantioselective allylation of a suitable *ortho*-substituted benzaldehyde would be a convenient method for the introduction of a stereogenic center and would provide a useful chiral intermediate that would ultimately be transformed into the desired target(s). Specifically, our goal was to synthesize the known intermediate **3** for the sertraline synthesis (Scheme 1). Retrosynthetic analysis anticipated the following steps: (a) ring-closing metathesis of the *ortho*-vinyl benzyl alcohol and (b) enantioselective allylation of *ortho*-vinyl benzaldehyde.

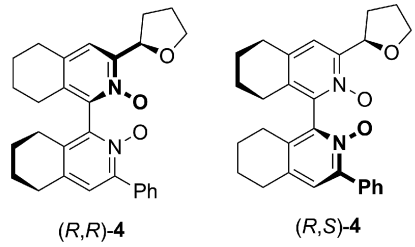


Scheme 1. Retrosynthetic analysis of sertraline **2**.

Results and Discussion

Lewis-Base-Catalyzed Enantioselective Allylations

Given that no systematic study regarding enantioselective allylation of *ortho*-substituted benzaldehydes **5** has been previously undertaken, we initially screened various substrates and reaction conditions. Two diastereoisomeric *N*,*N*′-dioxides, (*R*,*R*)-**4** and (*R*,*S*)-**4** (Figure 2), that were able to induce a high level of asymmetric induction in the allylation of *para*-substituted benzaldehydes, were chosen as catalysts.[14e]



(*R*,*R*)-**4** (*R*,*S*)-**4**

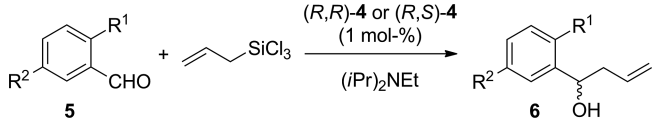
Figure 2. Catalysts (*R*,*R*)-**4** and (*R*,*S*)-**4**.

Initially, allylation of *ortho*-substituted halobenzaldehydes was carried out. Surprisingly, one of the highest asymmetric inductions was achieved in the case of *o*-fluorobenzaldehyde **5a**: 82% *ee* for (*R*,*R*)-**4** and 66% *ee* for (*R*,*S*)-**4** (Table 1, entry 1). In the case of *o*-chloro, and *o*-iodobenzaldehydes **5b** and **5d** the asymmetric induction decreased (entries 2 and 4). Strangely, *o*-bromobenzaldehyde **5c** did not react at all under any conditions (entry 3). Although speculative, the observed decrease in stereoselectivity could be explained by the increasing atomic size of the halogen atom. This assumption was supported by the allylation of *o*-trifluoromethylbenzaldehyde **5e**, which proceeded with low enantioselectivity: 4% *ee* for (*R*,*R*)-**4** and 22% *ee* for (*R*,*S*)-**4** (entry 5). Interestingly, in both cases, the same enantiomer was obtained as the major product. In the next step, enantioselective allylation of 2-iodo-4-methoxybenzaldehyde (**5f**), which is relevant for the synthesis of **3**, was studied. The allylation catalyzed by (*R*,*R*)-**4** gave **6f** in low yield (5%) and moderate asymmetric induction (56% *ee*); on the other hand, the use of (*R*,*S*)-**4** proceeded with reasonable yield (53%) and gave rather good enantioselectivity (80% *ee*; entry 6). Attempts to increase the asymmetric induction by changing the reaction conditions did not meet with success. The reaction carried out in toluene did not proceed (entry 7), and the reaction in dichloromethane proceeded with low enantioselectivity of 41% for (*R*,*R*)-**4** and 4% for (*R*,*S*)-**4** (entry 8). A change of configuration of the product upon change of solvent was reported by us previously[14b–14h] and probably indicates a different course of the reaction mechanism in each solvent.[35] It should also be added that such a phenomenon is not uncommon and has also been observed in other catalytic reactions.[36] Notably, in cases of allylations catalyzed by other *N*-oxide bases, the reactions in tetrahydrofuran (THF) either proceeded very sluggishly or it did not proceed at all.

The allylation of *ortho*-vinylbenzaldehyde (**5g**) in the presence of (*S*,*R*)-**4** proceeded with reasonable yields (40%) and moderate enantioselectivity (72 and 76% *ee*) (entry 9). Surprisingly, the reaction with 5-methoxy-2-vinylbenzaldehyde (**5h**) did not proceed and the starting material was recovered unchanged (entry 10).

Allylation of benzaldehydes **5i**–**n**, bearing alkynyl groups in the *ortho* position, in the presence of (*R*,*R*)-**4** or (*R*,*S*)-**4** proceeded with low asymmetric induction (Table 1, entries 11–16). The highest *ee* achieved with (*R*,*R*)-**4** was 42% *ee* for **5k** and with (*R*,*S*)-**4** it was 60% *ee* for **5m**. Together,

Table 1. Enantioselective allylation of *ortho*-substituted benzaldehydes with (*R*,*R*)-**4** and (*R*,*S*)-**4**.



5 6

Entry	5	R^1	R^2	6	(*R*,*R*)-**4**[a] Yield [%][b]	*er*[c]	*ee* [%][d]	(*R*,*S*)-**4**[a] Yield [%][b]	*er*[c]	*ee* [%][d]
1	**5a**	F	H	**6a**	48	9:91	82 (+)-*R*	34	83:17	66 (–)-*S*
2	**5b**	Cl	H	**6b**	75	6.5:93.5	46 (+)-*R*[e]	78	96:4	14 (–)-*S*[e]
3	**5c**	Br[f]	H	**6c**	0	–	–	0	–	–
4	**5d**	I	H	**6d**	52	42:58	16 (+)-*R*	51	75.45	30 (–)-*S*
5	**5e**	CF_3	H	**6e**	5	52:48	4 (–)-*S*	20	61.39	22 (–)-*S*
6	**5f**	I	OMe	**6f**	5	78:22	56 (+)-*R*	53	10.90	80 (–)-*S*
7[g]	**5f**	I	OMe	**6f**	0	–	–	0	–	
8[h]	**5f**	I	OMe	**6f**	70	29.5:70.5	41 (–)-*S*	40	48.52	4 (–)-*R*
9	**5g**	$CH=CH_2$	H	**6 g**	40	14:86	72 (+)-*R*[i]	40	88.12	76 (–)-*S*
10	**5h**	$CH=CH_2$	OMe	**6h**	0	–	–	0	–	–
11	**5i**	C≡CTMS	H	**6i**	57	54:46	8 (+)-*R*[j]	45	42.58	16 (–)-*S*
12	**5j**	C≡CH	OMe	**6j**	70	71:29	18 (+)-*R*[j]	10	37.63	27 (–)-*S*
13	**5k**	C≡CPh	OMe	**6k**	50	71:29	42 (+)-*R*[j]	65	25.75	50 (–)-*S*
14	**5l**	C≡C-*t*Bu	OMe	**6l**	33	46:54	8 (+)-*R*[j]	34	40.60	20 (–)-*S*
15	**5m**	C≡CTMS	OMe	**6m**	60	61:39	22 (+)-*R*[j]	73	20.80	60 (–)-*S*
16	**5n**	C≡CTBDMS	OMe	**6n**	30	59:41	18 (+)-*R*[j]	60	31.69	38 (–)-*S*
17	**5o**	H	OMe	**6o**	60	92.5:7.5	85 (+)-*R*	60	6.94	88 (–)-*S*

