Studies on Transition Metal-catalyzed Carbon–Carbon Bond Forming Reactions through Intramolecular Activation of Organosilicon Compounds

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Contents

Abbreviations

Ac	acetyl
acac	acetylacetonato
aq.	aqueous
Ar	aryl
BINAP (binap)	2,2'-bis(diphenylphosphino)-1,1'-binaphthyl
B(pin)	4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl
Bu	butyl
br	broad
ca.	about (circa)
cat.	catalyst
cod	1,5-cyclooctadiene
Cp	cyclopentadienyl
Cy	cyclohexyl
d	doublet
δ	scale (NMR)
dba	dibenzylideneacetone
DIBAL-H	diisobutylaluminium hydride
DMAP	4-dimethylaminopyridine
DMF	*N*,*N*-dimethylformamide
DMSO	dimethyl sulfoxide
dppb	1,4-bis(diphenylphosphino)butane
dppf	1,1'-bis(diphenylphosphino)-ferrocene
dppp	1,3-bis(diphenylphosphino)propane
dvds	1,3-divinyl-1,1,3,3-tetramethyldi-siloxane
ee	enantiomeric excess
EI	electron impact ionization
Eq.	equation
equiv	equivalent
Et	ethyl
FAB	fast atom bombardment
GC	gas chromatography
GPC	gel permeation chromatography
Hex	hexyl
HMPA	hexamethylphosphoric triamide
HPLC	high-performance liquid chromatography
HRMS	high-resolution mass spectra
Hz	hertz
IR	infrared
J	coupling constant (NMR)
L	ligand or litre
lit.	literature
m	multiplet
M(m)	metal
Me	methyl
mp	melting point
MS	mass spectrometry
MS 4A	molecular sieves 4A
NMR	nuclear magnetic resonance
Oct	octyl
Pent	pentyl
PG	protecting group
Ph	phenyl
Phth	phthalimide
PPTS	pyridinium *p*-toluenesulfonate
Pr	propyl
q	quartet
quint	quintet
R_f	retention factor
rt	room temperature
RuPhos	[2,6-bis(1-methylethoxy)[1,1-bi-phenyl]-2-yl]dicyclohexyl-phosphine
s	singlet

sat.	saturated
sext	sextet
S_N2	bimolecular nucleophilic substitution
t	triplet
TASF	tris(diethylamino)sulfonium difluorotrimethylsilicate
TBAF	tetrabutylammonium fluoride
TBDMS	*t*-butyldimethylsilyl
THF	tetrahydrofuran
TLC	thin-layer chromatography
TMS	trimethylsilyl
THP	tetrahydropyran-2-yl
2-Th	2-thienyl

Chapter 1

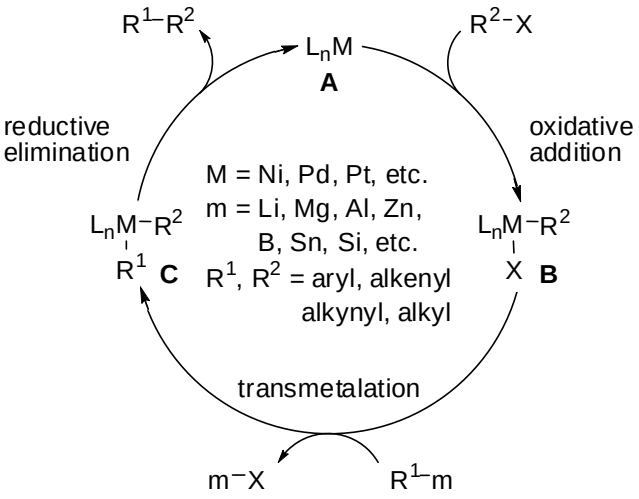
Introduction and General Summary

–carbon bond forming reaction is the most important transformation in organic synthesis in view that carbon–carbon bonds constitute the framework of organic molecules.[1] Of many synthetic transformations leading to the bond formation, those which employ organometallic reagents of main group elements are playing indispensable roles, since these readily react with a diverse range of electrophiles to form various types of carbon–carbon bonds. The synthetic value of organometallics of main group elements is further enhanced by transmetalation, which allows transfer of organic groups from main group elements to transition metals. The resulting carbon–transition metal bonds exhibit unique and versatile reactivities and selectivities that are inaccessible with organometallics of main group elements.[2]

Cross-coupling reaction

Transition metal-catalyzed cross-coupling reactions of organometallic reagents with organic halides or pseudohalides are one of the most important catalytic transformations that involve transmetalation. The reaction generally proceeds via oxidative addition of electrophiles R^2–X to active transition metal catalysts L_nM (**A**), transmetalation of the resulting complex **B** with nucleophiles R^1–m to give **C**, and reductive elimination of two organic groups R^1 and R^2 in **C** to produce coupled products R^1–R^2 and regenerate catalytically active species **A** (Scheme 1). Various main group organometallic reagents, such as organomagnesium, -lithium, -aluminum, -zinc, -bo

Scheme 1.



ron, -tin and -silicon compounds, have been found to undergo transmetalation, and thus are successfully employed in the cross-coupling reaction.[3] Recently, in addition to the original coupling partners, those containing aromatic, vinylic, and even aliphatic C–H bonds are found to participate in the cross-coupling reaction.[4]

From the early stage of studies on the cross-coupling chemistry, organomagnesium,[5] -lithium,[6] and -aluminum[7] reagents have been employed, because these are nucleophilic enough to undergo transmetalation smoothly. However, poor chemoselectivity associated with these nucleophiles have often been problematic particularly when applied to synthesis of highly functionalized target molecules. Later, organozinc reagents were introduced as alternative cross-coupling reagents, which tolerated a wide range of electrophilic functional groups such as ketones, esters, and nitriles, although they are not always useful enough in view of their preparation and handling: strictly anhydrous reaction conditions are required during these manipulations.[8]

Subsequently, organotin reagents were shown to be more useful in view of their stability, reactivity, and chemoselectivity.[9] They are shown to be completely inert to moisture, to participate in the cross-coupling reaction under neutral conditions, and to tolerate almost all kinds of functional groups on both coupling partners, and thus have been utilized in synthesis of highly functionalized compounds including complex natural products.[10] A critical drawback in use of organotin reagents is toxicity of not only the reagents but their residues, triorganohalostannanes,[11] thus making this protocol less attractive in view of industrial production. In spite of many efforts made to overcome this disadvantage,[12] use of organotin reagents is currently limited mainly to laboratory-scale syntheses.

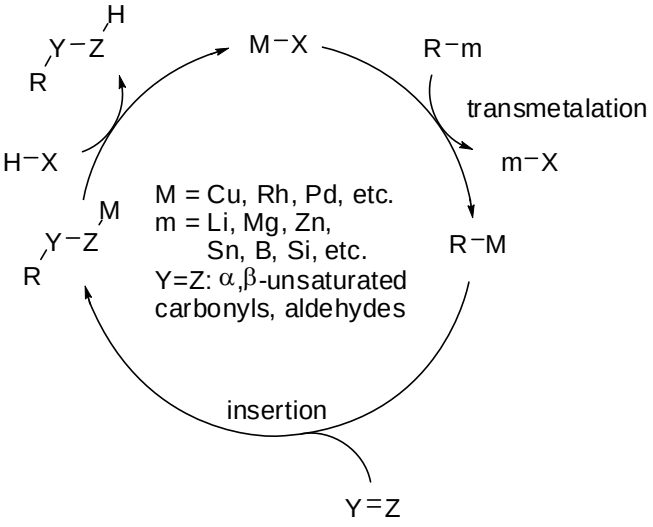
Nowadays, organoboron reagents are used most extensively in the cross-coupling reaction.[13] Although co-use of activators such as inorganic bases is necessary to promote transmetalation, organoborane reagents exhibit chemoselectivity, stability, availability, and less toxicity, and thus have attracted attention of many synthetic chemists and stimulated them to apply the reaction even to industrial production.[14]

Organosilicon reagents also can participate in the cross-coupling reactions. Details will be discussed later.

1,4- and 1,2-Addition reactions

Another important transition metal-catalysis involving transmetalation is 1,4- and 1,2-addition reactions (Scheme 2).[15] Although many main group organometallic reagents can undergo the addition reactions without catalysts, it is not always easy to control their reaction modes: 1,2- vs 1,4-addition or nucleophilic addition vs proton-abstraction. Copper was first introduced as a transition metal-catalyst for 1,4-addition reaction of organomagnesium reagents. The reaction proceeds generally with excellent regio- and chemoselectivities.[16] Enantioselective additions have also been achieved, using chiral phosphorous ligands.[17] A serious limitation of the copper catalysis is that the reaction is limited mostly to primary alkyl groups. Recently, rhodium catalysis has gained significant attention as an alternative to the copper catalysis to compensate for this limitation.[18] The rhodium catalysis allows installation of alkenyl and aryl groups through transmetalation from highly mild nucleophiles such as organoboron, -tin, and -silicon reagents. Not only 1,4-addition but also 1,2-addition reactions have been attained with rhodium catalysts.[19] Most importantly, high enantioselectivities have been attained with chiral rhodium catalysts.[20] A few examples of palladium-catalyzed 1,4-addition reactions also are reported.[21]

Scheme 2.



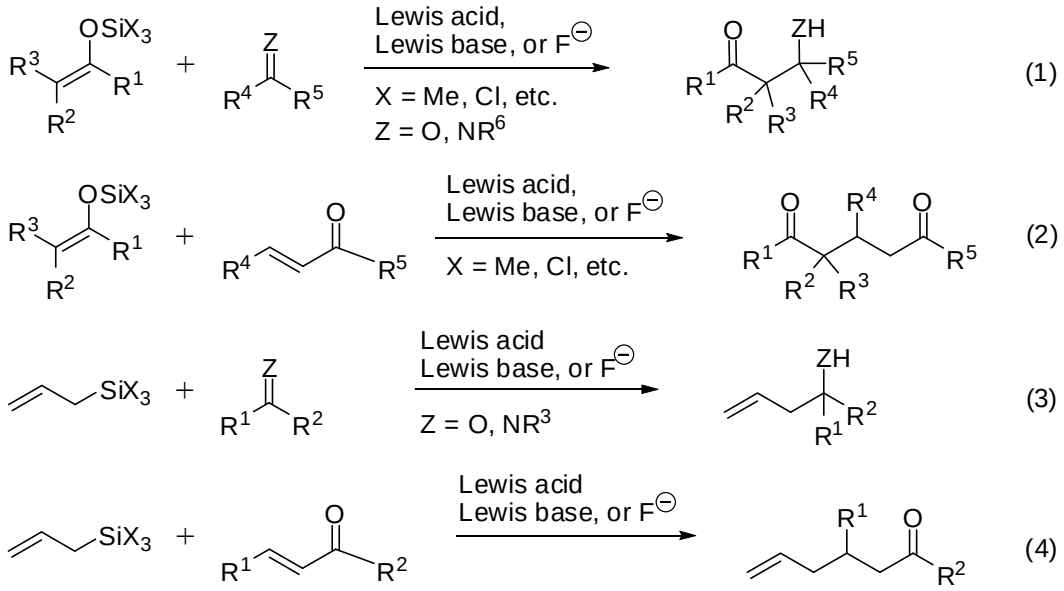
Both of the catalytic transformations discussed above have extensively been studied and now grown to be the standard tool in modern organic synthesis in terms of reactivity and selectivity achieved by transition metal-catalysts. On the other hand, new

main group organometallic reagents that fulfill high reactivity, chemoselectivity, availability, stability, and non-toxicity have remained yet to be explored. In addition, none of the precedents has demonstrated recovery and reuse of metallic residues, which are always co-generated in stoichiometric amounts.

Based on these historical backgrounds, the author designed new organometallic reagents that satisfy all of these requirements and focused especially on organosilicon reagents.

Use of organosilicon reagents in C–C bond forming reactions

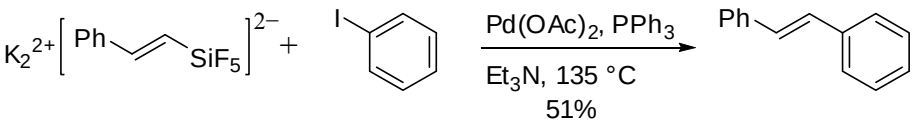
In view of their high stability and non-toxicity as well as natural abundance of silicon,[22] organosilicon reagents have gained significant importance and interest in organic synthesis. Accordingly, carbon–carbon bond forming reactions using organosilicon reagents have been extensively studied in the past three decades. As a result, synthetically valuable reactions using organosilicon reagents such as the Mukaiyama aldol reaction (Eqs. 1 and 2)[23] and the Hosomi-Sakurai allylation reaction (Eqs. 3 and 4)[24] have been developed and extensively used in organic synthesis. In these reactions, electron-rich double bonds react with electrophilic functionalities activated often by a Lewis acid by virtue of β-carbocation-stabilizing silyl groups.



Another strategy to activate organosilicon reagents to be nucleophilic enough is to convert them to silicate species. This strategy is also employed in the Mukaiyama and Hosomi-Sakarai reactions. Compared with other main group organometallic reagents, organosilicon reagents are inert under ambient conditions due to less polarized C–Si bonds, as is recognized by the fact that triorganosilyl groups are most frequently used as protecting groups.[25] On the other hand, penta- and hexacoordinate silicates may transfer organic groups to participate in the reactions with electrophiles and to form C–C bonds. Such nucleophilic silicates also may undergo transmetalation to achieve cross-coupling reactions and 1,4- and 1,2-reactions.

Cross-coupling reaction using organosilicon reagents

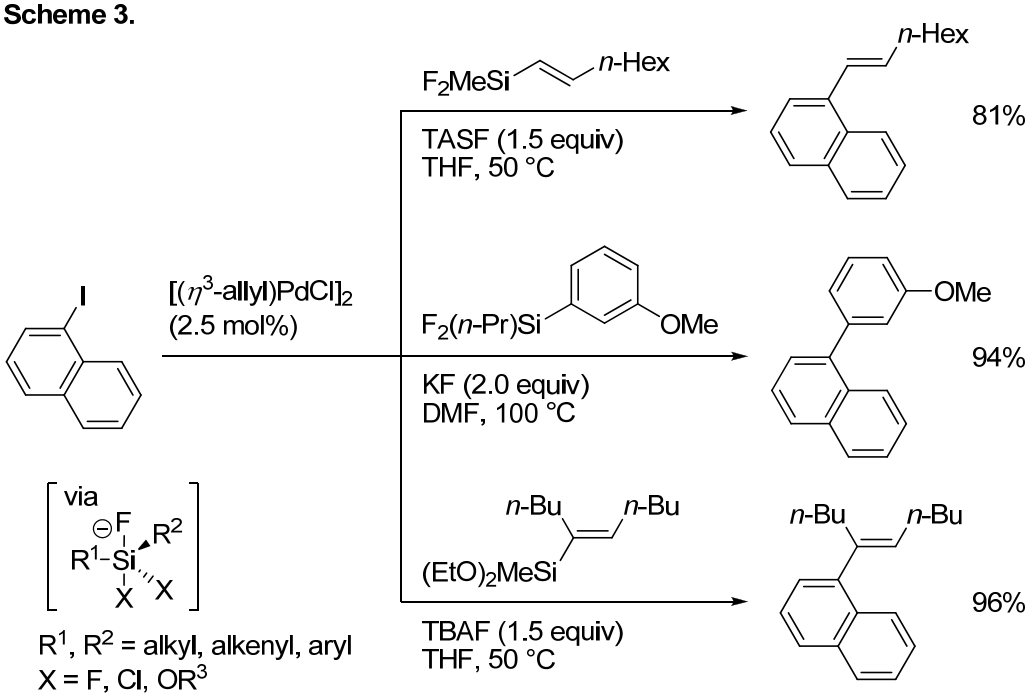
The silicon-based cross-coupling reaction has been extensively studied in the past two decades.[26] The first cross-coupling reaction using organosilicon compounds was reported by Tamao and Kumada using dipotassium pentafluorostyrylsilicate, a hexacoordinate silicate species. This paper clearly indicated that silicate species might participate in transmetalation with palladium(II) species generated by oxidative addition of organic halides to palladium(0) (Eq. 5).[27] Unfortunately, this protocol was not widely applicable, due possibly to saturated nature of hexacoordinate silicate.



(5)

In 1988, Hiyama and Hatanaka disclosed a different strategy for the silicon-based cross-coupling reaction producing pentacoordinate silicates in situ from tetragonal organofluorosilanes with a fluoride activator. Since then, this strategy has become the standard protocol for the silicon-based cross-coupling reaction (Scheme 3).[28] Later, this method has also been extended to the cross-coupling reaction of organoalkoxysilanes.[29]

Scheme 3.

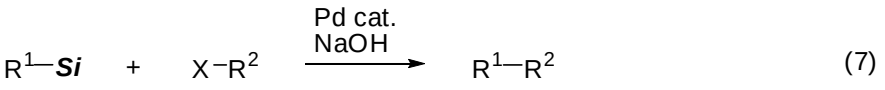


More recently, Mori/Hiyama and Denmark independently reported the use of organosilanols as the coupling agents.[30] Silanols, though relatively stable compared with halosilanes and alkoxysilanes, undergo the cross-coupling reaction even at room temperature, significantly milder reaction conditions than those reported for halosilanes and alkoxysilanes (Eq. 6).

$$R^1{-}Si(OH)R^2_2 \quad + \quad I{-}R^3 \xrightarrow[\text{rt to 60 °C}]{\text{Pd cat.}\ \text{TBAF}} R^1{-}R^3 \qquad (6)$$

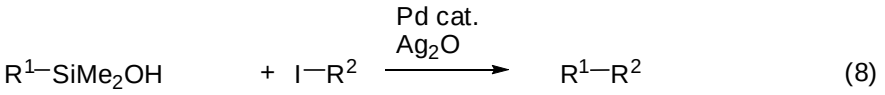
R^1 = alkenyl, aryl, alkynyl; R^2 = Me, *i*-Pr; R^3 = alkenyl, aryl

Although a fluoride additive successfully promotes the cross-coupling reaction of orgnanosilicon reagents, they are relatively expensive and often incompatible with several functional groups including common silyl protectors. Accordingly, application of the silicon-based protocol to multi-step organic synthesis of functionalized compounds has been hampered. To develop fluoride-free conditions, many efforts have been made: such bases as sodium hydroxide,[31] silver oxide,[30a,b] silanolate,[32] and cesium carbonate[33] were successfully demonstrated to be alternative promoters particularly for the cross-coupling reactions of halosilanes, alkoxysilanes, and silanols (Eqs. 7–10).



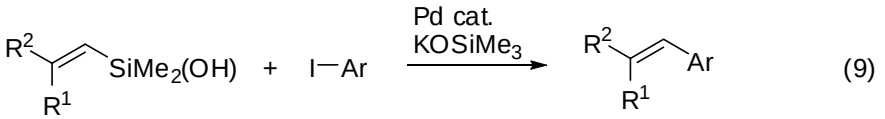
(7)

R^1 = aryl, alkenyl; ***Si*** = $SiEtCl_2$, $SiMeCl_2$, $Si(OMe)_3$
X = Cl, Br, I; R^2 = aryl, alkenyl

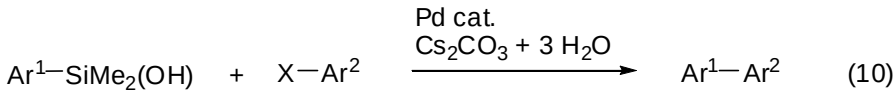


(8)

R^1 = aryl, alkenyl; R^2 = aryl, benzyl



(9)

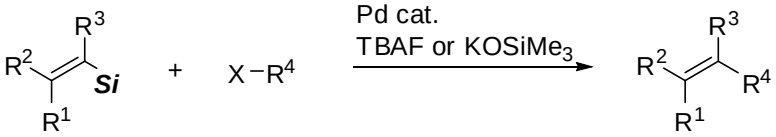


(10)

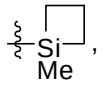
X = I, Br

Of many types of organosilicon compounds, tetraorganosilanes are considered to be ideal in view of their high stability and easy handling. Alkenyl- and aryltriorganosilanes survive many synthetic transformations, as is the case with triorganosilyl protecting groups, allowing their installation of a triorganosilyl group at even an early stage of complex natural product syntheses.[34] A wide range of (*E*)-, (*Z*)-, and α-substituted triorgano(vinyl)silanes are readily available by virtue of recent progress in transition metal-catalyzed hydrosilylation of alkynes.[35] Whereas a classical strategy involving silylation of arylmagnesium or -lithium reagents with triorganosilyl halides still serves as a convenient access to simple aryltriorganosilanes, the metal-catalyzed silylation of aryl halides with disilanes[36] or hydrosilanes[37] and direct silylation of Ar-H bonds[38] have gained significant synthetic value as highly chemoselective and atom economical alternatives to classical arylsilane synthesis. Highly stable alkenyl(triorgano)silanes that contain labile silacyclobutyl,[39] 2-pyridyl,[40] 2-thienyl,[41] electron-poor aryl,[42] benzyl,[43] and even phenyl[31b] groups have further raised the synthetic potential of tetraorganosilanes as the cross-coupling reagents because of their greater stability and robustness than conventional halosilanes, alkoxysilanes, and silanols (Eq. 11). They are considered to be convertible into organosilanols in situ upon treatment with TBAF or $KOSiMe_3$ and then to undergo cross-coupling reaction under mild conditions. Triallyl(aryl)silanes have also been introduced as stable but reactive

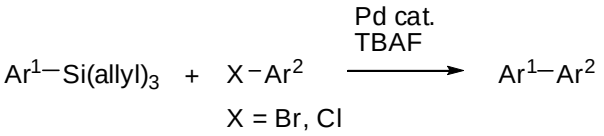
aryl(triorgano)silane reagents in the presence of TBAF (Eq. 12).[44]



(11)

Si =  ,  (R = 2-pyridyl, 2-thienyl, 3,5-$(CF_3)_2$-C_6H_3, benzyl, Ph)

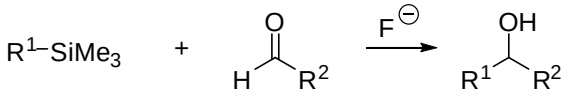
X = I, Br; R^4 = alkenyl, aryl



(12)

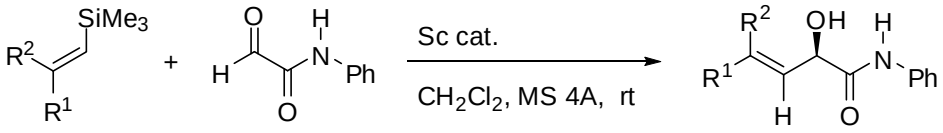
1,4- and 1,2-Addition reaction of organosilicon reagents

Organosilicon reagents undergo 1,4- and 1,2-addition reactions also. Not only enol silyl ethers and allylsilanes shown in Equations 1–3 but also vinyl- and arylsilanes participate in the reaction with aldehydes and ketones in the presence of fluoride activators,[45] Lewis acid catalysts,[46] or copper catalysts[47] (Eqs. 13–15). However, the scope is rather limited.



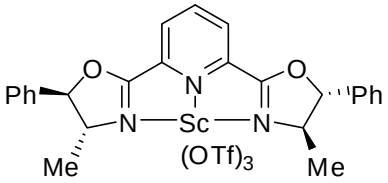
(13)

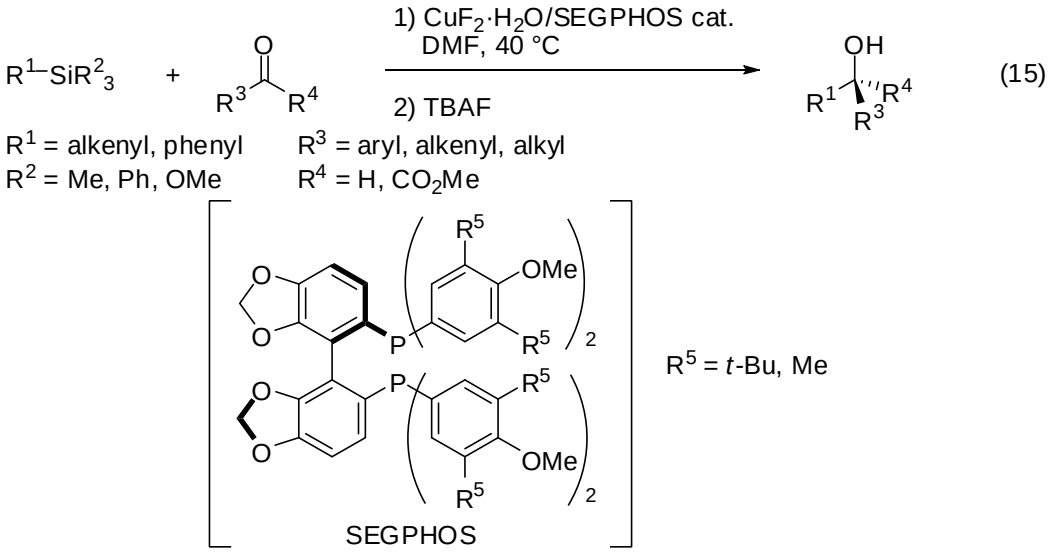
R^1 = alkenyl, aryl; R^2 = aryl, alkyl



(14)

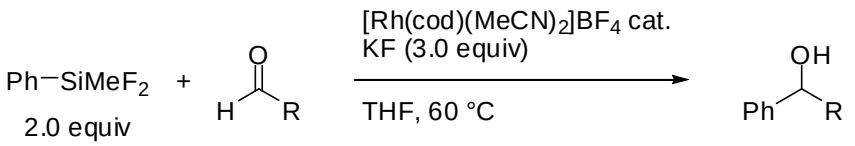
R^1, R^2 = alkyl, aryl





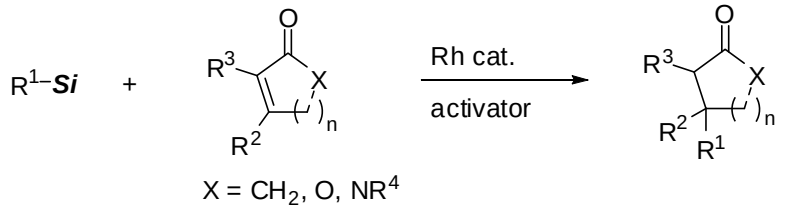
(15)

As is observed with the reactions of organoboron reagents, rhodium catalysis is also versatile and effective for 1,2-addition reactions of aryldifluorosilanes to aldehydes (Eq. 16)[48] and 1,4-addition reactions of arylsilanediols to α,β-unsaturated carbonyl compounds as reported first by Mori in 2001 (entry 1 of Table 1).[49] Chlorosilanes,[50] silicones,[51] and trialkoxy(organo)silanes[52] were also demonstrated to undergo the rhodium-catalyzed 1,4-addition reactions (entries 2– 4). By using (*S*)-binap as a ligand, highly enantioselective 1,4-addition reactions have been achieved with trialkoxy(organo)silanes (Eq. 17).[53] Nevertheless, stable tetraorganosilicon reagents remained yet to be employed for the rhodium-catalyzed reactions. The synthetic utility of the silicon-based rhodium-catalyzed reactions has been limited, due mostly to instability of these silicon reagents towards moisture, acid and/or base, to required use of fluoride additives in some cases to accelerate transmetalation to rhodium(I) species, and also to relatively harsh reaction conditions.

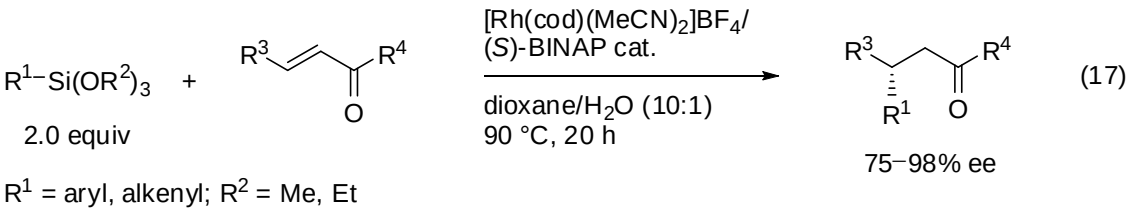


(16)

Table 1. Rhodium-catalyzed 1,4-addition reaction of organosilicon reagents to α,β-unsaturated compounds



entry	R^1–***Si*** (equiv)	electrophile	Rh cat.	activator	temp. (°C)
1[49]	Ar**SiEt(OH)$_2$** (1.0)	α,β-unsaturated esters, amides, and ketones	$[Rh(OH)(cod)]_2$	none	70
2[50]	Ph**SiCl$_2$Ph** (4.0)	α,β-unsaturated esters, amides, and ketones	$Rh(cod)_2BF_4$	NaF	100
3[51]	(Ph**SiMeO**)$_n$ (3.0)	α,β-unsaturated esters, and ketones	$[Rh(OH)(cod)]_2$	K_2CO_3	120
4[52]	R**Si(OR')$_3$** (2.0)	α,β-unsaturated esters, amides, and ketones	$[Rh(cod)(MeCN)_2]BF_4$	none	90



R^1 = aryl, alkenyl; R^2 = Me, Et

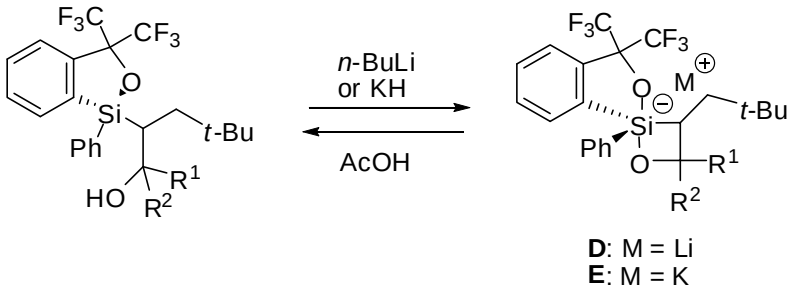
Thus, the silicon reagents employed in the transition metal-catalyzed transformations discussed above are mostly sensitive to moisture, base, and acid due to the presence of electron-withdrawing heteroatoms on silicon, need to be activated by highly nucleophilic or basic activators, and consequently, appear less attractive for synthetic chemists. The author has considered that an ideal organosilicon reagent should be stable tetraorganosilanes which can undergo transmetalation by the aid of a mild activator. A clue to this goal turned out to be available by virtue of intramolecular activation of organosilicon compounds.

Intramolecular activation of organosilicon compounds in organic synthesis

Structures of pentacoordinate silicon species have extensively studied by generation through intramolecular coordination of negatively charged oxygen atoms.[54]

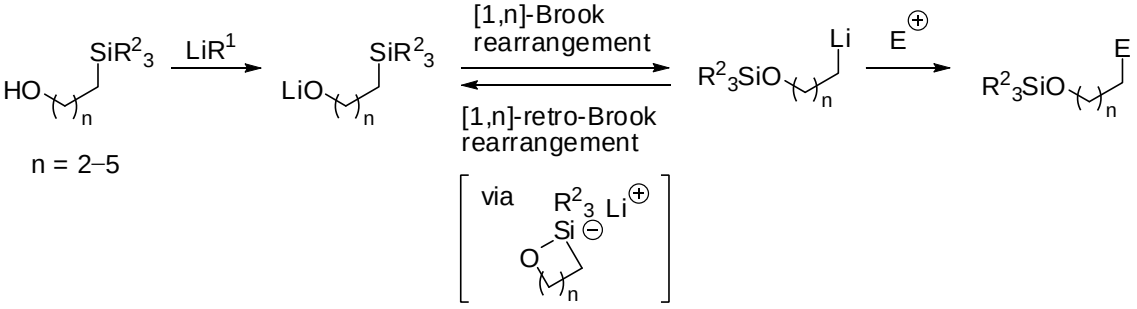
For example, Kawashima, Iwama, and Okazaki reported synthesis and X-ray crystallographic analysis of pentacoordinate 1,2-oxasiletanides **D** and **E** as models of possible intermediates of the Peterson olefination (Scheme 4).[55] X-Ray analysis of **E** has indicated that it contains a distorted trigonal bipyramidal structure, wherein electron-withdrawing two oxygen atoms occupy apical positions.

Scheme 4.

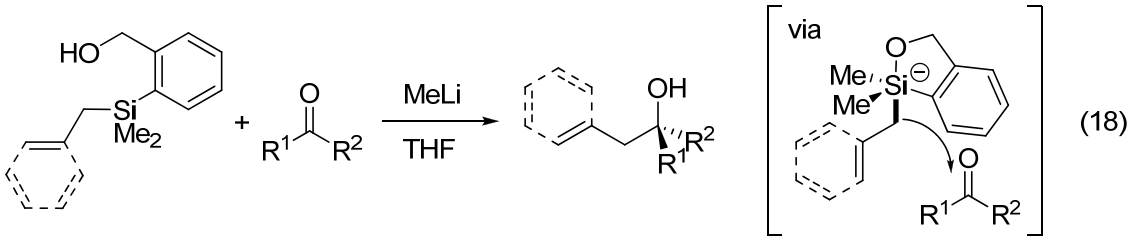


The Brook rearrangement, an intramolecular transfer of silyl groups from carbon to oxygen, is an example of an intramolecular attack of a negatively charged oxygen atom to silicon. This transformation was applied to organic synthesis by converting organosilicon compounds having a proximal hydroxy group into reactive organometallic species to form C–C bonds upon reaction with various electrophiles (Scheme 5).[56] Further studies have shown that various organolithium compounds having siloxy groups at different positions can be prepared in situ by the [1,n]-Brook rearrangement (n = 2–5) of lithium alkoxides bearing a C–Si bond. Formation of Si–O bonds that are stronger than Si–C bonds is a driving force.[57]

Scheme 5.



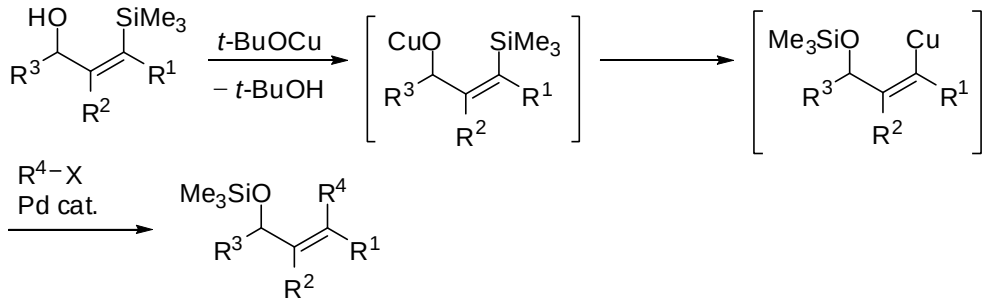
Such intramolecular activation is applied to cleavage of a C–Si bond to produce highly nucleophilic species. Hudrlik and coworkers showed that allyl- and benzyl[2-(hydroxymethyl)phenyl]dimethylsilanes transfer allylic and benzylic groups to carbonyls upon treatment with a base presumably via pentacoordinate silicate intermediates (Eq. 18).[58]



(18)

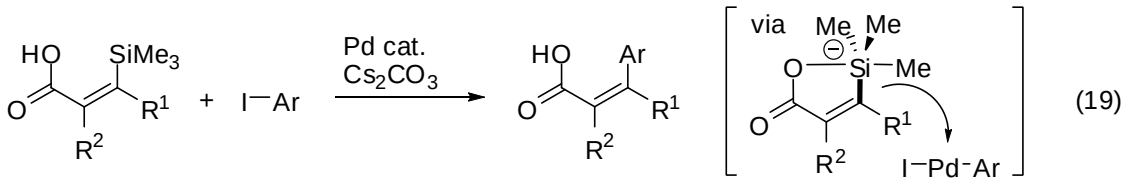
The presence of a proximal hydroxy group has also been reported to promote the transmetalation from silicon to late transition metals by Takeda and coworkers. They observed that copper(I) *t*-butoxide treatment of trimethylsilylalkenes having a proximal hydroxy group *cis* to the silyl group induced the cross-coupling reaction with aryl and alkenyl halides in the presence of a palladium catalyst (Scheme 6) and attributed the successful reaction to alkenylcopper species generated through the Brook-type rearrangement.[59]

Scheme 6.



R^4 = aryl, alkenyl; X = I, Br

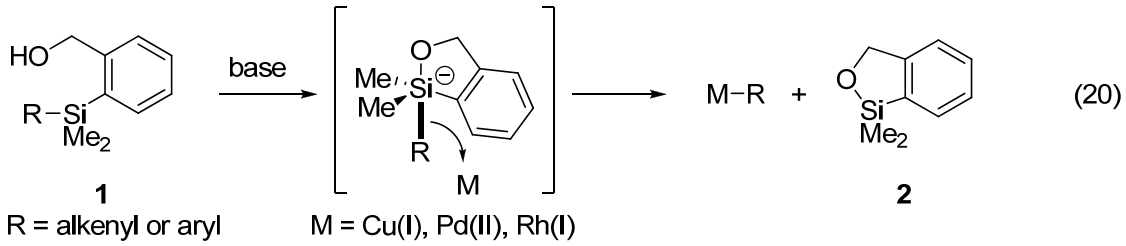
Shindo and coworkers also demonstrated a similar effect of a proximal carboxyl group and achieved a fluoride-free cross-coupling reaction of alkenyl(trimethyl)silanes with aryl iodides (Eq. 19).[60]



(19)

Apparently, these proximal oxygen nucleophiles accelerate transmetalation from stable tetraorganosilicon reagents to late transition metals without fluoride activators. A severe limitation in these examples is that the silylalkenes must always contain a nucleophilic oxygen moiety.

With these facts in mind, the author envisioned that alkenyl- or aryl[2-(hydroxymethyl)phenyl]dimethylsilanes (**1**) would be able to transfer the activator-free alkenyl and aryl groups selectively to a late transition metal catalyst via intramolecular coordination of the hydroxy group upon base treatment (Eq. 20).



1
R = alkenyl or aryl

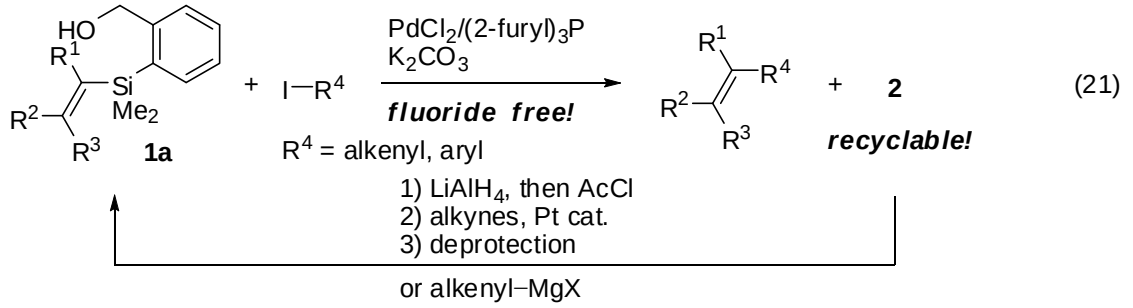
M = Cu(I), Pd(II), Rh(I)

2

(20)

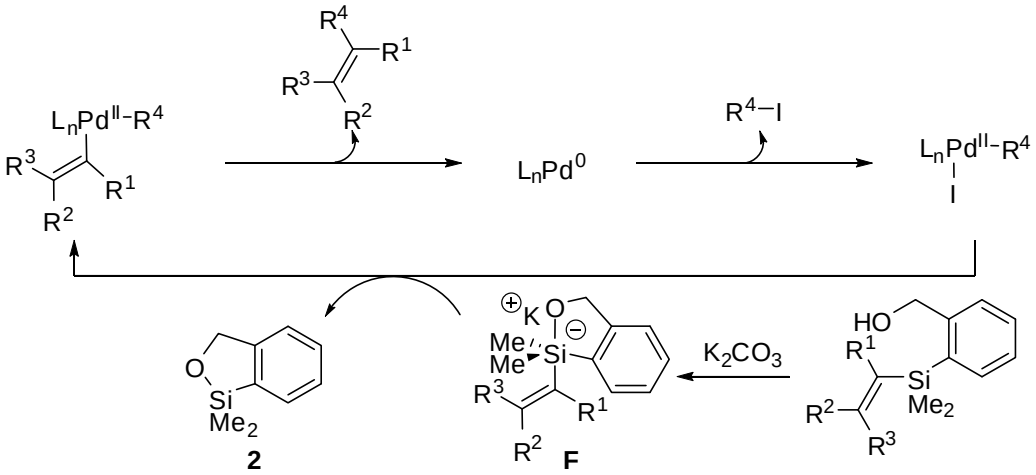
This reagent design has been demonstrated to work well as expected. For example, the cross-coupling reaction of alkenyl[2-(hydroxymethyl)phenyl]dimethylsilanes with aryl and alkenyl iodides proceeds in the presence of a palladium catalyst prepared *in situ* from $PdCl_2$ and $(2\text{-furyl})_3P$ and a K_2CO_3 mild base in DMSO in highly regio- and stereospecific manners (Eq. 21).[61] Details will be described in Chapter 2. The reaction tolerates a diverse range of functional groups including silyl ethers, which are incompatible with the conventional fluoride activation. Cyclic silyl ether **2**, a silicon residue of the present protocol, is readily recovered by distillation on gram-scale experiments and converted back to organosilicon reagents through reduction with $LiAlH_4$ followed by hydrosilylation of alkynes. The reaction of **2** with alkenyl nucleophiles such as Grignard reagents provides an alternative access back to the alkenylsilanes. Intramolecular coordination of an alkoxide derived from the proximal hydroxy group takes place upon treatment with a base to efficiently form

pentacoordinate silicate species **F** having a transferable alkenyl group possibly at its apical position, and thus responsible for the cross-coupling reaction under the conditions significantly milder than those ever reported for the silicon-based reactions (Scheme 7).

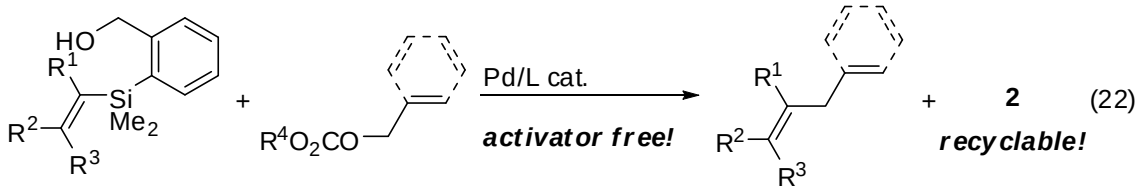


(21)

Scheme 7.

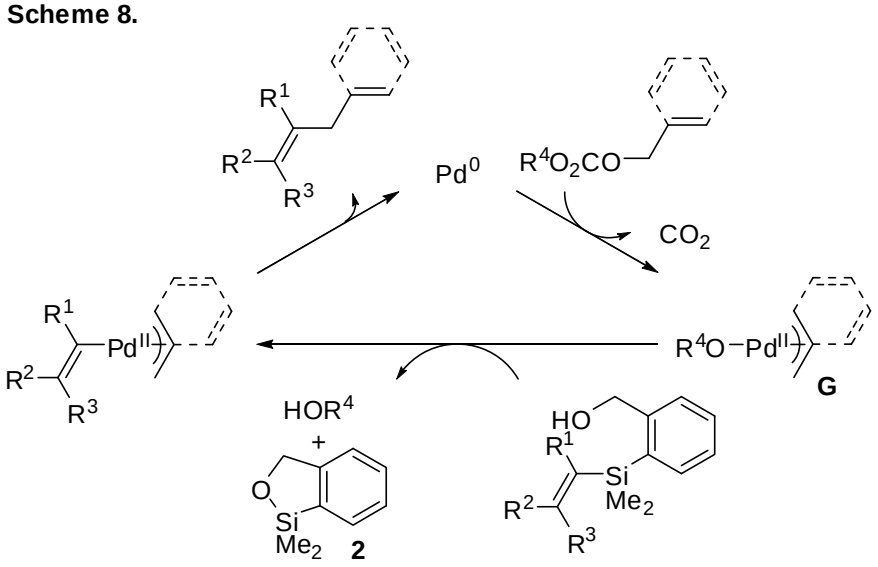


Also demonstrated is the cross-coupling reaction of alkenylsilanes with allylic and benzylic carbonates in the absence of a base to give a diverse range of 1,4-diene and 3-arylpropene products (Eq. 22).[62] In this particular transformation, the oxidative addition of allylic and benzylic carbonates to palladium(0) is accompanied by decarboxylation to generate palladium alkoxide **G**, which acts as a base to promote the intramolecular activation–transmetalation (Scheme 8).

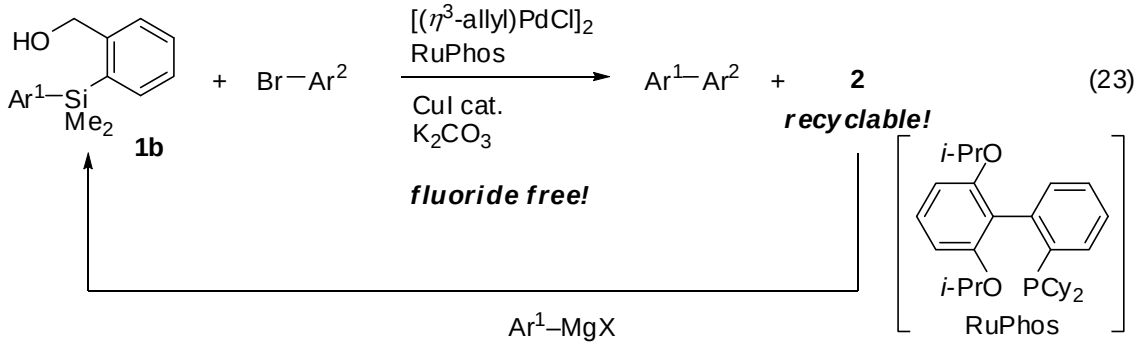


(22)

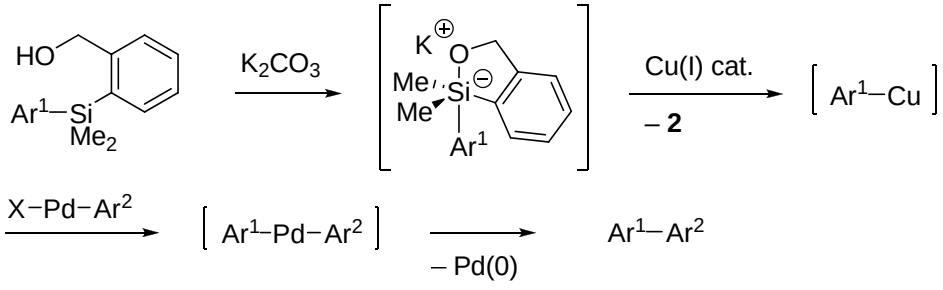
Scheme 8.



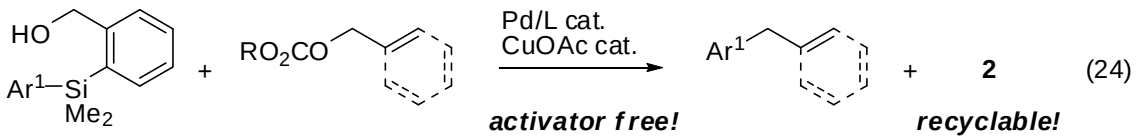
In Chapter 3, the cross-coupling reaction of aryl[2-(hydroxymethyl)phenyl]dimethylsilanes is discussed (Eq. 23). Use of a copper(I) co-catalyst is essential for the success of the present cross-coupling reaction. Transmetalation is considered to proceed from silicon to copper and then to palladium (Scheme 9).[63] Cyclic silyl ether **2** is again readily recovered and reused to produce the starting arylsilanes by the reaction with various aryl Grignard reagents.



Scheme 9.



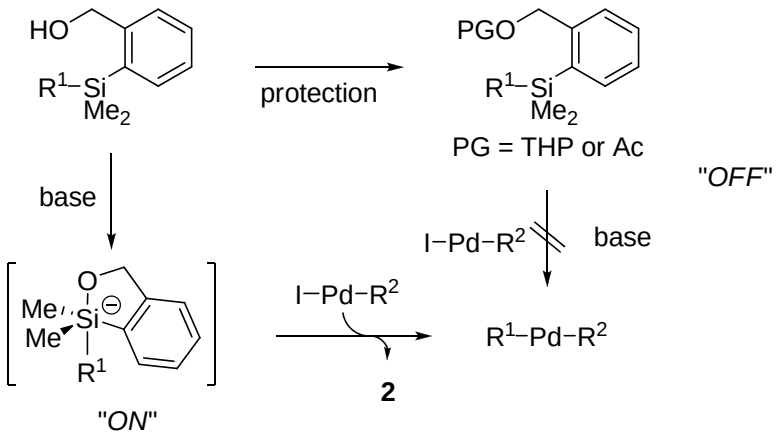
Arylsilanes also participate in the cross-coupling reaction with allylic and benzylic carbonates in the presence of palladium and copper catalysts without any activator to afford a wide variety of 3-arylpropenes and diarylmethanes (Eq. 24).



(24)

The present biaryl synthesis is further extended to a synthetic protocol for sequence-defined oligoarenes. Since the enhanced reactivity of the silicon reagents can be "turned off" simply upon protection of the hydroxy group (Scheme 10), the compounds having halogen and OH-protected groups are found to serve as promising coupling partners for the iterative cross-coupling sequence. Deprotection followed by subsequent cross-coupling with the brominated arylsilanes allows an iterative approach to oligoarenes (Scheme 11). Both THP-protection and acetyl-protection tolerate the present conditions, showing the flexibility of the present method depending on the functional groups of target molecules. Unsymmetrically disilylated quinquethiophene **3** and highly conjugated protected oligoarenylsilane **4** are thus efficiently synthesized (Figure 1).[64]

Scheme 10.



Scheme 11.

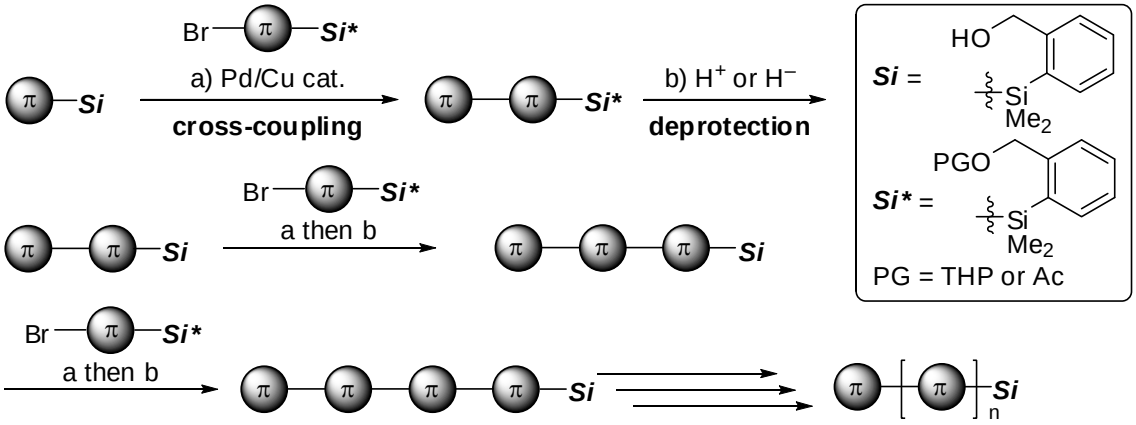
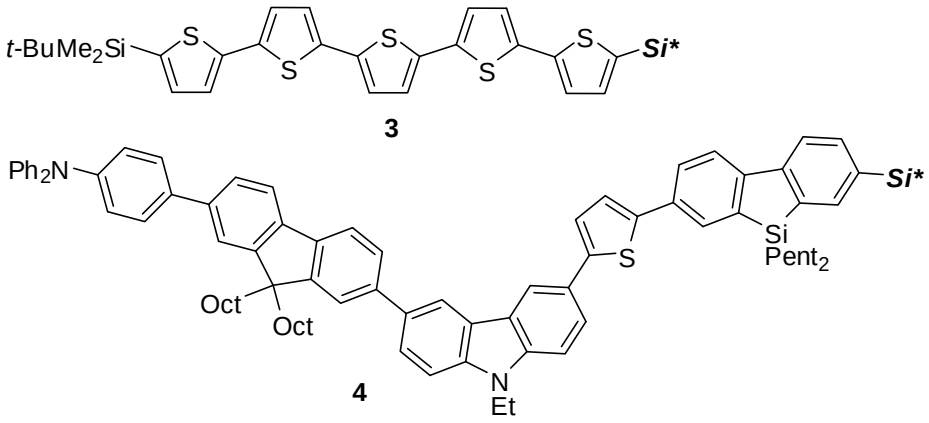
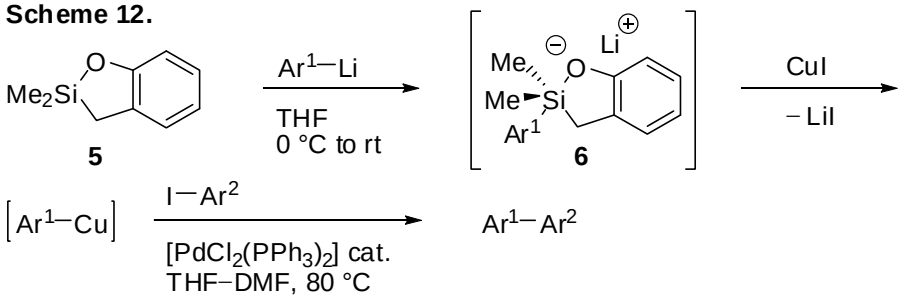


Figure 1.



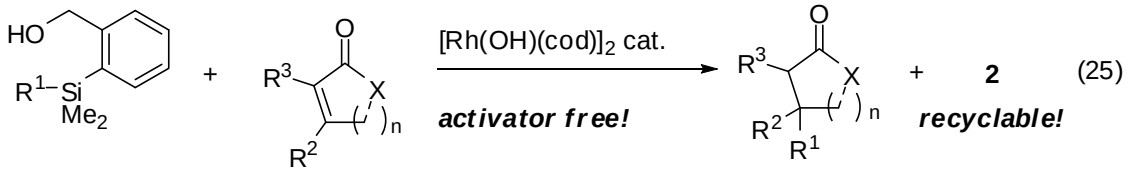
Intramolecular activation strategy for cross-coupling reaction has been studied independently by Tamao and his coworkers, who have demonstrated that arylsilicates **6** generated in situ from cyclic silyl ether **5** and Ar^1–Li undergo transmetalation with Cu(I) and the resulting arylcopper species participate in the palladium-catalyzed cross-coupling reaction with aryl iodides to afford biaryls (Scheme 12).[65]

Scheme 12.



Chapter 4 describes that rhodium-catalyzed 1,4-addition reaction of

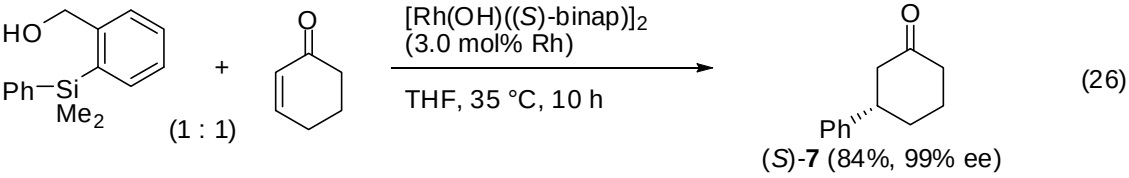
tetraorganosilicon reagents across various electron-deficient olefins proceeds smoothly with high chemoselectivity under mild conditions and is applicable to gram-scale synthesis without any activators (Eq. 25).[66] It is worth noting that the silicon reagents are more reactive than such conventional organosilicon reagents as aryl(trialkoxy)silanes, and competitive to arylboronic acids, which are most frequently used for rhodium-catalyzed reactions. Moreover, α-substituted vinylsilanes can be successfully applied to the present reaction, whereas the corresponding vinylboronic acids are thermally unstable and thus rarely used in the similar transformations.[67]



(25)

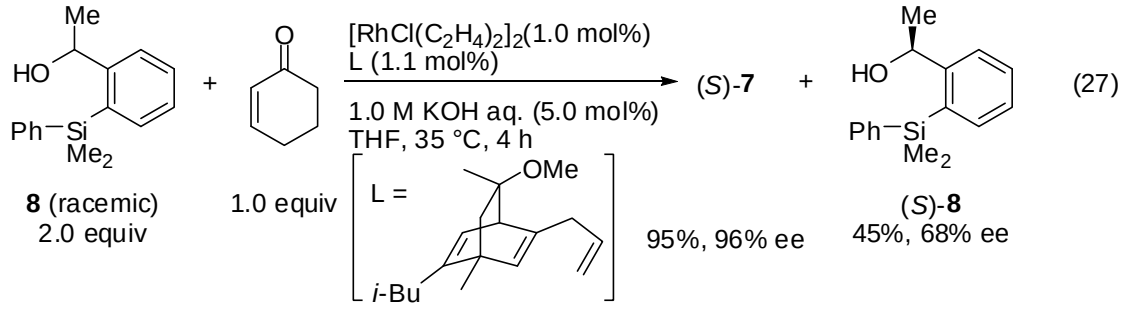
R^1 = alkenyl, aryl, $PhSiMe_2$; X = CH_2, O, NR^4

Using a $[Rh(OH)((S)\text{-binap})]_2$ as a catalyst, enantioselective 1,4-addition reaction of phenylsilane to 2-cyclohexen-1-one was successfully carried out to afford the corresponding optically active ketone (*S*)-**7** of 99% ee in 84% yield (Eq. 26).



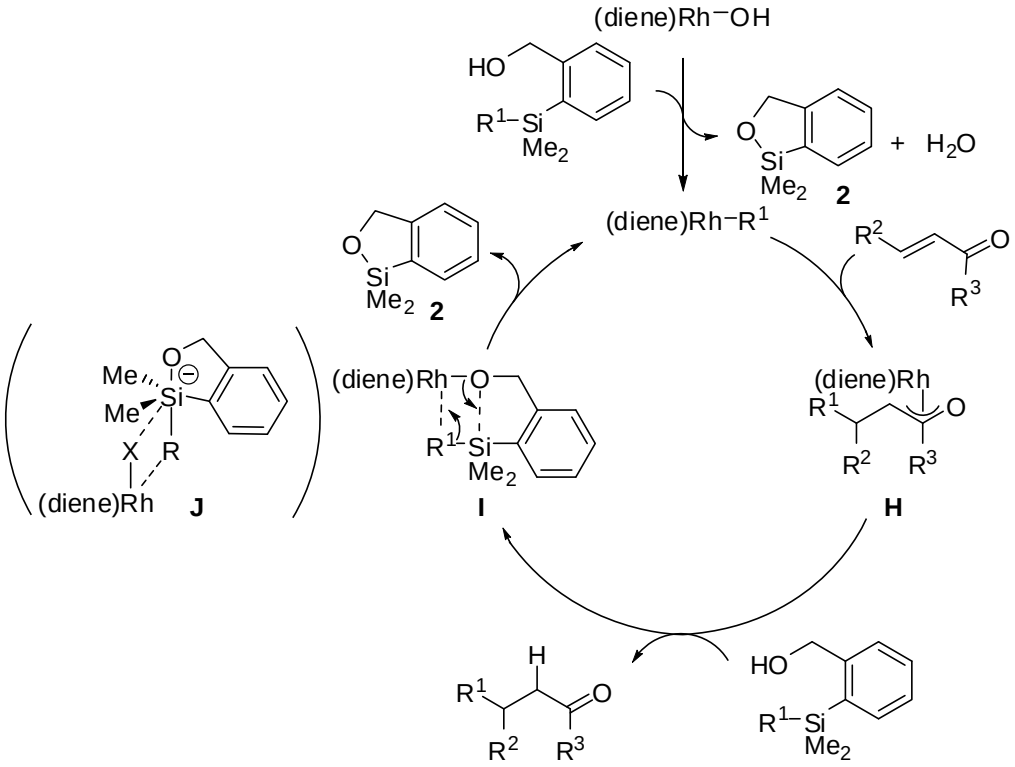
(26)

Based on the observed kinetic resolution of racemic chiral phenylsilane reagent **8** in the presence of a rhodium/chiral diene catalyst (Eq. 27), a catalytic cycle is proposed that involves rhodium enolate **H**, which acts as a base to form probably R-equatorial pentacoordinate silicate–rhodium species **I** rather than R-apical species **J** (Scheme 13).



(27)

Scheme 13.



In summary, the present Thesis demonstrates highly stable organo[2-(hydroxymethyl)phenyl]dimethylsilanes undergo transition metal-catalyzed reactions through smooth transmetalation by the aid of the proximal hydroxy group. The reagents allow cross-coupling and 1,4-addition reactions in excellent chemo-, stereo- and regioselective manners under conditions significantly milder than those ever reported for other silicon-based reagents. The fact is also significant that cyclic silyl ether **2**, a silicon residue of the present protocol, is readily recovered by distillation on gram-scale experiments and is converted back to the organosilicon reagents, because no precedents are available of such metallic recycle system in the cross-coupling and 1,4-addition reactions. In view of green chemistry, these characteristic features of the tetraorganosilicon reagents are definitely attractive for many synthetic chemists as a favorable alternative to other conventional organometallic reagents.

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Chapter 2

Palladium-catalyzed Cross-coupling Reactions of Alkenyl[2-(hydroxymethyl)phenyl]dimethylsilanes

Easily accessible and highly stable alkenyl[2-(hydroxymethyl)phenyl]dimethylsilanes smoothly undergo transmetalation with a palladium catalyst and participate in the cross-coupling reaction with various aryl and alkenyl iodides in highly regio- and stereospecific manners in the presence of K_2CO_3 as a mild basic activator. This activator is not necessary for the cross-coupling reaction of the alkenylsilanes with allylic and benzylic carbonates. These reactions tolerate a wide range of functional groups including silyl ethers. The co-produced silicon residue is readily isolated in gram-scale experiments and reused for the synthesis of the alkenylsilane reagents. Intramolecular coordination of a proximal hydroxy group to a silicon atom is considered to efficiently form pentacoordinate silicates having a transferable alkenyl group possibly at an apical position, and thus responsible for the cross-coupling reaction under the conditions significantly milder than those ever reported for the silicon-based reactions.

