Silicalite, either method gave the same % CE values. For Silicalite, a simple CH_2Cl_2 extraction failed to remove sufficient organic material for analysis. For this zeolite, we found that a simple MeOH extraction gave the same % CE values as from a Soxhlet extraction.

Analysis of AA, AB, and BB ratios were carried out by using a Varian Aerograph 3700 gas chromatograph. To check for possible interconversion of AA, AB, and BB on the zeolite, a known mixture of AA, AB, and BB (obtained via photolysis of 4-MeDBK in benzene) was deposited on the zeolites and reextracted via the above described procedures. Interconversion of AA, AB, and BB was not observed on any of the zeolites. A 5-10% loss of AA was observed on Silicalite, but % CE's are only affected by <4% due to this "preferential adsorption" of AA. Thus, no corrections were applied to the apparent % CE's observed for Silicalite.

^{13}C-Enrichment Studies. DBK-^{13}C (**2'**) was deposited on zeolites and photolyzed in the same manner as described above. ^{13}C-Content was determined by mass spectrometry using a Finnegan 3300 GC/MS system (SE-30 column; multiple ion detection mode). The details in calculating α are available elsewhere.[21-25] The identity of PMAP was confirmed by coinjection with an authentic sample of the compound. An additional isomer (as determined by its mass spectrum) (~1%) was observed on photolysis in Na^+-X, and is believed to be the ortho analogue of PMAP. However, due to the low yield observed, direct confirmation of its structure was not feasible. Conversions were >80% for all the zeolites except Silicalite, in which case <30% conversion was used. We found that it was not possible to take Silicalite to high conversion. The probable reason for this is that homogeneous tumbling of Silicalite samples proved to be problematic due to the extreme powdery form of the sample.

Adsorption Isotherms. For adsorption isotherm studies, 2,2,4-trimethylpentane (isooctane) was chosen as the solvent since it is known that the kinetic diameter is >6.2 Å based on the fact that for neopentane, the kinetic diameter is 6.2 Å.[14,16] A preweighed amount of DBK dissolved in 30 mL of isooctane was added to 100 mg of zeolite and stirred rigorously with a magnetic stirring bar at room temperature (25 ± 3 °C) for 15 h. The slurry was then filtered by using a microfiltration apparatus, and dodecane internal standard was added. After removal of most of the solvent, the mixture was analyzed for DBK content via GLC (capillary SE-30 column; Varian Aerograph Model 3700). The amount of DBK adsorbed was calculated by taking the difference of the amount of DBK exposed to the zeolite and the amount recovered in the solvent filtrate. Decomposition of DBK was not observed during the period of the experiment.

Acknowledgment. We thank the National Science Foundation and the Air Force Office of Scientific Research for their generous support of this work. P.W. thanks NSERC (Canada) for a postdoctoral fellowship (1983-1984). Additional thanks are due to Dr. Edith Flanigen, Union Carbide Corp., Tarrytown, NY, for stimulating discussions concerning zeolite structure and catalysis and their potential use in organic photochemistry. Dr. Chao Chung is thanked for performing some initial, exploratory investigations.

Registry No. 1, 35730-02-0; **2**, 102-04-5.

Enantioselective Synthesis of 2,2',6-Trisubstituted Biphenyls

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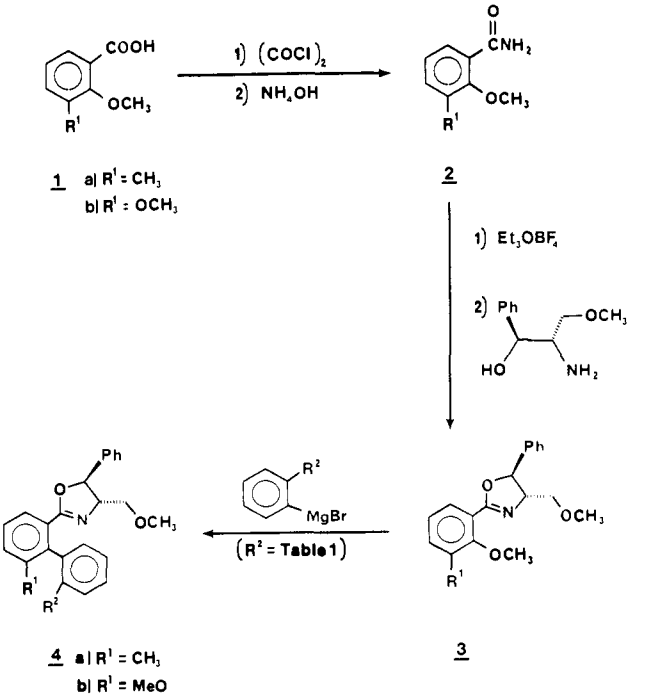
Abstract: A general procedure is described for the synthesis of chiral biphenyls via nucleophilic aromatic substitution of an *o*-methoxy group by an aryl Grignard reagent with an oxazoline as a chiral auxiliary.

