Synthesis, resolution, and application of 2,2′-bis(diphenylphosphino)-3,3′-binaphtho[*b*]furan (BINAPFu)[1]

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Abstract: (±)-2,2′-Bis(diphenylphosphino)-3,3′-binaphtho[2,1-*b*]furan (BINAPFu) was synthesized from 2-naphthoxyacetic acid in a five-step sequence in 62% overall yield. A variety of reported resolution procedures for biaryl bisphosphines did not work with (±)-BINAPFu; thus, a new resolution method was developed, involving the Staudinger reaction of the aforementioned racemate of BINAPFu with an enantiopure camphor sulfonyl azide derivative. The resulting diastereomeric phosphinimines were separated by flash chromatography. Subsequent hydrolysis to the corresponding bis-phosphine oxide and trichlorosilane reduction provided enantiopure BINAPFu. The absolute stereochemical configuration of BINAPFu was established by X-ray crystallography. BINAPFu was compared with commercially available 2,2′-bis(diphenylphosphino)-1,1′-binaphthalene (BINAP) in Pd(0)-catalyzed intermolecular Heck reactions. Investigation of the Heck arylation of 2,3-dihydrofuran showed BINAPFu to be more efficacious than BINAP in dioxane at 30 °C. A variety of phosphorus selenides were prepared, and the $^1J_{P\text{-}Se}$ coupling constants measured, to obtain a comparative scale of parent phosphine basicity. The phosphorus atoms in BINAPFu were found to be electron deficient when compared with BINAP but slightly more electron rich than trifurylphosphine.

Key words: naphthofurans, atropisomers, electron-deficient phosphines, asymmetric Heck reactions, Staudinger reaction.

Résumé : Utilisant l'acide 2-naphtoxyacétique comme produit de départ, on a réalisé la synthèse en cinq étapes du (±)-2,2′-bis(diphénylphosphino)-3,3′-binaphto[2,1-*b*]furane (BINAPFu), avec un rendement global de 62 %. Plusieurs méthodes connues de résolutions ont été tentées sans succès sur le (±)-BINAPFu; on a donc développé une nouvelle méthode de résolution impliquant la réaction du (±)-BINAPFu avec un dérivé énantiopur de l'azoture de camphresulfonyle. On a séparé les phosphinimines diastéréomères résultantes par chromatographie éclair. L'hydrolyse subséquente de l'oxyde de bis-phosphine correspondante et une réduction à l'aide de trichlorosilane ont conduit au BINAPFu énantiopur. La configuration stéréochimique absolue du BINAPFu a été établie par diffraction des rayons X. On a comparé le BINAPFu au 2,2′-bis(diphénylphosphino)-1,1′-binaphtalène (BINAP) dans les réactions intermoléculaires de Heck catalysées par le Pd(0). Une étude de l'arylation de Heck du 2,3-dihydrofurane a montré que le BINAPFu est plus efficace que le BINAP, dans le dioxane, à 30 °C. On a préparé une variété de séléniures de phosphore et on a mesuré les constantes de couplage $^1J_{P\text{-}Se}$ afin d'obtenir une échelle comparative de la basicité de la phosphine de base. On a trouvé que les atomes de phosphore du BINAPFu sont déficients en électron par comparaison avec le BINAP, mais qu'ils sont plus riches en électrons que la trifurylphosphine.

Mots clés : naphtofuranes, atropisomères, phosphine déficiente en électron, réaction de Heck asymétriques, réaction de Staudinger.

[Traduit par la Rédaction]

Introduction

Since Noyori and co-workers' (1) introduction of 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl (BINAP) as a chiral ligand for asymmetric catalysis, numerous workers have shown that remarkably high degrees of enantioselectivity can be obtained using this phosphine in a wide variety of transition-metal-mediated organic reactions (2). Based on the superior results often realized using BINAP in asymmetric transformations, coupled with the recent interest in 2-furyl phosphine ligands (3), a project was undertaken to develop an axially stereogenic diphosphine ligand that incorporates the 2-furyl group. At the onset of this endeavor, a literature search revealed that no such structure had ever been reported. Moreover, it was clear that very little was known about how phosphine σ-donor ability affected the

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Dedicated to Dr. E. Piers for his outstanding chemistry contributions and to him as an invaluable mentor over the years.

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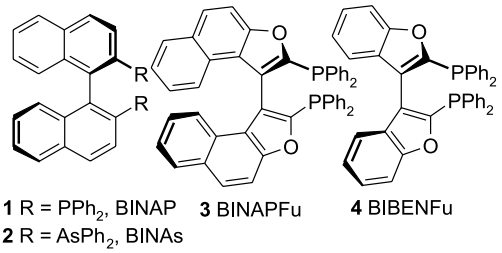
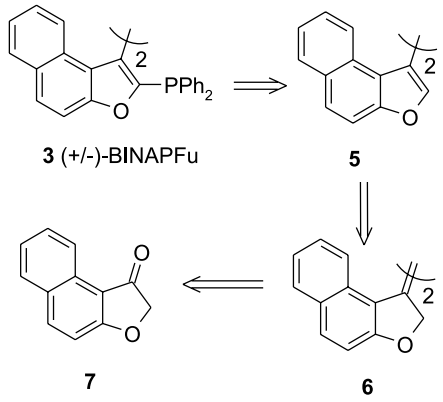
course of enantioselective reactions. However, many workers have now sought to develop chiral 2-furyl phosphine ligands for asymmetric synthesis, and several reports of asymmetric reactions using these ligands have recently been disclosed (4, 5). These investigations have been prompted, in part, by recent evidence that suggests that less electron-rich ligands are or should be advantageous in some metal-mediated organic processes. For example, Shibasaki and co-workers (6) have recently developed 2,2′-bis(diphenylarsino)-1,1′-binaphthyl (**1**, BINAs) and have shown this poorly donating ligand to be more effective than BINAP **2** for an intramolecular asymmetric Heck reaction (Scheme 1) (7). In addition, Amatore and co-workers (8) have studied the oxidative addition of phenyl iodide with in situ generated palladium(0) complexes of triphenylphosphine and TFP, showing that in DMF, $\{Pd(dba)_2 + n(trifurylphosphine)\}$ is always more reactive than $\{Pd(dba)_2 + nPPh_3\}$, for $n \geq 2$ (7). These reports, in conjunction with our interests in the asymmetric polyene cyclization (9), led to the development of a novel 3,3′-bifuryl-derived diphosphine analogue of BINAP (Scheme 1), namely, BINAPFu **3** (10).

To develop a C_2-symmetric furyl phosphine analogue of BINAP, it was conceived that a prudent design would retain the bis(diphenylphosphino) moieties and incorporate the furyl functionality into the biaryl framework. In this way, it was felt that the electronic properties of the phosphine ligand could be altered with minimal perturbation of the chiral pocket structure. Since Benincori and co-workers (5*i*, 11) have concluded that the BIBENFu **4** ligand is not configurationally stable at room temperature, it was decided to prepare the more sterically bulky bisnaphtho[*b*]furan skeleton, as PM3 semi-empirical calculations on **3** indicated that the rotational energy of the bifuryl bond in **3** would be quite high. This paper describes the design aspects, synthesis, resolution, and application of the BINAPFu **3** ligand.

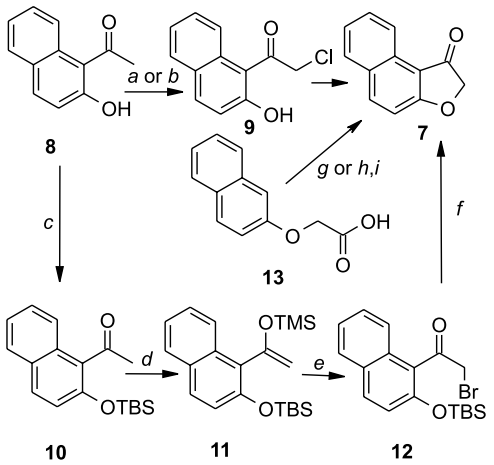
Scheme 1.



Scheme 2.



Scheme 3. (*a*) 1–5 equiv SO_2Cl_2, DCM, reflux, 4.5–12 h, <5%; (*b*) 2 equiv hexachloro-2,4-cyclohexadienone, EtOH, reflux, 18 h, 30%; (*c*) 1.1 equiv TBSCl, Et_3N, DCM, rt, 18 h, 89%; (*d*) 1.0 equiv TMSOTf, Et_3N, DCM, rt, 2 h; (*e*) 1 equiv Br_2, CCl_4; (*f*) 1 equiv TBAF, THF, rt, 0.5 h, 72% (2 steps); (*g*) excess P_2O_5, MsOH, rt, 18 h, 68%; (*h*) 2 equiv $SOCl_2$, benzene, catalytic (cat) Py, reflux, 2 h; (*i*) 1.5 equiv $AlCl_3$, benzene, rt, 12 h, 95% (2 steps).



Synthesis of (±)-BINAPFu 3

Two initial routes to the synthesis of **3** were unsuccessful (12) and led to a design in which the key reaction involved a McMurry coupling. The low-valent titanium homocoupling of aldehydes and ketones, developed independently by Mukaiyama et al. (13), Tyrlik et al. (14), and McMurry et al. (15), has been applied in a wide variety of contexts to prepare symmetrical olefins (16). It was thought that the BINAPFu bifuryl bond could be constructed via a McMurry coupling of ketone **7** followed by DDQ oxidation of the resultant olefin **6** (Scheme 2). Finally, introduction of the diphenylphosphino groups into **5** would give (±)-BINAPFu **3**.

Although ketone **7** has been previously reported (17), the syntheses were characterized by low product yields (<35%) and difficult isolation procedures. It was therefore decided that a new, efficient synthesis of the required ketone **7** should be developed. Since 1-acetyl-2-hydroxynaphthalene (**8**) was readily available, it was reasoned that α-chlorination of the ketone function to give **9**, followed by 5-*exo-trig* ring closure, would provide an expedient route to the desired ketone **7** (Scheme 3). Unfortunately, several chlorination reagents, including sulfuryl chloride (18) and hexachloro-2,4-cyclohexadienone (19), failed to provide α-chloroketone **9** in good yields. Recourse was sought in the three-step α-bromination of ketone **10** via TMS enol ether **11** (Scheme 3). Treatment of hydroxy-ketone **8** with 1.1 equiv of *tert*-butyldimethylsilyl chloride in CH_2Cl_2 and Et_3N furnished TBS ether **10** in 89% yield. Although the TMS enol ether **11** could be formed using LHMDS and TMSCl in an ethereal solvent, much more consistent results were obtained when ketone **10** was treated with TMSOTf in a mixture of CH_2Cl_2 and triethylamine. Bromination of enol silyl ether **11** with

1 equiv of Br_2 in CCl_4 proceeded with loss of TMSBr to furnish α-bromo ketone **12** in modest yield. Cleavage of the TBS ether under standard conditions occurred with concomitant ring closure, to provide the desired naphthoketone **7** in 61% overall yield. Although this four-step synthetic sequence provided the desired ketone **7** in moderate yield, without the need for costly purification routines, the use of expensive protecting groups and reagents rendered this method somewhat infeasible for large-scale preparation.

To address these concerns, an alternative synthesis of compound **7** was conceived whereby readily available 2-naphthoxyacetic acid (**13**) could be subjected to Friedel–Crafts acylation conditions to provide the desired compound directly (Scheme 3). Treatment of acid **13** with Eaton's reagent (20) at ambient temperature for 18 h afforded the desired ketone **7** in 68% yield. Alternatively, preparation of the corresponding acyl chloride, under standard conditions, and subsequent reaction with $AlCl_3$ gave naphthoketone **7** in 95% yield. Interestingly, in both cases, acylation occurred regiospecifically in the 1-position to give the desired product **7** with remarkable purity. This procedure, which does not require any purification steps, can easily be performed on a 50 g scale to provide ketone **7** in excellent yield.

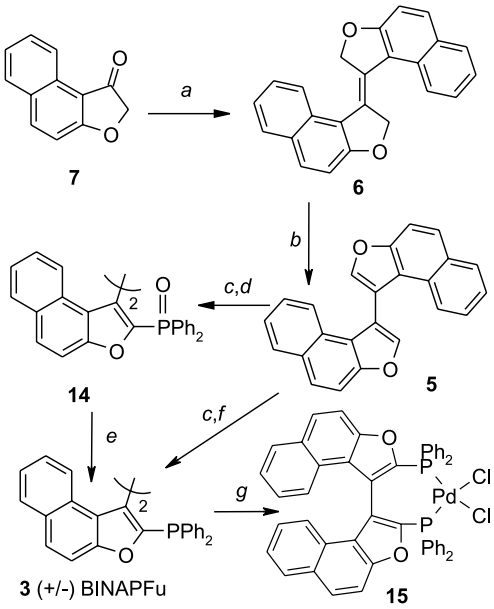
Reductive coupling of compound **7** with $TiCl_4$ and zinc–copper couple (21) in refluxing DME smoothly provided olefin **6** in good yield (Scheme 4). Activated zinc dust (22) worked equally as well for this purpose, giving biaryl **5** in 78% isolated yield after DDQ oxidation (23). ^{1}H NMR analysis of compound **6** showed that the product had been formed essentially as a single isomer (>95%), which was assigned the *E* configuration on the basis of steric arguments. Owing to facile carbon-carbon double bond migration, olefin **6** could not be fully characterized. Upon oxidation with DDQ, the broad singlet (δ: 5.25 ppm) that integrated as four protons in the ^{1}H NMR spectrum of **6** was replaced by a sharp singlet (δ: 7.87 ppm) that represented the two furan α-protons in biaryl **5**.

Installation of the bis(diphenylphosphino) moieties was accomplished by lithiation of the biaryl scaffold **5** with 2.5 equiv of *t*-BuLi and subsequent treatment of the resulting dianion with freshly distilled diphenylphosphinic chloride. This provided phosphine oxide **14** in 88% yield (Scheme 4). Reduction of the oxide **14** with trichlorosilane in a mixture of xylenes and triethylamine furnished (±)-BINAPFu (**3**) in >95% yield. Alternatively, lithiation of biaryl **5** followed by treatment of the resultant dianion with 2.0 equiv of chlorodiphenylphosphine gave (±)-BINAPFu **3** directly in 91% yield.

