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Asymmetric 1,4-addition of organoboronic acids to α,β-unsaturated ketones and 1,2-addition to aldehydes catalyzed by a palladium complex with a ferrocene-based phosphine ligand

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ABSTRACT

A combination of palladium with ferrocene-based phosphine ligand with a carbon–bromine bond was found to be a good catalyst for the 1,4-addition of arylboronic acids to α,β-unsaturated ketones and the 1,2-addition to aldehydes. Using $Pd(dba)_2$ and (S,R_p)-[1-(2-bromoferrocenyl)ethyl]diphenylphosphine (S,R_p)-**1**, 3-phenylcyclohexanone was obtained from the reaction of 2-cyclohexen-1-one with phenylboronic acid in the presence of K_2CO_3 in toluene at room temperature after 3 h in 92% yield with 76% ee. In the 1,2-addition of 4-methylphenylboronic acid to benzaldehyde, 96% of (4-methylphenyl)phenylmethanol was afforded after 24 h, while the enantiomeric excess was only 6%.

1. Introduction

Transformations using an organometallic nucleophile catalyzed by transition metal complexes are indispensable techniques in present organic syntheses. Among them, various kinds of reactions using organoboronic acid have been developed.[1] An asymmetric carbon–carbon bond-forming reaction using organoboronic acid is especially useful for making a skeleton of optically active organic compounds because of their commercial availability, stability, nontoxicity, and allowance for many functional groups.[2]

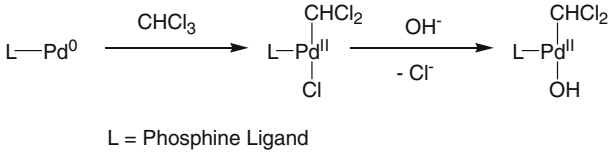
The combination of rhodium catalysts and organoboronic acids has emerged as a powerful and ideal catalytic system in carbon–carbon bond-forming reactions. The 1,4-additions of aryl- and 1-alkenylboron compounds to α,β-unsaturated carbonyl compounds,[3,4] aldehydes,[5] and aldimines[6] have been developed. In the last few years, various groups have reported the use of inexpensive metals in comparison to rhodium, such as nickel,[7] ruthenium,[8] platinum,[9] and palladium[10] catalysts for the 1,4-additions to α,β-unsaturated carbonyl compounds with organoboron compounds. Additionally, copper,[11] iron,[12] platinum,[13] ruthenium,[14] palladium,[15] and nickel[16] have been reported to catalyze the 1,2-additions of organoboron compounds to aldehydes, ketones, imines, and nitriles. However, these addition reactions with organoboron compounds by metals other than rhodium are still under development.

We have also developed a new palladium catalyst system for 1,2- and 1,4-addition reactions.[10e,15b] In our system, chloroform is a crucial activation reagent for conventional palladium species. We also developed a new catalyst system combined with a palladium precursor with a phosphine having a carbon–bromine bond by utilizing the chloroform effect and reported the preliminary results.[10f] Herein, we report the addition reaction of organoboronic acid to α,β-unsaturated ketones and to aldehydes catalyzed by a combination of palladium and ferrocene-based phosphine ligands.

2. Results and discussion

2.1. Design of ferrocene ligand

In our previous research, conventional palladium complexes were activated by the addition of a catalytic amount of chloroform in the presence of triphenylphosphine for the reaction of 1,2- and 1,4-additions of arylboronic acids to α,β-unsaturated carbonyl compounds and aldehydes.[10e,15b] The best catalytic activity was achieved using one equimolar amount of triphenylphosphine to a palladium atom. The oxidative addition of chloroform to palladium is considered essential for the activation (Scheme 1). From these hypotheses, a ferrocene-based phosphine with a carbon–bromine



Scheme 1. Plausible formation of catalytically active species.

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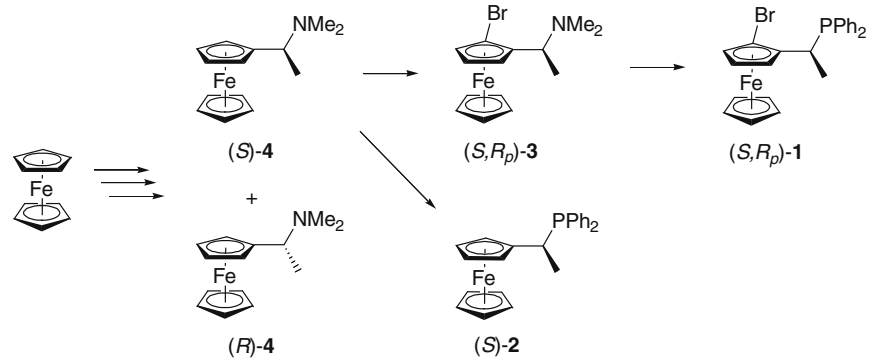
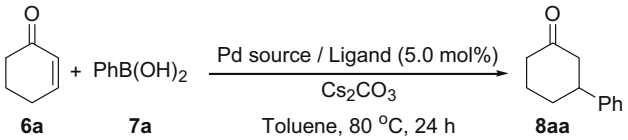


Scheme 2. Preparation of compounds **1**–**4**.

bond **1** was selected. Ferrocene-based ligand **1** was readily accessible by a reported procedure (Scheme 2).[17]

2.2. Palladium-catalyzed addition reaction of phenylboronic acid to 2-cyclohexen-1-one

We screened the use of phosphine and ferrocene-based ligands **1**–**4** in the palladium-catalyzed addition reaction of phenylboronic acid **7a** to 2-cyclohexen-1-one **6a** (Eq. 1). All the reactions were performed with 5 mol% of Pd source and racemic ligand. The results are summarized in Table 1.



(1)

In the presence of triphenylphosphine, the reaction did not proceed (Table 1, entry 1). Bidentate phosphine ligands such as DPPP, DPPB, DPPF, and BINAP were not effective at all (Table 1, entries 2–5). The reaction progressed when a ferrocene-based phosphine ligand with a carbon–bromine bond [1-(2-bromoferrocenyl)ethyl]-diphenylphosphine **1** was employed, and 1,4-addition product 3-phenylcyclohexanone **8aa** was obtained in 82% isolated yield (Table 1, entry 6). On the other hand, the yield was dramatically decreased with ligand **2** which had no carbon–bromine bond (Table 1, entry 7). The reaction did not proceed when using ligand **3** which has no phosphine substituent but a carbon–bromine bond (Table 1, entry 8). Moreover, the combination of triphenylphosphine and ligand **3** gave no reaction at all. These results indicate that the effective ligand for this addition reaction should simultaneously have a carbon–bromine bond and a phosphine substituent. In addition, we examined other Pd sources such as $PdCl_2$ and $Pd(OAc)_2$ (Table 1, entries 11–13). However, the combination of $PdCl_2$, $Pd(OAc)_2$, and ligand **1** or **2** did not give good results.