1. Introduction

The transition metal-catalyzed cross-coupling reaction of alkenylmetals of main group elements with organic halides or pseudohalides provides a regio- and stereochemically well-defined access to a range of substituted ethenes including conjugated arylethenes and dienes as well as non-conjugated 1,4-dienes and 3-arylpropenes that are ubiquitous in organic materials, pharmaceuticals, pesticides, and natural products.[1] Among many protocols, the one based on silicon is gaining increasing importance and interest in view of high stability and non-toxicity of silicon reagents.[2] Another beneficial aspect of the transformation is well-established metal-catalyzed alkyne-hydrosilylation chemistry that makes a variety of alkenylsilanes readily available in regio-, stereo-, and chemoselective manners.[3] However, the silicon-based protocol has rarely been employed by synthetic chemists irrespective of such attractive properties of organosilicon compounds. Since the pioneering work by Hiyama and Hatanaka,[4] in situ formation of pentacoordinate silicates by use of alkenyl(halo)silanes or alkenyl(alkoxy)silanes in the presence of a fluoride activator has been the standard strategy for the silicon-based cross-coupling.[2] However, halosilanes and alkoxysilanes suffer from drawbacks like sensitivity to moisture, base, and/or acid. Recently, a significant breakthrough has been achieved that uses relatively stable alkenylsilanols[5] or "masked-alkenylsilanols",[6] highly stable tetraorganosilicon reagents. These new technologies have raised the synthetic potential of alkenylsilanes as the cross-coupling reagents for synthesis of conjugated organic materials and natural products.[7] Thus, the remaining synthetic problem in the silicon-based protocol is the use of fluoride activators that are relatively expensive and incompatible with some functional groups including common silyl ethers. Fluoride-free cross-coupling reaction of alkenylsilanes has been realized but in limited examples. Hereby activation is achieved with NaOH,[8] $KOSiMe_3$,[9] or stoichiometric amounts of transition metal promoters[10] particularly for alkenyl(halo)silanes, alkenyl(alkoxy)silanes, or alkenylsilanols.

Recently, Takeda[11] and Shindo[12] reported fluoride-free cross-coupling reactions through intramolecular coordination of trimethylsilylalkenes having a proximal hydroxy group *cis* to the silyl group (Figure 1). These examples clearly show that intramolecular coordination by a negatively charged oxygen nucleophile accelerates transmetalation from silicon to a late transition metal in highly efficient manners. However, these

precedents are restricted to silylalkenes that have an oxygen activating functionality at an appropriate position. Accordingly, the author has embarked on design of stable tetraorganosilicon reagents that have an activating organofunctional group and an independent transferable group. A proto-type of this design was suggested by Hudrlik and coworkers, who showed that allyl- or benzyl[2-(hydroxymethyl)phenyl]dimethylsilanes could transfer an allyl or benzyl group to carbonyl compounds.[13] The author envisioned that upon treatment with a certain base alkenyl[2-(hydroxymethyl)-phenyl]dimethylsilanes would form penta coordinate silicate intermediates having a rather electron-withdrawing alkenyl group at an apical position, and thus selectively transfer the alkenyl group. The reagent should be able to deliver a variety of alkenyl groups to electrophiles, since the hydroxy group functions only as an activator and has nothing to do with alkenyl groups. This reagent design was found to work well as the author expected.[14]

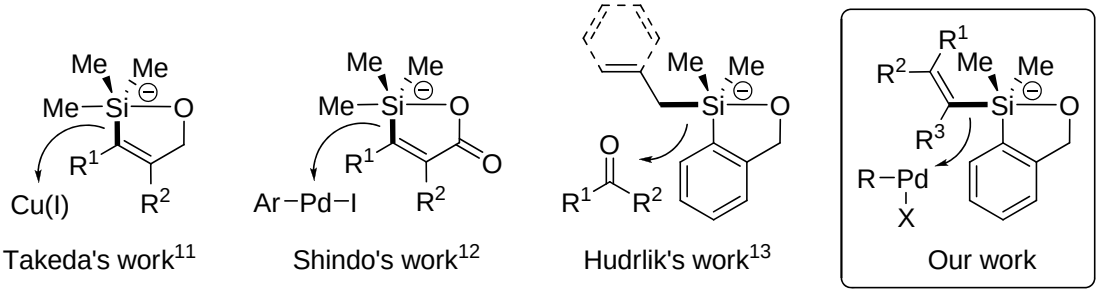


Figure 1. Organic group transfer from silicon to an electrophile assisted by an intramolecular attack of a negatively charged oxygen.

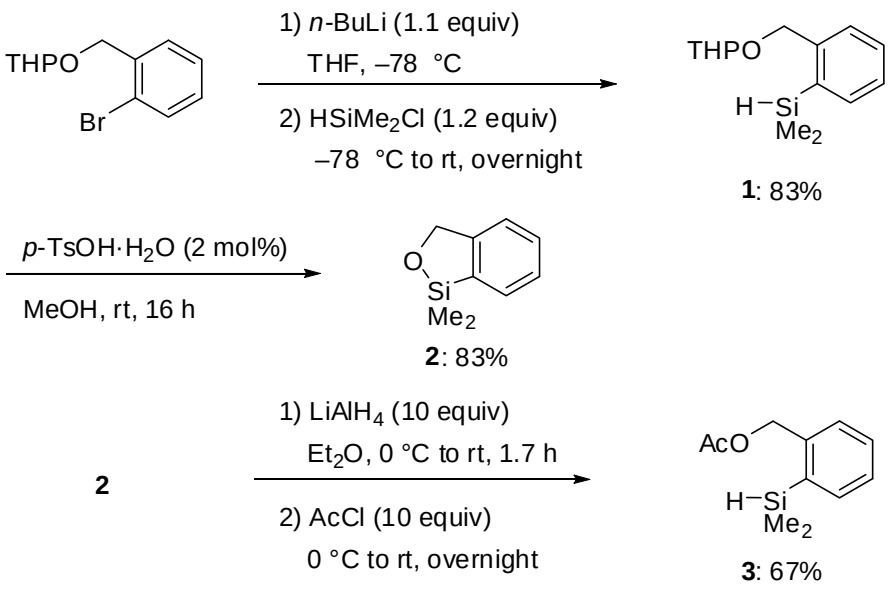
In this Chapter, the author first describes the synthesis of the alkenylsilanes by transition metal-catalyzed stereo- and regioselective hydrosilylation of alkynes or by ring-opening reaction of cyclic silyl ether, 1,1-dimethyl-2-oxa-1-silaindan, with various alkenyl Grignard reagents. He then discusses in detail the palladium-catalyzed cross-coupling reactions of thus prepared alkenylsilanes with aryl and alkenyl iodides as well as allylic and benzylic carbonates. He also demonstrates recovery and reuse of the silicon residue, cyclic silyl ether, by gram-scale experiments.

2. Results and discussion

2.1 Preparation of alkenyl[2-(hydroxymethyl)phenyl]dimethylsilanes

Key synthetic precursors **1**–**3** of alkenyl[2-(hydroxymethyl)phenyl]dimethylsilanes are readily prepared from 2-bromobenzyl alcohol (Scheme 1). Dimethyl[2-(2-tetrahydro-2*H*-pyran-2-yloxymethyl)phenyl]silane (**1**) was obtained by lithiation of THP-protected 2-bromobenzyl alcohol followed by trapping with chloro(dimethyl)silane. Attempted THP deprotection of **1** to obtain an unprotected hydrosilane failed but gave cyclic silyl ether **2**, which turned out to be another versatile starting silicon reagent for the alkenylsilanes (vide infra). Treatment of **2** with $LiAlH_4$ followed by in situ acetylation using acetyl chloride afforded acetyl-protected hydrosilane **3**, a reagent complementary to THP-protected hydrosilane **1**.

Scheme 1.

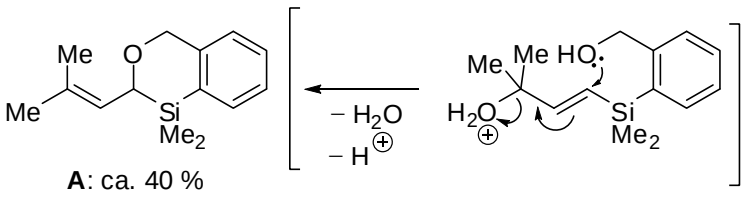


With the key starting silicon reagents in hand, the author then examined hydrosilylation of alkynes using hydrosilane **1** or **3** to prepare alkenyl[2-(hydroxymethyl)phenyl]dimethylsilanes (Table 1). At the onset, the author envisaged that protected hydrosilanes **1** and **3** would act in a manner similar to phenyl(dimethyl)silane, a hydrosilane frequently used for hydrosilylation of alkynes. Indeed, the equimolar reaction of hydrosilane **1** with 1-octyne in the presence of 0.1 mol% of platinum–1,3-divinyl-1,1,3,3-tetramethyldisiloxane [Pt(dvds)] and P(*t*-Bu)$_3$ in hexane at 0 °C to room temperature gave (*E*)-[2-(hydroxymethyl)phenyl]dimethyl(1-octen-1-yl)-silane (**4a**) in 81% yield with excellent regio- and stereoselectivities after acidic

deprotection of the THP group with *p*-TsOH in MeOH (entry 1). The same hydrosilylation procedure with **3** followed by basic deprotection of the acetyl group with K_2CO_3 in MeOH–H_2O also afforded **4a** in 82% yield (entry 2). Thus, it is possible to choose either of the hydrosilane reagent, **1** or **3**, depending on the functional group involved in a target alkenylsilane. Fair stability of the silicon reagents toward an acid or base is demonstrated by the facts that **4a** can be purified by silica gel column chromatography without any decomposition and that **4a** can be quantitatively recovered after treatment with a stoichiometric amount of an aq. 1 M HCl or 1 M NaOH solution in THF at 50 °C for 24 h.

Under the standard conditions, alkenyl[2-(hydroxymethyl)phenyl]dimethylsilanes (**4b**–**4f**) having a functional group such as cyano, ester, chloro, siloxy, or *N*-phthalimide were prepared in good yields (entries 3–7), whereas acetate **4g** was obtained in only 27% yield due to formation of a significant amount of deacetylated product during THP deprotection (entry 8). Hydrosilylation of 1-methyl-3-butyn-2-ol gave the corresponding alkenylsilane (**4h**) in 43% yield and allylsilane **A** (ca. 40% yield), derived probably from an intramolecular S_N2' type attack of the hydroxy group assisted by an acid catalyst (entry 9 and Scheme 2). Conjugated butadienylsilane **4i** and (*E*)-styrylsilane **4j** were prepared in good yields from 2-methyl-1-buten-3-yne and phenylacetylene, respectively (entries 10 and 11). An internal alkyne, 4-octyne, also underwent the present hydrosilylation stereoselectively to give (*E*)-4-octenylsilane **4k** (entry 12).

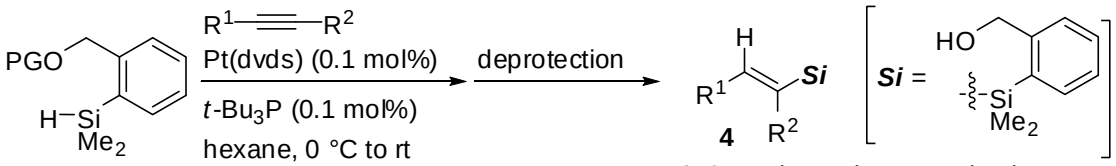
Scheme 2.



A: ca. 40 %

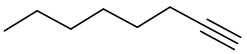
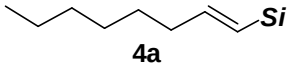
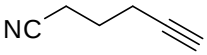
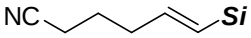
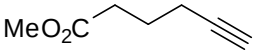
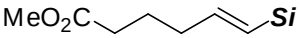
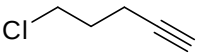
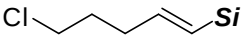
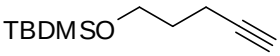
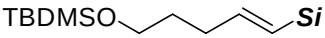
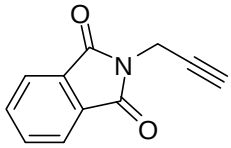
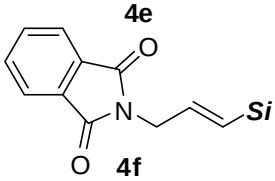
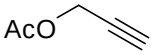
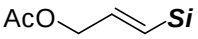
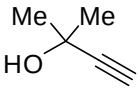
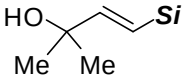
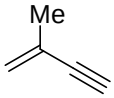
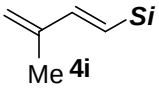
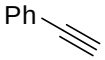
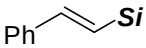
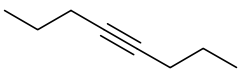
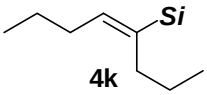
Ruthenium-catalyzed hydrosilylation has recently emerged as a unique tool for preparation of (*Z*)-alkenylsilanes via *trans*-addition of hydrosilanes across alkynes.[15] Employing the procedure reported by Ozawa and coworkers,[6f] (*Z*)-styrylsilane **4l** was prepared in 72% yield by the hydrosilylation of phenylacetylene with **1** in the presence of a ruthenium catalyst followed by acidic deprotection (Eq. 1).

Table 1. Preparation of alkenyl[2-(hydroxymethyl)phenyl]dimethylsilanes **4** via hydrosilylation of alkynes catalyzed by Pt/*t*-Bu_3P using hydrosilane **1** or **3** followed by deprotection[a]

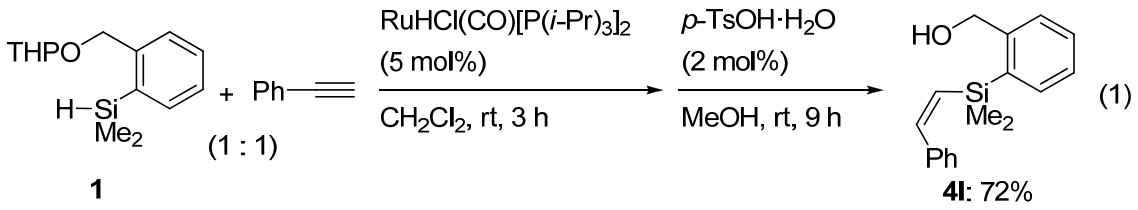


PG = THP (**1**); Ac (**3**)

>95% regio- and stereoselective

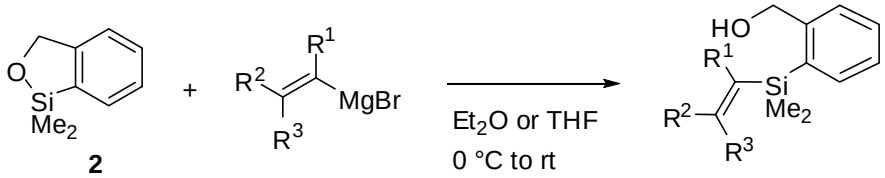
entry	alkyne	hydrosilane	time (h)	alkenylsilane	yield (%)[b]
1		**1**	2	 **4a**	81
2		**3**	4		82
3		**1**	22[c]	 **4b**	84
4		**1**	22	 **4c**	68
5		**1**	3	 **4d**	71
6		**3**	3	 **4e**	93
7		**1**	3	 **4f**	72
8		**1**	3	 **4g**	27[d]
9		**1**	5	 **4h**	43
10		**1**	24	 **4i**	57
11		**1**	2	 **4j**	84
12		**1**	18[e]	 **4k**	81

[a]The reaction was carried out using an alkyne (1.0 equiv), a hydrosilane (1.0 equiv), Pt(dvds) (0.1 mol%), and P(*t*-Bu)$_3$ (0.1 mol%) in hexane at 0 °C to rt. Deprotection was carried out using *p*-toluenesulfonic acid monohydrate (2 mol%) in MeOH at rt for 2–12 h (for **1**) or K_2CO_3 (20 equiv) in MeOH–H_2O (1 : 1) at 50 °C for 24–60 h (for **3**). [b]Isolated yields. [c]Hydrosilylation was carried out at rt for 19 h and then at 50 °C for 3 h. [d]Deacetylated product was also obtained in 49% yield. [e]Hydrosilylation was carried out at rt for 4 h and then at 50 °C for 14 h.



(1)

Ring-opening reactions of cyclic silyl ether **2** with alkenyl Grignard reagents represent another way to prepare various alkenyl[2-(hydroxymethyl)phenyl]dimethylsilanes (Eq. 2). The procedure is straightforward and useful particularly when the corresponding Grignard reagents and/or alkenyl halides are readily available from commercial sources.



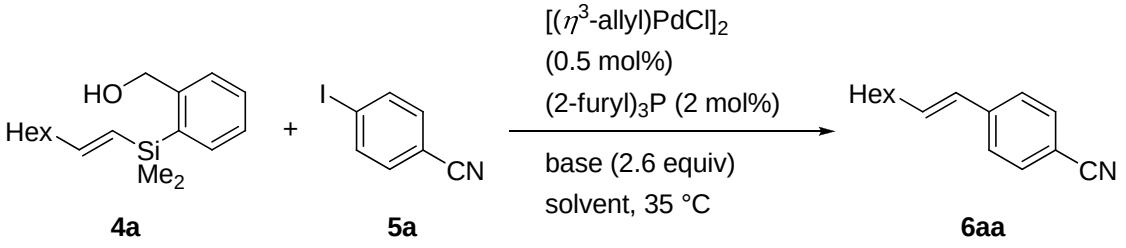
(2)

$R^1 = R^2 = R^3 = H$: **4m** (81%)
$R^1 = R^2 = H$; $R^3 = Me$: **4n** (94%, *Z* : *E* = 94 : 6)
$R^1 = Me$; $R^2 = R^3 = H$: **4o** (89%)
$R^1 = Ph$; $R^2 = R^3 = H$: **4p** (56%)
$R^1 = H$; $R^2 = R^3 = Me$: **4m** (71%)

2.2 Cross-coupling reaction of alkenyl[2-(hydroxymethyl)phenyl]dimethylsilanes with aryl and alkenyl iodides

To prove the viability of the above discussed reagent design, examined first was the reaction of (*E*)-1-octenylsilane **4a** (0.39 mmol) with 4-cyanoiodobenzene (**5a**: 0.30 mmol) in the presence of $[(\eta^3\text{-allyl})PdCl]_2$ (0.5 mol%), tri-2-furylphosphine (2.0 mol%), and a metal carbonate salt (0.78 mmol) at 35 °C (Table 2). Among the bases examined, use of inexpensive K_2CO_3 in a polar DMSO solvent turned out to be satisfactory and gave (*E*)-1-(4-cyanophenyl)-1-octene (**6aa**) quantitatively (entry 3), whereas relatively more basic Cs_2CO_3 was best in THF (entry 4). Na_2CO_3 was completely ineffective for the present coupling reaction even in DMSO (entry 1). Stronger bases like NaOH and *n*-BuLi were also effective in THF (entries 5 and 6), showing base flexibility to tune reaction conditions depending on substrate structures.

Table 2. Cross-coupling reaction of (*E*)-[2-(hydroxymethyl)phenyl]dimethyl(1-octenyl)silane (**4a**) with 4-cyanoiodobenzene (**5a**)[a]



4a **5a** **6aa**

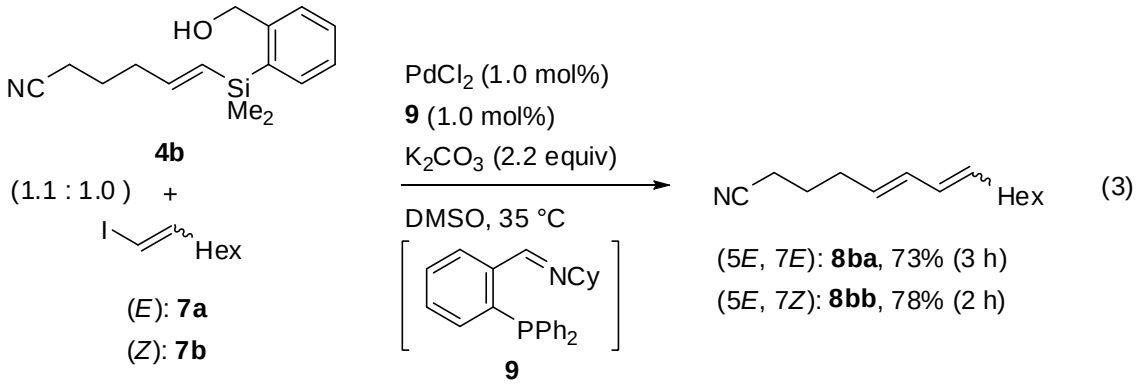
entry	base	solvent	time (h)	yield (%)[b]
1	Na_2CO_3	DMSO	31	5
2	K_2CO_3	THF	48	44
3	K_2CO_3	DMSO	5	100
4	Cs_2CO_3	THF	19	88
5	10 M NaOH aq.	THF	5	93
6[c]	*n*-BuLi	THF	1.5	96

[a]The reaction was carried out using **4a** (0.39 mmol), **5a** (0.30 mmol), a base (0.78 mmol), [(η^3-allyl)PdCl]$_2$ (0.5 μmol), and (2-furyl)$_3$P (2.0 μmol) in a solvent (0.75 mL) at 35 °C. [b]Estimated by GC using pentadecane as an internal standard. [c]**4a** was treated with *n*-BuLi (0.39 mmol) in THF at 0 °C to room temperature before addition of **5a**, $PdCl_2$, and (2-furyl)$_3$P.

The author further found that $PdCl_2$ was as effective as [(η^3-allyl)PdCl]$_2$ on a larger scale (entry 1 of Table 3), and then extended the reaction of alkenyl[2-(hydroxymethyl)-phenyl]dimethylsilanes (1.1 mmol) to various aryl iodides (1.0 mmol) under the optimized conditions employing mild and inexpensive K_2CO_3 as a base (Table 3). Aryl iodides having electron-withdrawing or -donating groups such as ester, keto, formyl, nitro, chloro, and methoxy also underwent the reaction in good yields (entries 2–7). It is worth noting that both silyl-protected and unprotected hydroxy groups tolerated the present protocol (entries 8 and 9). *ortho*-Substituents did not affect the reaction (entries 10 and 11); such heteroaryl iodides as 3-iodopyridine and 2-iodothiophene reacted in good yields (entries 12 and 13). Functional groups in alkenyl[2-(hydroxymethyl)phen-yl]dimethylsilanes are also compatible with the present conditions (entries 14–20); arylethene **6gb** having an allyl acetate moiety may find further applications as a substrate for π-allylpalladium chemistry (entry 19). Vinylsilane **4m** and other mono- and disubstituted alkenylsilanes **4i**–**4q** also reacted with ethyl 4-iodobenzoate (**5b**) in stereo- and regiospecific manners, giving the desired arylethenes in good yields (entries

21–30). Especially, the regiospecific reaction of **4p** with both activated and unactivated aryl iodides is remarkable in view that the corresponding coupling of fluorosilanes results in *cine*-substitution to some extent (entries 28 and 29).[16]

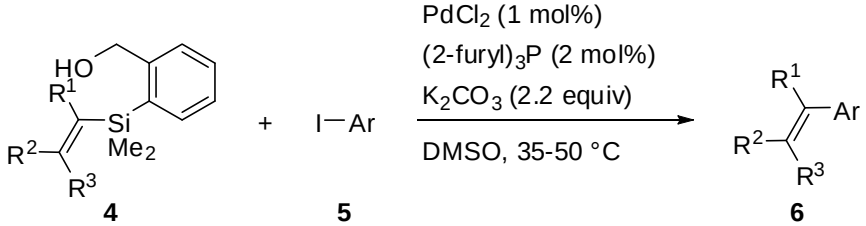
The cross-coupling reactions of **4b** with (*E*)- and (*Z*)-1-iodo-1-octene (**7a** and **7b**) also proceeded stereospecifically to give 1,4-disubstituted 1,3-dienes **8ba** and **8bb**, respectively (Eq. 3). Use of *N*-(2-diphenylphosphinobenzylidene)cyclohexylamine (**9**) as a ligand rather than tri(2-furyl)phosphine was found effective for the present diene formation.[17]



(3)

A gram-scale synthesis was carried out using 9.1 g (33 mmol) of **4a** and 8.3 g (30 mmol) of **5b** under the identical conditions. Cyclic silyl ether **2** was recovered by vacuum distillation in 62% yield based on **4a**; the residue was chromatographed to give the desired coupling product **6ab** in 97% yield (Eq. 4). As demonstrated above (Scheme 1 and Eq. 2), cyclic silyl ether **2** serves as a starting reagent for synthesis of the alkenylsilanes **4**. As illustrated herein, metal residue of the cross-coupling reaction is demonstrated for the first time to be reusable for the next coupling.

Table 3. Cross-coupling reaction of alkenyl[2-(hydroxymethyl)phenyl]dimethylsilanes **4** with aryl iodides **5**[a]



4 **5** **6**

Ar = 4-NC–C_6H_4 (**5a**); 4-EtO_2C–C_6H_4 (**5b**); 4-Ac–C_6H_4 (**5c**); 4-OHC–C_6H_4 (**5d**); 4-O_2N–C_6H_4 (**5e**); 4-Cl–C_6H_4 (**5f**); 4-MeO–C_6H_4 (**5g**); 3-*t*-$BuMe_2SiOCH_2$–C_6H_4 (**5h**); 3-$HOCH_2$–C_6H_4 (**5i**); 2-Me–C_6H_4 (**5j**); 1-naphthyl (**5k**); 3-pyridyl (**5l**); 2-thienyl (**5m**)

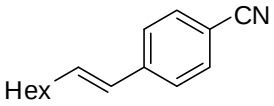
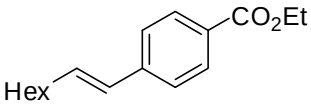
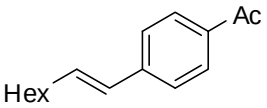
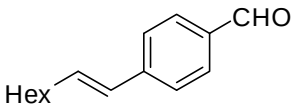
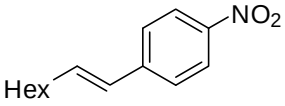
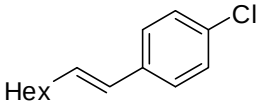
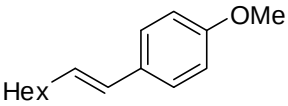
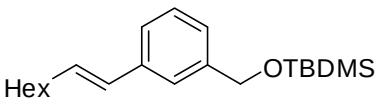
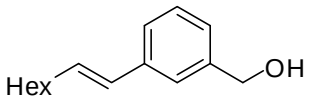
entry	**4**	**5**	time (h)	product	yield (%)[b]
1	**4a**	**5a**	20		93 (**6aa**)
2	**4a**	**5b**	18		96 (**6ab**)
3	**4a**	**5c**	17		94 (**6ac**)
4	**4a**	**5d**	20		94 (**6ad**)
5	**4a**	**5e**	26		99 (**6ae**)
6	**4a**	**5f**	19		93 (**6af**)
7	**4a**	**5g**	40		89 (**6ag**)
8	**4a**	**5h**	23		98 (**6ah**)
9	**4a**	**5i**	47		88 (**6ai**)

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Table 3. (*continued*)

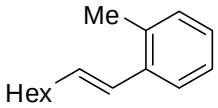
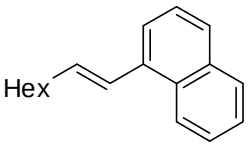
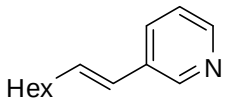
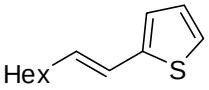
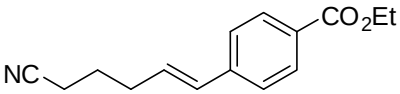
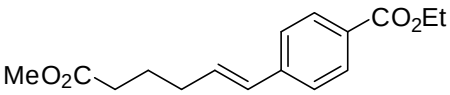
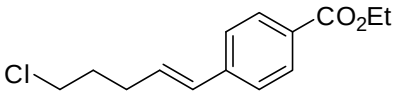
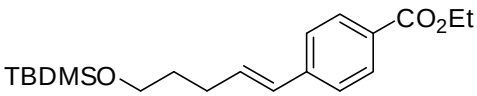
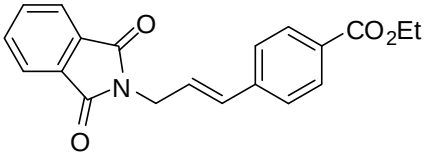
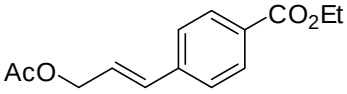
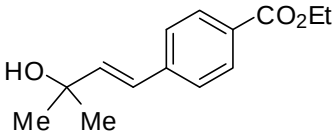
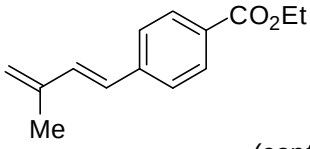
entry	**4**	**5**	time (h)	product	yield (%)[b]
10	**4a**	**5j**	47		94 (**6aj**)
11	**4a**	**5k**	23		91 (**6ak**)
12	**4a**	**5l**	23		80 (**6al**)
13	**4a**	**5m**	23		99 (**6am**)
14	**4b**	**5b**	19		95 (**6bb**)
15	**4c**	**5b**	18		92 (**6cb**)
16	**4d**	**5b**	50		92 (**6db**)
17	**4e**	**5b**	31		90 (**6eb**)
18	**4f**	**5b**	24		93 (**6fb**)
19[c]	**4g**	**5b**	25		93 (**6gb**)
20[d,e]	**4h**	**5b**	72		92 (**6hb**)
21	**4i**	**5b**	25		93 (**6ib**)

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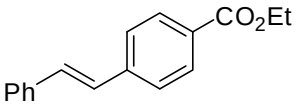
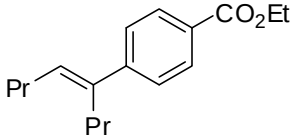
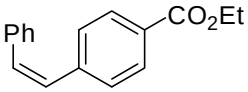
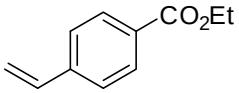
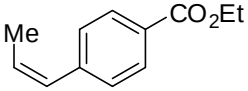
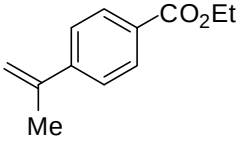
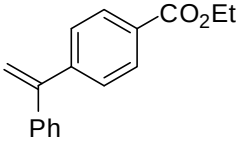
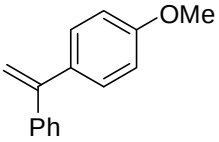
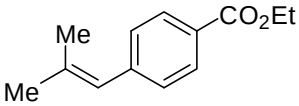
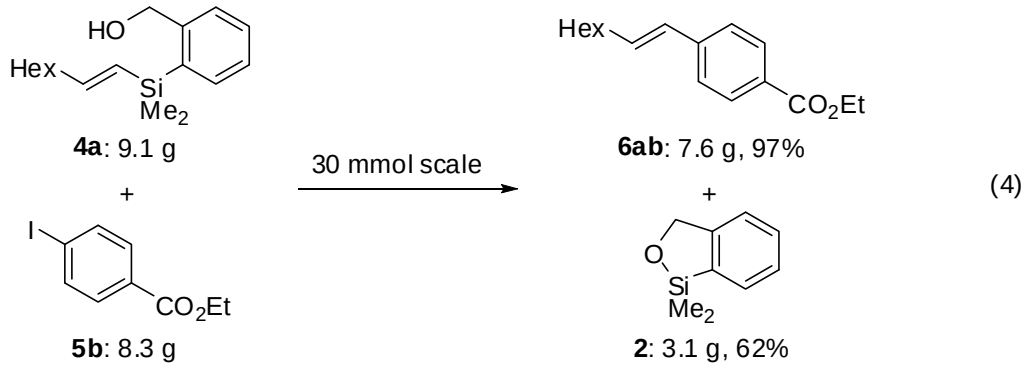
Table 3. (*continued*)

entry	**4**	**5**	time (h)	product	yield (%)[b]
22	**4j**	**5b**	19		88 (**6jb**)
23[d]	**4k**	**5b**	29		92 (**6kb**)
24	**4l**	**5b**	11		92 (**6lb**)
25	**4m**	**5b**	19		87 (**6mb**)
26	**4n**	**5h**	19		91 (**6nb**)[f]
27	**4o**	**5b**	24		96 (**6ob**)
28	**4p**	**5b**	25		95 (**6pb**)
29[c,d]	**4p**	**5g**	12		80 (**6pg**)[g]
30	**4q**	**5b**	25		96 (**6qb**)

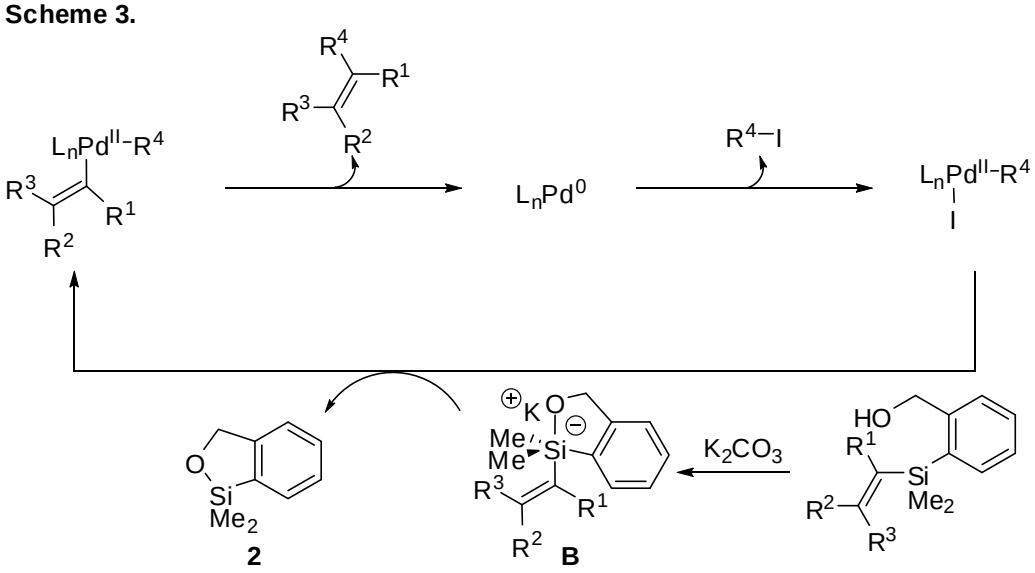
[a]The reaction was carried out using an alkenylsilanes (1.1 mmol), an aryl iodide (1.0 mmol), K_2CO_3 (2.2 mmol), $PdCl_2$ (10 μmol), and (2-furyl)$_3$P (20 μmol) in DMSO (2.5 mL) at 35 °C. [b]Isolated yields based on an aryl iodide. [c]The alkenylsilane (1.3 mmol) was used. [d]The reaction was carried out at 50 °C. [e]$PdCl_2$ (50 μmol) and (2-furyl)$_3$P (0.10 mmol) were used. [f]*Z* : *E* = 94 : 6 estimated by GC. [g]Formation of *cine*-product was at best 4% yield.



(4)

Key of the successful cross-coupling is an intramolecular coordination of an alkoxide derived from the proximal hydroxy group upon treatment with a base, efficiently forming pentacoordinate silicate species **B** that contains a transferable alkenyl group possibly at its apical position. **B** is thus responsible for the cross-coupling reaction under the conditions significantly milder than those ever reported for the silicon-based reactions (Scheme 3).

Scheme 3.



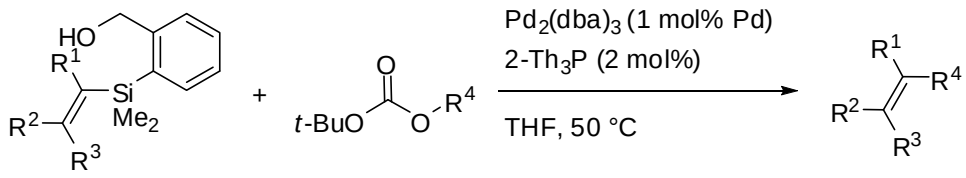
2.3 Cross-coupling reaction with allylic and benzylic carbonates

The author subsequently envisaged the cross-coupling reaction of alkenylsilanes with allylic electrophiles, and thus examined reaction of (*E*)-[2-(hydroxymethyl)phenyl]dimethyl(1-octenyl)silane (**4a**: 1.0 mmol) with allyl *t*-butyl carbonate (**10a**: 1.0 mmol) in the presence of 0.5 mol% of $Pd_2(dba)_3$ and 2.0 mol% of $(2\text{-thienyl})_3P$ as a ligand. He was delighted to obtain (*E*)-1,4-undecadiene (**11aa**) in 85% yield after 2 h

(entry 1 of Table 4). The reaction with a (2-furyl)$_3$P ligand resulted in a slightly lower yield. *O*-Allylation of **4** was observed in less than 5%, if any. Excellent chemoselectivity was observed with (*E*)-alkenylsilanes having such a group as cyano, siloxy, chloro, or phthalimide, giving various 1,4-dienes in good yields (entries 2–5). Free hydroxy group that may serve as a nucleophile in the allylpalladium chemistry also was compatible (entry 6). (*E*)- and (*Z*)-β-Styryl-, α-phenylvinyl-, and (*E*)-4-octenylsilanes participated in the reaction with **10a** in good yields with perfect regioselectivity and stereospecificity (entries 7–10). (*E*)-Cinnamyl (**10b**) carbonate similarly reacted with **4a** to give linear (*E*)-1-phenyl-1,4-undecadiene (**11ab**) in 93% yield irrespective of reaction scale (1 and 10 mmol) (entry 11). The reaction on a 10 mmol scale allowed isolation of cyclic silyl ether **2** (80% yield). *t*-Butyl 2-cyclohexenyl carbonate (**10c**) readily participated in the reaction to give the corresponding coupling product in 92% yield (entry 12), whereas crotyl methyl carbonate (**10d**) gave a mixture of linear and branched products (entry 13).

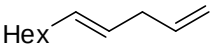
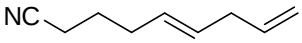
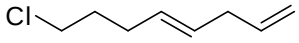
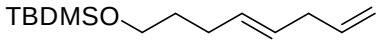
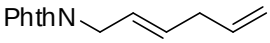
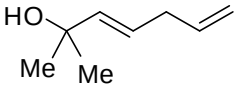
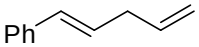
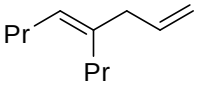
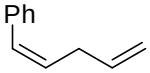
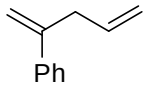
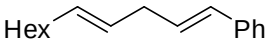
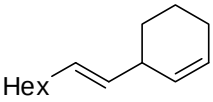
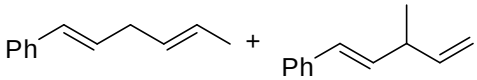
The author then turned his attention to the cross-coupling reaction with benzylic carbonates. Recently, Kuwano and Yokogi have revealed that benzylic carbonates serve as electrophiles for the cross-coupling chemistry by employing a Pd/bisphosphine system.[18] After survey of several combinations of a palladium catalyst and a bisphosphine ligand, a combination of (η^5-cylcopentadienyl)(η^3-allyl)palladium [Cp(allyl)Pd] and 1,10-bis(diphenylphosphino)ferrocene (dppf) turned out to be optimum. Thus, the reaction of (*E*)-1-octenylsilane **4a** with benzyl methyl carbonate (**12a**) in the presence of 5 mol% of Cp(allyl)Pd and dppf in THF at 80 °C for 18 h gave (*E*)-1-phenyl-2-nonene (**13aa**) in 87% yield (Eq. 5). To the best of his knowledge, this is the first example of silicon-based cross-coupling reaction successfully carried out with a benzylic electrophile. Under the similar conditions, 4-methoxyphenyl (**12b**), 2,4,6-trimethylphenyl (**12c**), and 2-pyridyl (**12d**) carbonate also cross-coupled with **4a** to give the corresponding (*E*)-1-aryl-2-nonenes **13** in good yields (Eq. 5).

Table 4. Cross-coupling reaction of alkenyl[2-(hydroxymethyl)phenyl]dimethylsilanes (**4**) with allylic carbonates **10**[a]

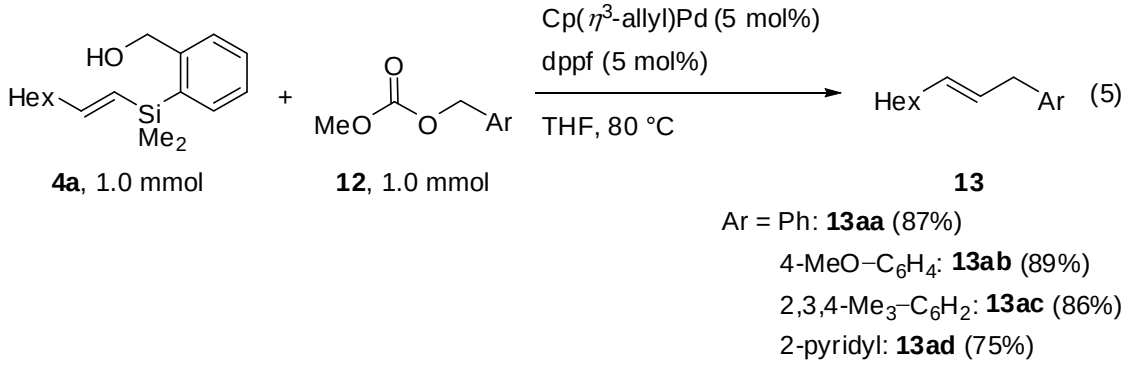


4 **10** **11**

R^4 = allyl (**10a**); (*E*)-cinnamyl (**10b**); 2-cyclohexenyl (**10c**); crotyl (**10d**)

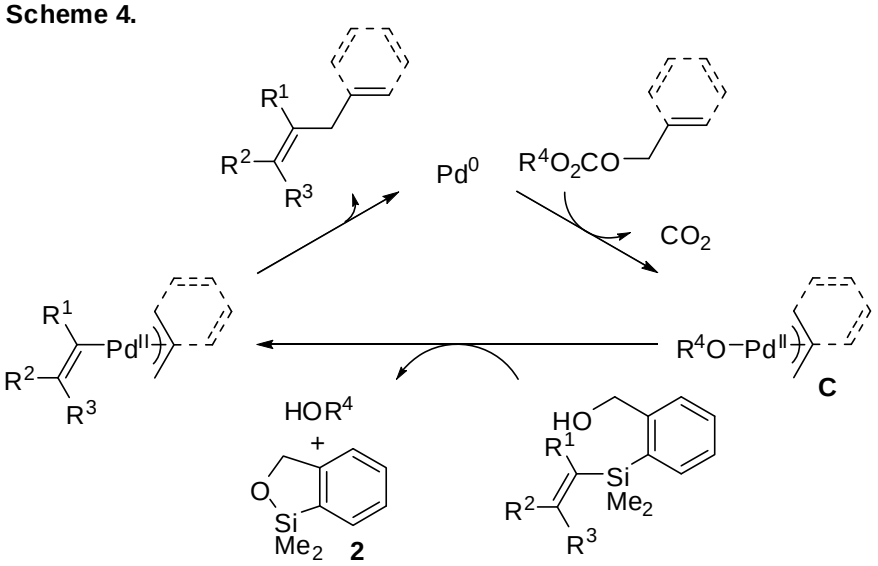
entry	**4**	**10**	time (h)	product	yield (%)[b]
1	**4a**	**10a**	2		85 (**11aa**)
2	**4b**	**10a**	4		85 (**11ba**)
3	**4d**	**10a**	2		74 (**11da**)
4	**4e**	**10a**	2		72 (**11ea**)
5	**4f**	**10a**	3		85 (**11fa**)
6	**4h**	**10a**	4		53 (**11ha**)
7	**4j**	**10a**	2		91 (**11ja**)
8	**4k**	**10a**	24		78 (**11ka**)
9	**4l**	**10a**	2		92 (**11la**)
10	**4p**	**10a**	3		81 (**11pa**)
11	**4a**	**10b**	3		93 (**11ab**)[c]
12	**4a**	**10c**	4		92 (**11ac**)
13	**4j**	**10d**[d]	7		68 (**11gd**)[e]

[a]The reaction was carried out using an alkenylsilane (1.0 mmol), an allylic carbonate (1.0 mmol), $Pd_2(dba)_3$ (5 μmol), and 2-Th_3P (20 μmol) at 50 °C. [b]Isolated yields. [c]Cyclic silyl ether **2** was also isolated in 80% yield on a 10 mmol scale. [d]Crotyl methyl carbonate was applied. [e]The ratio of isomers was determined to be 73 : 27 by ^{1}H NMR.



The author hypothesized that a palladium alkoxide species **C** should be generated by oxidative addition of allylic and benzylic carbonates to Pd^0 and then act as a base to allow the cross-coupling reaction of the silicon reagents with these carbonate esters under neutral conditions (Scheme 4).[19]

Scheme 4.



3. Conclusion

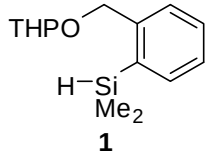
A new silicon-based cross-coupling protocol is demonstrated that employs alkenyl[2-(hydroxymethyl)phenyl]dimethylsilanes and K_2CO_3 base in addition to a Pd catalyst. Highly chemoselective transformations using the highly stable alkenylsilane reagents certainly allow convenient synthesis of a wide range of functionalized arylethenes, 1,3-dienes, 1,4-dienes, and 3-arylpropenes, and thus will find a widespread synthetic applications both in academia and industry. Use of the readily accessible, highly stable, and recyclable tetraorganosilicon compounds under mild fluoride-free conditions is definitely an attractive feature that may replace the conventional protocols.

4. Experimental

4.1 General remarks compatible to all the experimental part in the present Thesis

All the manipulation with oxygen- and moisture-sensitive materials were conducted by a standard Schlenk technique under an argon atmosphere. Flash column chromatography was performed using Merck silica gel 60 (40–63 μm), Kanto Chemical silica gel (spherical, 40–50 μm), or Merck aluminium oxide 90 neutral (20–63 μm). Analytical thin layer chromatography (TLC) was performed on Merck Kieselgel 60 F254 (0.25 mm) plates. Visualization was performed with a UV light (254 nm) and/or an aq. alkaline $KMnO_4$ solution followed by heating. Proton and carbon nuclear magnetic resonance spectra (^{1}H NMR and ^{13}C NMR) were recorded on a Varian Mercury 400 (^{1}H NMR, 400 MHz; ^{13}C NMR, 101 MHz) spectrometer with a solvent signal as the internal standard (^{1}H NMR, $CHCl_3$ at 7.26 ppm; ^{13}C NMR, $CDCl_3$ at 77.0 ppm). ^{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. Melting points were determined using a YANAKO MP-500D. Mass spectra were obtained with a JEOL JMS-700 (EI at 70 eV unless otherwise stated or CI) or JEOL JMS-HX110A (FAB) spectrometer. Unless otherwise noted, reagents were commercially available and were used without purification. THF and diethyl ether were distilled from sodium/benzophenone ketyl right before use. Anhydrous DMSO was purchased from Aldrich and used without further purification. *N*-(2-Diphenylphosphinobenzylidene)-cyclohexylamine (**9**),[20] RuHCl(CO)[P(*i*-Pr)$_3$]$_2$,[21] *t*-butyl allylic carbonates (**10**),[22] arylmethyl methyl carbonates (**12**),[23] and Cp(η^3-allyl)Pd[24] were prepared according to the reported procedures.

4.2 Preparation of alkenyl[2-(hydroxymethyl)phenyl]dimethylsilanes



1

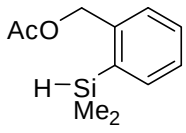
Dimethyl[2-(2-tetrahydro-2*H*-pyran-2-yloxymethyl)phenyl]silane (1). To a mixture of 2-bromophenylmethanol (34 g, 0.180 mol) and 3,4-dihydro-2*H*-pyran (18.2 g, 0.22

mol) were added 10 drops of concentrated hydrochloric acid, and the resulting mixture was stirred at rt overnight. The mixture was diluted with diethyl ether, neutralized with a sat. NH_4Cl aq. solution, dried over anhydrous $MgSO_4$, and concentrated in vacuo to give 2-(2-tetrahydro-2*H*-pyran-2-yloxymethyl)bromobenzene, which was dissolved in THF (450 mL). To the solution was added a 1.6 M *n*-BuLi solution in hexane (124 mL, 0.20 mol) over 40 min at –78 °C, and the resulting solution was stirred for 50 min before addition of chlorodimethylsilane (20 g, 0.22 mol) at –78 °C. The mixture was warmed gradually at rt overnight and quenched with H_2O. After evaporation of the solvents, the residue was extracted with diethyl ether, and the combined organic layers were washed with brine and dried over anhydrous $MgSO_4$. Distillation under vacuum gave **1** (38 g, 83%) as a colorless oil, bp 135 °C (1.0 mmHg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (dd, *J* = 7.2, 1.4 Hz, 1H), 7.44 (dd, *J* = 7.5, 0.5 Hz, 1H), 7.37 (td, *J* = 7.5, 1.5 Hz, 1H), 7.29 (td, *J* = 7.3, 1.3 Hz, 1H), 4.86 (d, *J* = 11.9 Hz, 1H), 4.73 (t, *J* = 3.6 Hz, 1H), 4.59 (d, *J* = 11.7 Hz, 1H), 4.56–4.51 (m, 1H), 3.98–3.89 (m, 1H), 3.60–3.52 (m, 1H), 1.94–1.45 (m, 6H), 0.364 (d, *J* = 3.7 Hz, 3H), 0.360 (d, *J* = 3.7 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.6, 136.5, 134.7, 129.4, 128.3, 127.0, 98.1, 69.1, 62.1, 30.6, 25.5, 19.3, –3.0, –3.1; IR (neat) 2943, 2124, 1250, 1202, 1119, 1080, 1055, 1026, 974, 885, 837, 752 cm^{-1}; MS (EI) *m*/*z* (%) 250 (M^+, 0.1), 164 (12), 163 (14), 150 (17), 149 (100), 85 (22). Anal. Calcd. for $C_{14}H_{22}O_2Si$: C, 67.15; H, 8.86. Found: C, 67.44; H, 8.91%.

2

1,1-Dimethyl-2-oxa-1-silaindan (2). *p*-Toluenesulfonic acid monohydrate (1.14 g, 6.0 mmol) was added portionwise to **1** (75 g, 0.30 mol) dissolved in MeOH (500 mL) at rt, and the mixture was stirred for 16 h before concentration in vacuo. The residue was distilled to give **2** (41 g, 83%) as a colorless oil, bp 45 °C (2.0 mmHg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (dd, *J* = 7.1, 0.4 Hz, 1H), 7.42–7.37 (m, 1H), 7.33–7.28 (m, 1H), 7.23 (dd, *J* = 7.5, 0.7 Hz, 1H), 5.16 (s, 2H), 0.40 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.7, 135.0, 131.0, 129.5, 126.8, 121.6, 71.5, 0.6; IR (neat) 3360, 3057, 2953, 2897, 2860, 1701, 1593, 1445, 1350, 1252, 1200, 1134, 1067, 1051, 1024, 858, 829, 791, 748,

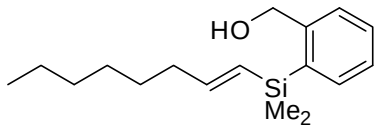
692, 652 cm^{-1}; MS (EI) *m*/*z* (%) 165 (M^+, 9), 164 (58), 163 (26), 151 (13), 150 (45), 149 (100), 105 (15). Anal. Calcd. for $C_9H_{12}OSi$: C, 65.80; H, 7.36. Found: C, 65.60; H, 7.34%.



3

Dimethyl[2-(2-acetoxymethyl)phenyl]silane (3). To a suspension of $LiAlH_4$ (0.38 g, 10.0 mmol) in diethyl ether (30 mL) was added **2** (1.64 g, 10.0 mmol) at 0 °C, and the resulting mixture was stirred at rt for 100 min before addition of acetyl chloride (7.1 mL, 100 mmol) at 0 °C. Stirring was continued at rt overnight, and the mixture was filtered through a Celite and then through a silica gel pad. The residue was purified by flash chromatography on silica gel to give **3** (1.39 g, 67%) as a colorless oil, R_f 0.30 (hexane–ethyl acetate = 20 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 7.0 Hz, 1H), 7.42–7.32 (m, 3H), 5.20 (s, 2H), 4.58–4.51 (m, 1H), 2.10 (s, 3H), 0.37 (d, *J* = 3.8 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.8, 140.9, 137.2, 135.0, 129.6, 129.1, 127.8, 66.6, 21.1, –3.1; IR (neat) 2959, 2127, 1742, 1437, 1379, 1362, 1236, 1130, 1080, 1026, 966, 887, 839, 756 cm^{-1}; MS (EI) *m*/*z* (%) 208 (M^+, 6), 207 (37), 194 (14), 193 (81), 165 (59), 163 (24), 152 (25), 151 (98), 150 (29), 149 (100), 148 (24), 147 (27), 145 (12), 135 (27), 134 (12), 133 (55), 131 (11), 123 (14), 121 (14), 119 (13), 117 (38), 105 (20), 91 (34), 75 (46). Anal. Calcd. for $C_{11}H_{16}O_2Si$: C, 63.42; H, 7.74. Found: C, 63.48; H, 7.74%.

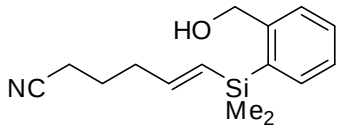
Preparation of (*E*)-alkenyl[2-(hydroxymethyl)phenyl]dimethylsilanes by platinum-catalyzed hydrosilylation with 1



4a

(*E*)-[2-(Hydroxymethyl)phenyl]dimethyl(1-octen-1-yl)silane (4a). To a solution of hydrosilane **1** (10.0 g, 0.040 mol) and 1-octyne (4.4 g, 0.040 mol) in hexane (4 mL) were added a 10% hexane solution of *t*-Bu_3P (80 mg, 0.040 mmol) and a 0.01 M hexane

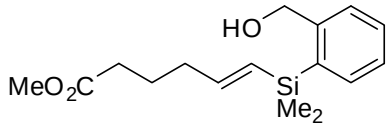
solution of platinum(0)–1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex (4.0 mL, 0.040 mmol) at 0 °C. The resulting mixture was stirred at rt for 2 h, filtered through a Florisil pad, and concentrated in vacuo. The residue was dissolved in MeOH (140 mL) and treated with *p*-toluenesulfonic acid monohydrate (152 mg, 0.80 mmol) at rt for 4 h. After removal of the solvent in vacuo, the residue was purified by flash chromatography on silica gel to give the title compound (9.0 g, 81%) as a colorless oil, R_f 0.25 (hexane–ethyl acetate = 10 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (dd, *J* = 7.3, 1.3 Hz, 1H), 7.46 (dd, *J* = 7.5, 0.7 Hz, 1H), 7.40 (td, *J* = 7.5, 1.5 Hz, 1H), 7.28 (td, *J* = 7.3, 1.3 Hz, 1H), 6.15 (dt, *J* = 18.7, 6.4 Hz, 1H), 5.83 (dt, *J* = 18.7, 1.5 Hz, 1H), 4.74 (s, 2H), 2.17–2.12 (m, 2H), 1.63 (br s, 1H), 1.42–1.25 (m, 8H), 0.90–0.83 (m, 3H), 0.39 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.7, 146.4, 137.1, 135.1, 130.0, 128.2, 128.0, 127.0, 65.4, 36.8, 31.7, 28.9, 28.5, 22.6, 14.1, –1.2; IR (neat) 3329, 2957, 2926, 2855, 1614, 1466, 1435, 1248, 1126, 1078, 991, 841, 783, 746, 687 cm^{-1}; MS (EI) *m*/*z* (%) 276 (M^+, 0.1), 261 (32), 243 (14), 199 (12), 177 (13), 173 (11), 166 (27), 165 (66), 164 (51), 163 (44), 160 (11), 159 (42), 151 (25), 150 (30), 149 (100), 148 (27), 147 (50), 146 (16), 145 (51), 137 (12), 135 (31), 133 (14), 131 (22), 129 (18), 105 (16), 91 (18), 75 (32), 61 (39), 59 (13), 55 (11). Anal. Calcd. for $C_{17}H_{28}OSi$: C, 73.85; H, 10.21. Found: C, 73.86; H, 10.42%.



4b

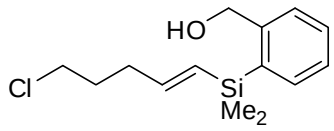
(*E*)-5-Cyano-1-penten-1-yl[2-(hydroxymethyl)phenyl]dimethylsilane (4b). Following the procedure for **4a**, the reaction using hydrosilane **1** (1.25 g, 5.0 mmol) and 5-hexynenitrile (0.46 g, 5.0 mmol) gave **4b** (1.09 g, 84%) as a colorless oil, R_f 0.30 (hexane–ethyl acetate = 4 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 7.2 Hz, 1H), 7.46 (d, *J* = 7.2 Hz, 1H), 7.40 (td, *J* = 7.4, 1.2 Hz, 1H), 7.29 (td, *J* = 7.4, 1.2 Hz, 1H), 6.06 (dt, *J* = 18.5, 6.0 Hz, 1H), 5.95 (d, *J* = 18.4 Hz, 1H), 4.73 (s, 2H), 2.33 (q, *J* = 7.2 Hz, 4H), 1.79 (quint, *J* = 7.2 Hz, 2H), 1.60 (br s, 1H), 0.40 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.4, 145.6, 136.2, 135.0, 131.2, 129.7, 127.7, 126.9, 119.5, 65.1, 35.2, 24.0, 16.4, –1.3; IR (neat) 3443, 2953, 2249, 1618, 1433, 1250, 1124, 1078, 991, 910, 827, 733 cm^{-1}; MS (EI) *m*/*z* (%) 259 (M^+, 0.3), 244 (33), 242 (18), 226 (24), 165 (39), 164

(44), 163 (22), 150 (15), 149 (100), 147 (25), 145 (20), 135 (11). Anal. Calcd. for $C_{15}H_{21}NOSi$: C, 69.45; H, 8.16. Found: C, 69.68; H, 8.15%.



4c

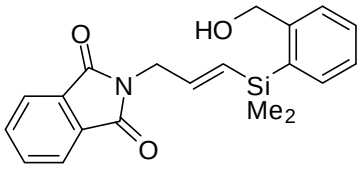
Methyl (*E*)-6-([2-(hydroxymethyl)phenyl]dimethylsilyl)-5-hexenoate (4c). Following the procedure for **4a**, the reaction using hydrosilane **1** (2.5 g, 10.0 mmol) and methyl 5-hexynoate (1.26 g, 10.0 mmol) gave **4c** (2.0 g, 68%) as a colorless oil, R_f 0.38 (hexane–ethyl acetate = 3 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (dd, *J* = 7.4, 1.4 Hz, 1H), 7.47 (d, *J* = 7.1 Hz, 1H), 7.40 (td, *J* = 7.4, 1.5 Hz, 1H), 7.28 (td, *J* = 7.5, 1.3 Hz, 1H), 6.10 (dt, *J* = 18.7, 6.2 Hz, 1H), 5.87 (dt, *J* = 18.7, 1.5 Hz, 1H), 4.74 (s, 2H), 3.65 (s, 3H), 2.31 (t, *J* = 7.5 Hz, 2H), 2.19 (td, *J* = 7.4, 6.2 Hz, 2H), 1.76 (quint, *J* = 7.4 Hz, 2H), 1.66 (bs, 1H), 0.39 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.0, 147.6, 146.5, 136.7, 135.1, 129.8, 129.7, 127.9, 127.0, 65.3, 51.5, 35.9, 33.4, 23.7, –1.2; IR (neat) 3447, 2951, 1738, 1616, 1437, 1250, 1202, 1078, 991, 839, 750 cm^{-1}. Anal. Calcd. for $C_{16}H_{24}O_3Si$: C, 65.71; H, 8.27. Found: C, 65.66; H, 8.12%.



4d

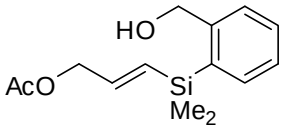
(*E*)-5-Chloro-1-pentenyl[2-(hydroxymethyl)phenyl]dimethylsilane (4d). The procedure for **4a** was applied to the reaction of hydrosilane **1** (2.5 g, 10.0 mmol) and 5-chloro-1-pentyne (1.03 g, 10.0 mmol) to give the title compound (1.91 g, 71%) as a colorless oil, R_f 0.15 (hexane–ethyl acetate = 10 : 1). ^{1}HNMR (400 MHz, $CDCl_3$) δ 7.54 (dd, *J* = 7.3, 1.3 Hz, 1H), 7.47 (dd, *J* = 7.5, 0.6 Hz, 1H), 7.40 (td, *J* = 7.5, 1.3 Hz, 1H), 7.29 (td, *J* = 7.3, 1.5 Hz, 1H), 6.10 (dt, *J* = 18.7, 6.2 Hz, 1H), 5.92 (dt, *J* = 18.5, 1.5 Hz, 1H), 4.74 (s, 2H), 3.53 (t, *J* = 6.6 Hz, 2H), 2.31 (tdd, *J* = 6.6, 6.2, 1.5 Hz, 2H), 1.89 (quint, *J* = 6.6 Hz, 2H), 1.59 (bs, 1H), 0.40 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.9, 146.4, 136.7, 135.1, 130.2, 129.7, 128.0, 127.0, 65.4, 44.4, 33.7, 31.3, –1.2; IR (neat) 3369, 2955, 1614, 1435, 1250, 1124, 1078, 991, 839, 750, 650 cm^{-1}. Anal. Calcd.

for $C_{14}H_{21}ClOSi$: C, 62.54; H, 7.87. Found: C, 62.31; H, 7.70%.



