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P-Chiral, Monodentate Ferrocenyl Phosphines, Novel Ligands for Asymmetric Catalysis†

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Eight *P*-chiral monodentate ferrocenyl phosphines (**1a**−**h**) were prepared in high enantiomeric excess (>95% ee in most cases) by way of an ephedrine-based oxazaphospholidine borane complex. Primary alkyl, secondary alkyl, and substituted aromatic substituents were successfully introduced at the phosphorus center, along with ferrocenyl and phenyl groups, generating phosphines of the general structure FcP(Ph)(R) (Fc = ferrocenyl, R = aryl, alkyl). The synthetic route employed provides facile access to a previously undeveloped class of chiral monophosphines. These compounds were evaluated as ligands in asymmetric catalytic reductive coupling of alkynes and aldehydes and were found to provide the desired chiral allylic alcohols with good regioselectivity and ee in many cases and with complete (*E*)-selectivity (>98:2) in all cases.

Introduction

Chiral phosphines have proven to be effective and highly selective ligands for a wide variety of enantioselective transition metal-catalyzed reactions.[1] Since the introduction of DIOP in the early 1970s by Kagan,[2] bidentate phosphines have been the center of considerable attention. The exceptional enantioselectivities observed with chiral bisphosphines have often overshadowed the utility of chiral monophosphine ligands. Certain metal-catalyzed reactions, however, are inhibited or completely suppressed by bisphosphine ligands yet proceed smoothly and with high enantioselectivity when monophosphines are used.[3] Examples include rhodium-catalyzed hydrogenation of olefins and carbonyls, palladium-catalyzed hydrosilylation of olefins, rhodium-catalyzed hydrosilylation of carbonyls, nickel-catalyzed cross-coupling reactions, and palladium-catalyzed allylic substitution reactions.[4]

Monophosphines containing a ferrocenyl moiety have been particularly effective ligands for several catalytic, asymmetric metal-catalyzed reactions, such as dialkylzinc additions to aldehydes, allylic alkylations, cross-coupling reactions, and α-isocyanocarboxylate aldol reactions.[5,6] We have found that achiral ferrocenyl phosphines (e.g., $FcPPh_2$, Fc = ferrocenyl)[7] promote nickel-catalyzed, intermolecular reductive coupling reactions of alkynes and aldehydes.[8] Taking $FcPPh_2$ as a lead structure, we targeted several *P*-chiral ferrocenyl phosphines in order to investigate their steric and electronic effects on these and other catalytic reactions. Compounds **1a**−**h** (Chart 1) are representative members of a class of *P*-chiral monodentate phosphines that has not been thoroughly explored to date.[9]

Results and Discussion

Synthesis of *P*-Chiral, Monodentate Ferrocenyl Phosphines. The van Leeuwen[10] and Mezzetti[11] laboratories recently described procedures for preparing related bidentate *P*-chiral ferrocenyl bisphosphines using Jugé's ephedrine-based method[12] for the enantioselective synthesis of PAMP[13] and other *P*-chiral phosphines. Our initial investigations began with one of van Leeuwen's intermediates, (*R*)-methyl (ferrocenylphenyl)phosphinite

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† Dedicated to the memory of Professor Henry Rapoport.

[1] (a) Noyori, R. *Asymmetric Catalysis in Organic Synthesis*; Wiley & Sons: New York, 1994; Chapter 2. (b) *Catalytic Asymmetric Synthesis*; Ojima, I., Ed.; VCH Publishers: Weinheim, 1993; Chapter 1. (c) Pietrusiewicz, K. M.; Zablocka, M. *Chem. Rev.* **1994**, *94*, 1375−1411. (d) Ohff, M.; Holz, J.; Quirmbach, M.; Börner, A. *Synthesis* **1998**, 1391−1415. (e) Yamanoi, Y.; Imamoto, T. *Rev. Heteroat. Chem.* **1999**, *20*, 227−248. (f) Brunel, J. M.; Buono, G. In *Topics in Current Chemistry*; Springer-Verlag: New York, 2002; pp 79−105.

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[7] Both achiral and chiral (racemic) ferrocenyl monophosphines are highly effective for Pd-catalyzed arylation and cross-coupling reactions; see: (a) Stambuli, J. P.; Stauffer, S. R.; Shaughnessy, K. H.; Hartwig, J. F. *J. Am. Chem. Soc.* **2001**, *123*, 2677−2678. (b) Stauffer, S. R.; Beare, N. A.; Stambuli, J. P.; Hartwig, J. F. *J. Am. Chem. Soc.* **2001**, *123*, 4641−4642. (c) Beare, N. A.; Hartwig, J. F. *J. Org. Chem.* **2002**, *67*, 541−555. (d) Kataoka, N.; Shelby, Q.; Stambuli, J. P.; Hartwig, J. F. *J. Org. Chem.* **2002**, *67*, 5553−5566.

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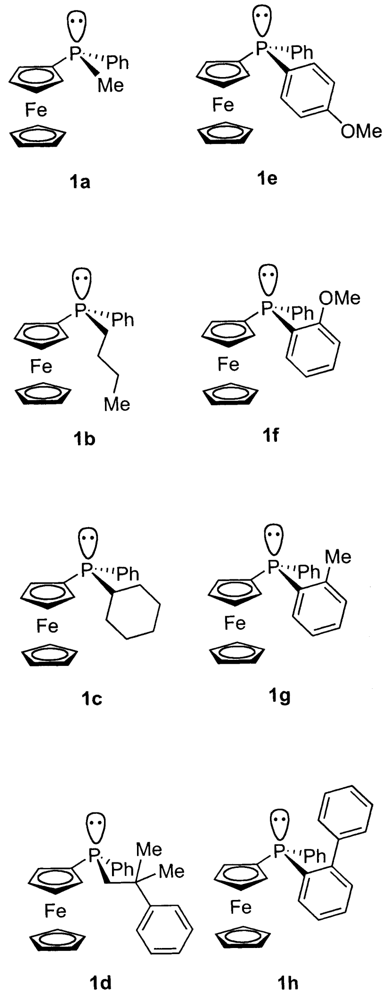
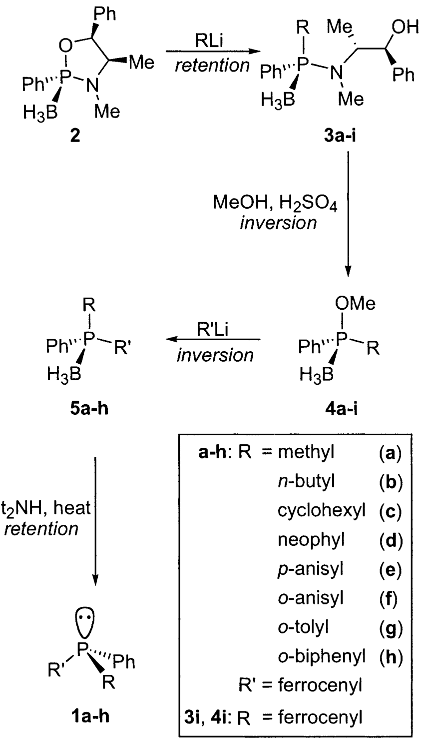
CHART 1



SCHEME 1



borane (**4i**).[10c] Using this strategy (Scheme 1), the ferrocenyl and phenyl groups of all the ligands would be installed first to allow for straightforward variation of the third group from a common intermediate. However, as observed by van Leeuwen, we found that the acid-promoted methanolysis of phosphinamide borane **3i** ((R_p,1*R*,2*S*)-*N*-methyl-*N*-(1-hydroxy-1-phenyl)prop-2-yl-*P*-(ferrocenyl)-*P*-(phenyl)-phosphinamide borane), the precursor to key intermediate **4i**, was sluggish and low yielding (approximately 30% yield of **4i**, 35% recovered **3i**).

Accordingly, to prepare the ligands in a quantity suitable for thorough study, we investigated an alternative strategy that installs the ferrocenyl group later in the synthesis.[14] As shown in Scheme 1, treatment of oxazaphospholidine borane **2** with the appropriate organolithium reagent (retention of stereochemistry)[15] was followed by acid-promoted methanolysis of the resulting phosphinamide borane product **3** (inversion). It should be noted that preparation of cyclohexyllithium and 2-methyl-2-phenyl-1-propyllithium (neophyllithium) was best accomplished using a naphthalene-catalyzed oxidative addition of lithium metal[16] to chlorocyclohexane and 1-chloro-2-methyl-2-phenylpropane, respectively.

Methanolysis of aryl- and primary alkyl-substituted phosphinamide boranes **3a,b** and **3d**−**h** proceeded smoothly, but formation of methyl-cyclohexylphenylphosphinite borane **4c** was lower yielding. Secondary and tertiary alkyl-substituted phosphinamide boranes are notoriously difficult to convert to phosphinite boranes and usually require heating to obtain the desired product, often in low yield.[17]

Completion of the phosphine syntheses required installation of the ferrocenyl substituent. Although methods of direct deprotonation of ferrocene with *sec*-butyllithium or *tert*-butyllithium are commonly used to generate ferrocenyllithium (FcLi), we found that FcLi prepared via

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[9] To the best of our knowledge, only the *o*-anisyl derivative **1e** has been previously reported (92% ee): (a) Brown, J. M.; Laing, J. C. P. *J. Organomet. Chem.* **1997**, *529*, 435−444. Racemic **1a** and **1b** have also been synthesized previously, but not in enantiomerically enriched form. (b) (±)-**1a**: Seyferth, D.; Withers, H. P., Jr. *Organometallics* **1982**, *1*, 1275−1282. (c) (±)-**1b**: Chacon, S. T.; Cullen, W. R.; Bruce, M. I.; Shawkataly, O. B. *Can. J. Chem.* **1990**, *68*, 2001−2010.

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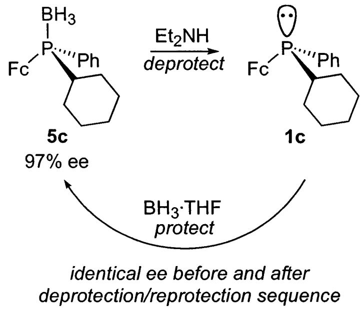
TABLE 1. Summary of Synthetic Operations[a]

RLi addition			methanolysis		FcLi addition			BH$_3$ removal			overall yield (4 steps, %)
compd	yield (%)	dr[b]	compd	yield (%)	compd	yield (%)	ee (%)[c]	compd	yield (%)	ee (%)[c]	
3a	79	9:1	**4a**	75	**5a**	58	83	**1a**	93	>**95**[d]	32
3b	80	16:1	**4b**	62	**5b**	90	77	**1b**	88	**80**	39
3c	88	>98:2	**4c**	29	**5c**	66	97	**1c**	83	**98**	14
3d	72	>98:2	**4d**	65	**5d**	79	98	**1d**	>99	**96**	37
3e	80	>98:2	**4e**	77	**5e**	85	95	**1e**	95	**94**	50
3f	93	>98:2	**4f**	77	**5f**	92	>98	**1f**	83	>**98**	55
3g	80	>98:2	**4g**	87	**5g**	70	83	**1g**	>99	>**98**[e]	48
3h	81	>98:2	**4h**	77	**5h**	69	98	**1h**	94	**96**	40

[a] See Scheme 1. [b] Determined by ^{1}H NMR. [c] Determined by HPLC. [d] Recrystallized from hexane. [e] Crystallized from diethylamine upon standing after BH$_3$ removal.

SCHEME 2



metal−halogen exchange of commercially available bromoferrocene and *tert*-butyllithium provided the desired substitution products (inversion of configuration) in superior yields.[18] The metal−halogen exchange can also be performed with *n*-butyllithium, but in the case of ferrocenylmethylphenylphosphine (**1a**) we observed significant amounts (>30%) of an *n*-pentyl-containing product, which likely arose from ferrocenyl substitution, deprotonation of one of the methyl protons, and alkylation of the resulting lithium anion by *n*-butyl bromide.[19]

In all cases, the BH$_3$ group facilitated chromatographic purification, providing the corresponding complexes of the phosphines as orange, air-stable compounds. Removal of the BH$_3$ group by heating in the presence of diethylamine proceeded in good to excellent yield in all cases, providing the free phosphines. The enantiomeric excesses of **1a**−**h** were determined by reprotection with BH$_3$ (retention) and subsequent measurement via HPLC. As shown in Scheme 2, comparison of the enantiomeric excesses of **5a**−**h** before and after the deprotection-reprotection sequence confirmed the preservation of stereochemical integrity during the diethylamine-mediated BH$_3$ removal (below limit of detection).