Table 1
Palladium-catalyzed 1,4-addition reaction of phenylboronic acid to 2-cyclohexen-1-one[a]

Entry	Ligand	Pd source	Yield[b] (%)
1	PPh_3	$Pd(dba)_2$	0
2	DPPP[c]	$Pd(dba)_2$	0
3	DPPB[d]	$Pd(dba)_2$	0
4	DPPF[e]	$Pd(dba)_2$	0
5	*rac*-BINAP[f]	$Pd(dba)_2$	0
6	*rac*-**1**	$Pd(dba)_2$	82[g]
7	*rac*-**2**	$Pd(dba)_2$	3
8	*rac*-**3**	$Pd(dba)_2$	0
9	*rac*-**3** + PPh_3	$Pd(dba)_2$	0
10	*rac*-**4**	$Pd(dba)_2$	0
11	*rac*-**1**	$PdCl_2$	8
12	*rac*-**1**	$Pd(OAc)_2$	18
13	*rac*-**2**	$PdCl_2$	17

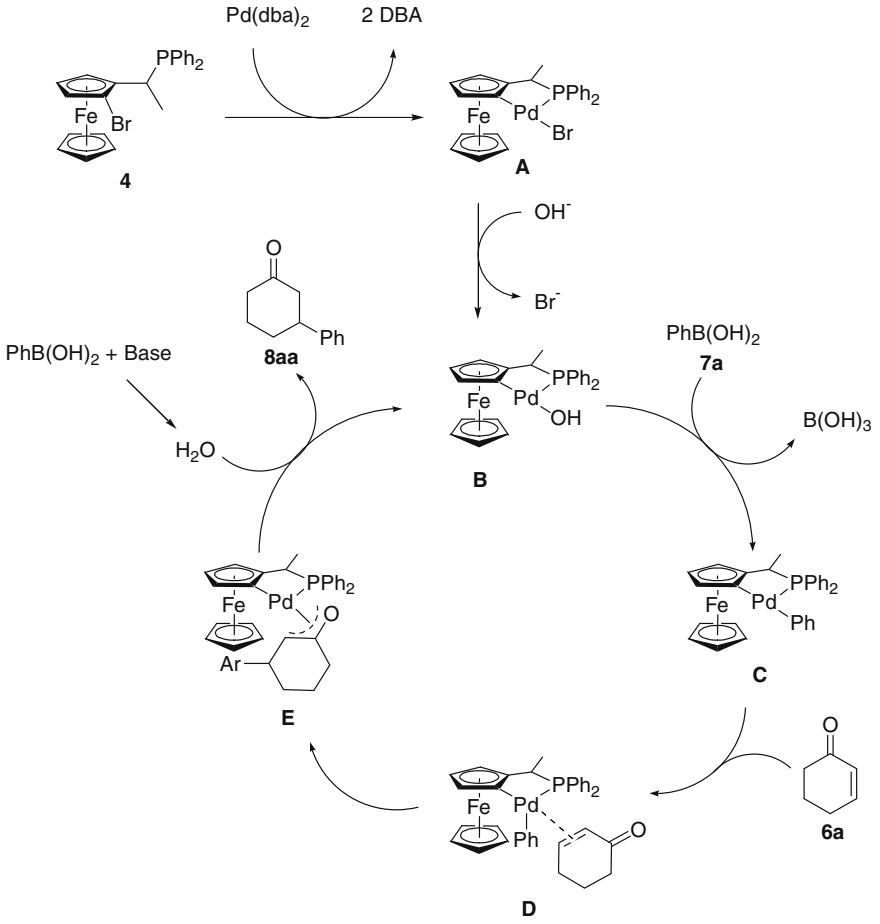
[a] The reaction was carried out with 2-cyclohexen-1-one (1.0 mmol), phenylboronic acid (2.0 mmol), a Pd source (0.05 mmol), ligand (0.05 mmol), and Cs_2CO_3 (1.0 mmol) in 2 mL of toluene at 80 °C for 24 h.
[b] Determined by ^1H NMR.
[c] 1,3-Bisdiphenylphosphinopropane.
[d] 1,4-Bisdiphenylphosphinobutane.
[e] 1,1′-Bisdiphenylphosphinoferrocene.
[f] 2,2′-Bis(diphenylphosphino)-1,1′-binaphthyl.
[g] Isolated yield.

2.3. Plausible reaction mechanism

From the above results, we propose this reaction's catalytic cycle in Scheme 3. First, palladacycle **A**, which is generated by the oxidative addition of a carbon–bromine bond in ligand **1** to $Pd(dba)_2$, is converted to hydroxypalladium species **B** by ligand exchange with a hydroxide anion. Then the transmetallation between phenylboronic acid **7a** and hydroxypalladium species **B** occurs to generate phenylpalladium intermediate **C**. The coordination and the insertion of the 2-cyclohexen-1-one **6a** into the carbon–palladium bond afford intermediate **E** which is hydrolyzed by water generated from boronic acid and the base to give the corresponding carbonyl compound 3-phenylcyclohexanone **8aa** to regenerate the hydroxypalladium species **B**

2.4. Optimization of the reaction conditions

We optimized the reaction conditions using chiral ligand (S,R_p)-**1** (Table 2). First, the reaction was carried out in the presence of Cs_2CO_3 at 80 °C for 24 h, and the desired product **8aa** was obtained in 82% yield with 42% ee. The product **8aa** was gained in identical yield with similar ee at 60 °C, and higher enantioselectivity was recorded at room temperature even with a similar yield of the product (Table 2, entries 1–3). At a lower temperature (0 °C), the reaction did not proceed at all. We found that the reaction was relatively quick, that is, when the reaction time was shortened from 24 h to 6, 3, and 1 h, it proceeded smoothly to give the product in 81%, 80%, and 60% yields, respectively, with the same enantioselectivities (Table 2, entries 3–6). These results allowed us to conduct the reaction for 3 h. In the experiments to determine the solvent effect, toluene, ethanol, and 1,4-dioxane were good solvents with regard to yield and enantioselectivity (Table 2, entries 5, 9, and 10). When DMF and acetonitrile were used as solvents, both yield and enantioselectivity decreased (Table 2, entries 8 and 11). When phenylboronic acid was examined, the kind of base was crucial for reactivity and selectivity. Therefore, we examined the base effect. Bases which included potassium usually gave



Scheme 3. Plausible reaction mechanism.

