Diastereoselective Amidoalkylation Reactions of Electrochemically Methoxylated Chiral 2-Oxazolidinones with Organocopper Reagents

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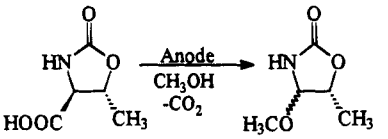
(4*RS*,5*R*)-4-Methoxy-5-methyl-2-oxazolidinone (**2ab**), easily obtained by electrochemical decarboxylative methoxylation of the cyclic L-threonine derivative (4*S*,5*R*)-5-methyl-2-oxazolidinone-4-carboxylic acid (**1**), acts as effective diastereoselective amidoalkylation reagent. The methoxy group exchange in **2ab** can be performed with higher order organocuprates (R_3Cu_2Li) in the presence of $BF_3{\cdot}OEt_2$. The 4-alkyl- or 4-aryl-substituted 2-oxazolidinones **3**–**6** can be obtained with *trans* diastereoselectivities between 75 and 98% in S_N1 fashion via the intermediate *N*-acylimine. On the contrary, the N-methylated (4*RS*,5*R*)-4-methoxy-3,5-dimethyl-2-oxazolidinone (**7ab**) undergoes methoxy group exchange under identical conditions mainly via the S_N2 mechanism. Thus, starting from *trans*-**7a** mainly *cis*-**8b** is formed with 76% ds. The described procedures make *cis*- or *trans*-4-alkyl-5-methyl-2-oxazolidinones and the respective dichiral 2-amino alcohols selectively available by a short reaction sequence.

Introduction

N-Acyliminium ions are established as valuable amidoalkylation reagents,[1] especially if they are chiral. They can be stored in the form of *N*,*O*-acetals which can be obtained most easily by anodic methoxylation of amides or carbamates[2] or by electrochemical decarboxylative methoxylation of amino acid derivatives (Hofer–Moest reaction).[3] In the latter case, chiral amidoalkylation reagent can be obtained using naturally occuring α-amino acid derivatives with a second stereocenter. Especially, cyclic derivatives which are fixed in their conformation guarantee high diastereoselectivities. This has, for example, been demonstrated in the case of proline and hydroxyproline derivatives[4] or for cyclic dipeptide structures.[5]

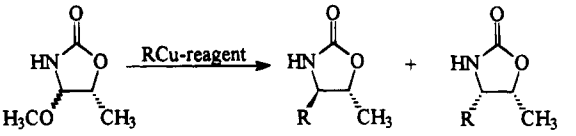
For the asymmetric synthesis of certain dichiral 2-amino alcohols we followed this line by using the easily accessible 5-methyl-2-oxazolidinone-4-carboxylic acid **1** as a building block starting from L-threonine followed by cyclization with methyl chloroformate.[6] The key reaction for the transformation of the free acid into a versatile chiral amidoalkylation reagent is the anodic decarboxylative methoxylation by which **1** is directly oxidized at the surface of the electrode to form a diastereomeric mixture of the *N*-acyl-*N*,*O*-acetal **2ab** in almost quantitative yield [*cis*(**2b**):*trans*(**2a**) = 23:77] (Scheme 1).

Scheme 1



1 **2a = trans** **2b = cis**

Scheme 2



2ab **3a-6a trans** **3b-6b cis**

In our previous synthetic investigations, the substitution of the methoxy group in **2ab** took place under S_N1-conditions and allowed introduction of nucleophiles like dibenzoylmethane in the presence of Brönsted acids or furan and allyltrimethylsilane under Lewis acid catalysis in high yields and high *trans*-diastereoselectivities.[6]

For the synthetically highly desirable introduction of alkyl or aryl groups into the 2-amino alcohol building block, we report here the reaction of organocopper reagents as nucleophiles with **2ab** and its N-methylated derivative **7a**.

