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Catalytic Asymmetric Epoxidation of α,β-Unsaturated Phosphane Oxides with a Y(O-*i*Pr)$_3$/Biphenyldiol Complex

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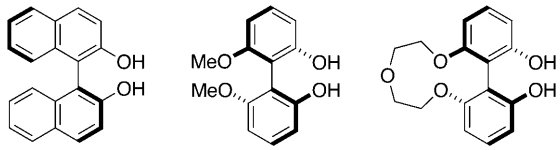
Dedicated to Professor Ryoji Noyori on the occasion of his 70th birthday

Abstract: A rare-earth-metal-catalyzed asymmetric epoxidation of α,β-unsaturated phosphane oxides is described. The appropriate selection of a chiral ligand and an achiral additive is important for achieving good reactivity and enantioselectivity. A Y(O-*i*Pr)$_3$/biphenyldiol complex with an achiral phosphane oxide additive afforded β-aryl α,β-epoxy phosphane oxides in 77–99% yield and with 96–98% *ee*. With β-alkyl substrates, the reaction proceeded smoothly in the absence of an achiral additive, and β-alkyl α,β-epoxy phosphane oxides were obtained in 94–99% yield and with 87–95% *ee*.

Keywords: asymmetric catalysis · biaryldiols · epoxidation · organophosphorus compounds · yttrium

Introduction

Organophosphorus compounds are important substrates in biochemical processes, and optically active tetracoordinate pentavalent phosphorus compounds are widely used as biologically active compounds.[1] For example, β-amino phosphonic acids, phosphonates, and phosphane oxides are important classes of compounds as isosteres of β-amino acids and β-amino ketones.[1,2] α,β-Epoxy phosphorus compounds are useful precursors for the synthesis of various functionalized phosphorus compounds, including β-amino adducts.[1] Although several diastereoselective methods have been reported for the synthesis of optically active α,β-epoxy phosphorus compounds,[3] only a few catalytic asymmetric methods are available.[4–6] Among them, the most practical approach to a *cis*-epoxy phosphonate was accomplished by Noyori and co-workers through Ru/binap-catalyzed (binap = 2,2′-bis(diphenylphosphanyl)-1,1′-binaphthyl) asymmetric hydrogenation of an α-bromo-β-oxo phosphonate.[4] For the synthesis of chiral α,β-epoxy phosphorus compounds, the most straightforward synthetic method can be a catalytic asymmetric epoxidation[7,8] of α,β-unsaturated phosphorus compounds. Chiral catalysts for the epoxidation of α,β-unsaturated phosphorus compounds are, however, rare, and there remains much room for improvement in substrate scope, yield, and enantioselectivity.[6] Therefore, the development of a new catalyst for the catalytic asymmetric epoxidation of α,β-unsaturated phosphorus compounds is highly desirable.[9] Herein, we report the use of a new Y(O-*i*Pr)$_3$/biphenyldiol complex **1a** (Scheme 1) in the catalytic asymmetric epoxidation of α,β-unsaturated phosphane oxides **2**. α,β-Epoxy phosphane oxides **3** with various β-substituents were obtained in good yield (up to 99%) and with good enantioselectivity (up to 98% *ee*). The use of biphenyl-



(*S*)-binol (*S*)-**1a** (*S*)-**1b**

Scheme 1. Structures of (*S*)-binol, *S* biphenyldiol **1a**, and *S* biphenyldiol **1b**.

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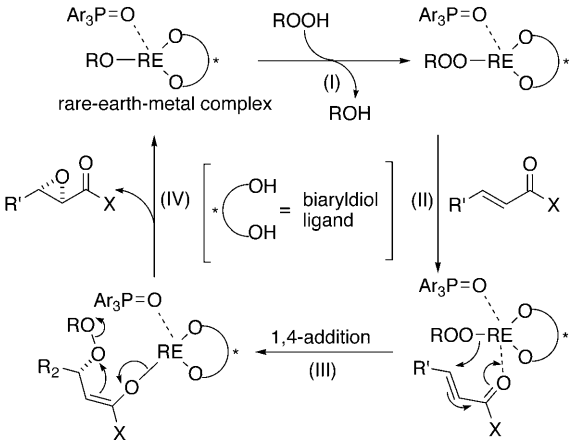
diol **1a** was essential for high enantioselectivity. Transformations of α,β-epoxy phosphane oxides are also described.

