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Enantioselective 1,4-addition of arylboronic acids to α,β-unsaturated carbonyl compounds catalyzed by rhodium(I)-chiral phosphoramidite complexes

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Abstract

A chiral bidentate phosphoramidite (5a) was synthesized from Shibasaki's linked-(R)-BINOL and P(NMe₂)₃ as a new ligand for rhodium(I)-catalyzed asymmetric 1,4-addition of arylboronic acids to α,β-unsaturated carbonyl compounds. The effects of 5a and Feringa's monodentate phosphoramidite (4, R¹, R²=Et) on the yields and enantioselectivities were fully investigated. The reaction was significantly accelerated in the presence of a base such as KOH and Et₃N, allowing the reaction to be completed at the lower temperatures than 50 °C. The addition to cyclic enones such as 2-cyclopentenone, 2-cyclohexenone and 2-cycloheptenone at 50 °C in the presence of an [Rh(coe)₂Cl]₂-4 (R¹, R²=Et) complex resulted in enantioselectivities up to 98%, though it was less effective for acyclic enones (0-70% ee). On the other hand, a complex between [Rh(nbd)₂]BF₄ and 5a completed the addition to cyclic enones within 2 h at room temperature in the presence of Et₃N with 86-99% yields and 96-99.8%ee. This catalyst was also effective for acyclic enones, resulting in 62-98% yields and 66-94%ee. The 1,4-additions of arylboronic acids to unsaturated lactones and acyclic esters with rhodium(I)-phosphoramidites complexes were also investigated.

Key words: arylboronic acids, rhodium catalyst, phosphoramidite, asymmetric, conjugate addition

1. Introduction

Metal-catalyzed conjugate addition reactions of carbon nucleophiles to α,β-unsaturated compounds are the most widely used methods for asymmetric carbon-carbon bond formation [1]. The reactions catalyzed by copper [2], rhodium [3], and palladium [4] complexes are of great value for asymmetric syntheses because of the availability of chiral ligands. Rhodium(I)-binap catalysts were found to be excellent catalysts for 1,4-addition reactions of aryl- and 1-alkenylboronic acids to
electron-deficient alkenes [3, 5]. Other catalysts that are effective for arylboronic acids are rhodium(I) complexes of mono-phosphoramidites [6], chiral P-P ligands such as chiraphos [7] and diphosphonites [8], P-N ligands of amidomonophosphines [9], bis(alkene) ligands based on a norbornadiene skeleton [10], and carbene ligands derived from bicsyclophane imidazolium salts [11]. Among these chiral auxiliaries for metal-catalyzed conjugate additions, phosphoramidites developed by Feringa [6, 12], such as 4, are the only ligands for which monodentate form exhibit high enantioselectivity for a large number of asymmetric transformations, including copper- and rhodium-catalyzed conjugate addition of organozinc and -boron compounds, though the efficiency of a bidentate ligand bridged by diamine [12a] was reported in copper-catalyzed reaction of diethylzinc with cyclic enones. Herein we report the performance of monodentate and bidentate phosphoramidite ligands for asymmetric addition of arylboronic acids to α,β-unsaturated carbonyl compounds (Scheme 1) [6a, 13]. A bidentate bisphosphoramidite 5a newly synthesized from Shibasaki’s linked-BINOL was found to be an excellent ligand for both cyclic and acyclic enones.

<<Scheme 1>>

2. Results and discussion

2.1. Monodentate phosphoramidites for asymmetric 1,4-addition to enones

The effects of monodentate phosphoramidite ligands (4) on 1,4-addition of arylboronic acids to enones are summarized in Table 1. The catalyst was prepared in situ by mixing [Rh(coe)Cl]₂ (1.5 mol%) and four equivalents of 4 at room temperature for 1 h. The addition of arylboronic acid, enone, and aqueous KOH was then followed at room temperature. After being stirred for 6 h at 50 °C, the products were isolated and analyzed by a chiral stationary column. Since the enantioselectivity was reduced by raising the reaction temperature, the presence of a base was critical to carry out the reaction under mild conditions and to achieve high enantioselective. The reaction was completed within 6 h at 50 °C in the presence of 1 equivalent of KOH, K₃PO₄ or K₂CO₃ in striking contrast to the reaction occurring at 90 °C in the absence of a base. Rh(acac)(coe)₂, [RhCl(C₂H₄)₂]₂, [Rh(OH)(cod)]₂ and Rh(acac)(C₂H₄)₂ also gave yields and enantioselectivities analogous to those of [Rh(coe)Cl]₂. The enantioselectivities dramatically changed in a series of N,N-dialkylamino derivatives for 2-cyclohexenone (entries 1-8). Among the ligands employed, N,N-diethylamine and morpholine derivative exhibited the best enantioselectivity (91% ee, entries 2 and 8), and the selectivities were reduced by increasing the bulkiness of amino groups (entries 5-7). The diethylamino ligand (4, R¹, R²=Et) was also effective for other cyclic
enones such as 2-cyclopentenone (75-95% ee, entries 9-11) and 2-cycloheptenone (94% ee, entry 12),
giving yields and selectivities comparable to those of 2-cyclohexenone. It is interesting that the
substituents on aromatic rings significantly affected the enantioselectivity. 3-Methoxy-, 3-chloro,
and 4-tolylboronic acid resulted in apparently higher enantioselectivities than that of phenylboronic
acid (entries 2-4 and 9-11). The phosphoramidites derived from (R)-(+) -BINOL afforded
(R)-3-phenylcyclohexanone for a series of dialkylamino derivatives (entries 1, 2, 5, 7, 8), though the
diisopropyl derivative exceptionally gave an S isomer with a very low selectivity (entry 6).

