Recent Progress in the Cross-Coupling Reaction Using Triorganosilyl-Type Reagents
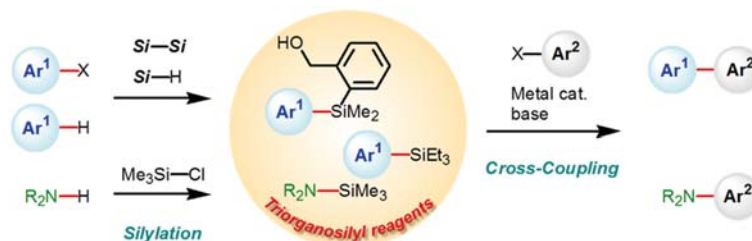
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Abstract The silicon-based cross-coupling reaction has attracted much attention over recent decades because there are many advantages in using organosilicon compounds. However, the use of reagents with a triorganosilyl group as a key function remains to be established. This account summarizes our recent progress in cross-coupling chemistry with such silyl reagents.

1   Introduction
2   Preparation of HOMSi Reagents from Aryl Bromides and Disilanes
3   HOMSi Reagents from Heteroaromatics and Hydrosilanes
4   Cross-Coupling Polymerization with HOMSi Reagents
5   Cross-Coupling with Aryl(triethyl)silanes
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1   Introduction

The cross-coupling reaction has been developed as a common tool to form carbon–carbon and carbon–heteroatom bonds in π-conjugate systems and allows the construction of a wide variety of frameworks of potent pharmaceuticals, agrochemicals, and electronic materials.[1] To achieve the bond formation, the use of nucleophilic organometallic reagents such as lithium, magnesium, zinc, aluminum, tin, boron, silicon, zirconium, indium and others is essential. Among them, silicon is attractive as it is an earth-abundant element and organosilicon reagents are superior in terms of stability, solubility, ease of handling, and accessibility. Nowadays, many types of organosilicon reagents are available for alkenylation, arylation, alkynylation, and alkylation of organic halides.[2] For successful reactions, a nucleophilic activator such as a fluoride or hydroxide ion is generally employed. To assist the silicon–activator interaction, one to three electronegative heteroatoms such as a halogen or oxygen are often introduced at the silicon center, mainly for the sake of easy formation of the pentacoordinate silicate species responsible for transmetalation to a transition-metal catalyst. As a result, these silicon reagents become reactive enough to accomplish the cross-coupling, but meanwhile they become air- and moisture-sensitive. Therefore, careful attention is required in the preparation and handling of the halo- and oxysilanes.

In contrast, tetraorganosilanes are characterized by their robustness and low toxicity. Accordingly, in terms of stability and ease of handling, they are favorable. However, such reagents generally do not show enough reactivity for the cross-coupling due possibly to inferior silicate formation. In order to find cross-coupling-active alkenyl(triorgano)silanes and appropriate activators, many chemists have made efforts to find a solution. Some triorganosilyl-type reagents are summarized in Figure 1. Hatanaka and Hiyama first discovered that structurally simple vinyl(trimethyl)silanes coupled with aryl iodides upon activation by tris(dimethylamino)sulfonium difluorotrimethylsilicate (TASF).[3] More than a decade later, Denmark disclosed that 1-alkenyl-1-methyl-silacyclobutanes underwent cross-coupling in the presence of tetrabutylammonium fluoride (TBAF)[4] and observed a ring-opening reaction of the four-membered silacycle by water in TBAF to produce a silanol. They considered that this silanol[2c] was the true active species.[4b] Similarly, 2-pyridyl,[5] 2-thienyl,[6] benzyl,[7] phenyl,[8,9] 3,5-bis(trifluoromethyl)phenyl,[10] allyl,[11] and pentafluorophenyl[12] groups are shown to act as a leaving group to generate cross-coupling-active fluorosilanes and/or silanols in situ. A substituent-induced intramolecular activation strategy is also effective for the coupling. Shindo found that a carboxyl group β-cis to the silicon in alkenyl(trimethyl)silanes promoted the cross-coupling through intramolecular

activation with Cs_2CO_3.[13] Nakao and Hiyama invented alkenyl[2-(**H**ydr**O**xy**M**ethyl)phenyl]dimethyl**Si**lanes (alkenyl-HOMSi), which underwent the cross-coupling reaction even in the presence of K_2CO_3.[14]

Cross-coupling-active aryl(triorgano)silanes were also disclosed as in the case with the alkenyl silanes. Such active arylsilanes are summarized in Figure 2. Arylsilanes bearing allyl,[15,16] 2-(hydroxymethyl)phenyl,[14] or (2-hydroxyprop-2-yl)cyclohexyl[17] groups can be used to connect a wide range of aryl groups to various aryl halides. Simple 2-pyridyl-[18] and 2-benzofuryltrimethylsilanes[19] were employed for cross-coupling with aryl iodides in the presence of not only a palladium catalyst, but also a stoichiometric transition-metal mediator. A *tert*-butyldimethylsilyl group was used in the cross-coupling only in the case of using 8-hydroxy-1-naphthyl as an electrophile.[20] Aryl(triorgano)silanes substi-

tuted by a heteroaryl, or 3,5-bistrifluoromethylphenyl group were suggested by Murata,[21] Gevorgyan,[22] and Murai and Takai.[23]

As described above, organo-HOMSis are examples of cutting-edge reagents for silicon-based cross-couplings (Scheme 1). This type of cross-coupling reagent is applicable not only to alkenylation and arylation, but also to alkylation.[14g] The organo-HOMSi reagents are stable but become highly reactive to effect the cross-coupling upon activation by a weak base such as potassium carbonate.[14] Moreover, the silicon residue, cyclic silyl ether **1**, is recoverable and recyclable to any organo-HOMSi reagents by treatment with an organolithium or organomagnesium reagent.

Protection of the proximal hydroxy group makes the HOMSi totally cross-coupling inactive.[14e,f] Orthogonally removable protecting groups such as tetrahydropyranyl (THP), methoxymethyl (MOM), acetyl (Ac), and silyl (SiR$_3$) are applicable. This flexibility permits the construction of a

Biographical Sketches

Takeshi Komiyama was born in Saitama in 1991, and is a Ph.D. student at Chuo University guided by Professors Tamejiro Hiyama and Yasunori Minami. His research interest is the exploitation of novel synthetic transformations of organosilicon compounds by transition-metal catalysis. He received a Poster Award at the 5th CSJ Chemistry Festa (2015), the Gakuin Kaicho Award from the Head of Chuo University Alumni Association (2016), the Student Presentation Award at the 71th Kanto Branch Symposium organized by the Association of Synthetic Organic Chemistry, Japan (2016), the Shibuya Ken-ichi Award for Encouragement presented by the Director of Chuo University (2017), and the Presentation Award (Industry Division) at the 97th CSJ Annual Meeting (2017).

Yasunori Minami was born in Mie prefecture in 1982. He spent three months at the Laboratories of Professor John F. Hartwig (University of Illinois at Urbana-Champaign) as a visiting student in 2009, before receiving his Ph.D. from Osaka University in 2010 under the supervision of Professor Nobuaki Kambe. He then joined RDI at Chuo University as an assistant professor. His current research interests are synthetic organic chemistry using transition-metal catalysts and main group elements.

Tamejiro Hiyama was born in Osaka in 1946. He was appointed Associate Professor at Kyoto University in 1972, completed his Ph.D. under the supervision of Professor Hitosi Nozaki at Kyoto University in 1975, and spent a postdoctoral year at Harvard University working with Professor Yoshito Kishi. In 1981, he started his research as a Principal Investigator at the Sagami Chemical Research Center. In 1992, he moved to the Research Laboratory for Resources Utilization, Tokyo Institute of Technology, as a full professor and then to the Graduate School of Engineering, Kyoto University, in 1997. Since retirement from Kyoto University in 2010, he has been at Chuo University as an RDI Professor. His research stems from the invention of synthetic methods for the synthesis of biologically active agents and liquid crystalline and light-emitting materials.
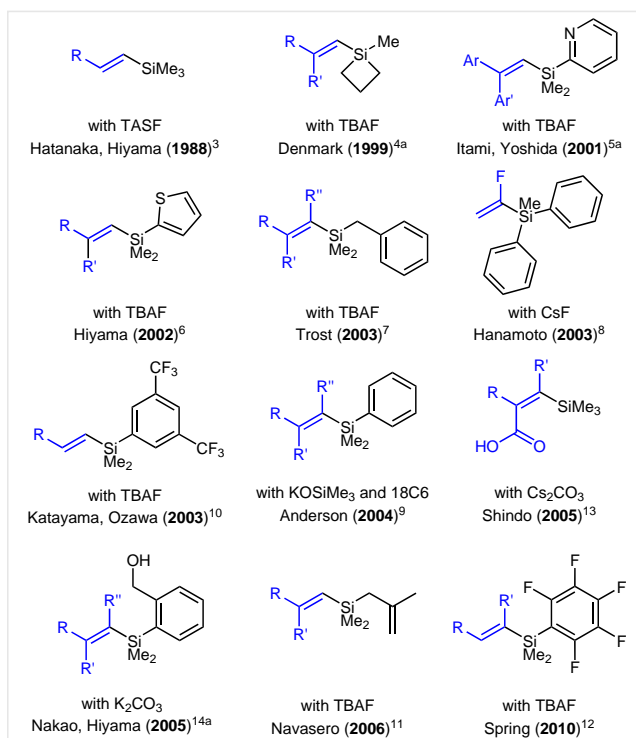
Figure 1 Cross-coupling-active alkenyl(triorgano)silanes and their activators. Blue units are utilized as coupling partners
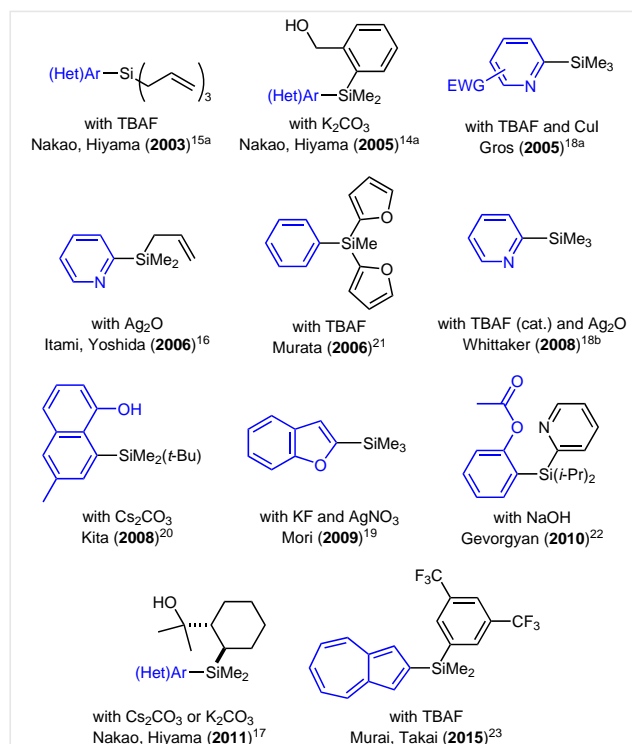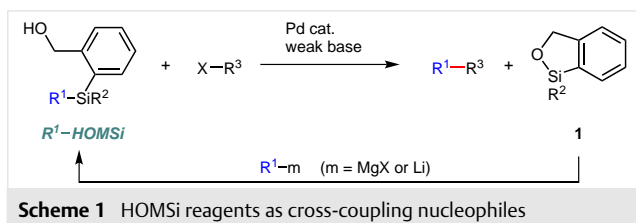