Table 2
Optimization of reaction condition[a]

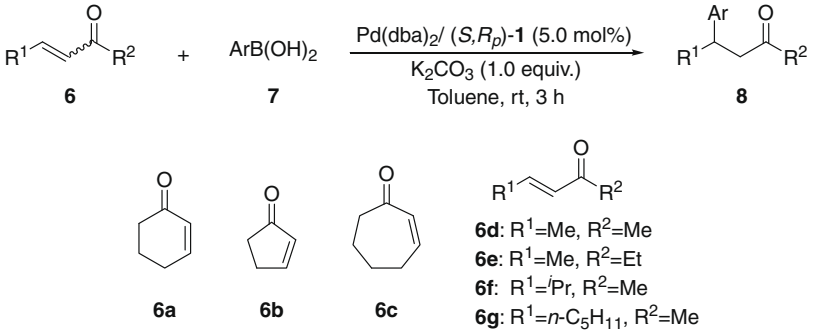
Entry	Temp (°C)	Time (h)	Solvent	Base	Yield[b] (%)	ee[c] (%)
1	80	24	Toluene	Cs_2CO_3	82	42 (*S*)
2	60	24	Toluene	Cs_2CO_3	83	46 (*S*)
3	rt	24	Toluene	Cs_2CO_3	79	66 (*S*)
4	rt	6	Toluene	Cs_2CO_3	81	67 (*S*)
5	rt	3	Toluene	Cs_2CO_3	80	66 (*S*)
6	rt	1	Toluene	Cs_2CO_3	60	65 (*S*)
7	rt	3	THF	Cs_2CO_3	70	62 (*S*)
8	rt	3	DMF	Cs_2CO_3	32	49 (*S*)
9	rt	3	Ethanol	Cs_2CO_3	77	66 (*S*)
10	rt	3	1,4-Dioxane	Cs_2CO_3	80	61 (*S*)
11	rt	3	Acetonitrile	Cs_2CO_3	48	30 (*S*)
12	rt	3	Toluene	K_2CO_3	92	76 (*S*)
13	rt	3	Toluene	Na_2CO_3	52	73 (*S*)
14	rt	3	Toluene	$CaCO_3$	17	75 (*S*)
15	rt	3	Toluene	K_3PO_4	85	72 (*S*)
16	rt	3	Toluene	KOH	91	75 (*S*)
17	rt	3	Toluene	$Ca(OH)_2$	64	76 (*S*)
18	rt	3	Toluene	KO^{t}Bu	69	66 (*S*)

[a] The reaction was carried out with 2-cyclohexen-1-one (1.0 mmol), phenylboronic acid (2.0 mmol), $Pd(dba)_2$ (0.05 mmol), ligand **1** (0.05 mmol), and base (1.0 mmol) in 2 mL of solvent.
[b] Isolated yield.
[c] Determined by HPLC.

better enantioselectivities than the common base Cs_2CO_3 for the reaction using phenylboronic acid. Among the bases tested, K_2CO_3 gave the best yield and enantioselectivity (Table 2, entries 5 and 12–18). When Na_2CO_3 was used, the product yield became lower. The use of $CaCO_3$ made the reaction sluggish, while the use of $Ca(OH)_2$ afforded the product in better yield. The optimum reaction conditions were finalized when the reaction was carried out in toluene in the presence of K_2CO_3 at room temperature for 3 h.

2.5. 1,4-Addition of arylboronic acid to α,β-unsaturated ketones

After the determination of the optimized reaction conditions, the scope of this palladium-catalyzed asymmetric 1,4-addition of arylboronic acid **7** to α,β-unsaturated ketones **6** was examined (Scheme 4). The results are summarized in Table 3. First, 2-cyclohexen-1-one **6a** was used as an α,β-unsaturated ketone, and the substituent effects on 4-carbon in phenylboronic acid were tested. When such substrates with electron-donating groups such as methyl, methoxy, and *tert*-butyl were employed for this reaction, almost identical yields and enantioselectivities were recorded (Table 3, entries 1–4). The enantioselectivity increased to 79% from the reaction with 4-*tert*-butylphenylboronic acid **7d**. The reaction with 4-trifluoromethylphenylboronic acid **7e** proceeded smoothly in 81% yield with very low enantioselectivity, 4% ee, and the reaction with 4-fluorophenylboronic acid **7f** proceeded slowly with good enantioselectivity, 68% ee. 2-Naphthylboronic acid **7g** was examined for this reaction and converted to 3-(2-naphthyl)cyclohexanone **8ag** in 80% yield with 42% ee. Then several cyclic and acyclic α,β-unsaturated ketones were allowed to react with phenylboronic acid. In comparison with 2-cyclohexen-1-one **6a**, the reaction of 2-cyclophenten-1-one **6b** and 2-cycloepten-1-one **6c**



Scheme 4. 1,4-Additon of arylboronic acids **7** to α,β-unsaturated ketones **6** catalyzed by palladium-(S,R_p)-**1**.

Table 3
1,4-Addition of arylboronic acids **7** to α,β-unsaturated ketones **6** catalyzed by palladium-(S,R_p)-**1**[a]

Entry	Substrate **6**	Boronic acid **7**		Ketone **8**	Yield[b] (%)	ee[c] (%)
			R=			
1	**6a**	**7a**	C_6H_5	**8aa**	92	76 (*S*)
2	**6a**	**7b**	4-$CH_3C_6H_4$	**8ab**	89	78 (*S*)
3	**6a**	**7c**	4-$CH_3OC_6H_4$	**8ac**	83	76 (*S*)
4	**6a**	**7d**	4-*tert*-$C_4H_9C_6H_4$	**8ad**	92	79 (*S*)
5	**6a**	**7e**	4-$CF_3C_6H_4$	**8ae**	81	4 (*S*)
6	**6a**	**7f**	4-FC_6H_4	**8af**	45	68 (*S*)
7	**6a**	**7g**	1-Naphthyl	**8ag**	80	42 (*S*)
8	**6b**	**7a**	C_6H_5	**8ba**	94	54 (*S*)
9	**6c**	**7a**	C_6H_5	**8ca**	90	38 (*S*)
10	**6d**	**7a**	C_6H_5	**8da**	53	44 (*S*)
11	**6e**	**7a**	C_6H_5	**8ea**	62	47 (*S*)
12	**6f**	**7a**	C_6H_5	**8fa**	70	52 (*S*)
13	**6g**	**7a**	C_6H_5	**8ga**	99	42 (*S*)