Structural characterization of (±)-BINAPFu 3

As stated previously, a fundamental aspect of the ligand design required that the 2-furyl groups be incorporated in such a way that the electronic properties of the phosphorus atoms may be altered with as little perturbation of the chiral pocket structure as possible. To investigate the success of the ligand design with respect to this requirement, the palladium(II) chloride complex of BINAPFu **15** was prepared (5*i*) and analyzed by single crystal X-ray diffraction (Fig. 1). Crystals of compound **15** were obtained by slow diffusion of

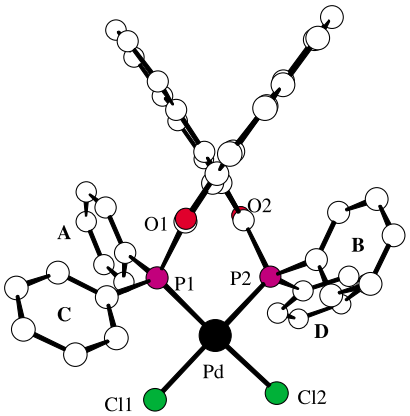
Scheme 4. 8.2 equiv Zn dust, 2.0 equiv $TiCl_4$, DME, reflux, 18 h; (*b*) 1.0 equiv DDQ, benzene, reflux, 4 h, 78% (2 steps); (*c*) 2.5 equiv *t*-BuLi, Et_2O, rt, 2 h; (*d*) 2.0 equiv $PPh_2(O)Cl$, rt, 12 h, 88%; (*e*) 20 equiv $SiCl_3H$, 24 equiv Et_3N, xylenes, 150 °C, 3 h, >95%; (*f*) 2.0 equiv PPh_2Cl, rt, 12 h, 91%; (*g*) 1.0 equiv $(CH_3CN)_2PdCl_2$, DCM, rt, 28 h, 93%.



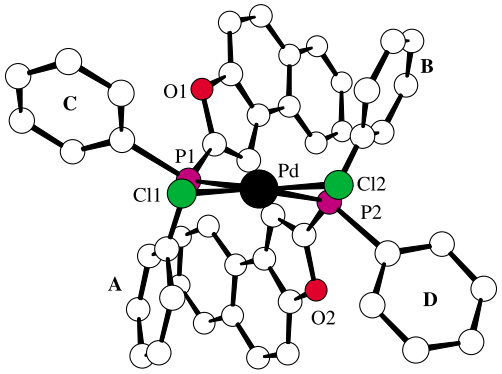
Et_2O into an acetone-saturated solution of the complex under an argon atmosphere.

Comparing the projections of [(±)-BINAPFu]$PdCl_2$ (**15**) with Hayashi's [(*R*)-BINAP]$PdCl_2$ structure **16** (24), a few structural differences are immediately apparent. Whereas two of the phenyl rings (A and B) in the [(*R*)-BINAP]$PdCl_2$ complex **16** π-stack with the binaphthalene framework, the corresponding phenyl groups in compound **15** (A and B) do not show perpendicular relationships with the binaphtho[*b*]furan system. Also noteworthy in the [(±)-BINAPFu]$PdCl_2$ structure **15** is that the square planar geometry about the palladium atom seems to be less distorted than in the corresponding (*R*)-BINAP complex **16**. These observations suggest that the chiral pocket formed in the [BINAPFu]$PdCl_2$ complex **15** is somewhat less rigid than that obtained with the BINAP ligand **16**. However, several similarities are also observed upon comparing [BINAP]$PdCl_2$ **16** and [BINAPFu]$PdCl_2$ **15**. In both structures, two of the phenyl rings (C and D) project outward toward the coordination sites occupied by the chloride ligands. The [BINAP]$PdCl_2$ **16** bite angle (25), defined by the P1-Pd-P2 vertex, of 92.7° compares well with that measured for the [BINAPFu]$PdCl_2$ **15** (93.4°). Values for the Pd—P (**16**: 2.245 Å; **15**: 2.264 Å) and Pd—Cl (**16**: 2.350 Å; **15**: 2.333 Å) bond lengths compare quite favorably, although slight differences can be seen because of the reduced electron-donor ability of the BINAPFu ligand. As expected, the mean Pd—P bond length is slightly longer in the [BINAPFu]$PdCl_2$ complex, owing to the reduced σ-donor ability of the phosphorus atoms relative to BINAP. As a result, the Pd—Cl bond lengths are slightly shorter in compound **15**. Given the structural changes that had to be made to incorporate the 2-furyl moieties, it was felt that the struc-

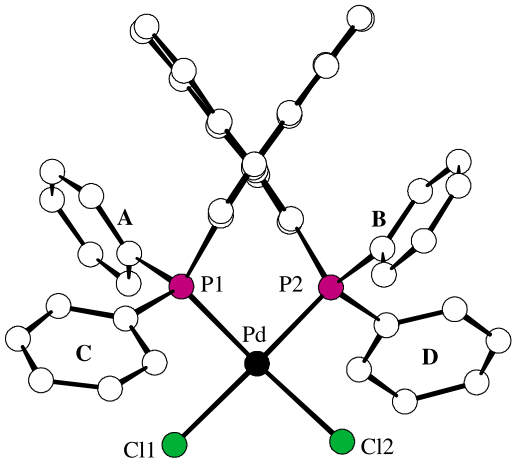
Fig. 1. X-ray crystal structure of [(±)-BINAPFu]$PdCl_2$ (15) vs. Hayashi's (24) [(±)-BINAP]$PdCl_2$ (16) structure (hydrogen atoms omitted for clarity).



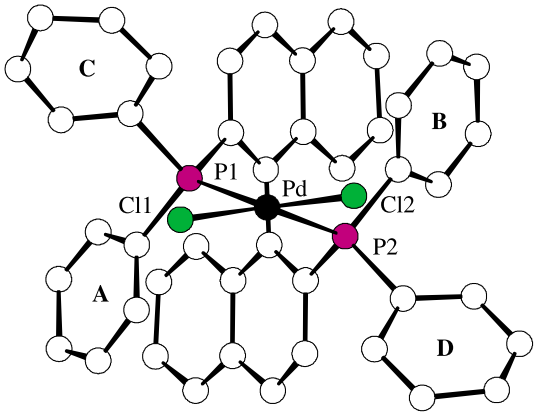
[(±)-BINAPFu]$PdCl_2$ (**15**) top view



[(±)-BINAPFu]$PdCl_2$ (**15**) side view



[(*R*)-BINAP]$PdCl_2$ (**16**) top view



[(*R*)-BINAP]$PdCl_2$ (**16**) side view

tural homology between the two organometallic complexes was great enough to warrant further investigation with the BINAPFu ligand.

Resolution of (±)-BINAPFu 3

Subsequent to developing a simple, highly efficient synthesis of (±)-BINAPFu **3**, attention focused on finding a method for obtaining the two pure optical antipodes. To achieve this goal, it was first necessary to find a convenient method for determining the enantiopurity of diphosphine **3**. Fortunately, (±)-BINAPFu **3** could be readily separated by analytical HPLC using a Chiralcel® OJ column (25 °C; 95:5 MeOH:EtOH; 0.5 mL min^{-1}; 270 nm UV detection), indicating that the rotational barrier of the biaryl axis was of sufficient magnitude to impart optical activity at room temperature. Although preparative HPLC columns employing similar chiral stationary phases are commercially available (26), optical resolution of the BINAPFu ligand in large quantities using this method was deemed to be infeasible.

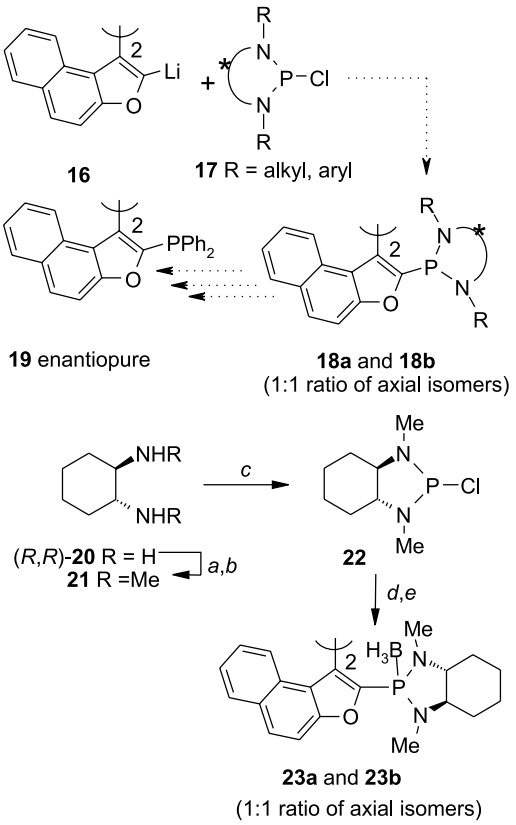
Although several methods for achieving optical resolution of stereogenic organophosphorus compounds are known (27), efforts were initially focused on procedures that have been applied to BINAP and related C_2-symmetric diphosphines. Unfortunately, the following reported procedures did not afford a suitable resolution method for (±)-BINAPFu **3**: (*a*) co-crystallization of phosphine oxide **14** with (–)-DBTA or (1*S*)-(+)-10-camphorsulfonic acid (28); (*b*) using enantiopure palladium(II) complexes with (*S*)-*N*,*N*-dimethyl-α-phenylethylamine or (*S*)-*N*,*N*-dimethyl-α-(2-naphthyl)ethylamine (29–31); (*c*) via formation of phosphonium salts with enantiopure organohalides like (*S*)-(+)-citronellyl bromide, (*S*)-(+)-citronellyl iodide (32), or (*S*)-(+)-1-iodo-2-methylbutane; and (*d*) attempts to resolve the bis-phosphonium salt

of **3** (generated with 2 equiv of iodomethane) by reaction with silver hydrogen dibenzoyl-L-tartrate (Ag-DBHT) (33) or silver (1*S*)-(+)-10-camphorsulfonate (34).

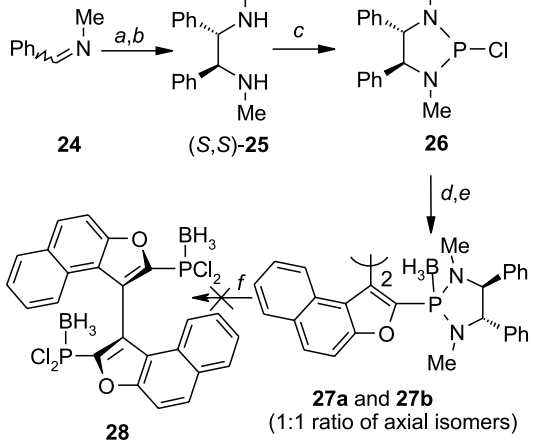
Although the synthesis developed for the BINAPFu ligand (vide supra) is short and efficient, failure to identify a suitable method for obtaining the optically pure material via known resolution methods led to the consideration of alternative synthetic routes. It was postulated that an enantiopure electrophile of type **17** could potentially be reacted with lithiated biaryl **16** to give bis-phosphonamide **18** as a 1:1 mixture of diastereomers (35) (Scheme 5). Such an approach would thus install the required 2,2′-phosphorus atoms while appending a chiral auxiliary for optical resolution. Separation of the resulting diastereomer mixture and subsequent synthetic manipulation of each pure isomer, **18a** and **18b**, would then provide routes to the optically pure BINAPFu antipodes. Following this general scheme, commercially available *trans*-1,2-cyclohexane diamine was resolved (36), and the (*R*,*R*)-isomer (37) **20** was converted to the corresponding *N*,*N*′-dimethyl derivative **21** according to a literature procedure (38) (Scheme 5). Diamine **21**, thus obtained, was treated with 1 molar equivalent of phosphorus trichloride, according to a standard procedure (39), to furnish chlorophosphine **22** in 72% isolated yield. This highly moisture- and oxygen-sensitive (39) compound was prepared using Schlenk techniques under an atmosphere of argon and was used without purification. Trapping dianion **16**, prepared as previously described, with 1,3-diazaphopholidine derivative **22** and subsequent reaction with BH_3·DMS provided a 1:1 mixture of diastereomers **23a** and **23b**, respectively (Scheme 5). Bis-borane complex **23** was prepared in situ to prevent potential complications due to air oxidation of the phosphine precursor (39). Although separation of compounds **23a** and **23b** could not be achieved using standard recrystallization or flash chromatographic techniques, a small sample (~3 mg) of each pure diastereomer was obtained by preparative HPLC, using a reversed-phase C_{18} column. While this labor-intensive and costly separation technique clearly did not provide large quantities of resolved material, the obtainment of diastereomerically pure borane adducts **23a** and **23b** was highly encouraging. Moreover, it was postulated that by simply changing the diamine used to prepare phosphoramidous chloride **17** (Scheme 5), it may be possible to prepare a more readily separable mixture of axial diastereomers.

Diamine **25** was prepared from **24** (40) and resolved (41) according to standard literature procedures (Scheme 6). Diazaphospholidine **26** (42) was subsequently prepared upon treatment of (*S*,*S*)-(–)-diamine **25** with 1 equiv of phosphorus trichloride in Et_3N–Et_2O solution. Further reaction with 2,2′-dilithiated binaphthofuran **16** and BH_3·DMS furnished a 1:1 mixture of axially isomeric borane adducts **27a** and **27b** in 71% yield. Fortunately, separation of stereoisomers **27a** and **27b** was facile by fractional crystallization from a $CHCl_3$–hexanes solvent system. Under these conditions, compound **27a** selectively crystallized, leaving highly enriched (>95%) isomer **27b** in the mother liquor. The latter compound could be further purified by flash chromatography. With pure borane adducts **27a** and **27b** in hand, attention was focused on removing the diamine moiety and installing the required phenyl substituents.