<<Table 1>>

In contrast to the excellent performance of the N,N-diethylamino ligand for cyclic enones, it
was not effective for acyclic enones (entries 13-20). Acyclic enones such as (E)-3-nonen-2-one
unfortunately resulted in a racemic product (entry 13). Since the reactions were very slow when the
bulkiness of two alkyl groups of 4 were increased (e.g., R^1, R^2 = benzyl, i-propyl). A series of
methylalkylamine derivatives was synthesized to optimize the best ligand (entries 14-20). The
N,N-t-butylmethylamino derivative was found to result in 70% ee (entry 20); however, none of the
enantioselectivities were a practical level. The absolute configuration of product (3h) determined by
specific rotations was reversed from S to R by increasing bulkiness of the ligand.

2.2 Preparation of bidentate phosphoramidites and their rhodium(I) complexes

The use of a rigid bidentate ligand can be critical to achieve high enantioselectivity for
flexible acyclic substrates. Thus, bidentate bisphosphoramidites 5 were newly synthesized on the
basis of linked-BINOL (6), which was obtained from optically active BINOL by the procedures of
Shibasaki [14] (Scheme 2).

<<Scheme 2>>

The two methods pioneered by Feringa [15, 12c] were used for conversion of
linked-BINOL to the corresponding phosphoramidites (5). A mixture of P(NMe_2)_3 or P(NEt_2)_3
and an (R, R)-O-linked-BINOL (6) was refluxed in toluene in the presence of a catalytic amount
of NH_4Cl to give air and moisture-stable bisphosphoramidite 5a (74%) and 5b (56%). The protocol
failed to give an N,N-diisopropyl derivative (5c). Thus, 5c was synthesized in 11% yield by a
two-step method that involves chlorophosphonylation of 6 at -60 °C and amidation with lithium
diisopropylamide [12c].

The reaction of 5a with [Rh(nbd)_2]BF_4 in CD_2Cl_2 gave the desired [Rh(4a)(nbd)]BF_4 (7a)
as a fine powder. ^31P NMR exhibited a single signal at 142.4 ppm (d, J_{Rh-P}=248.9 Hz), thus
suggesting the intramolecular complexation of two phosphorous atoms to a rhodium metal center.
The formation of a 1:1 complex was also confirmed by mass spectroscopy (FAB), which showed a molecular weight of 955.1913 (M$^+–$BF$_4^−$). The corresponding neutral complex [Rh(Cl)(5a)] (7b) was synthesized by analogous reaction of 5a with [Rh(Cl)(coe)$_2$], which exhibited a single signal at 153.7 ppm (d, $J_{Rh-P}=296.3$ Hz). A mixture of [Rh(nbd)$_2$]BF$_4$ and 4b also gave a single signal (142.3 ppm, d, $J=248.9$ Hz) analogous to that of 5a, but 4c exhibited multiple signals at 24.8, 111.0 and 134.1 ppm due to formation of a mixture of intra- and intermolecular coordination.

2.3. Bidentate phosphoramidites for asymmetric 1,4-addition to enones

The effects of 5, rhodium catalysts and bases in the reaction of 2-cyclohexenone and phenylboronic acid in aqueous 1,4-dioxane are shown in Table 2. The catalysts were prepared in situ by mixing a rhodium precursor and 10% excess of 5 since they resulted in yields and enantioselectivities that were same as those of isolated complexes (7a, 7b). The neutral complex thus prepared from [RhCl(coe)$_2$] and 5a did not catalyze the reaction (entry 1), but the reaction was initiated by addition of a base at 50 °C with yields increasing in the order of basic strength (entries 2-4). Finally, aqueous KOH was recognized to be the best base for a neutral catalyst (entry 4), as was previously demonstrated in analogous conjugated addition catalyzed by Rh(I)-phosphine complexes. A combination of a cationic rhodium(I) complex and 5 provided a much more active catalyst than a neutral one. The reaction was completed within 0.5 h at room temperature when [Rh(nbd)$_2$]BF$_4$ and 5a were used in the presence of Et$_3$N [5k] (entries 5 and 6). A perfect enantioselectivity that close to 100%ee was obtained at room temperature (entry 6). On the other hand, $N,N$-diethyl (5b) and $N,N$-diisopropyl (5c) derivatives were less effective than the $N,N$-dimethyl ligand (5a) (entries 7 and 8).

The effects of catalyst amounts and reaction rates are shown in Figure 1. The addition of phenylboronic acid (1.5 equivalents) to 2-cyclohexenone completed within 30 min when a 3 mol% of [Rh(nbd)$_2$]BF$_4$–5a was used at 25 °C. The use of 0.5 mol% complex completed the reaction within 3 h at 50 °C, though it was very slow at 25 °C. However, the reaction resulted in less than 5% yields even at temperatures higher than 50 °C when catalyst loading was reduced to 0.1 mol%.