Substituted biphenyls have been synthesized by a variety of methods,[1] most notable of which are the Ullmann reaction,[2] the Kumada coupling[3] of aryl Grignard reagents with aryl halides in the presence of a nickel phosphine catalyst, and the nucleophilic addition of an aryl Grignard reagent to *o*-methoxyaryloxazolines.[4] As part of a program directed toward the synthesis of (-)-steganone, we were interested in developing a general enantioselective synthesis of substituted biphenyls which are chiral by virtue of hindered rotation about the central bond.

Based on work described by Adams and co-workers,[5] we decided that a minimum of three ortho substituents would be required to impart a sufficient barrier to rotation to avoid racemization. Although 2,2'-disubstituted biphenyls have been resolved, they are generally not sufficiently stable toward racemization. Frejd[6] has recently demonstrated that optically pure 2,2'-dilithio-6,6'-dimethylbiphenyl is stable toward racemization at -10 °C and can be iodinated to provide optically pure 2,2'-diiodo-6,6'-dimethylbiphenyl. This approach can presumably be extended to provide a number of chiral biphenyls yet requires an optically pure biphenyl as the starting material. Indeed a number of optically active biphenyls have been prepared in the literature, but this is usually the result of a classical or kinetic resolution.[7]

Scheme I



Analogous to the recently reported preparation of optically active binaphthyls,[8] we chose to prepare the chiral biphenyls **4**

(1) Sainsbury, M. *Tetrahedron* **1980**, *36*, 3327.
(2) Fanta, P. E. *Chem. Rev.* **1946**, *38*, 139; **1964**, *64*, 613.
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Table I. Chiral Biphenyloxazolines **4** from Phenyloxazolines **3** and Phenyl Grignard Reagents

biphenyl-oxazoline	R^1	R^2	% yield	diastereo-meric, ratio[a]	IR ($CHCl_3$), cm^{-1}	H NMR ($CDCl_3$), δ
4a	CH_3	CH_3	59	68:32	3020, 1645	2.00 (s, 6 H), 3.33 (s, 3 H), 3.21–3.55 (m, 2 H), 3.82–4.22 (m, 1 H), 5.02 (d, J = 6 Hz, 0.68 H), 5.10 (d, J = 6 Hz, 0.32 H), 6.65–7.80 (m, 12 H)
4b	CH_3	OCH_3	72	96:4	2910, 1640	2.07 (s, 3 H), 3.34 (s, 3 H), 3.47–3.65 (m, 2 H), 3.65 (s, 3 H), 3.95–4.25 (m, 1 H), 4.99 (d, J = 6 Hz, 0.96 H), 5.17 (d, J = 6 Hz, 0.04 H), 6.65–7.80 (m, 12 H)
4c	OCH_3	CH_3	75	80:20	3020, 1645	2.07 (s, 3 H), 3.30 (s, 3 H), 3.30–3.65 (m, 2 H), 3.67 (s, 3 H), 3.90–4.35 (m, 1 H), 5.08 (d, J = 6 Hz, 0.80 H), 5.18 (d, J = 6 Hz, 0.2 OH), 6.70–7.60 (m, 12 H)
4d	OCH_3	OCH_3	85	50:50	3000, 1645	3.33 (s, 3 H), 3.35–3.62 (m, 2 H), 3.63 (s, 1.5 H,) 3.66 (s, 1.5 H) 3.69 (s, 3 H), 3.97–4.20 (m, 1 H), 5.03 (d, J = 6 Hz, 0.50 H), 5.17 (d, J = 6 Hz, 050 H), 6.70–7.60 (m, 12 H)
4e	OCH_3	CH_2OSiMe_2-t-Bu	85	79:21	3020, 1650	−0.02 (s, 3 H), 0.15 (s, 3 H), 1.00 (s, 9 H) 3.37 (s, 3 H), 3.40–3.65 (m, 2 H), 3.73 (s, 3 H), 3.95–4.35 (m, 1 H), 4.53 (s, 2 H), 5.00 (d, J = 6 Hz, 0.79 H), 5.07 (d, J = 6 Hz, 0.21 H), 6.80–7.70 (m, 12)
4f	CH_3	$CH_2OCH_2OCH_3$	95	84:16	3050, 1645	2.02 (s, 3 H), 3.19–3.54 (m, 2 H), 3.19 (s, 3 H), 3.32 (s, 3H), 3.90–4.10 (m, 1 H), 4.27 (s, 2 H), 4.48 (s, 2 H), 5.04 (d, J = 6 Hz, 0.84 H), 5.12 (d, J = 6 Hz, 0.16 H), 6.80–7.60 (m, 12 H)

