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博士論文 (要約)

Development of Organic Reactions through Nucleophilic Activation by Alkoxide

(アルコキシドを用いた求核的活性化を経る
有機合成反応の開発)

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Abstract

The nucleophilic activation of a metal complex increases the nucleophilicity of the metal center and of the ligands, resulting in the high reactivity toward electrophilic species. Nucleophilic activation of a metal complex has been achieved by various nucleophiles, and among these an alkoxide has been used as a nucleophile for this purpose. An alkoxide is a readily available anionic reagent, and versatile tuning of its structure is a good feature for nucleophilic activation of a metal complex to control the reactivity. The purpose of this thesis is to demonstrate the potential of utilizing nucleophilic activation with an alkoxide for difficult organic transformations under simple reaction conditions.

Chapter 1 describes the importance of nucleophilic activation of a metal complex by an alkoxide in order to achieve difficult organic transformations under simple reaction conditions, together with current challenges for this methodology and the goal of this study.

Chapter 2 describes the utilization of nucleophilic activation of an iron catalyst by an alkoxide for borylation of low-reactive aryl chlorides. In the presence of a catalytic amount of iron salt and a stoichiometric amount of an alkoxide, the borylation of low-reactive and readily available aryl chlorides was achieved.

Chapter 3 describes the utilization of electron-rich iron-alkoxide species in order to generate an organic radical species from perfluoroalkyl halides, to achieve intermolecular carboamination and carboalkoxylation of an alkene. In the presence of a catalytic amount of an iron salt, the three-component coupling reaction proceeded to give complex molecules from simple molecular building blocks.

Chapter 4 describes the nucleophilic activation of a monoorganosilane by an alkoxide, and its application for silylation of aryl halides. Aryl halides are easily silylated in the presence of a monoorganosilane and a lithium alkoxide without any transition metal catalyst. Based on a mechanistic study, a reaction mechanism in good agreement with the experimental results was proposed.

Finally, Chapter 5 summarizes the present studies and gives a future perspective.

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Abbreviations

Ac: acetyl
APCI: atmospheric pressure chemical ionization
Ar: aryl
acac: acetylacetonate
$\mathrm{B_2Pin_2}$: bis(pinacolato)diboron
Bu: butyl
Bpin: pinacolatoboron
cod: 1,5-cyclooctadiene
Cy: cyclohexyl
DCE: 1,2-dichloroethane
dcpe: 1,2-bis(dicyclohexylphosphino)ethane
DMF: *N,N*-dimethylformamide
DMPU: 1,3-dimethyltetrahydropyrimidin-2(*1H*)-one
DMSO: dimethyl sulfoxide
dppe: 1,2-bis(diphenylphosphino)ethane
dppm: 1,2-bis(diphenylphosphino)methane
DPV: differential pulse voltammetry
Et: ethyl
ESR: electron spin resonance
EWG: electron-withdrawing group
eq: equation
GC: gas chromatography
GC–MS: gas chromatography-mass spectrometry
GPC: gel permeation chromatography
h: hour(s)
ICP-AES: inductively coupled plasma-atomic emission spectrometry
IR: infrared spectroscopy
HFIP: 1,1,1,3,3,3-hexafluoro-2-propanol
HRMS: high-resolution mass spectrometry
HOMO: highest occupied molecular orbital
Hz: hertz

LUMO: lowest unoccupied molecular orbital
M: mol/L
Me: methyl
Mes: mesityl
min: minute(s)
MS: mass spectroscopy
NHC: *N*-heterocyclic carbene
NMR: nuclear magnetic resonance
Nu: nucleophile
OTf: triflate
OTs: tosylate
Ph: phenyl
ppm: perts per million
pr: propyl
rt: room temperature
selectfluor: 1-chloromethyl-4-fluoro-1,4-diazoniabicyclo[2.2.2]octane bis(tetrafluoroborate)
TBAF: tetrabutylammonium fluoride
TBME: *tert*-butyl methyl ether
TBS: *tert*-butyldimethylsilyl
TEMPO: 2,2,6,6-tetramethylpiperidine 1-oxyl
THF: tetrahydrofuran
TM: transition metal
TMEDA: *N,N,N',N'*-tetramethylethylenediamine
TMS: trimethylsilyl

Chapter 1

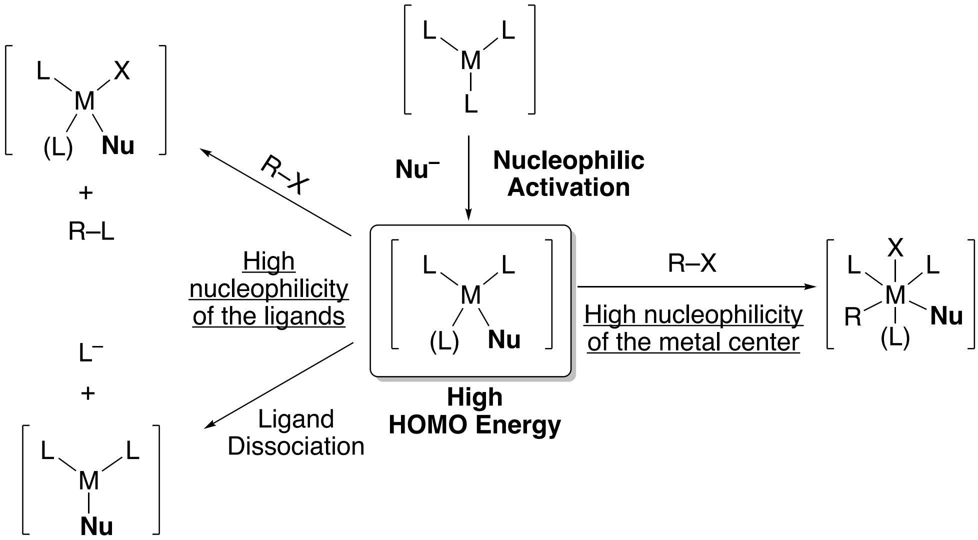
General Introduction

1-1. Nucleophilic activation of a metal complex

Organometallic chemistry[1] has become one of the most important research areas in organic chemistry nowadays. For the past two decades, three research areas related to organometallic chemistry have been awarded the Nobel Prize: palladium-catalyzed cross couplings in organic synthesis in 2010,[2] development of the metathesis method in organic synthesis in 2005,[3] and hydrogenation or oxidation reactions with chiral ligands in 2001.[4] Organometallic compounds are widely used in the field of academia and chemical industry[5] for the synthesis of complex natural products, functional materials, polymers, bioactive compounds, etc. An important feature of a metal is its d orbitals that are accessible to interaction with s or p orbitals of other atoms. Therefore, a variety of organic molecules can coordinate to a metal center, and the resulting organometallic complex has a rich reactivity, tunable both by the selection of the metal and of the ligand. A large variety of ligands have been developed to control the reactivity of a metal complex, in order to be exploited for various organic transformations as a catalyst or a reagent.

Metals generally receive electrons from a ligand into their vacant d orbital. By coordination of a strong anionic ligand to a metal complex, the HOMO energy level of the metal complex is increased by σ and π donation from the ligand. HOMO is delocalized over the metal center and the ligands, resulting in an increase in electron density of both of them. Thus, both the metal center and the ligands are nucleophilically activated, for example this activation mode has been often used for the activation of a metal carbonyl.[6] Through the nucleophilic activation of a metal complex, two important reactivities can be induced (Figure 1). First, the metal center has increased nucleophilicity, and therefore it can easily react with various electrophilic species. Second, the ligands also have increased nucleophilicity, as compared with the corresponding neutral metal complex. Especially when the affinity between the nucleophile and the metal is high, the ligands attached to the metal are sometimes dissociated from the complex. The resulting metal complex generally shows higher nucleophilicity compared to the original metal complex, and the dissociated anionic ligands can be utilized for organic synthesis. Based on these induced reactivities, a variety of transformations have been developed.[7–14]

Figure 1. Two reactivities induced by nucleophilic activation



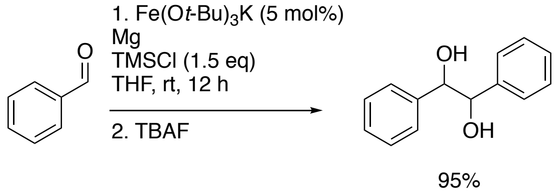
1-2. Increased nucleophilicity of the metal center through nucleophilic activation

Through nucleophilic activation, the HOMO energy level of a metal complex is increased, typically resulting in high nucleophilicity of the metal center. Therefore, the activated metal complex can react with electrophiles more easily as compared to the corresponding neutral metal complex. Thus, this nucleophilic activation strategy is a promising approach to achieve difficult organic transformations with low-reactive electrophiles.

For example, Uchiyama *et al.* previously reported that an iron complex activated by an alkoxide or a Grignard reagent has a strong reducing power, as compared with the corresponding neutral iron halide complex.[7] Only one chloride ligand was replaced with a methyl group on the iron complex, but the reducing power was dramatically increased. Also, the methyliron ate complex showed a strong reducing power as compared to the neutral dimethyliron complex. The iron alkoxide ate complex also showed a strong reducing power, which is similar with the neutral dimethyliron complex. These iron complexes are nucleophilic enough to reduce organic ketones or organic halides through one-electron transfer (Figure 2).

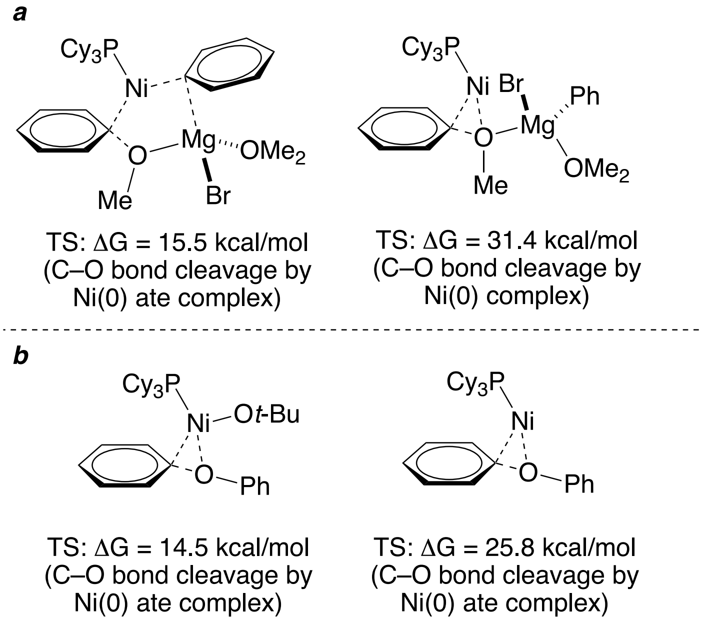
Figure 2. Nucleophilically-activated iron complex shows a strong reducing power

Species	*E*°
$FeCl_2$	+ 0.15
MeFeCl	– 1.38
Me_2Fe	– 1.93
Me_3FeLi	– 2.50
$Fe(Ot\text{-}Bu)_3K$	– 1.86



Another example is a nickel-catalyzed carbon-carbon bond forming reaction via carbon-oxygen bond cleavage.[8] A nucleophilically-activated low-valent nickel was suggested as an important reaction intermediate in this transformation. Wang and Uchiyama *et al* suggested that generation of a phenylnickel(0) ate complex bearing a phosphine ligand is important to achieve cross coupling of unreactive aryl ethers with Grignard reagents based on theoretical study (Figure 3 (a)).[9] Chung *et al* suggested that generation of a nickel(0)–alkoxide ate complex bearing a phosphine ligand is important to achieve hydrogenolysis of aryl ethers based on theoretical study (Figure 3 (b)).[10] In both cases, they compared the activation energy for carbon-oxygen bond cleavage step using the nucleophilically-activated catalyst and the corresponding neutral catalyst, to reveal that nucleophilic activation significantly decreased the activation energy for the carbon-oxygen bond cleavage step. Although these theoretical studies were not supported by direct experimental evidence, they showed that high nucleophilicity can be expected by nucleophilic activation of a metal complex. In this case, the nucleophile actually acts as a ligand to the metal complex, and during the reaction, an alkoxide coordinates to the metal complex to increase its reactivity.

Figure 3. Nucleophilically-activated low-valent nickel complex shows lower activation energy toward carbon-oxygen bond cleavage, as suggested by a theoretical study



TS: ΔG = 15.5 kcal/mol (C–O bond cleavage by Ni(0) ate complex)

TS: ΔG = 31.4 kcal/mol (C–O bond cleavage by Ni(0) complex)

TS: ΔG = 14.5 kcal/mol (C–O bond cleavage by Ni(0) ate complex)

TS: ΔG = 25.8 kcal/mol (C–O bond cleavage by Ni(0) ate complex)

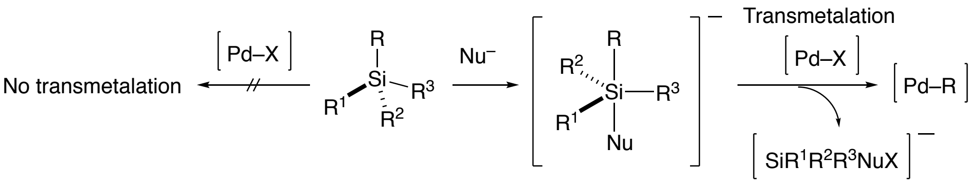
These reports are just selected examples and there are many examples about the utilization of nucleophilically activated metal center[11] for the organic synthesis such as direct metalation,[12] addition type reaction[13], cross-coupling type reaction[14] and so on.

1-3. Increased nucleophilicity of a ligand through nucleophilic activation

Through nucleophilic activation of a metal complex, the nucleophilicity of a ligands is also increased. Therefore, the reactivity of a ligand toward electrophiles is also increased and as mentioned in the **1-1** section, ligand dissociation from the metal complex sometimes occurs via nucleophilic activation.

The famous reaction to utilize this feature is the Hiyama cross-coupling reaction.[15] Organosilane compounds themselves are stable and cannot transmetalate with a transition metal catalyst. On the other hand, the addition of a Lewis base such as an alkoxide or a fluoride generates a silicate, which is active for transmetalation with a transition metal catalyst because the nucleophilicity of the organic group attached to the silicon atom is increased via nucleophilic activation by a Lewis base (Figure 4). Thus, the reaction of a ligand originally attached to a metal complex is enabled by nucleophilic activation of the metal complex.

Figure 4. Nucleophilic activation of an organosilane for transmetalation



The other famous reaction to utilize this feature is the Suzuki-Miyaura cross-coupling reaction.[16] Although detailed reaction mechanism is under investigation,[17] it is considered that nucleophilic activation by a Lewis base is necessary to generate a borate in order to achieve facile transmetalation with a transition metal catalyst.

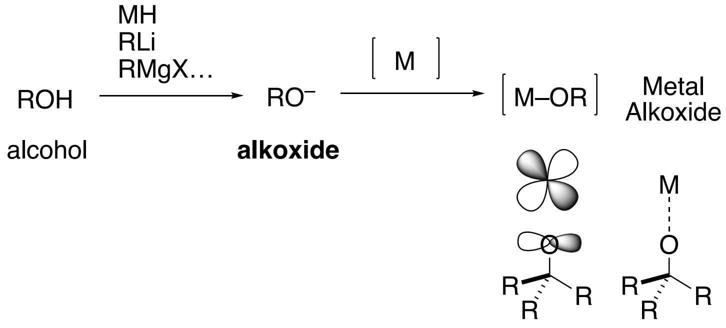
In both cases, the metal atom is nucleophilically activated by a Lewis base and nucleophilicity of organic group attached to the metal atom is increased. It enables facile transmetalation with a transition metal catalyst.

1-4. Use of an alkoxide for nucleophilic activation of a metal complex

In the previous two sections, I described that nucleophilic activation of a metal complex can be utilized for various organic transformations. Nucleophilic activation is achieved by various nucleophiles such as halide anions and carbanions; among these, an alkoxide is an important nucleophile for this purpose.

An alkoxide[18] is an anionic species, the conjugate base of an alcohol. This class of compounds is widely used as a strong base for deprotonation of organic compounds,[19] and as a precursor to ceramic materials.[20] An alkoxide shows lower reactivity toward functional groups compared to the reactive organometallic reagents that are sometimes used for nucleophilic activation of a metal complex. The strong π-donating ability due to its lone pairs enhances the interaction with the *d* orbitals of the metal center[21] and increases the nucleophilicty of the metal complex. Therefore, an alkoxide is utilized as a readily available nucleophile or ligand for a metal complex (Figure 5).[22]

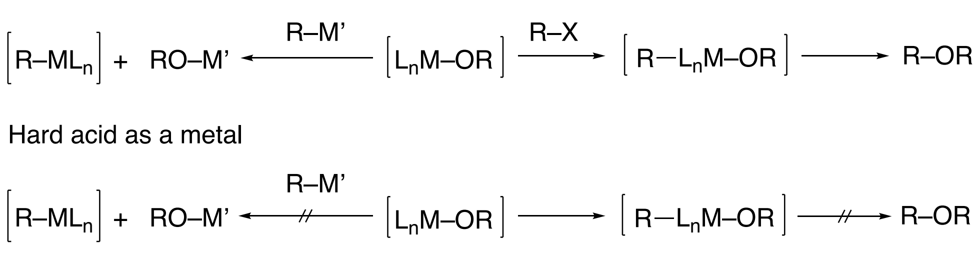
Figure 5. The preparation of an alkoxide and its use as a ligand for a metal complex



Versatile structural tuning of the structure of the alkoxide is a good feature for its use as a nucleophile for nucleophilic activation of a metal complex. Both the reactivity of the alkoxide itself and of the metal-alkoxide complex can be tuned by the selection of the organic group bonded to the oxygen atom. For example, in order to decrease the nucleophilicity of an alkoxide itself toward electrophilic species, a sterically-hindered organic group is often used. The organic group bonded to the oxygen atom also can tune the aggregation state of an alkoxide and a metal-alkoxide complex.

The selection of the metal is also important in order to determine the reactivity of a metal-alkoxide complex. When a soft acid[23] such as palladium or platinum are used, the metal-alkoxide bond is not strong, and therefore transmetalation with organometallic reagents[24] or reductive elimination[25] are likely to occur. This reactivity is utilized for Suzuki-Miyaura cross-coupling reaction[16] or Buchwald-Hartwig cross-coupling reaction.[27] On the other hand, when a hard acid such as a first-row transition metal, boron atom, or silicon atom is used as a metal, the metal-alkoxide bond becomes strong because this bond is nearly ionic bond (Figure 6). Therefore, transformations related to the dissociation of an alkoxide from the metal center such as transmetalation or reductive elimination are difficult.

Figure 6. Reactivity difference of metal alkoxides



Another important point is the large availability of an alkoxide. Recently, sustainable development[28] became an important goal of our society, and this concept has also gained much attention in organometallic chemistry and organic synthesis. However, the preparation of an engineered nucleophile generally requires multi-step synthesis and/or toxic reagents from expensive precursors resulting in consumption of large amounts of chemicals, energy and time resources. In some cases, the availability of nucleophiles is lower than that of the metal. As a result, the total cost of transformation is increased and this is incompatible with the concept of sustainable development. On the other hand, several alkoxides can be purchased from commercial suppliers, and can be easily prepared from the readily available corresponding alcohol and a strong base such as metal hydrides, Grignard reagents, or organolithium reagents.

As described in this section, the use of an alkoxide as a nucleophile to a metal complex for nucleophilic activation is a good approach, because of versatile structural tuning of the structure of the alkoxide and relatively lower reactivity of the alkoxide compared to the reactive organometallic reagents. Also, an alkoxide is largely available, and they do not require multi-step synthesis, decreasing the total cost of the transformation. Indeed, many organic transformations have been reported by utilizing nucleophilic activation by an alkoxide.[7,15,16]

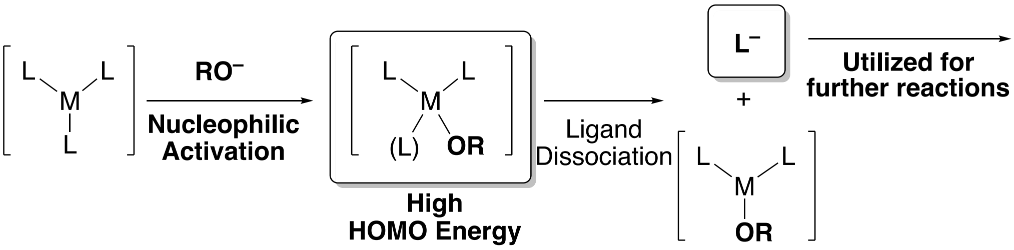
1-5. Objective of survey in this thesis

As I mentioned in the previous section, the concept of sustainability is important in modern organometallic chemistry and organic synthesis. Therefore, achieving difficult organic transformations under simple reaction conditions is desirable.[29] For example, the design and use of a tailored ligand is a general method to achieve difficult organic transformations.[30] However, multi-step synthesis and/or the use of toxic reagents from expensive precursors are necessary for ligand synthesis, which is incompatible with the concept of sustainability. In another example, the use of transition metal as a catalyst is sometimes problematic and therefore, development of transition-metal-free reactions is important research area in today’s organic synthesis.[31] In order to achieve difficult organic transformations under simple reaction conditions, the use of nucleophilic activation by an alkoxide would be promising approach.

An alkoxide can coordinate to the metal center strongly especially when a hard metal is used, and therefore it can work as a ligand during the reaction. When an alkoxide works as a ligand, the nucleophilicity of the metal center is increased and it shows high reactivity toward an electrophilic species. Therefore, it is possible to achieve difficult organic transformations with low-reactive electrophilic species in the absence of an external ligand utilizing nucleophilic activation by an alkoxide.

Ligand dissociation from a nucleophilically-activated metal complex is also promising to achieve difficult organic transformations without transition metal catalyst under simple reaction conditions. This ligand dissociation can generate unstable and reactive anionic species from two stable compounds and these species can be used for difficult organic reactions under simple reaction conditions (Figure 7).[32]

***Figure** 7*. Further utilization of a generated anionic species



Therefore, the objective of survey in this thesis is to demonstrate the potential of nucleophilic activation of a metal complex with an alkoxide for difficult organic transformations under simple reaction conditions.

1-6. Difficulty in the use of an alkoxide to achieve difficult organic transformations under simple reaction conditions

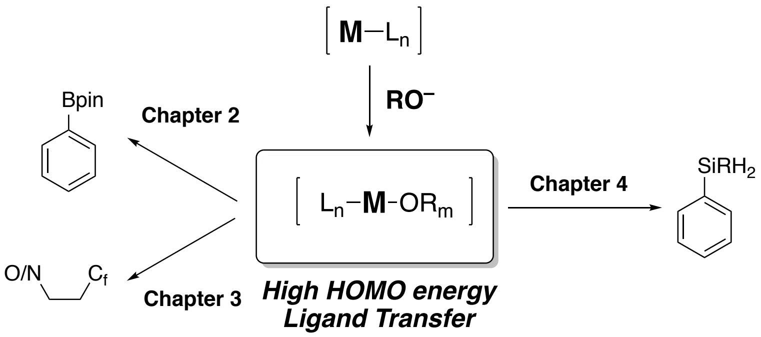
An alkoxide and a metal-alkoxide complex have high tendency to make a bridge-structure.[33] Such an aggregated structure is often structurally stable and hence unreactive for organic reactions. In addition, it tends to show poor solubility in common organic solvents. To achieve alkoxide-mediated reactions under simple reaction conditions, controlling the aggregation state of the reaction system is necessary. The key to achieve this is the choice of an alkoxide and a solvent, which can change the aggregation state of an alkoxide or a metal alkoxide complex.[34] The use of a bulky alkoxide or a coordinating solvent generally suppresses generating an aggregation of an alkoxide or a metal alkoxide complex.

1-7. Subjects of survey in this thesis

During my Ph. D. course, I have investigated three different organic transformations, which cannot be achieved by previous methods, by utilizing two important features of nucleophilic activation of a metal complex. In all cases, difficult transformations were accomplished through a proper selection of an alkoxide and the reaction solvent, under simple reaction conditions.

Through nucleophilic activation, the high reactivity of the metal center and of the ligands toward electrophilic species is an important feature. Therefore, my first target reaction was the coupling reaction of low-reactive aryl chlorides, which are representative low-reactive electrophilic species. The combination of an alkoxide with an iron salt enabled the synthesis of arylboron reagents from low reactive, inexpensive and readily available aryl chlorides in the absence of an external ligand (Chapter 2). The selection of the base was the most important factor in order to achieve high reaction efficiency, emphasizing the importance of the generation of a highly reductive iron-alkoxide complex. Thereafter, I focused on utilizing the strong reducing power of an iron-alkoxide complex for a radical-mediated coupling reaction, and a rare example of intermolecular carboamination and carboalkoxylation reaction with perfluoroalkyl halides, functionalized alkenes and amines or phenols was achieved (Chapter 3). In Chapters 2 and 3, I demonstrated the high reactivity of an iron-alkoxide system toward organic halides. To utilize both nucleophilically-activated ligands and metals by an alkoxide, I designed a silylation reaction in the presence of an iron salt. Finally, I developed the silylation of aryl halides with monoorganosilanes in the presence of an alkoxide via nucleophilic activation of silane reagents in the absence of a transition metal catalyst (Chapter 4). A mechanistic study showed that nucleophilic activation of monoorganosilanes by an alkoxide increases the nucleophilicity of the hydride ligands attached to the silicon atom, important for achieving this intriguing transformation. The reactions described herein demonstrate the importance and potential of nucleophilic activation of a metal complex using an alkoxide for difficult organic transformations under simple reaction conditions (Figure 8).

Figure 8. Overview of this thesis



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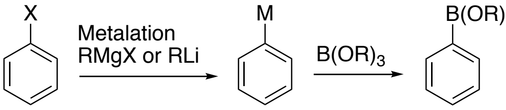
Chapter 2

Iron-Catalyzed Borylation of Aryl Chlorides

2-1. Introduction

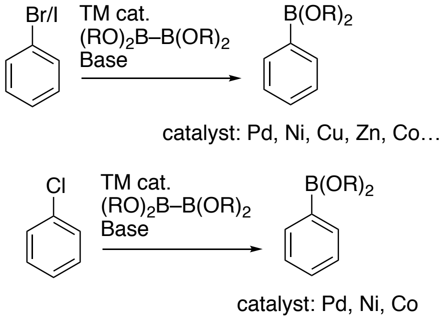
Aryl- and heteroaryl boronic acid derivatives are widely used as building blocks[1] for a variety of synthetic transformations such as Suzuki-Miyaura reaction[2] and Chan-Lam-Evans reaction.[3] Therefore, many researchers have focused on developing synthetic methods for these derivatives. The conventional synthetic method for preparing these derivatives is the coupling reaction of a highly reactive organomagnesium or organolithium compound with an alkoxyborane (Eq. 1). However, this method requires multi-step synthesis of the desired boron compounds and suffers from low functional group tolerance.



(1)

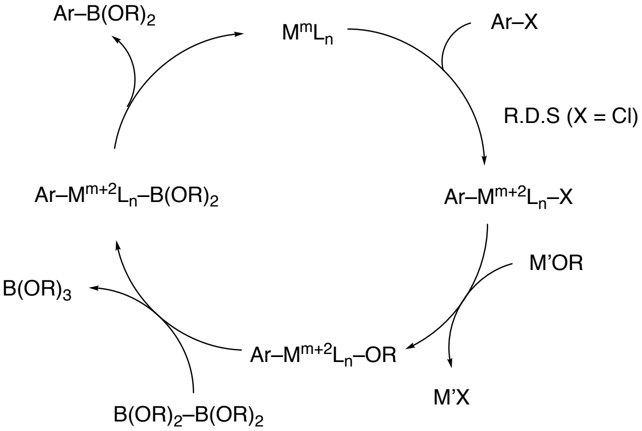
An alternative approach is the transition-metal-catalyzed borylation of aryl halides.[4] This transformation can omit the metalation step and the use of reactive organometallic reagents. However, the reaction typically proceeds well only with aryl iodides and bromides, while readily available and inexpensive aryl chlorides are more difficult substrates. To date, transition-metal-catalyzed borylation of aryl chlorides has been achieved with palladium,[5] nickel,[6] and cobalt catalysis.[7] These methods require expensive and toxic transition metal catalysis, tailored ligands, special additives and preparation of the metal complex in advance (Scheme 1).

Scheme 1. Reported methods for transition-metal-catalyzed borylation of aryl halides



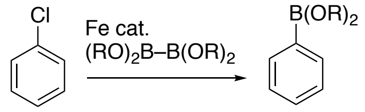
The general catalytic cycle for the transition-metal-catalyzed borylation of aryl halides is shown in the Figure 1. The reaction mechanism is similar to the transition-metal-catalyzed cross-coupling reaction.[8] In the case of aryl chlorides, the most difficult step is the oxidative addition of the metal species to the low reactive carbon-chloride bond. To overcome this difficult step, expensive and toxic transition metal catalysis with tailored ligands, special additives (e.g. $TMSOCH_2CF_3$), reactive organometallic reagents (e.g. methyl lithium) and preparation of the metal complex in advance are necessary.

Figure 1. Proposed mechanism for the transition-metal-catalyzed borylation of aryl halides



Taking these backgrounds into consideration, I decided to investigate the iron-catalyzed borylation of aryl chlorides because iron is inexpensive and benign metal (Figure 2).

Figure 2. Target reaction

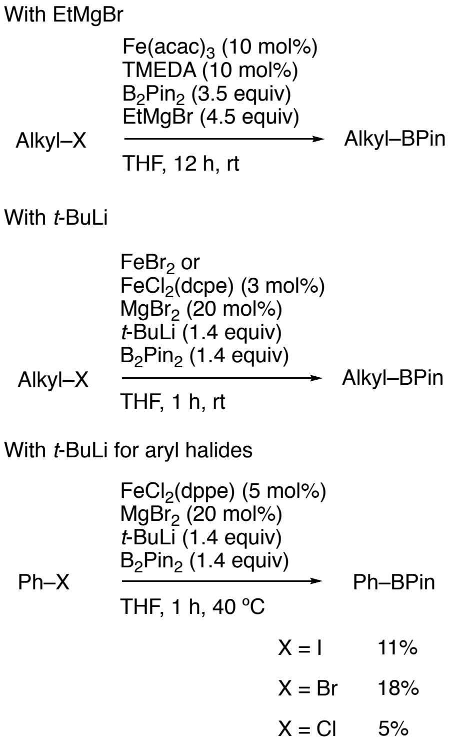


○ The use of inexpensive and low toxic iron
○ Inexpensive and redialy availble substrates

Recently, iron-catalyzed cross-coupling reactions[9] have been receiving much attention.[10] In contrast to other transition metal catalysis, the iron-catalyzed cross coupling with aryl electrophiles is uncommon because oxidative addition of organoiron species to aryl electrophiles is difficult, and homocoupling of the substrates readily proceeds.[11] This is problematic because the reaction mechanism of transition-metal-catalyzed borylation of aryl halides is similar with that of cross-coupling reaction.

Regarding the borylation of organic halides using iron catalysis, only two catalytic systems have been reported, which used reactive organometallic reagents such as ethyl magnesium bromide[12] and *tert*-butyllithium.[13] These reagents are necessary to activate the boron reagent and reduce iron to the low-valent state.[14] However, such catalytic systems could not achieve efficient borylation of aryl chlorides (e.g., 18% yield for bromobenzene, 5% yield for chlorobenzene even in the presence of *tert*-butyllithium) (Figure 3).[13]

Figure 3. Reported methods for iron-catalyzed borylation of alkyl and aryl halides



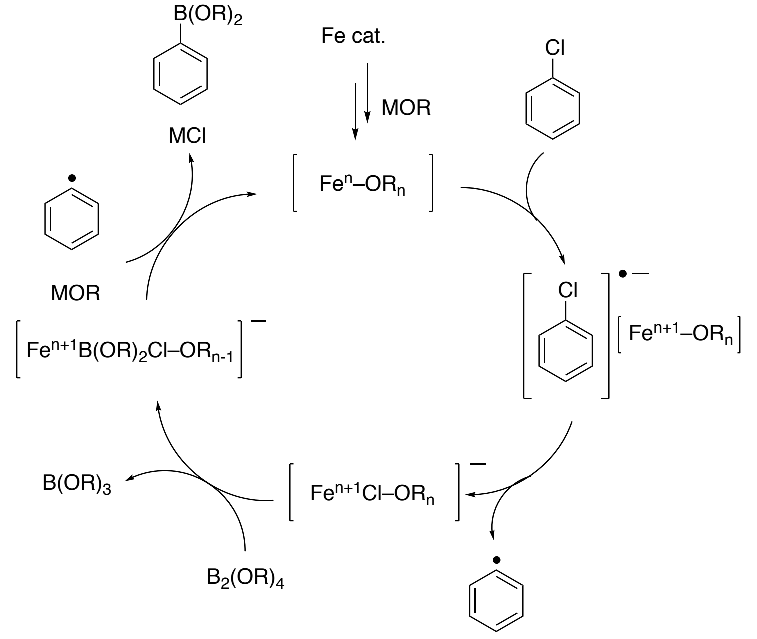
2-2. Reaction design for iron-catalyzed borylation of aryl chlorides

To achieve this difficult transformation, I envisioned using nucleophilic activation of an iron catalyst with an alkoxide. The key to achieve this transformation is the cleavage of the carbon–chloride bond, because oxidative addition is difficult by iron catalysis. Another promising pathway for cleaving the carbon-chloride bond is an electron transfer to an aryl halide from electron-rich species. By mixing an iron precatalyst such as an iron-halide complex and an alkoxide, an iron-alkoxide complex is easily generated.[15] A previous report suggested that an iron-alkoxide system is effective to generate an aryl radical from an aryl halide.[16] While the detailed mechanism was not discussed in the previous report, based on the relevant reports,[17] this reaction is initiated by an electron transfer to an aryl halide to give an aryl halide radical anion, and following elimination of the halide anion gives the aryl radical. Therefore, it is possible to cleave a carbon–halide bond by using the highly reductive iron-alkoxide complex.

Another important issue that must be solved in order to achieve this borylation reaction is how to generate an iron-boron complex, which is an important intermediate for the borylation reaction. In general, a transition metal-boron complex is generated by metathesis of a transition metal alkoxide with a diboron reagent. A theoretical study by the density functional theory (DFT) calculation showed that the generation of a thermodynamically stable alkoxide-boron is the driving force of this metathesis step.[18] Therefore, it is considered that transmetalation between an iron alkoxide complex and a diboron reagent is difficult because the energy gain obtained by generation of stable alkoxide-boron is low due to the strong bond between an iron atom and a boron atom. Notably, Nakamura *et al.* reported that an iron-alkoxide complex can transmetalate with diboron reagents to give an iron-boron complex, as supported by a theoretical study, and they used this catalytic system to achieve diboration and carboboration of alkenes.[19] If this generated aryl-boron complex reacts with aryl radical, borylation reaction takes place. Therefore, it is possible to generate an iron-boron complex from an iron-alkoxide complex.

Based on these considerations, my reaction design is shown in Figure 4. The aryl radical generated from an aryl halide in the presence of an iron salt and an alkoxide reacts with an iron-boron complex generated from an iron alkoxide complex and a diboron reagent to give the desired borylated product. Based on this reaction design, I expected that the use of additional ligands or reactive organometallic reagents is not required for any step of this reaction.

Figure 4. A reaction design for iron-catalyzed borylation of aryl chlorides

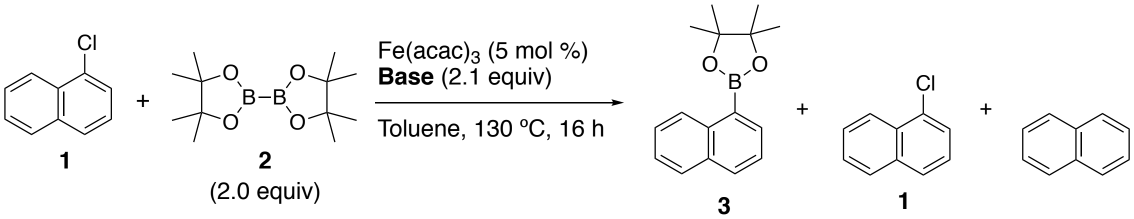


2-3. Effects of base

Based on the reaction design mentioned above, the choice of base would be critical because it coordinates to the iron center and determines the reactivity of the catalytic species. The results are summarized in Table 1.

It was found that simple reaction conditions are effective to promote iron-catalyzed borylation of aryl chlorides. Thus, a mixture of Fe(acac)$_3$ (5 mol%), potassium *tert*-butoxide (2.1 equiv), 1-chloronaphthalene (**1**) (1.0 equiv), bis(pinacolato)diboron (**2**) (2.0 equiv) in toluene was stirred at 130 ºC for 16 h to obtain borylated naphthalene (**3**) in 80% yield (entry 1). In contrast to the previously described transition-metal-catalyzed borylation of aryl halides, external ligands, special additives and preparation of the metal complex in advance are not necessary in this transformation. The use of high purity potassium *tert*-butoxide (entry 2) gave the desired product in a similar yield. This suggests that contamination in the base did not play a critical role for the borylation reaction. The desired product was obtained in a similar yield using lithium *tert*-butoxide (entry 3), but sodium *tert*-butoxide did not give the product at all (entry 4). The reactivity difference between sodium *tert*-butoxide and potassium *tert*-butoxide can be derived from the different iron alkoxide species obtained. Potassium methoxide reduced the reactivity and yielded the product in lower yield (entry 5). When alkoxides were used as a base, no precipitation was observed during the reaction. Therefore, the solubility difference is not important. Therefore, these results suggested that the importance of an iron-alkoxide complex. The use of other inorganic bases was totally ineffective for the borylation reaction (entries 6–8). Basicity of tertiary metal alkoxides is higher than that of primary metal alkoxides or other bases, therefore, it is considered that these are effective to generate reactive iron active species via nucleophilic activation.

Table 1. Effects of base[a]



entry	base	**3** (%)^b	**1** (%)^b	Naphthalene (%)^b
1	KO*t*-Bu	80	0	20
2	KO*t*-Bu^c	78	0	19
3	LiO*t*-Bu	77	0	16
4	NaO*t*-Bu	0	97	0
5	KOMe	13	65	21
6	NaOMe	0	91	0
7	KF	0	87	0
8	K_2CO_3	0	93	0

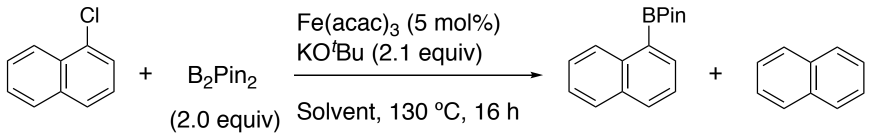
[a] Reaction conditions: 1-chloronaphthalene (**1**, 0.2 mmol), bis(pinacolato)diboron (**2**, 0.4 mmol), iron(III) acetylacetonate (0.01 mmol), base (0.42 mmol) in toluene (1.0 mL) at 130 °C for 16 h. [b] Yield determined by GC in the presence of tridecane as an internal standard. [c] The use of potassium *tert*-butoxide (purity 99.9%).

Dehalogenated product (naphthalene) was the main byproduct of this catalytic reaction, and to suppress the generation of this is important to improve the reaction efficiency. One possible hydrogen source is the solvent, therefore the effects of solvent was investigated next.

2-4. Effects of solvent

The effects of solvent were investigated to clarify the hydrogen source (Table 2). Solvents also can coordinate to the metal center to change the aggregation state of a metal-alkoxide complex, and therefore it can be critical reaction parameter. Because benzyilic hydrogen of toluene is sometimes reactive, *tert*-butyl benzene was used as a solvent. However, generation of naphthalene was not suppressed by changing the solvent. Indeed, using toluene-d^8 confirmed that toluene is not hydrogen source of naphthalene. The use of tetrahydrofuran also cannot suppress the generation of dehalogenated product. The use of cyclohexane actually gave a similar result. In this case, the selection of solvent is not so critical for the reaction efficiency compared to the selection of base.

Table 2. Effects of solvent[a]



Toluene	*t*-Butyl benzene	THF	Cyclohexane
80% (20%)	48% (31%)	37% (48%)	70% (25%)

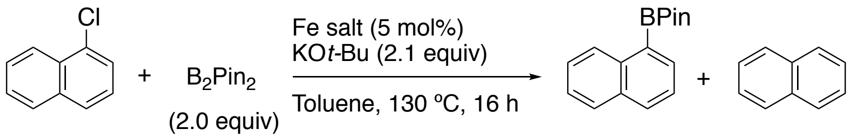
[a]Reaction conditions: 1-chloronaphthalene (0.2 mmol), bis(pinacolato)diboron (0.4 mmol), Fe(acac)$_3$ (0.01 mmol), potassium *tert*-butoxide (0.42 mmol) in solvent (1.0 mL) at 130 °C for 16 h. [b]Yield determined by GC in the presence of tridecane as an internal standard. The value in the parenthesis is yield of naphthalene.

2-5. Effects of inorganic iron source

Compared to the nature of the base, the selection of the iron precatalyst should not be so important, because based on the working hypothesis the iron precatalyst should be transformed to the active species with an alkoxide and a dibroron reagent. The results are summarized in Table 3.

In all cases, the reaction proceeded to some extent. Notably, the use of Fe(acac)$_2$ and iron (II) chloride gave similar results to that of Fe(acac)$_3$. This suggests that reactive iron active species is not an iron precatalyst itself but in situ generated species from an alkoxide or a borylating reagent. Although the valence of iron precatalyst is different, reduction by bis(pinacolato)diboron[20] can give the same iron species.

Table 3. Effects of iron precatalyst[a]



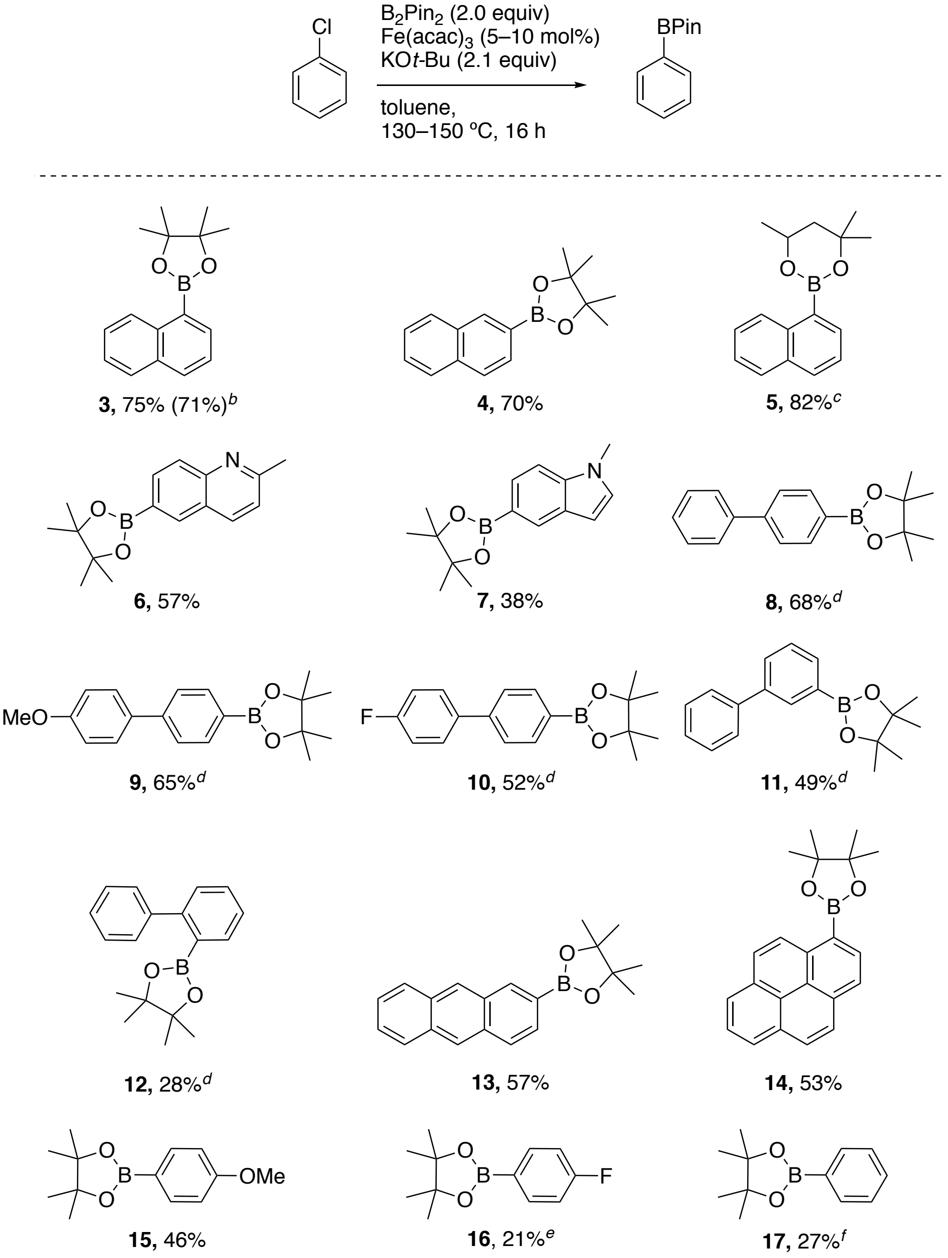
Fe(acac)$_3$	Fe(acac)$_2$	FeCl$_2$	Fe(OAc)$_2$	FeBr$_2$
80%[b]	78%[b]	75%[b]	59%[b]	57%[b]
(20%)	(21%)	(30%)	(23%)	(19%)

[a]Reaction conditions: 1-chloronaphthalene (0.2 mmol), bis(pinacolato)diboron (0.4 mmol), catalyst (0.01 mmol), potassium *tert*-butoxide (0.42 mmol) in toluene (1.0 mL) at 130 °C for 16 h. [b]Yield determined by GC in the presence of tridecane as an internal standard. The value in the parenthesis is yield of naphthalene.

2-6. Substrate scope

With the optimized conditions in hand, the scope of aromatic chlorides and borylating reagents was investigated (Figure 5). This transformation can be carried out on 10 mmol scale without significant reducing the reaction efficiency. 1-Chloronaphthalene and 2-chloronaphthalene gave the corresponding borylated compounds in a regioselective manner (**3** and **4**). This result rules out the possibility for the generation of a benzyne intermediate. Bis(hexylenepinaolato)diboron gave the borylated product in slightly higher yield (**5**). Quinoline- or indole-based heteroaromatic chlorides gave the borylated product in lower yield due to the recovery of the starting materials (**6** and **7**). To obtain a sufficient conversion, increase of the reaction temperature is necessary for biphenyl chlorides (**8**–**12**). In the presence of an electron-donating group (**9**), the borylated product is obtained in slightly higher yield compared to the electron-deficient substrates (**10**). Meta- or ortho-substituted biphenyl leads to the lower yield due to the recovery of the starting materials (**11** and **12**). This suggested the iron catalytic species is sensitive to the presence of steric hindrance. Polycyclic aromatic hydrocarbon (PAH) chlorides reacted smoothly to give corresponding conjugated borylated product, which is interested in the materials science,[21] in slightly lower yield compared to chloronaphthalenes due to slightly large amount of dehalogenated byproduct (**13** and **14**). With simple aryl chlorides, lower yield and large amount of recovery of the starting material were observed (**15**–**17**). Although the reason is unclear, in this case the electron-rich aryl chloride (**15**) also shows better reactivity than the electron-deficient aryl chloride (**17**).