With these optimized conditions, the scope of reaction was investigated by using representative arylboronic acids, $\alpha,\beta$-unsaturated carbonyl compounds, and an [Rh(nbd)$_2$]BF$_4$–5a catalyst (Table 3). There was no difficulty in obtaining high chemical yields and high enantioselectivities for cyclic enones within 2 h at room temperature (entries 1-7). The catalyst was
especially effective for 2-cyclohexenone, easily achieving over 99%ee for various arylboronic acids (entries 1-4). The catalyst was less effective for acyclic enones; however, the selectivities were comparable to or even higher than those of mono-phosphoramidites 4 or previously reported bisphosphine ligands such as BINAP [5-11]. For example, the use of a catalyst obtained from 1/2[RhCl(coe)]₂ and 4 resulted in 0-70%ee (Table 1, entries 13-20), and the use of Rh(1)-BINAP catalyst resulted in 83%ee for (E)-C₅H₁₁CH=CHCOCH₃ [5k], whereas [Rh(nbd)₂]BF₄/5a gave 74%ee at 25 °C (entry 8) and 84%ee at 5 °C (entry 9). The enantioselectivities for acyclic (E)-enones were dependent on the β-substituent (R₁) and a substituent on ketone carbonyls (R₃). The effect of R₁ increased in the order of Ph < n-C₅H₁₁ < isopropyl for a series of methyl ketones (entries 10, 15 and 19). Steric balance between R₁ and R₃ was also an important factor affecting the selectivity. The selectivities were improved by increasing the bulkiness of R₃ for enones having a primary alkyl group at the β-carbon (entries 10 and 13), but enones possessing a hindered substituent (R₁=isopropyl and phenyl) reduced the selectivity by increasing the bulkiness of R₃ groups (CH₃ > Ph > cyclohexyl) (entries 15, 17, 18, 19 and 20). The para- and meta-substituents in arylboronic acids affected enantioselectivities (entries 8-12). The enantioselectivities of meta-substituted arylboronic acids were generally higher than that of para-substituted boronic acids, as shown in Table 1 and as previously reported for related rhodium- and palladium-catalyzed reactions [4, 5].

2.4. Asymmetric addition to α,β-unsaturated esters

Asymmetric 1,4-additions to acyclic and cyclic α,β-unsaturated esters are shown in Scheme 3. The reaction was slower than that for enones, but high enantioselectivities comparable to those of the corresponding enones were easily obtained. Methyl crotonate, 5H-furan-2-one, and 5,6-dihydro-2H-pyran-2-one afforded 3v (75%ee), 3w (77%ee), 3x (89%ee) and 3y (91%ee), respectively, in the presence of [Rh(nbd)₂]BF₃-5a and Et₃N at room temperature. On the other hand, the use of monodentate phosphoramidites such as 4 (R₁, R²=Et) resulted in no reaction for 5H-furan-2-one and 35% yield and 72%ee for 5,6-dihydro-2H-pyran-2-one at 50 °C in the presence of Rh(acac)(coe)₂ and Et₃N in dioxane-H₂O (6/1).

3. Conclusion

In conclusion, the effects of catalysts, phosphoramidites (4, 5) and bases on reaction rates
and enantioselectivities in the rhodium-catalyzed 1,4-addition of arylboronic acids to enones were investigated in detail. Although traditional monodentate phosphoramidite ligands (4) gave good enantioselectivities for cyclic enones, we have shown that bidentate phosphoramidite (5a), first prepared from Shibasaki’s linked-BINOL, is an excellent ligand for both cyclic and acyclic enones and enable the reaction to be completed in a short time at room temperature. Works aimed at characterization of the catalysts by X-ray analysis are in progress to elucidate the enantioselection mechanism.

4. Experimental

4.1. Reagents

[RhCl(coe)₂]₂ [16] and [Rh(nbd)₂]BF₄ [17] were prepared by the reported procedures. Chiral phosphoramidites (4) were obtained from (R)-BINOL and the corresponding amines by the method of Feringa [15]. (R, R)-O-linked-BINOL (6) was synthesized from (R)-BINOL by the method of Shibasaki [14].

4.2. Bidentate phosphoramidites (5, Scheme 2)

4.2.1. N,N-Dimethyl (R, R)-O-linked-phosphoramidite (5a)

3,3"-(Oxydimethylene)-di-1,1'-bi-2-naphthol (6, (R,R)-O-linked-BINOL) (1 mmol), NH₄Cl (0.01 g) and P(NMe₂)₃ (2.8 mmol) in dry toluene (10 ml) were refluxed for 12 h under nitrogen. The crude solid obtained by evaporation of the solvent was crystallized from CH₂Cl₂/pentane to give 5a as white crystals (74%). ¹H-NMR (400 MHz, CD₂Cl₂): δ = 2.23-2.39 (m, 12 H), 4.82 (d, J=13.3 Hz, 2H), 5.02 (d, J=13.3 Hz, 2H), 7.07-7.39 (m, 14H), 7.76-7.86 (m, 6H), 8.15 (s, 2H); ¹³C NMR (100 MHz, CD₂Cl₂) δ = 35.7, 35.9, 69.2, 122.1, 122.9, 124.2, 125.1, 126.2, 126.5, 126.8, 127.0, 128.2, 128.7, 129.3, 130.6, 130.9, 131.0, 131.8, 132.3, 133.1, 148.0, 148.1, 149.7; ³¹P NMR (161.7 Hz, CD₂Cl₂) δ= 149.4; MS (m/z) 46 (33), 136 (31), 154 (41), 266 (27), 282 (47), 329 (100), 388 (25), 716 (28), 761 (16, [M+H]+); exact mass calcd for C₄₆H₃₈N₂O₅P₂: 760.2256; found 760.2275; [α]D²¹ = -522.5 ° (C=0.56, CHCl₃).

4.2.2. N,N-Diethyl (R, R)-O-linked-phosphoramidite (5b)

An analogous method used for preparation of 5a gave 5b in 56% yield. ¹H-NMR (400 MHz, CD₂Cl₂) δ= 0.75-0.91 (m, 12 H), 2.64-2.95 (m, 8H), 4.89 (d, J=13.6 Hz, 2H), 5.06 (d, J=13.6
Hz, 2H), 7.09-7.41 (m, 14H), 7.79-7.87 (m, 6H), 8.15 (d, J=8.8 Hz, 2H); $^{13}$C NMR (100 MHz, CD$_2$Cl$_2$) δ= 15.0, 39.1, 39.3, 69.1, 122.3, 124.3, 125.0, 125.1, 126.0, 126.4, 126.9, 127.1, 127.8, 128.7, 130.3, 130.6, 130.9, 131.2, 131.7, 132.3, 133.1, 148.4, 148.5, 149.9; $^{31}$P NMR (161.7 MHz, CD$_2$Cl$_2$) δ= 150.1; MS (m/z) 72 (31), 266 (38), 282 (51), 329 (100), 416 (15), 744 (28), 817 (10, [M+H]$^+$); exact mass calcd for C$_{50}$H$_{47}$N$_2$O$_5$P$_2$ ([M+H]$^+$): 817.2961; found 817.2981; $^{[\alpha]}$D$^{22}$ = -414.4˚ (C=0.50, CHCl$_3$).

