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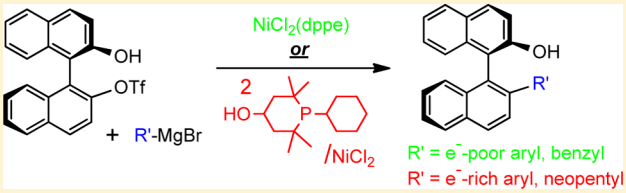
Access to 2′-Substituted Binaphthyl Monoalcohols via Complementary Nickel-Catalyzed Kumada Coupling Reactions under Mild Conditions: Key Role of a P,O Ligand

Sachin Handa, Yohan L. N. Mathota Arachchige, and LeGrande M. Slaughter*

Department of Chemistry, Oklahoma State University, Stillwater, Oklahoma 74078, United States

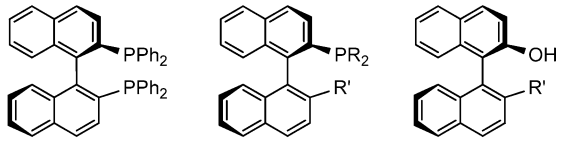
Supporting Information

ABSTRACT: Two complementary Kumada coupling methods for the conversion of monotriflated 1,1′-binaphthalene-2,2′-diol (BINOL) into 2′-substituted binaphthyl monoalcohols under mild conditions are reported. A protocol using $NiCl_2$(dppe), in combination with an improved preparation of the monotriflate, is effective for 1,1′-binaphthalene-2-ols containing unsubstituted or electron-poor aryl or benzyl 2′-substituents. An alternative procedure, using a potentially hemilabile-bidentate phosphinan-4-ol ligand, is superior for products containing neopentyl or electron-rich aryl 2′-substituents. The obtained binaphthyl alcohols represent potentially useful synthons for chiral ligands and auxiliaries.



The 1,1′-binaphthyl moiety is a ubiquitious design element in chiral auxiliaries and catalysts.[1,2] For derivatives with substituents at the 2- and 2′-positions, restricted rotation about the 1,1′-bond prevents racemization,[3] enforcing a sterically pronounced, axially chiral conformation that can engender highly asymmetric environments at metal-based or organocatalytic active sites.[4] The vast majority of binaphthyl derivatives used in asymmetric synthesis contain Lewis basic substituents at both the 2- and 2′-positions.[5] This is exemplified by chiral diphosphine ligands such as 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl (BINAP; **1**),[6] in which chelation to a catalytic metal constrains the binaphthyl unit to a rigid, C_2-symmetric geometry and creates a static binding pocket that is favorable for chiral induction.[7] Monodentate binaphthyl-based ligands are less developed[8] but could provide advantages when the metal is intrinsically low-coordinate or forms underligated catalytic intermediates.[9] Here, attention has focused on ligand designs that tie the binaphthyl unit into phosphite,[10] phosphonite,[11] or phosphoramidite[12] structures via P−O linkages at the 2,2′-positions, also rigidifying the chiral backbone. Monodentate binaphthyl ligands with donor substituents only at the 2-position are rare.[13−19] The most notable examples are the MOP family of monophosphines (**2**),[13−15] some of which have delivered high enantioselectivities for certain palladium-catalyzed reactions[14] despite the greater conformational flexibility arising from the noncoordinated second naphthyl ring. We have recently reported evidence that this kind of flexibility can be advantageous in binaphthyl-based monodentate carbene ligands, where it facilitates noncovalent interactions of the 2′-substituent with the metal active site that may contribute to highly enantioselective catalysis.[19]

Toward a goal of further exploring monodentate binaphthyl-based ligands in asymmetric catalysis, we sought preparative routes to 1,1′-binaphthalene-2-ols with electronically and sterically diverse aryl and alkyl substituents at the 2′-position (**3**). Only a few such binaphthyl monoalcohols are known,[20−27] and no broadly applicable synthetic method for installing nonheteroatom groups at the 2′-position of a binaphthyl unit has been reported, in contrast to well-developed methods for modification at the 3,3′-[1,28] and 6,6′-positions.[1] Most reported alcohols of type **3** have been obtained by nickel-catalyzed Kumada−Corriu coupling reactions[29] of Grignard reagents with derivatives of 1,1′-binaphthalene-2,2′-diol (BINOL: **4**, Table 1), a widely used binaphthyl precursor that is readily available in enantiomerically pure form.[2] The 2′-phenyl-substituted alcohol was prepared in two steps from BINOL, via the monotriflate **5**, using mild Kumada coupling conditions of 2 mol % $NiCl_2$(dppe) catalyst [dppe = bis(diphenylphosphino)-ethane] and 35 °C.[20] A derivative with a bulky silyl substituent at the *para* position of the 2′-phenyl group required slightly more stringent conditions (5 mol % catalyst, 66 °C).[21] One example with an electron-deficient aryl substituent [R′ = 3,5-$(CF_3)_2C_6H_3$] was synthesized similarly, but pretreatment of **5** with MeMgI prior to coupling was needed, and the yield was modest (59%).[22] Two variants of **3** with electronic-deficient 2′-aryl groups were obtained by palladium-catalyzed Suzuki



1 (*R*)-BINAP **2** MOP (R' = aryl, aryloxy, OMe) **3**

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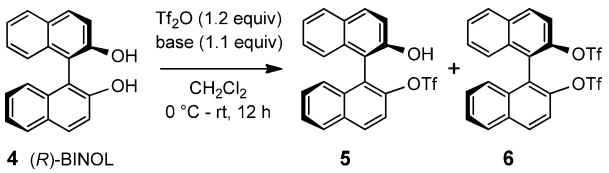
Table 1. Optimization of Reaction Conditions for Synthesis of Monotriflated BINOL (5)[a]



4 (*R*)-BINOL 5 6

entry	base	% yield 5	% yield 6	% recovered 4
1	Et_3N	65	10	12
2	iPr_2NH	69	10	10
3	iPr_2NEt	89	<2	–
4	pyridine	60	20	18
5	2,6-lutidine	62	15	17

[a]Reactions were conducted with 2.0 g of **4**.