Figure 5**.** Iron-catalyzed borylation of various aryl and heteroaryl chlorides[a]



3, 75% (71%)[b]

4, 70%

5, 82%[c]

6, 57%

7, 38%

8, 68%[d]

9, 65%[d]

10, 52%[d]

11, 49%[d]

12, 28%[d]

13, 57%

14, 53%

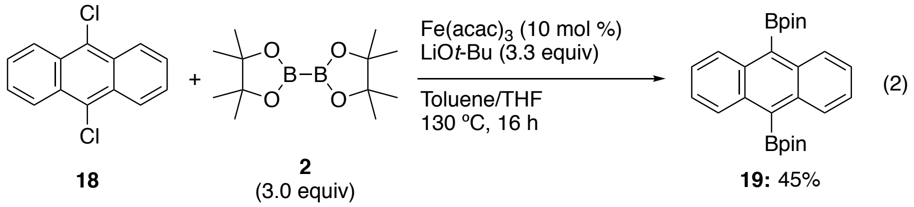
15, 46%

16, 21%[e]

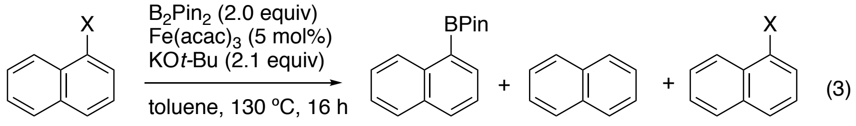
17, 27%[f]

[a]Reaction conditions: aryl chloride (0.4 mmol), bis(pinacolato)diboron (**2**, 0.8 mmol), Fe(acac)$_3$ (5–10 mol %), pottasium *tert*-butoxide (0.84 mmol) in toluene (2.0 mL) at 130 °C for 16 h, unless mentioned otherwise. See the experimental section for details. [b]Reaction with 10 mmol of the substrate. [c]Bis(hexylenepinacolato)diboron was used instead of bis(pinacolato)diboron. [d]Reaction temperature was 150 °C. [e]Yield was determined by ^{19}F NMR using trifluorotoluene as an internal standard. [f]Yield was determined by GC in the presence of tridecane as an internal standard.

Two-fold borylation took place with 3.0 equiv of lithium *tert*-butoxide and 3.3 equiv of bis(pinacolato)diboron to give the diborylated compound (**19**) in 45% yield (Eq. 2).



1-Bromonaphthalene and 1-iodonaphthalene gave the borylated products in moderate yield because a large amount of a dehalogenated product was obtained as a byproduct. Aryl tosylate was a low reactive substrate and the desired product was obtained in 12% yield (Eq. 3).

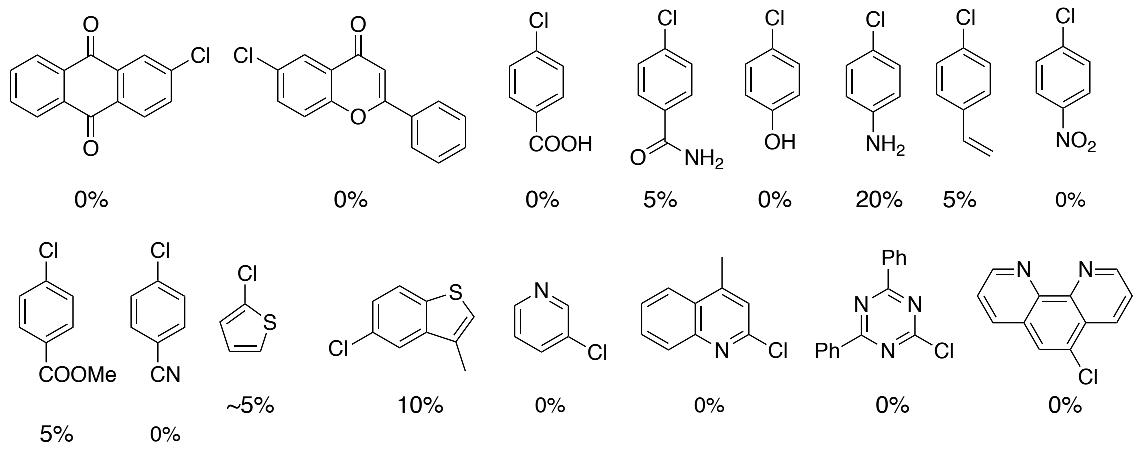


X = Br	41%	54%	0%
X = I	20%	67%	0%
X = OTs	12%	1%	80%

Yield is determined by GC in the presence of tridecane

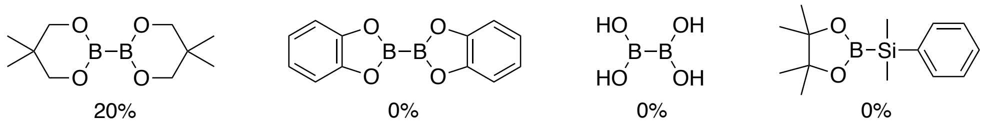
The substrates that did not show sufficient reactivity under the reaction conditions are listed in Figure 6. The presence of reactive functional group such as ketone, carboxylic acid, amide, hydroxyl, amine, vinyl, nitro, ester and cyano group, generally retarded or shut down the borylation reaction. I speculate that these reactive functional groups interact with the iron catalyst to suppress the formation of active species or functional groups react with an alkoxide. Also, nitrogen- or sulfur-containing heteroaromatic halide derivatives did not give the product due to the poisoning effect by a sulfur atom or a nitrogen atom, or reactive heteroaromatic halides cannot be tolerated in the presence of a strong base.

Figure 6. Aryl chlorides of unsatisfactory reactivity



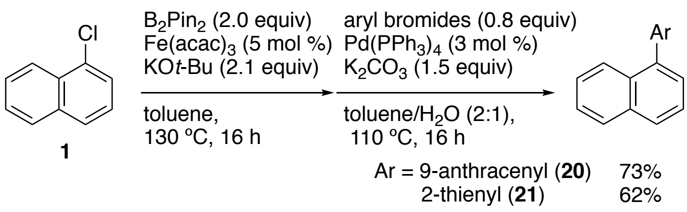
The scope of the borylating reagent was also examined. However, a variety of borylating reagents only gave the product in low yield, and large amount of starting material was recovered (Figure 7).

Figure *7*. Borylating reagents of unsatisfactory reactivity



2-7. One-pot Suzuki-Miyaura cross-coupling reaction

To investigate the utility of this transformation, I utilized the synthesized boron compound for a further transformation. The synthesized arylboronic acid pinacol esters can be used for Suzuki-Miyaura cross-coupling reaction without isolation, in an one-pot reaction. After iron-catalyzed borylation of 1-chloronaphtalene, a catalytic amount of a palladium catalyst, potassium carbonate, water, and an aryl bromide were added to the reaction mixture. By heating at 110 ºC for 16 h, the cross-coupling reaction proceeded. After isolation of the product, the desired π-conjugated molecules were obtained in 73% and 62% yield respectively (yields are based on the aryl halides) (Eq. 4).



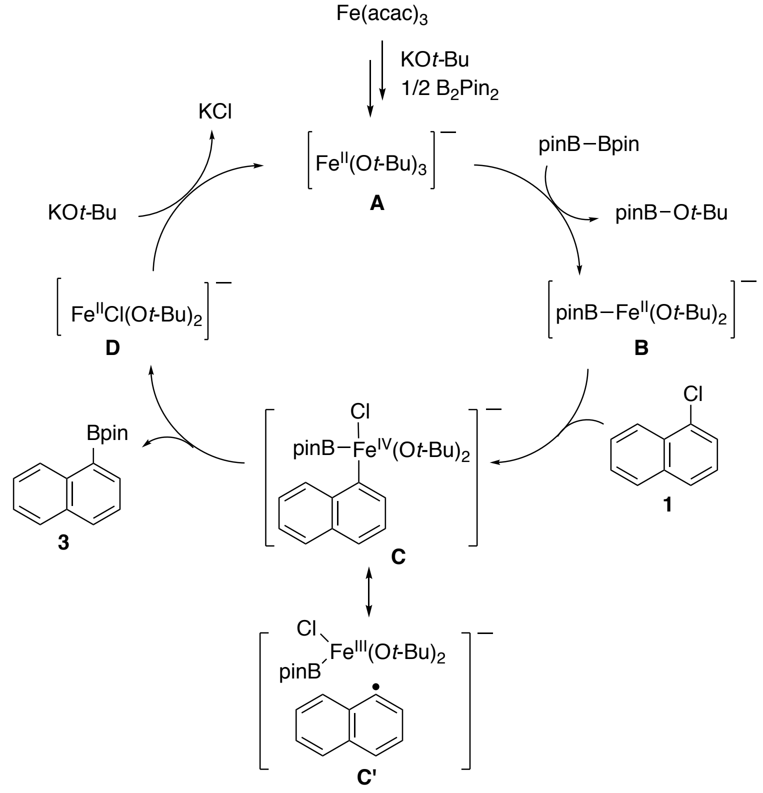
(4)

2-8. Proposed reaction mechanism

I propose two possible catalytic cycles based on several previous reports.[22–25] The first mechanism is based on the cross-coupling-type mechanism and the second mechanism is based on the radical chain mechanism.

The first possible catalytic cycle is shown in Figure 8. First, Fe(acac)$_3$ undergoes ligand exchange and reduction in the presence of an excess amount of potassium *tert*-butoxide and bis(pinacolato)diboron, to give an iron alkoxide ate complex **A**. This complex is known as a strong reductant for the pinacol coupling reaction.[22] The complex **A** transmetalates with the diboron reagent to generate a boryliron ate complex **B**.[19] This complex **B** reacts with an aryl chloride to give complex **C** or **C'**, which is in resonance structure with each other. Oxidative addition of an iron (II) complex to an aryl fluoride to generate an iron (IV) complex was suggested based on a previous computational study.[23] Reductive elimination then gives the desired borylated product **3** and complex **A** is regenerated via complex **D**.

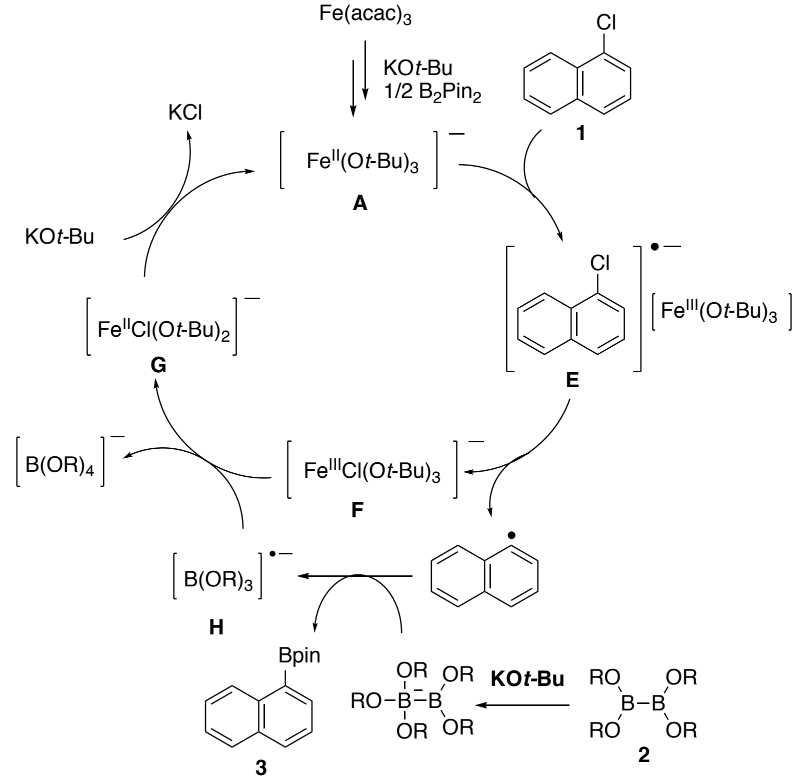
Figure 8. The first proposed mechanism



The second proposed mechanism is shown in Figure 9. The first step is the same with the first mechanism. The electron-rich iron-alkoxide complex directly transfers the electron to an aryl chloride to produce **E**.[24] Elimination of the chloride anion takes place faster to generate an aryl radical and an iron ate complex **F**. The resulting aryl radical reacts with the nucleophilically-activated borate to give the desired product **3** and a boryl radical anion **H** stabilized by an alkoxide anion.[25] Finally, the reduction of complex **F** by **H** gives the complex **G**. After ligand exchange, **E** is regenerated. Also, direct electron transfer from **H** to aryl chlorides is a possible pathway. In this case, iron actually acts as an initiator for this transformation rather than a catalyst.

In both cases, an aryl radical is important intermediate. However, homocoupling product of an aryl radical was not observed. Therefore, it suggested that lifetime of an aryl radical is short and it easily reacts with borylating reagent.

Figure 9. The second proposed mechanism



2-9. Conclusion

In conclusion, an iron-catalyzed borylation of aryl chlorides was developed. Inexpensive, low-reactive aryl chlorides could be used as an electrophile. The key to success was the nature of the alkoxide, rather than that of the solvent or of the iron precatalyst, in order to promote the desired borylation reaction. Based on several previous reports,[22–24] two reaction mechanisms assuming active participation of an iron alkoxide complex, which behaves as an effective reducing agent via nucleophilic activation, were proposed. This transformation demonstrates the high and unique reactivity of an iron alkoxide complex toward low-reactive electrophilic species, and this reactivity can be utilized for further development of cross-coupling type reaction under simple reaction conditions.

2-10. Experimental part

Material and methods

All reactions dealing with air- or moisture-sensitive compounds were carried out in a dry reaction vessel under argon. The water content of the solvent was confirmed with a Karl-Fischer Moisture Titrator (MKC-210, Kyoto Electronics Company) to be less than 20 ppm. Analytical thin-layer chromatography was performed on glass plates coated with 0.25 mm 230–400 mesh silica gel containing a fluorescent indicator (Merck). Gas-liquid chromatographic (GLC) analysis was performed on a Shimadzu GC-2014 or GC-2025 machine equipped with glass capillary column HR-1 (0.25-mm i.d. ´25 m). Flash silica gel column chromatography was performed on silica gel 60N (Kanto, spherical and neutral, 140–325 mesh) as described by Still.[26] The melting points of solid materials were determined on a Mel-Temp capillary melting-point apparatus. NMR spectra were measured on ECZ-500 and reported in parts per million from tetramethylsilane. ^{1}H NMR spectra in $CDCl_3$ were referenced internally to tetramethylsilane as a standard, and ^{13}C NMR spectra to the solvent resonance. Mass spectra (GC MS) are taken at SHIMADZU Parvum 2 gas chromatograph mass spectrometer.

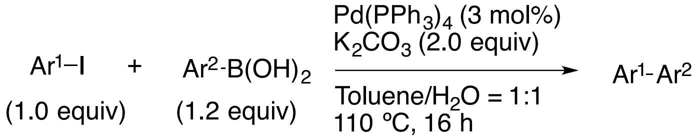
Unless otherwise noted, materials were purchased from Tokyo Kasei Co., Aldrich Inc., and other commercial suppliers. Anhydrous toluene was purchased from WAKO Pure Chemical and purified by a solvent purification system (GlassContour)[27] equipped with columns of activated alumina and supported copper catalyst (Q-5) prior to use. Iron(III) acetylacetonate (99.9%) was purchased from Aldrich Inc. Bis(pinacolato)diboron was purchased from Tokyo Kasei Co., and recrystallized from hexane before use. Potassium *tert*-butoxide (>97%) was purchased from Tokyo Kasei Co., and used without purification. We also confirmed that this reaction gives the same result when using potassium *tert*-butoxide in tetrahydrofuran (1M) from Tokyo Kasei Co., or potassium *tert*-butoxide (99.99%) from Aldrich Inc.

Caution: This reaction is sensitive to the quality of the alkoxide base. Old potassium *tert*-butoxide (generally, it cannot work after 3 months have passed since purchase) resulted in no reaction and total recovery of starting materials. If potassium *tert*-

butoxide is introduced as a solid, it should be rapidly weighted. Generally, a color change of the reaction mixture to black after 10 min indicates progress of the reaction.

Preparation of starting materials

Chlorobiphenyl derivatives were prepared by Suzuki-Miyaura coupling under standard conditions from the corresponding organic halides and organoboronic acids, as shown in the scheme below. 1-Chlropyrene was prepared by chlorination of pyrene with a stoichiometric amount of copper (II) chloride.[28] Other starting materials were purchased from Tokyo Kasei Co., Aldrich Inc., and other commercial suppliers.



Iron-catalyzed borylation of aryl chlorides on 10 mmol scale.

In an oven-dried 100 mL two-neck flask fitted with a reflux condenser, $Fe(acac)_3$ (175 mg, 0.49 mmol), potassium *tert*-butoxide (2.30 g, 20.5 mmol), and bis(pinacolato)diboron (5.10 g, 20.1 mmol) were added. The reaction vessel was evacuated and refilled with argon, then 1-chloronaphthalene (1.59 g, 9.8 mmol) and toluene (50 mL) were added successively. The resulting mixture was stirred at 130 °C under reflux for 16 h. After cooling the reaction mixture to room temperature, saturated ammonium chloride aqueous solution (50 mL) was added. The organic phase was extracted with ethyl acetate (3×50 ml), and the organic layer was dried over magnesium sulfate. After filtering off the solids, the volatiles were removed *in vacuo* to obtain an oily residue. The crude mixture was purified by column chromatography on silica gel (hexane/ethyl acetate = 97:3) to afford the desired compound as a colorless solid in 71% yield (1.76 g). The compound data was in good accordance with the literature.[29]

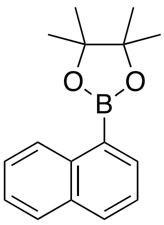
General procedure for borylation of aryl chlorides

In an oven-dried Schlenk tube, $Fe(acac)_3$ (0.02–0.04 mmol), potassium *tert*-butoxide (0.84 mmol), and bis(pinacolato)diboron (0.80 mmol) were added. The reaction vessel was evacuated and refilled with argon, then aromatic chloride (0.40

mmol) and toluene (2.0 mL) were added successively. The resulting mixture was stirred at 130 °C for 16 h. After cooling to room temperature, saturated ammonium chloride aqueous solution (3.0 mL) was added. The organic phase was extracted with ethyl acetate (3×5 ml), and the organic layer was passed over a pad of Florisil. The volatiles were removed *in vacuo* to obtain an oily residue. The crude mixture was purified by column chromatography on silica gel (typically hexane/ethyl acetate = 97:3) to afford the desired compound.

Compound data

1-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolane-2-yl)naphthalene (3)



Fe(acac)$_3$ (7.2 mg), potassium *tert*-butoxide (94 mg), bis(pinacolato)diboron (204 mg), 1-chloronaphthalene (64 mg) and toluene (2.0 mL) were used. The crude product was purified by column chromatography on silica gel (hexane/ethyl acetate = 97:3) to afford the desired compound as a white plate solid in 75% yield (75 mg). The compound data was in good accordance with the literature.[29]

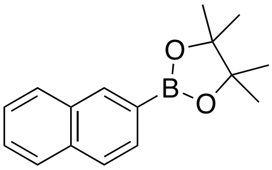
^{1}H NMR (500 MHz, CDCl$_3$): δ 8.77–8.75 (d, J = 8.5 Hz, 1H), 8.09–8.07 (m, 1H), 7.94–7.92 (d, J = 8.3 Hz, 1H), 7.84–7.82 (m, 1H), 7.55–7.45 (m, 3H), 1.42 (s, 12 H);

^{13}C NMR (125 MHz, CDCl$_3$): δ 136.9, 135.6, 133.2, 131.6, 128.4, 128.3, 126.3, 125.5, 124.9, 83.7, 25.0.

Melting point: 53–55 ºC (hexane, lit 54–55 ºC)

GC MS (EI) *m/z* (relative intensity): 239 (1), 196 (7), 139 (6), 84 (89), 83 (100).

2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolane-2-yl)naphthalene (4)



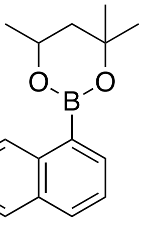
Fe(acac)$_3$ (14.3 mg), potassium *tert*-butoxide (90 mg), bis(pinacolato)diboron (208 mg), 2-chloronaphthalene (65 mg) and toluene (2.0 mL) were used. The crude product was purified by column chromatography on silica gel (hexane/ethyl acetate = 95:5) to afford the desired compound as a white granular solid in 70% yield (71 mg). The compound data was in good accordance with the literature.[29 above]

^{1}H NMR (500 MHz, CDCl$_3$): δ 8.74 (s, 1H), 7.89–7.87 (m, 1H), 7.86–7.82 (m, 3H), 7.53–7.46 (m, 2H), 1.36 (s, 12H).

^{13}C NMR (125 MHz, CDCl$_3$): δ 136.2, 135.0, 132.8, 130.4, 128.6, 127.7, 126.97, 126.95, 125.8, 83.9, 24.9.

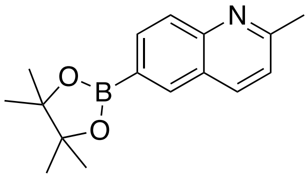
Melting Point: 64–66 ºC (hexane, lit 64–65 ºC)
GC MS (EI) *m/z* (relative intensity): 254 (41), 239 (8), 154 (100), 85 (8).

4,4,6-Trimethyl-2-(naphthalen-1-yl)-1,3,2-dioxaborinane (5)



Fe(acac)$_3$ (7.2 mg), potassium *tert*-butoxide (89 mg), bis(hexyleneglycolato)diboron (203 mg), 1-chloronaphthalene (64 mg) and toluene (2.0 mL) were used. The crude product was purified by column chromatography on silica gel (hexane/ethyl acetate = 95:5) to afford the desired compound as a white fiber solid in 82% yield (82 mg). The compound data was in good accordance with the literature.[30]
^{1}H NMR (500 MHz, CDCl$_3$): δ 8.79–8.78 (d, *J* = 8.6 Hz, 1H), 8.03–8.01 (m, 1H), 7.87–7.86 (d, *J* = 8.1 Hz, 1H), 7.81–7.80 (m, 1H), 7.50–7.42 (m, 3H), 4.49–4.45 (m, 1 H), 1.96-1.93 (dd, *J* = 14.0 Hz, 2.9 Hz, 1H), 1.74–1.69 (m, 1H), 1.47 (s, 6H), 1.44–1.42 (d, *J*= 6.3 Hz, 3H);
^{13}C NMR (125 MHz, CDCl$_3$): δ 136.7, 134.2, 133.4, 130.1, 128.38, 128.34, 125.8, 125.1, 124.9, 71.5, 65.3, 46.0, 31.4, 28.3, 23.3.
Melting point: 51–53 ºC (hexane, the melting point was not reported in the literature)
GC MS (EI) *m/z* (relative intensity): 254 (72), 154 (100).

2-Methyl-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)quinolone (6)



Fe(acac)$_3$ (14.3 mg), potassium *tert*-butoxide (96 mg), bis(pinacolato)diboron (204 mg), 6-chloro-2-methyl quinoline (70 mg) and toluene (2.0 mL) were used. The crude product was purified by column chromatography on silica gel (hexane/ethyl acetate = 80:20) to afford the desired compound as a white fiber solid in 57% yield (61 mg). The compound data was in good accordance with the literature.[29]

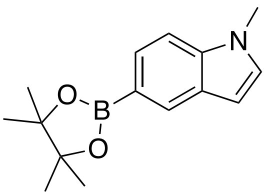
^{1}H NMR (500 MHz, $CDCl_3$): δ 8.29 (s, 1H), 8.08–8.04 (m, 2H), 8.00–7.98 (m, 1H), 7.29–7.26 (m, 1H), 2.75 (s, 3H), 1.39 (s, 12 H);

^{13}C NMR (126 MHz, $CDCl_3$): δ 160.1, 149.3, 136.8, 135.8, 134.3, 127.6, 125.9, 122.1, 84.1, 25.5. 24.9.

Melting point: 105–106 ºC (hexane, the melting point was not reported in the literature)

GC MS (EI) *m/z* (relative intensity): 269 (40), 254 (16), 183 (98), 169 (100).

1-Methyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-indole (7)



Fe(acac)$_3$ (14.2 mg), potassium *tert*-butoxide (90 mg), bis(pinacolato)diboron (202 mg), 5-chloro-1-methyl indole (79 mg) and toluene (2.0 mL) were used. Crude product was purified by column chromatography on silica gel (hexane/ethyl acetate = 95:5 to 80:20) to afford the desired compound as a yellow granular solid in 38% yield (40 mg). The compound data was in good accordance with the literature.[31]

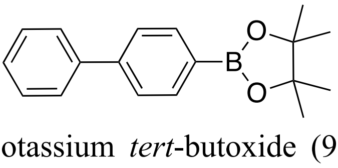
^{1}H NMR (500 MHz, $CDCl_3$): δ 8.16 (s, 1H), 7.67–7.65 (m, 1H), 7.33–7.31 (m, 1H), 7.04–7.03 (m, 1H), 6.50–6.49 (m, 1H), 3.79 (s, 3 H), 1.37 (s, 12H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 138.6, 128.9, 128.8, 128.2, 127.6, 108.6, 101.6, 83.4, 24.9.

Melting point: 108–109 ºC (hexane, lit 112 ºC)

GC MS (EI) *m/z* (relative intensity): 257 (82), 184 (21), 171 (35), 157 (100).

2-(Biphenyl-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (8)



Fe(acac)$_3$ (14.4 mg), potassium *tert*-butoxide (92 mg), bis(pinacolato)diboron (204 mg), 4-chloro-1,1’-biphenyl (75 mg) and toluene (2.0 mL) were used. The reaction temperature was 150 ºC. Crude product was purified by column chromatography on silica gel (hexane/ethyl acetate = 94:6) to afford the desired compound as a white granular solid in 68% yield (76 mg). The compound data was in good accordance with the literature.[32]

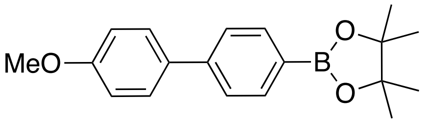
^{1}H NMR (500 MHz, CDCl$_3$): δ 7.89–7.88 (d, J = 8.3 Hz, 2H), 7.63–7.60 (m, 4H), 7.46–7.43 (m, 2H), 7.37–7.34 (m, 1 H) , 1.36 (s, 12 H);

^{13}C NMR (126 MHz, CDCl$_3$): δ 143.9, 141.0, 135.2, 128.8, 127.5, 127.2, 126.4, 83.8, 24.9.

Melting point: 102–103 ºC (hexane, lit 102–104 ºC)

GC MS (EI) *m/z* (relative intensity): 280 (55), 265 (23), 194 (64), 180 (100).

2-(4’-Methoxybiphenyl-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (9)



Fe(acac)$_3$ (14.1 mg), potassium *tert*-butoxide (89 mg), bis(pinacolato)diboron (204 mg), 4-chloro-4’-methoxy-1,1’-biphenyl (88 mg) and toluene (2.0 mL) were used. The reaction temperature was 150 ºC. The crude product was purified by column chromatography on silica gel (hexane/ethyl acetate = 94:6) to afford the desired compound as a white amorphous solid in 65% yield (80 mg). The compound data was in good accordance with the literature.[32]

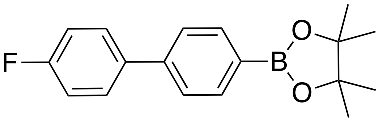
^{1}H NMR (500 MHz, CDCl$_3$): 7.87–7.85 (d, J = 7.5 Hz, 2H), 7.57–7.55 (m, 4H), 6.99–6.97 (m, 2H), 3.85 (s, 3 H) , 1.36 (s, 12 H);

^{13}C NMR (126 MHz, CDCl$_3$): 159.4, 143.4, 135.2, 133.5, 128.2, 126.0, 114.2, 83.8, 55.3, 24.9.

Melting point: 134–136 ºC (hexane, lit 130–134 ºC)

GC MS (EI) *m/z* (relative intensity): 310 (100), 224 (32), 210 (85), 195 (18), 167 (16).

2-(4’-Fluorobiphenyl-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (10)



Fe(acac)$_3$ (14.1 mg), potassium *tert*-butoxide (91 mg), bis(pinacolato)diboron (204 mg), 4-chloro-4’-fluoro-1,1’-biphenyl (82 mg) and toluene (2.0 mL) were used. Reaction temperature was 150 ºC. The crude product was purified by column chromatography on silica gel (hexane/ethyl acetate = 98:2) to afford the desired compound as a white amorphous solid in 52% yield (62 mg). The compound data was in good accordance with the literature.[33]

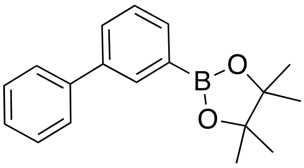
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.89–7.88 (d, J = 5.4 Hz, 2H), 7.61–7.55 (m, 4H), 7.14–7.11 (m, 2H), 1.36 (s, 12 H);

^{13}C NMR (126 MHz, $CDCl_3$): δ 162.6 (d, J = 245 Hz), 142.8, 137.1 (d, J = 3.6 Hz), 135.3, 128.8 (d, J = 8.4 Hz), 127.2, 126.3, 115.6 (d, J = 21.6 Hz), 83.8, 24.9.

Melting point: 91–92 ºC (hexane, the melting point was not reported in the literature)

GC MS (EI) *m/z* (relative intensity): 298 (53), 283 (25), 212 (57), 198 (100).

2-(Biphenyl-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (11)



Fe(acac)$_3$ (14.1 mg), potassium *tert*-butoxide (92 mg), bis(pinacolato)diboron (204 mg), 3-chloro-1,1'-biphenyl (71 mg), and toluene (2.0 mL) were used. Reaction temperarature was 150 °C. The crude product was purified by column chromatography on silica gel (hexane/ethyl acetate = 98:2) to afford the desired compound as a yellow needle solid in 49% yield (52 mg). The compound data was in good accordance with the literature.[34]

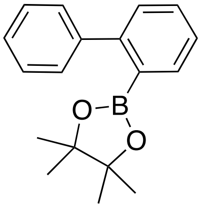
^{1}H NMR (500 MHz, $CDCl_3$): δ 8.05 (s, 1H), 7.80–7.79 (d, J = 7.5 Hz, 1H), 7.70–7.69 (d, J = 7.5 Hz, 1H), 7.64–7.62 (m, 2H), 7.47–7.41 (m, 3 H), 7.35–7.33 (m, 1 H), 1.36 (s, 12 H);

^{13}C NMR (126 MHz, $CDCl_3$): δ 141.1, 140.5, 133.6, 133.5, 130.0, 128.6, 128.2, 127.3, 127.2, 83.9, 24.9.

Melting point: 84–85 ºC (hexane, the melting point was not reported in the literature)

GC MS (EI) *m/z* (relative intensity): 280 (60), 194 (80), 180 (100), 152 (26), 85 (14).

2-(Biphenyl-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (12)



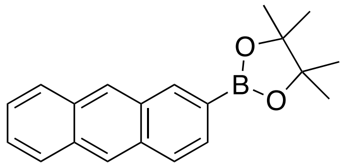
$Fe(acac)_3$ (14.0 mg), potassium *tert*-butoxide (91 mg), bis(pinacolato)diboron (204 mg), 2-chloro-1,1'-biphenyl (73 mg) and toluene (2.0 mL) were used. Reaction temperature was 150 °C. The crude product was purified by column chromatography on silica gel (hexane/ethyl acetate = 98:2) to afford the desired compound as a colorless oil in 28% yield (30 mg). The compound data was in good accordance with the literature.[29]

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.72–7.71 (d, J = 7.2 Hz, 1H), 7.45–7.43 (m, 1H), 7.41–7.32 (m, 7H), 1.20 (s, 12 H);

^{13}C NMR (126 MHz, $CDCl_3$): δ 147.5, 143.2, 134.4, 130.0, 129.1, 128.9, 127.7, 126.8, 126.3, 83.7, 24.6.

GC MS (EI) *m/z* (relative intensity): 280 (35), 265 (12), 194 (21), 179 (40), 164 (100)

2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolane-2-yl)anthracene (13)



$Fe(acac)_3$ (14.1 mg), potassium *tert*-butoxide (90 mg), bis(pinacolato)diboron (204 mg), 2-chloroanthracene (84 mg) and toluene (2.0 mL) were used. The crude product was purified by column chromatography on silica gel (hexane/ethyl acetate = 98:2) to afford the desired compound as a yellow granular solid in 57% yield (69 mg). The compound data was in good accordance with the literature.[35]

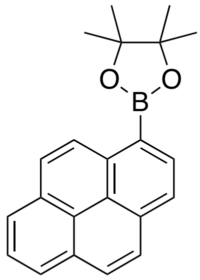
^{1}H NMR (500 MHz, $CDCl_3$): δ 8.56 (s, 1H), 8.47 (s, 1H), 8.40 (s, 1H), 8.03-7.97 (m, 3H), 7.80–7.78 (m, 1H), 7.48-7.45 (m, 1H), 1.41 (s, 12 H);

^{13}C NMR (126 MHz, $CDCl_3$): δ 137.3, 132.7, 132.4, 131.6, 131.1, 129.2, 128.5, 128.1, 127.4, 127.1, 125.9, 125.8, 125.2, 84.0, 24.9.

Melting point: 105–106 ºC (hexane, the melting point was not reported in the literature)

GC MS (EI) *m/z* (relative intensity): 304 (100), 204 (84).

1-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolane-2-yl)pyrene (14)



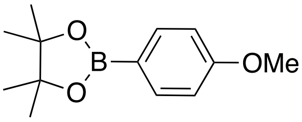
Fe(acac)$_3$ (14.2 mg), potassium *tert*-butoxide (91 mg), bis(pinacolato)diboron (204 mg), 1-chloropyrene (94 mg) and toluene (2.0 mL) were used. The crude product was purified by column chromatography on silica gel (hexane/ethyl acetate = 98:2) to afford the desired compound as a pale red oil in 53% yield (69 mg). The compound data was in good accordance with the literature.[36]

^{1}H NMR (500 MHz, CDCl$_3$): δ 9.08–9.06 (d, J = 9.1 Hz, 1H), 8.54–8.53 (d, J = 7.8 Hz, 1H), 8.23–8.06 (m, 6H), 8.03–8.00 (t, J = 7.8 Hz 1H), 1.49 (s, 12 H);

^{13}C NMR (126 MHz, CDCl$_3$): δ 136.4, 133.8, 133.4, 131.1, 130.8, 128.5, 128.0, 127.8, 127.5, 125.7, 125.3, 125.2, 124.6, 124.4, 124.1, 83.9, 25.1.

GC MS (EI) *m/z* (relative intensity): 328 (100), 255 (32), 228 (98).

2-(4-Methoxyphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (15)



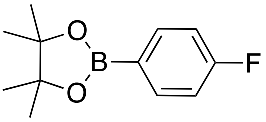
Fe(acac)$_3$ (14.2 mg), potassium *tert*-butoxide (92 mg), bis(pinacolato)diboron (204 mg), 4-chloroanisole (55 mg) and toluene (2.0 mL) were used. The crude product was purified by column chromatography on silica gel (hexane/ethyl acetate = 95:5) to afford the desired compound as a colorless oil in 46% yield (42 mg). The compound data was in good accordance with the literature.[29]

^{1}H NMR (500 MHz, CDCl$_3$): δ 7.76–7.74 (dd, J = 6.9 Hz, J = 1.7 Hz, 2H), 6.90–6.89 (dd, J = 6.9 Hz, J = 2.0 Hz, 1H), 3.82 (s, 3 H), 1.33 (s, 12 H);

^{13}C NMR (126 MHz, CDCl$_3$): δ 162.1, 136.5, 113.3, 83.5, 55.1, 24.8.

GC MS (EI) *m/z* (relative intensity): 234 (65), 219 (49), 148 (66), 134 (100).

2-(4-Fluorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (16)

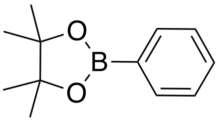


Fe(acac)$_3$ (14.2 mg), potassium *tert*-butoxide (91 mg), bis(pinacolato)diboron (202 mg), 1-chloro-4-fluorobenzene (52 mg) and toluene (2.0 mL) were used. After cooling the reaction mixture to room temperature, saturated ammonium chloride solution (3.0 mL) was added. The organic phase was extracted with ethyl acetate (3×5 ml), and the organic layer was passed over a pad of Florisil. The volatiles were removed *in vacuo* to obtain an oily residue. The yield was determined by ^{19}F NMR in the presence of benzotrifluoride as an internal standard. The title product was obtained in 21% yield. The compound data was in good accordance with the literature.[37]

^{19}F NMR (470 MHz, CDCl$_3$): δ −109.42

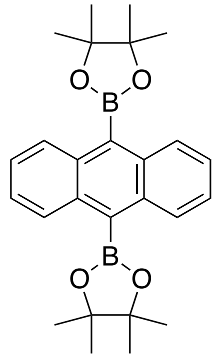
GC MS (EI) *m/z* (relative intensity): 222 (10), 207 (58), 136 (33), 123 (100).

2-Phenyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (17)



Fe(acac)$_3$ (14.1 mg), potassium *tert*-butoxide (91 mg), bis(pinacolato)diboron (205 mg), 4-chlorobenzotrifluoride (38 mg) and toluene (2.0 mL) were used. After cooling the reaction mixture to room temperature, saturated ammonium chloride aqueous solution (3.0 mL) was added. The organic phase was extracted with ethyl acetate (3×5 ml), and the organic layer was passed over a pad of Florisil. The volatiles were removed *in vacuo* to obtain an oily residue. The yield was determined by GC, calibrated in the presence of tridecane as an internal standard. The title product was obtained in 27% yield.

Iron-Catalyzed Borylation of 9,10-Dichloroanthracene (19)



In an oven-dried Schlenk tube, Fe(acac)$_3$ (14.0 mg, 0.04 mmol), bis(pinacolato)diboron (302 mg, 1.20 mmol) and 9,10-dichloroanthracene (100 mg, 0.40 mmol) were added. The reaction vessel was evacuated and refilled with argon, then lithium *tert*-butoxide in THF (1.0 M) (1.3 mL, 1.3 mmol) and toluene (2.0 mL) were added successively. The resulting mixture was stirred at 130 °C for a 16 h. After cooling to room temperature, saturated ammonium chloride aqueous solution (3.0 mL) was added. The organic phase was extracted with toluene (3×5 ml), and the organic layer was passed over a pad of Florisil. The volatiles were removed *in vacuo* to obtain an oily residue. The crude mixture was purified by column chromatography on silica gel (hexane/ethyl acetate = 95:5) to afford the desired compound as a white granular solid in 45% yield (76 mg). The compound data was in good accordance with the literature.[38]

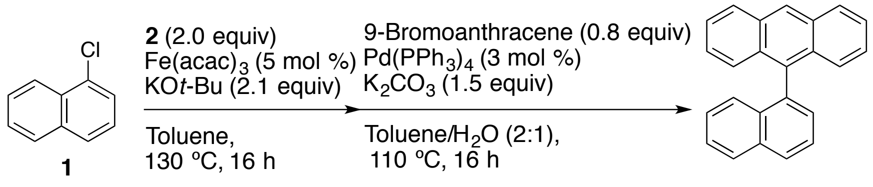
^{1}H NMR (500 MHz, CDCl$_3$): δ 8.34–8.32 (m, 4H), 7.46–7.44 (m, 4H), 1.58 (s, 24 H);

^{13}C NMR (126 MHz, CDCl$_3$): δ 134.9, 128.8, 125.1, 84.5, 25.2.

Melting Point: >300 ºC (hexane, lit 325–328 ºC)

GC MS (EI) *m/z* (relative intensity): 430 (100), 230 (23), 101 (30), 83 (18).

One-pot Suzuki-Miyaura cross-coupling with 9-Bromoanthracene under palladium catalysis (20)



20: 73% yield

In an oven-dried Schlenk tube, Fe(acac)$_3$ (0.02 mmol, 7.2 mg), potassium *tert*-butoxide (0.84 mmol, 92 mg), and bis(pinacolato)diboron (0.80 mmol, 205 mg) were added. The reaction vessel was evacuated and refilled with argon, 1-chloronaphthalene (0.40 mmol, 65 mg) and toluene (2.0 mL) were added successively. The resulting mixture was stirred at 130 °C for a 16 h. After cooling the reaction mixture to room temperature, $Pd(PPh_3)_4$ (0.011 mmol, 13.2 mg), potassium carbonate (0.6 mmol, 83 mg), 9-bromoanthracene (0.31 mmol, 81 mg) and water (1 mL) were added. The resulting mixture was stirred at 110 °C for a 16 h. After cooling the reaction mixture to room temperature, saturated NH_4Cl aqueous solution was added. The organic phase was extracted with ethyl acetate (3×5 ml), and the organic layer was passed over a pad of Florisil. The volatiles were removed *in vacuo* to obtain an oily residue. The crude mixture was purified by column chromatography on silica gel (hexane 100%) to afford the desired compound as a white needle solid in 73% yield (70.1 mg). The compound date was in good accordance with literature.[39]

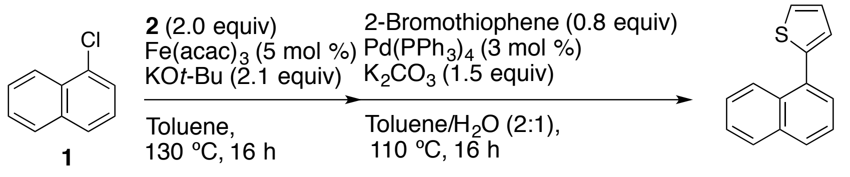
^{1}H NMR (500 MHz, $CDCl_3$): δ 8.58 (s, 1H), 8.10–8.09 (d, J = 8.6 Hz, 2H), 8.06–8.04 (d, J = 8.3 Hz, 1H), 8.01–7.99 (d, J = 8.3 Hz, 1H), 7.70–7.67 (m, 1H), 7.53–7.51 (m, 1H), 7.48–7.43 (m, 3H), 7.40–7.39 (d, J = 8.9 Hz, 2H), 7.26–7.20 (m, 5H), 7.19–7.17 (m, 1H), 7.07–7.05 (d, J = 8.3 Hz, 1H);

^{13}C NMR (126 MHz, $CDCl_3$): δ 136.5, 134.9, 133.6, 133.5, 131.4, 131.0, 129.1, 128.4, 128.2, 128.1, 126.89, 126.87, 126.5, 126.2, 125.9, 125.52, 125.47, 125.2.

Melting Point: 148–150 ºC (hexane, lit 160–161 ºC)

GC MS (EI) *m/z* (relative intensity): 304 (100), 289 (9), 259 (9), 150 (34).

One-pot Suzuki-Miyaura cross-coupling with 2-bromothiophene under palladium catalysis (21)



21: 62% yield

In an oven-dried Schlenk tube, $Fe(acac)_3$ (0.02 mmol, 7.2 mg), potassium *tert*-butoxide (0.84 mmol, 91 mg), and bis(pinacolato)diboron (0.80 mmol, 203 mg) were added. The reaction vessel was evacuated and refilled with argon, then 1-chloronaphthalene (0.40 mmol, 65 mg) and toluene (2.0 mL) were added successively. The resulting mixture was stirred at 130 °C for a 16 h. After cooling the reaction mixture to room temperature, $Pd(PPh_3)_4$ (0.01 mmol, 11.2 mg), potassium carbonate (0.6 mmol, 84 mg), 2-bromothiophene (0.31 mmol, 50 mg), and water (1 mL) were added. The resulting mixture was stirred at 110 °C for a 16 h. After cooling the reaction mixture to room temperature, saturated NH_4Cl aqueous solution was added. The organic phase was extracted with ethyl acetate (3×5 ml), and the organic layer was passed over a pad of Florisil. The volatiles were removed *in vacuo* to obtain an oily residue. The crude mixture was purified by column chromatography on silica gel (hexane 100%) to afford the desired compound as colorless oil in 62% yield (40.6 mg). The compound date was in good accordance with literature.[40]

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.23–8.21 (m, 1H), 7.91–7.87 (m, 2H), 7.58–7.57 (m, 1H), 7.53–7.47 (m, 3H), 7.44–7.42 (m, 1H), 7.53–7.51 (m, 1H), 7.48–7.43 (m, 3H), 7.40–7.39 (d, J = 8.9 Hz, 2H), 7.26–7.25 (m, 1H), 7.20–7.18 (m, 1H);

^{13}C NMR (126 MHz, $CDCl_3$): δ 141.8, 133.8, 132.4, 131.9, 128.4, 128.3, 128.2, 127.4, 127.3, 126.4, 126.0, 125.7, 125.6, 125.2.

GC MS (EI) *m/z* (relative intensity): 210 (100), 165 (30), 104 (12).

