中央大学博士論文

Synthetic Applications of Silicon-Based Cross-Coupling Reaction

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Contents

List of Abbreviations

Ac	acetyl
Ar	aryl
BINAP	2,2'-Bis(diphenylphosphino)binathtyl
Bn	benzyl
Bz	benzoyl
(*R*,*R*)-Bn-bod*	(1*R*,4*R*)-2,5-dibenzylbicyclo[2.2.2]octa-2,5-diene
Boc	*tert*-butylcarbonyl
Bu	butyl
t-Bu	*tert*-butyl
cod	1,4-cycoctadiene
Cp	η^5-cyclopentadienyl
Cy	cyclohexyl
CyPF-*t*-Bu	(*R*)-1-[(S_p)-2-(dicyclohexylphosphino)ferrocenyl]ethyl-di-*tert*-butylphosphine
Davephos	2-dicyclohexyl-2'-dimethylaminobiphenyl
dba	dibenzylydeneacetone
DIBAL-H	diisobutylaluminium hydride
dpca	[*N*-(2-diphenylphosphino)benzylidene]cyclohexylamine
DME	1,2-dimethylethane
DMF	dimethylformamide
DMI	1,3-dimethyl-2-pyroridinone
DMPU	*N*,*N*'-dimethylpropyleneurea
DMSO	dimethylsulfoxide
dppf	1,1'-bis(diphenylphosphino)ferrocene
dpppz	1,2-bis(diphenylphosphino)benzene
dvds	1,3-divinyl-1,1,3,3-tetramethyldisiloxane
E	electrophile
ee	enantiomer excess
Et	ethyl
FET	field-effect transistors
FG	functional group
Hex	hexyl
hfacac	hexafluoroacethylacetone
HMDS	1,1,1,3,3,3-hexamethyldisilazane

HMPA	hexamethylphosphoric triamide
Jonphos	(2-biphenyl)di-*tert*-butylphosphine
Me	methyl
M_n	number average molecular weight
M_w	weight average molecular weight
NMP	*N*-mehtyl-pyrroridone
Ns	2-nitorobenzenesulfonyl
Oct	octyl
Pent	pentyl
c-Pent	cyclopentyl
PDI	polydispersity index
PG	protecting group
Ph	phenyl
(*R*,*R*)-Ph-bod*	(1*R*,4*R*)-2,5-diphenylbicyclo[2.2.2]octa-2,5-diene
(*S*,*S*)-Ph-bnd*	(1*S*,5*S*)-2,6-diphenylbicyclo[3.3.1]nona-2,6-diene
PPTS	pyridinium *p*-toluenesulfonate
Pr	Propyl
i-Pr	isopropyl
PTSA	*p*-toluenesulfonic acid
PVC	photovoltaic cell
Py	pyridyl
Ruphos	2-dicyclohexylphosphino-2',6'-di-*iso*-propoxybiphenyl
$scCO_2$	supercritical carbon dioxide
TASF	tris(dimethylamino)sulfonium difluorotrimethylsilicate
TBAF	tetrabutylammonium fluoride
TBDPS	*tert*-butyldiphenylsilyl
TBS	*tert*-buthyldimethylsilyl
TIPS	tri-*iso*-propylsilyl
THF	tetrahydrofuran
THP	tetrahydropyran-2-yl
TMEDA	*N*,*N*,*N*',*N*'-tetramethylethylenediamine
TMS	trimethylsilyl
X	halogen
Xphos	2-dicyclohexylphosphino-2',4',6'-tri-*iso*-propylbiphenyl

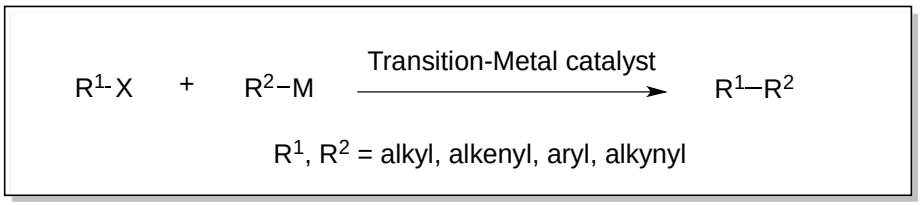
Chapter 1

General Introduction

Organic synthesis has definitely influenced on modern science and technology particularly pharmaceutical and material industry and brought various innovations. It should be noted that current organic synthesis made it possible to transform straghtforwardly by a variety of metal-catalyzed reactions. High selectivity and efficiency are attained by the well-designed catalytic reactions using specific organometallic complexes with appropriate ligands. Typical examples are asymmetric synthesis, metathesis, and cross-coupling reactions, to which the Nobel Prize in Chemistry was given in 2001, 2005, and 2010, respectively. However, along with economic and industrial developments, we are faced with environmental problems such as global warming and energy resource issues. Chemists are requested to solve these problems. With the background mentioned above, the author has struggled with these problems through studied on more efficient and environmentally benign cross-coupling reaction.

1. 1 Cross-Coupling Reaction

Cross-coupling reaction is the one that combines nucleophilic organometallic reagents with electrophiles like organic halides in the presence of transition metal catalysts such as palladium, nickel, cobalt, or iron. The reaction usually takes place at the original position stereospecifically with retention of configuration. Thus, this reaction is considered now the most reliable and straightforward carbon–carbon bond forming transformation and is widely applied to synthesis of a wide variety of π-electron conjugated organic materials and pharmaceuticals. It should be noted that many Japanese chemists have contributed to the advances in the cross-coupling reaction as summarized in Figure 1.

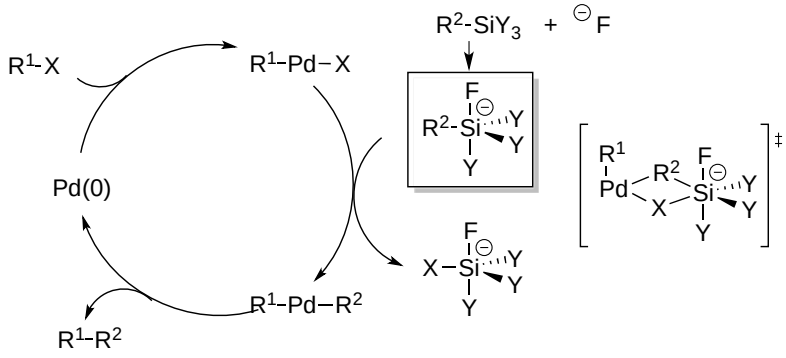


Organometallic reagents and Catalyst（additive）	Name Reaction
RMgX, Ni	Kumada-Tamao-Corriu Coupling
RLi, Pd	Murahashi Coupling
RZnX, R_3Zr, Pd	Negishi Coupling
$RSnY_3$, Pd	Migita-Kosugi-Stille Coupling
$RB(OY)_2$, Pd (OH^-)	Suzumi-Miyaura Coupling
$RSiY_3$, Pd (F-, OH^-)	Hiyama Coupling

Figure 1. Cross-coupling reactions

Historically, the first protocol was disclosed in 1972 by the group of Kumada and Tamao and by Corriu independently, using Grignard reagents (RMgX) and nickel catalysts. Shortly thereafter, Murahashi used organolithium reagents and palladium catalysts. Negishi screend combination of various transition and main group metals to find in 1976 organozinc reagents and palladium catalysts were the best. Next year the group of Migita and Kosugi and two years later Stille reported that organotin reagents were superior in stability along with enough reactivity. Suzuki and Miyaura joined the game in 1979 to show that organoboron compounds are the best in handling and reactivity when they are activated by a base. Silicon reagents remained inapplicable for long time due to lack of general reactivity, though they are considered to be ideal in view of availability, stability and nontoxicity. Hiyama and Hatanaka reported in 1988 that tetragonal organosilicon reagents participate in the palladium-catalyzed cross-coupling reaction in the presence of a fluoride activator.[1)] The reactivity of organometallics falls roughly in the order of $R^2Li > R^2MgX > R^2ZnX > R^2SnR^3_3 > R^2B(OR^3)_2 \simeq R^2SiR^3_3$. Namely, the less nucleophilic reagents show the more chemoselectivity that are preferable in view of storage and selective use. From the viewpoint of manufacturing, ready accessibility of elements, stability of reagents, nontoxicity, and easy waste recovery and storage are the essentials of choice. In this respect, organosilicon reagents have advantages: rich natural abundance, non- or low toxicity, and high chemoselectivity. Thus, the cross-coupling reaction with organosilicon reagents have attracted much interest recently[2)].

Silicon is an element at the 14th group, right below carbon, in the Periodic Table. Thus, saturated organosilicon compounds have a tetrahedral structure which is extremely stable and inert under various conditions. However, once a nucleophile like fluoride ion is present, some portion of the silicon compound is converted to a pentacoordinate silicate, to undergo transmetalation to transition metals as disclosed by Hiyama and Hatanaka. Scheme 1 summarizes the well-accepted mechanism of the silicon-based cross-coupling reaction: oxidative addition of Pd(0) complex to electrophile R^1–X to



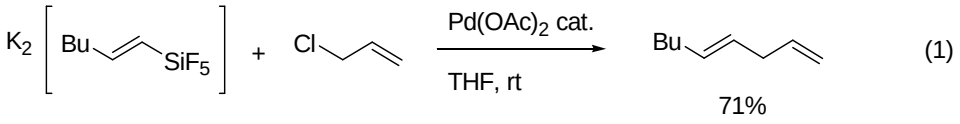
Scheme 1. Catalytic cycle for silicon-based cross-coupling reaction

give R^1-Pd(II)-X, (2) transmetalation with a pentacoordinate silicate, transferring organic group R from Si possibly via a 4-membered transition state[3] to give R^1-Pd-R^2, (3) reductive elimination to give a coupled product and reproduce the starting Pd(0) complex. In order to undergo the transmetalation smoothly, it is essential to make pentacoordinate silicate more electrophilic. To this end, one to three heteroatom substituents like halogen or alkoxy are better present on silicon. In the following sections, reactivity of the organosilicon reagents is reviewed, depending on the kind of organic group to react with.

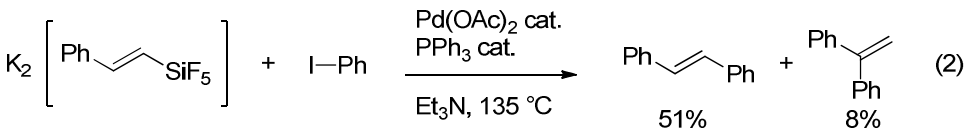
1. 2 Intermolecular Activation of Organosilicon Reagents

1. 2. 1 Organohalosilanes

Electronegative halogens on silicon make the silicon center more electrophilic. Accordingly, the reaction in Eq 1[4] reported by Kumada and Tamao is not surprising: alkenylpentafluorosilicate couples with allyl chloride with the aid of palladium(II) acetate at room temperature. The hexacoordinate silicate was considered to be nucleophilic enough to undergo transmetalation. This is the first to show highly coordinated silicate can transmetalate to palladium to effect cross-coupling reaction. However, a radical mechanism via single electron-transfer may be an alternative.

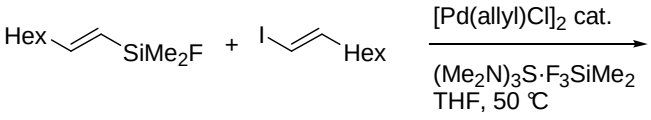


The same silicate cross-couples with phenyl iodide at 135 °C to give *trans*-stilbene and a cine-coupled product in a small amount[4] (Eq 2). High reaction temperature was necessary possibly for the porpose of the removing one fluoride from the hexacoordinate species. This reaction was not well-appreciated, because synthesis of pentacoordinate silicates is tedious and thus lacks the general potential.



Trimethylvinylsilane was first employed for the cross-coupling reaction, using tris(dimethylamino)sulfonium difluorotrimethylsilicate ($(Et_2N)_3S\cdot F_2SiMe_3$, TASF) activator in HMPA. To extend the scope of the reaction, one to three fluorines were intro-

duced on silicon; tetrabutylammonium fluoride ($Bu_4N \cdot F$, TBAF) or potassium fluoride was later used as a fluoride ion source; simple THF as the solvent was found satisfactory, all for the formation of pentacoordinate silicates in-situ through the reaction of tetragonal silanes with a fluorine activator.[5] An example is the coupling of (*E*)-1-iodo-1-octene with (*E*)-1-dimethylfluorosilyl-1-octene to give a coupled 1,3-diene in a high yield (Eq 3). The fluorine on the silicon is definitely making the silicon center be more reactive for transmetalation than trimethylsilyl as is shown in Eq 4.



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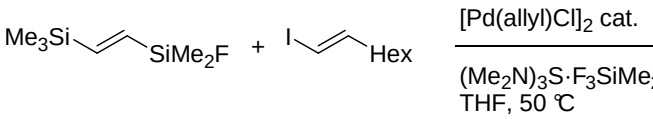
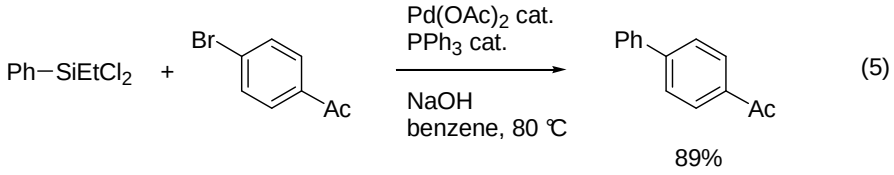


(4)

Fluorine atoms on the silicon can be replaced by chlorine atoms, and a fluoride activator may be replaced by a hydroxide ion as illustrated by Eq 5.[6] This particular example suggests a high potential of the silicon-based cross-coupling reaction for industrial applications.



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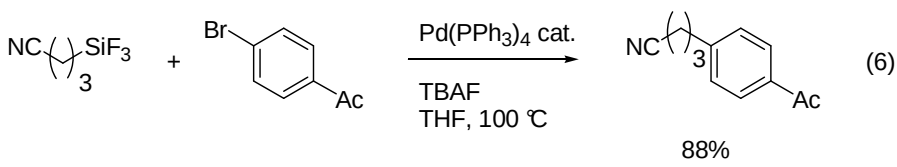
Alkyl cross-coupling using alkylsilanes is achieved using trifluorosilyl reagents. The next example demonstrates high chemoselectivity of the coupling reaction.

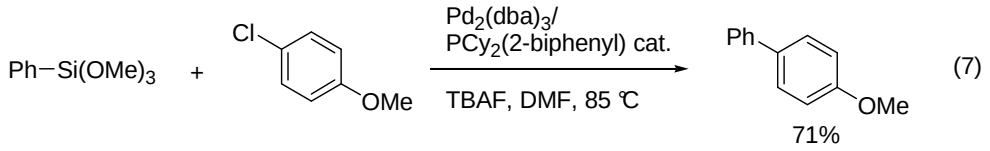


(6)

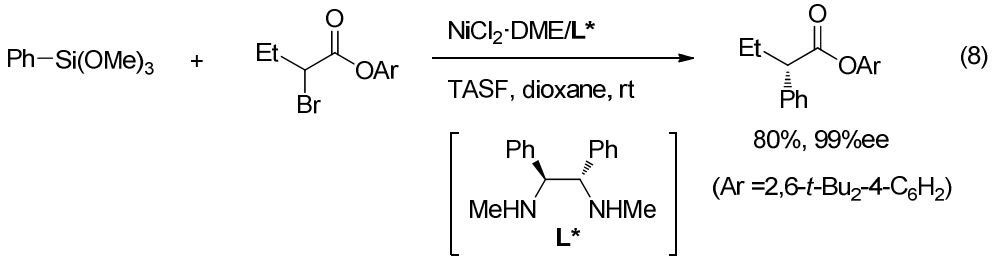
1. 2. 2 Organoalkoxysilanes

Organoalkoxysilanes are more stable than halosilanes but equally applicable to the cross-coupling reaction due to the enhanced Lewis acidity at the silicon center by oxy-

gen. Using inexpensive trialkoxyphenylsilanes and aryl chlorides,[7a] tosylate[7b] or mesylate,[7c] biaryls have become readily accessible (Eq 7).

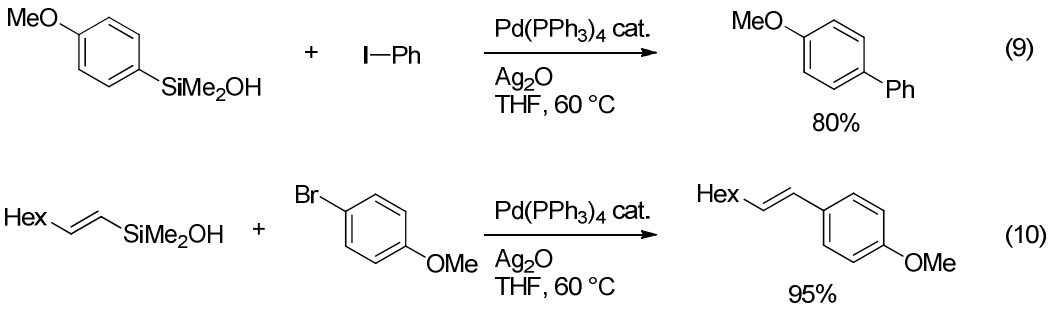


Fu disclosed that a Ni/chiral diamine-catalyzed enantioselective cross-coupling reaction of α-bromobutyrates with phenyl(trimethoxy)silane to obtain α-phenylbutyrates with high enantioselectivity (Eq 8).[8]

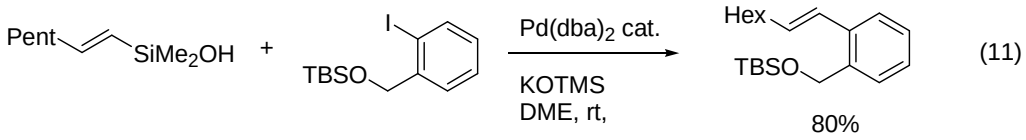


1. 2. 3 Organosilanols and silanolates

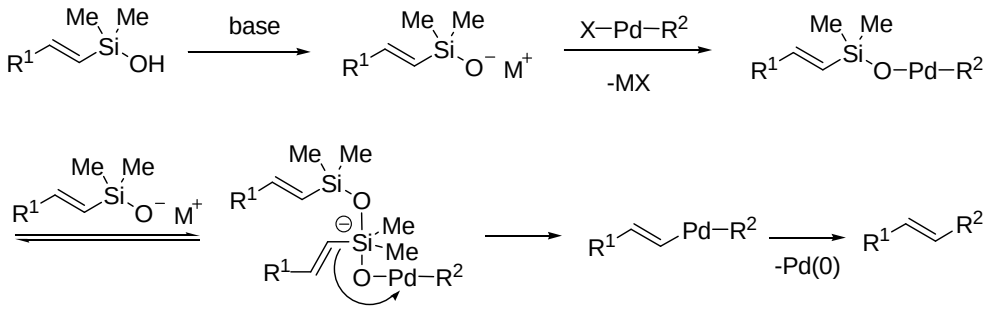
Orgonosilanols are shown by Hiyama and Mori to be equally effective for the cross-coupling reaction. The reaction of aryl halides with arylsilanols in the presence of a palladium catalyst and a silver oxide activator.[9] Alkneylsilanols also are applicable to the corresponding cross-coupling reaction (Eqs 9, 10).



Meanwhile Denmark achieved the cross-coupling reaction using organosilanols,[10] which react with organic halides in the presence of a palladium catalyst and $KOSiMe_3$ (KOTMS) as a base in place of a fluorine activator (Eq 11). It is worth to note that TBS silyl ethers are tolerated under the conditions.



The reaction is considered to involve silanolates which substitute X in R^2-Pd-X to give R^1-Pd-$OSiMe_2CH{=}CHR^1$. This Pd(II) complex is attacked by another silanolate to complete transmetalation (Scheme 2).

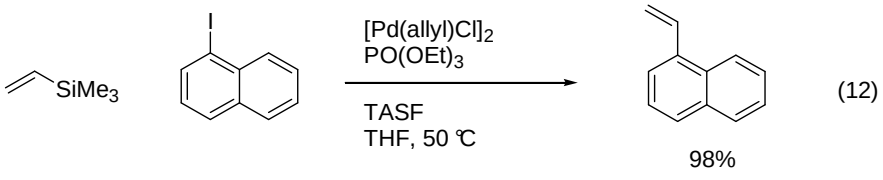


Scheme 2. Plausible mechanism of the cross-coupling of alkenylsilanolates

Denmark later employed organolsilanolates directly as the coupling reagent and in fact demonstrated that the cross-coupling reaction smoothly proceeded with potassium organosilanolates without an additional base.[11)]

1. 2. 4 Organo(trimethyl)silanes

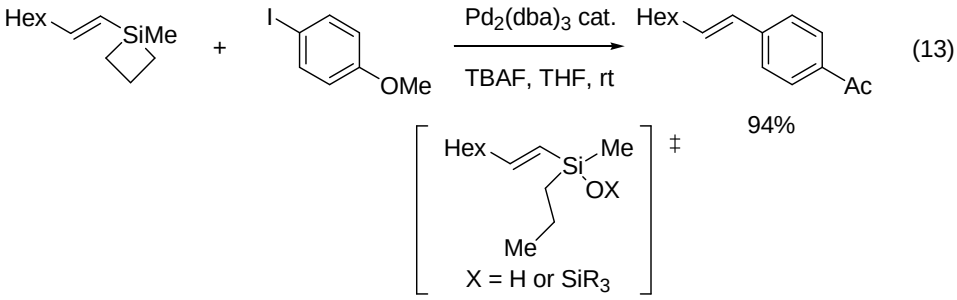
As described in 1.2.1, tetraorganosilanes were initially employed for the silicon-based cross-coupling reaction.[2)] For instance, the reaction of 2-iodonaphthalene with vinyl(trimethyl)silane in the presence of a palladium(II)/triethylphosphite catalyst and TASF produced 1-vinylnaphthalene in a quantitative yield (Eq 12).



1. 2. 5 Masked silanols

More than 10 years later Denmark reported that the cross-coupling reaction of aryl iodides with 1-alkenyl-1-methylsilacyclobutanes proceeded smoothly to give sty-

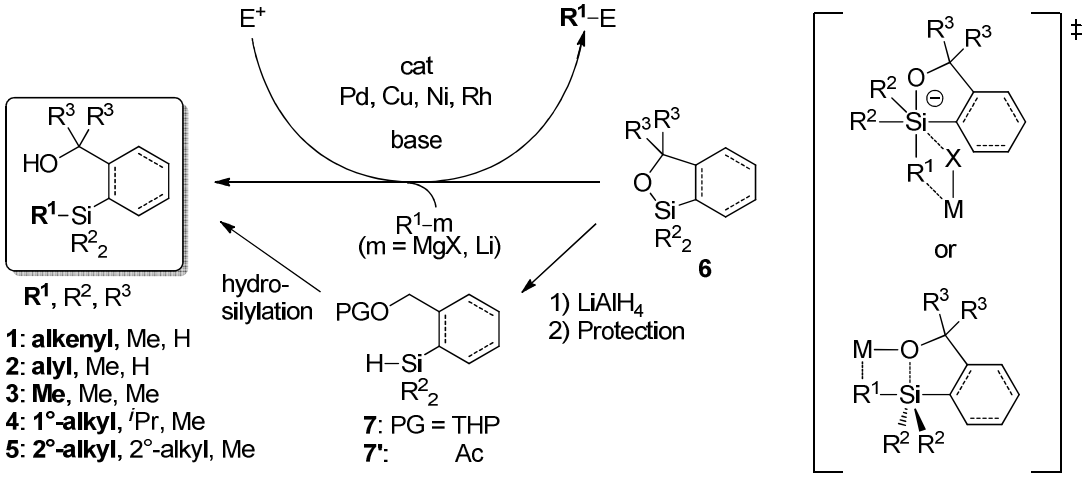
renes.[13a] However, the silacyclobutane reagents were shown to decompose by a contaminant water in TBAF·THF solution to give silanols or siloxanes, which turned out to be real active species for the cross-coupling reaction (Eq 13). [13b]



Tetraorganosilanes with such substituent as 2-pyridyl,[14] 2-thienyl,[15] allyl,[16] 3,5-bis(trifluoromethyl)phenyl,[17] and benzyl[18] are used for the Pd-catalyzed TBAF-mediated cross-coupling: hereby these organic groups are converted to fluorosilanes or silanols before transmetalation for the cross-coupling.

1. 3 Organo[2-(hydroxymethyl)phenyl]dimethylsilanes (HOMSi reagents)

As described above, the cross-coupling reactions with organosilicon reagents such as halosilanes and silanols proceed successfully as these heteroatoms assist pentacoordinate silicate formation. Because tetraorgonosilicon reagents are desirable in terms of stability, easy handling and storage, the cross-coupling reaction with tetraorganosilanes has remained challenging for some time.

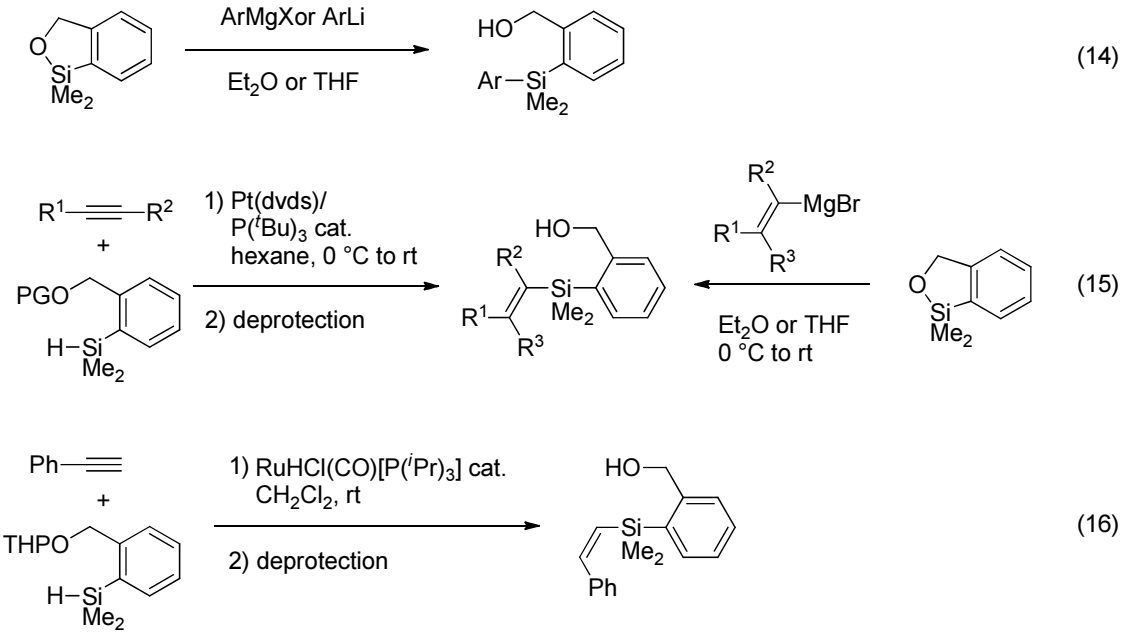


Scheme 3. Transition-metal catalyzed C-C bond formation with HOMSi reagent

In 2005, Hiyama and Nakao achieved the cross-coupling reaction with organo[2-(***h***ydr***o***xy***m***ethyl)phenyl]dimethyl***si***lanes, so called HOMSi reagent (**1**~**5**). HOMSi reagents react in the presence of a weak base and readily form cyclic pentacoordinate silicates by intramolecular nucleophilic attack of a hydroxyl group. Co-generated silicon residue is cyclic silyl ether **6**, which can be used for synthesis of the same or other HOMSi reagents as summarized in Scheme 3.

In the following sections, synthetic methods of HOMSi reagents and details of the cross-coupling reaction with HOMSi reagents are discussed.

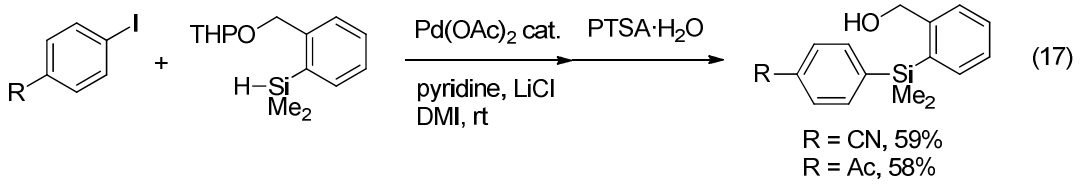
Aryl substituted HOMSi reagents (Ar-HOMSi) can be easily prepared by the reaction of such organometallic reagents as arylmagnesium halides or aryllithiums with the cyclic silyl ether (Eq 14). [19-20] Alkenyl-HOMSi reagents are prepared by platinum-catalyzed hydrosilylation of alkynes with protected hydrosilanes derived from the cyclic silyl ether or alternatively by the reaction of the cyclic silyl ether with alkenylmagnesium halides (Eq 15).[19,21] Ru-Catalyzed hydrosilylation is recently shown to give (*Z*)-alkenyl-HOMSi selectively (Eq 16).[21]



Kondo demonstrated a Pd-catalyzed dehydrohalogenative silylation of electron-deficient aryl iodides using protected H-HOMSi reagents (Eq 17).[22] Deprotection provides the coupling active form of aryl-HOMSi reagents.

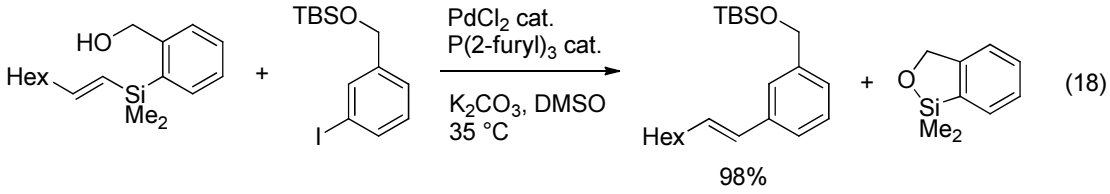
With the limited number of synthetic methods for HOMSi reagents, it is desirable to

exploit novel straightforward preparation of HOMSi reagents starting with disilanes or hydrosilanes. This is the target of the present Disseration and will be discussed in Chapter 2.



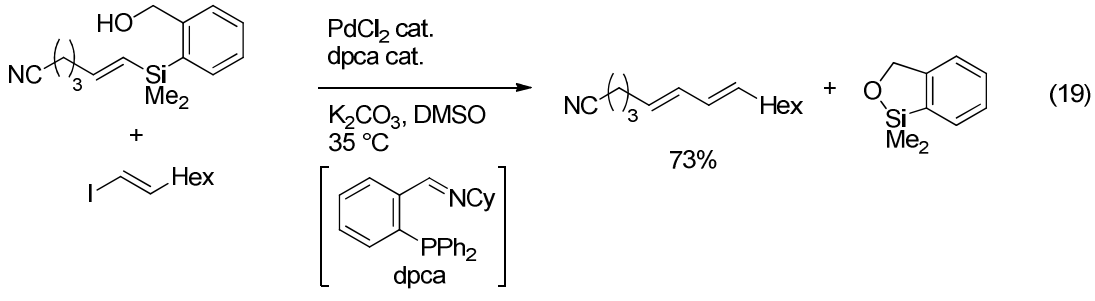
(17)

In the presence of a palladium catalyst and a weak base, the cross-coupling reaction of aryl iodides with HOMSi reagents proceeds smoothly to give coupled products in good yields.[19-21] For example, *m*-TBSoxymethylphenyl iodide react with a 1-octenyl-HOMSi reagent to give an octenylated benzyl silyl ether and the cyclic silyl ether in an excellent yield using $PdCl_2$, $P(2\text{-furyl})_3$ and K_2CO_3 (Eq 18). The silyl protecting group is tolerated under the conditions.



(18)

For the reaction of 1-iodo-1-octene, a dcpa ligand is effective for the reaction and the coupled 1,3-diene is obtained regio- and stereoselectively (Eq 19).



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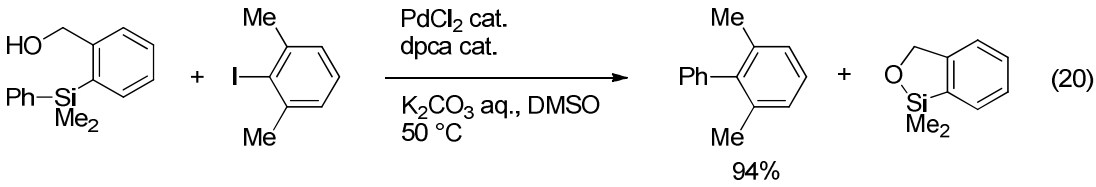
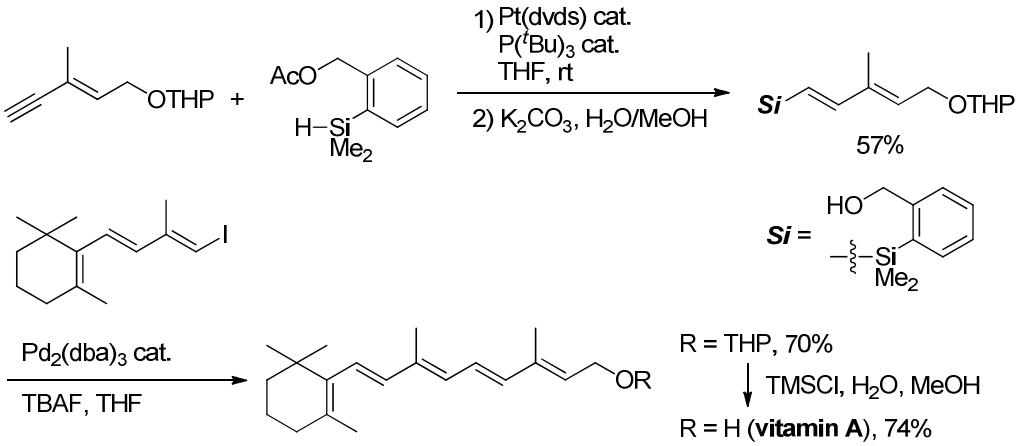


(20)

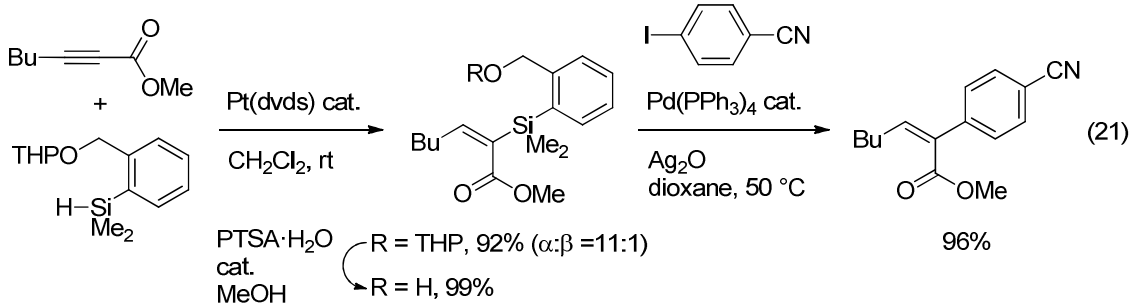
Aryl-HOMSi reagents also react with iodoarenes to give biaryls. Sterically hindered 2,6-dimethyliodobenzene gives 2,6-dimethylbiaryl in 94% yield (Eq 20).