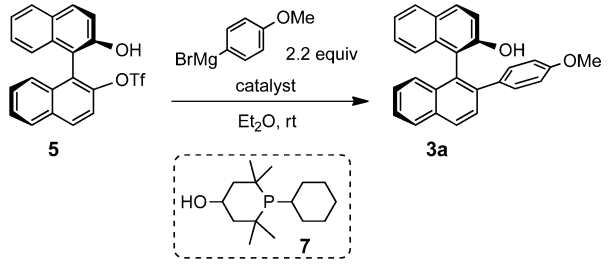
coupling, but formation of the 2′-iodide was necessary in addition to an alcohol protection step.[23] The only reported synthesis of a binaphthyl alcohol with an electron-rich 2′-aryl substituent (R′ = 2-methoxyphenyl) used an arylzinc reagent and harsh catalytic conditions, with 20 mol % $NiCl_2$(dppe) and extended reflux in THF.[24] Similarly forcing conditions were required for installation of electron-rich aryl groups at the 2′-position of MOP-type ligands via Kumada coupling reactions of 2-(diphenylphosphino)-1,1′-binaphthyl-2′-triflate.[15] Three 2′-alkyl versions of **3** (R′ = Me, Et, *i*Pr) have also been prepared by Kumada coupling with $NiCl_2$(dppe), but protection of the 2-hydroxy group and extended heating at 60 °C were necessary.[25,26] The 2′-benzyl derivative has been obtained by a three-step, noncatalytic route that is not applicable for nonbenzylic 2′-groups.[27]

Herein we report two complementary procedures that provide access to binaphthyl monoalcohols having a range of 2′-substituents via room temperature, nickel-catalyzed Kumada couplings of monotriflated BINOL **5**. An optimized version of the literature protocol, involving $NiCl_2$(dppe) catalyst and an improved synthesis of **5**, is effective for attachment of unsubstituted or electron-deficient aryl or benzyl substituents at the binaphthyl 2′-position. A new Kumada coupling procedure, using a potentially hemilabile-bidentate phosphinan-4-ol ligand in combination with nickel, provides superior yields for binaphthyl alcohols containing alkyl or electron-rich aryl 2′-substituents. Monotriflate **5** represents a challenging Kumada substrate due to the presence of a bulky naphthyl substituent *ortho* to the reactive carbon−oxygen bond,[29] and it is notable that no catalyst systems other than $NiCl_2$(dppe) have been previously reported for cross-coupling reactions of this useful chiral building block.

Our first goal was to identify conditions for synthesis of monotriflated BINOL **5** using triflic anhydride, which is significantly less expensive than the $PhNTf_2$ used as a sulfonating agent in the literature procedure.[20] Several bases were tested in reactions of (*R*)-BINOL with Tf_2O, and most of them afforded material contaminated with substantial amounts of ditriflate **6**[30] as well as unreacted BINOL (Table 1). The ditriflate was difficult to remove chromatographically, and trace amounts negatively impacted yields in subsequent catalytic reactions. However, the use of iPr_2NEt as a base led to isolation of **5** in 89% yield with only traces of **6** present. The minor ditriflate impurity in the optimized reaction is readily removed by flash chromatography, affording very pure monotriflate **5** even when the reaction is conducted on a 12 g scale. Notably, iPr_2NEt has been used previously to generate **5** in situ,[22] but not to prepare it as a pure material. Monotriflate **5** is isolated as a crystalline solid in our optimized protocol, whereas the literature procedure describes it as an oil.[20]

We examined the synthesis of *p*-methoxyphenyl-substituted binaphthyl alcohol **3a** as a test case for the identification of mild Kumada coupling conditions. Although **3a** has not been previously reported, literature precedent indicates that similar Kumada coupling reactions of binaphthyl triflates with aryl Grignard reagents containing electron-donating groups typically require forcing conditions.[15,24] Use of the standard Kumada catalyst $NiCl_2$(dppe) in 5 mol % at 25 °C with 2.2 equiv of aryl Grignard afforded **3a** in only 25% yield after 20 h (entry 1, Table 2). The related catalyst $NiCl_2$(dppp) [dppp = bis(diphenylphosphino)propane], which is known to provide superior activities in some Kumada coupling reactions involving electron-rich and/or hindered coupling partners,[31] was even less effective in this case, resulting in no detectable formation of **3a** (entry 2). These disappointing results prompted us to examine phosphinan-4-ol **7** as a ligand in the test reaction. Ligand **7** and variants were recently shown by McNulty and coworkers to be effective for the synthesis of electron-rich and sterically hindered biaryls by palladium-catalyzed Suzuki−Miyaura coupling.[32,33] The use of phosphinan-4-ol ligands in Ni-catalyzed coupling processes has not been previously reported, but reports of room-temperature Kumada couplings with nickel[34−37] or palladium[36,38−40] complexes of other potentially bifunctional P,O-type ligands encouraged us to try **7**. We were gratified to find that a catalyst system comprising 5 mol % $NiCl_2$ in combination with 10 mol % **7** provided binaphthyl alcohol **3a** in 79% yield after 60 min at 25 °C (entry 3).

