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Highly Efficient Asymmetric Synthesis of Vinylic Amino Alcohols by Zn-Promoted Benzoyloxyallylation of Chiral *N*-*tert*-Butanesulfinyl Imines: Facile and Rapid Access to (−)-Cytoxazone

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Abstract: An efficient and convenient α-hydroxyallylation approach for the asymmetric synthesis of a variety of β-amino-α-vinyl alcohols has been successfully developed. A wide range of vinylic amino alcohol derivatives could be obtained in very good yields and with excellent diastereomeric ratios of up to 99:1 in favor of *anti* isomers by highly diastereoselective Zn-promoted benzoyloxyallylation of chiral *N*-*tert*-butanesulfinyl imines with 3-bromopropenyl benzoate at room temperature. In particular, excellent enantioinduction of the two new stereogenic centers was observed, with up to 98% *ee*. The method provides a new route for the direct α-hydroxyallylation of imines in a highly stereoselective manner. Moreover, the synthetic value of the method has also been demonstrated by the most concise and straightforward synthesis of (−)-cytoxazone yet reported.

Keywords: amino alcohols · asymmetric synthesis · chiral auxiliaries · (−)-cytoxazone · hydroxyallylation

Introduction

β-Amino alcohols are important structural motifs present in many natural products and pharmaceutical compounds.[1] They have also been used as powerful chiral ligands or auxiliaries in asymmetric synthesis.[2] Over the past two decades, the asymmetric synthesis of β-amino alcohol derivatives has attracted much attention.[3] Among the successful strategies developed for obtaining optically active β-amino alcohols—such as asymmetric aminohydroxylation,[4] ring-opening of chiral epoxides[5] or aziridines,[6] nucleophilic addition to protected α-hydroxyimines or α-aminocarbonyls,[7] α-alkoxyenolate addition to imine derivatives,[8] catalytic asymmetric Mannich-type reactions of α-hydroxyketones and imines,[9] and direct asymmetric pinacol-type cross-coupling between carbonyls and imines[10]—those with broad reaction scope and, particularly, that allow substrates containing certain functional groups are of great interest. Although considerable efforts have been made to explore the functionality limitations in many methods, the current achievements remain far from satisfactory.

β-Amino alcohol compounds containing α-vinyl groups are an important class of densely functionalized materials. They serve as precursors for α-hydroxy-β-amino acids,[11] β-hydroxy-γ-amino acids,[12] and many related natural products of biological interest. Unfortunately, despite the potential significance of β-amino-α-vinyl alcohols as valuable building blocks for organic synthesis and medicinal chemistry, methods for their highly stereoselective preparation are very limited.[13] In the literature, simple and direct additions of vinylmetal reagents such as vinylmagnesium halides to enantiomerically pure *N*-protected α-amino aldehydes are often used in the synthesis of β-amino-α-vinyl alcohol derivatives, but mostly low to moderate diastereoselectivities are afforded.[14] Moreover, the use of enantiopure starting α-amino aldehydes could sometimes be a disadvantage because of their relatively poorer availability.

The addition of an α-hydroxyallyl carbanion to a carbonyl imino compound (Scheme 1) represents another, very straightforward, type of route to β-amino-α-vinyl alcohol derivatives, but less progress with this approach has been achieved because of the poorer electrophilicities of imines rela-

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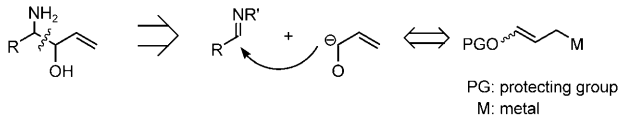
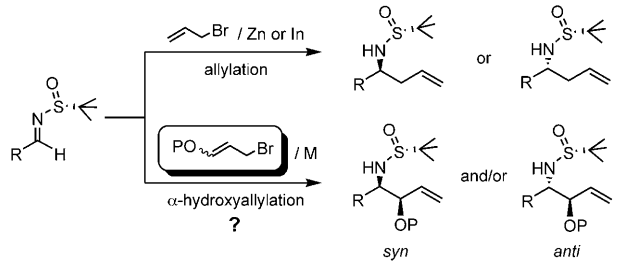


Scheme 1. Direct α-hydroxyallylation approach.

tive to the corresponding carbonyl compounds and also because of severe difficulties in regio- and diastereoselectivity control.[15,16] In particular, direct asymmetric α-hydroxyallylation of imino derivatives is far more rarely encountered in the literature.[17] Excellent stereoselectivities have been obtained only in some cases of reagent-controlled asymmetric α-alkoxyallylation of azomethine derivatives with enantioenriched γ-oxygenated allylic stannanes and boranes.[17a–c] Several examples of the use of chiral imines as substrates have been described, but these reactions have often given only low to moderate levels of stereocontrol.[15c,17d–e] Although the ring-opening of chiral vinylaziridines with oxygen nucleophiles provides an alternative route to β-amino-α-vinyl alcohols,[18] multiple synthetic operations are required. As such, new strategies for accessing β-amino-α-vinyl alcohol compounds with high optical purity are greatly desirable. Here we report an efficient and convenient approach for the asymmetric synthesis of a variety of β-amino-α-vinyl alcohols by highly diastereoselective Zn-promoted α-hydroxyallylation of *N-tert*-butanesulfinyl imines at room temperature.

N-tert-Butanesulfinyl imines have recently shown versatile applicability in the asymmetric synthesis of various chiral amines.[19,20] In an earlier work, we successfully developed an efficient method for the highly diastereoselective synthesis of chiral homoallylic amines by Zn-mediated allylation of enantioenriched *N-tert*-butanesulfinyl imines at room temperature.[20d] More recently, we reported our further discovery of a simple and mild system in aqueous media for In-mediated asymmetric allylation of *N*-sulfinyl imines to give chiral homoallylic amines and 3-allylisoindolinone derivatives with excellent diastereoselectivity.[20e] Encouraged by these successes in allylation chemistry, we wondered whether this *N*-sulfinyl imine strategy could be extended to asymmetric α-hydroxyallylation for the synthesis of optically active β-amino-α-vinyl alcohols (Scheme 2).

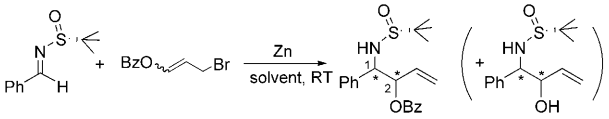


Scheme 2. Proposed asymmetric α-hydroxyallylation procedure.

Results and Discussion

It is known that 3-bromopropenyl benzoate (3-benzoyloxyallyl bromide)[21] is an ideal α-hydroxyallyl reagent for acyloxyallylation because of its easy preparation, high stability, and remarkable reactivity. We initially examined the reaction between the (*R*)-*N-tert*-butanesulfinyl imine **1a** and (*E*)-3-benzoyloxyallyl bromide [(*E*)-**2**] in THF in the presence of zinc metal at room temperature (Table 1). To our

Table 1. Initial examination of benzoyloxyallylation.