Cross-coupling with HOMSi has recently been applied to the synthesis of vitamin A by López (Scheme 4).[23] An alkenyl-HOMSi reagent was prepared by the Pt-catalyzed hydrosilylation of 1,3-eneyne with a protected H-HOMSi reagent followed by deprotection. The tetraene skeleton of vitamin A was constructed by the Pd-catalyzed cross-coupling of 1-iodo-1,3-diene with the alkenyl-HOMSi reagent. The coupling yield is 70% and is compared favorably with the Suzuki-Miyaura coupling or Migita-Kosugi-Stille coupling. The reaction conditions are the mildest among these, and thus the silicon-based coupling is evaluated to be the best.

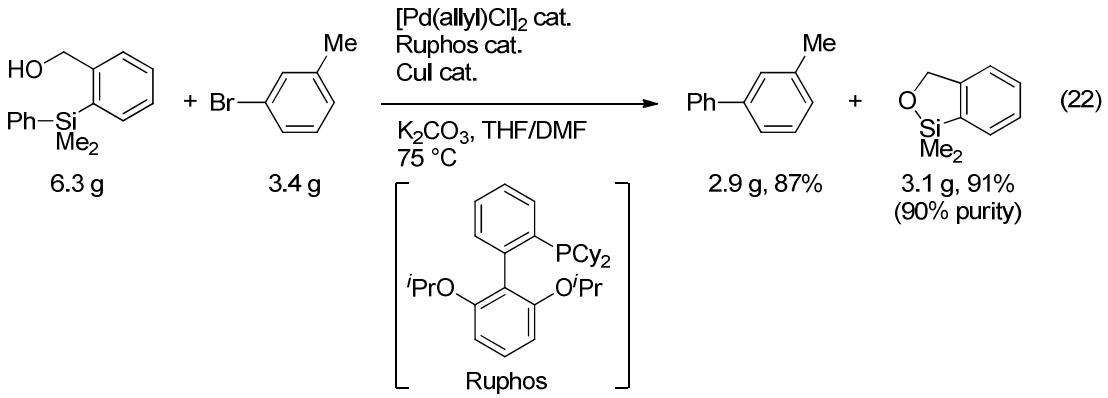


Scheme 4. Vitamin A synthesis via cross-coupling reaction with HOMSi reagent

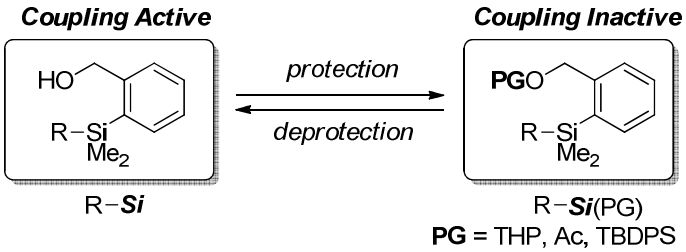
Because regioselectivity in hydrosilylation of internal alkynes is hardly controlled, synthesis of alkenyl-HOMSis by hydrosilylation remained restricted to terminal and symmetrical internal alkynes. Recently, however, regioselective hydrosilylation of unsymmetrical alkynes is attained to facilitate the synthesis of alkenyl-HOMSi reagents.[24] Hydrosilylation of 2-alkanoates with hydrosilanes is demonstrated to proceed high regioselectively to give α-silylalkanoates. The resulting functionalized HOMSi reagent can be converted into α-arylalkanoates by the cross-coupling with aryl iodides. An example is shown in Eq 21. [24]



The HOMSi-based cross-coupling reaction is applicable also to aryl bromides.[25] For example, 3-bromotoluene is cross-coupled with Ph-HOMSi with the aid of a Pd/Cu catalyst mixture to give the corresponding biaryl and the cyclic silyl ether (Eq 22).



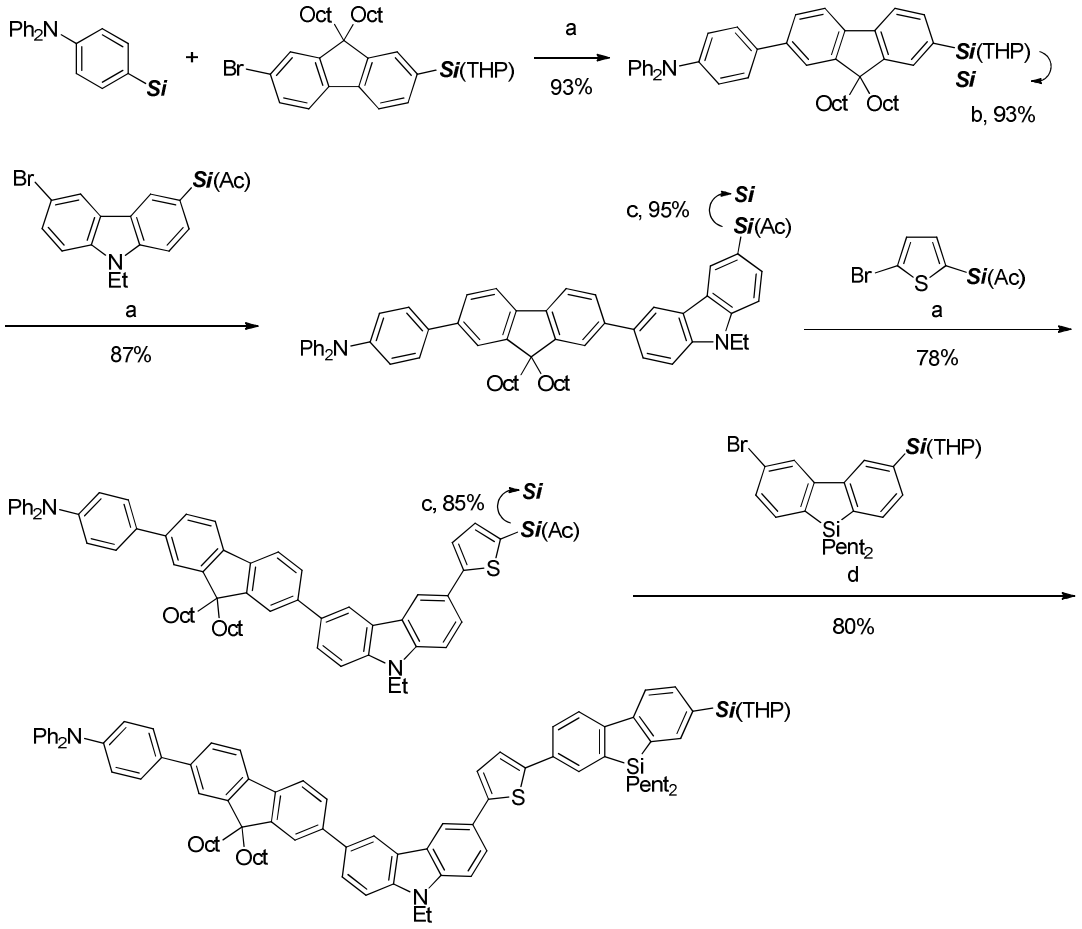
Whereas HOMSis are excellent coupling reagent, protection of the hydroxyl group as a silyl ether, acetate ester, or THP or MOM ether makes the silicon moiety totally inactive; deprotection under different conditions produces specifically activated HOMSi reagent being ready for cross-coupling (Scheme 5).



Scheme 5. Orthogonal protection and deprotection of HOMSi reagents

Using various protected halo-aryl-HOMSi reagents, a variety of oligo-arenes can readily be prepared according to a blue print of total synthesis by repeating cross-coupling and deprotection. [26-27] An example is illustrated in Scheme 6.

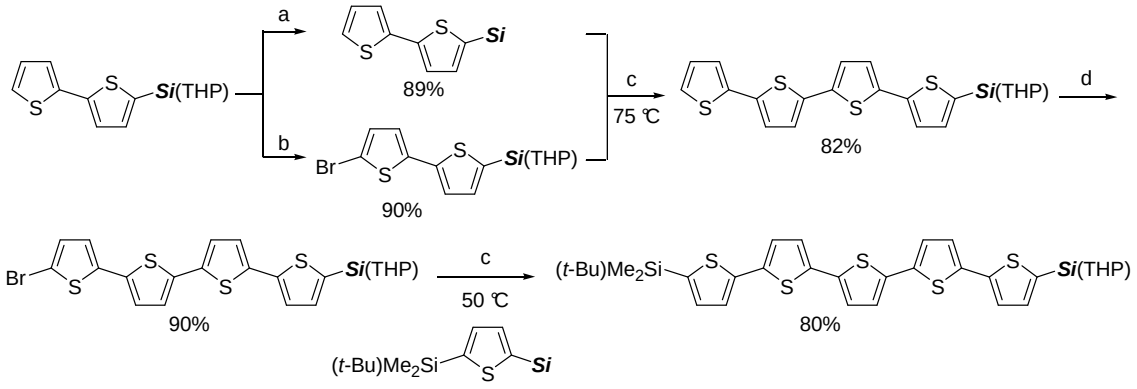
Repeating the procedure of protection/cross-coupling and protection/halogenation, oligothiophenes are readily prepared. Scheme 7 demonstrates a convergent synthesis of a quinquethiophene with silyl groups on the both ends. The material has an excellent character for three-dimensional holographic recording.[26-27]



Si = [2-(HOCH$_2$)C$_6$H$_4$]SiMe$_2$; ***Si***(THP) = [2-(THPOCH$_2$)C$_6$H$_4$]SiMe$_2$; ***Si***(Ac) = [2-(AcOCH$_2$)C$_6$H$_4$]SiMe$_2$

(a) [Pd(allyl)Cl]$_2$ (1 or 5 mol% Pd), Ruphos (2 or 11 mol%), CuI (3 or 5 mol%), K_2CO_3 (2.5 eq), THF/DMF, 75 °C; (b)PTSA·H_2O (2 mol%), MeOH/CH_2Cl_2, rt, overnight; (c)DIBAL-H (1.1 eq), CH_2Cl_2, -78 °C, 2h; (d)$PdCl_2$(dppf)·CH_2Cl_2 (5 mol%), CuI (5 mol%),K_2CO_3 (2.5 eq), THF/DMF, 75 °C, 24 h.

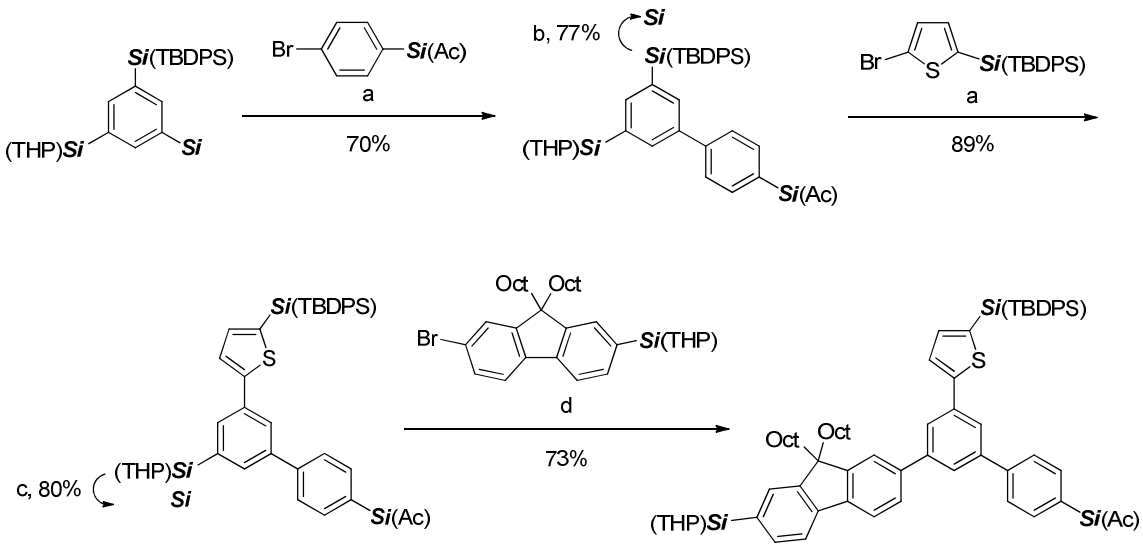
Scheme 6. Iterative cross-coupling–deprotection sequence



(a) PPTS (20 mol%), MeOH, 40 ℃, 2 h; (b) *n*-BuLi, TMEDA, THF, -40 ℃ to rt, 1 h, then BrCF_2CF_2Br, -40 ℃, 1 h; (c) $PdCl_2$(dppf)·CH_2Cl_2 (3 or 5 mol%), CuI (9 or 5 mol%), K_2CO_3 (2.5 eq), THF-DMF; (d) *n*-BuLi, TMEDA, THF, -78 ℃, 5 min, then BrCF_2CF_2Br, -40 ℃, 1 h.

Scheme 7. Convergent synthesis of disilylated quinquethiophene

Orthogonally protected HOMSi reagents are used to connect any desired π-electron systems as demonstrated in Scheme 8.

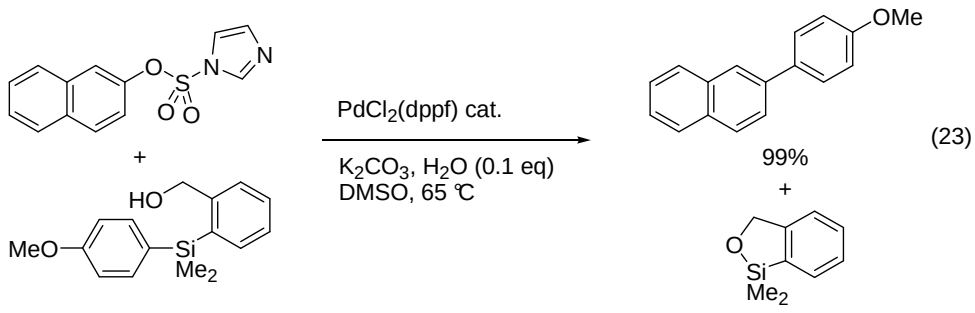


Si(TBDPS) = [2-(*t*-BuPh$_2$SiOCH$_2$)C$_6$H$_4$]SiMe$_2$

(a) [Pd(ally)Cl]$_2$ (5 mol% Pd), Ruphos (11 mol%), CuI (5 mol%), K$_2$CO$_3$ (2.5 eq), THF/DMF, 50 °C; (b)TBAF (2.0 eq), THF, rt, 1h; (c)PPTS (20 mol%), MeOH, 40 °C, overnight; (d)PdCl$_2$(dppf)·CH$_2$Cl$_2$ (5 mol%), CuI (5 mol%),K$_2$CO$_3$ (2.5 eq), THF/DMF, 50 °C, 24 h.

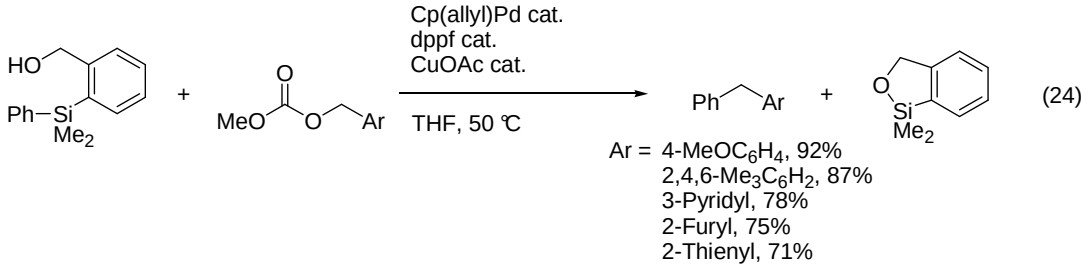
Scheme 8. Stepwise synthesis of trisilylated Oligoarene

A modification of the HOMSi coupling is recorded by Williams who used aryl sulfamate as an electrophile. The electrophile allows to run the HOMSi coupling without a copper co-catalyst (Eq 23). [28)]

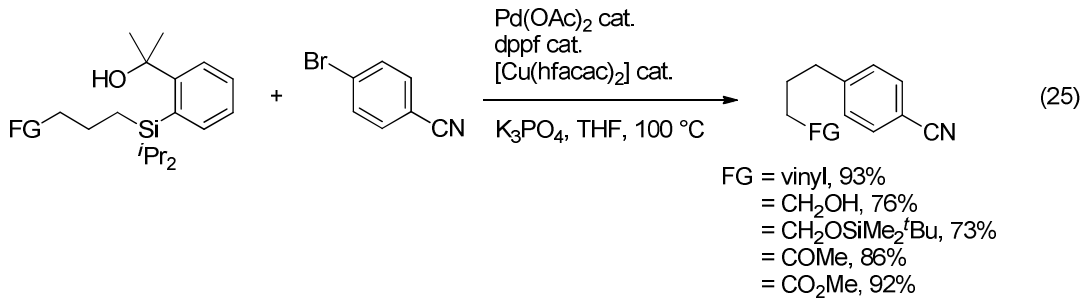


(23)

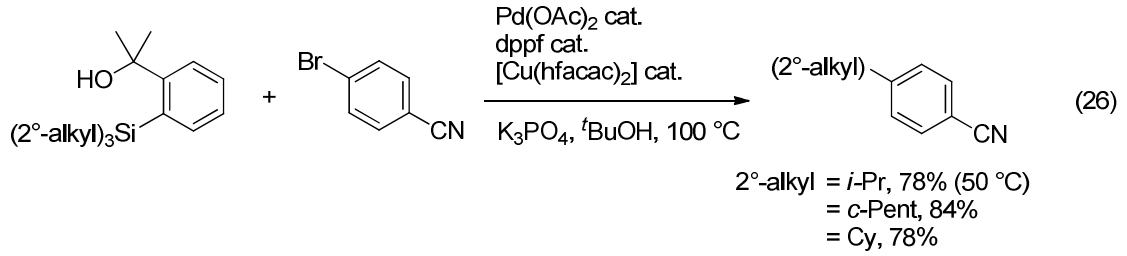
Cross-coupling of Ar-HOMSi reagents with benzyl carbonates proceeds in the absence of a base, as a methoxide ion is produced by oxidative addition of the benzyl–O bond to palladium catalyst followed by decarboxylation, giving rise to diarylmethanes (Eq 24)[29)].

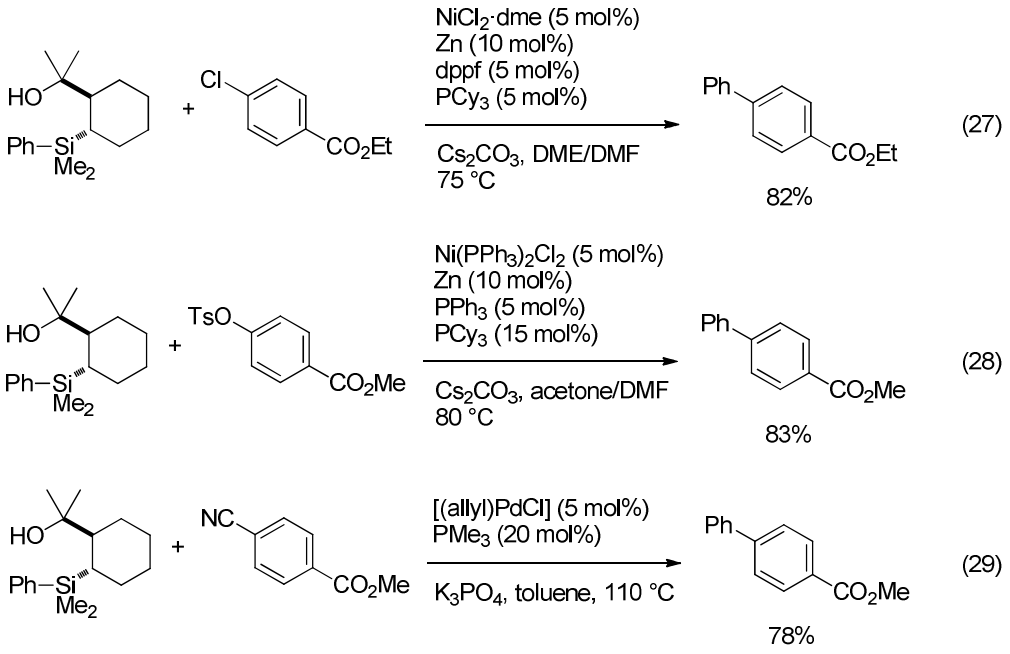


Alkyl-aryl coupling using alkylsilanes was attained initially by means of alkyltrifluorosilanes.[6b)] In contrast, modification of HOMSi reagents by introducing a dimethylmethylene in place of the benzylic methylene and diisopropyl in lieu of the dimethyl on silicon, made it more facile.[30)] For example, bromobenzonitrile is alkylated using various functionalized primary alkyl-HOMSi reagents (Eq 25).



Secondary alkyl coupling is achieved with the similarly modified HOMSi reagents. Use of *t*-butyl alcohol as the solvent allowed alkylation of aryl halides with triisopropyl-, tricyclopentyl-, and tricyclohexyl-HOMSi reagents (Eq 26).





Robust HOMSi reagents are prepared based on the molecular design based on a cyclohexane ring in place of the benzene moiety. The new HOMSi reagents allow the use of nickel catalyst and aryl chlorides (Eq 27) or sulfonates (Eq 28). [32] This sort of HOMSi reagents can undergo cross-coupling with aryl cyanides in the presence of a palladium-trimethylphosphine catalyst (Eq 29). [33]

As discussed above, the silicon residue is recovered as a cyclic silyl ether after the cross-coupling reaction. Smith, III, took advantage of the characteristic features and applied to a silicon-mediated cross-coupling of organolithium reagents with aryl halides using various cyclic silyl ethers listed in Fig 2.[34a]

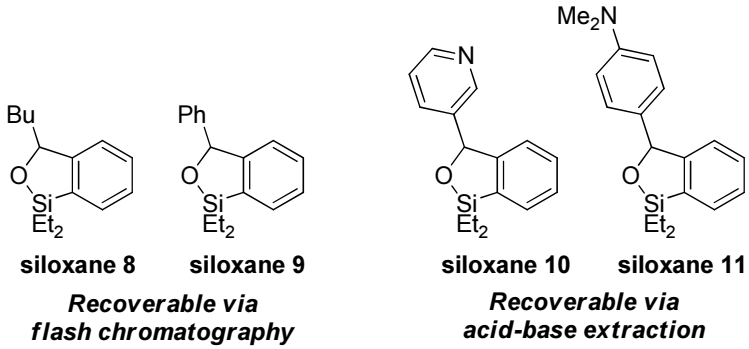
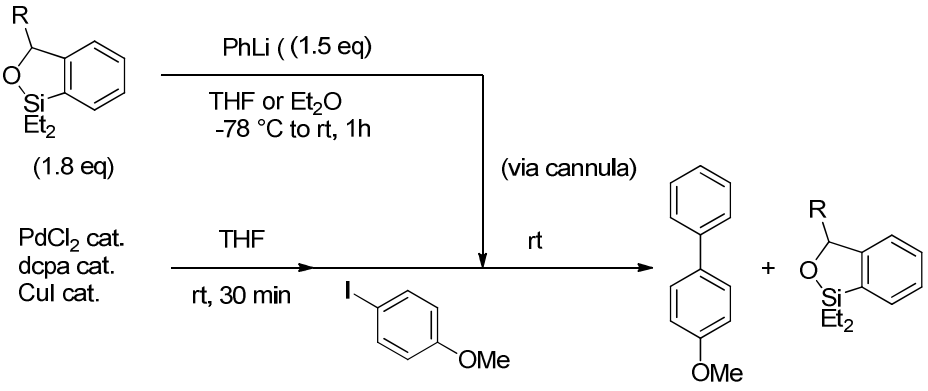


Figure 2. Recoverable siloxanes

One of these cyclic silyl ethers is allowed to react first with aryllithium reagents to

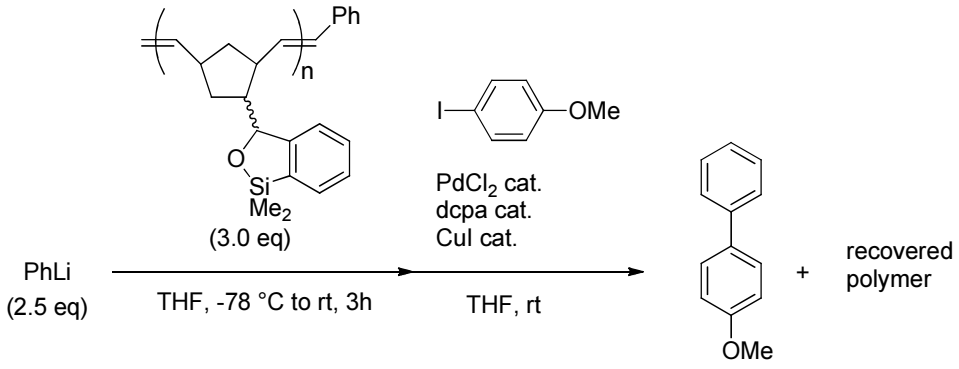
generate pentacoordinate form of a HOMSi reagent, which readily couples with aryl iodides to give biaryls. [34b] The cyclic silyl ether is easily separated from the coupled product by acid/alkaline extraction and/or chromatography (Scheme 9).



Recovered via flash chromatography	**siloxane 8 (**R = Bu)	96%	81%
	siloxane 9 (R = Ph)	98%	85%
Recovered via acid-base extraction	**siloxane 10** (R = 3-Py)	98%	76%
	siloxane 11 (R = 4-$Me_2NC_6H_4$)	98%	96%

Scheme 9. Cross-coupling reaction using recoverable siloxanes

Recovery of the cyclic silyl ether is facilitayed by supporting on polystyrene.[34c] The cross-coupling reaction is repeated three times without loss of the high efficiency (Scheme 10).



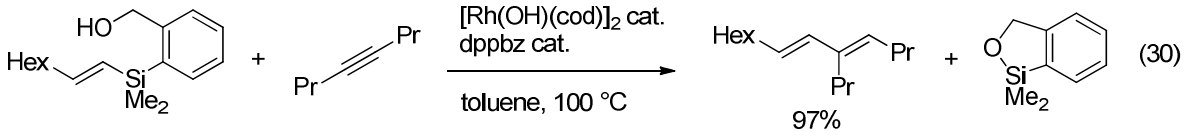
cycle	coupling product	recovered polymer
0		(Mn = 63500, PDI = 1.2)
1	98%	98% (Mn = 73000, PDI =1.6)
2	91%	99% (Mn = 104400, PDI = 2.3)
3	81%	99% (mn = 94600, PDI = 2.6)

Scheme 10. Recyclability of polymer-supported HOMSi reagents

As discussed above, the carbon–carbon bond formation with organosilicon reagents is almost established. However, its application to polymer synthesis or manufacturing is still rare due possibly to inefficiency of the reaction. Thus, it is essential to truly establish the best conditions for stoichiometric reaction by the organosilicon reagents. This problem as well as some solutions will be discussed will be discussed in Chapter 3.

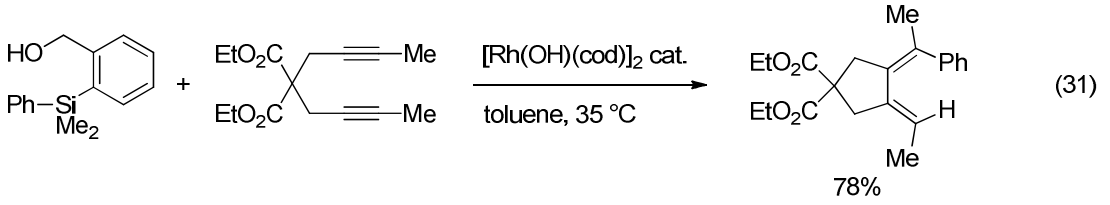
1. 4 Additional Carbon–Carbon Bond-Forming Reactions with HOMSi Reagents

HOMSi reagents undergo transmetalation to transition metals other than palladium catalysts to effect synthetic transformations characteristic of the metal. For example, a (hydroxo)rhodium(I) complex catalyzes alkenylrhodation of internal alkynes by alkenyl-HOMSi to give 1,3-dienes stereoselectively (Eq 30).



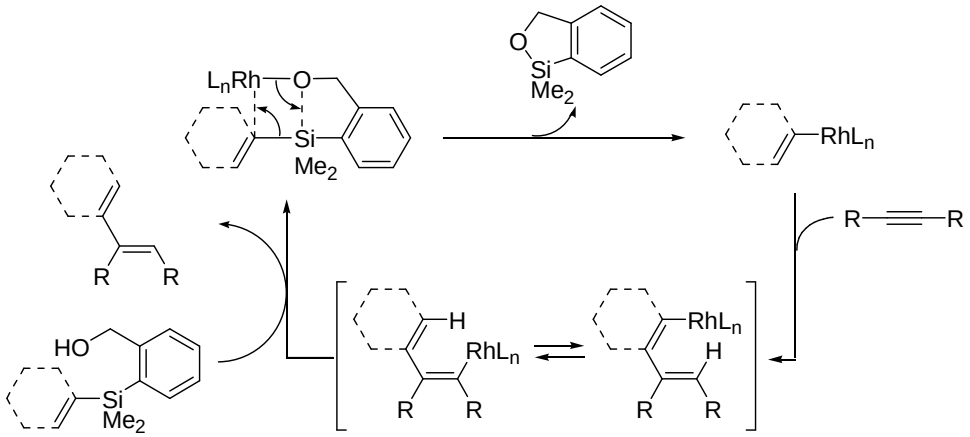
(30)

Under similar conditions, 1,6-diynes react with Ph-HOMSi to induce cyclization to give 1,2-bismethylenecyclopentanes (Eq 31). The mechanism of the cyclization is considered in a following way: after transmetalation, phenylrhodium is produced, which undergoes phenylrhodation at one of the alkyne moieties. The resulting alkenylrhodium attacks another alkyne intramolecularly, namely alkenylrhodation proceeds. Finally, the resulting dienylrhodium is protonated by the HOMSi reagent to provide with the final product.



