Synthesis, Resolution, and Determination of Absolute Configuration of a Vaulted 2,2′-Binaphthol and a Vaulted 3,3′-Biphenanthrol (VAPOL)

Jianming Bao,[†] William D. Wulff,*[,†] James B. Dominy,[†] Michael J. Fumo,[†] Eugene B. Grant,[†] Alexander C. Rob,[†] Mark C. Whitcomb,[†] Siu-Man Yeung,[†] Robert L. Ostrander,[‡] and Arnold L. Rheingold[‡]

Contribution from the Searle Chemistry Laboratory, Department of Chemistry, University of Chicago, Chicago, Illinois 60637, and Department of Chemistry, The University of Delaware, Newark, Delaware 19716

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Abstract: Two methods for the synthesis of vaulted biaryls were developed involving the reactions of carbene complexes with alkynes and the [2 + 2] cycloaddition of ketenes. The final step in the synthesis of 3,3′-diphenyl-[2,2′-binaphthalene]-1,1′-diol (**39**) and 2,2′-diphenyl-[3,3′-biphenanthrene]-4,4′-diol (**47**) (VAPOL) was phenol coupling of the 3-phenyl-1-naphthol (**14**) and the 2-phenyl-4-phenanthrol (**28**), respectively. The naphthol **14** could be prepared from the thermolysis of phenylacetyl chloride in the presence of phenylacetylene or from the benzannulation of the pentacarbonyl(phenylmethoxymethylene)chromium(0) (**15**) with phenylacetylene which upon an acetylative workup gives *O*-acetyl-4-methoxy-2-phenyl-1-naphthol (**16**). The reductive cleavage of the acetoxy group in **16** was unexpectedly affected by aluminum chloride and ethanethiol which were used to cleave the methyl ether. In a similar manner, the phenanthrol **28** could either be prepared from the 1-naphthylacetyl chloride (**30**) or pentacarbonyl-(1-naphthylmethoxymethylene)chromium(0) (**21**). A new procedure for the preparation of carbene complexes was developed utilizing dimethyl sulfate as methylating agent. Unlike the benzannulation of the phenyl complex **15**, the benzannulation of the naphthylcarbene complex **21** with phenylacetylene gave a side product which resulted from the incorporation of 2 equiv of the alkyne. This side product could be minimized by the proper control of the concentration of the alkyne. The phenol coupling of the 3-phenyl-1-naphthol with ferric chloride gave 2,2′-diphenyl-[2,2′-binaphthalene]-4,4′-diol (**38**) and with air as oxidant gave the of 3,3′-diphenyl-[2,2′-binaphthalene]-1,1′-diol (**39**). Oxidative coupling of the 2-phenyl-4-phenanthrol (**28**) with air gave 2,2′-diphenyl-[3,3′-biphenanthrene]-4,4′-diol (**47**) (VAPOL), but the same coupling with 2-*tert*-butyl-4-phenanthrol (**34**) failed. The 2,2′-binaphthol **39** was resolved via its cyclic diester with phosphoric acid by salt formation with (−)-brucine, and the 3,3′-biphenanthrol **47** was resolved via its cyclic deiester with phosphoric acid (**49**) by salt formation with (−)-cinchonidine. The configuration of (−)-**39** was shown to be *S* from an X-ray analysis of the brucine salt, and the configuration of (+)-**47** was shown to be *S* from an X-ray analysis the amide (*S*,*S*)-**54** derived from **49** and (*S*)-α-methylbenzylamine.

The enantiomeric atropisomers of 1,1′-binapth-2-ol are among the most widely used ligands in asymmetric synthesis. The binaphthol **1a** (Chart 1) has been used as a ligand for both stoichiometric and catalytic asymmetric reactions with success achieved over a truly impressive range of reactions.[1] The current use of 1,1′-binaphthol is so pervasive that a comprehensive citation is not possible here. The range of applications that have appeared since 1994 for 1,1′-binaphthol and its derivatives[2] includes Diels−Alder,[4] aldol,[5] Michael,[6] Ene reactions,[7] carbonyl additions,[8] carbonyl reductions,[9] heteroatom Diels−Alder,[10] alkylations,[11] π-allyl additions,[12] [3 + 2]-cycloadditions,[13] [2 + 2]-cycloadditions,[14] Claisen rearrangements,[15] reductive cyclization,[16] olefin additions,[17] epoxidation,[18] epoxide opening,[19] asymmetric protonation,[20] hydrosilylation,[21] hydroformylation,[22] ring opening metathesis polymerization,[23] group transfer polymerization,[24] alkene, diene, and alkyne polymerization,[25] molecular recognition,[26] nonlinear optical and other materials,[27] phase transition induction,[28] and membrane bilayers.[29]

[†] University of Chicago.

[‡] The University of Delaware.

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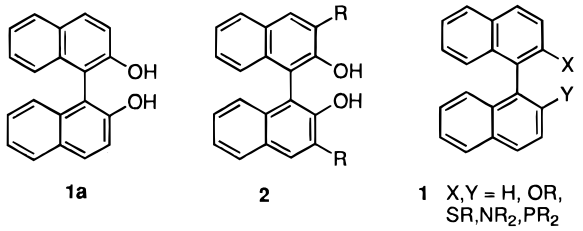
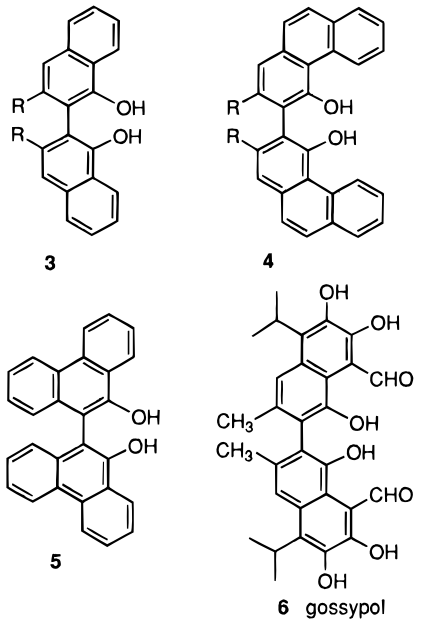
Chart 1



1a **2** **1** X,Y = H, OR, SR,NR_2,PR_2

A few years ago we began work on a program to prepare and evaluate a series of new biaryl ligands of the type **3** and **4** where the phenol functions were embedded within a chiral pocket created by the walls of the biaryl unit. When this work was initially conceived, a search of the literature revealed that no examples of the vaulted biaryls **3** or **4** were known except for the parent 2,2′-binaphthol (**3**) (R = H).[32] This included a search for 3,3′-biphenanthrols in which all of the aryl sites were left open. However, when all sites were left open in the search for 2,2′-binaphthols the 6,6′-biphenanthrol (**5**) and gossypol (**6**) were identified as well as a large number of derivatives of gossypol (Chart 2). Gossypol is abundant in cotton seeds and has received considerable attention for its male antifertility activity.[33] While neither gossypol or its derivatives have been investigated as chiral ligands in catalysis, the biphenanthrol (**5**) has received some such attention. This compound contains both 1,1′-binaphthol and 2,2′-binaphthol units, and the studies of this compound as a chiral ligand have not revealed any significant advantages over the 1,1′-binaphthol (**1a**).[34] In contrast, we

Chart 2



recently reported that both of the vaulted biaryls **3** and **4** (R = Ph) are superior to the linear biaryls **1a** or **2** (R = Ph_3Si) as a ligand in Lewis acid-catalyzed Diels−Alder reactions.[30] We report herein the preparation, resolution, and determination of the absolute configuration of the vaulted 2,2′-binaphthol **3** (R = Ph) and the vaulted 3,3′-biphenanthrol **4** (R = Ph).

The two synthetic approaches to the vaulted biaryls **3** and **4** are outlined in Scheme 1 and have in common the last step

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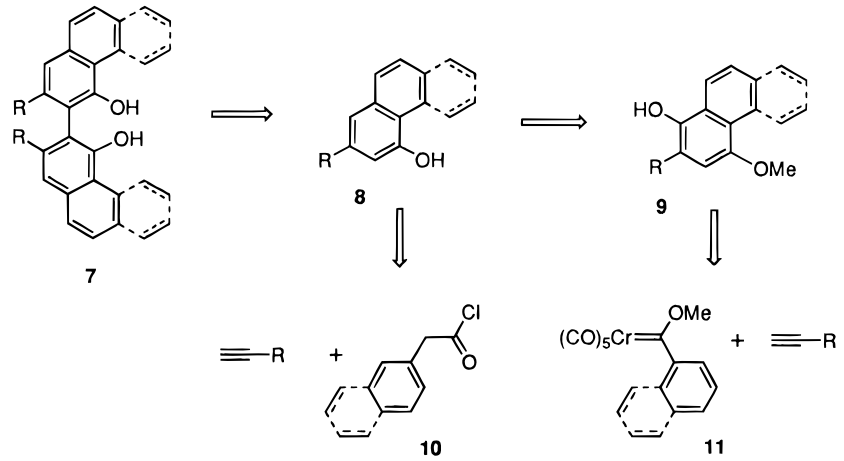
Scheme 1



which is an oxidative phenol coupling reaction.[35] One approach to the monomeric phenol intermediate **8** is a benzannulation process that in the retrosynthetic analysis requires a [2 + 2] cycloaddition of a terminal acetylene with an aryl ketene generated from the corresponding acid chloride **10**.[36,37] The second approach to be considered is the benzannulation of an arylcarbene complex with an alkyne which would initially produce the *p*-methoxyphenol intermediate **9**.[38] The use of **9** as a precursor of **8** would require the reduction of the phenol function and a deprotection of the methyl aryl ether. Both of these approaches have been evaluated for the synthesis of **3** and **4**, and the relative merits of each will be discussed. Since the resolution of **3** and **4** into atropisomers will require that the substituent R be non-hydrogen and since it is desirable that the enantiomers of **3** and **4** be robust with respect to racemization, the synthetic approaches outlined in Scheme 1 will be evaluated with R = Ph and R = *t*-Bu.

Both of the approaches outlined in Scheme 1 are viable for the preparation of 3-phenyl-1-naphthol (**14**), the monomer required for the preparation of 2,2′-binaphthol **39** (**3**, R = Ph). The preparation of **14** from phenylacetyl chloride **12** and phenylacetylene has been previously reported and can be obtained in 56% overall yield from **12**.[36] The reaction is thought to involve the [2 + 2] cycloaddition of phenylketene and phenylacetylene, electrocyclic ring opening, and finally an electrocyclic ring closure of the β-phenylvinylketene species **18**. The benzannulation reaction of the chromium carbene complex **15** with phenylacetylene is carried out as indicated in the presence of acetic anhydride and triethylamine to give the acylated naphthol **16** in 93% yield. The last step in this process is related mechanistically to that for the conversion of **12** to **13** and is thought to involve the cyclization of the metal-complexed β-phenylvinylketene species **20**.[38,39] The naphthol formed from the reaction of complex **15** and phenylacetylene was trapped as its acetate by the method of Yamashita[40] in preparation for the cleavage of the methyl ether. The treatment of naphthol derivative **16** with aluminum chloride and ethanethiol was performed to cleave the methyl ether, but much to our surprise this resulted in a reduction of the acetoxyl group as well.[41] This of course was a much welcomed result since, as outlined in Scheme 1, the synthetic plan for the removal of this group anticipated that at least two additional steps would be required via procedures that involved the reduction of an aryl triflate.[42] The demethylation occurs first since with insufficient reaction times, varying amounts of the 4-acetoxyphenol **19** can be isolated from the reaction. For the large scale synthesis of **14**, the route starting from phenylacetyl chloride is the most desirable. It is necessary for the oxidative coupling step that the naphthol **14** be quite pure, and on a large scale it was possible to obtain sufficiently pure material without column chromatography only from the crude mixture obtained from the reaction of phenylacetyl chloride and phenylacetylene.

The synthesis of a phenanthrol monomer of the type **8** (Scheme 1) from the benzannulation reaction of a carbene

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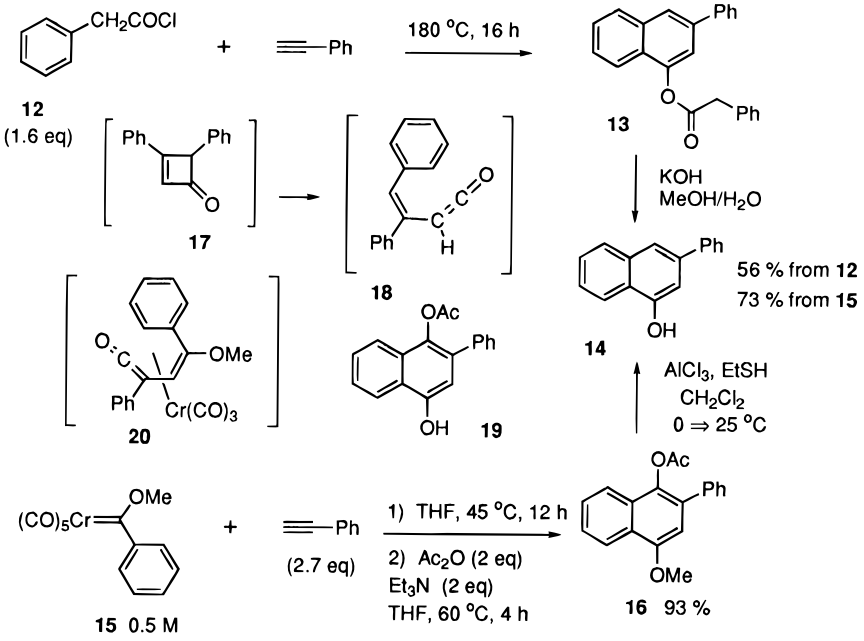
Scheme 2

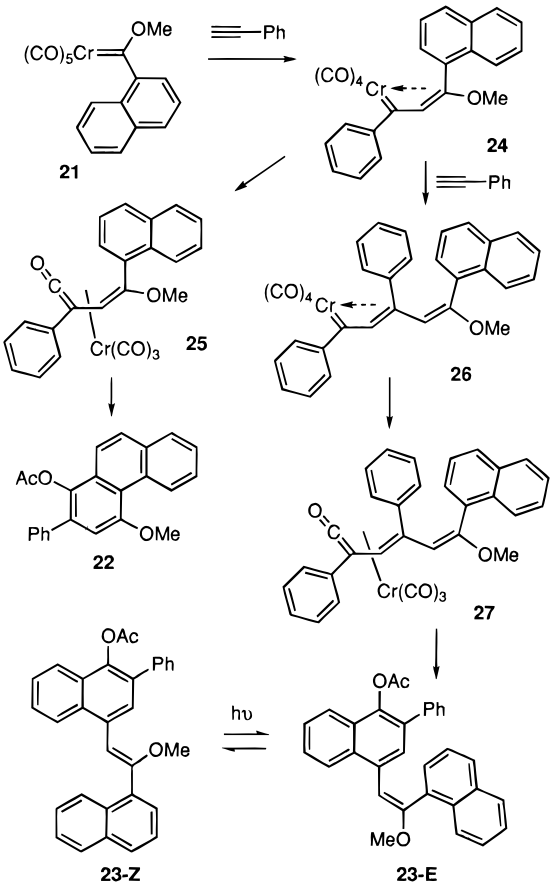


complex was pursued with the unsubstituted 1-naphthylcarbene complex **21**. Complex **21** is a known compound,[44] but we have developed a new procedure for the synthesis of this complex that involves the use of dimethyl sulfate as methylating agent. This was developed in an effort to minimize cost and maximize convenience for large-scale throughput. Dimethyl sulfate has not been previously used as a methylation agent due to poor yields and low reactivity.[45] This has been overcome by generating the more reactive potassium salt of the metal acylate by washing the lithium acylate with aqueous HCl to generate a solution of a hydroxycarbene complex and directly exposing this solution to solid potassium carbonate and dimethyl sulfate.

