Allylation of Exocyclic *N*-Acyliminium Ions Generated from Chiral *N*-[1-(Phenylsulfonyl)alkyl]oxazolidin-2-ones†

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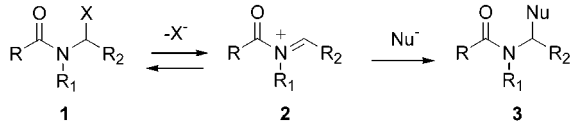
N-[1-(Phenylsulfonyl)alkyl]oxazolidin-2-ones are successfully prepared by condensation of the corresponding optically active oxazolidin-2-ones with aldehydes and benzenesulfinic acid. At low temperature, in the presence of titanium tetrachloride, these sulfones are converted into *N*-acyliminium ions, which react with allyltrimethylsilane with a variable degree of stereoselectivity. The best results are obtained with (*R*)-5,5-dimethyl-4-phenyloxazolidin-2-one as a chiral auxiliary. Cleavage of the oxazolidin-2-one ring with lithium/ammonia affords the corresponding homoallylamines, which reveal an absolute configuration opposite that expected on the basis of the usual steric effects. A complexation of the Lewis acid with the *N*-acyliminium ion may be responsible of this rather unusual stereochemical outcome.

Introduction

Electrophilic substrates featuring carbon−nitrogen double bonds as *N*-acyliminium ions have found a widespread utilization as reactive intermediates for the synthesis of functionalized amino derivatives.[1] In comparison with the usual imino derivatives, these reagents possess an enhanced reactivity that allows them to react even with weak nucleophiles at low temperatures. *N*-Acyliminium ion **2** is usually generated by an acid-promoted elimination of α-substituted amido derivative **1** and is immediately made to react with a nucleophile to the addition product **3** (Scheme 1).

Scheme 1



1 **2** **3**

The choice of a suitable leaving group X in the amido derivative **1** is mandatory since it can affect the equilibrium in which the iminium ion is involved. α-Alkoxy amides[2] are the most popular precursors for *N*-acyliminium ions even though the alkoxy group can sometimes be substituted with other reactive leaving groups such as halogens[3] and amides.[4] Particularly interesting is the utilization of the phenylsulfonyl group for this purpose since it acts as a good leaving group and its derivatives are mostly stable solids easy to purify by crystallization.[5]

The chemistry of *N*-acyliminium ions has been mainly addressed in regard to the synthesis of nitrogenated heterocyclic compounds owing to their importance as biologically active substances.[6] This led to the development of many stereoselective syntheses in which cyclic *N*-acyliminium ions were involved.[7] Much less attention has been devoted to acyclic stereoselection produced by optically active linear *N*-acyliminium ions[8] or chiral nucleophilic reagents with achiral *N*-acyliminium ions.[9] In this paper we report the synthesis of optically active (phenylsulfonyl)alkyloxazolidin-2-ones and their utiliza-

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† Dedicated to Professor Giuseppe Bartoli on the occasion of his 60th birthday.

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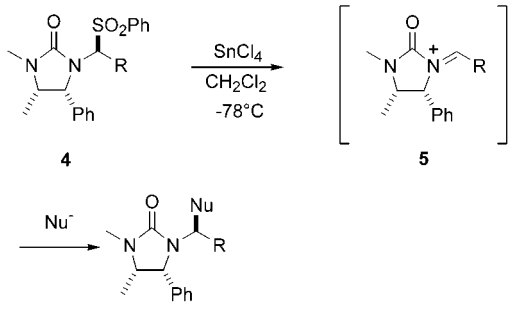
Scheme 2



tion as precursors of *N*-acyliminium ions in the reaction with allyltrimethylsilane.

Results and Discussion

Synthesis of *N*-[1-(Phenylsulfonyl)alkyl]oxazolidin-2-ones. Recently, we have reported that chiral exocyclic *N*-acyliminium ions **5** can be generated starting from *N*-[1-(phenylsulfonyl)alkyl] imidazolidin-2-ones **4**[10] in the presence of tin tetrachloride.[11] These electrophilic ions have been made to react with different nucleophiles, giving the corresponding addition products **6** in good yields and high diastereoselectivities (Scheme 2). Unfortunately, the imidazolidin-2-one ring has proved to be resistant to various cleavage conditions, and therefore, the preparation of primary amino derivatives is not achievable by this method. Thus, we turned our attention to the use of oxazolidin-2-ones as chiral auxiliaries[12] since they are readily available compounds and are cleavable under reductive conditions.[13]

Classical methods used for the synthesis of phenylsulfonyl derivatives of imidazolidin-2-ones and cogeners usually involve a reaction with an aldehyde and sodium benzenesulfinate in aqueous solutions.[10,11] However, these conditions are totally uneffective when 4-substituted oxazolidin-2-ones are used as substrates probably because of the unfavorable equilibrium that hinders the formation of the phenylsulfonyl derivative in water.[14] For this reason we decided to exploit the formation of (phenylsulfonyl)alkyloxazolidin-2-ones in organic solvents using benzenesulfinic acid in place of its sodium salt. Oxazolidin-2-ones **7** react with aldehydes **8** and benzenesulfinic acid in dry dichloromethane and in the presence of magnesium sulfate, which acts as a water scavenger,

Scheme 3

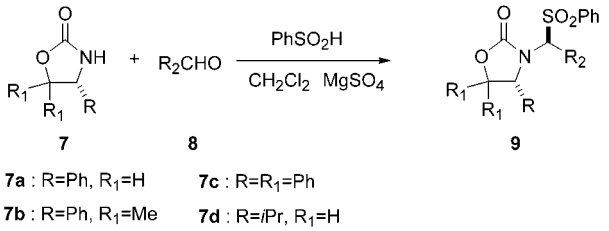


Table 1. Synthesis of Phenylsulfonyloxazolidin-2-ones 9

entry	7	aldehyde **8**	9	dr[a]	yield,[b] %
1	**7a**	EtCHO (**8a**)	**9a**	85:15	95
2	**7a**	$(CH_3)_2CHCH_2CHO$ (**8b**)	**9b**	85:15	86
3	**7a**	$(CH_3)_2CHCHO$ (**8c**)	**9c**	80:20	70
4	**7a**	$PhCH_2CH_2CHO$ (**8d**)	**9d**	90:10	68
5	**7a**	n-$C_7H_{15}CHO$ (**8e**)	**9e**	90:10	80
6	**7a**	$Cl(CH_2)_5CHO$ (**8f**)	**9f**	90:10	72
7	**7a**	$CH_2{=}CH(CH_2)_7CHO$ (**8g**)	**9g**	90:10	78
8	**7b**	**8b**	**9h**	80:20	75
9	**7b**	**8c**	**9i**	90:10	65
10	**7b**	**8d**	**9j**	75:25	83
11	**7b**	**8e**	**9k**	75:25	95
12	**7c**	**8b**	**9l**	80:20	68
13	**7d**	**8b**	**9m**	80:20	83