1a **2** **3a** **4a**

Entry[a]	Solvent	*t* [h]	Yield [%][b]	dr[c]	*ee* [%][d]
1[e]	THF	3	69	98:2	84
2[e]	HMPA[g]	12	95	99:1	96
3[f]	THF	3	85	99:1	79
4[f]	HMPA[g]	12	96	98:2	92
5[e,h]	HMPA	12	95	99:1	96
6[e,i]	THF	12	41	99:1	97

[a] The reaction was performed with imine **1a** (0.25 mmol) and Zn/**2** (0.5 mmol) in dry solvent (5 mL) at RT, unless otherwise noted. [b] Isolated yield of product **3a**. [c] Diastereomeric ratio for the acetate derivative of product **3a** after the removal of the sulfinyl moiety. [d] Enantiomeric excess for the acetate derivative of compound **3a** after the removal of the sulfinyl moiety. [e] Pure *E* isomer of **2** was used. [f] *E*/*Z* mixture (31:69) of **2** was used. [g] H_2O (10 μL) was used as additive. [h] The reaction was performed with imine **1a** (5 mmol) and (*E*)-**2** (10 mmol) in HMPA (100 mL) containing H_2O (0.2 mL) at RT. [i] In was used instead of Zn.

delight, the reaction proceeded well and afforded the expected benzoyloxyallylation product with excellent *syn*/*anti* diastereoselectivity in 69% yield (Table 1, entry 1), although minor formation of the hydrolysis product **4a** (about 10%) was also detected. When HMPA was used as solvent, very gratifyingly, the reaction gave solely the benzoyloxyallylation product **3a** in 95% yield (entry 2). Unlike in reported cases of allylation of benzylideneanilines,[15b] it is noteworthy that no internal migration of the benzoyl group was observed either in THF or in HMPA systems, probably as a result of the decreased nucleophilic capability of the sulfinyl nitrogen.

To improve understanding of the stereochemical outcome of the reaction, the benzoyloxyallylation product **3a** obtained in entry 1 of Table 1 was chosen for conversion into a related cyclic compound for further NMR studies. As illustrated in Scheme 3, removal of the sulfinyl group under acidic conditions, followed by acetyl protection, afforded the corresponding vinylic amino alcohol **5a** in good yield. The use of LC-MS and chiral HPLC analysis of **5a** clearly revealed the diastereoselectivity (98:2 dr) and enantioselectivity (84% *ee*) of asymmetric benzoyloxyallylation in THF (Table 1, entry 1). Subsequent debenzoylation of derivative **5a** in NaOH/MeOH and cyclization of the resulting product

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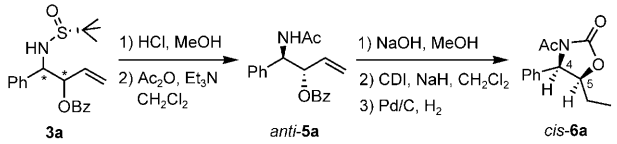


Scheme 3. Stereochemistry determination.

with CDI (1,1′-carbonyldiimidazole), followed by hydrogenation, provided the *cis*-configured oxazolidinone derivative **6a**. The *cis* configuration of **6a** was confirmed by the coupling constant ($J_{4,5}=7.6$ Hz) between H-4 and H-5,[22] and by NOE experimentation. Accordingly, the major diastereoisomer **5a** was assigned as *anti*. By the same method and through comparison with the HPLC trace of **5a**, the benzoyloxyallylic addition in HMPA was also found to be highly *anti*-selective (99:1). To our pleasure, the reaction provided a much improved enantioselectivity, and an excellent *ee* value of 96% was obtained (Table 1, entry 2). It should be noted that a reversal of stereofacial selectivity was again achieved as we had previously found in the simple allylic addition (entry 2 vs entry 1), suggesting different transition states in THF and HMPA. Fortunately, with a single crystal of the benzoyloxyallylation product **3a** obtained from (*S*)-*N*-sulfinyl imine **1a** in the HMPA system, the absolute configuration of the two newly generated stereocenters was unambiguously determined by X-ray crystallography to be (1*R*,2*S*) (Figure 1). Thus, treatment of the enantiopure (*R*)-

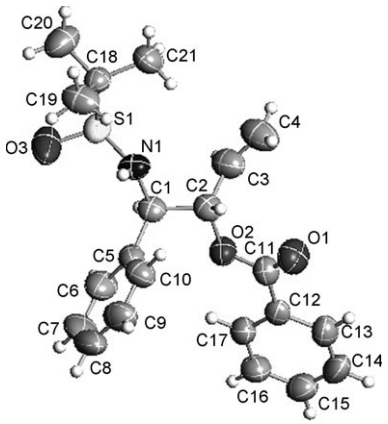


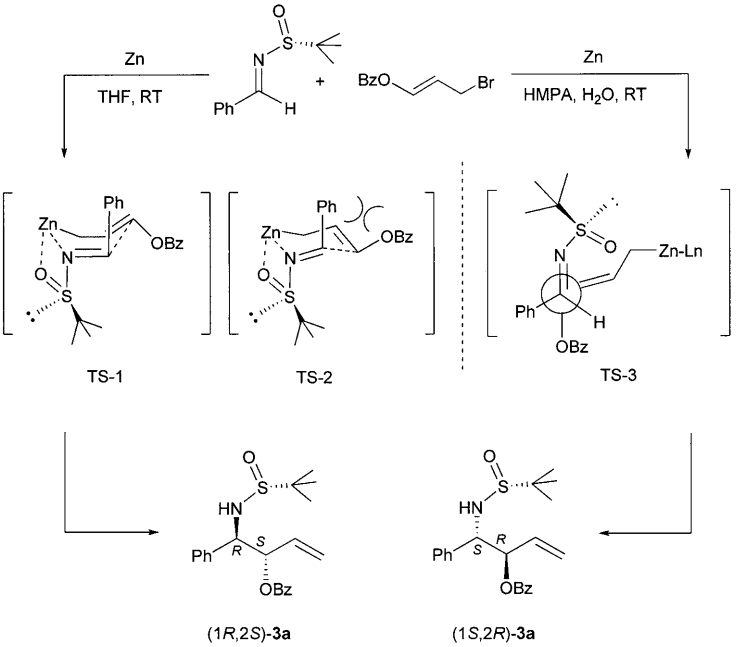
Figure 1. X-ray crystal structure of **3a** produced from the (*S*)-*N*-sulfinyl imine with the HMPA system.

N-sulfinyl imine **1a** with 3-benzoyloxyallyl bromide (**2**) in the presence of zinc at room temperature either in THF or in HMPA gave the major products (1*R*,2*S*)-*anti*-**3a** and (1*S*,2*R*)-*anti*-**3a**, respectively.

We also examined the benzoyloxyallylation of the (*R*)-*N*-*tert*-butanesulfinyl imine **1a** with an *E*/*Z* mixture (~31:69) of 3-benzoyloxyallyl bromide (**2**) rather than the *E* isomer, both in THF and in HMPA systems. Although the same excellent levels of diastereoselectivity were observed, the enantioselectivities were slightly reduced, by about 5% in both cases (Table 1, entries 3 and 4). Notably, with the *E* isomer of **2** the same levels both of diastereoselectivity (99:1 dr) and of enantioselectivity (96% *ee*) could be obtained in HMPA even on a gram scale (Table 1, entry 5).

In addition, replacement of zinc with indium in the same benzoyloxyallylation reaction was also tested. Interestingly, excellent stereoselectivities (99:1 dr, 97% *ee*) could be achieved in THF, but the yield was not ideal (41%) even after 12 h (entry 6). When HMPA was used as solvent, no reaction was observed.

To explain the observed results, we proposed two different transition state models—TS-1 and TS-3 (Scheme 4)—for the reactions under different conditions. As described in the



Scheme 4. Mechanistic proposals relating to reaction stereocontrol.

previous studies[20d] of simple allylation of *N*-sulfinyl imines with allyl bromide, in a THF system a six-membered cyclic chair transition state model is believed to be preferred and the allylzinc is thought to coordinate both to the imine nitrogen and to sulfinyl oxygen. In the benzoyloxyallylation reaction, however, because of the steric repulsion between the imine phenyl group and the benzoyloxy group attached to the allylzinc reagent (see TS-2), a six-membered boat-like transition state (TS-1) should be favored, accordingly leading to the dominance of the (1*R*,2*S*)-*anti*-amino alcohol product when the (*R*)-*N*-*tert*-butanesulfinyl imine is employed. In a HMPA system, according to our previous hypothesis, the acyclic *anti* periplanar transition state TS-3, in which the allylzinc moiety is coordinated to the Lewis base (HMPA) rather than to the sulfinyl oxygen, is likely to be involved. As depicted, the nucleophilic attack of the corresponding benzoyloxyallylzinc reagent would be expected to take place predominately from the less sterically hindered

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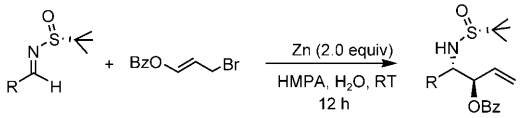
re-face of the imine to deliver the (1*S*,2*R*)-*anti*-amino alcohol product. Thus, simply by tuning the reaction solvent it is possible to achieve a remarkable reversal of diastereofacial selectivity to afford the desired stereochemical outcome.