The benzannulation of the naphthylcarbene complex **21** with phenylacetylene produced an additional product which was not observed in the reactions of the phenylcarbene complex **15**. In addition to the desired 1,2,4-trisubstituted phenanthrene **22**, the bis(naphthyl)ethylene **23** was also isolated from this reaction as a single stereoisomer whose stereochemistry was determined to be *E* as will be described below. This product results from the incorporation of 2 equiv of phenylacetylene and a cyclization with CO insertion onto the phenyl ring of the first phenylacetylene unit that was incorporated. This type of product has been seen previously, but significant formation of this type of product has only been seen when the normal cyclization is not possible.[46]

As indicated in Scheme 3, it was found that the stereochemistry of the olefin product **23** has the *E*-configuration. This was confirmed when the product obtained from the reaction was photolyzed in benzene to produce its olefin isomer which was separated and characterized. The stereochemistry of these olefin isomers was assigned on the basis of NOE studies which revealed that only one of the isomers displayed an enhancement at the vinyl hydrogen when the methoxyl group was irradiated. Since the primary product **23** has the *E*-configuration, it must

Scheme 3



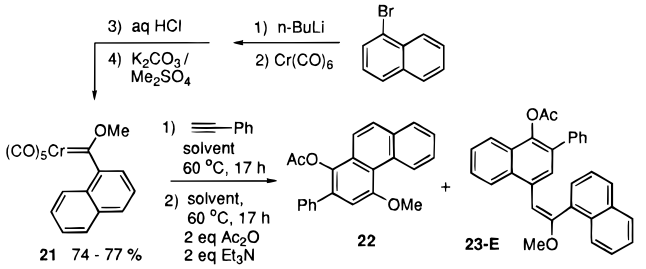
have arisen from a vinylcarbene-complexed intermediate (**24**) that has an *E*-configuration, the necessary stereochemistry for cyclization to the phenanthrol product **22**. The branchpoint in the mechanism thus is the vinylcarbene complex **24**, and the product distribution is thus determined by the relative rates of a unimolecular CO insertion to give the vinyl ketene complexed intermediate **25** and a bimolecular reaction with phenylacetylene to give homologated vinyl carbene complexed intermediate **26**. These mechanistic considerations lead to the prediction that product distribution will be concentration dependent with lower

(44) Fischer, E. O.; Kreiter, C. G.; Kollmeier, H. J.; Muller, J.; Fischer, R. D. *J. Organomet. Chem.* **1971**, *28*, 237.

(45) Hoye, T. R.; Chen, K.; Vyvyan, J. R. *Organometallics* **1993**, *12*, 2806.

(46) (a) Challener, C. A.; Wulff, W. D.; Anderson, B. A.; Chamberlin, S.; Faron, K. L.; Kim, O. K.; Murray, C. K.; Xu, Y.-C.; Yang, D. C.; Darling, S. D. *J. Am. Chem. Soc.* **1993**, *115*, 1359. (b) Dietz, R.; Dötz, K. H.; Neugebauer, D. *Nouv. J. Chim.* **1978**, *2*, 59. (c) Wulff, W. D.; Kaesler, R. W.; Peterson, G. A.; Tang, P. C. *J. Am. Chem. Soc.* **1985**, *107*, 1060.

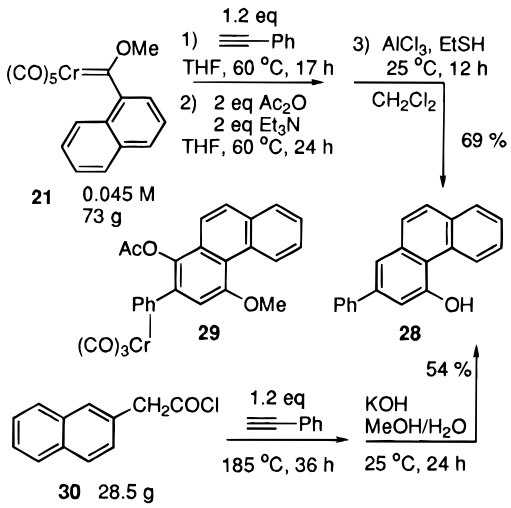
Table 1. Benzannulation of Naphthylcarbene Complex **21** with Phenylacetylene[a]



[**21**] (M)	[alkyne] (M)	solvent	yield of **22** (%)	yield of **23**-*E* (%)	yield of **23**-*Z* (%)
0.005[b]	0.01	THF	79	<1.2	ND[c]
0.03[d]	0.06	THF	65	8	ND
0.05	0.10	THF	66	<13	ND
0.5	1.0	THF	38	32	ND
0.5[e]	0.6	THF	74	8[f]	<0.5[f]
0.5	1.0	benzene	36	25	<1.7[f]
0.5	1.0	CH_3CN	22	18	<2.8[f]

[a] Unless otherwise specified, all yields are isolated. [b] 0.1 equiv of DMAP was included in the acetylation step. [c] Not determined. [d] Concurrent reaction: reagents for acetylation were added with the alkyne. [e] The alkyne (1.2 equiv) was added via syringe pump over 6 h at 65 °C and then stirred for 1 h longer before acetylation. [f] Maximum yield determined on crude reaction mixture by ^{1}H NMR.

Scheme 4



concentration favoring the phenanthrol product **22**. The data in Table 1 show that this is the case and that the distribution drops from nearly an equal mixture at a starting carbene complex concentration of 0.5 M with 2 equiv of alkyne to at least a 66:1 ratio in favor of the phenanthrol when the concentration is lowered by a factor of 100. For the purposes of large-scale preparation, the reaction can be run at high concentrations, avoiding the need for large volumes of solvent, and without the formation of an unduly large amount of the side product **23** if the phenyacetylene is added slowly to a refluxing solution of the carbene complex (entry 5, Table 1).

The synthesis of 2-phenyl-4-phenanthrol (**28**) from the benzannulation reaction of the naphthylcarbene complex **21** was accomplished in 69% overall yield on a 73 g scale as indicated in Scheme 4. While small-scale reactions gave the desired phenanthrol acetate **22** that had been completely divested of the metal, larger scale reactions gave varying amounts of the metal complex **29** where the chromium tricarbonyl group had migrated to the phenyl substituent. It was not necessary to separate **22** and **29** and/or to drive the demetalation to completion by heating in the presence of air since the latter occurred under the reduction conditions. Treatment with aluminum chloride and ethanethiol gave phenanthrol **28** in 69% overall yield. The free vinylketene approach to the synthesis of phenanthrol **28** was also successful, providing a 54% overall yield of **28** from 2-naphthyl acetyl chloride (**30**). However, it was not possible to purify **28** from the black tarry material obtained from this reaction without careful column chromatography. Thus, in this case it was found that for large-scale preparation it was best to utilize the route from the carbene complex.

The *tert*-butyl-substituted phenanthrol **34** was prepared as a potential precursor to the 3,3′-biphenanthrol **4** (Chart 2, R = *tert*-Bu) since the *tert*-butyl group, like a phenyl group, would be expected to provide a high barrier to racemization. The benzannulation of the naphthylcarbene complex with *tert*-butylacetylene gave a 91% total yield of the phenanthrol **31** and the metal complex **32** (Scheme 5). Despite the presence of the free phenol function on the benzene ring coordinated by the chromium tricarbonyl group, complex **32** is surprisingly stable to air and silica gel, presumably due to the steric bulk of the *tert*-butyl group. The acetylization of this mixture occurred with loss of the metal to give **33** in 54% overall yield from the carbene complex **21**. Demethylation and deacetoxylation with ethanethiol and aluminum chloride occurred smoothly to provide the phenanthrol **34** in 85% yield.

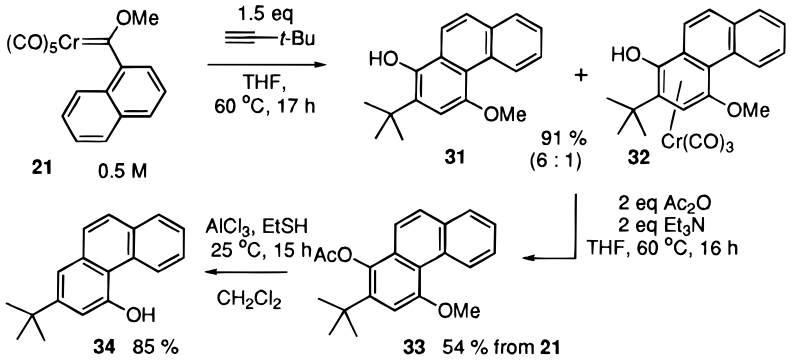
The 1,1′-binaphthol **1a** is prepared by an oxidative coupling of β-naphthol which was first reported by Pummerer in 1928 who used ferric chloride to give **1a** in greater than 90% yield.[47] Interestingly, the oxidative coupling of α-naphthol **35** was reported approximately 50 years earlier by Dainin to give the para,para-coupling product **36**.[32a] Some 70 years later, Edwards and Cashaw demonstrated that this reaction also produces the ortho,ortho-coupling product **37** as a minor product in the oxidative coupling; however, the ratio of the two products were never reported.[32c] This precedent did not bode well for the proposed oxidative coupling of the 3-phenyl-1-naphthol (**14**). Even with the knowledge of this precedent, it was disappointing to find that the coupling of **14** with ferric chloride gave the para,para-coupled product **38** in 62% yield (Scheme 6). Two minor products were observed in this reaction which remain unidentified, but it was determined that neither was the desired ortho,ortho-coupled product **39**. One solution to this problem would involve a slight adjustment of the target vaulted biaryl. Retention of the oxygen substituent in the 4-position of the product **9** (Scheme 1) makes para,para coupling impossible and would produce vaulted biaryl **7** with an oxygen substituent in the 4- and 4′-positions. While this might produce vaulted biaryl derivatives with quite different electronic properties, it would not solve the problem for the general case.

In their studies on the synthesis of gossypol, Edwards and Cashaw found that the 3-methyl-1-naphthol derivative **40** gave a low yield of the ortho,ortho-coupled product **41** when treated with ferric chloride.[48] However, they reported that a quantitative yield of **41** could be obtained if the monomer **40** was oxidized by air by simply placing **40** in a test tube and placing it in an oil bath and heating until a melt was obtained and then after 20 min the product **41** resolidified in the test tube.[48b] Despite the high selectivity of this reaction, it was not clear how this would translate to the oxidative air coupling of **14**. It would be reasonable to argue that the oxidative coupling of **40** would be

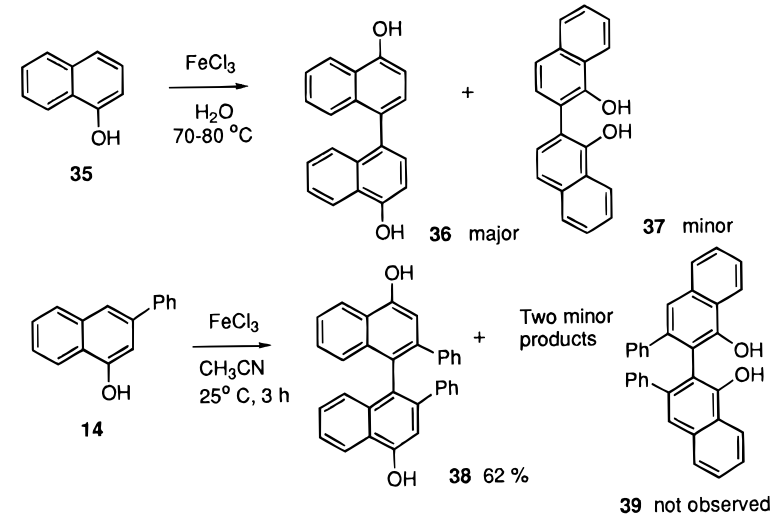
(47) Pummerer, R.; Prell, E.; Reiche, A. *Ber*. **1926**, *59B*, 2159.

(48) (a) Edwards, J. D., Jr. *J. Am. Chem. Soc*. **1958**, *80*, 3798. (b) Edwards, J. D., Jr.; Cashaw, J. L. *J. Am. Chem. Soc*. **1957**, *79*, 2283. For recent citations, see: (c) Ognyanov, V.; Petrov, O.; Tikholov, E.; Mollov, N. *Helv. Chim. Acta* **1989**, *72*, 353.

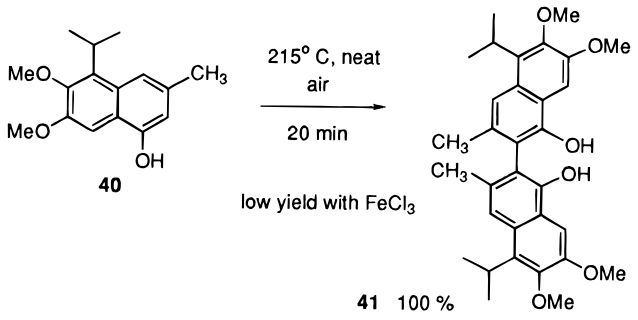
Scheme 5



Scheme 6



Scheme 7



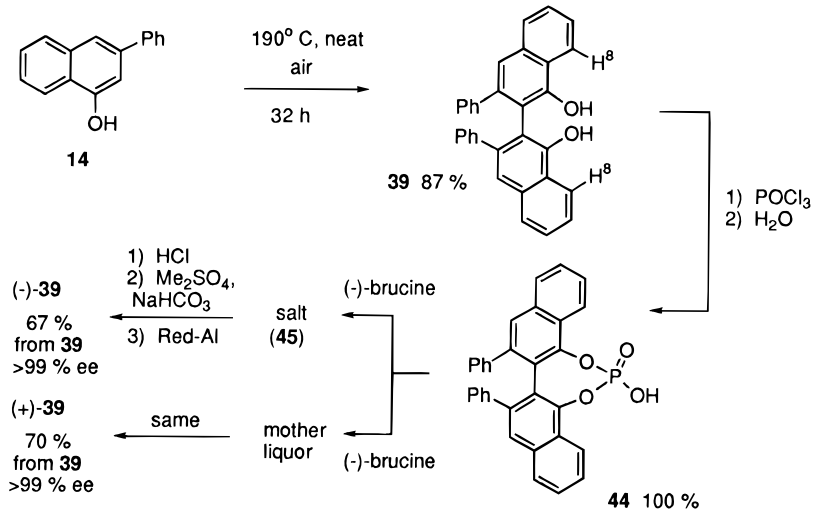
expected to favor the ortho,ortho-coupled product **41** since the formation of the para,para-coupled product would presumably be strongly disfavored of the presence of the isopropyl groups (Scheme 7).

