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New Chiral Auxiliaries Based on Conformation Control, a C_2-Symmetric 2,2-Dimethylimidazolidine and 4-Chiral 2,2-Dialkyloxazolidines. Synthesis and Conformational Analysis of Acrylamide Derivatives

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Abstract: New chirality-controlling auxiliaries, a C_2-symmetric 2,2-dimethylimidazolidine and 4-chiral 2,2-dialkyloxazolidines, are readily prepared from a C_2-symmetric 1,2-ethanediamine and naturally occurring α-amino acids, respectively. Conformational analysis of their *N*-acryloyl derivatives has been carried out on the basis of dynamic ^{1}H NMR spectroscopy and molecular mechanics calculations using MM2 program. Proper choice of the substituents at 2-, 4-, and 5-positions, in the oxazolidine cases, leads to the most effective chiral shielding of a diastereotopic acryloyl face.

Development of a new methodology for enantio-controlled 1,3-dipolar cycloaddition reaction is important for the construction of optically active heterocyclic compounds. Only quite limited examples are known so far for the effective asymmetric 1,3-dipolar cycloaddition reactions.[1] Although several asymmetric dipolar cycloadditions utilizing chiral dipoles have been recently reported,[2] more useful so far from the standpoint of synthetic application would be the reactions with optically active dipolarophiles.[3-6]

Dipolar cycloaddition and Diels-Alder reaction are both frontier orbital-controlled pericyclic ring-forming processes including 6 pi electrons. However, chemical properties as Lewis bases of the 4 pi components, dipoles and dienes, are quite different. Diene is a relatively weak Lewis base, even when activated by alkoxyl moieties, so that the Lewis acid-catalyzed Diels-Alder reactions have provided numerous successful results leading to highly stereoselective elegant ring formation.[7] In the catalyzed Diels-Alder reactions using chiral dienophiles, the catalyst acts not only to activate the dienophiles but also to stabilize their stereogenic diastereofaces. On the other hand, dipole is a much stronger Lewis base than dienophile so that its ready complexation with Lewis acid (or metallic reagent) leads to deactivation of dipole. Only limited examples are known for the metal-assisted dipolar cycloadditions,[8] and catalytic dipolar reactions are even fewer.[9] Accordingly, the same chiral dienophiles that have been effectively utilized in Lewis acid-catalyzed asymmetric Diels-Alder reactions would not be always useful in asymmetric dipolar cycloadditions. Accordingly, it is desired to develop a new chirality-controlling auxiliary that can be effectively used in noncatalyzed, or without the aid of metallic additive, asymmetric reactions.

The Curran's acrylamide **A** is the best among electron-deficient dipolarophiles ever used in asymmetric dipolar cycloadditions (Fig. 1). The exclusively high diastereoselectivity (ds = ~100%) has been recorded in its cycloaddition with benzonitrile oxide.[10] One disadvantage is the rather complicated synthetic route which starts from the naturally occurring Kemp's triacid. This discourages its wide use in asymmetric reactions. The acrylate **B** bearing a C_2-symmetric 2-imidazolidinyl chiral controller at 3-position shows also the exclusive diastereoselectivity (ds = ~100%) in nitrile oxide cycloaddition, while regioselectivity of this reaction is inevitably poor.[11] The acrylamides derived from the Oppolzer's chiral sultams **C**[12] and **D**[13] are satisfactory

both from the viewpoints of high diastereoselectivity and acceptably short synthesis. In these cases, chiral discrimination is made in their *anti*-conformations by the electrostatic force of repulsion operating between nucleophiles and the pseudoaxial sulfonamide oxygen. This point should be emphasized because it makes a striking contrast with the Curran's chiral acrylamide A in which face selection is simply based on the steric shielding in the *anti*-conformation.

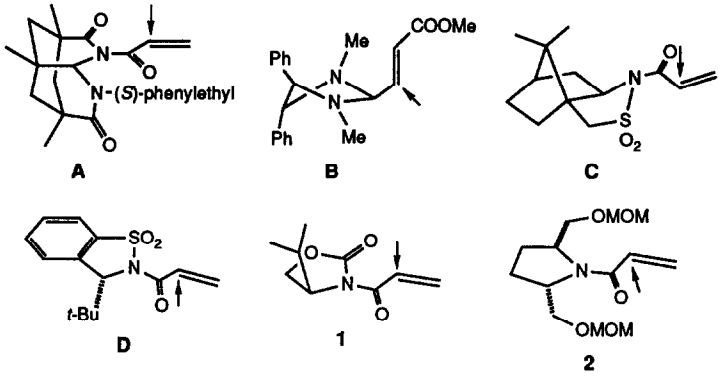
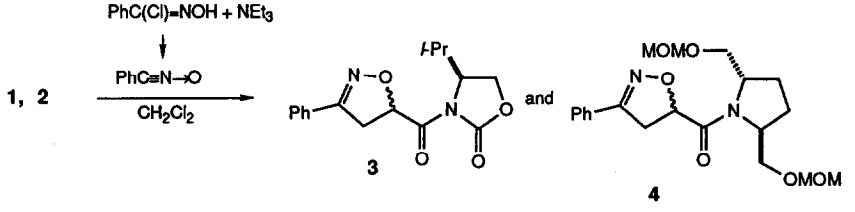


Figure 1. Several known chiral α,β-unsaturated carbonyl compounds ever utilized in asymmetric cycloadditions.

Two acrylamides **1** and **2**, derived from the known chirality-controlling heterocyclic molecules such as 4-isopropyl-2-oxazolidinone (the Evans' chiral auxiliary)[14] and *trans*-2,5-di(methoxymethoxymethyl)pyrrolidine (the Katsuki's chiral auxiliary),[15] have found wide synthetic applications in a variety of asymmetric reactions.[16,17] In the nitrile oxide cycloadditions of these acrylamides **1** and **2**, it is of special interest how satisfactory diastereoselectivity they will record under noncatalyzed conditions (or without the aid of metallic additive). We first of all employed these two chiral acrylamides in dipolar cycloadditions (Scheme 1). Thus, benzonitrile oxide, generated in situ from benzohydroximoyl chloride and triethylamine, readily reacted with **1** or **2** at a low temperature in dichloromethane to give mixture of diastereomers of regioselectively pure cycloadducts **3** (94% at –30 °C) and **4** (78% at –78 °C). The diastereoselectivities (ds) observed were not higher than 75% for both **3** (ds = 73%) and **4** (ds = 70%).[18] It is now concluded that synthetic potential of **1** and **2** in asymmetric reactions with nucleophiles in the absence of metallic additive is not excellent.



Scheme 1.

We have started the research program of molecular design of new chiral dipolarophiles based on a new concept of diastereofacial discrimination. Our work bases on the use of conformation-controlled *N*-acryloyl derivatives **E** of chiral heterocycles such as C_2-symmetric imidazolidine (X = NR, one of $R^5 = R^4$) and 4-chiral oxazolidines (X = O) as shown in Fig. 2.

The present paper describes the design and synthesis of such new heterocyclic chiral auxiliaries. Proper choice of a set of substituents to attain high diastereofacial selectivity in dipolar cycloaddition has been guided by the conformational analysis of *N*-acryloyl derivatives. For the analysis, dynamic ^{1}H NMR spectroscopy and molecular mechanics calculation have been utilized.

RESULTS AND DISCUSSION

Among all the bonds involved in acrylamides **E**, the amide nitrogen-carbonyl carbon bond is no doubt most restricted, and the sp^2-sp^2 single bond of the *N*-acryloyl moiety may be the second. With respect to the amide conformation, *syn*-conformer *syn*-**E** must be much more stabilized than *anti*-conformer *anti*-**E** in which serious steric congestion exists between the α-carbon of vinyl substituent and the two alkyl substituents R^2 at 2-position. In addition, the *N*-acryloyl moiety may take *s-cis*-conformation, either in *syn*-**E** or *anti*-**E**, since *s-trans*-conformation causes unfavorable steric repulsion against R^2 or R^4. The preference for *syn*-conformation and *s-cis*-geometry is confirmed by ^{1}H NMR spectroscopy as well as molecular mechanics calculation (MM2 calculation). This will be discussed below. Since the least hindered approach to **E** by a nucleophilic reagent must take place from the side opposite to R^4 in the *syn*-conformer, such heterocycles with two substituents at 2-position are expected to work as effective chiral auxiliaries.