Figure 2 Cross-coupling-active aryl(triorgano)silanes and their activators. Blue units are utilized as coupling partners

**Scheme 1** HOMSi reagents as cross-coupling nucleophiles

variety of oligoarenes easily. For example, 2-thienyl-HOMSi undergoes cross-coupling with THP-protected 2-(5-bromothienyl)-HOMSi in the presence of a catalyst consisting of palladium, CuI, and RuPhos to give the protected bithienyl-HOMSi, which can be deprotected to give cross-coupling-active bithienyl-HOMSi (Scheme 2).

A similar idea of intramolecular activation was also developed by Tamao, who noted that *ortho*-oxybenzyl-substituted phenylsilanes generated in situ from cyclic silyl ether **2**, phenyllithium, and copper iodide, undergo cross-coupling with iodoarenes (Equation 1).[24] Smith applied this basic concept to cyclic silyl ether **3**, which was easily converted into aryl-(lithioxy-methylphenyl)diisopropylsilanes upon treatment with an aryllithium and then cross-coupled with aryl chlorides (Equation 2).[25]
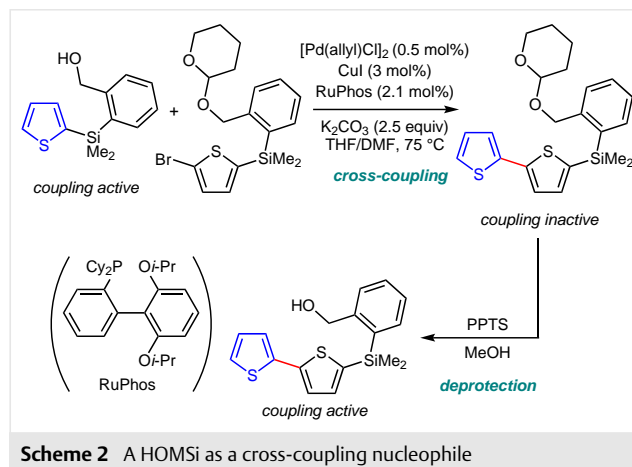

Scheme 2 A HOMSi as a cross-coupling nucleophile

As discussed before, some tetraorganosilanes are active for the cross-coupling but lack the generality. Herein, we briefly review our recent progress in the development of synthetic methods for triorganosilyl-type reagents and their cross-coupling chemistry, taking advantage of such silicon reagents.
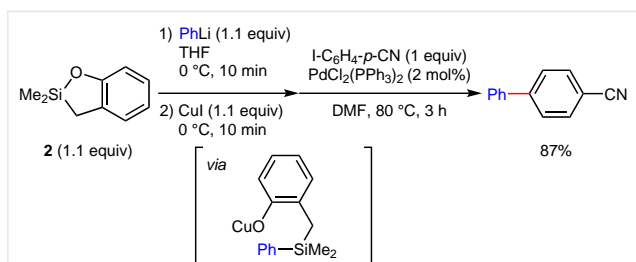
Equation 1
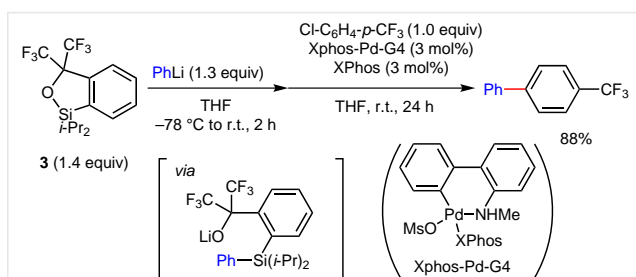
Equation 2

## 2 Preparation of HOMSi Reagents from Aryl Bromides and Disilanes

The reaction of the cyclic silyl ether **1** with organometallic reagents in Scheme 1 is a typical procedure to prepare any HOMSi reagent. However, it is not suitable in the case of reagents containing a reactive functional group such as formyl or cyano. To overcome this drawback, transition-metal-catalyzed silylation of aryl electrophiles with hydrosilanes,[26] disilanes,[27] or silylboranes[28] is feasible. Indeed, Kondo reported that the Pd-catalyzed silylation of aryl bromides using hydrido[2-(hydroxymethyl)phenyl]dimethylsilane (H-HOMSi) gave Ar-HOMSis containing acetyl and cyano groups,[29] although the yields are moderate in the two examples shown. We decided to scrutinize the catalytic conditions for the synthesis of Ar-HOMSi and found that a Pd/Cu dual catalytic system was effective for the silylation of aryl bromides with protected HOMSi-type disilanes **4$_{PG}$** and could be used to prepare various protected aryl-HOMSi reagents **5** (Scheme 3).[30] For example, 4-bromotoluene reacted with THP-protected disilanes **4$_{THP}$** in the presence of [Pd(allyl)Cl]$_2$ (2.5 mol%), RuPhos (10 mol%), CuI (10 mol%), K$_2$CO$_3$ (2.2 equiv), H$_2$O (4 equiv), and dioxane/NMP co-solvents to give THP-protected tolyl-HOMSi **5aa** in 73% yield. The disilane **4$_{THP}$** was prepared easily by the reaction of dichlorotetramethylsilane with the corresponding aryllithium. Based on the fact that CuI as a co-catalyst is particularly effective for the silylation, a silyl copper reagent is probably produced as an active nucleophile by the reaction of **4**, CuI, and K$_2$CO$_3$. Other protecting groups such as methoxymethyl (MOM), acetyl, and *t*-butyl(diphenyl)silyl (TBDPS) are also

available for this reaction. This method allows the preparation of phenyl-HOMSi reagents containing any electron-donating or electron-withdrawing reactive functional group. RuPhos was effective for arenes with an electron-donating aryl group and DavePhos for those with an electron-withdrawing group. When RuPhos was used, HOMSi reagents with OMe, NPh$_2$, and NHBoc groups at *para* positions (**5ba–da**) were obtained in good yields, whereas the synthesis of a HOMSi reagent with a CF$_3$ group did not proceed effectively; the example with a bulky 2-tolyl aryl group reduced the reactivity to afford low yields of the product.
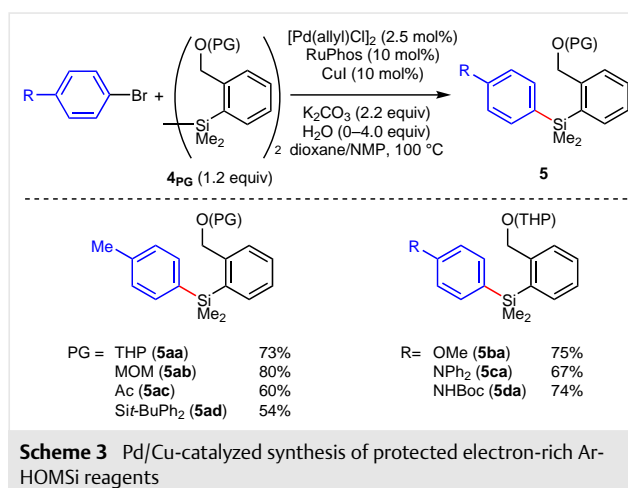