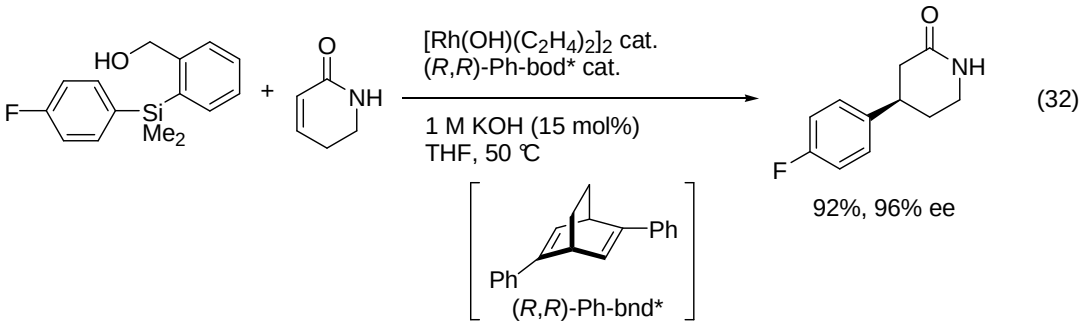
(31)

These reactions are considered to proceed through transmetalation of HOMSi to the Rh catalyst to give an alkenyl- or aryl-Rh which undergo carbometalation of alkynes. The resulting alkenylrhodium intermediates are then protonated by another molecule of HOMSi to generate the Rh(I) catalyst (Scheme 11).[35)]



Scheme 11. Plausible reaction mechanism

Rhodium(I) complexes catalyze the Michael addition of HOMSi reagents to α,β-unsaturated substrates. In particular, using a chiral diene ligand, asymmetric 1,4-addition of extremely high enantioselectivity is attained and applied to the synthesis of pharmaceutical intermediates (Eqs 32 and 33).[36)]



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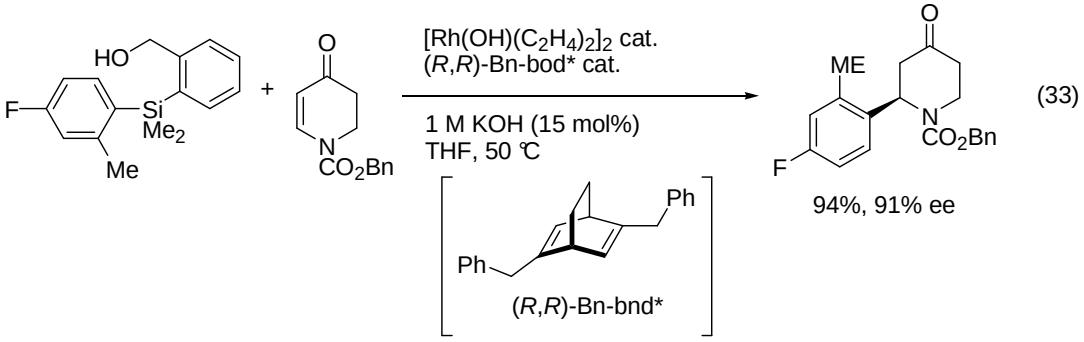
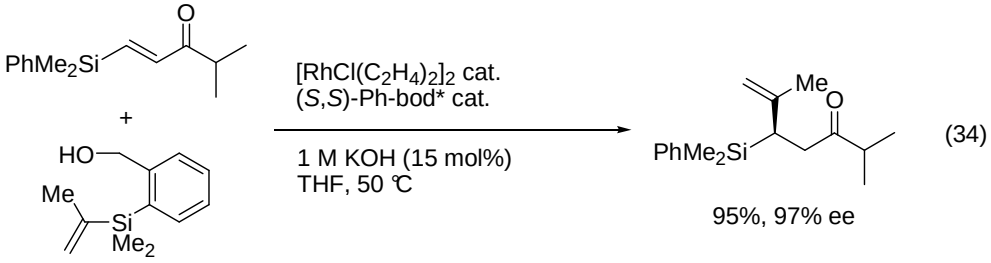


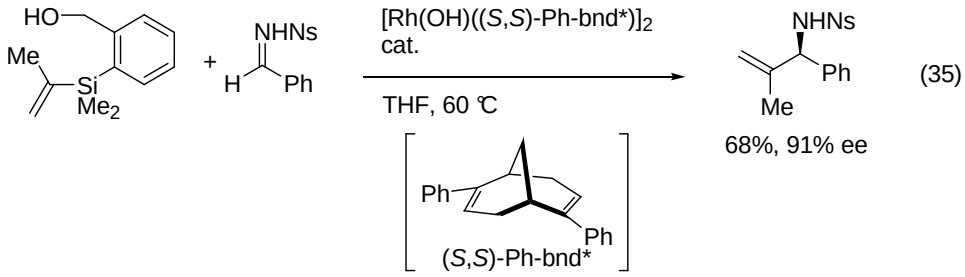
(33)

α-Substituted vinyl-HOMSis achieve a high level of enantioselective conjugate addition in sharp contrast to the corresponding vinylboronic acids which fail to give the corresponding adduct. When applied to a β-silyl enone in Eq 34, a highly enan-

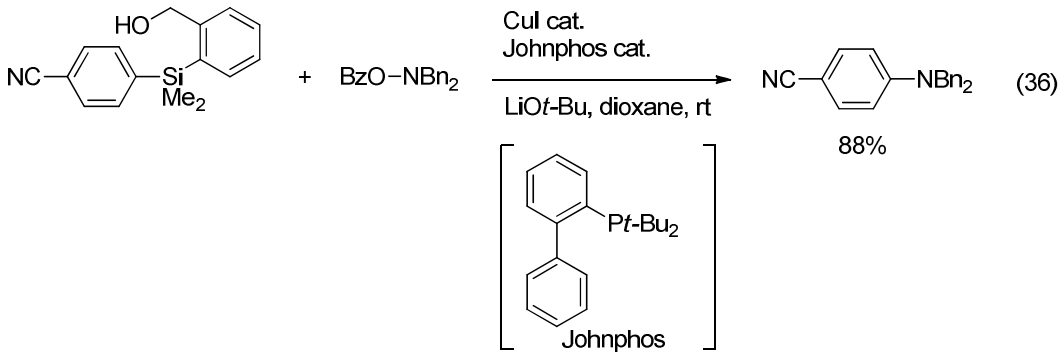
tio-enriched allylic silane is produced.[37)]



The rhodium catalysis also enables 1,2-addition of HOMSi reagents to imines also. Alkenyl-HOMSi reagents provide allylamines in high yields and high enantioselectivity (Eq 35). [38)]

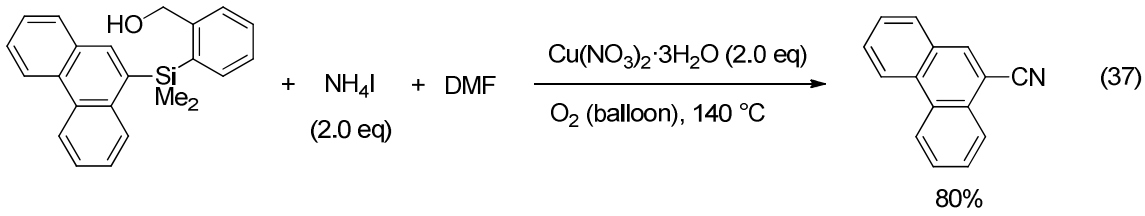


HOMSi reagents can be applicable to copper-catalyzed carbon-nitrogen bond forming reactions. Miura has used aryl-HOMSi for transmetalation to copper to give arylcopper intermediates which react with BzO-NBu_2 to give arylamines. As aryltrimethylsilanes and -trimethoxysilanes fail to react, transmetalation with HOMSi reagents through intramolecular activation is definitely effective (Eq 36).[39)]



In a similar manner, a copper(II) salt catalyzes the reaction of HOMSi reagents with

DMF and ammonia in an aerobic atmosphere to give arenecarbonitriles (Eq 37).[40] Cyanide ion, derived from DMF, ammonia, and oxygen, is considered to couple with aryl-HOMSi reagents with the aid of the copper catalyst.



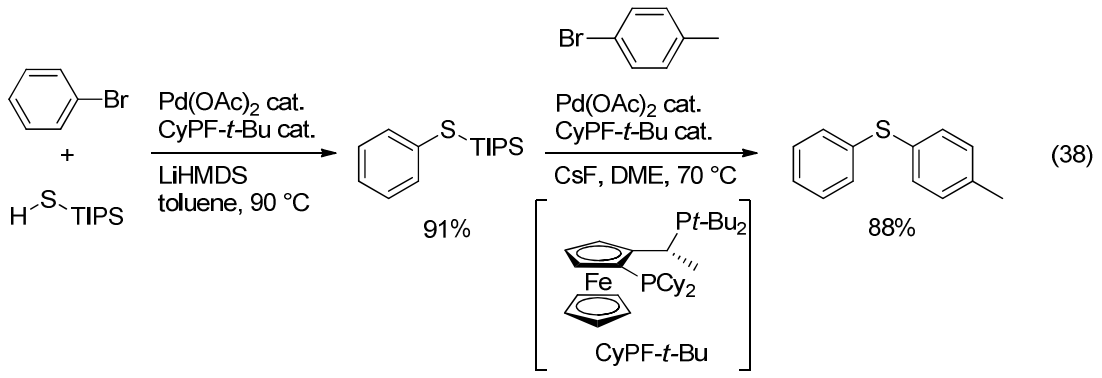
(37)

As discussed above, the organic groups in HOMSi reagents can be readily transferred to transition metals to effect synthetic reactions such as cross-coupling and conjugate addition depending on the catalyst metal. This design concept of reaction will lead to invention of novel synthetic methods characteristic of the metal in the future. Since the HOMSi reagent has a character appropriate to Green Chemistry, the chemistry with HOMSis will play important role in organic synthesis. It should be noted that the concept of intramolecular activation of C–Si bonds is discussed also by Takeda, [41] Shindo,[42] Tamao,[43] and Brown.[44]

1. 5 Carbon–Heteroatom Bond-Forming Reaction with Heteroatom–Silicon Reagents

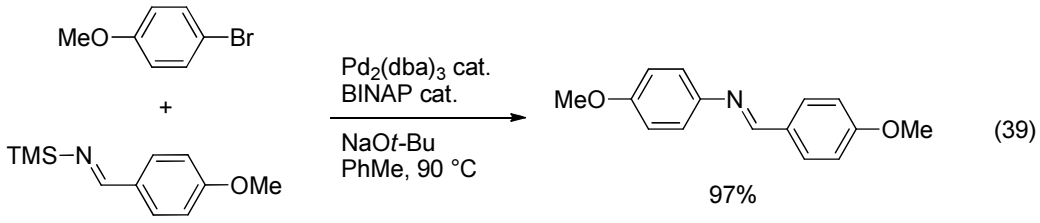
Silicon-based cross-coupling reaction is applicable not only to carbon-carbon bond formation but also carbon-heteroatom bond formation.

Hartwig attained the cross-coupling of TIPS thioether of benzenethiol, derived from bromobenzene and triisopropylsilylmercaptan by the Buchwald-Hartwig reaction, with *p*-bromotoluene in the presence of Pd(II)/CyPF-*t*-Bu catalyst, and cesium fluoride to give unsymmetrical diaryl sulfides (Eq 38).[45]

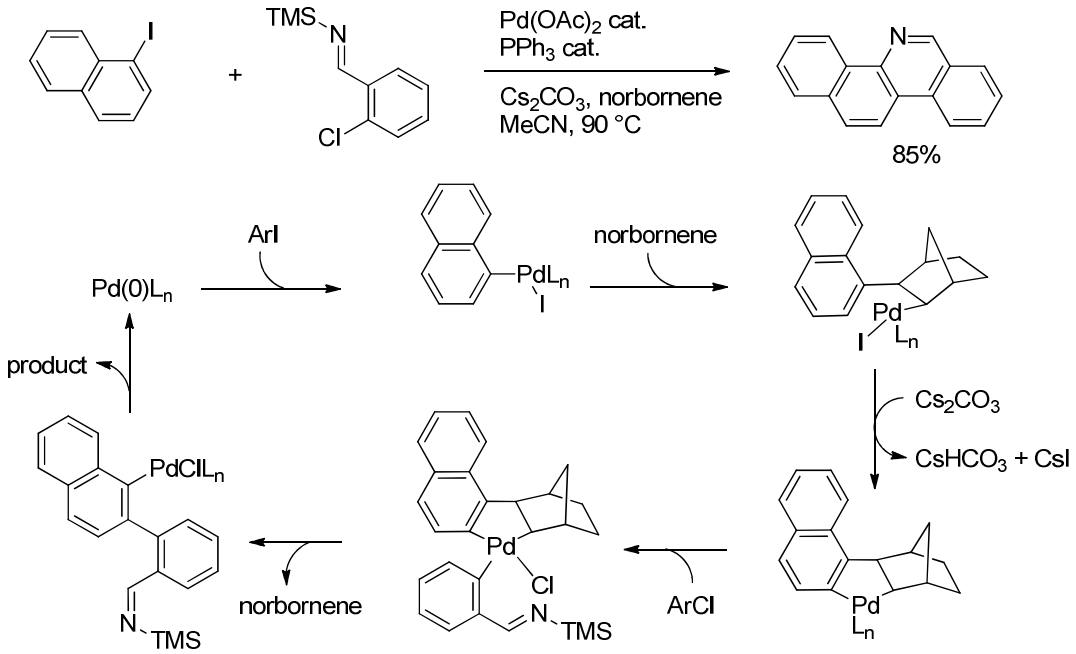


(38)

Barluenga et al. found *N*-TMS-aldimines to undergo coupling with aryl halides in the presence of a Pd/BINAP catalyst and NaO*t*-Bu to give *N*-arylaldimines, which upon hydrolysis were transformed to primary amines, demonstrating that *N*-TMS-aldimines are a synthetic equivalent of ammonia (Eq 39).[46)]

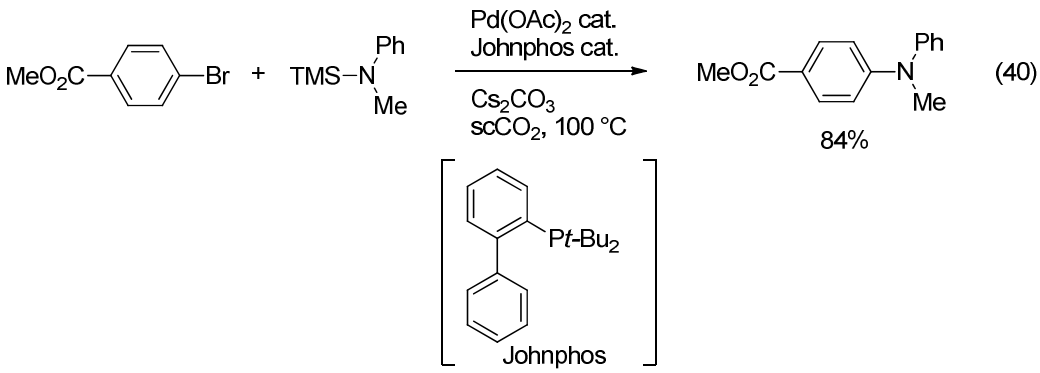


The C–N coupling using *N*-TMS-imines followed by the Catallani reaction is applied to synthesis of phenanthridines (Eq 40).[47)]



Scheme 12. C-N coupling via Catallani type reaction

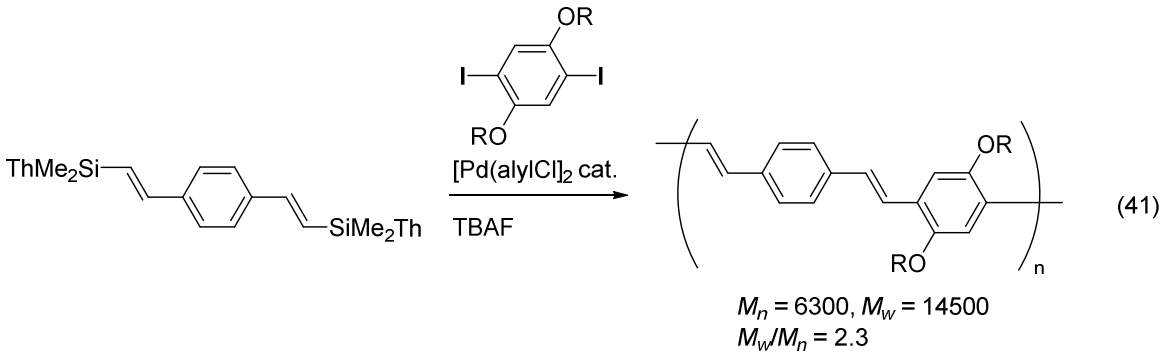
Simple C–N coupling is achieved with *N*-TMS secondary amines with aryl bromides using a palladium(II) catalyst/Johnphos, cesium carbonate in supercritical carbon dioxides ($scCO_2$). The same coupling carried out in a common solvent fails to give the C–N coupled products (Eq 40).[48)]



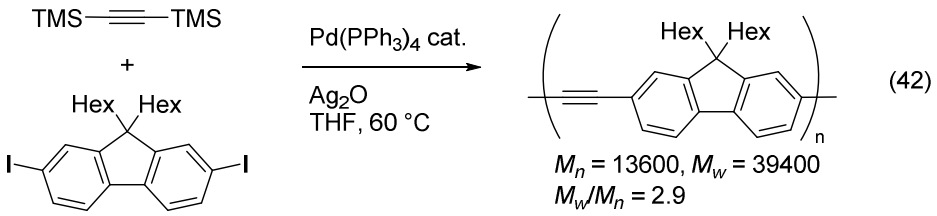
In view that the study on the carbon-heteroatom coupling using silyl-heteroatom reagents is relatively rare and this approach is of great significance, the author has considered more precise examination will lead to invention of a highly efficient and straightforward strategy.

1. 6 Cross-Coupling Polycondensation

Cross-coupling polycondensation has been an important tool for the synthesis of various polymer materials, and thus, much attention has been focused on preparation of π-conjugated polymer materials for light-emitting diodes, photovoltaics. Various types of cross-coupling reaction have been employed for condensation reaction. Notably, the reaction which involves boron, stannane, and magnesium reagents are often employed for these polymer synthesis. However, these organometallic reagents have disadvantages in stability, toxicity, and waste problems of the co-produced metallic salt. Thus, innovation in the cross-coupling reaction with other organometallic reagents is requested for cross-coupling polymerization. In this regard, the silicon-based cross-coupling reaction is ideal. However, only a few examples have been employed for the polymerization. Ozawa reported that palladium-catalyzed cross-coupling polycondensation of diiodobenzene with bifunctional (*E*)- or (*Z*)-alkenylsilane to give corresponding poly(arylene-vinylene)s (Eq 41).[49)]



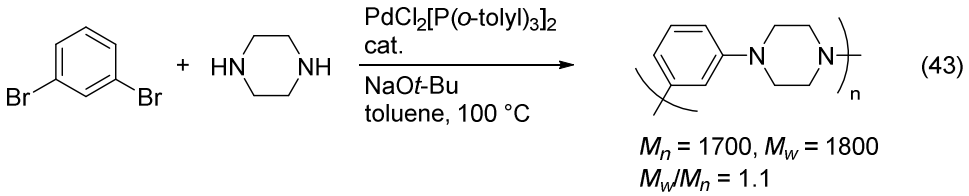
The cross-coupling polymerization of bifunctionalized trimethylsilylalkynes with arylene iodides in the presence of palladium-catalyst and silver(I) oxide as an activator is demonstrated by Mori (Eq 42).[50)]



(42)

Although ary-aryl bond-forming cross-coupling polycondensation with bifuntional organometallic reagent is essential for synthesis of polyarylenes for organic functionalized materials, silicon-based cross-coupling polymerization has remained to be studied.

Cross-coupling polymerization is employied not only carbon-carbon bond-forming reaction but also carbon-heteroatom bond-forming reaction. For example, Kanbara demonstrated that palladium-catalyzed C-N-coupling polymerization. Cross-coupling reaction of *m*-dibromobenzene with piperazine in the presence of $PdCl_2[P(o\text{-tolyl})_3]_2$ and NaO*t*-Bu gave poly(aryleneamine) with M_w 1800 (Eq 43).[51)] In a manner similar to amines, primary and secondary phosphines are also employed for the polymerization with arylene dihalide.[52)]



(43)

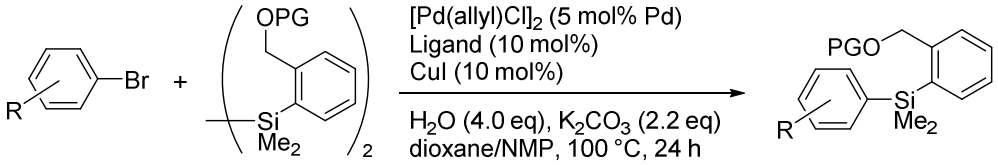
Whereas carbon-carbon bond-forming cross-coupling polymerizations with various organometallic reagents are extensively studied, carbon-heteroatom coupling reaction is limited to that which uses H-heteroatom reagent. To enhance the efficiency of carbon-heteroatom cross-coupling polymerization, novel heteroatom nucleophiles likes silylamines should be employed for polymerization.

1. 7 Outline of this Dissertation

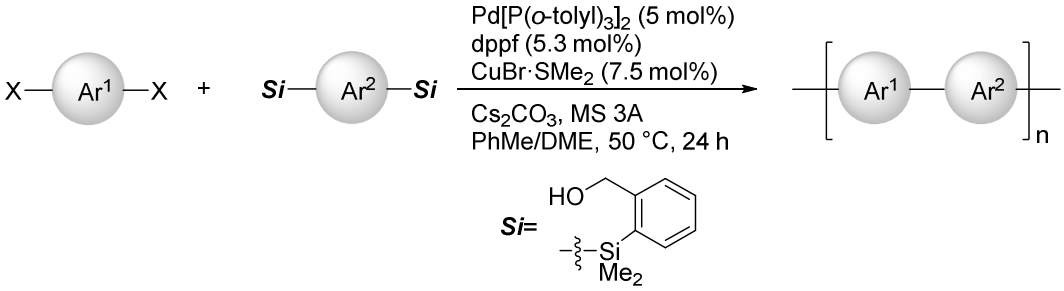
In this Chapter the author has so far reviewed the reactions of carbon–carbon cross-coupling and carbon-heteroatom coupling reactions with organosilicon reagents. It

is obvious that among many types of organosilicon compounds, the HOMSi reagent has an advantage in environmentally benign characters, which will allow HOMSi reagents find much more applications in manufacturing materials and pharmaceuticals. Also he has focused on the future possibility of carbon-heteroatom bond formation by means of *N*-TMS-heteroatom reagents.

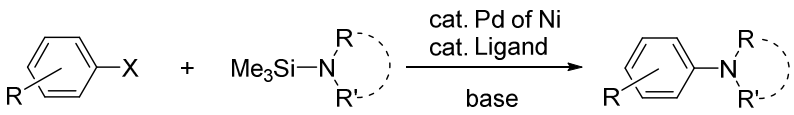
In Chapter 2 is described novel synthesis of HOMSi reagents by the transition metal catalysis, starting with disilane analogs of HOMSi reagents. Highly functionalized HOMSi reagents are readily accessible by this method.



Chapter 3 is attributed to the study directed to double and multiple carbon–carbon bond formation with HOMSi reagents and subsequently polyarylene synthesis is demonstrated to be accessible using double functionalized HOMSi reagents.



Chapter 4 describes the C–N coupling using *N*-TMS-diarylamines and -carbazoles using palladium or nickel catalysts and a nucleophilic activator in common solvents. The findings are further applied to polyarylamine synthesis.



The final Chapter summarizes the chemistry discussed in the Dissertation.

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Chapter 2
Novel Synthetic Method of HOMSi Reagents

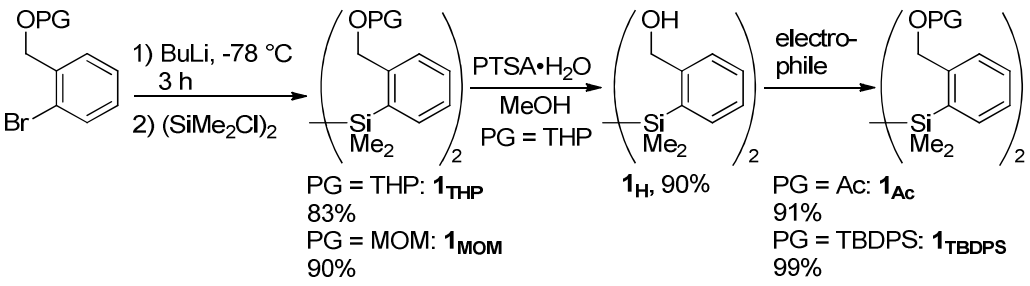
Silylation of aryl bromides with disilanes of type [{2-(PGOCH$_2$)C$_6$H$_4$}Me$_2$Si]$_2$ (PG: protecting group) is successfully found to take place in the presence of a Pd/Ruphos or Davephos/CuI catalytic system to give HOMSi reagents containing various functional groups in good yields. BisHOMSi reagents also are prepared directly from the corresponding arylene dibromides.

2.1 Introduction

Silicon-based cross-couplilng reaction is useful and environmentally bengine method for new carbon-carbon bond formation as discussed in Chapter 1.[1)] Particularly, organo [(2-hydroxymethyl)phenyl]dimethylsilanes (HOMSi reagents) are superior to other silicon reagents in nature regarding to handling, recovery and reuse of the Si residue.[2,3)] In addition, HOMSi reagents are now commercially available worldwide. Ar-HOMSi reagents have a great potential for the synthesis of various biaryls and functionalized oligoarenes. A general synthetic method of Ar-HOMSi reagents is the reaction of organometallic reagents such as aryl-Grignard reagents and aryllithiums with the cyclic silyl ether (*cf*. Eq 14, Chapter 1). Therefore, it is not easy to synthesize the functionalized arylHOMSi reagents without problem. To overcome this disadvantage, transition metal-catalyzed silylation of organic halides with disilanes[4-6)] or hydrosilanes[7)] has an advantage for the synthesis of complex organosilicon compounds. Thus, Kondo reported a preparative method of aryl HOMSi reagents by the cross-coupling of bromoarenes with a hydrosilane. However, yields remain only moderate and the scope is limited to two examples.[7k)] In view that disilanes are also applicable to such silylation, in this chapter, the authour has focused on the use of disilanes for the silylation of aryl halides and describes a new synthesis of Ar-HOMSi reagents by the palladium/copper-catalyzed silylation of organic halides.

2.2 Results and discussions

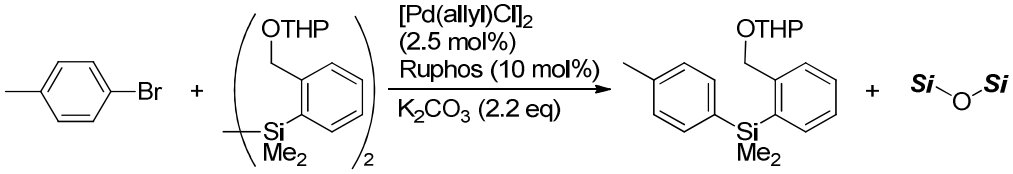
Bisarylated tetramethyl disilane protected by THP group **1THP** was prepared by the reaction of 1,2-dichlorotetramethyldisilane with the 2-Li-$C_6H_4CH_2O$-THP prepared by the lithiation of THP-protected 2-bromobenzylalcohol with butyllithium in 83% yield (Scheme 1). In a similar way, MOM-protected disilane (**1MOM**) was prepared in 90% yield. Other protected disilanes having acetyl (**1Ac**), and TBDPS (**1TBDPS**) were synthesized in high yields by the deprotection of **1THP** mediated by *p*-toluenesulfonic acid, followed by acetylation and silylation, of **1H** with corresponding electrophiles.



Scheme 1. Preparation of Disilanes **1**

First, the author applied the reported conditions[4f,4g,4h,4j] to the silylation of *p*-bromotoluene **2a** using $\mathbf{1_{THP}}$ in the presence of a base and was disappointed to find that no trace or small amounts of the desired product, 4-silyltoluene (**3a**) was formed. Thus, he searched other activation methods to use of **1** as the silylation reagent. To this end, silylcopper reagents were formed under the reaction of disilanes with Cu(OTf) reported by Hosomi.[8] He considered a HOMSi copper reagent is proceeded by the treatment of disilyl reagents **2** with Cu(I) for the silylation of organo halides.[9] Of many catalysts and additives examined, he found that reaction conditions consisting of $[Pd(allyl)Cl]_2$, Ruphos (2-Dicyclohexylphosphino-2′,6’-diisopropoxybiphenyl), CuI, K_2CO_3 and THP/DMF (3:1) as a solvent are patented to show the catalytic activity to give **3a** in 34% NMR yield together with the generation of siloxane **4** in 92% yield (Table 1,entry 1). Other copper reagents such as CuBr, $CuBr\cdot SMe_2$ and CuCl were less effective. In the absece of CuI, palladium or

Table 1. Reaction of **2a** with $\mathbf{1_{THP}}$[a]



2a | $\mathbf{1_{THP}}$ (1.2 eq) | **3a** | **4**

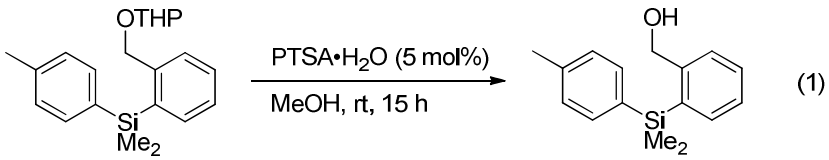
Si = {2-(THPOCH$_2$)C$_6$H$_4$}Me$_2$Si

Entry	Additive	Solvent	Temp. (°C)	Time (h)	Yield (%)[b] **3a**	**4**[c]
1	CuI (10 mol%)	THF/DMF[d]	80	24	34	92
2	-	THF/DMF[d]	80	24	0	71
3[e]	CuI (10 mol%)	THF/DMF[d]	80	24	0	72
4[f]	CuI (10 mol%)	THF/DMF[d]	80	24	0	13
5	CuI (10 mol%)	dioxane/NMP[g]	100	24	80	85
6	-	dioxane/NMP[g]	100	24	52	76
7	CuI (10 mol%) H_2O (4 eq)	dioxane/NMP[g]	100	2	83	11
8	CuI (10 mol%) H_2O (4 eq)	dioxane/NMP[g]	100	24	87 (73)[h]	77

[a] Unless otherwise noted, a mixture of **2a**, $\mathbf{1_{THP}}$ (1.2 eq), $[Pd(allyl)Cl]_2$ (2.5 mol%), ligand (10 mol%), CuI (10 mol%), K_2CO_3 (2.2 eq) and solvent (0.36 M) was heated at 80-100 °C. [b] NMR yield. [c] Yields based on $\mathbf{1_{THP}}$. [d] 3:1. [e] without $[Pd(allyl)Cl]_2$. [f] without K_2CO_3. [g] 4:1. [h] Isolated yield.

K_2CO_3, **3a** was not produced, wheres **4** was generated (entries 1, 3 and 4). These results indicate that the silyl copper reagent is formed as an active silyl nucleophile via the reaction of **2(THP)** with CuI maybe in the presence of K_2CO_3. To enhance yield of **3a**, he examined various solvents and found dioxane/NMP (4:1) at 100 ºC, **3a** was obtained in 80% yield (entry 5). In the absence of CuI, yield of **3a** was in 52% yield (entry 6). These results suggest that highly polar solvents enhances the silylation efficiency: as is evidenced by the additive of H_2O increased the yield in a shorter reaction time (entry 7). Finally, under the reaction in the presence H_2O at 24 h the yield was improved upto 87% (entry 8).

Of note, deprotection of **3a** mediated by *para*-toluenesulfonic acid in methanol gave active HOMSi reagent **5**, 4-tolyl-2-(hydroxymethyl)phenyl}dimethylsilane, in high yield (Eq 1).

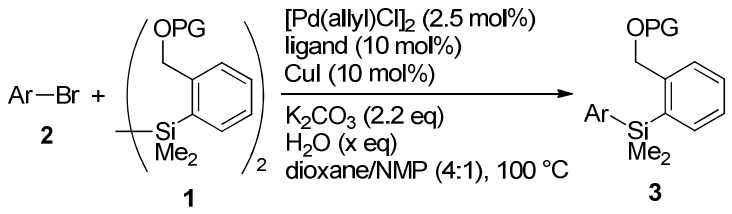


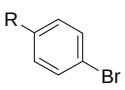
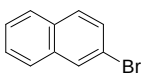
3a **5**, 80% (NMR) (1)

Scope and limitations of the reaction under the optimized conditions are summarized in Table 2. Protected disilanes $\mathbf{1}_{\mathbf{MOM}}$, $\mathbf{1}_{\mathbf{Ac}}$ and $\mathbf{1}_{\mathbf{TBDPS}}$ reacted with **2a** smoothly to give the corresponding products **6a**, **7a** and **8a** in moderate to high yields (entries 1-3). Using $\mathbf{1}_{\mathbf{THP}}$ as a silylation reagent, the reaction of various organic bromides was examined. Electron-donating groups such as *p*-MeO, *p*-NHBoc and *p*-Ph_2N did not hamper the reaction in the presence of Ruphos, and the corresponding HOMSi reagents **3b**-**3d** were isolated in moderate to good yields (entries 4-6). In the case of 3,5-xylyl bromide **2e**, H_2O did not show any advantage: **3e** was isolated in 63% yield in the absence of H_2O (entries 7). On the contrary, when electron-neutral and electron-deficient aryl bromides were used under the conditions with Ruphos, the corresponding silylarenes were obtained but in very low yields. The author further screened ligands for the silylation using these bromides and found that Davephos, 2-dicyclohexylphosphino-2′-(*N*,*N*-dimethylamino)biphenyl, led to improvement in the catalytic activity. Bromobenzene **2g** upon this reaction using Davephos gave Ph-HOMSi reagent **3g** in 64% yield (entry 8). Electron-deficient aryl bromides preferred the reaction in the absence or in the presence of 1 equiv amount of H_2O (entries 9-15). The reaction of 1-bromo-4-fluorobenzene **2g** gave 4-F-C_6H_4-HOMSi reagent **3g** in 60% yield

(entry 9). Other electron-deficient groups such as chloro, phenyl, acetyl, cyano, trifluoromethyl and formyl tolerated well the

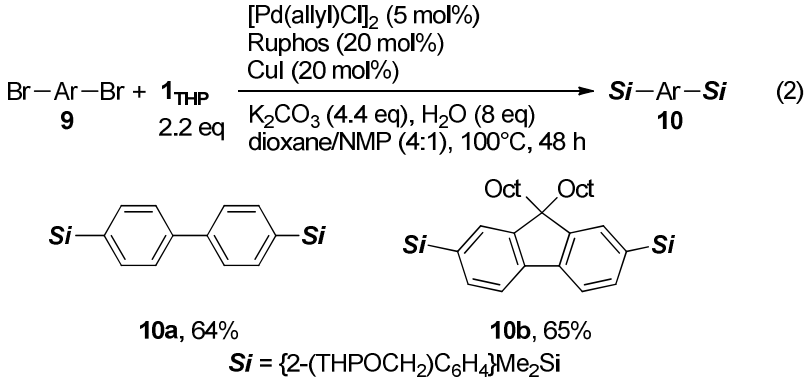
Table 2. Silylation of organobromides **2** using disilane **1**[a]



Entry	1	2	ligand	H_2O (x eq)	time (h)	Product (%)[b]
1	$\mathbf{1}_{MOM}$	**2a**	**L1**	4	24	**6a**, 80%
2	$\mathbf{1}_{Ac}$	**2a**	**L1**	4	24	**7a**, 60%
3	$\mathbf{1}_{TBDPS}$	**2a**	**L1**	4	24	**8a**, 54%
						
4	$\mathbf{1}_{THP}$	**2b**: R = OMe	**L1**	4	24	**3b**, 75%
5	$\mathbf{1}_{THP}$	**2c**: R = NH(Boc)	**L1**	4	13	**3c**, 74%
6	$\mathbf{1}_{THP}$	**2d**: R = NPh_2	**L1**	4	16	**3d**, 67%
7	$\mathbf{1}_{THP}$	**2e**: R = 3,5-xylyl	**L1**	0	24	**3e**, 63%
8	$\mathbf{1}_{THP}$	**2f**: R = H	**L2**	4	24	**3f**, 64%
9[c]	$\mathbf{1}_{THP}$	**2g**: R = F	**L2**	0	24	**3g**, 60%
10[c]	$\mathbf{1}_{THP}$	**2h**: R = Cl	**L2**	0	16	**3h**, 63%
11	$\mathbf{1}_{THP}$	**2i**: R = Ph	**L2**	0	24	**3i**, 70%
12	$\mathbf{1}_{MOM}$	**2j**: R = Ac	**L2**	0	48	**6j**, 35%
13[d]	$\mathbf{1}_{THP}$	**2k**: R = CN	**L2**	1	31	**3k**, 26%
14[d]	$\mathbf{1}_{THP}$	**2l**: R = CF_3	**L2**	1	23	**3l**, 63%
15	$\mathbf{1}_{THP}$	**2m**: R = CHO	**L2**	0	48	**3m**, 27%
16	$\mathbf{1}_{THP}$	 **2n**	**L2**	0	24	**3n**, 70%
17	$\mathbf{1}_{THP}$	 **2o**	**L1**	4	24	**3o**, 42%

[a] Unless otherwise noted, **2** (0.5 mmol), **1** (0.6 mmol), $[Pd(allyl)Cl]_2$ (0.0125 mmol), ligand (0.05 mmol),CuI (0.05 mmol), K_2CO_3 (1.1 mmol), and 1,4-dioxane/NMP (4:1, 1.4 mL) were heated at 100 °C. [b] Isolated yield. [c] 120 °C. [d] 80 °C. **L1** = Ruphos. **L2** = Davephos.

silylation with $\mathbf{1}_{\mathbf{THP}}$ and $\mathbf{1}_{\mathbf{MOM}}$ to give the corresponding HOMSi reagents **3h**-**3i**, **6j** and **3k**-**3m** in 26-70% yields (entries 10-15). The reaction of 2-bromonapthalene (**2n**) gave **3n** in 70% yield (entry 16). 3-Bromothiophene (**2o**) was silylated with $\mathbf{1}_{\mathbf{THP}}$ in the presence of Ruphos and 4 equiv. of H_2O to afford 3-thienyl-HOMSi reagent **3o** in 42% yield (entry 17).



