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Regioselective Sequential Silylation and Borylation of Aromatic Aldimines as a Strategy for Programming Synthesis of Multifunctionalized Benzene Derivatives

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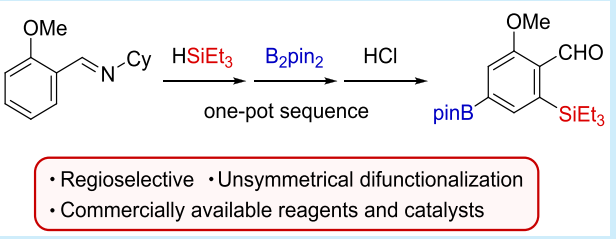
Supporting Information

ABSTRACT: Regioselective difunctionalization of two different C−H bonds in one pot using a three-component coupling reaction is described. The reaction order is important for controlling the reactivity and regioselectivity, and the first silylation promotes the second borylation. The introduced formyl, silyl, and boryl functional groups could be independently converted to other functional groups, and the substitution pattern for the resulting benzenes is difficult to access by conventional methods.



Synthetic methods that are based on multiple transformations in a single reaction vessel without the need for workup or product isolation between successive steps have received considerable attention, especially in the field of process chemistry.[1] Such techniques reduce the amount of solvent required for the workup and purification of intermediates, avoid the formation of associated chemical waste, and significantly reduce the overall working time and effort involved in the synthesis process.

In this work, a programmed one-pot synthesis of multifunctionalized benzene derivatives from simple and readily available aromatic compounds is examined. Considerable attention has been paid to difunctionalization via inter- or intramolecular addition to unsaturated π-bonds for the regioselective installation of two different functional groups (Figure 1a), while difunctionalization via the substitution of two different C−H bonds present in one molecule remains challenging (Figure 1b).[2] This is because catalysts and directing groups, which are indispensable for controlling the regioselectivity of most C−H bond functionalization reactions, are highly specific for one reaction. Another difficulty is that the intermediate in the initial functionalization often hampers the efficiency of the second functionalization. Therefore, most unsymmetrical difunctionalization reactions have been achieved by the introduction of similar functional groups at the *ortho* position of directing groups, and incorporation of two different functional groups in a one-pot operation is typically difficult.[2] The previous approach to overcoming these difficulties is a one-pot sequential reaction that involves rapid intramolecular hydroarylation followed by an intermolecular coupling reaction (Scheme 1a).[3] Difunctionalization of C−H bonds by a three-component coupling reaction, i.e., two successive intermolecular functionalization reactions, was achieved by only Ackerman et al. (Scheme 1b)[4] and us (Scheme 1c)[5] in 2018.

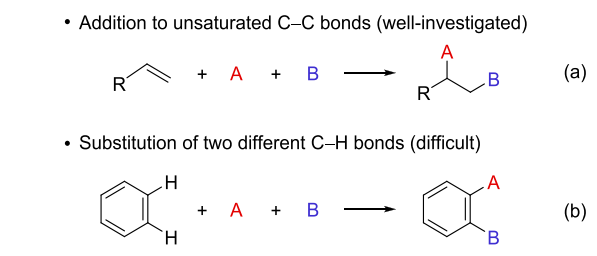


Figure 1. Regioselective difunctionalization.

On the basis of our previous report,[5] we envisioned that the programmed synthesis of highly functionalized benzenes could be achieved by the sequential silylation and borylation in one pot. We are particularly interested in the synthesis of multifunctionalized arylaldehydes, considering their high utility as building blocks. Due to the high reactivity of the formyl group, an efficient approach toward highly functionalized arylaldehydes in a short step remains challenging. Our approach is to utilize arylimines, which can be easily prepared from generally cheap and commercially available monofunctionalized arylaldehydes as platforms for sequential silylation and borylation. This is a novel example of the difunctionalization of C−H bonds by a three-component coupling reaction. The regioselectivity of the initial silylation could be controlled by chelation with an imino group, and that of the second