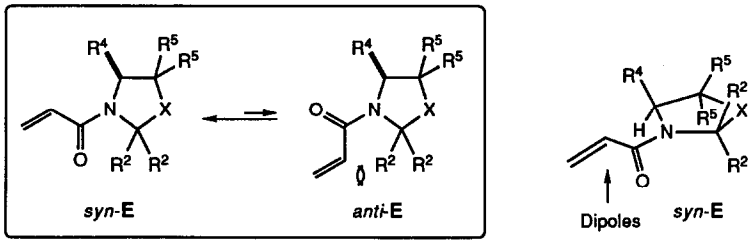


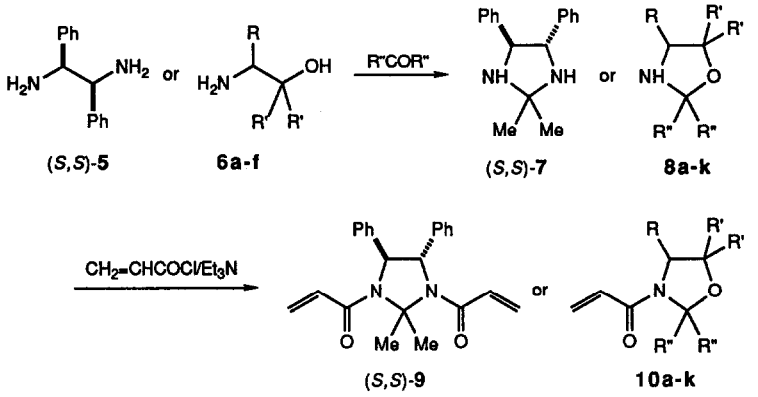
Figure 2. Chiral acrylamides utilized for asymmetric addition by nucleophiles without the aid of metallic reagent.

Finally, degree of diastereoselectivity should depend upon 1) the *syn/anti* conformer ratio, 2) the stability of *s-cis*-conformation of the sp^2-sp^2 single bond of the *N*-acryloyl moiety, and 3) the efficiency of chiral shielding by R^4. When X is oxygen atom, so oxazolidine cases, such chiral olefins **E** bearing a variety of substituents R^4 are readily available by starting from optically pure natural α-amino acids. This is a high synthetic advantage.

Synthesis. The C_2-symmetric 1,2-diamine (*S,S*)-**5**, which is commercially available in optically pure form but expensive, was prepared from benzil according to the reported procedure[7o,19] followed by optical resolution.[20] Optically pure β-amino alcohol (*R*)-**6a** and (*S*)-**6b,c** were readily prepared without racemization by reduction of the corresponding α-amino esters with sodium borohydride[21] or the corresponding α-amino acids with sodium borohydride in the presence of chlorotrimethylsilane.[22] Action of methylmagnesium iodide onto methyl (*S*)-phenylalanine led to α-amino alcohol (*S*)-**6d**. Both *rac*-**6e,f** were prepared in racemates by alkylation of ethyl *N*-benzylideneglycinate[23] and subsequent reduction with sodium borohydride. The last two were used without optical resolution.

Condensation of diamine (*S,S*)-**5** with acetone took place readily at room temperature in the presence of anhydrous $MgSO_4$ in dichloromethane to produce (*S,S*)-**7** in a quantitative yield (Scheme 2). Since purification of (*S,S*)-**7** by column chromatography on silica gel caused partial hydrolytic decomposition to (*S,S*)-**5** and acetone, (*S,S*)-**7** was employed without further purification to the subsequent *N*-acryloylation

with acryloyl chloride and Et_3N in dichloromethane at room temperature to give diacrylamide (*S,S*)-**9** in 60% yield. The amide (*S,S*)-**9** has high chemical stability enough to be purified by silica gel column chromatography without trouble.



6a-f:

a:	R = Ph, R' = H
b:	R = *i*-Pr, R' = H
c:	R = $PhCH_2$, R' = H
d:	R = $PhCH_2$, R' = Me
e:	R = Ph_2CH, R' = H
f:	R = 9-Fluorenyl, R' = H

8a-k, 10a-k:

a:	R = Ph, R' = H, R" = Me
b:	R = Ph, R' = H, R"$_2$ = $(CH_2)_5$
c:	R = *i*-Pr, R' = H, R" = Me
d:	R = $PhCH_2$, R' = H, R" = Me
e:	R = $PhCH_2$, R' = R" = Me
f:	R = $PhCH_2$, R' =Me, R" = Et
g:	R = R" = $PhCH_2$, R' =Me
h:	R = $PhCH_2$, R' = Me, R"$_2$ = $(CH_2)_5$
I:	R = Ph_2CH, R' = H, R" = Me
J:	R = Ph_2CH, R' = H, R"$_2$ = $(CH_2)_5$
k:	R = 9-Fluorenyl, R' = H, R" = Me

Scheme 2.

Amino alcohols **6a-f** underwent successful condensation with acetone under reflux in acetone itself or with cyclohexanone under reflux in dichloromethane, both in the presence of a catalytic amount of *p*-toluenesulfonic acid (PTSA). The resulting 2,2-disubstituted oxazolidines **8a-k** were again unstable against hydrolysis. They were immediately transformed to *N*-acryloyl derivatives **10a-k** without further purification (Scheme 2).

Conformational Analysis. The ^1H NMR spectra recorded at room temperature showed that some of 3-acryloyl-2,2-dialkyloxazolidines **10a-k** existed as mixtures of conformers. Such conformational isomerism must have arisen from the restricted rotation around the amide nitrogen-carbonyl carbon bond. Fixation of the amide bond as *syn*-conformers should be essential to attain highly diastereoselective reactions at one of the stereogenic acryloyl faces; the contribution by *anti*-conformers is not desired.

First of all, the MM2 molecular mechanics calculation was performed for several derivatives of 3-acryloyl-2,2-dialkyloxazolidines **10a-k**.[24] *Trans*-1,3-diacryloyl-2,2-dimethyl-4,5-diphenylimidazolidine **9** was also calculated as a reference compound since its nitrile oxide cycloaddition was previously examined.[18] Results are summarized in Table 1. Conformer ratios were measured at various temperatures and rotation barriers with respect to the amide nitrogen-carbonyl carbon bond were estimated. Based on the inspection of these ^1H NMR spectra, structures of the major conformers were assigned (Table 1).

The C_2-symmetric 1,3-diacryloyl-2,2-dimethylimidazolidine **9** existed as single conformer of C_2-symmetric structure at room temperature. Protons of **9** all appeared as sharp signals. Since notable NOE enhancement was observed between H-4 (or H-5, δ 5.37) and the acryloyl Hα (6.12), the *syn,syn*-conformer *syn,syn*-**9**

was found to be much more favored than either of the *anti,anti*- and *anti,syn*-conformers. This is consistent with the calculated relative stability of *syn,syn*-**9** (entry 1).

No minor conformers were detected in the case of 3-acryloyl-2,2-dimethyl-4-phenyloxazolidine (**10a**). Acryloyl protons of **9** and **10a** showed similar chemical shifts to each other (Table 1, entries 1 and 2), confirming that **9** exists as single *syn*-conformer and that the *N*-acryloyl moieties of **9** and **10a** are located almost in the same chiral shielding zone of the phenyl substituents. Accordingly, it is not so difficult to anticipate that similar levels of diastereoselectivities would result in noncatalyzed dipolar cycloadditions of **9** and **10a**. No substantial change of conformation was detected when the methyl substituents at 2-position of **10a** were replaced by a pentamethylene group to give **10b** (entry 3), while the MM2 calculation indicated the increase of *syn/anti* ratio.

More efficient chiral shielding, so magnetic shielding as well, is expected when the 4-chiral substituent is benzylic and when its phenyl plane is forced to face the *N*-acryloyl plane. In such case, chemical shifts of the acryloyl protons can be used as a convenient indicator for the effectiveness of chiral shielding.

Table 1. Conformational Analysis of 1,3-Diacryloyl-2,2-dimethylimidazolidine **9** and 3-Acryloyl-2,2-dialkyloxazolidines **10a-k**.

		Chemical shift (δ)[a]			*Syn/anti* ratio at various temperature					MM2 Calculation
Entry	**9/10**	$=CH_2^t$	$=CH_2^c$	=CH–	27 °C	0 °C	–30 °C	–50 °C	–80 °C	ΔG (G_{anti} - G_{syn})[b]
1	**9**[c]	6.31	5.48	6.12	*syn* only[c]					3.24[d]
2	**10a**[c]	6.30	5.47	6.10	*syn* only[c]					2.65
3	**10b**[c]	6.28	5.44	6.09	*syn* only[c]					2.71
4	**10c**[c]	6.42	5.68	6.41	-[c,e]					1.25
5	**10d**	6.35	5.72	6.56	91:9	92:8	94:6	95:5		2.92
		6.41	5.74	6.58						
6	**10e**	5.76	5.02	5.71	94:6[f]	95:5	97:3	97:3		2.59
		6.34	-[g]	6.57						
7	**10f**	6.13	5.47	6.31	-[d]	81:19	81:19			2.34
		6.38	5.69	6.54						
8	**10g**	6.53	5.71	6.50	single	single	single	single	single	2.71
9	**10h**	5.76	5.01	5.71	-[d]	96:4	96:4	97:3		2.81
		6.31	5.69	6.65						
10	**10i**	5.70	4.91	5.62	94:6[f]	94:6	96:4	98:2	98:2	2.67
		6.20	-[g]	6.42						
11	**10j**	5.67	4.86	5.61	-[h]	95:5	96:4	97:3		2.82
		6.12	-[g]	6.47						
12	**10k**	6.22	5.47	6.17	70:30	71:29	74:26	79:21		2.98
		6.52	5.86	6.70						

[a]The upper and lower lines are for major and minor conformers, respectively. ^1H NMR Spectrum was recorded at –30 °C in CD_2Cl_2 solution unless otherwise noted. [b]Energy calculation was made for the most stable conformer each for the *syn*- and *anti*-isomers (kcal/mole). [c]Measured only at 27 °C. Solvent: $CDCl_3$. [d]The energy difference between *syn,syn*-**9** and *anti,syn*-**9**. [e]No *syn/anti* ratio was given because of peak coalescence. [f]Measured at 21 °C. [g]Overlapping with other signals. [h]Not measured.

