Tetrahedron: *Asymmetry* 21 (2010) 2690–2695

Contents lists available at ScienceDirect

Tetrahedron: *Asymmetry*

journal homepage: www.elsevier.com/locate/tetasy

Palladium catalyzed asymmetric sulfonylation mediated chiral β-hydroxy- and β-(*o*-diphenylphosphino)benzoyloxy (*o*-diphenyl phosphino)benzamides

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ARTICLE INFO

Article history:
Received 24 September 2010
Accepted 26 October 2010
Available online 20 November 2010

ABSTRACT

The palladium catalyzed asymmetric allylic sulfonylation reaction has been investigated employing β-hydroxy- and β-(*o*-diphenylphosphino)benzoyloxy (*o*-diphenyl phosphino)benzamides as chiral, non-racemic ligands. The bisphosphine β-benzoyloxybenzamide ligands proved to be the best ligands for this process. Competitive transition states for the (1*S*,2*R*)-norephedrine derived ligand **14** are compared and a rationale is provided for the observed enantioselectivities.

1. Introduction

The remarkable success of Tsuji-Trost palladium catalyzed asymmetric reactions with allylic substrates has spurred the development and application of a broad range of phosphorus containing ligand frameworks.[1–4] Burke et al.[5] recently developed a series of monophosphine ligands **1** that were successfully employed in the asymmetric alkylation of 1,3-diphenylpropenyl acetate with malonate nucleophiles (Fig. 1). This work inspired our group to explore the use of *Ephedra* derivatives and commercially available β-amino alcohols as templates for making both β-hydroxy(*o*-diphenylphosphino)benzamides **2** and β-(*o*-diphenylphosphino)benzoyloxy (*o*-diphenylphosphino)benzamides **3**.[6,7] We learned that these easily prepared mono- and bisphosphine ligands could indeed serve as effective ligands in the palladium catalyzed asymmetric allylic alkylation of dimethyl malonate and afforded enantioselectivities of up to 96% ee.[8]

We became interested in determining the efficacy of the *Ephedra* based phosphines and other related β-amino alcohol derived phosphines in the asymmetric allylic sulfonylation reaction that was pioneered by Hiroi and Makino (Fig. 2).[9] Eichelmann and Gais[10] as well as Bondarev et al have also made contributions in this field.[11,12] We describe herein our efforts to employ β-hydroxy- and β-(*o*-diphenylphosphino)benzoyloxy(*o*-diphenyl phosphino) benzamides as chiral, non-racemic ligands in this area.

2. Results and discussion

We began our investigation by employing triphenylphosphine as a ligand in the palladium catalyzed allylic sulfonylation of the substrate 1,3-diphenylpropenyl acetate as a test reaction (Table 1). The substrate was added to a solution containing the palladium pre-catalyst $[(\eta^3\text{-}(C_3H_5)PdCl)]_2$ and triphenylphosphine. Finally, the nucleophile (either anhydrous sodium *p*-toluenesulfinate or the monohydrate of sodium *p*-toluenesulfinate) was added to the reaction mixture. The anhydrous material gave a better yield (42%) of target compound **9** to reactions involving the hydrated salt. The catalysis reactions involving the ligands **2a** and **2b** did not yield any product when either nucleophile was applied. It is postulated that the β-hydroxy component of ligands **2a** and **2b** is responsible for deactivation of the catalytic system. The origin of this deactivation is not clear as these same ligands afforded the product in good yield and enantiomeric excess when the asymmetric alkylation of 1,3-diphenylpropenyl acetate with dimethyl malonate was carried out.[7]

To determine why the catalysis process was unsuccessful, (1*S*,2*R*)-norephedrine was acylated with *o*-(diphenylphosphino)benzoic acid (Scheme 1). The resultant amide was esterified at the benzylic alcohol by treatment with benzoyl chloride to yield the target compound in 49% isolated yield. This 'capped' variant of the β-hydroxy(*o*-diphenylphosphino)benzamide ligand was then employed in the asymmetric sulfonylation reaction with $[(\eta^3\text{-}(C_3H_5)PdCl)]_2$ and 1,3-diphenylpropenyl acetate to afford the sulfonylated product **9** in 46% yield and 78% ee favoring the (*R*)-enantiomer. Interestingly, the application of the related *O*-naphthoyl capped variant in the asymmetric sulfonylation process afforded **9** in only 5% yield and 23% ee favoring the (*S*)-enantiomer.

