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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 $P(NMe_2)_3$ 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**, R^1, $R^2 = Et$) on the yields and enantioselectivities were fully investigated. The reaction was significantly accelerated in the presence of a base such as KOH and Et_3N, 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** (R^1, $R^2 = Et$) 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 $[Rh(nbd)_2]BF_4$ and **5a** completed the addition to cyclic enones within 2 h at room temperature in the presence of Et_3N 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.

Keywords: 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 monophosphoramidites [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 biscyclophane 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

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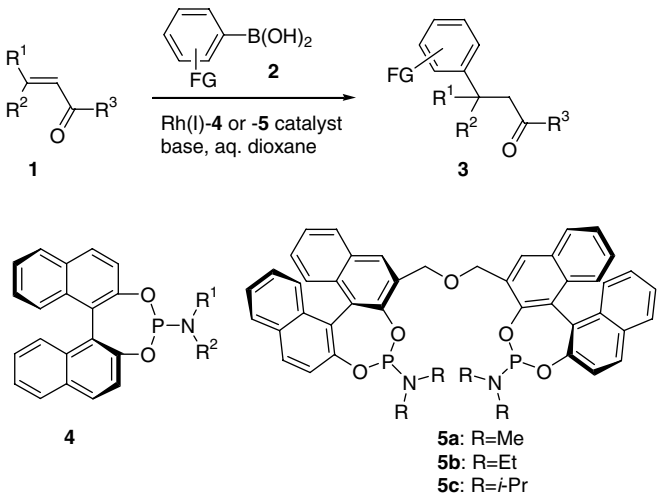
addition of arylboronic acids to α,β-unsaturated carbonyl compounds (Scheme 1) [6a,13]. A bidentate bisphosphoramidite **5a** newly synthesized from Shibasaki's linked-BINOL was found to be an excellent ligand for both cyclic and acyclic enones.

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 $[Rh(coe)_2Cl]_2$ (1.5 mol%) and 4 equiv 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 equiv of KOH, K_3PO_4 or K_2CO_3 in striking contrast to the reaction occurring at 90 °C in the absence of a base. $Rh(acac)(coe)_2$, $[RhCl(C_2H_4)_2]_2$, $[Rh(OH)(cod)]_2$ and $Rh(acac)(C_2H_4)_2$ also gave yields and enantioselectivities analogous to those of $[Rh(coe)_2Cl]_2$. The enantioselectivities dramatically changed in a series of *N*,*N*-dialkylamino derivatives for 2-cyclohexenone (entries 1–8). Among the ligands employed,



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

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**, R^1, R^2 = 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

Table 1
1,4-Addition of arylboronic acid to α,β-unsaturated carbonyl compounds catalyzed by Rh(I)-**4** complexes[a]

Entry	Carbonyl compound	Ligand (**1**)		$ArB(OH)_2$, X=	Product no.	Yield/%[b]	% ee[c]
		R^1=	R^2=				
1	2-Cyclohexenone	Me	Me	H	**3a**	85	85 (*R*)
2	2-Cyclohexenone	Et	Et	H	**3a**	89	91 (*R*)
3	2-Cyclohexenone	Et	Et	3-MeO	**3b**	85	98
4	2-Cyclohexenone	Et	Et	4-Me	**3c**	95	96
5	2-Cyclohexenone	CH_2Ph	CH_2Ph	H	**3a**	45	57 (*R*)
6	2-Cyclohexenone	*i*-Pr	*i*-Pr	H	**3a**	11	4 (*S*)
7	2-Cyclohexenone	$-CH_2CH_2CH_2CH_2CH_2-$		H	**3a**	83	68 (*R*)
8	2-Cyclohexenone	$-CH_2CH_2NCH_2CH_2-$		H	**3a**	89	91 (*R*)
9	2-Cyclopentenone	Et	Et	H	**3d**	95	75
10	2-Cyclopentenone	Et	Et	3-Cl	**3e**	98	81
11	2-Cyclopentenone	Et	Et	3-MeO	**3f**	97	95
12	2-Cycloheptenone	Et	Et	H	**3g**	90	94
13	(*E*)-$C_5H_{11}CH{=}CHCOCH_3$	Et	Et	H	**3h**	96	0
14	(*E*)-$C_5H_{11}CH{=}CHCOCH_3$	Me	Et	H	**3h**	99	16 (*S*)
15	(*E*)-$C_5H_{11}CH{=}CHCOCH_3$	Me	*n*-Pr	H	**3h**	95	24 (*S*)
16	(*E*)-$C_5H_{11}CH{=}CHCOCH_3$	Me	CH_2Ph	H	**3h**	94	10 (*S*)
17	(*E*)-$C_5H_{11}CH{=}CHCOCH_3$	Me	Ph	H	**3h**	28	29 (*R*)
18	(*E*)-$C_5H_{11}CH{=}CHCOCH_3$	Me	*i*-Pr	H	**3h**	94	35 (*R*)
19	(*E*)-$C_5H_{11}CH{=}CHCOCH_3$	Me	1-Adamantyl	H	**3h**	55	47 (*R*)
20	(*E*)-$C_5H_{11}CH{=}CHCOCH_3$	Me	*t*-Bu	H	**3h**	41	70 (*R*)