This silylation can be applied to the synthesis of bis-HOMSi reagents **10** by the reaction of dibromoarenes **9**. For example, 4,4'-dibromobiphenyl (**9a**) reacted with 2.2 equiv. of $\mathbf{1}_{\mathbf{THP}}$ under the optimized conditions using Ruphos to give bissilylated biphenyl **10a** in 64% yield (Eq 2). Similarly, 2,7-dibromo-9,9-dioctyl-9*H*-fluorene (**9b**) was double silylated to form the corresponding product **10b** in 65% yield.

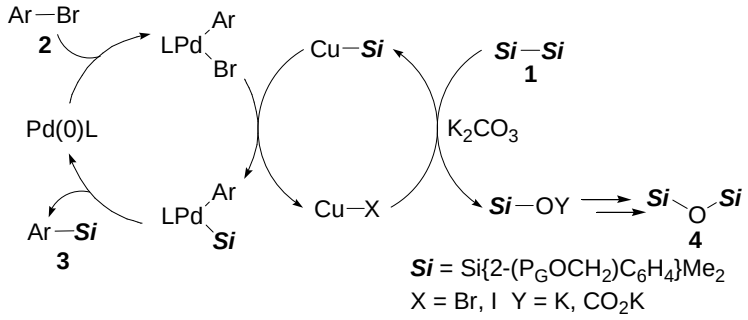


Figure 1. Proposed reaction mechanism

The author proposes a reaction mechanism illustrated in Figure 1. Oxidative addition of aryl bromide **2** to palladium(0) complex forms an Ar-Pd-Br complex, which transmetalates to the silylcopper(I) reagent derived from the reaction of disilane **1** with Cu-X and K_2CO_3 to give Ar-Pd-*Si* complex with the generation of an oxysilane (*Si*-OY) and Cu-X. Finally, reductive elimination of Ar-Pd-*Si* complex produces HOMSi rea-

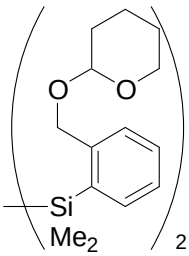
gents **3** and regenerates palladium(0) to complete the catalytic cycle. The coproduced oxysilane appears to be converted readily into siloxane **4**.[10] The effect of the additive H_2O may be attributed to enhancement of solubility of K_2CO_3 to promote the reactivity of **1** toward Cu(I) and K_2CO_3.

In conclusion, the author has demonstrated that the silylation of aryl bromides with disilanes is a powerful and straightforward approch for the preparation of aryl-HOMSi reagents. This method allows us to synthesize variously functionalized aryl-HOMSi reagents useful for the C-C bond-forming cross-coupling with aryl bromides after deprotection. Furthermore, bisHOMSi reagents also are readily prepared and conveniently used for polyarylene synthesis.

Experimental

General. The following apparatus and purification procedures apply to all the experiments described in this Dissertaion. All manipulations of oxygen- and moisture-sensitive materials were conducted with a standard Schlenk technique or in a dry box under an argon atmosphere. Flash column chromatography was performed using Kanto Chemical silica gel (spherical, 50 μm), silica gel neutral (spherical, 50 μm) or Merck aluminium oxide 90 active neutral. Analytical TLC was performed on Merck Kieselgel 60 F254 (0.25 mm) plates. Preparative TLC was carried out using Wakogel B-5F silica gel. Visualization was accomplished with UV light (254 nm).

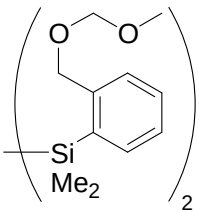
Apparatus. ^{1}H and ^{13}C NMR spectra in $CDCl_3$ and benzene-d_6 were recorded with Varian Mercury 400 spectrometer. The chemical shifts in the ^{1}H NMR spectra were recorded relative to Me_4Si as an internal standard, and the chemical shifts in the ^{13}C NMR spectra were recorded relative to $CHCl_3$ (δ 77.16). ^{1}H NMR data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sext = sextet, sept = septet, br = broad, m = multiplet), coupling constants (Hz), and integration. The IR spectra were measured by JASCO FT/IR-4200. GCMS were measured on Agilent 6890N/5975B. High-resolution mass spectra (HRMS) were measured by JEOL JMS-T100LC AccuTOF. Melting points were measured by a MPA100 Optimelt Automated Melting Point System.

Preparation of 1,2-bis[2-{(2-tetrahydropyranyloxy)methyl}phenyl]-1,1,2,2-tetramethyldisilane ($\mathbf{1}_{THP}$). 

(Tetrahydropyran-2-yloxy)methylbromotoluene (27.2 g, 100 mmol) was dissolved in the Et_2O (250 mL) and cooled to –78 °C. After the addition of a solution of BuLi in hexane (2.69 M, 37.2 mL, 100 mmol) over 30 minutes, the solution was stirred at –78 °C for 3 h. 1,2-Dichlorotetramethylsilane (9.3 mL, 50 mmol) was added dropwise over 10 minutes, and the resulting mixture was stirred at room temperature overnight. After the addition of water, the mixture was extracted with hexane, washed with brine, dried over $MgSO_4$, evaporated and dried *in vacuo*. The residue was purified by flash column chromatography on silica gel using hexane and ethyl acetate (10:1) as an eluent to give $\mathbf{1}_{THP}$ (20.7 g, 83%), as a colorless oil. R_f 0.21 (hexane–ethyl acetate = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.38 (s, 6H), 0.39 (s, 6H), 1.51-1.73 (m, 10H), 1.80-1.88 (m, 2H), 3.50 (ddd, *J* = 4.0, 6.4, 11.2 Hz, 2H), 3.87 (ddd, *J* = 2.8, 8.0, 11.2 Hz, 2H), 4.22 (d, *J* = 12.0 Hz, 1H), 4.23 (d, *J* = 12.0 Hz, 1H), 4.50 (t, *J* = 3.6 Hz, 2H), 4.59 (d, *J* = 12.0

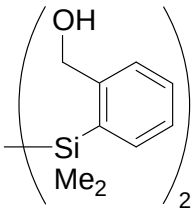
Hz, 1H), 4.60 (d, *J* = 12.0 Hz, 1H), 7.22 (ddd, *J* = 1.2, 7.2, 7.6 Hz, 2H), 7.34 (ddd, *J* = 1.2, 7.2, 7.6 Hz, 2H), 7.39 (dd, *J* = 1.2, 7.6 Hz, 2H), 7.45 (ddd, *J* = 1.2, 7.6 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ -1.81, -1.68, 19.5, 25.6, 30.7, 62.3, 69.3, 98.1, 126.9, 127.9, 129.1, 134.6, 137.0, 137.6, 144.0; IR (neat) 3055, 2944, 1439, 1349, 1249, 1200, 1117, 1077, 1031, 976, 870, 793, 748, 466, 455, 428 cm^{-1}. MS (EI, 70 eV) *m/z* (%) 296 (M^+ - 2(THPO), 0.5), 193 (6), 179 (13), 165 (48), 147 (36), 133 (26), 105 (8), 85 (100), 67 (9), 57 (9). HRMS calcd for $C_{28}H_{42}NaO_4Si_2$ (M + Na) 521.2519, found 521.2503.

1,2-Bis{(2-methoxymethoxymethyl)phenyl}-1,1,2,2-tetramethyldisilane (1$_{MOM}$). A



colorless oil. R_f 0.32 (hexane–ethyl acetate = 10 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.39 (t, *J* = 3.2 Hz, 12H), 3.36 (s, 6H), 4.34 (s, 4H), 4.54 (s, 4H), 7.23 (ddd, *J* = 1.2, 7.2, 7.2 Hz, 2H), 7.34 (ddd, *J* = 1.2, 7.2, 7.6 Hz, 2H), 7.38-7.41 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ -1.80, 55.5, 69.7, 96.0, 127.1, 128.1, 129.1, 134.7, 137.1, 143.5; IR (neat) 3056, 2948, 2886, 2822, 1467, 1437, 1402, 1377, 1249, 1209, 1150, 1123, 1102, 1076, 1046, 919, 834, 794, 751, 477, 463, 444, 435, 428, 420, 408 cm^{-1}. MS (EI, 70 eV) *m/z* (%) 357 (M^+ - OCH_2OCH_3, 0.002), 209 (17), 180 (17), 179 (100), 163 (41), 149 (53), 133 (20), 105 (17), 89 (13). HRMS calcd for $C_{22}H_{34}NaO_4Si_2$ (M + Na) 441.1893, found 441.1888.

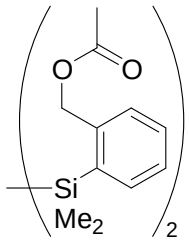
Preparation of 1,2-bis{2-(hydroxymethyl)phenyl}-1,1,2,2-tetramethyldisilane (1$_H$).



To a solution of **1$_{THP}$** (8.31 g, 16.7 mmol) in methanol (85 mL) 4-toluenesulfonic acid monohydrate (0.15 mg, 0.84 mmol) was added at room tempreture, and the resulting solution was stirred for 3 h. After the addition of sat. NH_4Cl at 0 °C, the mixture was extracted with diethyl ether, washed with brine, dried over $MgSO_4$, evaporated and dried *in vacuo*. The residue was purified by flash column chromatography on silica gel using hexane and ethyl acetate (3:1) as an eluent to give **1$_H$** (4.97 g, 90%), as a colorless solid. R_f 0.13 (hexane–ethyl acetate = 3:1). mp 82.9-83.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.43 (s, 12H), 1.08 (s, 2H), 4.24 (s, 4H), 7.25-7.29 (m, 2H), 7.33-7.35 (m, 4H), 7.45 (dd, *J* = 0.8, 8.0 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ -1.90, 65.5, 127.1, 127.2, 129.4, 134.5, 136.5, 146.9; IR (KBr) 3302, 3057, 2952, 2893, 1434, 1407, 1251, 1200, 1251, 1200, 1121, 1074, 1035, 1001, 834, 789, 742, 687, 638, 453, 423 cm^{-1}. MS (EI, 70 eV) *m/z* (%) 299 (M^+ - $2CH_3$ - H, 2.3), 207 (29), 179 (28), 165 (62), 164 (15), 163 (18), 150 (16), 149 (100), 148 (37), 147 (70), 145 (36), 135 (14), 133 (39), 131 (11), 105 (14). HRMS calcd for $C_{18}H_{26}NaO_2Si_2$ (M + Na) 353.1369, found

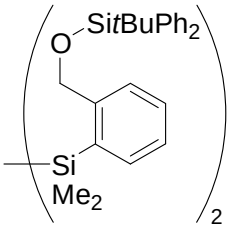
353.1365.

Preparation of 1,2-bis{(2-acetoxymethyl)phenyl}-1,1,2,2-tetramethyldisilane ($\mathbf{1_{Ac}}$).



Unprotected disilane $\mathbf{1_H}$ (1.65 g, 5.00 mmol) was dissolved in the Et_2O (10 mL) and cooled to 0 °C. 4-Dimethylaminopyridine (DMAP) (6.1 mg, 0.050 mmol), pyridine (8.0 mL, 10 mmol) and acetyl chloride (0.40 mL, 5.5 mmol) were added to the solution, and the resultant mixture was stirred for 5 h at room temperature. After 1M HCl was added, the reaction mixture was extracted with diethyl ether. The organic phase was washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by flash column chromatography on silica gel using hexane and ethyl acetate (5:1) as an eluent to give $\mathbf{1_{Ac}}$ (1.89 g, 91%), as a colorless solid. R_f 0.29 (hexane–ethyl acetate = 10 : 1). mp 54.4-55.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.41 (s, 12H), 2.03 (s, 6H), 4.75 (s, 4H), 7.25-7.30 (m, 4H), 7.33 (dd, *J* = 1.6, 7.2 Hz, 2H), 7.41 (dd, *J* = 1.6, 7.2 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ -1.87, 21.2, 66.8, 127.8, 129.2, 129.3, 135.0, 137.8, 141.0, 170.8; IR (KBr) 3441, 3080, 3069, 3012, 2960, 2941, 2902, 2332, 1946, 1732, 1470, 1436, 1383, 1076, 1024, 963, 925, 882, 838, 792, 761, 737, 686, 651, 637, 607, 588, 525, 469, 445, 429, 411 cm^{-1}. MS (EI, 70 eV) *m/z* (%) 399 (M^+ - CH_3, 0.001), 208 (10), 207 (60), 166 (15), 165 (100), 147 (36), 145 (14), 133 (10). HRMS calcd for $C_{22}H_{30}NaO_4Si_2$ (M + Na) 437.1580, found 437.1588.

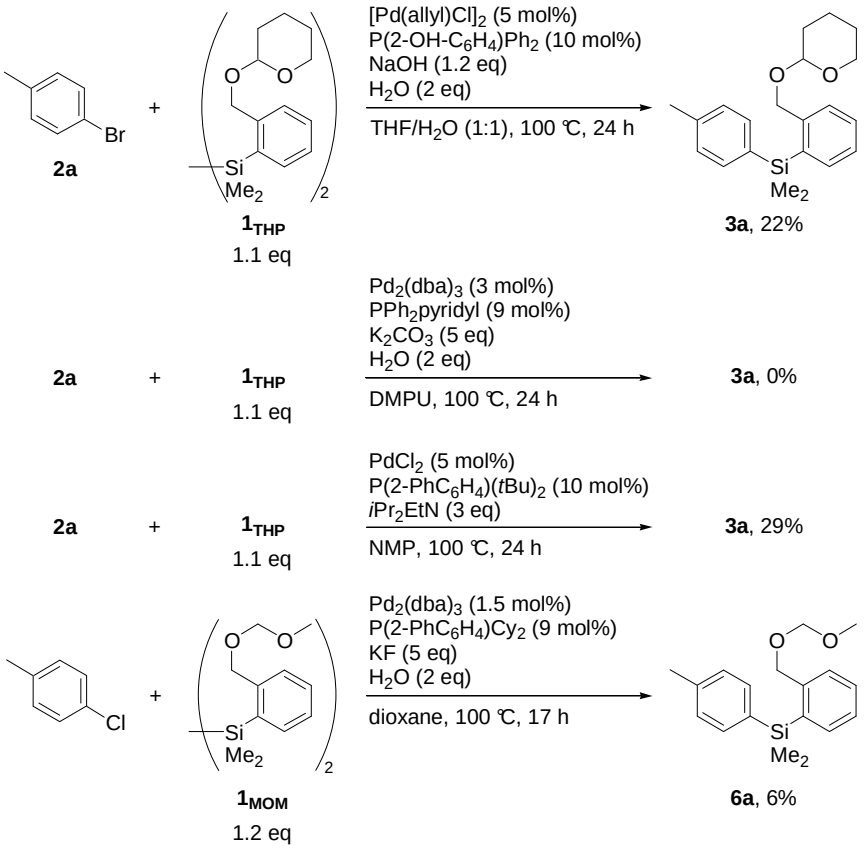
Preparation of 1,2-bis{2-(*t*-butyldiphenylsiloxymethyl)phenyl}-1,1,2,2-tetra-



methyldisilane ($\mathbf{1_{TBDPS}}$). Unprotected disilane $\mathbf{1_H}$ (1.32 g, 4.00 mmol) and imidazole (1.10 g, 16.0 mmol) were dissolved in DMF (7.0 mL). After the addition of a solution of chloro-*t*-butyldiphenylsilane (2.40 g, 8.73 mmol), the resultant solution was stirred for 5 min at room temperature. After the addition of water, the mixture was extracted with CH_2Cl_2. The organic phase was washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. The residue was recrystalized with CH_2Cl_2-hexane to give $\mathbf{1_{TBDPS}}$ (3.20 g, 99%), as a colorless solid. R_f 0.24 (hexane–ethyl acetate = 10 : 1). mp 139.3-139.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ -0.032 (s, 12H), 1.08 (s, 18H), 4.45 (s, 4H), 7.04 (ddd, *J* = 1.2, 6.8, 7.6 Hz, 2H), 7.12 (dd, *J* = 1.6, 7.6 Hz, 2H), 7.26-36 (m, 10H), 7.39-7.43 (m, 4H), 7.59-7.62 (m, 10H); ^{13}C NMR (101 MHz, $CDCl_3$) δ -2.01, 19.2, 19.4, 26.7, 27.0, 66.0, 121.3, 125.6, 126.3, 127.8, 129.1, 129.7, 129.8, 133.6, 134.2, 134.3, 135.0, 135.8, 146.5. IR (KBr) 3134, 3051, 2932, 2895, 2857, 1964, 1894, 1587, 1472, 1427, 1390, 1372, 1362, 1253, 1203,

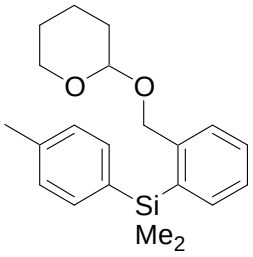
1188, 1115, 1087, 1060, 1107, 940, 837, 822, 787, 770, 702, 688, 622, 507, 494, 476, 449, 435 cm^{-1}. HRMS calcd for $C_{50}H_{62}O_2Si_4$ (M + Na) 829.3725, found 829.3746.

Examination of Silylation of Haloarenes under the Reported Conditions[4f,4g,4h,4j]



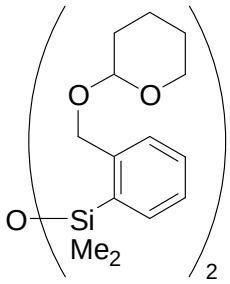
Silylation of *p*-tolyl bromide (2a) using 1_{THP} to give 4-tolyl-(2-tetrahydropyranyloxy)methylphenyldimethylsilane (3a) (Table 1). ***A general procedure for the synthesis of protected HOMSi reagents.*** An aryl bromide (0.50 mmol), disilane (0.55 mmol) and K_2CO_3 (1.1 mmol) were added sequentially to a solution of $[Pd(allyl)Cl]_2$ (12.5 μmol), ligand (50 μmol) and CuI (0.10 mmol) in 1,4-dioxane and NMP (4:1, 1.4 mL) placed in a 3 mL-vial in a dry box. The vial was closed with a screw PTFE septum cap, taken outside the dry box. H_2O was added to the mixture via syringe and the resultant mixture was heated at 80-100 °C for the time specified in Table 1. The resultant mixture was filtered through Celite, and the filtrate was evaporated and dried *in vacuo*. The desired products were isolated in yields listed in Table 1 by Preparative TLC and HPLC.

4-Tolyl[2-(2-tetrahydropyranyloxymethyl)phenyl]dimethylsilane (3a). a yellow oil.



R_f 0.15 (hexane–ethyl acetate = 20 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.57 (s, 3H), 0.58 (s, 3H), 1.43-1.66 (m, 5H), 1.75-1.84 (m, 1H), 2.34 (s, 3H), 3.41 (ddd, *J* = 4.8, 5.2, 11.2 Hz, 1H), 3.76 (ddd, *J* = 5.2, 8.4, 11.2 Hz, 1H), 4.38 (d, *J* = 12.0 Hz, 1H), 4.44 (t, *J* = 3.6 Hz, 1H), 4.66 (d, *J* = 12.0 Hz, 1H), 7.15 (d, *J* = 7.6 Hz, 2H), 7.27 (ddd, *J* = 1.2, 7.2, 7.6 Hz, 1H), 7.38 (d, *J* = 7.6 Hz, 2H), 7.40 (ddd, J = 1.2, 7.2, 7.6 Hz, 1H), 7.49 (dd, *J* = 1.2, 7.6 Hz, 1H), 7.52 (dd, *J* = 1.2, 7.6 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ -0.88, -0.75, 19.5, 21.6, 25.6, 30.6, 62.1, 68.9, 98.0, 126.9, 128.7, 128.8, 129.7, 134.2, 135.3, 135.6, 136.5, 139.0, 144.3. IR (neat) 2945, 2924, 2870, 1489, 1259, 1250, 1200, 1127, 1118, 1106, 1078, 1055, 1027, 976, 906, 870, 836, 821, 797, 773, 754, 509, 497, 482, 473, 466, 453, 440, 420, 404 cm^{-1}. MS (EI, 70 eV) *m/z* (%) 326 (M^+ -CH_2, 0.3), 241 (43), 239 (21), 224 (13), 223 (57), 165 (14), 164 (12), 163 (46), 149 (38), 91 (16), 85 (100), 55 (10). HRMS calcd for $C_{21}H_{28}NaO_2Si$ (M + Na) 363.1756, found 363.1773.

1,3-Bis[2-{(2-Tetrahydropyranyloxy)methyl}phenyl]-1,1,3,3-tetramethylsiloxane

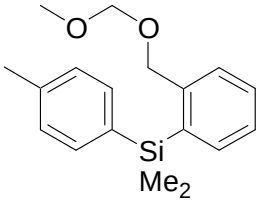


(4). A colorless oil. R_f 0.22 (hexane–ethyl acetate = 10 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.41 (s, 12H), 1.50-1.74 (m, 10H), 1.84-1.87 (m, 2H), 3.49 (ddd, *J* = 5.2, 5.2, 11.6 Hz, 2H), 3.88 (ddd, *J* = 2.0, 6.8, 11.6 Hz, 2H), 4.62 (d, *J* = 12.0 Hz, 2H), 4.62 (s, 2H), 4.87 (d, *J* = 12.0 Hz, 2H), 7.26 (dd, *J* = 7.2, 7.6 Hz, 2H), 7.38 (dd, *J* = 7.2, 7.6 Hz, 2H), 7.50 (d, *J* = 7.6 Hz, 2H), 7.58 (d, *J* = 7.2 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 2.31, 19.6, 25.6, 30.7, 62.3, 68.7, 98.0 (d, 2.2 Hz), 126.8, 128.1, 129.7, 134.3, 137.7, 143.5. IR (KBr) 3448, 3057, 2944, 2871, 1627, 1627, 1591, 1466, 1454, 1439, 1386, 1350, 1323, 1284, 1258, 1201, 1182, 1155, 1128, 1119, 1079, 1054, 1028, 976, 956, 934, 906, 870, 834, 817, 792, 753, 701, 688, 649, 504, 494, 482, 471, 458, 429, 416, 410 cm^{-1}. MS (EI, 70 eV) *m/z* (%) 399 (M^+ -CH_2OTHP, 0.05), 237 (8), 165 (8), 164 (20), 163 (23), 150 (14), 149 (100), 133 (9), 85 (37), 84 (11). HRMS calcd for $C_{28}H_{42}NaO_5Si_2$ (M + Na) 537.2469, found 537.2448.

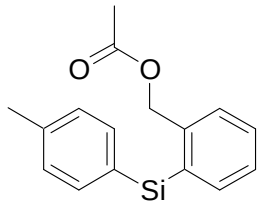
Deprotection of 3a. 4-Toluenesulfonic acid monohydroxide (3.2 mg, 0.017 mmol) was added to a solution of **3a** (102 mg, 0.300 mmol) in methanol (1.0 mL) at room tempreture, and the resulting solution was stirred for 16 h. The mixture was concentrated *in vacuo* to give **4-Tolyl(2-hydroxymethyl)phenyldimethylsilane (5)**

CAS registry number: 1217863-38-1.

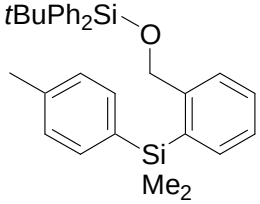
4-Tolyl(2-methoxymethoxymethyl)phenyldimethylsilane (6a). A colorless oil. R_f 0.38 (hexane–ethyl acetate = 10 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.57 (s, 6H), 2.34 (s, 3H), 3.29 (s, 3H), 4.47 (s, 2H), 4.50 (s, 2H), 7.15 (d, *J* = 8.0 Hz, 2H), 7.29 (ddd, *J* = 1.2, 7.2, 7.6 Hz, 1H), 7.38 (d, *J* = 8.0 Hz, 2H), 7.40 (ddd, *J* = 1.2, 7.2, 7.6 Hz, 1H), 7.45 (d, *J* = 7.2 Hz, 1H), 7.54 (d, *J* = 7.2 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ -0.80, 21.6, 55.5, 69.4, 95.9, 127.1, 128.6, 128.8, 129.7, 134.1, 135.2, 135.7, 136.6, 139.0, 143.8; IR (neat) 2951, 2927, 2884, 1465, 1438, 1392, 1379, 1257, 1250, 1149, 1105, 1047, 920, 836, 821, 797, 773, 754, 495, 485, 463, 455, 442, 426, 414, 404 cm^{-1}. MS (EI, 70 eV) *m/z* (%) 300 (M^+, 0.02), 255 (26), 239 (28), 224 (12), 223 (48), 209 (16), 179 (32), 165 (13), 164 (12), 163 (71), 149 (46), 105(100). HRMS calcd for $C_{18}H_{24}NaO_2Si$ (M + Na) 323.1443, found 323.1439.



4-Tolyl(2-acetoxymethyl)phenyldimethylsilane (7a). A colorless oil. R_f 0.20 (hexane–ethyl acetate = 10 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.59 (s, 6H), 1.93 (s, 3H), 2.34 (s, 3H), 4.98 (s, 2H), 7.16 (d, *J* = 8.0 Hz, 2H), 7.31-7.43 (m, 5H), 7.58 (d, *J* = 7.2 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ -0.89, 21.0, 21.6, 66.7, 127.7, 128.9, 129.6, 129.8, 134.1, 135.9, 137.6, 139.1, 141.4, 170.8. IR (neat) 3011, 2956, 2925, 2860, 2373, 2351, 2323, 1738, 1248, 1738, 1378, 1027, 1248, 1234, 1105, 1027, 835, 820, 797, 774, 756, 539, 512, 498, 486, 480, 472, 465, 453, 439, 418, 404 cm^{-1}. 283 (M^+ - CH_3, 8.2), 241 (5), 223 (100), 207 (34), 195 (6), 179 (6), 165 (24), 163 (22), 149 (8). HRMS calcd for $C_{18}H_{22}NaO_2Si$ (M + Na) 321.1287, found 321.1301.

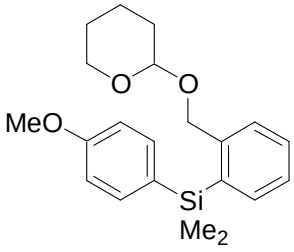


4-Tolyl(2-*t*-butyldiphenylsiloxymethyl)phenyldimethylsilane (8a). A colorless solid. R_f 0.28 (hexane–ethyl acetate = 10:1). mp 113.6-114.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.37 (s, 6H), 1.04 (s, 9H), 2.28 (s, 3H), 4.58 (s, 2H), 7.00 (d, *J* = 7.6 Hz, 2H), 7.18 (d, *J* = 7.6 Hz, 2H), 7.25 (dd, *J* = 6.0, 7.2 Hz, 1H), 7.30-7.34 (m, 4H), 7.38-7.47 (m, 3H), 7.48 (dd, *J* = 1.2, 7.2 Hz, 1H), 7.538 (d, *J* = 8.0 Hz, 2H), 7.542 (d, *J* = 8.0 Hz, 2H), 7.73 (d, *J* = 7.6 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ -1.36, 19.4, 21.6, 27.0, 65.7, 125.6, 126.2, 127.7, 128.8, 129.7, 129.8, 133.6, 134.0, 134.2, 134.7, 135.0, 135.6, 138.8, 147.1. IR (neat) 3096, 3012, 2958, 2930, 2857, 1906,



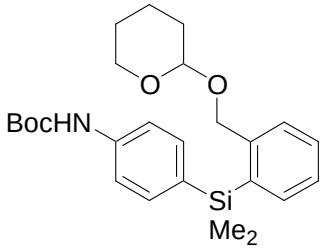
1821, 1590, 1471, 1428, 1390, 1250, 1204, 1106, 1007, 822, 742, 702, 622, 616, 603, 591, 506, 497, 488, 480, 471, 463 cm^{-1}. MS (EI, 70 eV) *m/z* (%) 437 (M^+ - *t*Bu), 359 (100), 345 (69), 285 (17), 267 (48), 223 (15), 209 (16), 197 (13), 181 (12), 165 (15), 149 (28), 135 (20), 105 (20). HRMS calcd for $C_{32}H_{38}NaOSi_2$ (M + Na) 517.2359, found 517.2352.

4-Methoxyphenyl[2-(2-tetrahydropyranyloxymethyl)phenyl]dimethylsilane (3b). A



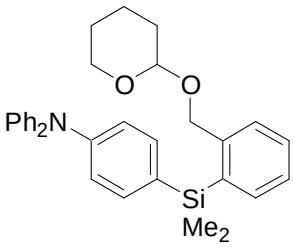
yellow oil. R_f 0.23 (hexane–ethyl acetate = 20 : 1). ^1H NMR (400 MHz, $CDCl_3$) δ 0.567 (s, 3H), 0.571 (s, 3H), 1.45-1.67 (m, 5H), 1.75-1.81 (m, 1H), 3.42 (ddd, *J* = 4.0, 6.0, 11.2 Hz, 1H), 3.77 (ddd, *J* = 3.2, 8.8, 11.2 Hz, 1H), 3.79 (s, 3H), 4.39 (d, *J* = 12.0 Hz, 1H), 4.46 (t, *J* = 3.6 Hz, 1H), 4.66 (d, *J* = 12.0 Hz, 1H), 6.88 (d, *J* = 8.8 Hz, 2H), 7.27 (ddd, *J* = 1.2, 7.2, 7.6 Hz, 1H), 7.38-7.43 (m, 3H), 7.49 (d, *J* = 7.6 Hz, 1H), 7.52 (d, *J* = 7.6 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ -0.77, -0.66, 19.5, 25.6, 30.6, 55.1, 62.1, 68.9, 98.0, 113.7, 126.9, 128.6, 129.69, 129.74, 135.6, 136.6, 144.3, 160.5. IR (neat) 3056, 2949, 1594, 1564, 1503, 1464, 1440, 1396, 1349, 1310, 1279, 1248, 1220, 1182, 1112, 1078, 1031, 976, 906, 870, 818, 774, 756, 688, 660, 607, 526, 501, 488, 473, 458, 450, 431, 419 cm^{-1}. MS (EI, 70 eV) *m/z* (%) 341 (M^+ - CH_3, 1.2), 257 (32), 239 (20), 225 (12), 165 (14), 164 (14), 163 (41), 149 (48), 108 (16), 85 (100), 84 (14), 55 (21). HRMS calcd for $C_{21}H_{28}NaO_3Si$ (M + Na) 379.1705, found 379.1696.

4-*t*-Butoxycarbonylaminophenyl[2-(2-tetrahydropyranyloxymethyl)phenyl]di-



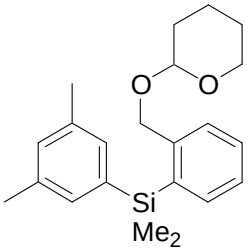
methylsilane (3c). A yellow viscous oil. R_f 0.17 (hexane–ethyl acetate = 10 : 1). ^1H NMR (400 MHz, $CDCl_3$) δ 0.560 (s, 3H), 0.563 (s, 3H), 1.46-1.71 (m, 14H), 1.78-1.81 (m, 1H), 3.43 (ddd, *J* = 4.8, 5.2, 11.2 Hz, 1H), 3.78 (ddd, *J* = 2.8, 8.0, 11.2 Hz, 1H), 4.38 (d, *J* = 12.0 Hz, 1H), 4.47 (t, *J* = 3.6 Hz, 1H), 4.66 (d, *J* = 12.0 Hz, 1H), 6.56 (s, 1H), 7.22 (dd, *J* = 6.4, 7.6 Hz, 1H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.34-7.41 (m, 3H), 7.48 (d, *J* = 8.0 Hz, 1H), 7.50 (d, *J* = 8.4 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ -0.89, -0.77, 19.5, 25.5, 28.4, 30.6, 62.1, 68.9, 80.9, 97.9, 117.9, 126.9, 128.6, 129.7, 132.7, 135.0, 135.7, 136.4, 139.3, 144.2, 152.7. IR (neat) 3295, 3163, 3052, 2941, 1732, 1589, 1520, 1391, 1317, 1254, 1323, 1157, 1111, 1051, 1023, 976, 910, 868, 834, 813, 782, 754, 691, 521, 488, 461, 424 cm^{-1}. HRMS calcd for $C_{25}H_{35}NNaO_4Si$ (M + Na) 464.2233, found 464.2230.

4-Diphenylaminophenyl[2-(2-tetrahydropyranyloxymethyl)phenyl]dimethylsilane



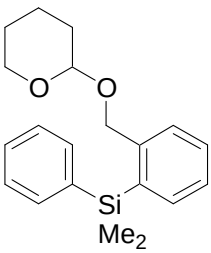
(3d). A colorless viscous oil. R_f 0.43 (hexane–ethyl acetate = 10 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.568 (s, 3H), 0.574 (s, 3H), 1.49-1.65 (m, 5H), 1.78-1.86 (m, 1H), 3.47 (ddd, *J* = 4.8, 5.2, 11.2 Hz, 1H), 3.83 (ddd, *J* = 2.8, 8.4, 11.2 Hz, 1H), 4.45 (d, *J* = 12.0 Hz, 1H), 4.53 (t, *J* = 3.6 Hz, 1H), 4.70 (d, *J* = 12.0 Hz, 1H), 6.99-7.04 (m, 4H), 7.10 (d, *J* = 7.6 Hz, 4H), 7.22-7.33 (m, 7H), 7.40 (dd, *J* = 7.2, 7.6 Hz, 1H), 7.50 (d, *J* = 8.0 Hz, 1H), 7.55 (d, *J* = 7.2 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ -0.87, -0.69, 19.4, 25.6, 30.6, 62.0, 68.8, 97.9, 122.5, 123.1, 124.7, 126.9, 128.4, 129.3, 129.6, 131.4, 135.0, 135.5, 136.4, 144.2, 147.6, 148.6. IR (neat) 3059, 2947, 2871, 2246, 1548, 1454, 1548, 1455, 1439, 1386, 1326, 1279, 1200, 1181, 1154, 1115, 1077, 1055, 1027, 976, 870, 834, 774, 697, 665, 637, 621, 525, 500, 488, 480, 473, 465, 417, 406 cm^{-1}. HRMS calcd for $C_{32}H_{35}NNaO_2Si$ (M + Na) 516.2335, found 516.2329.