[a] The reactions were carried out with 1 mol-% catalyst in THF at –78 °C for 20 h, unless otherwise mentioned. [b] Isolated yield. [c] Enantiomeric ratio. The ratio numbers refer to the order of the peaks in the ^{19}F NMR spectra. [d] The assignment of the absolute configuration was based on the fact that it is known that compounds **6** having the sign of rotation '+' possess *R* configuration and those with sign '–' *S* configuration unless otherwise mentioned. [e] These results were reported previously.[14d] [f] The reaction was attempted several times with the purified reactants, but it did not proceed. [g] The reaction was carried out in toluene. [h] The reaction was carried out in dichloromethane. [i] Configuration assigned by comparison with known data.[7,32] [j] The tentative assignment of configuration was based on the results from the TRIP-PA catalyzed reactions (see the Supporting Information).

these results indicate that it is not possible to sensibly rationalize the influence of the substituent on the triple bond on asymmetric induction.

The results described above indicated that that the use of (*R*,*S*)-**4** catalysts in allylation reactions proceeded, in general, with higher asymmetric induction than those with (*R*,*R*)-**4**. This phenomenon has also been observed in previous cases;[14d,14e,14g] however, exceptions have also been observed.[14d,14g] A possible, albeit speculative, explanation could be rationalized in terms of a conformationally and thermodynamically more favorable and more rigid transition state in which the chiral information is transferred from the ligand into the product.

Lewis-Acid-Catalyzed Enantioselective Allylations

Lewis-acid-catalyzed allylation is associated mainly with the Keck protocol. The method is based on the reaction of allyltributylstannane with carbonyl compounds catalyzed by chiral titanium species prepared in situ from Ti(O-*i*Pr)$_4$ and binol. This procedure usually furnished the corresponding homoallylic alcohols in high yields and enantioselectivities.[37]

Given that, to our knowledge, there are no reports on enantioselective allylation of *ortho*-substituted benzaldehydes, we screened various Keck allylation protocols (Conditions A, B, and C) to find the best conditions for high asymmetric induction. Aldehydes **5f**–**g**, and **5m**, which could be used as building blocks for the synthesis of structurally more complex compounds, were chosen as model compounds. It should be noted that the reaction rates were very slow in all cases and the reactions had to be carried out for at least seven days to achieve reasonable conversion and to obtain the corresponding homoallylic alcohols **6** in sensible isolated yields.

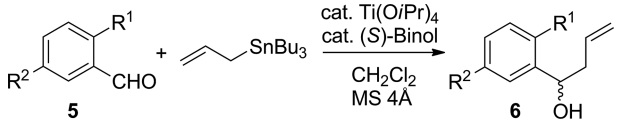
In the case of allylation of aldehyde **5f** to homoallylic alcohol **6f**, a mediocre asymmetric induction (60% *ee*) was achieved under classical Keck conditions A (Table 2, entry 1) and also modified conditions C (entry 3).[37a–37c]

Attempts to carry out the reaction in toluene and THF failed, as the reactions did not proceed. The use of conditions B (catalyst/ligand ratio, 1:2) and C, which were reported to induce higher asymmetric induction,[38] proved to give either inferior (46% *ee*; Table 2, entry 2) or the same results (60% *ee*, entry 3).

A similar trend was also observed during the allylation of other aldehydes. Thus, allylation of **5g** provided the corresponding homoallylic alcohol **6g** with a nice enantioselectivity of 88% *ee* (Table 2, entry 4) under conditions A, whereas under conditions C the enantioselectivity was only 42% *ee* (entry 5). In view of these results, the remaining aldehyde **5m** was allylated only using conditions A with rather low enantioselectivity of 24% *ee* (entry 6).

The question remains how to improve the enantioselectivity of the Keck allylation. One possible pathway could rely on the use of binols possessing bulky substituents

Table 2. Enantioselective allylation of *ortho*-substituted benzaldehydes by using the Keck protocol.



Entry	5	Condition[a]	Yield [%][b]	*er*[c]	*ee* [%]
1	**5f**	A	80	80:20	60 (+)-*R*
2	**5f**	B	55	73:27	46 (+)-*R*
3	**5f**	C	70	80:20	60 (+)-*R*
4	**5g**	A	55	94:6	88 (+)-*R*
5	**5g**	C	60	71:29	42 (+)-*R*
6	**5m**	A	80	62:38	24 (+)-*R*

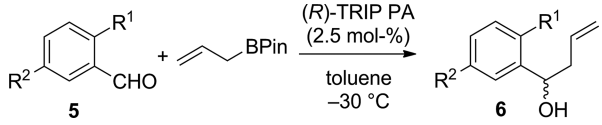
[a] Reaction conditions A: $Ti(OiPr)_4$ (10 mol-%), (*S*)-Binol (10 mol-%), CH_2Cl_2, 4 Å MS, –20 °C, 7 d. Reaction conditions B: $Ti(OiPr)_4$ (10 mol-%), (*S*)-Binol (20 mol-%), CH_2Cl_2, 4 Å MS, –20 °C, 7 d. Reaction conditions C: $Ti(OiPr)_4$ (7.5 mol-%), $TiCl_4$ (2.5 mol-%), (*S*)-Binol (10 mol-%), Ag_2O (5 mol-%), 4 Å, –10 °C, 7 d. [b] Isolated yield. [c] Enantiomeric ratio. The ratio numbers refer to the order of the peaks in the ^{19}F NMR spectra.

in positions 3 and 3′. However, available studies that would provide leads in this direction have, to our knowledge, not been undertaken. Moreover, allylations of ketones under Keck conditions with variously substituted binols suggest that attachment of substituents in the position mentioned above resulted in lower levels of asymmetric induction.[39] Nevertheless, allylations of **5f** were carried out under Keck conditions A by using (*R*)-3,3-bis[3,5-bis(trifluormethyl)-phenyl]binol and (*R*)-3,3-dibromobinol. In the former case, the reaction did not proceed and in the latter case 30% of the product was formed with *ee* of approximately 20%. These results thus support the speculations mentioned above on lower activity of substituted binols.

