JOC The Journal of Organic Chemistry

NOTE

pubs.acs.org/joc

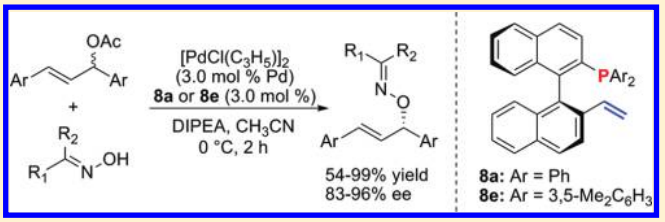
Pd-Catalyzed Asymmetric Allylic Etherizations with Oximes by Chiral Alkene-Phosphine Ligands

Ziping Cao, Zhaoqun Liu, Yilin Liu, and Haifeng Du*

Beijing National Laboratory of Molecular Sciences, CAS Key Laboratory of Molecular Recognition and Function, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China

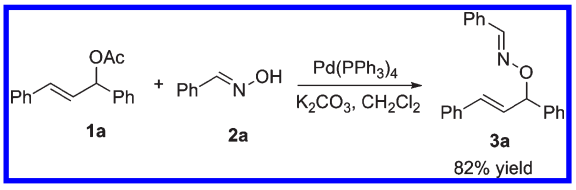
Supporting Information

ABSTRACT: Palladium-catalyzed asymmetric allylic etherizations with a variety of oximes as nucleophiles utilizing a chiral alkene-phosphine hybrid ligand have been successfully achieved for the first time to afford the optical active oxime ethers in high yields with good to excellent enantioselectivities.



Pd-catalyzed asymmetric allylic substitutions provide a practical and efficient approach to construct the C−C, C−N, and C−O bonds enantioselectively from readily available starting materials.[1−3] Oximes can be easily obtained by a simple condensation of aldehydes or ketones with hydroxylamine and have been widely utilized in synthetic chemistry.[4−8] In 2004, Takemoto and co-workers described the first Ir-catalyzed allylic substitutions with oximes.[9] Therein, they also reported one example of allylic substitution catalyzed by $Pd(PPh_3)_4$ (Scheme 1).[9] Soon after that, Takemoto and co-workers realized the Ir-catalyzed asymmetric transformation.[10−13] However, to the best of our knowledge, few applications of oximes as nucleophiles in Pd-catalyzed asymmetric allylic substitutions that would provide access to useful optically active oxime ethers[14−20] have been reported. The key point to achieve this enantioselective transformation is to determine suitable chiral ligands.

Scheme 1. Pd-Catalyzed Allylic Etherization with Oxime 2a



Chiral olefins as one type of lately emerging ligands have attracted intensive attention.[21−24] Both chiral diene[25−31] and hybrid olefin ligands incorporated with heteroatoms such as phosphorus[32−35] or nitrogen[36,37] have been well developed and successfully applied in asymmetric catalysis. Recently, our group developed a variety of acyclic chiral diene ligands for Rh-catalyzed asymmetric additions.[38−41] Particularly, a strategy was adopted in our group for the exploring of novel alkene-phosphine hybrid ligand by the combination of the terminal alkene and the phosphorus atom. These resulting ligands showed high activities and selectivities in palladium-catalyzed asymmetric allylic substitutions.[42,43] On the basis of our previous study, we envision that chiral terminal-alkene-phosphine hybrid ligands will be suitable for Pd-catalyzed asymmetric allylic etherizations with oximes. Herein, we report our efforts on this subject.

Because $Pd(PPh_3)_4$ was an efficient catalyst for the allylic etherization of 1,3-diphenyl-2-propenyl acetate (**1a**) with oxime **2a** (Scheme 1),[9] initially, various well-established chiral phosphine ligands[44−48] were subjected to this reaction to examine the activity and selectivity (Scheme 2). It was disappointing to find that ligands **4**−**7** led to only 6−29% yields with 13−76% ee's, which indicated that the challenge still remained in this asymmetric transformation. We were pleased to find that alkene/phosphine hybrid ligand **8a**[43] was highly effective for this reaction to give the desired oxime ether **3a** in 95% yield with 83% ee, while a control experiment with **8b**[43] as a ligand afforded only a small amount of product **3a** with 8% ee (Scheme 2). The terminal alkene moieties in ligand **8a** proved to be essential for the observed high activity and selectivity.

To further improve the enantioselectivities, various reaction conditions were then optimized. As shown in Table 1, both base and solvent had some impact on the reactivity and enantioselectivity. We found that the allylic etherization of 1,3-diphenyl-2-propenyl acetate (**1a**) with oxime **2a** under the catalysis of **8a**/Pd (3.0 mol %) using *N*,*N*-diisopropylethylamine (DIPEA) as a base and CH_3CN as a solvent went smoothly to give the best enantioselectivity (Table 1, entry 11).

Under optimized conditions, chiral alkene/phosphine ligands were subsequently evaluated to search for more effective ligands. Compared with ligand **8a**, ligand **8c**[43] gave a similar yield but a lower ee, and ligand **8e**[43] gave a little higher ee (Figure 1). Ligand **8f**[43] containing an internal double bond led to only 10% yield

Received: May 6, 2011
Published: June 13, 2011

Scheme 2. Pd-Catalyzed Asymmetric Allylic Etherization with Oxime 2a

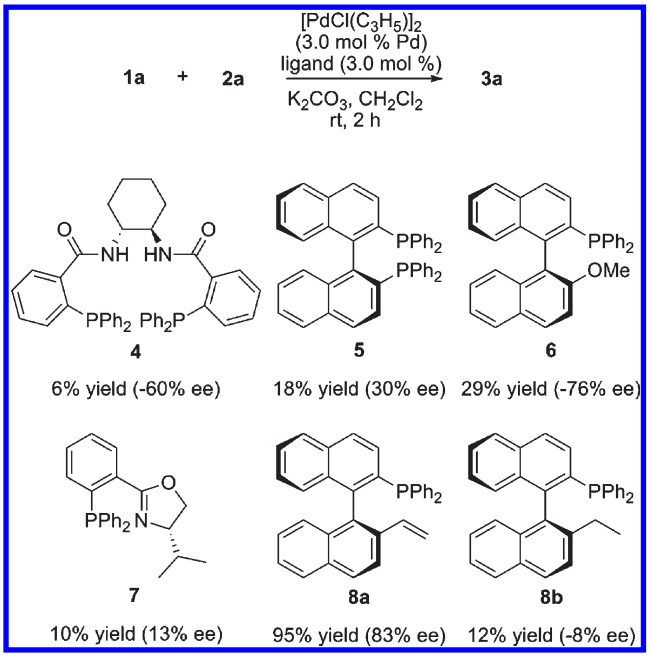


Table 1. Optimization of Reaction Conditions[a]

entry	base	solvent	yield (%)[b]	ee (%)[c]
1	K_2CO_3	CH_2Cl_2	95	83
2	Na_2CO_3	CH_2Cl_2	86	85
3	Li_2CO_3	CH_2Cl_2	50	86
4	Cs_2CO_3	CH_2Cl_2	99	84
5	KOAc	CH_2Cl_2	96	83
6	Et_3N	CH_2Cl_2	87	84
7	DIPEA	CH_2Cl_2	>99	85
8	DIPEA	THF	98	86
9	DIPEA	toluene	99	86
10	DIPEA	dioxane	82	87
11	**DIPEA**	**CH_3CN**	**91**	**90**