Scheme 5. (*a*) 2.1 equiv ethyl chloroacetate, 4.6 equiv NaOH, H_2O, 0 °C, 2 h, 82%; (*b*) 8.5 equiv $LiAlH_4$, THF, rt, 1 h, 92%; (*c*) 1.0 equiv PCl_3, 2 equiv NEt_3, Et_2O, –40 °C, 72%; (*d*) 0.5 equiv compound **16**, Et_2O, rt, 1.5 h; (*e*) 2 equiv BH_3·DMS, rt, 24 h, 74% (2 steps).



Scheme 6. (*a*) 1.5 equiv Mg, 1.5 equiv $TiCl_4$, 4 mol% $HgCl_2$, THF, 0 °C, 12 h, 61%; (*b*) optical resolution with L-(+)-tartaric acid; (*c*) 1.0 equiv PCl_3, 2 equiv NEt_3, Et_2O, –40 °C, 81%; (*d*) 0.5 equiv compound **16**, Et_2O, rt, 1.5 h; (*e*) 2 equiv BH_3·DMS, rt, 24 h, 71% (2 steps); (*f*) 8 equiv anhyd HCl, Et_2O.



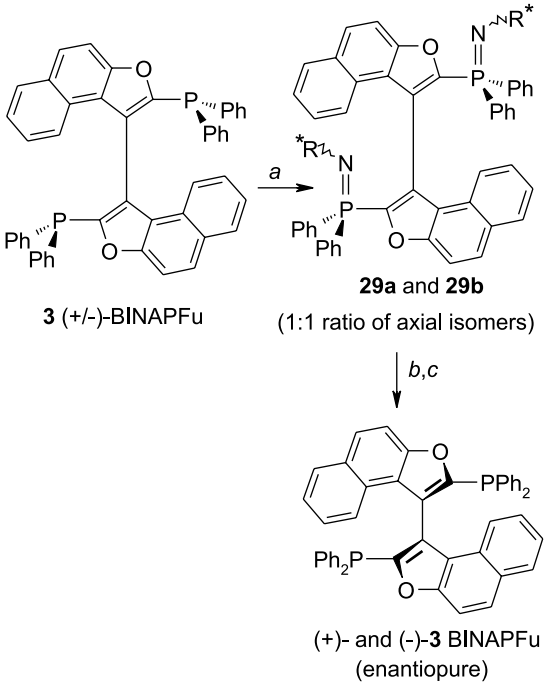
Supported by literature precedent (35, 43), it was envisioned that the diamine chiral auxiliary could be cleaved from borane adduct **27a** upon treatment with anhyd HCl, providing enantiopure chloride **28** (Scheme 6). Subsequent

reaction of **28** with 4 equiv of phenyllithium or phenyl Grignard and removal of the BH_3 protecting group would then furnish the desired BINAPFu **3** in optically pure form. Following this approach, isomerically pure compound **27a** was treated with 8 molar equivalents of HCl (1.0 mol L^{-1} solution in Et_2O) at 0 °C for 1 h. The mixture thus obtained was filtered under argon to remove (1*S*,2*S*)-*N*,*N*′-dimethyl-1,2-diphenylethylenediamine dihydrochloride, and the filtrate was treated with 5 equiv of phenyllithium at –40 °C. Under these conditions, a complex mixture of products was obtained, as evidenced by ^{31}P NMR analysis. Lowering the reaction temperature to –40 °C for the acid addition or using phenyl Grignard in place of phenyllithium failed to improve this result. Employing anhyd HCl(g) instead of the 1.0 mol L^{-1} ethereal solution also afforded a complex mixture of products. In all cases, isolation of the unwanted amine hydrochloride salt confirmed that cleavage of the P—N bonds was occurring under the reaction conditions. Low temperature ^{31}P NMR analysis indicated that complex mixture formation was occurring previous to the addition of the organometallic reagent. Other Brönsted acids, including MsOH and TFA in methanolic solution, afforded similar results. The failure to identify suitable conditions for cleaving the diamine chiral auxiliary from borane adduct **27a** led to the development of a new resolution procedure for phosphines.

As several of the known methods for phosphine resolution were unsuccessful, we decided to develop a new resolution to obtain enantiopure BINAPFu **3**. Consideration of the resolution methods already attempted (vide supra) suggested that a newly developed procedure should ideally act directly on BINAPFu **3** or the corresponding bis-phosphine oxide **14** to minimize the number of synthetic steps. Moreover, owing to the difficulties experienced in the CSA and DBTA resolution techniques, it was concluded that a successful route would likely involve appending the resolving agent via a covalent linkage, thus providing two discrete diastereomeric compounds. Based on unsuccessful attempts with the *ortho*-palladated resolving agents (29–31), the diastereomeric compounds obtained by appending a resolving agent to the phosphine ligand should be neutral intermediates, to allow for possible chromatographic separation. Finally, considering the impasse reached with diazaphospholidine compound **27a**, cleavage of the chiral auxiliary to furnish the desired optically pure phosphine **3** or phosphine oxide **14** should not require strongly acidic reaction conditions. With these parameters in mind, it was conceived that a Staudinger reaction (44) between (±)-BINAPFu **3** and 2 equiv of an enantiopure organoazide could potentially give a 1:1 mixture of diastereomeric phosinimines **29a** and **29b** (Scheme 7) if the P=N bond rotational barrier was low enough to prevent geometrical isomerism. A literature survey revealed that the P=N rotational barrier for simple phosphinimines has been calculated to be ca. 2.54 kcal mol^{-1} (45). Hence it was rationalized that P=N geometrical isomerism would likely not complicate the proposed resolution technique. Separation of the phosphinimine mixture and subsequent reductive cleavage of the resolving agent from each pure isomer with $LiAlH_4$ would then furnish the desired, enantiomerically pure antipodes.

To develop a resolution procedure for (±)-BINAPFu based on phosphinimine formation, a readily available and optically pure organoazide needed to be identified (46). (1*S*)-10-camphorsulfonyl azide was chosen as a possible resolving agent; it can be prepared in a single step from commercially available (1*S*)-(+)-10-camphorsulfonyl chloride (47). Treatment of (±)-BINAPFu **3** with 2 molar equivalent of enantiopure sulfonyl azide **30** smoothly provided a 1:1 mixture of diastereomeric phosphinimines **31a** and **32b** in near quantitative yield (Scheme 8). Fortunately, phosphinimines **31a** and **31b** could be readily separated by flash chromatography on silica gel using a 9:1 $CHCl_3$–CH_3CN eluent mixture. With isomerically pure phosphinimines **31a** and **32b** in hand, attention was now focused on identifying a method for removing the chiral auxiliary to give optically pure BINAPFu **3** or the corresponding phosphine oxide **14**.

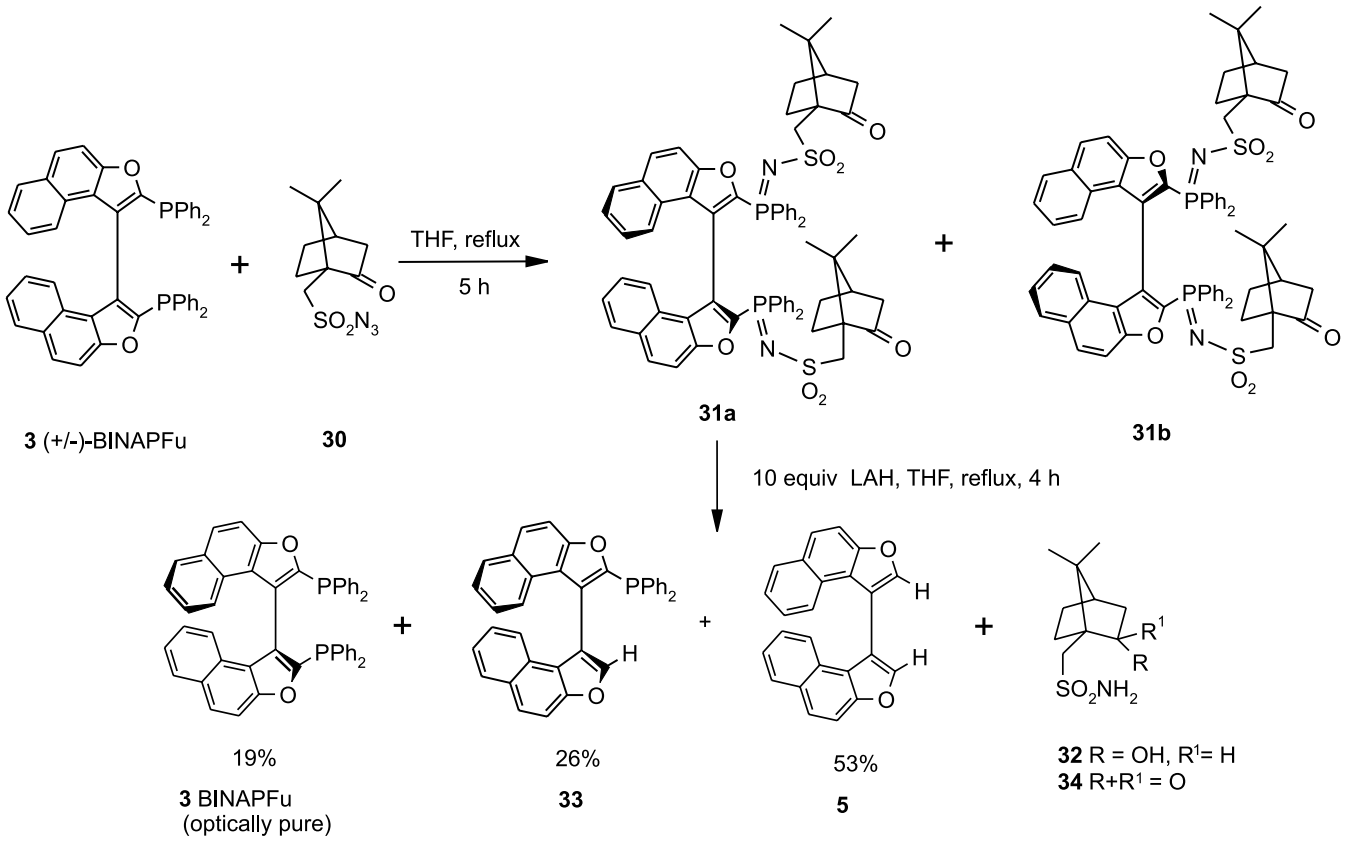
Scheme 7. (*a*) 2 equiv enantiopure azide ($*RN_3$); (*b*) separate axial stereoisomers; (*c*) H^- reduction, Et_2O.



It was postulated that treatment of isomerically pure phosphinimine **31a** with excess $LiAlH_4$ would provide optically pure BINAPFu **3** along with isobornyl-10-sulfonamide **32** (Scheme 8) (48). Interestingly, heating compound **31a** with 10 equiv of LAH in THF resulted in the unexpected formation of 3,3′-binaphtho[*b*]furan (**5**) and monophosphine **33**. Although a small amount of the desired product was obtained and shown to be optically pure by HPLC analysis (Chiralcel® OJ column; 25 °C; 95:5 MeOH:EtOH; 0.5 mL min^{-1}; 270 nm UV detection), conditions to attenuate the formation of byproducts **5** and **33** could not be found. Performing this reaction at ambient temperature resulted in a similar product mixture, while employing weaker reducing agents, such as DIBAL or $NaBH_4$, failed to cleave the P=N bond.

Faced with the failure to prepare optically pure BINAPFu **3** in good yield via direct reduction of phosphinimine **31a**, it was postulated that the P=N bond could be cleaved using an aza-Wittig process (49). Hence, reaction of either compound **31a** or **31b** with CO_2 would afford optically pure phosphine

Scheme 8.



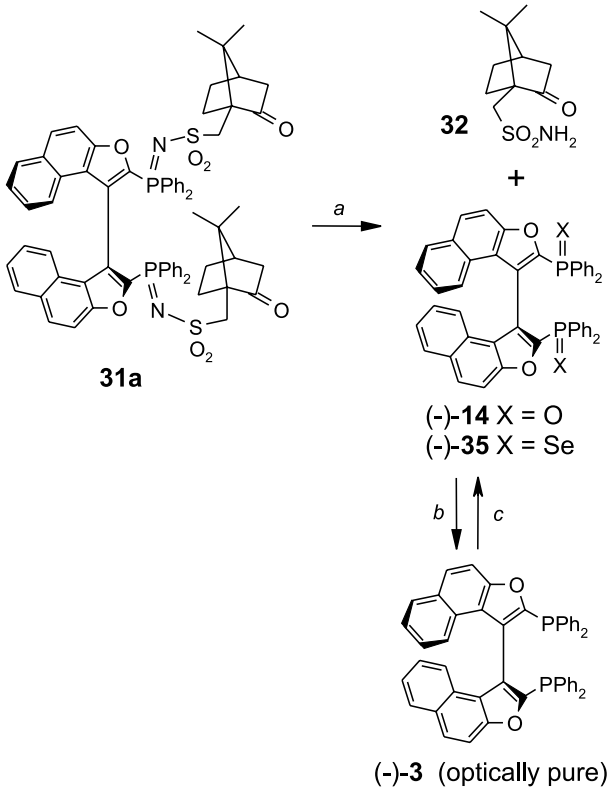
oxide **14** along with (1*S*)-10-camphorsulfonamide **34** (Scheme 8). Subsequent trichlorosilane reduction of phosphine oxide **14** thus obtained would then furnish the desired enantiopure BINAPFu ligand **3**. Surprisingly, bubbling CO_2 gas through a solution of isomerically pure phosphinimine **31a** in THF for a period of 4 h failed to cause any detectable cleavage of the P=N bond. Changing the solvent to acetone and lengthening the exposure time did not improve this result. Moreover, no reaction was observed upon refluxing compound **31a** in carbon disulfide for 24 h, suggesting that an aza-Wittig approach toward cleaving the phosphinimine moiety was not going to be feasible.