[a] Determined by 100-MHz ^1H NMR spectroscopy using the 5 H benzylic doublet (J = 6 Hz) at δ 5.00–5.20.

Table II. Chiral Biphenylaldehydes **9** from Chiral Biphenyloxazolines **4**

biphenyl-aldehyde	% yield	% ee	$[\alpha]_D$ ($CHCl_3$), deg	IR ($CHCl_3$), cm^{-1}	^1H NMR ($CDCl_3$), δ
9a	72[a]	36[g]	+4.14 (c 8.60)	3020, 1680	2.00 (s, 3 H), 2.03 (s, 3 H), 6.90–7.95 (m, 7 H), 9.57 (s, 1 H)
9b	59[b]	0[h]	−13.1 (c 10.5)[j]	3010, 1680	2.10 (s, 3 H), 3.67 (s, 3 H), 6.80–7.95 (m, 7 H), 9.63 (s, 1 H)
9c	63[c]	60[i]	+50.2 (c 12.6)	3020, 1685	2.07 (s, 3H), 3.75 (s, 3 H), 7.00–7.74 (m, 7 H), 9.57 (s, 1 H)
9d	63[d]	0	0	3010, 1680	3.67 (s, 3 H), 3.72 (s, 3 H), 6.71–7.67 (m, 7 H), 9.63 (s, 1 H)
9e	56[e]	52[j]	+36.5 (c 17.5)	3020, 1680	0.00 (s, 6 H), 0.93 (s, 9 H), 3.80 (s, 3 H), 4.47 (d, J = 2 Hz, 2 H), 7.70–7.75 (m, 7 H), 9.60 (s, 1 H)
9f	64[f]	64[k]	+3.01 (c 7.9)	2920, 1685	2.07 (s, 3 H), 3.17 (s, 3 H), 4.20 (s, 2 H), 4.43 (s, 2 H), 7.00–7.95 (m, 7 H), 9.57 (s, 1 H)

[a] anal. Calcd for $C_{15}H_{14}O$: C, 85.68; H, 6.71. Found: C, 85.89; H, 7.11. [b] Anal. Calcd for $C_{15}H_{14}O_2$: C, 79.62; H, 6.24. Found: C, 79.54; H, 6.25. [c] Anal. Calcd for $C_{15}H_{14}O_2$: C, 79.62; H, 6.24. Found: C, 79.67; H, 6.19 [d] Anal. Calcd for $C_{15}H_{14}O_3$: C, 74.36; 5.82. Found: C, 74.41; H, 5.93. [e] Anal. Calcd for $C_{21}H_{28}O_3Si$: C, 70.74; H, 7.92. Found: C, 70.70; H, 8.18. [f] Anal. Calcd for $C_{17}H_{18}O_3$: C, 75 53; H, 6.71. Found: C, 75.20; H, 6.64. [g] Determined by 360-MHz ^1H NMR spectroscopy using the diastereomeric methyl singlets at δ 1.87 and 1.89 of the Mosher esters (see Experimental Section). [h] Determined by 360-MHz ^1H NMR spectroscopy using the methyl singlets at δ 3.66 and 3.69 of the Mosher esters. [i] Determined by 360-MHz ^1H NMR spectroscopy using the methyl singlets at δ 1.93 and 1.95 of the Mosher esters. [j] Determined by 360-MHz ^{19}F NMR spectroscopy using the trifluorometry singlets at 4.35 and 4.43 (downfield from TFA) of the Mosher esters. [k] Determined by 360-MHz ^{19}F NMR spectroscopy using the trifluoromethyl singlets at δ 4.30 and 4.40 (downfield from TFA) of the Mosher esters. [l] Observed immediately upon preparation of the aldehyde but asymmetric induction is lost in conversion to Mosher ester.

via nucleophilic addition of appropriately substituted aryl Grignard reagents to 3-substituted 2-methoxyphenyloxazoline, **3**. We were particularly interested in determining which substitution patterns would allow for the preparation of optically stable biphenyls.

