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Tunable phosphinite, phosphite and phosphoramidite ligands for the asymmetric hydrovinylation reactions

Haengsoon Park, Ramaiah Kumareswaran and T. V. RajanBabu*

Department of Chemistry, The Ohio State University, 100 W. 18th Avenue, Columbus, OH 43210, USA

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Abstract—Only a limited number of ligands have been successfully employed for the Ni-catalyzed asymmetric hydrovinylation reaction. Diarylphosphinites, carrying β-acylamino groups prepared from readily available carbohydrates, in conjunction with highly dissociated counteranions $\{[(3,5\text{-}(CF_3)_2C_6H_3]_4B^-$ or $SbF_6^-\}$, effect the hydrovinylation of vinylarenes under ambient pressure of ethylene with high enantioselectivity. Nitrogen substituents such as $-COCF_3$ and COPh groups lead to isomerization of the primary products (3-arylbutenes) to *Z*- and *E*-2-aryl-2-butenes. In a prototypical synthesis of a 2-arylproionic acid, (*S*)-3-(4-bromophenyl)-1-butene (89% ee) has be transformed into (*R*)-ibuprofen by Ni-catalyzed cross-coupling with *i*-BuMgBr, followed by oxidation of the double bond with $NaIO_4$ and $KMnO_4$. Asymmetric codimerization of norbonene and ethylene using binaphthol-derived phosphoramidites as ligands gives 1:1, 2:1 or polymeric adducts depending on the relative configurations and nature of the BINAP and amine moieties. With one of the phosphoramidite–Ni complexes, counteranions BAr_4^- [Ar = 3,5-$(CF_3)_2C_6H_3$] and SbF_6^-, which had been used interchangeably in other reactions, give either a 1:1 adduct or a 2:1 adduct, respectively.

1. Introduction

Development of new asymmetric catalytic processes depends on the availability of enantiomerically pure ligand precursors that are amenable to fine-tuning for optimum performance.[1] Once the essential features of the ligand system are identified, substantial modifications in the scaffolding and in the steric and electronic environments around the chelating atoms are often necessary to achieve acceptable levels of catalytic efficiency and enantioselectivity. Nowhere is such a strategy more important than in the discovery of new catalytic processes that involve the use of relatively stable carbon feedstocks such as HCN, CO or olefins for selective C–C bond-forming reactions. At the appropriate stages in the catalytic cycle, the ligand should promote activation of the substrate(s) and induce high *selectivity* in the bond-forming process. Following the pioneering works of Cullen[2] and Selke,[3] we have invested considerable effort in the design and use of readily available carbohydrates as precursors[4] for variety diarylphosphinite and phospholane[5] ligands. Thus electronically tuned glucose- and fructose-derived phosphinites (e.g., Fig. 1) were found to be excellent ligands for Ni(0)-catalyzed asymmetric hydrocyanation of vinylarenes[6] and Rh(I)-catalyzed hydrogenation of dehydroamino acids.[7] These studies also provided some of the first demonstrable examples[8] of electronic tuning of asymmetric catalysts for not only hydrocyanation and hydrogenation but also hydroformylation[9] and Pd-catalyzed asymmetric allylation reactions.[10]

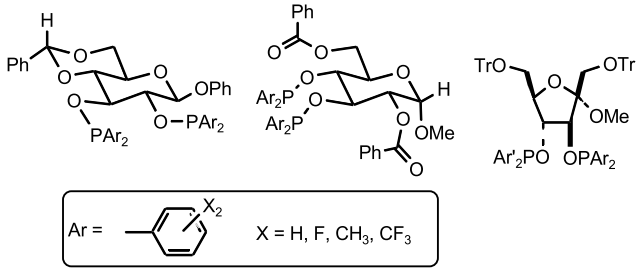
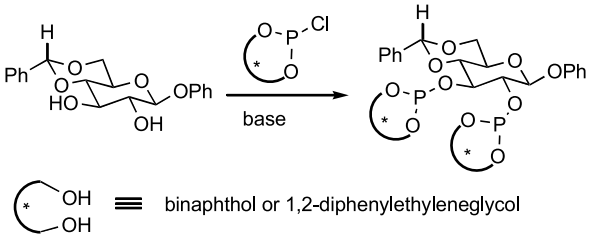


Figure 1. Diarylphosphinite ligands for hydrogenation and hydrocyanation reactions.



(1)

As early as 1991, during the initial studies of asymmetric hydrocyanation we also recognized that the hydroxyl groups

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* Corresponding author. Tel.: +1 614 688 3543; fax: +1 614 292 1685; e-mail: rajanbabu.1@osu.edu

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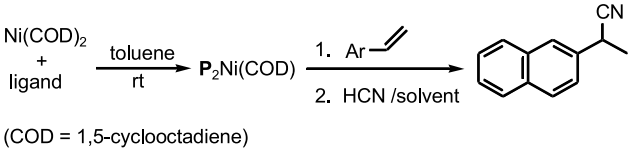
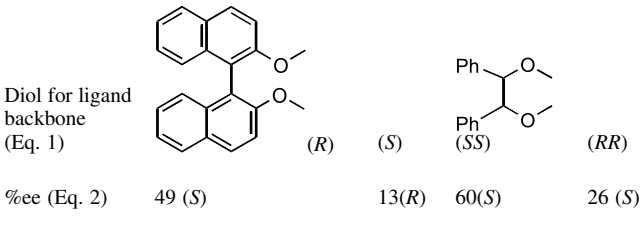
on carbohydrates can be readily converted into phosphite esters (Eq. 1), and depending on the source of the (RO)P(OR′)-Cl,[11] additional elements of chirality can be introduced into the ligand.[12] As can be expected from such modular ligands, which combine two chiral fragments, the sense and extent of asymmetric induction will depend on whether the two elements are matching or mismatching (Eq. 2).[13] Mono- and bis-phosphites of this structural type have since been found to have wide applications in enantioselective Rh-catalyzed hydrogenation reactions.[14]



(2)



In related developments, Feringa et al. have reported the synthesis and applications of highly versatile phosphoramidite ligands derived from binaphthol and various chiral amines.[15] Mono- and bi-dentate analogs of Feringa's ligands have been used in a number of reactions including hydrogenations,[16] conjugate addition reactions,[17] and Ir-catalyzed allylation reactions.[18]

In a study that is especially relevant to this report, Leitner et al. found that the Feringa's phosphoramidites are excellent ligands for the asymmetric hydrovinylation of vinylarenes.[19] Ni-catalyzed asymmetric hydrovinylation is a very demanding reaction with only a limited number of ligands giving acceptable selectivity for the desired 3-arylbutenes.[20] In this paper, we disclose the full details of our own studies on the application of carbohydrate-derived phosphinite and phosphite ligands for the asymmetric hydrovinylation reaction.[21] Phosphoramidite ligands are suitable also for hydrovinylation of norbornene.[21b] In this instance, dramatic changes on the course of the reaction with minor changes in the structure of the ligand and nature of the counteranion were noticed. The details of this study are also reported here.[22]

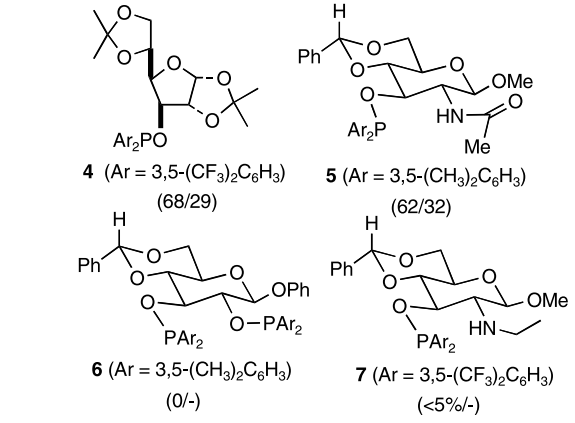
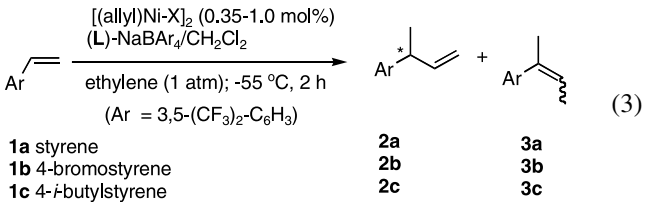


Figure 2. Diarylphosphinite ligands for hydrovinylation (yield of product/ee for hydrovinylation of styrene (Eq. 3) are shown in brackets).



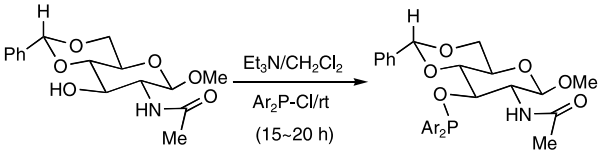
(3)

2. Results

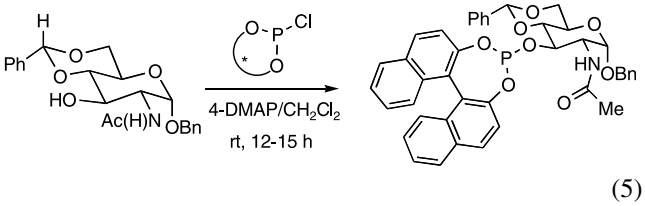
2.1. Hydrovinylation of vinylarenes

2.1.1. Ligands from monosaccharides. In our initial survey of ligands prepared from several monosaccharide derivatives it became apparent that simple monodentate diarylphosphinites like **4** and **5** (Fig. 2) were viable ligands for the hydrovinylation of styrene under our standard conditions (Eq. 3), where as bidentate bisphosphinites[23] like **6**, or β-amino-phosphinites like **7** were not.[24]

Among the various ligands we examined, the β-acetamido-diarylphosphinites (e.g., **5**) showed the most promise, and thus were chosen for further development. The syntheses of this type of ligands were carried out as follows: inside a drybox, to a solution of 1 equiv each of the alcohol and triethylamine in CH_2Cl_2 is added 1 equiv of the chlorodiarylphosphine[6a] in CH_2Cl_2 (Eq. 4). The resulting mixture is stirred overnight at rt and is subsequently concentrated in vacuo. The residue is then dissolved in a small amount of toluene, filtered through a pad of celite to remove the amine hydrochloride. Further concentration and recrystallization from cyclohexane or hexane gives the pure ligand.



(4)



(5)

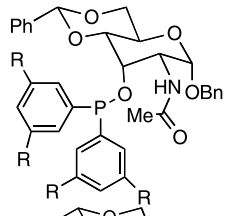
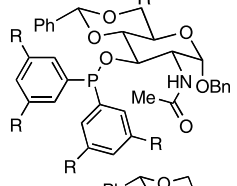
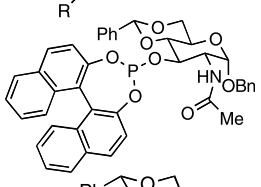
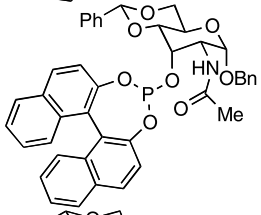
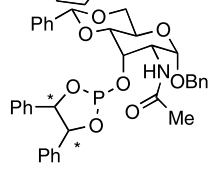
Syntheses of the phosphite ligands were accomplished by adding a solution of the chlorodioxophospholane[11a] (from (*R*/*S*) binaphthol or (*RR*/*SS*)-hydrobenzoin) in CH_2Cl_2 to an equimolar mixture of the sugar and 4-dimethylaminopyridine (Eq. 5). The mixture is stirred overnight and subsequently worked up as described before. The pure

phosphite ligands were obtained by column chromatography inside the drybox.

