A Simple Resolution Procedure Using the Staudinger Reaction for the Preparation of *P*-Stereogenic Phosphine Oxides

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Received July 10, 2001

The resolution of a variety of (±)-*P*-stereogenic phosphines is achieved by exploiting the Staudinger reaction of a (±)-phosphine with enantiopure (1*S*,2*R*)-*O*-(*tert*-butyldimethylsilyl)isobornyl-10-sulfonyl azide. The resulting mixtures of diastereomeric phosphinimines are generally separable by fractional crystallization or flash chromatography. Subsequent acid-catalyzed hydrolysis provides the corresponding optically pure phosphine oxides in high yields.

Introduction

The use of enantiomerically pure phosphine ligands in asymmetric syntheses mediated by transition metals has become very popular among the various strategies available for performing asymmetric transformations.[1] Therefore, much effort has been directed toward the rational design, synthesis, and testing of new enantiomerically pure phosphines for various synthetic purposes. A large number of enantiomerically pure phosphines are now available commercially, and many other ligands have been reported in the literature.[1d,2] The vast majority of these compounds have carbon-based central or axial chirality rather than *P*-stereogenic phosphorus atoms. However, efforts to use *P*-stereogenic phosphines in enantioselective transformations have been infrequent due, in part, to the relative difficulty of obtaining these compounds by resolution procedures or diastereoselective synthesis.[3] While there have been several recent advances in the diastereoselective synthesis of *P*-stereogenic materials,[4,5] there are still relatively few resolution methods available for obtaining enantiomerically pure tertiary phosphines. Since reliable methods have been developed to stereospecifically reduce *P*-stereogenic phosphine oxides to the corresponding phosphines with either retention or inversion of configuration,[6] new methods for the preparation of optically pure phosphine oxides are highly valuable. Of the few strategies reported for obtaining enantiomerically pure phosphines via resolution techniques, the most popular these days uses orthometalated palladium(II)−amine complexes.,[7,8,9] The main disadvantage of this strategy is that it requires the use of stoichiometric amounts of palladium, which is quite expensive. On a project involving the preparation of electron deficient phosphines containing an axis of chirality, we required a method for resolving the enantiomers of BINAPFu **1**.[10] Upon exhausting several of the known methods for phosphine resolution without success,[11] it was necessary to design a new optical resolution procedure to obtain the enantiopure BINAPFu ligand. We

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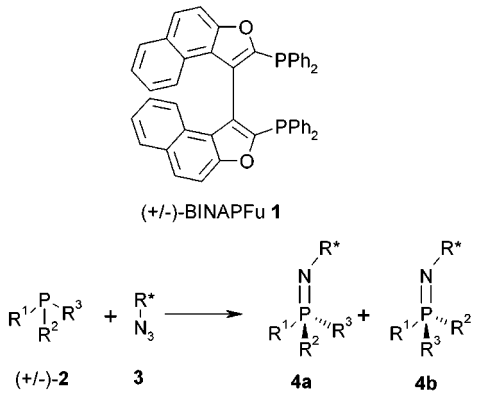
10.1021/jo015909u CCC: $20.00
Published on Web 10/10/2001

Scheme 1

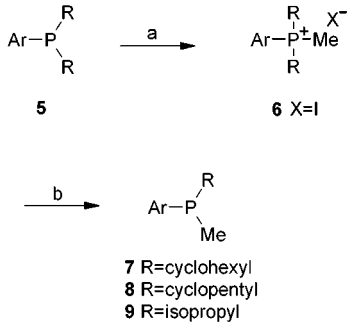


conceived that a Staudinger[12] reaction between a racemic phosphine (±)-**2** and an enantiopure organoazide **3** should provide a 1:1 mixture of diastereomeric phosphinimines **4a** and **4b** if the P═N bond rotational barrier was low enough to prevent geometrical isomerism (Scheme 1). A literature survey revealed that the P═N rotational barrier for simple phosphinimines has been calculated to be ca. 2.54 kcal/mol.[13] Hence it was rationalized that P═N geometrical isomerism would likely not complicate the proposed resolution technique. By judicious choice of the organoazide, the diastereomers formed from the Staudinger reaction would be separable by column chromatography or crystallization. Once separated the phosphinimines would be hydrolyzed to provide optically pure phosphine oxides. We herein provide a full account of our new resolution procedure[14] via the Staudinger reaction for application with either *P*-stereogenic phosphines or phosphines within molecules containing an axis of chirality.

Synthesis of *P*-Stereogenic Phosphines. Unfortunately, a commercial source of (±)-*P*-stereogenic tertiary phosphines could not be identified and thus these materials had to be synthesized according to known general methods.[15] Phosphines containing two alkyl substituents, one of which was methyl, and an aryl group were prepared via $LiAlH_4$ reduction of a suitably substituted phosphonium salt **6** (Scheme 2) that was generated from phosphine **5**. In this manner, racemic phosphines **7**−**9** were prepared and exhibited physical and spectral properties consistent with the literature.[16]

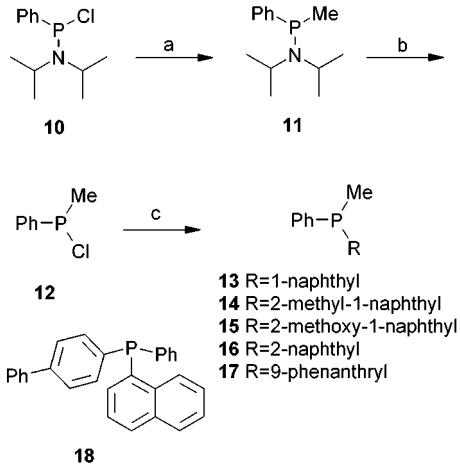
Phosphines bearing two or more aryl substituents were prepared in a stepwise fashion starting with phosphonamidous chloride reagent **10**[17] (Scheme 3). Treatment of compound **10** with 1 equiv of MeMgBr (Et_2O, −40 °C, 1 h) afforded phosphonamide **11** in 85% yield. Subsequent reaction with 2.2 equiv of anhydrous HCl (1.0 M solution in Et_2O) furnished chloromethylphenylphosphine (**12**).[18] Treatment of **12** (ether, −40 °C) with a

Scheme 2[a]



[a] Conditions: (a) 2 equiv of MeI, $CHCl_3$, rt, 24 h. (b) 5 equiv of $LiAlH_4$, Et_2O, reflux, 6 h.

Scheme 3[a]



[a] Conditions: (a) 1.0 equiv of MeMgBr, Et_2O, −40 °C, 1 h, 85%. (b) 2.2 equiv of HCl (1.0 M solution in Et_2O), 0 °C, 1 h. (c) 1.2 equiv of RMgBr, Et_2O, −40 °C, 3 h, 32−67% (two steps).

variety of freshly prepared aryl Grignard reagents afforded racemic phosphines **13**−**17** in 32−67% yield.[18−22] Triaryl phosphine **18**[20] was prepared in a similar stepwise manner with the exception that 1-naphthylmagnesium bromide was used in place of MeMgBr (step a, Scheme 3) and biphenyl was used in **10** instead of a phenyl ring.

Attempted Resolution of Cyclohexylmethylphenylphosphine (7) Using Various Organo Azides. Efforts were directed at identifying an organoazide resolving agent, which would be highly general for a wide variety of racemic phosphines. To this end, (+)-neomenthyl azide (**19**),[23] 3*β*-azido-5α-cholestane (**20**),[24] 6-azido-6-deoxy-1,2,3,4-di-*O*-isopropylidene-α-D-galactopyranose (**21**),[25] and (1*S*)-10-camphorsulfonyl azide (**22**)[26] were prepared according to literature procedures and screened as potential

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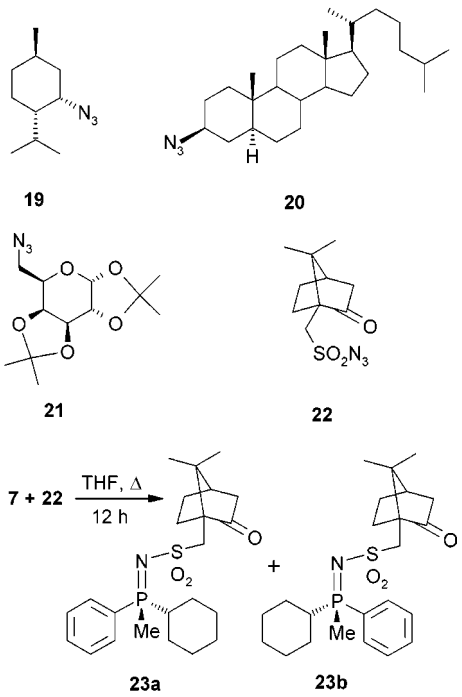
Scheme 4

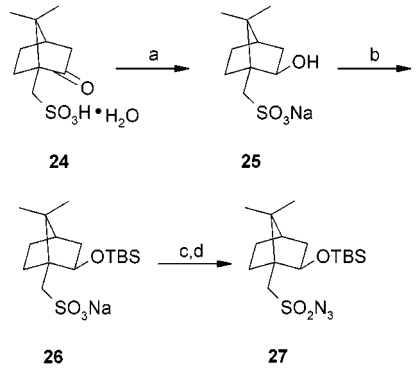


resolving agents. Unfortunately, azides **19**−**21** were unsuccessful in this endeavor. Treatment of cyclohexylmethylphenylphosphine (**7**) with (1*S*)-10-camphorsulfonyl azide (**22**) gave a 1:1 mixture of diastereomeric phosphinimines **23a** and **23b** (by ^{1}H and ^{31}P NMR) (Scheme 4), but unfortunately, the two diastereomers could not be separated. Attention was focused on derivatizing azide **22** in hopes of identifying a more general phosphine resolving agent.

