Tetrahedron Letters 53 (2012) 4562–4564

Contents lists available at SciVerse ScienceDirect

Tetrahedron Letters

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

Chiral dihydrobenzofuran-based diphosphine (BICMAP): optical resolution and application to rhodium(I)-catalyzed asymmetric 1,4-addition of aryl- and alkenylboronic acids to cyclic enones

Takashi Mino *, Masatoshi Hashimoto, Katsunori Uehara, Yoshiaki Naruse, Shohei Kobayashi, Masami Sakamoto, Tsutomu Fujita

Department of Applied Chemistry and Biotechnology, Graduate School of Engineering, Chiba University, 1-33, Yayoi-cho, Inage-ku, Chiba 263-8522, Japan

ARTICLE INFO

Article history:
Received 16 May 2012
Revised 7 June 2012
Accepted 13 June 2012
Available online 18 June 2012

Keywords:
Rhodium catalyst
Diphosphine
Asymmetric reaction
1,4-Addition

ABSTRACT

Chiral dihydrobenzofuran-based diphosphine ligand (BICMAP) **1** was used as a ligand for the rhodium(I)-catalyzed asymmetric 1,4-addition of arylboronic acids to cyclic enones up to 99% ee. We also found that the BICMAP-rhodium system was an efficient catalyst for the 1,4-addition of alkenylboronic acids to 2-cyclohexenone in good enantioselectivities.

The 1,4-addition to α,β-unsaturated carbonyl compounds is considered one of the most important C–C bond formations in organic synthesis. After the discovery of the BINAP-rhodium(I)-catalyzed asymmetric 1,4-addition of aryl- and alkenylboronic acids by Hayashi and Miyaura in 1998,[1] many diphosphine ligands have been used for the rhodium(I)-catalyzed asymmetric 1,4-addition of boronic acids.[2] On the other hand, we recently reported the synthesis of an atropisomeric diphosphine ligand (BICMAP) **1** bearing a dihydrobenzofuran (coumaran) core and its use in the palladium-catalyzed Suzuki-Miyaura reaction and the Hartwig–Buchwald amination.[3] Here we report the rhodium-catalyzed asymmetric 1,4-addition of aryl- and alkenylboronic acids to cyclic enones using (*S*)-BICMAP ((*S*)-**1**) as a chiral ligand (Fig. 1).

Although we previously reported that the optical resolution of (±)-**1** was also carried out by HPLC with a chiral stationary phase column,[3] we herein tried optical resolution using *O*,*O*′-dibenzoyltartaric acid (DBTA) (Scheme 1). We added (−)-DBTA in EtOAc to the solution of (±)-**2** in $CHCl_3$ at room temperature, filtered the formed solid, washed it with $CHCl_3$, and dried it under vacuum to give (+)-**2**/(−)-DBTA complex. This complex was converted into the desired (+)-**2** using a KOH solution. (−)-**2** was also obtained by a similar method using (+)-DBTA and enriched (−)-**2** from the mother liquor.[4]

The absolute configuration of (+)-**2** was determined by X-ray analysis of the (+)-**2**/(−)-DBTA complex. From an internal comparison with (−)-DBTA, the absolute configuration of (+)-**2** was defined to be *R* (Fig. 2).[5]

The X-ray structure of the (+)-**2**/(−)-DBTA complex also showed that diphosphine oxide **2** and DBTA molecules were connected by hydrogen bonds (O···H = 1.701 Å). The resolved diphosphine oxides (*R*)-(+)-**2** and (*S*)-(−)-**2** were converted into diphosphine (*R*)-(+)-**1** and (*S*)-(−)-**1** using trichlorosilane-triethylamine. (*R*)-(+)-**1** and (*S*)-(−)-**1** were enantiomerically pure (>99% ee) according to the chiral phase HPLC after recrystallization.[6]