Table 2. Catalyst Optimization for Kumada Coupling of 5 with an Electron-Rich Aryl Grignard[a]



5 3a 7

entry	catalyst	time (h)	% yield 3a
1	5 mol % $NiCl_2$(dppe)	20	25
2	5 mol % $NiCl_2$(dppp)	20	–
3	5 mol % anhyd $NiCl_2$ + 10 mol % **7**	1	78

[a]Reactions were conducted with 100 mg of **5**.

We next examined the effectiveness of the $NiCl_2/(7)_2$ catalyst system in room-temperature Kumada coupling reactions of **5** with a range of Grignard reagents in comparison with the standard $NiCl_2$(dppe) catalyst. The results show that the two catalyst systems are complementary (Table 3). In couplings of aryl Grignard reagents with **5**, the $NiCl_2/(7)_2$ system provides significantly better yields when electron-donating methoxy or methyl groups are present (entries 1−6), whereas $NiCl_2$(dppe) is superior for unsubstituted or electron-deficient aryl groups (entries 7−12). Notably, the P,O ligand allowed formation of the known *o*-methoxyphenyl derivative **3b** in comparable yield to that previously reported

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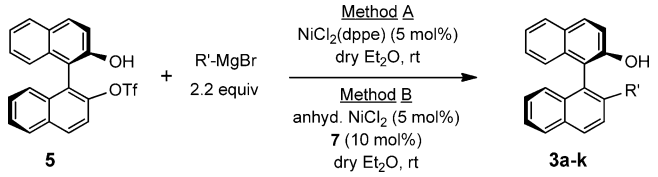
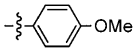
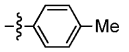
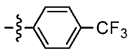
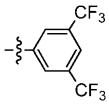
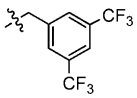
Table 3. Scope of 2′-Substituted Binaphthyl Alcohol Synthesis Using Complementary Kumada Coupling Methods



5 **3a-k**

entry	R′	product	method[a]	time (min)	yield (%)
1		**3a**	A	120	25
2			B	60	78
3		**3b**[b]	A	60	40
4			B	39	70
5		**3c**	A	80	30
6			B	40	91
7		**3d**	A	50	80
8			B	100	25
9		**3e**	A	65	51
10			B	45	10
11		**3f**	A	45	89
12			B	45	22
13		**3g**	A	35	50
14			B	30	83
15		**3h** (R′=*i*Pr)/**3i** (R′=*n*Pr)[c]	A	30	26 (18:82)[d,e]
16			B	30	49 (29:71)[d,f]
17		**3j**	A	70	81
18			B	60	85
19		**3k**	A	70	50
20			B	45	22

[a]Reaction conditions: 100 mg of **5** (0.20 M in dry Et_2O). Method A: 2.2 equiv of R′-MgBr (1.0 M in dry Et_2O), 5 mol % $NiCl_2$(dppe), rt. Method B: 2.2 equiv of R′-MgBr (1.0 M in dry Et_2O), 5 mol % anhydrous $NiCl_2$, 10 mol % **7**, rt. [b]Exists as a 50:50 mixture of two diastereomeric rotamers that are interconverting on the ^{1}H NMR time scale, consistent with published spectral data (ref 24). [c]Obtained as a mixture of the two isomers that could not be chromatographically separated. [d]Combined yield, with isomeric ratio of **3h** to **3i** given. [e]Binaphthalen-2-ol (ref 13) was also obtained in 32% yield. [f]Use of *n*PrMgBr resulted in an identical product ratio.

with $NiCl_2$(dppe),[24] but without the need for heating, high catalyst loading, or conversion of the Grignard to an arylzinc reagent (entry 4); by contrast, $NiCl_2$(dppe) was much less effective under the same conditions (entry 3). The $NiCl_2/(7)_2$ catalyst also gave significantly higher yields with alkyl Grignard reagents, including one example without β-hydrogens (R′ = neopentyl, entries 13, 14) and one with β-hydrogens (R′ = *i*Pr, entries 15, 16), although the yield was still modest (49%) in the latter case. For R′ = *i*Pr, a competing β-hydrogen elimination/alkene reinsertion process resulted in a mixture of the *i*Pr- and *n*Pr-substituted products with both catalysts. The high *n*Pr:*i*Pr ratios obtained are in agreement with previous reports of facile isomerization to the linear alkyl group in nickel-catalyzed alkyl−aryl Kumada couplings.[41] The coupling of **5** with benzyl Grignard was the only case in which both catalysts gave good yields of the desired product (entries 17, 18). However, coupling reactions of 3,5-bis(trifluoromethyl)benzyl Grignard exhibited catalyst-dependent differences in activity similar to those seen for electron-deficient aryl Grignard reagents, with a significantly higher yield obtained using the $NiCl_2$(dppe) catalyst (entries 19, 20). Finally, the use of highly pure **5** as a precursor appeared to improve the performance of the catalyst even when the standard $NiCl_2$(dppe) system was employed. For example, the synthesis of **3d** (R′ = Ph, entry 7) used a lower excess of Grignard reagent, and **3f** [R′ = 3,5-bis$(CF_3)_2C_6H_3$, entry 12] formed in higher yield without the need to pretreat **5** with MeMgI, in comparison to literature procedures using the same catalyst.[20,22]