Scheme 3 Pd/Cu-catalyzed synthesis of protected electron-rich Ar-HOMSi reagents

In the case of DavePhos as a ligand, Ar-HOMSi reagents **5ea–ia** with an electron-neutral or electron-deficient substituent such as CF$_3$, CN, Cl, Ac, and CHO were obtained in moderate to good yields (Scheme 4), whereas the reagent with an NO$_2$ group was hard to prepare by the present method.
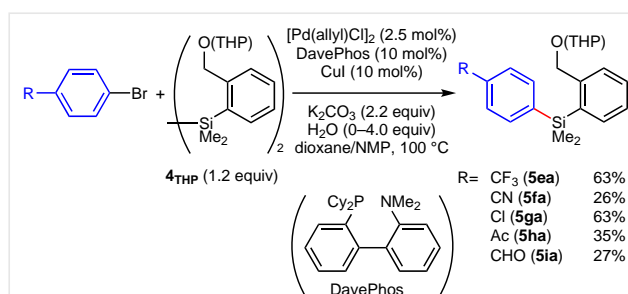
**Scheme 4** Pd/Cu-catalyzed synthesis of protected electron-neutral and electron-deficient Ar-HOMSi reagents

Bis-HOMSi reagents were also successfully prepared. For example, 2,7-dibromo-9,9-dioctylfluorene was doubly silylated smoothly under conditions similar to those in Scheme 3 and gave THP-protected bis-HOMSi **6a** (Equation 3), which was employed for polyarylene synthesis (vide infra, see section 4).[31]

Equation 3
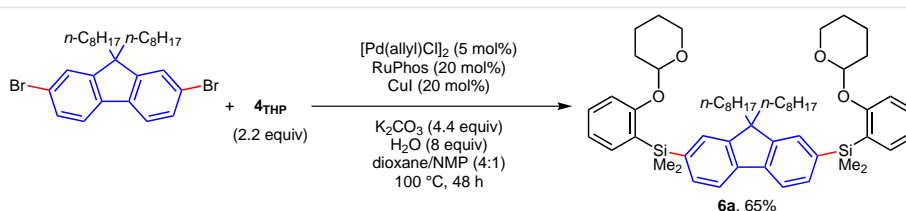
3 HOMSi Reagents from Heteroaromatics and Hydrosilanes

In contrast to the preparation of Ar-HOMSi reagents starting with aryl halides, catalytic C–H silylation of aromatic hydrocarbons is more attractive in view of green chemistry.[32] This type of transformation is made possible by C–H silylation of arenes catalyzed by a transition-metal complex,[33] t-BuOK,[34] B(C_6F_5)$_3$,[35] or a Brønsted acid.[36] HOMSi-type hydrosilanes, H-HOMSi **7**, accessible by hydride reduction of **1** followed by protection of the resulting OH group, are an appropriate form for the straightforward synthesis of Ar-HOMSi. The total transformation is considered a sustainable silicon cross-coupling protocol (Scheme 5). Therefore, we decided to develop the straightforward synthesis of Ar-HOMSi reagents.[37]
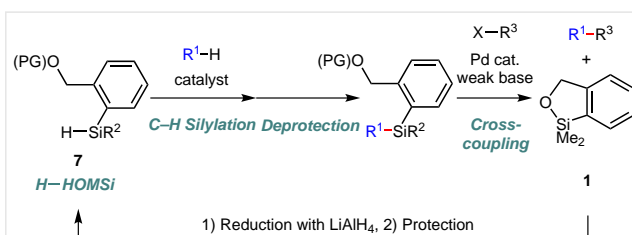
Scheme 5 A HOMSi-based sustainable cross-coupling cycle

According to Falck's protocol,[33c] we first examined the reaction of benzothiophene with MOM-protected hydrosilanes **7$_{MOM}$** using the [Ir(OMe)cod]$_2$/4,7-di-$tert$-butyl-bypyridyl (dtbpy) catalytic system and isolated the desired product in <10% yield. Optimization of the conditions led to the isolation of THP-protected benzothienyl-HOMSi **5ja** in 89% yield: [Ir(OMe)cod]$_2$ (5 mol%), Me$_4$phen (10 mol%), norbornene (1.5 equiv) in (i-Pr)$_2$O (2 M) at 80 °C (Scheme 6). An acetyl group is also a pertinent protecting group. Five-membered heteroaromatics such as benzofuran, indole, and 2-bromo-3-dodecylthiophene gave C2-silylated products in good to excellent yields. The carbon–bromine bond did not interfere with this silylation, whereas pyridine, pentafluorobenzene, and 1,4-dimethoxybenzene failed to undergo silylation.

Scheme 6 Straightforward syntheses of protected Ar-HOMSis via Ir-catalyzed C–H silylation
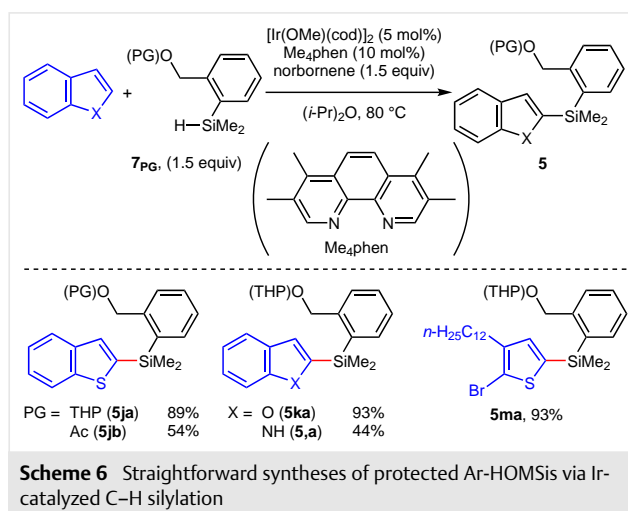
Using three equivalents of **7$_{THP}$** and norbornene, disilylation was successfully effected to give Ar(HOMSi)$_2$. Indeed, Ar(HOMSi)$_2$ reagents **6b–e** were readily accessible, originating from 3-bromothiophene, benzodithiophene, 3,4-ethylenedioxythiophene, and 4,7-dithienylbenzothiadiazole (Figure 3) under the conditions in Scheme 6. The resulting Ar(HOMSi)$_2$ compounds are potential monomers for the synthesis of π-conjugated polymers used for organic electronics.
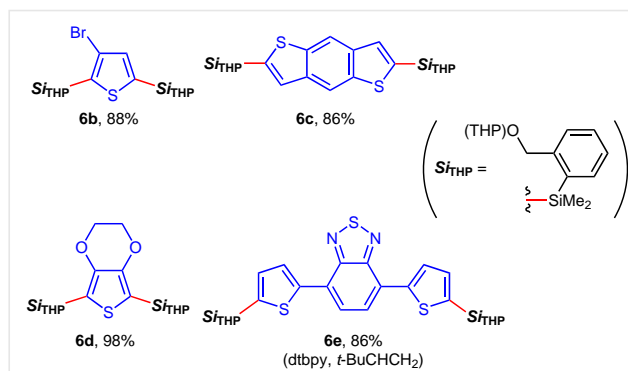

**Figure 3** Bis-HOMSi reagents via Ir-catalyzed double C–H silylation

4   Cross-Coupling Polymerization with HOMSi Reagents

Polyarylenes play a significant role in organic electronics. To construct such π-conjugated molecules, cross-coupling using organoboron or organotin reagents is the standard approach at present.[38] When organoboron monomers suffer from low solubility owing to their planar and rigid skeletons, organotin reagents containing alkyl chains on the tin center are preferably employed. However, organotin reagents are toxic in general so that they are not suitable for mass production in industry. In contrast, organosilicon compounds are in general stable and easy to handle without such toxicity problems. However, silicon-based polymerization leading to polyarylenes has remained almost unexplored except for a few efforts.[39] To achieve successful high-molecular-weight-polymer synthesis, we applied the HOMSi-based cross-coupling. However, the reaction conditions shown in Scheme 2 require strictly stoichiometric organometallic reagents based on organic halides, whereas the original HOMSi-based coupling requires loading of silicon regents in a slight excess. Therefore, we pursued optimization of the reaction conditions to achieve cross-coupling polymerization using Ar-HOMSi reagents and examined double cross-coupling reactions using stoichiometric amounts of Ar-HOMSi and dibromoarenes. As a result, 2.1 equivalents of phenyl-HOMSi turned out to doubly couple with dibromoarenes in the presence of Pd[P(o-tolyl)$_3$]$_2$ (2 mol%), DPPF (2.1 mol%), CuBr·SMe$_2$ (3.0 mol%), Cs$_2$CO$_3$ (4.2 equiv), 3 Å MS, and THF/NMP co-solvent in high efficiency (Scheme 7). For instance, 1,4-dibromo-2,5-dihexylbenzene, 2,7-dibromo-9,9-dioctylfluorene, and 2,5-dibromothiophene were applicable to the coupling of Ph-HOMSi and gave products **8a–c** in yields higher than 90%. Moreover, 4,7-dibromobenzothiadiazole smoothly reacted with 2-thienyl-HOMSi, 4-diphenylaminophenyl-HOMSi, and 9,9-dioctyl-2-fluorenyl-HOMSi to furnish teraryls **8d–f** in good to excellent yields.
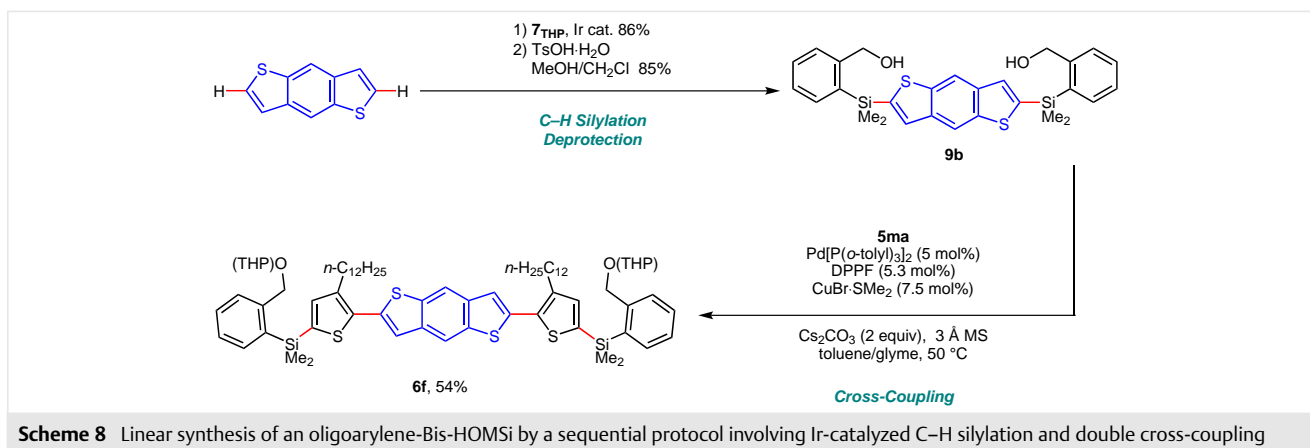
Bis-4,7-(fluorenylene)HOMSi **9** underwent double coupling with 4-bromobenzothiadiazole to give teraryl **8g** in an excellent yield (Equation 4).