Typically, the catalyst precursor is prepared by mixing stoichiometric amounts of allyl nickel bromide dimer and the ligand (1:1 Ni/**L**) in CH_2Cl_2, followed by exchanging the bromide ion by addition of Na^+ Ar_4B^- (Ar=3,5-$(CF_3)_2$-C_6H_3) or another appropriate Ag salt (Eq. 3). The precipitated salts are removed by filtration through celite. Oxygen-free ethylene is then introduced into the flask after cooling the Ni-complex to the appropriate temperature (−70 to −55 °C), followed by the substrate dissolved in CH_2Cl_2. After ~2 h, the reaction is quenched with ammonium chloride, the product is isolated by evaporation of the solvent. Selectivity factors are determined by NMR spectroscopy, GC and HPLC.

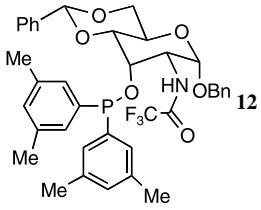
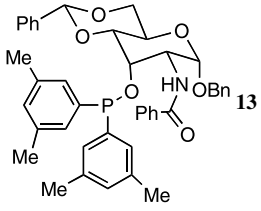
2.1.2. Asymmetric hydrovinylation of prototypical vinylarenes. Table 1 shows the yields and ee's obtained when various β-acetamidophosphinites are used as ligands for the Ni(II)-catalyzed asymmetric hydrovinylation of various vinylarenes (Eq. 3). In this study, two series of sugars were examined, the *allo*-series (entries 1, 4 and 5) and *gluco*-series (entries 2 and 3). In general, outstanding selectivity for the primary product, 3-aryl-1-butene (**2**) is observed with the diarylphosphinite ligands as long as the *N*-substituent is an acetyl group (vide infra for other acyl groups). In overall yield and selectivity, in the phosphinite series, the *allo*-derivatives (entry 1) are better than the *gluco*-derivatives (entry 2). Whether a 3,5-bis-CH_3-C_6H_3-substituent or a 3,5-bis-CF_3-C_6H_3-substituent on phosphorus is better depends on the configuration of the carbon to which is attached the diarylphosphinite moiety. In the *gluco*-series (entry 2), for both styrene and 4-bromostyrene, the CF_3-aromatic substituent is better, whereas in the *allo*-series (entry 1) the CH_3-aromatic substituent is clearly superior. In the hybrid ligands carrying the sugar and the BINAPO moieties, the combination of the (*R*)-BINAP and D-gluco appear to give the best yield and selectivity for styrene hydrovinylation (entries 3 and 4). The hydrobenzoin-derived phosphite generally gave poor selectivity, the best result coming from a combination of (*SS*)-hydrobenzoin and the D-allopyranoside (entry 5, ligand **11D**).

Table 1. Asymmetric hydrovinylation of vinylarenes using phosphinite and phosphite ligands[a]

Entry	Ligand		Styrene		4-Br-styrene		4-*i*-Bu-styrene	
			Yield[b]	%ee	Yield	%ee	Yield	%ee
1.		**8A** R=CH_3 **8B** R=CF_3	89[c] 95	81 (*S*) 62 (*S*)	94 19	89 (*S*) 43 (*S*)	99 99	74(*S*) 59 (*S*)
2.		**9A** R=CH_3 **9B** R=CF_3	93 93	9 (*S*) 45(*S*)	88	13 (*S*) 47(*S*)	— 36	— 61(*S*)
3.		**10A** =(*R*)-$BINAPO_2$ **10B** =(*S*)-$BINAPO_2$	95 26	62(*S*) 2 (*R*)	— —	— —	— —	— —
4.		**11A** =(*R*)-$BINAPO_2$ **11B** =(*S*)-$BINAPO_2$	84 83[d]	44 (*S*) 19 (*S*)	— —	— —	99 —	38 (*S*) —
5.		**11C**=(*RR*) **11D**=(*SS*)	53 83	5 (*R*) 30 (*S*)	— —	— —	— —	— —

[a] For typical reaction conditions see Eq. 3. Yield of 3-arylbutene (**2**). Selectivity for **2** >99% unless otherwise mentioned.
[b] Some of the variable yields of 3-phenylbutene reflect the volatility of the product.
[c] Selectivity 89%; rest **3a**.
[d] Selectivity 83%; rest **3a**.

Table 2. Asymmetric hydrovinylation of vinylarenes. Effect of *N*-substituent

Entry	Ligand, **L**	Conver. (%)	Selectivity		
			% **2a**	% c/t-**3a**	% ee (**2a**)
1.	 **12**	>99[a]	~40	~60	87 (*S*)
2.	 **13**	>99[b] >99[c]	~66 ~23	34 77	80 (*S*) 82 (*S*)

[a] Conditions: see Eq. 3. 2 mol% [(η^3-allyl)Ni**L**]BARF/2 h.
[b] 3 mol% [(η^3-allyl)Ni**L**/BARF]/0.5 h.
[c] 3 mol% [(η^3-allyl)Ni**L**/BARF]/2.0 h.

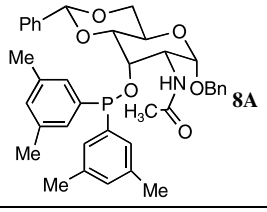
2.1.3. Effect of *N*-acyl substituent: isomerization of the primary product. Having identified **8A** (entry1, Table 2) as the best ligand for hydrovinylation of styrene, 4-bromostyrene and 4-isobutylstyrene, we decided to examine the effect of nitrogen substituents on the course of the reaction. We find that a seemingly minor change in the *N*-substituent has a profound effect on the overall utility of the reaction. The results obtained upon substituting the $-COCH_3$ group with $-COCF_3$ and –COPh groups are shown in Table 2. Even though the *N*-C(O)CF_3 ligand **12** gave 3-phenyl-1-butene (**2a**) with one of the highest enantioselectivities we have observed (87%, entry 1), isomerization of this product to 2-phenyl-2-butene (**3a**) significantly erodes the overall selectivity for the reaction. Ligand **13** with an *N*-C(O)Ph group also behaves in a similar fashion. Quenching the reaction at various times (30 or 120 min) seems to indicate that both enantiomers of 3-phenylbutenes undergo the isomerization with nearly equal facility (entry 2).

2.1.4. Effect of counteranion. We have previously shown that counteranions play a very significant role in the efficiency and selectivity of the hydrovinylation reaction and there is a synergistic relation between the nature of the ligand and the counteranion.[23,24] The effect of the counteranion was examined in the context of hydrovinylation of 4-bromostyrene using the best ligand, **8A**.

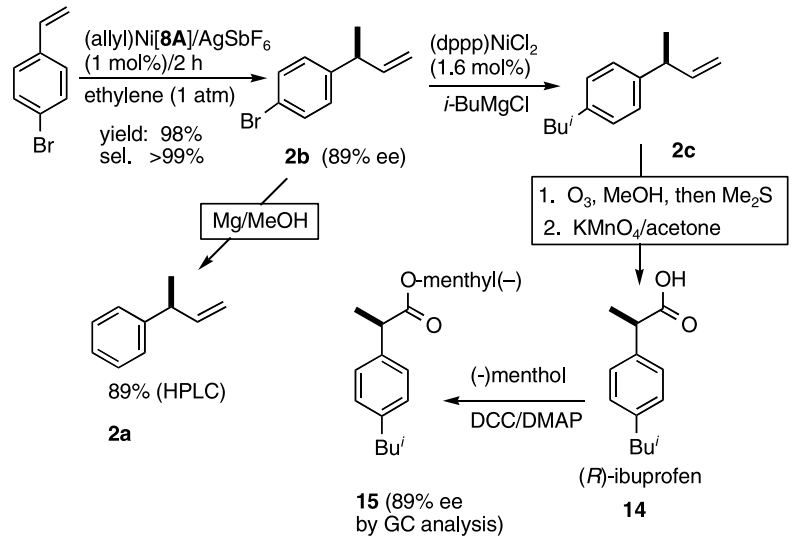
The results are shown in Table 3. These results confirm the marginally superior effect of SbF_6 as a counteranion in the hydrovinylation of 4-bromostyrene. Thus the use of Ar_4B resulted in up to 6% formation of the isomerized product **3b**, while SbF_6 gave an exquisite reaction with >99% selectivity for the desired 3-(4-bromophenyl)butene in 89% ee (entry 2). Both BF_4 and OTf gave lower conversions and selectivities under identical conditions (entries 3 and 4).

2.1.5. Asymmetric hydrovinylation of 4-bromostyrene and identification of the major product. The enantiomeric excess of 3-(4-bromophenyl)-but-1-ene (**2b**), a key compound {($[\alpha]_D^{25}$ +9.9±1 (*c* 7.02, $CHCl_3$)}, from which several 2-arylpropionic acids could be prepared by cross-coupling chemistry (vide infra), was determined by three independent methods, all agreeing within experimental error. The ee's for compound **2b** and the corresponding debrominated derivative, 3-phenyl-1-butene (**2a** prepared by treatment of **2b** with Mg in MeOH, >99% yield) were determined by HPLC on chiralcel OJ column. Kumada coupling of **2b** and *i*-BuMgBr in the presence of 1.6 mol% of (dppe)$NiCl_2$ gave **2c**[25] (89%ee, HPLC). Subsequent ozonolysis and oxidation of the resulting aldehyde[26] gave ibuprofen (Scheme 1), whose configuration and enantiomeric excess were established by conversion to the known (−)-menthyl esters.[27] Gas chromatographic analysis of

Table 3. Asymmetric hydrovinylation of vinylarenes. Effect of counteranions[a]

Entry	Ligand	Counteranion X	4-Bromostyrene		
			Conversion (%)	Selectivity (% **3a**)	% ee
1	 **8A**	BARF	>99	94	89 (*S*)
2		SbF_6	98	>99	89 (*S*)
3		BF_4	24	>99	86 (*S*)
4		OTf	70	>99	74 (*S*)

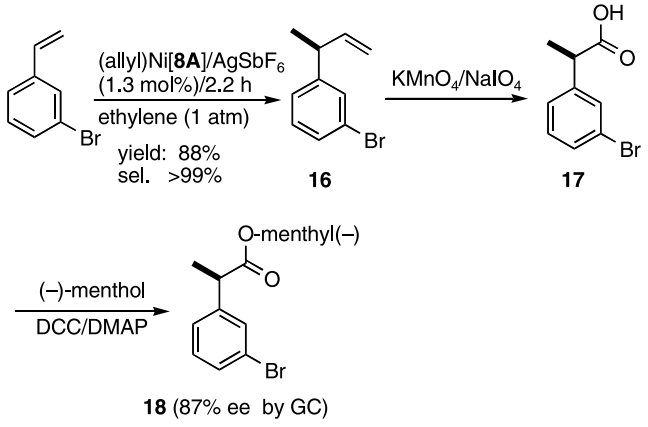
[a] Conditions: see Scheme 1, step 1. 1 mol% [(η^3-allyl)Ni**L**X]$_2$/CH_2Cl_2, −55 °C/2 h.



Scheme 1. Asymmetric hydrovinylation of 4-bromostyrene.

(−)-menthyl esters of ibuprofen using chiralsil-*L*-val column revealed baseline separation, with a diastereomeric excess of 89% for the (*R*)-ibuprofen ester. This confirms the overall selectivity and the absolute configuration of the primary product of hydrovinylation.