The ability of related P,O-type ligands to promote room-temperature Kumada-Corriu coupling reactions has been attributed to enhancement of the oxidative addition rate of the electrophile, either through formation of reactive anionic M^0 species upon deprotonation of ligand hydroxy groups[38] or through cooperative C−X activation involving O-bound Mg ions.[35,37,39] However, the electrophile (i.e., **5**) is identical for all reactions in this study, suggesting that other steps in the catalytic cycle underlie the improved activities observed with ligand **7**. The Ni^{II}-bound binaphthyl ligand formed from **5** will be highly electron-rich upon deprotonation of the 2-hydroxy group by excess Grignard reagent, and C−C reductive eliminations are known to be slow when two electron-rich aryl ligands are involved.[42] We hypothesize that **7** promotes reductive elimination of electron-rich aryl groups by acting as a hemilabile-bidentate ligand (Scheme 1). A chair−boat conformational change allows the oxygen of one ligand to bind Ni^{II}, forming a 5-coordinate intermediate from which reductive elimination may be faster.[43] McNulty previously proposed that **7** stabilizes reactive Pd^0 species through this type of conformational flip.[32,33] Retardation of the transmetalation step due to bidentate binding and/or the stronger donicity of **7** may outweigh the improved reductive elimination rates in some cases, potentially explaining why poorer results were obtained

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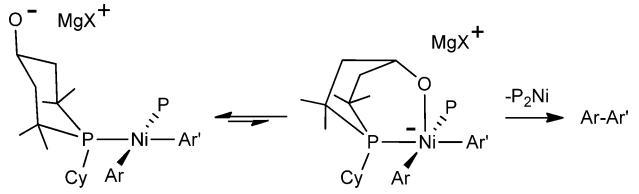
Scheme 1



with **7** versus dppe when electron-poor Grignard reagents were employed.[44]

The complementary Kumada coupling protocols presented herein expand the number of accessible 2′-substituted binaphthyl alcohols while also improving upon existing routes to these chiral synthons. Both procedures use inexpensive nickel as a catalyst but avoid the high catalyst loadings,[24] larger excesses of Grignard reagent,[20] or alcohol protection steps[23,25,26] used in some reported syntheses. The mild catalytic conditions preclude high temperatures that could lead to loss of enantiomeric purity. Ligand **7**, which improves access to variants of **3** with alkyl or electron-rich aryl 2′-substituents, is easily prepared in two steps from commercial materials, although it requires air-sensitive handling; detailed synthetic procedures and characterization data are provided below, as these are not available in the original report of **7**.[32] The syntheses of all alcohols except **3b** and **3h**/**3i**, including five previously unreported compounds (**3a**,**c**,**e**,**g**,**k**), were scaled up to 1−4 g with no appreciable loss of yield (see the Experimental Section). These binaphthyl monoalcohols represent potential synthons for a range of new monodentate chiral ligands and auxiliaries, since the hydroxyl group or its sulfonated derivatives can be readily converted into a variety of donor functionalities including phosphines,[6] amines,[45] and carbenes.[19]

EXPERIMENTAL SECTION

General Experimental Methods. Manipulations were performed under dry nitrogen in oven-dried glassware using freshly distilled dry solvents unless otherwise noted. (*R*)-BINOL **4** (>99%) was purchased from Chem-Impex International, Inc., and checked for optical purity prior to reaction. $NiCl_2$ (anhydrous, >99%) was purchased from Strem. $NiCl_2$(dppe) was synthesized in *i*PrOH/MeOH using a literature procedure.[46] Preparative flash column chromatography was performed on silica gel 60 (230−400 mesh) using solvent mixtures that gave optimal separations by TLC (specified below). For development of chiral HPLC separation conditions used for confirmation of enantiomeric purity, racemic samples of **3a**−**k** were prepared from commercial *rac*-BINOL using the methods reported in Table 3.

(*R*)-2′-Trifluoromethanesulfonyl-[1,1′-binaphthalene]-2-ol (5). A three-neck flask was fitted with two dropping funnels, which contained solutions of Tf_2O (5.90 mL, 34.9 mmol) in 50 mL of CH_2Cl_2 and *i*Pr_2NEt (6.10 mL, 34.9 mL) in 49 mL of CH_2Cl_2, respectively. A solution of (*R*)-BINOL **4** (10.0 g, 34.9 mmol) in CH_2Cl_2 (350 mL) was added to the flask. The flask was cooled to 0 °C, and the solutions of Tf_2O and *i*Pr_2NEt were slowly added together over a period of 30 min. The reaction mixture was slowly warmed to 25 °C and then stirred for an additional 9 h. After complete consumption of **4**, the mixture was diluted with 150 mL of CH_2Cl_2 and then sequentially washed with cold 1.0 N HCl and 0.5 N $NaHCO_3$. The organic layer was dried over Na_2SO_4, and the solvent was removed under vacuum. The oily crude product was purified by flash chromatography to yield a white solid (12.1 g, 89%). Optical rotation and ^{1}H NMR data were in agreement with published values:[20] R_f 0.50 (2:3 CH_2Cl_2/hexanes); mp = 38−39 °C; $[\alpha]_D^{23}$ = +12.7 (*c* = 4.0, $CHCl_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.9, 146.3, 133.4, 133.3, 133.1, 131.8, 131.6, 129.3, 128.6, 128.4, 128.4, 127.7, 127.2, 126.6, 125.3, 124.3, 123.9, 119.9, 118.4 (q, $J_{(C,F)}$ = 319 Hz), 118.1, 112.2; HRMS (ESI-orbitrap) *m*/*z* calcd for $C_{21}H_{13}F_3O_4SNa$ 441.0384 $[M + Na]^+$, found 441.0386.

