

Chiral Auxiliary-Bearing Isocyanides as Synthons: Synthesis of Strongly Fluorescent (+)-5-(3,4-Dimethoxyphenyl)-4-[[N-[(4S)-2-oxo-4-(phenylmethyl)-2-oxazolidinyl]]carbonyl]oxazole and Its Enantiomer

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Received August 9, 1996[®]

Both (4S-(+)-3-(isocyanoacetyl)-4-(phenylmethyl)-2-oxazolidinone (*R*)-**1** and its enantiomer (*S*)-**1** have been synthesized as potentially useful synthons in asymmetric synthesis. Optically active (+)-5-(3,4-dimethoxyphenyl)-4-[[N-[(4S)-2-oxo-4-(phenylmethyl)-2-oxazolidinyl]]carbonyl]oxazole (*S*)-**2** and its enantiomer (*R*)-**2** obtained by treating 3,4-dimethoxybenzoyl chloride with (*S*)-**1** and (*R*)-**1**, respectively, in the presence of the nonionic superbases P(MeNCH₂CH₂)₃N, have high fluorescence quantum yields. The molecular structure of (*S*)-**2** obtained by X-ray means is also presented.

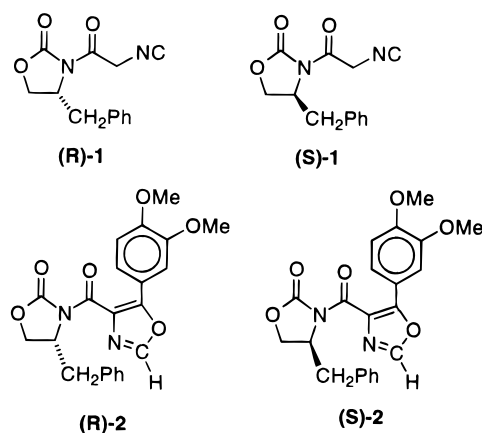
Introduction

Being both nucleophilic and electrophilic, α -metalated isocyanides can add to polar double bonds, forming a variety of heterocycles such as 2-oxazolines, 2-imidazolines, 2-thiazolines, oxazoles, thiazoles, triazoles, imidazolinones, pyrroles, pyrrolines, 1,3-oxazines, and imidazolidinones.¹ Oxazolines and oxazoles are not only pharmaceutically interesting classes of heterocyclic compounds, but they are also useful intermediates to α -amino acids and α -acylamino acids,² while thiazolines are key intermediates to penicillin antibiotics and their structural variants.¹ α -Metalated isocyanides are also used for the preparation of 1,2- and 1,3-amino alcohols, 1,2-diamines, and 2,3-diaminoalkenoic acids.¹ Recently, there has arisen considerable interest in the asymmetric aldol addition of isocyanide enolates to aldehydes for producing optically active 2-oxazoline-4-carboxylates or 4-carbamides which upon hydrolysis give proteinogenic or non-proteinogenic amino acids. Moreover, considerable efforts have been devoted to developing effective chiral catalysts such as ferrocenyldiphosphine gold(I) complexes for asymmetric aldol reactions.³ Yet, there has been no report on the use of a chiral auxiliary-bearing isocyanide enolate for such asymmetric syntheses. Here, we report the synthesis of the chiral auxiliary-bearing isocyanides (*R*)-**1** and (*S*)-**1**. We also report the synthesis of a new type of optically active fluorescence system, namely, (*R*)-**2** and (*S*)-**2** derived from (*R*)-**1** and (*S*)-**1**, the fluorescence quantum yields of (*R*)-**2** and (*S*)-**2**, and the crystal structure of (*S*)-**2**. (*R*)-**2** and (*S*)-**2** are potentially useful in fluorescence-detected circular dichroism for on-column capillary electrophoresis.⁴

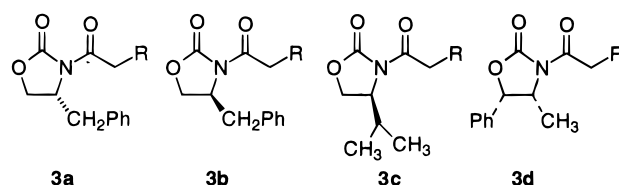
Results and Discussion

Synthesis of Chiral Auxiliary-Bearing Isocyanides.