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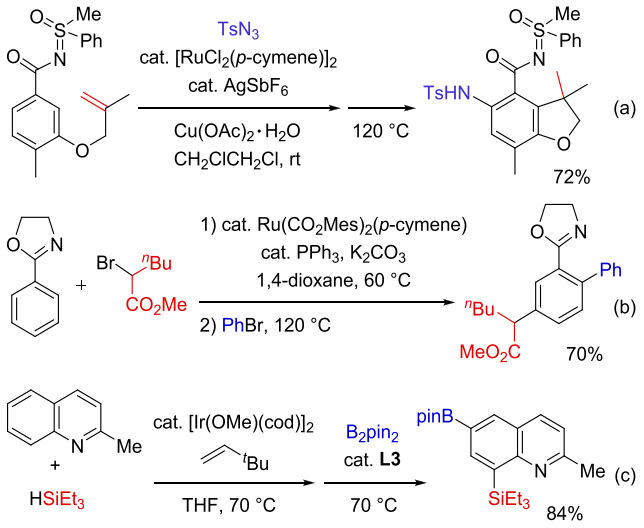
Scheme 1. Previous Difunctionalization with Incorporation of Two Different Functional Groups in a One-Pot Operation (see Table 1 for the structure of L3)



borylation could be controlled by steric repulsion from the initially incorporated silyl group (Figure 2). The substitution pattern for the resultant functionalized benzenes is difficult to access by the conventional electrophilic functionalization of arenes.

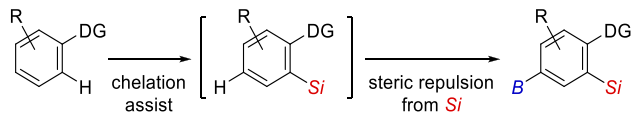
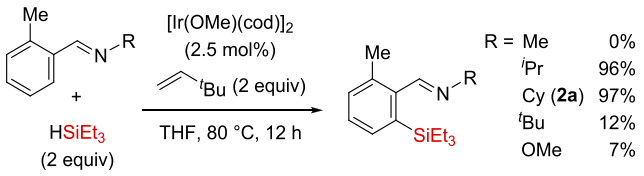


Figure 2. Programmed synthesis of tetrafunctionalized benzenes (*Si* = SiR_3, and *B* = Bpin).

The study presented here began with iridium-catalyzed regioselective dehydrogenative silylation of aldimines derived from 2-tolualdehyde to obtain insight into the effect of the substituents on the nitrogen atom (Scheme 2).[6] Note that the

Scheme 2. Effect of Substituents on the Nitrogen Atom in the Chelation-Assisted Dehydrogenative Silylation of Aldimines[a]

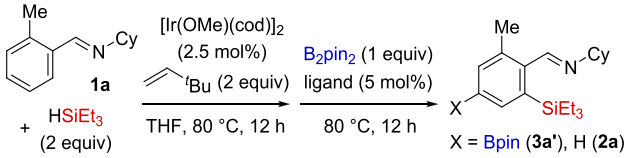


[a]Yields were determined by ^{1}H NMR of the crude products in C_6D_6.

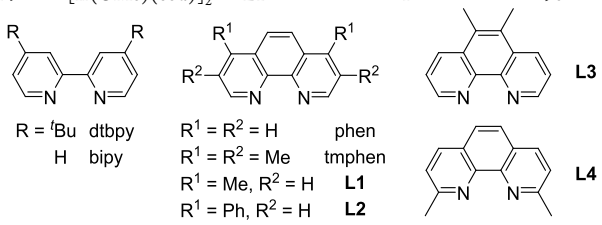
ortho-selective dehydrogenative silylation of 2-arylpyridines has been well-investigated,[7] while the corresponding reaction of arylimines is rare probably due to the competitive hydrosilylation reaction. The results revealed that branched alkyl groups that possess moderate steric hindrance, such as isopropyl and cyclohexyl groups, were optimal, and the formation of benzylsilyl ethers by hydrosilylation of aldimines was not observed in these reactions. Silylation did not proceed at 80 °C with bulkier *N*-*tert*-butylimine, whereas *N*-methylimine was decomposed under the reaction conditions presented here. While dehydrogenative silylation of aldimines, including *N*-(*tert*-butyl)- and *N*-(4-methoxyphenyl)aldimines, has been reported,[8,9] the silylation protocol proposed here with easily hydrolyzed *N*-(*sec*-alkyl)aldimines is practicable when considering the ease of functionalization of the products.