We investigated the ability of chiral diphosphine **1** as a chiral ligand for the rhodium(I)-catalyzed asymmetric 1,4-addition of boronic acids to cyclic enones. Phenylboronic acid and 2-cyclohexenone were chosen as model substrates with 3 mol % of rhodium source and 3.3 mol % of (*S*)-(−)-**1** in dioxane/H_2O for 5 h under an argon atmosphere at 100 °C (Table 1). Using $[RhCl(C_2H_4)_2]_2$ as a rhodium source[2h] with KOH as a base, we observed that the 1,4-addition proceeded to give the corresponding product **3a** in 91% yield with good

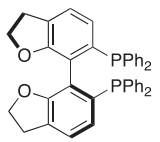
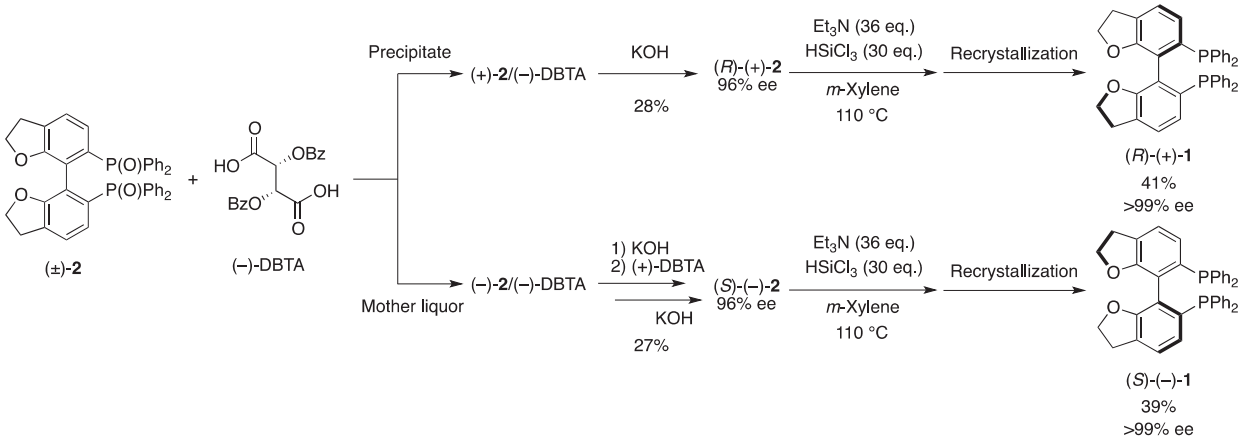


Figure 1. (*S*)-BICMAP ((*S*)-**1**).

* Corresponding author. Tel.: +81 43 290 3385; fax: +81 43 290 3401.
E-mail address: tmino@faculty.chiba-u.jp (T. Mino).

0040-4039/$ - see front matter © 2012 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.tetlet.2012.06.064



Scheme 1. Optical resolution of (±)-**2** and preparation of (*R*)-(+)-**1** and (*S*)-(−)-**1**.

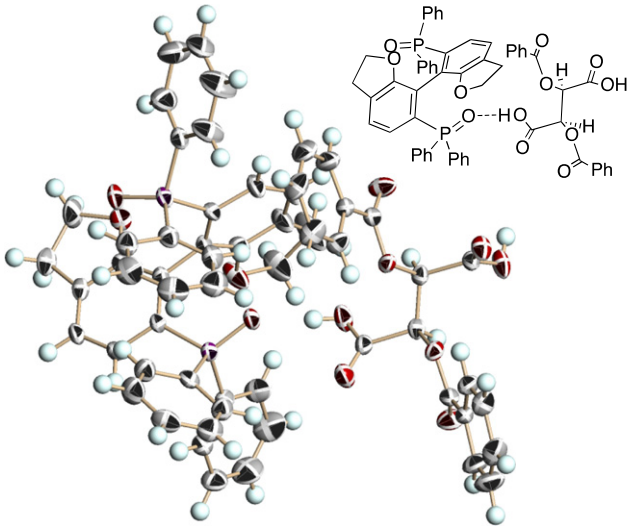
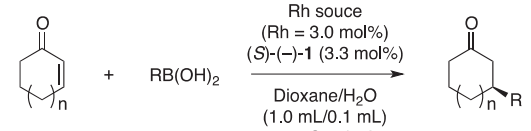