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Chapter 3

本章については，５年以内に雑誌等で刊行予定のため

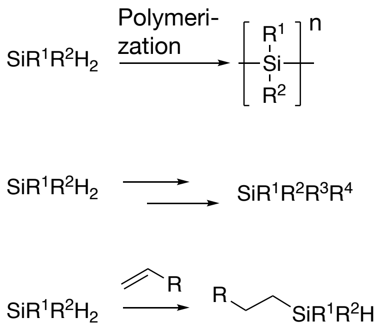
Chapter 4

Silylation of Aryl Halides with Monoorganosilanes Activated by Lithium Alkoxide

4-1. Introduction

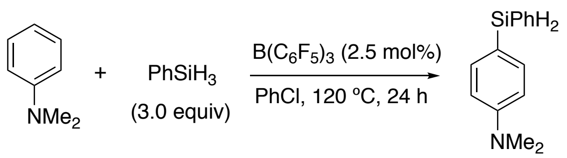
Diorganosilanes are important synthetic intermediates for the synthesis of organosilanes,[1] important compounds for organic synthesis,[2] medicinal chemistry,[3] materials science[4] and polymer chemistry (Figure 1).[5]

Figure 1. Utilization of diorganosilanes

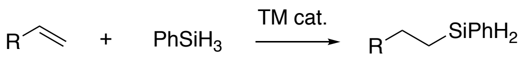


There have been however only limited synthetic approaches[6] to this class of compounds: substitution (Eq. 1),[7] Friedel-Crafts-type reaction (Eq. 2),[8] and transition-metal-catalyzed hydrosilylation of an alkene or alkyne with monoorganosilanes (Eq. 3).[9] The substitution reaction requires reactive organometallic reagents such as Grignard reagents or organolithium reagents, and stepwise synthesis is necessary to obtain the desired diorganosilanes. The Friedel-Crafts-type reaction suffers from narrow scope, and the substrates are limited to electron-rich arenes. The hydrosilylation reaction can only be applied to the synthesis of alkylated diorganosilanes. Thus, there is no general method for the synthesis of diorganosilanes.

$$R{-}X \xrightarrow{\text{Metalation}} R{-}M \xrightarrow{SiCl_4} R_2SiCl_2 \xrightarrow{\text{Reduction}} R_2SiH_2 \qquad (1)$$

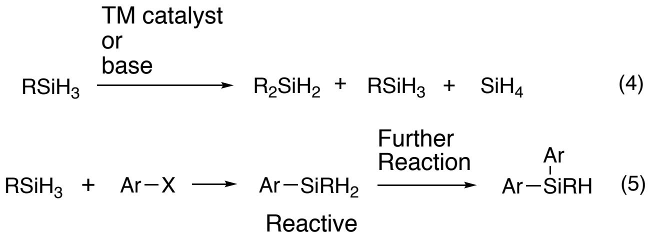


(2)



(3)

The synthetic difficulty arises because of the high reactivity of monoorganosilanes and diorganosilanes, which causes in many cases the disproportionation of silanes or formation of tri- or tetraorganosilanes via overreaction (Eq. 4 and Eq. 5). For example, transition-metal-catalyzed silylation of aryl halides is a powerful method to produce aryl silanes. However, coupling of monoorganosilanes with aryl halides gave a mixture of several arylated silanes.[10]



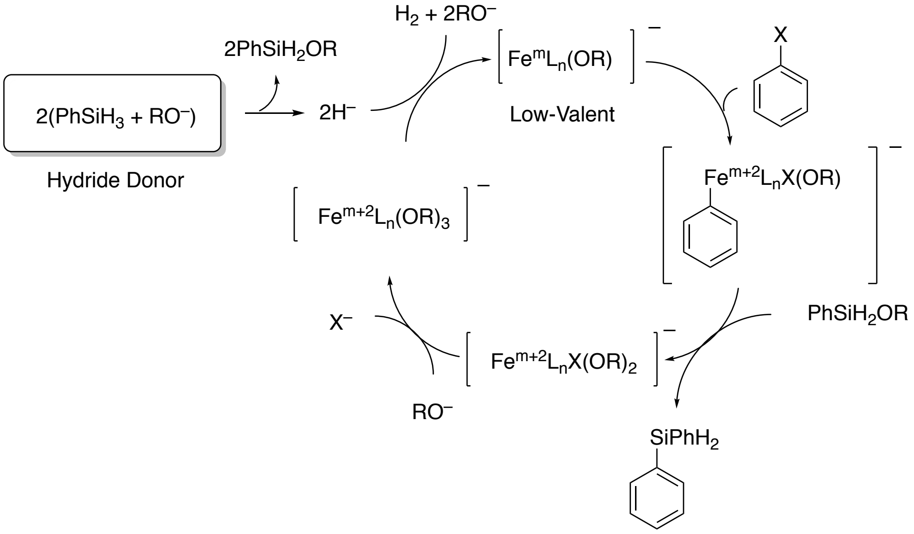
$$RSiH_3 \xrightarrow{\text{TM catalyst or base}} R_2SiH_2 + RSiH_3 + SiH_4 \quad (4)$$

$$RSiH_3 + Ar{-}X \longrightarrow \underset{\text{Reactive}}{Ar{-}SiRH_2} \xrightarrow{\text{Further Reaction}} Ar{-}\overset{Ar}{Si}RH \quad (5)$$

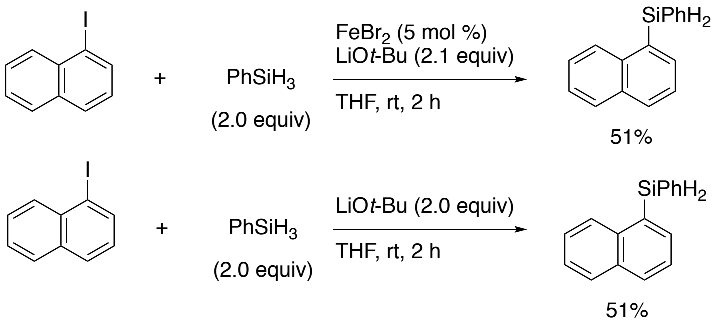
4-2. Initial finding

My initial idea was to generate a low-valent iron catalyst in order to achieve silylation of aryl halides via nucleophilic activation of a hydrosilane by an alkoxide (Figure 2). Recently, Thomas *et al.* reported[11] that the combination of hydrosilane and metal alkoxide can reduce an iron catalyst to the low-valent state and the low-valent iron is active catalyst for various reactions. A nucleophilically-activated hydrosilane shows hydride character because the nucleophilicity of the hydride ligand attached to the silicon atom is increased. The generated low-valent iron has high nucleophilicity, and therefore it can easily react with an aryl halide to give a nucleophilic aryl group. The resulting nucleophilic aryl group reacts with an in situ-generated alkoxysilane to give the silylated product.

Figure 2. Initial idea for iron-catalyzed silylation



Based on this reaction design, the silylation of aryl halides proceeded in the presence of a catalytic amount of iron salt (Eq. 6). However, a control experiment revealed that this reaction did not require any iron catalyst (Eq. 7).



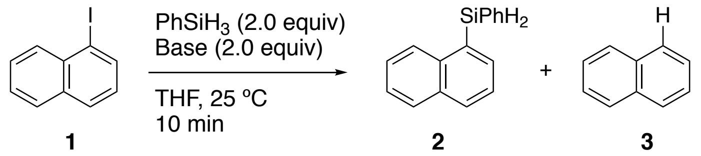
Yield is estimated by GC in the presence of tridecane

I considered that this result is important, considering the challenging synthesis of diorganosilanes mentioned in the previous section. In this transformation, disproportionated products or overreacted products were not observed. Although the reaction mechanism was unclear at that time, I hypothesized that nucleophilic activation of a hydrosilane with an alkoxide is important to produce the desired silylated product. Recently, Grubbs and Stoltz *et al.* reported a related reactivity, the C–H silylation of heteroaromatics by an earth-abundant metal catalyst such as potassium *tert*-butoxide.[12] Based on the mechanistic study, two possible reaction mechanisms were proposed.[13] In both cases, generation of a silicate through nucleophilic activation of a hydrosilane by an alkoxide was suggested by IR or MS techniques and it was proposed as an important reaction intermediate. Although present reaction condition is slightly different from that of C–H silylation reactions, similar reaction mechanism is expected and nucleophilic activation of a hydrosilane by an alkoxide is important step. Therefore, it is considered that selection of base or solvent should be important to control the aggregation state of a metal alkoxide and reaction efficiency of this transformation.

4-3. Effects of alkoxide

The effects of alkoxide were examined (Table 1). After the reaction, the starting material (**1**), silylated product (**2**), dehalogenated product (**3**) were obtained and disproportionated products or overreacted products were not observed by GC, GC–MS and NMR. In the absence of a base, no reaction occurred and the starting material was recovered (entry 1). Both secondary and tertiary lithium alkoxides reacted well and similar results were obtained (entries 2 and 3). On the other hand, the use of lithium ethoxide or lithium phenoxide did not give the desired product at all (entries 4 and 5). Based on these results, it is considered that generation of a monomeric alkoxide is important to achieve this reaction. Less bulky base easily aggregates to make a metal cluster, which may be unreactive toward phenylsilane. This hypothesis is also supported by the experimental results described in next section. Other possible reason of these reactivity differences is derived from high basicity of an alkoxide. Generally, basicity of secondary and tertiary lithium alkoxides is higher than that of primary lithium alkoxides. Therefore, high basicity is effective to activate a silane reagent via nucleophilic activation. Addition of 12-crown-4-ether, which is known as a trapping reagent for the lithium cation,[14] did not affect the reaction outcome (entry 6). Potassium *tert*-butoxide and sodium *tert*-butoxide gave the product in lower yield and generated disproportionated products such as silane, diphenylsilane and triphenylsilane.

Table 1. Effects of alkoxide[a]



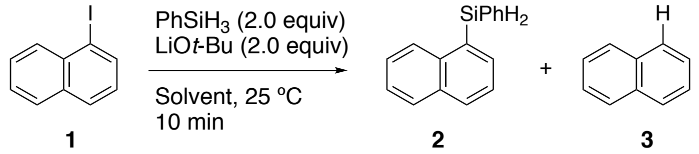
entry	base	**2** (%)[b]	**3** (%)[b]
1	none	0	0
2	LiO*t*-Bu	51	50
3	LiO*i*-Pr	50	40
4	LiOEt	0	0
5	LiOPh	0	0
6[c]	LiO*t*-Bu	26	63
7	KO*t*-Bu	19	44
8	NaO*t*-Bu	3	26

[a] 1-Iodonaphthalene (**1**, 0.20 mmol), phenylsilane (0.40 mmol), base (0.40 mmol) in tetrahydrofuran (0.40 mL) at 25 ºC under argon for 10 min. [b] GC yield with tridecane as an internal standard. [c] Addition of 2.0 equiv of 12-crown-4-ether.

4-4. Effects of solvent

The choice of solvent was also critical for this transformation (Table 2). The use of solvents other than tetrahydrofuran did not give the desired silylated product nor reduced product at all (entries 2–8). When 1,3-dimethyltetrahydropyrimidin-2(*1H*)-one (DMPU) was used as a solvent, only the dehalogenated product (**3**) was obtained in high yield. This reaction system is also promising for the mild reduction method of aryl halides (entry 9). This solvent effect can also be explained by the importance of generation of a monomeric base. Highly coordinating solvents such as tetrahydrofuran (entry 1) or DMPU (entry 9) can coordinate to lithium atom to lead generation of a monomeric base.

Table 2. Effects of solvent[a]



entry	solvent	**2** (%)[b]	**3** (%)[b]
1	THF	51	43
2	Hexane	0	0
3	Toluene	0	0
4	CH_2Cl_2	0	0
5	EtOH	0	0
6	Et_2O	0	0
7	*t*-BuOMe	0	0
8	Dioxane	0	0
9	DMPU	0	92

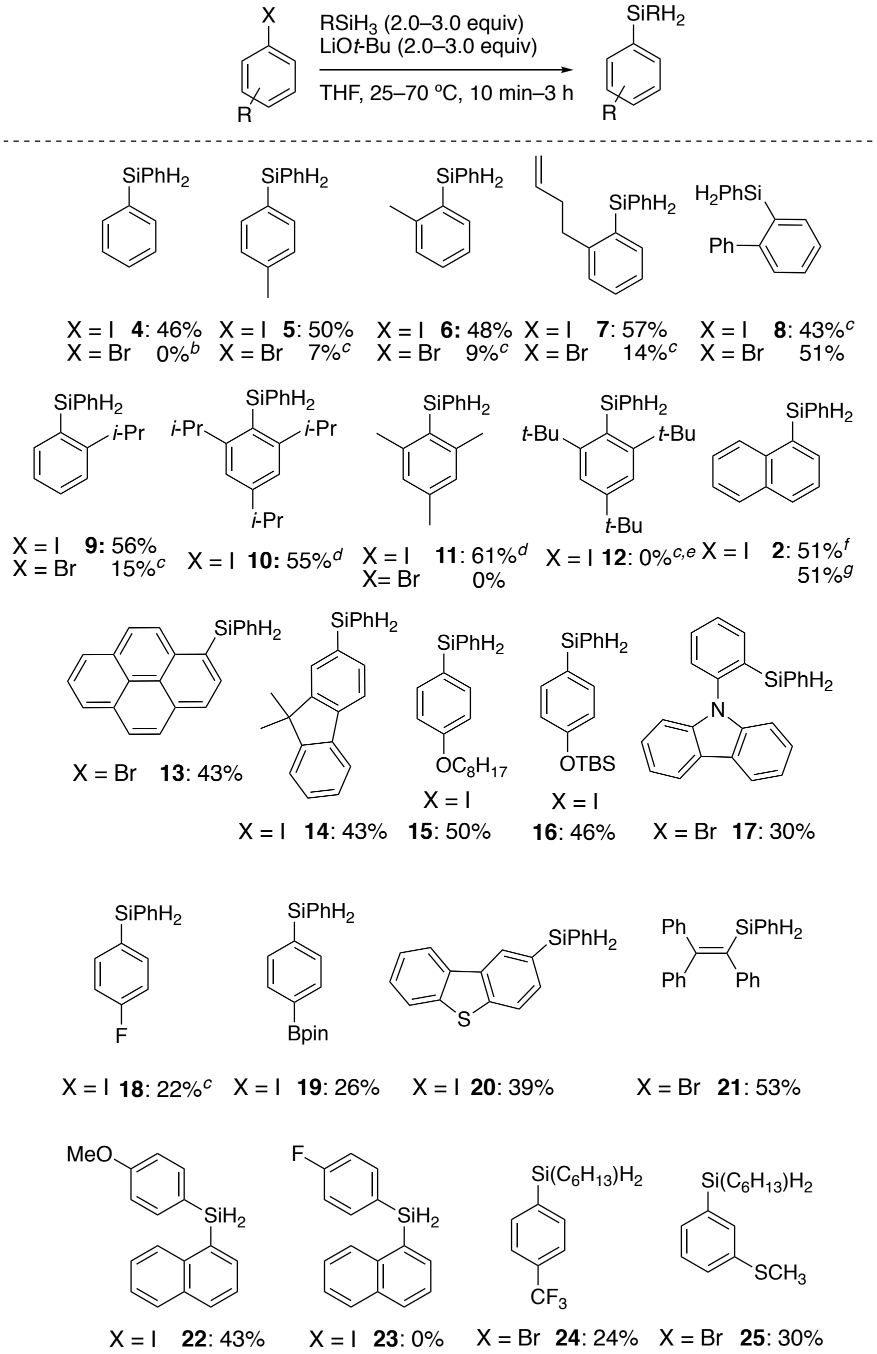
[a] 1-Iodonaphthalene (**1**, 0.20 mmol), phenylsilane (0.40 mmol), lithium-*tert* butoxide (0.40 mmol) in solvent (0.40 mL) at 25 °C under argon for 10 min. [b] GC yield with tridecane as an internal standard.

4-5. Substrate scope

After extensive investigation, the generation of dehalogenated product could not be suppressed. With the optimized conditions in hand, I next investigated the substrate scope of this reaction (Figure 3). For all reactions, the conversion of the starting material was 100% (except for **23** (no reaction) and some aryl bromides, **4**–**7**, **9**, **11**). The reduction product was the main byproduct, which accounted for the decrease in reaction yield. The reduction products and the generated alkoxysilane could be separated by column chromatography in most of the cases, but additional GPC separation was sometimes necessary to obtain a pure silylated product. Iodobenzene and iodotoluenes gave the product in about 50% yield (**4**–**6**), while the corresponding aryl bromides were unreactive. An alkene-containing substrate gave the silylated product without generation of a cyclized product (**7**). Although increasing the reaction temperature was sometimes necessary, the reaction proceeded in the presence of an ortho substituent, which even improves the ratio of silylation product and reduction product (cf. **5** vs. **6**–**11**). 2,4,6-Tri-*tert*-butyliodobenzene was too hindered to give the reduced product in high yield (**12**). This reaction could be scaled up to at least 10 mmol scale (**2**). Polycyclic aromatic hydrocarbon (PAH) halides could be converted to conjugated silyl compounds (**13**, **14**). Electron-deficient aryl iodides gave the silylated products in lower yield due to large amount of dehalogenated product (**18** vs **15**).

Silicon-, boron- and sulfur-containing substrates reacted well under these reaction conditions (**16**, **20** and **25**). A tri-substituted alkenyl bromide was converted to a tri-substituted alkenyl silane, which cannot be synthesized by hydrosilylation of alkynes (**21**). Further reaction such as hydrosilylation of an alkene did not occur. Hexylsilane could be used as the silylating reagent to give alkylarylsilanes in lower yield due to the difficulty of isolation (**24**, **25**).

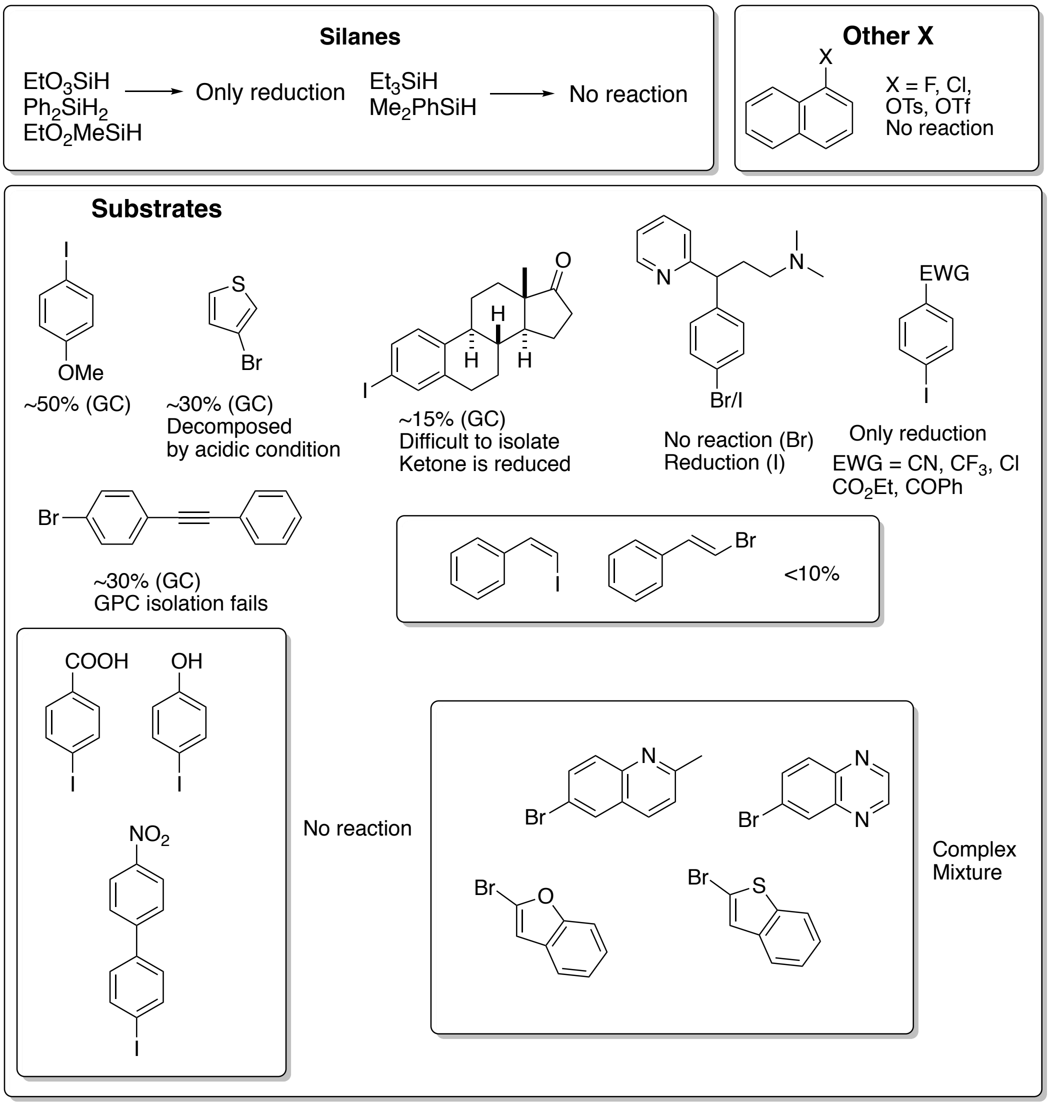
Figure 3. Scope of silylation of aryl halides and an alkenyl halide with monoorganosilanes[a]



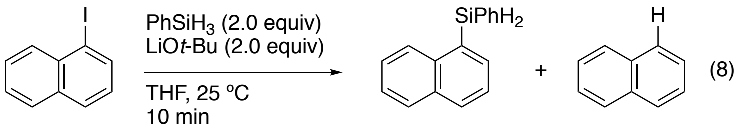
[a]Aryl iodide (0.5 mmol), silane (1.0 mmol), lithium *tert*-butoxide (1.0 mmol) in tetrahydrofuran (1.0 mL) at 25 ºC under argon for 10 min, unless mentioned otherwise. Aryl or alkenyl bromides: aryl bromide (0.5 mmol), silane (1.5 mmol), lithium *tert*-butoxide (1.5 mmol) in tetrahydrofuran (1.5 mL) at 70 ºC under argon for 3 h. [b]25 ºC, 3 h. [c]Yield determined by ^{1}HNMR with 1,1,2,2-tetrachloroethane as an internal standard. [d]50 ºC, 1 h. [e]70 ºC, 3 h. [f]1 mmol scale. [g]10 mmol scale.

The substrates that did not show sufficient reactivity under the reaction conditions are summarized in Figure 4. Regarding the silane source, only monoorganosilanes gave the silylated product. Chloro, fluoro, tosyl and trifluoromethanesulfonate compounds resulted in the total recovery of the starting material and no silylated product was obtained. 3-Bromothiophene gave the product as judged by GC and GC-MS, but this product could not be isolated, as it may decompose by column chromatography. A ketone-containing substrate gave a mixture of reduced products and isolation failed. Drug derivatives containing pyridine and dimethylamino moiety, did not give any silylated product. In the presence of strong electron withdrawing groups, only reduced products were obtained. An alkyne-containing substrate gave the silylated product, but isolation failed. Simple alkenyl halides are less reactive toward this system, and the desired products were obtained in low yield and large amount of starting materials were recovered. Substrates containing a reactive functional group, such as carboxylic acid, hydroxyl group and nitro group did not give the product at all. Heteroaromatic halides gave a complex mixture because the reactive heteroaromatic part can be reacted under these reaction conditions.

Figure 4. Substrates of unsatisfactory reactivity



This reaction took place under dry air (The reaction vessel was connected to atmospheric air through an anhydrous calcium chlorides) and this reaction was sensitive to moisture in air (Eq. 8).



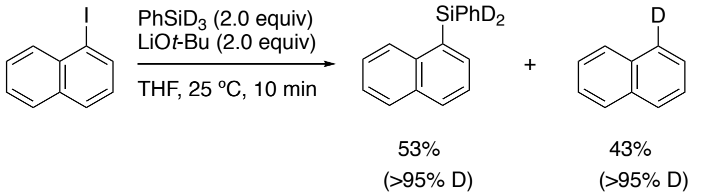
1

argon	**2**: 51%	**3**: 43%
dry air	50%	50%
air	44%	53%

Although reaction efficiency is moderate due to the large amount of the dehalogenated product, there are several synthetic merits that this reaction can proceed under simple reaction conditions, within 10 min at ambient temperature for aryl iodides without addition of a transition metal catalyst.

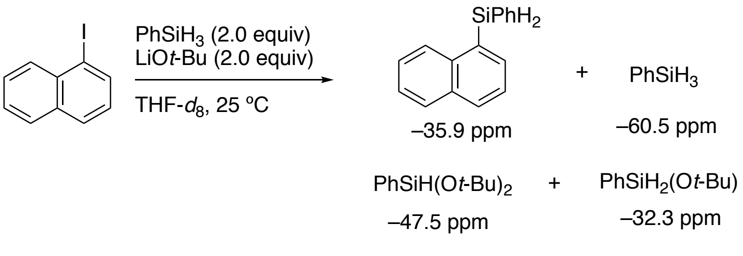
4-6. Mechanistic study

In order to explain this intriguing reactivity, I decided to investigate the reaction mechanism. First, I carried out this reaction using deuterated phenyl silane (Eq. 9). Deuterium incorporation was very high in silylated product and reduced product. Importantly, the product ratio between silylated product and reduced product was similar when phenyl silane was used as a silane reagent.



(9)

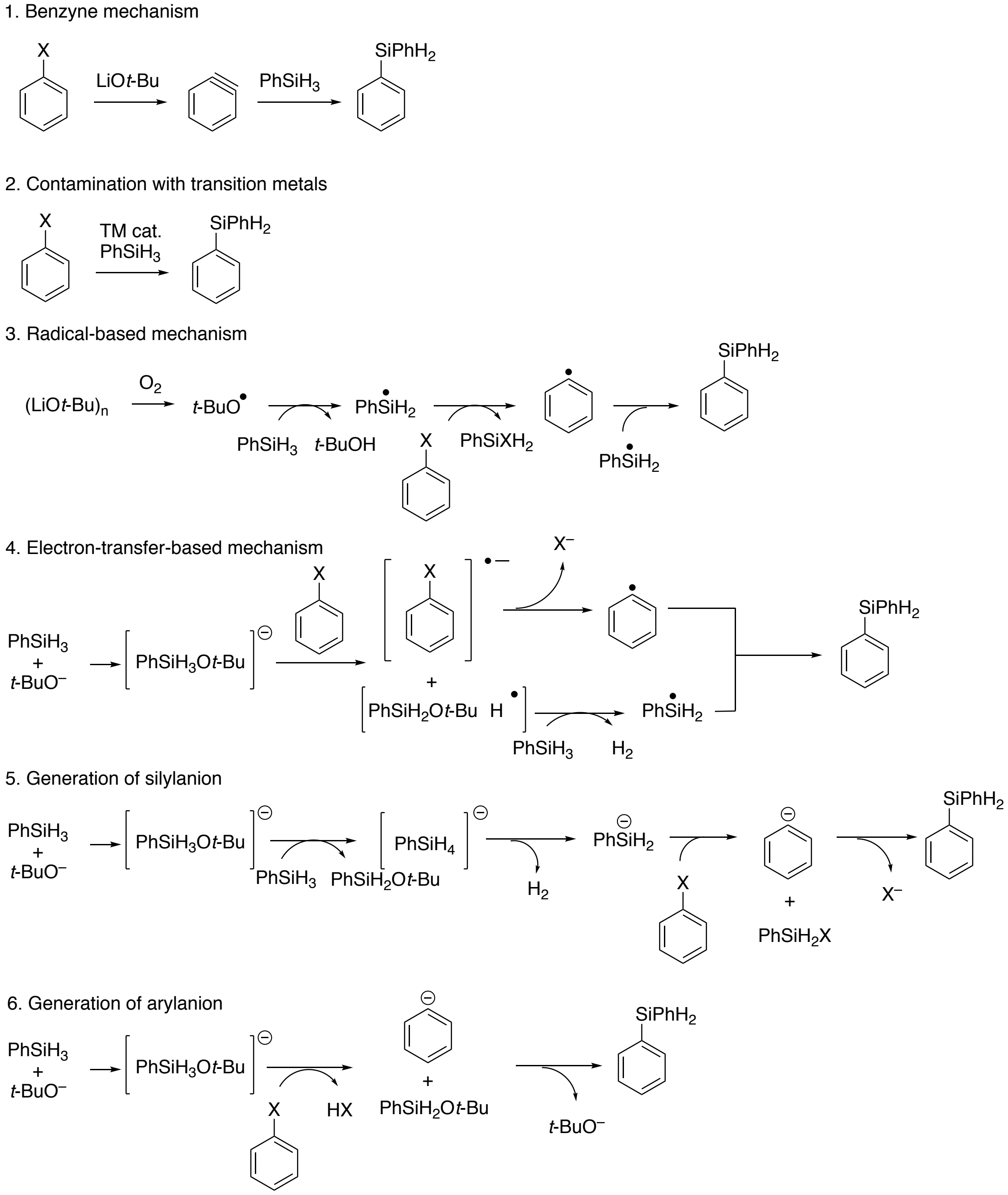
To obtain mechanistic insight, in situ ^{29}Si NMR measurement was carried out during reaction (Eq. 10). Silylated product and phenylsilane were observed and two alkoxy silanes were also observed. Di(*tert*-butoxy)phenyl silane was obtained after the reaction, which was confirmed by GC or GC–MS, while (*tert*-butoxy)phenyl silane was only observed during the reaction. This alkoxy silane should be important reaction intermediate to achieve this transformation.



(10)

Based on these observations, all possible reaction mechanistic scenarios are listed in Figure 5.

Figure 5. All possible reaction mechanisms



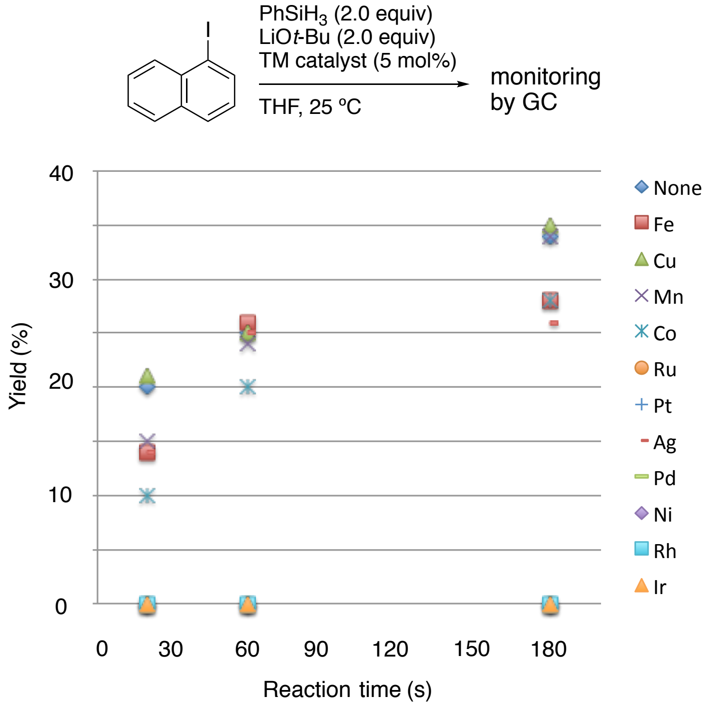
A mechanism involving a benzyne intermediate (1)[15] was ruled out because 2,4,6-trimethyliodobenzene, which cannot generate a benzyne intermediate, gave the silylated product. The other possible mechanisms were investigated by both experimental study and theoretical study.

4-6-1. Contamination with transition metals

A small amount of transition metal contaminating the reaction system sometimes functions as an important catalyst or additive.[16] To investigate this possibility, three experiments were carried out.

The first experiment is the addition of catalytic amount of a transition metal to the reaction mixture to confirm whether transition metal catalysis can promote this reaction or not. Eleven transition metals were examined, and reactions were monitored by GC after 20 s, 60 s and 120 s, respectively. After monitoring the reaction, yield and reaction time were plotted (Figure 6). As a result, no acceleration was observed in all cases.

Figure 6. Addition of a transition metal catalyst[a]



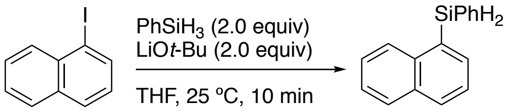
	none	$Fe(acac)_3$	CuI	$Mn(acac)_3$	$Co(acac)_2$	$RuCl_3$•H_2O
Yield at 20 s	20	14	21	15	10	0
Yield at 60 s	25	26	25	24	20	0
Yield at 180 s	34	28	35	34	28	0

	$PtCl_2(cod)$	Ag_2CO_3	$Pd(OAc)_2$	$Ni(acac)_2$	$RhCl(PPh_3)_2$	$[IrCl(cod)]_2$
Yield at 20 s	0	14	0	0	0	0
Yield at 60 s	0	25	0	0	0	0
Yield at 180 s	0	26	0	0	0	0

[a] Yield is estimated by GC in the presence of tridecane. Experimental detail is shown in the experimental section.

Since the reaction proceeded with various aryl halides and hydrosilanes, the contaminates may be contained in the lithium *tert*-butoxide. To examine this possibility, I used several commercially available lithium *tert*-buoxide from different suppliers, and I also used a reagent prepared form *tert*-butyl alcohol and butyllithium for this transformation (Scheme 1). In all cases, similar results were obtained.

Scheme 1. The use of several lithium *tert*-butoxide

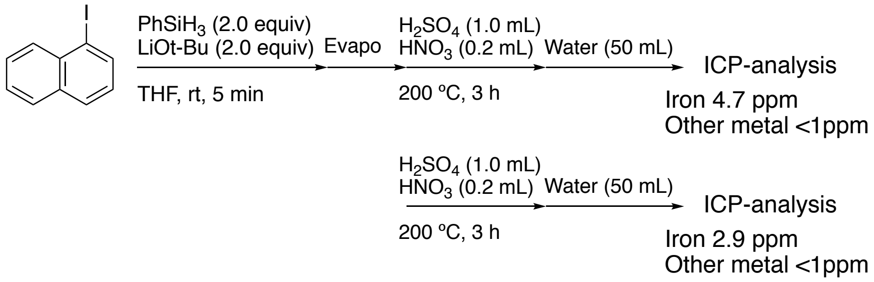


LiO*t*-Bu from TCI (solution)	51
LiO*t*-Bu from Aldrich (solution)	48
LiO*t*-Bu from Wako (solid)	49
LiOt-Bu from BuLi and *t*-BuOH	49

Yield is estimated by GC in the presence of tridecane

Finally, ICP-AES analysis was carried out to determine the amount of transition metals in the reaction mixture. While a slightly large amount of iron was observed by this experiment, a blank test also detected a similar amount of iron atom (Scheme 2, details shown in the experimental part). Notably, addition of a catalytic amount of iron salt did not accelerate the reaction (Figure 6).

Scheme 2. ICP-AES analysis of the reaction mixture



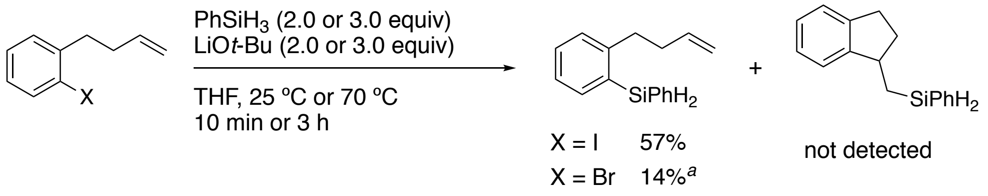
Thus, it is unlikely that a trace amount of transition metal actually catalyzes this transformation.

4-6-2. Radical-based mechanism

For the potassium *tert*-butoxide-catalyzed C–H silylation, a silyl radical chain mechanism was proposed based on a combined experimental and computational study.[13(a)] First step is the generation of *tert*-butoxy radical from potassium *tert*-butoxide and a trace amount of oxygen. The generated radical abstracts hydrogen from the hydrosilane to give a silyl radical. Finally, this silyl radical reacts with heteroaromatics. This radical chain mechanism was supported by several experiments such as radical probe experiments and a computational study. Although present reaction was not catalytic with respect to lithium *tert*-butoxide, this possibility should be taken into account. To investigate this possibility, three experiments were carried out.

The first experiment was a radical probe experiment.[17] If an aryl radical is generated in the reaction mixture, fast cyclization should take place to give a cyclized product. Two substrates containing iodide and bromide respectively were prepared and subjected to this transformation. As a result, only silylated products, reduced products and recovery of the starting material were obtained without the formation of a cyclized product (Scheme 3).

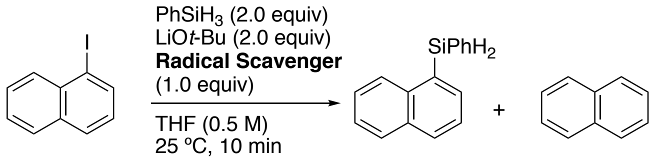
Scheme 3**.** Radical probe experiment



^{a}Estimated by GC in the presence of tridecane

Another experiment was the addition of several radical scavengers. If radical intermediates are involved in the reaction, they easily react with these radical scavengers and the desired silylation reaction was retarded. For this experiment, three radical scavengers were used. As a result, these scavengers did not suppress the reaction, while a slight decrease in yield was observed (Scheme 4).

Scheme 4. Addition of radical scavengers



TEMPO	38	45
1,1-diphenylethylene	42	42
9.10-dihydroanthracene	42	43

Estimated by GC in the presence of tridecane as an internal standard

Finally, the reaction mixture was transferred to an ESR tube under air, and subjected to the ESR measurement at 25 ºC. This measurement cannot detect any peaks (detail is shown in the experimental part).

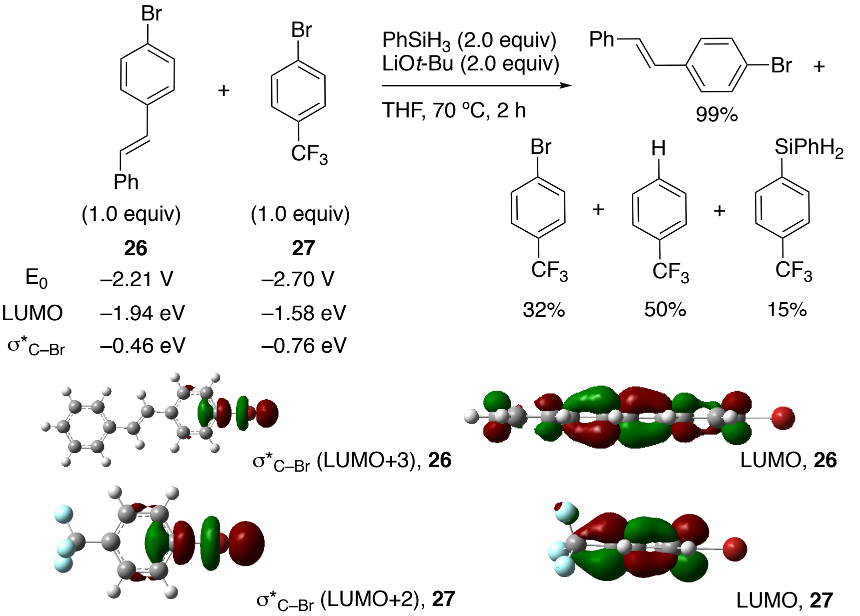
These experimental results are totally different from those of the previous reports about C–H silylation.[12,13] Based on these observations, the involvement of a radical intermediate is unlikely.

4-6-3. Electron-transfer-based mechanism

The coupling reaction of aryl halides sometimes occurs via direct electron transfer to an aryl halide from an electron-rich species, followed by generation of an aryl radical species via elimination of the halide anion.[18] To examine this possibility, a competition experiment between 4-bromostilbene and 4-bromobenzotrifluoride was conducted. DPV measurement of these two compounds showed that 4-bromostilbene was easily reduced compared to the 4-bromobenzotrifluoride. This result was also supported by computation, which showed a lower LUMO energy for 4-bromostilbene. On the other hand, 4-bromobenzotrifuoride has higher electrophilicity at the carbon atom bonded to the bromide and it was also supported by computation. Thus, a competition experiment between these two substrates was used as a support to judge the reaction mechanism.[19]

The competition experiment between 4-bromostilbene and 4-trifluoromethylbromobenzene showed that only 4-trifluoromethylbromobenzene reacted well to give the starting material, the dehalogenated product and the silylated product (Figure 7). 4-bromostilbene did not give the product at all. If single electron transfer to an aryl halide is main pathway to generate the silylated product, 4-bromostilbene is more reactive due to its low LUMO energy. Thus, the carbon–bromide bond cleavage step is not driven by the direct electron transfer to an aryl halide.

***Figure** 7*. Competition experiment to examine the possibility for electron transfer[a]

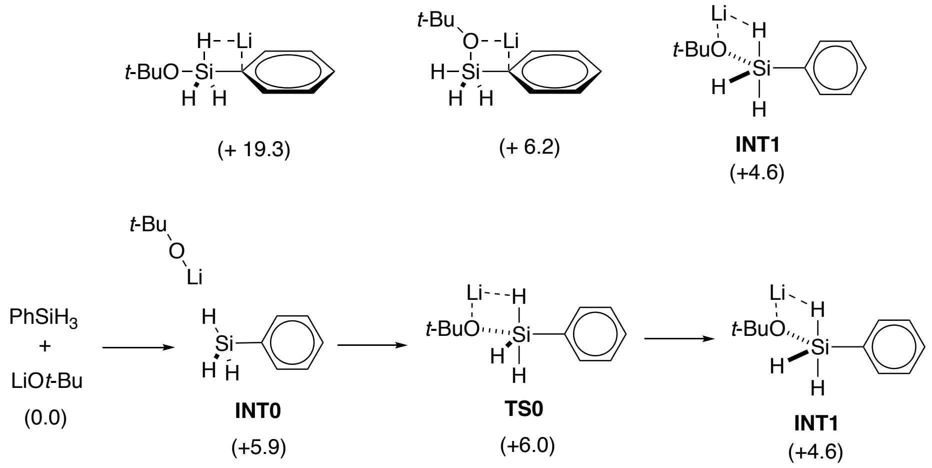


[a]Yield is estimated by GC in the presence of tridecane. Experimental detail and theoretical detail is shown in the experimental section.

4-7. Theoretical study

In the previous section, several possible reaction mechanisms were investigated and four possible reaction mechanisms were ruled out by several experiments. In this section, a theoretical study to investigate the remaining two reaction mechanisms is described. Although the stable structure of lithium *tert*-butoxide in tetrahydrofuran is unknown,[20] a monomeric base was used for the theoretical study, because alkoxysilane was generated during the reaction, implying the intermediacy of a monomeric alkoxide. The first step is generation of a silicate from lithium *tert*-butoxide and phenylsilane, which is involved in both reaction mechanisms. To find a stable silicate intermediate, optimization of the silicate structure from several initial structures was carried out. As a result, three stable structures were found. The most stable silicate is **INT1**, which is generated from **INT0** and **TS0** (Figure 8).

Figure 8. Generation of a silicate[a]



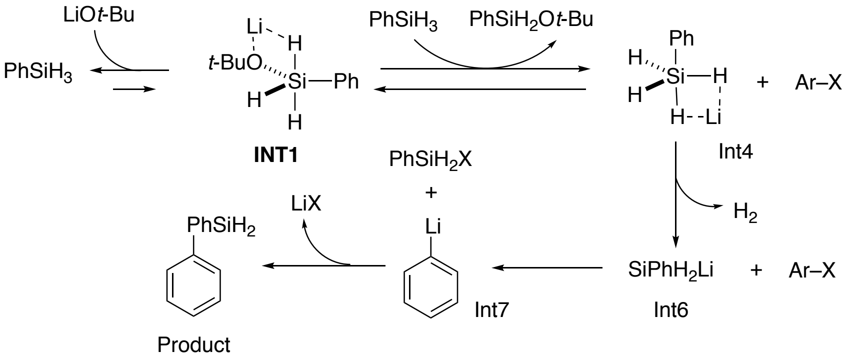
[a]The value in the parenthesis is Gibbs free energies in kcal/mol. Detail is shown in the experimental section.

Computational detail is summarized in experimental part. In this section, I described only the important points to select a computational method. Basis sets for geometry optimization and single point energies calculation are 6-31++G(d) and 6-311++G(d,p) respectively except for iodide atom because hydride may be generated during the reaction. M06-2X was used for single point energies calculation because considering dispersion forces is necessary based on the proposed reaction mechanism.

4-7-1. Generation of silyl anion

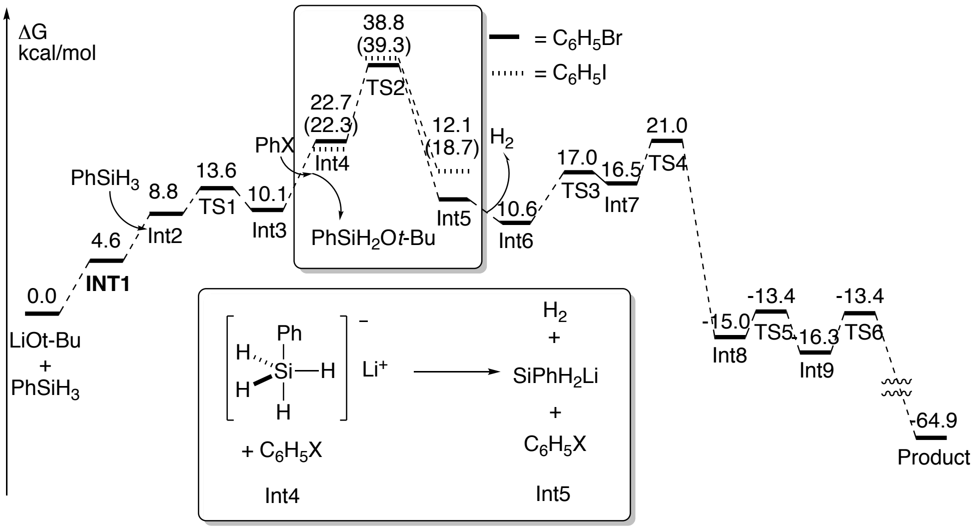
Recently, Ito *et al* reported the silylation of aryl and alkenyl halides with silyllithium.[21] Also, generation of silyllithium from hydrosilicate was suggested by a previous report.[22] Based on these previous reports, it is possible that silyllithium is an important intermediate for this transformation (Figure 9). After generation of silicate (**INT1**), hydride ligands of **INT1** can attack to another phenylsilane due to high nucleophilicity of hydride ligands to generate tetrahydrosilicate (Int4). The generated tetrahydrosilicate can decompose into silyllithium (Int6),[22] which can react with an aryl halide to give the silylated product via aryllithium.

Figure 9. Possible pathway via silyllithium intermediate



To probe this reaction mechanism, a theoretical study was conducted (Figure 10). The generation of silyl anion ($SiPhH_2Li$) from $[PhSiH_4]^{-}Li^{+}$ is the most difficult step (Int4 → TS2). The Gibbs free activation energy for iodobenzene or bromobenzene was calculated as 38.8 kcal/mol and 39.3 kcal/mol respectively. This value is too high for a fast room-temperature reaction. Also, this theoretical result cannot explain the experimentally observed difference in reactivity between bromobenzene and iodobenzene: the total activation energy is similar for bromobenzene and iodobenzene, while the experimental reactivity difference between bromobenzene (conversion: 0%) and iodobenzene (conversion: 100%) is obvious. Indeed, a previous report[21] on silylation of aryl halides by silyllithium described that the reaction easily proceeded with bromobenzene. Based on these considerations, this pathway is also unlikely.

Figure 10. Gibbs free energy diagram for silylanion mechanism



[a]Gibbs free energies are obtained by DFT calculations (M06-2X/6-311++G(d,p)//B3LYP/6-31++G(d) for I atom: SDD and ECP46MWB, Gas phase, 1 atm, 298 K) and shown in kcal/mol.

4-7-2. Generation of aryl anion

This reaction mechanism is proposed based on two previous studies on transition-metal-free borylation of aryl halides.[23] According to these reports, an aryl anion is generated from an aryl halide by the in situ-generated silyl anion or carbanion through halide abstraction. The generated aryl anion reacts with in situ-generated alkoxyborane to give the aryl boronic acid derivatives without the need of a transition metal catalyst.

Based on these previous reports,[23] the reaction mechanism of the silylation reaction via an aryl anion intermediate can be divided into three steps. The first step is the generation of a silicate[24] from a hydrosilane and an alkoxide, and the hydride ligand attached to the silicon atom is dissociated from the silicon atom (**a**).[25] These steps are energetically unfavorable, therefore no reaction intermediate was observed by NMR measurement. In the second step, this intermediate (**INT2**) reacts with an aryl halide via **TS1** to give the aryl anion, alkoxysilane and hydrogen halide (**b**). The generated lithium hydride donates electrons to the σ^* orbital of the carbon-halide bond and finally, the negative charge transfers to the aromatic ring. This reaction pathway is similar to the halogen-metal exchange reaction between aryl halides and organolithium reagents.[26] If the generated aryl anion reacts with the generated hydrogen halide, the reduced product is obtained. If the generated aryl anion reacts with the alkoxysilane, the silylated product is obtained (**c**). Because controlling the reactivity of these intermediates is difficult, it is considered that improving the ratio of silylated product and reduced product is difficult (Figure 11, 12).