Results and Discussion

Our group has been working on rare-earth-metal-catalyzed asymmetric epoxidations of α,β-unsaturated carbonyl compounds, such as enones,[10–12] α,β-unsaturated amides,[13] α,β-unsaturated *N*-acyl pyrroles,[14] and α,β-unsaturated esters.[15] In these reactions, the suitable selection of RE(O-*i*Pr)$_3$ (RE = rare-earth metal), binol (1,1′-bi-2,2′-naphthol), or biphenyldiol chiral ligands and achiral phosphane oxide or arsine oxide additives was important for achieving optimum yield and enantioselectivity. The postulated catalytic cycle of the asymmetric epoxidation of α,β-unsaturated carbonyl compounds is shown in Scheme 2. The rare-earth-metal alk-

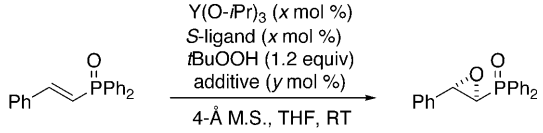


Scheme 2. Postulated catalytic cycle of rare-earth-metal-catalyzed asymmetric epoxidation of α,β-unsaturated carbonyl compounds.

oxide moiety functions as a Brønsted base to generate a rare-earth-metal peroxide from *t*BuOOH through proton exchange (I). The rare-earth-metal–binol complex also functions as a Lewis acid to activate electron-deficient olefins through monodentate coordination (II). Enantioselective 1,4-addition of the rare-earth-metal peroxide gives an intermediate enolate (III), followed by epoxide formation to regenerate the catalyst (IV). We hypothesized that the rare-earth-metal complex would be applicable not only to α,β-unsaturated carbonyl compounds, but also to other electron-deficient olefins, such as α,β-unsaturated phosphorus compounds.

On the basis of our most recent reports on the asymmetric epoxidation of α,β-unsaturated esters with Y(O-*i*Pr)$_3$ and either biphenyldiol **1b** or binol (Scheme 1),[15] we screened for a suitable catalyst for the epoxidation of α,β-unsaturated phosphane oxide **2a** (Table 1). In contrast to α,β-unsaturated esters, **2a** was much less reactive. A 1:1 Y(O-*i*Pr)$_3$/binol complex with either $Ph_3As(O)$ or $Ph_3P(O)$ as an additive,[16] which was the previously optimized condition for various

Table 1. Optimization of reaction conditions.

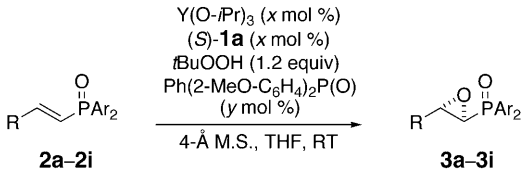


Entry	Ligand ([mol%])	Additive ([mol%])	*t* [h]	Yield[a] [%]	*ee*[b] [%]
1	binol (10)	$Ph_3As(O)$ (10)	24	trace	N.D.
2	binol (10)	$Ph_3P(O)$ (30)	24	trace	N.D.
3	binol (10)	$PhAr_2P(O)$ (30)[c]	24	13	35
4	**1b** (10)	$PhAr_2P(O)$ (30)[c]	24	44	83
5	**1b** (10)	$PhAr_2P(O)$ (90)[c]	24	78	89
6	**1a** (10)	$PhAr_2P(O)$ (90)[c]	21	89[d]	96
7	**1a** (20)	none	20	10	N.D.
8	**1a** (10)	$Ph_3P(O)$ (90)	21	85	95
9	**1a** (10)	$Ph_3As(O)$ (10)	21	23	95
10	**1a** (10)	$Ar_3P(O)$ (90)[c]	21	4	N.D.

[a] Yield based on conversion was determined by ^{1}H NMR spectroscopic analysis unless otherwise noted. [b] Determined by chiral HPLC analysis. [c] Ar = 2-MeO-C_6H_4. [d] Yield of isolated analytically pure compound after column chromatography. M.S. = molecular sieves, N.D. = not determined.