4f

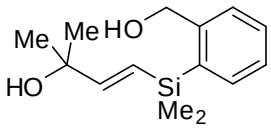
(*E*)-*N*-[3-([2-(Hydroxymethyl)phenyl]dimethylsilyl)-2-propenyl]phthalimide (4f). Following the procedure for **4a**, the reaction using hydrosilane **1** (2.5 g, 10.0 mmol) and *N*-propargylphthalimide (1.85 g, 10.0 mmol) gave **4f** (2.5 g, 72%) as a colorless solid, mp 88.6–89.2 °C, R_f 0.10 (hexane–ethyl acetate = 5 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88–7.82 (m, 2H), 7.75–7.69 (m, 2H), 7.49 (dd, *J* = 7.3, 1.3 Hz, 1H), 7.46 (d, *J* = 7.0 Hz, 1H), 7.38 (td, *J* = 7.3, 1.3 Hz, 1H), 7.26 (td, *J* = 7.3, 1.3 Hz, 1H), 6.12 (dt, *J* = 18.6, 4.5 Hz, 1H), 6.00 (dt, *J* = 18.6, 1.4 Hz, 1H), 4.69 (s, 2H), 4.37 (dd, *J* = 4.5, 1.3 Hz, 2H), 1.79 (bs, 1H), 0.38 (s, 6H); ^{13}C NMR(101 MHz, $CDCl_3$) δ 168.1, 146.6, 140.0, 135.9, 135.0, 134.0, 132.0, 131.0, 129.8, 128.2, 126.9, 123.4, 65.1, 42.0, –1.5; IR (KBr) 3518, 2930, 1767, 1705, 1423, 1393, 1337, 1250, 1082, 1038, 993, 935, 841, 816, 779, 745, 727, 530 cm^{-1}. Anal. Calcd. for $C_{20}H_{21}NO_3Si$: C, 68.35; H, 6.02. Found: C, 68.41; H, 6.12%.



4g

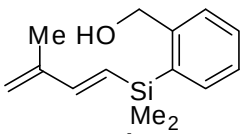
(*E*)-3-([2-(Hydroxymethyl)phenyl]dimethylsilyl)-2-propenyl acetate (4g). Following the procedure for **4a**, the reaction using hydrosilane **1** (2.5 g, 10.0 mmol) and propargyl acetate (0.98 g, 10.0 mmol) gave **4g** (0.71 g, 27%) and (*E*)-[2-(hydroxymethyl)phenyl](3-hydroxypropenyl)dimethylsilane, a deacetylated product (1.08 g, 49%). **4g** was a colorless oil and showed R_f 0.18 (hexane–ethyl acetate = 5 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 7.3 Hz, 1H), 7.47 (d, *J* = 7.5 Hz, 1H), 7.41 (td, *J* = 7.4, 1.1 Hz, 1H), 7.29 (td, *J* = 7.4, 1.1 Hz, 1H), 6.14 (s, 2H), 4.72 (s, 2H), 4.63 (dd, *J* = 1.7, 0.7 Hz, 2H), 2.09 (s, 3H), 1.64 (bs, 1H), 0.43 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.8, 146.5, 141.0, 135.9, 135.1, 131.7, 129.9, 128.1, 127.1, 66.6, 65.3, 20.9, –1.4; IR (neat) 3427, 2953, 1744, 1624, 1435, 1379, 1236, 1126, 1078, 1028, 839, 785, 750 cm^{-1}. HRMS (FAB$^+$) Calcd. for $C_{14}H_{21}O_3Si$: $[M+H]^+$, 265.1260. Found: *m*/*z* 265.1257.

(*E*)-[2-(Hydroxymethyl)phenyl](3-hydroxypropenyl)dimethylsilane was a colorless solid, mp 65.2–65.7 °C, and showed R_f 0.25 (hexane–ethyl acetate = 2 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (dd, *J* = 7.4, 0.6 Hz, 1H), 7.43 (d, *J* = 7.5 Hz, 1H), 7.39 (td, *J* = 7.5, 1.7 Hz, 1H), 7.28 (td, *J* = 7.3, 1.3 Hz, 1H), 6.26 (dt, *J* = 18.8, 4.2 Hz, 1H), 6.12 (dt, *J* = 18.8, 1.3 Hz, 1H), 4.71 (s, 2H), 4.17 (dt, *J* = 4.0, 0.8 Hz, 2H), 2.19 (br s, 2H), 0.41 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.5, 146.3, 136.3, 135.0, 129.8, 128.2, 128.1, 127.0, 65.2, 65.1, –1.4; IR (neat) 3308, 3194, 2949, 2899, 1624, 1429, 1342, 1250, 1200, 1128, 1074, 1026, 1009, 997, 847, 826, 791, 766, 739, 637, 463, 426 cm^{-1}. HRMS (FAB$^-$) Calcd. for $C_{12}H_{17}O_2Si$: $[M–H]^+$, 221.0998. Found: *m*/*z* 221.0998.



4h

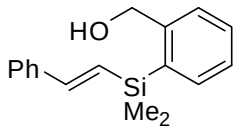
(*E*)-3-Hydroxy-3-methyl-1-butenyl[2-(hydroxymethyl)phenyl]dimethylsilane (4h). The procedure for **4a** was successfully applied to the reaction of hydrosilane **1** (2.5 g, 10.0 mmol) and 2-methyl-3-butyn-2-ol (0.84 g, 10.0 mmol), and **4h** (1.08 g, 43%) was isolated as a colorless oil, R_f 0.25 (hexane–ethyl acetate = 2 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (dd, *J* = 7.3, 1.3 Hz, 1H), 7.46 (d, *J* = 7.1 Hz, 1H), 7.40 (td, *J* = 7.3, 1.1 Hz, 1H), 7.29 (td, *J* = 7.3, 1.3 Hz, 1H), 6.24 (d, *J* = 18.8 Hz, 1H), 6.04 (d, *J* = 19.0 Hz, 1H), 4.71 (s, 2H), 2.04 (s, 1H), 1.68 (s, 1H), 1.31 (s, 6H), 0.41 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.8, 146.4, 136.4, 135.0, 129.7, 128.2, 126.9, 123.6, 71.9, 65.0, 29.1, –1.3; IR (neat) 3323, 2964, 1611, 1433, 1375, 1259, 1215, 1022, 826, 750 cm^{-1}. Anal. Calcd. for $C_{14}H_{22}O_2Si$: C, 67.15; H, 8.86. Found: C, 67.28; H, 8.88%.



4i

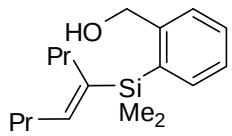
(*E*)-[2-(Hydroxymethyl)phenyl]dimethyl(3-methyl-1,3-butadienyl)silane (4i). Following the procedure for **4a**, the reaction using hydrosilane **1** (2.5 g, 10.0 mmol) and 2-methyl-1-buten-3-yne (0.66 g, 10.0 mmol) gave **4i** (1.31 g, 57%) as a colorless oil, R_f 0.20 (hexane–ethyl acetate = 10 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 7.3 Hz,

1H), 7.47 (d, *J* = 7.7 Hz, 1H), 7.41 (td, *J* = 7.4, 1.1 Hz, 1H), 7.30 (t, *J* = 7.3 Hz, 1H), 6.70 (d, *J* = 18.8 Hz, 1H), 6.01 (dt, *J* = 18.7 Hz, 1H), 5.10 (s, 1H), 5.03 (s, 1H), 4.74 (s, 2H), 1.86 (s, 3H), 1.58 (bs, 1H), 0.45 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.1, 146.4, 143.2, 136.5, 135.1, 129.7, 127.9, 127.7, 127.0, 118.0, 65.3, 17.9, –1.3; IR (neat) 3333, 2955, 1574, 1435, 1248, 1202, 1124, 1078, 988, 893, 835, 748 cm^{-1}. Anal. Calcd. for $C_{14}H_{20}OSi$: C, 72.36; H, 8.67. Found: C, 72.27; H, 8.50%.



4j

(*E*)-[2-(Hydroxymethyl)phenyl]dimethyl(2-phenylethenyl)silane (4j). Following the procedure for **4a**, the reaction using hydrosilane **1** (0.55 g, 2.2 mmol) and phenylacetylene (0.20 g, 2.0 mmol) gave **4j** (0.45 g, 84%) as a colorless oil, R_f 0.20 (hexane–ethyl acetate = 10 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (dd, *J* = 7.4, 1.3 Hz, 1H), 7.51–7.41 (m, 4H), 7.37–7.27 (m, 4H), 6.97 (d, *J* = 19.2 Hz, 1H), 6.67 (d, *J* = 19.2 Hz, 1H), 4.79 (s, 2H), 1.67 (br s, 1H), 0.52 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.5, 145.2, 138.0, 136.4, 135.3, 130.0, 128.6, 128.3, 127.9, 127.8, 127.1, 126.5, 65.4, –1.2; IR (neat) 3444, 3055, 2955, 2359, 1605, 1572, 1495, 1447, 1435, 1248, 1198, 1124, 1076, 1028, 991, 847, 831, 812, 777, 748, 691 cm^{-1}; MS (EI) *m*/*z* (%) 268 (M^+, 0.5), 253 (11), 235 (15), 165 (14), 164 (29), 163 (19), 150 (15), 149 (100), 147 (13), 137 (35), 135 (10), 105 (11), 104 (25), 103 (12), 91 (24). Anal. Calcd. for $C_{17}H_{20}OSi$: C, 76.07; H, 7.51. Found: C, 75.73; H, 7.55%.

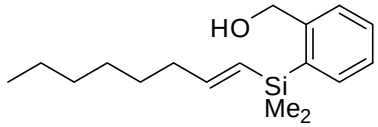


4k

(*E*)-[2-(Hydroxymethyl)phenyl]dimethyl(4-octen-4-yl)silane (4k). Following the procedure for **4a**, the reaction using hydrosilane **1** (0.55 g, 2.2 mmol) and 4-octyne (0.22 g, 2.0 mmol) gave **4k** (0.45 g, 81%) as a colorless oil, R_f 0.25 (hexane–ethyl acetate = 10 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (dd, *J* = 7.2, 1.2 Hz, 1H), 7.47 (dd, *J* = 7.2, 1.2 Hz, 1H), 7.40 (td, *J* = 7.3, 1.4 Hz, 1H), 7.30–7.26 (m, 1H), 5.80 (t, *J* = 7.2

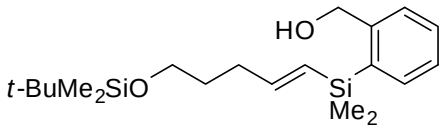
Hz, 1H), 4.70 (s, 2H), 2.12–2.06 (m, 4H), 1.60 (br s, 1H), 1.38 (m, 2H), 1.28–1.18 (m, 2H), 0.90 (t, J = 7.4 Hz, 3H), 0.83 (t, J = 7.2 Hz, 3H), 0.40 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.6, 142.8, 140.2, 136.7, 135.3, 129.6, 128.0, 126.9, 65.2, 32.1, 30.8, 23.4, 22.6, 14.5, 14.0, –1.2; IR (neat) 3319, 2957, 2930, 2870, 1611, 1466, 1435, 1377, 1248, 1124, 1078, 1015, 833, 816, 770, 750, 687 cm^{-1}; MS (EI) *m*/*z* (%) 276 (M^+, 0.1), 261 (19), 166 (15), 165 (100), 164 (15), 163 (24), 151 (22), 150 (12), 149 (79), 148 (13), 147 (61), 145 (30), 135 (19), 91 (11), 75 (14), 61 (19), 59 (10), 55 (10). Anal. Calcd. for $C_{17}H_{28}OSi$: C, 73.85; H, 10.21. Found: C, 73.67; H, 10.06%.

Alternative preparation of (*E*)-alkenyl[2-(hydroxymethyl)phenyl]dimethylsilanes



4a

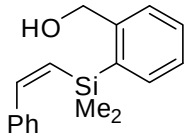
(*E*)-[2-(Hydroxymethyl)phenyl]dimethyl(1-octen-1-yl)silane (4a). A 1.0 M solution of 1-octyne in hexane (0.50 mL, 0.50 mmol) was added dropwise to a mixture of **3** (104 mg, 0.50 mmol), *t*-Bu_3P (10% hexane solution, 10.0 mg, 5.0 μmol), and platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex (0.01 M hexane solution, 0.50 mL, 5.0 μmol) at 0 °C. The resulting mixture was stirred at rt for 4 h, filtered through a Florisil pad, and concentrated in vacuo. The residue was dissolved in MeOH (2.5 mL) and water (2.5 mL) and treated with K_2CO_3 (1.38 g, 10.0 mmol) at 50 °C for 24 h. The mixture was extracted with diethyl ether, and the combined organic layers were washed with water and brine and dried over anhydrous $MgSO_4$; the residue was purified by flash chromatography on silica gel to give **4a** (113 mg, 82%).



4e

(*E*)-5-*t*-Butyldimethylsiloxy-1-pentenyl[2-(hydroxymethyl)phenyl]dimethylsilane (4e). The above procedure for **4a** was applied to the reaction of hydrosilane **3** (1.48 g, 7.0 mmol) and 5-*t*-butyldimethylsiloxy-1-pentyne (1.39 g, 7.0 mmol) to give **4e** (2.4 g, 93%) as a colorless oil, R_f 0.40 (hexane–ethyl acetate = 4 : 1). ^{1}H NMR (400 MHz,

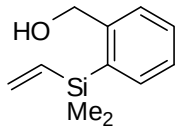
$CDCl_3$) δ 7.54 (d, *J* = 7.3 Hz, 1H), 7.46 (d, *J* = 7.7 Hz, 1H), 7.40 (td, *J* = 7.5, 1.3 Hz, 1H), 7.31–7.26 (m, 1H), 6.15 (dt, *J* = 18.5, 6.2 Hz, 1H), 5.86 (d, *J* = 18.5 Hz, 1H), 4.74 (s, 2H), 3.61 (t, *J* = 6.5 Hz, 2H), 2.20 (td, *J* = 6.5, 6.2 Hz, 2H), 1.63 (quint, *J* = 6.5 Hz, 2H), 1.57 (bs, 1H), 0.87 (s, 9H), 0.39 (s, 6H), 0.04 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.8, 146.4, 136.9, 135.1, 129.6, 128.7, 128.0, 127.0, 65.4, 62.5, 33.0, 31.7, 26.0, 18.3, –1.2, –5.3; IR (neat) 3358, 2953, 2930, 2856, 1616, 1472, 1254, 1105, 837, 777 cm^{-1}. Anal. Calcd. for $C_{20}H_{36}O_2Si_2$: C, 65.87; H, 9.95. Found: C, 65.98; H, 9.65%.



4l

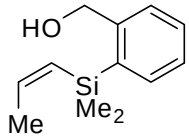
Preparation of (*Z*)-[2-(hydroxymethyl)phenyl]dimethyl(2-phenylethenyl)silane (4l) by ruthenium-catalyzed hydrosilylation of 1.[6f] A mixture of hydrosilane **1** (1.25 g, 5.0 mmol), phenylethyne (0.51 g, 5.0 mmol), and RuHCl(CO)[P(*i*-Pr)$_3$]$_2$ (0.122 g, 0.25 mmol) in CH_2Cl_2 (25 mL) was stirred at rt for 3 h before filtration through a silica gel pad and concentration in vacuo. The residue was dissolved in MeOH (15 mL) and treated with *p*-toluenesulfonic acid monohydrate (18.8 mg, 0.100 mmol) at rt for 9 h. After removal of the solvents in vacuo, the residue was purified by flash chromatography on silica gel to give **4l** (0.97 g, 72%) as a colorless oil, R_f 0.20 (hexane–ethyl acetate = 10 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (dd, *J* = 7.1, 1.1 Hz, 1H), 7.46 (dd, *J* = 15.0 Hz, 1H), 7.43–7.36 (m, 2H), 7.30 (td, *J* = 7.1, 2.0 Hz, 1H), 7.17–7.09 (m, 5H), 6.08 (d, *J* = 15.2 Hz, 1H), 4.69 (s, 2H), 1.54 (brs, 1H), 0.33 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.7, 146.1, 138.9, 137.4, 134.6, 131.2, 129.7, 128.2, 127.9, 127.8, 127.6, 127.1, 65.5, –0.3; IR (neat) 3331, 3055, 2959, 1591, 1568, 1493, 1435, 1250, 1124, 1078, 1028, 814, 758, 698 cm^{-1}. Anal. Calcd. for $C_{17}H_{20}OSi$: C, 76.07; H, 7.51. Found: C, 75.80; H, 7.59%.

Preparation of alkenyl[2-(hydroxymethyl)phenyl]dimethylsilanes by the reaction of 2 with Grignard reagents



4m

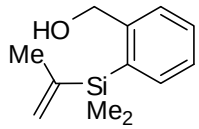
[2-(Hydroxymethyl)phenyl]dimethyl(vinyl)silane (4m). To a solution of **2** (2.5 g, 15.0 mmol) in THF (30 mL) was added a 1.0 M solution of vinylmagnesium bromide in THF (16.5 mL, 16.5 mmol) at 0 °C, and the resulting mixture was stirred at rt overnight. The mixture was diluted with diethyl ether, washed with a sat. NH_4Cl aq. solution, water, and brine, and dried over anhydrous $MgSO_4$. After removal of the solvents in vacuo, the residue was purified by flash chromatography on silica gel to give **4m** (2.3 g, 81%) as a colorless oil, R_f 0.30 (hexane–ethyl acetate = 7 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (dd, *J* = 7.3, 1.3 Hz, 1H), 7.46 (dd, *J* = 7.1, 0.7 Hz, 1H), 7.41 (td, *J* = 7.4, 1.5 Hz, 1H), 7.30 (td, *J* = 7.3, 1.5 Hz, 1H), 6.39 (dd, *J* = 20.3, 14.6 Hz, 1H), 6.08 (dd, *J* = 14.6, 3.7 Hz, 1H), 5.79 (dd, *J* = 20.3, 3.7 Hz, 1H), 4.74 (s, 2H), 1.71 (br s, 1H), 0.43 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.4, 139.0, 136.2, 135.2, 132.8, 129.8, 128.0, 127.0, 65.3, −1.6; IR (neat) 3321, 3051, 2957, 1404, 1250, 1078, 1009, 820, 775, 754 cm^{-1}. Anal. Calcd. for $C_{11}H_{16}OSi$: C, 68.69; H, 8.39. Found: C, 68.43; H, 8.36%.



4n

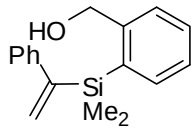
(*Z*)-[2-(Hydroxymethyl)phenyl]dimethyl(propen-1-yl)silane (4n). A solution of (*Z*)-propenylmagnesium bromide in THF (70 mL) [prepared from (*Z*)-1-bromopropene (6.0 g, 50 mmol) and Mg turnings (1.71 g, 50 mmol)][25] was added to a THF (20 mL) solution of **2** (5.8 g, 35 mmol) at 0 °C, and the resulting mixture was stirred at rt overnight. The mixture was diluted with diethyl ether (90 mL) and filtered to remove the remaning magnesium metal; the filtrate was washed with a sat. NH_4Cl aq. solution, then with water and finally with brine and dried over anhydrous $MgSO_4$. After removal of the solvents in vacuo, the residue was purified by flash chromatography on silica gel to give **4n** [6.8 g, as a 94%, (*Z*) : (*E*) = 94 : 6 as estimated by GC] as a colorless oil, R_f 0.26 (hexane–ethyl acetate = 7 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (dd, *J* = 7.3, 1.5 Hz, 1H), 7.47 (d, *J* = 7.6 Hz, 1H), 7.41 (td, *J* = 7.5, 1.5 Hz, 1H), 7.29 (td, *J* = 7.3, 1.3 Hz,

1H), 6.52 (dq, *J* = 13.9, 7.0 Hz, 1H), 5.76 (dq, *J* = 13.9, 1.5 Hz, 1H), 4.72 (s, 2H), 1.79 (br d, *J* = 4.9 Hz, 1H), 1.64 (dd, *J* = 6.8, 1.6 Hz, 3H), 0.45 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.3, 145.1, 137.5, 134.7, 129.7, 129.3, 128.2, 127.0, 65.4, 19.1, –0.2; IR (neat) 3319, 3055, 2961, 2910, 1609, 1435, 1248, 1200, 1124, 1078, 1034, 826, 777, 746, 696, 658 cm^{-1}; MS (EI) *m*/*z* (%) 206 (M^+, 0.1), 191 (12), 173 (29), 166 (10), 165 (62), 164 (37), 163 (18), 150 (15), 149 (100), 148 (11), 147 (39), 145 (48), 135 (16), 131 (14), 105 (11), 91 (11), 75 (43), 61 (19). Anal. Calcd. for $C_{12}H_{18}OSi$: C, 69.84; H, 8.79. Found: C, 69.82; H, 8.81%.



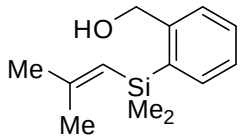
4o

[2-(Hydroxymethyl)phenyl]dimethyl(propen-2-yl)silane (4o). To a solution of **2** (7.5 g, 46 mmol) in THF (50 mL) was added a 0.5 M solution of 2-propenylmagnesium bromide in THF (100 mL, 50 mmol) at 0 °C, and the resulting mixture was stirred at rt for 9 h. The mixture was diluted with diethyl ether, washed sequentially with a sat. NH_4Cl aq. solution, water, and brine, and then dried over anhydrous $MgSO_4$. After removal of the solvents in vacuo, the residue was distilled under vacuum to give **4o** (8.4 g, 89%) as a colorless oil, bp 75 °C (0.4 mmHg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (dd, *J* = 7.4, 1.2 Hz, 1H), 7.48 (ddd, *J* = 7.7, 1.3, 0.5 Hz, 1H), 7.42 (td, *J* = 7.5, 1.5 Hz, 1H), 7.30 (td, *J* = 7.3, 1.5 Hz, 1H), 5.71 (dq, *J* = 3.1, 1.6 Hz, 1H), 5.37 (dq, *J* = 3.1, 1.3 Hz, 1H), 4.72 (s, 2H), 1.92 (br s, 1H), 1.82 (dd, *J* = 1.6, 1.3 Hz, 3H), 0.44 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.3, 146.6, 135.4, 135.3, 129.7, 127.9, 126.9, 126.6, 65.1, 22.5, –2.1; IR (neat) 3329, 2951, 1435, 1248, 1126, 1078, 1034, 924, 835, 818, 775, 754, 696, 662 cm^{-1}; MS (EI) *m*/*z* (%) 206 (M^+, 0.3), 191 (26), 189 (14), 173 (39), 166 (17), 165 (100), 164 (17), 163 (23), 150 (13), 149 (75), 148 (17), 147 (78), 146 (12), 145 (61), 135 (18), 131 (14), 105 (10), 75 (30). Anal. Calcd. for $C_{12}H_{18}OSi$: C, 69.84; H, 8.79. Found: C, 69.82; H, 8.56%.



4p

[2-(Hydroxymethyl)phenyl]dimethyl(1-phenylethenyl)silane (4p). To a solution of 1-phenylethenylmagnesium bromide in THF (18 mL), prepared from α-bromostyrene (4.3 g, 24 mmol) and Mg turnings (0.60 g, 25 mmol),[26] was added a THF (10 mL) solution of **2** (3.5 g, 21 mmol) at rt, and the resulting mixture was stirred at rt for 4.5 h. The mixture was diluted with diethyl ether and filtered to remove the remaining magnesium; the filtrate was washed with a sat. NH_4Cl aq. solution, water, and brine and dried over anhydrous $MgSO_4$. After removal of the solvents in vacuo, the residue was purified by flash chromatography on silica gel to give **4p** (3.2 g, 56%) as a colorless oil, R_f 0.28 (hexane–ethyl acetate = 5 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (dd, *J* = 7.4, 1.3 Hz, 1H), 7.48 (dd, *J* = 7.6, 0.8 Hz, 1H), 7.43 (td, *J* = 7.4, 1.3 Hz, 1H), 7.31 (td, *J* = 7.3, 1.5 Hz, 1H), 7.25–7.15 (m, 3H), 7.13–7.08 (m, 2H), 6.04 (d, *J* = 1.4 Hz, 1H), 5.71 (d, *J* = 1.4 Hz, 1H), 4.73 (s, 2H), 1.55 (br s, 1H), 0.48 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.0, 146.5, 143.6, 135.8, 135.3, 129.9, 128.8, 128.2, 128.1, 127.1, 126.72, 126.65, 65.2, –0.8; IR (neat) 3339, 3055, 2955, 1597, 1489, 1439, 1408, 1250, 1200, 1124, 1078, 1028, 934, 831, 812, 781, 754, 708, 633 cm^{-1}; MS (EI) *m*/*z* (%) 268 (M^+, 0.2), 253 (6), 235 (25), 209 (10), 166 (15), 165 (100), 163 (22), 149 (32), 148 (11), 147 (60), 145 (23), 137 (22), 135 (12), 104 (20). Anal. Calcd. for $C_{17}H_{20}OSi$: C, 76.07; H, 7.51. Found: C, 76.31; H, 7.48%.



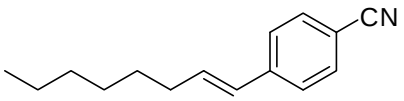
4q

[2-(Hydroxymethyl)phenyl]dimethyl(2-methylpropen-1-yl)silane (4q). A 0.5 M THF solution of 2-methylpropen-1-ylmagnesium bromide (100 mL, 50 mmol) was added to a solution of **2** (7.5 g, 46 mmol) in THF (50 mL) at 0 °C, and the resulting mixture was stirred at rt overnight before dilution with diethyl ether. The mixture was washed with a sat. NH_4Cl aq. solution, water, and brine and dried over anhydrous $MgSO_4$. After removal of the solvents in vacuo, flash chromatography of the residue on neutral

aluminium oxide (activity grade III) gave **4q** (7.1 g, 71%) as a colorless oil, R_f 0.26 (hexane–ethyl acetate = 5 : 1). ^{1}H NMR (400 MHz, C_6D_6) δ 7.57 (d, *J* = 7.3 Hz, 1H), 7.45 (d, *J* = 7.7 Hz, 1H), 7.22 (t, *J* = 7.4 Hz, 1H), 7.13 (d, *J* = 7.4 Hz, 1H), 5.41 (s, 1H), 4.63 (d, *J* = 5.9 Hz, 2H), 1.78 (t, *J* = 5.9 Hz, 1H), 1.66 (s, 3H), 1.46 (s, 3H), 0.37 (s, 6H); ^{13}C NMR (101 MHz, C_6D_6) δ 153.4, 147.3, 137.5, 134.9, 129.7, 128.0, 127.0, 123.8, 65.3, 29.3, 23.2, 0.0; IR (neat) 3238, 2953, 2907, 1620, 1437, 1371, 1246, 1123, 1076, 1036, 858, 833, 816, 800, 773, 745, 700, 644, 459 cm^{-1}; MS (EI) *m*/*z* (%) 220 (M^+, 0.04), 205 (10), 165 (28), 164 (32), 163 (17), 150 (14), 149 (100), 148 (10), 147 (25), 145 (30), 135 (10), 105 (10), 75 (27), 61 (16). Anal. Calcd. for $C_{13}H_{20}OSi$: C, 70.85; H, 9.15. Found: C, 70.83; H, 9.23%.

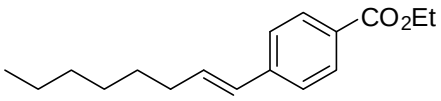
4.3 Cross-coupling reaction of alkenyl[2-(hydroxymethyl)phenyl]dimethylsilanes.

Cross-coupling reaction with aryl or alkenyl iodides. *A general procedure.* To a mixture of K_2CO_3 (0.30 g, 2.2 mmol), [(2-furyl)$_3$P (4.6 mg, 0.020 mmol) or **9** (3.7 mg, 0.010 mmol), and $PdCl_2$ (1.8 mg, 0.010 mmol) in DMSO (2.5 mL) were added an alkenylsilane (1.10 mmol) and an aryl or alkenyl iodide (1.00 mmol) sequentially, and the resulting mixture was stirred at 35 °C. After the time specified in Table 3 and Eq. 3, the mixture was diluted with diethyl ether, washed with water and brine, and dried over anhydrous $MgSO_4$. Concentration in vacuo followed by flash chromatography on silica gel gave the corresponding coupling product in a yield listed in Table 3 and Eq. 3.



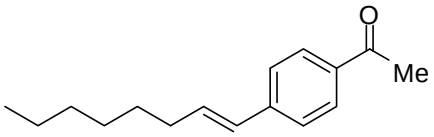
6aa

(*E*)-1-(4-Cyanophenyl)-1-octene (6aa). A colorless oil, R_f 0.31 (hexane–ethyl acetate = 20 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 8.4 Hz, 2H), 7.39 (d, *J* = 8.4 Hz, 2H), 6.38–6.35 (m, 2H), 2.24–2.20 (m, 2H), 1.50–1.42 (m, 2H), 1.40–1.25 (m, 6H), 0.92–0.86 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.4, 135.5, 132.2, 128.3, 126.3, 119.1, 109.8, 33.1, 31.6, 28.9, 28.8, 22.5, 14.0; IR (neat) 2955, 2928, 2855, 2226, 1649, 1605, 1502, 1466, 1412, 1175, 966, 856, 733, 552 cm^{-1}; MS (EI) *m*/*z* (%) 213 (M^+, 18), 143 (11), 142 (34), 130 (19), 129 (100), 116 (14), 115 (11). Anal. Calcd. for $C_{15}H_{19}N$: C, 84.46; H, 8.98. Found: C, 84.37; H, 8.96%.



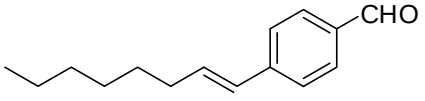
6ab

(*E*)-1-(4-Ethoxycarbonylphenyl)-1-octene (6ab). A colorless oil, R_f 0.40 (hexane–ethyl acetate = 20 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.4 Hz, 2H), 7.38 (d, *J* = 7.0 Hz, 2H), 6.45–6.32 (m, 2H), 4.37 (q, *J* = 7.2 Hz, 2H), 2.23 (q, *J* = 7.2 Hz, 2H), 1.53–1.28 (m, 11H), 0.94–0.86 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.5, 142.4, 134.2, 129.8, 129.0, 128.5, 125.7, 60.8, 33.2, 31.7, 29.1, 28.9, 22.6, 14.3, 14.1; IR (neat) 2957, 2928, 2855, 1715, 1607, 1466, 1412, 1366, 1275, 1177, 1107, 1020, 968, 957, 864, 762, 696 cm^{-1}; MS (EI) *m*/*z* (%) 261 (M^++1, 14), 260 (M^+, 76), 215 (37), 177 (16), 176 (100), 161 (11), 148 (45), 145 (23), 132 (10), 131 (55), 129 (16), 128 (13), 118 (10), 117 (86), 116 (23), 115 (49), 91 (18). Anal. Calcd. for $C_{17}H_{24}O_2$: C, 78.42; H, 9.29. Found: C, 78.45; H, 9.41%.



6ac

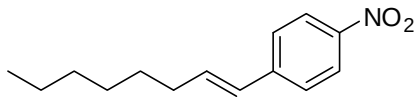
(*E*)-1-(4-Acetylphenyl)-1-octene (6ac). A colorless oil, R_f 0.30 (hexane–ethyl acetate = 20 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.4 Hz, 2H), 7.39 (d, *J* = 8.4 Hz, 2H), 6.43–6.33 (m, 2H), 2.57 (s, 3H), 2.23 (q, *J* = 6.4 Hz, 2H), 1.52–1.42 (m, 2H), 1.40–1.25 (m, 6H), 0.92–0.86 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.5, 142.6, 135.3, 134.5, 128.8, 128.7, 125.8, 33.1, 31.7, 29.1, 28.9, 26.5, 22.6, 14.0; IR (neat) 2957, 2926, 2855, 1682, 1603, 1410, 1358, 1267, 1180, 966, 592 cm^{-1}; MS (EI) *m*/*z* (%) 231 (M^++1, 12), 230 (M^+, 73), 216 (11), 215 (72), 148 (10), 147 (15), 146 (56), 145 (11), 134 (11), 131 (100), 128 (11), 117 (19), 116 (12), 115 (36). Anal. Calcd. for $C_{16}H_{22}O$: C, 83.43; H, 9.63. Found: C, 83.72; H, 9.74%.



6ad

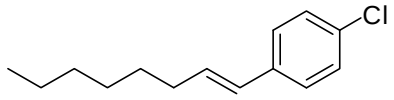
(*E*)-1-(4-Formylphenyl)-1-octene (6ad). A colorless oil, R_f 0.30 (hexane–ethyl acetate = 30 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.96 (s, 1H), 7.80 (d, *J* = 8.4 Hz, 2H), 7.48 (d,

J = 8.4 Hz, 2H), 6.64–6.42 (m, 2H), 2.28–2.22 (m, 2H), 1.53–1.44 (m, 2H), 1.40–1.25 (m, 6H), 0.92–0.86 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.7, 144.1, 135.4, 134.8, 130.1, 128.9, 126.3, 33.2, 31.7, 29.0, 28.9, 22.6, 14.1; IR (neat) 2955, 2926, 2855, 1697, 1603, 1568, 1304, 1213, 1167, 966, 851, 802 cm^{-1}; MS (EI) *m*/*z* (%) 216 (M^+, 43), 133 (14), 132 (100), 131 (39), 117 (62), 116 (11), 115 (29), 91 (19). Anal. Calcd. for $C_{15}H_{20}O$: C, 83.28; H, 9.32. Found: C, 83.40; H, 9.37%.



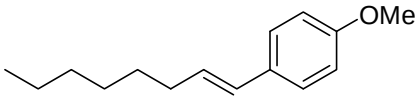
6ae

(*E*)-1-(4-Nitrophenyl)-1-octene (6ae). A colorless oil, R_f 0.17 (hexane–ethyl acetate = 30 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, J = 8.8 Hz, 2H), 7.44 (d, J = 8.8 Hz, 2H), 6.46–6.42 (m, 2H), 2.30–2.20 (m, 2H), 1.54–1.42 (m, 2H), 1.40–1.24 (m, 6H), 0.93–0.87 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.3, 144.4, 136.7, 128.0, 126.3, 123.9, 33.2, 31.6, 28.91, 28.87, 22.6, 14.0; IR (neat) 2955, 2928, 2855, 1649, 1597, 1518, 1466, 1342, 1109, 968, 955, 860, 824, 745, 689 cm^{-1}; MS (EI) *m*/*z* (%) 234 (M^++1, 11), 233 (M^+, 67), 151 (12), 150 (40), 149 (100), 137 (29), 129 (13), 128 (17), 119 (22), 117 (19), 116 (79), 115 (70), 103 (13), 91 (11), 55 (11); HRMS (FAB^+) Calcd for $C_{14}H_{20}NO_2$: $[M+H]^+$, 234.1494. Found: *m*/*z* 234.1497.



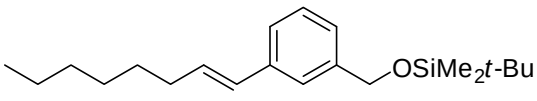
6af

(*E*)-1-(4-Chlorophenyl)-1-octene (6af). A colorless oil, R_f 0.60 (hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (s, 4H), 6.33 (dt, J = 15.5, 1.2 Hz, 1H), 6.21 (dt, J = 15.5, 6.8 Hz, 1H), 2.20 (q, J = 6.8 Hz, 2H), 1.52–1.42 (m, 2H), 1.40–1.23 (m, 6H), 0.94–0.88 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.4, 132.2, 132.0, 128.54, 128.49, 127.1, 33.0, 31.7, 29.2, 28.9, 22.6, 14.1; IR (neat) 2957, 2926, 2855, 1709, 1491, 1466, 1404, 1092, 1013, 964, 845, 820, 802, 735 cm^{-1}; MS (EI) *m*/*z* (%) 224 (M^++2, 15), 222 (M^+, 44), 153 (29), 152 (12), 151 (88), 140 (31), 139 (10), 138 (100), 129 (10), 125 (17), 117 (11), 116 (36), 115 (46); HRMS (EI) Calcd. for $C_{14}H_{19}Cl$: M^+, 222.1175. Found: *m*/*z* 222.1172.



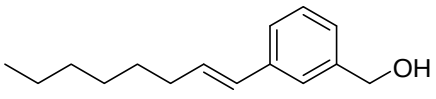
6ag

(*E*)-1-(4-Methoxyphenyl)-1-octene (6ag). A colorless oil, R_f 0.36 (hexane–ethyl acetate = 50 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (d, *J* = 8.7 Hz, 2H), 6.84 (d, *J* = 8.7 Hz, 2H), 6.33 (d, *J* = 15.7 Hz, 1H), 6.09 (dt, *J* = 15.7, 7.0 Hz, 1H), 3.81 (s, 3H), 2.19 (q, *J* = 7.5 Hz, 2H), 1.50–1.42 (m, 2H), 1.40–1.26 (m, 6H), 0.93–0.88 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.6, 130.8, 129.1, 129.0, 126.9, 113.9, 55.2, 33.0, 31.8, 29.5, 28.9, 22.6, 14.1; IR (neat) 2955, 2926, 2855, 1609, 1510, 1466, 1248, 1175, 1038, 964, 841 cm^{-1}; MS (EI) *m*/*z* (%) 218 (M^+, 39), 148 (12), 147 (100), 134 (14), 121 (15), 91 (10). Anal. Calcd. for $C_{15}H_{22}O$: C, 82.52; H, 10.16. Found: C, 82.52; H, 9.98%.



6ah

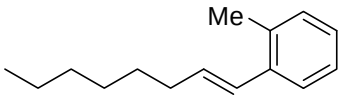
(*E*)-1-[3-(*t*-Butyldimethylsiloxymethyl)phenyl]-1-octene (6ah). A colorless oil, R_f 0.35 (hexane–ethyl acetate = 50 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (s, 1H), 7.25–7.13 (m, 3H), 6.37 (d, *J* = 15.7 Hz, 1H), 6.22 (dt, *J* = 15.7, 6.9 Hz, 1H), 4.72 (s, 2H), 2.20 (q, *J* = 7.7 Hz, 2H), 1.50–1.42 (m, 2H), 1.38–1.26 (m, 6H), 0.95 (s, 9H), 0.39 (t, *J* = 6.9 Hz, 3H), 0.10 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.5, 137.8, 131.2, 129.7, 128.3, 124.49, 124.47, 123.5, 64.9, 33.0, 31.7, 29.3, 28.9, 26.0, 22.6, 18.4, 14.1, –5.2; IR (neat) 2955, 2928, 2856, 1462, 1256, 1105, 1080, 962, 837, 777 cm^{-1}; MS (EI) *m*/*z* (%) 332 (M^+, 2), 276 (27), 275 (100), 245 (16), 201 (34). Anal. Calcd. for $C_{21}H_{36}OSi$: C, 75.84; H, 10.91. Found: C, 75.97; H, 11.13%.



6ai

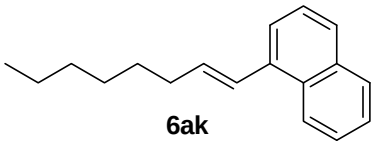
(*E*)-1-[3-(Hydroxymethyl)phenyl]-1-octene (6ai). A colorless oil, R_f 0.30 (hexane–ethyl acetate = 5 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (s, 1H), 7.32–7.27 (m, 2H), 7.21–7.18 (m, 1H), 6.38 (d, *J* = 15.6 Hz, 1H), 6.26 (dt, *J* = 16.0, 6.8 Hz, 1H), 4.68 (s, 2H), 2.21 (q, *J* = 7.2 Hz, 2H), 1.62 (br s, 1H), 1.51–1.42 (m, 2H), 1.40–1.26 (m, 6H), 0.93–0.87 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.0, 138.3, 131.7, 129.4, 128.7,

125.35, 125.32, 124.4, 65.4, 33.0, 31.7, 29.3, 28.9, 22.6, 14.1; IR (neat) 3329, 2955, 2926, 2855, 1466, 1433, 1020, 962, 775, 733, 696 cm^{-1}; MS (EI) *m*/*z* (%) 218 (M^+, 36), 134 (42), 132 (16), 131 (16), 129 (24), 128 (12), 118 (14), 117 (100), 115 (22), 105 (10), 91 (20). Anal. Calcd. for $C_{15}H_{22}O$: C, 82.52; H, 10.16. Found: C, 82.63; H, 10.40%.



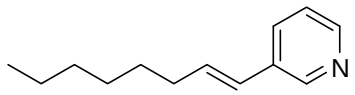
6aj

(*E*)-1-(2-Methylphenyl)-1-octene (6aj). A colorless oil, R_f 0.71 (hexane). ^1H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 7.2 Hz, 1H), 7.19–7.10 (m, 3H), 6.57 (d, *J* = 15.6 Hz, 1H), 6.10 (dt, *J* = 15.6, 6.8 Hz, 1H), 2.34 (s, 3H), 2.23 (q, *J* = 7.2 Hz, 2H), 1.54–1.42 (m, 2H), 1.40–1.26 (m, 6H), 0.92–0.88 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.1, 134.8, 132.6, 130.1, 127.5, 126.7, 126.0, 125.4, 33.3, 31.7, 29.4, 28.9, 22.6, 19.8, 14.1; IR (neat) 3020, 2957, 2926, 2855, 1485, 1460, 1377, 962, 745 cm^{-1}; MS (EI) *m*/*z* (%) 202 (M^+, 42), 132 (13), 131 (100), 129 (12), 118 (51), 117 (18), 116 (17), 115 (18), 105 (16), 91 (15). Anal. Calcd. for $C_{15}H_{22}$: C, 89.04; H, 10.96. Found: C, 88.97; H, 11.18%.



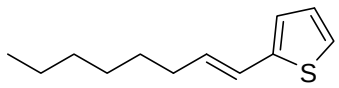
6ak

(*E*)-1-(1-Naphthyl)-1-octene (6ak). A colorless oil, R_f 0.50 (hexane). ^1H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 7.6 Hz, 1H), 7.84 (d, *J* = 7.2 Hz, 1H), 7.74 (d, *J* = 8.0 Hz, 1H), 7.58–7.40 (m, 4H), 7.11 (d, *J* = 15.2 Hz, 1H), 6.24 (dt, *J* = 16.0, 7.2 Hz, 1H), 2.33 (q, *J* = 7.6 Hz, 2H), 1.60–1.52 (m, 2H), 1.46–1.32 (m, 6H), 0.94–0.88 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.8, 134.6, 133.6, 131.1, 128.4, 127.1, 126.8, 125.74, 125.65, 125.58, 124.0, 123.5, 33.5, 31.8, 29.4, 29.0, 22.7, 14.1; IR (neat) 3059, 3044, 2955, 2926, 2855, 1591, 1508, 1466, 1394, 964, 775, 727 cm^{-1}; MS (EI) *m*/*z* (%) 238 (M^+, 44), 168 (17), 167 (100), 166 (15), 165 (35), 154 (21), 153 (24), 152 (22), 141 (13). Anal. Calcd. for $C_{18}H_{22}$: C, 90.70; H, 9.30. Found: C, 90.61; H, 9.32%.



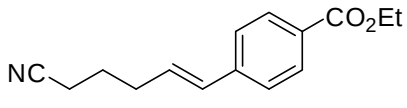
6al

(*E*)-1-(3-Pyridyl)-1-octene (6al). A colorless oil, R_f 0.35 (hexane–ethyl acetate = 5 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (br s, 1H), 8.42 (br d, *J* = 3.7 Hz, 1H), 7.65 (d, *J* = 7.9 Hz, 1H), 7.22 (dd, *J* = 7.8, 4.8 Hz, 1H), 6.38–6.26 (m, 2H), 2.26–2.20 (m, 2H), 1.52–1.43 (m, 2H), 1.40–1.26 (m, 6H), 0.92–0.86 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.8, 147.7, 133.8, 133.5, 132.5, 126.1, 123.4, 33.1, 31.7, 29.1, 28.9, 22.6, 14.1; IR (neat) 3024, 2955, 2926, 2855, 2359, 2341, 1653, 1568, 1466, 1414, 1022, 964, 708 cm^{-1}; MS (EI) *m*/*z* (%) 189 (M^+, 46), 146 (10), 132 (10), 130 (10), 119 (14), 118 (87), 117 (37), 106 (27), 105 (100), 93 (14), 91 (15). Anal. Calc. for $C_{13}H_{19}N$: C, 82.48; H, 10.12. Found: C, 82.20; H, 10.06%.



6am

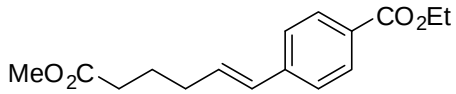
(*E*)-1-(2-Thienyl)-1-octene (6am). A colorless oil, R_f 0.70 (hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.08 (d, *J* = 5.2 Hz, 1H), 6.95–6.91 (m, 1H), 6.86 (d, *J* = 3.2 Hz, 1H), 6.50 (d, *J* = 15.6 Hz, 1H), 6.07 (dt, *J* = 15.6, 6.8 Hz, 1H), 2.17 (q, *J* = 7.2 Hz, 2H), 1.52–1.41 (m, 2H), 1.40–1.24 (m, 6H), 0.94–0.86 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 131.3, 127.2, 124.1, 123.0, 122.9, 108.2, 32.9, 31.7, 29.2, 28.9, 22.6, 14.1; IR (neat) 2955, 2926, 2855, 1724, 1686, 1676, 1466, 1437, 1420, 1377, 1211, 1042, 953, 853, 723, 692 cm^{-1}; MS (EI) *m*/*z* (%) 194 (M^+, 41), 147 (10), 124 (12), 123 (100), 110 (46), 97 (14), 73 (18); HRMS (EI) Calcd for $C_{12}H_{18}S$: M^+, 194.1129. Found: *m*/*z* 194.1126.



6bb

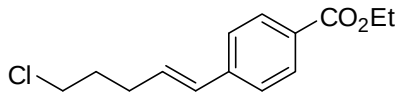
(*E*)-6-(4-Ethoxycarbonylphenyl)-5-hexenenitrile (6bb). A colorless oil, R_f 0.30 (hexane–ethyl acetate = 5 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.4 Hz, 2H), 7.39 (d, *J* = 8.4 Hz, 2H), 6.50 (d, *J* = 16.0 Hz, 1H), 6.31–6.22 (m, 1H), 4.36 (q, *J* = 7.2 Hz, 2H), 2.44–2.38 (m, 4H), 1.86 (quint, *J* = 7.2 Hz, 2H), 1.39 (t, *J* = 7.2 Hz, 3H); ^{13}C

NMR (101 MHz, $CDCl_3$) δ 166.4, 141.4, 131.2, 130.4, 129.9, 129.1, 125.9, 119.4, 60.9, 31.7, 24.8, 16.5, 14.3; IR (neat) 2984, 2937, 2907, 2243, 1711, 1607, 1458, 1437, 1414, 1366, 1271, 1180, 1126, 1109, 1092, 1024, 968, 955, 768, 750, 694 cm; MS (EI) *m*/*z* (%) 244 (M^++1, 14), 243 (M^+, 81), 199 (15), 198 (100), 197 (16), 196 (19), 170 (12), 157 (14), 145 (15), 130 (14), 129 (43), 128 (22), 117 (57), 116 (16), 115 (40); HRMS (EI) Calcd for $C_{15}H_{17}NO_2$: M^+, 243.1259. Found: *m*/*z* 243.1259.



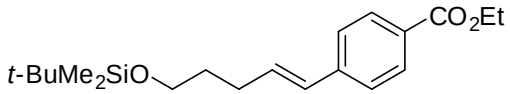
6cb

Methyl (*E*)-6-(4-ethoxycarbonylphenyl)-5-hexenoate (6cb). A colorless oil, R_f 0.32 (hexane–ethyl acetate = 5 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.4 Hz, 2H), 7.38 (d, *J* = 8.4 Hz, 2H), 6.44 (d, *J* = 15.8 Hz, 1H), 6.31 (dt, *J* = 15.8, 6.8 Hz, 1H), 4.37 (q, *J* = 7.1 Hz, 2H), 3.66 (s, 3H), 2.37 (t, *J* = 6.8 Hz, 2H), 2.29 (q, *J* = 6.8 Hz, 2H), 1.84 (quint, *J* = 6.8 Hz, 2H), 1.39 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.9, 166.5, 141.9, 132.4, 130.1, 129.8, 128.8, 125.8, 60.8, 51.5, 33.4, 32.4, 24.3, 14.3; IR (neat) 2982, 2951, 1736, 1717, 1607, 1275, 1178, 1107, 1020, 970, 860, 760 cm^{-1}. HRMS (EI) Calcd for $C_{16}H_{20}O_4$: M^+, 276.1362. Found: *m*/*z* 276.1359.



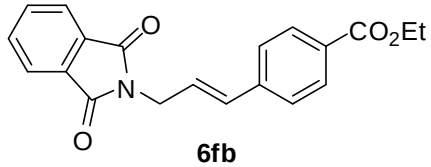
6db

(*E*)-5-Chloro-1-(4-ethoxycarbonylphenyl)-1-pentene (6db). A colorless oil, R_f 0.25 (hexane–ethyl acetate = 10 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.3 Hz, 2H), 7.39 (d, *J* = 8.3 Hz, 2H), 6.48 (d, *J* = 15.9 Hz, 1H), 6.31 (dt, *J* = 15.9, 6.3 Hz, 1H), 4.37 (q, *J* = 7.1 Hz, 2H), 3.59 (t, *J* = 6.3 Hz, 2H), 2.42 (q, *J* = 6.3 Hz, 2H), 1.97 (quint, *J* = 6.3 Hz, 2H), 1.39 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.4, 141.8, 131.5, 130.5, 129.9, 129.0, 125.8, 60.9, 44.2, 31.8, 30.1, 14.3; IR (neat) 2982, 2959, 2937, 1715, 1607, 1277, 1178, 1107, 1020, 970, 758 cm^{-1}. Anal. Calcd. for $C_{14}H_{17}ClO_2$: C, 66.53; H, 6.78. Found: C, 66.61; H, 6.71%.



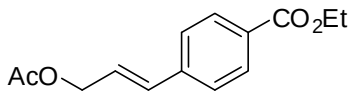
6eb

(*E*)-5-*t*-Butyldimethylsiloxy-1-(4-ethoxycarbonylphenyl)-1-pentene (6eb). A colorless oil, R_f 0.23 (hexane–ethyl acetate = 20 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.3 Hz, 2H), 7.38 (d, *J* = 8.3 Hz, 2H), 6.43 (d, *J* = 15.9 Hz, 1H), 6.31 (dt, *J* = 15.9, 6.3 Hz, 1H), 4.36 (q, *J* = 7.1 Hz, 2H), 3.67 (t, *J* = 6.3 Hz, 2H), 2.31 (q, *J* = 7.0 Hz, 2H), 1.74–1.65 (m, 2H), 1.39 (t, *J* = 7.1 Hz, 3H), 0.91 (s, 9H), 0.06 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.6, 142.3, 133.5, 129.9, 129.4, 128.7, 125.7, 62.4, 60.8, 32.2, 29.5, 26.0, 18.4, 14.4, –5.3; IR (neat) 2955, 2930, 2895, 2856, 1719, 1607, 1275, 1177, 1105, 1020, 968, 837, 775 cm^{-1}; HRMS (CI) Calcd for $C_{20}H_{33}O_3Si$: $[M+H]^+$, 349.2199. Found: *m*/*z* 349.2193.



6fb

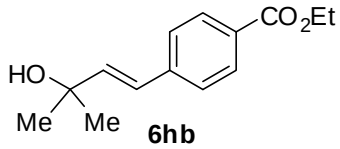
(*E*)-*N*-[3-(4-Ethoxycarbonylphenyl)-2-propen-1-yl]phthalimide (6fb). A colorless solid, mp 124.0–125.0 °C, R_f 0.72 (hexane–ethyl acetate = 3 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.3 Hz, 2H), 7.90–7.80 (m, 2H), 7.76–7.66 (m, 2H), 7.40 (d, *J* = 8.3 Hz, 2H), 6.68 (d, *J* = 15.9 Hz, 1H), 6.37 (dt, *J* = 15.9, 6.4 Hz, 1H), 4.48 (d, *J* = 6.4 Hz, 2H), 4.36 (q, *J* = 7.1 Hz, 2H), 1.38 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.8, 166.3, 140.6, 134.1, 132.7, 132.1, 129.8, 129.7, 126.4, 125.4, 123.4, 60.9, 39.5, 14.3; IR (KBr) 2968, 1773, 1728, 1703, 1470, 1427, 1396, 1367, 1294, 1265, 1180, 1109, 980, 955, 746, 727, 710, 530 cm^{-1}. Anal. Calcd. for $C_{20}H_{17}NO_4$: C, 71.63; H, 5.11. Found: C, 71.58; H, 5.18%.



6gb

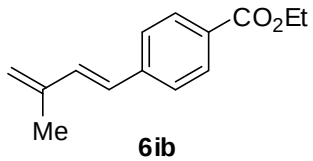
(*E*)-3-(4-Ethoxycarbonylphenyl)-2-propen-1-yl acetate (6gb). A colorless oil, R_f 0.31 (hexane–ethyl acetate = 5 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.3 Hz, 2H), 7.44 (d, *J* = 8.3 Hz, 2H), 6.68 (d, *J* = 15.9 Hz, 1H), 6.39 (dt, *J* = 15.9, 6.2 Hz, 1H), 4.75

(d, J = 6.2 Hz, 2H), 4.37 (q, J = 7.1 Hz, 2H), 2.11 (s, 3H), 1.39 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.7, 166.3, 140.5, 132.8, 129.9, 129.8, 126.4, 125.8, 64.7, 61.0, 20.9, 14.3; IR (neat) 2982, 2937, 1742, 1715, 1609, 1366, 1277, 1229, 1178, 1107, 1024, 970, 866, 760, 698 cm^{-1}. Anal. Calcd. for $C_{14}H_{16}O_4$: C, 67.73; H, 6.50. Found: C, 67.88; H, 6.44%.



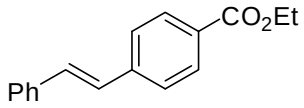
6hb

(*E*)-4-(4-Ethoxycarbonylphenyl)-2-methyl-3-buten-2-ol (6hb). A colorless solid, mp 38.0–38.8 °C, R_f 0.29 (hexane–ethyl acetate = 2 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, J = 8.3 Hz, 2H), 7.43 (d, J = 8.3 Hz, 2H), 6.64 (d, J = 16.1 Hz, 1H), 6.46 (d, J = 16.1 Hz, 1H), 4.37 (q, J = 7.1 Hz, 2H), 1.57 (br s, 1H), 1.44 (s, 6H), 1.39 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.4, 141.4, 140.0, 129.9, 129.2, 126.2, 125.6, 71.1, 60.9, 29.9, 14.3; IR (KBr) 3311, 2980, 1712, 1609, 1366, 1281, 1180, 1146, 1111, 1020, 974, 903, 872, 764, 698 cm^{-1}. HRMS (EI) Calcd for $C_{14}H_{18}O_3$: M^+, 234.1256 Found: *m*/z 234.1248.



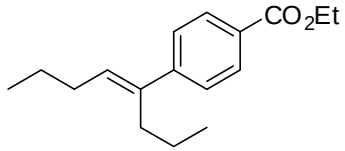
6ib

(*E*)-1-(4-Ethoxycarbonylphenyl)-3-methyl-1,3-butadiene (6ib). A colorless solid, mp 43.5–44.5 °C C, R_f 0.23 (hexane–ethyl acetate = 20 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, J = 8.4 Hz, 2H), 7.48 (d, J = 8.4 Hz, 2H), 6.97 (d, J = 16.1 Hz, 1H), 6.55 (d, J = 16.1 Hz, 1H), 5.19 (s, 1H), 5.15 (s, 1H), 4.37 (q, J = 7.1 Hz, 2H), 1.98 (s, 3H), 1.40 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.4, 141.80, 141.77, 134.0, 129.9, 129.1, 127.7, 126.2, 118.9, 60.9, 18.5, 14.3; IR (KBr) 2984, 1705, 1605, 1288, 1263, 1184, 1130, 1109, 1022, 986, 880, 772, 708, 536 cm^{-1}. Anal. Calcd. for $C_{14}H_{16}O_2$: C, 77.75; H, 7.46. Found: C, 77.48; H, 7.39%.



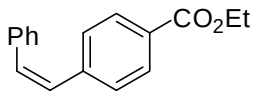
6jb

(*E*)-4-Ethoxycarbonylstilbene (6jb). A colorless solid, mp 106.0–106.5 °C, R_f 0.30 (hexane–ethyl acetate = 20 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.4 Hz, 2H), 7.58–7.52 (m, 4H), 7.41–7.36 (m, 2H), 7.32–7.27 (m, 1H), 7.22 (d, *J* = 16.4 Hz, 1H), 7.13 (d, *J* = 16.4 Hz, 1H), 4.39 (q, *J* = 7.1 Hz, 2H), 1.41 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.4, 141.7, 136.7, 131.1, 130.0, 129.2, 128.8, 128.2, 127.6, 126.8, 126.3, 60.9, 14.4; IR (KBr) 2976, 1705, 1607, 1367, 1283, 1180, 1130, 1109, 1024, 976, 770, 696, 527 cm^{-1}; MS (EI) *m*/*z* (%) 253 (M^++1, 20), 252 (M^+, 100), 208 (12), 207 (65), 180 (10), 179 (54), 178 (57). Anal. Calcd. for $C_{17}H_{16}O_2$: C, 80.93; H, 6.39. Found: C, 81.18; H, 6.27%.



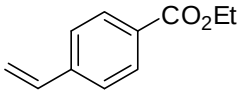
6kb

(*E*)-4-(4-Ethoxycarbonylphenyl)-4-octene (6kb). A colorless oil, R_f 0.40 (hexane–ethyl acetate = 30 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.6 Hz, 2H), 7.39 (d, *J* = 8.8 Hz, 2H), 5.76 (t, *J* = 7.3 Hz, 1H), 4.37 (q, *J* = 7.1 Hz, 2H), 2.49 (t, *J* = 7.5 Hz, 2H), 2.19 (q, *J* = 7.3 Hz, 2H), 1.53–1.42 (m, 2H), 1.41–1.32 (m, 5H), 0.97 (t, *J* = 7.3 Hz, 3H), 0.88 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.6, 148.0, 139.4, 131.1, 129.5, 128.4, 126.2, 60.8, 31.4, 30.7, 22.9, 21.8, 14.4, 14.0, 13.9; IR (neat) 2959, 2932, 2872, 1720, 1607, 1462, 1408, 1366, 1273, 1180, 1107, 1020, 858, 772, 706 cm^{-1}; MS (EI) *m*/*z* (%) 261 (M^++1, 15), 260 (M^+, 79), 231 (16), 217 (44), 215 (31), 190 (21), 189 (15), 187 (51), 173 (30), 159 (16), 157 (13), 146 (13), 145 (100), 143 (17), 131 (35), 130 (15), 129 (46), 128 (32), 127 (10), 117 (63), 116 (11), 115 (31), 91 (19). Anal. Calcd. for $C_{17}H_{24}O_2$: C, 78.42; H, 9.29. Found: C, 78.28; H, 9.14%.



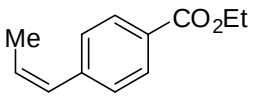
6lb

(*Z*)-4-Ethoxycarbonylstilbene (6lb). A colorless oil, R_f 0.33 (hexane–ethyl acetate = 20 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.4 Hz, 2H), 7.30 (d, *J* = 8.4 Hz, 2H), 7.24–7.19 (m, 5H), 6.71 (d, *J* = 12.4 Hz, 1H), 6.60 (d, *J* = 12.4 Hz, 1H), 4.36 (q, *J* = 7.1 Hz, 2H), 1.38 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.4, 142.0, 136.7, 132.1, 109.5, 129.3, 128.9, 128.83, 128.79, 128.3, 127.5, 60.9, 14.3; IR (neat) 2980, 1717, 1607, 1366, 1275, 1178, 1103, 1020, 781, 714, 698 cm^{-1}. Anal. Calcd. for $C_{17}H_{16}O_2$: C, 80.93; H, 6.39. Found: C, 80.70; H, 6.27%.



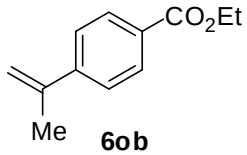
6mb

Ethyl 4-vinylbenzoate (6mb).[27] A colorless oil, R_f 0.30 (hexane–ethyl acetate = 30 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.4 Hz, 2H), 7.46 (d, *J* = 8.4 Hz, 2H), 6.75 (dd, *J* = 17.6, 11.2 Hz, 1H), 5.86 (d, *J* = 17.2 Hz, 1H), 5.38 (d, *J* = 10.8 Hz, 1H), 4.37 (q, *J* = 7.2 Hz, 2H), 1.40 (t, *J* = 7.2 Hz, 3H).



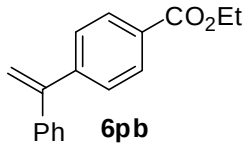
6nb

1-(4-Ethoxycarbonylphenyl)propene [(*Z*) : (*E*) = 94 : 6] (6nb). A colorless oil, R_f 0.33 (hexane–ethyl acetate = 20 : 1). (*Z*)-Isomer showed: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (dd, *J* = 8.4 Hz, 2H), 7.35 (d, *J* = 8.2 Hz, 2H), 6.46 (dd, *J* = 11.8, 1.8 Hz, 1H), 5.90 (dq, *J* = 11.8, 7.2 Hz, 1H), 4.38 (q, *J* = 7.2 Hz, 2H), 1.91 (dd, *J* = 7.2, 1.8 Hz, 3H), 1.40 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.5, 142.2, 129.4, 129.1, 129.0, 128.7, 128.3, 60.8, 14.8, 14.3; IR (neat) 2980, 1715, 1609, 1367, 1310, 1277, 1178, 1105, 1020, 866, 773, 733, 721, 700 cm^{-1}; MS (EI) *m*/*z* (%) 190 (M^+, 50), 162 (12), 146 (13), 145 (100), 117 (20), 115 (25), 91 (10). Anal. Calcd. for $C_{12}H_{14}O_2$: C, 75.76; H, 7.42. Found: C, 75.90; H, 7.44%.