Figure 2. The ORTEP drawing of (+)-2/(−)-DBTA complex (CCDC 878593).

enantioselectivity (96% ee) (entry 1). When the reaction was carried out using $[Rh(OH)(cod)]_2$ as a rhodium source[7] without adding KOH, the enantioselectivity slightly decreased (95% ee) (entry 2). We tested $Rh(acac)(C_2H_4)_2$ as a rhodium source[1] and found that the reaction proceeded with high enantioselectivity (99% ee) with good yield (entry 3). Under optimized reaction conditions, we investigated the asymmetric 1,4-addition of various arylboronic acids to 2-cyclohexenone (entries 4–11).[8] The reactions with 4-methylphenylboronic acid and 3-methylphenylboronic acid gave corresponding products **3b** and **3c** in high enantioselectivities with good yields (entries 4 and 5). Unfortunately, the reaction with 2-methylphenylboronic acid led to moderate yield with 89% ee (entry 6). When we used 3,5-dimethylphenylboronic acid, the reaction gave product **3e** with high enantioselectivity (entry 7). On the other hand, the reaction with 4-methoxyphenylboronic acid gave product **3f** in moderate yield with good enantioselectivity (entry 8). Using 4-biphenylboronic acid led to good yield of product **3g** in high enantioselectivity (entry 9). When 4-chloro- and 3-chlorophenylboronic acids were used, the reactions gave products **3h** and **3i** in low-to-moderate yields with good enantioselectivities (entries 10 and 11). On the other hand, the reactions of 2-cyclopentenone and 2-cycloheptenone with phenylboronic acid gave products **3j** and **3k** with good enantioselectivities (entries 12 and 13). We also tested the reaction of 2-cyclohexenone with various alkenylboronic acids

Table 1
Rhodium(I)-catalyzed asymmetric 1,4-addition to cyclic enones using (*S*)-(−)-**1**



0.40 mmol 2.0 mmol **3**

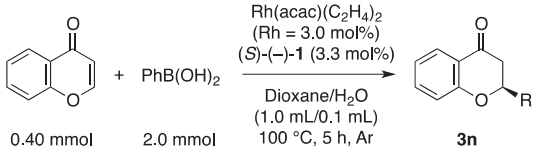
Entry	Rh source	*n*	*R*	Yield[a] (%)	Ee[b] (%)
1[c]	$[RhCl(C_2H_4)_2]_2$	1	Ph	91 (**3a**)	96
2	$[Rh(OH)(cod)]_2$	1	Ph	92 (**3a**)	95
3	$Rh(acac)(C_2H_4)_2$	1	Ph	98 (**3a**)	99
4	$Rh(acac)(C_2H_4)_2$	1	*p*-MeC_6H_4	80 (**3b**)	97
5	$Rh(acac)(C_2H_4)_2$	1	*m*-MeC_6H_4	89 (**3c**)	99
6	$Rh(acac)(C_2H_4)_2$	1	*o*-MeC_6H_4	50 (**3d**)	89
7	$Rh(acac)(C_2H_4)_2$	1	3,5-$DiMeC_6H_3$	96 (**3e**)	99
8	$Rh(acac)(C_2H_4)_2$	1	*p*-$MeOC_6H_4$	64 (**3f**)	96
9	$Rh(acac)(C_2H_4)_2$	1	*p*-PhC_6H_4	93 (**3g**)	98
10	$Rh(acac)(C_2H_4)_2$	1	*p*-ClC_6H_4	31 (**3h**)	98
11	$Rh(acac)(C_2H_4)_2$	1	*m*-ClC_6H_4	61 (**3i**)	98
12	$Rh(acac)(C_2H_4)_2$	0	Ph	96 (**3j**)	94
13	$Rh(acac)(C_2H_4)_2$	2	Ph	84 (**3k**)	95
14	$Rh(acac)(C_2H_4)_2$	1	*trans*-PhCH=CH	78 (**3l**)	89
15	$Rh(acac)(C_2H_4)_2$	1	*trans*-*n*-$C_6H_{13}CH$=CH	79 (**3m**)	93