In light of the uncertain prediction that arose from the consideration discussed above, it was a delight to find that when 3-phenyl-1-naphthol (**14**) was melted at 190 °C in a test tube in the presence of air the 2,2′-binaphthol **39** was obtained in 87% yield. Although the difference in regiochemistry between oxidation with air and with iron(III) is not understood, it may be due to the fact that a metal-free phenol radical is not generated in the latter. The resolution of acid **44** was achieved with (−)-brucine which led to the selective precipitation of a single diastereomer of the brucine salt **45** which, with one crystallization, was free of the other diastereomer as indicated by ^{31}P NMR. The levorotatory enantiomer of **39** was released from the salt **45** by treatment with acid, conversion to the methyl ester, and then reduction.[49] This resolution procedure gave (−)-**39** in 67% overall yield from racemic **39** with an optical purity that is greater than 99% ee as determined by HPLC on a Pirkle D-phenylglycine column (retention times: (−)-**39** t_R = 7.80 min; (+)-**39**, t_R = 7.26 min) (Scheme 8). The (+) enantiomer of **39** can be easily recovered from the filtrate that produced salt **45**. Without purification, the crude solution of the soluble diastereomer of the brucine salt is treated with acid, esterified, and then reduced to give the free (+)-binaphthol **39**. A single crystallization gives a 70% overall yield of (+)-**39** from racemic **39** in greater than 99% ee as determined by HPLC.

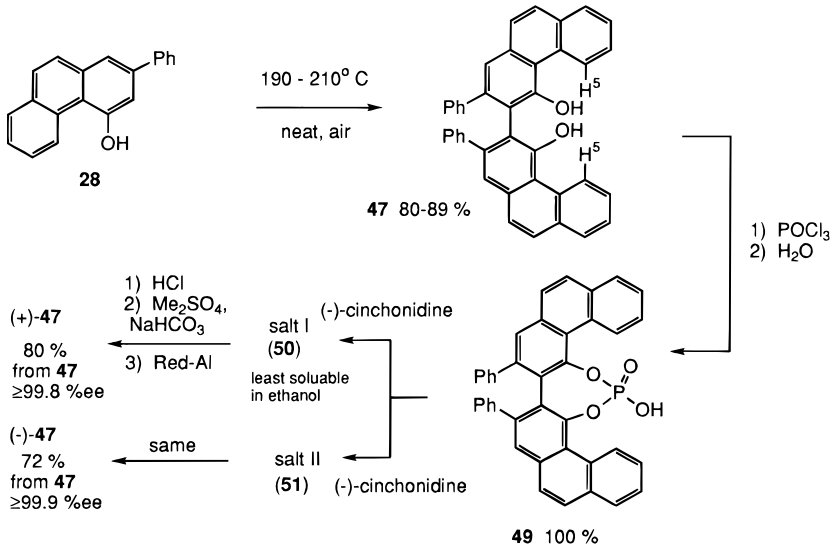
The oxidative coupling of **28** with ferric chloride, unlike that of **14**, did not produce a predominate product but rather several different products in more or less equal amounts, and as a result the disposition of this reaction was not further pursued. The oxidative coupling of the *tert*-butyl-substituted phenanthrol **34** in air was not clean and produced more than six compounds in approximately equal amounts as judged by the number of bay region doublets between 9 and 10 ppm in the ^{1}H NMR spectrum of the crude reaction mixture. The oxidative coupling of the phenanthrol **28** in air, on the other hand, was quite clean, and like the oxidation of **14**, gave the ortho,ortho-product in high yield. The phenanthrol **28** (mp = 154−55 °C) is simply placed in a beaker and then melted by placing the beaker in an oil bath at 190 °C. The reaction mixture solidifies prior to completion of the reaction due to the higher melting point of the product (mp > 250 °C). For multigram preparations, this can cause the reaction to slow down due to insufficient diffusion of air into the mixture. Deliberate injection of air or oxygen into the sample has deleterious effects on the yield which is likely due to overoxidation. This can be overcome by the

(49) (a) Jacques, J.; Fouquey, C. *Org. Synth.* **1988**, *67*, 1. (b) Truesdale, L. K. *Org. Synth.* **1968**, *67*, 13.

Scheme 8



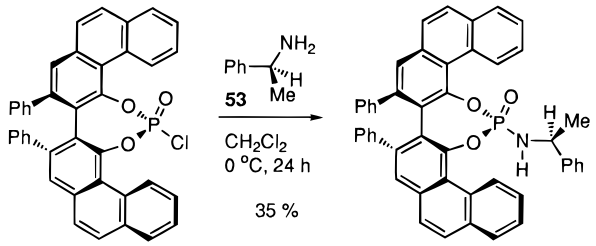
Scheme 9



addition of glass beads and stirring the reaction mixture with a large magnetic stir bar. With this technique, an 89% yield of **47** can be obtained on a 10 g scale.

The resolution of **47** can be accomplished in a manner similar to that described above for **39** except that (−)-cinchonidine is required to give crystalline salts with the cyclic phosphoric acid derivative **49**. Another difference is that in this case both diastereomers of the salt are crystalline solids which can be separated by fractional crystallization. The least soluble salt gives rise to (+)-**47** by the procedure outlined in Scheme 9 in 80% overall yield from racemic **47** in ≥99.8% ee. In a similar manner, (−)-**47** can be obtained from the second salt **51** in 72% overall yield in ≥99.9% ee as determined by HPLC with a Pirkle D-phenylglycine column. The biphenanthrol **47** apparently strongly interacts with the D-phenylglycine residues on the Pirkle column since the retention times for (−)-**47** and (+)-**47** are 12.1 and 19.8 min, respectively. As an indicator of how much more inaccessible the hydroxy groups in **47** are than those in **39**, it was found that the H^5 protons in **47** (δ = 9.71 ppm) were completely unaffected by even large excesses of $Eu(hfc)_3$. The corresponding protons H^8 in **39** (Scheme 8) are readily shifted by the same reagent and can be used in the analysis of enantiomeric purity. The enantiomeric purity of **47** can be determined by ^1H NMR with (−)-1-phenylethylamine as chiral solvating agent.[50]

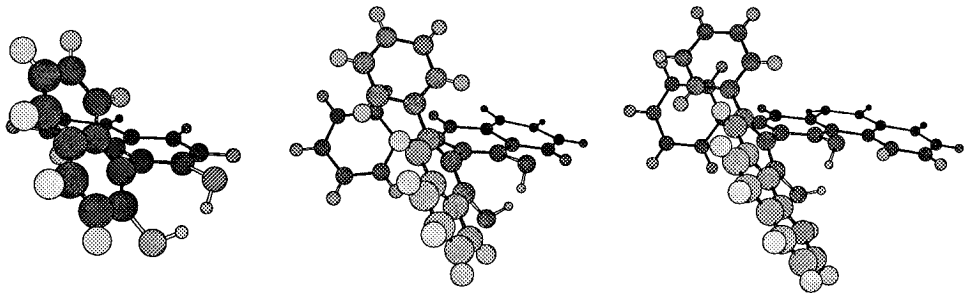
Scheme 10



The ease with which highly optically pure enantiomers of **47** can be obtained is a consequence of the large solubility difference between the racemate and each pure enantiomer. The pure enantiomers of **47** are freely soluble in hexane but the reacemate is not. For example, if a scalemic sample of 150 mg of **47** of 84% ee is washed three times with 5 mL of hexane, there remains 58 mg of undissolved **47** of 57% ee and the hexane solution contains 90 mg of **47** that is ∼100% ee. Thus, final purification to nearly complete optical purity can easily be obtained by hexane extraction or by chromatography on silica gel from which the racemate elutes much more slowly with hexane than the pure enantiomers.

(50) Pirkle, W. H.; Hoekstra, M. S. *J. Magn. Reson.* **1975**, *18*, 396.

Chart 3



The absolute configuration of the enantiomers of the biphenanthrol **47** where determined by an X-ray structure of the (*S*,*S*)-isomer of **54** which was prepared by the reaction of the acid chloride **48** (obtained from (+)-**47**) with (*S*)-1-phenylethylamine (**53**).[51] It is interesting to note that the acid chloride **48** is stable to silica gel and will not react with the lithium salt of (+)-*sec*-phenylethyl alcohol. The amide **54** was only obtained in 35% yield, (Scheme 10), but perhaps this could be improved if the reaction was performed with the amide anion generated from **53**.[52] Since **54** contains the *S*-configuration about the biaryl axis, the dextrorotatory enantiomer of **47** must also have the *S*-configuration as (*S*,*S*)-**54** was prepared from (+)-**47**. In contrast, the absolute configuration of the dextrorotatory enantiomer of **39** was found to have the *R*-configuration. This was determined by an X-ray diffraction of the salt **45** prepared from the phosphoric acid derivative **44** and (−)-brucine, and the details can be found in the supporting information. The salt **45** contains an *S*-configuration about the biaryl axis and thus so must the levorotatory enantiomer of the vaulted biaryl **39**.

The enantiomers of **39** and **47** are quite robust with respect to thermal racemization. The thermal isomerization of the atropisomers of **39** was examined. A sample of (−)-**39** was dissolved in octane and sealed in a tube and heated at 200 °C. After 3 h, 10% racemization was observed, and after 15 h 30% racemization was observed. Assuming an Arrhenius preexponential factor of 10^{13}, this rate of racemization corresponds to a rotation barrier of approximately 40 kcal/mol.[53]

As is illustrated in Chart 3, the *R*-enantiomer of **39** has the same sign of optical rotation as the *R*-enantiomer of **1a**, whereas the *R*-enantiomer of **47** has the opposite sign of rotation as the *R*-enantiomer of **1a**. This is consistent with the fact that catalysts derived from diethylaluminum chloride and the (+)-enantiomers of **39** and **47** give opposite enantiomers of the Diels−Alder adduct from the reaction of methacrolein and cyclopentadiene.[30a] The fact that catalysts derived from bromoborane and the *R*-enantiomers of **1a** and **39** give different enantiomers of cycloadducts in the same Diels−Alder reaction apparently has an alternate explanation.[30b]

We have described herein methods for the synthesis and resolution of the first members of the vaulted biaryls of the type **3** and **4**. The monomer **14** for the preparation of the 2,2′-binaphthol **39** is best prepared by a benzannulation reaction of the acid chloride **12** with phenylacetylene. The monomer **28** for the preparation of the 3,3′-biphenanthrol (**47**) (VAPOL) is best prepared by the benzannulation reaction of the carbene complex **21** with phenylacetylene. The oxidative coupling of both monomers is most efficient with air as oxidant, and the resolution of the resulting vaulted biaryls **39** and **47** was realized in each case by a classical resolution of their cyclic phosphoric acid derivatives **44** and **49**. In this manner the optically pure 2,2′-binaphthol **39** can be obtained in 36% overall yield from bromobenzene which includes the four chemical steps for the preparation of racemic **39** and the resolution via the acid **44**. Optically pure 3,3′-biphenanthrol (**47**) (VAPOL) can be obtained in 40% overall yield from 1-bromonaphthalene which includes the four chemical steps for the preparation of racemic **47** and the resolution via the acid **49**. Given the efficacy of catalysts derived from the VAPOL ligand **47** in the Diels−Alder reaction,[30] the relatively straightforward procedure for the large scale preparation of **47** described herein should be important in providing quantities of **47** sufficient for the evaluation of its use in other asymmetric catalytic reactions. The most cumbersome aspect of the synthesis of the VAPOL ligand **47** is the resolution and other methods of deriving optical pure **47** from the racemate are currently being evaluated.

Experimental Section

All reagents were obtained from commercial suppliers and used without further purification unless otherwise indicated. Tetrahydrofuran, ether, and benzene were distilled from benzophenone ketyl under nitrogen. Dichloromethane and hexane were distilled from calcium hydride. Proton NMR data were obtained either on a University of Chicago built DS-1000 500 MHz instrument or a QE-300 MHz instrument. Carbon-13 spectral data were obtained on the QE-300 instrument at 75 MHz. Infrared spectra were taken on a Nicolet 20SX FTIR. Low-resolution mass spectra were recorded on a Finnigan 1015 mass spectrometer. High-resolution mass spectra were recorded on a VG 70-250 instrument or obtained from the Midwest center for Mass Spectrometry in Lincoln, NE. Elemental analyses were done by Galbraith Laboratories, Knoxville, TN. Optical rotations were obtained on a Perkin-Elmer 141 polarimeter at 589 nm (sodium D line) using 1.0 dm cells. Specific rotations, $[\alpha]^D$, are reported in degrees per decimeter at 25 °C, and the concentration (*c*) is given in grams per 100 mL.

The Preparation of Acetylated Naphthol 16. A 20 mL single-necked flask equipped with a threaded high vacuum stopcock was charged with (phenylmethoxy)chromium complex **15**[54] (1.44 g, 4.62 mmol) and phenylacetylene (1.01 mL, 9.21 mmol) and diluted with THF until the solution was 0.5 M in **15** (9.3 mL). The red solution was deoxygenated by the freeze-thaw method (three cycles) and the flask backfilled with argon at room temperature and sealed. After the flask was heated at 45 °C for 11.5 h, the flask was allowed to cool, and acetic anhydride (0.87 mL, 9.2 mmol) and triethylamine (1.28 mL, 9.2 mmol) were added to the mixture under argon. The solution was heated at 60 °C for an additional 4 h. After the removal of all volatiles, the residue was loaded onto a silica gel column and eluted with a 1:9 mixture of EtOAc/hexane to give 1.25 g (4.28 mmol, 93% yield) of

(51) The details of the X-ray structure of (*S*,*S*)-**54** have been published.[30a]

(52) (a) Toda, F.; Tanaka, K.; Mak, T. C. W. *Chem. Lett.* **1984**, 2085. (b) Toda, F.; Tanaka, K.; Nagamatsu, S. *Tetrahedron Lett.* **1984**, *25*, 4929.

(53) (a) Schwartz, L. H.; Koukotas, C.; Yu, C.-S. *J. Am. Chem. Soc.* **1977**, *99*, 7710. (b) Oki, M. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 87.

