

/ Review

Development of Efficient Catalytic Arylation of Aldehydes with Thioether-Imidazolium Carbene Ligands

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Effective methods of ligand design have been highly sought due to the significant roles of ligands in controlling metal catalyses. In particular, easy-to-handle ligands to realize high reaction efficacy, substrate tolerance, and environmental friendliness are desirable. Novel bidentate ligands containing *N*-heterocyclic carbene and thioether moieties were developed based on findings of hemilabile coordination, whose precursors were crystalline solids stable enough to handle and store in the air. The thioether-imidazolium carbene ligand successfully brought out high catalyst performance of palladium in the catalytic arylation of aldehydes with organoboron reagents, which tolerated a diverse range of substrates including poorly reactive, sterically hindered, and heterocyclic compounds. This process was applied to gram-scale synthesis using only water as solvent with high efficiency and also achieved the effective one-pot synthesis of 3-arylphthalides known as useful biologically active agents and important synthetic intermediates for naturally occurring compounds.

Key words hemilabile ligand; *N*-heterocyclic carbene; thioether; palladium; arylation; organoboron reagent

Introduction

The discovery and development of efficient catalytic systems are important issues in synthetic organic chemistry. In the establishment of synthetic methods including catalytic processes, the design of ligands has received much attention because these molecules play significant roles in controlling metal catalyses.^{1–3} Hybrid ligands bearing two different donors have some coordination manners, such as monodentate, bidentate, and bridging behaviors. Especially, hetero-bidentate ligands with a strongly coordinating donor and labile group could show hemilabile properties, in which the labile donor has a fluxional process involving dissociation and recoordination.^{4,5} In 2001, we found that the chiral monophosphine ligand (*S*)-**1** (Fig. 1) gave superior catalytic performance compared with (*S*)-binap in rhodium-catalyzed asymmetric conjugate addition with longer heatup time.⁶ Physicochemical investigation on the behavior of (*S*)-**1** in the neutral complex showed that the amide carbonyl oxygen was coordinatively labile whereas the phosphorus atom bonded to rhodium tightly⁷ (Fig. 2). In addition, steric tuning in which *L*-valine derivative was introduced to the chiral monophosphine ligand in possession of the amide carbonyl group at the appropriate position realized the rhodium-catalyzed asymmetric 1,2-addition to imines with high catalyst efficiency.⁸ These results indicate that the labile coordination of hetero atoms to metal centers was quite important in controlling the catalyst function and performance. Therefore we attempted to develop new bidentate ligands that are easy to handle and educe excellent

efficiency of transition metal catalysis on the basis of our accumulated findings on hemilabile coordination.

Novel thioether-imidazolium carbene ligands were designed as bidentate hemilabile ligands focusing on practical utility based on the lesson that phosphine donors are normally unstable, expensive, and inflexible about structure modification (Fig. 3). The *N*-heterocyclic carbene (NHC) was adopted as a main framework due to the high stability and easy preparation of its precursor in addition to the pronounced σ -donating property. The thioether moiety was expected to be a superior labile donor,⁹ because it is electronically softer and could show more appropriate affinity to transition metals, giving distinctive effects such as the facilitation of substrate replacement, protection of vacant coordination sites, and dynamic electron-state control. While sulfur species are known

