

การสังเคราะห์เฮไลโซเลนแบบวันพอดและการประยุกต์



นายวีรชัย พงษ์กิตติพันธ์

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วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญามหาบัณฑิต

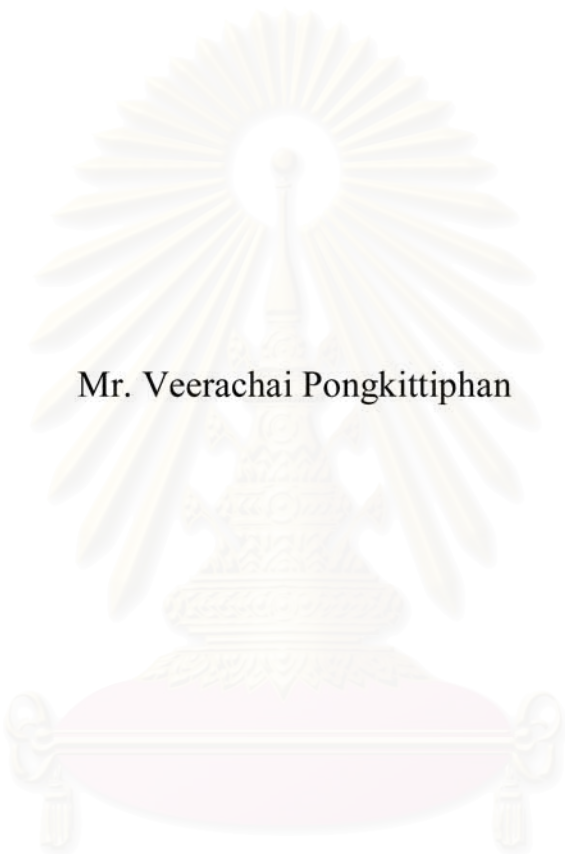
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ONE- POT SYNTHESIS OF HALOSILANES AND APPLICATION



Mr. Veerachai Pongkittiphan

สถาบันวิทยบริการ  
จุฬาลงกรณ์มหาวิทยาลัย

A Thesis Submitted in Partial Fulfillment of the Requirements  
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By                                      Mr. Veerachai Pongkittiphan  
Field of Study                      Chemistry  
Thesis Advisor                      Assistant Professor Warinthorn Chavasiri, Ph.D.

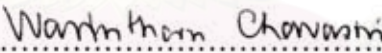
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(Professor Supot Hannongbua, Dr. rer. nat.)

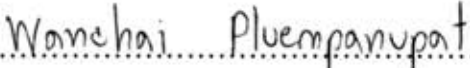
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ได้ทดสอบคลอรีนทิงเอเจนต์ 15 ชนิดสำหรับการเปลี่ยนไฮโดรไซเลนเป็นคลอโรไซเลน ในบรรดาคลอรีนทิงเอเจนต์ที่ศึกษา การใช้เฮกซะคลอโรอีเทนร่วมกับ  $\text{PdCl}_2$  ในปริมาณตัวเร่งปฏิกิริยา พบว่ามีประสิทธิภาพสูงสุดได้คลอโรไซเลนที่สอดคล้องกันในปริมาณสูง ภายใต้ภาวะที่ไม่รุนแรง ใช้ระยะเวลาสั้น วิธีการนี้สามารถประยุกต์สำหรับสังเคราะห์คลอโรไซเลนจากไฮโดรไซเลนที่มีโครงสร้างหลากหลาย ได้เสนอกลไกการเกิดปฏิกิริยาโดยทั่วไปว่าเกิดขึ้นจากการทำปฏิกิริยาระหว่างคลอรีนทิงเอเจนต์กับ  $\text{Pd}(0)$  ผ่านปฏิกิริยาออกซิเดทีฟแอคดิชัน ตามด้วยปฏิกิริยารีดักทีฟอีลิมีเนชันเพื่อทำให้เกิด  $\text{Pd}(0)$  ใหม่ นอกจากนี้สามารถใช้เฮกซะโบรโมเอซิโตนเป็นโบรมินทิงเอเจนต์ร่วมกับแสงยูวี (254 นาโนเมตร) เพื่อสังเคราะห์โบรโมไซเลนจากไฮโดรไซเลนได้ในปริมาณสูง ภายใต้ภาวะที่ไม่รุนแรง ใช้ระยะเวลาสั้น วิธีการนี้ได้พัฒนาสำหรับเตรียมคลอโรไซเลนนี้สามารถประยุกต์ต่อสำหรับสังเคราะห์อนุพันธ์ซิลิล ได้แก่ ซิลิลอีเทอร์และซิลิลเอสเทอร์ในปฏิกิริยาแบบวันพอด

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ภาควิชา ..... เคมี .....

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VEERACHAI PONGKITTIPHAN: ONE-POT SYNTHESIS OF  
HALOSILANES AND APPLICATION. ADVISOR: ASST.PROF.  
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Fifteen chlorinating agents were screened for conversion hydrosilanes to chlorosilanes. Among them, the use of hexachloroethane with catalytic amount of  $\text{PdCl}_2$  was disclosed to be the highest efficiency furnishing the corresponding chlorosilanes in high yield under mild conditions with short reaction time. This method could be applied for the synthesis of chlorosilane from structurally diverse hydrosilanes. The general mechanism was proposed to occur by the interaction of chlorinating agents with  $\text{Pd}(0)$  by oxidative addition, followed by reductive elimination to regenerate  $\text{Pd}(0)$ . Moreover, hexabromoacetone could be utilized as a brominating agent in the presence of UV light (254 nm) to synthesize bromosilanes from hydrosilanes in high yield under mild conditions with short reaction time. This developed methodology for preparation of chlorosilanes could further be efficiently applied for synthesis of silyl derivatives including silyl ethers and silyl esters in one-pot reaction.

สถาบันวิทยบริการ  
จุฬาลงกรณ์มหาวิทยาลัย

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จุฬาลงกรณ์มหาวิทยาลัย

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**LIST OF ABBREVIATIONS**

%	percent
°C	degree of Celsius
br s	broad singlet (NMR)
$\delta$	chemical shift
<i>J</i>	coupling constant (NMR)
d	doublet (NMR)
dd	doublet of doublet (NMR)
eq	equivalent (s)
g	gram (s)
h	hour (s)
HPLC	High performance liquid chromatography
Hz	hertz
m.p.	melting point
mmol	millimole (s)
min	minute (s)
m	multiplet (NMR)
nm	nanometer
NMR	nuclear magnetic resonance
ppm	part per million
q	quartet (NMR)
RT	room temperature
s	singlet (NMR)
t	triplet (NMR)
TLC	thin layer chromatography
UV	ultra violet
W	watt
$\alpha$	alpha
conc.	concentrated
ml	milliliter (s)
quant	quantitative
N	normal

## CHAPTER I

### INTRODUCTION

#### 1.1 Introduction of halosilanes

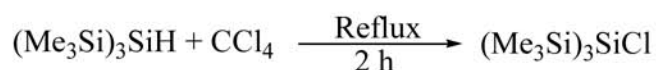
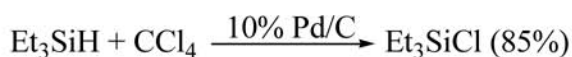
Halosilanes are very useful as starting materials in the field of organosilicon chemistry [1] such as organometallic, silicone and polymer chemistry or as versatile reagents in synthetic organic chemistry [2]. For example, they can be served as protecting agent, hydrosilylating agent or deoxygenating agent. Among halosilanes, only chlorosilanes are supplied by an industrial process, so-called 'the direct process' [3], and are widely used for the synthesis of organosilicon compounds or polymers. Thus, enormous examples for the synthetic utility of chlorosilanes have been reported to date.

#### 1.2 Classical Methods for the Preparation of Halosilanes

Halosilanes can be prepared from several sources of starting materials, including hydrosilanes, alkoxy silanes, and silicon tetrachloride. These general protocols can be achieved by simple substitution reaction using Grignard reagent or other organometallics [4].

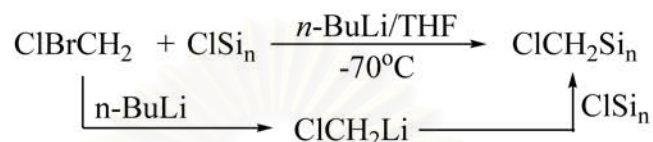
##### 1.2.1 The Synthesis of Chlorosilanes by Classical Procedures

The synthesis of chlorosilanes from hydrosilanes using chlorinating agents in combination with transition metal as a catalyst was the most common procedure. For instance, Pd/C catalyst [5] was used for the preparation of Et<sub>3</sub>SiCl from Et<sub>3</sub>SiH in high yield with several chlorinating agents including CCl<sub>4</sub>, CHCl<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub>, CH<sub>3</sub>CCl<sub>3</sub>, *n*-BuCl, PhCl and PhCH<sub>2</sub>Cl *etc.* The order of reactivity was CCl<sub>4</sub> > CHCl<sub>3</sub> >> CH<sub>2</sub>Cl<sub>2</sub> > *n*-BuCl. However, the toxicity of CCl<sub>4</sub> was the drawback for this protocol.

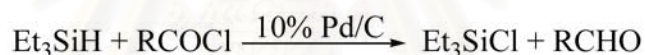




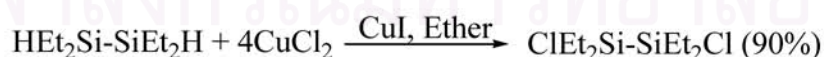
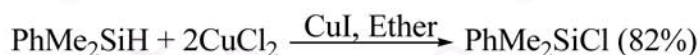
The example of using *n*-butyl lithium to synthesize chlorosilane could be viewed from the reaction between silylchloride and (chloromethyl)lithium generated *in situ* from bromochloromethane and *n*-BuLi to provide (chloromethyl)silanes in high yield [6]. However, the active species of alkyl lithium in this reaction can produce more substituent products of chlorosilane which was hard to control the selectivity of reaction.



Several acyl chlorides [7] including  $\text{CH}_3\text{COCl}$ ,  $\text{PhCOCl}$ ,  $n\text{-C}_7\text{H}_{15}\text{COCl}$ , and  $(\text{CH}_3)_3\text{CCOCl}$  *etc.* could be used as chlorinating agents in combination with Pd/C catalyst to prepare  $\text{Et}_3\text{SiCl}$  from  $\text{Et}_3\text{SiH}$  in high yield. The corresponding aldehyde was obtained as a by-product. Nonetheless, the acidic properties and less stability of acyl chlorides made this procedure not very useful in practical sense.



Another alternative method to prepare chlorosilane [8] in high yield was reported by reacting hydrosilane with 2 equivalents of  $\text{CuCl}_2$  in the presence of a catalytic amount of CuI. For the preparation of dihydrosilanes, 4 equivalents of  $\text{CuCl}_2$  were needed.



Siloxanes could be converted to silyl chloride by chlorination with  $\text{SOCl}_2$  in the presence of quinoline hydrochloride [9]. In addition, silanol derived from the cleavage of organosilyl protecting groups could be efficiently reconverted into chlorosilanes by treatment with  $\text{SOCl}_2$  [10] or  $\text{HCl}$  [11].



### 1.2.2 Classical Procedures for Synthesis of Bromosilanes

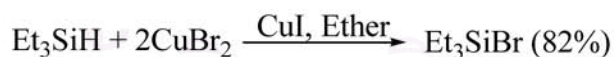
The classical way to prepare  $\text{CH}_3\text{SiBr}_3$  was carried out by the reaction of  $\text{SiBr}_4$  and  $\text{CH}_3\text{MgBr}$  [12]. However, this method possessed less selectivity producing a mixture of undesired products such as di- or tri-alkylsilylbromide.



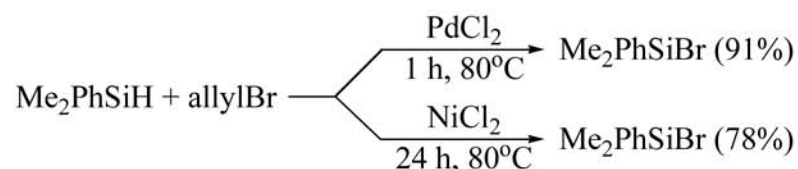
Chlorosilanes can also be converted to bromosilanes by bromination with certain brominating agents such as  $\text{AlBr}_3$  or  $\text{HBr}$  [13]. In addition,  $(\text{CH}_3)_3\text{SiBr}$  could be synthesized by the cleavage of Si-O bond in hexamethylsiloxane with  $\text{PBr}_3$  or by cleavage of Si-Ph bond in  $(\text{CH}_3)_3\text{SiPh}$  with  $\text{Br}_2$  [14]. However, these methods had disadvantages such as brominating agents were quite toxic, hard to handle and high reactivity of reagents. Another protocol utilized  $\text{HgX}_2$  [15] such as  $\text{HgBr}_2$  as a halogenating agent to prepare  $n\text{-BuSiBr}_3$  from  $n\text{-BuSiH}_3$ .

### 1.3 Literature Reviews on the Conversion of Hydrosilanes into Halosilanes

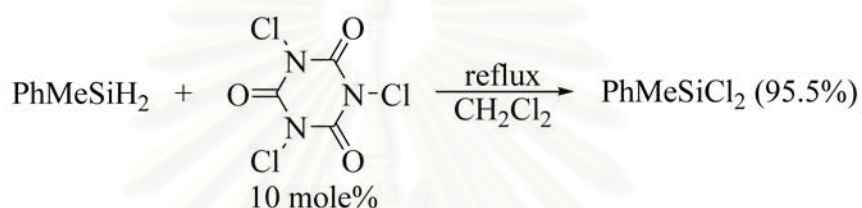
Kunai and Ohshita [16] addressed the use of  $\text{CuBr}_2$  in the presence of a catalytic amount of  $\text{CuI}$  to synthesize bromosilane at RT. The selectivity towards the bromination could be controlled by a stoichiometric amount of reagents.



$\text{PdCl}_2$  and  $\text{NiCl}_2$  were reported to utilize in combination with some brominating agents such as  $\text{EtBr}$ ,  $n\text{-PrBr}$  and  $\text{allyl-Br}$  to prepare bromosilanes.  $\text{PdCl}_2$  exhibited higher efficiency under mild conditions than  $\text{NiCl}_2$ .

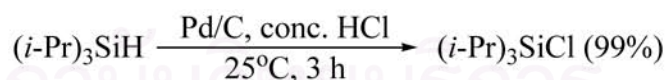


Varaprath and Stutts [17] introduced trichloroisocyanuric acid (TCCA) as a chlorination agent for efficient conversion of hydrosilane and siloxane to the corresponding Si-Cl. Compared with other reported chlorinating agents, TCCA was inexpensive resulting in a much faster reaction and producing essentially almost quantitative yield of product.



However, those mentioned reactions needed THF to homogenize and the reactions must be performed at or below  $-20^\circ\text{C}$  and then allowed to warm to RT. This was due to the very exothermic reaction. At ambient temperature, in the absence of any silane, TCCA reacted with THF exothermically to form mono and disubstituted products.

Masaoka and Banno [18] used concentrated HCl as a chlorinating agent to synthesize trialkylchlorosilanes from trialkylhydrosilanes in the presence of a Pd catalyst in high yields.