Results and Discussion

The requisite chiral phenyloxazolines **3** were prepared from the corresponding benzoic acids **1** by initally converting them to the benzamide **2** and then treating them with Meerwein's reagent to form the imidate salt. The latter was treated with (+)-1-methoxy-2-amino-3-phenyl-3-hydroxypropane[9] to afford the chiral phenyloxazolines **3** in 65–84% yield from **1** (Scheme I).

The biphenyloxazolines **4** were prepared by addition of a tetrahydrofuran solution of phenyloxazoline **3** to an ethereal solution of aryl Grignard reagent derived from the corresponding aryl bromide. Reaction conditions were carefully studied and optimized for chemical yields and diastereoselectivity. Stoichiometry of the reactants and reaction temperature mattered little, but of paramount importance was the use of aryl Grignard reagents as opposed to aryllithium reagents. In all cases, the use of aryllithium reagents gave the biphenyls but resulted in little or no diastereoselectivity, presumably due to the rapid rate of reaction and thus poor selectivity.[8] Tetrahydrofuran was required as the cosolvent since ether alone resulted in precipitation of the primary complex between the oxazoline and Grignard reagent.

As seen in Table I, several 2,2',6-trisubstituted biphenyls **4** have been prepared by this method, resulting in good yields and useful disastereoselectivity. The lack of selectivity in the case of **4d** undoubtedly represents the inability of the smaller methoxy groups to inhibit racemization. Particularly useful are the biphenyloxazolines **4e** and **4f** which allow for further elaboration after the coupling is performed. Separation of the diastereomeric biphenyloxazolines **4a–f** proved difficult on a preparative scale; however, biphenyloxazoline **4e** was deprotected with HF to give the corresponding hydroxymethylene derivatives which were separable by silica gel thin-layer chromatography. The 4:1 ratio of diastereomers thus isolated was in good agreement with the diastereoselectivity observed by 100-MHz ^1H NMR spectroscopy, substantiating the integrity of this analytical method.

The synthesis of 2,2',6,6'-tetrasubstituted biphenyls was attempted but resulted in poor yields due to steric crowding. Little or no diastereoselectivity was observed presumably due to a comparative lack of diastereofacial bias on the part of the incoming aryl Grignard reagent (i.e., sterically, the difference between alkyl groups and hydrogen is much greater than that between two alkyl groups).

Removal of the chiral auxiliary, by acidic or basic hydrolysis at elevated temperatures, in most cases resulted in racemic carboxylic acids. However, use of methodology previously developed in these laboratories[10] for the reductive cleavage of aryloxazolines