Since phosphinimine **31a** was inert towards aza-Wittig conditions, recourse was sought in the hydrolytic cleavage of the P=N bond using mineral acids (50). Stirring a solution of compound **31a** in THF and 1.5 mol L^{-1} H_2SO_4 at ambient temperature for 24 h failed to give any reaction, as evidenced by ^{31}P NMR analysis. Although this experiment did not result in the cleavage of the P=N bond, it is noteworthy that the binaphtho[*b*]furan system withstood the reaction conditions and was therefore more stable to acid than previously anticipated. Performing the reaction in refluxing THF, under otherwise identical conditions, cleanly provided the desired phosphine oxide, albeit in poor conversion (~15%). Subsequent experimentation revealed phosphine oxide **14** could be obtained in near quantitative yield by refluxing compound **31a** in a 3:2 mixture of 1,4-dioxane and 3 mol L^{-1} H_2SO_4 for 24 h (Scheme 9). Subsequent chromatographic removal of sulfonamide **32** and trichlorosilane reduction of the resulting phosphine oxide **14** provided BINAPFu **3** in excellent yield. HPLC analysis (vide supra) of the bisphosphine thus obtained showed a single peak at R_T = 23.7 min. Finally, optical rotation data revealed that phosphinimine **31a** yielded (–)-BINAPFu ($[\alpha]_D^{19}$ –203.0 (*c* 1.09, $CHCl_3$)). Performing the same hydrolysis–reduction sequence on phosphinimine **31b** provided (+)-BINAPFu **3** in near quantitative yield ($[\alpha]_D^{20}$ +201.8 (*c* 1.28, $CHCl_3$)). Heating the enantiopure (–)-BINAPFu ligand in *p*-xylenes at 150 °C for 7 days did not result in any racemization of the chiral axis, as evidenced by optical rotation and HPLC analysis.

Physical characterization of the BINAPFu ligand: Investigation of the σ-donor ability and absolute configuration assignment

Allen and Taylor (51) have reported that the $^1J(^{31}P\text{-}^{77}Se)$ coupling constant of phosphorus selenides may be used as a measure of parent phosphine basicity. A large coupling constant indicates high *s*-character of the phosphorus lone-pair orbital. In other words, poorly donating phosphine ligands exhibit large $^1J(^{31}P\text{-}^{77}Se)$ coupling constants. To gauge the donor ability of the BINAPFu ligand, a solution of optically pure (–)-**3** in $CHCl_3$ was heated with 10 molar equivalent of selenium powder for 5 h to afford bis-selenide **35** (Scheme 8). ^{31}P NMR analysis of selenide **35** clearly showed a strong singlet at +19.4 ppm with a satellite doublet ($^1J_{P\text{-}Se}$ = 762 Hz) due to $^{31}P\text{-}^{77}Se$ coupling. Performing the same reaction and ^{31}P NMR analysis on a variety of other commonly used phosphine ligands yielded the $^1J_{P\text{-}Se}$ coupling constants shown in Fig. 2. As the data clearly indi-

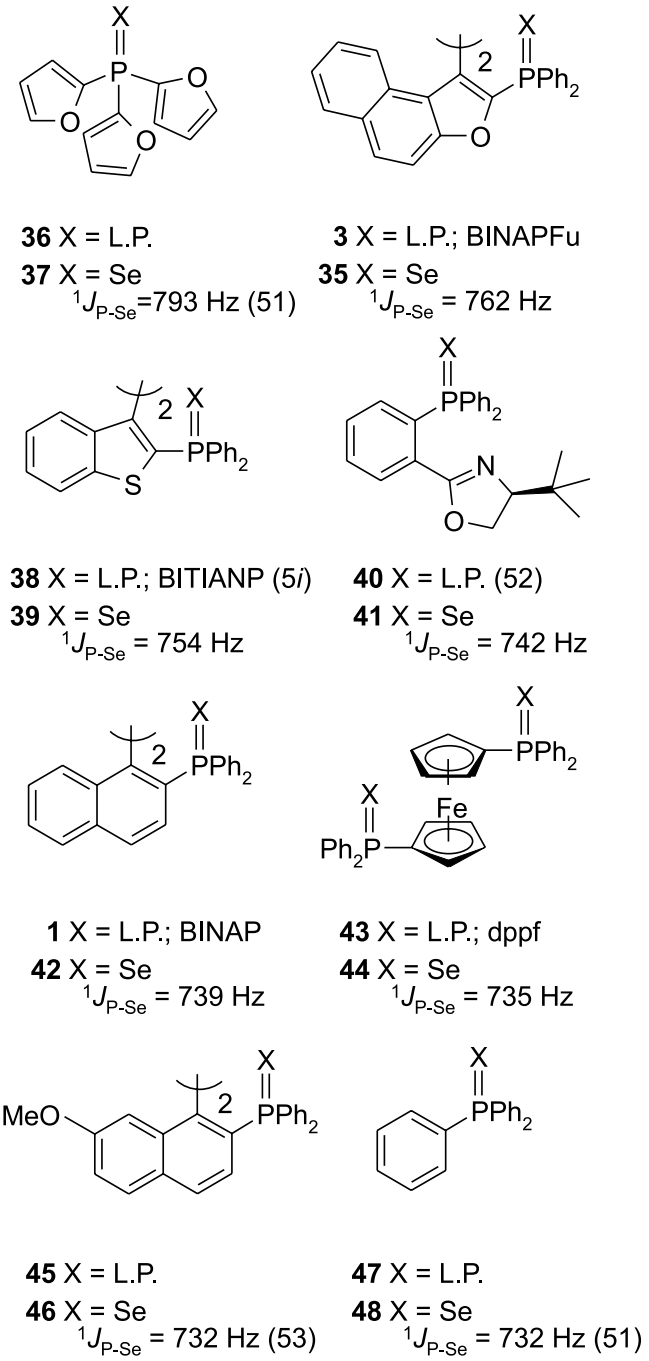
Scheme 9. (*a*) 3 mol L^{-1} H_2SO_4, 1,4-dioxane, 100 °C, 24 h, >95%; (*b*) 20 equiv $SiCl_3H$, 24 equiv Et_3N, xylenes, 150 °C, 3 h, >95%; (*c*) 10 equiv Se powder (100 mesh), $CHCl_3$, 60 °C, 5 h, 97%.



cates, the BINAPFu ligand **3** is far less basic than both triphenylphosphine (**47**) and BINAP (**1**). Moreover, BINAPFu **3** is significantly less basic that Benincori's benzothiophene-derived ligand BITIANP (**38**) (5*i*). Phosphinoaryl oxazoline ligand **40**, which has gained much attention in enantioselective allylic alkylation reactions (52), is also less basic than triphenylphosphine but significantly more basic than either BINAPFu or BITIANP. The small difference observed between the coupling constants for bis-selenides **42** and **46** suggest that this measure of σ-donor ability can be quite a sensitive technique. The latter selenide, derived from 7,7′-dimethoxy-2,2′-bis(diphenylphosphino)-1,1′-binaphthalene (**45**) (53), is slightly more basic than BINAP, owing to the electron-donating capacity of the remote 7,7′-methoxy substituents.

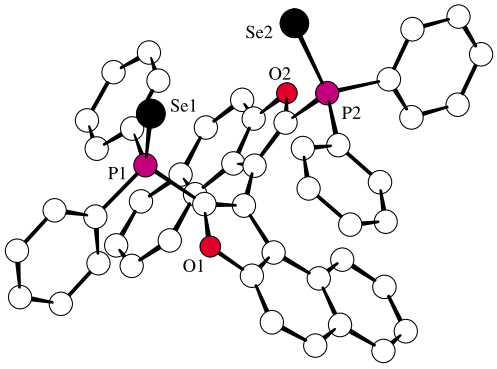
Having demonstrated that the electronic properties of BINAPFu **3** and BINAP **1** are dissimilar, with the former ligand resembling those of tri-2-furylphosphine (**36**), attention was focused on the final task of characterization. The absolute configuration of the biaryl axis needed to be elucidated. With phosphine selenide **35** in hand, prepared from optically pure (–)-BINAPFu (vide supra), it was rationalized that X-ray diffraction using the Bijvoet method (54) could determine the stereochemical assignment. Single crystal analysis of compound **35** furnished the structure depicted in Fig. 3. By refining the inverted structure and evaluating the Flack parameter, it was shown that the *S*-configuration was present in the crystal. Hence, phosphinimine **31a** corresponds to (*S*)-(–)-BINAPFu, while phosphinimine **31b** corresponds to (*R*)-(+)-BINAPFu. This relationship was verified via single crystal X-ray diffraction analysis of phosphinimine **31a** (Fig. 3). In this case, Bijvoet analysis was not required since the absolute stereochemistry of the biaryl axis could be ascertained by simple comparison with the known configurations of the camphor residues. Since (1*S*)-(+)-10-camphorsulfonyl chloride was used to prepare resolving agent **30**, it follows from Fig. 3 that phosphinimine **31a** is the *S*-axial diastereomer.

Fig. 2. $^1J_{P\text{-}Se}$ coupling constants for selected phosphine selenides.

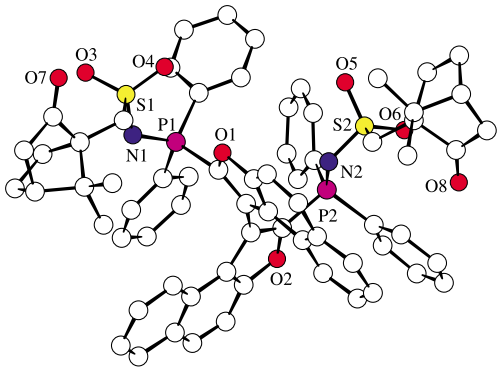


Having attained the goal of preparing and optically resolving a C_2-symmetric bifuran analogue of BINAP, the task of

Fig. 3. X-ray crystal structures of phosphine selenide **35** (one solvent molecule of crystallization (CH_3CN) omitted for clarity) and phosphinimine **31a** (unit cell contains two identical molecules of compound **31a** and five molecules of CH_3CN (not shown)); hydrogen atoms omitted for clarity.



35



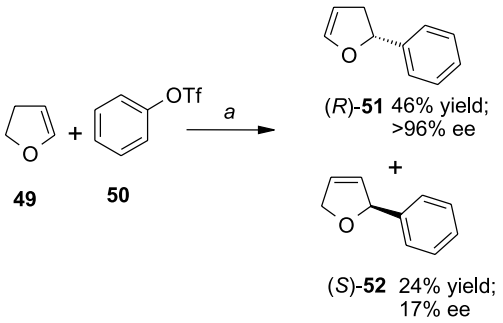
31a

evaluating the performance of this ligand in metal-mediated asymmetric transformations remained.

Application of BINAPFu in the Heck arylation of 2,3-dihydrofuran using (*R*)-BINAP and (*R*)-BINAPFu

The asymmetric Heck arylation of 2,3-dihydrofuran (**49**), first reported by Hayashi and co-workers (24, 55), has been studied extensively and was therefore chosen as a suitable reaction to study using the BINAPFu ligand (Scheme 10). The Heck arylation of 2,3-dihydrofuran (**49**) was performed under a variety of reaction conditions (Table 1) on a 1.0 mmol scale (based on PhOTf) in sealed, screw-cap sample vials. In all cases, the Pd-catalysts (3 mol%) were formed in situ at 60 °C in the presence of an amine base under argon for 30 min. In general, catalysts formed using (*R*)-BINAP were bright orange in color, while catalysts derived from (*R*)-BINAPFu were bright yellow in color. After formation of the catalyst, PhOTf and 2,3-dihydrofuran

Scheme 10. (*a*) 3.0 equiv DIPEA, 3 mol% $Pd(OAc)_2$, 6 mol% (*R*)-BINAP, C_6H_6, 30 °C, 66 h.

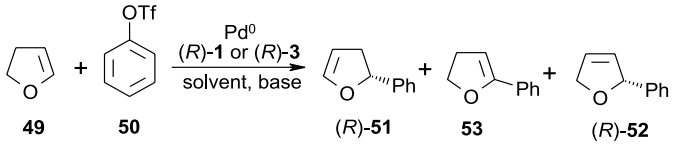


(5.1 mmol) were carefully added by microlitre-syringe. The argon-purged vessels were subsequently sealed and placed in a thermostatically controlled oil bath for a specified period. In light of our inability to repeat Hayashi's experimental results, coupled with the fact that the reported ee values were ascertained using the chiral shift NMR analysis method, it was deemed prudent to perform control experiments using commercially supplied (*R*)-BINAP. To this end, all experiments were performed in parallel, using both the (*R*)-BINAP and (*R*)-BINAPFu catalyst systems, and were analyzed using chiral GC analysis conditions.

Employing Hayashi's original Heck arylation conditions with the (*R*)-BINAP ligand afforded 2,3-dihydrofuran product **51** in 27% yield and 86% ee (entry 1b). However, the reaction was only 30% complete after a 9 day period at 30 °C. In our hands, neither Hayashi's reported yield (78%) (55*a*) nor the enantiomeric excess of the 2,3-dihydrofuran product **51** (93%) (55*a*) were attainable under these reaction conditions. Utilizing (*R*)-BINAPFu under otherwise identical conditions afforded a 21% yield of product **51**, favoring the *R*-configuration in >97% ee. Extraordinarily, the enantiomeric purity of the minor isomer **52** was also greater than when (*R*)-BINAP was employed, and the sense of enantioselection was reversed. In other words, both products **51** and **52** were enriched in the *R*-configuration, suggesting that the reaction with BINAPFu may not follow Hayashi's proposed kinetic resolution mechanism. Repeating this experiment using Proton Sponge® (3.0 equiv) as the base provided much lower product conversion factors (entries 2a and 2b). Since the conditions reported in the literature for this reaction failed to give useful product conversions, alternative palladium sources, solvents, bases, and reaction temperatures were investigated.

A significant increase in product conversion was observed upon using a polar solvent such as 1,4-dioxane with DIPEA as the base (entry 3). The effect was more pronounced for the (*R*)-BINAPFu catalyst, giving a 61% yield of the 2,3-dihydrofuran product **51** (97% ee, entry 3a). Under identical conditions, the (*R*)-BINAP catalyst afforded only 43% yield of **51** (73% ee, entry 3b), albeit with higher regioselectivity. Again, the 2,5-dihydrofuran product **52** was formed with *S*-configuration selectivity using the (*R*)-BINAP catalyst, while the *R*-configuration was preferred with the (*R*)-BINAPFu catalyst. Since NMP has been used successfully in the Stille reaction with trifurylphosphine-derived catalysts (56), it was conceived that this polar solvent may also work well in the present case. Employing NMP as the solvent also afforded

Table 1. Asymmetric Heck results with BINAPFu (3) and BINAP (1).