(*E*)-*N*-Cyclohexyl-1-(2-tolyl)methanimine **1a** was next chosen as a model substrate for the study of sequential silylation and borylation of two different C−H bonds in a one-pot process (Table 1). The preliminary study of the second

Table 1. Optimization of Reaction Conditions for One-Pot Sequential Silylation and Borylation of Aldimine 1a



entry	IrL_n	ligand	yield of **2a**[a] (%)	yield of **3a′**[a] (%)
1	$[Ir(OMe)(cod)]_2$	dtbpy	12	73
2	$[IrCl(cod)]_2$	dtbpy	14	72
3	$[Ir(cod)_2]BF_4$	dtbpy	35	46
4	$[Cp^*IrCl_2]_2$	dtbpy	74	0
5	$[Ir(OMe)(cod)]_2$	bipy	31	61
6	$[Ir(OMe)(cod)]_2$	phen	33	53
7	$[Ir(OMe)(cod)]_2$	tmphen	12	77
8	$[Ir(OMe)(cod)]_2$	**L1**	14	80
9	$[Ir(OMe)(cod)]_2$	**L2**	32	41
10	$[Ir(OMe)(cod)]_2$	**L3**	61	8
11	$[Ir(OMe)(cod)]_2$	**L4**	75	3
12[b]	$[Ir(OMe)(cod)]_2$	**Ll**	20	63
13[c]	$[Ir(OMe)(cod)]_2$	**L1**	8	88
14[c,d]	$[Ir(OMe)(cod)]_2$	**L1**	<1	90



[a]Determined by ^{1}H NMR of the crude products in C_6D_6. [b]Norbornene was used in place of 3,3-dimethyl-1-butene. [c]$HSiEt_3$ and 3,3-dimethyl-1-butene (1.8 equiv each) at 100 °C. Excess $HSiEt_3$ and 3,3-dimethyl-1-butene were removed in vacuo before borylation. [d]B_2pin_2 (1.1 equiv).

borylation step using *ortho*-silylated *N*-cyclohexylaldimines suggested that borylation requires 1,10-phenanthroline-based bidentate ligands. **3a′** was not obtained with phosphine-based bidentates or in the absence of ligands. Therefore, the one-pot silylation and borylation reaction was tested by the addition of B_2pin_2 and diamine ligands after the completion of the initial dehydrogenative silylation. Among the iridium precatalysts and diamine ligands that were screened, the combination of $[Ir(OMe)(cod)]_2$ and 3,4,7,8-tetramethyl-1,10-phenanthroline (tmphen) or 4,7-dimethyl-1,10-phenanthroline (**L1**) was most effective (entries 7 and 8). The site selectivity of the second borylation step was completely controlled by steric effects, and no formation of regioisomers was observed. The use of 2-norbornene in place of 3,3-dimethyl-1-butene as a hydrogen acceptor for the dehydrogenative silylation decreased the yield

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of **3a′** (entry 12), which implied that the olefins employed in the initial silylation step affected the efficiency of the second borylation step. As expected, a decrease in the amount of $HSiEt_3$ and 3,3-dimethyl-1-butene and evacuation of the latter after completion of the initial silylation step increased the efficiency of the overall reaction (entry 13). Finally, the yield of **3a′** reached 90% with an increase in the amount of B_2pin_2 to completely consume **2a** (entry 14). The corresponding tetrasubstituted benzene **3a** with formyl, silyl, and boryl functionalities was isolated in 87% yield after hydrolysis with hydrochloric acid (Figure 3).