With optimal conditions identified, we turned our attention to investigation of the reaction scope and generality. As summarized in Table 2, a series of (*R*)-*N*-*tert*-butanesulfinyl imines bearing a range of R substituents were examined in reactions with (*E*)-3-benzoyloxyallyl bromide (**2**) in HMPA in the presence of zinc (2 equiv). In most cases, the benzoyloxyallylation proceeded in good yields and with excellent diastereoselectivities to afford various highly optically active β-amino-α-vinyl alcohol products. For aromatic substrates, it was found that the position and property of the substituent on the benzene ring did not significantly affect either the reactivity or the selectivity of the reaction (entries 1–15). Very high enantioselectivities (98% *ee*) were achieved in the cases of imines **1f**, **1i**, and **1j** (entries 6, 9, and 10).

The use of aliphatic substrates were also examined (entries 16–19). Decreases both in diastereoselectivity (78:22–79:21 dr) and in enantioselectivity (80–87% *ee*) were observed with use of the less sterically hindered *N*-sulfinyl imines of 3-phenylpropanal (**1p**), butanal (**1q**), and 3-methylbutanal (**1r**) (entries 16–18). When the more bulky cyclohexyl imine (**1s**) was employed (entry 19), the reaction diastereoselectivity was dramatically improved to 98:2, but the enantioselectivity remained moderate (81% *ee*).

Table 2. Diastereoselective benzoyloxyallylation of (*R*)-*N*-*tert*-butanesulfinyl imines in the HMPA system.



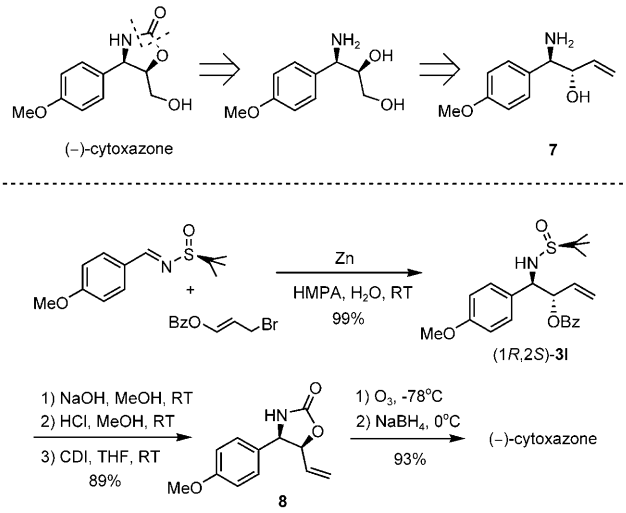
1 2 3

Entry[a]	1	R	3	Yield[b] [%]	*anti*/*syn*[c]	*ee* [%][d]
1	**1a**	C_6H_5	**3a**	95	99:1	96
2	**1b**	4-FC_6H_4	**3b**	99	98:2	93
3	**1c**	2-ClC_6H_4	**3c**	99	97:3	93
4	**1d**	3-ClC_6H_4	**3d**	99	95:5	93
5	**1e**	4-ClC_6H_4	**3e**	98	98:2	95
6	**1f**	3-BrC_6H_4	**3f**	99	95:5	98
7	**1g**	4-BrC_6H_4	**3g**	99	97:3	96
8	**1h**	2-$CH_3C_6H_4$	**3h**	98	99:1	90
9	**1i**	4-$CH_3C_6H_4$	**3i**	96	99:1	98
10	**1j**	4-$CH_3SC_6H_4$	**3j**	98	98:2	98
11	**1k**	3-$MeOC_6H_4$	**3k**	99	99:1	92
12	**1l**	4-$MeOC_6H_4$	**3l**	99	99:1	93
13	**1m**	2,4-$(MeO)_2C_6H_3$	**3m**	75	99:1	86
14	**1n**	2,4-$Cl_2C_6H_3$	**3n**	99	99:1	93
15	**1o**	β-naphthyl	**3o**	96	98:2	95
16	**1p**	$C_6H_5CH_2CH_2$	**3p**	98	79:21	87
17	**1q**	$CH_3CH_2CH_2$	**3q**	90	79:21	80
18	**1r**	$(CH_3)_2CHCH_2$	**3r**	89	78:22	85
19	**1s**	C_6H_{11}	**3s**	94	98:2	81

[a] The reaction was performed with imine **1** (0.25 mmol), Zn/**2** (0.5 mmol), and H_2O (10 μL) in dry HMPA (5 mL) at RT. [b] Isolated yield. [c] Diastereomeric ratio for the acetate derivative of product **3** after the removal of the sulfinyl moiety. [d] Enantiomeric excess for the acetate derivative of product **3** after the removal of the sulfinyl moiety.

With this highly diastereoselective and enantioselective Zn-promoted α-hydroxyallylation approach to hand, we sought to demonstrate its synthetic utility by the efficient asymmetric synthesis of (−)-cytoxazone. Cytoxazone is a selective modulator of Th2 cytokine secretion isolated from *Streptomyces* sp.[23] Because of its important biological activity, the development of efficient asymmetric routes to cytoxazone and its stereoisomers have recently attracted considerable attention from organic chemists.[24] Despite the progress achieved, a method for convenient and rapid access to the optically active cytoxazone target is still in great demand.

According to the retrosynthetic analysis of the (−)-cytoxazone molecule (Scheme 5), an expedient synthesis should be readily achievable through the use of the corresponding *anti*-β-amino-α-vinyl alcohol **7** as the key intermediate. Indeed, as indicated in entry 12 of Table 2, asymmetric benzoyloxyallylation of the (*R*)-*N*-sulfinyl imine **1l** with (*E*)-3-benzoyloxyallyl bromide **2** provided the (1*S*,2*R*)-*anti*-amino alcohol **3l** in excellent yield (99%), diastereoselectivity (99:1 dr), and enantioselectivity (93% *ee*). Accordingly, the benzoyloxyallylation of the corresponding (*S*)-*N*-sulfinyl imine was carried out also under HMPA conditions to give the desired (1*R*,2*S*)-*anti*-amino alcohol product with 98:2 dr and 92% *ee*. Removal of the benzoyl group with NaOH in methanol (1%) and of the sulfinyl group under acidic conditions (HCl/MeOH), followed by treatment with CDI (1,1′-carbonyldiimidazole), gave the enantiomerically enriched oxazolidone **8** in 89% yield, and this was smoothly converted into (−)-cytoxazone by oxidation of the double bond with O_3 and subsequent reduction of the ozonide with sodium borohydride by the literature procedure.[24g] On comparison of the optical rotation, the absolute stereochemistry of the prepared compound was found to be fully consis-



Scheme 5. Synthesis of (−)-cytoxazone through asymmetric benzoyloxyallylation.