[a] All reactions were carried out with **1a** (0.24 mmol), **2a** (0.20 mmol), Pd/**8a** = 1/1 (3 mol % Pd), base (0.40 mmol), and solvent (1.0 mL) at room temperature for 2 h. [b] Yield based on oxime **2a**. [c] The ee was determined by chiral HPLC (Chiralpak IC column).

with 66% ee for the reverse absolute configuration, which was probably the result of the steric hindrance on the double bond.

With the optimized condition and the best ligand in hand, the substrate scope for Pd-catalyzed asymmetric allylic etherization with oximes was examined, and all the results are summarized in Table 2. It was found that oximes derived from aromatic aldehydes or ketones were effective substrates to give the desired products in 54−99% yields with 89−96% ee's (Table 2, entries 1−15, 18−20), and enantiomerically pure oxime ethers were obtained after a single recrystallization in hexanes (Table 2, entries 1 and 14). It is worth noting that α-carbonyloximes **2p**−**2r** were also suitable substrates for this reaction to give the corresponding products in good yields and ee's (Table 2, entries 16−18). However, using cyclohex-2-enyl actetate as a substrate

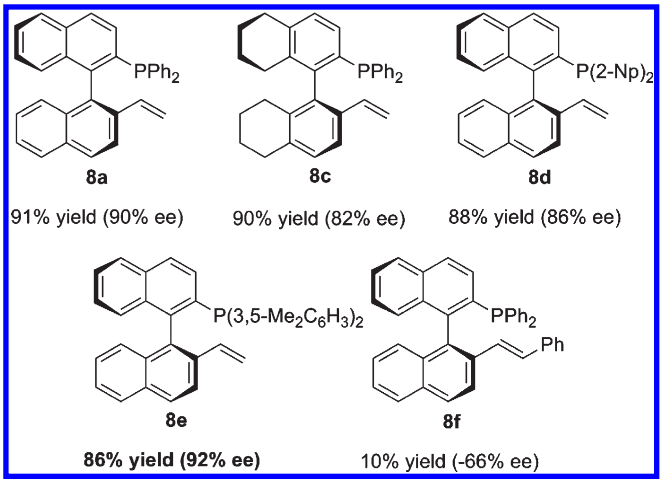
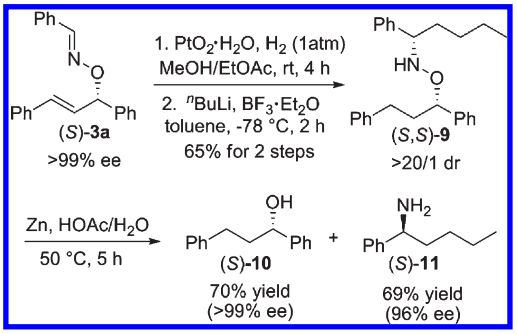


Figure 1. Evaluation of chiral alkene-phosphine ligands for Pd-catalyzed asymmetric etherization with oxime **2a**.

Scheme 3. Synthesis of Chiral Amine from the Oxime Ether



gave only low yield and ee (Table 2, entry 21). Oximes derived from aliphatic aldehydes or ketones were ineffective for the current system, and the reason still awaits further investigation. The absolute configuration of product **3l** was determined as *S* by the X-ray structure of derivatives (Supporting Information), and the configurations of other products were tentatively assigned by analogy.

The resulting oxime ethers provide access to optically active amines. For example, compound **3a** can be easily converted to compound **9** in a reasonable yield with excellent diastereoselectivity after hydrogenation with H_2 and addition with *n*-butyllithium (Scheme 3). The N−O bond was then cleaved efficiently by treating with Zn/HOAc according to the reported methods[10,15−20] to afford both optically active alcohol **10** and amine **11**.

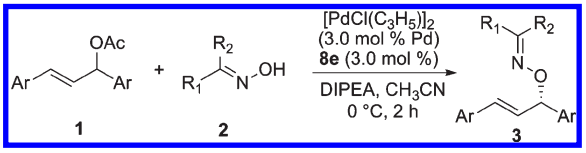
In conclusion, terminal-alkene-phosphine hybrid ligands proved to be highly effective for palladium-catalyzed asymmetric allylic etherizations of 1,3-diaryl-2-propenyl acetates with oximes to give optically active oxime ethers in high yields and ee's. Importantly, the current study also provides an attractive approach for the synthesis of optically active amines.

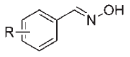
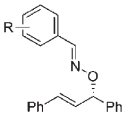
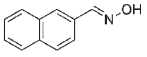
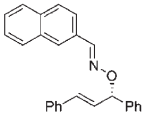
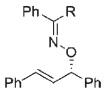
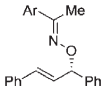
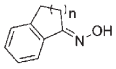
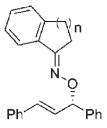
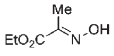
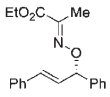
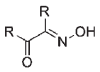
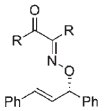
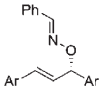
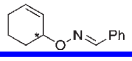
EXPERIMENTAL SECTION

General Procedure for 8e/Pd-Catalyzed Asymmetric Allylic Etherization with Oxime. To a dried Schlenk flask charged with $[PdCl(C_3H_5)]_2$ (0.0022 g, 0.006 mmol, 3.0 mol % Pd) and ligand **8e** (0.0062 g, 0.012 mmol, 3 mol %) was added distilled CH_3CN

dx.doi.org/10.1021/jo200925q |J. Org. Chem. 2011, 76, 6401–6406

Table 2. Pd/8e-Catalyzed Asymmetric Allylic Etherization with Oximes[a]



entry	oxime (**2**)	product (**3**)[c]	yield (%)[d]	ee (%)[e]
1			97	93(>99)[f]
2	**2a**: R = H		92	94
3	**2b**: R = 4-CH_3		99	93
4	**2c**: R = 4-Cl		98	92
5	**2d**: R = 3-Cl		96	94
6	**2e**: R = 2-CH_3		93	92
	2f: R = 2-Cl			
7	 **2g**		98	94
				
