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Development of 4,4′-Substituted-XylBINAP Ligands for Highly Enantioselective Hydrogenation of Ketones

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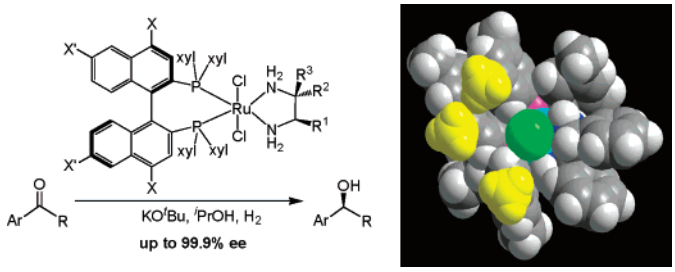

A family of 4,4′-substituted-xylBINAPs was synthesized in multistep sequences and characterized by NMR spectroscopy and mass spectrometry. Ru(diphosphine)(diamine)Cl_2 complexes based on these 4,4′-substituted-xylBINAPs and chiral diamines (DPEN and DAIPEN) were synthesized by treatment of [(benzene)$RuCl_2$]$_2$ with 4,4′-substituted-xylBINAP followed by chiral diamine, and characterized by ^{1}H and ^{31}P NMR spectroscopy and mass spectrometry. These Ru complexes were used for asymmetric hydrogenation of aromatic ketones in a highly enantioselective manner with complete conversion. With 0.1% catalyst loading, complete conversion and enantioselectivity greater than 99% were obtained for most of the aromatic ketones examined. These Ru catalysts thus gave the highest ee for asymmetric hydrogenation of aromatic ketones among all of the catalysts reported in the literature. A single-crystal X-ray diffraction study of Ru[(*R*)-**L**$_4$][(*R*,*R*)-DPEN]Cl_2 indicated that the 4-methyl group of the naphthyl ring and the methyl groups of the two xylyl moieties form a fence on the opposite side of the DPEN ligand of the Ru center. These three methyl groups will have significant repulsive interactions with the bulky aryl ring of the hydrogen-bonded aromatic ketone in the disfavored transition state. These results support our hypothesis of combining dual modes of enantiocontrol (i.e., the substituents on 4,4′-positions of the binaphthyl framework and the methyl groups on the bis(xylyl)phosphino moieties) to achieve higher stereoselectivity in the hydrogenation of aromatic ketones.

1. Introduction

Homogeneous asymmetric catalysis has undergone tremendous growth over the past four decades.[1] Many highly enantioselective asymmetric catalytic processes are now available for the synthesis of a wide variety of chiral compounds for the pharmaceutical, agrochemical, and other industries. Among these processes, catalytic asymmetric hydrogenation is undoubtedly the most mature technology,[2] as exemplified by numerous successful industrial processes such as the synthesis of *L*-Dopa[2a] and (*S*)-Metolachlor.[3] An industrially useful asymmetric catalyst needs to have both high activity (TON) and high enantioselectivity. A practically useful asymmetric catalyst thus either needs to have an extremely high turnover number (TON) or can be readily recycled and reused.

In 1995, Noyori et al. disclosed one of the most powerful methods for the production of chiral secondary alcohols

(1) (a) Hayashi, T.; Tomioka, K.; Yonemitsu, O. *Asymmetric Synthesis*: *Graphical Abstracts and Experimental Methods*; Gordon and Beach Science Publishers: Amsterdam, The Netherlands, 1998. (b) Ojima, I., Ed. *Catalytic Asymmetric Synthesis*; VCH: New York, 1993. (c) Lin, G.-O.; Li, Y.-M.; Chan, A. S. C. *Principles of Applications Asymmetric Synthesis*; Wiley-Interscience: John Wiley & Sons: New York, 2001.

(2) (a) Knowles, W. S. *Adv. Synth. Catal.* **2003**, *345*, 3. (b) Noyori, R. *Angew. Chem., Int. Ed.* **2002**, *41*, 2008. (c) Zhou, Y. G.; Tang, W.; Wang, W. B.; Li, W.; Zhang, X. *J. Am. Chem. Soc.* **2002**, *124*, 4952. (d) Ireland, T.; Tappe, K.; Grossheimann, G.; Knochel, P. *Chem. Eur. J.* **2002**, *8*, 843. (e) Ohkuma, T.; Koizumi, M.; Muniz, K.; Hilt, G.; Kabuto, C.; Noyori, R. *J. Am. Chem. Soc.* **2002**, *124*, 6508.

(3) (a) Togni, A.; Breutel, C.; Schnyder, A.; Spindler, F.; Landert, H.; Tijani, A. *J. Am. Chem. Soc.* **1994**, *116*, 4062. (b) Blaser, H.-U. *Adv. Synth. Catal.* **2002**, *344*.

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SCHEME 1

via the asymmetric reduction of aromatic ketones using molecular hydrogen (Scheme 1).[4] For example, a combination of Ru[(*S*)-BINAP](DMF)$_n$Cl$_2$, (*S*,*S*)-1,2-diphenylethylenediamine (DPEN), and KOH in 2-propanol catalyzed the asymmetric hydrogenation of 1-acetonaphthone to give (*R*)-1-(1-naphthyl)ethanol in 97% ee and >99% conversion (Scheme 1).[4] Optimal homochiral Ru(xylBINAP)(DAIPEN)Cl$_2$ complex (DAIPEN is (2*R*)-(−)-1,1-bis-(4-methoxyphenyl)-3-methyl-1,2-butanediamine) catalyzes the hydrogenation of a variety of simple aromatic ketones in the presence of strong bases such as KOH, KO-*i*-C_3H_7, or KO-*t*-C_4H_9 in 2-propanol to give secondary alcohols of >95% ee.[5]

Since Noyori's original disclosure, much effort has been devoted to further tuning of the Ru(diphosphine)(diamine)Cl$_2$ catalyst system as well as understanding the mechanism of this powerful catalytic system.[6] Seminal contributions by Noyori and others have established that this catalyst system follows a nonclassical metal−ligand bifunctional mechanism, whereby a hydride on the Ru and a proton of the NH_2 group are simultaneously transferred to the C=O function through a six-membered hydrogen-bonded transition state.[7] Although many other chiral diphosphines have also been examined for the highly asymmetric hydrogenation of aromatic ketones, there is no consensus on exactly how enantiocontrol occurs in this interesting catalytic system. As shown in Scheme 2, many phosphine systems including BINAP,[4] HexaPHEMP,[8] P-Phos,[9] PhanePhos,[10] and SpiroPhos[11] gave good to excellent enantioselectivity. All these efficient diphosphines share a common feature of possessing bis(xylyl)phosphino moieties.

Our work on heterogeneous asymmetric hydrogenation of aromatic ketones unexpectedly showed that solid Ru-precatalyst with 4,4′-substituted BINAP exhibited much higher ee values than its parent homogeneous BINAP system.[12] Our group has since then examined homogeneous asymmetric hydrogenation of aromatic ketones using a family of tunable 4,4′-substituted BINAP ligands.[13] These Ru(4,4′-substituted BINAP)(diamine)Cl$_2$ complexes exhibited ee values comparable to those of the best catalysts prepared by Noyori et al. More importantly, an entirely new approach toward enantiocontrol was achieved by relying on repulsive interactions between the aryl group of aromatic ketones and bulky substituents on the 4,4′-positions of BINAP in the disfavored transition state. In this paper, we would like to report our efforts in the design of a family of 4,4′-substituted-XylBINAP ligands and in combining two modes of enantiocontrol (i.e., the substituents on 4,4′-postions of the binaphthyl framework and the methyl groups on the bis(xylyl)phosphino moieties) to design highly enantioselective Ru catalysts for the reduction of aromatic ketones.

2. Results and Discussion

2.1. Synthesis of 4,4′-Substituted-xylBINAP Ligands. A family of 4,4′-substituted-xylBINAP ligands was obtained in multistep sequences starting from known enantiopure BINOL derivatives in relatively high yield for each step. All the intermediates and final ligands were readily purified by using silica gel chromatography and characterized by ^{1}H and ^{13}C{^{1}H} NMR spectroscopy and mass spectrometry. Phosphorus-containing compounds were also characterized by ^{31}P{^{1}H} NMR spectroscopy.

Enantiopure 4,4′-bis(TMS)-2,2′-bis[bis(xylyl)phosphino]-1,1′-binaphthyl ligand, $\mathbf{L_1}$, was synthesized in 7 steps starting from known 6,6′-dichloro-4,4′-dibromo-2,2′-bis-(TBDMS)-1,1′-binaphthalene[14] in 27.6% overall yield (Scheme 3). Lithiation of 6,6′-dichloro-4,4′-dibromo-2,2′-bis(TBDMS)-1,1′-binaphthalene by ^{n}BuLi at −78 °C in THF followed by the addition of trimethylsilyl bromide afforded 6,6′-dichloro-4,4′-bis(TMS)-2,2′-bis(TBDMS)-1,1′-binaphthalene, **1**. The TBDMS groups in **1** were deprotected with ^{n}Bu$_4$NF in THF to afford the dihydroxy intermediate **2**, which was hydrodechlorinated in the presence of Pd/C catalyst to give 4,4′-bis(TMS)-2,2′-dihydroxy-1,1′-binaphthalene (**3**). The dihydroxy groups in **3** were converted to triflate groups by treatment with triflic anhydride (Tf$_2$O). The resulting 4,4′-bis(TMS)-2,2′-bis(triflato)-1,1′-binaphthalene (**4**) was reacted with bis-(xylyl)phosphine oxide in the presence of Pd(OAc)$_2$, 1,4-bis(di-phenylphosphino)butane (dppb), and Hünig's base (NEt$_2$^{i}Pr) in DMSO at 110 °C for 3 days to afford 4,4′-bis(TMS)-2-triflato-2′-bis(xylyl)phosphinyl-1,1′-binaphthyl (**5**). **5** was then reduced with (EtO)$_3$SiH in the presence of Ti(O^{i}Pr)$_4$ to give 4,4′-bis(TMS)-2-triflato-2′-bis(xylyl)phosphino-1,1′-binaphthyl (**6**).[15] **6** was finally treated with (xyl)$_2$PH in the presence of Ni(dppe)Cl$_2$ catalyst and 1,4-diazabicyclo[2.2.2]octane (DABCO) in DMF to afford the desired ligand $\mathbf{L_1}$.

4-TMS-2,2′-bis[bis(xylyl)phosphino]-1,1′-binaphthyl ($\mathbf{L_2}$) was synthesized in 9 steps starting from 4-bromo-6,6′-

(4) (a) Ohkuma, T.; Ooka, H.; Ikariya, T.; Noyori, R. *J. Am. Chem. Soc*. **1995**, *117*, 10417. (b) Doucet, H.; Ohkuma, T.; Murata, K.; Yokozawa, T.; Kozawa, M.; Katayama, E.; England, A. F.; Ikariya, T.; Noyori, R. *Angew. Chem., Int. Ed*. **1998**, *37*, 1703. (c) Ohkuma, T.; Ishii, D.; Takeno, H.; Noyori, R. *J. Am. Chem. Soc*. **2000**, *122*, 6510.

(5) Ohkuma, T.; Koizumi, M.; Doucet, H.; Pham, T.; Kozawa, M.; Murata, K.; Katayama, E.; Yokozawa, T.; Ikariya, T.; Noyori, R. *J. Am. Chem. Soc.* **1998**, *120*, 13529.

(6) (a) Genov, D. G.; Ager, D. J. *Angew. Chem., Int. Ed*. **2004**, *43*, 2816. (b) Scalone, M.; Waldmeier, P. *Org. Process Res. Dev*. **2003**, *7*, 418. (c) Wu, J.; Ji, J.-X.; Guo, R.; Yeung, C.-H.; Chan, A. S. C. *Chem Eur. J*. **2003**, *9*, 2963. (d) Chaplin, D.; Harrison, P.; Henschke, J. P.; Lennon, I. C.; Meek, G.; Moran, P.; Pilkington, C. J.; Ramsden, J. A.; Watkins, S.; Zanotti-Gerosa, A. *Org. Process Res. Dev*. **2003**, *7*, 89. (e) Wu, J.; Chen, H.; Kwok, W.; Guo, R.; Zhou, Z.; Yeung, C.-H.; Chan, A. S. C. *J. Org. Chem*. **2002**, *67*, 7908.

(7) (a) Sandoval, C. A.; Ohkuma, T.; Muniz, K.; Noyori, R. *J. Am. Chem. Soc.* **2003**, *125*, 13490. (b) Abdur-Rashid, K.; Clapham, S. E.; Hadzovic, A.; Harvey, J. N.; Lough, A. J.; Morris, R. H. *J. Am. Chem. Soc*. **2002**, *124*, 15104-15118· (c) Abdur-Rashid, K.; Faatz, M.; Lough, A. J.; Morris, R. H. *J. Am. Chem. Soc*. **2001**, *123*, 7473−7474.

(8) Henschke, J. P.; Burk, M. J.; Malan, C. G.; Herzberg, D.; Peterson, J. A.; Wildsmith, A. J.; Cobley, C. J.; Casy, G. *Adv. Synth. Catal.* **2003**, *345*, 300.

(9) (a) Pai, C.-C.; Lin, C.-W.; Lin, C.-C.; Chen, C.-C.; Chan, A. S. C. *J. Am. Chem. Soc*. **2000**, *122*, 11513. (b) Wu, J.; Chen, H.; Kwok, W. H.; Lam, K. H.; Zhou, Z. Y.; Yeung, C. H.; Chan, A. S. C. *Tetrahedron Lett.* **2002**, *43*, 1539.