[a] All reactions were carried out at 50 °C for 6 h in the presence of enone (1 mmol), arylboronic acid (1.5 mmol), $[Rh(coe)Cl]_2$ (0.015 mmol, 3 mol%), **4** (0.066 mmol) and KOH (1 mmol) in dioxane–H_2O (6/1).

[b] Isolated yields based on enones.

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

phosphoramidites derived from (*R*)-(+)-BINOL afforded (*R*)-3-phenylcyclohexanone for a series of dialkylamino derivatives (entries 1, 2, 5, 7 and 8), though the diisopropyl derivative exceptionally gave an *S* isomer with a very low selectivity (entry 6).

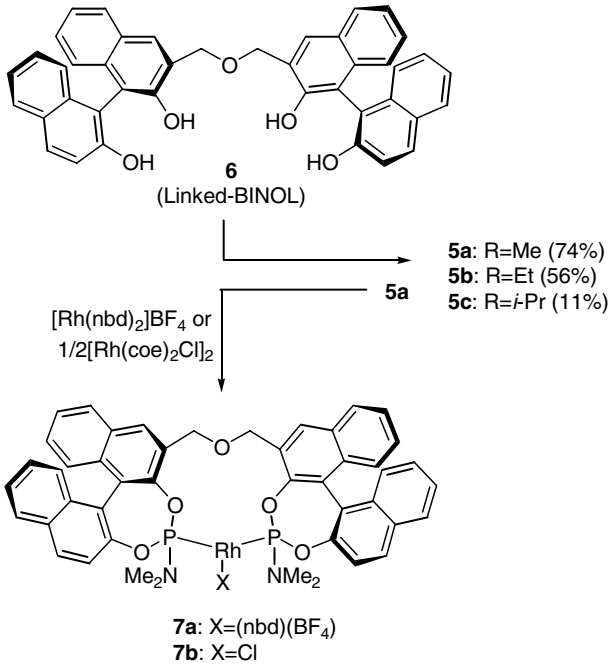
In contrast to the excellent performance of the *N*,*N*-diethylamino ligand for cyclic enones, it was not effective for acyclic enones (entries 13–20). Acyclic enones such as (*E*)-3-nonen-2-one unfortunately resulted in a racemic product (entry 13). Since the reactions were very slow when the bulkiness 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).

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 $[Rh(\mathbf{4a})(nbd)]BF_4$ (**7a**) as a fine powder. ^{31}P 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 $[Rh(Cl)(coe)_2]_2$, 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.



Scheme 2. Phosphoramidites based on linked-BINOL.

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%

Table 2
Effects of catalysts and bases[a]

Entry	Rhodium complex	Base	°C/h	Yield/%	% ee
1	1/2[RhCl(coe)]$_2$/**5a**	none	50/16	0	–
2	1/2[RhCl(coe)]$_2$/**5a**	Et_3N	50/16	46	97 (*R*)
3	1/2[RhCl(coe)]$_2$/**5a**	K_2CO_3	50/16	26	98 (*R*)
4	1/2[RhCl(coe)]$_2$/**5a**	KOH	50/16	84	98 (*R*)
5	$[Rh(nbd)_2]BF_4$/**5a**	Et_3N	50/16	94	99 (*R*)
6	$[Rh(nbd)_2]BF_4$/**5a**	Et_3N	25/0.5	99	99.6 (*R*)
7	$[Rh(nbd)_2]BF_4$/**5b**	Et_3N	25/2	62	83 (*R*)
8	$[Rh(nbd)_2]BF_4$/**5c**	Et_3N	25/2	Trace	–

[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_2O (6/1).