8	**2h**: R = CH_3		90	93
9	**2i**: R = C_2H_5		54	94
10	**2j**: R = Ph		99	92
				
11	**2k**: Ar = 4-$CH_3C_6H_4$		84	94
12	**2l**: Ar = 4-ClC_6H_4		96	94
13	**2m**: Ar = 1-Naphthyl		73	93
				
14	**2n**: n = 1		89	95(>99)[f]
15	**2o**: n = 2		88	96
				
16	**2p**		96	88
				
17			94	83
18	**2q**: R = CH_3		89	91
	2r: R = Ph			
				
19[b]	**2a**		89	89
20[b]		Ar = 4-$CH_3C_6H_4$	99	91
		Ar = 3-ClC_6H_4		
21[b,g]	**2a**		32	33

[a] All reactions were carried out with **1** (0.48 mmol), oxime **2** (0.40 mmol), $[PdCl(C_3H_5)]_2$ (0.006 mmol), **8e** (0.012 mmol), DIPEA (0.80 mmol), and CH_3CN (2.0 mL) at 0 °C for 2 h unless otherwise noted. [b] Ligand **8a** was used. [c] The absolute configuration was tentatively assigned by analogy with (*S*)-**3l**. [d] Yield based on oxime. [e] The ee values were determined by chiral HPLC. [f] The ee in parentheses was determined after a single recrystallization in hexanes (75% yield for entry 1, 74% yield for entry 14). [g] The reaction was conducted with 5 mol % catalyst at room temperature for 8 h.

dx.doi.org/10.1021/jo200925q |*J. Org. Chem.* 2011, 76, 6401–6406

(0.6 mL) under argon, and the resulting mixture was stirred at room temperature for 20 min before being cooled to 0 °C. Then a solution of 1,3-diphenyl-2-propenyl acetate **1a** (0.1210 g, 0.48 mmol) and oxime **2** (0.4 mmol) in CH_3CN (1.40 mL) and DIPEA (0.1032 g, 0.8 mmol) was added. After 2 h of stirring at 0 °C, the reaction mixture was concentrated under reduced pressure, and the crude residue was purified by flash chromatography on silica gel to afford the desired product **3**.

Benzaldehyde *O*-[(1*S*,2*E*)-1,3-Diphenyl-2-propen-1-yl]oxime (Table 2, entry 1). White solid, mp 70−71 °C, $[\alpha]^{20}_D$ +39.4 (*c* 0.66, CH_2Cl_2) (93% ee); IR (film) 1494, 1447 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.22 (s, 1H), 7.60−7.54 (m, 2H), 7.47 (d, *J* = 7.2 Hz, 2H), 7.44−7.28 (m, 10H), 7.27−7.21 (m, 1H), 6.68 (d, *J* = 16.0 Hz, 1H), 6.52 (dd, *J* = 16.0, 6.8 Hz, 1H), 5.89 (d, *J* = 6.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.4, 140.6, 136.8, 132.7, 132.5, 130.0, 129.2, 128.8, 128.7, 128.6, 128.1, 128.0, 127.6, 127.3, 126.9, 86.1. Anal. Calcd for $C_{22}H_{19}NO$: C, 84.31; H, 6.11; N, 4.47. Found: C, 84.34; H, 6.04; N, 4.46.

4-Methylbenzaldehyde *O*-[(1*S*,2*E*)-1,3-Diphenyl-2-propen-1-yl]oxime (Table 2, entry 2). White solid, mp 81−82 °C, $[\alpha]^{20}_D$ +50.7 (*c* 0.42, CH_2Cl_2) (94% ee); IR (film) 1604, 1494, 1450 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.24 (s, 1H), 7.54−7.48 (m, 4H), 7.48−7.39 (m, 4H), 7.38−7.31 (m, 3H), 7.30−7.23 (m, 1H), 7.18 (d, *J* = 8.0 Hz, 2H), 6.72 (d, *J* = 16.0 Hz, 1H), 6.56 (dd, *J* = 16.0, 6.4 Hz, 1H), 5.92 (d, *J* = 6.4 Hz, 1H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.5, 140.7, 140.2, 136.9, 132.6, 129.7, 129.5, 129.3, 128.7, 128.6, 128.0, 127.9, 127.6, 127.3, 126.9, 86.0, 21.6. Anal. Calcd for $C_{23}H_{21}NO$: C, 84.37; H, 6.46; N, 4.28. Found: C, 84.32; H, 6.45; N, 4.25.

4-Chlorobenzaldehyde *O*-[(1*S*,2*E*)-1,3-Diphenyl-2-propen-1-yl]oxime (Table 2, entry 3). White solid, mp 113−115 °C, $[\alpha]^{20}_D$ +49.2 (*c* 0.33, CH_2Cl_2) (93% ee); IR (film) 1597, 1492, 1450, 1299 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.19 (s, 1H), 7.54−7.46 (m, 4H), 7.46−7.38 (m, 4H), 7.38−7.30 (m, 5H), 7.26 (dd, *J* = 8.0, 6.4 Hz, 1H), 6.70 (d, *J* = 16.0 Hz, 1H), 6.53 (dd, *J* = 16.0, 6.8 Hz, 1H), 5.90 (d, *J* = 6.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.2, 140.5, 136.7, 135.8, 132.8, 131.0, 129.1, 129.0, 128.7, 128.6, 128.5, 128.2, 128.1, 127.5, 126.9, 86.3. Anal. Calcd for $C_{22}H_{18}ClNO$: C, 75.97; H, 5.22; N, 4.03. Found: C, 76.13; H, 5.24; N, 4.00.

3-Chlorobenzaldehyde *O*-[(1*S*,2*E*)-1,3-Diphenyl-2-propen-1-yl]oxime (Table 2, entry 4). Colorless oil, $[\alpha]^{20}_D$ +35.7 (*c* 0.98, CH_2Cl_2) (92% ee); IR (film) 1596, 1563, 1494, 1480, 1450 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.16 (s, 1H), 7.59 (m, 1H), 7.46 (d, *J* = 8.0 Hz, 2H), 7.44−7.37 (m, 5H), 7.36−7.28 (m, 4H), 7.28−7.21 (m, 2H), 6.67 (d, *J* = 16.0 Hz, 1H), 6.50 (d, *J* = 16.0, 6.8 Hz, 1H), 5.88 (d, *J* = 6.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.1, 140.4, 136.7, 134.9, 134.3, 132.8, 130.1, 130.0, 128.9, 128.7, 128.2, 128.1, 127.5, 127.0, 126.9, 125.6, 86.4. Anal. Calcd for $C_{22}H_{18}ClNO$: C, 75.97; H, 5.22; N, 4.03. Found: C, 75.93; H, 5.28; N, 4.02.