Figure 11. Proposed reaction mechanism

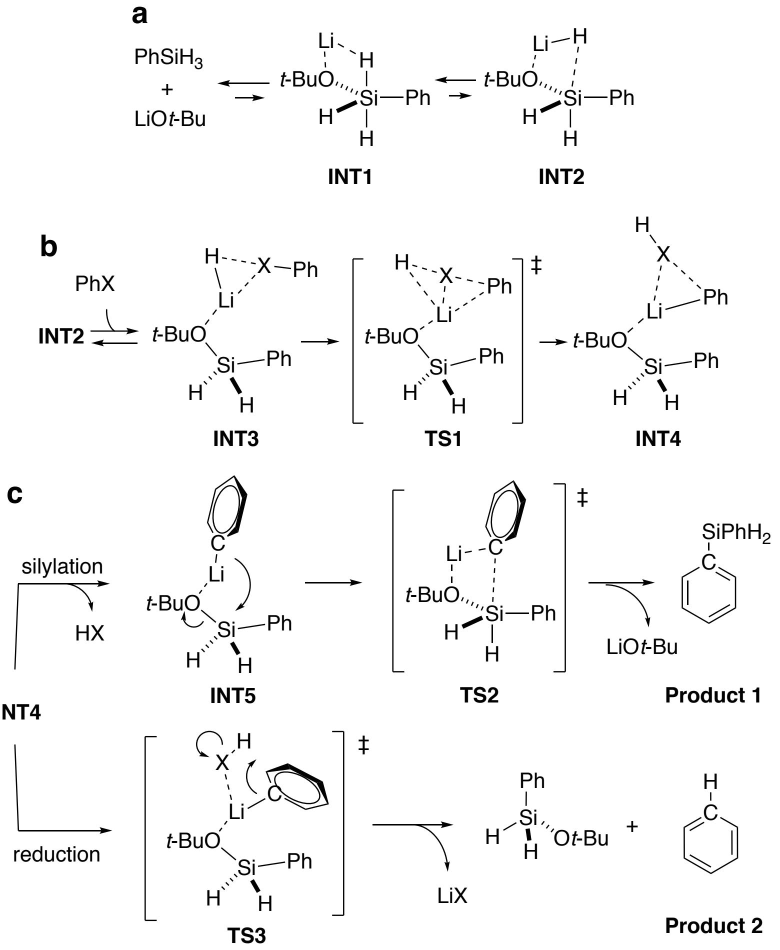
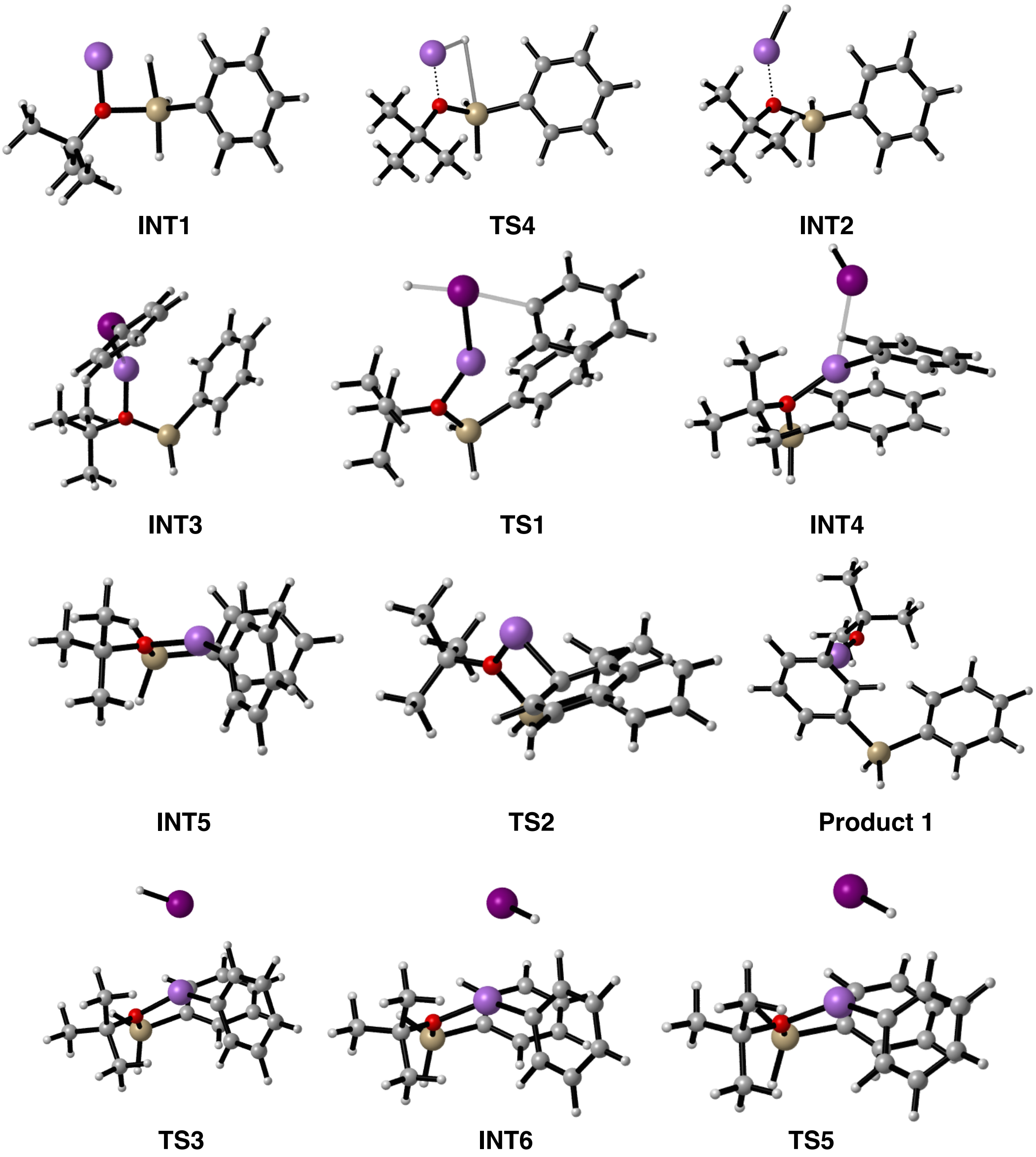


Figure 12. Structure of intermediates and transition states



INT1 TS4 INT2

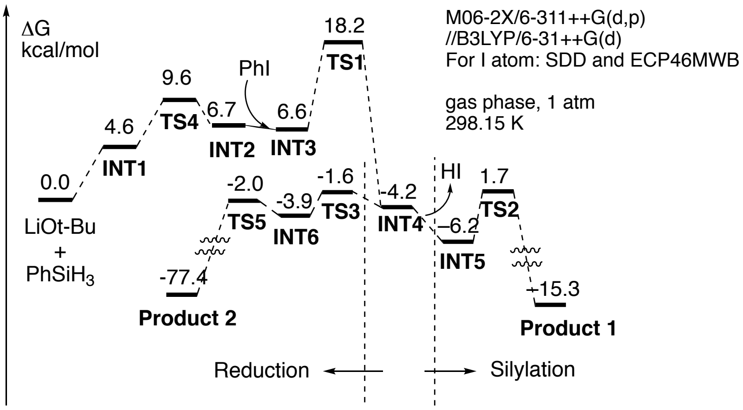
INT3 TS1 INT4

INT5 TS2 Product 1

TS3 INT6 TS5

Based on this proposed mechanism, Gibbs free energy diagram for the overall pathway using iodobenzene as a substrate was shown in Figure 13. The total activation energy for this mechanism is calculated as 18.2 kcal/mol. This value is in good accordance with the experimental result; 25 ºC is enough to achieve this silylation reaction. Also, as there is no stable reaction intermediate, any intermediates cannot be detected by NMR studies. Importantly, step **b** (**INT2 → INT4**) is the rate determining step and step **c** (**INT4 → Product 1** or **Product 2)** is the product-selectivity determining step.

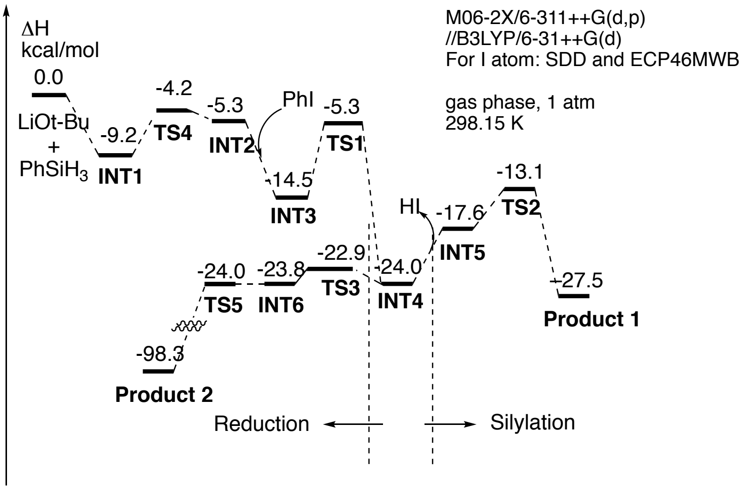
Figure 13. Gibbs free energy diagram for overall pathway using iodobenzene in gas phase[a]



[a]Gibbs free energies are obtained by DFT calculations (M06-2X/6-311++G(d,p)//B3LYP/6-31++G(d) for I atom: SDD and ECP46MWB, Gas phase, 1 atm, 298 K) and shown in kcal/mol.

In enthalpy diagram, product is extremely stable than starting point. Indeed this reaction is strong exothermic reaction (Figure 14).

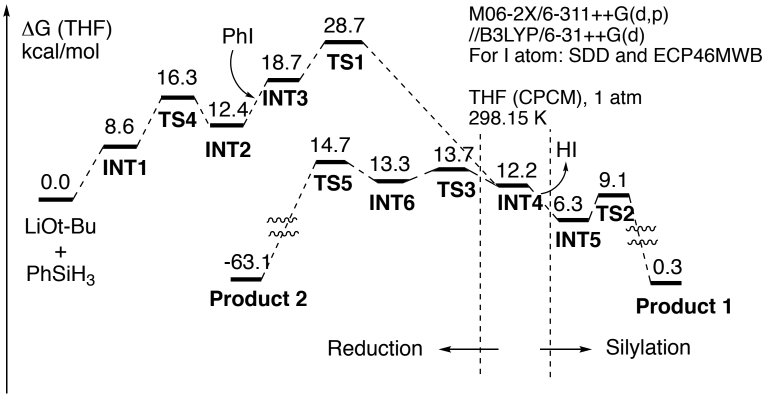
Figure 14. Enthalpy diagram for overall pathway using iodobenzene in gas phase[a]



[a]Enthalpy are obtained by DFT calculations (M06-2X/6-311++G(d,p)//B3LYP/6-31++G(d) for I atom: SDD and ECP46MWB, Gas phase, 1 atm, 298 K) and shown in kcal/mol.

Importantly, this energy profile described in Figure 13 was calculated in the gas phase. In order to take solvent effects into account, C-PCM[27] method was used for single point energies calculation (Figure 15).

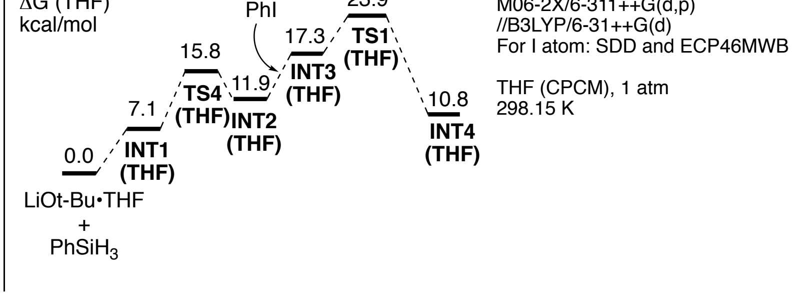
Figure 15. Solvent effect is taken into consideration using the C-PCM model with iodobenzene, without THF coordination to lithium.



[a]Gibbs free energies are obtained by DFT calculations (M06-2X/6-311++G(d,p)(C-PCM-THF)//B3LYP/6-31++G(d) for I atom: SDD and ECP46MWB, 1 atm, 298 K) and shown in kcal/mol.

The value of calculated activation energy with C-PCM method is higher than that of calculated activation energy in gas phase and it seems that the activation energy is too high for room-temperature reaction. However, current theoretical model is simplified because solvent coordination to the lithium atom was not taken into consideration. Indeed, one molecule of tetrahydrofuran coordinating to the lithium atom stabilizes each intermediate and transition state and the value of total activation energy was slightly decreased (Figure 16) and it is enough low to achieve room-temperature reaction.

Figure 16. Solvent effect is taken into consideration using the C-PCM model with iodobenzene, with one molecule of THF coordinating to lithium[a]



[a]Gibbs free energies are obtained by DFT calculations (M06-2X/6-311++G(d,p)(C-PCM-THF)//B3LYP/6-31++G(d) for I atom: SDD and ECP46MWB, 1 atm, 298 K) and shown in kcal/mol.

Importantly, the activation energy for silylation pathway is lower than that for reduction pathway with C-PCM model (Figure 15). On the other hand, the activation energy for silylation pathway is higher than that for reduction pathway in gas phase (Figure 13). This means this computational method is not good enough to discuss the ratio of the silylated product and the reduced product. Further study is necessary to discuss the ratio of the silylated product and the reduced product.

4-7-3. Comparison with the experimental results

Using the aryl anion reaction mechanism, the theoretically predicted reaction outcome was compared with several experimental results. First, the total activation energy for each substrate was calculated and compared with the experimental conversion data. As a result, the calculated data show good accordance with the experimental results, that is, reaction conversion is low when calculated total activation energy is high (Table 3).

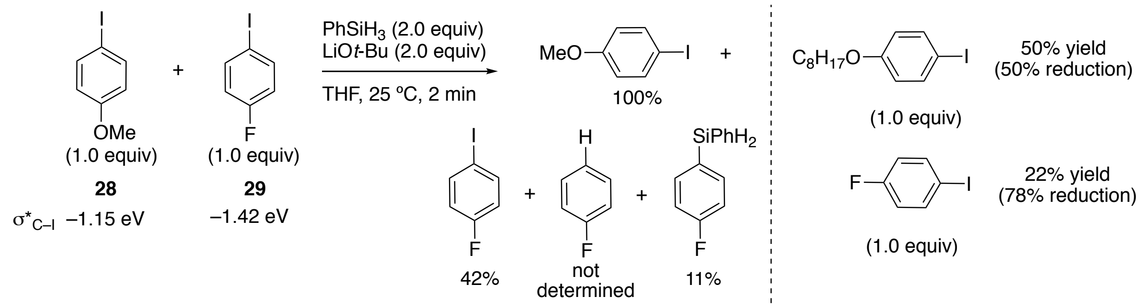
Table 3. Reactivity difference between different substrates

Substrate	Total activation energy[a]		Conversion[b]	
1-Iodonaphthalene	13.4 kcal/mol		100%	⇑
1-Iodobenzene	18.2 kcal/mol		100%	
Mesityl Iodide	20.8 kcal/mol		80%	
1-Bromonaphthalene	23.0 kcal/mol		28%	
1-Bromobenzene	25.2 kcal/mol	⇓	0%	

[a]Gibbs free energies are obtained by DFT calculations (M06-2X/6-311++G(d,p)//B3LYP/6-31++G(d) for I atom: SDD and ECP46MWB, Gas phase, 1 atm, 298 K) and shown in kcal/mol. [b]Reaction condition: $PhSiH_3$ and lithium *tert*-butoxide (2.0 equiv), 25 ºC, 30 min.

Second, a competition experiment was carried out (Figure 17). Electron-rich aryl iodide and electron-deficient aryl iodide were mixed and subjected to the silylation reaction. As a result, the electron-rich aryl iodide was totally recovered and silylated electron-deficient aryl iodide was obtained. On the other hand, for a parallel reaction, electron-rich aryl iodide gave the silylated product in higher yield because electron-deficient aryl iodide gave a large amount of reduced product. This means that electron-deficient aryl iodide reacts faster (related to **TS1**) and silylation is more difficult compared to dehalogenation (related to **TS2**)

Figure 17. A competition experiment between electron-rich aryl iodide and electron-deficient aryl iodide[a]

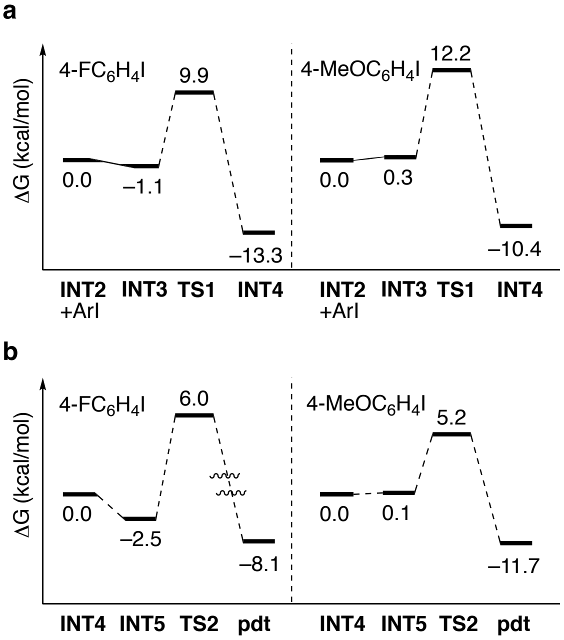


[a]Yield is estimated by GC in the presence of tridecane. Experimental detail and theoretical detail is shown in the experimental section.

The proposed reaction mechanism provides a reasonable account for this intriguing reactivity (Figure 18). As mentioned in the previous section, the reaction rate is determined by **TS1**. In this step, the aromatic ring receives electrons from the hydride. Therefore, the presence of an electron-withdrawing group lowers the activation energy because the LUMO energy of the aryl halide decreases. The theoretical study also supports this explanation (Figure 18a). As a result, the reaction itself is faster with an electron-deficient aryl halide.

The product selectivity also can be explained well. The substituents group can change the activation energy for the silylation pathway. That is, electron-withdrawing group stabilize the reaction intermediate and retard the silylation pathway. Theoretical study also supports this explanation (Figure 18b). This is totally different trend to the one found for carbon-halide bond cleavage step.

Figure 18. Gibbs free energy diagram for a competition experiment[a]



[a]Gibbs free energies are obtained by DFT calculations (M06-2X/6-311++G(d,p)//B3LYP/6-31++G(d)) and shown in kcal/mol.

4-8. Conclusion

In conclusion, a new procedure for silylation of aryl bromides and aryl iodides with monoorganosilanes was developed. The reaction procedure is simple and scalable, and the reaction proceeds rapidly under very mild conditions. The choice of base and solvent was crucial for promoting the reaction. While the yields are moderate due to generation of the dehalogenated product, this reaction enables the selective synthesis of diorganosilanes, which has been difficult using transition metal catalysis. Based on experimental and theoretical studies, I proposed a concerted metal/halide exchange to smoothly generate an aryl anion intermediate, which then reacts with a proximal electrophilic silicon, successfully outcompeting the more common protonation pathway. Nucleophilic activation of monoorganosilane using a monomeric base is a key step based on the experimental results. Thus, I believe that this work offers a unique insight and a new perspective into the alkoxide-promoted reaction of organosilanes, and that it would provide chemists an incentive to develop further the reactions based on the proposed reaction mechanism through nucleophilic activation.

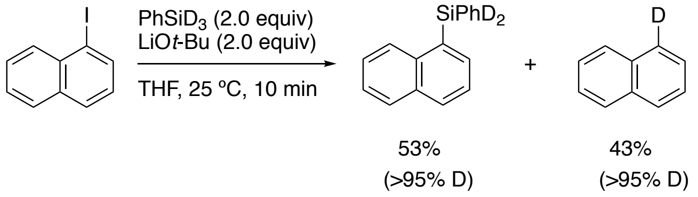
4-9. Experimental part

General. All reactions dealing with air- or moisture-sensitive compounds were carried out in a dry reaction vessel under argon. The water content of the solvent was confirmed with a Karl-Fischer Moisture Titrator (MKC-210, Kyoto Electronics Company) to be less than 20 ppm. Analytical thin-layer chromatography was performed on glass plates coated with 0.25 mm 230–400 mesh silica gel containing a fluorescent indicator (Merck). Gas-liquid chromatographic (GLC) analysis was performed on a Shimadzu GC-2014 or GC-2025 machine equipped with glass capillary column HR-1 (0.25-mm i.d. ´ 25 m). Flash silica gel column chromatography was performed on silica gel 60N (Kanto, spherical and neutral, 140–325 mesh) as described by Still.[28] Gel permeation column chromatography was performed on a Japan Analytical Industry LC-908 (eluent: chloroform) with JAIGEL 1H and 2H polystyrene columns. NMR spectra were measured on ECZ-500 and reported in parts per million from tetramethylsilane. ^{1}H NMR spectra in $CDCl_3$ were referenced internally to tetramethylsilane as a standard, ^{13}C NMR spectra to the solvent resonance and ^{29}Si NMR spectra in $CDCl_3$ were referenced internally to tetramethylsilane or phenylsilane as a standard. Mass spectra (GC MS) are taken at SHIMADZU Parvum 2 gas chromatograph mass spectrometer and JEOL JMS-T100LC (AccuTOF) spectrometer with a calibration standard of Reserpine (MW 609).

Materials. Unless otherwise noted, materials were purchased from Tokyo Kasei Co., Aldrich Inc., and other commercial suppliers. Anhydrous tetrahydrofuran was purchased from WAKO Pure Chemical and purified by a solvent purification system (GlassContour)[29] equipped with columns of activated alumina and supported copper catalyst (Q-5) prior to use. Phenylsilane was purchased from Tokyo Kasei Co., and hexylsilane was purchased from Aldrich Inc. Lithium *tert*-butoxide in tetrahydrofuran (1M) was purchased from Tokyo Kasei Co. Use of solid lithium *tert*-butoxide instead of tetrahydrofuran solution gave similar results.

Mechanistic investigations

Reaction using deuterated phenylsilane

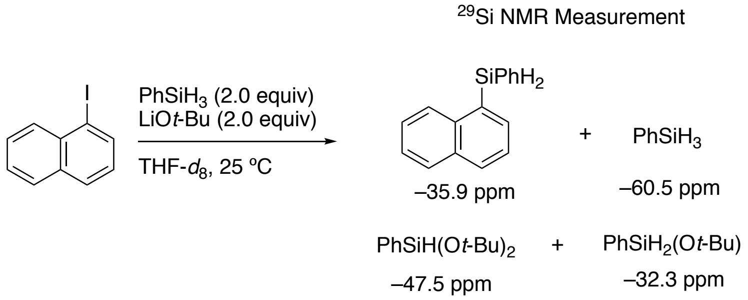


An oven-dried Schlenk tube was evacuated and filled with argon three times, then lithium *tert*-butoxide (0.40 mmol, 0.40 mL, 1.0 M) was added, and then phenylsilane-d_3 (0.40 mmol, 0.050 mL) was added slowly. Finally, 1-iodonaphthalene (0.20 mmol) was added slowly, and the resulting mixture was stirred at 25 ºC for 10 min. Saturated ammonium chloride solution (2.0 mL) was added, the organic phase was extracted with ethyl acetate (3×5.0 ml), and the organic layer was passed over a pad of Florisil. This solution was subjected to GC analysis in the presence of tridecane as an internal standard.

GC MS of naphthalene-d_1 (EI) *m*/*z* (relative intensity): 129 (100), 128 (24).

GC MS of 1-naphtylphenylsilane-d_3 (EI) *m*/*z* (relative intensity): 236 (100), 235 (14), 234(7)

^{29}Si NMR Measurement during Reaction



A dried NMR tube was evacuated and filled with argon three times, then lithium *tert*-butoxide (0.20 mmol, 0.20 mL, 1.0 M) was added. Next, THF was removed *in vacuo*, and THF-d_8 (0.75 mL) and phenylsilane (0.2 mmol, 0.025 mL) were added slowly. Finally, 1-iodonaphthalene (0.10 mmol) was added, and the resulting reaction mixture was subjected to ^{29}Si NMR Measurement. The compounds data except for $PhSiH_2$(O*t*-Bu) was in good accordance with the data of the isolated products. The peak of $PhSiH_2$(O*t*-Bu) was assigned by comparison with an authentic sample, as shown below.

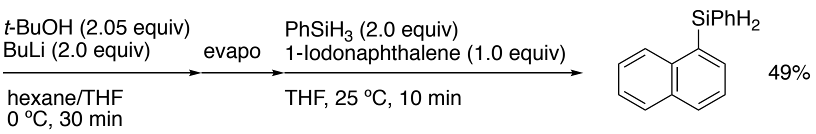
Synthesis of (*tert*-butoxy)phenylsilane[30]

The title compound was synthesized according to the procedure in the literature.[30] An oven-dried Schlenk tube was evacuated and filled with argon three times, then 1,3-bis(2,6-diisopropylphenyl)imidazolium chloride (0.020 mmol, 8.6 mg) and potassium *tert*-butoxide (0.020 mmol, 2.5 mg) were added. Next phenylsilane (0.40 mmol, 0.049 mL) and *tert*-butyl alcohol (0.40 mmol, 0.040 mL) were added, and the resulting mixture was stirred at 25 ºC for 1 h. Then saturated ammonium chloride solution (2.0 mL) was added, the organic phase was extracted with ethyl acetate (3×5.0 ml), and the organic layer was passed over a pad of Florisil. The volatiles were removed *in vacuo*, and the remaining solids were dissolved in THF-d_8. Phenylsilane (2 μl) was added to this sample as an internal standard, ^{29}Si NMR was measured. The main peak ($PhSiH_2$O*t*-Bu) had the same chemical shift with the reaction intermediate.

Addition of several transition-metal catalysts

An oven-dried Schlenk tube was evacuated and filled with argon three times, then lithium *tert*-butoxide in tetrahydrofuran (0.40 mmol, 0.40 mL, 1.0 M) was added. Phenylsilane (0.40 mmol) was added slowly, and a transition metal catalyst (5.0 mol%) was added. Finally, 1-iodonaphthalene (0.20 mmol) was added slowly. The reaction was monitored at 20s, 60s and 180s by GC in the presence of tridecane as an internal standard. No acceleration of the reaction was observed in the presence of several transition-metal catalysts.

Control reaction with *tert*-butyl alcohol and butyllithium.



Yield was detemined by GC in the presence of tridecane as an internal standard

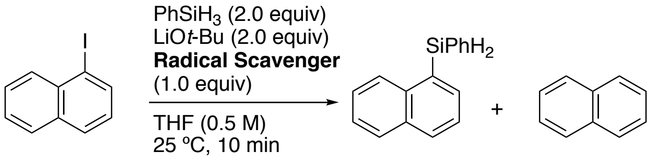
An oven-dried Schlenk tube was evacuated and filled with argon three times, then *tert*-butyl alcohol (0.42 mmol) and tetrahydrofuran (0.50 mL) were added. Next, butyllithium in hexane (0.25 mL, 0.40 mmol, 1.6 M) was slowly added at 0 ºC. The resulting mixture was stirred at 0 ºC for 30 min. After removal of tetrahydrofuran, hexane, *tert*-butyl alcohol *in vacuo*, tetrahydrofuran (0.40 mL) were added. Next, phenylsilane (0.40 mmol) and 1-iodonaphthalene (0.20 mmol) were added slowly. The resulting mixture was stirred at 25 ºC for a 10 min, and then saturated ammonium chloride solution (2.0 mL) was added. The resulting organic layer was extracted by ethyl acetate and subjected to GC analysis. The desired product was obtained in 49% yield.

ICP-AES analysis of the reaction mixture.

An oven-dried Schlenk tube was evacuated and filled with argon three times, then lithium *tert*-butoxide in tetrahydrofuran (0.40 mmol, 0.40 mL, 1.0 M) was added. Phenylsilane (0.40 mmol) and 1-iodonaphthalene (0.20 mmol) were added slowly, and an exothermic reaction smoothly started. The resulting mixture was stirred at 25 °C for a 10 min. Then tetrahydrofuran and phenylsilane were evaporated, sulfuric acid (1.0 mL) and nitric acid (0.30 mL) were added, and the mixture was heated to 200 ºC for 3 h. After cooling to room temperature, mixture was diluted to 50 mL with Milli Q water, and the sample was analyzed on Shimadzu ICPS-7510 spectrometer. The amount of all transition metals was smaller than 1 ppm except for iron, which was detected as 5 ppm; analysis of a blank sample also detected 3 ppm of iron.

	Mn	Fe	Co	Ni	Cu	Zn	Ru	Rh	Pd	Ag	Ir	Pt	Au
Reaction Mixture (ppm)	0.11	4.7	—	—	—	0.37	0.15	—	—	—	0.19	—	0.29
Blank (ppm)	—	2.9	—	—	0.40	0.36	—	0.12	—	—	0.16	0.25	—

Reaction in the presence of a radical scavenger



TEMPO	38	45
1,1-diphenylethylene	42	42
9.10-dihydroanthracene	42	43

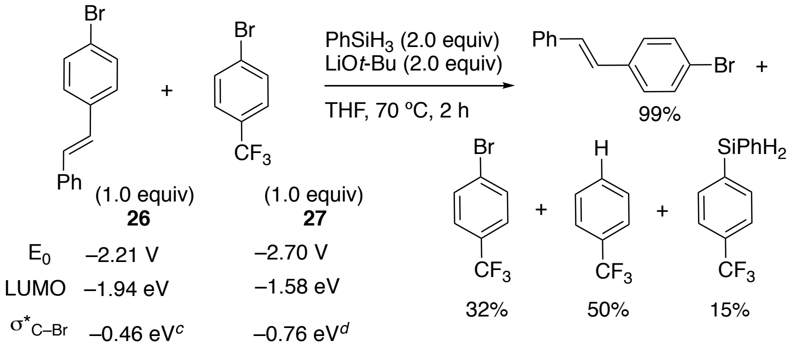
Estimated by GC in the presence of tridecane as an internal standard

An oven-dried Schlenk tube was evacuated and filled with argon three times, then lithium *tert*-butoxide in tetrahydrofuran (0.40 mmol, 0.40 mL, 1.0 M) was added. Then phenylsilane (0.40 mmol, 0.049 mL), a radical scavenger (0.20 mmol), and 1-iodonaphthalene (0.20 mmol) were added slowly. The resulting mixture was stirred at 25 °C for 10 min, then saturated ammonium chloride solution (2.0 mL) was added. The organic phase was extracted with ethyl acetate (3×5.0 ml), and the organic layer was passed over a pad of Florisil. The yield was estimated by GC in the presence of tridecane.

ESR measurement

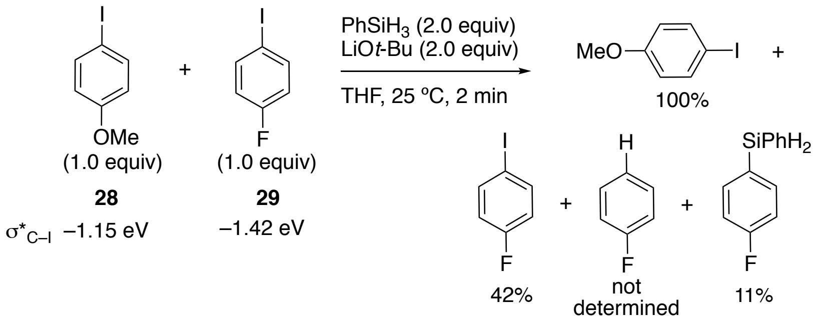
An oven-dried Schlenk tube was evacuated and filled with argon three times, then lithium *tert*-butoxide in tetrahydrofuran (0.60 mmol, 0.60 mL, 1.0 M) was added. Next, phenylsilane (0.60 mmol, 0.074 mL) and 1-bromonaphthalene (0.20 mmol) were added slowly. The resulting mixture was stirred at 70 °C for 5 min. After cooling to room temperature, the resulting mixture was transferred to ESR tube in air and the measurement was performed at 25 ºC. No peak was observed.

Competition experiment between 4-bromostilbene and 4-bromo(trifluoromethyl)benzene



An oven-dried Schlenk tube was evacuated and filled with argon three times, then 4-bromostilbene (0.20 mmol, 52 mg), 4-bromo(trifluoromethyl)benzene (0.20 mmol, 45 mg), and lithium *tert*-butoxide in tetrahydrofuran (0.40 mmol, 0.40 mL, 1.0 M) were added. Finally, phenylsilane (0.40 mmol, 0.049 mL) was added slowly, and the resulting mixture was stirred at 70 °C for 2 h. After cooling to room temperature, a saturated ammonium chloride solution (2.0 mL) was added. The organic phase was extracted with ethyl acetate (3×5.0 ml), and the organic layer was passed over a pad of Florisil. The combined organic layer was analyzed by GC and GC-MS in the presence of tridecane as an internal standard.

Competition experiment between 4-methoxyiodobenzene and 4-fluoroiodobenzene



An oven-dried Schlenk tube was evacuated and filled with argon three times, then 4-fluoroiodobenzene (0.20 mmol, 45 mg), 4-methoxyiodobenzene (0.20 mmol, 47 mg), lithium *tert*-butoxide in tetrahydrofuran (0.40 mmol, 0.40 mL, 1.0 M) and tetrahydrofuran (1.6 mL) were added. Finally, phenylsilane (0.40 mmol, 0.049 mL) was added slowly, and the resulting mixture was stirred at 25 °C for 2 min. After cooling to room temperature, saturated ammonium chloride solution (2.0 mL) was added. The organic phase was extracted with ethyl acetate (3×5.0 ml), and the organic layer was passed over a pad of Florisil. The combined organic layer was analyzed by GC and GC-MS in the presence of hexadecane as an internal standard. 100% of 4-methoxyiodobenzene and 42% of 4-fluoroiodobenzene were recovered. Although reduced product of 4-fluoroiodobenzene could not be detected due to its high volatility, the silylated product of 4-fluoroiodobenzene was obtained in 11% yield.

Preparation of the starting materials

2,4,6-triisopropyl-iodobenzene was prepared by iodination of 2,4,6-triisoproylbenzene.[31] 2,4,6-tri(*tert*-Butyl)-iodobenzene was prepared by lithiation of the corresponding bromide followed by addition of iodine.[32] 1-(3-Butenyl)-2-iodobenzene and 1-(3-butenyl)-2-bromobenzene were prepared from 2-iodobenzylbromide or 2-bromobenzylbromide and allylmagnesium bromide according to the literature procedure.[33] 1-Iodo-4-(octyloxy)benzene and (4-*tert*-butyldimethylsiloxy)iodobenzene were prepared from 4-iodophenol according to the literature procedure.[34,35] 2-Bromobenzyl *tert*-butyldimethylsilyl ether was prepared according to the literature.[36] 4-Methoxyphenylsilane and 4-fluorophenylsilane were prepared by the reaction of the corresponding Grignard reagent with tetrachlorosilane, followed by reduction with lithium aluminum hydride.[37] The data for all compounds was in good accordance with the literature.

10 mmol scale silylation of 1-iodonaphthalene

An oven-dried 100 mL two-neck flask was evacuated and filled with argon three times, then lithium *tert*-butoxide in tetrahydrofuran (20 mmol, 20 mL, 1.0 M) was added. Next, phenylsilane (20 mmol, 2.5 mL) was added over a 1 min. Evolution of a small amount of gas was observed. Finally, 1-iodonaphthalene (10 mmol, 2.51 g) was added over 20 sec. Evolution of gas was observed, and an exothermic reaction smoothly started. During the reaction, the reaction mixture stayed as a clear solution and no precipitation was observed. The reaction mixture was stirred at 25 ºC for 20 min, and then a saturated ammonium chloride solution (20 mL) was added slowly. The organic phase was extracted with ethyl acetate (3×20 ml), and the organic layer was dried over $MgSO_4$. After filtration, the volatiles were removed *in vacuo* to obtain an oily residue. The crude mixture was purified by column chromatography (hexane 100%) to afford the desired compound as colorless oil in 51% yield (1.18 g). The compound data was in good accordance with the literature.[38]

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.06–8.04 (m, 1H), 7.96–7.95 (d, J = 8.3 Hz, 1H), 7.90–7.88 (m, 1H), 7.84–7.82 (m, 1H), 7.64–7.62 (m, 2H), 7.53–7.47 (m, 3H), 7.43–7.35 (m, 3H), 5.26 (s, 2H);

^{13}C NMR (125 MHz, $CDCl_3$): δ 137.2, 136.8, 135.7, 133.1, 131.4, 130.9, 130.0, 129.9, 128.8, 128.1, 127.9, 126.4, 125.8, 125.3;

^{29}Si NMR (100 MHz, $CDCl_3$): δ –35.6;

GC MS (EI) *m/z* (relative intensity): 234 (70), 202 (6), 156 (100), 128 (28), 105 (39), 77 (7).

General procedure for silylation of aryl iodide

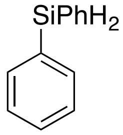
An oven-dried Schlenk tube was evacuated and filled with argon three times, then lithium *tert*-butoxide in tetrahydrofuran (1.0 mmol, 1.0 mL, 1.0 M) was added, and then phenylsilane (1.0 mmol, 0.12 mL) and the substrate (0.50 mmol) were added slowly. The resulting mixture was stirred at 25 °C for 10 min, then a saturated ammonium chloride solution (2.0 mL) was added. The organic phase was extracted with ethyl acetate (3×5 ml), and the organic layer was passed over a pad of Florisil. The volatiles were removed *in vacuo* to obtain an oily residue. The crude mixture was purified by column chromatography (typically hexane 100%) to afford the desired compound.

General procedure for silylation of aryl bromide

An oven-dried Schlenk tube was evacuated and filled with argon three times, then lithium *tert*-butoxide in tetrahydrofuran (1.5 mmol, 1.5 mL, 1.0 M) was added, and then phenylsilane (1.5 mmol, 0.19 mL) and the aryl bromide (0.50 mmol) were added slowly. The resulting mixture was stirred at 70 °C for 3 h, then a saturated ammonium chloride solution (2.0 mL) was slowly added. The organic phase was extracted with ethyl acetate (3×5 ml), and the organic layer was passed over a pad of Florisil. The volatiles were removed *in vacuo* to obtain an oily residue. The crude mixture was purified by column chromatography (typically hexane 100%) to afford the desired compound.

Caution: Some silane compounds may slowly decompose under acidic conditions, including column chromatography on silica gel. Therefore, quick extraction and column chromatography is necessary after quenching the reaction.

Diphenylsilane (4)



Iodobenzene (101 mg) and 2.0 equiv of phenylsilane and lithium *tert*-butoxide were used. Crude product was purified by column chromatography (hexane 100%) to afford the desired compound as a colorless liquid in 46% yield (42 mg). The compound data was in good accordance with the literature.[38]

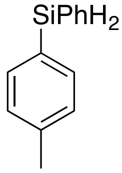
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.61–7.59 (m, 4H), 7.43–7.36 (m, 6H), 4.92 (s, 2H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 135.7, 131.5, 129.9, 128.1;

^{29}Si NMR (100 MHz, $CDCl_3$): δ –34.8;

GC MS (EI) *m/z* (relative intensity): 184 (40), 106 (100).

4-(Methylphenyl)phenylsilane (5)



4-Iodotoluene (110 mg) and 2.0 equiv of phenylsilane and lithium *tert*-butoxide were used. Crude product was purified by column chromatography (hexane 100%) to afford the desired compound as a colorless liquid in 50% yield (50 mg).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.60–7.58 (m, 2H), 7.53–7.49 (m, 2H), 7.42–7.34 (m, 3H), 7.20–7.19 (m, 2H), 4.90 (s, 2H), 2.36 (s, 3H);

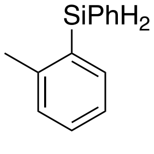
^{13}C NMR (125 MHz, $CDCl_3$): δ 139.9, 135.7, 135.6, 131.8, 129.8, 129.0, 128.1, 127.7, 21.5.

^{29}Si NMR (100 MHz, $CDCl_3$): δ –35.1;

GC MS (EI) *m/z* (relative intensity): 198 (54), 120 (100), 105 (93).

HRMS (APCI): Calcd for $C_{13}H_{15}Si^+$ [$M+H^+$] 199.0943 found, 199.0947.

2-(Methylphenyl)phenylsilane (6)



2-Iodotoluene (110 mg) and 2.0 equiv of phenylsilane and lithium *tert*-butoxide were used. Crude product was purified by column chromatography (hexane 100%) to afford the desired compound as a colorless liquid in 48% yield (50 mg). The compound data was in good accordance with the literature.[38]

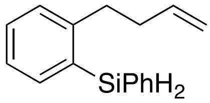
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.59–7.53 (m, 3H), 7.42–7.32 (m, 4H), 7.20–7.17 (m, 2H), 4.95 (s, 2H), 2.40 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 144.4, 137.1, 135.6, 131.5, 130.8, 130.5, 129.7, 129.4, 128.1, 125.2, 22.6;

^{29}Si NMR (100 MHz, $CDCl_3$): δ –37.7;

GC MS (EI) *m/z* (relative intensity): 198 (32), 120 (96), 105 (100).

(2-(3-Butenyl)phenyl)(phenyl)silane (7)



1-(3-butenyl)-2-iodobenzene (105 mg) and 2.0 equiv of phenylsilane and lithium *tert*-butoxide were used. Crude product was purified by column chromatography (hexane 100%) to afford the desired compound as a colorless liquid in 57% yield (55 mg).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.58–7.54 (m, 3H), 7.42–7.34 (m, 4H), 7.25–7.18 (m, 2H), 5.83–5.74 (m, 1H), 4.98 (s, 2H), 4.97–4.92 (m, 2H), 2.79–2.76 (t, J = 7.7 Hz, 2H), 2.28–2.23 (q, J = 7.7 Hz, 2H);

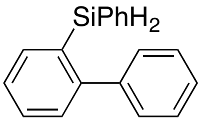
^{13}C NMR (125 MHz, $CDCl_3$): δ 148.4, 137.8, 137.4, 135.6, 131.8, 130.49, 130.47, 129.8, 128.7, 128.1, 125.5, 114.9, 36.1, 35.8;

^{29}Si NMR (100 MHz, $CDCl_3$): δ –37.6;

GC MS (EI) *m/z* (relative intensity): 195 (59), 160 (76), 129 (97), 105 (100).

HRMS (APCI): Calcd for $C_{16}H_{17}Si^+$ [$M+H–H_2^+$] 237.1100 found, 237.1086.

(2-(1,1'-Biphenyl)(phenyl)silane (8)

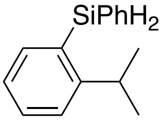


2-Bromobiphenyl (116 mg) and 3.0 equiv of phenylsilane and lithium *tert*-butoxide were used. Crude product was purified by column chromatography (hexane 100%) to afford the desired compound as a colorless liquid in 51% yield (66 mg).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.67–7.65 (m, 1H), 7.49–7.46 (m, 1H), 7.38–7.32 (m, 8H), 7.30–7.25 (m, 4H), 4.74 (s, 2H);

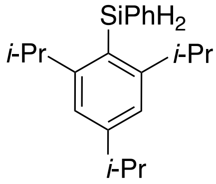
^{13}C NMR (125 MHz, $CDCl_3$): δ 149.8, 143.1, 137.3, 135.5, 132.2, 130.8, 130.1, 129.5, 129.3, 129.0, 128.0, 127.8, 127.2, 126.5;
^{29}Si NMR (100 MHz, $CDCl_3$): δ –36.0;
GC MS (EI) *m/z* (relative intensity): 260 (25), 182 (100), 181 (91), 155 (15), 129 (10), 105 (22).
HRMS (APCI): Calcd for $C_{18}H_{15}Si^+$ [$M+H–H_2^+$] 259.0943 found, 259.0942.

(2-Isopropylphenyl)phenylsilane (9)



2-Iodocumene (122 mg) and 2.0 equiv of phenylsilane and lithium *tert*-butoxide were used. Crude product was purified by column chromatography (hexane 100%) to afford the desired compound as a colorless liquid in 56% yield (63 mg).
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.57–7.51 (m, 3H), 7.44–7.32 (m, 5H), 7.20–7.17 (m, 1H), 4.99 (s, 2H), 3.10–3.08 (m, 1H), 1.18 (s, 3H), 1.16 (s, 3H);
^{13}C NMR (125 MHz, $CDCl_3$): δ 155.5, 137.3, 135.6, 132.1, 130.9, 129.69, 129.68, 128.1, 125.5, 124.8, 34.7, 24.1;
^{29}Si NMR (100 MHz, $CDCl_3$): δ –37.5;
GC MS (EI) *m/z* (relative intensity): 226 (5), 148 (66), 133 (100), 119 (31), 105 (69), 78 (44).
HRMS (APCI): Calcd for $C_{15}H_{19}Si^+$ [$M+H^+$] 227.1256 found, 227.1246.

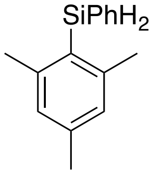
(2,4,6-Triisopropylphenyl)(phenyl)silane (10)



2,4,6-Triisopropyl-iodobenzene (171 mg) and 2.0 equiv of phenylsilane and lithium *tert*-butoxide were used at 50 ºC for 1 h. Crude product was purified by column chromatography (hexane 100%) to afford the desired compound as a colorless liquid in 55% yield (88 mg).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.54–7.52 (m, 2H), 7.35–7.30 (m, 3H), 7.07 (s, 2H), 5.03 (s, 2H), 3.36–3.27 (sep, 2H), 2.94–2.86 (sep, 1H), 1.28 (s, 3H), 1.27 (s, 3H), 1.21 (s, 6H), 1.19 (s, 6H);
^{13}C NMR (125 MHz, $CDCl_3$): δ 156.1, 151.2, 135.2, 133.1, 129.4, 128.0, 124.1, 120.9, 34.43, 34.36, 24.5, 23.8;
^{29}Si NMR (100 MHz, $CDCl_3$): δ –52.0;
GC MS (EI) *m/z* (relative intensity): 310 (2), 232 (60), 217 (46), 203 (24), 189 (100), 105 (32), 78 (33).
HRMS (APCI): Calcd for $C_{21}H_{31}Si^+$ [$M+H^+$] 311.2195, found, 311.2210.