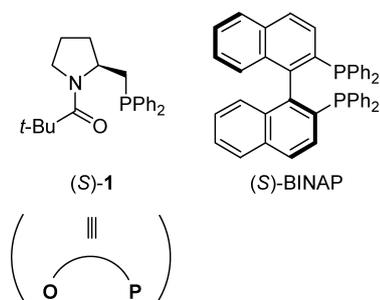


Fig. 1. Chiral Phosphine Ligands

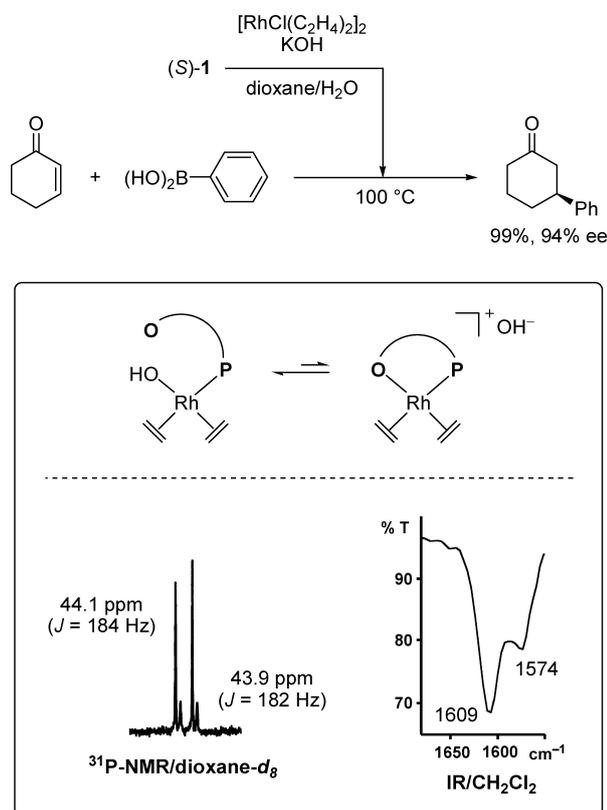


Fig. 2. Hemilabile Coordination of (S)-1

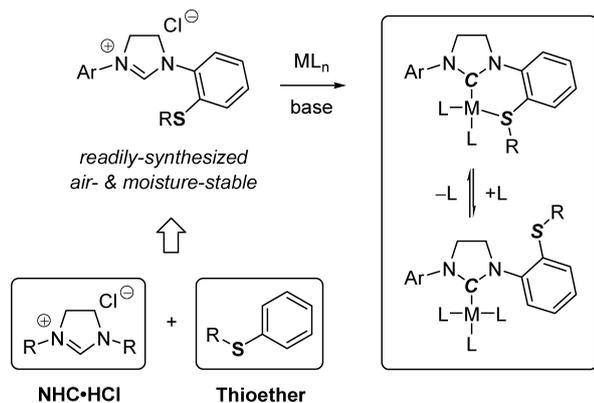


Fig. 3. Design of Thioether-Imidazolium Carbene Ligand

as catalyst poisons leading to significant deactivation of transition metals, the fine function of thiol moiety in switching between the active and passive mode in a metalloenzyme was investigated,¹⁰ which convinced us that the proper arrangement could make the thioether group work as an effective labile donor for transition metals.

Transition metal catalysts are one of the most important synthetic tools for carbon–carbon bond formation.¹¹ Since Miyaura and co-workers reported rhodium-catalyzed 1,2-addition in 1998,¹² the transition metal-catalyzed 1,2-addition reactions of organoboronic acids to aldehydes have been attracting much attention.^{13–15} Due to the advantages of organoboron reagents such as low toxicity, superior stability, and widespread availability,^{16–18} and the significance of adducts as intermediates for the synthesis of biologically active compounds,^{19–21} several types of active catalysts have been developed for this kind of reaction, such as palladium,²² nickel,²³ and copper²⁴ complexes in addition to recently found effective metal species following our report.^{25–28} However, they did not achieve adequate level performance and high catalyst loading was usually required to obtain sufficient results. In addition, successful examples with sterically hindered, heterocyclic, and synthetically applicable substrates were quite limited and more active and efficient catalyst systems were desired to give superior alternatives to traditional 1,2-addition with organolithium and magnesium reagents.

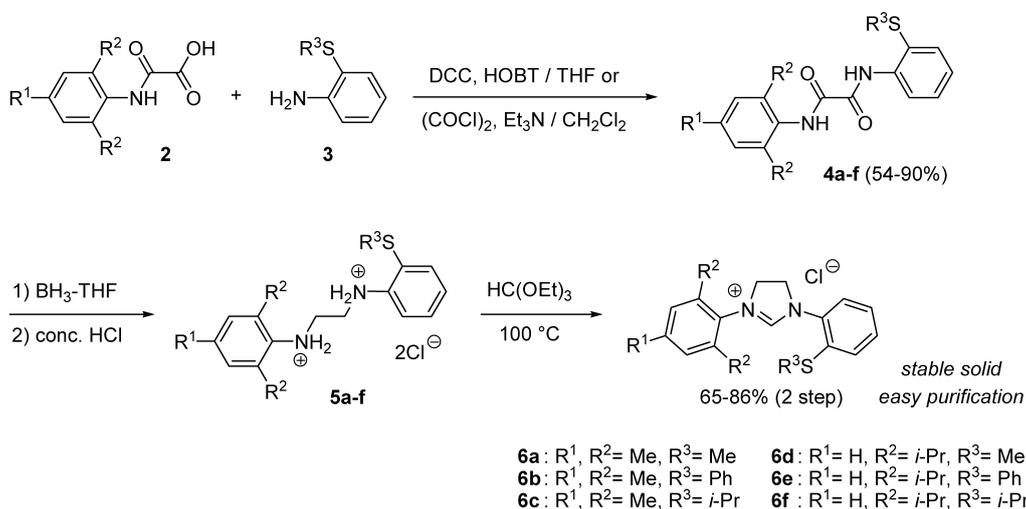
1. Synthesis of Thioether-Imidazolium Chlorides as Ligand Precursors