2-Methylbenzaldehyde *O*-[(1*S*,2*E*)-1,3-Diphenyl-2-propen-1-yl]oxime (Table 2, entry 5). Colorless oil, $[\alpha]^{20}_D$ +32.1 (*c* 0.39, CH_2Cl_2) (94% ee); IR (film) 1494, 1453, 1292 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.56 (s, 1H), 7.73 (d, *J* = 7.6 Hz, 1H), 7.56 (d, *J* = 7.2 Hz, 2H), 7.51−7.43 (m, 4H), 7.42−7.33 (m, 3H), 7.30 (t, *J* = 7.2 Hz, 2H), 7.23 (dd, *J* = 8.0, 7.6 Hz, 2H), 6.77 (d, *J* = 16.0 Hz, 1H), 6.61 (dd, *J* = 16.0, 6.8 Hz, 1H), 5.98 (d, *J* = 6.8 Hz, 1H), 2.46 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.5, 140.6, 137.0, 136.8, 132.7, 131.0, 130.6, 129.7, 129.2, 128.7, 128.6, 128.1, 128.0, 127.6, 127.3, 126.9, 126.2, 86.1, 20.2. Anal. Calcd for $C_{23}H_{21}NO$: C, 84.37; H, 6.46; N, 4.28. Found: C, 84.45; H, 6.56; N, 4.17.

2-Chlorobenzaldehyde *O*-[(1*S*,2*E*)-1,3-Diphenyl-2-propen-1-yl]oxime (Table 2, entry 6). Colorless oil, $[\alpha]^{20}_D$ +22.2 (*c* 0.56, CH_2Cl_2) (92% ee); IR (film) 1600, 1494, 1471, 1449 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.65 (s, 1H), 7.85 (d, *J* = 7.6 Hz, 1H), 7.48 (d, *J* = 7.6 Hz, 2H), 7.45−7.38 (m, 4H), 7.38−7.29 (m, 4H), 7.29−7.24 (m, 2H), 7.22 (dd, *J* = 7.6, 7.2 Hz, 1H), 6.69 (d, *J* = 16.0 Hz, 1H), 6.52 (dd, *J* = 16.0, 6.8 Hz, 1H), 5.90 (d, *J* = 6.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.4, 140.4, 136.7, 134.0, 132.8, 130.9, 130.2, 129.9, 129.0, 128.7, 128.2, 128.1, 127.6, 127.5, 127.0, 126.9, 86.5. Anal. Calcd for $C_{22}H_{18}ClNO$: C, 75.97; H, 5.22; N, 4.03. Found: C, 76.02; H, 5.30; N, 3.91.

2-Naphthaldehyde *O*-[(1*S*,2*E*)-1,3-Diphenyl-2-propen-1-yl]oxime (Table 2, entry 7). White solid, mp 74−75 °C, $[\alpha]^{20}_D$ +35.5 (*c* 0.4, CH_2Cl_2) (94% ee); IR (film) 1510, 1494, 1449 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.85 (s, 1H), 8.55−8.51 (m, 1H), 7.86 (d, *J* = 7.6 Hz, 2H), 7.73 (d, *J* = 7.2 Hz, 1H), 7.54 (d, *J* = 8.0 Hz, 2H), 7.52−7.49 (m, 2H), 7.49−7.39 (m, 5H), 7.38−7.30 (m, 3H), 7.28−7.22 (m, 1H), 6.77 (d, *J* = 16.0 Hz, 1H), 6.59 (dd, *J* = 16.0, 6.8 Hz, 1H), 5.99 (d, *J* = 6.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.3, 140.6, 136.8, 134.0, 132.9, 130.8, 130.6, 129.2, 128.8, 128.7, 128.3, 128.1, 128.0, 127.9, 127.7, 127.2, 126.9, 126.3, 125.4, 125.0, 86.3. Anal. Calcd for $C_{26}H_{21}NO$: C, 85.92; H, 5.82; N, 3.85. Found: C, 86.16; H, 5.93; N, 3.88.

Acetophenone *O*-[(1*S*,2*E*)-1,3-Diphenyl-2-propen-1-yl]oxime (Table 2, entry 8). White solid, mp 103−104 °C, $[\alpha]^{20}_D$ +36.6 (*c* 0.68, CH_2Cl_2) (93% ee); IR (film) 1494, 1448, 1368 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.72−7.66 (m, 2H), 7.54 (d, *J* = 7.6 Hz, 2H), 7.51−7.42 (m, 4H), 7.42−7.33 (m, 6H), 7.32−7.26 (m, 1H), 6.74 (d, *J* = 16.0 Hz, 1H), 6.59 (d, *J* = 16.0, 6.8 Hz, 1H), 6.00 (d, *J* = 6.8 Hz, 1H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.2, 141.1, 136.9, 136.8, 132.2, 129.8, 129.2, 128.7, 128.6, 128.5, 127.9, 127.8, 127.4, 126.9, 126.3, 86.0, 13.3. Anal. Calcd for $C_{23}H_{21}NO$: C, 84.37; H, 6.46; N, 4.28. Found: C, 84.43; H, 6.58; N, 4.24.

Propiophenone *O*-[(1*S*,2*E*)-1,3-Diphenyl-2-propen-1-yl]oxime (Table 2, entry 9). White solid, mp 63−64 °C, $[\alpha]^{20}_D$ +28.3 (*c* 0.96, CH_2Cl_2) (94% ee); IR (film) 1494, 1449, 1339, 1300 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.67−7.61 (m, 2H), 7.49 (d, *J* = 7.2 Hz, 2H), 7.47−7.38 (m, 4H), 7.38−7.30 (m, 6H), 7.26 (dd, *J* = 8.0, 6.4 Hz, 1H), 6.69 (d, *J* = 16.0 Hz, 1H), 6.54 (dd, *J* = 16.0, 6.4 Hz, 1H), 5.93 (d, *J* = 6.4 Hz, 1H), 2.89 (q, *J* = 7.6 Hz, 2H), 1.23 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.2, 141.2, 137.0, 135.9, 132.1, 129.9, 129.2, 128.7, 128.6, 127.9, 127.8, 127.4, 126.9, 126.6, 85.9, 20.6, 11.4. Anal. Calcd for $C_{24}H_{23}NO$: C, 84.42; H, 6.79; N, 4.10. Found: C, 84.03; H, 6.71; N, 4.10.