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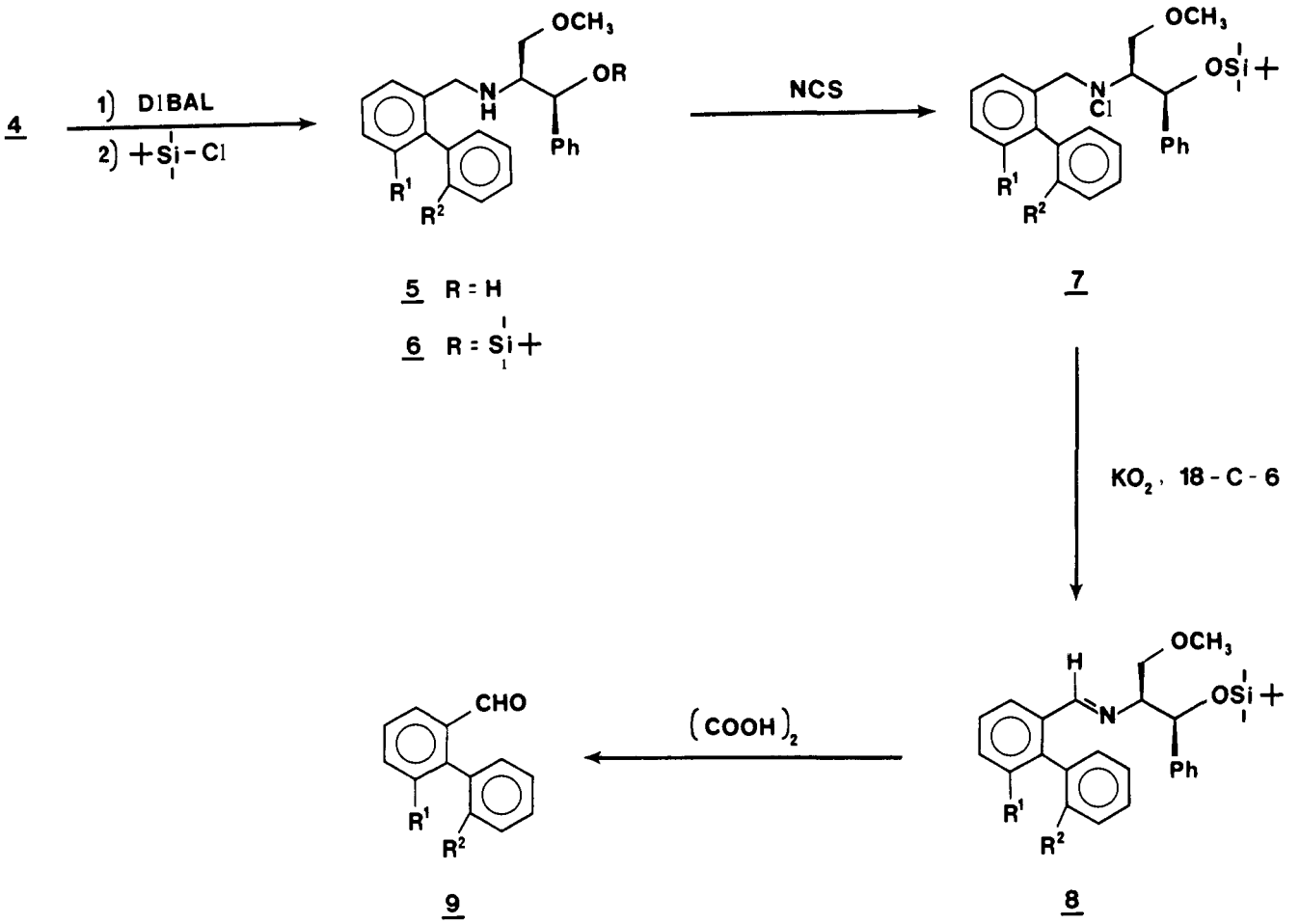
(9) Meyers, A. I.; Knaus, G.; Kamata, K.; Ford, M. E. *J. Am. Chem. Soc.* **1976**, *98*, 567.
(10) Meyers, A. I.; Himmelsbach, R. J.; Reuman, M. *J. Org. Chem.* **1983**, *48*, 4053.

Scheme II



to benzaldehydes provided biphenylaldehydes **9a–f** in 56–72% yield. The sequence, depicted in Scheme II, requires reduction of the oxazoline **4** to the amino alcohol **5** and protection of the alcohol as the *tert*-butyldimethylsilyl ether **6**. N-Chlorination of **6** afforded **7** and dehydrochlorination with potassium superoxide gave **8** which was hydrolyzed with oxalic acid to the biphenylaldehydes **9a–f**.

This sequence of reactions was carried out at room temperature or lower and minimized any chance for racemization. The results in Table II demonstrate the utility of this method. Most of the biphenyloxazolines **4** were cleaved in good yield with little or no racemization. The optical purity was determined by reducing the biphenylaldehyde **9** to the hydroxymethylene derivative and esterifying with (−)-α-methoxy-α-(trifluoromethyl)phenylacetyl chloride.[11,12] Diastereomers were distinguished by either 360-MHz ^{1}H NMR or 360-MHz ^{19}F NMR spectroscopy (Figure 1). The conversion of biphenyloxazoline **4b** to biphenylaldehyde **9b** gives material of undertermined optical purity since **9b** was found to racemize at room temperature. Although **9b** initially gives $[\alpha]_D$ 13.1°, the time involved in conversion to the Mosher ester results in racemic material.

