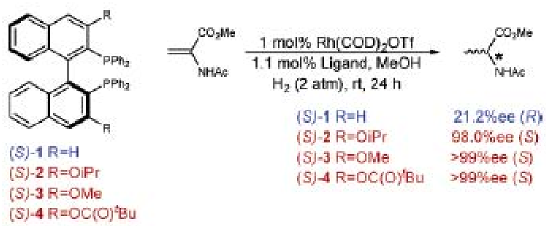
Access to full text denied by publisher.

Please contact your local library to acquire the following paper:

Citation:

3,3'-Disubstituted BINAP Ligands: Synthesis, Resolution, and Applications in Asymmetric Hydrogenation
J. Matthew Hopkins, Sean A. Dalrymple, Masood Parvez, and Brian A. Keay
pp 3765 – 3768.

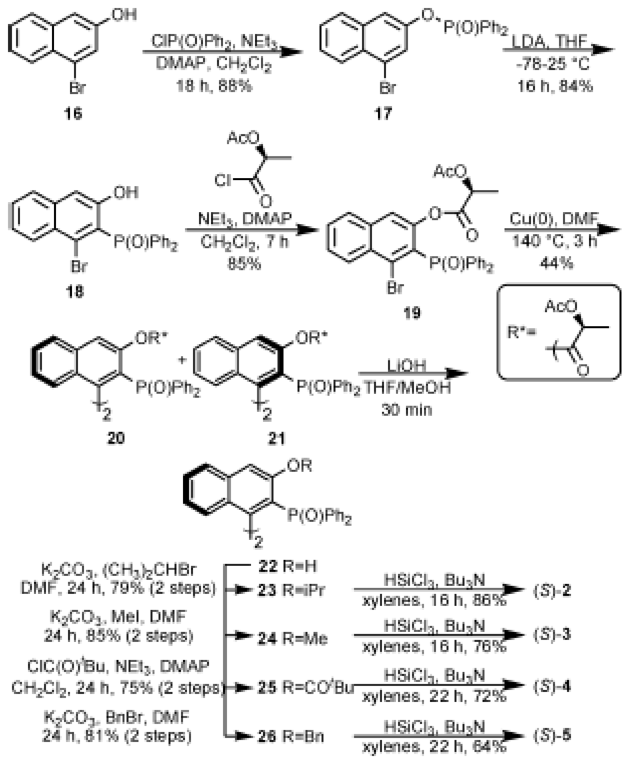
Abstract:



A novel family of BINAP ligands were prepared with alkoxy- and acetoxy-derived substituents in the 3,3′-positions. They were prepared through a convergent synthesis starting from readily available 4-bromo-2-naphthol. These ligands afforded excellent enantioselectivities in the asymmetric hydrogenation of substituted olefins. The presence of the 3,3′-substituents was shown to be beneficial by a direct comparison with the parent unsubstituted BINAP.

Schemes:

Scheme 1. Synthesis of 3,3′-Disubstituted BINAP Derivatives



Figures:

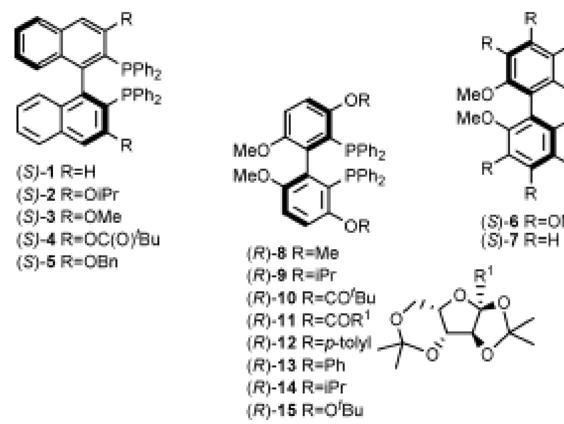


Figure 1. 3,3′-Disubstituted biaryl bisphosphine ligands.