Entry	Ligand	Solvent	T (°C)	Conversion (%)	Yield (% (% ee))		
					(*R*)-**51**	**53**	(*R*)-**52**
1a	(*R*)-**3**	C_6H_6[a]	30[b]	33	21 (>97)	1	11 (75)
1b	(*R*)-**1**	C_6H_6[a]	30[b]	30	27 (86)	0	3 (51)[c]
2a	(*R*)-**3**	C_6H_6[a]	30[d]	17	1 (—)	3	13 (93)
2b	(*R*)-**1**	C_6H_6[a]	30[d]	1	1 (—)	—	—
3a	(*R*)-**3**	Dioxane[a]	30[b]	71	61 (>97)	1	9 (57)
3b	(*R*)-**1**	Dioxane[a]	30[b]	46	43 (73)	1	2 (46)[c]
4a	(*R*)-**3**	NMP[a]	30[b]	41	32 (>79)	1	8 (22)
4b	(*R*)-**1**	NMP[a]	30[b]	69	67 (72)	1	1 (38)[c]
5a	(*R*)-**3**	Dioxane[e]	50[b]	30	25 (76)	0	5 (37)
5b	(*R*)-**1**	Dioxane[e]	50[b]	56	53 (66)	1	2 (15)
6a	(*R*)-**3**	C_6H_6[e]	70[b]	31	26 (74)	1	4 (61)
6b	(*R*)-**1**	C_6H_6[e]	70[b]	99	77 (54)	3	19 (35)
7a	(*R*)-**3**	THF[e]	70[b]	83	77 (75)	1	5 (61)
7b	(*R*)-**1**	THF[e]	70[b]	100	74 (53)	4	22 (71)
8a	(*R*)-**3**	DME[e]	85[b]	100	95 (73)	1	4 (64)
8b	(*R*)-**1**	DME[e]	85[b]	100	55 (48)	13	32 (72)
9a	(*R*)-**3**	Dioxane[e]	100[b]	100	90 (77)	1	10 (40)
9b	(*R*)-**1**	Dioxane[e]	100[b]	100	73 (41)	9	17 (26)
10a	(*R*)-**3**	DMF[e]	90[b]	100	94 (71)	3	3 (39)
10b	(*R*)-**1**	DMF[e]	90[b]	100	55 (35)	5	41 (47)
11a	(*R*)-**3**	Dioxane[e]	100[f]	100	83 (80)	3	14 (40)
11b	(*R*)-**1**	Dioxane[e]	100[f]	100	62 (50)	5	33 (11)
12a	(*R*)-**3**	Dioxane[e]	100[d]	100	66 (79)	1	33 (44)
12b	(*R*)-**1**	Dioxane[e]	100[d]	100	93 (54)	4	3 (23)
13a	(*R*)-**3**	Dioxane[a]	100[b]	100	94 (74)	1	7 (64)
13b	(*R*)-**1**	Dioxane[a]	100[b]	100	90 (57)	2	12 (79)

[a]3 mol% $Pd(OAc)_2$ for 9 days.
[b](i-Pr)$_2$NEt used as base.
[c]*S*-configuration was favoured.
[d]Proton sponge used as base.
[e]1.5 mol% Pd_2dba_3 for 7 days.
[f]PMP used as base.

higher conversion factors (entries 4a and 4b) than those observed using benzene (entries 1a and 1b), but the ee of the major product **51** was diminished (79%) relative to the result obtained with dioxane (97%). The same general trend in enantioselection was observed, wherein the absolute configuration of the 2,5-dihydrofuran product **52** differed between the two catalyst systems studied. The use of $Pd(OAc)_2$ as the pre-catalyst was not required to achieve good enantioselectivity. Utilizing the $Pd_2(dba)_3$–(*R*)-BINAPFu catalyst system in dioxane at 50 °C with DIPEA as the base afforded a 25% yield of compound **51** in 76% ee (entry 5a). The same conditions in conjunction with a $Pd_2(dba)_3$–(*R*)-BINAP catalyst system furnished compounds **51** and **52** in higher conversion and isomeric selectivity but with reduced enantioselectivity (entry 5b). Using these conditions, both catalysts provided 2,5-dihydrofuran product **52**, favoring the *R*-configuration. Virtually the same product conversion, regioselectivity, and ee were obtained using the (*R*)-BINAPFu ligand in benzene at 70 °C (entry 6a). However, a significant increase in conversion and decrease in isomer selectivity was observed using (*R*)-BINAP in benzene at 70 °C (entry 6b). Although the conversion was certainly poorer with the (*R*)-BINAPFu catalyst, it was encouraging to note that respectable enantioselectivities could also be achieved at higher temperatures. In other words, this result suggested that it may be possible to get this reaction to go to completion while still obtaining reasonable levels of enantioselection.

A study of various ethereal solvents at elevated temperature (entries 7–9) revealed that full conversion was attainable, without a significant loss in enantioselectivity, using 1,4-dioxane as the solvent at 100 °C (entries 9a and 9b). Moreover, at high temperatures, the (*R*)-BINAPFu catalyst

afforded less of the unwanted conjugated isomer **53** and afforded higher selectivity in favor of the 2,3-dihydrofuran product **51**. In all cases, utilization of high-temperature conditions (>50 °C) provided the 2,5-dihydrofuran product **52** enriched in the *R*-isomer, regardless of whether (*R*)-BINAP or (*R*)-BINAPFu was used as the ligand. Conducting the reaction in DMF at 90 °C with DIPEA as the base and an (*R*)-BINAPFu-derived catalyst afforded excellent isomer selectivity with a slight reduction in enantioselectivity (entry 10a). At elevated temperatures, the conditions that employed dioxane as the solvent and PMP as the tertiary amine base yielded the 2,3-dihydrofuran product **51** in 80% ee with only modest regioselectivity (entry 11a). Ozawa, Kubo, and Hayashi have reported (55*b*) higher degrees of enantioselection, at the expense of regioselectivity, using Proton Sponge® as the base. Using this base in dioxane at 100 °C with the (*R*)-BINAPFu catalyst did not result in increased enantioselectivity (entry 12a). However, in accordance with Hayashi's findings, a significant decrease in isomer selectivity was observed. Finally, changing back to the $Pd(OAc)_2$ catalyst and using dioxane as the solvent at 100 °C with DIPEA as the base gave a slight increase in product regioselectivity (entry 13a, cf. entry 9a).

Examining the results listed in Table 1 as a whole, a few general trends immediately emerge. Firstly, the enantiomeric purity of the 2,3-dihydrofuran isomer **51** was always higher when the (*R*)-BINAPFu-derived catalyst system was used. At low temperatures (<50 °C), employing dioxane as the solvent with DIPEA as the base afforded the best balance between conversion (71%) and enantioselectivity of the 2,3-dihydrofuran product **51** (97%). However, in this temperature domain, the (*R*)-BINAP catalyst generally affords a much higher isomer selectivity. The (*R*)-BINAPFu catalyst consistently provides products **51** and **52**, both enriched in the *R*-configuration. In contrast, the (*R*)-BINAP catalyst gives compounds **51** and **52** of opposite configuration only at low temperature (30 °C). At higher temperatures (>70 °C), full conversion of the phenyl triflate can be realized with either catalyst system. Under such conditions, the (*R*)-BINAPFu catalyst typically gives the major product in 71%–80% ee, while the (*R*)-BINAP catalyst produces product **51** in 35%–57% ee. High-temperature conditions, in conjunction with the (*R*)-BINAPFu catalyst system, give rise to higher isomeric ratios in favor of the 2,3-dihydrofuran product **51** and attenuated formation of the conjugated isomer **53**, relative to the corresponding reactions employing the (*R*)-BINAP-derived catalyst. Perhaps of greatest significance is the observation that high enantioselectivity for the 2,3-dihydrofuran isomer **51** does not seem to correlate with poor isomeric selectivity. Recall that Hayashi, Ozawa, and coworkers used this argument as strong evidence supporting a kinetic resolution mechanism (24). Notwithstanding our inability to repeat these workers' findings (vide supra), the experimental results obtained using the BINAPFu ligand suggest that this assertion may indeed be incorrect.

Conclusions

We have designed, synthesized, and resolved a new binaphthofuran ligand (BINAPFu) for use in asymmetric metal-catalyzed reactions. The ligand is easily prepared in 5 steps from readily available starting material. A new resolution procedure was designed for phosphines, involving the Staudinger reaction with a camphor sulfonyl azide derivative. BINAPFu outperformed BINAP in the Heck reaction between phenyl triflate and 2,3-dihydrofuran. Further structural modifications of BINAPFu are currently underway to improve the enantioselectivity of high-temperature Heck arylation reactions.

Experimental section

General comments

Melting points were determined using either an Electrothermal® melting point apparatus in sealed capillary tubes or an A.H. Thomas hot-stage and are uncorrected. Boiling points are uncorrected and refer to measured air-bath temperatures using a Kugelrohr short-path distillation apparatus. Optical rotation data was obtained on a Rudolph Autopol III polarimeter using a quartz cell with a 10 cm path length. Infrared spectra were recorded on a Mattson Galaxy Series 4030 FT-IR spectrometer. ^{1}H and ^{13}C NMR spectra were obtained on a Bruker ACE 200 (^{1}H, 200 MHz; ^{13}C, 50 MHz), a Bruker AM 400 (^{1}H, 400 MHz; ^{13}C, 100 MHz), or a Bruker DRX 400 (^{1}H, 400 MHz; ^{13}C, 100 MHz) spectrometer. Unless otherwise noted, deuteriochloroform was used as the NMR solvent. ^{31}P NMR spectra were obtained on a Varian XL 200 (^{31}P, 81 MHz), a Bruker AMX 300 (^{31}P, 121.5 MHz), or a Bruker DRX 400 (^{31}P, 162 MHz) spectrometer using an external reference of 30% H_3PO_4 in D_2O set to 0 ppm. Unless specified otherwise, ^{31}P NMR samples were prepared using deuteriochloroform as the solvent. GC–MS analysis was performed on a Hewlett-Packard 5890 Series II gas chromatograph equipped with a Hewlett-Packard OV 101, low polarity, 12 m × 0.2 mm column, in conjunction with a Hewlett-Packard 5971A mass selective detector. Low-resolution mass spectra on nonvolatile samples were obtained on a VG 7070 or a Kratos MS80 mass spectrometer using 70 eV ionization with direct probe sample introduction. HR-MS and FAB-MS analyses were obtained using a Kratos MS80 spectrometer. Elemental analyses were obtained from the University of Calgary's Control Equipment Corporation 440 Elemental Analyzer. X-ray structure determination[3] was performed by Dr. M. Parvez (University of Calgary), using a Rigaku AFC6S diffractometer with graphite monochromated Mo Kα radiation, or by Dr. R. McDonald (University of Alberta), using a Bruker P4 diffractometer equipped with a SMART 1000 CCD area detector and 18 kW rotating anode X-ray generator. Column chromatography was performed using silica gel 60 (E. Merck, 0.04–0.063 mm, 230–400 mesh), using the flash method (57). Sol-

[3] Supplementary data may be purchased from the Depository of Unpublished Data, Document Delivery, CISTI, National Research Council Canada, Ottawa, ON K1A 0S2, Canada (http://www.nrc.ca/cisti/irm/unpub_e.shtml for information on ordering electronically). CCDC 221199, 221200, and 147246 contain the supplementary data for this paper. These data can be obtained, free of charge, via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, U.K.; fax +44 1223 336033; or deposit@ccdc.cam.ac.uk).

vent systems refer to mixtures, by volume, of hexanes and ethyl acetate unless specified otherwise. Analytical HPLC analyses were performed on an ICI LC 1440 instrument equipped with an ICI LC 1150 HPLC Pump (C_{18} column or Chiralcel OJ column with an ICI LC 12010 UV–vis detector) or a Waters 4886 instrument (Nova-Pak C_{18} reverse-phase column or Chiralcel OB column with a Waters 486 UV detector). Preparative HPLC was done on the latter instrument equipped with a 25 mm × 100 mm Water Nova-Pak C_{18} reversed-phase column. Chiral gas chromatography was performed on either a Shimadzu GC-9A gas chromatograph (25 m × 0.33 mm (i.d.) Cydex-B fused silica column with a flame ionization detector) or a Varian Star 3400 CX instrument (30 m × 0.32 mm (i.d.) Cyclodex-B fused silica column with a flame ionization detector).

Chlorination of 1-acetyl-2-hydroxynaphthalene (8)

Method 1

To a solution of 1-acetyl-2-hydroxynaphthalene **8** (100 mg, 0.537 mmol) in CH_2Cl_2 (2 mL), H_2O (11 μL, 0.59 mmol), and MeOH (23 μL, 0.59 mmol), was added SO_2Cl_2 (53 μL, 0.65 mmol). The mixture was refluxed under an N_2 atmosphere for 1 h and subsequently quenched with H_2O (20 mL). The solution was extracted with ether (20 mL), washed with H_2O (2 × 20 mL), and dried ($MgSO_4$). Concentration of the organic phase afforded a greenish yellow oil. Only a trace amount of the desired product **9** was evident in the crude ^{1}H NMR spectrum.

Method 2

Hexachloro-2,4-cyclohexadienone (19) (111 mg, 0.371 mmol) was added to a solution of 1-acetyl-2-hydroxynaphthalene (69 mg, 0.37 mmol) in absolute ethanol (3 mL), and the mixture was refluxed under a nitrogen atmosphere for 15 h. The solvent was removed in vacuo to give a brown residue. ^{1}H NMR analysis showed that the major component of the mixture was unreacted starting material **8**, as well as a minor amount (<30%) of the desired α-chloroketone **9**, as evidenced by a singlet at 4.8 ppm corresponding to H-12. The product was not stable to column chromatography.