Mixed-donor ligands could be efficient systems in controlling transition metals due to the attractive and unique reactivity of their metal complexes arising from different functional groups. Although several bidentate NHC-based ligands bearing sulfur atoms have been reported, most of them were investigated in terms of coordination chemistry and the property and performance of their metal catalysts have been scarcely figured out.²⁹ We designed the synthetic route of novel thioether-imidazolium chlorides **6** to modify the subtle balance of steric and electronic effects flexibly, which were prepared in the three-step procedure as shown in Chart 1.³⁰ Bis-amides **4a–f** were obtained with 54–90% yields *via* the coupling of oxanilic acids **2** with *ortho*-substituted anilines **3** using *N,N'*-dicyclohexylcarbodiimide or oxalyl chloride. The reduction of bis-amides **4a–f** with borane-THF complex followed by acidification with concentrated hydrochloric acid gave ethylenediamine dihydrochlorides **5a–f**, then **5a–f** cyclized upon treatment with triethyl orthoformate to form thioether-imid-

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Chart 1. Synthesis of Thioether-Imidazolium Chlorides **6**

azolium chlorides **6a–f** in 65–86% yields (over two steps). These imidazolium chlorides **6a–f** are crystalline solids stable enough to handle and store in the air, which could be important advantages in terms of practical utility.

2. Palladium-Catalyzed 1,2-Addition of Organoboronic Acids to Aldehydes with Thioether-Imidazolium Carbene Ligands

Initially, the characteristic features of thioether-imidazolium chlorides **6** were examined in the catalytic 1,2-addition of phenylboronic acid **8a** to benzaldehyde **7a** using 1.0 mol% of the catalysts (Pd/L=1/1) generated *in situ* from thioether-imidazolium chlorides **6a–f** and allylpalladium(II) chloride dimer in the presence of cesium carbonate (Table 1). Then, the thioether-imidazolium chloride **6e** was proven to be a superior heterobidentate carbene ligand precursor, which

showed that the high bulkiness of aryl group and softer electronic condition of sulfur atom were necessary (entries 1–6).³¹⁾ The reaction using SIPr·HCl (1,3-bis(2,6-diisopropylphenyl)-imidazolium chloride), a simple monodentate carbene ligand precursor, gave the addition product **9aa** in only 8% yield (entry 7), which led to the suggestion that C,S-heterobidentate coordination was quite important in the achievement of high catalyst performance. A series of bases was examined and we found that cesium fluoride was the reagent of choice (entry 8). Investigation into the influence of solvents demonstrated that dioxane was most suitable, affording the adduct **9aa** in 99% yield (entry 9). Control experiments with thioanisole or no imidazolium chloride gave no conversion at all (entries 10 and 11), which indicated that active thioether-imidazolium carbene-palladium species were formed *in situ* under basic conditions. The experiments under low catalyst loading conditions

Table 1. Palladium-Catalyzed Phenylation of Benzaldehyde with Thioether-Imidazolium Carbene Ligands^{a)}

Entry	Ligand	Base	Solvent	Yield (%) ^{b)}
1	6a	Cs ₂ CO ₃	Toluene	12
2	6b	Cs ₂ CO ₃	Toluene	40
3	6c	Cs ₂ CO ₃	Toluene	20
4	6d	Cs ₂ CO ₃	Toluene	82
5	6e	Cs ₂ CO ₃	Toluene	95
6	6f	Cs ₂ CO ₃	Toluene	85
7	SIPr·HCl ^{c)}	Cs ₂ CO ₃	Toluene	8
8	6e	CsF	Toluene	97
9	6e	CsF	Dioxane	99
10	PhSMe	CsF	Dioxane	0
11	None	CsF	Dioxane	0
12 ^{d)}	6e	CsF	Dioxane	99
13 ^{e)}	6e	CsF	Dioxane	54

^{a)} Reaction conditions: **7a** (1.0 mmol), **8a** (1.5 mmol), ligand (1 mol%), [Pd(allyl)Cl]₂ (0.5 mol%), base (2.0 mmol), solvent (2.0 mL), 80 °C, 20 min. ^{b)} Isolated yield. ^{c)} 1,3-Bis(2,6-diisopropylphenyl)imidazolium chloride. ^{d)} The catalyst (0.05 mol%) was used. ^{e)} The catalyst (0.005 mol%) was used.