electron-deficient olefins, afforded trace amounts, if any at all, of epoxide **3a** from α,β-unsaturated phosphane oxide **2a** (Table 1, entries 1–2). The structures of achiral phosphane oxide additives are beneficial for improving reactivity and/or enantioselectivity in rare-earth-metal-catalyzed asymmetric reactions.[17] Therefore, we screened achiral phosphane oxide additives, and epoxide **3a** was obtained in 13% yield and with 35% *ee* with $Ph(2\text{-MeO-}C_6H_4)_2P(O)$ as an additive (Table 1, entry 3). Biphenyldiol **1b**, which was the best ligand in the asymmetric epoxidation of β-aryl α,β-unsaturated esters, gave slightly better results than binol (44% yield, 83% *ee*; Table 1, entry 4). Our previous mechanistic studies on rare-earth-metal-catalyzed asymmetric epoxidation suggest that achiral arsine oxide and/or phosphane oxide coordinate to the rare-earth-metal center, thereby increasing the nucleophilicity of the rare-earth-metal peroxide as well as improving the chiral environment around the rare-earth-metal center.[10b] We speculated that the amount of achiral phosphane oxide would be important in the present system with α,β-unsaturated phosphane oxides as substrates, owing to competitive coordination of α,β-unsaturated phosphane oxides and/or α,β-epoxy phosphane oxides to the yttrium metal center. By increasing the amount of $Ph(2\text{-MeO-}C_6H_4)_2P(O)$ to 90 mol%, the yield of epoxide **3a** improved to 78%; however, there remained room for improvement for the enantioselectivity (89% *ee*; Table 1, entry 5). Modification of chiral biphenyldiols was effective in improving enantioselectivity, and biphenyldiol **1a** produced the best yield and enantioselectivity:[18] thus, epoxide **3a** was obtained in 89% yield and with 96% *ee* (Table 1, entry 6). With ligand **1a**, we re-examined the effect of the achiral phosphane oxide additive (Table 1, entries 7–9). In the case of the β-aryl α,β-unsaturated phosphane oxide, the presence of the achiral phosphane oxide additive was crucial. A con-

Table 2. Catalytic asymmetric epoxidation of various α,β-unsaturated phosphane oxides **2a**–**2i**.[a]



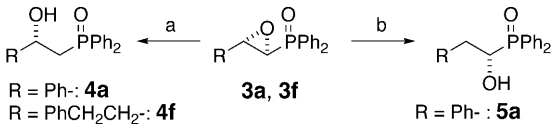
Entry	R	Ar	2	Cat. [mol%]	Additive [mol%]	t [h]	Yield[b] [%]	ee[c] [%]
1	Ph	Ph	**2a**	10	90	21	89	96
2	4-F-C_6H_4	Ph	**2b**	10	90	24	99	98
3	4-Me-C_6H_4	Ph	**2c**	10	90	24	77	97
4	3-thienyl	Ph	**2d**	10	90	18	85	95
5	Ph	*p*-Tol	**2e**	10	90	24	79	96
6	$PhCH_2CH_2$	Ph	**2f**	10	90	6	98	91
7	$PhCH_2CH_2$	Ph	**2f**	10	0	1.5	95	85
8	*n*-hexyl	Ph	**2g**	10	0	5	99	89
9	*i*Bu	Ph	**2h**	10	0	6	94	87
10	cyclohexyl	Ph	**2i**	10	0	5	99	95

[a] Reaction was performed with α,β-unsaturated phosphane oxide **2a** (0.2 mmol), *t*BuOOH (0.24 mmol, 1.2 equiv), $Y(O\text{-}iPr)_3$ (0.02 mmol, 10 mol%), ligand **1a** (0.02 mmol, 10 mol%), $Ph(2\text{-}MeO\text{-}C_6H_4)_2P(O)$ (for entries 1–6, 0.18 mmol), and 4-Å M.S. (100 mg) in THF at room temperature. [b] Yield of isolated analytically pure compound after column chromatography. [c] Determined by chiral HPLC analysis. Tol = tolyl.

trol experiment with the best ligand **1a** in the absence of $Ph(2\text{-}MeO\text{-}C_6H_4)_2P(O)$ resulted in only 10% yield (Table 1, entry 7). With **1a**, 90 mol% of $Ph_3P(O)$ as additive gave comparable results (85% yield, 95% *ee*; Table 1, entry 8) to $Ph(2\text{-}MeO\text{-}C_6H_4)_2P(O)$.[19] $Ph_3As(O)$ as an additive afforded epoxide **3a** with 95% *ee*, but the yield was unsatisfactory (23% yield; Table 1, entry 9).[20] $(2\text{-}MeO\text{-}C_6H_4)_3P(O)$ was not suitable as an additive, possibly due to its low solubility in THF (4% yield; Table 1, entry 10).