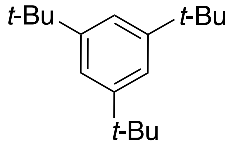
1-Mesitylphenylsilane (11)



1-Mesityliodide (122 mg) and 2.0 equiv of phenylsilane and lithium *tert*-butoxide were used at 50 ºC for 1 h. Crude product was purified by column chromatography (hexane 100%) to afford the desired compound as a colorless liquid in 61% yield (69 mg). The compound data was in good accordance with the literature.[38]

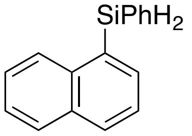
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.52–7.49 (m, 2H), 7.38–7.30 (m, 3H), 6.89 (s, 2H), 5.00 (s, 2H), 2.44 (s, 6H), 2.31 (s, 3H);
^{13}C NMR (125 MHz, $CDCl_3$): δ 145.1, 140.0, 135.2, 132.0, 129.5, 128.3, 128.1, 125.9, 23.8, 21.2;
^{29}Si NMR (100 MHz, $CDCl_3$): δ –50.3;
GC MS (EI) *m/z* (relative intensity): 226 (73), 148 (100), 133 (64), 119 (45), 105 (72).

1,3,5-Tri(*tert*-butyl)benzene (12)



2,4,6-tri(*tert*-butyl)-iodobenzene (171 mg) and 2.0 equiv of phenylsilane and lithium *tert*-butoxide were used at 70 ºC for 3 h. No silylated product is observed. NMR yield estimated in the presence of 1,1,2,2-tetrachloroethane of 1,3,5-tri(*tert*-butyl)benzene is 90%.

1-Naphtylphenylsilane (2)



1-Iodonaphthalene (252 mg) and 2.0 equiv of phenylsilane and lithium *tert*-butoxide were used. Crude product was purified by column chromatography (hexane 100%) to afford the desired compound as a colorless liquid in 51% yield (119 mg). The compound data was in good accordance with the literature.[38]

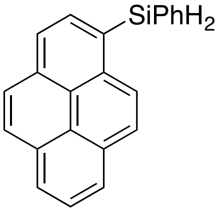
^{1}H NMR (500 MHz, $CDCl_3$): δ 8.06–8.04 (m, 1H), 7.96–7.95 (d, J = 8.3 Hz, 1H), 7.90–7.88 (m, 1H), 7.84–7.82 (m, 1H), 7.64–7.62 (m, 2H), 7.53–7.47 (m, 3H), 7.43–7.35 (m, 3H), 5.26 (s, 2H);

^{13}C NMR (125 MHz, $CDCl_3$): δ 137.2, 136.8, 135.7, 133.1, 131.4, 130.9, 130.0, 129.9, 128.8, 128.1, 127.9, 126.4, 125.8, 125.3;

^{29}Si NMR (100 MHz, $CDCl_3$): δ –35.6;

GC MS (EI) *m/z* (relative intensity): 234 (70), 202 (6), 156 (100), 128 (28), 105 (39), 77 (7).

(Phenyl)(1-pyrenyl)silane (13)



1-Bromopyrene (141 mg) and 3.0 equiv of phenylsilane and lithium *tert*-butoxide were used. Crude product was purified by column chromatography (hexane 100%) to afford the desired compound as a colorless liquid in 43% yield (66 mg).

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.31–8.28 (m, 2H), 8.21–8.16 (m, 3H), 8.12–8.06 (m, 3H), 8.03–8.00 (m, 1H), 7.65–7.63 (m, 2H), 7.42–7.33 (m, 3H), 5.45 (s, 2H);

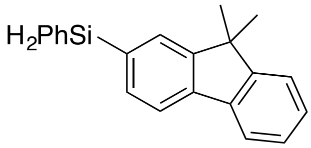
^{13}C NMR (125 MHz, $CDCl_3$): δ 136.4, 135.7, 135.0, 133.0, 131.6, 131.2, 130.7, 129.9, 128.4, 128.2, 127.9, 127.5, 127.4, 126.8, 126.0, 125.5, 125.4, 124.5, 124.4, 124.3;

^{29}Si NMR (100 MHz, $CDCl_3$): δ –37.0;

GC MS (EI) *m/z* (relative intensity): 308 (38), 202 (100), 105 (7).

HRMS (APCI): Calcd for $C_{22}H_{16}Si^+$ [M $^+$] 308.1021, found, 308.1019.

(2-(9,9-Dimethylfluorene))(phenyl)silane (14)



2-Iodo-9,9-dimethylfluorene (161 mg) and 2.0 equiv of phenylsilane and lithium *tert*-butoxide were used. Crude product was purified by column chromatography (hexane 100%) to afford the desired compound as a colorless liquid in 43% yield (64 mg).

^{1}H NMR (500 MHz, CDCl$_3$): δ 7.74–7.63 (m, 5H), 7.58–7.55 (m, 1H), 7.44–7.32 (m, 6H), 7.84–7.82 (m, 1H), 7.55–7.45 (m, 3H), 4.99 (s, 2H), 1.48 (s, 6H);

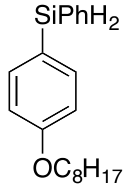
^{13}C NMR (125 MHz, CDCl$_3$): δ 153.8, 153.1, 141.0, 138.8, 135.7, 134.5, 131.8, 129.9, 129.85, 129.76, 128.1, 127.8, 127.0, 122.6, 120.3, 119.7, 46.9, 27.1;

^{29}Si NMR (100 MHz, CDCl$_3$): δ –34.3;

GC MS (EI) *m/z* (relative intensity): 300 (100), 285 (87), 257 (22), 207 (28), 194 (19), 179 (42), 107 (72).

HRMS (APCI): Calcd for $C_{21}H_{20}Si^+$ [M$^+$] 300.1334, found, 300.1346.

(4-(Octyloxy)phenyl)(phenyl)silane (15)



1-Iodo-4-(octyloxy)benzene (170 mg) and 2.0 equiv of phenylsilane and lithium *tert*-butoxide were used. Crude product was purified by column chromatography (hexane 100%) to afford the desired compound as a colorless liquid in 50% yield (80 mg).

^{1}H NMR (500 MHz, CDCl$_3$): δ 7.59–7.58 (m, 2H), 7.51–7.50 (m, 2H), 7.42–7.35 (m, 3H), 6.92–6.90 (m, 2H), 4.89 (s, 2H), 3.97–3.95 (t, J = 6.3H, 2H);

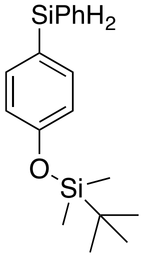
^{13}C NMR (125 MHz, CDCl$_3$): δ 160.7, 137.2, 135.6, 1321, 129.7, 128.1, 121.7, 114.5, 67.8, 31.8, 29.3, 29.22, 29.19, 26.0, 22.6, 14.1;

^{29}Si NMR (100 MHz, $CDCl_3$): δ –35.4;

GC MS (EI) *m/z* (relative intensity): 312 (29), 207 (31), 200 (34), 199 (78), 122 (100).

HRMS (APCI): Calcd for $C_{20}H_{29}OSi^+$ [$M+H^+$] 313.1998, found, 313.1995.

((4-*tert*-Butyldimethylsiloxy)phenyl)(phenyl)silane (16)



(4-*tert*-Butyldimethylsiloxy)iodobenzene (164 mg) and 2.0 equiv of phenylsilane and lithium *tert*-butoxide were used. Crude product was purified by column chromatography (hexane 100%) to afford the desired compound as a colorless liquid in 46% yield (76 mg).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.60–7.58 (dd, J = 7.8 Hz, J = 1.5 Hz, 2 H), 7.47–7.45 (d, J = 8.3 Hz, 2H), 7.41–7.36 (m, 3H), 6.86–6.85 (m, 2H), 4.98 (s, 2H), 0.98 (s, 9H), 0.20 (s, 6H).

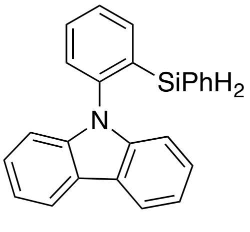
^{13}C NMR (125 MHz, $CDCl_3$): δ 157.4, 137.2, 135.6, 132.1, 129.7, 128.1, 122.7, 120.1, 25.6, 18.2, –4.4;

^{29}Si NMR (100 MHz, $CDCl_3$): δ –35.3, 19.7;

GC MS (EI) *m/z* (relative intensity): 314 (28), 257 (100), 195 (52), 179 (71).

HRMS (APCI): Calcd for $C_{18}H_{27}OSi^+$ [$M+H^+$] 315.1600, found, 315.1600.

9-(2-(Phenylsilyl)phenyl)-9*H*-carbazole (17)



9-(2-Bromophenyl)-9*H*-carbazole (161 mg) and 2.0 equiv of phenylsilane and lithium *tert*-butoxide were used. Crude product was purified by column chromatography (hexane 100%) followed by GPC (chloroform) to afford the desired compound as a colorless liquid in 30% yield (53 mg).

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.09–8.08 (d, J = 7.4 Hz, 2H), 7.81–7.80 (m, 1H), 7.62–7.59 (m, 1H), 7.53–7.50 (m, 1H), 7.34–7.33 (m, 1H), 7.29–7.21 (m, 4H), 7.18–7.15 (m, 1H), 7.05–7.00 (m, 4H), 6.94–6.92 (m, 2H), 4.60 (s, 2H);

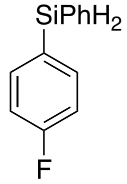
^{13}C NMR (125 MHz, $CDCl_3$): δ 143.1, 141.7, 138.1, 135.3, 134.2, 131.9, 130.0, 129.5, 129.4, 128.4, 127.6, 125.7, 122.9, 120.1, 119.5, 110.1;

^{29}Si NMR (100 MHz, $CDCl_3$): δ –34.8;

GC MS (EI) *m/z* (relative intensity): 349 (100), 270 (93), 241 (12), 135 (14).

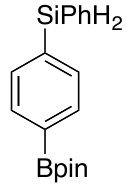
HRMS (APCI): Calcd for $C_{24}H_{20}NSi^{+}$ [M+H^{+}] 350.1365, found, 350.1355.

(*p*-Fluorophenyl)phenylsilane (18)



4-Fluoroiodobenzene (101 mg) and 2.0 equiv of phenylsilane and lithium *tert*-butoxide were used. NMR yield estimated in d^6 benzene in the presence of 1,1,2,2-tetrachloroethane is 22%.[39]

(Phenyl)(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)silane (19)



4-Iodophenyl boronic acid pinacol ester (164 mg) and 2.0 equiv of phenylsilane and lithium *tert*-butoxide were used. Crude product was purified by column chromatography (hexane 100%). After column chromatography, product was further purified by GPC (chloroform) to afford the desired compound as a colorless liquid in 26% yield (40 mg).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.81–7.80 (d, J = 7.8 Hz, 2H), 7.62–7.61 (m, 2H), 7.59–7.57 (m, 2H), 7.41–7.40 (m, 1H), 7.38–7.35 (m, 2H);

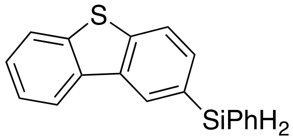
^{13}C NMR (125 MHz, $CDCl_3$): δ 135.7, 135.0, 134.9, 134.1, 131.3, 129.9, 128.1, 83.9, 24.8;

^{29}Si NMR (100 MHz, $CDCl_3$): δ –34.9;

GC MS (EI) *m/z* (relative intensity): 295 (3), 211 (11), 105 (23), 84 (100).

HRMS (APCI): Calcd for $C_{18}H_{24}BO_2Si^+$ [$M+H^+$] 311.1639, found, 311.1632.

(2-Dibenzothiophene)(phenyl)silane (20)



2-Iododibenzothiophene (154 mg) and 2.0 equiv of phenylsilane and lithium *tert*-butoxide were used. Crude product was purified by column chromatography (hexane 100%) to afford the desired compound as a colorless liquid in 39% yield (56 mg).

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.40 (s, 1H), 8.16–8.14 (m, 1H), 7.88–7.84 (m, 2H), 7.65–7.64 (d, J = 7.5 Hz, 3H), 7.46–7.38 (m, 5H), 5.08 (s, 2H);

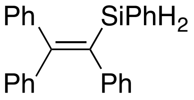
^{13}C NMR (125 MHz, $CDCl_3$): δ 141.5, 139.2, 135.7, 135.3, 135.1, 133.2, 131.5, 130.0, 129.0, 128.2, 126.9, 126.7, 124.5, 122.8, 122.6, 121.6;

^{29}Si NMR (100 MHz, $CDCl_3$): δ –33.8;

GC MS (EI) *m/z* (relative intensity): 290 (65), 257 (100), 212 (47), 184 (35), 105 (29).

HRMS (APCI): Calcd for $C_{18}H_{15}SSi^+$ [$M+H^+$] 291.0664, found, 291.0653.

(Phenyl)(1,2,2-triphenylvinyl)silane (21)

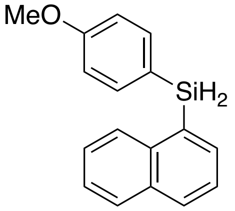


2-Bromo-1,1,2-triphenylethylene (167 mg) and 3.0 equiv of phenylsilane and lithium *tert*-butoxide were used. Crude product was purified by column chromatography (hexane 100%) to afford the desired compound as a colorless liquid in 53% yield (95 mg).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.34–7.22 (m, 10H), 7.16–7.13 (m, 2H), 7.10–7.01 (m, 6H), 6.93–6.91 (m, 2H), 4.55 (s, 2H);

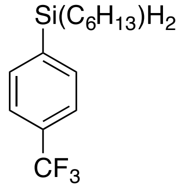
^{13}C NMR (125 MHz, $CDCl_3$): δ 156.7, 144.2, 143.4, 142.2, 136.6, 135.3, 132.7, 130.4, 129.8, 129.7, 129.3, 128.0, 127.9, 127.8, 127.7, 127.4, 126.7, 125.7;
^{29}Si NMR (100 MHz, $CDCl_3$): δ –38.9;
GC MS (EI) *m/z* (relative intensity): 362 (32), 284 (100), 206 (46), 181 (59), 105 (53).
HRMS (APCI): Calcd for $C_{26}H_{22}Si^+$ [$M+H^+$] 363.1569, found, 363.1566.

(4-Methoxyphenyl)(1-naphtyl)silane (22)



1-Iodonaphthalene (125 mg) and 2.0 equiv of 4-methoxyphenylsilane and lithium *tert*-butoxide were used. Crude product was purified by column chromatography (hexane/EtOAc = 97:3). After column chromatography, product was further purified by GPC (chloroform) to afford the desired compound as a colorless liquid in 43% yield (56 mg).
^1H NMR (500 MHz, $CDCl_3$): δ 8.04–8.02 (m, 1H), 7.94–7.92 (d, J = 8.0 Hz, 1H), 7.88–7.86 (m, 1H), 7.81–7.79 (m, 1H), 7.54–7.53 (m, 2H), 7.49–7.45 (m, 3H), 6.91–6.90 (m, 2H), 5.22 (s, 2H), 3.80 (s, 3H);
^{13}C NMR (125 MHz, $CDCl_3$): δ 161.1, 137.2, 136.7, 133.1, 130.8, 130.5, 128.8, 127.9, 126.3, 125.8, 125.3, 121.9, 114.0, 55.0;
^{29}Si NMR (100 MHz, $CDCl_3$): δ –35.3;
GC MS (EI) *m/z* (relative intensity): 264 (74), 155 (69), 136 (100), 77 (34).
HRMS (APCI): Calcd for $C_{17}H_{17}OSi^+$ [$M+H-H_2^+$] 263.0892, found, 263.0885.

Hexyl(4-trifluoromethylphenyl)silane (24)



1-Bromo-4-trifluoromethylbenzene (110 mg) and 3.0 equiv of hexylsilane and lithium *tert*-butoxide were used. Crude product was purified by column chromatography (hexane 100%) followed by GPC (chloroform) to afford the desired compound as a colorless liquid in 24% yield (31 mg).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.69–7.68 (d, J = 7.0 Hz, 2H), 7.61–7.59 (d, J = 6.9 Hz, 2H), 4.31 (s, 2H), 1.47–1.44 (m, 2H), 1.43–1.41 (m, 2H), 1.38–1.26 (m, 4H), 0.98–0.93 (m, 2H), 0.89–0.86 (m, 3H);

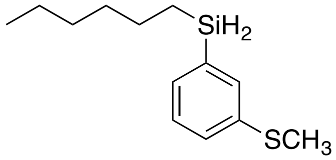
^{13}C NMR (125 MHz, $CDCl_3$): δ 137.9, 135.5, 131.4 (J = 32 Hz), 125.2 (q, J = 271 Hz), 124.4 (q, J = 4.4 Hz), 32.4, 31.4, 24.9, 22.5, 14.1, 9.7;

^{29}Si NMR (100 MHz, $CDCl_3$): δ –11.3;

GC MS (EI) *m/z* (relative intensity): 175 (67), 127 (100), 108 (52), 91 (32), 86 (32), 77 (26).

HRMS (APCI): Calcd for $C_{13}H_{20}F_3Si^+$ [M+H$^+$] 261.1286, found, 261.1279.

Hexyl(3-thioanisole)silane (25)



3-Bromothioanisole (101 mg) and 3.0 equiv of hexylsilane and lithium *tert*-butoxide were used. Crude product was purified by column chromatography (hexane 100%) followed by evaporation of thioanisole to afford the desired compound as a colorless liquid in 30% yield (35 mg).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.45–7.44 (m, 1H), 7.32–7.31 (m, 1H), 7.28–7.27 (m, 2H), 4.26 (s, 2H), 2.49 (s, 3H), 1.46–1.41 (m, 2H), 1.38–1.24 (m, 7H), 0.95–0.91 (m, 2H), 0.89–0.86 (t, J = 6.9 Hz, 3H);

^{13}C NMR (125 MHz, $CDCl_3$): δ 138.1, 133.7, 133.1, 131.8, 128.4, 127.7, 32.5, 31.4, 25.0, 22.5, 15.8, 14.1, 9.90;

^{29}Si NMR (100 MHz, $CDCl_3$): δ –31.8;

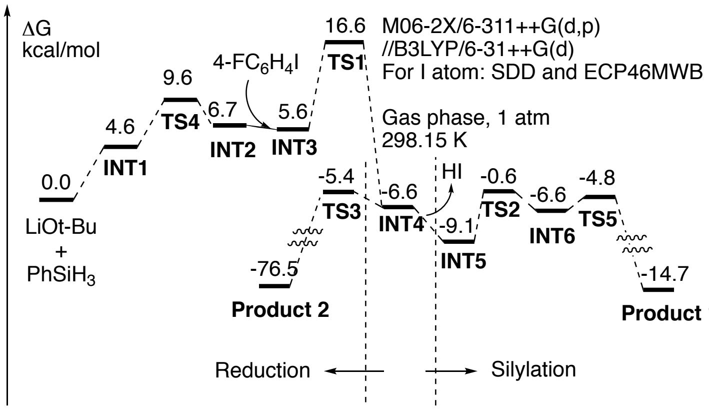
GC MS (EI) *m/z* (relative intensity): 238 (73), 153 (81), 139 (68), 124 (100), 105 (34), 91 (37).

HRMS (APCI): Calcd for $C_{13}H_{23}SSi^+$ [M+H$^+$] 239.1290, found, 239.1297.

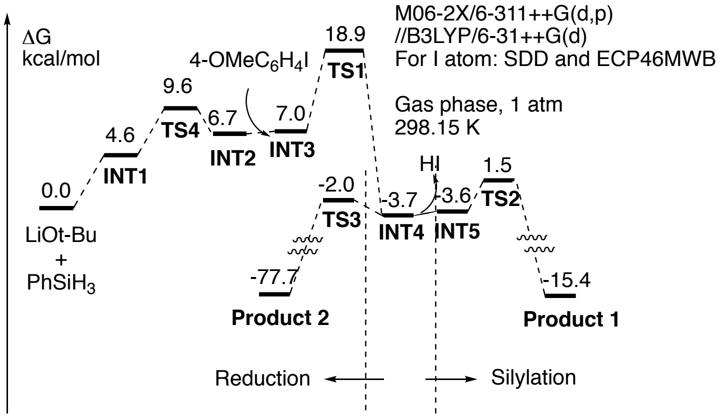
Theoretical study

Theoretical study was performed with the Gaussian 09 program package.[40] The density functional theory (DFT) method was employed using the B3LYP hybrid functional[41] or M06-2X.[42] Geometry optimizations were performed with the B3LYP method using the SDD basis set and the Stuttgard ECP46MWB effective core potential[43] for I atom and 6-31++G(d)[44] basis set for the rest. The use of 6-31++G(d) is necessary because hydride may be generated during the reaction. Each stationary point was characterized by normal coordinate analysis (no imaginary frequencies for an equilibrium structure and one imaginary frequency for a transition state structure. Single point energies calculation were performed with the M06-2X method using the SDD basis set and the Stuttgard ECP46MWB effective core potential for I atom and 6-311++G(d,p) basis set for the rest. Gibbs free energies at 298 K were calculated by adding thermochemical quantities derived from the B3LYP frequency calculation to the M06-2X electronic potential energy. The intrinsic reaction coordinate (IRC)[45] analysis was carried out to confirm that stationary points are smoothly connected to each other. The partial molecular geometries for the transition states were first estimated by Reaction plus software package[46], based on the nudged elastic band (NEB) method,[47] and were subsequently re-optimized using the Gaussian 09 program package.

Gas phase calculation with 4-fluoroiodobenzene without considering for THF coordination to lithium



Gas phase calculation with 4-methoxyiodobenzene without considering for THF coordination to lithium



References

[1] (a) Corey, J. Y. *Adv. Organomet. Chem.* **2004**, *51*, 1−52. (b) Nakajima, Y.; Shimada, S. *RSC Adv.* **2015**, *5*, 20603–20616. (c) Fukazawa, A.; Li, Y.; Yamaguchi, S.; Tsuji, H.; Tamao, K. *J. Am. Chem. Soc.* **2007**, *129*, 14164–14165. (d) Kuninobu, Y.; Yamauchi, K.; Tamura, N.; Seiki, T.; Takai, K. *Angew. Chem. Int. Ed.* **2013**, *52*, 1520–1522.

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Coordinates for the optimized structures

$PhSiH_3$

0 1

Si	-2.35151100	0.00036000	0.00447500
H	-2.88459200	-0.35307900	1.34922900
H	-2.84623600	1.35544800	-0.35612300
C	-0.46989500	-0.00009000	-0.01064700
H	-2.88227300	-0.99486400	-0.96566300
C	0.25711500	-1.20612900	-0.00752600
C	1.65392400	-1.20909800	0.00235900
C	0.25608000	1.20517200	-0.00761200
C	1.65441600	1.20828500	0.00231600
C	2.35591400	0.00027000	0.00827600
H	-0.26954600	-2.15895600	-0.01674800
H	2.19398500	-2.15289000	0.00324300
H	3.44313700	0.00004400	0.01429200
H	2.19382600	2.15244400	0.00311000
H	-0.27247700	2.15635200	-0.01698300

LiO*t*-Bu

0 1

O	-1.27615800	0.00169900	-0.00063300
C	0.11348800	0.00034400	-0.00001200
Li	-2.88076000	-0.00137300	-0.00039500
C	0.63387800	1.45587100	0.00082300
C	0.63343700	-0.72798000	-1.26041100
C	0.63233100	-0.72903100	1.26023800
H	0.26736300	-0.22150900	-2.16227200
H	0.26065900	-1.75986900	-1.27564900
H	1.73089500	-0.75663000	-1.30157600
H	0.26546900	-0.22330600	2.16219900
H	1.72975300	-0.75771700	1.30234600
H	0.25954200	-1.76093200	1.27429000
H	0.26424900	1.98473600	-0.88668300
H	1.73137200	1.50652100	0.00134600
H	0.26343900	1.98400900	0.88842500

LiO*t*-Bu•THF

0 1

O	-1.60750800	0.07394700	-0.05686900
C	-2.98679200	-0.00058000	0.01335200
Li	0.01565400	0.14735600	-0.13308300
C	-3.62149200	0.96580600	-1.01599300
C	-3.46454600	0.39001500	1.43298100
C	-3.45309000	-1.44403800	-0.29616900
H	-3.13785600	1.41140900	1.66625700
H	-3.01770500	-0.28522100	2.17381700
H	-4.55788800	0.34366600	1.53657300
H	-3.11555100	-1.73645200	-1.29867500
H	-4.54624800	-1.55135200	-0.25382200
H	-3.00926300	-2.14071900	0.42650700
H	-3.29736300	1.99377900	-0.80950200
H	-4.72021600	0.93882900	-0.99598400
H	-3.28734900	0.70298800	-2.02772300
C	2.67979300	-1.15677400	-0.20250200
O	1.92174500	0.08253600	-0.12807900
C	2.81649300	1.21081600	0.07916600
C	4.22805500	0.65669900	-0.12222700
C	4.07295000	-0.80881100	0.31957800
H	2.15412800	-1.90739300	0.39450700
H	2.70290200	-1.48247300	-1.24982200
H	2.54314600	1.99383700	-0.63414800
H	2.66228000	1.58389800	1.09891100
H	4.51531800	0.71037200	-1.17898900
H	4.97348300	1.20557600	0.46102500
H	4.84491400	-1.46603400	-0.09197600
H	4.10419000	-0.88743600	1.41275900

Iodobenzene

0 1

C	-1.26491500	-1.21633700	0.00000300
C	-0.58107500	0.00002600	0.00000500
C	-1.26493000	1.21634400	0.00000200
C	-2.66398300	1.20810500	-0.00000100
C	-3.36570100	-0.00000900	0.00000000
C	-2.66393900	-1.20813000	-0.00000300
H	-0.72381500	-2.15672200	0.00000800
H	-0.72389600	2.15676800	0.00000400
H	-3.20102100	2.15325100	-0.00000800
H	-4.45219700	-0.00004500	0.00000400
H	-3.20099500	-2.15326600	-0.00000800
I	1.56847500	0.00000000	-0.00000100

4-Fluoro-1-iodobenzene

0 1

C	0.89625700	-1.21509100	0.00000100
C	0.20868000	0.00000200	0.00000100
C	0.89625700	1.21509200	0.00000100
C	2.29451000	1.21736400	0.00000300
C	2.96371900	0.00000100	0.00000400
C	2.29450800	-1.21736300	0.00000200
H	0.35895500	-2.15746500	0.00000100
H	0.35895900	2.15746800	0.00000000
H	2.85635200	2.14604300	0.00000300
H	2.85635200	-2.14604100	0.00000300
I	-1.93675100	0.00000000	-0.00000200
F	4.32151300	-0.00000200	0.00000400

4-Methoxy-1-iodobenzene

0 1

C	-0.41670200	1.33826500	0.00005000
C	0.18915100	0.07778600	0.00005300
C	-0.58536800	-1.07744800	0.00006900
C	-1.98329600	-0.98353200	0.00002000
C	-2.59766200	0.27459800	-0.00001000
C	-1.80554700	1.43321700	-0.00004900
H	0.18325900	2.24257800	0.00003700
H	-0.12000900	-2.05756400	0.00004400
H	-2.56861800	-1.89618500	0.00003100
H	-2.29574500	2.40227200	-0.00005900
I	2.33111200	-0.07815100	-0.00001200
O	-3.94800300	0.47723200	0.00007200
C	-4.80608200	-0.65700300	-0.00007200
H	-4.65444700	-1.27151800	0.89698300
H	-5.82214500	-0.25923100	-0.00022600

H	-4.65415200	-1.27149000	-0.89709000

1-Iodonaphthalene

0 1

C	-3.32815900	-1.62831200	0.00049900
C	-3.41178700	-0.25806000	0.00049900
C	-2.23292100	0.53716900	0.00049900
C	-0.96759700	-0.10481100	0.00012900
C	-0.91032500	-1.52537700	-0.00002500
C	-2.06516800	-2.26861300	0.00026500
H	-3.27612100	2.44623800	0.00074200
H	-4.23858800	-2.24565100	0.00057900
H	-4.38876200	0.24815300	0.00072700
C	-2.29004200	1.95805600	0.00076200
C	0.21082600	0.69120500	0.00001400
H	0.07569600	-2.01345700	-0.00010700
H	-2.02449700	-3.36781400	0.00016300
C	0.12726100	2.06152000	0.00028700
C	-1.13598000	2.70176700	0.00074600
H	1.03767800	2.67882000	0.00046500
H	-1.17655200	3.80096500	0.00092800
I	2.07574500	-0.27423600	-0.00048200

Mesityl Iodide

0 1

C	0.85663600	1.23192100	-0.00459000
C	2.25958300	1.19776300	-0.01014200
C	2.97969000	0.00017500	-0.00934900
C	2.25961900	-1.19760000	-0.01012300
C	0.85682500	-1.23184300	-0.00459900
C	0.18357900	0.00007600	-0.00074500
H	2.79868500	-2.14313600	-0.01645000
H	2.79856200	2.14332300	-0.01647900
C	0.15007200	-2.56597000	-0.00672500
H	-0.49163500	-2.68307900	0.87459300
H	-0.49476800	-2.67911600	-0.88628400
H	0.87628300	-3.38468800	-0.00975400
C	4.49128800	-0.00007100	0.01911500
H	4.86701600	-0.01706700	1.05123700
H	4.90186000	-0.87820000	-0.49149000
H	4.90144000	0.89434300	-0.46255200
C	0.14992100	2.56606500	-0.00672000
H	-0.49498400	2.67919600	-0.88623200
H	-0.49171500	2.68323200	0.87464700
H	0.87615200	3.38476500	-0.00983200
I	-1.98434300	-0.00005000	0.00343100

1-bromonaphthalene

0 1

C	-3.14408600	-1.32184100	0.00000100
C	-3.02095500	0.04995100	0.00000300
C	-1.74280100	0.67404500	0.00000200
C	-0.56730200	-0.15509000	0.00000400
C	-0.72978900	-1.56670700	0.00000400
C	-1.98493700	-2.13566000	0.00000100
H	-2.50577500	2.70069700	0.00000600
H	-4.12848000	-1.78247700	0.00000100
H	-3.90568100	0.68265400	0.00000400
C	-1.60704200	2.08828400	0.00000600
C	0.69626100	0.50340400	0.00000900
H	0.15312500	-2.19481100	0.00000600
H	-2.08559800	-3.21787000	0.00000100
C	0.80644600	1.87519100	0.00000300
C	-0.36177900	2.67505900	0.00000400
H	1.78504400	2.34267500	0.00000100
H	-0.26128900	3.75690500	0.00000400
Br	2.31098700	-0.52593100	-0.00000700

Bromobenzene

0 1

C	1.21521200	2.17690700	0.00000000
C	1.21249600	0.77971900	0.00000000
C	0.00962200	2.88362200	0.00000000
C	-1.20048400	2.18552000	0.00000000
C	-1.20721200	0.78789000	0.00000000
C	0.00000000	0.08940000	0.00000000
H	2.16344600	2.70800600	0.00000000
H	2.14890900	0.22815400	0.00000000
H	-2.14772300	0.24331200	0.00000000
H	-2.14532200	2.72260600	0.00000000
H	0.01365800	3.97048400	0.00000000
Br	-0.00602200	-1.80831200	0.00000000

HI

0 1

H	0.00000000	0.00000000	-1.60690500
I	0.00000000	0.00000000	0.03031900

HBr

0 1

Br	0.00000000	0.00000000	0.03994600
H	0.00000000	0.00000000	-1.39811900

PhSiH_2O*t*-Bu

0 1

Si	-0.23731000	-0.87092500	-0.63071600
H	-0.53378700	-0.71056700	-2.08233800
H	-0.33505700	-2.31805600	-0.29438500
C	1.50067000	-0.29246100	-0.23226500
O	-1.28144900	0.05503400	0.28316800
C	1.89843300	1.04236400	-0.44758400
C	3.20183400	1.46172400	-0.16822600
C	2.45777700	-1.19310200	0.27201700
C	3.76543300	-0.77977300	0.55094600
C	4.13867500	0.54929100	0.33122100
H	1.18451500	1.76599600	-0.83620000
H	3.48778300	2.49649100	-0.34052300
H	5.15342600	0.87393000	0.54782700
H	4.48814000	-1.49224200	0.94104900
H	2.18317200	-2.23046600	0.45280200
C	-2.72507100	0.20366300	0.19819700
C	-3.13631400	0.91238800	1.49327700
C	-3.39502500	-1.17395700	0.10350200
C	-3.06651600	1.06877600	-1.02279500
H	-2.87195000	0.30304400	2.36480800
H	-4.21766700	1.09014500	1.50970400

H	-2.62581900	1.87812300	1.57862200
H	-3.10978900	-1.80270600	0.95443100
H	-3.11644000	-1.69392600	-0.82140300
H	-4.48582200	-1.06727000	0.10705300
H	-2.55593400	2.03623600	-0.95912700
H	-4.14633000	1.25138100	-1.07245200
H	-2.76388900	0.57909200	-1.95493800

H_2
0 1

H	0.00000000	0.00000000	0.37181000
H	0.00000000	0.00000000	-0.37181000

Generation of silicate from phenylsilane and lithium *tert*-butoxide.

INT0
0 1

Si	-1.60313100	1.84045400	-0.00995700
H	-1.64230400	2.68664200	1.20583400
H	-0.25235100	1.18214000	0.00305400
C	-2.94690200	0.54158200	-0.00352900
H	-1.63072600	2.66264600	-1.24241700
C	-3.45509100	0.02206600	-1.20943700
C	-4.44461200	-0.96398900	-1.20562200
C	-3.46526900	0.04475200	1.20760700
C	-4.45480500	-0.94126500	1.21400300
C	-4.94400800	-1.44803000	0.00676000
H	-3.08335100	0.39154400	-2.16319500
H	-4.82605100	-1.35181600	-2.14667200
H	-5.71507900	-2.21412200	0.01070700
H	-4.84426000	-1.31129600	2.15892900
H	-3.10163700	0.43221000	2.15735000
O	3.08128100	0.06166800	0.00735900
C	4.42048000	-0.29784100	0.00220600
Li	1.53216100	0.49891400	0.00973200
C	4.68885200	-1.29934500	-1.14539000
C	4.79015000	-0.95937000	1.35040500
C	5.29824400	0.95875700	-0.20489900
H	4.17081900	-1.85097900	1.51019200
H	4.59655200	-0.26070900	2.17411000
H	5.84636500	-1.25965500	1.39228100
H	5.04022700	1.44063600	-1.15640200
H	6.37116400	0.72163100	-0.21724400
H	5.11296100	1.68006500	0.60105000
H	4.06639800	-2.19323400	-1.01295400
H	5.74101900	-1.61341900	-1.18825300
H	4.42512800	-0.84262100	-2.10767100

TS0
0 1

Si	-0.09245000	0.26921500	0.48906800
H	-0.21848200	0.46125200	1.96463200
H	0.04787800	1.79915000	0.01434800
C	1.80588300	0.08518000	0.13285800
H	-0.38675500	-1.18307600	0.20982100
C	2.38680600	-1.19303700	0.05241100
C	3.76364500	-1.36563100	-0.12712500
C	2.66542300	1.18908700	0.00036000
C	4.04376900	1.03352200	-0.17723800
C	4.59766900	-0.24935800	-0.24084800
H	1.74834300	-2.07255900	0.13093700
H	4.18464200	-2.36761100	-0.18396700
H	5.66822100	-0.37730900	-0.38516300
H	4.68478900	1.90819600	-0.27065100
H	2.24806100	2.19593300	0.03562600
O	-1.87475400	0.66929000	-0.08789000
C	-3.04228200	-0.17356400	-0.11044300
Li	-1.50421300	2.32639900	-0.46470800
C	-3.22671000	-0.87002400	1.24773700
C	-2.92677100	-1.20388900	-1.24689700
C	-4.23736500	0.75804000	-0.37838100
H	-2.08025600	-1.87559700	-1.08284200
H	-2.77888000	-0.69563800	-2.20765700
H	-3.83969000	-1.80857200	-1.31614800
H	-4.32876700	1.50795100	0.41859800
H	-5.18021400	0.19964700	-0.42241000
H	-4.11650100	1.27519800	-1.34101200
H	-2.39788400	-1.55186600	1.45717200
H	-4.15794200	-1.44983200	1.25948800
H	-3.27200200	-0.12974900	2.05491500

INT1
0 1

Si	-0.16471700	-0.53183400	0.98220700
H	-0.24854300	-1.06342100	2.38369600
H	-0.48720100	0.92456300	1.28447200
C	1.60999600	-0.17992700	0.33697700
H	-0.00062800	-2.10775000	0.42157400
C	3.42130400	1.42789600	-0.03468900
C	2.45930500	-1.18283100	-0.16335300
C	3.76308500	-0.90020200	-0.58159200
C	4.24773500	0.41022000	-0.51988000
C	2.12054500	1.13083900	0.38482900
H	3.78883800	2.45089600	0.01470200
H	2.09279900	-2.20674600	-0.21973200
H	5.25963000	0.63601000	-0.84913500
H	1.48706400	1.93188800	0.76159900
H	4.40043000	-1.69873600	-0.95650400
Li	-1.34861900	-2.34389100	-0.55091100
O	-1.68266800	-0.69202800	-0.02608700
C	-2.75885200	0.25382200	-0.25366700
C	-3.77400600	-0.49054500	-1.13653600
H	-4.63707800	0.14342900	-1.37066200
H	-3.31538900	-0.78814000	-2.08975700
H	-4.15081100	-1.38676400	-0.62488300
C	-3.41370600	0.63958500	1.08035900
H	-3.76331500	-0.25573800	1.60820700
H	-2.70579300	1.16497800	1.72638000
H	-4.27669800	1.29459500	0.90780700
C	-2.23042500	1.48834600	-0.99881100
H	-1.72845200	1.18860700	-1.92636400
H	-3.05657000	2.16227400	-1.25777900
H	-1.51492000	2.04040900	-0.38491900

Generation of silylanion

Int2
0 1

Si	2.65918500	0.55621800	-1.05705800
H	3.70313700	1.58900800	-0.65119400
H	-2.66534100	-1.45674100	-2.28816600
C	3.62541900	-0.93434000	-0.31594400
O	1.33646300	1.54535500	-0.27123100
C	4.91049400	-0.73606100	0.22241700
C	5.66671900	-1.79754900	0.73024300
C	3.12312700	-2.24763400	-0.30954200
C	3.86910900	-3.31858600	0.19233800
C	5.14669300	-3.09515100	0.71556100
H	5.32605000	0.27002700	0.24064200
H	6.65873500	-1.61315400	1.13798800
H	5.72968800	-3.92414700	1.11099900
H	3.45621800	-4.32557900	0.17690600
H	2.12851700	-2.43436800	-0.71218400
C	1.39067400	2.86198300	0.33245200
C	-0.05490800	3.18724600	0.74227800
C	1.88395200	3.89399200	-0.69280400
C	2.28842900	2.83736900	1.57906700
H	-0.71608200	3.19434100	-0.13457000
H	-0.11908500	4.17455200	1.21483000
H	-0.43055100	2.44922100	1.46383400
H	1.24405500	3.88433500	-1.58330900
H	2.90897900	3.67698300	-1.00385400
H	1.85848700	4.90344400	-0.26360100
H	1.94027700	2.07346900	2.28452300
H	2.26485200	3.80975200	2.08679500
H	3.32361600	2.61137700	1.31245800
C	-4.87887500	-1.28313400	1.07252700
C	-6.15429900	-0.94047800	1.52804900
C	-5.33710600	-0.19389000	-1.03589100
C	-6.61302600	0.15002300	-0.58289300
C	-7.02210300	-0.22186000	0.70086700
C	-4.44743100	-0.91345900	-0.21557500
Si	-2.72781600	-1.34333100	-0.81232600
H	-8.01548500	0.04312900	1.05377200
H	-7.28704200	0.70356300	-1.23160500
H	-4.21954100	-1.84884600	1.72793600
H	-6.47097500	-1.23677400	2.52478000
H	-5.03858000	0.09778300	-2.04097500
H	-1.78479300	-0.22915600	-0.44367700
H	-2.19879400	-2.55902600	-0.15113900
Li	0.05020100	0.35349800	-0.55066100
H	1.35523700	-0.45274700	-1.26975000
H	2.78575100	0.70497100	-2.54713600

TS1
0 1

Si	2.65918500	0.55621800	-1.05705800
H	3.70313700	1.58900800	-0.65119400
H	-2.66534100	-1.45674100	-2.28816600
C	3.62541900	-0.93434000	-0.31594400
O	1.33646300	1.54535500	-0.27123100
C	4.91049400	-0.73606100	0.22241700
C	5.66671900	-1.79754900	0.73024300
C	3.12312700	-2.24763400	-0.30954200
C	3.86910900	-3.31858600	0.19233800
C	5.14669300	-3.09515100	0.71556100
H	5.32605000	0.27002700	0.24064200
H	6.65873500	-1.61315400	1.13798800
H	5.72968800	-3.92414700	1.11099900
H	3.45621800	-4.32557900	0.17690600
H	2.12851700	-2.43436800	-0.71218400
C	1.39067400	2.86198300	0.33245200
C	-0.05490800	3.18724600	0.74227800
C	1.88395200	3.89399200	-0.69280400
C	2.28842900	2.83736900	1.57906700
H	-0.71608200	3.19434100	-0.13457000
H	-0.11908500	4.17455200	1.21483000
H	-0.43055100	2.44922100	1.46383400
H	1.24405500	3.88433500	-1.58330900
H	2.90897900	3.67698300	-1.00385400
H	1.85848700	4.90344400	-0.26360100
H	1.94027700	2.07346900	2.28452300
H	2.26485200	3.80975200	2.08679500
H	3.32361600	2.61137700	1.31245800
C	-4.87887500	-1.28313400	1.07252700
C	-6.15429900	-0.94047800	1.52804900
C	-5.33710600	-0.19389000	-1.03589100
C	-6.61302600	0.15002300	-0.58289300
C	-7.02210300	-0.22186000	0.70086700
C	-4.44743100	-0.91345900	-0.21557500
Si	-2.72781600	-1.34333100	-0.81232600
H	-8.01548500	0.04312900	1.05377200
H	-7.28704200	0.70356300	-1.23160500
H	-4.21954100	-1.84884600	1.72793600
H	-6.47097500	-1.23677400	2.52478000
H	-5.03858000	0.09778300	-2.04097500
H	-1.78479300	-0.22915600	-0.44367700
H	-2.19879400	-2.55902600	-0.15113900
Li	0.05020100	0.35349800	-0.55066100
H	1.35523700	-0.45274700	-1.26975000
H	2.78575100	0.70497100	-2.54713600

Int3
0 1

Si	-2.54201900	0.66425500	1.30494600
H	-3.60210700	1.67070700	1.56030700
H	2.44600200	-0.82505900	3.07197800
C	-3.26346600	-0.76467600	0.34445100
O	-1.21305200	1.40745500	0.53729200
C	-4.61193600	-0.75169500	-0.05932200
C	-5.16835700	-1.83322600	-0.74779200
C	-2.48713800	-1.90207800	0.04201000
C	-3.03980400	-2.98255000	-0.64845900
C	-4.38098100	-2.94895400	-1.04423400
H	-5.23918700	0.10914900	0.16558100
H	-6.21216100	-1.80529300	-1.05037600
H	-4.81140800	-3.79208600	-1.57874900
H	-2.42615300	-3.85134500	-0.87225400
H	-1.44385700	-1.95049100	0.34899700
C	-1.23803500	2.45987900	-0.50275400
C	0.15346400	2.43553300	-1.14198300

C	-1.50227400	3.80030600	0.19028900
C	-2.31354400	2.14236300	-1.54574500
H	0.93958800	2.64414400	-0.40488700
H	0.22698300	3.20254800	-1.92041300
H	0.35539500	1.46442000	-1.60880900
H	-0.74282000	3.99676700	0.95480000
H	-2.48730200	3.81466900	0.66875200
H	-1.47119300	4.61666900	-0.54035400
H	-2.14491000	1.16217900	-2.00249000
H	-2.29157100	2.89837200	-2.33866500
H	-3.31918000	2.15518200	-1.11035800
C	4.48648500	-1.77425100	-0.14730000
C	5.61189300	-1.62754600	-0.96529900
C	4.39891900	0.60539000	0.17756000
C	5.53031600	0.76322800	-0.62846700
C	6.13876000	-0.35562600	-1.20682200
C	3.85442600	-0.66361600	0.44113800
Si	2.33087400	-0.94388000	1.58145800
H	7.01598000	-0.23664100	-1.83923600
H	5.93750000	1.75674600	-0.80682300
H	4.08915000	-2.76943700	0.04275800
H	6.07806700	-2.50392800	-1.41125900
H	3.92660800	1.48165800	0.61782100
H	2.09529500	0.78527200	1.53201500
H	2.37482700	-2.47634800	1.47849400
Li	0.48413300	0.75471700	1.09819800
H	0.82084400	-0.98067300	1.12698500
H	-1.91871500	0.20889600	2.56998200

Int4
0 1

C	3.32206400	0.68502500	0.93666800
C	4.26376500	1.50464600	0.30710100
C	4.91502900	1.06115400	-0.84752600
C	4.62362900	-0.20505300	-1.36355300
C	3.68106700	-1.01842600	-0.72772200
C	3.00877400	-0.59156500	0.43320200
Si	1.69941300	-1.67889500	1.26472100
H	2.83231400	1.04456200	1.84034300
H	4.49324800	2.48448000	0.71987700
H	5.65130800	1.69422000	-1.33694500
H	5.13342500	-0.56020700	-2.25623900
H	-0.55522600	-3.24383100	2.37151300
H	1.60318000	-1.29920100	2.68912400
H	3.47613200	-2.00555600	-1.13964600
H	0.40712400	-1.34374000	0.57099800
H	2.02924300	-3.09759800	1.01710500
Li	-1.22615800	-2.35131400	1.17974500
C	-3.15863600	1.11960400	0.79730100
C	-2.88961900	2.46784000	1.05204800
C	-1.91127600	3.14338200	0.31768200
C	-1.19689400	2.47188200	-0.67829700
C	-1.45438700	1.12418000	-0.94642500
C	-2.41987800	0.46916300	-0.18726200
H	-3.91992200	0.58942500	1.36020300
H	-3.45129100	2.98539100	1.82488000
H	-1.70694600	4.19100000	0.51991900
H	-0.43563400	2.99154700	-1.25345700
H	-0.90282800	0.59674500	-1.71747800
Br	-2.84197900	-1.36742200	-0.60042300

TS2
0 1

C	3.84558600	0.49968700	0.95877300
C	4.62907200	1.23067500	0.06006600
C	4.32810500	1.21960000	-1.30469600
C	3.24305800	0.46594300	-1.76391700
C	2.46938300	-0.26779400	-0.86076400
C	2.74191900	-0.25942800	0.52256600
Si	1.71149900	-1.29667700	1.73604700
H	4.09486600	0.52640600	2.01749000
H	5.47405800	1.80967600	0.42634000
H	4.93739100	1.78552100	-2.00525300
H	3.00820000	0.43970500	-2.82593300
H	0.11557900	-3.68125000	1.96845400
H	2.28607200	-1.07490000	3.09789900
H	1.64701900	-0.86961000	-1.24614700
H	0.36310300	-0.56383200	1.85401100
H	0.98593200	-2.91230400	1.72920800
Li	-0.59414700	-2.32042500	1.24107200
C	-3.53442800	0.48350800	0.37996300
C	-3.85559100	1.77554300	0.80699000
C	-2.92959300	2.81369100	0.67535400
C	-1.67966300	2.56504000	0.10251100
C	-1.34210300	1.28155000	-0.33804400
C	-2.27818300	0.26474000	-0.17820000
H	-4.24852700	-0.32767400	0.47690700
H	-4.83118600	1.96306800	1.24758800
H	-3.18353900	3.81461600	1.01207300
H	-0.95410000	3.36723700	-0.00143200
H	-0.36912300	1.08397300	-0.77509300
Br	-1.86656200	-1.50521200	-0.83907400

