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Michael Addition of Chloroalkyloxazolines to Electron-Poor Alkenes: Synthesis of Heterosubstituted Cyclopropanes†

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Lithiated 2-(1-chloroethyl)-4,4-dimethyl-2-oxazoline **7** adds to electron-poor alkenyl heterocycles to afford substituted cyclopropanes in excellent yields. A route to chiral nonracemic heterosubstituted cyclopropanes, starting from optically active 2-chloromethyl-2-oxazolines, is highlighted as well.

Introduction

Recent papers from our[1] and other research labs[2,3] have disclosed that certain metalated haloalkyl heterocycles, which proved to be good Darzens reagents and add to carbonyl compounds and imines to produce substituted oxiranes and aziridines[4] and to nitrones to give alkenyl heterocycles,[5] in the absence of external electrophiles tend to undergo a sort of "trimerization", giving cyclopropane derivatives. Such a remarkable propensity turned out to be very much dependent upon the α-substitution and the size and the nature of the heterocyclic system, so that metalated 2-(chloromethyl)-2-oxazolines do undergo cyclopropanation, while 2-(1-chloroethyl)-2-oxazoline,[1] 2-(chloromethyl)-5,6-dihydro-4*H*-[1,3]oxazine,[1] 2-(chloromethyl)pyridine,[2] and 2-(chloromethyl)triazine[3] do not or do in small percentages, undergoing mostly the "dimerization" reaction to give diheterosubstituted alkenes (Scheme 1). This has been rationalized in terms of a diverse electrophilicity of the corresponding alkenes that could be ascribed to the different endocyclic nature of the C−N double bond of the involved heterocyclic ring.[1]

Results and Discussion

In this paper we report the preparation of a number of substituted cyclopropanes based on the Michael addition of lithiated 2-(1-chloroalkyl)oxazolines to electron-poor alkenyl heterocycles. Our concern for heterosubstituted cyclopropanes is justified by the occurrence that chiral bisoxazolines and trisoxazolines have been successfully used in several catalytic asymmetric processes as bidentate and tridentate chiral ligands.[6] Moreover, it is well-known that the cyclopropyl moiety plays an important role in many natural and nonnatural products.[7] Despite this, while a number of methods exist for stereoselective preparation of disubstituted cyclopropanes, synthetic procedures to trisubstituted cyclopropane derivatives are rather limited.[8,9]

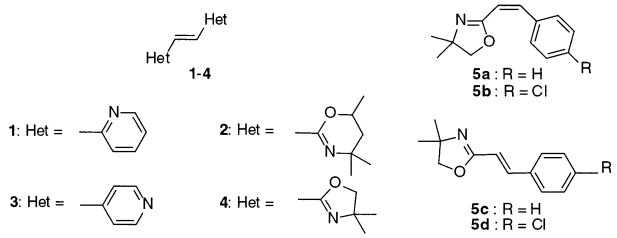

FIGURE 1.

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† Dedicated to Prof. A. I. Meyers on the occasion of his 70th birthday.

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(7) For examples of well-known cyclopropyl derivatives, see: Lin, H. W.; Walsh, C. T. In *The Chemistry of the Cyclopropyl Group*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1987; Vol. 16. Martel, J. In *Chirality in Industry*; Collins, A. N., Sheldrake, N. G., Crosby, J., Eds.; Wiley: Chichester, U.K., 1992; Chapter 4 and references therein. Barrett, A. G. M.; Kasdorf, J. *J. Am. Chem. Soc.* **1996**, *118*, 11030−11037 and references therein. Charette, A. B.; Lebel, H. *J. Am. Chem. Soc.* **1996**, *118*, 10327−10328 and references therein.

(8) For examples of direct carbene insertion into olefins from diazo precursors utilizing transition metals (stoichiometric and catalytic), see: Pfaltz, A. In *Comprehensive Asymmetric Catalysis I-III*; Chapter 16.1, Lydon, K. M., McKervey, M. A., Eds.; Chapter 16.2, Charette, A. B., Lebel, H., Eds.; Chapter 16.3, Jacobsen, E. N., Pfaltz, A., Yamamoto, H., Eds.; Springer-Verlag: Berlin, Heildelberg, New York, 2000.

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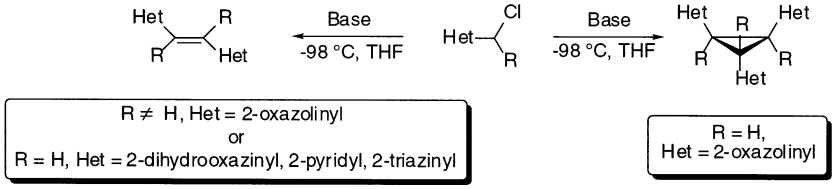
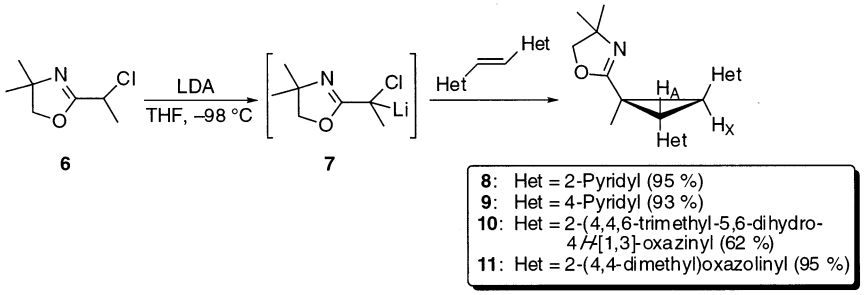
SCHEME 1



SCHEME 2



The needed alkenes for the cyclopropanation reaction under investigation were prepared as follows: *trans*-bis-(2-pyridyl)ethene **1** and *trans*-bis(dihydrooxazinyl)ethene **2** (Figure 1) were prepared in almost quantitative yields by treating 2-(chloromethyl)pyridine and 2-(chloromethyl)dihydrooxazine with potassium bis(trimethylsilyl)-amide, respectively; *trans*-bis(4-pyridyl)ethene **3** was commercially available, while bis(2-oxazolinyl)ethene **4**[1] and oxazolinylstyrenes **5a**−**d** were prepared as reported.[5]

We first investigated the reaction of lithiated 2-(1-chloroethyl)-4,4-dimethyl-2-oxazoline **7**, which was generated by lithiation of 2-(1-chloroethyl)-4,4-dimethyl-2-oxazoline (**6**) (LDA, THF, −98 °C), turned out to be quite stable at least at low temperature, and could be examined by NMR.[10,11] The addition of **7** to the *trans*-bis(2-pyridyl)-ethene **1** produced the *trans*-1-methyl-1-oxazolinyl-2,3-bis(2-pyridyl)cyclopropane **8** in an excellent yield (Scheme 2).