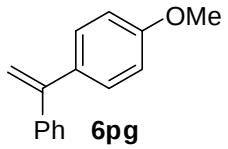
6ob

2-(4-Ethoxycarbonylphenyl)propene (6ob). A colorless oil, R_f 0.40 (hexane–ethyl acetate = 10 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (dd, *J* = 8.0 Hz, 2H), 7.52 (d, *J* = 8.2 Hz, 2H), 5.47 (dq, *J* = 1.3, 0.7 Hz, 1H), 5.19 (qd, *J* = 1.5, 1.3 Hz, 1H), 4.38 (q, *J* = 7.1 Hz, 2H), 2.17 (dd, *J* = 1.5, 0.7 Hz, 3H), 1.40 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.7, 145.8, 142.7, 129.8, 129.5, 125.6, 114.7, 61.1, 21.9, 14.6; IR (neat) 2980, 2359, 2341, 1715, 1609, 1367, 1275, 1184, 1123, 1103, 1020, 899, 860, 783, 719 cm^{-1}; MS (EI) *m*/*z* (%) 190 (M^+, 42), 162 (19), 146 (13), 145 (100), 115 (20); HRMS (FAB$^+$) Calcd for $C_{12}H_{14}O_2$: M^+, 190.0994. Found: *m*/*z* 190.0993.



6pb

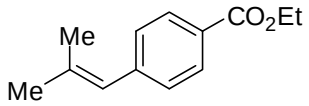
1-(4-Ethoxycarbonylphenyl)-1-phenylethene (6pb). A colorless solid, mp 46.7–47.3 °C, R_f 0.33 (hexane–ethyl acetate = 10 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.6 Hz, 2H), 7.41 (d, *J* = 8.6 Hz, 2H), 7.36–7.30 (m, 5H), 5.55 (d, *J* = 1.1 Hz, 1H), 5.54 (d, *J* = 1.1 Hz, 1H), 4.39 (q, *J* = 7.1 Hz, 2H), 1.41 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.4, 149.3, 145.9, 140.8, 129.7, 129.5, 128.3, 128.2, 128.0, 115.8, 60.9, 14.3; IR (KBr) 1717, 1279, 1105, 775, 702 cm^{-1}; MS (EI) *m*/*z* (%) 253 (M^++1, 18), 252 (M^+, 97), 224 (14), 208 (18), 207 (100), 179 (44), 178 (68), 177 (11), 176 (11). Anal. Calcd. for $C_{17}H_{16}O_2$: C, 80.93; H, 6.39. Found: C, 81.01; H, 6.47%.



6pg

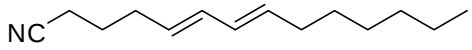
1-(4-Methoxyphenyl)-1-phenylethene (6pg). A colorless solid, mp 75.3–76.8 °C, R_f 0.39 (hexane–ethyl acetate = 15 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38–7.31 (m, 5H), 7.28 (d, *J* = 8.8 Hz, 2H), 6.87 (d, *J* = 8.8 Hz, 2H), 5.41 (d, *J* = 1.4 Hz, 1H), 5.36 (d, *J* = 1.4 Hz, 1H), 3.83 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.6, 149.7, 142.0, 134.2, 129.6, 128.6, 128.4, 127.9, 113.7, 113.2, 55.5; IR (KBr) 3005, 2951, 2835, 1908, 1811,

1605, 1572, 1508, 1491, 1456, 1441, 1290, 1250, 1180, 1028, 901, 843, 785, 708, 581, 552 cm^{-1}; MS (EI) *m*/*z* (%) 253 (M^++1, 18), 252 (M^+, 97), 224 (14), 208 (18), 207 (100), 179 (44), 178 (68), 177 (11), 176 (11). Anal. Calcd. for $C_{15}H_{14}O$: C, 85.68; H, 6.71. Found: C, 85.67; H, 6.73%.



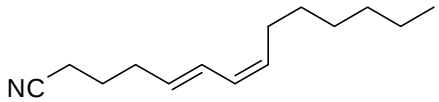
6qb

1-(4-Ethoxycarbonylphenyl)-2-methylpropene (6qb). A colorless oil, R_f 0.38 (hexane–ethyl acetate = 10 : 1). ^1H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.3 Hz, 2H), 7.28 (d, *J* = 8.3 Hz, 2H), 6.29 (s, 1H), 4.37 (q, *J* = 7.1 Hz, 2H), 1.93 (s, 3H), 1.88 (s, 3H), 1.39 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.6, 143.3, 137.9, 129.3, 128.5, 127.7, 124.6, 60.8, 27.1, 19.6, 14.3; IR (neat) 2980, 1715, 1607, 1410, 1366, 1275, 1178, 1103, 1020, 878, 760, 706 cm^{-1}; MS (EI) *m*/*z* (%) 205 (M^++1, 11), 204 (M^+, 78), 160 (14), 159 (100), 131 (32), 116 (12), 115 (19), 91 (16). Anal. Calcd. for $C_{13}H_{16}O_2$: C, 76.44; H, 7.90. Found: C, 76.24; H, 7.99%.



8ba

(5*E*,7*E*)-Tetradeca-5,7-dienenitrile (8ba). A colorless oil, R_f 0.42 (hexane–ethyl acetate = 5 : 1). ^1H NMR (400 MHz, $CDCl_3$) δ 6.11–5.94 (m, 2H), 5.63 (dt, *J* = 14.6, 7.0 Hz, 1H), 5.46 (dt, *J* = 14.8, 7.0 Hz, 1H), 2.34 (t, *J* = 7.1 Hz, 2H), 2.22 (q, *J* = 7.1 Hz, 2H), 2.06 (dt, *J* = 7.1, 7.0 Hz, 2H), 1.80–1.71 (m, 2H), 1.45–1.20 (m, 8H), 0.88 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 134.1, 132.6, 129.6, 128.5, 119.6, 32.6, 31.7, 31.2, 29.2, 28.9, 25.0, 22.6, 16.3, 14.1; IR (neat) 3017, 2957, 2926, 2855, 2247, 1456, 1437, 989, 733 cm^{-1}; MS (EI) *m*/*z* (%) 206 (M^++1, 10), 205 (M^+, 59), 204 (M^+–1, 13), 177 (37), 176 (34), 162 (13), 148 (36), 135 (16), 134 (100), 121 (29), 120 (60), 107 (15), 106 (16), 95 (15), 94 (26), 93 (52), 91 (25), 83 (21), 82 (10), 81 (67), 80 (45), 79 (39), 77 (22), 67 (45), 55 (15). Anal. Calcd. for $C_{14}H_{23}N$: C, 81.89; H, 11.29. Found: C, 82.18; H, 11.56%.



8bb

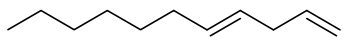
(5*E*,7*Z*)-Tetradeca-5,7-dienenitrile (8bb). A colorless oil, R_f 0.36 (hexane–ethyl acetate = 7 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.37 (ddq, *J* = 15.1, 10.9, 1.3 Hz, 1H), 5.94 (t, *J* = 10.9 Hz, 1H), 5.55 (dt, *J* = 15.0, 7.6 Hz, 1H), 5.37 (dt, *J* = 10.9, 7.6 Hz, 1H), 2.35 (t, *J* = 7.1 Hz, 2H), 2.27 (m, 2H), 2.16 (m, 2H), 1.77 (m, 2H), 1.41–1.21(m, 8H), 0.88 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 131.7, 130.8, 127.84, 127.81, 119.6, 31.7, 31.5, 29.6, 28.9, 27.7, 25.0, 22.6, 16.4, 14.1; IR (neat) 3020, 2957, 2928, 2855, 2247, 1456, 984, 949, 735 cm^{-1}; MS (EI) *m*/*z* (%) 205 (M^+, 43), 204 (M^+–1, 11), 177 (51), 176 (40), 162 (14), 148 (40), 135 (15), 134 (100), 121 (30), 120 (70), 107 (16), 106 (19), 95 (16), 94 (29), 93 (50), 91 (26), 83 (31), 82 (12), 81 (79), 80 (53), 79 (44), 77 (25), 67 (53), 55 (19), 54 (10). Anal. Calcd. for $C_{14}H_{23}N$: C, 81.89; H, 11.29. Found: C, 82.19; H, 11.18%.

Gram-scale cross-coupling reaction of 4a with 5b.

To a mixture of K_2CO_3 (9.1 g, 66 mmol), (2-furyl)$_3$P (138 mg, 0.60 mmol), and $PdCl_2$ (54 mg, 0.30 mmol) in DMSO (75 mL) were added **4a** (9.1 g, 33 mmol) and ethyl 4-iodobenzoate (**5b**, 8.3 g, 30 mmol) sequentially, and the resulting mixture was stirred at 35 °C for 21 h. The mixture was diluted with diethyl ether, washed with water and then with brine, and dried over anhydrous $MgSO_4$. Concentration in vacuo followed by distillation under vacuum (45 °C/1.0 mmHg) gave cyclic silyl ether **2** (3.1 g, 62%); the distillation residue was further purified by flash chromatography on silica gel (hexane–ethyl acetate = 20:1 as an eluent) to give **6ab** (7.6 g, 97%).

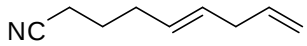
4.4 Cross-coupling reaction of alkenyl[2-(hydroxymethyl)phenyl]dimethylsilanes with allylic and benzylic carbonates. *A general procedure.* A solution of $Pd_2(dba)_3$ (4.6 mg, 5.0 μmol) and tri(2-thienyl)phosphine (5.6 mg, 20 μmol) in THF (2.0 mL) were added an organosilane (1.00 mmol) and a *t*-butyl allyl (or benzyl) carbonate (1.00 mmol) sequentially, and the resulting mixture was stirred at 50 °C. After the time specified in Table 1, the mixture was filtered through a silica gel pad and concentrated in vacuo. The residue was purified by flash chromatography on silica gel to afford the

corresponding adduct in a yield listed in Table 1. The spectra of **11gd** agreed well with those reported previously.[28]



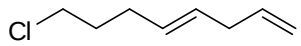
11aa

(*E*)-1,4-Undecadiene (11aa).[29] A colorless oil, R_f 0.65 (hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.90–5.77 (m, 1H), 5.51–5.36 (m, 2H), 5.08–4.94 (m, 2H), 2.75 (t, *J* = 6.3 Hz, 2H), 2.01 (q, *J* = 6.5 Hz, 2H), 1.42–1.21 (m, 8H), 0.89 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.4, 131.7, 127.3, 114.6, 36.9, 32.7, 31.8, 29.6, 29.0, 22.8, 14.3.



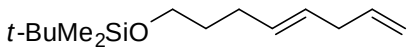
11ba

(*E*)-5,8-Nonadienenirtile (11ba). A colorless oil, R_f 0.41 (hexane–ethyl acetate = 5 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.87–5.75 (m, 1H), 5.53 (dtt, *J* = 15.4, 6.5, 1.3 Hz, 1H), 5.38 (dtt, *J* = 15.4, 6.9, 1.4 Hz, 1H), 5.07–4.97 (m, 2H), 2.79–2.72 (m, 2H), 2.33 (t, *J* = 7.2 Hz, 2H), 2.22–2.14 (m, 2H), 1.73 (quint, *J* = 7.2 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.8, 130.3, 128.6, 119.7, 115.2, 36.6, 31.2, 25.0, 16.3; IR (neat) 2937, 2247, 1638, 1427, 995, 972, 914, 735 cm^{-1}. HRMS (FAB^+) Calcd for $C_9H_{13}N$: M^+, 135.1048; Found: *m*/*z* 135.1043.



11da

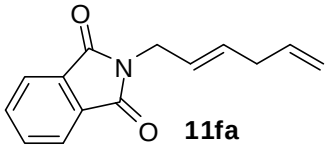
(*E*)-8-Chloro-1,4-octadiene (11da).[30] A colorless oil, R_f 0.29 (hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.88–5.76 (m, 1H), 5.50 (dt, *J* = 15.4, 6.3 Hz, 1H), 5.41 (dt, *J* = 15.4, 6.8 Hz, 1H), 5.07–4.96 (m, 2H), 3.54 (t, *J* = 6.7 Hz, 2H), 2.79–2.72 (m, 2H), 2.17 (q, *J* = 7.1 Hz, 2H), 1.84 (quint, *J* = 7.0 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.1, 129.5, 129.3, 115.0, 44.4, 36.7, 32.1, 29.6.



11ea

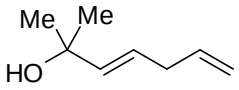
(*E*)-8-*t*-Butyldimethylsiloxy-1,4-octadiene (11ea).[29] A colorless oil, R_f 0.29 (hexane–ethyl acetate = 20 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.88–5.76 (m, 1H), 5.51–5.38 (m,

2H), 5.06–4.95 (m, 2H), 3.61 (t, J = 6.5 Hz, 2H), 2.78–2.71 (m, 2H), 2.11–2.01 (m, 2H), 1.59 (quint, J = 7.0 Hz, 2H), 0.89 (s, 9H), 0.04 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.4, 131.1, 127.9, 114.8, 62.6, 36.7, 32.5, 28.8, 26.0, 18.3, –5.3; IR (neat) 2955, 2930, 2895, 2858, 1638, 1472, 1256, 1105, 968, 912, 837, 775 cm^{-1}; Anal. Calcd for $C_{14}H_{28}OSi$; C, 69.93; H, 11.74. Found: C, 69.90; H, 11.81.



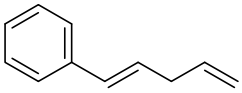
11fa

(*E*)-*N*-[2,5-Hexadien-1-yl]phthalimide (11fa). A pale yellow oil, R_f 0.35 (hexane–ethyl acetate = 5 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88–7.81 (m, 2H), 7.74–7.68 (m, 2H), 5.84–5.71 (m, 2H), 5.55 (dtt, J = 15.4, 6.1, 1.6 Hz, 1H), 5.06–4.97 (m, 2H), 4.26 (dq, J = 6.0, 1.1 Hz, 2H), 2.80–2.73 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.0, 135.9, 133.9, 132.3, 132.2, 124.3, 123.2, 115.8, 39.4, 36.1; IR (neat) 3005, 2978, 2924, 1771, 1713, 1468, 1429, 1393, 1356, 972, 937, 756, 719, 530 cm^{-1}; Anal. Calcd for $C_{14}H_{13}NO_2$; C, 73.99; H, 5.77. Found: C, 74.22; H, 5.76.



11ha

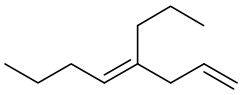
(*E*)-2-Methyl-3,6-heptadien-2-ol (11ha). A colorless oil, R_f 0.20 (hexane–ethyl acetate = 5 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.89–5.77 (m, 1H), 5.71–5.59 (m, 2H), 5.08–4.98 (m, 2H), 2.82–2.76 (m, 2H), 1.42 (br s, 1H), 1.33 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.9, 136.6, 124.6, 115.2, 70.7, 36.3, 29.9; IR (neat) 3373, 2974, 2928, 1638, 1373, 1362, 1231, 1148, 991, 972, 912, 735 cm^{-1}. HRMS (EI) Calcd for $C_8H_{14}O$: $[M–CH_3]^+$, 111.0810; Found: m/z 111.0811.



11ja

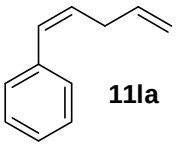
(*E*)-1-Phenyl-1,4-pentadiene (11ja).[29] A colorless oil, R_f 0.38 (hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39–7.27 (m, 4H), 7.24–7.18 (m, 1H), 6.42 (d, J = 15.7 Hz, 1H), 6.24

(dt, *J* = 15.9, 6.7 Hz, 1H), 5.99–5.85 (m, 1H), 5.17–5.04 (m, 2H), 2.98 (tq, *J* = 6.5, 1.5 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.4, 136.3, 130.7, 128.3, 128.0, 126.9, 125.9, 115.6, 37.1.



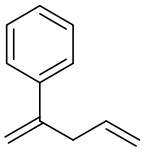
11ka

(*E*)-4-(2-Propen-1-yl)-4-octene (11ka).[31] A colorless oil, R_f 0.65 (hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.85–5.73 (m, 1H), 5.16 (t, *J* = 7.2 Hz, 1H), 5.06–4.96 (m, 2H), 2.72 (dd, *J* = 6.8, 1.2 Hz, 2H), 2.03–1.94 (m, 4H), 1.45–1.30 (m, 4H), 0.90 (t, *J* = 7.4 Hz, 3H), 0.89 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.64, 137.59, 126.2, 115.3, 41.5, 32.2, 29.9, 23.2, 21.4, 14.1, 13.9.



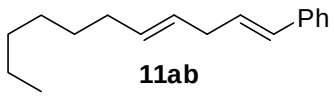
11la

(*Z*)-1-Phenyl-1,4-pentadiene (11la).[32] A colorless oil, R_f 0.43 (hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37–7.20 (m, 5H), 6.53 (d, *J* = 11.5 Hz, 1H), 5.98–5.86 (m, 1H), 5.71 (dt, *J* = 11.5, 7.6 Hz, 1H), 5.13 (ddt, *J* = 18.8, 1.8, 1.6 Hz, 1H), 5.07 (ddt, *J* = 10.1, 1.6, 1.6 Hz, 1H), 3.11–3.04 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.3, 136.6, 130.0, 129.5, 128.6, 128.2, 126.7, 115.3, 32.7.



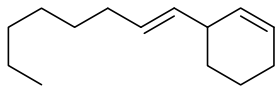
11pa

2-Phenyl-1,4-pentadiene (11pa).[33] A colorless oil, R_f 0.38 (hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47–7.41 (m, 2H), 7.37–7.24 (m, 3H), 5.98–5.85 (m, 1H), 5.40 (s, 1H), 5.16–5.05 (m, 3H), 3.26 (d, *J* = 6.6 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.3, 140.9, 136.2, 128.2, 127.4, 126.0, 116.4, 113.1, 39.5.



11ab

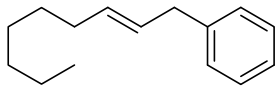
(1*E*,4*E*)-1-Phenyl-1,4-undecadiene (11ab).[30] A colorless oil, R_f 0.40 (hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38–7.25 (m, 5H), 7.23–7.16 (m, 1H), 6.38 (d, *J* = 15.9 Hz, 1H), 6.23 (dt, *J* = 15.7, 6.6 Hz, 1H), 5.57–5.43 (m, 2H), 2.90 (br t, *J* = 5.4 Hz, 2H), 2.03 (br q, *J* = 6.6 Hz, 2H), 1.42–1.23 (m, 8H), 0.89 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.8, 132.1, 130.1, 129.4, 128.5, 127.5, 126.9, 126.0, 35.9, 32.6, 31.7, 29.5, 28.9, 22.6, 14.1.



11ac

(*E*)-3-(1-Octen-1-yl)cyclohexene (11ac). A colorless oil, R_f 0.40 (hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.74–5.67 (m, 1H), 5.55 (dq, *J* = 10.1, 2.4 Hz, 1H), 5.46–5.31 (m, 2H), 2.78–2.67 (m, 1H), 2.04–1.93 (m, 4H), 1.84–1.63 (m, 2H), 1.59–1.47 (m, 1H), 1.44–1.20 (m, 9H), 0.88 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 134.2, 130.5, 129.8, 127.2, 38.3, 32.6, 31.7, 29.55, 29.49, 28.8, 25.1, 22.6, 20.6, 14.1; IR (neat) 3020, 2926, 2855, 1456, 1447, 1377, 966, 893, 723, 677 cm^{-1}. HRMS (EI) Calcd for $C_{14}H_{24}$: M^+, 192.1878; Found: *m*/*z* 192.1880.

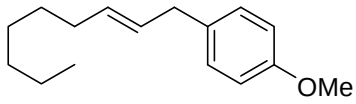
Palladium-catalyzed cross-coupling reaction of organo[2-(hydroxymethyl)phenyl]-dimethylsilanes with arylmethyl methyl carbonates. *A general procedure.* A solution of Cp(η^3-allyl)Pd (28 mg, 50 μmol) and dppf (6.1 mg, 50 μmol) in THF (1.0 mL) in a sealed tube were added an organosilane (1.00 mmol) and an arylmethyl methyl carbonates (1.00 mmol) sequentially, and the resulting mixture was stirred at 80 °C. After the time specified in Eq. 5, the mixture was filtered through a silica gel pad, and the filtrate was concentrated in vacuo. The residue was purified by flash chromatography on silica gel to give the corresponding adduct in a yield listed in Eq. 5.



13aa

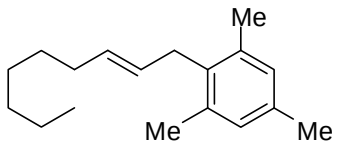
(*E*)-1-Phenyl-2-nonene (13aa).[34] A colorless oil, R_f 0.50 (hexane–ethyl acetate = 10 :

1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32–7.25 (m, 2H), 7.22–7.16 (m, 3H), 5.62–5.46 (m, 2H), 3.33 (d, *J* = 5.7 Hz, 2H), 2.02 (td, *J* = 7.2, 5.9 Hz, 2H), 1.42–1.20 (m, 8H), 0.88 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.1, 132.2, 128.6, 128.5, 128.3, 125.8, 39.1, 32.5, 31.7, 29.4, 28.9, 22.6, 14.1.



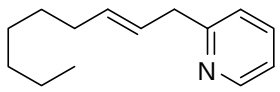
13ab

(*E*)-1-(4-Methoxyphenyl)-2-nonene (13ab). A colorless oil, R_f 0.29 (hexane–ethyl acetate = 50 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.10 (d, *J* = 8.2 Hz, 2H), 6.83 (d, *J* = 8.6 Hz, 2H), 5.59–5.44 (m, 2H), 3.80 (s, 3H), 3.27 (d, *J* = 5.9 Hz, 2H), 2.02 (td, *J* = 6.8, 6.6 Hz, 2H), 1.43–1.20 (m, 8H), 0.89 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.6, 133.1, 131.7, 129.2, 128.9, 113.6, 55.3, 38.2, 32.6, 31.8, 29.6, 29.0, 22.8, 14.2; IR (neat) 2955, 2926, 2855, 1611, 1512, 1466, 1439, 1300, 1246, 1175, 1040, 966, 820 cm^{-1}. Anal. Calcd for $C_{16}H_{24}O$; C, 82.70; H, 10.41. Found: C, 82.75; H, 10.31.



13ac

(*E*)-1-(2,4,6-Trimethylphenyl)-2-nonene (13ac). A colorless oil, R_f 0.58 (hexane–ethyl acetate = 50 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.82 (s, 2H), 5.41 (dtt, *J* = 15.2, 5.9, 1.3 Hz, 1H), 5.29 (dtt, *J* = 15.2, 6.6, 1.5 Hz, 1H), 3.27 (dd, *J* = 5.7, 1.1 Hz, 2H), 2.253 (s, 6H), 2.245 (s, 3H), 1.94 (q, *J* = 6.6 Hz, 2H), 1.36–1.17 (m, 8H), 0.86 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.2, 135.0, 133.9, 130.8, 128.6, 126.5, 32.7, 32.4, 31.8, 29.6, 29.0, 22.7, 21.0, 19.9, 14.2; IR (neat) 2957, 2924, 2855, 1483, 1458, 966, 851cm^{-1}. Anal. Calcd for $C_{18}H_{28}$; C, 88.45; H, 11.55. Found: C, 88.51; H, 11.57.



13ad

(*E*)-1-(2-Pyridyl)-2-nonene (13ad). A colorless oil, R_f 0.07 (hexane–ethyl acetate = 30 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (ddd, *J* = 4.9, 1.6, 0.9 Hz, 1H), 7.58 (td, *J* =

7.7, 1.8 Hz, 1H), 7.15 (d, *J* = 7.9 Hz, 1H), 7.09 (ddd, *J* = 7.5, 4.9, 1.1 Hz, 1H), 5.70–5.53 (m, 2H), 3.52 (d, *J* = 6.2 Hz, 2H), 2.04 (td, *J* = 7.3, 6.6 Hz, 2H), 1.46–1.20 (m, 8H), 0.87 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.9, 149.1, 136.2, 133.1, 126.8, 122.5, 120.9, 41.9, 32.7, 31.8, 29.4, 29.0, 22.8, 14.2; IR (neat) 2957, 2926, 2855, 1591, 1570, 1474, 1433, 968, 748 cm^{-1}. Anal. Calcd for $C_{16}H_{24}O$; C, 82.70; H, 10.41. Found: C, 82.95; H, 10.33.

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Chapter 3

Palladium-catalyzed Cross-coupling Reactions of Aryl[2-(hydroxymethyl)phenyl]dimethylsilanes

Taking advantage of the intramolecular activation discussed in Chapter 2, highly stable aryl[2-(hydroxylmethyl)phenyl]dimethylsilanes can also selectively transfer the aryl groups to palladium complexes to effect the cross-coupling reaction with various aryl halides (I, Br, and Cl) in the presence of a weak non-fluoride base and a copper co-catalyst. The reaction tolerates a wide range of functional groups to afford the corresponding functionalized biaryl products in high yields with high chemoselectivity. Aryl bromides having a pinacolateboryl or tributylstannyl group also participated in the silicon-based cross-coupling reaction to give the corresponding coupled products without loss of the metalloid group. This fact demonstrates that the arylsilanes become more reactive than organoboron and -tin reagents upon intramolecular activation of the present protocol. The coupling reaction with aryl bromides has led to a quantitative recovery of the cyclic silyl ether, which in contrast decomposed to some extent during the reaction with aryl iodides. The cross-coupling reaction of the arylsilanes with allylic and benzylic carbonates proceeds without any activator in good yields and with high chemoselectivity employing a Pd-Cu catalyst system. The present biaryl synthesis was successfully applied to precise synthesis of well-defined oligoarenes.

1. Introduction

The biaryl unit is widely present in natural products, polymers, advanced organic materials, ligands, and molecules of medicinal interest. In view of the tremendous importance of the biaryl structural motif, a number of catalytic methods have been developed in the last three decades for construction of the structures from monoaryl precursors. [1] In view that an S_N2 type reaction is not applicable to the preparation of biaryls, the cross-coupling chemistry has been extensively explored since the first report in 1972.[2] The transition metal-catalyzed cross-coupling reactions of arylmetals with organic halides or pseudohalides provide a regio- and sterochemically well-defined approach to the products that are hardly accessible by conventional methods. Various main group arylmetallic reagents undergo the cross-coupling reaction with a wide range of aryl electrophiles such as aryl chlorides, bromides, iodides, triflates, and tosylates in the presence of a catalytic amount of late transition metal catalysts such as palladium and nickel. Starting with highly nucleophilic aryl Grignard reagents, more chemoselective aryl nucleophiles such as arylstannanes and aryl boronic acids are derived and employed to the cross-coupling reaction. Nevertheless, stoichiometric amounts of metal wastes unavoidably form after the reaction. Especially, the metal wastes derived from toxic organostannane and -boron reagents burden the environmental problem.[3] In the past two decade, silicon-based methodology has gained increasing importance and interest due to inherent stability and non-toxicity of organosilicon compounds.[4] In early stages, heat-, moisture-, base, and/or acid-sensitive aryl(halo)silanes[5] or aryl(alkoxy)silanes[6] were used for the biaryl synthesis in the presence of a fluoride activator. Later relatively stable arylsilanols[7] or "masked arylsilanols" like triallyl(aryl)silanes[8] have proven to undergo cross-coupling reactions with aryl halides using a fluoride activator. However, as fluorides are relatively expensive and incompatible to several functional groups including common silyl protectors, the new protocol has limited yet widespread applications. Although efforts have been made for fluoride-free biaryl synthesis employing NaOH,[9] Cs_2CO_3,[7] or stoichiometric amounts of transition metal promoters[8,10] in combination with aryl(halo)silanes, aryl(alkoxy)silanes, or arylsilanols, successful examples are quite limited.

Recently, Takeda and coworkers reported that [2-(hydroxyalkyl)phenyl]trimethylsilanes underwent smooth transmetalation from silicon to copper without fluoride activators through intramolecular activation of the proximal negatively charged oxygen nucleophile and that the resulting copper reagents coupled with allyl chloride (Figure 1).[11] As was discussed in Chapter 2, the author disclosed that highly stable alkenyl[2-(hydroxymethyl)phenyl]dimethylsilanes behaved as a new class of silane coupling reagents for the fluoride-free palladium-catalyzed cross-coupling reaction with excellent regio- and stereoselectivities. The proximal hydroxyl group is supposed to be converted to an alkoxide upon treatment with a mild base, such as K_2CO_3, and coordinate to a nearby silicon atom to produce a requisite five-membered pentacoordinated silicate species. Encouraged by the given success of the alkenylsilanes in the cross-coupling chemistry, he envisioned that this reagent design may also be effective for arylsilanes that can selectively transfer the aryl group among four different organic substituents. This turned out to be the case. In this Chapter, he demonstrates the palladium-catalyzed cross-coupling reaction of aryl[2-(hydorxymethyl)phenyl]dimethylsilanes with various aryl halides proceeds in good yields with high selectivities using potassium carbonate as a mild base instead of fluoride activators with the aid of copper iodide as a co-catalyst. Especially, the silicon coupling was compared with the boron or stannane coupling. In addition, recovery of a cyclic silyl ether co-produced by the reaction is demonstrated in detail. In a manner similar to the alkenylsilanes discussed in Chapter 2, the arylsilanes also undergo the cross-coupling reaction with allylic and benzylic carbonates with the aid of a CuOAc co-catalyst to give 3-arylpropenes and diarylmethanes.[12]

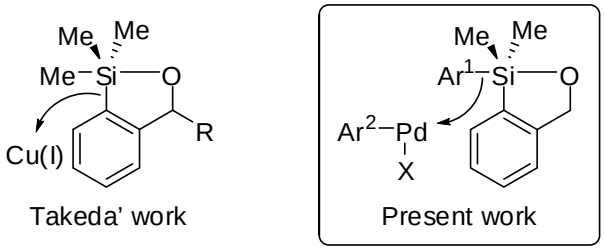
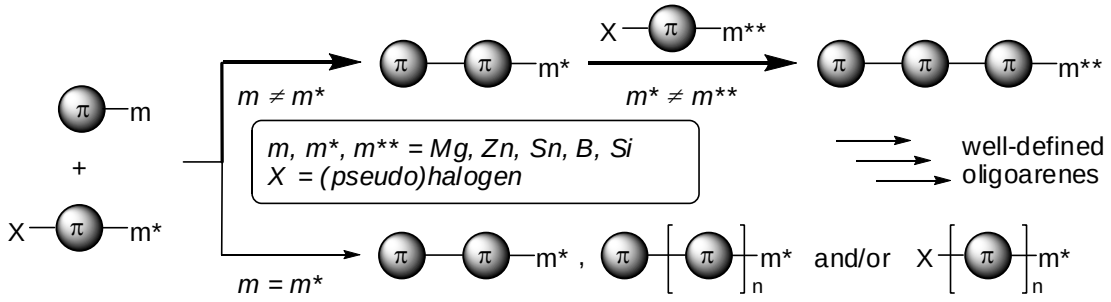


Figure 1. Transmetalation from silicon to a late transition metal assisted by an intramolecular coordination.

Conjugated oligoarenes containing biaryl units are playing key roles in photonic and optoelectronic materials such as organic light-emitting diodes, field-effect transistors, semiconductors, and fluorescent sensors.[13] Synthesis of oligoarenes relies

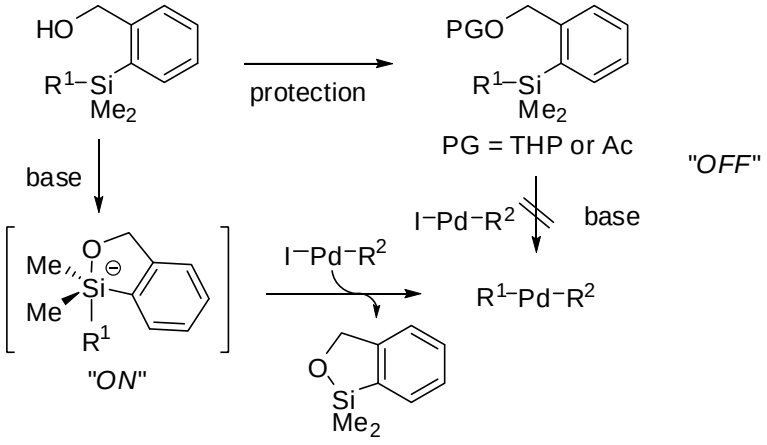
exclusively on the cross-coupling reaction, which allows direct connection of C(sp^2)–C(sp^2) bonds with high chemoselectivity and retention of stereo- and regiochemistry. However, installation of a leaving group and a metallic center at a specified arene position should always be performed to carry out the second cross-coupling reactions.[14] Accordingly, the whole sequence leading to the desired oligoarenes can't avoid tedious multi-step syntheses. Whereas iterative cross-coupling reactions of metalated organic halides would offer an efficient access to oligoarenes with well-defined structures (Scheme 1), it is hard to control their reaction modes (cross-coupling vs. homo-coupling, etc.) without precise discrimination of metallic centers. [15,16]

Scheme 1. Cross-coupling reaction with halogenated organometallics



Since the enhanced reactivity of the silicon reagents is "turned off" simply by protection of the hydroxy group (Scheme 2), the silicon reagents with halogen and protected OH groups are found to serve as promising coupling partners for the iterative cross-coupling sequence, leading to a silicon-based approach to well-defined oligoarenes that has rarely been addressed before.[17]

Scheme 2. Modulation of reactivity of organo[2-(hydroxymethyl)phenyl]dimethylsilanes



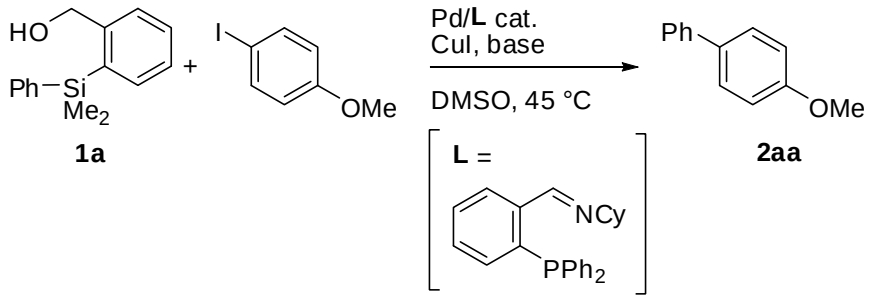
2. Results and discussion

2.1 Aryl–aryl cross-coupling

The author first examined the reaction of phenylsilane **1a** (0.13 mmol) with 4-iodoanisole (0.10 mmol) in the presence of $[(\eta^3\text{-allyl})PdCl]_2$ (2.5 mol%), tri-2-furylphosphine (15 mol%), CuI (20 mol%), and Cs_2CO_3 (0.24 mmol) in DMSO at 45 °C for 22 h. The reaction conditions were slightly modified from those for the successful cross-coupling of alkenylsilanes demonstrated in Chapter 2. Formation of the desired product 4-methoxybiphenyl **2aa** was estimated to be 79% yield by GC analysis of an aliquot of the reaction mixture (entry 1 of Table 1). Use of iminophosphine ligand **L** used in the reaction of alkenylsilanes in Chapter 2 was found also effective to increase the yield of **2aa** to 84% yield (entry 2). A copper co-catalyst was found essential for the present biaryl synthesis, since the absence of CuI resulted in no reaction (entry 3). He further found that use of K_2CO_3 (0.20 mmol) and $PdCl_2$ (3.0 mol%), an inexpensive combination of a base/palladium complex, was equally effective for the reaction even with smaller equivalents of these reagents and CuI (10 mol%) (entry 4). Finally, 96% GC yield of **2aa** was attained by addition of a small amount of H_2O (0.20 mmol) to the reaction mixture (entry 5); addition of an extra amount of H_2O (total 0.40 mmol) was futile (entry 6). Under the optimized conditions, the reaction in a preparative scale (0.70 mmol scale) gave **2aa** in 99% yield after isolation by silica gel column chromatography (entry 7).

It is highly intriguing that the desired aryl group exclusively coupled with the iodide with the hydroxymethylphenyl group remaining on silicon. The author proposes that pentacoordinated silicate intermediates like **A** having a rather electron-withdrawing aryl group (Ar^1) and the oxygen atom of 2-(hydroxymethyl)phenyl group at apical positions might be responsible for the selective aryl transfer (Scheme 3).[18] Transmetalation from silicon to copper appears likely rather than direct transmetalation from silicon to palladium.[10,11] Water might increase polarity of the reaction media to improve solubility of K_2CO_3 in the reaction mixture and thus accelerate the transmetalation step(s), though an excess amount of water likely induce protodesilylation of pentacoordinated silicate species **A** to reduce yields of biaryls (vide supra) (Fig. 1).

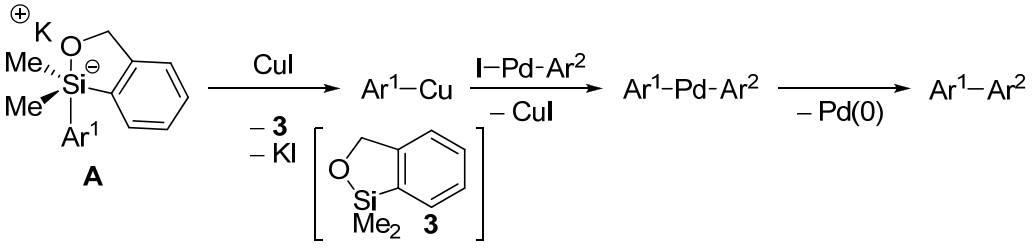
Table 1. Optimization of reaction conditions for the cross-coupling reaction of **1a** with 4-iodoanisole[a]



entry	Pd cat.	ligand	CuI	base	time (h)	yield of **2aa** (%)[b]
1	$[(\eta^3\text{-}C_3H_5)PdCl]_2$ (2.5 mol%)	$(2\text{-furyl})_3P$ (15 mol%)	20 mol%	Cs_2CO_3 (2.4 equiv)	22	79
2	$[(\eta^3\text{-}C_3H_5)PdCl]_2$ (2.5 mol%)	**L** (15 mol%)	20 mol%	Cs_2CO_3 (2.4 equiv)	22	84
3	$[(\eta^3\text{-}C_3H_5)PdCl]_2$ (2.5 mol%)	**L** (10 mol%)	None	Cs_2CO_3 (2.4 equiv)	20	<5
4	$PdCl_2$ (3.0 mol%)	**L** (4 mol%)	10 mol%	K_2CO_3 (2.0 equiv)	22	82
5[c]	$PdCl_2$ (3.0 mol%)	**L** (4 mol%)	10 mol%	K_2CO_3 (2.0 equiv)	22	96
6[d]	$PdCl_2$ (3.0 mol%)	**L** (4 mol%)	10 mol%	K_2CO_3 (2.0 equiv)	22	80
7[e]	$PdCl_2$ (3.0 mol%)	**L** (4 mol%)	10 mol%	K_2CO_3 (2.0 equiv)	16	99[f]

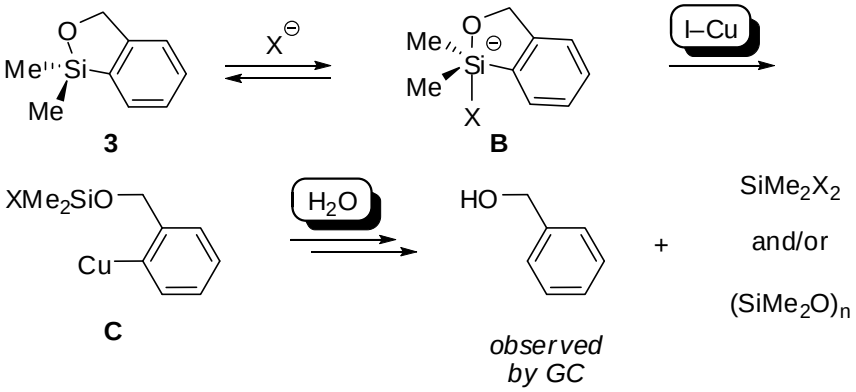
[a]The reaction was carried out using **1a** (0.13 mmol), 4-iodoanisole (0.10 mmol), a base, a palladium catalyst, a ligand, and CuI in DMSO at 45 °C. [b]Estimated by GC. [c]H_2O (0.20 mmol) was added. [d]H_2O (0.40 mmol) was added. [e]The reaction was carried out using **1a** (0.81 mmol), 4-iodoanisole (0.70 mmol), and H_2O (1.4 mmol) at 50 °C. [f]Isolated yield based on 4-iodoanisole.

Scheme 3. Plausible reaction pathway through selective aryl transfer



In principle, silicon residue liberated after the present coupling reaction should be cyclic silyl ether **3**. Indeed, the author succeeded in recovery of **3** by distillation of a crude product mixture as was described in Chapter 2. However, he did not observe the formation of **3** during the present biaryl synthesis. Instead, benzyl alcohol was detected as a plausible fate of **3**. At present, it looks reasonable to assume that cyclic silyl ether **3** would further accept coordination of a hydroxide, iodide, or chloride ion under the reaction conditions to form pentacoordinate silicate **B**, which would induce transmetalation to copper to give 2-(siloxymethyl)phenylcopper species **C** and then benzyl alcohol upon protonolysis (Scheme 4).[11]

Scheme 4. A possible fate of cyclic silyl ether **3** under the reaction conditions



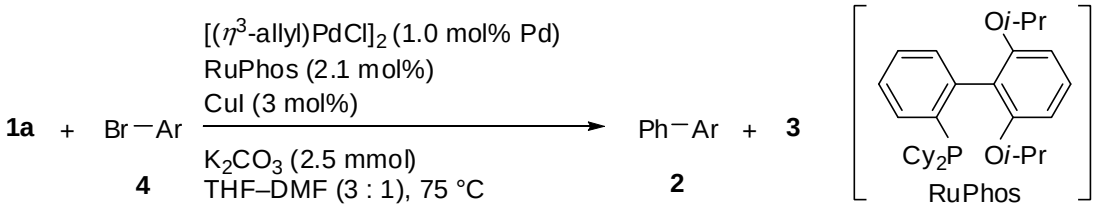
Having identified the necessity of copper(I) iodide in a transmetalation step and the role of water in acceleration of the reaction and decomposition of cyclic silyl ether **3**, the author turned his attention to the cross-coupling reaction of the arylsilane with more available aryl bromides and discovered conditions to avoid the decomposition of **3**. He first examined the optimum reaction conditions of phenylsilane **1a** and 4-bromoanisole **4** and found that the reaction proceeded smoothly in the presence of $[(\eta^3\text{-allyl})PdCl]_2$ (0.5 mol%), Ruphos ligand (2.1 mol%),[19] CuI (3.0 mol%), K_2CO_3 (2.5 mmol) in anhydrous THF–DMF (0.8 mL : 2.2 mL) at 75 °C for 23 h and isolated desired cross-coupling product **2aa** in 91% yield and cyclic silyl ether **3** in a synthetically valuable yield (Table 2, entry 1). As discussed above, lesser amount of CuI and absence of water are attributed to the successful recovery of **3**. With the optimized conditions in hands, the author further surveyed the scope of aryl bromides. Biphenyls having an electron-donating group at *para*-position were also isolated in good yields (entries 2–3). Various

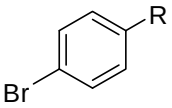
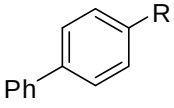
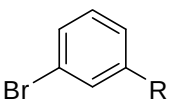
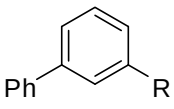
electron-withdrawing functional groups including cyano, ester, formyl, nitro, keto, trifluoromethyl, fluoro, and chloro at *para*-position of bromobenzene tolerated the present conditions to give the corresponding biaryls in excellent yields (entries 4–11). *Meta*-substitution by a free amino or hydroxy group did not affect the reaction (entries 12–15). It is worth noting that *t*-$BuMe_2Si$ ether, which is easily cleaved under the conventional fluoride activation protocols, survives completely (entry 14). *Ortho*-substituted aryl bromides also coupled with **1a** in good yields (entries 17 and 18). Heteroaryl groups such as pyridyl, thienyl, quinolyl, and 3-benzothienyl were also introduced successfully to give heterobiaryl compounds (entries 19–22). The present protocol is successfully applied to the recovery of cylic silyl ether **3** in good yields in most cases except entries 3 and 19.

In a manner similar to phenylsilane **1a**, phenylsilanes **1b**–**d** substituted by a methyl, fluoro, and cyano group, exclusively underwent the cross-coupling reaction with bromobenzene (**4y**) in good to excellent yields (Table 3, entries 1–4), regardless of the electronic nature of the substituents. Unfortunately, 2-thienylsilane **1f** and sterically hindered mesitylsilane **1g** were sluggish and furnished the desired coupled products **2at** and **2gy** in poor yields due possibly to competitive protodesilylation of arylsilanes under the present conditions.

Tolerance of stannyl and boryl functional groups was also examined under the present protocol (Scheme 5). The reaction of **1a** with 4-bromophenyl(tributyl)stannane **4w** afforded biphenyl(tributyl)stannane **2aw** in a high yield, whereas the reaction with 4-bromophenyl(pinacol)boronate **4x** gave a complex mixture owing probably to oligomerization of **4x**. However, pre-treatment of **1a** with an equimolar amount of butyl lithium, followed by cross-coupling with **4x**, gave biphenyl(pinacol)boronate in a good yield. Apparently, these results clearly indicate that the stannyl and boryl groups, which are considered to be more reactive than a silyl group, yielded the coupling reaction to silicon. Namely, an intramolecular activation by proximal hydroxy group significantly enhances the reactivity of organo[2-(hydroxymethyl)phenyl]dimethylsilanes to override stannyl and boryl groups.

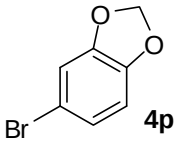
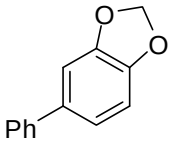
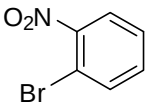
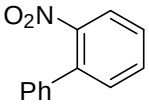
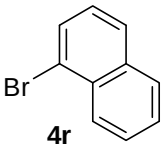
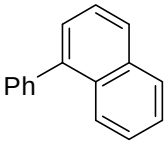
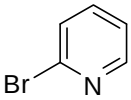
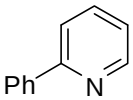
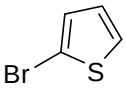
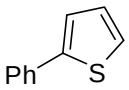
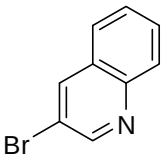
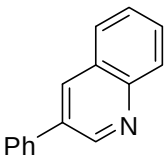
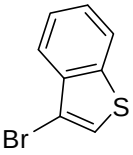
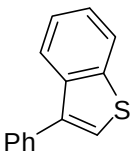
Table 2. Palladium-catalyzed cross-coupling reaction of **1a** with aryl bromides[a]



entry	aryl bromide	time (h)	product	yield of **2** (%)[b]	yield of **3**(%)[c]
					
1	R = OMe (**4a**)	23	R = OMe	91 (**2aa**)	72
2	Me (**4b**)	19	Me	86 (**2ab**)	71
3	*t*-Bu (**4c**)	56	*t*-Bu	82 (**2ac**)	46
4	CN (**4d**)	9	CN	92 (**2ad**)	81
5	COOEt (**4e**)	10	COOEt	81 (**2ae**)	79
6	CHO (**4f**)	9	CHO	91 (**2af**)	82
7	NO_2 (**4g**)	26	NO_2	97 (**2ag**)	70
8	Ac (**4h**)	26	Ac	87 (**2ah**)	88
9	CF_3 (**4i**)	12	CF_3	91 (**2ai**)	86
10	F (**4j**)	25	F	85 (**2aj**)	76
11	Cl (**4k**)	26	Cl	85 (**2ak**)	76
					
12	R = NH_2 (**4l**)	25	R = NH_2	95 (**2al**)	77
13	Me (**4m**)	14	Me	87 (**2am**)	90
14	$CH_2OTBDMS$ (**4n**)	13	$CH_2OTBDMS$	75 (**2an**)	75
15	CH_2OH (**4o**)	24	CH_2OH	92 (**2ao**)	68

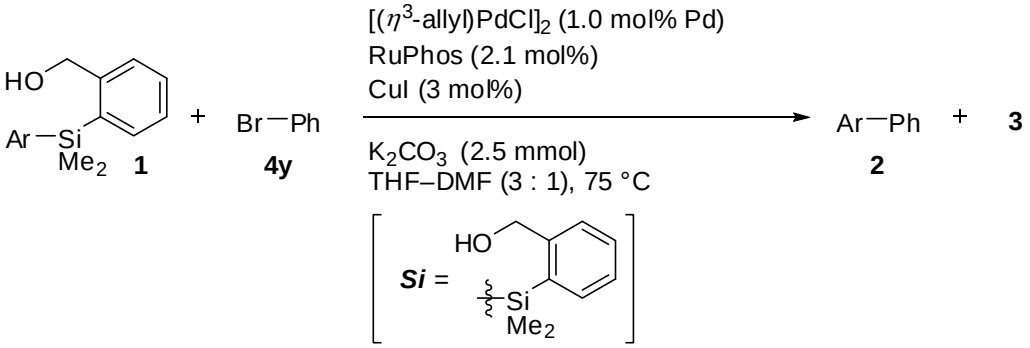
(*continued to the next page*)

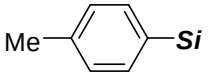
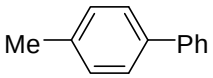
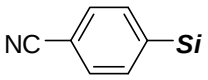
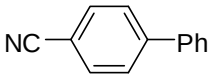
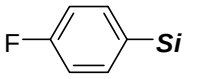
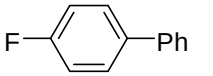
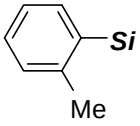
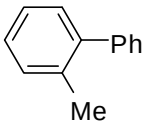
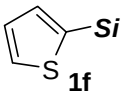
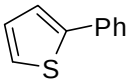
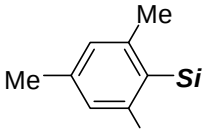
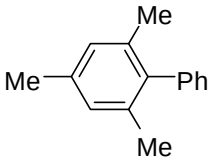
Table 2. (*continued*)

entry	aryl bromide	time (h)	product	yield of **2** (%)[b]	yield of **3**(%)[c]
16	 **4p**	27		88 (**2ap**)	91
17	 **4q**	7		80 (**2aq**)	73
18	 **4r**	13		88 (**2ar**)	100
19	 **4s**	13		65 (**2as**)	53
20	 **4t**	11		88 (**2at**)	89
21	 **4u**	17		97 (**2au**)	92
22	 **4v**	13		83 (**2av**)	70

[a]The reaction was carried out using phenylsilane **1a** (1.2−1.3 mmol) and an aryl bromide (1.0 mmol). [b]Isolated yields based on an aryl bromide. [c]Estimated by GC using nonane as an internal standard.

Table 3. Cross-coupling reaction of arylsilanes **1** with bromobenzene (**4y**)[a]



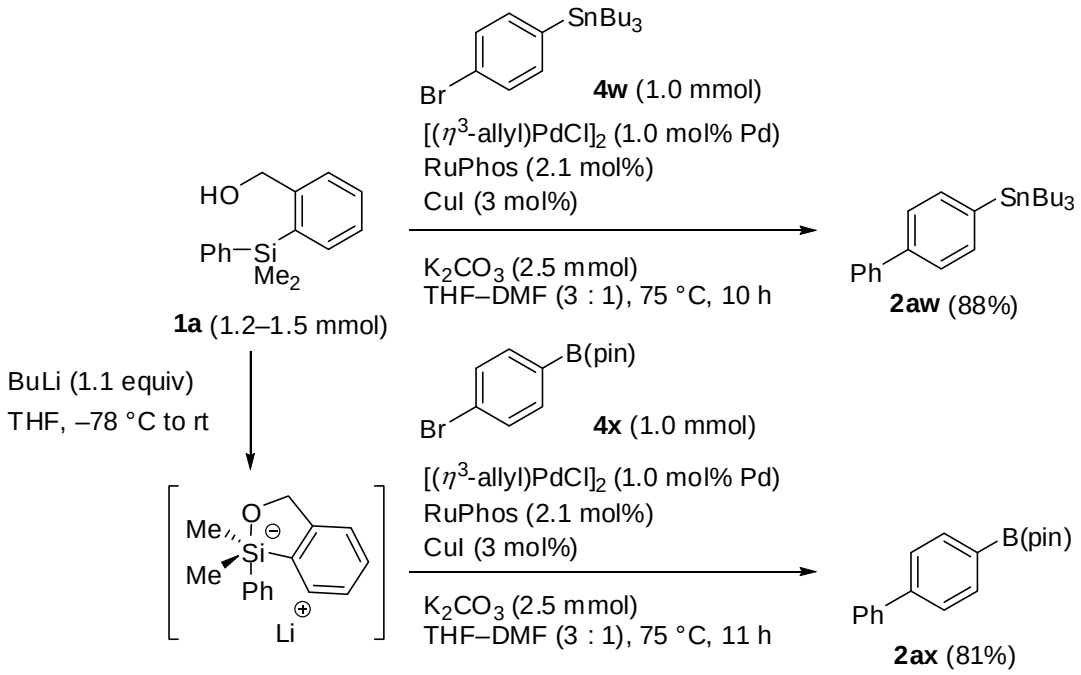
entry	arylsilane	time (h)	product	yield of **2** (%)[b]
1	 **1b**	22		88 (**2ab**)
2	 **1c**	22		97 (**2ad**)
3	 **1d**	25		95 (**2aj**)
4	 **1e**	14		85 (**2ey**)
5	 **1f**	24		21 (**2at**)
6	 **1g**	24		34 (**2gy**)

[a]The reaction was carried out using an arylsilane (1.2–1.5 mmol) and bromobenzene (**4y**) (1.0 mmol). [b]Isolated yield based on **4y**.

Although cyclic silyl ether **3** was recovered in most cases in yields of synthetic value by the cross-coupling with aryl[2-(hydroxymethyl)phenyl]dimethylsilanes, yields of **3** were not always satisfied: reactions with **4c**, **4o**, and **4s** co-produced benzyl alcohol significantly as detected by GC and ^{1}H NMR (entries 3, 15, and 19 in Table 2), possibly because nucleophilic attack of a hydroxide, iodide, and/or bromide ion caused the

decomposition of **3**. To improve the yield of **3**, the author designed a silicon reagent having bulky *i*-Pr group in place of methyl on silicon, and prepared **1'a** (Eq. 1). As demonstrated, the reactions proceeded equally well, and both **2** and **3'** were obtained in good to excellent yields.

Scheme 5. Cross-coupling reaction of phenylsilane with aryl bromides having a stannyl or boryl group



Aryl chlorides are an attractive coupling partner due to low cost and wide availability as compared with aryl iodides and bromides. However, they are less reactive towards the cross-coupling reaction and thus less employed. The poor reactivity is attributed to a stronger C–Cl bond [bond dissociation energies for Ph-X: Cl (96 kcal/mol); Br (81 kcal/mol); I (65 kcal/mol)].[20] The author examined the coupling reaction with aryl chlorides first applying the present standard protocol to find that a substituent on aryl chlorides significantly affected the reaction. The reaction with an electron-poor aryl chloride afforded the corresponding biaryl products in good to excellent yields (Table 4, entries 1–5), whereas the reaction with an electron-rich aryl chloride failed to give the biaryl products (entries 6 and 7).

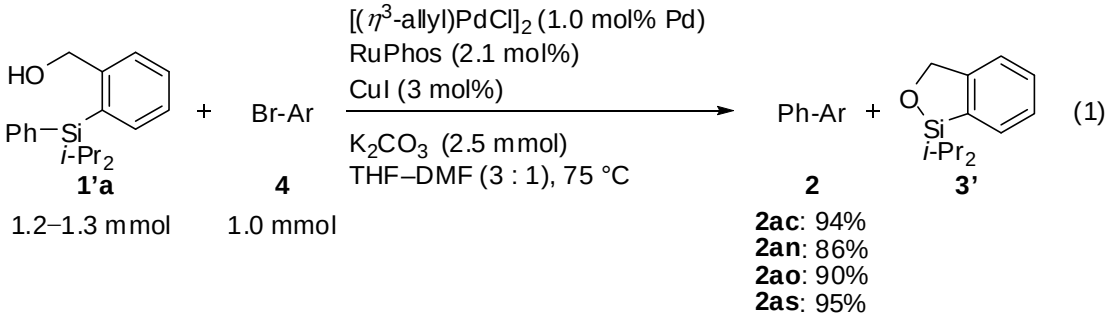
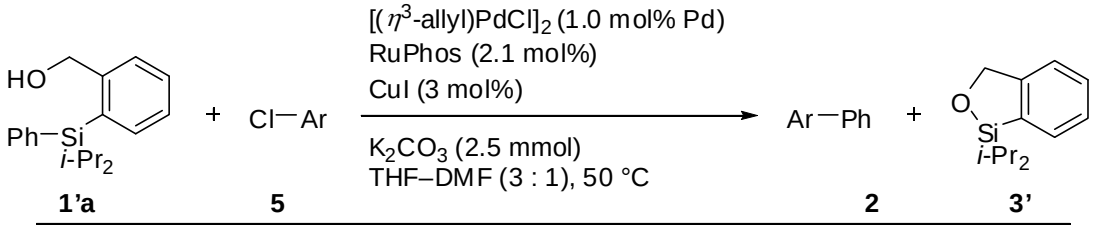
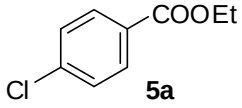
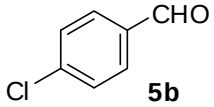
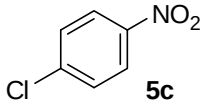
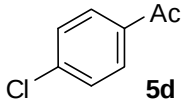
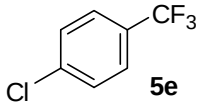
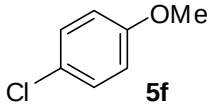
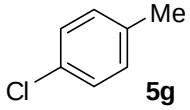


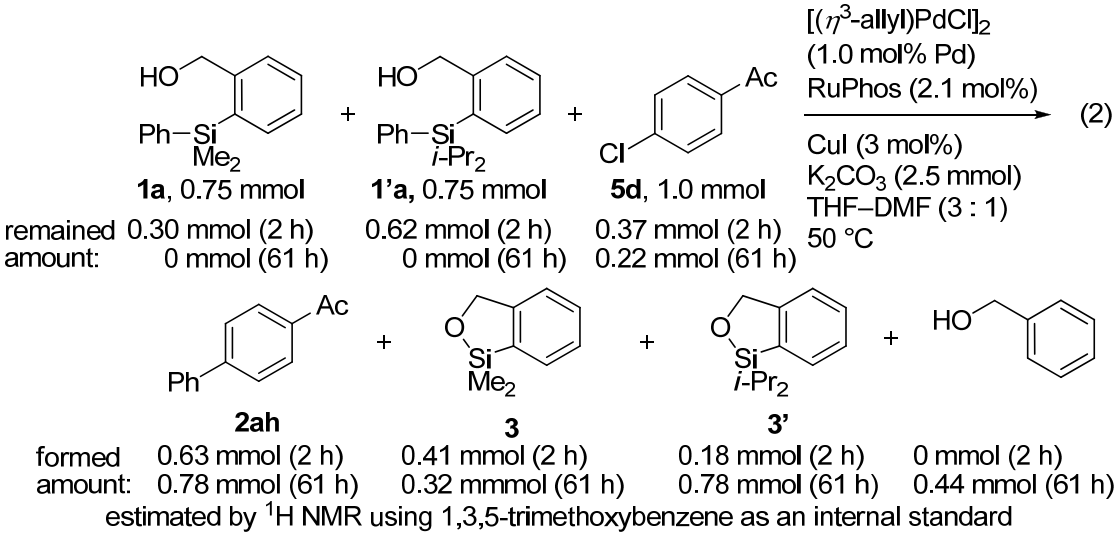
Table 4. Cross-coupling reaction of phenyl[2-(hydroxymethyl)phenyl]diisopropylsilanes (**1'a**) with aryl chlorides **5**[a]



entry	aryl chloride	time (h)	yield of **2** (%)[b]	yield of **3'** (%)[c]
1	 **5a**	15	99 (**2ae**)	100
2	 **5b**	24	90 (**2af**)	100
3	 **5c**	42	94 (**2ag**)	100
4	 **5d**	24	95 (**2ah**)	100
5	 **5e**	20	89 (**2ai**)	92
6	 **5f**	36	41 (**2aa**)[d]	100
7	 **5g**	65	70 (**2ab**)[d]	100

[a]The reaction was carried out using phenylsilane **1'a** (1.5 mmol) and an aryl chloride (1.0 mmol). [b]Isolated yield based on an aryl chloride. [c]Estimated by GC using tridecane as an internal standard. [d]Estimated by ^{1}H NMR using 1,3,5-trimethoxybenzene as an internal standard.

To compare the reactivity of **1a** and **1'a** as well as the stability of **3** and **3'** under the present protocol, we executed a competitive experiment. Cross-coupling reaction of **1a** (0.75 mmol) and **1'a** (0.75 mmol) with 4-acetylphenyl chloride **5d** (1.0 mmol) was carried out under the standard conditions to give the coupled product **2ah** (0.63 mmol), **3** (0.41 mmol), and **3'** (0.18 mmol), and, 0.30 mmol of **1a**, 0.62 mmol of **1'a**, and 0.37 mmol of **5d** remained after 2 h (Eq. 2). Formation of benzyl alcohol was not observed. These results show that consumed **1a** and **1'a** were quantitively converted to **3** and **3'**, and **2ah** quantitatively formed under the present conditions. Based on the consumption analysis of **1a** and **1'a**, it is obvious that **1a** is 3.5 times more reactive than **1'a**, indicating that a more bulky *i*-Pr group is responsible for less consumption of **1'a**. After 61 h, **1a** and **1'a** were completely consumed, 0.32 mmol of **3** and 0.78 mmol of **3'** remained, and 0.44 mmol of bezyl alcohol formed. Reversal of remained amount of **3'** compared to that of **3** explains that **3'** are stabler than **3** and almost does not decompose in view of attack of a hydroxide or halide ion under bulky *i*-Pr group' protection, while smaller methyl group makes **3** easier to be attacked to decompose to benzyl alcohol.