The optimized reaction conditions were applicable to various α,β-unsaturated phosphane oxides. With β-aryl and heteroaryl substituents, 10 mol% of $Y(O\text{-}iPr)_3$, 10 mol% of biphenyldiol **1a**, and 90 mol% of $Ph(2\text{-}MeO\text{-}C_6H_4)_2P(O)$ additive gave epoxides in 77–99% yield and with 95–98% *ee* (Table 2, entries 1–5).[21] Substrate **2b** with an electron-withdrawing group had high reactivity (99% yield, 98% *ee*; Table 2, entry 2), whereas **2c** with an electron-donating group resulted in only moderate yield (77%, 97% *ee*; Table 2, entry 3). The conditions were applicable not only to diphenylphosphane oxides, but also to di-*p*-tolylphosphane oxide **2e** (79% yield, 96% *ee*; Table 2, entry 5). β-Alkyl α,β-unsaturated phosphane oxides were more reactive than β-aryl substrates. The reaction of **2f** was complete within 6 h under the optimized reaction conditions for β-aryl substrates to give epoxide **3f** in 98% yield and with 91% *ee* (Table 2, entry 6). In contrast to β-aryl substrates, β-alkyl α,β-unsaturated phosphane oxides reacted smoothly even in the absence of the achiral phosphane oxide additive. The reaction was complete within 1.5 h, and epoxide **3f** was obtained in 95% yield, albeit with slightly lower enantioselectivity (85% *ee*; Table 2, entry 7). We speculate that β-alkyl α,β-unsaturated phosphane oxides play the same role as achiral phosphane oxides. The reaction was applicable to linear and branched β-alkyl substituents to give epoxides in 94–99% yield and with 87–95% *ee* without the use of an achiral phosphane oxide additive (Table 2, entries 8–10).

To demonstrate the utility of α,β-epoxy phosphane oxides, transformations of the epoxide moiety were investigated. As shown in Scheme 3, regioselective epoxide ring opening was accomplished with $LiAlH_4$[22] to give β-hydroxy phosphane oxides **4a** and **4f** in 99 and 87% yield, respectively. From β-aryl α,β-epoxy phosphane oxide **3a**, α-hydroxy phosphane oxide **5a** was selectively obtained in 79% yield by treatment with Pd/C under H_2 (1 atm).



Scheme 3. Ring opening of α,β-epoxy phosphane oxides. Reagents and conditions: a) $LiAlH_4$ (1.3 mol equiv), THF, 0°C; **4a**: 30 min, 99%; **4f**, 5 min, 87%; b) Pd/C, H_2 (1 atm), CH_3OH, room temperature, 3.5 h, 79% yield.

Conclusions

We have developed a catalytic asymmetric epoxidation of α,β-unsaturated phosphane oxides. Previously utilized rare-earth-metal/chiral-ligand (binol or biphenyldiol **1b**) combinations for α,β-unsaturated carbonyl compounds were not effective, and the appropriate selection of a chiral biphenyldiol ligand and an achiral additive was important for achieving good reactivity and enantioselectivity in the present reactions. The $Y(O\text{-}iPr)_3$/biphenyldiol complex **1a** with $Ph(2\text{-}MeO\text{-}C_6H_4)_2P(O)$ as an additive afforded β-aryl epoxides **3** in 77–99% yield and with 95–98% *ee*.[23] With β-alkyl substrates, the reaction proceeded smoothly in the absence of an achiral additive, and β-aryl epoxides were obtained in 94–99% yield and with 85–95% *ee*. Further studies to explore suitable catalysts for the catalytic asymmetric epoxidation of α,β-unsaturated phosphonates are ongoing.

Experimental Section

General

Infrared (IR) spectra were recorded on a JASCO FT/IR 410 Fourier transform IR spectrophotometer. NMR spectra were recorded in $CDCl_3$

on a JEOL JNM-LA500 spectrometer operating at 500 MHz for ^{1}H and 125.65 MHz for ^{13}C. Chemical shifts are reported relative to TMS (tetramethylsilane; 0 ppm) or $CHCl_3$ (7.24 ppm) for ^{1}H. For ^{13}C, chemical shifts are reported relative to $CHCl_3$ (77.0 ppm) as an internal reference. ESI mass spectra were recorded on a Waters-ZQ4000 spectrometer. FAB mass spectra were recorded on a JEOL JMS-700 spectrometer. Column chromatography was performed with silica gel Merck 60 (230–400 mesh ASTM). Reactions were carried out in dry solvents under argon atmosphere, unless otherwise stated. Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl. Y(O-*i*Pr)$_3$ was purchased from Kojundo Chemical Laboratory Co., Ltd. (e-mail: sales@kojundo.co.jp). Compounds **3a** (racemic), **4a**, and **5a** (racemic) are known.