#### 1.4 Introduction of Silyl Derivatives

Among organosilicon compounds, chlorosilanes are the most frequently used for a variety of functional group transformations [19]. Reactions involving nucleophilic attack by water, alcohols, organic acids, metallic oxides or organometallic reagents have been used in the synthesis of numerous substituted products.

Hydroxyl group protection is important in the synthesis of organic molecules. One way to protect hydroxyl groups is to transform the molecules to their

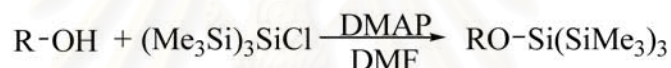


corresponding silyl ethers [20]. A large number of silylating agents exist for the introduction of the trimethylsilyl (TMS) group into alcohols [21].

#### 1.4.1 Preparation of Silyl Ethers and Silyl Esters

A number of hindered trialkylsilyl groups have been employed for the purpose of masking hydroxyl group. Triisopropylsilyl group [22] was prepared as a protecting group of alcohols. Triisopropylsilyl ethers were readily synthesized from appropriate triisopropylsilyl chlorides and alcohols in DMF in the presence of a catalytic amount of imidazole.

*Tris*(trimethylsilyl)silyl ethers [23] were prepared from the corresponding *tris*(trimethylsilyl)silyl chloride with the method commonly used for the preparation of silyl ethers. Conversion of alcohol to silyl ether was attempted using a number of bases such as  $\text{NEt}_3$ , imidazole and 4-dimethylaminopyridine (DMAP). DMAP was found to give the highest yield of protected alcohols in DMF as a solvent.



For the synthesis of silyl ester, some common reagents used for the conversion of alcohols to silyl ethers could be employed to silylate carboxylic acid [24]. For instance, *tert*-butyldimethylsilyl ester could be prepared by treating carboxylic acid with *tert*-butyldimethylsilyl chloride in the presence of imidazole in DMF [25].



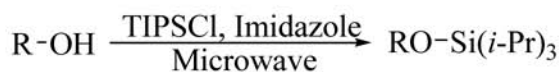
Hexamethyldisilazane [26] was reported as a new silylating agent with high efficiency and produced  $\text{NH}_3$  as a byproduct.



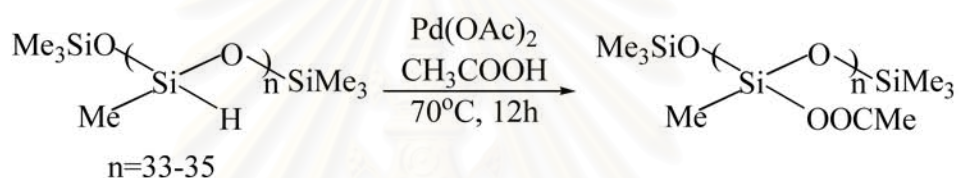
#### 1.4.2 Literature Reviews on the Synthesis of Silyl Derivatives

Khalafi-Nezhad and Alamdari [27] presented an efficient method for silylation of alcohols and phenols using triisopropylchlorosilane and imidazole under

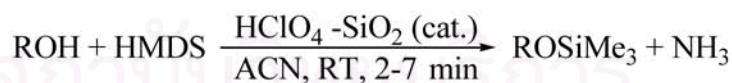
microwave irradiation. High selectivity was observed for silylation of primary and secondary alcohols and also for structurally different phenols.



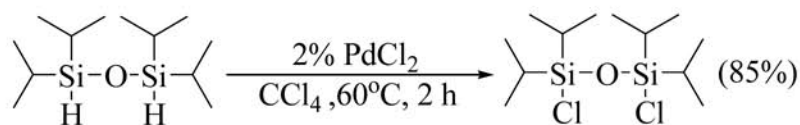
Chauhan and Boudjouk [28] reported a one-step, highly selective catalytic route to silyl esters. Commercially available silanes with Si-H functionality could be converted to silyl or siloxy esters in the presence of Pd(OAc)<sub>2</sub> under mild reaction conditions. This protocol was found to be equally applicable for the modification of multiple silicon centers in one framework and led to the corresponding polysilyl esters in high yields.



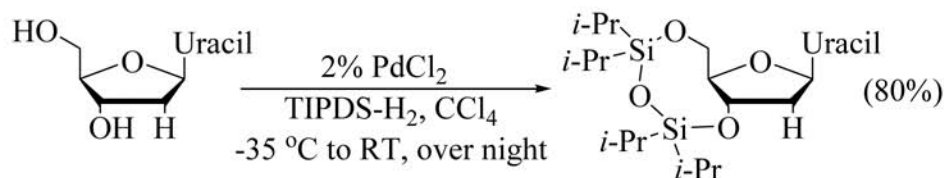
Shaterian and Shahrekipoor [29] presented the conversion of several alcohols, phenols, naphthols, and oximes into their corresponding trimethylsilyl ethers using hexamethyldisilazane (HMDS) in the presence of solid silica supported perchloric acid. The reaction proceeded under mild conditions at RT with short reaction time in excellent yields. The notable advantages of this protocol were easy procedure to work up and the catalyst could be recovered by simple filtration and reused.



Ferreri and co-workers [30] presented the reaction of the corresponding siloxane (TIPDS-H<sub>2</sub>) with CCl<sub>4</sub> in the presence of catalytic PdCl<sub>2</sub> affording the dichloride product (TIPDS-Cl<sub>2</sub>) under mild conditions in high yield after distillation. These systems can be successfully applied in one-pot silylation of nucleosides in high yield.







### 1.5 Recent Halogenating Agents

The systems containing certain halogenating agents such as  $\text{Cl}_3\text{CCCl}_3$ ,  $\text{Cl}_3\text{CCOCCl}_3$  or  $\text{Cl}_3\text{CCN}$  in combination with  $\text{PPh}_3$  have been reported as viable routes for the chlorination of alcohols with high efficiency [31]. These reagents are attractive since reactions could be formed under mild and acid-free conditions with good yields.

Pluempanapat [32] presented a new and convenient method for chlorination of alcohols utilizing  $\text{PPh}_3/\text{Cl}_3\text{CCONH}_2$ . Various alcohols could smoothly be converted into their corresponding alkyl chlorides in high yield with short reaction time.

Tongkate [33] described a new and efficient bromination reaction of alcohols and carboxylic acid utilizing  $\text{Br}_3\text{CCOCBr}_3/\text{PPh}_3$  and  $\text{Br}_3\text{CCO}_2\text{Et}/\text{PPh}_3$ . Various alcohols could be converted smoothly into their corresponding alkyl bromides in high yields. Carboxylic acids were transformed into their acid bromides which could then be trapped with amines, alcohols or thiols yielding amides, esters and thioesters, respectively under mild conditions in good to excellent yield with short reaction time.

### 1.6 The Objective of This Research

The objective of this research is to develop the methodology for the synthesis of halosilanes from hydrosilanes using halogenating agents in the presence of  $\text{PdCl}_2$  as a catalyst. The application of this developed methodology for the preparation of silyl derivatives as one-pot procedure including silyl ether and silyl ester is also examined.

## CHAPTER II

### EXPERIMENTAL

#### 2.1 Instruments and Equipment

All reactions were carried out under an atmosphere of N<sub>2</sub>. The <sup>1</sup>H- and <sup>13</sup>C-NMR spectra were performed in CDCl<sub>3</sub> with tetramethylsilane (TMS) as an internal reference on Varian nuclear magnetic resonance spectrometer, model Mercury plus 400 NMR spectrometer which operated at 399.84 MHz for <sup>1</sup>H and 100.54 MHz for <sup>13</sup>C nuclei. The chemical shifts (δ) are assigned by comparison with residue solvent protons. Yields of products were determined by <sup>1</sup>H-NMR technique using toluene as an internal standard.

Column chromatography was performed on silica gel (Merck's silica gel 60 G Art 7734 (70-230 mesh) and thin layer chromatography (TLC) was performed on aluminum sheets pre-coated with silica gel (Merck's, Kieselgel 60 PF<sub>254</sub>).

#### 2.2 Chemicals

All solvents were purified by standard methodology before use unless those were reagent grades. The reagents for synthesis were purchased from Fluka or Sigma-Aldrich chemical company and used without further purification.

#### 2.3 Preparation of Chlorinating and Brominating Agents

##### **Ethyl dichloroacetate, ethyl chloroacetate and ethyl tribromoacetate [34-35]**

In a round bottom flask connected with a condenser was added 0.6 eq (0.60 mmol, 50 mL) of a selected carboxylic acid, 2 eq (2 mmol) of EtOH and 5 mL of conc H<sub>2</sub>SO<sub>4</sub>. The mixture was stirred at reflux temperature for 24 h. When the reaction was completed, the reaction mixture was extracted with 1 N HCl, saturated aqueous NaHCO<sub>3</sub>, subsequently, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and evaporated. The residue was purified by reduced pressure distillation.

*Ethyl dichloroacetate*: colorless oil (42%),  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ )  $\delta$  (ppm): 1.35 (3H, t,  $J = 7.14$  Hz,  $\text{CH}_2\text{CH}_3$ ), 4.32 (2H, q,  $J = 7.20$  Hz,  $\text{CH}_2\text{CH}_3$ ), and 5.93 (1H, s,  $\text{Cl}_2\text{CH}$ ).  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ )  $\delta$  (ppm): 13.8, 63.7, 64.3 and 164.5.

*Ethyl chloroacetate*: colorless oil (44%),  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ )  $\delta$  (ppm): 1.28 (3H, t,  $J = 7.20$  Hz,  $\text{CH}_2\text{CH}_3$ ), 4.04 (2H, s,  $\text{ClCH}_2$ ) and 4.22 (2H, q,  $J = 7.15$  Hz,  $\text{CH}_2\text{CH}_3$ ).  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ )  $\delta$  (ppm): 14.0, 40.9, 62.3 and 167.3.

*Ethyl tribromoacetate*: colorless oil (69%),  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ )  $\delta$  (ppm): 1.36 (3H, t,  $J = 7.20$  Hz,  $\text{CH}_2\text{CH}_3$ ), and 4.46 (2H, q,  $J = 7.12$  Hz,  $\text{CH}_2\text{CH}_3$ ).  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ )  $\delta$  (ppm): 13.7, 29.5, 65.7 and 161.9.

### **Hexabromoacetone [36]**

Anhydrous NaOAc 7 g was mixed with 20 mL of glacial acetic acid. The reaction mixture was stirred and heated to 60 °C. Acetone 1.4 mL was added, followed by dropwise addition of  $\text{Br}_2$  5 mL over a 10 min period with stirring. The mixture was then heated to 95°C for 2 h. After which it was cooled to RT and mixed with 100 mL of water to precipitate the desired product as white solid. After air drying, the pure product was obtained upon recrystallization from hexane.

*Hexabromoacetone*: white solid (60%),  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ )  $\delta$  (ppm): 24.5 and 173.5.

### **2.4 General Procedure for Conversion of hydrosilane to halosilane**

A stirred solution of  $\text{Pd(II)Cl}_2$  1% mmol (w/w, 1.8 mg) and 0.50 eq (0.50 mmol) of selected halogenating agents was successively added hydrosilane 1 eq (1.0 mmol) at RT (28-30°C) under  $\text{N}_2$  atmosphere. After 1 h, the crude mixture was analyzed by  $^1\text{H-NMR}$  with the addition of toluene 1.0 mmol (106 $\mu\text{L}$ ) as an internal standard.



## 2.5 Studies on Conditions Optimization for the Synthesis of Chlorosilanes

### 2.5.1 Effect of Chlorinating Agents

The conversion of triisopropylhydrosilane (TIPS-H) into triisopropylsilyl chloride (TIPS-Cl) was carried out using the reaction conditions described in the general procedure. Fifteen different chlorinating agents including ethyl trichloroacetate ( $\text{Cl}_3\text{CCOOEt}$ ), acetyl chloride ( $\text{CH}_3\text{COCl}$ ), hexachloroacetone ( $\text{Cl}_3\text{CCOCCl}_3$ ), ethyl dichloroacetate ( $\text{Cl}_2\text{CHCOOEt}$ ), ethyl chloroacetate ( $\text{ClCH}_2\text{COOEt}$ ), trichloroacetic acid ( $\text{Cl}_3\text{CCOOH}$ ), trichloroacetonitrile ( $\text{Cl}_3\text{CCN}$ ), trichloroacetamide ( $\text{Cl}_3\text{CCONH}_2$ ), hexachloroethane ( $\text{Cl}_3\text{CCCl}_3$ ), 1,1,1-trichloroethane ( $\text{Cl}_3\text{CCH}_3$ ), 1,2-dichloroethane ( $\text{ClCH}_2\text{CH}_2\text{Cl}$ ), 1,1,2,2-tetrachloroethane ( $\text{Cl}_2\text{CHCHCl}_2$ ), chloroform ( $\text{CHCl}_3$ ), dichloro-methane ( $\text{CH}_2\text{Cl}_2$ ) and carbon tetrachloride ( $\text{CCl}_4$ ) were utilized.

### 2.5.2 Effect of Amount of $\text{PdCl}_2$ and Type of Pd(II) Catalyst

Two types of catalysts:  $\text{PdCl}_2$  and Pd/C were selected to compare their effects on the reaction efficiency. The amount of  $\text{PdCl}_2$  catalyst (0.5 and 1.0% mmol) was varied for the synthesis of TIPS-Cl from TIPS-H under standard conditions.

### 2.5.3 Effect of the amount of $\text{Cl}_3\text{CCCl}_3$

According to the general procedure, the amount variation of  $\text{Cl}_3\text{CCCl}_3$  as 0.125, 0.17, 0.25, 0.30, 0.50 and 0.75 mmol was explored to observe the effect of the amount of chlorinating agent on the chlorination of TIPS-H.

### 2.5.4 Effect of Solvent

The general reactions performed using various diverse solvents (1 mL) including benzene, THF, hexane and  $\text{CH}_3\text{CN}$  were carried out compared with that without solvent to observe the effect of solvent system.

## 2.6 Typical Procedure to Synthesize Chlorosilanes

The chlorination of different hydrosilanes (1 mmol) using  $\text{Pd(II)Cl}_2$  1% mmol (w/w, 1.8 mg) and  $\text{Cl}_3\text{CCCl}_3$  as a chlorinating agent in THF (or hexane) at RT for 1 h

was conducted. The quantity of chlorosilane in the crude mixture was determined by  $^1\text{H-NMR}$  using toluene as an internal standard.

*Triisopropylchlorosilane*: (quant),  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ )  $\delta$  (ppm): 1.11 (18H, d,  $J = 7.15$  Hz,  $\text{SiCH}(\underline{\text{CH}_3})_2$ ) and 1.23 (3H, m,  $\text{SiCH}(\underline{\text{CH}_3})_2$ ).

*Triethylhydrosilane*: (quant),  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ )  $\delta$  (ppm): 0.83 (6H, q,  $J = 7.82$  Hz,  $\text{SiCH}_2\underline{\text{CH}_3}$ ) and 1.05 (9H, t,  $J = 7.85$  Hz,  $\text{SiCH}_2\underline{\text{CH}_3}$ ).

*Tris-trimethylsilylchlorosilane*: (quant),  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ )  $\delta$  (ppm): 0.00 (27H, s,  $\text{Si-Si}(\underline{\text{CH}_3})_3$ ).