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tent with that of the known (−)-cytoxazone {$[\alpha]_D^{21}$ −70.0 (c= 0.1, MeOH); lit.[23] $[\alpha]_D^{25}$ −71 (c=0.1, MeOH); lit.[24l] $[\alpha]_D^{24}$ −70.9 (c=0.1, MeOH)}. The total synthesis of (−)-cytoxazone had thus been easily achieved in three linear steps (82% overall yield) from the (*S*)-*N*-*tert*-butanesulfinyl imine of *p*-anisaldehyde. Similarly, (+)-cytoxazone could be obtained in the same way. To the best of our knowledge, this approach represents one of the most convenient and efficient syntheses of cytoxazone reported to date.

Conclusions

In summary, we have developed an efficient approach for the asymmetric synthesis of β-amino alcohol compounds containing α-vinyl groups through highly diastereoselective Zn-promoted Barbier-type α-hydroxyallylations of *N*-*tert*-butanesulfinyl imines with 3-benzoyloxyallyl bromide at room temperature. The method provides a new route for the direct α-hydroxyallylation of imines in a highly stereoselective manner. With the effective stereocontrol provided by the *tert*-butanesulfinyl group, benzoyloxyallyl addition to imine derivatives offers an attractive route to a variety of *anti*-β-amino-α-vinyl alcohols with excellent yields, diastereoselectivities, and enantioselectivities. Moreover, the synthetic value of the protocol has been demonstrated by the most concise and straightforward synthesis to date of (−)-cytoxazone. We believe that this promising methodology and the obtained valuable vinylic amino alcohols will find widespread use in asymmetric synthesis. Further explorations are now in progress in our laboratories.

Experimental Section

General: Chiral *N*-*tert*-butanesulfinyl imines were prepared from the chiral *N*-*tert*-butanesulfinyl amine and the corresponding aldehydes by the known method.[25] THF was distilled from sodium/benzophenone, and HMPA (**Caution**: toxic compound) was distilled from CaH_2. Zinc dust was activated by stirring for 5 min with HCl (1 M), followed by washing successively with water, acetone, and ether and drying with a heat gun. Reactions were monitored by thin layer chromatography (TLC) on glass plates coated with silica gel with fluorescent indicator (Huanghai HSGF254). Flash chromatography was performed on silica gel (Huanghai 300–400) with hexane/EtOAc as eluent. Mass spectra were recorded on a HP-5989 instrument and HRMS were measured on a Finnigan MA+ mass spectrometer. Infrared spectra were measured on a Perkin–Elmer 983 spectrometer. NMR spectra were recorded on a Varian or a Bruker spectrometer (300 MHz, 400 MHz, or 500 MHz), and chemical shifts are reported in δ (ppm) referenced to an internal TMS standard for ^{1}H NMR and $CDCl_3$ (77.0 ppm) for ^{13}C NMR. Optical rotations were measured on a JASCO P-1030 polarimeter with a sodium lamp.

General procedure for Zn-promoted benzoyloxyallylation of chiral *N*-*tert*-butanesulfinyl imines in THF: Freshly distilled dry THF (5 mL) was added at room temperature under argon to a Schlenk flask containing activated zinc powder (32 mg, 0.5 mmol), 3-benzoyloxyallyl bromide (121 mg, 0.5 mmol), and the (*R*)-*N*-*tert*-butanesulfinyl imine (52 mg, 0.25 mmol). The mixture was then stirred at RT for 3 h, quenched with brine (5 mL), and extracted with ethyl acetate. The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated. The residue was purified by silica gel column chromatography to afford the corresponding benzoyloxyallylation product **3**.

General procedure for Zn-promoted benzoyloxyallylation of chiral *N*-*tert*-butanesulfinyl imines in HMPA: H_2O (10 μL) was added at room temperature under argon to a suspension of activated zinc powder (32 mg, 0.5 mmol), 3-benzoyloxyallyl bromide (121 mg, 0.5 mmol), and the (*R*)-*N*-*tert*-butanesulfinyl imine (0.25 mmol) in dry HMPA (5 mL, *Caution*: TOXIC). The reaction mixture was stirred at RT for 12 h, quenched with aqueous HCl (1 M, 5 mL), and extracted with ethyl acetate. The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated. The residue was purified by silica gel column chromatography to afford the corresponding benzoyloxyallylation product **3**.

(1*S*,2*R*)-1-((*R*)-1,1-Dimethylethylsulfinamido)-1-phenylbut-3-en-2-yl benzoate (3a): $[\alpha]_D^{28}$ 39.4 (c=1.02, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ= 1.19 (s, 9H), 3.77 (d, J=5.2 Hz, 1H), 4.79 (dd, J_1=J_2=5.0 Hz, 1H), 5.30 (d, J=10.6 Hz, 1H), 5.37 (d, J=17.2 Hz, 1H), 5.74–5.81 (m, 1H), 5.92–5.74 (m, 1H), 7.27–7.57 (m, 8H), 8.01–8.02 ppm (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ=22.6, 56.5, 61.3, 76.4, 119.3, 127.9, 128.2, 128.4, 128.5, 129.5, 129.9, 132.2, 133.1, 138.2, 165.4 ppm; FT-IR (film): $\tilde{\nu}$=3325, 2985, 1711, 1455, 1269, 1062, 718, 701 cm^{-1}; ESI-MS: m/z (%): 372.2 $[M+H]^+$, 394.2 $[M+Na]^+$; HRMS (MALDI): m/z: calcd for $C_{21}H_{25}NO_3SNa$: 394.1462 $[M+Na]^+$; found: 394.1447.

Crystallographic data for (1*R*,2*S*)-3a ($C_{21}H_{25}NO_3S$): T=293(2) K; wavelength: 0.71073 Å; crystal system: triclinic, space group: *P*1; unit cell dimensions: a=5.7901 (12), b=9.569(2), c=10.630(2) Å, α=106.961, β= 100.943, γ=107.012°; V=513.72(18) Å^3; Z=1; ρ_{calcd}=1.201 Mg m^{-3}; $F(000)$=198; final R indices [$I>2\sigma$ (I)]: R_1=0.0603, wR_2=0.1520; R indices (all data), R_1=0.0688, wR_2=0.1572; 2905 reflections measured, 2468 unique (R_{int}=0.1172).

(1*S*,2*R*)-1-((*R*)-1,1-Dimethylethylsulfinamido)-1-(4-fluorophenyl)but-3-en-2-yl benzoate (3b): $[\alpha]_D^{26}$ 31.8 (c=1.03, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ=1.19 (s, 9H), 3.74 (d, J=5.9 Hz, 1H), 4.77 (dd, J_1=J_2= 5.1 Hz, 1H), 5.30–5.39 (m, 2H), 5.73–5.80 (m, 1H), 5.89–5.91 (m, 1H), 7.04–7.08 (m, 2H), 7.41–7.46 (m, 4H), 7.56–7.59 (m, 1H), 7.99–8.01 ppm (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ=22.5, 56.5, 60.8, 76.3, 115.4, 115.5, 119.6, 128.5, 129.5, 129.6, 129.7, 129.8, 132.1, 133.2, 134.01, 134.03, 161.5, 163.5, 165.4 ppm; FT-IR (film): $\tilde{\nu}$=3434, 3313, 2968, 2928, 1708, 1512, 1049, 712 cm^{-1}; ESI-MS: m/z (%): 390.2 $[M+H]^+$, 412.2 $[M+Na]^+$; HRMS (MALDI): m/z: calcd for $C_{21}H_{24}NO_3SFNa$: 412.1373 $[M+Na]^+$; found: 412.1353.