(54) (a) Fischer, E. O.; Schubert, U.; Kleine, W.; Fischer, H. *Inorg. Synth.* **1979**, *19*, 164. (b) Fischer, E. O.; Heckl, B.; Dotz, K. H.; Muller, J.; Werner, H. *J. Organomet. Chem.* **1969**, *16*, P29.

acetylated naphthol **16** as a white solid. The same reaction in hexane gave a 90% yield. A reaction in THF at 0.03 M was performed by the addition of **15**, phenylacetylene, acetic anhydride, and triethylamine at the beginning of the reaction, and after 16 h at 60 °C a 72% yield of **16** was obtained. Spectral data for **16**: $R_f = 0.35$ (1:9 EtOAc:hexane); ^{1}H NMR ($CDCl_3$) δ 2.16 (s, 3 H), 3.97 (s, 3 H), 6.77 (s, 1 H), 7.32−7.51 (m, 7 H), 7.72 (d, 1 H, $J = 8.2$ Hz), 8.24 (d, 1 H, $J = 8.3$ Hz); ^{13}C NMR ($CDCl_3$) δ 20.62, 55.68, 105.52, 121.19, 122.35, 125.61, 125.67, 127.36, 127.46, 127.83, 128.33, 128.97, 130.72, 136.61, 138.35, 153.41, 169.61; IR (neat) 3060 w, 2938 w, 2844 w, 1762 s, 1630 w, 1596 m, 1500 w, 1450 m, 1445 m, 1399 w, 1365 s, 1279 w, 1229 w, 1204 s, 1167 m, 1150 w, 1102 m, 1052 m, 984 w, 895 w, 760 s, 700 m cm^{-1}; mass spectrum, *m*/*z* (rel intensity), 292 M^+(7), 264 (3), 250 (100), 235 (46), 218 (8), 205 (6), 189 (7), 178 (16), 105 (32), 76 (14); exact mass calcd for $C_{19}H_{16}O_3$ *m*/*z* 292.1099, found *m*/*z* 292.1146.

The Preparation of 3-Phenyl-1-naphthol (14) by the Reduction of 16 with Ethanethiol and Aluminum Chloride. To a red-orange solution of 0.275 g (0.94 mmol) of naphthol acetate **16** and 0.40 g (3.0 mmol) aluminum trichloride in 2 mL of methylene chloride at 0 °C was added 1.0 mL (13.5 mmol) of ethanethiol via syringe. After 0.5 h, the solution was warmed to 25 °C and stirred for an additional 2 h. The solution was then diluted with ether and washed with pH = 7 buffer solution, aqueous sodium bicarbonate, and brine and then dried with anhydrous $MgSO_4$. Upon removal of solvents, the residue was loaded on a silica gel column and eluted with a 1:1:4 mixture of ether/CH_2Cl_2/hexane to give 0.150 g (0.68 mmol, 73% yield) of 3-phenyl-1-naphthol (**14**) and 0.027 g (0.098 mmol, 10% yield) of 4-acetoxy-3-phenyl-1-naphthol (**19**) as white solids. On a larger scale (11.4 mmol) and with a reaction time of 3.5 h at 25 °C, a 78% yield of **14** was obtained (1.96 g) and **19** was not detected. Spectral data for **14**: white solid; mp 96−97.5 °C; $R_f = 0.16$ (1:1:8 ether:CH_2Cl_2:hexane); ^{1}H NMR ($CDCl_3$) δ 5.32 (s, 1 H), 7.06 (s, 1 H), 7.34 (t, 1 H), 7.41−7.50 (m, 4 H), 7.62 (s, 1 H), 7.64 (d, 2 H), 7.82 (d, 1 H), 8.13 (d, 1 H); ^{13}C NMR ($CDCl_3$) δ 108.41, 118.73, 121.39, 123.47, 125.34, 126.86, 127.20, 127.37, 127.99, 128.75, 134.85, 138.73, 140.67, 151.47; IR (neat) 3268 bs, 3058 w, 1597 m, 1497 m, 1399 m, 1284 m, 1082 m, 851 s, 762 vs, 689 s cm^{-1}; mass spectrum, *m*/*z* (rel intensity), 220 M^+ (100), 202 (2), 191 (38), 165 (14), 115 (6), 110 (7); exact mass calcd for $C_{16}H_{12}O$ *m*/*z* 220.0888, found *m*/*z* 220.0879. Spectral data for **19**: white solid; $R_f = 0.054$ (1:1:8 ether:CH_2Cl_2:hexane); ^{1}H NMR ($CDCl_3$) δ 2.18 (s, 3 H), 5.28 (s, 1 H), 6.82 (s, 1 H), 7.25−7.74 (m, 7 H), 7.74 (d, 1 H, $J = 8.4$ Hz), 8.15 (d, 1 H, $J = 8.5$ Hz); ^{13}C NMR ($CDCl_3$) δ 20.76, 110.15, 121.13, 122.27, 124.54, 125.52, 127.32, 127.47, 127.82, 128.31, 128.93, 130.81, 136.43, 137.68, 149.70, 170.55; IR (neat) 3401 s, 3055 m, 3021 w, 2922 w, 1757 s, 1634 w, 1598 s, 1499 m, 1446 w, 1397 m, 1367 s, 1313 w, 1223 s, 1168 s, 1071 s, 1050 s, 909 m, 817 w, 761 s, 739 w, 701 s cm^{-1}; mass spectrum, *m*/*z* (rel intensity), 278 M^+ (6), 250 (5), 236 (100), 220 (5), 207 (8), 178 (12), 105 (12); exact mass calcd for $C_{18}H_{14}O_3$ *m*/*z* 278.0943, found *m*/*z* 278.1030.

The Preparation of 3-Phenyl-1-naphthol (14) from Phenylacetyl Chloride and Phenylacetylene.[36] The following procedure is similar to that described in the original preparation of this compound.[36] A 100 mL recovery flask equipped with a condenser was charged with phenylacetyl chloride (20 mL, 151 mmol) and phenylacetylene (10 mL, 91 mmol). The condenser was connected to a drying tube. The flask was heated at 180 °C under nitrogen with an oil bath for 16 h. Upon being cooled to 25 °C, the dark brown mixture containing the acylated naphthol **13** was up in a solution prepared from 5 g (89 mmol) of potassium hydroxide, 10 mL of water, and 200 mL of methanol. The aqueous mixture was stirred for 12 h at 25 °C and then washed repeatedly with ether to extract the phenoxide. The organic layer was washed with 6 N aqueous HCl solution, pH = 7 buffer, and brine. The organic solution was dried with anhydrous magnesium sulfate and filtered through Celite. The filtrate was treated with activated charcoal and heated to reflux for 20 min. The mixture was filtered through Celite and concentrated, but the color was not diminished. The residue was loaded onto a silica gel column and eluted with a 1:1:8 mixture of ether:CH_2Cl_2:hexane to give 9.36 g (42.5 mmol, 56% yield) of naphthol **14** as a colored solid.

The following alteration of this procedure avoided a chromatography workup, could be scaled up to 100 g, and gave purer material. After the mixture was stirred with KOH for 12 h, the methanol was removed by rotatory evaporator. Additional aqueous KOH was added and the solution extracted with several portions of ether. The aqueous phase was neutralized with 6 N HCl and extracted with ether again. At this point ^{1}H NMR revealed that the ether layer contained the product **14** and phenylacetic acid which was removed by extraction (four times) with aqueous sodium bicarbonate. Removal of the ether gave the naphthol **14** as a white solid in 52% yield (2 g scale) which was pure by ^{1}H NMR.

The Preparation of the 1-Naphthylchromium Carbene Complex 21.[44] **Trimethyloxonium as Methylating Agent.**[44] To a solution of 1-bromonaphthalene (49.30 g, 238 mmol) in 500 mL of freshly distilled ether at −78 °C was added *n*-butyllithium (164 mL, 1.6 M in hexane, 262 mmol) under nitrogen. The mixture was stirred for 1.5 h from −78 to +25 °C. Then the milklike pale-orange solution was transferred into a flask containing chromium hexacarbonyl (52.5 g, 238 mmol) in 110 mL of freshly distilled ether at −78 °C via cannula. After 5 min, the cold bath was removed, and the solution was allowed to stir for an additional 2 h at 25 °C. The solution of the lithium acylate was stripped of solvent by rotary evaporator, the residue was taken up in 500 mL of water, and resulting solution was filtered through Celite to remove unreacted chromium hexacarbonyl. To the filtrate was added 500 mL of hexane and Meenwein salt (38.8 g, 264 mmol). This mixture was either stirred or shaken (separatory funnel) for several minutes, and then the layers were separated. The organic phase was extracted with hexane until all of the carbene complex was removed, and the combined organic layer was washed with water and brine. The organic phase was concentrated to one third of its original volume, and red crystals formed and were collected. This process was repeated to give 69.74 g (193 mmol, 81% yield) of carbene complex **21** from two crops. The naphthyl complex **21** is much more stable than phenyl complex **15**. The spectral data obtained for complex **21** match those previously reported for this compound.[44]

Methyl Triflate as Methylating Agent.[55] The ether solution of the lithium acylate (from 0.250 mmol of 1-bromonaphthalene) was cooled in an ice bath, and methyl triflate (30 mL, 0.265 mol) was added slowly. The solution was stirred at 0 °C for 15 min and then in a water bath (25 °C) for 30 min. The reaction mixture was filtered through Celite, washed with saturated aqueous $NaHCO_3$, water, and brine, and then dried over $MgSO_4$. The product was filtered through a short column of silica gel, and then the solvent was partially removed by rotary evaporator until a red solid formed. The product was collected by filtration and washed with small portions of cold hexane. This process was repeated until no more solid appeared upon concentration. The remainder of the product in the mother liquor was purified by flash chromatography on silica gel with hexane as eluent to give a 60% combined yield (54.16 g, 0.15 mmol) of carbene complex **21**. A repeat of this reaction on a similar scale gave a 70% yield.

Methyl Iodide As Methylating Agent.[45] The ether solution of the lithium acylate (from 0.025 mmol of 1-bromonaphthalene) was stripped of solvent under reduced pressure, and then the last trace of solvent was removed under high vacuum. The greenish-brown residue was dissolved in 50 mL of water in a 100 mL single-necked flask equipped with a threaded high vacuum stopcock to give a yellow solution. Tetrabutylammonium bromide (0.806 g, 2.5 mmol) was added followed by methyl iodide (3.11 mL, 50 mmol). The flask was sealed and immersed in a 70 °C oil bath and stirred for 2 h. The deep red lower layer was separated, and the top layer was extracted with hexane. The combined organic layer was dried over $MgSO_4$. The solution was filtered through a short column of silica gel, and the volatiles were evaporated to give a red liquid which was loaded onto a silica gel column. The product was flash eluted with hexane to give a 36% yield (3.30g, 9.11 mmol) of carbene complex **21**.

Methanol/Acetyl Bromide as Methylating Agents.[56a] The solution of the lithium acylate (from 0.050 mmol of 1-bromonaphthalene) was stripped of solvent under reduced pressure, and then the last trace of solvent was removed under vacuum. The greenish brown residue was dissolved in 200 mL of CH_2Cl_2, and the solution was cooled to −20 °C (in acetone/dry ice bath) under nitrogen in a flask equipped with a mechanical stirrer. TMEDA[56b] (7.55 mL, 50 mmol, distilled from KOH

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pellets) was added, and the solution became dark brown after 10 min. Freshly distilled and precooled (−20 °C) acetyl bromide (11.09 mL, 150 mmol) was added slowly via cannula. The dark reddish-brown slurry was allowed to stir for 30 min. Freshly distilled (from $Mg(OMe)_2$) and precooled (−20 °C) methanol (20.25 mL, 0.5 mol) was added, and the mixture was stirred at 0 °C for 1 h to produce a deep orange solution. The solution was poured into a separatory funnel containing saturated aqueous $NaHCO_3$. The CH_2Cl_2 layer was separated and stripped of volatiles, and then the residue was taken up in hexane. The hexane solution was washed with water and brine, dried over $MgSO_4$, and filtered through a short column of silica gel. The solvent was partially removed until a red solid formed which was collected. This process was repeated until no more solid appeared upon concentration. The remainder of the product in the mother liquor was purified by flash chromatography on silica gel with hexane as eluent to give a 52% total yield (9.44g, 26.5 mmol) of carbene complex **21**.

Dimethyl Sulfate as Methylating Agent. A solution of the lithium acylate (from 121 mmol of 1-bromonaphthalene) was generated as described above in 150 mL of THF, diluted with 200 mL of ether, and washed with 5% aqueous HCl (2 × 100 mL). The red organic layer was separated and stirred over solid potassium carbonate (35 g, 252 mmol, 2.0 equiv). Dimethyl sulfate (17 mL, 182 mmol, 1.5 equiv) was added via syringe and the reaction mixture allowed to stir for 12 h at 25 °C. The reaction mixture was washed with water (3 × 100 mL), filtered through a plug of silica, and concentrated in *vacuo*. Purification by crystallization from hexanes (two crops) afforded carbene complex **21** in 77% yield (34.0 g) as a red solid. A repeat of the reaction on the same scale gave **21** in 65% yield (one crop) if the reaction time with dimethyl sulfate was 2 h. On a 5 mmol scale a 73% yield of **21** was obtained with a 2 h reaction time. If either a THF or ether solution of the lithium acylate (5 mmol scale) is directly treated with dimethyl sulfate, an 18% yield of **21** is obtained with a 2 h reaction time and a 45% yield with a 12 h reaction time.