It is proposed that the origin of the difference in the chemical yield and enantioselectivity occurs during the course of the respective transition states and intermediates of the catalytic process (Fig. 3). In the case of the *O*-benzoyl ligand **12a**, it is believed that the ligand coordinates with palladium through the phosphino group and through the carbonyl of the benzoyl group. The potential bonding of the palladium center with the carbonyl is supported by the earlier mechanistic studies of Lloyd-Jones et al.[13] as well as by

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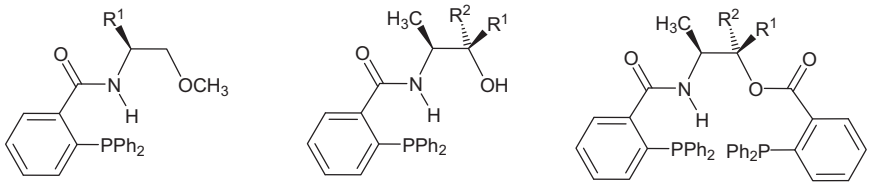
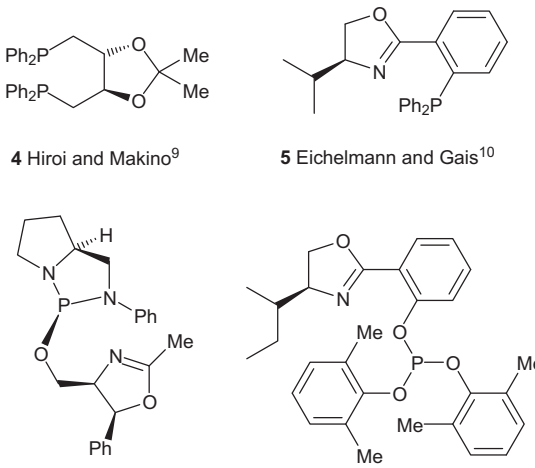
doi:10.1016/j.tetasy.2010.10.022



1a: R^1 = -*i*-Pr (Burke et al.)[1] **2a:** R^1 = -Ph, R^2 = -H **3a:** R^1 = -Ph, R^2 = -H
1b: R^1 = -Ph **2b:** R^1 = -H, R^2 = -Ph **3b:** R^1 = -H, R^2 = -Ph

Figure 1. Chiral, non-racemic phosphine ligands **1**–**3**.

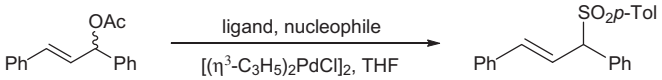


4 Hiroi and Makino[9] **5** Eichelmann and Gais[10]

6 Bondarev et al.[11] **7** Bondarev et al.[12]

Figure 2. Phosphorodiamidate and phosphite ligands employed in asymmetric sulfonylation reactions.

Table 1
Catalysis with triphenylphosphine and attempted catalysis with ligands **10**–**11**



8 **9**

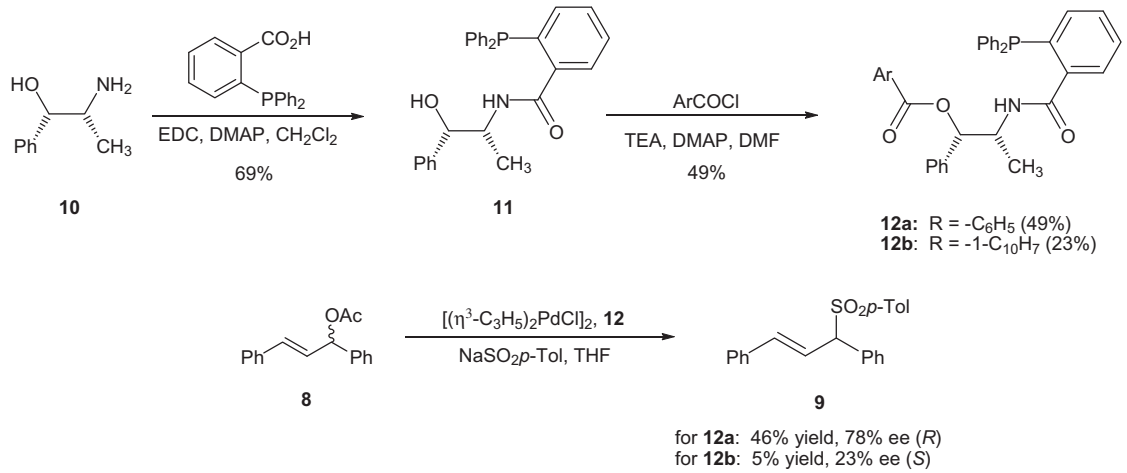
Entry	Ligand	Nucleophile	% Yield[a]
1	Ph_3P	$NaSO_2p$-Tol-H_2O	29
2	Ph_3P	$NaSO_2p$-Tol	42
3	**2a**	$NaSO_2p$-Tol-H_2O	NR
4	**2a**	$NaSO_2p$-Tol	NR
5	**2b**	$NaSO_2p$-Tol-H_2O	NR
6	**2b**	$NaSO_2p$-Tol	NR