It was postulated that increasing the steric size of the functional group at C-2 in azide **22** might indeed result in the production of a better, more stereodifferentiated resolving agent. (+)-CSA monohydrate (**24**) was reduced with $NaBH_4$ to give exclusively the exo alcohol **25**[27] (Scheme 5). Silylation of **25** followed by heating the sodium salt of silyl ether **26** with $SOCl_2$ (benzene, 12 h) furnished the corresponding sulfonyl chloride (not shown) which immediately reacted with NaN_3 in aqueous solution to provide the desired (1*S*,2*R*)-*O*-(*tert*-butyldimethylsilyl)isobornyl-10-sulfonyl azide (**27**) in 57% overall yield. With sulfonyl azide **27** in hand, attention was focused on the optical resolution *P*-stereogenic phosphines **7**−**9** and **13**−**18**.

Optical Resolution of *P*-Stereogenic Phosphines with Isobornyl Sulfonyl Azide 27. The phosphinimines formed using sulfonyl azide **27** were found to be stable toward flash chromatography on silica gel and prolonged storage under an ambient atmosphere. In addition, the diastereomeric phosphinimines produced from the reaction of racemic phosphines **7**−**9** and **13**−**18** with enantiopure azide **27** were readily separable by fractional crystallization or flash chromatography on silica gel (Table 1). For example, the phosphinimine mixture obtained upon treatment of phosphine **7** with azide **27** showed two strong singlets of equal intensity in the ^{31}P NMR spectrum at 23.3 and 23.2 ppm corresponding to compounds **28a** and **28b**, respectively (entry 1). Dissolving this mixture in petroleum ether and cooling the resulting solution to −5 °C resulted in the precipitation of diastereomerically pure phosphinimine **28a** in excellent yield. A second crop of crystals taken from the mother liquor afforded compound **28b** as thick colorless prisms with a melting point of 147−149 °C (total yield was 94%). Similar results were obtained using petroleum ether as a crystallization solvent for phosphinimines **29a** and **29b** (entry 2). However, phosphine **9** could not be fully resolved by this technique (entry 3). For this phosphinimine mixture, a single crystallization from petroleum ether provided pure compound **30a** in 43% yield leaving a ca. 7:1 ratio of diastereomers in the mother liquor. Under these circumstances, phosphinimine **30b** could not be further purified by crystallization. Many of the phosphinimine diastereomers were readily separable by simple flash chromatography on silica gel using mixtures of hexanes/ethyl acetate as eluent (entries 4−6, 8−9).[28] With isomerically pure phosphinimines **28**−**36** in hand, an investigation of the hydrolytic cleavage of these materials to provide the corresponding enantiopure phosphine oxides was initiated.

Scheme 5[a]



[a] Conditions: 2.4 equiv $NaBH_4$, H_2O, rt, 1 h, 95%. (b) 3.3 equiv TBSCl, Et_3N, DMF, rt, 3 h. (c) 6.0 equiv $SOCl_2$, C_6H_6, DMF, reflux, 12 h. (d) 3.2 equiv NaN_3, DMA, H_2O, 60 °C, 12 h, 57% (3 steps).

Treatment of phosphinimine **28a** with 3 M H_2SO_4 solution in refluxing dioxane smoothly afforded cyclohexylmethylphenylphosphine oxide (**37**) in 93% isolated yield after chromatographic removal of the sulfonamide byproduct **46** (Table 2, entry 1). The optical rotation of compound **37**, measured in MeOH at 20 °C, was +19.2, which compares very favorably to the reported α^{20}_{D} value of +19.0.[29] Moreover, since the absolute stereochemistry of phosphine oxide **37** has been previously established by Mislow and co-workers,[29] it can be concluded that the *R* isomer was obtained from phosphinimine **28a** in reasonably high optical purity. Similar hydrolytic cleavage of isomerically pure phosphinimines **29**−**36** provided optically active phosphine oxides **38**−**45**, respectively (Table 2). In general, the phosphine oxides obtained from the hydrolysis procedure exhibited optical rotation values, which closely matched the known specific rotations reported in the literature. Hence, it may be concluded that the phosphine oxide products obtained using this method are generally of high stereochemical purity. The stereochemical purity of phosphine oxides **38**, **41**, and **44**,

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(28) The first isomer to elute from the column was designated as phosphinimine "**a**" while the other diastereomer was designated as the "**b**" isomer.

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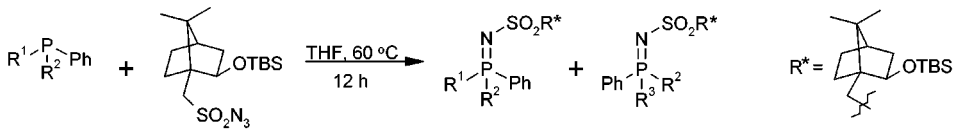
Table 1. Resolution of *P*-Stereogenic Phosphines with Sulfonyl Azide 27

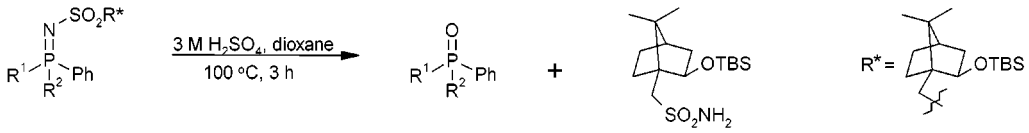


7-9 & 13-18 **27** **a** **b**

entry	SM	R^1	R^2	products[a]	separation method	yield (%)[b]
1	7	Me	C_6H_{11}	**28**a and **28b**	crystallization	94
2	8	Me	C_5H_9	**29a** and **29b**	crystallization	90
3	9	Me	$CH(CH_3)_2$	**30a** and **30b**	crystallization[c]	87
4	13	Me	1-Np	**31a** and **31b**	chromatography	94
5	14	Me	2-Me-1-Np	**32a** and **32b**	chromatography	91
6	15	Me	2-MeO-1-Np	**33a** and **33b**	chromatography	95
7	16	Me	2-Np	**34a** and **34b**	crystallization	87
8	17	Me	9-phenanthryl	**35a** and **35b**	chromatography	89
9	18	1-Np	*p*-PhC_6H_4	**36a** and **36b**	chromatography	89

[a] Diastereomer to elute first or crystallize first designated "**a**". [b] Combined isolated yield of both diastereomers. [c] Not fully separated.

Table 2. Hydrolysis of Isomerically Pure Phosphinimines



28-36 a or **b** diastereomerically pure **37-45** enantiomerically pure **46**

	SM	R^1	R^2	product	expt α^{20}_D; [*c*] (g/100 mL)[a]		lit. α^{20}_D	yield (%)[b,c]	SM config
1	28a	Me	C_6H_{11}	37	+19.2;	[0.93]	+19.0[28]	93 (*R*)	*S*
2	29b	Me	C_5H_9	38	+33.3;	[1.62]	- -	93	- -
3	30a	Me	$CH(CH_3)_2$	39	−22.6;	[1.00]	−21.2[30]	94 (*S*)	*R*
4	31a	Me	1-Np	40	+19.8;	[2.92]	+18.6[31]	96 (*S*)	*R*
5	32b	Me	2-Me-1-Np	41	−73.6;	[1.50]	- -	94	- -
6	33a	Me	2-MeO-1-Np	42	+128.0;	[1.58]	+128.0[19]	91 (*S*)	*R*
7	34a	Me	2-Np	43	−12.0;	[0.90]	−12.0[28]	96 (*S*)	*R*
8	35a	Me	9-phenanthryl	44	+71.4;	[1.14]	- -	99	- -
9	36b	1-Np	*p*-PhC_6H_4	45	+26.9;	[0.62][d]	+27.0[d,22]	93 (*R*)	*S*

[a] Rotation in methanol except as noted. [b] Isolated yields. [c] Phosphorus configuration assigned according to literature correlation. [d] Rotation in $CHCl_3$.

for which specific rotation data has not been reported,[30] is assumed to be high on the basis of the good agreement observed in the optical rotation data for known oxides **37**, **39**,[31] **40**,[32] **42**, **43**, and **45** (Table 2). Also, the phosphine oxides obtained from the hydrolysis of the opposite phosphinimine diastereomers, **29a**, **32b**, and **35a** provided oxides **38**, **41**, and **44**, respectively, with optical rotations equal in magnitude but opposite in sign to those reported in Table 2. It is clear from the data presented in Table 2 that the absolute configuration of the product cannot be predicted based on which phosphinimine diastereomer is hydrolyzed.