The substituted oxazolidinones **3** have proven to be versatile chiral auxiliaries for the construction of enantiomerically pure substances. The observation that eno-



late conjugates derived from these compounds react with a variety of carbon and heteroatomic electrophiles with

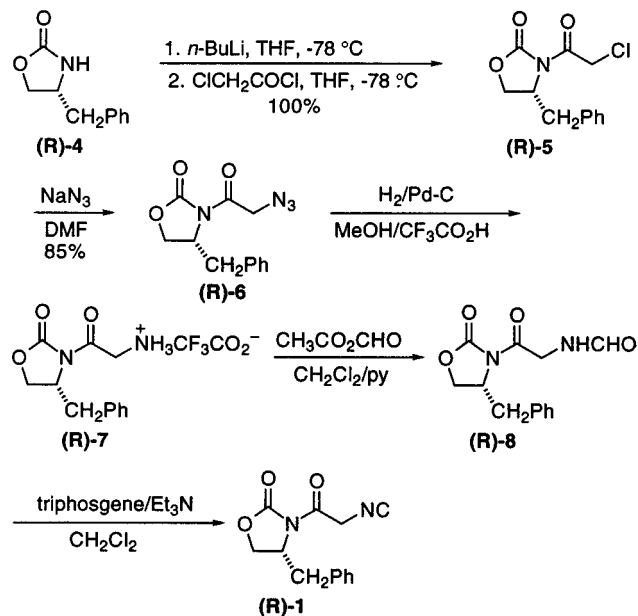


high diastereoselection led to the development of practical methods for asymmetric alkylation,⁵ acylation,⁶ aldol addition,^{5b,7} azidation,^{8,9} hydrazination,¹⁰ and hydroxylation.¹¹ Similarly, α,β -unsaturated *N*-acyloxazolidinones have proven to be useful dienophiles in Lewis acid-

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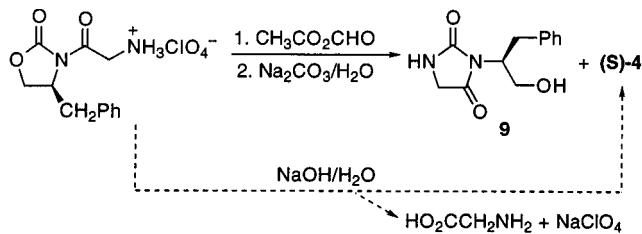
Scheme 1



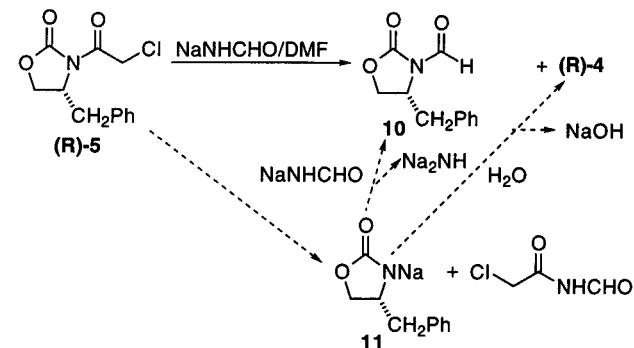
catalyzed Diels–Alder reactions.¹² However, R in **3** has been limited to alkyl, aryl, acyl, and isothiocyanato groups. Compound **1** (i.e., **3** with R = NC) though not previously reported, is potentially useful for the construction of many types of optically active substances, in view of the known wide range of reactivities of racemic isocyanides.¹