Benzophenone *O*-[(1*S*,2*E*)-1,3-Diphenyl-2-propen-1-yl]oxime (Table 2, entry 10). Colorless oil, $[\alpha]^{20}_D$ −2.6 (*c* 0.27, CH_2Cl_2) (92% ee); IR (film) 1600, 1494, 1445, 1327, 1301 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.61−7.51 (m, 7H), 7.51−7.35 (m, 12 H), 7.31 (dd, *J* = 7.6, 7.2 Hz, 1H), 6.72 (d, *J* = 16.0 Hz, 1H), 6.55 (dd, *J* = 16.0, 6.8 Hz, 1H), 6.07 (d, *J* = 6.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.4, 141.0, 136.9, 136.8, 133.7, 132.1, 129.6, 129.4, 128.9, 128.7, 128.5, 128.3, 128.2, 128.1, 127.9, 127.8, 127.3, 126.8, 86.4; HRMS (FT-ICRMS) calcd for $C_{28}H_{24}NO$ ($M + H^+$) 390.1850, found 390.1847.

1-(4-Methylphenyl)ethanone *O*-[(1*S*,2*E*)-1,3-Diphenyl-2-propen-1-yl]oxime (Table 2, entry 11). White solid, mp 105−107 °C, $[\alpha]^{20}_D$ +46.6 (*c* 0.67, CH_2Cl_2) (94% ee); IR (film) 1514, 1494, 1449, 1367, 1316 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 8.0 Hz, 2H), 7.46 (d, *J* = 8.0 Hz, 2H), 7.43−7.35 (m, 4H), 7.34−7.27 (m, 3H), 7.23 (dd, *J* = 7.2, 6.8 Hz, 1H), 7.14 (d, *J* = 8.0 Hz, 2H), 6.65 (d, *J* = 16.0 Hz, 1H), 6.51 (dd, *J* = 16.0, 6.4 Hz, 1H), 5.90 (d, *J* = 6.4 Hz, 1H), 2.34 (s, 3H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.2, 141.2, 139.2, 137.0, 134.1, 132.1, 129.9, 129.2, 128.7, 128.6, 127.9, 127.8, 127.4, 126.9, 126.2, 85.8, 21.4, 13.3. Anal. Calcd for $C_{24}H_{23}NO$: C, 84.42; H, 6.79; N, 4.10. Found: C, 84.09; H, 6.92; N, 4.20.

1-(4-Chlorophenyl)ethanone *O*-[(1*S*,2*E*)-1,3-Diphenyl-2-propen-1-yl]oxime (Table 2, entry 12). White solid, mp 129−130 °C, $[\alpha]^{20}_D$ +46.1 (*c* 0.59, CH_2Cl_2) (94% ee); IR (film) 1492, 1449, 1398, 1367, 1313 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.4 Hz, 2H), 7.49 (d, *J* = 7.2 Hz, 2H), 7.46−7.38 (m, 4H), 7.38−7.30

(m, 5H), 7.26 (dd, J = 7.6, 6.8 Hz, 1H), 6.69 (d, J = 16.0 Hz, 1H), 6.54 (d, J = 16.0, 6.4 Hz, 1H), 5.93 (d, J = 6.4 Hz, 1H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.1, 141.0, 136.9, 135.3, 135.2, 132.3, 129.6, 128.7, 128.6, 128.5, 128.0, 127.9, 127.6, 127.4, 126.9, 86.2, 13.1. Anal. Calcd for $C_{23}H_{20}ClNO$: C, 76.34; H, 5.57; N, 3.87. Found: C, 76.38; H, 5.61; N, 3.74.

1-(1-Naphthalenyl)ethanone *O*-[(1*S*,2*E*)-1,3-Diphenyl-2-propen-1-yl]oxime (Table 2, entry 13). Colorless oil, $[\alpha]^{20}_D$ +23.0 (c 0.50, CH_2Cl_2) (93% ee); IR (film) 1494, 1449, 1364, 1301 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, J = 8.4 Hz, 1H), 7.82 (d, J = 8.0 Hz, 2H), 7.52 (d, J = 7.2 Hz, 2H), 7.48−7.39 (m, 7H), 7.39−7.30 (m, 3H), 7.30−7.23 (m, 2H), 6.72 (d, J = 16.0 Hz, 1H), 6.58 (dd, J = 16.0, 6.4 Hz, 1H), 5.96 (d, J = 6.4 Hz, 1H), 2.47 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.1, 141.2, 136.9, 135.5, 134.0, 132.6, 131.0, 129.7, 129.2, 128.8, 128.7, 128.4, 128.0, 127.5, 126.9, 126.6, 126.2, 126.1, 125.9, 125.2, 85.9, 17.8; HRMS (FT-ICRMS) calcd for $C_{27}H_{24}NO$ (M + H$^+$) 378.1852, found 378.1857.

1-Indanone *O*-[(1*S*,2*E*)-1,3-Diphenyl-2-propen-1-yl]oxime (Table 2, entry 14). White solid, mp 106−108 °C, $[\alpha]^{20}_D$ +37.1 (c 0.58, CH_2Cl_2) (95% ee); IR (film) 1494, 1473, 1464, 1449, 1337, 1299 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, J = 7.6 Hz, 1H), 7.54 (d, J = 7.6 Hz, 2H), 7.49−7.41 (m, 4H), 7.39−7.31 (m, 5H), 7.31−7.23 (m, 2H), 6.73 (d, J = 16.0 Hz, 1H), 6.59 (dd, J = 16.0, 6.8 Hz, 1H), 5.96 (d, J = 6.8 Hz, 1H), 3.15−3.00 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.4, 148.4, 141.3, 137.0, 136.5, 132.1, 130.3, 129.9, 128.7, 128.6, 127.9, 127.8, 127.3, 127.0, 126.8, 125.6, 122.0, 85.8, 28.8, 27.0. Anal. Calcd for $C_{24}H_{21}NO$: C, 84.92; H, 6.24; N, 4.13. Found: C, 84.51; H, 6.34; N, 4.21.

1-Tetralone *O*-[(1*S*,2*E*)-1,3-Diphenyl-2-propen-1-yl]oxime (Table 2, entry 15). White solid, mp 67−68 °C, $[\alpha]^{20}_D$ +41.3 (c 0.46, CH_2Cl_2) (96% ee); IR (film) 1494, 1451, 1438, 1329, 1300 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, J = 8.0 Hz, 1H), 7.58 (d, J = 7.6 Hz, 2H), 7.54−7.44 (m, 4H), 7.43−7.34 (m, 3H), 7.31 (t, J = 7.6 Hz, 2H), 7.24 (dd, J = 7.2, 6.8 Hz, 1H), 7.19 (d, J = 7.2 Hz, 1H), 6.77 (d, J = 16.0 Hz, 1H), 6.63 (dd, J = 16.0, 6.4 Hz, 1H), 6.02 (d, J = 6.4 Hz, 1H), 3.06−2.91 (m, 2H), 2.87−2.80 (m, 2H), 1.99−1.91 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.5, 141.2, 139.6, 136.9, 132.1, 131.0, 129.9, 129.1, 128.7, 128.6, 128.5, 127.9, 127.8, 127.3, 126.8, 126.4, 124.6, 85.9, 29.9, 24.9, 21.6. Anal. Calcd for $C_{25}H_{23}NO$: C, 84.95; H, 6.56; N, 3.96. Found: C, 84.94; H, 6.56; N, 4.04.