[a] Isolated yields were determined after flash chromatography.

others.[14] The toluenesulfinate anion is believed to approach externally from this coordinated system.[9b,c] In contrast, the use of the *O*-1-naphthoyl ligand **12b** is proposed to lead to a palladium bound system, wherein the 1-naphthoyl group is omitted from the coordination sphere. It is believed that this is due to the steric environment of the C8 proton of the naphthyl substituent. Under these circumstances, it would be feasible that the toluenesulfinate anion becomes bound to the palladium, leading to an internal delivery of the nucleophile as a viable reaction pathway among others.[15]

At this time, we became interested in applying the bisphosphine ligands that we had developed earlier for palladium catalyzed asymmetric allylic alkylations with diethylmalonate.[8] Prior to our application of these ligands, the Trost ligand **13** was employed in the palladium catalyzed sulfonylation reaction (Table 2). This ligand was excellent in affording a near quantitative yield of the product with 93% enantiomeric excess in the formation of the (*R*)-enantiomer of homoallylic sulfone **9**.

The β-aminoalcohol derived bisphosphines were not as successful as in their application but still afforded results that were considered to be of interest (Table 2). For the bisphosphine ligands **14**–**18**, the use of anhydrous sodium *p*-toluenesulfinate provided a greater chemical yield and higher enantioselectivity than that of the monohydrate. This was consistent with the findings from the monophosphines. The most noteworthy item from the applica-



10 **11**

12a: R = -C_6H_5 (49%)
12b: R = -1-$C_{10}H_7$ (23%)

8 **9**

for **12a**: 46% yield, 78% ee (*R*)
for **12b**: 5% yield, 23% ee (*S*)

Scheme 1. Synthesis and application of the phosphine ligands **12** in asymmetric sulfonylation.

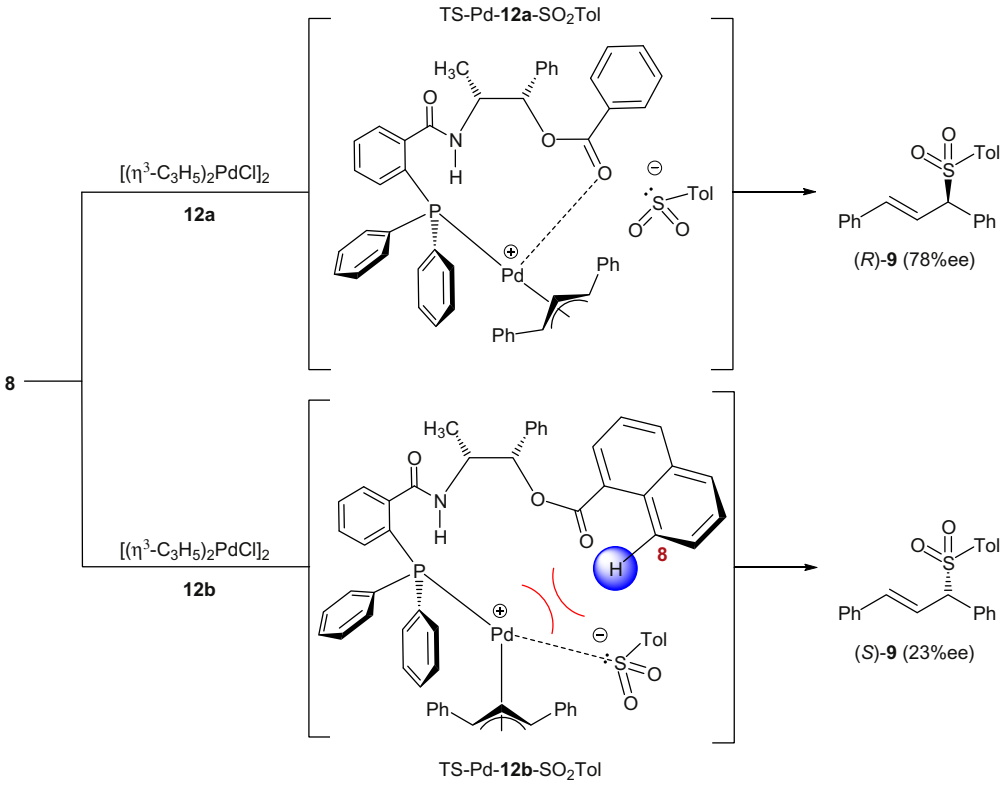


Figure 3. Proposed transition states for the application of **12a** and **12b**.

tion of the bisphosphine ligands was the application of the (1*S*,2*R*)-norephedrine derived bisphosphine **14**. This was the only entry, other than the test case of the Trost ligand, that yielded the (*S*)-enantiomer of the product (23% ee) when applied to the palladium catalyzed sulfonylation reaction. From the standpoint of the stereochemical constitution of **14**, the carbon bearing the amido group possesses an (*R*)-stereochemistry versus that the α-amino acid derived systems where the stereochemistry of the carbon bearing the amido group is the (*S*)-stereochemistry. Based on this assessment, it is logical that ligand **14** and ligands **15**–**18** would form **9** as opposing enantiomers.