To investigate the stereochemical course of the phosphinimine hydrolysis step, a single-crystal X-ray structure determination of compound **30a** was undertaken.[33] Since (1*S*,2*R*)-*O*-(*tert*-butyldimethylsilyl)isobornyl-10-sulfonyl azide (**27**) was used to prepare phosphinimine **30a**, it was unambiguously concluded from the X-ray analysis that the phosphorus stereocenter was of *R* configuration. Since the hydrolysis of phosphinimine **30a** provided (−)-isopropylmethylphenylphosphine oxide (**39**), known to be of *S* configuration,[31] it can be concluded that the hydrolysis proceeds stereospecifically with inversion at phosphorus.[34] Having shown that the hydrolysis step occurs with inversion of configuration, many of the stereochemical configurations of phosphinimines **28**−**36** may be assigned (Table 2) based on the optical rotation data reported for oxides **37**−**45** (vide supra).

Resolution of Axially Stereogenic Bidentate Phosphines. In addition to demonstrating the synthetic

(30) Unfortunately, assignment of the absolute configuration to phosphine oxide products **38**, **41**, and **44** was not possible since the relationship between rotation sign and configuration has not been deduced for these materials.

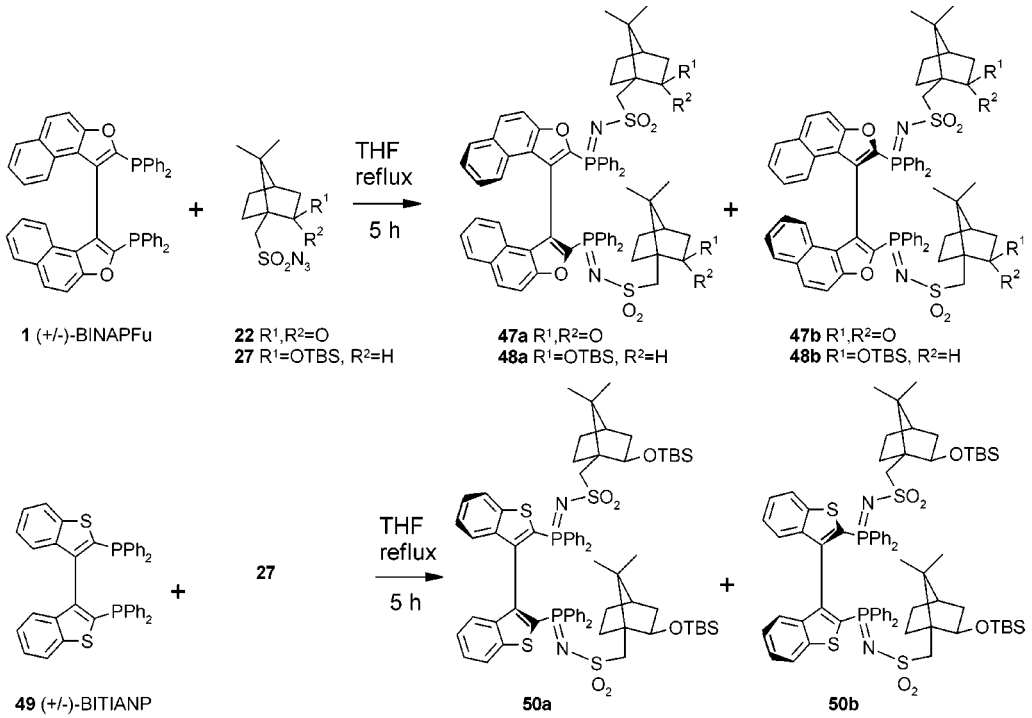
(31) Byrne, L. T.; Engelhardt, L. M.; Jacobsen, G. E.; Leung, W.-P.; Papasergio, R. I.; Raston, C. L.; Skelton, B. W.; Twiss, P.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1989**, 105.

(32) Luchenbach, R.; *Phosphorus* **1972**, *5*, 223.

(33) See Figure S1, Supporting Information. X-ray crystallographic analysis was performed by Dr. M. Parvez at the University of Calgary. The following crystal parameters were obtained: orthorhombic $P2_12_12_1$ (No. 19); $a = 12.337(4)$ Å, $b = 12.833(3)$ Å, $c = 18.751(2)$ Å, $V = 2969(1)$ Å^3; $Z = 4$; $R = 0.0459$; $wR = 0.1208$; Flack parameter = −0.03(2). Bijvoet analysis was performed. A refinement of the inverted structure was carried out and converged with $R = 0.0543$, $wR = 0.1427$ with Flack parameter = 1.03(3) and was therefore rejected as the absolute configuration present in the crystal.

(34) While the hydrolysis of phosphinimines under basic conditions has been shown to occur with inversion of configuration at phosphorus, such a relationship has not been previously established for acidic media. For more information, see: Horner, L.; Winkler, H. *Tetrahedron Lett.* **1964**, *3*, 175.

Scheme 6



utility of resolving agent **27** toward a variety of *P*-stereogenic phosphines, a project was undertaken to apply the Staudinger reaction in the resolution of C_2-symmetric diphosphines. Treatment of (±)-BINAPFu **1** with 2 equiv of enantiopure azide **22** smoothly provided a 1:1 mixture of diastereomeric phosphinimines **47a** and **47b** in near quantitative yield (Scheme 6). Phosphinimines **47a** and **47b** could be readily separated by flash chromatography on silica gel using a 9:1 $CHCl_3/CH_3CN$ eluent mixture.

Racemic BINAPFu (**1**) could also be resolved with 2 molar equiv of azide **27**; a 1:1 mixture of easily separable (by column chromatography) diastereomeric phosphinimines **48a** and **48b** were obtained (Scheme 6).

Application of resolving agent **27** to Sannicolò's BITIANP[35] ligand **49** was also successful giving phosphinimines **50a** and **50b**, which were separable by flash chromatography. Hydrolysis of phosphinimines **47**, **48**, and **50** after separation provided the enantiomerically pure bis-phosphine oxides of (*S*)-BINAPFu and (*S*)-BITIANP, respectively, as evidenced by optical rotation measurements.

Interestingly, the resolution of (±)-BINAP **51** and (±)-MeOBIPHEP **56**[36] using sulfonyl azide **27** did not proceed as planned. Treatment of racemic BINAP **51** with 2 equiv. of azide **27** afforded a mixture of four phosphinimine products **52**−**55** (Scheme 7). Fortunately, these materials could be separated by preparative TLC and were identified on the basis of their ^1H, ^{31}P, and ^{13}C NMR spectra. A mixture of mono-phosphine oxide, mono-phosphinimine **54** and **55**, and bis-phosphinimine products **52** and **53** had been isolated. This surprising result was initially attributed to partial air oxidation under the reaction conditions. Subsequent experimentation, with *rigorous* exclusion of oxygen, revealed that the source of oxidation must be internal to the reaction mixture. Similar results were obtained in the attempted resolution of (±)-MeOBIPHEP **56** using azide **27** (Scheme 7). Bis-phosphinimine product **57** was obtained in 19% yield after extensive chromatographic purification while products **58**−**60** could not be obtained in analytically pure form.

The resolution of 2,2′-bis(di-2-furylphosphino)-1,1′-binaphthalene **51a** was successful using resolving agent **27**. The diastereomers formed were easily separated and converted to their corresponding phosphine oxides upon treatment with 3 M sulfuric acid.[37]

The competitive formation of phosphine oxide products **54**, **55**, **59**, and **60** can be rationalized by considering the mechanism of the Staudinger reaction (Scheme 8). The first step involves nucleophilic attack of the phosphine on the terminal nitrogen of the azide reactant **27** producing a triazo intermediate **61**. Although some intermediates of type **61** have been isolated,[38] such compounds normally decompose rapidly through a four-membered transition state **62**[39] to provide the phosphinimine product **52**, **53** or **57**, **58** with the expulsion of N_2 gas. It is postulated that due to steric hindrance, a four-membered cyclic transition state **62** is not easily attained upon reacting BINAP **51** or MeOBIPHEP **56** with sulfonyl azide **27** through intermediate **61** (Scheme 8). Instead, a six-membered cyclic transition state **63** is possible leading to oxygen transfer from the sulfonyl moiety to the phosphorus atom. Such a hypothesis is consistent

(35) (a) Benincori, T.; Brenna, E.; Sannicolò, F.; Trimarco, L.; Antognazza, P.; Cesarotti, E.; Demartin, F.; Pilati, T. *J. Org. Chem.* **1996**, *61*, 6244. (b) Tietze, L. F.; Thede. K.; Sannicolò, F. *J. Chem. Soc., Chem. Commun.* **1999**, 1811. (c) Tietze, L. F.; Thede. K.; Schimpf, R.; Sannicolò, F. *J. Chem. Soc., Chem. Commun.* **2000**, 583.