Results and Discussion

We examined the reaction of **2ab** with Lipshutz and Gilman cuprates with and without addition of a Lewis acid according to Scheme 2 (Table 1). In a similar approach, Wistrand[4c–e] introduced alkyl substituents into 2-methoxypyrrolidine carbamates using a combination of RCu and $BF_3{\cdot}Et_2O$.

In the absence of $BF_3{\cdot}OEt_2$, the higher order cyano cuprate (entry 1) did not react with **2ab**, presumably because this reagent is not able to polarize or even to cleave the carbon–oxygen bond. However, modified

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0022-3263/94/1959-5658$04.50/0

Table 1. Reaction of 2ab with Various Organocopper Reagents

entry	RCu reagent	isolated yield of **3ab** (%)	ds for **3a** (%)
1	nBu$_2$Cu(CN)Li$_2$ (3)[a]	–	–
2	nBu$_3$Cu$_2$Li (3) BF$_3$·OEt$_2$ (2)	50	81
3	nBu$_3$Cu$_2$Li (3) BF$_3$·OEt$_2$ (1)	66	75

[a] Equivalents of reagent in parentheses with respect to substrate concentration.

Table 2. Reaction of 2ab with R$_3$Cu$_2$Li/BF$_3$·OEt$_2$

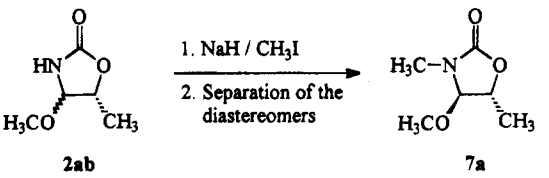
R	product	isolated yield (%)	ds for **3a**–**6a** (%)
nBu	**3ab**	66	75
CH$_3$	**4ab**	59	91
tBu	**5ab**	55	96
Ph	**6ab**	84	98

cuprates, formed by mixtures of Bu$_3$Cu$_2$Li and BF$_3$·OEt$_2$ in various amounts reacted smoothly. Thus, **2ab** was treated successfully with these more reactive complexes to obtain **3ab**. Encouraged by these results, we extended the described methodology according to Scheme 2 to a larger number of Lewis acid modified cuprates of the general structure R$_3$Cu$_2$Li (Table 2) thus demonstrating the versatility of the method.

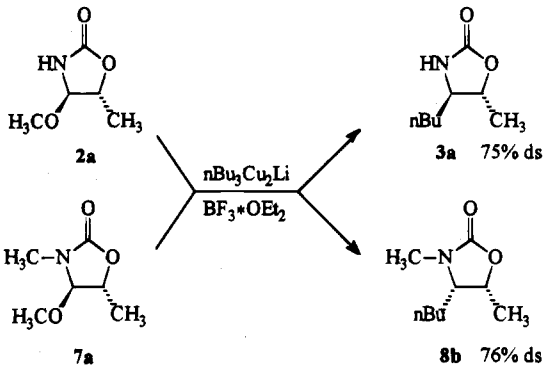
In all cases a high *trans* relationship between both ring-substituents was observed as expected and proved by nuclear Overhauser effects. Aside from simple alkyl groups like *n*-butyl (**3ab**) and methyl (**4ab**), it is possible to incorporate bulky ligands like *tert*-butyl (**6ab**) with a surprisingly high yield of 55% and a diastereoselectivity of 96%, although tertiary cuprates are usually very instable. It should also be point out that even the small methyl group was introduced to yield **4ab** with a 91% *trans* diastereoselectivity. This can be explained by the bulky structure of the newly formed cuprate–BF$_3$ complex. After removal of the methoxy group with 1 equiv of the complex, the sterically hindered cuprate–BF$_3$ complex transfers the nucleophile from the less hindered side of the ring via the S$_N$1-mechanism to the sp^2-hybridized C4.