Hydrovinylation of 3-bromostyrene under these conditions gave 88% yield of 3-(3-bromophenyl)-but-1-ene (**16**) with >99% selectivity for the 3-arylbut-1-ene. The enantioselectivity of the product (87% ee, *S*) was ascertained by first converting this into (−)-menthyl esters of the 2-(3-bromophenyl)-propionic acid. The diastereomeric (−)-menthyl esters were analyzed by gas chromatography (Scheme 2).[28] For comparison, authentic samples of racemic **17** and the corresponding (−)-methyl esters were prepared from racemic **16**.

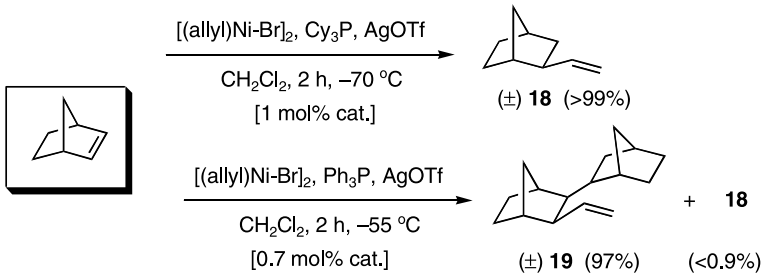


Scheme 2. Asymmetric hydrovinylation of 3-bromostyrene.

2.1.6. Hydrovinylation of norbornene. In 2003 we reported that hydrovinylation of norborne is an excellent reaction giving either a 1:1 (norbornene/ethylene) adduct or a 2:1 adduct depending on the size of the phosphine that is employed (Scheme 3).[22,29,30] As shown in Scheme 3, a bulky phosphine, Cy_3P (cone angle 180°), gives a 1:1 adduct whereas a smaller phosphine, Ph_3P (cone angle 145°), gave 2:1 adduct. We also reported that 2-benzyloxy-2′-diphenylphosphino-1,1′-binaphthyl gave ∼50% ee for the hydrovinylation product (−)**18**[31,32](Table 4, entry 1).

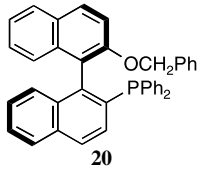
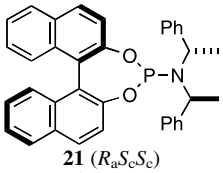
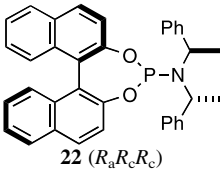
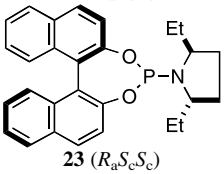
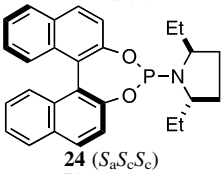
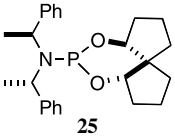
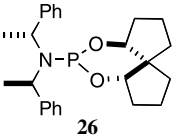
In view of the excellent results obtained by Leitner[19] on the use of binaphthol-derived phosphoramidites for the asymmetric hydrovinylation of styrene derivatives, we decided to examine these and related ligands for the hydrovinylation of norbornene under our reaction conditions (Scheme 4). The results are shown in Table 4.

The selectivities of these reactions under catalysis by phosphoramidite–Ni complexes (entries 2–7, Table 4) show remarkable dependence on the counteranion and the nature of the P–N appendages. Whereas the phosphoramidite **21**

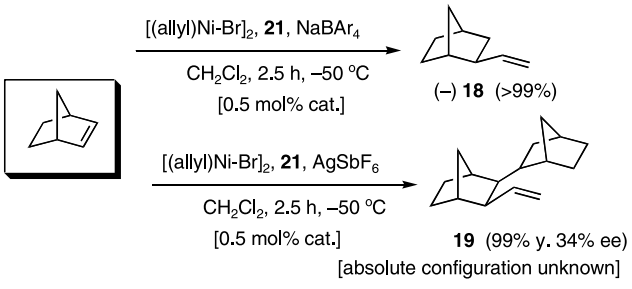


Scheme 3. Ligand dependence of hydrovinylation of norbornene.

Table 4. Asymmetric hydrovinylation of norbornene[a]

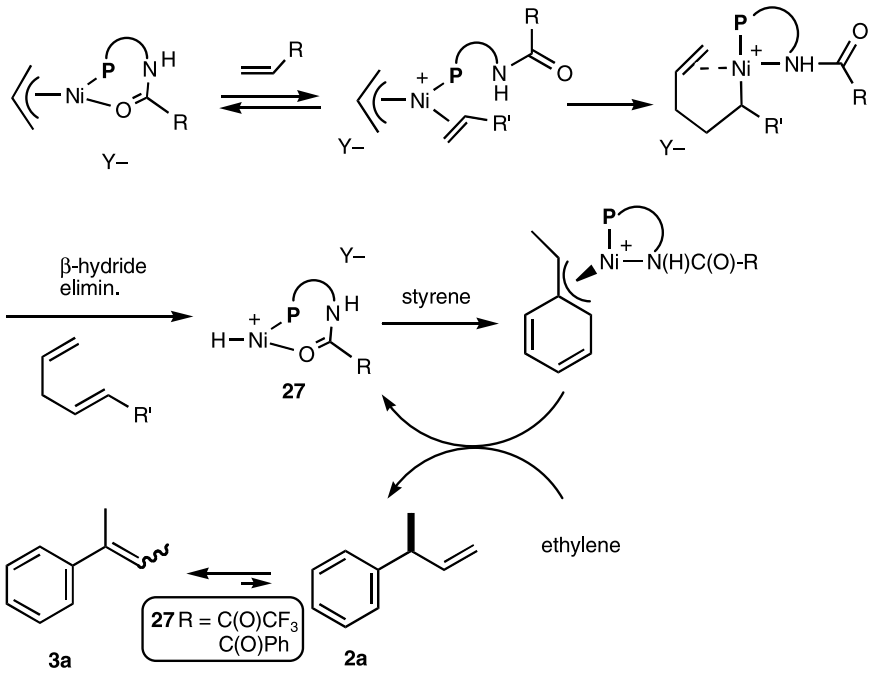
Entry	Ligand, **L**	Additive	*T* °C/t (h)	**18** (%)[b]	**19** (%)[b]	% ee[c]	Comments
1(a)	 **20**	NaBARF	−50/2.5	69[d]	0	44	
1(b)		$AgSbF_6$	−50/2.0	>99	0	50	Ref. 22
1(c)		$AgNTf_2$	−50/2.0	>99	0	50	
2(a)	 **21** ($R_aS_cS_c$)	NaBARF	−50/2.5	>99	0	80	—
2(b)		AgOTf	−50/2.5	20[d]	0	—	—
2(c)		$AgSbF_6$	−50/2.5	0	>99	34	—
3.	 **22** ($R_aR_cR_c$)	NaBARF	−50/2.5	<2%	0	—	—
4(a)	 **23** ($R_aS_cS_c$)	$AgSbF_6$ or	−50/3	0	0	—	Polymer (100%)
4(b)		NaBARF	−50/3	0	0	—	Polymer (100%)
5	 **24** ($S_aS_cS_c$)	$AgSbF_6$	−50/3	0	0	—	Polymer (100%)
6(a)	 **25**	$AgSbF_6$ or	−50/2.5	30	35	—	
6(b)		NaBARF	−50/2.5	1	—	—	—
7(a)	 **26**	$AgSbF_6$ or	−50/2.5	3	28	—	—
7(b)		NaBARF	−50/2.5	2	—	—	

[a] See Scheme 4 for typical procedure. Results of at least two experiments in each case.
[b] GC and NMR, isolated yield vary because of volatility of **18**.
[c] By NMR (see text).
[d] Rest starting material.



Scheme 4. Counteranion dependence of hydrovinylation of norbornene.

($R_aS_cS_c$) is a good ligand (entry 2a and 2c), the corresponding ($R_aR_cR_c$)-diastereomer **22** gives less than 2% of the product (entry 3). For the ligand **21**, the counteranion determines whether 1:1 or 1:2 adduct is produced (Scheme 3). With NaBARF as the additive, only 1:1 adduct **18** is produced (entry 2a), whereas with $AgSbF_6$, which we have successfully used in place of NaBARF in some of the early hydrovinylation experiments (Table 3, entries 1 and 2), the only product is the 2:1 adduct **19**, formed in nearly quantitative yield (entry 2c). Perhaps the most striking result is the effect of the amine component of the phosphoramidites (entries 4 and 5). Thus phosphoramidites derived from (2*S*,4*S*)-diethylpyrrolidine and either (*R*)-binaphthol or (*S*)-binaphthol (**23** and **24**) give none of the simple adducts **18** or **19**. Nearly quantitative yield of polymeric



Scheme 5. Abbreviated mechanism of asymmetric hydrovinylation and olefin isomerization.

materials were formed under the standard conditions (entries 6 and 7).[33]

Phosphoramidites **25** and **26** are poor ligands and showed no selectivity in the formation of either the 1:1 or the 2:1 adduct (entry 4). Clearly, $AgSbF_6$ appears to give better yields.

3. Discussion

While it is premature to propose models[23,34] for the asymmetric induction in any of the studies reported in this paper, some observations are worthy of note. The diarylphosphinite ligands derived from β-acylaminoalcohols are useful ligands for hydrovinylation of vinylarenes. The two asymmetric centers in the backbone, likely variations of the acyl group and the *P*-aryl-substituents provide myriad possibilities for further tuning of these ligands. We have not conclusively shown that the *N*-acyl group is the hemilabile group involved in the reaction. Yet, the complete lack of reactivity of a ligand with a β-amino group vis-à-vis a β-amido (e.g., **7** vs **5**, Fig. 2) group and the effect of the *N*-acyl groups (Table 2) are highly suggestive of a crucial role for this functionality.[35] It is conceivable that the $[\mathbf{L}Ni–H]^+$ species, **27** (Scheme 4), which is the presumed catalyst is more reactive with olefins when an *N*-C(O)CF_3 or *N*-C(O)Ph group is present at the β-position of the ligand, leading to indiscriminate addition–elimination reactions which results in isomerization of the primary product **2a** (Scheme 5).

Another notable observation is the counteranion effect seen in the hydrovinylation of norbornene using ligand **21** (Table 4, entry 2). At present we have no explanation for the fact that BARF anion gives a 1:1 adduct, **18**, and SbF_6 a 2:1 adduct, **19** (Scheme 3). However, one can speculate that the synergistic relationship between a possible hemilabile coordination of one of the Ph groups to Ni and each of the anions could be quite different. In the absence of such a phenyl group (for example, in ligands, **23** and **24**) a more active catalyst, not unlike the naked nickel catalyst popularized by Goodall et al. for polymerization of norbornene, is generated, and polymerization ensues (Table 4, entries 4, 5).[33b] Traditionally, these cationic Ni-complexes have only olefinic ligands and/or Ni–C σ-bonds, and the reaction is done in the presence of highly dissociated counter anions. Cationic Ni-complexes containing bulky phosphine ligands have recently been reported to be effective for non-living polymerization of styrene.[36] Without additional work, including a full characterization of the phosphoramide-derived catalyst precursor(s) and the norbornene polymers they produce, a discussion of the unusual ligand-dependent selectivity of the Ni(II)-complexes will be highly speculative. Further studies along these lines will be forthcoming.