There was a concern that **14** might be compromised based on the low level of enantioselection; as a result a test reaction was carried out (Table 3). Thus, the (1*S*,2*R*)-norephedrine based ligand **14** was applied to the asymmetric alkylation of allylic acetate **8** and dimethylmalonate. The result was compared to our earlier work involving the use of the (1*R*,2*S*)-norephedrine derived ligand **3a**. The results were virtually identical with those of the original observation; the formation of the opposite enantiomer was the only difference. This suggested that ligand **14** (*ent*-**3a**) was not compromised and that the observed result of the palladium catalyzed sulfonylation was valid. Ultimately, this would suggest that the palladium catalyzed alkylation with dimethyl malonate and the palladium catalyzed sulfonylation with sodium toluenesulfinate must have divergent pathways during the asymmetric induction event.

We propose that the coordination of the palladium with the bisphosphine and the ionized 1,3-diphenylpropenyl system is the same in both catalytic processes (Fig. 4). The key difference is in the type of nucleophile employed. In the case of the malonate nucleophile, the Lloyd-Jones–Norrby model[16] of amide-mediated external attack is proposed to be the dominant mode of attack. In contrast, the argument developed by Trost[15] in which the heteronucleophilic system of the toluenesulfinate nucleophile is capable of external and internal (palladium bound sulfinate) attack is proposed to be active. If an equilibrium between these two states were present (TS-**14**-A-Pd-suflinate vs TS-**14**-B-Pd-sulfinate), there would be a compromised level of enantioselection. It is noteworthy that the diastereomeric pseudonorephedrine derived ligand **15** afforded the sulfone product **9** in 84% ee favoring the (*R*)-enantiomer (Table 2). The significantly higher selectivity was attributed to the conformational differences between the ligands; apparently the *anti*-configured **15** does not exhibit the same level of competition between external and internal delivery of the toluenesulfinate nucleophile.

3. Conclusion

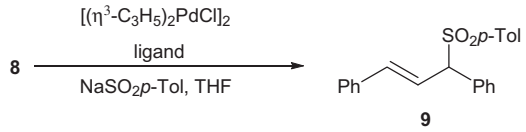
We have applied a series of monophosphine and bisphosphine ligands in the palladium catalyzed asymmetric sulfonylation reaction. The alcohol bearing monophosphines were ineffective in the catalysis process. It is believed that the appendant alcohol inhibited the process and prevented the formation of the product. The 'capped' monoligands proved to offer a better catalysis process although the acyl group bound to oxygen influences the overall level of enantioselection. The bisphosphines were the most effective ligands and generated enantioselectivities that ranged from 9% to 84% ee.

4. Experimentals

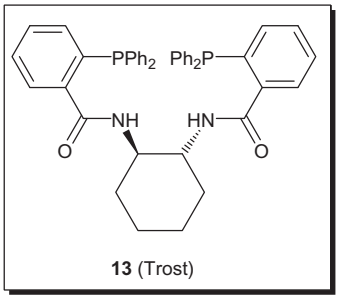
4.1. General remarks

Anhydrous THF was purchased as an anhydrous reagent and used without further purification. All reactions were run under a nitrogen atmosphere. Unless otherwise noted, all ^{1}H spectra were recorded in $CDCl_3$ using NMR spectrometer operating at 500 MHz. Chemical shifts were reported in parts per million (δ scale), and coupling constant (J values) are listed in Hertz (Hz). Tet-

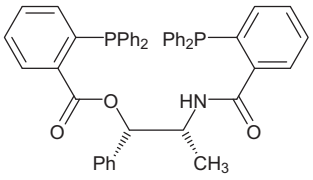
Table 2
Palladium catalyzed sulfonylation with phosphinobenzamides **14**–**19**



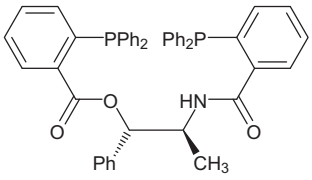
9



13 (Trost)