(1*S*,2*R*)-1-(2-Chlorophenyl)-1-((*R*)-1,1-dimethylethylsulfinamido)but-3-en-2-yl benzoate (3c): $[\alpha]_D^{26}$ 26.2 (c=0.97, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ=1.20 (s, 9H), 4.01 (d, J=7.4 Hz, 1H), 5.23 (dd, J=7.2, 5.7 Hz, 1H), 5.32 (d, J=10.5 Hz, 1H), 5.38 (d, J=17.1 Hz, 1H), 5.81–5.90 (m, 1H), 5.93–5.96 (m, 1H), 7.20–7.29 (m, 2H), 7.36–7.44 (m, 3H), 7.50–7.55 (m, 2H), 7.99–8.01 ppm (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=22.5, 56.7, 58.2, 75.4, 119.5, 126.9, 128.4, 129.3, 129.4, 129.6, 129.8, 129.9, 132.2, 133.1, 133.4, 136.1, 165.0 ppm; FT-IR (KBr): $\tilde{\nu}$=3318, 3085, 3044, 2964, 1716, 1269, 1066, 761, 718 cm^{-1}; ESI-MS: m/z (%): 406.2 $[M+H]^+$, 428.2 $[M+Na]^+$; HRMS (MALDI): m/z: calcd for $C_{21}H_{24}NO_3SClNa$: 428.1077 $[M+Na]^+$; found: 428.1058.

(1*S*,2*R*)-1-(3-Chlorophenyl)-1-((*R*)-1,1-dimethylethylsulfinamido)but-3-en-2-yl benzoate (3d): $[\alpha]_D^{26}$ 33.4 (c=1.05, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ=1.19 (s, 9H), 3.76 (d, J=5.9 Hz, 1H), 4.76 (dd, J=5.8, 4.2 Hz, 1H), 5.31–5.40 (m, 2H), 5.71–5.79 (m, 1H), 5.76–5.91 (m, 1H), 7.26–7.31 (m, 3H), 7.43–7.47 (m, 3H), 7.56–7.58 (m, 1H), 8.00–8.02 ppm (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=22.6, 56.7, 60.9, 76.1, 119.7, 126.3, 128.2, 128.5, 129.6, 129.8, 131.9, 133.3, 134.5, 140.2, 165.3 ppm; FT-IR (KBr): $\tilde{\nu}$=3428, 2960, 2922, 1709, 1262, 1115, 1051, 715, 699 cm^{-1}; ESI-MS: m/z (%): 406.2 $[M+H]^+$, 428.2 $[M+Na]^+$; HRMS (MALDI): m/z: calcd for $C_{21}H_{24}NO_3SClNa$: 428.1072 $[M+Na]^+$; found: 428.1058.

(1*S*,2*R*)-1-(4-Chlorophenyl)-1-((*R*)-1,1-dimethylethylsulfinamido)but-3-en-2-yl benzoate (3e): $[\alpha]_D^{26}$ 47.1 (c=1.03, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ=1.19 (s, 9H), 3.76 (d, J=6.1 Hz, 1H), 4.76 (dd, J=6.0, 4.4 Hz, 1H), 5.30–5.40 (m, 2H), 5.72–5.78 (m, 1H), 5.89–5.91 (m, 1H), 7.33–7.40 (m, 4H), 7.43–7.46 (m, 2H), 7.55–7.60 (m, 1H), 7.99–8.01 ppm (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=22.5, 56.6, 60.8, 76.2, 119.6, 128.5, 128.7,

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129.3, 129.5, 129.8, 132.0, 133.2, 134.1, 136.7, 165.3 ppm; FT-IR (film): $\tilde{\nu}$ = 3434, 2958, 1715, 1317, 1270, 1114, 1053, 931, 712 cm^{-1}; ESI-MS: *m/z* (%): 406.2 $[M+H]^+$, 428.2 $[M+Na]^+$; HRMS (MALDI): *m/z*: calcd for $C_{21}H_{25}ClO_3NS$: 406.1219 $[M+H]^+$; found: 406.1238.

(1*S*,2*R*)-1-(3-Bromophenyl)-1-((*R*)-1,1-dimethylethylsulfinamido)but-3-en-2-yl benzoate (3f): $[\alpha]_D^{25}$ 34.2 (*c* = 0.97, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ = 1.19 (s, 9H), 3.82 (d, *J* = 5.6 Hz, 1H), 4.74 (dd, $J_1 = J_2$ = 5.0 Hz, 1H), 5.30–5.39 (m, 2H), 5.71–5.79 (m, 1H), 5.89–5.92 (m, 1H), 7.24 (td, *J* = 5.7, 1.6 Hz, 1H), 7.36 (d, *J* = 7.8 Hz, 1H), 7.43–7.47 (m, 3H), 7.55–7.59 (m, 1H), 7.64 (s, 1H), 8.00–8.06 ppm (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 22.5, 56.5, 60.8, 76.0, 119.6, 122.5, 126.7, 128.4, 129.5, 129.7, 129.9, 131.1, 131.3, 131.9, 133.2, 140.4, 165.2 ppm; FT-IR (KBr): $\tilde{\nu}$ = 3337, 2926, 1712, 1519, 1320, 1267, 1061, 714, 684 cm^{-1}; ESI-MS: *m/z* (%): 450.1 $[M+H]^+$, 472.1$[M+Na]^+$; HRMS (MALDI): *m/z*: calcd for $C_{21}H_{24}NO_3SBrNa$: 472.0572 $[M+Na]^+$; found: 472.0553.

(1*S*,2*R*)-1-(4-Bromophenyl)-1-((*R*)-1,1-dimethylethylsulfinamido)but-3-en-2-yl benzoate (3g): $[\alpha]_D^{28}$ 48.9 (*c* = 1.05, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ = 1.18 (s, 9H), 3.73 (d, *J* = 5.1 Hz, 1H), 4.74 (dd, $J_1 = J_2$ = 5.2 Hz, 1H), 5.30–5.40 (m, 2H), 5.71–5.79 (m, 1H), 5.88–5.91 (m, 1H), 7.31–7.33 (m, 2H), 7.43–7.52 (m, 4H), 7.56–7.58 (m, 1H), 7.99–8.01 ppm (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 22.6, 56.6, 60.9, 76.2, 119.7, 122.3, 128.5, 129.6, 129.7, 129.8, 131.7, 132.0, 133.3, 137.3, 165.4 ppm; FT-IR (film): $\tilde{\nu}$ = 3339, 2956, 2923, 1713, 1267, 1064, 988, 714 cm^{-1}; ESI-MS: *m/z* (%): 450.2 $[M+H]^+$, 472.2 $[M+Na]^+$; HRMS (MALDI): *m/z*: calcd for $C_{21}H_{25}NO_3SBr$: 450.0752 $[M+H]^+$; found: 450.0733.

(1*S*,2*R*)-1-((*R*)-1,1-Dimethylethylsulfinamido)-1-*o*-tolylbut-3-en-2-yl benzoate (3h): $[\alpha]_D^{27}$ 26.0 (*c* = 1.03, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ = 1.18 (s, 9H), 2.50 (s, 3H), 3.73 (d, *J* = 5.2 Hz, 1H), 5.06 (dd, $J_1 = J_2$ = 4.6 Hz, 1H), 5.33 (d, *J* = 9.4 Hz, 1H), 5.42 (d, *J* = 15.4 Hz, 1H), 5.82–5.86 (m, 2H), 7.17–7.24 (m, 3H), 7.42–7.45 (m, 3H), 7.54–7.57 (m, 1H), 8.02 ppm (d, *J* = 7.7 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 19.7, 22.6, 56.3, 56.4, 76.0, 119.7, 126.2, 127.1, 127.9, 128.4, 129.6, 130.0, 130.7, 132.1, 133.1, 136.0, 136.8, 165.3 ppm; FT-IR (KBr): $\tilde{\nu}$ = 3323, 2983, 2965, 2928, 1718, 1268, 1112, 1064, 719, 706 cm^{-1}; ESI-MS: *m/z* (%): 386.2 $[M+H]^+$, 408.3 $[M+Na]^+$; HRMS (MALDI): *m/z*: calcd for $C_{22}H_{27}NO_3SNa$: 408.1623 $[M+Na]^+$; found: 408.1604.