Summarized in Table 1 are the results obtained for the synthesis leading to *P*-chiral phosphines **1a**−**h**. The average yield for the four-step sequences range from 75% to 86% per step in all but one case (R = c-C$_6$H$_{11}$, **1c**), and **1b** is the only ligand of the eight described that was not afforded in ≥94% ee at the end of the sequence. The majority of these ligands are moderately air-stable, and the corresponding BH$_3$ complexes (**5a**−**h**) are convenient for long-term storage of these novel *P*-chiral phosphines (Scheme 2).[20]

Asymmetric Catalytic Carbon−Carbon Bond-Forming Reactions. Chiral allylic alcohols[21] are useful building blocks in the preparation of a variety of organic molecules and are found in many natural products,[22−24] with potential therapeutic applications. Accordingly, several catalytic enantioselective methods of allylic alcohol synthesis have been described and can be divided into three types: additions of organometallic reagents to carbonyls, carbonyl reduction, and kinetic resolution of chiral allylic alcohols. The first of these also forms a carbon−carbon bond in the course of the reaction, with the Nozaki−Hiyama−Kishi (NHK) reaction being a well-known example,[25,26] but an enantioselective version of the NHK reaction has yet to be described.[27] The methods of Oppolzer[28] and Wipf[29] form a carbon−carbon bond using different transition metals, by first preparing organometallic reagents by way of hydrometalation of a terminal

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(18) For other selective methods of FcLi generation, see: (a) Sanders, R.; Mueller-Westerhoff, U. T. *J. Organomet. Chem.* **1996**, *512*, 219−224. (b) Chieffi, A.; Comasseto, J. V.; Snieckus, V. *Synlett* **2000**, *2*, 269−271. (c) Guillaneux, D.; Kagan, H. B. *J. Org. Chem.* **1995**, *60*, 2502−2505.

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(20) In two cases shown in Table 2, the diastereoselectivity of FcLi addition (for **3b** and **3g**) does not agree with the enantiomeric excess of the corresponding phosphine-borane complexes (**5b** and **5g**). It is possible that racemization may occur during the methanolysis step (giving **4b** and **4g**) in these cases. See ref 41 for similar observations.

(21) For reviews of useful reactions of allylic alcohols, see: (a) Brückner, R. In *Comprehensive Organic Synthesis*; Trost, B. M., Ed.; Pergamon: New York, 1991; Vol. 6, Chapter 4.6, pp 873−908. (b) Hill, R. K. In *Comprehensive Organic Synthesis*; Trost, B. M., Ed.; Pergamon: New York, 1991; Vol. 5, Chapter 7.1, pp 785−826. (c) Wipf, P. In *Comprehensive Organic Synthesis*; Trost, B. M., Ed.; Pergamon: New York, 1991; Vol. 5, Chapter 7.2, pp 827−873. (d) Hoveyda, A. H.; Evans, D. A.; Fu, G. C. *Chem. Rev.* **1993**, *93*, 1307−1370.

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(24) Epothilones: Bollag, D. M.; McQueney, P. A.; Zhu, J.; Hensens, O.; Koupal, L.; Liesch, J.; Goetz, M.; Lazarides, E.; Woods, C. M. *Cancer Res.* **1995**, *55*, 2325−2333.

(25) (a) Okude, Y.; Hirano, S.; Hiyama, T.; Nozaki, H. *J. Am. Chem. Soc.* **1977**, *99*, 3179−3181. (b) Jin, H.; Uenishi, J.; Christ, W. J.; Kishi, Y. *J. Am. Chem. Soc.* **1986**, *108*, 5644−5646. (c) Takai, K.; Tagashira, M.; Kuroda, T.; Oshima, K.; Utimoto, K.; Nozaki, H. *J. Am. Chem. Soc.* **1986**, *108*, 6048−6050. (d) Fürstner, A.; Shi, N. *J. Am. Chem. Soc.* **1996**, *118*, 2533−2534. (e) Fürstner, A.; Shi, N. *J. Am. Chem. Soc.* **1996**, *118*, 12349−12357.

(26) For related asymmetric catalytic reaction using benzylic and allylic Cr reagents (as opposed to vinylic) to give homoallylic alcohols (instead of allylic alcohols), see: Bandini, M.; Cozzi, P. G.; Umani-Ronchi, A. *Polyhedron* **2000**, *19*, 537−539.

(27) For examples of diastereoselective, catalytic couplings using chiral ligands, see: Kishi, Y. *Tetrahedron* **2002**, *58*, 6239−6258.

alkyne (hydroboration and hydrozirconation, respectively). In each case, transmetalation with a dialkylzinc reagent precedes addition of a chiral ligand and an aldehyde. The disubstituted allylic alcohol products are obtained in good to high yields and, in many cases, in very high enantiomeric excess. These procedures are not as effective with internal acetylenes (e.g., Ph-C≡C-Me) as interconversion of the (*E*) and (*Z*) isomers can occur to a significant degree upon transmetalation with the organozinc reagent.[30]

Chiral allylic alcohols can also be obtained by way of in situ reductive coupling of an alkyne and an aldehyde. Methods that involve stoichiometric use of transition metals have been described by Buchwald,[31] Livinghouse,[32] Negishi,[33] and Takai and Utimoto.[34] Sato demonstrated that certain optically enriched allylic alcohols could be obtained with stoichiometric use of chiral titanium-alkyne complexes.[35]

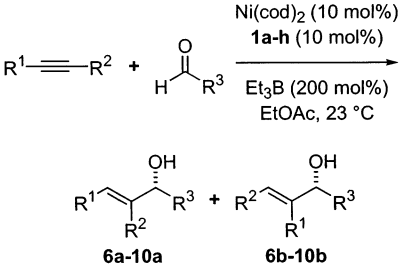
Catalytic methods for intramolecular[36] and intermolecular[8] reductive coupling of alkynes and aldehydes have also been described, but both of these methods are limited to the preparation of racemic allylic alcohols.[37]

To date, examples of asymmetric catalytic reductive or alkylative coupling of alkynes and aldehydes that do not involve an initial hydrometalation of the alkyne (see above) have not been described. Were this feasible, the convenient functional groups of alkynes and aldehydes could be assembled in a single catalytic operation to provide enantiomerically enriched, chiral allylic alcohols. In addition to enantioselectivity, the challenges associated with this approach include regioselectivity with respect to the alkyne substituents and *E*/*Z*-selectivity in formation of the double bond.

Since allylic alcohols corresponding to catalytic reductive couplings between aldehydes and "alkyl−alkyl" alkynes (alkyl-C≡C-alkyl′) are commonly found in natural products and related molecules, the enantioselective transformation depicted in Scheme 3 would constitute an efficient and rapid entry into these important functional group assemblies.[21−23]

Previously, we reported that tributylphosphine (Bu_3P) was an effective ligand for catalytic, intermolecular reductive couplings, providing chiral allylic alcohols in good yield and with exclusive cis addition across the alkyne.[8] Alkynes containing one aromatic subsituent or a trimethylsilyl group (or both) were obtained in high regioselectivity in these studies. In initial studies of couplings of "alkyl−alkyl" alkynes (Table 2), we observed that Bu_3P was effective in this catalytic reaction (Scheme 3) but afforded allylic alcohols **6a** and **6b** in low regioselectivity (entry 1). Similar regioselectivities were observed with other achiral phosphines (entries 2−4), yet it should be noted that in all cases the (*E*)-allylic alcohol (*cis* addition across the alkyne) was obtained exclusively (>98:2).

SCHEME 3



6a,b: $R^1 = c\text{-}C_6H_{11}$, $R^2 = Me$, $R^3 = i\text{-}Pr$
7: $R^1 = R^2 = n\text{-}Pr$, $R^3 = Ph$
8: $R^1 = R^2 = R^3 = n\text{-}Pr$
9: $R^1 = R^2 = n\text{-}Pr$, $R^3 = i\text{-}Pr$
10a,b: $R^1 = c\text{-}C_6H_{11}$, $R^2 = Me$, $R^3 = n\text{-}Pr$

Among these achiral ligands, (ferrocenyl)diphenylphosphine was the most selective ($FcPPh_2$, entry 4). Allylic alcohols **6a** and **6b** were obtained in good yield, complete (*E*)-selectivity, and 3:1 regioselectivity (favoring **6a**), the highest regioselectivity we had observed up to this point in our investigations of this particular coupling reaction.

Accordingly, as indicated above, we chose $FcPPh_2$ as the basis for the development of an asymmetric catalytic variant of this transformation. In these studies of **1a**−**h** (entries 5−12), we found *o*-tolyl ligand **1g** to be superior with respect to regio- and enantioselectivity, giving an 85:15 mixture of **6a** (55% ee) and **6b**. Phosphines **1a** (R = Me), **1f** (R = *o*-anisyl), and **1g** displayed nearly the same degrees of selectivity, with **1a** (entry 5) providing the best combination among these three ligands. For comparison, the three representative chiral monophosphines shown in Chart 2, (neomenthyl)diphenylphosphine[38] (NMDPP, **11**), ferrocenyl phosphine **12**,[39] and a proline-derived alkyldiphenylphosphine (**13**),[40] were used in similar experiments (entries 13−15). With a few exceptions, the regioselectivities and enantioselectivities were lower than those obtained with phosphines **1a**−**h**.

In all other catalytic coupling reactions examined to date, phosphine **1a** has afforded the highest enantioselectivities (entries 16, 21−23), perhaps because the difference in steric demand of the ferrocenyl group and

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[36] (a) Oblinger, E.; Montgomery, J. *J. Am. Chem. Soc.* **1997**, *119*, 9065−9066. (b) Review: Montgomery, J. *Acc. Chem. Res.* **2000**, *33*, 467−473. (c) Tang, X.-Q.; Montgomery, J. *J. Am. Chem. Soc.* **1999**, *121*, 6098−6099. (d) Tang, X.-Q.; Montgomery, J. *J. Am. Chem. Soc.* **2000**, *122*, 6950−6954. (e) Crowe, W. E.; Rachita, M. J. *J. Am. Chem. Soc.* **1995**, *117*, 6787−6788.

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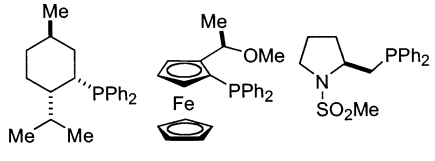
TABLE 2[a]

entry	ligand	product[b]	R^1	R^2	R^3	yield (%)[c]	**a**:**b**[d]	ee **a** (%)[e]	ee **b** (%)[f]
1	Bu_3P	**6a**, **6b**	c-C_6H_{11}	Me	i-Pr	55	2.0:1	na	na
2	$Ph_2P(n\text{-}Bu)$	**6a**, **6b**	c-C_6H_{11}	Me	i-Pr	56	1.9:1	na	na
3	$Ph_2P(Cy)$	**6a**, **6b**	c-C_6H_{11}	Me	i-Pr	62	2.0:1	na	na
4	$FcPPh_2$	**6a**, **6b**	c-C_6H_{11}	Me	i-Pr	60	3.0:1	na	na
5	**1a**	**6a**, **6b**	c-C_6H_{11}	Me	i-Pr	65	2.2:1	46	45
6	**1b**	**6a**, **6b**	c-C_6H_{11}	Me	i-Pr	27	1.8:1	8	12
7	**1c**	**6a**, **6b**	c-C_6H_{11}	Me	i-Pr	53	1.6:1	−34	−28
8	**1d**	**6a**, **6b**	c-C_6H_{11}	Me	i-Pr	33	1:1	−44	−10
9	**1e**	**6a**, **6b**	c-C_6H_{11}	Me	i-Pr	60	2.4:1	2	4
10	**1f**	**6a**, **6b**	c-C_6H_{11}	Me	i-Pr	60	3.8:1	−28	−17
11	**1g**	**6a**, **6b**	c-C_6H_{11}	Me	i-Pr	46	5.7:1	−55	−19
12	**1h**	**6a**, **6b**	c-C_6H_{11}	Me	i-Pr	33	1:1	−52	−37
13	**11**	**6a**, **6b**	c-C_6H_{11}	Me	i-Pr	50	2.0:1	−35	−38
14	**12**	**6a**, **6b**	c-C_6H_{11}	Me	i-Pr	40	1:1	−20	−17
15	**13**	**6a**, **6b**	c-C_6H_{11}	Me	i-Pr	22	1.2:1	−35	−39
16	**1a**	**7**	n-Pr	n-Pr	Ph	85	na	49	na
17	**1c**	**7**	n-Pr	n-Pr	Ph	80	na	−4	na
18	**1f**	**7**	n-Pr	n-Pr	Ph	81	na	12	na
19	**1g**	**7**	n-Pr	n-Pr	Ph	79	na	−28	na
20	**1h**	**7**	n-Pr	n-Pr	Ph	87	na	−36	na
21	**1a**	**8**	n-Pr	n-Pr	n-Pr	80	na	55	na
22	**1a**	**9**	n-Pr	n-Pr	i-Pr	80	na	55	na
23	**1a**	**10a**, **10b**	c-C_6H_{11}	Me	n-Pr	30	2.2:1	67	68

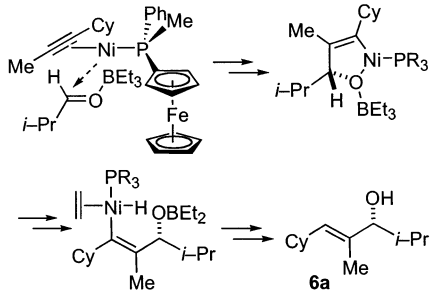
[a] All reactions were conducted using 10 mol % Ni(cod)$_2$, 10 mol % ligand, and 200 mol % Et_3B. See Scheme 3 and Experimental Section for details. Regioselectivities and enantioselectivities were determined for unpurified product mixtures. [b] Major and minor regioisomers. See Scheme 3. [c] Combined yield of all allylic alcohol products. [d] Regioselectivity (**a**:**b**) determined by ^{1}H NMR. [e] Enantiomeric excess of regioisomer **a**. Absolute configuration of **6a** assigned by Mosher ester analysis. Absolute configuration of **6b**, **7**−**9**, and **10a**−**b** assigned by analogy. Negative signs indicate opposite sense of induction. [f] Enantiomeric excess of regioisomer **b**.