The addition reaction was stereospecific: only the stereoisomer setting the two pyridyl rings trans on the cyclopropane ring was obtained. Equally stereospecific was the addition of **7** to the *trans*-bis(4-pyridyl)ethene **3**, affording the cyclopropane **9** in an almost quantitative yield. Moreover, the addition of **7** to the *trans*-bis(dihydrooxazinyl)ethene **2** and to the *trans*-bis(2-oxazolinyl)-ethene **4** afforded the cyclopropane **10** and tris(oxazolinyl)cyclopropane **11**, respectively, yet in a stereospecific way (Scheme 2).

The addition reaction of **7** to nonsymmetrical electron-poor alkenes was then considered worth investigation, and therefore, we decided to study the cyclopropanation reaction with *cis*- and *trans*-oxazolinylstyrenes **5a**−**d** (Figure 1). The reaction of lithiated 2-(1-chloroethyl)-oxazoline **7** with *cis*-oxazolinylstyrene **5a** in THF at −98 °C followed by warming to room temperature and quenching with saturated aq NH_4Cl furnished a 1:1 diastereomeric mixture of cyclopropanes **12a** and **13a** (Figure 2, Table 1, entry 1). It is worth noting that the reaction is stereospecific with reference to the geometry of the starting alkene but there is no stereoselection as far as the newly created stereogenic center. Comparable results were obtained when **7** was added to the *cis*-oxazolinyl-*p*-chlorostyrene **5b**, affording cyclopropanes **12b** and **13b**

TABLE 1. Synthesis of Heterosubstituted Cyclopropanes 12a,b and 13a,b from Oxazolinylstyrenes 5a−d

entry	base	solvent	styrene	yield[a] (%)	dr
1	LDA	THF	**5a**	**12a/13a**, 95	1:1[b]
2	LDA	THF	**5b**	**12b/13b**, 56	1:1[b]
3	LDA	THF	**5c**	**12a/13a**, 86	1:2[b]
4	LDA	THF	**5d**	**12b/13b**, 90	1:2[b]
5	$KN(SiMe_3)_2$	THF	**5d**	**12b/13b**, 85	1:3[b]
6	LDA	Et_2O	**5d**	**12b/13b**, 80	1:2[b]
7	$KN(SiMe_3)_2$	Et_2O	**5d**	**12b/13b**, 85	1:3[c]
8	$KN(SiMe_3)_2$	THF/HMPA	**5d**	**12b/13b**, 62	1:1.6[c]
9	LDA	toluene	**5c**		
10	LDA/Ti(O-*i*-Pr)$_4$	THF	**5c**		

[a] Isolated yields. [b] Diastereomeric ratio calculated on isolated products after column cromatography on silica gel. [c] Diastereomeric ratio calculated on the basis of ^{1}H NMR spectra of the crude reaction mixture.

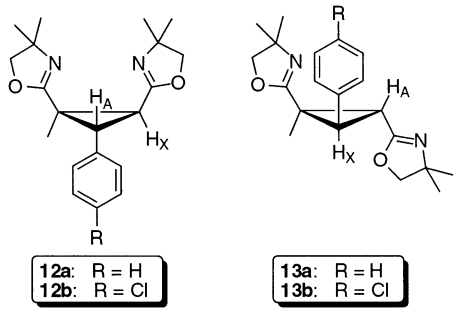
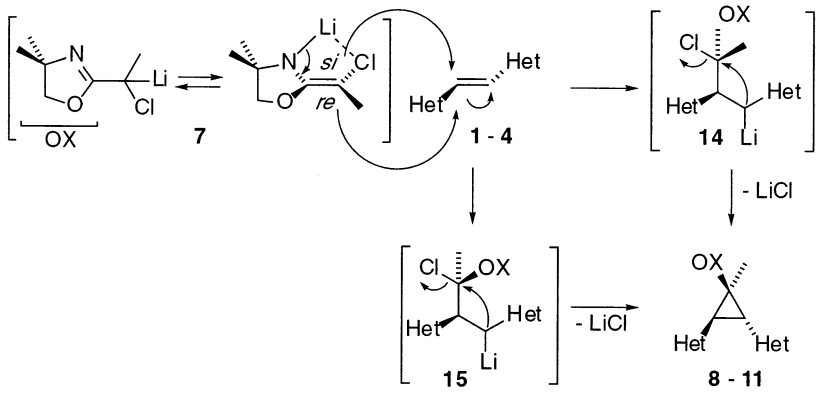


FIGURE 2.

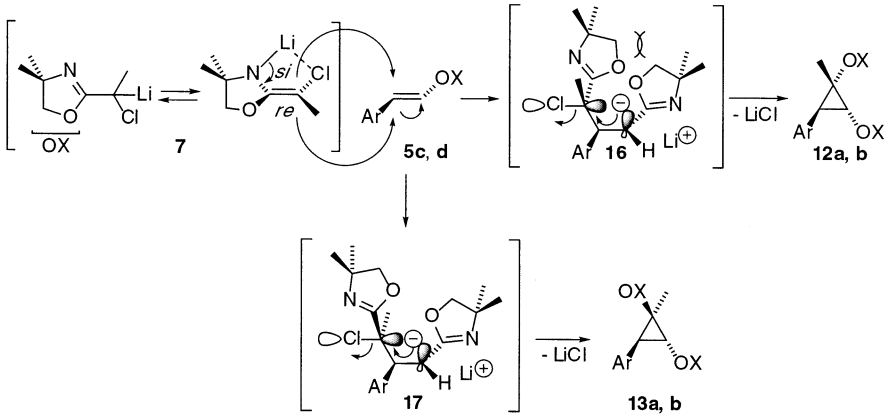
(10) Abbotto, A.; Bradamante, S.; Florio, S.; Capriati, V. *J. Org. Chem.* **1997**, *62*, 8937−8940.

(11) That lithiated 2-(1-chloroethyl)-2-oxazoline **7** is stable, at least at low temperature, so that it can be spectroscopically studied is well established. It was found (see ref 10) that the effect of H/Li exchange upon the ^{13}C chemical shift of the 2-(1-chloroethyl)-2-oxazoline C_α carbon atom was that of a low ^{13}C-deshielding ($\Delta\delta = 12.73$ ppm). This result could be accounted for in terms of a low carbenoid character (Boche, G.; Lohrenz, J. C. W. *Chem. Rev.* **2001**, *101*, 697−756) associated with the above-mentioned Li/Cl carbenoid species (in contrast to a higher one found in the case of the 2-chloromethyl-2-oxazoline; see ref 1) that would justify its greater thermodynamic stability and a less pronounced tendency toward an "eliminative dimerization" process so typical of carbenoid species.