(1*S*,2*R*)-1-((*R*)-1,1-Dimethylethylsulfinamido)-1-*p*-tolylbut-3-en-2-yl benzoate (3i): $[\alpha]_D^{29}$ 49.6 (*c* = 1.06, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ = 1.19 (s, 9H), 2.33 (s, 3H), 3.71 (d, *J* = 5.6 Hz, 1H), 4.75 (dd, $J_1 = J_2$ = 4.9 Hz, 1H), 5.27–5.39 (m, 2H), 5.74–5.82 (m, 1H), 5.90–5.92 (m, 1H), 7.15–7.18 (m, 2H), 7.32 (d, *J* = 7.7 Hz, 2H), 7.43 (t, *J* = 7.6 Hz, 2H), 7.54–7.58 (m,1H), 8.01–8.03 ppm (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.0, 22.5, 56.4, 61.1, 76.4, 119.2, 127.8, 128.4, 129.2, 129.5, 130.0, 132.3, 133.0, 135.2, 137.9, 165.4 ppm; FT-IR (film): $\tilde{\nu}$ = 3338, 3061, 2953, 2923, 2852, 1712, 1267, 1118, 1062, 987, 715, 700 cm^{-1}; ESI-MS: *m/z* (%): 386.3 $[M+H]^+$, 408.3 $[M+Na]^+$; HRMS (MALDI): *m/z*: calcd for $C_{22}H_{27}NO_3SNa$: 408.1621 $[M+Na]^+$; found: 408.1604.

(1*S*,2*R*)-1-((*R*)-1,1-Dimethylethylsulfinamido)-1-[4-(methylthio)phenyl]-but-3-en-2-yl benzoate (3j): $[\alpha]_D^{27}$ 60.2 (*c* = 1.05, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$): δ = 1.15 (s, 9H), 2.43 (s, 3H), 3.74 (d, *J* = 5.7 Hz, 1H), 4.70 (dd, $J_1 = J_2$ = 4.7 Hz, 1H), 5.25–5.37 (m, 2H), 5.68–5.79 (m, 1H), 5.73–5.89 (m, 1H), 7.21 (d, *J* = 7.8 Hz, 2H), 7.34 (d, *J* = 8.1 Hz, 2H), 7.41 (t, *J* = 3.8 Hz, 2H), 7.54 (t, *J* = 7.2 Hz, 1H), 7.99 ppm (d, *J* = 7.5 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 15.4, 22.4, 56.3, 60.7, 76.1, 119.3, 126.1, 128.2, 128.3, 129.4, 129.7, 132.0, 133.0, 134.7, 138.5, 165.2 ppm; FT-IR (film): $\tilde{\nu}$ = 3340, 2976, 2958, 2921, 1713, 1268, 1114, 1060, 717, 703 cm^{-1}; ESI-MS: *m/z* (%): 418.3 $[M+H]^+$, 440.3 $[M+Na]^+$; HRMS (MALDI): *m/z*: calcd for $C_{22}H_{27}O_3NS_2Na$: 440.1343 $[M+Na]^+$; found: 440.1325.

(1*S*,2*R*)-1-((*R*)-1,1-Dimethylethylsulfinamido)-1-(3-methoxyphenyl)but-3-en-2-yl benzoate (3k): $[\alpha]_D^{26}$ 33.9 (*c* = 0.96, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ = 1.19 (s, 9H), 3.75–3.80 (m, 4H), 4.77 (dd, $J_1 = J_2$ = 4.9 Hz, 1H), 5.31 (d, *J* = 10.6 Hz, 1H), 5.39 (d, *J* = 17.2 Hz, 1H), 5.76–5.83 (m, 1H), 5.91–5.93 (m, 1H), 6.84–6.86 (m, 1H), 6.94–7.03 (m, 2H), 7.27–7.30 (m, 1H), 7.44 (t, *J* = 7.7 Hz, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 8.02–8.04 ppm (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 22.5, 55.2, 56.5, 61.2, 76.4, 113.6, 113.7, 119.3, 120.1, 128.4, 129.5, 129.9, 132.2, 133.1, 139.8, 159.6, 165.3 ppm; FT-IR (film): $\tilde{\nu}$ = 3337, 2960, 2835, 1713, 1600, 1272, 1068, 717, 711 cm^{-1}; ESI-MS: *m/z* (%): 402.2 $[M+H]^+$, 424.2 $[M+Na]^+$; HRMS (MALDI): *m/z*: calcd for $C_{22}H_{27}NO_4SNa$: 424.1570 $[M+Na]^+$; found: 424.1553.

(1*S*,2*R*)-1-((*R*)-1,1-Dimethylethylsulfinamido)-1-(4-methoxyphenyl)but-3-en-2-yl benzoate (3l): $[\alpha]_D^{27}$ 41.9 (*c* = 1.03, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ = 1.19 (s, 9H), 3.68 (d, *J* = 5.5 Hz, 1H), 3.80 (s, 3H), 4.73 (dd, $J_1 = J_2$ = 4.9 Hz, 1H), 5.28–5.39 (m, 2H), 5.74–5.80 (m, 1H), 5.89–5.92 (m, 1H), 6.88–6.92 (m, 2H), 7.34–7.38 (m, 2H), 7.42–7.46 (m, 2H), 7.68–7.59 (m, 1H), 8.01–8.03 ppm (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 22.6, 55.2, 56.4, 60.9, 76.4, 113.9, 119.3, 128.4, 129.1, 129.6, 130.0, 130.3, 132.5, 133.1, 159.4, 165.4 ppm.; FT-IR (film): $\tilde{\nu}$ = 3431, 3310, 2958, 2929, 1710, 1261, 1051, 713 cm^{-1}; ESI-MS: *m/z* (%): 402.3 $[M+H]^+$, 424.2 $[M+Na]^+$; HRMS (MALDI): *m/z*: calcd for $C_{22}H_{27}NO_4SNa$: 424.1573 $[M+Na]^+$; found: 424.1553.

(1*S*,2*R*)-1-(2,4-Dimethoxyphenyl)-1-((*R*)-1,1-dimethylethylsulfinamido)-but-3-en-2-yl benzoate (3m): $[\alpha]_D^{25}$ −15.1 (*c* = 1.01, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$): δ = 1.19 (s, 9H), 3.73 (s, 3H), 3.81 (s, 3H), 4.23 (d, *J* = 8.7 Hz, 1H), 4.82 (dd, *J* = 8.3, 5.9 Hz, 1H), 5.23–5.34 (m, 2H), 5.80–5.94 (m, 2H), 6.40–6.45 (m, 2H), 7.23 (d, *J* = 8.1 Hz, 1H), 7.35–7.53 (m, 3H), 7.91–7.94 ppm (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 22.5, 55.3, 55.4, 56.4, 59.0, 75.9, 98.9, 104.5, 118.3, 119.4, 128.3, 129.5, 129.7, 129.8, 132.9, 133.5, 157.8, 160.6, 165.2 ppm; FT-IR (film): $\tilde{\nu}$ = 3336, 2958, 1712, 1519, 1267, 1118, 1061, 714 cm^{-1}; ESI-MS: *m/z* (%): 432.3 $[M+H]^+$, 454.3 $[M+Na]^+$; HRMS (MALDI): *m/z*: calcd for $C_{23}H_{29}NO_5SNa$: 454.1675 $[M+Na]^+$; found: 454.1659.