Ethyl-2-[(1′*S*,2′*E*)-1′,3′-diphenyl-2′-propen-1′-yloxyimino-]propanoate (Table 2, entry 16). White solid, mp 47−49 °C, $[\alpha]^{20}_D$ −2.4 (c 0.51, CH_2Cl_2) (88% ee); IR (film) 1717, 1495, 1450, 1367, 1319 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45−7.37 (m, 6H), 7.37−7.30 (m, 3H), 7.26 (dd, J = 7.6, 6.8 Hz, 1H), 6.64 (d, J = 16.0 Hz, 1H), 6.49 (dd, J = 16.0, 6.8 Hz, 1H), 6.04 (d, J = 6.8 Hz, 1H), 4.31 (q, J = 7.2 Hz, 2H), 2.19 (s, 3H), 1.34 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.0, 149.9, 140.0, 136.5, 132.9, 128.7, 128.6, 128.5, 128.2, 128.1, 127.3, 126.9, 87.3, 61.9, 14.3, 12.1. Anal. Calcd for $C_{20}H_{21}NO_3$: C, 74.28; H, 6.55; N, 4.33. Found: C, 74.17; H, 6.58; N, 4.21.

2-[(1′*S*,2′*E*)-1′,3′-Diphenyl-2′-propen-1′-yloxyimino]butan-2-one (Table 2, entry 17). Colorless oil, $[\alpha]^{20}_D$ −6.4 (c 0.72, CH_2Cl_2) (83% ee); IR (film) 1694, 1604, 1495, 1450, 1359, 1304 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49−7.40 (m, 6H), 7.39−7.32 (m, 3H), 7.28 (dd, J = 7.6, 7.2 Hz, 1H), 6.69 (d, J = 16.0 Hz, 1H), 6.53 (d, J = 16.0, 6.8 Hz, 1H), 5.95 (d, J = 6.8 Hz, 1H), 2.36 (s, 3H), 2.05 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.9, 156.1, 140.0, 136.5, 133.1, 128.8, 128.7, 128.5, 128.3, 128.2, 127.4, 126.9, 87.5, 25.2, 9.2. Anal. Calcd for $C_{19}H_{19}NO_2$: C, 77.79; H, 6.53; N, 4.77. Found: C, 78.02; H, 6.50; N, 4.74.

2-[(1′*S*,2′*E*)-1′,3′-Diphenyl-2′-propen-1′-yloxyimino]-1,2-diphenylethanone (Table 2, entry 18). Colorless oil, $[\alpha]^{20}_D$ −12.1 (c 0.37, CH_2Cl_2) (91% ee); IR (film) 1681, 1597, 1494, 1449 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, J = 7.2 Hz, 2H), 7.62 (dd, J = 7.6, 7.2 Hz, 1H), 7.56 (dd, J = 7.6, 1.6 Hz, 2H), 7.47 (dd, J = 8.0, 7.6 Hz, 2H), 7.39−7.32 (m, 3H), 7.31−7.24 (m, 7H), 7.24−7.16 (m, 3H), 6.48 (d, J = 16.0 Hz, 1H), 6.28 (dd, J = 16.0, 6.8 Hz, 1H), 5.86 (d, J = 6.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.3, 156.6, 140.2, 136.6, 135.0, 134.4, 132.4, 131.5, 130.5, 129.6, 129.1, 128.9, 128.7, 128.5, 128.0, 127.9, 127.3, 126.8, 126.7, 87.0; HRMS (FT-ICRMS) calcd for $C_{29}H_{24}NO_2$ (M + H$^+$) 418.1802, found 418.1795.

Benzaldehyde *O*-[(1*S*,2*E*)-1,3-Di(4-methylphenyl)-2-propen-1-yl]oxime (Table 2, entry 19). White solid, mp 121−123 °C, $[\alpha]^{20}_D$ +27.8 (c 0.54, CH_2Cl_2) (89% ee); IR (film) 1513, 1447, 1300, 1210 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (s, 1H), 7.62−7.55 (m, 2H), 7.41−7.30 (m, 7H), 7.22 (d, J = 7.6 Hz, 2H), 7.13 (d, J = 8.0 Hz, 2H), 6.66 (d, J = 16.0 Hz, 1H), 6.48 (dd, J = 16.0, 6.8 Hz, 1H), 5.87 (d, J = 6.8 Hz, 1H), 2.38 (s, 3H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.3, 137.8, 137.7, 134.1, 132.6, 132.4, 129.9, 129.4, 129.3, 128.8, 128.3, 127.6, 127.3, 126.8, 86.1, 21.4; HRMS (FT-ICRMS) calcd for $C_{24}H_{24}NO$ (M + H$^+$) 342.1852, found 342.1853.

Benzaldehyde *O*-[(1*S*,2*E*)-1,3-Di(3-chlorolphenyl)-2-propen-1-yl]oxime (Table 2, entry 20). Colorless oil, $[\alpha]^{20}_D$ +27.2 (c 1.18, CH_2Cl_2) (91% ee); IR (film) 1595, 1569, 1475, 1428 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (s, 1H), 7.59−7.54 (m, 2H), 7.44 (s, 1H), 7.40 (s, 1H), 7.38−7.33 (m, 3H), 7.33−7.27 (m, 3H), 7.27−7.20 (m, 3H), 6.61 (d, J = 16.0 Hz, 1H), 6.45 (dd, J = 16.0, 6.4 Hz, 1H), 5.83 (d, J = 6.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.9, 142.5, 138.4, 134.8, 134.7, 132.2, 131.6, 130.2, 130.04, 130.01, 130.0, 128.9, 128.3, 128.1, 127.6, 127.4, 126.8, 125.6, 125.1, 85.1. Anal. Calcd for $C_{22}H_{17}Cl_2NO$: C, 69.12; H, 4.48; N, 3.66. Found: C, 69.14; H, 4.36; N, 3.81.

Benzaldehyde *O*-Cyclohex-2-enyl Oxime (Table 2, entry 21). Colorless oil, $[\alpha]^{20}_D$ −72.2 (c 0.38, CH_2Cl_2) (33% ee); IR (film) 1447, 1309 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (s, 1H), 7.61−7.58 (m, 2H), 7.40−7.35 (m, 3H), 6.02−5.96 (m, 1H), 5.92−5.88 (m, 1H), 4.74 (brs, 1H), 2.15−2.07 (m, 1H), 2.06−1.96 (m, 1H), 1.96−1.90 (m, 2H), 1.84−1.74 (m, 1H), 1.68−1.52 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.6, 132.9, 132.6, 129.8, 128.8, 127.2, 126.6, 76.7, 28.5, 25.5, 18.9; HRMS (FT-ICRMS) calcd for $C_{13}H_{16}NO$ (M + H$^+$) 202.1226, found 202.1229.

