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Synthesis, resolution and application of 2,2′-bis(di-2-furylphosphino)-1,1′-binaphthalene

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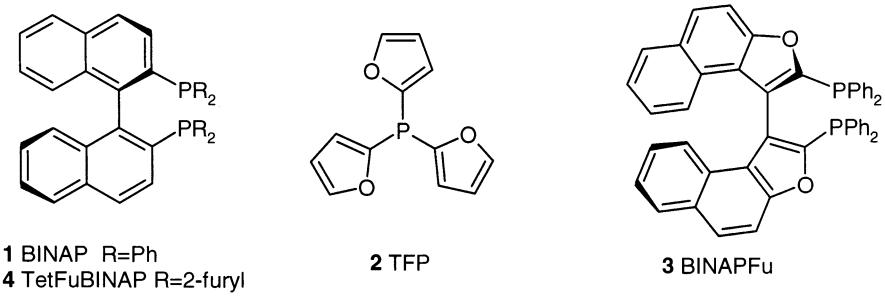
Abstract—A six step synthesis and resolution of (±)-2,2′-bis(di-2-furylphosphino)-1,1′-binaphthalene **4** (TetFuBINAP) is described along with its use in asymmetric inter- and intramolecular Heck reactions. © 2001 Elsevier Science Ltd. All rights reserved.

1. Introduction

Homochiral bidentate phosphine ligands play a vital role in homogeneous transition metal catalyzed asymmetric synthesis.[1] Since the initial reports with BINAP **1** (Scheme 1),[2] a wide variety of new biaryl, bidentate ligands have appeared in the literature.[3] However, evidence has been reported to suggest that less electron rich phosphines, like tri-2-furylphosphine **2** (TFP, Scheme 1), are advantageous for some transition metal mediated organic reactions.[4] These results, in conjunction with our interest in palladium catalyzed asymmetric polyene cyclizations,[5] led us to develop 2,2′-bis(diphenylphosphino)-3,3′-binaphtho[2,1-*b*]-furan **3** (BINAPFu, Scheme 1) as a new bidentate phosphine ligand in which the phosphorus atoms are less electron rich than in BINAP.[6] As BINAPFu **3** has only one furan ring attached directly to each phosphorus atom, we decided to synthesize 2,2′-bis(di-2-furylphosphino)-1,1′-binaphthalene **4** (TetFuBINAP, Scheme 1), which is functionalized with two furan rings on each phosphorus atom, and to compare the efficacy of TetFuBINAP **4** with BINAP **1**. We herein report the synthesis, resolution, and utility of TetFuBINAP **4** in inter- and intramolecular Heck reactions.

2. Results and discussion

(±)-TetFuBINAP **4** was prepared as outlined in Scheme 2. 2,2′-Dibromo-1,1′-binaphthalene **5**[7,8] was treated with magnesium metal in refluxing THF and the resulting Grignard reagent treated with chloro(di-2-furyl)phosphine[9] to provide (±)-**4** in 55% yield. TetFuBINAP was resolved, using our novel phosphine resolution procedure,[10] by treating (±)-**4** with (1*S*)-cam-



1 BINAP R=Ph
4 TetFuBINAP R=2-furyl

2 TFP

3 BINAPFu

Scheme 1.

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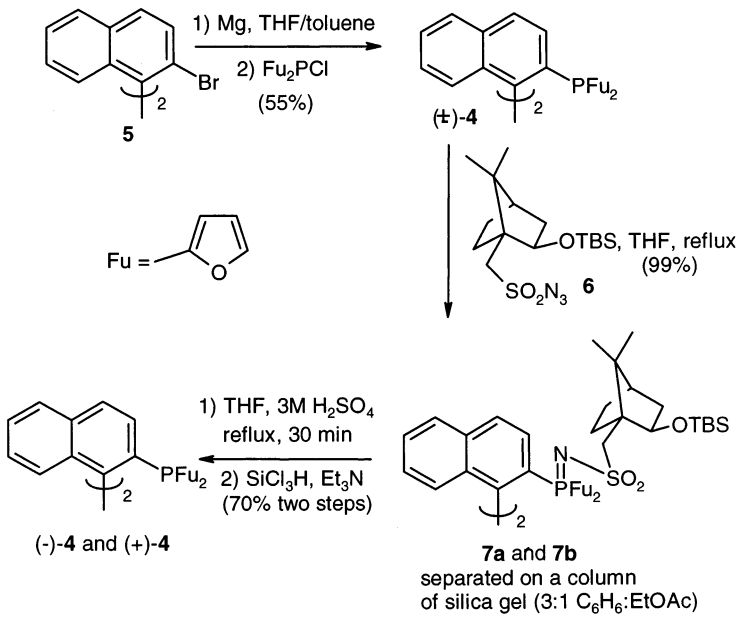