Int5
0 1

C	2.96038100	0.64170400	0.97185100
C	3.40165300	1.70362500	0.17354500
C	3.50963600	1.54688900	-1.21209600
C	3.17251100	0.31520300	-1.78506400
C	2.72975700	-0.73732900	-0.97774200
C	2.61017800	-0.60891100	0.42271100
Si	1.87895600	-2.03246500	1.49422900
H	2.89959400	0.78633200	2.04943800
H	3.67751000	2.64993900	0.63628900
H	3.86051800	2.36671500	-1.83478600
H	3.26258600	0.17272300	-2.86050600
H	-2.40233600	-2.35391200	2.42630500
H	2.71682200	-3.22120700	1.08769500
H	2.48066200	-1.68740000	-1.45057600
H	2.43232500	-1.72061400	2.86368900
H	-1.84097400	-2.50541000	2.89438900
Li	-0.58398300	-2.12061100	1.10906700
C	-3.11531200	1.00798600	0.39027900
C	-3.02258000	2.33312800	0.82441900
C	-1.80839400	3.02104400	0.74048000
C	-0.68380500	2.38811800	0.20674400

C	-0.75781800	1.06776000	-0.25134000
C	-1.97418600	0.40260200	-0.13116100
H	-4.05426200	0.46721900	0.44922400
H	-3.90336300	2.82158600	1.23301000
H	-1.74170100	4.04925000	1.08436600
H	0.26602100	2.90998900	0.13764400
H	0.11857900	0.58109300	-0.66732900
Br	-2.12735900	-1.39973900	-0.81517100

Int6
0 1

C	3.04757600	1.23635800	-0.96729300
C	2.32602100	2.43226600	-0.98929700
C	1.50168400	2.78796500	0.08637300
C	1.40975500	1.92683500	1.18228300
C	2.13244400	0.72562600	1.19393800
C	2.99226300	0.34326200	0.13154400
Si	3.75205300	-1.44658600	0.08434600
H	3.69078700	0.99411200	-1.81122400
H	2.41315500	3.09783000	-1.84618500
H	0.94419000	3.72104200	0.06931600
H	0.78392200	2.19056200	2.03270400
H	2.06641500	0.08760700	2.08000600
H	4.57730300	-1.47793200	1.34561600
Li	1.33614300	-1.26923100	-0.00047300
H	4.79175900	-1.30964400	-0.99622400
C	-3.34138200	1.18944100	1.20426900
C	-2.56985900	0.02438500	1.16214500
C	-3.14187000	1.42517200	-1.19717100
C	-2.37142400	0.26001300	-1.25569500
C	-2.08789300	-0.40903600	-0.06918000
C	-3.62566100	1.88974900	0.02871400
H	-2.34805900	-0.52786600	2.06940400
H	-3.72037200	1.54310900	2.15921500
H	-1.99569500	-0.10958900	-2.20422500
H	-3.36341900	1.96353200	-2.11451900
H	-4.22639700	2.79414400	0.06764400
Br	-1.07944800	-2.05426300	-0.14556400

TS3
0 1

C	-3.16222000	0.51871400	1.20369300
C	-3.05564000	1.91486100	1.20781800
C	-2.97504900	2.63009300	0.00108600
C	-3.05304600	1.91614000	-1.20656600
C	-3.15959900	0.51998500	-1.20414900
C	-3.17568700	-0.24538300	-0.00065400
Si	-2.61722500	-2.07836500	-0.00107200
H	-3.19235000	-0.00601300	2.15718800
H	-3.02985400	2.44975200	2.15509700
H	-2.87951600	3.71191700	0.00176200
H	-3.02521900	2.45202500	-2.15322600
H	-3.18765200	-0.00373200	-2.15826000
H	-3.35972500	-2.63958500	-1.18936900
Li	-1.17629800	0.52312800	0.00218500
H	-3.36226900	-2.64096900	1.18497500
C	4.25592500	0.76142300	-1.21055200
C	3.00780300	0.12908900	-1.21468200
C	4.25729600	0.75867800	1.21072400
C	3.00916800	0.12635000	1.21484700
C	2.39898600	-0.17535000	0.00008100
C	4.87943200	1.07821000	0.00009500
H	2.52302200	-0.12830300	-2.15237800
H	4.73976700	1.00145600	-2.15413300
H	2.52545800	-0.13315400	2.15251300
H	4.74221300	0.99656700	2.15429700
H	5.85014700	1.56680800	0.00010100
Br	0.64176600	-1.10559700	-0.00001600

Int7
0 1

C	-2.94173700	0.60010500	1.20539300
C	-2.71789300	1.98197900	1.21001000
C	-2.57121000	2.68827500	0.00032300
C	-2.71838200	1.98223400	-1.20945000
C	-2.94222900	0.60035500	-1.20503600
C	-3.01523100	-0.16192400	0.00011300
Si	-2.68257700	-2.04236700	-0.00011700
H	-3.01414600	0.08025700	2.15865100
H	-2.64417300	2.51339100	2.15648200
H	-2.38558700	3.75803400	0.00039900
H	-2.64502800	2.51384200	-2.15584100
H	-3.01500900	0.08071000	-2.15837800
H	-3.49715800	-2.50185100	-1.18624300
Li	-1.01710000	0.81537400	-0.00036800
H	-3.49675300	-2.50204900	1.18621000
C	4.14162600	0.65535700	-1.21051900
C	2.87730900	0.05569900	-1.21427600
C	4.14192800	0.65437500	1.21063700
C	2.87764800	0.05463300	1.21421400
C	2.25765000	-0.23026400	-0.00006900
C	4.77310400	0.95649500	0.00010400
H	2.38760300	-0.19163200	-2.15249100
H	4.63275000	0.88079000	-2.15407000
H	2.38820000	-0.19351700	2.15234900
H	4.63329800	0.87901200	2.15425000
H	5.75667700	1.41872400	0.00017000
Br	0.47232000	-1.13178900	-0.00021200

TS4
0 1

C	-2.63652900	0.28164000	-0.00001900
C	-2.36808300	0.98238700	-1.20275200
C	-1.83493500	2.27833400	-1.20942100
C	-1.54728500	2.93308800	0.00017100
C	-1.83507700	2.27822000	1.20966900
C	-2.36822100	0.98227300	1.20281300
Si	-2.78028600	-1.61897000	-0.00012200
H	-3.59455600	-1.96917300	-1.20984500
H	-3.59467700	-1.96930200	1.20948200
H	-2.55025500	0.49105900	-2.15631800
H	-1.63668400	2.77721500	-2.15523200
H	-1.13105000	3.93647000	0.00024200
H	-1.63693800	2.77701100	2.15555100
H	-2.55050500	0.49085500	2.15631000
Br	-0.06654900	-1.51232100	-0.00002400

C	1.95158500	-0.45149700	0.00002500
C	2.58547000	-0.14069600	-1.20694000
C	3.84039200	0.48494100	-1.21164900
C	4.46714800	0.79608800	-0.00006000
C	3.84069800	0.48447700	1.21157100
C	2.58577200	-0.14114600	1.20694900
H	2.11204900	-0.39824600	-2.15507800
H	4.33018300	0.72060300	-2.15483900
H	5.44311000	1.27572000	-0.00009100
H	4.33073300	0.71977600	2.15472600
H	2.11258300	-0.39903400	2.15511000
Li	-0.15545800	0.84507300	0.00012400

Int8
0 1

C	1.77824600	1.30264000	0.24285800
C	0.97940400	1.60620600	1.36539400
C	-0.00663900	2.59245600	1.29526400
C	-0.21656500	3.28707400	0.10166300
C	0.56166700	2.99805900	-1.02341800
C	1.55006400	2.01365900	-0.95531800
Si	3.06340700	-0.03876700	0.32696700
H	3.57468200	-0.25392900	1.69603200
H	4.14469600	0.14490000	-0.66332900
H	1.12782200	1.07286100	2.30213100
H	-0.62137800	2.80462400	2.16508900
H	-0.99434000	4.04314900	0.04395500
H	0.39706300	3.53590400	-1.95315600
H	2.15476000	1.80754100	-1.83657300
Br	1.98519700	-1.96024500	-0.25911700
C	-2.14129100	-0.55903000	-0.30229700
C	-2.71647600	-1.27542200	0.77829200
C	-4.09568600	-1.33395400	1.02706600
C	-4.98540800	-0.66722600	0.17928700
C	-4.47392700	0.05108200	-0.90656900
C	-3.09001900	0.09340400	-1.12878800
H	-2.06802900	-1.82088400	1.47133200
H	-4.47740400	-1.90106700	1.87647500
H	-6.05808100	-0.70735800	0.36043900
H	-5.15428100	0.57299400	-1.58007100
H	-2.74609500	0.66768400	-1.99406600
Li	-0.16973900	-0.48959300	-0.47910900

TS5
0 1

C	-1.90882400	1.18805700	0.35552600
C	-2.12193100	2.07422700	-0.72120900
C	-1.30839600	3.19598500	-0.89120500
C	-0.26338100	3.44554700	0.00447200
C	-0.03483900	2.57674600	1.07423400
C	-0.85123900	1.45724600	1.24932600
Si	-2.96435500	-0.32487100	0.56636200
H	-4.22983900	-0.24329500	-0.19190700
H	-3.17252000	-0.69796200	1.98046900
H	-2.93101900	1.89331500	-1.42610900
H	-1.48553900	3.87141700	-1.72406200
H	0.37716900	4.31181300	-0.13614400
H	0.78740600	2.75717000	1.76012400
H	-0.65937300	0.79337700	2.09005800
Br	-1.80244500	-2.06594400	-0.35514100
C	2.25937700	-0.49339500	-0.36520600
C	3.17820800	0.24590900	-1.15130500
C	4.55207900	0.31551600	-0.87986600
C	5.08356100	-0.37229100	0.21614400
C	4.22376700	-1.12184600	1.02458700
C	2.85330600	-1.17196400	0.72960400
H	2.81805800	0.80080900	-2.02242900
H	5.20939600	0.90126800	-1.52293500
H	6.14906400	-0.32685500	0.43433900
H	4.62201500	-1.66743600	1.88044800
H	2.22856400	-1.77789900	1.39357000
Li	0.30101800	-0.59930300	-0.62839200

Int9
0 1

C	3.99133100	-0.22337000	1.30845100
C	2.87437500	-0.94597000	0.86344700
C	4.66618100	0.62730100	0.42768400
C	4.20928800	0.73849900	-0.88963600
C	3.08899600	0.00473700	-1.30601300
C	2.36580700	-0.87266500	-0.45820300
Si	-1.66072800	-0.67733700	1.21666700
C	-1.60337100	1.03047900	0.51027900
C	-2.79679500	1.74613700	0.28823100
C	-2.76185400	3.04883300	-0.21114300
C	-1.53367800	3.65235600	-0.50042000
C	-0.34221000	2.95211700	-0.29007400
C	-0.37269100	1.65035700	0.21451600
H	-2.94155900	-0.95787800	1.89977100
H	-0.48750200	-1.04348300	2.03112400
H	0.56433100	1.11799900	0.36339500
H	0.61449800	3.41661900	-0.51328000
H	-1.50642900	4.66778100	-0.88781200
H	-3.68926700	3.59292000	-0.37195200
H	-3.75924100	1.29099800	0.51397300
H	2.38966300	-1.60141700	1.59323100
H	2.77558300	0.13049800	-2.34627400
H	4.72732500	1.39397400	-1.58973800
H	5.53531400	1.19141000	0.76086700
H	4.33691400	-0.32531900	2.33710700
Li	0.76899200	-1.89626800	-1.05366600
Br	-1.66653400	-2.23301300	-0.49730000

TS6
0 1

C	3.48777200	-1.27899400	0.91121900
C	2.12273500	-1.51117400	1.12688300
C	3.94355900	-0.94651900	-0.37024500
C	3.02792400	-0.86118000	-1.42297900
C	1.66716500	-1.09473400	-1.17706700
C	1.15897300	-1.43527000	0.09938200
Si	-1.19058600	-0.18940800	1.19653300
C	-0.51305800	1.40509800	0.48513900
C	-1.46202000	2.32618400	-0.00262000
C	-1.07360600	3.58376700	-0.46898700
C	0.27375900	3.95377000	-0.43517100

C	1.22541900	3.06051800	0.06439900
C	0.83805500	1.79395100	0.50851300
H	-2.46899900	0.25779100	1.82687800
H	-0.51300300	-0.96156000	2.25675900
H	1.59423700	1.10512500	0.86897300
H	2.27470300	3.34287600	0.09865500
H	0.57905800	4.93509700	-0.79041200
H	-1.82168400	4.27537500	-0.84924600
H	-2.51788000	2.06378400	-0.01569300
H	1.80429300	-1.75126000	2.14510600
H	0.98045300	-0.98267600	-2.02322100
H	3.37042600	-0.59658900	-2.42253200
H	5.00116100	-0.76109100	-0.54559000
H	4.19495100	-1.35014900	1.73663200
Li	-0.30728000	-2.64541400	-0.39927000
Br	-2.37336300	-1.51317900	-0.39287900

Product

0 1

C	3.26338900	-1.66976900	-0.20828900
C	2.07505200	-1.62894300	-0.95142900
C	3.21401500	-1.69032400	1.19276900
C	1.97053200	-1.67065900	1.84123700
C	0.78739700	-1.63442600	1.08895600
C	0.81232700	-1.61240800	-0.32194100
Si	-0.79315500	-1.54137200	-1.34932300
C	-2.13793700	-0.58777300	-0.45975800
C	-1.94533700	0.75329500	-0.06837800
C	-2.95347200	1.45095800	0.60054400
C	-4.17490700	0.82946800	0.87850400
C	-4.38367500	-0.49843600	0.49633700
C	-3.37093100	-1.20094300	-0.16370500
H	-0.41348400	-0.96524100	-2.66406700
H	-1.26286300	-2.93793900	-1.56109300
H	-3.54820200	-2.23497300	-0.45365800
H	-5.33094700	-0.98703400	0.71167600
H	-4.96128100	1.37817900	1.39133300
H	-2.78327700	2.48311800	0.89581900
H	-1.00650700	1.26544200	-0.27300900
H	2.13752600	-1.57573500	-2.03544900
H	-0.16558900	-1.59558100	1.61079500
H	1.92255500	-1.67197200	2.92691100
H	4.13289300	-1.70221400	1.77211900
H	4.22207000	-1.66408900	-0.71949700
Li	2.03802700	0.38675900	0.46542000
Br	1.51738500	2.44533500	-0.21876300

Generation of aryl anion

TS4

0 1

Si	-0.21478900	0.52796800	-1.12177000
H	-0.30919900	1.52749600	-2.20183300
H	-0.52850600	-0.78775300	-1.76503200
C	1.48811000	0.20348800	-0.38126600
H	0.00003300	2.89531800	-0.02249500
C	3.24913900	-1.44555600	0.04311200
C	2.33578900	1.19441200	0.15079500
C	3.61471300	0.87426800	0.61255200
C	4.07380600	-0.44608500	0.56491000
C	1.97405700	-1.11945400	-0.42917500
H	3.59760700	-2.47494600	-0.00159100
H	1.96816100	2.21548400	0.20557500
H	5.06791300	-0.69365100	0.93045500
H	1.35362100	-1.90934200	-0.84800700
H	4.25399400	1.65778800	1.01342700
Li	-1.34047400	2.34930500	0.72934400
O	-1.54334900	0.68482700	-0.01155400
C	-2.60067200	-0.28331800	0.28308300
C	-3.44519600	0.38145200	1.37936300
H	-4.27943400	-0.26295900	1.67755200
H	-2.84071600	0.57250300	2.27604400
H	-3.87524900	1.32746800	1.02289100
C	-3.45073400	-0.51905000	-0.97148100
H	-3.85044800	0.42900100	-1.34893100
H	-2.86260700	-0.98611000	-1.76660100
H	-4.29459500	-1.18040000	-0.74120500
C	-1.98975900	-1.58841600	0.80713300
H	-1.35664400	-1.39602300	1.68027200
H	-2.78296500	-2.28525100	1.10337200
H	-1.38122500	-2.07714500	0.04112500

INT2

0 1

Si	0.25877700	-0.27641500	1.42400500
H	0.27303300	0.46377400	2.70482400
H	0.55291900	-1.71628500	1.63929900
C	-1.37083800	-0.11330800	0.52696200
H	0.69429800	3.73543100	0.81088700
C	-3.36276200	-1.14780300	-0.43528200
C	-1.89058700	1.15243900	0.18348000
C	-3.12300300	1.26140600	-0.46490600
C	-3.85987000	0.11351300	-0.77468800
C	-2.12753000	-1.25750700	0.20952800
H	-3.93331400	-2.04248800	-0.67241000
H	-1.33117100	2.05925000	0.41620900
H	-4.81982700	0.20223500	-1.27764900
H	-1.75282200	-2.24716800	0.46614000
H	-3.50784800	2.24426100	-0.72486300
Li	1.56830800	2.35088300	0.71340100
O	1.56174700	0.44927400	0.58673700
C	2.39673300	-0.14295000	-0.47335600
C	3.18177500	1.03181100	-1.06801500
H	3.85062700	0.68497100	-1.86284400
H	2.50910800	1.77919900	-1.50856300
H	3.80684600	1.51460400	-0.30508100
C	3.34650200	-1.15881600	0.16934200
H	3.94484500	-0.68353800	0.95415300
H	2.79595600	-1.99489900	0.61235000
H	4.02929300	-1.56832600	-0.58403200
C	1.50902100	-0.79283800	-1.53919600
H	0.79586600	-0.07115400	-1.94980600
H	2.12817300	-1.17286900	-2.35989100
H	0.94559100	-1.63971900	-1.13212400

INT3

0 1

Si	3.42171000	0.71669200	1.12507400
H	4.82946000	0.97587800	0.73070600
H	3.32596800	0.57631100	2.59829100
C	2.25849300	2.04758300	0.52340700
H	0.78501600	-0.82649700	-2.34205600
C	0.38529800	3.56304500	0.91765500
C	2.33144300	2.53057300	-0.80039300
C	1.44415200	3.50674100	-1.25953000
C	0.47214600	4.02418200	-0.39899600
C	1.26893800	2.58225600	1.37289700
H	-0.37409400	3.96067900	1.58573900
H	3.08818100	2.14658300	-1.48254600
H	-0.22058600	4.78190400	-0.75582500
H	1.18516700	2.22880400	2.39844900
H	1.50926200	3.85788000	-2.28571400
C	-3.61538000	-1.50826700	0.97629500
C	-4.77470900	-1.38792800	1.75170900
C	-3.27766000	-0.50681200	0.06260300
C	-4.10195600	0.61249300	-0.07778000
C	-5.60014000	-0.26827300	1.61481400
C	-5.26141700	0.73083300	0.69780300
H	-2.98221800	-2.38511800	1.08685400
H	-6.50141600	-0.17643900	2.21586700
H	-5.90014800	1.60393400	0.58163200
H	-3.84748900	1.39323300	-0.79018200
H	-5.03277500	-2.17238700	2.46009100
Li	1.38108000	-0.34728700	-0.83837900
O	2.86348800	-0.68425300	0.34896000
C	3.53779000	-2.00201700	0.25998000
C	2.42123900	-3.02141900	0.02338000
H	2.84657400	-4.02657800	-0.07521400
H	1.71695200	-3.02797600	0.86277700
H	1.86911700	-2.79766700	-0.89786500
C	4.50118800	-1.94969400	-0.92978000
H	3.95852000	-1.71024000	-1.85049100
H	5.28386500	-1.19812200	-0.77640700
H	4.98951800	-2.92193500	-1.06353500
C	4.27238400	-2.29299200	1.57193900
H	3.58224000	-2.28243200	2.42250100
H	4.73389500	-3.28545800	1.52376900
H	5.07589000	-1.57040600	1.76056300
I	-1.44239300	-0.69101100	-1.16549100

TS1

0 1

Si	2.79740200	1.92356600	0.33991900
H	3.80670000	2.26593200	-0.69171200
H	3.20056100	2.46617300	1.65838600
C	1.09259900	2.47464600	-0.19186700
H	0.83867800	-2.77069200	-1.77220500
C	-1.30510400	2.67868900	0.26282000
C	0.85894400	2.96792200	-1.49294300
C	-0.42891200	3.32108700	-1.90388900
C	-1.50955600	3.17034500	-1.02955700
C	-0.01289200	2.34621800	0.68010300
H	-2.14624200	2.53503200	0.93419000
H	1.68727500	3.07680700	-2.18982800
H	-2.51427400	3.42200600	-1.35708100
H	0.12983700	1.98832100	1.69947600
H	-0.59074700	3.69967200	-2.90973000
C	-2.51151500	-0.73383100	1.70354900
C	-3.48918300	-0.02063100	2.41543800
C	-2.54785900	-0.84205800	0.30585400
C	-3.61363200	-0.22159100	-0.36195700
C	-4.54113000	0.59507300	1.72814300
C	-4.60371600	0.48817800	0.33314800
H	-1.71306300	-1.22199700	2.26802500
H	-5.30918400	1.14013600	2.27285600
H	-5.42798000	0.95194300	-0.20831700
H	-3.68613800	-0.28697300	-1.44888900
H	-3.44050100	0.04270100	3.50234100
Li	0.78144200	-0.09926900	-0.10895800
O	2.57307600	0.24139300	0.44974100
C	3.60751200	-0.80869600	0.65616800
C	2.91228300	-1.93625000	1.42063700
H	3.61969900	-2.75220700	1.60586000
H	2.54022100	-1.58011800	2.38801300
H	2.07631400	-2.35006400	0.84626700
C	4.06697300	-1.27121700	-0.72919800
H	3.22679200	-1.67894100	-1.30311400
H	4.51686700	-0.44537300	-1.29262400
H	4.82050500	-2.06136500	-0.63092500
C	4.76601900	-0.23030900	1.47370100
H	4.42526900	0.13398200	2.44892000
H	5.51514600	-1.00997400	1.64934300
H	5.27130200	0.58877900	0.94666900
I	-0.74310500	-2.01099000	-0.90692000

INT4

0 1

Si	-3.15783200	0.38572500	0.43861800
H	-4.18334100	0.29237900	-0.62927200
H	-3.74490000	1.00793500	1.65133900
C	-2.45218700	-1.30652900	0.78765600
H	1.21756000	-1.55790300	-3.51306500
C	-1.15098800	-2.82440100	2.19079100
C	-2.69991000	-2.38012000	-0.09167300
C	-2.18521100	-3.65277100	0.16420400
C	-1.40965400	-3.87481800	1.30571600
C	-1.67055200	-1.55310500	1.93545600
H	-0.54538100	-2.99251700	3.07711600
H	-3.30357200	-2.22269500	-0.98324500
H	-1.00513000	-4.86397500	1.50418800
H	-1.46239200	-0.75062100	2.64065100
H	-2.38634100	-4.46829700	-0.52567400
C	2.54448000	1.73398300	0.83697200
C	3.65044700	1.92784500	1.67678000
C	1.74147100	0.56701000	0.85428400
C	2.16643000	-0.41287000	1.78602800
C	4.01578600	0.93281800	2.58858700
C	3.26726800	-0.24704900	2.63860900
H	2.31369900	2.54047300	0.13505000
H	4.87406100	1.07150300	3.24329100
H	3.54522200	-1.03682100	3.33665800
H	1.62319200	-1.35891200	1.85518800
H	4.22914500	2.84956000	1.61765300

Li	-0.11475100	0.41921200	0.01695200
O	-1.83848200	1.31640200	-0.08479200
C	-1.81306000	2.78711000	-0.27276800
C	-0.70141000	3.05212800	-1.29071100
H	-0.61747500	4.12721200	-1.48490400
H	0.27002700	2.70808300	-0.91894500
H	-0.91334200	2.54722600	-2.23940000
C	-3.16293000	3.26440000	-0.81743400
H	-3.40550800	2.77018300	-1.76439100
H	-3.97874600	3.08435600	-0.10694600
H	-3.12477800	4.34410000	-0.99931000
C	-1.49165700	3.42550200	1.08217800
H	-0.54264600	3.04381400	1.47343300
H	-1.40531300	4.51321100	0.97602900
H	-2.28000000	3.22057600	1.81515800
I	1.55090100	-0.84325800	-2.03626100

INT5

0 1

Si	-2.61592100	-0.54335700	-0.37150800
H	-3.77969100	-0.88374600	0.48235100
H	-2.88924600	-0.92170700	-1.78051700
C	-2.18848400	1.26652400	-0.19298100
C	-0.96491600	3.24501400	-0.94326600
C	-2.70074800	2.02704100	0.87835100
C	-2.35531600	3.37116200	1.03520700
C	-1.48543200	3.97959600	0.12508400
C	-1.31723900	1.90241900	-1.10237600
H	-0.28145300	3.71178000	-1.64695100
H	-3.37886100	1.56746400	1.59480400
H	-1.21044100	5.02351200	0.25092500
H	-0.90798800	1.35062900	-1.94697000
H	-2.76080500	3.94195100	1.86664200
C	2.83380000	0.19275200	-1.01851400
C	4.20891800	0.37566900	-1.22782600
C	2.22547200	0.16030000	0.26264900
C	3.14102100	0.33195300	1.33193800
C	5.06292700	0.53973000	-0.13296800
C	4.52008600	0.51719400	1.15589200
H	2.21457900	0.07149500	-1.91415600
H	6.13191200	0.68233600	-0.28126200
H	5.17159600	0.64434100	2.02081800
H	2.77276200	0.32457400	2.36221800
H	4.61420700	0.39013300	-2.24001700
Li	0.24881400	-0.09433700	0.45492600
O	-1.21733700	-1.33106300	0.17170300
C	-0.89297000	-2.77672900	0.09271600
C	0.09098700	-3.04061400	1.23482500
H	0.39363900	-4.09387900	1.23366800
H	0.99561200	-2.43070900	1.12375500
H	-0.37127900	-2.81864900	2.20358900
C	-2.17158200	-3.60029200	0.27252500
H	-2.65740000	-3.37501500	1.22820600
H	-2.88992100	-3.42504600	-0.53808000
H	-1.92601900	-4.66789200	0.26277200
C	-0.24084500	-3.03216800	-1.26938700
H	0.66057200	-2.42087800	-1.38381700
H	0.04954100	-4.08559600	-1.35628000
H	-0.93023400	-2.80389800	-2.09020200

TS2

0 1

Si	0.65850600	0.21528100	1.04471900
H	1.72782100	0.94990400	1.81647200
H	0.11188200	-0.67193600	2.09560200
C	-0.41048800	1.64903800	0.45365700
C	-2.45348100	2.98042800	0.60785200
C	0.08857500	2.59237000	-0.46293800
C	-0.66998600	3.70096200	-0.85323900
C	-1.94369800	3.90011000	-0.31408100
C	-1.69761700	1.86512400	0.97853900
H	-3.44451200	3.12643900	1.03167400
H	1.08783100	2.46987800	-0.87761500
H	-2.53391000	4.76460400	-0.60869200
H	-2.12398500	1.14682900	1.67533400
H	-0.26295100	4.41250500	-1.56851500
C	-1.12068500	-2.68658300	0.37184000
C	-2.25436600	-3.51090300	0.35460600
C	-1.09820400	-1.38323200	-0.18028900
C	-2.31276200	-0.96920900	-0.77415800
C	-3.43592000	-3.04997600	-0.23449600
C	-3.46214100	-1.77253800	-0.80250900
H	-0.22624600	-3.07548200	0.86915800
H	-4.32473000	-3.67742900	-0.24898200
H	-4.37728200	-1.40231600	-1.26326100
H	-2.38140600	0.02634700	-1.21616800
H	-2.22125500	-4.50242500	0.80481800
Li	0.54261100	-1.24563300	-1.28206000
O	1.71743000	-0.46328100	-0.17126000
C	3.17972500	-0.53424100	-0.17499300
C	3.52509000	-1.38144000	-1.40808300
H	4.60952700	-1.49560700	-1.51451200
H	3.09442000	-2.38825400	-1.32441000
H	3.15392200	-0.90491300	-2.32568200
C	3.77997900	0.86993100	-0.31656900
H	3.40802300	1.35785100	-1.22499100
H	3.52918100	1.49733200	0.54249700
H	4.87252100	0.80715400	-0.38811000
C	3.67154300	-1.23281100	1.09892000
H	3.20878200	-2.22122600	1.19981800
H	4.75915700	-1.36706200	1.06139200
H	3.43348000	-0.64516100	1.99000400

Product1

0 1

Si	1.87646600	1.38820600	1.24830000
H	1.38487900	1.16448500	2.63351800
H	2.99944300	2.36373700	1.29943500
C	2.48276600	-0.17553800	0.41098900
C	4.32784100	-1.51173200	-0.47180300
C	1.59608300	-1.21600400	0.06341300
C	2.07147000	-2.38268400	-0.54092300
C	3.43589300	-2.53363600	-0.80758900
C	3.85287900	-0.34342800	0.13117600
H	5.38953400	-1.62209700	-0.67932300
H	0.52525000	-1.12853600	0.25041800

H	3.80197000	-3.44369500	-1.27688300
H	4.55976300	0.44446400	0.38467400
H	1.37121600	-3.17199900	-0.80170300
C	-0.66138100	2.74834200	0.98402000
C	-1.74475600	3.30950500	0.29444200
C	0.42470400	2.16567200	0.29784700
C	0.38482400	2.17124200	-1.11297500
C	-1.76472200	3.29847700	-1.10575200
C	-0.69508800	2.72907300	-1.80933300
H	-0.67684300	2.74283100	2.07131700
H	-2.61058900	3.71791200	-1.64337800
H	-0.70895100	2.70582200	-2.89570600
H	1.19287600	1.71102200	-1.67671000
H	-2.57717900	3.73557000	0.84789600
Li	-1.56258100	0.78949800	-0.30271500
O	-2.05226300	-0.74623300	-0.01665700
C	-2.83133100	-1.87975700	0.15596100
C	-3.98419300	-1.89138200	-0.87670800
H	-4.63024700	-2.77502100	-0.77708700
H	-4.60534000	-0.99506500	-0.75001500
H	-3.57236600	-1.87777200	-1.89390700
C	-1.97058000	-3.15086300	-0.04134000
H	-1.52594700	-3.14541700	-1.04476400
H	-1.15638000	-3.17043600	0.69413900
H	-2.55604600	-4.07383300	0.07180900
C	-3.43125000	-1.89580900	1.58244700
H	-4.05034800	-1.00244900	1.73557200
H	-4.05378900	-2.78267600	1.76677300
H	-2.62452800	-1.87922500	2.32591000

TS3

0 1

Si	-1.33208500	2.43451000	0.94564400
H	-2.62104600	2.87601300	0.35629400
H	-0.78032400	3.52019300	1.79511900
C	-1.58999600	0.83878000	1.88134300
H	-1.50839200	-1.14629400	-3.21098000
C	-0.73044800	-0.99431800	3.25027200
C	-2.85923300	0.22575000	1.91117500
C	-3.06487400	-0.96923700	2.60485000
C	-1.99858400	-1.58126900	3.27267700
C	-0.53030500	0.20902600	2.56748800
H	0.10535200	-1.47097700	3.75463900
H	-3.69500900	0.68396900	1.38645700
H	-2.15558300	-2.51505700	3.80665800
H	0.46565600	0.64692500	2.57088400
H	-4.05158600	-1.42525900	2.61916700
C	2.79495200	-1.75983600	-0.46793600
C	4.04455600	-2.34178800	-0.20685800
C	2.31709600	-0.59128600	0.17891000
C	3.22548700	-0.05857400	1.12938000
C	4.89860200	-1.76867700	0.74142800
C	4.48134200	-0.61603200	1.41468700
H	2.16847300	-2.25310200	-1.21662600
H	5.87031600	-2.21180000	0.95201800
H	5.13246700	-0.15451500	2.15772300
H	2.95570400	0.84448000	1.68934500
H	4.35319800	-3.24119400	-0.74036800
Li	0.51191200	0.23777500	-0.15012300
O	-0.21102400	2.05028400	-0.26745900
C	0.54123200	3.00305600	-1.11641100
C	0.99116700	2.19727200	-2.33838300
H	1.56682100	2.83501800	-3.01860200
H	1.63639500	1.36094800	-2.04165700
H	0.12498500	1.80966800	-2.88775800
C	-0.38065800	4.15322800	-1.53453800
H	-1.26750600	3.77899400	-2.05787300
H	-0.70703300	4.74908600	-0.67327400
H	0.15371400	4.82824000	-2.21216200
C	1.74910600	3.50376500	-0.31770900
H	2.38109000	2.66347300	-0.01273400
H	2.35276300	4.18070100	-0.93372600
H	1.43605700	4.05372200	0.57683300
I	-1.48021700	-1.81719100	-1.71944600

INT6

0 1

Si	-2.63496800	1.37997300	0.63520400
H	-3.86711700	1.11190500	-0.14761400
H	-2.84139700	2.58152900	1.48279600
C	-2.18513000	-0.13975200	1.62214000
H	1.80871700	-1.87735700	-1.37259100
C	-0.73760600	-1.30311000	3.20944700
C	-2.95965400	-1.31243600	1.51550000
C	-2.63687000	-2.45654600	2.24833600
C	-1.52284400	-2.45287300	3.09331100
C	-1.07070100	-0.15488300	2.48623100
H	0.13632200	-1.29760200	3.85480600
H	-3.82384300	-1.33308900	0.85448900
H	-1.26514400	-3.34588800	3.65699200
H	-0.44680200	0.72944800	2.60039000
H	-3.24759400	-3.35097000	2.15472700
C	3.24516000	-0.20328200	0.08602500
C	4.54953500	-0.04129300	0.57287400
C	2.13911900	0.58247500	0.47558900
C	2.47206600	1.57858400	1.43040800
C	4.81405300	0.95876600	1.51356700
C	3.76244900	1.77354400	1.94421600
H	3.10811800	-1.00966000	-0.65271100
H	5.82051900	1.09979100	1.90273600
H	3.94927100	2.55831000	2.67754400
H	1.69148100	2.24914300	1.80688100
H	5.35387200	-0.68806300	0.22309700
Li	0.20083000	0.43458200	-0.10763500
O	-1.30891900	1.64280300	-0.38989100
C	-1.06637200	2.83452700	-1.23796400
C	-0.05484300	2.38665000	-2.29584800
H	0.17921300	3.21940500	-2.96857500
H	0.88392800	2.06072100	-1.83113100
H	-0.45879900	1.56457100	-2.89754700
C	-2.38015200	3.27072500	-1.89396300
H	-2.81409300	2.45836800	-2.48707200
H	-3.11968600	3.59688500	-1.15237600
H	-2.19527300	4.11867700	-2.56263000
C	-0.48204900	3.93984400	-0.35281500
H	0.44568500	3.60288300	0.12014800

H	-0.25441600	4.82480300	-0.95841100
H	-1.18752400	4.24088100	0.42943300
I	0.25634000	-2.19709700	-1.82427400

TS5

0 1

Si	-2.85372500	0.64940100	0.84628400
H	-3.96407400	-0.00503700	0.11024700
H	-3.39789100	1.74938900	1.68182800
C	-1.92196100	-0.62938300	1.83656800
H	2.00340700	-1.51845700	-1.34788900
C	-0.13900100	-1.24113400	3.39114600
C	-2.28922600	-1.98896600	1.76932300
C	-1.60135900	-2.95667000	2.50497700
C	-0.52432700	-2.58230600	3.31504600
C	-0.83602600	-0.27284600	2.66345900
H	0.70676000	-0.94689300	4.00615200
H	-3.11903100	-2.29571700	1.13582200
H	0.01737500	-3.33562000	3.88133500
H	-0.51869200	0.76499700	2.74120500
H	-1.89922800	-4.00010200	2.44102500
C	3.14455500	0.18888600	0.30376000
C	4.43478700	0.59236000	0.67669300
C	1.99013100	0.99863000	0.40413300
C	2.25730200	2.28571300	0.93947000
C	4.63364000	1.87591700	1.19507300
C	3.53153700	2.72681000	1.32675900
H	3.05791600	-0.83929600	-0.07916400
H	5.62769000	2.20572000	1.49074600
H	3.66634600	3.73114800	1.72880800
H	1.43573600	2.99842300	1.06759600
H	5.27859200	-0.08880400	0.56810100
Li	0.07697500	0.49865700	-0.03782700
O	-1.70362500	1.28388100	-0.22895500
C	-1.85986200	2.47632400	-1.09250700
C	-0.75011700	2.37411200	-2.14209200
H	-0.79147100	3.23604100	-2.81745200
H	0.24204700	2.36406000	-1.67451800
H	-0.86419900	1.46498200	-2.74325500
C	-3.23975200	2.44624900	-1.75817500
H	-3.37878100	1.52435100	-2.33322700
H	-4.05072900	2.52575300	-1.02375700
H	-3.33887600	3.29389800	-2.44533100
C	-1.68125100	3.72616200	-0.22381800
H	-0.70478000	3.71437000	0.27082700
H	-1.73732700	4.62734600	-0.84535800
H	-2.46042300	3.79823900	0.54269900
I	0.57821600	-1.99899200	-2.01732400

Product2

0 1

Si	1.16119900	0.04694300	2.35069000
H	0.56173900	-1.01279700	3.19233300
H	1.88958700	1.02118000	3.20190800
C	2.32756200	-0.66420900	1.07680600
H	0.34458800	-0.47745800	-2.50474300
C	4.43339000	-0.53005100	-0.15492600
C	2.04761500	-1.87615300	0.41328000
C	2.94019200	-2.39956500	-0.52696100
C	4.13323200	-1.72881300	-0.81057000
C	3.53694500	-0.00404500	0.77819600
H	5.36494100	-0.01062900	-0.36646000
H	1.12357600	-2.41316800	0.61678600
H	4.83013100	-2.14079800	-1.53636300
H	3.78715300	0.92668400	1.28408100
H	2.70221300	-3.33182500	-1.03246200
C	1.29545400	1.45259000	-2.25165000
C	1.12464600	2.83986200	-2.31158000
C	0.21380800	0.60268800	-2.52040400
C	-1.04084700	1.14154500	-2.84018900
C	-0.12469100	3.37702800	-2.64038800
C	-1.20704600	2.52979200	-2.90237000
H	2.26624300	1.03131400	-2.00480300
H	-0.25423600	4.45530400	-2.69433600
H	-2.17656400	2.94882800	-3.15958200
H	-1.87526700	0.47449000	-3.03843300
H	1.96428300	3.50006300	-2.10880700
Li	-0.66577300	0.07682800	-0.15577700
O	-0.07173000	0.87074700	1.50536700
C	-1.05342000	1.79880200	2.11528800
C	-2.11854200	2.03100200	1.03974300
H	-2.87257900	2.73872600	1.40080200
H	-1.67409200	2.46073500	0.13319200
H	-2.63924200	1.09842700	0.78656800
C	-1.67696700	1.15063800	3.35550200
H	-2.12335400	0.18280700	3.10559900
H	-0.93873700	1.00113000	4.15237200
H	-2.46336000	1.80014200	3.75645300
C	-0.33611900	3.10971300	2.45433400
H	0.14355800	3.52658100	1.56228500
H	-1.05798600	3.84334400	2.83143500
H	0.42824300	2.96766900	3.22507900
I	-2.03750400	-2.06470500	-0.39495900

INT1(THF)

0 1

Si	-1.30337500	0.55992700	-1.07745500
H	-1.28189200	0.57355700	-2.58271000
H	-2.18278600	1.78998700	-0.87516400
C	-2.60474100	-0.65671100	-0.33536600
H	-0.20441700	-0.65639800	-1.04813100
C	-4.86524200	-1.04792300	0.52870100
C	-2.35410200	-2.02953600	-0.16370800
C	-3.32944000	-2.90147600	0.33038300
C	-4.59168500	-2.41068300	0.67972700
C	-3.88032900	-0.18850600	0.03036600
H	-5.84345900	-0.65591500	0.80084600
H	-1.37346700	-2.42279300	-0.42929200
H	-5.35304200	-3.08326900	1.06917300
H	-4.10478700	0.87110600	-0.08118400
H	-3.10738200	-3.96106900	0.44503100
Li	1.20656000	-0.02108300	-0.28948500
O	0.09793900	1.40390000	-0.25782300
C	0.21308300	2.77120700	0.19894400
C	1.65212100	2.91567100	0.72178900
H	1.83785600	3.93038400	1.09396200

H	1.83426700	2.21714500	1.54936800
H	2.37632800	2.71366500	-0.07844000
C	-0.00865500	3.74446900	-0.96979500
H	0.68973900	3.52404300	-1.78612000
H	-1.02685800	3.66363700	-1.35838600
H	0.15801300	4.77976200	-0.64599700
C	-0.77772100	3.03733800	1.34373900
H	-0.62137700	2.31847800	2.15708800
H	-0.63723600	4.04824400	1.74738100
H	-1.80960700	2.94294100	0.99755000
C	4.10752600	-0.34915000	0.51643400
O	2.86521000	-0.89165200	-0.01155000
C	3.04836000	-2.28373800	-0.40371700
C	4.56084700	-2.49487800	-0.43456100
C	5.04247900	-1.54896100	0.67845400
H	4.49454900	0.37900000	-0.20652200
H	3.88154400	0.16527700	1.45465500
H	2.56027900	-2.91751700	0.34652200
H	2.55321100	-2.42562300	-1.36772000
H	4.83566400	-3.53949000	-0.25991100
H	4.97217900	-2.19088400	-1.40445600
H	4.90487300	-2.01339200	1.66210700
H	6.09518500	-1.26732600	0.57982300

TS4(THF)

0 1

Si	-1.12748800	0.24930100	-1.24112700
H	-0.41167100	-0.46599000	-2.31386400
H	-1.76132200	1.44078300	-1.88913500
C	-2.59720200	-0.63741400	-0.46648300
H	0.40736000	-1.82823100	-0.15576400
C	-5.02282200	-0.66188700	-0.12876700
C	-2.52163700	-1.86549700	0.21975200
C	-3.67320700	-2.47767800	0.72129900
C	-4.92551900	-1.87839000	0.55142600
C	-3.86930600	-0.05209900	-0.63130700
H	-5.99226600	-0.18882000	-0.26897200
H	-1.54354000	-2.32368300	0.34827700
H	-5.81971900	-2.35675100	0.94516900
H	-3.96604900	0.89297400	-1.16274200
H	-3.59215400	-3.42704300	1.24639000
Li	1.27995200	-0.45051800	0.22901200
O	0.03894000	0.94571400	-0.18251800
C	0.01440100	2.29093000	0.39431700
C	1.06536700	2.27684200	1.51140600
H	1.12871500	3.25959000	1.99243200
H	0.80430900	1.54043200	2.28076400
H	2.05820200	2.03206700	1.11646700
C	0.39735200	3.30842100	-0.68843100
H	1.37748000	3.06421100	-1.11394100
H	-0.33686000	3.31810200	-1.49958100
H	0.44930700	4.31847300	-0.26415200
C	-1.36790600	2.59663200	0.98598400
H	-1.65426200	1.83191100	1.71561700
H	-1.35109900	3.56869300	1.49311000
H	-2.13901600	2.63893400	0.21103200
C	4.19017500	0.09162900	-0.38500100
O	3.20108800	-0.54240600	0.46678900
C	3.62609500	-1.89446400	0.80518800
C	4.65688000	-2.25826200	-0.25857400
C	5.34832600	-0.90713800	-0.51079500
H	3.72070400	0.29673300	-1.35487700
H	4.48436400	1.04116900	0.07465400
H	4.06398900	-1.87650000	1.81235500
H	2.72785700	-2.51805700	0.79687400
H	5.34871700	-3.03678700	0.07832500
H	4.15214900	-2.61312800	-1.16472600
H	6.10604900	-0.71681900	0.25885600
H	5.83752400	-0.84712800	-1.48807200

INT2(THF)

0 1

Si	-0.96154100	0.08603500	-1.24417200
H	-0.07040900	-0.94575600	-1.82378400
H	-1.37169700	1.04704100	-2.30508600
C	-2.51460700	-0.63904700	-0.49773600
H	0.71454200	-1.81944900	1.48326200
C	-4.94561500	-0.87384100	-0.53165800
C	-2.46257400	-1.54257900	0.58414900
C	-3.63785200	-2.09664700	1.09804300
C	-4.87841000	-1.76489600	0.54319000
C	-3.77122600	-0.31605500	-1.04525800
H	-5.90747300	-0.61288000	-0.96693100
H	-1.49798000	-1.80523000	1.02264300
H	-5.79017400	-2.19977600	0.94647200
H	-3.83920000	0.37941800	-1.88065000
H	-3.58251900	-2.79066900	1.93342800
Li	1.29949600	-0.42966900	0.71733800
O	0.07661500	0.86823200	-0.15005200
C	-0.06169800	2.21070100	0.42715000
C	0.85828600	2.22722200	1.65309900
H	0.82495000	3.20683000	2.14278900
H	0.54381300	1.47209200	2.38358900
H	1.89802500	2.03085500	1.36553800
C	0.40387300	3.23189100	-0.61779300
H	1.43151000	3.01771400	-0.93136300
H	-0.23826000	3.21459700	-1.50496300
H	0.37556000	4.24533400	-0.20026200
C	-1.51295500	2.46768000	0.84870500
H	-1.85882300	1.70166800	1.54935800
H	-1.58863900	3.44520700	1.33918600
H	-2.19061700	2.47856900	-0.01245200
C	3.81064000	-0.16576300	-0.95343900
O	3.21138800	-0.30615800	0.36011000
C	3.95173000	-1.28709800	1.14287000
C	4.68043000	-2.13729000	0.10772600
C	5.03168500	-1.09773400	-0.97057500
H	3.06137400	-0.45779400	-1.69909500
H	4.06910500	0.88762800	-1.10710500
H	4.65184100	-0.75085100	1.79846200
H	3.21299600	-1.82931900	1.73968900
H	5.56112400	-2.63851300	0.52201000
H	4.00351300	-2.90158900	-0.29183800
H	5.93816700	-0.54841500	-0.68891900
H	5.19808600	-1.53805300	-1.95887800

INT3(THF)