[a] The diastereomeric ratio was evaluated by ^{1}H NMR analysis [b] Yields of pure, isolated products.

giving (phenylsulfonyl)alkyloxazolidin-2-ones **9** in good yield (Scheme 3, Table 1). However, unlike (phenylsulfonyl)alkylimidazolidin-2-ones **4**, which are formed as single diastereomers, compounds **9** are produced as epimeric mixtures with variable stereoselectivity. The utilization of trisubstituted oxazolidin-2-ones **7b,c**, which have been recently introduced as chiral auxiliaries,[4b,d] does not seem to offer any beneficial effect on the stereoselectivity of sulfonyl derivatives **9h**−**k**. Pure samples of the major diastereomer can be obtained for analytical purposes by repeated crystallizations in ethyl acetate. The stereochemistry of the newly formed stereocenter in sulfones **9** is *S* in the major stereoisomer as confirmed by the X-ray crystallographic analysis carried out for compound **9h**.

Allylation of Chiral (Phenylsulfonyl)alkyloxazolidin-2-ones 9. The formation of *N*-acyliminium ions from their precursors strongly depends on the nature of the Lewis acid used. Tin tetrachloride works very efficiently with derivatives **4** and unsubstituted (phenylsulfonyl)alkyloxazolidin-2-ones **9** (Scheme 3; R = R_1 = H; R_2 = Et) since a slight excess (1.25 equiv) of this Lewis acid is usually required to afford the corresponding addition products **6** in good yield.[11] However, substituted (phenylsulfonyl)alkyloxazolidin-2-ones **9** necessitate a large excess (5 equiv) of tin tetrachloride to be converted into the allyl derivatives **11**. The yields of allylated products **11** obtained are quite modest, and furthermore, the elevated amounts of tin salts employed make the

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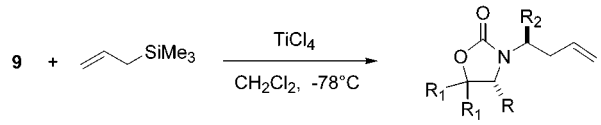
Table 2. Synthesis of Allyloxazolidin-2-ones 11

entry	sulfone **9**	allyl derivative **11**	dr[a]	yield,[b] %
1	**9a**	**11a**	70:30	73
2	**9b**	**11b**	65:35	78
			70:30[c]	46[c]
3	**9c**	**11c**	55:45	85
4	**9d**	**11d**	80:20	66
5	**9e**	**11e**	75:25	70
6	**9f**	**11f**	60:40	91
7	**9g**	**11g**	70:30	80
8	**9h**	**11h**	90:10	93
			90:10[c]	55[c]
9	**9i**	**11i**	95:5	73
10	**9j**	**11j**	85:15	78
11	**9k**	**11k**	90:10	79
12	**9l**	**11l**	65:35	58
13	**9m**	**11m**	75:25	68

[a] The diastereomeric ratio was evaluated by ^{1}H NMR analysis. [b] Yields of pure, isolated products. [c] Values obtained using 5 equiv of tin tetrachloride as activator.

Scheme 4



10 **11**

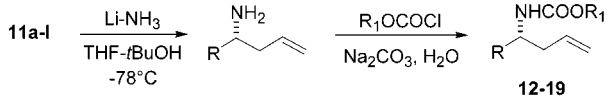
11a: R=Ph; R_1=H; R_2=Et
11b: R=Ph; R_1=H; R_2=Me_2CHCH_2
11c: R=Ph; R_1=H; R_2= Me_2CH
11d: R=Ph; R_1=H; R_2=$PhCH_2CH_2$
11e: R=Ph; R_1=H; R=*n*-C_7H_{15}
11f: R=Ph; R_1=H; R_2=$Cl(CH_2)_5$
11g: R=Ph; R_1=H; R_2=CH_2=$CH(CH_2)_7$
11h: R=Ph; R_1=Me; R_2=Me_2CHCH_2
11i: R=Ph; R_1=Me; R_2=Me_2CH
11j: R=Ph; R_1=Me; R_2=$PhCH_2CH_2$
11k: R=Ph; R_1=Me; R_2=*n*-C_7H_{15}
11l: R=R_1=Ph; R_2=Me_2CHCH_2
11m: R=*i*-Pr; R_1=H; R_2=Me_2CHCH_2

usual workup procedures rather troublesome (Table 2, entries 2 and 8). Conversely, titanium tetrachloride (2 equiv) is able to turn sulfones **9** into the corresponding *N*-acyliminium ions in dichloromethane at −78 °C, which, upon reaction with allyltrimethylsilane **10**, give the addition products **11** in good yields (Scheme 4, Table 2).