SCHEME 3



SCHEME 4



(Figure 2, Table 1, entry 2). An appreciable stereoselection could be observed in the reaction of **7** with *trans*-oxazolinylstyrenes **5c** and **5d**: diastereomeric cyclopropanes **12a**/**13a** and **12b**/**13b** were smoothly obtained in a 1:2 stereoisomeric ratio (Table 1, entries 3 and 4). Diastereomers **12a** and **13a** (as well as **12b** and **13b**) could be easily separated by column chromatography on silica gel. Relative configurations to all cyclopropanes **8**−**13** could be assigned by ^{1}H and ^{13}C NMR. The vicinal coupling constant values between the cyclopropane ring hydrogens H_A and H_X ($^3J_{H_A-H_X}$ = 6.8−7.2 Hz) (Scheme 2 and Figure 2) were diagnostic of a trans configuration as previously reported for similarly substituted cyclopropanes.[1,12] Furthemore, the two different small long-range $^3J_{CH}$ coupling constants[13] ($^3J_{CH_3-H_X}$ = 5.2 Hz, $^3J_{CH_3-H_A}$ = 1.9 Hz) between the methyl group and the above-mentioned hydrogens definitively proved a trans−trans arrangement.[14]

With the aim of increasing the diastereomeric ratio of the addition reaction, we studied the addition of metalated 2-(1-chloroethyl)oxazoline **7** to the *trans*-oxazolinyl-*p*-chlorostyrene **5d** under different experimental conditions in terms of solvent, cosolvent, reaction time, and temperature (Table 1, entries 5−10). The best results in stereoselection were obtained by using $KN(SiMe_3)_2$ as the metalating agent (Table 1, entries 5 and 7).

The stereospecific outcome of the reaction of **7** with the Michael-type acceptors **1**−**4** to give cyclopropane derivatives **8**−**11** might reasonably be accounted for with a nucleophilic 1,4-addition reaction leading to the lithium derivatives **14** and **15** (Scheme 3). The cyclopropanation that follows results from the intramolecular nucleophilic S_N2 displacement of chlorine, as proposed for the reported cyclopropanation reaction of metalated 2-chloromethyloxazoline.[1] It might be useful to point out that with symmetrical Michael acceptors such as **1**−**4** it does not matter which face (*si* or *re*) the reagent **7**, which is known to equilibrate between the iminic and the enaminic forms, shows to the reaction partner as the same product will result.

The lack of stereoselection or the modest diastereoselection of the reactions of **7** with both unsymmetrical *cis*- and *trans*-styrenes **5a**−**d**, affording cyclopropanes **12a,b** and **13a,b**, as well as the relevant regioselectivity deserves some remarks. First of all, we observed that the addition of **7** to alkenes **5** in all cases occurs in a completely regioselective fashion at the aryl-bearing carbon atom, thus leading to the carbanionic intermediate α to the heterocyclic ring (Schemes 4 and 5). This can reasonably be explained with the stronger electron-withdrawing ability of the oxazolinyl group with respect to that of the aryl group. Support for this comes from

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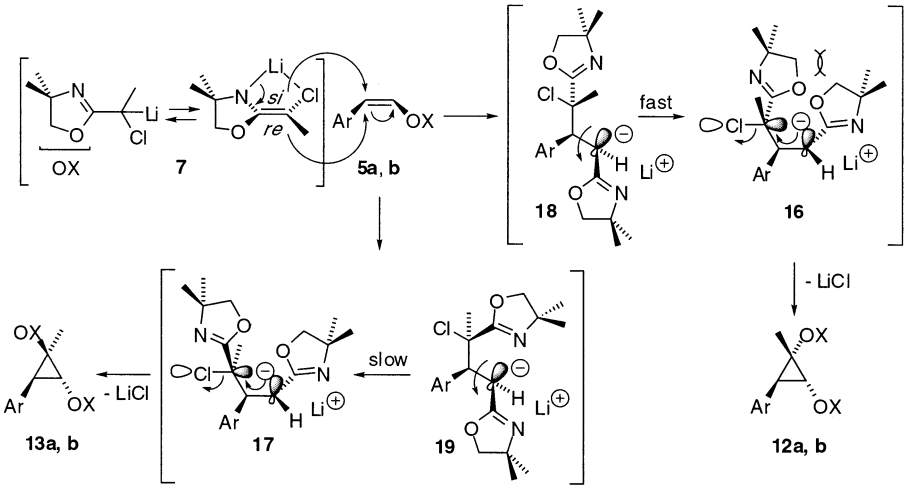
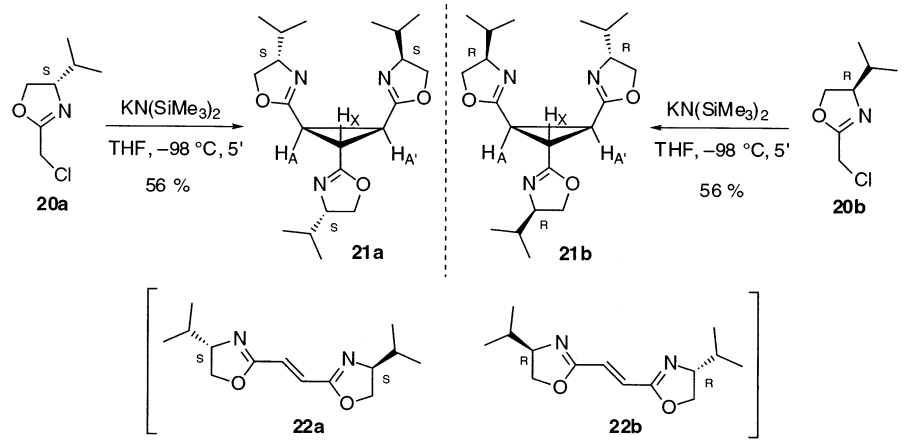
(13) Kingsbury, C. A.; Durham, D. L.; Hutton, R. *J. Org. Chem.* **1978**, *43*, 4696−4700.

(14) NOESY phase-sensitive experiments performed on compounds **8**, **12a**, and **13a** also showed that, as a general pattern, the most deshielded cyclopropane ring hydrogen was always the one between the two heterocyclic rings, and that an oxazoline ring had, on the other hydrogen, a greater shielding effect with respect to a phenyl-substituted ring.

SCHEME 5



SCHEME 6



the reported higher acidity of hydrogens α to the oxazoline ring[15] with respect to those α to the aryl group.[16] In a recent work from our laboratory we reported that the base-promoted deprotonation of *cis*- and *trans*-oxazolinylaryloxiranes takes place α to the oxazolinyl group.[17] Moreover, the negative charge demand, a quantitative measure of the electron-withdrawing capability, reported for pyridyl and other heterocyclic groups,[10,18] provides a reasonable explanation for the observed regioselectivity.

Concerning the reaction of **7** with *trans*-alkenes **5c** and **5d**, leading to cyclopropanes **12a**, **13a** and **12b**, **13b** (Scheme 4), respectively, all setting the oxazolinyl group belonging to the starting alkene and the aryl group trans to each other, the observed diastereoselectivity could be explained considering that **7** approaches the alkene showing its *re* or *si* face to give carbanionic diastereomeric intermediates **16** and **17** and, then, after the intramolecular nucleophilic S_N2 displacement of chlorine, the cyclopropanes **12a,b** and **13a,b** (Scheme 4).