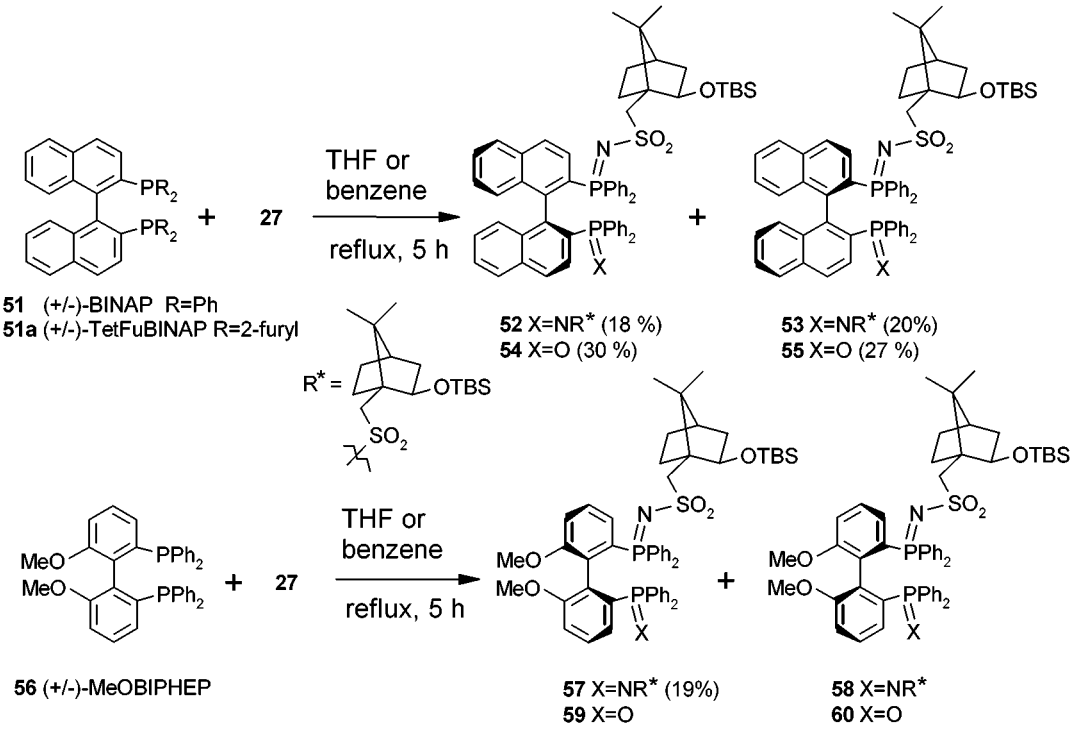
(36) The (±)-MeOBIPHEP ligand was prepared by Dr. D. Che according to literature proceedure. See: Schmid, R.; Foricher, M.; Cereghetti, M.; Schönholzer, P. *Helv. Chim. Acta* **1991**, *74*, 370.

(37) Andersen, N. G.; McDonald, R.; Keay, B. A. *Tetrahedron: Asymm.* **2001**, *12*, 263.

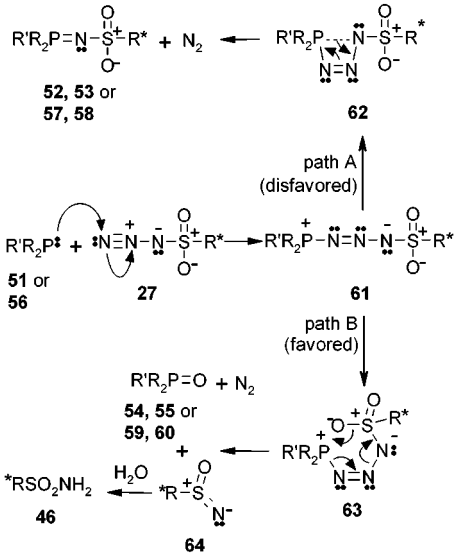
(38) (a) Leffler, J. E.; Tsuno, Y. *J. Org. Chem.* **1963**, *28*, 902. (b) Leffler, J. E.; Hosenberg, U.; Tsuno, Y.; Forsblad, I. *J. Org. Chem.* **1961**, *26*, 4811.

(39) Leffler, J. E.; Temple, R. D. *J. Am. Chem. Soc.* **1967**, *89*, 5235.

Scheme 7



Scheme 8



with ^{31}P NMR studies of the (±)-BINAP/azide **27** reaction mixture, which showed the formation of all four products **52**−**55** prior to workup. Sulfonamide **46** was also obtained from the reaction mixture and presumably formed via hydration of intermediate **64**.

Conclusions

By use of the Staudinger reaction between racemic tertiary phosphines and an enantiomerically pure organoazides **22** or **27**, a 1:1 mixture of diastereomeric phosphinimines can be formed and separated by either crystallization or flash chromatography. Subsequent hydrolysis of the isomerically pure phosphinimines gives enantiopure phosphine oxides with inversion of configuration at phosphorus. Although this method works very well for *P*-stereogenic systems, its use is somewhat limited for axially stereogenic diphosphines such as BINAP **51** and MeOBIPHEP **56**; however, BINAPFu, TetFuBINAP, and BITIANP could be resolved via this procedure. In principle, the Staudinger resolution method should be applicable to tertiary phosphines bearing substituents other than alkyl and aryl groups and work is currently in progress to test this hypothesis.

Experimental Section

General Details. Infrared spectra were recorded on a FT-IR spectrometer. Solid samples were handled as pressed KBr pellets or as CCl_4 thin films while liquid samples were analyzed neat between NaCl plates. Nuclear magnetic resonance (NMR) spectra were recorded on a 200 MHz (^{1}H), 50 MHz (^{13}C), 400 MHz (^{1}H), 100 MHz (^{13}C), 81 MHz (^{31}P), or 162 MHz (^{31}P) spectrometer. All spectra were obtained in $CDCl_3$ unless otherwise mentioned and the chemical shifts (ppm) are relative to the C*H*Cl_3 peak as an internal reference (7.27 ppm for ^{1}H 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. Low resolution MS, HRMS, and FAB-MS analyses were obtained at the University of Calgary. All melting and boiling points 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 polarimeter using a quartz cell with a 10 cm path length. Elemental analyses were performed by Ms. D. Fox at the University of Calgary. X-ray structure determination was performed by Dr. M. Parvez (University of Calgary) using a diffractometer with graphite monochromated Mo−Kα radiation.

Cyclohexylmethylphenylphosphine[15a] (**7**), cyclopentylmethylphenylphosphine[16] (**8**), isopropylmethylphenylphosphine[16] (**9**), chloro(diisopropylamino)phenylphosphine[17] (**10**), chloromethylphenylphosphine[18] (**12**), methyl-1-naphthylphenylphosphine[18] (**13**), methyl(2-methoxy-1-naphthyl)phenylphosphine[19] (**15**), methyl-2-naphthylphenylphosphine[20] (**16**), methyl-9-phenanthrylphenylphosphine[21] (**17**), 4-biphenyl-1-naphthylphenylphosphine[22] (**18**), sodium (1*S*,2*R*)-isobornyl-10-sulfonate[27] (**25**), BITIANP[35] (**49**), and MeOBIPHEP[36] (**56**) were prepared according to known procedures and exhibited spectral

properties consistent with those reported in the literature. (*R*)-Cyclohexylphenylphosphine oxide[29] (**37**), (*S*)-isopropylmethylphenyl phosphine oxide[31] (**39**), (*S*)-methyl-1-naphthylphenylphosphine oxide[32] (**40**), methyl(2-methyl-1-naphthyl)phenylphosphine oxide[40] (**41**) (*S*)-methyl(2-methoxy-1-naphthyl)phenylphosphine oxide[19] (**42**), (*S*)-methyl-2-naphthylphenylphosphine oxide[29] (**43**), methyl-9-phenanthrylphenylphosphine oxide[21] (**44**), and (*R*)-4-biphenyl-1-naphthylphenylphosphine oxide[22] (**45**) exhibited physical and spectral properties consistent with those reported in the literature.

Methyl (2-Methyl-1-naphthyl)phenylphosphine (14). To a solution of chloromethylphenylphosphine[18] (**12**) (0.238 g, 1.5 mmol) in dry Et_2O (10 mL) at −40 °C was added a freshly prepared solution of 2-methyl-1-naphthylmagnesium bromide (0.080 M solution in THF, 20 mL, 1.6 mmol). The resulting mixture was warmed to room temperature and stirred for a 3 h period. The mixture was quenched with 10% HCl and extracted with Et_2O. The combined organic extracts were dried ($MgSO_4$) and concentrated under reduced pressure to afford a thick yellow oil. The product was purified by flash chromatography (19:1 hexanes:benzene) to afford the analytically pure **14** (0.246 g, 62%). mp 190−191 °C ($CHCl_3$); IR (KBr) 2954, 1114, 748 cm^{-1}; ^1H NMR (400 MHz) δ 1.94 (d, J = 4.8 Hz, 3H), 2.80 (s, 3H), 7.20−7.54 (m, 8H), 7.88 (d, J = 8.3 Hz, 2H), 8.38 (dd, J = 8.5, 3.6 Hz, 1H); ^{13}C NMR (100 MHz) ppm 10.8 (d, J = 17 Hz), 24.3 (d, J = 26 Hz), 125.2, 126.4, 126.8 (d, J = 2 Hz), 128.1 (d, J = 17 Hz), 128.9 (d, J = 4 Hz), 129.4, 129.6 (d, J = 15 Hz), 129.9 (d, J = 6 Hz), 131.2, 131.8 (d, J = 20 Hz), 133.4 (d, J = 3 Hz), 136.4 (d, J = 7 Hz), 142.9 (d, J = 13 Hz), 145.4 (d, J = 22 Hz); ^{31}P NMR (162 MHz) ppm −41.4; mass spectrum, *m*/*z* (relative intensity, %) 264 (26, M^+), 263 (100, $M^+ - H$), 215 (13), 170 (7). Exact mass calcd for $C_{18}H_{17}P$: 264.1068. Found: 264.1066.