Our results contrast with studies by Yamamoto[7] on related N-methylated 2-oxazolidinone systems which suggests an interesting difference. In similar substitution reactions, he examined a methoxy exchange by modified cuprates that mainly showed *cis* stereoselectivity. This was explained by postulating a S$_N$2-mechanism.[7] Because these results seemed to be contradictory, we compared the stereochemical outcome of the methoxy substitution under identical conditions starting from pure **2a** and the N-methylated analog **7a**. Therefore, **2ab** was methylated with iodomethane in the presence of sodium hydride. The *trans* diastereomer **7a** was separated by flash chromatography. The exchange of the methoxy group in **7a** to yield **8** was carried out identically to the transformation of **2** to **3**. In contrast to the latter case, the reaction of **7** to form **8** is very slow. Even after 3 days, the conversion was incomplete. We were able to isolate 24% of the expected product as a mixture of the *cis*(**8b**) and *trans*(**8a**) diastereoisomers in a 76 to 24% ratio (**8b**:**8a**) besides large quantities of starting material. This was confirmed by the ^{1}H-NOE spectra of the isolated isomers. Thus, contrary to the diastereoselectivity observed for the unprotected ring system **2**, the N-methylated *trans* isomer **7a** mainly reacts to give the *cis* product **8b**. This confirms the S$_N$2-mechanism proposed by Yamamoto for the N-methylated compounds[7] (Scheme 4).

Scheme 3



Scheme 4



As the S$_N$2-reaction of **7a** cannot proceed via the *N*-acyliminium ion, the S$_N$1-type reaction of **2a** must depend on the availability of the hydrogen in 3-position. This indicates that most likely the imine is formed as an intermediate which is attacked by the nucleophile from the less hindered side. For the selective formation of the *trans* adduct it is neither possible nor necessary to consider an organocopper π-system to block one side of the molecule as described for proline derivatives.[4c–e] It has been shown that the methyl group in 5-position alone can direct the attack of other nucleophiles with similar diastereoselectivities.[6]

By blocking the N-position of the ring a different reaction mechanism can be forced upon the molecule which is also very interesting from a synthetic standpoint. Thus, a versatile product spectrum with the desired diastereoselectivity (*trans* or *cis*) can be obtained. Products **3**–**6** may easily be transformed to the dichiral 2-amino alcohols employing the method of Kunieda[8] or mild hydrolysis by NaOH.[6]

Experimental Section

General Methods. ^{1}H NMR spectra were recorded at 200 MHz with tetramethylsilane as internal reference. Data are reported as follows: chemical shift (δ) in ppm, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quin = quintet, br = broad), coupling constants in Hertz, integration. ^{13}C NMR spectra were recorded using broad-band proton-decoupling at 50.3 MHz with the solvent resonance as internal reference. Optical rotations were measured in absolute CHCl$_3$. Melting points are uncorrected. Thin-layer chromatography was performed on Merck ^{60}F$_{254}$ (0.2 mm) sheets, which were visualized with ethanolic molybdophosphoric acid, I$_2$, and UV light. Preparative flash column chromatography was performed on Merck (0.04–0.063 mm) silica gel using a positive pressure of air. Elemental analyses were performed by the Central service of the Institute. Unless otherwise noted, all chemicals were used of the highest commercially available

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purity and without further purification. Solvents, used for chromatography, were distilled before use. THF was distilled from potassium/benzophenone. BF_3·OEt_2 was distilled before use and stored under an atmosphere of argon. Organolithium reagents were commercially available. The ratios of diastereomers were determined *before* their purification by NMR spectra and the relative configurations identified by nuclear Overhauser effects.