The Preparation of the Acetylated Phenanthrol 22 from the Reaction of the 1-Naphthylcarbene Complex 21 with Phenylacetylene. Slow Addition of Phenylacetylene. The naphthyl carbene complex **21** (5 g, 13.8 mmol) was placed in a 250 mL round-bottom flask equipped with a reflux condenser. The whole system was purged with nitrogen for 5 min, and then 27.6 mL of dry THF was added under nitrogen to make a solution 0.5 M in **21**. The solution was heated in an oil bath at 65 °C under nitrogen. Phenylacetylene (1.8 mL, 16.6 mmol) was added slowly by means of a syringe pump over 6 h, and then reflux was maintained for an additional hour. Upon cooling and examination by TLC to confirm that consumption of the carbene complex was complete, triethylamine (6 mL, 41.4 mmol) and acetic anhydride (4 mL, 41.4 mmol) were added and the resulting solution was refluxed for 13 h under nitrogen. The THF was partially removed by rotary evaporator, and then the solution was diluted with ether and washed with water and brine. This solution was dried over $MgSO_4$ and filtered through a short column of SiO_2 to remove a green insoluble material, and then the solvent was removed to give a brown residue. The ^{1}H NMR of the crude reaction mixture reveals the presence of **22** and **23-*E*** in a 9:1 ratio and that the ratio of the *E* and *Z* isomers of **23** is ≥16:1. Ether (50 mL) was added to the residue to give a light brown solution and a pale yellow material that did not dissolve which was found to be pure **22**. Addition of hexane (25 mL) caused precipitation of additional **22**. Collection of this solid gave 3.3 g of pure product. Additional **22** (0.21 g) was obtained from the mother liquor by flash chromatography (1:9 EtOAc:hexane) to give a total isolated yield of 3.51 g of **22** (74.3%). On a larger scale (30 g of **21**), this reaction gave a 65% yield of **22**. Spectral data for **22**: R_f = 0.23 (1:9 EtOAc:hexane); white solid; mp = 160−161 °C; ^{1}H NMR ($CDCl_3$) δ 2.19 (s, 3 H), 4.14 (s, 3 H), 7.13 (s, 1 H), 7.36 (t, 1 H, J = 7.3 Hz), 7.43 (t, 2 H, J = 7.6 Hz), 7.53−7.63 (m, 4 H), 7.70 (d, 1 H, J = 8.9 Hz), 7.78 (d, 1 H, J = 9.0 Hz), 7.85 (d, 1 H, J = 7.8 Hz), 9.62 (d, 1 H, J = 8.8 Hz); ^{13}C NMR ($CDCl_3$) δ 20.74, 55.98, 109.56, 119.50, 120.95, 126.30, 126.89, 127.52, 127.63, 128.35, 128.43, 128.56, 129.06, 129.30, 130.09, 131.93, 132.47, 137.34, 138.02, 156.65, 169.70; IR (neat) 3056 w, 2929 w, 2844 w, 1762 s, 1598 w, 1498 w, 1451 w, 1367 m, 1213 m, 1196 vs, 1174 m, 1157 m, 1100 w, 1049 m, 815 w, 745 w, 700 m cm^{-1}; mass spectrum, *m*/*z* (rel intensity), 342 M^+ (8), 300 (100), 285 (46), 268 (8), 255 (6), 239 (10), 226 (12), 191 (2), 155 (27), 126 (18); exact mass calcd for $C_{23}H_{18}O_3$ *m*/*z* 342.1256, found *m*/*z* 342.1253. Anal. Calcd for $C_{23}H_{18}O_3$: C, 80.68; H, 5.30. Found: C, 80.76, H, 5.42.

Initial Addition of Phenylacetylene. A 50 mL single-necked flask equipped with a threaded high vacuum stopcock was charged with (1-naphthylmethoxy)chromium complex **21** (3.04 g, 8.4 mmol), phenylacetylene (1.84 mL, 16.7 mmol), and 16.7 mL of THF to make a solution 0.5 M in **21**. The solution was deoxygenated via the freeze-thraw method (three cycles), although this was found not to be necessary as indicated by the above procedure. The flask was sealed with the threaded stopcock at 25 °C under argon and then heated at 60 °C in an oil bath for 19 h. Acetic anhydride (1.59 mL, 168 mmol) and triethylamine (2.34 mL, 168 mmol) were added, and the solution was heated at 60 °C for 17 h. The crude reaction mixture was worked up as described above, and after removal of volatiles the residue was loaded onto a silica gel column and eluted with a 1:9 mixture of EtOAc:hexane to give 1.08 g (3.16 mmol, 38% yield) of acetylated phenanthrol **22** and 1.20 g (2.70 mmol, 32% yield) of the bis(naphthyl)ethylene **23-*E*** as a white solid. The results from other runs at different concentrations and in different solvents are tabulated in Table 1. Spectral data for **23-*E***: R_f = 0.15 (1:9 EtOAc:hexane); mp = 150−151 °C; ^{1}H NMR ($CDCl_3$) δ 2.10 (s, 3 H), 4.01 (s, 3 H), 6.57 (s, 1 H), 6.58 (d, 2 H, J = 6.6 Hz), 6.75 (s, 1 H), 7.05−7.11 (m, 3 H), 7.20−7.23 (m, 2 H), 7.36−7.40 (m, 2 H), 7.48−7.53 (m, 2 H), 7.71 (d, 1 H, J = 7.8 Hz), 7.74−7.81 (m, 1 H), 7.80 (d, 1 H, J = 7.5 Hz), 7.99 (d, 1 H, J = 8.1 Hz), 8.24 (d, 1 H, J = 8.0 Hz); ^{1}H NMR (C_6D_6) δ 1.79 (s, 3 H), 3.63 (s, 3 H), 6.56 (s, 1 H), 6.94−6.95 (m, 3 H), 7.06−7.30 (m, 7 H), 7.46−7.54 (m, 3 H), 7.65 (d, 1 H, J = 6.8 Hz), 8.01 (d, 1 H, J = 8.0 Hz), 8.26 (d, 1 H, J = 7.1 Hz), 8.39 (d, 1 H, J = 8.1 Hz); ^{13}C NMR ($CDCl_3$) δ 20.42, 55.47, 100.33, 121.80, 124.58, 125.25, 125.35, 125.72, 125.98, 126.31, 126.40, 126.85, 126.96, 127.79, 128.01, 128.43, 128.54, 128.69, 128.97, 129.68, 131.80, 131.87, 132.30, 133.44, 133.76, 137.40, 141.27, 158.39, 169.03; IR (neat) 3059 s, 3001 w, 2956 w, 2934 w, 1761 s, 1705 w, 1633 s, 1618 s, 1595 s, 1579 m, 1506 m, 1445 m, 1366 s, 1265 m, 1237 s, 1196 s, 1051 s, 1033 m, 902 s, 803 s, 779 s cm^{-1}; mass spectrum, *m*/*z* (rel intensity), 444 (20) M^+, 402 (100), 369 (14), 359 (12), 341 (13), 339 (12), 202 (13); exact mass calcd for $C_{31}H_{24}O_3$ *m*/*z* 444.1726, found *m*/*z* 444.1733. Anal. Calcd for $C_{31}H_{24}O_3$: C, 83.76; H, 5.44. Found: C, 83.81, H, 5.50.

Isomerization of Alkene 23 and Stereochemical Assignment of the *E*- and *Z*-Isomers. A solution of alkene **23-*E*** (0.08g) in 100 mL of benzene was irradiated in a quartz tube for 18 h using a Rayonet photochemical reactor. A mixture of alkenes was produced which were separated on silica gel by flash column chromatography using a 1:9 mixture of EtOAc:hexanes as eluant. Spectral data for **23-*Z***: R_f = 0.23 (1:9 EtOAc:hexane); white gum; ^{1}H NMR ($CDCl_3$) δ 2.25 (s, 3 H), 3.44 (s, 3 H), 6.38 (s, 1 H), 7.37−7.56 (m, 8 H), 7.62 (d, 2 H, J = 7.3 Hz), 7.68 (d, 1 H, J = 6.8 Hz), 7.86−7.92 (m, 3 H), 8.15 (d, 1 H, J = 8.1 Hz), 8.26 (s, 1 H), 8.30 (d, 1 H, J = 7.6 Hz); ^{1}H NMR (C_6D_6) δ 1.92 (s, 3 H), 3.13 (s, 3 H), 6.54 (s, 1 H), 7.26−7.48 (m, 8 H), 7.60 (d, 1 H, J = 6.9 Hz), 7.76 (d, 2 H, J = 7.8 Hz), 7.81 (d, 2 H, J = 7.5 Hz), 8.13−8.16 (m, 2 H), 8.52 (d, 1 H, J = 8.3 Hz), 8.73 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 20.76, 56.88, 107.33, 121.88, 124.59, 125.28, 125.59, 126.13, 126.21, 126.38, 126.86, 127.35, 127.99, 128.32, 128.36, 128.75, 129.24, 129.36, 130.67, 130.93, 131.87, 132.12, 133.38, 134.14, 138.48, 141.87, 156.71, 169.35, 1 aryl C not assigned; IR (neat) 1764 s, 1365 s, 1201 s, 1176 s, 1051 s, 780 s, 762 s cm^{-1}; mass spectrum, *m*/*z* (rel intensity), 444 (30) M^+, 403 (30), 402 (100), 387 (5), 369 (7), 357 (5), 341 (5).

The stereochemistry of the isomers of **23** was assigned by NOE experiments. Samples of each isomer were dissolved in C_6D_6 in a 5 mm NMR tube, and the solutions were deoxygenated by means of the freeze-thraw method (three cycles). *E*-Isomer: Irradiation at the methoxy proton (δ = 3.63) gave rise to a 20% enhancement of the vinyl proton (δ = 6.56). Irradiation at the vinyl proton at δ = 6.56 gave rise to a 10% enhancement of the methoxy proton at δ = 3.63 as well as a 13% enhancement of the aromatic proton at δ = 8.39. Irradiation at the aromatic proton (δ = 8.39) gave rise to an enhancement of the vinyl proton (δ = 6.56). *Z*-Isomer: Irradiation at either the methoxy proton (δ = 3.13), the vinyl proton (δ = 6.54), or the aromatic proton (δ = 8.73) gave no observable enhancements for any of the protons in the spectrum.

The Preparation of 3-Phenylphenanthrol (28) by Reduction of Acetylated Phenanthrol 22 with Ethanethiol and Aluminum Chloride. To a solution of the acetylated phenanthrol **22** (0.3144 g, 0.92 mmol) and aluminum chloride (0.42 g, 3.1 mmol) in 2 mL of dichloromethane was added 2 mL of ethanethiol. The solution was stirred at 25 °C for 4.5 h and was then diluted with dichloromethane. The reaction mixture was then washed with aqueous sodium bicarbonate and brine and then dried with anhydrous $MgSO_4$. After the removal of solvent, the residue was loaded onto a silica gel column and eluted with a 1:5 mixture of EtOAc:hexane to give 0.2386 g (0.88 mmol, 96% yield) of phenanthrol **28** and 0.0045 g (0.014 mmol, 1.5% yield) of a compound that was tentatively identified as 4-acetoxy-3-phenylphenanthrol (**55**), both as white solids. Spectral data for **55**: ^{1}H NMR ($CDCl_3$) δ 2.20 (s, 3 H), 5.82 (s, 1 H), 6.96 (s, 1 H), 7.34 (t, 1 H, J = 7.5 Hz), 7.40 (t, 2 H, J = 7.1 Hz), 7.48 (d, 2 H, J = 7.3 Hz), 7.55 (t, 1 H, J = 7.4 Hz), 7.58 (t, 1 H, J = 7.1 Hz), 7.67 (d, 1 H, J = 9.0 Hz), 7.75 (d, 1 H, J = 9.1 Hz), 7.83 (d, 1 H, J = 7.7 Hz), 9.55 (d, 1 H, J = 8.6 Hz). Spectral data for **28**: R_f = 0.33 (1:5 EtOAc:hexane); mp = 154−155 °C; ^{1}H NMR ($CDCl_3$) δ 5.71 (s, 1 H), 7.18 (s, 1 H), 7.35 (t, 1 H, J = 7.5 Hz), 7.45 (t, 2 H, J = 7.6 Hz), 7.55 (t, 1 H, J = 7.2 Hz), 7.72 (t, 1 H, J = 7.4 Hz), 7.64−7.70 (m, 5 H), 7.84 (d, 1 H, J = 7.8 Hz), 9.58 (d, 1 H, J = 8.5 Hz); ^{13}C NMR ($CDCl_3$) δ 112.20, 118.52, 119.86, 125.99, 126.65, 127.21 (two carbons), 127.62, 128.25, 128.42, 128.89, 130.13, 132.57, 135.27, 139.17, 140.09, 154.61 (one carbon not located); IR (neat) 3521 s, 3061 w, 2028 w, 1604 w, 1564 m, 1524 w, 1411 w, 1391 s, 1331 m, 1278 m, 1225 s, 1178 m, 1125 w, 1019 m, 745 s cm^{-1}; mass spectrum, *m*/*z* (rel intensity), 270 (100) M^+, 241 (23), 165 (8), 135 (12), 120 (11), 84 (43); exact mass calcd for $C_{20}H_{14}O$ *m*/*z* 270.1045, found *m*/*z* 270.1074. Anal. Calcd for $C_{20}H_{14}O$: C, 88.86; H, 5.22. Found: C, 88.52, H, 5.31.

A Large Scale Preparation of 3-Phenylphenanthrol (28). A dry 5000 mL round-bottomed flask equipped with a reflux condensor was charged with naphthylchromium complex **21** (73.10 g, 202 mmol), phenylacetylene (26.6 mL, 243 mmol), and 4500 mL of THF (predistilled from CaH_2) under nitrogen. The solution was heated to reflux for 17 h. Upon cooling, triethylamine (87.3 mL, 626 mmol) and acetic anhydride (57.2 mL, 606 mmol) were added under nitrogen, and the solution was heated to reflux for 24 h. The THF was removed by rotary evaporator to give an oily residue. Upon addition of ether a yellow solid precipitated which was collected to give 13.95 g (29.2 mmol, 14% yield) of a compound which was tentatively identified as the arene chromium complex **29**. Spectral data for **29**: R_f = 0.036 (1:9 EtOAc:hexane); ^{1}H NMR ($CDCl_3$) δ 2.32 (s, 3 H), 4.20 (s, 3 H), 5.28 (t, 2 H), 5.45 (t, 1 H), 5.76 (brd s, 2 H), 7.21 (s, 1 H), 7.58−7.67 (m, 3 H), 7.79 (d, 1 H), 7.86 (d, 1 H), 9.61 (d, 1 H); IR (neat) 1963 s, 1882 s, 1761 m, 1449 w, 1368 w, 1196 m, 1174 w, 1142 w, 1049 w, 817 w, 732 w, 701 w, 660 m cm^{-1}. The mother liquor was washed with aqueous saturated sodium bicarbonate and brine and then dried with anhydrous $MgSO_4$ and filtered through Celite. Upon concentration, crystals of the phenanthrol **22** began to separate, and collection of two crops of these crystals gave 39.42 g (115 mmol, 57% yield) of the acetylated phenanthrol **22**. The acetylated phenanthrol **22** and the arene complex **29** were combined and dissolved in 200 mL of dichloromethane. To this solution was added aluminum trichloride (40 g, 300 mmol) and ethanethiol (200 mL, 2.7 mol), and the resulting solution was stirred at 25 °C for 12 h under an inert atmosphere. The crude reaction mixture was quenched with 1 N aqueous HCl (slowly in a ice bath). The organic layer was washed with aqueous saturated sodium bicarbonate and brine and then dried with anhydrous $MgSO_4$. After filtration through Celite and removal of solvent, the residue was chromatographed on a 50 mm diameter silica gel column with a 1:9 mixture of EtOAc/hexane to remove base line impurities to give 37.74 g (140 mmol) of phenanthrol **28** as a white solid in 69% yield from the carbene complex **21**. Presumably, the amount of solvent for this reaction could be reduced by at least a factor of 10 if slow addition of phenylacetylene was employed as described above. Also, it has been found phenanthrol **28** obtained by this reaction is pure enough to be successfully employed in the synthesis of **47** without purification by silica gel chromatography.