[a] Isolated yields.
[b] Determined by HPLC analysis using a chiral column.
[c] 2.3 equiv of KOH was added.

(entries 14 and 15). The reactions gave corresponding products **3l** and **3m** with 89% ee and 93% ee.

Finally, we tried the synthesis of flavanone. There have been only a few reports for the synthesis of flavanone via rhodium(I)-catalyzed asymmetric 1,4-addition of chromone, which has an electron-donating group at the γ-position, with phenylboronic acid.[9] We applied the reaction of chromone with phenylboronic acid using (*S*)-BICMAP as a chiral ligand (Scheme 2). The reaction gave flavanone (**3n**) in 31% yield with 99% ee.

In summary, we described the optical resolution of BICMAP (**1**) using DBTA and determined the absolute configuration. We found



0.40 mmol 2.0 mmol **3n**

Scheme 2. Synthesis of flavanone (**3n**).

that BICMAP-rhodium system was an efficient catalyst for the rhodium(I)-catalyzed asymmetric 1,4-addition of aryl- and alkenylboronic acids to cyclic enones including chromone up to 99% ee.

Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2012.06.064.

References and notes

1. Takaya, Y.; Ogasawara, M.; Hayashi, T.; Sakai, M.; Miyaura, N. *J. Am. Chem. Soc.* **1998**, *120*, 5579–5580.
2. (a) d'Herouville, F. L. B.; Millet, A.; Scalone, M.; Michelet, V. *J. Org. Chem.* **2011**, *76*, 6925–6930; (b) Berhal, F.; Wu, Z.; Genet, J.-P.; Ayad, T.; Ratovelmanana-Vidal, V. *J. Org. Chem.* **2011**, *76*, 6320–6326; (c) Berhal, F.; Esseiva, O.; Martin, C.-H.; Tone, H.; Genet, J.-P.; Ayad, T.; Ratovelomanana-Vidal, V. *Org. Lett.* **2011**, *13*, 2806–2809; (d) Gök, Y.; Noël, T.; Van der Eycken, J. *Tetrahedron: Asymmetry* **2010**, *21*, 2768–2774; (e) Korenaga, T.; Maenishi, R.; Hayashi, K.; Sakai, T. *Adv. Synth. Catal.* **2010**, *352*, 3247–3254; (f) Korenaga, T.; Osaki, K.; Maenishi, R.; Sakai, T. *Org. Lett.* **2009**, *11*, 2325–2328; (g) Imamoto, T.; Saioh, Y.; Koide, A.; Ogura, T.; Yoshida, K. *Angew. Chem., Int. Ed.* **2007**, *46*, 8636–8639; (h) Vandyck, K.; Matthy, B.; Willen, M.; Robeyns, K.; Van Meervelt, L.; Van der Eycken, J. *Org. Lett.* **2006**, *8*, 363–366; (i) Shimada, T.; Suda, M.; Nagano, T.; Kakiuchi, K. *J. Org. Chem.* **2005**, *70*, 10178–10181; (j) Imamoto, T.; Sugita, K.; Yoshida, K. *J. Am. Chem. Soc.* **2005**, *127*, 11934–11935; (k) Otomaru, Y.; Senda, T.; Hayashi, T. *Org. Lett.* **2004**, *6*, 3357–3359.