Diastereomeric intermediate **17**, leading to the predominant cyclopropanes **13a**,**b**, seems to be more favored with respect to **16**, leading to cyclopropanes **12a**,**b**, for steric reasons (Scheme 4). Indeed, looking at the intermediate **16**, the appropriate orbital alignment allowing the overlap of the carbanion lone pair with the antibonding orbital of the C−Cl bond is somehow hindered by the steric interactions between the two oxazolinyl groups. Such a steric repulsion is absent in the intermediate **17**.

The absence of stereoselection of the reaction of **7** with *cis*-alkenes **5a** and **5b**, affording cyclopropanes **12a**, **13a** and **12b**, **13b** (Scheme 5), respectively, could be ascribed to the fact that carbanionic intermediates **18** and **19**, generated by the syn 1,4-addition of **7** to **5a** and **5b**, before undergoing cyclization rotate around the newly formed σ bond to put the oxazolinyl and the aryl group in a more stable trans arrangement as that found in the final product. It could be that the rotation transforming **18** into **16** is faster than that converting **19** into **17** (having the suitable stereoelectronic arrangement for the S_N2 chlorine displacement) for steric reasons. The observed lack of steroselection might result from a balance between the higher reactivity of **17** with respect to **16** and the slower transformation of **19** into **17** with respect to that of **18** into **16**.

The treatment of (4*S*)-2-chloromethyl-4-isopropyl-2-oxazoline (**20a**) with $KN(SiMe_3)_2$ in THF at low temper-

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(16) Bordwell, F. G. *Acc. Chem. Res.* **1988**, *21*, 456−463.
(17) Capriati, V.; Degennaro, L.; Favia, R.; Florio, S.; Luisi, R. *Org. Lett.* **2002**, *4* (9), 1551−1554.
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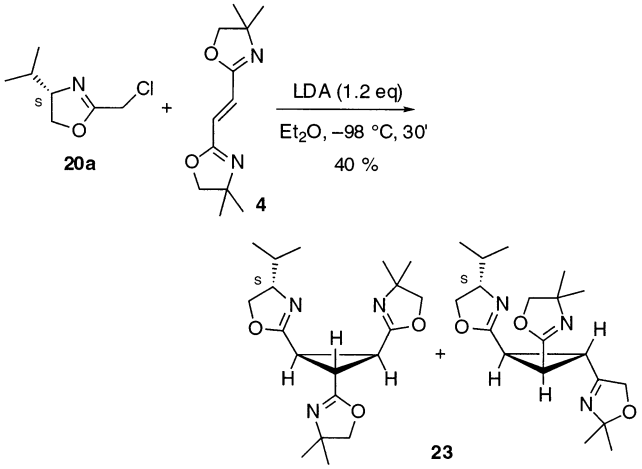
SCHEME 7



ature produced the *trans*-tris(oxazolinyl)cyclopropane **21a** (one predominant stereoisomer) (Scheme 6) in a good yield. Similarly, the reaction of (4*R*)-2-chloromethyl-4-isopropyl-2-oxazoline (**20b)** with $KN(SiMe_3)_2$ gave rise to the *trans*-tris(oxazolinyl)cyclopropane **21b** (one predominant stereoisomer). Moreover, it is interesting to point out that **21a** and **21b** are enantiomers (same ^1H and ^{13}C NMR, opposite optical activity). Compounds **21a** and **21b** are likely the result of a sort of "trimerization" reaction of metalated **20a** and **20b** passing, most probably, through the corresponding *trans*-bis(oxazolinyl)alkenes **22a** and **22b**, as demonstrated for 2-chloromethyl-4,4-dimethyl-2-oxazoline.[1]

Taking into consideration that the cyclopropanation reaction occurs via a 1,4-addition of the metalated 2-chloromethyl-2-oxazoline **20a** (or **20b**) to the corresponding alkene intermediate (**22a** or **22b**, respectively),[1] we evaluated the possibility of preparing cyclopropanes bearing a different chiral oxazolinyl appendage, by choosing the appropriate reaction conditions to avoid the self-trimerization. We were pleased to find that treatment of a mixture of **20a** and *trans*-bis(oxazolinyl)ethene **4** with LDA in Et_2O at −98 °C (Barbier's technique) afforded *trans*-tris(oxazolinyl)cyclopropane **23** (40% yield) as an equimolar mixture of two diastereoisomers, as determined by ^1H and ^{13}C NMR, and the unreacted (40%) starting ethene **4** (Scheme 7). We presumed that **20a** was partially consumed in the self-trimerization to give **21a**.

Conclusions

In conclusion, in this paper we report a simple synthesis of heterosubstituted cyclopropanes and demonstrate the synthetic potential of alkenyloxazolines as electron-poor alkenes for the cyclopropanation reaction. Work is at present in progress exploring the synthetic utility of the above triheterosubstituted cyclopropanes as ligands and as potential precursors of functionalized cyclopropanes. Results will be reported in due course.

Experimental Section

General Information. Tetrahydrofuran (THF) and diethyl ether (Et_2O) were freshly distilled under a nitrogen atmosphere over sodium/benzophenone ketyl. (*E*)-1,2-Bis(oxazolinyl)ethene[1] (**4**), (*Z*)-1-(4,4-dimethyl-2-oxazolin-2-yl)-2-phenylethene[5] (**5a**), (*Z*)-1-(4,4-dimethyl-2-oxazolin-2-yl)-2-(4-chlorophenyl)ethene[5] (**5b**), (*E*)-1-(4,4-dimethyl-2-oxazolin-2-yl)-2-phenylethene[5] (**5c**), (*E*)-1-(4,4-dimethyl-2-oxazolin-2-yl)-2-(4-chlorophenyl)ethene[5] (**5d**), 2-(1-chloroethyl)-4,4-dimethyl-2-oxazoline[10] (**6**), (4*S*)-2-chloromethyl-4-isopropyl-2-oxazoline[4d] (**20a**), and (4*R*)-2-chloromethyl-4-isopropyl-2-oxazoline[19] (**20b**) were prepared as reported. All other chemicals were of commercial grade and were used without further purification. Petroleum ether refers to the 40−60 °C boiling fraction. A commercial solution of *n*-BuLi (2.5 M solution in hexanes) was titrated by using *N*-pivaloyl-*o*-toluidine prior to use.[20] For ^1H and ^{13}C NMR spectra (^1H NMR, 300 and 500 MHz; ^{13}C NMR, 75.4 and 125 MHz) $CDCl_3$ was used as solvent. GC−MS spectrometry analyses were performed on a gas chromatograph (MS capillary column, 30 m, 0.25 mm i.d. × 0.25 μm) equipped with a 5973 mass selective detector operating at 70 eV (EI). TLC was performed on Merck silica gel plates with F-254 indicator; visualization was accomplished by UV light (254 nm) and by exposure to I_2 vapor. All reactions involving air-sensitive reagents were performed under nitrogen in oven-dried glassware using the syringe−septum cap technique.