The Preparation of 3-Phenylphenanthrol (28) from 2-Naphthylacetic acid and Phenylacetylene. A mixture of 28.5 g (153 mmol) of naphthylacetic acid and thionyl chloride (40 mL, 548 mmol) was heated to reflux for 1 h, at which point all starting material had been consumed as indicated by ^{1}H NMR. All of the volatiles were removed by high vacuum to leave a yellow solid which appeared to be a single compound by ^{1}H NMR. To this solid was added phenylacetylene (10.1 mL, 92.0 mmol), and the resulting mixture was heated at 185 °C for 16 h under nitrogen. The ^{1}H NMR spectrum indicated that a substantial amount of the acid chloride remained unreacted. More phenylacetylene (10 mL, 91.1 mmol) was added, and the mixture was heated at 185 °C for 20 h after which time the ^{1}H NMR indicated that the reaction was complete. To the reaction mixture (black oil) was added KOH (8.5 g, 152 mmol), 200 mL of water, and 400 mL of methanol. After being stirred at room temperature for 20 h, the solution was concentrated by rotary evaporator. Ether was added, and the organic layer was washed with water and brine. After removal of the solvents, the product **28** could be purified from the residue by flash chromatography on a silica gel column with a 1:9 mixture of EtOAc/hexane and then on a second silica gel column with a 1:1:8 mixture of CH_2Cl_2/ether/hexane to give 11.09 g (41.1 mmol, 54%) of phenanthrol **28** as a brown solid. Attempts to purify phenanthrol **28** by extraction from ether with aqueous potassium hydroxide were not successful. The phenanthrol **28** purified from this reaction by chromatography on silica gel was not suitable for the oxidative coupling to **47**.

The Reaction of 1-Naphthylcarbene Complex 21 with *tert*-Butylacetylene. According to the procedure described above for the reaction of **21** with phenylacetylene, the reaction of complex **21** (1.12 g, 3.1 mmol) with *tert*-butylacetylene (0.57 mL, 4.6 mmol) in 6.2 mL of THF was carried out at 60 °C for 17 h. The crude mixture was stirred in air for 0.5 h and then filtered through Celite. Upon removal of solvent, the residue was loaded onto a silica gel column and eluted with a 1:1:16 mixture of Et_2O:CH_2Cl_2:hexane to give three compounds: **31** (0.6784 g, 2.42 mmol, 78% yield), **32** (0.167g, 0.40 mmol, 13% yield, yellow solid), and an unidentified material (0.182 g). Spectral data for **32**: R_f = 0.06 (1:1:16 Et_2O:CH_2Cl_2:hexane); ^{1}H NMR ($CDCl_3$) δ 1.56 (s, 9 H), 4.10 (s, 3 H), 5.01 (s, 1 H), 5.41 (t, 1 H, J = 6.9 Hz), 5.56 (t, 1 H, J = 6.2 Hz), 5.96 (d, 1 H, J = 6.2 Hz), 7.17 (s, 1 H), 7.29 (d, 1 H, J = 9.1 Hz), 7.88 (d, 1 H, J = 7.2 Hz), 7.96 (d, 1 H, J = 9.0 Hz); IR (neat) 3583 w, 2969 w, 1951 s, 1874 s, 1440 w, 1362 w, 1228 w, 1055 w, 732 w, 713 w, 664 m cm^{-1}.

The three compounds were combined and dissolved in 20 mL of THF. To this solution were added acetic anhydride (0.58 mL, 6.15 mmol) and triethylamine (0.86 mL, 6.17 mmol). The solution was heated to reflux for 16 h. All volatiles were removed, and the residue was dissolved in ether. The solution was washed with aqueous saturated sodium bicarbonate, water, and brine. After drying with $MgSO_4$ and removal of solvent, the residue was loaded onto a silica gel column and eluted with a 1:9 mixture of EtOAc:hexane to give 0.541 g (1.79 mmol, 54% from **21**) of acetylated phenanthrol **33** as a light yellow solid. Spectral data for **33**: R_f = 0.38 (1:9 EtOAc:hexane); ^{1}H NMR ($CDCl_3$) δ 1.48 (s, 9 H), 2.49 (s, 3 H), 4.11 (s, 3 H), 7.17 (s, 1H), 7.45 (d, 1 H, J = 9.2 Hz), 7.53 (t, 1 H, J = 6.1 Hz), 7.58 (t, 1 H, J = 6.4 Hz), 7.69 (d, 1 H, J = 9.2 Hz), 7.80 (d, 1 H, J = 7.3 Hz), 9.55 (d, 1 H, J = 8.6 Hz); ^{13}C NMR ($CDCl_3$) δ 21.55, 21.87, 30.49, 34.85, 119.84, 120.88, 122.62, 126.01, 126.81, 127.05, 128.02, 128.69, 128.74, 132.40, 139.15, 143.00, 145.69, 169.38, 169.78; IR (neat) 3053 w, 2963 w, 2869 w, 1764 s, 1717 w, 1598 w, 1357 m, 1191 s, 1157 m, 1136 m, 1037 w, 1018 w, 912 w, 820 w, 732 w cm^{-1}.

The Preparation of the *tert*-Butylphenanthrol (34) by Reduction of Acetylated Phenanthrol 33. To a solution of the acetylated phenanthrol **33** (0.54 g, 1.68 mmol) and aluminum chloride (0.54 g, 4.05 mmol) in 3 mL of dichloromethane was added ethanethiol (5 mL, 72 mmol). The solution was stirred at 25 °C for 15 h, and then the volatiles were removed under vacuum. The residue was diluted with ether, and the solution was washed with aqueous sodium bicarbonate, water, and brine. After drying with $MgSO_4$ and removal of solvent, the residue was loaded onto a silica gel column and eluted with a 1:1:16 mixture of ether:CH_2Cl_2:hexane to give 0.36 g (1.44 mmol, 85% yield) of phenanthrol **34** as a white solid. Spectral data for **34**: R_f = 0.21 (1:9 EtOAc:hexane); ^{1}H NMR ($CDCl_3$) δ 1.44 (s, 9 H), 5.67 (s, 1 H), 7.01 (d, 1 H, J = 1.5 Hz), 7.45 (s, 1 H), 7.54 (t, 1 H, J = 7.1 Hz), 7.62 (t, 1 H, J = 8.0 Hz), 7.63−7.70 (m, 2 H), 7.84 (d, 1 H, J = 8.5 Hz), 9.56 (d, 1 H, J = 8.4 Hz); ^{13}C NMR ($CDCl_3$) δ 31.28, 34.54, 111.55, 117.30, 117.77, 125.56, 126.39, 127.29, 127.83, 128.10, 128.22,

130.17, 132.33, 134.71, 149.71, 153.92; IR (neat) 3508 s, 3057 w, 2953 s, 2893 m, 2866 m, 1627 w, 1599 w, 1570 m, 1460 m, 1420 m, 1397 s, 1345 m, 1283 m, 1239 s, 1229 s, 1179 s, 1110 m, 1050 w, 1015 m, 867 m, 851 s, 811 s, 746 s, 715 cm^{-1}.

The Preparation of 4,4′-Binaphthol 38 by Oxidative Coupling of 3-Phenyl-1-naphthol (14) with Ferric Chloride. To 0.245 g (1.11 mmol) of 3-phenyl-1-naphthol (**14**) in 30 mL of acetonitrile was added 1.66 g (6.15 mmol) of $FeCl_3 \cdot 6H_2O$ at 25 °C. The solution was stirred at 25 °C for 16 h. The crude reaction mixture was diluted with ether, and the solution was washed with water and dried over anhydrous $MgSO_4$. Upon removal of solvent, the residue was loaded onto a silica gel column and eluted with a 1:1:4 mixture of ether:CH_2Cl_2:hexane to give 0.1529 g (0.35 mmol, 62% yield) of 4,4′-binaphthol **38**. Two minor products were also observed which were not characterized but whose properties were not consistent with those known for 2,2′-binaphthol **39** (*vide infra*). Spectral data for **38**: white solid; mp = 240−241 °C; R_f = 0.23 (1:1:4 ether:CH_2Cl_2:hexane); ^{1}H NMR ($CDCl_3$) δ 5.35 (s, 2 H), 6.37 (d, 4 H, J = 7.7 Hz), 6.66 (s, 2 H), 6.83 (t, 4 H, J = 7.6 Hz), 6.97 (t, 2 H, J = 7.2 Hz), 7.30 (t, 2 H, J = 7.2 Hz), 7.37 (d, 2 H, J = 8.4 Hz), 7.45 (t, 2 H, J = 7.3 Hz), 8.23 (d, 2 H, J = 8.3 Hz); ^{13}C NMR ($CDCl_3$) δ 111.09, 121.74, 123.45, 124.76, 125.98, 126.68, 126.95, 127.01, 127.45, 128.94, 135.99, 141.10, 141.42, 151.09; IR (neat) 3518 bs, 3058 w, 1621 w, 1596 s, 1513 w, 1497 m, 1444 w, 1380 s, 1357 m, 1288 w, 1230 s, 1146 w, 1064 s, 908 m, 859 w, 732 s, 702 s cm^{-1}; Mass spectrum, *m*/*z* (rel intensity), 438 M^+ (85), 322 (7), 247 (25), 220 (100), 205 (16), 191 (23), 97 (38), 84 (64), 71 (63); exact mass calcd for $C_{32}H_{22}O_2$ *m*/*z* 438.1620, found *m*/*z* 438.1632.

The Preparation of 2,2′-Binaphthol 39 by Oxidative Coupling of 3-Phenyl-1-naphthol (14) with Air.[48b] 3-Phenyl-1-naphthol (**14**) (0.98 g, 4.45 mmol) was introduced into an 18 × 150 mm culture tube which was placed in an oil bath at 190 °C. After 16 h, TLC indicated only 50% conversion, but after an additional 16 h at 200 °C the reaction was complete. The crude reaction mixture was directly loaded onto a silica gel column and eluted with a 1:15 mixture of EtOAc:hexane to give 0.0474 g (0.11 mmol, 2.5%) of a product **56** which was tentatively identified as the furan resulting from the dehydration of **39**, 0.856 g (1.95 mmol, 87% yield) of the 2,2′-bi-1-naphthol **39**, and 0.0458 g of an unknown compound. Spectral data for **56**: R_f = 0.70 (1:9 EtOAc: hexane); ^{1}H NMR ($CDCl_3$) δ 6.91−6.92 (m, 6 H), 7.18−7.21 (m, 4 H), 7.55 (t 2 H, J = 7.4 Hz), 7.59 (s, 2 H), 7.65 (t, 2 H, J = 7.4 Hz), 7.92 (d, 2 H, J = 8.1 Hz), 8.64 (d, 2 H, J = 8.1 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 118.10, 120.30, 120.79, 125.79, 126.30, 126.47, 126.97, 128.00, 128.09, 128.47, 132.08, 135.99, 141.81, 152.85; Mass spectrum, *m*/*z* (rel intensity), 420 M^+ (100), 389 (8), 342 (7), 313 (5), 171 (15); exact mass calcd for $C_{32}H_{20}O$ *m*/*z* 420.1514, found *m*/*z* 420.1505. Spectral data for **39**: R_f = 0.36 (1:9 EtOAc:hexane); white solid; mp = 231−233 °C; ^{1}H NMR ($CDCl_3$) δ 5.83 (s, 2 H), 6.61 (d, 4 H, J = 7.2 Hz), 6.93 (t, 4 H, J = 7.7 Hz), 7.03 (t, 2 H, J = 7.3 Hz), 7.29 (s, 2 H), 7.50−7.54 (m, 4 H), 7.73−7.75 (m, 2 H), 8.30−8.32 (m, 2 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 112.64, 122.00, 122.78, 122.86, 125.66, 126.59, 127.43, 127.51, 127.67, 128.86, 134.56, 140.12, 140.65, 150.33; IR (neat) 3508 s, 3054 m, 3030 w, 1948 w, 1630 w, 1502 m, 1569 m, 1493 s, 1439 w, 1383 s, 1285 m, 1233 m, 1221 m, 1192 m, 1140 m, 1062 m, 1020 w, 947 m, 908 s, 879 m, 853 w, 798 w, 759 s cm^{-1}; mass spectrum, *m*/*z* (rel intensity), 438 M^+ (2), 420 (15), 408 (2), 389 (2), 234 (5), 206 (30, 83 (100), 71 (9); exact mass calcd for $C_{32}H_{22}O_2$ *m*/*z* 438.1620, exact *m*/*z* 438.1610. Anal. Calcd for $C_{32}H_{22}O_2$: C, 87.65; H, 5.06. Found: C, 87.89; H, 5.10.