4. Conclusions

Diarylphosphinites, carrying a β-acylamino groups prepared from readily available carbohydrates, in conjunction with highly dissociated counterions $\{[(3,5\text{-}(CF_3)_2C_6H_3]_4B^-$ or $SbF_6^-\}$, effect the hydrovinylation of vinylarenes under ambient pressure of ethylene with the high enantioselectivity. Nitrogen substituents such as $–COCF_3$ and COPh groups lead to isomerization of the primary products (3-arylbutenes) to *Z*- and *E*-2-aryl-2-butenes. The intermediate 3-arylbutenes are useful for the synthesis of anti-inflammatory 2-arylpropionic acids. Asymmetric codimerization of norbonene and ethylene using binaphthol-derived phosphoramidites as ligands gives 1:1, 2:1 or polymeric adducts depending on the relative configurations and nature of the BINAP and amine moieties. With one of

the phosphoramidite–Ni complexes, counteranions BAr_4^- [Ar=3,5-$(CF_3)_2C_6H_3$] and SbF_6^-, which had been used interchangeably in other reactions, give either a 1:1 adduct or a 2:1 adduct, respectively.

5. Experimental

5.1. General procedures

Reactions requiring air-sensitive manipulations were conducted under an inert atmosphere of nitrogen in a Vacuum Atmospheres drybox or by using Schlenk techniques. Methylene chloride and toluene were distilled from calcium hydride under nitrogen and stored over molecular sieves. Tetrahydrofuran, diethyl ether, and hexane were distilled under nitrogen from sodium/benzophenone ketyl. Ethylene (99.5%) was purchased from Matheson Inc., and passed through Drierite before use. Styrene was purchased from Aldrich, vacuum-transferred, and stored at −30 °C. For ozonolysis, ozone gas was delivered using a Welsbach ozone generator. Analytical TLC was performed on E. Merck precoated (0.25 mm) silica gel 60 F_{254} plates. Flash column chromatography was carried out on silica gel 40 (Scientific Adsorbents Incorporated, Microns Flash). Gas chromatographic analyses were performed on a Hewlett-Packard 5890 equipped with an HP-ultra-1 crosslinked methyl silicone capillary column (25 m length×0.2 mm i.d.) and a FID detector connected to a HP 3396 integrator. Helium was used as the carrier gas. Chiral gas chromatographic separations of the (−)-menthol esters 2-arylpropionic acids were accomplished using Chirasil-L-Val on WCOT fused silica (25 m×0.25 mm, 0.12 μm film thickness) capillary GC column purchased from Chrompack (1130 Route 202 South Raritan, New Jersey 08869). The absolute configuration of 3-phenyl-1-butene was determined by GC analysis using a 50 m Lipodex C capillary column (conditions: 1.5 mL helium/min, 35 °C (50 min), 0.1 °C/min (60 min), 41 °C (30 min); retention times: *R*-isomer 95.8 min, *S*-isomer 97.2 min). Determination of the configuration of other compounds is described under the appropriate experiments. Enantiomeric excesses of 3-aryl-1-butenes were determined by HPLC using a Daicel Chiralcel OJ column using hexane as the solvent where base-line separation was obtained. Optical rotations were recorded on a Perkin–Elmer Model 241 polarimeter at the sodium D line in chloroform treated with 4 Å molecular sieves. Compounds for which an exact mass is reported exhibited no significant peaks at *m/z* greater than that of the parent. Elemental analyses were done by Atlantic Microlab, Inc., Norcross, GA.

Starting materials diphenylchlorophosphine, 2-acetamido-2-deoxy-α-D-glucopyranose, 1,2:5,6-*O*-diisopropylidene-D-glucofuranose, (*S*,*S*)-(−)-hydrobenzoin and (*R*,*R*)-(+)-hydrobenzoin, 4-bromostyrene, 3-bromostyrene, 2-vinylnaphthalene, norbornene and (−)-menthol and various silver salts were purchased from commercial sources. The following compounds were prepared by the procedures from the references cited: chloro-bis-[3,5-*di*-(trifluoromethyl)-phenyl]phosphine,[4a] chloro-bis-(3,5-dimethylphenyl)phosphine,[4a] chloro-dioxophospholanes[11a] from binaphthol and hydroxybenzoin, (*R*)- and (*S*)-binaphthols,[37] sugar precursors benzyl 2-acetamido-2-deoxy-4,6-*O*-phenylmethyl-α-D-glucopyranoside,[38] 2-amino-2-deoxy-4,6-*O*-phenylmethyl-α-D-glucopyranoside,[38] benzyl 2-acetamido-2-deoxy-4,6-*O*-phenylmethyl-α-D-allopyranoside,[39] diarylphosphinite ligand **6**,[6a] phosphoramidites ligands[40] **21** and **22**, 4-*i*-butylstyrene,[41] $NaBAr_4$ (Ar=3,5-$(CF)_3$–C_6H_3).[42]

5.2. Synthesis of phosphinite and phosphite ligands

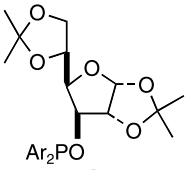
The preparations of all air-sensitive trivalent phosphorus compounds were carried out under an inert atmosphere of nitrogen in a Vacuum Atmospheres drybox. Since air-sensitive phosphorus compounds result in poor C, H-analysis, the purities of the ligands were confirmed by ^1H and ^{31}P NMR, and in most instances the ligands are >95% pure. The phosphinite ligands were synthesized according to one of the following procedures unless stated otherwise.[6a]

Procedure A. To a solution of 1.0 equiv of a chlorodiarylphosphine and 1.0 equiv of 4-dimethylaminopyridine (DMAP) in toluene (5 mL) was added dropwise 1.0 equiv of the alcohol in toluene (2 mL). The mixture was stirred for 6–10 h at rt and filtered through a short pad of Celite to remove the precipitated DMAP·HCl. The filtrate was concentrated to dryness in vacuo, and the crude product was recrystallized from cyclohexane and/or hexane inside the drybox to afford the corresponding phosphinite as a white crystalline solid.

Procedure B. To a solution of 1 equiv of an alcohol and 1 equiv of triethylamine (TEA) or DMAP in dichloromethane (5 mL) was added dropwise 1 equiv of a chlorodiarylphosphine in dichloromethane (2 mL). The resulting mixture was stirred overnight at rt and was concentrated in vacuo. The residue was suspended in a small amount of toluene, filtered through a short pad of Celite to remove TEA hydrochloride or DMAP hydrochloride, and then was concentrated to dryness in vacuo. The crude product was purified by recrystallization inside the drybox from cyclohexane and/or hexane to afford the corresponding phosphinite as a white crystalline solid.

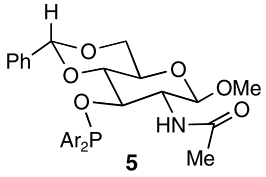
Procedure C. To a solution of 1 equiv of an alcohol and 1 equiv of DMAP in dichloromethane (5 mL) was added, dropwise, 1 equiv of chlorodiarylphosphonite in dichloromethane (2 mL). The resulting mixture was stirred overnight at rt and concentrated in vacuo. The residue was suspended in a small amount of toluene, filtered through a short pad of Celite to remove DMAP hydrochloride, and then concentrated to dryness in vacuo. The crude product was chromatographed (inside drybox) to afford the corresponding phosphite as a white crystalline solid.

5.2.1. 3-*O*-[bis-(α,α,α,α′,α′,α′-Hexafluoro-3,5-xylyl)phosphino]-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose [4, Ar=3,5-$(CF_3)_2C_6H_3$)]. *Procedure B*. 73% Yield; ^1H NMR (300 MHz, $CDCl_3$) δ 8.00–7.90 (m, 6H, aromatic), 5.92 (d, *J*=3.6 Hz, 1H), 4.63 (dd, *J*=3.6, 1.8 Hz, 1H), 4.54 (dd, *J*=9.1, 2.7 Hz, 1H), 4.25–4.20 (m, 1H), 4.14–4.02 (m, 3H), 1.51 (s, 3H, Me), 1.40 (s, 3H, Me), 1.30 (s, 3H, Me) 1.17 (s, 3H, Me); ^{31}P NMR (101 MHz, $CDCl_3$) δ 105.8 (s, 1P).



4

5.2.2. Methyl 2-acetamido-4,6-*O*-benzylidene-2-deoxy-3-*O*-(di-3,5-xylylphosphino)-β-D-glucopyranoside [5, Ar = 3,5-$(CH_3)_2C_6H_3$)]. *Procedure B*. 92% Yield; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.51–6.82 (m, 11H, aromatic), 5.46 (s, 1H, benzylic), 5.24 (br d, J = 8.0 Hz, 1H, NH), 4.91 (d, J = 8.3 Hz, 1H, H-1), 4.66 (td, J = 9.4, 9.1 Hz, 1H, H-3), 4.36 (dd, J = 10.4, 4.9 Hz, 1H, H-6eq), 3.77 (t, J = 10.2 Hz, 1H, H-6ax), 3.75 (t, J = 9.2 Hz, 1H, H-4), 3.59–3.44 (m, 2H, H-2, H-5), 3.49 (s, 3H, OMe), 2.29 (s, 6H, 2Me), 2.06 (s, 6H, 2Me), 1.59 (s, 3H, CH_3CO); ^{31}P NMR (101 MHz, $CDCl_3$) δ 120.9 (s, 1P).



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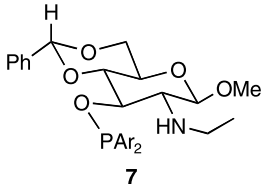
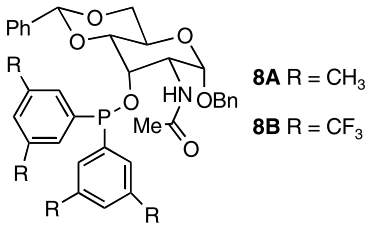
5.2.3. Methyl 4,6-*O*-benzylidene-3-*O*-[bis(α,α,α,α′,α′,α′-hexafluoro-3,5-xylyl)phosphino]-2-deoxy-2-(ethylamino)-β-D-glucopyranoside (7, Ar = 3,5-$(CF_3)_2C_6H_3$). *Procedure B*. 90% Yield; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.97–7.05 (m, 11H, aromatic), 5.30 (s, 1H, benzylic), 5.10 (d, 8 Hz), 4.38–4.31 (m, 2H), 4.13 (m, 1H), 3.81–3.71 (m, 2H), 3.56 (s, 3H, OMe), 3.43 (m, 1H), 2.87–2.78 (m, 2H), 2.45 (m, 1H), 0.82 (t, 3H, CH_3); ^{31}P NMR (101 MHz, $CDCl_3$) δ 106.2 (s, 1P).



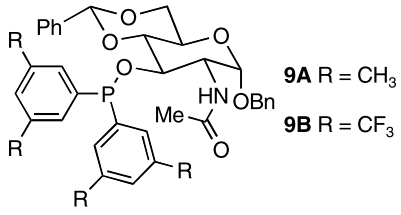
7

5.2.4. Benzyl 2-acetamido-4,6-*O*-benzylidene-2-deoxy-3-*O*-(di-3,5-xylylphosphino)-α-D-allopyranoside (8A). *Procedure B*. 90% Yield; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.51–6.97 (m, 16H, aromatic), 5.59 (d, J = 8.5 Hz, 1H, NH), 5.56 (s, 1H, benzylic), 4.85 and 4.53 (AB, J = 12.0 Hz, 2H, OCH_2Ph), 4.84 (d, J = 3.9 Hz, 1H, H-1), 4.60–4.42 (m, 2H, H-2, H-3), 4.39–4.23 (m, 2H, H-5, H-6eq), 3.77–3.69 (m, 2H, H-4, H-6ax), 2.18 (s, 6H, 2Me), 2.16 (s, 6H, 2Me), 1.34 (s, 3H, CH_3CO); ^{31}P NMR (101 MHz, $CDCl_3$) δ 123.6 (s, 1P).