Table 2. Scope of Organoboronic Acids^{a)}

Entry	8	9	Cat. (mol%)	Time (h)	Yield (%) ^{b)}
1		8b → 9bb	0.5	3.0	98
2		8c → 9bc	0.5	3.0	98
3		8d → 9bd	0.5	3.0	84
4 ^{c)}		8e → 9be	1.0	3.5	95
5		8f → 9bf	1.5	0.5	92
6		8g → 9bg	1.5	0.5	93
7		8h → 9bh	2.0	2.0	75
8 ^{d)}		8i → 9bi	1.0	2.0	82
9 ^{e)}		8j → 9bj	1.5	2.0	93
10		8k → 9bk	1.0	2.0	99

^{a)} Reaction conditions: **7b** (1.0 mmol), **8** (1.5 mmol), ligand **6e** (1 mol%), [Pd(allyl)Cl]₂ (0.5 mol%), CsF (2.0 mmol), dioxane (2.0 mL), 80 °C. ^{b)} Isolated yield. ^{c)} 100 °C. ^{d)} Boronic acid (2.5 mmol) was used. ^{e)} Water (0.2 mL) was added.

were conducted and the addition reactions using 0.05 mol% and 0.005 mol% of the catalyst led to 99% (turnover number (TON): 2.0×10^3) and 54% yields (TON: 1.1×10^4), respectively (entries 12 and 13).

The influence of varying aryl and alkenyl boronic acids in the addition reactions with 0.5–2.0 mol% of the catalyst using 2-naphthaldehyde **7b** was investigated (Table 2). The reaction using sterically hindered 2-biphenylboronic acid **8b** gave the adduct **9bb** with 98% yield (entry 1). Both the electron-rich and -poor arylboronic acids substituted at 2-position **8c** and **8d** were converted efficiently (entries 2 and 3). The quite sterically hindered 2,6-dimethoxyphenyl boronic acid **8e** also reacted readily to afford 95% yield (entry 4), although the palladium-catalyzed arylation with 2,6-disubstituted arylboronic acid was known as a difficult task. The alkenyl boronic acids **8f** and **8g** also gave the adducts **9bf** and **9bg** with high yields (entries 5 and 6). Then, heteroaryl boronic acids containing nitrogen, oxygen, and sulfur atoms were examined. The reaction with *N*-protected 3-indoleboronic acid **8h** proceeded smoothly leading to 75% yield (entry 7). To obtain the adduct **9bi** with

82% yield, 2.5 eq of 3-furanboronic acid **8i** were needed (entry 8). 2-Furanboronic acid **8j** and 3-thiophenylboronic acid **8k** afforded excellent results (entries 9 and 10).

Investigation of aldehydes in the addition reactions of arylboronic acids using 0.5–1.5 mol% of the palladium/thioetherimidazolium chloride system was also conducted (Table 3). Both the electron-rich and poor aromatic aldehydes **7c** and **7d** were easily converted (entries 1 and 2). The sterically hindered and electron-rich 2-methoxybenzaldehyde **7e** reacted with the *ortho*-substituted phenylboronic acid **8c**, efficiently (entry 3). Moreover, the addition to quite sterically hindered and weakly-reactive 2,6-dimethoxybenzaldehyde **7f** with phenylboronic acid **8a** led to 98% yield (entry 4) although it was reported that the addition to this class of aromatic aldehyde was sluggish. On the other hand, the addition reaction of **8c** to **7f** gave the product **9fc** with acceptable yield (entry 5). Phenyl group was introduced to the aliphatic aldehydes **7g** and **7h**, affording the adducts **9ga** and **9ha** with high yields (entries 6 and 7). The heteroaromatic aldehydes **7i–k**, which have not been examined in previous reports, were also good

Table 3. Scope of Aldehydes^{a)}

$\text{R-CHO} + (\text{HO})_2\text{B-Ar} \xrightarrow[\text{CsF (2 equiv), dioxane, 80 }^\circ\text{C, 3 h}]{\text{6e, [Pd(allyl)Cl]}_2} \text{R-CH(OH)-Ar}$