4.2.3. N,N-Diisopropyl (R, R)-O-linked-phosphoramidite (5c)

To a mixture of PCl$_3$ (2 mmol) and Et$_3$N (4 mmol) in toluene (3 ml) was added a solution of 3,3"-(oxydimethylene)-di-1,1'-bi-2-naphthol (6, (R, R)-O-linked-BINOL) (1 mmol) in toluene (10 ml) at -60 °C. After being stirred for 2 h, the reaction mixture was allowed to warm up to room temperature. The precipitates were removed by filtration. The filtrate was treated with n-BuLi (2 mmol) and i-Pr$_2$NH (3 mmol) at -40 °C. After being stirred for 16 h at room temperature, the crude solids obtained by evaporation of the solvent was crystallized from CH$_2$Cl$_2$/pentane to give 5c as white crystals (11%). $^1$H-NMR (400 MHz, CD$_2$Cl$_2$); δ 0.75-1.36 (m, 24 H), 3.24-3.32 (m, 4H), 5.03 (s, 4H), 7.12-7.39 (m, 14H), 7.92-7.97 (m, 6H), 8.23 (s, 2H); $^{13}$C NMR (100 MHz, CD$_2$Cl$_2$) δ= 24.4, 24.5, 24.6, 24.7, 45.2, 24.3, 69.1, 69.2, 122.6, 124.7, 125.1, 126.1, 126.2, 127.3, 128.6, 128.8, 129.1, 130.0, 131.0, 131.2, 131.4, 132.6, 132.8, 133.1, 148.7, 150.9, 157.9; $^{31}$P NMR (161.7 MHz, CD$_2$Cl$_2$) δ= 150.7; MS (m/z) 43 (31), 57 (32), 71 (26), 149 (100), 266 (27), 281 (49), 329 (87), 391 (28), 444 (50), 772 (18), 873 (43, [M+H]$^+$); exact mass calcd for C$_{54}$H$_{55}$N$_2$O$_5$P$_2$ ([M+H]$^+$): 873.3586; found 873.3604.

4.3 Rhodium complexes (7, Scheme 2)

4.3.1. Complex between [Rh(nbd)$_2$]BF$_4$ and 5a (7a)

To a solution of 5a (0.05 mmol) in CD$_2$Cl$_2$ was added [Rh(nbd)$_2$]BF$_4$ (0.05 mmol) under atmosphere of argon. The solvent was evaporated to dryness in vacuo to give solids of 7a. All attempts at synthesizing single crystals were failed. $^{31}$P NMR (161.7 MHz, CD$_2$Cl$_2$) δ= 142.4 (d, $J_{Rh-P}$=248.9 Hz); exact mass calcd for C$_{53}$H$_{46}$BF$_4$N$_2$O$_5$P$_2$Rh ([M$^+$–BF$_4$]): 955.1938; found 955.1913

4.3.2. Complex between [Rh(coe)$_2$Cl]$_2$ and 5a (7b)

$^{31}$P NMR (161.7 MHz) of a mixture between 5a (0.05 mmol) and [RhCl(coe)$_2$]$_2$ (0.025 mmol) in CD$_2$Cl$_2$ exhibited a signal at δ= 153.7 (d, $J_{Rh-P}$=296.3 Hz).
4.3.3. Complex between [Rh(nbd)₂]BF₄ and 5b

³¹P NMR (161.7 MHz) of a mixture between 5b (0.05 mmol) and [Rh(nbd)₂]BF₄ (0.05 mmol) in CD₂Cl₂ exhibited a signal at δ= 142.3 (d, J_Rh-P=248.9 Hz).

4.3.4. Complex between [Rh(nbd)₂]BF₄ and 5c

³¹P NMR (161.7 MHz) of a mixture between 5c (0.05 mmol) and [Rh(nbd)₂]BF₄ (0.05 mmol) in CD₂Cl₂ exhibited three signals at δ=24.8, 111.0, 134.1.

4.4. General procedure for asymmetric 1,4-addition (Table 1)

A flask charged with [Rh(coe)₂Cl]₂ (0.015 mmol), 4 (R¹, R²=Et) (0.066 mmol) was flushed with argon. 1,3-Dioxane (2.6 ml) was then added. After being stirred for 1 h at room temperature, arylboronic acid (1.5 mmol), enone (1.0 mmol), and aqueous KOH (2.4M, 0.43 ml, 1 mmol) were added. The resulting mixture was stirred for 6 h at 50 °C. Isolated yields determined by chromatography on silica gel are shown in Table 1. Enantiomer excess was determined by HPLC analyses using a chiral stationary column (Dicel Chiralpak AD and Chiralcel OD-H or OB-H).

We previously reported the spectral data of 3a [5l], 3b [5l], 3c [5l], 3d [5a], 3e [5l], 3f [4f], 3g [5a], and 3h [5l]. The specific rotations of these compounds were 3a ([α]_D²¹= +20.4 ° (c=1.03, CHCl₃)), 3b ([α]_D²²= +13.6 ° (c=0.98, CHCl₃)), 3c ([α]_D²²= +17.3 ° (c=0.96, CHCl₃)), 3d ([α]_D²¹= +79.9 ° (c=1.13, CHCl₃)), 3e ([α]_D²¹= +71.4 ° (c=0.92, CHCl₃)), 3f ([α]_D²²= +58.8 ° (c=1.07, CHCl₃)), 3g ([α]_D²³= +59.3 ° (c=1.00, CHCl₃)), and 3h ([α]_D²¹= +16.1 ° (c=0.97, CHCl₃)).