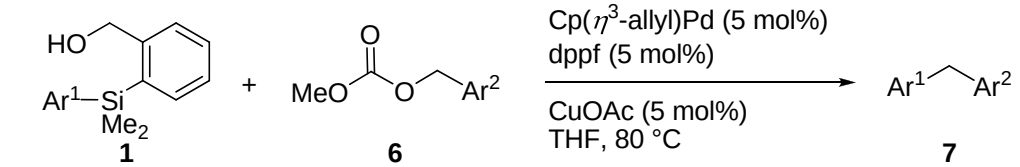


2.2 Aryl-allyl and aryl-benzyl coupling

Like the alkenylsilane reagents discussed in Chapter 2, the corresponding arylsilanes undergo the cross-coupling reaction with allylic and benzylic carbonates with the aid of a CuOAc co-catalyst. The author first examined the reaction of **1a** with (4-methoxyphenyl)methyl methyl carbonate **6a**. The reaction took place smoothly in the

presence of Cp(η^3-allyl)Pd (5 mol%), dppf (5 mol%), and CuOAc (5 mol%) in THF at 80 °C to give diarylmethane **7aa** in 92% yield after 8 h (entry 1, Table 5). Mesityl group did not hinder the catalytic reaction (entry 2). Chloro functional group was tolerated under the present protocol (entry 3). Heteroarylmethyl carbonate derived from 3-pyridyl-, 2-furyl-, or 2-thienylmethanol, similarly reacted with **1a** or **1h** to give the corresponding diarylmethane **7** in good yields (entries 4–6).

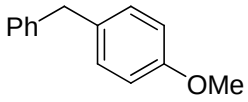
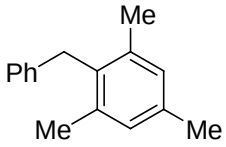
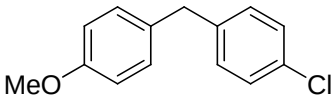
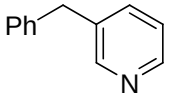
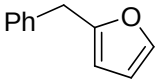
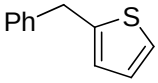
Table 5. Cross-coupling reaction of aryl[2-(hydroxymethyl)phenyl]dimethylsilanes (**1**) with benzyl carbonates **6**[a]



1 **6** **7**

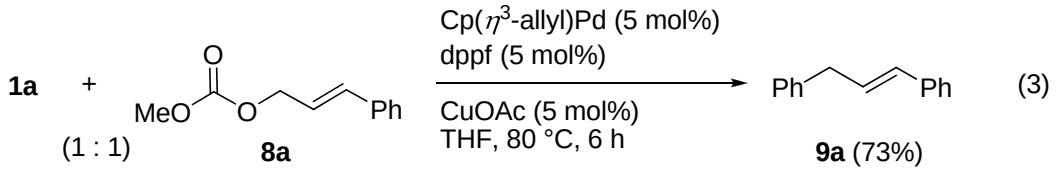
Ar^1 = Ph (**1a**); 4-MeO–C_6H_4 (**1h**)

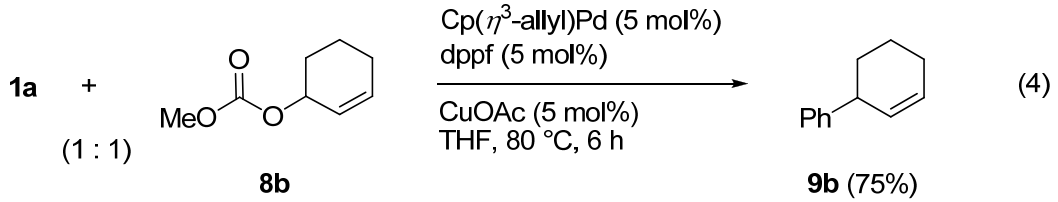
Ar^2 = 4-MeO–C_6H_4 (**6a**); 2,4,6-Me_3–C_6H_2 (**6b**); 4-Cl–C_6H_4 (**6c**); 3-pyridyl (**6d**); 2-furyl (**6e**); 2-thienyl (**6f**)

entry	**1**	**6**	time (h)	product	yield (%)[b]
1	**1a**	**6a**	8		92 (**7aa**)
2	**1a**	**6b**	8		87 (**7ab**)
3	**1h**	**6c**	13		70 (**7hc**)
4	**1a**	**6d**	8		78 (**7ad**)
5	**1a**	**6e**	9		75 (**7ae**)
6	**1a**	**6f**	8		71 (**7af**)

[a]The reaction was carried out using an arylsilane (1.0 mmol) and an benzylic carbonate (1.0 mmol). [b]Isolated yields.

Under the similar conditions, (*E*)-cinnamyl methyl carbonate (**8a**) and 2-cyclohexenyl methyl carbonate (**8b**) also cross-coupled with **1a** to give allylated benzenes in good yields (Eqs. 3 and 4).

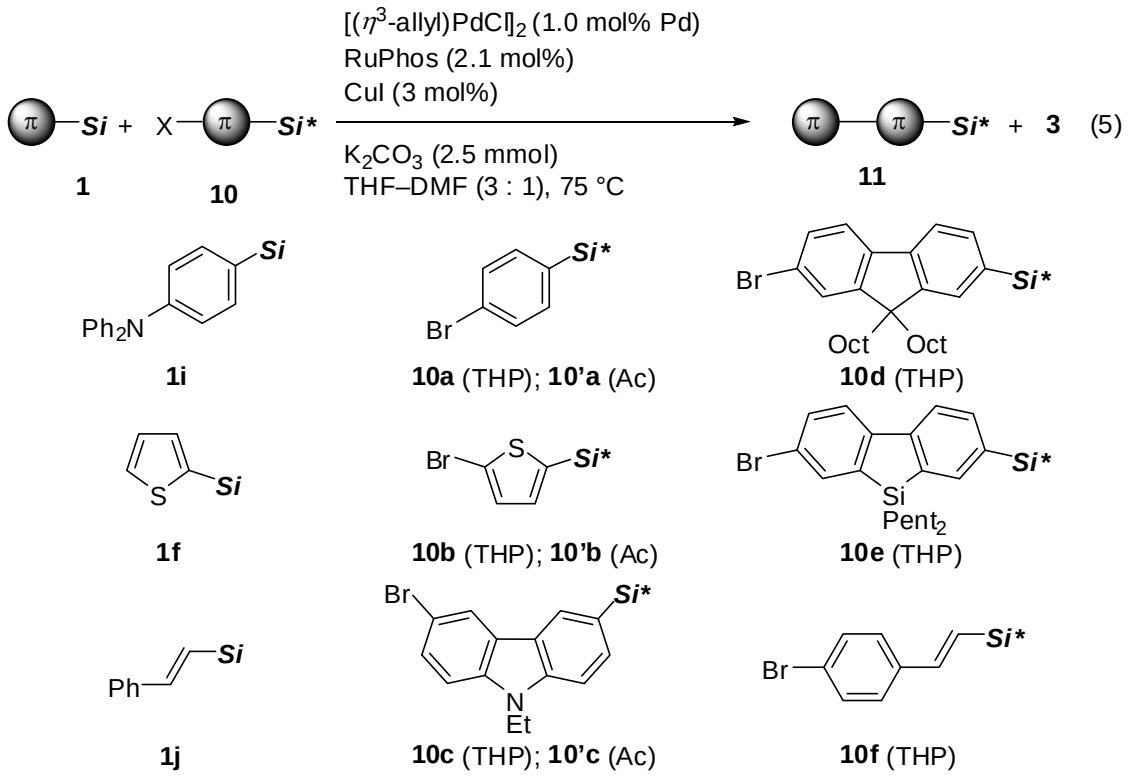




2.3 Oligoarene synthesis by iterative cross-coupling

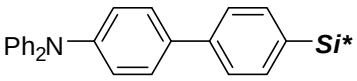
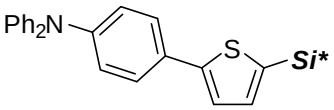
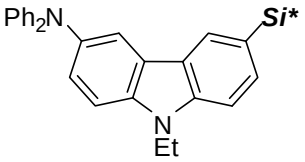
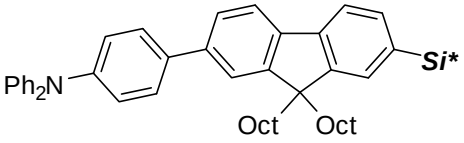
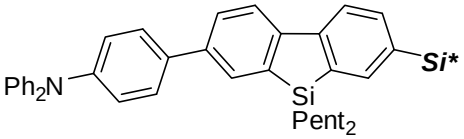
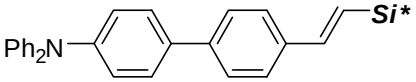
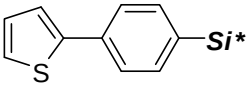
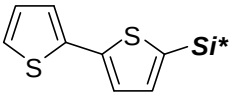
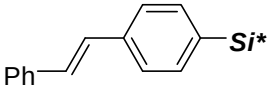
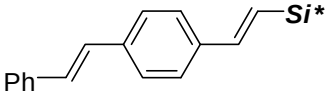
To verify the strategy shown in Scheme 1, the author synthesized various bromoaryl- and bromoheteroaryl[(2-hydroxymethyl)phenyl]dimethylsilanes bearing either THP (for acidic deprotection) **10a**–**10f** or acetyl (for basic deprotection) protecting group **10'a**–**10'c**, and examined their cross-coupling reactions (Eq. 5 and Table 6). The reaction of 4-(diphenylamino)phenylsilane **1i** (12 mmol) with THP-protected 4-bromophenylsilane **10a** (10 mmol) proceeded smoothly in the presence of $[(\eta^3\text{-allyl})PdCl]_2$ (1.0 mol % Pd), RuPhos (2.1 mol %), CuI (3.0 mol %), and K_2CO_3 (2.5 mmol) in THF–DMF (3 : 1) at 75 °C for 7 h to give 4-silylated biphenyl **11ia** in 88% yield (entry 1). Recyclable silicon residue **3** was also isolated in 86% yield. The acetyl-protected silicon reagent **10'a** also tolerated the present conditions to give the corresponding biaryl **11'ia** in 93% yield (entry 2), demonstrating flexibility of the present protocol adaptable to functional groups in target molecules. Coupling of **1i** with various brominated arylsilanes even in a gram scale also met with success, giving a variety of silylated biaryls in a highly chemoselective manner in good to excellent yields (entries 3–8). It is worth noting that the mild reaction conditions utilizing K_2CO_3 as the base for the present silicon-based cross-coupling technology allow participation of silafluorene **10e** with its C–Si bonds in the ring system being completely intact (entry 8). The alkenylsilane moiety in **10f** becomes inert upon THP protection of the hydroxy group, and the cross-coupling reaction between **10f** and **1i** successfully took place (entry 9). Thienylsilane **1f** also cross-coupled even on a gram-scale with e.g. **10b** successfully to give silylated bithiophene **11fb** which is ready for further homologation (entries 10 and 11). Similar cross-coupling reactions with (*E*)-styrylsilane **1j** took place in the

absence of a copper cocatalyst to give phenylenevinylenes **11ja** and **11jf** with a silyl terminus for next coupling (entries 12 and 13)



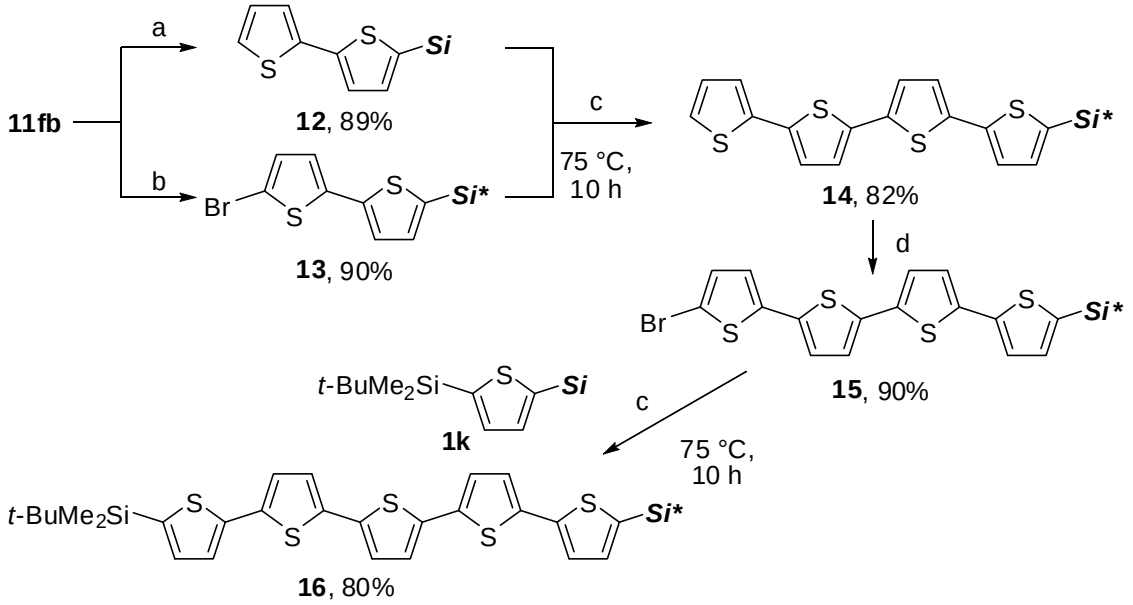
Second cross-coupling of the silylated biaryls **11** thus obtained was examined subsequently. For example, deprotection of **11fb** with PPTS and MeOH proceeded smoothly to give silylbithiophene **12** bearing a free hydroxy group, whereas lithiation of **11fb** with *n*-BuLi followed by bromination with 1,2-dibromo-1,1,2,2-tetrafluoroethane afforded 5-bromo-5'-silyl-2,2'-bithiophene **13** (Scheme 6). High stability of silylated biaryls **11fb**, **12**, and **13** under acidic or basic conditions is remarkable and ascribed definitely to tetraorganosilane structure. The coupling reaction of **12** with **13** succesfully gave silylated quarterthiophene **14**. Bromination leading to **15** followed by further cross-coupling with 2,5-disilyl thiophene **1k** gave unsymmetrically disilylated quinquethiophene **16**, which would enjoy potential application to stepwise two-photon holographic recording.[21] On the other hand, linear extention of silylated biaryl **11id** was performed with the deprotection–cross-coupling sequence employing **10'c**, **10'b**, and **10e**, affording highly conjugated protected oligoarenylsilane **19** in an efficient manner (Scheme 7).

Table 6. Cross-coupling reaction of organo[2-(hydroxymethyl)phenyl]dimethylsilanes (**1**) with halogenated organo[2-(hydroxymethyl)phenyl]dimethylsilanes (**10**)

entry	**1** (equiv)	**10**	time (h)	product	yield (%)[a]
1[b]	**1i** (1.2)	**10a**	7		88 (**11ia**)
2	**1i** (1.2)	**10'a**	22		93 (**11'ia**)
3[c]	**1i** (1.2)	**10b**	8		81 (**11ib**)
4[c]	**1i** (1.2)	**10'b**	7		81 (**11'ib**)
5	**1i** (1.2)	**10c**	22		85 (**11ic**)
6	**1i** (15)	**10'c**	18		94 (**11'ic**)
7[d]	**1i** (1.5)	**10d**	30		93 (**11id**)
8[e,f]	**1i** (1.5)	**10e**	24		82 (**11ie**)
9	**1i** (1.2)	**10f**	17		93 (**11if**)
10[g]	**1f** (1.2)	**10a**	6		96 (**11fa**)
11[h]	**1f** (1.2)	**10b**	6		96 (**11fb**)
12[i]	**1j** (1.2)	**10a**	7		90 (**11ja**)
13[i]	**1j** (1.2)	**10f**	22		90 (**11jf**)

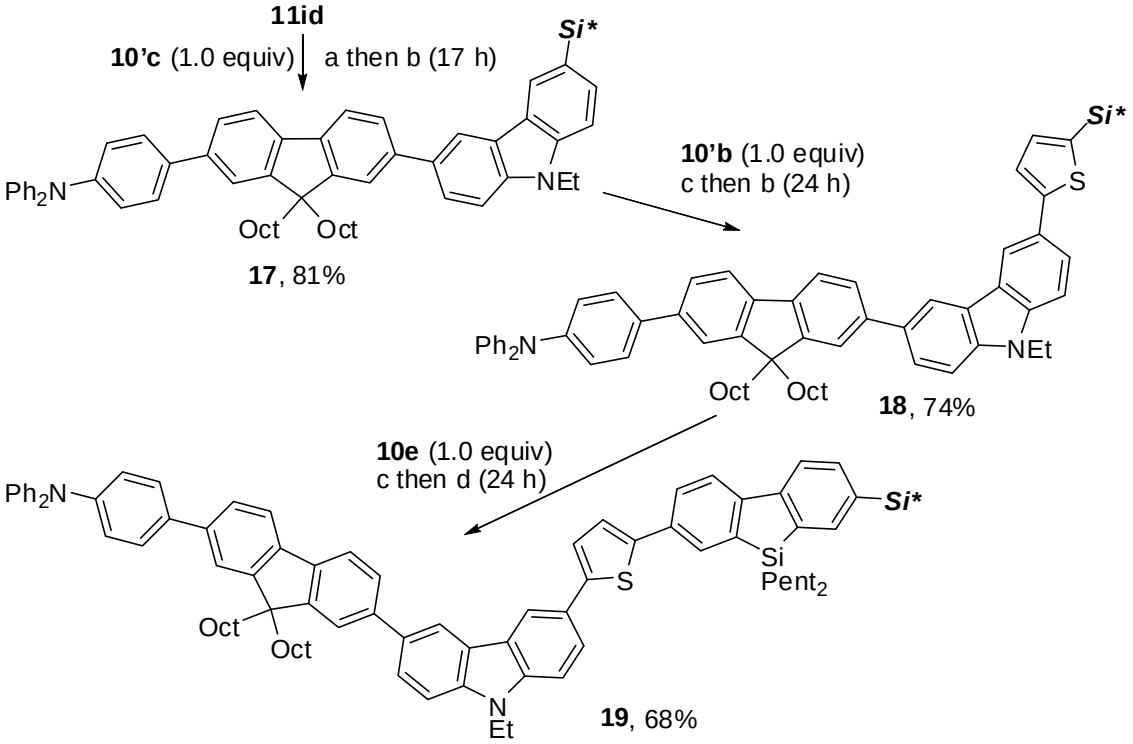
[a]Isolated yields based on **10**. [b]The reaction was carried out on a 10 mmol scale, and **3** was also isolated in 86% yield based on the conversion of **1i** (88%). [c]Reaction run using 3 mol% Pd. [d]Reaction run on a 20 mmol scale. [e]Reaction run on a 0.10 mmol scale. [f]Reaction run using 5 mol% Pd. [g]The reaction was carried out using (dppf)$PdCl_2 \cdot CH_2Cl_2$ (3 mol%) at 50 °C. [h]The reaction was carried out using (dppf)$PdCl_2 \cdot CH_2Cl_2$ (1 mol%) on a 20 mmol scale. [i]Without CuI.

Scheme 6. Convergent synthesis of disilylated quinquethiophene[a]



[a]Reagents and conditions: (a) PPTS (20 mol%), MeOH, 40 °C, 2 h; (b) *n*-BuLi, TMEDA, THF, –40 °C to rt, 1 h, then $BrCF_2CF_2Br$, –40 °C, 1 h; (c) (dppf)$PdCl_2 \cdot CH_2Cl_2$ (3 or 5 mol%), CuI (9 or 5 mol%), K_2CO_3, (2.5 equiv), THF–DMF (3 : 1); (d) *n*-BuLi, TMEDA, THF, –78 °C, 5 min, then $BrCF_2CF_2Br$, –40 °C, 1 h.

Scheme 7. Stepwise synthesis of oligoarenylsilane by iterative cross-coupling–deprotection sequence[a]



[a]Reagents and Conditions: (a) $TsOH \cdot H_2O$ (2 mol%), MeOH–CH_2Cl_2 (1 : 1), rt; (b) [(η^3-allyl)$PdCl]_2$ (5 mol% Pd), RuPhos (11 mol%), CuI (5 mol%), K_2CO_3 (2.5 equiv), THF–DMF (3 : 1), 75 °C; (c) DIBAL-H (1.1 equiv), CH_2Cl_2, –78 °C; (d) (dppf)$PdCl_2 \cdot CH_2Cl_2$ (5 mol%), CuI (5 mol%), K_2CO_3 (2.5 equiv), THF–DMF (3 : 1), 75 °C.

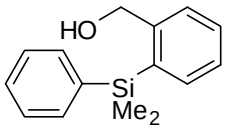
3. Conclusion

In summary, the author have demonstrated the palladium-catalyzed cross-coupling reactions of aryl[2-(hydroxymethyl)phenyl]dimethylsilanes is highly effective for those with aryl halides, allylic and benzylic carbonates. The use of readily accessible, highly stable, and recyclable tetraorganosilicon reagents under mild conditions free of fluoride activators is definitely an attractive feature that may replace the conventional protocols that employ boron, tin, zinc, and magnesium reagents. The iterative cross-coupling strategy utilizing organo[(2-hydroxymethyl)phenyl]dimethylsilanes has been demonstrated to be an efficient silicon-based entry to oligoarenes of well-defined structure. Mild and divergent conditions for the cross-coupling and deprotection steps clearly show that the stable tetraorganosilicon-type reagents have high potency in applications to creation of new functional materials.

4. Experimental section

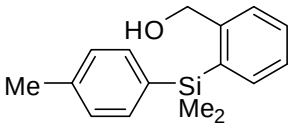
Chemicals. RuPhos were prepared according to the reported procedures.[20]

4.1 Preparation of aryl[2-(hydroxymethyl)phenyl]dimethylsilane (1) using 1,1-dimethyl-2-oxa-1-silaindan (3)



1a

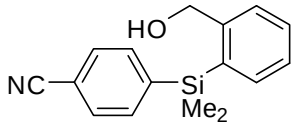
[2-(Hydroxymethyl)phenyl]dimethyl(phenyl)silane (1a). A 1.0 M solution of phenylmagnesium bromide in THF (65 mL, 65 mmol) was added over 15 min to a solution of **3** (9.9 g, 60 mmol) in diethyl ether (250 mL) at −78 °C. The mixture was stirred at −78 °C for 2 h and then at rt overnight before quenching with a sat. NH_4Cl aq. solution (40 mL) at 0 °C. The aq. layer was extracted two times with diethyl ether (60 mL), and the combined organic layers were washed with water (75 mL) and then with brine (50 mL) and dried over anhydrous $MgSO_4$. After concentration in vacuo, the residue was purified by flash chromatography on silica gel to afford **1a** (13.8 g, 95%) as a colorless solid, mp 53.0–54.0 °C, R_f 0.39 (hexane–ethyl acetate = 4 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, J = 7.6 Hz, 1H), 7.54‑7.41 (m, 4H), 7.41‑7.29 (m, 4H), 4.54 (s, 2H), 1.38‑1.22 (br s, 1H), 0.62 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.5, 139.0, 135.8, 135.5, 133.8, 130.0, 129.2, 128.1, 128.0, 127.0, 65.3, −1.1; IR (KBr) 3298, 2953, 1427, 1250, 1111, 1076, 1018, 826, 777, 739, 702, 640, 482, 419 cm^{-1}; MS (EI, 70 eV) *m*/*z* (%) 243 (M^+, 0.1), 227 (39), 211 (12), 210 (21), 209 (100), 165 (47), 164 (11), 149 (28), 147 (18), 135 (11), 105 (12). Anal. Calcd. for $C_{15}H_{18}OSi$; C, 74.33; H, 7.49. Found: C, 74.18; H, 7.52.



1b

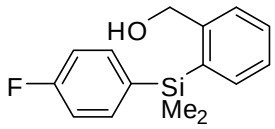
[2-(Hydroxymethyl)phenyl]dimethyl(4-methylphenyl)silane (1b). Following the procedure for **1a**, the reaction using a 0.5 M solution of *p*-tolylmagnesium bromide in

diethyl ether (100 mL, 50 mmol) and **3** (7.5 g, 46 mmol) gave **1b** (9.7 g, 83%) as a colorless solid, mp 55.6–56.5 °C, R_f 0.19 (hexane–ethyl acetate = 5 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61–7.56 (m, 1H), 7.48–7.37 (m, 4H), 7.32 (td, *J* = 7.0, 2.0 Hz, 1H), 7.20–7.16 (m, 1H), 4.54 (d, *J* = 6.0 Hz, 2H), 2.36 (s, 3H), 1.28 (t, *J* = 6.0 Hz, 1H), 0.61 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.3, 139.0, 136.0, 135.3, 135.1, 133.7, 129.8, 128.8, 128.1, 126.9, 65.3, 21.6, –0.9; IR (KBr) 3285, 3059, 2951, 1599, 1435, 1258, 1248, 1128, 1105, 1078, 1018, 826, 797, 775, 756, 745, 660, 500, 490 cm^{-1}; MS (EI) *m*/*z* (%) 243 (4), 242 (15), 241 (M^+–Me, 69), 225 (7), 224 (20), 223 (100), 105 (3), 91 (7); HRMS (EI) Calcd. for $C_{16}H_{20}OSi$: M^+, 256.1283. Found: *m*/*z* 256.1289.



1c

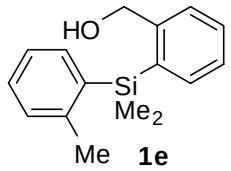
(4-Cyanophenyl)[2-(hydroxymethyl)phenyl]dimethylsilane (1c). To a solution of *p*-iodobenzonitrile (4.1 g, 18 mmol) in THF (50 mL) was added a 0.68 M solution of *i*-PrMgBr (58 mL, 39 mmol) at –20 °C, and the resulting mixture was stirred at the same temperature for 10 h. A solution of *p*-cyanophenylmagnesium bromide[22] thus prepared was transferred dropwise to a solution of **3** (2.5 g, 15 mmol) in THF (50 mL) at –20 °C, and the resulting mixture was stirred at rt overnight. After a standard work-up procedure and purification by flash chromatography on silica gel, **1c** was obtained (3.5 g, 87%) as a white solid, mp 38.4–39.4 °C, R_f 0.50 (hexane–ethyl acetate = 2 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63–7.52 (m, 5H), 7.49–7.42 (m, 2H), 7.36–7.29 (m, 1H), 4.52 (s, 2H), 1.57 (br s, 1H), 0.63 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.5, 146.2, 135.7, 134.32, 134.28, 131.1, 130.4, 128.0, 127.3, 118.9, 112.7, 65.3, –1.3; IR (KBr) 3489, 3466, 3416, 3051, 2964, 2232, 1385, 1258, 1124, 1096, 1078, 1036, 814, 779, 750, 704, 554 cm^{-1}. Anal. Calcd. for $C_{16}H_{17}NOSi$; C, 71.87; H, 6.41. Found: C, 71.58; H, 6.56.



1d

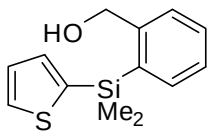
[2-(Hydroxymethyl)phenyl]dimethyl(4-fluorophenyl)silane (1d). Following the

procedure for **1a**, the reaction using a 2.0 M solution of 4-fluorophenylmagnesium bromide in diethyl ether (17 mL, 33 mmol) and **3** (4.9 g, 30 mmol) gave **1d** (6.8 g, 86%) as a colorless oil, R_f 0.17 (hexane–ethyl acetate = 4 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 7.7 Hz, 1H), 7.51‑7.41 (m, 4H), 7.32 (td, *J* = 7.0, 1.8 Hz, 1H), 7.08‑7.01 (m, 2H), 4.54 (s, 2H), 1.44 (br s, 1H), 0.61 (s, 6H); ^{13}C NMR (101MHz, $CDCl_3$) δ 163.7 (d, *J* = 248.4 Hz), 146.5, 135.8 (d, *J* = 7.6 Hz), 135.5, 134.4 (d, *J* = 3.8 Hz), 130.1, 128.0, 127.1, 115.2 (d, *J* = 19.9 Hz), 65.2, –0.9; IR (neat) 3331, 2955, 1587, 1499, 1261, 1250, 1231, 1163, 1103, 1078, 826, 812, 775, 756, 517 cm^{-1}; MS (EI) *m*/*z* (%) 245 (M^+–Me, 87), 243 (14), 229 (14), 228 (22), 227 (100), 183 (10), 149 (24), 147 (12), 79 (11). Anal. Calcd. for $C_{15}H_{17}FOSi$; C, 69.19; H, 6.58. Found: C, 69.03; H, 6.58.



1e

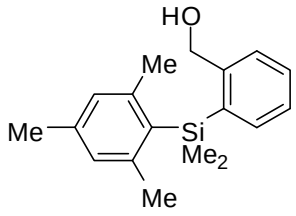
[2-(Hydroxymethyl)phenyl]dimethyl(2-methylphenyl)silane (1e). Following the procedure for **1a**, the reaction with **3** (4.9 g, 30 mmol) and a 2.0 M solution of 2-methylphenylmagnesium bromide in THF (17 mL, 33 mmol) gave **1e** (7.6 g, 99%) as a colorless oil, R_f 0.36 (hexane–ethyl acetate = 5 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64–7.55 (m, 2H), 7.45–7.39 (m, 2H), 7.35–7.30 (m, 2H), 7.23 (t, *J* = 7.4 Hz, 1H), 7.13 (d, *J* = 7.5 Hz, 1H), 4.46 (s, 2H), 2.17 (s, 3H), 1.34 (br s, 1H), 0.64 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.3, 143.8, 137.0, 136.7, 135.0, 134.6, 130.1, 129.8, 128.3, 127.2, 125.5, 65.2, 22.8, –0.6; IR (neat) 3339, 3055, 2955, 1589, 1437, 1258, 1128, 1078, 1032, 835, 818, 773, 745, 691, 642 cm^{-1}; MS (EI) *m*/*z* (%) 256 (M^+, 0.03), 242 (11), 241 (51), 225 (10), 224 (21), 223 (100), 179 (11), 178 (10), 166 (10), 165 (44), 164 (16), 163 (13), 149 (57), 147 (26), 145 (10), 105 (13), 92 (14), 91 (26). Anal. Calcd. for $C_{16}H_{20}OSi$; C, 74.95; H, 7.86. Found: C, 75.24; H, 7.94.



1f

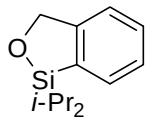
[2-(Hydroxymethyl)phenyl]dimethyl(2-thienyl)silane (1f). A solution of 2-thienyl-

magnesium bromide in THF (23 mL) [prepared from 2-bromothiophene (5.4 g, 33 mmol) and Mg (0.82 g, 34 mmol)] was added to **3** (4.9 g, 30 mmol) in THF (10 mL) at 0 °C, and the resulting mixture was stirred at rt for 22 h. The mixture was diluted with diethyl ether, washed with a sat. NH_4Cl aq. solution, water, and brine, and dried over anhydrous $MgSO_4$. After removal of the solvent in vacuo, flash chromatography on silica gel gave **1f** (5.9 g, 79%) as a colorless oil, R_f 0.21 (hexane–ethyl acetate = 5 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (dd, *J* = 4.6, 0.9 Hz, 1H), 7.57 (dd, *J* = 7.4, 0.7 Hz, 1H), 7.50–7.41 (m, 2H), 7.34–7.28 (m, 2H), 7.20 (dd, *J* = 4.6, 3.4 Hz, 1H), 4.64 (s, 2H), 1.47 (s, 1H), 0.68 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.5, 138.5, 135.6, 135.3, 131.3, 130.2, 128.4, 128.2, 127.1, 65.3, 0.2; IR (neat) 3337, 2955, 1435, 1406, 1252, 1213, 1126, 1080, 991, 833, 812, 777, 754, 710, 654 cm^{-1}; MS (EI) *m*/*z* (%) 233 (M^+–Me, 42), 231 (15), 217 (14), 216 (19), 215 (100), 164 (19), 163 (12), 150 (10), 149 (73). Anal. Calcd. for $C_{13}H_{16}OSSi$; C, 62.85; H, 6.49. Found: C, 62.96; H, 6.49.



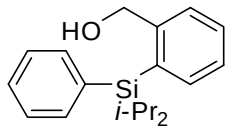
1g

[2-(Hydroxymethyl)phenyl]dimethyl(2,4,6-trimethylphenyl)silane (1g). Following the procedure for **1b**, the reaction with a 1.0 M solution of 2,4,6-trimethylphenylmagnesium bromide in diethyl ether (33 mL, 33 mmol) and **3** (4.9 g, 30 mmol) gave **1g** (4.3 g, 50%) as a colorless solid, mp 60.0–60.7 °C, R_f 0.20 (hexane–ethyl acetate = 5 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (dt, *J* = 7.1, 1.1 Hz, 1H), 7.42–7.27 (m, 3H), 6.81 (s, 2H), 4.43 (s, 2H), 2.26 (s, 6H), 2.25 (s, 3H), 1.53 (br s, 1H), 0.66 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.4, 144.3, 140.0, 139.4, 133.8, 131.6, 129.6, 129.3, 128.5, 127.3, 65.3, 24.5, 20.9, 3.3; IR (KBr) 3292, 2961, 1684, 1506, 1456, 1248, 1074, 1011, 841, 820, 777 cm^{-1}. Anal. Calcd. for $C_{18}H_{24}OSi$; C, 76.00; H, 8.50. Found: C, 76.01; H, 8.45.



3'

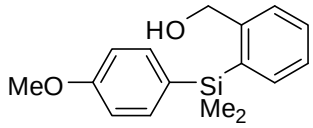
1,1-Diisopropyl-2-oxa-1-silaindan (3'). Following the similar procedure for **3** described in Chapter 2, a 1.6 M *n*-BuLi solution in hexane (12.7 mL, 20 mmol) was added to the solution of 2-(2-tetrahydro-2*H*-pyran-2-yloxymethyl)bromobenzene (5.0 g, 18.4 mmol) in THF (3.8 mL) over 5 min at –78 °C, and the resulting solution was stirred for 2 h before the addition of chlorodiisopropylsilane (3.3 g, 22 mol) at –78 °C. The mixture was warmed gradually at rt overnight. The mixture was diluted with diethyl ether and washed with a sat. $NaHCO_3$ aq. solution, water, and brine and dried over anhydrous $MgSO_4$. After concentration in vacuo, the residue was dissolved in MeOH (74 mL). To the solution was portionwise added *p*-toluenesulfonic acid monohydrate (175 mg, 0.92 mmol) at rt, and the mixture was stirred overnight before concentration in vacuo. The residue was distilled to give **3'** (4.1 g, 82%) as a colorless oil, bp 75 °C (3.0 mmHg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59–7.55 (m, 1H), 7.42–7.36 (m, 1H), 7.31–7.21 (m, 2H), 5.15 (s, 2H), 1.25 (sept, J = 7.3 Hz, 2H), 1.04 (d, J = 7.3 Hz, 6H), 1.01 (d, J = 7.3 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.5, 132.0, 131.6, 129.3, 126.4, 121.4, 72.5, 17.1, 13.2; IR (neat) 2941, 2864, 1464, 1443, 1067, 1049, 880, 781, 746, 716, 667, 642 cm^{-1}; MS (EI) *m*/*z* (%) 222 (M^+, 2), 221 (6), 220 (33), 179 (32), 178 (82), 177 (100), 151 (24), 150 (75), 149 (99), 105 (22), 91 (44); HRMS (EI) Calcd. for $C_{13}H_{20}OSi$: M^+, 220.1283. Found: *m*/*z* 220.1285.



1'a

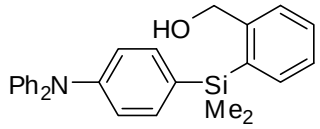
[2-(Hydroxymethyl)phenyl]diisopropyl(phenyl)silane (1'a). Following the procedure for **1a**, the reaction with a 1.07 M solution of phenylmagnesium bromide in THF (51 mL, 55 mmol) and 1,1-diisopropyl-2-oxa-1-silaindan (**3'**, 11.0 g, 50 mmol) gave the **1'a** (13.5 g, 90%) as a colorless solid, mp 119.0–119.6 °C, R_f 0.69 (hexane–ethyl acetate = 2 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67–7.56 (m, 1H), 7.53–7.29 (m, 3H), 4.40 (d, J = 5.6 Hz, 2H), 1.67 (sept, J = 7.2 Hz, 2H), 1.40 (t, J = 5.8 Hz, 1H), 1.00 (d, J = 7.2 Hz, 6H), 0.98 (d, J = 7.2 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.6, 136.7, 134.9, 134.8,

130.9, 129.6, 129.1, 128.6, 127.7, 126.5, 65.6, 18.0, 17.9, 10.7; IR (KBr) 3364, 2953, 2862, 1427, 1105, 1015, 995, 878, 745, 708, 687, 656, 615, 517 cm^{-1}; MS (EI) *m*/*z* (%) 257 (6), 256 (21), 255 (M^+–*i*-Pr, 100), 239 (2), 238 (5), 237 (27), 105 (5), 91 (8); HRMS (EI) Calcd. for $C_{23}H_{24}BrNOSi$: M^+, 298.1753. Found: *m*/*z* 298.1758.



1h

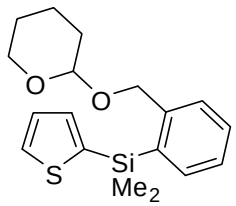
[2-(Hydroxymethyl)phenyl]dimethyl(4-methoxyphenyl)silane (1h). To a solution of 1,1-dimethyl-2-oxa-1-silaindan (**3**, 3.3 g, 20 mmol) in THF (60 mL) was added a 0.5 M solution of 4-methoxyphenylmagnesium bromide in THF (44 mL, 22 mmol) over 30 min at 0 °C. The resulting mixture was stirred at 0 °C for 1 h and then at rt overnight. The reaction was quenched with a sat. NH_4Cl aq. solution (20 mL) at 0 °C. The aq. layer was extracted with diethyl ether (100 mL), and the combined organic layers were washed with water (20 mL) and brine (20 mL) and dried over anhydrous $MgSO_4$. After concentration in vacuo, the residue was purified by flash chromatography on silica gel to afford **1h** (4.9 g, 90%) as a colorless solid, mp 43.4–44.4 °C, R_f 0.23 (hexane–ethyl acetate = 5 : 1). ^1H NMR (400 MHz, $CDCl_3$) δ 7.62–7.55 (m, 1H), 7.48–7.38 (m, 4H), 7.31 (td, *J* = 7.1, 1.6 Hz, 1H), 6.91 (d, *J* = 8.6 Hz, 2H), 4.55 (s, 2H), 3.81 (s, 3H), 1.46 (br s, 1H), 0.59 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.5, 146.5, 136.2, 135.5, 135.3, 129.9, 129.6, 128.2, 127.0, 113.8, 65.2, 55.0, –0.9; IR (KBr) 3285, 2947, 1593, 1502, 1277, 1246, 1182, 1111, 1018, 824, 814, 775, 756, 745 cm^{-1}. Anal. Calcd. for $C_{16}H_{20}O_2Si$; C, 70.54; H, 7.46. Found: C, 70.29; H, 7.46.



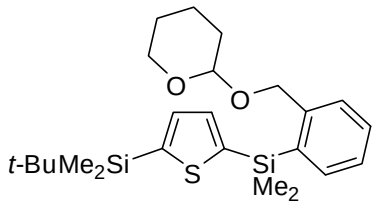
1i

[2-(Hydroxymethyl)phenyl]dimethyl[4-(diphenylamino)phenyl]silane (1i).[23] To a suspension of Mg turnings (1.9 g, 79 mmol) in Et_2O (160 mL) was added a solution of 4-bromo-*N*,*N*-diphenylaniline (25 g, 77 mmol) in THF (60 mL) at rt, and the resulting mixture was stirred at 60 °C for 4 h. The mixture was cooled to 0 °C, and then 1,1-dimethyl-2-oxa-1-silaindan (**3**, 12.1 g, 73 mmol) was added. After being stirred at rt

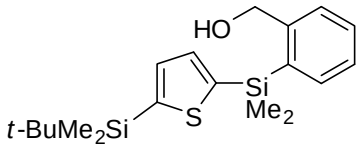
overnight, the reaction mixture was quenched with a sat. NH_4Cl aq. solution at 0 °C. The aq. layer was extracted with diethyl ether, and the combined organic layers were dried over anhydrous $MgSO_4$, and concentrated in vacuo. The residue was purified by flash chromatography on silica gel to afford **1a** (30 g, 95%) as a colorless viscous oil, R_f 0.70 (hexane–ethyl acetate = 1 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 7.3 Hz, 1H), 7.48–7.37 (m, 2H), 7.31 (d, *J* = 8.4 Hz, 2H), 7.23 (t, *J* = 7.8 Hz, 5H), 7.08 (d, *J* = 8.2 Hz, 4H), 7.01 (t, *J* = 7.5 Hz, 4H), 4.58 (s, 2H), 1.33 (br s, 1H), 0.59 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.6, 147.2, 146.3, 136.2, 135.3, 134.6, 130.9, 129.8, 129.2, 128.2, 126.9, 124.7, 123.1, 122.1, 65.4, –0.8; IR (neat) 3398, 3057, 3011, 2955, 1585, 1489, 1327, 1315, 1279, 1254, 1196, 1109, 1076, 1028, 812, 754, 696, 665, 621 cm^{-1}. Anal. Calcd. for $C_{27}H_{27}NOSi$; C, 79.17; H, 6.64. Found: C, 79.21; H, 6.80.



Dimethyl[2-(tetrahydro-2*H*-pyran-2-yloxymethyl)phenyl](2-thienyl)silane. To a mixture of **1f** (20 g, 80 mmol) and 3,4-dihydro-2*H*-pyran (13.5 g, 160 mmol) were added 4 drops of conc. HCl at rt, and the resulting mixture was stirred at rt for 4 h, diluted with Et_2O, neutralized with $NaHCO_3$, dried over anhydrous $MgSO_4$, and filtered through a Celite pad. After concentration in vacuo, the residue was purified by flash chromatography on silica gel to afford the title compound (22 g, 82%) as a colorless oil, R_f 0.30 (hexane–ethyl acetate = 20 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (dd, *J* = 4.6, 0.6 Hz, 1H), 7.53–7.46 (m, 2H), 7.40 (td, *J* = 7.5, 1.3 Hz, 1H), 7.29–7.22 (m, 2H), 7.17 (dd, *J* = 4.5, 3.4 Hz, 1H), 4.73 (d, *J* = 12.1 Hz, 1H), 4.53 (t, *J* = 3.5 Hz, 1H), 4.47 (d, *J* = 12.1 Hz, 1H), 3.85–3.77 (m, 1H), 3.50–3.42 (m, 1H), 1.88–1.75 (m, 1H), 1.72–1.42 (m, 5H), 0.652 (s, 3H), 0.651 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.9, 138.2, 135.7, 135.20, 135.15, 130.9, 129.7, 128.5, 128.0, 126.7, 97.8, 68.7, 62.1, 30.6, 25.6, 19.5, 0.4, 0.3; IR (neat): 2943, 2870, 1437, 1406, 1350, 1252, 1213, 1202, 1119, 1078, 1026, 989, 907, 833, 812, 777, 756, 708, 656 cm^{-1}. Anal. Calcd. for $C_{18}H_{24}O_2SSi$: C, 65.01; H, 7.27. Found: C, 64.88; H, 7.06.



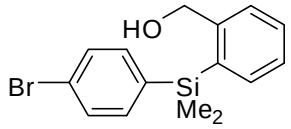
5-(*t*-Butyldimethylsilyl)-2-(dimethyl[2-(tetrahydro-2*H*-pyran-2-yloxymethyl)phenyl]silyl)thiophene. To a solution of dimethyl[2-(tetrahydro-2*H*-pyran-2-yloxymethyl)-phenyl](2-thienyl)silane (1.56 g, 4.7 mmol) in Et_2O (5 mL) were added TMEDA (0.63 g, 5.4 mmol) and a 1.6 M solution of *n*-BuLi (5.2 mmol) in hexane at –40 °C. The resulting mixture was stirred at rt for 1 h, and then a solution of *t*-$BuMe_2SiCl$ (0.85 g, 5.6 mmol)in Et_2O (4 mL) was added at –40 °C. The resulting mixture was stirred at the same temperature for 30 min and then at rt overnight, diluted with diethyl ether, washed with water and brine, and then dried over anhydrous $MgSO_4$. Concentration in vacuo followed by flash chromatography on silica gel afforded the title compound (1.74 g, 83%) as a colorless oil, R_f 0.37 (hexane–ethyl acetate = 5 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56–7.43 (m, 2H), 7.39 (td, *J* = 7.5, 1.4 Hz, 1H), 7.32–7.18 (m, 3H), 4.72 (d, *J* = 12.1 Hz, 1H), 4.52 (t, *J* = 3.6 Hz, 1H), 4.46 (d, *J* = 12.1 Hz, 1H), 3.86–3.75 (m, 1H), 3.50–3.39 (m, 1H), 1.87–1.74 (m, 1H), 1.70–1.40 (m, 5H), 0.91 (s, 9H), 0.653 (s, 3H), 0.649 (s, 3H), 0.29 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.91, 143.85, 143.4, 136.04, 135.98, 135.9, 135.1, 129.6, 128.4, 126.7, 97.8, 68.8, 62.1, 30.6, 26.5, 25.6, 19.5, 17.0, 0.6, 0.4, –4.5; IR (neat) 2953, 2928, 2855, 1470, 1250, 1202, 1119, 1078, 1055, 1026, 1007, 976, 907, 835, 804, 773, 752, 675 cm^{-1}. Anal. Calcd. for $C_{24}H_{38}O_2SSi_2$; C, 64.52; H, 8.57. Found: C, 64.51; H, 8.37.



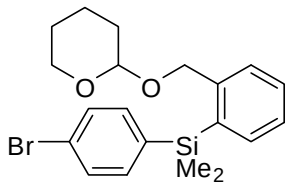
1k

5-(*t*-Butyldimethylsilyl)-2-[2-(hydroxymethyl)phenyl]dimethylsilyl)thiophene (1k). A solution of 5-(*t*-butyldimethylsilyl)-2-(dimethyl[2-(tetrahydro2*H*-pyran-2-yl-oxymethyl)phenyl]silyl)thiophene (1.51 g, 34 mmol) and PPTS (171 mg, 0.68 mmol) in methanol (10 mL) was stirred at 40 °C for 2 h and then concentrated in vacuo. The residue was purified by flash chromatography on silica gel to afford **1k** (1.13 g, 92%) as

a colorless solid, mp 50.3–51.5 °C, R_f 0.26 (hexane–ethyl acetate = 5 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 7.3 Hz, 1H), 7.47–7.38 (m, 2H), 7.36–7.25 (m, 3H), 4.61 (d, *J* = 6.2 Hz, 2H), 1.38 (t, *J* = 6.0 Hz, 1H), 0.90 (s, 9H), 0.67 (s, 6H), 0.29 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.4, 144.0, 143.9, 136.2, 136.0, 135.7, 135.1, 130.0, 128.3, 127.0, 65.4, 26.5, 17.0, 0.5, –4.6; IR (KBr) 3321, 2953, 2928, 2856, 1250, 1204, 1007, 835, 822, 808, 777 cm^{-1}. Anal. Calcd. for $C_{19}H_{30}OSSi_2$; C, 62.92; H, 8.34. Found: C, 62.89; H, 8.17.



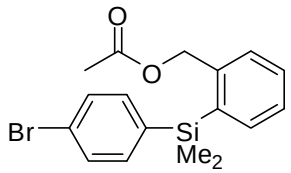
(4-Bromophenyl)[2-(hydroxymethyl)phenyl]dimethylsilane. To a solution of 2,6-dibromobenzene (12.4 g, 53 mmol) in THF (100 mL) was added a 1.6 M solution of *n*-BuLi in hexane (33 mL, 53 mmol) over 30 min at –78 °C, and the resulting mixture was stirred at –78 °C for 2 h. To this was added a solution of **3** (8.2 g, 50 mmol) in THF (50 mL) over 30 min at –78 °C. The resulting mixture was stirred at –78 °C for 2 h, warmed slowly to rt, and stirred overnight. Following the standard work-up procedure, a crude product was purified by flash chromatography on silica gel to give the title compound (14.6 g, 91%) as a colorless solid, mp 55.1–55.8 °C, R_f 0.31 (hexane–ethyl acetate = 5 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 7.5 Hz, 1H), 7.51–7.41 (m, 4H), 7.38–7.29 (m, 3H), 4.53 (s, 2H), 1.49 (br s, 1H), 0.60 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.5, 137.9, 135.6, 135.4, 135.1, 131.1, 130.1, 128.0, 127.1, 124.0, 65.2, –1.1; IR (KBr) 3308, 3057, 2951, 1570, 1479, 1375, 1258, 1126, 1076, 1067, 1022, 1009, 833, 824, 806, 775, 758, 745, 723, 650, 488 cm^{-1}. Anal. Calcd. for $C_{15}H_{17}BrOSi$; C, 56.08; H, 5.33. Found: C, 55.80; H, 5.27.



10a

(4-Bromophenyl)dimethyl[2-(tetrahydro-2*H*-pyran-2-yloxymethyl)phenyl]silane (8a). To a mixture of (4-bromophenyl)[2-(hydroxymethyl)phenyl]dimethylsilane (6.4 g,

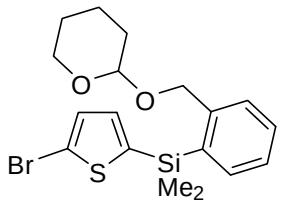
20 mmol) and 3,4-dihydro-2*H*-pyran (2.0 g, 24 mmol) was added a drop of concentrated hydrochloric acid at rt, and the resulting mixture was stirred at rt overnight. The mixture was diluted with Et_2O, neutralized with $NaHCO_3$, dried over anhydrous $MgSO_4$, and filtered through a Celite pad. After concentration in vacuo, the residue was purified by flash chromatography on silica gel to afford **8a** (7.3 g, 90%) as a colorless oil, R_f 0.29 (hexane–ethyl acetate = 10 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54–7.37 (m, 5H), 7.36–7.25 (m, 3H), 4.62 (d, *J* = 12.1 Hz, 1H), 4.43 (t, *J* = 3.3 Hz, 1H), 4.33 (d, *J* = 11.9 Hz, 1H), 3.78–3.68 (m, 1H), 3.45–3.36 (m, 1H), 1.84–1.70 (m, 1H), 1.67–1.40 (m, 5H), 0.58 (s, 3H), 0.57 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.9, 137.7, 135.5, 135.3, 130.8, 129.7, 128.6, 126.8, 123.7, 97.8, 68.7, 62.1, 30.6, 25.5, 19.5, –0.9, –1.0; IR (neat): 2943, 2870, 1570, 1479, 1439, 1377, 1258, 1202, 1119, 1078, 1067, 1026, 1011, 974, 907, 835, 818, 806, 775, 754, 723 cm^{-1}. Anal. Calcd. for $C_{20}H_{25}BrO_2Si$: C, 59.25; H, 6.22. Found: C, 59.09; H, 6.22.



10'a

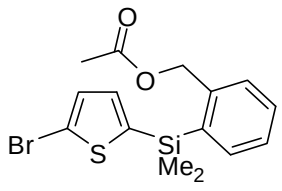
[2-(Acetoxymethyl)phenyl](4-bromophenyl)dimethylsilane (10'a). To a solution of (4-bromophenyl)[2-(hydroxymethyl)phenyl]dimethylsilane (3.2 g, 10 mmol) in Et_2O (20 mL) were added DMAP (12.2 mg, 0.10 mmol), pyridine (1.58 g, 20 mmol), and acetyl chloride (0.86 g, 11 mmol) at 0 °C. The resulting mixture was stirred at rt overnight, diluted with Et_2O, neutralized with a 1 M HCl aq. solution (20 mL), and washed with water and then with brine. The organic layer was dried over anhydrous $MgSO_4$, filtered through a Celite pad, and then concentrated in vacuo. The residue was purified by flash chromatography on silica gel to afford **10'a** (3.7 g, 100%) as a colorless solid, mp 57.4–58.0 °C, R_f 0.44 (hexane–ethyl acetate = 10 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 7.3 Hz, 1H), 7.49–7.28 (m, 7H), 4.94 (s, 2H), 1.92 (s, 3H), 0.59 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.4, 141.1, 137.2, 136.4, 135.6, 135.4, 130.9, 129.9, 129.6, 127.6, 123.9, 66.5, 20.9, –1.0; IR (KBr): 2959, 1730, 1566, 1481, 1377, 1259, 1244, 1069, 1034, 1011, 837, 824, 800, 762, 721, 494 cm^{-1}. Anal. Calcd.

for $C_{17}H_{19}BrO_2Si$: C, 56.20; H, 5.27. Found: C, 56.19; H, 5.22.



10b

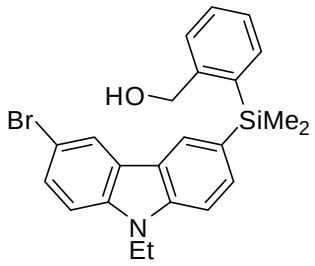
(5-Bromo-2-thienyl)dimethyl[2-(tetrahydro-2*H*-pyran-2-yloxymethyl)phenyl]silane (10b). To a solution of dimethyl[2-(tetrahydro-2*H*-pyran-2-yloxymethyl)phenyl](2-thienyl)silane (1.56 g, 4.7 mmol) in Et_2O (5 mL) were added TMEDA (0.63 g, 5.4 mmol) and a 1.6 M solution of *n*-BuLi (5.2 mmol) in hexane at –40 °C. The mixture was stirred at rt for 2 h and then treated with 1,2-dibromo-1,1,2,2-tetrafluoroethane (7.8 g, 30 mmol) at –40 °C. The resulting mixture was stirred at the same temperature for further 1 h before quenching with a sat. $Na_2S_2O_3$ aq. solution (100 mL) and then dilution with diethyl ether (300 mL). The organic layer was dried over anhydrous $MgSO_4$ and concentrated in vacuo. The residue was purified by flash chromatography on silica gel to afford **10b** (9.3 g, 90%) as a yellowish oil, R_f 0.27 (hexane–ethyl acetate = 15 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (t, *J* = 7.6 Hz, 2H), 7.41 (td, *J* = 7.5, 1.0 Hz, 1H), 7.27 (t, *J* = 7.3 Hz, 1H), 7.06 (d, *J* = 3.5 Hz, 1H), 6.97 (d, *J* = 3.5 Hz, 1H), 4.73 (d, *J* = 12.1 Hz, 1H), 4.54 (t, *J* = 3.5 Hz, 1H), 4.46 (d, *J* = 12.1 Hz, 1H), 3.87–3.75 (m, 1H), 3.52–3.42 (m, 1H), 1.88–1.75 (m, 1H), 1.72–1.41 (m, 5H), 0.62 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.9, 141.6, 135.5, 135.2, 134.9, 131.1, 129.9, 128.7, 126.9, 117.3, 97.8, 68.7, 62.2, 30.6, 25.6, 19.5, 0.2, 0.1 cm^{-1}; IR (neat): 2943, 2870, 1439, 1406, 1350, 1259, 1204, 1119, 1078, 1026, 974, 953, 907, 870, 837, 812, 779, 754, 691, 656 cm^{-1}. Anal. Calcd. for $C_{18}H_{23}BrO_2SSi$: C, 52.55; H, 5.63. Found: C, 52.72; H, 5.63.



10'b

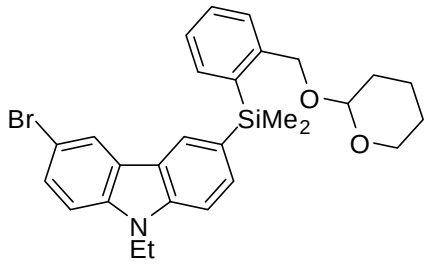
[2-(Acetoxymethyl)phenyl](5-bromo-2-thienyl)dimethylsilane (10'b). To a solution of diisopropylamine (0.53 g, 5.3 mmol) in THF (3 mL) was added a 1.6 M solution of

n-BuLi (3.3 mmol) in hexane at –40 °C, and the resulting mixture was stirred for 30 min. To this was added 2-bromothiophene (0.82 g, 5.0 mmol) at –70 °C, and the resulting mixture was stirred at –40 °C for 30 min before addition of magnesium bromide etherate (1.4 g, 5.3 mmol) at –30 °C. The resulting mixture was stirred at –30 °C for another 30 min, treated with **3** (0.82 g, 5.0 mmol) at the same temperature, and stirred at rt overnight. Acetyl chloride (0.39 g, 5.0 mmol) was added at 0 °C, and then the resulting mixture was stirred at rt for additional 6 h. The mixture was diluted with diethyl ether, washed with a sat. $NaHCO_3$ aq. solution, water, and brine, and the organic layer was dried over anhydrous $MgSO_4$. After concentration in vacuo, the residue was purified by flash chromatography on silica gel to afford **10b** (1.14 g, 62%) as a yellowish oil, R_f 0.29 (hexane–ethyl acetate = 10 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 7.3 Hz, 1H), 7.48–7.31 (m, 3H), 7.09 (d, *J* = 3.5 Hz, 1H), 6.99 (d, *J* = 3.7 Hz, 1H), 5.07 (s, 2H), 2.02 (s, 3H), 0.65 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.4, 141.0, 135.9, 135.6, 135.4, 131.2, 130.1, 129.6, 127.7, 117.6, 66.5, 21.0, 0.1 cm^{-1}; IR (neat): 3057, 2957, 1736, 1437, 1404, 1379, 1362, 1286, 1227, 1128, 1078, 1069, 1026, 999, 955, 837, 810, 779, 756, 692, 656 cm^{-1}. Anal. Calcd. for $C_{15}H_{17}BrO_2SSi$: C, 48.78; H, 4.64. Found: C, 48.72; H, 4.67.



(3-Bromo-9-ethyl-9*H*-carbazol-6-yl)[2-(hydroxymethyl)phenyl]dimethylsilane. To a solution of 3,6-dibromo-9-ethyl-9*H*-carbazole[24] (7.7 g, 22 mmol) in THF (60 mL) was added a 1.6 M solution of *n*-BuLi in hexane (14 mL, 22 mmol) over 30 min at –78 °C, and the resulting mixture was stirred at –78 °C for 1 h. To this was added **3** (3.6 g, 22 mmol) at –78 °C, and the resulting mixture was warmed slowly to rt, stirred overnight, and then quenched with a sat. NH_4Cl aq. solution at 0 °C. The aq. layer was extracted three times with diethyl ether (90 mL), and the combined organic layer was dried over anhydrous $MgSO_4$. After concentration in vacuo, the residue was purified by flash chromatography on silica gel to afford the title compound (8.6 g, 90%) as a colorless

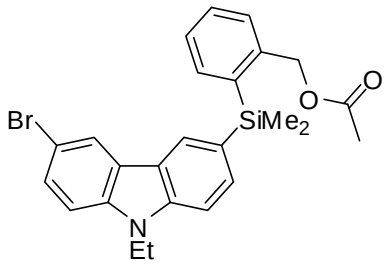
solid, mp 49.2–51.0 °C, R_f 0.37 (hexane–ethyl acetate = 2 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (s, 2H), 7.63 (d, *J* = 7.5 Hz, 1H), 7.56 (d, *J* = 8.1 Hz, 1H), 7.52 (dd, *J* = 8.6, 1.6 Hz, 1H), 7.48–7.22 (m, 4H), 4.55 (d, *J* = 4.4 Hz, 2H), 4.32 (q, *J* = 7.1 Hz, 2H), 1.41 (t, *J* = 7.1 Hz, 3H), 1.24 (br, *J* = 5.3 Hz, 1H), 0.69 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.4, 140.8, 138.4, 136.3, 135.4, 131.5, 129.8, 128.3, 128.1, 127.7, 126.9, 126.3, 124.3, 123.1, 121.9, 111.8, 109.8, 108.6, 65.3, 37.8, 13.9, 0.2; IR (KBr): 3418, 2972, 2951, 1587, 1474, 1435, 1346, 1286, 1275, 1232, 1157, 1097, 847, 802, 773, 754 cm^{-1}; HRMS (FAB^+) Calcd. for $C_{23}H_{24}BrNOSi$: M^+, 437.0811. Found: *m*/*z* 437.0807.



10c

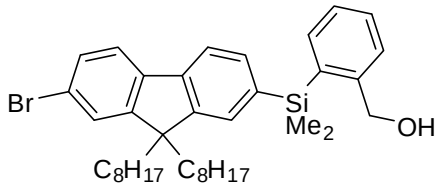
(3-Bromo-9-ethyl-9*H*-carbazol-6-yl)dimethyl[2-(tetrahydro-2*H*-pyran-2-yloxymethyl)phenyl]silane (10c). To a mixture of (3-bromo-9-ethyl-9*H*-6-carbazolyl)[2-(hydroxymethyl)phenyl]dimethylsilane (5.6 g, 13 mmol) and 3,4-dihydro-2*H*-pyran (1.29 g, 15.4 mmol) were added 3 drops of conc. HCl at rt, and the resulting mixture was stirred at rt overnight. The mixture was diluted with diethyl ether (50 mL), neutralized with $NaHCO_3$, dried over anhydrous $MgSO_4$, and filtered through a Celite pad. Concentration in vacuo followed by purification of the residue by flash chromatography on silica gel afforded **10c** (6.1 g, 91%) as a colorless viscous oil, R_f 0.19 (hexane–ethyl acetate = 15 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (s, 1H), 8.17 (s, 1H), 7.60–7.46 (m, 4H), 7.41 (td, *J* = 7.4, 1.4 Hz, 1H), 7.36 (d, *J* = 8.1 Hz, 1H), 7.32–7.23 (m, 2H), 4.67 (d, *J* = 11.9 Hz, 1H), 4.44–4.37 (m, 2H), 4.32 (q, *J* = 7.1 Hz, 2H), 3.73–3.64 (m, 1H), 3.35–3.26 (m, 1H), 1.80–1.67 (m, 1H), 1.62–1.31 (m, 8H), 0.68 (s, 3H), 0.67 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.0, 140.7, 138.3, 136.6, 135.4, 131.8, 129.5, 128.5, 128.1, 127.8, 126.7, 126.5, 124.4, 123.1, 121.7, 111.7, 109.7, 108.3, 97.8, 68.8, 62.0, 37.7, 30.5, 25.5, 19.4, 13.9, –0.3, –0.4; IR (neat): 3053, 3009, 2947, 2872, 1620, 1589, 1564, 1470, 1435, 1381, 1346, 1286, 1275, 1259, 1232, 1200, 1182, 1157, 1128, 1097, 1078, 1053, 1024, 976, 907, 870, 847, 800, 754, 689, 667, 635, 569 cm^{-1}. Anal. Calcd.

for $C_{28}H_{32}BrNO_2Si$: C,64.36; H, 6.17. Found: C, 64.10; H, 6.05.