Scheme 2.

phorsulfonyl azide derivative **6** in refluxing THF to provide a mixture of diastereomers **7a** and **7b**. Diastereomers **7a** and **7b** were easily separated on a column of silica gel (3:1 benzene:EtOAc; **7a** R_f 0.59; **7b** R_f 0.47). Hydrolysis of the phosphinimines **7a** and **7b** (refluxing THF, 3 M H_2SO_4, 30 min) followed by reduction of the resulting phosphine oxides ($SiCl_3H$, Et_3N) provided (−)-**4** and (+)-**4** in 70% yield (two steps).[11]

The chiroptical property of circular dichroism, which is a measure of the differential absorption of left-handed and right-handed circularly polarized light as a function of wavelength, has been used to assign the absolute stereochemistry of biaryl compounds.[12] The absolute stereochemistry of (−)-**4** was assigned as S_a by comparison of the CD spectrum of (−)-**4** with the CD spectrum of (−)-S_a-BINAP **1**. The CD spectra of these two solutions, measured in EtOH at 25°C under a nitrogen

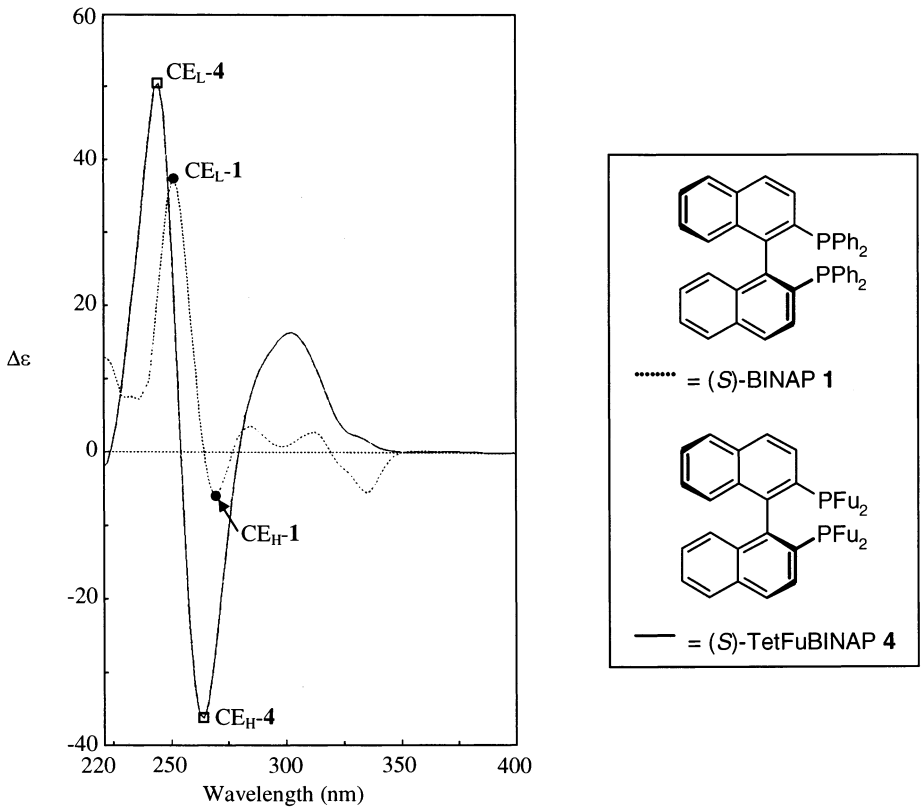
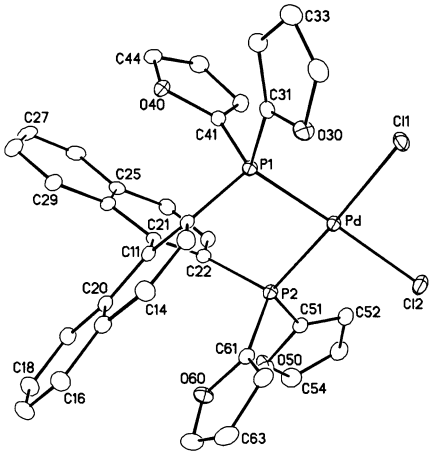


Figure 1. CD spectra of (*S*)-BINAP and (*S*)-TetFuBINAP in EtOH at 25°C.