[a] The reaction was carried out with α,β-unsaturated ketone (1.0 mmol), phenylboronic acid (2.0 mmol), $Pd(dba)_2$ (0.05 mmol), ligand **1** (0.05 mmol), and K_2CO_3 (1.0 mmol) in 2 mL of toluene at rt for 3 h.
[b] Isolated yield.
[c] Determined by HPLC.

gave the corresponding products in similar yields with lower enantioselectivities of 54% and 38% ee, respectively. Acyclic substrates **6d**–**6g** also smoothly reacted with phenylboronic acid **7a** to give the desired products **8da**–**8ga** in moderate to good yields but with lower enantioselectivities than cyclic **6a** but with similar selectivities to the five- and seven-membered substrates **6b** and **6c**.

2.6. 1,2-Addition of arylboronic acid to aldehydes

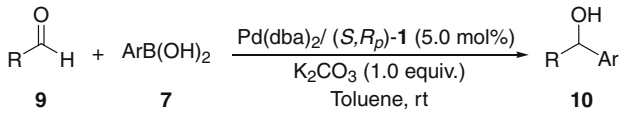
This catalyst system was applied to the 1,2-addition of arylboronic acids to aldehydes, and the results are summarized in Table 4. First, the addition of phenylboronic acid **7a** to benzaldehyde **9a** was tested under the standard reaction condition described in the 1,4-addition reaction. The reaction proceeded successfully to give the desire product diphenylmethanol **10aa** in high yield (Table 4, entry 1), but slower than the 1,4-addition. Therefore, the reaction time was prolonged to 24 h as a standard reaction condition. The addition of arylboronic acids **7b**–**d** and **7g** was proceeded smoothly to give the corresponding diarylmethanols **10ab**–**10ad** and **10ag** in high yield (Table 4, entries 2–5). Unfortunately, enantioselectivity was quite low. Various arylaldehydes **9b**–**9i** underwent the addition reaction of phenylboronic acid **7a**. All products **10ba**–**10ia** were obtained in high yield with low enantioselectivity (Table 4, entries 6–13). Even with low enantioselectivity, the reaction of aldehyde **9b** and boronic acid **7a** produced the product **10ba** with the same structure as that of **10ab**,

Table 4
1,2-Additon of arylboronic acids **7** to aldehydes **9** catalyzed by palladium-**1**[a]

Entry	Aldehyde		Boronic acid	Product	Yield[b] (%)	ee[c] (%)
	R=					
1	**9a**	C_6H_5	**7a**	**10aa**	95	—
2	**9a**	C_6H_5	**7b**	**10ab**	96	6 (*R*)
3	**9a**	C_6H_5	**7c**	**10ac**	81	8 (*R*)
4	**9a**	C_6H_5	**7d**	**10ad**	92	4 (−)
5	**9a**	C_6H_5	**7g**	**10ag**	71	11 (*R*)
6	**9b**	4-$CH_3C_6H_4$	**7a**	**10ba**	78	5 (*S*)
7	**9c**	4-CNC_6H_4	**7a**	**10ca**	93	9 (*S*)
8	**9d**	4-$NO_2C_6H_4$	**7a**	**10da**	80	8 (*S*)
9	**9e**	4-$CH_3OC_6H_4$	**7a**	**10ea**	83	11 (*S*)
10	**9f**	4-ClC_6H_4	**7a**	**10fa**	>99	5 (*S*)
11	**9g**	4-BrC_6H_4	**7a**	**10ga**	51	7 (*S*)
12	**9h**	1-Naphthyl	**7a**	**10ha**	91	6 (*S*)
13	**9i**	2-Naphthyl	**7a**	**10ia**	90	11 (*S*)
14	**9j**	Cyclohexyl	**7a**	**10ja**	78	3 (*R*)
15	**9k**	*tert*-C_4H_9	**7a**	**10ka**	54	4 (*R*)
16	**9l**	*iso*-C_3H_7	**7a**	**10la**	19	2 (*R*)
17	**9m**	2-Furyl	**7a**	**10ma**	68	3 (*R*)
18	**9n**	2-Thiophenyl	**7a**	**10na**	61	6 (*R*)

[a] The reaction was carried out with an aldehyde (1.0 mmol), phenylboronic acid (2.0 mmol), $Pd(dba)_2$ (0.05 mmol), ligand **1** (0.05 mmol), and K_2CO_3 (1.0 mmol) in 2 mL of toluene at rt for 24 h.
[b] Isolated yield.
[c] Determined by HPLC.

and the product had an opposite configuration (Table 4, entries 2 and 6). Similarly, **10ea** and **10ha** had the opposite configurations of **10ac** and **10ag** (Table 4, entries 3 and 9, 5, and 12). Ligand **1** has the potential to control the configuration of the products. A high yield was also observed from the reaction of cyclohexanecarbaldehyde **9j** (Table 4, entries 14). Acyclic alkylaldehydes **9k** and **9l** produced the **10ka** and **10la** in moderate to low yields (Table 4, entries 15 and 16). In addition, furan-2-carbaldehyde **9m** and thiophene-2-carbaldehyde **9n** were converted to the desired products in moderate yields (Scheme 5).



Scheme 5. 1,2-Addition of arylboronic acids **7** to aldehydes **9** catalyzed by palladium-**1**.

3. Conclusion

We have achieved an efficient addition reaction to α,β-unsaturated ketones and aldehydes with an arylboronic acid catalyzed by palladium complex having a ferrocene-based phosphine ligand,

which has an oxidative addition ability to the palladium center. The asymmetric 1,4-addition of arylboronic acids to α,β-unsaturated ketones proceeded smoothly at room temperature for 3 h to give the addition products in good yields with good enantioselectivities. For the 1,2-addition of arylboronic acids to aldehydes, the products were obtained in high yields but the enantioselectivities were low. Further applications and the development of efficient ligands continue.