4.5. General procedure for asymmetric 1,4-addition (Table 3 and Scheme 3)

A flask charged with [Rh(nbd)₂]BF₄ (0.03 mmol, 3 mol%) and 5a (0.033 mmol) was flushed with argon. 1,3-Dioxane (2.6 ml) and water (0.43 ml) were then added. After being stirred for 0.5 h, arylboronic acid (1.5 mmol), α,β-unsaturated carbonyl compound (1.0 mmol) and triethylamine (1 mmol) were successively added. The resulting mixture was stirred at 5 °C or 25 °C. Isolated yields determined by chromatography on silica gel are shown in Table 2. Enantiomer excess was determined by HPLC analyses using a chiral stationary column (Dicel Chiralpak AD and Chiralcel OD-H or OB-H).

4.5.1. 4-(3-Fluorophenyl)nonan-2-one (3m)

[α]_D²¹= +14.8 ° (c=1.00, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 0.74-0.77 (m, 3H), 1.02-1.18 (m, 6H), 1.43-1.54 (m, 2H), 1.96 (s, 3H), 2.63 (d, J=7.3 Hz, 2H), 3.02-3.09 (m, 1H),
6.78-6.89 (m, 3H), 7.13-7.19 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 14.0, 22.4, 26.9, 30.6, 31.6, 36.2, 40.9, 50.6, 113.1 (d, $J$=20.7 Hz), 114.1 (d, $J$=21.5 Hz), 123.3 (d, $J$=2.5 Hz), 129.8 (d, $J$=8.3 Hz), 147.4, 162.9 (d, $J$=245.6 Hz), 207.4; MS (m/z) 43 (54), 55 (9), 109 (43), 122 (64), 135 (19), 165 (63), 178 (100), 236 (11, M$^+$); exact mass calcd for C$_{13}$H$_{21}$FO: 236.1576; found 236.1575.

4.5.2. 3-(4-Methoxyphenyl)-1-phenyloctan-1-one (3n)

$[\alpha]_D^{22}$ = -2.9 ° (c=0.97, CHCl$_3$); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 0.81-0.84 (m, 3H), 1.21-1.27 (m, 6H), 1.59-1.73 (m, 3H), 3.17-3.34 (m, 3H), 3.78 (s, 3H), 6.71-6.84 (m, 3H), 7.18-7.55 (m, 4H), 7.89-7.91 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 14.06, 22.51, 27.17, 31.78, 36.20, 41.31, 45.93, 55.11, 111.14, 113.58, 119.98, 128.1, 128.5, 129.35, 132.90, 137.23, 146.77, 159.58, 199.15; MS (m/z) 55 (13), 77 (44), 105 (75), 121 (11), 135 (27), 190 (100), 205 (33), 239 (49), 310 (29, M$^+$); exact mass calcd for C$_{21}$H$_{26}$O$_2$: 310.1933; found 310.1931

4.5.3. 5-Methyl-3-(3-fluorophenyl)hexan-2-one (3q)

$[\alpha]_D^{21}$ = +25.7 ° (c=0.95, CHCl$_3$); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 0.67 (d, $J$=6.95 Hz, 3H), 0.86 (d, $J$=6.95 Hz, 3H), 1.69-1.78 (m, 1H), 1.93 (s, 3H), 2.65-2.77 (m, 2H), 2.83-2.89 (m, 1H), 6.76-6.86 (m, 3H), 7.12-7.19 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 20.3, 20.6, 30.6, 33.2, 47.4, 47.6, 113.1 (d, $J$=21.5 Hz), 114.9 (d, $J$=21.5 Hz), 124.0 (d, $J$=3.3 Hz), 129.5 (d, $J$=8.3 Hz), 146.1 (d, $J$=6.6 Hz), 162.7 (d, $J$=245.7 Hz), 207.7; MS (m/z) 43 (70), 109 (23), 123 (32), 135 (11), 150 (100), 166 (15), 208 (4, M$^+$); exact mass calcd for C$_{13}$H$_{17}$FO: 208.1263; found 208.1264.

4.5.4. 1-Cyclohexyl-4-methyl-3-(3-methoxyphenyl)pentan-1-one (3r)

$[\alpha]_D^{22}$ = +54.5 ° (c=0.50, CHCl$_3$); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 0.74 (d, $J$=6.8 Hz, 3H), 0.92 (d, $J$=6.6 Hz, 3H), 1.06-1.29 (m, 4H), 1.56-1.85 (m, 7H), 2.19-2.21 (m, 1H), 2.79 (d, $J$=7.3 Hz, 2H), 2.93 (dt, $J$=7.3 Hz, 7.1 Hz, 1H), 3.79 (s, 3H), 6.68-6.74 (m, 3H), 7.15-7.26 (m, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 20.4, 20.8, 25.59, 25.61, 25.8, 28.1, 28.2, 33.0, 44.8, 47.5, 51.2, 55.1, 111.0, 114.3, 120.8, 128.9, 145.6, 159.3, 213.1; MS (m/z) 55 (22), 83 (51), 121 (30), 162 (100), 177 (17), 288 (16, M$^+$); exact mass calcd for C$_{19}$H$_{28}$O$_2$: 288.2089; found 288.2099.

