8.8 Hz, CHC=O), 3.94 (ddd, 1 H, J = 6.8, 7.8, and 8.3 Hz, one of CH_2O), 4.08 (ddd, 1 H, J = 6.4, 7.3, and 8.3 Hz, one of CH_2O), 4.99 (d, 1 H, J = 7.3 Hz, CHPh), 7.25–7.36 (m, 5 H, Ph); ^{13}C NMR ($CDCl_3$) δ 28.5, 30.3, 60.2, 68.3, 82.5, 125.8, 127.8, 128.5, 141.5, 207.7; HRMS calcd for $C_{12}H_{14}O_2$ 190.0983, found 190.0983.

***cis*-3-Benzoyl-2-(*p*-chlorophenyl)tetrahydrofuran (*cis*-9c).** This compound was obtained by TLC as a mixture with *trans*-**9c** (cis:trans = 1:1): mp 38–40 °C; IR (KBr) 1065, 1675 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.15–2.23 (m, 1 H, one of CH_2), 2.63–2.73 (m, 1 H, one of CH_2), 4.00 (ddd, 1 H, J = 6.8, 8.3, and 8.8 Hz, one of CH_2O), 4.40 (td, 1 H, J = 7.8 and 6.8 Hz, one of CH_2O), 4.46 (ddd, 1 H, J = 3.9, 7.8, and 8.3 Hz, CHC=O); 5.28 (d, 1 H, J = 7.8 Hz, CHAr), 6.92–7.83 (m, 9 H, Ar); HRMS calcd for $C_{17}H_{15}ClO_2$ 286.0761, found 286.0777.

***trans*-3-Benzoyl-2-(*p*-chlorophenyl)tetrahydrofuran (*trans*-9c).** This compound was obtained by TLC as a mixture with *cis*-**9c** (cis:trans = 1:1): mp 38–40 °C; IR 1065, 1680 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.24–2.34 (m, 1 H, one of CH_2), 2.43–2.53 (m, 1 H, one of CH_2), 3.85 (td, 1 H, J = 7.3 and 9.3 Hz, CHC=O), 4.07 (td, 1 H, J = 7.8 and 6.8 Hz, one of CH_2O), 4.25 (ddd, 1 H, J = 5.4, 7.8, and 8.3 Hz, one of CH_2O), 5.25 (d, 1 H, J = 7.3 Hz, CHAr), 6.92–7.83 (m, 9 H, Ar); HRMS calcd for $C_{17}H_{15}ClO_2$ 286.0761, found 286.0717.

***cis*-2-(*p*-Nitrophenyl)-3-benzoyltetrahydrofuran (*cis*-9d).** This compound was isolated by TLC as a mixture with *trans*-**9d** (cis:trans = 2:1): mp 86–88 °C; IR (KBr) 1060, 1670 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.23–2.32 (m, 1 H, one of CH_2), 2.60–2.70 (m, 1 H, one of CH_2), 4.08 (td, 1 H, J = 14.7 and 7.3 Hz, one of CH_2O), 4.47–4.56 (m, 2 H, one of CH_2O and CHC=O), 5.38 (d, 1 H, J = 7.8 Hz, CHAr), 7.20–8.16 (m, 9 H, Ar); HRMS calcd for $C_{17}H_{15}NO_4$ 297.1501, found 297.0972.

***trans*-2-(*p*-Nitrophenyl)-3-benzoyltetrahydrofuran (*trans*-9d).** This compound was obtained by TLC as a mixture with *cis*-**9d** (cis:trans = 2:1): mp 86–88 °C; IR (KBr) 1060, 1670 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.23–2.32 (m, 1 H, one of CH_2), 2.49–2.58 (m, 1 H, one of CH_2), 3.85 (td, 1 H, J = 7.3 and 9.8 Hz, CHC=O), 4.25–4.36 (m, 2 H, CH_2O), 5.45 (d, 1 H, J = 7.3 Hz, CHAr), 7.20–7.86 (m, 10 H, Ar); HRMS calcd for $C_{17}H_{15}NO_4$ 297.1001, found 297.0995.

***cis*-3-Benzoyl-2-phenyltetrahydropyran (*cis*-11).** To a solution of Bu_3SnOMe (0.96 g, 3 mmol) in dry THF (3 mL) under N_2 atmosphere was added PhN=C=NPh (0.58 g, 3 mmol) at 0 °C. After 10 min, **10** (0.86 g, 3 mmol), **3a** (0.32 g, 3 mmol), and HMPA (0.54 g, 3 mmol) were added to the mixture. After being heated at 60 °C for 3 h, the solvent was evaporated, and the mixture was chromatographed on a silica gel column. Bu_3SnI was eluted by hexane (200 mL). Subsequent elution with hexane/EtOAc (1:1 v/v, 200 mL) gave a almost pure mixtures of *cis*- and *trans*-**11** (0.43 g, 54% cis:trans = 21:79). Further purification was performed by preparative TLC with 4:1 hexane/ethyl ether, and a mixture (cis:trans = 1:5) was obtained. The relative stereochemistry of diastereomers was assigned by ^1H NMR spectra: wax; IR (neat) 1095, 1680 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.83–2.14 (m, 4 H, CH_2), 3.68–3.78 (m, 2 H, CHC=O and one of CH_2O), 4.20 (ddd, 1 H, J = 2.0, 2.4, and 11.7 Hz, one of CH_2O), 4.71 (d, 1 H, J = 9.8 Hz, CHPh), 7.11–7.67 (m, 10 H, Ph); ^{13}C NMR ($CDCl_3$) δ 25.2, 28.7, 50.9, 68.6, 81.8, 127.0, 127.9, 128.0, 128.3, 128.4, 132.9, 136.7, 140.7, 202.2; HRMS calcd for $C_{18}H_{18}O_2$ 266.1308, found 266.1305.

***trans*-3-Benzoyl-2-phenyltetrahydropyran (*trans*-11).** This compound was obtained by TLC as a mixture with *cis*-**11** (cis:trans = 1:5): wax; IR (neat) 1095, 1680 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.84–2.44 (m, 4 H, CH_2), 3.70 (td, 1 H, J = 2.4 and 11.2 Hz, one of CH_2O), 3.97 (td, 1 H, J = 3.0 and 5.4 Hz, one of CHC=O), 4.33 (ddd, 1 H, J = 4.4, 4.9, and 6.8 Hz, one of CH_2O), 4.78 (d, 2 H, J = 3.0 Hz, CHPh), 7.16–7.60 (m, 10 H, Ph); ^{13}C NMR ($CDCl_3$) 21.6, 26.6, 4.9, 68.9, 80.1, 125.8, 127.1, 127.8, 128.0, 128.2, 132.2, 137.9, 140.6, 200.9; HRMS calcd for $C_{18}H_{18}O_2$ 266.1307, found 266.1317.

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Supplementary Material Available: ^1H NMR spectra and HRMS data for **4a–f**, **6a–d**, **9a–d**, and **11** (34 pages). This material is contained in many 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.

Synthesis of Optically Active Arylglycines by Photolysis of Optically Active (β-Hydroxyamino) Carbene–Chromium(0) Complexes

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Photolysis of [(amino)(aryl)carbene]chromium complexes having the optically active amino alcohol (1*R*,2*S*)-(−)- or (1*S*,2*R*)-(+)-2-amino-1,2-diphenylethanol as the amino group produced aryl-substituted oxazinones in good yield with reasonable diastereoselectivity. Facile separation of diastereoisomers followed by mild reductive cleavage produced several arylglycines, having either electron-donating or withdrawing groups on the aromatic ring, in good overall yield and with excellent enantiomeric excess.

Introduction

Although arylglycines are nonproteinogenic amino acids, they are found in a number of important biologically active compounds, including the vancomycins,[1] amoxicillins,[2] nocardicins,[3] and cephalecins.[4] The asymmetric synthesis of this class of compounds[5] is complicated by the lability of the α-proton, and syntheses involving basic conditions are compromised by attendant racemization. Because of

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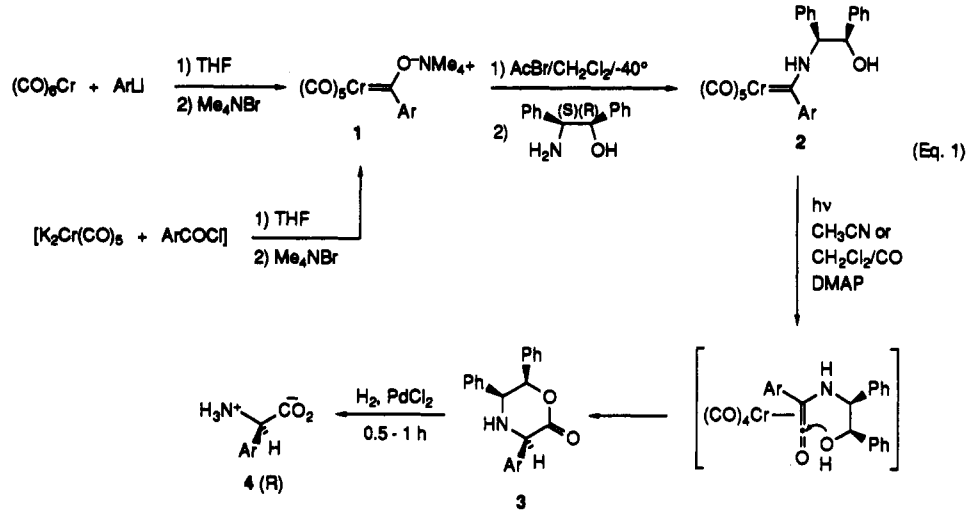