7c-k **8a:** R' = H
8c: R' = OMe **9**

Entry	7	8	9	Cat. (mol%)	Yield (%) ^{b)}
1		8a	9ca	0.5	99
2		8a	9da	0.5	98
3		8c	9ec	1.0	99
4		8a	9fa	0.5	98
5 ^{c)}		8c	9fc	1.5	65
6		8a	9ga	1.0	98
7		8a	9ha	1.0	85
8		8a	9ia	0.5	98
9		8a	9ja	0.5	99
10		8a	9ka	0.5	99

^{a)} Reaction conditions: **7** (1.0 mmol), **8** (1.5 mmol), ligand **6e** (1 mol%), [Pd(allyl)Cl]₂ (0.5 mol%), CsF (2.0 mmol), dioxane (2.0 mL), 80 °C, 3 h. ^{b)} Isolated yield. ^{c)} 100 °C.

acceptors, being converted to the addition products **9ia–9ka** with excellent yields (entries 8–10).

These results suggest that a high level of catalyst performance was attainable in the palladium-catalyzed 1,2-addition of organoboronic acids to aldehydes with thioether-imidazolium chloride **6e** as heterobidentate carbene ligand precursor. This process tolerated a diverse range of substrates including poorly reactive, sterically hindered, and heterocyclic compounds. This initial investigation also revealed that the thioether-imidazolium carbene is a promising class of heterobidentate ligand systems for transition metal-catalyzed reactions.

3. Palladium-Catalyzed 1,2-Addition of Organoboronic Acids to Aldehydes with Thioether-Imidazolium Carbene Ligands in Water

Environmentally benign synthetic methods are desirable from the viewpoint of green chemistry.³²⁾ Organic chemical

reactions in aqueous media have been focused due to advantages of water as solvent such as its low cost, safety, and innocuity in addition to unique reactivity observed therein.^{33–37)} Especially, the development of more efficient and sustainable catalysts that are effective in only water has been desired.^{38–42)} However, the achievement of high reaction efficiency with metal catalysts in water is not easy. To overcome the poor solubility of organic compounds and deleterious effects for metal catalysts in water, ingenious aids such as microwave heating, organic co-solvents, and surfactants are often necessary.^{33–42)} Despite these efforts, reported examples of transition metal-catalyzed arylation of aldehydes with organoboron reagents in only water are quite scarce and have unresolved issues in reaction systems and substrate generality.^{43,44)}

The performance of palladium/thioether-imidazolium chloride system was examined in the phenylation of 2-naphthaldehyde **7b** using water as solvent (Table 4). Then, only thioether-imidazolium chloride **6e** was proven to be an

effective *N*-heterocyclic carbene ligand precursor (entries 1–6).⁴⁵) Evaluation on the effect of organic solvents revealed that smooth reaction progress required appropriate solvent polarity (entries 7–9). Interestingly, dimethyl sulfoxide (DMSO) gave a quite poor result although the reaction in more highly polar water proceeded efficiently, which could be achieved by hydrophobic effects. As expected, decrease of water had no

Table 4. Palladium-Catalyzed Phenylation of 2-Naphthaldehyde with Thioether-Imidazolium Carbene Ligands in Water^{a)}

Entry	Ligand	Solvent	Yield (%) ^{b)}
1	6a	H ₂ O	0
2	6b	H ₂ O	5
3	6c	H ₂ O	20
4	6d	H ₂ O	9
5	6e	H ₂ O	90
6	6f	H ₂ O	13
7	6e	Toluene	90
8	6e	Dioxane	95
9	6e	DMSO	25
10 ^{c)}	6e	H ₂ O	90
11 ^{d)}	6e	H ₂ O	91

a) Reaction conditions: **7b** (1.0 mmol), **8a** (1.5 mmol), ligand **6** (1 mol%), [Pd(allyl)Cl]₂ (0.5 mol%), Cs₂CO₃ (2.0 mmol), solvent (2.0 mL), 100 °C, 2 h. b) Isolated yield. c) Water (1 mL) was used. d) Large-scale reaction conditions: **7b** (10 mmol), **8a** (15 mmol), ligand **6e** (1 mol%), [Pd(allyl)Cl]₂ (0.5 mol%), Cs₂CO₃ (20 mmol), water (15 mL), 100 °C, 8 h.

influence on the reaction rate, which could make large-scale synthesis easier to conduct (entry 10). Gram-scale reaction with 10 mmol of aldehyde **7b** was achieved with excellent efficacy to afford the desired product **9ba** in 91% yield (entry 11). Therefore this catalytic system could be quite advantageous for the practical synthesis of carbinol derivatives.