(10) Burk, M. J.; Hems, W.; Herzberg, D.; Malan, C.; Zanotti-Gerosa, A. *Org. Lett.* **2000**, *2*, 4173.

(11) Xie, J.-H.; Wang, L.-X.; Fu, Y.; Zhu, S.-F.; Fan, B.-M.; Duan, H.-F.; Zhou, Q.-L. *J. Am. Chem. Soc*. **2003**, *125*, 4404.

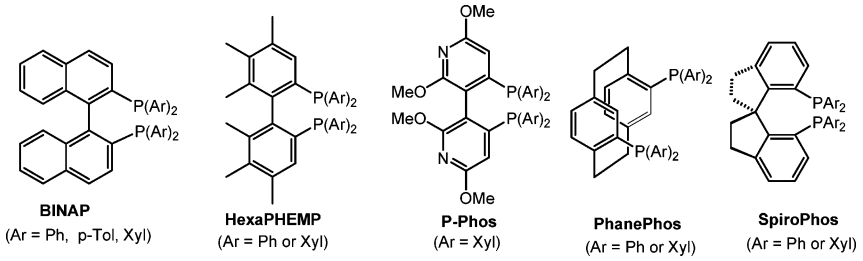
(12) Hu, A.; Ngo, H. L.; Lin, W. *J. Am. Chem. Soc.* **2003**, *125*, 11490.

(13) Hu, A.; Ngo, H. L.; Lin, W. *Org. Lett.* **2004**, *6*, 2937.

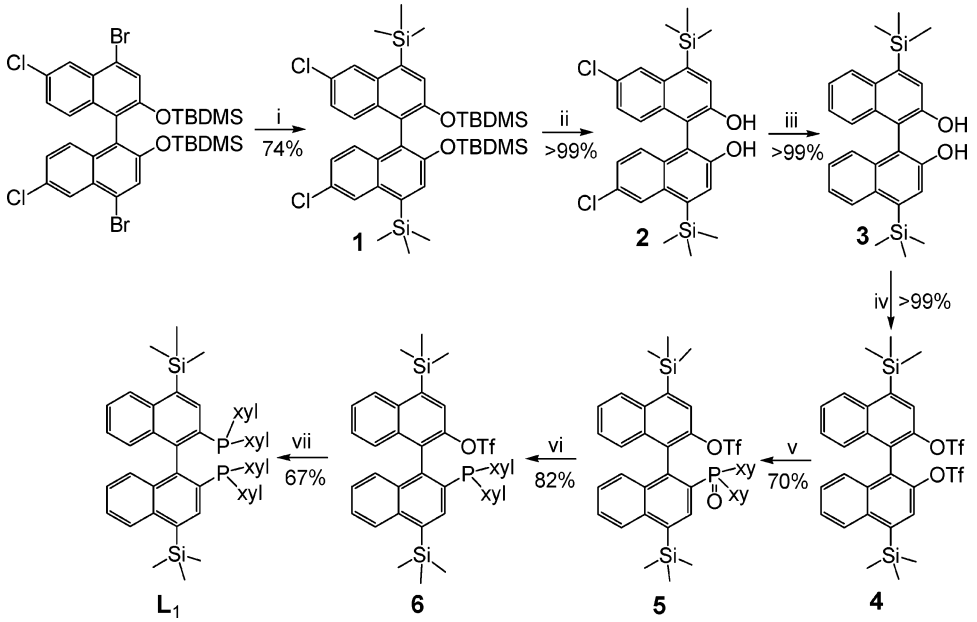
(14) Lee, S. J.; Hu, A.; Lin, W. *J. Am. Chem. Soc.* **2002**, *124*, 12948.

(15) Allen, A., Jr.; Ma, L.; Lin, W. *Tetrahedron Lett*. **2002**, *43*, 3707.

SCHEME 2



SCHEME 3[a]



[a] Reagents and conditions: (i) (a) ^{n}BuLi/hexane, −78 °C; (b) $(CH_3)_3SiBr$, THF, −78 °C to rt, 12 h; (ii) $^n Bu_4NF$, THF, rt, 1 h; (iii) H_2, Pd/C, Et_3N, MeOH, rt, 12 h; (iv) $(Tf)_2O$, pyridine, CH_2Cl_2, rt, 12 h; (v) HP(O)$(Xyl)_2$, $Pd(OAc)_2$, dppb, Et_2N^iPr, DMSO, 110 °C, 3 days; (vi) $(EtO)_3SiH$, $Ti(O^iPr)_4$, benzene, reflux for 4 h; (vii) $HP(Xyl)_2$, Ni(dppe)Cl_2, DABCO, DMF, 110 °C, 3 days.

dichloro-2,2′-diethoxy-1,1′-binaphthalene[16] with an overall yield of 31% (Scheme 4). The reaction sequences leading to 4-TMS-2,2′-bis(triflato)-1,1′-binaphthalene (**12**) were the same as for the synthesis of 4,4′-bis(TMS)-2,2′-bis(triflato)-1,1′-binaphthalene (**4**). Pd-catalyzed monophosphinylation of 4-TMS-2,2′-bis(triflato)-1,1′-binaphthalene with $(xyl)_2POH$, however, gave a mixture of two separable regioisomers, 4-TMS-2-triflato-2′-bis(xylyl)-phosphinyl-1,1′-binaphthyl (**13a**) and 4-bis(TMS)-2-bis-(xylyl)phosphinyl-2′-triflato-1,1′-binaphthyl (**13b**), in roughly 1:1 ratio. Ti-mediated reduction of this mixture of regioisomers with $(EtO)_3SiH$ led to a mixture of monophosphino products (**14a** and **14b**), which was directly treated with $(xyl)_2PH$ in the presence of Ni(dppe)Cl_2 catalyst and DABCO in DMF to afford the desired $\mathbf{L_2}$.

4,4′-Diphenyl-6,6′-dichloro-2,2′-bis(bis(xylyl)phosphino)-1,1′-binaphthyl ligand ($\mathbf{L_3}$) was obtained in 6 steps starting from 4,4′-dibromo-6,6′-dichloro-2,2′-diethoxy-1,1′-binaphthalene[13] with an overall yield of 21.4%. Suzuki coupling of 4,4′-dibromo-6,6′-dichloro-2,2′-diethoxy-1,1′-binaphthalene with $PhB(OH)_2$ in the presence of Pd-$(PPh_3)_4$ in DME afforded 4,4′-diphenyl-6,6′-dichloro-2,2′-diethoxy-1,1′-binaphthalene (**15**) in 73% yield. The ethoxy groups in **15** were deprotected with BBr_3 in CH_2Cl_2 and then converted to triflate groups with use of Tf_2O. Pd-catalyzed monophosphinylation of 4,4′-diphenyl-6,6′-dichloro-2,2′-bis(triflato)-1,1′-binaphthalene (**17**) with $(xyl)_2POH$, followed by Ti-mediated reduction with (Et_3O)-SiH gave 6,6′-dichloro-4,4′-diphenyl-2-triflato-2′-bis(xyl)-phosphino-1,1′-binaphthyl (**19**), which was then treated with $(xyl)_2PH$ in the presence of Ni catalyst to give the desired ligand $\mathbf{L_3}$.

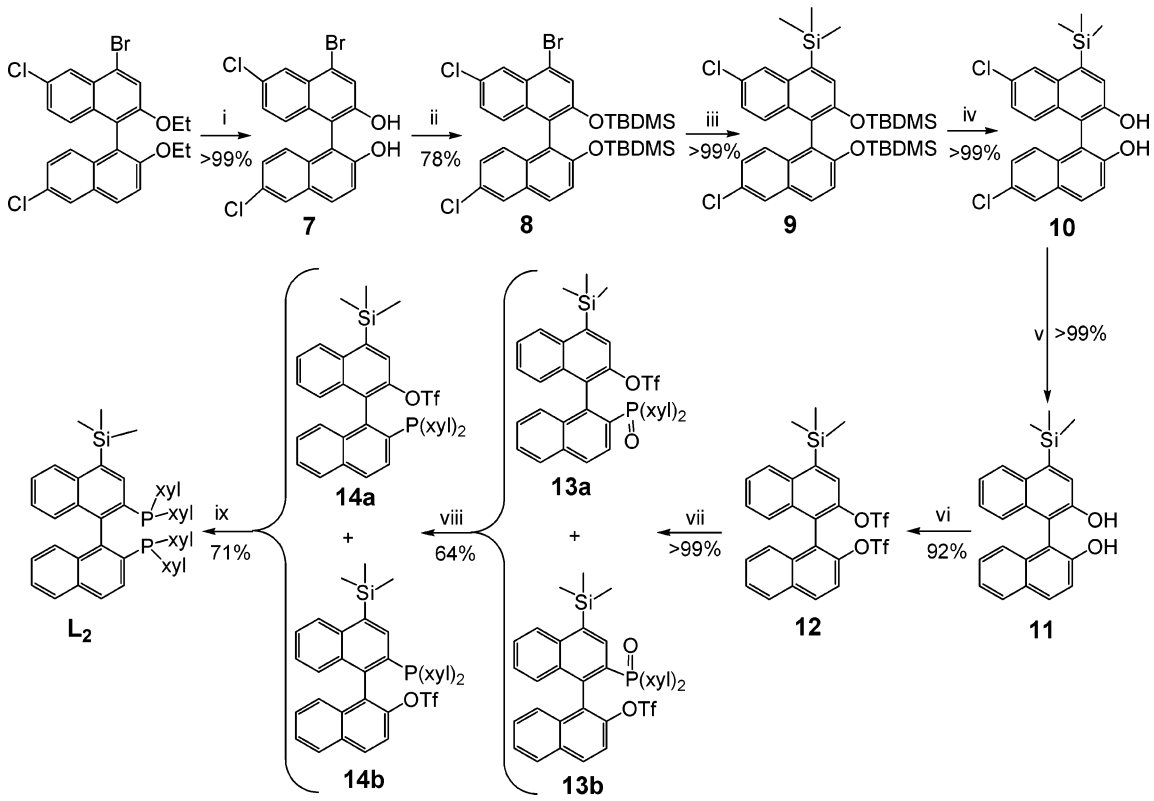
4,4′,6,6′-Tetramethyl-2,2′-bis[bis(xylyl)phosphino]-1,1′-binaphthyl ($\mathbf{L_4}$) was synthesized in 6 steps starting from 4,4′,6,6′-tetrabromo-2,2′-diethoxy-1,1′-binaphthalene[17] with an overall yield of 31.5% (Scheme 6). Pd-catalyzed coupling of 4,4′,6,6′-tetrabromo-2,2′-diethoxy-1,1′-binaphthalene with trimethyboroxine in DME gave 4,4′,6,6′-tetramethyl-2,2′-diethoxy-1,1′-binaphthalene (**20**) in very high yield. Subsequent steps leading to the desired $\mathbf{L_4}$ ligand were analogous to those for the synthesis of $\mathbf{L_1}$.

2.2. Synthesis and Characterization of Ru Precatalysts Based on 4,4′-Substituted-xylBINAP Ligands. Ru(diphosphine)(diamine)Cl_2 precatalysts were prepared by the following procedure (Scheme 7). First, a mixture of 4,4′-substituted-xylBINAP ligand and 0.5 equiv of $[Ru(benzene)Cl_2]_2$ was heated in anhydrous DMF at 100 °C for 1 h and then cooled to room temperature.

(16) Lee, S. J. Ph.D. Thesis, University of North Carolina at Chapel Hill, 2003.

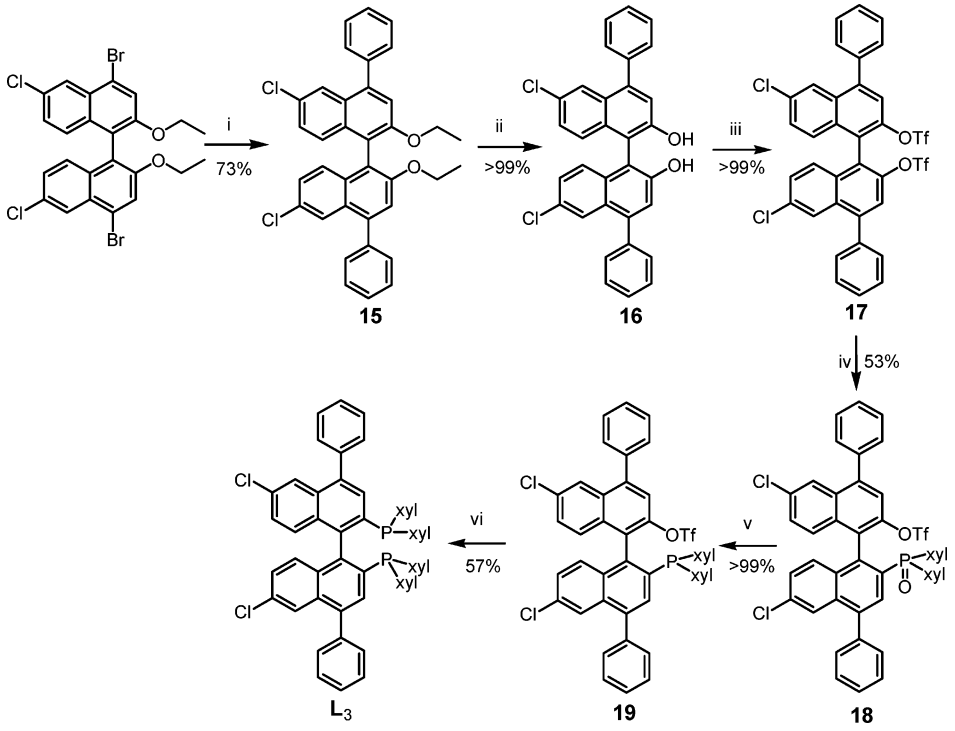
(17) Gong, L.-Z.; Hu, Q.-S.; Pu, L. *J. Org. Chem*. **2001**, *66*, 2358.