Other Lewis acids tested as BF_3·Et_2O or $AlCl_3$ gave only poor yields of allylated products **11** as previously observed with compounds **4.**[11] Unsatisfactory results have been obtained using allyltributylstannane as allylating reagent with various Lewis acids at different temperatures. Sulfones **9a**−**g** obtained from (*R*)-4-phenyloxazolidin-2-one (**7a**) (Table 2, entries 1−7) afford the corresponding allyl derivatives **11a**−**g** only with modest diastereoselectivity. It is interesting to note that the diasteromeric ratio of allylated products **11** is not affected by the diastereomeric composition of sulfones **9**. Indeed, pure (4*R*,1′*S*)-**9e** gives the allylated product **11e** (Table 2, entry 5) in a 75:25 diastereomeric ratio, a value similar to that obtained using variable diastereomeric mixtures of **9e**. This result clearly indicates that the stereochemical outcome of our reaction is governed only by the diastereomeric composition of *N*-acyliminium ion formed as well as the diastereofacial preference of the subsequent nucleophilic addition. Sulfones **9h**−**k** obtained from (*R*)-5,5-dimethyl-4-phenyloxazolidin-2-one (**7b**) (Table 1, entries 8−11) have been converted into the corresponding allyl derivatives **11h**−**k** using the usual procedure in good yields (Table 2, entries 8−11). The diastereoselectivity of allyl derivatives **11h**−**k** obtained is higher than that previously observed using unsubstituted oxazolidin-2-one **7a**. The utilization of other chiral auxiliaries such as (4*R*)-4,5,5-triphenyloxazolidin-2-one (**7c**) and (4*S*)-4-isopropyloxazolidin-2-one (**7d**) (Table 2, entries 12 and 13) did not introduce any improvement compared to that of 5,5-dimethyl derivative **7b**. The assignment of the absolute configuration of the newly formed stereocenter in compounds **11** was rather troublesome since any attempt to obtain crystals suitable for an X-ray analysis from these allyl derivatives failed.[15]

Therefore, we sought a chemical correlation that could enable us to elucidate the stereochemistry of compounds **11**. Cleavage of the 4-phenyloxazolidin-2-one ring in compounds **11a**−**l** has been efficiently carried out under reductive conditions using Li/NH_3 in a mixture of THF/*t*-BuOH at −78 °C.[13a] (Scheme 5).

Scheme 5



12: R=Et ; R_1=Me
13: R=Me_2CHCH_2 ; R_1=Bn
14: R= Me_2CH; R_1=Bn
15: R=$PhCH_2CH_2$; R_1=Me
16: R=*n*-C_7H_{15}; R_1=Me
17: R=$Cl(CH_2)_5$; R_1=Bn
18: R=CH_2=$CH(CH_2)_7$; R_1=Me
19: R=Me_2CHCH_2 ; R_1=Me

Table 3. Synthesis of Carbamates 13 by Reductive Cleavage of Allyloxazolidin-2-ones 11

entry	allyl derivative **11**	carbamate **12**−**19**	er[a]	yield,[b] %
1	**11a**	**12**	75:25	78
2	**11b**	**13**	70:30	72
3	**11c**	**14**	58:42	80
4	**11d**	**15**	78:22	71
5	**11e**	**16**	70:30	75
6	**11f**	**17**	*c*	51
7	**11g**	**18**	74:26	76
8	**11h**	**19**	92:8	82
9	**11i**	**14**	94:6	88
10	**11j**	**15**	88:12	77
11	**11k**	**16**	90:10	75
12	**11l**	**19**	68:22	70

[a] The enantiomeric ratio was evaluated by GLC analysis on a chiral column (see the Experimental Section). [b] Yields of pure, isolated products. [c] Not evaluated.

Cleavage of 4-phenyloxazolidin-2-ones using metals in liquid ammonia usually occurs with complete retention of the configuration at the stereocenter adjacent to the nitrogen atom.[13] This behavior has been confirmed by evaluating the enantiomeric ratio of carbamates **12**−**19** by GLC analysis using a chiral capillary column (Table 3). A comparison between the sign of the optical rotation of these *N*-protected homoallylamines with that available in the literature for the same compound demonstrated that the absolute configuration of carbamate **19** obtained from **11h** is *S*[16] and that of carbamate **14** obtained from **11i** is *R*.[17] The stereochemistry of other carbamates, **12**, **13**, and **15**−**18**, has been inferred by analogy with **14** and **19** considering that the same mechanism operates for the allylation process. Surprisingly, this result is the opposite

(15) Compounds **11** are mostly oils or low melting point solids. Derivative **11m** is actually a solid (mp 213 °C), but it does not give crystals in any of the solvents tested.

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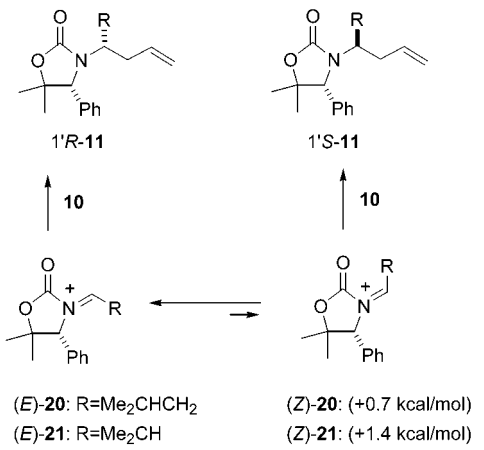
Scheme 6



of what is expected on the basis of the structural features of the *N*-acyliminium ions involved in the process. Assuming as the most probable an attack from the upper face of the *N*-acyliminium ion intermediate, the prevailing diastereomer (1′*S*)-**11** would be formed by reaction of (*Z*)-**20** and (*Z*)-**21** with allyltrimethylsilane (Scheme 6).