3-Acryloyl-4-benzyloxazolidine (**10d**) is a 94:6 conformer mixture at –30 °C. The major conformer was assigned as *syn*-**10d**, and hence the minor one *anti*-**10d**, since H-4 (δ 4.14) of the major conformer appears in higher field than that of the minor isomer (4.44). The deshielding of H-4 in *anti*-conformer *anti*-**10d** is caused by anisotropy of the proximate amide carbonyl oxygen.

Acryloyl protons of **10d** all appeared in lower fields than those of 4-phenyl substituted oxazolidine **10a** and imidazolidine **9**, indicating that the benzylic phenyl plane stays far from the *N*-acryloyl moiety.

Substitution by two methyl substituents at 5-position must inhibit the escape of benzylic phenyl group from the *N*-acryloyl reaction site. In other words, the antiperiplanar conformer *ap*-**10e** (*syn*) should be destabilized due to the steric repulsion of benzyl group to 5-Me so that the synclinal conformer *sc*-**10e** (*syn*) becomes the major contributor (Fig. 2). As a result, much effective chiral shieldings is expected in the case of *syn*-**10e**, and *syn*-**10h** as well. According to MM2 calculation, *sc*-**10e** (*syn*) is more stabilized than *ap*-**10e** (*syn*) by 1.76 kcal/mole.

Such expectation was true. The acryloyl protons of **10e,h** were all intensely shielded compared with those of **10d** (entries 5 vs 6 and 9). In addition, although not expected, the *syn/anti* ratio of **10e**, and that of **10h** as well, was even higher at room temperature than that of 5-unsubstituted derivative **10d**.

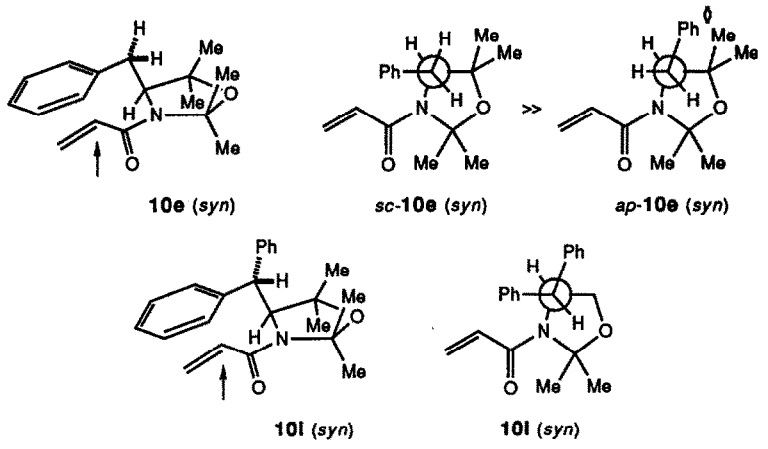


Figure 3. Stabilization of the synclinal conformation *sc*-**10e** (*syn*) by introduction of two methyl substituents at 5-position.

When the 4-benzyl group is replaced by a diphenylmethyl substituent, one of the two phenyl groups is induced to cover the acryloyl plane as shown with the examples of **10i** in Fig. 3 and **10j**. No substituents are necessary at 5-position to direct the chiral shielding substituent toward the *N*-acryloyl moiety. However, it was feared that the relative stability of *syn*-conformers, e.g. *syn*-**10i,j**, would decrease due to the increased steric repulsion since the diphenylmethyl moiety is a secondary and bulky substituent. Nevertheless, almost identical *syn/anti* ratios (96:4 at –30 °C) were actually observed (entries 10 and 11). This is consistent with the MM2 calculations.

Chiral shielding, evaluated by magnetic shielding, by the dipheylmethyl moiety was also about the same to that of **10e** at –30 °C (entries 6 and 10). However, **10i** showed more effective shielding at room temperature (**10e**: δ 5.14, 5.78, 5.96; **10i**: 4.98, 5.63, 5.84 for $=CH_2^c$, =CH-, $=CH_2^t$, respectively). This indicates the higher thermal stability of diphenylmethyl substituent for chiral shielding than benzyl substituent. At room temperature the phenyl plane of benzyl group of **10e** rotates fast around the C-1/benzylic carbon bond, and consequently fails to cover the *N*-acryloyl face. On the other hand, thermal movement of one phenyl group of **10i**, the one shielding the *N*-acryloyl moiety, is restricted by the other geminal phenyl group. Accordingly, 4-(diphenylmethyl)oxazolidines **10i,j** would become better chiral acrylamides than 4-benzyl derivatives **10e,h**, especially in the reactions performed at relatively high reaction temperatures.

Introduction of a 9-fluorenyl group at 4-position caused the extremely decreased *anti/syn* ratio (entry 12). It is certain that the steric size of fluorenyl substituent is a major reason. In addition, chiral shielding by the fluorenyl moiety toward the *N*-acryloyl moiety, evaluated by the chemical shifts, is not enough in the major conformer *syn*-**10k** (entry 12).

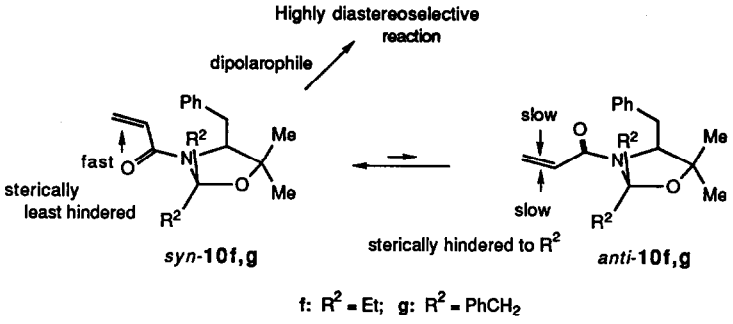


Figure 4. Relative reaction rates for both acryloyl faces in *syn*- and *anti*-conformers (*syn*-**10f,g** and *anti*-**10f,g**).

Two substituents at 2-position, e.g. substituent R^2 in Figs. 2 and 4, serve to control the *syn/anti* ratio in favor of *syn*-conformer. In the cases of 4-benzyloxazolidines **10f,g**, the bulkier substituent R^2 becomes, the more favored *syn*-conformers *syn*-**10f,g** should be (Fig. 4). The sterically least hindered nucleophilic attack occurs at the face opposite to 4-benzyl moiety in *s-cis* conformer of *syn*-**10f,g**. Since *syn*-conformers are generally more favored than *anti*-conformers for a variety of substituents R^2 and R^4, high diastereoselectivities would result when the chiral shielding by R^4 is efficient. However, it is still certain that participation of *anti*-conformer in the reaction lowers selectivity. To suppress the less selective undesired reaction from *anti*-**E**, we planned to introduce two bulky substituents at 2-position. 2,2-Diethyl and 2,2-bibenzyl derivatives, **10f** and **10g**, are the cases. In such acrylamides, the nucleophilic attack in *anti*-conformers is expected to become quite difficult at both acryloyl faces.

It was disappointing, however, that not only *syn/anti* conformer ratio but also chiral shielding, evaluated by magnetic shielding, was poor for the diethyl derivative **10f** (entry 7). The dibenzyl derivative **10g** existed as single conformer in the temperature range of 27 to –80 °C. Based on the fact that the *syn/anti* conformer ratio was lowered when the 2-substituents were replaced from methyl to ethyl (entries 6 and 7), it is difficult to assume that *syn*-**10g** has been much more stabilized than *anti*-**10g**. Probably, the rotation barrier should be relatively lowered in **10g** since the stability of flat amide structure decreases due to the increased steric repulsion in the ground states, both for *syn*- and *anti*-conformers. According to MM2 calculation, torsion angles for the amide moieties, C(2)-N(3)-C(CO)-O(CO) are calculated as –5.7°, –7.4°, and –10.5° for *syn*-conformers and C(4)-N(3)-C(CO)-O(CO) are –4.7°, –7.7°, and –2.3° for *anti*-conformers of **10e**, **10f**, and **10g**, respectively.[25] Such deviation from the flat amide plane causes the aforementioned less effective magnetic shielding.