1-Cyclohexyl-2,2,6,6-tetramethylphosphinan-4-ol (7). Neat cyclohexylphosphine (1.0 g, 7.2 mmol) and freshly distilled 2,6-dimethylhepta-2,5-dien-4-one (phorone, 0.84 g, 7.2 mmol) were added to a sealable reaction vessel under argon counterflow. The vessel was sealed, and the reaction mixture was heated at 130 °C for 8 h. The reaction mixture was then cooled to room temperature, and the intermediate 1-cyclohexyl-2,2,6,6-tetramethylphosphinan-4-one[47] (0.80 g, 44% yield, air-sensitive waxy solid) was obtained by vacuum distillation (120 °C, 10 mtorr) under rigorous exclusion of air: ^{1}H NMR (400 MHz, CD_2Cl_2) δ 2.56 (dd, *J* = 12, 3.4 Hz, 2H), 2.13 (dd, *J* = 17, 12 Hz, 2H), 1.98−1.91 (m, 2H), 1.88−1.76 (m, 3H), 1.70−1.64 (m, 1H), 1.48−1.36 (m, 2H), 1.34−1.22 (m, 3H), 1.22 (d, $J_{(P,H)}$ = 16 Hz, 6H), 1.17 (d, $J_{(P,H)}$ = 4.0 Hz, 6H). For the next step, dry THF (20 mL) was transferred to a two-neck flask, and $LiAlH_4$ (180 mg, 4.72 mmol) was added under argon counterflow. The resulting slurry was stirred for 5 min at 0 °C, and a solution of the phosphinan-4-one intermediate (0.60 g, 2.4 mmol) in 5.0 mL of THF was slowly added. The reaction mixture was stirred for 30 min at 25 °C and then for a further 1 h at 50 °C. After complete consumption of the starting material as judged by disappearance of the carbonyl IR stretch at 1723 cm^{-1}, the reaction mixture was cooled to 0 °C, quenched with 1.0 mL of degassed water, and stirred for 30 min at 25 °C. The mixture was then filtered through a glass frit under argon, and the solvent was removed in vacuo. The crude product was recrystallized from dry hexanes to afford **7** as a white, air-sensitive solid (0.20 g, 33%): mp = 55−57 °C (decomp, under N_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.07 (m, 1H), 3.21 (br s, 1H), 2.23−2.10 (m, 3H), 1.95−1.71 (m, 6H), 1.60−1.48 (m, 2H), 1.32 (d, $J_{(P,H)}$ = 11 Hz, 6H), 1.30−1.18 (m, 4H), 1.26 (d, $J_{(P,H)}$ = 13 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 63.7 (d, $J_{(C,P)}$ = 4.4 Hz), 48.9, 39.0 (d, $J_{(C,P)}$ = 56 Hz), 35.4 (d, $J_{(C,P)}$ = 54 Hz), 27.8 (d, $J_{(C,P)}$ = 2.2 Hz), 27.7, 27.6, 26.5, 26.4; ^{31}P NMR (101 MHz, $CDCl_3$) δ 29.8; HRMS (ESI-orbitrap) *m*/*z* calcd for $C_{15}H_{30}OP$ 257.2034 $[M + H]^+$, found 257.2028.

General Procedure for Grignard Reagent Preparation. Magnesium turnings were activated by washing with 1.0 M HNO_3, water, and acetone, followed by drying in vacuo, and 1.5 equiv (relative to R′-Br) were placed in a two-neck flask fitted with a reflux condenser. Dry Et_2O (10 mL per mmol of R′-Br) was transferred into the flask by vacuum distillation. Half of the R′-Br was introduced slowly with stirring, and the reaction mixture was heated at reflux in a 48 °C oil bath until initiation of the reaction (time specific to R′-Br). After initiation, the remaining R′-Br was added dropwise, and the mixture was stirred for an additional 30 min to 2 h (time specific to R′-Br). After cooling, the Grignard solution was used immediately in a Kumada coupling reaction.

General Procedure for Kumada Coupling (Method A). To a stirred solution of **5** in dry Et_2O (6.0 mL per mmol of **5**) were added $NiCl_2$(dppe) (5.0 mol %) and freshly prepared Grignard reagent (2.2 equiv) under argon counterflow. The reaction mixture was stirred at 25 °C until **5** had been completely consumed as judged by TLC (30−120 min; see Table 3). The reaction mixture was then quenched with saturated aqueous NH_4Cl and extracted with Et_2O and water. The organic layer was dried over Na_2SO_4 and concentrated under reduced pressure to obtain the crude product, which was purified by flash chromatography.

General Procedure for Kumada Coupling (Method B). To a solution of **5** in dry Et_2O (6.0 mL per mmol of **5**) were added anhydrous $NiCl_2$ (5.0 mol %) and **7** (10 mol %) under argon counterflow. The mixture was stirred at 25 °C for 15 min, and a small portion (~5% of 2.2 equiv total) of freshly prepared Grignard reagent was introduced. After appearance of a deep brown color (5−10 min), the remaining Grignard was added. Stirring was continued until **5** had been completely consumed as judged by TLC (30−120 min; see Table 3). The reaction mixture was then quenched with saturated aqueous NH_4Cl and extracted with Et_2O and water. The organic layer was dried

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over Na_2SO_4 and concentrated under reduced pressure to obtain the crude product, which was purified by flash chromatography.