Scheme 7 Pd-catalyzed double cross-coupling of aryl dibromides with Ar-HOMSi
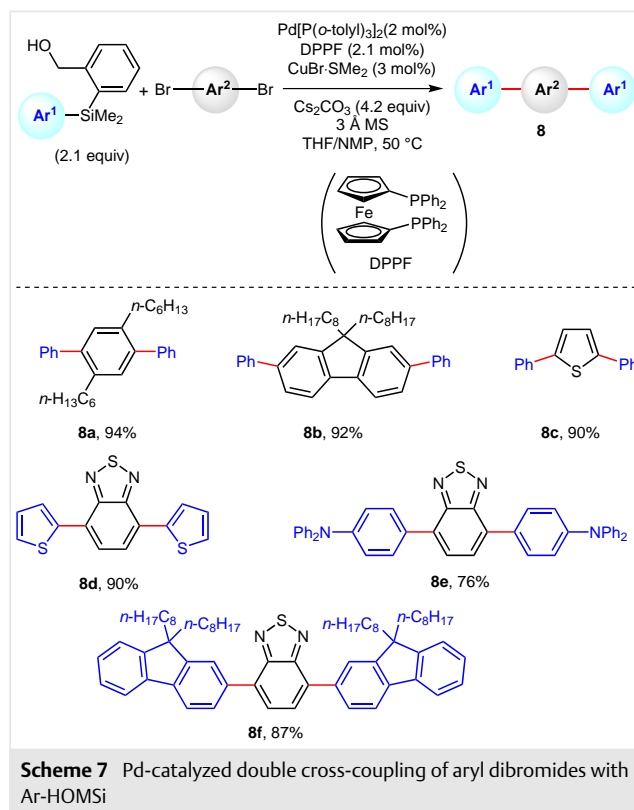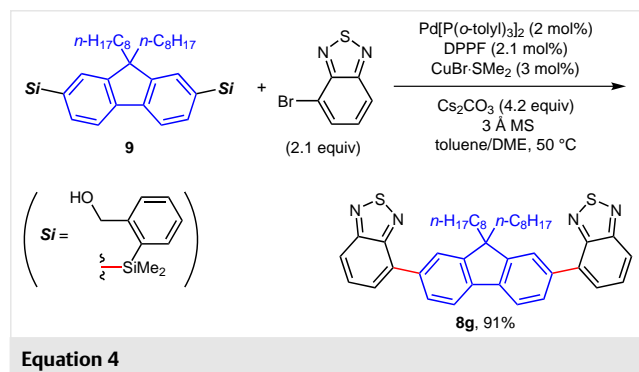
With optimized coupling conditions in hand, we next studied the synthesis of polyarylenes. Cross-coupling polymerization of **9** with 4,7-dibromobenzothiadiazole produced in a quantitative yield poly(9,9-dioctyl-fluorene-co-benzothiadiazole),[40] also known as light-emitting material F8BT (Equation 5).

Equation 5
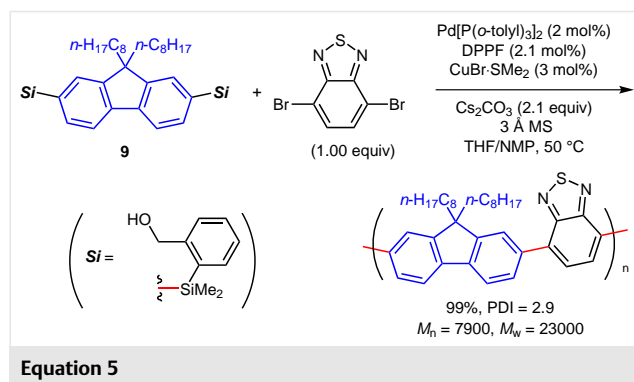
Combined with this double-coupling protocol and the straightforward disilylation described in Section 3, the linear synthesis of an oligo(arylene)-based bis-HOMSi was easily achieved via a net C–Br/C–H coupling (Scheme 8). Double silylation product **6c** (see Figure 3) was deprotected to give cross-coupling-active benzodithienylene-bis-HOMSi (**9**), which underwent double cross-coupling with THP-pro-

Equation 4

Scheme 8 Linear synthesis of an oligoarylene-Bis-HOMSi by a sequential protocol involving Ir-catalyzed C–H silylation and double cross-coupling

tected 5-bromo-4-dodecyl-2-thienyl-HOMSi **5ma** (see Scheme 6), withstanding the steric repulsion between the dodecyl groups, to produce the coupled product **6f**. This oligoarene unit is a part of a polymer for a solar cell.[41]
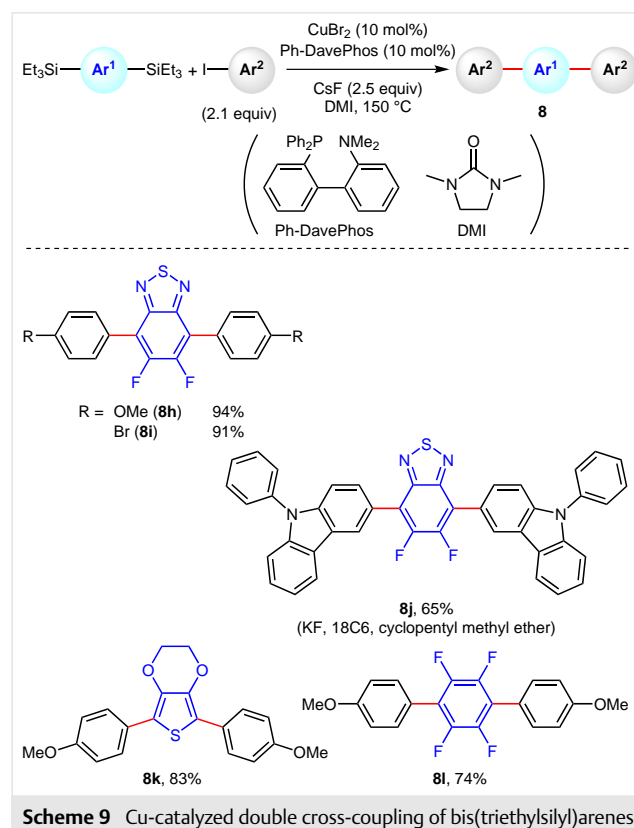
5 Cross-Coupling with Aryl(triethyl)silanes

During the studies described in Sections 2, 3, and 4, we were challenged repeatedly to prepare 4,7-benzothiadiazole-based bis-HOMSi reagents by lithiation followed by the reaction with **1**, Pd/Cu-catalyzed silylation of bromobenzothiadiazoles as described in Section 2, and Ir-catalyzed silylation of benzothiadiazoles, but all attempts failed. A great deal of effort led to the Ir-catalyzed C–H silylation of 5,6-difluorobenzothiadiazole using triethylsilane as a silylation reagent (Equation 6). Since the cross-coupling of aryl(triethyl)silanes had no precedent, we decided to find appropriate catalytic conditions for the cross-coupling of aryl(triethyl)silanes.

Equation 6
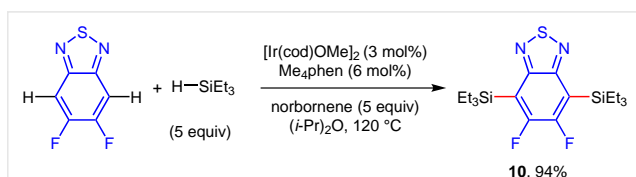
As discussed previously, the coupling with trialkylsilyl-type reagents has been a long-standing synthetic challenge; a successful outcome would be anticipated to enhance the availability of not only organosilicon chemistry but also synthetic organic chemistry. Thus, we focused on the development of the cross-coupling reaction with trialkylsilylarenes with aryl halides. We were soon pleased to find that CuBr$_2$ was a crucial catalyst for the targeted reaction.[42] For example, the reaction of 4,7-bis(triethylsilyl)-5,6-difluoro-

benzothiadiazole (**10**) with 4-iodoanisole and 4-iodobromobenzene took place in the presence of CuBr$_2$ (10 mol%), Ph-DavePhos (10 mol%), CsF (2.5 equiv) in 1,3-dimethyl-2-imidazolidinone (DMI) to give teraryls **8h** and **8i** in excellent yields (Scheme 9). The coupling of **10** with 3-iodocarbazole produced **8j** in a good yield using KF, 18-crown-6 (18C6), and cyclopentyl methyl ether (CPME) instead of CsF and DMI. Double cross-coupling of 2,5-bis(triethylsilyl)-3,4-ethylenedioxythiophene and 1,4-bis(triethylsilyl)tetrafluorobenzene, both prepared by the Ir-catalyzed C–H silylation, proceeded to give **8k** and **8l**.