Preparation of (*E*)-1,2-Bis(2-pyridyl)ethene (1) and (*E*)-1,2-Bis(4,4,6-trimethyl-5,6-dihydro-4*H*-[1,3]oxazin-2-yl)ethene (2). To a precooled (−98 °C, with a methanol−liquid nitrogen bath) solution of potassium bis(trimethylsilyl)amide (1.1 g, 5.72 mmol) in 10 mL of dry THF was added dropwise a solution of 2-(chloromethyl)pyridine (0.47 g, 2.86 mmol) [or 2-(chloromethyl)-4,4,6-trimethyl-5,6-dihydro-4*H*-[1,3]oxazine] in 10 mL of dry THF, under N_2 and magnetic stirring. The reaction mixture was slowly allowed to warm to room temperature and after 7 h was quenched with saturated aq NH_4Cl. The aqueous layer was extracted with AcOEt (3 × 20 mL), and the combined organic extracts were dried ($MgSO_4$) and concentrated in vacuo to give the crude **1** (or **2**). Compounds **1** and **2** were purified by crystallization (Et_2O) (221 mg, 85% yield, and 234 mg, 90% yield, respectively). Compound **1** is commercially available; the spectroscopic data of **2** matched very well those reported in the literature.[21]

Preparation of Heterosubstituted Cyclopropanes 8−13. General Procedure. To a precooled (−98 °C) solution of LDA [prepared from *n*-BuLi (0.81 mmol) and *i*-Pr_2NH (0.81 mmol) in 3 mL of dry THF (or dry Et_2O), under N_2 at 0 °C] was added dropwise a solution of **6** (0.12 g, 0.74 mmol) in 2 mL of dry THF. After 30 min at this temperature, a solution of **1** (0.13 g, 0.74 mmol) in 3 mL of dry THF was added dropwise, and the resulting mixture was slowly allowed to warm to room temperature under magnetic stirring and quenched with saturated aq NH_4Cl. The resulting mixture was extracted with AcOEt (3 × 15 mL) and the combined organic extracts dried (Na_2SO_4) and concentrated in vacuo. The crude product so obtained was purified by column chromatography [silica gel; petroleum ether/acetone, 1/1, in the case of **8** (95% yield); petroleum ether/acetone, 6/4, in the case of **10** (mixture of four diasteroisomers, 62% overall yield)]. No further purification was needed in the case of **11** (95% yield). Compound **9** was purified by crystallization (AcOEt) (white solid, 93% yield).

Compounds **12a** and **13a** were separated by column chromatography on silica gel (petroleum ether/acetone, 1/1): 95% overall yield, dr(**12a**/**13a**) = 1/1, from **5a**; 86% overall yield, dr(**12a**/**13a**) = 1/2, from **5c**.

Compounds **12b** and **13b** were also easily separated by column chromatography on silica gel (petroleum ether/acetone, 7/3): 56% overall yield, dr(**12b**/**13b**) = 1/1, from **5b**; 90% overall yield, dr(**12b**/**13b**) = 1/2, from **5d**.

Data for (2*R,3*R**)-1-methyl-1-(4,4-dimethyl-2-oxazolin-2-yl)-*trans*-2,3-bis(2-pyridyl)cyclopropane (8):** yield 216 mg (95%); yellow oil; ^1H NMR (500 MHz) δ 0.93 (s, 3 H, CH_3), 1.07 (s, 3 H, CH_3), 1.35 (s, 3 H, CH_3), 3.32 (d, J = 6.8

(19) **20b** {$[\alpha]^{25}_D$ = +97.8 (*c* 5, $CHCl_3$)} was prepared as reported in the case of **20a** (see ref 4d).

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(21) Malone, G. R.; Meyers, A. I. *J. Org. Chem.* **1974**, *39*, 618−628.

Hz, 1 H, C*H* cyclopropyl), 3.52 (d, J = 8.0 Hz, 1 H, CH_2O), 3.62 (d, J = 8.0 Hz, 1 H, CH_2O), 3.77 (d, J = 6.8 Hz, 1 H, C*H* cyclopropyl), 7.03−7.06 (m, 1 H, C*H* pyridyl), 7.08−7.11 (m, 1 H, C*H* pyridyl), 7.31 (d, J = 7.9 Hz, 1 H, C*H* pyridyl), 7.45 (d, J = 7.9 Hz, 1 H, C*H* pyridyl), 7.51−7.54 (m, 1 H, C*H* pyridyl), 7.57−7.60 (m, 1 H, C*H* pyridyl), 8.46−8.47 (m, 1 H, C*H* pyridyl), 8.51−8.52 (m, 1 H, C*H* pyridyl); ^{13}C NMR (125 MHz) δ 16.1 (*C*H$_3$), 28.0 (*C*H$_3$), 28.2 (*C*H$_3$), 31.3 (*C* cyclopropyl), 33.9 (*C*H cyclopropyl), 36.8 (*C*H cyclopropyl), 66.7 (*C*-4 oxazolinyl), 78.9 (*C*H$_2$O), 121.2 (*C*H pyridyl), 121.4 (*C*H pyridyl), 123.9 (*C*H pyridyl), 125.0 (*C*H pyridyl), 135.7 (*C*H pyridyl), 135.9 (*C*H pyridyl), 148.7 (*C*H pyridyl), 148.8 (*C*H pyridyl), 156.8 (*C*=N pyridyl), 157.3 (*C*=N pyridyl), 165.3 (*C*=N oxazolinyl); GC−MS (70 eV) *m*/*z* (rel intens) 307 (M$^+$, 3), 292 (24), 209 (44), 208 (100), 161 (49); FT-IR (film, cm^{-1}) 2967, 1655 (C=N), 1590, 1474, 1434.

Data for (2*R,3*R**)-1-methyl-1-(4,4-dimethyl-2-oxazolin-2-yl)-*trans*-2,3-bis(4-pyridyl)cyclopropane (9):** yield 211 mg (93%); mp 137−138 °C (AcOEt); ^{1}H NMR (500 MHz) δ 0.83 (s, 3 H, C*H*$_3$), 1.06 (s, 3 H, C*H*$_3$), 1.18 (s, 3 H, C*H*$_3$), 2.59 (d, J = 7.2 Hz, 1 H, C*H* cyclopropyl), 3.49 (d, J = 8.0 Hz, 1 H, CH_2O), 3.50 (d, J = 7.2 Hz, 1 H, C*H* cyclopropyl), 3.56 (d, J = 8.0 Hz, 1 H, CH_2O), 7.16−7.19 (m, 4 H, 4 C*H* pyridyl), 8.43−8.50 (m, 4 H, 4 C*H* pyridyl);^{13}C NMR (125 MHz) δ 17.0 (*C*H$_3$), 28.0 (*C*H$_3$), 28.2 (*C*H$_3$), 29.9 (*C* cyclopropyl), 31.1 (*C*H cyclopropyl), 34.4 (*C*H cyclopropyl), 66.9 (*C*-4 oxazolinyl), 78.9 (*C*H$_2$O), 123.9 (*C*H pyridyl), 124.0 (*C*H pyridyl), 124.2 (*C*H pyridyl), 124.3 (*C*H pyridyl), 145.4 (2 *C* pyridyl), 149.2 (2 *C*H pyridyl), 149.6 (2 *C*H pyridyl), 163.9 (*C*=N oxazolinyl); GC−MS (70 eV) *m*/*z* (rel intens) 307 (M$^+$, 100), 292 (26), 252 (32), 229 (24), 215 (22); FT-IR (KBr, cm^{-1}) 2971, 1646 (C=N), 1597, 1414, 1365, 1121, 992, 804. Anal. Calcd for $C_{19}H_{21}N_3O$: C, 74.24; H, 6.89; N, 13.67. Found: C, 74.22; H, 7.15; N, 13.45.