(*R*)-2′-(4-Methoxyphenyl)-[1,1′-binaphthalen]-2-ol (3a). Method B (Grignard preparation: initiation 45 min, reaction time 120 min): R_f 0.52 (2:3 CH_2Cl_2/hexanes); 2.7 g, 79%; white solid, mp = 78−79 °C, $[\alpha]_D^{24}$ = +67.2 (*c* = 0.5, THF); *er* 0.2(*S*):99.8(*R*), determined by chiral HPLC (Chiralpak IC column, 4.6 × 250 mm, 5 μm particle size, 25 °C, hexanes/*i*PrOH 95:5, pressure = 3.4 MPa, flow rate 1.0 mL min^{-1}, $t_R(S)$ = 5.7 min, $t_R(R)$ = 7.0 min); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 8.8 Hz, 1H), 7.97 (d, *J* = 8.4 Hz, 1H), 7.80 (d, *J* = 8.4 Hz, 1H), 7.79 (d, *J* = 9.2 Hz, 1H), 7.70 (d, *J* = 8.8 Hz, 1H), 7.49 (ddd, *J* = 8.1, 6.7, 1.6 Hz, 1H), 7.33−7.25 (m, 3H), 7.22 (ddd, *J* = 8.1, 6.8, 1.2 Hz, 1H), 7.15 (d, *J* = 9.2 Hz, 1H), 7.09 (d, *J* = 8.8 Hz, 1H), 7.06 (m, 2H), 6.60 (m, 2H), 4.82 (s, 1H), 3.67 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.6, 151.0, 141.2, 134.34, 133.4, 133.3, 133.2, 129.9 (2C), 129.5, 128.9, 128.8, 128.3, 128.3, 128.2, 127.2, 126.7, 126.4, 126.4, 125.2, 123.3, 118.0, 117.4, 113.3, 55.2. Anal. Calcd for $C_{27}H_{20}O_2$·0.1(C_6H_{14}) (solvent content by ^{1}H NMR; not removable under a vacuum): C, 86.09; H, 5.60%. Found: C, 85.85; H, 5.99%.

(*R*)-2′-(2-Methoxyphenyl)-[1,1′-binaphthalen]-2-ol (3b). Method B (Grignard preparation: initiation 45 min, reaction time 50 min): R_f 0.51 (2:3 CH_2Cl_2/hexanes); 0.23 g, 61%; white solid, mp = 78−79 °C, $[\alpha]_D^{24}$ = +17.0 (*c* = 0.5, THF); *er* 0.1(*S*):99.9(*R*), determined by chiral HPLC (Phenomenex Lux Cellulose-1 column, 4.6 × 250 mm, 3 μm particle size, 25 °C, hexanes/*i*PrOH 99:1, pressure = 5.7 MPa, flow rate 1.0 mL min^{-1}, $t_R(S)$ = 11.4 min, $t_R(R)$ = 12.5 min); Optical rotation and ^{1}H NMR data were in agreement with published values;[24] HRMS (ESI-orbitrap) *m*/*z* calcd for $C_{27}H_{20}O_2Na$ 399.1361 $[M + Na]^+$, found 399.1372.

(*R*)-2′-(*p*-Tolyl)-[1,1′-binaphthalen]-2-ol (3c). Method B (Grignard preparation: initiation 40 min, reaction time 90 min): R_f 0.31 (2:3 EtOAc/hexanes); 3.9 g, 90%; white solid, mp = 92−93 °C, $[\alpha]_D^{25}$ = +56.6 (*c* = 0.5, THF); *er* 0.2(*S*):99.8(*R*), determined by chiral HPLC (Phenomenex Lux Cellulose-1 column, 4.6 × 250 mm, 3 μm particle size, 25 °C, hexanes/*i*PrOH 98:2, pressure = 2.8 MPa, flow rate 0.5 mL min^{-1}, $t_R(S)$ = 6.8 min, $t_R(R)$ = 7.5 min); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 8.8 Hz, 1H), 7.97 (d, *J* = 8.0 Hz, 1H), 7.79 (d, *J* = 8.8 Hz, 2H), 7.70 (d, *J* = 8.8 Hz, 1H), 7.50 (ddd, *J* = 8.3, 6.6, 1.6 Hz, 1H), 7.33−7.25 (m, 3H), 7.23 (ddd, *J* = 8.3, 6.6, 1.6 Hz, 1H), 7.15 (d, *J* = 8.8 Hz, 1H), 7.10 (d, *J* = 8.4 Hz, 1H), 7.03 (m, 2H), 6.87 (m, 2H), 4.83 (s, 1H), 2.18 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.0, 141.6, 138.0, 136.8, 134.4, 133.3, 133.3, 129.9, 129.5, 128.9, 128.8, 128.6 (2C), 128.4, 128.3, 128.2, 127.2, 126.7, 126.5, 126.4, 125.2, 123.3, 118.0, 117.3, 21.2. Anal. Calcd for $C_{27}H_{20}O$: C, 89.97; H, 5.59%. Found: C, 89.89; H, 5.91%.

(*R*)-2′-Phenyl-[1,1′-binaphthalen]-2-ol (3d). Method A (Grignard preparation: initiation 20 min, reaction time 60 min): R_f 0.58 (2:3 CH_2Cl_2/hexanes); 1.9 g, 80%; white solid, mp = 174−175 °C; $[\alpha]_D^{25}$ = +26.1 (*c* = 0.5, CH_2Cl_2); *er* 0.2(*S*):99.8(*R*), determined by chiral HPLC (Chiralpak IC column, 4.6 × 250 mm, 5 μm particle size, 25 °C, hexanes/*i*PrOH 95:5, pressure = 3.4 MPa, flow rate 1.0 mL min^{-1}, $t_R(S)$ = 4.6 min, $t_R(R)$ = 5.1 min); Melting point, optical rotation, and ^{1}H NMR data were in agreement with published values;[20] ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.1, 141.8, 141.0, 134.4, 133.4, 133.3, 130.1, 129.6, 128.9, 128.8 (2C), 128.7, 128.4, 128.3, 127.9, 127.4, 127.2, 126.8, 126.6, 126.5, 125.2, 123.4, 117.9, 117.4. Anal. Calcd for $C_{26}H_{18}O$: C, 90.14; H, 5.24%. Found: C, 90.21; H, 5.41%.