SCHEME 4[a]



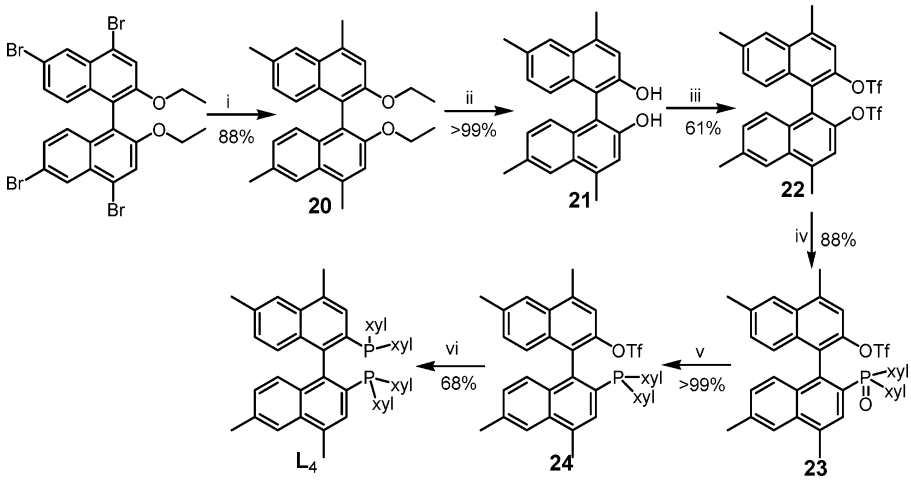
[a] Reagents and conditions: (i) BBr_3, CH_2Cl_2, rt, 12 h; (ii) $^tBu(CH_3)_2SiCl$, imidazole, DMAP, CH_2Cl_2, reflux for 12 h; (iii) (a) ^{n}BuLi/hexane, −78 °C; (b) $(CH_3)_3SiBr$, THF, −78 °C to rt, 12 h; (iv) $^nBu_4NF$, THF, rt, 1 h; (v) H_2(g), Pd/C, Et_3N, MeOH, rt, 12 h; (vi) $(Tf)_2O$, pyridine, CH_2Cl_2, rt, 12 h; (vii) $HP(O)(Xyl)_2$, $Pd(OAc)_2$, dppb, Et_2N^iPr, DMSO, 110 °C, 3 days; (viii) $(EtO)_3SiH$, $Ti(O^iPr)_4$, benzene, reflux for 4 h; (ix) $HP(Xyl)_2$, $Ni(dppe)Cl_2$, DABCO, DMF, 110 °C, 3 days.

SCHEME 5[a]



[a] Reagents and conditions: (i) $Pd(PPh_3)_4$, $PhB(OH)_2$, ethanol, 2M Na_2CO_3/H_2O, DME, reflux for 2 days; (ii) BBr_3, CH_2Cl_2, rt, 12 h; (iii) Tf_2O, pyridine, CH_2Cl_2, rt, 12 h; (iv) $HP(O)(Xyl)_2$, $Pd(OAc)_2$, dppb, Et_2N^iPr, DMSO, 110 °C, 3 days; (v) $(EtO)_3SiH$, $Ti(O^iPr)_4$, benzene, reflux for 4 h; (vi) $HP(Xyl)_2$, $Ni(dppe)Cl_2$, DABCO, DMF, 110 °C, 3 days.

SCHEME 6[a]



[a] Reagents and conditions: (i) trimethylboroxine, $Pd(PPh_3)_4$, 2 M Na_2CO_3/H_2O, DME, reflux for 2 days; (ii) BBr_3, CH_2Cl_2, rt, 1 h; (iii) Tf_2O, pyridine, CH_2Cl_2, rt, 12 h; (iv) $HP(O)(Xyl)_2$, $Pd(OAc)_2$, dppb, Et_2N^iPr, DMSO, 110 °C, 3 days; (v) $Ti(O^iPr)_4$, $(EtO)_3SiH$, benzene, reflux for 4 h; (vi) $HP(Xyl)_2$, $Ni(dppe)Cl_2$, DABCO, DMF, 110 °C, 3 days.

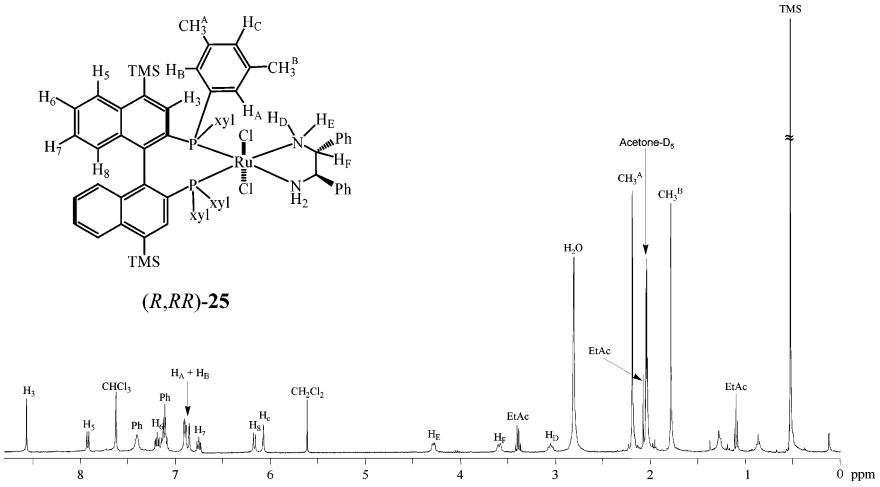


FIGURE 1. Tentative assignments of the $^1H\{^{31}P\}$ NMR spectrum of (*R,RR*)-**25** in acetone-d_6.

SCHEME 7

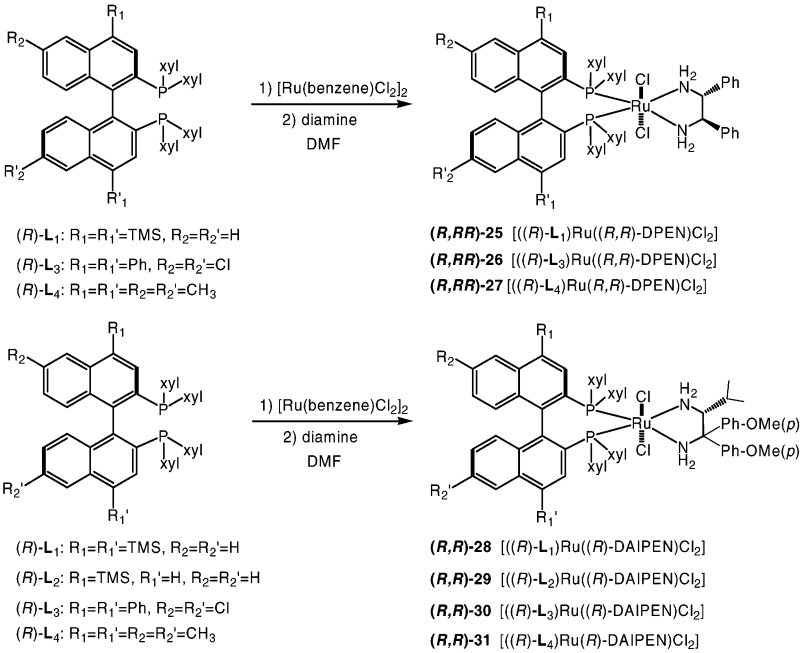
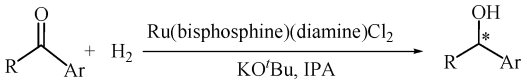


TABLE 1. Asymmetric Hydrogenation of Aromatic Ketones by Ru(4,4′-Substituted-xylBINAP)-Based Catalysts



aromatic ketone	L_1 DAIPEN	L_1 DPEN	L_4 DAIPEN	L_4 DPEN	L_3 DAIPEN	L_3 DPEN	L_2 DAIPEN	XylBINAP DAIPEN[5]
R = CH_3, Ar = Ph	**99.8**	98.4	**99.6**	98.5	89.9	87.9	98.4	*99*
R = CH_3, Ar = 1-Np	**99.9**	99.1	**99.5**	99.1	91.9	90.1	99.1	*99*
R = CH_3, Ar = 2-Np	**99.3**	97.7	**99.5**	94.1	65.9	85.1	97.9	*98*
R = CH_3, Ar = *p*-OMe-Ph	**98.7**	96.7	**99.0**	92.1	58.1	85.5	94.9	*100*
R = CH_3, Ar = *p*-Cl-Ph	**99.5**	97.1	**99.1**	96.1	71.5	86.3	97.1	*98*
R = CH_3, Ar = *p*-Me-Ph	**99.2**	98.2	**99.4**	96.1	61.7	96.5	97.9	*98*
R = CH_3, Ar = *p*-*t*Bu-Ph	**98.7**	97.1	**99.8**	97.3	64.9	86.1	96.3	*N/A*
R = CH_2CH_3, Ar = Ph	**99.6**	99.1	**99.6**	98.7	76.5	93.5	98.9	*99*
R = cyclopropyl, Ar = Ph	**96.2**	95.9	**96.5**	96.5	29.9	77.3	95.1	*N/A*
R = benzyl, Ar = Ph			**99.1**	95.7	63.3			*N/A*
R = $NMe_2C_2H_4$−, Ar = Ph			**95.5**	98.3	47.5			*95.9*
R = CH_3, Ar = *p*-NO_2-Ph	**99.5**		**99.8**					*99*

One equivalent of chiral diamine was added to the mixture, which was then heated at 80 °C for 3 h. After removing the DMF under vacuum at 50 °C, the desired Ru(diphosphine)(diamine)Cl_2 precatalysts were purified by using silica gel column chromatography in air. Typical yields for the Ru precatalysts range from 50% to 60%.

All of the Ru(diphosphine)(diamine)Cl_2 precatalysts were characterized by ^1H, $^1H\{^{31}P\}$, and $^{31}P\{^1H\}$ NMR spectroscopy and MALDI-TOF mass spectrometry. As shown in Figure 1 for the representative Ru(diphosphine)(diamine)Cl_2 precatalysts (*R*,*RR*)-**25**, a single set of signals was observed for both 4,4′-substituted-xylBINAP and DPEN ligands, consistent with the C_2 symmetric nature of these precatalysts. Tentative assignments for the proton signals of (*R*,*RR*)-**25** were made based on chemical shifts and $^1H-^1H$ and $^1H-^{31}P$ coupling patterns (Figure 1). It is worth noting that two sets of xylyl and NH_2 protons were observed owing to their diastereotopic nature. In contrast to the C_2 symmetric nature of **25**−**27**, precatalysts **28**−**31** are C_1 symmetric and its $^1H\{^{31}P\}$ NMR spectra are much more complicated. The proton spectral assignments and purity of the Ru(diphosphine)(diamine)Cl_2 precatalysts are supported by their $^{31}P\{^1H\}$ NMR spectra. For example, precatalysts **25**−**27** show a single $^{31}P\{^1H\}$ signal at ~45 ppm, consistent with their C_2 symmetric nature. Precatalysts **28**, **30**, and **31** on the other hand show two doublets in their $^{31}P\{^1H\}$ spectrum owing to different chemical environments of the two bis(xylyl)phosphino moieties.

Dark yellow crystals of (*R*)-(*R*,*R*)-**27**·2-propanol were obtained by recrystallization from a dichloromethane/2-propanol mixture and crystallized in the *R*3 space group with two molecules of **27** and two molecules of disordered 2-propanol in the asymmetric unit. The Ru centers of **27** adopt an octahedral coordination environment with the P atoms of ligand L_4 and the N atoms of DPEN in the equatorial positions and the two chlorine atoms trans to each other (Figure 2). The bond distances and angles around the Ru center are within the normal range expected for a six-coordinate Ru(II) complex. One of the L_4 ligands has a dihedral angle of 75.3° between the naphthyl rings, while the other L_4 ligand adopts a dihedral angle of 76.3° between the naphthyl rings. It is clear from the space-filling model of **27** that the 4-methyl group of the naphthyl ring and the methyl groups of the two xylyl moieties form a fence on the opposite side of the DPEN ligand of the Ru center. These three methyl groups will have significant repulsive interactions with the bulky aryl ring of the hydrogen-bonded aromatic ketone in the disfavored transition state. We believe that such a repulsive interaction is responsible for very high

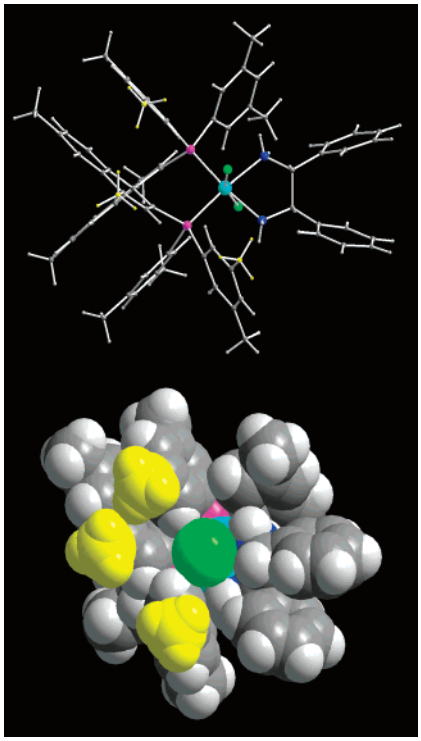


FIGURE 2. Ball-and-stick presentation (top) and space-filling model (bottom) for one of the two crystallographically independent **27** molecules in the single crystal of (*R*)-(*R*,*R*)-**27**·2-isopropanol. Key: red, Ru; green, Cl; blue, N; purple, P; medium gray, C; light gray, H. The 4-methyl groups of the naphthyl ring and of the two xylyl moieties are highlighted in yellow. Key bond distances and angles: Ru1−N2, 2.111(9) Å; Ru1−N1, 2.16(1) Å; Ru1−P2, 2.226(8) Å; Ru1−P1, 2.227(8) Å; Ru1−Cl1, 2.39(2) Å; Ru1−Cl3, 2.40(2) Å; N2−Ru1−N1, 78.3(2)°; N2−Ru1−P2, 172.3(2)°; N1−Ru1−P2, 94.4(2)°; N2−Ru1−P1, 94.3(2)°; N1−Ru1−P1, 172.0(2)°; P2−Ru1−P1, 93.10(9)°; N2−Ru1−Cl1, 84.2(3)°; N1−Ru1−Cl1, 82.8(2)°; P2−Ru1−Cl1, 97.7(2)°; P1−Ru1−Cl1, 93.6(2)°; N2−Ru1−Cl3, 83.2(2)°; N1−Ru1−Cl3, 84.4(3)°; P2−Ru1−Cl3, 93.5(2)°; P1−Ru1−Cl3, 97.8(2)°; Cl1−Ru1−Cl3, 163.6(2)°.

enantioselectivity in the hydrogenation of aromatic ketones by the **27** precatalyst (see below).