3,5-Xylyl[2-(2-tetrahydropyranyloxymethyl)phenyl]dimethylsilane (3e). A yellow



oil. R_f 0.17 (hexane–ethyl acetate = 20 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.568 (s, 3H), 0.572 (s, 3H), 1.43-1.67 (m, 5H), 1.75-1.85 (m, 1H), 2.28 (s, 6H), 3.41-3.43 (m, 1H), 3.75-3.80 (m, 1H), 4.39 (d, *J* = 12.0 Hz, 1H), 4.46 (s, 1H), 4.67 (d, *J* = 12.0 Hz, 1H), 6.99 (s, 1H), 7.10 (s, 2H), 7.28 (dd, *J* = 7.2, 7.6 Hz, 1H), 7.40 (dd, *J* = 7.6, 7.6 Hz, 1H), 7.48-7.54 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ -0.90, -0.75, 19.5, 21.5, 25.6, 30.6, 62.1, 69.0, 98.0, 126.9, 128.6, 129.7, 130.9, 131.9, 135.6, 136.6, 137.2, 138.6, 144.3. IR (neat) 3055, 3013, 2923, 2870, 1592, 1466, 1454, 1439, 1401, 1350, 1322, 1258, 1249, 1200, 1182, 1138, 1127, 1118, 1078, 1055, 1027, 976, 906, 864, 830, 817, 799, 774, 754, 697, 651, 482, 463, 453, 447, 435, 421, 412, 407 cm^{-1}. MS (EI, 70 eV) *m/z* (%) 339 (M^+ - CH_3, 0.3), 255 (40), 253 (27), 237 (35), 165 (11), 164 (11), 163 (56), 149 (55), 85 (100), 67 (10), 55 (11). HRMS calcd for $C_{22}H_{30}NaO_2Si$ (M + Na) 377.1913, found 377.1916.

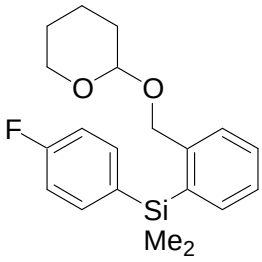
Phenyl[2-(2-tetrahydropyranyloxymethyl)phenyl]dimethylsilane (3f). A colorless



oil. R_f 0.46 (hexane–ethyl acetate = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.588 (s, 3H), 0.593 (s, 3H), 1.43-1.64 (m, 5H), 1.77-1.80 (m, 1H), 3.40 (ddd, *J* = 4.8, 5.6, 11.2 Hz, 1H), 3.75 (ddd, *J* = 4.0, 8.4, 11.2 Hz, 1H), 4.38 (d, *J* = 12.0 Hz, 1H), 4.44 (t, *J* = 3.2 Hz, 1H), 4.65 (d, *J* = 12.0 Hz, 1H), 7.25-7.35 (m, 4H), 7.39-7.42 (m, 1H),

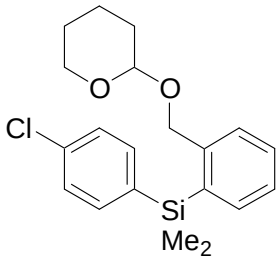
7.47-7.50 (m, 3H), 7.53 (d, *J* = 7.2 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ -0.98, -0.85, 19.4, 25.5, 30.6, 62.0, 68.9, 97.9, 126.9, 127.9, 128.6, 129.1, 129.8, 134.1, 135.6, 136.2, 139.0, 144.3. IR (neat) 3051, 2946, 1428, 1349, 1257, 1200, 1116, 1078, 1026, 906, 835, 816, 776, 731, 701, 499, 484, 473, 467, 459, 450, 438, 430, 414, 406 cm^{-1}. MS (EI, 70 eV) *m/z* (%) 325 (M^+ - H, 0.004), 227 (22), 225 (22), 210 (15), 209 (16), 173 (36), 165 (28), 164 (13), 149 (26), 135 (11), 105 (11), 85 (100), 55 (13). HRMS calcd for $C_{20}H_{26}NaO_2Si$ (M + Na) 349.1600, found 349.1597.

4-Fluorophenyl[2-(2-tetrahydropyranyloxymethyl)phenyl]dimethylsilane (3g). A



colorless oil. R_f 0.43 (hexane–ethyl acetate = 10 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.579 (s, 3H), 0.584 (s, 3H), 1.46-1.66 (m, 5H), 1.74-1.80 (m, 1H), 3.41 (ddd, *J* = 4.8, 5.6, 11.2 Hz, 1H), 3.75 (ddd, *J* = 4.8, 7.2, 11.2 Hz, 1H), 4.35 (d, *J* = 12.0 Hz, 1H), 4.45 (t, *J* = 3.2 Hz, 1H), 4.64 (d, *J* = 12.0 Hz, 1H), 7.02 (ddt, *J* = 2.0, 8.8, 9.2 Hz, 2H), 7.29 (ddt, *J* = 1.2, 7.2, 7.6 Hz, 1H), 7.40-7.47 (m, 3H), 7.49 (d, *J* = 7.6 Hz, 1H), 7.52 (dd, *J* = 1.6, 7.2 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ -0.83, -0.72, 19.4, 25.5, 30.6, 62.1, 68.8, 98.0, 115.1 (d, *J* = 19.3 Hz), 127.0, 128.7, 129.9, 134.5 (d, *J* = 3.7 Hz), 135.6, 135.9, 136.1 (d, *J* = 7.4 Hz), 144.3, 163.8 (d, *J* = 247 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -112.2-112.1 (m, 1F). IR (neat) 3058, 2948, 2871, 1588, 1498, 1439, 1407, 1387, 1350, 1261, 1231, 1201, 1183, 1119, 1103, 1078, 1955, 1027, 975, 906, 870, 825, 813, 776, 756, 825, 659, 516, 500, 494, 484, 472, 456, 445, 439, 423, 409 cm^{-1}. MS (EI, 70 eV) *m/z* (%) 329 (M^+ - CH_3, 0.1), 277 (38), 254 (21), 165 (43), 164(17), 163 (32), 149 (51), 96 (21), 91 (14), 85 (100), 84 (16) , 79 (16), 77 (20), 55 (20). HRMS calcd for $C_{20}H_{25}FNaO_2Si$ (M + Na) 367.1506, found 367.1488.

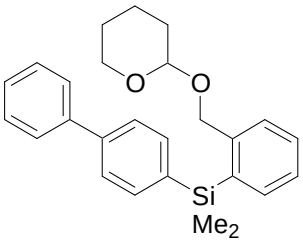
4-Chlorophenyl[2-(2-tetrahydropyranyloxymethyl)phenyl]dimethylsilane (3h). A



yellow oil. R_f 0.15 (hexane–ethyl acetate = 10 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.58 (s, 6H), 1.46-1.66 (m, 5H), 1.73-1.81 (m, 1H), 3.41 (ddd, *J* = 4.4, 5.6, 11.2 Hz, 1H), 3.74 (ddd, *J* = 2.0, 7.6, 11.2 Hz, 1H), 4.35 (d, *J* = 12.0 Hz, 1H), 4.44 (s, 1H), 4.64 (d, *J* = 12.0 Hz, 1H), 7.27-7.31 (m, 3H), 7.39-7.44 (m, 3H), 7.49 (d, *J* = 7.2 Hz, 1H), 7.52 (d, *J* = 7.6 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ -0.98, -0.87, 19.4, 25.5, 30.6, 62.1, 68.8, 98.0, 127.0, 128.2, 130.0, 135.4, 135.5, 135.6, 135.7, 137.5, 144.2. IR (neat) 3056, 2945, 1577, 1484, 1381, 1349, 1257, 1200, 1119, 1084, 1026, 809, 453, 451, 444, 439, 434 cm^{-1}. MS (EI, 70 eV)

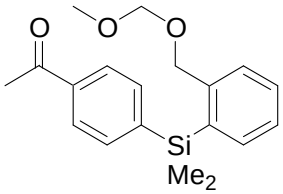
m/z (%) 345 (M^+ - CH_3, 0.04), 234 (11), 165 (16), 149 (15), 85 (100), 84 (16), 57 (10), 55 (25). HRMS calcd for $C_{21}H_{25}ClNaO_2Si$ (M + Na) 383.1210, found 383.1220.

Biphen-4-yl[2-(2-tetrahydropyranyloxymethyl)phenyl]dimethylsilane (3i). A



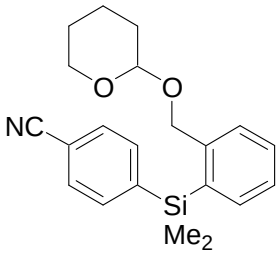
colorless oil. R_f 0.42 (hexane–ethyl acetate = 10 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.62 (s, 3H), 0.63 (s, 3H), 1.43-1.64 (m, 5H), 1.72-1.81 (m, 1H), 3.40 (ddd, *J* = 4.8, 5.2, 11.2 Hz, 1H), 3.74 (ddd, *J* = 2.8, 8.4, 11.2 Hz, 1H), 4.42 (d, *J* = 12.0 Hz, 1H), 4.45 (t, *J* = 3.6 Hz, 1H), 4.79 (d, *J* = 12.0 Hz, 1H), 7.31 (ddd, *J* = 1.2, 7.6, 7.6 Hz, 1H), 7.35 (tt, *J* = 2.0, 7.6 Hz, 1H), 7.41-7.46 (m, 3H), 7.50 (d, *J* = 7.6 Hz, 1H), 7.56-7.60 (m, 7H); ^{13}C NMR (101 MHz, $CDCl_3$) δ -0.90, -0.78, 19.4, 25.5, 30.6, 62.1, 68.9, 98.0, 126.6, 127.0, 127.2, 127.5, 128.8, 128.9, 129.8, 134.6, 135.6, 136.2, 137.8, 141.2, 141.8, 144.3. IR (neat) 3057, 3013, 2948, 2871, 1597, 1484, 1439, 1385, 1484, 1439, 1385, 1254, 1200, 1182, 1153, 1117, 1077, 1182, 1026, 975, 906, 870, 815, 776, 756, 697, 664, 636, 553, 516, 506, 498, 486, 468, 454, 438, 428 cm^{-1}. MS (EI, 70 eV) *m/z* (%) 387 (M^+ - CH_3, 0.4), 304 (21), 303 (79), 287 (14), 286 (81), 241 (18), 165 (15), 164 (31), 163 (55), 154 (22), 153 (19), 149 (62), 85 (100), 55 (15). HRMS calcd for $C_{26}H_{30}NaO_2Si$ (M + Na) 425.1913, found 425.1894.

4-Acetylphenyl[(2-methoxymethoxymethyl)phenyl]dimethylsilane (6j). A yellow oil.



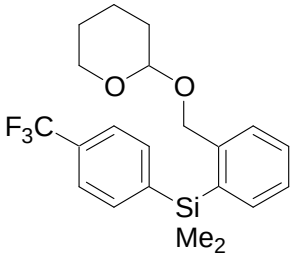
R_f 0.23 (hexane– ethyl acetate = 10 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.62 (s, 6H), 2.60 (s, 3H), 3.27 (s, 3H), 4.40 (s, 2H), 4.46 (s, 2H), 7.32 (ddd, *J* = 2.0, 6.8, 7.2 Hz, 1H), 7.41-7.47 (m, 2H), 7.55 (d, *J* = 8.0 Hz, 1H), 7.59 (d, *J* = 8.0 Hz, 2H), 7.70 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ -1.06, 26.8, 55.5, 69.3, 95.7, 127.3, 127.4, 128.9, 130.1, 134.3, 135.4, 135.7, 137.4, 143.7, 146.0, 198.5. IR (neat) 3055, 2925, 2853, 1726, 1685, 1594, 1549, 1436, 1388, 1357, 1258, 1209, 1149, 1106, 1105, 1042, 957, 920, 814, 778, 756, 690, 657, 607, 514, 493, 446 cm^{-1}. MS (EI, 70 eV) *m/z* (%) 313 (M^+ - CH_3, 22), 283 (16), 267 (38), 251 (39), 251 (98), 209 (22), 179 (39), 163 (100), 149 (37), 133 (22), 119 (8), 105 (13), 91 (9). HRMS calcd for $C_{19}H_{24}NaO_3Si$ (M + Na) 351.1392, found 351.1386

4-Cyanophenyl[2-(2-tetrahydropyranyloxymethyl)phenyl]dimethylsilane (3k). A



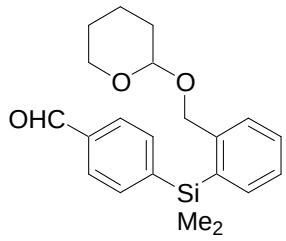
yellow oil. R_f 0.23 (hexane–ethyl acetate = 10 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.611 (s, 3H), 0.612 (s, 3H), 1.44-1.63 (m, 5H), 1.68-1.77 (m, 1H), 3.41 (ddd, *J* = 4.4, 5.2, 11.2 Hz, 1H), 3.72 (ddd, *J* = 2.8, 8.4, 11.2 Hz, 1H), 4.32 (d, *J* = 12.0 Hz, 1H), 4.43 (t, *J* = 2.8 Hz, 1H), 4.62 (d, *J* = 12.0 Hz, 1H), 7.31 (dt, *J* = 1.2, 7.6 Hz, 1H), 7.44 (dt, *J* = 1.2, 7.6 Hz, 1H), 7.49 (d, *J* = 7.6 Hz, 1H), 7.52 (d, *J* = 7.6 Hz, 1H), 7.58 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ -1.23, -1.12, 19.4, 25.4, 30.5, 62.1, 68.8, 97.9, 112.6, 119.1, 127.2, 129.0, 130.2, 131.1, 134.57, 134.61, 135.6, 144.2, 146.3. IR (neat) 2945, 2870, 2227, 1744, 1466, 1454, 1439, 1386, 1350, 1260, 1201, 1182,1119, 1078, 1028, 974, 906, 870, 837, 826, 816, 778, 758, 689, 655, 554, 518, 507, 499, 448, 445, 427, 409 cm^{-1}. MS (EI, 70 eV) *m/z* (%) 351 (M^+, 0.1), 250 (89), 234 (100), 220 (9), 206 (6), 190 (11), 165 (25), 163 (28), 149 (15), 85 (87), 55 (14). HRMS calcd for $C_{21}H_{25}NaNO_2Si$ (M + Na) 374.1552, found 374.1548.

4-Trifluoromethylphenyl[2-(2-tetrahydropyranyloxy)methylphenyl]dimethylsilane



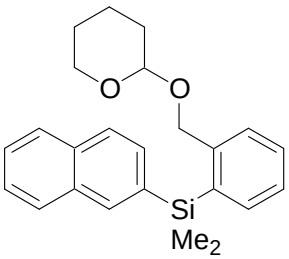
(3l). A yellow oil R_f 0.41 (hexane–ethyl acetate = 10 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.61 (s, 3H), 0.62 (s, 3H), 1.39-1.62 (m, 5H), 1.69-1.80 (m, 1H), 3.38 (ddd, *J* = 4.8, 5.2, 11.2 Hz, 1H), 3.74 (ddd, *J* = 2.8, 8.4, 11.2 Hz, 1H), 4.33 (d, *J* = 11.6 Hz, 1H), 4.41 (t, *J* = 3.2 Hz, 1H), 4.63 (d, *J* = 11.6 Hz, 1H), 7.31 (ddd, *J* = 1.2, 7.6, 7.6 Hz, 1H), 7.43 (ddd, *J* = 1.2, 7.2, 7.6 Hz, 1H), 7.49 (dd, *J* = 1.2, 7.6 Hz, 1H), 7.53 (dd, *J* = 1.2, 7.2 Hz, 1H), 7.56 (d, *J* = 8.8 Hz, 2H), 7.60 (d, *J* = 8.8 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ -1.11, -1.01, 19.4, 25.5, 30.5, 62.1, 68.8, 97.9, 124.35 (q, *J* = 274 Hz), 124.42 (q, *J* = 3.73 Hz), 127.2, 129.0, 130.1, 131.0 (q, *J* = 32.3 Hz), 134.4, 135.2, 135.6, 144.2, 144.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.9 (s, 3F). IR (neat) 2943, 1439, 1401, 1386, 1349, 1324, 1401, 1386, 1349, 1324, 1285, 1255, 1251, 1201, 1182, 1155, 1126, 1201, 1182, 1155, 1032, 977, 906, 870, 834, 817, 793, 749, 687, 667, 652, 639, 609, 546, 535, 520, 509, 496, 484, 479, 466, 449, 433, 417, 407 cm^{-1}. MS (EI, 70 eV) *m/z* (%) 394 (M^+, 0.04), 293 (19), 277 (24), 215 (21), 196 (18), 165 (26), 163 (23), 149 (15), 137 (9), 127 (9), 85 (100), 55 (17). HRMS calcd for $C_{21}H_{25}F_3NaO_2Si$ (M + Na) 417.1474, found 417.1474.

4-Formylphenyl[2-(2-tetrahydropyranyloxymethyl)phenyl]dimethylsilane (3m). A



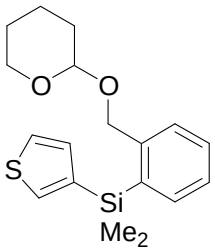
colorless oil. R_f 0.17 (hexane–ethyl acetate = 10 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.626 (s, 3H), 0.633 (s, 3H), 1.41-1.62 (m, 5H), 1.70-1.79 (m, 1H), 3.39 (ddd, *J* = 5.2, 5.6, 11.2 Hz, 1H), 3.72 (ddd, *J* = 2.0, 8.8, 11.2 Hz, 1H), 4.33 (d, *J* = 12.0 Hz, 1H), 4.43 (t, *J* = 2.6 Hz, 1H), 4.63 (d, *J* = 12.0 Hz, 1H), 7.31 (ddd, *J* = 1.6, 7.2, 7.6 Hz, 1H), 7.44 (ddd, *J* = 1.6, 7.2, 7.6 Hz, 1H), 7.49 (dd, *J* = 0.8, 8.0 Hz, 1H), 7.53 (dd, *J* = 0.8, 8.0 Hz, 1H), 7.66 (d, *J* = 8.0 Hz, 2H), 7.82 (d, *J* = 8.0 Hz, 2H), 10.0 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ -1.15, -1.02, 19.4, 25.5, 30.5, 62.1, 68.8, 97.9, 127.1, 128.8, 128.9, 130.1, 134.6, 135.1, 135.6, 136.6, 144.2, 148.0, 192.7. IR (neat) 2951, 2851, 1704, 1596, 1557, 1496, 1466, 1455, 1430, 1384, 1351, 1322, 1310, 1284, 1259, 1211, 1202, 1174, 1153, 1127, 1119, 1100, 1078, 1055, 1026, 975, 906, 870, 834, 807, 777, 756, 717, 694, 489, 458 cm^{-1}. MS (EI, 70 eV) *m/z* (%) 339 (M^+ - CH_3, 0.4), 238 (13), 227 (18), 209 (17), 165 (10), 164 (23), 163 (13), 149 (59), 85 (100), 84 (18), 57 (21), 55 (30). HRMS calcd for $C_{21}H_{26}NaO_3Si$ (M + Na) 377.1549, found 377.1556.

2-Naphthyl[2-(2-tetrahydropyranyloxymethyl)phenyl]dimethylsilane (3n). A yellow



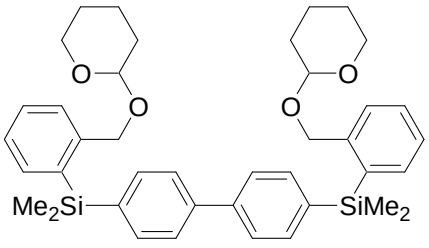
oil. R_f 0.16 (hexane–ethyl acetate = 20 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.668 (s, 3H), 0.672 (s, 3H), 1.35-1.55 (m, 5H), 1.67-1.76 (m, 1H), 3.27 (ddd, *J* = 5.2, 5.2, 11.2 Hz, 1H), 3.64 (ddd, *J* = 3.2, 8.4, 11.2 Hz, 1H), 4.36 (t, *J* = 3.6 Hz, 1H), 4.39 (d, *J* = 12.0 Hz, 1H), 4.67 (d, *J* = 12.0 Hz, 1H), 7.30 (ddd, *J* = 1.6, 7.2, 7.6 Hz, 1H), 7.42 (ddd, *J* = 1.6, 7.6, 7.6 Hz, 1H), 7.49-7.51 (m, 3H), 7.54 (dd, *J* = 0.8, 8.0 Hz, 1H), 7.57 (dd, *J* = 1.2, 7.6 Hz, 1H), 7.78-7.82 (m, 3H), 8.00 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ -0.89, -0.79, 19.4, 25.5, 30.5, 62.1, 68.9, 98.0, 126.0, 126.5, 127.0, 127.2, 127.8, 128.2, 128.8, 129.9, 130.4, 133.1, 133.8, 134.0, 135.7, 136.3, 136.5, 144.4. IR (neat) 3052, 2948, 2870, 2795, 2740, 2657, 1927, 1821, 1804, 1738, 1626, 1590, 1566, 1498, 1465, 1454, 1439, 1385, 1350, 1324, 1257, 1200, 1182, 1153, 1119, 1081, 1023, 975, 905, 869, 855, 833, 808, 777, 753, 688, 659, 631, 448, 472, 465, 454, 448, 436, 420, 414 cm^{-1}. MS (EI, 70 eV) *m/z* (%) 361 (M^+ - CH_3, 0.6), 277 (33), 259 (30), 215 (24), 163 (22), 149 (91), 128 (100), 85 (69), 67 (8), 55 (36). HRMS calcd for $C_{24}H_{28}NaO_2Si$ (M + Na) 399.1756, found 399.1739.

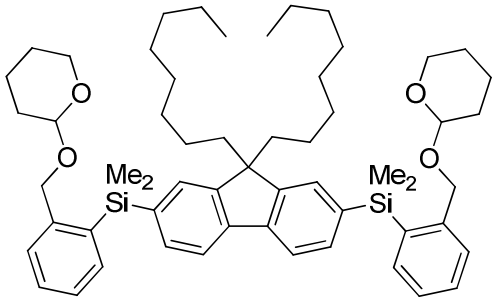
3-Thienyl[2-(2-tetrahydropyranyloxymethyl)phenyl]dimethylsilane (3o). A yellow oil. R_f 0.39 (hexane–ethyl acetate = 10 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.59 (s, 3H), 0.60 (s, 3H), 1.46-1.70 (m, 5H), 1.77-1.87 (m, 1H), 3.46 (ddd, *J* = 4.0, 5.2, 11.2 Hz, 1H), 3.81 (ddd, *J* = 3.2, 8.4, 11.2 Hz, 1H), 4.42 (d, *J* = 12.0 Hz, 1H), 4.50 (t, *J* = 3.6 Hz, 1H), 4.70 (d, *J* = 12.0 Hz, 1H), 7.15 (dd, *J* = 1.2, 4.4 Hz, 1H), 7.27 (ddd, *J* = 1.6, 7.2, 7.6 Hz, 1H), 7.39 (ddd, *J* = 0.8, 4.8, 4.8 Hz, 1H), 7.40 (ddd, *J* = 1.6, 7.2, 7.6 Hz, 1H), 7.45 (dd, *J* = 0.8, 2.4 Hz, 1H), 7.48-7.50 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ -0.37, -0.28, 19.5, 25.6, 30.6, 62.2, 68.8, 98.0, 125.9, 127.0, 128.6, 129.8, 132.1, 132.8, 135.4, 136.4, 139.6, 144.2. IR (neat) 3056, 2942, 1590, 1438, 1349, 1251, 1200, 1119, 1078, 1032, 900, 823, 772, 688, 496, 484, 479, 473, 459, 452, 449 cm^{-1}. MS (EI, 70 eV) *m/z* (%) 332 (M^+, 0.04), 233 (17), 231 (18), 215(50), 163(54), 149(43) 141(21), 84(19), 85(100), 57(17), 55(12). HRMS calcd for $C_{18}H_{24}NaSO_2Si$ (M + Na) 355.1164, found 355.1154.



Cross-coupling of dibromoarene 9 with 1_{THP}. ***A general procedure.*** Dibromoarene (0.50 mmol), disilane (1.1 mmol) and K_2CO_3 (2.2 mmol) were added sequentially to a solution of $[Pd(allyl)Cl]_2$ (0.025 mol), ligand (0.10 mol) and CuI (0.10 mol) in 1,4-dioxane and NMP (4:1, 2.75 mL) prepared in a 3 mL-vial in a dry box. The vial was closed with a screw cap, taken outside the dry box, and heated at 100 °C for 48 h. The resultant mixture was filtered through Celite, and the filtrate was evaporated and dried *in vacuo*. The desired products were obtained by Preparative TLC and HPLC.

4,4'-Bis[2-{(2-tetrahydropyranyloxy)methyl}phenyldimethylsilyl]biphenyl (10a). A yellow oil. R_f 0.20 (hexane–ethyl acetate = 10 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.617 (s, 6H), 0.623 (s, 6H), 1.40-1.64 (m, 10H), 1.72-1.81 (m, 2H), 3.40 (ddd, *J* = 1.6, 5.2, 11.2 Hz, 2H), 3.74 (ddd, *J* = 3.2, 8.4, 11.2 Hz, 2H), 4.41 (d, *J* = 12.0 Hz, 2H), 4.45 (t, *J* = 3.2 Hz, 2H), 4.69 (d, *J* = 12.0 Hz, 2H), 7.30 (ddd, *J* = 1.2, 7.2, 7.2 Hz, 2H), 7.42 (ddd, *J* = 1.2, 7.2, 8.0 Hz, 2H), 7.50 (dd, *J* = 0.8, 8.0 Hz, 2H), 7.55-7.58 (m, 10H); ^{13}C NMR (101 MHz, $CDCl_3$) δ -0.93, -0.81, 19.4, 25.5, 30.5, 62.0, 68.9, 97.9, 126.6, 127.0, 128.7, 129.8, 134.6, 135.6, 136.1, 137.9, 141.6, 144.2. IR (neat) 3057, 3014, 2946, 2246, 1922, 1594, 1439, 1384, 1350, 1322, 1256, 1182, 1116, 1078, 1026, 907, 870, 835, 815, 775, 756, 733, 699, 645, 524, 493 cm^{-1}. HRMS calcd for $C_{40}H_{50}NaO_4Si_2$ (M + Na) 673.3145, found 673.3165.



3,7-Bis[2-{(2-tetrahydropyranyloxy)methyl}phenyldimethylsilyl]-9,9-dioctyl-9*H*-fluorene (10b). 

A yellow oil. R_f 0.22 (hexane–ethyl acetate = 10 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.64 (s, 12H), 0.83 (t, *J* = 7.2 Hz, 6H), 0.997-1.23 (m, 20H), 1.45-1.65 (m, 14H), 1.81-1.89 (m, 6H), 3.44 (ddd, *J* = 4.4, 5.2, 11.2 Hz, 2H), 3.80 (ddd, *J* = 2.8, 8.4, 11.2 Hz, 1H), 4.42 (d, *J* = 12.0 Hz, 2H), 4.51 (t, *J* = 3.2 Hz, 2H), 4.68 (d, *J* = 12.0 Hz, 2H), 7.23 (d, *J* = 8.0 Hz, 2H), 7.40 (dd, *J* = 7.2, 7.6 Hz, 2H), 7.44-7.50 (m, 8H), 7.67 (d, *J* = 7.6 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ -0.76, -0.67, 14.3, 19.4, 22.8, 25.6, 29.3, 29.4, 30.1, 30.6, 31.9, 40.1, 55.0, 62.0, 68.9, 97.9, 119.4, 126.9, 128.5, 128.7, 129.6, 132.8, 135.8, 136.9, 137.7, 142.0, 144.3, 150.3. IR (neat) 3054, 2026, 2853, 1730, 1591, 1462, 1440, 1396, 1385, 1350, 1322, 1259, 1250, 1200, 1182, 1119, 1090, 906, 870, 832, 814, 752, 668, 498, 491, 482, 472, 461, 454, 434 cm^{-1}. HRMS calcd for $C_{57}H_{82}NaO_4Si_2$ (M + Na) 909.5649, found 909.5631.

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Chapter 3
Polyarylene Synthesis by Cross-Coupling Reaction with HOMSi Reagents

Cross-coupling reaction of diboromoarenes with HOMSi-reagents (namely, organo(2-hydroxymethylphenyl)dimethylsilanes), or alternatively, bromoarenes with arylene-bisHOMSi reagents, proceeds smoothly in the presence of a Pd catalyst and a weak base, and ter- or quarterarenes are produced in excellent yields. The present reaction is successfully applied to the polyarylene synthesis using a 2,7-fluorenylene-bisHOMSi reagent along 4,7-dibromobenzothiadiazole or a 2,7-dibromofluorene derivative.

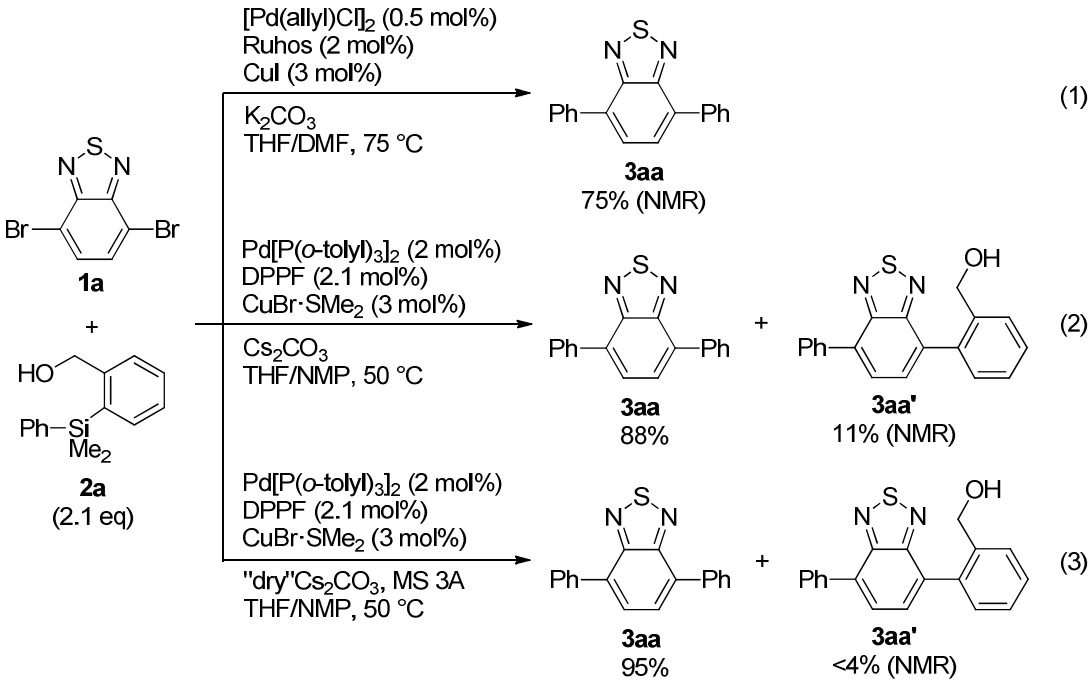
3.1 Introduction

Polymers containing conjugated π-electron systems play key roles in many electronic organic materials such as sensors, semiconductors, photovoltaic cells (PVC), field-effect transistors (FET), and optical devices (e.g., organic light-emitting diodes).[1] Thus invention of efficient synthetic methods for π-conjugated polymers has grown to be an important issue in synthetic organic chemistry. Metal catalyzed cross-coupling reaction of dihaloarenes with organobimetallic reagents is a powerful tool to synthesize polyarylenes straightforwardly.[2,3] In order to obtain high-molecular-weight polymers, use of highly reactive cross-coupling reaction is essential. To this end, the Suzuki-Miyaura coupling is extensively employed so far. However, the polymer synthesis is often accompanied by more than trace contaminant formation attributed mainly to the boron reagents.[4,5] In this sense, organosilicon-based cross-coupling is considered to be advantageous. In particular, recently invented aryl-HOMSi reagents, smoothly cross-couple with a range of haloarenes to give the corresponding biaryls in the presence of a Pd catalyst and weak base in preference to the coupling active groups like boryl and stannyl groups.[6,7] Thus, it is reasonable to apply the HOMSi-based cross-coupling to simultaneous multiple bond forming reactions and polymer synthesis. Herein the author describes that the Pd catalyzed cross-coupling reaction of dihaloarenes with HOMSi reagents, or haloarenes with arylene-bisHOMSi reagents, work well to give ter- to quinuquaryl derivatives. The cross-coupling reaction is finally shown to be applicable to polyarylene synthesis.

3.2 Results and Discussions

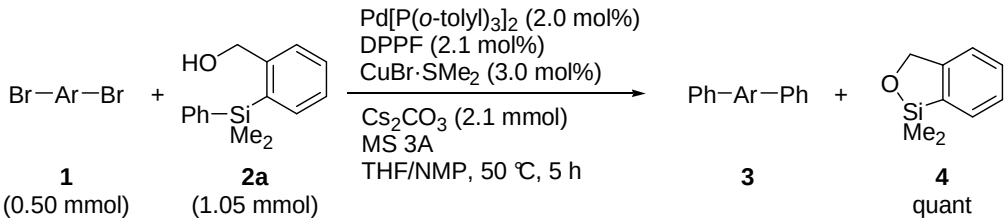
It is well recognized that the polymer synthesis by the cross-coupling reaction requests a careful design of a catalyst system including ligand and base in addition to stoichimetic ratio of dihaloarenes and organobimetalic reagents for the preparation of high-molecular-weight polymers. In this regard, HOMSi reagents have advantages of easy handing and purification as well as cyclic silyl ether formation. On the other hand, for a single carbon-carbon bond formation, HOMSi reagents are generally used slightly in excess.[6] Thus, the author started his research by scrutinizing the cross-coupling conditions for the stoichiometric coupling of 4,7-dibromobenzothiadiazole **1a** with phenyl-HOMSi reagent **2a**. Hiyama and Nakao employed $[Pd(allyl)Cl]_2$/Ruphos/CuI catalyst systems for the reaction of **1a** with 2.1 eq of **2a**. The reaction gave **3aa** in 75% yield, a level of unstisfaction (Eq 1). After screening various parameters of reaction conditions, the author found that $Pd[P(o\text{-tolyl})_3]_2$/DPPF/CuBr·$SMe_2$ catalyst system is more efficient for the reaction, giving **3aa** in 88% yield (Eq 2). However, the reaction produced

byproduct **3aa',** a product derived from the cross-coupling of 2-hydroxymethylphenyl group on the HOMSi reagent. The author envisaged that a part of the Ph-HOMSi reagent might have decomposed by a small amout of concominat water to produce 2-hydroxymethyldimethylsilanol[8], which cross-coupled with the aryl bromide to givie **3aa'**. Thus, he dried Cs_2CO_3 thoroghly with vacuum oven and added molecular sives 3A in the reaction mixture (Eq 3). Yield of **3aa** was much improved; **3aa'** formation was almost suppressed. Based on these results, the author has concluded that use of **1a** and **2a** in a molar ratio of 1.0 : 2.1 with Pd[P(*o*-tolyl)$_3$]$_2$ (2.0 mol%), DPPF (2.1 mol%), CuBr·SMe$_2$ (3.0 mol%), Cs_2CO_3 (4.2 eq), MS 3A (200 mg/mmol) in THF/NMP at 50 °C is the optimal reaction conditions.