(*R*)-2′-[4-(Trifluoromethyl)phenyl]-[1,1′-binaphthalen]-2-ol (3e). Method A (Grignard preparation: initiation 35 min, reaction time 60 min): R_f 0.56 (2:3 CH_2Cl_2/hexanes); 1.2 g, 50%; white solid, mp = 146−147 °C, $[\alpha]_D^{24}$ = +21.5 (*c* = 0.5, CH_2Cl_2); *er* 0.1(*S*):99.9(*R*), determined by chiral HPLC (Chiralpak IC column, 4.6 × 250 mm, 5 μm particle size, 25 °C, hexanes/*i*PrOH 95:5, pressure = 1.7 MPa, flow rate 0.5 mL min^{-1}, $t_R(S)$ = 8.4 min, $t_R(R)$ = 9.5 min); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 8.4 Hz, 1H), 8.01 (d, *J* = 8.4 Hz, 1H), 7.80 (d, *J* = 9.2 Hz, 1H), 7.79 (d, *J* = 7.2 Hz, 1H), 7.67 (d, *J* = 8.4 Hz, 1H), 7.55 (ddd, *J* = 8.2, 6.6, 1.6 Hz, 1H), 7.38−7.27 (m, 5H), 7.26−7.20 (m, 3H), 7.14 (d, *J* = 8.8 Hz, 1H), 7.06 (d, *J* = 8.4 Hz, 1H), 4.77 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.1, 144.6, 140.2, 134.1, 133.6, 133.2, 130.3, 129.8, 129.1, 129.0, 129.0 (q, $J_{(C,F)}$ = 32 Hz), 128.8, 128.4, 128.3, 128.1, 127.6, 126.9, 126.9, 126.5, 124.8, 124.7 (q, $J_{(C,F)}$ = 3.7 Hz), 124.2 (q, $J_{(C,F)}$ = 272 Hz), 123.5, 117.3, 117.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ −63.5. Anal. Calcd for $C_{27}H_{17}F_3O$: C, 78.25; H, 4.14%. Found: C, 78.08; H, 4.31%.

(*R*)-2′-[3,5-Bis(trifluoromethyl)phenyl]-[1,1′-binaphthalen]-2-ol (3f). Method A (Grignard preparation: initiation 10 min, reaction time 40 min): R_f 0.61 (2:3 CH_2Cl_2/hexanes); 3.2 g, 92%; white solid, mp = 96−97 °C, $[\alpha]_D^{24}$ = −17.0 (*c* = 0.5, THF); *er* 0.2(*S*):99.8(*R*), determined by chiral HPLC (Phenomenex Lux Cellulose-1 column, 4.6 × 250 mm, 3 μm particle size, 25 °C, hexanes/EtOH 97:3, pressure = 5.8 MPa, flow rate 1.0 mL min^{-1}, $t_R(S)$ = 9.9 min, $t_R(R)$ = 9.3 min); ^{1}H AND ^{13}C NMR data were in agreement with published values;[22] ^{19}F NMR (376 MHz, $CDCl_3$) δ −64.1. Anal. Calcd for $C_{28}H_{16}F_6O$: C, 69.71; H, 3.34%. Found: C, 69.61; H, 3.42%.

(*S*)-2′-Neopentyl-[1,1′-binaphthalen]-2-ol (3g). Method B (Grignard preparation: initiation 10 min, reaction time 60 min): R_f 0.48 (2:3 CH_2Cl_2/hexanes); 2.3 g, 82%; white solid, mp = 75−76 °C, $[\alpha]_D^{25}$ = +86.0 (*c* = 0.15, THF; α observed to fluctuate at higher concentrations); *er* 99.7(*S*):0.3(*R*), determined by chiral HPLC (Phenomenex Lux Cellulose-1 column, 4.6 × 250 mm, 3 μm particle size, 25 °C, hexanes/*i*PrOH 95:5, pressure = 4.0 MPa, flow rate 0.7 mL min^{-1}, $t_R(S)$ = 7.6 min, $t_R(R)$ = 8.5 min); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.4 Hz, 1H), 7.92 (d, *J* = 8.4 Hz, 2H), 7.87 (d, *J* = 8.0 Hz, 1H), 7.63 (d, *J* = 8.4 Hz, 1H), 7.47 (ddd, *J* = 7.8, 6.4, 1.2 Hz, 1H), 7.34 (d, *J* = 8.8 Hz, 1H), 7.34−7.20 (m, 4H), 7.04 (d, *J* = 8.4 Hz, 1H), 4.84 (s, 1H), 2.49 (AB, *J* = 13 Hz, 2*C* = 32 Hz, 2H),[48] 0.76 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.2, 139.7, 133.9, 133.0, 132.8, 130.3, 130.1, 129.9, 129.2, 128.3, 128.2 (2C), 126.9, 126.6, 126.2, 125.9, 125.5, 123.4, 118.0, 117.5, 47.0, 33.0, 30.3. Anal. Calcd for $C_{25}H_{24}O$: C, 88.20; H, 7.11%. Found: C, 88.36; H, 7.44%.