Table I

1, % yield[a]	2, % yield[a]	3, % yield[a]	de[b] (ratio)	3′, % yield[c]	4, % yield[a,d]	ee (Mosher's amide)[e]
1a, Ph, 62	a, 79	a, 81	64 (82:18)	67	69 (23)[d]	94
1b, *p*-MeOPh, 78	b, 81	b, 82	76 (88:12)	72	91 (41)	96
1c, *p*-ClPh, 64	c, 73	c, 73	60 (80:20)	59	81 (22)	84
1d, *p*-FPh, 62	d, 77	d, 77	72 (86:14)	69	80 (26)	98
1e, *p*-CF_3Ph, 80	e, 84	e, 84	60 (80:20)	73	86 (42)	98
1f, *o*-MeOPh, 81	f, 86	f, 78	76 (88:12)	61	24[f] (11)	64[g]
1g, 2,6-F_2Ph, 63	g, 78	g, 62	64 (82:18)	63	95 (29)	56
1h, 1-Naphth, 75	h, 51	h, 76	62 (81:19)	66	40[h] (10)	91
1i, 3-thienyl, 80	i, 55	i, 75	66 (83:17)	62	*h,i*	

[a] Reported yields are for isolated, purified materials. [b] Determined by integration of appropriate signals in the ^1H NMR spectrum in the crude reaction mixture. [c] Yield of isolated, pure, single (major) diastereoisomer based on 2. [d] Overall yield of amino acid, from ArLi + $Cr(CO)_6$. [e] Determined by integration of appropriate peaks in ^1H NMR spectra of the Mosher's amide. [f] As the hydrochloride salt. The free amino acid was unstable. [g] The amino acid decomposed during conversion to Mosher's amide, complicating the ee determination. [h] Oxidative removal of the chiral auxiliary was used. [i] Deprotection was unsuccessful; see text.

this, a wide array of synthetic approaches to these compounds, each with its own limitations, have been developed.[6] Recently, an unconventional synthetic approach to amino acids, involving photolysis of optically active (amino alcohol)carbene–chromium complexes, was reported from these laboratories.[7] The use of this reaction to synthesize optically active arylglycines is described below.

Results and Discussion

The approach to optically active arylglycines is summarized in eq 1. (Aryl)carbene complexes 1 are readily available, in good yield, by the reaction of aryllithium reagents with chromium hexacarbonyl[8] (they can also be prepared from acid chlorides and the chromium pentacarbonyl dianion,[9] although this route was not used in this study). O–Acylation of complexes 1[10] followed by displacement of the acetoxy group[11] with the amino group of the chiral auxilliary produced carbene complexes 2 in fair to good yield (Table I). (In some cases, two rotamers about the C–N bond of these complexes were obtained and could be separated. Photolysis of each gave identical yields and with comparable diastereoselectivities; thus, separation was not necessary.) Photolysis of carbene complexes 2 (450-W Hanovia lamp, Pyrex reaction vessel and wells) produced oxazinones 3 in good yield. However, under standard reaction conditions,[7,11] these products were complexed to chromium in some fashion. Separation by chromatographic methods failed, and oxidative removal of the chromium resulted in partial epimerization as well as oxidation of the product. This problem was solved by carrying out the photolysis in the presence of 1 equiv of 4–(dimethylamino)pyridine (DMAP) to scavenge the chromium carbonyl fragments. When the photolysis was carried out in methylene chloride solvent under an atmosphere of carbon monoxide, oxazinones 3 were isolated in good yield, free from the easily recovered $Cr(CO)_5$DMAP complex, which could be recycled.

The diastereoselectivity of the process was only modest, ranging from 88:12 (76% de) to 80:20 (60% de), and always favored the all syn product. This stands in contrast to the use of these N-protected oxazinones as electrophilic glycine equivalents[6] for which the anti product predominates. However, the diastereomers of 3 separated virtually quantitatively during chromatographic (Silica gel column) removal of the $(CO)_5$CrDMAP complex from the crude reaction mixture, making further purification unnecessary. Because of the efficiency of the photo reaction, and the ease of separation, good yields of diastereomerically pure 3′ could be obtained in spite of the less-than-perfect diastereoselectivity.

The final step in the synthesis of arylglycines by this procedure is removal of the chiral auxilliary. The standard

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(9) Semmelhack, M. F.; Lee, G. R. *Organometallics* **1987**, *6*, 1839.
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procedures developed by Williams[12] consist of either a dissolving metal reduction or catalytic hydrogenolysis of the benzylic amine and ester bonds. However, arylglycines pose a special problem since, in these, the amino acid C–N bond is also benzylic, making selective cleavage difficult. Indeed, in the Williams synthesis of arylglycines,[6] oxidative (periodate) removal of the chiral auxilliary from the anti analogs of **3** was required in all but two cases. In marked contrast, the syn isomers produced in this study were selectively cleaved to the amino acid in high yield under very mild reductive conditions (1 atm of H_2, $PdCl_2$ cat. 0.25–1 h) in all but two cases. This facility of hydrogenolysis is likely due to the syn disposition of all three aryl groups in **3**, allowing easy access to a face of these compounds by the catalyst which is not available in the anti isomer. The naphthyloxazinone **3h** did not cleave cleanly under these conditions, and the periodate cleavage of Williams[6] was used. The (3-thienyl)oxazinone **3i** could not be cleaved to the free amino acid under either set of conditions. Oxidative procedures led to decomposition, while catalytic hydrogenolysis did not proceed at all, probably because the thiophene group acted as a catalyst poison. The (*o*-methoxyphenyl)oxazinone **3f** was easily cleaved, but the free amino acid was unstable and difficult to handle. This material was isolated and characterized as the hydrochloride salt.

The enantiomeric excess of the final amino acid was determined by conversion to the corresponding Moser's amide and analysis by both ^1H and ^{19}F NMR spectroscopy. Authentic racemic amino acids were synthesized using the racemic amino alcohol chiral auxillary, and carried through to the corresponding Mosher's amide, to provide reference peaks for the minor diastereoisomers. Since diastereoisomerically pure **3'** was used, and since hydrogenolysis under neutral conditions should not lead to racemization, the free amino acids obtained *should* be optically pure. The observed enantiomeric excesses of the Mosher's amides of 90–98% indicates some loss of stereochemistry in the conversion of **3'** to **4**, as had previously been observed.[6] The substantial loss of stereochemistry observed in the (2,6-difluorophenyl)glycine (**4g**) is an indication of the increased acidity of the α-proton due to the strong electron-withdrawing effects of the fluoro groups. Remarkably, the (4-fluorophenyl)glycine (**4d**) and the [4-(trifluoromethyl)phenyl]glycine (**4e**) suffered only minor racemization during the conversion of **3'** to **4**. The (*o*-methoxyphenyl)glycine (**4f**) was unstable as the free amino acid and rapidly decomposed upon production from the hydrochloride salt. Direct conversion of the salt to Moser's amide was accompanied by substantial loss of stereochemistry.

The absolute stereochemistry of the amino acids **4** was determined in several cases by comparison to authentic material[13] and was, as anticipated from previous studies,[7] *R* when (1*R*,2*S*)-(−)-2-amino-1,2-diphenylethanol was used and *S* when (1*S*,2*R*)-(+)-amino alcohol was used. This confirms that the oxazinones **3** have the syn stereochemistry shown, exactly opposite that found in the Williams[6] case. As a cross check, (*S*)-amino acids **4b** and **4d** were prepared using the (1*S*,2*R*)-(+)-amino alcohol and were formed in similar yields and with identical stereoselectivity as were their (*R*) analogs, indicating that both (*S*)- or (*R*)-substituted phenylglycines are accessible by this methodology. Application of this methodology to the synthesis of other classes of optically active amino acids is under investigation.

Experimental Section

Materials. The following compounds were prepared according to literature procedures: tetramethylammonium salt of [(oxo)(phenyl)carbene]pentacarbonylchromium(0) (**1a**),[8] [(oxy)(*o*-methoxyphenyl)carbene]pentacarbonylchromium(0) (**1f**);[14] [(oxy)[*p*-(trifluoromethyl)phenyl]carbene]pentacarbonylchromium(0) (**1e**);[15] *o*-methoxyphenyllithium;[16a] *p*-chlorophenyllithium;[16b] *p*-fluorophenyllithium;[16c] 1-lithionaphthalene;[16d] and 3-lithiothiophene.[16e]

General Procedure for the Synthesis of the Tetramethylammonium Salt of [(Oxy)(aryl)carbene]pentacarbonylchromium(0) 1. All procedures were carried out under an atmosphere of argon using degassed solvents. An ethereal solution of aryllithium (1.1 equiv) was added to a suspension of hexacarbonylchromium (1 equiv) in ether at 0 °C. The solution became yellow and then rapidly turned brown. The reaction time and temperature are given in each synthesis. The solvent was then removed under reduced pressure. The dark brown residue was dissolved in a minimum amount of cold, degassed water, and tetramethylammonium bromide (1.1 equiv) was added slowly. The solution was stirred for 20 min at 0 °C and extracted with methylene chloride (3×), and the methylene chloride extracts were dried over $MgSO_4$. The solvent was removed under reduced pressure, and the residue was recrystallized from CH_2Cl_2/Et_2O. Most of these complexes were relatively unstable and were used soon after preparation.