Conclusion. A variety of new chiral auxiliaries based on conformation control have been described in the present work. Important factors to effect the chirality discrimination at the *N*-acryloyl faces by a substituent at 4-position are: 1) High *syn/anti* conformer ratio can be accomplished enough by introduction of two methyl groups or a pentamethylene group at 2-position. Substituents bulkier than methyl group at 2-position improve neither *syn/anti* conformer ratio nor chiral shielding. 2) A benzyl group at 4-position works as excellent chiral shielding substituent if two methyl groups are introduced at 5-position. 3) Introduction of a bulky substituent at 4-position does not always affect the stability of *syn*-conformation. 4) A diphenylmethyl substituent at 4-position is effective even when no 5-substituents exist. 5) The diphenylmethyl group behaves as thermally rigid shielding substituent.

Porter and coworkers have recently demonstrated the sufficient use of the *N*-acryloyl derivatives of 4-(*t*-butyl)-2,2-dimethyloxazolidine in highly diastereoselective free radical reactions.[26] They conclude that the

pseudoaxial methyl group at 2-position shields, in the *anti*-conformer, the same diastereoface that the *tert*-butyl group protects in the *syn*-conformer.

Diastereoselective nitrile oxide cycloaddition reactions using above chiral acrylamides are reported in the succeeding paper in this journal.

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EXPERIMENTAL

General. Melting points were recorded on a Yanagimoto melting point apparatus and are uncorrected. IR spectra were taken with JASCO IRA-1 and A-702 spectrometers. ^1H and ^{13}C NMR spectra were recorded with JEOL JNM EX-90 (^1H NMR: 90 MHz) and JEOL GSX-270 (270 MHz for ^1H NMR and 67.94 MHz for ^{13}C NMR) instruments. Chemical shifts are reported in parts per million downfield (δ) from internal tetramethylsilane at 27 °C unless otherwise stated. Mass spectra were recorded with a JEOL-01SG-2 spectrometer operating at an ionization energy of 75 eV unless otherwise stated. Elemental analyses were performed with a Hitachi 026 CHN analyzer. Optical rotations were recorded with a Horiba SEPA-200 polarimeter. High performance liquid chromatography (HPLC) was performed on TOSOH SC-8010 or JASCO FAMILIC-300S equipped with a column Hibar LiChrosorb^R Si 60 (Cica Merck). Chiral HPLC was performed with Chiralcel^R OB and OD (both Dicel). Flash chromatography was performed with an Eyera EF-10 apparatus on a 20x180 mm column packed with 0.04-0.063 mm silica gel 60. For preparative column chromatography, Merck silica gel 60 was used. Micro vacuum distillation was performed with a Sibata GTO-250R Kugelrohr distilling apparatus.

General Procedure for the Acetalization of (S,S)-5 and 6a-f Leading to (S,S)-7 and 8a-k. As a typical procedure the reaction of **6a** is presented. A solution of (*R*)-**6a** (0.206 g, 1.5 mmol) in acetone (10 ml) containing PTSA (0.03 g) was refluxed for 12 h. The acetone was removed by evaporation in vacuo. To the residue were added CH_2Cl_2 (20 ml) and saturated aqueous $NaHCO_3$. The CH_2Cl_2 was separated and the aqueous layer was extracted with CH_2Cl_2 (4 x 15 ml). The combined extracts were dried ($MgSO_4$) and evaporated in vacuo to give (*R*)-**8a** (0.239 g, 69%).

Other imidazolidine (*S,S*)-**7** and oxazolidines **6b-k** were similarly prepared. In the cases of **6b,h,j** which bear a pentamethylene moiety, cyclohexanone diluted with CH_2Cl_2 was employed instead of acetone. These *N*-unsubstituted imidazolidine and oxazolidines are all too labile against hydrolysis. However, their purity was satisfactory enough to be used without further purification for the following *N*-acryloylations. Only ^1H NMR spectra ($CDCl_3$) are shown below: (*S,S*)-2,2-dimethyl-4,5-diphenylimidazolidine [(*S,S*)-**7**]: δ = 1.52 (6H, s, Me), 2.06 (2H, br, NH), 4.22 (2H, s, H-4 and H-5), and 7.22 (10H, s, Ph); (*R*)-2,2-dimethyl-4-phenyloxazolidine [(*R*)-**8a**]: δ = 1.43, 1.50 (each 3H, s, Me), 2.80 (1H, br, NH), 3.67 (1H, t, $J_{gem} = J_{5\text{-}4(cis)} = 8.0$ Hz, one of H-5), 4.23 (1H, t, $J_{gem} = J_{5\text{-}4(trans)} = 8.0$ Hz, the other of H-5), 4.50 (1H, t, $J_{4\text{-}5} = 8.0$ Hz, H-4), and 7.20 - 7.40 (5H, s, Ph); *rac*-2,2-pentamethylene-4-phenyloxazolidine (*rac*-**8b**): δ = 1.40 - 1.74 (10H, m, CH_2), 1.99 (1H, s, NH), 3.66 (1H, t, $J_{gem} = J_{5\text{-}4(cis)} = 8.1$Hz, one of H-5), 4.24 (1H, dd, $J_{gem} = 8.1$ and $J_{5\text{-}4(trans)} = 7.0$ Hz, the other H-5), 4.48 (1H, dd, $J_{4\text{-}5} = 8.1$and 7.0 Hz, H-4), and 7.23 - 7.63 (5H, m, Ph); (*S*)-4-isopropyl-2,2-dimethyloxazolidine [(*S*)-**8c**]: δ = 0.91, 1.04 (each 3H, d, *J* = 6.6 Hz, *i*-Pr), 1.31, 1.43 (each 3H, s, Me), 1.56 (1H, m, *i*-Pr), 1.85 (1H, br, NH), 3.10 (1H, dd, $J_{gem} = 8.4$ and $J_{5\text{-}4(trans)} = 7.0$ Hz, one of H-5), 3.33 (1H, dd, $J_{gem} = 8.4$ and $J_{5\text{-}4(cis)} = 7.7$ Hz, the other of H-5), and 3.93 (1H, dd, $J_{4\text{-}5} = 7.7$ and 7.0 Hz, H-4); (*S*)-4-benzyl-2,2-dimethyloxazolidine [(*S*)-**8d**]: δ = 1.32, 1.46 (each 3H, s, Me), 1.95 (1H, br, NH), 2.71 (1H, dd, $J_{gem} = 12.0$ and $J_{CH2\text{-}4} = 7.3$ Hz, one of $PhCH_2$), 3.01 (1H, dd, $J_{gem} = 12.0$ and $J_{CH2\text{-}4} = 6.3$ Hz, the other of $PhCH_2$), 3.37 (1H, t, $J_{gem} = J_{5\text{-}4(cis)} = 8.0$ Hz, one of H-5), 3.75 (1H, m, H-4), 3.88 (1H, dd, $J_{gem} = 8.0$ and $J_{4\text{-}5(trans)} = 6.0$ Hz, the other of H-5), and 7.10 - 7.45 (5H, m, Ph); (*S*)-4-benzyl-2,2,5,5-tetramethyloxazolidine [(*S*)-**8e**]: δ = 1.09, 1.13, 1.29, 1.43 (each 3H, Me), 1.95 (1H, br, NH), 2.66 (1H, dd, $J_{gem} = 14.3$ and $J_{CH2\text{-}4} = 5.9$ Hz, one of $PhCH_2$), 2.75 (1H, dd, $J_{gem} = 14.3$ and $J_{CH2\text{-}4} = 8.1$ Hz, the other of $PhCH_2$), 3.38 (1H, dd, $J_{gem} = 8.7$ and $J_{CH2\text{-}4} = 6.9$ Hz, one of H-5), 3.72 (1H, dd, $J_{gem} = 8.7$ and $J_{CH2\text{-}4} = 8.0$ Hz, the other