(1*S*,2*R*)-*O*-(*tert*-Butyldimethylsilyl)isobornyl-10-sulfonyl Azide (27). To a solution of sodium (1*S*,2*R*)-isobornyl-10-sulfonate[27] **25** (5.56 g, 21.7 mmol) in DMF (150 mL) and Et_3N (15 mL) was added TBSCl (10.84 g, 71.92 mmol). The resulting mixture was stirred for 3 h at room temperature, and the solvents were removed in vacuo (55 °C, 0.05 mmHg). The residue was taken up into ether, filtered through a pad of Celite, and concentrated under reduced pressure to afford a thick orange oily residue. The crude silyl ether was dissolved in benzene (150 mL), and DMF (5 drops) was added followed by $SOCl_2$ (9.5 mL, 0.13 mmol). The resulting solution was heated to reflux for 12 h, quenched with saturated brine, and extracted with ether. The combined organic extracts were dried ($MgSO_4$), filtered, and concentrated in vacuo to afford the desired product (7.76 g, 82% from compound **25**). The crude sulfonyl chloride was dissolved in DMA (80 mL) and H_2O (40 mL). To the solution was added NaN_3 (4.54 g, 69.8 mmol), and the resulting mixture was heated to 60 °C for 12 h. The cooled mixture was then extracted with Et_2O, washed with brine, dried ($MgSO_4$), and concentrated to furnish a light yellow oil. The product was purified by column chromatography (15:1, hexanes:ethyl acetate) to afford 6.13 g (70%) of azide **27** as a colorless oil: α^{20}_D −36.2 (*c* 5.5, $CHCl_3$); IR (KBr) 2954, 2131 (N_3) cm^{-1}; ^1H NMR (200 MHz) δ 0.08 (s, 3H), 0.11 (s, 3H), 0.89 (s, 3H), 0.90 (s, 9H), 1.05 (s, 3H), 1.06−1.47 (m, 3H), 1.49−1.86 (m, 3H), 1.88−2.10 (m, 1H), 3.12 (d, J = 14.0 Hz, 1H), 3.97 (d, J = 14.0 Hz, 1H), 4.06 (m, 1H); ^{13}C NMR (50 MHz) ppm −5.4, −4.1, 17.8, 20.1, 20.6, 25.8, 27.2, 28.6, 41., 44.5, 49.3, 50.4, 54.9, 75.8; mass spectrum, *m*/*z* (relative intensity, %) 345 (1, $M^+ - N_2$), 288 (44), 115 (66), 73 (100). Exact mass calcd for $C_{12}H_{22}N_3O_3SSi$ ($M^+ - C_4H_9$): 316.1151. Found: 316.1120.

General Procedure for the Preparation of Phosphinimines Using Azide 27. To a solution of the tertiary phosphine (1.0 mmol) in dry THF (10 mL) is *cautiously* added a solution of azide **27** (1.1 mmol) in THF (5 mL) at ambient temperature. The mixture is then heated to 60 °C under an inert atmosphere for 12 h. Removal of the solvent under reduced pressure gives the crude phosphinimine mixture, which may be purified by fractional crystallization or flash chromatography.

(S_P)-[(1*S*,2*R*)-*O*-(*tert*-Butyldimethylsilyl)isobornyl-10-sulfonamidyl]cyclohexylmethylphenylphosphinimine (28a) and (R_P)-[(1*S*,2*R*)-*O*-(*tert*-Butyldimethylsilyl)isobornyl-10-sulfonamidyl]cyclohexylmethylphenylphosphinimine (28b). Phosphinimines **28a** and **28b** were prepared according to the general procedure using cyclohexylmethylphenylphosphine[15a] **7** (1.07 g, 5.20 mmol) and azide **27** (2.04 g, 5.46 mmol). Separation of the product diastereomers was achieved by recrystallization from petroleum ether. The first diastereomer to crystallize, compound **28a**, was obtained as fine, colorless needles (1.39 g, 49%) and exhibited the following analytical data: α^{20}_D −39.7 (*c* 0.86, $CHCl_3$); mp 175−177 °C (petroleum ether); IR (KBr) 2930, 1452, 1110 cm^{-1}; ^1H NMR (200 MHz) δ 0.06 (s, 3H), 0.16 (s, 3H), 0.82 (s, 3H), 0.91 (s, 9H4), 1.00 (s, 3H), 1.07−1.90 (m, 15H), 2.04 (d, J = 11.2 Hz), 1.91−2.24 (m, 3H), 2.81 (d, J = 13.8 Hz, 1H), 3.70 (dd, J = 13.8, 2.0 Hz, 1H), 4.19 (m, 1H), 7.66−7.45 (m, 3H), 7.72-7.90 (m, 2H); ^{13}C NMR (50 MHz) ppm −4.9, −4.4, 10.3 (d, J = 58 Hz), 17.9, 20.3, 20.9, 25.0 (d, J = 3 Hz), 25.1 (d, J = 3 Hz), 25.6, 26.0, 26.2, 27.4, 28.1, 38.7 (d, J = 71 Hz), 42.2, 44.6, 48.5, 50.4, 53.8 (d, J = 5 Hz), 76.3, 127.7 (d, J = 86 Hz), 128.7 (d, J = 12 Hz), 131.1 (d, J = 9 Hz), 134.2 (d, J = 3 Hz); ^{31}P NMR (81 MHz) ppm +23.3; mass spectrum, *m*/*z* (relative intensity, %) 551 (0.2, M^+), 536 (1, $M^+ - CH_3$), 494 (53, $M^+ - C_4H_9$), 268 (64), 73 (100). Exact mass calcd for $C_{25}H_{41}NO_3PSSi$ ($M^+ - C_4H_9$): 494.2314. Found: 494.2339. Compound **28b** was recovered from the mother liquor by recrystallization (1.30 g, 45%) as colorless prisms and exhibited the following characteristics: α^{20}_D −10.0 (*c* 1.06, $CHCl_3$); mp 147−149 °C (petroleum ether); IR (KBr) 2930, 1452, 1110 cm^{-1}; ^1H NMR (200 MHz) δ 0.06 (s, 3H), 0.14 (s, 3H), 0.85 (s, 3H), 0.87 (s, 9H), 0.99 (s, 3H), 1.02−1.98 (m, 15H), 1.98−2.26 (m, 3H), 2.03 (d, J = 13 Hz, 3H), 2.81 (d, J = 13.8 Hz, 1H), 3.67 (dd, J = 13.8, 2.4 Hz, 1H), 4.10 (m, 1H), 7.41−7.64 (m, 3H), 7.70-7.82 (m, 2H); ^{13}C NMR (50 MHz) ppm −4.9, −4.4, 10.3 (d, J = 59 Hz), 17.9, 20.3, 20.9, 25.0 (d, J = 3 Hz), 25.2 (d, J = 3 Hz), 25.6, 26.0, 26.2, 27.4, 28.3, 38.7 (d, J = 72 Hz), 42.2, 44.6, 48.5, 50.4, 53.9 (d, J = 5 Hz), 76.4, 127.7 (d, J = 86 Hz), 128.7 (d, J = 12 Hz), 131.1 (d, J = 10 Hz), 132.3 (d, J = 3 Hz); ^{31}P NMR (81 MHz) ppm 23.2; mass spectrum, *m*/*z* (relative intensity, %) 551 (0.2, M^+), 536 (1, $M^+ - CH_3$), 494 (53, $M^+ - C_4H_9$), 268 (64), 73 (100). Exact mass calcd for $C_{25}H_{41}NO_3PSSi$ ($M^+ - C_4H_9$): 494.2314. Found: 494.2365.