Syntheses

Typical procedure for enantioselective epoxidation: 4-Å M.S. (100 mg, powder) were flame-dried for 10 min under reduced pressure (0.6 kPa) prior to use. Y(O-*i*Pr)$_3$ (0.10 mL, 0.02 mmol, 0.2 M solution in THF) was added to a stirred suspension of 4-Å M.S., *S* biphenyldiol **1a** (4.9 mg, 0.02 mmol), and Ph(2-MeO-C$_6$H$_4$)$_2$P(O) (60.9 mg, 0.18 mmol) in THF (0.51 mL) at room temperature. After the mixture was stirred for 30 min at room temperature, *t*BuOOH (60 μL, 0.24 mmol, 4.0 M solution in toluene) was added. After the mixture was stirred for 10 min, α,β-unsaturated phosphane oxide **2a** (0.2 mmol) was added, and the mixture was stirred at room temperature. After 21 h, the reaction was quenched with saturated aqueous NH_4Cl. The reaction mixture was diluted with CH_2Cl_2 and extracted with CH_2Cl_2 (3×10 mL). The combined organic layers were washed with brine and dried over Na_2SO_4. After evaporation under reduced pressure, the residue was purified by silica-gel flash column chromatography (hexane/EtOAc=1:1) to give epoxide **3a** (89%, 96% *ee*) as a colorless solid. $[\alpha]_D^{21}=-56.3$ ($c=1.83$, $CHCl_3$); HPLC (DAICEL CHIRALCEL OD-H, 2-propanol/hexane=1:4, flow rate 0.5 mL min^{-1}, detection at 220 nm): $t_R=20.6$ (*S*,*S*), 23.0 min (*R*,*R*).

3b: Colorless solid. $[\alpha]_D^{20}=-60.8$ ($c=2.48$, $CHCl_3$); IR (KBr): $\tilde{\nu}=2969$, 1514, 1438, 1190 cm^{-1}; ^{1}H NMR ($CDCl_3$): $\delta=7.86$–7.81 (m, 4H), 7.61–7.49 (m, 6H), 7.26–7.23 (m, 2H), 7.03–6.98 (m, 2H), 4.02 (dd, $J=4.0$, 2.5 Hz, 1H), 3.54 ppm (dd, $J=30$, 2.5 Hz, 1H); ^{13}C NMR ($CDCl_3$): $\delta=$ 163.0 (d, $^1J_{C,F}=247$ Hz), 132.6, 132.6, 131.8 (d, $^3J_{C,P}=10.3$ Hz), 131.2 (d, $^3J_{C,P}=9.3$ Hz), 130.9, 130.9 (d, $^1J_{C,P}=103$ Hz), 128.9 (d, $^2J_{C,P}=11.3$ Hz), 128.9 (d, $^1J_{C,P}=104$ Hz), 128.7 (d, $^2J_{C,P}=12.4$ Hz), 127.6 (d, $^3J_{C,F}=7.9$ Hz), 115.7 (d, $^2J_{C,F}=21.7$ Hz), 58.3 (d, $^1J_{C,P}=98.1$ Hz), 55.6 ppm; MS (ESI): *m*/*z*=361 $[M+Na]^+$; HRMS (FAB+): *m*/*z* calcd for $C_{20}H_{17}FO_2P^+$: 339.0945 $[M+H]^+$; found: 339.0939; HPLC (DAICEL CHIRALCEL OD-H, 2-propanol/hexane=1:4, flow rate 0.5 mL min^{-1}, detection at 220 nm): $t_R=$ 18.3 (major), 20.4 min (minor).

3c: Colorless solid. $[\alpha]_D^{20}=-67.6$ ($c=1.98$, $CHCl_3$); IR (KBr): $\tilde{\nu}=2974$, 1438, 1188, 1122 cm^{-1}; ^{1}H NMR ($CDCl_3$): $\delta=7.87$–7.80 (m, 4H), 7.60–7.47 (m, 6H), 7.16 (d, $J=8.3$ Hz, 2H), 7.03–6.98 (m, 2H), 4.03 (dd, $J=$ 4.0, 2.3 Hz, 1H), 3.57 (dd, $J=31$, 2.3 Hz, 1H), 2.31 ppm (s, 3H); ^{13}C NMR ($CDCl_3$): $\delta=138.8$, 132.5, 132.5, 132.1, 131.8 (d, $^3J_{C,P}=9.3$ Hz), 131.2 (d, $^3J_{C,P}=9.3$ Hz), 131.0 (d, $^1J_{C,P}=102$ Hz), 129.3, 129.1 (d, $^1J_{C,P}=$ 102 Hz), 128.9 (d, $^2J_{C,P}=11.4$ Hz), 128.7 (d, $^2J_{C,P}=12.4$ Hz), 58.2 (d, $^1J_{C,P}=$ 98.1 Hz), 56.1, 21.2 ppm; MS (ESI): *m*/*z*=357 $[M+Na]^+$; HRMS (FAB+): *m*/*z* calcd for $C_{21}H_{19}O_2PCs^+$: 467.0177 $[M+Cs]^+$; found: 467.0167; HPLC (DAICEL CHIRALCEL OD-H, 2-propanol/hexane= 1:9, flow rate 0.3 mL min^{-1}, detection at 220 nm): $t_R=42.6$ (major), 47.8 min (minor).