(1*S*,2*R*)-1-(2,4-Dichlorophenyl)-1-((*R*)-1,1-dimethylethylsulfinamido)but-3-en-2-yl benzoate (3n): $[\alpha]_D^{26}$ 34.5 (*c* = 0.99, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$): δ = 1.20 (s, 9H), 4.05 (d, *J* = 7.8 Hz, 1H), 5.19–5.23 (m, 1H), 5.32–5.41 (m, 2H), 5.78–5.94 (m, 2H), 7.26–7.30 (m, 1H), 7.39–7.48 (m, 4H), 7.55–7.60 (m, 1H), 7.99–8.02 ppm (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 22.5, 56.8, 57.7, 75.2, 119.7, 127.3, 128.4, 129.5, 129.6, 130.4, 131.9, 133.3, 134.1, 134.5, 134.8, 165.0 ppm; FT-IR (film): $\tilde{\nu}$ = 2923, 1722, 1561, 1475, 1268, 1110, 1026, 711 cm^{-1}; ESI-MS: *m/z* (%): 440.2 $[M+H]^+$, 462.2 $[M+Na]^+$; HRMS (MALDI): *m/z*: calcd for $C_{21}H_{23}NO_3SNaCl_2$: 462.0685 $[M+Na]^+$; found: 462.0668.

(1*S*,2*R*)-1-((*R*)-1,1-Dimethylethylsulfinamido)-1-(naphthalen-2-yl)but-3-en-2-yl benzoate (3o): $[\alpha]_D^{27}$ 59.2 (*c* = 1.00, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ = 1.21 (s, 9H), 3.89 (d, *J* = 5.7 Hz, 1H), 4.97 (dd, $J_1 = J_2$ = 4.9 Hz, 1H), 5.30 (d, *J* = 10.6 Hz, 1H), 5.39 (d, *J* = 17.2 Hz, 1H), 5.76–5.84 (m, 1H), 6.02–6.04 (m, 1H), 7.42–7.51 (m, 4H), 7.55–7.60 (m, 2H), 7.83–7.90 (m, 4H), 8.03–8.05 ppm (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 22.6, 56.6, 61.3, 76.4, 119.5, 125.6, 126.3, 126.4, 127.3, 127.7, 128.1, 128.4, 128.5, 129.6, 129.9, 132.1, 133.10, 133.12, 133.2, 135.6, 165.5 ppm; FT-IR (film): $\tilde{\nu}$ = 3464, 3345, 3046, 2952, 1713, 1266, 1115, 1060, 715 cm^{-1}; ESI-MS: *m/z* (%): 422.2 $[M+H]^+$, 444.3 $[M+Na]^+$; HRMS (MALDI): *m/z*: calcd for $C_{25}H_{27}NO_3SNa$: 444.1621 $[M+Na]^+$; found: 444.1604.

4-((*R*)-1,1-Dimethylethylsulfinamido)-6-phenylhex-1-en-3-yl benzoate (3p): $[\alpha]_D^{26}$ −20.9 (*c* = 1.03, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ = 1.21 (s, 9H), 1.82–1.96 (m, 1H), 2.03–2.14 (m, 1H), 2.76–3.00 (m, 2H), 3.24 (d, *J* = 7.2 Hz, 1H), 3.56–3.66 (m, 1H), 5.29–5.42 (m, 2H), 5.54–5.57 (m, 1H), 5.82–5.94 (m, 1H), 7.16–7.22 (m, 1H), 7.25–7.30 (m, 4H), 7.41–7.47 (m, 2H), 7.54–7.60 (m, 1H), 8.01–8.05 ppm (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 22.6, 31.7, 33.8, 56.2, 58.9, 77.3, 119.1, 126.0, 128.3, 128.4, 128.5, 129.5, 129.9, 132.4, 133.1, 141.0, 165.3 ppm; FT-IR (film): $\tilde{\nu}$ = 3494, 3130, 3027, 2955, 2860, 1712, 1266, 1027, 713 cm^{-1}; ESI-MS: *m/z* (%): 400.3 $[M+H]^+$, 422.3 $[M+Na]^+$; HRMS (MALDI): *m/z*: calcd for $C_{23}H_{29}NO_3SNa$: 422.1778 $[M+Na]^+$; found: 422.1760.

4-((*R*)-1,1-Dimethylethylsulfinamido)hept-1-en-3-yl benzoate (3q): ^1H NMR (400 MHz, $CDCl_3$): δ = 0.95 (t, *J* = 7.0 Hz, 3H), 1.18 (s, 9H), 1.40–1.69 (m, 4H), 3.08 (d, *J* = 6.4 Hz, 1H), 3.57–3.63 (m, 1H), 5.33 (d, *J* = 10.8 Hz, 1H), 5.38 (d, *J* = 17.2 Hz, 1H), 5.51–5.52 (m, 1H), 5.85–5.94 (m, 1H), 7.40–7.44 (m, 2H), 7.53–7.57 (m, 1H), 8.02 ppm (d, *J* = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.7, 19.0, 22.6, 34.4, 56.1, 58.9, 77.2, 119.1, 128.3, 129.5, 132.2, 133.0, 133.4, 165.4 ppm; FT-IR (KBr): $\tilde{\nu}$ = 3233, 3070, 2959, 2872, 1721, 1270, 1111, 1069, 713 cm^{-1}; ESI-MS: *m/z* (%): 338.2 $[M+H]^+$, 360.2 $[M+Na]^+$; HRMS (MALDI): *m/z*: calcd for $C_{18}H_{27}NO_3SNa$: 360.1604 $[M+Na]^+$; found: 360.1612.

4-((*R*)-1,1-Dimethylethylsulfinamido)-6-methylhept-1-en-3-yl benzoate (3r): ^1H NMR (400 MHz, $CDCl_3$): δ = 0.93–0.99 (m, 6H), 1.18 (s, 9H),

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1.46–1.52 (m, 2H), 1.83–1.93 (m, 1H), 3.05 (d, $J=7.2$ Hz, 1H), 3.64–3.70 (m, 1H), 5.34 (d, $J=10.4$ Hz, 1H), 5.38 (d, $J=17.2$ Hz, 1H), 5.50–5.51 (m, 1H), 5.85–5.94 (m, 1H), 7.41–7.46 (m, 2H), 7.53–7.57 (m, 1H), 8.03 ppm (d, $J=7.2$ Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=21.7$, 22.6, 23.1, 24.0, 41.4, 56.1, 57.1, 77.4, 119.2, 128.3, 129.5, 132.2, 133.0, 133.4, 165.4 ppm; FT-IR (KBr): $\tilde{\nu}=3231$, 3068, 2957, 2869, 1720, 1270, 1111, 1069, 713 cm^{-1}; ESI-MS: m/z (%): 352.2 $[M+H]^+$, 374.2 $[M+Na]^+$; HRMS (MALDI): m/z: calcd for $C_{19}H_{29}NO_3SNa^+$: 374.1760 $[M+Na]^+$; found: 374.1779.

(1*S*,2*R*)-1-Cyclohexyl-1-((*R*)-1,1-dimethylethylsulfinamido)but-3-en-2-yl benzoate (3s): $[\alpha]_D^{28}$ −5.9 ($c=1.07$, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): $\delta=1.10$–1.38 (m, 15H), 1.52–1.55 (m, 1H), 1.66 (m, 1H), 1.82–1.85 (m, 3H), 2.00 (d, $J=12.6$ Hz, 1H), 3.20 (d, $J=7.6$ Hz, 1H), 3.44–3.49 (m, 1H), 5.35–5.51 (m, 2H), 5.65–5.67 (m, 1H), 5.91–6.01 (m, 1H), 7.41–7.48 (m, 2H), 7.54–7.58 (m, 1H), 8.05 ppm (d, $J=7.6$ Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta=22.8$, 25.9, 26.0, 26.1, 29.1, 30.3, 39.8, 56.4, 63.8, 75.9, 119.3, 128.3, 129.6, 130.1, 132.6, 133.0, 165.5 ppm; FT-IR (film): $\tilde{\nu}=$ 3249, 3072, 2927, 2854, 1716, 1451, 1273, 1113, 1069, 713 cm^{-1}; ESI-MS: m/z (%): 378.3 $[M+H]^+$, 400.3 $[M+Na]^+$; HRMS (MALDI): m/z: calcd for $C_{21}H_{31}NO_3SNa$: 400.1936 $[M+Na]^+$; found: 400.1917.