2.3. Asymmetric Hydrogenation of Aromatic Ketones with Use of 4,4′-Substituted-xylBINAP-Based Catalysts. Ru complexes of 4,4′-substituted-xylBINAP and chiral diamines **25**−**31** were used in asymmetric hydrogenation reactions of a variety of unfunctionalized ketones. As shown in Table 1, a variety of aromatic ketones with various substituents can be effectively hydrogenated with the present Ru(diphosphine)(diamine)Cl_2 precatalysts. With 0.1 mol % catalyst loading, all the ketones in Table 1 were completely hydrogenated under a hydrogen pressure of 700 psi in 20 h. The combination of (*R*)-**L$_1$** and (*R*)-DAIPEN and (*R*)-**L$_4$** and (*R*)-DAIPEN gave the best ee values, greater than 99% for most of the substrates examined. This level of enantioselectivity compares favorably with the performance of the Ru(xylBINAP)(DAIPEN)Cl_2 system (last column in Table 1). To the best of our knowledge, the enantioselectivity seen for (*R*,*RR*)-**25** and (*R*,*RR*)-**27** is the highest ever reported. We have also carried out hydrogenation reactions with 0.01% catalyst loading, and aromatic ketones were hydrogenated with complete conversions and ee values similar to those listed in Table 1.

The 6,6′-$(Cl)_2$-4,4′-$(Ph)_2$-xylBINAP catalyst systems, however, performed very poorly. We believe that the phenyl groups may form π-edge interactions with the aromatic groups of the ketones to stabilize the undesired diastereomeric transition state and thus reduce the ee values significantly. The 4-TMS-xylBINAP system performed slightly worse than the Ru(xylBINAP)(DAIPEN)-Cl_2 system, probably a result of adoption of an unfavorable dihedral angle by the naphthyl rings owing to the TMS group in the 4-position. In this case, the ketone substrate will most likely attack from the catalyst side without the TMS substituent. The TMS group thus will not have any beneficial effect except for forcing the adoption of unfavorable dihedral angle between the naphthyl rings.

We have also tested the performance of the mismatched catalyst systems. Ru complexes of (*R*)-4,4′-bis-(TMS)(xylBINAP)/(*S,S*)-DPEN and (*R*)-4-TMS-xylBINAP/(*S,S*)-DPEN combinations gave 27.7% and 17.9% ee for the reduction of acetophenone, respectively. These values are significantly lower than those of the matched pairs. The match/mismatch behaviors exhibited by the Ru-(diphosphine)(diamine)Cl_2 catalyst systems based on 4,4′-substituted-xylBINAP are similar to those reported earlier, such as Xyl-PhanePhos-Ru-DPEN and Xyl-Spiro-Phos-Ru-DPEN catalyst systems.[11,12]

3. Conclusions

We have designed and synthesized a family of 4,4′-substituted-xylBINAPs in multistep sequences. Ru(diphosphine)(diamine)Cl_2 complexes based on these 4,4′-substituted-xylBINAPs gave the best enantioselectivity for the hydrogenation of aromatic ketones among all the chiral diphosphines that have been reported in the literature. These results support our hypothesis of combining dual modes of enantiocontrol (i.e., the substituents on 4,4′-postions of the binaphthyl framework and the methyl groups on the bis(xylyl)phosphino moieties) to achieve higher stereoselectivity in the hydrogenation of aromatic ketones. Future work is directed at extending this concept to the asymmetric hydrogenation of other more difficult substrates such as alkyl ketones and imines.

4. Experimental Section

4.1. Synthesis of 4,4′-Bis(trimethylsilyl)-2,2′-[bis(bis-(xylyl)phosphino)]-1,1′-binaphthyl (L$_1$). (a) Synthesis of (*R*)-6,6′-Dichloro-4,4′-bis(trimethylsilyl)-2,2′-bis(*tert*-butyldimethylsiloxy)-1,1′-binaphthalene, 1. To a solution of (*R*)-6,6′-dichloro-4,4′-dibromo-2,2′-bis(*tert*-butyldimethylsiloxy)-1,1′-binaphthalene (2.0 g, 2.7 mmol) in 60 mL of anhydrous THF at −78 °C was added 2.4 mL of 2.5 M ^{n}BuLi in hexane dropwise. After the addition, the reaction mixture was allowed to stir at −78 °C for an additional 4 h, then 0.89 mL (5.0 mmol) of $(CH_3)_3SiBr$ was added dropwise over a period of half an hour. The reaction mixture was allowed to slowly warm to room temperature and stirred for 12 h, and then it was quenched with water and extracted with EtOAc and washed with water 3 times. The organic layer was dried over $MgSO_4$ and the organic volatiles were removed under reduced pressure. The crude product was purified by silica gel column chromatography (hexane) to give 1.4 g (74% yield) of pure **1**. ^{1}H NMR ($CDCl_3$) δ 8.17 (d, $^4J_{H-H}$ = 4 Hz, 2H), 7.55 (s, 2H), 7.39 (d, $^3J_{H-H}$ = 8 Hz, 2H), 7.32 (dd, $^3J_{H-H}$ = 8 Hz, $^4J_{H-H}$ = 4 Hz, 2H), 0.67 (s, 18H), 0.578 (s, 18H), 0.17 (s, 6H), 0.069 (s, 6H). ^{13}C-{^{1}H} NMR ($CDCl_3$) δ 150.4 (s), 139.1 (s), 133.2 (s), 133.1 (s), 128.8 (s), 128.5 (s), 128.3 (s), 126.7 (s), 126.1 (s), 122.9 (s), 0.993 (s), 0.147 (s), −4.24 (s), −4.31 (s). MS *m/z* 728.9 (calcd *m/z* 728.1 for $[M]^+$).

(b) Synthesis of (*R*)-6,6′-Dichloro-4,4′-bis(trimethylsilyl)-2,2′-dihydroxy-1,1′-binaphthalene, 2. To a solution of **1** (1.4 g, 1.9 mmol) in 20 mL of anhydrous THF at room temperature was added 4.0 mL (4 mmol) of 1 M ^{n}Bu$_4$NF in THF via a syringe. The reaction mixture was allowed to stir at room temperature for another hour and quenched with water. The mixture was extracted with EtOAc and washed with NH_4Cl twice and then with water. The organic layer was dried over $MgSO_4$ and the organic volatiles were removed under reduced pressure to give pure product of **2** in quantitative yield (0.96 g, >99% yield). ^{1}H NMR ($CDCl_3$) δ 8.10 (d, $^4J_{H-H}$ = 2.1 Hz, 2H), 7.60 (s, 2H), 7.25 (dd, $^3J_{H-H}$ = 9 Hz and $^4J_{H-H}$ = 1.2 Hz, 2H), 7.1 (d, $^3J_{H-H}$ = 9.6 Hz, 2H), 4.99 (s, 2H), 0.560 (s, 18H). ^{13}C{^{1}H} NMR ($CDCl_3$) δ 151.7 (s), 142.3 (s), 133.5 (s), 131.9 (s), 129.6 (s), 127.5 (s), 127.4 (s), 126.7 (s), 126.1 (s), 112.3 (s), 0.131 (s). MS *m/z* 499.7 (calcd *m/z* 499.6 for $[M]^+$).

(c) Synthesis of (*R*)-4,4′-Bis(trimethylsilyl)-2,2′-bis-(hydroxyl)-1,1′-binaphthalene, 3. A mixture of anhydrous MeOH (40 mL) and Et_3N (0.84 mL, 6 mmol) was added to **2** (0.8 g, 1.6 mmol) and 0.34 g (0.032 mmol) of 10% Pd on activated carbon. A balloon of H_2 was connected to the reaction mixture after outgassing 3 times to remove oxygen, and the reaction mixture was allowed to stir at room temperature for 12 h. The mixture was filtered through Celite and the solvent was removed under reduced pressure. The residue was then dissolved in EtOAc and washed with water 3 times. The organic layer was dried over $MgSO_4$ and the organic volatiles were removed under reduced pressure to obtain pure product of **3** in quantitative yield. ^{1}H NMR (acetone-d_6) δ 8.15 (d, $^3J_{H-H}$ = 8.1 Hz, 2H), 7.60 (s, 2H), 7.40 (t, $^3J_{H-H}$ = 9 Hz, 2H), 7.30 (t, $^3J_{H-H}$ = 8.4 Hz, 2H), 7.22 (dd, $^3J_{H-H}$ = 8.7 Hz and $^4J_{H-H}$ = 0.9 Hz), 0.56 (s, 18H). ^{13}C{^{1}H} NMR (acetone-d_6) δ 153.1 (s), 140.4 (s), 135.5 (s), 132.9 (s), 128.8 (s), 126.6 (s), 126.3 (s), 126.2 (s), 123.2 (s), 116.4 (s), 0.246 (s). MS *m/z* 430 (calcd *m/z* 430.2 for $[M]^+$).

(d) Synthesis of (*R*)-4,4′-Bis(trimethylsilyl)-2,2′-bis-(triflato)-1,1′-binaphthalene, 4. To a solution of **3** (0.65 g, 1.5 mmol) in 1 mL of pyridine and 10 mL of CH_2Cl_2 at 0 °C was added 1.1 mL (6.2 mmol) of $(Tf)_2O$ via a syringe. The reaction mixture was stirred at room temperature for 12 h, extracted with CH_2Cl_2, and washed with water 3 times. The organic layer was dried over $MgSO_4$ and the filtrate was removed under reduced pressure to give pure product of **4** in

quantitative yield. ^{1}H NMR ($CDCl_3$) δ 8.23 (d, $^3J_{H-H}$ = 9 Hz, 2H), 7.75 (s, 2H), 7.60 (t, $^3J_{H-H}$ = 8.4 Hz, 2H), 7.39 (t, $^3J_{H-H}$ = 9 Hz, 2H), 7.31 (d, $^3J_{H-H}$ = 7.5 Hz, 2H), 0.58 (s, 18H). ^{13}C{^{1}H} NMR ($CDCl_3$) δ 145.1 (s), 144.9 (s), 135.9 (s), 133.3 (s), 128.4 (s), 127.9 (s), 127.1 (s), 126.8 (s), 125.7 (s), 124.5 (s), 118.2 (q, $^1J_{C-F}$ = 318 Hz), −0.0362 (s). MS *m/z* 694.7 (calcd *m/z* 694.8 for $[M]^+$).

(e) Synthesis of (*R*)-4,4′-Bis(trimethylsilyl)-2-triflato-2′-bis(xyl)phosphinyl-1,1′-binaphthyl, 5. A mixture of **4** (0.5 g, 0.72 mmol), $HOP(xyl)_2$ (0.37 g, 1.4 mmol), $Pd(OAc)_2$ (0.032 g, 0.14 mmol), dppb (0.061 g, 0.14 mmol), Et_2N^iPr (0.48 mL, 2.9 mmol), and 1 mL of DMSO was prepared in a glovebox. The reaction mixture was then heated at 110 °C for 3 days, allowed to cool to room temperature, and then extracted with EtOAc and washed with water 5 times. The organic layer was dried over $MgSO_4$ and the organic volatiles were removed under reduced pressure. The residue was purified by using silica gel chromatography with CH_2Cl_2/acetone (20:1) to give pure product of **5** (0.4 g, 70% yield). ^{1}H{^{31}P} NMR ($CDCl_3$) δ 8.4 (m, 1H), 8.35 (m, 1H), 7.89 (m, 1H), 7.54 (m, 1H), 7.42 (m, 2H), 7.23 (m, 2H), 7.1 (m, 7H), 6.93 (m, 2H), 2.18 (s, 6H), 2.11 (s, 6H), 0.55 (s, 9H), 0.4 (s, 9H). ^{31}P{^{1}H} NMR ($CDCl_3$) δ +29 (s). ^{13}C{^{1}H} NMR ($CDCl_3$) δ 145.5 (s), 142.8 (s), 139.2 (m), 137.5 (m), 135.8 (m), 135.2 (s), 134.2 (s), 133.8 (s), 133.1 (m), 131.9 (s), 129.9 (s), 129.6 (m), 128.8 (m), 128.3 (m), 127.9 (m), 126.2 (m), 125,2 (s), 118.2 (q, $^1J_{C-F}$ = 330 Hz), 20.2 (m), 0.11 (m). MS *m/z* 803.8 (calcd *m/z* 803.0 for $[M]^+$).