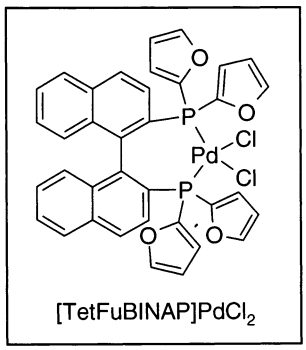


Figure 2. X-Ray crystal structure of [(±)-TetFuBINAP]$PdCl_2$.

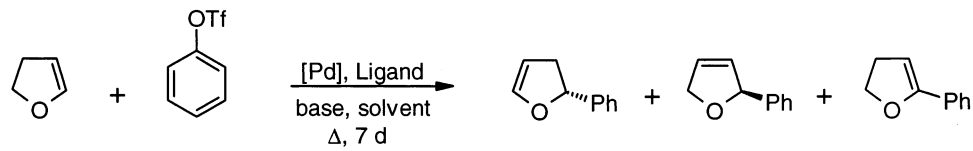
atmosphere, are shown in Fig. 1. The (*S*)-BINAP spectrum exhibits 'negative' chirality with Cotton effects at 265 nm ($\Delta\varepsilon$ −6) and 252 nm ($\Delta\varepsilon$ +37), respectively. The solution of (−)-TetFuBINAP displayed a very similar CD spectrum with Cotton effects at 264 nm ($\Delta\varepsilon$ −36) and 244 nm ($\Delta\varepsilon$ 51). It was therefore concluded that these two compounds share a common configurational assignment and (−)-TetFuBINAP was assigned as the (*S*)-axial isomer.

Allen and Taylor have reported[13] that an increase in the $^1J(^{31}P–^{77}Se)$ coupling constant of phosphine selenides indicates an increase in the *s*-character of the phosphorus lone pair orbital (i.e. less basic phosphine). A comparison of the $^1J(^{31}P–^{77}Se)$ coupling values for selenium derivatives[14] of BINAP (738 Hz),[6] BINAPFu (762 Hz),[6] TetFuBINAP (767 Hz) and TFP (793 Hz)[13] shows that the phosphorus atoms in TetFuBINAP **4** are less basic than those in BINAP **1** and BINAPFu **3** but are more basic than the phosphorus atom in TFP **2**.

An X-ray crystal structure of [TetFuBINAP]$PdCl_2$ (Fig. 2)[15] was obtained in order to determine if the bite angle,[16] defined by the P–Pd–P vertex, would be significantly altered by the replacement of four benzene rings with four furan rings. The [TetFuBINAP]$PdCl_2$ bite angle of 91.7° compared well to that measured for the [BINAP]$PdCl_2$ structure[17] (92.7°). Therefore, any change in activity observed between TetFuBINAP and BINAP should be either due to the reduction in the size of a furan ring relative to a benzene ring or due to stereoelectronic effects due to the presence of the furan rings.

With enantiomerically pure TetFuBINAP **4** in hand, attention was now directed at the application of this novel ligand in the asymmetric Heck arylation of 2,3-dihydrofuran **8** with phenyltriflate **9**.[18] Employing (*R*)-TetFuBINAP at 30°C in either dioxane or C_6H_6 with DIPEA as the base afforded only unreacted PhOTf after 7 days of reaction. Hence, the TetFuBINAP lig-

Table 1. Application of (*R*)-TetFuBINAP in the Heck arylation of 2,3-dihydrofuran

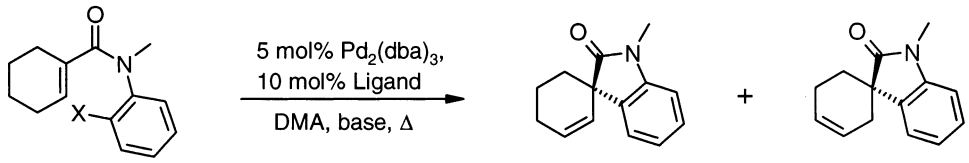


8 **9** **10** **11** **12**

Entry	Pd source	Ligand	Cond.[a]	Conv. (%)[b]	Ratio **10**/**11**	% Yield[c] (% e.e.)[c]		
						(*R*)-**10**	**12**	(*S*)-**11**
1	$Pd_2(dba)_3$	(*R*)-TetFuBINAP	i	22	3.4	17 (89)	0	5 (63)
		(*R*)-BINAP		56	27	53 (66)	1	2 (15)
2	$Pd_2(dba)_3$	(*R*)-TetFuBINAP	ii	100	2.3	60 (19)	14	26 (2)
		(*R*)-BINAP		100	4.1	73 (41)	9	18 (26)
3	$Pd(OAc)_2$	(*R*)-TetFuBINAP	ii	100	2.5	64 (49)	10	26 (16)
		(*R*)-BINAP		100	7.2	86 (57)	2	12 (79)

[a] Conditions: (i) dioxane, 3.0 equiv. DIPEA, 50°C, 7 days; (ii) dioxane, 3.0 equiv. DIPEA, 100°C, 7 days.
[b] Based on unreacted PhOTf.
[c] Based on GC analysis.