CHART 2



11 (NMDPP) **12** **13**

SCHEME 4



the varied group is the greatest in this case (Fc vs R = Me). The superiority of ligand **1a** and the sense of induction observed in the formation of **6a** (Mosher ester analysis) are consistent with the model shown in Scheme 4, in which a Et_3B-aldehyde complex approaches an alkyne-Ni(0)-phosphine complex such that the Et_3B group approaches *syn* to a small Me group, away from a much larger Fc group. Investigation of the mechanistic details and further development of these novel phosphines are ongoing in our laboratory.[41]

Conclusions

In four steps from oxazaphospholidine-borane **2**, *P*-chiral ferrocenyl phosphines can be synthesized in 14−55% overall yield and in good to very high enantiomeric excess. When used as ligands in the catalytic reactions described above, these compounds are superior in every respect to any other class of chiral phosphine we have evaluated for an important class of alkynes, affording certain types of chiral allylic alcohols in good to high yield, good regioselectivity and enantioselectivity in most cases, and with complete (*E*)-selectivity (>98:2) in every case. Our continued investigations in this area will be facilitated by the synthetic sequence leading to ligands **1a**−**h**, as it is amenable to steric and electronic variation of the substituents on phosphorus. These novel *P*-chiral, monodentate ferrocenyl phosphines may also find utility in other asymmetric catalytic reactions.

Experimental Section

General. All reactions were carried out under an inert atmosphere of argon using Schlenk techniques and oven-dried glassware. Tetrahydrofuran and diethyl ether were distilled from sodium/benzophenone ketyl. Diethylamine and methanol were purchased in 99.5% purity and were degassed before use by bubbling argon through for 20 min. Ethyl acetate was distilled from $CaSO_4$ and degassed before use by bubbling argon through for 20 min. NMR spectra were recorded on 300 and 500 MHz instruments. ^{1}H NMR positive chemical shifts in ppm are downfield from tetramethylsilane; ^{31}P NMR positive chemical shifts in ppm are downfield from an external 85% phosphoric acid standard. IR spectra were recorded on a

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(41) Several mechanistic frameworks for Ni-catalyzed coupling reactions involving carbonyl addition have been proposed. See ref 36 and (a) Tsuda, T.; Kiyoi, T.; Saegusa, T. *J. Org. Chem.* **1990**, *55*, 2554. (b) Sato, Y.; Takimoto, M.; Hayashi, K.; Katsuhara, T.; Takagi, K.; Mori, M. *J. Am. Chem. Soc.* **1994**, *116*, 9771. (c) Kimura, M.; Ezoe, A.; Shibata, K.; Tamaru, Y. *J. Am. Chem. Soc.* **1998**, *120*, 4033. (d) Sato, Y.; Takanashi, T.; Mori, M. *Organometallics* **1999**, *18*, 4891. (e) Sato, Y.; Saito, N.; Mori, M. *J. Am. Chem. Soc.* **2000**, *122*, 2371. (f) Chowdhury, S. K.; Amarasinghe, K. K. D.; Heeg, M. J.; Montgomery, J. *J. Am. Chem. Soc.* **2000,** *122*, 6775. (g) Amarasinghe, K. K. D.; Chowdhury, S. K.; Heeg, M. J.; Montgomery, J. *Organometallics* **2001**, *20*, 370.

FTIR instrument using NaCl plates. Melting points were measured on a capillary melting point apparatus. HPLC was performed on a chromatograph equipped with a variable wavelength detector and Chiracel OD, OJ, or AD column (0.46 cm × 25 cm). Analysis by chiral GC was performed on a chromatograph equipped with a Chiradex B-PH column.

(2S_p,4*R*,5*S*)-(−)-3,4-Dimethyl-2,5-diphenyl-1,3,2-oxazaphospholidine Borane (2).[12] A solution of dichlorophenylphosphine (10.8 mL, 80 mmol) in 400 mL of tetrahydrofuran was cooled to 0 °C. (+)-Ephedrine (13.2 g, 80 mmol) was added in one portion, causing a white precipitate to form. Diisopropylethylamine (28 mL, 160 mmol) was added via syringe, and the heterogeneous mixture was allowed to warm to ambient temperature and then refluxed 24 h (solids dissolved upon heating). After the mixture cooled to ambient temperature, BH_3·THF was added (80 mL, 1.0 M in THF, 80 mmol), and the heterogeneous mixture was stirred for 18 h. H_2O was added, and the aqueous layer was extracted with diethyl ether. The combined organic layers were washed with saturated aqueous NaCl, dried with $MgSO_4$, filtered, and concentrated in vacuo. Recrystallization from methanol provided the title compound (8.57 g, 30.0 mmol, 38% yield) as a white crystalline solid. Mp: 103−104 °C. R_f (80:20 hexane/EtOAc) = 0.23. IR (thin film): 3428, 2381, 1644, 1454, 1436 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz): δ 7.84−7.81 (m, 2H), 7.55−7.50 (m, 3H), 7.40−7.28 (m, 5H), 5.60 (dd, J = 3.1, 6.0 Hz, 1H), 3.71−3.67 (m, 1H), 2.69 (d, J = 11.0 Hz, 3H), 0.84 (d, J = 6.7 Hz, 3H), 1.3−0.7 (br m, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 136.4 (d, J = 5.4 Hz), 132.6 (d, J = 2.2 Hz), 131.1 (d, J = 12.1 Hz, 2C), 128.8 (d, J = 9.8 Hz, 2C), 128.54 (s, 2C), 125.52, 126.8 (s, 2C), 84.5 (d, J = 7.6 Hz), 59.3 (d, J = 1.9 Hz), 29.9 (d, J = 8.1 Hz), 14.0 (d, J = 3.6 Hz). ^{31}P NMR ($CDCl_3$, 121 MHz): δ 132.8 (br q, J = 87 Hz).

Synthesis of Phosphinamides 3a−h (Typical Procedure). A 1.0 M solution of **2** (20 mmol) in tetrahydrofuran was cooled to −78 °C before addition of a solution of alkyl- or aryllithium (40 mmol, commercially available unless noted). The mixture was allowed to stir for 3 h, warming slowly to 0 °C. Water was added, and the aqueous phase was extracted with diethyl ether. The combined organic layers were washed with saturated aqueous NaCl, dried over $MgSO_4$, filtered, and concentrated in vacuo. The crude residue was purified via column chromatography.

(S_p,1*S*,2*R*)- *N*-Methyl-*N*-(1-hydroxy-1-phenyl)prop-2-yl-*P*-(methyl)-*P*-(phenyl)-phosphinamide Borane (3a).[12] Purification: column chromatography (elution with 95:5 toluene/EtOAc). Small scale yield: 79% (0.10 g, 0.33 mmol), prepared and purified for spectral analysis. Large scale crude yield: >99% (6.0 g, 20 mmol), used without purification. The diastereomeric ratio of the isolated material was determined to be 9:1 by ^1H NMR integration. Mp: 108−109 °C. R_f (95:5 toluene/EtOAc) = 0.17. IR (NaCl): 3446, 2968, 2369 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz): δ 7.46−7.26 (m, 8H), 7.11−7.07 (m, 2H), 4.74 (dd, 1H, J = 3.4, 7.2 Hz), 4.06−4.01 (m, 1H), 2.47 (d, 3H, J = 8.5 Hz), 1.94 (d, 1H, J = 3.7 Hz), 1.52 (d, 3H, J = 9.0 Hz), 1.24 (d, 3H, J = 6.7 Hz), 1.1−0.4 (br m, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 143.3, 133.5 (d, J = 65.6 Hz), 131.3, 131.2, 131.0, 130.9, 129.3, 129.2, 129.1, 129.1, 128.7, 127.5, 78.5 (d, J = 6.3 Hz), 58.7 (d, J = 8.6 Hz), 29.7, 14.8, 12.0 (d, J = 41.5 Hz). ^{31}P NMR ($CDCl_3$, 121 MHz): δ 66.1 (br q, J = 77 Hz). HRMS (ESI) $[M + Na]^+$: *m*/*z* calcd for $C_{17}H_{25}BNNaOP$ 324.1659, obsd 324.1652.

(S_p,1*S*,2*R*)-*N*-Methyl-*N*-(1-hydroxy-1-phenyl)prop-2-yl-*P*-(*n*-butyl)-*P*-(phenyl)-phosphinamide Borane (3b).[12] Purification: column chromatography (95:5 toluene/EtOAc). Yield: 80% (1.67 g, 4.9 mmol), isolated as a colorless oil. The diastereomeric ratio of the isolated material was determined to be 16:1 by ^1H NMR integration. R_f (95:5 toluene/EtOAc) = 0.25. IR (thin film): 3503, 2957, 2872, 2379, 1455, 1436, 1025 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz): δ 7.44−7.42 (m, 2H), 7.36−7.28 (m, 8H), 4.87 (dd, J = 3.7, 5.5 Hz, 1H), 4.07−4.02 (m, 1H), 2.57 (d, J = 7.6 Hz, 3H), 2.00−1.96 (m, 1H), 1.88−1.84 (m, 1H), 1.83 (d, J = 3.6 Hz, 1H), 1.69−1.62 (m, 1H), 1.47−1.38 (m, 3H), 1.19 (d, J = 6.7 Hz, 3H), 0.95 (t, J = 7.3 Hz, 3H), 1.05−0.4 (br m, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 143.2, 133.0 (d, J = 60.9 Hz), 131.2, 131.11, 131.10, 129.22, 129.19, 129.14, 126.7, 127.1 (2C), 79.4 (d, J = 4.0 Hz), 58.8 (d, J = 8.6), 30.0 (d, J = 2.9 Hz), 25.8 (d, J = 42.0 Hz), 25.5, 25.0 (d, J = 15.6 Hz), 14.4, 13.6 (d, J = 2.8 Hz). ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 70.3 (br q, J = 73 Hz). HRMS (ESI) $[M + Na]^+$: *m*/*z* calcd for $C_{20}H_{31}BNNaOP$ 366.2129, obsd 366.2123.

(S_p,1*S*,2*R*)-*N*-Methyl-*N*-(1-hydroxy-1-phenyl)prop-2-yl-*P*-(cyclohexyl)-*P*-(phenyl)-phosphinamide Borane (3c). Cyclohexyllithium was prepared from chlorocyclohexane and lithium-naphthalenide.[16] Lithium (35 mmol) and naphthalene (0.35 mmol) were combined in 7 mL of tetrahydrofuran. The mixture was vigorously stirred at ambient temperature until it turned dark green, at which point the mixture was cooled to −78 °C. Chlorocyclohexane was added dropwise via syringe (3.5 mmol), and the mixture was stirred for 3 h at −78 °C to generate cyclohexyllithium, which was added to a solution of **2** (1.7 mmol) at −78 °C. Purification: gradient silica gel chromatography (90:10 hexane/EtOAc, polarity gradually increased to 50:50 hexane/EtOAc). Yield: 88% (0.57 g, 1.5 mmol), isolated as a white foam. Only one diastereomer was detected by ^1H NMR integration. R_f (80:20 hexane/EtOAc) = 0.24. IR (NaCl): 3495, 2934, 2854, 2382, 1480, 1435, 1023 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz): δ 7.56−7.52 (m, 2H), 7.43−7.33 (m, 5H), 7.27−7.18 (m, 3H), 4.74 (d, J = 4.6 Hz, 1H), 4.09−4.04 (m, 1H), 2.60 (d, J = 7.0 Hz, 3H), 2.35 (dd, J = 2.6, 12.4 Hz, 1H), 2.0 (br s, 1H), 2.00−1.88 (m, 1H), 1.75 (m, 3H), 1.58−1.50 (m, 2H), 1.45−1.38 (m, 1H), 1.33−1.23 (m, 3H), 1.12 (d, J = 7.0 Hz, 3H), 1.1−0.5 (br m, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 142.7, 131.4 (d, J = 9.2 Hz), 131.1 (d, J = 40.1 Hz), 130.7 (d, J = 1.7 Hz), 128.5 (d, J = 9.2 Hz), 128.4 (s, 2C), 127.6, 126.3 (s, 2C), 78.8, 58.5 (d, J = 8.6 Hz), 32.7 (d, J = 43.7 Hz), 29.5 (d, J = 3.5 Hz), 27.2 (d, J = 12.1 Hz), 26.93 (d, J = 8.6 Hz), 26.86, 26.2, 26.1, 12.4 (d, J = 4.0 Hz). ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 72.2 (br q, J = 66 Hz). HRMS (ESI) $[M + Na]^+$: *m*/*z* calcd for $C_{22}H_{33}BNNaOP$ 392.2285, obsd 392.2290.