A successful synthesis of (R)-**1** reported herein is shown schematically in Scheme 1. Its enantiomer (S)-**1** was synthesized similarly. (R)-**5** and (S)-**5** were prepared from their corresponding optically pure 2-oxazolidinones in high yields by use of a procedure previously reported for (S)-**5**.^{7b} The synthesis of (S)-**6**, also reported previously,^{7b} was carried out by the reaction of (S)-**5** with sodium azide in 1:1 CH₂Cl₂/H₂O using the phase transfer catalyst *n*-Bu₄NHSO₄. Since NaN₃–CH₂Cl₂ is a dangerously explosive mixture,¹³ we modified the procedure by using DMF as the solvent and eliminating the use of a phase transfer catalyst. In this way (R)-**6** and (S)-**6** were isolated in 85–90% yields. (R)-**6** and (S)-**6** were conveniently transformed into (R)-**7** and (S)-**7**, respectively, by use of a modified literature procedure used previously for the preparation of the corresponding perchlorate salt.^{7b} An attempt to convert [(S)-**7**]ClO₄ to (S)-**8** with CH₃CO₂CHO in HCO₂H, followed by treatment with Na₂CO₃/H₂O, resulted in the formation of **9** and (S)-**4** (Scheme 2). Apparently, neutralization of the ammonium group in [(S)-**7**]ClO₄ facilitated conversion of the (CO)–O linkage to the more thermodynamically stable C(O)–N bond. The formation of (S)-**4** from [(S)-**7**]ClO₄ suggests that the exo-acylimide bond is labile in an alkaline environment. An attempt to convert (R)-**5** to (R)-**8** directly with NaNHCHO in DMF resulted in the formation of **10** and (R)-**4**, suggesting the exo-acylimide bond is also labile to the strongly nucleophilic NaNHCHO (Scheme 3). Formation of **10** in this reaction should be

Scheme 2



Scheme 3



accompanied by ClCH₂CONHCHO, but the latter was not isolated. [(R)-**7**]CF₃CO₂ and [(S)-**7**]CF₃CO₂ were successfully converted in high yield to (R)-**8** and (S)-**8**, respectively, with CH₃CO₂CHO in CH₂Cl₂ in the presence of pyridine. Transformation of a formamide group to an isocyanato group is well documented,¹⁴ and herein both (R)-**8** and (S)-**8** were converted to the desired crystalline (R)-**1** and (S)-**1** in ~60% yield with triphosgene¹⁵ in CH₂Cl₂ in the presence of Et₃N.

Before we devised the strategy shown in Scheme 1, the method shown in Scheme 4 for the synthesis of (R)-**1** was tried unsuccessfully. Though the reaction of isocyanacetamide (derived from CNCH₂CO₂K and [Me₂N=CHCl]Cl) with amines provides isocyanacetamides in high yield,¹⁶ (R)-**1** was not formed by treating Li[(R)-**4**] with CNCH₂CO₂K/[Me₂N=CHCl]Cl in THF. Formation of (R)-**4** suggests a proton transfer from CNCH₂COCl to Li[(R)-**4**] due to the high acidity of the methylene protons in CNCH₂COCl. While the reaction of Li[(R)-**4**] with the anhydride of hexenoic acid and trimethylacetic acid gives 2-hexenylacetyloxazolidine in 93% yield,^{7b} treatment of Li[(R)-**4**] with CNCH₂CO₂C(O)CMe₃ resulted in the formation of (R)-**4**, supporting the idea of proton transfer from the acidic methylene in CNCH₂CO₂(CO)CMe₃ to Li[(R)-**4**].

Synthesis, Quantum Yield, and Crystal Structure of Optically Active Oxazoles. Optically active fluorescence materials with high quantum yields and/or strong circular dichroism signals are rare but they are important as standards in fluorescence-detected circular dichroism for on-column detection in capillary electrophoresis (FDCD-CE). This newly developed method, widely useful in biology, medicine, and in the pharmaceutical industry, enjoys several advantages over traditional detection methods. In FDCD-CE, riboflavin (which has a low quantum yield and a weak CD signal) is used as the optically active fluorescence standard. The intro-

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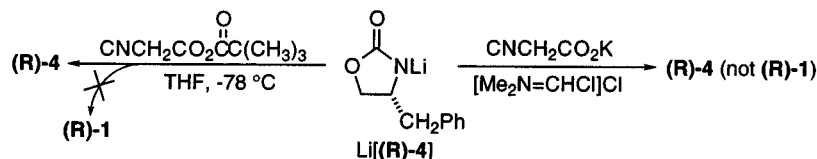
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Scheme 4