(4*S*,5*R*)-5-Methyl-2-oxazolidinone-4-carboxylic Acid (1). To a solution of 2.38 g (20 mmol) of L-threonine and a trace of thymolphthalein as indicator in 30 mL of 2 N NaOH at 0 °C was added 2.4 mL (30 mmol) of methyl chloroformate dropwise. To maintain pH 10, it was necessary to add more NaOH several times. The solution was allowed to slowly warm to rt and stirred overnight. The reaction was neutralized with dilute HCl. After evaporation of the solvent, a white precipitate was obtained. The product was extracted with 250 mL of ethyl acetate which was acidified by HCl. The solvent was again evaporated and the white product was recrystallized in ethyl acetate/petroleum ether (40/60) affording 2.18 g (75%) of **1**, mp 138 °C (lit.[9] 139 °C): ^{1}H NMR ($CDCl_3$ + CD_3OD) δ 1.44 (d, J = 6.25 Hz, 3H), 3.85 (d, J = 6.25 Hz, 1H), 4.63 (quin, J = 6.25 Hz, 1H), 7.07 (br, 1H); ^{13}C NMR ($CDCl_3$ + CD_3OD) δ 21.1, 60.6, 76.1, 159.6, 172.1. Anal. Calcd for $C_5H_7NO_4$: C, 41.38; H, 4.86; N, 9.65. Found: C, 41.32; H, 4.89; N, 9.62.

(4*RS*,5*R*)-4-Methoxy-5-methyl-2-oxazolidinone (2ab). A stirred solution of 2.9 g (20 mmol) of **1** in 500 mL of 0.02 N NaOAc/MeOH was electrolyzed at rt under galvanostatic conditions using graphite electrodes (3 × 30 × 100 mm) in an undivided cell. After consumption of 3F/mol at a current density of 5 mA/cm^2, the solvent was evaporated, the white residue was purified, and the diastereomers were separated by flash chromatography on silica gel with Et_2O as eluent to afford 2.1 g (88%) of **2ab** as white crystals, mp 87–90 °C. The 4*R*,5*R*-product **2a** was formed with 77% ds.

***trans*-2a**: ^{1}H NMR ($CDCl_3$) δ 1.39 (d, J = 6.6 Hz, 3H), 3.32 (s, 1H), 4.50 (ddq, J = 6.6, 1.6, 0.5 Hz, 1H), 4.62 (dd, J = 1.7, 1.6 Hz, 1H), 7.1–7.2 (br, 1H); ^{13}C NMR $CDCl_3$) δ 18.9, 54.7, 79.5, 89.5, 159.3; $[\alpha]^{20}_D$ = +144.1°, c = 1.025 ($CHCl_3$).

***cis*-2b**: ^{1}H NMR ($CDCl_3$) δ 1.41 (d, J = 6.6 Hz, 3H), 3.34 (s, 1H), 4.68 (dq, J = 6.6, 5.5 Hz, 1H), 4.77 (dd, J = 5.5, 1.1 Hz, 1H), 7.25–7.35 (br, 1H); ^{13}C NMR ($CDCl_3$) δ 13.3, 55.4, 77.9, 85.4, 159.9; $[\alpha]^{17}_D$ = −139.0°, c = 1.025 ($CHCl_3$); HRMS calcd for $C_5H_9NO_3$ (M^+) 131.0582, found 131.0580.

(4*RS*,5*R*)-4-Methoxy-3,5-dimethyl-2-oxazolidinone (7ab). To a solution of 1.453 g (11.08 mmol) of **2ab** in 30 mL of dry THF under an argon atmosphere was added 2.5 mL (40 mmol) of CH_3I and an excess of NaH carefully at rt. After stirring 4 h, the reaction mixture was quenched by dropwise addition of ethanol, diluted with water, and extracted three times with CH_2Cl_2. The organic layer was washed with water, separated, and dried over $MgSO_4$. The residue was purified and the diastereomers were separated by flash chromatography on silica gel (Et_2O) to afford 1.086 g (68%) of **7ab**. The (4*R*,5*R*)-product *trans*-**7a** was obtained with 85% ds.

***trans*-7a**: mp 28 °C; ^{1}H NMR ($CDCl_3$) δ 1.36 (d, J = 6.8 Hz, 3H), 2.82 (s, 3H), 3.28 (s, 3H), 4.40 (dq, J = 6.8, 2.1 Hz, 1H), 4.57 (d, J = 2.1 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 19.2, 28.5, 52.5, 74.6, 93.1, 157.0; $[\alpha]^{17}_D$ = +56.85°, c = 1.45 ($CHCl_3$).