The Preparation of 2,2′-Binaphthylphosphoric Acid 44 and Its Conversion to the 2,2′-Binaphthyl Methyl Phosphate 46. To a solution of the 2,2′-binaphthol **39** (4.6 g, 10.5 mmol) in 30 mL of pyridine was added phosphorus oxychloride (1.37 mL, 14.7 mmol) at 0 °C under argon. This solution was heated at 90 °C for 2.5 h. Upon cooling, 0.5 mL of water was added and the solution was heated to 90 °C for 1.5 h. After the pyridine was removed under vacuum, the residue was taken up in 150 mL of aqueous HCl (6 N, 900 mmol). This solution was heated to reflux for 1.5 h, and after the solution was cooled the acid **44** precipitated as a white solid. The product was collected, washed with water, and dried under high vacuum overnight to give 5.3 g (10.6 mmol, 100%) of acid **44**. Spectral data for **44**: white solid; mp = 220 °C dec; ^{1}H ($CDCl_3$) δ 5.80 (brd s, 1 H), 6.45 (d, 4 H, J = 7.5 Hz), 6.88 (t, 4 H, J = 7.4 Hz), 7.06 (t, 2 H, J = 7.2 Hz), 7.47 (s, 2 H), 7.49−7.51 (m, 4 H), 7.77 (d, 2 H, J = 7.4 Hz), 8.46 (d, 2 H, J = 7.3 Hz). The acid **44** was taken on directly to **46**. To a potassium hydroxide solution (4.0 g, 71.4 mmol, in 10 mL of water) was added 15 mL of ether. The two-phase mixture was cooled to 0 °C, and *N*-nitroso-*N*-methylurea (1.4 g, 13.5 mmol) was added. The mixture was stirred for 25 min, and the organic layer was separated and dried over potassium hydroxide pellets. The organic phase was then added to a solution of phosphoric acid **44** (0.2312 g, 0.46 mmol) in 20 mL of methylene chloride at 25 °C. After 10 min, the reaction was quenched with acetic acid until bubbling stopped. The mixture was diluted with ether and washed with aqueous saturated sodium bicarbonate, water, and brine. The solution was dried over anhydrous $MgSO_4$ and filtered through Celite. Upon removal of solvent, the residue was loaded onto a silica gel column and eluted with a 1:3 mixture of EtOAc:hexane to give 0.210 g (0.41 mmol, 88% yield) of phosphate ester **46** as a white solid. Spectral data for **46**: white solid; R_f = 0.07 (1:1:4 CH_2Cl_2: ether:hexane); ^{1}H NMR ($CDCl_3$) δ 4.04 (d, 3 H, J = 11.5 Hz), 6.43 (t, 4 H, J = 7.4 Hz), 6.89 (q, 4 H, J = 7.2 Hz), 7.06 (q, 2 H, J = 7.0 Hz), 7.47 (s, 2 H), 7.55−7.65 (m, 4 H), 7.80 (t, 2 H, J = 8.6 Hz), 8.31 (d, 1 H, J = 8.3 Hz), 8.38 (d, 1 H, J = 8.3 Hz); ^{13}C NMR ($CDCl_3$) δ 56.19 (d, J_{P-C} = 5.7 Hz), 121.74, 122.29, 122.49, 122.51, 125.24, 125.28, 125.66, 125.70, 126.56, 126.64, 127.02, 127.06, 127.30, 127.34, 127.51, 127.60, 127.70, 127.78, 127.99, 128.94, 128.96, 134.12, 134.29, 139.69, 139.94, 140.17, 144.58, 144.69, 145.72, 145.87; IR (neat) 3053 w, 2948 w, 2848 w, 2244 w, 1582 w, 1566 w, 1488 m, 1451 w, 1383 m, 1337 w, 1303 s, 1291 s, 1263 w, 1110 w, 1093 w, 1056 s, 1043 s, 969 s, 944 m, 911 s, 875 m, 864 m, 795 w, 774 m, 761 s, 730 s cm^{-1}; mass spectrum, *m*/*z* (rel intensity) 514 M^+ (100), 436 (12), 420 (10), 389 (6), 33 (12), 218 (11); exact mass calcd for $C_{33}H_{23}O_4P$ *m*/*z* 514, 1334, found 514.1334. Anal. Calcd for $C_{33}H_{23}O_4P$: C, 77.04; H, 4.51; P, 6.02. Found: C, 76.52; H, 4.79; P, 6.31.

The Resolution of 3,3′-Diphenyl-2,2′-binaphthalene-1,1′-diol (39). Preparation of Salt 45 from Acid 44 and Brucine. A mixture of the binaphthylphosphoric acid **44** (53.7 mmol), prepared from 23.51 g of racemic binaphthol **39** as described above, and brucine (22.3 g, 51.8 mmol as dihydrate) in 1000 mL of ethanol was heated to a boil. A white solid begin to separate even with slight cooling. Upon cooling to room temperature, the white solid was collected and then redissolved in a small amount of CH_2Cl_2, and then ethanol was added. Methylene chloride was removed via gentle vacuum until the solution was saturated at ambient temperature. After a few hours, the fine crystals of the salt **45** were collected, washed with ethanol, and dried under high vacuum overnight to give 20.48 g (22.9 mmol, 85% yield). These crystals were of X-ray quality. An X-ray diffraction analysis was performed, and the details can be found in the supporting information. The X-ray analysis revealed that the 2,2′-binaphthol chiral axis in salt **45** has an *S*-configuration.

Isolation of Resolved Acid (+)-44. The above crystals of salt **45** (δ = 7.25 ppm) were determined by ^{31}P NMR to be free of the soluble diastereomer (δ = 7.31). All of the above crystals of salt **45** were slurried in 200 mL of boiling ethanol. Not all of the salt dissolved even at the boiling point. Hydrochloric acid (200 mL, 6 N) was added by dropping funnel, and at one point during the addition all of the solid disappeared, but the solution became cloudy again upon further addition of acid. After cooling to 25 °C, the white solid was collected and washed with water. The filtrates were combined and concentrated. A second crop of the resolved acid **44** was collected and washed. The two crops were combined and dried under high vacuum to give 10.81 g (21.6 mmol, 81% yield) of (+)-**44**: $[\alpha]_D$ = 20.4 ($CHCl_3$, c = 1.5).

The Liberation of Binaphthol (−)-39 from Acid (+)-44. The resolved binaphthol phosphoric acid (+)-**44** (10.81 g, 21.6 mmol) was taken up in 100 mL of *N*,*N*-dimethylacetamide, and dimethyl sulfate (4.08 mL, 43.2 mmol) was added. Sodium bicarbonate (4.0 g, 47.6 mmol) was then added, and the mixture was stirred for 12 h at 25 °C at which point the reaction was complete as indicated by ^{1}H NMR. The solvent was removed by rotary evaporator at 55 °C, and the residue was dissolved in dichloromethane. This solution was washed with water and brine and then dried with anhydrous $MgSO_4$ and filtered through Celite. After removal of solvent, the residue was redissolved in 60 mL of toluene, and then 15 mL of Red-Al (3.4 M in toluene, 51 mmol) was introduced dropwisely at room temperature. After the solution was stirred for 12 h it was diluted with ethyl acetate. The reaction

mixture was washed with 1 N hydrochloric acid, aqueous saturated sodium bicarbonate, and water and then dried over anhydrous $MgSO_4$. Upon removal of solvent, the residue was loaded onto a silica gel column and eluted with a 1:9 mixture of EtOAc:hexane to give 9.26 g (21.1 mmol, 98%) of (−)-**39** as a crystalline white solid: $[\alpha]_D = -372.3$ (THF, $c = 1.0$). It was found that resolved **39** was much more soluble than the racemate, and thus resolved **39** can be easily loaded onto a column with a small portion of ethyl acetate. The optical purity of (−)-**39** was determined to be greater than 98% by ^{1}H NMR in $CDCl_3$ with Eu(hfc)$_3$. The optical purity of (−)-**39** was determined to be greater than 99% by HPLC on a Pirkle D-phenylglycine column with a 30:70 mixture of 2-propanol and hexane (550 psi, 0.9 mL/min) under which conditions the retention time of (−)-**39** is 7.83 min and that for (+)-**39** is 7.26 min.

Racemization of Binaphthol (−)-39 in Octane. A 15 mL Kontes flask was charged with (−)-**39** (0.020 g, 0.046 mmol) and 5 mL of octane. The solution was deoxygenated by the freeze-thaw method (two cycles) and was sealed under argon at 25 °C. The solution was heated to 150 °C for 2 h. After cooling and removal of solvent, the residue was dissolved in $CDCl_3$ and Eu(hfc)$_3$ was added. The ^{1}H NMR spectrum showed that no detectable amount of racemization had occurred. The same procedure was repeated as follows: 180 °C for 2 h, no racemization; 200 °C for 3 h, 10% racemization (95:5); 200 °C for 15 h, 30% racemization (85:15).

The Recovery of Binaphthol (+)-39 from the Mother Liquor. The mother liquor remaining after the removal of salt **45** was concentrated, and 300 mL of 6 N hydrochloric acid was added. The mixture was heated to boiling, and the remaining ethanol was evaporated. Upon cooling, the white solid that formed was collected, washed with water, and dried to give 13.0 g (26 mmol) of the nearly resolved binaphthol phosphoric acid (−)-**44**. This material was converted to (+)-**39** by the procedure described above for (−)-**39**. Purification of (+)-**39** was accomplished by chromatography on silica gel with a 1:9 mixture of EtOAc-hexane. As the fractions of **39** were collected, a small amount of crystals came out of solution which were collected to give 0.45 g of material that by ^{1}H NMR ($CDCl_3$) in the presence of the chiral shift reagent Eu(hfc)$_3$ was determined to be a mixture of (−)-**39** and (+)-**39**. Removal of solvent from the filtrate from all of the fractions and drying of the residue gave 8.27 g (18.9 mmol, 70% from racemic **39**) of optically pure binaphthol (+)-**39**: $[\alpha]_D = 362.0$ ($c = 1.0$, THF). The optical purity of (+)-**39** was determined to be greater than 98% by ^{1}H NMR in $CDCl_3$ with Eu(hfc)$_3$ ((−)-**39** could not be detected). The optical purity of (+)-**39** was determined to be greater than 99% by HPLC under the conditions described for (−)-**39**.

The Preparation of 3,3′-Biphenanthrol 47 by Oxidative Coupling of Phenanthrol 28 with Air. A mixture of **28** (9.94 g, 36.8 mmol) and glass beads (∼50 beads) in a beaker (800 mL) was stirred with a large magnetic stirring bar until a uniform layer of **28** (∼2 mm thick) had formed on each bead. The resulting mixture was heated to 190 °C in air with continuous stirring. After 18 h, the reaction mixture was allowed to cool to 25 °C, and the resulting dark solid layer was ground to break up the fused coated-bead particles and then suspended in EtOAc (∼25 mL). The beaker was covered with a watch glass and slowly lowered back into the 190 °C oil bath to prevent spattering as the ethyl acetate was boiled off. The reaction was monitored while being heated at 190 °C for 16 h to ensure that continuous stirring was maintained. An ^{1}H NMR analysis revealed complete consumption of starting material. The resulting dark brown reaction mixture was extracted with EtOAc (4 × 100 mL), and the combined EtOAc layer was filtered through filter paper and stripped of solvent to afford bis-(phenanthrol) **47** (8.78 g, 9.89 g theor, 89%) as a light-brown solid. This material was pure by ^{1}H NMR and was used directly in the resolution with (−)-cinchonidine. Further purification could be achieved by crystallization from EtOAc. If continuous stirring was not maintained during the reaction or if enough surface area was not provided, small amounts of side products could be observed by ^{1}H NMR. Spectral data for **47**: white solid; mp > 250 °C; $R_f = 0.29$ (1:9 EtOAc:hexane); ^{1}H NMR ($CDCl_3$) δ 6.59 (s, 2 H), 6.66 (d, 4 H, $J = 7.7$ Hz), 6.93 (t, 4 H, $J = 7.5$ Hz), 7.04 (t, 2 H, $J = 7.4$ Hz), 7.42 (s, 2 H), 7.61 (t, 2 H, $J = 7.3$ Hz), 7.64−7.67 (m, 4 H), 7.79 (d, 2 H, $J = 8.8$ Hz), 7.91 (d, 2 H, $J = 7.7$ Hz), 9.71 (d, 2 H, $J = 8.4$ Hz); ^{13}C NMR ($CDCl_3$) δ 115.77, 118.09, 123.23, 126.36, 126.81, 126.99, 127.03, 127.53, 128.44, 128.82, 129.29, 130.28, 132.80, 135.27, 139.70, 141.56, 153.41 (one carbon not located); IR (neat) 3473 s, 3049 m, 1611 w, 1590 w, 1555 w, 1372 m, 1330 m, 1246 w, 1210 w, 1175 m, 1027 w, 816 w, 774 m, 731 m, 665 m cm^{-1}; mass spectrum, *m*/*z* (rel intensity), 538 (18) M$^+$, 520 (5), 370 (3), 270 (100), 241 (30), 215 (7), 165 (10); exact mass calcd for $C_{40}H_{26}O_2$ *m*/*z* 538.1933, found *m*/*z* 538.1933. Anal. Calcd for $C_{40}H_{26}O_2$: C, 89.19; H, 4.87. Found: C, 88.43, H, 5.29.

The Preparation of 3,3′-Biphenanthrylphosphoric Acid 49 and Its Conversion to the 3,3′-Biphenanthrol Methyl Phosphate 52. To a solution of biphenanthrol **47** (15.93 g, 29.6 mmol) in 120 mL of pyridine was added phosphorus oxychloride (3.9 mL, 41.8 mmol). After this solution was stirred at room temperature for 2 h, it was heated to 90 °C for 1 h. Upon cooling to 25 °C, 25 mL of water was added with a noticable heat release and then the solution was heated to 95 °C for 1.5 h. The pyridine was removed under vacuum, and the residue was taken up in 200 mL of aqueous 6 N HCl solution and then heated to reflux for 2 h in a 140 °C oil bath. The solution was cooled to room temperature and filtered. The solid that was collected was washed with water and dried under high vacuum to give 18.06 g (30.1 mmol, 100% yield) of the phosphoric acid **49** as a white solid (mp > 275 °C). Spectral data for **49**: ^{1}H NMR ($CDCl_3$) δ 1.95 (brd s, 1 H), 6.49 (d, 4 H, $J = 7.4$ Hz), 6.87 (t, 4 H, $J = 7.6$ Hz), 7.23 (t, 2 H, $J = 7.7$ Hz), 7.39−7.43 (m, 4 H), 7.53−7.59 (m, 4 H), 7.66 (d, 2 H, $J = 8.8$ Hz), 7.76 (d, 2 H, $J = 7.5$ Hz), 9.87 (d, 2 H, $J = 8.5$ Hz); IR (neat) 3054 w, 3022 w, 2612 bs, 2133 w, 1616 w, 1597 w, 1487 m, 1375 m, 1288 m, 1246 m, 1131 w, 1075 w, 1023 m, 900 m, 750 s, 697 s cm^{-1}.

A small portion of acid **49** (0.162 g, 0.27 mmol) was converted to the methyl ester **52** with CH_2N_2 by the procedure described above for the preparation of **46**. The product was purified on a silica gel column with a 1:5 mixture of EtOAc:hexane to give 0.1106 g (0.18 mmol, 67% yield) of the biphenanthrol methyl phosphate **52** as a white solid. Spectral data for **52**: $R_f = 0.12$ (1:5 EtOAc:hexane); white solid mp > 300 °C; ^{1}H NMR ($CDCl_3$) δ 3.76 (d, 3 H, $J_{P-H} = 11.6$ Hz), 6.46 (d, 2 H, $J = 7.4$ Hz), 6.50 (d, 2 H, $J = 7.8$ Hz), 6.91 (m, 4 H), 7.05 (m, 2 H), 7.539 (s, 1 H), 7.54 (s, 1 H), 7.63−7.79 (m, 8 H), 7.92 (d, 1 H, $J = 7.8$ Hz), 7.95 (d, 1 H, $J = 8.1$ Hz), 9.51 (d, 1 H, $J = 8.6$ Hz), 9.59 (d, 1 H, $J = 8.6$ Hz); ^{13}C NMR ($CDCl_3$) δ 56.19 (d, $J_{P-C} = 5.4$ Hz), 121.19, 121.24, 121.76, 121.80, 125.54, 125.56, 125.65, 125.68, 126.63, 126.72, 126.78, 127.12, 127.19, 127.41, 127.48, 127.63, 127.66, 127.78, 127.92, 128.16, 128.65, 128.92, 128.97, 129.01, 129.17, 129.39, 133.31, 133.41, 134.50, 134.80, 139.31, 141.15, 141.32, 146.74, 147.64, 147.80; IR (neat) 3056 m, 2957 w, 2851 w, 1611 w, 1590 w, 1442 m, 1379 m, 1298 s, 1231 m, 1125 w, 1045 s, 1021 s, 911 s, 895 m, 868 m, 813 m, 732 s, 697 s cm^{-1}; mass spectrum, *m*/*z*) (rel intensity), 614 (100) M$^+$, 520 (15), 443 (5), 268 (7), 221 (6); exact mass calcd for $C_{41}H_{27}O_4P$ *m*/*z* 614.1647, found *m*/*z* 614.1619. Anal. Calcd for $C_{41}H_{27}O_4P$: C, 80.12; H, 4.43; P, 5.04. Found: C, 80.03; H, 4.59; P, 4.88.