Scheme 5

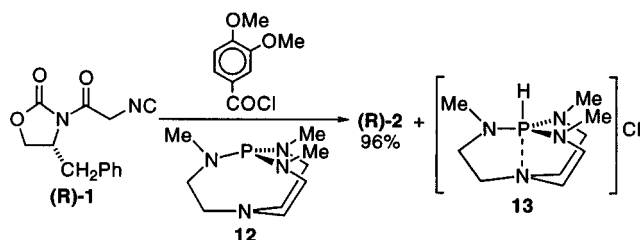


Table 1. UV Spectral, FL Spectral, and Quantum Yield Data for (R)-2, (S)-2, 14, 15 and PBD

compound ^a	solvent	λ_{\max} UV	λ_{\max} FL	FL emission range (nm)	Φ (315 nm)
(S)-2	EtOH	313	397	330–650	0.99
(R)-2	etoh	313	397	330–650	0.99
14	etoh	277	346	<300–500	<i>b</i>
15	EtOH	291	410	326–600	0.30
PBD	cyclohexane	301	355	310 to 530	0.83 ^c

^a Concentration: 2.0×10^{-6} M. ^b The Φ value was not measured because this compound has no UV absorption at 315 nm. ^c Reference 19.

Table 2. Selected Mean Deviations and Interplanar Angles to the plane O1–N1–C1–C2–C3

least-square plane	mean deviations (Å)	interplanar angles (deg)
O1–N1–C1–C2–C3	0.0052	0
C3–C4–O2–N2	0.0033	83.0
C8–C9–C10–C11–C12–C13	0.0069	22.5
O2–C4–N2–C5–O3	0.0198	81.7

duction of a standard having a higher fluorescence quantum yield and/or a stronger circular dichroism could enhance the detection sensitivity, thereby improving detection limits.⁴ For this purpose, (R)-2 and (S)-2 were conveniently synthesized in high yields from (R)-1 and (S)-1 by a reaction we studied previously^{2b} (Scheme 5).

The maximum UV absorption ($\lambda_{UV_{\max}}$) and fluorescence (FL) emission ($\lambda_{FL_{\max}}$), fluorescence quantum yields Φ , and FL emission ranges for (R)-2, (S)-2, 14, 15, and 2-(4-biphenyl)-5-phenyl-1,3,4-oxadiazole (PBD), a standard for Φ measurements, are summarized in Table 1. The $\lambda_{UV_{\max}}$ red-shifts from 276.8 nm for 14 to 291.0 nm for 15 as OMe groups are added to the phenyl group. Replacement of the ester group in 15 with an 2-oxo-oxazolidin-3-yl acyl group in (R)-2 or (S)-2, further red-shifts $\lambda_{UV_{\max}}$ to 315.4 nm. It is interesting to note the $\lambda_{FL_{\max}}$ red-shift from 14 to 15, the $\lambda_{FL_{\max}}$ blue-shift from 15 to (R)-2 or (S)-2, and the quantum yield increase from $\Phi = 0.30$ for 15 to $\Phi = 0.99$ for (R)-2 or (S)-2. The high fluorescence quantum yields suggest the potential use of (R)-2 and (S)-2 as optically active fluorescence standards in FDCE.

The bond lengths and bond angles for (S)-2 are unremarkable. The ground state for the five-membered oxazole ring is essentially planar. The dimethoxyphenyl group plane is twisted 22.5° away from the oxazole plane

and the plane containing the two carbonyl groups (O2–C4–N2–C5–O3) is almost perpendicular (81.7°) to the oxazole plane.

Experimental Section

General. All reactions and solvent treatments were done under a nitrogen or argon atmosphere. THF and diethyl ether were refluxed with sodium in the presence of benzophenone and freshly distilled. CH₂Cl₂, pyridine, triethylamine, and cyclohexane were refluxed with CaH₂ and freshly distilled. Methyl alcohol and ethyl alcohol were refluxed with sodium and then freshly distilled. Compounds 14,^{2b} 15,^{2b} and trimethyl-pro-azaphosphatane 12¹⁷ were prepared as described as previously. Elemental analyses were performed by Desert Analytics. The X-ray data collection and structure solution was carried out in the Iowa State University Molecular Structure Laboratory. All melting points are uncorrected.