*Triphenylchlorosilane*: (quant),  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ )  $\delta$  (ppm): 7.44 (9H, m, Ar-H) and 7.66 (6H, d,  $J = 6.54$  Hz, Ar-H).

*Dimethylphenylchlorosilane*: (67%),  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ )  $\delta$  (ppm): 0.35 (6H, s,  $\text{Si}(\underline{\text{CH}_3})_2$ ), 7.10 (3H, m, Ar-H) and 7.30 (2H, q,  $J = 7.66$  Hz, Ar-H).

*tert-Butyldimethylchlorosilane*: (86%),  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ )  $\delta$  (ppm): 0.27 (6H, s,  $\text{Si}(\underline{\text{CH}_3})_2$ ) and 0.88 (9H, s,  $\text{SiC}(\underline{\text{CH}_3})_3$ ).

*Diphenylchlorosilane*: (83%),  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ )  $\delta$  (ppm): 5.78 (1H, s,  $\text{Ph}_2\text{SiCH}$ ), 7.48 (6H, m, Ar-H) and 7.70 (4H, d,  $J = 6.74$  Hz, Ar-H).

*Dichlorodiphenylsilane*: (45%),  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ )  $\delta$  (ppm): 7.56 (6H, m, Ar-H) and 7.77 (4H, d,  $J = 6.81$  Hz, Ar-H).

*Chloro(2-(dimethylsilyl)phenyl)dimethylsilane*: (35%),  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ )  $\delta$  (ppm): 0.34 (6H, d,  $J = 6.35$  Hz,  $\text{ArSiH}(\underline{\text{CH}_3})_2$ ), 0.41 (12H, s,  $\text{ArSiCl}(\underline{\text{CH}_3})_2$ ), 4.46 (1H, m,  $\text{ArSiH}(\underline{\text{CH}_3})_2$ ), 7.26 (2H, d,  $J = 6.98$  Hz, Ar-H) and 7.44 (2H, d,  $J = 7.35$  Hz, Ar-H).

*1,2-Bis(chlorodimethylsilyl)benzene*: (24%),  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ )  $\delta$  (ppm): 0.46 (12H, s,  $\text{ArSiCl}(\underline{\text{CH}_3})_2$ ), 7.35 (2H, d,  $J = 7.43$  Hz, Ar-H) and 7.53 (2H, d,  $J = 8.75$  Hz, Ar-H).



*1,1,3,3-Tetraisopropylchlorosiloxane*: (61%),  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ )  $\delta$  (ppm): 1.04 (28H, m,  $\text{CH}(\text{CH}_3)_2$ ) and 4.32 (1H, s,  $\text{OSiH}(i\text{-Pr})_2$ ).

*1,1,3,3-tetraisopropyldichlorosiloxane*: (22%),  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ )  $\delta$  (ppm): 1.10 (28H, m,  $\text{CH}(\text{CH}_3)_2$ ).

*Diethylchlorosilane*: (54%),  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ )  $\delta$  (ppm): 0.85 (4H, m,  $\text{SiCH}_2\text{CH}_3$ ) and 1.04 (6H, m,  $\text{SiCH}_2\text{CH}_3$ ).

*Dichlorodiethylchlorosilane*: (62%),  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ )  $\delta$  (ppm): 1.10 (10H, s,  $\text{SiCH}_2\text{CH}_3$ ).

## 2.7 Typical Procedure to Synthesize Bromosilanes

The synthesis of bromosilanes was carried out by using the same general procedure as that described for chlorination. Four brominating agents including  $\text{CBr}_4$ ,  $\text{Br}_3\text{CCOOEt}$ ,  $\text{Br}_3\text{CCOOH}$  and  $\text{Br}_3\text{CCOCBr}_3$  were examined.

An alternative procedure for the preparation of bromosilanes was the irradiation of a mixture of TIPS-H (1 mmol) and  $\text{Br}_3\text{CCOCBr}_3$  (0.25 mmol) in THF with UV lamp (234 nm, 6 W). The yield of bromosilane was analyzed by  $^1\text{H-NMR}$  using toluene as an internal standard.

*Triisopropylbromosilane*: (96%),  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ )  $\delta$  (ppm): 1.09 (18H, d,  $J = 7.33$  Hz,  $\text{SiCH}(\text{CH}_3)_2$ ) and 1.26 (3H, m,  $\text{SiCH}(\text{CH}_3)_2$ ).

## 2.8 Application of Halosilanes for the One-pot Synthesis of Silyl Derivatives

A one-pot synthesis of silyl derivatives was divided into 2 steps.

**Step 1** Synthesis of halosilane: TIPS-H 1 eq (1.50 mmol) as a substrate, halogenating agent 0.25 eq (0.375 mmol) and 1% $\text{PdCl}_2$  (2.6 mg) for 1 h at RT.

**Step 2** The transformation to silyl derivatives: the reaction of the *in situ* generated chlorosilane with selected alcohols or carboxylic acids (1.0 mmol) under suitable conditions.

### 2.8.1 Synthesis of Silyl Ether Derivatives

Three selected alcohols (1.0 mmol): geraniol, 2-phenylethanol and cinamyl alcohol were used to synthesize silyl ether derivatives. Several factors in step 2 including reaction temperature and time, the amount and type of base, and the amount of THF were varied to explore the efficiency of the reaction. After the reaction was finished, all silyl ether products were extracted with 1 N HCl, saturated aqueous NaHCO<sub>3</sub>, subsequently, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and evaporated. The residue was purified by column chromatography using hexane as a solvent system.

*Triisopropyl(phenethoxy)silane*: colorless oil (82%), <sup>1</sup>H-NMR (CDCl<sub>3</sub>) δ (ppm): 1.05 (21H, d, *J* = 5.07 Hz, SiCH(CH<sub>3</sub>)<sub>2</sub>), 2.86 (2H, t, *J* = 7.22 Hz, PhCH<sub>2</sub>CH<sub>2</sub>OSi), 3.88 (2H, t, *J* = 7.21 Hz, PhCH<sub>2</sub>CH<sub>2</sub>OSi) and 7.25 (5H, m, Ar-H).

*Cinnamyloxytriisopropylsilane*: colorless oil (75%), <sup>1</sup>H-NMR (CDCl<sub>3</sub>) δ (ppm): 1.08 (21H, d, *J* = 5.97 Hz SiCH(CH<sub>3</sub>)<sub>2</sub>), 4.43 (2H, d, *J* = 3.32 Hz, CHCH<sub>2</sub>OSi), 6.29 (1H, dt, *J* = 15.86, 4.67 Hz, CHCH<sub>2</sub>OSi), 6.63 (1H, d, *J* = 15.85 Hz, PhCHCH) and 7.34 (5H, m, Ar-H).

*trans-(3,7-dimethylocta-2,6-dienyloxy)triisopropylsilane*: colorless oil (80%), <sup>1</sup>H-NMR (CDCl<sub>3</sub>) 1.05 (21H, d, *J* = 4.83 Hz, SiCH(CH<sub>3</sub>)<sub>2</sub>), 1.59 (1H, s, CH<sub>3</sub>CCH<sub>2</sub>), 1.64 (1H, s, CH<sub>3</sub>CCH<sub>3</sub>), 2.00 (2H, t, *J* = 6.93 Hz, CHCH<sub>2</sub>CH<sub>2</sub>CCH<sub>3</sub>), 2.07 (2H, t, *J* = 7.17 Hz, CHCH<sub>2</sub>CH<sub>2</sub>CCH<sub>3</sub>), 5.09 (1H, t, *J* = 6.53 Hz, CH=CCH<sub>3</sub>) and 5.32 (1H, t, *J* = 5.71 Hz, C=CHCH<sub>2</sub>OSi).

### 2.8.2 Synthesis of Silyl Ester Derivatives

Four carboxylic acids (1.0 mmol): 2-phenylacetic acid, 2-methylbenzoic acid, *trans*-4-methoxycinnamic acid and 3-methoxybenzoic acid were used as a model to synthesize silyl esters. A general procedure was carried out as the same manner as the synthesis of silyl ethers except for THF was used as a solvent in step 2. The yields of silyl ester product were quantified by <sup>1</sup>H-NMR.

*Triisopropylsilyl 2-methylbenzoate*: (quant), <sup>1</sup>H-NMR (CDCl<sub>3</sub>) 1.15 (21H, d, *J* = 7.51 Hz, SiCH(CH<sub>3</sub>)<sub>2</sub>), 2.63 (3H, s, Ar-CH<sub>3</sub>), 7.26 (2H, m, Ar-H), 7.40 (1H, t, *J* = 7.41 Hz, Ar-H) and 7.97 (1H, d, *J* = 7.10 Hz, Ar-H).

*Triisopropylsilyl 3-methoxybenzoate*: (quant),  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ) 1.15 (21H, d,  $J = 7.54$  Hz,  $\text{SiCH}(\text{CH}_3)_2$ ), 3.85 (3H, s,  $\text{Ar-OCH}_3$ ), 7.12 (1H, d,  $J = 8.26$ , Ar-H), 7.35 (1H, t,  $J = 7.87$ , Ar-H), 7.61 (1H, s, Ar-H) and 7.67 (1H, d,  $J = 7.55$ , Ar-H).

*trans-Triisopropylsilyl-3-(4-methoxyphenyl)acrylate*: (quant),  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ) 1.13 (21H, d,  $J = 7.53$  Hz,  $\text{SiCH}(\text{CH}_3)_2$ ), 3.84 (3H, s,  $\text{Ar-OCH}_3$ ), 6.32 (1H, d,  $J = 15.83$  Hz,  $\text{CH}=\text{CHCOOSi}$ ), 6.90 (2H, d,  $J = 8.59$ , Ar-H), 7.48 (2H, d,  $J = 8.61$ , Ar-H), 7.62 (1H, d,  $J = 15.84$ ,  $\text{CH}=\text{CHCOOSi}$ ).



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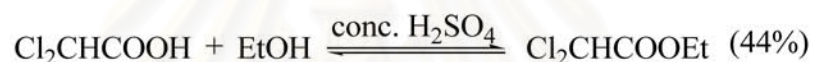
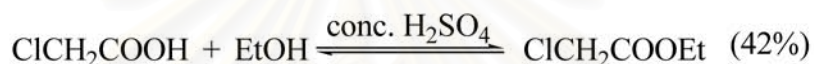
## CHAPTER III

### RESULTS AND DISCUSSION

#### Part I Synthesis of Chlorosilanes

##### 3.1 The Synthesis of Chlorinating Agents

Two chlorinating agents used in this research:  $\text{Cl}_2\text{CHCOOEt}$  and  $\text{ClCH}_2\text{COOEt}$  were synthesized by reacting  $\text{Cl}_2\text{CHCOOH}$  and  $\text{ClCH}_2\text{COOH}$  with  $\text{EtOH}$  in the presence of conc.  $\text{H}_2\text{SO}_4$  as a catalyst. The desired products were purified by vacuum distillation.



Two synthesized esters were well-characterized. To illustrate this, the  $^1\text{H}$ -NMR spectrum of  $\text{Cl}_2\text{CHCOOEt}$  revealed three peaks of a methyl group resonating at  $\delta_{\text{H}} 1.35$  ( $t$ ,  $J = 7.14$  Hz, 3H), a methylene group at  $\delta_{\text{H}} 4.32$  ( $q$ ,  $J = 7.20$  Hz, 2H) and -CH- group at  $\delta_{\text{H}} 5.93$  (s). The  $^{13}\text{C}$ -NMR spectrum exhibited a carbonyl carbon at  $\delta_{\text{C}} 164.5$  whereas the carbon bearing two chlorine atoms at  $\delta_{\text{C}} 64.3$  and two peaks at 63.7 and 13.8 belonging to methylene and methyl carbons, respectively were detected.

Three peaks visualized from the  $^1\text{H}$ -NMR spectrum of  $\text{ClCH}_2\text{COOEt}$  could be assigned for methyl protons resonating at  $\delta_{\text{H}} 1.28$  ( $t$ ,  $J = 7.20$  Hz, 3H), methylene protons at  $\delta_{\text{H}} 4.04$  (s, 2H) on the carbon bearing a chlorine atom and at  $\delta_{\text{H}} 4.22$  ( $q$ ,  $J = 7.15$  Hz, 2H) connecting to a methyl group. The  $^{13}\text{C}$ -NMR spectrum displayed a carbonyl carbon at  $\delta_{\text{C}} 167.3$  while the carbon bearing a chlorine atom at  $\delta_{\text{C}} 62.3$  and two peaks at  $\delta_{\text{C}} 40.9$  and 14.0 assigned for methylene and methyl carbons, respectively could be clearly observed.

##### 3.2 Conditions Optimization Study

Several parameters including type of chlorinating agents, molar ratio of chlorinating agents, reaction time, reaction media, ratio of  $\text{PdCl}_2$  and temperature



were investigated to optimize the reaction conditions for conversion of hydrosilanes to chlorosilanes.

### 3.2.1 The Effect of Chlorinating Agents

Various commercially available chlorinating agents such as  $\text{Cl}_3\text{CCOCCl}_3$ ,  $\text{CH}_3\text{COCl}$ ,  $\text{Cl}_3\text{CCOOEt}$ ,  $\text{Cl}_3\text{CCN}$ ,  $\text{Cl}_3\text{CCONH}_2$ ,  $\text{Cl}_3\text{CCCl}_3$ ,  $\text{Cl}_3\text{CCH}_3$  and  $\text{CCl}_4$  were selected to explore the effect of chlorinating agents on the conversion of TIPS-H to triisopropylsilyl chloride (TIPS-Cl). The other two chlorinating agents as mentioned above,  $\text{Cl}_2\text{CHCOOEt}$  and  $\text{ClCH}_2\text{COOEt}$  were synthesized. The results are presented in Table 3.1.

The yield of TIPS-Cl could be quantified by  $^1\text{H-NMR}$  spectrum. According to this developed analytical method, toluene 1 mmol (106  $\mu\text{L}$ ) as an internal standard was added to the completed reaction. A few drops of the reaction mixture were then taken and analyzed by  $^1\text{H-NMR}$  technique as depicted in Fig 3.1. From the calculation, the peak area of methyl protons of toluene was compared with the area of the interested peak which can further calculate the percentage yield by the relative ratio of integration and number of proton shown in equation 3.1.