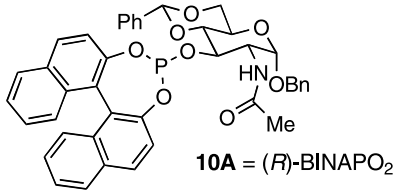
5.2.5. Benzyl 2-acetamido-4,6-*O*-benzylidene-3-*O*-[bis(α,α,α,α′,α′,α′-hexafluoro-3,5-xylyl)phosphino]-2-deoxy-α-D-allopyranoside (8B). *Procedure B*. 75% Yield; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.45–6.94 (m, 16H, aromatic), 5.62 (d, J = 8.5 Hz, 1H, NH), 5.46 (s, 1H, benzylic), 4.89 (d, J = 4.8 Hz, 1H, H-1), 4.88 and 4.70 (AB, J = 12.0 Hz, 2H, OCH_2Ph), 4.75 (m, 1H, H-3), 4.39–4.17 (m, 3H, H-2, H-5, H-6eq), 3.75 (dd, J = 9.5, 2.6 Hz, 1H, H-4), 3.67 (t, J = 10.2 Hz, 1H, H-6ax), 1.56 (s, 3H, CH_3CO); ^{31}P NMR (101 MHz, $CDCl_3$) δ 106.9 (s, 1P).

5.2.6. Benzyl 2-acetamido-4,6-*O*-benzylidene-2-deoxy-3-*O*-(di-3,5-xylylphosphino)-α-D-glucopyranoside (9A). *Procedure B*. 92% Yield; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37–6.82 (m, 16H, aromatic), 5.53 (br d, J = 9.2 Hz, 1H, NH), 5.44 (s, 1H, benzylic), 4.95 (d, J = 3.6 Hz, 1H, H-1), 4.71 and 4.45 (AB, J = 11.8 Hz, 2H, OCH_2Ph), 4.48 (td, J = 10.1, 3.6 Hz, 1H, H-2), 4.35 (td, J = 9.5, 9.2 Hz, 1H, H-3), 4.23 (dd, J = 10.1, 4.6 Hz, 1H, H-6eq), 3.93 (td, J = 9.8, 4.6 Hz, 1H, H-5), 3.78 (t, J = 9.1 Hz, 1H, H-4), 3.76 (t, J = 10.1 Hz, 1H, H-6ax), 2.30 (s, 6H, 2Me), 2.07 (s, 6H, 2Me), 1.50 (s, 3H, CH_3CO); ^{31}P NMR (101 MHz, $CDCl_3$) δ 120.8 (s, 1P)



5.2.7. Benzyl 2-acetamido-4,6-*O*-benzylidene-3-*O*-[bis(α,α,α,α′,α′,α′-hexafluoro-3,5-xylyl)phosphino)-2-deoxy-α-D-glucopyranoside (9B). *Procedure B*. 89% Yield; ^{1}H NMR (300 MHz, C_6D_6) δ 8.40–6.84 (m, 16H, aromatic), 5.10 (s, 1H, benzylic), 5.00 (br d, J = 10.0 Hz, 1H, NH), 4.71 (td, J = 10.2, 3.8 Hz, 1H, H-2), 4.61 (d, J = 3.8 Hz, 1H, H-1), 4.31 and 3.98 (AB, J = 11.6 Hz, 2H, OCH_2Ph), 4.26 (m, 1H, H-3), 4.00 (m, 1H, H-6eq), 3.86 (td, J = 9.8, 4.9 Hz, 1H, H-5), 3.40 (t, J = 10.2 Hz, 1H, H-4), 3.34 (t, J = 9.3 Hz, 1H, H-6ax), 1.13 (s, 3H, CH_3CO); ^{31}P NMR (101 MHz, C_6D_6) δ 105.8 (s, 1P).

5.2.8. Benzyl 2-acetamido-4,6-*O*-benzylidene-2-deoxy-α-D-glucopyrano-side cyclic (*R*)-[1,1′-binaphthalene]-2,2′-diyl Phosphite (10A). *Procedure C*. 70% Yield; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.99–7.20 (m, 22H, aromatic), 5.80 (d, J = 9.4 Hz, 1H, NH), 5.56 (s, 1H, benzylic), 4.98 (d, J = 3.5 Hz, 1H, H-1), 4.72 and 4.48 (AB, J = 11.7 Hz, 2H, OCH_2Ph), 4.61–4.44 (m, 2H, H-2, H-3), 4.27 (dd, J = 10.1, 4.7 Hz, 1H, H-6eq), 3.91 (td, J = 9.9, 4.7 Hz, 1H, H-5), 3.74 (t, J = 10.2, 1H, H-6ax), 3.71 (t, J = 9.2 Hz, 1H, H-4), 2.09 (s, 3H, CH_3CO); ^{31}P NMR (101 MHz, $CDCl_3$) δ 148.2 (s, 1P).

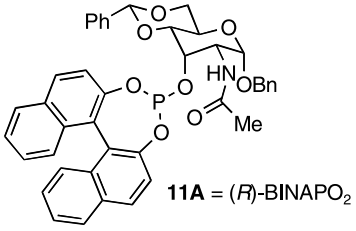


10A = (*R*)-BINAPO$_2$

10B = (*S*)-BINAPO$_2$

5.2.9. Benzyl 2-acetamido-4,6-*O*-benzylidene-2-deoxy-α-D-glucopyranoside cyclic (*S*)-[1,1′-binaphthalene]-2,2′-diyl phosphite (10B). *Procedure C*. Quantitative yield; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.94–7.14 (m, 22H, aromatic), 5.67 (s, 1H, benzylic), 5.55 (d, J=9.1 Hz, 1H, NH), 4.97 (d, J=3.7 Hz, 1H, H-1), 4.73 and 4.48 (AB, J=11.7 Hz, 2H, OCH_2Ph), 4.52 (q, J=9.7 Hz, 1H, H-3), 4.38–4.25 (m, 2H, H-2, H-6eq), 3.99 (td, J=9.9, 4.7 Hz, 1H, H-5), 3.85 (t, J=10.2 Hz, 1H, H-6ax), 3.77 (t, J=9.3 Hz, 1H, H-4), 1.78 (s, 3H, CH_3CO); ^{31}P NMR (101 MHz, $CDCl_3$) δ 150.9 (s, 1P).

5.2.10. Benzyl 2-acetamido-4,6-*O*-benzylidene-2-deoxy-α-D-allopyranoside cyclic (*R*)-[1,1′-binaphthalene]-2,2′-diyl phosphite (11A). *Procedure C*. 80% Yield; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.98–6.86 (m, 22H, aromatic), 5.78 (d, J=9.5 Hz, 1H, NH), 5.71 (s, 1H, benzylic), 4.86 (dt, J=9.5, 3.0 Hz, 1H, H-2), 4.78 (d, J=4.5 Hz, 1H, H-1), 4.58 and 4.30 (AB, J=12.2 Hz, 2H, OCH_2Ph), 4.45–4.27 (m, 3H, H-3, H-5, H-6eq), 3.84–3.75 (m, 2H, H-4, H-6ax), 1.67 (s, 3H, CH_3CO); ^{31}P NMR (101 MHz, $CDCl_3$) δ 156.0 (s, 1P).

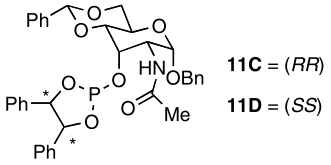


11A = (*R*)-BINAPO$_2$

11B = (*S*)-BINAPO$_2$

5.2.11. Benzyl 2-acetamido-4,6-*O*-benzylidene-2-deoxy-α-D-allopyranoside cyclic (*S*)-[1,1′-binaphthalene]-2,2′-diyl phosphite (11B). *Procedure C*. 88% Yield; ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.82–6.88 (m, 22H, aromatic), 6.09 (d, J=9.4 Hz, 1H, NH), 5.54 (s, 1H, benzylic), 4.79 (dt, J=8.7, 2.9 Hz, 1H, H-2), 4.72 (d, J=4.4 Hz, 1H, H-1), 4.43 and 4.24 (AB, J=12.5 Hz, 2H, OCH_2Ph), 4.34 (m, 1H, H-3), 4.08–3.98 (m, 2H, H-5, H-6eq), 3.64–3.57 (m, 2H, H-4, H-6ax), 1.97 (s, 3H, CH_3CO); ^{13}C NMR (71.6 MHz, $CDCl_3$) δ 169.3, 148.1, 147.4, 137.4, 137.3, 132.8, 131.5, 130.9, 130.3, 129.3, 129.2, 128.4, 128.3, 128.3, 128.2, 127.5, 127.2, 127.1, 127.0, 126.6, 126.3, 126.2, 126.0, 125.0, 124.9, 121.9, 121.9, 121.5, 101.6, 96.4, 77.2, 71.6, 71.4, 69.8, 68.9, 57.7, 48.9, 48.9; ^{31}P NMR (101 MHz, $CDCl_3$) δ 150.6 (s, 1P).

5.2.12. Benzyl 2-acetamido-4,6-*O*-benzylidene-2-deoxy-α-D-allopyranoside cyclic (*R*,*R*)-1,2-diphenylethylene phosphite (11C). *Procedure C*. 84% Yield; ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.36–7.03 (m, 20H, aromatic), 5.99 (d, J=9.45 Hz, 1H, NH), 5.47 (s, 1H, benzylic), 5.19 (d, J=9.6 Hz, 1H), 4.82 (d, J=4.5 Hz, 1H), 4.76 and 4.54 (AB, J=12.2 Hz, 2H, OCH_2Ph), 4.68–4.63 (m, 2H), 4.35 (m, 1H), 4.19–4.09 (m, 2H), 3.66–3.36 (m, 2H), 1.71 (s, 3H, CH_3CO); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.1, 137.6, 137.5, 137.3, 136.7, 136.7, 129.5, 129.1, 129.0, 128.8, 128.8, 128.6, 128.3, 127.0, 102.5, 96.8, 87.4, 82.8, 77.6, 70.8, 70.0, 69.8, 69.5, 58.5, 49.5; ^{31}P NMR (101 MHz, $CDCl_3$) δ 144.0 (s, 1P).

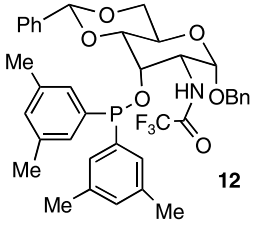


11C = (*RR*)

11D = (*SS*)

5.2.13. Benzyl 2-acetamido-4,6-*O*-benzylidene-2-deoxy-α-D-allopyranoside cyclic (*S*,*S*)-1,2-diphenylethylene phosphite (11D). *Procedure C*. 83% Yield; ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.45–6.83 (m, 20H, aromatic), 6.06 (d, J=9.5 Hz, 1H, NH), 5.54 (s, 1H, benzylic), 4.93 (d, J=9.2 Hz, 1H), 4.80–4.68 (m, 3H), 4.52 and 4.27 (AB, J=11.7 Hz, 2H, OCH_2Ph), 4.37–4.15 (m, 3H), 3.72–3.64 (m, 2H), 1.82 (s, 3H, CH_3CO); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.2, 138.1, 137.6, 137.5, 137.0, 136.9, 129.6, 129.0, 128.9, 128.9, 128.7, 128.6, 128.5, 128.3, 127.4, 127.3, 126.9, 102.7, 97.7, 87.3, 83.7, 71.5, 71.1, 70.9, 69.7, 66.3, 58.8, 49.7; ^{31}P NMR (101 MHz, $CDCl_3$) δ 144.9 (s, 1P).