(f) Synthesis of (*R*)-4,4′-Bis(trimethylsilyl)-2-triflato-2′-bis(xyl)phosphino-1,1′-binaphthyl, 6. To a solution of **5** in 20 mL of anhydrous benzene were added 82 μL (0.28 mmol) of $Ti(O^iPr)_4$ and 0.5 mL (2.7 mmol) of $(EtO)_3SiH$ via a syringe. The reaction mixture was heated to reflux for 4 h. The solvent was removed under reduced pressure and passed through a short silica gel column with CH_2Cl_2. The solvent was removed under reduced pressure to give 0.32 g (82% yield) of pure **6**. ^{1}H{^{31}P} NMR ($CDCl_3$) δ 8.15 (m, 2H), 7.71 (m, 2H), 7.5 (m, 2H), 7.15 (m, 3H), 7.13 (m, 1H), 7.04 (m, 1H), 6.92 (m, 3H), 6.78 (s, 1H), 6.62 (s, 1H), 2.25 (s, 6H), 2.1 (s_2, 6H), 0.58 (s, 9H), 0.39 (s, 9H). ^{31}P{^{1}H} NMR ($CDCl_3$) δ −11.8 (s). MS *m/z* 787.0 (calcd *m/z* 787.0 for $[M]^+$).

(g) Synthesis of (*R*)-4,4′-Bis(trimethylsilyl)-2,2′-bis(bis-(xylyl)phosphino)-1,1′-binaphthyl, L_1. A mixture of **6** (170 mg, 0.22 mmol), $HP(Xyl)_2$ (0.078 mL, 0.32 mmol), $Ni(dppe)Cl_2$ (12 mg, 0.022 mmol), and DABCO (48 mg, 0.43 mmol) was prepared in a glovebox. The reaction mixture was then dissolved in 1 mL of anhydrous DMF and heated at 110 °C for 2 days. The reaction mixture was allowed to cool to room temperature, extracted with EtOAc, and washed with water 4 times. The organic layer was dried with $MgSO_4$ and the volatiles were removed under reduced pressure. The residue was then passed through a short silica gel column with CH_2Cl_2 and then with hexane/EtOAc (1:1). The solvents were removed under reduced pressure to give 120 mg (67% yield) of pure L_1. ^{1}H{^{31}P} NMR ($CDCl_3$) δ 8.11 (m, 2H), 7.78 (s, 2H), 7.40 (m, 2H), 7.02 (m, 4H), 6.75 (m, 12H), 2.16 (s, 12H), 2.10 (s, 12H), 0.34 (s, 18H). ^{31}P{^{1}H} NMR ($CDCl_3$) δ −14.6 (s). ^{13}C-{^{1}H} NMR ($CDCl_3$) δ 138.5 (m), 137.6 (s), 137.3 (s), 137 (m), 136.7 (m), 136.7 (s), 132 (m), 131.9 (s), 131.8 (m), 130.7 (m), 129.9 (s), 128.9 (s), 127.8 (s), 125.9 (s), 124.8 (s), 21.2 (s), 0.41 (s). MS *m/z* 879 (calcd *m/z* 879.2 for $[M]^+$).

4.2. Synthesis of 4-Trimethylsilyl-2,2′-Bis[bis(xylyl)-phosphino]-1,1′-binaphthal (L_2). (a) Synthesis of (*R*)-6,6′-Dichloro-4-bromo-2,2′-dihydroxy-1,1′-binaphthalene, 7. To a solution of (*R*)-6,6′-dichloro-4-bromo-2,2′-diethoxy-1,1′-binaphthalene (0.43 g, 0.88 mmol) in 10 mL of CH_2Cl_2 at room temperature was added 0.25 mL (2.7 mmol) of BBr_3 via a syringe. The reaction mixture was allowed to stir at room temperature for 1 h. The mixture was quenched with ice water, extracted with CH_2Cl_2, and washed with water 3 times. The organic layer was dried over $MgSO_4$ and the organic volatiles were removed under reduced pressure to give pure product of **7** in quantitative yield. ^{1}H NMR ($CDCl_3$) δ 8.27 (d, $^4J_{H-H}$ = 4 Hz, 1H), 7.86 (m, 2H), 7.74 (s, 1H), 7.37 (m, 1H), 7.25 (m, 2H), 7.01 (m, 2H), 5 (m, 2H). ^{13}C{^{1}H} NMR ($CDCl_3$) δ 152.8 (s), 152.5 (s), 132.3 (s), 131.7 (s), 131.5 (s), 130.9 (s), 130.2 (s), 130.1 (s), 129.2 (s), 128.9 (s), 128.6 (s), 127.2 (s), 126.8 (s), 126.3 (s), 125.6 (s), 124.5 (s), 123 (s), 119 (s), 110.9 (s), 110 (s). MS *m/z* 434 (calcd *m/z* 434.1 for $[M]^+$).

(b) Synthesis of (*R*)-6,6′-Dichloro-4-bromo-2,2′-bis(*tert*-butyldimethylsiloxy)-1,1′-binaphthalene, 8. 7 (0.38 g, 0.88 mmol), 2.6 mL (2.6 mmol) of 1 M ^{t}Bu$(CH_3)_2$SiCl in THF, 0.19 g (2.8 mmol) of imidazole, and 0.09 mg (0.7 μmol) of DMAP were dissolved in 10 mL of CH_2Cl_2. The mixture was heated to reflux for 12 h, cooled to room temperature, extracted with CH_2Cl_2, and washed with water 3 times. The organic layer was dried over $MgSO_4$ and the volatiles were removed under reduced pressure to give 0.45 g (78% yield) of **7**. ^{1}H NMR ($CDCl_3$) δ 8.23 (d, $^4J_{H-H}$ = 2 Hz, 1H), 7.81 (d, $^4J_{H-H}$ = 2 Hz, 1H), 7.75 (d, $^3J_{H-H}$ = 12 Hz, 1H), 7.55 (s, 1H), 7.16 (m, 5H), 0.504 (s, 9H), 0.49 (s, 9H), 0.061 (s, 3H), 0.041 (s, 3H), −0.123 (s, 3H), −0.132 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$) δ 151.4 (s), 151.1 (s), 133.3 (s), 132.5 (s), 130.9 (s), 129.7 (s), 129.2 (s), 128.6 (s), 128.4 (s), 127.9 (s), 127.7 (s), 127.1 (s), 127 (s), 126.5 (s), 126 (s), 125.5 (s), 122.1 (s), 121.4 (s), 121.4 (s), 120.9 (s), 24.94 (m), 24.91 (m,), 17.6 (s), 4.33 (s), −4.43 (s), −4.54 (s). MS *m/z* 662.6 (calcd *m/z* 662.6 for $[M]^+$).

(c) Synthesis of (*R*)-6,6′-Dichloro-4-trimethylsilyl-2,2′-bis(*tert*-butyldimethylsiloxy)-1,1′-binaphthalene, 9. To a solution of 0.45 g (0.68 mmol) of **8** in 10 mL of THF at −78 °C was added 0.46 mL of 2.5 M *n*BuLi in hexane dropwise. After the addition, the reaction mixture was allowed to stir at −78 °C for an additional 4 h. Then 0.14 mL (1.1 mmol) of $(CH_3)_3$-SiBr was then added dropwise over a period of a half hour. The reaction mixture was allowed to warm to room temperature and stirred for 12 h, and then quenched with water and extracted with EtOAc and washed with water 3 times. The organic layer was dried over $MgSO_4$ and the organic volatiles were removed under reduced pressure. The crude product was purified by using silica gel column chromatography (hexane) to give 0.45 g (>99% yield) of pure **9**. ^{1}H NMR ($CDCl_3$) δ 8.05 (d, $^4J_{H-H}$ = 2 Hz, 1H), 7.83 (d, $^4J_{H-H}$ = 2 Hz, 1H), 7.75 (d, $^3J_{H-H}$ = 8 Hz, 1H), 7.45 (s, 1H), 7.21 (m, 5H), 0.553 (s, 9H), 0.525 (s, 9H), 0.453 (s, 9H), 0.0661 (s, 3H), 0.0446 (s, 3H), −0.0584 (s, 3H), −0.0996 (s, 3H). ^{13}C{^{1}H} NMR ($CDCl_3$) δ 151.3 (s), 150.5 (s), 139.1 (s), 133.3 (s), 133.2 (s), 132.7 (s), 129.7 (s), 129.1 (s), 128.8 (s), 128.6 (s), 128.2 (s), 128 (s), 127.5 (s), 126.8 (s), 126.7 (s), 126.4 (s), 126.1 (s), 122.7 (s), 122 (s), 121.5 (s), 25 (s), 24.9 (s), 17.6 (s), 17.5 (s), 0.186 (s), −4.18 (s), −4.27 (s), −4.3 (s), −4.45 (s). MS *m/z* 640.6 (calcd *m/z* 640.9 for $[M]^+$).

(d) Synthesis of (*R*)-6,6′-Dichloro-4-trimethylsilyl-2,2′-dihydroxy-1,1′-binaphthalene, 10. To a solution of **9** (0.45 g, 0.69 mmol) in 10 mL of THF at room temperature was added 2 mL (2 mmol) of 1 M ^{n}Bu$_4$NF in THF via a syringe. The reaction mixture was allowed to stir at room temperature for another hour and quenched with water. The mixture was extracted with EtOAc and washed with NH_4Cl twice and then with water. The organic layer was dried over $MgSO_4$ and the organic volatiles were removed under reduced pressure to give a pure product of **10** in quantitative yield. ^{1}H NMR ($CDCl_3$) δ 8.1 (d, $^4J_{H-H}$ = 2 Hz, 1H), 7.82 (m, 1H), 7.6 (s, 1H), 7.34 (m, 1H), 7.15 (m, 5H), 5.27 (s, 2H), 0.561 (s, 9H). ^{13}C{^{1}H} NMR ($CDCl_3$) δ 152.8 (s), 151.8 (s), 142.4 (s), 133.5 (s), 131.9 (s), 131.7 (s), 130.4 (s), 129.9 (s), 129.8 (s), 129.4 (s), 128.2 (s), 127.5 (s), 127 (s), 126.6 (s), 126.2 (s), 125.9 (s), 119 (s), 112 (s), 111.3 (s), 0.136 (s). MS *m/z* 428.5 (calcd *m/z* 428.6 for $[M]^+$).

(e) Synthesis of (*R*)-4-Trimethylsilyl-2,2′-dihydroxyl-1,1′-binaphthalene, 11. A mixture of anhydrous MeOH (5 mL) and Et_3N (0.16 mL, 0.93 mmol) was added to a mixture of **10** (0.16 g, 0.37 mmol) and 10% Pd on activated carbon (0.079 g, 0.078 mmol). A balloon of H_2 was then attached to the reaction mixture and after outgassing 3 times to remove the oxygen, the reaction mixture was allowed to stir at room temperature for 12 h. The mixture was filtered through Celite and the solvents were removed under reduced pressure. The residue was then extracted with EtOAc and washed with water 3 times. The organic layer was dried over $MgSO_4$ and the

organic volatiles were removed under reduced pressure to obtain pure product of **11** in quantitative yield. ^{1}H NMR (acetone-d_6) δ 8.14 (d, $^3J_{H-H}$ = 7.5 Hz, 1H), 7.89 (m, 3H), 7.58 (s, 1H), 7.33 (m, 4H), 7.14 (d, $^3J_{H-H}$ = 8.1 Hz, 1H), 7.05 (d, $^3J_{H-H}$ = 8.8 Hz, 1H), 0.546 (s, 9H). ^{13}C{^{1}H} NMR (acetone-d_6) δ 154.2 (s), 153.2 (s), 140.4 (s), 135.6 (s), 135.2 (s), 133 (s), 130.3 (s), 129.7 (s), 128.8 (s), 128.7 (s), 126.8 (s), 126.6 (s), 126.3 (s), 125.2 (s), 123.5 (s), 123.2 (s), 119.2 (s), 116.3 (s), 114.9 (s), 0.218 (s). MS *m/z* 358.6 (calcd *m/z* 358.5 for [M]$^+$).

(f) Synthesis of (*R*)-4-Trimethylsilyl-2,2′-bis(triflato)-1,1′-binaphthalene, 12. To a solution of **11** (0.08 g, 0.31 mmol) in 1 mL of pyridine and 10 mL of CH_2Cl_2 at 0 °C was added 0.2 mL (1.1 mmol) of $(Tf)_2O$ via a syringe. The reaction mixture was stirred at room temperature for 12 h, then extracted with CH_2Cl_2 and washed with water 3 times. The organic layer was dried over $MgSO_4$ and the filtrate was removed under reduced pressure to give 0.12 g (92% yield) of pure **12**. ^{1}H NMR ($CDCl_3$) δ 8.27 (d, $^4J_{H-H}$ = 7.7 Hz, 1H), 8.15 (d, $^4J_{H-H}$ = 9.9 Hz, 1H), 8.02 (d, $^4J_{H-H}$ = 9 Hz, 1H), 7.79 (s, 1H), 7.65 (d, $^4J_{H-H}$ = 9 Hz, 1H), 7.62 (m, 2H), 7.43 (m, 2H), 7.32 (m, 2H), −0.609 (s, 9H). ^{13}C{^{1}H} NMR ($CDCl_3$) δ 145.4 (s), 145.1 (s), 145.06 (s), 135.9 (s), 133.3 (s), 133.2 (s), 132.3 (s), 131.9 (s), 128.5 (s), 128.3 (s), 127.9 (s), 127.8 (s), 127.3 (s), 127.2 (s), 126.9 (s), 125.7 (s), 124.4 (s), 123.6 (s), 119.3 (s), −0.0442 (s). MS *m/z* 622.7 (calcd *m/z* 622.6 for [M]$^+$).