Equation 3.1

$$\% \text{ Yield A} = \frac{\text{Integration of A}}{\text{Integration of Internal std}} \times \frac{\#H \text{ of Internal std}}{\#H \text{ of A}} \times 100$$

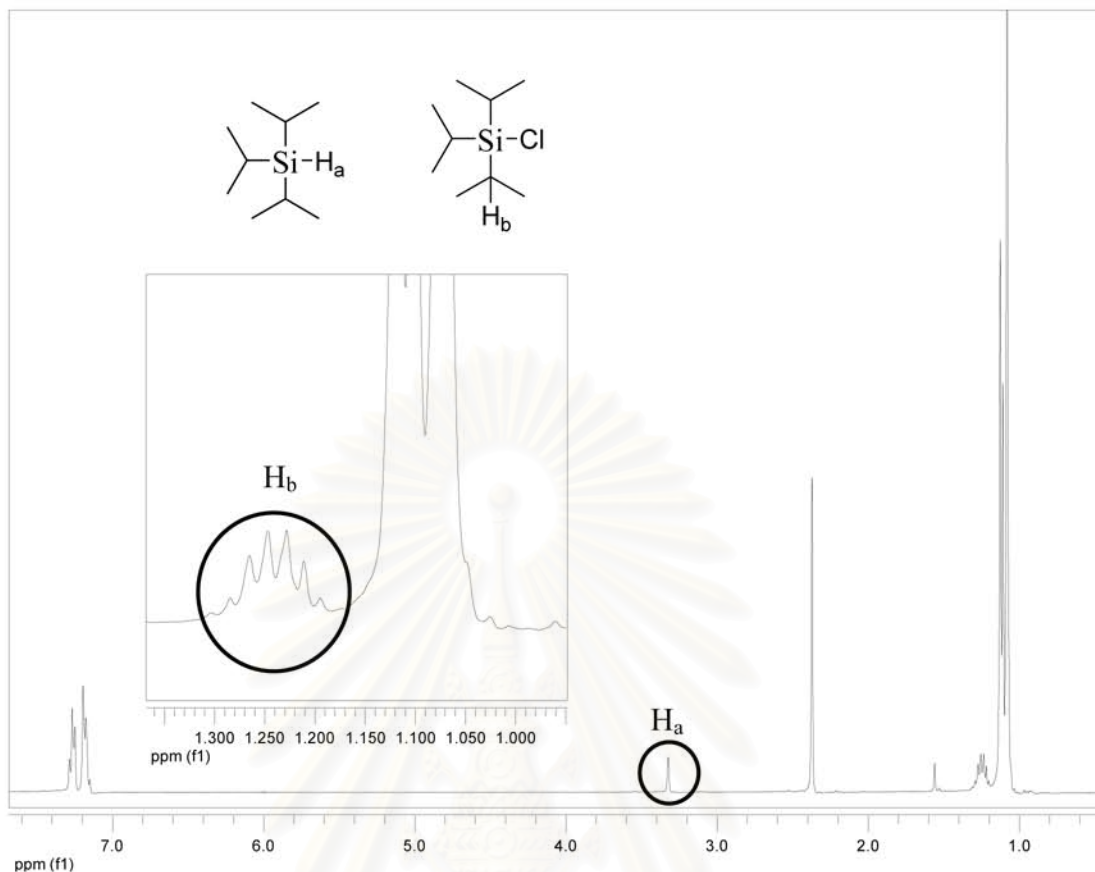
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**Table 3.1** The effect of chlorinating agents on the conversion of TIPS-H to TIPS-Cl
$$(i\text{-Pr})_3\text{SiH} \xrightarrow[\text{RT, 60 min}]{\substack{1\% \text{ PdCl}_2 \\ \text{Chlorinating agents}}} (i\text{-Pr})_3\text{SiCl}$$

Entry	Chlorinating agents	Equivalent (mmol)	% Yield <sup>a</sup>		Total
			Si-Cl	Si-H	
1	None	-	13	92	105
2	CH <sub>3</sub> COCl	0.75	67	36	103
		1.50	quant	0	100
3	Cl <sub>3</sub> CCOCCl <sub>3</sub>	0.50	19 (58) <sup>b</sup>	84 (40) <sup>b</sup>	103 (98) <sup>b</sup>
			(94) <sup>c</sup>	(10) <sup>c</sup>	(104) <sup>c</sup>
4	Cl <sub>3</sub> CCOOEt	0.50	15 (41) <sup>b</sup>	85 (63) <sup>b</sup>	100 (104) <sup>b</sup>
			(37) <sup>c</sup>	(68) <sup>c</sup>	(105) <sup>c</sup>
5	Cl <sub>3</sub> CCOOH	0.50	19	85	104
6	Cl <sub>2</sub> CHCOOEt	0.50	88	18	106
7	ClCH <sub>2</sub> COOEt	0.50	10	89	99
		1.50	25	79	104
8	Cl <sub>3</sub> CCN	0.50	11	93	104
9 <sup>d</sup>	Cl <sub>3</sub> CCONH <sub>2</sub>	0.50	16	87	103
10	ClCH <sub>2</sub> CH <sub>2</sub> Cl	0.50	17	84	101
11	Cl <sub>2</sub> CHCHCl <sub>2</sub>	0.50	32	68	100
12	Cl <sub>3</sub> CCCl <sub>3</sub>	0.50	quant	0	100
13	CCl <sub>4</sub>	0.50	17	81	98
14	CHCl <sub>3</sub>	0.50	66	36	102
15	CH <sub>2</sub> Cl <sub>2</sub>	0.50	15	90	105
16	Cl <sub>3</sub> CCH <sub>3</sub>	0.50	51	44	95

<sup>a</sup> % yield was determined by <sup>1</sup>H-NMR using toluene as an internal standard <sup>b</sup> the reaction was carried out at 55°C for 3 h <sup>c</sup> the reaction was carried out at 55°C for 6 h <sup>d</sup> not completely soluble

From Fig 3.1, the peak areas of H<sub>a</sub> (δ<sub>H</sub> 3.28) and H<sub>b</sub> (δ<sub>H</sub> 1.24) were taken to calculate for the percentage yield of product and substrate, respectively.



**Figure 3.1** The  $^1\text{H}$ -NMR spectrum of the reaction mixture containing toluene, TIPS-H and TIPS-Cl

As aforementioned, TIPS-H was used as a model to investigate the effect of chlorinating agents in the presence of 1%PdCl<sub>2</sub> as a catalyst for 1 h at RT. Entry 1 manifestly revealed that in the absence of a chlorinating agent, only 13% of the desired product was detected. The use of CH<sub>3</sub>COCl 0.75 mmol as chlorinating agent was accomplished providing 67% yield of TIPS-Cl. The increased amount of this chlorinating agent to 1.50 mmol fruitfully achieved the quantitative yield of the target product. Even though CH<sub>3</sub>COCl provided a high yield of product under these reaction conditions, this reagent itself had some drawbacks including toxicity and acidity of reagent which were sometime not compatible to handle.[7]

A set of chlorinating agents which were previously reported to display high efficiency to convert alcohol to alkyl chloride [32] including Cl<sub>3</sub>CCOCCl<sub>3</sub>, Cl<sub>3</sub>CCOOEt, Cl<sub>3</sub>CCN, and Cl<sub>3</sub>CCONH<sub>2</sub> (entries 3, 4, 8 and 9) was chosen to utilize as a chlorinating agent to synthesize chlorosilane. The results, however, demonstrated



that these reagents gave the desired product in trace amount. In addition,  $\text{Cl}_3\text{CCONH}_2$  (entry 9) was insoluble under the reaction conditions studied. In order to investigate the effects of temperature and reaction time, two chlorinating agents,  $\text{Cl}_3\text{CCOCCl}_3$  and  $\text{Cl}_3\text{CCOOEt}$  were selected (entries 3 and 4). With these two less reactive chlorinating agent, to prolong the reaction time at higher temperature made the chlorination of hydrosilane more efficient. For instance, using  $\text{Cl}_3\text{CCOCCl}_3$ , more yield of TIPS-Cl could be lifted up from 58% to 94% when the reaction was carried out at  $55^\circ\text{C}$  for 3 and 6 h, respectively (entry 3). In case of  $\text{Cl}_3\text{CCOOEt}$ , the yield of the desired product was arose from 15% to approximately 40% upon prolonging the reaction time (entry 4).

Three ethyl chloroacetates including  $\text{Cl}_3\text{CCOOEt}$ ,  $\text{Cl}_2\text{CHCOOEt}$ , and  $\text{ClCH}_2\text{COOEt}$  (entries 4, 6, and 7) were comparatively studied for their efficiency towards this transformation. Interestingly, 88% yield of chlorosilane was detected when using  $\text{Cl}_2\text{CHCOOEt}$ , while only 25% yield was obtained in the case of  $\text{ClCH}_2\text{COOEt}$  (entry 7). The attempt to raise up the product yield using the latter reagent was not successful even in the case that the amount of the reagent was increased up to 1.50 mmol. The reaction with  $\text{Cl}_3\text{CCOOEt}$  which in fact had more Cl atoms also provided a lower yield, only 15%.

The examination on the effect of chloroethanes ( $\text{ClCH}_2\text{CH}_2\text{Cl}$ ,  $\text{Cl}_2\text{CHCHCl}_2$ , and  $\text{Cl}_3\text{CCCl}_3$ ) was conducted (entries 10, 11, and 12). It should be mentioned at this point that at the first stage of the reaction,  $\text{Cl}_3\text{CCCl}_3$ , a solid reagent, was not completely homogeneous in the reaction mixture. Nonetheless, the reaction could eventually become homogeneous within 30 min and furnished the quantitative yield of the desired products. The efficiency of this mentioned reagent was much more potent than those of  $\text{ClCH}_2\text{CH}_2\text{Cl}$  and  $\text{Cl}_2\text{CHCHCl}_2$ .

The last group of chlorinating agents studied was  $\text{CCl}_4$ ,  $\text{CHCl}_3$ , and  $\text{CH}_2\text{Cl}_2$  (entries 13, 14 and 15). The outcome revealed that  $\text{CHCl}_3$  provided 66% yield of the target product which was much higher than those using  $\text{CCl}_4$  (17%) or  $\text{CH}_2\text{Cl}_2$  (15%).

From the aforementioned results,  $\text{Cl}_3\text{CCCl}_3$  displayed as the highest efficient reagent to prepare TIPS-Cl than various chlorinating agents screened. This reagent is



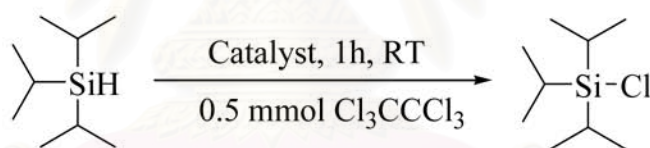
a solid which is in fact very easy to handle; nevertheless, a solubility may perhaps be its disadvantage.

The intriguing points on the mechanistic viewpoint was also arose from the observation that chlorinating agents containing more Cl atoms providing lower yield of chlorosilanes than those bearing less Cl atoms such as  $\text{CCl}_4$  vs  $\text{CHCl}_3$  or  $\text{Cl}_3\text{CCOOEt}$  vs  $\text{Cl}_2\text{CHCOOEt}$ . More details of mechanistic interpretation will be discussed in section 3.3.

### 3.2.2 The Effect of Amount and Type of Catalyst

Preliminary results revealed that in the absence of palladium catalyst, the transformation from TIPS-H to TIPS-Cl did not take place. The amount and type of palladium catalyst was thus investigated to search for optimum conditions as presented in Table 3.2.

**Table 3.2** The effect of the amount and type of catalyst to convert TIPS-H to TIPS-Cl



Entry	Catalyst (%mmol)	%Yield <sup>a</sup>		Total
		Si-Cl	Si-H	
1	none	NR	100	100
2	1.0% PdCl <sub>2</sub>	quant	0	100
3	0.5% PdCl <sub>2</sub>	84	20	104
4	1.0% Pd/C	quant	0	100

<sup>a</sup> %yield was determined by <sup>1</sup>H-NMR using toluene as an internal standard

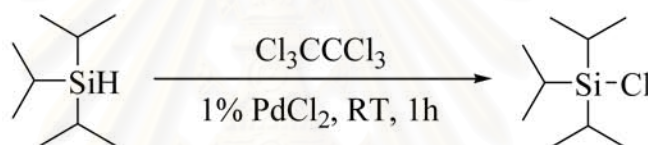
Entry 1 confirms the previous study that the target product could not be formed in the absence of palladium catalyst. Two types of catalyst examined were PdCl<sub>2</sub> and Pd/C which were previously reported in the synthesis of chlorosilane.[5,7,18] Reactions using 1%PdCl<sub>2</sub> and 1%Pd/C provided alike quantitative yield (entries 2 and 4). The yield of product was reduced when 0.5%PdCl<sub>2</sub> was employed (entry 3). Considering two palladium catalysts used, although Pd/C which can be reused provided the overall yield as same as that obtained

from PdCl<sub>2</sub>, the amount of Pd/C (10 mg) used was in fact higher than that of PdCl<sub>2</sub> (1.8 mg). Moreover, the reused Pd/C catalyst may render its activity and efficiency due to the contamination from the reaction. Accordingly, PdCl<sub>2</sub> was a suitable catalyst and was used for further exploration.

### 3.2.3 The Effect of the Amount of Cl<sub>3</sub>CCCl<sub>3</sub>

In order to find out the optimized conditions, the amount of Cl<sub>3</sub>CCCl<sub>3</sub> was one of crucial parameters for the reaction that needed to examine. The outcome is presented in Table 3.3.

**Table 3.3** The effect of the amount of Cl<sub>3</sub>CCCl<sub>3</sub> on the conversion of TIPS-H to TIPS-Cl



Entry	Cl <sub>3</sub> CCCl <sub>3</sub> (mmol)	% Yield <sup>a</sup>		Total
		Si-Cl	Si-H	
1	0.125	50	55	105
2	0.17	72	32	104
3	0.25	91	12	103
4	0.30	95	10	105
5	0.50	quant	0	100
		quant	0	100 <sup>b</sup>
6	0.75	quant	0	100

<sup>a</sup> %yield was determined by <sup>1</sup>H-NMR using toluene as an internal standard

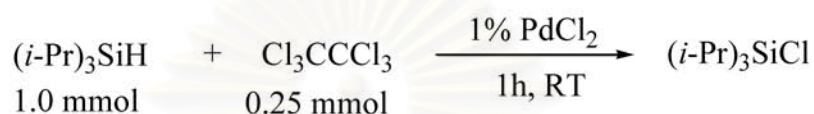
<sup>b</sup> Reaction time: 30 min

The yield of the desired product (TIPS-Cl) was increased from 50 to 95% upon raising the amount of a chlorinating agent, Cl<sub>3</sub>CCCl<sub>3</sub> from 0.125 to 0.30 mmol. The use of this chlorinating agent more than 0.5 mmol gave quantitative yield of the target molecule. It was also important to note that employing 0.5 mmol of Cl<sub>3</sub>CCCl<sub>3</sub>, the reaction time required for producing a quantitative yield of TIPS-Cl was only 30 min at RT.

### 3.2.4 The Effect of Solvent

In certain cases where hydrosilanes were solid such as triphenylsilane ( $\text{Ph}_3\text{SiH}$ ), the reaction was invariably required solvent to assist the reaction become homogenous with  $\text{Cl}_3\text{CCl}_3$ . Various solvents were tried to observe their effects on the outcome of the reaction and the results are presented in Table 3.4.