3. Mino, T.; Naruse, Y.; Kobayashi, S.; Oishi, S.; Sakamoto, M.; Fujita, T. *Tetrahedron Lett.* **2009**, *50*, 2239–2241.
4. *Resolution of (±)-***2**: To the solution of (±)-**2**[3] (0.375 g, 0.59 mmol) in $CHCl_3$ (5 mL) was added (−)-DBTA (0.211 g, 0.59 mmol) in EtOAc (5 mL) and stirred for 1 h at room temperature. The mixture was diluted in $CHCl_3$ (6 mL) and EtOAc (9 mL). After 14 h at room temperature, the solid was filtered, washed with $CHCl_3$ and dried under vacuum to give (+)-**2**/(−)-DBTA complex. The solution of complex in $CHCl_3$ (5 mL) was added 2 M NaOH aq (2 mL) and stirred for 1 h at room temperature. The organic layer was dried over $MgSO_4$, and concentrated under reduced pressure to give (*R*)-(+)-**2**: 0.107 g, 0.17 mmol, 28% as a white solid; mp 156–158 °C; 96% ee, $[\alpha]_D^{20}$ +149 (*c* 0.5, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.94–3.17 (m, 4H), 3.79 (dd, *J* = 8.6, 18.7 Hz, 2H), 4.18–4.26 (m, 2H), 6.76 (dd, *J* = 7.6 and 13.7 Hz, 2H), 7.03 (dd, *J* = 2.6 and 7.6 Hz, 2H), 7.24–7.30 (m, 4H), 7.33–7.49 (m, 8H), 7.59–7.65 (m, 4H), 7.69–7.75 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 29.8 (s, Cx2), 70.5 (s, Cx2), 121.5 (d, *J* = 3.6 Hz), 121.6 (d, *J* = 4.1 Hz), 123.8 (d, *J* = 15.9 Hz Cx2), 126.5 (d, *J* = 12.6 Hz Cx2), 127.8 (d, *J* = 12.0 Hz Cx8), 130.2 (d, *J* = 105.9 Hz Cx2), 130.3 (d, *J* = 1.8 Hz Cx2), 130.9 (d, *J* = 2.6 Hz Cx4), 132.2 (d, *J* = 9.5 Hz Cx4), 132.3 (d, *J* = 10.0 Hz Cx4), 134.4 (d, *J* = 105.3 Hz Cx2), 134.9 (d, *J* = 104.1 Hz, Cx2), 158.7 (d, *J* = 15.1 Hz Cx2), ^{31}P NMR (121 MHz, $CDCl_3$) δ 29.9; EI-MS *m*/*z* (rel intensity) 638 (M^+, 23); HRMS (ESI-TOF-MS) *m*/*z* Calcd for $C_{40}H_{32}O_4P_2$+H 639.1849. Found 639.1826; HPLC (Daicel CHIRALPAK® IC, 0.46 φ × 25 cm, Hexane:EtOH = 25:75, 0.3 mL/min, UV 254 nm) t_R = 19.9 min (major), t_R = 29.6 min (minor). The combined filtrates were concentrated in vacuum. The solution of residue in $CHCl_3$ (5 mL) was added 2 M KOH aq (2 mL) and stirred for 1 h at room temperature. The organic layer was dried over $MgSO_4$, and concentrated under reduced pressure. To the solution of solid (0.241 g, 0.38 mmol) in $CHCl_3$ (5 mL) was added (+)-DBTA (0.135 g, 0.38 mmol) in EtOAc (5 mL) and stirred for 1 h at room temperature. The mixture was diluted in $CHCl_3$ (6 mL) and EtOAc (9 mL). After 14 h at room temperature, the solid was filtered, washed with $CHCl_3$ and dried under vacuum to give (−)-**2**/(+)-DBTA complex. The solution of complex in $CHCl_3$ (5 mL) was added 2 M KOH aq (2 mL) and stirred for 1 h at room temperature. The organic layer was dried over $MgSO_4$, and concentrated under reduced pressure to give (*S*)-(−)-**2**: 0.102 g, 0.16 mmol, 27% as a white solid; mp 156–158 °C; 96% ee, $[\alpha]_D^{20}$ −154 (*c* 0.5, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.94–3.16 (m, 4H), 3.78 (dd, *J* = 8.6, 18.7 Hz, 2H), 4.18–4.26 (m, 2H), 6.76 (dd, *J* = 7.6 and 13.7 Hz, 2H), 7.03 (dd, *J* = 2.6 and 7.6 Hz, 2H), 7.24–7.30 (m, 4H), 7.33–7.46 (m, 8H), 7.59–7.65 (m, 4H), 7.69–7.75 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 29.8 (s, Cx2), 70.5 (s, Cx2), 121.6 (d, *J* = 3.6 Hz), 121.7 (d, *J* = 4.3 Hz), 123.8 (d, *J* = 15.9 Hz Cx2), 126.5 (d, *J* = 12.7 Hz Cx2), 127.8 (d, *J* = 11.7 Hz Cx8), 130.2 (d, *J* = 104.9 Hz Cx2), 130.3 (d, *J* = 2.4 Hz Cx2), 130.9 (d, *J* = 2.8 Hz Cx4), 132.2 (d, *J* = 9.8 Hz Cx4), 132.3 (d, *J* = 10.0 Hz Cx4), 134.5 (d, *J* = 103.1 Hz Cx2), 134.9 (d, *J* = 104.4 Hz, Cx2), 158.7 (d, *J* = 15.2 Hz Cx2), ^{31}P NMR (121 MHz, $CDCl_3$) δ 30.0; EI-MS *m*/*z* (rel intensity) 638 (M^+, 22); HRMS (ESI-TOF-MS) *m*/*z* Calcd for $C_{40}H_{32}O_4P_2$+H 639.1849. Found 639.1835; HPLC (Daicel CHIRALPAK® IC, 0.46 φ × 25 cm, UV 254 nm, Hexane:EtOH = 25:75, 0.3 mL/min) t_R = 19.9 min (minor), t_R = 29.3 min (major).
5. *(+)-***2**/*(−)-DBTA complex*: A white solid; mp 165–166 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.90–3.10 (m, 4H), 3.78 (dd, *J* = 9.2 and 18.4 Hz, 2H), 4.15 (dd, *J* = 8.7 and 16.6 Hz, 2H), 5.80 (s 2H), 6.64 (dd, *J* = 7.7 and 14.2 Hz, 2H), 6.96 (dd, *J* = 2.4 and 7.6 Hz, 2H), 7.10–7.65 (m, 28H), 8.03 (d, *J* = 7.3 Hz, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 29.6 (s, Cx2), 70.6 (s, Cx2), 71.9 (s, Cx2), 120.9 (d, *J* = 1.8 Hz), 121.1 (d, *J* = 3.7 Hz), 124.1 (d, *J* = 16.9 Hz, Cx2), 126.7 (d, *J* = 13.4 Hz, Cx2), 127.6 (s, Cx2), 127.8 (d, *J* = 12.3 Hz, Cx4), 127.9 (d, *J* = 12.4 Hz, Cx4), 128.2 (s, Cx4), 129.0 (s, Cx2), 129.4 (s, Cx2), 130.1 (s, Cx4), 131.3 (d, *J* = 2.5 Hz, Cx2), 131.3 (d, *J* = 2.6 Hz, Cx2), 131.4 (d, *J* = 2.1 Hz, Cx2), 132.1 (d, *J* =10.2 Hz, Cx4), 132.3 (d, *J* =10.2 Hz, Cx4), 133.1 (s, Cx2), 133.5 (d, *J* = 8.6 Hz, Cx2), 158.8 (d, *J* = 15.5 Hz, Cx2), 165.2 (s, Cx2), 167.1 (s, Cx2); ^{31}P NMR (121 MHz, $CDCl_3$) δ 33.3; $[\alpha]_D^{20}$ +69.9 (*c* 0.5, $CHCl_3$) Anal. Calcd for $C_{58}H_{46}Cl_{15}O_{12}P_2$·5/6$CHCl_3$: C, 64.45; H, 4.31. Found: C, 64.52; H, 4.17; X-ray diffraction analysis data. Colorless prismatic crystals, monoclinic space group P6(1) *a* = 13.1422(11) Å, *b* = 13.1422(11) Å, *c* = 53.315(4) Å, *V* = 7974.7(12) Å^3, *Z* = 6, γ = 1.395 g/cm^3, μ (MoKα) = 2.97 cm^{-1}. The structure was solved by the direct method of full-matrix least–squares, where the final *R* and *Rw* were 0.0566 and 0.1376 for 45483 reflections.