***cis*-7b**: colorless oil; ^{1}H NMR ($CDCl_3$) δ 1.39 (d, J = 6.8 Hz, 3H), 2.93 (s, 3H), 3.44 (s, 3H), 4.53 (dq, J = 6.8, 5.8 Hz, 1H), 4.69 (d, J = 5.8 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 13.2, 28.9, 57.4, 74.7, 90.4, 157.4; $[\alpha]^{17}_D$ = −42.21°, c = 0.995 ($CHCl_3$); HRMS calcd for $C_6H_{11}NO_3$(M^+) 145.0739, found 145.0739.

Nucleophilic Exchange. General Procedure. In a dry Schlenk tube, the organolithium compound was added to a stirred grey suspension of CuI in dry THF at −50 °C under argon atmosphere. After the mixture was stirred for 15 min and cooled down to −78 °C, BF_3·OEt_2 was added dropwise through a septum followed by **2ab** or **7a** in THF slowly over 10 min using a syringe. The mixture was stirred for several hours in a Dewar vessel, cooled with CO_2/MeOH and then treated with 3 × 30 mL concd NH_3/NH_4Cl (1:1) until a clear solution was formed. The phases were separated, the organic layer was extracted with water and dried over $MgSO_4$. The crude material obtained after evaporation of the solvent was purified by flash chromatography on silica gel.

(4*RS*,5*R*)-4-*n*-Butyl-5-methyl-2-oxazolidinone (3ab). Following the general procedure **2ab** (0.393 g, 3 mmol) was reacted with CuI (3.425 g, 18 mmol), 15% *n*-butyllithium in hexane (16.5 mL, 27 mmol), and BF_3·OEt_2 (0.4 mL, 3 mmol) in 30 mL of THF. The reaction was complete after 3 h, and the (4*R*,5*R*)-product *trans*-**3a** was obtained in 75% ds. Purification of the crude product and separation of the diastereomers by flash chromatography on silica gel (cyclohexane:ethyl acetate 3:2) afforded 0.312 g (66%) of **3ab** as a colorless oil.

***trans*-3a**: ^{1}H NMR ($CDCl_3$) δ 0.87 (t, J = 6.7 Hz, 3H), 1.2–1.34 (m, 4H), 1.38 (d, J = 6.7 Hz, 3H), 1.43–1.59 (m, 2H), 3.35 (q, J = 6.3 Hz, 1H), 4.26 (quin, J = 6.3 Hz, 1H), 6.72 (br, 1H); ^{13}C NMR ($CDCl_3$) δ 13.8, 20.2, 22.4, 27.4, 34.6, 59.8, 79.0, 160.0; $[\alpha]^{17}_D$ = +43.6°, c = 2.425 ($CHCl_3$).

***cis*-3b**: ^{1}H NMR ($CDCl_3$) δ 0.89 (t, J = 6.7 Hz, 3H), 1.31 (d, J = 6.7 Hz, 3H), 1.13–1.54 (m, 6H), 3.74 (q, J = 6.7 Hz, 1H), 4.75 (quin, J = 6.7 Hz, 1H), 6.33 (br, 1H); ^{13}C NMR ($CDCl_3$) δ 13.8, 14.8, 22.5, 28.1, 29.5, 55.8, 76.3, 160.2; HRMS calcd for $C_8H_{15}NO_2$ (M^+) 157.1103, found 157.1106.

(4*RS*,5*R*)-4,5-Dimethyl-2-oxazolidinone (4ab). Following the general procedure, **2ab** (0.524 g, 4 mmol) was reacted with CuI (4.56 g, 24 mmol), 1.6 M methyllithium in diethyl ether (24 mL, 27 mmol), and BF_3·OEt_2 (0.6 mL, 4 mmol) in 40 mL THF. The reaction was complete after 24 h. Purification of the crude product by flash chromatography on silica gel (CH_2Cl_2:MeOH 20:1) afforded 0.271 g (59%) of **4ab** as white crystals, mp 63–80 °C (lit.[10] colorless oil). The (4*R*,5*R*)-product *trans*-**4a** was obtained in 91% ds.