4. Experimental

4.1. General procedure

All reactions with air- or moisture-sensitive materials were carried out under argon using standard Schlenk techniques. All compounds are commercially available, and are used without purification. All solvents were dried by standard methods and distilled under argon. Nuclear magnetic resonance spectra were measured on a Varian MERCURY plus 300-4N spectrometer (^{1}H: 300 MHz, ^{13}C: 75 MHz). Exact mass spectrometry was performed on a JEOL JMS-700 (FAB-MS, matrix: m-NBA, reference: PEG-400). All substrates are commercially available and are used without purification. *N,N*-Dimethy-1-ferrocenylethylamine **4**, (*S*,R_p)-*N,N*-dimethyl-1-(2-bromoferrocenyl)ethylamine (*S*,R_p)-**3**, (*S*,R_p)-[1-(2-Bromoferrocenyl)ethyl]diphenylphosphine (*S*,R_p)-**1**, and (*S*,R_p)-(1-ferrocenylethyl)diphenylphosphine ((*S*,R_p)-**2**) were prepared according to the literature.[17]

4.2. 1,4-Addition of organoboronic acid to α,β-unsaturated ketone

In a 80 mL Schlenk tube were placed the α,β-unsaturated ketone (1.0 mmol), arylboronic acid (2.0 mmol), $Pd(dba)_2$ (0.0288 g, 0.05 mmol), ligand (0.0239 g, 0.05 mmol), K_2CO_3 (0.1382 g, 1.0 mmol), and solvent (2 mL). The resulting solution was stirred at room temperature for 3 h. The analytically pure ketone was obtained by chromatography on silica gel.

4.3. 1,2-Addition of organoboronic acid to aldehyde

In a 80 mL Schlenk tube were placed the aldehyde (1.0 mmol), arylboronic acid (2.0 mmol), $Pd(dba)_2$ (0.0288 g, 0.05 mmol), ligand (0.0239 g, 0.05 mmol), K_2CO_3 (0.1382 g, 1.0 mmol), and solvent (2 mL). The resulting solution was stirred at room temperature for 24 h. The analytically pure alcohol was obtained by chromatography on silica gel.

4.4. (*S*)-3-Phenylcyclohexanone 8aa[4a]

^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 1.69–1.90 (m, 2H), 2.07–2.17 (m, 2H), 2.31–2.60 (m, 4H), 2.94–3.05 (m, 1H), 7.19–7.23 (m, 3H), 7.29–7.34 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 25.9, 33.1, 41.5, 45.1, 49.3, 126.8, 126.9, 128.9, 144.5, 211.2. GC–MS (*M*/*Z*) 174. The enantiomeric ratio was determined by HPLC using a chiral column (Daicel Chiralcel OD-H), hexane/2-propanol 98:2, 0.5 mL/min, 254 nm, 30.6 min (major), 33.0 min (minor). $[\alpha]_D^{25} = -17.2$ (*c* 1.05, $CHCl_3$) for 76% ee [lit.: $[\alpha]_D^{20} = -21$ (*c* 0.96, $CHCl_3$) for 97% ee in the (*S*)-isomer].

4.5. (*S*)-3-(4-Methyphenyl)cyclohexanone 8ab[18]

^{1}H NMR (300 MHz, $CDCl_3$) δ 1.69–1.86 (m, 2H), 2.00–2.14 (m, 2H), 2.30 (s, 3H), 2.30–2.58 (m, 4H), 2.89–2.99 (m, 1H), 7.06–7.13 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.4, 25.9, 33.2, 41.5, 44.7, 49.4, 126.6, 129.5, 136.3, 141.6, 211.1. GC–MS (*M*/*Z*) 188. The enantiomeric ratio was determined by HPLC using a chiral column (Daicel Chiralpak AD-H), hexane/2-propanol 98:2, 0.5 mL/min, 254 nm, 13.0 min (major), 14.6 min (minor). $[\alpha]_D^{25} = -12.0$ (*c* 1.00, $CHCl_3$) for 78% ee [lit.: $[\alpha]_D^{23} = -15.0$ (*c* 1.09, $CHCl_3$) for 94% ee in the (*S*)-isomer].

4.6. (*S*)-3-(4-Methoxyphenyl)cyclohexanone 8ac[18]

^{1}H NMR (300 MHz, $CDCl_3$) δ 1.69–1.86 (m, 2H), 2.01–2.15 (m, 2H), 2.30–2.58 (m, 4H), 2.89–2.98 (m, 1H), 3.76 (s, 3H), 6.82–6.87 (m, 2H), 7.09–7.14 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 25.7, 33.2, 41.5, 44.3, 49.3, 55.5 126.7, 136.7, 158.3 211.2. GC–MS (*M*/*Z*) 204. The enantiomeric ratio was determined by HPLC using a chiral column (Daicel Chiralpak AD-H), hexane/2-propanol 90:10, 0.5 mL/min, 254 nm, 13.7 min (major), 14.6 min (minor). $[\alpha]_D^{25} = -11.0$ (*c* 1.00, $CHCl_3$) for 76% ee [lit.: $[\alpha]_D^{23} = -14.2$ (*c* 1.02, $CHCl_3$) for 92% ee in the (*S*)-isomer].

4.7. (*S*)-3-(4-*t*-Butylphenyl)cyclohexanone 8ad[19]

^{1}H NMR (300 MHz, $CDCl_3$) δ 1.31 (s, 9H), 1.74–1.89 (m, 2H), 2.06–2.18 (m, 2H), 2.31–2.63 (m, 4H), 2.93–3.04 (m, 1H), 7.13–7.16 (m, 2H), 7.33–7.35 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 25.9, 31.8, 33.2, 34.8, 41.6, 44.6, 49.3, 125.8, 126.4, 141.5, 149.6, 211.3. GC–MS (*M*/*Z*) 230. The enantiomeric ratio was determined by HPLC using a chiral column (Daicel Chiralpak AS-H), hexane/2-propanol 98:2, 0.5 mL/min, 254 nm, 22.9 min (minor), 30.5 min (major). $[\alpha]_D^{25} = -12.0$ (*c* 1.00, $CHCl_3$) for 79% ee [lit.: $[\alpha]_D^{20} = +11.9$ (*c* 0.68, $CHCl_3$) for 99% ee in the (*R*)-isomer].

4.8. (*S*)-3-(4-Trifluoromethylphenyl)cyclohexanone 8ae[18]

^{1}H NMR (300 MHz, $CDCl_3$) δ 1.77–1.94 (m, 2H), 2.07–2.18 (m, 2H), 2.34–2.62 (m, 4H), 3.05–3.12 (m, 1H), 7.32–7.25 (m, 2H), 7.56–7.59 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 25.7, 32.8, 41.4, 44.8, 48.8, 126.0, 127.2, 129.1, 148.3, 210.6. ^{19}F NMR (282 MHz, $CDCl_3$) δ −62.98. GC–MS (*M*/*Z*) 242. The enantiomeric ratio was determined by HPLC using a chiral column (Daicel Chiralcel OD-H), hexane/2-propanol 98:2, 0.5 mL/min, 254 nm, 18.7 min (minor), 19.9 min (major). $[\alpha]_D^{25} = -1.0$ (*c* 1.00, $CHCl_3$) for 4% ee [lit.: $[\alpha]_D^{23} = -11.4$ (*c* 0.95, $CHCl_3$) for 95% ee in the *S*-isomer].