(g) Synthesis of (*R*)-4-Trimethylsilyl-2-triflato-2′-bis(xyl)phosphinyl-1,1′-binaphthyl, 13a, and (*R*)-4-Trimethylsilyl-2-bis(xyl)phosphinyl-2′-triflato-1,1′-binaphthyl, 13b. A mixture of **12** (0.07 g, 0.11 mmol), $HOP(Xyl)_2$ (0.06 g, 0.23 mmol), $Pd(OAc)_2$ (0.0052 g, 0.023 mmol), dppb (0.007 g, 0.016 mmol), Et_2N^iPr (0.072 mL, 0.44 mmol), and 1 mL of DMSO was prepared in a glovebox. The reaction mixture was heated at 110 °C for 3 days, allowed to cool to room temperature, and then extracted with EtOAc and washed with water 5 times. The organic layer was dried over $MgSO_4$ and the organic volatiles were removed under reduced pressure. The residue was purified by using silica gel chromatography with CH_2Cl_2:acetone (20:1) to give a mixture of **13a** and **13b** in 1:1 ratio and 99% total yield.

13a: ^{1}H{^{31}P} NMR ($CDCl_3$) δ 8.15 (d, $^3J_{H-H}$ = 9.3 Hz, 1H), 8.09 (d, $^3J_{H-H}$ = 9.8 Hz, 1H), 7.99 (d, $^3J_{H-H}$ = 9.8 Hz, 1H), 7.85 (d, $^3J_{H-H}$ = 6.8 Hz, 1H), 7.61 (t, $^3J_{H-H}$ = 7.4, 6.8 Hz, 1H), 7.53 (m, 2H), 7.2 (m, 9H), 6.97 (s, 1H), 2.27 (s, 6H), 2.23 (s, 6H), 0.619 (s, 9H). ^{31}P{^{1}H} NMR ($CDCl_3$) δ +31.5 (s). ^{13}C{^{1}H} NMR ($CDCl_3$) δ 145.5 (s), 142.8 (s), 137.6 (m), 137.2 (m), 136.2 (m), 135.2 (s), 134.4 (m), 133.7 (s), 133.1 (m), 132.8 (m), 131.7 (s), 131.5 (s), 130.5 (s), 129.5 (m), 128.7 (m), 128.1 (m), 127.8 (s), 127.2 (s), 126.9 (s), 126.3 (s), 126.1 (s), 125.1 (s), 21.1 (s), −0.078 (s). MS *m/z* 730.1 (calcd *m/z* 730.8 for [M]$^+$).

13b: ^{1}H{^{31}P} NMR ($CDCl_3$) δ 8.15 (d, $^3J_{H-H}$ = 7.4 Hz, 1H), 7.9 (s, H_3, 1H), 7.82 (m, 2H), 7.55 (t, $^3J_{H-H}$ = 6.9 Hz, 1H), 7.42 (t, $^3J_{H-H}$ = 7.9 Hz, 1H), 7.25 (m, 4H), 7.05 (m, 5H), 6.93 (m, 2H), 2.15 (s, 6H), 2.16 (s, 6H), 0.41 (s, 9H). ^{31}P{^{1}H} NMR ($CDCl_3$) δ +28.4 (s). ^{13}C{^{1}H} NMR ($CDCl_3$) δ 149.7 (s), 142.7 (m), 141.5 (m), 141 (m), 139.3 (m), 137.2 (s), 136.7 (s), 136.3 (m), 135.8 (m), 135.3 (s), 134.9 (s), 133.9 (s), 133.4 (s), 132.5 (m), 131.1 (m), 130.9 (m), 130.6 (m), 130.2 (s), 129.5 (s), 129.4 (s), 129.2 (s), 121.1 (s), 120.5 (q, $^1J_{C-F}$ = 328 Hz), 17.7 (s), −4.67 (s). MS *m/z* 730.4 (calcd *m/z* 730.8 for [M]$^+$).

(h) Synthesis of (*R*)-4-Trimethylsilyl-2-triflato-2′-bis(xyl)phosphino-1,1′-binaphthyl, 14a. To a solution of **13a** (0.050 g, 0.11 mmol) in 2 mL of anhydrous benzene were added 8 μL (0.061 mmol) of $Ti(O^iPr)_4$ and 0.11 mL (0.59 mmol) of $(EtO)_3SiH$ via a syringe. The reaction mixture was heated to reflux for 4 h. The solvents were removed under reduced pressure and the residue was passed through a short silica gel column with CH_2Cl_2. The solvent was removed under reduced pressure to give **14a** (0.035 g, 60% yield). ^{1}H{^{31}P} NMR ($CDCl_3$) δ 8.25 (d, $^3J_{H-H}$ = 8.32 Hz, 1H), 7.99 (m, 2H), 7.79 (s, 1H), 7.59 (m, 4H), 7.37 (m, 1H), 7.27 (m, 1H), 7.20 (t, $^3J_{H-H}$ = 8 Hz, 1H), 7.05 (m, 4H), 6.86 (s, 1H), 6.71 (s, 2H), 2.33 (s, 6H), 2.18 (s, 6H), 0.669 (s, 9H). ^{31}P{^{1}H} NMR ($CDCl_3$) δ −11.2 (s). ^{13}C{^{1}H} NMR ($CDCl_3$) δ 144.9 (s), 142.9 (s), 137.9 (s), 137.6 (m), 137.3 (m), 136.8 (m), 136.4 (m), 135.6 (s), 134.8 (s), 133.5 (s), 132.7 (m), 131.8 (s), 131.6 (s), 131.2 (m), 130.9 (s), 130.7 (s), 130.3 (s), 130.1 (s), 129.9 (s), 129.1 (s), 128.3 (s), 128.1 (s), 127.9 (s), 126.8 (m), 126.4 (s), 126.1 (m), 125.9 (s), 118.2 (q, $^1J_{C-F}$ = 318 Hz), 21.2 (s), 21.1 (s), 1.0 (s). MS *m/z* 714.6 (calcd *m/z* 714.8 for [M]$^+$).

(i) Synthesis of (*R*)-4-Trimethylsilyl-2-bis(xyl)phosphino-2′-triflato-1,1′-binaphthyl, 14b. To a solution of **13b** (0.08 g, 0.11 mmol) in 5 mL of anhydrous benzene were added 18 μL (0.061 mmol) of $Ti(O^iPr)_4$ and 0.11 mL (0.59 mmol) of $(EtO)_3SiH$ via a syringe. The reaction mixture was heated to reflux for 4 h. The solvents were removed under reduced pressure and the residue was passed through a short silica gel column with CH_2Cl_2. The solvent was removed under reduced pressure to give **14b** (0.05 g, 64% yield). ^{1}H{^{31}P} NMR ($CDCl_3$) δ 8.26 (d, $^3J_{H-H}$ = 8.4 Hz, 1H), 8.14 (d, $^3J_{H-H}$ = 8 Hz, 1H), 8.01 (d, $^3J_{H-H}$ = 8.4 Hz, 1H), 7.88 (s, 1H), 7.67 (d, $^3J_{H-H}$ = 8 Hz, 1H), 7.62 (t, $^3J_{H-H}$ = 7.3, 7.4 Hz, 1H), 7.55 (t, $^3J_{H-H}$ = 7.8, 7.4 Hz, 1H), 7.36 (m, 2H), 7.26 (t, $^3J_{H-H}$ = 8.3 Hz, 1H), 7.12 (d, $^3J_{H-H}$ = 8.4 Hz, 1H), 7.05 (s, 3H), 6.88 (s, 1H), 6.76 (s, 1H), 2.37 (s, 6H), 2.21 (s, 6H), 0.51 (s, 9H). ^{31}P{^{1}H} NMR ($CDCl_3$) δ −12.1 (s). ^{13}C{^{1}H} NMR ($CDCl_3$) δ 145.0 (s), 139 (m), 138.7 (s), 137.5 (m), 137.2 (m), 136.9 (m), 135.8 (m), 133.9 (s), 132.5 (m), 132.1 (s), 131.8 (s), 131.5 (s), 131.1 (s), 130.9 (s), 130.5 (s), 130.2 (m), 129.8 (s), 128.1 (s), 127.8 (m), 127.3 (s), 126.8 (s), 126.6 (s), 126.4 (s), 125.7 (s), 119.3 (s), 118 (q, $^1J_{C-F}$ = 318 Hz), 21.1 (s), 21 (s), 0.99 (s). MS *m/z* 714.6 (calcd *m/z* 714.8 for [M]$^+$).

(j) Synthesis of (*R*)-4-Trimethylsilyl-2,2′-bis(bis(xylyl)phosphino)-1,1′-binaphthyl ((*R*)-L$_2$). A mixture of **14** (0.075 mg, 0.11 mmol), $HP(Xyl)_2$ (25 μL, 0.17 mmol), $Ni(dppe)Cl_2$ (0.0034 g, 0.011 mmol), and DABCO (0.016 g, 0.22 mmol) was prepared in a glovebox. The reaction mixture was then dissolved in 1 mL of anhydrous DMF and heated at 110 °C for 2 days. The reaction mixture was allowed to cool to room temperature and was extracted with EtOAc and washed with water 4 times. The organic layer was dried over $MgSO_4$ and the volatiles were removed under reduced pressure. The residue was then passed through a short silica gel column with CH_2Cl_2 and then with hexane:EtOAc (1:1). The solvent was removed under reduced pressure to obtain pure product of **L$_2$** (0.06 g, 71% yield). ^{1}H{^{31}P} NMR ($CDCl_3$) δ 8.07 (d, $^4J_{H-H}$ = 7.5 Hz, 1H), 7.84 (m, 2H), 7.77 (s, 1H), 7.52 (m, 1H), 7.32 (m, 2H), 7.0 (m, 5H), 6.8 (m, 2H), 6.7 (m, 8H), 2.34 (s, 12H), 2.17 (s, 12H), 0.27 (s, 9H). ^{31}P{^{1}H} NMR ($CDCl_3$) δ −12.2 (d, $^5J_{P-P}$ = 24 Hz), −13.2 (d, $^5J_{P-P}$ = 21 Hz). ^{13}C{^{1}H} NMR ($CDCl_3$) δ 138.5 (m), 137.1 (m), 133.2 (m), 132.1 (m), 131.8 (m), 130.7 (m), 130 (m), 128.9 (m), 127.9 (m), 126.3 (s), 125.9 (s), 125.5 (s), 124.7 (s), 21.2 (m), 0.38 (s). MS *m/z* 807.6 (calcd *m/z* 807.1 for [M]$^+$).

4.3. Synthesis of 4,4′-Diphenyl-6,6′-dichloro-2,2′-bis(bis(xyl)phosphino)-1,1′-binaphthyl (L$_3$). (a) Synthesis of (*R*)-4,4′-Diphenyl-6,6′-dichloro-2,2′-diethoxy-1,1′-binaphthalene, 15. A mixture of 4,4′-dibromo-6,6′-dichloro-2,2′-diethoxy-1,1′-binaphthalene (2.0 g, 3.5 mmol), phenylboronic acid (0.92 g, 6.7 mmol), $Pd(PPh_3)_4$ (0.2 g, 0.18 mmol), 3 mL of 2 M Na_2CO_3, 1 mL of ethanol, and 10 mL of DME was prepared in a two-neck flask, degassed for ∼3 min, and then heated to reflux for 2 days. The reaction mixture was extracted with EtOAc and washed with water 3 times. The organic layer was dried over $MgSO_4$ and the organic volatiles were removed under reduced pressure. The residue was purified with silica gel chromatography with hexane:EtOAc (20:1) to give pure **15** (1.4 g, 73% yield). ^{1}H NMR ($CDCl_3$) δ 7.87 (s, 2H), 7.58 (m, 10H), 7.39 (s, 2H), 7.19 (s, 4H), 4.11 (m, 4H), 1.14 (t, $^3J_{H-H}$ = 6 Hz, 6H). ^{13}C{^{1}H} NMR ($CDCl_3$) δ 153.9 (s), 141 (s), 140.1 (s), 132.8 (s), 130 (s), 129.6 (s), 128.5 (s), 128.1 (s), 127.7 (s), 127.4 (s), 126.9 (s), 124.9 (s), 119.4 (s), 117.5 (s), 65.1 (s), 14.9 (s). MS *m/z* 563.4 (calcd *m/z* 563.5 for [M]$^+$).

(b) Synthesis of (*R*)-4,4′-Diphenyl-6,6′-dichloro-2,2′-dihydroxy-1,1′-binaphthalene, 16. To a solution of **15** (0.70 g, 1.2 mmol) in 10 mL of CH_2Cl_2 at room temperature was added 0.45 mL (4.8 mmol) of BBr_3 via a syringe. The reaction

mixture was stirred at room temperature for 12 h, quenched with ice water, extracted with CH_2Cl_2, and washed with water 3 times. The organic layer was dried over $MgSO_4$ and the organic volatiles were removed under reduced pressure to give pure **16** in quantitative yield. ^{1}H NMR ($CDCl_3$) δ 7.92 (d, $^4J_{H-H}$ = 2 Hz, H_5, 2H), 7.59 (m, 10H), 7.39 (s, H_3, 2H), 7.29 (dd, $^3J_{H-H}$ = 8 Hz and $^4J_{H-H}$ = 2 Hz, H_7, 2H), 7.21 (d, $^3J_{H-H}$ = 8 Hz, H_8, 2H), 5.2 (s, $-OH$, 2H). ^{13}C{^{1}H} NMR ($CDCl_3$) δ 152.3 (s), 143.1 (s), 139.1 (s), 132.3 (s), 130.2 (s), 129.8 (s), 128.6 (s), 128 (s), 126.2 (s), 125.6 (s), 126.3 (s), 125.6 (s), 119.8 (s), 110.7 (s). MS *m/z* 507.5 (calcd *m/z* 507.4 for $[M]^+$).