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_3N [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 Fig. 1. The addition of phenylboronic acid (1.5 equiv) 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, α,β-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 monophosphoramidites **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(I)-BINAP catalyst resulted in 83% ee for (*E*)-$C_5H_{11}CH{=}CHCOCH_3$ [5k], whereas $[Rh(nbd)_2]BF_4$/**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 (R^1) and a substituent on ketone carbonyls (R^3). The effect of R^1

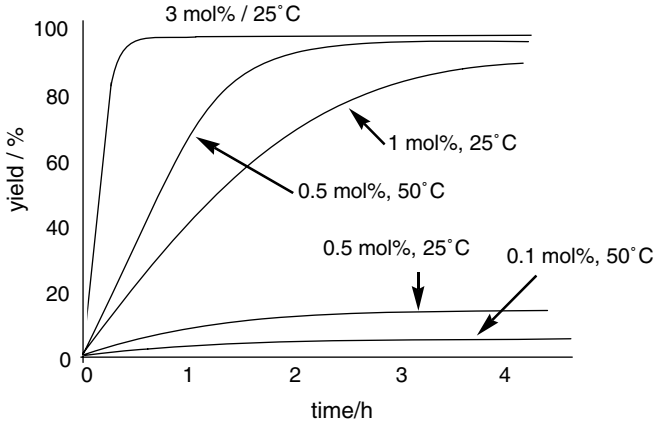


Fig. 1. Amounts of catalyst loading and reaction rates.

Table 3
1,4-Addition of arylboronic acid to α,β-unsaturated carbonyl compounds catalyzed by a Rh(+)-**5a** complex[a]

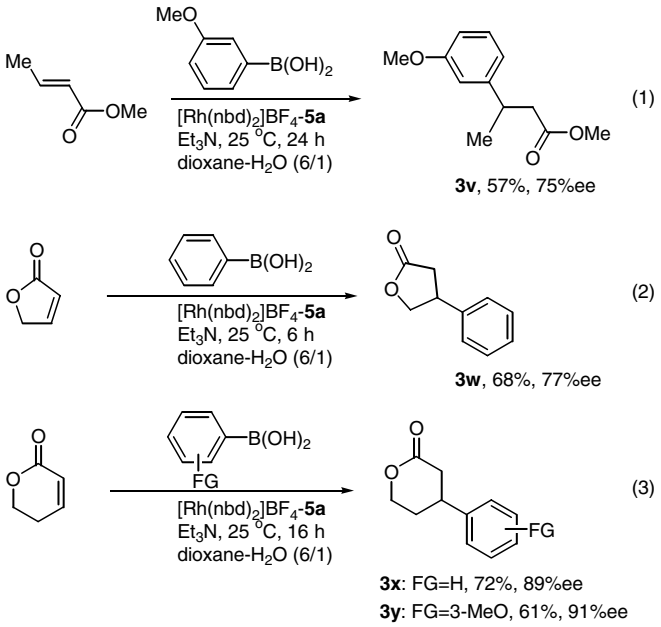
Entry	Carbonyl compound	$ArB(OH)_2$, X=	°C/h	Product no.	Yield/%[b]	% ee[c]
1	2-Cyclohexenone	H	25/0.5	**3a**	99	99.6 (*R*)
2	2-Cyclohexenone	3-MeO	25/2	**3b**	90	99.5 (*R*)
3	2-Cyclohexenone	4-MeO	25/2	**3i**	99	99.8
4	2-Cyclohexenone	3-Cl	25/2	**3j**	86	99.8
5	2-Cyclopentenone	3-Cl	25/2	**3e**	99	96
6	2-Cyclopentenone	4-MeO	25/2	**3k**	99	96
7	2-Cycloheptenone	H	25/2	**3g**	90	98
8	(*E*)-$C_5H_{11}CH{=}CHCOCH_3$	H	25/2	**3h**	87	74
9	(*E*)-$C_5H_{11}CH{=}CHCOCH_3$	H	5/48	**3h**	42	84
10	(*E*)-$C_5H_{11}CH{=}CHCOCH_3$	3-MeO	25/2	**3l**	98	80
11	(*E*)-$C_5H_{11}CH{=}CHCOCH_3$	3-MeO	5/48	**3l**	65	83
12	(*E*)-$C_5H_{11}CH{=}CHCOCH_3$	3-F	25/2	**3m**	97	81
13	(*E*)-$C_5H_{11}CH{=}CHCOPh$	3-MeO	25/2	**3n**	91	85
14	(*E*)-$(CH_3)_2CHCH{=}CHCOCH_3$	H	25/6	**3o**	80	92 (*R*)
15	(*E*)-$(CH_3)_2CHCH{=}CHCOCH_3$	3-MeO	25/16	**3p**	78	94
16	(*E*)-$(CH_3)_2CHCH{=}CHCOCH_3$	3-F	25/16	**3q**	71	90
17	(*E*)-$(CH_3)_2CHCH{=}CHCOC_6H_{11}$	3-MeO	25/2	**3r**	62	81
18	(*E*)-$(CH_3)_2CHCH{=}CHCOPh$	3-MeO	25/6	**3s**	98	85
19	(*E*)-$PhCH{=}CHCOCH_3$	3-MeO	25/2	**3t**	99	78
20	(*E*)-$PhCH{=}CHCOPh$	3-MeO	25/6	**3u**	98	66