However, the *Z* stereoisomer of these reactive ions seems to be less stable than the *E* one probably because of the 1,3-allylic strain between the alkyl chain and the carbonyl oxygen.[10,11] This assumption is also supported by semiempirical calculations (PM3)[18] made on intermediates **20** and **21**, which show for the *Z* stereoisomers energy levels 0.7 and 1.4 kcal/mol higher than those of the *E* stereoisomers. On the other hand, since an *N*-acyliminium ion is also involved in the formation of sulfones **9**, the stereochemistry of the additional stereocenter in these compounds confirms the preference for the *E* configuration of this reactive intermediate even at room temperature. It is interesting to note that the utilization of tin tetrachloride as activator leads to the synthesis of allyl derivatives **11b,h** with almost the same diastereomeric ratio and, most importantly, with the same diastereofacial preference observed with titanium tetrachloride. The nature of the actual interaction existing between the *N*-acyliminium ion and the Lewis acid is unknown, but it is evident that even the introduction of small structural modifications in the core structure of the heterocyclic ring of the chiral auxiliary leads to a consistent change in the conformation of the reactive intermediate. In particular, titanium shows a marked coordinating ability and, especially when it is used in low ionizating solvents as dichloromethane, could give rise to tight ionic pair couples with the carbonyl group of the oxazolidin-2-one.[19] In this couple, the metal and its ligands may force the alkyl chain to occupy the upper side face of the *N*-acyliminium ion (*si*-*si*), thus fostering the nucleophilic attack from the opposite face (*re*-*re*). This hypothesis would also explain the improved diastereoselectivity experienced using sulfones **9h**−**k** obtained from **7b**. Indeed, to relieve the eclipsing interation between the phenyl and the *cis*-methyl in **7b**, the heterocycle should constrain the *trans*-methyl to assume an axial position that cooperates to facilitate the attack of allyltrimethylsilane on the same side of the aromatic ring. An alternative explanation of this unusual stereochemical outcome could be found in a higher reactivity of the (*Z*)-*N*-acyliminium ion (e.g., **20**, Scheme 6), which reacts faster than the *E* stereoisomer, thus shifting the equilibrium toward the formation of the observed major diastereomer 1′*S*-**11**. The lack of reactivity displayed by other nucleophilic reagents such as silyl enol ethers may be ascribed to the low rate by which the *N*-acyliminium ion is formed from **9**, which favors a decomposition of the silyl enol ether by the excess of the Lewis acid used.[20]

In summary, condensation of optically active oxazolidin-2-ones **7** with an aldehyde in the presence of benzenesulfinic acid leads to the synthesis of (phenylsulfonyl)-alkyloxazolidin-2-ones **9** in good yield. These sulfonyl derivatives react with titanium tetrachloride at low temperature, giving the corresponding *N*-acyliminium ions, which are allylated using allyltrimethylsilane. The diastereomeric ratio of allyl derivatives **11** is quite modest using oxazolidin-2-one **7a** as chiral auxiliary, while satisfactory results are obtained using **7b**. The diastereofacial preference experienced in the formation of allyl derivatives **11** is opposite that observed in similar adducts observed from sulfones **4**. Cleavage of the oxazolidin-2-one ring of allyl derivatives **11** affords the corresponding optically active homoallylamines, which have been isolated as the corresponding carbamates **12**−**19**.

Experimental Section

^{1}H NMR was performed at 300 MHz in $CDCl_3$ as solvent.^{13}C NMR was performed at 75 MHz in $CDCl_3$ as solvent. The enantiomeric ratio of carbamates **12**−**19** was evaluated by GLC using a chiral column (30:70 dimethylpentylbetacyclodextrin−OV1701, 0.25 μm × 0.25 mm i.d., length 25 m, ΔT = 50−180 °C at 2 °C/min). Dichloromethane was dried by refluxing it over calcium hydride and then distilled. All chemicals used are available commercially. Oxazolidin-2-ones **7b**−**d** were prepared using a literature method.[12d]

Preparation of Benzenesulfinic Acid from Its Sodium Salt. Sodium benzenesulfinate (1.64 g, 10 mmol) was dissolved in water (5 mL), and then 6 N H_2SO_4 was added until the pH reached 1. The white suspension was extracted with $CHCl_3$ and dried over $MgSO_4$. Removal of the solvent at reduced pressure afforded 1.35 g of benzenesulfinic acid (95%).

General Procedure for the Preparation of Phenylsulfonyl Derivatives 9. Oxazolidin-2-one **7** (5 mmol) was dissolved in dichloromethane (15 mL), and then benzenesulfinic acid (10 mmol), the appropriate aldehyde (7.5 mmol), and anhydrous $MgSO_4$ (0.5 g) were sequentially added at room temperature. The mixture was stirred for 36 h at room temperature and then filtered over a short pad of Florisil. Removal of the solvent afforded the crude sulfone **9**, which was purified by crystallization (4:1 hexanes−ethyl acetate) or column chromatography (7:3 hexanes−ethyl acetate).

Data for (4*R*)-3-[1-(Phenylsulfonyl)propyl]-4-phenyloxazolidin-2-one (9a): mixture of 1′*S* and 1′*R* (85:15) diastereomers; yield 95%; oil; $[\alpha]^{20}_D = -90$ (*c* 1.6, $CHCl_3$); IR (cm^{-1},

(18) Semiempirical PM3 calculations were performed with Spartan 5.0.3, Wavefunction Inc., 18401 Von Karmen Ave., no. 370, Irvine, CA 92715.

(19) According to the observations of Denmark and Almstead, a 1:1 complex between $TiCl_4$ and aldehydes is formed in dichloromethane. Furthermore, the formation of allyltrichlorotitanium species, which could lead to an intramolecular delivery of the allyl group, can be definitely ruled out. Denmark, S. E.; Almstead, N. G. *Tetrahedron* **1992**, *48*, 5565−5578.

(20) We thank a reviewer for this useful suggestion. It is known that increasing the electron-withdrawing aptitude of the acyl group usually leads to a decrease in the *N*-acyliminium ion stability. Therefore, imidazolidinones would be more efficient than oxazolidinones in promoting the formation of *N*-acyliminium ions (see ref 1b). Preliminary results also indicate that electron-rich aromatic derivatives are able to react with sulfones **9**, giving the corresponding addition products.

neat) 1695, 1375, 1145; ^{1}H NMR (1′*S*) δ (ppm) 0.53 (t, 3H, J = 7.3 Hz), 1.28−1.44 (m, 1H), 1.75−1.91 (m, 1H), 4.18 (dd, 1H, J = 9.3, 4.4 Hz), 4.49 (t, 1H, J = 8.9 Hz), 4.97 (dd, 1H, J = 1.7, 4.0 Hz), 5.34 (dd, 1H, J = 8.9, 4.3 Hz), 7.30−7.43 (m, 5H), 7.52−7.59 (m, 2H), 7.63−7.67(m, 1H), 7.91−7.97 (m, 2H); ^{13}C NMR δ (ppm) 10.3, 18.6, 57.2, 71.2, 76.8, 127.4, 128.6, 129.2, 129.3, 129.4, 129.5, 134.5, 137.1, 139.5, 158.3. Anal. Calcd for $C_{18}H_{19}NO_4S$ (345.41): C, 62.59; H, 5.54; N, 4.06. Found: C, 62.65; H, 5.51; N, 3.99.