(S_p,1*S*,2*R*)-*N*-Methyl-*N*-(1-hydroxy-1-phenyl)prop-2-yl-*P*-(2-methyl-2-phenyl-1-propyl)-*P*-(phenyl)-phosphinamide Borane (3d). Neophyllithium was prepared from 1-chloro-2-methyl-2-phenylpropane (neophyl chloride) and lithium-naphthalenide as described for **3c**. Purification: gradient silica gel chromatography (90:10 hexane/EtOAc, polarity gradually increased to 50:50 hexane/EtOAc). Yield: 72% (1.53 g, 3.7 mmol), isolated as a white foam. Only one diastereomer was detected by ^1H NMR integration. R_f (90:10 hexane/EtOAc) = 0.12. IR (NaCl): 3511, 2968, 2389, 1601, 1496, 1450, 1435 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz): δ 7.67−7.63 (m, 2H), 7.46−7.40 (m, 6H), 7.36−7.31 (m, 4H), 7.27−7.21 (m, 3H), 5.12 (br s, 1H), 4.09−4.07 (m, 1H), 2.70 (t, J = 16.3 Hz, 1H), 2.65 (d, J = 7.0 Hz, 3H), 2.25 (dd, J = 2.1, 15.3 Hz, 1H), 1.87 (d, J = 2.1 Hz, 1H), 1.67 (s, 3H), 1.64 (s, 3H), 0.95 (d, J = 7.0 Hz, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 150.9 (d, J = 7.5 Hz), 142.8, 135.4 (d, J = 59.9 Hz), 130.5 (d, J = 8.6 Hz, 2C), 130.3 (d, J = 1.7 Hz), 128.7 (d, J = 9.2 HZ, 2C), 128.4 (d, J = 4.0 Hz, 2C), 127.4, 126.2, 125.9 (s, 2C), 125.6 (s, 2C), 79.8, 58.2 (d, J = 10.4 Hz), 41.1 (d, J = 36.3 Hz), 38.0, 31.2 (d, J = 5.2 Hz), 31.1 (d, J = 3.5 Hz), 28.4 (d, J = 4.6 Hz), 10.4 (d, J = 5.2 Hz). ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 67.4 (br q, J = 53 Hz). HRMS (ESI) $[M + Na]^+$: *m*/*z* calcd for $C_{26}H_{35}BNNaOP$ 442.2442, obsd 442.2464.

(R_p,1*S*,2*R*)-*N*-Methyl-*N*-(1-hydroxy-1-phenyl)prop-2-yl-*P*-(4-methoxyphenyl)-*P*-(phenyl)-phosphinamide Borane (3e). A 1.0 M solution of 4-bromoanisole (10 mmol) in diethyl ether was cooled to −78 °C and treated with a solution of *tert*-butyllithium (20 mmol). The solution was allowed to stir 15 min at −78 °C, warmed to 0 °C, and stirred for an additional 30 min producing a clear, yellow solution of *p*-anisyllithium. The aryllithium reagent was transferred via cannula to a 1.0 M solution of **2** in tetrahydrofuran (5.0 mmol) at −78 °C. The mixture was allowed to stir 30 min at −78 °C, warmed to 0 °C to increase the solubility of salts, and stirred for an additional 2 h. Water and diethyl ether were added, and the solution was warmed to ambient temperature. Purification: gradient silica gel chromatography (90:10 hexane/EtOAc, polarity gradually increased to 50:50 hexane/EtOAc). Yield: 80% (1.6 g, 4.0 mmol), isolated as a white solid. Mp: 51−52 °C. Only one diastereomer was detected by ^{1}H NMR integration. R_f (80:20 hexane/EtOAc) = 0.14. IR (thin film): 3457, 2969, 2384, 1596, 1501, 1255 cm^{-1}. ^{1}H NMR (CDCl$_3$, 500 MHz): δ 7.55−7.46 (m, 4H), 7.41−7.25 (m, 6H), 7.14−7.10 (m, 2H), 6.95 (dd, J = 1.7, 8.7 Hz, 2H), 4.82 (dd, J = 4.0, 6.3 Hz, 1H), 4.33−4.28 (m, 1H), 3.85 (s, 3H), 2.46 (d, J = 7.9 Hz, 3H), 1.85 (d, J = 4.0 Hz, 1H), 1.24 (d, J = 6.7 Hz, 3H), 1.3−0.7 (br m, 3H). ^{13}C NMR (CDCl$_3$, 125 MHz): δ 162.0, 142.7, 134.5 (d, J = 11.5 Hz, 2C), 132.1 (d, J = 9.8 Hz, 2C), 130.7, 128.8 (s, 2C), 128.4 (d J = 10.9 Hz, 2C), 128.1, 127.0 (s, 2C), 122.0 (d, J = 63.9 Hz), 114.2 (d, J = 10.9, 2C), 78.9 (d, J = 6.3 Hz), 58.2 (d, J = 10.4 Hz), 55.5, 30.4 (d, J = 4.0 Hz), 13.8. ^{31}P NMR (CDCl$_3$, 121.5 MHz): δ 69.2 (br q, J = 95 Hz). HRMS (ESI) [M + Na]$^+$: *m/z* calcd for C$_{23}$H$_{29}$BNNaO$_2$P 416.1921, obsd 416.1918.

(R_p,1S,2R)-N-Methyl-N-(1-hydroxy-1-phenyl)prop-2-yl-P-(2-methoxyphenyl)-P-(phenyl)-phosphinamide Borane (3f).[9a,10a,b,12] *o*-Anisyllithium was prepared from the corresponding bromide, and the reaction was carried out as described for **3e**. Purification: gradient silica gel chromatography (90:10 hexane/EtOAc, polarity gradually increased to 50:50 hexane/EtOAc). Yield: 93% (1.46 g, 3.7 mmol), isolated as a white solid. Only one diastereomer was detected by ^{1}H NMR integration. Mp: 108 °C. R_f (80:20 hexane/EtOAc) = 0.18. IR (thin film): 3416, 3060, 2940, 2376, 1589, 1477, 1431, 1276, 1251 cm^{-1}. ^{1}H NMR (CDCl$_3$, 500 MHz): δ 7.57 (ddd, J = 1.8, 7.6, 12.7 Hz), 7.50−7.46 (m, 3H), 7.39−7.23 (m, 8H), 7.03 (tdd, J = 0.9, 1.5, 7.5 Hz, 1H), 6.92 (dd, J = 4.1, 7.8 Hz), 4.91 (d, J = 5.2 Hz, 1H), 4.37−4.32 (m, 1H), 3.59 (s, 3H), 2.56 (d, J = 7.9 Hz), 1.91 (br s, 1H), 1.23 (d, J = 7.0 Hz, 3H). ^{13}C NMR (CDCl$_3$, 125 MHz): δ 135.10 (d, J = 10.4 Hz), 133.4, 132.4 (d, J = 71.4), 131.0 (d, J = 10.4, 2C), 130.1, 128.5 (s, 2C), 128.1 (d, J = 10.9, 2C), 127.8, 126.8 (s, 2C), 121.0 (d, J = 10.9 Hz), 118.7 (d, J = 57 Hz), 111.7 (d, J = 4.6 Hz), 79.0 (d, J = 5.2 Hz), 58.3 (d, J = 10.4 Hz), 55.2, 31.1 (d, J = 4.0), 12.7. ^{31}P NMR (CDCl$_3$, 121.5 MHz): δ 68.5 (br q, J = 84 Hz). HRMS (ESI) [M + Na]$^+$: *m/z* calcd for C$_{23}$H$_{29}$BNNaO$_2$P 416.1921, obsd 416.1920.

(R_p,1S,2R)-N-Methyl-N-(1-hydroxy-1-phenyl)prop-2-yl-P-(2-methylphenyl)-P-(phenyl)-phosphinamide Borane (3g).[42] *o*-Tolyllithium was prepared from the corresponding iodide, and the reaction was carried out as described for **3e**. Purification: gradient silica gel chromatography (90:10 hexane/EtOAc, polarity gradually increased to 50:50 hexane/EtOAc). Yield: 80% (1.2 g, 3.2 mmol). Only one diastereomer was detected by ^{1}H NMR integration. Mp: 118 °C. R_f (90:10 hexane/EtOAc) = 0.09. IR (NaCl, thin film): 3507, 3059, 2979, 2391, 1451, 1436, 1384, 1069, 1024 cm^{-1}. ^{1}H NMR (CDCl$_3$, 500 MHz): δ 7.64−7.60 (m, 2H), 7.51−7.47 (m, 1H), 7.44−7.21 (m, 11H), 4.95 (t, J = 3.7 Hz, 1H), 4.39−4.35 (m, 1H), 2.65 (d, J = 7.3 Hz, 3H), 2.33 (s, 1H), 1.77 (d, J = 3.7 Hz, 1H), 1.26 (d, J = 6.7 Hz, 3H). ^{13}C NMR (CDCl$_3$, 125 MHz): δ 142.7, 142.4 (d, J = 12.7 Hz), 132.8 (d, J = 8.1 Hz), 132.5, 132.4 (d, J = 9.2 Hz), 132.0 (d, J = 9.8 Hz, 2C), 131.1 (d, J = 2.3 Hz), 131.0 (d, J = 2.3 Hz), 129.1, 128.6 (d, J = 10.4 Hz, 2C), 128.4 (s, 2C), 127.6, 126.2 (s, 2C), 125.8 (d, J = 9.8 Hz), 79.1 (d, J = 2.3 Hz), 58.2 (d, J = 9.8 Hz), 31.5 (d, J = 3.5 Hz), 22.2 (d, J = 3.5 Hz), 11.7 (d, J = 4.6 Hz). ^{31}P NMR (CDCl$_3$, 121.5 MHz): δ 69.9 (br q, J = 78 Hz). HRMS (ESI) [M + Na]$^+$: *m/z* calcd for C$_{23}$H$_{29}$BNNaOP 400.1972, obsd 400.1962.

(R_p,1S,2R)-N-Methyl-N-(1-hydroxy-1-phenyl)prop-2-yl-P-(2-biphenylyl)-P-(phenyl)-phosphinamide Borane (3h).[10b] *o*-Biphenyllithium was prepared from the corresponding bromide, and the reaction was carried out as described for **3e**. Purification: gradient silica gel chromatography (90:10 hexane/EtOAc, polarity gradually increased to 80:20 hexane/EtOAc). Yield: 81% (1.8 g, 4.1 mmol). Mp: 110 °C. R_f (80:20 hexane/EtOAc) = 0.24. IR (thin film): 3566, 3058, 2983, 2366, 1465, 1445, 1436, 1179, 1068, 1026 cm^{-1}. ^{1}H NMR (CDCl$_3$, 500 MHz): δ 7.72−7.68 (m, 2H), 7.51−7.47 (m, 1H), 7.44−7.18 (m, 16H), 4.88−4.87 (m, 1H), 3.97−3.93 (m, 1H), 2.57 (d, J = 7.3 Hz, 3H), 1.50 (d, J = 3.1 Hz, 1H), 1.4−0.8 (br m, 3H), 0.69 (d, J = 7.0 Hz, 3H). ^{13}C NMR (CDCl$_3$, 125 MHz): δ 147.6 (d, J = 9.8 Hz), 142.7, 141.6 (d, J = 2.9 Hz), 134.3 (d, J = 9.8 Hz), 133.6 (d, J = 58.2 Hz), 132.9 (d, J = 8.6 Hz), 132.4 (d, J = 9.8 Hz, 2C), 130.74 (d, J = 2.3 Hz), 130.70 (d, J = 2.3 Hz), 129.8, 129.0 (d, J = 66.2 Hz), 128.4, 128.31 (s, 2C), 128.29, 127.6 (s, 2C), 127.5, 127.3, 127.0 (d, J = 9.8 Hz), 125.8 (s, 2C), 79.0, 58.2 (d, J = 10.4 Hz), 32.0 (d, J = 4.0 Hz), 10.0 (d, J = 6.9 Hz). ^{31}P NMR (CDCl$_3$, 121.5 MHz): δ 70.1 (br q, J = 55 Hz). HRMS (ESI) [M + Na]$^+$: *m/z* calcd for C$_{28}$H$_{31}$BNNaOP 462.2129, obsd 462.2127.