[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.

increased in the order of Ph < n-C_5H_{11} < isopropyl for a series of methyl ketones (entries 10, 15 and 19). Steric balance between R^1 and R^3 was also an important factor affecting the selectivity. The selectivities were improved by increasing the bulkiness of R^3 for enones having a primary alkyl group at the β-carbon (entries 10 and 13), but enones possessing a hindered substituent (R^1 = isopropyl and phenyl) reduced the selectivity by increasing the bulkiness of R^3 groups (CH_3 > Ph > cyclohexyl) (entries 15, 17–20). 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, 5*H*-furan-2-one, and 5,6-dihydro-2*H*-pyran-2-one afforded **3v** (75% ee), **3w** (77% ee), **3x** (89% ee) and **3y** (91% ee), respectively, in the presence of $[Rh(nbd)_2]BF_3$-**5a** and Et_3N at room temperature. On the other hand, the use of monodentate phosphoramidites such as **4** (R^1, R^2 = Et) resulted in no reaction for 5*H*-furan-2-one and 35% yield and 72% ee for 5,6-dihydro-2*H*-pyran-2-one at 50 °C in the presence of Rh(acac)(coe)$_2$ and Et_3N in dioxane-H_2O (6/1).



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

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 $[Rh(nbd)_2]BF_4$ [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), NH_4Cl (0.01 g) and $P(NMe_2)_3$ (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 CH_2Cl_2/pentane to give **5a** as white crystals (74%). ^1H NMR (400 MHz, CD_2Cl_2): 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); ^{13}C NMR (100 MHz, CD_2Cl_2) 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; ^{31}P NMR (161.7 Hz, CD_2Cl_2) 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 $C_{46}H_{38}N_2O_5P_2$: 760.2256; found 760.2275; $[\alpha]_D^{21} = -522.5$ (*c* 0.56, $CHCl_3$).

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, CD_2Cl_2) δ = 0.75–0.91 (m, 12H), 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_2Cl_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_2Cl_2) $\delta = 150.1$; MS (*m*/*z*) 72 (31), 266 (38), 282 (51), 329 (100), 416 (15), 744 (28), 817 (10, $[M+H]^+$); exact mass calcd for $C_{50}H_{47}N_2O_5P_2$ ($[M+H]^+$): 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_3N (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_2NH (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_2Cl_2/pentane to give **5c** as white crystals (11%). ^{1}H NMR (400 MHz, CD_2Cl_2); δ 0.75–1.36 (m, 24H), 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_2Cl_2) $\delta = 24.4$, 24.5, 24.6, 24.7, 45.2, 45.3, 69.1, 69.2, 122.6, 124.7, 125.1, 126.1, 126.2, 127.0, 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, 167.9; ^{31}P NMR (161.7 MHz, CD_2Cl_2) $\delta = 150.7$; 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 $C_{54}H_{55}N_2O_5P_2$ ($[M+H]^+$): 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_2Cl_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_2Cl_2) $\delta = 142.4$ (d, $J_{Rh-P} = 248.9$ Hz); exact mass calcd for $C_{53}H_{46}BF_4N_2O_5P_2Rh$ ($[M^+-BF_4]$): 955.1938; found 955.1913.