Data for (4*R*,1′*S*)-3-[1-(Phenylsulfonyl)-3-methylbutyl]-4-phenyloxazolidin-2-one (9b): purified by crystallization; yield 86%; mp 121 °C; $[\alpha]^{20}_D$ = −44 (*c* 1.5, $CHCl_3$); IR (cm^{-1}, KBr) 1690, 1377, 1133; ^{1}H NMR δ (ppm) 0.22 (d, 3H, J = 6.4 Hz), 0.67 (d, 3H, J = 6.4 Hz), 1.02−1.14 (m, 1H), 1.38−1.46 (m, 2H), 4.21 (dd, 1H, J = 8.9, 4.3 Hz), 4.48 (t, 1H, J = 8.9 Hz), 5.12−5.19 (m, 1H), 5.36 (dd, J = 8.9, 4.3), 7.32−7.43 (m, 5H), 7.55−7.61 (m, 2H), 7.65−7.69 (m, 1H), 7.92−7.97 (m, 2H); ^{13}C NMR δ (ppm) 20.6, 22.4, 24.6, 32.8, 57.0, 71.2, 73.6, 127.4, 128.6, 129.3, 129.5, 134.5, 137.1, 139.5, 158.3. Anal. Calcd for $C_{20}H_{23}NO_4S$ (373.46): C, 64.32; H, 6.21; N, 3.75. Found: C, 64.28; H, 6.24; N, 3.77.

Data for (4*R*)-3-[1-(Phenylsulfonyl)-2-methylpropyl]-4-phenyloxazolidin-2-one (9c): mixture of 1′*S* and 1′*R* (80:20) diastereomers; yield 70%; oil; $[\alpha]^{20}_D$ = −80 (*c* 1.2, $CHCl_3$); IR (cm^{-1}, neat) 1692, 1373, 1136; ^{1}H NMR δ (ppm) 0.57 (d, 3H, J = 6.6 Hz), 0.98 (d, 3H, J = 6.6 Hz), 1.89−2.08 (m, 1H), 4.26 (dd, 1H, J = 8.7, 4.3 Hz), 4.37 (t, 1H, J = 8.8 Hz), 4.97 (d, 1H, J = 10.7 Hz), 5.25 (dd, 1H, J = 8.8, 4.3 Hz), 7.35−7.50 (m, 5H), 7.54−7.72 (m, 3H), 7.95−8.01 (m, 2H); ^{13}C NMR δ (ppm) 20.0, 20.8, 27.8, 57.8, 71.5, 81.8, 127.9, 128.1, 129.3, 129.4, 129.5, 134.3, 139.1, 139.5, 159.0. Anal. Calcd for $C_{19}H_{21}NO_4S$ (359.44): C, 63.49; H, 5.89; N, 3.90. Found: C, 63.55; H, 5.91; N, 3.86.

Data for (4*R*,1′*S*)-5,5-Dimethyl-3-[1-(phenylsulfonyl)-3-methylbutyl]-4-phenyloxazolidin-2-one (9h): purified by crystallization; yield 75%; mp 122 °C; $[\alpha]^{20}_D$ = −26.3 (*c* 2.9, $CHCl_3$); IR (cm^{-1}, KBr) 1690, 1377, 1133; ^{1}H NMR δ (ppm) 0.19 (d, 3H, J = 6.1 Hz), 0.55 (d, 3H, J = 6.1 Hz), 1.01 (s, 3H), 1.12−1.41 (m, 3H), 1.65 (s, 3H), 4.97 (s, 1H), 5.23 (d, 1H, 10.6 Hz), 7.25−7.44 (m, 5H), 7.53−7.70 (m, 3H), 7.93−7.99 (m, 2H); ^{13}C NMR δ (ppm) 21.1, 22.7 24.1, 24.6, 28.6, 34.7, 66.5, 73.5, 83.8, 126.9, 128.8, 129.3, 129.7, 130.1, 134.4, 135.0, 137.9, 158.5. Anal. Calcd for $C_{22}H_{27}NO_4S$ (401.52): C, 65.81; H, 6.78; N, 3.49. Found: C, 65.87; H, 6.84; N, 3.53.

Data for (4*R*,1′*S*)-5,5-Dimethyl-3-[1-(phenylsulfonyl)-3-phenylpropyl]-4-phenyloxazolidin-2-one (9j): purified by repeated cystallizations; yield 83%; mp 96 °C; $[\alpha]^{20}_D$ = +7.2 (*c* 2.1, $CHCl_3$); IR (cm^{-1}, KBr) 1691, 1378, 1135; ^{1}H NMR δ (ppm) 1.01 (s, 3H), 1.68 (s, 3H), 1.73−1.84 (m, 1H), 2.12−2.40 (m, 2H), 2.72−2.84 (m, 1H), 5.03 (s, 1H), 5.19 (dd, 1H, J = 9.5, 3.7 Hz), 6.48−6.53 (m, 2H), 6.97−7.06 (m, 3H), 7.11−7.27 (m, 2H), 7.32−7.43 (m, 3H), 7.45−7.64 (m, 3H), 7.80−7.89 (m, 2H); ^{13}C NMR δ (ppm) 24.2, 27.6, 29.0, 31.9, 66.9, 73.9, 83.5, 126.2, 126.4, 128.0, 128.3, 128.6, 128.8, 129.2, 129.5, 129.7, 134.3, 137.2, 139.1, 158.1. Anal. Calcd for $C_{26}H_{27}NO_4S$ (449.56): C, 69.46; H, 6.05; N, 3.12. Found: C, 69.44; H, 6.01; N, 3.15.