4.9. (*S*)-3-(4-Fluorophenyl)cyclohexanone 8af[20]

^{1}H NMR (300 MHz, $CDCl_3$) δ 1.72–1.88 (m, 2H), 2.04–2.18 (m, 2H), 2.31–2.59 (m, 4H), 2.93–3.02 (m, 1H), 6.99 (m, 2H), 7.13–7.19 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 25.7, 33.2, 41.4, 44.3, 49.4, 115.6, 128.1, 140.2, 161.6, 210.8. ^{19}F NMR (282 MHz, $CDCl_3$) δ −161.6. GC–MS (*M*/*Z*) 192. The enantiomeric ratio was determined by HPLC using a chiral column (Daicel Chiralpak AD-H), hexane/2-propanol 99:1, 0.5 mL/min, 254 nm, 20.3 min (major), 27.1 min (minor). $[\alpha]_D^{25} = -17.7$ (*c* 0.51, $CHCl_3$) for 68% ee [lit.: $[\alpha]_D^{20} = -21.3$ (*c* 0.50, $CHCl_3$) for 88% ee in the (*S*)-isomer].

4.10. (*S*)-3-(1-Naphthyl)cyclohexanone 8ag[18]

^{1}H NMR (300 MHz, $CDCl_3$) δ 1.86–2.08 (m, 2H), 2.15–2.30 (m, 2H), 2.41–2.82 (m, 4H), 3.81–3.92 (m, 1H), 7.38–7.57 (m, 4H), 7.76 (d, *J* = 8.1 Hz, 1H), 7.88 (d, *J* = 8.9 Hz, 1H), 8.05 (d, *J* = 8.4 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 25.7, 32.5, 39.6, 41.7, 48.8, 122.8, 125.8, 126.4, 127.4, 129.3, 131.1, 134.1, 140.2, 211.3. GC–MS (*M*/*Z*) 224. The enantiomeric ratio was determined by HPLC using a chiral column (Daicel Chiralpak AD-H), hexane/2-propanol 99:1, 0.5 mL/min, 230 nm, 33.1 min (major), 36.2 min (minor). $[\alpha]_D^{25} = -39.0$ (*c* 1.00, $CHCl_3$) for 42% ee [lit.: $[\alpha]_D^{23} = -31.7$ (*c* 0.97, $CHCl_3$) for 52% ee in the (*S*)-isomer].

4.11. (*S*)-3-Phenylcyclopentanone 8ba[4a]

^{1}H NMR (300 MHz, $CDCl_3$) δ 1.88–2.02 (m, 2H), 2.19–2.47 (m, 4H), 2.63 (dd, J = 18.6 Hz, 7.5 Hz, 1H), 3.32–3.44 (m, 1H), 7.18–7.23 (m, 3H), 7.29–7.33 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 31.5, 39.2, 42.5, 46.1, 126.9, 128.8, 143.2, 218.5. GC–MS (*M*/*Z*) 160. The enantiomeric ratio was determined by HPLC using a chiral column (Daicel Chiralcel OB-H), hexane/2-propanol 99.5:0.5, 0.7 mL/min, 210 nm, 37.0 min (major), 40.2 min (minor). $[\alpha]_D^{25} = -45.5$ (*c* 1.01, $CHCl_3$) for 54% ee [lit.: $[\alpha]_D^{20} = -92$ (*c* 0.96, $CHCl_3$) for 97% ee in the (*S*)-isomer].

4.12. (*S*)-3-Phenylcycloheptanone 8ca[20]

^{1}H NMR (300 MHz, $CDCl_3$) δ 1.43–1.58 (m 1H), 1.66–1.82 (m, 2H), 1.96–2.14 (m, 3H), 2.86–2.99 (m, 2H), 7.16–7.24 (m, 3H), 7.26–7.31 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 24.3, 29.4, 39.4, 42.9, 44.1, 51.4, 126.5, 128.8, 147.1, 213.5. GC–MS (*M*/*Z*) 188. The enantiomeric ratio was determined by HPLC using a chiral column (Daicel Chiralcel OD-H), hexane/2-propanol 95:5, 0.7 mL/min, 210 nm, 10.7 min (major), 11.8 min (minor). $[\alpha]_D^{25} = -28.2$ (*c* 1.10, $CHCl_3$) for 38% ee [lit.: $[\alpha]_D^{20} = -61.3$ (*c* 1.00, $CHCl_3$) for 90% ee in the (*S*)-isomer].

4.13. (*S*)-4-Phenyl-2-pentanone 8da[21]

^{1}H NMR (300 MHz, $CDCl_3$) δ 1.23 (d, J = 6.9 Hz, 3H), 2.01 (s, 3H), 2.61 (dd, J = 16.2 Hz, 7.9 Hz, 1H), 2.71 (dd, J = 16.2 Hz, 6.5 Hz, 1H), 3.26 (m, 1H), 7.16–7.25 (m, 5H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.9, 30.4, 35.3, 51.9, 126.2, 126.6, 128.4, 146.0, 207.6. GC–MS (*M*/*Z*) 162. The enantiomeric ratio was determined by HPLC using a chiral column (Daicel Chiralcel OJ-H), hexane/2-propanol 99:1, 0.5 mL/min, 210 nm, 24.9 min (major), 26.4 min (minor). $[\alpha]_D^{25} = 14.0$ (*c* 0.50, $CHCl_3$) for 44% ee [lit.: $[\alpha]_D^{20} = 38.8$ (*c* 0.4, $CHCl_3$) for 97% ee in the (*S*)-isomer].