Preparation of the Tetramethylammonium Salt of [(Oxy)(*p*-methoxyphenyl)carbene]pentacarbonylchromium(0) (1b). Following the general procedure, 1.52 g (3.90 mmol, 78%) of **1b** was produced as a yellow brown solid from an etheral solution of *p*-methoxyphenyllithium (5.00 mmol, 15.63 mL, 0.32 M), hexacarbonylchromium (1.10 g, 5.00 mmol), and tetramethylammonium bromide (0.79 g, 5.10 mmol). ^1H NMR (300 MHz, $(CD_3)_2CO$): δ 3.37 (s, 12 H, NMe_4), 3.77 (s, 3 H, OMe) 6.82 (d, J = 6 Hz, 2 H, ArH), 7.50 (d, J = 6 Hz, 2 H, ArH). ^{13}C NMR (75.5 MHz, $(CD_3)_2CO$): δ 54.77 (OCH_3), 55.27 (NMe_4), 112.24, 126.98, 147.99, 159.83 (Ar), 223.69 (M=CO cis), 228.03 (M=CO trans), 287.76 (Cr=C). Assignments for **1c–1i** follow directly from these.

Preparation of the Tetramethylammonium Salt of [(Oxy)(*p*-chlorophenyl)carbene]pentacarbonylchromium(0) (1c). Following the general procedure, 1.28 g (3.18 mmol, 64%) of **1c** was produced as a yellow brown solid from an etheral solution of *p*-chlorophenyllithium (5.00 mmol, 20.00 mL, 0.25 M), 1.10 g (5.00 mmol) of chromium hexacarbonyl, and 0.79 g (5.10 mmol) of tetramethylammonium bromide. ^1H NMR (300 MHz, $(CD_3)_2CO$): δ 2.59 (s, 12 H); 6.46 (m, 4 H). ^{13}C NMR (75.5 MHz, $(CD_3)CO$): δ 55.80, 126.09, 127.77, 146.47, 154.47, 223.57, 228.29, 288.79.

Preparation of the Tetramethylammonium Salt of [(Oxy)(*p*-fluorophenyl)carbene]pentacarbonylchromium(0) (1d). Following the general procedure, 1.21 g (3.10 mmol, 62%) of the tetramethylammonium salt **1d** was produced as a yellow brown solid from an etheral solution of *p*-fluorophenyllithium (5.00 mmol, 17.86 mL, 0.28 M), 1.10 g (5.00 mmol) of chromium hexacarbonyl, and 0.79 g (5.10 mmol) of tetramethylammonium bromide. ^1H NMR (300 MHz, $(CD_3)_2CO$): δ 2.63 (s, 12 H), 6.18 (m, 2 H), 6.62 (m, 2 H). ^{13}C NMR (75.5 MHz, $(CD_3)_2CO$): δ 55.44,

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113.83 (d, J = 21 Hz), 126.67 (d, J = 9 Hz), 152.08, 162.55 (d, J = 240 Hz), 223.48, 228.05, 228.44.

Preparation of the Tetramethylammonium Salt of [(Oxy)(2,6-difluorophenyl)carbene]pentacarbonylchromium(0) (1g). A solution of 2,6-difluorobromobenzene (2.00 g, 10.30 mmol) in THF (40 mL) was treated with t-BuLi (20.60 mmol, 9.81 mL, 2.1 M) at −78 °C and stirred at this temperature for 2 h. Then this solution was added to chromium hexacarbonyl (2.27 g, 10.31 mmol) in THF (100 mL) at −78 °C. After 0.5 h at this temperature, the reaction mixture was allowed to warm to room temperature and was stirred 1 h at this temperature. The solvent was removed under vacuum. The dark red residue was dissolved in cold, degassed water (50 mL) and filtered through Celite, and tetramethylammonium bromide (1.74 g, 11.30 mmol) was added. The solution was stirred for 20 min at 0 °C. Workup as usual gave 2.65 g (6.51 mmol, 63%) of **1g** as a green yellow solid. This material was unstable and was used immediately. ^{1}H NMR (300 MHz, $(CD_3)_2CO$): δ 3.54 (s, 12 H), 6.79 (m, 1 H), 7.03 (m, 1 H), 7.47 (m, 1 H).

Preparation of the Tetramethylammonium Salt of [(Oxy)(1-naphthyl)carbene]pentacarbonylchromium(0) (1h). Following the general procedure 1.58 g (3.75 mmol, 75%) of the tetramethylammonium salt **1h** was produced as a brown solid from an etheral solution of 1-lithionaphthalene (5.00 mmol, 19.23 mL, 0.26 M), 1.10 g (5.00 mmol) of chromium hexacarbonyl, and 0.79 g (5.10 mmol) of tetramethylammonium bromide. ^{1}H NMR (300 MHz, $(CD_3)_2CO$): δ 3.21 (s, 12 H), 7.19 (d, J = 8 Hz, 1 H), 7.39 (m, 3 H), 7.59 (d, J = 5 Hz, 1 H), 7.77 (d, J = 8 Hz, 1 H), 8.04 (d, J = 8 Hz, 1 H). ^{13}C NMR (75.5 MHz, $(CD_3)_2CO$): δ 55.36, 118.72, 125.02, 125.09, 125.35, 125.48, 126.03, 126.86, 127.99, 134.33, 158.76, 222.86, 228.24, 298.45.

Preparation of the Tetramethylammonium Salt of [(Oxy)(3-thienyl)carbene]pentacarbonylchromium(0) (1i). Following the general procedure, 1.51 g (4.00 mmol, 80%) of the tetramethylammonium salt **1i** was produced as a yellow brown solid from an etheral solution of 3-thienyllithium (5.00 mmol, 23.8 mL, 0.21 M), 1.10 g (5.00 mmol) of chromium hexacarbonyl, and 0.79 g (5.10 mmol) of tetramethylammonium bromide. ^{1}H NMR (300 MHz, $(CD_3)_2CO$): δ 3.44 (s, 12 H), 7.18 (m, 2 H), 7.64 (m, 1 H). ^{13}C NMR (75.5 MHz, $(CD_3)_2CO$): δ 55.62, 123.44, 125.56, 126.37, 160.53, 223.89, 228.12, 280.08.

General Procedure for the Synthesis of (Amino alcohol)carbene Complexes 2. An Airlessware flask was fitted with a rubber septum, stirring bar, and an argon-filled balloon. The apparatus was charged with the tetramethylammonium salt of [(oxy)(aryl)carbene]pentacarbonylchromium(0) and freshly distilled, degassed dichloromethane (0.06 M solution). The solution was saturated with argon and was then cooled to −15 °C in a −40 °C bath. Freshly distilled acetyl bromide was slowly injected, and the mixture was stirred at −40 °C for 0.5 h. The amino alcohol (either (1S,2R)-(+)- or (1R,2S)-(−)-2-amino-1,2-diphenylethanol) was transferred by cannula as a degassed 0.25 M dichloromethane solution to the acetoxycarbene complex. This solution was warmed to 0 °C over 4 h and then quickly to room temperature. It was then placed in a separatory funnel and was washed with Ar-flushed distilled water (50 mL) and with Ar-flushed 5% aqueous $NaHCO_3$ (ca. 50 mL). Each aqueous layer was extracted with CH_2Cl_2. After being dried over Na_2SO_4, the organic solution was concentrated to give a slightly dark yellow foam. Chromatography of the crude product on silica gel (20 g) under Ar pressure with CH_2Cl_2 gave the pure chromium complex which was collected under a gentle flow of argon. The solvent was removed by rotary evaporation, and the product was dried under vacuum and was stored at −15 °C under argon. Slow decomposition prevented acceptable elemental analyses, and these complexes were prepared and photolyzed as needed.

Preparation of (Phenyl)aminocarbene Complex 2a. Following the general procedure, 0.39 g (0.79 mmol, 79%) of the aminocarbene complex **2a** was produced as a yellow solid from 0.37 g (1.00 mmol) of **1a**, 0.12 g (1.00 mmol) of acetyl bromide, and 0.21 g (1.00 mmol) of (1R,2S)-(−)-2-amino-1,2-diphenylethanol. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.34 (brs, 1 H, OH), 4.55 (dd, J = 5 and 10 Hz, 1 H, NCHPh), 4.94 (d, J = 5 Hz, 1 H, OCHPh), 6.79 (m, 2 H, ArH), 6.91 (m, 2 H, ArH), 7.03–7.20 (m, 11 H, ArH), 9.69 (br s, 1 H, NH). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 68.56 (NCHPh), 76.14 (OCHPh), 126.36, 126.66, 127.24, 128.14, 128.59, 128.68, 128.78, 135.79, 137.98, 149.41 (Ar), 216.96 (CO cis), 223.41 (CO trans), 283.78 (Cr=C). Assignments for **2b–2i** follow these directly. IR (KBr): ν 3430, 3339, 2055, 1919, 1596, 1498, 1454, 1437, 1419 cm^{-1}. Mass spectrum (NH_3-CI): 511 (M + NH_4^+), 494 (M + 1), 493 (M).

Preparation of (p-Methoxyphenyl)aminocarbene Complex 2b. Following the general procedure, 0.21 g (0.40 mmol, 81%) of the aminocarbene complex **2b** was produced as a yellow solid from 0.20 g (0.50 mmol) of **1b**, 61.5 mg (0.50 mmol) of acetyl bromide, and 0.11 g (0.50 mmol) of the (1R,2S)-(−)-amino alcohol. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.29 (br s, 1 H), 3.78 (s, 3 H), 4.70 (dd, J = 5 and 9 Hz, 1 H), 5.04 (d, J = 5 Hz, 1 H), 6.44 (m, 2 H), 6.78 (m, 2 H), 6.92 (m, 2 H), 7.02 (m, 2 H), 7.30 (m, 6 H), 9.75 (br s, 1 H). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 55.18, 68.33, 76.34, 113.46, 121.17, 126.37, 127.23, 128.38, 128.60, 128.70, 128.78, 135.91, 138.01, 142.46, 158.24, 217.11, 223.41, 284.63. IR (KBr): ν 3433, 3341, 2054, 1923, 1603, 1507, 1454, 1408 cm^{-1}. Mass spectrum (NH_3-CI): 541 (M + NH_4^+), 524 (M + 1), 523 (M).