of H-5), 3.82 (1H, m, H-4), and 7.17 - 7.34 (5H, m, Ph): (*S*)-4-benzyl-2,2-diethyl-5,5-dimethyloxazolidine [(*S*)-**8f**]: δ = 0.94, 1.05 (each 3H, t, J = 6.7 Hz, Et), 1.10, 1.11 (each 3H, s, Me), 1.60 (4H, m, Et), 1.80 (1H, br, NH), 2.60 (1H, dd, J_{gem} = 14.3 and $J_{CH2\text{-}4}$ = 6.6 Hz, one of $PhCH_2$), 2.81 (1H, dd, J_{gem} = 14.3 and $J_{CH2\text{-}4}$ = 6.8 Hz, the other of $PhCH_2$), 3.35 (1H, dd, $J_{4\text{-}CH2}$ = 6.8 and 6.6 Hz, H-4), and 7.14 - 7.43 (5H, m, Ph): (*S*)-2,2,4-tribenzyl-5,5-dimethyloxazolidine [(*S*)-**8g**]: δ = 0.50, 1.05 (each 3H, s, Me), 1.99 (1H, br, NH), 2.30 - 3.20 (7H, m, $PhCH_2$ and H-4), and 6.65 - 7.60 (15H, m, Ph); (*S*)-4-benzyl-5,5-dimethyl-2,2-pentamethyleneoxazolidine [(*S*)-**8h**]: δ = 1.09, 1.11 (each 3H, s, Me), 1.20 - 2.10 (11H, m, CH_2 and NH), 2.30 (1H, dd, J_{gem} = 7.5 and $J_{CH2\text{-}4}$ = 7.0 Hz, one of $PhCH_2$), 2.69 (1H, dd, J_{gem} = 7.5 and $J_{CH2\text{-}4}$ = 6.5 Hz, the other of $PhCH_2$), 3.30 (1H, dd, $J_{4\text{-}CH2}$ = 7.0 and 6.5 Hz, H-4), and 7.05 - 7.40 (5H, m, Ph); *rac*-2,2-dimethyl-4-(diphenylmethyl)oxazolidine (*rac*-**8i**): δ = 1.32, 1.38 (each 3H, s, Me), 1.88 (1H, br, NH), 3.40 (H, dd, J_{gem} = 9.9 and $J_{5\text{-}4}$ = 7.5 Hz, one of H-5), 3.76 (1H, dd, J_{gem} = 9.9 and $J_{5\text{-}4}$ = 6.0 Hz, the other of H-5), 3.81 (1H, d, $J_{CH\text{-}4}$ = 9.0 Hz, Ph_2CH), 4.20 (1H, m, H-4), and 6.95 - 7.40 (10H, m, Ph); *rac*-2,2-pentamethylene-4-(diphenylmethyl)oxazolidine (*rac*-**8j**): δ = 0.90 - 2.00 (10H, m, CH_2), 2.31 (1H, br, NH), 3.42 (1H, dd, J_{gem} = 10.3 and $J_{5\text{-}4}$ = 7.5 Hz, one of H-5), 3.76 (1H, dd, J_{gem} = 10.3 and $J_{5\text{-}4}$ = 7.3 Hz, the other of H-5), 3.84 (1H, d, $J_{CH\text{-}4}$ = 8.0 Hz, Ph_2CH), 4.20 (1H, m, H-4), and 6.95 - 7.42 (10H, m, Ph); *rac*-4-(9-fluorenyl)-2,2-dimethyloxazolidine (*rac*-**8k**): δ = 1.31, 1.39 (each 3H, s, Me), 1.87 (1H, br, NH), 3.40 (1H, dd, J_{gem} = 10.5 and $J_{5\text{-}4}$ = 4.8 Hz, one of H-5), 3.48 (1H, dd, J_{gem} = 10.5 and $J_{5\text{-}4}$ = 6.0 Hz, the other of H-5), 3.88 (1H, m, H-4), 4.16 (1H, d, $J_{CH\text{-}4}$ = 5.5 Hz, fluorenyl CH), and 7.05 - 7.90 (8H, m, Ar).

***N*-Acryloylation of (*S,S*)-7 Leading to (*S,S*)-9.** To a mixture of (*S,S*)-**7** (0.62 g, 2.5 mmol) and NEt_3 (0.91 ml, 6.5 mmol) in CH_2Cl_2 (15 ml) was added slowly, at –78 °C under nitrogen in a period of 1 h, acryloyl chloride (0.543 g, 6 mmol) in CH_2Cl_2 (15 ml). The mixture was stirred at –78 °C for 1 h, poured to saturated aqueous $NaHCO_3$ (20 ml), and extracted with CH_2Cl_2 (5 x 20 ml). The combined extracts were dried ($MgSO_4$) and evaporated in vacuo. The residue was purified by column chromatography on silica gel with CH_2Cl_2-EtOAc (20:1 v/v) to give (*S,S*)-**9** (0.537 g, 60%).

(S,S)-1,3-Diacryloyl-2,2-dimethyl-4,5-diphenylimidazolidine [(S,S)-9]. Colorless prisms (*i*-PrOH); mp 221-222 °C; $[\alpha]_D^{24}$ = –119.5° (c = 1.05, $CHCl_3$); IR (KBr) 3000, 1630, 1605, 1400, 1360, 1325, 1295, 1180, 950, 780, 710, and 690 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 2.26 (6H, s, Me), 5.37 (2H, s, H-4 and H-5), 5.48 (2H, dd, J_{cis} = 10.3 and J_{gem} = 1.8 Hz, $=CH_2$), 6.12 (2H, dd, J_{trans} = 16.5 and J_{cis} = 10.3 Hz, =CH-), 6.31 (2H, dd, J_{trans} = 16.5 and J_{gem} = 1.8 Hz, $=CH_2$), and 7.40-7.45 (10H, m, Ph); ^{13}C NMR ($CDCl_3$) δ = 25.54 (Me), 68.58 (C-4 and C-5), 77.51 (C-2), 128.29, 128.61, 129.17, 129.25, 141.32 (Ph and =CH), and 163.93 (NCO); MS (rel intensity, %) m/z 360 (M^+, 2), 346 (26), 345 (base peak), 292 (15), 291 (67), 237 (41), 201 (31), 196 (13), 146 (41), 104 (11), 91 (21), 90 (10), and 55 (53). Anal. Calcd for $C_{23}H_{24}N_2O_2$: C, 76.64; H, 6.71; N, 7.77%. Found: C, 77.07; H, 6.83; N, 7.85%.

General Procedure for the N-Acryloylation of 8a-k Leading to 10a-k. As a typical example the reaction of (*R*)-**8a** is presented. To a mixture of (*R*)-**8a** (1.099 g, 6.2 mmol) and NEt_3 (1.05 ml, 7.5 mmol) in CH_2Cl_2 (20 ml) was added slowly, in a period of 10 min at 0 °C under nitrogen, acryloyl chloride (0.679 g, 7.5 mmol) in CH_2Cl_2 (10 ml). The mixture was stirred at 0 °C for 1 h, poured to saturated aqueous $NaHCO_3$ (20 ml), and extracted with CH_2Cl_2 (3 x 20 ml). The combined extracts were dried ($MgSO_4$) and evaporated in vacuo. The residue was purified by column chromatography on silica gel with hexane-EtOAc (6:1 v/v) to give (*R*)-**10a** (1.223 g, 85%).

N-Acryloylations of other oxazolidines **8b-k** were similarly performed. The yields of **10b-k** based on **8b-k** as well as the eluents used for silica gel column chromatography are given in each section.

(R)-3-Acryloyl-2,2-dimethyl-4-phenyloxazolidine [(R)-10a]. Colorless prisms (hexane); mp 47-48 °C; $[\alpha]_D^{24}$ = –85.4° (c = 1.01, $CHCl_3$); IR (KBr) 2950, 1640, 1600, 1420, 1350, 1240, 1050, and 960 cm^{-1}; ^1H NMR ($CDCl_3$, 27 °C) δ = 1.70, 1.90 (each 3H, s, Me), 3.94 (1H, dd, J_{gem} = 9.2 and $J_{5\text{-}4(trans)}$ = 2.2 Hz, one of H-5), 4.40 (1H, dd, J_{gem} = 9.2 and $J_{5\text{-}4(cis)}$ = 6.6 Hz, the other of H-5), 5.02 (1H, dd, $J_{4\text{-}5}$ = 6.6 and 2.2 Hz, H-4), 5.47 (1H, dd, J_{cis} = 9.9 and J_{gem} = 2.0 Hz, $=CH_2$), 6.10 (1H, dd, J_{trans} = 16.6 and J_{cis} = 9.9 Hz, =CH-), 6.30 (1H, dd, J_{trans} = 16.6 and J_{gem} = 2.0 Hz, $=CH_2$), and 7.26-7.40 (5H, m, Ph); ^{13}C NMR ($CDCl_3$, 27 °C) δ = 23.31, 25.26 (Me), 61.21 (C-5), 71.43 (C-4), 96.28 (C-2), 125.90,127.86, 127.92, 128.97, 129.80, 141.49 (Ph and =CH), and 163.46 (NCO); MS (20 eV, rel intensity, %) m/z 231 (M^+, 7), 217 (15), 216 (base peak), 173 (10), and 162 (21). Anal. Calcd for $C_{14}H_{17}NO_2$: C, 72.70; H, 7.41; N, 6.06%. Found: C, 72.88; H, 7.45; N, 6.08%.