4.14. (*S*)-5-Phenyl-3-hexanone 8ea[22]

^{1}H NMR (300 MHz, $CDCl_3$) δ 0.96 (t, J = 7.2 Hz, 3H), 1.24 (d, J = 6.9 Hz, 3H), 2.21–2.38 (m, 2H), 2.57–2.74 (m, 2H), 3.25–3.37 (m, 1H), 7.13–7.29 (m, 5H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 8.01, 22.2, 35.8, 37.1, 51.3, 126.4, 127.0, 128.7, 146.4, 210.4. GC–MS (*M*/*Z*) 176. The enantiomeric ratio was determined by HPLC using a chiral column (Daicel Chiralpak AD-H), hexane/2-propanol 99:1, 0.5 mL/min, 210 nm, 9.2 min (major), 9.9 min (minor). $[\alpha]_D^{25} = +26.0$ (*c* 0.50, $CHCl_3$) for 47% ee [lit.: $[\alpha]_D^{25} = -49.5$ (*c* 1.00, $CHCl_3$) for 98% ee in the (*R*)-isomer].

4.15. (*S*)-5-Methyl-4-phenyl-2-hexanone 8fa[18]

^{1}H NMR (300 MHz, $CDCl_3$) δ 0.73 (d, J = 6.6 Hz, 3H), 0.93 (d, J = 6.6 Hz, 2H), 1.79–1.83 (m, 1H), 1.95 (s, 3H), 2.77–2.79 (m, 2H), 2.88–2.95 (m, 1H), 7.11–7.18 (m, 3H), 7.22–7.27 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.3, 20.7, 30.6, 33.3, 47.6, 48.0, 126.2, 128.1, 128.4, 143.3, 208.3. GC–MS (*M*/*Z*) 176. The enantiomeric ratio was determined by HPLC using a chiral column (Daicel Chiralcel OJ-H), hexane/2-propanol 99:1, 0.5 mL/min, 210 nm, 14.2 min (major), 17.3 min (minor). $[\alpha]_D^{25} = -16.0$ (*c* 0.50, $CHCl_3$) for 52% ee [lit.: $[\alpha]_D^{22} = -26.3$ (*c* 1.18, $CHCl_3$) for 77% ee in the *S*-isomer].

4.16. (*S*)-4-Phenyl-2-nonanone 8ga[23]

^{1}H NMR (300 MHz, $CDCl_3$) δ 0.81 (t, J = 6.7 Hz, 3H), 1.05–1.27 (m, 6H), 1.50–1.67 (m, 2H), 2.01 (s, 3H), 2.71 (d, J = 7.2 Hz, 2H), 3.04–3.16 (m, 1H), 7.14–7.21 (m, 3H), 7.25–7.31 (m, 2H). GC–MS (*M*/*Z*) 218. The enantiomeric ratio was determined by HPLC using a chiral column (Daicel Chiralcel OD-H), hexane/2-propanol 95:5, 0.5 mL/min, 210 nm, 7.2 min (major), 7.5 min (minor). $[\alpha]_D^{25} = +20.0$ (*c* 0.50, $CHCl_3$) for 42% ee.

4.17. Diphenylmethanol 10aa

^{1}H NMR (300 MHz, $CDCl_3$) δ 2.35 (br s, 1H), 5.80 (s, 1H), 7.20–7.43 (m, 10H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 76.3, 126.6, 127.6, 128.5, 143.8. GC–MS (*M*/*Z*) 184.

4.18. (*R*)-4-Methylphenyl(phenyl)methanols 10ab and 10ba

^{1}H NMR (300 MHz, $CDCl_3$) δ 2.21 (br s, 1H), 2.32 (s, 3H), 5.79 (s, 1H), 7.11–7.38 (m, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.5, 76.4, 126.65, 126.72, 127.6, 128.6, 129.4, 137.5, 141.1 144.1. GC–MS (*M*/*Z*) 198. The enantiomeric ratio was determined by HPLC using a chiral column (Daicel Chiralcel OD-H), hexane/2-propanol 90:10, 0.5 mL/min, 254 nm, 19.4 min (minor), 21.2 min (major).

4.19. (*R*)-4-Methoxyphenyl(phenyl)methanols 10ac and 10ea

^{1}H NMR (300 MHz, $CDCl_3$) δ 2.34 (br s, 1H), 3.75 (s, 3H), 5.74 (s, 1H), 6.83 (d, J = 8.4, 2H), 7.20–7.35 (m, 7H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 55.6, 76.1, 114.1, 126.6, 127.6, 128.1, 128.6, 136.4, 144.2, 159.2. GC–MS (*M*/*Z*) 214. The enantiomeric ratio was determined by HPLC using a chiral column (Daicel Chiralcel OJ), hexane/2-propanol 90:10, 0.7 mL/min, 254 nm, 50.5 min (major), 63.6 min (minor).

4.20. (−)-4-*t*-Butylphenyl(phenyl)methanol 10ad

^{1}H NMR (300 MHz, $CDCl_3$) δ 1.30 (s, 9H), 2.15 (br s, 1H), 5.81 (s, 1H), 7.20–7.44 (m, 9H). GC–MS (*M*/*Z*) 240. The enantiomeric ratio was determined by HPLC using a chiral column (Daicel Chiralpak AD-H), hexane/2-propanol 95:5, 0.7 mL/min, 254 nm, 15.4 min (minor), 17.5 min (major).

4.21. (*R*)-1-Naphthyl(phenyl)methanols 10ag and 10ha

^{1}H NMR (300 MHz, $CDCl_3$) δ 2.39 (br s, 1H), 5.98 (s, 1H), 7.25–7.55 (m, 8H), 7.78–7.93 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 73.3, 124.0, 124.5, 125.3, 125.5, 125.8, 127.0, 127.5, 127.6, 128.4, 128.6, 130.4, 133.6, 138.8, 143.2. GC–MS (*M*/*Z*) 234. The enantiomeric ratio was determined by HPLC using a chiral column (Daicel Chiralcel OJ), hexane/2-propanol 80:20, 0.7 mL/min, 254 nm, 22.9 min (minor), 36.9 min (major).

4.22. (*S*)-4-Cyanophenyl(phenyl)methanol 10ca

^{1}H NMR (300 MHz, $CDCl_3$) δ 2.63 (br s, 1H), 5.78 (s, 1H), 7.23–7.35 (m, 5H), 7.43–7.55 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 75.81, 113.13, 119.11, 127.08, 123.45, 129.06, 132.46, 143.00, 149.26. GC–MS (*M*/*Z*) 209. The enantiomeric ratio was determined by HPLC using a chiral column (Daicel Chiralcel OD-H), hexane/2-propanol 85:15, 0.5 mL/min, 254 nm, 23.8 min (minor), 26.5 min (major).