Rates of racemization of these biphenyls were measured at 110 °C in toluene. Adams and co-workers[5] have measured the rates of racemization of a number of substituted biphenyls and determined that the capacity of an ortho group to inhibit internal rotation is steric in nature and parallels the van der Waals radius of that group, yielding the following order of substituents in descending effective radius:

$$Br \gg CH_3 > Cl > NO_2 > CO_2 \gg OCH_3 > F$$

The results of the kinetic study are presented in Table III and substantiate those of Adams. Rates of racemization were measured in toluene at 110 °C and were found to be first order in biphenyl concentration. In general, those biphenyls in which the

Table III. Rate Constants for Racemization of Biphenyloxazolines **4** and Biphenylaldehydes **9** in Toluene at 110 °C

biphenyl	4		9	
	k_i, S^{-1} [b]	$T^{1/2}$, h	k, s^{-1}	$T^{1/2}$, h
a		∞[a]		∞[a]
b	$(8.19 \pm 0.27) \times 10^{-5}$	2.35		<0.1
c	$(4.95 \pm 0.17) \times 10^{-6}$	38.5	$(6.57 \pm 0.25) \times 10^{-5}$	2.93
e	$(2.56 \pm 0.11) \times 10^{-6}$	74.0	$(3.87 \pm 0.21) \times 10^{-5}$	4.96
f		∞[a]		∞[a]

[a] No observable loss in optical activity after 48 h. [b] Errors represent 95% confidence limit.

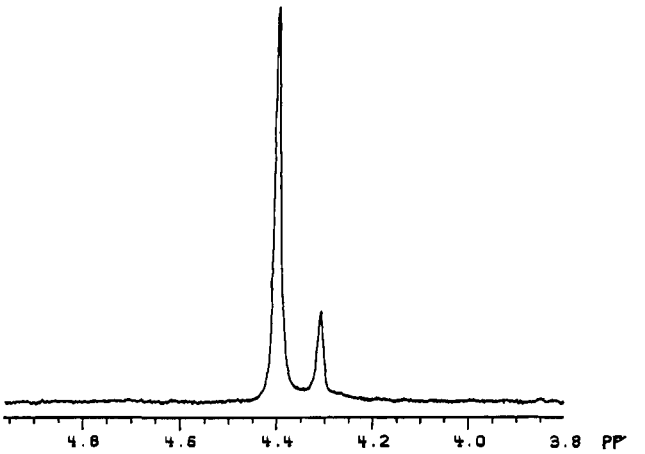


Figure 1. ^{19}F NMR spectrum (360 MHz) of the diastereomeric Mosher ester of the aldehyde **9f** in $CDCl_3$ using TFA as internal standard.

(11) Dale, J. A.; Dull, D. L.; Mosher, H. S. *J. Org. Chem.* **1969**, *34*, 2543.
(12) Heitner, C.; Leffek, K. T. *Can J. Chem.* **1966**, *44*, 2567.

monosubstituted aromatic ring had an sp^3 carbon in the ortho position were stable toward racemization while those which had a methoxy group in this position showed a much greater propensity to racemize. Of further interest is the greater stability of the biphenyloxazolines **4** compared to the biphenylaldehydes **9** presumably due to the ability of the substituents on the oxazoline ring to augment hindrance to rotation.

In summary, we have introduced methodology which allows for the general, enantioselective preparation of 2,2',6-trisubstituted biphenyls. Careful optimization of experimental parameters has afforded these biphenyls in good chemical yields and useful ee's. Kinetic studies have elucidated the nature of the substitution pattern needed to achieve thermal stability and should prove useful in designing a synthesis which contains this moiety. Further studies are currently under investigation in the laboratories.