**Table 3.4** The effect of solvent on the conversion of TIPS-H to TIPS-Cl



Entry	solvent (1 mL)	% Yield <sup>a</sup>		Total
		Si-Cl	Si-H	
1	none	91	12	103
2	benzene	27	72	99
3	THF	85	20	105
4	hexane	77	27	104
5 <sup>b</sup>	$\text{CH}_3\text{CN}$	5	100	105

<sup>a</sup> % yield is determined by  $^1\text{H-NMR}$  using toluene as an internal standard

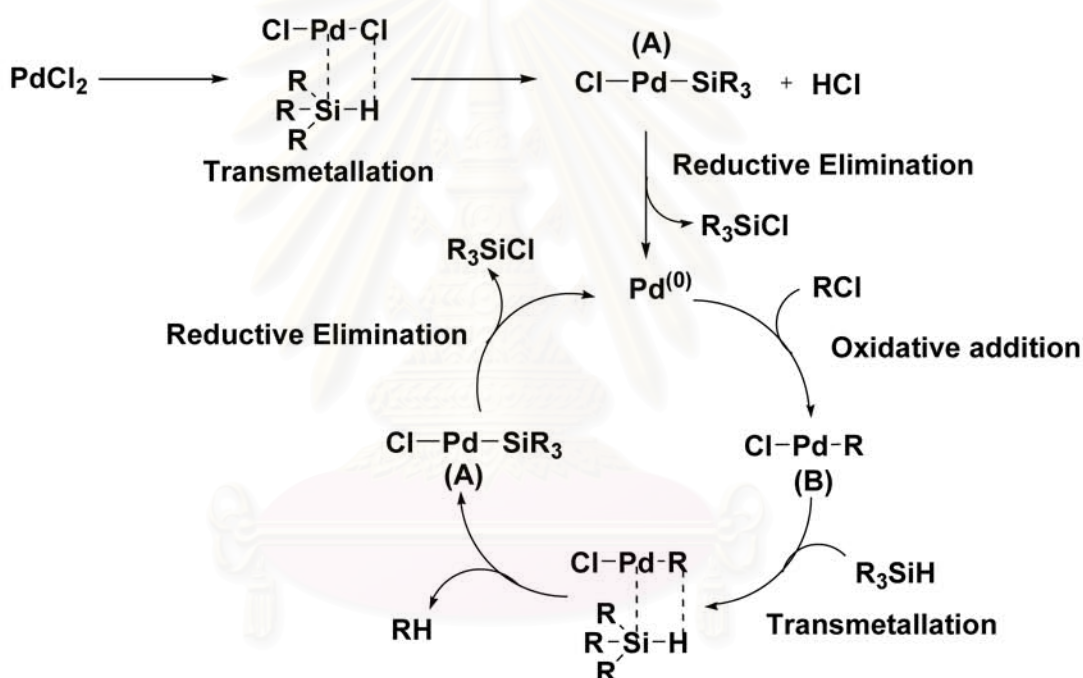
<sup>b</sup> Not completely soluble

In the reaction that solvent is required, the yield of TIPS-Cl was found to be lower than the neat reaction (entry 1). Four solvents including benzene, THF, hexane and  $\text{CH}_3\text{CN}$  were selected to employ as a reaction media.  $\text{CH}_3\text{CN}$ , a polar organic solvent could not homogenize with  $\text{Cl}_3\text{CCl}_3$  (entry 5), while benzene (entry 2), a non-polar solvent gave a trace amount of the desired product. The rest solvents: THF and hexane provided satisfactorily 85% and 77% yield of the desired product (entries 3 and 4). THF was then selected for the next study.



### 3.3 The Proposed Mechanism

Scheme 3.1 presents the proposed mechanism for the conversion of hydrosilane to chlorosilane.  $\text{PdCl}_2$  underwent transmetalation with the starting material, hydrosilane to furnish  $\text{HCl}$  and  $\text{Pd(II)}$  complex (A), followed by reductive elimination to generate chlorosilane as a product and  $\text{Pd(0)}$  as an active species. Thereupon,  $\text{Pd(0)}$  involved into the catalytic cycle by firstly undergo oxidative addition with chlorinating agents to generate  $\text{Pd(II)}$  complex (B) which reacted with hydrosilane by transmetalation to reproduce  $\text{Pd(II)}$  complex (A). Finally, this complex released chlorosilane and  $\text{Pd(0)}$ . [38]



**Scheme 3.1** The proposed mechanistic pathway towards the conversion of hydrosilanes to chlorosilanes

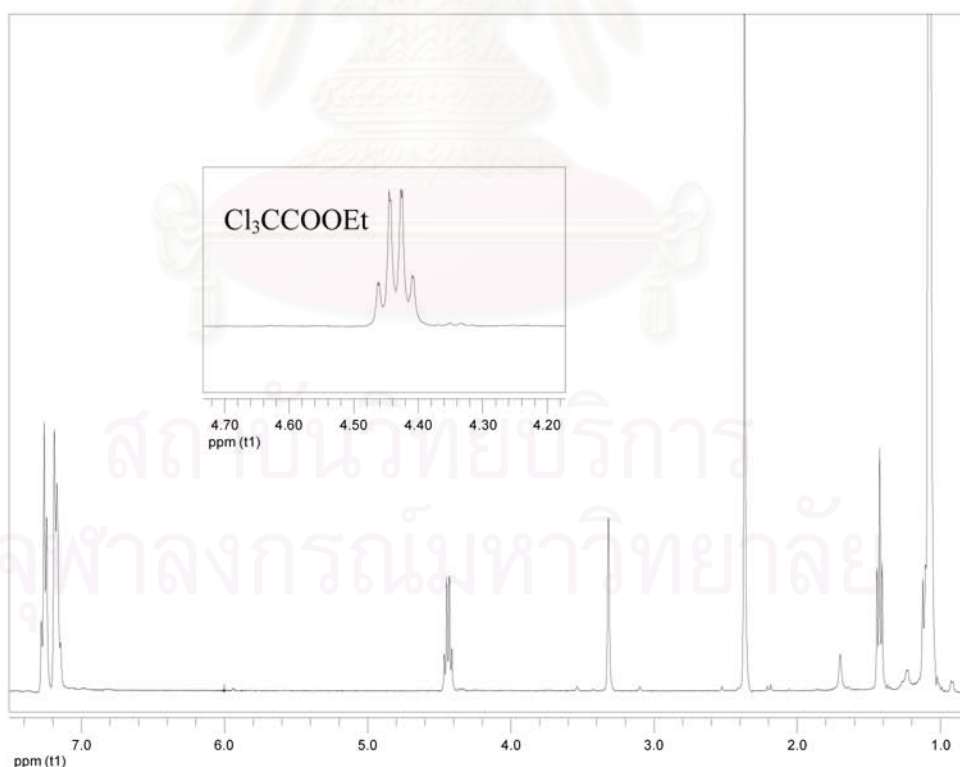
According to this proposed mechanism (Scheme 3.1), it could be noticed that only one chlorine atom involved. Therefore, it was rationalized that chlorinating agents with several chlorine atoms may be used in less amount than those containing less chlorine atoms. That was probably because  $\text{Pd(0)}$  still could react with the remained chlorine atom in chlorinating agent. However, as above-mentioned in section 3.2.1,  $\text{Cl}_3\text{CCOOEt}$  produced lower yield of  $\text{TIPS-Cl}$  than  $\text{Cl}_2\text{CHCOOEt}$



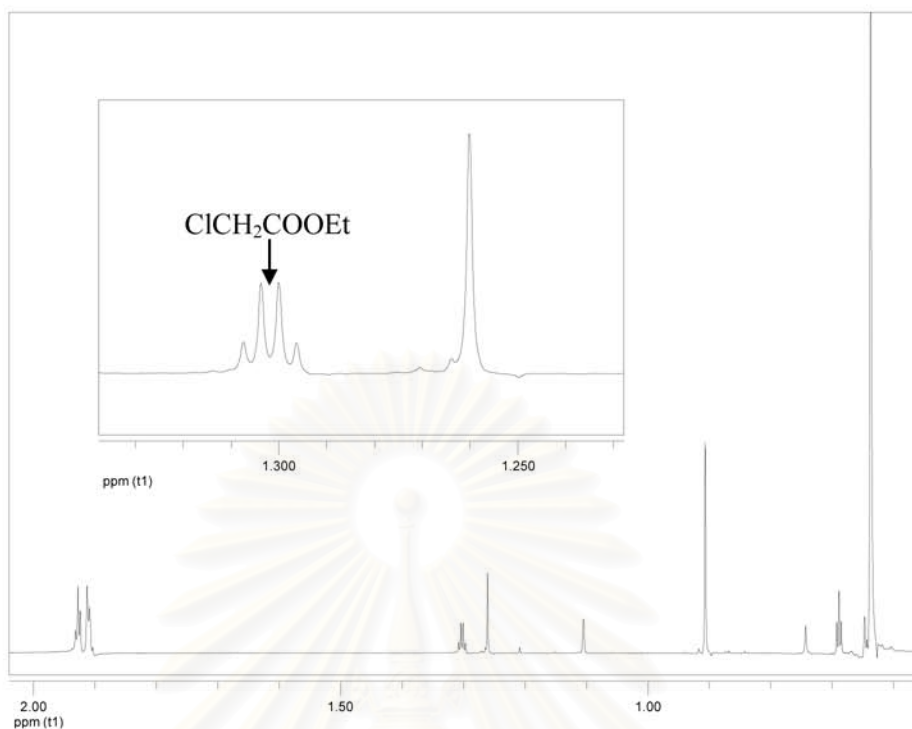
(Table 3.1, entries 4 and 6). The same observation could also clearly be seen from the experiments using  $\text{CCl}_4$  and  $\text{CHCl}_3$  (Table 3.1, entries 13 and 14).

To investigate more insight to the mechanistic pathway of this chlorination, the  $^1\text{H-NMR}$  spectra of the crude reactions using these chlorinating agents (Figs 3.2 and 3.3) were examined. For the reaction employing  $\text{Cl}_3\text{CCOOEt}$ , the methylene proton signal of the ethyl group of  $\text{Cl}_2\text{CHCOOEt}$  or  $\text{ClCH}_2\text{COOEt}$  should be detected if the reaction occurred. Nonetheless, those mentioned peaks could not be detected in the  $^1\text{H-NMR}$  spectrum (Fig 3.2). This implied that  $\text{Pd}(0)$  did not react with this chlorinating agent. In the case of  $\text{ClCH}_2\text{COOEt}$ , the same explanation could be applied (Fig 3.3).

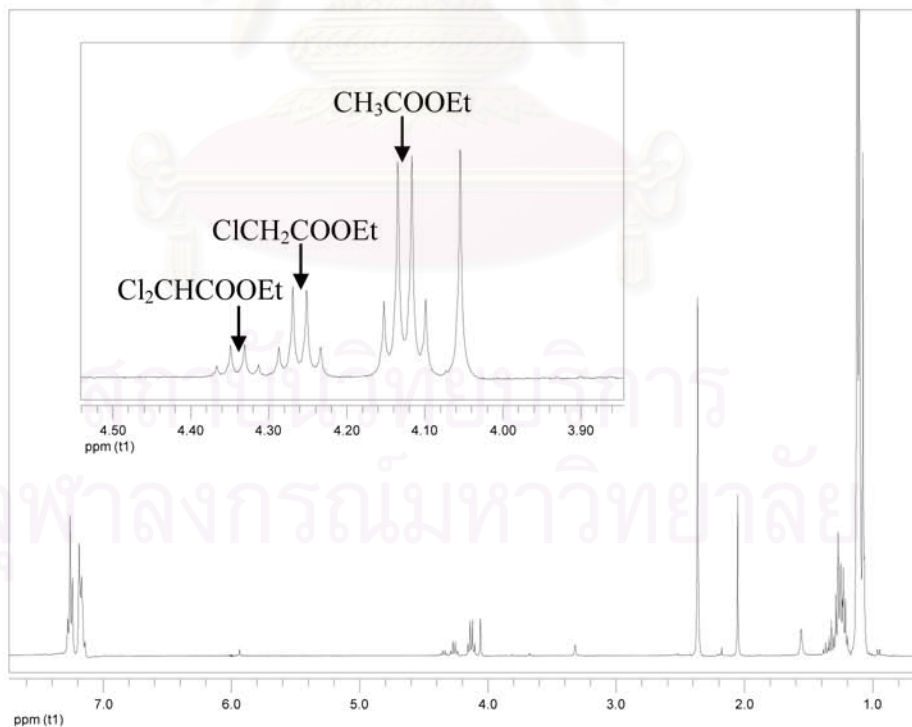
Meanwhile, the  $^1\text{H-NMR}$  spectrum (Fig 3.4) taken from the crude reaction mixture using  $\text{Cl}_2\text{CHCOOEt}$  clearly displayed the signal of  $\text{ClCH}_2\text{COOEt}$  and  $\text{CH}_3\text{COOEt}$  which should occur from the reaction between  $\text{Pd}(0)$  and  $\text{Cl}_2\text{CHCOOEt}$ , and thus providing a chlorosilane product.



**Figure 3.2** The  $^1\text{H-NMR}$  spectrum of the reaction mixture using  $\text{Cl}_3\text{CCOOEt}$  (0.50 mmol) for 1 h at RT in the presence of 1% $\text{PdCl}_2$

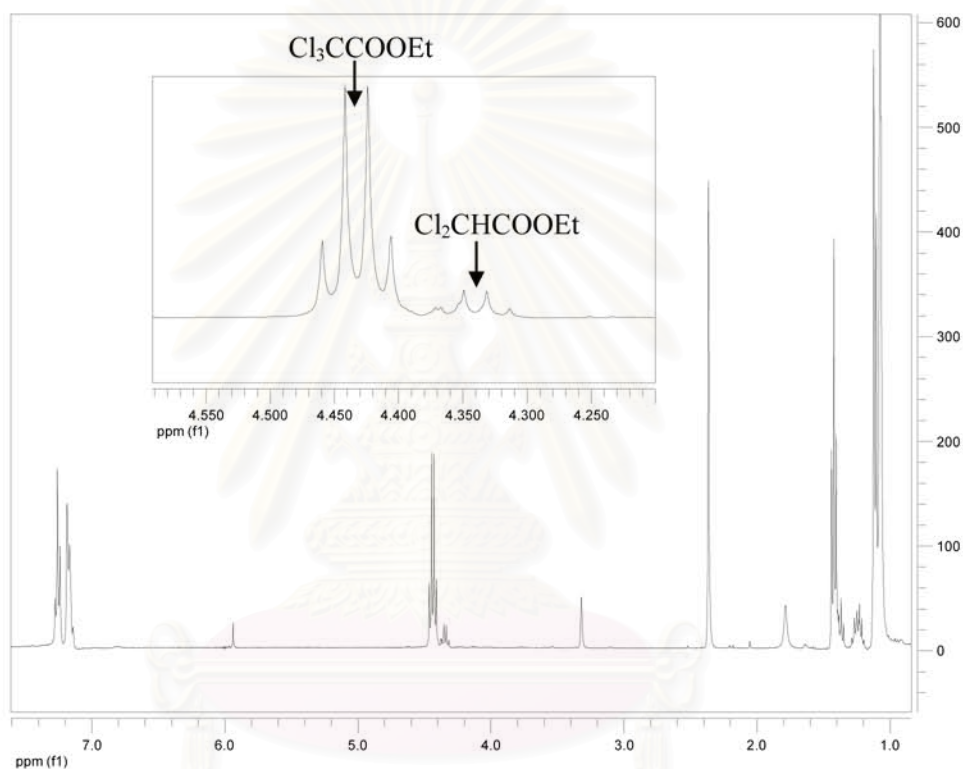


**Figure 3.3** The <sup>1</sup>H-NMR spectrum of the reaction mixture using ClCH<sub>2</sub>COOEt (0.50 mmol) for 1 h at RT with 1%PdCl<sub>2</sub>



**Figure 3.4** The <sup>1</sup>H-NMR spectrum of the reaction mixture between using Cl<sub>2</sub>CHCOOEt (0.50 mmol) for 1 h at RT with 1%PdCl<sub>2</sub>

Interestingly, in the case of using  $\text{Cl}_3\text{CCOOEt}$ , the methylene proton signal of the ethyl group of  $\text{Cl}_2\text{CHCOOEt}$  could be observed when the reaction temperature increased to  $55^\circ\text{C}$  for 3 h (Fig 3.5). This implied that lower efficient chlorinating agents could be employed, but more drastic reaction conditions such as higher temperature and longer reaction time were required. In addition, the above mentioned outcome displayed that a number of Cl and H atom in chlorinating agents had affected on the reactivity of chlorination.