4.5.5. 4-Methyl-3-(3-methoxyphenyl)-1-phenyloctan-1-one (3s)

$[\alpha]_D^{21}$ = -1.8 ° (c=0.92, CHCl$_3$); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 0.800 (d, $J$=6.6 Hz, 3H), 0.98 (d, $J$=6.8 Hz, 3H), 1.86-1.97 (m, 1H), 3.11-3.17 (dd, $J$=7.2, 14.3 Hz, 1H), 3.34 (d, $J$=6.8 Hz, 2H), 3.76 (s, 3H), 6.68-6.79 (m, 3H), 7.16 (t, $J$=7.8 Hz, 1H), 7.39-7.43 (m, 2H), 7.50-7.54 (m, 1H),
7.84-7.94 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 20.5, 20.9, 33.3, 42.5, 47.8, 55.1, 111.1, 114.4, 120.8, 128.0, 128.5, 129.0, 132.8, 137.3, 145.4, 159.3, 199.4; MS (m/z) 77 (35), 105 (100), 162 (91), 177 (8), 239 (8), 282 (10, M$^+$); exact mass calcd for C$_{19}$H$_{22}$O$_2$: 282.1620; found 282.1623.

4.5.6. *Methyl-3-((3-methoxyphenyl)butanoate (3v)*

$[\alpha]_{D}^{21}$ = +23.0° (c=0.56, CHCl$_3$); $^1$H NMR (400 MHz, CDCl$_3$) δ 1.29 (d, J=7.1 Hz, 3H), 2.56 (dd, J=8.3, 15.2 Hz, 1H), 2.63 (dd, J=6.6, 15.3 Hz, 1H), 3.21-3.30 (m, 1H), 3.63 (s, 3H), 3.80 (s, 3H), 6.74-6.83 (m, 3H), 7.20-7.26 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 21.7, 36.4, 42.6, 51.5, 55.1, 111.4, 112.7, 119.0, 129.5, 147.4, 159.6, 172.8; MS (m/z) 77 (10), 91 (13), 105 (26), 121 (11), 135 (84), 148 (100), 208 (57, M$^+$); exact mass calcd for C$_{12}$H$_{16}$O$_3$: 208.1099; found 208.1091.

4.5.7. 4-Phenyldihydropyran-2-one (3w)

$[\alpha]_{D}^{22}$ = -39.2° (c=0.99, CHCl$_3$); $^1$H NMR (400 MHz, CDCl$_3$) δ 2.60 (dd, J=9.3, 17.6 Hz, 1H), 2.85 (dd, J=8.8, 8.8 Hz, 1H), 3.68-3.76 (m, 1H), 4.60 (dd, J=7.8, 9.02 Hz, 1H), 4.20 (dd, J=7.8, 8.8 Hz, 1H), 7.15-7.32 (m, 5H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 35.7, 41.0, 74.0, 126.7, 127.7, 129.1, 139.4, 176.4; MS (m/z) 51 (12), 78 (12), 104 (100), 162 (23, M$^+$); exact mass calcd for C$_{10}$H$_{10}$O$_2$: 162.0681; found 162.0695.

4.5.8. 4-Phenyltetrahydropyran-2-one (3x)

$[\alpha]_{D}^{22}$ = -2.8° (c=1.01, CHCl$_3$); $^1$H NMR (400 MHz, CDCl$_3$) δ 1.91-2.01 (m, 1H), 2.07-2.14 (m, 1H), 2.56 (dd, J=10.7, 17.6 Hz, 1H), 3.15 (ddd, J=17.6, 5.9, 1.7 Hz, 1H), 3.12-3.20 (m, 1H), 4.31 (ddd, J=11.8, 10.9, 3.9 Hz, 1H), 4.43 (ddd, J=11.5, 5.0, 3.9 Hz, 1H), 7.13-7.22 (m, 3H), 7.26-7.30 (m, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 30.2, 37.3, 47.4, 68.6, 126.4, 127.1, 128.9, 142.7, 170.6; MS (m/z) 51 (9), 78 (20), 92 (26), 104 (65), 117 (87), 130 (16), 158 (16), 176 (100, M$^+$); exact mass calcd for C$_{12}$H$_{14}$O$_2$: 176.0837; found 176.0836.

4.5.9. 4-(3-Methoxyphenyl)tetrahydropyran-2-one (3y)

$[\alpha]_{D}^{22}$ = +4.0° (c=0.51, CHCl$_3$); $^1$H NMR (400 MHz, CDCl$_3$) δ 1.98-2.08 (m, 1H), 2.14-2.21 (m, 1H), 2.63 (dd, J=10.7, 17.6 Hz, 1H), 2.92 (ddd, J=17.7, 5.85, 1.46 Hz, 1H), 3.17-3.25 (m, 1H), 4.38 (ddd, J=11.0, 11.0, 3.7 Hz, 1H), 4.50 (ddd, J=11.5, 4.6, 3.9 Hz, 1H), 6.74-6.83 (m, 3H), 7.14-7.36 (m, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 30.2, 37.4, 55.2, 68.6, 112.1, 112.7, 118.6, 130.0, 144.4, 160.0, 170.6; MS (m/z) 65 (18), 77 (19), 91 (35), 121 (38), 134 (86), 150 (31), 163 (25), 206 (100, M$^+$); exact mass calcd for C$_{12}$H$_{14}$O$_2$: 206.0943; found 206.0937.
The spectral data of $3i$ [5l], $3j$ [5l], $3k$ [5b], $3l$ [5l], $3o$ [5l], $3p$ [5l], $3t$ [4f] and $3u$ [4f] were reported previously. The specific rotations of these compounds were $3i$ ($[\alpha]_D^{22} = +17.5^\circ$ (c=0.97, CHCl$_3$)), $3j$ ($[\alpha]_D^{21} = +16.4^\circ$ (c=0.93, CHCl$_3$)), $3k$ ($[\alpha]_D^{22} = +70.8^\circ$ (c=1.02, CHCl$_3$)), $3l$ ($[\alpha]_D^{23} = +15.9^\circ$ (c=0.93, CHCl$_3$)), $3o$ ($[\alpha]_D^{21} = +32.4^\circ$ (c=0.98, CHCl$_3$)), $3p$ ($[\alpha]_D^{21} = +18.2^\circ$ (c=0.51, CHCl$_3$)), $3t$ ($[\alpha]_D^{23} = -1.6^\circ$ (c=0.51, CHCl$_3$)) and $3u$ ($[\alpha]_D^{22} = -4.4^\circ$ (c=0.91, CHCl$_3$)).