Table 2. Results obtained for the asymmetric Heck cyclization of haloanilides **14** and **15** using (*R*)-BINAP and (*R*)-TetFuBINAP derived catalysts



14 X=I
15 X=Br

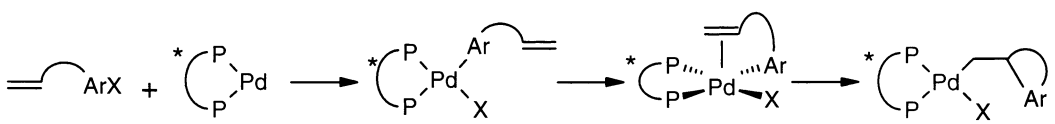
16 **17**

Entry	X	Ligand	Solvent	Base	Ratio **16**/**17**[a]	% Yield **16**[b]	% E.e. **16** (Config.)[c]
1	I	(*R*)-TetFuBINAP	DMA	PMP	5.6	74	85 (*R*)
		(*R*)-BINAP			0.8	39	85 (*R*)
2	I	(*R*)-TetFuBINAP	DMF	PMP	5.3	65	90 (*R*)
		(*R*)-BINAP			0.6	31	82 (*R*)
3	Br	(*R*)-TetFuBINAP	DMA	PMP	1.6	57	64 (*R*)
		(*R*)-BINAP			1.9	61	18 (*R*)
4	Br	(*R*)-TetFuBINAP	DMF	PMP	0.9	45	61 (*R*)
		(*R*)-BINAP			1.0	46	36 (*R*)

[a] Based on ^{1}H NMR analysis of the crude reaction mixture.
[b] Isolated yield.
[c] Enantiomeric purity determined by ^{1}H NMR analysis at 200 MHz in the presence of Eu(hfc)$_3$.

and presents a less active Pd catalyst than the corresponding (*R*)-BINAP and (*R*)-BINAPFu derived systems. Performing the reaction with a $Pd_2(dba)_3$/(*R*)-TetFuBINAP catalyst system at 50°C in dioxane for 7 days yielded only 17% of the desired product **10** (Table 1, entry 1). Although the reaction did not go to completion, the enantiomeric purity of 2,3-dihydrofuran product **10** exceeded the values obtained using (*R*)-BINAP **1** under identical conditions. However, (*R*)-TetFuBINAP **4** provided a lower level of isomer selectivity. Conducting the reaction at a higher temperature (100°C) solved the conversion problem but resulted in an unexpected enantioselectivity trend (entry 2). The (*R*)-TetFuBINAP **4** derived catalyst afforded 2,3-dihydrofuran product **10** in only 19% e.e. in favor of the (*R*)-configuration. In addition, poor isomeric selectivity was observed with an increased production of 4,5-dihydrofuran product **12**. Similar results were obtained using $Pd(OAc)_2$ as the pre-catalyst (entry 3). Clearly, factors other than phosphine σ-donor capacity also play a significant role in determining the reaction outcome. Since TetFuBINAP **4** provided the highest enantioselectivity at 50°C (entry 1), it follows that incorporation of the four furyl moieties into the ligand design did not compromise the phosphine's ability to discriminate between the two enantiotopic faces of 2,3-dihydrofuran **8**. However, it is clear that reduced phosphine donor capacity has an adverse effect upon the rate of conversion.

The best results with TetFuBINAP **4** were obtained in an intramolecular asymmetric Heck reaction (Table 2).[19] Overman et al. have extensively studied the asymmetric Heck cyclization of various (*E*)-α,β-unsaturated 2-haloanilides for the production of enantio-enriched spirocyclic heterocycles. Rigorous investigation of these systems has provided much insight into the possible mechanistic pathways surrounding Heck ring closure reactions. Of particular significance was the discovery that either enantiomer of spirocyclic product **16** could be prepared with good selectivity using an (*R*)-BINAP derived catalyst. Overman et al. explained this result by postulating that silver salts cause the reaction to occur via a cationic mechanism while tertiary amine bases such as PMP result in a neutral pathway. Previous to this discovery, Hayashi[18] and Shibasaki[20] had proposed that cationic intermediates were obligatory for realizing high enantioselection in asymmetric Heck reactions of halide substrates. The fact that (*R*)-**16** could be obtained with an e.e. of 89–95% from aryl iodide **14**, without the presence of silver ions, implied that the bidentate (*R*)-BINAP ligand had to be fully coordinated to the Pd center during the stereochemistry determining step. To this end, it was proposed that the neutral pathway proceeds through a five-coordinate



13

Scheme 3.

intermediate **13** whereby the halide ligand is displaced by axial association of the olefin function (Scheme 3). Intrigued by Overman's involution of a fifth coordination site, it was reasoned that increasing the electrophilicity of the metal center by employing a poorer σ-donor ligand than BINAP might serve to enhance this mode of reactivity.