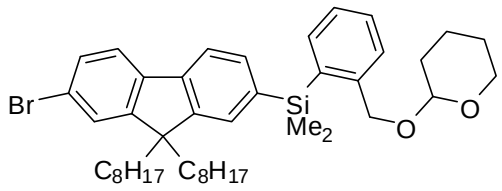
10'c

[2-(Acetoxymethyl)phenyl](3-bromo-9-ethyl-9*H*-carbazol-6-yl)dimethylsilane (10'c). To a solution of 3,6-dibromo-9-ethyl-9*H*-carbazole (7.0 g, 20 mmol) in THF (60 mL) was added a 1.6 M solution of *n*-BuLi in hexane (12.5 mL, 20 mmol) over 30 min at −78 °C, and the resulting mixture was stirred at −78 °C for 1 h. To this was added **3** (3.3 g, 20 mmol) at −78 °C. The resulting mixture was warmed slowly to rt, stirred overnight, and then quenched with a sat. NH_4Cl aq. solution at 0 °C. The aq. layer was extracted three times with diethyl ether (80 mL), and the combined organic layer was dried over anhydrous $MgSO_4$ before concentration in vacuo. The residue was purified by flash chromatography on silica gel to afford **10'c** (8.8 g, 92%) as a colorless viscous oil, R_f 0.44 (hexane–ethyl acetate = 5 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, *J* = 1.6 Hz, 1H), 8.14 (s, 1H), 7.62 (d, *J* = 7.3 Hz, 1H), 7.56 (d, *J* = 8.2 Hz, 1H), 7.51 (dd, *J* = 8.5, 1.8 Hz, 1H), 7.45–7.32 (m, 4H), 7.28–7.23 (m, 1H), 4.99 (s, 2H), 4.32 (q, *J* = 7.1 Hz, 2H), 1.84 (s, 3H), 1.41 (t, *J* = 7.1 Hz, 3H), 0.69 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.4, 141.2, 140.8, 138.3, 137.7, 135.7, 131.6, 129.6, 129.4, 128.2, 127.5, 127.3, 126.5, 124.4, 123.1, 121.8, 111.7, 109.8, 108.5, 66.6, 37.7, 20.9, 13.9, –0.4; IR (neat) 3055, 2974, 2897, 1732, 1622, 1589, 1474, 1435, 1379, 1346, 1286, 1275, 1232, 1157, 1128, 1097, 1024, 849, 802, 773, 756, 691, 635 cm^{-1}. Anal. Calcd. for $C_{25}H_{26}BrNO_2Si$: C, 62.49; H, 5.45. Found: C, 62.79; H, 5.44.



(2-Bromo-9,9'-dioctyl-9*H*-fluoren-7-yl)[2-(hydroxymethyl)phenyl]dimethylsilane.

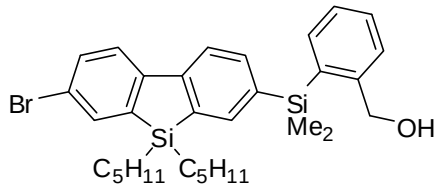
To a solution of 2,7-dibromo-9,9'-dioctyl-9*H*-fluorene (22 g, 40 mmol) in THF (120 mL) was added a 1.6 M solution of *n*-BuLi in hexane (25 mL, 40 mmol) over 30 min at −78 °C, and the resulting mixture was stirred at −78 °C for 1 h. To this was added **3** (6.6 g, 40 mmol) at −78 °C, and the resulting mixture was warmed slowly to rt, stirred overnight, and then quenched with a sat. NH_4Cl aq. solution at 0 °C. The aq. layer was extracted with diethyl ether, and the combined organic layer was dried over anhydrous $MgSO_4$. After concentration in vacuo, the residue was purified by flash chromatography on silica gel to afford the title compound (25 g, 100%) as a colorless viscous oil, R_f 0.25 (hexane–ethyl acetate = 10 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 7.5 Hz, 1H), 7.57–7.50 (m, 2H), 7.48–7.38 (m, 6H), 7.28 (td, *J* = 7.1, 2.0 Hz, 1H), 4.52 (d, *J* = 5.7 Hz, 2H), 1.97–1.80 (m, 4H), 1.30–0.94 (m, 21H), 0.83 (t, *J* = 7.1 Hz, 6H), 0.68–0.48 (m, 4H), 0.65 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.9, 149.6, 146.4, 141.0, 139.7, 137.8, 136.2, 135.5, 132.5, 129.81, 129.79, 128.1, 128.0, 126.9, 126.1, 121.2, 121.1, 119.3, 65.3, 55.4, 40.1, 31.9, 30.0, 29.28, 29.25, 23.8, 22.7, 14.2, –0.7; IR (neat): 3393, 3053, 2955, 2926, 2855, 1601, 1560, 1454, 1396, 1377, 1256, 1200, 1126, 1092, 1078, 1061, 1003, 876, 814, 777, 752, 689, 646 cm^{-1}. Anal. Calcd. for $C_{38}H_{53}BrOSi$: C, 72.01; H, 8.43. Found: C, 71.90; H, 8.39.



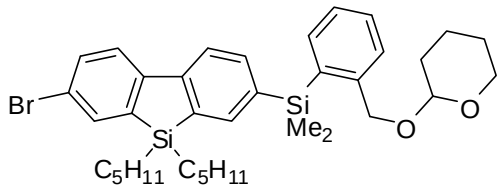
10d

(2-Bromo-9,9'-dioctyl-9*H*-fluoren-7-yl)dimethyl[2-(tetrahydro-2*H*-pyran-2-yloxy-methyl)phenyl]silane (10d). To a mixture of (2-bromo-9,9'-dioctyl-9*H*-7-fluorenyl)[2-(hydroxymethyl)phenyl]dimethylsilane (21 g, 32 mmol) and 3,4-dihydro-2*H*-pyran (3.3 g, 39 mmol) were added 2 drops of conc. HCl at rt, and the resulting mixture was stirred at rt overnight. The mixture was diluted with Et_2O, neutralized with $NaHCO_3$, dried over anhydrous $MgSO_4$, and filtered through a Celite pad. After concentration in vacuo, the residue was purified by flash chromatography on silica gel to afford **10d** (22 g, 95%) as a colorless viscous oil, R_f 0.34 (hexane–ethyl acetate = 20 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 7.3 Hz, 1H), 7.54 (d, *J* = 8.6 Hz, 1H), 7.50–7.35 (m, 7H),

7.26–7.20 (m, 1H), 4.66 (d, J = 12.1 Hz, 1H), 4.50 (t, J = 3.2 Hz, 1H), 4.40 (d, J = 12.1 Hz, 1H), 3.84–3.74 (m, 1H), 3.47–3.39 (m, 1H), 1.96–1.75 (m, 5H), 1.69–1.41 (m, 5H), 1.28–0.94 (m, 20H), 0.83 (t, J = 7.2 Hz, 6H), 0.68–0.52 (m, 4H), 0.63 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.0, 149.4, 144.0, 140.7, 139.8, 137.8, 136.4, 135.5, 132.7, 129.7, 129.4, 128.4, 128.2, 126.6, 126.1, 121.0, 119.1, 109.7, 97.6, 68.8, 61.9, 55.4, 40.1, 31.9, 30.6, 30.0, 29.31, 29.28, 25.6, 23.9, 22.7, 19.4, 14.2, –0.65, –0.73; IR (neat) 2926, 2853, 1452, 1258, 1200, 1119, 1092, 1078, 1055, 1026, 1003, 836, 814, 777, 752, 646 cm^{-1}. Anal. Calcd. for $C_{43}H_{61}BrO_2Si$; C, 71.94; H, 8.56. Found: C, 71.96; H, 8.73.

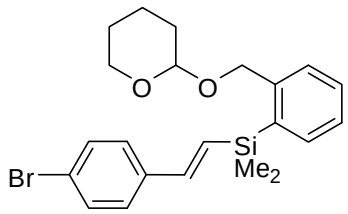


[2-(Hydroxymethyl)phenyl]dimethyl(2-bromo-9,9'-dipentyl-9*H*-9-silafluoren-7-yl)-silane. To a solution of 2,7-dibromo-9,9'-dioctyl-9*H*-9-silafluorene[25] (2.5 g, 5.2 mmol) in THF (16 mL) was added a 1.6 M solution of *n*-BuLi in hexane (3.3 mL, 5.2 mmol) over 30 min at –78 °C, and the resulting mixture was stirred at –78 °C for 1 h. To this was added **3** (0.85 g, 5.2 mmol) at –78 °C. The resulting mixture was warmed slowly to rt, stirred overnight, and the quenched with a sat. NH_4Cl aq. solution at 0 °C. The aq. layer was extracted with diethyl ether, and the combined organic layer was dried over anhydrous $MgSO_4$. After concentration in vacuo, the residue was purified by flash chromatography on silica gel to afford the title compound (1.79 g, 61%) as a viscous oil, R_f 0.32 (hexane–ethyl acetate = 5 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, J = 8.2 Hz, 2H), 7.63 (d, J = 8.4 Hz, 2H), 7.57–7.46 (m, 3H), 7.45–7.36 (m, 2H), 7.28 (t, J = 7.2 Hz, 1H), 4.53 (d, J = 7.5 Hz, 2H), 1.34–1.13 (m, 13H), 0.92–0.84 (m, 4H), 0.77 (t, J = 6.8 Hz, 6H), 0.61 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.1, 146.6, 146.4, 141.0, 138.6, 137.7, 136.8, 135.86, 135.83, 135.6, 135.4, 132.7, 129.8, 128.1, 126.9, 122.5, 122.0, 120.3, 65.4, 35.5, 23.6, 22.2, 14.1, 12.1, –0.8; IR (neat) 3377, 3057, 2955, 2922, 2870, 2856, 1582, 1458, 1443, 1379, 1366, 1250, 1113, 1076, 999, 837, 827, 775, 750, 646 cm^{-1}. Anal. Calcd. for $C_{31}H_{41}BrOSi_2$; C, 65.81; H, 7.30. Found: C, 65.94; H, 7.51.



10e

(2-Bromo-9,9'-dipentyl-9*H*-9-silafluoren-7-yl)dimethyl[2-(tetrahydro-2*H*-pyran-2-yloxymethyl)phenyl]silane (10e). To a solution of [2-(hydroxymethyl)phenyl]dimethyl(2-bromo-9,9'-dipentyl-9*H*-9-silafluoren-7-yl)silane (1.36 g, 2.4 mmol) and 3,4-dihydro-2*H*-pyran (0.4 g, 4.8 mmol) in Et_2O (2.4 mL) were added 2 drops of conc. HCl at rt, and the resulting mixture was stirred at rt overnight. The mixture was diluted with Et_2O, neutralized with $NaHCO_3$, dried over anhydrous $MgSO_4$, and filtered through a Celite pad. After concentration in vacuo, the residue was purified by flash chromatography on silica gel to afford **10e** (1.47 g, 94%) as a colorless oil, R_f 0.35 (hexane–ethyl acetate = 20 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75–7.62 (m, 4H), 7.57–7.44 (m, 4H), 7.39 (t, *J* = 7.4 Hz, 1H), 7.30–7.22 (m, 1H), 4.67 (d, *J* = 12.1 Hz, 1H), 4.47 (t, *J* = 3.2 Hz, 1H), .4.41 (d, *J* = 12.1 Hz, 1H), 3.80–3.70 (m, 1H), 3.44–3.25 (m, 1H), 1.84–1.70 (m, 1H), 1.66–1.02 (m, 17H), 0.95–0.85 (m, 6H), 0.84–0.74 (m, 4H), 0.620 (s, 3H), 0.617 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.8, 146.8, 144.0, 141.1, 138.7, 137.8, 136.4, 136.1, 136.0, 135.6, 135.4, 132.7, 129.5, 128.5, 126.7, 122.4, 121.9, 120.0, 97.7 68.8, 61.9, 35.6, 30.6, 25.5, 23.6, 22.2, 19.4, 14.1, 12.2, –0.7, –0.8; IR (neat) 2955, 2922, 2870, 2856, 1441, 1250, 1200, 1115, 1078, 1026, 837, 816, 775, 750 cm^{-1}. Anal. Calcd. for $C_{36}H_{49}BrO_2Si_2$; C, 66.54; H, 7.60. Found: C, 66.39; H, 7.42.

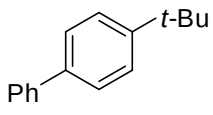


10f

(*E*)-2-[(4-Bromophenyl)ethenyl][2-(tetrahydro-2*H*-pyran-2-yloxymethyl)phenyl]dimethylsilane (10f). To a solution of dimethyl[2-tetrahydro-2*H*-pyran-2-yloxymethyl)-phenyl]silane (0.79 g, 3.2 mmol) and 1-bromo-4-ethynylbenzene (0.54 g, 3.0 mmol) in hexane (0.3 mL) were slowly added a 10% hexane solution of *t*-Bu_3P (6.1 mg, 3 μmol) and a 0.01 M hexane solution of platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane

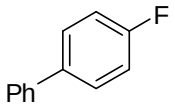
complex (0.3 mL, 3 μmol) at –40 °C for 30 min. The resulting mixture was stirred at the same temperature for further 30 min and then at rt for 3 h, filtered through a Florisil pad. After concentration in vacuo followed by flash chromatography gave **10f** (1.23 g, 95%) as a yellow oil, R_f 0.13 (hexane–ethyl acetate = 30 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (dd, *J* = 7.4, 1.4 Hz, 1H), 7.50 (d, *J* = 7.5 Hz, 1 H), 7.47–7.37 (m, 3H), 7.32–7.27 (m, 3H), 6.86 (d, *J* = 19.0 Hz, 1H), 6.65 (d, *J* = 19.0 Hz, 1H), 4.86 (d, *J* = 12.1 Hz, 1H), 4.65 (t, *J* = 3.6 Hz, 1H), 4.59 (d, *J* = 11.9 Hz, 1H), 3.98–3.82 (m, 1H), 3.52–3.42 (m, 1H), 1.91–1.77 (m, 1H), 1.76–1.43 (m, 5H), 0.50 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.8, 143.3, 137.0, 136.3, 134.9, 131.4, 129.4, 128.9, 128.4, 127.8, 126.8, 121.8, 97.9, 68.9, 62.2, 30.7, 25.6, 19.5, –1.1, –1.2; IR (neat) 2947, 2870, 1603, 1485, 1439, 1396, 1350, 1248, 1200, 1117, 1074, 1026, 1009, 988, 961, 907, 845, 818, 785, 752 cm^{-1}. Anal. Calcd. for $C_{22}H_{27}BrO_2Si$; C, 61.25; H, 6.31. Found: C, 61.52 ; H, 6.32.

4.2 Cross-coupling reaction of 1 with aryl bromides. *A general procedure.* To a mixture of **1** (1.2–1.5 mmol), K_2CO_3 (0.35 g, 2.5 mmol), [(η^3-allyl)PdCl]$_2$ (1.8 mg, 5.0 μmol), RuPhos (9.8 mg, 21 μmol), and CuI (5.7 mg, 30 μmol) in DMF (0.8 mL) and THF (2.2 mL) was added **4** (1.0 mmol), and the resulting mixture was stirred at 75 °C. After the time specified in Tables 2 and 3, the mixture was filtered through a Florisil pad, diluted with Et_2O, washed with water and then with brine, and dried over anhydrous $MgSO_4$. Concentration in vacuo followed by flash chromatography on silica gel afforded the corresponding coupled product in a yield listed in Table 2. The spectra of the biaryls shown in entries 1–10, 13, 15, and 17–22 of Table 2 agreed well with those reported previously.



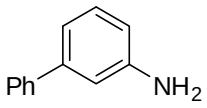
2ac

4-*t*-Butylbiphenyl (2ac).[26] A colorless solid, mp 49.5–50.5 °C, R_f 0.38 (hexane–ethyl acetate = 100 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63–7.53 (m, 4H), 7.51–7.41 (m, 4H), 7.34 (tt, *J* = 6.6, 1.3 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.1, 140.9, 138.2, 128.5, 126.9, 126.8, 126.6, 125.6, 34.6, 31.5.



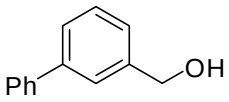
2aj

3-(*t*-Butyldimethylsiloxymethyl)biphenyl (2aj).[27] A colorless solid, mp 73.2–73.8 °C, R_f 0.39 (hexane–ethyl acetate = 100 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58–7.52 (m, 4H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.35 (tt, *J* = 6.6, 1.3 Hz, 1H), 7.13 (t, *J* = 8.8 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.2 (*J* = 245.5 Hz), 140.1, 137.1, 128.7, 128.6, 128.5, 127.1, 126.9, 115.5 (*J* = 20.7 Hz).



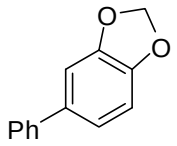
2al

3-Aminobiphenyl (2al).[28] A off-white solid, mp 29.5–30.6 °C, R_f 0.19 (hexane–ethyl acetate = 5 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58–7.54 (m, 2H), 7.45–7.39 (m, 2H), 7.33 (tt, *J* = 6.6, 1.4 Hz, 1H), 7.23 (t, *J* = 7.8 Hz, 1H), 7.00 (ddd, *J* = 4.5, 1.6, 0.9 Hz, 1H), 6.92 (t, *J* = 2.0 Hz, 1H), 6.92 (ddd, *J* = 7.9, 2.4, 0.9 Hz, 1H), 3.75 (br s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.5, 142.2, 141.2, 129.5, 128.5, 127.1, 127.0, 117.6, 114.0, 113.8.



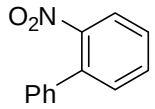
2ao

3-(Hydroxymethyl)biphenyl (2ao).[29] A colorless solid, mp 49.1–49.9 °C, R_f 0.23 (hexane–ethyl acetate = 3 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63–7.58 (m, 3H), 7.54 (dt, *J* = 7.7, 1.5 Hz, 1H), 7.48–7.42 (m, 3H), 7.39–7.33 (m, 2H), 4.78 (s, 2H), 1.77 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.4, 141.2, 140.8, 128.9, 128.6, 127.2, 127.0, 126.4, 125.72, 125.66, 65.4; IR (KBr) 3381, 3302, 3061, 3034, 2883, 1479, 1454, 1421, 1348, 1186, 1028, 1009, 901, 756, 721, 700, 617 cm^{-1}; MS (EI) *m*/*z* (%) 185 (13), 184 (M^+, 100), 168 (1), 167 (7), 154 (7), 153 (14), 78 (4), 77 (8); HRMS (EI) Calcd. for $C_{13}H_{12}O$: M^+, 184.0888, Found: *m*/*z* 184.0889.



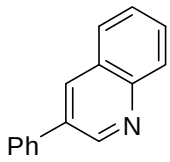
2ap

3,4-Methylenedioxybiphenyl (2aq).[30] A colorless oil, R_f 0.38 (hexane–ethyl acetate = 20 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54–7.50 (m, 2H), 7.44–7.38 (m, 2H), 7.31 (tt, *J* = 6.6, 1.3 Hz, 1H), 7.09–7.05 (m, 2H), 6.91–6.87 (m, 1H), 6.00 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.1, 147.0, 140.9, 135.6, 128.7, 126.91, 126.87, 120.6, 108.6, 107.7, 101.1.



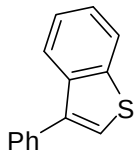
2aq

2-Nitrobiphenyl (2aq).[31] A pale yellow solid, mp 37.3–38.0 °C, R_f 0.31 (hexane–ethyl acetate = 10 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.1 Hz, 1H), 7.62 (t, *J* = 7.5 Hz, 1H), 7.52–7.48 (m, 5H), 7.32–7.29 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ. 149.5, 137.4, 136.3, 132.3, 131.9, 128.7, 128.2, 128.1, 127.9, 124.1.



2au

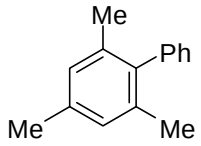
3-Phenylquinoline (2au).[32] A colorless oil, R_f 0.38 (hexane–ethyl acetate = 2 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.20 (d, *J* = 1.2 Hz, 1H), 8.32 (d, *J* = 2.2 Hz, 1H), 8.15 (d, *J* = 8.4 Hz, 1H), 7.90 (d, *J* = 8.1 Hz, 1H), 7.76–7.70 (m, 3H), 7.62–7.51 (m, 3H), 7.45 (tt, *J* = 6.8, 1.3 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.7, 147.1, 137.7, 133.1, 129.2, 129.08, 129.03, 128.0, 127.9, 127.3, 126.9.



2av

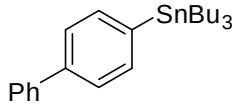
3-Phenyl-1-benzothiophene (2av).[33] A colorless oil, R_f 0.51 (hexane–ethyl acetate =

20 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96–7.90 (m, 2H), 7.63–7.58 (m, 2H), 7.53–7.47 (m, 2H), 7.45–7.37 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.5, 137.9, 137.7, 135.8, 128.6, 127.4, 124.3, 124.2, 123.3, 122.8.



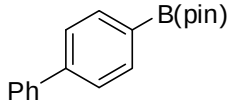
2gy

2,4,6-Trimethylbiphenyl (2gy).[34] A colorless oil, R_f 0.22 (hexane–ethyl acetate = 50 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45–7.39 (m, 2H), 7.33 (tt, *J* = 6.6, 1.3 Hz, 2H), 7.17–7.12 (m, 2H), 2.34 (s, 3H), 2.01 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.1, 139.0, 136.5, 136.0, 129.3, 128.3, 128.0, 126.5, 21.0, 20.7.



2aw

4-Tributylstannylbiphenyl (2aw). A colorless oil, R_f 0.35 (hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63–7.41 (m, 8H), 7.37–7.30 (m, 1H), 1.68–1.47 (m, 6H), 1.35 (sext, *J* = 7.3 Hz, 6H), 1.18–1.00 (m, 6H), 0.91 (t, *J* = 7.3 Hz, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.3, 140.9, 140.7, 136.9, 128.7, 127.15, 127.09, 126.6, 29.1, 27.4, 13.7, 9.6; IR (neat) 2955, 2922, 2870, 2851, 1481, 1458, 1377, 1076, 1007, 822, 756, 696 cm^{-1}; MS (EI) *m*/*z* (%) 444 (M^+, 0.5), 442 (0.3), 440 (0.2), 387 (100), 385 (77), 383 (42) . Anal. Calcd. for $C_{24}H_{36}Sn$: C, 65.03; H, 8.19. Found: C, 65.29; H, 8.11.



2ax

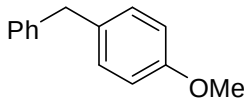
4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-1,1'-biphenyl (2ax). A colorless oil, R_f 0.23 (hexane–ethyl acetate = 20 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93–7.88 (m, 2H), 7.66–7.60 (m, 4H), 7.48–7.43 (m, 2H), 7.39–7.34 (m, 1H), 1.39 (s, 12H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.7, 140.8, 135.1, 128.6, 127.4, 127.1, 126.3, 83.8, 25.0; IR (neat) 2978, 2928, 1609, 1398, 1362, 1321, 1144, 1092, 962, 860, 768, 735, 696, 658

cm^{-1}; MS (EI) *m*/*z* (%) 281 (71), 280 (M+, 100), 279 (78), 266 (21), 265 (80), 264 (25) . Anal. Calcd. for $C_{18}H_{21}BO_2$: C, 77.17; H, 7.55. Found: C, 77.41; H, 7.27.

Cross-coupling reaction of 1a and 1' with 4-acetylphenyl chloride (5d). To a mixture of **1a** (0.22 g, 0.75 mmol), **1'** (0.182 g, 0.75 mmol), K_2CO_3 (0.35 g, 2.5 mmol), [(η^3-allyl)PdCl]$_2$ (1.8 mg, 5.0 μmol), RuPhos (9.8 mg, 21 μmol), and CuI (5.7 mg, 30 μmol) in DMF (0.8 mL) and THF (2.2 mL) was added **5d** (1.0 mmol), and the resulting mixture was stirred at 50 °C for 2 h. Remained amount of **1a**, **1'**, and **5d** and produced amount of **2ah**, **3**, and **3'** were estimated by ^{1}H NMR analysis and listed in Eq. 2.

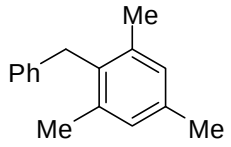
4.3 Cross-coupling reaction of 1a and 1h with allylic and benzylic carbonates

Palladium-catalyzed cross-coupling reaction of 1a and 1h with arylmethyl methyl carbonates 6. *A general procedure.* A solution of Cp(allyl)Pd (28 mg, 50 μmol) and dppf (6.1 mg, 50 μmol) in THF (1.0 mL) were added an organosilane **1** (1.00 mmol) and an arylmethyl methyl carbonate **6** (1.00 mmol) sequentially, and the resulting mixture was stirred at 80 °C in a sealed tube. After the time specified in Table 5, the mixture was filtered through a silica gel pad and concentrated in vacuo. The residue was purified by flash chromatography on silica gel to afford the corresponding adduct **7** in a yield listed in Table 5.



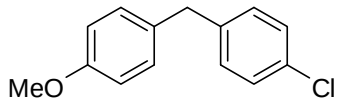
7aa

1-Benzyl-4-methoxybenzene (7aa).[35] A colorless oil, R_f 0.33 (hexane–ethyl acetate = 30 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30–7.12 (m, 5H), 7.09 (d, *J* = 8.8 Hz, 2H), 6.81 (d, *J* = 8.6 Hz, 2H), 3.92 (s, 2H), 3.77 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.7, 141.4, 133.1, 129.7, 128.7, 128.3, 125.8, 113.8, 55.3, 41.1.



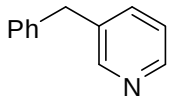
7ab

1-Benzyl-2,4,6-trimethylbenzene (7ab).[36] A colorless oil, R_f 0.36 (hexane–ethyl acetate = 30 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (d, *J* = 8.4 Hz, 2H), 7.11–7.03 (m, 4H), 6.82 (d, *J* = 8.6 Hz, 2H), 3.87 (s, 2H), 3.77 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.9, 139.9, 132.5, 131.6, 129.98, 129.66, 128.4, 113.8, 55.3, 40.4.



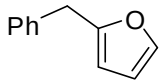
7hc

1-Chrolo-4-(4-methoxyphenylmethyl)benzene (7hc).[35] A pale yellow oil, R_f 0.62 (hexane–ethyl acetate = 30 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25–7.17 (m, 2H), 7.16–7.10 (m, 1H), 7.00 (d, *J* = 7.1 Hz, 2H), 6.87 (s, 2H), 4.00 (s, 2H), 2.35 (s, 3H), 2.28 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.9, 136.9, 135.5, 133.6, 128.7, 128.2, 127.7, 125.5, 34.8, 21.0, 20.3.



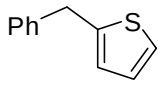
7ad

3-Benzylpyridine (7ad).[37] A pale yellow oil, R_f 0.27 (hexane–ethyl acetate = 2 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (d, *J* = 1.8 Hz, 1H), 8.44 (dd, *J* = 4.8, 1.6 Hz, 1H), 7.48–7.42 (m, 1H), 7.33–7.26 (m, 2H), 7.24–7.14 (m, 3H), 3.97 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.0, 147.4, 139.6, 136.3, 136.2, 128.7, 128.5, 126.3, 123.3, 39.1.



7ae

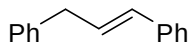
2-Benzylfuran (7ae).[38] A colorless oil, R_f 0.33 (hexane–ethyl acetate = 30 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33–7.18 (m, 6H), 6.27 (dd, *J* = 2.7, 1.8 Hz, 1H), 5.99 (d, *J* = 3.1 Hz, 1H), 3.96 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.4, 141.3, 138.0, 128.6, 128.4, 126.3, 110.1, 106.1, 34.6.



7af

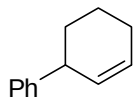
2-Benzylthiophene (7af). A yellow oil, R_f 0.54 (hexane–ethyl acetate = 30 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32–7.21 (m, 5H), 7.13 (dd, *J* = 5.1, 1.1 Hz, 1H), 6.91 (dd, *J* = 5.2, 3.4 Hz, 1H), 6.80–6.77 (m, 1H), 4.15 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.7, 140.0, 128.3, 128.2, 126.5, 126.2, 124.8, 123.6, 35.9; IR (neat) 3063, 3028, 2907, 1603, 1495, 1452, 1437, 1074, 1038, 1030, 851, 739, 696 cm^{-1}. Anal. Calcd. for $C_{11}H_{10}S$; C, 75.82; H, 5.78. Found: C, 75.58; H, 6.02.

Palladium-catalyzed cross-coupling reaction of 1a with methyl allyl carbonates 8. *A general procedure.* A solution of $Pd_2(dba)_3$ (4.6 mg, 5.0 μmol) and tri(2-thienyl)phosphine (5.6 mg, 20 μmol) in THF (2.0 mL) were added an organosilane **1** (1.00 mmol) and a methyl allyl carbonate (1.00 mmol) sequentially, and the resulting mixture was stirred at 50 °C. After the time specified in Eqs. 3 and 4, the mixture was filtered through a silica gel pad, and the filtrate was concentrated in vacuo. The resulting residue was purified by flash chromatography on silica gel to afford the corresponding adduct **9**.



9a

(*E*)-1,3-Diphenylpropene (9a).[39] A colorless oil, R_f 0.50 (hexane–ethyl acetate = 50 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38–7.17 (m, 10H), 6.46 (d, J = 15.9 Hz, 1H), 6.36 (dt, *J* = 15.7, 6.4 Hz, 1H), 3.55 (d, *J* = 6.6 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.2, 137.5, 131.1, 129.2, 128.7, 128.5, 127.1, 126.2, 126.1, 39.3.

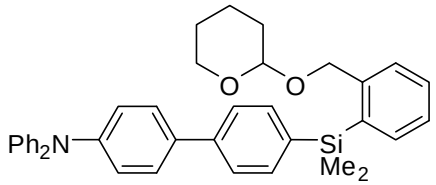


9b

3-Phenylcyclohexene (9b).[39] A pale yellow oil, R_f 0.50 (hexane). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32–7.15 (m, 5H), 5.93–5.84 (m, 1H), 5.76–5.67 (m, 1H), 3.45–3.34 (m, 1H), 2.18–1.96 (m, 3H), 1.81–1.49 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.5, 130.0, 128.0, 128.1, 127.6, 125.8, 41.9, 32.7, 25.1, 21.3.

4.4 Cross-coupling reaction of 1i with bromoaryl- and bromoheteroaryl [2-(alkoxymethyl)phenyl]dimethylsilanes (10). *A general procedure.* To a mixture of **1i** (1.2–1.5 mmol), K_2CO_3 (0.35 g, 2.5 mmol), [(η^3-allyl)PdCl]$_2$ (1.8 mg, 5.0 μmol), RuPhos (9.8 mg, 21 μmol), and CuI (5.7 mg, 30 μmol) in DMF (0.8 mL) and THF (2.2 mL) was added **10** (1.0 mmol), and the resulting mixture was stirred at 75 °C. After the time specified in Table 6, the mixture was filtered through a Florisil pad, diluted with Et_2O, washed with water and then with brine, and dried over anhydrous $MgSO_4$. Concentration in vacuo followed by flash chromatography on silica gel afforded the corresponding coupling product **11** in a yield listed in Table 6.

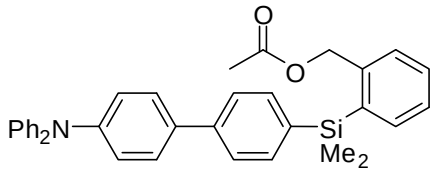
Gram-scale Cross-coupling reaction of 1i with 10a. To a solution of **1i** (4.9 g, 12 mmol), K_2CO_3 (3.5 g, 2.5 mmol), [(η^3-allyl)PdCl]$_2$ (18 mg, 50 μmol), RuPhos (98 mg, 0.21 mmol), and CuI (57 mg, 0.30 mmol) in DMF (8 mL) and THF (22 mL) was added **10a** (4.1 g, 10 mmol), and the resulting mixture was stirred at 75 °C for 7 h. The mixture was filtered through a Florisil pad, diluted with Et_2O, washed with water for 5 times and brine, and dried over anhydrous $MgSO_4$. Concentration in vacuo followed by distillation under vacuum (3.0 mmHg) gave cyclic silyl ether **3** (1.50 g, 86% based on consumed **1i**). The residue was further purified by flash chromatography on silica gel (hexane–ethyl acetate = 20 : 1 → 10 : 1 → 2 : 1 as eluents) to give **11ia** (5.0 g, 88%) and unreacted **1i** (0.58 g, 12%).



11ia

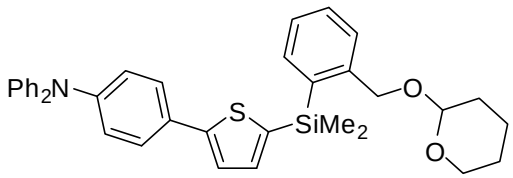
4-(Diphenylamino)-4'-([2-(tetrahydro-2*H*-pyran-2-yloxymethyl)phenyl]dimethylsilyl)biphenyl (11ia). A colorless solid, mp 52.6–53.5 °C, R_f 0.18 (hexane–ethyl acetate = 15 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58–7.37 (m, 8H), 7.34–7.20 (m, 6H), 7.16–7.07 (m, 6H), 7.02 (t, *J* = 7.3 Hz, 2H), 4.68 (d, *J* = 11.9 Hz, 1H), 4.46–4.37 (m, 2H), 3.80–3.70 (m, 1H), 3.45–3.35 (m, 1H), 1.84–1.69 (m, 1H), 1.66–1.38 (m, 5H), 0.62 (s, 3H), 0.61 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.4, 147.1, 144.0, 141.0,

136.9, 136.0, 135.4, 134.7, 134.4, 129.5, 129.1, 128.4, 127.6, 126.7, 125.9, 124.4, 123.6, 122.8, 97.8, 68.8, 62.0, 30.6, 25.5, 19.4, –0.7, –0.8; IR (KBr): 3470, 2945, 1589, 1489, 1325, 1277, 1115, 1026, 835, 812, 775, 754, 696, 521 cm^{-1}. Anal. Calcd. for $C_{38}H_{39}NO_2Si$: C, 80.10; H, 6.90. Found: C, 80.07; H, 6.80.



11'ia

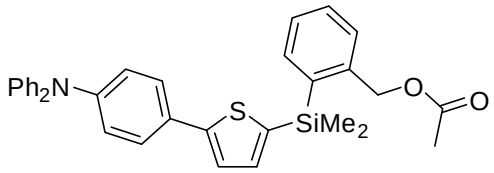
4-{[2-Acetoxymethyl)phenyl]dimethylsilyl}-4'-(diphenylamino)biphenyl (11'ia). A colorless solid, mp 43.4–45.3 °C, R_f 0.26 (hexane–ethyl acetate = 5 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 7.1 Hz, 1H), 7.56–7.31 (m, 9H), 7.29–7.21 (m, 4H), 7.17–7.08 (m, 6H), 7.02 (t, *J* = 7.3 Hz, 2H), 5.00 (s, 2H), 1.91 (s, 3H), 0.63 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.4, 147.4, 147.2, 141.1, 137.2, 136.4, 135.6, 134.5, 134.3, 129.7, 129.5, 129.1, 127.58, 127.56, 126.0, 124.4, 123.6, 122.9, 66.7, 21.0, –0.8; IR (KBr): 3456, 3057, 3032, 2955, 1736, 1589, 1518, 1489, 1379, 1327, 1317, 1277, 1250, 1234, 1113, 1026, 835, 810, 775, 754, 696, 521 cm^{-1}. Anal. Calcd. for $C_{35}H_{33}NO_2Si$: C, 79.66; H, 6.30. Found: C, 79.48; H, 6.27.



11ib

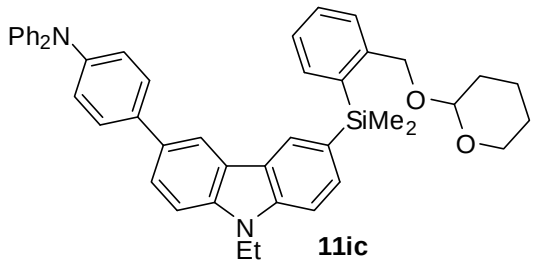
2-{Dimethyl[2-(tetrahydro-2*H*-pyran-2-yloxymethyl)phenyl]silyl}-5-[4-(diphenylamino)phenyl]thiophene (11ib). A pale yellow viscous oil, R_f 0.13 (hexane–ethyl acetate = 20 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (dd, *J* = 7.3, 1.1 Hz, 1H), 7.53–7.43 (m, 3H), 7.41 (td, *J* = 7.5, 1.3 Hz, 1H), 7.31–7.22 (m, 6H), 7.18 (d, *J* = 3.5 Hz, 1H), 7.14–7.08 (m, 4H), 7.07–6.99 (m, 4H), 4.78 (d, *J* = 11.9 Hz, 1H), 4.58 (t, *J* = 3.6 Hz, 1H), 4.53 (d, *J* = 12.1 Hz, 1H), 3.88–3.79 (m, 1H), 3.54–3.42 (m, 1H), 1.90–1.76 (m, 1H), 1.73–1.44 (m, 5H), 0.67 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.0, 147.3, 147.1, 143.9, 137.2, 136.3, 135.7, 135.2, 129.7, 129.1, 128.5, 128.3, 126.8, 126.6, 124.3,

123.54, 123.45, 122.9, 97.8, 68.8, 62.1, 30.6, 25.6, 19.5, 0.3, 0.2; IR (neat) 3055, 2941, 2868,1589, 1529, 1489, 1431, 1327, 1313, 1277, 1277, 1200, 1117, 1076, 1026, 955, 949, 835, 810, 773, 752, 731, 696 cm^{-1}. HRMS (FAB^+) Calcd. for $C_{36}H_{37}BrNO_2SSi$: M^+ 575.2314, Found 575.2327.



11'ib

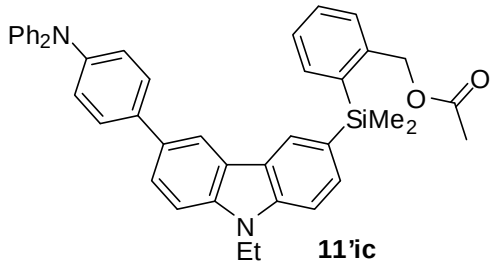
2-{[2-(Acetoxymethyl)phenyl]dimethylsilyl}-5-[4-(diphenylamino)phenyl]thiophene (11'ib). A pale yellow viscous oil, R_f 0.13 (hexane–ethyl acetate = 20 : 1). ^1H NMR (400 MHz, $CDCl_3$) δ 7.61 (dd, *J* = 7.4, 0.8 Hz, 1H), 7.59–7.37 (m, 5H), 7.34 (td, *J* = 7.1, 1.9 Hz, 1H), 7.29-7.22 (m, 5H), 7.18 (d, *J* = 3.5 Hz, 1H), 7.13–7.08 (m, 4H), 7.06–7.00 (m, 4H), 5.10 (s, 2H), 2.02 (s, 3H), 0.68 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.5, 150.3, 147.3, 147.1, 141.1, 136.7, 136.6, 136.3, 135.4, 129.9, 129.5, 129.1, 128.2, 127.6, 126.6, 124.4, 123.5, 122.9, 66.6, 21.1. 0.2; IR (neat) 3057, 3034, 2961, 1738, 1591, 1529, 1495, 1433, 1327, 1315, 1279, 1259, 1234, 1078, 1026, 995, 951, 835, 808, 779, 754, 696 cm^{-1}. HRMS (EI) Calcd. for $C_{33}H_{31}NO_2SSi_2$: M^+, 533.1845. Found: *m*/*z* 533.1846.



11ic

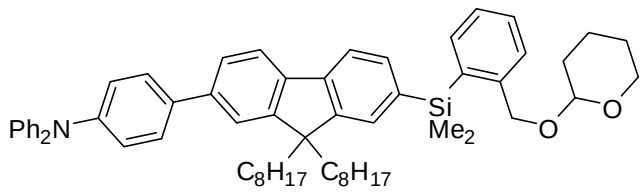
6-[4-(Diphenylamino)phenyl]-3-{[2-(tetrahydro-2*H*-pyran-2-yloxymethyl)phenyl]-dimethylsilyl}-9-ethyl-9*H*-carbazole (11ic). A pale yellow viscous oil, R_f 0.42 (hexane–ethyl acetate = 10 : 1). ^1H NMR (400 MHz, $CDCl_3$) δ 8.27 (s, 1H), 8.25 (d, *J* = 1.1 Hz, 1H), 7.67 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.61–7.53 (m, 4H), 7.49 (d, *J* = 7.5 Hz, 1H), 7.46–7.35 (m, 3H), 7.32–7.22 (m, 5H), 7.20–7.11 (m, 6H), 7.01 (t, *J* = 7.3 Hz, 2H), 4.69 (d, *J* = 12.1 Hz, 1H), 4.46–4.32 (m, 4H), 3.74–3.65 (m, 1H), 3.35–3.27 (m, 1H),

1.80–1.67 (m, 1H), 1.62–1.23 (m, 8H), 0.688 (s, 3H), 0.685 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.6, 146.1, 144.0, 140.9, 139.0, 136.9, 136.4, 135.5, 131.9, 131.3, 129.4, 129.1, 128.4, 127.8, 127.2, 126.6, 126.3, 124.7, 124.4, 124.0, 123.2, 122.8, 122.5, 118.5, 108.5, 108.2, 97.8, 68.9, 62.0, 37.7, 30.6, 25.5, 19.4, 14.0, –0.3, –0.4; IR (neat): 2947, 2870, 1593, 1479, 1275, 1232, 1128, 1117, 1078, 1026, 837, 806, 752, 696 cm^{-1}. Anal. Calcd. for $C_{46}H_{46}N_2O_2Si$: C, 80.43; H, 6.75. Found: C, 80.20; H, 6.77.



11'ic

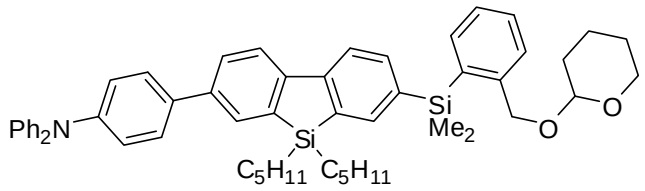
3-{[2-(Acetoxymethyl)phenyl]dimethylsilyl}-6-[(4-diphenylamino)phenyl]-9-ethyl-9*H*-carbazole (11'ic). A colorless solid, mp 75.3–76.4 °C, R_f 0.29 (hexane–ethyl acetate = 5 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (d, *J* = 1.5 Hz, 1H), 8.24 (s, 1H), 7.67 (dd, *J* = 8.5, 1.7 Hz, 1H), 7.63 (dd, *J* = 7.2, 1.0 Hz, 1H), 7.60–7.52 (m, 3H), 7.45–7.31 (m, 5H), 7.30–7.22 (m, 4H), 7.19–7.11 (m, 6H), 7.01 (tt, *J* = 7.2, 1.1 Hz, 2H), 5.01 (s, 2H), 4.37 (q, *J* = 7.1 Hz, 2H), 1.84 (s, 3H), 1.45 (t, *J* = 7.2 Hz, 3H), 0.70 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.4, 147.6, 146.1, 141.2, 141.0, 139.0, 138.0, 136.3, 135.7, 132.0, 131.1, 129.5, 129.4, 129.1, 127.8, 127.5, 126.7, 126.3, 124.8, 124.4, 124.0, 123.1, 122.9, 122.5, 118.5, 108.5, 108.3, 66.7, 37.7, 21.0, 14.0, –0.4; IR (KBr): 3452, 1736, 1591, 1479, 1277, 1232, 837, 806, 754, 696 cm^{-1}. Anal. Calcd. for $C_{43}H_{40}N_2O_2Si$: C, 80.09; H, 6.25. Found: C, 80.07; H, 6.34.



11id

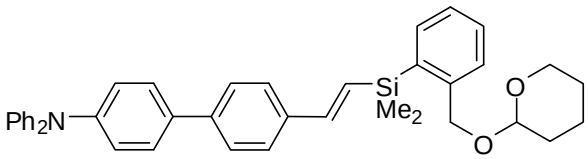
7-[(4-Diphenylamino)phenyl]-2-{[2-(tetrahydro-2*H*-pyran-2-yloxymethyl)phenyl]-dimethylsilyl}-9,9'-dioctyl-9*H*-fluorene (11id). A pale yellow viscous oil, R_f 0.22 (hexane–ethyl acetate = 9 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 7.7 Hz, 1H),

7.66 (d, *J* = 7.5 Hz, 1H), 7.57–7.42 (m, 8H), 7.38 (t, *J* = 7.5 Hz, 1H), 7.30–7.20 (m, 5H), 7.14 (t, *J* = 7.4 Hz, 6H), 7.02 (t, *J* = 7.3 Hz, 2H), 4.68 (d, *J* = 12.1 Hz, 1H), 4.51 (t, *J* = 3.4 Hz, 1H), 4.43 (d, *J* = 12.1 Hz, 1H), 3.86–3.74 (m, 1H), 3.48–3.39 (m, 1H), 2.00–1.75 (m, 5H), 1.70–1.40 (m, 5H), 1.34–0.93 (m, 20H), 0.81 (t, *J* = 7.2 Hz, 6H), 0.74–0.58 (m, 10H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.4, 145.0, 147.5, 146.9, 144.0, 141.6, 139.7, 139.5, 137.0, 136.7, 135.52, 135.47, 132.6, 129.4, 129.1, 128.4, 128.1, 127.6, 126.6, 125.3, 124.2, 123.9, 122.8, 120.8, 119.9, 119.0, 97.6, 68.8, 61.9, 55.1, 40.3, 31.9, 30.6, 30.1, 29.34, 29.31, 25.6, 24.0, 22.7, 19.4, 14.2, –0.6, –0.7; IR (KBr): 3458, 2926, 2853, 1591, 1514, 1493, 1464, 1281, 1028, 837, 816, 752, 696 cm^{-1}. Anal. Calcd. for $C_{61}H_{75}NO_2Si$: C, 83.04; H, 8.57. Found: C, 83.14; H, 8.55.



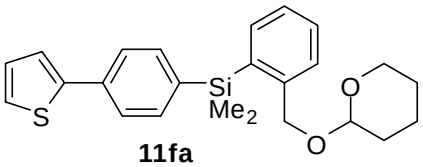
11ie

7-[4-(Diphenylamino)phenyl]-2-{[2-(tetrahydro-2*H*-pyran-2-yloxymethyl)phenyl]-dimethylsilyl}-9,9'-dipentyl-9*H*-9-silafluorene (11ie). A pale yellow viscous liquid, R_f 0.27 (hexane–ethyl acetate = 10 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.1 Hz, 1H), 7.81-7.71 (m, 1H), 7.61 (dd, *J* = 8.1, 1.3 Hz, 1H), 7.57–7.46 (m, 1H), 7.39 (t, *J* = 7.4 Hz, 1H), 7.31–7.21 (m, 5H), 7.18–7.09 (m, 6H), 7.02 (t, *J* = 7.2 Hz, 2H), 4.69 (d, *J* = 12.1 Hz, 1H), 4.48 (t, *J* = 3.4 Hz, 1H), 4.43 (d, *J* = 11.9 Hz, 1H), 3.82–3.71 (m, 1H), 3.46–3.36 (m, 1H), 1.85–1.72 (m, 1H), 1.67–1.16 (m, 17H), 0.98–0.89 (m, 4H), 0.85–0.75 (m, 6H), 0.630 (s, 3H), 0.626 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.9, 147.8, 147.2, 147.1, 144.3, 139.6, 139.01, 139.03, 137.33, 137.30, 136.6, 136.2, 135.8, 135.4, 131.5, 129.7, 129.4, 128.7, 128.6, 127.8, 127.0, 124.5, 124.2, 123.1, 121.4, 120.4, 98.0, 69.1, 62.3, 35.9, 30.9, 25.9, 24.0, 22.6, 19.7, 14.4, 12.7, –0.3, –0.4; IR (KBr): 3450, 2953, 2922, 2870, 2855, 1591, 1510, 1493, 1452, 1325, 1279, 1117, 1076, 1026, 837, 816, 752, 696, 498 cm^{-1}. Anal. Calcd. for $C_{54}H_{63}NO_2Si_2$: C, 79.65; H, 7.80. Found: C, 79.65; H, 7.80.



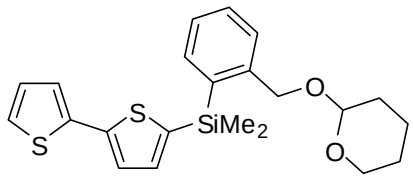
11if

(*E*)-4-(Diphenylamino)-4'-[2-{[2-(tetrahydro-2*H*-pyran-2-yloxymethyl)phenyl]dimethylsilyl}ethenyl]biphenyl (11if). A yellow solid, mp 47.0–49.2 °C, R_f 0.21 (hexane–ethyl acetate = 10 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 7.3 Hz, 1H), 7.57–7.44 (m, 7H), 7.40 (td, *J* = 7.5, 1.4 Hz, 1H), 7.33–7.22 (m, 5H), 7.16–7.08 (m, 6H), 7.03 (t, *J* = 7.3 Hz, 2H), 6.96 (d, *J* =19.0 Hz, 1H) , 6.68 (d, *J* =19.0 Hz, 1H), 4.88 (d, *J* = 11.9 Hz, 1H), 4.67 (t, *J* = 3.5 Hz, 1H), 4.63 (d, *J* = 11.9 Hz, 1H), 3.94–3.84 (m, 1H), 3.53–3.43 (m, 1H), 1.90–1.78 (m, 1H) 1.75–1.43 (m, 5H), 0.51 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.4, 147.1, 144.2, 143.8, 140.1, 136.63, 136.60, 134.9, 134.3, 129.4, 129.1, 128.4, 127.5, 127.4, 126.81, 126.76, 126.5, 124.3, 123.7, 122.8, 97.9, 68.9, 62.2, 30.7, 25.6, 19.5, –1.0, –1.1; IR (KBr) 3055, 3032, 2943, 2868, 1589, 1489, 1325, 1277, 1200, 1180, 1117, 1076, 1024, 988, 905, 818, 752, 694 cm^{-1}. HRMS (EI) Calcd. for $C_{40}H_{41}NO_2Si$: M^+, 595.2907. Found: *m*/*z* 595.2902.



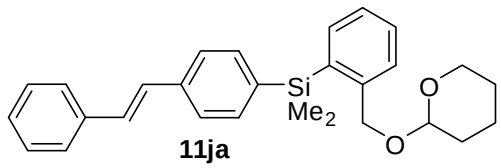
11fa

Dimethyl[2-(tetrahydro-2*H*-pyran-2-yloxymethyl)phenyl][4-(2-thienyl)phenyl]silane (11fa). A pale yellow viscous oil, R_f 0.13 (hexane–ethyl acetate = 20 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60–7.46 (m, 6H), 7.42 (td, *J* = 7.5, 1.5 Hz, 1H), 7.34–7.24 (m, 3H), 7.08 (dd, *J* = 5.0, 3.6 Hz, 1H), 4.68 (d, *J* = 12.1 Hz, 1H), 4.45 (t, *J* = 3.6 Hz, 1H) , 4.40 (d, *J* = 11.9 Hz, 1H) , 3.79–3.71 (m, 1H), 3.45–3.37 (m, 1H), 1.84–1.72 (m, 1H), 1.67–1.39 (m, 5H), 0.620 (s, 3H), 0.615 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.2, 144.0, 138.0, 135.8, 135.3, 134.7, 134.5, 129.6, 128.5, 127.9, 126.7, 125.1, 124.8, 123.1, 97.8, 68.8, 62.0, 30.6, 25.5, 19.4, –0.8, –0.9; IR (neat) 3055, 3013, 2945, 2870, 1597, 1433, 1394, 1350, 1258, 1200, 1117, 1078, 1026, 974, 907, 870, 833, 812, 775, 756, 729, 696, 654, 534 cm^{-1}. Anal. Calcd. for $C_{24}H_{28}O_2SSi_2$: C, 70.54; H, 6.91. Found: C, 70.46; H, 6.84.



11fb

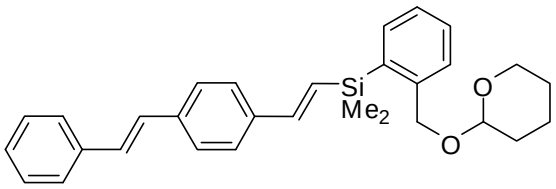
5-{[2-(Tetrahydro-2*H*-pyran-2-yloxymethyl)phenyl]dimethylsilyl}-2,2'-bithiophene (9fb). To a mixture of **1f** (6.0 g, 24 mmol), K_2CO_3 (6.9 g, 50 mmol), (dppf)$PdCl_2 \cdot CH_2Cl_2$ (163 mg, 0.20 mmol), and CuI (114 mg, 0.60 mmol) in DMF (16 mL) and THF (44 mL) was added **10b** (20 mmol), and the resulting mixture was stirred at 75 °C for 6 h. The mixture was filtered through a Florisil pad, diluted with Et_2O, washed with water and brine, dried over anhydrous $MgSO_4$, and then concentrated in vacuo. The residue was purified by flash chromatography on silica gel to afford **11fb** (8.0 g, 96%) as a colorless viscous oil, R_f 0.20 (hexane–ethyl acetate = 15 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (dd, *J* = 7.3, 1.3 Hz, 1H), 7.49 (d, *J* = 7.7 Hz, 1H), 7.41 (td, *J* = 7.5, 1.3 Hz, 1H), 7.28 (td, *J* = 7.3, 1.1 Hz, 1H), 7.21 (d, *J* = 3.5 Hz, 1H), 7.19 (dd, *J* = 5.1, 1.1 Hz, 1H), 7.15 (dd, *J* = 3.7, 1.1 Hz, 1H), 7.12 (d, *J* = 3.5 Hz, 1H), 6.99 (dd, *J* = 5.0, 3.6 Hz, 1H), 4.77 (d, *J* = 11.9 Hz, 1H), 4.56 (t, *J* = 3.6 Hz, 1H), 4.51 (d, *J* = 11.9 Hz, 1H), 3.86–3.77 (m, 1H), 3.51–3.41 (m, 1H), 1.88–1.75 (m, 1H), 1.72–1.41 (m, 5H), 0.66 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.9, 142.9, 137.9, 137.1, 135.9, 135.4, 135.2, 129.8, 128.6, 127.7, 126.8, 124.9, 124.3, 123.7, 97.8, 68.8, 62.1, 30.6, 25.6, 19.5, 0.3, 0.2; IR (neat): 2943, 2870, 2849, 1439, 1252, 1200, 1119, 1078, 1026, 988, 907, 837, 812, 777, 756, 692 cm^{-1}. Anal. Calcd. for $C_{22}H_{26}O_2S_2Si$: C, 63.72; H, 6.32. Found: C, 63.47; H, 6.32.



11ja

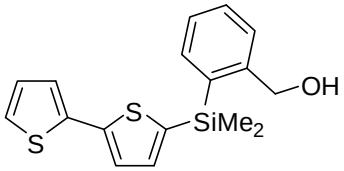
(*E*)-4-{Dimethyl[2-(tetrahydro-2*H*-pyran-2-yloxymethyl)phenyl]silyl}stilbene (11ja). A pale yellow viscous oil, R_f 0.10 (hexane–ethyl acetate = 20 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57–7.45 (m, 8H), 7.42 (td, *J* = 7.6, 1.4 Hz, 1H), 7.39–7.33 (m, 2H), 7.32–7.23 (m, 2H), 7.14 (d, *J* = 16.3, 1H), 7.09 (d, *J* = 16.3 Hz, 1H), 4.68 (d, *J* = 12.1 Hz, 1H), 4.59 (t, *J* = 3.5, 1H), 4.40 (d, *J* = 11.9 Hz, 1H), 3.80–3.71 (m, 1H), 3.46–3.37 (m, 1H), 1.82–1.73 (m, 1H), 1.69–1.41 (m, 5H), 0.62 (s, 3H), 0.61 (s, 3H); ^{13}C NMR

(101 MHz, $CDCl_3$) δ 144.0, 138.2, 137.7, 137.1, 135.9, 135.3, 134.3, 129.5, 128.9, 128.54, 128.48, 128.4, 127.5, 126.7, 126.4, 125.7, 97.8, 68.8, 62.0, 30.6, 25.5, 19.4, –0.8, –0.9; IR (neat) 3057, 3024, 2949, 2870, 1597, 1495, 1466, 1448, 1439, 1396, 1348, 1258, 1200, 1117, 1078, 1026, 964, 907, 870, 835, 806, 775, 754, 718, 692, 646, 577, 536 cm^{-1}. Anal. Calcd. for $C_{28}H_{32}O_2Si$: C, 78.46; H, 7.52. Found: C, 78.40; H, 7.59.



11jf

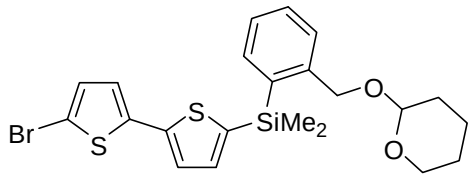
(*E*)-4-(2-(*E*)-{[2-(Tetrahydro-2*H*-pyran-2-yloxymethyl)phenyl]dimethylsilyl}ethenyl)stilbene (11jf). A yellow solid, mp 53.2–56.5 °C, R_f 0.13 (hexane–ethyl acetate = 20 : 1). ^1H NMR (400 MHz, $CDCl_3$) δ 7.59 (dd, *J* = 7.4, 1.2 Hz, 1H), 7.56–7.22 (m, 8H), 7.13 (d, *J* =16.3 Hz, 1H), 7.08 (d, *J* =16.3 Hz, 1H), 6.93 (d, *J* =19.2 Hz, 1H), 6.67 (d, *J* =19.0 Hz, 1H), 4.87 (d, *J* =11.9 Hz, 1H), 4.67 (t, *J* =3.5 Hz, 1H), 4.62 (d, *J* =11.9 Hz, 1H), 3.93–3.84 (m, 1H), 3.52–3.44 (m, 1H), 1.92–1.78 (m, 1H), 1.76–1.43 (m, 5H), 0.51 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.2, 143.8, 137.4, 137.1, 137.0, 136.6, 134.9, 129.4, 128.6, 128.4, 128.1, 127.7, 127.5, 126.8, 126.7, 126.5, 126.4, 97.9, 68.9, 62.2, 30.7, 25.6, 19.5, –1.0, –1.1; IR (KBr): 3053, 3022, 2941, 2891, 2868, 1597, 1508, 1448, 1437, 1342, 1250, 1200, 1117, 1076, 1055, 1028, 991, 966, 907, 868, 837, 820, 793, 752, 731, 708, 689, 534 cm^{-1}. Anal. Calcd. for $C_{30}H_{34}O_2Si_2$: C, 79.25; H, 7.54. Found: C, 79.10; H, 7.46.



12

5-{[2-(Hydroxymethyl)phenyl]dimethylsilyl}-2,2'-bithiophene (12). A solution of **11fb** (3.4 g, 8.3 mmol) and PPTS (0.42 g, 1.65 mmol) in MeOH (41 mL) was stirred at 40 °C for 2 h, and then concentrated in vacuo. The resulting residue was purified by flash chromatography on silica gel to give **12** (2.4 g, 89%) as a colorless solid, mp 47.2–

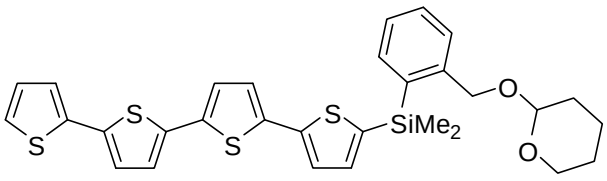
48.0 °C, R_f 0.30 (hexane–ethyl acetate = 5 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 7.3 Hz, 1H), 7.50–7.39 (m, 2H), 7.30 (t, *J* = 7.2 Hz, 1H), 7.21 (d, *J* = 3.5 Hz, 1H), 7.19 (d, *J* = 5.1 Hz, 1H), 7.15 (d, *J* = 3.5 Hz, 1H), 7.13 (d, *J* = 3.5 Hz, 1H), 6.98 (dd, *J* = 4.8, 3.8 Hz, 1H), 4.67 (d, *J* = 5.5 Hz, 2H), 1.53 (t, *J* = 5.8 Hz, 1H), 0.67 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.4, 143.1, 137.8, 136.9, 135.9, 135.2, 135.0, 130.1, 128.0, 127.7, 127.0, 125.0, 124.5, 123.9, 65.3, 0.3; IR (KBr): 3329, 3057, 2947, 1439, 1418, 1217, 1200, 1126, 1078, 1015, 989, 839, 810, 779, 758, 746, 708, 691 cm^{-1}. Anal. Calcd. for $C_{17}H_{18}OS_2Si$: C, 61.77; H, 5.49. Found: C, 61.58; H, 5.48.