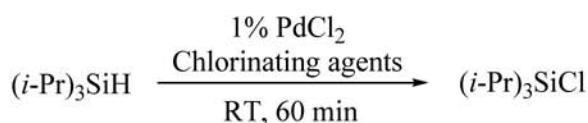


**Figure 3.5** The  $^1\text{H}$ -NMR spectrum of the reaction mixture using  $\text{Cl}_3\text{CCOOEt}$  (0.50 mmol) for 3 h at  $55^\circ\text{C}$  with 1%  $\text{PdCl}_2$

### 3.3.1 The Effect of Electron Withdrawing Groups in Chlorinating Agents

Another set of interesting observation was derived from the experiments with various ethyl chloroacetates. The results are collected in Table 3.5.

**Table 3.5** The effect of carboxyl group in chlorinating agents on chlorination of TIPS-H



Entry	Chlorinating agents	Equivalent (mmol)	% Yield <sup>a</sup>		Total
			Si-Cl	Si-H	
1	Cl <sub>2</sub> CHCOOEt	0.50	87	18	105
2	Cl <sub>2</sub> CHCOOH	0.50	60	44	104
3	Cl <sub>3</sub> CCOOEt	0.50	16	86	102
4	Cl <sub>3</sub> CCOOH	0.50	10	81	101
5	ClCH <sub>2</sub> COOEt	0.50	10	89	99
6	ClCH <sub>2</sub> COOH	1.00	NR	100	100

<sup>a</sup> %yield was determined by <sup>1</sup>H-NMR using toluene as an internal standard

The results manifestly displayed that all chloroacetic acids provided lower yield of a chlorosilane product than that achieved from ethyl chloroacetates. Among chloroacetic acids, Cl<sub>2</sub>CHCOOH produced the highest yield. This similar trend could be notified from Cl<sub>2</sub>CHCOOEt. Those implied that an electron withdrawing group such as a carboxyl group in chlorinating agents decreased the reactivity of reaction. The observed outcome implied that the oxidative addition of Pd(0) with the chlorinating agent containing two chlorine atoms may take place and transformed to Pd(II) complex as a facile step. This phenomena was previously reported in the metathesis reaction of chloroacetic acids with zinc [38] and found that Zn(0) reacted with Cl<sub>3</sub>CCOOH providing (Cl<sub>2</sub>CHCOO)<sub>2</sub>Zn, followed by the rearrangement in which hydrogen and zinc exchange process took place. According to this previous postulation, it was rationalized that Pd(0) may be occurred with Cl<sub>3</sub>CCOOH yielding (Cl<sub>2</sub>CHCOO)<sub>2</sub>Pd which perhaps had less reactivity or strong complex to react *via* metathesis with hydrosilanes. Therefore, the reaction using Cl<sub>3</sub>CCOOH as a chlorinating agent provided a low yield of product.

### 3.3.2 The Proposed Mechanistic Pathway Involving the Use of Cl<sub>3</sub>CCCl<sub>3</sub>

As aforementioned, Cl<sub>3</sub>CCCl<sub>3</sub> was the most efficient chlorinating agent. From the general mechanism described in Scheme 3.1, the <sup>1</sup>H-NMR spectrum of the reaction using Cl<sub>3</sub>CCCl<sub>3</sub> should observe the fragments of chlorinating agent occurred



from  $\text{Cl}_3\text{CCCl}_3$  reacted with  $\text{Pd}(0)$  such as  $\text{Cl}_2\text{CHCCl}_3$ ,  $\text{CH}_3\text{CCl}_3$ ,  $\text{ClCH}_2\text{CH}_2\text{Cl}$ ,  $\text{Cl}_2\text{CHCHCl}_2$  etc. Nonetheless, no detectable signal could be seen except for the signals belonging to those of product and starting material. Furthermore, the reactions using  $\text{Cl}_2\text{CHCHCl}_2$  and  $\text{ClCH}_2\text{CH}_2\text{Cl}$  (entries 10 and 11 in Table 3.1) provided only low yields of product. This observation implied that the exchange process between Cl atom and  $\text{Pd}(0)$  maybe not occurred through these chlorinating agents or it took place very fast.

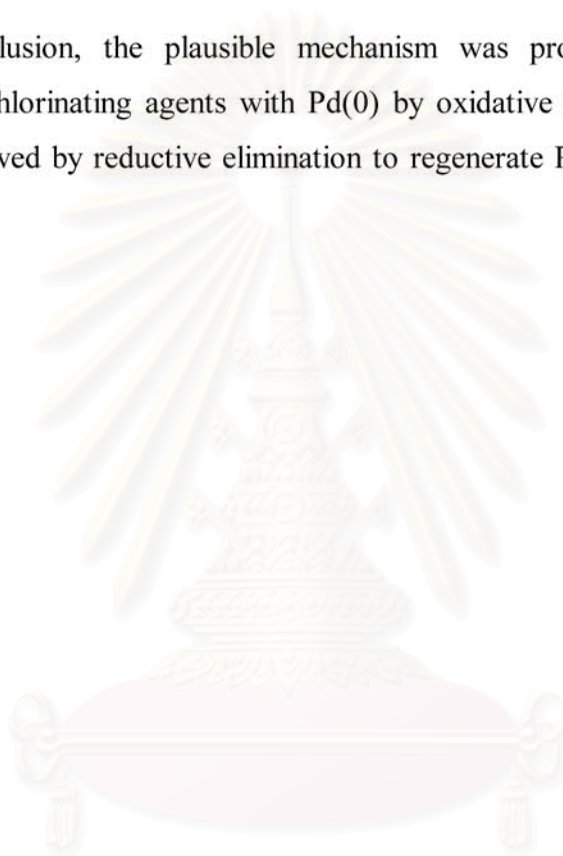
According to these obtained results,  $\text{Cl}_3\text{CCCl}_3$  and the fragments of chlorinating agents perhaps had very high reactivity; thus could not be detected. It was rationalized that if more equivalents of  $\text{Cl}_3\text{CCCl}_3$  were used in the reaction, certain fragments of chlorinating agents which should have less reactivity than  $\text{Cl}_3\text{CCCl}_3$  may be detected. Therefore, this hypothesis brought to the proposed mechanism that the exchange process took place *via* the mechanism proposed in Scheme 3.2 (pathway A), and  $\text{Cl}_3\text{CCCl}_3$  had higher reactivity than other species,  $\text{Pd}(0)$  would react with the remaining  $\text{Cl}_3\text{CCCl}_3$  providing certain fragments with lower reactivity which could be observed from  $^1\text{H-NMR}$ .

To prove this hypothesis, the reaction was carried out by using excess  $\text{Cl}_3\text{CCCl}_3$  (2 mmol) in benzene- $d_6$  (2 mL) and 1% $\text{PdCl}_2$  at RT for 1 h. The complete reaction mixture was detected by  $^1\text{H-NMR}$  and found that 60% yield of product was obtained without other signals including those of the fragments of chlorinating agents in the spectrum. This result clearly demonstrated that  $\text{Pd(II)}$  complex might not be occurred in the step of reductive elimination by pathway A to regenerate  $\text{Pd}(0)$ , but it might be occurred through insertion addition by pathway B. The latter proposed pathway was a possible hypothesis in case of using  $\text{Cl}_3\text{CCCl}_3$ .  $\text{Pd}(0)$  should react with three terminal Cl atoms and produce  $\text{CH}_3\text{CCl}_3$  which had higher reactivity than  $\text{Cl}_3\text{CCCl}_3$ . Nonetheless, the absence of the signal corresponding to  $\text{CH}_3\text{CCl}_3$  was observed in the  $^1\text{H-NMR}$  spectrum.



Cl atoms. Finally  $\text{CH}_3\text{CH}_3$  was generated from the reaction which should not be easily detected. By this proposed pathway, employing chlorinating agents in a group of chloroethane and chloromethane, no signal of chlorinating agents derived from reductive elimination should not be detected. This observation could also be seen from the reaction using  $\text{Cl}_3\text{CCOCCl}_3$  (entry 3 in Table 3.1) as a chlorinating agent, no other signal derived from the fragments of  $\text{Cl}_3\text{CCOCCl}_3$  was observed.

In conclusion, the plausible mechanism was proposed to occur by the interaction of chlorinating agents with Pd(0) by oxidative addition until no Cl atom remained, followed by reductive elimination to regenerate Pd(0) as shown in Scheme 3.2.



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### 3.4 The Synthesis of Chlorosilanes

#### 3.4.1 The Synthesis of Chlorosilanes from Monohydrosilanes

Several monohydrosilanes including phenyldimethylhydrosilane ( $\text{Ph}(\text{Me})_2\text{SiH}$ ), *tert*-butyldimethylhydrosilane (*t*- $\text{Bu}(\text{Me})_2\text{SiH}$ ), triethylhydrosilane ( $\text{Et}_3\text{Si-H}$ ), chlorodiphenyl-silane ( $\text{Ph}_2\text{SiClH}$ ), *tris*-trimethylsilylhydrosilane ( $(\text{Me}_3\text{Si})_3\text{SiH}$ ) and triphenylhydrosilane ( $\text{Ph}_3\text{SiH}$ ) were selected to explore the scope of this developed methodology. The results are presented in Table 3.6.

**Table 3.6** The conversion of monohydrosilane to chlorosilane

Hydrosilane + $\text{Cl}_3\text{CCCl}_3$		$\xrightarrow[1\text{h, RT}]{1\% \text{ PdCl}_2}$		Chlorosilane	
1.0 mmol		0.25 mmol			
Entry	Hydrosilane	Solvent (0.25 mL)	% Yield <sup>a</sup> Si-Cl	% Recovery Si-H	Total
1	$\text{Et}_3\text{SiH}$	-	78	22	100
2		-	quant	0	105 <sup>b</sup>
3	$(\text{Me}_3\text{Si})_3\text{SiH}$	-	quant	0	105
4		THF	quant	0	102
5	$\text{Ph}_3\text{SiH}$	THF	quant	0	101
6		THF	30	70	100
7	$\text{Ph}(\text{Me})_2\text{SiH}$	THF	67	34	101 <sup>b</sup>
8		THF	57	46	103 <sup>b,d</sup>
9		THF	63	41	104 <sup>e</sup>
10		THF	63	42	105 <sup>f</sup>
11	<i>t</i> - $\text{Bu}(\text{Me})_2\text{SiH}$	-	68	33	101 <sup>c</sup>
12		THF	83	13	96
13		THF	86	10	96 <sup>b</sup>
14		THF	79	20	99 <sup>b,d</sup>
15	$\text{Ph}_2\text{SiClH}$	-	89	11	100
16		THF	77	23	100
17		THF	83	17	100 <sup>b</sup>
18		THF	78	23	101 <sup>b,d</sup>

<sup>a</sup> % yield is determined by <sup>1</sup>H-NMR using toluene as an internal standard

<sup>b</sup> Using 0.50 mmol of  $\text{Cl}_3\text{CCCl}_3$  <sup>c</sup> The reaction was carried out in ice bath.

<sup>d</sup> The reaction was carried out for 2 h <sup>e</sup> Using 0.75 mmol of  $\text{Cl}_3\text{CCCl}_3$

<sup>f</sup> Using 1.00 mmol of  $\text{Cl}_3\text{CCCl}_3$

All reactions were performed under optimal conditions:  $\text{Cl}_3\text{CCCl}_3$  0.25 mmol in combination with 1%PdCl<sub>2</sub> at RT for 1 h without any extra solvent or otherwise stated.  $\text{Et}_3\text{SiH}$  could be transformed to its chloro derivative in 78% yield. The

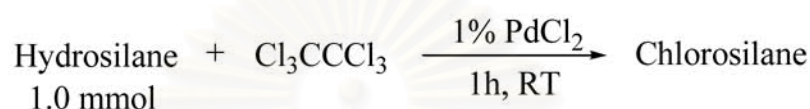


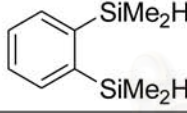
quantitative yield of this desired product could be fruitfully achieved by increasing the amount of  $\text{Cl}_3\text{CCl}_3$  to 0.50 mmol (entries 1-2).  $(\text{Me}_3\text{Si})_3\text{SiH}$  could also be converted to its chloro analogue in quantitative yield under this optimal conditions using THF as an extra solvent or under neat conditions (entries 3-4). For  $\text{Ph}_3\text{SiH}$ , a solid hydrosilane, the reaction could proceed smoothly using THF to accomplish a quantitative yield of  $\text{Ph}_3\text{SiCl}$  (entry 5). The chlorination of  $\text{Ph}(\text{Me})_2\text{SiH}$  or *tert*- $\text{Bu}(\text{Me})_2\text{SiH}$  afforded the chloro derivative in 30% and 83% yield, respectively under standard conditions (entries 6 and 12). The attempt to increase the yield was carried out by varying the amount of chlorinating agent and reaction time. In the case of  $\text{Ph}(\text{Me})_2\text{SiH}$ , the standard conditions could be employed, but doubling the amount of chlorinating agent was required (entry 7). For *tert*- $\text{Bu}(\text{Me})_2\text{SiH}$ , the best yield of the desired product was achieved from the chlorination using THF as a solvent (entry 12). Increasing the amount of chlorinating agent or prolong the reaction time did however not assist the increment of the yield of the corresponding chlorosilane (entries 13-14). The chlorination of  $\text{Ph}_2\text{SiClH}$  was successfully furnishing the chlorosilane product with 89% yield (entry 15).

### 3.4.2 The Synthesis of Chlorosilanes from Dihydrosilanes

The chlorination of three selected dihydrosilanes: diphenylhydrosilane ( $\text{Ph}_2\text{SiH}_2$ ), 1,2-*bis*(dimethylsilyl)benzene, diethylhydrosilane ( $\text{Et}_2\text{SiH}_2$ ) and 1,1,3,3-tetraisopropyldihydro-siloxane ( $((i\text{-Pr})_2\text{SiH})_2\text{O}$ ) was carried out. The results are presented in Table 3.7.

**Table 3.7** The chlorination of dihydrosilane



Entry	dihydrosilane	$\text{Cl}_3\text{CCCl}_3$ (mmol)	Solvent (0.25 mL)	% Yield <sup>a</sup>		% Recovery	
				Mono Cl	Di Cl	Si-H	Total
1		0.25	-	30	63	7	100
2		0.50	-	31	61	8	100
3		0.25	Hex	43	16	41	100
4	$\text{Ph}_2\text{SiH}_2$	0.50	Hex	41	45	11	97
5		0.25	THF	24	40	34	98
6		0.50	THF	39	47	9	95
7		0.50	THF	45	55	0	100 <sup>b</sup>
8		0.25	THF	19	17	67	103
9		0.50	-	35	20	50	105
10		0.50	THF	27	24	53	104
11	$((i\text{-Pr})_2\text{SiH})_2\text{O}$	0.25	-	60	13	29	102
12		0.50	-	61	22	19	102

<sup>a</sup> % yield is determined by  $^1\text{H-NMR}$  using toluene as an internal standard

<sup>b</sup> The reaction was performed for 6 h.