***trans*-4a**: ^{1}H NMR ($CDCl_3$) δ 1.25 (d, J = 7.0 Hz, 3H), 1.39 (d, J = 7.0 Hz, 3H), 3.52 (dquin, J = 7.0, 1.7 Hz, 1H), 4.20 (quin, J = 7.0 Hz, 1H), 5.98 (br, 1H); ^{13}C NMR ($CDCl_3$) δ 19.2, 19.7, 55.2, 80.4, 159.7.

***cis*-4b**: ^{1}H NMR ($CDCl_3$) δ 1.15 (d, J = 7.0 Hz, 3H), 1.32 (d, J = 7.0 Hz, 3H), 3.92 (quin, J = 7.0 Hz, 1H), 4.76 (quin, J = 7.0 Hz, 1H), 7.42 (br, 1H); ^{13}C NMR ($CDCl_3$) δ 15.5, 18.6, 51.1, 79.2, 159.7; HRMS calcd for $C_5H_9NO_2$ (M^+) 115.0633, found 115.0632. Anal. Calcd for $C_5H_9NO_2$: C, 52.16; H, 7.88; N, 12.17. Found: C, 51.82; H, 7.73; N, 12.12.

(4*RS*,5*R*)-4-*tert*-Butyl-5-methyl-2-oxazolidinone (5ab). Following the general procedure, **2ab** (0.262 g, 2 mmol) was reacted with CuI (2.282 g, 12 mmol), 1.7 M *tert*-butyllithium in pentane (5.3 mL, 9 mmol), and BF_3·OEt_2 (0.6 mL, 4 mmol) in 20 mL of THF. The reaction was complete after 12 h. Purification of the crude product and separation of the diastereomers by flash chromatography on silica gel (ethyl acetate:cyclohexane 1:1) afforded 0.171 g (55%) of **5ab** as white crystals, mp 118 °C (diastereomeric mixture). The (4*R*,5*R*)-product *trans*-**5a** was obtained in 96% ds.

***trans*-5a**: ^{1}H NMR ($CDCl_3$) δ 0.88 (s, 9H), 1.39 (d, J = 6.6 Hz, 3H), 3.08 (dd, J = 4.4, 1.1 Hz, 1H), 4.44 (dq, J = 6.6, 4.4 Hz, 1H), 6.56 (br, 1H); ^{13}C NMR ($CDCl_3$) δ 22.3, 24.9, 33.5, 68.7, 74.7, 160.1; $[\alpha]^{17}_D$ = +34.4°, c = 1.02 ($CHCl_3$).

***cis*-5b**: ^{1}H NMR ($CDCl_3$) δ 1.10 (s, 9H), 1.49 (d, J = 7.0 Hz, 3H), 3.49 (dd, J = 7.0 Hz, 1.1 Hz, 1H), 4.76 (quin, J = 7.0 Hz, 1H), 6.36 (br, 1H); ^{13}C NMR ($CDCl_3$) δ 16.6, 26.6, 33.7, 65.1, 77.7, 160.8; HRMS calcd for $C_8H_{15}NO_2$ (M^+) 157.1102, found 157.1108. Anal. Calcd for $C_8H_{15}NO_2$: C, 61.12; H, 9.62; N, 8.91. Found: C, 60.98; H, 9.59; N, 8.83.