Synthesis of Phosphinite Boranes 4a−h (Typical Procedure). Concentrated sulfuric acid (120 mol %) was added slowly to a solution of phosphinamide borane **3** in methanol (0.1 M) at ambient temperature. The solution was allowed to stir 18 h and partitioned between dichloromethane and water, and the aqueous phase was extracted with dichloromethane. The combined dichloromethane layers were washed with saturated aqueous sodium bicarbonate, dried with MgSO$_4$, and concentrated. The crude residue was purified via column chromatography (elution with 90:10 hexane/EtOAc) to give clear, colorless oils (unless otherwise specified).

(R)-Methyl-(methylphenyl)phosphinite Borane (4a).[12] The general procedure was followed, except **3a** was used without purification. Yield over two steps: 75% (2.52 g, 15 mmol). R_f (95:5 hexane/EtOAc) = 0.42. IR (neat): 3058, 2988, 2944, 2842, 2382, 1037 cm^{-1}. ^{1}H NMR (CDCl$_3$, 500 MHz): δ 7.82−7.78 (m, 2H), 7.58−7.49 (m, 3H), 3.58 (d, 3H, J = 12.2 Hz), 1.71 (d, 3H, J = 9.2 Hz), 1.1−0.5 (br m, 3H). ^{13}C NMR (CDCl$_3$, 125 MHz): δ 132.9 (d, J = 65.6 Hz), 131.5, 131.4, 129.53, 129.45, 54.4 (d, J = 2.9 Hz), 16.8 (d, J = 47.2 Hz). ^{31}P NMR (CDCl$_3$, 121 MHz): δ 113 (br q, J = 72 Hz). HRMS (EI) [M − H$^+$]: *m/z* calcd for C$_8$H$_{13}$BOP 167.0792, obsd 167.0794.

(R)-Methyl-(n-butylphenyl)phosphinite Borane (4b).[12] Yield: 62% (0.6 g, 2.9 mmol). R_f (90:10 hexane/EtOAc) = 0.32. IR (thin film): 2958, 2872, 2375, 1437, 1033 cm^{-1}. ^{1}H NMR (CDCl$_3$, 300 MHz): δ 7.79−7.73 (m, 2H), 7.55−7.45 (m, 3H), 3.60 (d, J = 11.9 Hz, 3H), 2.00−1.86 (m, 2H), 1.52−1.32 (m, 4H), 0.88 (t, J = 7.2 Hz, 3H), 1.2−0.3 (br m, 3H). ^{13}C NMR (CDCl$_3$, 125 MHz): δ 132.1 (d, J = 2.3 Hz), 131.5, 131.1 (d, J = 10.4 Hz, 2C), 128.9 (d, J = 9.8 Hz, 2C), 54.0 (d, J = 2.9 Hz), 30.4 (d, J = 45.5 Hz), 24.14, 24.11 (d, J = 13.8 Hz), 13.7. ^{31}P NMR (CDCl$_3$, 121.5 MHz): δ 116.6 (br q, J = 72 Hz). HRMS (ESI) [M + Na]$^+$: *m/z* calcd for C$_{11}$H$_{20}$BNaOP 233.1237, obsd 233.1235.

(R)-Methyl-(cyclohexylphenyl)phosphinite Borane (4c). The general procedure was followed, except that the reaction was heated to 45 °C after addition of sulfuric acid. Yield: 29% (0.2 g, 0.9 mmol). R_f (90:10 hexane/EtOAc) = 0.38. IR (NaCl, thin film): 2933, 2855, 2383, 1728, 1450, 1437, 1114, 1067, 1034, 1003 cm^{-1}. ^{1}H NMR (CDCl$_3$, 500 MHz): δ 7.72−7.68 (m, 2H), 7.54−7.46 (m, 3H), 3.61 (d, J = 12.1 Hz), 1.93−1.86 (m, 2H), 1.81−1.78 (m, 1H), 1.73 (br s, 1H), 1.66−1.61 (m, 2H), 1.34−1.30 (m, 1H), 1.26−1.13 (m, 4H), 1.1−0.4 (br m, 3H). ^{13}C NMR (CDCl$_3$, 125 MHz): δ 131.9 (d, J = 2.3 Hz), 131.5 (d, J = 10.4 Hz, 2C), 130.3 (d, J = 51.2 Hz), 128.7 (d, J = 9.8 Hz, 2C), 54.3 (d, J = 3.5 Hz), 39.2 (d, J = 45.5 Hz), 26.5 (d, J = 4.5 Hz), 26.4 (d, J = 5.2 Hz), 26.0, 25.6, 25.2. ^{31}P NMR (CDCl$_3$, 121.5 MHz): δ 119.5 (br q, J = 75 Hz). HRMS (ESI) [M + Na]$^+$: *m/z* calcd for C$_{13}$H$_{22}$BNaOP 259.1394, obsd 259.1384.

(R)-Methyl-[(2-methyl-2-phenyl-1-propyl)phenyl]phosphinite Borane (4d). Yield: 65% (0.67 g, 2.3 mmol). R_f (90:10 hexane/EtOAc) = 0.29. IR (NaCl): 3058, 2967, 2945, 2384, 1496, 1437, 1065, 1035 cm^{-1}. ^{1}H NMR (CDCl$_3$, 500 MHz): δ 7.62−7.58 (m, 2H), 7.47−7.44 (m, 1H), 7.40−7.7.37 (m, 2H),

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[42] Moulin, D.; Bago, S.; Bauduin, C.; Darcel, C.; Jugé, S. *Tetrahedron: Asymmetry* **2000**, *11*, 3939−3956.

7.31−7.29 (m, 2H), 7.24−7.21 (m, 2H), 7.16−7.13 (m, 1H), 3.42 (d, J = 11.9 Hz, 3H), 2.51 (t, J = 14.8 Hz, 1H), 2.31 (dd, J = 5.2, 15.2 Hz, 1H), 1.55 (s, 3H), 1.50 (s, 3H), 1.2−0.5 (br m, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 148.6, 133.1 (d, J = 55.8 Hz), 131.6 (d, J = 2.9 Hz), 130.6 (d, J = 10.4 Hz, 2C), 128.7 (d, J = 9.8 Hz, 2C), 128.2 (s, 2C), 126.1, 125.8 (s, 2C), 53.7, 47.3 (d, J = 38.6 Hz), 37.7, 30.4 (d, J = 5.2 Hz), 30.2 (d, J = 5.8 Hz). ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 114.5 (br q, J = 69 Hz). HRMS (ESI) [M + Na]$^+$: *m/z* calcd for $C_{17}H_{24}BNaOP$ 309.1550, obsd 309.1551.

(*S*)-Methyl-[(4-methoxyphenyl)phenyl]phosphinite Borane (4e). Yield: 77% (0.7 g, 2.7 mmol). R_f (80:20 hexane/EtOAc) = 0.31. IR (thin film): 3059, 3008, 2944, 2840, 2383, 1595, 1503 cm^{-1}. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.74−7.67 (m, 4H), 7.52−7.45 (m, 3H), 7.0−6.96 (m, 2H), 3.85 (s, 3H), 3.72 (d, J = 12.2 Hz, 3H), 1.3−0.7 (br m, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 162.6 (d, J = 2.2 Hz), 133.5 (d, J = 12.6, 2C), 131.8 (d, J = 2.4 Hz), 132.1 (d, J = 65.6 Hz), 131.1 (d, J = 11.2 Hz, 2C), 128.7 (d, J = 10.5 Hz, 2C), 122.3 (d, J = 67.7 Hz), 114.4 (d, J = 11.4 Hz), 55.6, 54.1. ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 105.9 (br q, J = 76 Hz). HRMS (ESI) [M + Na]$^+$: *m/z* calcd for $C_{14}H_{18}BNNaO_2P$ 283.1030, obsd 283.1024.

(*S*)-Methyl-[(2-methoxyphenyl)phenyl]phosphinite Borane (4f).[9a,10a,b,12] Yield: 76% (0.53 g, 2.0 mmol). R_f (10:90 hexane/EtOAc) = 0.18. IR (thin film): 3060, 2943, 2840, 2382, 1590, 1478, 1432, 1278, 1252, 1064, 1033 cm^{-1}. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.81 (ddd, J = 1.7, 7.6, 12.4, 1H) 7.77−7.73 (m, 2H), 7.53−7.47 (m, 2H), 7.45−7.42 (m, 2H), 7.08 (tdd, J = 0.9, 1.8, 7.5, 1H), 6.88 (dd, J = 4.3, 8.2 Hz, 1H), 3.75 (d, J = 12.2 Hz, 3H), 3.64 (s, 3H), 1.3−0.7 (br m, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 161.2 (d, J = 3.5 Hz), 134.13 (d, J = 1.7 Hz), 134.13 (d, J = 10.9 Hz), 132.2 (d, J = 66.2 Hz), 131.5 (d, J = 2.3 Hz), 131.3 (d, J = 11.5 Hz, 2C), 128.3 (d, J = 10.9 Hz, 2C), 121.0 (d, J = 10.9 Hz), 119.5 (d, J = 63.3 Hz), 111.8 (d, J = 5.2 Hz), 55.7, 54.1 (d,J = 2.9 Hz). ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 105.8 (br q, J = 76 Hz). HRMS (ESI) [M + Na]$^+$: *m/z* calcd for $C_{14}H_{18}BNNaO_2P$ 283.1030, obsd 283.1026.

(*S*)-Methyl-[(2-methylphenyl)phenyl]phosphinite Borane (4g). Yield: 87% (0.62 g, 2.5 mmol). R_f (10:90 hexane/EtOAc) = 0.37. IR (thin film): 3058, 2944, 2385, 1438, 1137, 1067, 1033 cm^{-1}. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.90 (dd, J = 7.6, 12.8, 1H, 7.68−7.64 (m, 2H), 7.54−7.51 (m, 1H), 7.47−7.44 (m, 3H), 7.34 (t, J = 7.3, 1H), 6.22 (dd, J = 3.7, 7.3 Hz, 1H), 3.76 (d, J = 12.2 Hz, 3H), 2.25 (s, 3H), 1.3−0.7 (br m, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 142.1 (d, J = 8.1 Hz), 133.9 (d, J = 15.0 Hz), 132.5 (d, J = 2.3 Hz), 132.0 (d, J = 64.5 Hz), 131.9 (d, J = 2.3 Hz), 131.8 (d, J = 8.6 Hz), 131.4 (d, J = 11.5, 2C Hz), 129.2 (d, J = 60.4 Hz), 128.8 (d, J = 10.4 Hz, 2C), 125.9 (d, J = 11.5 Hz), 54.0, 21.4 (d, J = 4.0 Hz). ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 109.5 (br q, J = 72 Hz). HRMS (ESI) [M + Na]$^+$: *m/z* calcd for $C_{14}H_{18}BNaOP$ 267.1081, obsd 267.1089.

(*S*)-Methyl-[(2-biphenylyl)phenyl]phosphinite Borane (4h).[10b] Yield: 77% (0.95 g, 3.1 mmol), isolated as a white solid. Mp: 62−63 °C. R_f (90:10 hexane/EtOAc) = 0.34. IR (thin film): 3056, 2943, 2383, 1465, 1438, 1131, 1114, 1064, 1033 cm^{-1}. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.10−8.06 (m, 1H), 7.57−7.50 (m, 2H), 7.39−7.31 (m, 3H), 7.27−7.21 (m, 4H), 7.14−7.11 (m, 2H), 6.94−6.92 (m, 2H), 3.58 (d, J = 12.2 Hz, 3H), 1.2−0.8 (br m, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 146.8 (d, J = 7.5 Hz), 140.5 (d, J = 2.9 Hz), 133.7 (d, J = 5.0 Hz), 132.4 (d, J = 67.3 Hz), 131.8 (d, J = 7.4 Hz), 131.7 (d, J = 2.3 Hz), 131.3 (d, J = 2.3 Hz), 131.1 (d, J = 10.9 Hz, 2C), 130.3 (d, J = 60.4 Hz), 129.7 (s, 2C), 128.3 (d, J = 10.9 Hz, 2C), 127.4, 127.35 (s, 2C), 127.2 (d, J = 11.5 Hz), 53.8. ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 108.6 (br q, J = 69 Hz). HRMS (ESI) [M + Na]$^+$: *m/z* calcd for $C_{19}H_{20}BNaOP$ 329.1237, obsd 329.1251.