1-Acetyl-2-[(*tert*-butyldimethylsilyl)oxy]naphthalene (10)

To a solution of 1-acetyl-2-hydroxynaphthalene (**8**) (21.9 g, 0.117 mol) in Et_3N (75 mL, 0.538 mol) and CH_2Cl_2 (500 mL) was added TBSCl (19.4 g, 0.129 mmol). The mixture was stirred at room temperature (rt) for 18 h before it was quenched with H_2O (500 mL). The mixture was then stirred for 1 h and extracted with ether (3 × 500 mL), and the pooled organic extracts were washed with a 10% HCl solution (2 × 500 mL) and H_2O (2 × 500 mL). The organic layer was dried ($MgSO_4$) and concentrated under reduced pressure to give 31.4 g (89%) of the TBS ether **10** as a light yellow oil. ^{1}H NMR (200 MHz) δ: 0.28 (s, 6H), 1.02 (s, 9H), 2.68 (s, 3H), 7.10 (d, J = 12 Hz, 1H), 7.47 (m, 2H), 7.76 (m, 2H), 7.78 (d, J = 12 Hz, 1H). This material was used in the next step without further purification.

1-[(1-Trimethylsilyl)oxy]ethenyl-2-[(*tert*-butyldimethylsilyl)oxy]naphthalene (11)

To a solution of silyl ether **10** (31.4 g, 0.105 mol) in CH_2Cl_2 (600 mL) and Et_3N (73 mL, 0.52 mol) at 0 °C was added TMSOTf (24 mL, 0.13 mol). The mixture was warmed to rt and stirring was continued for 1 h under an N_2 atmosphere. The mixture was diluted with $CHCl_3$ (100 mL), washed with brine (2 × 300 mL), dried (Na_2SO_4), and evaporated to dryness under reduced pressure to give crude enol ether **11** in quantitative yield. ^{1}H NMR (200 MHz) δ: 0.18 (s, 9H), 0.27 (s, 6H), 1.09 (s, 9H), 4.39 (s, 1H), 4.74 (s, 1H), 7.07 (d, J = 11 Hz, 1H), 7.45 (m, 2H), 7.71 (m, 2H), 8.08 (d, J = 11 Hz, 1H). Trimethylsilyl enol ether **11** was used directly in the subsequent step.

1-(2-Bromoacetyl)-2-[(*tert*-butyldimethylsilyl)oxy]naphthalene (12)

In a flask equipped with a dropping funnel, TMS enol ether **11** (38.9 g, 0.105 mol) was dissolved in CCl_4 (450 mL) and cooled to 0 °C. A solution of bromine (5.66 mL, 0.119 mol) in CCl_4 (100 mL) was placed in the dropping funnel, and 20 mL of this solution was added to the reaction mixture; after warming to rt, the remaining 80 mL of the bromine solution was added over a 30 min period. The mixture was stirred for a further 30 min and diluted with H_2O (200 mL), and the layers were separated. The aqueous layer was extracted with $CHCl_3$ (2 × 100 mL), and the combined organic layers were washed with an $Na_2S_2O_3$ solution (200 mL) and H_2O (2 × 200 mL). The organic fraction was dried (Na_2SO_4) and concentrated in vacuo to furnish 39.5 g of compound **12** as a light orange oil. ^{1}H NMR (200 MHz) δ: 0.29 (s, 6H), 1.05 (s, 9H), 4.58 (s, 2H), 7.08 (d, J = 11 Hz, 1H), 7.50 (m, 2H), 7.78 (m, 2H), 7.85 (d, J = 11 Hz, 1H).

Naphtho[2,1-*b*]furan-3(2H)-one (7) from bromide 12

To a solution of compound **12** (39.7 g, 0.105 mol) in THF (400 mL) at 0 °C was slowly added TBAF (1.0 mol L^{-1} solution in THF, 110 mL, 0.110 mol) under an N_2 atmosphere. The mixture was allowed to stir at 0 °C for 10 min and at rt for 15 min. The dark purple solution was then quenched with NH_4Cl solution (100 mL), and the THF was removed in vacuo. The remaining residue was extracted with ether (3 × 100 mL), and the combined ether layers were washed with brine (100 mL) and H_2O (3 × 150 mL), dried ($MgSO_4$), and evaporated under reduced pressure. The crude product was purified by column chromatography (20:1, hexanes – ethyl acetate) to give 15.1 g (72% from compound **11**) of cyclized ketone **7** as a light yellow solid: mp 133 °C (lit (58) 133 °C). IR (KBr) (cm^{-1}): 1688. ^{1}H NMR (200 MHz, $CDCl_3$) δ: 8.75 (d, J = 8.2 Hz, 1H), 8.05 (d, J = 9.0 Hz, 1H), 7.82 (d, J = 8.0 Hz, 1H), 7.66 (dt, J = 7.6, 0.9 Hz, 1H), 7.47 (dt, J = 7.6, 1.0 Hz, 1H), 7.24 (dd, J = 7.8, 2.4 Hz, 1H), 4.77 (s, 2H). ^{13}C NMR (50 MHz, $CDCl_3$) δ: 199.9 (C), 176.6 (C), 139.7 (CH), 129.8 (CH), 129.2 (C), 129.1 (C), 126.4 (CH), 125.4 (CH), 123.1 (CH), 113.9 (CH), 113.5 (C), 75.5 (CH_2). MS, m/z (relative intensity, %): 184 ($[M]^+$, 74), 155 (87), 126 (100). Exact mass calcd for $C_{12}H_8O$: 184.0524; found: 184.0520.

Naphtho[2,1-*b*]furan-3(2H)-one (7) from 2-naphthoxyacetic acid (13)

2-Naphthoxyacetic acid (20.1 g, 99.3 mmol) in dry benzene (1000 mL) was treated with a catalytic amount of pyridine and 2 equiv $SOCl_2$ (14.4 mL, 198.6 mmol) at reflux under an N_2 atmosphere for 2 h. The cooled solution was

then concentrated in vacuo, and the resulting residue was taken up into C_6H_6 (500 mL) and cooled to 0 °C. To the solution was then added $AlCl_3$ (19.8 g, 148.9 mmol), and the resulting solution was stirred for 12 h at ambient temperature. The mixture was then quenched with brine and extracted with benzene (2 × 100 mL). The combined organic extracts were then washed with water (2 × 100 mL) and filtered through neutral alumina. The filtrate was then concentrated under reduced pressure to afford the desired product **7** (17.2 g, 95%), which was found to be clean by ^{1}H NMR analysis. Spectra were identical to compound **7** made from bromide **12**.

3,3′-Binaphtho[2,1-*b*]furan (5)

Into a 1 L, 3-neck round-bottom flask equipped with an addition funnel was weighed activated zinc dust (29.3 g, 0.448 mol) and DME (300 mL). The mixture was cooled to –78 °C, and to it was carefully added $TiCl_4$ dropwise via syringe over a 30 min period. The resulting blue mixture was warmed to reflux, and the starting naphthoketone **7** (10.0 g, 54.4 mmol in 100 mL DME) was added dropwise over a 20 min period. The resulting mixture was heated to reflux under an N_2 atmosphere for 18 h. The cooled mixture was then filtered through a coarse sintered glass funnel, and the filtrate was concentrated under reduced pressure to give **6** as an orange, gummy residue. This residue was immediately dissolved in C_6H_6 (300 mL) and treated with DDQ (6.17 g, 27.2 mmol) at reflux under an N_2 atmosphere for 4 h. The cooled mixture was then quenched with saturated $Na_2S_2O_3$ and extracted with ether (3 × 100 mL). The combined organic extracts were dried ($MgSO_4$) and concentrated to afford the crude title compound. The product **5** was readily purified by flash chromatography (100:1 hexanes – ethyl acetate) to afford the analytically pure biaryl (7.13 g, 78%). mp 292–294 °C. IR (KBr) (cm^{-1}): 2850, 1436. ^{1}H NMR (200 MHz, $CDCl_3$) δ: 7.94 (d, *J* = 8.2 Hz, 1H), 7.86 (s, 1 H), 7.84 (m, 2H), 7.75 (d, *J* = 8.5 Hz, 1H), 7.35 (dt, *J* = 7.5, 1.0 Hz, 1H), 7.09 (dt, *J* = 7.7, 1.3 Hz, 1H). ^{13}C NMR (50 MHz, $CDCl_3$) δ: 153.5 (C), 142.8 (CH), 130.8 (C), 128.6 (CH), 128.4 (C), 126.4 (CH), 126.3 (CH), 124.5 (CH), 123.3 (CH), 112.1 (C), 113.9 (C), 112.6 (CH). MS, *m*/*z* (relative intensity, %): 334 ([M]$^+$, 100), 305 (31), 276 (32), 138 (18). Exact mass calcd for $C_{24}H_{14}O_2$: 334.0994; found: 334.0970. Anal calcd for $C_{24}H_{14}O_2$: C 86.20, H 4.22; found: C 85.96, H 4.04.

2,2′-Bis(diphenylphosphonyl)-3,3′-binaphtho[2,1-*b*]furan (14)

3,3′-Binaphtho[2,1-*b*]furan **5** (0.593 g, 1.776 mmol) in dry Et_2O (30 mL) was lithiated with *t*-BuLi (2.61 mL, 4.440 mmol, 1.7 mol L^{-1} solution in hexanes) at 0 °C. After 1 h at 0 °C, the vessel was warmed to rt and stirred for a further 2 h under an N_2 atmosphere. To the mixture was then added freshly distilled diphenylphosphinic chloride (0.85 mL, 4.440 mmol), and the resulting white slurry was stirred overnight at room temperature. The reaction mixture was then quenched with water and extracted with $CHCl_3$ (3 × 50 mL). The combined organic extracts were washed with 10% $NaHCO_3$, water, and brine. The organic phase was then dried ($MgSO_4$) and concentrated in vacuo to afford a light yellow solid residue. The crude material **14** was purified by column chromatography (3:1 CH_2Cl_2–EtOAc → 19:1 CH_2Cl_2–MeOH) to afford the title compound (1.150 g, 88%). mp 289–290 °C. IR (KBr) (cm^{-1}): 2924, 1437, 1120. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.87 (d, *J* = 8.1 Hz, 1H), 7.83 (d, *J* = 9.1 Hz, 1H), 7.72 (m, 2H), 7.64 (d, *J* = 9.0 Hz, 1H), 7.56 (d, *J* = 7.3 Hz, 1H), 7.53 (d, *J* = 7.3 Hz, 1H), 7.46 (d, *J* = 8.3 Hz, 1H), 7.36 (m, 2H), 7.23 (m, 3H), 7.06 (t, *J* = 7.6 Hz, 1H), 6.96 (dt, *J* = 7.7, 3.1 Hz, 2H). ^{13}C NMR (50 MHz, $CDCl_3$) δ: 155.5 (d, *J* = 8 Hz, C), 145.8 (d, *J* = 128 Hz, C), 132.1 (CH), 132.1 (d, *J* = 35 Hz, C), 132.0 (CH), 131.9 (d, *J* = 3 Hz, CH), 130.8 (C), 129.9 (d, *J* = 31 Hz, C), 128.7 (CH), 128.1 (d, *J* = 13 Hz, CH), 127.6 (d, *J* = 13 Hz, CH), 126.9 (CH), 124.8 (CH), 124.6 (C), 122.7 (CH), 121.5 (d, *J* = 8 Hz, C), 112.6 (CH). ^{31}P NMR (81 MHz, $CDCl_3$) δ: 16.5. MS, *m*/*z* (relative intensity, %): 533 ([M$^+$ – P(O)Ph_2], 100), 201 (54). Exact mass calcd for $C_{48}H_{32}P_2O_4$: 734.1778; found: 734.1731.

(±)-2,2′-Bis(diphenylphosphino)-3,3′-binaphtho[2,1-*b*]furan (3)

3,3′-Binaphtho[2,1-*b*]furan **5** (3.4 g, 10.2 mmol) in dry Et_2O (130 mL) was lithiated with *t*-BuLi (11.2 mL, 22.4 mmol, 2.0 mol L^{-1} solution in hexanes) at 0 °C. After 1 h at 0 °C, the vessel was warmed to rt and stirred for a further 2 h under an N_2 atmosphere. To the mixture was then added freshly distilled chlorodiphenylphosphine (4.0 mL, 22.4 mmol), and the resulting white slurry was stirred overnight at room temperature. The reaction mixture was quenched with water and extracted with $CHCl_3$ (3 × 125 mL). The combined organic extracts were washed with 10% $NaHCO_3$, water, and brine. The organic phase was dried ($MgSO_4$) and concentrated in vacuo to afford a light brown solid residue. The crude material (±)-**3** was purified by crystallization ($CHCl_3$–MeOH) to afford the title compound (6.49 g, 91%). mp 228–229 °C. IR (KBr) (cm^{-1}): 3052, 1433. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.90 (d, *J* = 8.1 Hz, 1H), 7.84 (d, *J* = 9.0 Hz, 1H), 7.76 (d, *J* = 9.1 Hz, 1H), 7.62 (d, *J* = 8.3 Hz, 1H), 7.37 (m, 2H), 7.35–7.30 (m, 4H), 7.24–7.14 (m, 5H), 7.04 (td, *J* = 7.4, 1.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 156.3 (C), 152.9 (d, *J* = 34 Hz, C), 135.4 (d, *J* = 71 Hz, C), 133.7 (CH), 133.6 (CH), 133.5 (CH), 130.7 (C), 128.6 (d, *J* = 4 Hz, CH), 128.5 (CH), 128.3 (C), 128.1 (d, *J* = 2 Hz, CH), 127.4 (CH), 126.5 (d, *J* = 35 Hz, C), 126.7 (CH), 124.5 (CH), 123.0 (CH), 122.5 (C), 112.9 (CH). ^{31}P NMR (81 MHz, $CDCl_3$) δ: –32.3. MS, *m*/*z* (relative intensity, %): 625 ([M$^+$ – Ph], 1), 517 (37), 408 (79), 183 (100). Exact mass calcd for $C_{48}H_{32}P_2O_2$: 702.1878; found: 702.1841.