Scheme 9 Cu-catalyzed double cross-coupling of bis(triethylsilyl)arenes

The results of the mono-coupling of aryl(triethyl)silanes with 4-iodoanisole are summarized in Figure 4. 2-Benzothienyl, 2-indolyl, 2- and 3-pyridyl-, 3,5-bis(trifluoromethyl)phenyl-, and 4-cyanophenyl(triethyl)silanes gave the corresponding biaryls in moderate to excellent yields. Whereas 2-pyridylboronic acids and esters were not sufficiently stable to effect the Suzuki–Miyaura coupling, 2-pyridyltrimethylsilane is stable and easy to handle, and smoothly participates in the cross-coupling.[43] We should note that electron-neutral and electron-rich arylsilanes such as 2-naphthyl-, 4-biphenyl-, and 4-diphenylaminophenyl-(triethyl)silanes failed to react, probably due to the low electrophilicity of the silicon center.
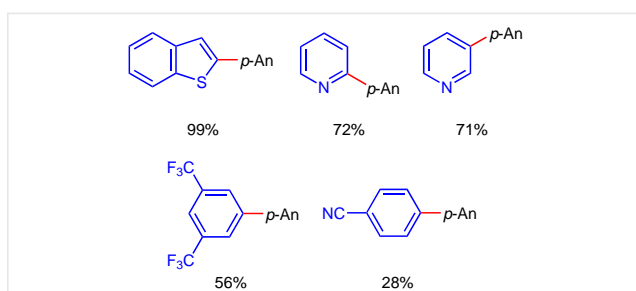

Figure 4 Biaryls synthesized by Cu-catalyzed coupling of aryl(triethyl)silanes with 4-iodoanisole. p-An = 4-MeOC$_6$H$_4$

In addition to 4,7-bis(triethylsilyl)-5,6-benzothiadiazole (**10**), its phenyldimethylsilyl analog **10′** cross-couples with 4-iodoanisole to give 4,7-(di-4-anisyl)benzothiadiazole **8h** in 63% yield along with 4-methoxybiphenyl (4% yield) (Equation 7). Probably a more electron-deficient aryl group on the silicon center was transmetalated to the Pd center faster than an electron-rich one. This reactivity order contrasts sharply to that in transmetalation in the Pd-catalyzed cross-coupling of arylsilanes.[44] Because the coupling of **10** with 4-iodoanisole is not catalyzed by CuI or CuBr, the mechanism of the Cu(II)-catalyzed reaction is definitely different from the recorded Cu(I)-catalyzed silicon-based cross-coupling, which is considered to proceed through a Cu(I)/Cu(III) cycle.[45]
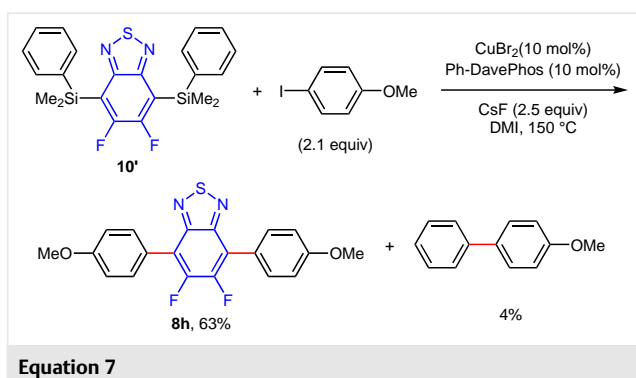
Equation 7

We propose the catalytic cycle shown in Scheme 10, which consists of three steps: (1) single-electron transfer from Ar^1(fluoro)silicate to CuX$_2$ (X = Br, I) to generate radical species **II** and/or **III** and Cu(I)X, (2) oxidative addition of Ar^2–I to Cu(I)X to form Ar^2–Cu(III), and (3) coupling of **II** and/or **III** with Ar^2–Cu(III) to form the coupled Ar^1–Ar^2 product and reproduce Cu(II)X$_2$.
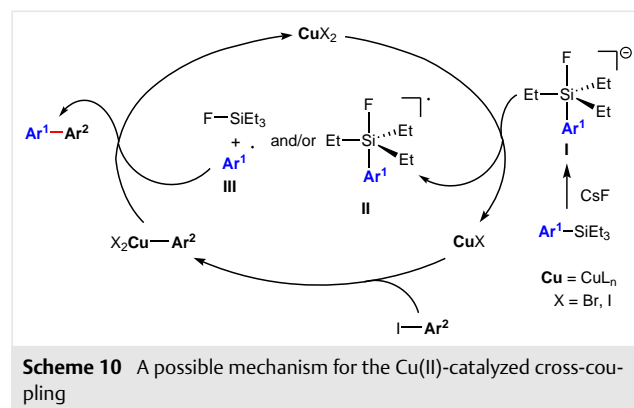

Scheme 10 A possible mechanism for the Cu(II)-catalyzed cross-coupling

6   Amination of Aryl Halides with *N*-TMS-Amines

The concept of the silicon-based cross-coupling is applicable to formation of not only C–C bonds, but also carbon–heteroatom bonds including C–S,[46] C–O,[47] and C–N[48] bonds. As for C–N bond-forming reactions, the Buchwald–Hartwig amination is well described, which generally requires the use of a strong base.[49] On the other hand, Pd-catalyzed amination using an *N*-silylamine takes place upon activation with a base such as a fluoride ion. Indeed, Smith observed that *N*-TMS-amines couple with aryl bromides in the presence of a palladium catalyst and Cs$_2$CO$_3$ or CsF in supercritical carbon dioxide.[48b,c] This observation is seminal but it is a drawback to use a pressure bottle for supercritical CO$_2$. In addition, the reactivity of silylamines remains to be improved. Thus, we decided to improve the conditions for the C–N bond-forming cross-coupling reaction using *N*-TMS-amines.[50] *N*-TMS-amines can be prepared by lithiation of *N*-H-amines followed by reaction with chlorotrimethylsilane.

After screening the reaction conditions, we found that amination of 4-bromotoluene took place with *N*-TMS-diphenylamine (1.1 equiv), Pd(dba)$_2$ (1 mol%), XPhos (2 mol%), CsF (1.5 equiv), and DMI as a general organic solvent (Scheme 11) to give 4-methyltriphenylamine in 97% yield. Various bromoarenes such as 4-BrC$_6$H$_4$NPh$_2$, 2-BrC$_6$H$_4$Me, and 1- and 2-bromonaphthalenes were applicable to the reaction, whereas 2- or 3-bromothiophene, 3-bromopyridine, and bulky 1-bromo-2,6-dimethylbenzene proved unreactive. It is noteworthy that 4-chlorotoluene undergoes the amination without any serious problems. Other *N*-TMS-

Scheme 11 Pd-catalyzed C–N bond-forming cross-coupling of aryl bromides with *N*-TMS-amines
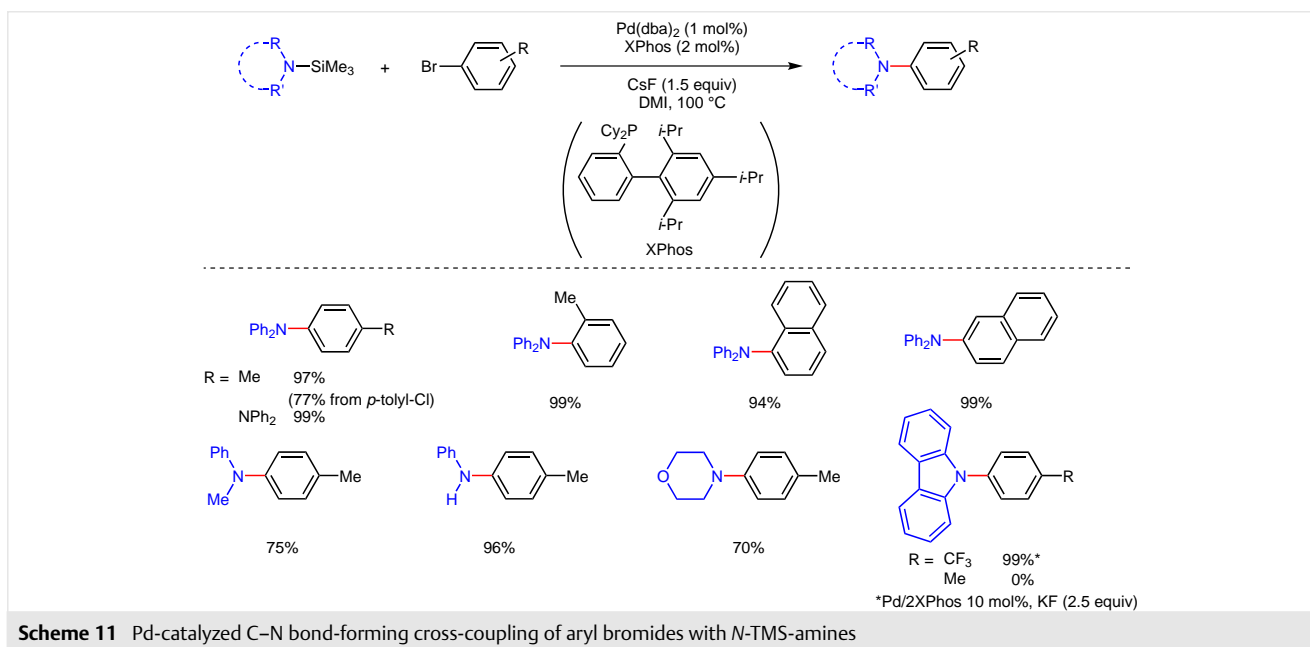
amines such as *N*-TMS-*N*-methylaniline, *N*-TMS-aniline, *N*-TMS-morphine, and *N*-TMS-carbazole are applicable to this amination. Although an *N*-arylcarbazole unit is an important motif in organic electronics,[51] *N*-TMS-carbazole could only be applied to the reaction with electron-deficient aryl bromides under the palladium catalytic conditions.