(c) Synthesis of (*R*)-4,4′-Diphenyl-6,6′-dichloro-2,2′-bis-(triflato)-1,1′-binaphthalene, 17. To a solution of **16** (0.63 g, 1.2 mmol) in 1 mL of pyridine and 10 mL of CH_2Cl_2 at 0 °C was added 0.7 mL (3.6 mmol) of $(Tf)_2O$ via a syringe. The reaction mixture was stirred at room temperature for 12 h, extracted with CH_2Cl_2, and washed with water 3 times. The organic layer was dried over $MgSO_4$ and the organic volatiles were removed under reduced pressure to give pure product of **17** in quantitative yield. ^{1}H NMR ($CDCl_3$) δ 8.02 (d, $^4J_{H-H}$ = 4 Hz, 2H), 7.73 (m, 12H), 7.55 (dd, $^3J_{H-H}$ = 8 Hz and $^4J_{H-H}$ = 4 Hz, 2H), 7.48 (d, $^3J_{H-H}$ = 8 Hz, 2H). ^{13}C{^{1}H} NMR ($CDCl_3$) δ 144.9 (s), 144.4 (s), 137.9 (s), 134 (s), 132 (s), 131.8 (s), 129.9 (s), 129.0 (s), 128.9 (s), 128.8 (s), 128.7 (s), 125.8 (s), 122.4 (s), 121.3 (s), 118.2 (q, $^1J_{C-F}$ = 318 Hz). MS *m/z* 771.4 (calcd *m/z* 771.5 for $[M]^+$).

(d) Synthesis of (*R*)-4,4′-Diphenyl-6,6′dichloro-2-triflato-2′-bis(xyl)phosphinyl-1,1′-binaphthyl, 18. A mixture of **17** (0.15 g, 0.19 mmol), $HOP(xyl)_2$ (0.065 g, 0.25 mmol), $Pd(OAc)_2$ (0.004 g, 0.019 mmol), dppb (0.008 g, 0.019 mmol), Et_2N^iPr (0.48 mL, 0.57 mmol), and 1 mL of DMSO was prepared in a glovebox. The reaction mixture was then heated at 110 °C for 3 days. The mixture was then extracted with EtOAc and washed with water 5 times. The organic layer was dried over $MgSO_4$ and the organic volatiles were removed under reduced pressure. The residue was purified by using silica gel chromatography with CH_2Cl_2:acetone (20:1) to give 0.09 g (53% yield) of pure **18**. ^{1}H{^{31}P} NMR ($CDCl_3$) δ 7.95 (d, $^4J_{H-H}$ = 2 Hz, 1H), 7.88 (d, $^4J_{H-H}$ = 2 Hz, 1H), 7.73 (s, H_3, 1H), 7.5 (m, 10H), 7.25 (m, 2H), 7.15 (m, 2H), 7.0 (m, 7H), 2.2 (s, 6H), 2.1 (s, 6H). ^{31}P{^{1}H} NMR ($CDCl_3$) δ +29.2 (s). ^{13}C{^{1}H} NMR ($CDCl_3$) δ 145.3 (s), 142.5 (s), 141.8 (s), 140.4 (s), 140.3 (s), 139.3 (s), 139.2 (s), 138.9 (s), 138.5 (s), 138.4 (s), 138.2 (s), 137.9 (s), 137.8 (s), 137.7 (s), 137.6 (s), 137.3 (s), 137.2 (s), 135.3 (m), 134.8 (s), 134.4 (m), 133.8 (m), 133.4 (m), 133 (s), 132.8 (s), 132.3 (s), 131.6 (s), 131.5 (s), 131.3 (s), 130.9 (m), 130.8 (m), 130 (s), 129.5 (m), 129.1 (m), 128.5 (m), 128.8 (m), 127 (m), 125.9 (s), 125.3 (m), 125 (m), 124.4 (m), 120.6 (s), 118 (q, $^1J_{C-F}$ = 320 Hz), 22.2 (s). MS *m/z* 879.7 (calcd *m/z* 879.7 for $[M]^+$).

(e) Synthesis of (*R*)-4,4′-Diphenyl-6,6′dichloro-2-triflato-2′-bis(xyl)phosphino-1,1′-binaphthyl, 19. To a solution of **18** (0.09 g, 0.1 mmol) in 5 mL of anhydrous benzene were added 16 μL (0.054 mmol) of $Ti(O^iPr)_4$ and 99 μL (0.53 mmol) of $(EtO)_3SiH$ via a syringe. The reaction mixture was heated to reflux for 4 h. The solvent was removed under reduced pressure and the residue was then passed through a short silica gel column with CH_2Cl_2. CH_2Cl_2 was removed under reduced pressure to give 0.08 g (>99% yield) of pure **19**. ^{1}H{^{31}P} NMR ($CDCl_3$) δ 8.0 (m, 2H), 7.6 (m, 13H), 7.31 (m, 2H), 7.1 (m, 1H), 6.95 (m, 4H), 6.85 (s, 1H), 6.65 (m, 1H), 2.25 (s, 6H), 2.15 (s, 6H). ^{31}P{^{1}H} NMR ($CDCl_3$) δ −10.4 (s). ^{13}C{^{1}H} NMR ($CDCl_3$) δ 144.4 (s), 142.8 (s), 140.5 (s), 139.7 (s), 138.3 (m), 136.6 (m), 133.5 (s), 133.4 (m), 132.2 (m), 131.8 (m), 130.8 (m), 130.2 (m), 129.4 (m), 127.9 (m), 127.4 (s), 125.3 (m), 121.4 (s), 21.5 (s). MS *m/z* 863.6 (calcd *m/z* 863.8 for $[M]^+$).

(f) Synthesis of (*R*)-4,4′-Diphenyl-6,6′dichloro-2,2′-bis-(bis(xyl)phosphino)-1,1′-binaphthyl ((*R*)-L$_3$). A mixture of **19** (80 mg, 0.093 mmol), $HP(Xyl)_2$ (34 μL, 0.14 mmol), Ni(dppe)-Cl_2 (12 mg, 9.3 μmol), and DABCO (24 mg, 0.19 mmol) was prepared in a glovebox. The reaction mixture was then dissolved in 1 mL of anhydrous DMF and heated at 110 °C for 2 days. The reaction mixture was allowed to cool to room temperature and then extracted with EtOAc and washed with water 4 times. The organic layer was dried with $MgSO_4$ and the volatiles were removed under reduced pressure. The residue was then passed through a short silica gel column with CH_2Cl_2. The solvent was removed under reduced pressure to obtain pure product of *R*-**L$_3$** (0.051 g, 57% yield). ^{1}H{^{31}P} NMR ($CDCl_3$) δ 7.91 (s, 2H), 7.57 (s, 2H), 7.49 (m, 12H), 6.85 (m, 4H), 6.8 (s, 4H), 6.74 (s, 2H), 6.68 (s, 2H), 2.12 (s, 12H), 2.08 (s, 12H). ^{31}P{^{1}H} NMR ($CDCl_3$) δ −12.4 (s). ^{13}C{^{1}H} NMR ($CDCl_3$) δ 140.1 (s), 139.3 (s), 137.4 (m), 137.2 (m), 132.5 (m), 131.9 (m), 130.2 (m), 129.4 (m), 129.3 (s), 128.4 (s), 127.5 (s), 126.1 (s), 124.6 (s), 21.2 (s), 21.1 (s). MS *m/z* 956 (calcd *m/z* 956 for $[M]^+$).

4.4. Synthesis of 4,4′,6,6′-Tetramethyl-2,2′-bis(bis(xyl)-phosphino)-1,1′-binaphthyl (L$_4$). (a) Synthesis of (*R*)-4,4′,6,6′-Tetramethyl-2,2′-diethoxy-1,1′-binaphthalene, 20. A mixture of 4,4′,6,6′-tetrabromo-2,2′-diethoxy-1,1′-binaphthalene (1.5 g, 2.4 mmol), trimethylboroxine in 50 wt % THF (4 mL), $Pd(PPh_3)_4$ (0.14 g, 0.012 mmol), and 2 M Na_2CO_3 (4.5 mL) was dissolved in 20 mL of DME. The reaction mixture was degassed for ~3 min, heated to reflux for 2 days, extracted with EtOAc, and washed with water 3 times. The organic layer was dried over $MgSO_4$ and the volatiles were removed under reduced pressure. The crude product was purified by using silica gel column with toluene to give 1.2 g (88% yield) of **20**. ^{1}H NMR ($CDCl_3$) δ 7.78 (s, 2H), 7.28 (s, 2H), 7.07 (s, 4H), 4.2 (m, 4H), 2.80 (s, 6H), 2.49 (s, 6H), 1.8 (m, 6H). ^{13}C{^{1}H} NMR ($CDCl_3$) δ 153.3 (s), 134.5 (s), 132.6 (s), 132.5 (s), 128.6 (s), 127.9 (s), 126.2 (s), 123.1 (s), 119.2 (s), 117.4 (s), 65.3 (s), 21.7 (s), 19.9 (s), 15.1 (s). MS *m/z* 370 (calcd *m/z* 370.5 for $[M]^+$).

(b) Synthesis of (*R*)-4,4′,6,6′-Tetramethyl-2,2′-dihydroxy-1,1′-binaphthalene, 21. To a solution of **20** (1.2 g, 3.2 mmol) in 10 mL of CH_2Cl_2 at room temperature was added 2 mL (13 mmol) of BBr_3 via a syringe. The reaction mixture was allowed to stir at room temperature for 12 h, quenched with ice water, then extracted with CH_2Cl_2, and washed with water 3 times. The organic layer was dried over $MgSO_4$ and the volatiles were removed under reduced pressure to give pure product of **21** in quantitative yield. ^{1}H NMR ($CDCl_3$) δ 7.8 (s, 2H), 7.22 (s, 2H), 7.15 (dd, $^3J_{H-H}$ = 9 Hz and $^4J_{H-H}$ = 3 Hz, 2H), 7.08 (d, $^3J_{H-H}$ = 9 Hz, 2H), 2.77 (s, 6H), 2.50 (s, 6H). ^{13}C{^{1}H} NMR ($CDCl_3$) δ 151.6 (s), 137.4 (s), 133.2 (s), 131.8 (s), 129.1 (s), 128.9 (s), 124.8 (s), 123.8 (s), 118.3 (s), 109.0 (s), 21.6 (s), 19.5 (s). MS *m/z* 342.4 (calcd *m/z* 342.4 for $[M]^+$).

(c) Synthesis of (*R*)-4,4′,6,6′-Tetramethyl-2,2′-bis(triflato)-1,1′-binaphthalene, 22. To a solution of **21** (0.46 g, 1.3 mmol) in 1 mL of pyridine and 10 mL of CH_2Cl_2 at 0 °C was added 1 mL of $(Tf)_2O$ via a syringe. The reaction mixture was stirred for an additional 12 h. The reaction mixture was then extracted with CH_2Cl_2 and washed with water 3 times. The organic layer was dried over $MgSO_4$ and the volatiles were removed under reduced pressure to give 0.5 g (61% yield) of **22**. ^{1}H NMR ($CDCl_3$) δ 7.88 (s, 2H), 7.40 (s, 2H), 7.22 (d, $^3J_{H-H}$ = 9.9 Hz and $^4J_{H-H}$ = 1.5 Hz, 2H), 7.15 (d, $^3J_{H-H}$ = 9.0 Hz, 2H), 2.84 (s, 6H), 2.54 (s, 6H). ^{13}C{^{1}H} NMR ($CDCl_3$) δ 144.4 (s), 138.5 (s), 136.9 (s), 131.9 (s), 131.5 (s), 129.7 (s), 127.4 (s), 123.7 (s), 121.5 (s), 119.7 (s), 21.9 (s), 19.7 (s). MS *m/z* 606.8 (calcd *m/z* 606.6 for $[M]^+$).

(d) Synthesis of (*R*)-4,4′,6,6′-Tetramethyl-2-triflato-2′-bis(xylyl)phosphinyl-1,1′-binaphthyl, 23. A mixture of **22** (0.3 g, 0.49 mmol), $HOP(xyl)_2$ (0.26 g, 0.9 mmol), $Pd(OAc)_2$ (0.022 g, 0.097 mmol), dppb (0.042 g, 0.099 mmol), Et_2N^iPr (0.33 mL, 2.0 mmol), and 1 mL of DMSO was prepared in a glovebox. The reaction mixture was then heated at 110 °C for 3 days, extracted with EtOAc, and washed with water 5 times. The organic layer was dried over $MgSO_4$ and the volatiles were removed under reduced pressure. The residue was purified by using silica gel chromatography with CH_2Cl_2:acetone (20:1) to give 0.31 g (88% yield) of **23**. ^{1}H{^{31}P} NMR ($CDCl_3$) δ 7.85 (s, 1H), 7.76 (s, H_3, 1H), 7.62 (s, 1H), 7.10 (m, 4H), 6.10 (m, 5H), 6.82 (m, 2H), 2.74 (s), 2.63 (s), 2.52 (s), 2.49 (s), 2.20 (s, 6H), 2.04 (s, 6H). ^{31}P{^{1}H} NMR ($CDCl_3$) δ +30.8 (s). ^{13}C{^{1}H} NMR ($CDCl_3$) δ 144.7 (s), 137.9 (s), 137.6 (s), 137.4 (s), 136.9 (s), 136.8

(s), 136.7 (s), 136.1 (s), 134.6 (s), 134.4 (s), 133.9 (m), 132.9 (m), 132.4 (s), 132.2 (m), 131.2 (s), 129.5 (m), 128.9 (s), 128.6 (s), 127.8 (s), 123.3 (s), 123 (s), 118.9 (s), 21.9 (s), 21.7 (s), 21 (s), 20.9 (s), 19.7 (s), 19.5 (s). MS *m/z* 715.2 (calcd *m/z* 714.8 for $[M]^+$).