3d: Colorless solid. $[\alpha]_D^{26}=-60.6$ ($c=2.47$, $CHCl_3$); IR (KBr) $\tilde{\nu}=2976$, 1437, 1189, 1122 cm^{-1}; ^{1}H NMR ($CDCl_3$): $\delta=7.88$–7.83 (m, 4H), 7.62–7.57 (m, 2H), 7.55–7.50 (m, 4H), 7.32 (dd, $J=3.1$, 1.2 Hz, 1H), 7.30 (dd, $J=5.2$, 3.1 Hz, 1H), 6.97 (dd, $J=5.2$, 1.2 Hz, 1H), 4.11 (dd, $J=4.3$, 2.4 Hz, 1H), 3.69 ppm (dd, $J=30$, 2.4 Hz, 1H); ^{13}C NMR ($CDCl_3$): $\delta=$ 136.8, 132.6, 132.5, 131.8 (d, $^3J_{C,P}=9.3$ Hz), 131.1 (d, $^3J_{C,P}=10.3$ Hz), 130.9 (d, $^1J_{C,P}=103$ Hz), 128.9 (d, $^2J_{C,P}=12.4$ Hz), 128.8 (d, $^1J_{C,P}=103$ Hz), 128.7 (d, $^2J_{C,P}=12.4$ Hz), 126.7, 124.8, 124.0, 57.5 (d, $^1J_{C,P}=98.1$ Hz), 53.0 ppm; MS (ESI): *m*/*z*=349 $[M+Na]^+$; HRMS (FAB+): *m*/*z* calcd for $C_{18}H_{15}O_2PCsS^+$: 458.9585 $[M+Cs]^+$; found: 458.9595; HPLC (DAICEL CHIRALPAK AD-H, 2-propanol/hexane=1:4, flow rate 0.5 mL min^{-1}, detection at 220 nm): $t_R=39.8$ (major), 47.7 min (minor).

3e: Colorless solid. $[\alpha]_D^{20}=-54.5$ ($c=1.35$, $CHCl_3$); IR (KBr) $\tilde{\nu}=2976$, 1186, 1119 cm^{-1}; ^{1}H NMR ($CDCl_3$): $\delta=7.68$–7.62 (m, 4H), 7.28–7.18 (m, 9H), 3.98 (dd, $J=4.3$, 2.5 Hz, 1H), 3.47 (dd, $J=30$, 2.5 Hz, 1H), 2.35 (s, 3H), 2.33 ppm (s, 3H); ^{13}C NMR ($CDCl_3$): $\delta=143.1$, 143.1 135.4, 131.8 (d, $^3J_{C,P}=9.6$ Hz), 131.2 (d, $^3J_{C,P}=10.8$ Hz), 129.6 (d, $^2J_{C,P}=13.2$ Hz), 129.4 (d, $^2J_{C,P}=13.2$ Hz), 128.8, 128.6, 127.7 (d, $^1J_{C,P}=106$ Hz), 125.8 (d, $^1J_{C,P}=$ 107 Hz), 125.8, 58.5 (d, $^1J_{C,P}=98.7$ Hz), 56.1, 21.7 ppm; MS (ESI): *m*/*z*= 371 $[M+Na]^+$; HRMS (FAB+): *m*/*z* calcd for $C_{22}H_{21}CsO_2P^+$: 481.0333 $[M+Cs]^+$; found: 481.0331; HPLC (DAICEL CHIRALPAK OD-H, 2-propanol/hexane=1:9, flow rate 0.5 mL min^{-1}, detection at 220 nm): $t_R=$ 27.6 (major), 38.1 min (minor).