Then, a series of arylboronic acids and aldehydes was examined in the catalytic arylation reactions of aldehydes using water as solvent (Table 5). Although the sterically hindered 2-methylphenylboronic acid **8n** was less reactive in water (entry 3), various arylboronic acids were successfully applied, leading to good to excellent yields (entries 1, 2, and 4–6). On the other hand, a wide range of aldehydes bearing sterically hindered, electron-donating, and heterocyclic moieties were available in high yields (entries 7–12). In particular, 2,4-dichlorobenzaldehyde **7n** was converted efficiently without the generation of Suzuki–Miyaura coupling or dehalogenation products and the electron-withdrawing cyano group was also tolerated under the reaction conditions though they have high reactivity towards organolithium and magnesium reagents (entries 9 and 10). Thus the palladium/thioether-imidazolium chloride system showed high catalyst efficiency even in only water with no further aid, such as microwave heating, organic co-solvents, and surfactants.

4. Palladium-Imidazolium Carbene-Catalyzed 1,2-Addition of Potassium Organotrifluoroborates to Aldehydes in Aqueous Media

Recently, potassium organotrifluoroborates have attracted much attention as alternatives to organoboronic acids because of their superior features.^{46–48}) Boronic acids often dimerize and trimerize to form boronic acid anhydrides and

Table 5. Scope of Substrates^{a)}

Entry	7	8	9	Yield (%) ^{b)}	Entry	7	8	9	Yield (%) ^{b)}
1	7b	(HO) ₂ B--Me 8l	9bl	81	7	7l	8a	9la	92
2	7b	(HO) ₂ B--Me 8m	9bm	85	8 ^{c)}	7m	8a	9ma	81
3 ^{c)}	7b	(HO) ₂ B--Me 8n	9bn	35	9	7n	8a	9na	92
4	7b	(HO) ₂ B--OMe 8o	9bo	61	10	7d	8a	9da	87
5	7b	(HO) ₂ B--F 8p	9bp	96	11 ^{c)}	7g	8a	9ga	96
6	7b	(HO) ₂ B--S 8k	9bk	76	12 ^{c)}	7o	8a	9oa	93

a) Reaction conditions: **7** (1.0 mmol), **8** (1.5 mmol), ligand **6e** (2 mol%), [Pd(allyl)Cl]₂ (1 mol%), Cs₂CO₃ (2.0 mmol), water (2.0 mL), 100 °C, 2 h. b) Isolated yield. c) The catalyst (3 mol%) was used.

Table 6. Palladium-Imidazolium Carbene-Catalyzed Arylation of Aldehydes with Potassium Organotrifluoroborates in Aqueous Media^{a)}

Entry	7	10	9	Yield (%) ^{b)}	Entry	7	10	9	Yield (%) ^{b)}		
1 ^{c)}	7b		10a	9ba	95	7	7e		10a	9ea	94
2	7b		10n	9bn	83	8	7p		10a	9pa	88
3	7b		10o	9bo	90	9	7g		10a	9ga	58
4	7b		10p	9bp	83	10	7i		10a	9ia	93
5	7b		10f	9bf	92	11	7q		10a	9qa	99
6	7b		10k	9bk	82	12	7o		10a	9oa	96

^{a)} Reaction conditions: **7** (0.6 mmol), **10** (0.9 mmol), ligand **6e** (0.5 mol%), [Pd(allyl)Cl]₂ (0.25 mol%), Cs₂CO₃ (1.8 mmol), toluene (1.5 mL), water (0.25 mL), 100°C, 2 h. ^{b)} Isolated yield. ^{c)} 0.5 h.

boroxines,⁴⁹⁾ which make difficulties in the direct purification and determination of exact chemical amount. On the other hand, potassium organotrifluoroborates are highly air- and moisture-stable crystalline solids^{50–52)} and more easily prepared, purified, and handled although these compounds are less soluble in organic solvents and require protic solvents for their dissolution.^{46–48)} In spite of these advantages, only two kinds of rhodium(I)-phosphine catalysts for the 1,2-addition to aldehydes with potassium organotrifluoroborates have been reported.^{53,54)} Because the palladium/thioether-imidazolium chloride system had high tolerance for water, it was expected to be a suitable catalyst system for this type of reagent.