6. *Preparation of (R)-(+)-***1**: To a mixture of (*R*)-(+)-**2** (383 mg, 0.60 mmol) and triethylamine (3.0 mL, 21.6 mmol) in *m*-xylene (6 mL) was added trichlorosilane (1.82 mL, 18.0 mmol) at 0 °C under an Ar atmosphere. The reaction mixture was stirred for 18 h at 110 °C. After being cooled to room temperature, the mixture was quenched with 2 M NaOH aq (10 mL) and diluted with chloroform and water. The organic layer was dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by silica gel chromatography (elution with *n*-hexane/ethyl acetate = 15/1) and recrystallization from *n*-hexane/ $CHCl_3$: 149 mg, 0.246 mmol, 41% as a white solid; mp 229–231 °C; >99% ee, $[\alpha]_D^{20}$ +58.3 (*c* 0.5, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 2.91–3.02 (m, 2H), 3.08–3.20 (m, 2H), 3.74 (dd, *J* = 8.9 and 18.7 Hz, 2H), 4.26–4.34 (m, 2H), 6.60 (dt, *J* = 1.6 and 7.5 Hz, 2H), 7.08 (d, *J* = 7.5 Hz, 2H), 7.17–7.27 (m, 20H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 29.8 (s, Cx2), 70.7 (s, Cx2), 124.0 (t, *J* = 21.7 Hz Cx4), 124.7 (s, Cx2), 126.7 (s, Cx2), 127.8 (d, *J* = 1.0 Hz Cx2), 127.9 (t, *J* = 3.6 Hz, Cx4), 128.0 (s, Cx2), 128.1 (t, *J* = 3.0 Hz, Cx4), 133.3 (t, *J* = 10.3 Hz, Cx4), 134.0 (t, *J* = 10.5 Hz, Cx4), 137.3 (dd, *J* = 3.5 and 4.5 Hz Cx2), 137.7 (dd, *J* = 5.4 and 6.6 Hz Cx2), 138.6 (dd, *J* = 6.2 and 7.3 Hz, Cx2), 158.6 (t, *J* = 6.4 Hz, Cx2) ^{31}P NMR (121 MHz, $CDCl_3$) δ −13.0; FD-MS *m*/*z* (rel intensity) 606 (M^+, 100); HRMS (ESI-TOF-MS) *m*/*z* Calcd for $C_{40}H_{32}O_2P_2$+H 607.1950. Found 607.1945; HPLC (Daicel CHIRALPAK® IC, 0.46 φ × 25 cm, UV 254 nm, Hexane:EtOH:MTBE = 89:1:10, 0.5 mL/min) t_R = 8.5 min (*R*) (CD: λ_{ext} (Δε) 254 (−)): *Preparation of (S)-(−)-***1**: To a mixture of (*R*)-(−)-**2** (74.9 mg, 0.12 mmol) and triethylamine (0.6 mL, 4.2 mmol) in *m*-xylene (1.6 mL) was added trichlorosilane (0.35 mL, 3.5 mmol) at 0 °C under an Ar atmosphere. The reaction mixture was stirred for 6 h at 110 °C. After being cooled to room temperature, the mixture was quenched with 6 M NaOH aq (3 mL) and diluted with chloroform