3f: Colorless solid. $[\alpha]_D^{21}=-67.2$ ($c=1.83$, $CHCl_3$); IR (KBr) $\tilde{\nu}=2976$, 1437, 1197, 1121 cm^{-1}; ^{1}H NMR ($CDCl_3$): $\delta=7.83$–7.72 (m, 4H), 7.58–7.43 (m, 6H), 7.22–7.09 (m, 5H), 3.32 (dd, $J=29$, 4.8 Hz, 1H), 3.07–3.04 (m, 1H), 2.78–2.66 (m, 2H), 2.04–1.96 (m, 1H), 1.95–1.86 ppm (m, 1H); ^{13}C NMR ($CDCl_3$): $\delta=140.3$, 132.3, 132.3, 131.6 (d, $^3J_{C,P}=9.6$ Hz), 131.1 (d, $^1J_{C-P}=105$ Hz), 131.0 (d, $^3J_{C,P}=9.6$ Hz), 128.8 (d, $^1J_{C,P}=105$ Hz), 128.7 (d, $^2J_{C,P}=12.0$ Hz), 128.4 (d, $^2J_{C,P}=12.0$ Hz), 128.4, 128.1, 126.0, 55.8, 53.7 (d, $^1J_{C,P}=103$ Hz), 33.5, 31.9 ppm; MS (ESI): *m*/*z*=371 $[M+Na]^+$; HRMS (FAB+): *m*/*z* calcd for $C_{22}H_{22}O_2P^+$: 349.1352 $[M+H]^+$; found: 349.1362; HPLC (DAICEL CHIRALCEL OD-H, 2-propanol/hexane= 1:4, flow rate 1.0 mL min^{-1}, detection at 220 nm): $t_R=8.9$ (major), 12.5 min (minor).

3g: Colorless solid. $[\alpha]_D^{24}=-64.7$ ($c=2.27$, $CHCl_3$); IR (KBr): $\tilde{\nu}=2976$, 1438, 1187, 1120 cm^{-1}; ^{1}H NMR ($CDCl_3$): $\delta=7.85$–7.74 (m, 4H), 7.58–7.43 (m, 6H), 3.27 (dd, $J=29$, 2.6 Hz, 1H), 3.04–2.99 (m, 1H), 1.73–1.64 (m, 1H), 1.61–1.53 (m, 1H), 1.43–1.33 (m, 2H), 1.29–1.18 (m, 6H), 0.83 ppm (t, $J=6.9$ Hz, 3H); ^{13}C NMR ($CDCl_3$): $\delta=132.4$, 132.4, 131.7 (d, $^3J_{C,P}=9.6$ Hz), 131.4 (d, $^1J_{C,P}=103$ Hz), 131.1 (d, $^3J_{C,P}=9.6$ Hz), 129.0 (d, $^1J_{C,P}=105$ Hz), 128.8 (d, $^2J_{C,P}=12.0$ Hz), 128.5 (d, $^2J_{C,P}=12.0$ Hz), 56.4, 53.7 (d, $^1J_{C,P}=105$ Hz), 31.8, 31.6, 28.9, 25.7, 22.4, 14.0 ppm; MS (ESI): *m*/*z*=351 $[M+Na]^+$; HRMS (FAB+): *m*/*z* calcd for $C_{20}H_{26}O_2P^+$: 329.1665 $[M+H]^+$: found: 329.1667; HPLC (DAICEL CHIRALCEL, 2-propanol/hexane=1:4, flow rate 0.7 mL min^{-1}, detection at 220 nm): $t_R=$ 8.0 (major), 9.5 min (minor).

3h: Colorless solid. $[\alpha]_D^{23}=-75.6$ ($c=2.02$, $CHCl_3$); IR (KBr): $\tilde{\nu}=2942$, 1437, 1189, 889 cm^{-1}; ^{1}H NMR ($CDCl_3$): $\delta=7.85$–7.75 (m, 4H), 7.57–7.43 (m, 6H), 3.24 (dd, $J=29$, 2.6 Hz, 1H), 3.08–3.04 (m, 1H), 1.81–1.72 (m, 1H), 1.59–1.53 (m, 1H), 1.48–1.41 ppm (m, 1H); ^{13}C NMR ($CDCl_3$): $\delta=$ 132.4, 132.4, 131.7 (d, $^3J_{C,P}=9.6$ Hz), 131.3 (d, $^1J_{C,P}=106$ Hz), 131.1 (d, $^3J_{C,P}=9.6$ Hz), 129.1 (d, $^1J_{C,P}=105$ Hz), 128.8 (d, $^2J_{C,P}=12.0$ Hz), 128.5 (d, $^2J_{C,P}=12.0$ Hz), 55.4, 53.7 (d, $^1J_{C,P}=105$ Hz), 53.3, 40.9, 26.4, 22.7, 22.4 ppm; MS (ESI): *m*/*z*=323 $[M+Na]^+$; HRMS (FAB+): *m*/*z* calcd for $C_{18}H_{21}CsO_2P^+$: 433.0333 $[M+Cs]^+$; found: 433.0333; HPLC (DAICEL CHIRALCEL OD-H, 2-propanol/hexane=1:9, flow rate 0.5 mL min^{-1}, detection at 220 nm): $t_R=16.5$ (major), 21.6 min (minor).