Heating iodoanilide **14** and PMP (5.0 equiv.) in dimethylacetamide at 110°C with a $Pd_2(dba)_3$/(*R*)-TetFuBINAP catalyst system for 3 days furnished cyclized products **16** and **17** in a 5.6:1 ratio as evidenced by ^1H NMR analysis (Table 2, entry 1). Chromatographic separation of the product mixture afforded a 74% yield of the desired $\Delta^{2,3}$-isomer **16** having an e.e. of 85% in favor of the (*R*)-configuration. Under otherwise identical conditions, employing an (*R*)-BINAP derived catalyst also resulted in high enantioselectivity (85% e.e., (*R*)-product), but diminished isomer selectivity. Performing the reaction in DMF at 110°C for 3 days resulted in nearly identical results (entry 2). (*R*)-TetFuBINAP **4** catalyst provided cyclized product **16** in reasonably high enantioselectivity. However, similar to the results obtained for the 2,3-dihydrofuran Heck arylation reaction, using (*R*)-TetFuBINAP as the chiral modifying ligand resulted in reduced catalyst activity. Therefore, in order to force the reaction to completion, it was necessary to employ long reaction times at elevated temperatures, resulting in heightened production of the unwanted $\Delta^{3,4}$-isomer **17**.

The cyclization of bromoanilide **15** in DMA at 110°C for 3 days furnished cyclized product **15** in 57% isolated yield with e.e. of 64% (entry 3). Although this enantioselectivity is clearly modest in comparison to the results obtained with iodide precursor **14**, the cyclization of bromide **15** with an (*R*)-BINAP derived catalyst afforded product **17** in only 18% e.e. Overman has reported[20] that the PMP promoted cyclization of bromide **15** in DMA (120°C) with (*R*)-BINAP as the catalyst optimally provides product **16** in 51% yield having an e.e. of 32% in favor of the (*R*)-configuration. Moreover, using these conditions, isomer **17** was also produced in 36% yield. In short, employing TetFuBINAP **4** for the Heck cyclization of bromoanilide **15** has improved upon the best reported e.e. for this reaction by a factor of two. Similar results were obtained performing the reaction in DMF at 110°C with a $Pd_2(dba)_3$/(*R*)-TetFuBINAP catalyst (entry 4).

3. Conclusions

In conclusion, we have synthesized and resolved a new chiral binaphthalene ligand **4** that has two furyl groups attached to the phosphorus atoms and is abbreviated TetFuBINAP. The catalyst afforded higher enantioselectivity but lower overall yield in the intermolecular Heck reaction with 2,3-dihydrofuran **8** and much improved enantioselectivity in the intramolecular Heck reaction with **15** (X = Br) when compared to results obtained with BINAP. Further applications of TetFuBINAP and the preparation of other chiral ligands containing the electron deficient phosphine moiety are currently under investigation.

4. Experimental

Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker ACE-200 (^1H, 200 MHz; ^{13}C, 50 MHz) spectrometer, Bruker DRX 400 (^1H, 400 MHz; ^{13}C, 100 MHz) spectrometer, Varian XL-200 (^{31}P, 81 MHz), or a Bruker DRX 400 (^{31}P, 162 MHz) spectrometer. All spectra were obtained in $CDCl_3$ unless otherwise mentioned and the chemical shifts (ppm) are relative to the $C\underline{H}Cl_3$ peak as an internal reference (7.27 ppm for ^1H and 77.00 for ^{13}C). The external standard for ^{31}P NMR spectra was a solution of 30% H_3PO_4 in D_2O. Mass spectra (MS) were run on either a Varian CH5 or a VG 7070 instrument. All melting and boiling points are uncorrected. Anhydrous THF was distilled from sodium benzophenone ketyl. Anhydrous toluene, diethyl ether and xylenes were freshly distilled from calcium hydride. X-Ray structure determination was performed 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.