(4R)-(-)-3-(Chloroacetyl)-4-(phenylmethyl)-2-oxazolidinone (R)-1. (4R)-(-)-4-(phenylmethyl)-2-oxazolidinone (R)-4 (4.00 g, 0.0226 mol) and Ph₃CH (15 mg, indicator) were dissolved in dry THF (50 mL) at room temperature and then cooled to -78 °C. To this solution was added dropwise *n*-BuLi (14 mL of a 1.6 M solution in hexanes 0.023 mol, 1.0 equiv) giving an orange solution. Chloroacetyl chloride (2.83 g, 0.0248 mol, 1.10 equiv) was added by syringe over 2 min at -78 °C to give a yellowish solution which was stirred at -78 °C for 20 min. The dry ice-acetone bath was removed, and the solution was stirred for 2.5 h and finally quenched with saturated aqueous ammonium chloride (25 mL). After volatiles were removed in vacuo at room temperature, the residue was diluted with distilled water (20 mL) and extracted with CH₂Cl₂ (100 mL and then 50 mL). The combined extracts were dried with anhydrous Na₂SO₄ overnight and filtered. The filtrate was concentrated at 40 °C in vacuo to give crude solid (R)-5 (5.71 g, 100%) which was used directly for further reactions because ¹H NMR spectra indicated nearly pure material. For analyses, 0.76 g of crude (R)-5 was recrystallized from CH₂Cl₂-hexane in a freezer to give colorless crystals. The supernatant was removed by syringe while it was still cold, and the colorless crystals remaining weighed 0.49 g after being dried in vacuo. Mp 74–5 °C, $R_f = 0.48$ (ethyl acetate:hexane = 1:2). $[\alpha]_D^{25} -87.2$ (CH₂Cl₂, *c* = 0.620 g/mL). Anal. Calcd: C, 56.91; H, 5.01; N, 5.80. Found: C, 56.85; H, 4.87; N, 5.39.

(4R)-(-)-3-(Azidoacetyl)-4-(phenyl)methyl-2-oxazolidinone (R)-6. **Method A:** Although this method is less safe

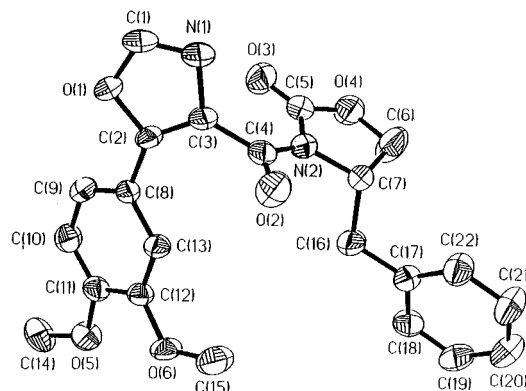


Figure 1. Computer drawing of (S)-2 (C₂₂H₂₀N₂O₆; fw, 408.4; monoclinic, *P*₂₁₂₁₂₁; colorless; *a* = 7.863(1) Å, *b* = 10.059(1) Å, *c* = 25.218(3) Å; *Z* = 4; *R* = 3.85%; GOF = 1.82). Ellipsoids are drawn at the 50% probability level.

than method B, it is given here for completeness. To a solution of crude (4R)-(-)-3-(chloroacetyl)-4-(phenylmethyl)-2-oxazolidinone (*R*)-5 (7.1 g, 0.028 mol) in dry CH₂Cl₂ (30 mL) were added sequentially water (30 mL), NaN₃ (9.2 g, 0.14 mol, 5.0 equiv) and the phase-transfer catalyst (*n*-Bu)₄NHSO₄ (0.96 g, 0.0028 mol, 0.10 equiv). The reaction mixture was stirred vigorously with a mechanical stirrer for 1.5 h. The organic layer was separated, and the aqueous layer was extracted with CH₂Cl₂ (100 mL). The combined organic layers were concentrated in vacuo, and the resulting residual brownish oil was filtered through a short silica gel column (50 × 50 mm) using CH₂Cl₂ as the eluent to give crude (*R*)-6 (7.1 g, 97%) as white crystals. For analysis, 0.42 g of crude (*R*)-6 was recrystallized from ethyl acetate-hexane to give 0.35 g of pure (*R*)-6. Mp 62–63 °C, *R*_f = 0.48 (hexane:ethyl acetate = 2:1). [α]_D²⁵ = -93.9 (CH₂Cl₂, *c* = 0.917 g/mL). Anal. Calcd: C, 55.38; H, 4.65; N, 21.52. Found: C, 55.17; H, 4.68; N, 21.30.