Synthesis of Phosphine Boranes 5a−h (Typical Procedure). A 0.075 M solution of bromoferrocene (8 mmol) in diethyl ether was prepared and cooled to −78 °C. *tert*-Butyllithium (16 mmol) was slowly added, and the solution was stirred for 10 min at −78 °C. The solution was warmed to 0 °C and stirred for an additional 15 min to generate FcLi. A 1.0 M solution of **4** (4 mmol) in THF was cooled to −78 °C, and the FcLi solution was transferred to it via cannula over 10 min. The solution was allowed to warm to ambient temperature and stirred for 14 h. Water was added, and the aqueous phase was extracted with diethyl ether. The combined organic layers were washed with saturated aqueous NaCl, dried with $MgSO_4$, filtered, and concentrated in vacuo. The crude residue was purified via gradient column chromatography (elution with 80:20 hexane/CH_2Cl_2, polarity gradually increased to 50:50).

(*S*)-Ferrocenylmethylphenylphosphine Borane (5a). Yield: 58% (0.75 g, 2.3 mmol), isolated as an orange oil that was crystallized from hexane. Enantiomeric excess: 83% ee by HPLC analysis (Chiracel OJ, isocratic, hexane/2-propanol 95:5, t_R [(*R*)-**5a**] = 16.8 min, t_R [(*S*)-**5a**] = 24.7 min). Mp: 73−74 °C. R_f (1:1 hexane/CH_2Cl_2) = 0.35. IR (thin film): 3096, 2919, 2379 cm^{-1}. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.67−7.63 (m, 2H), 7.44−7.40 (m, 3H), 4.51−4.48 (m, 3H), 4.45 (m, 1H), 4.29−4.28 (s, 5H), 1.80 (d, 3H, J = 10.4 Hz), 1.2−0.7(br m, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 133.1 (d, J = 56 Hz), 131.8 (d, 2C, J = 6.3 Hz), 131.5 (d, 1C, J = 2.8 Hz), 129.3 (d, 2C, J = 13.8 Hz), 72.5 (d, 1C, J = 8.6 Hz), 72.2 (d, 1C, J = 6.9 Hz), 71.1 (d, 1C, J = 6.3 Hz), 70.5 (5C), 13.9 (d, J = 42 Hz). ^{31}P NMR δ ($CDCl_3$, 121 MHz): 6.2 (br q, J = 76 Hz). $[\alpha]^{20}_D$ = −32.3 (*c* 0.60; CH_2Cl_2). HRMS (EI): *m/z* calcd for $C_{17}H_{20}BFeP$ 322.0740, obsd 322.0750.

(*S*)-*n*-Butylferrocenylphenylphosphine Borane (5b). Yield: 90% (0.7 g, 1.8 mmol), isolated as an orange oil. Enantiomeric excess: 77% ee by HPLC analysis (Chiracel OJ, isocratic, hexane/2-propanol 97.5:2.5, t_R [(*R*)-**5b**] = 10.0 min, t_R [(*S*)-**5b**] = 12.0 min). R_f (50:50 hexane/CH_2Cl_2) = 0.36. IR (NaCl): 3386, 3097, 2957, 2870, 2380, 1436, 1172, 1107, 1065 cm^{-1}. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.79−7.75 (m, 2H), 7.49−7.44 (m, 3H), 4.56−4.55 (m, 1H), 4.47−4.46 (m, 1H), 4.44−4.42 (m, 1H), 4.37−4.36 (m, 1H), 4.18 (s, 5H), 2.09−2.03 (m, 2H), 1.60−1.57 (m, 1H), 1.40−1.30 (m, 3H), 0.88 (t, J = 7.2 Hz, 3H), 1.3−0.7 (br m, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 132.2 (d, J = 8.6 Hz, 2C), 131.1 (d, J = 2.3 Hz), 130.6 (d, J = 2.9 Hz), 128.7 (d, J = 9.8 Hz, 2C), 71.9 (d, J = 9.8 Hz), 71.8 (d, J = 3.5 Hz), 71.7, 71.3 (d, J = 7.5 Hz), 69.9 (s, 5C), 27.7 (d, J = 39.1 Hz), 25.5, 24.5 (d, J = 14.4 Hz), 13.8. ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 11.9 (br q, J = 75 Hz). $[\alpha]^{20}_D$ = −48.4 (*c* 1.10; CH_2Cl_2). HRMS (EI): *m/z* calcd for $C_{20}H_{26}BFeP$ 364.1209, obsd 364.1194.

(*S*)-Cyclohexylferrocenylphenylphosphine Borane (5c). Yield: 66% (1.0 g, 2.6 mmol), isolated as an orange solid. Enantiomeric excess: 97% ee by chiral HPLC analysis (Chiracel OJ, isocratic, hexane/2-propanol 97.5:2.5, t_R [(*R*)-**5c**] = 8.3 min, t_R [(*S*)-**5c**] = 10.0 min). R_f (50:50 hexane/CH_2Cl_2) = 0.33. Mp: 95−96 °C. IR (NaCl): 2931, 2854, 2381 cm^{-1}. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.95−7.91 (m, 2H), 7.54−7.53 (m, 3H), 4.66 (br s, 1H), 4.43 (br s, 1H), 4.40 (br s, 1H), 4.24 (br s, 1H), 3.97 (s, 5H), 2.03 (dd, J = 12.4, 26 Hz, 1H), 1.77−1.76 (m, 1H), 1.70−1.62 (m, 3H), 1.44−1.23 (m, 3H), 1.20−1.12 (m, 3H), 1.1−0.6 (br m, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 132.8 (d, J = 8.6 Hz, 2C), 131.3 (d, J = 2.9 Hz), 129.3 (d, J = 55.9 Hz), 128.7 (d, J = 9.2 Hz, 2C), 74.6 (d, J = 15.0 Hz), 71.8 (d, J = 6.3 Hz), 70.9 (d, J = 8.6 Hz), 70.6 (d, J = 4.0 Hz), 69.8 (s, 5C), 69.2 (d, J = 62.8 Hz), 37.2 (d, J = 37.4 Hz), 27.1, 26.9 (d, J = 4.6 Hz), 26.9 (d, J = 19.6 Hz), 26.7, 26.0 (d, J = 1.2 Hz). ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 19.3 (br q, J = 67 Hz). $[\alpha]^{20}_D$ = −281.8 (*c* 0.55; CH_2Cl_2). HRMS (EI): *m/z* calcd for $C_{22}H_{28}BFeP$ 390.1366, obsd 390.1351.

(*S*)-Ferrocenylphenyl(2-methyl-2-phenyl-1-propyl)phosphine Borane (5d). Yield: 79% (0.66 g, 1.5 mmol), isolated as an orange oil. Enantiomeric excess: 98% ee by chiral HPLC analysis (Chiracel AD, isocratic, hexane/2-propanol 98:2, t_R [(*R*)-**5d**] = 7.3 min, t_R [(*S*)-**5d**] = 7.8 min). R_f (80:20 hexane/CH_2Cl_2) = 0.06. IR (NaCl): 3088, 3057, 2965, 2389, 1496, 1437, 1387, 1171, 1107, 1063 cm^{-1}. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.74−7.70 (m, 2H), 7.41−7.40 (m, 1H), 7.36−7.33 (m, 2H), 7.26−7.24 (m, 2H), 7.20−7.16 (m, 2H), 7.13−7.11 (m, 1H), 4.55−4.54 (m, 1H), 4.41−4.40 (m, 1H), 4.37 (m, 2H), 4.10 (s, 5H), 2.72 (t, $J = 14.2$ Hz, 1H), 2.63 (dd, $J = 9.2$, 14.6 Hz, 1H), 1.54 (s, 3H), 1.43 (s, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 148.8 (d, $J = 6.9$ Hz), 132.0 (d, $J = 11.4$ Hz, 2C), 131.6, 130.7 (d, $J = 2.3$ Hz), 128.4 (d, $J = 9.8$ Hz, 2C), 128.2 (s, 2C), 126.1, 125.7 (s, 2C), 72.6 (d, $J = 66.2$ Hz), 71.9 (d, $J = 10.4$ Hz), 71.6 (d, $J = 7.5$ Hz), 71.5 (d, $J = 9.2$ Hz), 70.9 (d, $J = 7.5$ Hz), 69.8 (s, 5C), 43.6 (d, $J = 32.2$ Hz), 38.3, 31.0 (d, $J = 5.2$ Hz), 29.2 (d, $J = 4.6$ Hz). ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 6.3 (br q, $J = 70$ Hz). $[\alpha]^{20}_{D} = -72.3$ (c 0.90; CH_2Cl_2). HRMS (ESI) $[M + Na]^+$: m/z calcd for $C_{26}H_{30}BFeNaP$ 463.1420, obsd 463.1418.

(*R*)-Ferrocenyl(4-methoxyphenyl)phenylphosphine Borane (5e). Yield: 85% (0.56 g, 1.4 mmol), isolated as an orange oil. Enantiomeric excess: 95% ee by chiral HPLC analysis (Chiracel OJ, isocratic, hexane/2-propanol 90:10, t_R [(*S*)-**5e**] = 22.8 min, t_R [(*R*)-**5e**] = 30.3 min). R_f (50:50 hexane/CH_2Cl_2) = 0.30. IR (thin film): 3056, 2960, 2838, 2384, 1596, 1570, 1501, 1293, 1256, 1181, 1109, 1062 cm^{-1}. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.58−7.53 (m, 4H), 7.45−7.43 (m, 1H), 7.41−7.38 (m, 2H), 6.95 (dd, $J = 1.8$, 8.9 Hz, 2H), 4.52−4.50 (m, 2H), 4.46−4.45 (m, 1H), 4.37 (m, 1H), 4.13 (s, 5H), 3.84 (s, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 161.9, 134.6 (d, $J = 10.9$ Hz, 2C), 132.5 (d, $J = 9.2$ Hz, 2C), 132.2 (d, $J = 59.9$ Hz), 130.8, 128.5 (d, $J = 9.8$ Hz, 2C), 121.9 (d, $J = 64.5$ Hz), 114.2 (d, $J = 10.9$ Hz, 2C), 73.1 (d, $J = 10.9$ Hz), 72.6 (d, $J = 9.2$ Hz), 72.0, 71.9, 71.84, 69.9 (s, 5C), 55.5. ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 14.8 (br q, $J = 65$ Hz). $[\alpha]^{20}_{D} = +20.0$ (c 0.25; CH_2Cl_2). HRMS (EI): m/z calcd for $C_{23}H_{24}BFeOP$ 414.1002, obsd 414.0999.

(*R*)-Ferrocenyl(2-methoxyphenyl)phenylphosphine Borane (5f).[9a] Yield: 92% (0.38 g, 0.9 mmol). Enantiomeric excess: >98% ee by chiral HPLC analysis (Chiracel OJ, isocratic, hexane/2-propanol 99:1, t_R [(*R*)-**5f**] = 43.8 min, t_R [(*S*)-**5f**] = 56.9 min). R_f (90:10 hexane/EtOAc) = 0.18. Mp: 140 °C. IR (thin film): 3434, 3074, 2938, 2382, 1736, 1589, 1574, 1478, 1432, 1277, 1251, 1170, 1107, 1061 cm^{-1}. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.82−7.77 (m, 1H), 7.55−7.48 (m, 3H), 7.40−7.33 (m, 3H), 7.09−7.06 (m, 1H), 6.89 (dd, $J = 3.8$, 8.1 Hz, 1H), 4.70−4.69 (m, 1H), 4.54 (br s, 1H), 4.51−4.49 (m, 2H), 4.04 (s, 5H), 3.47 (s, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 135.6, 133.5, 131.5 (d, $J = 9.8$ Hz, 2C), 130.1, 128.0 (d, $J = 10.9$ Hz, 2C), 121.0 (d, $J = 10.9$ Hz, 1C), 112.0, 74.1 (d, $J = 12.1$ Hz), 73.6 (d, $J = 8.6$ Hz), 71.8 (d, $J = 7.5$ Hz), 71.6 (d, $J = 8.1$ Hz), 69.9 (s, 5C), 55.5.^{31}P NMR ($CDCl_3$, 121 MHz): δ 14.1 (br q, $J = 55$ Hz). $[\alpha]^{20}_{D} = +60.0$ (c 0.25; CH_2Cl_2). HRMS (EI): m/z calcd for $C_{23}H_{24}BFeOP$ 414.1002, obsd 414.1004.