Preparation of (p-Chlorophenyl)aminocarbene Complex 2c. Following the general procedure, 0.38 g (0.72 mmol, 72%) of the aminocarbene complex **2c** was produced as a yellow solid from 0.41 g (1.00 mmol) of **1c**, 0.12 g (1.00 mmol) of acetyl bromide, and 0.21 g (1.00 mmol) of the (1R,2S)-(−)-amino alcohol. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.19 (br s, 1 H), 4.60 (dd, J = 4 and 8 Hz, 1 H), 5.10 (d, J = 4 Hz, 1 H), 6.87 (m, 2 H), 7.02 (m, 2 H), 7.30 (m, 10 H), 9.77 (br s, 1 H). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 68.73, 76.26, 120.77, 126.40, 127.16, 128.44, 128.58, 128.73, 128.82, 128.98, 132.49, 135.69, 137.80, 147.59, 216.82, 223.07, 283.64. IR (KBr): ν 3433, 3336, 2056, 1919, 1699, 1682, 1658, 1588, 1508, 1498, 1485, 1458 cm^{-1}. Mass spectrum (NH_3-CI): 336 (M + 1 − $Cr(CO)_5$).

Preparation of (p-Fluorophenyl)aminocarbene Complex 2d. Following the general procedure, 0.79 mg (1.54 mmol, 77%) of the aminocarbene complex **2d** was produced from 0.78 g (2.00 mmol) of **1d**, 0.25 g (2.00 mmol) of acetyl bromide, and 0.43 g (2.00 mmol) of the (1R,2S)-(−)-amino alcohol. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.19 (br s, 1 H), 4.62 (dd, J = 5 and 9 Hz, 1 H), 5.10 (d, J = 5 Hz, 1 H), 6.95 (m, 2 H), 7.08 (m, 2 H), 7.36 (m, 10 H), 9.80 (br s, 1 H). ^{13}C NMR (300 MHz, $CDCl_3$): δ 68.70, 76.09, 115.22 (d, J = 21 Hz), 121.22 (d, J = 8 Hz), 126.35, 127.17, 128.51, 128.65, 128.76, 128.87, 135.74, 137.88, 145.51, 161.15 (d, J = 247 Hz), 216.88, 223.22, 283.95. IR (KBr): ν 3444, 3339, 2056, 1924, 1654, 1599, 1500, 1454, 1419 cm^{-1}. Mass spectrum (NH_3-CI): 529 (M + NH_4^+), 511 (M).

Preparation of [p-(Trifluoromethyl)phenyl]aminocarbene Complex 2d. Following the general procedure, 0.47 g (0.84 mmol, 84%) of the aminocarbene complex **2d** was produced as a yellow solid from 0.44 g (1.00 mmol) of **1d**, 0.12 g (1.00 mmol) of acetyl bromide, and 0.21 g (1.00 mmol) of the (1R,2S)-(−)-amino alcohol. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.21 (br s, 1 H), 4.56 (dd, J = 5 and 9 Hz, 1 H), 5.01 (d, J = 5 Hz, 1 H), 6.82 (m, 2 H), 7.00 (m, 2 H), 7.27 (m, 10 H), 9.76 (br s, 1 H). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 69.11, 75.96, 119.60 (q, J = 4 Hz), 123.83 (q, J = 267 Hz), 126.41, 127.10, 128.63, 128.70, 128.83, 128.96, 128.59 (q, J = 11 Hz), 135.59, 137.72, 152.09, 216.62, 223.07, 282.42. IR (KBr): ν 3433, 3335, 2058, 1925, 1686, 1647, 1612, 1498, 1456, 1402 cm^{-1}. Mass spectrum (NH_3-CI): 367 (M + 2 − $Cr(CO)_5$).

Preparation of (o-Methoxyphenyl)aminocarbene Complex 2f. Following the general procedure, 0.44 g (0.86 mmol, 86%) of two rotamers (1:1, not separable by chromatography on silica) of the aminocarbene complex **2f** was produced as a yellow solid from 0.40 g (1.00 mmol) of **1f**, 0.12 g (1.00 mmol) of acetyl bromide, and 0.21 g (1.00 mmol) of the (1R,2S)-(−)-amino alcohol. ^{1}H NMR (300 MHz, $CDCl_3$): (two rotamers) δ 2.15 (br s, 1 H), 2.68 (br s, 1 H), 3.05 (s, 3 H), 3.85 (s, 3 H), 4.51 (m, 2 H), 4.95 (br s, 1 H), 5.03 (br s, 1 H), 6.15 (m, 1 H), 6.39 (m, 1 H), 6.55 (m, 1 H), 6.68–7.20 (m, 25 H), 9.61 (br s, 1 H), 9.78 (br s, 1 H, NH). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 53.88, 55.54, 68.58, 68.98, 76.14, 76.34, 110.06, 110.87, 120.19, 120.52, 120.57, 120.87, 126.15, 126.43, 127.40, 128.18, 128.23, 128.41, 128.58, 135.23, 135.60, 137.71, 137.86, 137.94, 138.18, 148.06, 148.70, 217.14, 223.51, 282.32. IR (KBr): ν 3435, 3333, 2054, 1919, 1685, 1654, 1636, 1596, 1508, 1498, 1476, 1457, 1435 cm^{-1}. Mass spectrum (NH_3-CI): 541 (M + NH_4^+), 530 (M + 1), 529 (M − 1).

Preparation of (2,6-Difluorophenyl)aminocarbene Complex 2g. [(2,6-Difluorophenyl)(methoxy)carbene]pentacarbonylchromium(0)[17] (0.41 g, 1.00 mmol) was dissolved in DMF

(125 mL). The solution was degassed, and the (1*R*,2*S*)-(−)-amino alcohol (0.21 g, 1.00 mmol) was added. The solution was stirred at room temperature and after 2 h the solution was diluted with Et_2O (75 mL) and washed with water (50 × 3). The organic layer was dried on $MgSO_4$, concentrated under vacuum, and purified by chromatography on silica using CH_2Cl_2 as eluent to give the aminocarbene complex **2g** (0.41 g, 0.78 mmol, 78%) as a yellow solid. **Less polar rotamer.** ^1H NMR (300 MHz, C_6D_6): δ 2.19 (br s, 1 H), 5.01 (q, *J* = 4 Hz, 1 H), 5.08 (br s, 1 H), 6.65 (m, 1 H), 6.95 (m, 2 H), 7.11 (m, 2 H), 7.31 (m, 2 H), 7.35 (m, 6 H), 10.97 (br s, 1 H). ^{13}C NMR (75.5 MHz, C_6D_6): δ 70.33, 75.89, 111.44 (dd, *J* = 4 and 25 Hz), 112.04 (dd, *J* = 4 and 25 Hz), 126.46, 127.96, 128.38, 128.48, 128.56, 128.65, 129.30 (t, *J* = 8 Hz), 134.57, 138.36, 150.39 (dd, *J* = 8 and 247 Hz), 217.01, 223.23, 275.18. IR (KBr): ν 3441, 3340, 2059, 1924, 1618, 1528, 1463 cm^{-1}. **More polar rotamer.** ^1H NMR (300 MHz, C_6D_6): δ 2.14 (br s, 1 H), 5.05 (br s, 1 H), 5.92 (d, *J* = 8 Hz, 1 H), 6.59 (m, 4 H), 6.98 (m, 9 H), 9.92 (br s, 1 H). ^{13}C NMR (75.5 MHz, C_6D_6): δ 71.89, 76.32, 111.99 (d, *J* = 21 Hz), 126.41, 128.28, 128.48, 128.57, 129.30 (t, *J* = 10 Hz), 131.08 (t, *J* = 22 Hz), 134.31, 139.17, 154.04 (dd, *J* = 7 and 246 Hz), 216.72, 223.64, 271.79. IR (KBr): ν 3447, 3280, 2060, 1924, 1618, 1581, 1527, 1463 cm^{-1}. Mass spectrum (NH_3-Cl): 537 (M + NH_4^+), 530 (M + 1), 529 (M).

Preparation of (1-Naphthyl)aminocarbene Complex 2h. Following the general procedure, 0.28 g (0.51 mmol, 51%) of the aminocarbene complex **2h** was produced as a yellow solid from 0.42 g (1.00 mmol) of **1h**, 0.12 g (1.00 mmol) of acetyl bromide, and 0.21 g (1.00 mmol) of the (1*R*,2*S*)-(−)-amino alcohol. Two rotamers were produced (40/60), partially separable by chromatography on silica. **Less polar rotamer.** ^1H NMR (300 MHz, C_6D_6): δ 1.34 (br s, 1 H), 4.26 (br s, 1 H), 4.43 (br s, 1 H), 6.34–7.83 (m, 17 H), 10.4 (br s, 1 H). ^{13}C NMR (75.5 MHz, C_6D_6): δ 69.19, 75.94, 117.28, 124.52, 124.90, 125.17, 126.26, 126.66, 126.77, 127.18, 127.59, 128.19, 128.37, 128.45, 128.48, 128.51, 129.12, 133.65, 136.36, 138.18, 146.63, 217.67, 223.36, 285.53. IR (KBr) ν 3425, 3336, 3059, 2055, 1925, 1685, 1654, 1636, 1560, 1508, 1497, 1457 cm^{-1}. **More polar rotamer.** ^1H NMR (300 MHz, C_6D_6): δ 1.36 (br s, 1 H), 4.39 (m, 2 H), 6.36–7.45 (m, 17 H), 10.20 (br s, 1 H). ^{13}C NMR (75.5 MHz, C_6D_6): δ 69.44, 76.61, 117.21, 125.07, 125.25, 126.09, 126.49, 126.59, 127.78, 128.27, 128.46, 128.50, 128.59, 133.51, 134.93, 138.64, 146.62, 217.65, 223.41, 284.65. IR (KBr): ν 3518, 3425, 1995, 1895, 1685, 1654, 1560, 1519, 1484, 1456, 1425 cm^{-1}. Mass spectrum (NH_3–Cl): 352 (M + 2 − $Cr(CO)_5$).