Optimization of reaction conditions using potassium organotrifluoroborates showed that the mixed solvent of toluene and water and three equivalent of cesium carbonate were required while the catalyst amount was reduced to 0.5 mol% even in aqueous condition (Table 6).⁵⁵⁾ A variety of potassium aryl- and alkenyltrifluoroborate salts including sterically hindered, electron-donating, electron-withdrawing, and heterocyclic moieties were applied successfully (entries 1–6). While the aliphatic aldehyde **7g** led to moderate result (entry 9), weakly reactive and heteroaromatic aldehydes were proven to be excellent acceptors (entries 7 and 10–12). Especially, the reaction with 2-bromobenzaldehyde **7p** proceeded efficiently with high chemoselectivity to give no by-product although its halogen moiety was highly activated by the electron-withdrawing formyl group (entry 8). The compatibility of organoboron reagents was achieved by minor optimization of reaction conditions, which showed considerable potential of

this catalyst system.

5. One-Pot Synthesis of 3-Arylphthalides via Palladium-Imidazolium Carbene-Catalyzed 1,2-Addition of Organoboronic Acids to Aldehydes

Subsequently, this reaction system was applied to the development of effective synthetic methods for useful building blocks of biologically active agents. Phthalides substituted at C-3 are important heterocycles possessing interesting biological activities and found in various naturally occurring compounds such as alcyopterosin E, cytosporone E, fuscinarin, rubiginone H, isopestacin, and cryphonectric acid.⁵⁶⁾ Especially, 3-arylphthalides are also known as useful intermediates for the synthesis of tri- and tetracyclic natural products such as anthracycline antibiotics.^{57–60)} Because of their significance, various methods for the synthesis of 3-arylphthalides have been reported. However, not many transition metal-catalyzed synthetic reactions for 3-arylphthalides have been developed,^{61–65)} although catalytic methods could be highly efficient processes. In particular, there were only a few reports on the synthesis of 3-arylphthalides using transition metal-catalyzed 1,2-addition as key reaction,^{66–69)} and more catalytically active and practically advantageous processes have been desirable. Recently, a few additional catalytic methods have emerged following our report.^{70–72)}

Initially, we examined two applicable synthetic methods for 3-arylphthalides using the palladium-catalyzed arylation of aldehydes with thioether-imidazolium chloride **6e** (Chart 2).⁷³⁾ While the synthesis of 3-phenylphthalide **11ra**

lactone products (entries 6–8).

Furthermore, the influence of the electron-rich aldehyde, methyl 6-formyl-2,3-dimethoxybenzoate **7s**, was investigated (Table 7, entries 9–12). No significant decrease in yield for the reaction of the aldehyde **7s** and phenylboronic acid **8a** was observed, affording the product **11sa** with 85% yield (entry 9). While the reaction of sterically hindered 2-biphenylboronic acid **8b** proceeded with good yield (entry 10), the transformation using 3-thiopheneboronic acid **8k** afforded the desired lactone product in moderate yield (entry 11). In the case of 3-alkenylphthalide **8g**, the cyclization following addition was relatively slow. The crude product contained the uncyclized adduct, which was then dissolved in chloroform and converted to the cyclized product **11sg** in 88% yield (entry 12). These results demonstrate that this catalyst system was applicable to one-pot multi-step synthetic methods for heterocyclic structures keeping its efficacy.

6. Conclusion

Novel thioether-imidazolium carbene ligands were designed and synthesized on the basis of findings about hemilabile coordination, whose precursors were crystalline solids stable enough to handle and store in the air. The catalyst system generated from the thioether-imidazolium chloride and palladium(II) complex showed high-level performance in the catalytic arylation of aldehydes with organoboron reagents, even when applied to a diverse range of substrates including poorly-reactive, sterically hindered, and heterocyclic compounds. In addition to the high compatibility of boron reagents, this process still gave high efficiency even in the gram-scale reaction using only water as solvent with no further aid. Moreover, effective one-pot synthesis of heterocyclic building blocks was achieved *via* palladium-catalyzed arylation with the thioether-imidazolium carbene. We believe that this simple ligand design strategy would open new possibilities for the development of efficient, practical, and environmentally benign synthetic methods.

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