Method B: To a stirred solution of crude (*R*)-5 (27.3 g, 0.108 mol) in DMF (100 mL) was added NaN₃ (35.1 g, 0.540 mol, 5.00 equiv). After the mixture was stirred vigorously with a mechanical stirrer for 10 min, the liquid layer changed from colorless to brownish. The mixture was further stirred at room temperature for 11 h and filtered through Celite in vacuo to remove inorganic salts and then ethyl acetate (100 mL × 2) was passed through the Celite. The filtrate was washed with 25% sodium chloride solution (300 mL). The organic phase was separated, and the aqueous phase was extracted with ethyl acetate (100 mL). The combined organic phases were dried with anhydrous Na₂SO₄ and then concentrated in vacuo at 35 °C. The residual oil was crystallized from ethyl acetate and hexane (1:1) in a freezer to give (*R*)-6 as white crystals (12.25 g). The supernatant was concentrated in vacuo at 25 °C to 30 °C, and the residue was flash-chromatographed on a silica gel column (45 × 150 mm) using a 2:1 ratio of CH₂Cl₂:hexane as eluent to give 11.4 g of (*R*)-6 as a white solid. The total yield of (*R*)-6 was 85%.

[[[(4R)-(-)-4-(Phenylmethyl)-2-oxooxazolidin-3-yl]carboxylmethyl]ammonium Trifluoroacetate [(*R*)-7]CF₃CO₂. To a solution of crude (4R)-(-)-3-(azidoacetyl)-4-(phenylmethyl)-2-oxazolidinone (*R*)-6 (5.31 g, 0.0205 mol) in anhydrous methanol (160 mL) was added CF₃CO₂H (4.8 mL, 0.062 mol, 3.0 equiv), and then 10% palladium-carbon (1.30 g) was added slowly with a spatula. The reaction flask was stoppered with a septum, and air inside the flask was removed by flushing with argon. The flask was then purged with hydrogen for 10 min by bubbling hydrogen through a long needle inlet and out via a short needle. The mixture was then stirred under a hydrogen atmosphere (by attaching a hydrogen balloon to a needle through the septum) for 23.5 h. The Pd/C catalyst was filtered through Celite and was washed with methanol (30 mL). The filtrate and washing solution were combined and rotary-evaporated at room temperature using ice-water as a recycling coolant. The residue was then evacuated under oil pump pressure (0.4 torr) at room temperature to afford white foamy particles (7.1 g, 100%) which were not further purified but were used directly for the formylation reaction that followed.

(4R)-(-)-3-[(Formylamino)acetyl]-4-(phenylmethyl)-2-oxazolidinone (*R*)-8. To a suspension of crude [(*R*)-7]CF₃CO₂ (7.2 g, 0.020 mol) in dry CH₂Cl₂ (100 mL) was added by syringe CH₃CO₂CHO¹⁸ (20.4 g, 0.232 mol). The reaction mixture was placed in a dessicator containing CaSO₄ and the dessicator was placed in a freezer. After 2 min a clear solution formed which was allowed to cool to 0 °C and then dry pyridine (18.5 g, 0.235 mol) was added by syringe over a period of 2 min. The solution was further stirred at 0 °C for 45 min and then at room temperature for 1 h. Finally it was poured into 10% hydrochloric acid (85 mL). The organic phase was separated and the aqueous phase was extracted with CH₂Cl₂ (2 × 100 mL). The combined organic phases were dried overnight with anhydrous Na₂SO₄ after which volatiles were removed at 30 °C in vacuo. To remove any acetic acid remaining, 30 mL of ethyl acetate/toluene (1:2) was added and

the mixture was rotary-evaporated at 30 °C using ice-water as the coolant. Final evaporation was carried out under oil pump pressure at 0.4 torr. This two-fold evaporation procedure was repeated three times. The resulting oil was flash-chromatographed on a silica gel column (50 × 50 mm) using hexane:ethyl acetate (3:1 to 1:1) to give the product as a colorless oil (4.85 g, 93%). *R*_f = 0.29 (hexane:ethyl acetate = 1:3). [α]_D²⁵ = -86.0 (CH₂Cl₂, *c* = 0.812 g/mL). Anal. Calcd C, 59.54; H, 5.38; N, 10.68. Found: C, 59.42; H, 5.48; N, 10.23.