Procedure for the Synthesis of Chiral Amine from Oxime Ether. To a solution of the oxime ether **3a** (0.0939 g, 0.3 mmol, >99% ee) in MeOH/EtOAc (3.0 mL, v/v = 1/1) was added $PtO_2 \cdot H_2O$ (0.0037 g, 5 mol %) under H_2 atmosphere, and the resulting mixture was stirred at room temperature for 4 h. Then the mixture was filtered, washed with ethyl ether (10 mL), dried over $MgSO_4$, filtered, and concentrated. The residue was dissolved in toluene (1.5 mL) and cooled to −78 °C. $BF_3 \cdot Et_2O$ (0.1278 g, 0.9 mmol, 3 equiv) was then added dropwise, and the mixture was stirred for 10 min before ^{n}BuLi (0.36 mL, 0.9 mmol, 3 equiv, 2.5 M in hexanes) was added dropwise. The resulting mixture was continued to stir for 2 h at this temperature before water (1.0 mL) was added to quench the reaction. The mixture was then extracted with ethyl ether (5 mL × 3), and the organic phase was dried over $MgSO_4$, filtered, and concentrated. The crude residue was purified by flash chromatography on silica gel (petroleum ether/ethyl ether = 20:1, v/v) to afford the desired product **9** as a colorless oil (0.0728 g, 65% for 2 steps, >20/1 dr).

(1*S*,1′*S*)-*N*-(1′,3′-Diphenylpropan-1′-oxy)-1-phenylpentan-1-amine (9). $[\alpha]^{20}_D$ −51.0 (c 0.49, CH_2Cl_2); IR (film) 1494, 1454 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40−7.10 (m, 15H), 5.38 (brs, 1H), 4.60 (dd, J = 7.6, 6.0 Hz, 1H), 3.98 (dd, J = 8.8, 5.6 Hz, 1H), 2.80−2.66 (m, 1H), 2.66−2.53 (m, 1H), 2.30−2.10 (m, 1H), 2.00−1.80 (m, 2H), 1.75−1.55 (m, 1H), 1.40−1.05 (m, 4H), 0.88 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.7, 142.2, 141.9, 128.6, 128.5, 128.4, 128.3, 128.0, 127.6, 127.5, 127.0, 125.9, 84.8, 65.9, 37.9, 33.7, 32.4, 28.5, 22.9, 14.2; HRMS (FT-ICRMS) calcd for $C_{26}H_{32}NO$ (M + H$^+$) 374.2478, found 374.2470.

To a solution of **9** (0.0597 g, 0.16 mmol) in HOAc/H_2O (1.0 mL, v/v = 1/1) was added zinc dust (0.4160 g, 6.4 mmol), and the resulting mixture was stirred at 50 °C for 5 h. Then the mixture was filtered and washed with H_2O (2 mL) and EtOAc (5 mL), the organic phase was separated, and the aqueous layer was extracted with EtOAc (5 mL × 2). The combined organic solution was dried over $MgSO_4$, filtered and concentrated. The crude residue was purified by flash chromatography on silica gel (petroleum ether/ethyl ether = 10:1 to 5:1, v/v) to afford the desired alcohol product **10** as a white solid (0.0237 mg, 70% yield, >99% ee). The aqueous layer was neutralized with saturated $NaHCO_3$ aqueous solution and extracted with CH_2Cl_2 (5 mL × 3). The organic phase was dried over $MgSO_4$, filtered, and concentrated to give amine **11** as a colorless oil (0.0180 g, 69% yield, 96% ee).

(1*S*)-1,3-Diphenylpropan-1-ol (10). $[\alpha]^{20}_D$ −27.1 (*c* 0.52, $CHCl_3$) (>99% ee) [$[\alpha]^{20}_D$ +13.4 (*c* 0.22, $CHCl_3$) 47% ee for *R*-isomer[49]]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40−7.33 (m, 4H), 7.33−7.24 (m, 3H), 7.24−7.15 (m, 3H), 4.70 (dd, *J* = 6.8, 5.6 Hz, 1H), 2.82−2.63 (m, 2H), 2.22−2.11 (m, 1H), 2.11−1.98 (m, 1H), 1.92 (brs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.8, 142.0, 128.7, 128.6, 128.5, 127.8, 126.1, 126.0, 74.1, 40.7, 32.3.

(*S*)-1-Phenylpentan-1-amine (11). $[\alpha]^{20}_D$ −23.6 (*c* 0.64, CH_2Cl_2) (96% ee) [$[\alpha]^{27}_D$ −17.4 (*c* 1.9, CH_2Cl_2) 94% ee for *S*-isomer[50]]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38−7.20 (m, 5H), 3.87 (dd, *J* = 7.2, 6.8 Hz, 1H), 1.72−1.60 (m, 4H), 1.38−1.18 (m, 4H), 0.87 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.1, 128.6, 127.0, 126.5, 56.5, 39.6, 29.0, 22.9, 14.2.

■ ASSOCIATED CONTENT

Supporting Information. Data for the determination of enantiomeric excess and X-ray data for **3l** in CIF format, along with NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author
*E-mail: haifengdu@iccas.ac.cn.

■ ACKNOWLEDGMENT

The authors are thankful for financial support from the National Science Foundation of China (20802079, 21072194), the National Basic Research Program of China (2010CB833 300), and the Scientific Research Foundation for the Returned Overseas Chinese Scholars.