4.1. Chlorodi-2-furylphosphine

The following preparation of chlorodi-2-furylphosphine is based on an unpublished procedure kindly provided by Dr. M. Scalone (Hoffmann-La Roche).[9] To a solution of furan (5.8 mL, 80 mmol) in Et_2O (50 mL) at −40°C was added *n*-BuLi (1.50 M solution in hexanes, 43 mL, 65 mmol) under an argon atmosphere. The mixture was warmed to 10°C and stirred for 2 h. In a 1 L three-necked flask, equipped with an inert atmosphere filtering tube, were placed freshly distilled phosphorus trichloride (2.9 mL, 33 mmol) and ether (300 mL). The PCl_3 solution was then cooled to −78°C under argon and to it was added the 2-furyllithium slurry over a 1 h period using a wide bore cannula. The transfer vessel was rinsed with dry Et_2O (40 mL) and the washings were added to the reaction vessel. Upon complete addition, the temperature of the mixture was raised to −60°C for 15 min and subsequently cooled to −78°C for 1 h. The resulting mixture was then slowly warmed to rt over a 4 h period and stirred for 14 h. The reaction mixture was then filtered under an atmosphere of argon and the filtrate was concentrated in vacuo. The remaining thick yellow oil was transferred via cannula into a 50 mL single neck round bottomed flask using a small volume of dry Et_2O. The ether was again removed under reduced pressure and the residual oil was fractionally distilled under high vacuum (0.2 mmHg). The product was collected between 100 and 120°C as a clear colorless oil (3.5 g, 53%). ^1H NMR (200 MHz) δ 6.50 (m, 1H), 7.04 (m, 1H), 7.78 (m, 1H, H-4); ^{31}P NMR (81 MHz) ppm +14.4.

4.2. (±)-2,2′-Bis(di-2-furylphosphino)-1,1′-binaphthalene 4

(±)-2,2′-Dibromo-1,1′-binaphthalene **5**[7] (1.007 g, 2.44 mmol) and 1,2-dibromoethane (50 μL, 0.58 mmol) in a mixture of dry toluene (20 mL) and THF (2 mL) were treated with excess magnesium powder (0.238 g, 9.78 mmol) at 85°C for 5 h. The resulting Grignard slurry was cooled to rt and transferred via cannula into a vessel (−30°C) containing solution of chlorodi(2-furyl)phosphine (1.03 g, 5.13 mmol) in THF (5 mL). The reaction mixture was then warmed to rt over 30 min and left to stir for 12 h under an argon atmosphere. The mixture was then quenched with $NaHCO_3$ solution and extracted with $CHCl_3$ (3×100 mL). The combined organic extracts were dried ($MgSO_4$) and concentrated in vacuo to afford a bright yellow solid residue. The crude material was purified by flash chromatography (25:1) to afford the title compound **4** as a white amorphous powder (0.783 g, 55%). The product exhibited the following analytical properties: mp 190–191°C; IR (KBr) 2922, 1454, 1006, 741 cm^{-1}; ^1H NMR (400 MHz) δ 5.98 (m, 1H), 6.00 (m, 1H), 6.44 (m, 1H), 6.71 (d, $J=3.3$ Hz, 1H), 6.81 (d, $J=8.5$ Hz, 1H), 7.02 (t, $J=7.7$ Hz, 1H), 7.32 (m, 1H), 7.37 (t, $J=7.5$ Hz, 1H), 7.73 (m. 1H), 7.81 (d, $J=8.7$ Hz, 1H), 7.84 (d, $J=8.2$ Hz, 1H), 7.95 (d, $J=8.6$ Hz, 1H); ^{13}C NMR (100 MHz) ppm 110.6 (t, $J=4$ Hz), 111.2 (t, $J=3$ Hz), 121.3 (t, $J=15$ Hz), 121.4 (d, $J=108$ Hz), 122.1 (t, $J=13$ Hz), 126.5, 126.8, 127.2, 128.1, 128.7, 130.1, 133.1, 133.8, 142.9 (t, $J=20$ Hz), 147.3, 147.8, 150.4 (t, $J=7$ Hz), 151.3 (t, $J=5$ Hz); ^{31}P NMR (162 MHz) ppm −58.6; mass spectrum, m/z (relative intensity, %) 582 (0.2, M^+), 515 (0.3, M^+–Fu), 417 (100, M^+–PFu_2). Exact mass calcd for $C_{28}H_{18}O_2P$ (M^+–PFu_2): 417.1044. Found: 417.1027.