(S_{ax})-[(1*S*,2*R*)-*O*-(*tert*-Butyldimethylsilyl)isobornyl-10-sulfonamidyl]-[3,3′-binaphtho[2,1-*b*]furan]-2,2′-diylbis-[diphenylphosphinimine] (48a) and (R_{ax})-[(1*S*,2*R*)-*O*-(*tert*-Butyldimethylsilyl)isobornyl-10-sulfonamidyl]-[3,3′-binaphtho[2,1-*b*]furan]-2,2′diylbis[diphenylphosphinimine] (48b). To a solution of racemic BINAPFu[10] (**1**) (0.242 g, 0.345 mmol) in DME (2.5 mL) was added a solution of azide **27** (0.284 g, 0.759 mmol) in 7.5 mL of DME. The resulting mixture was heated to reflux under a N_2 atmosphere for 12 h. The cooled mixture was then concentrated in vacuo to afford a thick yellow oil. Separation of the product diastereomers was achieved by column chromatography (3:1, hexanes:ethyl acetate). The first isomer to elute from the column, compound **48a**, was obtained as white solid (0.224 g, 49%), which gave the following analytical data: mp 196−198 °C (CH_3CN/H_2O); IR (KBr) 2954, 1437, 1120 cm^{-1}; ^1H NMR (400 MHz) δ −0.27 (s, 3H), −0.10 (s, 3H), 0.57 (s, 3H), 0.70 (s, 9H), 0.79 (s, 3H), 1.28−1.37 (m, 2H), 1.38−1.63 (m, 4H), 1.70−1.86 (m, 1H), 2.01 (d, J = 13.6 Hz, 1H), 2.83 (d, J = 13.6 Hz, 1H), 3.85 (m, 1H), 6.72−6.87 (m, 2H), 7.03−7.15 (m, 1H), 7.29−7.43 (m, 1H), 7.44−7.70 (m, 7H), 7.78−7.90 (m, 5H); ^{13}C NMR (100 MHz) ppm −4.7, −4.3, 18.1, 20.5, 21.1, 26.4, 27.8, 29.0, 42.8, 44.8, 48.8, 50.6, 53.4 (d, J = 5 Hz), 76.4, 112.7, 122.2 (d, J = 8 Hz), 123.6, 125.9, 127.0 (d, J = 105 Hz), 127.2 (d, J = 15 Hz), 128.0, 128.1 (d, J = 10 Hz), 128.3 (d, J = 105 Hz), 129.0, 129.2, 129.3, 130.2, 131.2, 132.8 (d, J = 3 Hz), 133.3 (d, J = 3 Hz), 133.9 (d, J = 12 Hz), 134.1 (d, J = 10 Hz), 140.8 (d, J = 151 Hz), 156.1 (d, J = 9 Hz); ^{31}P NMR (162 MHz) ppm +4.9; FAB-MS, *m*/*z* (relative intensity, %) 1393 (2, $M+H^+$). Phosphinimine **48b** was

(40) Pescher, P.; Caude, M.; Rosset, R.; Tambuté, A. *J. Chromatogr.* **1986**, *371*, 159.

obtained as a pale yellow solid (0.198 g, 43%), which was recrystallized from CH_3CN/H_2O as long white needles with the following properties: mp 176−178 °C (CH_3CN/H_2O); IR (KBr) 2954, 1438, 1118 cm^{-1}; ^1H NMR (400 MHz) δ 0.05 (s, 3H), 0.11 (s, 3H), 0.35 (s, 3H), 0.81 (s, 3H), 0.91 (s, 9H), 1.07−1.78 (m, 7H), 1.99 (d, J = 13.3 Hz, 1H), 2.85 (d, J = 13.3 Hz, 1H), 3.90 (m, 1H), 6.56−6.77 (m, 2H), 7.04 (t, J = 7.1 Hz, 1H), 7.30−7.47 (m, 4H), 7.51 (td, J = 7.3, 3.2 Hz, 2H), 7.59 (td, J = 6.9, 1.7 Hz, 1H), 7.66 (d, J = 9.1 Hz, 1H), 7.71 (d, J = 8.2 Hz, 1H), 7.78 (d, J = 7.4 Hz, 1H), 7.81 (d, J = 7.5 Hz, 1H), 7.87 (d, J = 9.1 Hz, 1H), 7.91 (d, J = 8.0 Hz, 1H); ^{13}C NMR (100 MHz) ppm −4.2, 18., 20.5, 20.9, 26.7, 27.6, 29.5, 42.7, 44.9, 48.8, 50.7, 54.3 (d, J = 2 Hz), 76.6, 113.1, 122.1 (d, J = 8 Hz), 123.8, 125.8, 126.3 (d, J = 107 Hz), 126.9 (d, J = 16 Hz), 127.8, 127.8 (d, J = 105 Hz), 128.0 (d, J = 9 Hz), 128.9, 129.1 (d, J = 14 Hz), 129.5, 130.0, 131.2, 132.6 (d, J = 3 Hz), 133.2 (d, J = 3 Hz), 133.7 (d, J = 12 Hz), 134.1 (d, J = 12 Hz), 140.9 (d, J = 145 Hz), 156.1 (d, J = 9 Hz); ^{31}P NMR (162 MHz) ppm +5.8; FAB-MS, *m*/*z* (relative intensity, %) 1393 (2, M + H^+). Anal. Calcd for $C_{80}H_{94}N_2O_8P_2S_2Si_2 + 2H_2O$: C, 67.20; H, 6.91; N, 1.96. Found: C, 67.36; H, 6.80; N, 2.01. To establish absolute stereochemistry, phosphinimine **48a** (0.155 g, 0.111 mmol) was subjected to acid hydrolysis, according to the general procedure for the preparation of phosphine oxides from phosphinimines to afford (*S*)-2,2′-bis(diphenylphosphinyl)-3,3′-binaphtho[2,1-*b*]furan (0.076 g, 93%) with α^{22}_D −170.4.

(S_{ax})-[(1*S*,2*R*)-*O*-(*tert*-Butyldimethylsilyl)isobornyl-10-sulfonamidyl]-[3,3′-bibenzo[*b*]thiophene]-2,2′-diylbis[diphenylphosphinimine] (50a) and (R_{ax})-[(1*S*,2*R*)-*O*-(*tert*-Butyldimethylsilyl)isobornyl-10-sulfonamidyl]-[3,3′-bibenzo[*b*]thiophene]-2,2′-diylbis[diphenylphosphinimine] (50b). To a solution of racemic BITIANP[35] (**49**) (0.247 g, 0.389 mmol) in THF (2.5 mL) was added a solution of azide **27** (0.320 g, 0.855 mmol) in 7.5 mL of THF. The resulting mixture was heated to reflux under a N_2 atmosphere for 24 h. The cooled mixture was then concentrated in vacuo to afford a thick yellow oil. Separation of the product diastereomers was achieved by column chromatography (3:1, hexanes:ethyl acetate). The first isomer to elute from the column, compound **50a**, was obtained as a white solid (0.240 g, 47%), which gave the following analytical data: mp 277−279 °C (CH_3CN/H_2O); IR (KBr) 2927, 1438, 1121, 1086 cm^{-1}; ^1H NMR (400 MHz) δ −0.05 (s, 3H), −0.01 (s, 3H), 0.67 (s, 3H), 0.84 (s, 9H), 0.90 (s, 3H), 1.38 (m, 1H), 1.62 (m, 5H), 2.02 (m, 1H), 2.17 (d, J = 13.8 Hz, 1H), 3.01 (d, J = 13.8 Hz, 1H), 3.95 (m, 1H), 7.00 (td, J = 7.7, 3.2 Hz), 7.20 (t, J = 7.4 Hz), 7.32 (d, J = 8.2 Hz), 7.38 (t, J = 7.5 Hz), 7.50 (td, J = 7.5, 3.3 Hz), 7.60 (d, J = 7.4 Hz), 7.63 (d, J = 7.5 Hz), 7.75 (d, J = 8.2 Hz), 7.78 (d, J = 7.4 Hz); ^{13}C NMR (100 MHz) ppm −4.4, −4.1, 18.3, 20.8, 21.3, 26.5, 27.7, 29.2, 42.8, 44.9, 48.9, 50.7, 53.5 (d, J = 7 Hz), 76.7, 122.2 (d, J = 2 Hz), 125.6, 125.8, 127.7, 127.8 (d, J = 123 Hz), 127.9 (d, J = 102 Hz), 128.2 (d, J = 13 Hz), 129.1 (d, J = 13 Hz), 129.6 (d, J = 104 Hz), 132.7 (d, J = 3 Hz), 133.3 (d, J = 3 Hz), 133.7 (d, J = 12 Hz), 133.9 (d, J = 12 Hz), 140.4 (dd, J = 7, 2 Hz), 141.6 (d, J = 13 Hz), 142.2 (d, J = 7 Hz); ^{31}P NMR (162 MHz) ppm +8.1; FAB-MS, *m*/*z* (relative intensity, %) 1325 (2, M + H^+). Anal. Calcd for $C_{72}H_{90}N_2O_6P_2S_4Si_2 + H_2O$: C, 64.35; H, 6.90; N, 2.08. Found: C, 64.57; H, 6.69; N, 2.18. Phosphinimine **50b** was obtained as a colorless solid (0.208 g, 40%) with the following properties: mp 220−222 °C (CH_3CN/H_2O); IR (KBr) 2927, 1438, 1122, 1086 cm^{-1}; ^1H NMR (400 MHz) δ 0.05 (s, 3H), 0.15 (s, 3H), 0.52 (s, 3H), 0.86 (s, 3H), 0.92 (s, 9H), 1.21 (m, 1H), 1.35−1.70 (m, 6H), 2.01 (d, J = 13.7 Hz, 1H), 3.01 (d, J = 13.7 Hz, 1H), 3.94 (m, 1H), 6.88 (td, J = 7.7, 3.4 Hz), 7.14 (d, J = 8.1 Hz), 7.18 (d, J = 7.7 Hz), 7.25 (d, J = 8.7 Hz), 7.31−7.42 (m, 3H), 7.51 (dt, J = 7.6, 3.3 Hz), 7.57−7.63 (m, 1H), 7.74 (d, J = 7.7 Hz), 7.77 (d, J = 7.3 Hz); ^{13}C NMR (100 MHz) ppm −4.2, −4.0, 18.4, 20.7, 21.1, 26.7, 27.7, 29.4, 42.8, 44.9, 48.9, 50.7, 54.1 (d, J = 3 Hz), 76.7, 122.4, 125.2, 125.4, 127.3 (d, J = 104 Hz), 127.5, 127.8 (d, J = 124 Hz), 128.0 (d, J = 13 Hz), 128.7 (d, J = 100 Hz), 129.0 (d, J = 13 Hz), 132.5 (d, J = 3 Hz), 133.3 (d, J = 3 Hz), 133.3 (d, J = 12 Hz), 134.4 (d, J = 11 Hz), 140.0 (dd, J = 8, 2 Hz), 141.3 (d, J = 14 Hz), 142.3 (d, J = 7 Hz); ^{31}P NMR (162 MHz) ppm +9.8; FAB-MS, *m*/*z* (relative intensity, %) 1325 (2, M + H^+). To establish absolute stereochemistry, phosphinimine **50a** (0.110 g, 0.083 mmol) was subjected to acid hydrolysis, according to the general procedure for the preparation of phosphine oxides from phosphinimines, to afford (*S*)-2,2′-bis(diphenylphosphinyl)-3,3′-bibenzo[*b*]thiophene (0.050 g, 91%) with α^{22}_D −324.2 (lit.[35] α^{25}_D −329.0).