Data for (4*R*)-5,5-Dimethyl-3-[1-(phenylsulfonyl)octyl]-4-phenyloxazolidin-2-one (9k): mixture of 1′*S* and 1′*R* (75:25) diastereomers; yield 95%; oil; $[\alpha]^{20}_D$ = −19.3 (*c* 2, $CHCl_3$); IR (cm^{-1}, neat) 1688, 1375, 1134; ^{1}H NMR δ (ppm) 0.77 (t 3H, J = 7.2 Hz), 0.92−1.03 (m, 2H), 0.97 (s, 3H), 1.05−1.36 (m, 8H), 1.52−1.59 (m, 2H), 1.60 (s, 3H), 4.94 (s, 1H), 5.13 (dd, 1H, J = 10.8, 2.9 Hz), 7.32−7.39 (m, 5H), 7.537.67 (m, 3H), 7.86−7.95 (m, 2H); ^{13}C NMR δ (ppm) 14.0, 22.4, 24.1, 25.7, 26.0, 27.0, 28.5, 28.9, 31.5, 66.9, 74.7, 83.2, 128.7, 128.9, 129.2, 129.4, 134.2, 137.3, 158.0. Anal. Calcd for $C_{25}H_{33}NO_4S$ (443.60): C, 67.69; H, 7.50; N, 3.16. Found: C, 67.75; H, 7.46; N, 3.20.

Data for (4*R*,1′*S*)-3-[1-(Phenylsulfonyl)-3-methylbutyl]-4,5,5-triphenyloxazolidin-2-one (9l): purified by crystallization; yield 68%; mp 123 °C; $[\alpha]^{20}_D$ = −123.3 (*c* 1.8, $CHCl_3$); IR (cm^{-1}, KBr) 1690, 1377, 1133; ^{1}H NMR δ (ppm) 0.16 (d, 3H, J = 6.7 Hz), 0.77 (d, 3H, J = 6.4 Hz), 1.16−1.30 (m, 2H), 1.74−1.72 (m, 1H), 5.19 (dd, 1H, J = 10.8, 2.3 Hz), 6.29 (s, 1H), 6.86−7.22 (m, 8H), 7.34−7.55 (m, 6H), 7.66−7.72 (m, 4H), 7.83−7.87 (m, 2H). Anal. Calcd for $C_{32}H_{31}NO_4S$ (525.66): C, 73.12; H, 5.94; N, 2.66. Found: C, 73.07; H, 5.99; N, 2.70.

Data for (4*R*,1′*S*)-3-[1-(Phenylsulfonyl)-3-methylbutyl]-4-isopropyloxazolidin-2-one (9m): purified by a preliminary column chromatography and successively by crystallization; yield 83%; mp 87 °C; $[\alpha]^{20}_D$ = −21 (*c* 1.0, $CHCl_3$); IR (cm^{-1}, KBr) 1690, 1377, 1133; ^{1}H NMR δ (ppm) 0.87 (d, 3H, J = 6.4 Hz), 0.88 (d, 3H, J = 6.7 Hz), 0.92 (d, 3H, J = 6.4 Hz), 0.93 (d, 3H, J = 6.7 Hz), 1.63−2.08 (m, 3H), 4.03 (d, 1H, J = 8.9 Hz), 4.13 (dd, J = 8.9, 2.7 Hz), 4.18−4.30 (m, 1H), 5.18−5.24 (m, 1H), 7.53−7.60 (m, 2H), 7.63−7.61 (m, 1H), 7.87−7.95 (m, 2H). Anal. Calcd for $C_{17}H_{25}NO_4S$ (339.45): C, 60.15; H, 7.42; N, 4.13. Found: C, 60.11; H, 7.37; N, 4.14.

General Procedure for the Preparation of Allyloxazolidin-2-ones 11. Sulfone **9** (2 mmol) was dissolved in CH_2Cl_2 (20 mL), and the solution was cooled to −78 °C. $TiCl_4$ (4 mmol) was then added dropwise in 15 min, and the temperature was kept at −78 °C for 30 min. Allyltrimethylsilane (4 mmol) dissolved in CH_2Cl_2 (10 mL) was then added dropwise, and after 1 h at −78 °C the temperature was slowly raised to 0 °C. The reaction mixture was then diluted with CH_2Cl_2 (20 mL) and washed with brine (10 mL), and the organic phase was dried over $MgSO_4$. After removal of the solvent at reduced pressure, the allylation product **11** obtained was purified by column chromatography (7:3 hexanes−ethyl acetate).

Data for (4*R*)-3-(1-Ethylbut-3-enyl)-4-phenyloxazolidin-2-one (11a): mixture of 1′*S* and 1′*R* (70:30) diastereomers; yield 73%; oil $[\alpha]^{20}_D$ = −26.1 (*c* 2.3, $CHCl_3$); IR (cm^{-1}, neat) 1692; ^{1}H NMR (1′*S*) δ (ppm) 0.80 (t, 3H, J = 7.3 Hz), 1.55−1.76 (m, 2H), 1.81−1.90 (m, 1H), 2.09−2.18 (m, 1H), 3.32−3.41 (m, 1H), 4.13 (dd, 1H, J = 8.5, 6.7 Hz), 4.55 (t, 1H, J = 9.0 Hz), 4.71 (dd, 1H, J = 8.9, 6.4 Hz), 4.86−5.02 (m, 2H), 5.60−5.72 (m, 1H), 7.31−7.42 (m, 5H); ^{13}C NMR δ (ppm) 11.3, 24.5, 37.6, 56.7, 59.8, 70.1, 117.5, 127.7, 129.0, 129.1, 135.3, 139.2, 158.2. Anal. Calcd for $C_{15}H_{19}NO_2$ (245.32): C, 73.44; H, 7.81; N, 5.71. Found: C, 73.50; H, 7.86; N, 5.68.

Data for (4*R*)-3-(1-Phenethylbut-3-enyl)-4-phenyloxazolidin-2-one (11d): mixture of 1′*S* and 1′*R* (80:20) diastereomers; yield 66%; mp 72 °C; $[\alpha]^{20}_D$ = −18.7 (*c* 2.5, $CHCl_3$); IR (cm^{-1}, KBr) 1690; ^{1}H NMR (1′*S*) δ (ppm) 1.86−2.84 (m, 4H), 2.38−2.61 (m, 2H), 3.43−3.48 (m, 1H), 4.17 (dd, 1H, J = 8.6, 6.6 Hz), 4.49 (t, 1H, J = 8.8 Hz), 4.70 (dd, 1H, J = 8.9, 6.6 Hz), 4.91−5.08 (m, 2H), 5.55−5.83 (m, 1H), 7.31−7.43 (m, 10H); ^{13}C NMR δ (ppm) 33.1, 37.5, 54.9, 60.2, 70.0, 117.8, 125.9, 127.7, 128.2, 128.4, 129.1, 129.2, 135.0, 139.1, 141.2, 158.0. Anal. Calcd for $C_{21}H_{23}NO_2$ (321.41): C, 78.47; H, 7.21; N, 4.36. Found: C, 78.50; H, 7.24; N, 4.37.