Data for (2*R,3*R**)-1-methyl-1-(4,4-dimethyl-2-oxazolin-2-yl)-*trans*-2,3-bis(4,4,6-trimethyl-5,6-dihydro-4*H*-[1,3]-oxazin-2-yl)cyclopropane (10):** yield 185 mg (62%); yellow oil, mixture of four inseparable diastereoisomers; ^{1}H NMR (500 MHz) (selected signals) δ 1.11−1.22 (two groups of singlets, 24 H, 8 C*H*$_3$), 1.32−1.38 [m, 5 H, C*H*$_3$ + (2 CH_aH$_b$ oxazinyl)], 1.58−1.68 (m, 2 H, CH$_a$*H*$_b$ oxazinyl), 2.21, 2.25, and 2.28 (3 d, J = 6.7 Hz, 1 H, C*H*'s cyclopropyl of three main diastereoisomers), 2.61, 2.65, and 2.66 (3 dd, J = 6.7, 0.6 Hz, 1 H, C*H*'s cyclopropyl of three main diastereoisomers), 3.71−4.12 [m, 4 H, CH_2O oxazolinyl + (2 C*H*O) oxazinyl]; ^{13}C NMR (125 MHz) (selected signals) δ 16.3, 16.4, 16.5, 16.6 (4 s, *C*H$_3$'s cyclopropyl), 21.2$_0$, 21.2$_4$, 21.3$_0$, 21.3$_5$ (4 s overlapping, *C*H$_3$CH's oxazinyl), 27.9−33.0 (29 s overlapping, *C*H$_3$'s oxazolinyl + *C*H$_3$'s oxazinyl + *C*H's cyclopropyl + *C*'s cyclopropyl), 41.6, 41.7, 41.8, 41.9, 42.0, 42.1 (6 s overlapping, *C*H$_2$'s oxazinyl), 49.7, 49.8, 50.1 (3 s overlapping, *C*'s oxazinyl), 66.9$_0$, 66.9$_6$, 67.4, 67.6, 67.7, 68.0 (6 s overlapping, *C*HO's oxazinyl + *C*'s oxazolinyl), 78.5, 78.7 (2 s overlapping, *C*H$_2$O's oxazolinyl), 153.5, 153.8, 153.9$_4$, 153.9$_9$, 154.0$_2$, 154.0$_5$ (6 s overlapping, *C*=N's oxazinyl), 165.5, 165.6$_1$, 165.6$_7$, 165.7 (4 s, *C*=N's oxazolinyl); GC−MS (four diastereoisomers) (70 eV) *m*/*z* (rel intens) 403 (M$^+$, 32), 388 (27), 304 (32), 277 (39), 205 (23), 178 (19), 124 (17), 98 (9), 83 (47), 55 (100), 41 (87); FT-IR (four diastereoisomers) (film, cm^{-1}) 2970, 1660 (C=N), 1543, 1453, 1363, 1262, 1188, 998.

Data for (2*R,3*R**)-1-methyl-*trans*-1,2,3-tris(4,4-dimethyl-2-oxazolin-2-yl)cyclopropane (11):** yield 243 mg (95%); yellow oil; ^{1}H NMR (500 MHz) δ 1.12 (s, 3 H, C*H*$_3$), 1.13 (s, 3 H, C*H*$_3$), 1.15 (s, 6 H, 2 C*H*$_3$), 1.16 (s, 3 H, C*H*$_3$), 1.19 (s, 3 H, C*H*$_3$), 1.39 (s, 3 H, C*H*$_3$), 2.27 (d, J = 6.7 Hz, 1 H, C*H* cyclopropyl), 2.77 (d, J = 6.7 Hz, 1 H, C*H* cyclopropyl), 3.73−3.88 (m, 6 H, 3 CH_2O); ^{13}C NMR (125 MHz) δ 16.2 (*C*H$_3$), 25.1 (*C* cyclopropyl), 27.5, 27.8, 27.9, 28.0$_6$, 28.1$_0$, 28.2, 28.3, 28.4, 67.0 (*C*-4 oxazolinyl), 67.2 (*C*-4 oxazolinyl), 67.3 (*C*-4 oxazolinyl), 78.9 (*C*H$_2$O), 79.0 (*C*H$_2$O), 79.1 (*C*H$_2$O), 161.1 (*C*=N), 161.4 (*C*=N), 164.0 (*C*=N); GC−MS (70 eV) *m*/*z* (rel intens) 347 (M$^+$, 8), 332 (100), 260 (34), 219 (44), 188 (37); FT-IR (film, cm^{-1}) 2970, 1661 (C=N), 1462, 1365, 1190, 1120, 999, 733.

Data for (1*R,2*S**,3*R**)-1-methyl-*cis*-1,2-bis(4,4-dimethyl-2-oxazolin-2-yl)-*trans*-3-phenylcyclopropane (12a):** yield 69.5 mg (29%); yellow oil; ^{1}H NMR (300 MHz) δ 0.87 (s, 3 H, C*H*$_3$), 1.02 (s, 3 H, C*H*$_3$), 1.26 (s, 3 H, C*H*$_3$), 1.30 (s, 3 H, C*H*$_3$), 1.56 (s, 3 H, C*H*$_3$), 2.84 (d, J = 7.0 Hz, 1 H, C*H* cyclopropyl), 3.01 (d, J = 7.0 Hz, 1 H, C*H* cyclopropyl), 3.35 (d, J = 7.9 Hz, 1 H, CH_2O), 3.53 (d, J = 7.9 Hz, 1 H, CH_2O), 3.93 and 3.99 (2 d, AB system, J = 8.0 Hz, 2 H, CH_2O), 7.10−7.21 (m, 5 H, 5 C*H* phenyl); ^{13}C NMR (125 MHz) δ 16.7 (*C*H$_3$), 24.5 (*C*H cyclopropyl), 27.9 (*C*H$_3$), 28.2 (*C*H$_3$), 28.3 (*C*H$_3$), 28.6 (*C*H$_3$), 29.4 (*C* cyclopropyl), 35.9 (*C*H cyclopropyl), 66.8 (*C*-4 oxazolinyl), 67.2 (*C*-4 oxazolinyl), 78.8 (*C*H$_2$O), 79.1 (*C*H$_2$O), 126.5 (*C*H phenyl), 127.6 (2 *C*H phenyl), 128.7 (2 *C*H phenyl), 135.7 (*C* ipso), 163.1 (*C*=N), 164.2 (*C*=N); GC−MS (70 eV) *m*/*z* (rel intens) 326 (M$^+$, 53), 311 (23), 227 (100), 166 (75), 160 (67), 138 (27), 112 (29), 77 (81), 55 (18); FT-IR (film, cm^{-1}) 2968, 1657 (C=N), 1462, 1365, 1120, 993, 733.