Preparation of bis-*P*-borane-(R^*_{ax})-2,2′-bis[(8*R*,9*R*)-*N*,*N*′-dimethyl-1,3-diazahexahydro-2-phosphinoindan-2-yl]-3,3′-binaphtho[2,1-*b*]furan complex (23a) and bis-*P*-borane-(S^*_{ax})-2,2′-bis[(8*R*,9*R*)-*N*,*N*′-dimethyl-1,3-diazahexahydro-2-phosphinoindan-2-yl]-3,3′-binaphtho[2,1-*b*]furan complex (23b)

To a solution of naphtho[*b*]furan **5** (0.173 g, 0.518 mmol) in Et_2O (5.0 mL) at –78 °C was added 2.05 equiv of *t*-BuLi (1.7 mol L^{-1} in hexanes, 0.62 mL, 1.1 mmol). The resulting mixture was warmed to 0 °C and stirred under an atmosphere of nitrogen for 1.5 h. To the vessel was then added enantiopure 2-chloro-2,2′-bis[8*R*,9*R*]-*N*,*N*′-dimethyl-1,3-diazahexahydro-2-phosphinoindane (**22**) (38, 39) (0.219 g,

1.06 mmol). The reaction contents were allowed to warm to rt over a 1 h period and subsequently left to stir for 24 h. To the vessel was then added borane – dimethyl sulfide complex (2.0 mol L^{-1} solution in THF, 0.531 mL, 1.06 mmol), and the resulting mixture was left to react for a further 24 h. The reaction contents were then quenched with brine (50 mL) and extracted with $CHCl_3$ (3 × 50 mL). The combined organic extracts were dried ($MgSO_4$) and concentrated under reduced pressure to afford a light yellow oil. The crude material was purified by column chromatography (15:1) to afford a 1:1 mixture of the title compounds (0.270 g, 74%). A small sample (~3 mg) of each pure diastereomer was obtained by exhaustive preparative high performance liquid phase chromatography (Nova-Pak C_{18}, 93:7 $CH_3CN:H_2O$, 1.0 mL min^{-1}, 320 nm detection). The first isomer to elute, compound **23a**, was obtained as a colorless film exhibiting the following analytical data: IR (KBr) (cm^{-1}): 2937, 2387 (BH_3), 1462, 1025. ^{1}H NMR (400 MHz) δ: –0.50 to 0.63 (bq, 3H), 1.10–1.62 (m, 4H), 1.89 (t, *J* = 12.9 Hz, 2H), 2.00–2.13 (m, 2H), 2.19 (d, *J* = 14.5 Hz, 3H), 2.48 (td, *J* = 10.4, 3.0 Hz, 1H), 2.74 (d, *J* = 12.8 Hz, 3H), 3.18 (t, *J* = 9.6 Hz, 1H), 7.02 (t, *J* = 7.0 Hz, 1H), 7.32 (t, *J* = 7.0 Hz, 1H), 7.58 (d, *J* = 7.8 Hz, 1H), 7.82 (d, *J* = 9.1 Hz, 1H), 7.90 (d, *J* = 9.1 Hz, 1H), 7.91 (d, *J* = 7.8 Hz, 1H). ^{13}C NMR (100 MHz) (ppm): 24.7 (CH_2), 24.8 (CH_2), 29.0 (d, *J* = 8 Hz, CH_2), 29.3 (d, *J* = 5 Hz, CH_2), 30.4 (d, *J* = 3 Hz, CH_3), 32.6 (d, *J* = 10 Hz, CH_3), 65.8 (d, *J* = 3 Hz, CH), 68.4 (CH), 113.4 (CH), 122.8 (C), 122.9 (C), 123.5 (CH), 125.1 (CH), 126.4 (d, *J* = 19 Hz, C), 126.8 (CH), 128.9 (CH), 129.3 (CH), 131.3 (C), 150.4 (d, *J* = 30 Hz, C), 155.5 (d, *J* = 4 Hz, C). ^{31}P NMR (162 MHz) (ppm): +94.1 (q, *J* = 71 Hz). FAB-MS, *m/z* (relative intensity, %): 725 (48, $[M + Na]^+$). Compound **23b**, also obtained as a colorless film, had the following properties: IR (KBr) (cm^{-1}): 2935, 2390 (BH_3), 1461, 1003. ^{1}H NMR (400 MHz) δ: –0.48 (qd, *J* = 12.3, 3.6 Hz, 1H), 0.08 (m, 1H), 0.20–1.20 (bq, 3H), 0.78–0.97 (m, 2H), 1.28 (d, *J* = 8.6 Hz, 1H), 1.39 (d, *J* = 9.8 Hz, 2H), 1.65 (d, *J* = 8.9 Hz, 1H), 2.10 (td, *J* = 12.0, 3.2 Hz, 1H), 2.26 (m, 1H), 2.36 (d, *J* = 13.1 Hz, 3H), 2.62 (d, *J* = 14.2 Hz, 3H), 7.13 (t, *J* = 8.0 Hz, 1H), 7.36 (t, *J* = 7.1 Hz, 1H), 7.55 (d, *J* = 8.3 Hz, 1H), 7.88 (ABq, *J* = 9.2 Hz, 2H), 7.94 (d, *J* = 8.1 Hz, 1H). ^{13}C NMR (100 MHz) (ppm): 23.7 (CH_2), 24.1 (CH_2), 27.3 (d, *J* = 5 Hz, CH_2), 28.2 (d, *J* = 8 Hz, CH_2), 30.3 (d, *J* = 2 Hz, CH_3), 32.8 (d, *J* = 10 Hz, CH_3), 64.1 (d, *J* = 3 Hz, CH), 68.2 (CH), 113.5 (CH), 123.1 (d, *J* = 5 Hz, C), 123.2 (d, *J* = 9 Hz, C), 123.7 (CH), 125.3 (CH), 127.1 (CH), 128.7 (CH), 129.0 (C), 129.5 (CH), 131.5 (C), 150.3 (d, *J* = 40 Hz, C), 155.5 (d, *J* = 6 Hz, C). ^{31}P NMR (162 MHz) (ppm): +98.7 (q, *J* = 74 Hz). FAB-MS, *m/z* (relative intensity, %): 725 (7, $[M + Na]^+$).

2-Chloro-1,3-dimethyl-4,5-diphenyl-1,3,2-diazaphospholidine (26)

Under an argon atmosphere, (1*S*,2*S*)-*N*,*N*-dimethyl-1,2-diphenylethylenediamine (**25**) (40, 41) (1.59 g, 6.63 mmol) was dissolved in freshly distilled Et_2O (40 mL) and Et_3N (1.85 mL, 13.3 mmol). The reaction mixture was then cooled to –40 °C; phosphorus trichloride (0.578 mL, 6.63 mmol) was added; and the resultant thick white slurry was stirred for 30 min at –40 °C, for 1 h at 0 °C, and for 24 h at room temperature. The slurry was filtered under an atmosphere of argon, and the filtrate was concentrated under reduced pressure in an inert atmosphere to give a bright yellow solid residue. Crude phosphoramidous chloride **26**: ^{1}H NMR (200 MHz) δ: 2.55 (d, *J* = 19.5 Hz, 3H), 4.28 (d, *J* = 7.4 Hz, 1H), 7.11–7.40 (m, 5H). ^{13}C NMR (50 MHz) (ppm): 31.8 (d, *J* = 21 Hz, CH_3), 78.1 (d, *J* = 11 Hz, CH), 128.2 (CH), 128.7 (CH), 128.8 (CH), 137.1 (d, *J* = 2 Hz, C). ^{31}P NMR (62 MHz) (ppm): +173.6. Compound **26** was used in the subsequent step without further purification.

Bis-*P*-borane-(R^*_{ax})-2,2′-bis[(4*R*,5*R*)-1,3-dimethyl-4,5-diphenyl-1,3,2-diazaphospholidin-2-yl]-3,3′-binaphtho-[2,1-*b*]furan complex (27a) and bis-*P*-borane-(S^*_{ax})-2,2′-bis[(4*R*,5*R*)-1,3-dimethyl-4,5-diphenyl-1,3,2-diazaphospholidin-2-yl]-3,3′-binaphtho[2,1-*b*]furan complex (27b)

To a solution of naphtho[*b*]furan (**5**) (0.245 g, 0.734 mmol) in Et_2O (8.0 mL) at –78 °C was added 2.2 equiv of *t*-BuLi (1.7 mol L^{-1} in hexanes, 0.949 mL, 1.61 mmol). The resulting mixture was warmed to 0 °C and stirred under an atmosphere of nitrogen for 1.5 h. To the vessel was then added enantiopure diazaphospholidine reagent **26** (0.491 g, 1.61 mmol). The reaction contents were allowed to warm to rt over a 1 h period and subsequently left to stir for 3 h. To the vessel was then added borane – dimethyl sulfide complex (2.0 mol L^{-1} solution in THF, 1.10 mL, 2.20 mmol), and the resulting mixture was left to react for a further 4 h. The reaction contents were then quenched with brine (50 mL) and extracted with $CHCl_3$ (3 × 75 mL). The combined organic extracts were dried ($MgSO_4$) and concentrated in vacuo to afford a light yellow solid residue. The crude material was purified by column chromatography (15:1) to afford a 1:1 mixture of the title compounds. Separation of the mixture was achieved by recrystallization from a binary mixture of $CHCl_3$ and hexanes. Under these conditions, compound **27a** crystallized, diastereomerically pure, as long white needles (0.304 g, 46%) characterized by the following analytical data: mp 123–124 °C. IR (KBr) (cm^{-1}): 2869, 2392 (BH_3), 1455, 1147. ^{1}H NMR (300 MHz) δ: –0.32 to 0.84 (bs, 3H), 2.02 (d, *J* = 11.3 Hz, 3H), 2.71 (d, *J* = 13.3 Hz, 3H), 4.00 (d, *J* = 8.7 Hz, 1H), 4.80 (d, *J* = 8.7 Hz, 1H), 7.02–7.45 (m, 12H), 7.74 (d, *J* = 7.9 Hz, 1H), 7.84–8.10 (m, 3H). ^{13}C NMR (75 MHz) (ppm): 31.8 (d, *J* = 3 Hz, CH_3), 32.7 (d, *J* = 11 Hz, CH_3), 75.1 (d, *J* = 3 Hz, CH), 76.3 (CH), 112.7 (CH), 122.4 (C), 122.5 (C), 122.8 (CH), 124.8 (CH), 126.2 (C), 126.9 (CH), 127.7 (CH), 128.0 (CH), 128.5 (CH), 128.6 (CH), 128.8 (CH), 129.1 (CH), 131.1 (C), 137.6 (d, *J* = 9 Hz, C), 138.5 (d, *J* = 4 Hz, C), 151.6 (d, *J* = 26 Hz, C), 155.0 (d, *J* = 3 Hz, C). ^{31}P NMR (81 MHz) (ppm): +98.7 (bs). FAB-MS, *m/z* (relative intensity, %): 899 (1, $[M + H]^+$). Borane adduct **27b** was obtained isomerically pure after flash chromatographic (15:1) purification of the mother liquor. The following analytical data were recorded for this compound: mp 138–140 °C ($CHCl_3$–hexanes). IR (KBr) (cm^{-1}): 2869, 2390 (BH_3), 1455, 1146. ^{1}H NMR (400 MHz) δ: –0.32–1.00 (bs, 3H), 2.11 (d, *J* = 13.7 Hz, 3H), 2.86 (d, *J* = 11.1 Hz, 3H), 4.15 (d, *J* = 8.7 Hz, 1H), 4.61 (d, *J* = 8.7 Hz, 1H), 6.99 (t, *J* = 7.2 Hz, 1H), 7.12–7.23 (m, 2H), 7.25–7.34 (m, 4H), 7.35–7.50 (m, 5H), 7.70 (d, *J* = 8.2 Hz, 1H), 7.91–8.03 (m, 3H). ^{13}C NMR (100 MHz) (ppm): 31.8 (d, *J* = 5 Hz, CH_3), 33.4 (d, *J* = 11 Hz, CH_3), 75.1 (d, *J* = 2 Hz, CH), 76.4 (CH), 113.3

(CH), 122.9 (C), 123.0 (C), 123.5 (CH), 125.2 (CH), 126.7 (C), 126.9 (CH), 128.5 (CH), 128.6 (CH), 128.7 (CH), 128.8 (CH), 128.9 (CH), 129.3 (CH), 129.4 (CH), 131.5 (C), 137.6 (d, J = 9 Hz, C), 138.6 (d, J = 4 Hz, C), 151.3 (d, J = 26 Hz, C), 155.6 (d, J = 3 Hz, C). ^{31}P NMR (81 MHz) (ppm): +91.3 (bs). FAB-MS, *m/z* (relative intensity, %): 899 (4, [M + H]$^+$).