(*S*)-2′-Isopropyl-[1,1′-binaphthalen]-2-ol (3h, minor, 29%) and (*S*)-2′-Propyl-[1,1′-binaphthalen]-2-ol (3i, major, 71%). Method B (used commercial Grignard reagent: *i*PrMgBr, 0.5 M in THF): R_f 0.44 (2:3 CH_2Cl_2/hexanes; both isomers eluted together); 0.37 g, 45% (**3h**/**3i** 29:71); white solid, mp = 78−79 °C, $[\alpha]_D^{25}$ = −82.0 (*c* = 0.1, CH_2Cl_2); *er* (**3h**) 99.8(*S*):0.2(*R*), *er* (**3i**) >99.9-(*S*):0.1(*R*), determined by chiral HPLC (Chiralpak IC column, 4.6 × 250 mm, 5 μm particle size, 25 °C, hexanes/*i*PrOH 99:1, pressure = 3.4 MPa, flow rate 1.0 mL min^{-1}, t_R[(*S*)-**3h**] = 6.1 min, t_R[(*R*)-**3h**] = 5.2 min, t_R[(*S*)-**3i**] = 5.8 min, t_R[(*R*)-**3i**] = 5.6 min); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.4 Hz, 1H minor), 7.98 (d, *J* = 8.4 Hz, 1H major), 7.94−7.90 (m, 2H major + minor), 7.88 (d, *J* = 8.4 Hz, 1H major + minor), 7.69 (d, *J* = 8.8 Hz, 1H minor), 7.59 (d, *J* = 8.4 Hz, 1H major), 7.47−7.42 (m, 1H major + minor), 7.37−7.21 (m, 4H major + minor), 7.20−7.14 (m, 1H major + minor), 7.02−6.98 (m, 1H major + minor), 4.76 (br s, 1H major), 4.75 (br s, 1H minor), 2.74 (septet, *J* = 6.8 Hz, 1H minor), 2.41 (m, 2H major), 1.48 (m, 2H major), 1.19 (d, *J* = 6.8 Hz, 3H minor), 1.07 (d, *J* = 6.8 Hz, 3H minor), 0.73 (t, *J* = 7.6 Hz, 3H major); ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.2, 151.1, 147.8, 142.0, 134.1, 133.4, 133.2, 132.7, 129.9, 129.8, 129.3, 129.2, 129.2, 128.2, 128.2, 127.1, 127.0, 126.9, 126.7, 126.1, 125.9, 125.8, 124.9, 124.4, 123.6, 123.5, 117.6, 117.4, 36.0, 31.1, 25.4, 24.2, 23.9, 22.8; HRMS (ESI-orbitrap) *m*/*z* calcd for $C_{23}H_{20}ONa$ 335.1412 $[M + Na]^+$, found 335.1454. Anal. Calcd for $C_{23}H_{20}O$: C, 88.43; H, 6.45%. Found: C, 88.51; H, 6.59%.

(*S*)-2′-Benzyl-[1,1′-binaphthalen]-2-ol (3j). Method B (Grignard preparation: initiation 12 min, reaction time 60 min): R_f 0.41 (2:3 CH_2Cl_2/hexanes); 2.6 g, 85%; white solid, mp = 138−139 °C; $[\alpha]_D^{25}$ = +130.0 (*c* = 0.4, THF); *er* 99.9(*S*):0.1(*R*), determined by chiral HPLC (Phenomenex Lux Cellulose-1 column, 4.6 × 250 mm, 3 μm particle size, 25 °C, hexanes/*i*PrOH 95:5, pressure = 4.0 MPa, flow rate 0.7 mL min^{-1}, $t_R(S)$ = 12.7 min, $t_R(R)$ = 11.9 min); ^{1}H and ^{13}C NMR data were in agreement with published values;[27] melting point and optical rotation were not previously reported. Anal. Calcd for $C_{27}H_{20}O$: C, 89.97; H, 5.59%. Found: C, 89.68; H, 5.72%.

(*S*)-2′-[3,5-Bis(trifluoromethyl)benzyl]-[1,1′-binaphthalen]-2-ol (3k). Method A (Grignard preparation: initiation 15 min, reaction time 40 min): R_f 0.61 (1:1 CH_2Cl_2/hexanes); 1.0 g, 49%; viscous oil;

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$[\alpha]_D^{24}$ = −117.2 (*c* = 0.5, CH_2Cl_2); *er* 99.8(*S*):0.2(*R*), determined by chiral HPLC (Phenomenex Lux Cellulose-1 column, 4.6 × 250 mm, 3 μm particle size, 25 °C, hexanes/EtOH 99:1, pressure = 5.8 MPa, flow rate 1.0 mL min^{-1}, $t_R(S)$ = 19.2 min, $t_R(R)$ = 21.4 min); ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.07 (d, *J* = 8.4 Hz, 1H), 7.98 (d, *J* = 8.4 Hz, 1H), 7.92 (d, *J* = 8.8 Hz, 1H), 7.83 (d, *J* = 8.4 Hz, 1H), 7.64 (d, *J* = 8.4 Hz, 1H), 7.53−7.48 (m, 2H), 7.34−7.21 (m, 4H), 7.17 (s, 2H), 7.09 (ddd, *J* = 8.4, 6.9, 1.3 Hz, 1H), 6.73 (d, *J* = 8.4 Hz, 1H), 4.74 (s, 1H), 3.95 (AB, *J* = 15 Hz, 2*C* = 18 Hz, 2H);[48] ^{13}C NMR (101 MHz, CD_2Cl_2) δ 151.4, 143.1, 138.6, 133.8, 133.6, 133.6, 131.2 (q, $J_{(C,F)}$ = 33 Hz), 130.8, 130.6, 130.1, 129.4, 129.1, 128.9, 128.7, 128.6, 127.5, 127.2, 126.7, 125.9, 124.5, 123.8, 123.7 (q, $J_{(C,F)}$ = 273 Hz), 120.2 (septet, $J_{(C,F)}$ = 3.7 Hz), 111.7, 117.1, 40.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ −63.9. HRMS (ESI-orbitrap) *m*/*z* calcd for $C_{29}H_{18}F_6O$ 497.1340 $[M + H]^+$, found 497.1349.

■ ASSOCIATED CONTENT

Supporting Information

^{1}H and ^{13}C NMR spectra of newly characterized compounds; ^{1}H NMR spectra of known compounds synthesized by new routes; chiral HPLC chromatograms. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: lms@chem.okstate.edu.

Notes

The authors declare no competing financial interest.

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