13

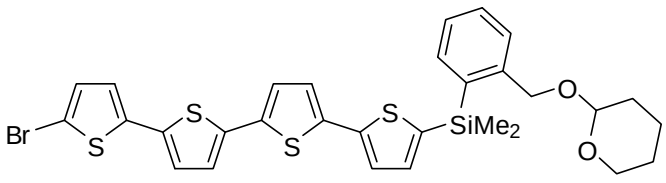
5-Bromo-5'-{dimethyl[2-(tetrahydro-2*H*-pyran-2-yloxymethyl)phenyl]silyl}-2,2'-bithiophene (13). To a solution of **11fb** (4.6 g, 11 mmol) in Et_2O (33 mL) was added TMEDA (1.41 g, 12.1 mmol) and a 1.6 M solution of *n*-BuLi (7.2 mL, 11.6 mmol) in hexane at –40 °C, and the resulting mixture was stirred at –40 °C for 30 min and then at rt for 30 min. To this was added 1,2-dibromo-1,1,2,2-tetrafluoroethane (3.1 g, 12.1 mmol) at –40 °C, and the resulting mixture was stirred at –40 °C for 1 h before quenching with a sat. $Na_2S_2O_3$ aq. solution (20 mL). The aq. layer was extracted 3 times with diethyl ether (120 mL). The combined organic layer was dried over anhydrous $MgSO_4$, and then concentrated in vacuo. The residue was purified by flash chromatography on silica gel to give **13** (4.9 g, 90%) as a colorless oil, R_f 0.22 (hexane–ethyl acetate = 15 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 7.3 Hz, 1H), 7.50 (d, *J* = 7.5 Hz, 1H), 7.42 (td, *J* = 7.4, 1.0 Hz, 1H), 7.29 (t, *J* = 7.3 Hz, 1H), 7.15 (d, *J* = 3.5 Hz, 1H), 7.12 (d, *J* = 3.5 Hz, 1H), 6.95 (d, *J* = 3.8 Hz, 1H), 6.90 (d, *J* = 3.8 Hz, 1H), 4.77 (d, *J* = 12.1 Hz, 1H), 4.56 (t, *J* = 3.5 Hz, 1H), 4.50 (d, *J* = 12.1 Hz, 1H), 3.88–3.76 (m, 1H), 3.52–3.42 (m, 1H), 1.73–1.42 (m, 5H), 1.88–17.5 (m, 1H), 0.67 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.9, 141.8, 138.63, 138.60, 135.9, 135.22, 135.17, 130.5, 129.9, 128.6, 126.8, 125.1, 123.8, 110.9, 97.8, 68.7, 62.1, 30.6, 25.5, 19.5, 0.3, 0.2 ; IR (neat): 3055, 2943, 2870, 2849, 1441, 1418, 1350, 1252, 1200, 1119, 1078, 1026, 988, 970, 905, 870, 835, 812, 754, 691, 654, 530 cm^{-1}. Anal. Calcd. for $C_{22}H_{25}BrO_2S_2Si$: C,

53.54; H, 5.11. Found: C, 53.77; H, 5.19.



14

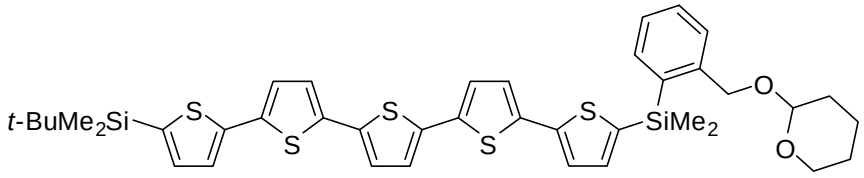
5-{[2-(Tetrahydro-2*H*-pyran-2-yloxymethyl)phenyl]dimethylsilyl}-2,2':5',2'':5'',2'''-quarterthiophene (14). To a solution of **12** (3.9 g, 11.9 mmol), K_2CO_3 (3.4 g, 25 mmol), (dppf)$PdCl_2$ · CH_2Cl_2 (0.25 g, 0.30 mmol), CuI (0.17 g, 0.89 mmol) in DMF (7.9 mL) and THF (22 mL) was added **13** (4.9 g, 9.9 mmol), and the resulting mixture was stirred at 75 °C for 10 h before filtration through a Florisil pad. After concentration in vacuo, the residue was filtered through a short silica gel column and further purified by preparative GPC to afford **14** (4.7 g, 82%) as a a yellow solid, mp 111.0–111.7 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (dd, *J* = 7.5, 1.2 Hz, 1H), 7.50 (d, *J* = 7.6 Hz, 1H), 7.42 (td, *J* = 7.5, 1.3 Hz, 1H), 7.29 (td, *J* = 7.3, 1.3 Hz, 1H), 7.23–7.18 (m, 2H), 7.16 (dd, *J* = 3.7, 1.1 Hz, 1H), 7.13 (d, *J* = 3.5 Hz, 1H), 7.09–7.03 (m, 4H), 7.02 (dd, *J* = 5.1, 3.7 Hz, 1H), 4.77 (d, *J* = 11.9 Hz, 1H), 4.56 (t, *J* = 3.6 Hz, 1H), 4.51 (d, *J* = 11.9 Hz, 1H), 3.85–3.77 (m, 1H), 3.51–3.42 (m, 1H), 1.87–1.75 (m, 1H), 1.72–1.42 (m, 5H), 0.67 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.9, 142.5, 138.3, 136.9, 136.1, 136.03, 136.01, 135.8, 135.7, 135.3, 135.2, 129.8, 128.6, 127.8, 126.8, 124.9, 124.43, 124.40, 124.3, 124.2, 124.1, 123.6, 97.8, 68.8, 62.1, 30.6, 25.6, 19.5, 0.3, 0.2; IR (KBr): 3452, 2949, 833, 793, 687 cm^{-1}. Anal. Calcd. for $C_{30}H_{30}O_2S_4Si$: C, 62.24; H, 5.22. Found: C, 62.00; H, 4.95.



15

5-Bromo-5'''-{dimethyl[2-(tetrahydro-2*H*-pyran-2-yloxymethyl)phenyl]silyl}-2,2':5',2'':5'',2'''-quarterthiophene (15). To a solution of **14** (0.70 g, 1.2 mmol) in THF (14.4 mL) were added TMEDA (153 mg, 1.32 mmol) and a 1.6 M solution of *n*-

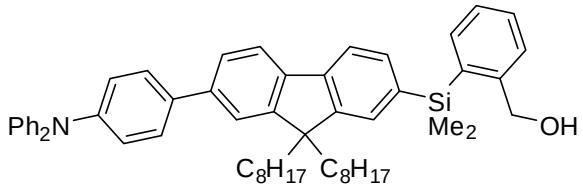
BuLi (1.32 mmol) in hexane at –78 °C, and the resulting mixture was stirred at the same temperature for 5 min. To this was added $BrCF_2CF_2Br$ (0.37 g, 1.44 mmol), and the resulting mixture was stirred at –40 °C for 1 h and then quenched with a sat. $Na_2S_2O_3$ aq. solution (2 mL). The aq. layer was extracted with diethyl ether (20 mL), and the organic layer was dried over anhydrous $MgSO_4$ and concentrated in vacuo. The residue was purified by preparative GPC to give **15** (0.71 g, 90%) as a yellow solid, mp 112.4–115.7 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (dd, *J* = 7.3, 1.1 Hz, 1H), 7.50 (d, *J* = 8.1 Hz, 1H), 7.41 (td, *J* = 7.5, 1.3 Hz, 1H), 7.29 (td, *J* = 7.4, 1.0 Hz, 1H), 7.21 (d, *J* = 3.5 Hz, 1H), 7.13 (d, *J* = 3.5 Hz, 1H), 7.08–7.02 (m, 3H), 7.00 (d, *J* = 3.7 Hz, 1H), 6.97 (d, *J* = 3.8 Hz, 1H), 6.90 (d, *J* = 3.8 Hz, 1H), 4.77 (d, *J* = 12.1 Hz, 1H), 4.56 (t, *J* = 3.5 Hz, 1H), 4.51 (d, *J* = 11.9 Hz, 1H), 3.86–3.77 (m, 1H), 3.51–3.43 (m, 1H), 1.86–1.74 (m, 1H), 1.72–1.42 (m, 5H), 0.67 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.9, 142.3, 138.4, 138.3, 136.3, 136.2, 136.0, 135.4, 135.3, 135.2, 134.9, 130.5, 129.8, 128.6, 126.8, 124.9, 124.5, 124.38, 124.37, 124.0, 123.6, 111.0, 97.8, 68.7, 62.1, 30.6, 25.5, 19.5, 0.3, 0.2; IR (KBr): 3450, 3061, 2943, 2870, 1427, 1254, 1117, 1078, 1028, 989, 843, 835, 814, 789, 756, 465 cm^{-1}. HRMS (FAB$^+$) Calcd. $C_{30}H_{29}BrO_2S_4Si$: M^+ 656.0003. Found: *m*/*z* 656.0024.



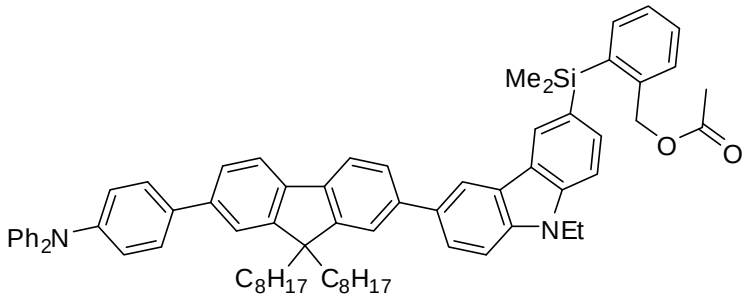
16

5’’’’-(*t*-Butyldimethylsilyl)-5-{dimethyl[2(tetrahydro-2*H*-pyran-2-yloxymethyl)-phenyl]silyl}-2,2’:5’,2’’:5’’,2’’’:5’’’,2’’’’-quinquethiophene (16). The standard cross-coupling procedure employing **15** (66 mg, 0.10 mmol) and **1k** (44 mg, 0.12 mmol) gave **16** (62 mg, 80%) as an orange solid, mp 128.5–130.3 °C, R_f 0.32 (hexane–ethyl acetate = 5 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 7.3 Hz, 1H), 7.50 (d, *J* = 7.5 Hz, 1H), 7.42 (t, *J* = 7.5 Hz, 1H), 7.29 (t, *J* = 7.3 Hz, 1H), 7.23 (d, *J* = 3.3 Hz, 1H), 7.21 (d, *J* = 3.5 Hz, 1H), 7.13 (d, *J* = 3.5 Hz, 1H), 7.11–7.01 (m, 7H), 4.77 (d, *J* = 11.9 Hz, 1H), 4.56 (t, *J* = 3.4 Hz, 1H), 4.51 (d, *J* = 11.9 Hz, 1H), 3.87–3.77 (m, 1H), 3.51–3.42 (m, 1H), 1.88–1.75 (m, 1H), 1.73–1.43 (m, 5H), 0.95 (s, 9H), 0.67 (s, 6H), 0.31 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.9, 142.5, 141.9, 138.3, 137.0, 136.2, 136.1, 136.0, 135.9,

135.79, 135.76, 135.7, 135.6, 135.3, 135.2, 129.8, 128.6, 126.8, 124.9, 124.7, 124.4, 124.3, 124.23, 124.21, 124.17, 124.12, 97.8, 68.8, 62.1, 30.6, 26.4, 25.6, 19.5, 17.1, 0.3, 0.20, –4.8; IR (KBr): 3059, 2951, 2926, 2855, 1427, 1078, 986, 833, 804, 791, 773, 473 cm^{-1}. Anal. Calcd. for $C_{40}H_{46}O_2S_5Si_2$: C, 61.97; H, 5.98. Found: C, 61.85; H, 6.08.



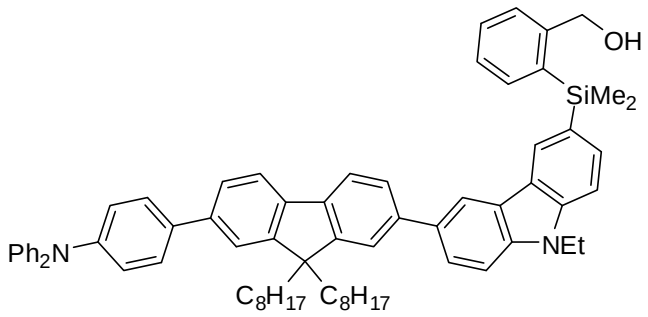
2-(4-Diphenylaminophenyl)-7-(2-hydroxymethylphenyl)dimethylsilyl-9,9'-dioctyl-9*H*-fluorene. To a solution of **11id** (0.88 g, 1.0 mmol) in MeOH (3 mL) and CH_2Cl_2 (3 mL) was added *p*-TsOH・H_2O (3.8 mg, 20 μmol), and the resulting mixture was stirred at rt overnight. Concentration in vacuo followed by flash chromatography on silica gel to afford the title compound, OH-free **11id** (0.74 g, 93%) as a viscous oil, R_f 0.27 (hexane–ethyl acetate = 3 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 7.9 Hz, 1H), 7.67 (d, *J* = 7.3 Hz, 1H), 7.59–7.38 (m, 9H), 7.32–7.21 (m, 5H), 7.18–7.09 (m, 6H), 7.02 (t, *J* = 7.2 Hz, 2H), 4.54 (d, *J* = 5.9 Hz, 2H), 2.01–1.98 (m, 4H), 1.30–0.94 (m, 21H), 0.81 (t, *J* = 7.0 Hz, 6H), 0.74–0.54 (m, 10H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.4, 150.2, 147.5, 146.9, 146.5, 141.8, 139.6, 139.5, 136.9, 136.4, 135.5, 135.4, 132.4, 129.8, 129.1, 128.2, 128.0, 127.6, 126.8, 125.3, 124.2, 123.9, 122.8, 120.8, 120.0, 119.2, 65.4, 55.2, 40.3, 31.9, 30.1, 29.31, 29.28, 23.9, 22.7, 14.2, –0.7; IR (neat): 3450, 2953, 2926, 2853, 1591, 1514, 1493, 1464, 1331, 1315, 1279, 837, 816, 752, 696, 502 cm^{-1}. Anal. Calcd. for $C_{56}H_{67}NOSi$: C, 84.26; H, 8.46. Found: C, 84.24; H, 8.23.



17

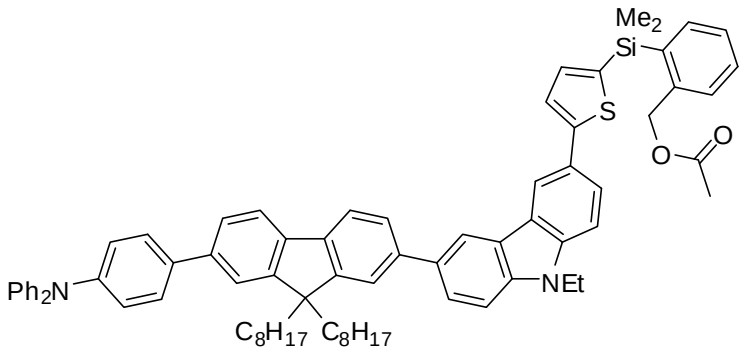
7-[6-(2-Acetoxymethylphenyl)dimethylsilyl-9-ethylcarbazol-3-yl]-2-(4-diphenyl-aminophenyl)-9,9'-dioctyl-9*H*-fluorene (17). To a mixture of deproteced **11id** (8.0 g,

10 mmol), K_2CO_3 (3.5 g, 25 mmol), [(η^3-allyl)PdCl]$_2$ (18 mg, 50 μmol), RuPhos (98 mg, 0.21 mmol), and CuI (57 mg, 0.30 mmol) in DMF (8 mL) and THF (22 mL) was added **10'c** (4.8 g, 10 mmol), and the resulting mixture was stirred at 75 °C for 17 h, filtered through a Florisil pad, diluted with Et_2O, washed with water and then with brine, and dried over anhydrous $MgSO_4$. Concentration in vacuo followed by flash chromatography on silica gel gave **17** (9.0 g, 87%) as a colorless solid, mp 70.8–73.6 °C, R_f 0.37 (hexane–ethyl acetate = 5 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (s, 1H), 8.30 (s, 1H), 7.81–7.72 (m, 3H), 7.71–7.62 (m, 3H), 7.61–7.51 (m, 5H), 7.50–7.32 (m, 5H), 7.31–7.22 (m, 4H), 7.20–7.11 (m, 6H), 7.03 (t, *J* = 7.3 Hz, 2H), 5.03 (s, 2H), 4.42 (q, *J* = 7.1 Hz, 2H), 2.13–1.99 (m, 4H), 1.86 (s, 3H), 1.47 (t, *J* = 7.1 Hz, 3H), 1.23–0.98 (m, 20H), 0.84–0.68 (m, 16H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.4, 151.5, 151.4, 147.5, 146.8, 141.2, 141.0, 139.8, 139.2, 139.1, 139.0, 138.0, 135.8, 135.6, 133.0, 131.2, 129.6, 129.4, 129.1, 127.6, 127.5, 126.7, 126.4, 126.0, 125.34, 125.31, 124.2, 123.9, 123.2, 123.0, 122.7, 121.5, 120.8, 119.74, 119.71, 118.9, 108.5, 108.4, 66.7, 55.3, 40.6, 37.8, 31.9, 30.2, 29.35, 29.32, 24.0, 22.7, 21.0, 14.2, 14.1, –0.4; IR (KBr): 3452, 2926, 2852, 1738, 1593, 1493, 1464, 1275, 1232, 818, 806, 754, 696 cm^{-1}. Anal. Calcd. for $C_{72}H_{80}N_2O_2Si$: C, 83.67; H, 7.80. Found: C, 83.92; H, 7.91.



2-(4-Diphenylaminophenyl)-7-[6-(2-hydroxymethylphenyl)dimethylsilyl-9-ethylcarbazol-3-yl]-9,9'-dioctyl-9*H*-fluorene. To a solution of **17** (9.0 g, 8.7 mmol) in CH_2Cl_2 (17.4 mL) was added DIBAL–H (9.6 mmol) in toluene at –78 °C, and the resulting mixture was stirred at the same temperature for 2 h. The reaction was quenched with a sat. NH_4Cl aq. solution at –78 °C, diluted with Et_2O, and slowly warmed to rt. The aq. layer was extracted with diethyl ether, and the combined organic layer was dried over anhydrous $MgSO_4$. Concentratiion in vacuo followed by flash chromatography on silica gel afforded the title compound, OH-free **17**, (0.82 g, 95%) as

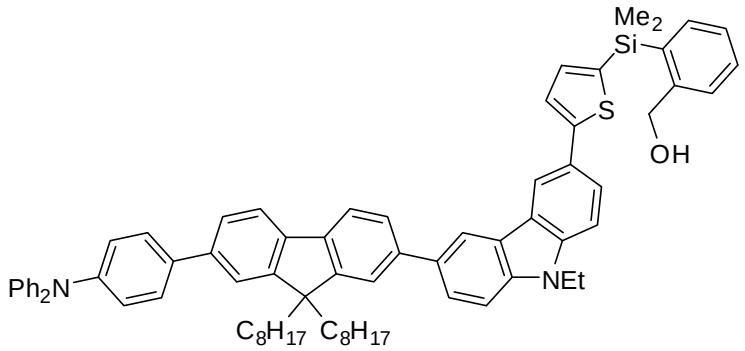
a colorless solid, mp 81.9–83.5 °C, R_f 0.52 (hexane–ethyl acetate = 3 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (s, 1H), 8.34 (s, 1H), 7.81–7.72 (m, 3H), 7.71–7.62 (m, 3H), 7.61–7.52 (m, 5H), 7.51–7.40 (m, 4H), 7.37–7.22 (m, 5H), 7.20–7.11 (m, 6H), 7.03 (t, *J* = 7.2 Hz, 2H), 4.57 (s, 2H), 4.40 (q, *J* = 7.1 Hz, 2H), 2.13–1.97 (m, 4H), 1.47 (t, *J* = 7.1 Hz, 3H), 1.29–0.98 (m, 21H), 0.82–0.66 (m, 16H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.5, 151.4, 147.5, 146.8, 146.5, 141.0, 140.7, 139.8, 139.2, 139.1, 139.0, 136.7, 135.6, 135.5, 133.0, 131.0, 129.8, 129.1, 128.2, 127.6, 127.2, 126.9, 126.2, 126.0, 125.4, 125.3, 124.2, 123.9, 123.1, 122.7, 121.5, 120.8, 119.8, 119.7, 118.9, 108.6, 65.4, 55.3, 40.6, 37.8, 31.9, 30.2, 29.35, 29.32, 24.0, 22.7, 14.2, 14.1, –0.4; IR (KBr): 3450, 2926, 2853, 1593, 1493, 1464, 1275, 1232, 820, 804, 752, 696 cm^{-1}. Anal. Calcd. for $C_{70}H_{78}N_2OSi$: C, 84.80; H, 7.93. Found: C, 84.79; H, 7.84.



18

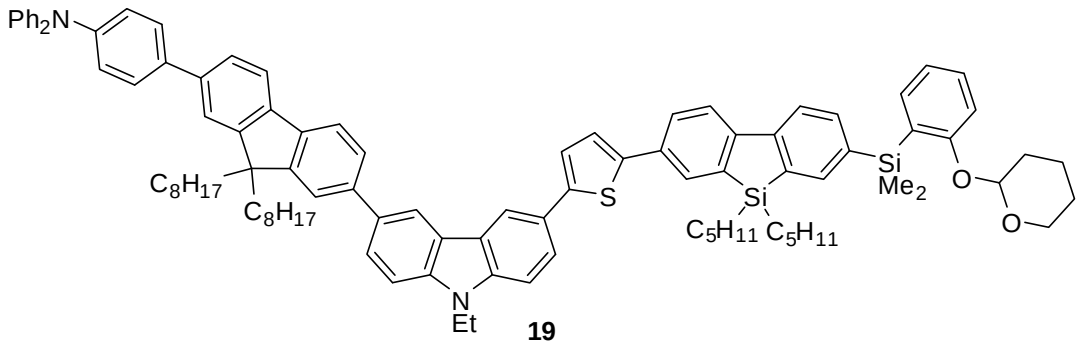
7-(6-{[5-(2-Acetoxymethylphenyl)dimethylsilyl]-2-thienyl}-9-ethylcarbazol-3-yl)-2-(4-diphenylaminophenyl)-9,9'-dioctyl-9*H*-fluorene 18. To a mixture of OH-free **17** (0.99 g, 1.0 mmol), K_2CO_3 (0.99 g, 1.0 mmol), [(η^3-allyl)PdCl]$_2$ (1.8 mg, 5.0 μmol), RuPhos (9.8 mg, 21 μmol), and CuI (5.7 mg, 30 μmol) in DMF (0.8 mL) and THF (2.2 mL) was added **10'b** (0.37 g, 1.0 mmol), and the resulting mixture was stirred at 75 °C for 24 h. The mixture was filtered through a Florisil pad, diluted with Et_2O, washed with water and brine, and dried over anhydrous $MgSO_4$. After concentration in vacuo, the residue was purified by flash chromatography on silica gel to give **18** (0.87 g, 78%) as a yellow solid, mp 71.8–73.6 °C, R_f 0.38 (hexane–ethyl acetate = 5 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (d, *J* = 1.1 Hz, 1H), 8.39 (s, 1H), 7.83–7.52 (m, 11H), 7.51–7.32 (m, 6H), 7.31–7.21 (m, 5H), 7.20–7.11 (m, 6H), 7.03 (t, *J* = 7.3 Hz, 2H), 5.14 (s, 2H), 4.40 (q, *J* = 7.1 Hz, 2H), 2.15–1.96 (m, 7H), 1.48 (t, *J* = 7.2 Hz, 3H), 1.22–0.99 (m,

24H), 0.77 (t, J = 7.0 Hz, 6H), 0.72 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.5, 151.8, 151.5, 151.4, 147.5, 146.8, 141.1, 140.6, 139.9, 139.7, 139.6, 139.2, 139.0, 136.9, 136.4, 136.1, 135.6, 135.5, 133.0, 129.9, 129.5, 129.1, 127.6, 126.0, 125.5, 125.3, 124.4, 124.2, 123.9, 123.40, 123.36, 122.7, 121.4, 120.8, 119.8, 119.7, 118.9, 118.0, 108.8, 66.6, 55.3, 40.6, 37.9, 31.9, 30.2, 29.34, 29.32, 24.0, 22.7, 21.1, 14.2, 14.1, 0.3; IR (KBr): 3466, 2926, 2855, 1736, 1593, 1493, 1483, 1466, 1275, 1252, 1231, 804, 752, 696 cm^{-1}. Anal. Calcd. for: C, 81.82; H, 7.41. Found: C, 81.57; H, 7.51.



2-(4-Diphenylaminophenyl)-7-(6-{[5-(2-hydroxymethylphenyl)dimethylsilyl]-2-thienyl}-9-ethylcarbazol-3-yl)-9,9'-dioctyl-9*H*-fluorene. To a solution of **18** (0.82 g, 0.74 mmol) in CH_2Cl_2 (2 mL) was added a 1.5 M solution of DIBAL–H (0.81 mmol) in toluene at –78 °C, and the resulting mixture was stirred at the same temperature for 2 h. The reaction was quenched with a sat. NH_4Cl aq. solution at –78 °C, diluted with Et_2O, and slowly warmed to rt The aq. layer was extracted with diethyl ether, and the combined organic layer was dried over anhydrous $MgSO_4$. After concentration in vacuo, the residue was purified by flash chromatography on silica gel to afford the title compound, OH-free **18**, (0.68 g, 85%) as a yellow solid, mp 86.7–88.0 °C, R_f 0.50 (hexane–ethyl acetate = 3 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (s, 1H), 8.39 (s, 1H) 7.83–7.37 (m, 15H), 7.36–7.21 (m, 7H), 7.20–7.10 (m, 6H), 7.03 (td, J = 7.3, 1.0 Hz, 2H), 4.72 (d, J = 5.9 Hz, 2H), 4.41 (q, J = 7.1 Hz, 2H), 2.14–1.98 (m, 4H), 1.48 (t, J = 7.2 Hz, 3H), 1.22–0.99 (m, 25H), 0.77 (t, J = 6.8 Hz, 6H), 0.72 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.5, 151.4, 149.5, 147.5, 146.8, 145.6, 140.6, 139.8, 139.72, 139.65, 139.2, 139.0, 135.6, 134.9. 133.0, 130.8, 129.4, 129.1, 127.9, 127.6, 126.7, 126.0, 125.7, 125.6, 125.4, 124.4, 124.2, 123.9, 123.5, 123.4, 123.3, 122.7, 121.9, 121.51, 121.48, 120.8, 119.8, 119.7, 118.9, 118.0, 108.80, 108.77, 71.5, 55.3, 40.6, 37.9, 31.9, 30.2, 29.4,

29.3, 24.0, 22.7, 14.2, 14.0, 0.7.; IR (KBr): 3452, 2926, 2853, 1593, 1493, 1466, 1275, 804, 752, 696 cm^{-1}. Anal. Calcd. for $C_{74}H_{80}N_2OSSi$: C, 82.79; H, 7.51. Found: C, 82.53; H, 7.54.



19

3-[2-(4-Diphenylaminophenyl)-9,9'-dioctyl-9*H*-fluoren-7-yl]-9-ethyl-6-(5-{7-[2-(tetrahydropyran-2-yloxymethyl)phenyl]dimethylsilyl-9,9'-dipentyl-9*H*-silafluoren-2-yl}-2-thienyl)carbazole (19). To a mixture of deprotected **18** (107 mg, 0.10 mmol), K_2CO_3 (35 mg, 0.25 mmol), (dppf)$PdCl_2$ · CH_2Cl_2 (4.1 mg, 5.0 μmol), and CuI (1.0 mg, 5.0 μmol) in DMF (80 μL) and THF (0.22 mL) was added **10e** (65 mg, 0.10 mmol), and the resulting mixture was stirred at 75 °C for 24 h. The mixture was filtered through a Florisil pad, diluted with Et_2O, washed with water and brine, and dried over anhydrous $MgSO_4$. Concentration in vacuo followed by flash chromatography on silica gel gave **19** (0.118 g, 80%) as a yellow solid, mp 91.7–94.0 °C, R_f 0.35 (hexane–ethyl acetate = 10 : 1). ^1H NMR (400 MHz, $CDCl_3$) δ 8.45 (s, 1H), 8.43 (s, 1H), 7.91–7.65 (m, 10H), 7.62–7.33 (m, 12H), 7.32–7.11 (m, 12H), 7.03 (t, *J* = 7.2 Hz, 2H), 4.70 (d, *J* = 11.9 Hz, 2H), 4.51–4.38 (m, 4H), 3.82–3.72 (m, 1H), 3.46–3.36 (m, 1H), 2.18–1.99 (m, 4H), 1.85–1.72 (m, 1H), 1.68–0.91 (m, 47H), 0.89–0.70 (m, 12H), 0.63 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.5, 151.4, 148.5, 147.5, 147.2, 146.8, 144.7, 144.0, 142.5, 140.6, 139.8, 139.72, 139.68, 139.2, 139.1, 138.9, 138.7, 137.2, 136.9, 136.3, 136.0, 135.6, 135.5, 133.3, 133.0, 129.9, 129.4, 129.1, 128.4, 127.6, 127.1, 126.7, 126.0, 125.7, 125.6, 125.4, 124.2, 124.0, 123.9, 123.7, 123.5, 123.3, 122.8, 122.7, 121.4, 121.2, 120.8, 120.0, 119.8, 119.7, 118.9, 117.6, 108.9, 108.8, 97.7, 68.8, 62.0, 55.3, 40.6, 37.9, 35.6, 31.9, 30.6, 30.2, 29.8, 29.3, 25.5, 24.0, 23.7, 22.7, 22.3, 19.4, 14.2, 14.13, 14.07, 12.4, –0.7, –0.8; IR (KBr): 2924, 2855, 1591, 1493, 1462, 1292, 1277, 1232, 837, 820, 802, 752, 694 cm^{-1}. Anal. Calcd. for: C, 81.82; H, 7.41. Found: C, 81.57; H, 7.51.

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Chapter 4

Rhodium-catalyzed 1,4-Addition Reactions of Organo[2-(hydroxymethyl)phenyl]dimethylsilanes

Tetraorganosilicon reagents, alkenyl-, aryl-, and silyl[2-(hydroxymethyl)phenyl]dimethylsilanes, are found to undergo transmetalation with rhodium complexes under mild conditions and thus to participate in 1,4-addition reactions to various electron-deficient olefins without any activator. The reaction tolerates a wide range of functional groups, and the cyclic silyl ether is recovered in good yields on gram-scale synthesis. Use of an (*S*)-binap ligand or chiral diene ligand allows to achieve the corresponding enantioselective transformation using the tetraorganosilicon reagents, providing a silicon-based approach to optically active ketones and substituted piperidones that serve as synthetic intermediates for potent pharmaceuticals. The kinetic resolution of a racemic chiral phenylsilane was studied in the enantioselective 1,4-addition reaction under the rhodium–chiral diene catalysis to suggest that a rhodium alkoxide species would be responsible for transmetalation step.

2. Introduction

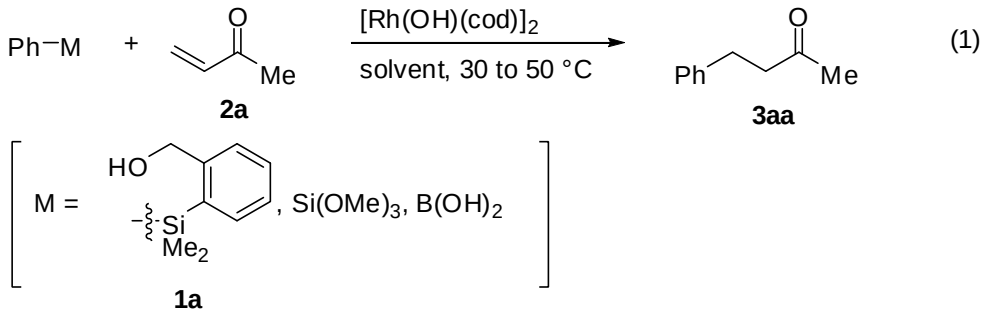
Transition metal-catalyzed addition reactions of organometallic reagents to electron-deficient olefins have attracted much attention and have been developed extensively in the last decade. Especially, since the landmark report by Miyaura and his coworkers in 1997,[1] use of organoboron reagents has found many synthetic applications including asymmetric 1,2- and 1,4-additions because of their tolerance toward many functional groups as well as easy handling and ready availability.[2–4] Alternative organometallic reagents have also been developed including silicon[3d,f,5] titanium,[6] zinc,[7] zirconium,[8] indium,[9] tin,[10] lead,[11] and bismuth.[12] Among these, organosilicon reagents should have significant importance in view of stability and non-toxicity as well as natural abundance of silicon element. Nevertheless, reported examples of such silicon-based reactions rely on the use of acid-, base-, and/or moisture-sensitive organotri(alkoxy)silanes,[5a–g] -silanediols,[5h] and chlorosilanes[5i] in excess under relatively harsh conditions. Furthermore, use of highly nucleophilic activators including metal fluorides in a stoichiometric amount is essential in some cases[3f,5f,h,l,m] to activate the silicon reagents to be reactive enough to undergo transmetalation to rhodium(I) or palladium(II) species. Thus, the development of new silicon reagents that are highly stable but reactive enough at the same time have remained elusive.

With the given success of organo[2-(hydroxymethyl)phenyl]dimethylsilanes **1** in the cross-coupling chemistry, the author envisioned the use of **1** as a new entry to silicon-based rhodium-catalyzed 1,4-addition reactions. In this Chapter, the author demonstrates the rhodium-catalyzed conjugate addition reaction using **1** under mild conditions without any activators to produce a wide range of adducts in good yields with excellent chemoselectivities. Enantioselective 1,4-addition reactions are also achieved by means of a rhodium/(*S*)-binap or chiral diene catalyst.

2. Results and discussion

2.1 Rhodium-catalyzed 1,4-addition reactions of organo[2-(hydroxymethyl)phenyl]dimethylsilanes.

At the onset, the author assessed the reactivity of **1** by the reaction of phenyl[2-(hydroxymethyl)phenyl]dimethylsilane (**1a**) with an excess amount of methyl vinyl ketone (**2a**) in the presence of $[Rh(OH)(cod)]_2$ as a catalyst (Eq. 1). The reaction was carried out in 1,4-dioxane at 30 °C and monitored with a reaction calorimeter (Omnical SuperCRC).[13] Almost quantitative conversion of **1a** was observed after 3 h (curve c, Figure 1), whereas the reaction using trimethoxy(phenyl)silane, a representative silicon



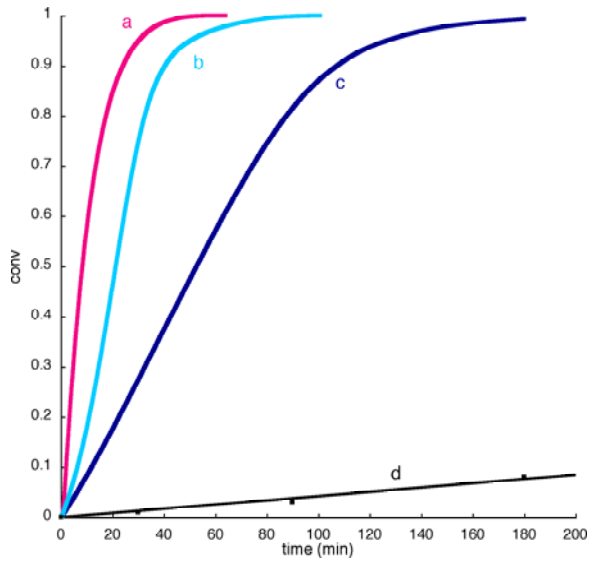
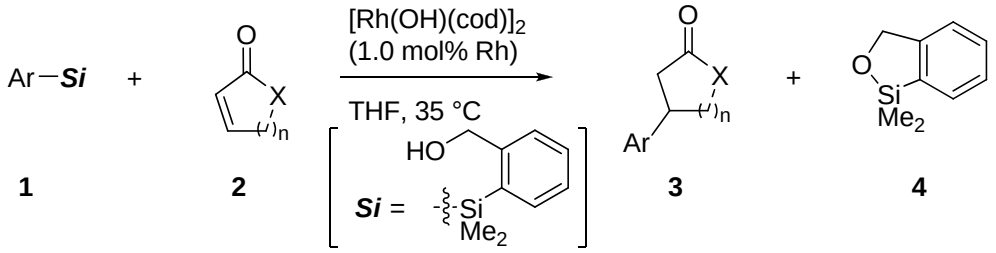


Figure 1. Conversion vs time for the reactions of a phenylmetal reagent ($[Ph–M]_0$ = 67 mM) with methyl vinyl ketone ($[\mathbf{2a}]_0$ = 201 mM) in the presence of a rhodium catalyst ($[Rh]_{total}$ = 2.7 mM) at 30 or 50 °C: (a) $PhB(OH)_2$ as the nucleophile and $[Rh(OH)(cod)]_2$ as the catalyst in 1,4-dioxane/H_2O (10/1) at 30 °C in the presence of $[B(OH)_3]_0$ = 536 mM (for the reaction conditions see ref 14); (b) **1a** as the nucleophile and $[Rh(OH)(cod)]_2$ as the catalyst in 1,4-dioxane at 50 °C; (c) **1a** as the nucleophile and $[Rh(OH)(cod)]_2$ as the catalyst in THF at 30 °C; (d) $PhSi(OMe)_3$ as the nucleophile and $[Rh(cod)(MeCN)_2]BF_4$ as the catalyst in 1,4-dioxane/H_2O (10/1) at 50 °C.

reagent frequently used for rhodium-catalyzed transformations,[5a–g] in the presence of cationic $[Rh(cod)(MeCN)_2]BF_4$ as a catalyst in 1,4-dioxane/H_2O (10/1)[5a] showed less than 10% yield of 1,4-adduct **3aa** by ^1H NMR analysis even at 50 °C (curve d). The author further found that the rate of the reaction using **1a** at 50 °C was comparable with that using phenylboronic acid[14] at 30 °C (curve a vs curve b). Apparently, these results indicate a prominent reactivity of organo[2-(hydroxymethyl)phenyl]dimethylsilanes as alternatives of organoboronic acids, compared with conventional silicon reagents such as trialkoxy(organo)silanes.

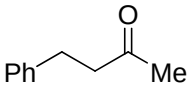
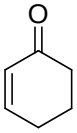
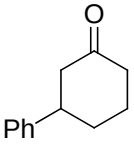
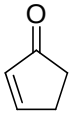
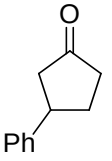
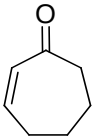
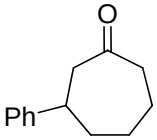
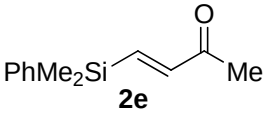
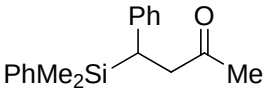
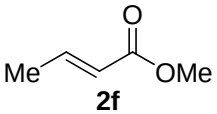
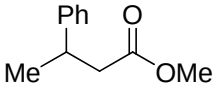
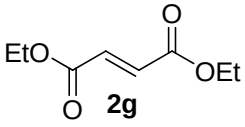
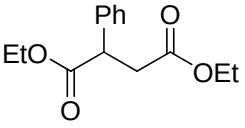
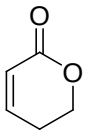
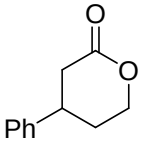
Indeed, the equimolar reaction of **1a** with **2a** on a 1.0 mmol scale in the presence of $[Rh(OH)(cod)]_2$ (1.0 mol% Rh) in THF at 35 °C gave **3aa** in 94% yield after 4 h (entry 1 of Table 1). The observed excellent reactivity of the silicon reagent under mild conditions prompted the author to further investigate the scope of both silicon reagents and electrophiles. The addition of **1a** across 2-cyclohexen-1-one (**2b**) also took place smoothly under the similar conditions to give 3-phenylcyclohexanone (**3ab**) in 90% yield (entry 2). The same reaction on a gram-scale (10 mmol scale) allowed him to isolate cyclic silyl ether **4**, a silicon residue of the reaction, in 92% yield by distillation of the crude product and **3ab** in 92% yield by flash chromatography on silica gel of the residue (entry 3). As already demonstrated in Chapter 3, **4** serves as a silylating agent of various aryl Grignard reagents to give the arylsilane reagents employed in this study. The metal residue of the 1,4-addition reaction is demonstrated to be recyclable for the first time. Reactions of **1a** met success not only with cyclic or acyclic enones (entries 4–6) but also with various α,β-unsaturated esters, amides, and nitrile in good yields (entries 7–14). Phenylsilanes having methoxy (**1b**), fluoro (**1c**), bromo (**1d**), cyano (**1e**), and pinacolatoboryl (**1f**) at the *para*-position all reacted with **2b**, these functional groups being intact during the reactions (entries 15–19). Sterically highly demanding 2,4,6-trimethylphenylsilane **1g** gave the corresponding adduct (**3gb**) in 85% yield although extra loading of **1g** (total 1.5 equiv.) was necessary (entry 20). It should be noted that transmetalation to rhodium(I) proceeds very efficiently without the aid of other metal cocatalyst, in sharp contrast to the transmetalation of arylsilanes **1** to a palladium(II) complex which requires the use of a copper(I) cocatalyst for the success of cross-coupling.

Table 1. Rhodium-catalyzed 1,4-addition reactions of aryl[2-(hydroxymethyl)phenyl]-dimethylsilanes to electron-deficient olefins **2**[a]



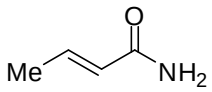
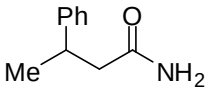
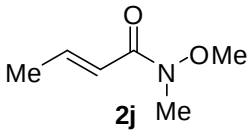
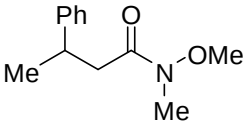
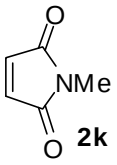
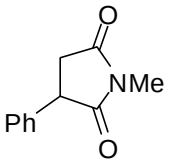
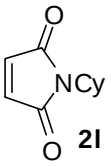
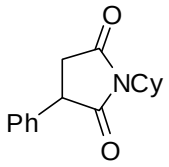
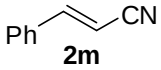
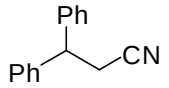
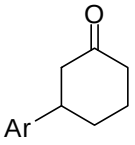
1 **2** **3** **4**

Ar = Ph (**1a**); 4-MeO–C_6H_4 (**1b**); 4-F–C_6H_4 (**1c**); 4-Br–C_6H_4 (**1d**); 4-NC–C_6H_4 (**1e**); 4-(pin)B–C_6H_4 (**1f**); 2,4,6-Me_3–C_6H_2 (**1g**)

entry	**1**	**2**	time (h)	product	yield (%)[b]
1	**1a**	**2a**	4		94 (**3aa**)
2	**1a**	 **2b**	5		90 (**3ab**)
3[c]	**1a**		6		92 (**3ab**)[d]
4	**1a**	 **2c**	4		95 (**3ac**)
5	**1a**	 **2d**	5		86 (**3ad**)
6	**1a**	 **2e**	4		90 (**3ae**)
7	**1a**	 **2f**	4		86 (**3af**)
8	**1a**	 **2g**	8		98 (**3ag**)
9[e]	**1a**	 **2h**	4		91 (**3ah**)

(*continued to the next page*)

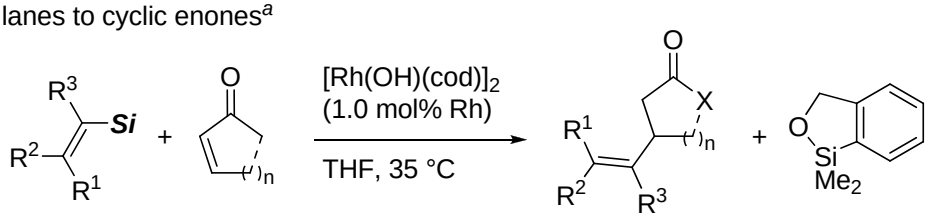
Table 1. (*continued*)

entry	1	2	time (h)	product	yield (%)[b]
10	**1a**	 **2i**	4		80 (**3ai**)
11[f]	**1a**	 **2j**	4		100 (**3aj**)
12	**1a**	 **2k**	4		78 (**3ak**)
13	**1a**	 **2l**	4		74 (**3al**)
14[g]	**1a**	 **2m**	7		94 (**3am**)
15	**1b**	**2b**	4	 Ar = 4-MeO–C_6H_4	96 (**3bb**)
16	**1c**	**2b**	6	4-F–C_6H_4	89 (**3cb**)
17	**1d**	**2b**	4	4-Br–C_6H_4	90 (**3db**)
18	**1e**	**2b**	6	4-NC–C_6H_4	93 (**3eb**)
19	**1f**	**2b**	18	4-(pin)B–C_6H_4	69 (**3fb**)
20[h]	**1g**	**2b**	4	2,4,6-Me_3–C_6H_2	85 (**3gb**)

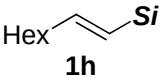
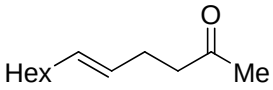
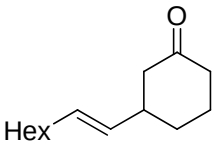
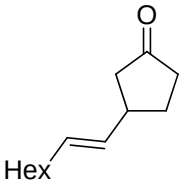
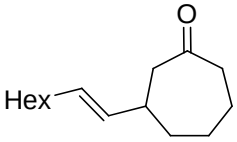
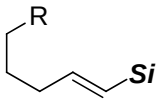
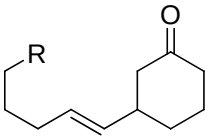
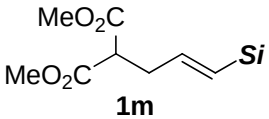
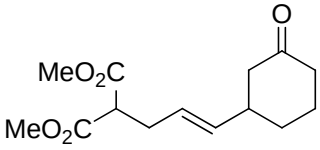
[a]Unless otherwise noted, all the reaction was carried out in THF (0.5 mL) using an arylsilane **1** (1.0 mmol) and an electron-deficient olefins **2** (1.0 mmol) in the presence of $[Rh(OH)(cod)]_2$ (1.0 mol% Rh) at 35 °C. [b]Isolated yields. [c]The reaction was carried out on a 10 mmol scale. [d]Cyclic silyl ether **4** was also isolated in 92% yield. [e]The reaction was carried out using $[Rh(OH)(cod)]_2$ (3.0 mol% Rh) at 50 °C. [f]The reaction was carried out using 1.2 mmol of **1a**. [g]The reaction was carried out using 1.3 mmol of **1a** at 60 °C. [h]The reaction was carried out using 1.5 mmol of **1g**.

The author then examined the 1,4-addition reaction using alkenylsilanes (Table 2). The reaction of (*E*)-[2-(hydroxymethyl)phenyl]dimethyl(1-octenyl)silane (**1h**) (1.0 mmol) with **2a** (1.0 mmol) in the presence of $[Rh(OH)(cod)]_2$ (1.0 mol% Rh) in THF at 35 °C gave the corresponding adduct **3ha** in 67% yield after 4 h (entry 1 of Table 2). The reaction of **1h** with **2b** proceeded successfully irrespective of its reaction scale (entries 2 and 3), and cyclic silyl ether **4** was again recovered in 80% yield (entry 3). Reusability of **4** for preparation of the alkenylsilane reagents has been demonstrated in Chapter 2. Cyclic enones, **2c** and **2d**, also underwent the 1,4-addition reaction of **1h** to give the corresponding adducts in good yields (entries 4 and 5). The author then surveyed the scope of alkenylsilanes, which were readily accessible by platinum-catalyzed hydrosilylation of the corresponding alkynes as demonstrated in Chapter 2. Excellent chemoselectivity was observed with (*E*)-alkenylsilanes having a functional group, such as cyano, ester, chloro, siloxy, malonate, phthalimide, or free hydroxy, giving rise to various 3-alkenylcyclohexanones in good yields (entries 6–12). Conjugated 1,3-dienylsilane **1p**, (*E*)-styrylsilane **1q**, and (*Z*)-propenylsilane **1r** added to **2b** with retention of the olefinic configuration (entries 13–15). (*Z*)-Styrylsilane (**1s**) also gave **3sb** as a major product (~95%) albeit being contaminated by a small amount (~5%) of its stereoisomer **3qb** (entry 16). The isomer would be derived from partial isomerization of (*Z*)-styrylrhodium intermediate via a plausible rhodium carbene species.[15] Ethenylsilanes having substituent(s) like 1-methyl, 1-phenyl, 2,2-dimethyl, and (*E*)-1,2-dipropyl participated in the reaction with **2b** with perfect regio- and stereospecificities in good yields (entries 17–20). Especially, successful addition of α-substituted vinylsilanes, **1t** and **1u**, is worth noting, because the corresponding vinylboronic acids are thermally unstable,[16] and thus have rarely been employed in the rhodium-catalyzed transformations.

Table 2. Rhodium-catalyzed 1,4-addition reactions of alkenyl[2-(hydroxymethyl)phenyl]dimethylsilanes to cyclic enones[a]

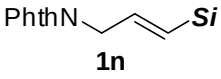
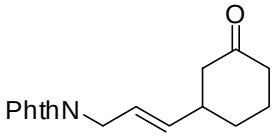
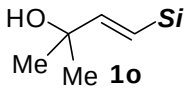
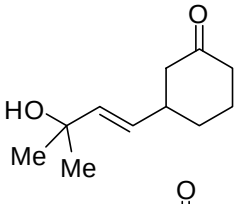
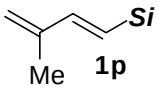
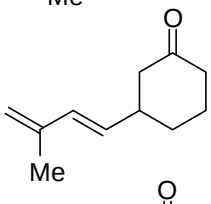
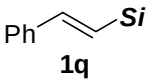
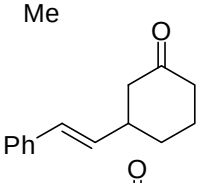
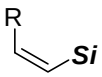
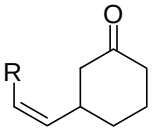
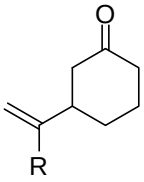
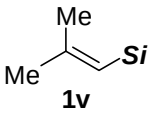
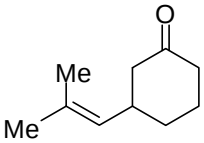
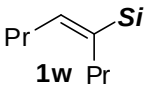
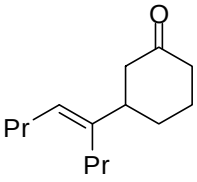


1 **2** **3** **4**

entry	1	2	time (h)	product	yield (%)[b]
1	 **1h**	**2a**	4		67 (**3ha**)
	1h				
2		**2b**	2		89 (**3hb**)
3[c]	**1h**	**2b**	5		79 (**3hb**)[d]
4	**1h**	**2c**	3		85 (**3hc**)
5	**1h**	**2d**	3		78 (**3hd**)
					
6	R = CN (**1i**)	**2b**	3	R = CN	87 (**3ib**)
7	CO_2Me (**1j**)	**2b**	3	CO_2Me	89 (**3jb**)
8	Cl (**1k**)	**2b**	3	Cl	92 (**3kb**)
9	OTBDMS (**1l**)	**2b**	3	OTBDMS	94 (**3lb**)
10	 **1m**	**2b**	6		91 (**3mb**)

(*continued to the next page*)

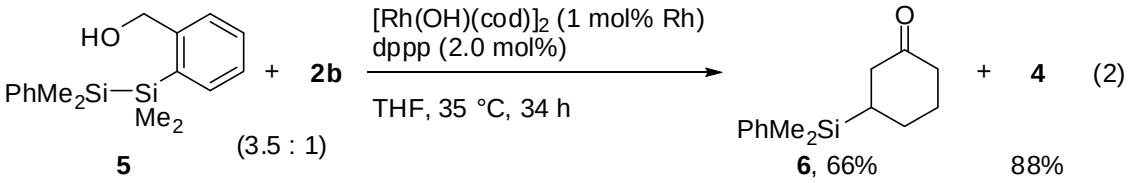
Table 2. (*continued*)

entry	1	2	time (h)	product	yield (%)[b]
11	 **1n**	**2b**	3		84 (**3nb**)
12	 **1o**	**2b**	3		81 (**3ob**)
13	 **1p**	**2b**	3		81 (**3pb**)
14	 **1q**	**2b**	3		87 (**3qb**)
					
15	R = Me (**1r**)	**2b**	3	R = Me	77 (**3rb**)
16	Ph (**1s**)	**2b**	3	Ph	94 (**3sb**)[e]
					
17	R = Me (**1t**)	**2b**	3	R = Me	75 (**3tb**)
18	Ph (**1u**)	**2b**	3	Ph	85 (**3ub**)
19	 **1v**	**2b**	3		79 (**3vb**)
20	 **1w**	**2b**	3		90 (**3wb**)

[a]Unless otherwise noted, all the reaction were carried out in THF (0.5 mL) using an alkenylsilane **1** (1.0 mmol) and an enone **2** (1.0 mmol) in the presence of $[Rh(OH)(cod)]_2$ (1.0 mol% Rh) at 35 °C. [b]Isolated yields. [c]The reaction was carried out on a 10 mmol scale. [d]Cyclic silyl ether **4** was also isolated in 80% yield. [e]Contaminated by 5% of **3qb**.

The author also applied the present protocol to 1,4-addition of a silyl group to

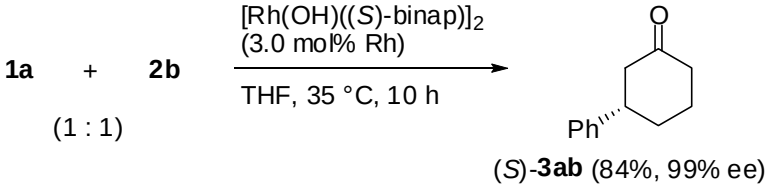
enones.[17] Disilane reagent **5** was prepared by the reaction of cyclic silyl ether **4** with dimethylphenylsilyllithium and was subjected to the reaction with **2b** using 1,3-bis(diphenylphosphino)propane (dppp) as a ligand (Eq. 2).[17a] Desired adduct **6** was obtained in a moderate yield, although extra loading of **5** (3.5 molar equivalents to **2b**) was necessary due to competitive protonolysis of the dimethylphenylsilyl group of **5** leading to dimethylphenylsilane as a byproduct. The formation of silicon residue **4** was confirmed by GC analysis of the crude mixture.



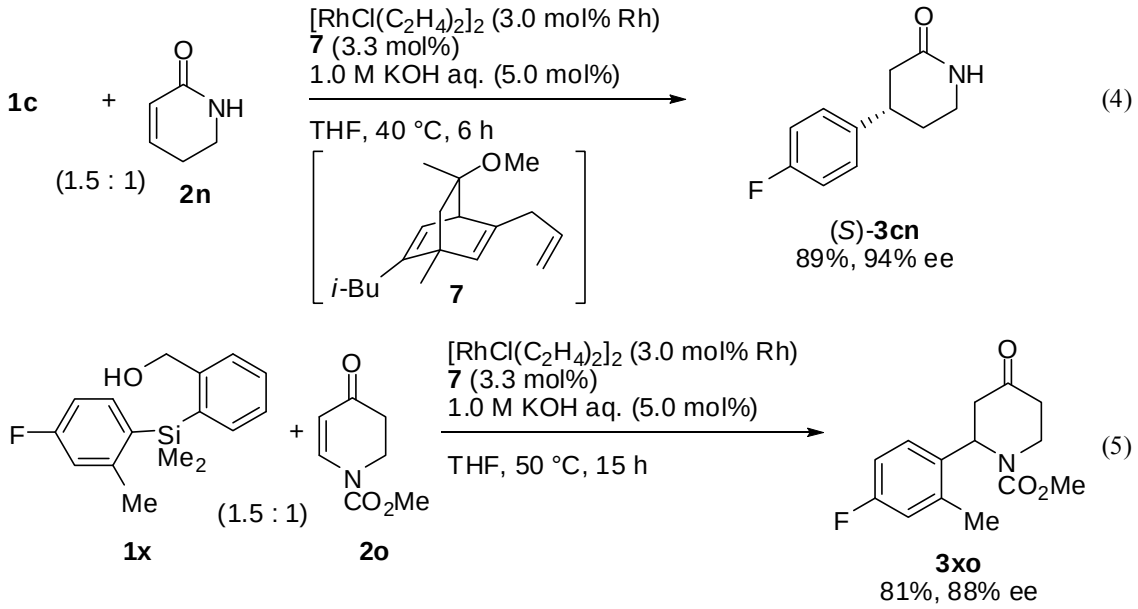
(2)

Enantioselective 1,4-addition reactions of aryl[2-(hydroxymethyl)phenyl]dimethylsilanes.

The success with the 1,4-addition reactions of the silicon reagents under mild reaction conditions encouraged the author to turn his attention to the application of **1** to asymmetric synthesis. Using [Rh(OH)((*S*)-binap)]$_2$[18] as a catalyst, the enantioselective addition of **1a** to **2b** was readily achieved to give (*S*)-**3ab** of 99% ee in 84% yield (Eq. 3). The recent innovation in the highly reactive and enantioselective rhodium-catalysis with chiral diene ligands[19–21] also prompted him to utilize this chemistry for the asymmetric transformations using **1**. Thus, the reaction of phenylsilane **1c** or **1x** with nitrogen-containing substrates **2n** or **2o** in the presence of [RhCl(C_2H_4)]$_2$ (1.0 mol% Rh), Carreira's chiral diene ligand **7**[21a-d] (1.1 mol%), and a 1.0 M aq. solution of KOH (5 mol%) in THF gave optically active substituted piperidones, (*S*)-**3cn**[22] and **3xo**[7], in highly enantioselective manners, respectively (Eqs. 4 and 5). The absolute configuration of **3xo** was not further determined. (*R*)-**3cn** is the synthetic intermediate of (–)-paroxetine, whereas (*R*)-**3xo** serves as that of a tachykinin antagonist developed by Glaxo Group Ltd., UK.

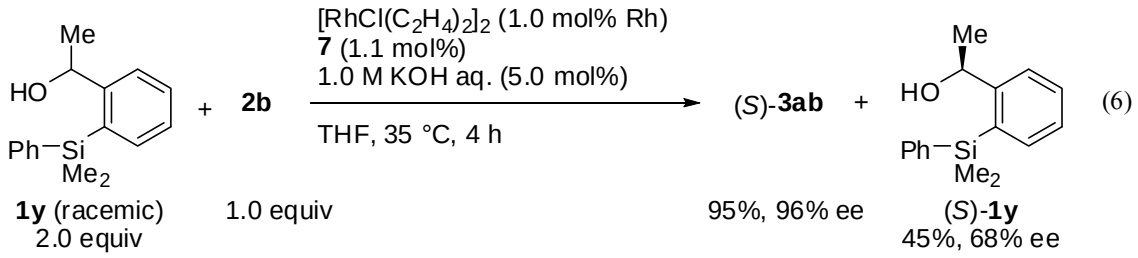


(3)

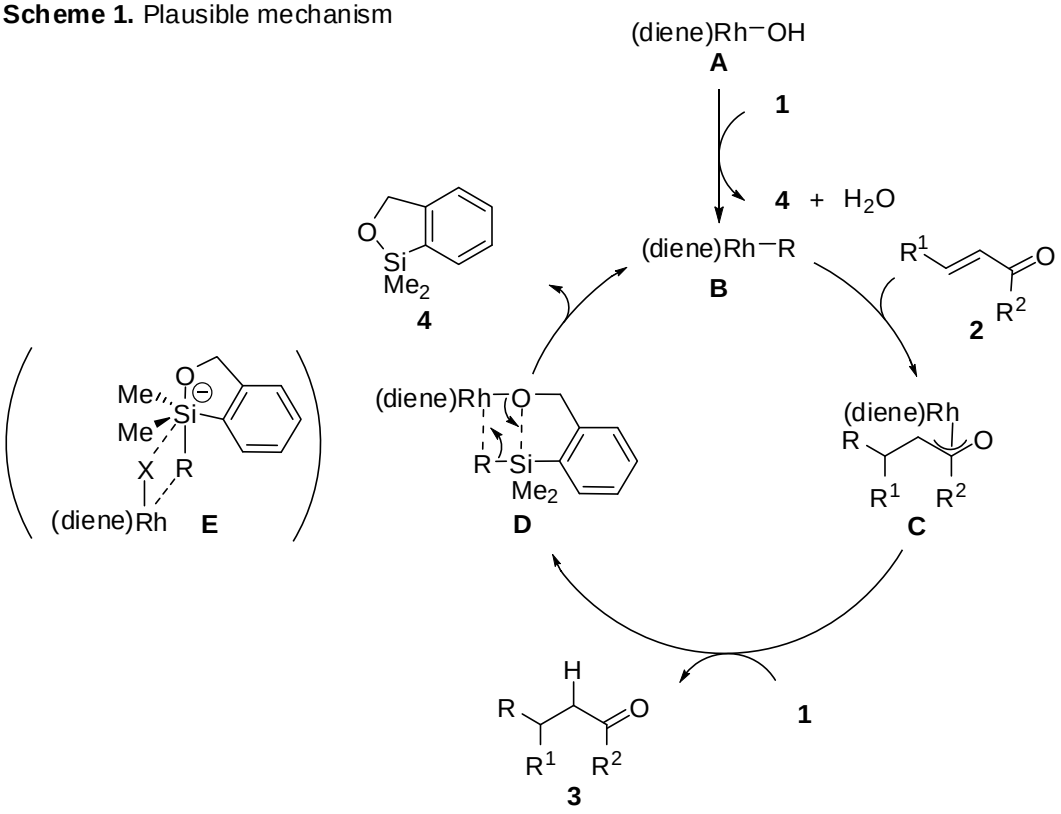


2.3 Reaction mechanism.

The catalytic cycle of the present reaction should be initiated by the reaction of rhodium hydroxide **A** with silane reagent **1** to give organorhodium intermediate **B**. Michael addition of the R group in **B** to an enone gives rhodium enolate **C**,[18] which acts as a base and reacts with **1** to give adduct **3** and rhodium alkoxide **D**. Transmetalation of R from silicon to rhodium would take place by the aid of the proximal hydroxy group to regenerate **B** and to complete the catalytic cycle. To gain a mechanistic insight into the transmetalation step, the author examined the enantioselective addition of 2.0 molar equivalents of racemic chiral phenylsilane reagent **1y** to **2b** using Carreira's chiral diene ligand **7** to give the corresponding adduct (*S*)-**3yb** of 96% ee in 95% yield, and unreacted (S)-**1y** of 68% ee ($[\alpha]^{26}_{D}$ –32.0; *c* 1.00, $CHCl_3$) was recovered in 45% yield based on the amount of loaded **1y** (Eq. 6). The absolute configuration has been determined based on the optical rotation compared with that of authentic (*S*)-**1y** ($[\alpha]^{20}$D –52.6; *c* 1.02, $CHCl_3$), synthesized from commercially available (*S*)-2-bromo-α-methyl-benzylalcohol. The observed kinetic resolution of **1y** appears to support that rhodium alkoxide species **D** would be responsible for the transmetalation step, recognizing the chirality of **1y** effectively by the optically pure diene ligand. Transfer of the R group via pentacoordinate silicate intermediate **E** is anothor possibility in this particular transformation.[23]



Scheme 1. Plausible mechanism

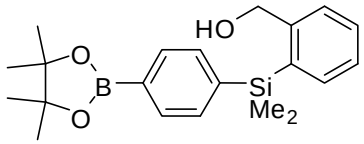


3. Conclusion

In summary, the author has demonstrated that organo[2-(hydroxymethyl)phenyl]dimethylsilanes serve as efficient reagents for the rhodium-catalyzed 1,4-addition reactions. All the reactions proceed in high chemoselective manners under mild conditions in good yields using equimolar amounts of the silane reagents in most cases. Ready accessibility and high stability toward acid, base, and moisture of the present tetraorganosilicon compounds compared to conventional ones definitely present the characteristic features of the silane reagents as an attractive alternative to organoboron reagents.