1-Acetamido-1-phenylbut-3-en-2-yl benzoate (*anti*-5a): A solution of HCl in 1,4-dioxane (4N, 0.2 mL) was added to a solution of the benzoyloxyallylation product **3a** (74 mg, 0.2 mmol) obtained from the THF system (Table 1, entry 1) in dry methanol (2 mL). The mixture was stirred at RT for 0.5 hour and the solvent was removed in vacuo. Triethylamine (0.4 mL) and acetic anhydride (40 μL, 0.4 mmol) were added to the solution of the resulting crude product dissolved in fresh CH_2Cl_2 (2 mL). The mixture was stirred at RT for 3 h, followed by the addition of ethyl acetate (30 mL). The solution was washed with brine, dried, filtered, and concentrated in vacuo. Purification by flash column chromatography gave the major product *anti*-**5a** as a white solid (61 mg, 99%). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=2.02$ (s, 3H), 5.28–5.45 (m, 3H), 5.73–5.87 (m, 2H), 6.19 (d, $J=8.0$ Hz, 1H), 7.26–7.46 (m, 7H), 7.57 (t, $J=7.6$ Hz, 1H), 7.99 ppm (d, $J=7.2$ Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=23.4$, 55.7, 76.5, 119.1, 127.4, 127.9, 128.5, 128.6, 129.7, 129.8, 132.4, 133.3, 137.5, 165.6, 169.3 ppm; FT-IR (film): $\tilde{\nu}=3271$, 3071, 1713, 1648, 1272, 1106, 713, 698 cm^{-1}; ESI-MS: m/z (%): 332.0 $[M+Na]^+$, 347.8 $[M+K]^+$, 364.0 $[M+MeOH+Na]^+$; HRMS (MALDI): m/z: calcd for $C_{19}H_{19}NO_3Na^+$: 332.12572 $[M+Na]^+$; found: 332.1257.

(4*R*,5*S*)-3-Acetyl-5-ethyl-4-phenyloxazolidin-2-one (*cis*-6a): Compound *anti*-**5a** (46 mg, 0.15 mol), obtained as above, was added to sodium hydroxide in methanol (1%). After the system had been stirred at RT for 40 min, the solvent was removed in vacuo and H_2O (5 mL) was added to the residue. The solution was extracted with ethyl acetate, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was dissolved in anhydrous THF (5 mL) and mixed with 1,1′-carbonyldiimidazole (CDI, 49 mg, 0.30 mmol) and NaH (36 mg, 1.5 mmol). The resulting suspension was stirred under argon at RT for 18 h and filtered. The filter cake was rinsed with ethyl acetate. The combined organic phases were washed with HCl (1N) and sat. aqueous $NaHCO_3$, dried, filtered, and concentrated. Purification by silica gel column chromatography gave the unsaturated oxazolidinone product in 71% yield (25 mg). Pd/C (5 mg, 10 wt.% Pd) was carefully added to a solution of this unsaturated oxazolidinone product (23 mg, 0.1 mmol) in MeOH (5 mL). The reaction mixture was stirred under H_2 for 12 h and filtered through celite. The combined organic phases were concentrated. Purification by flash column chromatography gave the saturated oxazolidinone derivative **6a** (21 mg, 92%). $[\alpha]_D^{22}$ −63.4 ($c=0.46$, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=0.92$ (t, $J=7.4$ Hz, 3H), 1.21–1.27 (m, 2H), 2.53 (s, 3H), 4.65 (dt, $J=5.7$, 7.6 Hz, 1H), 5.38 (d, $J=7.6$ Hz, 1H), 7.17–7.19 (m, 2H), 7.33–7.39 ppm (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=9.0$, 22.78, 22.82, 60.1, 79.7, 126.0, 127.7, 127.8, 134.2, 153.0, 168.5 ppm; FT-IR (film): $\tilde{\nu}=3034$, 2973, 1782, 1709, 1372, 1317, 1201, 1047, 706 cm^{-1}; ESI-MS: m/z (%): 234.0 $[M+H]^+$, 256.0 $[M+Na]^+$; HRMS (MALDI): m/z: calcd for $C_{13}H_{15}NO_3Na$: 256.09441 $[M+Na]^+$; found: 256.09470.

(4*R*,5*S*)-4-(4-Methoxyphenyl)-5-vinyloxazolidin-2-one (8): The benzoyloxyallylation product (1*R*,2*S*)-**3l** (1.965 g, 4.9 mol) was added to sodium hydroxide in methanol (1%). After the system had been stirred at RT for 40 min, the solvent was removed in vacuo, and H_2O (10 mL) was added. The solution was extracted with ethyl acetate, dried over anhydrous Na_2SO_4, and concentrated in vacuo. The residue was dissolved in methanol (5 mL) and mixed with a solution of dry HCl in 1,4-dioxane (4N, 5 mL). The mixture was stirred at RT for 0.5 h, neutralized with ammonia, and extracted with EtOAc. After concentration of the combined organic phases under reduced pressure, 1,1-carbonyldiimidazole (CDI, 6 mmol, 810 mg) and *N*,*N*-4-dimethylaminopyridine (DMAP, 1 mmol, 122 mg) were added to a solution of the resulting crude product in fresh THF (10 mL). The mixture was stirred at room temperature for 18 h and was then quenched with saturated aqueous NH_4Cl (10 mL). The aqueous phase was extracted with EtOAc, washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. Purification by flash column chromatography gave oxazolidone **8** as a pale yellow solid (0.974 g, 89%). $[\alpha]_D^{24}$ −12.0 ($c=1.01$, $CHCl_3$); ^{1}HNMR (300 MHz, $CDCl_3$): $\delta=3.81$ (s, 3H), 4.94 (d, $J=7.5$ Hz, 1H), 5.11–5.15 (m, 1H), 5.22–5.36 (m, 3H), 5.51 (brs, 1H), 6.89 (d, $J=8.4$ Hz, 2H), 7.13 ppm (d, $J=8.7$ Hz, 2H); EI-MS: m/z (%): 219 (14.59) $[M]^+$, 162 (92.70), 135 (100.00).

(−)-Cytoxazone: Ozone was bubbled through a solution of **8** (0.876 g, 4.0 mmol) in anhydrous CH_2Cl_2 (10 mL) and MeOH (20 mL) at −78°C until the blue color persisted, the excess was then purged out with N_2 until decolorization, and $NaBH_4$ (1.52 g, 40 mmol) was added at −78°C. The reaction mixture was slowly warmed to 0°C, stirred at 0°C for 1 h, and concentrated in vacuo. The residue was dissolved in H_2O (30 mL) and EtOAc (200 mL), and the organic layer was separated and washed with H_2O and brine, dried over anhydrous Na_2SO_4, and concentrated in vacuo. The residue was purified by column chromatography to give (−)-cytoxazone (0.83 g, 93%) as a white solid. $[\alpha]_D^{21}$ −70.0 ($c=0.1$, MeOH); ^{1}H NMR (300 MHz, [D$_6$]DMSO): $\delta=2.94$–2.98 (m, 2H), 3.75 (s, 3H), 4.67–4.72 (m, 1H), 4.85–4.87 (m, 1H), 4.91 (d, $J=8.4$ Hz, 1H), 6.94 (d, $J=8.1$ Hz, 2H), 7.15 (d, $J=8.4$ Hz, 2H), 8.08 ppm (s, 2H); ^{13}C NMR (100 MHz, [D$_6$]DMSO): $\delta=55.0$, 56.1, 61.0, 80.0, 113.6, 128.0, 129.2, 158.8, 159.0 ppm; EI-MS: m/z (%): 223 (17.90) $[M]^+$, 163 (32.59), 135 (100.00).

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