14



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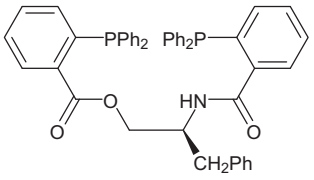

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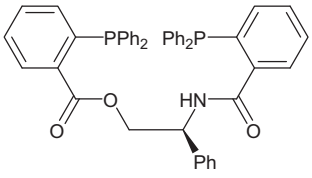

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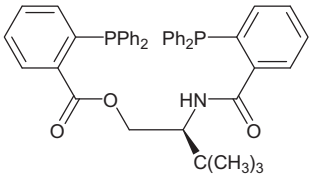


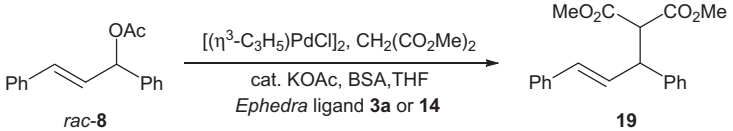
18

Entry	Ligand	Nucleophile	%Yield[a]	%ee[b]	Abs Config.[c]
1	**13**	$NaSO_2p$-Tol	99	90	(*S*)
2	**14**	$NaSO_2p$-Tol	33	23	(*S*)
3	**15**	$NaSO_2p$-Tol·H_2O	37	49	(*R*)
4	**15**	$NaSO_2p$-Tol	81	84	(*R*)
5	**16**	$NaSO_2p$-Tol·H_2O	39	9	(*R*)
6	**16**	$NaSO_2p$-Tol	14	51	(*R*)
7	**17**	$NaSO_2p$-Tol·H_2O	33	59	(*R*)
9	**17**	$NaSO_2p$-Tol	96	76	(*R*)
10	**18**	$NaSO_2p$-Tol·H_2O	36	59	(*R*)
11	**18**	$NaSO_2p$-Tol	53	75	(*R*)

[a] Isolated yields were determined after flash chromatography and recrystallization.
[b] Enantiomeric excesses were determined by chiral stationary phase HPLC (Chiralcel OD-H).
[c] The identity of the enantiomer was based on the elution from the CSP HPLC column.

ramethylsilane (TMS) was used as internal standard ($\delta = 0$ ppm). Infrared spectra are reported in reciprocal centimeters (cm^{-1}) and are measured either as nujol mull or as neat liquid. Melting points were recorded on a Mel-Temp apparatus and are uncorrected. Optical activities were measured at 589 nm using digital polarimeter. Enantiomeric ratios of the asymmetric catalyses were determined using chiral stationary phase HPLC using AD or OD-H column. High resolution mass spectra were obtained from the mass spectrometry laboratory, School of Chemical Science, University of Illinois, Urbana-Champaign. Anhydrous THF was used for the catalysis reaction. Ligands **15**, **17**, and **18** were characterized and previously described.[7,8]

Table 3
Palladium catalyzed alkylation with **3a** and **14** (*ent*-**3a**)



rac-**8** **19**

Entry	Ligand	Yield[b] (%)	e.r. [c] (% ee)	Enantiomer[d]
1	**3a**	51	94.0:6.0 (88)	(*S*)
2	**14**	50	6.0:94.0 (86)	(*R*)

[a] All reactions were conducted in THF at 25 °C.
[b] Isolated yield after flash chromatography.
[c] Enantiomeric ratios determined by CSP HPLC (Chiralcel AD column).
[d] The identity of the enantiomer was based on elution from the CSP HPLC column.