(4R)-(-)-3-(Isocyanoacetyl)-4-(phenylmethyl)-2-oxazolidinone (*R*)-1. To a solution of (4R)-(-)-3-[(formylamino)acetyl]-4-(phenylmethyl)-2-oxazolidinone (0.21 g, 0.80 mmol) in dry CH₂Cl₂ (27 mL) was added by syringe dry Et₃N (0.21 g, 2.0 mmol, 2.5 equiv). The solution was cooled to 0 °C, and a solution of triphosgene (0.095 g, 0.32 mmol, 1.2 equiv) which was weighed in a hood into dry CH₂Cl₂ (5 mL) was added dropwise. The reaction mixture was stirred at room temperature for 24 h and filtered through a short silica gel column with 1:1 hexane/ethyl acetate to remove salts. The eluents were combined and concentrated in vacuo. The residue was flash chromatographed on a silica gel column (45 × 130 mm) with hexane:ethyl acetate (2:1) to give colorless crystals (0.13 g, 67%). Mp 277.0–278.0 °C, *R*_f = 0.62 (hexane:ethyl acetate = 1:1). [α]_D²⁵ = -95.0 (CH₂Cl₂, *c* = 0.500 g/mL). Anal. Calcd C, 63.92; H, 4.95; N, 11.47. Found: C, 63.72; H, 4.88; N, 11.40.

(4S)-(+)-3-(Azidoacetyl)-4-(phenylmethyl)-2-oxazolidinone (*S*)-6. The synthesis of (*S*)-6 was similar to that of (*R*)-6 using method B (overall yield from (*R*)-4, 90%). *R*_f = 0.48 (hexane:ethyl acetate = 2:1). [α]_D²⁵ = +93.6 (CH₂Cl₂, *c* = 0.917 g/mL).

(4S)-(+)-3-[(Formylamino)acetyl]-4-(phenylmethyl)-2-oxazolidinone (*S*)-8. The synthesis of (*S*)-8 was similar to that of (*R*)-8 (overall yield from (*S*)-6, 90%). *R*_f = 0.29 (ethyl acetate:hexane = 3:1). [α]_D²⁵ = +86.5 (CH₂Cl₂, *c* = 0.812 g/mL).

(4S)-(+)-3-(Isocyanoacetyl)-4-(phenylmethyl)-2-oxazolidinone (*S*)-1. The synthesis of (*S*)-1 was similar to that of (*R*)-1. Yield = 53%. [α]_D²⁵ = +195.3 (CH₂Cl₂, *c* = 0.500 g/mL).

(+)-5-(3,4-Dimethoxyphenyl)-4-[N-[(4S)-2-oxo-4-(phenylmethyl)-2-oxazolidinyl]carbonyloxazole (*S*)-2. To a stirred solution of trimethyl-pro-azaphosphatane **12**¹⁷ (0.23 g, 0.0011 mol) in dry THF (5 mL) at 0 °C was added under nitrogen colorless crystals of (4S)-3-(isocyanoacetyl)-4-(phenylmethyl)-2-oxazolidinone, (*S*)-1 (0.26 g, 0.0010 mol). After 5 min, a colorless solution of 3,4-dimethoxybenzoyl chloride (0.22 g, 1.1 mmol) in dry THF (5 mL) was added dropwise to give an orange solution plus a white precipitate. The mixture was stirred at 0 °C for 20 min and then at room temperature for 30 min. The volatiles were removed in vacuo, and the resulting residue was treated with water (5 mL). The solution was then extracted with ethyl acetate (25 mL × 2). The combined extracts were dried overnight with anhydrous Na₂SO₄ and flash chromatographed on a silica gel column (25 × 130 mm) with ethyl acetate/hexane (1:1) to afford 0.39 g (96%) of (*S*)-2 as colorless crystals. *R*_f = 0.20 (ethyl acetate:hexane = 1:1). The solution was blue under UV light (254 nm). Anal. Calcd C, 64.68; H, 4.94; N, 6.86. Found: C, 64.79; H, 4.83; N, 6.72. [α]_D²⁵ = +68.9 (*c* = 0.80 g/mL). Pertinent UV spectral, FL spectral, and fluorescence quantum yield data are summarized in Table 1.