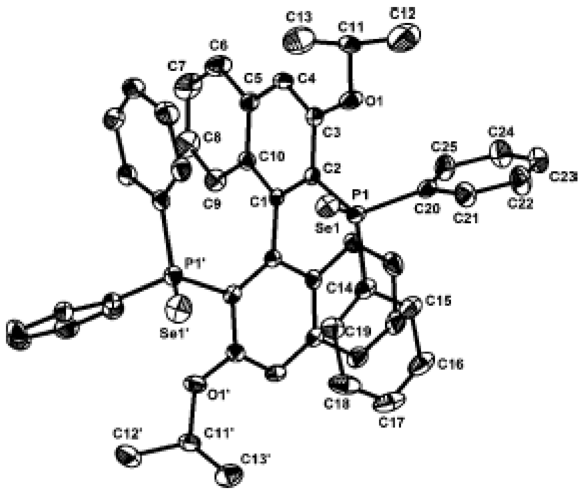
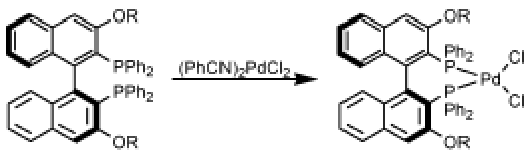


Figure 2. X-ray crystal structure of the phosphine selenide of (*S*)-**2**.

Tables:

Table 1. Structural Parameters for $PdCl_2$ Complexes of (*S*)-1−3

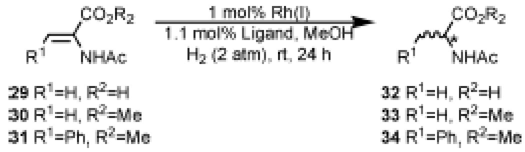


(*S*)-**2** R=iPr
(*S*)-**3** R=Me

(*S*)-**27** R=iPr
(*S*)-**28** R=Me

entry	3,3′-substituent	average Pd−P (Å)	average Pd−Cl (Å)	ligand bite angle (deg)	torsion angle (deg)
1	H	2.245	2.350	92.77	68.42
2	OiPr	2.290	2.338	89.91	62.64
3	OMe	2.270	2.355	88.09	60.25

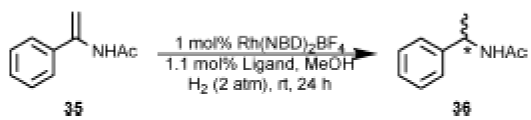
Table 2. Asymmetric Hydrogenation of 2-Acetamidoacrylic Acid Derivatives with Ligands (*S*)-**1**−**5**



entry[a]	ligand	olefin	ee (%)[b]
1	(*S*)-**1**	29[c]	33.8 (*R*)
2		30	21.2 (*R*)
3		31	14.8 (*R*)
4	(*S*)-**2**	29[c]	94.9 (*S*)
5		30	98.0 (*S*)
6		31	23.2 (*S*)
7	(*S*)-**3**	29[c]	98.6 (*S*)
8		30	>99 (*S*)
9		31	32.8 (*S*)
10	(*S*)-**4**	29[c]	>99 (*S*)
11		30	>99 (*S*)
12		31	74.7 (*S*)
13	(*S*)-**5**	29[c]	92.3 (*S*)
14		30	96.3 (*S*)
15		31	44.8 (*S*)

[a] All reactions proceeded with complete conversion. Reactions of olefins **29** and **30** used $Rh(COD)_2OTf$ as the Rh source. Reactions of olefin **31** used $Rh(NBD)_2BF_4$ as the Rh source. [b] For 33, determined by chiral GC on a Cyclodex B column; for 34, determined by chiral HPLC on a Chiralcel OD column. [c] Ee determined upon conversion to the methyl ester.

Table 3. Asymmetric Hydrogenation of *N*-Acetyl-phenylethenamide with Ligands (*S*)-**1**−**5**



entry[a]	ligand	ee (%)[b]
1	(*S*)-**1**	10.7 (*R*)
2	(*S*)-**2**	89.9 (*S*)
3	(*S*)-**3**	26.9 (*S*)
4	(*S*)-**4**	85.6 (*S*)
5	(*S*)-**5**	59.6 (*S*)

[a] All reactions proceeded with complete conversion. [b] Determined by chiral GC using a Cyclodex B column.

DOI: 10.1021/ol051413d