4.23. (*S*)-4-Nitrophenyl(phenyl)methanol 10da

^{1}H NMR (300 MHz, $CDCl_3$) δ 2.39 (br s, 1H), 5.93 (s, 1H), 7.33–7.38 (m, 5H), 7. 59 (d, J = 6.9 Hz, 2H), 8.21 (d, J = 6.9 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 75.5, 123.6, 126.7, 127.0, 128.4, 128.7, 142.7, 150.5. GC–MS (*M*/*Z*) 229. The enantiomeric ratio was determined by HPLC using a chiral column (Daicel Chiralpak AD-H), hexane/2-propanol 80:20, 0.5 mL/min, 254 nm, 14.6 min (minor), 18.0 min (major).

4.24. (*S*)-4-Chlorophenyl(phenyl)methanol 10fa

^{1}H NMR (300 MHz, $CDCl_3$) δ 2.34 (s, 1H), 5.76 (s, 1H), 7.24–7.29 (m, 5H), 7.31–7.33 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 75.5, 126.4, 127.8, 128.5, 128.6, 133.2, 142.1, 143.4. GC–MS (*M*/*Z*) 218. The enantiomeric ratio was determined by HPLC using a chiral column (Daicel Chiralcel OB-H), hexane/2-propanol 90:10, 0.7 mL/min, 254 nm, 32.5 min (minor), 47.7 min (major).

4.25. (*S*)-4-Bromophenyl(phenyl)methanol 10ga

^{1}H NMR (300 MHz, $CDCl_3$) δ 2.30 (d, J = 2.9 Hz, 1H), 5.77 (d, J = 2.9 Hz, 1H), 7.24 (d, J = 8.4 Hz, 2H), 7.22–7.31 (m, 5H), 7.42 (d, J = 8.4 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 75.8, 121.7, 126.8, 128.1, 128.6, 128.9, 131.9, 143.0, 143.6. GC–MS (*M*/*Z*) 262. The enantiomeric ratio was determined by HPLC using a chiral column (Daicel Chiralcel OB-H), hexane/2-propanol 90:10, 0.7 mL/min, 254 nm, 19.1 min (minor), 27.6 min (major).

4.26. (*S*)-2-Naphthyl(phenyl)methanol 10ia

^{1}H NMR (300 MHz, $CDCl_3$) δ 2.36 (br s, 1H), 5.98 (s, 1H), 7.23–7.49 (m, 8H), 7.76–7.88 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 76.7, 125.2, 126.2, 126.4, 126.9, 127.9, 128.3, 128.5, 128.8, 133.1, 133.4, 141.3, 143.8. GC–MS (*M*/*Z*) 234. The enantiomeric ratio was determined by HPLC using a chiral column (Daicel Chiralcel OJ), hexane/2-propanol 80:20, 0.7 mL/min, 254 nm, 31.1 min (major), 39.3 min (minor).

4.27. (*R*)-Cyclohexyl(phenyl)methanol 10ja

^{1}H NMR (300 MHz, $CDCl_3$) δ 0.90–1.36 (m, 5H), 1.38–1.48 (m, 1H), 1.60–1.76 (m, 3H), 1.78–1.87 (m, 2H), 2.00 (m, 1H), 4.39 (d, J = 7.4 Hz, 1H), 7.20–7.38 (m, 5H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 26.0, 26.1, 26.4, 28.8, 29.3, 44.9, 79.4, 126.6, 127.4, 128.2, 142.2. GC–MS (*M*/*Z*) 190. The enantiomeric ratio was determined by HPLC using a chiral column (Daicel Chiralcel OD-H), hexane/2-propanol 99:1, 0.5 mL/min, 254 nm, 29.1 min (minor), 40.1 min (major).

4.28. (*R*)-*t*-Butyl(phenyl)methanol 10ka

^{1}H NMR (300 MHz, $CDCl_3$) δ 0.93 (s, 9H), 1.83 (d, J = 3.0 Hz, 1H), 4.40 (d, J = 3.0 Hz, 1H), 7.25–7.35 (m, 5H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 25.9, 35.6, 82.4, 127.2, 127.5, 127.6, 142.2. GC–MS (*M*/*Z*) 164. The enantiomeric ratio was determined by HPLC using a chiral column (Daicel Chiralcel OD-H), hexane/2-propanol 99:1, 0.5 mL/min, 254 nm, 24.1 min (minor), 32.6 min (major).

4.29. (*R*)-Phenyl(*i*-propyl)methanol 10la

^{1}H NMR (300 MHz, $CDCl_3$) δ 0.80 (d, J = 6.9 Hz, 3H), 1.00 (d, J = 6.9 Hz, 3H), 1.81 (br s, 1H), 1.96 (m, 1H), 4.36 (d, J = 6.9 Hz, 1H), 7.24–7.37 (m, 5H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 17.2, 18.0, 34.2, 79.0, 125.5, 126.4, 127.2, 142.6. GC–MS (*M*/*Z*) 150. The enantiomeric ratio was determined by HPLC using a chiral column (Daicel Chiralcel OD-H), hexane/2-propanol 98:2, 0.7 mL/min, 254 nm, 12.0 min (minor), 15.3 min (major).

4.30. (*R*)-2-Furyl(phenyl)methanol 10ma

^{1}H NMR (300 MHz, $CDCl_3$) δ 2.54 (br s, 1H), 5.82 (br s, 1H), 6.11 (dd, J = 3.1, 0.8 Hz, 1H), 6.32 (dd, J = 3.2, 2.1 Hz, 1H), 7.30–7.47 (m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 70.1, 107.3, 110.2, 126.5, 127.9, 128.4, 140.8, 142.4, 155.9, GC–MS (*M*/*Z*) 174. The enantiomeric ratio was determined by HPLC using a chiral column (Daicel Chiralcel OD-H), hexane/2-propanol 95:5, 0.5 mL/min, 254 nm, 9.3 min (minor), 10.4 min (major).

4.31. (*R*)-Phenyl(2-thiophenyl)methanol 10na

^{1}H NMR (300 MHz, $CDCl_3$) δ 2.43 (d, J = 2.9 Hz, 1H), 6.12 (d, J = 2.9 Hz, 1H), 6.92–6.94 (m,1H), 6.96–6.98 (m, 1H), 7.28–7.49 (m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 72.7, 125.2, 125.7, 126.5, 126.9, 128.3, 128.8, 142.2. GC–MS (*M*/*Z*) 190. The enantiomeric ratio was determined by HPLC using a chiral column (Daicel Chiralcel OD-H), hexane/2-propanol 98:2, 0.7 mL/min, 254 nm, 30.3 min (minor), 34.4 min (major).

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