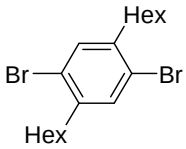
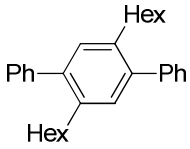
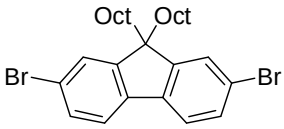
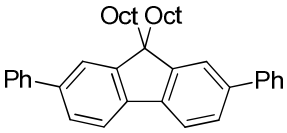
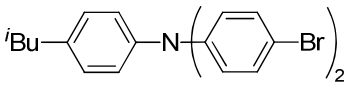
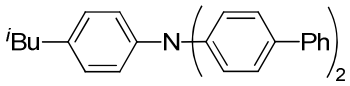
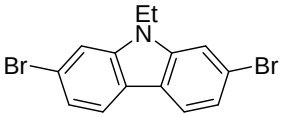
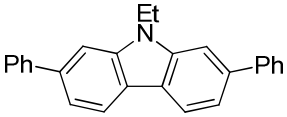
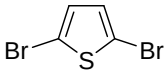
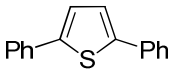


The scope of dibromoarenes **1** was proved broad enough as demonstrated in Table 1. Substituted aryl electrophiles such as 1,4-dibromo-2,5-dihexylbenzene (**1b**) and 2,7-dibromo-9,9'-dioctyl-fluorene (**1c**) gave the corresponding terphenyl and quarterphenyl derivatives (**3ba** and **3ca**) in 94% and 92% yields respectively (entries 1 and 2). Dibromo derivative of triarylamine **1d** reacted with **2a** to afford **3da** in a quantitative yield (entry 3). Dibromoheteroarenes **1e** and **1f** also underwent the phenyl coupling in excellent yields (entries 4 and 5).

Table 1. Cross-coupling reaction of dihaloarenes **1** with **2a**.[a]



1 (0.50 mmol) **2a** (1.05 mmol) **3** **4** quant

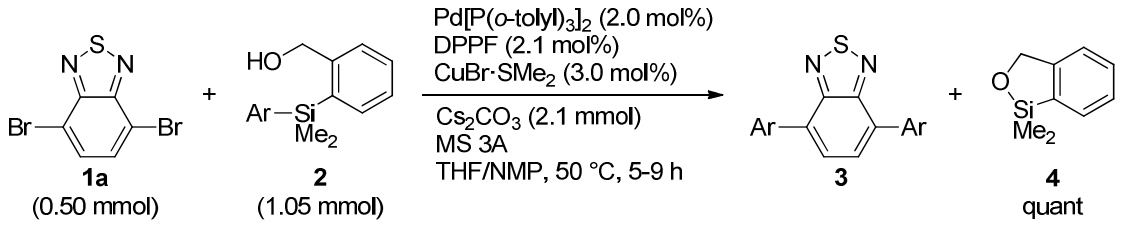
Entry	**1**		**3**		Yield (%)[b]
1		**1b**		**3ba**	94
2		**1c**		**3ca**	92
3		**1d**		**3da**	98
4		**1e**		**3ea**	90
5		**1f**		**3fa**	90

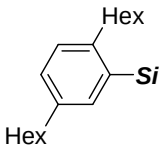
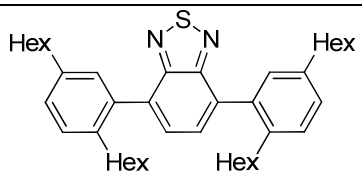
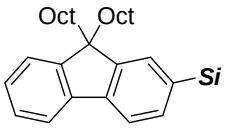
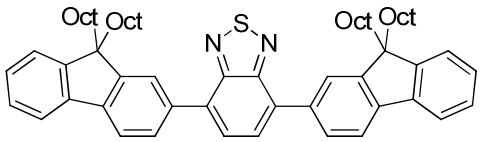
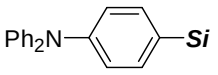
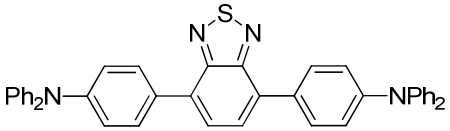
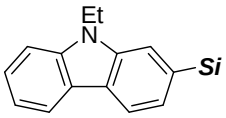
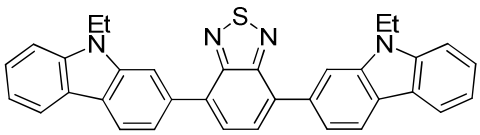
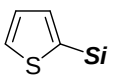
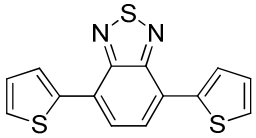
[a]Unless otherwise noted, a mixture of **1** (0.50 mmol), **2a** (1.05 mmol), Pd[P(*o*-tolyl)$_3$]$_2$ (0.010 mmol), DPPF (0.011 mmol), CuBr·SMe$_2$ (0.015 mmol), Cs_2CO_3 (2.10 mmol), MS 3A (100 mg), THF (0.75 mL) and NMP (0.25mL) was heated at 50 °C for 5 h. [b]Isolated yield. NMP = *N*-methyl-pyrrolidone.

Having succeeded in the cross-coupling of dibromoarenes with phenyl-HOMSi reagent **2a**, the author turned his attention to the reaction of other aryl and heteroaryl-HOMSi reagents (**2b**-**2f**) with 2,7-dibromobenzothiadiazole (**1a**) as a coupling partner.[9] As summarized in Table 2, the teraryl and quarteraryl synthesis proceeded without any problem. Perturbation by an *ortho* substituent is minimum (entry 1). When fluorenyl -HOMSi reagent **2c** was used, the corresponding quinquaryl derivative **3ac** was obtained in 87% yield (entry 2). Diphenylamino group did not hamper the reaction, but the isolated yield of **3ad** was slightly lower (entry 3). Heteroaryl groups such as 2-thienyl and

2-carbazoyl groups tolerated the coupling reaction conditions to give **3ae** and **3af** in 91% and 99% yields, respectively (entries 4 and 5). To the best of his knowledge, the cross-coupling reaction of 4,7-dibromobenzothiadiazole with a 2-thienylsilane reagent have never been performed before.

Table 2. Cross-coupling reaction of **1a** with **2**



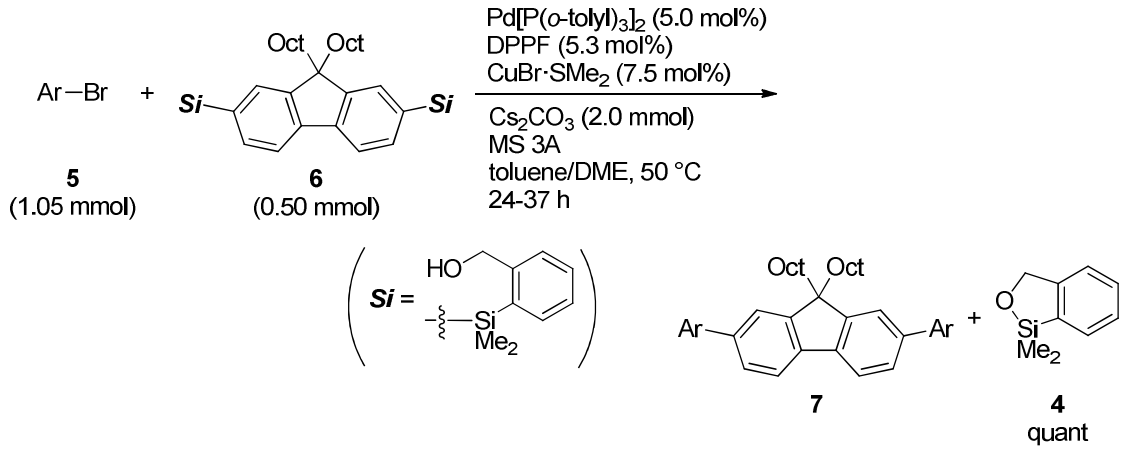
Entry	2		3		Yield (%)[b]
1		**2b**		**3ab**	99
2		**2c**		**3ac**	87
3		**2d**		**3ad**	76
4		**2e**		**3ae**	91
5		**2f**		**3af**	99

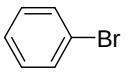
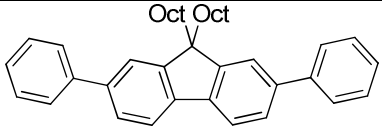
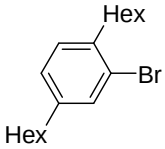
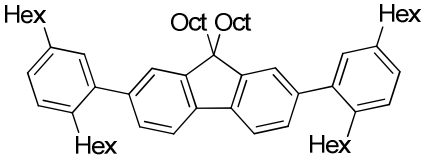
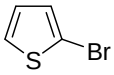
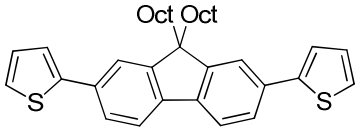
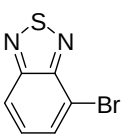
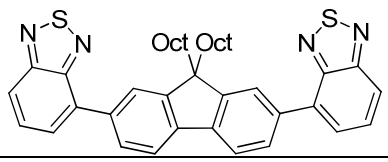
[a]Unless otherwise noted, a mixture of **1a** (0.50 mmol), **2** (1.05 mmol), Pd[P(*o*-tolyl)$_3$]$_2$ (0.010 mmol), DPPF (0.011 mmol), CuBr·SMe$_2$ (0.015 mmol), Cs_2CO_3 (2.1 mmol), MS 3A (100 mg), THF (0.75 mL) and NMP (0.25mL) was heated at 50 °C for 5-9 h. [b]Isolated yield.

The scope of the reaction of bromoarenes with a fluorenylene-bisHOMSi reagent **6**, as an organobimetallic coupling partner is summarized in Table 3. The reaction of **6** (0.50 mmol) with bromobenzene **5a** (1.05 mmol) proceeded smoothly in the presence of

$Pd[P(o\text{-tolyl})_3]_2$ (5 mol%), DPPF (5.3 mol%), $CuBr \cdot SMe_2$ (7.5 mol%), Cs_2CO_3 (4.0 equiv.) and MS 3A (200 mg/mmol) in toluene/DME at 50 ºC for 24 h to give **7a** (identical to **3ca**) in 91% yield (entry 1). Dihexyl substituents in bromobenzene **5b** did not seriously hamper the reaction to give the corresponding bisarylated fluorene (**7b**) in 72% yield (entry 2). Heteroaryl electrophiles also reacted with **6** to give the correspondingquateraryls **7c** and **7d** in good to excellent yields (entries 3 and 4).

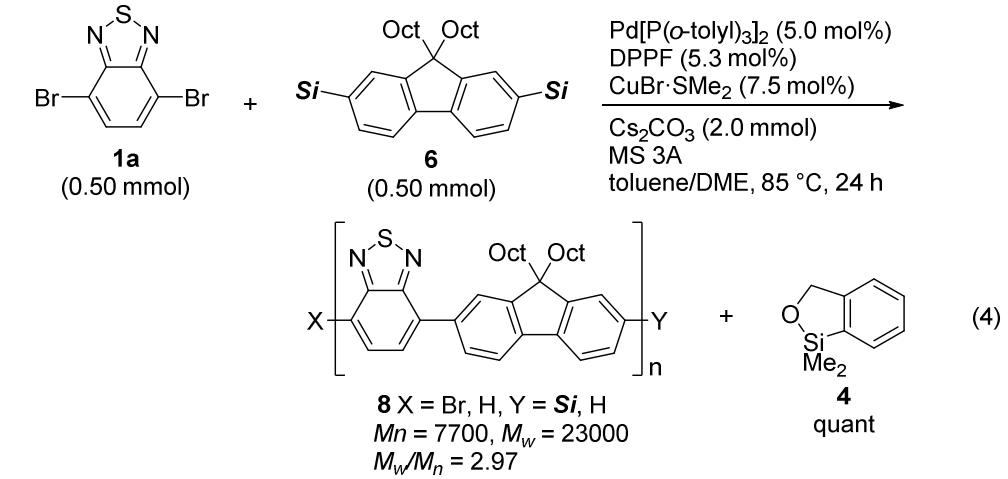
Table 3. Cross-coupling reaction of bromoarenes **5** with **6**.

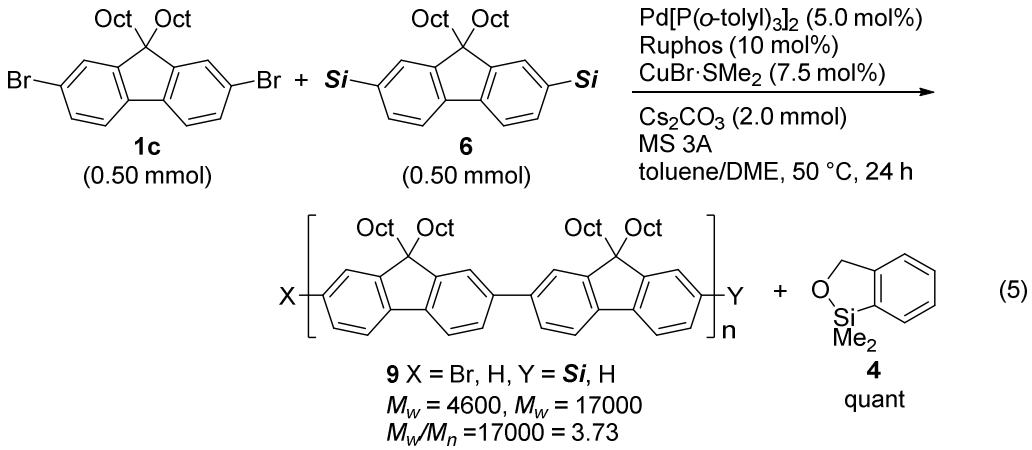


Entry	5		7		Yield (%)[b]
1		**5a**		**7a** (= **3ca**)	91
2		**5b**		**7b**	72
3		**5c**		**7c**	80
4[c]		**5d**		**7d**	94

[a]Unless otherwise noted, a mixture of **5** (1.05 mmol), **6** (0.50 mmol), $Pd[P(o\text{-tolyl})_3]_2$ (0.025 mmol), DPPF (0.026 mmol), $CuBr \cdot SMe_2$ (0.038 mmol), Cs_2CO_3 (2.0 mmol), MS 3A (100 mg), PhMe (0.75 mL) and DME (0.25mL) was heated at 50 °C. DME = 1,2-dimethoxyethane. [c]Reaction run on a 0.20 mmol scale.

Present cross-coupling reaction was applied to dibromoarenes **1** and fluorenylene-bisHOMSi reagent **6** to give the corresponding conjugated polyarylenes (Eq 4 and 5). Co-polymerization of **1a** and **6** in a strictly equimolar ratio under the optimized conditions proceeded smoothly to give poly(9,9-dioctylfluorene-*co*-benzothiadiazole) (F8BT) with Mw of 23000 (PDI 2.97) (Eq 2).[10] F8BT is attracting special interest as a photovoltaic and light-emitting materials.[11] 4,7-Dibromo-9,9'-dioctylfluorene **1c** also reacted with **6** to give a polyfluorene with Mw of 17000 (PDI 3.73) in almost quantitative yield (eq. 3).

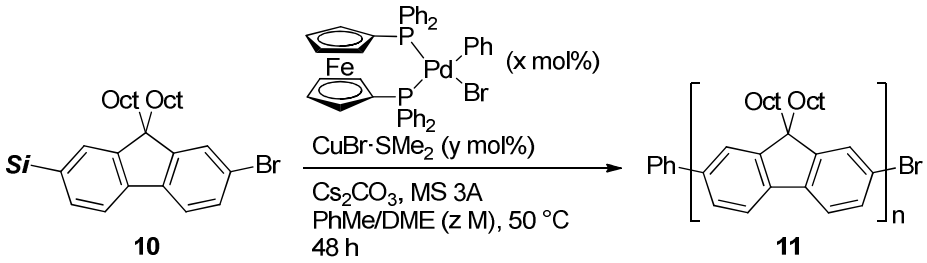




Co-polymerization of dihaloarelenes with bisHOMSi reagents resulted in broad PDI. For materials use, narrow PDI is suitable. Thus, the present cross-coupling reaction was examined whether the chain-growth polymerization takes place.[12] This polymerization method is demonstrated to give polymers with well controlled molecular weight and

narrow PDI. Polymerization of bromofluorenyl-HOMSi reagent **10** was carried out in the presence of (dppf)Pd(Ph)(Br)[13] and CuBr·SMe$_2$ as catalysts (Table 4). When **10** was polymerized in the presence of Pd catalyst (5 mol%), Cu catalyst (7.5 mol%), Cs_2CO_3 (2.0 eq), and MS 3A (200 mg/mol) in toluene/DME (1 M, 3/1) at 50 °C, the polymerization gave polymer **11** with relatively narrow PDI (1.78) (entry 1). Although, the polymerization diluted in a toluene/DME solution gave the desired polymer, PDI turned out to be 3.03 (entry 2). Perhaps, free palladium(0) species might have formed through reductive elimination of Ar-Pd-fluorene complex before participation in oxidative addition to C-Br bond of other monomer. As the cross-coupling reaction with aryl-HOMSi ragents is considerd to proceed via aryl copper intermediate, formation of aryl-copper species might be assumed to be slow. In addition, Ar-Pd-Br complex might undergo reductive elimination to form free Pd(0) and Ar-Br. Thus, the author repeated the polymerization using 50 mol% of Cu catalyst so as to form exess aryl-copper species. However, the copper so-catalyst was ineffective in the present polymerization (entries 3 and 4). In the presence of less amount of Pd and Cu catalysts, the reaction was extreamely slow (entry 5). According to these experimets, chain-growth polymerization

Table 4. Chain-growth polymerization of **10**



10 **11**

Entry	Pd complex (x mol%)	CuBr·SMe$_2$ (y mol%)	PhMe/DME (z M)	yield (%)	M_n	M_w	PDI
1	5.0	7.5	1	>99	4200	7600	1.78
2	5.0	7.5	0.5	98	4700	14000	3.03
3	5.0	50	1	46	5100	12700	2.49
4	5.0	50	2	45	4600	10100	2.19
5	1.0	1.5	1	43	600	7800	14.1

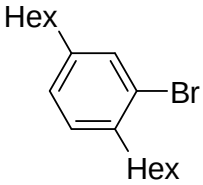
[a]Unless otherwise noted, a mixture of **10** (0.50 mmol), (dppf)Pd(Ph)(Br) (0.025 mmol), CuBr·SMe$_2$, Cs_2CO_3 (1.0 mmol), MS 3A (100 mg), PhMe/ DME (3/1) was heated at 50 °C for 48 h. DME = 1,2-dimethoxyethane.

dose not appear to proceed under the present conditions.

In summary, the author has demonstrated that HOMSi-based cross-coupling reaction is an efficient and straightforward strategy for simultaneous multiple cross-coupling and polymer synthesis. Double cross-coupling of dibromoarenes with HOMSi reagents proceeds smoothly to give ter- and quarter aryls in high yields. When the fluorenlene-bisHOMSi reagent is used in the reaction, various double arylated fluorenes are smoothly obtained. The present reaction is demonstrated to be applicable to synthesis of π-conjugated polymers for electron organic materials.

3.3 Experimetal

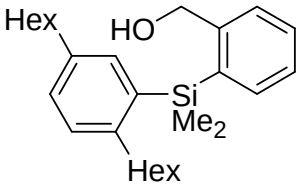
Preparation of 2,5-Dihexylbromobenzene (5b).



5b

To a solution of 2,5-dihexyl-1,4-dibromobenzene (**1b**) (1.5 g, 3.7 mmol) in THF (37 mL) was added a 2.69 M solution of *n*-BuLi in hexane (1.4 mL, 3.7 mmol) at -78 °C, and the mixture was stirred at -78 °C for 1 h, and then quenched with MeOH at -78 °C. The resulting mixture was added to H_2O at rt. The aqueous layer was extracted three times with Et_2O, and the combined organic extracts were dried over anhydrous $MgSO_4$. After concentration in vacuo, the residue was purified by flash column chromatography on silica gel to give **5b** (1.1 g, 89%) as a colorless oil. R_f 0.58 (hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.82-0.94 (m, 6H), 1.23-1.41 (m, 12H) 1.52-1.63 (m, 4H) 2.53 (t, *J* = 7.6 Hz, 2H), 2.67 (t, *J* = 8.0 Hz, 2H), 7.02 (dd, *J* = 1.6, 8.0 Hz, 1H), 7.10 (d, *J* = 7.6 Hz 1H), 7.34 (d, *J* = 1.8 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 14.24, 14.25, 22.7, 22.8, 29.1, 29.3, 30.2, 31.4, 31.8, 35.2, 35.9, 124.3, 127.6, 130.1, 132.6, 139.3, 142.5. One alkyl carbon signal is overlapping other signals. IR (neat) 2955, 2927, 2856, 1606, 1557, 1491, 1465, 1400, 1378, 1038, 882, 724, 674 cm^{-1}. MS (EI, 70 eV) *m/z* (%) 325 (M^+, 40), 254 (100), 175 (56), 170 (20), 115 (15), 104 (19), 91 (12).

Preparation of [(2,5-Dihexyl)phenyl][2-(hydroxymethyl)phe-nyl]dimethylsilane (2b). ***A general procedure for preparation of HOMSi reagents.***

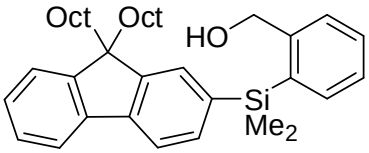


To a solution of 2,5-dihexylbromobenzene (1.3 g, 4.0 mmol) in THF (5 mL) was added a 1.65 M solution of *n*-BuLi in hexane (2.5 mL, 4.1 mmol) at -78 °C, and the mixture was stirred at -78 °C for 2 h. To this was added 1,1-dimethyl-2-oxa-1-silaindan (**4**, 1.3 g, 8.0 mmol). The resulting mixture was warmed slowly to rt and stirred for 17 h, and then quenched with H_2O at 0 °C. The aqueous layer was extracted thrice with Et_2O, and the combined organic layer was dried over anhydrous $MgSO_4$. After concentration in vacuo, the residue was purified by flash column chromatography on silica gel to give **2b** (1.3 g, 78%), as a colorless oil. R_f 0.45 (hexane-ethyl acetate = 10 :1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.62 (s, 6H), 0.82 (t, *J* = 7.4 Hz, 3H), 0.89 (t, *J* = 6.8 Hz, 3H), 0.97-1.40 (m, 15H), 1.55-1.65 (m, 2H), 2.35-2.41 (m, 2H), 2.58 (t, *J* = 8.0 Hz, 2H), 4.45 (d, *J* = 6.0 Hz, 2H), 7.08 (d, *J* = 7.6 Hz, 1H), 7.16 (dd, *J* = 1.6, 7.6 Hz, 1H), 7.27-7.34 (m, 1H), 7.36 (d, *J* = 2.0 Hz, 1H), 7.37-7.43 (m, 3H), 7.62 (d, *J* = 7.2 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 0.2, 14.2, 14.3, 22.7, 22.8, 29.2, 29.6, 31.7, 31.8, 31.9, 32.2, 35.8, 35.9, 65.4, 127.3, 128.4, 128.9, 129.9, 130.0, 134.8, 134.9, 136.4, 137.6, 139.9, 146.4, 146.6. IR (neat) 3375, 3001, 2955, 2927, 2856, 1477,

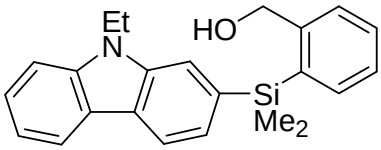
1466, 1436, 1396, 1378, 1255, 1250, 1199, 1146, 1125, 1077, 1029, 1012, 833, 813, 773, 754, 647 cm^{-1}. MS (EI, 70 eV) *m/z* (%) 395 (36), 293 (12), 246 (30), 175 (100), 149 (75), 105 (19), 91 (27). HRMS calcd for $C_{27}H_{42}NaOSi$ (M + Na) 433.2903, found 433.2904.

Other HOMSi reagents were prepared by the similar procedures.

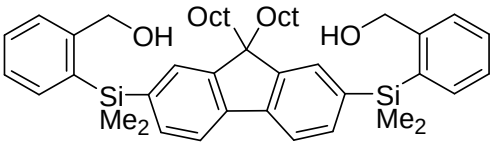
2-[(2-Hydroxymethylphenyl)dimethylsily]-9,9-dioctyl-9*H*-fluorene (2c). A colorless viscous oil. R_f 0.45 (hexane-ethyl acetate = 10 : 1). ^1H NMR (400 MHz, $CDCl_3$) δ 0.55-0.69 (m, 4H), 0.65 (s, 6H), 0.82 (t, *J* = 7.2 Hz, 6H), 0.97-1.29 (m, 21H), 1.87-1.98 (m, 4H), 4.53 (d, *J* = 5.6 Hz, 2H), 7.26-7.35 (m, 4H), 7.39-7.48 (m, 4H), 7.57 (d, *J* = 7.2 Hz, 1H), 7.66-7.73 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ -0.7, 14.2, 22.8, 23.9, 29.3, 30.1, 31.9, 40.3, 55.0, 55.2, 65.5, 119.5, 120.0, 123.0, 126.9, 127.1, 127.5, 128.3, 128.4, 130.0, 132.6, 135.8, 136.7, 137.4, 140.9, 142.4, 146.8, 150.4, 151.0. IR (neat) 3357, 3056, 3016, 3003, 2954, 2926, 2854, 1600, 1590, 1562, 1464, 1399, 1376, 1255, 1250, 1125, 1090, 1077, 1023, 1003, 818, 774, 742, 688, 644 cm^{-1}. HRMS calcd for $C_{38}H_{54}NaOSi$ (M + Na) 577.3842, found 577.3850.



2-[2-(Hydroxymethyl)phenyl]dimethylsilyl]-9-ethyl-9*H*-carbazole (2e). A pale yellow viscous oil. R_f 0.11 (hexane-ethyl acetate = 10 : 1). ^1H NMR (400 MHz, $CDCl_3$) δ 0.71 (s, 6H), 1.23 (t, *J* = 6.0 Hz, 1H), 1.41 (t, *J* = 7.2 Hz, 3H), 4.36 (q, *J* = 7.2 Hz, 2H), 4.55 (d, *J* = 6.0 Hz, 2H), 7.18-7.26 (m, 1H), 7.29-7.51 (m, 6H), 7.55 (s, 1H), 7.64 (d, *J* = 7.2 Hz, 1H), 8.07-8.13 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ -0.6, 14.0, 37.5, 65.5, 108.7, 113.7, 119.0, 120.3, 120.8, 122.8, 124.0, 124.1, 126.2, 127.1, 128.5, 130.1, 135.7, 135.9, 136.6, 139.8, 140.2, 146.8. IR (KBr) 3430, 3052, 2972, 2952, 2933, 2892, 2873, 1637, 1622, 1591, 1559, 1553, 1491, 1473, 1454, 1431, 1378, 1364, 1346, 1324, 1127, 1092, 1078, 1056, 1044, 1020, 998, 834, 818, 791, 776, 766, 746, 727, 687, 663, 489, 437, 431 cm^{-1}. HRMS calcd for $C_{23}H_{25}NaOSi$ (M + Na) 382.1603, found 382.1600.



Preparation of

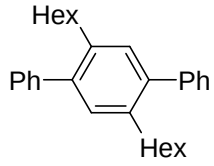


2,7-Bis[(2-hydroxymethylphenyl)dimethylsilyl]-(9,9-dioctyl-9*H*-fluorene (6). To a solution of 9,9-dioctyl-2,7-dibromofluorene (5.5 g, 10 mmol) in THF (40 mL) was added a 2.69 M solution of *n*-BuLi in hexane (7.5 mL, 20 mmol) at -78 °C, and the mixture was stirred at -78 °C for 2 h. To this was added 1,1-dimethyl-2-oxa-1-silaindan (6.6 g, 40 mmol). The resulting mixture was warmed slowly to -10 °C and stirred for 36 h, and then quenched with H_2O at 0 °C. The aqueous layer was extracted three times with Et_2O, and the combined organic layers were dried over anhydrous $MgSO_4$. After concentration in vacuo, the residue was purified by flash chromatography on silica gel to afford the title compound **6** (4.3 g, 60%), as a colorless solid. mp 73-74 °C. R_f 0.07 (hexane-ethyl acetate = 10 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.52-0.62 (m, 4H), 0.65 (s, 12H), 0.83 (t, *J* = 7.2 Hz, 6H), 0.95-1.29 (m, 22H), 1.84-1.94 (m, 4H), 4.53 (d, *J* = 6.0 Hz, 4H), 7.29 (dt, *J* = 2.0, 7.2 Hz, 2H), 7.39-7.48 (m, 8H), 7.56 (d, *J* = 7.6 Hz, 2H), 7.68 (d, *J* = 7.6 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ -0.7, 14.3, 22.8, 23.9, 29.30, 29.31, 30.0, 31.9, 40.1, 55.1, 65.5, 119.7, 127.1, 128.37, 128.41, 130.1, 132.6, 135.7, 136.6, 137.9, 142.1, 146.8, 150.5. IR (KBr) 3387, 3281, 3055, 2950, 2922, 2899, 2869, 2852, 2363, 1464, 1432, 1399, 1375, 1259, 1250, 1205, 1162, 1125, 1091, 1076, 1009, 847, 832, 818, 802, 777, 754, 727, 687, 643, 606, 435 cm^{-1}. HRMS calcd for $C_{47}H_{66}NaO_2Si_2$ (M + Na) 741.4499, found 741.4478.

Cross-coupling reaction of 2,7-dibromobenzothiadiazole (1a) with phenyl-HOMSi reagent 2a. ***A general procedure of cross-coupling reaction of 1a with 2*.** To a mixture of **1a** (147 mg, 0.50 mmol), Cs_2CO_3 (684 mg, 2.10 mmol), Pd[P(*o*-tolyl)$_3$]$_2$ (7.2 mg, 10 μmol), DPPF (5.8 mg, 11 μmol), CuBr·SMe_2 (3.1 mg, 15 μmol), Molecular Sieves 3A (100 mg) in THF (0.75 mL) and NMP (0.25 mL) in a screw vial was added **2a** (255 mg, 1.05 mmol), and the mixture was stirred at 50 °C for 6 h. The resultant solution was filtered through a Florisil pad, and diluted with dichloromethane. Concentration in vacuo followed by preparative TLC gave the corresponding coupling product **3aa** (137 mg, 95%).

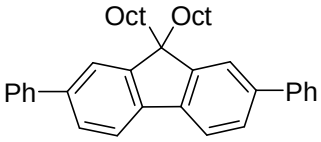
4,7-Diphenyl-benzo[1,2,5]thiadiazole (3aa). CAS registry number: 287976-96-9.

2',5'-Dihexyl-1,1':4',1"-terphenyl (3ba). A colorless oil. R_f 0.43 (hexane). ^{1}H NMR



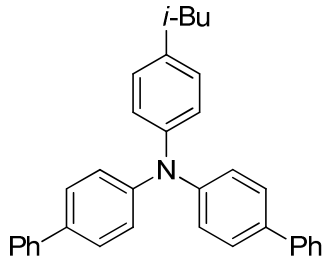
(400 MHz, $CDCl_3$) δ 0.81 (t, *J* = 7.2 Hz, 6H), 1.09-1.25 (m, 12H), 1.47 (quint, *J* = 7.2 Hz, 4H), 2.53-2.61 (m, 4H), 7.13 (s, 2H), 7.32-7.38 (m, 6H), 7.39-7.45 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 14.1, 22.6, 29.3, 31.5, 31.7, 32.9, 126.8, 128.1, 129.5, 131.0, 137.6, 141.0, 142.4; IR (neat) 2954, 2926, 2857, 1481, 701 cm^{-1}. MS (EI, 70 eV) *m/z* (%) 398 (M^+, 100), 372 (16), 255 (13), 243 (94), 165 (11). HRMS calcd for $C_{30}H_{38}$ (M) 398.2974, found 398.2946.

9,9-Dioctyl-2,7-diphenyl-9*H*-fluorene (3ca). A colorless oil. R_f 0.23 (hexane). ^{1}H



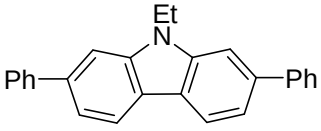
NMR (400 MHz, $CDCl_3$) δ 0.68-0.82 (m, 4H), 0.79 (t, *J* = 7.2 Hz, 6H), 1.00-1.28 (m, 20H), 2.00-2.08 (m, 4H), 7.36 (tt, *J* = 1.2, 7.2 Hz, 2H), 7.48 (t, *J* = 7.6 Hz, 4H), 7.54-7.61 (m, 4H), 7.65-7.74 (m, 4H), 7.77 (dd, *J* = 0.4, 7.6 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 14.1, 22.7, 24.1, 29.3, 30.2, 31.9, 40.6, 55.5, 120.1, 121.8, 126.3, 127.3, 127.4, 128.9, 140.3, 140.4, 142.0, 151.9. One alkyl carbon signal is overlapping other signals. IR (neat) 3058, 3029, 2953, 2926, 2853, 1598, 1501, 1464, 1412, 1377, 1252, 1075, 1024, 889, 824, 760, 729, 709, 697 cm^{-1}. HRMS calcd for $C_{41}H_{50}$ (M) 542.3913, found 547. 3914.

Bis(biphenyl-4-yl)(4-isobutylphenyl)amine (3da). A pale yellow solid. mp 88-89 °C.