Four selected dihydrosilanes could be classified into two groups according to the number of hydrogen on Si. The first group including  $\text{Ph}_2\text{SiH}_2$  and  $\text{Et}_2\text{SiH}_2$  possessed 2 H atoms on Si whereas the other bearing only one H atom on Si: 1,2-*bis*(dimethyl-silyl)benzene and 1,1,3,3-tetraisopropyldihydrosiloxane. According to the outcome presented in Table 3.7, a higher yield of mono- and dichlorosilanes could be detected when increasing the equivalent of  $\text{Cl}_3\text{CCCl}_3$ . For  $\text{Ph}_2\text{SiH}_2$  (entries 1-7), the reaction performed in neat could provide  $\text{Ph}_2\text{SiCl}_2$  in higher yield than  $\text{Ph}_2\text{SiHCl}$ . However, the decrease of  $\text{Ph}_2\text{SiCl}_2$  and the increase of  $\text{Ph}_2\text{SiHCl}$  could be observed when solvent was employed. The use of THF provided more  $\text{Ph}_2\text{SiCl}_2$  than using

hexane. That maybe because THF could stabilize Pd(0). [39] Therefore, the reaction could be controlled to attain monosilane,  $\text{Ph}_2\text{SiHCl}$  as a major product by using hexane as a reaction media and low equivalent of  $\text{Cl}_3\text{CCCl}_3$  (entry 3). On the other hand, dichlorosilane,  $\text{Ph}_2\text{SiCl}_2$  could be produced as a major product when higher equivalent of  $\text{Cl}_3\text{CCCl}_3$  and no extra solvent were used. Based on the mechanism proposed,  $\text{Ph}_2\text{SiCl}_2$  was occurred by double chlorination of  $\text{Ph}_2\text{SiH}_2$  (*via*  $\text{Ph}_2\text{SiHCl}$ ). Therefore, the examination on the reactivity of chlorination between  $\text{Ph}_2\text{SiHCl}$  and  $\text{Ph}_2\text{SiH}_2$  may give clue for this aspect. The chlorination of  $\text{Ph}_2\text{SiHCl}$  yielding  $\text{Ph}_2\text{SiCl}_2$  must be a faster process than that of  $\text{Ph}_2\text{SiH}_2$  giving  $\text{Ph}_2\text{SiHCl}$ . This was stemmed from the experimental fact to detect a higher yield of  $\text{Ph}_2\text{SiCl}_2$  than  $\text{Ph}_2\text{SiH}_2$ . This could be explained by the mechanism in the step of transmetallation that Si-H bond strength was decreased in the presence of chlorine substituent on Si atom. Thus, transmetallation step of the substrate bearing an electron withdrawing group in the molecule should occurred more rapidly.

For 1,2-*bis*(dimethylsilyl)benzene, the reaction provided only trace amount of product even the amount of  $\text{Cl}_3\text{CCCl}_3$  was increased from 0.25 to 0.50 mmol or the reaction was performed in THF or neat (entries 8-10). In the case of 1,1,3,3-tetraisopropyldihydrosiloxane (entries 11-12), the reaction provided mainly monochlorosilane in moderate yield with less dihydrosilane. The main reason for the reactions of dihydrosilane substrates in this group providing a moderate yield of product was probably the steric hindrance of substrates.

### 3.4.3 Optimal Conditions for Controlling the Distribution of Chlorosilanes

$\text{Et}_2\text{SiH}_2$  was selected as a model to study the favorable conditions to synthesize a particular chlorosilanes. Several factors were explored including amount of  $\text{Cl}_3\text{CCCl}_3$ , reaction time, ratio of  $\text{PdCl}_2$  and amount of THF. The results are exhibited in Table 3.8.



**Table 3.8** Optimal conditions study for controlling the distribution of chlorosilanes

$$\text{Et}_2\text{SiH}_2 + \text{Cl}_3\text{CCCl}_3 \xrightarrow[1\text{h, RT}]{1\% \text{ PdCl}_2} \text{Product}$$

1.0 mmol

Entry	THF (mL)	Cl <sub>3</sub> CCCl <sub>3</sub> (mmol)	%Yield <sup>a</sup>		% Recovery	Total
			Mono Cl	Di Cl	Si-H	
1	-	0.25	31	27	45	103
		0.50	27	43	30	100
		0.65	22	62	15	99
2	0.10	0.50	34	37	31	102
		0.65	35	32	33	100
3	0.25	0.25	36	7	60	103
		0.50	40	17	44	101
		0.50	47	6	47	100 <sup>b</sup>
		0.50	38	25	38	101 <sup>c</sup>
		0.65	42	30	28	100
4	0.50	0.50	47	3	52	102
		0.65	54	10	36	100

<sup>a</sup> %yield was determined by <sup>1</sup>H-NMR using toluene as an internal standard

<sup>b</sup> Using 2%mmol PdCl<sub>2</sub>

<sup>c</sup> The reaction was carried out for 2 h

Table 3.8 displays that under neat conditions, higher yield of Et<sub>2</sub>SiCl<sub>2</sub> could be obtained when more equivalents of Cl<sub>3</sub>CCCl<sub>3</sub> was used. The reaction carried out using THF as a solvent gave lower yield. The more THF, the less product attained. This was understandable that the reaction containing solvent made the dilution and thus the rate of reaction was decreased. When 0.50 mmol of Cl<sub>3</sub>CCCl<sub>3</sub> was used (entry 3), the reaction gave higher yield of Et<sub>2</sub>SiCl<sub>2</sub>. With longer reaction time or increasing the amount of PdCl<sub>2</sub>, not significant increment of the desired product was observed.

Therefore, it could be seen that Et<sub>2</sub>SiCl<sub>2</sub> could be produced as a major product when more equivalent of Cl<sub>3</sub>CCCl<sub>3</sub> and long reaction time were utilized in the absence of any extra solvent. On the other hand, the using THF as a solvent would be a choice for the formation of Et<sub>2</sub>SiHCl as a major product.

## Part II Synthesis of Bromosilanes

### 3.5 The Synthesis of Brominating Agents

Two brominating agents: Br<sub>3</sub>CCOOEt and Br<sub>3</sub>CCOCBr<sub>3</sub> were synthesized. The former was obtained from the esterification of Br<sub>3</sub>CCOOH with EtOH in the



presence of conc  $\text{H}_2\text{SO}_4$  as a catalyst [34-35], whereas the latter was gained from the bromination of acetone. [36]

The  $^1\text{H}$ -NMR spectrum of  $\text{Br}_3\text{CCOOEt}$  reveals two peaks of a methylene group resonating at  $\delta_{\text{H}}$  4.46 ( $q$ ,  $J = 7.20$  Hz) and a methyl group at  $\delta_{\text{H}}$  1.36 ( $t$ ,  $J = 7.20$  Hz). The  $^{13}\text{C}$ -NMR spectrum exhibits a carbonyl carbon at  $\delta_{\text{C}}$  161.9, the carbon atom bearing three bromine atoms at  $\delta_{\text{C}}$  65.7 and two peaks at 29.5 and 13.7 belonging to methylene and methyl carbons, respectively.

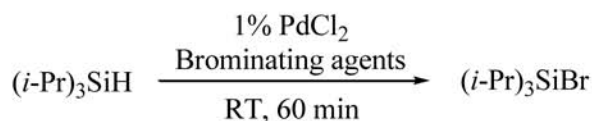
The  $^{13}\text{C}$ -NMR spectrum of  $\text{Br}_3\text{CCOCBr}_3$  exhibits a carbonyl carbon at  $\delta_{\text{C}}$  173.5 and the other peak of the carbon bearing bromine atoms at  $\delta_{\text{C}}$  24.5.

### 3.6 The Synthesis of Bromosilanes

Generally, bromosilanes had a higher reactivity than chlorosilane as a result of a good leaving group of bromine atom. Based on literature review, bromosilanes could be synthesized from hydrosilanes by using  $\text{CuBr}_2/\text{CuI}$  as a catalyst or  $\text{CBr}_4$  as brominating agent in the presence of  $\text{PdCl}_2$  as a catalyst.

As previously stated, chlorosilanes could be accomplishedly synthesized from hydrosilanes using this developed methodology. To extend the utilization of this method, the synthesis of bromosilanes from hydrosilanes was explored. Several brominating agents including  $\text{CBr}_4$ ,  $\text{Br}_3\text{CCOOH}$ ,  $\text{Br}_3\text{CCOOEt}$  and  $\text{Br}_3\text{CCOCBr}_3$  were examined. TIPS-H was used as a model to synthesize TIPS-Br. The results are accumulated in Table 3.9.

TIPS-Br was attained in 30% yield from the reaction of TIPS-H and  $\text{CBr}_4$  in THF (entry 1). Only 9% was obtained when the reaction was carried out in the absence of  $\text{PdCl}_2$  catalyst (entry 2). This also confirmed the essence of Pd in this bromination catalytic cycle. The reaction employing  $\text{Br}_3\text{CCOOH}$  under standard conditions provided 54% yield of product, whereas adding THF as an extra solvent and in the absence of  $\text{PdCl}_2$  rendered the reaction efficiency giving 30% and 0% yield of the target molecule, respectively (entries 3-5). The use of  $\text{Br}_3\text{CCOOEt}$  did not either give TIPS-Br in good yield under these conditions examined (entry 6). Interesting results could be observed from the utilization of  $\text{Br}_3\text{CCOCBr}_3$  (entries 7-10).

**Table 3.9** The conversion of hydrosilanes to bromosilanes

Entry	brominating agents	Equivalent (mmol)	%Yield <sup>a</sup> % Recovery		Total
			Si-Br	Si-H	
1	CBr <sub>4</sub>	0.50	30	70	100 <sup>b</sup>
2			9	91	100 <sup>b,c</sup>
3			54	41	95
4	Br <sub>3</sub> CCOOH	0.50	30	72	102 <sup>b</sup>
5			0	97	97 <sup>b,c</sup>
6	Br <sub>3</sub> CCOOEt	0.50	10	85	95
7			30	70	100
8	Br <sub>3</sub> CCOCBr <sub>3</sub>	0.25	49	56	105 <sup>b</sup>
9			49	56	105 <sup>b,c</sup>
10			96	7	103 <sup>b,c,d</sup>

<sup>a</sup> %yield was determined by <sup>1</sup>H-NMR using toluene as an internal standard

<sup>b</sup> Using THF 0.25 mL as solvent

<sup>c</sup> The reaction was carried out in the absence of PdCl<sub>2</sub>

<sup>d</sup> Using UV light at 254 nm

Under the optimal conditions, only 30% yield of product was achieved; that might be because of non-homogeneity of the reaction mixture. This insolubility of the reagent could be solved by using THF, resulting in giving TIPS-Br approximately 50%. More intriguingly, in the absence of Pd catalyst, unlike other cases, the amount of the desired product was attained in the same level as that observed in the presence of catalyst. This observation strongly implied that the use of Br<sub>3</sub>CCOCBr<sub>3</sub> may not need to incorporate with Pd catalyst, but perhaps involving a radical process. To prove this hypothesis, the reaction was allowed to carry out in the same manner under UV light (254 nm) in the absence of Pd catalyst. TIPS-Br was obtained in almost quantitative yield (96%). Thus, it could confirm that the mechanistic pathway operated in this special case occurred through a radical process. To our best knowledge, there was no report concerning the use of Br<sub>3</sub>CCOCBr<sub>3</sub> in bromination of hydrosilanes activating by UV. Thus, this was the first report of the synthesis of bromosilane by this unique methodology.

### 3.7 Applications of the developed methodologies for the synthesis of silyl ethers and silyl esters

This disclosed methodology for the preparation of halosilanes directly from hydrosilanes was further applied for one-pot synthesis of silyl ether and silyl ester. The former could be accomplished by the reaction of the *in situ* generated halosilanes with alcohols, while the latter could be fruitfully synthesized by those with the corresponding carboxylic acids.

For the one-pot synthesis of silyl derivatives, the reaction constituted of two steps.

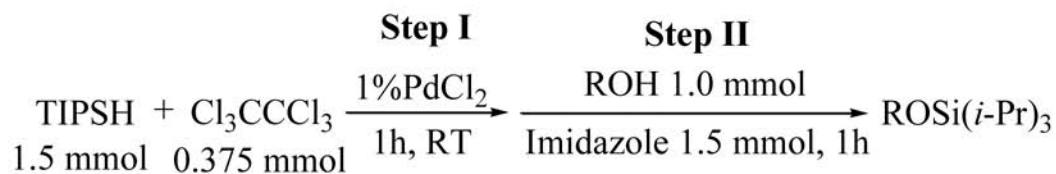
Step I: the preparation of chlorosilane using TIPS-H 1 eq (1.50 mmol) as a substrate, chlorinating agent 0.25 eq (0.375 mmol), 1%PdCl<sub>2</sub> (2.6 mg) for 1 h at RT.

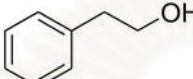
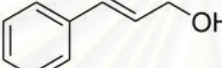
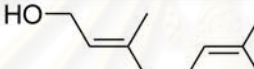
Step II: The synthesis of silyl derivatives was completed from the reaction of the received chlorosilane with selected alcohol or carboxylic acid (1.0 mmol) under optimal conditions.

#### 3.7.1 The one-pot synthesis of silyl ethers

TIPS-H was used as a model compound reacting with Cl<sub>3</sub>CCCl<sub>3</sub> in the same fashion under the optimal conditions described earlier. After the reaction was completed in the first step, a selected alcohol and imidazole were added to the reaction mixture and stirred for another 1 h to furnish the desired silyl ethers. All silyl ethers were extracted with 1 N HCl, saturated aqueous NaHCO<sub>3</sub>, subsequently, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and evaporated. The residue was purified by column chromatograph using hexane as an eluent. The results of the conditions optimization including the effect of type of alcohols, temperature and an additive, DMAP on the outcome of the reaction are displayed in Table 3.10.