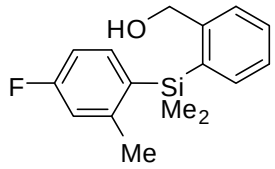
4. Experimental section

Chemicals. Unless otherwise described below, organo[2-(hydroxymethyl)phenyl]dimethylsilanes were described in Chapters 2 and 3. (*E*)-4-(Dimethylphenylsilyl)-3-buten-2-one (**2e**),[24] *N*-methoxy-*N*-methyl-2-butenamide (**2j**),[20c] Carreira's chiral diene ligand **7**[21b] 5,6-dihydro-2(1*H*)-pyridone (**2p**),[25] and 3,4-dihydro-4-oxo-1(2*H*)-pyridinecarboxylic acid benzyl ester (**2q**)[26] were prepared according to the reported procedures.



1f

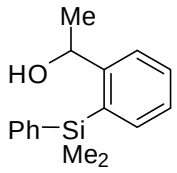
[2-(Hydroxymethyl)phenyl]dimethyl[4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl]silane (1f). To a solution of 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)iodobenzene (2.2 g, 6.8 mmol) in THF (14 mL) was added a 1.0 M solution of *i*-PrMgCl・LiCl (11 mL, 11 mmol) at –78 °C, and the resulting mixture was stirred for 4 h. To a solution of 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenylmagnesium chloride[27] thus prepared was added **4** (1.1 g, 6.8 mmol) over 30 min, and the whole was stirred for 2 h at –78 °C and then at rt overnight. After a standard work-up procedure and purification by flash chromatography on silica gel, **1f** was obtained (1.7 g, 67%) as a colorless solid, mp 93.7–95.3 °C, R_f 0.21 (hexane–ethyl acetate = 5 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 7.0 Hz, 2H), 7.62–7.39 (m, 5H), 7.38–7.26 (m, 1H), 4.52 (s, 2H), 1.52 (br s, 1H), 1.34 (s, 12H), 0.60 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.6, 142.7, 135.59, 135.53, 134.1, 133.1, 130.0, 128.0, 127.0, 83.8, 65.2, 24.8, –1.2; IR (KBr) 3483, 2980, 1601, 1385, 1360, 1315, 1296, 1144, 1070, 856, 810, 777, 750, 660 cm^{-1}. Anal. Calcd for $C_{21}H_{29}BO_3Si$; C, 68.47; H, 7.94. Found: C, 68.19; H, 7.76.



1x

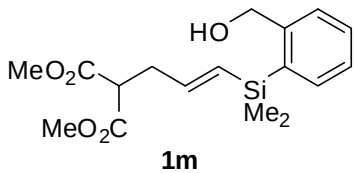
[2-(Hydroxymethyl)phenyl]dimethyl(4-fluoro-2-methylphenyl)silane (1x). A solution of 2-bromo-5-fluorotoluene (2.5 g, 13.2 mmol) in THF (13 mL) was added dropwise to Mg turnings (0.33 g, 13.4 mmol) at rt, and the resulting mixture was heated

to reflux for 30 min. To this was added a solution of **4** (1.97 g, 12 mmol) in THF (12 mL) at 0 °C, and the resulting mixture was stirred at rt overnight. A standard work-up procedure followed by purification by flash chromatography on silica gel gave **1x** (2.8 g, 85%) as a white solid, mp 38.1–39.1 °C, R_f 0.54 (hexane–ethyl acetate = 2 : 1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65–7.38 (m, 4H), 7.36–7.28 (m, 1H), 6.97–6.81 (m, 2H), 4.47 (s, 2H), 2.16 (s, 3H), 1.38 (br s, 1H), 0.62 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.9 (d, J = 248.4 Hz), 146.6 (d, J = 6.9 Hz), 146.2, 136.5 (d, J = 7.7 Hz), 136.3, 135.0, 132.5 (d, J = 3.0 Hz), 129.9, 128.0, 127.2, 117.0 (d, J = 19.2 Hz), 112.3 (d, J = 19.2 Hz), 65.1, 22.8 (d, J = 1.5 Hz), –0.5; IR (KBr) 3373, 3057, 2959, 2918, 1593, 1578, 1481, 1435, 1279, 1256, 1223, 1078, 1030, 951, 835, 812.0, 775, 756 cm^{-1}. Anal. Calcd for $C_{16}H_{19}FOSi$; C, 70.03; H, 6.98. Found: C, 69.90; H, 6.97.



1y

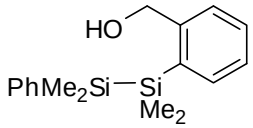
[2-(1-Hydroxyethyl)phenyl]dimethyl(phenyl)silane (1y). Following the procedure for **1b**, the reaction using a 1.0 M solution of phenylmagnesium bromide in THF (22 mL, 22 mmol) and 1,1,3-trimethyl-2-oxa-1-silaindan (prepared in a similar manner as **4**, 3.6 g, 20 mmol) gave **1y** (5.1 g, 99%) as a colorless oil, R_f 0.38 (hexane–ethyl acetate = 5 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63–7.44 (m, 5H), 7.41–7.28 (m, 4H), 4.96 (q, J = 6.3 Hz, 1H), 1.57 (br s, 1H), 1.26 (d, J = 6.3 Hz, 3H), 0.62 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.8, 139.1, 135.1, 134.7, 133.7, 130.3, 129.2, 128.0, 127.0, 125.5, 69.5, 24.4, –0.7, –0.8; IR (neat) 3383, 2970, 1429, 1258, 1107, 1070, 835, 816, 768, 733, 702 cm^{-1}. Anal. Calcd for $C_{16}H_{20}OSi$; C, 74.95; H, 7.86. Found: C, 74.69; H, 7.92.



1m

(*E*)-[4-Bis(methoxycarbonyl)-1-buten-1-yl]dimethylsilane (1m). To a solution of dimethyl[2-(2-tetrahydro-2*H*-pyranoxymethyl)phenyl]silane (3.8 g, 15 mmol) and dimethyl propargylmalonate (2.6 g, 15 mmol) in hexane (1.5 mL) were added a 10%

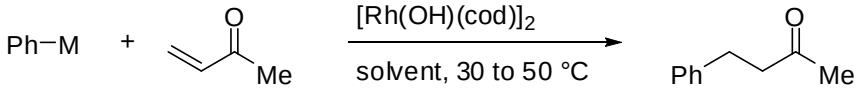
hexane solution of *t*-Bu_3P (30 mg, 0.015 mmol) and a 0.01 M hexane solution of platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex (1.5 mL, 0.015 mmol) at 0 °C. The resulting mixture was stirred at rt for 10 h, filtered through a Florisil pad, and concentrated in vacuo. The residue was dissolved in MeOH (60 mL) and treated with *p*-toluenesulfonic acid monohydrate (57 mg, 0.30 mmol) at rt for 14 h. After removal of the solvent in vacuo, the residue was purified by flash chromatography on silica gel to give **1m** (3.0 g, 59%) as a colorless oil, R_f 0.15 (hexane–ethyl acetate = 3 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55–7.44 (m, 2H), 7.39 (td, *J* = 7.5, 1.3 Hz, 1H), 7.27 (td, *J* = 7.4, 0.9 Hz, 1H), 6.03 (dt, *J* = 18.7, 5.8 Hz, 1H), 5.94 (d, *J* = 18.7 Hz, 1H), 4.69 (s, 2H), 3.69, (s, 6H), 3.51 (t, *J* = 7.5 Hz, 1H), 2.73 (t, *J* = 6.6 Hz, 2H), 2.04, (br s, 1H), 0.37 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.3, 146.7, 143.0, 135.9, 135.0, 132.6, 129.7, 127.7, 126.9, 65.0, 52.6, 51.0, 35.4, –1.4; IR (neat) 3422, 2953, 1751, 1736, 1684, 1653, 1437, 1250, 1225, 1202, 1151, 827, 750 cm^{-1}. Anal. Calcd for $C_{17}H_{24}O_5Si$; C, 60.69; H, 7.19. Found: C, 60.83; H, 7.25.



5

1-[2-(Hydroxymethyl)phenyl]-1,1,2,2-tetramethyl-2-phenyldisilane (5). To a solution of **4** (3.4 g, 21 mmol) in THF (5 mL) was added a solution of dimethylphenylsilyllithium in THF (15 mL)[28] prepared from chlorodimethylphenylsilane (3.4 g, 20 mmol) and lithium (0.49 g, 70 mmol) at 0 °C. The resulting mixture was stirred at rt overnight, then diluted with diethyl ether, and quenched with a sat. NH_4Cl aq. solution at –78 °C. The aq. layer was extracted with diethyl ether, and the combined organic layer was washed with water and brine and dried over anhydrous $MgSO_4$. After concentration in vacuo, the residue was purified by flash chromatography on silica gel to afford **5** (3.0 g, 50%) as a pale yellow oil, R_f 0.23 (hexane–ethyl acetate = 10 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46–7.22 (m, 9H), 4.38 (s, 2H), 0.40 (s, 6H), 0.34 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.4, 139.1, 136.4, 134.7, 133.8, 129.2, 128.5, 127.8, 127.4, 126.9, 65.7, –2.1, –3.7; IR (neat) 3356, 3051, 2951, 2893, 1427, 1246, 1105, 833, 793, 762, 733, 698 cm^{-1}. Anal. Calcd for $C_{17}H_{24}OSi_2$; C, 67.94; H, 8.05. Found: C, 68.04; H, 7.97.

Kinetic Study on the Reactions below Using Reaction Calorimetry



Reactions were performed in an Omnical SuperCRC reaction calorimeter. The instrument contains a differential scanning calorimeter (DSC), which compares the heat released or consumed in a sample vessel to a reference vessel. The reaction vessels were 16 mL borosilicate screw-thread vials fit with opentop black phenolic screw caps and white PTFE septa charged with Teflon stir bars. Sample volumes did not exceed 3.5 mL. In a typical calorimetry experiment, a reaction vessel containing a solution of $[Rh(OH)(cod)]_2$ (2.06 mg, 9.03 μmol Rh) in a solvent (2.2 mL) was placed in the calorimeter and stirred for over 30 min, allowing the contents of the vessel to reach thermal equilibrium. The vessel containing the same amount of the solvent (2.2 mL) was prepared as a reference vessel. A syringe containing a solution of phenylmetal reagent (0.225 mmol) and methyl vinyl ketone (56.2 μL, 0.675 mmol) in the solvent (1.1 mL) was placed in the sample injection port of the calorimeter for the reaction vessel and a syringe containing the same chemical was placed in the sample injection port of the calorimeter for the reference vessel. These two syringes were allowed to thermally equilibrate. The reaction was initiated by injecting the solution of the phenylmetal reagent and methyl vinyl ketone into the reaction and the reference vessels at the same time. The temperature of the DSC was held constant at 30 or 50 °C using Titec CL-150F (water circulator), ensuring that the reaction would proceed under isothermal conditions. A raw data curve was produced by measuring the heat flow from the sample vessel every 3 seconds during the reaction. Due to the delay between the instantaneous moment heat is evolved from the reaction vessel and the time the thermophile sensor detects the heat flow, the raw data curve must be calibrated. To accomplish this calibration, a constant amount of current was passed through a resistor in the sample chamber of the calorimeter thereby producing a known quantity of heat. This process results in a response curve, which is then transformed into a square wave allowing for the response time of the instrument to be calculated using the WinCRC software. Application of the response time to the raw data results in a "tau corrected data curve." The tau corrected data curve is a plot of heat flow (mJ/s) versus time. The reaction rate, which is directly proportional to the heat flow (eq 1), fraction conversion

(eq 2) and instantaneous concentrations of reactants/products can all be calculated from this tau corrected data curve.

$$q = \Delta H_{rxn} \cdot V \cdot v \qquad (1)$$

where q is the reaction heat flow, ΔH_{rxn} is the heat of reaction, V is the reaction volume, and v is the reaction rate.

$$conversion = \frac{\int_0^t q(t)dt}{\int_0^{tf} q(t)dt} \qquad (2)$$

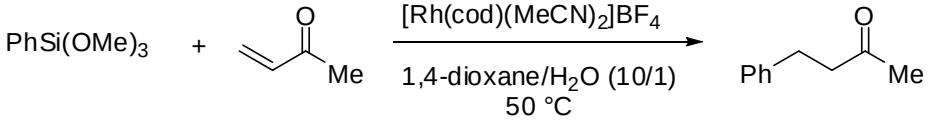
The numerator represents the area under the heat flow to any time point t and the denominator represents the total area under the heat flow curve.

$PhB(OH)_2$ as the nucleophile at 30 °C: the reaction was in 1,4-dioxane/H_2O (10/1) in the presence of $B(OH)_3$ (111 mg, 1.80 mmol).

1r as the nucleophile at 30 °C: the reaction was performed in THF.

1r as the nucleophile at 50 °C: the reaction was performed in 1,4-dioxane.

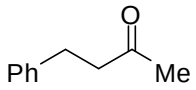
Experimental Procedure for Kinetic Studies Using ^{1}H NMR



Methyl vinyl ketone (56.2 μL, 0.675 mmol) and phenyl(trimethoxy)silane (42.0 μL, 0.225 mmol) were added to a solution of $[Rh(cod)(MeCN)_2]BF_4$ (3.4 mg, 9.0 μmol Rh) in 1,4-dioxane (3.0 mL) and H_2O (0.30 mL). The mixture was stirred at 50 °C for 30 min, 90 min, or 180 min, and then passed through a pad of silica gel with EtOAc. After removing the solvent under vacuum, yield was estimated by ^{1}H NMR using $MeNO_2$ as an internal standard.

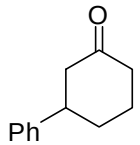
Rhodium-catalyzed 1,4-addition of organo[2-(hydroxymethyl)phenyl]dimethyl-silanes. *A general procedure.* To a solution of $[Rh(OH)(cod)]_2$ (2.3 mg, 5.0 μmol) in

THF (0.5 mL) were added an organosilane **1** (1.00 mmol) and an enone **2** (1.00 mmol) sequentially, and the resulting mixture was stirred at 35 °C. After the time specified in Tables 1 and 2, the mixture was filtered through a silica gel pad, and the filtrate was concentrated in vacuo. The residue was purified by flash chromatography on silica gel to afford the corresponding adduct **3** in a yield listed in Tables 1 and 2.



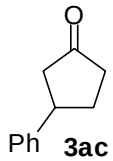
3aa

4-Phenylbutan-2-one (3aa).[29] A colorless oil, R_f 0.36 (hexane–ethyl acetate = 5 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31–7.25 (m, 2H), 7.22–7.16 (m, 3H), 2.90 (t, *J* = 7.7 Hz, 1H), 2.76 (t, *J* = 7.5 Hz, 1H), 2.14 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 207.9, 141.0, 128.5, 128.3, 126.1, 45.2, 30.1, 29.7.



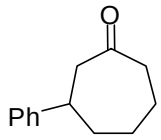
3ab

3-Phenylcyclohexanone (3ab).[18a] A colorless oil, R_f 0.26 (hexane–ethyl acetate = 5 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37–7.30 (m, 2H), 7.27–7.20 (m, 3H), 3.07–2.95 (m, 1H), 2.64–2.32 (m, 4H), 2.21–2.05 (m, 2H), 1.92–1.72 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 211.1, 144.3, 128.7, 126.7, 126.6, 48.9, 44.7, 41.2, 32.8, 25.5.



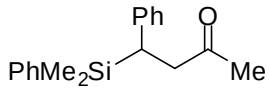
3ac

3-Phenylcyclopentanone (3ac).[18a] A colorless oil, R_f 0.28 (hexane–ethyl acetate = 5 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38–7.30 (m, 2H), 7.29–7.21 (m, 3H), 3.49–3.35 (m, 1H), 2.67 (dd, *J* = 18.2, 7.4 Hz, 1H), 2.54–2.22 (m, 4H), 2.06–1.91 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 218.4, 143.0, 128.7, 126.7, 45.8, 42.2, 38.9, 31.2.



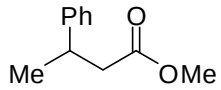
3ad

3-Phenylcycloheptanone (3ad).[18a] A colorless oil, R_f 0.31 (hexane–ethyl acetate = 5 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34–7.26 (m, 2H), 7.23–7.15 (m, 3H), 2.98–2.85 (m, 2H), 2.71–2.52 (m, 3H), 2.14–1.94 (m, 3H), 1.80–1.64 (m, 2H), 1.62–1.42 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 213.5, 146.9, 128.6, 126.4, 126.3, 51.2, 43.9, 42.7, 39.2, 29.2, 24.2.



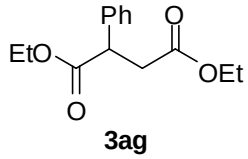
3ae

4-(Dimethylphenylsilyl)-4-phenylbutan-2-one (3ae).[20e] A pale yellow oil, R_f 0.43 (hexane–ethyl acetate = 5 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42–7.30 (m, 5H), 7.19 (t, *J* = 7.5 Hz, 2H), 7.08 (tt, *J* = 7.3, 1.4 Hz, 1H), 6.96–6.91 (m, 2H), 2.96–2.83 (m, 2H), 2.69–2.57 (m, 1H), 1.94 (s, 3H), 0.24 (s, 3H), 0.21 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 208.2, 142.0, 136.6, 134.1, 129.3, 128.2, 127.7, 127.5, 124.9, 43.9, 31.4, 30.0, –4.1, –5.4.



3af

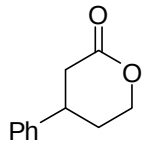
Methyl 3-phenylbutanoate (3af).[30] A colorless oil, R_f 0.34 (hexane–ethyl acetate = 5 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34–7.27 (m, 2H), 7.25–7.17 (m, 3H), 3.63 (s, 3H), 3.28 (sext, *J* = 7.2 Hz, 1H), 2.63 (dd, *J* = 15.2, 7.2 Hz, 1H), 2.55 (dd, *J* = 15.2, 8.2 Hz, 1H), 1.30 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.8, 145.7, 128.5, 126.7, 126.4, 51.5, 42.7, 36.4, 21.8.



3ag

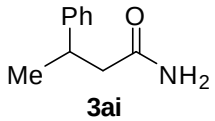
Diethyl phenylsuccinate (3ag).[31] A colorless oil, R_f 0.43 (hexane–ethyl acetate = 5 :).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35–7.24 (m, 5H), 4.22–4.03 (m, 5H), 3.18 (dd, *J* = 16.8, 10.2 Hz, 1H), 2.65 (dd, *J* = 16.8, 5.3 Hz, 1H), 1.22 (t, *J* = 7.1 Hz, 3H), 1.20 (t, *J* = 7.1, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.9, 171.5, 137.8, 128.8, 127.7, 127.5, 61.1, 60.7, 47.2, 37.8, 14.1, 14.0.



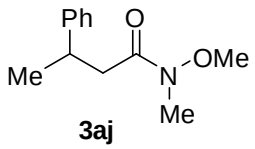
3ah

4-Phenyl-tetrahydro-2*H*-pyran-2-one (3ah).[32] A colorless oil, R_f 0.44 (hexane–ethyl acetate = 1 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41–7.17 (m, 5H), 4.51 (ddd, *J* = 11.3, 4.8, 3.8 Hz, 1H), 4.39 (ddd, *J* = 11.3, 10.4, 3.9 Hz, 1H), 3.30–3.18 (m, 1H), 2.92 (ddd, *J* = 17.6, 5.8, 1.6 Hz, 1H), 2.64 (dd, *J* = 17.6, 10.6 Hz, 1H), 2.24–2.14 (m, 1H), 2.11–1.98 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.7, 142.7, 129.0, 127.2, 126.4, 68.6, 37.5, 37.4, 30.3.



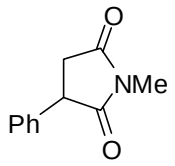
3ai

3-Phenylbutanamide (3ai).[33] A colorless solid, mp 107.7–109.4 °C (lit.[18] 103–104 °C), R_f 0.19 (ethyl acetate). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35–7.18 (m, 5H), 5.27 (br, 2H), 3.29 (sext, *J* = 7.2 Hz, 1H), 2.52 (dd, *J* = 9.9, 7.4 Hz, 1H), 2.44 (dd, *J* = 14.3, 7.4, 1H), 1.34 (d, *J* = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.0, 145.7, 128.6, 126.7, 126.5, 44.8, 36.8, 21.8.



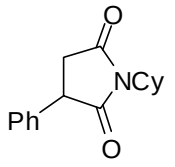
3aj

***N*-Methoxy-*N*-methyl-3-phenylbutanamide (3aj)**.[20c] A pale yellow oil, R_f 0.38 (hexane–ethyl acetate = 1 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34–7.16 (m, 5H), 3.58 (s, 3H), 3.38 (sext, *J* = 7.1 Hz, 1H), 3.14 (s, 3H), 2.74 (br dd, *J* = 15.2, 6.2 Hz, 1H), 2.65 (br dd, *J* = 15.2, 8.2 Hz, 1H), 1.32 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.1, 146.5, 128.4, 127.6, 126.94, 126.87, 126.2, 61.1, 40.3, 35.8, 32.1, 21.6.



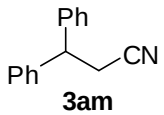
3ak

***N*-Methylphenylsuccinimide (3ak)**.[19b] A pale yellow solid, mp 67.9–69.0 °C (lit.[34] 71–73 °C), R_f 0.50 (hexane–ethyl acetate = 1 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41–7.28 (m, 3H), 7.25–7.19 (m, 2H), 4.03 (dd, *J* = 9.5, 4.8 Hz, 1H), 3.21 (dd, *J* = 18.4, 9.5 Hz, 1H), 3.07 (s, 3H), 2.84 (dd, *J* = 18.4, 4.8 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.8, 176.2, 137.0, 129.2, 128.0, 127.4, 45.9, 37.1, 25.2.



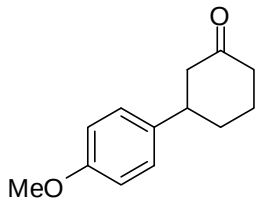
3al

***N*-Cyclohexyl-2-phenylsuccinimide (3al)**.[19b] A colorless solid, mp 84.5–85.1 °C, R_f 0.29 (hexane–ethyl acetate = 5 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40–7.27 (m, 3H), 7.22–7.16 (m, 2H), 4.04 (tt, *J* = 12.4, 3.8, 1H), 3.93 (dd, *J* = 9.7, 4.6 Hz, 1H), 3.14 (dd, *J* = 18.4, 9.7 Hz, 1H), 2.75 (dd, *J* =18.4, 4.6 Hz, 1H), 2.27–2.10 (m, 2H), 1.94–1.76 (m, 2H), 1.74–1.55 (m, 3H), 1.42–1.14 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.8, 176.4, 137.8, 129.2, 127.8, 127.2, 52.0, 45.5, 37.1, 28.9, 28.7, 25.82, 25.80, 25.0.



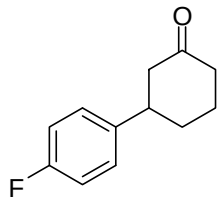
3am

3,3-Diphenylpropanitrile (3am). A colorless solid, mp 85.1–86.7 °C (lit.[35] 87–90 °C), R_f 0.25 (hexane–ethyl acetate = 10 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38–7.31 (m, 4H), 7.30–7.21 (m, 6H), 4.39 (t, *J* = 7.7 Hz, 1H), 3.05 (d, *J* = 7.7 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.2, 128.9, 127.5, 127.4, 118.4, 47.1, 24.2; IR (KBr): 3055, 3024, 2245, 1495, 1456, 1447, 1427, 1086, 783, 754, 739, 704, 635, 592, 507 cm^{-1}. Anal. Calcd for $C_{15}H_{13}N$: C, 86.92; H, 6.32. Found: C, 86.76; H, 6.36.



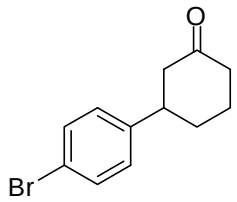
3bb

3-(4-Methoxyphenyl)cyclohexanone (3bb).[36] A pale yellow solid, mp 43.4–44.4 °C, R_f 0.23 (hexane–ethyl acetate = 5 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14 (d, *J* = 8.7 Hz, 2H), 6.87 (d, *J* = 8.7 Hz, 2H), 3.80 (s, 3H), 3.02–2.89 (m, 1H), 2.62–2.29 (m, 4H), 2.20–1.99 (m, 2H), 1.88–1.68 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 211.2, 158.2, 136.6, 127.5, 114.0, 55.3, 49.2, 44.0, 41.2, 33.0, 25.5.



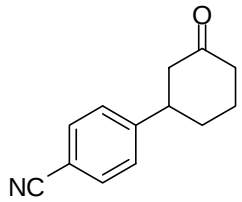
3cb

3-(4-Fluorophenyl)cyclohexanone (3cb).[3g] A yellow oil, R_f 0.29 (hexane–ethyl acetate = 5 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22–7.13 (m, 2H), 7.05–6.97 (m, 2H), 3.07–2.93 (m, 1H), 2.64–2.30 (m, 4H), 2.22–2.00 (m 2H), 1.89–1.70 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 210.7, 161.5 (d, *J* = 246.6 Hz), 140.0 (d, *J* = 3.1 Hz), 128.0 (d, *J* = 7.7 Hz), 115.4 (d, *J* = 20.7 Hz), 49.1, 44.0, 41.1, 32.9, 25.4.



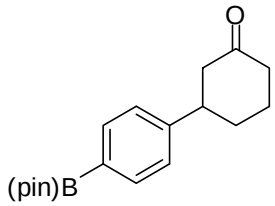
3db

3-(4-Bromophenyl)cyclohexanone (3db). A pale yellow oil, R_f 0.24 (hexane–ethyl acetate = 5 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.3 Hz, 2H), 7.09 (d, *J* = 8.3 Hz, 2H), 3.05–2.91 (m, 1H), 2.64–2.29 (m, 4H), 2.22–2.00 (m, 2H), 1.90–1.70 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 210.5, 143.2, 131.7, 128.3, 120.4, 48.7, 44.1, 41.1, 32.6, 25.4; IR (neat): 2937, 2864, 1713, 1489, 1223, 1074, 1009, 822 cm^{-1}. Anal. Calcd for $C_{12}H_{13}BrO$: C, 56.94; H, 5.18. Found: C, 56.66; H, 5.16.



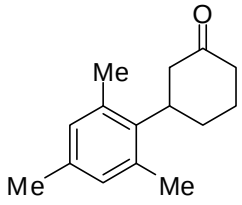
3eb

[3-(4-Cyanophenyl)cyclohexanone (3eb).[37] A pale yellow solid, mp 38.4–39.4 °C, R_f 0.28 (hexane–ethyl acetate = 2 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.3 Hz, 2H), 7.33 (d, *J* = 8.3 Hz, 2H), 3.15–3.00 (m, 1H), 2.64–2.30 (m, 4H), 2.24–2.01 (m, 2H), 1.93–1.71 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 209.7, 149.5, 132.5, 127.4, 118.7, 110.6, 48.1, 44.6, 41.0, 32.2, 25.2.



3fb

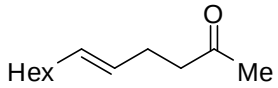
3-[4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl]cyclohexanone (3fb). A colorless solid, mp 86.4–88.3 °C, R_f 0.24 (hexane–ethyl acetate = 5 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.1 Hz, 2H), 7.24 (d, *J* = 8.1 Hz, 2H), 3.09–2.93 (m, 1H), 2.64–2.30 (m, 4H), 2.21–2.02 (m, 2H), 1.94–1.68 (m, 2H), 1.34 (s, 12H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 210.9, 147.5, 135.2, 126.0, 114.6, 83.8, 48.7, 44.9, 41.2, 32.6, 25.6, 24.8; IR (KBr): 2980, 2932, 2862, 1713, 1611, 1393, 1360, 1323, 1146, 1088, 860, 658 cm^{-1}. HRMS (EI) Calcd for $C_{18}H_{25}BO_3$: M^+, 300.1897. Found: *m/z* 300.1902.



3gb

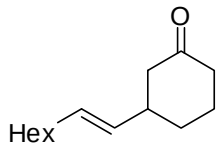
3-(2,4,6-Trimethylphenyl)cyclohexanone (3gb). A colorless solid, mp 48.7–49.7 °C, R_f 0.26 (hexane–ethyl acetate = 7 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.84 (s, 2H), 3.40 (tt, *J* = 13.8, 4.0 Hz, 1H), 2.94 (t, *J* = 13.8 Hz, 1H), 2.62–2.00 (m, 5H), 2.24 (s, 9H), 1.94–1.65 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 211.2, 136.4, 136.0 (br), 135.8, 45.7,

41.5, 40.7, 29.1, 26.3, 21.7 (br), 20.6; IR (KBr): 2951, 2864, 1705, 1611, 1481, 1448, 1420, 1342, 1306, 1219, 853, 573, 503 cm^{-1}. Anal. Calcd for $C_{15}H_{20}O$: C, 83.28; H, 9.32. Found: C, 83.58; H, 9.62.



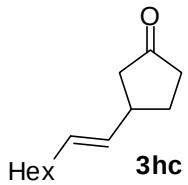
3ha

(*E*)-5-Dodecen-2-one (3ha).[38] A colorless oil, R_f 0.32 (hexane–ethyl acetate = 5 : 1). ^1H NMR (400 MHz, $CDCl_3$) δ 5.49–5.31 (m, 2H), 2.48 (t, *J* = 7.3 Hz, 2H), 2.25 (dt, *J* = 7.1, 6.8 Hz, 2H), 2.13 (s, 3H), 1.95 (dt, *J* = 7.0, 6.5 Hz, 2H), 1.37–1.18 (m, 8H), 0.87 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 208.7, 131.6, 128.1, 43.6, 32.5, 31.7, 29.9, 29.4, 28.8, 26.8, 22.6, 14.1.



3hb

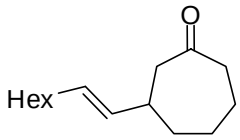
(*E*)-3-(1-Octen-1-yl)cyclohexanone (3hb). A colorless oil, R_f 0.35 (hexane–ethyl acetate = 10 : 1). ^1H NMR (400 MHz, $CDCl_3$) δ 5.54–5.38 (m, 2H), 2.85–2.73 (m, 1H), 2.42–2.24 (m, 2H), 2.21–2.19 (m, 2H), 2.05–1.94 (m, 3H), 1.77–1.62 (m, 1H), 1.40–1.18 (m, 8H), 0.93–0.82 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 219.4, 131.9, 130.7, 45.0, 39.8, 38.2, 32.5, 31.7, 30.0, 29.3, 28.8, 22.6, 14.1; IR (neat) 2957, 2926, 2855, 1744, 1458, 1404, 1377, 1277, 1232, 1157, 1094, 968, 756, 725 cm^{-1}. Anal. Calcd for $C_{14}H_{24}O$; C, 80.71; H, 11.61. Found: C, 80.93; H, 11.74.



3hc

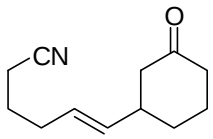
(*E*)-3-(1-Octen-1-yl)cyclopentanone (3hc). A colorless oil, R_f 0.30 (hexane–ethyl acetate = 10 : 1). ^1H NMR (400 MHz, $CDCl_3$) δ 5.47–5.32 (m, 2H), 2.50–2.13 (m, 5H), 2.08–1.94 (m, 3H), 1.93–1.85 (m, 1H), 1.74– 1.61 (m, 1H), 1.54–1.42 (m, 1H), 1.38–1.21 (m, 8H), 0.88 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 211.6, 132.9,

130.0, 47.7, 41.6, 41.3, 32.5, 31.7, 31.6, 29.3, 28.7, 25.0, 22.6, 14.1; IR (neat) 2926, 2855, 1715, 1448, 1421, 1344, 1313, 1223, 966 cm^{-1}. HRMS (EI) Calcd for $C_{13}H_{22}O$: M^+, 194.1670. Found: *m/z* 194.1673.



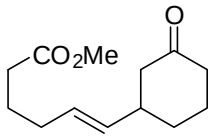
3hd

(*E*)-3-(1-Octen-1-yl)cycloheptanone (3hd). A colorless oil, R_f 0.38 (hexane–ethyl acetate = 10 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.45–5.31 (m, 2H), 2.58–2.45 (m, 4H), 2.38–2.28 (m, 1H), 1.99–1.82 (m, 5H), 1.69–1.57 (m, 1H), 1.49–1.19 (m, 10H), 0.91–0.84 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 214.2, 134.2, 129.2, 49.9, 44.1, 39.0, 37.4, 32.5, 31.7, 29.4, 28.7, 28.4, 24.1, 22.6, 14.1; IR (neat) 2926, 2855, 1701, 1456, 1447, 1346, 1288, 1248, 1198, 1161, 966, 934, 725 cm^{-1}. Anal. Calcd for $C_{15}H_{26}O$; C, 81.02; H, 11.79. Found: C, 80.97; H, 12.04.



3ib

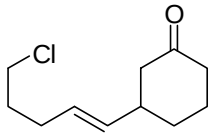
(*E*)-3-(5-Cyano-1-penten-1-yl)cyclohexanone (3ib). A colorless oil, R_f 0.30 (hexane–ethyl acetate = 3 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.49 (dd, *J* = 15.4, 6.2 Hz, 1H), 5.36 (dt, *J* = 15.6, 6.6 Hz, 1H), 2.13–2.54 (m, 9H), 2.09–2.00 (m, 1H), 1.94–1.86 (m, 1H), 1.77–1.63 (m, 3H), 1.55–1.45 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 211.0, 135.5, 127.0, 119.5, 47.4, 41.4, 41.2, 31.3, 31.1, 24.87, 24.84, 16.3; IR (neat) 2936, 2866, 2245, 1713, 1447, 1423, 1346, 1315, 1223, 1188, 1053, 1029, 972 cm^{-1}. Anal. Calcd for $C_{12}H_{17}NO$; C, 75.35; H, 8.96. Found: C, 75.16; H, 8.82.



3jb

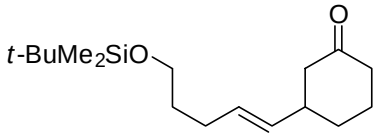
(*E*)-3-(5-Methoxycarbonyl-1-penten-1-yl)cyclohexanone (3jb). A colorless oil, R_f

0.40 (hexane–ethyl acetate = 3 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.40–5.37 (m, 2H), 3.66 (s, 3H), 2.50–2.13 (m, 7H), 2.09–1.98 (m, 3H), 1.92–1.83 (m, 1H), 1.74–1.59 (m, 3H), 1.53–1.42 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 211.3, 174.0, 134.2, 128.5, 51.5, 47.6, 41.5, 41.2, 33.3, 31.8, 31.5, 24.9, 24.5; IR (neat) 2937, 2864, 1738, 1713, 1435, 1315, 1223, 1153, 1053, 970 cm^{-1}. HRMS (EI) Calcd for $C_{13}H_{20}O_3$: M^+, 224.1412. Found: *m/z* 224.1414.



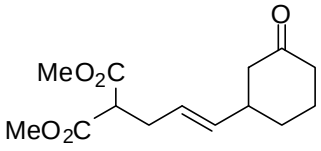
3kb

(*E*)-3-(5-Chloro-1-penten-1-yl)cyclohexanone (3kb). A colorless oil, R_f 0.25 (hexane–ethyl acetate = 10 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.48–5.35 (m, 2H), 3.52 (t, *J* = 6.6 Hz, 2H), 2.52–2.13 (m, 7H), 2.09–2.00 (m, 1H), 1.93–1.79 (m, 3H), 1.75–1.63 (m, 1H), 1.54–1.44 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 211.3, 134.6, 127.8, 47.5, 44.3, 41.5, 41.2, 32.0, 31.5, 29.5, 24.9; IR (neat) 2936, 2866, 1713, 1447, 1429, 1344, 1313, 1288, 1223, 1186, 1053, 970, 868, 723, 652 cm^{-1}. Anal. Calcd for $C_{11}H_{17}ClO$; C, 65.83; H, 8.54. Found: C, 65.59; H, 8.49.



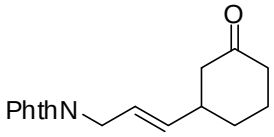
3lb

(*E*)-3-(5-*t*-Butyldimethylsiloxy-1-penten-1-yl)cyclohexanone (3lb). A colorless oil, R_f 0.30 (hexane–ethyl acetate = 10 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.47–5.34 (m, 2H), 3.59 (t, J = 6.5 Hz, 2H), 2.50–2.14 (m, 5H), 2.09–2.00 (m, 3H), 1.93–1.85 (m, 1H), 1.74–1.42 (m, 4H), 0.89 (s, 9H), 0.04 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 211.5, 133.3, 129.3, 62.4, 47.7, 41.6, 41.3, 32.4, 31.6, 28.7, 25.9, 25.0, 18.3, –5.3; IR (neat) 2930, 2895, 2856, 1717, 1472, 1256, 1223, 1103, 968, 837, 775 cm^{-1}. Anal. Calcd for $C_{17}H_{32}O_2Si$; C, 68.86; H, 10.88. Found: C, 68.59; H, 10.95.



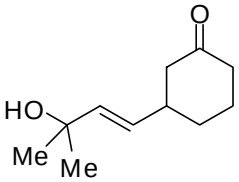
3mb

(*E*)-3-[4-Bis(methoxycarbonyl)-1-buten-1-yl]cyclohexanone (3mb). A colorless oil, R_f 0.24 (hexane–ethyl acetate = 2 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.49 (dd, *J* = 15.4, 6.4 Hz, 1H), 5.38 (dtd, *J* = 15.4, 6.8, 1.0 Hz, 1H), 3.72, (s, 6H), 3.40 (t, *J* = 7.6 Hz, 1H), 2.58 (dd, *J* = 7.5, 6.8 Hz, 2H), 2.49–2.09 (m, 5H), 2.08–1.97 (m, 1H), 1.91–1.79 (m, 1H), 1.74–1.58 (m, 1H), 1.52–1.39 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 211.0, 169.2, 136.6, 124.8, 52.5, 51.7, 47.3, 41.4, 41.2, 31.7, 31.2, 24.8; IR (neat): 2953, 2866, 1736, 1713, 1437, 1342, 1231, 1155, 1030, 972 cm^{-1}. Anal. Calcd for $C_{14}H_{20}O_5$: C, 62.67; H, 7.51. Found: C, 62.87; H, 7.66.



3nb

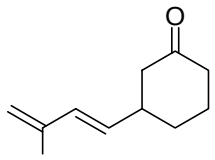
(*E*)-3-(3-*N*-Phthalimidoylpropen-1-yl)cyclohexanone (3nb). A colorless solid, mp 105.0–106.0 °C, R_f 0.20 (hexane–ethyl acetate = 3 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (dd, *J* = 5.6, 3.0 Hz, 2H), 7.71 (dd, *J* = 5.5, 3.1 Hz, 2H), 5.70 (dd, *J* = 15.4, 6.2 Hz, 1H), 5.52 (dtd, *J* = 15.6, 6.0, 1.3 Hz, 1H), 4.24 (d, *J* = 6.0 Hz, 2H), 2.52–2.29 (m, 3H), 2.28–2.12 (m, 2H), 2.07–1.98 (m, 1H), 1.93–1.85 (m, 1H), 1.71–1.59 (m, 1H), 1.54–1.42 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 210.6, 167.9, 137.2, 133.9, 132.1, 123.3, 122.7, 46.9, 41.2, 40.9, 39.3, 30.9, 24.8; IR (KBr) 2952, 2923, 2856, 1766, 1709, 1612, 1463, 1425, 1396, 1350, 1227, 1190, 1074, 964, 939, 725, 530 cm^{-1}. Anal. Calcd for $C_{17}H_{17}NO_3$; C, 72.07; H, 6.05. Found: C, 72.09; H, 5.98.



3ob

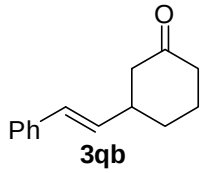
(*E*)-3-(3-Hydroxy-3-methyl-1-penten-1-yl)cyclohexanone (3ob). A colorless oil, R_f 0.13 (hexane–ethyl acetate = 3 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.64–5.55 (m, 2H),

2.54–2.15 (m, 5H), 2.10–2.01 (m, 1H), 1.95–1.87 (m, 1H), 1.72–1.62 (m, 1H), 1.55–1.45 (m, 2H), 1.30 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 211.1, 137.3, 129.6, 70.6, 47.4, 41.2, 41.1, 31.3, 29.9, 24.9; IR (neat) 3423, 2968, 2934, 2866, 1709, 1448, 1419, 1360, 1223, 1156, 972, 914 cm^{-1}. Anal. Calcd for $C_{11}H_{18}O_2$; C, 72.49; H, 9.95. Found: C, 72.22; H, 10.18.



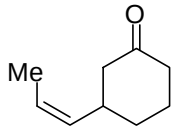
3pb

(*E*)-3-(3-Methyl-1,3-butadien-1-yl)cyclohexanone (3pb). A colorless oil, R_f 0.32 (hexane–ethyl acetate = 10 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.14 (d, J = 16.1 Hz, 1H), 5.58 (dd, J = 15.7, 7.0 Hz, 1H), 4.92 (s, 2H), 2.62–2.51 (m, 1H), 2.49–2.42 (m, 1H), 2.41–2.33 (m, 1H), 2.32–2.19 (m, 2H), 2.12–2.02 (m, 1H), 1.99–1.90 (m, 1H), 1.84 (t, J = 1.0 Hz, 3H) , 1.77–1.64 (m, 1H), 1.60–1.48 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 210.9, 141.6, 132.8, 132.0, 115.8, 47.4, 41.7, 41.2, 31.4, 25.0, 18.6; IR (neat) 2939, 2864, 1715, 1609, 1448, 1425, 1315, 1223, 966, 887 cm^{-1}. Anal. Calcd for $C_{11}H_{16}O$; C, 80.44; H, 9.82. Found: C, 80.55; H, 9.89.



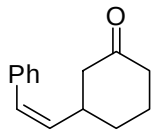
3qb

(*E*)-3-(2-Phenylethenyl)cyclohexanone (3qb). A colorless solid, mp 48.8–49.6 °C, R_f 0.20 (hexane–ethyl acetate = 10 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37–7.28 (m, 4H), 7.22 (tt, *J* = 7.1, 1.6 Hz, 1H), 6.39 (d, *J* = 16.1 Hz, 1H), 6.16 (dd, *J* = 15.9, 6.8 Hz, 1H), 2.73–2.63 (m, 1H), 2.57–2.49 (m, 1H), 2.45–2.27 (m, 3H), 2.15–2.07 (m, 1H), 2.06–1.98 (m, 1H), 1.81–1.69 (m, 1H), 1.68–1.57 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 210.8, 137.1, 132.9, 129.1, 128.5, 127.3, 126.1, 47.3, 41.9, 41.3, 31.4, 25.0; IR (KBr) 2950, 2864, 1707, 1493, 1447, 1425, 1313, 1279, 1238, 1220, 1177, 1049, 970, 752, 696, 538 cm^{-1}. Anal. Calcd for $C_{14}H_{16}O$; C, 83.96; H, 8.05. Found: C, 83.67; H, 7.99.



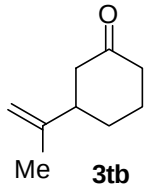
3rb

(*Z*)-3-(Propen-1-yl)cyclohexanone (3rb). A colorless oil, R_f 0.35 (hexane–ethyl acetate = 10 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.44 (dqd, *J* = 10.8, 6.8, 1.0 Hz, 1H), 5.26 (ddq, *J* = 10.6, 9.2, 1.8 Hz, 1H), 2.86–2.74 (m, 1H), 2.48–2.10 (m, 5H), 1.86–1.64 (m, 2H), 1.61 (dd, *J* = 6.9, 1.7 Hz, 3H), 1.53–1.42 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 211.3, 133.4, 124.0, 47.8, 41.2, 37.0, 31.5, 25.4, 12.9; IR (neat) 3011, 2936, 2864, 1715, 1447, 1423, 1315, 1221, 1184, 1055, 953, 716 cm^{-1}. Anal. Calcd for $C_9H_{14}O$; C, 78.21; H, 10.21. Found: C, 78.07; H, 10.45.



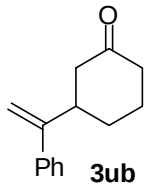
3sb

(*Z*)-3-(2-Phenylethenyl)cyclohexanone (3sb). A colorless oil, R_f 0.20 (hexane–ethyl acetate = 10 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36–7.30 (m, 2H), 7.25–7.18 (m, 3H), 6.42 (d, *J* = 11.5 Hz, 1H), 5.51 (dd, *J* = 11.3, 10.2 Hz, 1H), 3.12–3.01 (m, 1H), 2.50–2.20 (m, 4H), 2.12–2.04 (m, 1H), 1.95–1.87 (m, 1H), 1.76–1.53 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 210.6, 137.0, 135.0, 128.8, 128.41, 128.35, 126.9, 47.8, 41.2, 37.8, 31.7, 25.1; IR (neat) 2936, 1713, 1493, 1447, 1423, 1317, 1223, 945, 800, 772, 700 cm^{-1}. Anal. Calcd for $C_{14}H_{16}O$; C, 83.96; H, 8.05. Found: C, 83.76; H, 8.04.



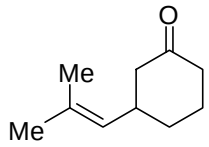
3tb

3-(Propen-2-yl)cyclohexanone (3tb). A colorless oil, R_f 0.28 (hexane–ethyl acetate = 10 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.79–4.77 (m, 1H), 4.74–4.72 (m, 1H), 2.24–2.47 (m, 5H), 2.12–2.04 (m, 1H), 1.98–1.89 (m, 1H), 1.74 (s, 3H), 1.72–1.53 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 211.6, 147.5, 110.0, 46.7, 45.7, 41.3, 30.0, 25.1, 20.6; IR (neat) 3082, 2939, 2864, 1717, 1645, 1448, 1315, 1223, 1182, 1057, 893 cm^{-1}. HRMS (EI) Calcd for $C_9H_{14}O$: M^+, 138.1045. Found: *m/z* 138.1048.



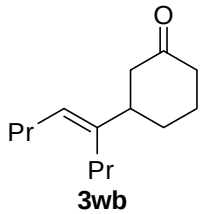
3ub

3-(1-Phenylethenyl)cyclohexanone (3ub). A colorless oil, R_f 0.15 (hexane–ethyl acetate = 10 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36–7.27 (m, 5H), 5.24 (s, 1H), 5.06 (d, J = 1.3 Hz, 1H), 3.03–2.94 (m, 1H), 2.59–2.52 (m, 1H), 2.44–2.27 (m, 3H), 2.10–1.95 (m, 2H), 1.76–1.64 (m, 1H), 1.62–1.53 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 211.3, 152.0, 141.5, 128.4, 127.5, 126.6, 112.1, 47.0, 42.8, 41.3, 30.5, 24.9; IR (neat) 2939, 2864, 1713, 1626, 1493, 1447, 1420, 1313, 1225, 1028, 905, 779, 706 cm^{-1}. Anal. Calcd for C14H16O; C, 83.96; H, 8.05. Found: C, 83.70; H, 8.07.



3vb

3-(2-Methyl-1-propen-1-yl)cyclohexanone (3vb). A colorless oil, R_f 0.28 (hexane–ethyl acetate = 10 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.99 (d, *J* = 9.0 Hz, 1H), 2.71–2.60 (m, 1H), 2.39–2.21 (m, 3H), 2.14–2.01 (m, 2H), 1.84–1.63 (m, 5H), 1.60 (d, *J* = 1.1 Hz, 3H), 1.50–1.38 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 211.7, 131.8, 127.8, 48.2, 41.2, 38.3, 31.8, 25.7, 25.4, 17.8; IR (neat) 2932, 2864, 1715, 1447, 1421, 1377, 1344, 1313, 1257, 1221, 1042, 868, 822 cm^{-1}. Anal. Calcd for $C_{10}H_{16}O$; C, 78.90; H, 10.59. Found: C, 78.62; H, 10.32.

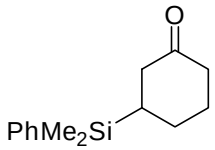


3wb

(*E*)-3-(4-Octen-4-yl)cyclohexanone (3wb). A colorless oil, R_f 0.30 (hexane–ethyl acetate = 10 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.15 (t, *J* = 7.0 Hz, 1H), 2.41–2.22 (m, 5H), 2.10–1.85 (m, 6H), 1.70–1.48 (m, 2H), 1.43–1.38 (m, 4H), 0.895 (t, *J* = 7.3 Hz, 3H), 0.890 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 212.3, 141.7, 124.8, 47.8, 45.1, 41.3, 31.9, 31.1, 29.8, 25.4, 23.1, 22.4, 14.3, 13.8; IR (neat) 2957, 2870, 1713,

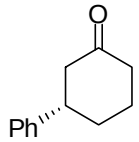
1456, 1421, 1377, 1344, 1317, 1261, 1220, 893 cm^{-1}. HRMS (EI) Calcd for $C_{14}H_{24}O$: M^+, 208.1827. Found: *m/z* 208.1825.

Gram-scale 1,4-addition of 1a and 1h to 2-cyclohexen-1-one (2b). A solution of $[Rh(OH)(cod)]_2$ (23 mg, 0.05 mmol) in THF (5 mL) were added an organosilane (**1a**, 2.4 g; **1h**, 2.8 g, 10.0 mmol) and **2b** (1.0 g, 10.0 mmol) sequentially, and the resulting mixture was stirred at 35 °C for 4 h. The mixture was filtered through a silica gel pad, concentrated in vacuo, and distilled under vacuum (2 mmHg) to give cyclic silyl ether **4**; the residue was further purified by flash chromatography on silica gel (hexane–ethyl acetate = 5 : 1 as an eluent) to give the corresponding adduct. The results are listed in entry 3, Table 1, and entry 3, Table 2, respectively.



6

Rhodium-catalyzed 1,4-addition of disilane 5 to 2-cyclohexen-1-one (2b). To a solution of $[Rh(OH)(cod)]_2$ (2.3 mg, 5.0 μmol) and dppp (8.2 mg, 20 μmol) in THF (0.5 mL) was added **2b** (96 mg, 1.00 mmol). To this was added **5** (1.05 g, 3.5 mmol) dropwise via a syringe pump over 20 h at 35 °C, and the resulting mixture was further stirred at the same temperature for 14 h. The mixture was concentrated in vacuo, and the residue was purified by flash chromatography on silica gel followed by preparative recycling silica gel chromatography to afford **6**[24e] (153 mg, 66%) as a colorless oil, R_f 0.34 (hexane–ethyl acetate = 5 : 1. ^1H NMR (400 MHz, $CDCl_3$) δ 7.51–7.44 (m, 2H), 7.42–7.33 (m, 3H), 2.41–2.20 (m, 3H), 2.19–2.04 (m, 2H), 1.86–1.58 (m, 2H), 1.48–1.21 (m, 2H), 0.31 (s, 3H), 0.30 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 212.8, 136.6, 133.9, 129.3, 127.9, 42.4, 41.9, 29.8, 27.6, 26.0, –5.3, –5.4.

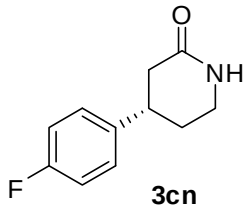


(*S*)-**3yb**

Enatioselective 1,4-addition of 1a to 2-cyclohexen-1-one (2b) using [Rh(OH)(*S*)-

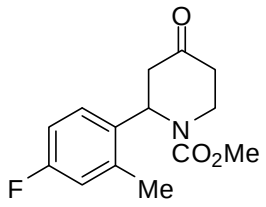
binap]$_2$ as a catalyst. To a solution of [Rh(OH)(*S*)-binap]$_2$ (22 mg, 15 μmol) in THF (0.5 mL) were sequentially added **1a** (0.24 g, 1.00 mmol) and **2b** (96 mg, 1.00 mmol). The resulting mixture was stirred at 35 °C for 10 h, and then filtered through a silica gel pad. The filtrate was concentrated in vacuo. The residue was purified by flash chromatography on silica gel to afford (*S*)-**3ab** (146 mg, 84%). Ee was determined on a Daicel Chiralpak AD-H column with hexane–2-propanol = 98 : 2, flow = 0.6 mL/min. Retention times: 14.3 min [(*S*)-enantiomer], 17.0 min [(*R*)-enantiomer]. 99% ee. $[\alpha]^{27}_{D}$ –20 (*c* 1.00, $CHCl_3$) [lit.[18a] $[\alpha]^{20}_{D}$ –21 (*c* 0.96, $CHCl_3$) for (*S*)-**3ab**].

Enatioselective 1,4-addition of organo[2-(hydroxymethyl)phenyl]dimethylsilanes. A solution of $[RhCl(C_2H_4)_2]_2$ (1.7 mg, 8.7 μmol Rh) and **7** (11 μmol) in THF (0.30 mL) was stirred for 5 min at room temperature. To the mixture were added **2** (0.30 mmol), organosilane **1** (0.30 mmol), and KOH (45 μL, 45 μmol; 1.0 M aq.). The resulting mixture was stirred for 5–12 h at 40 °C before filteration through a silica gel pad with EtOAc. The filtrate was concentrated under vacuum, and the residue was chromatographed on silica gel to afford 1,4-adduct **3**.



3cn

4-(4-Fluorophenyl)-2-piperidinone (3cn).[22b] A pale yellow solid, mp 168.0–169.4 °C, R_f 0.18 (ethyl acetate). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 (dd, *J* = 8.5, 5.2 Hz, 2H), 7.03 (t, *J* = 8.7 Hz, 2H), 6.29 (br s, 1H), 3.48–3.35 (m, 2H), 3.10 (tdd, *J* = 11.2, 5.1, 3.1 Hz, 1H), 2.68 (ddd, *J* = 17.6, 5.3, 1.8 Hz, 1H), 2.45 (dd, *J* = 17.6, 11.0 Hz, 1H), 2.13–2.00 (m, 1H), 1.97–1.85 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.8, 161.6 (d, *J* = 245.4 Hz), 139.2 (d, *J* = 3.1 Hz), 128.0 (d, *J* = 7.7 Hz), 115.6 (d, *J* = 21.5 Hz), 41.3, 38.9, 37.7, 29.6. Ee was determined by HPLC on a Daicel Chiralcel AD-H column with hexane–2-propanol = 85 : 15, flow = 0.6 mL/min, detection at 220 nm. Retention times: 37.7 min [(*R*)-enantiomer], 42.1 min [(*S*)-enantiomer]. 94% ee. $[\alpha]^{20}_{D}$ –16.0 (*c* 0.95, $CHCl_3$) {lit.[22b] $[\alpha]^{20}_{D}$ +19 (*c* 1.02, $CHCl_3$) for (*R*)-**3cn**}.



3xo

Methyl 2-(4-Fluoro-2-methylphenyl)-4-oxopiperidine-1-carboxylate (3xo). A colorless solid, mp 100.8–101.8 °C, R_f 0.36 (hexane–ethyl acetate = 1 : 1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.11 (dd, *J* = 8.6, 5.7 Hz, 1H), 6.93–6.80 (m, 2H), 5.78 (br s, 1H), 4.20 (br s, 1H), 3.77 (s, 3H), 3.11 (br t, *J* = 11.3 Hz, 1H), 2.88–2.76 (m, 2H), 2.60–2.38 (m, 2H), 2.33 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 207.8, 162.0 (d, *J* = 246.1 Hz), 155.8, 139.4 (br), 134.0, 127.9 (d, *J* = 8.4 Hz), 118.0 (d, *J* = 21.5 Hz), 112.6 (d, *J* = 20.7 Hz), 53.2, 52.3, 44.8, 40.9, 38.7, 19.4; IR (KBr): 2963, 2909, 1693, 1589, 1497, 1474, 1447, 1398, 1315, 1273, 1211, 1196, 1169, 1138, 1040, 1013, 978, 957, 880, 870, 831, 775, 754, 642, 594, 517 cm^{-1}; Anal. Calcd for $C_{14}H_{16}FNO_3$: C, 63.39; H, 6.08. Found: C, 63.10; H, 5.94. Ee was determined by HPLC on a Daicel Chiralcel OJ-H column with hexane–2-propanol = 85 : 15, flow = 0.6 mL/min, detection at 220 nm. Retention times: 25.6 min, 30.3 min. 88% ee. $[\alpha]^{20}_D$ −79.3 (*c* 1.00, $CHCl_3$).

Enatioselective 1,4-addition of 1y to 2-cyclohexen-1-one (2b) and kinetic resolution of 1y using Rh/Carreira's chiral diene catalyst. A solution of $[RhCl(C_2H_4)_2]_2$ (0.4 mg, 1 μmol) and **7** (0.6 mg, 2 μmol) in THF (0.1 mL) were added **1y** (103 mg, 0.40 mmol), **2b** (19.2 mg, 0.20 mmol), and a 1.0 M KOH aq. solution (10 μL, 10 μmol) sequentially, and the resulting mixture was stirred at 35 °C for 4 h. The mixture was filtered through a silica gel pad and concentrated in vacuo. The residue was purified by flash chromatography on silica gel to afford (*S*)-**3yb** (33 mg, 95%, 96% ee) and recovered sample of (*S*)-**1y** (46 mg, 45%). Ee of **1y** was determined on a Daicel Chiralcel OD-H column with hexane–2-propanol = 98 : 2, flow = 0.6 mL/min. Retention times: 12.0, 13.7 min. 68% ee. $[\alpha]^{26}_D$ –32.0 (*c* 1.00, $CHCl_3$). The authentic (*S*)-**1y** {$[\alpha]^{20}_D$ –52.6 (*c* 0.96, $CHCl_3$)} was synthesized from commercially available (*S*)-2-bromo-α-methylbenzyl alcohol.

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List of Publications

Ⅰ. Parts of the present Thesis have been or are to be published in the following journals.

Chapter 2

(1) Synthesis and Cross-coupling Reaction of Alkenyl[2-(hydroxymethyl)phenyl]dimethylsilanes

Nakao, Y.; Imanaka, H.; Chen, J.; Yada, A.; Hiyama, T. *J. Organomet. Chem*. **2007**, *692*, 585–603.

(2) Cross-coupling Reaction of Allylic and Benzylic Carbonates with Organo[2-(hydroxymethyl)phenyl]dimethylsilanes

Nakao, Y.; Ebata, S.; Chen J.; Imanaka, H.; Hiyama, T. *Chem. Lett.* **2007**, *36*, 606–607.

Chapter 3

(3) Biaryl Synthesis Using Highly Stable Aryl[2-(hydroxymethyl)phenyl]dimethylsilanes and Aryl Iodides under Fluoride-free Conditions

Nakao, Y.; Sahoo, A. K.; Yada, A.; Chen J.; Hiyama, T. *Sci. Technol. Adv. Mater.* **2006**, *7*, 536–543.

(2) Cross-coupling Reaction of Allylic and Benzylic Carbonates with Organo[2-(hydroxymethyl)phenyl]dimethylsilanes

Nakao, Y.; Ebata, S.; Chen J.; Imanaka, H.; Hiyama, T. *Chem. Lett.* **2007**, *36*, 606–607.

(4) A Silicon-based Approach to Oligoarenes by Iterative Cross-coupling Reactions of Halogenated Organo[2-(hydroxymethyl)phenyl]dimethylsilanes

Nakao, Y.; Chen, J.; Tanaka, M.; Hiyama, T. *J. Am. Chem. Soc.* **2007**, *129*, 11694–11695.

Chapter 4

(5) Organo[2-(hydroxymethyl)phenyl]dimethylsilanes as Mild and Reproducible Agents for Rhodium-catalyzed 1,4-Addition Reactions

Nakao, Y.; Chen, J.; Imanaka, H.; Hiyama, T.; Ichikawa, Y.; Duan, W.-L.; Shintani,

R.; Hayashi, T. *J. Am. Chem. Soc.* **2007**, *129*, 9137–9143.

Ⅱ. Following publications are not included in this Thesis.

(6) Rhodium-catalyzed Addition of Organo[2-(hydroxymethyl)phenyl]dimethylsilanes to Arenesulfonylimines
Nakao, Y.; Takeda, M.; Chen, J.; Hiyama, T.; Ichikawa, Y.; Shintani, R.; Hayashi T. *Chem. Lett.* **2008**, in press.

(7) Rhodium-catalyzed Hydroarylation and -alkenylation of Alkynes Using Organo[2-(hydroxymethyl)phenyl]dimethylsilanes
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