Brønsted Acid (TRIP PA) Catalyzed Enantioselective Allylations

For comparison with the experiments described above, allylations catalyzed by a chiral Brønsted acid, (*R*)-TRIP PA,[21] were also carried out with selected benzaldehydes (Table 3). Allylation of aldehydes **5a**, **5d**, **5e**–**g**, **5i**, **5j**, and **5m**–**p**, proceeded with high yields and with asymmetric induction in the range of 9–90% *ee* with several exceptions. In some cases these values were lower than or comparable to those obtained with (*R*,*R*)-**4** or (*R*,*S*)-**4** (Table 1, entries 1, 5, 6, 15, and 16). In the case of aldehydes **5d**, **5g**, **5i**, **5j**, and **5o**, the asymmetric induction was higher than those obtained with (*R*,*R*)-**4** or (*R*,*S*)-**4** (Table 1, entries 4, 9, 11, 12, 17). The lower asymmetric induction in allylation of **5g** in comparison with previously reported results[32] might be caused by the lower load of the catalyst (2.5 vs. 5 mol-%). In this respect, the authors also observed a drop in asymmetric induction. In addition, allylation of aldehyde **5p** was undertaken to compare this protocol with the recently reported Ag-catalyzed methodology.[29b] In this case, asymmetric induction was also lower (65% *ee*) than the reported value (74% *ee*).

Table 3. Enantioselective allylation of *ortho*-substituted benzaldehydes by using (*R*)-TRIP PA.

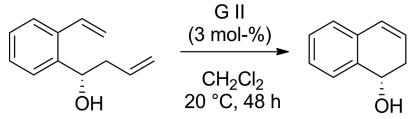


Entry	5	Yield [%][a]	*er*[b]	*ee* [%][c]
1	**5a**	95	27:73	46 (+)-*R*
2	**5d**	99	24.5:75.5	51 (+)-*R*
3	**5e**	59	40.5:59.5	18 (+)-*R*
4	**5f**	66	71:29	42 (+)-*R*
5	**5g**	96	9:91	82 (+)-*R*
6	**5i**	93	37:63	26 (+)-*R*
7	**5j**	98	82:18	64 (+)-*R*
8	**5m**	94	70.5:29.5	41 (+)-*R*
9	**5n**	98	54.5:45.5	9 (+)-*R*
10	**5o**	95	5:95	90 (+)-*R*
11	**5p**[d]	94	82.5:17.5	65 (+)-*R*

[a] Isolated yield. [b] Enantiomeric ratio. The ratio numbers refer to the order of the peaks in the ^{19}F NMR spectra. [c] For assignment of the configuration, see the Supporting Information. [d] R^1 = Br, R^2 = OMe.

Synthesis of a Sertraline Intermediate

Given that allylation of 2-vinylbenzaldehyde **5g** under Keck conditions provided the corresponding homoallylic alcohol **6g** with a reasonable enantioselectivity (88% *ee*) and isolated yield (55%), it was decided to use this substrate for the synthesis of sertraline intermediate (Scheme 2). The prepared compound **6g** was subjected to ring-closing metathesis by using Grubbs 2nd generation catalysts (G II) (2 mol-%) under standard conditions in CH_2Cl_2 at 20 °C for 48 h. The reaction proceeded smoothly and the corresponding dihydronaphthalene **3** was obtained in 79% isolated yield and 84% *ee*. Notably, a slight loss of enantiopurity during ring-closing metathesis reactions have previously been observed in this laboratory,[14e] and we do not currently have reasonable explanation for this phenomenon.



Scheme 2. Synthesis of the sertraline intermediate **3**.

Conclusions

We have shown that catalytic allylation of *ortho*-substituted benzaldehydes under selected Lewis basic and acid catalysts provides the corresponding homoallylic alcohols with reasonable enantioselectivity depending on the nature of the *ortho*-substituent. However, it seems difficult to correlate the level of asymmetric induction with respect to the steric bulk of the substituent. In addition, the obtained results also indicate difficulties regarding the choice of a suitable catalyst with which to achieve highly enantioselective

allylation. In some cases the use of *N*,*N*′-dioxide catalysts gives better optical purity; in others, Keck or Brønsted acid allylation seems to provide better results. The advantage of the *N*,*N*′-dioxide catalysts is in their rather low loading, with only 1 mol-% being sufficient to bring about the desired allylation. In contrast, the Keck allylation suffers from high catalyst loadings (usually 10 mol-%) and long reaction times (one week). As far as TRIP PA is concerned, it has been published that this reagent usually gives the product with high enantiopurity, but the level of asymmetric induction depends on the catalyst loading, as has been noted by us and by others. The optimal amount of TRIP PA to achieve high asymmetric induction in the allylation of *ortho*-substituted benzaldehydes is 10 mol-%,[32] which can be considered to be a high loading. In summary, although progress has been made, the development of a highly catalytically active and general system for the allylation of *ortho*-substituted arylaldehydes that provides products with high optical purity remains to be solved.

Experimental Section

General: All solvents – unless otherwise stated – were used as obtained. THF and Et_2O were distilled from $LiAlH_4$, DCM and Et_3N from CaH_2, toluene from sodium benzophenone ketyl. All other reagents and starting materials {e.g. (2-iodophenyl)methanol, (2-bromo-5-methoxyphenyl)methanol, and 2-[(trimethylsilyl)ethynyl] benzaldehyde} were obtained from commercial sources. ^1H, ^{19}F and ^{13}C NMR spectra were recorded with a Varian UNITY 400 (^1H at 400 MHz, ^{13}C at 100.6 MHz) and a Varian UNITY 300 (^1H and ^{19}F at 300 MHz, ^{13}C at 75 MHz) as solutions in $CDCl_3$ or C_6D_6 at 25 °C. Chemical shifts are given on the δ-scale, coupling constants J are given in Hz. Melting points (uncorrected) were determined by using a Kofler apparatus. Mass spectra were recorded with a ZAB-SEQ (VG-Analytical) instrument. Infrared spectra were recorded with a Bruker IFS 55 spectrometer as THF solutions and are reported in wavenumbers (cm^{-1}). Fluka 60 silica gel was used for flash chromatography. TLC was performed on silica gel 60 F_{254} coated aluminum sheets (Merck). Specific rotation values were determined with an Autopol III automatic polarimeter (Rudolph Research Analytical), the samples were dissolved in $CHCl_3$ (concentrations in g/100 mL). All reactions were carried out under argon.