Acknowledgments

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References

   (b) K. Tomioka, Y. Nagaoka in: E. N. Jacobsen, A. Pfalts, H. Yamamoto (Eds),  


   (d) T. Nishikata, Y. Yamamoto, N. Miyaura, Organometallics 23 (2004) 4317;  


Scheme 1. Asymmetric 1,4-addition of arylboronic acids to enones catalyzed by Rh(I)-phosphoramidite complexes
Scheme 2. Phosphoramidites based on Linked-BINOL

5a: R=Me (74%)
5b: R=Et (56%)
5c: R=\text{-}Pr (11%)

7a: X=(nbd)(BF₄)
7b: X=Cl
Scheme 3. Asymmetric 1,4-addition to unsaturated esters
Figure 1. Amounts of catalyst loading and reaction rates
<table>
<thead>
<tr>
<th>entry</th>
<th>carbonyl compound</th>
<th>ligand (I)</th>
<th>ArB(OH)$_2$, product</th>
<th>yield%$^{[b]}$</th>
<th>%ee$^{[c]}$</th>
</tr>
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<td>R$^2$=</td>
<td>X=</td>
<td>No</td>
<td></td>
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<td>Me</td>
<td>Me</td>
<td>H</td>
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<td>2-cyclohexenone</td>
<td>Et</td>
<td>Et</td>
<td>H</td>
<td>3a</td>
</tr>
<tr>
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<td>Et</td>
<td>3-MeO</td>
<td>3b</td>
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<td>Et</td>
<td>4-Me</td>
<td>3c</td>
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<td>CH$_2$Ph</td>
<td>H</td>
<td>3a</td>
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<td>6</td>
<td>2-cyclohexenone</td>
<td>i-Pr</td>
<td>i-Pr</td>
<td>H</td>
<td>3a</td>
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<td>2-cyclohexenone</td>
<td>-CH$_2$CH$_2$CH$_2$CH$_2$-</td>
<td>H</td>
<td>3a</td>
<td>83</td>
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<td>Et</td>
<td>H</td>
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<td>Et</td>
<td>Et</td>
<td>3-Cl</td>
<td>3e</td>
</tr>
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<td>Et</td>
<td>Et</td>
<td>3-MeO</td>
<td>3f</td>
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<td>12</td>
<td>2-cycloheptenone</td>
<td>Et</td>
<td>Et</td>
<td>H</td>
<td>3g</td>
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<td>(E)-C$_5$H$_11$CH=CHCOCH$_3$</td>
<td>Et</td>
<td>Et</td>
<td>H</td>
<td>3h</td>
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<td>(E)-C$_5$H$_11$CH=CHCOCH$_3$</td>
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<td>Et</td>
<td>H</td>
<td>3h</td>
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<td>n-Pr</td>
<td>H</td>
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<td>CH$_2$Ph</td>
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<td>3h</td>
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<td>Ph</td>
<td>H</td>
<td>3h</td>
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<td>18</td>
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<td>Me</td>
<td>i-Pr</td>
<td>H</td>
<td>3h</td>
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<td>Reaction Conditions</td>
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<td>19</td>
<td>(E)-C₅H₁₁CH=CHCOCH₃ Me 1-adamantyl H 3h 55 47 (R)</td>
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<td></td>
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</table>

[a] All reactions were carried out at 50 °C for 6 h in the presence of enone (1 mmol), arylboronic acid (1.5 mmol), [Rh(coc)Cl]₂ (0.015 mmol, 3 mol%), 4 (0.066 mmol) and KOH (1 mmol) in dioxane-H₂O (6/1).

[b] Isolated yields based on enones.

[c] Enantiomer excess determined by a chiral stationary column.
Table 2. Effects of catalysts and bases\(^{[a]}\)

<table>
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<tr>
<th>entry</th>
<th>rhodium complex</th>
<th>base</th>
<th>°C/h</th>
<th>yield/%</th>
<th>%ee</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1/2[RhCl(coe)](_2/5)a</td>
<td>none</td>
<td>50/16</td>
<td>0</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>1/2[RhCl(coe)](_2/5)a</td>
<td>Et(_3)N</td>
<td>50/16</td>
<td>46</td>
<td>97 ((R))</td>
</tr>
<tr>
<td>3</td>
<td>1/2[RhCl(coe)](_2/5)a</td>
<td>K(_2)CO(_3)</td>
<td>50/16</td>
<td>26</td>
<td>98 ((R))</td>
</tr>
<tr>
<td>4</td>
<td>1/2[RhCl(coe)](_2/5)a</td>
<td>KOH</td>
<td>50/16</td>
<td>84</td>
<td>98 ((R))</td>
</tr>
<tr>
<td>5</td>
<td>[Rh(nbd)(_2)]BF(_4/5)a</td>
<td>Et(_3)N</td>
<td>50/16</td>
<td>94</td>
<td>99 ((R))</td>
</tr>
<tr>
<td>6</td>
<td>[Rh(nbd)(_2)]BF(_4/5)a</td>
<td>Et(_3)N</td>
<td>25/0.5</td>
<td>99</td>
<td>99.6 ((R))</td>
</tr>
<tr>
<td>7</td>
<td>[Rh(nbd)(_2)]BF(_4/5)b</td>
<td>Et(_3)N</td>
<td>25/2</td>
<td>62</td>
<td>83 ((R))</td>
</tr>
<tr>
<td>8</td>
<td>[Rh(nbd)(_2)]BF(_4/5)c</td>
<td>Et(_3)N</td>
<td>25/2</td>
<td>trace</td>
<td>-</td>
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</tbody>
</table>