rac-3-Acryloyl-2,2-pentamethylene-4-phenyloxazolidine [rac-10b]. Separated and purified by silica gel column chromatography using hexane-EtOAc (10:1 v/v). Yield 83%. Colorless needles (hexane); mp 107-108 °C; IR (KBr) 2960, 1640, 1610, 1420, 1070, 990, 740, and 700 cm^{-1}; ^1H NMR ($CDCl_3$, 27 °C) δ = 1.27-2.93 (10H, m, CH_2), 3.92 (1H, dd, J_{gem} = 8.8 and $J_{5\text{-}4(trans)}$ = 2.0 Hz, one of H-5), 4.35 (1H, dd, J_{gem} = 8.8 and $J_{5\text{-}4(cis)}$ = 6.4 Hz, the other of H-5), 5.02 (1H, dd, $J_{4\text{-}5}$ = 6.4 and 2.0 Hz, H-4), 5.44 (1H, dd, J_{cis} = 10.1 and J_{gem} = 2.2 Hz, $=CH_2$), 6.09 (1H, dd, J_{trans} = 16.5 and J_{cis} = 10.1 Hz, =CH), 6.28 (1H, dd, J_{trans} = 16.5 and J_{gem} = 2.2 Hz, $=CH_2$), and 7.27-7.38 (5H, m, Ph); ^{13}C NMR ($CDCl_3$, 27 °C) δ = 23.15, 23.43, 24.72, 29.98, 33.78 (each CH_2), 61.21 (C-5), 71.21 (C-4), 97.94 (C-2), 125.96, 127.74, 128.89, 130.26, 141.69 (Ph and =CH), and 163.67 (NCO); MS (rel intensity, %) *m/z* 272 (M^+ + 1, 10), 271 (M^+, 51), 229 (15), 228 (90), 215 (base peak), 214 (45), 187 (12), 174 (74), 120 (31), 104 (71), 103 (15), 91 (16), and 55 (62). Anal. Calcd for $C_{17}H_{21}NO_2$: C, 75.25; H, 7.80; N, 5.16%. Found: C, 75.51; H, 7.80; N, 5.09%.

(S)-3-Acryloyl-4-isopropyl-2,2-dimethyloxazolidine [(S)-10c]. Separated and purified by silica gel column chromatography using hexane-EtOAc (7:1 v/v). Yield 60%. Purification by a vacuum distillation (bulb-to-bulb) was also useful. Yield 60%. Colorless liquid; bp 100 °C / 0.3 Torr; $[\alpha]_D^{25}$ = −56.9° (*c* = 1.09, $CHCl_3$); IR (neat) 2920, 1630, 1590, 1405, 1350, 1225, 1060, 960, 830, and 780 cm^{-1}; ^1H NMR ($CDCl_3$, 27 °C) δ = 0.94, 0.96 (each 3H, d, *J* = 7.0 and 6.6 Hz, *i*-Pr), 1.56, 1.72 (each 3H, s, Me), 2.02 (1H, m, *i*-Pr), 3.82 (1H, m, H-4), 3.94, 3.97 (each 1H, br, H-5), 5.68 (1H, dd, J_{cis}= 7.3 and J_{gem} = 4.8 Hz, $=CH_2$), and 6.42 (2H, m, $=CH_2$ and =CH-); ^{13}C NMR ($CDCl_3$, 27 °C) δ = 17.05, 19.64 (each *i*-Pr), 22.78, 25.77 (each Me), 31.86 (*i*-Pr), 62.04 (C-5), 64.21 (C-4), 95.36 (C-2), 127.65, 129.60 ($=CH_2$ and =CH-), and 162.89 (NCO); MS (rel intensity, %) *m/z* 197 (M^+, 27), 182 (61), 154 (72), 128 (base peak), 100 (46), 96 (66), 83 (20), and 55 (84). Anal. Calcd for $C_{11}H_{19}NO_2$: C, 66.97; H, 9.71; N, 7.10%. Found: C, 66.55; H, 9.81; N, 7.20%.

(S)-3-Acryloyl-4-benzyl-2,2-dimethyloxazolidine [(S)-10d]. Separated and purified by silica gel column chromatography using hexane-EtOAc (9:1 v/v). Yield 81%. Colorless liquid; bp 135 °C / 0.2 Torr; $[\alpha]_D^{24}$ = −162.6° (*c* = 1.03, $CHCl_3$); IR (neat) 3000, 1650, 1610, 1420, 1365, 1245, and 970 cm^{-1}; ^1H NMR (CD_2Cl_2, −30 °C) *syn*: δ = 1.54, 1.73 (each 3H, s, Me), 2.86 (1H, dd, J_{gem} = 13.6 and $J_{CH2\text{-}4}$ = 9.9 Hz, one of $PhCH_2$), 2.97 (1H, dd, J_{gem} = 13.6 and $J_{CH2\text{-}4}$ = 4.2 Hz, the other of $PhCH_2$), 3.85 (2H, br s, H-5), 4.13 (1H, m, H-4), 5.72 (1H, dd, J_{cis} = 9.2 and J_{gem} = 2.9 Hz, $=CH_2$), 6.35 (1H, dd, J_{trans} = 16.5 and J_{gem} = 2.9 Hz, $=CH_2$), 6.56 (1H, dd, J_{trans} = 16.5 and J_{cis} = 9.2 Hz, =CH-), and 7.18-7.36 (5H, m, Ph). *anti*: δ = 1.67, 2.33 (each 3H, s, Me), 2.63 (1H, dd, J_{gem} = 12.9 and $J_{CH2\text{-}4}$ = 10.4 Hz, one of $PhCH_2$), 3.43 (1H, dd, J_{gem} = 12.9 and $J_{CH2\text{-}4}$ = 2.3 Hz, the other of $PhCH_2$), 4.43 (1H, m, H-4), 5.74 (1H, dd, J_{cis} = 9.9 and J_{gem} = 2.3 Hz, $=CH_2$), 6.41 (1H, dd, J_{trans} = 16.5 and J_{gem} = 2.3 Hz, $=CH_2$), 6.58 (1H, dd, J_{trans} = 16.5 and J_{cis} = 9.9 Hz, =CH-). Other signals are overlapping with those of *syn*-conformer; ^{13}C NMR ($CDCl_3$, 27 °C) δ = 23.11, 26.74 (each Me), 40.89 ($PhCH_2$), 59.00 (C-5), 66.39 (C-4), 95.71 (C-2), 126.99, 128.17, 128.91, 129.00, 129.23, 137.27 (Ph and =CH), and 162.30 (NCO); MS (rel intensity, %) *m/z* 245 (M^+, 19), 176 (22), 155 (10), 154 (base peak), 100 (38), 96 (51), 91 (16), 83 (15), and 55 (54). Anal. Calcd for $C_{15}H_{19}NO_2$: C, 73.44; H, 7.81; N, 5.71%. Found: C, 73.26; H, 7.91; N, 5.55%.

(S)-3-Acryloyl-4-benzyl-2,2,5,5-tetramethyloxazolidine [(S)-10e]. Separated and purified by silica gel column chromatography using hexane-EtOAc (9:1 v/v). Purification by a vacuum distillation (bulb-to-bulb) was also useful. Yield 89%. Colorless prisms; mp 38-39 °C (bp 140 °C / 0.2 Torr); $[\alpha]_D^{25}$ = −197.7° (*c* = 1.00, $CHCl_3$); IR (neat) 3000, 1640, 1610, 1420, 1370, 1270, 1200, 1140, and 1000 cm^{-1}; ^1H NMR (CD_2Cl_2, −30 °C) *syn*: δ = 1.32, 1.36, 1.69, 1.75 (each 3H, s, Me), 2.77 (1H, dd, J_{gem} = 13.5 and $J_{CH2\text{-}4}$ = 9.6 Hz, one of $PhCH_2$), 3.01 (1H, dd, J_{gem} = 13.5 and $J_{CH2\text{-}4}$ = 5.3 Hz, the other of $PhCH_2$), 3.98 (1H, dd, $J_{4\text{-}CH2}$ = 9.6 and 5.3 Hz, H-4), 5.02 (1H, dd, J_{cis} = 8.9 and J_{gem} = 3.3 Hz, $=CH_2$), 5.71 (1H, dd, J_{trans} = 16.5 and J_{cis} = 8.9 Hz, =CH-), 5.76 (1H, dd, J_{trans} = 16.5 and J_{gem} = 3.3 Hz, $=CH_2$), and 7.15-7.29 (5H, m, Ph). *anti*: δ = 1.17, 1.24 (each 3H, s, Me), 2.19 (6H, each s, Me), 4.54 (1H, dd, $J_{4\text{-}CH2}$ = 8.6 and 4.3 Hz, H-4), 6.34 (1H, dd, J_{trans} = 16.5 and J_{gem} = 2.0 Hz, $=CH_2$), 6.57 (1H, dd, J_{trans} = 16.5 and J_{cis} = 10.2 Hz, =CH-). Other signals are overlapping with those of *syn*-conformer; ^{13}C NMR ($CDCl_3$, 27 °C) δ = 24.20, 27.88, 28.80, 29.30 (each Me), 38.66 ($PhCH_2$), 66.52 (C-4), 80.42 (C-5), 94.58 (C-2), 125.74, 126.72, 128.00, 128.78, 129.59, 137.54 (Ph and =CH), and 163.64 (NCO); MS (20eV, rel intensity, %)

m/z 273 (M^+, 10), 258 (6), 204 (5), 183 (12), 182 (base peak), 128 (12), and 124 (20). Anal. Calcd for $C_{17}H_{23}NO_2$: C, 74.69; H, 8.48; N, 5.12%. Found: C, 74.89; H, 8.47; N, 5.04%.