General Procedure for Allylation with *N*,*N*′-Dioxides: To a solution of bis(tetrahydroisoquinoline)-*N*,*N*′-dioxides (*R*,*R*)-**4** or (*S*,*R*)-**4** (0.0023 mmol, 1 mg) in THF, toluene, or CH_2Cl_2 (1 mL), the corresponding aldehyde (0.23 mmol) and diisopropylethylamine (0.26 mmol, 47 μL, 35 mg) were added at –78 or –40 °C. Allyltrichlorosilane (0.26 mmol, 40 μL, 49 mg) was then added and the reaction mixture was stirred for 4–20 h at the same temperature, unless otherwise stated. The reaction was quenched with brine (4 mL) and the mixture was extracted with EtOAc (3 × 5 mL), the combined organic fractions were dried with $MgSO_4$ and volatiles were removed under reduced pressure. Column chromatography of the residue on silica gel (hexane/EtOAc, 5:1) gave the product as a yellowish liquid or colorless solid. Enantiomeric excess was determined by ^{19}F NMR analysis of the corresponding Mosher acid esters or by GC analysis.

Allylation of *ortho*-Substituted Benzaldehydes Catalyzed by (*S*,*R*)-4. (*S*)-(–)-1-(2-Fluorophenyl)but-3-en-1-ol (6a): Column chromatography on silica gel afforded the title compound (13 mg, 34%) as a colorless liquid. The spectral characteristics are in agreement with the previously reported data.[40] 66% *ee* [Mosher ester: ^{19}F NMR (300 MHz): δ = –71.37 (83%), –71.51 (17%) ppm].

(*S*)-(–)-1-(2-Iodophenyl)but-3-en-1-ol (6d): Column chromatography on silica gel afforded the title compound (32 mg, 51%) as a colorless liquid. The spectral characteristics are in agreement with the previously reported data.[41] 30% *ee* [Mosher ester: ^{19}F NMR (300 MHz): δ = –71.23 (75%), –71.32 (45%) ppm].

(*S*)-(–)-1-[2-(Trifluoromethyl)phenyl]but-3-en-1-ol (6e): Column chromatography on silica gel afforded the title compound (10 mg, 20%) as a colorless liquid. The spectral characteristics are in agreement with the previously reported data.[40] 22% *ee* [Mosher ester: ^{19}F NMR (300 MHz): δ = –71.25 (61%), –71. 34 (39%) ppm].

(*S*)-(–)-1-(2-Iodo-5-methoxyphenyl)but-3-en-1-ol (6f): Column chromatography on silica gel afforded the title compound (37 mg, 53%) as a pale solid; m.p. 28–29 °C; $[\alpha]_D$ = –32.0 (c = 0.98, $CHCl_3$). ^1H NMR (300 MHz): δ = 2.25–2.33 (m, 2 H), 2.54–2.65 (m, 1 H), 3.79 (s, 3 H), 4.85–4.89 (m, 1 H), 5.16–5.24 (m, 2 H), 5.83–5.95 (m, 1 H), 6.58 (dd, J = 8.7, 3.0 Hz, 1 H), 7.12 (d, J = 3 Hz, 1 H), 7.65 (d, J = 8.7 Hz, 1 H) ppm. ^{13}C NMR (75 MHz): δ = 42.3, 55.4, 76.2, 85.5, 112.7, 115.6, 118.7, 134.3, 139.7, 146.7, 160.3 ppm. IR (THF): $\tilde{\nu}$ = 801, 1007, 1268, 1291, 1468, 1590, 2931, 3078 cm^{-1}. MS: *m*/*z* (%) = 123.1 (100), 283.1 (23), 301.1 (70), 341.3 (54), 368.2 (25), 418.3 (58). HRMS (ESI): *m*/*z* calcd for $C_{11}H_{13}O_2INa$ 326.98524; found 326.98511. 80% *ee* [Mosher ester: ^{19}F NMR (300 MHz): δ = –71.15 (10%), –71. 27 (90%) ppm].

(*S*)-(–)-1-(2-Vinylphenyl)but-3-en-1-ol (6g): Column chromatography on silica gel afforded the title compound (16 mg, 40%) as a colorless liquid. The spectral characteristics are in agreement with the previously reported data.[30] 76% *ee* [Mosher ester: ^{19}F NMR (300 MHz): δ = –71.22 (88%), –71.47 (12%) ppm].

(*S*)-(–)-1-{2-[2-(Trimethylsilyl)ethynyl]phenyl}but-3-en-1-ol (6i): Column chromatography on silica gel afforded the title compound (24 mg, 45%) as a colorless liquid. The spectral characteristics are in agreement with the previously reported data.[42] 16% *ee* [Mosher ester: ^{19}F NMR (300 MHz): δ = –71.22 (42%), –71.36 (58%) ppm].

(*S*)-(–)-1-(2-Ethynyl-5-methoxyphenyl)but-3-en-1-ol (6j): Column chromatography on silica gel afforded the title compound (5 mg, 10%) as a colorless liquid. $[\alpha]_D$ = –58 (c = 0.3, $CHCl_3$). ^1H NMR (300 MHz): δ = 2.21–2.22 (m, 1 H), 2.40–2.45 (m, 1 H), 2.63–2.65 (m, 1 H), 3.26 (s, 1 H), 3.84 (s, 3 H), 5.15–5.22 (m, 3 H), 5.80–5.96 (m, 1 H), 6.77 (dd, J = 8.4, 2.7 Hz, 1 H), 7.08–7.09 (m, 1 H), 7.42 (d, J = 8.4 Hz, 1 H) ppm. ^{13}C NMR (75 MHz): δ = 42.7, 55.3, 71.0, 80.9, 81.4, 110.7, 111.4, 113.0, 118.4, 134.3, 134.6, 148.3, 160.3 ppm. IR (THF): $\tilde{\nu}$ = 819, 1030, 1233, 1276, 1489, 1605, 1733, 2099, 2854, 2926, 3073 cm^{-1}. MS: *m*/*z* (%) = 203.1 (100) [M^+]. HRMS (ESI): *m*/*z* calcd for $C_{13}H_{14}O_2$ 203.10666; found 203.10660. 27% *ee* [Mosher ester: ^{19}F NMR (300 MHz): δ = –71.22 (37%), –71. 32 (63%) ppm].