Experimental Section

2,3-Disubstituted Phenyloxazolines 3a and 3b. To 21.5 g (0.13 mol) of 2-methoxy-3-methylbenzoic acid in 150 mL of CH_2Cl_2 at 0 °C, in an inert atmosphere, was slowly added 21.4 g (0.17 mol) of oxalyl chloride. The reaction mixture was stirred for 14 h, allowing to warm to room temperature. After cooling to 0 °C, 150 mL of 30% ammonium hydroxide solution was cautiously added over a 15-min period. The mixture was poured into 800 mL of water and extracted with 2 × 1000 mL of ether. Drying over magnesium sulfate and concentrating afforded the benzamide as a white solid (mp 100–101 °C, 87%). Then, 6.30 g (0.038 mol) of the benzamide was added to a solution of 7.26 g (0.038 mol) of triethyloxonium tetrafluoroborate in 250 mL of 1,2-dichloroethane at room temperature under an inert atmosphere. This was stirred for 22 h, and 7.61 g (0.042 mol) of (+)-1-methoxy-2-amino-3-phenyl-3-hydroxypropane[9] was added. The mixture was heated to reflux for 24 h, cooled, poured into 250 mL of CH_2Cl_2, washed with saturated sodium bicarbonate, dried over magnesium sulfate, and concentrated. Silica gel flash column chromatography (35% EtOAc/hexanes) afforded 11.4 g (96%) of phenyloxazoline **3a** as an oil: PMR ($CDCl_3$) δ 2.30 (s, 3 H), 3.38 (s, 3 H), 3.52–4.05 (m, 2 H), 3.77 (s, 3 H), 4.20–4.60 (m, 1 H), 5.47 (d, J = 6 Hz, 1 H), 6.85–7.90 (m, 8 H); IR ($CHCl_3$) 3000, 1640 cm^{-1}.

In the same manner, 2,3-dimethoxybenzoic acid was first converted to the benzamide (mp 132–134 °C, 74%) which was converted to the phenyloxazoline **3b** in 88% yield: PMR ($CDCl_3$) δ 3.40 (s, 3 H), 3.60–3.85 (m, 2 H), 3.83 (s, 6 H), 4.18–4.55 (m, 1 H), 5.50 (d, J = 6 Hz, 1 H), 6.98–7.65 (m, 8 H); IR ($CHCl_3$) 3000, 1640 cm^{-1}.

General Procedure for Coupling Biphenyls 4. To 2.2 mmol of magnesium turnings in 3 mL of dry ether at 20 °C, under an inert atmosphere, was added 2.0 mmol of aryl bromide. The reaction was allowed to stir for 1 h for Grignard formation. To this solution was added 1.0 mmol of aryloxazoline in 3 mL of dry THF. The resulting mixture was then stirred for 24 h. The solution was poured into saturated ammonium chloride and extracted with Et_2O. The organic layer was washed with brine, dried over potassium carbonate, and concentrated. Purification by silica gel flash column chromatography (35% or 50% EtOAc/hexanes) afforded the mixture of diastereomeric biphenyloxazolines **4** as oils.

In one case, diasteromeric biphenyls were separable by silica gel chromatography. Deprotection of the (*tert*-butyldimethylsilyl)biphenyl **4e** with 2% HF in acetonitrile at room temperature for 30 min gave the corresponding (hydroxymethylene)biphenyls which were separated by silica gel chromatography. Developing twice in diethyl ether gave the minor diastereomer (18.5%) (R_f 0.54; NMR ($CDCl_3$) δ 3.16 (s, 3 H), 2.80–3.40 (m, 2 H), 3.70 (s, 3 H), 3.90–4.11 (m, 1 H), 4.36 (s, 2 H), 4.46 (br s, 1 H), 5.22 (d, J = 7 Hz, 1 H), 6.70–7.60 (m, 12 H)) and the major diastereomer (73.5%) (R_f 0.43; NMR ($CDCl_3$), 3.32 (s, 3 H), 3.32–3.48 (m, 2 H), 3.70 (s, 3 H), 3.70–3.90 (m, 1 H), 4.36 (s, 2 H), 4.92 (br s, 1 H), 5.22 (d, J = 7 Hz, 1 H), 6.70–7.60 (m, 12 H)). The relative ratios of the hydroxymethylenebiphenyls (80:20) reflect very closely the ratio observed for the (*tert*-butyldimethylsilyl)biphenyls **4e** (79:21).

Reductive Cleavage of Biphenyloxazolines 4. General Procedure. The procedure used was one recently reported by us and is herein described in condensed form.[10] To 1 mmol of biphenyloxazoline **4** in 5 mL of ether at 0 °C, under an inert atmosphere, was added 5 mmol of a 1 M solution of DIBAL. The reaction was allowed to stir at room temperature and was monitored for the disappearance of the biphenyloxazoline by thin-layer chromatography on silica gel. The solution was cooled to 0 °C and was slowly quenched with 1 M HCl. The layers were separated, and the aqueous layer was made alkaline with 5 M NaOH and was extracted with K_2CO_3 to give, after concentration, the biphenylamino alcohol **5**.