Preparation of Aminocarbene Complex 2i. Following the general procedure, 0.28 g (0.55 mmol, 55%) of the aminocarbene complex **2i** was produced as a yellow solid from 0.33 g (1.00 mmol) of **1i**, 0.12 g (1.00 mmol) of acetyl bromide, and 0.21 g (1.00 mmol) of the racemic erythro amino alcohol. ^1H NMR (300 MHz, DMSO-d_6): δ 2.27 (s, 1 H), 4.67 (dd, *J* = 5 and 9 Hz, 1 H), 4.97 (d, *J* = 5 Hz), 6.31 (d, *J* = 2 Hz, 1 H), 6.43 (d, *J* = 5 Hz, 1 H), 6.82 (m, 2 H), 6.90 (m, 2 H), 7.13 (m, 7 H), 9.71 (br s, 1 H). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 68.73, 76.21, 114.78, 122.77, 126.36, 126.41, 127.19, 128.43, 128.76, 128.81, 136.01, 137.99, 149.66, 217.01, 223.27, 280.25. IR (KBr): ν 3535, 3344, 2054, 1918, 1890, 1500, 1453, 1375 cm^{-1}.

General Procedure for the Synthesis of Lactones 3. The aminocarbene complex (2) (1 equiv) and (dimethylamino)pyridine (1.1 equiv) were placed in a 20-mL Pyrex tube, which was sealed with a rubber septum. The vessel was evacuated and purged with argon (three cycles). Dry, degassed acetonitrile or dichloromethane was added via a cannula to produce a 0.02–0.03 M solution. The solution was irradiated for 18 h, and the reaction was followed by TLC (silica gel). The bright yellow color of the aminocarbene solution turned to a more intense yellow due to the formation of the (dimethylamino)pyridinechromium complex. After irradiation, the solvent was removed under reduced pressure, and the residue was purified by chromatography on silica gel (ICN Silitech 32-63D 60 Å, 10 g/0.1 g of product to be separated, 2.0-cm diameter column) using the appropriate eluant as described in each synthesis. One-mL fractions were taken, and these fractions were screened by analytical TLC for their contents. The $Cr(CO)_5$DMAP eluted with the solvent front, followed by the minor anti isomer, followed by the major syn isomer.

(17) Fischer, E. O.; Kreiter, C. G.; Kollmerer, J.; Müller, J.; Fischer, R. D. *J. Organomet. Chem.* **1971**, *28*, 237.

Preparation of the (3*R*,5*S*,6*R*)-2,3,5,6-Tetrahydro-3,5,6-triphenyl-1,4-oxazin-2-one (3a). Following the general procedure, 180 mg (0.36 mmol) of the aminocarbene complex **2a** and 49 mg (0.40 mmol) of (dimethylamino)pyridine in dry acetonitrile (10 mL) were irradiated for 18 h. The crude product was purified by chromatography on silica using methylene chloride as eluant to yield 81 mg (0.24 mmol, 67%) of the syn-isomer **3a** and 17 mg (0.051 mmol, 14%) of the anti-isomer **3a** as white solids and 50 mg (0.15 mmol, 42%) of the [(dimethylamino)pyridine]pentacarbonylchromium complex as a yellow solid. *syn*-**3a**. ^1H NMR (300 MHz, $CDCl_3$): δ 1.91 (br s, 1 H, NH), 4.71 (s, 1 H, CHPh), 4.91 (d, *J* = 4 Hz, 1 H, NCHPh), 5.51 (d, *J* = 4 Hz, OCHPh), 6.79 (m, 2 H, ArH), 6.90 (m, 2 H, ArH), 7.08 (m, 6 H, ArH), 7.31 (m, 3 H, ArH), 7.55 (m, 2 H, ArH). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 61.59 (NCHPh), 64.61 (OCHPh), 85.10 (CHPh), 127.18, 127.32, 127.76, 127.96, 128.02, 128.10, 128.42, 128.46, 128.53, 134.91, 137.10, 137.20 (Ar), 168.55 (C=O). Assignments for **3b–3i** follow these directly. IR (KBr): ν 3433, 3314, 1736 cm^{-1}. $[\alpha]^{22}_D$ + +66.0° (*c* = 1, CH_2Cl_2). Anal. Calcd for $C_{22}H_{19}NO_2$: C, 80.21; H, 5.81; N, 4.25. Found: C, 79.98; H, 6.07; N, 4.16. *anti*-**3a**. ^1H NMR (300 MHz, $CDCl_3$): δ 2.29 (br s, 1 H), 4.65 (d, *J* = 5 Hz, 1 H), 5.14 (s, 1 H), 5.63 (d, *J* = 5 Hz, 1 H), 6.84 (m, 2 H), 6.90 (m, 2 H), 7.05–7.12 (m, 7 H), 7.29 (m, 2 H), 7.52 (m, 2 H). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 57.91, 60.34, 82.89, 126.69, 126.80, 127.66, 127.74, 128.00, 128.16, 128.32, 128.99, 134.96, 137.62, 137.98, 169.52. IR (KBr): ν 3433, 3333, 1716 cm^{-1}.

Preparation of the (3*R*,5*S*,6*R*)-2,3,5,6-Tetrahydro-3-(*p*-methoxyphenyl)-5,6-diphenyl-1,4-oxazin-2-one (3b). Following the general procedure, 209 mg (0.40 mmol) of the aminocarbene complex **2b** and 50 mg (0.41 mmol) of (dimethylamino)pyridine in dry acetonitrile (10 mL) were irradiated for 18 h. The crude product was purified by chromatography on silica using CH_2Cl_2 to elute the chromium complex of (dimethylamino)pyridine (42 mg, 0.13 mmol, 32%) as a yellow solid, followed by hexane/EtOAc (3/1), yielding 14 mg (0.04 mmol, 10%) of the anti-isomer **3b** and 103 mg (0.29 mmol, 72%) of the syn-isomer **3b** as white solids. *syn*-**3b**. ^1H NMR (300 MHz, $CDCl_3$): δ 2.35 (br s, 1 H), 3.82 (s, 3 H), 4.75 (d, *J* = 4 Hz, 1 H), 5.17 (s, 1 H), 5.65 (d, *J* = 4 Hz, 1 H), 6.79 (m, 2 H), 6.90 (m, 4 H), 7.08 (m, 6 H), 7.50 (m, 2 H). ^{13}C NMR (75.5 MHz, $CDCl_3$): 55.49, 60.55, 62.09, 84.72, 111.32, 121.07, 125.53, 127.35, 127.39, 127.76, 127.86, 127.94, 128.14, 129.93, 130.22, 135.25, 137.51, 157.21, 169.02. IR (KBr) ν 3433, 3312, 1736 cm^{-1}. $[\alpha]^{22}_D$ = +45.6° (*c* = 1, CH_2Cl_2). Anal. Calcd for $C_{23}H_{21}NO_3$: C, 76.85; H, 5.89; N, 3.89. Found: C, 76.76; H, 5.83; N, 3.91. *anti*-**3b**. ^1H NMR (300 MHz, $CDCl_3$): δ 2.25 (br s, 1 H), 3.79 (s, 3 H), 4.63 (d, *J* = 4 Hz, 1 H), 5.28 (s, 1 H), 5.72 (d, *J* = 4 Hz, 1 H), 6.85–7.26 (m, 14 H). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 55.55, 56.57, 57.70, 85.17, 111.33, 120.69, 123.13, 127.22, 127.58, 127.86, 127.92, 127.95, 128.23, 129.48, 129.78, 135.02, 137.22, 156.75, 169.44. IR (KBr): ν 3483, 3313, 1729 cm^{-1}.