We compared the reactivity of *N*-TMS-amines with respect to the rate of amination of 4-bromotoluene using TMS-NPh$_2$, TMS-NMePh, TMS-NHPh, and *N*-TMS-morpholine. The results are shown in Figure 5,[50b] which shows that the reaction rates are in the order of TMS-NPh$_2$ > TMS-NMePh ≈ TMS-NHPh > *N*-TMS-morpholine. In contrast, diarylamines are less reactive in the Buchwald–Hartwig amination than alkyl(aryl)amines and monoaryl amines.[52] The opposite reactivity order of *N*-TMS-amines is attributed to the basicity of amines, which may contribute to the smooth activation of silicon by a fluoride ion.
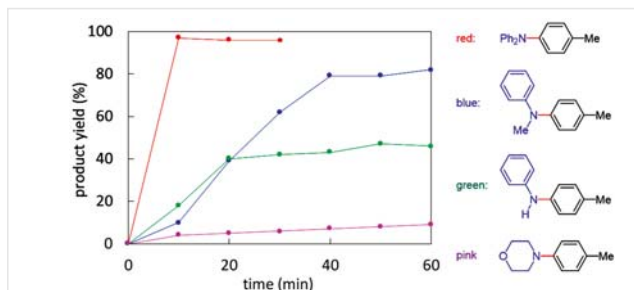

Figure 5 Time courses for the formation of 4-tolyl-NPh$_2$ (red), 4-tolyl-NMePh (blue), 4-tolyl-NHPh (green), and *N*-(4-tolyl)morpholine (pink) by Pd-catalyzed amination of 4-bromotoluene with the corresponding silylamines

The present C–N bond-forming coupling was applied to poly(arylene-imine)[53] synthesis (Scheme 12). Under the optimized conditions, 2,7-dibromo-9,9-dioctylfluorene reacted with *N,N*-bis(TMS)-anilines or *N*-TMS-*N'*-TMS-*para*-phenylenediamine to produce the corresponding polymers, which might be employed as organic electron-conducting materials.[54]

Scheme 12 Poly(arylene-imine) synthesis
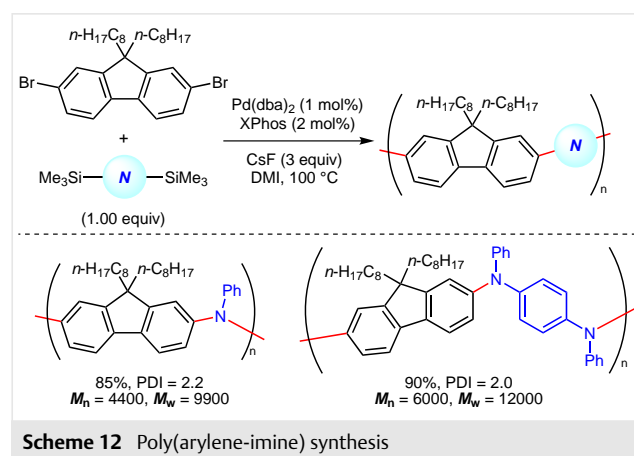
As mentioned above, the Pd-catalyzed amination protocol does not work well with *N*-TMS-carbazole and electron-rich aryl bromides. We were pleased to find that nickel catalysis is especially effective for the amination of aryl bromides with *N*-TMS-carbazole.[55] In fact, *N*-TMS-carbazole coupled with both electron-rich and electron-deficient aryl

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bromides using an SIPr-ligated nickel(0) complex generated in situ (Scheme 13). This novel amination proceeds in the presence of a weak base, sodium acetate.
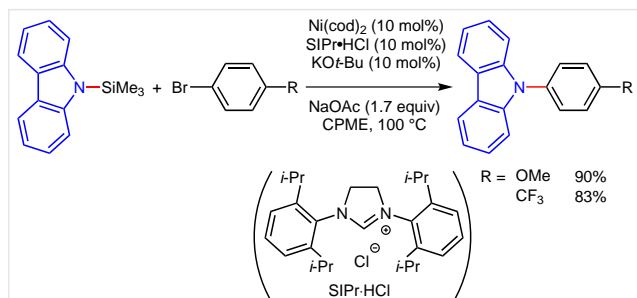
Scheme 13 Pd-catalyzed C–N bond-forming cross-coupling of aryl bromides with *N*-TMS-amines

7   Conclusion and Perspective

Recent contributions to silicon-based cross-coupling chemistry are briefly reviewed mainly from our view point. Sections 2, 3 and 4 demonstrate that a wide variety of HOMSi reagents are readily accessible via two catalytic approaches and that they are applicable to teraryl and poly-arylene synthesis. Section 5 shows that simple trialkylsilyl-arenes can be utilized for the cross-coupling with iodo-arenes in the presence of a copper(II) catalyst. Section 6 deals with the amination of aryl halides with *N*-TMS-amines. This transformation is an alternative procedure for triarylamine synthesis because such reactions proceed in the presence of a fluoride ion. The C–C and C–N bond-forming procedure will provide stable tetraorganosilanes that are potentially applicable to various transition-metal-catalyzed reactions, allowing the possibility for novel methodologies to construct complex molecules such as π-conjugated organic materials and nitrogen-linked compounds.

References

(1) (a) Diederich, F.; Stang, P. J. In *Metal-Catalyzed Cross-Coupling Reactions*; Wiley-VCH: Weinheim, **1998**. (b) de Meijere, A.; Diederich, F. In *Metal-Catalyzed Cross-Coupling Reactions*; Wiley-VCH: Weinheim, **2004**, 2nd ed..
(2) For recent reviews, see: (a) Nakao, Y.; Hiyama, T. *Chem. Soc. Rev.* **2011**, *40*, 4893. (b) Sore, H. F.; Galloway, W. R. J. D.; Spring, D. R. *Chem. Soc. Rev.* **2012**, *41*, 1845. (c) Denmark, S. E.; Ambrosi, A.