(*S*)-(–)-1-[5-Methoxy-2-(2-phenylethynyl)phenyl]but-3-en-1-ol (6k): Column chromatography on silica gel afforded the title compound (34 mg, 65%) as a pale solid; m.p. 57–59 °C; $[\alpha]_D$ = –12.6 (c = 0.33, $CHCl_3$). ^1H NMR (300 MHz): δ = 2.25–2.27 (m, 1 H), 2.45–2.50 (m, 1 H), 2.72–2.75 (m, 1 H), 3.85 (s, 3 H), 5.16–5.28 (m, 3 H), 5.82–6.00 (m, 1 H), 6.78–6.82 (m, 1 H), 7.11–7.13 (m, 1 H), 7.32–7.38 (m, 3 H), 7.43–7.52 (m, 3 H) ppm. ^{13}C NMR (75 MHz): δ = 42.8, 55.4, 71.4, 87.1, 93.2, 110.7, 112.5, 113.1, 118.4, 123.5, 128.1, 128.4 (2C), 131.3 (2C), 133.6, 134.7, 147.7. 160.1 ppm. IR (THF): $\tilde{\nu}$ = 686, 753, 820, 921, 1057, 1171, 1234, 1296, 1463, 1503, 1608, 1895, 2210, 2837, 2924, 3048, 3276 cm^{-1}. MS: *m*/*z* (%) = 301.1 (100)

[M^+]. HRMS: *m*/*z* calcd for $C_{19}H_{18}O_2Na$ 301.11990; found 301.11989. 50% *ee* [Mosher ester: ^{19}F NMR (300 MHz): δ = –71.23 (25%), –71.29 (75%) ppm].

(*S*)-(–)-1-{5-Methoxy-2-[2-(*tert*-butyl)ethynyl]phenyl}but-3-en-1-ol (6l): Column chromatography on silica gel afforded the title compound (20 mg, 34%) as a colorless liquid. $[\alpha]_D$ = –6.0 (*c* = 0.18, $CHCl_3$). ^1H NMR (300 MHz): δ = 1.24 (s, 9 H), 2.27–2.38 (m, 2 H), 2.51–2.62 (m, 1 H), 3.73 (s, 3 H), 5.00–5.14 (m, 3 H), 5.74–5.87 (m, 1 H), 5.81 (dd, *J* = 8.4, 2.7 Hz, 1 H), 6.95–6.96 (m, 1 H), 7.19–7.22 (m, 1 H) ppm. ^{13}C NMR (75 MHz): δ = 28.2, 31.1 (3C), 40.9, 42.5, 55.3, 71.4, 102.4, 110.6, 112.7, 113.2, 118.0, 133.3, 135.0, 147.4, 159.3 ppm. IR (THF): $\tilde{\nu}$ = 820, 912, 1037, 1158, 1230, 1288, 1492, 1606, 2835, 2866, 2904, 2968, 3072, 3415 cm^{-1}. MS: *m*/*z* (%) = 281.1 (100) [M^+]. HRMS: *m*/*z* calcd for $C_{17}H_{22}O_2Na$ 281.15120; found 281.15108. 20% *ee* [Mosher ester: ^{19}F NMR (300 MHz): δ = –71.21 (40%), –71.23 (60%) ppm].

(*S*)-(–)-1-{5-Methoxy-2-[2-(trimethylsilyl)ethynyl]phenyl}but-3-en-1-ol (6m): Column chromatography on silica gel afforded the title compound (40 mg, 73%) as a pale solid. The spectral characteristics are in agreement with the previously reported data.[42] 60% *ee* [Mosher ester: ^{19}F NMR (300 MHz): δ = –71.20 (20%), –71.25 (80%) ppm].

(*S*)-(–)-1-{5-Methoxy-2-[2-(*tert*-butyldimethylsilyl)ethynyl]phenyl}-but-3-en-1-ol (6n): Column chromatography on silica gel afforded the title compound (44 mg, 60%) as a colorless liquid. $[\alpha]_D$ = –8.2 (*c* = 0.84, $CHCl_3$). ^1H NMR (300 MHz): δ = 0.18 (s, 6 H), 1.00 (s, 9 H), 2.25–2.27 (m, 1 H), 2.35–2.44 (m, 1 H), 2.67–2.71 (m, 1 H), 3.82 (s, 3 H), 5.15–5.30 (m, 3 H), 5.80–5.92 (m, 1 H), 6.72–6.75 (m, 1 H), 7.05–7.06 (m, 1 H), 7.37–7.40 (m, 1 H) ppm. ^{13}C NMR (75 MHz): δ = –4.5, 16.7, 26.1 (3C), 42.7, 55.3, 71.2, 96.3, 103.4, 110.6, 112.5, 112.9, 118.4, 134.1, 134.6, 148.2, 160.1 ppm. IR (THF): $\tilde{\nu}$ = 775, 832, 1035, 1250, 1488, 1606, 2149, 2894, 2927, 2951, 3077, 3406 cm^{-1}. MS: *m*/*z* (%) = 123.1 (100), 257.0 (26), 339.2 (60) [M^+]. HRMS (ESI): *m*/*z* calcd for $C_{19}H_{28}O_2NaSi$: 339.17508; found: 339.17502. 38% *ee* [Mosher ester: ^{19}F NMR (300 MHz): δ = –71.17 (31%), –71.23 (69%) ppm].

(*S*)-(–)-1-(3-Methoxyphenyl)but-3-en-1-ol (6o): Column chromatography on silica gel afforded the title compound (24 mg, 60%) as a colorless liquid. The spectral characteristics are in agreement with the previously reported data.[43] 88% *ee* [GC (HP-Chiral β column; 30 m × 0.25 mm; oven: 80 °C for 1 min, then 1 °C/min to 160 °C, 5 min at the same temperature): t_R = 69.25 (+), 69.66 (–) min].

General Procedure for Keck Allylation. Conditions A: To a solution of $Ti(OiPr)_4$ (0.1 mmol, 28 mg) in CH_2Cl_2 (5 mL), (*S*)-binol (0.1 mmol, 28 mg) and 4Å molecular sieves (200 mg) were added. The mixture was sealed in a pressure tube and heated to 50 °C for 2 h, then cooled to –10 °C and the corresponding benzaldehyde (1 mmol) and allyltributyltin (360 mg, 1.1 mmol) or allenyltrimethyltin (358 mg, 1.1 mmol) were added. The pressure tube was again sealed and left at –18 °C (freezer) for 7 d. HCl (0.5%, 20 mL) was then added and the reaction mixture was extracted with CH_2Cl_2 (3 × 10 mL). The combined organic fractions were dried with anhydrous Na_2SO_4 and volatiles were removed under reduced pressure. Residue mixtures were purified by column chromatography on silica gel.

Conditions B: Procedure was the same as described for Conditions A, but (*S*)-binol (0.2 mmol, 56 mg) was used.