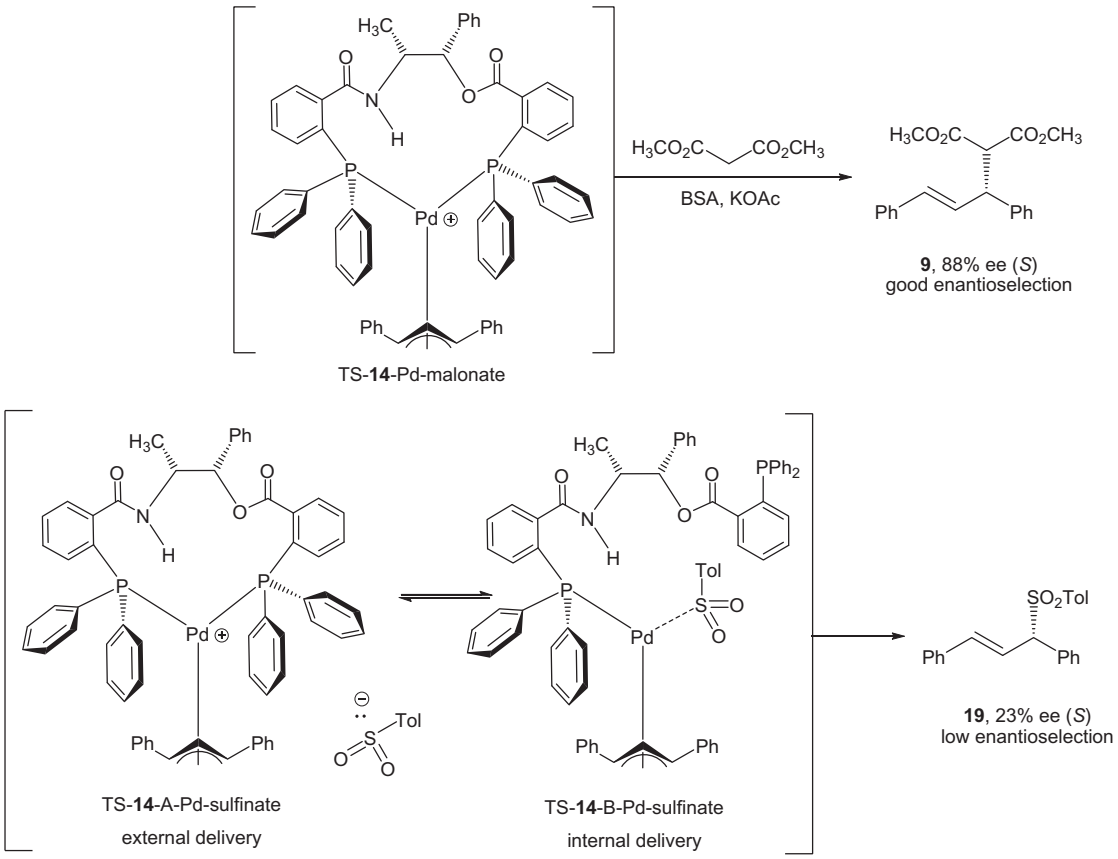


Figure 4. Proposed transitions states involving **14**.

4.2. 2-(Diphenylphosphino)-*N*-((1*S*,2*R*)-1-hydroxy-1-phenyl-2-propyl)benzamide 11

In a 100 mL flame dried nitrogen purged round bottom flask were added (1*S*,2*R*)-norephedrine (0.500 g, 3.31 mmol), dichloromethane (16.5 mL), DMAP (0.161 g, 1.32 mmol), 2-(diphenylphosphino)benzoic acid (1.011 g, 3.31 mmol), and EDC (0.634 g, 3.31 mmol). The reaction mixture was allowed to stir for 72 h and then quenched with the addition of 3 M HCl (50 mL × 2). The organic layer was diluted with dichloromethane (100 mL), washed with brine (50 mL), and dried over magnesium sulfate ($MgSO_4$). The solvents were removed via rotary evaporation and the product was purified by trituration (hexanes/EtOAc, 3:1). White solid (69%), mp: 170–173 °C. $[\alpha]_D^{23} = +34.9$ (*c* 0.38, $CHCl_3$). IR (nujol mull) (cm^{-1}): 3324, 1623, 1525, 1008, 749, 699. ^1H NMR (500 MHz, $CDCl_3$) (ppm): 0.85 (d, *J* = 6.9 Hz, 3H), 3.20 (s (br), 1H), 4.29 (dp, *J* = 2.7, 7.0 Hz, 1H), 4.89 (d, *J* = 2.6 Hz, 1H), 6.01 (d, *J* = 5.7 Hz, 1H), 6.97 (ddd, *J* = 1, 4.3, 7.6 Hz, 1H), 7.23–7.42 (m, 17H), 7.60–7.62 (m, 1H). ESI-HRMS calcd for $C_{28}H_{26}NO_2P$ $(M+H)^+$: 440.1779. Found: 440.1784.