Org. Process Res. Dev. **2015**, *19*, 982. (d) Foubelo, F.; Najera, C.; Yus, M. *Chem. Rec.* **2016**, *16*, 2521. (e) Komiyama, T.; Minami, Y.; Hiyama, T. *ACS Catal.* **2017**, *7*, 631.
(3) Hatanaka, Y.; Hiyama, T. *J. Org. Chem.* **1988**, *53*, 918.
(4) (a) Denmark, S. E.; Choi, Y. *J. Am. Chem. Soc.* **1999**, *121*, 5821. (b) Denmark, S. E.; Wehrli, D.; Choi, Y. *Org. Lett.* **2000**, *2*, 2491.
(5) (a) Itami, K.; Nokami, T.; Ishimura, Y.; Mitsudo, K.; Kamei, T.; Yoshida, J. *J. Am. Chem. Soc.* **2001**, *123*, 11577. (b) Itami, K.; Kamei, T.; Yoshida, J. *J. Am. Chem. Soc.* **2003**, *125*, 14670.
(6) Hosoi, K.; Nozaki, K.; Hiyama, T. *Chem. Lett.* **2002**, *31*, 138.
(7) Trost, B. M.; Machacek, M. R.; Ball, Z. T. *Org. Lett.* **2003**, *5*, 1895.
(8) Hanamoto, T.; Kobayashi, T. *J. Org. Chem.* **2003**, *68*, 6354.
(9) Anderson, J. C.; Munday, R. H. *J. Org. Chem.* **2004**, *69*, 8971.
(10) Katayama, H.; Nagao, M.; Moriguchi, R.; Ozawa, F. *J. Organomet. Chem.* **2003**, *676*, 49.
(11) Li, L.; Navasero, N. *Org. Lett.* **2006**, *8*, 3733.
(12) Sore, H. F.; Blackwell, D. T.; MacDonald, S. J. F.; Spring, D. R. *Org. Lett.* **2010**, *12*, 2806.
(13) Shindo, M.; Matsumoto, K.; Shishido, K. *Synlett* **2005**, 176.
(14) (a) Nakao, Y.; Imanaka, H.; Sahoo, A. K.; Yada, A.; Hiyama, T. *J. Am. Chem. Soc.* **2005**, *127*, 6952. (b) Nakao, Y.; Sahoo, A. K.; Yada, A.; Chen, J.; Hiyama, T. *Sci. Technol. Adv. Mater.* **2006**, *7*, 536. (c) Nakao, Y.; Imanaka, H.; Chen, J.; Yada, A.; Hiyama, T. *J. Organomet. Chem.* **2007**, *692*, 585. (d) Nakao, Y.; Ebata, S.; Chen, J.; Imanaka, H.; Hiyama, T. *Chem. Lett.* **2007**, *36*, 606. (e) Nakao, Y.; Chen, J.; Tanada, M.; Hiyama, T. *J. Am. Chem. Soc.* **2007**, *129*, 11694. (f) Chen, J.; Tanaka, M.; Sahoo, A. K.; Takeda, M.; Yada, A.; Nakao, Y.; Hiyama, T. *Bull. Chem. Soc. Jpn.* **2010**, *83*, 554. (g) Nakao, Y.; Takeda, M.; Matsumoto, T.; Hiyama, T. *Angew. Chem. Int. Ed.* **2010**, *49*, 4447.
(15) (a) Nakao, Y.; Oda, T.; Sahoo, A. K.; Hiyama, T. *J. Organomet. Chem.* **2003**, *687*, 570. (b) Sahoo, A. K.; Nakao, Y.; Hiyama, T. *Chem. Lett.* **2004**, *33*, 632. (c) Hiyama, T.; Sahoo, A. K.; Oda, T.; Nakao, Y. *Adv. Synth. Catal.* **2004**, *346*, 1715.
(16) Nokami, T.; Tomida, Y.; Kamei, T.; Itami, K.; Yoshida, J. *Org. Lett.* **2006**, *8*, 729.
(17) (a) Tang, S.; Takeda, M.; Nakao, Y.; Hiyama, T. *Chem. Commun.* **2011**, *47*, 307. (b) Ohgi, A.; Semba, K.; Hiyama, T.; Nakao, Y. *Chem. Lett.* **2016**, *45*, 973.
(18) (a) Pierrat, P.; Gros, P.; Fort, Y. *Org. Lett.* **2005**, *7*, 697. (b) Napier, S.; Marcuccio, S. M.; Tye, H.; Whittaker, M. *Tetrahedron Lett.* **2008**, *49*, 6314.
(19) Matsuda, S.; Takahashi, M.; Monguchi, D.; Mori, A. *Synlett* **2009**, 1941.
(20) Akai, S.; Ikawa, T.; Takayanagi, S.; Morikawa, Y.; Mohri, S.; Tsubakiyama, M.; Egi, M.; Wada, Y.; Kita, Y. *Angew. Chem. Int. Ed.* **2008**, *47*, 7673.
(21) Murata, M.; Ohara, H.; Oiwa, R.; Watanabe, S.; Matsuda, Y. *Synthesis* **2006**, 1771.
(22) Chernyak, N.; Dudnik, A. S.; Huang, C.; Gevorgyan, V. *J. Am. Chem. Soc.* **2010**, *132*, 8270.
(23) Murai, M.; Takami, K.; Takeshima, H.; Takai, K. *Org. Lett.* **2015**, *17*, 1798.
(24) Son, E. C.; Tsuji, H.; Saeki, T.; Tamao, K. *Bull. Chem. Soc. Jpn.* **2006**, *79*, 492.
(25) (a) Smith, A. B. III.; Hoye, A. T.; Martinez-Solorio, D.; Kim, Q.-S.; Tong, R. *J. Am. Chem. Soc.* **2012**, *134*, 4533. (b) Martinez-Solorio, D.; Hoye, A. T.; Nguyen, M. H.; Smith, A. B. III *Org. Lett.* **2013**, *15*, 2454. (c) Nguyen, M. H.; Smith, A. B. III *Org. Lett.* **2013**, *15*, 4258. (d) Nguyen, M. H.; Smith, A. B. III *Org. Lett.* **2013**, *15*, 4872. (e) Nguyen, M. H.; Smith, A. B. III *Org. Lett.* **2014**, *16*, 2070. (f) Martinez-Solorio, D.; Melillo, B.; Sanchez, L.; Liang, Y.; Lam, E.; Houk, K. N.; Smith, A. B. III *J. Am. Chem. Soc.* **2016**, *138*, 1836.

(26) For recent examples, see: (a) Iranpoor, N.; Firouzabadi, H.; Azadi, R. *J. Organomet. Chem.* **2010**, *695*, 887. (b) Lesbani, A.; Kondo, H.; Sato, J.; Yamanoi, Y.; Nishihara, H. *Chem. Commun.* **2010**, *46*, 7784. (c) Lesbani, A.; Kondo, H.; Yabusaki, Y.; Nakai, M.; Yamanoi, Y.; Nishihara, H. *Chem. Eur. J.* **2010**, *16*, 13519. (d) Huang, C.; Chernyak, N.; Dudnik, A. S.; Gevorgyan, V. *Adv. Synth. Catal.* **2011**, *353*, 1285. (e) Kurihara, Y.; Nishikawa, M.; Yamanoi, Y.; Nishihara, H. *Chem. Commun.* **2012**, *48*, 11564. (f) Inubushi, H.; Kondo, H.; Lesbani, A.; Miyachi, M.; Yamanoi, Y.; Nishihara, H. *Chem. Commun.* **2013**, *49*, 134.

(27) For recent examples, see: (a) Gooßen, L. J.; Ferwanah, A.-R. S. *Synlett* **2000**, 1801. (b) Shirakawa, E.; Kurahashi, T.; Yoshida, H.; Hiyama, T. *Chem. Commun.* **2000**, 1895. (c) Denmark, S. E.; Kallemeyn, J. M. *Org. Lett.* **2003**, *5*, 3483. (d) Iwasawa, T.; Komano, T.; Tajima, A.; Tokunaga, M.; Obora, Y.; Fujihara, T.; Tsuji, Y. *Organometallics* **2006**, *25*, 4665. (e) Kashiwabara, T.; Tanaka, M. *Organometallics* **2006**, *25*, 4648. (f) McNeill, E.; Barder, T. E.; Buchwald, S. L. *Org. Lett.* **2007**, *9*, 3785. (g) Yamamoto, Y.; Matsubara, H.; Murakami, K.; Yorimitsu, H.; Osuka, A. *Chem. Asian J.* **2015**, *10*, 219.

(28) (a) Zarate, C.; Martin, R. *J. Am. Chem. Soc.* **2014**, *136*, 2236. (b) Guo, L.; Chatupheeraphat, A.; Rueping, M. *Angew. Chem. Int. Ed.* **2016**, *55*, 11810.

(29) Iizuka, M.; Kondo, Y. *Eur. J. Org. Chem.* **2008**, 1161.

(30) Minami, Y.; Shimizu, K.; Tsuruoka, C.; Komiyama, T.; Hiyama, T. *Chem. Lett.* **2014**, *43*, 201.

(31) Shimizu, K.; Minami, Y.; Nakao, Y.; Ohya, K.; Ikehira, H.; Hiyama, T. *Chem. Lett.* **2013**, *42*, 45.

(32) For recent reviews, see: (a) Cheng, C.; Hartwig, J. F. *Chem. Rev.* **2015**, *115*, 8946. (b) Bähr, S.; Oestreich, M. *Angew. Chem. Int. Ed.* **2017**, *56*, 52.

(33) For selected examples of intermolecular catalytic dehydrogenative silylation of arenes without any directing group, see: (a) Tsukada, N.; Hartwig, J. F. *J. Am. Chem. Soc.* **2005**, *127*, 5022. (b) Murata, M.; Fukuyama, N.; Wada, J.; Watanabe, S.; Masuda, Y. *Chem. Lett.* **2007**, *36*, 910. (c) Lu, B.; Falck, J. R. *Angew. Chem. Int. Ed.* **2008**, *47*, 7508. (d) Ishiyama, T.; Saiki, T.; Kishida, E.; Sasaki, I.; Ito, H.; Miyaura, N. *Org. Biomol. Chem.* **2013**, *11*, 8162. (e) Klare, H. F. T.; Oestreich, M.; Ito, J.-i.; Nishiyama, H.; Ohki, Y.; Tatsumi, K. *J. Am. Chem. Soc.* **2011**, *133*, 3312. (f) Cheng, C.; Hartwig, J. F. *Science* **2014**, *343*, 853. (g) Cheng, C.; Hartwig, J. F. *J. Am. Chem. Soc.* **2015**, *137*, 592. (h) Murai, M.; Takami, K.; Takeshima, H.; Takai, K. *Org. Lett.* **2015**, *17*, 1798. (i) Murai, M.; Takami, K.; Takai, K. *Chem. Eur. J.* **2015**, *21*, 4566. (j) Yin, Q.; Klare, H. F. T.; Oestreich, M. *Angew. Chem. Int. Ed.* **2016**, *55*, 3204. (k) Lee, K.-S.; Katsoulis, D.; Choi, J. *ACS Catal.* **2016**, *6*, 1493. (l) Fang, H.; Guo, L.; Zhang, Y.; Yao, W.; Huang, Z. *Org. Lett.* **2016**, *18*, 5624.

(34) Toutov, A. A.; Liu, W.-B.; Betz, K. N.; Fedorov, A.; Stoltz, B. M.; Grubbs, R. H. *Nature* **2015**, *518*, 80.

(35) Ma, Y.; Wang, B.; Zhang, L.; Hou, Z. *J. Am. Chem. Soc.* **2016**, *138*, 3663.

(36) Chen, Q.-A.; Klare, H. F. T.; Oestreich, M. *J. Am. Chem. Soc.* **2016**, *138*, 7868.