4.3.2. Complex between $[Rh(coe)_2Cl]_2$ 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_2Cl_2 exhibited a signal at $\delta = 153.7$ (d, $J_{Rh-P} = 296.3$ Hz).

4.3.3. Complex between $[Rh(nbd)_2]BF_4$ and **5b**

^{31}P NMR (161.7 MHz) of a mixture between **5b** (0.05 mmol) and $[Rh(nbd)_2]BF_4$ (0.05 mmol) in CD_2Cl_2 exhibited a signal at $\delta = 142.3$ (d, $J_{Rh-P} = 248.9$ Hz).

4.3.4. Complex between $[Rh(nbd)_2]BF_4$ and **5c**

^{31}P NMR (161.7 MHz) of a mixture between **5c** (0.05 mmol) and $[Rh(nbd)_2]BF_4$ (0.05 mmol) in CD_2Cl_2 exhibited three signals at $\delta = 24.8$, 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** (R^1, R^2 = 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 (2.4 M, 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** ($[\alpha]_D^{21} = +20.4$ (*c* 1.03, $CHCl_3$)), **3b** ($[\alpha]_D^{22} = +13.6$ (*c* 0.98, $CHCl_3$)), **3c** ($[\alpha]_D^{22} = +17.3$ (*c* 0.96, $CHCl_3$)), **3d** ($[\alpha]_D^{21} = +79.9$ (*c* 1.13, $CHCl_3$)), **3e** ($[\alpha]_D^{21} = +71.4$ (*c* 0.92, $CHCl_3$)), **3f** ($[\alpha]_D^{22} = +58.8$ (*c* 1.07, $CHCl_3$)), **3g** ($[\alpha]_D^{23} = +59.3$ (*c* 1.00, $CHCl_3$)), and **3h** ($[\alpha]_D^{21} = +16.1$ (*c* 0.97, $CHCl_3$)).

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

A flask charged with $[Rh(nbd)_2]BF_4$ (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**)

$[\alpha]_D^{21} = +14.8$ (*c* 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) 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, $CDCl_3$) δ 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 $C_{15}H_{21}FO$: 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, $CDCl_3$) δ 0.81–0.84 (m, 3H), 1.21–1.27 (m, 6H), 1.59–1.73 (m, 2H), 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, $CDCl_3$) δ 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, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 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, $CDCl_3$) δ 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, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 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, $CDCl_3$) δ 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-phenylpentan-1-one (**3s**)*

$[\alpha]_D^{21} = -1.8$ (*c* 0.92, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 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, $CHCl_3$); ^1H 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-Phenyldihydrofuran-2-one (**3w**)*

$[\alpha]_D^{22} = -39.2$ (*c* 0.99, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ2.60 (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, $CHCl_3$); ^1H 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, $CHCl_3$); ^1H 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 $C_{12}H_{14}O_3$: 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** ($[\alpha]_D^{22} = +17.5$ (*c* 0.97, $CHCl_3$)), **3j** ($[\alpha]_D^{21} = +16.4$ (*c* 0.93, $CHCl_3$)), **3k** ($[\alpha]_D^{22} = +70.8$ (*c* 1.02, $CHCl_3$)), **3l** ($[\alpha]_D^{23} = +15.9$ (*c* 0.93, $CHCl_3$)), **3o** ($[\alpha]_D^{21} = +32.4$ (*c* 0.98, $CHCl_3$)), **3p** ($[\alpha]_D^{21} = +18.2$ (*c* 0.51, $CHCl_3$)), **3t** ($[\alpha]_D^{23} = -1.6$ (*c* 0.51, $CHCl_3$)) and **3u** ($[\alpha]_D^{22} = -4.4$ (*c* 0.91, $CHCl_3$)).

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