(S)-3-Acryloyl-4-benzyl-2,2-diethyl-5,5-dimethyloxazolidine [(S)-10f]. Separated and purified by silica gel column chromatography using hexane-EtOAc (9:1 v/v). Yield 57%. Colorless liquid; $[\alpha]_D^{25} = -177.2°$ (*c* = 1.06, $CHCl_3$); IR (neat) 2950, 1640, 1605, 1410, 1140, and 690 cm^{-1}; ^1H NMR (CD_2Cl_2, –30 °C) *syn*: δ = 0.90, 0.98 (each 3H, t, *J* = 7.3 Hz, Et), 1.22, 1.34 (each 3H, s, Me), 1.82-2.52 (4H, m, Et), 2.94 (1H, dd, J_{gem} = 14.9 and $J_{CH2\text{-}4}$ = 5.3 Hz, one of $PhCH_2$), 3.08 (1H, dd, J_{gem} = 14.9 and $J_{CH2\text{-}4}$ = 9.2 Hz, the other of $PhCH_2$), 4.19 (1H, dd, $J_{4\text{-}CH2}$ = 9.2 and 5.3 Hz, H-4), 5.47 (1H, dd, J_{cis} = 9.9 and J_{gem} = 2.3 Hz, $=CH_2$), 6.13 (1H, dd, J_{trans} = 16.5 and J_{gem} = 2.3 Hz, $=CH_2$), 6.31 (1H, dd, J_{trans} = 16.5 and J_{cis} = 9.9 Hz, =CH), and 7.10-7.40 (5H, m, Ph). *anti*: δ = 1.16, 1.26 (each 3H, s, Me), 2.74 (1H, dd, J_{gem} = 13.9 and $J_{CH2\text{-}4}$ = 10.6 Hz, one of $PhCH_2$), 3.28 (1H, d, J_{gem} = 13.9 Hz, the other of $PhCH_2$), 4.43 (1H, d, $J_{4\text{-}CH2}$ = 10.6 Hz, H-4), 5.69 (1H, dd, J_{cis} = 9.9 and J_{gem} = 2.3 Hz, $=CH_2$), 6.38 (1H, dd, J_{trans} = 16.5 and J_{gem} = 2.3 Hz, $=CH_2$), 6.54 (1H, dd, J_{trans} = 16.5 and J_{cis} = 9.9 Hz, =CH). Other signals are overlapping with those of *syn*-conformer; MS (rel intensity, %) *m/z* 301 (M^+, 3), 273 (22), 272 (base peak), 218 (29), and 210 (22). Anal. Calcd for $C_{19}H_{27}NO_2$: C, 75.71; H, 9.63; N, 4.65%. Found: C, 75.72; H, 8.81; N, 4.57%.

(S)-3-Acryloyl-2,2,4-tribenzyl-5,5-dimethyloxazolidine [(S)-10g]. Separated and purified by silica gel column chromatography using hexane-EtOAc (9:1 v/v). Yield 53% based on **6d**. Colorless prisms (hexane); mp 98-99 °C; $[\alpha]_D^{24} = -208.2°$ (*c* = 1.01, $CHCl_3$); IR (KBr) 2960, 1630, 1590, 1400, 1130, 960, and 690 cm^{-1}; ^1H NMR (CD_2Cl_2, –30 °C) *syn*: δ = 0.78 (1H, dd, J_{gem} = 15.0 and $J_{CH2\text{-}4}$ = 12.0 Hz, one of 2-$PhCH_2$), 0.87, 1.45 (each 3H, s, Me), 1.94 (1H, J_{gem} = 15.0 Hz, the other of 4-$PhCH_2$), 2.71, 3,13, 3,69, 4.07 (each 1H, d, J_{gem} = 13.6 and 13.1 Hz, 2-$PhCH_2$), 4.13 (1H, d, $J_{4\text{-}CH2}$ = 12.0 Hz, H-4), 5.75 (1H, dd, J_{cis} = 8.1 and J_{gem} = 4.0 Hz, $=CH_2$), 6.50 (1H, dd, J_{trans} = 16.8 and J_{cis} = 8.1 Hz, =CH), 6.53 (1H, dd, J_{trans} = 16.8 and J_{gem} = 4.0 Hz, $=CH_2$), 6.84 (2H, d, *J* = 7.0 Hz, *o*-H of Ph), and 7.01-7.41 (13H, m, Ph); ^{13}C NMR ($CDCl_3$, 27 °C) δ = 24.94, 31.60, 37.09, 41.78, 43.84 (each $PhCH_2$), 65.04 (C-4), 81.61 (C-5), 99.38 (C-2), 126.22, 126.42, 126.62, 127.86, 128.00, 128.10, 128.25, 128.49, 128.71, 129.61, 131.33, 131.77, 137.40, 137.59, 138.31 (Ph and =CH), and 163.46 (NCO); MS (20eV, rel intensity, %) *m/z* 425 (M^+, 1), 335 (25), 334 (base peak), 280 (12), and 216 (1). Anal. Calcd for $C_{29}H_{31}NO_2$: C, 81.85; H, 7.34; N, 3.29%. Found: C, 81.76; H, 7.31, N, 3.34%.

(S)-3-Acryloyl-4-benzyl-5,5-dimethyl-2,2-pentamethyleneoxazolidine [(S)-10h]. Separated and purified by silica gel column chromatography using hexane-EtOAc (9:1 v/v). Yield 69%. Colorless prisms (hexane); mp 93-94 °C; $[\alpha]_D^{24} = -172.6°$ (*c* = 1.00, $CHCl_3$); IR (KBr) 2930, 1640, 1605, 1410, 1140, 935, 740, and 690 cm^{-1}; ^1H NMR (CD_2Cl_2, –30 °C) *syn*: δ = 1.32, 1.34 (each 3H, s, Me), 1.63-2.70 (10H, m, CH_2), 2.84 (1H, dd, J_{gem} = 13.8 and $J_{CH2\text{-}4}$ = 8.6 Hz, one of $PhCH_2$), 2.99 (1H, dd, J_{gem} = 13.8 and $J_{CH2\text{-}4}$ = 5.3 Hz, the other of $PhCH_2$), 3.98 (1H, dd, $J_{4\text{-}CH2}$ = 8.6 and 5.3 Hz, H-4), 5.01 (1H, dd, J_{cis} = 6.9 and J_{gem} = 5.3 Hz, $=CH_2$), 5.71 (1H, dd, J_{trans} = 16.5 and J_{cis} = 6.9 Hz, =CH), 5.76 (1H, dd, J_{trans} = 16.5 and J_{gem} = 5.3 Hz, $=CH_2$), and 7.15-7.28 (5H, m, Ph). *anti*: δ = 2.14 (6H, s, Me), 4.55 (1H, dd, $J_{4\text{-}CH2}$ = 7.5 and 4.0 Hz, H-4), 5.69 (1H, dd, J_{cis} = 10.2 and J_{gem} = 2.0 Hz, $=CH_2$), 6.31 (1H, dd, J_{trans} = 16.5 and J_{gem} = 2.0 Hz, $=CH_2$), 6.65 (1H, dd, J_{trans} = 16.5 and J_{cis} = 10.2 Hz, =CH). Other signals are overlapping with those of *syn*-conformer; ^{13}C NMR ($CDCl_3$, 27 °C) δ = 23.24, 23.56, 24.54, 24.85, 29.57, 33.97, 37.11 (Me and CH_2), 39.06 ($PhCH_2$), 66.32 (C-4), 80.08 (C-5), 96.33 (C-2), 125.45, 126.62, 128.69, 129.17, 129.64, 137.75 (Ph and =CH), and 163.91 (NCO); MS (rel intensity, %) *m/z* 314 (M^+ + 1, 18), 313 (M^+, 75), 270 (80), 257 (base peak), 256 (40), 222 (76), 216 (41), 168 (22), 145 (81), 124 (85), 91 (98), and 55 (88). Anal. Calcd for $C_{20}H_{27}NO_2$: C, 76.64; H, 8.68; N, 4.47%. Found: C, 76.63; H, 8.72; N, 4.27%.