(4*RS*,5*R*)-5-Methyl-4-phenyl-2-oxazolidinone (6ab). Following the general procedure, **2ab** (0.393 g, 3 mmol) was reacted with CuI (3.425 g, 18 mmol), 2 M phenyllithium in cyclohexane/diethyl ether (13.5 mL, 27 mmol), and BF_3·OEt_2 (0.4 mL, 3 mmol) in 35 mL of THF. The reaction was complete after 17 h. Purification of the diastereomers by flash chromatography on silica gel (CH_2Cl_2:Et_2O 5:1) afforded 0.445 g (84%) of **6ab** as white crystals, mp 132 °C (acetone/*n*-hexane) (lit.[11] 125 °C). The (4*R*,5*R*)-product *trans*-**6a** was obtained in 98% ds.

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***trans*-6a**: ^{1}H NMR ($CDCl_3$) δ 1.48 (d, J = 6.2 Hz, 3H), 4.42 dq, J = 6.2, 7.7 Hz, 1H), 4.46 (d J = 7.7 Hz, 1H), 5.88 (br, 1H), 7.28–7.47 (m, 5H); ^{13}C NMR ($CDCl_3$) δ = 19.3, 64.1, 81.8, 126.2 (2C), 128.9, 129.2 (2C), 138.8, 159.4; $[\alpha]^{17}_D = -35.36°$, c = 1.04 ($CHCl_3$).

***cis*-6b**: ^{1}H NMR ($CDCl_3$) δ 0.93 (d, J = 6.7 Hz, 3H), 4.88–5.18 (m, 2H), 5.75 (br, 1H), 7.28–7.47 (m, 5H); HRMS calcd for $C_{10}H_{11}NO_2$ (M^+) 177.0790, found 177.0795. Anal. Calcd for $C_{10}H_{11}NO_2$: C, 67.78; H, 6.26; N, 7.90. Found: C, 67.50; H, 6.15; N, 7.64.

(4*RS*,5*R*)-4-*n*-Butyl-3,5-dimethyl-2-oxazolidinone (8ab). Following the general procedure, **7a** (0.453 g, 3.12 mmol) was reacted with CuI (3.560 g, 18.72 mmol), 1.6 M *n*-butyllithium in heptane (16.85 mL 28.08 mmol), and BF_3·OEt_2 (0.41 mL 3.12 mmol) in 40 mL of THF. The reaction was stopped after 66 h. Purification of the crude product and separation of the diastereomers by flash chromatography on silica gel (cyclohexane:ethylacetate 2:1) afforded 0.127 g (24%) of **8ab** as a colorless oil. The (4*S*,5*R*)-product *cis*-**8b** was obtained in 76% ds.

***cis*-8b**: ^{1}H NMR ($CDCl_3$) δ 0.91 (t, J = 7.0 Hz, 3H), 1.30 (d, J = 6.6 Hz, 3H), 1.14–1.74 (m, 6H), 2.81 (s, 3H), 3.56 (dt, J = 7.4, 4.9 Hz, 1H), 4.63 (dq, J = 7.4, 6.6 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 14.6, 20.8, 22.8, 27.1, 27.6, 29.4, 60.4, 73.5, 158.5.

***trans*-8a**: ^{1}H NMR ($CDCl_3$) δ 0.91 (t, J = 7.0 Hz, 3H), 1.37 (d, J = 6.3 Hz, 3H), 1.15–1.78 (m, 6H), 2.81 (s, 3H), 3.16 (ddd, J = 6.3, 5.6, 3.5 Hz, 1H), 4.20 (quin, J = 6.3 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 13.8, 20.8, 22.6, 26.0, 28.9, 31.2, 64.0, 75.1, 157.8; HRMS calcd for $C_9H_{17}NO_2$ (M^+) 171.1259, found 171.1259.

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Supplementary Material Available: Copies of the 200 MHz ^{1}H NMR spectra of those compounds lacking combustion data, including NOE difference spectra of compounds **3a**, **3b**, **5a**, **8b**, and **8ab**, as well as the MS, and IR data, together with R_f values (TLC), and 200 MHz ^{1}H and 50.3 MHz ^{13}C NMR spectra including peak assignments for compounds **1**–**8** (14 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.