Data for (1*R,2*S**,3*R**)-1-methyl-*cis*-1,2-bis(4,4-dimethyl-2-oxazolin-2-yl)-*trans*-3-(4-chlorophenyl)cyclopropane (12b):** yield 74 mg (28%); yellow oil; ^{1}H NMR (300 MHz) δ 0.92 (s, 3 H, C*H*$_3$), 1.05 (s, 3 H, C*H*$_3$), 1.27 (s, 3 H, C*H*$_3$), 1.32 (s, 3 H, C*H*$_3$), 1.56 (s, 3 H, C*H*$_3$), 2.80 (d, J = 7.0 Hz, 1 H, C*H* cyclopropyl), 2.98 (d, J = 7.0 Hz, 1 H, C*H* cyclopropyl), 3.40 (d, J = 8.0 Hz, 1 H, CH_2O), 3.58 (d, J = 8.0 Hz, 1 H, CH_2O), 3.94 and 4.00 (2 d, AB system, J = 8.1 Hz, 2 H, CH_2O), 7.14−7.21 (m, 4 H, 4 C*H* phenyl); ^{13}C NMR (75.4 MHz) δ 16.1 (*C*H$_3$), 24.8 (*C*H cyclopropyl), 28.0, 28.3, 28.7, 29.5 (*C*H cyclopropyl), 35.3 (*C*H cyclopropyl), 67.0 (*C*-4 oxazolinyl), 67.3 (*C*-4 oxazolinyl), 78.9 (*C*H$_2$O), 79.1 (*C*H$_2$O), 127.8 (2 *C*H phenyl), 130.1 (2 *C*H phenyl), 132.4 (*C* ipso), 134.5 (*C* ipso), 162.7 (*C*=N), 164.0 (*C*=N); GC−MS (70 eV) *m*/*z* (rel intens) 362 (M$^+$ + 2, 17), 360 (M$^+$, 48), 261 (100), 194 (65), 166 (77); FT-IR (film, cm^{-1}) 2968, 1658 (C=N), 1495, 1364, 1190, 1121, 1089, 992, 736.

Data for (1*R,2*R**,3*S**)-1-methyl-*trans*-1,2-bis(4,4-dimethyl-2-oxazolin-2-yl)-*cis*-3-phenylcyclopropane (13a):** yield 137.5 mg (57%); yellow oil; ^{1}H NMR (300 MHz) δ 1.07 (s, 3 H, C*H*$_3$), 1.20 (s, 3 H, C*H*$_3$), 1.21 (s, 3 H, C*H*$_3$), 1.22 (s, 6 H, 2 C*H*$_3$), 2.14 (d, J = 7.0 Hz, 1 H, C*H* cyclopropyl), 3.32 (d, J = 7.0 Hz, 1 H, C*H* cyclopropyl), 3.80−3.84 (m, 4 H, 2 CH_2O), 7.17−7.22 (m, 5 H, 5 C*H* phenyl);^{13}C NMR (75.4 MHz) δ 17.5 (*C*H$_3$), 27.2 (*C*H cyclopropyl), 28.1, 28.2, 28.4, 32.9 (*C*H cyclopropyl), 67.0 (*C*-4 oxazolinyl), 67.1 (*C*-4 oxazolinyl), 78.9 (*C*H$_2$O), 79.0 (*C*H$_2$O), 126.7 (*C*H phenyl), 128.0 (2 *C*H phenyl), 129.4 (2 *C*H phenyl), 135.3 (*C* ipso), 162.7 (*C*=N), 165.4 (*C*=N); GC−MS (70 eV) *m*/*z* (rel intens) 326 (M$^+$, 44), 311 (14), 227 (100), 166 (53), 160 (49), 138 (26), 128 (19), 112 (22), 77 (67), 55 (15); FT-IR (film, cm^{-1}) 2969, 1664 (C=N), 1462, 1364, 1118, 994, 733.

Data for (1*R,2*R**,3*S**)-1-methyl-*trans*-1,2-bis(4,4-dimethyl-2-oxazolin-2-yl)-*cis*-3-(4-chlorophenyl)cyclopropane (13b):** yield 165 mg (62%); yellow oil; ^{1}H NMR (300 MHz) δ 1.11 (s, 3 H, C*H*$_3$), 1.23 (s, 3 H, C*H*$_3$), 1.24 (s, 9 H, 3 C*H*$_3$), 2.14 (d, J = 6.9 Hz, 1 H, C*H* cyclopropyl), 3.30 (d, J = 6.9 Hz, 1 H, C*H* cyclopropyl), 3.85−3.93 (m, 4 H, 2 CH_2O), 7.18−7.27 (m, 4 H, 4 C*H* phenyl);^{13}C NMR (75.4 MHz) δ 17.7 (*C*H$_3$), 27.6 (*C*H cyclopropyl), 28.1, 28.2, 28.3, 28.5, 32.4 (*C*H cyclopropyl), 67.2 (*C*-4 oxazolinyl), 67.3 (*C*-4 oxazolinyl), 79.1 (*C*H$_2$O), 79.2 (*C*H$_2$O), 128.3 (2 *C*H phenyl), 130.5 (2 *C*H phenyl), 132.7 (*C* ipso), 134.1 (*C* ipso), 162.5 (s, *C*=N), 165.2 (*C*=N); GC−MS (70 eV) *m*/*z* (rel intens) 362 (M$^+$ + 2, 12), 360 (M$^+$, 33), 261 (100), 194 (56), 166 (64); FT-IR (film, cm^{-1}) 2968, 1663 (C=N), 1495, 1364, 1191, 1118, 1089, 995, 736.

Reaction of 2-(1-Chloroethyl)-4,4-dimethyl-2-oxazoline (6) with KN(SiMe$_3$)$_2$ and (*E*)-1-(4,4-Dimethyl-2-oxazolin-2-yl)-2-(*p*-chlorophenyl)ethene (5d). To a precooled (−98 °C) solution of potassium bis(trimethylsilyl)amide (75 mg, 0.37 mmol) in 5 mL of dry THF was added dropwise (Barbier's tecnique) under N_2 a solution of **6** (34 mg, 0.21 mmol) and **5d** (50 mg, 0.21 mmol) in 2 mL of dry THF. The reaction mixture was slowly allowed to warm to room temperature, quenched with saturated aq NH_4Cl (10 mL), and extracted with AcOEt

(3 × 15 mL). The combined organic extracts were dried (Na_2SO_4) and evaporated in vacuo. The slurry was then purified by chromatography on silica gel (petroleum ether/acetone, 7/3), affording diastereomeric compounds **12b** (15 mg, 20%) and **13b** (50 mg, 65%) in an overall yield of 85%.