4.3. (S_{ax})-[(1*S*,2*R*)-*O*-(*t*-Butyldimethylsilyl)isobornyl-10-sulfonamidyl]-[1,1′-binaphthalene]-2,2′-diylbis[di-2-furylphosphinimine] 7a and (R_{ax})-[(1*S*,2*R*)-*O*-(*t*-butyldimethylsilyl)isobornyl-10-sulfonamidyl]-[1,1′-binaphthalene]-2,2′-diylbis[di-2-furylphosphinimine] 7b

To a solution of (±)-2,2′-bis(di-2-furylphosphino)-1,1′-binaphthyl **4** (0.791 g, 1.36 mmol) in THF (20 mL) was added (1*S*,2*R*)-*O*-(*t*-butyldimethylsilyl)isobornyl-10-sulfonyl azide **6**[10] (1.12 g, 2.99 mmol). The resulting solution was heated to reflux under an argon atmosphere for 24 h. The cooled solution was then concentrated under reduced pressure to afford the crude phosphinimine mixture. Separation of the diastereomeric products was achieved by flash chromatography (3:1 benzene:ethyl acetate) to afford **7a** (0.86 g, 50%) and **7b** (0.84 g, 49%). The first diastereomer to elute from the column, compound **7a**, had: mp 250–252°C; IR (KBr) 2926, 1456, 695 cm^{-1}; ^1H NMR (400 MHz) δ 0.05 (s, 3H), 0.11 (s, 3H), 0.71 (s, 3H), 0.90 (s, 9H), 0.96 (s, 3H), 1.12–1.35 (m, 2H), 1.48–1.76 (m, 4H), 1.90 (t, $J=14$ Hz, 1H), 2.36 (d, $J=13.8$ Hz, 1H), 3.32 (d, $J=13.8$ Hz, 1H), 4.01 (m, 1H), 6.16 (s, 1H), 6.34 (s, 1H), 6.61 (s, 1H), 6.90 (d, $J=8.5$ Hz, 1H), 7.03 (s, 1H), 7.11 (t, $J=7.6$ Hz, 1H), 7.45 (d, $J=13.1$ Hz, 2H), 7.50 (d, $J=7.4$ Hz, 1H), 7.86 (d, $J=8.1$ Hz, 1H), 7.92 (d, $J=6.7$ Hz, 1H), 8.20 (dd, $J=13.8$, 8.8 Hz, 1H); ^{13}C NMR (100 MHz) ppm −4.1, −4.4, 18.4, 20.7, 21.3, 26.5, 27.7, 28.9, 42.7, 44.9, 48.9, 50.7, 53.8 (d, $J=5$ Hz), 76.7, 111.7 (d, $J=9$ Hz), 111.9 (d, $J=9$ Hz), 124.3 (d, $J=131$ Hz), 126.3, 126.5, 127.0, 127.2, 127.6, 127.9, 128.1, 128.2, 128.9, 129.1 (d, $J=8$ Hz), 129.3 (d, $J=6$ Hz), 134.0 (d, $J=14$ Hz), 135.0 (d, $J=2$ Hz), 139.8 (dd, $J=10$,6 Hz), 142.1 (d, $J=148$ Hz), 142.7 (d, $J=144$ Hz), 149.3 (d, $J=8$ Hz), 149.7 (d, $J=8$ Hz); ^{31}P NMR (162 MHz) ppm −17.1; mass spectrum, m/z (relative intensity, %) 596 (2), 417 (65), 57 (100). Compound **7b** exhibited the following properties: mp 241–243°C; IR (KBr) 2925, 1456, 1123, 637 cm^{-1}; ^1H NMR (400 MHz) δ −0.01 (s, 3H), 0.00 (s, 3H), 0.69 (s, 3H), 0.85 (s, 9H), 0.95 (s, 3H), 1.28–1.40 (m, 2H), 1.53–1.78 (m, 4H), 1.92 (t, $J=14$ Hz, 1H), 2.24 (d, $J=13.8$ Hz, 1H), 3.16 (d, $J=13.8$ Hz, 1H), 3.96 (m, 1H), 6.17 (s, 1H), 6.36 (s, 1H), 6.72 (s, 1H), 6.91 (d, $J=8.5$ Hz, 1H), 7.11 (d, $J=7.7$ Hz, 1H), 7.14 (s, 1H), 7.48–7.57 (m, 3H), 7.87 (d, $J=8.1$ Hz, 1H), 7.94 (d, $J=7.0$ Hz, 1H), 8.11 (dd, $J=14.0$, 8.8 Hz, 1H); ^{13}C NMR (100 MHz) ppm −4.5, −4.2, 18.3, 20.7, 21.3, 26.5, 27.7, 28.7, 42.7, 44.9, 48.9, 50.7, 53.5 (d, $J=5$ Hz), 76.6, 111.7 (d, $J=7$ Hz), 111.8 (d, $J=7$ Hz), 124.2 (d, $J=134$ Hz), 126.6, 126.8, 127.2, 127.6, 127.8, 128.0, 128.1, 128.9 (d, $J=13$ Hz), 129.0, 129.1 (d, $J=13$ Hz), 134.1 (d, $J=14$ Hz), 135.0 (d, $J=2$ Hz), 140.1 (dd, $J=10$,6 Hz), 142.4 (d, $J=143$ Hz), 142.5 (d, $J=144$ Hz), 149.4 (d, $J=8$ Hz), 149.7 (d, $J=8$ Hz); ^{31}P NMR (162 MHz) ppm −17.7; mass spectrum, m/z (relative intensity, %) 596 (2), 449 (13), 417 (65), 57 (100).