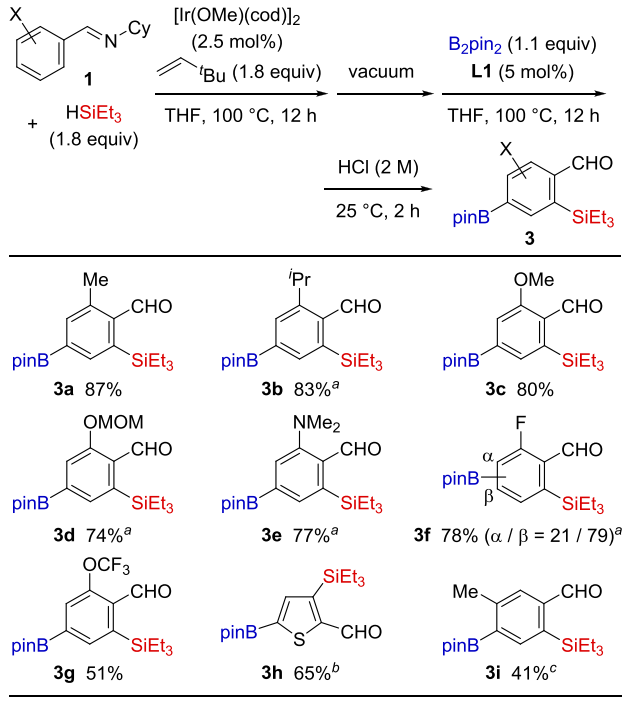
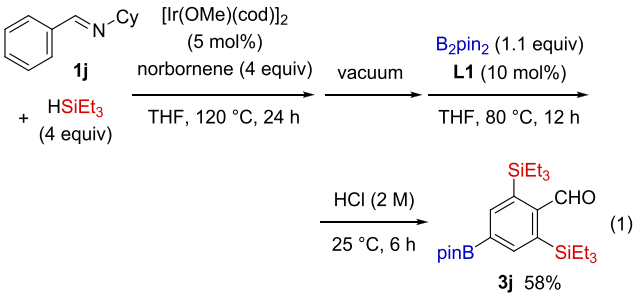
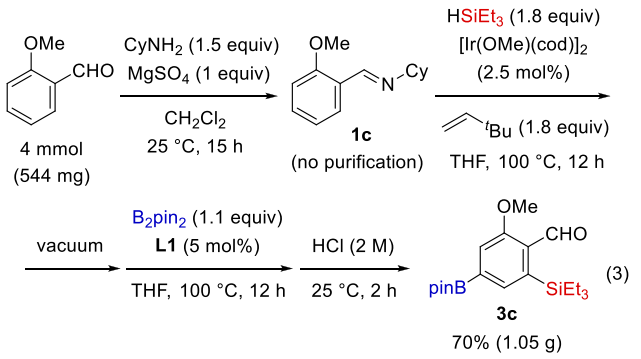


Figure 3. Optimization of reaction conditions for one-pot sequential silylation and borylation of aldimine **1a**. The reaction was conducted on a 0.20 mmol scale in a test tube with a screw cap. [a]3,4,7,8-Tetramethyl-1,10-phenanthroline (tmphen) was used in place of **L1** as a ligand. [b]With 1.4 equiv of $HSiEt_3$ and 3,3-dimethyl-1-butene. [c]Bolylation at 120 °C.

Under the optimized reaction conditions listed in entry 14 of Table 1, the corresponding tetrasubstituted benzene derivatives **3** were obtained by the regioselective silylation and borylation of C−H bonds of **1** in a one-pot synthesis followed by hydrolysis of aldimines (Figure 3). The overall reaction efficiency was generally dependent on the efficiency of the first dehydrogenative silylation step.[10] Electron-rich aldimines, such as **1c**, gave the expected products in higher yields because they were inherently more reactive toward chelation-assisted silylation, which reflects the coordination ability of their nitrogen atoms. Borylation was sluggish with the aldimines **1b**, **1d**, and **1e**, which have relatively bulky substituents on the benzene ring, and the use of more electron-rich tmphen as a ligand gave better results. Note that the reaction proceeded regioselectively even with **1d** and **1e** that have potentially coordinating methoxymethoxy and amino groups. On the other hand, **3f** was obtained as a mixture of two regioisomers from the sequential silylation and borylation of arylimine **1f** derived from 2-fluorobenzaldehyde. In this case, the site selectivity of the second borylation was affected by the electronic factor of the fluoride group as well as by steric factors. As expected, **1g** with the oxytrifluoromethyl group, which is sterically more hindered and electron-withdrawing, was converted to the expected **3g** as a single isomer. The current sequential silylation and borylation can be applied to five-membered ring heterocycles. To suppress the formation of disilylated products, the amount of $HSiEt_3$ and 3,3-dimethyl-1-butene was decreased, and the corresponding **3h** was obtained in 65% yield from 2-thiophenecarboxaldehyde. The sequential silylation and borylation of *m*-tolualdehyde (**1i**) were sluggish and required a higher temperature (120 °C) for the second borylation step. The expected **3i** was obtained as a single regioisomer albeit in low yield. Sequential silylation and borylation of aldimine **1j** derived from benzaldehyde provided disilylated **3j** via the regioselective activation of three different C−H bonds (eq 1).