3i: Colorless solid. $[\alpha]_D^{24}=-62.8$ ($c=2.12$, $CHCl_3$); IR (KBr): $\tilde{\nu}=2924$, 1438, 1194, 1123 cm^{-1}; ^{1}H NMR ($CDCl_3$): $\delta=7.82$–7.74 (m, 4H), 7.57–7.43 (m, 6H), 3.31 (br d, $J=30$ Hz, 1H), 2.93 (br s, 1H), 1.81–1.61 (m, 5H), 1.33–1.05 ppm (m, 6H); ^{13}C NMR ($CDCl_3$): $\delta=132.4$, 132.4, 131.7 (d, $^3J_{C,P}=9.6$ Hz), 131.3 (d, $^1J_{C,P}=105$ Hz), 131.1 (d, $^3J_{C,P}=9.6$ Hz), 129.2 (d, $^1J_{C,P}=105$ Hz), 128.8 (d, $^2J_{C,P}=12.0$ Hz), 128.5 (d, $^2J_{C,P}=12.0$ Hz), 60.4, 52.8 (d, $^1J_{C,P}=103$ Hz), 39.8, 29.3, 28.8, 26.0, 25.5, 25.3 ppm; MS (ESI): *m*/*z*=349 $[M+Na]^+$; HRMS (FAB+): *m*/*z* calcd for $C_{20}H_{23}CsO_2P^+$: 459.0490 $[M+H]^+$; found: 459.0478; HPLC (DAICEL CHIRALCEL OD-H, 2-propanol/hexane=1:9, flow rate 0.5 mL min^{-1}, detection at 220 nm): $t_R=18.9$ (major), 22.2 min (minor).

4f: Colorless solid. $[\alpha]_D^{21}=+15.8$ ($c=1.37$, $CHCl_3$); IR (KBr): $\tilde{\nu}=3292$, 2911, 2849, 1434, 1119 cm^{-1}; ^{1}H NMR ($CDCl_3$): $\delta=7.73$–7.09 (m, 15H), 4.54 (br s, 1H), 4.13–4.06 (m, 1H), 2.76 (ddd, $J=14$, 10, 5.8 Hz, 1H), 2.63 (ddd, $J=14$, 10, 6.1 Hz, 1H), 2.46 (ddd, $J=15$, 12, 10 Hz, 1H), 2.36 (ddd, $J=15$, 7.7, 1.9 Hz, 1H), 1.97–1.78 (m, 1H), 1.80–1.72 ppm (m, 1H); ^{13}C NMR ($CDCl_3$): $\delta=141.7$, 133.2 (d, $^1J_{C,P}=101$ Hz), 132.1 (d, $^4J_{C,P}=$ 2.4 Hz), 132.0 (d, $^4J_{C,P}=2.4$ Hz), 131.8 (d, $^1J_{C,P}=99.9$ Hz), 130.9 (d, $^3J_{C,P}=$ 9.6 Hz), 130.3 (d, $^3J_{C,P}=9.6$ Hz), 128.8 (d, $^2J_{C,P}=12.0$ Hz), 128.8 (d, $^2J_{C,P}=$ 12.0 Hz), 128.3, 128.3, 125.7, 66.4, 40.3 (d, $^2J_{C,P}=14.5$ Hz), 36.3 (d, $^1J_{C,P}=$ 71.0 Hz), 31.5 ppm; MS (ESI): *m*/*z*=373 $[M+Na]^+$; HRMS (FAB+): *m*/*z* calcd for $C_{22}H_{24}O_2P^+$: 351.1508 $[M+H]^+$; found: 351.1506.

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[20] Y(O-*i*Pr)$_3$/Ph$_3$As(O) = 1:1 was used in Table 1, entry 9 because our previous studies suggest that excess Ph$_3$As(O) has adverse effects on the reactivity of the rare-earth-metal catalyst; see references [10b] and [16].

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