The Resolution of 2,2′-Diphenyl-[3,3′-biphenanthrene]-4,4′-diol (47). Preparation of Salts 50 and 51 from Acid 49 and (−)-Cinchonidine. To a solution of acid **49** (17.8 g, 29.6 mmol) in 300 mL of ethanol was added (−)-cinchonidine (8.73 g, 29.6 mmol). The solution was heated to the boiling point to ensure complete dissolution of all solids and then allowed to cool on the benchtop for 12 h. Crystals were collected and shown by ^{1}H NMR to be salt **50**. The mother solution was concentrated on a rotary evaporator to the saturation point and then allowed to sit at room temperature for a few hours. The crystals that were collected were shown by ^{1}H NMR to be salt **51**. In both cases, the enrichment was greater than 40:1. The filtrate was concentrated again to give additional crystals of salt **50**. This process was repeated until there was 2.67 g of a mixture of salts left which by ^{1}H NMR was shown to consist of **50** and **51** in a 1:4 ratio. Salt **50**: ^{1}H NMR ($CDCl_3$) δ 0.85−0.95 (m, 1H), 1.25−1.30 (m, 1H), 1.50−1.60 (m, 1H), 1.65−1.75 (m, 2H), 1.91−1.95 (m, 2H), 2.21−2.23 (m, 1H), 2.45−2.55 (m, 1H), 2.73−2.83 (m, 2H), 4.10 (m, 1H), 4.70 (d, 1H, $J = 17.1$ Hz), 4.83 (d, 1H, $J = 10.3$ Hz), 5.08−5.12 (m, 1H), 5.92 (br s, 1H), 6.37 (br s, 1H), 6.49 (d, 4H, $J = 7.8$ Hz), 6.77 (t, 1H, $J = 7.7$ Hz), 6.85 (t, 4H, $J = 7.6$ Hz), 7.01 (t, 2H, $J = 7.3$ Hz), 7.15 Hz, (t, 2H, $J = 7.4$ Hz), 7.58 (s, 2H), 755−7.61 (m, 7H), 7.75 (d, 1H, $J = 8.4$ Hz), 8.67 (d, 1H, $J = 4.4$ Hz), 10.03 (d, 2H, $J = 8.6$ Hz). Salt **51**: ^{1}H NMR ($CDCl_3$) δ 1.02−1.05 (m, 1H), 1.30−1.40 (m, 1H), 1.65−

1.72 (m, 1H), 1.65−1.73 (m, 2H), 2.04−2.07 (m, 1H), 2.18−2.19 (m, 1H), 2.40−2.50 (m, 3H), 3.10−3.15 (m, 1H), 4.05−4.15 (m, 1H), 4.75 (d, 1H, J = 17.2 Hz), 4.81 (d, 1H, J = 10.4 Hz), 5.22−5.32 (m, 1H), 6.33 (s, 1H), 6.40 (br s, 1H), 6.55 (d, 4H, J = 7.4 Hz), 6.89 (t, 4H, J = 7.6 Hz), 6.98 (t, 2H, J = 7.8 Hz), 7.04 (t, 2H, J = 7.3 Hz), 7.36−7.31 (m, 4H), 7.48 (s, 2H), 7.59−7.68 (m, 6H), 7.75 (d, 2H, J = 7.8 Hz), 8.11 (d, 1H, J = 7.7 Hz), 8.35 (d, 1H, J = 7.9 Hz), 8.72 (d, 1H, J = 5.0 Hz), 9.94 (d, 2H, J = 8.6 Hz).

Biphenanthrol (+)-47 from Salt 50. All crops of salt **50** were combined and recrystalized from ethanol. The ^{1}H NMR and ^{31}P NMR spectra of the salt **50** indicated that the purity was greater than 98%. The salt **50** was then treated with 6 N aqueous HCl solution and heated to reflux for 1 h. The white solid that formed was collected and dried under high vacuum to give 7.08 g (11.8 mmol, 80% yield) of the resolved acid **49**. All of this acid was dissolved in 100 mL of *N*,*N*-dimethylacetamide, and then sodium bicarbonate (1.97 g, 23.4 mmol) and dimethyl sulfate (2.23 mL, 23.4 mmol) were added. The solution was stirred at room temperature for 20 h, and then the solvent was removed by rotary evaporator at 55 °C. The residue was dissolved in dichloromethane and was washed wtih aqueous saturated sodium bicarbonate, water, and brine. After it was dried over $MgSO_4$ and stripped of all volatiles, the ester was dissolved in 150 mL of toluene, and then Red-Al (12.5 mL, 42.5 mmol as a 3.4 M solution in toluene) was added. The solution was allowed to stir at room temperature for 10 h and then was diluted with ethyl acetate and quenched with 1 N aqueous HCl. The organic layer was washed with aqueous saturated sodium bicarbonate, water, and brine and then dried ($MgSO_4$). After removal of solvent, the residue was loaded onto a silica gel column and eluted with a 1:5 mixture of EtOAc:hexane to give 6.36 g (11.8 mmol, 99% yield) of resolved bisphenanthrol (+)-**47** as a white crystalline solid: $[\alpha]_D$ = 124.96 (c = 1.0, THF). The optical purity of (+)-**47** was determined to be greater than 98% by ^{1}H NMR with an excess of (*S*)-(−)-α-methylbenzylamine as chiral shift reagent (no detectable amount of (−)-**47** was present). The optical purity by HPLC was found to be greater than 99.8% by using a Pirkle D-phenylglycine colum with the following conditions: 254 nm, 148 psi, 1.5 mL/min, 60:40 mixture of 2-propanol and hexane (t_R = 19.8 min for (+)-**47** and t_R = 12.1 min for (−)-**47**). The configuration of (+)-**47** was determined to be *S* by its conversion to the amide (*S*,*S*)-**54** with (*S*)-1-phenylethyl amine as described below. It was also noted that the racemate of **47** and the pure enanatiomers of **47** eluted with different rates on a silica gel column. The elution by flash chromatography on silica gel with a 1:1 mixture of methylene chloride and hexanes of a sample of **47** with an optical purity of 89.7% ee into four fractions gave a distribution of optical purities which in order of elution where 95.6%, 90.7%, 88.8%, and 82.9%.

Enrichment of (*S*)-3,3′-Biphenanthrol (+)-47 by Hexane Extraction. The following experiment illustrates that essentially optically pure **47** can be obtained from a scalemate by simple washing with hexane. A 150 mg sample of **47** that was enriched in (+)-**47** to 83.8% ee was washed with three 5 mL portions of hexane. The combined hexane layer was filtered, the filtrate was found to contain 89.6 mg of (+)-**47** of greater than 99.8% ee, and the remaining solid consisted of 57.5 mg of (+)-**47** of 56.5% ee.

Biphenanthrol (−)-47 from Salt 51. All crops of salt **51** were combined and recrystallized once from ethanol to give material that ^{1}H NMR indicated was greater than 98% free of salt **50**. The salt **51** was then converted to (−)-**47** with the procedure described above for (+)-**47**. The (−)-**47** obtained was purified on silica gel (1:5 mixture of EtOAc/hexane) to give 5.75 g (10.7 mmol, 72% from racemic **47**) of bis(phenanthrol) (−)-**47** as a white solid: $[\alpha]_D$ = −123.37 (c = 1.0, THF). The optical purity of (−)-**47** was determined to be greater than 98% by ^{1}H NMR with an excess of (*S*)-(−)-α-methylbenzylamine as chiral shift reagent (no detectable amount of (+)-**47** was present). The optical purity by HPLC was found to be greater than 99.9% utilizing the conditions described for the analysis of (+)-**47**.

The Preparation of Phosphoric Amide (*S*,*S*)-54 from the Resolved Biphenanthrol (+)-47. To a solution of resolved bis(phenanthrol) (+)-**47** (0.220 g, 0.41 mmol) in 4 mL of methylene chloride at ambient temperature were added triethylamine (0.137 mL, 0.98 mmol) and phosphorus oxychloride (0.053 mL, 0.57 mmol). After the solution was stirred for 1 h at 25 °C, it was cooled to 0 °C and (*S*)-α-methylbenzylamine was added. The solution was stirred for 24 h, and then it was diluted with dichloromethane, was washed with water and brine, and dried with anhydrous $MgSO_4$. Upon removal of solvent, the residue was loaded onto a silica gel column and eluted with a 1:4 mixture of EtOAc:hexane to give, in order of elution, 0.0385 g (0.062 mmol, 15%) of acid chloride **48**, 0.1014 g (0.14 mmol, 35% yield) of (*S*,*S*)-**54**, and 0.1146 g of an unidentified compound. Crystals were grown from a solution of (*S*,*S*)-**54** in CH_2Cl_2, and an X-ray crystal structure was obtained which revealed that the chiral axis in this compound has an *S* configuration and the details have been previously published.[30a] Spectral data for **48**: R_f = 0.57 (1:2 EtOAc:hexane); ^{1}H NMR ($CDCl_3$) δ 6.46 (d, 2 H, J = 7.5 Hz), 6.49 (d, 2 H, J = 7.5 Hz), 6.90 (t, 4 H, J = 7.4 Hz), 7.05−7.09 (m, 2 H), 7.59 (d, 2 H, J = 5.2 Hz), 7.65−7.84 (m, 8 H), 7.94 (t, 2 H, J = 7.9 Hz), 9.49 (d, 1 H, J = 9.0 Hz), 9.51 (d, 1 H, J = 8.8 Hz); ^{13}C NMR ($CDCl_3$) δ 126.45, 126.54, 126.97 (two carbons), 127.47, 127.59, 127.75 (two carbons), 127.80, 127.89, 127.96, 128.09, 128.49, 128.56, 128.76, 128.80, 128.91, 128.93, 129.06, 129.40 (two carbons), 129.46, 129.69, 129.83, 133.52, 134.81, 134.99, 139.00, 139.08, 141.28, 141.39, 141.42 (4 carbons not located); IR (neat) 3076 w, 3048 m, 1613 w, 1597 w, 1384 w, 1319 m, 1302 s, 1230 m, 1119 m, 1051 w, 1017 m, 917 s, 910 s, 868 m, 825 m, 780 w, 748 m, 738 s, 697 s cm^{-1}; mass spectrum, *m*/*z* (rel intensity), 618 (1) M^+, 490 (12), 467 (7), 415 (5), 372 (18), 121 (100), 105 (24). Spectral data for (*S*,*S*)-**54**: R_f = 0.38 (1:2 EtOAc:hexane); mp > 250 °C; ^{1}H NMR ($CDCl_3$) δ 0.89 (d, 3 H, J = 6.8 Hz), 3.11 (dd, 1 H, J = 9.6, 11.6 Hz), 4.54−4.59 (m, 1 H), 6.46 (d, 2 H, J = 7.4 Hz), 6.50 (d, 2 H, J = 7.4 Hz), 6.87−6.91 (m, 4 H), 7.03−7.09 (m, 4 H), 7.15−7.21 (m, 3 H), 7.39 (t, 1 H, J = 8.3 Hz), 7.52 (d, 2 H, J = 7.8 Hz), 7.57 (t, 1 H, J = 7.5 Hz), 7.63−7.67 (m, 3 H), 7.75−7.79 (m, 3 H), 7.87 (d, 1 H, J = 8.1 Hz), 7.90 (d, 1 H, J = 8.2 Hz), 9.40 (d, 1 H, J = 8.7 Hz), 9.75 (d, 1 H, J = 8.6 Hz); ^{13}C NMR ($CDCl_3$) δ 24.43 (d, J = 7.0 Hz), 52.24, 121.50, 121.54, 121.88, 121.92, 125.28, 125.56, 125.61, 126.30, 126.33, 126.61, 126.74, 126.90, 126.98, 127.13, 127.21, 127.55, 127.60, 127.65, 127.81, 128.25, 128.41, 128.77, 128.82, 129.01, 129.21, 129.24, 129.32, 129.39, 133.18, 133.31, 134.44, 134.46, 134.60, 134.61, 139.41, 139.48, 140.99, 141.01, 141.34, 141.35, 144.52, 144.56, 146.90, 147.02, 147.43, 147.57; IR (neat) 3366 w, 3175 w, 3057 m, 3031 w, 2968 w, 2925 m, 2855 w, 2246 w, 1616 w, 1598 w, 1557 w, 1494 w, 1487 w, 1450 w, 1423 w, 1375 m, 1330 w, 1283 s, 1232 s, 1206 w, 1120 m, 1075 m, 1053 s, 1024 s, 989 m, 902 s, 847 s, 813 m, 781 w, 731 s, 697 s, 645 m cm^{-1}; mass spectrum, *m*/*z* (rel intensity), 703 (8) M^+, 199 (100), 149 (25), 97 (40), 83 (43), 69 (69); exact mass calcd for $C_{48}H_{34}O_3NP$, *m*/*z*, 703.2276, found *m*/*z* 703.2269.

The same procedure was carried out on racemic **47** (0.38 mmol) to provide a sample of (*R*,*S*)-**54** (18%) and also an 11% yield of the less polar (*S*,*S*)-**54**. Spectral data for (*R*,*S*)-**54**: R_f = 0.26 (1:2 EtOAc:hexane); ^{1}H NMR ($CDCl_3$) δ 0.73 (d, 3 H, J = 7.0 Hz), 3.36 (dd, 1 H, J = 9.0, 12.0 Hz), 3.57−3.62 (m, 1 H), 6.44 (d, 2 H, J = 7.5 Hz), 6.50 (d, 2 H, J = 7.5 Hz), 6.82 (d, 2 H, J = 7.1 Hz), 6.88−6.91 (m, 4 H), 7.03−7.11 (m, 6 H), 7.44−7.48 (m, 2 H), 7.55−7.77 (m, 6 H), 7.81 (d, 1 H, J = 8.8 Hz), 7.84 (d, 1 H, J = 7.5 Hz), 7.93 (d, 1 H, J = 7.3 Hz), 8.95 (d, 1 H, J = 8.6 Hz), 9.77 (d, 1 H, J = 8.5 Hz).

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Supporting Information Available: X-ray data for compound **45**, including fractional coordinates, isotropic and anisotropic thermal parameters, and bond distances and bond angles; listing of observed and calculated structure factors (15 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.

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