The current sequential silylation and borylation can be conducted even on a large scale (eq 2). 544 mg of *o*-anisaldehyde with cyclohexylamine afforded aldimine **1c** quantitatively. Purification with chromatography, distillation, or recrystallization was not required, and simple filtration to remove $MgSO_4$ followed by concentration was sufficinet to obtain **1c** in adequately pure form for the following transformation. **1c** was then sequentially treated with $HSiEt_3$ and B_2pin_2 in a 15 mL test tube with a screw cap under standard reaction conditions to give 1.05 g of **3c** in 70% yield (the yield was based on the amount of *o*-anisaldehyde employed).



Although silylation and borylation were reported to proceed under similar conditions using iridium catalysts,[11] the reaction order is important for controlling the reactivity and selectivity during the current sequential C−H difunctionalization. For example, the treatment of **1a** with B_2pin_2 provided an inseparable mixture of borylated compounds with or without **L1** and 3,3-dimethyl-1-butene. Due to the high reactivity of

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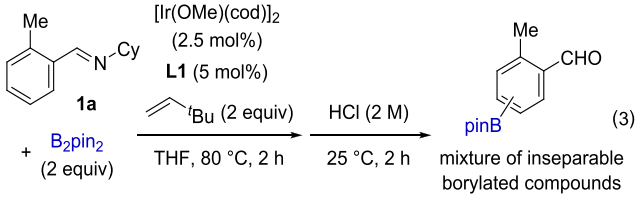
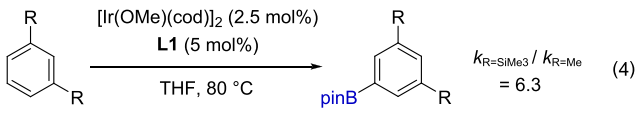
generated boryliridium species, assistance of chelation by an imino group was not sufficient to control the regioselectivity of the reaction (eq 3).



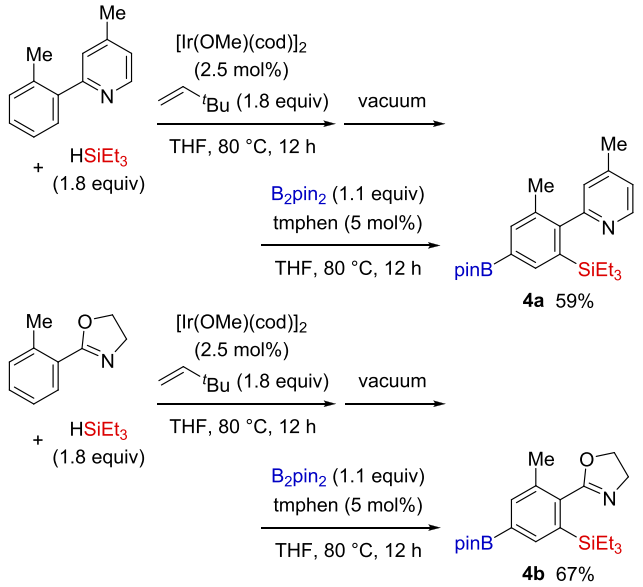
The presence of a silyl group on the benzene ring promoted the borylation of C−H bonds. The initial rate of borylation for 1,3-bis(trimethylsilyl)benzene and *m*-xylene was compared and revealed that the former proceeded more than 6 times faster than the latter (eq 4). Silyl groups increase the electron density



in benzene rings, which could promote the approach of the reactive electron-deficient boryliridium species to the C−H bonds of an aromatic ring.