Preparation of the (3*R*,5*S*,6*R*)-2,3,5,6-Tetrahydro-3-(*p*-chlorophenyl)-5,6-diphenyl-1,4-oxazin-2-one (3c). Following the general procedure, 106 mg (0.20 mmol) of the aminocarbene **2c** and 27 mg (0.22 mmol) of (dimethylamino)pyridine in dry acetonitrile (8 mL) were irradiated for 18 h. The crude product was purified by chromatography on silica using CH_2Cl_2 as eluant yielding 9 mg (0.025 mmol, 12%) of a mixture of 60/40 anti-/syn-**3c** and 43 mg (0.12 mmol, 59%) of the syn-isomer **3c** as white solids. *syn*-**3c**. ^1H NMR (300 MHz, $CDCl_3$): δ 2.07 (br s, 1 H), 4.85 (d, *J* = 4 Hz, 1 H), 5.05 (d, *J* = 4 Hz, 1 H), 5.64 (d, *J* = 4 Hz, 1 H), 6.88 (m, 2 H), 6.98 (m, 2 H), 7.14–7.23 (m, 6 H), 7.41 (m, 2 H), 7.68 (m, 2 H). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 61.72, 63.97, 85.28, 127.32, 127.40, 127.79, 128.13, 128.80, 129.79, 134.45, 134.81, 135.65, 136.94, 168.16. IR (KBr): ν 3460, 3370, 1740 cm^{-1}. $[\alpha]^{22}_D$ = +33.3° (*c* = 1, CH_2Cl_2). Anal. Calcd for $C_{22}H_{18}ClNO_2$: C, 72.62; H, 4.98; N, 3.85. Found: C, 72.41; H, 5.12; N, 3.85. *anti*-**3c**. ^1H NMR (300 MHz, $CDCl_3$): δ 2.32 (br s, 1 H), 4.61 (d, *J* = 5 Hz, 1 H), 5.13 (s, 1 H), 5.70 (d, *J* = 5 Hz, 1 H), 6.84 (m, 2 H), 6.90 (m, 2 H), 7.10 (m, 6 H), 7.32 (m, 2 H), 7.52 (m, 2 H). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 57.97, 59.50, 82.88, 126.56, 127.42, 127.60, 127.84, 128.10, 128.28, 128.39, 128.84, 129.01, 129.80, 134.08, 134.73, 136.32, 137.34, 169.14. IR (KBr): ν 3441, 3289, 1737 cm^{-1}.

Preparation of the (3*R*,5*S*,6*R*)-2,3,5,6-Tetrahydro-3-(*p*-fluorophenyl)-5,6-diphenyl-1,4-oxazin-2-one (3d). Following the general procedure, 180 mg (0.35 mmol) of the aminocarbene complex **2d** and 48 mg (0.39 mmol) of (dimethylamino)pyridine

in dry methylene chloride (9 mL) were irradiated for 18 h. The crude product was purified by chromatography on silica using CH_2Cl_2 as eluant, yielding 48 mg (0.15 mmol, 41%) of the chromium complex of (dimethylamino)pyridine as a yellow solid, 16 mg (0.046 mmol, 13%) of the anti-isomer **3d**, and 84 mg (0.24 mmol, 69%) of the syn-isomer **3d** as white solids. *syn*-**3d**. ^1H NMR (300 MHz, $CDCl_3$): δ 1.96 (br s, 1 H), 4.87 (d, J = 4 Hz, 1 H), 5.08 (s, 1 H), 5.67 (d, J = 4 Hz, 1 H), 6.83 (m, 2 H), 6.98 (m, 2 H), 7.07 (m, 8 H), 7.65 (m, 2 H). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 61.80, 63.97, 85.25, 115.52 (d, J = 22 Hz), 127.31, 127.40, 127.59, 127.79, 128.10, 128.25, 130.12 (d, J = 8 Hz), 132.98, 134.89, 137.02, 162.78 (d, J = 247 Hz), 168.48. IR (KBr): ν 3448, 3332, 1736 cm^{-1}. $[\alpha]^{22}_D$ = +64.4° (c = 1, CH_2Cl_2). Anal. Calcd for $C_{22}H_{18}FNO_2$: C, 76.06; H, 5.22; N, 4.03. Found: C, 75.83; H, 5.07; N, 4.00. *anti*-**3d**: ^1H NMR (300 MHz, $CDCl_3$): δ 2.25 (br s, 1 H), 4.62 (d, J = 4 Hz, 1 H), 5.09 (s, 1 H), 5.65 (d, J = 4 Hz, 1 H), 6.84 (m, 2 H), 6.87 (m, 2 H), 7.08 (m, 8 H), 7.53 (m, 2 H). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 57.88, 59.46, 82.95, 115.80 (d, J = 22 Hz), 126.56, 127.61, 127.83, 128.06, 128.55 (d, J = 8 Hz), 133.58, 134.79, 137.33, 162.54 (d, J = 246 Hz), 177.52. IR (KBr): ν 3445, 3331, 1726 cm^{-1}.

Preparation of the (3*R*,5*S*,6*R*)-2,3,5,6-Tetrahydro-3-[*p*-(trifluoromethyl)phenyl]-5,6-diphenyl-1,4-oxazin-2-one (3e). Following the general procedure, 160 mg (0.28 mmol) of the aminocarbene complex **2e** and 37 mg (0.30 mmol) of (dimethylamino)pyridine in dry methylene chloride (8 mL) were irradiated for 18 h. The crude product was purified by chromatography on silica using CH_2Cl_2 as eluant, yielding 40 mg (0.12 mmol, 43%) of the chromium complex of (dimethylamino)pyridine as a yellow solid, 11 mg (0.028 mmol, 10%) of the anti-isomer **3e**, 10 mg (0.025 mmol, 9%) of a mixture of anti/syn (45/55), and 65 mg (0.16 mmol, 58%) of the syn-isomer **3e** as white solids. *syn*-**3e**. ^1H NMR (300 MHz, $CDCl_3$): δ 2.01 (s, 1 H), 4.80 (d, J = 4 Hz), 5.06 (s, 1 H), 5.58 (d, J = 4 Hz, 1 H), 6.73 (m, 2 H), 6.91 (m, 2 H), 7.07 (m, 6 H), 7.59 (m, 2 H), 7.70 (m, 2 H). ^{13}C NMR (300 MHz, $CDCl_3$): δ 61.54, 64.08, 85.31, 123.98 (q, J = 273 Hz), 125.50 (q, J = 4 Hz), 127.32, 127.37, 127.74, 128.16, 128.26, 128.31, 128.87, 130.30 (q, J = 33 Hz), 134.71, 136.80, 141.06, 167.81. IR (KBr): ν 3386, 1740 cm^{-1}. $[\alpha]^{22}_D$ = +49.7° (c = 1, CH_2Cl_2). Anal. Calcd for $C_{23}H_{18}F_3NO_2$: C, 69.51; H, 4.56; N, 3.52. Found: C, 69.76; H, 4.64; N, 3.54. *anti*-**3e**. ^1H NMR (300 MHz, $CDCl_3$): δ 2.49 (s, 1 H), 4.72 (t, J = 4 Hz, 1 H), 5.27 (d, J = 4 Hz, 1 H), 5.74 (d, J = 4 Hz, 1 H), 6.96 (m, 4 H), 7.24 (m, 6 H), 7.76 (m, 4 H). ^{13}C NMR (300 MHz, $CDCl_3$): δ 58.08, 59.68, 82.95, 123.97 (q, J = 271 Hz), 125.85 (q, J = 4 Hz), 126.52, 127.35, 127.56, 127.79, 127.90, 128.15, 128.18, 128.36, 130.46 (q, J = 32 Hz), 134.60, 137.18, 141.78, 168.83. IR (KBr): ν 3386, 1736 cm^{-1}. Anal. Calcd for $C_{23}H_{18}F_3NO_2$: C, 69.51; H, 4.56; N, 3.52. Found: C, 69.76; H, 4.64; N, 3.54.

Preparation of the (3*R*,5*S*,6*R*)-2,3,5,6-Tetrahydro-3-(*o*-methoxyphenyl)-5,6-diphenyl-1,4-oxazin-2-one (3f). Following the general procedure, 178 mg (0.34 mmol) of the aminocarbene complex **2f** and 43 mg (0.35 mmol) of (dimethylamino)pyridine in dry CH_2Cl_2 (7 mL) were irradiated for 24 h. The crude product was purified by chromatography on silica using CH_2Cl_2 to elute the chromium complex of (dimethylamino)pyridine (52 mg, 0.16 mmol, 47%) and hexane/ethyl acetate (3/1) to elute the product, yielding 11 mg (0.038 mmol, 10%) of the anti-isomer **3f**, 6 mg (0.017 mmol, 5%) of a mixture of 60/40 anti/syn, and 75 mg (0.21 mmol, 61%) of the syn-isomer **3f** as white solids. *syn*-**3f**. ^1H NMR (300 MHz, $CDCl_3$): δ 2.33 (br s, 1 H), 3.81 (s, 3 H, OCH_3), 4.74 (d, J = 5 Hz, 1 H), 5.17 (s, 1 H), 5.64 (d, J = 5 Hz, 1 H), 6.92 (m, 6 H), 7.08 (m, 6 H), 7.24 (m, 1 H), 7.44 (m, 1 H). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 55.48, 60.64, 62.10, 84.71, 111.32, 120.98, 125.50, 127.31, 127.68, 127.75, 128.03, 129.84, 130.15, 135.26, 137.45, 157.21, 169.01. IR (KBr): ν 3429, 3350, 1737 cm^{-1}. $[\alpha]^{22}_D$ = +114.2° (c = 1, CH_2Cl_2). Anal. Calcd for $C_{28}H_{21}NO_3$: C, 76.85; H, 5.89; N, 3.89. Found: C, 76.62; H, 6.04; N, 3.94. *anti*-**3f**. ^1H NMR (300 MHz, $CDCl_3$): δ 2.23 (br s, 1 H), 3.79 (s, 3 H, OCH_3), 4.63 (d, J = 5 Hz, 1 H), 5.28 (s, 1 H), 5.72 (d, J = 5 Hz, 1 H), 6.92 (m, 6 H), 7.10 (m, 6 H), 7.26 (m, 2 H). ^{13}C NMR (300 MHz, $CDCl_3$): δ 55.56, 56.58, 57.70, 85.16, 111.34, 120.69, 127.22, 127.38, 127.58, 127.86, 127.95, 128.23, 129.45, 129.78, 135.61, 137.22, 156.75, 169.44. IR (KBr): ν 3425, 3314, 1715 cm^{-1}.