Phosphinimine 31a and 31b

BINAPFu (±)-**3** (2.65 g, 3.78 mmol) in THF (60 mL) was treated with (1*S*)-camphor-10-sulfonyl azide (59) (1.95 g, 7.55 mmol) at reflux under an N_2 atmosphere for 12 h. The cooled mixture was then concentrated under reduced pressure to afford a 1:1 mixture of **31a** and **31b** in quantitative yield. The diastereomeric products were separated by flash chromatography (9:1 $CHCl_3$–CH_3CN). The first spot off the column, **31a**, was determined to be the *S* axial isomer by single crystal X-ray analysis and afforded the following analytical data: mp 175–177 °C. $[\alpha]_D^{21}$ –72.1 (*c* 4.13, $CHCl_3$). IR (KBr) (cm^{-1}): 1745. ^{1}H NMR (200 MHz, $CDCl_3$) δ: 7.97–7.52 (m, 11H), 7.44 (t, J = 8.0 Hz, 1H), 7.38 (d, J = 8.4 Hz, 1H), 7.17 (t, J = 6.6 Hz, 1H), 6.88 (m, 2H), 2.51–2.26 (m, 2H), 2.18 (dt, J = 16.0, 3.0 Hz, 1H), 1.94–1.54 (m, 4H), 1.50–1.07 (m, 2H), 0.90 (s, 3H), 0.53 (s, 3H). ^{13}C NMR (50 MHz, $CDCl_3$) δ: 214.8 (C), 156.3 (d, J = 10 Hz, C), 140.1 (d, J = 154 Hz, C), 134.1 (CH), 134.0 (CH), 133.9 (CH), 133.8 (CH), 133.6 (CH), 133.0 (d, J = 1 Hz, CH), 131.2 (C), 129.9 (CH), 129.5 (CH), 129.4 (CH), 129.3 (CH), 129.0 (C), 128.5 (CH), 128.4 (CH), 128.0 (CH), 127.9 (d, J = 15 Hz, C), 127.4 (d, J = 81 Hz, C), 126.3 (d, J = 84 Hz, C), 125.9 (CH) 123.7 (CH), 122.5 (d, J = 8 Hz, C), 112.5 (CH), 78.0 (CH_2), 58.7 (C), 51.7 (d, J = 4 Hz, CH_2), 47.8 (C), 42.9 (CH), 27.3 (CH_2), 24.6 (CH_2), 20.4 (CH_3), 20.2 (CH_3). ^{31}P NMR (81 MHz, $CDCl_3$) δ: 5.7. MS, *m/z* (relative intensity, %): 531 ([$M^+ - C_{32}H_{40}NO_6PS_2$], 1). FAB-MS, *m/z* (relative intensity, %): 1161 ([M]$^+$, 31), 531 (68). Compound **31b** gave the following analytical data: mp 229 °C (decomposition (dec.)). $[\alpha]_D^{21}$ +66.5 (*c* 1.55, $CHCl_3$). IR (KBr) (cm^{-1}): 1743. ^{1}H NMR (200 MHz, $CDCl_3$) δ: 7.93 (t, J = 9.6, 2H), 7.78 (t, J = 8.5, 4H), 7.70–7.29 (m, 7H), 7.11 (t, J = 8.0, 1H), 6.89–6.71 (m, 2H), 2.59–2.32 (m, 2H), 2.21 (dt, J = 16.0, 3.0, 1H), 1.93–1.60 (m, 4H), 1.49–1.08 (m, 2H), 0.71 (s, 3H), 0.45 (s, 3H). ^{13}C NMR (50 MHz, $CDCl_3$) δ: 215.0 (C), 156.5 (d, J = 9 Hz, C), 140.0 (d, J = 151 Hz, C), 134.1 (CH), 134.0 (CH), 133.7 (CH), 133.6 (CH), 133.5 (CH), 132.9 (d, J = 1 Hz, CH), 130.5 (CH), 129.6 (CH), 129.3 (CH), 129.2 (CH), 128.9 (C), 128.3 (CH), 128.2 (CH), 127.8 (d, J = 15 Hz, C), 127.8 (CH), 127.2 (C), 126.5 (C), 125.7 (CH), 125.5 (C), 123.7 (CH), 122.2 (d, J = 8 Hz, C), 112.6 (CH), 58.3 (C), 51.7 (d, J = 3 Hz, CH_2), 47.6 (C), 42.6 (CH_2), 42.5 (CH), 27.2 (CH_2), 24.8 (CH_2), 20.4 (CH_3), 20.2 (CH_3). ^{31}P NMR (81 MHz, $CDCl_3$) δ: 4.9. MS, *m/z* (relative intensity, %): 531 ([$M^+ - C_{32}H_{40}NO_6PS_2$], 1). FAB MS, *m/z* (relative intensity, %): 1161 ([M]$^+$, 38), 531 (72). Anal calcd for $C_{68}H_{62}P_2S_2O_8N_2$ + $CHCl_3$: C 64.61, H 5.11, N 2.18; found: C 64.75, H 4.98, N 2.37.

X-ray crystallographic analysis on **31a** was performed at the University of Alberta on a Bruker P4 diffractometer equipped with a SMART 1000 CCD area detector, using graphite-monochromated Mo Kα radiation. The following crystal parameters were obtained: monoclinic, $P2_1$ (No. 4); a = 16.248(2) Å; b = 11.0208(16) Å; c = 35.643(5) Å; V = 6372.8(15) Å^3; Z = 4; R = 0.0696; Rw = 0.2355.

(–)-2,2′-Bis(diphenylphosphonyl)-3,3′-binaphtho[2,1-*b*]furan (14)

Phosphinimine **31a** (1.44 g, 1.24 mmol) in dioxane (50 mL) was treated with 3 mol L^{-1} aqueous H_2SO_4 (35 mL), and the resulting mixture was heated to reflux for 12 h. The cooled mixture was then quenched with 10% NaOH and extracted with $CHCl_3$ (3 × 100 mL). The combined organic extracts were dried ($MgSO_4$) and concentrated in vacuo to afford the crude phosphine oxide. The product was purified by flash chromatography on basic alumina (1:1 hexanes – ethyl acetate → 9:1 $CHCl_3$–MeOH) to afford the desired phosphine oxide (–)-**14** in quantitative yield. $[\alpha]_D^{19}$ –166.6 (*c* 1.01, $CHCl_3$). ^{1}H and ^{13}C spectra were indentical to those of (±)-**14**.

(–)-2,2′-Bis(diphenylphosphino)-3,3′-binaphtho[2,1-*b*]furan (3)

Phosphine oxide (–)-**14** (821 mg, 1.12 mmol) was dissolved in a mixture of xylenes (25 mL) and Et_3N (3.75 mL, 26.8 mmol). To the solution was added $SiCl_3H$ (2.26 mL, 22.4 mmol), and the resulting mixture was heated to 100 °C under argon for 1 h. The mixture was then heated to 150 °C for 3 h and subsequently cooled to 65 °C. To the vessel was then added dropwise 30% NaOH (60 mL). The resulting mixture was vigorously stirred for 1 h at 65 °C. The cooled reaction mixture was extracted with $CHCl_3$ (3 × 100 mL), and the combined organic phases were dried ($MgSO_4$) and concentrated in vacuo. The product (–)-**3** was purified by flash chromatography (20:1 hexanes – ethyl acetate) to afford the optically pure (*S*)-BINAPFu (785 mg, 100%). $[\alpha]_D^{19}$ –203.0 (*c* 1.09, $CHCl_3$). Heating the enantiopure ligand in *p*-xylenes at 150 °C for 7 days did not result in any racemization of the chiral axis, as evidenced by optical rotation and HPLC analysis (Chiralcel® OJ, 95:5 MeOH:EtOH, 0.5 mL min^{-1}, 270 nm detection). ^{1}H and ^{13}C spectra were identical to those of (±)-**3**.

(±)-Dichloro[2,2′-bis(diphenylphosphino)-3,3′-binaphtho[2,1-*b*]furan]-palladium (II) (15)

(±)-2,2′-Bis(diphenylphosphino)-3,3′-binaphtho[2,1-*b*]furan (**3**) (300 mg, 0.427 mmol) and bis(acetonitrile)dichloropalladium(II) (111 mg, 0.427 mmol) were stirred in CH_2Cl_2 (20 mL) at rt for 15 h. The solution was concentrated in vacuo, and the residue was purified by recrystallization from acetone–ether to give 349 mg (93%) of palladium adduct **15** as orange crystals: mp 312–314 °C. IR (KBr) (cm^{-1}): 3056, 1095, 999, 690. ^{1}H NMR (400 MHz) δ: 6.59 (m, J = 6.9 Hz, 2H), 6.82 (t, J = 7.3 Hz, 1H), 7.08 (t, J = 7.6 Hz, 1H), 7.27–7.52 (m, 6H), 7.65 (d, J = 7.5 Hz, 1H), 7.67 (d, J = 8.4 Hz, 1H), 7.77 (d, J = 9.1 Hz, 1H), 7.91 (d, J = 8.1 Hz, 1H), 8.11 (d, J = 7.6 Hz, 1H), 8.15 (d, J = 7.6 Hz, 1H). ^{13}C NMR (100 MHz) (ppm): 112.6 (CH), 122.0 (d, J = 2 Hz, C), 123.8 (dd, J = 7, 6 Hz, C), 124.3 (dd, J = 62, 4 Hz, C), 125.8 (CH), 126.8 (dd, J = 68, 5 Hz, C), 127.8 (CH), 128.1 (C), 128.3 (t, J = 6 Hz, CH), 128.5 (t, J = 6 Hz, CH), 128.9 (CH), 129.2 (CH), 131.2 (d, J = 2 Hz, C), 131.6 (CH), 132.0 (CH), 134.3 (t, J = 5 Hz, CH), 136.3 (t, J = 7 Hz, CH), 147.4 (d, J = 73 Hz, C), 158.1 (dd, J = 4, 3 Hz, C). ^{31}P

NMR (162 MHz) (ppm): +11.3. FAB-MS, *m/z* (relative intensity, %): 901 (9, $[M(^{35}Cl_2) + Na]^+$), 878 (9, $[M^+(^{35}Cl_2)]$).

X-ray crystallographic analysis on **15** was performed at the University of Calgary on an Enraf-Nonius CAD-4 diffractometer with graphite monochromated Cu Kα radiation. The following crystal parameters were obtained: monoclinic, $P2_1/n$ (No. 14); a = 16.673(5) Å, b = 18.478(7) Å, c = 13.702(3) Å; V = 4134(2) Å^3; Z = 4; R = 0.053; Rw = 0.041.

(–)-(S_{ax})-2,2′-Bis(selenodiphenylphosphinyl)-3,3′-binaphtho[2,1-*b*]furan (35)

The following procedure is based on a method reported by Allen and Taylor (51). To a 0.02 mol L^{-1} solution of the BINAPFu (–)-**3** (0.119 g, 0.170 mmol) in $CHCl_3$ was added 10 molar equivalents of Se dust (100 mesh). The resulting mixture was heated to reflux under an atmosphere of argon gas for a 5 h period. The cooled mixture was filtered through a pad of Celite®, and the filterings were washed with a small volume of $CHCl_3$. Concentration of the filtrate under reduced pressure furnished the crude phosphine selenide (–)-**35**. The crude product was recrystallized from CH_3CN to furnish the analytically pure product (0.142 g, 97%). X-ray diffraction analysis of a single crystal thus obtained, using the Bijvoet method, showed the *S*-configuration for the biaryl axis. Phosphine selenide (–)-**35** gave the following analytical data: mp 176–178 °C (CH_3CN). IR (KBr) (cm^{-1}): 2923, 1435, 1095, 1003. ^{1}H NMR (400 MHz) δ: 7.04–7.15 (m, 6H), 7.19–7.26 (m, 1H), 7.35 (t, J = 8.0 Hz, 1H), 7.49 (d, J = 8.2 Hz, 1H), 7.61 (d, J = 9.1 Hz, 1H), 7.67–7.79 (m, 4H), 7.82 (d, J = 9.1 Hz, 1H), 7.87 (d, J = 8.1 Hz, 1H). ^{13}C NMR (50 MHz) δ: 112.9 (CH), 122.5 (C), 122.6 (C), 123.2 (CH), 124.9 (d, J = 16 Hz, C), 125.4 (CH), 127.3 (CH), 128.1 (d, J = 3 Hz, CH), 128.2 (CH), 128.3 (CH), 129.2 (d, J = 3 Hz, CH), 129.2 (d, J = 21 Hz, C), 130.3 (d, J = 30 Hz, C), 131.2 (d, J = 3 Hz, C), 131.8 (d, J = 3 Hz, CH), 132.0 (d, J = 3 Hz, CH), 133.1 (d, J = 12 Hz, CH), 133.7 (d, J = 12 Hz, CH), 142.1 (d, J = 99 Hz, C), 155.2 (d, J = 7 Hz, C). ^{31}P NMR (162 MHz) (ppm): +19.4 ($^1J_{P\text{-}Se}$ = 762 Hz). MS, *m/z* (relative intensity, %): 597 (47, $[M^+ - PPh_2Se]$), 517 (100, $[M^+ - PPh_2Se_2]$). Exact mass calcd for $[M^+ - PPh_2{}^{80}Se]$: 597.0523; found: 597.0520. Anal calcd for $C_{48}H_{32}O_2P_2Se_2 + CH_3CN$: C 66.60, H 3.91, N 1.55; found: C 66.41, H 3.91, N 1.70.

X-ray crystallographic analysis on **35** was performed at the University of Calgary on a Rigaku AFC6S diffractometer with graphite-monochromated Mo Kα radiation. The following crystal parameters were obtained: monoclinic, $P2_1$ (No. 4); a = 9.842(4) Å; b = 21.045(5) Å; c = 10.347(3) Å; V = 2031(1) Å^3; Z = 2; R = 0.0406; Rw = 0.0915; Flack parameter (60) = 0.006(19). Bijvoet analysis was performed. A refinement of the inverted structure was carried out and converged with R = 0.0465 (Rw = 0.1043 with Flack parameter = 0.20(2)) and was therefore rejected as the absolute configuration present in the crystal.

General procedure for the Heck arylation of 2,3-dihydrofuran

Into a 2 dram (1 dram = 1.771845 g) screw-cap vial was measured $Pd(OAc)_2$ (2.2 mg, 9.97 μmol), (*S*)-BINAPFu (21.0 mg, 29.9 μmol), Hunig's base (255 μL, 1.46 mmol), and 1,4-dioxane (2.5 mL). The resulting mixture was heated to 60 °C under an argon atmosphere for 30 min. To the vessel was then added 2,3-dihydrofuran (189 μL, 2.50 mmol) and phenyl triflate (79 μL, 0.488 mmol). The mixture was thermostatically heated to 100 °C for a 7 day period. The crude mixture was filtered through a pad of celite and analyzed by chiral GC (Cyclodex B column, 80 °C start temperature, 2 min initial hold time, 1 °C min^{-1} ramp rate, 220 °C final temperature). The reaction products eluted in the following order: (*S*)-2-phenyl-2,3-dihydrofuran T_r = 26.1 min; (*R*)-5-phenyl-2,3-dihydrofuran T_r = 26.7 min; 2-phenyl-4,5-dihydrofuran T_r = 28.9 min; (*R*)-2-phenyl-2,5-dihydrofuran T_r = 31.2 min; (*S*)-2-phenyl-2,5-dihydrofuran T_r = 31.6 min.

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