R_f 0.34 (hexane-ethyl acetate = 20 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.87 (t, *J* = 7.4 Hz, 3H), 1.25 (d, *J* = 6.9 Hz, 3H), , 1.596 (quint, *J* = 7.0 Hz, 1H) 1.600 (quint, *J* = 7.0 Hz, 1H), 2.58 (sext, *J* = 7.0 Hz, 1H), 7.11 (s, 4H) 7.17 (dt, *J* = 2.0, 8.8 Hz, 4H), 7.30 (tt, *J* = 1.2, 7.6 Hz, 2H), 7.37-7.45 (m, 4H), 7.47 (dt, *J* = 2.0, 8.8 Hz, 4H), 7.55-7.61 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 12.5, 21.9, 31.4, 41.2, 123.9, 125.1, 126.8, 126.9, 127.9, 128.1, 128.9, 135.1, 140.8, 143.1, 145.2, 147.3. IR (KBr) 3056, 3030, 2957, 2925, 2870, 1598, 1517, 1509, 1485, 1460, 1450, 1407, 1376, 1320, 1281, 1265, 1187, 1178, 1109, 1075, 1005, 995, 832, 763, 744, 718, 693, 641, 618, 551, 499, 475, 456, 409 cm^{-1}. HRMS calcd for $C_{34}H_{31}NNa$ (M + Na) 476.2354, found 476.2348.

9-Ethyl-2,7-diphenyl-9*H*-carbazole (3ea). A pale yellow solid. mp 194-195 °C. R_f

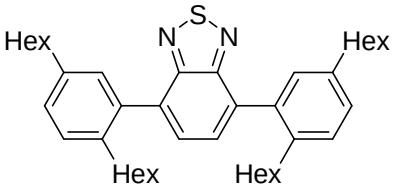


0.13 (hexane-dichloromethane = 4 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.49 (t, *J* = 7.2 Hz, 3H), 4.46 (q, *J* = 7.2 Hz, 2H), 7.34-7.41 (m, 2H), 7.45-7.53 (m, 6H), 7.59 (s, 2H), 7.70-7.77

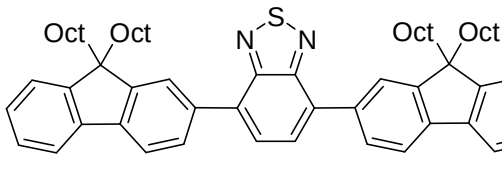
(m, 4H), 8.14 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 14.1, 37.7, 107.2, 118.9, 120.8, 122.1, 127.2, 127.8, 128.9, 139.3, 141.1, 142.4. IR (KBr) 3057, 3029, 2974, 2945, 2929, 2869, 2362, 1626, 1602, 1561, 1508, 1501, 1481, 1460, 1440, 1428, 1379, 1344, 1330, 1309, 1256, 1221, 1126, 1092, 1085, 1076, 1062, 1021, 993, 927, 916, 853, 818, 809, 740, 720, 698, 680, 644, 613, 593, 520, 455 cm^{-1}. MS (EI, 70 eV) *m/z* (%) 347 (M^+, 100), 332 (80), 173 (15), 165 (19). HRMS calcd for $C_{26}H_{21}NNa$ (M + Na) 370.1572, found 370.1589.

2,5-Diphenylthiophene (3fa). CAS registry number: 1445-78-9

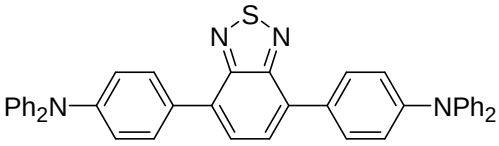
4,7-Bis(2,5-Dihexylphenyl)benzo[1,2,5]thiadiazole (3ab). A pale green oil. R_f 0.43 (hexane-ethyl acetate = 20 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.76 (t, *J* = 7.2 Hz, 6H), 0.88 (t, *J* = 6.8 Hz, 6H), 0.99-1.18 (m, 12H), 1.25-1.48 (m, 16H), 1.66 (quint, *J* = 7.6 Hz, 4H), 2.45 (t, *J* = 7.6 Hz, 4H), 2.65 (t, *J* = 7.6 Hz, 4H), 7.18 (d, *J* = 2.0 Hz, 2H), 7.21-7.26 (m, 2H), 7.31 (d, *J* = 7.8 Hz, 2H), 7.54 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 14.1, 14.3, 22.6, 22.8, 29.2, 29.3, 31.2, 31.57, 31.58, 31.9, 33.3, 35.7, 128.7, 129.3, 130.45, 130.48, 134.6, 137.0, 138.6, 140.3, 154.5. IR (neat) 3013, 2955, 2926, 2855, 1486, 1465, 1377, 896, 856, 824, 733 cm^{-1}. HRMS calcd for $C_{42}H_{60}N_2NaS$ (M + Na) 647.4375, found 647.4376.



4,7-Bis(9,9-dioctyl-9*H*-fluoren-2-yl)-benzo[1,2,5]-thiadiazole (3ac). A yellow-green oil. R_f 0.45 (hexane-ethyl acetate = 20 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.68-0.90 (m, 20H), 1.05-1.29 (m, 40H), 1.95-2.22 (m, 8H), 7.30-7.42 (m, 6H) 7.77 (d, *J* = 6.4 Hz, 2H), 7.80-7.92 (m, 4H), 7.98 (s, 2H), 8.03 (d, *J* = 7.8 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 14.2, 22.7, 24.0, 29.37, 29.39, 30.2, 32.0, 40.4, 55.3, 119.8, 120.1, 123.1, 124.0, 127.0, 127.4, 128.0, 128.3, 133.7, 136.3, 140.8, 141.5, 151.2, 151.4, 154.5. IR (neat) 2954, 2925, 2852, 1466, 1451, 826, 739 cm^{-1}. HRMS calcd for $C_{64}H_{84}N_2NaS$ (M + Na) 935.6253, found 935.6290.

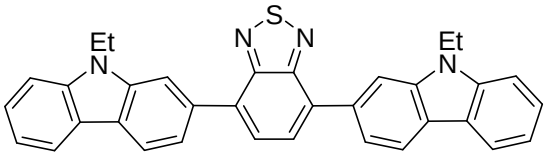


4,7-Bis[(4-diphenylamino)phenyl](benzo-[1,2,5]thiadiazole (3ad). An orange solid. mp 232-233 °C. R_f 0.14 (hexane-dichloromethane = 2 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) 7.07 (tt, *J* = 1.2, 7.2 Hz, 4H),



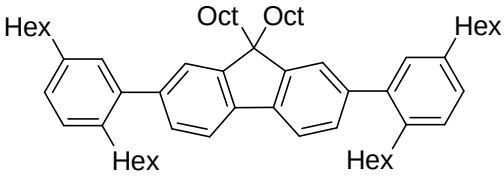
7.17-7.24 (m, 12H), 7.27-7.34 (m, 8H), 7.75 (s, 2H), 7.88 (d, *J* = 8.8 Hz, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 123.1, 123.4, 125.0, 127.6, 129.5, 130.0, 131.1, 132.3, 147.6, 148.1, 154.3. IR (KBr) 1588, 1515, 1485, 1460, 1346, 1333, 1316, 1277, 1178, 883, 837, 823, 754, 732, 697, 621, 523, 513 cm^{-1}. HRMS calcd for $C_{42}H_{30}N_2NaS$ (M + Na) 645.2089, found 645.2115.

4,7-Bis(9-ethyl-9*H*-carbazol-2-yl)benzo[1,2,5]-thiadiazole (3ae). A yellow solid. mp 234-236 °C. R_f 0.14 (hexane-dichloromethane = 2 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.50 (t, *J* = 7.2 Hz, 6H), 4.47 (q, *J* = 7.2 Hz, 4H), 7.27 (t, *J* = 7.6 Hz, 2H), 7.42-7.54 (m, 4H), 7.82 (dd, *J* = 1.2, 8.0 Hz, 2H), 7.95 (s, 2H), 8.11 (s, 2H), 8.16 (d, *J* = 7.8 Hz, 2H), 8.25 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 14.1, 37.8, 108.7, 109.7, 119.1, 120.4, 120.6, 120.8, 122.9, 123.2, 126.1, 128.6, 134.1, 135.1, 140.3, 140.8, 154.6. IR (KBr) 2366, 2360, 1598, 1485, 1469, 1450, 1442, 1350, 1328, 1231, 1157, 1129, 1085, 881, 844, 822, 813, 795, 768, 746, 725 cm^{-1}. HRMS calcd for $C_{34}H_{26}N_4NaS$ (M + Na) 545.1776, found 545.1809.



4,7-Bis(thiophen-2-yl)benzo[1,2,5]thiadiazole (3af). CAS registry number: 165190-76-1

2,7-Bis(2,5-dihexylphenyl)-9,9-Dioctyl-9*H*-fluorene (7b). A colorless oil. R_f 0.45 (pentane). ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.68-0.80 (m, 4H), 0.806 (t, *J* = 7.2 Hz, 6H), 0.810 (t, *J* = 7.2 Hz, 6H), 0.89 (t, *J* = 7.2 Hz, 6H), 1.00-1.50 (m, 48H), 1.66 (m, 4H), 1.93-2.01 (m, 4H), 2.53-2.68 (m, 8H), 7.09-7.16 (m, 4H), 7.22 (d, *J* = 7.6 Hz, 2H), 7.25-7.31 (m, 4H), 7.74 (dd, *J* = 1.2, 7.2 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 14.2, 14.3, 22.7, 22.77, 22.80, 24.1, 29.4, 29.48, 29.53, 30.3, 31.7, 31.88, 31.92, 32.0, 33.2, 35.7, 40.7, 55.2, 119.3, 124.0, 127.4, 128.1, 129.4, 130.2, 137.8, 139.6, 140.3, 141.1, 142.3, 150.6. Three alkyl carbon signals are overlapping each other. IR (neat) 3008, 2955, 2925, 2855, 1608, 1497, 1467, 1377, 907, 894, 826, 759, 735, 723 cm^{-1}. HRMS calcd for $C_{85}H_{99}$ (M + H) 305.1937, found 305.1956



2,7-Bis(thiophen-2-yl)-9,9-dioctyl-9*H*-fluorene (7c). CAS registry number: 338469-45-7

4,7-Bis(benzo[1,2,5]thiadiazol-2-yl)-9,9-dioctyl-9*H*-fluorene (7d). CAS registry number: 1088119-02-1

Poly[2,7-(9,9-dioctylfluorenylene)-*co*-(4,7-benzothiadiazolylene)] (8). CAS registry number: 210347-52-7

Poly(9,9-diocty-2,7-lfluorenylene) (9). CAS registry number: 12386-00-6

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Chapter 4
Silicon-Based C-N coupling Reaction

Palladium-catalyzed C–N bond-forming cross-coupling reaction of *N*-trimethylsilyl-substituted secondary and primary arylamines with aryl bromides and chlorides is found to proceed in the presence of a fluoride activator in DMI, giving tri-arylamines in excellent yields. When aryl bromide and bis(silyl)amine are used in this reaction, double C–N bond forming products are obtained in high yields. The present reaction is successfully applied to C–N bond-forming polymerization.

4.1 Introduction

Arylamines are an important structural motif for various pharmaceuticals, natural products, dyes, agrochemicals and functionalized polymers,[1] and can be prepared straightforwardly by the metal-catalyzed cross-coupling reaction of aryl halides or pseudohalides with nitrogen nucleophiles.[2,3] Particularly, the Pd-catalyzed reaction, so called Buchwald-Hartwig amination,[2] is of great significance because of straightforward approach and better functional group compatibility. The reaction usually requires strong bases for effective aromatic amination. Naturally, base-sensitive functional groups cannot tolerate the presence of such bases. In order to overcome this drawback, milder reaction conditions were developed: use of active catalyst systems[4] and/or weak bases[5] and aqueous conditions.[6] However, improvement of nucleophilic nitrogen source is almost unchanged since stannylamines were applied by Migita, Kosugi et al.[7]

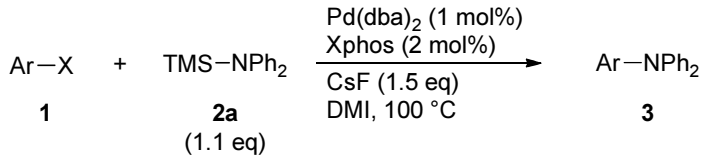
Hiyama and his coworkers have studied the silicon-based C–C bond-forming cross-coupling reaction.[8] This particular reaction proceeds under mild conditions since carbon nucleophiles are generated smoothly by the reaction of orgonosilicon compounds with a fluoride activator. The concept of organosilicon/fluoride activator to generate active nucleophiles has been applied to C–N coupling reaction with limited success. Barluenga and co-workers reported that cross-coupling reaction of aryl halides with silylaldimines to give *N*-arylated aldimines.[9] Smith, Holmes and coworkers developed the reaction of aryl halides with silylamines in supercritical carbon dioxide ($scCO_2$).[10] The latter is seminal. However, the use of $scCO_2$ limits its scope: substrates such as monosilyl primary amines are not applicabl as they react with $scCO_2$. Moreover, the reaction needs special pressure bottles. Thus, the author has decided to study the Pd-catalyzed cross-coupling reaction of aryl halides with silylamines and found the reaction is achieved under mild conditions in DMI.

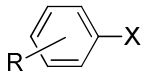
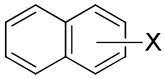
4.2 Results and Discussion

On the basis of the silicon-based cross-coupling reaction, the author examined the prototypical standard reaction conditions and soon found that 4-bromotoluene (**1a**) coupled with *N*-TMS-diphenylamine (**2a**) in the presence of $Pd(dba)_2$ (1 mol%), Xphos (2-dicyclohexylphosphino-2',4',6'-triisopropylbiphenyl)[11] (2 mol%), and CsF (1.5 eq) in DMI at 100 °C for 30 min to give diphenyl(*p*-tolyl)amine (**3aa**) in 97% yield (Table 1, entry 1). The reaction conditions were applied to various aryl halides. Less reactive 4-chlorotoluene (**1'a**) also underwent the C–N coupling to form **3aa** in 77% yield (entry 2). Phenyl and electron-rich aryl bromides having OMe, NMe_2 and NPh_2 groups at a *para* positions did not hamper the reaction to give the corresponding coupling products

in excellent yields (entries 3-6). Substrates with base-sensitive carbonyl groups (**1f** and **1g**)[4b] smoothly reacted to give **3fa** and **3ga** quantitatively (entries 7 and 8). Electron-withdrawing groups such as CF_3 and NO_2 did not interfere with the reaction (entries 9 and 10). Sterically hindered 2-bromotoluene (**1j**) reacted without any problem, and coupling product **3ja** was obtained in 99% yield (entry 11). *meta*-Dimethylphenyl bromide (**1k**) gave **3ka** in 98% yield (entry 12). 1- and 2-Bromonaphthalenes (**1l** and **1m**) gave corresponding C–N coupling products **3la** and **3ma** in 94% and 99% yields, respectively (entries 13 and 14).

Table 1. Cross-coupling reaction of aryl halides **1** with *N*-TMS-diphenylamine **2a**.

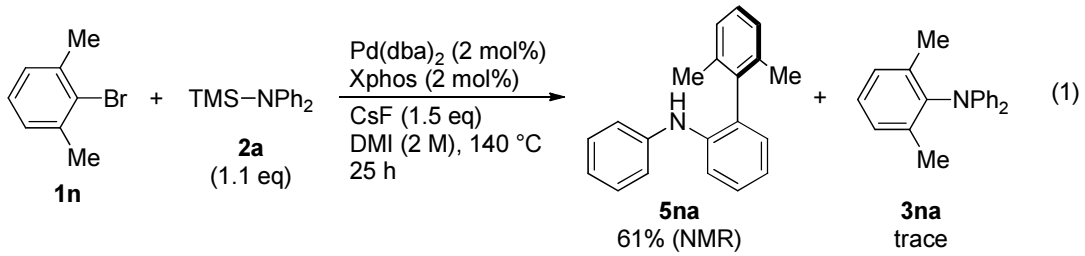


Entry	**1**	Ar	X	Time (h)	**3**	Yield (%)[b]
						
1	**1a**	R = 4-Me	Br	0.5	**3aa**	97
2	**1'a**	R = 4-Me	Cl	4	**3aa**	77
3	**1b**	R = H	Br	1	**3ba**	97
4	**1c**	R = 4-MeO	Br	1	**3ca**	94
5	**1d**	R = 4-NMe_2	Br	1	**3da**	89
6	**1e**	R = 4-NPh_2	Br	3	**3ea**	99
7	**1f**	R = 4-CO_2Me	Br	0.5	**3fa**	99
8	**1g**	R = 4-PhCO	Br	0.5	**3ga**	99
9	**1h**	R = 4-CF_3	Br	0.5	**3ha**	98
10	**1i**	R = 4-NO_2	Br	0.5	**3ia**	97
11	**1j**	R = 2-Me	Br	12	**3ja**	99
12	**1k**	R = 3,5-Me_2	Br	1	**3ka**	98
						
13	**1l**	1-X	Br	3	**3la**	94
14	**1m**	2-X	Br	1	**3ma**	99

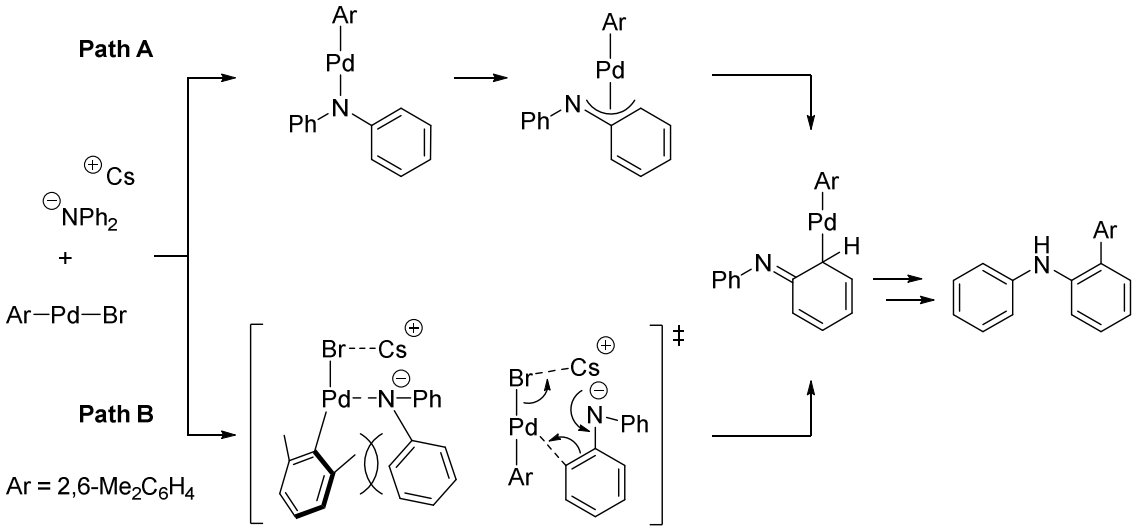
[a]Unless otherwise noted, a mixture of **1** (0.50 mmol), **2a** (0.55 mmol), $Pd(dba)_2$ (5.0 μmol), Xphos (10 μmol), CsF (0.75 mmol) and DMI (0.50 mL) were heated at 100 °C. [b]Isolated yield.

When sterically hindered bromide, 2,6-dimethylbromobenzene (**1n**) was used in this

reaction, a quite different coupling was observed. The reaction of **1n** with **2a** was carried out in the presence of $Pd(dba)_2$ (2 mol%), Xphos (2 mol%), CsF (1.5 eq) and DMI (2 M) at 140 °C to give *ortho*-arylated product **5na** in 61% NMR yield (Eq. 1). This type of coupling reaction is unprecedent but may be understood in analogy to *β*-selective cross-coupling reaction of aryl halide with allylmetal reagents.[12] According to this analogy, the author proposes two reaction mechanisms for *ortho*-arylation of diphenylamine shown in Scheme 1. Path A involves normal transmetalation of Ar-Pd-Br with pentacoordinated silicate to give Ar-Pd-NPh_2, which then undergoes reductive elimination at less hindered *ortho*-position of the amine. The resulting imine isomerizes to *ortho*-arylated arylamine via 1,3-H-shift. Path B proceeds through transmetalation of Ar-Pd-Br with silicate directly at the *ortho*-position of the amine. The following reductive elimination and 1,3-H-shift give the ortho-arylated amine. The details of the mechanism is the topic of future work.

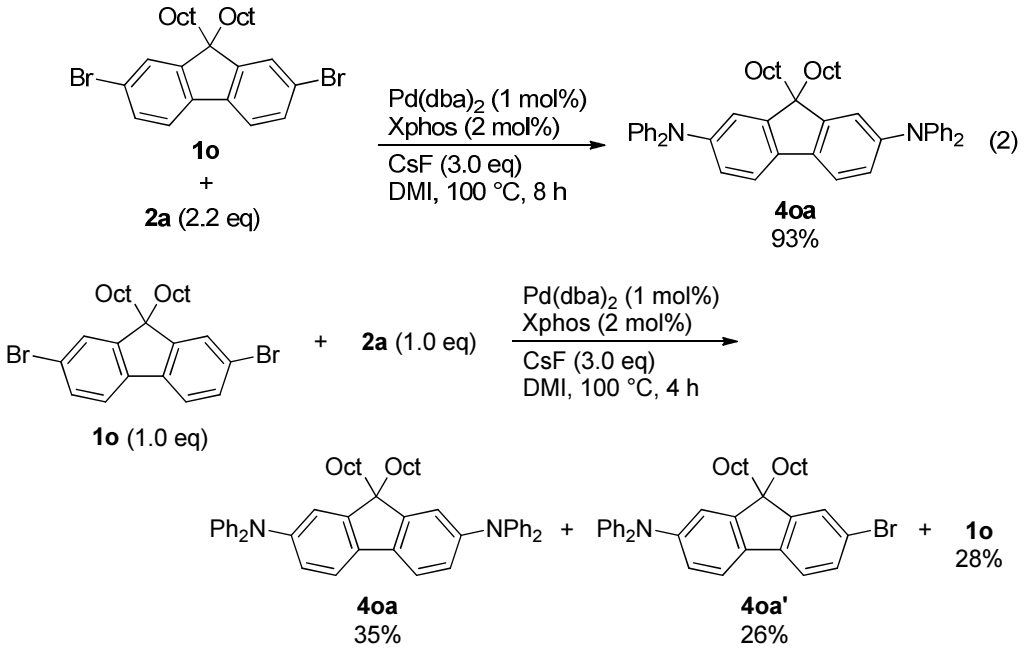


Scheme 1. Plausible reaction mechanism of *ortho*-arylation of diphenylamine



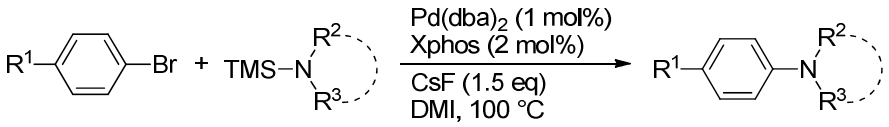
With arylene dibromides, double C–N bond-forming reaction readily takes place as was seen with 2,7-dibromo-9,9-dioctylfluorene (**1o**), which underwent sequential dou-

ble amination smoothly to give bis(diphenylamino) derivative **4oa** in 93% yield without formation of a mono-amination or reduction product (Eq 2). When an equal molar mixture of dibromofluorene **1o** and *N*-TMS-diphenylamine **2a** was applied, **4oa** was obtained as main coupling product. Mono coupling product **4oa'** was obtained in 26% yield and **1o** was recovered in 28% yield (Eq 3).

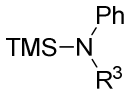
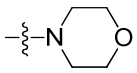
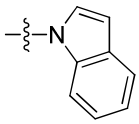
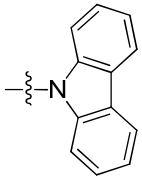


Scope of silylamine was next examined and the results are summarized in Table 2. *N*-TMS-diarylamines **2b** (R^2 = Ph, R^3 = *m*-tolyl) and **2c** (R^2 = Ph, R^3 = 1-naphthyl) gave smoothly the corresponding triarylamines (**3ab** and **3ac)** in 90% and 99% yields, respectively (entries 1 and 2). *N*-TMS-phenylmethylamine (**2d**) cross-coupled with phenyl bromide to form coupling product **3ad** in 75% yield (entry 3). *N*-TMS-aniline **2e** gave mono arylated product **3ae** in 96% yield without double arylation (entry 4). Even when 2.0 eq. of **1a** was used in the reaction with **2e**, **3ae** was formed in a high yield; triarylamine formation was hardly observed. These results clearly demonstrate that an N–$SiMe_3$ bond undergoes the C-N coupling in preference to an N–H bond. *N*-TMS-morpholine (**2f**) was successfully converted to **3af** in 70% yield (entry 5). *N*-TMS-azole derivatives are also applicable to this reaction. For example, the reaction of 1-TMS-indole (**2g**) with **1h** gave *N*-arylated indol **3hg** in 76% yield (entry 6); *N*-Trimethylsilylcarbazole **2h** coupled in the presence of double amount of the palladium catalyst to afford *N*-(4-trifluoromethylphenyl)carbazole (**3hh**) in 99% yield (entry 7).

Table 2. Cross-coupling reaction aryl bromides **1** with *N*-silylamines **2**



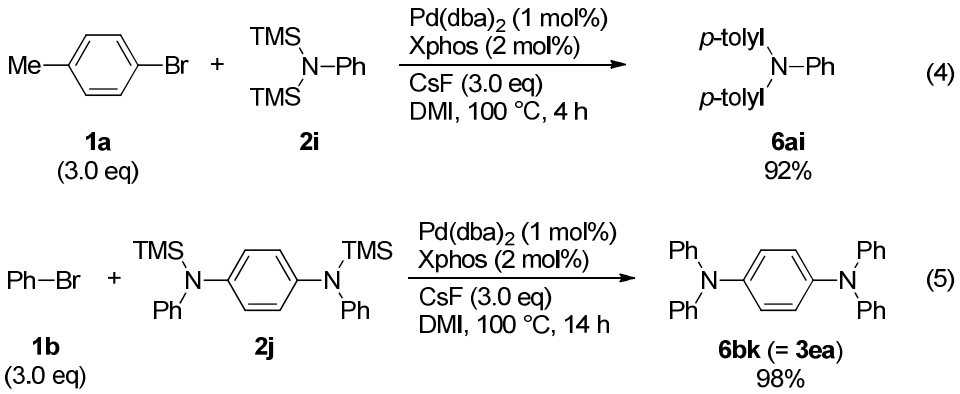
1 **2** (1.1 eq) **3**

entry	**1**	**2**	R^2, R^3	time (h)	**3**	yield (%)[b]
						
1	**1a**	**2b**	R^3 = *m*-tolyl	0.5	**3ab**	90
2	**1a**	**2c**	R^3 = 1-naphthyl	0.5	**3ac**	99
3	**1a**	**2d**	R^3 = Me	1	**3ad**	75
4	**1a**	**2e**	R^3 = H	5.5	**3ae**	96
5	**1a**	**2f**		12	**3af**	70
6	**1h**	**2g**		13	**3hg**	76
7[c]	**1h**	**2h**		24	**3hh**	99

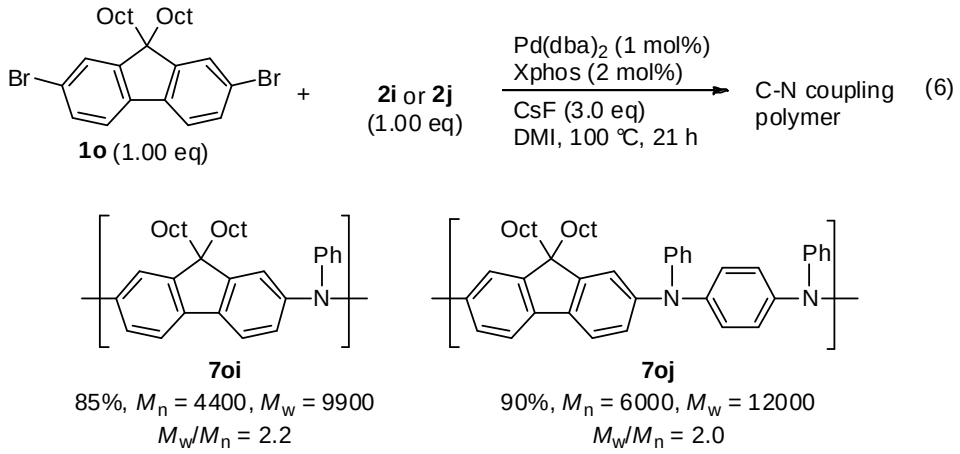
[a]Unless otherwise noted, a mixture of 1 (0.50 mmol), 2 (0.55 mmol), $Pd(dba)_2$ (5.0 μmol), Xphos (10 μmol), CsF (0.75 mmol) and DMI (0.50 mL) were heated at 100 °C. [b]Isolated yield. [c]$Pd(dba)_2$ (10 μmol), Xphos (20 μmol) and KF (2.50 mmol) were used.

In the case of *N*-trimethylsilylcarbazole, less basic KF gave better results than CsF.As *N*-arylcarbazoles have received much attention as electronic materials.[13] The present C-N coupling reaction of *N*-TMS-carbazole should be a facile entry for preparation of such triaryamine.[3,14]

The reaction of 3.0 eq. of **1a** with *N*,*N*-bis(TMS)aniline **2i** took place in freshly distilled DMI using rigorously dried CsF to give triarylamine **6ai** in 92% via double C-N bond formation (Eq 4). In this case, direct use of commercially available "dry" DMI and CsF resulted in low yields, since **2i** is extremely moisture sensitive. Similarly, *N*,*N*'-bis(TMS)-*p*-phenylenediamine (**2j**) gave *N*,*N*,*N*',*N*'-tetraphenyl-*p*-phenylenediamine (**6bk**) in 98% yield (Eq 5).



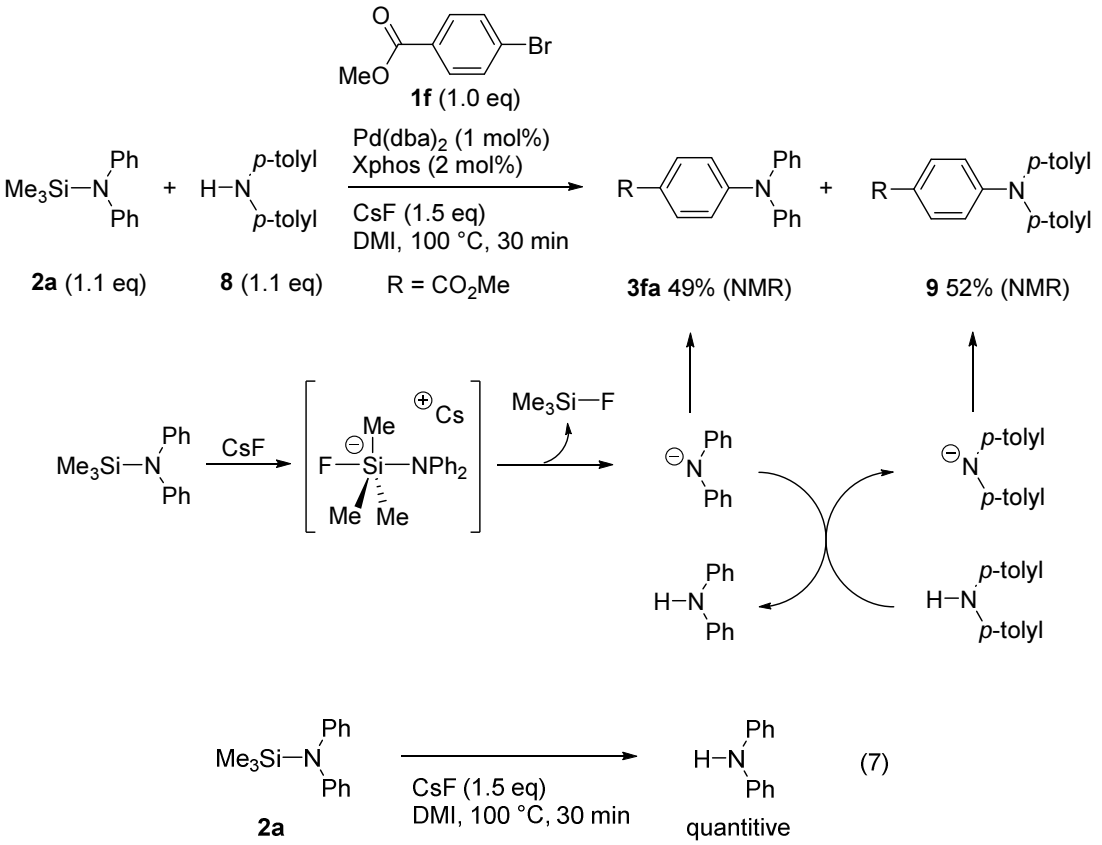
The present reaction was applied to the cross-coupling polymerization to synthesize poly(triarylamine)s[15] which are considered to be unique organic materials as electron carriers (Eq 6).[16] The reaction of 2,7-fluorenylidene dibromide (**1o**) with bis(TMS)aniline (**2i**) gave copolymer **7oi** with M_n = 4400, M_w = 9900 and M_w/M_n = 2.2 in 85% yield. *p*-Phenylenediamine-based bis(silyl)amine **2j** also reacted with **1o** to give copolymer **7oj** with M_n = 6000, M_w = 12000 and M_w/M_n = 2.0 in 90%.



To research reaction mechanism of C-N coupling using silylamines, conpetition reaction of *N*-TMS-diphenyamine and ditolylamine were examined (Schem 2). Surprisingly, *N*-(4-methoxycarbonylpheny)dipneylamine **3fa** (48%) and N-(4-methoxycarbonylpheny)ditolylamine **9** (52%) were obtained. The result suggestesd that trimethylaminosilicate was not coupling active species. Perhaps, trimethylaminosilicate generares tirimethylsiliy fluoride and diarylaminoanion. The diarylamino anion cross-couples with ArPdBr to give triarylamines. *N*-TMS-diphenylamine reacted with CsF smoothly to afford diphenylamine (Eq 7). This result also supports that

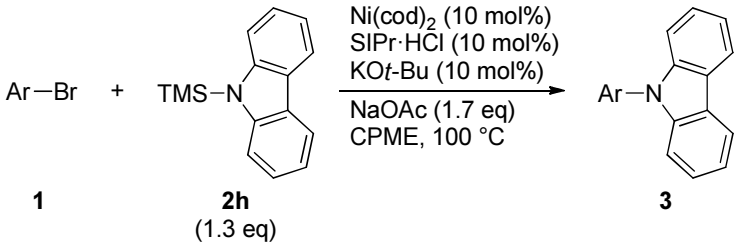
diarylamino anion is coupling active species.