5.2.14. Benzyl 4,6-*O*-benzylidene-2-deoxy-3-*O*-(di-3,5-xylylphosphino)-2-(2,2,2-trifluoroacetamido)-α-D-allopyranoside (12). *Procedure B*. 81% Yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29–6.90 (m, 16H, aromatic), 6.46 (d, J=9.4 Hz, 1H, NH), 5.47 (s, 1H, benzylic), 4.82 (d, J=4.3 Hz, 1H, H-1), 4.80 and 4.51 (AB, J=12.0 Hz, 2H, OCH_2Ph), 4.53 (m, 1H, H-3), 4.41 (td, J=10.2, 5.1 Hz, 1H, H-5), 4.26 (dt, J=9.5, 3.9 Hz, 1H, H-2), 4.19 (dd, J=10.3, 5.2 Hz, 1H, H-6eq), 3.68–3.64 (m, 2H, H-4, H-6ax), 2.12 (s, 6H, 2Me), 2.08 (s, 6H, 2Me); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.1, 144.6, 141.0, 140.1, 139.8, 139.6, 134.4, 133.3, 131.5, 131.3, 130.9, 130.8, 130.7, 130.6, 130.4, 130.1, 129.9, 129.0, 104.7, 98.2, 80.8, 72.9, 71.8, 68.5, 61.0, 52.3, 23.9, 23.8; ^{31}P NMR (162 MHz, $CDCl_3$) δ 126.1 (s, 1P).



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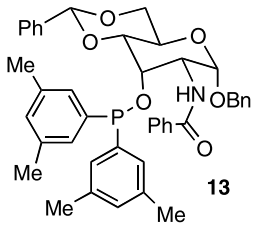
5.2.15. Benzyl 2-benzamido-4,6-*O*-benzylidene-2-deoxy-3-*O*-(di-3,5-xylylphosphino)-α-D-allopyranoside (13). *Procedure B*. 77% Yield; ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.34–6.82 (m, 21H, aromatic), 6.35 (d, J=9.2 Hz, 1H, NH), 5.45 (s, 1H, benzylic), 4.89 (d, J=4.2 Hz, 1H, H-1), 4.70 and 4.48 (AB, J=12.0 Hz, 2H, OCH_2Ph), 4.61–4.41 (m, 3H, H-2, H-3, H-5), 4.17 (dd, J=10.2, 5.2 Hz, 1H, H-6eq), 3.72–3.61 (m, 2H, H-4, H-6ax), 2.07 (s, 6H, 2Me), 1.99 (s, 6H, 2Me); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.8, 144.0, 142.9, 138.8, 138.1, 138.9, 137.6, 133.7, 131.9, 131.8, 130.9, 129.1, 128.9, 128.7, 128.6, 128.4, 128.3, 128.2, 128.1, 127.8, 127.5, 127.2, 126.8, 102.5, 97.3, 78.8, 70.7, 70.7, 66.3, 58.9, 50.3, 21.7, 21.6; ^{31}P NMR (101 MHz,

$CDCl_3$) δ 123.6 (s, 1P).



5.3. Hydrovinylation reactions

The preparations of all hydrovinylation catalysts were carried out under a nitrogen atmosphere in a Vacuum Atmospheres drybox. The hydrovinylation reactions were conducted under an inert atmosphere of nitrogen using Schlenk techniques.

Procedure A. Use of triphenylphosphine and AgOTf[23]. The following is a typical procedure for the Ni(II)-catalyzed hydrovinylation reactions. To a red solution of 0.0035 equiv of $[Ni(allyl)Br]_2$ in dichloromethane (1.5 mL) was added a solution of 0.0070 equiv of triphenylphosphine in dichloromethane (1.5 mL). Then, the resulting yellow solution was added to a suspension of 0.0080 equiv of silver triflate in dichloromethane (2 mL). After 1.5 h of stirring at rt, the brown suspension was filtered through a short pad of Celite into a Schlenk flask, removed from the drybox, and cooled to −55 °C. Oxygen-free ethylene (≈1 atm) was then introduced into the yellow catalyst solution, and 1.0 mmol of a hydrovinylation substrate was added dropwise through a rubber septum with a syringe. The resulting reaction mixture was stirred for 2 h at −55 °C under an ethylene atmosphere (≈1 atm), quenched with half-saturated aqueous ammonium chloride solution (5 mL), and product was extracted with diethyl ether or dichloromethane (50 mL). The organic phase was dried over magnesium sulfate, analyzed by GC to determine the conversion of the substrate, and concentrated under reduced pressure to afford the corresponding hydrovinylation product.

Procedure B. Typical for asymmetric hydrovinylation reactions. The following is a typical procedure for the Ni(II)-catalyzed asymmetric hydrovinylation reactions of norbornene and 4-bromostyrene using NaBARF as the additive. To a red solution of 0.01 equiv of $[Ni(allyl)Br]_2$ in dichloromethane (1.5 mL) was added a solution of 0.021 equiv of a chiral phosphorus ligand (**L**) in dichloromethane (1.5 mL). Then, the resulting orange solution was added to a suspension of 0.029 equiv of the additive in dichloromethane (2 mL). The mixture was stirred for 1.5 h at rt, filtered through a short pad of celite into a Schlenk flask, and taken out of the drybox. Oxygen-free ethylene (≈1 atm) was then introduced to the orange catalyst solution at the appropriate temperatures shown in Tables 3 and 4. The hydrovinylation substrate (1 mmol) was added dropwise via a syringe. The resulting reaction mixture was stirred for the indicated times at low temperature under an ethylene atmosphere (≈1 atm). The reaction was quenched with half-saturated aqueous ammonium chloride (5 mL), and the product was extracted with diethyl ether or dichloromethane (50 mL). The organic layer was dried over magnesium sulfate, analyzed by GC to determine the conversion of the substrate. ^{1}H NMR spectra was also used to determine the isomeric rations. The organic extract was concentrated under reduced pressure to afford the corresponding hydrovinylation product. Enantiomeric excesses were determined by HPLC using a Daicel Chiralcel OJ column eluting with hexane (0.3–0.6 mL/min) for styrene derivatives.

Procedure C. Use of $AgSbF_6$ and $AgBF_4$ in Ni-catalyzed hydrovinylations of 4-bromostyrene (Table 3). A solution of 0.0050 equiv of $[Ni(allyl)Br]_2$ and 0.010 equiv of ligand **8A** in dichloromethane (3 mL) was stirred for 30 min at rt and then added to a suspension of 0.011 equiv of a silver salt in dichloromethane (2 mL). The resulting brown suspension was stirred for 5 min, filtered through a short pad of celite into a Schlenk flask, and then taken out of the drybox. Oxygen-free ethylene (≈1 atm) was introduced into the yellow-brown catalyst solution at −55 °C, and 1.0 mmol of 4-bromostyrene was added dropwise via a syringe. The resulting reaction mixture was stirred for 2 h at −55 °C under an ethylene atmosphere (≈1 atm), quenched with half-saturated aqueous ammonium chloride (5 mL), and extracted with dichloromethane (50 mL). The concentrated solution was analyzed as described before.

5.3.1. [(*S*)-1-Methylallyl]benzene. *Procedure B* (**L**=**8A**). 0.030 equiv of catalyst used; reaction temperature: −70 °C; quantitative yield (89% of 3-phenylbut-1-ene), ee=81% (*S*); ^{1}H NMR (300 MHz, $CDCl_3$) of 3-phenylbut-1-ene: δ 7.37–7.21 (m, 5H, aromatic), 6.06 (ddd, J_{trans}=17.0 Hz, J_{cis}=10.3 Hz, J=6.5 Hz, 1H), 5.10 (dt, J_{trans}=17.1 Hz, J=1.6 Hz, 1H), 5.07 (dt, J_{cis}=10.3 Hz, J=1.5 Hz, 1H), 3.51 (m, 1H), 1.41 (d, J=7.0 Hz, 3H); NMR spectra of minor impurities useful for determining selectivity: (*E*)-2-phenylbut-2-ene: δ 7.41–7.20 (m, 5H, aromatic), 5.89 (qq, J=6.9, 1.4 Hz, 1H), 2.07 (m, 3H), 1.82 (dq, J=6.8, 1.2 Hz, 3H); (*Z*)-2-phenylbut-2-ene: δ 7.41–7.20 (m, 5H, aromatic), 5.58 (qq, J=6.9, 1.4 Hz, 1H), 2.07 (m, 3H), 1.62 (dq, J=6.8, 1.5 Hz, 3H).

The absolute configuration of 3-phenyl-1-butene was determined by GC analysis using a 50 m Lipodex C capillary column[25] [conditions: 1.5 mL helium/min, 35 °C (50 min), 0.1 °C/min (60 min), 41 °C (30 min); retention times: *R*-isomer 95.8 min, *S*-isomer 97.2 min].

5.4. Reactions using ligands 12 and 13 with β-NHC(O)CF_3 and β-NHC(O)Ph groups (Table 2)

Procedure B (**L**=**12**). 0.020 equiv of catalyst used; >99% yield (40% of (*S*)-3-phenylbut-1-ene, 60% of (*E*)- and (*Z*)-2-phenylbut-2-ene); ee=87% (*S*).

Procedure B (**L**=**13**, 30 min.): 0.030 equiv of catalyst used; >99% yield (66% of (*S*)-3-phenylbut-1-ene, 34% of (*E*)- and (*Z*)-2-phenylbut-2-ene); ee=80% (*S*).

Procedure B (**L**=**13**, 120 min): 0.030 equiv of catalyst used; >99% yield (23% of (*S*)-3-phenylbut-1-ene, 77% of (*E*)- and (*Z*)-2-phenylbut-2-ene); ee=82% (*S*).

5.4.1. 1-Bromo-4-[(*S*)-1-methylallyl]benzene (2b).

Procedure B (**L**=**8A**, SbF_6 counteranion). 0.010 equiv of catalyst used; quantitative yield (~98% yield of 3-(4-bromophenyl)but-1-ene, ee=89% (*S*)); ^{1}H NMR (300 MHz, $CDCl_3$) of 3-(4-bromophenyl)but-1-ene δ 7.48–7.40 (m, 2H, aromatic), 7.12–7.06 (m, 2H, aromatic), 5.97 (ddd, J_{trans}=17.7 Hz, J_{cis}=9.8 Hz, J=6.4 Hz, 1H), 5.05 (dt, J_{trans}=17.6 Hz, J=1.5 Hz, 1H), 5.05 (dt, J_{cis}=9.9 Hz, J=1.5 Hz, 1H), 3.44 (quin, J=6.9 Hz, 1H), 1.35 (d, J=7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.2, 150.3, 139.1, 136.7, 127.5, 121.3, 50.3, 28.3; Purity by GC and NMR >98%; Anal. Found (calcd) C 57.00 (56.90), H 5.30 (5.25), Br 37.72 (37.85); $[\alpha]_D^{18}$ +9.9±0.1 (*c* 7.02, $CHCl_3$).