Reaction of (±)-BINAP (51) with (1*S*,2*R*)-*O*-(*tert*-Butyldimethylsilyl)isobornyl-10-sulfonyl Azide (27). To a solution of racemic BINAP (**51**) (0.247 g, 0.397 mmol) in degassed toluene (10 mL) was added azide **27** (0.326 g, 0.873 mmol), and the mixture was heated to reflux under an argon atmosphere for 48 h. The cooled mixture was concentrated under reduced pressure to afford a thick yellow oil. ^{31}P NMR analysis of the crude material showed the complete consumption of starting material to yield four products **52**−**55** in an approximate 2:2:3:3 ratio. Subjecting the mixture to flash chromatography (4:1, hexanes:ethyl acetate) afforded bis-phosphinimine products **52** and **53** in isomerically pure form along with a third fraction containing compounds **54** and **55**. The first isomer to elute from the column, compound **52**, was obtained as a colorless film (0.940 g, 18%) with the following properties: mp 176−178 °C ($CHCl_3$); IR (KBr) 2926, 1438, 1085 cm^{-1}; ^1H NMR (400 MHz) δ 0.04 (s, 3H), 0.10 (s, 3H), 0.50 (s, 3H), 0.91 (s, 3H), 0.93 (s, 3H), 1.27 (m, 1H), 1.37−1.65 (m, 6H), 1.71 (d, J = 13.6 Hz, 1H), 2.78 (d, J = 13.6 Hz, 1Hb), 3.91 (m, 1H), 6.87−6.99 (m, 2H), 7.14 (t, J = 7.1 Hz, 1H), 7.35−7.51 (m, 5H), 7.55 (td, J = 7.9, 1.4 Hz, 2H), 7.69 (d, J = 7.3 Hz, 2H), 7.72 (d, J = 7.3 Hz, 2H), 7.82 (t, J = 7.1 Hz, 2H); ^{13}C NMR (100 MHz) ppm −4.1, −3.9, 18.4, 20.8, 21.1, 26.7, 27.7, 29.7, 43.0, 44.9, 48.9, 50.9, 53.8 (d, J = 4 Hz), 76.8 (CH), 124.2 (d, J = 114 Hz), 127.3, 128.2 (d, J = 13 Hz), 128.5 (d, J = 10 Hz), 128.7, 128.7 (d, J = 101 Hz), 128.8, 128.8 (d, J = 14 Hz), 129.0, 129.9 (d, J = 14 Hz), 130.9 (d, J = 95 Hz), 131.9 (d, J = 3 Hz), 132.5 (d, J = 3 Hz), 133.9 (d, J = 13 Hz), 134.0 (d, J = 11 Hz), 134.4 (d, J = 2 Hz), 134.9 (d, J = 12 Hz), 142.8 (dd, J = 6, 4 Hz); ^{31}P NMR (162 MHz) ppm +15.9; FAB-MS, *m*/*z* (relative intensity, %) 1313 (4, M + H^+). Bis-phosphinimine **53** was obtained as a colorless amorphous solid (0.105 g, 20%) with the following characteristics: mp 148−151 °C ($CHCl_3$); IR (KBr) 2926, 1438, 1120, 1086 cm^{-1}; ^1H NMR (400 MHz) δ −0.18 (s, 3H), −0.05 (s, 3H), 0.69 (s, 3H), 0.81 (s, 3H), 0.98 (s, 3H), 1.11−1.30 (m, 2H), 1.42−1.66 (m, 5H), 2.02 (d, J = 13.8 Hz, 1H), 2.70 (d, J = 13.8 Hz, 1H), 3.85 (m, 1H), 7.15 (td, J = 8.9, 3.6 Hz, 4H), 7.23 (d, J = 6.7 Hz, 1H), 7.40 (td, J = 7.6, 3.1 Hz, 2H), 7.45−7.57 (m, 3H), 7.64−7.74 (m, 4H), 7.82 (t, J = 8.4 Hz, 2H); ^{13}C NMR (100 MHz) ppm −4.2, 18.2, 20.9, 21.5, 26.6, 27.7, 29.2, 43.1, 44.7, 49.1, 50.7, 53.3 (d, J = 8 Hz, CH_2), 76.6, 124.3 (d, J = 116 Hz), 127.4, 128.2, 128.5, 128.5 (d, J = 6 Hz), 128.6, 128.7 (d, J = 96 Hz), 128.8, 128.9, 129.0, 129.5 (d, J = 16 Hz), 131.0 (d, J = 98 Hz), 132.3 (d, J = 3 Hz), 133.7 (d, J = 11 Hz, 134.2 (d, J = 12 Hz), 134.3, 134.8 (d, J = 12 Hz), 143.2 (t, J = 5 Hz); ^{31}P NMR (162 MHz) ppm +14.6; FAB-MS, *m*/*z* (relative intensity, %) 1313 (6, M + H^+). The third fraction obtained from the column contained a mixture of compounds **54** and **55**. This mixture was separated by repeated preparative TLC (7:3 $CHCl_3/CH_3CN$). The less polar fraction, compound **54**, was obtained as a colorless solid (0.118 g, 30%) and exhibited the following analytical data: mp 212−214 °C ($CHCl_3$); IR (KBr) 2951, 1437, 1118 cm^{-1}; ^1H NMR (400 MHz) δ 0.07 (s, 3H), 0.13 (s, 3H), 0.52 (s, 3H), 0.89 (s, 3H), 0.91 (s, 3H), 1.33−1.44 (m, 1H), 1.50−1.71 (m, 5H), 1.88−1.98 (m, 1H), 2.22 (d, J = 13.4 Hz, 1H), 3.45 (d, J = 13.4 Hz, 1H), 4.07 (m, 1H), 6.29 (d, J = 8.5 Hz, 1H), 6.44 (td, J = 8.5, 1.3 Hz, 1H), 6.65 (td, J = 8.0, 3.6 Hz, 2H), 6.89 (td, J = 8.4, 1.6 Hz, 1H), 7.05−7.25 (m, 7H), 7.36−7.71 (m, 13H), 7.73 (t, J = 8.2 Hz, 2H), 7.97 (dd, J = 8.4, 2.1 Hz, 1H), 8.19 (d, J = 13.1 Hz, 1H), 8.22 (d, J = 13.1 Hz, 1H), 8.33−8.45 (m, 2H); ^{13}C NMR (100 MHz) ppm −4.3, −4.2, 18.4, 20.8, 21.1, 26.5, 27.7, 29.0, 42.7, 44.9, 48.8, 50.8, 53.8 (d, J = 4 Hz), 76.9, 125.8, 126.5 (d, J = 129 Hz), 127.3, 127.4, 127.7, 127.9 (d, J = 6 Hz), 128.0, 128.1 (d, J = 5 Hz), 128.2, 128.3, 128.4, 128.6, 128.7, 128.8 (d, J = 115 Hz), 128.9, 129.6, 130.6 (d, J = 13 Hz), 131.1 (d, J = 3 Hz), 131.4 (d, J = 3 Hz), 131.5 (d, J = 9 Hz), 131.6 (d, J = 98 Hz), 132.0 (d, J = 3 Hz), 132.4 (d, J = 3 Hz), 132.68 (d, J = 12 Hz), 132.72 (d, J = 9 Hz), 133.1, 133.5 (d, J = 11 Hz), 133.6