Data for (4*R*,1′*S*)-5,5-Dimethyl-3-(1-isobutylbut-3-enyl)-4-phenyloxazolidin-2-one (11h): yield 93%; oil; $[\alpha]^{20}_D$ = −23.4 (*c* 2.2, $CHCl_3$); IR (cm^{-1}, neat) 1695; ^{1}H NMR δ (ppm) 0.81 (d, 3H J = 6.4 Hz), 0.85 (d, 3H, J = 6.3 Hz), 0.94 (s, 3H), 1.48−1.63 (m, 3H), 1.50 (s, 3H), 1.74−1.90 (m, 1H), 2.26−2.45 (m, 1H), 3.47−3.62 (m, 1H), 4.34 (s, 1H), 4.93−5.05 (m, 2H), 5.61−5.78 (m, 1H), 7.32−7.40 (m, 5H); ^{13}C NMR δ (ppm) 22.7, 23.2, 24.5, 25.6, 29.6, 38.4, 41.5, 53.4, 70.0, 81.4, 118.1, 128.6, 129.0, 129.3, 136.0, 137.6, 157.8 Anal. Calcd for $C_{19}H_{27}NO_2$ (301.42): C, 75.71; H, 9.03; N, 4.65. Found: C, 75.74; H, 9.00; N, 4.63.

Data for (4*R*,1′*S*)-5,5-Dimethyl-3-(1-phenethylbut-3-enyl)-4-phenyloxazolidin-2-one (11j): yield 78%; oil; $[\alpha]^{20}_D$ = −20.7 (*c* 2.0, $CHCl_3$); IR (cm^{-1}, KBr) 1691; ^{1}H NMR δ (ppm) 0.97 (s, 3H), 1.57 (s, 3H), 1.94−2.13 (m, 4H), 2.37−2.51 (m, 2H), 2.54−2.68 (m, 2H), 3.38−3.51 (m, 1H), 4.40 (s, 1H), 4.95−5.06 (m, 2H), 5.62−5.68 (m, 1H), 6.97−7.40 (m, 10H); ^{13}C NMR δ (ppm) 23.7, 28.9, 32.9, 33.1, 33.4, 37.1, 54.4, 68.3, 69.8, 81.0, 117.7, 125.7, 127.9, 128.0, 128.1, 128.2, 128.4, 128.7, 128.8, 135.0, 136.4, 140.9, 157.1. Anal. Calcd for $C_{23}H_{27}NO_2$ (349.47): C, 79.05; H, 7.79; N, 4.01. Found: C, 79.10; H, 7.83; N, 4.06.

Data for (4*R*,1′*S*)-5,5-Dimethyl-3-(1-heptylbut-3-enyl)-4-phenyloxazolidin-2-one (11k): yield 79%; oil; $[\alpha]^{20}_D$ = −22.4 (*c* 4.6, $CHCl_3$); IR (cm^{-1}, neat) 1695; ^{1}H NMR δ (ppm) 0.87 (t, 3H, J = 6.5 Hz), 0.94 (s, 3H), 1.10−1.37 (m, 10H), 1.53 (s, 3H), 1.55−1.71 (m, 2H), 1.75−1.96 (m, 1H), 2.24−2.46 (m,

1H), 3.35−3.52 (m, 1H), 4.36 (s, 1H), 4.97−5.04 (m, 2H), 5.59−5.57 (m, 1H), 7.34−7.40 (m, 5H); ^{13}C NMR δ (ppm) 14.1, 22.6, 24.0, 26.8, 29.1, 29.3, 31.8, 37.8, 55.0, 69.5, 80.9, 113.7, 117.6, 128.5, 128.8, 129.0, 135.6, 137.0, 157.4. Anal. Calcd for $C_{22}H_{33}NO_2$ (343.51): C, 76.92; H, 9.68; N, 4.08. Found: C, 76.86; H, 9.71; N, 4.12.

Data for (4*R*)-3-(1-Isobutylbut-3-enyl)-4,5,5-triphenyloxazolidin-2-one(11l): mixture of 1′*S* and 1′*R* (65.35) diastereomers; yield 58%; mp 213 °C; $[\alpha]^{20}_D = +61$ (*c* 1.3, $CHCl_3$); IR (cm^{-1}, KBr) 1693; ^{1}H NMR (1′*S*) δ (ppm) 0.49 (d, 3H J = 6.4 Hz), 0.58 (d, 3H, J = 6.4 Hz), 1.23−1.37 (m, 2H), 1.58−1.69 (m, 1H), 1.99−2.10 (m, 1H), 2.16−2.27 (m, 1H), 3.61−3.73 (m, m, 1H), 4.69−4.83 (m, 2H), 5.26 (s, 1H), 5.40−5.57 (m, 1H), 6.95−7.25 (m, 11H), 7.27−7.40 (m, 2H), 7.60−7.75 (m, 2H). Anal. Calcd for $C_{29}H_{31}NO_2$ (425.57): C, 81.85; H, 7.34; N, 3.29. Found: C, 81.84; H, 7.31; N, 3.33.

Data for (4*R*)-3-(1-Isobutylbut-3-enyl)-4-isopropyloxazolidin-2-one (11m): mixture of 1′*S* and 1′*R* (75:25) diastereomers; yield 68%; oil; $[\alpha]^{20}_D = +13.3$ (*c* 1.8, $CHCl_3$); IR (cm^{-1}, neat) 1690; ^{1}H NMR (1′*S*) δ (ppm) 0.87 (d, 3H, J = 6.4 Hz), 0.89 (d, 3H, J = 6.4 Hz), 0.93 (d, H, J = 6.6 Hz), 0.95 (d, 3H, J = 6.7 Hz), 1.48−1.66 (m, 3H), 1.91−2.04 (m, 1H), 2.13−2.23 (m, 1H), 2.49−2.59 (m, 1H), 3.49−3.74 (m, 2H), 4.03 (dd, 1H, J = 8.9, 4.3 Hz), 4.09 (d, 1H, J = 8.9 Hz), 5.01−5.12 (m, 2H), 5.71−5.79 (m, 1H). Anal. Calcd for $C_{14}H_{25}NO_2$ (239.36): C, 70.25; H, 10.53; N, 5.85. Found: C, 70.21; H, 10.49; N, 5.88.