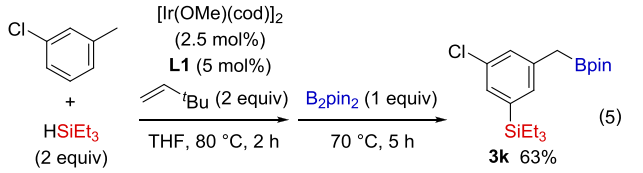
Other than the imino group, 2-pyridyl or 4,5-dihydro-2-oxazolyl groups could be used as effective directing groups for sequential silylation and borylation (Scheme 3). As expected,

Scheme 3. Sequential Silylation and Borylation of Aromatic Compounds with Various Directing Groups



silylation proceeded under chelation control, and borylation was accomplished under steric control to afford the expected **4a** and **4b** in moderate yields. The use of tmphen as a ligand again gave a better result in these reactions.

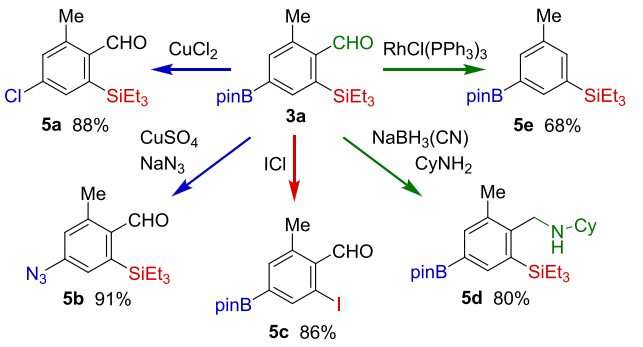
The use of 3-chlorotoluene as a substrate resulted in the introduction of a silyl group onto the benzene ring and a boryl group into the benzylic C(sp^3)−H bond (eq 5). The addition of **L1** was required for the first silylation and second borylation



steps, and the regioselectivity of both reactions was controlled by steric factors. Adducts derived from the competitive reductive dechlorination were not observed, and **3k** was obtained in 63% yield. This is a very rare example of the sequential difunctionalization of two C−H bonds that involves C(sp^3)−H bond activation.[12]

Derivatization of the resulting tetrasubstituted benzenes with formyl, silyl, and boryl functionalities was examined to illustrate their synthetic utility (Scheme 4). Treatment with

Scheme 4. Derivatization of the Product (see the Supporting Information for details)



$CuCl_2$ or NaN_3 in the presence of $CuSO_4$ converted the boryl group of **3a** into chloride or azide groups to yield **5a** or **5b**, respectively, with no effect on the formyl or silyl groups.[13] Selective conversion of silyl groups by iododesilylation with ICl proceeded smoothly to afford **5c** in 86% yield.[14] The formyl groups could be utilized for C−N bond formation via reductive amination to yield **5d**.[15] The formyl groups could be also selectively removed by simple heating with a Wilkinson catalyst to yield **5e**.[16] Selective installation of boryl and silyl groups at these positions is difficult without the current difunctionalization protocol.

In conclusion, simple programmed synthesis of tetrasubstituted benzenes was demonstrated by sequential silylation, borylation, and hydrolysis of functionalized aldimines. The reaction order is important for controlling the reactivity and regioselectivity, and the first silylation reaction promotes the second borylation reaction. The regioselectivity was well-controlled by a single iridium catalyst, and silylation proceeded under chelation control with an imino group, whereas borylation was accomplished under steric control by the initially incorporated silyl group. The formyl, silyl, and boryl functional groups could be independently converted to other functional groups, and the proposed method opens up new perspectives for the development of pot-economical rapid approaches to synthetically useful building blocks.

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■ ASSOCIATED CONTENT

Supporting Information

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Experimental procedures, spectroscopic data for all new compounds, and copies of ^{1}H and ^{13}C NMR spectra (PDF)

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Notes

The authors declare no competing financial interest.

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