(*R*)-Ferrocenyl(2-methylphenyl)phenylphosphine Borane (5g). Yield: 70% (0.50 g, 1.3 mmol). Enantiomeric excess: 83% ee by chiral HPLC analysis (Chiracel OJ, isocratic, hexane/2-propanol 99:1, t_R [(*R*)-**5g**] = 14.0 min, t_R [(*S*)-**5g**] = 20.3 min). R_f (80:20 hexane/EtOAc) = 0.50. Mp: 168−169 °C. IR (thin film): 3055, 2393, 1437, 1171, 1107, 1063 cm^{-1}. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.80−7.76 (m, 2H), 7.58−7.54 (m, 1H), 7.52−7.49 (m, 2H), 7.33−7.11 (m, 2H), 7.08−7.04 (m, 1H), 4.77−4.76 (m, 1H), 4.59−4.58 (m, 1H), 4.50−4.49 (m, 1H), 4.08−4.07 (m, 1H), 4.07 (s, 5H), 2.09 (s, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 141.8 (d, $J = 10.4$ Hz), 133.4 (d, $J = 8.1$ Hz), 132.8 (d, $J = 9.8$ Hz, 2C), 131.7 (d, $J = 9.2$ Hz), 131.3, 130.9, 130.8, 130.4 (d, $J = 16.1$ Hz), 128.8 (d, $J = 9.8$ Hz, 2C), 125.7 (d, $J = 9.8$ Hz), 72.2 (d, $J = 6.3$ Hz), 72.0 (d, $J = 10.4$ Hz), 71.8, 70.1 (d, $J = 70.2$ Hz), 70.0 (s, 5C), 22.2 (d, $J = 4.6$ Hz). ^{31}P NMR ($CDCl_3$, 121 MHz): δ 17.1 (br q, $J = 60$ Hz). $[\alpha]^{20}_{D} = -269.3$ (c 0.15; CH_2Cl_2). HRMS (ESI) $[M + Na]^+$: m/z calcd for $C_{23}H_{24}BFeNaP$ 421.0950, obsd 421.0952.

(*R*)-Ferrocenyl(2-biphenylyl)phenylphosphine Borane (5h). Yield: 69% (0.54 g, 1.2 mmol). Enantiomeric excess: 98% ee by chiral HPLC analysis (Chiracel AD, isocratic, hexane/2-propanol 99.4:0.6, t_R [(*R*)-**5h**] = 13.2 min, t_R [(*S*)-**5h**] = 14.3 min). R_f (50:50 hexane/CH_2Cl_2) = 0.34. M.p. 135−137 °C. IR (thin film): 3055, 2385, 1464, 1438, 1169, 1108, 1060 cm^{-1}. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.64−7.60 (m, 2H), 7.46−7.40 (m, 2H), 7.36−7.33 (m, 2H), 7.31−7.26 (m, 2H), 7.18−7.15 (m, 1H), 7.13−7.10 (m, 1H), 7.04−7.01 (m, 2H), 6.94 (br s, 2H), 4.75 (br s, 1H), 4.49 (br s, 1H), 4.43 (br s, 1H), 4.10 (br s, 1H), 3.90 (s, 5H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 146.7 (d, $J = 9.2$ Hz), 140.5 (d, $J = 3.5$ Hz), 133.5 (d, $J = 8.6$ Hz), 133.0 (d, $J = 9.2$ Hz, 2C), 131.80 (d, $J = 8.1$ Hz), 131.79, 131.3 (d, $J = 18.4$ Hz), 130.9 (d, $J = 2.3$ Hz), 130.7, 130.15, 130.1 (d, $J = 2.3$ Hz), 128.1 (d, $J = 10.4$ Hz, 2C), 127.1 (s, 2C), 127.0, 126.9 (d, $J = 9.2$ Hz). ^{31}P NMR ($CDCl_3$, 121 MHz): δ 18.1 (br s). $[\alpha]^{20}_{D} = -180.8$ (c 0.40; CH_2Cl_2). HRMS (ESI) $[M + Na]^+$: m/z calcd for $C_{28}H_{26}BFeNaP$ 483.1107, obsd 483.1107.

Synthesis of Phosphines 1a−h (Typical Procedure). Diethylamine was degassed, and a 0.1 M solution of **5** was prepared (1 mmol in 10 mL diethylamine). The solution was heated at reflux 14 h and cooled to ambient temperature, and the diethylamine was removed by evaporation under reduced pressure. The crude orange residue was taken up in a solution of 95:5 hexane/EtOAc (degassed) and passed through a short column of silica gel eluting, under argon, with 95:5 hexane/EtOAc (also degassed) to yield an orange solid (unless otherwise noted). The enantiomeric excess was determined by reprotection with BH_3·THF and analysis by chiral HPLC.

(*S*)-Ferrocenylmethylphenylphosphine (1a). Yield: 93% (0.343 g, 1.1 mmol). Enantiomeric excess: 87% ee determined by chiral HPLC (Chiracel OJ, isocratic, hexane/2-propanol 95:5, t_R [(*R*)-**5a**] = 16.8 min, t_R [(*S*)-**5a**] = 24.7 min). Recrystallization from hexane (90% yield) provided **1a** in 96% ee. R_f (95:5 hexane/EtOAc) = 0.42. Mp: 84−85 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.40−7.34 (m, 3H), 7.31−7.25 (m, 2H), 4.39−4.30 (m, 4H), 4.22−4.21 (s, 5H), 1.64 (d, 3H, $J = 3.0$ Hz). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 131.3 (d, $J = 18.4$ Hz, 2C), 130.2 (d, $J = 9.2$ Hz), 128.5 (d, $J = 11.5$ Hz), 128.3 (d, $J = 6.7$ Hz, 2C), 74.5 (d, $J = 28.5$ Hz), 71.2, 69.8, 12.6 (d, $J = 8.1$ Hz). ^{31}P NMR ($CDCl_3$, 121 MHz): δ −37.4. HRMS (EI): m/z calcd for $C_{17}H_{17}FeP$ 308.0412, obsd 308.0422.

(*S*)-*n*-Butylferrocenylphenylphosphine (1b). Yield: 88% (0.35 g, 1 mmol), isolated as an orange oil. Enantiomeric excess: 80% ee determined by chiral HPLC (Chiracel OJ, isocratic, hexane/2-propanol 97.5:2.5, t_R [(*R*)-**5b**] = 10.0 min, t_R [(*S*)-**5b**] = 12.0 min). R_f (90:10 hexane/EtOAc) = 0.48. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.53−7.50 (m, 2H), 7.34−7.33 (m, 3H), 4.40−4.38 (m, 2H), 4.33 (br s, 1H), 4.18 (br s, 1H), 4.16 (s, 5H), 2.03−1.96 (m, 2H), 1.55−1.40 (m, 4H), 0.92 (t, $J = 7.0$ Hz, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 140.2 (d, $J = 13.8$ Hz), 132.8 (d, $J = 19.6$ Hz, 2C), 128.7, 128.2 (d, $J = 6.9$ Hz, 2C), 77.6 (d, $J = 8.1$ Hz), 73.2 (d, $J = 20.1$ Hz), 70.7 (d, $J = 4.6$ Hz), 70.4 (d, $J = 8.1$ Hz), 70.1 (d, $J = 2.3$ Hz), 69.2 (s, 5C), 28.8 (d, $J = 11.5$ Hz), 28.7 (d, $J = 2.3$ Hz), 24.5 (d, $J = 13.2$ Hz), 14.0. ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ −27.1 (br s). HRMS (EI): m/z calcd for $C_{20}H_{23}FeP$ 350.0881, obsd 350.0880.

(*S*)-Cyclohexylferrocenylphenylphosphine (1c). Yield: 84% (0.35 g, 0.9 mmol). Enantiomeric excess: 98% ee by chiral HPLC (Chiracel OJ, isocratic, hexane/2-propanol 97.5:2.5, t_R [(*R*)-**5c**] = 8.3 min, t_R [(*S*)-**5c**] = 10.0 min). Mp: 99−101 °C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.67−7.63 (m, 2H), 7.42−7.39 (m, 3H), 4.37−4.36 (m, 1H), 4.34−4.43 (m, 1H) 4.28−4.26 (m, 1H), 4.03−4.02 (m, 1H), 4.00 (s, 5H), 1.96−1.93 (m, 1H), 1.86−1.84 (m, 1H), 1.79−1.78 (m, 1H), 1.68−1.66 (m, 2H), 1.48−1.45 (m, 1H), 1.29−1.17 (m, 4H), 1.09−1.05 (m, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 137.4 (d, $J = 10.9$ Hz), 134.5 (d, $J = 20.7$ Hz, 2C), 129.2, 128.2 (d, $J = 8.1$ Hz, 2C), 76.6 (d, $J = 11.5$ Hz), 74.1 (d, $J = 24.8$ Hz), 71.1 (d, $J = 2.9$ Hz), 70.5 (d, $J = 1.7$ Hz), 70.0 (d, $J = 6.3$ Hz), 69.2 (s, 5C), 38.1 (d, $J = 6.3$ Hz), 30.3, 30.2, 27.0 (d, $J = 12.1$ Hz), 26.9, 26.6. ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ −12.0. HRMS (EI): m/z calcd for $C_{22}H_{25}FeP$ 376.1038, obsd 376.1030.

(*S*)-Ferrocenylphenyl(2-methyl-2-phenyl-1-propyl)phosphine (1d). Yield: >99% (0.40 g, 0.94 mmol), isolated as an orange oil. Enantiomeric excess: 96% ee by chiral HPLC analysis (Chiracel AD, isocratic, hexane/2-propanol 98:2, t_R [(*R*)-**5d**] = 7.3 min, t_R [(*S*)-**5d**] = 7.8 min). R_f (90:10 hexane/EtOAc) = 0.47. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.46−7.43 (m, 2H), 7.35−7.33 (m, 2H), 7.27−7.23 (m, 5H), 7.17−7.16 (m, 1H), 4.28−4.27 (m, 1H), 4.25−4.23 (m, 2H), 4.09−4.06 (m, 1H), 4.05 (s, 5H), 2.57 (dd, J = 6.3, 13.9 Hz, 1H), 2.43 (d, J = 13.7 Hz, 1H), 1.46 (s, 3H), 1.43 (s, 3H).^{13}C NMR ($CDCl_3$, 125 MHz): δ 145.5 (d, J = 3.4 Hz), 133.6 (d, J = 21.3 Hz, 2C), 128.8, 128.2 (d, J = 7.5 Hz, 2C), 128.0 (d, J = 1.2 Hz, 2C), 126.0, 72.8 (d, J = 19.0 Hz), 70.9 (d, J = 11.5 Hz), 70.6 (d, J = 5.2 Hz), 70.0 (d, J = 2.9 Hz), 69.1 (s, 5C), 46.3 (d, J = 12.1 Hz), 38.2 (d, J = 15.5 Hz), 30.3, 30.2. ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ −36.3. HRMS (EI): m/z calcd for $C_{26}H_{27}FeP$ 426.1194, obsd 426.1197.

(*R*)-Ferrocenyl(4-methoxyphenyl)phenylphosphine (1e). Yield: 95% (86 mg, 0.21 mmol), isolated as an orange oil. Enantiomeric excess: 94% ee by chiral HPLC (Chiracel OJ, isocratic, hexane/2-propanol 90:10, t_R [(*S*)-**5e**] = 22.8 min, t_R [(*R*)-**5e**] = 30.3 min). R_f (95:5 hexane/EtOAc) = 0.25. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.40−7.30 (m, 7H), 6.91 (d, J = 7.9 Hz, 2H), 4.40−4.39 (m, 1H), 4.38−4.37 (m, 1H), 4.18−4.17 (m, 1H), 4.11 (s, 5H), 4.10−4.07 (m, 1H), 3.83 (s, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 160.4, 135.5 (d, J = 21.3 Hz, 2C), 133.0 (d, J = 19.0 Hz, 2C), 128.3, 128.2 (d, J = 6.3 Hz, 2C), 114.0 (d, J = 8.1 Hz, 2C), 73.4 (d, J = 18.4 Hz, 1C), 72.4 (d, J = 10.9 Hz, 1C), 70.9 (d, J = 4.0 Hz, 2C), 69.3 (s, 5C), 55.3. ^{31}P NMR ($CDCl_3$, 121 MHz): δ −17.7. HRMS (EI): m/z calcd for $C_{23}H_{21}FeOP$ 400.0674, obsd 400.0672.