0 1

Si	-3.82983300	-0.06523900	-1.62137800
H	-5.18938600	0.51469700	-1.46835300
H	-3.81652200	-0.94557900	-2.81697500
C	-2.59388800	1.33241000	-1.75104200
H	-0.33170100	-1.52729700	0.46469100
C	-0.29671900	2.14760000	-1.91676600
C	-3.04025100	2.66741100	-1.81519300
C	-2.13442100	3.72444500	-1.93961400
C	-0.76096800	3.46437600	-1.98795400
C	-1.20578400	1.09088300	-1.81043300
H	0.76866100	1.93581300	-1.94206500
H	-4.10539000	2.88623100	-1.76841600
H	-0.05451000	4.28576600	-2.07989800
H	-0.81587800	0.07520500	-1.76247700
H	-2.49863300	4.74749800	-1.99515400
C	4.75675600	-0.93497900	-1.46142100
C	6.10579400	-0.63996000	-1.69090200
C	4.14229500	-0.54836900	-0.26617200
C	4.89047300	0.13177600	0.69970900
C	6.85160300	0.04239500	-0.72537100
C	6.23972800	0.42703700	0.47115700
H	4.18750000	-1.46895300	-2.21858900
H	7.89980900	0.27068900	-0.90283000
H	6.81218200	0.95604700	1.23062500
H	4.42646000	0.43341800	1.63597300
H	6.57297600	-0.94624100	-2.62475300
Li	-1.68606900	-0.49382300	0.67292100
O	-3.39501200	-0.96153900	-0.25496600
C	-3.88220900	-2.31958900	0.08067400
C	-3.12712500	-3.33337700	-0.78507700
H	-3.40572400	-4.35379700	-0.49592700
H	-3.36400500	-3.21006700	-1.84747300
H	-2.04765000	-3.21167800	-0.64566000
C	-3.54654600	-2.51856400	1.56171300
H	-2.46059600	-2.50426600	1.71786300
H	-4.01334200	-1.73905600	2.17456300
H	-3.91502300	-3.49234000	1.90365900
C	-5.39656800	-2.38700500	-0.14251500
H	-5.66110100	-2.24334200	-1.19730600
H	-5.77152100	-3.37306300	0.15400800
H	-5.91771800	-1.63014600	0.45436200
I	2.00763000	-1.01772400	0.08897100
C	-1.78630500	2.21729900	2.05219700
O	-1.62834500	0.78097400	2.12740500
C	-0.72820400	0.43656400	3.22584500
C	-0.33472900	1.76670900	3.88216000
C	-0.55423900	2.78616200	2.75133200
H	-1.86957800	2.49088400	0.99759300
H	-2.71366700	2.50017700	2.57074000
H	-1.26304500	-0.23685400	3.90348800
H	0.12277900	-0.09428800	2.78966900
H	-0.99233100	1.99218800	4.73050500
H	0.69599900	1.75027600	4.24898100
H	-0.71294700	3.80632000	3.11568700
H	0.30008000	2.79111900	2.06504200

TS1(THF)

0 1

Si	-0.55938500	-2.06972900	2.22303200
H	-1.59251100	-3.03039800	2.68082900
H	0.41856700	-1.82576800	3.31138400
C	0.24628100	-2.76080900	0.68627700
H	-1.66320400	3.27878600	-1.07424600
C	2.07953500	-2.86742400	-0.92264100
C	-0.36148600	-3.84535400	0.01839400
C	0.24047900	-4.43421100	-1.09557400
C	1.46408600	-3.94451600	-1.56606200
C	1.48025800	-2.28353300	0.19826700
H	3.02816100	-2.47805600	-1.28039500
H	-1.30938700	-4.24124300	0.37763700
H	1.93791200	-4.40517000	-2.42967900
H	1.98746400	-1.45484800	0.68672500
H	-0.23824900	-5.27570900	-1.59062500
C	2.62119800	1.26405800	1.33290100
C	3.85792400	0.68909700	1.66542600
C	2.19550100	1.39459200	0.00106000
C	3.07504700	0.94128500	-0.99505800
C	4.71215300	0.23735900	0.65313900
C	4.31801900	0.36983000	-0.68365000
H	1.98670500	1.62410300	2.14499000
H	5.67618500	-0.20120900	0.90195500
H	4.98460900	0.03769300	-1.47969900
H	2.79900900	1.03828800	-2.04730200
H	4.16052700	0.60264200	2.70879200
Li	-0.85012100	0.05711200	0.00238300
O	-1.29610300	-0.59532700	1.79287200
C	-2.02773800	0.29859000	2.72845700
C	-1.01124600	1.24788400	3.36880300
H	-1.52207900	1.94665600	4.04169900
H	-0.26808500	0.69545200	3.95402800
H	-0.49033400	1.83079800	2.60365100
C	-3.04198300	1.06154400	1.87200100
H	-2.55078500	1.67351300	1.10702400
H	-3.73704200	0.36727000	1.38598600
H	-3.62625600	1.74254500	2.50090100
C	-2.75691000	-0.53163800	3.79133600
H	-2.06039000	-1.08079300	4.43610600
H	-3.33570200	0.13761500	4.43737700
H	-3.45056700	-1.24616900	3.33560900
I	0.04656300	2.53618400	-0.61962900
C	-1.01041300	-0.87086000	-2.74610500
O	-1.78828200	-0.54137300	-1.55938000
C	-3.03522800	0.11022800	-1.94484500
C	-3.14270500	-0.07036400	-3.45980800
C	-1.66673400	-0.10078800	-3.89078300
H	0.02762200	-0.58034000	-2.56163100
H	-1.05948100	-1.95661100	-2.88974300
H	-3.84461200	-0.36813000	-1.38496800
H	-2.96683200	1.16885700	-1.66704600
H	-3.63657900	-1.01873900	-3.70497700
H	-3.70822900	0.74124200	-3.92760400
H	-1.51069800	-0.58759500	-4.85880300
H	-1.26300000	0.91621600	-3.94436300

INT4(THF)

0 1

Si	2.55946100	1.81292200	-1.13835500
H	3.46444100	2.91555300	-0.72734200
H	2.42920800	1.80501000	-2.61701400
C	3.28766900	0.21197500	-0.50474600
H	-4.87423800	0.38924200	0.84997100
C	3.60181500	-2.20517800	-0.62876600
C	4.23093900	0.24866100	0.54282000
C	4.84921400	-0.91799500	0.99880300
C	4.53427900	-2.14745700	0.41080400
C	2.98625800	-1.03620000	-1.08531100
H	3.34961200	-3.15763500	-1.08732500
H	4.49437500	1.19969600	1.00218700
H	5.01799200	-3.05693900	0.75953300
H	2.25758800	-1.10564300	-1.88829200
H	5.57914200	-0.86770800	1.80339800
C	-0.55553700	-0.89194800	-2.56628000
C	-0.59153000	-1.92496400	-3.51472400
C	-0.61813600	-1.10058600	-1.16457400
C	-0.75208500	-2.46494500	-0.80223700
C	-0.70424700	-3.25405900	-3.09391700
C	-0.79047400	-3.52158900	-1.72413900
H	-0.47165200	0.12594800	-2.95585600
H	-0.73501800	-4.06436500	-3.81999300
H	-0.89318900	-4.55011300	-1.37713800
H	-0.83959100	-2.73493500	0.25437400
H	-0.53435900	-1.69535100	-4.57900500
Li	0.09338900	0.32857400	0.17325400
O	1.03156400	2.04956800	-0.43820200
C	0.15958100	3.22110200	-0.65493800
C	-0.68482500	2.96939200	-1.90875500
H	-1.37734500	3.80373400	-2.07198100
H	-0.05217300	2.87622200	-2.79811600
H	-1.27170700	2.05180800	-1.80603100
C	-0.72179800	3.31596800	0.59376400
H	-1.34455400	2.42247200	0.71192100
H	-0.10583900	3.44118100	1.49095200
H	-1.39834200	4.17462700	0.51604600
C	0.99432600	4.49945900	-0.80183900
H	1.62225900	4.48005200	-1.70007000
H	0.32451600	5.36191800	-0.89220900
H	1.63827500	4.65894700	0.06966200
I	-3.43585700	-0.10847400	0.16900700
C	0.97134400	-1.28296900	2.45063100
O	0.35104500	-0.02330000	2.08186200
C	-0.43455900	0.48587000	3.19119700
C	-0.24474600	-0.51101100	4.34304700
C	0.12960600	-1.80997500	3.60914700
H	0.97219200	-1.92081900	1.56424300
H	2.00843500	-1.08790200	2.75346000
H	-0.07970100	1.49367300	3.43173100
H	-1.47811900	0.54166800	2.86225500
H	0.57587200	-0.19410300	4.99796700
H	-1.14702100	-0.60642200	4.95505400
H	0.68039900	-2.51582400	4.23915900
H	-0.76710500	-2.31297700	3.22910200

INT2 4-fluoroiodobenzene

0 1

Si	3.66559100	0.69794900	1.24325500
H	5.09052900	0.94121100	0.90540200
H	3.50749200	0.56401300	2.71150500
C	2.53811000	2.03476000	0.58857300
H	1.14102700	-0.81885000	-2.31599500
C	0.67073700	3.57611100	0.90301100
C	2.65774800	2.49849500	-0.73885000
C	1.79592400	3.47741700	-1.23903600
C	0.80347400	4.01744700	-0.41662000
C	1.52860600	2.59228600	1.39922100
H	-0.10393600	3.99204600	1.54175900
H	3.43182000	2.09785100	-1.39144200
H	0.13118600	4.77791900	-0.80520400
H	1.40932200	2.25514500	2.42676600
H	1.89729800	3.81367100	-2.26724100
C	-3.45303800	-1.47850300	0.66432400
C	-4.66682800	-1.36274300	1.35263200
C	-3.03687700	-0.47858200	-0.21884200
C	-3.84551000	0.64373200	-0.41828600
C	-5.44573900	-0.23408900	1.13357500
C	-5.06289300	0.77586900	0.26057500
H	-2.83726500	-2.35971800	0.82501100
H	-5.70522600	1.63970500	0.11635900
H	-3.53648300	1.42697200	-1.10557500
H	-5.00704700	-2.13022100	2.04171900
Li	1.69414400	-0.34032600	-0.79198600
O	3.12476700	-0.69960100	0.44762300
C	3.78896300	-2.02457300	0.38981500
C	2.67331300	-3.03256600	0.10506300
H	3.09157300	-4.04251800	0.02803400
H	1.93218400	-3.02931100	0.91208900
H	2.16571800	-2.80572900	-0.84058700
C	4.80465500	-1.98397500	-0.75603400
H	4.30627500	-1.73930800	-1.70015100
H	5.58833900	-1.24123200	-0.56880700
H	5.28753700	-2.96164400	-0.86804000
C	4.46088900	-2.32090700	1.73363100
H	3.73345500	-2.30143500	2.55238600
H	4.91341100	-3.31828600	1.70773400
H	5.26265800	-1.60641800	1.95728200
I	-1.10755300	-0.66963900	-1.30438800
F	-6.62973100	-0.11306300	1.80027000

INT3 4-fluoroiodobenzene

0 1

Si	3.66559100	0.69794900	1.24325500
H	5.09052900	0.94121100	0.90540200
H	3.50749200	0.56401300	2.71150500
C	2.53811000	2.03476000	0.58857300
H	1.14102700	-0.81885000	-2.31599500
C	0.67073700	3.57611100	0.90301100
C	2.65774800	2.49849500	-0.73885000
C	1.79592400	3.47741700	-1.23903600
C	0.80347400	4.01744700	-0.41662000
C	1.52860600	2.59228600	1.39922100
H	-0.10393600	3.99204600	1.54175900

H	3.43182000	2.09785100	-1.39144200
H	0.13118600	4.77791900	-0.80520400
H	1.40932200	2.25514500	2.42676600
H	1.89729800	3.81367100	-2.26724100
C	-3.45303800	-1.47850300	0.66432400
C	-4.66682800	-1.36274300	1.35263200
C	-3.03687700	-0.47858200	-0.21884200
C	-3.84551000	0.64373200	-0.41828600
C	-5.44573900	-0.23408900	1.13357500
C	-5.06289300	0.77586900	0.26057500
H	-2.83726500	-2.35971800	0.82501100
H	-5.70522600	1.63970500	0.11635900
H	-3.53648300	1.42697200	-1.10557500
H	-5.00704700	-2.13022100	2.04171900
Li	1.69414400	-0.34032600	-0.79198600
O	3.12476700	-0.69960100	0.44762300
C	3.78896300	-2.02457300	0.38981500
C	2.67331300	-3.03256600	0.10506300
H	3.09157300	-4.04251800	0.02803400
H	1.93218400	-3.02931100	0.91208900
H	2.16571800	-2.80572900	-0.84058700
C	4.80465500	-1.98397500	-0.75603400
H	4.30627500	-1.73930800	-1.70015100
H	5.58833900	-1.24123200	-0.56880700
H	5.28753700	-2.96164400	-0.86804000
C	4.46088900	-2.32090700	1.73363100
H	3.73345500	-2.30143500	2.55238600
H	4.91341100	-3.31828600	1.70773400
H	5.26265800	-1.60641800	1.95728200
I	-1.10755300	-0.66963900	-1.30438800
F	-6.62973100	-0.11306300	1.80027000

TS1 4-Fluoroiodobenzene
0 1

Si	2.88552500	2.07079400	0.36837900
H	3.94614100	2.41763600	-0.60858800
H	3.15499700	2.70976100	1.67733300
C	1.19299200	2.48171700	-0.31015400
H	1.34972200	-2.80498500	-1.65159500
C	-1.23638900	2.58200600	-0.02127900
C	1.01973100	2.86686900	-1.65645600
C	-0.25492200	3.11549600	-2.17180900
C	-1.38138600	2.96758000	-1.35689100
C	0.04066500	2.35339600	0.49908200
H	-2.11113000	2.44432900	0.60690700
H	1.88524900	2.97445600	-2.30682300
H	-2.37394900	3.14027700	-1.76304500
H	0.13515700	2.07823900	1.54923300
H	-0.36955000	3.41263100	-3.21088900
C	-2.39479600	-0.87012200	1.46522400
C	-3.46936200	-0.20015500	2.07489100
C	-2.30040500	-1.02649600	0.07509700
C	-3.34275700	-0.49822100	-0.70039900
C	-4.46840400	0.30960500	1.25561600
C	-4.43513600	0.17191900	-0.12722200
H	-1.62166000	-1.28455300	2.11602300
H	-5.24807800	0.57340500	-0.72776800
H	-3.32211200	-0.60212600	-1.78605100
H	-3.54450500	-0.08530800	3.15368900
Li	1.03272600	-0.08925400	-0.11274000
O	2.75225800	0.38585100	0.56027100
C	3.82327400	-0.58703500	0.90661700
C	3.12992000	-1.71575100	1.67131400
H	3.86287900	-2.47829900	1.95701700
H	2.65821000	-1.33585100	2.58466800
H	2.36922300	-2.20592000	1.05384900
C	4.42401200	-1.08864900	-0.40940200
H	3.66001800	-1.57435700	-1.02728500
H	4.87190500	-0.26590400	-0.97867800
H	5.21038800	-1.82480400	-0.20654500
C	4.87403200	0.09914100	1.78429600
H	4.43217400	0.48889300	2.70777300
H	5.64773900	-0.62497300	2.06144800
H	5.37588700	0.92076600	1.25788100
I	-0.32240700	-2.11993800	-0.94528000
F	-5.52457300	0.96726800	1.82987700

INT4 4-Fluoroiodobenzene
0 1

Si	3.18067800	0.85214900	-0.76095800
H	4.32693200	0.74419600	0.17398300
H	3.56064200	1.67063700	-1.93901500
C	2.59948000	-0.85144700	-1.25435500
H	0.07740600	-2.31107800	3.32378800
C	1.33306600	-2.32090900	-2.73888300
C	3.01036200	-1.98814800	-0.52915800
C	2.59164700	-3.26782500	-0.89993700
C	1.75172400	-3.43416400	-2.00439500
C	1.75569600	-1.04236100	-2.36837600
H	0.67939400	-2.44763700	-3.59769700
H	3.66472300	-1.87454500	0.33277600
H	1.42218800	-4.42923100	-2.29175900
H	1.42535800	-0.18872000	-2.95743700
H	2.91750500	-4.13244900	-0.32757800
C	-2.73604300	1.24776100	0.26160900
C	-4.03555700	1.39417300	-0.24869000
C	-1.74309900	0.42292000	-0.32086300
C	-2.17899800	-0.27596000	-1.47418700
C	-4.36984400	0.68146900	-1.39124200
C	-3.46597700	-0.16106400	-2.02275400
H	-2.50873000	1.81161700	1.16969300
H	-3.76871400	-0.70940900	-2.91185600
H	-1.49334800	-0.95602800	-1.98513800
H	-4.77458000	2.03683400	0.22388400
Li	0.25144400	0.47404600	0.09372600
O	1.85258400	1.57180200	0.01571300
C	1.71218700	3.00313000	0.37726300
C	0.67801200	3.04330400	1.50447400
H	0.52940100	4.07499600	1.84215800
H	-0.29259900	2.66479800	1.16501100
H	1.01179900	2.44747800	2.36121400
C	3.05905700	3.54783700	0.86242800
H	3.43063400	2.97673200	1.72006400
H	3.81830100	3.52865600	0.07124800
H	2.94307900	4.59152000	1.17454300
C	1.20984700	3.75249700	-0.86081100

H	0.26550900	3.32387800	-1.21248600
H	1.03713500	4.80772900	-0.61932400
H	1.93976300	3.70959200	-1.67668600
I	-0.69149700	-1.45394100	2.11393400
F	-5.63292600	0.80949100	-1.90934300

INT5 4-fluoroiodobenzene
0 1

Si	-3.05807900	-0.17942000	-0.25064800
H	-4.15923300	-0.34135800	0.72917200
H	-3.54036900	-0.48839000	-1.62016800
C	-2.32503700	1.53432900	-0.13053200
C	-0.92689600	3.31629900	-1.04899900
C	-2.53627500	2.33141200	1.01351100
C	-1.95614300	3.59703700	1.12470800
C	-1.14935900	4.08838600	0.09414800
C	-1.51297800	2.05327700	-1.16101100
H	-0.29471000	3.69286500	-1.84826800
H	-3.16302300	1.96348600	1.82357700
H	-0.69147500	5.06991800	0.18348500
H	-1.33603500	1.47042600	-2.06345200
H	-2.13015000	4.19718400	2.01401400
C	2.56245000	-0.00579700	-1.03113200
C	3.95989100	0.03921300	-1.16693900
C	1.88407100	-0.12532800	0.20790600
C	2.75198700	-0.19809800	1.32632200
C	4.72767200	-0.03765200	-0.01415200
C	4.15346000	-0.15650800	1.24317100
H	1.98821700	0.05903800	-1.96006100
H	4.78834200	-0.21364000	2.12451900
H	2.33275800	-0.29144300	2.33183500
H	4.44632000	0.13133300	-2.13550900
Li	-0.11400900	-0.16361500	0.33511800
O	-1.75095400	-1.18641900	0.14115200
C	-1.66808400	-2.66269100	0.02836300
C	-0.62011300	-3.09678400	1.05536600
H	-0.48108100	-4.18303000	1.01411400
H	0.34896800	-2.62433600	0.85532200
H	-0.93878000	-2.83129800	2.06987300
C	-3.03315800	-3.27941800	0.34656100
H	-3.37122700	-2.99687100	1.34942900
H	-3.79797100	-2.97974000	-0.38074400
H	-2.96164300	-4.37199200	0.31009100
C	-1.21798000	-2.99195200	-1.39804900
H	-0.25124200	-2.52451600	-1.61334700
H	-1.10529600	-4.07554400	-1.51880700
H	-1.95014400	-2.64483000	-2.13594700
F	6.09660900	0.00471800	-0.12111900

TS2 4-fluoroiodobenzene
0 1

Si	1.07334800	0.04575600	1.07340000
H	2.33801500	0.52696300	1.73971900
H	0.39897900	-0.63694000	2.20264800
C	0.36673300	1.68848000	0.47209300
C	-1.38372400	3.39259400	0.46105300
C	1.16998300	2.56529200	-0.28027700
C	0.70240500	3.82149900	-0.67965800
C	-0.57663800	4.24019200	-0.30458800
C	-0.92016000	2.12822500	0.83244100
H	-2.37991200	3.71150700	0.75898000
H	2.18053800	2.27172800	-0.55770400
H	-0.94146000	5.21996900	-0.60384400
H	-1.57468500	1.47015800	1.39812000
H	1.33965800	4.47515700	-1.27133200
C	-1.89001700	-1.70787700	0.98151700
C	-3.27474000	-1.90196500	0.88293000
C	-1.12572800	-1.02961200	0.00730000
C	-1.86528300	-0.55933600	-1.10530800
C	-3.92557600	-1.40803700	-0.24120500
C	-3.25068300	-0.73602700	-1.25035900
H	-1.39707700	-2.08895300	1.87847300
H	-3.79825000	-0.35451900	-2.10845000
H	-1.36149300	0.01045200	-1.89214800
H	-3.84378400	-2.41860700	1.65184100
Li	0.46000700	-1.75065800	-0.93087500
O	1.85251400	-0.97323800	-0.12094200
C	3.26530500	-1.33802900	-0.23822900
C	3.31521400	-2.32257500	-1.41589900
H	4.34081500	-2.65844600	-1.60412900
H	2.71454200	-3.21906900	-1.20626000
H	2.94805800	-1.84860400	-2.33573400
C	4.11200100	-0.09991200	-0.55609500
H	3.74308100	0.39532700	-1.46144800
H	4.09003200	0.61723100	0.26842900
H	5.15535700	-0.39072800	-0.72732700
C	3.73570300	-2.02845700	1.04848900
H	3.10662600	-2.89770400	1.27339600
H	4.76984000	-2.37559400	0.93676600
H	3.69688300	-1.34450800	1.90055900
F	-5.27572600	-1.58825000	-0.35480300

INT6 4-fluoroiodobenzene
0 1

Si	-0.78984200	-0.26094500	-0.96362500
H	-2.18958600	-0.82623400	-1.16708500
H	-0.38324800	-0.27775200	-2.41685400
C	-1.49027300	1.43969600	-0.35821800
C	-1.34337700	3.86370000	-0.00208400
C	-2.83150000	1.51555200	0.06220400
C	-3.41760100	2.72119200	0.46287400
C	-2.67327800	3.90295100	0.42870400
C	-0.76357800	2.64739500	-0.37516000
H	-0.75790300	4.78004700	-0.04559800
H	-3.43562900	0.61021500	0.06388300
H	-3.12492900	4.84579400	0.72930600
H	0.27509300	2.64620100	-0.69754800
H	-4.45476200	2.73923500	0.79193100
C	2.18939500	-0.00341500	-1.35182600
C	3.53982500	0.21570400	-1.03597100
C	1.14477700	0.17121700	-0.42023100
C	1.54042100	0.57372600	0.87857200
C	3.85676300	0.61057500	0.25767200
C	2.88111400	0.79483500	1.23241900
H	1.93783200	-0.30468100	-2.36849900
H	3.16716900	1.12088100	2.22878400

H	0.77679700	0.75099200	1.63630200
H	4.33032400	0.08906500	-1.77065800
Li	1.29162600	-1.74536900	0.48213000
O	-0.40899900	-1.81906500	0.00722700
C	-1.23375800	-2.98720900	0.24277300
C	-0.34177600	-3.95393300	1.04471500
H	-0.86958500	-4.88349300	1.28718500
H	0.55112900	-4.23620400	0.46543500
H	-0.03025200	-3.50020000	1.99717200
C	-2.46626600	-2.61669500	1.08158200
H	-2.16098900	-2.11317700	2.00667700
H	-3.12578200	-1.94560800	0.52711700
H	-3.03340400	-3.51654300	1.35102100
C	-1.63526900	-3.64416100	-1.08661700
H	-0.74396300	-3.88983300	-1.67688200
H	-2.19128600	-4.57238300	-0.90398200
H	-2.26339200	-2.97407900	-1.67793500
F	5.16083700	0.82142400	0.58425700

TS5 4-fluoroiodobenzene
0 1

Si	-0.43348700	0.80767300	0.80215100
H	-0.97351500	2.22308600	0.73335500
H	-0.21337100	0.67980500	2.28338700
C	-2.16669900	0.08202200	0.29610600
C	-3.82789900	-1.72121000	0.17026100
C	-3.15145000	0.94882900	-0.21257300
C	-4.43750700	0.50360900	-0.53976300
C	-4.78107200	-0.83625800	-0.34511500
C	-2.54081700	-1.26614900	0.47084400
H	-4.08777500	-2.76509400	0.33563100
H	-2.90844600	2.00190500	-0.34536300
H	-5.78092900	-1.18848400	-0.58917800
H	-1.81785500	-1.97927200	0.86208200
H	-5.17043100	1.20198100	-0.93918000
C	1.42075800	-1.48652900	1.31749800
C	2.21902400	-2.60859300	1.03760000
C	0.55714200	-0.90489700	0.36483200
C	0.54338900	-1.51449300	-0.91116600
C	2.15865400	-3.15632100	-0.23818500
C	1.33313200	-2.63072700	-1.22778600
H	1.46507100	-1.05669600	2.31767500
H	1.30321800	-3.09569000	-2.20936500
H	-0.11919900	-1.12146900	-1.68125100
H	2.86813400	-3.05362400	1.78673500
Li	2.21936800	0.18598400	-0.39796800
O	1.14550300	1.53202100	-0.01128400
C	1.52556100	2.91381700	-0.19651100
C	2.96580700	2.87411600	-0.74362300
H	3.35887300	3.88095600	-0.92729200
H	3.64344400	2.38911100	-0.02490500
H	3.00480400	2.33418400	-1.70209400
C	0.60924100	3.59214300	-1.22810000
H	0.60815900	3.02513700	-2.16708700
H	-0.41792700	3.64660500	-0.86059900
H	0.95536800	4.61109500	-1.44319200
C	1.50957000	3.66441300	1.14455900
H	2.14921700	3.15444700	1.87494800
H	1.88157400	4.68911400	1.01868300
H	0.49724500	3.71187200	1.55272400
F	2.93111300	-4.23701700	-0.53054600

Product 1 4-fluoroiodobenzene
0 1

Si	1.32545400	1.69239500	1.46515000
H	1.00989900	1.05709900	2.77099000
H	1.91875200	3.03262900	1.72279500
C	2.51893200	0.69999200	0.41549000
C	4.70152600	0.47974300	-0.65888300
C	2.17445300	-0.57605000	-0.07759100
C	3.08094700	-1.30735900	-0.84941200
C	4.34431700	-0.78275400	-1.13978200
C	3.79460000	1.21367700	0.11129100
H	5.68214700	0.89287700	-0.88262800
H	1.19528900	-1.01079900	0.12783800
H	5.04762000	-1.35586600	-1.73924700
H	4.08667500	2.19601300	0.47776300
H	2.79620000	-2.28826000	-1.22124100
C	-1.55324100	1.95078000	1.30788600
C	-2.79137500	2.12822200	0.67701100
C	-0.34357400	1.92324900	0.58125700
C	-0.42427500	2.07753900	-0.81980200
C	-2.81199300	2.28635200	-0.70638700
C	-1.64992000	2.25541600	-1.47396200
H	-1.53922100	1.81066500	2.38595000
H	-1.71132200	2.36506600	-2.55226700
H	0.48152200	2.03774500	-1.41983300
H	-3.72161100	2.13781600	1.23644800
Li	-1.49265500	-0.10710800	-0.13057200
O	-1.24268900	-1.71154400	0.03687200
C	-1.43825800	-3.08052500	0.15504800
C	-2.67034900	-3.51122400	-0.67584800
H	-2.86221800	-4.59156000	-0.61396100
H	-3.56388600	-2.98279500	-0.31882900
H	-2.51857900	-3.24772200	-1.73032300
C	-0.19413300	-3.84069000	-0.36355600
H	-0.00348300	-3.57187100	-1.41035700
H	0.68836500	-3.56460000	0.22732300
H	-0.31693600	-4.93083400	-0.30414500
C	-1.67292300	-3.45190900	1.63846900
H	-2.55828300	-2.92651500	2.01892700
H	-1.82455900	-4.53090800	1.78157000
H	-0.81044600	-3.14124100	2.24131500
F	-4.00013400	2.46071500	-1.32675700

TS3 4-fluoroiodobenzene
0 1

Si	-2.09818200	2.07515600	1.05216000
H	-3.48783400	2.21001800	0.54917100
H	-1.76021100	3.24932000	1.89532300
C	-1.91760600	0.45459000	1.96353200
H	-1.54772600	-1.49607500	-3.17652800
C	-0.57902600	-1.12285500	3.26547800
C	-2.99563900	-0.45132500	2.03082500
C	-2.87283900	-1.66641500	2.70921700
C	-1.66240500	-2.00386700	3.32421000

C	-0.70879100	0.09850400	2.59793300
H	0.36731600	-1.38336600	3.73102200
H	-3.94052900	-0.20672200	1.55007400
H	-1.56388400	-2.95184800	3.84696800
H	0.14735300	0.76969800	2.57378400
H	-3.71659900	-2.35034500	2.75370700
C	2.86052100	-0.93328800	-0.70066900
C	4.23240800	-1.18962300	-0.54066900
C	2.14115100	0.04630400	0.02928200
C	2.94029600	0.75866300	0.95872400
C	4.93238100	-0.43927500	0.39381300
C	4.31420700	0.54014000	1.15785500
H	2.33953100	-1.54486400	-1.44150800
H	4.89393100	1.10887400	1.88149600
H	2.48777200	1.53942400	1.57914400
H	4.75062500	-1.95024000	-1.12036200
Li	0.16920900	0.40557200	-0.16354500
O	-0.99472100	1.97246500	-0.23259200
C	-0.55883600	3.07260800	-1.12391200
C	0.00558500	2.38886300	-2.37235300
H	0.35698100	3.14122900	-3.08728300
H	0.85913000	1.74851100	-2.11706900
H	-0.76539200	1.78506100	-2.86531500
C	-1.76416800	3.94743800	-1.48340700
H	-2.55623700	3.35420700	-1.95366400
H	-2.18034000	4.45286900	-0.60341200
H	-1.45829900	4.72644400	-2.19049200
C	0.52937500	3.87223400	-0.40031800
H	1.37020000	3.22284000	-0.13620300
H	0.90466700	4.67047600	-1.05140600
H	0.14234100	4.33851400	0.51248200
I	-1.29561300	-2.12571200	-1.68823900
F	6.27440800	-0.67289600	0.56784500

Product 2 4-fluoroiodobenzene

0 1

Si	1.25614100	1.06466200	2.22912100
H	2.48390800	0.33724400	2.62286100
H	0.76867400	1.88665600	3.36483600
C	1.54829000	2.16279200	0.74628000
H	-0.30748800	0.47741700	-2.40086200
C	1.22557400	4.30832900	-0.37786000
C	2.33643900	1.74112600	-0.34423200
C	2.55393100	2.58384100	-1.43843000
C	2.00135500	3.86756700	-1.45535700
C	1.00039800	3.46149700	0.71009400
H	0.80246200	5.30994300	-0.38364600
H	2.77738700	0.74651200	-0.35313200
H	2.17877200	4.52543100	-2.30260500
H	0.39844900	3.82038200	1.54286800
H	3.15876300	2.23629900	-2.27184600
C	-2.08706100	-0.70742300	-2.11470900
C	-3.40312800	-0.73496400	-1.64151100
C	-1.31746600	0.45916600	-1.99774700
C	-1.86544200	1.60229000	-1.39942600
C	-3.91693000	0.41713300	-1.05569200
C	-3.17864000	1.58796400	-0.91909600
H	-1.65458600	-1.59240000	-2.57239000
H	-3.62956100	2.45938600	-0.45470100
H	-1.27153200	2.50772300	-1.31270700
H	-4.02280200	-1.62230300	-1.72478500
Li	0.03540800	-0.61566700	-0.06433700
O	0.04700400	-0.05345600	1.78435000
C	-0.64870200	-0.98938600	2.70205800
C	-1.47611900	-1.90534800	1.79582000
H	-2.05586000	-2.61168100	2.39968400
H	-2.18938700	-1.32507800	1.19702600
H	-0.83286200	-2.49629800	1.13060100
C	0.38591600	-1.80131100	3.48697400
H	1.07016700	-2.31908400	2.80712900
H	0.97422900	-1.16750300	4.16062500
H	-0.12247900	-2.55166600	4.10302500
C	-1.56262200	-0.17831200	3.62594400
H	-2.25569900	0.43613900	3.04126700
H	-2.15154900	-0.85509200	4.25524100
H	-0.99158800	0.47939700	4.28904500
I	1.62216600	-2.26676800	-1.18961300
F	-5.19391300	0.39743200	-0.59068600

INT3 4-methoxyiodobenzene

0 1

Si	3.84974000	0.73464600	1.36645100
H	5.29833700	0.94361700	1.11628900
H	3.59932200	0.64734600	2.82586900
C	2.78999400	2.07405500	0.61109700
H	1.63106200	-0.82058500	-2.35634300
C	0.99903800	3.72241300	0.80257700
C	2.94116600	2.44060400	-0.74305100
C	2.13091300	3.42327200	-1.31683000
C	1.16149400	4.06622600	-0.54259900
C	1.80314400	2.73273600	1.37183600
H	0.24156200	4.21772800	1.40442600
H	3.69721600	1.95929900	-1.36139000
H	0.52985300	4.83023600	-0.98836400
H	1.65903100	2.47004600	2.41778600
H	2.25404900	3.68112600	-2.36507500
C	-3.13477600	-1.60930700	0.42239500
C	-4.36749600	-1.52403600	1.06638000
C	-2.69550300	-0.57660700	-0.41442000
C	-3.50765200	0.53964600	-0.59607800
C	-5.18343000	-0.39841900	0.88062000
C	-4.75203700	0.63808900	0.04508500
H	-2.51837200	-2.49172600	0.57453500
H	-5.36342500	1.51924900	-0.11871200
H	-3.18708400	1.35223200	-1.24322500
H	-4.71796800	-2.32162100	1.71581100
Li	2.00163900	-0.34575000	-0.78008000
O	3.33867700	-0.67525400	0.57554500
C	3.99858500	-2.00337700	0.57811000
C	2.89588300	-3.01150500	0.24687500
H	3.31153500	-4.02511400	0.21825000
H	2.10589900	-2.98589100	1.00561600
H	2.45081400	-2.80334300	-0.73389800
C	5.07788600	-1.98769700	-0.50863200
H	4.63459200	-1.75295700	-1.48234300

H	5.85616200	-1.24848600	-0.28783500
H	5.55775100	-2.97081800	-0.57913500
C	4.58989800	-2.27860200	1.96372200
H	3.81606200	-2.24004900	2.73813400
H	5.03678700	-3.27871700	1.98219100
H	5.38171600	-1.56414300	2.22066700
I	-0.74235200	-0.72175500	-1.43811800
O	-6.37634600	-0.40909400	1.55610300
C	-7.25439400	0.69460600	1.39502800
H	-8.12939800	0.47070200	2.00819900
H	-6.79355300	1.62820000	1.74530500
H	-7.56350200	0.81113600	0.34754100

TS1 4-methoxyiodobenzene

0 1

Si	2.97259100	2.23286500	0.39419700
H	4.03331100	2.64958900	-0.55532600
H	3.16428000	2.89449600	1.70590900
C	1.27821800	2.52688000	-0.33750400
H	1.88578800	-2.83851100	-1.51033100
C	-1.16027600	2.41284700	-0.14353100
C	1.12393200	2.93420900	-1.67932000
C	-0.14693400	3.09045900	-2.23831200
C	-1.28654700	2.82374300	-1.47341400
C	0.11150400	2.28008100	0.42165400
H	-2.04213200	2.17663300	0.44428300
H	2.00123800	3.13024100	-2.29212500
H	-2.27405600	2.92096000	-1.91553600
H	0.18848800	1.98516400	1.46806200
H	-0.24712000	3.40593900	-3.27354200
C	-2.10181400	-1.00112200	1.36468100
C	-3.24326900	-0.38955300	1.89436600
C	-1.93794200	-1.21996200	-0.01285200
C	-2.98485100	-0.80748300	-0.84145800
C	-4.27702300	0.01431700	1.03716400
C	-4.15016100	-0.19721700	-0.34157800
H	-1.32770200	-1.32427700	2.06484300
H	-4.94096100	0.09414800	-1.02719000
H	-2.91830400	-0.95701000	-1.92040700
H	-3.36339000	-0.23343300	2.96457800
Li	1.27978500	-0.06399800	-0.11284300
O	2.94985900	0.54451800	0.59447800
C	4.08215800	-0.34501700	0.97339000
C	3.46017900	-1.51221700	1.74144200
H	4.24364200	-2.21152900	2.05410400
H	2.94165700	-1.15641200	2.63901700
H	2.75421200	-2.06912900	1.11607600
C	4.74100500	-0.81770400	-0.32523100
H	4.02575500	-1.36861000	-0.94689200
H	5.13629800	0.02849000	-0.89927300
H	5.57634500	-1.49065100	-0.09917000
C	5.06398400	0.42650500	1.86013700
H	4.57826600	0.79234400	2.77129300
H	5.88342800	-0.23592600	2.15938300
H	5.51376300	1.27693600	1.33237600
I	0.12788500	-2.22555600	-0.89923900
O	-5.36642100	0.60133600	1.64236700
C	-6.47231900	0.95959900	0.83200100
H	-7.22115400	1.37174300	1.51200200
H	-6.19988400	1.72220700	0.08841000
H	-6.89186300	0.08596300	0.31433000

INT4 4-methoxyiodobenzene

0 1

Si	3.18924100	1.17878600	-1.10821000
H	4.50972000	1.19383400	-0.43228600
H	3.22201400	2.06910000	-2.29558600
C	2.73044900	-0.57441100	-1.55528900
H	0.89487000	-2.64601000	3.10675400
C	1.29089400	-2.16873500	-2.71791300
C	3.49577400	-1.65811900	-1.08016600
C	3.16828600	-2.97307500	-1.41836500
C	2.06405900	-3.22863900	-2.23604600
C	1.62393400	-0.85394100	-2.38389200
H	0.42989100	-2.36444200	-3.35128600
H	4.35715500	-1.47481700	-0.44107300
H	1.80460600	-4.25175700	-2.49553000
H	1.01434900	-0.04249600	-2.77782900
H	3.77018100	-3.79611000	-1.04173200
C	-2.45032000	1.09448300	0.83082700
C	-3.80008400	1.23111100	0.49840700
C	-1.52249900	0.31470400	0.09179200
C	-2.10242400	-0.34369700	-1.01506900
C	-4.30942900	0.56514400	-0.62404800
C	-3.45433000	-0.23408900	-1.38897600
H	-2.11827200	1.62640200	1.72649100
H	-3.81892400	-0.77314300	-2.25919900
H	-1.48519100	-0.99528500	-1.63914400
H	-4.47617400	1.84096700	1.09432100
Li	0.50593000	0.44419600	0.21997900
O	1.96904100	1.70089800	-0.05107000
C	1.73463700	3.09286700	0.40539000
C	1.01462100	2.96867700	1.75000200
H	0.80852300	3.96380200	2.15971000
H	0.05407600	2.45374300	1.63892000
H	1.63002300	2.42089400	2.47216700
C	3.07436900	3.81532700	0.57890900
H	3.71837500	3.29099900	1.29324100
H	3.61191700	3.91752400	-0.37162200
H	2.89905100	4.82689800	0.96124400
C	0.85002100	3.78281400	-0.63761300
H	-0.08926400	3.23530300	-0.76838200
H	0.60994500	4.80226500	-0.31374300
H	1.35676500	3.84816800	-1.60703500
I	-0.06474700	-1.69582200	2.11148600
O	-5.64898700	0.75534000	-0.88442000
C	-6.21631000	0.08478900	-1.99555800
H	-7.27140200	0.36750800	-2.01012200
H	-5.74436300	0.39489200	-2.93863700
H	-6.13376900	-1.00643200	-1.89382300

INT5 4-methoxyiodobenzene

0 1

Si	-2.24097200	-0.07918100	-1.45232100
H	-3.61928200	-0.15946300	-1.99901500
H	-1.23313500	-0.27810800	-2.51701100

C	-2.02168100	1.55207000	-0.57334700
C	-0.61510100	3.14719900	0.62047800
C	-3.08643100	2.46960200	-0.48796800
C	-2.92193900	3.70645300	0.14158000
C	-1.68498800	4.04479000	0.69747800
C	-0.77858300	1.91300300	-0.01263800
H	0.34988500	3.40733100	1.04769300
H	-4.05581100	2.22140800	-0.91727100
H	-1.55393000	5.00665000	1.18726800
H	0.06929900	1.23081300	-0.06584600
H	-3.75502500	4.40292900	0.19685500
C	2.67727700	-1.12970300	-1.06112100
C	4.00383800	-0.66736000	-0.97415800
C	1.76265400	-1.15020700	0.01571100
C	2.31434900	-0.65025500	1.22601400
C	4.47967300	-0.18841400	0.24988200
C	3.62447900	-0.18101900	1.35902000
H	2.36359000	-1.49099500	-2.04470000
H	4.00490600	0.19138000	2.30844400
H	1.69795500	-0.61916500	2.12945800
H	4.63988700	-0.68766300	-1.85485700
Li	-0.11085200	-1.80392800	-0.14585100
O	-1.95666300	-1.43149900	-0.44412600
C	-2.92012500	-2.13101800	0.42384900
C	-2.06821500	-3.02851500	1.32891000
H	-2.70472400	-3.61261400	2.00179900
H	-1.48093000	-3.74426900	0.73821000
H	-1.38891700	-2.43438900	1.95333600
C	-3.70892600	-1.11859000	1.26013700
H	-3.03746200	-0.48581000	1.84912600
H	-4.32898300	-0.47127400	0.63016600
H	-4.37852800	-1.64647900	1.94873000
C	-3.84289300	-2.97508500	-0.46168500
H	-3.25872300	-3.66704400	-1.07812500
H	-4.53015500	-3.56296400	0.15754300
H	-4.44402000	-2.34544000	-1.12549400
O	5.75562700	0.29170000	0.46457100
C	6.65836000	0.29743300	-0.62609700
H	6.29601700	0.93086000	-1.44833000
H	7.59412600	0.70830900	-0.23971000
H	6.83793800	-0.71760200	-1.00804800

TS2 4-methoxyiodobenzene

0 1

Si	-1.39442400	-0.05820500	-1.07116800
H	-2.69380600	0.22914800	-1.77873100
H	-0.58581200	-0.65587300	-2.15771100
C	-0.95775300	1.67723000	-0.47084600
C	0.56560200	3.57708300	-0.27176800
C	-1.97202700	2.48656200	0.07606800
C	-1.72200500	3.80463500	0.47026800
C	-0.45009600	4.35497700	0.29252400
C	0.31608300	2.25155900	-0.63617600
H	1.55763800	3.99836100	-0.41748900
H	-2.97839300	2.08930800	0.19265300
H	-0.25255000	5.38283400	0.58802800
H	1.12616600	1.65258600	-1.04140900
H	-2.52105600	4.40311300	0.90247400
C	1.84193300	-1.31418000	-0.90010400
C	3.24210200	-1.27287300	-0.79354500
C	0.96121500	-0.83599800	0.08778400
C	1.61244300	-0.30698300	1.23364200
C	3.82556500	-0.73924400	0.36221400
C	3.00057700	-0.25432000	1.38590800
H	1.43482000	-1.72655300	-1.82668500
H	3.46360300	0.16856000	2.27480400
H	1.01860300	0.12399400	2.04701800
H	3.85520000	-1.65146400	-1.60619200
Li	-0.55476500	-1.75413600	0.94286600
O	-2.03496400	-1.17923100	0.11088100
C	-3.38144400	-1.74103100	0.21440100
C	-3.30363700	-2.72048100	1.39502200
H	-4.27255400	-3.19973600	1.57296200
H	-2.57823100	-3.52173100	1.19451300
H	-3.01800000	-2.19753100	2.31712400
C	-4.39852600	-0.63456500	0.51852800
H	-4.10762400	-0.08132700	1.41864000
H	-4.47597300	0.06931300	-0.31419100
H	-5.39034700	-1.07003800	0.68937300
C	-3.73639700	-2.49457700	-1.07386200
H	-2.98643000	-3.26442500	-1.28990100
H	-4.71072200	-2.98671600	-0.96899100
H	-3.78923500	-1.81426100	-1.92820600
O	5.17832000	-0.64462900	0.58310600
C	6.06055200	-1.10706000	-0.42712400
H	5.92402400	-0.55215400	-1.36532600
H	7.06864500	-0.93109400	-0.04598000
H	5.92629700	-2.18056600	-0.61851400

Product 1 4-methoxyiodobenzene

0 1

Si	1.85198300	-0.61314000	1.39157100
H	1.25973300	-1.97422500	1.33099300
H	2.06517600	-0.23638600	2.81438700
C	3.46862100	-0.63526800	0.43352600
C	5.57635300	0.41586800	-0.21599400
C	3.80172900	-1.73169300	-0.38396100
C	4.99760400	-1.75650100	-1.10873500
C	5.88641500	-0.68219200	-1.02529600
C	4.38011600	0.43671100	0.50404400
H	6.26716000	1.25244700	-0.14451400
H	3.12434700	-2.58040000	-0.45453900
H	6.81807800	-0.70024400	-1.58529600
H	4.15821200	1.29939600	1.13002500
H	5.23448600	-2.61402800	-1.73369400
C	-0.26581200	1.34604800	1.50194600
C	-1.19712500	2.26351400	0.99330700
C	0.63989500	0.65525100	0.67550100
C	0.57989900	0.93939900	-0.70948100
C	-1.22793400	2.52936500	-0.38592600
C	-0.33375300	1.84983400	-1.23617500
H	-0.26739700	1.16314200	2.57426300
H	-0.37790200	2.05003300	-2.30251000
H	1.25778200	0.43479400	-1.39400100
H	-1.88471600	2.75407100	1.67264800
Li	-1.64993800	-0.08601400	-0.01130500

O	-2.86327300	-1.16351200	-0.07753900
C	-3.86017100	-2.11898900	-0.15039700
C	-5.08505900	-1.54815200	-0.90580600
H	-5.90332000	-2.27710100	-0.99221400
H	-5.46565000	-0.66268900	-0.38055800
H	-4.78787600	-1.24015800	-1.91626100
C	-3.34070000	-3.36768300	-0.90405400
H	-3.02559200	-3.08582700	-1.91678900
H	-2.46864700	-3.78026200	-0.38089600
H	-4.10106300	-4.15744400	-0.98540700
C	-4.29743800	-2.53720600	1.27448400
H	-4.66624000	-1.66067300	1.82248400
H	-5.09074200	-3.29808600	1.26400000
H	-3.43756600	-2.94174900	1.82337500
O	-2.07452300	3.39777100	-0.98836000
C	-3.08182400	4.03977800	-0.20443200
H	-2.63392100	4.68672200	0.55973000
H	-3.65329900	4.64701500	-0.90701900
H	-3.74152500	3.30107400	0.26561700