4.4. (S_{ax})-(−)-2,2′-Bis(di-2-furylphosphinyl)-1,1′-binaphthalene

Diastereomerically pure phosphinimine **7a** (1.01 g, 0.794 mmol) in THF (50 mL) was treated with 3 M H_2SO_4 (3.0 mL, 9.0 mmol) and stirred under reflux for 0.5 h. The resulting solution was quenched with $NaHCO_3$ solution and concentrated under reduced pressure. The residual aqueous phase was extracted with $CHCl_3$ (3×50 mL) and the combined organic extracts were dried ($MgSO_4$). Subsequent concentration and chromatographic purification (9:1 $CHCl_3$:MeOH) afforded the desired phosphine oxide as a white foam in near quantitative yield. The phosphine oxide of (−)-**4** displayed the following properties: IR (KBr) 3101, 1582, 1490, 800 cm^{-1}; ^1H NMR (400 MHz, THF-d_8) δ 6.34 (m, 1H), 6.57 (m, 1H), 6.72 (m, 1H), 7.00 (d, $J=8.5$ Hz, 1H), 7.15 (m, 1H), 7.21 (t, $J=7.6$ Hz, 1H), 7.86 (m, 2H), 7.58 (m. 2H), 8.05 (d, $J=8.1$ Hz, 1H), 8.12 (d, $J=7.7$ Hz, 1H); ^{13}C NMR (100 MHz, THF-d_8) ppm 108.7 (d, $J=9$ Hz), 108.9 (d, $J=9$ Hz), 120.9 (d, $J=20$ Hz), 121.9 (d, $J=21$ Hz), 124.4, 124.9, 125.2 (d, $J=14$ Hz), 125.7 (d, $J=123$ Hz), 125.9, 126.0, 126.3 (d, $J=14$ Hz), 131.6 (d, $J=13$ Hz), 132.8 (d, $J=2$ Hz), 139.2 (dd, $J=8$,5 Hz), 144.5 (d, $J=79$ Hz), 146.0 (d, $J=80$ Hz), 146.4 (d, $J=8$ Hz), 146.6 (d, $J=8$ Hz); ^{31}P NMR (162 MHz, THF-d_8) ppm +2.2; mass spectrum m/z (relative intensity, %) 614 (0.2, M^+), 547 (0.5,

M^+–Fu), 433 (100, M^+–P(O)Fu_2). Exact mass calcd for $C_{28}H_{18}O_3P$ (M^+–P(O)Fu_2): 433.1038. Found: 433.1057.

4.5. (S_{ax})-(−)-2,2′-Bis(di-2-furylphosphino)-1,1′-binaphthalene (−)-4

(*S*)-Phosphine oxide (0.407 g, 0.663 mmol) in xylenes (25 mL) was treated with Et_3N (2.22 mL, 15.9 mmol) and $SiCl_3H$ (1.34 mL, 13.3 mmol) at 150°C for 3 h. To the cooled mixture was then added 30% NaOH solution (25 mL) and the resulting mixture was stirred at 65°C for 30 min. The mixture was then extracted with $CHCl_3$ (3×75 mL). The combined organic extracts were dried ($MgSO_4$), and concentrated under reduced pressure to afford a light yellow solid, which was purified by column chromatography (25:1) to give the title compound (−)-**4** (0.272 g, 70%): mp 190–191°C; $[\alpha]_D^{19}$ −78.3 (*c* 0.95, $CHCl_3$). Trichlorosilane reduction of (+)-phosphine oxide furnished (*R*)-TetFuBINAP (+)-**4** in 77% yield: $[\alpha]_D^{17}$ +77.5 (*c* 1.03, $CHCl_3$). In both cases, the products exhibited NMR spectral characteristics consistent with those above.

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