Conditions C: To a the solution of $Ti(OiPr)_4$ (0.075 mmol, 21 mg) and $TiCl_4$ (0.025 mmol, 5 mg) in CH_2Cl_2 (5 mL), (*S*)-binol (0.1 mmol, 28 mg), Ag_2O (0.05 mmol, 12 mg) and 4Å molecular sieves (200 mg) were added. The mixture was sure-sealed in a pressure tube and heated to 50 °C for 2 h, then it was cooled to –10 °C and the substituted benzaldehyde (1 mmol) and allyltributyltin (360 mg, 1.1 mmol) or allenyltrimethyltin (358 mg, 1.1 mmol) were added. The mixture was sure-sealed and left at –18 °C (freezer) for 7 d. Work-up was the same as described for Conditions A.

(*R*)-(+)-1-(2-Iodo-5-methoxyphenyl)but-3-en-1-ol (6f): Conditions A: yield 80%. The spectral characteristics are in agreement with the previously reported data.[30] 60% *ee* [Mosher ester: ^{19}F NMR (300 MHz): δ = –71.17 (80%), –71.30 (20%) ppm. Conditions B: yield 55%; 46% *ee*. Conditions C: yield 70%; 60% *ee*.

(*S*)-(–)-1-(2-Vinylphenyl)but-3-en-1-ol (6g): Conditions A: yield 55%. The spectral characteristics are in agreement with the previously reported data.[30] 88% *ee* [Mosher ester: ^{19}F NMR (300 MHz): δ = –71.24 (94%), –71.49 (6%) ppm]. Conditions C: yield 60%; 42% *ee*.

(*R*)-(+)-1-{5-Methoxy-2-[(trimethylsilyl)ethynyl]phenyl}but-3-en-1-ol (6m): Conditions A: yield 80%. The spectral characteristics are in agreement with the previously reported data.[42] 24% *ee* [Mosher ester: ^{19}F NMR (300 MHz): δ = –71.21 (62%), –71.26 (38%) ppm].

General Procedure for Allylboration of Aldehydes: (*R*)-TRIP-PA catalyst (3.2 mg, 0.0042 mmol, 2.5 mol-%) and the corresponding benzaldehyde (0.17 mmol) were dissolved in toluene (3 mL) and cooled to –30 °C. Pinacol allylboronate (0.038 mL, 0.20 mmol) was added dropwise and the reaction mixture was stirred for 16 h while maintaining –30 °C, then the mixture was warmed to room temperature. The solvent was evaporated under reduced pressure and column chromatographic purification of the residue on silica gel (hexane/EtOAc, 5:1) furnished the homoallylic alcohol as a colorless oil. The *ee* values were determined by ^{19}F NMR analysis of the corresponding Mosher esters. The absolute configurations were tentatively assigned primarily according to the known fact that (*R*)-TRIP PA catalyzed allylation of benzaldehydes provides the corresponding homoallylic alcohols with *R*-configuration. For other supporting data regarding the assigned configuration, see references in individual cases.

(*R*)-(+)-1-(2-Fluorophenyl)but-3-en-1-ol (6a): Isolated yield 95%. The spectral[40] and optical characteristics[24] are in agreement with the previously reported data. $[\alpha]_D$ = +28.5 (*c* = 3.3, $CHCl_3$); 46% *ee* [Mosher ester: ^{19}F NMR (300 MHz): δ = –71.38 (27%), –71.52 (73%) ppm].

(*R*)-(+)-1-(2-Iodophenyl)but-3-en-1-ol (6d): Isolated yield 99%. The spectral[41] and optical[29] characteristics are in agreement with the previously reported data. $[\alpha]_D$ = +36.8 (*c* = 14.1, $CHCl_3$); 51% *ee* [Mosher ester: ^{19}F NMR (300 MHz): δ = –71.24 (24.5%), –71.33 (75.5%) ppm].

(*R*)-(+)-1-(2-(Trifluoromethyl)phenyl)but-3-en-1-ol (6e): Isolated yield 59%. The spectral[40] and optical characteristics are in agreement with the previously reported data.[24] $[\alpha]_D$ = +13.2 (*c* = 1.9, $CHCl_3$); 19% *ee* [Mosher ester: ^{19}F NMR (300 MHz): δ = –71.25 (40.5%), –71.34 (59.5%) ppm].

(*R*)-(+)-1-(2-Iodo-5-methoxyphenyl)but-3-en-1-ol (6f): Isolated yield 66%. 42% *ee* [Mosher ester: ^{19}F NMR (300 MHz): δ = –71.16 (71%), –71.29 (29%) ppm].

(*R*)-(+)-1-(2-Vinylphenyl)but-3-en-1-ol (6g): Isolated yield 96%. The spectral[30] and optical characteristics[32] are in agreement with the previously reported data. Configuration was also assigned according to analogy with a related compound.[44] $[\alpha]_D$ = +50.2 (*c* = 4.3, $CHCl_3$); 82% *ee* [Mosher ester: ^{19}F NMR (300 MHz): δ = –71.24 (9%), –71.48 (91%) ppm].

(*R*)-(+)-1-{2-[2-(Trimethylsilyl)ethynyl]phenyl}but-3-en-1-ol (6i): Isolated yield 93%. The spectral characteristics are in agreement with the previously reported data.[42] $[\alpha]_D$ = +23.5 (c = 3.4, $CHCl_3$); 26% *ee* [Mosher ester: ^{19}F NMR (300 MHz): δ = –71.22 (37%), –71.36 (63%) ppm].

(*R*)-(+)-1-(2-Ethynyl-5-methoxyphenyl)but-3-en-1-ol (6j): Isolated yield 98%. 64% *ee* [Mosher ester: ^{19}F NMR (300 MHz): δ = –71.23 (82%), –71.33 (18%) ppm].

(*R*)-(+)-1-{5-Methoxy-2-[2-(trimethylsilyl)ethynyl]phenyl}but-3-en-1-ol (6m): Isolated yield 94%. The spectral characteristics are in agreement with the previously reported data.[42] 41% *ee* [Mosher ester: ^{19}F NMR (300 MHz): δ = –71.20 (70.5%), –71.25 (29.5%) ppm].

(*R*)-(+)-1-{5-Methoxy-2-[2-(*tert*-butyldimethylsilyl)ethynyl]phenyl}-but-3-en-1-ol (6n): Isolated yield 98%. 9% *ee* [Mosher ester: ^{19}F NMR (300 MHz): δ = –71.19 (54.5%), –71.24 (45.5%) ppm].

(*R*)-(+)-1-(3-Methoxyphenyl)but-3-en-1-ol (6o): Isolated yield 95%. The spectral and optical[43] characteristics are in agreement with the previously reported data. $[\alpha]_D$ = +49.0 (c = 3.1, $CHCl_3$); 90% *ee* [Mosher ester: ^{19}F NMR (300 MHz): δ = –71.33 (5%), –71.47 (95%) ppm].