rac-3-Acryloyl-5,5-dimethyl-4-(diphenylmethyl)oxazolidine (rac-10i). Separated and purified by silica gel column chromatography using hexane-EtOAc (5:1 v/v). Yield 68%. Colorless plates (*i*-PrOH); mp 168-169 °C; IR (KBr) 3000, 1630, 1595, 1420, 1360, 1220, 1055, and 700 cm^{-1}; ^1H NMR (CD_2Cl_2, –30 °C) *syn*: δ = 1.55, 1.86 (each 3H, s, Me), 3.84 (1H, d, J_{gem} = 9.2 Hz, H-5 (trans)), 4.04 (1H, dd, J_{gem} = 9.2 and $J_{5\text{-}4(cis)}$ = 4.5 Hz, H-5 (cis)), 4.23 (1H, d, $J_{CH\text{-}4}$ = 10.6 Hz, Ph_2CH), 4.66 (1H, dd, $J_{4\text{-}CH}$ = 10.6 and $J_{4\text{-}5}$ = 4.5 Hz, H-4), 4.91 (1H, dd, J_{cis} = 8.9 and J_{gem} = 3.3 Hz, $=CH_2$), 5.62 (1H, dd, J_{trans} = 16.5 and J_{cis} = 8.9 Hz, Hz, =CH), 5.70 (1H, dd, J_{trans} = 16.5 and J_{gem} = 3.3 Hz, $=CH_2$), and 7.10-7.28 (10H, m, Ph). *anti*: δ = 1.45, 1.48 (each 3H, s, Me), 3.94 (1H, d, J_{gem} = 9.2

Hz, H-5 (trans)), 4.50 (1H, d, J_{CH-4} = 9.9 Hz, Ph_2CH), 6.20 (1H, dd, J_{trans} = 16.5 and J_{gem} = 2.3 Hz, $=CH_2$), 6.42 (1H, dd, J_{trans} = 16.5 and J_{cis} = 10.2 Hz, =CH-). Other signals are overlapping with those of *syn*-conformer; ^{13}C NMR ($CDCl_3$, 27 °C) δ = 23.27, 27.00 (each Me), 54.38 (Ph_2CH), 60.98 (C-5), 67.30 (C-4), 96.17 (C-2), 125.29, 127.01, 127.09, 127.63, 128.59, 128.85, 128.98, 129.56, 140.41, 140.74 (Ph_2CH and =CH), and 163.78 (NCO); MS (rel intensity, %) *m/z* 321 (M^+, 4), 167 (21), 165 (17), 154 (base peak), 100 (22), 96 (31), 83 (10), and 55 (33). Anal. Calcd for $C_{21}H_{23}NO_2$: C, 78.47; H, 7.21; N, 4.36%. Found: C, 78.34; H, 7.20; N, 4.40%.

rac-3-Acryloyl-5,5-pentamethylene-4-(diphenylmethyl)oxazolidine (rac-10j). Separated and purified by silica gel column chromatography using hexane-EtOAc (6:1 v/v). Yield 81%. Colorless prisms (*i*-PrOH); mp 160-161 °C; IR (KBr) 2970, 1630, 1600, 1420, 1360, 1220, 1050, and 700 cm^{-1}; ^1H NMR (CD_2Cl_2, –30 °C) *syn*: δ = 1.19-3.00 (10H, br, CH_2), 3.79 (1H, d, J_{CH-4} = 9.2 Hz, Ph_2CH), 3.98 (1H, dd, J_{4-CH} = 9.2 and J_{4-5} = 4.6 Hz, H-4), 4.22 (1H, d, J_{gem} = 10.8 Hz, H-5 (trans)), 4.65 (1H, dd, J_{gem} = 10.8 and $J_{5-4(cis)}$ = 4.6 Hz, H-5 (cis)), 4.86 (1H, dd, J_{cis} = 7.6 and J_{gem} = 4.6 Hz, $=CH_2$), 5.61 (1H, dd, J_{trans} = 16.5 and J_{cis} = 7.6 Hz, =CH-), 5.67 (1H, dd, J_{trans} = 16.5 and J_{gem} = 4.6 Hz, $=CH_2$), and 7.14-7.38 (10H, m, Ph). *anti*: δ = 4.70 (1H, d, J_{gem} = 9.9 Hz, H-5 (trans)), 6.12 (1H, dd, J_{trans} = 16.5 and J_{gem} = 1.7 Hz, $=CH_2$), 6.47 (1H, dd, J_{trans} = 16.5 and J_{cis} = 10.0 Hz, =CH-). Other signals are overlapping with those of *syn*-conformer; ^{13}C NMR ($CDCl_3$, 27 °C) δ = 23.33, 23.47, 24.65, 29.26, 35.67(each CH_2), 54.54 (Ph_2CH), 60.89 (C-5), 67.11 (C-4), 97.79 (C-2), 124.86, 126.91, 126.99, 127.99, 128.48, 128.79, 128.98, 129.72, 140.41, 140.86 (Ph and =CH), and 163.98 (NCO); MS (rel intensity, %) *m/z* 361 (M^+, 3), 195 (13), 194 (base peak), 167 (13), 165 (10), 140 (10), 123 (21), 96 (33), and 55 (19). Anal. Calcd for $C_{24}H_{27}NO_2$: C, 79.74; H, 7.53; N, 3.87%. Found: C, 79.91; H, 7.63; N, 3.71%.

rac-3-Acryloyl-4-(9-fluorenyl)-5,5-dimethyloxazolidine (rac-10k). Separated and purified by silica gel column chromatography using hexane-EtOAc (4:1 v/v). Yield 70%. Colorless prisms (hexane); mp 76-77 °C; IR (neat) 3000, 1640, 1610, 1415, 1350, 1240, 1060, and 730 cm^{-1}; ^1H NMR (CD_2Cl_2, –30 °C) *syn*: δ = 1.56, 1.75 (each 3H, s, Me), 3.51 (1H, dd, J_{gem} = 9.2 and $J_{5-4(cis)}$ = 7.3 Hz, H-5 (cis)), 3.89 (1H, dd, J_{gem} = 9.2 and $J_{5-4(trans)}$ = 5.6 Hz, H-5 (trans)), 4.38 (2H, m, H-4 and fluorenyl CH), 5.47 (1H, dd, J_{cis} = 8.9 and J_{gem} = 3.3 Hz, $=CH_2$), 6.17 (1H, dd, J_{trans} = 16.5 and J_{cis} = 8.9 Hz, =CH-), 6.22 (1H, dd, J_{trans} = 16.5 and J_{gem} = 3.3 Hz, $=CH_2$), and 7.25-7.58 and 7.73-7.77 (8H, m, Ar). *anti*: δ = 1.48, 1.54 (each 3H, s, Me), 2.60 (1H, dd, J_{gem} = 9.6 and J_{5-4} = 6.6 Hz, one of H-5), 6.04 (2H, m, H-4 and fluorenyl CH), 5.86 (1H, dd, J_{cis} = 9.9 and J_{gem} = 2.0 Hz, $=CH_2$), 6.52 (1H, dd, J_{trans} = 16.5 and J_{gem} = 2.0 Hz, $=CH_2$), 6.70 (1H, dd, J_{trans} = 16.5 and J_{cis} = 9.9 Hz, =CH-); ^{13}C NMR ($CDCl_3$, 27 °C) *syn*: δ = 23.86, 25.64 (each Me), 49.96 (fluorenyl CH), 59.81 (C-5), 66.10 (C-4), 96.53 (C-2), and 163.98 (NCO); *anti*: δ = 27.11, 28.37 (each Me), 45.57 (fluorenyl CH), 60.80 (C-5), 67.14 (C-4), 94.44 (C-2), and 164.72 (NCO). Overlapping signals: δ = 120.11, 125.50, 125.74, 126.98, 127.34, 127.94, 128.09, 129.50, 141.31, 141.65, and 142.73 (Ar and =CH). MS (rel intensity, %) *m/z* 320 (M^+ + 1, 4), 319 (M^+, 14), 165 (38), 154 (base peak), 100 (38), 96 (59), 83 (152), and 55 (48). Anal. Calcd for $C_{21}H_{21}NO_2$: C, 78.97; H, 6.63; N, 4.39%. Found: C, 78.68; H, 6.53; N, 3.93%.

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24. Chem3D Plus™ version 3.0 was used for the MM2 calculation.
25. For 3-acryloyl-4-benzyloxazolidines with *S* configuration, all the amide nitrogen-carbonyl carbon bonds rotate anticlockwise in order to avoid steric repulsion against the 4-substituent. Plus sign was given to the clockwise rotation.
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