TS3 4-methoxyiodobenzene

0 1

Si	-2.23341300	2.09869000	1.18200900
H	-3.65337200	2.29113900	0.79481600
H	-1.79080000	3.24793000	2.01137800
C	-2.04715900	0.45831500	2.05572600
H	-2.09224200	-1.45963700	-3.10225200
C	-0.67614800	-1.21694600	3.18996400
C	-3.16661400	-0.37890300	2.23788500
C	-3.04759700	-1.60787800	2.89156800
C	-1.80036400	-2.02864400	3.36539700
C	-0.80038600	0.01904900	2.54846900
H	0.29792000	-1.54232100	3.54436200
H	-4.14077800	-0.07064600	1.86388800
H	-1.70490900	-2.98794800	3.86780700
H	0.09036700	0.63291900	2.43174000
H	-3.92301900	-2.23846900	3.02476300
C	2.54122800	-0.94378200	-0.99263400
C	3.91290200	-1.20413100	-0.91907100
C	1.86355900	0.01693000	-0.19437900
C	2.72421400	0.69203200	0.70025300
C	4.70797800	-0.49545500	-0.00879200
C	4.11011700	0.46421000	0.81303000
H	1.97653100	-1.53342200	-1.72002500
H	4.69488900	1.03307700	1.53101800
H	2.31849000	1.45767600	1.37170900
H	4.38761000	-1.95043700	-1.55355600
Li	-0.10837300	0.39118200	-0.26311600
O	-1.24166700	1.98427800	-0.18888000
C	-0.84055500	3.09275100	-1.08662000
C	-0.39852500	2.42311400	-2.39086600
H	-0.08798800	3.18222000	-3.11761400
H	0.45701900	1.75769300	-2.21972900
H	-1.22309300	1.84913100	-2.83003700
C	-2.04044100	4.01405800	-1.33020100
H	-2.88695300	3.45886100	-1.74930700
H	-2.36904100	4.51086000	-0.40902000
H	-1.76431200	4.80028200	-2.04157400
C	0.32668600	3.83917400	-0.43279000
H	1.16075900	3.15495200	-0.24657700
H	0.67950900	4.63878800	-1.09481500
H	0.02533600	4.29746900	0.51571500
I	-1.74177100	-2.08948500	-1.63386300
O	6.05155700	-0.81357100	0.00018100
C	6.89440800	-0.12043100	0.90047200
H	7.89879700	-0.52078700	0.74225700
H	6.89943600	0.96080800	0.70035900
H	6.59765200	-0.28908500	1.94579400

Product 2 4-methoxyiodobenzene

0 1

Si	-1.03536400	-1.19428600	2.23226300
H	-2.47704100	-0.94794900	2.45408000
H	-0.39333500	-1.62758300	3.49985400
C	-0.75796600	-2.49633900	0.91997400
H	0.12836300	-0.17579300	-2.57821000
C	0.48721700	-4.43511000	0.10722200
C	-1.59017000	-2.58911500	-0.21398300
C	-1.38033900	-3.58168300	-1.17617000
C	-0.34396900	-4.50593400	-1.01589400
C	0.28083100	-3.43824200	1.06373200
H	1.28851700	-5.15819800	0.23966600
H	-2.40093400	-1.87798700	-0.35826400
H	-0.18717900	-5.28291700	-1.76021700
H	0.93116000	-3.40002500	1.93575200
H	-2.03032700	-3.63334100	-2.04581000
C	1.50425200	1.44695200	-2.18286100
C	2.73952800	1.81534200	-1.65746500
C	1.07854900	0.10784100	-2.13222900
C	1.90901700	-0.84944500	-1.54187900
C	3.57206500	0.84592900	-1.07145700
C	3.15348900	-0.49076100	-1.00801900
H	0.86334200	2.19670200	-2.63904900
H	3.77981800	-1.25282600	-0.55791100
H	1.59437100	-1.88881400	-1.49908300
H	3.08606400	2.84391400	-1.69655800
Li	-0.44294500	0.60969300	-0.21004300
O	-0.27887800	0.23576500	1.69240500
C	-0.02310000	1.43284000	2.52896600
C	0.34413300	2.54864400	1.54691900
H	0.58481900	3.46826300	2.09133600
H	1.22803500	2.27732400	0.95625800
H	-0.49210200	2.77546400	0.87301100
C	-1.28995200	1.80068900	3.30776600
H	-2.13491100	1.94620600	2.62736600
H	-1.55606600	1.02883300	4.03976800
H	-1.12718200	2.73262100	3.86112300
C	1.15303700	1.12510800	3.46121000
H	2.03187100	0.82108600	2.88248900
H	1.41505200	2.01733900	4.04157200
H	0.90981500	0.32578200	4.16847500
I	-2.67903300	1.32527900	-1.24139500
O	4.76226900	1.30601900	-0.58767200
C	5.68157000	0.37478200	-0.02845500
H	6.55505800	0.96084600	0.26155100
H	5.26207500	-0.11808400	0.85832900

H	5.97711700	-0.38299200	-0.76528800

INT3 1-Iodonaphthalene
0 1

Si	3.89794700	1.27862700	1.03887200
H	5.10373200	1.95495700	0.49749800
H	4.02195800	1.10946300	2.50665200
C	2.33142300	2.19944700	0.61253600
H	1.59301100	-1.00582500	-2.25318000
C	0.07344100	2.92028700	1.20195500
C	2.17829500	2.84065800	-0.63489200
C	0.99406500	3.50636700	-0.95988800
C	-0.05818000	3.54625800	-0.04091300
C	1.25719900	2.25392600	1.52439600
H	-0.74718500	2.94456800	1.91376300
H	2.99036800	2.82689300	-1.35985900
H	-0.98273700	4.05799700	-0.29447200
H	1.34465500	1.77231100	2.49622900
H	0.89224500	3.98843700	-1.92850300
Li	2.10879900	-0.31141800	-0.79955800
O	3.69930100	-0.22752500	0.28289500
C	4.70962400	-1.29980600	0.11168400
C	3.91360500	-2.60236600	0.00182000
H	4.59511900	-3.44713400	-0.14977600
H	3.33999500	-2.78494200	0.91750000
H	3.22146000	-2.57150300	-0.84873200
C	5.47733800	-1.00745100	-1.18108000
H	4.78929600	-0.95896700	-2.03191300
H	6.02245500	-0.05906200	-1.11357000
H	6.20644600	-1.80259700	-1.37552400
C	5.64020500	-1.33058200	1.32758400
H	5.07755500	-1.49223400	2.25334400
H	6.35788500	-2.15151500	1.22120800
H	6.21947000	-0.40396300	1.42415500
C	-2.49715300	-2.16454300	1.16521200
C	-2.43766900	-1.20515600	0.17702400
C	-3.52099100	-0.29424300	-0.01189700
C	-4.66788700	-0.40438100	0.85395400
C	-4.68996600	-1.40515700	1.86271100
C	-3.62835300	-2.26783800	2.01446600
H	-2.68359700	0.81207300	-1.67541500
H	-1.67179300	-2.85894000	1.30003500
C	-3.53783200	0.71900400	-1.01295000
C	-5.75868800	0.49262800	0.68000000
H	-5.56197000	-1.47923700	2.50903900
H	-3.65014200	-3.03582100	2.78441100
C	-5.73744100	1.45907100	-0.30137200
C	-4.61326200	1.57013800	-1.15616000
H	-6.61867700	0.39740900	1.34014500
H	-6.58084000	2.13414300	-0.42379000
H	-4.60080800	2.32980200	-1.93405700
I	-0.59880400	-1.14302300	-1.08658500

TS1 1-Iodonaphthalene
0 1

Si	3.22752000	2.16288500	0.15472500
H	4.05280400	2.60470700	-0.99555000
H	3.72135300	2.76998700	1.41265800
C	1.41291100	2.48621000	-0.14626400
H	1.59374000	-2.67975100	-1.66224800
C	-0.89801200	2.45830500	0.66159200
C	0.93054600	2.83405700	-1.42637300
C	-0.43805400	2.99776200	-1.65529100
C	-1.35194900	2.80229200	-0.61522900
C	0.47212800	2.31117300	0.89481800
H	-1.60804100	2.28361600	1.46438500
H	1.62773100	2.97571300	-2.24965700
H	-2.41788100	2.89540500	-0.80106000
H	0.80883200	2.05944600	1.90002000
H	-0.79306600	3.26015800	-2.64833500
Li	1.42876500	-0.07480000	-0.05295100
O	3.22645200	0.46616300	0.29001500
C	4.39329600	-0.45037700	0.38022400
C	3.90063800	-1.67349400	1.15601200
H	4.71374100	-2.39968400	1.26606900
H	3.56024900	-1.38858400	2.15810700
H	3.08200300	-2.17583700	0.62844200
C	4.79574400	-0.82169500	-1.04973000
H	3.96520400	-1.30927200	-1.57239800
H	5.10373600	0.06395800	-1.61745600
H	5.63963300	-1.52105300	-1.03263400
C	5.53351400	0.24672800	1.12757600
H	5.22368200	0.55335300	2.13246300
H	6.37860300	-0.44245800	1.23106000
H	5.89993600	1.12815700	0.58645700
C	-1.68034800	-1.16152800	2.00459200
C	-1.86144400	-1.13787100	0.63335000
C	-3.03044900	-0.49009900	0.12260600
C	-3.96913600	0.13787400	1.02060800
C	-3.72197800	0.08645900	2.42119300
C	-2.60198900	-0.55671400	2.90384600
H	-2.61916800	-0.90870100	-1.95927400
H	-0.80865900	-1.66374200	2.43033300
C	-3.31386200	-0.43094300	-1.27411900
C	-5.11899500	0.78764600	0.48874700
H	-4.43457400	0.55081700	3.10085600
H	-2.42478400	-0.60708300	3.97769600
C	-5.35209500	0.82270800	-0.87054800
C	-4.43920800	0.20300500	-1.76150600
H	-5.82227000	1.25325800	1.17792300
H	-6.23927100	1.31659800	-1.26047400
H	-4.63305800	0.22326700	-2.83167600
I	-0.01549400	-2.10069000	-0.74075000

INT4 1-Iodonaphthalene
0 1

Si	-3.09458400	1.42788800	-1.02300800
H	-4.44118000	1.41953000	-0.39920900
H	-3.19693700	1.90721100	-2.42265200
C	-1.88610400	2.49444300	-0.08565600
H	-0.46913900	-2.05996600	3.63586600
C	-0.30110600	4.35106400	-0.04797900
C	-1.69587300	2.34245800	1.30364100
C	-0.82124700	3.17494500	2.00389300
C	-0.12584800	4.18247900	1.32775100
C	-1.17212000	3.51249300	-0.74782300

H	0.24539100	5.12719600	-0.57704200
H	-2.23508900	1.56942700	1.84783000
H	0.55566900	4.83070300	1.87253900
H	-1.29300600	3.65196800	-1.81991200
H	-0.68033800	3.03724900	3.07256500
Li	-0.58818500	-0.36200700	-0.51890700
O	-2.46922900	-0.15460700	-0.98109000
C	-3.22194600	-1.38178200	-1.34074600
C	-2.16708800	-2.47023500	-1.54621600
H	-2.64951400	-3.41153500	-1.83127300
H	-1.46366600	-2.19557900	-2.33967800
H	-1.60267400	-2.65880700	-0.62534800
C	-4.15020800	-1.73413400	-0.17372200
H	-3.57475200	-1.85571700	0.75001600
H	-4.90913300	-0.96161300	-0.01200300
H	-4.66995700	-2.67701500	-0.37913400
C	-4.00409900	-1.14258700	-2.63633800
H	-3.33402400	-0.84145400	-3.44855200
H	-4.51123700	-2.06570700	-2.93811200
H	-4.77575300	-0.37293800	-2.51478300
C	1.63926800	-2.17864700	-1.33214900
C	1.35532600	-0.91910700	-0.80193000
C	2.46556400	0.00541700	-0.80119300
C	3.75899500	-0.34651400	-1.33117000
C	3.94786000	-1.65208500	-1.86169700
C	2.90602100	-2.55260900	-1.85886200
H	1.35725500	1.60071700	0.14939000
H	0.86186900	-2.94700000	-1.35472800
C	2.32251300	1.32053100	-0.26923200
C	4.81392700	0.60849000	-1.31237900
H	4.92308900	-1.92561800	-2.26183000
H	3.05238400	-3.55538700	-2.25923700
C	4.62458900	1.87051100	-0.78962500
C	3.36083800	2.23024500	-0.25918500
H	5.78357700	0.32383600	-1.71895400
H	5.44183900	2.58843800	-0.78068100
H	3.21341100	3.22422200	0.15800200
I	0.25130000	-1.69267900	2.17524900

INT3 Mesityliodide
0 1

Si	3.90336700	0.60310900	1.27077100
H	5.31882500	0.87872100	0.91743700
H	3.79223400	0.31942600	2.72264200
C	2.76693900	2.00943000	0.80323600
H	1.46193700	-0.53102300	-2.45741400
C	0.94910100	3.53941100	1.36624100
C	2.83402300	2.60661800	-0.47330700
C	1.97055400	3.64632700	-0.82670200
C	1.03010700	4.11476500	0.09476700
C	1.80736500	2.49439500	1.71464200
H	0.21410900	3.89890700	2.08166400
H	3.56643800	2.26322400	-1.20208300
H	0.35772800	4.92362300	-0.17918600
H	1.72866800	2.05247900	2.70578000
H	2.03068200	4.08564500	-1.81864900
C	-3.03944200	-1.37198300	0.80022400
C	-4.25117900	-1.30083800	1.50683100
C	-2.80649500	-0.43454400	-0.21902200
C	-3.75645800	0.55394700	-0.53029400
C	-5.22096200	-0.33573400	1.22419900
C	-4.95151900	0.58248200	0.20445600
H	-5.69145300	1.34625500	-0.03203100
H	-4.43736900	-2.02437600	2.29936800
Li	1.91379900	-0.22406300	-0.86644000
O	3.33508700	-0.70369000	0.35263900
C	4.00401400	-2.00831100	0.12560700
C	2.88297400	-2.99076200	-0.22104000
H	3.30357100	-3.98250100	-0.42259700
H	2.17524000	-3.08090300	0.61047400
H	2.33813100	-2.66829000	-1.11689000
C	4.97083100	-1.83590700	-1.04980500
H	4.43144100	-1.49408900	-1.93973000
H	5.75942300	-1.11213100	-0.81459300
H	5.45125800	-2.79242800	-1.28642100
C	4.73155700	-2.44106300	1.40182500
H	4.03785900	-2.51675700	2.24628100
H	5.18700100	-3.42582100	1.24967900
H	5.53881800	-1.74806100	1.66936700
I	-0.90627100	-0.50908300	-1.36787600
C	-3.54228900	1.58021900	-1.62046800
H	-4.40706000	2.24772700	-1.69739200
H	-2.65341700	2.19345300	-1.42914700
H	-3.39113600	1.10537100	-2.59715000
C	-2.04182700	-2.44756700	1.16737500
H	-1.09274100	-2.01623400	1.50941100
H	-2.43377700	-3.08136300	1.96995700
H	-1.80634700	-3.08946600	0.31024400
C	-6.53253200	-0.30001500	1.97640400
H	-6.85150600	0.72898200	2.18036300
H	-7.33542200	-0.77972200	1.39991900
H	-6.45857400	-0.82629100	2.93452700

TS1 Mesityliodide
0 1

Si	3.04382800	2.11129900	0.40949500
H	4.09597500	2.53571800	-0.54601900
H	3.31833600	2.66102400	1.75775500
C	1.34820700	2.55844100	-0.23729000
H	1.47910500	-2.77404100	-1.77243600
C	-1.08722700	2.56563400	0.02665300
C	1.18103200	3.08628700	-1.53486800
C	-0.09351000	3.36305400	-2.03589100
C	-1.22534200	3.09727100	-1.25887800
C	0.19044300	2.31390900	0.53628400
H	-1.96521400	2.32916100	0.62044000
H	2.05089900	3.28214100	-2.15820900
H	-2.21734700	3.28993700	-1.65765300
H	0.27854700	1.92769300	1.55179500
H	-0.20393600	3.77180300	-3.03695300
C	-2.18559700	-0.78674400	1.50525000
C	-3.25105600	-0.08472300	2.10040400
C	-2.12126000	-0.93170700	0.10686500
C	-3.15638300	-0.37861000	-0.67263100
C	-4.27939000	0.47363400	1.33321300
C	-4.21413000	0.31329100	-0.05698000

H	-5.01222900	0.73009600	-0.67369200
H	-3.28777600	0.01590900	3.18634000
Li	1.19072400	-0.03924700	-0.16579500
O	2.92485200	0.41666600	0.48780100
C	4.00927800	-0.56864900	0.75181100
C	3.35405000	-1.71964500	1.51654200
H	4.09847900	-2.49346100	1.73483600
H	2.93567300	-1.36919900	2.46682200
H	2.55740600	-2.18639300	0.92740900
C	4.53975500	-1.02895100	-0.60874400
H	3.74519300	-1.49842700	-1.20033400
H	4.95648800	-0.18757800	-1.17470700
H	5.33604300	-1.76965700	-0.47087200
C	5.10666100	0.08815300	1.59403000
H	4.71675200	0.44464600	2.55358700
H	5.89315000	-0.64497900	1.80325000
H	5.57999500	0.92728400	1.06905900
I	-0.16834100	-2.06334800	-0.99029200
C	-3.16279500	-0.51755100	-2.18376400
H	-4.05706200	-0.05999300	-2.62372500
H	-2.28240500	-0.04445200	-2.63780500
H	-3.13950600	-1.57148400	-2.48658600
C	-1.12523200	-1.38611600	2.41401200
H	-0.14146900	-0.90973800	2.28015900
H	-1.39551300	-1.27444100	3.47075400
H	-0.97973800	-2.45306300	2.20986100
C	-5.44951400	1.17940300	1.98446800
H	-5.81358800	2.01108900	1.36880700
H	-6.29645200	0.49493600	2.13406900
H	-5.18024300	1.58084000	2.96868200

INT4 Mesityliodide
0 1

Si	3.81248800	-0.22237000	0.24548700
H	4.61152600	-0.77630400	-0.87707000
H	4.60919100	-0.25969900	1.49546800
C	3.25065200	1.50540300	-0.16912900
H	-2.97037300	-3.43303300	-1.64403700
C	2.19604300	3.61608200	0.46079400
C	3.50569500	2.04751400	-1.44505300
C	3.12083300	3.35218800	-1.76129300
C	2.46318400	4.13562500	-0.80864600
C	2.59391900	2.31615000	0.77914500
H	1.67242500	4.21731600	1.19867200
H	4.01114700	1.44786200	-2.19938700
H	2.15307600	5.14733000	-1.05684100
H	2.38659600	1.93594300	1.77781300
H	3.32649600	3.75368100	-2.75023000
C	-1.83423400	0.78983000	1.66474100
C	-2.92748300	1.65613800	1.83062600
C	-1.08725200	0.73581100	0.45919500
C	-1.52894700	1.60989300	-0.56896400
C	-3.34184600	2.50886900	0.80120800
C	-2.62280000	2.47400100	-0.39908800
H	-2.92372300	3.13448300	-1.21429800
H	-3.46950300	1.67040000	2.77786000
Li	0.70405900	-0.20534600	0.30529500
O	2.39917900	-1.14769200	0.46894900
C	2.35382800	-2.62317800	0.63689500
C	1.13479100	-2.90849500	1.51560100
H	1.03573500	-3.98714700	1.68131900
H	1.23426400	-2.41970700	2.49061700
H	0.20598400	-2.56682000	1.04524200
C	2.19528700	-3.23422200	-0.75873000
H	1.28473600	-2.86553700	-1.24288800
H	3.05291600	-2.99172900	-1.39595900
H	2.12236700	-4.32568000	-0.68895600
C	3.63011300	-3.12292100	1.32225200
H	3.76383700	-2.65947000	2.30518700
H	3.56232700	-4.20664700	1.46742600
H	4.52482700	-2.93289900	0.71763800
I	-2.38188300	-2.04739900	-0.95097500
C	-0.79779800	1.63232300	-1.90263200
H	-1.21917900	2.37470400	-2.59239000
H	0.26615800	1.87576700	-1.77313000
H	-0.84987100	0.65558500	-2.40334700
C	-1.45665900	-0.11231700	2.82980900
H	-0.40226600	0.01707500	3.11529700
H	-2.06292900	0.08938200	3.72196400
H	-1.59268400	-1.17241400	2.57458200
C	-4.54344900	3.41301500	0.96866200
H	-4.44575700	4.32708600	0.37028000
H	-5.46973100	2.91461200	0.64829700
H	-4.68150400	3.70847400	2.01588000

INT3 Bromonaphthalene
0 1

Si	2.97160800	0.93774400	1.40209300
H	4.25026100	1.67924800	1.54807600
H	2.60821300	0.30586900	2.69452000
C	1.58925300	2.04674300	0.81273100
H	1.85885700	-0.22240600	-2.95844400
C	-0.71919000	2.82667100	0.96777200
C	1.79827600	2.96696000	-0.23591700
C	0.76658700	3.79749300	-0.68003000
C	-0.49181200	3.72842700	-0.07577500
C	0.31163500	1.99197700	1.40466900
H	-1.69983400	2.76601800	1.43203700
H	2.77505000	3.04365300	-0.71067000
H	-1.29566400	4.37443200	-0.41947700
H	0.11629900	1.28947100	2.21205900
H	0.94514700	4.49433700	-1.49456500
Li	1.91821300	0.05092500	-1.31070100
Br	-0.43329000	-0.99385900	-1.54304900
O	3.12345900	-0.22559200	0.18288900
C	4.23707000	-1.18098200	-0.02935000
C	3.62761300	-2.37176400	-0.77290700
H	4.40732400	-3.10787400	-1.00048200
H	2.86285600	-2.86089600	-0.15908600
H	3.17103600	-2.05344600	-1.71854600
C	5.29005100	-0.47353000	-0.88795200
H	4.85150800	-0.15297000	-1.83919600
H	5.69878500	0.40328500	-0.37245600
H	6.12067900	-1.15501700	-1.10583800
C	4.80691300	-1.61697800	1.32412600
H	4.03406300	-2.08118400	1.94669900

H	5.60230100	-2.35430100	1.16882000
H	5.24633200	-0.77656400	1.87555800
C	-1.47196100	-2.23653800	0.82001300
C	-1.75597600	-1.29990400	-0.14737000
C	-2.99825600	-0.60066800	-0.17381100
C	-3.95028700	-0.90052900	0.86150800
C	-3.62754600	-1.86117900	1.85849800
C	-2.41706300	-2.51679000	1.83715000
H	-2.63806700	0.57903400	-1.95295900
H	-0.52389500	-2.76511000	0.80087300
C	-3.34726600	0.36069400	-1.16217600
C	-5.20032800	-0.22063300	0.86446400
H	-4.35925500	-2.07748000	2.63381400
H	-2.17869400	-3.25837600	2.59531200
C	-5.51016300	0.70050900	-0.11193700
C	-4.57441100	0.98831100	-1.13616000
H	-5.91431300	-0.44970100	1.65270400
H	-6.47235300	1.20615600	-0.10076700
H	-4.82514600	1.71269800	-1.90684600

TS1 Bromonaphthalene

0 1

Si	3.28924000	1.52479400	0.95885400
H	4.38233800	2.23717000	0.25274700
H	3.56663400	1.46912800	2.41329200
C	1.62996800	2.28153200	0.55044900
H	1.20238900	-1.43119100	-2.74609800
C	-0.80403500	2.31319700	0.80894000
C	1.50919700	3.28394100	-0.43456800
C	0.25827200	3.79877800	-0.78244400
C	-0.89753500	3.31055400	-0.16532400
C	0.44961000	1.81018300	1.16844400
H	-1.70056100	1.91446900	1.27293700
H	2.39765300	3.66572800	-0.93307400
H	-1.87248000	3.69632700	-0.44955200
H	0.49944500	1.04863100	1.94638900
H	0.18426500	4.57173400	-1.54300600
Li	1.33832700	-0.12615200	-0.41029700
Br	-0.13497800	-1.40151800	-1.65007800
O	3.08584800	-0.04890000	0.35008000
C	4.10476400	-1.11550200	0.18116000
C	3.33929700	-2.43719900	0.26394700
H	4.02902400	-3.27829700	0.13231600
H	2.85275200	-2.54470100	1.23981000
H	2.57765500	-2.50647600	-0.52069100
C	4.73994500	-0.92476800	-1.19905100
H	3.97862300	-0.98093900	-1.98500400
H	5.25044900	0.04242400	-1.27121200
H	5.47988500	-1.71151600	-1.38583200
C	5.14227700	-1.01383700	1.30208500
H	4.67316800	-1.10370200	2.28768500
H	5.87316300	-1.82353800	1.20121400
H	5.69849300	-0.06892900	1.26088900
C	-1.52599100	-2.08263600	1.13700400
C	-1.76264600	-1.32499600	0.00699200
C	-2.99797600	-0.61233700	-0.08431700
C	-3.95353300	-0.67375700	0.99253600
C	-3.64882500	-1.46230100	2.13749300
C	-2.46184300	-2.15962200	2.20557000
H	-2.62106600	0.20479200	-2.04808300
H	-0.60413200	-2.66386600	1.21886600
C	-3.33149200	0.17285100	-1.22647400
C	-5.17303000	0.05283800	0.88440400
H	-4.37330400	-1.51670700	2.94860900
H	-2.24172000	-2.77475800	3.07749300
C	-5.45739000	0.80039500	-0.23938700
C	-4.52757700	0.85686100	-1.30872000
H	-5.88816200	0.00171000	1.70428400
H	-6.39721100	1.34339000	-0.31070200
H	-4.76293800	1.43972700	-2.19667200

INT4 Bromonaphthalene

0 1

Si	-2.85839500	0.82716300	-1.36040800
H	-4.30489200	0.97333000	-1.06103400
H	-2.65124600	0.84221200	-2.82877500
C	-1.83530600	2.17273400	-0.57248000
H	-0.83779100	-0.40843700	3.66822200
C	-0.24785400	4.01529000	-0.78556300
C	-1.93061800	2.45426100	0.80594800
C	-1.19877700	3.49476400	1.37938100
C	-0.35644900	4.27668200	0.58236800
C	-0.97962100	2.97072500	-1.35635800
H	0.41154500	4.61621500	-1.40610700
H	-2.58558100	1.85929300	1.43924600
H	0.21743200	5.08458000	1.02902000
H	-0.87703100	2.77370800	-2.42121200
H	-1.28170200	3.69465600	2.44452500
Li	-0.51885900	-0.66823600	0.02832700
Br	0.03015900	-0.68929900	2.51869600
O	-2.31467900	-0.64167800	-0.69724500
C	-3.02523600	-1.93850100	-0.78437700
C	-2.00075500	-3.00560400	-0.39383300
H	-2.46046300	-3.99912400	-0.43537200
H	-1.14250600	-3.00051100	-1.07418000
H	-1.63677300	-2.85460200	0.62944800
C	-4.19105900	-1.91640300	0.20968400
H	-3.82521000	-1.72053700	1.22342400
H	-4.92876900	-1.14960100	-0.04787800
H	-4.70142700	-2.88633800	0.21209400
C	-3.50774500	-2.16078800	-2.22115800
H	-2.66925300	-2.12200300	-2.92446100
H	-3.98015200	-3.14563500	-2.30711800
H	-4.25297400	-1.41485100	-2.52264700
C	1.74759800	-2.61107600	-0.11948100
C	1.43157200	-1.25338400	-0.07619400
C	2.52658300	-0.36427000	-0.37926600
C	3.83157000	-0.84908100	-0.75142400
C	4.05006200	-2.25319700	-0.79719900
C	3.02565000	-3.11803900	-0.48088800
H	1.37820600	1.43173700	-0.02674700
H	0.98531400	-3.35486800	0.12810200
C	2.35202300	1.04993700	-0.32787300
C	4.86719300	0.07742800	-1.05881300
H	5.03279000	-2.62812000	-1.07930800
H	3.19480900	-4.19431300	-0.50868300

C	4.64612400	1.43773300	-1.00548600
C	3.37094200	1.93032200	-0.63110900
H	5.84704700	-0.30744700	-1.33893200
H	5.44828400	2.13298700	-1.24356300
H	3.20093000	3.00377300	-0.57900500

INT3 Bromobenzene

0 1

Si	2.44929900	0.94814400	1.31775300
H	3.80243100	1.56119900	1.31801200
H	2.08327300	0.56099600	2.70298300
C	1.14480400	2.08409100	0.61096700
H	1.29384800	-0.46337400	-2.89811000
C	-0.99561500	3.23874500	0.82084800
C	1.28478700	2.64093400	-0.67756400
C	0.29554100	3.46901400	-1.21400100
C	-0.84243900	3.77270900	-0.46221300
C	-0.01428000	2.39656700	1.34808600
H	-1.88279100	3.46871300	1.40538200
H	2.16825100	2.42892600	-1.27800500
H	-1.60968200	4.42206800	-0.87641100
H	-0.15428800	1.97797600	2.34252500
H	0.41349900	3.87062200	-2.21663900
C	-2.58192700	-2.00788200	0.70123600
C	-3.60764400	-2.07337100	1.64949400
C	-2.58494200	-0.97480800	-0.23514000
C	-3.59564600	-0.01429900	-0.24394500
C	-4.62648500	-1.11613500	1.65586400
C	-4.61897300	-0.09036900	0.70598400
H	-1.79549200	-2.75642800	0.68647700
H	-5.42494700	-1.17386300	2.39071100
H	-5.41200300	0.65363600	0.69945700
H	-3.58693500	0.77834100	-0.98576800
H	-3.61114000	-2.87908100	2.37976500
Li	1.26295000	-0.16538400	-1.25445600
Br	-1.18534500	-0.88804800	-1.57779200
O	2.43197100	-0.38795700	0.28039300
C	3.43345800	-1.47581400	0.18246300
C	2.69313800	-2.66110400	-0.44205200
H	3.38041100	-3.50532900	-0.56998500
H	1.86765200	-2.98516600	0.20184100
H	2.29254000	-2.39772200	-1.42922500
C	4.56143100	-0.98841200	-0.73206300
H	4.16053900	-0.71298800	-1.71363200
H	5.07580700	-0.12127100	-0.30240200
H	5.30273900	-1.78347600	-0.87454800
C	3.94484500	-1.82649700	1.58285900
H	3.12127300	-2.12762600	2.23969000
H	4.65050000	-2.66237100	1.52039600
H	4.47647700	-0.98651900	2.04691700

TS1 Bromobenzene

0 1

Si	2.70425900	1.56556000	0.70520500
H	3.79483800	2.08170900	-0.15812300
H	3.03763700	1.77292600	2.13409600
C	1.06118500	2.31046200	0.21234400
H	0.64850300	-1.98746800	-2.43149300
C	-1.36734600	2.44050000	0.49858400
C	0.94510300	3.15223500	-0.91303100
C	-0.30026500	3.64100800	-1.31509200
C	-1.45528300	3.28154200	-0.61384000
C	-0.11770800	1.97174400	0.91404200
H	-2.26314400	2.13468300	1.03027800
H	1.83174600	3.42669400	-1.48061400
H	-2.42548600	3.64548100	-0.94073500
H	-0.06959600	1.33652900	1.79832100
H	-0.37110700	4.29025500	-2.18392300
C	-2.47062400	-1.40843300	1.29187800
C	-3.53149000	-1.08305300	2.15145200
C	-2.49810700	-1.07043100	-0.06627200
C	-3.63015400	-0.40418800	-0.55120500
C	-4.64944100	-0.40668200	1.65123000
C	-4.70052700	-0.07362800	0.29184300
H	-1.61804300	-1.95753700	1.70022200
H	-5.47973700	-0.15793900	2.30874900
H	-5.57557800	0.43898500	-0.10738800
H	-3.69089600	-0.13866000	-1.60819600
H	-3.49134600	-1.36149900	3.20441800
Li	0.65642500	-0.20526300	-0.33973800
Br	-0.76093500	-1.64241300	-1.45843700
O	2.40788200	-0.08090900	0.41238700
C	3.36849900	-1.21487800	0.43132200
C	2.54432200	-2.44887200	0.80228500
H	3.18827100	-3.33496700	0.82785300
H	2.08957600	-2.32970500	1.79230600
H	1.75338100	-2.63405900	0.06734200
C	3.95530200	-1.33809300	-0.97743200
H	3.16181500	-1.52114500	-1.71105400
H	4.49855500	-0.42908900	-1.26059900
H	4.65827600	-2.17811100	-1.02013000
C	4.45422000	-0.94769100	1.47688800
H	4.02315100	-0.81419600	2.47493400
H	5.14083200	-1.80021900	1.51729200
H	5.05302300	-0.06222100	1.22900600

INT4 Bromobenzene

0 1

Si	2.67178600	0.85984200	0.91599300
H	3.93651600	0.98989700	0.14875700
H	2.95591100	0.92714900	2.36973200
C	1.42203500	2.16327100	0.44510500
H	-0.23456500	-0.72910700	-3.63807200
C	-0.26762000	3.80644000	1.08267400
C	1.19573200	2.50036800	-0.90558800
C	0.25534200	3.47017100	-1.25734200
C	-0.47651800	4.12429700	-0.26196600
C	0.67253600	2.83434000	1.43197200
H	-0.84143300	4.30794800	1.85740700
H	1.76081900	2.00526700	-1.69285900
H	-1.21318600	4.87559700	-0.53456000
H	0.81856700	2.59328600	2.48267200
H	0.09086300	3.71210100	-2.30399800
C	-2.46916800	-1.96086100	0.79742700
C	-3.73585400	-2.11292600	1.37872200
C	-1.89806100	-0.70490500	0.48253800

C	-2.73103500	0.40187300	0.77636500
C	-4.51141600	-0.98406100	1.66183000
C	-4.00269500	0.28185700	1.35434600
H	-1.90802800	-2.87589200	0.58681200
H	-5.49772200	-1.08965100	2.11006900
H	-4.59761600	1.17116300	1.56413000
H	-2.37965800	1.41226800	0.55204800
H	-4.12067500	-3.10704800	1.60678700
Li	0.05902700	-0.40276000	0.05678300
Br	-0.88595300	-0.73043900	-2.31795800
O	1.92456900	-0.61154500	0.51904600
C	2.52979900	-1.95956300	0.51860600
C	1.35723600	-2.94364000	0.51533100
H	1.73200400	-3.97318400	0.52367400
H	0.72276200	-2.80265100	1.39672300
H	0.73712400	-2.82368800	-0.38041300
C	3.36903500	-2.10358000	-0.75541700
H	2.74606700	-1.94263100	-1.64189100
H	4.19618800	-1.38581200	-0.77671200
H	3.79574900	-3.11140200	-0.81539900
C	3.37979700	-2.13747300	1.78013300
H	2.77817400	-1.97918400	2.68144500
H	3.78627800	-3.15430700	1.81570000
H	4.23068400	-1.44553500	1.80146200

Competition experiment (b)

4-bromostilbene

0 1

C	-2.43066500	1.31312700	-0.00019200
C	-1.04228400	1.44216900	-0.00023400
C	-0.19248700	0.31915700	-0.00004900
C	-0.79829600	-0.95384700	0.00018100
C	-2.18225000	-1.09862000	0.00022500
C	-2.99315900	0.03863000	0.00006200
H	-3.06640600	2.19210200	-0.00034500
H	-0.60665100	2.43890800	-0.00040900
H	-0.18544000	-1.85026800	0.00033500
H	-2.63085500	-2.08634600	0.00038700
C	1.25813000	0.53172600	-0.00007300
H	1.55383900	1.57996200	-0.00008700
C	2.22032000	-0.41545000	-0.00001600
H	1.92469200	-1.46401300	0.00003200
C	3.67197600	-0.20306100	0.00003700
C	4.51770000	-1.32944300	-0.00020600
C	4.27654300	1.07112900	0.00023900
C	5.90668300	-1.19615000	-0.00021400
H	4.07461700	-2.32329800	-0.00038900
C	5.66263700	1.20625500	0.00022800
H	3.66016700	1.96549800	0.00040700
C	6.48711600	0.07423700	0.00001100
H	6.53404900	-2.08396700	-0.00039800
H	6.10436600	2.19973100	0.00038700
H	7.56835100	0.18441400	0.00000100
Br	-4.88864300	-0.15862500	0.00000200

4-trifluoromethylbromobenzene

0 1

C	-1.44503500	0.01750000	-0.02381500
C	-0.75216000	-1.19856400	-0.01864300
C	0.64118100	-1.20766700	-0.00941000
C	1.33389500	0.00440800	-0.00646700
C	0.65262100	1.22064300	-0.00867300
C	-0.74310200	1.22543800	-0.01841300
H	-1.29656800	-2.13809800	-0.02498300
H	1.18488000	-2.14622600	-0.00871800
H	1.20411600	2.15465600	-0.00762500
H	-1.27806700	2.16920700	-0.02460400
Br	3.23419400	-0.00470700	0.00555500
C	-2.94999300	0.00317100	-0.00014700
F	-3.46314300	-0.90761500	-0.86699700
F	-3.48619400	1.20509200	-0.31970800
F	-3.43239700	-0.32685100	1.22947400

Energies of Stationary Points

Table S1. Electronic Energies (E), Zero-point Energy Corrected Energies (E+ZPE), Electronic and Thermal Enthalpies (H), Gibbs Free Energies (G) of Stationary Points (in hartrees) Calculated at the M062X/6-311++G(d,p)//B3LYP/6-31++G(d) level of theory (SDD basis set and ECP46MWB are used for I atom).

Structures	E	E+ZPE	H	G	Imaginary Frequency (cm^{-1})
$PhSiH_3$	-522.872479	-522.756975	-522.748998	-522.789348	
LiO*t*-Bu	-240.586501	-240.460798	-240.452128	-240.491577	
Iodobenzene	-242.965622	-242.875397	-242.868566	-242.907167	
4-Fluoro-1-iodobenzene	-342.207135	-342.125315	-342.117629	-342.158383	
4-Methoxy-1-iodobenzene	-357.478786	-357.356059	-357.346588	-357.391396	
1-Iodonaphthalene	-396.579653	-396.442517	-396.433133	-396.477741	
Mesityl Iodide	-360.889231	-360.716113	-360.704130	-360.755167	
1-bromonaphthalene	-2959.393911	-2959.254266	-2959.245378	-2959.288346	
Bromobenzene	-2805.776451	-2805.684217	-2805.677787	-2805.714938	
HI	-11.958361	-11.953404	-11.950099	-11.973564	
HBr	-2574.770609	-2574.764700	-2574.761395	-2574.783944	
INT0	-763.465537	-763.223359	-763.205603	-763.271494	
TS0	-763.474604	-763.221363	-763.215187	-763.271382	-41.82
INT1	-763.476132	-763.231544	-763.215814	-763.273613	
TS4	-763.465528	-763.223615	-763.207892	-763.265694	-315.95
INT2	-763.467673	-763.226651	-763.209636	-763.270234	
INT3	-1006.449897	-1006.117548	-1006.092788	-1006.177532	
TS1	-1006.433594	-1006.102015	-1006.078096	-1006.159094	-65.28
INT4	-1006.465545	-1006.133275	-1006.107990	-1006.194855	
INT5	-994.495471	-994.169661	-994.147682	-994.224480	
TS2	-994.487359	-994.161167	-994.140497	-994.211808	-111.60
Product 1	-994.511478	-994.185513	-994.163470	-994.238983	
TS3	-1006.462777	-1006.131065	-1006.106166	-1006.190691	-78.16
INT6	-1006.464784	-1006.132985	-1006.107641	-1006.194309	
TS5	-1006.464070	-1006.132537	-1006.107919	-1006.191424	-31.61
Product 2	-1006.590630	-1006.250971	-1006.226333	-1006.311386	
INT3 4-fluoroiodobenzene	-1105.693006	-1105.368921	-1105.343338	-1105.430430	
TS1 4-fluoroiodobenzene	-1105.678015	-1105.354781	-1105.329975	-1105.412907	-62.00
INT4 4-Fluoroiodobenzene	-1105.711214	-1105.387144	-1105.361024	-1105.449866	
INT5 4-fluoroiodobenzene	-1093.741187	-1093.423590	-1093.400749	-1093.480179	
TS2 4-fluoroiodobenzene	-1093.733003	-1093.414864	-1093.393433	-1093.466646	-100.46
INT6 4-fluoroiodobenzene	-1093.743257	-1093.424506	-1093.402699	-1093.476189	
TS5 4-fluoroiodobenzene	-1093.742789	-1093.424097	-1093.403119	-1093.473325	-25.57

Product1 4-fluoroiodobenzene	-1093.751976	-1093.434247	-1093.411335	-1093.489158	
TS3 4-fluoroiodobenzene	-1105.708683	-1105.385395	-1105.359486	-1105.447785	-82.14
Product2 4-fluoroiodobenzene	-1105.833269	-1105.501694	-1105.476322	-1105.563265	
INT3 4-methoxyiodobenzene	-1120.962907	-1120.597880	-1120.570560	-1120.661157	
TS1 4-methoxyiodobenzene	-1120.946316	-1120.582112	-1120.555605	-1120.642244	-66.18
INT4 4-methoxyiodobenzene	-1120.979147	-1120.614010	-1120.586310	-1120.678237	
INT5 4-methoxyiodobenzene	-1109.006713	-1108.647747	-1108.623395	-1108.704480	
TS2 4-methoxyiodobenzene	-1109.001398	-1108.642325	-1108.619156	-1108.696358	-104.01
Product1 4-methoxyiodobenzene	-1109.021706	-1108.663433	-1108.638509	-1108.723220	
TS3 4-methoxyiodobenzene	-1120.975350	-1120.611122	-1120.583546	-1120.675460	-106.63
Product2 4-methoxyiodobenzene	-1121.105938	-1120.733471	-1120.706416	-1120.796120	
INT3 1-Iodonaphthalene	-1160.068736	-1159.689238	-1159.661988	-1159.752751	
TS1 1-iodonaphthalene	-1160.056653	-1159.678105	-1159.651667	-1159.737339	-60.76
INT4 1-Iodonaphthalene	-1160.087594	-1159.708528	-1159.680679	-1159.772426	
INT3 Mesityliodide	-1124.372331	-1123.956770	-1123.927054	-1124.021415	
TS1 Mesityliodide	-1124.355442	-1123.941097	-1123.912106	-1124.002949	-60.96
INT4 Mesityliodide	-1124.384560	-1123.970056	-1123.939275	-1124.037969	
INT3 1-Bromonaphthalene	-3722.873820	-3722.494152	-3722.466929	-3722.556356	
TS1 1-Bromonaphthalene	-3722.851355	-3722.472175	-3722.445787	-3722.532657	-156.97
INT4 1-Bromonaphthalene	-3722.895328	-3722.514438	-3722.487162	-3722.575804	
INT3 Bromobenzene	-3569.255883	-3568.923240	-3568.898599	-3568.982350	
TS1 Bromobenzene	-3569.230063	-3568.898549	-3568.874903	-3568.954335	-142.90
INT4 Bromobenzene	-3569.272704	-3568.938780	-3568.913962	-3568.997027	

Chapter 5

Conclusions and Perspectives

Based on the concept of sustainability, development of difficult organic transformations under simple reaction conditions is important. I hypothesized that nucleophilic activation of a metal complex by an alkoxide is effective for difficult organic transformations under simple reaction conditions based on the features of nucleophilically-activated metal complex. Throughout my Ph.D. studies, I have investigated the development of three organic reactions through nucleophilic activation of a metal complex by an alkoxide under simple reaction conditions. In Chapters 2 and 3, the high nucleophilicity of the metal center was utilized to achieve difficult organic transformations with organic halides and in Chapter 4, the high nucleophilicity of ligands was utilized to achieve challenging organic transformation without transition metal catalysis.

In Chapter 2, I described the iron-catalyzed borylation of low-reactive and readily available aryl chlorides. Borylation of aryl chlorides have been achieved with expensive and toxic transition metal catalysts, tailored ligands, special additives and reactive organometallic reagents. On the other hand, borylation of aryl chlorides was achieved in the presence of an iron salt and an alkoxide in this study. The selection of a precise alkoxide and nucleophilic activation of a metal complex is key to achieve this transformation.

In Chapter 3, I described the iron-mediated carboamination and carboalkoxylation of an alkene with a perfluoroalkyl halide. Intermolecular carboamination and carboalkoxylation of an alkene is efficient method to construct a complex molecule from a simple molecule. Three-component coupling reaction with perfluoroalkyl halides, alkenes and amines or phenols was achieved in the presence of an iron salt and an alkoxide in this study. The selection of a precise alkoxide and solvent system is key to achieve this transformation efficiently. Several experiments suggested the intermediacy of a radical intermediate.

In Chapter 4, I described the silylation of aryl halides with monoorganosilanes. Synthesis of diorganosilanes is difficult due to the high reactivity of monoorganosilanes (starting material) and diorganosilanes (product). Synthesis of diorganosilanes from monoorganosilanes and aryl halides was achieved in the presence of an alkoxide in this study. The selection of a precise alkoxide and solvent system is critical to achieve this transformation. Both experimental and theoretical study was carried out and proposed reaction mechanism can explain several experimental results well.

In conclusion, the present study has revealed the importance of nucleophilic activation of a metal complex by an alkoxide to achieve difficult organic transformations under simple reaction conditions. The important points to utilize nucleophilic activation of a metal complex by an alkoxide are the selection of the base and solvent. The present study provides important and useful insights for the design of novel and difficult organic transformations under simple reaction conditions through nucleophilic activation of a metal complex by an alkoxide.

List of Publications

Chapter 2.

1. "Iron-Catalyzed Borylation of Aryl Chlorides in the Presence of Potassium *t*-Butoxide",
   Takumi Yoshida.; Laurean Ilies.; Eiichi Nakamura.
   ACS Catal. **2017**, *7*, 3199–3203.
   (**One of the most read articles in April 2017**, highlighted in SYNFACTS, **2017**, *13*, 639)

Chapter 4.

1. "Silylation of Aryl halides with Monoorganosilanes Activated by Lithium Alkoxide",
   Takumi Yoshida.; Laurean Ilies.; Eiichi Nakamura.
   Org. Lett. **2018**, *20*, 2844–2847.

Other publications not included in this thesis.

1. "Iron-Catalyzed Chemo- and Stereoselective Hydromagnesiation of Diarylalkynes and Diynes",
   Laurean Ilies.; Takumi Yoshida.; Eiichi Nakamura.
   J. Am. Chem. Soc. **2012**, *134*, 16951–16954.
   (**One of the most read articles in October 2012**, highlighted in SYNFACTS, **2013**, *9*, 88)

2. "Synthesis of Polysubstituted Enynes via Iron-Catalyzed Carbomagnesiation of Conjugated Diynes",
   Laurean Ilies.; Takumi Yoshida.; Eiichi Nakamura.
   Synlett **2014**, *25*, 527–530.

3. "Manganese-Catalyzed Directed Methylation of C(sp2)–H Bonds at 25 ºC with High Catalytic Turnover",
   Takenari Sato.; Takumi Yoshida.; Hamad H. Al Mamari.; Laurean Ilies.; Eiichi Nakamura. *Org. Lett.* **2017**, *19*, 5458–5461.

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