(e) Synthesis of (*R*)-4,4′,6,6′-Tetramethyl-2-triflato-2′-bis(xyl)phosphino-1,1′-binaphthyl, 24. To a solution of **23** (0.31 g, 0.43 mmol) in 5 mL of anhydrous benzene were added 72 μL (0.24 mmol) of $Ti(O^iPr)_4$ and 0.5 mL (2.7 mmol) of $(EtO)_3SiH$ via a syringe. The reaction mixture was then heated to reflux for 4 h. The organic solvents were removed under reduced pressure and the crude product was passed through a short silica gel column with CH_2Cl_2. The solvent was then removed under reduced pressure to give 0.30 g (>99% yield) of **24**. $^1H\{^{31}P\}$ NMR ($CDCl_3$) δ 7.80 (m, 2H), 7.31 (m, 2H), 7.1 (s, 2H), 6.91 (m, 6H), 6.63 (s, 2H), 2.80 (s, 3H), 2.65 (s, 3H), 2.49 (s, 3H), 2.48 (s, 3H), 2.23 (s, 12H), 2.10 (s, 12H). $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ −11.0 (s). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 144.2 (m), 137.5 (m), 137(m), 136.3 (m), 135.3 (m), 134.5 (s), 133.1 (s), 132.5 (s), 131.3 (m), 130 (m), 129.9 (m), 129.7 (m), 127.5 (s), 123.3 (m), 119.7 (s), 21.9 (s), 21.8 (s), 21.2 (s), 21.1 (s), 19.7 (m). MS *m/z* 699 (calcd *m/z* 698.8 for $[M]^+$).

(f) Synthesis of (*R*)-4,4′,6,6′-Tetramethyl-2,2′-bis(bis-(xyl)phosphino)-1,1′-binaphthyl ((*R*)-L$_4$). A mixture of **24** (0.3 g, 0.4 mmol), $HP(Xyl)_2$ (0.18 mL, 0.6 mmol), $Ni(dppe)Cl_2$ (0.06 g, 0.04 mmol), and DABCO (0.12 g, 0.8 mmol) was prepared in a glovebox. One milliliter of anhydrous DMF was added to the reaction mixture and the resulting mixture was heated at 110 °C for 2 days. The reaction mixture was allowed to cool to room temperature and then extracted with EtOAc and washed with water 4 times. The organic layer was dried over $MgSO_4$ and the volatiles were removed under reduced pressure. The residue was then passed through a short silica gel column with CH_2Cl_2, and the solvent was then removed under reduced pressure to give 0.23 g (68% yield) of **L$_4$**. $^1H\{^{31}P\}$ NMR ($CDCl_3$) δ 7.78 (s, 2H), 7.35 (s, 2H), 6.97 (m, 4H), 6.82 (m, 12H), 2.72 (s, 6H), 2.56 (s, 6H), 2.23 (s, 12H), 2.10 (s, 12H). $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ −10.3 (s). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 144.7 (m), 144.3 (m), 138.4 (m), 137.9 (m), 137 (m), 136.8 (m), 135.9 (s), 134.2 (m), 133.2 (s), 132.9 (s), 132 (m), 131.5 (s), 131.3 (s), 130.6 (m), 129.9 (s), 128.7 (s), 127.2 (s), 123.3 (s), 21.9 (s), 21.2 (s), 21.1 (s), 19.7 (s). MS *m/z* 791.1 (calcd *m/z* 791 for $[M]^+$). $[\alpha]_D$ +210.6 (CH_2Cl_2, *c* 0.05).

4.5. A Typical Procedure for the Synthesis of Ru-4,4′-Substituted-xylBINAP-Diamine Precatalysts. A mixture of $[Ru(benzene)Cl_2]_2$[18] (7.1 mg, 0.014 mmol) and **L$_1$** (37.4 mg, 0.029 mmol) in anhydrous DMF (2 mL) was heated at 100 °C under nitrogen for 1 h and was then cooled to room temperature. (*R*,*R*)-DPEN (6.3 mg, 0.025 mmol) was added to the mixture. With stirring, DPEN slowly dissolved in the solution in approximately 15 min and the color of the solution changed from orange-red to yellow. After the mixture was stirred at 80 °C for 3 h and at room temperature for 12 h, DMF was removed under vacuum at room temperature and then at 50 °C. The residue was purified with silica gel column chromatography in air with a mixture of hexane:EtAOc (4:1) to give 23 mg (61% yield) of pure (*R*,*RR*)-**25** precatalyst.

Ru[(R)-L$_1$)][(R,R)-DPEN]Cl$_2$, 25: $^1H\{^{31}P\}$ NMR (acetone-d_6) δ 8.54 (s, 2H), 7.90 (d, $^3J_{H-H}$ = 8.8 Hz, 2H), 7.38 (m, 5H), 7.20 (t, $^3J_{H-H}$ = 7.3 and 7.8 Hz, 2H), 7.15 (m, 5H), 6.87 (m, 8H), 6.73 (t, $^3J_{H-H}$ = 7.4 and 7.9 Hz, 2H), 6.14 (d, $^3J_{H-H}$ = 8.3 Hz, 2H), 6.05 (s, 4H), 4.26 (m, 2H), 3.56 (m, 2H), 3.03 (m, 2H), 2.26 (s, 12H), 1.78 (s, 12H), 0.51 (s, 18H). $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ +46.5 (s). MS *m/z* 1226.7 (calcd *m/z* 1226.9 for $[M - Cl]^+$).

Ru[(R)-L$_3$)][(R,R)-DPEN]Cl$_2$, 26: $^1H\{^{31}P\}$ NMR ($CDCl_3$) δ 8.40 (s, 2H), 7.88 (s, 2H), 7.84 (m, 2H), 7.66 (s, 4H), 7.61 (m, 4H), 7.5 (m, 6H), 7.07 (m, 6H), 6.78 (m, 6H), 6.72 (m, 2H), 6.28 (d, $^3J_{H-H}$ = 9.2 Hz, 2H), 6.05 (s, 4H), 4.22 (m, 2H), 3.27 (m, 2H), 3.04 (m, 2H), 2.20 (s, 12H), 1.77 (s, 12H). $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ +43.9 (s). MS *m/z* 1340.8 (calcd *m/z* 1340.2 for $[M]^+$).

(18) Zelonka, R. A.; Baird, M. C. *Can. J. Chem.* **1972**, *50*, 3063.

Ru[(R)-L$_4$)][(R,R)-DPEN]Cl$_2$, 27: $^1H\{^{31}P\}$ NMR ($CDCl_3$) δ 8.15 (s, 2H), 7.68 (s, 8H), 7.55 (s, 2H), 7.04 (m, 5H), 6.81 (m, 5H), 6.51 (d, $^3J_{H-H}$ = 8.8 Hz, 2H), 6.03 (d, $^3J_{H-H}$ = 9.7 Hz, 2H), 5.83 (s, 4H), 4.18 (m, 2H), 3.16 (m, 2H), 3.0 (m, 2H), 2.77 (s, 6H), 2.37 (s, 6H), 2.26 (s, 12H), 1.78 (s, 12H). $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ +44.1 (s). MS *m/z* 1139.9 (calcd *m/z* 1139.4 for $[M - Cl]^+$).

Ru[(R)-L$_1$)][(R)-DAIPEN]Cl$_2$, 28: $^1H\{^{31}P\}$ NMR (acetone-d_6) δ 8.80 (s, 1H), 8.68 (s, 1H), 8.02 (m, 2H), 7.77 (s, 2H), 7.59 (s, 2H), 7.44 (m, 5H), 7.24 (m, 2H), 7.12 (s, 1H), 6.92 (m, 4H), 6.79 (m, 2H), 6.6 (m, 2H), 6.06 (m, 4H), 5.68 (s, 2H), 4.64 (m, 1H), 4.16 (m, 1H), 3.93 (s, 3H), 3.82 (s, 3H), 3.3 (m, 1H), 2.83 (m, 3H), 2.67 (m, 1H), 2.52 (m, 1H), 2.35 (m, 3H), 2.0 (s, 12H), 1.82 (s, 12H), 0.66 (s, 9H), 0.57 (s, 9H). $^{31}P\{^1H\}$ NMR (acetone-d_6) δ +47.8 (d, $^5J_{P-P}$ = 40 Hz) and +45.3 (d, $^5J_{P-P}$ = 40 Hz). MS *m/z* 1294.1 (calcd *m/z* 1294.5 for $[M - 2Cl]^+$).

Ru[(R)-L$_2$)][(R)-DAIPEN]Cl$_2$, 29: $^1H\{^{31}P\}$ NMR (acetone-d_6) $^1H\{^{31}P\}$ NMR spectrum indicated that there are two diastereometers. Phosphorus proton decoupled spectrum showed four sets of phosphorus peaks. $^{31}P\{^1H\}$ NMR (acetone-d_6) δ +48.1 (d, $^5J_{P-P}$ = 38 Hz), +46.8 (d, $^5J_{P-P}$ = 37 Hz), +45.8 (d, $^5J_{P-P}$ = 38 Hz), and +44.4 (d, $^5J_{P-P}$ = 38 Hz). MS *m/z* 1292.1 (calcd *m/z* 1292.4 for $[M]^+$).

Ru[(R)-L$_3$)][(R)-DAIPEN]Cl$_2$, 30: $^1H\{^{31}P\}$ NMR ($CDCl_3$) δ 8.50 (s, 1H), 8.37 (s, 1H), 7.82 (m, 4H), 7.75 (m, 2H), 7.7 (s, 2H), 7.53 (m, 10H), 7.35 (m, 4H), 6.92 (s, 1H), 6.78 (m, 7H), 6.65 (m, 2H), 6.13 (m, 2H), 6.05 (s, 1H), 5.99 (s, 1H), 4.25 (m, 1H), 4.58 (m, 2H), 4.08 (m, 2H), 3.85 (s, 3H), 3.75 (s, 3H), 3.27 (m, 2H), 2.5 (m, 3H), 2.26 (s, 6H), 2.23 (m, 3H), 1.99 (s, 6H), 1.77 (s, 6H), 1.72 (s, 6H). $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ +46 (d, $^5J_{P-P}$ = 37 Hz) and +43.8 (d, $^5J_{P-P}$ = 38 Hz). MS *m/z* 1442.7 (calcd *m/z* 1442.3 for $[M]^+$).

Ru[(R)-L$_4$)][(R)-DAIPEN]Cl$_2$, 31: $^1H\{^{31}P\}$ NMR ($CDCl_3$) δ 8.21 (s, 1H), 8.05 (s, 1H), 7.70 (s, 2H), 7.63 (s, 1H), 7.59 (s, 1H), 7.56 (s, 2H), 7.35 (m, 5H), 7.04 (s, 1H), 6.84 (m, 5H), 6.71 (m, 2H), 6.54 (m, 2H), 5.98 (m, 4H), 4.52 (m, 1H), 4.04 (m, 1H), 3.84 (s, 3H), 3.74 (s, 3H), 3.32 (m, 1H), 2.74 (m, 6H), 2.65 (m, 1H), 2.34 (m, 1H), 2.35 (s, 6H), 2.28 (s, 6H), 1.74 (m, 24H). $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ +47.4 (d, $^5J_{P-P}$ = 39 Hz) and +45.2 (d, $^5J_{P-P}$ = 36 Hz). MS *m/z* 1206.1 (calcd *m/z* 1206.5 for $[M - 2Cl]^+$).

4.6. A Typical Procedure for Asymmetric Hydrogenation of Aromatic Ketones. Ru(disphosphine)(diamine)Cl_2 precatalyst (3.3 mg, 3.3 μmol) and 2 mol % of KO^{t}Bu were transferred into a 1-dram vial in a glovebox. After the addition of 1-acetonaphthone (0.5 mL, 3.3 mmol), the reaction mixture was quickly transferred into a stainless steel autoclave and sealed. After purging with H_2 six times, the final H_2 pressure was adjusted to 700 psi. After 24 h, the autoclave was depressurized and the reaction mixture was washed with diethyl ether and water twice. The diethyl ether layer was then passed through a mini silica gel column. An aliquot was analyzed on GC to give conversion and ee values. The absolute configurations of enantioenriched products from the present experiments were assigned based on GC to be same as those samples obtained from Ru-BINAP catalyzed reactions.

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Supporting Information Available: Detailed chiral GC conditions, $^1H\{^{31}P\}$ NMR spectra of (*R*)-**L$_{1-4}$**, $^{31}P\{^1H\}$ NMR spectra of (*R*,*RR*)-**25**, **-27**, and **-28**, representative chiral GC traces for the secondary alcohol products with (*R*,*R*)-**28**, and crystallographic data (CIF file). This material is available free of charge via the Internet at http://pubs.acs.org.

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