5.4.2. 1-Isobutyl-4-[(*S*)-1-methylallyl]benzene (2c). *Procedure B* (**L**=**8A**). 0.020 equiv of catalyst used; quantitative yield; ee=74% (*S*); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.14–7.05 (m, 4H, aromatic), 6.01 (ddd, J_{trans}=17.0 Hz, J_{cis}=10.3 Hz, J=6.5 Hz, 1H), 5.05 (dt, J_{trans}=17.2 Hz, J=1.6 Hz, 1H), 5.02 (dt, J_{cis}=10.3 Hz, J=1.5 Hz, 1H), 3.45 (m, 1H), 2.44 (d, J=7.2 Hz, 2H), 1.85 (sept, J=6.8 Hz, 1H), 1.35 (d, J=7.0 Hz, 3H), 0.91 (d, J=6.0 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.0, 143.2, 139.8, 129.5, 127.3, 113.2, 45.5, 43.2, 30.6, 22.8, 21.2); Purity by GC and NMR: >99%; $[\alpha]_D^{18}$ +6.8±0.1(*c* 2.1, $CHCl_3$).

5.4.3. Conversion to 2b to 2a [(*S*)-1-methylallyl]benzene. In a Schlenk flask was charged compound **2b** (45 mg, 0.21 mmol) in methanol (6 mL) and attached a vigreux column with a balloon of nitrogen. Mg turnings (350 mg) were added in small portion, and stirring was continued for 1 d at rt. The reaction mixture was diluted with diethyl ether (30 mL) and water (5 mL). The organic layer was dried over magnesium sulfate, and concentrated under reduced pressure to afford 25 mg (89%) of 3-phenyl-1-butene as a colorless oil. The product was analyzed by GC (>99% yield) and HPLC (ee=89% (*S*).

5.4.4. Conversion of 2b to 2c (*S*)-(1-isobutyl-4-[1-methylallyl]benzene). A solution of isobutyl bromide (400 mg, 2.92 mmol) in diethyl ether (5 mL) was added to Mg turnings (100 mg, 4.11 mmol) in diethyl ether (5 mL). The mixture was stirred overnight at rt and added dropwise to a mixture of compound **2b** (360 mg, 1.7 mmol) and (dppp) $NiCl_2$ (15 mg, 0.028 mmol) in diethyl ether (10 mL). The resulting reaction mixture was heated at reflux overnight, quenched with half-saturated aqueous ammonium chloride, and extracted with diethyl ether (50 mL). The organic phase was dried over magnesium sulfate and concentrated under reduced pressure. The crude product and chromatographed on silica with hexane as solvent to afford 300 mg (95% yield) of (*S*)-**2c** as a colorless oil, ascertained by HPLC of having ee of 89% (*S*).

5.4.5. (*R*)-2-(4-Isobutylphenyl)propionic acid (14).[21] A solution of compound **2c** (170 mg, 1.06 mmol) in dichloromethane–methanol (2:1, 30 mL) was cooled to −78 °C, and ozone was passed through the solution until the blue color persisted. It was stirred for 30 min at −78 °C, nitrogen was purged for few minutes to remove excess ozone, and dimethylsulfide (0.5 mL) was added to the mixture. The resulting mixture was permitted to warm to 0 °C, and stirring was continued for 1 h at 0 °C and for another hour at rt. It was concentrated under reduced pressure, diluted with water, and extracted with petroleum ether (bp 40–60 °C). The organic extract was washed with saturated aqueous sodium bicarbonate, dried over magnesium sulfate, and concentrated to dryness in vacuo to afford 153 mg (96%) of the intermediate aldehyde as a colorless oil. The crude product was used for the next step without further purification.

To a suspension of aldehyde from the above step (100 mg, 0.67 mmol) and magnesium sulfate (123 mg, 0.5 mmol) in acetone (15 mL) was added dropwise a solution of potassium permanganate (116 mg, 0.734 mmol) in acetone (10 mL) for 30 min. The resulting mixture was stirred for 2 h at rt, and the solvent was removed under reduced pressure. The residue was extracted with hot water (3× 20 mL) and filtered. The filtrate was washed with chloroform (10 mL), acidified with 1 N aqueous hydrochloric acid to pH 2, and then extracted with chloroform (3×30 mL). The combined organic extracts were dried over magnesium sulfate and concentrated to dryness in vacuo to afford 70 mg (66%) of **14** as an off white solid. To ascertain the absolute configuration and the enantioselectivity, the crude product **14** (0.5 mg in 100 μL of dichloromethane) was converted to the corresponding ibuprofen (−)-menthyl esters by mixing with 100 μL of an esterification solution, prepared as described below, and then stirring the resulting mixture for 30 min. The esterification solution was prepared by dissolving 3.5 g of (−)-menthol, 0.12 g of dicyclohexylcarbodiimide, 6 mg of 4-dimethylaminopyridine, and 25 μL of 1 M HCl in 1 mL of dichloromethane. The diastereomeric menthyl esters were analyzed by GC on a Chirasil-L-Val column (conditions: 150 °C; retention times: *R*-acid ester 29.9 min, *S*-acid ester 30.9 min). The major acid isomer was identified as *R*-ibuprofen (89% ee) by comparison of retention times with that of authentic samples. Correspondingly, the olefin product, **2c** (3-(4-isobutylphenyl)-but-1-ene), was established as having the *S* configuration.

5.4.6. 2-(3-Bromophenyl)-1-butene (16, racemic). To a solution of allylnickel bromide (2.2 mg, 0.0061 mmol) in CH_2Cl_2 (1.0 mL), was added a solution of triphenylphosphine (3.2 mg, 0.0122 mmol) in CH_2Cl_2 (2.0 mL). The resulting orange solution was added to a suspension of silver triflate (3.8 mg, 0.015 mmol) in CH_2Cl_2 (1.0 mL), and the resulting mixture was stirred at rt for 1.5 h. The mixture was filtered through celite to get a clear yellow solution which was subsequently cooled to −52 °C. Ethylene was introduced to the reaction followed by addition of 3-bromostyrene (**1**, 148 mg, 0.86 mmol) in 0.5 mL of CH_2Cl_2. The reaction was stirred at −52 °C for 3 h and was quenched by adding saturated aqueous NH_4Cl solution (5 mL). The mixture was extracted twice with ether. GC showed >99% conversion and >99% selectivity. The dried organic layer was evaporated to afford crude product (**16**, 170 mg, 99%). ^{1}H NMR (400 MHz, $CDCl_3$): 1.35 (d, J=7.0, 3H); 3.45 (q, J=6.8, 1H); 5.03–5.13 (m, 2H); 7.10–7.21 (m, 2H); 7.31–7.42 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): 20.80; 43.10; 114.03; 112.72; 126.18; 129.44; 130.18; 130.60; 142.57; 148.15.

5.4.7. 2-(3-Bromophenyl)-propionic acid (17, racemic). To a solution of 2-(3-bromophenyl)-1-butene (racemic **16**, 47 mg, 0.22 mmol) in 1:2 *t*-butanol/H_2O (18 mL), was added $KMnO_4$ (108 mg, 0.68 mmol), $NaIO_4$ (880 mg, 4.1 mmol) and K_2CO_3 (223 mg, 1.6 mmol). The pH of the reaction solution was adjusted to 8 with 3 M NaOH aqueous solution. The reaction was stirred for 3 h at rt. Concentrated HCl was added to adjust the pH of the solution to 1, and $NaHSO_3$ was added to reduce $KMnO_4$ until the reaction mixture turned yellow greenish. The mixture was extracted with ether and the ether layer was extracted with 3 M NaOH aqueous solution. The aqueous layer was acidified with concentrated HCl and then extracted with ether. The dried organic layer was evaporated and the product was subjected to chromatography (10:1 CH_2Cl_2/MeOH) to get 2-(3-bromophenyl)-propionic acid (36 mg, 72%). ^1H NMR (400 MHz, $CDCl_3$): 1.40 (d, 3H); 3.58 (q, 1H); 7.03–7.21 (m, 2H); 7.23–7.44 (m, 2H).

5.4.8. (−)-Menthyl (*R*+*S*) 2-(3-bromophenyl)-propionate (18). To a mixture of 2-(3-bromophenyl)-propionic acid from the previous step (36 mg, 0.16 mmol), (−)-menthol (62 mg, 0.40 mmol), DCC (1,3-dicyclohexylcarbodiimide, 49 mg, 0.24 mmol) and a few crystals of DMAP, was added anhydrous CH_2Cl_2 (2.0 mL). The resulting mixture was stirred for 15 h at rt. The reaction mixture was filtered to remove the urea. The filtrate was evaporated and the residue was dissolved in ether. After filtration to remove the insoluble materials, the filtrate was washed with 0.5 M HCl twice and then with saturated $NaHCO_3$. The dried organic layer was evaporated and chromatography (10:1 hexanes/ether) of the residue afforded the desired product as a 1:1 mixture of diastereomers (55 mg, 95%). The two isomers were cleanly separated on chirasil-*S*-val- column (R_T ester from (*R*)-acid 20.41 min.; ester from (*S*)-acid 21.86 min). ^1H NMR (250 MHz, $CDCl_3$): 0.57 (d, 3H); 0.71–2.16 (m, 16H), 3.68 (quint, 1H), 4.66 (dq, 1H), 7.12–7.28 (m, 2H); 7.37–7.52 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): 16.04; 16.40; 18.23; 18.59; 20.85; 20.94; 22.17; 22.21; 23.38; 23.58; 25.99; 26.43; 31.54; 31.60; 34.42; 34.44; 40.65; 41.62; 45.73; 45.79; 47.15; 47.34; 74.96; 75.04; 122.70; 126.39; 130.20; 130.31; 130.86; 131.90; 143.21; 143.32; 173.58; 173.67.

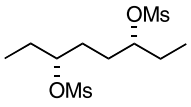
5.4.9. (*S*)-2-(3-Bromophenyl)-1-butene (16). To a solution of allylnickel bromide (1.8 mg, 0.0050 mmol) in CH_2Cl_2 (1.0 mL), was added a solution of **8A** ligand in CH_2Cl_2 (1.5 mL) at rt. The resulting solution was stirred for 30 min. before it was added to a suspension of $AgSbF_6$ (3.8 mg, 0.011 mmol) in CH_2Cl_2 (1.0 mL). The mixture was stirred for 5 min before it was filtered through celite into a Schlenk tube. The celite pad was washed with CH_2Cl_2 (1.5 mL). The solution was cooled down to −52 °C and ethylene was introduced. 3-Bromostyene (138 mg, 0.75 mmol) in CH_2Cl_2 (0.5 mL) was added slowly. The reaction was stirred for 2.2 h before it was quenched with saturated NH_4Cl (5 mL) and extracted twice with ether. The dried ether layer was evaporated to get crude product (157 mg, 99%), GC of which showed 88% conversion with >99% selectivity. ^1H and ^{13}C NMR are consistent with the structure. ^1H NMR (400 MHz, $CDCl_3$): 1.36 (d, 3H); 3.45 (quint, 1H), 5.02–5.12 (m, 2H), 5.93–6.08 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): 20.80; 43.10; 114.03; 122.72; 126.18; 129.44; 130.18; 130.60; 142.57; 148.15.

5.4.10. (−)-Menthyl (*R*)-2-(3-bromophenyl)-propionate (18). The optically enriched (*S*)-2-(3-bromophenyl)-1-butene (**16**) was also oxidized and esterified with (−)-menthol to the (−)-menthyl ester as described for the racemic counterpart. Gas chromatography on chirasil *S*-Val column showed this material to be of 87% ee.