**Table 3.10** The one-pot synthesis of silyl ethers

Entry	Alcohol	Temp (°C)	DMAP (mmol)	%Isolated yield
1			-	65 <sup>a</sup>
2		RT	-	64
3			0.50	70
4			0.50	82 <sup>b</sup>
5		55	0.50	79
6			0.50	NR <sup>c</sup>
7		55	0.50	75 (103) <sup>d</sup>
8		55	0.50	80 (100) <sup>d</sup>

<sup>a</sup> Using THF 0.50 mL <sup>b</sup> The reaction was performed for 2 h <sup>c</sup> The reaction was performed in one step for 1 h <sup>d</sup> % yield is determined by <sup>1</sup>H-NMR using toluene as an internal standard

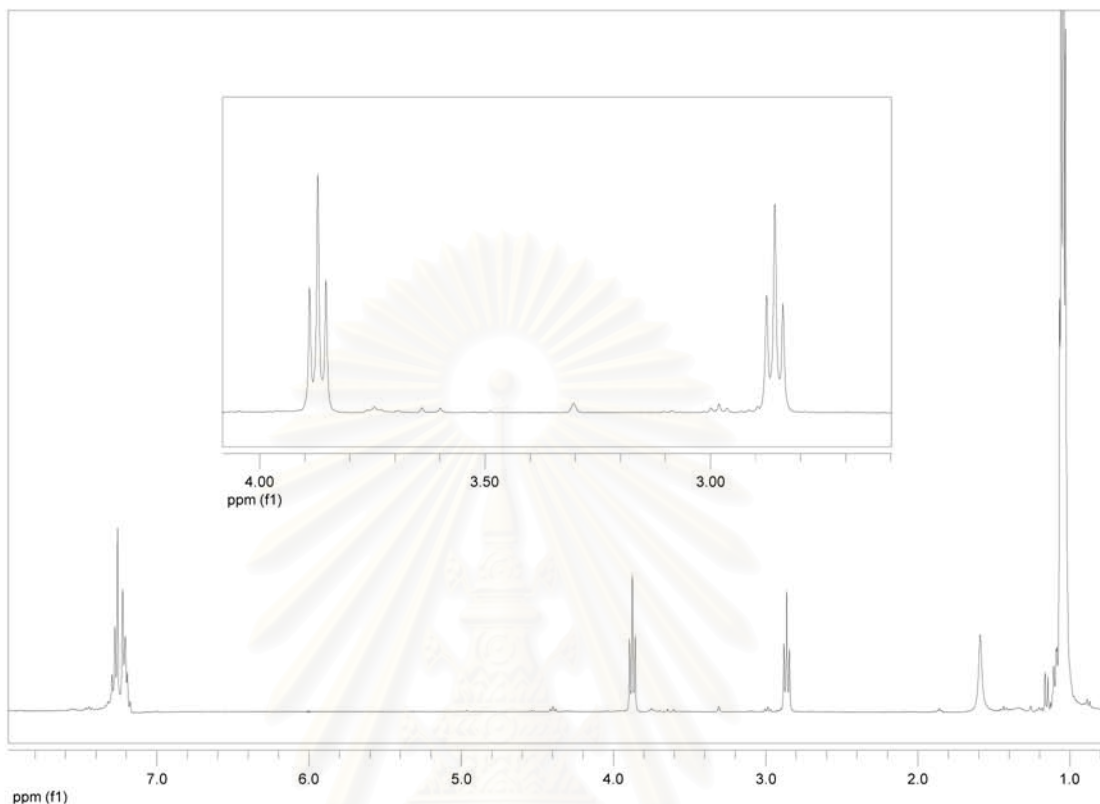
To search for optimal conditions and the scope of this one-pot protocol, particularly in step II, 2-phenylethanol was chosen as a model. The reactions carried out at RT provided the same result approximately 65% yield of the target product either using THF as an extra solvent or not. The addition of DMAP (0.5 mmol) as a co catalyst furnished 70% yield. More impressive result could be attained from prolonging the reaction to 2 h (82%). Lifting the reaction temperature to 55°C also made the yield of the desired silyl ether higher to 79% (reaction time 1 h). The reaction was however totally not occurred when it was consolidated in one step.

Under these particular optimal conditions above, this protocol was tested for other two chosen alcohols: cinnamyl alcohol and geraniol, and the desired silyl ethers could be successfully obtained in quantitative yield (NMR) and 75% and 80% isolated yield, respectively.

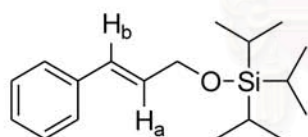
Four peaks visualized from the <sup>1</sup>H-NMR spectrum of triisopropyl(phenethoxy)silane (Fig 3.6) could be assigned for the isopropyl protons resonating at  $\delta_{\text{H}}$  1.05 (*d*,  $J = 5.07$  Hz, 21H), methylene protons at  $\delta_{\text{H}}$  2.86 (*t*,  $J = 7.22$



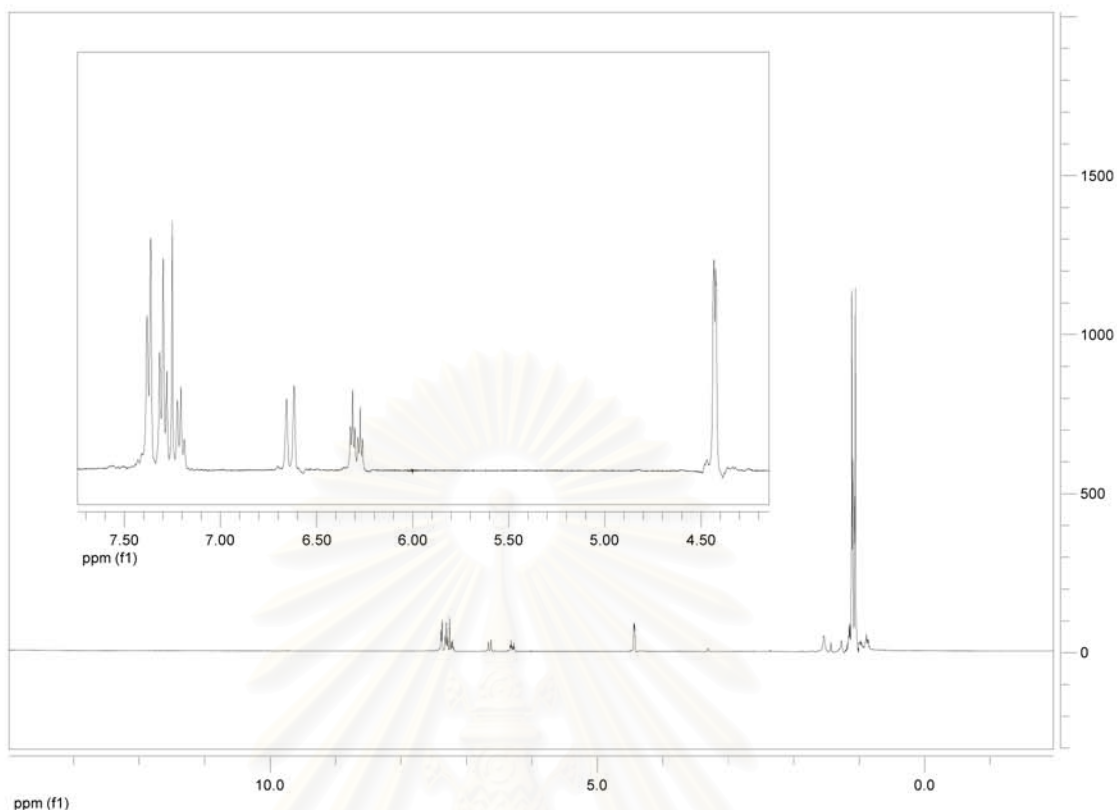
Hz, 2H, H<sub>a</sub>) on the carbon bearing a phenyl group, methylene protons at  $\delta_{\text{H}}$  3.88 (*t*,  $J = 7.21$  Hz, 2H, H<sub>b</sub>) connecting to siloxyl group and phenyl protons at  $\delta_{\text{H}}$  7.25 (*m*, 5H).



**Figure 3.6** The <sup>1</sup>H-NMR spectrum of triisopropyl(phenethoxy)silane

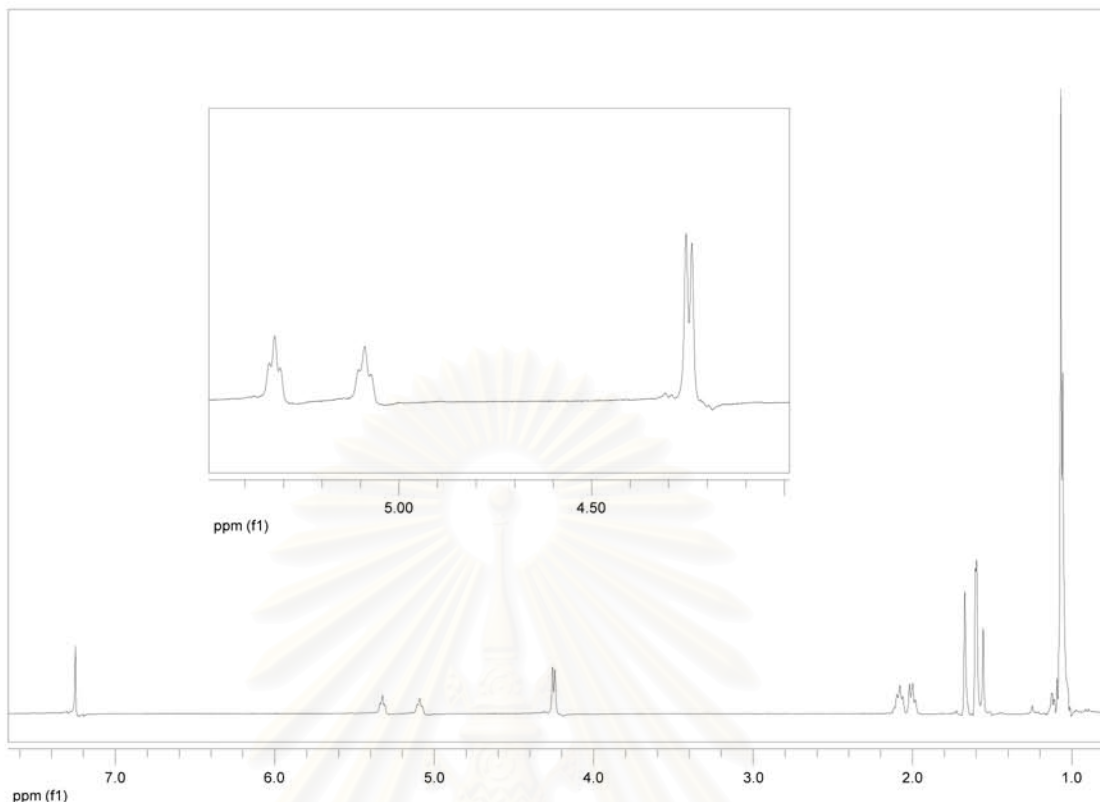


The <sup>1</sup>H-NMR spectrum of cinnamyloxytriisopropylsilane (Fig 3.7) revealed five peaks of the isopropyl protons detecting at  $\delta_{\text{H}}$  1.08 (*d*,  $J = 5.97$  Hz, 21H), two methylene protons on the carbon bearing a siloxyl group at  $\delta_{\text{H}}$  4.43 (*d*,  $J = 3.32$  Hz, 2H),  $\text{-CH-}$  on the carbon nearing the methylene group at  $\delta_{\text{H}}$  6.29 (*dt*,  $J = 15.86, 4.67$  Hz, H<sub>a</sub>),  $\text{-CH-}$  connecting to phenyl group at  $\delta_{\text{H}}$  6.63 (*d*,  $J = 15.85$  Hz, H<sub>b</sub>), and phenyl protons at  $\delta_{\text{H}}$  7.34 (*m*, 5H).



**Figure 3.7** The  $^1\text{H}$ -NMR spectrum of cinnamyloxytriisopropylsilane

Seven peaks observed from the  $^1\text{H}$ -NMR spectrum of *trans*-(3,7-dimethylocta-2,6-dienyloxy)triisopropylsilane (Fig 3.8) could be assigned for the protons of isopropyl group resonating at  $\delta_{\text{H}}$  1.05 (*d*,  $J = 4.83$  Hz, 21H). The methyl protons at  $\delta_{\text{H}}$  1.59 (*s*, 3H,  $\text{H}_{\text{a}}$ ) and two methyl protons ( $\text{H}_{\text{b}}$ ) at  $\delta_{\text{H}}$  1.64 (*s*, 6H), the methylene protons ( $\text{H}_{\text{c}}$ ) at  $\delta_{\text{H}}$  2.00 (*t*,  $J = 6.93$  Hz, 2H), the methylene protons ( $\text{H}_{\text{d}}$ ) at  $\delta_{\text{H}}$  2.07 (*t*,  $J = 7.17$  Hz, 2H,  $\text{H}_{\text{d}}$ ),  $-\text{CH}_{\text{e}}=$  at  $\delta_{\text{H}}$  5.09 (*t*,  $J = 6.53$  Hz) and  $-\text{CH}_{\text{f}}=$  at  $\delta_{\text{H}}$  5.32 (*t*,  $J = 5.71$  Hz) on the carbon bearing a methylene group connecting to a siloxyl group could be clearly detected.



**Figure 3.8** The  $^1\text{H-NMR}$  spectrum of *trans*-(3,7-dimethylocta-2,6-dienyloxy)triisopropylsilane

### 3.7.2 The one-pot synthesis of silyl esters

By the same fashion, the *in situ* generated chlorosilane was allowed to react with carboxylic acid to produce silyl ester. The quantification of the yield of silyl ester was done by  $^1\text{H-NMR}$  technique since the unstable silyl ester product could not purify by column chromatograph. Four carboxylic acids including 2-phenylacetic acid, 2-methylbenzoic acid, *trans*-3-(4-methoxyphenyl) acrylic acid and 3-methoxybenzoic acid were selected as a model to synthesize silyl esters. The results are presented in Table 3.11.





## CHAPTER IV

### CONCLUSION

The purpose of this research is to develop the new methodology to synthesize halosilanes from hydrosilanes in combination with  $\text{PdCl}_2$  as a catalyst and to explore the optimum conditions under mild conditions. The application of the developed methodology for the one-pot synthesis of silyl derivatives including silyl ether and silyl ester was also carefully explored.

The conversion of hydrosilanes into their chlorosilanes utilizing a combination of  $\text{Cl}_3\text{CCCl}_3$  with  $\text{PdCl}_2$  could be smoothly converted to the corresponding chlorosilanes in high yield under mild conditions at RT with short reaction time. The plausible mechanism was proposed to occur by the interaction of chlorinating agents with  $\text{Pd}(0)$  by oxidative addition until no Cl atom remained, followed by reductive elimination to regenerate  $\text{Pd}(0)$ .

The reactions of dihydrosilanes providing a moderate yield of product was probably due to steric hindrance of substrates. For controlling the distribution of chlorosilanes from dihydrosilanes, it could be seen that  $\text{Et}_2\text{SiCl}_2$  could be produced as a major product when more equivalent of  $\text{Cl}_3\text{CCCl}_3$  and long reaction time were utilized in the absence of any extra solvent. On the other hand, using THF as a solvent would be a choice for the formation of  $\text{Et}_2\text{SiHCl}$  as a major product.

The utilizing of  $\text{Br}_3\text{CCOCBr}_3$  with the irradiation of UV light (254 nm) could also be another viable tool for synthesis of bromosilanes from the corresponding hydrosilanes in high yield under mild conditions at RT. The mechanistic pathway operated was occurred *via* a radical process.

This general methodology of synthesis of chlorosilanes could also be further applied for the preparation of silyl derivative as silyl ether from alcohol and silyl ester from carboxylic acid as a one-pot reaction in high yield.

### Proposal for the Further Work

This research concerns with the development of methodology for synthesis of halosilanes from hydrosilanes and application of this methodology to prepare silyl derivative in one-pot reaction. This outcome opened many possibilities to deal with further exploration. This methodology should be applied with Mukayama aldol condensation and developed the new combination reaction for one-pot synthesis.



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