and water. The organic layer was dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by silica gel chromatography (elution with *n*-hexane/EtOAc = 10/1) and recrystallization from *n*-hexane/$CHCl_3$: 27.5 mg, 45.3 μmol, 39% as a white solid; mp 229–231 °C; >99% ee, $[\alpha]_D^{20}$ −63.3 (*c* 0.5, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 2.91–3.02 (m, 2H), 3.08–3.20 (m, 2H), 3.74 (dd, *J* = 8.8 and 18.7 Hz, 2H), 4.26–4.34 (m, 2H), 6.60 (dt, *J* = 1.7 and 7.5 Hz, 2H), 7.08 (d, *J* = 7.5 Hz, 2H), 7.16–7.30 (m, 20H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 29.8 (s, Cx2), 70.7 (s, Cx2), 124.0 (t, *J* = 21.6 Hz Cx4), 124.7 (s, Cx2), 126.7 (s, Cx2), 127.8 (d, *J* = 1.4 Hz Cx2), 127.9 (t, *J* = 3.6 Hz, Cx4), 128.0 (s, Cx2), 128.1 (t, *J* = 3.0 Hz, Cx4), 133.3 (t, *J* = 10.4 Hz, Cx4), 134.0 (t, *J* = 10.4 Hz, Cx4), 137.3 (dd, *J* = 3.5 and 4.5 Hz Cx2), 137.7 (dd, *J* = 5.5 and 6.6 Hz Cx2), 138.6 (dd, *J* = 6.2 and 7.5 Hz, Cx2), 158.6 (t, *J* = 6.5 Hz, Cx2) ^{31}P NMR (121 MHz, $CDCl_3$) δ −13.0; EI-MS *m*/*z* (rel intensity) 606 (M^+, 6); HRMS (ESI-TOF-MS) *m*/*z* Calcd for $C_{40}H_{32}O_2P_2$+H 607.1950. Found 607.1954; HPLC (Daicel CHIRALPAK® IA, 0.46 φ × 25 cm, UV 254 nm, Hexane:EtOH = 97:3, 0.3 mL/min) t_R = 23.6 min (*S*) (CD: λ_{ext} (Δε) 254 (+)).
7. Duan, W.-L.; Iwamura, H.; Hayashi, T. *J. Am. Chem. Soc.* **2007**, *129*, 2130–2138.
8. *General procedure for the rhodium(I)-catalyzed asymmetric 1,4-addition to cyclic enones using (S)-(−)-1*: To a mixture of aryl- or alkenylboronic acid (2.0 mmol), $Rh(acac)(C_2H_4)_2$ (3.09 mg, 12.0 μmol), and (*S*)-(−)-1 (8.08 mg, 13.3 μmol) in a dioxane (1.0 mL) and H_2O (0.1 mL) was added cyclic enone (0.40 mmol) at room temperature under an Ar atmosphere. The reaction mixture was stirred for 5 h at 100 °C. After being cooled to room temperature, the mixture was quenched with sat. $NaHCO_3$ aq and diluted with EtOAc. The organic layer was washed with water and brine, and dried over Na_2SO_4. The filtrate was concentrated with a rotary evaporator and the residue was purified by column chromatography (elution with *n*-hexane/EtOAc = 15-6/1).
9. (a) Han, F.; Chen, G.; Zhang, X.; Liao, J. *Eur. J. Org. Chem.* **2011**, 2928–2931; (b) Korenaga, T.; Hayashi, K.; Akaki, Y.; Maenishi, R.; Sakai, T. *Org. Lett.* **2011**, *13*, 2022–2025; (c) Chen, J.; Chen, J.; Lang, F.; Zhang, X.; Cun, L.; Zhu, J.; Deng, J.; Liao, J. *J. Am. Chem. Soc.* **2010**, *132*, 4552–4553.