To 1.0 mmol of the amino alcohol **5** in 5 mL of THF was added 2.1 mmol of imidazole, and the reaction was stirred for 12 h at room temperature under a nitrogen atmosphere. The mixture was diluted with ether, washed with saturated sodium bicarbonate and brine, and dried over magnesium sulfate. Purification by silica gel column chromatography (25% EtOAc hexane) afforded the silyl ether 6. To 1.0 mmol of silyl ether **6** in 2 mL of CH_2Cl_2 was added 1.0 mmol of *N*-chlorosuccimide, and the reaction was stirred for 15 min. Filtration was through a small plug of silica gel, and concentration afforded the chloramine **7**. This was dissolved in 5 mL of ether, 2.2 mmol of potassium superoxide and 5 mg of 18-crown-6 were added, and the reaction was stirred at room temperature under an inert atmosphere for 3–6 h. Filtration and concentration afforded the imine **8**, which was directly hydrolyzed to the aldehyde **9** by stirring in 1:1 saturated oxalic acid–pentane at room temperature for 12 h. The organic layer was separated, washed with sodium bicarbonate, dried ($MgSO_4$), and concentrated to afford the aldehyde **9**, which was purified by silica gel thin-layer chomatography (25% Et_2O/hexane).

Conversion of Biphenylaldehydes 9 to Mosher Esters. General Procedure. To 0.10 of mmol of biphenylaldehyde **9** in 1 mL of absolute EtOH at room temperature was added 0.10 mmol of sodium borohydride. The reaction mixture was stirred for 0.5 h and poured into saturated sodium bicarbonate. The biphenyl alcohol was extracted with Et_2O and dried over $MgSO_4$. Filtration and concentration afforded the biphenyl alcohol in greater than 90% yield. To the biphenyl alcohol in 0.5 mL of carbon tetrachloride and 0.5 mL of pyridine was added 1.20 equiv of (−)-α-methoxy-α-(trifluoromethyl)phenylacetyl chloride. The reaction was stirred at room temperature for 12 h and poured into 1 M HCl. Extraction with ether followed by washing with saturated sodium bicarbonate, drying over magnesium sulfate, and concentrating afforded the crude ester. Purification of the ester was carried out by silica gel thin-layer chromatography using 3–5% Et_2O–CCl_4 as the eluant. The Mosher ester was thus prepared in greater than 90% yield.

Kinetic Measurements on Rates of Biphenyloxazolines 4 and Biphenylaldehydes 9. The kinetic runs were carried out at a concentration of 0.1 M and were run in toluene at 110 °C using a constant temperature bath. Solution samples were heated under a nitrogen atmosphere and were periodally monitored by immersing the reaction vessel in an ice bath, removing the toluene under reduced pressure, and measuring the optical activity in chloroform. The chloroform was then removed under reduced pressure and the sample redissolved in toluene and immersed in the constant temperature bath. The time involved in this operation was not counted in the reaction time, and the induction period involved with the cooling and heating processes did not appear to significantly affect the results as evidenced by the standard deviation of the slope of the kinetic plots. The rate constants were calculated by the method of least-squares from the equation

$$2kt = \ln \frac{\alpha_0 - \alpha_\infty}{\alpha_t \alpha_\infty}$$

where k is the first-order rate constant, t is the time, and α_0, α_t, and α_∞ are the optical rotations at the kinetic zero, time t, and after ten half-lives, respectively. The errors represent the 95% confidence limit from the least-squares analysis. Interestingly, the oxazolines measured all racemized to a 1:1 mixture of diastereomers, indicating that the chiral oxazoline has no influence on the thermodynamic stability of one diastereomer with respect to the other.

Acknowledgment. We are grateful to the National Institutes of Health for financial support of this work and to the Colorado State University Regional NMR Center funded by the National Science Foundation.

Supplementary Material Available: Complete spectroscopic data for amino alcohols **5**, silyl ethers **6**, Mosher esters of **9**, four additional chiral biphenyloxazolines, not taken to aldehydes **9**, and a graphic description of the kinetic data for the rate of racemization of **9e** (5 pages). Ordering information given on any current masthead page.