(*R*)-(+)-1-(2-Bromo-5-methoxyphenyl)but-3-en-1-ol (6p): Isolated yield 94%. Spectral and optical data are in accordance with previously published data.[29] $[\alpha]_D$ = +48.5 (c = 2.2, $CHCl_3$); 65% *ee* [Mosher ester: ^{19}F NMR (300 MHz): δ = –71.17 (82.5%), –71.29 (17.5%) ppm].

Supporting Information (see footnote on the first page of this article): Preparation of the starting aldehydes **5**, all experimental procedures regarding allylations, copies of ^1H and ^{13}C NMR spectra of hitherto unreported compounds.

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[1] A. de Fátima, A. A. M. Lapis, R. A. Pilli, *J. Braz. Chem. Soc.* **2005**, *16*, 495–499.
[2] a) A. de Fatima, R. A. Pilli, *Tetrahedron Lett.* **2003**, *44*, 8721–8724; b) E. Sundby, L. Perk, T. Anthonsen, A. J. Aasen, T. V. Hansen, *Tetrahedron* **2004**, *60*, 521–524; c) P. Harsch, G. A. O'Doherty, *Tetrahedron* **2009**, *65*, 5051–5055.
[3] A. de Fatima, L. K. Kohn, M. A. Antônio, J. E. de Carvalho, R. A. Pilli, *Bioorg. Med. Chem.* **2004**, *12*, 5437–5442.
[4] K. B. Sawant, M. P. Jennings, *J. Org. Chem.* **2006**, *71*, 7911–7914.
[5] X. Tian, S. D. Rychnowsky, *Org. Lett.* **2007**, *9*, 4955–4958.
[6] A. Ditto, V. Bellosta, J. Cossy, *Synlett* **2008**, 2459–2460.
[7] M. Inoue, M. Nakada, *J. Am. Chem. Soc.* **2007**, *129*, 4164–4165.
[8] S. E. Denmark, T. Kobayashi, C. S. Regens, *Tetrahedron* **2010**, *66*, 4745–4759.
[9] For reviews, see: a) S. E. Denmark, J. Fu, *Chem. Rev.* **2003**, *103*, 2763–2793; b) M. Yus, J. C. González-Goméz, F. Foubelo, *Chem. Rev.* **2011**, *111*, 7774–7854.
[10] a) N. Nakajima, M. Saito, M. Shiro, S. Hashimoto, *J. Am. Chem. Soc.* **1998**, *120*, 6419–6420; b) N. Nakajima, M. Saito, M. Shiro, S. Hashimoto, *Chem. Pharm. Bull. Chem. Soc.* **2000**, *48*, 306–307; c) N. Nakajima, M. Saito, M. Uemura, S. Hashimoto, *Tetrahedron Lett.* **2002**, *43*, 8827–8829.
[11] a) T. Shimada, A. Kina, S. Ikeda, T. Hayashi, *Org. Lett.* **2002**, *4*, 2799–2801; b) T. Shimada, A. Kina, T. Hayashi, *J. Org. Chem.* **2003**, *68*, 6329–6337; c) T. Shimada, A. Kina, T. Hayashi, *Adv. Synth. Catal.* **2004**, *346*, 1169–1174.
[12] a) A. V. Malkov, L. Dufková, L. Farrugia, P. Kočovský, *Angew. Chem. Int. Ed.* **2003**, *42*, 3674–3676; *Angew. Chem.* **2003**, *115*, 3802; b) A. V. Malkov, M. Orsini, D. Pernazza, K. W. Muir, V. Langer, P. Meghani, P. Kočovský, *Org. Lett.* **2002**, *4*, 1047–1049; c) A. V. Malkov, M. Bell, M. Orsini, D. Pernazza, A. Massa, P. Hermann, P. Meghani, P. Kočovský, *J. Org. Chem.* **2003**, *68*, 9659–9668; d) A. V. Malkov, M. Bell, F. Castelluzzo, P. Kočovský, *Org. Lett.* **2005**, *7*, 3219–3222; e) A. V. Malkov, P. Ramírez-López, L. Biedermannová, L. Rulíšek, L. Dufková, M. Kotora, F. Zhu, P. Kočovský, *J. Am. Chem. Soc.* **2008**, *130*, 5341–5348.
[13] a) T. Bao, M. M.-C. Lo, G. C. Fu, *J. Am. Chem. Soc.* **2001**, *123*, 353–354; b) Q. Chai, C. Song, Z. Sun, Y. Ma, C. Ma, Y. Dai, M. B. Andrus, *Tetrahedron Lett.* **2006**, *47*, 8611–8615; c) G. Chelucci, S. Baldino, S. A. Pinna, M. Benanglia, L. Buffa, S. Guizetti, *Tetrahedron Lett.* **2008**, *64*, 7574–7582.
[14] a) R. Hrdina, I. Valterová, J. Hodačová, M. Kotora, *Adv. Synth. Catal.* **2007**, *349*, 822–826; b) R. Hrdina, M. Dračínský, I. Valterová, J. Hodačová, I. Císařová, M. Kotora, *Adv. Synth. Catal.* **2008**, *350*, 1449–1456; c) A. Kadlčíková, M. Kotora, *Molecules* **2009**, *14*, 2918–2926; d) A. Kadlčíková, R. Hrdina, I. Valterová, M. Kotora, *Adv. Synth. Catal.* **2009**, *351*, 1279–1283; e) A. Kadlčíková, I. Valterová, L. Ducháčková, J. Roithová, M. Kotora, *Chem. Eur. J.* **2010**, *16*, 9442–9445; f) K. Vlašaná, R. Hrdina, L. Valterová, M. Kotora, *Eur. J. Org. Chem.* **2010**, 7040–7044; g) F. Hessler, A. Korotvička, D. Nečas, I. Valterová, M. Kotora, *Eur. J. Org. Chem.* **2014**, 2543–2548; h) P. Motloch, I. Valterová, M. Kotora, *Adv. Synth. Catal.* **2014**, *356*, 199–204.
[15] A. Traverse, Y. Zhao, A. H. Hoveyda, M. L. Snapper, *Org. Lett.* **2005**, *7*, 3151–3154.
[16] V. Simonini, M. Benaglia, L. Pignataro, S. Guizzetti, G. Celentano, *Synlett* **2008**, 1061–1065.
[17] P. Kwiatkowski, P. Mucha, G. Mloston, J. Jurczak, *Synlett* **2009**, 1757–1760.
[18] *S*-oxide: a) P. Wang, J. Chen, L. Cun, J. Deng, J. Zhu, J. Liao, *Org. Biomol. Chem.* **2009**, *7*, 3741–3747; b) A. Massa, L. Capozzolo, A. Scettri, *Cent. Eur. J. Chem.* **2010**, *8*, 1210–1215.
[19] *P*-oxide: K. Iseki, Y. Kuroki, M. Takahashi, S. Kishimoto, Y. Kobayashi, *Tetrahedron* **1997**, *53*, 3513–3527.
[20] Alcohol: L. Liu, J. Sun, N. Liu, W. Chang, J. Li, *Tetrahedron: Asymmetry* **2007**, *18*, 710–716.
[21] Brønsted acid: a) P. Jain, J. C. Antilla, *J. Am. Chem. Soc.* **2010**, *132*, 11884–11886; b) C. Ke, T. Fan, J. Sun, *Chin. J. Chem.* **2011**, *29*, 1669–1671.
[22] Ti complex: Y.-Y. Yin, G. Zhao, Y. Qian, W. Yin, *J. Fluorine Chem.* **2003**, *120*, 117–120.
[23] In complex: a) L. C. Hirayama, S. Gamsey, D. Knueppel, D. Steiner, K. DeLaTorre, B. Singaram, *Tetrahedron Lett.* **2005**, *46*, 2315–2318; b) T. D. Haddad, L. C. Hirayama, B. Singaram, *J. Org. Chem.* **2010**, *75*, 642–649.
[24] Sn complex: V. Rauniyar, H. Zhai, D. G. Hall, *J. Am. Chem. Soc.* **2008**, *130*, 8481–8490.
[25] Cr complex: a) G. Xia, H. Yamamoto, *J. Am. Chem. Soc.* **2006**, *128*, 2554–2555; b) P. Kwiatkowski, W. Chaladaj, J. Jurczak, *Tetrahedron* **2006**, *62*, 5116–5125; c) X. Huang, C. Chen, *Tetrahedron: Asymmetry* **2010**, *21*, 2999–3004; d) J. D. White, S. Shaw, *Org. Lett.* **2011**, *13*, 2488–2491; e) X.-R. Huang, X.-H. Pan, G.-H. Lee, C. Chen, *Adv. Synth. Catal.* **2011**, *353*, 1949–1954.
[26] Rh complex: Y. Motoyama, H. Narusawa, H. Nishiyama, *Chem. Commun.* **1999**, 131–132.
[27] Pd complex: S.-F. Zhu, X.-C. Qiao, Y.-Z. Zhang, L.-X. Wang, Q.-L. Zhou, *Chem. Sci.* **2011**, *2*, 1135–1140.
[28] Bi complex: Z. Li, B. Planq, T. Ollevier, *Chem. Eur. J.* **2012**, *18*, 3144–3147.