■ REFERENCES

(1) Trost, B. M.; Van Vranken, D. L. *Chem. Rev.* **1996**, *96*, 395–422.
(2) Trost, B. M.; Crawley, M. L. *Chem. Rev.* **2003**, *103*, 2921–2944.
(3) Lu, Z.; Ma, S. *Angew. Chem., Int. Ed.* **2008**, *47*, 258–297.
(4) Yang, S. H.; Chang, S. *Org. Lett.* **2001**, *3*, 4209–4211.
(5) Ramalingan, C.; Park, Y.-T. *J. Org. Chem.* **2007**, *72*, 4536–4538.
(6) Pohjakallio, A.; Pihko, P. M. *Chem.—Eur. J.* **2009**, *15*, 3960–3964.
(7) Ramón, R. S.; Bosson, J.; Díez-González, S.; Marion, N.; Nolan, S. P. *J. Org. Chem.* **2010**, *75*, 1197–1202.
(8) Zhang, F.-G.; Yang, Q.-Q.; Xuan, J.; Lu, H.-H.; Duan, S.-W.; Chen, J.-R.; Xiao, W.-J. *Org. Lett.* **2010**, *12*, 5636–5639.
(9) Miyabe, H.; Matsumura, A.; Yoshida, K.; Yamauchi, M.; Takemoto, Y. *Synlett* **2004**, 2123–2126.
(10) Miyabe, H.; Matsumura, A.; Moriyama, K.; Takemoto, Y. *Org. Lett.* **2004**, *6*, 4631–4634.
(11) Miyabe, H.; Yoshida, K.; Reddy, V. K.; Matsumura, A.; Takemoto, Y. *J. Org. Chem.* **2005**, *70*, 5630–5635.
(12) Miyabe, H.; Matsumura, A.; Yoshida, K.; Takemoto, Y. *Tetrahedron* **2009**, *65*, 4464–4470.
(13) Miyabe, H.; Takemoto, Y. *Synlett* **2005**, 1641–1655.
(14) Hanessian, S.; Lu, P.-P.; Sancéau, J.-Y.; Chemla, P.; Gohda, K.; Fonne-Pfister, R.; Prade, L.; Cowan-Jacob, S. W. *Angew. Chem., Int. Ed.* **1999**, *38*, 3159–3162.
(15) Moody, C. J.; Gallagher, P. T.; Lightfoot, A. P.; Slawin, A. M. Z. *J. Org, Chem.* **1999**, *64*, 4419–4425.
(16) Yamazaki, N.; Atobe, M.; Kibayashi, C. *Tetrahedron Lett.* **2001**, *42*, 5029–5032.
(17) Hunt, J. C. A.; Laurent, P.; Moody, C. J. *J. Chem. Soc., Perkin Trans. 1* **2002**, 2378–2389.
(18) Cooper, T. S.; Laurent, P.; Moody, C. J.; Takle, A. K. *Org. Biomol. Chem.* **2004**, *2*, 265–276.
(19) Atobe, M.; Yamazaki, N.; Kibayashi, C. *J. Org. Chem.* **2004**, *69*, 5595–5607.
(20) Miyata, O.; Hashimoto, J.; Iba, R.; Naito, T. *Tetrahedron Lett.* **2005**, *46*, 4015–4018.
(21) Glorius, F. *Angew. Chem., Int. Ed.* **2004**, *43*, 3364–3366.
(22) Johnson, J. B.; Rovis, T. *Angew. Chem., Int. Ed.* **2008**, *47*, 840–871.
(23) Defieber, C.; Grützmacher, H.; Carreira, E. M. *Angew. Chem., Int. Ed.* **2008**, *47*, 4482–4502.
(24) Shintani, R.; Hayashi, T. *Aldrichimica Acta* **2009**, *42*, 31–38.
(25) Hayashi, T.; Ueyama, K.; Tokunaga, N.; Yoshida, K. *J. Am. Chem. Soc.* **2003**, *125*, 11508–11509.
(26) Fischer, C.; Defieber, C.; Suzuki, T.; Carreira, E. M. *J. Am. Chem. Soc.* **2004**, *126*, 1628–1629.
(27) Wang, Z.-Q.; Feng, C.-G.; Xu, M.-H.; Lin, G.-Q. *J. Am. Chem. Soc.* **2007**, *129*, 5336–5337.
(28) Gendrineau, T.; Chuzel, O.; Eijsberg, H.; Genet, J.-P.; Darses, S. *Angew. Chem., Int. Ed.* **2008**, *47*, 7669–7672.
(29) Luo, Y.; Carnell, A. J. *Angew. Chem., Int. Ed.* **2010**, *49*, 2750–2754.
(30) Pattison, G.; Piraux, G.; Lam, H. W. *J. Am. Chem. Soc.* **2010**, *132*, 14373–14375.
(31) Li, Q.; Dong, Z.; Yu, Z.-X. *Org. Lett.* **2011**, *13*, 1122–1125.
(32) Maire, P.; Deblon, S.; Breher, F.; Geier, J.; Böhler, C.; Rüegger, H.; Schönberg, H.; Grützmacher, H. *Chem.—Eur. J.* **2004**, *10*, 4198–4205.
(33) Shintani, R.; Duan, W.-L.; Nagano, T.; Okada, A.; Hayashi, T. *Angew. Chem., Int. Ed.* **2005**, *44*, 4611–4614.
(34) Defieber, C.; Ariger, M. A.; Moriel, P.; Carreira, E. M. *Angew. Chem., Int. Ed.* **2007**, *46*, 3139–3143.
(35) Minuth, T.; Boysen, M. M. K. *Org. Lett.* **2009**, *11*, 4212–4215.
(36) Maire, P.; Breher, F.; Schönberg, H.; Grützmacher, H. *Organometallics* **2005**, *24*, 3207–3218.
(37) Hahn, B. T.; Tewes, F.; Fröhlich, R.; Glorius, F. *Angew. Chem., Int. Ed.* **2010**, *49*, 1143–1146.
(38) Hu, X.; Zhuang, M.; Cao, Z.; Du, H. *Org. Lett.* **2009**, *11*, 4744–4747.
(39) Hu, X.; Cao, Z.; Liu, Z.; Wang, Y.; Du, H. *Adv. Synth. Catal.* **2010**, *352*, 651–655.
(40) Cao, Z.; Du, H. *Org. Lett.* **2010**, *12*, 2602–2605.
(41) Wang, Y.; Hu, X.; Du, H. *Org. Lett.* **2010**, *12*, 5482–5485.
(42) Liu, Z.; Du, H. *Org. Lett.* **2010**, *12*, 3054–3057.
(43) Cao, Z.; Liu, Y.; Liu, Z.; Feng, X.; Zhuang, M.; Du, H. *Org. Lett.* **2011**, *13*, 2164–2167.
(44) Trost, B. M.; Van Vranken, D. L.; Bingel, C. *J. Am. Chem. Soc.* **1992**, *114*, 9327–9343.
(45) Miyashita, A.; Yasuda, A.; Takaya, H.; Toriumi, K.; Ito, T.; Souchi, T.; Noyori, R. *J. Am. Chem. Soc.* **1980**, *102*, 7932–7934.
(46) Uozumi, Y.; Hayashi, T. *J. Am. Chem. Soc.* **1991**, *113*, 9887–9888.
(47) Reiser, O. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 547–549.
(48) von Matt, P.; Pfaltz, A. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 566–568.
(49) Node, M.; Nishide, K.; Shigeta, Y.; Shiraki, H.; Obata, K. *J. Am. Chem. Soc.* **2000**, *122*, 1927–1936.
(50) Gonzalez, A. Z.; Soderquist, J. A. *Org. Lett.* **2007**, *9*, 1081–1084.