Schem 2. Competition reaction of *N*-TMS-diphenylamine and ditolylamine.

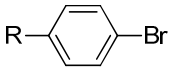
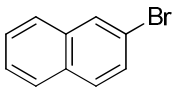
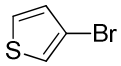


The author next focused on the cross-coupling reaction of aryl bromide with *N*-TMS-carbazole. In the view of material science, synthetic method of carbazole derivatives is important issue.[14] The electron-deficient aryl bromides with *N*-TMS-carbazole proceeded smoothly in the presence of a palladium catalyst as shown in Table 2. However, electron-rich aryl bromide such as bromotoluene and bromoanisole resulted in low yield. The author immediately screened suitable reaction conditions for cross-coupling reaction with *N*-TMS-carbazole and found that Ni(0)/SIPr system promotes the reaction with *N*-TMS-carbazole. Cross-coupling reaction of various aryl bromide **1** with *N*-TMS-carbazole **2h** were shown in Table 3.

Table 3. Cross-coupling reaction of aryl bromide **1** with *N*-TMS-carbazole **2h**

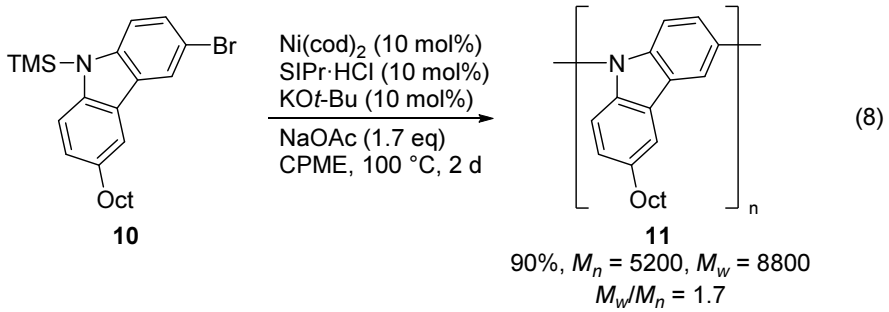


1 **2h** (1.3 eq) **3**

Entry	**1**	Ar	Time (h)	**3**	Yield (%)[b]
					
1	**1a**	R = Me	24	**3ah**	96
2	**1b**	R = H	18	**3bh**	88
3	**1c**	R = MeO	12	**3ch**	90
4	**1d**	R = NMe_2	18	**3dh**	77
5	**1e**	R = NPh_2	24	**3ea**	99
6	**1h**	R = CF_3	18	**3hh**	83
7	**1i**	R = NO_2	72	**3ih**	39
8	**1m**		24	**3mh**	90
9	**1p**		36	**3ph**	67

[a]Unless otherwise noted, a mixture of **1** (0.50 mmol), **2h** (0.63 mmol), $Ni(cod)_2$ (50 μmol), SIPr·HCl (50 μmol), KO*t*-Bu (50 μmol), NaOAc (0.85 mmol) and CPME (0.50 mL) were heated at 100 °C. [b]Isolated yield.

The reaction of bromotoluene (**1a**) with **2h** proceeded smoothly to give *N*-(4-tolyl)-carbazole (**3ah**) in 96% in the presence of $Ni(cod)_2$ (10 mol%), SIPr·HCl (10 mol%), KO*t*-Bu (10 mol%), NaOAc (1.7 eq) and CPME at 100 °C (entry 1). In the case of Ni-catalyzed reaction, fluorine activators such as KF and CsF afforded no coupling product. Perhaps, unreactive NiF_2 prevented the reaction. Bromobenzene also gave coupling product **3bh** in high yield (entry 2). An electron-donating group such as OMe, NMe_2, and NPh_2 did not hamper the reaction (entries 3-5). Electron-deficient aryl bromides (**1h** and **1i)** also reacted with **2h** to afford carbazole derivatives (**3hh** and **3ih**) in high and moderate yields, respectively (entries 6 and 7). 2-Bromonaphthalene gave *N*-(2-naphthyl)-carbazole (**3mh)** in 90% yield (entry 8). When 3-bromothiophwas ene applied, the desired heteroarylated carbazole (**3ph)** was obtained in a moderate yield (entry 9).



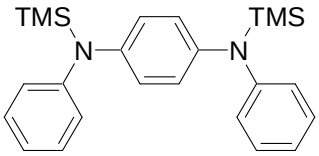
(8)

Finally, the Ni-catalyzed reaction was applied to cross-coupling polymerization. *N*-TMS-3-bromo-6-octylcarbazole (**10)** was allowed to react under the optimized conditions to afford C-N coupled polycarbazole **11** with Mw 8800 and PDI 1.7 in 90% (Eq 8). This type of oligocarbazole was prepared by Lu and co-worker,[17)] but their synthetic method is stepwisw and thus impractical. In this sense, the present reaction is useful method for synthesis of this type of polycarbazole.

In conclusion, the author has disclosed that the Pd(0)-catalyzed C-N bond-forming cross-coupling of aryl halides with *N*-trimethylsilylamines proceeds smoothly in the presence of a Pd catalyst and cesium fluoride in a common solvent. The feature of the present C–N coupling is attributed to a high reactivity of nitrogen nucleophiles generated by the fluoride-mediated desilylation of *N*-TMS amines. In addition, the present reaction allows him to use variously functionalized substrates and thus demonstrates wide applicability which might lead to invention of novel functionalized organic materials by double and multiple C–N bond-forming couplings. Moreover, Ni/NHC system is found to be efficient for the cross-coupling reaction with *N*-TMS-carbazole. Currently, his interest is focused on the extension of scope of the reaction.

4.3 Experimental

Preparation of *N*,*N*'-bis(trimethylsilyl)-*N*,*N*'-diphenyl-4,4'-phenylendiamine (2j).



To a solution of *N*,*N*'-diphenyl-4,4'-phenylendiamine (7.81 g, 30.0 mmol) in THF (80 mL) was added a 2.69 M solution of *n*-BuLi in hexane (27.0 mL, 72.0 mmol) at -78 °C, and the mixture was stirred at -78 °C for 5 h. To this was added trimethylchlorosilane (11.0 mL, 120 mmol). The resulting mixture was warmed slowly to room temperature and stirred for 14 h, and then excess trimethylchlorosilane and THF were removed under reduced pressure. Desired chemical **2j** was isolated in 70% yield (8.46 g, 21.0 mmol) by recrystallization using hot toluene. A colorless solid. R_f 0.14 (hexane). mp 128.1-129.7 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.24 (s, 18H), 6.81-6.85 (m, 4H), 6.86 (s, 4H), 6.87-6.92 (m, 2H), 7.18-7.25 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 1.23, 120.5, 121.8, 127.6, 129.0, 143.2, 149.5. IR (KBr) 3449, 3058, 2953, 1598, 1497, 1284, 1211, 1091, 1035, 962, 891, 843, 747, 692, 625, 556, 522 cm^{-1}. MS (EI, 70 eV) *m/z* (%) 404 (M^+, 100), 389 (10), 332 (10), 225 (17), 73 (54). HRMS calcd for $C_{24}H_{32}N_2Si_2$ (M + H) 405.2182, found 405.2166.

Cross-coupling reaction of aryl halide with *N*-trimethylsilylamine. ***A general procedure for synthesis of arylamines.*** To a mixture of aryl halide **1** (0.50 mmol), CsF (0.75 mmol), $Pd(dba)_2$ (5.0 μmol), Xphos (10 μmol), and DMI (0.50 mL) placed in a screw vial was added *N*-trimethylsilylamine **2** (0.55 mmol), and the whole mixture was stirred at 100 °C for the time specified in Tables 1 and 2. The resultant mixture was quenched with H_2O. The aqueous layer was extracted with Et_2O, and washed with brine. The combined organic layers were dried over anhydrous $MgSO_4$. After concentration in vacuo, the residue was purified by flash chromatography on silica gel or preparative TLC to give arylamine **3**.

***N*-(4-Tolyl)diphenylamine (3aa)**. CAS registry number: 4316-53-4.

Triphenylamine (3ba). CAS registry number: 603-34-9.

***N*-(4-Methoxyphenyl)diphenylamine (3ca)**. CAS registry number: 4316-51-2.

***N*,*N*-Dimethyl-*N*',*N*'-diphenyl-*p*-phenylenediamine (3da)**. CAS registry number: 4316-50-1.

***N*,*N*,*N*',*N*'-Tetraphenyl-*p*-phenylenediamine (3ea)**. CAS registry number: 14118-16-2.

***N*-(4-Methoxycarbonylphenyl)diphenylamine (3fa)**. CAS registry number: 25069-30-1.

***N*-(4-Benzoylphenyl)diphenylamine (3ga)**. CAS registry number: 16911-33-4.

***N*-(4-Trifluoromethylphenyl)diphenylamine (3ha)**. CAS registry number: 36809-32-2.

***N*-(4-Nitrophenyl)diphenylamine (3ia)**. CAS registry number: 4316-57-8.

***N*-(2-Tolyl)diphenylamine (3ja)**. CAS registry number: 4316-55-6.

***N*-(3,5-Dimethylphenyl)diphenylamine (3ka)**. CAS registry number: 92115-22-5.

***N*-(1-Naphthyl)diphenylamine (3la)**. CAS registry number: 6940-30-3.

***N*-(2-Naphthyl)diphenylamine (3ma)**. CAS registry number: 61231-45-6.

***N*-Methyl-*N*-(4-tolyl)aniline (3ad)**. CAS registry number: 38158-65-5

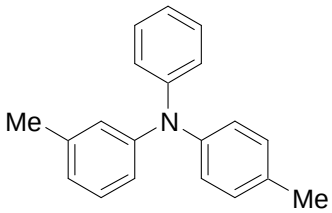
***N*-(4-Tolyl)aniline (3ae)**. CAS registry number: 620-84-8

***N*-(4-Methylphenyl)morpholine (3af)**. CAS registry number: 3077-16-5

***N*-(4-Trifluoromethylphenyl)-1*H*-indole (3ig)**. CAS registry number: 174621-55-7

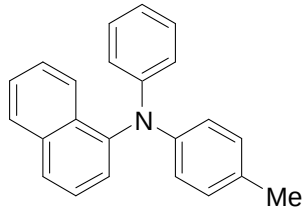
***N*-(4-Trifluoromethylphenyl)-9*H*-carbazole (3ih)**. CAS registry number: 264066-03-5

***N*-(3-Tolyl)-*N*-(4-tolyl)aniline (3ab)**. A yellow oil. R_f 0.52 (hexane-ethyl acetate = 20 : 1).



^{1}H NMR (400 MHz, $CDCl_3$) δ 2.24 (s, 3H), 2.31 (s, 3H), 6.80 (d, *J* = 7.6 Hz, 1H), 6.86 (dd, *J* = 2.0, 8.0 Hz, 1H), 6.89 (s, 1H), 6.92-7.03 (m, 3H), 7.03-7.08 (m, 4H), 7.11 (t, *J* = 7.6 Hz, 1H), 7.18-7.24 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 21.0, 21.6, 121.1, 122.2, 123.4, 123.6, 124.5, 125.0, 129.1, 129.2, 130.0, 132.7, 139.1, 145.5, 148.1, 148.3. IR (neat) 3025, 2918, 2860, 1692, 1594, 1491, 1274, 1213, 1110, 1028, 750, 696, 622, 511 cm^{-1}. MS (EI, 70 eV) *m/z* (%) 273 (M^+, 100), 180 (7), 167 (5). HRMS calcd for $C_{20}H_{20}N$ (M + H) 274.1598, found 274.1587.

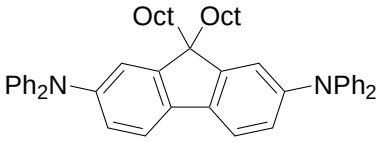
***N*-(4-Tolyl)-*N*-(1-naphthyl)aniline (3ac)**. A yellow oil. R_f 0.42 (hexane-ethyl acetate = 20 : 1).



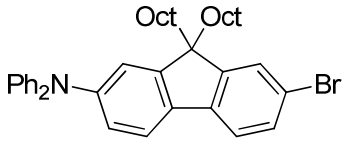
^{1}H NMR (400 MHz, $CDCl_3$) δ 2.26 (s, 3H), 6.86 (ddt, *J* = 1.2, 7.6, 7.6 Hz, 1H), 6.92-7.03 (m, 6H), 7.09-7.17 (m, 2H), 7.26-7.35 (m, 2H), 7.38-7.45 (m, 2H), 7.72 (d, *J* = 8.0 Hz, 1H), 7.84 (d, *J* = 8.4 Hz, 1H), 7.94 (d, *J* = 8.4 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 20.9, 121.09, 121.12, 122.8, 124.5, 126.2, 126.3, 126.4, 126.5, 127.1, 128.5, 129.1, 129.9, 131.3, 131.7, 135.4, 143.9, 146.0, 148.9. IR (neat) 3034, 2919, 2858, 2244, 1931, 1593, 1491, 1392, 1292, 1088, 1016, 908, 773, 732, 695, 679, 617 cm^{-1}. MS (EI, 70 eV) *m/z* (%) 309 (M^+, 100), 293 (11), 217 (10). HRMS calcd for $C_{23}H_{20}N$ (M + H) 310.1596, found 310.1578.

Cross-coupling of 2,7-dibromo-9,9-dioctylfluorene 1o with *N*-trimethylsilyl- diphenylamine (2a). To a mixture of 1n (274 mg, 0.500 mmol), CsF (228 mg, 1.50 mmol), $Pd(dba)_2$ (2.9 mg, 5.0 μmol), Xphos (4.8 mg, 10 μmol), and DMI (0.50 mL) in a screw vial was added **2a** (266 mg, 1.10 mmol). The resultant mixture was stirred at 100 °C for 8 h, then quenched with H_2O. The aqueous layer was extracted Et_2O, then washed with brine. The combined organic layers were dried over anhydrous $MgSO_4$. After concentration in vacuo, the residue was purified by preparative TLC to afford **4oa** in 93% yield (336 g, 0.463 mmol).

9,9-Dioctyl-2,7-bis(diphenylamino)-*9H*-fluorene (4oa). A colorless solid. R_f 0.38 (hexane-ethyl acetate = 20 : 1). mp 100.4-104.4 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.65-0.73 (m, 4H), 0.85 (t, *J* = 7.2 Hz, 6H), 0.99-1.29 (m, 20H), 1.72-1.78 (m, 4H), 6.95-7.02 (m, 6H), 7.06-7.15 (m, 10H), 7.19-7.26 (m, 8H), 7.47 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 14.3, 22.8, 24.0, 29.4, 29.5, 30.1, 32.0, 40.3, 55.1, 119.6, 119.9, 122.4, 123.8, 129.2, 136.4, 146.5, 148.2, 152.2. One signal derived from sp^2 carbon is overlapped with other signals. IR (KBr) 3435, 3033, 2925, 2852, 1587, 1492, 1434, 1332, 1273, 818, 752, 694, 501 cm^{-1}. HRMS calcd for $C_{53}H_{61}N_2$ (M + H) 725.4835, found 725.4814.



2-Bromo-9,9-dioctyl-7-diphenylamino-*9H*-fluorene (4oa'). A colorless viscus oil. R_f 0.40 (hexane-ethyl acetate = 20 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.56-0.72 (m, 4H), 0.84 (t, *J* = 7.6 Hz, 6H), 0.96-1.29 (m, 20H), 1.75-1.99 (m, 4H), 6.97-7.05 (m, 3H), 7.06-7.15 (m, 5H), 7.20-7.29 (m, 4H), 7.41 (dd, *J* = 2.0, 6.4 Hz, 2H), 7.45 (dd, *J* = 2.4, 6.4 Hz, 2H), 7.51 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ14.3, 22.8, 23.9, 29.37, 29.40, 30.1, 31.9, 40.3, 55.5, 119.2, 120.3, 120.5, 120.6, 122.8, 123.6, 124.0, 126.1, 129.3, 130.0, 135.2, 140.1, 147.6, 148.0. 151.9, 153.0. IR (neat) 3035, 2925, 2854, 1589, 1492, 1455, 1431, 1403, 1376, 1341, 1257, 1219, 1118, 1062, 1028, 877, 812, 753, 696, 508, 440, 423, 405 cm^{-1}. HRMS calcd for $C_{41}H_{51}Br_1N_1$ (M + H) 636.3177, found 6936.3205.



Cross-coupling reaction of 4-bromotoluene (1a) with *N*,*N*-bis(trimethylsilyl)aniline (2i). ***A general procedure for the synthesis of diarylated amines.*** To a mixture of **1a** (257 mg, 1.50 mmol), CsF (228 mg, 1.50 mmol), $Pd(dba)_2$ (2.9 mg, 5.0 μmol), Xphos (4.8 mg, 10 μmol), and DMI (0.50 mL) in a screw vial was added **2i** (137 mg, 0.577

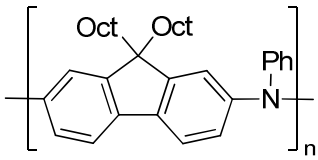
mmol), and the mixture was stirred at 100 °C for 4 h, then quenched with H_2O. The aqueous layer was extracted Et_2O, then washed with brine. The combined organic layers were dried over anhydrous $MgSO_4$. After concentration in vacuo, the residue was purified by Preparative TLC to afford **5ai** in 92% yield (145 mg, 0.530 mmol).

***N,N*-Bis(4-tolyl)aniline (5ai)**. CAS registry number: 20440-95-3

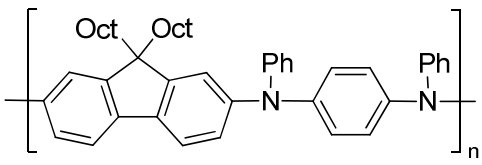
The reaction of **1b** with **2j** was performed by the similar procedure.

Cross-coupling polymerization of 9,9-dioctyl-2,7-dibromo-*9H*-fluorene (1o) with bis(trimethylsilyl)amine. ***A general procedure for the synthesis of poly(triarylamine).*** To a mixture of **1o** (274.2 mg, 0.500 mmol), CsF (227.9 mg, 1.50 mmol), $Pd(dba)_2$ (2.9 mg, 5.0 μmol), Xphos (4.8 mg, 10 μmol), and DMI (0.50 mL) in a screw vial was added **2** (0.50 mmol), and the mixture was stirred at 100 °C for 22 h. The crude polymer was precipitated into methanol to afford poly(triarylamine).

Poly(fluorene-aniline) (6oi). A yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.58-0.95 (m, 10H), 0.95-1.32 (m, 20H), 1.67-2.10 (m, 4H), 6.90-7.09 (m, 3H), 7.10-7.32 (m, 6H), 7.47 (d, J = 8.0 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 14.3, 22.8, 24.2, 29.5, 29.6, 30.2, 32.0, 40.4, 55.1, 119.0, 119.8, 122.1, 123.3, 129.2, 136.1, 146.6, 148.5, 152.0. One signal derived from sp^2 carbon is overlapped with other signal. IR (KBr) 3465, 2925, 2852, 1595, 1492, 1465, 1229, 816, 744, 695 cm^{-1}. M_n = 4400, M_n/M_w = 2.2.



Poly(fluorene-phenylendiamine) (6oj). A yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.63-0.76 (m, 4H), 0.79 (t, J = 7.2 Hz, 6H), 0.99-1.35 (m, 20H), 1.70-1.90 (m, 4H), 6.89-7.19 (m, 14H), 7.19-7.30 (m, 4H), 7.49 (d, J = 8.0 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 14.3, 22.7, 24.1, 29.4, 29.5, 30.2, 31.9, 40.3, 55.1, 119.4, 119.8, 122.0, 123.0, 123.5, 125.1, 129.2, 136.2, 142.9, 152.1. Two signals derived from sp^2 carbon is overlapped with other signal. IR (KBr) 3424, 3034, 2924, 2852, 1594, 1503, 1465, 1265, 815, 747, 694, 511 cm^{-1}. M_n = 6000, M_n/M_w = 2.0.

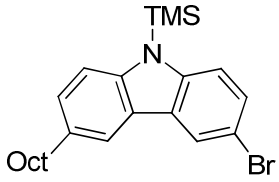


Ni-catalyzed cross-coupling of aryl halide with *N*-trimethylsilylcarbazole 2h. ***A general procedure for the synthesis of arylamines.*** A mixture of $Ni(cod)_2$ (50 μmol), SIPr·HCl (50 μmol), KO*t*-Bu (50 μmol), and CPME was stirred at rt for 30 min. To this

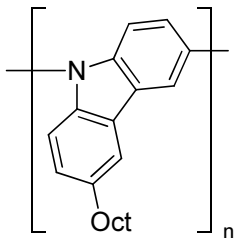
was added NaOAc (0.85 mmol), aryl bromide **1** (0.50 mmol), and *N*-trimethylsilylcarbazole **2h** (0.63 mmol)**.** Then, the resultant mixture was was stirred at 100 °C for the time specified in Tables 3. The resultant mixture was quenched with H_2O. The aqueous layer was extracted with Et_2O, and washed with brine. The combined organic layers were dried over anhydrous $MgSO_4$. After concentration in vacuo, the residue was purified by flash chromatography on silica gel or preparative TLC to afford arylamine **3**.

***N*-(4-Tolyl)-carbazole (3ah)**. CAS registry number: 19264-73-4
***N*-Phenyl-carbazole (3bh).** CAS registry number: 1150-62-5
***N*-(4-Anisyl)-carbazole (3ch).** CAS registry number: 19264-74-5
***N*-[4-(*N*, *N*-Dimethylamino)phenyl]-carbazole (3dh)**. CAS registry number: 53167-75-2
***N*-[4-(*N*, *N*-Diphenylamino)phenyl]-carbazole (3eh)**. CAS registry number: 212385-56-3
***N*-(4-Nitrophenyl)-carbazole (3ih)**. CAS registry number: 16982-76-6
***N*-(2-Naphthyl)-carbazole (3mh)**. CAS registry number: 34292-03-0
***N*-(3-Thienyl)-carbazole (3ph)**. CAS registry number: 1165806-09-6

Preparation of *N*-trimethylsilyl-2-bromo-6-octylcarbazole (10). To a solution of NaH (480 mg, 12.0 mmol) in THF (80 mL) was added 2-bromo-6-octylcarbazole (3.58 g, 10.0 mmol) at 0 °C, and the mixture was stirred at rt for 2 h. To this was added trimethylchlorosilane (1.73 mL, 20 mmol). The resulting mixture was stirred for 12 h, and then excess trimethylchlorosilane and THF were removed under reduced pressure. The residue was purified by flash chromatography on neutral silica gel to afford desired chemical **8** in 65% yield (2.80 g, 6.51 mmol). A colorless viscus oil. R_f 0.50 (hexane-ethyl acetate = 10 : 1). ^{1}H NMR(400 MHz, $CDCl_3$) δ, 0.67 (s, 9H), 0.88 (t, *J* = 7.0 Hz, 3H), 1.20-1.42 (m, 10H), 1.65-1.72 (m, 2H), 2.75 (t, *J* = 7.6 Hz, 2H), 7.22 (d, *J* = 8.4 Hz, 1H), 7.38-7.45 (m, 2H), 7.50 (d, *J* = 8.4 Hz, 1H), 7.80 (s, 1H), 8.15 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 1.7, 14.3, 22.9, 29.45, 29.52, 29.7, 32.1, 32.3, 35.9, 112.4, 113.0, 114.5, 119.6, 122.8, 125.3, 127.1, 127.9, 128.2, 134.7, 143.0, 143.2. IR (neat) 2954, 2925, 2853, 1482, 1467, 1467, 1440, 1274, 1257, 1218, 1138, 1063, 1024, 971, 843, 802, 763, 699, 634 cm^{-1}. HRMS calcd for $C_{23}H_{33}Br_1N_1Si_1$ (M + H) 430.1566, found 430.1547.

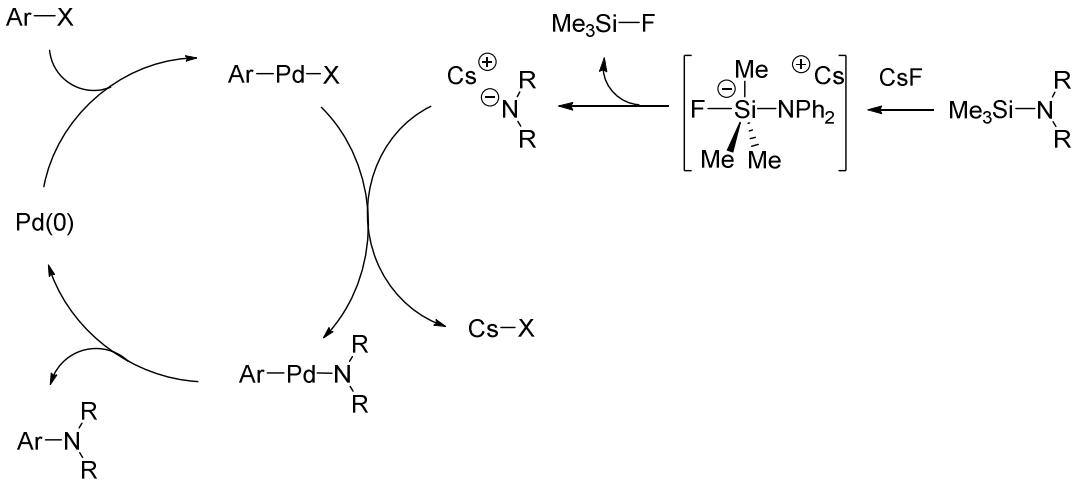


Cross-coupling polymerization of *N*-trimethylsilyl-2-bromo-6-octylcarbazole (10). A mixture of $Ni(cod)_2$ (50 μmol), SIPr·HCl (50 μmol), KO*t*-Bu (50 μmol), and CPME was stirred at rt for 30 min. To this was added NaOAc (0.85 mmol), *N*-trimethylsilyl-2-bromo-7-octylcarbazole (**10).** Then, the resultant mixture was was stirred at 100 °C for 2 days. The crude polymer was precipitated into methanol to afford polycarbazole **11**.

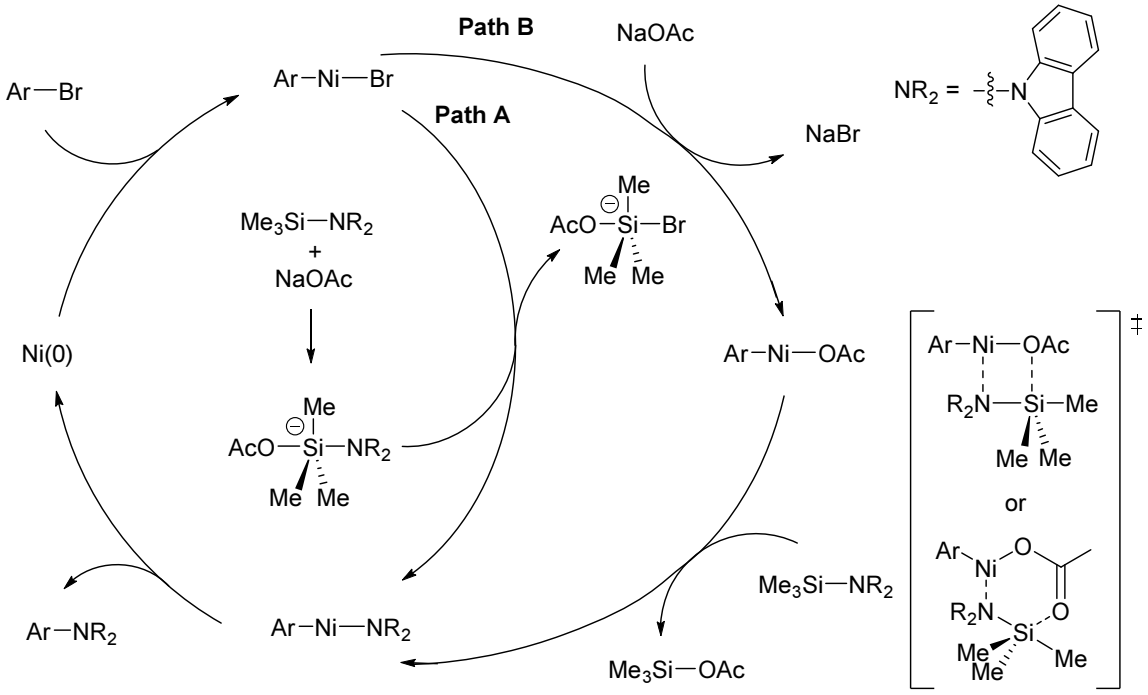


Poly(3-octylcarbazole) (11). A brown solid. δ, 0.82-0.95 (m, 3H), 1.20-1.42 (m, 10H), 1.65-1.78 (m, 2H), 2.72-2.88 (m, 2H), 7.20-7.68 (m, 4H), 7.85-8.02 (m, 1H), 8.20-8.42 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.3, 22.8, 29.45, 29.54, 29.7, 32.1, 32.5, 32.6, 36.2, 110.2, 111.2, 119.5, 119.9, 122.8, 124.1, 125.2, 127.6, 129.2, 135.0, 140.9, 141.4. IR (KBr) 2922, 2851, 1628, 1575, 1491, 1473, 1324, 1300, 1273, 1240, 1147, 1024, 874, 808, 722, 654, 605, 573, 492, 458, 445, 420, 404 cm^{-1}. M_n = 5200, M_n/M_w = 1.7.

Plausible reaction mechanism of Pd-catalyzed C-N coupling using *N*-TMS-amines



Plausible reaction mechanism of Ni-catalyzed C-N coupling using *N*-TMS-carbazoles



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Chapter 5
Conclusion

In this Dissertation, the author has reviewed first the history of the cross-coupling reactions and then focused on the one that uses organosilicon reagents to point out problems of the silicon-based cross coupling reaction. Various synthetic aspects are discussed in Chapter 1.

In Chapter 2, the author has described a new synthetic method of HOMSi reagents through palladium/copper-catalyzed silylation of aryl bromides with disilanes analogs of HOMSi reagents. The reaction enables preparation of functionalized aryl-HOMSi reagents which have been hardly accessible. A variety of functionalized aryl bromides and disilanes with different protecting group can be employed as a coupling partner in this reaction. The protected-HOMSi reagents obtained are readily applicable to cross-coupling reaction after deprotection. With arylene dibromides, simultaneous double silylation proceeds smoothly to give arylene-bisHOMSi reagents in good yields.

In Chapter 3, the author has discussed simultaneous double cross-coupling reaction and cross-coupling polymerization. Reaction conditions are thoroughly scrutinized to obtain the coupled products in stoichiometric ratio, which is essential for cross-coupling polymerization. Double cross-coupling reactions using bifunctionalized coupling species such as arylene dibromides and arylene-bisHOMSi reagents take place smoothly under the optimized reaction conditions. With the reaction conditions in hand, HOMSi-based cross-coupling reaction is applied to cross-coupling polycondensation, giving π-conjugated polymers.

In Chapter 4, the author has disclosed that the C-N bond-forming cross-coupling reaction is readily achieved using *N*-silylamines. The reaction of aryl halides with silylamines is shown to proceed smoothly in the presence of palladium catalyst under in DMI. Various functionalized triarylamines are thus obtained by the reaction. The reaction of aryl halides bearing base-sensitive functional group take place without any problem. Silylamines, prepared from diarylamine, dialkylamine, primary arylamine, and azole, are found to couple smoothly to give coupled products in all cases. The reaction with bis(silyl)amine form new two C-N bonds at one time. The C-N coupling reaction is applied to C-N coupling polymerization. In the case of raction of *N*-TMS-carbazole, Ni/SIPr catalyst system is sutable. Cross-coupling reaction of various aryl bromide with *N*-TMS-carbazole proceeded smoothly to give *N*-arylated carbazoles.

Publication List

(1)
Kenta Shimizu, Yasunori Minami, Yoshiaki Nakao, Ken-ichiro Ohya, Hideyuki Ikehira, and Tamejiro Hiyama
"**Polyarene Synthesis by Cross-Coupling Reaction using HOMSi reagents**"
Chemistry Letters, **2013**, *42*, 45.

(2)
Yasunori Minami, Kenta Shimizu, Chisato Tsuruoka, Takeshi Komiyama, and Tamejiro Hiyama
"**Synthesis of HOMSi Reagents by Pd/Cu-Catalyzed Silylation of Bromoarenes with Disilanes**"
Chemistry Letters, **2014**, *43*, 201.

(3)
Kenta Shimizu, Yasunori Minami, Osamu Goto, Hideyuki Ikehira, and Tamejiro Hiyama
"**Silicon-Based C-N Coupling Reaction**"
Chemistry Letters, in press**.**

The following publications are not included in this disserration.

(1)
Shin-ich Fukuzawa, Ichiro Oura, Kenta Shimizu, Minoru Kato, and Ken-ichi Ogata
"**Divalent Samarium Triflate Mediated Stereoselective Pinacol Coupling of Planar Chiral Phosphanyl and Phosphoryl Ferrocenecarbaldehyde**"
European Journal of Organic Chemistry, **2009**, 716.

(2)
Ichiro Oura, Kenta Shimizu, Ken-ichi Ogata, and Shin-ich Fukuzawa
"**Highly Endo-Selective and Enantioselective 1,3-Dipolar Cycloaddition of Azomethine Ylide with α-Enones Catalyzed by a Silver(I)/ThioClickFerrophos Complex"**
Organic Letters, **2010**, *12*, 1752.

(3)
Kenta Shimizu, Ken-ichi Ogata, and Shin-ich Fukuzawa
"**Ag/ThioClickFerrophos catalyzed highly enantioselective 1,3-dipolar cycloaddition of azomethine ylides with alkenes**"
Tetrahedron Letters, **2010**, *51*, 5068.

(4)
Imae Kazumi, Kenta Shimizu, Ken-ichi Ogata, and Shin-ich Fukuzawa
"**Ag/ThioClickFerrophos-Catalyzed Enantioselective Mannich Reaction and Amination of Glycine Schiff Base**"
The Journal of Organic Chemistry, **2011**, *76*, 3604.

(5)
Takashi Konno, Kenta Shimizu, Ken-ichi Ogata, and Shin-ich Fukuzawa
"**Rhodium-Catalyzed Enantioselective Hydrogenation of Unsaturated Phosphorates by ClickFerrophos Ligands**"
The Journal of Organic Chemistry, **2012**, *77*, 3318.

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