Preparation of the (3*R*,5*S*,6*R*)-2,3,5,6-Tetrahydro-3-(2,6-difluorophenyl)-5,6-diphenyl-1,4-oxazin-2-one (3g). Following the general procedure, 180 mg (0.34 mmol) of the aminocarbene complex **2g** and 43 mg (0.35 mmol) of (dimethylamino)pyridine in dry CH_2Cl_2 (8 mL) were irradiated for 24 h. The crude product was purified by chromatography on silica using CH_2Cl_2/hexane (60/40), yielding 48 mg (0.15 mmol, 43%) of the (dimethylamino)pyridinechromium complex as a yellow solid, 10 mg (0.027 mmol, 8%) of the anti-isomer **3g**, 12 mg (0.033 mmol, 10%) of a mixture of 40/60 anti/syn, and 78 mg (0.21 mmol, 63%) of the syn-isomer **3g** as white solids. *syn*-**3g**. ^1H NMR (300 MHz, $CDCl_3$): δ 2.29 (br s, 1 H), 4.84 (d, J = 4 Hz, 1 H), 5.37 (s, 1 H), 5.75 (d, J = 4 Hz, 1 H), 6.85–7.25 (m, 13 H). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 54.67, 62.40, 85.07, 111.80 (d, J = 24 Hz), 113.11 (t, J = 18 Hz), 126.89, 127.29, 127.42, 127.63, 127.66, 127.71, 128.06, 128.18, 128.33, 130.69 (t, J = 10 Hz), 134.78, 136.82, 161.28 (dd, J = 7 and 250 Hz), 167.46. IR (KBr): ν 3448, 3309, 1731 cm^{-1}. $[\alpha]^{22}_D$ = +127° (c = 1, CH_2Cl_2). Anal. Calcd for $C_{22}H_{17}F_2NO_2$: C, 72.32; H, 4.69; N, 3.83. Found: C, 72.17; H, 4.69; N, 3.91. *anti*-**3g**. ^1H NMR (300 MHz, $CDCl_3$): δ 1.53 (br s, 1 H), 4.81 (d, J = 4 Hz, 1 H), 5.35 (t, J = 3 Hz, 1 H), 5.71 (d, J = 4 Hz, 1 H), 6.88–7.34 (m, 13 H). IR (KBr): ν 3448, 3317, 1741 cm^{-1}.

Preparation of the (3*R*,5*S*,6*R*)-2,3,5,6-Tetrahydro-3-(1-naphthyl)-5,6-diphenyl-1,4-oxazin-2-one (3h). Following the general procedure, 160 mg (0.29 mmol) of the aminocarbene complex **2h** and 39 mg (0.32 mmol) of (dimethylamino)pyridine in dry CH_2Cl_2 (7 mL) were irradiated 24 h. The crude product was purified by chromatography on silica using CH_2Cl_2/hexane (70/30), yielding 33 mg (0.10 mmol, 34%) of the (dimethylamino)pyridinechromium complex as a yellow solid and 87 mg (0.22 mmol, 76%) of a mixture of syn/anti-**3h** (80/20) as a white solid. In this case the diastereoisomers are not separable by chromatography on silica, and just 41 mg (0.11 mmol, 38%) of the pure syn-isomer was isolated. *syn*-**3h**. ^1H NMR (300 MHz, $CDCl_3$): δ 1.95 (br s, 1 H), 4.83 (t, J = 3 Hz, 1 H), 5.62 (d, J = 4 Hz, 1 H), 5.70 (d, J = 4 Hz, 1 H), 6.88 (m, 4 H), 7.11 (m, 6 H), 7.42 (m, 3 H), 7.80 (m, 2 H), 7.93 (m, 1 H), 8.09 (m, 1 H). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 60.93, 62.09, 85.31, 123.77, 125.36, 125.44, 125.79, 126.48, 127.35, 127.62, 127.85, 128.07, 128.20, 128.75, 129.82, 131.91, 133.47, 133.90, 135.07, 137.12, 168.28. IR (KBr): ν 3348, 3312, 1736 cm^{-1}. $[\alpha]^{22}_D$ = −88.0° (c = 0.5, CH_2Cl_2). Anal. Calcd for $C_{26}H_{21}NO_2$: C, 82.29; H, 5.58; N, 3.69. Found: C, 82.08; H, 5.67; N, 3.63. *anti*-**3h**. ^1H NMR (300 MHz, $CDCl_3$): δ 2.05 (br s, 1 H), 4.65 (t, J = 3 Hz, 1 H), 5.77 (d, J = 4 Hz, 1 H), 5.86 (d, J = 4 Hz, 1 H), 6.84–8.11 (m, 17 H). ^{13}C NMR (75.5 MHz, $CDCl_3$): (some carbons are unassignable but some differences appear) δ 56.55, 58.73, 84.94, 122.79, 123.95, 125.75, 126.06, 126.94, 130.74, 133.33, 136.87, 168.34.

Preparation of the 2,3,5,6-Tetrahydro-3-(3-thienyl)-5,6-diphenyl-1,4-oxazin-2-one (3i). Following the general procedure, 134 mg (0.27 mmol) of the aminocarbene complex **2i** and 33 mg (0.28 mmol) of (dimethylamino)pyridine in dry CH_2Cl_2 (6 mL) were irradiated for 18 h. The crude product was purified by chromatography on silica using CH_2Cl_2 as eluant, yielding 38 mg (0.11 mmol, 41%) of the (dimethylamino)pyridinechromium complex as a yellow solid, 13 mg (0.043 mmol, 16%) of the anti-isomer **3i**, and 52 mg (0.17 mmol, 62%) of the syn-isomer **3i** as white solids. *syn*-**3i**. ^1H NMR (300 MHz, $CDCl_3$): δ 2.08 (br s, 1 H), 4.77 (d, J = 4 Hz, 1 H), 5.16 (s, 1 H), 5.57 (d, J = 4 Hz, 1 H), 6.77 (m, 2 H), 6.92 (m, 2 H), 7.18 (m, 6 H), 7.33 (d, J = 4 Hz, 2 H), 7.51 (s, 1 H). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 55.32, 55.84, 114.47, 127.04, 127.42, 128.47, 128.65, 129.54, 132.41, 160.06, 166.06, 174.80. IR (KBr): ν 3346, 1732 cm^{-1}. *anti*-**3i**. ^1H NMR (300 MHz, $CDCl_3$): δ 2.30 (br s, 1 H), 4.68 (t, J = 5 Hz, 1 H), 5.18 (d, J = 4 Hz, 1 H), 5.65 (d, J = 4 Hz, 1 H), 6.80 (m, 1 H), 6.88 (m, 1 H), 7.14–7.35 (m, 11 H). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 57.28, 57.40, 83.84, 122.51, 126.58, 126.80, 126.90, 127.45, 127.76, 128.02, 128.14, 128.34, 134.79, 137.30, 138.90, 191.94. IR (KBr): ν 3350, 1717 cm^{-1}.

General Procedure for the Preparation of Arylglycines 4. To a suspension of the oxazinone (syn-isomer) (1 equiv) in a 1:1 mixture of EtOH/THF (0.05–0.06 M) was added $PdCl_2$ (0.3 equiv). The mixture was exposed to 1 atm of hydrogen for 15 min to 1 h. The reaction mixture was purged with Argon and filtered through Celite. Then, several drops of 1 N HCl was added to the filtrate and the mixture was evaporated under reduced pressure (15 mmHg). The resulting solid was triturated three times with Et_2O to give the hydrochloride salt of the aryl glycine.

The amine salt was dissolved in a minimum amount of methanol, and the same quantity of propylene oxide was added. After heating at reflux for 20 min the free amino acid precipitated and was isolated by filtration.

General Procedure for the Preparation of the Mosher Amide. The amino acid (1 equiv), the Mosher's acid chloride (0.9 equiv), and propylene oxide (4 equiv) were heated at reflux in THF for 30 min. The resulting solution was filtered through Celite, yielding the desired Mosher's amide after evaporation of the solvent, usually as a white solid. The % ee were determined by an examination of the ^{19}F NMR spectrum.

(*R*)-Phenylglycine Hydrochloride (4·HCl) (Oxidative Cleavage). A 75-mg portion of *syn*-**3a** (0.23 mmol) was dissolved in THF (4 mL) and treated with 10% HCl (15 mL). The solution was heated at reflux for 0.5 h, cooled, and concentrated under reduced pressure (15 mmHg). The resulting cream solid was dissolved in H_2O (5 mL), and 107 mg of sodium periodate (0.50 mmol, 2.20 equiv) was added. The pH was adjusted to 3.0, and the resulting solution was stirred at room temperature for 36 h. Then the pH was adjusted to 5.5, and 10 drops of ethylene glycol was added to destroy the excess of sodium periodate. The resulting mixture was washed with ethyl acetate (3 × 15 mL) and concentrated under reduced pressure (15 mmHg). The resulting white solid was purified via ion-exchange chromatography (HCl 10%, Amberlite IRA-45) yielding 29 mg of the pure amino acid (0.16 mmol, 69%). This was identical in all respects to authentic material.[13a]

(*R*)-(*p*-Methoxyphenyl)glycine[13b] (4b). Following the general procedure, 80 mg (0.23 mmol) of the syn-isomer (**3b**) in THF (2 mL) and EtOH (2 mL) and 12 mg (0.066 mmol, 0.3 equiv) of $PdCl_2$ was hydrogenated for 1 h to give the hydrochloride salt. After treatment with methanol (2 mL) and propylene oxide (2 mL), 36 mg (0.20 mmol, 91%) of the free amino acid was isolated as a white amorphous solid.