(*R*)-Ferrocenyl(2-methoxyphenyl)phenylphosphine (1f).[9a] Yield: 83% (0.26 g, 0.65 mmol). Enantiomeric excess: >98% ee by chiral HPLC analysis (Chiracel OJ, isocratic, hexane/2-propanol 99:1, t_R [(*R*)-**5f**] = 43.8 min, t_R [(*S*)-**5f**] = 56.9 min). R_f (90:10 hexane/EtOAc) = 0.31. Mp: 128−130 °C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.50−7.46 (m, 2H), 7.35−7.29 (m, 4H), 6.94−6.91 (m, 1H), 6.89−6.87 (m, 1H), 6.85−6.83 (m, 1H), 4.41−4.40 (m, 1H), 4.35−4.34 (m, 1H), 4.30−4.29 (m, 1H), 4.12 (s, 5H), 3.85−3.84 (m, 1H), 3.73 (s, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 160.9 (d, J = 15.5 Hz), 138.0, 133.8 (d, J = 20.1 Hz, 2C), 130.2, 128.6, 128.0 (d, J = 7.5 Hz, 2C), 120.9, 110.3 (d, J = 1.7 Hz), 74.1 (d, J = 24.7 Hz), 72.3 (d, J = 4.6 Hz), 71.1 (d, J = 5.8 Hz), 70.6 (s, 1C), 69.3 (s, 5C), 55.8. ^{31}P NMR ($CDCl_3$, 121 MHz): δ −28.8 (s). HRMS (EI): m/z calcd for $C_{23}H_{21}FeOP$ 400.0674, obsd 400.0672.

(*R*)-Ferrocenyl(2-methylphenyl)phenylphosphine (1g). Yield: >99% (0.42 g, 1.1 mmol), crystallized from diethylamine upon cooling and standing. The crystals were purified via column chromatography. Enantiomeric excess: >98% ee by chiral HPLC analysis (Chiracel OJ, isocratic, hexane/2-propanol 99:1, t_R [(*R*)-**5g**] = 14.0 min, t_R [(*S*)-**5g**] = 20.3 min). R_f (90:10 hexane/EtOAc) = 0.42. Mp: 116−117 °C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.54−7.51 (m, 2H), 7.40−7.38 (m, 3H), 7.25−7.21 (m, 1H), 7.15−7.11 (m, 2H), 6.99−6.97 (m, 1H), 4.48−4.47 (m, 1H), 4.41−4.38 (m, 2H), 4.14 (s, 5H), 3.80−3.79 (m, 1H), 2.31(s, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 141.1 (d, J = 23.6 Hz), 138.8 (d, J = 11.5 Hz), 136.8 (d, J = 7.5 Hz), 134.5 (d, J = 19.6 Hz, 2C), 132.1, 130.0 (d, J = 4.0 Hz), 129.1, 128.4, 128.3 (d, J = 7.5 Hz, 2C), 125.7, 75.8 (d, J = 4.0 Hz), 74.7 (d, J = 30.5 Hz), 71.9, 71.4 (d, J = 6.9 Hz), 70.7, 69.3 (s, 5C), 24.2 (d, J = 20.1 Hz). ^{31}P NMR ($CDCl_3$, 121 MHz): δ −23.4 (s). HRMS (EI): m/z calcd for $C_{23}H_{21}FeP$ 384.0725, obsd 384.0735.

(*R*)-Ferrocenyl(2-biphenylyl)phenylphosphine (1h). Yield: 94% (0.30 g, 0.7 mmol). Enantiomeric excess: 96% ee by chiral HPLC analysis (Chiracel AD, isocratic, hexane/2-propanol 99.4:0.6, t_R [(*R*)-**5h**] = 13.2 min, t_R [(*S*)-**5h**] = 14.3 min). R_f (90:10 hexane/EtOAc) = 0.40. Mp: 63−65 °C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.38−7.23 (m, 11H), 7.21−7.18 (m, 1H), 7.13−7.12 (m, 2H), 4.43−4.43 (m, 1H), 4.37−4.36 (m, 1H), 4.34−4.33 (m, 1H), 4.0 (s, 5H), 3.86−3.85 (m, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 146.9 (d, J = 24.4 Hz), 141.9 (d, J = 5.2 Hz), 139.1 (d, J = 15.0 Hz), 138.3 (d, J = 8.1 Hz), 134.5 (d, J = 20.1 Hz, 2C), 132.9, 130.0 (d, J = 3.5. Hz), 129.8 (d, J = 3.5 Hz, 2C), 128.7, 128.2, 128.0 (d, J = 8.1 Hz, 2C), 127.7 (s, 2C), 127.1 (s, 2C), 76.6 (d, J = 7.5 Hz), 74.9 (d, J = 31.9 Hz), 72.0, 71.2 (d, J = 6.9 Hz), 70.7, 69.2 (s, 5C). ^{31}P NMR ($CDCl_3$, 121 MHz): δ −22.0 (s). HRMS (EI): m/z calcd for $C_{28}H_{23}FeP$ 446.0887, obsd 446.0871.

Synthesis of Allylic Alcohols 6a,b, 7−9, 10a,b (Typical Procedure). In a glovebox, Ni(cod)$_2$ (14 mg, 0.05 mmol) and solid ligand (0.05 mmol) were placed into a flask, which was then sealed with a rubber septum and removed from the glovebox. If a liquid phosphine was employed, it was added via syringe immediately after removal from the glovebox. A 2.0 M solution of Et_3B in EtOAc was added (0.5 mL, 1.0 mmol), and the mixture was stirred for 10 min at ambient temperature. The aldehyde (1.0 mmol) and alkyne (0.5 mmol) were added via syringe in succession, and the reaction was stirred for 14 h at ambient temperature. After this time, the solution was allowed to stir open to the air for 1 h. The solvent was evaporated, and the crude residue was purified via gradient column chromatography (50:1 hexanes/EtOAc, polarity gradually increased to 9:1) to afford the desired alcohol as a clear, colorless oil. The enantiomeric excess of **6a,b**, **7**−**9**, and **10a,b** was determined by chiral GC or chiral HPLC analysis.

(*E*)-1-Cyclohexyl-2,4-dimethyl-pent-1-en-3-ol (6a) and (*E*)-4-Cyclohexyl-2-methyl-hex-4-en-3-ol (6b). Enantiomeric excess determined by chiral GC analysis (B-PH, isothermal, 140 °C, t_R [(*R*)-**6b**] = 6.85 min, t_R [(*S*)-**6b**] = 7.04 min, t_R [(*R*)-**6a**] = 9.36 min, t_R [(*S*)-**6a**] = 9.64 min). IR (thin film): 3383, 2925, 2852, 1448, 1010 cm^{-1}. R_f (90:10 hexane/EtOAc) = 0.38. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 5.46 (q, 1H, **6b,** J = 7.0 Hz), 5.18 (d, 1H, **6a**, J = 9.2 Hz), 3.65 (d, 1H, **6b,** J = 7.6 Hz), 3.29 (d, 1H, **6a**, J = 8.2 Hz), 2.34−2.28 (m, 1H, **6b**), 2.23−2.16 (m, 1H, **6a**), 1.87−0.99 (m, 18H, **6a, 6b**), 0.83 (d, 1H, **6b**, J = 6.7 Hz), 0.77 (d, 1H, **6a**, J = 6.7 Hz). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 146.7, 134.6, 134.1, 120.6, 84.4, 80.0, 39.1, 36.7, 33.2, 32.2, 31.6, 31.3, 31.2, 27.20, 27.19, 26.4, 26.3, 26.17, 26.14, 20.5, 19.6, 18.9, 18.2, 13.7, 11.4. HRMS (ESI) [M + Na]$^+$: m/z calcd for $C_{13}H_{24}NaO$ 219.1719, obsd 219.1723.

(*E*)-1-Phenyl-2-propyl-hex-2-en-1-ol (7).[43] Enantiomeric excess determined by chiral HPLC analysis (Chiracel OD, isocratic, 99:1 hexane/2-propanol, 0.8 mL/min, t_R [(*R*)-**7**] = 15.7 min, t_R [(*S*)-**7**] = 17.4 min). R_f (90:10 hexane/EtOAc) = 0.28. IR (thin film): 3365, 2958, 2930, 2871, 1493, 1453, 1377, 1035 cm^{-1}. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.38−7.31 (m, 4H), 7.29−7.25 (m, 1H), 5.64 (5, 1H, J = 7.3 Hz), 5.17 (d, 1H, J = 3.1 Hz), 2.09−2.05 (m, 2H), 2.01−1.96 (m, 1H), 1.86−1.81 (m, 1H), 1.81 (d, 1H, J = 3.1 Hz), 1.48−1.40 (m, 2H), 1.34−1.19 (m, 3H), 0.94 (t, 3H, J = 7.3 Hz), 0.83 (t, 3H, J = 7.3 Hz). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 143.0, 141.4, 128.4, 127.54, 127.49, 126.8, 78.4, 30.2, 29.9, 23.2, 23.0, 14.7, 14.2. HRMS (ESI) [M + Na]$^+$: m/z calcd for $C_{15}H_{22}NaO$ 241.1564, obsd 241.1564.

(*E*)-5-Propyl-non-5-en-4-ol (8). Enantiomeric excess determined from the chloroacetate derivative by chiral GC analysis (B-PH, isothermal, 120 °C, t_R [(*S*)-**8**] = 21.2 min, t_R [(*R*)-**8**] = 21.9 min). R_f (90:10 hexane/EtOAc) = 0.25. IR (thin film): 3357, 2958, 2872, 1465, 1378, 1017 cm^{-1}. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 5.39 (t, 1H, J = 7.3 Hz), 4.03 (td, 1H, J = 2.5, 6.5 Hz), 2.07−1.94 (m, 4H), 1.54−1.50 (m, 2H), 1.46−1.53 (m, 5H) 1.33−1.26 (m, 2H), 0.95−0.90 (m, 9H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 142.2, 127.0, 76.9, 38.2, 29.9, 29.8, 23.5, 23.2, 19.4, 14.9, 14.3, 14.1. HRMS (ESI) [M + Na]$^+$: m/z calcd for $C_{12}H_{24}NaO$ 207.1719, obsd 207.1723.

(*E*)-2-Methyl-4-propyl-oct-4-en-3-ol (9). Enantiomeric excess determined from the chloroacetate derivative by chiral GC analysis (B-PH, 90 °C for 30 min then 140 °C for 15 min, t_R [(*S*)-**9**] = 38.4 min, t_R [(*R*)-**9**] = 38.9 min). R_f (90:10 hexane/EtOAc) = 0.34. IR (thin film): 3409, 2958, 2931, 2872, 1466, 1379, 1005 cm^{-1}. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 5.35 (t, 1H, J = 7.3 Hz), 3.65 (d, 1H, J = 7.3 Hz), 2.05−1.92 (m, 4H), 1.81−1.75 (m, 1H), 1.47−1.35 (m, 5H) 0.98−0.89 (m, 9H), 0.83 (t, 3H, J = 7.0 Hz). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 141.4, 127.9, 83.0, 31.8, 30.3, 29.8, 23.5, 20.1, 18.3, 14.9, 14.1. HRMS (ESI) [M + Na]$^+$: m/z calcd for $C_{12}H_{24}NaO$ 207.1719, obsd 207.1716.

(*E*)-1-Cyclohexyl-2-methyl-hex-1-en-3-ol (10a) and (*E*)-3-Cyclohexyl-hept-2-en-4-ol (10b). Enantiomeric excess determined by chiral GC analysis (B-PH, isothermal, 140 °C, t_R

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[43] Srebnik, M. *Tetrahedron Lett.* **1991**, *32*, 2449−2452.

[(*R*)-**10b**] = 7.86 min, t_R [(*S*)-**10b**] = 8.03 min, t_R [(*R*)-**10a**] = 11.40 min, t_R [(*S*)-**10a**] = 11.66 min,). IR (thin film): 3348, 2926, 2852, 1448 cm^{-1}. R_f (90:10 hexane/EtOAc) = 0.33. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 5.51 (q, 1H, **10b,** $J = 7.0$ Hz), 5.20 (d, 1H, **10a**, $J = 8.8$ Hz), 4.05 (t, 1H, **10b**, $J = 5.5$ Hz), 3.96 (t, 1H, **10a,** $J = 6.7$ Hz), 2.37−2.33 (m, 1H, **10b**), 2.21−2.15 (m, 1H, **10a**), 1.78−0.87 (m, 21H, **10a, 10b**). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 148.0, 135.4, 133.1, 119.6, 78.0, 73.6, 39.4, 38.9, 37.2, 36.7, 33.3, 33.2, 31.6, 31.4, 27.2, 26.4, 26.3, 26.18, 26.17, 19.7, 19.2, 14.28, 14.25, 13.5, 12.8, 11.3. HRMS (ESI) [M + Na]$^+$: *m*/*z* calcd for $C_{13}H_{24}NaO$ 219.1719, obsd 219.1724.

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Supporting Information Available: ^{1}H, ^{13}C, and ^{31}P NMR spectra for **1a−h**, **3a−h**, **4a−h**, and **5a−h**; ^{1}H and ^{13}C NMR spectra for **6a,b**, **7−9**, and **10a,b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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