(37) Minami, Y.; Komiyama, T.; Hiyama, T. *Chem. Lett.* **2015**, *44*, 1065.

(38) For recent reviews on the cross-coupling polymerization, see: (a) Sakamoto, J.; Rehahn, M.; Wegner, G.; Schlüter, A. D. *Macromol. Rapid Commun.* **2009**, *30*, 653. (b) Robb, M. J.; Ku, S.-Y.; Hawker, C. J. *Adv. Mater.* **2013**, *25*, 5686. (c) Carsten, B.; He, F.; Son, H. J.; Xu, T.; Yu, L. *Chem. Rev.* **2011**, *111*, 1493. (d) Bryan, Z. J.; McNeil, A. J. *Macromolecules* **2013**, *46*, 8395. (e) Yokozawa, T.; Nanashima, Y.; Ohta, Y. *ACS Macro Lett.* **2012**, *1*, 862.

(39) (a) Sengupta, S.; Sadbukhan, S. K. *J. Chem. Soc., Perkin Trans. 1* **1999**, 2235. (b) Nishihara, Y.; Ando, J.-i.; Kato, T.; Mori, A.; Hiyama, T. *Macromolecules* **2000**, *33*, 2779. (c) Mori, A.; Kondo, T.; Kato, T.; Nishihara, Y. *Chem. Lett.* **2001**, *30*, 286. (d) Babudri, F.; Colangiuli, D.; Lorenzo, P. A. D.; Farinola, G. M.; Omarb, O. H.; Naso, F. *Chem. Commun.* **2003**, *39*, 130. (e) Katayama, H.; Nagao, M.; Moriguchi, R.; Ozawa, F. *J. Organomet. Chem.* **2003**, *676*, 49.

(40) (a) Kim, Y.; Cook, S.; Choulis, S. A.; Nelson, J.; Durrant, J. R.; Bradley, D. D. C. *Chem. Mater.* **2004**, *16*, 4812. (b) Kabra, D.; Lu, L. P.; Song, M. H.; Snaith, H. J.; Friend, R. H. *Adv. Mater.* **2010**, *22*, 3194. (c) Gwinner, M. C.; Kabra, D.; Roberts, M.; Brenner, T. J. K.; Wallikewitz, B. H.; McNeill, C. R.; Friend, R. H.; Sirringhaus, H. *Adv. Mater.* **2012**, *24*, 2728.

(41) Wang, N.; Chen, Z.; Wei, W.; Jiang, Z. *J. Am. Chem. Soc.* **2013**, *135*, 17060.

(42) Komiyama, T.; Minami, Y.; Hiyama, T. *Angew. Chem. Int. Ed.* **2016**, *55*, 15787.

(43) (a) Knapp, D. M.; Gillis, E. P.; Burke, M. D. *J. Am. Chem. Soc.* **2009**, *131*, 6961. (b) Dick, G. R.; Knapp, D. M.; Gillis, E. P.; Burke, M. D. *Org. Lett.* **2010**, *12*, 2314. (c) Dick, G. R.; Woerly, E. M.; Burke, M. D. *Angew. Chem. Int. Ed.* **2012**, *51*, 2667.

(44) Hatanaka, Y.; Goda, K.-i.; Okahara, Y.; Hiyama, T. *Tetrahedron* **1994**, *50*, 8301.

(45) For reactions via single-electron transfer from silicates, see: (a) Yoshida, Y.; Tamao, K.; Kakui, T.; Kurita, A.; Murata, M.; Yamada, K.; Kumada, K. *Organometallics* **1982**, *1*, 369. (b) Corc, V.; Chamoreau, L.; Derat, E.; Goddard, J.-P.; Ollivier, C.; Fensterbank, L. *Angew. Chem. Int. Ed.* **2015**, *54*, 11414. (c) Jouffroy, M.; Primer, D. N.; Molander, G. A. *J. Am. Chem. Soc.* **2016**, *138*, 475. (d) Patel, N. R.; Kelly, C. B.; Jouffroy, M.; Molander, G. A. *Org. Lett.* **2016**, *18*, 764. (e) Xu, P.; Wang, F.; Fan, G.; Xu, X.; Tang, P. *Angew. Chem. Int. Ed.* **2017**, *56*, 1101.

(46) F.-Rodríguez, M. A.; Shen, Q.; Hartwig, J. F. *J. Am. Chem. Soc.* **2006**, *128*, 2180.

(47) (a) Milton, E. J.; Fuentes, J. A.; Clarke, M. L. *Org. Biomol. Chem.* **2009**, *7*, 2645. (b) Bhadra, S.; Dzik, W. I.; Gooßen, L. J. *J. Am. Chem. Soc.* **2012**, *134*, 9938.

(48) (a) Barluenga, J.; Aznar, F.; Valadés, C. *Angew. Chem. Int. Ed.* **2004**, *43*, 343. (b) Smith, C. J.; Early, T. R.; Holmes, A. B.; Shute, R. E. *Chem. Commun.* **2004**, 1976. (c) Smith, C. J.; Tsang, M. W. S.; Holmes, A. B.; Danheiser, R. L.; Tester, J. W. *Org. Biomol. Chem.* **2005**, *3*, 3767.

(49) For reviews, see: (a) Ley, S. V.; Thomas, A. W. *Angew. Chem. Int. Ed.* **2003**, *42*, 5400. (b) Evano, G.; Blanchard, N.; Toumi, M. *Chem. Rev.* **2008**, *108*, 3054. (c) Hartwig, J. F. *Acc. Chem. Res.* **2008**, *41*, 1534. (d) Surry, D. S.; Buchwald, S. L. *Angew. Chem. Int. Ed.* **2008**, *47*, 6338. (e) Monnier, F.; Taillefer, M. *Angew. Chem. Int. Ed.* **2009**, *48*, 6954. (f) Surry, D. S.; Buchwald, S. L. *Chem. Sci.* **2010**, *1*, 13. (g) Sadig, J. E. R.; Willis, M. C. *Synthesis* **2011**, 1. (h) Surry, D. S.; Buchwald, S. L. *Chem. Sci.* **2011**, *2*, 27. (i) Beletskaya, I. P.; Cheprakov, A. V. *Organometallics* **2012**, *31*, 7753. (j) Rauws, T. R. M.; Maes, B. U. W. *Chem. Soc. Rev.* **2012**, *41*, 2463. (k) Ruiz-Castillo, P.; Buchwald, S. L. *Chem. Rev.* **2016**, *116*, 12564.

(50) (a) Shimizu, K.; Minami, Y.; Goto, O.; Ikehira, H.; Hiyama, T. *Chem. Lett.* **2014**, *43*, 438. (b) Minami, Y.; Komiyama, T.; Shimizu, K.; Hiyama, T.; Goto, O.; Ikehira, H. *Bull. Chem. Soc. Jpn.* **2015**, *88*, 1437.

(51) For selected examples, see: (a) Adhikari, R. M.; Neckers, D. C. *J. Org. Chem.* **2009**, *74*, 3341. (b) Jiang, W.; Duan, L.; Qiao, J.; Dong, G.; Zhang, D.; Wang, L.; Qiu, Y. *J. Mater. Chem.* **2011**, *21*, 4918. (c) Uoyama, H.; Goushi, K.; Shizu, K.; Nomura, H.; Adachi, C. *Nature* **2012**, *492*, 234. (d) Chen, Q.; Luo, M.; Hammaeshøj, P.; Zhou, D.; Han, Y.; Laursen, B. W.; Yan, C.-G.; Han, B.-H. *J. Am.*

Chem. Soc. **2012**, *134*, 6084. (e) Komino, T.; Tanaka, H.; Adachi, C. *Chem. Mater.* **2014**, *26*, 3665. (f) Ishimatsu, R.; Matsunami, S.; Kasahara, T.; Mizuno, J.; Edura, T.; Adachi, C.; Nakano, K.; Imato, T. *Angew. Chem. Int. Ed.* **2014**, *53*, 6993.

(52) Hooper, M. W.; Utsunomiya, M.; Hartwig, J. F. *J. Org. Chem.* **2003**, *68*, 2861.

(53) For pioneering work on the Pd-catalyzed C–N cross-coupling polymerization, see: (a) Kanbara, T. *Honma A.* **1996**, 1135. (b) Goodson, F. E.; Hauck, S. I.; Hartwig, J. F. *J. Am. Chem. Soc.* **1999**, *121*, 7527.

(54) (a) Chen, S.-A.; Chuang, K.-R.; Chao, C.-I.; Lee, H.-T. *Synth. Met.* **1996**, *82*, 207. (b) Tu, G.; Zhou, Q.; Chen, Y.; Wang, L.; Ma, D.; Jing, X.; Wang, F. *Appl. Phys. Lett.* **2004**, *85*, 2172. (c) Lee, S. K.; Hwang, D.-H.; Jung, B.-J.; Cho, N. S.; Lee, J.; Lee, J.-D.; Shim, H.-K. *Adv. Funct. Mater.* **2005**, *15*, 1647. (d) Liu, J.; Zhou, Q.; Cheng, Y.; Geng, Y.; Wang, L.; Ma, D.; Jing, X.; Wang, F. *Adv. Mater.* **2005**, *17*, 2974.

(55) Minami, Y.; Komiyama, T.; Shimizu, K.; Uno, S.; Hiyama, T.; Goto, O.; Ikehira, H. *Synlett* **2017**, DOI: 10.1055/s-0036-1588417.