General Procedure for the Reductive Cleavage of the Oxazolidin-2-one Ring. Allyl derivative **11** (2 mmol) was dissolved in a mixture of THF (80 mL) and *t*-BuOH (10 mL), and then Li shots (20 mmol) were added in one portion. After the mixture was cooled to −78 °C, NH_3 (100 mL) was condensed, and the blue solution was stirred at this temperature for 1 h. The reaction mixture was then quenched by addition of solid NH_4Cl (2 g) and warmed to room temperature, and then the volume of the solvent was reduced to about 20 mL by evaporation at reduced pressure. Na_2CO_3 (2 N, 20 mL) was added followed by the appropriate chloroformate (6 mmol), the mixture was stirred overnight and then concentrated at reduced pressure. The resulting aqueous solution was extracted with CH_2Cl_2 and then dried over $MgSO_4$. After evaporation of the solvent at reduced pressure, the crude carbamate was purified by column chromatography (9:1 hexanes−ethyl acetate).

Data for (*R*)-Benzyl-1-isopropylbut-3-enylcarbamate (14): obtained by reductive cleavage of **11i**; yield 88%, oil; $[\alpha]^{20}_D = -27.1$ (*c* 1.5, $CHCl_3$); IR (cm^{-1}, neat) 3300, 1690; ^{1}H NMR δ (ppm) 0.90 (d, 3H, J = 6.7 Hz), 0.93 (d, 3H, J = 6.7 Hz), 1.70−1.82 (m, 1H), 2.08−2.15 (m, 1H), 2.21−2.28 (m, 1H), 3.53−3.59 (m, 1H), 4.64 (d, 1H, J = 9.5 Hz), 5.01−5.11 (m, 2H), 5.10 (s, 2H), 5.70−5.76 (m, 1H), 7.28−7.36 (m, 5H); ^{13}C NMR δ (ppm) 17.6, 19.0, 19.3, 31.5, 36.9, 55.7, 66.5, 117.4, 127.96, 127.98, 128.3, 128.6, 134.8, 136.8, 156.5. Anal. Calcd for $C_{15}H_{21}NO_2$ (247.33): C, 72.84; H, 8.56; N, 5.66. Found: C, 72.89; H, 8.53; N, 5.71.

Data for (*S*)-Methyl-1-Phenethylbut-3-enylcarbamate (15): obtained by reductive cleavage of **11j**; yield 77%; oil; $[\alpha]^{20}_D = -9.7$ (*c* 2.5, $CHCl_3$); IR (cm^{-1}, neat) 3310, 1685; ^{1}H NMR δ (ppm) 1.65−1.91 (m, 2H), 2.17−2.40 (m, 2H), 2.56−2.81 (m, 2H), 3.69 (s, 3H), 3.75−3.88 (m, 1H), 4.64 (d, 1H, J = 8.9 Hz), 5.05−5.15 (m, 2H), 5.69−5.86 (m, 1H), 7.18−7.35 (m, 5H); ^{13}C NMR δ (ppm) 32.1, 36.3, 39.3, 50.2, 51.8, 117.9, 125.7, 128.1, 128.2, 133.8, 141.5, 156.5. Anal. Calcd for $C_{14}H_{19}NO_2$ (233.31): C, 72.07; H, 8.21; N, 6.00. Found: C, 72.13; H, 8.23; N, 5.96.

Data for (S)-Methyl-1-heptylbut-3-enylcarbamate (16): obtained by reductive cleavage of **11k**; yield 75%; mp 38 °C; $[\alpha]^{20}_D = -15.1$ (*c* 1.8, $CHCl_3$); IR (cm^{-1}, KBr) 3305, 1695; ^{1}H NMR δ (ppm) 0.84 (t, 3H, J = 6.7 Hz), 1.23−1.71 (m, 12H), 2.09−2.28 (m, 2H), 3.44−3.60 (m, 1H), 3.62 (s, 3H), 4.46 (d, 1H, J = 8.0 Hz), 5.00−5.07 (m, 2H), 5.67−5.80 (m, 1H); ^{13}C NMR δ (ppm) 14.1, 22.6, 25.8, 29.2, 29.4, 31.8, 34.6, 39.5, 50.6, 51.9, 117.7, 134.3, 156.4. Anal. Calcd for $C_{13}H_{25}NO_2$ (227.34): C, 68.68; H, 11.08; N, 6.16. Found: C, 68.75; H, 11.01; N, 6.19.

Data for (*S*)-Methyl-1-isobutylbut-3-enylcarbamate (19): yield 82%; oil; $[\alpha]^{20}_D = -28.3$ (*c* 2.4, $CHCl_3$); IR (cm^{-1}, neat) 3300, 1690; ^{1}H NMR δ (ppm) 0.85 (d, 3H, J = 6.4 Hz), 0.86 (d, 3H, J = 6.4 Hz), 1.18−1.25 (m 2H), 1.56−1.66 (m, 1H), 2.09−2.23 (m, 2H), 3.60 (s, 3H), 3.64−3.78 (m, 1H), 4.42 (d, 1H, J = 7.8 Hz), 4.98−5.04 (m, 2H), 5.67−5.76 (m, 1H); ^{13}C NMR δ (ppm) 22.1, 23.1, 24.8, 40.1, 44.0, 48.7, 51.9, 117.8, 134.3, 156.5. Anal. Calcd for $C_{10}H_{19}NO_2$ (185.26): C, 64.83; H, 10.34; N, 7.56. Found: C, 64.86; H, 10.30; N, 7.60.

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Supporting Information Available: Spectral and physical data for compounds not included in the Experimental Section and X-ray molecular structure and crystal data of compound **9h**. This material is available free of charge via the Internet at http://pubs.acs.org.

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