4b Hydrochloride Salt. ^1H NMR (300 MHz, DMSO): δ 3.77 (s, 3 H, OMe), 4.98 (s, 1 H, CH), 6.99 (d, J = 10 Hz, ArH), 7.41 (d, J = 10 Hz, 2 H), 8.7 (br s, $^+NH_3$). ^{13}C NMR (75.5 MHz, DMSO): δ 54.91 (CH), 55.30 (OMe), 114.22, 125.06, 129.51, 159.86 (Ar), 169.93 (C=O). IR (KBr): ν 3447, 3003, 2924, 1740, 1617 cm^{-1}.

4b Free Amino Acid. IR (KBr): ν 3413, 2955, 1626, 1603, 1586 cm^{-1}. Mass spectrum (NH_3-CI) 181 (M). $[\alpha]^{22}_D$ = −150° (c = 1, 3 N HCl). Anal. Calcd for $C_9H_{11}NO_3$: C, 59.66; H, 6.11; N, 7.73. Found: C, 59.26; H, 6.11; N, 7.69.

(*S*)-(*p*-Methoxyphenyl)glycine (4b'). Prepared by the same procedure as **4b** from (+)-(L)-erythro amino alcohol. (3*S*,5*R*,6*S*)-oxazinone (**3b'**) was obtained in the same yield and with the same diastereoselectivity.

^1H and ^{13}C NMR spectra are identical to those of the *R* enantiomer. $[\alpha]^{22}_D$ = −45.9° (c = 1, CH_2Cl_2).

Free (*S*) amino acid **4b'**. $[\alpha]^{22}_D$ = +156° (c = 1,3 N HCl).

(*R*)-(*p*-Chlorophenyl)glycine[13a] (4c). Following the general procedure, 55 mg (0.15 mmol) of the syn-isomer **3c** and 8 mg (0.045 mmol) of $PdCl_2$ in THF (1.5 mL) and EtOH (1.5 mL) was hydrogenated for 1 h to give 39 mg (0.17 mmol, 115%) of the hydrochloride salt. The free amino acid, 22 mg (0.12 mmol, 81%), was obtained by the usual method.

4c Hydrochloride Salt. ^1H NMR (300 MHz, DMSO): δ 3.32 (br s, HCl), 5.08 (s, 1 H, CH), 7.48 (m, 4 H, ArH), 8.83 (br s, $^+NH_3$). ^{13}C NMR (75.5 MHz, DMSO): δ 55.56 (CH), 128.14, 128.97, 130.14, 132.18, 133.18 (Ar), 169.74 (C=O). IR (KBr): ν 3413, 3002, 2594, 1736, 1597 cm^{-1}.

4c Free Amino Acid. IR (KBr): 3426, 2934, 2620, 1609, 1096 cm^{-1}. Mass spectrum (NH_3-Cl): 186 (M). $[\alpha]^{22}_D$ = −142° (c = 0.5, 1 N, HCl).

(*R*)-(*p*-Fluorophenyl)glycine (4d). Following the general procedure, 50 mg (0.14 mmol) of the syn-isomer **3d** and 8 mg (0.045 mmol) of $PdCl_2$ in THF (1.5 mL) and EtOH (1.5 mL) was hydrogenated for 1 h to give 34 mg (0.17 mmol, 115%) of the crude hydrochloride salt. The free amino acid, 20 mg (0.12 mmol, 82%), was obtained by the usual method.

4d Hydrochloride Salt. ^1H NMR (300 MHz, DMSO): δ 5.11 (s, 1 H, CH), 7.29 (m, 2 H, ArH), 7.56 (m, 2 H, ArH), 8.92 (br s, NH_3^+). ^{13}C NMR (75.5 MHz, DMSO): 54.76 (CH), 115.70 (d, J = 22 Hz, Ar), 129.68 (Ar), 130.51 (d, J = 8 Hz, Ar), 162.38 (d, J = 245 Hz, Ar), 169.45 (C=O). IR (KBr): ν 3421, 2926, 1736, 1698, 1654, 1636, 1605 cm^{-1}. Anal. Calcd for $C_8H_9ClFNO_2$: C, 46.73; H, 4.41; N, 6.81. Found: C, 46.79; H, 4.58; N, 6.59.

4d Free Amino Acid. IR (KBr): ν 3442, 2932, 2614, 1610, 1552 cm^{-1}. Mass spectrum (NH_3-CI): 169 (M). $[\alpha]^{22}_D$ = −135° (c = 0.5, 1 N HCl).

(*R*)-[(*p*-Trifluoromethyl)phenyl]glycine (4e). Following the general procedure, 58 mg (0.15 mmol) of the syn-isomer **3e**, 8 mg (0.045 mmol) of $PdCl_2$ in THF (2 mL), and EtOH (2 mL) was hydrogenated for 30 min to give 38 mg (0.15 mmol, 100%) of the hydrochloride salt. This salt was dissolved in MeOH (2 mL), and propylene oxide (2 mL) was added. The mixture was refluxed for 30 min and cooled, and 5 mL of Et_2O was added to give after filtration to give 27 mg (0.13 mmol, 86%) of the free amino alcohol as a white amorphous solid.

4e Hydrochloride Salt. ^1H MMR (300 MHz, DMSO): δ 5.18 (s, 1 H, CH), 7.80 (m, 4 H, ArH), 9.03 (br s, $^+NH_3$). ^{13}C NMR (75.5 MHz, DMSO): δ 55.19 (CH), 123.97 (q, J = 272 Hz, CF_3), 125.65 (q, J = 4 Hz, Ar), 129.14 (Ar), 129.47 (q, J = 32 Hz, Ar), 138.05 (Ar), 168.93 (C=O). IR (KBr): ν 3423, 3018, 2607, 1736, 1624, 1602 cm^{-1}.

4e Free Amino Acid. IR (KBr): 3427, 2979, 2667, 1624, 1589 cm^{-1}. Mass spectrum (NH_3-CI): 219 (M). $[\alpha]^{22}_D$ = −109° (c = 0.5, 1 N HCl).

(*S*)-[*p*-(Trifluoromethyl)phenyl]glycine (4e'). Prepared by the same procedure as **4e** from (+)-(L)-erythro-amino alcohol. (3*S*,5*R*,6*S*)-Oxazinone **3e'** was obtained with the same yield and the same diastereoselectivity. $[\alpha]^{22}_D$ = −50.3° (c = 1, CH_2Cl_2).

(*S*)-Amino Acid 4e. $[\alpha]^{22}_D$ = +104° (c = 0.5, 1 N HCl).

(*R*)-(*o*-Methoxyphenyl)glycine Hydrochloride Salt (4f). Following the general procedure, 56 mg (0.16 mmol) of the syn-isomer **3f** and 9 mg (0.05 mmol) of $PdCl_2$ in THF (2 mL) and EtOH (2 mL) was hydrogenated for 1 h to give 32 mg (0.15 mmol, 24%) of the hydrochloride salt **4f** as a white solid.

4f Hydrochloride Salt. ^1H NMR (300 MHz, DMSO): δ 3.80 (s, 3 H, OMe), 5.15 (s, 1 H, CH), 7.02 (t, J = 7 Hz, 1 H, ArH), 7.10 (d, J = 8 Hz, 1 H, ArH), 7.39 (m, 2 H, ArH), 8.55 (br s, $^+NH_3$). IR (KBr): ν 3421, 2926, 2585, 1736, 1605, 1598 cm^{-1}. $[\alpha]^{22}_D$ = −83° (c = 1, 3 N HCl). Mass spectrum (NH_3-CI): 181 (M − HCl). The free amino acid was quite unstable and could not be characterized. The salt was directly converted to the Mosher's amide for determination of ee.

(*R*)-(2,6-Difluorophenyl)glycine (4g). Following the general procedure, 60 mg (0.16 mmol) of **3g** and 9 mg (0.049 mmol) of $PdCl_2$ in THF (2 mL) and EtOH (2 mL) was hydrogenated for 1 h to give 35 mg (0.15 mmol, 94%) of the hydrochloride salt **4g**. This salt was dissolved in MeOH (2 mL), and propylene oxide (2 mL) was added. The mixture was stirred at room temperature for 3 h, and Et_2O (6 mL) was added to precipitate the product. 30 mg (0.15 mole, 95%) of the free amino acid was isolated as a white amorphous solid.

4g Hydrochloride Salt. ^1H NMR (300 MHz, DMSO): δ 5.26 (s, 1 H, CH), 7.21 (m, 2 H, ArH), 7.56 (m, 1 H, ArH), 9.04 (br s, $^+NH_3$). ^{13}C NMR (75.5 MHz, DMSO): δ 44.99 (CH), 109.98 (t, J = 18 Hz, Ar), 112.08 (d, J = 24 Hz, Ar), 132.52 (t, J = 10 Hz, Ar), 160.49 (dd, J = 7 and 250 Hz, Ar), 168.01 (C=O). IR (KBr): ν 3425, 2960, 2685, 2621, 1752, 1631, 1592 cm^{-1}.

4g Free Amino Acid. IR (KBr): ν 3425, 3072, 2344, 1647, 1629, 1593 cm^{-1}. $[\alpha]^{22}_D$ = −55° (c = 0.5, 1 N HCl) (56% ee after conversion to Mosher's amide). Mass spectrum (NH_3-CI): 187 (M).

(*R*)-Naphthylglycine 4h. The oxidation cleavage of Williams[6] was followed exactly to give a 40% yield of the free amino acid.

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Supplementary Material Available: NMR spectra of **2a–i**, **3h–i**, and **4d–g** (37 pages). This material is contained in many 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.