(+)-5-(3,4-Dimethoxyphenyl)-4-[[N-(4R)-2-oxo-4-(phenylmethyl)-2-oxazolidinyl]carbonyloxazole (*R*)-2. (*R*)-2 was synthesized similarly. Yield, 96%; [α]_D²⁵ = -68.8 (*c* = 0.80 g/mL). Pertinent UV spectral, FL spectral, and fluorescence quantum yield data are summarized in Table 1.

Ultraviolet Spectra, Fluorescent Spectra, and Fluorescence Yield of (*R*)-2, (*S*)-2, 14, 15 and 2-(4-Biphenyl)-5-phenyl-1,3,4-oxadiazole (PBD). The concentrations of (*R*)-2, (*S*)-2, 14, 15, and PBD in cyclohexane were all 2.0 × 10⁻⁶ M. Ultraviolet spectra and absorbances were measured with a Shimadzu UV-240 Ultra-Via spectrometer, and fluorescent

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spectra and intensities (area integration) were measured with a Spex FluoroMax spectrometer using 315 nm as the exciting wavelength. Fluorescent quantum yields were calculated using the following equation:²⁰

$$\Phi_f = \Phi_f^\circ \frac{F(1 - 10^{-A_0}) n_i^2}{F_0(1 - 10^{-A}) n_0^2} \quad (1)$$

where Φ_f and Φ_f° are fluorescent quantum yields of the specimen and the standard (PBD, $\Phi_f^\circ = 0.83^{19}$), respectively, F and F_0 are total fluorescent intensities of the specimen and the standard (PBD), respectively, A and A_0 are the absorbances of the specimen and the standard (PBD) at 315 nm, respectively, and n_i and n_0 are the refractive indices of the specimen solution in ethanol and the standard (PBD) solution in cyclohexane, respectively. Since all the solutions used were quite dilute, the solvent refractive indices²¹ of pure ethanol ($n = 1.3600$) and cyclohexane ($n_0 = 1.4246$) were used in the calculations. The pertinent results are summarized in Table 1.

Molecular Structure of (S)-2. A crystal of the compound was attached to the tip of a glass fiber and mounted on the P4RA diffractometer for data collection at 295 ± 1 K. The cell constants for the data collection were determined from reflections found from a 360° rotation photograph. High-angle cell constants were determined from a subset of intense reflections in the range of 35.0 to 50.0° (2θ). Lorentz and polarization corrections were made, and a nonlinear correction based on the decay in the standard reflections was also applied to the data. A series of azimuthal reflections was collected. An

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absorption correction was not deemed necessary. The space group $P2_12_12_1$ was chosen based on systematic absences and intensity statistics. This assumption proved to be correct as determined by a successful direct-method solution and subsequent refinement. All non-hydrogen atoms were placed directly from the E-map. All non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogen atoms were refined as riding atoms with C-H distances of 0.96 \AA and individual isotropic displacement parameters. Each methoxy group was refined torsionally in order to find the best placement of the hydrogen atoms. Conversion was then made to a riding atom model with group isotropic displacement parameters. Refinement calculations were performed on a Digital Equipment MicroVAX 3100 computer using the SHELX-TL-Plus programs.^{22,23}

Acknowledgment. The authors are grateful to the Donors of the Petroleum Research Foundation, administered by the American Chemical Society, and the National Science Foundation for grant support of this research.

Supporting Information Available: ^1H and ^{13}C NMR data, mass spectral molecular weights, and details of attempted syntheses (7 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.

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(22) SHELXTL-Plus, Siemens Analytical X-ray Inc., Madison, WI.

(23) The author has deposited atomic coordinates for this structure with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.