4.3. (1*S*,2*R*)-2-(2-(Diphenylphosphino)benzamido)-1-phenylpropyl benzoate 12a

In a 50 mL flame dried nitrogen purged round bottom flask were added 2-(diphenylphosphino-*N*-((1*S*, 2*R*)-1-hydroxy-1-phenylpropan-2-yl)benzamide (0.500 g, 1.14 mmol), dimethylformamide (7 mL), DMAP (0.028 g, 0.23 mmol), benzoyl chloride (0.26 mL, 2.28 mmol), and triethylamine (0.32 mL, 2.28 mmol). The reaction mixture was heated at reflux and allowed to stir overnight. The reaction mixture was diluted with ethyl acetate (50 mL) washed with HCl (2 × 50 mL), and brine (50 mL). The organic layer was dried over magnesium sulfate ($MgSO_4$). The solvents were removed via rotary evaporation and the product was recrystallized (hexanes/CH_2Cl_2, 3:1). White solid (49%), mp: 188–190 °C. $[\alpha]_D^{23} = -31.0$ (*c* 0.98, $CHCl_3$). IR (nujol mull) (cm^{-1}): 3337, 1713, 1645, 1524, 1273, 744, 701. ^1H NMR (500 MHz, $CDCl_3$) δ (ppm): 1.05 (d, *J* = 6.8 Hz, 3H), 4.59–4.66 (m, 1H), 6.09 (d, *J* = 3.6 Hz, 1H), 6.18 (d, *J* = 6.8 Hz, 1H), 6.89–6.91 (m, 1H), 7.18–7.37 (m, 17H), 7.45–7.48 (m, 2H), 7.51–7.54 (m, 1H), 7.58–7.61 (m, 1H), 8.09–8.11 (m, 2H). ESI-HRMS calcd for $C_{35}H_{30}NO_3P$ $(M+H)^+$: 544.2042. Found: 544.2033.

4.4. (1*S*,2*R*)-2-(2-(Diphenylphosphino)benzamido)-1-phenylpropyl 1-napthoate 12b

In a 100 mL flame dried nitrogen purged round bottom flask were added 2-(diphenylphosphino-*N*-((1*S*,2*R*)-1-hydroxy-1-phenyl-2-propyl)benzamide (0.450 g, 1.02 mmol), dimethylformamide (5 mL), DMAP (0.024 g, 0.20 mmol), 1-naphthoyl chloride (0.389 g, 2.04 mmol), and triethylamine (0.28 mL, 2.04 mmol). The reaction mixture was heated at reflux and allowed to stir overnight. The reaction mixture was diluted with ethyl acetate (50 mL), washed with 1 M HCl (2 × 50 mL), and brine (50 mL). The organic layer was dried over magnesium sulfate ($MgSO_4$). The solvents were removed via rotary evaporation. The crude mixture was purified by column chromatography (hexane/EtOAc, 80:20) and was recrystallized twice (hexanes/CH_2Cl_2, 3:1). ^1H NMR contamination with 1-napthoic acid (~20%). White solid (23%), mp: 163–165 °C. $[\alpha]_D^{23} = -10.5$ (*c* 0.35, $CHCl_3$). IR (nujol mull) (cm^{-1}): 3349, 1706, 1643, 1524, 1277, 1247, 778, 741, 700. ^1H NMR (500 MHz, $CDCl_3$) (ppm): 1.05 (d, *J* = 6.8 Hz, 3H), 4.52–4.71 (m, 1H), 6.21–6.25 (m,

1H), 6.90 (dd, J = 4.1, 7.6 Hz, 1H), 7.16–7.66 (m, 16H), 7.86–7.89 (m, 1H), 8.05 (d, J = 8.3 Hz, 1H), 8.34–8.37 (m, 1H), 8.90–8.93 (m, 1H). ESI-HRMS calcd for $C_{39}H_{32}NO_3P$ ($M+H^+$): 594.2198. Found: 594.2203.

4.5. (1*S*,2*R*)-2-(2-(Diphenylphosphino)benzamido)-1-phenylpropyl 2-(diphenylphosphino) benzoate 14

In a 100 mL flame dried nitrogen purged round bottom flask was added (1*S*,2*R*)-norephedrine (0.500 g, 3.31 mmol), dichloromethane (16.5 mL), DMAP (0.161 g, 1.32 mmol), 2-(diphenylphosphino)benzoic acid (2.223 g, 7.28 mmol), and EDC (1.396 g, 7.28 mmol). The reaction mixture was allowed to stir for 24 h and was quenched with the addition of 3 M HCl (50 mL × 2). The organic layer was diluted with dichloromethane (100 mL), washed with brine (50 mL), and dried over magnesium sulfate ($MgSO_4$). The solvents were removed via rotary evaporation and the product was isolated by flash column chromatography (hexanes/EtOAc, 8:2). Viscous wax (50%), $[\alpha]_D^{23} = -10.8$ (c 1.00, $CHCl_3$). IR (nujol mull) (cm^{-1}): 1715, 1652, 1248, 743, 696. ^1H NMR (500 MHz, $CDCl_3$) δ (ppm): 0.81 (d, J = 6.9 Hz, 3H), 4.50–4.57 (m, 1H), 6.10 (d, J = 3.4 Hz, 1H), 6.77 (d, J = 8.7 Hz, 1H), 6.92–6.95 (m, 1H), 7.01 (dd, J = 3.9, 7.5 Hz, 1H), 7.11–7.14 (m, 1H), 7.06 (d, J = 6.9 Hz, 2H), 7.16–7.34 (m, 26H), 7.39–7.46 (m, 2H), 7.52–7.57 (m, 1H), 8.10–8.13 (m, 1H). ESI-HRMS calcd for $C_{47}H_{39}NO_3P_2$ ($M+H^+$): 728.2483. Found: 728.2479.