Preparation of (4′*S*)-*trans*-1,2,3-Tris(4-isopropyl-2-oxazolin-2-yl)cyclopropane (21a) and (4′*R*)-*trans*-1,2,3-Tris-(4-isopropyl-2-oxazolin-2-yl)cyclopropane (21b). To a stirred solution of potassium bis(trimethylsilyl)amide (0.55 g, 2.78 mmol) in 10 mL of dry THF (−98 °C) was added dropwise under N_2 a solution of **20a** (0.3 g, 1.86 mmol) in 10 mL of dry THF. After 5 min, the reaction mixture was quenched with saturated aq NH_4Cl (20 mL), the cooling bath was removed, and the reaction mixture was allowed to warm to room temperature. The aqueous layer was extracted with AcOEt (3 × 20 mL), and the combined organic extracts were dried (Na_2SO_4) and evaporated in vacuo to give **21a** as a dark-yellow oil which was purified by flash chromatography (silica gel; acetone/petroleum ether, 1/9; R_f = 0.52), affording **21a** (130 mg, 56% yield). The same procedure, starting from **20b**, was followed for the synthesis of **21b** obtained in similar yield (56%).

Data for 21a: light yellow oil; $[\alpha]^{25}_D = -112$ (*c* 1, $CHCl_3$); ^{1}H NMR (500 MHz) δ 0.78−0.81 (m, 9 H, 3 CH_3), 0.89−0.91 (m, 9 H, 3 CH_3), 1.58−1.68 [m, 3 H, 3 CH(CH_3)$_2$], 2.44 (dd, J = 10.0, 6.0 Hz, 1 H, CH cyclopropyl), 2.48 (ddd, J = 10.0, 6.0, 0.5 Hz, 1 H, CH cyclopropyl), 2.78 (t, J = 6.0 Hz, 1 H, CH cyclopropyl), 3.75−3.86 (m, 6 H, 3 CH_2O), 4.11−4.17 (m, 3 H, 3 CHN); ^{13}C NMR (125 MHz) δ 18.0 (*C*H_3), 18.2 (*C*H_3), 18.3 (*C*H_3), 18.8 (2 *C*H_3), 18.9 (*C*H_3), 20.7 (*C*H cyclopropyl), 22.4 (*C*H cyclopropyl), 22.7 (*C*H cyclopropyl), 32.4 [*C*H(CH_3)$_2$], 32.6 [*C*H(CH_3)$_2$], 32.7 [*C*H(CH_3)$_2$], 70.2 (*C*H_2O), 70.4 (*C*H_2O), 70.5 (*C*H_2O), 72.3 (2 *C*HN), 72.4 (*C*HN), 162.2 (2 *C*═N), 163.9 (*C*═N); GC−MS (70 eV) *m*/*z* (rel intens) 375 (M^+, 1), 350 (11), 332 (100), 291 (41), 246 (16), 263 (5), 160 (14), 135 (5), 69 (13), 43 (8); FT-IR (film, cm^{-1}) 2960, 1651 (C═N), 1557, 1469, 1367, 1073, 733.

Data for 21b: $[\alpha]^{25}_D = +116$ (*c* 1, $CHCl_3$).

Preparation of (4′*S*,2*S,3*R**)-1-[4-Isopropyl-2-oxazolin-2-yl]-*trans*-2,3-bis(4,4-dimethyl-2-oxazolin-2-yl)cyclopropane (23).** To a precooled (−98 °C) solution of LDA [prepared from *n*-BuLi (2.2 M, 0.65 mmol) and *i*-Pr_2NH (0.65 mmol) in 2 mL of dry Et_2O, under N_2 at 0 °C] was added dropwise a solution of **20a** (87 mg, 0.54 mmol) and **4** (120 mg, 0.54 mmol) in 2 mL of dry Et_2O (Barbier's technique). After 30 min at this temperature, the mixture was quenched with saturated aq NH_4Cl (5 mL), the cooling bath was removed, and the reaction mixture was allowed to warm to room temperature. The aqueous layer was extracted with AcOEt (3 × 10 mL), and the combined organic extracts were dried (Na_2SO_4) and evaporated in vacuo to give a slurry which was purified by column chromatography (silica gel; petroleum ether/acetone, 7/3) to give cyclopropane **23** as an equimolar mixture of the two inseparable diasteroisomers (75 mg, 40% overall yield) and 42% (50 mg) of the starting unreacted alkene **4**.

Data for 23: yellow oil; ^{1}H NMR (300 MHz) δ 0.80 [(d, J = 6.7 Hz, 6 H, (CH_3)$_2$CH), diastereomer A], 0.90 (d, J = 6.7 Hz, 3 H, CH_3CH, diastereomer B), 0.92 (d, J = 6.7 Hz, 3 H, CH_3CH, diastereomer B), 1.18, 1.19, and 1.20 (3 s, 24 H, 8 CH_3, diastereomers A + B), 1.55−1.72 (m, 2 H, 2 CH_3C*H*, diastereomers A + B), 2.43−2.46 (m, 4 H, 4 C*H* cyclopropyl, diastereomers A + B), 2.69−2.73 (m, 2 H, 2 C*H* cyclopropyl, diastereomers A + B), 3.76−3.87 (m, 12 H, 6 CH_2O, diastereomers A + B), 4.10−4.16 (m, 2 H, 2 C*H*N, diastereomers A + B); ^{13}C NMR (75.4 MHz) (diastereomers A + B) δ 18.0, 18.2, 18.8, 18.9, 20.5, 22.1, 22.4, 22.5, 27.8, 28.0, 28.1, 32.3, 32.5, 67.1, 70.1, 70.3, 72.2, 72.4, 79.1, 79.1, 79.2, 160.8, 160.9, 162.3, 162.6; GC−MS (70 eV) (diastereomers A + B) *m*/*z* (rel intens) 347 (M^+, 1), 332 (7), 304 (100), 260 (9), 233 (12), 160 (48), 133 (5), 108 (2), 73 (4), 55 (9), 43 (4); FT-IR (film, cm^{-1}) (diastereomers A + B) 2970, 1664 (C═N), 1463, 1363, 1170, 1000, 943, 755.

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Supporting Information Available: Spectroscopic data (^{1}H or ^{13}C NMR) for compounds **8**, **10**, **11**, **12a**, **12b**, **13a**, **13b**, **21a**, **21b**, and **23**. This material is available free of charge via the Internet at http://pubs.acs.org.

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