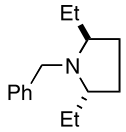
5.5. Synthesis of phosphoramidite ligands

5.5.1. Synthesis of 2,5-diethylpyrrolidine·HCl. (−)-(2*S*, 5*S*)-2,5-Diethylpyrrolidine·HCl was synthesized from (3*R*, 6*R*)-octane-3,6-diol by following the literature procedure[43] described for (+)-(2*R*, 5*R*)-2, 5-dimethylpyrrolidine. HCl, via mesylation of the diol, reaction of the dimesylate with benzyl amine to get *N*-benzyl-(2*S*, 5*S*)-2, 5-diethylpyrrolidine followed by debenzylation and salt formation.

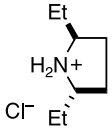
5.5.2. Dimesylate of (*RR*)-octane-3,6-diol. The crude product was found to be pure by NMR. Yield ~100%. ^1H NMR (400 MHz, $CDCl_3$) δ 4.72–4.69 (m, 2H), 3.01 (s, 6H), 1.75 (dd, J=3, 2.7 Hz, 4H), 1.72–1.65 (m, 4H), 0.93 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 84.2, 39, 29.5, 27.8, 9.7.



5.5.3. (+)-*N*-Benzyl-(2*S*, 5*S*)-2,5-diethylpyrrolidine. The product was isolated in 72% yield as an oil by flash column chromatography (SiO_2, 3% EtOAc in hexanes). ^1H NMR (400 MHz, $CDCl_3$) δ 7.28 (d, J=7.2 Hz, 2H), 7.19 (t, J=7.2 Hz, 2H), 7.1 (t, J=7.2 Hz, 1H), 3.73 (d, J=14 Hz, 1H), 3.58 (d, J=14 Hz, 1H), 2.71 (br s, 2H), 1.83–1.72 (m, 2H), 1.56–1.47 (m, 2H), 1.42–1.36 (m, 2H), 1.13–1.02 (m, 2H), 0.7 (t, J=7.6 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.8, 128.7, 128.4, 126.7, 62.2, 51.6, 28, 23.5, 10.8. $[\alpha]_D^{22}$ +111.9 (*c* 3, CH_2Cl_2).



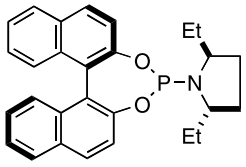
5.5.4. (−)-(2*S*, 5*S*)-2,5-Diethylpyrrolidine·HCl. The product was obtained as a pale yellowish solid in 82% yield after crystallization from a 4:1 solvent mixture of CH_2Cl_2, hexanes. ^1H NMR (400 MHz, $CDCl_3$) δ 9.38 (br s, 2H), 3.55 (br s, 2H), 2.15–2 (m, 4H), 1.72–1.6 (m, 4H), 0.99 (t, J=7 Hz, 6H); ^{13}C NMR (100, $CDCl_3$) δ 61.4, 30.3, 26.1, 11.4. $[\alpha]_D^{22}$ −2.87 (*c* 3, CH_2Cl_2); mp 222–226 °C.



5.6. Preparation of binaphthyl-*O*, *O*′-dioxo-*N*-[(2*S*, 5*S*)-diethylpyrrolidino]phospholidines

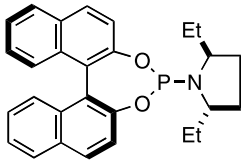
In a flame dried two necked flask equipped with a stirring bar, long reflux condenser attached to a guard tube filled with NaOH pellets, were placed binaphthol (286 mg, 1 mmol) and 5 mL of freshly purified PCl_3. The mixture was refluxed at 82 °C for 4 h. After cooling to rt, the reaction flask was tightly closed and taken inside a glove box. Removal of PCl_3 under high vacuum afforded 355 mg of colorless solid (^{31}P NMR: δ 176, s) which was redissolved in dry toluene (6 mL) and cooled to approximately −20 °C in the freezer. To this cold solution 164 mg (1 mmol) of (2*S*, 5*S*)-2, 5-diethylpyrrolidine. HCl and triethylamine (3 mL) were added successively, and stirred at rt for 20 h. Toluene was removed under reduced pressure. To the residue 3× 3 mL portions of a mixture of hexanes, ether (3:1) was added to dissolve the product leaving most of the $Et_3N\cdot HCl$. Filtration, concentration of the filtrate followed by flash column chromatographic purification (SiO_2, 100% hexanes) afforded phosphoramidite **23** [from (*R*)-binaphthol] or **24** [from (*S*)-binaphthol] as a colorless solid in 40–45% yield.

5.6.1. (*R*)-2,2′-*O*, *O*-(1, 1′-Binaphthyl)-*O*, *O*′-dioxo-*N*-[(2*S*, 5*S*)-2,5-diethylpyrrolidino]phospholidine (23). ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.94–7.84 (m, 4H), 7.47–7.2 (m, 8H), 3.52–3.45 (m, 2H), 1.9–1.72 (m, 2H), 1.55–1.41 (m, 4H), 1.3–1.18 (m, 2H), 0.65 (t, J=7.5 Hz, 6H); ^{31}P NMR (101 MHz, $CDCl_3$) δ 149.9.



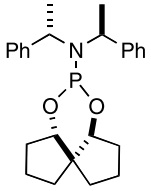
23 ($R_aS_cS_c$)

5.6.2. (*S*)-2,2′-*O*, *O*-(1, 1′-Binaphthyl)-*O*, *O*′-dioxo-*N*-[(2*S*, 5*S*)-2,5-diethylpyrrolidino]-phospholidine (24). ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.87–7.76 (m, 4H), 7.32–7.09 (m, 8H), 3.16 (br s, 2H), 1.71–1.64 (m, 4H), 1.5–1.22 (m, 4H), 0.55 (t, J=7.5 Hz, 6H); ^{31}P NMR (101 MHz, $CDCl_3$) δ 155.9.



24($S_aS_cS_c$)

5.6.3. 1,6-*O*, *O*-(1*S*, 5*S*, 6*S*)-*cis*,*cis*-spiro[4.4]nonyl-*O*, *O*′-Dioxo-*N*, *N*-bis[(1*S*)-phenylethyl]-aminophospholidine (25). In a Schlenk flask equipped with a stirring bar and a rubber septum was placed PCl_3 (0.39 mmol, 34 μL) in toluene (2 mL) at −60 °C under N_2. Triethylamine (0.77 mmol, 107 μL) in neat was introduced through a syringe followed by a toluene (2 mL) solution of (1*S*, 5*S*, 6*S*)-spiro[4.4]nonane-1,6-diol (0.35 mmol, 55 mg).[44] The resultant mixture was stirred at −60 °C for 2 h. The rubber septum was quickly replaced by a glass stopper while flushing N_2 and the reaction flask was taken inside a glove box. Toluene was removed under vacuum and the residue was added 3×3 mL of 3:1 hexanes, ether and filtered through cotton. The filtrate was concentrated to dryness. The residue was dissolved in 3 mL of toluene and cooled to approximately −20 °C. Triethylamine (0.3 mL) and (*R*)-bis(α-methylbenzyl) amine (0.7 mmol, 158 mg) in 2 mL of toluene were added successively and the resultant mixture was stirred at rt overnight. Toluene was removed under reduced pressure and to the residue was added 3× 3 mL of 3:1 hexanes, ether mixture. Filtration through cotton and concentration of the filtrate gave a crude product which was purified by flash column chromatography (SiO_2, 100% hexanes) to afford 82 mg (57%) of pure **25** as a colorless solid. ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.1 (s, 10H), 4.62–4.45 (m, 3H), 4.15–4.13 (m, 1H), 2.04–1.6 (m, 10H), 1.72 (d, J=7.25 Hz, 6H), 1.43–1.36 (m, 2H); ^{13}C NMR (63 MHz, $CDCl_3$) δ 144.3, 128.2, 128, 126.5, 81.9 and 81.8, 53.6 and 53.4, 37.6 and 36.8, 34.9 and 34.8, 33.4 and 33.3, 23.9 and 22.9, 22.7 and 22.5; ^{31}P NMR (101 MHz, $CDCl_3$) δ 130.



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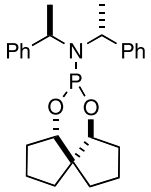
5.6.4. 1,6-*O*, *O*-(1*S*, 5*S*, 6*S*)-*cis*, *cis*-spiro[4.4]nonyl-*O*, *O*′-dioxo-*N*, *N*-bis[(1*R*)-phenylethyl]aminophospholidine (26). Following the above procedure **26** (172 mg, 61%) was obtained as a colorless solid starting from PCl_3 (0.76 mmol, 66 μL), triethylamine (1.52 mmol, 0.21 mL), (1*S*, 5*S*, 6*S*)-spiro[4.4]nonane-1,6-diol (0.69 mmol, 108 mg) and then triethylamine (0.5 mL), (*S*)-bis(α-methylbenzyl) amine (1.4 mmol, 315 mg).[1]H NMR (250 MHz $CDCl_3$) δ 7.19–7.05 (m, 10H), 4.75–4.62 (m, 2H), 4.35 (dd, J=4.75, 2.75 Hz, 1H), 4.12 (dd, J=3.5, 1.75 Hz, 1H), 2.06–1.88 (m, 6H), 1.9–1.62 (m, 4H), 1.72 (d, J=7.25 Hz, 6H), 1.5–1.35 (m, 2H); ^{13}C NMR (63 MHz, $CDCl_3$) δ 142, 128.3, 128, 126.6, 82.3 and 81.2, 57, 52.4 and 52.3, 37.8 and 37, 34.7 and 33.8, 24.1 and 23.1, 22.5 and 22.3; ^{31}P NMR (101 MHz, $CDCl_3$) δ 126.1.



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Acknowledgements

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28. We thank Dr. Xiufeng Sun for this experiment.
29. Hydrovinylation of norbornene is one of the first asymmetric, metal-catalyzed C–C bond-forming reactions reported. See:

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30. For other reports of hydrovinylation of norbornene, see: (a) Müller, G.; Ordinas, J. I. *J. Mol. Catal.* **1997**, *125*, 97–108. (b) Yi, C. S.; He, Z.; Lee, D. W. *Organometallics* **2001**, *20*, 802–804. For hydrovinylation of norbornadiene, see, Ref. 29 and, Pillai, S. M.; Tembe, G. L.; Ravindranathan, M. *J. Mol. Catal.* **1993**, *84*, 77–86.
31. For identification of the relative and absolute configuration of (−)-**18** and relative configuration **19**, see Ref. 22. The absolute configuration of **19** has not been determined.
32. For other asymmetric catalyzed reactions of norbornene see: Hydrocyanation: Hodgson, M.; Parker, D.; Taylor, R. J.; Ferguson, G. *Organometallics* **1988**, *7*, 1761–1766. Baker, M. J.; Pringle, P. G. *J. Chem. Soc., Chem. Commun.* **1991**, 1292–1293. Horiuchi, T.; Shirakawa, E.; Nozaki, K.; Takaya, H. *Tetrahedron: Asymmetry* **1997**, *8*, 57–63. Yan, M.; Xu, Q.-Y.; Chan, A. S. C. *Tetrahedron: Asymmetry* **2000**, *11*, 845–849. Hydrosilylation: Hayashi, T. *Acta Chem. Scand.* **1996**, *50*, 259–266. Hydroalkenylation: Ozawa, F.; Kabatake, Y.; Kubo, A.; Hayashi, T. *J. Chem. Soc., Chem. Commun.* **1994**, 1323–1324.
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