4.6. (*S*)-2-(2-(Diphenylphosphino)benzamido)-3-phenylpropyl 2-(diphenylphosphino) benzoate 16

In a 100 mL flame dried nitrogen purged round bottom flask were added (*S*)-2-amino-3-phenyl-1-propanol (0.500 g, 3.31 mmol), dichloromethane (16.5 mL), DMAP (0.161 g, 1.32 mmol), 2-(diphenylphosphino)benzoic acid (2.230 g, 7.28 mmol), and EDC (1.396 g, 7.28 mmol). The reaction mixture was allowed to stir for 24 h and was quenched with the addition of 3 M HCl (50 mL × 2). The organic layer was diluted with dichloromethane (100 mL), washed with brine (50 mL), and dried over magnesium sulfate ($MgSO_4$). The solvents were removed via rotary evaporation and the product was isolated by flash column chromatography (hexanes/EtOAc, 9:1) and recrystallized (hexanes/CH_2Cl_2, 3:1). White solid (26%), mp: 172–173 °C. $[\alpha]_D^{23} = +4.5$ (c 1.00, $CHCl_3$). IR (nujol mull) (cm^{-1}): 3347, 1712, 1636, 1258, 743, 696. ^1H NMR (500 MHz, $CDCl_3$) δ (ppm): 2.55 (dd, J = 4.7, 13.7 Hz, 1H), 2.74 (dd, J = 8.0, 13.7 Hz, 1H), 4.02 (dd, J = 7.7, 11.4 Hz, 1H), 4.10 (dd, J = 7.1, 11.5 Hz, 1H), 4.48–4.54 (m, 1H), 6.64 (d, J = 8.7 Hz, 1H), 6.91–6.97 (m, 2H), 7.06 (d, J = 6.9 Hz, 2H), 7.14–7.32 (m, 25H), 7.38–7.44 (m, 2H), 7.52–7.56 (m, 1H), 8.10–8.13 (m, 1H). ESI-HRMS calcd for $C_{47}H_{39}NO_3P_2$ ($M+H^+$): 728.2483. Found: 728.2443.

4.7. General procedure for the catalytic asymmetric allylic sulfonylation reactions 9

In a 100 mL flame dried, nitrogen purged round bottom flask were added the ligand (0.049 g, 0.067 mmol), anhydrous THF (4 mL), and $[(\eta^3\text{-}C_3H_5)PdCl]_2$ (0.025 g, 0.067 mmol). The mixture was allowed to stir for 15 min. 1,3-Diphenylpropenyl acetate was dissolved in THF (1 mL) and added to the reaction mixture. The mixture was allowed to stir for an additional 30 min. Sodium *p*-toluenesulfinate (0.595 g, 3.34 mmol) was added and the reaction mixture was allowed to stir overnight at room temperature. The reaction was diluted with dichloromethane (50 mL), washed with water (3 × 50 mL), and dried with magnesium sulfate ($MgSO_4$). The solvents were removed via rotary evaporation and the product was isolated by flash column chromatography (hexanes/EtOAc, 9:1) and recrystallized (hexanes/CH_2Cl_2, 3:1). The products were analyzed by HPLC using a Chiralcel OD-H column (hexanes/*i*-PrOH, 95:5, 0.5 mL/min). White solid (29%), mp: 161–163 °C. IR (nujol mull) (cm^{-1}): 1596, 1494, 748, 700, 666. ^1H NMR (500 MHz, $CDCl_3$) δ (ppm): 2.38 (s, 3H), 4.82 (d, J = 8.2 Hz, 1H), 6.59–6.60 (m, 2H), 7.19 (d, J = 8.1 Hz, 2H), 7.24–7.27 (m, 1H), 7.29–7.36 (m, 9H), 7.53 (d, J = 8.3 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): 21.6, 75.4, 120.3, 126.8, 128.46, 128.64, 128.69, 128.87, 129.31, 129.34, 129.73, 132.5, 134.5, 136.0, 138.0. ESI-HRMS calcd for $C_{22}H_{20}O_2S$ ($M+Na^+$): 371.1082. Found: 371.1082.

Acknowledgements

The authors gratefully acknowledge financial support from the National Science Foundation (Grant CHE-644950). The 500 MHz NMR spectroscopic data collected in this work are based upon work supported by the National Science Foundation under Grant CHE-0722385.

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