\(^{[a]}\)All reactions were carried out in the presence of 2-cyclohexenone (1 mmol), phenylboronic acid (1.5 mmol), rhodium(I) catalyst (3 mol\%), ligand (5, 3.3 mol\%), and base (if used, 1 mmol) in dioxane-H\(_2\)O (6/1).
Table 3. 1,4-Addition of arylboronic acid to α,β-unsaturated carbonyl compounds catalyzed by a Rh(+)–5a complex[^a]

<table>
<thead>
<tr>
<th>entry</th>
<th>carbonyl compound</th>
<th>ArB(OH)$_2$, X=</th>
<th>°C/h</th>
<th>product No</th>
<th>yield/%[^b]</th>
<th>%ee[^c]</th>
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<tbody>
<tr>
<td>1</td>
<td>2-cyclohexenone</td>
<td>H</td>
<td>25/0.5</td>
<td>3a</td>
<td>99</td>
<td>99.6 (R)</td>
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<tr>
<td>2</td>
<td>2-cyclohexenone</td>
<td>3-MeO</td>
<td>25/2</td>
<td>3b</td>
<td>90</td>
<td>99.5 (R)</td>
</tr>
<tr>
<td>3</td>
<td>2-cyclohexenone</td>
<td>4-MeO</td>
<td>25/2</td>
<td>3i</td>
<td>99</td>
<td>99.8</td>
</tr>
<tr>
<td>4</td>
<td>2-cyclohexenone</td>
<td>3-Cl</td>
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<td>86</td>
<td>99.8</td>
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<tr>
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<td>2-cyclopentenone</td>
<td>3-Cl</td>
<td>25/2</td>
<td>3e</td>
<td>99</td>
<td>96</td>
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<tr>
<td>6</td>
<td>2-cyclopentenone</td>
<td>4-MeO</td>
<td>25/2</td>
<td>3k</td>
<td>99</td>
<td>96</td>
</tr>
<tr>
<td>7</td>
<td>2-cycloheptenone</td>
<td>H</td>
<td>25/2</td>
<td>3g</td>
<td>90</td>
<td>98</td>
</tr>
<tr>
<td>8</td>
<td>(E)-C$<em>5$H$</em>{11}$CH=CHCOCH$_3$</td>
<td>H</td>
<td>25/2</td>
<td>3h</td>
<td>87</td>
<td>74</td>
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<tr>
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<td>(E)-C$<em>5$H$</em>{11}$CH=CHCOCH$_3$</td>
<td>H</td>
<td>5/48</td>
<td>3h</td>
<td>42</td>
<td>84</td>
</tr>
<tr>
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<td>3-MeO</td>
<td>25/2</td>
<td>3l</td>
<td>98</td>
<td>80</td>
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<tr>
<td>11</td>
<td>(E)-C$<em>5$H$</em>{11}$CH=CHCOCH$_3$</td>
<td>3-MeO</td>
<td>5/48</td>
<td>3l</td>
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<td>83</td>
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<td>3m</td>
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<td>3n</td>
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<td>25/6</td>
<td>3o</td>
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<td>92 (R)</td>
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<td>15</td>
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<td>25/16</td>
<td>3p</td>
<td>78</td>
<td>94</td>
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<tr>
<td>16</td>
<td>(E)-(CH$_3$)$_2$CHCH=CHCOCH$_3$</td>
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<td>25/16</td>
<td>3q</td>
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<td>90</td>
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<td>17</td>
<td>(E)-(CH$_3$)$_2$CHCH=CHCOC$<em>6$H$</em>{11}$</td>
<td>3-MeO</td>
<td>25/2</td>
<td>3r</td>
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<td>81</td>
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<tr>
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<td>3s</td>
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<td>3t</td>
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</tbody>
</table>

[a] All reactions were carried out in the presence of enone (1 mmol), arylboronic acid (1.5 mmol), [Rh(nbd)_2]BF_4 (0.03 mmol, 3 mol%), 5a (0.033 mmol) and Et_3N (1 mmol) in dioxane (2.6 ml) and H_2O (0.43 ml).

[b] Isolated yields based on enones.

[c] Enantiomer excess determined by a chiral stationary column.
Figure Captions Page

**Scheme 1.** Asymmetric 1,4-addition of arylboronic acids to enones catalyzed by Rh(I)-phosphoramidite complexes

**Scheme 2.** Phosphoramidites based on Linked-BINOL

**Scheme 3.** Asymmetric 1,4-addition to unsaturated esters

**Figure 1.** Amounts of catalyst loading and reaction rates

**Table 1.** 1,4-Addition of arylboronic acid to $\alpha,\beta$-unsaturated carbonyl compounds catalyzed by Rh(I)-4 complexes$^{[a]}$

**Table 2.** Effects of catalysts and bases$^{[a]}$

**Table 3.** 1,4-Addition of arylboronic acid to $\alpha,\beta$-unsaturated carbonyl compounds catalyzed by a Rh(+)5a complex$^{[a]}$
Chiral bidentate phosphoramidites (2) were newly synthesized for the rhodium(I)-catalyzed asymmetric 1,4-addition of arylboronic acids to $\alpha,\beta$-unsaturated carbonyl compounds. The complex between $[\text{Rh(nbd)}_2]\text{BF}_4$ and 2 (R=Me) completed the addition to cyclic enones within 2 h at room temperature in the presence of $\text{Et}_3\text{N}$ with 96-99.8% ee. The catalyst resulted in 66-94% ee for acyclic enones.