[29] Ag complex: a) M. Wadamoto, N. Ozasa, A. Yanagisawa, H. Yamamoto, *J. Org. Chem.* **2003**, *68*, 5593–5601; b) R. Mirabdolbaghi, T. Dudding, *Tetrahedron* **2012**, *68*, 1988–1991.
[30] N. T. Barczak, E. R. Jarvo, *Eur. J. Org. Chem.* **2008**, 5507–5510.
[31] a) J. Blanco-Urgoiti, L. Casarrubios, G. Domínguez, J. Pérez-Castells, *Tetrahedron Lett.* **2001**, *42*, 3315–3317; b) M. Rosillo, L. Casarrubios, G. Domínguez, J. Pérez-Castells, *Tetrahedron Lett.* **2001**, *42*, 7029–7031; c) M. Rosillo, G. Domínguez, L. Casarrubios, U. Amador, J. Pérez-Castells, *J. Org. Chem.* **2004**, *69*, 2084–2093; d) R. J. Blanco-Urgoiti, D. Abdi, G. Omínguez, J. Pérez-Castells, *Tetrahedron* **2008**, *64*, 67–74.
[32] S. Fustero, E. Rodríguez, R. Lázaro, L. Herrera, S. Catalán, P. Barrio, *Adv. Synth. Catal.* **2013**, *355*, 1058–1064.
[33] L. F. Tietze, G. Brasche, A. Grube, N. Böhnke, C. Stadler, *Chem. Eur. J.* **2007**, *13*, 8543–8563.
[34] a) M. Lautens, T. Rovis, *J. Org. Chem.* **1997**, *62*, 5246–5247; b) M. Lautens, T. Rovis, *Tetrahedron* **1999**, *55*, 8967–8976; c) E. A. Garcia, S. Ouizem, X. Cheng, P. Romanens, E. P. Kündig, *Adv. Synth. Catal.* **2010**, *352*, 2306–2314; d) S. H. Lee, I. S. Kim, Q. R. Li, G. R. Dong, L. S. Jeong, J. H. Jung, *J. Org. Chem.* **2011**, *76*, 10011–10019.
[35] a) R. Hrdina, F. Opekar, J. Roithová, M. Kotora, *Chem. Commun.* **2009**, 2314–2316; b) L. Ducháčková, A. Kadlčíková, M. Kotora, J. Roithová, *J. Am. Chem. Soc.* **2010**, *132*, 12660–12667.
[36] M. Bartók, *Chem. Rev.* **2010**, *110*, 1663–1705.
[37] a) G. E. Keck, K. H. Tarbet, L. S. Geraci, *J. Am. Chem. Soc.* **1993**, *115*, 8467–8468; b) G. E. Keck, D. Krishnamurthy, M. C. Grier, *J. Org. Chem.* **1993**, *58*, 6543–6544; c) G. E. Keck, L. S. Geraci, *Tetrahedron Lett.* **1993**, *34*, 7827–7828.
[38] H. Hanzawa, D. Uraguchi, S. Konishi, T. Hashimoto, K. Maruoka, *Chem. Eur. J.* **2003**, *9*, 4405–4413.
[39] J. G. Kim, E. H. Camp, P. J. Walsh, *Org. Lett.* **2006**, *8*, 4413–4416.
[40] H. Doucet, M. Santelli, *Tetrahedron: Asymmetry* **2000**, *11*, 4163–4169.
[41] a) L. E. Overman, D. J. Ricca, V. D. Tran, *J. Am. Chem. Soc.* **1997**, *119*, 12031–12040; b) N. Kurono, E. Honda, F. Komatsu, K. Orito, M. Tokuda, *Tetrahedron* **2004**, *60*, 1791–1801.
[42] M. Rosillo, G. Dominguez, L. Casarrubios, U. Amadour, J. Perez-Castells, *J. Org. Chem.* **2004**, *69*, 2084–2093.
[43] T.-P. Loh, J.-R. Zhou, Z. Yin, *Org. Lett.* **1999**, *1*, 1855–1857.
[44] S. Obika, H. Kono, Y. Yasui, R. Yanada, Y. Takemoto, *J. Org. Chem.* **2007**, *72*, 4462–4468.

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