(d, J = 101 Hz), 134.3 (d, J = 11 Hz), 134.6 (d, J = 34 Hz), 134.7 (d, J = 36 Hz), 134.9 (d, J = 11 Hz), 141.4 (dd, J = 8, 5 Hz), 142.2 (dd, J = 7, 5 Hz); ^{31}P NMR (162 MHz) ppm +12.9 (P-15), +26.1 (P-26); FAB-MS, *m*/*z* (relative intensity, %) 984 (47, M + H$^+$). The less polar material, compound **55**, was obtained as a colorless solid (0.107 mg, 27%) with the following properties: mp 189−191 °C ($CHCl_3$); IR (KBr) 2926, 1437, 1117 cm^{-1}; ^{1}H NMR (400 MHz) δ −0.07 (s, 3H), −0.01 (s, 3H), 0.63 (s, 3H), 0.83 (s, 9H), 0.98 (s, 3H), 1.20−1.40 (m, 1H), 1.47−1.71 (m, 5H), 1.96−2.07 (m, 1H), 2.33 (d, J = 13.9 Hz, 1H), 2.98 (d, J = 13.9 Hz, 1H), 3.93 (m, 1H), 6.36 (d, J = 8.5 Hz, 1H), 6.50 (t, J = 7.5 Hz, 1H), 6.96 (td, J = 7.6, 3.0 Hz, 2H), 7.08−7.26 (m, 7H), 7.28−7.57 (m, 10H), 7.58−7.98 (m, 7H), 8.07 (dd, J = 12.7, 5.3 Hz, 2H); ^{13}C NMR (100 MHz) ppm −4.3, −4.2, 18.3, 20.8, 21.4, 26.6, 27.8, 29.0, 42.9, 44.8, 49.0, 50.7, 53.6 (d, J = 4 Hz, CH_2), 76.8, 124.8, 125.9, 127.7 (d, J = 5 Hz), 127.75 (d, J = 7 Hz), 127.84, 127.9, 128.0, 128.1 (d, J = 4 Hz), 128.2 (d, J = 12 Hz), 128.3 (d, J = 3 Hz), 128.6, 128.7, 128.9 (d, J = 12 Hz), 129.2 (d, J = 76 Hz), 129.6 (d, J = 15 Hz), 130.3 (d, J = 97 Hz), 131.3 (d, J = 3 Hz), 131.7 (d, J = 3 Hz), 131.8 (d, J = 4 Hz), 131.9 (d, J = 9 Hz), 132.0 (d, J = 24 Hz), 132.2 (d, J = 3 Hz), 132.8 (d, J = 10 Hz), 132.0 (d, J = 8 Hz), 133.2, 133.4 (d, J = 63 Hz), 134.1 (d, J = 2 Hz), 134.2 (d, J = 3 Hz), 134.5 (d, J = 53 Hz), 134.6 (d, J = 53 Hz), 134.8 (d, J = 10 Hz), 142.6 (dd, J = 7, 5 Hz), 143.2 (dd, J = 6, 4 Hz); ^{31}P NMR (162 MHz) ppm +13.2 (P-15), +27.1 (P-26); FAB-MS, *m*/*z* (relative intensity, %) 984 (21, M + H$^+$).

Reaction of (±)-BIPHEP (56) with (1*S*,2*R*)-*O*-(*tert*-Butyldimethylsilyl)isobornyl-10-sulfonyl Azide (27). To a solution of racemic MeOBIPHEP[36] (**56**) (0.304 g, 0.546 mmol) in degassed toluene (10 mL) was added azide **27** (0.448 g, 1.20 mmol). The mixture was then heated to reflux under an argon atmosphere for 48 h. The cooled mixture was concentrated under reduced pressure to afford a thick yellow oil. ^{31}P NMR analysis of the crude material showed the complete consumption of starting material to yield four products **57**−**60** in an approximate 2:2:3:3 ratio. Subjecting the mixture to exhaustive flash chromatography (4:1, hexanes:ethyl acetate) afforded bis-phosphinimine product **57** and an inseparable mixture of the diastereomeric bis-phosphinimine **58**, and mono-phosphine oxides **59** and **60**. Compound **57** had: IR (KBr) 2928, 1470, 1110 cm^{-1}; ^{1}H NMR (400 MHz) δ 0.05 (s, 3H), 0.08 (s, 3H), 0.58 (s, 3H), 0.88 (s, 3H), 0.91 (s, 9H), 1.22−1.31 (m, 1H), 1.45−1.70 (m, 5H), 1.78−1.92 (m, 1H) 2.08 (d, J = 13.5 Hz, 1H), 3.29 (d, J = 13.5 Hz, 1H), 3.47 (s, 3H), 3.99 (m, 1H), 6.81 (d, J = 8.1 Hz, 1H), 7.09 (td, J = 7.5, 3.1 Hz, 2H) 7.15−7.32 (m, 3H), 7.40−7.55 (m, 3H), 7.58 (d, J = 7.6 Hz, 1H), 7.61 (d, J = 7.8 Hz, 1H), 7.86 (d, J = 7.1 Hz, 1H), 7.89 (d, J = 7.1 Hz, 1H); ^{13}C NMR (100 MHz) ppm −3.9, −4.3, 18.4, 20.9, 21.4, 26.6, 27.8, 29.6, 43.0, 44.9, 49.0, 50.8, 53.6 (d, J = 5 Hz, CH_2), 55.5, 76.5, 113.9 (d, J = 3 Hz, CH), 126.8 (d, J = 114 Hz), 127.1 (d, J = 13 Hz), 128.4 (d, J = 13 Hz), 128.6 (d, J = 7 Hz), 128.9 (d, J = 17 Hz), 129.5 (dd, J = 7, 4 Hz), 130.8 (d, J = 81 Hz), 130.8 (d, J = 117 Hz), 131.9 (d, J = 3 Hz), 132.4 (d, J = 3 Hz), 133.7 (d, J = 11 Hz), 134.6 (d, J = 11 Hz), 157.9 (d, J = 16 Hz); ^{31}P NMR (162 MHz) ppm +14.0; FAB-MS, *m*/*z* (relative intensity, %) 1273 (5, M$^+$), 1216 (9, M$^+$ − C_4H_9), 70 (100).

General Procedure for the Hydrolysis of Isomerically Pure (1*S*,2*R*)-*O*-(*tert*-Butyldimethylsilyl)isobornyl-10-sulfonamidyl Phosphinimines To Give Enantiomerically Pure Phosphine Oxides and (1*S*,2*R*)-*O*-(*tert*-Butyldimethylsilyl)isobornyl-10-sulfonamide (46). The isomerically pure phosphinimine starting material (1.0 mmol) in *p*-dioxane (20 mL) is treated with 3 M H_2SO_4 solution (7 mL), and the resulting mixture is heated to 100 °C for 3 h. The cooled reaction mixture is quenched with $NaHCO_3$ solution and extracted with $CHCl_3$. The combined organic extracts are then dried ($MgSO_4$) and concentrated in vacuo to afford the crude mixture of the desired phosphine oxide and (1*S*,2*R*)-*O*-(*tert*-butyldimethylsilyl)isobornyl-10-sulfonamide (**46**). Compound **46** can ordinarily be removed from the phosphine oxide product by flash chromatography (1:1, hexane:ethyl acetate). The phosphine oxide, which typically remains at the baseline, can be flushed from the column using 9:1 $CHCl_3$/MeOH as the eluent. The sulfonamide byproduct **46** exhibits the following characteristics: mp 113−115 °C ($CHCl_3$); IR (KBr) 3430, 3371, 2929, 1385, 1089 cm^{-1}; ^{1}H NMR (400 MHz) δ 0.07 (s, 3H), 0.10 (s, 3H), 0.87 (s, 3H), 0.90 (s, 9H), 1.02 (s, 3H), 1.02−1.13 (m, 1H), 1.30−1.42 (m, 1H), 1.62−1.80 (m, 4H), 1.90−2.03 (m, 1H), 2.96 (d, J = 14.0 Hz, 1H), 3.77 (d, J = 14.0 Hz, 1H), 4.05 (m, 1H), 4.62 (s, 2H); ^{13}C NMR (50 MHz) ppm −4.8, −3.7, 18.3, 20.5, 21.1, 26.3, 27.6, 28.8), 42.3, 44.9, 49.3, 50.6, 54.0, 76.4; mass spectrum, *m*/*z* (relative intensity, %) 290 (1, M$^+$ − C_4H_9), 226 (27), 135 (100). Exact mass calcd for $C_{12}H_{24}NO_3SSi$ (M$^+$ − C_4H_9): 290.1246. Found: 290.1236.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada (NSERC) for financial support. N.G.A. gratefully acknowledges receipt of a NSERC scholarship, Ralph Steinhauer Award of Distinction from the Alberta Heritage Foundation and an Honorary Killam Fellowship. P.D.R. gratefully acknowledges the receipt of an NSERC summer studentship.

Supporting Information Available: Experimental details and data for **29a**, **29b**, **30a**, **31**−**36 (a**,**b)**, **37**−**45** and an ORTEP diagram of **30a**. This material is available free of charge via the Internet at http://pubs.acs.org.

JO015909U