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Selective mono- and di-allylation and allenylation of chlorosilanes using indium

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ABSTRACT

Allyl and allenyl groups have been introduced into silicon systems by the allylation and allenylation of chlorosilanes using allyl bromide or propargyl bromide with indium. The allylation of chlorosilanes afforded a variety of aryl, aralkyl, and alkenyl substituted allylsilanes. By applying this method, the reactions of 1-bromo-3-methylbut-2-ene, 3-bromo-2-methylprop-1-ene and 3-bromobut-1-ene with chlorosilanes also proceed smoothly to give regioselectively allylic rearrangement products in good yields. Mediated by indium, dichlorosilanes (R_2SiCl_2) and trichlorosilanes ($RSiCl_3$) can either afford monoallylated silanes or diallylated silanes depending on the amount of allyl bromide and indium used.

1. Introduction

Allylsilanes have become a commonly used class of organosilicon reagents as applied to organic synthesis. Hydrolysis and dehydration of di- and tri-chloroallylsilanes yield polysiloxanes which retain the unsaturated groups, permitting additional polymerization across the double bonds to synthesize the functional polymers [1]. A variety of methods have been used for the preparation of allylsilanes. Among them, the reactions of allylic Grignard reagents with chlorosilanes and alkoxysilanes offer a convenient route to the synthesis of various industrial useful organosilicon compounds. However, only moderate yields of the products could be obtained in the preparation of allylic chlorosilanes with this method [2]. Allyltrichlorosilane can be prepared readily using Cu mediated reaction of allyl chloride with trichlorosilane [3]. Sakurai reported the selective allylation of polychlorosilanes by an organozinc procedure [4]. Recently, some modified approaches have been reported for the synthesis of unsaturated organosilicon compounds, such as hydrosilylation and silylmetallation and/or carbosilylation of alkynes or hydrometallation and hydrogenation of alkynylsilanes [5,6]. These methods are useful for the preparation of novel and well-known silicon-containing alkenes, but it did not work well for synthesis of unsaturated chlorosilanes [7,8]. We previously found that allylsamarium bromide was a versatile reagent for the allylation of chlorosilanes with allyl bromide, but when $RCH{=}CHCH_2Br$ or 3-bromoprop-1-yne was used, this method failed [9]. Herein we reported the organoindium mediated selective mono- and di-allylation and allenylation of chlorosilanes into allylsilanes and allenylsilanes.

2. Results and discussion

2.1. Indium induced allylation of chlorosilanes (R_3SiCl) with allyl bromide

The reactions of various trisubstituted chlorosilanes (R_3SiCl) with allyl bromide were carried out in the presence of indium in DMF at room temperature. After stirring for several hours, the reaction mixture was quenched with 0.1 M hydrochloric acid and extracted with diethyl ether. The ether was evaporated and purified by column chromatography to give the corresponding allylsilanes in good yields. The products were identified by comparing their IR, NMR, MS spectra. The results are summarized in Table 1.

When chlorodiphenylsilane was treated with allyl bromide in the presence of indium powder in DMF or DMI (1,3-dimethylimidazolidine) at room temperature, allyldiphenylsilane was obtained in 98% and 82% isolated yields, respectively. When the reaction was performed in THF under the similar reaction conditions, no reaction took place (Scheme 1). The chlorodiphenylsilane, indium and allyl bromide were used in a ratio of 1:1:1.5. The aliphatic chlorosilane such as chlorotrimethylsilane also reacted with allyl bromide giving the corresponding allyltrimethylsilane (**3e**) in good yield (entry 5). The reactions of 1-bromo-3-methylbut-2-ene, 3-bromo-2-methylprop-1-ene and 3-bromobut-1-ene with chlorodiphenylsilane also proceed smoothly to give the corresponding allylation products in good yields (entries 6–8). Noteworthy is that the products of the allylic rearrangement were obtained regioselectively exclusively. Thus, the reactions gave (2-methylbut-3-en-2-yl)-diphenylsilane (**3f**), (2-methylallyl)diphenylsilane (**3g**) and (*E*)-but-2-enyldiphenylsilane (**3h**), respectively, but no (3-methylbut-2-enyl)diphenylsilane, (2-methylallyl)diphenylsilane or but-3-en-2-yldiphenyl silane was detected in the products. When a mixture of 3-bromocy-

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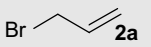
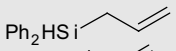
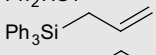
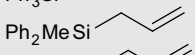
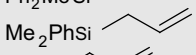
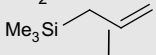
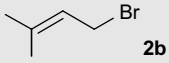
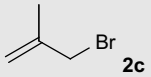
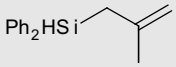
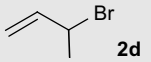
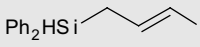
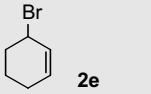
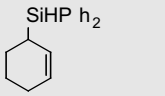
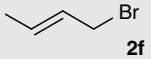
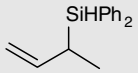
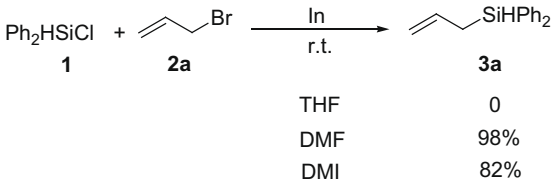
Table 1
Allylation of trisubstituted chlorosilanes (R_3SiCl)[a]

Entry	Allyl bromide	Substrate	Product	Yields[b] (%)
1	 **2a**	Ph_2HSiCl	 **3a**	98
2	**2a**	Ph_3SiCl	 **3b**	97
3	**2a**	$Ph_2MeSiCl$	 **3c**	98
4	**2a**	$PhMe_2SiCl$	 **3d**	87
5	**2a**	Me_3SiCl	 **3e**	78
6	 **2b**	Ph_2HSiCl	**3f**	96
7	 **2c**	Ph_2HSiCl	 **3g**	94
8	 **2d**	Ph_2HSiCl	 **3h**	93[c]
9	 **2e**	Ph_2HSiCl	 **3i**	92
10	 **2f**	Ph_2HSiCl	 **3j**	94

[a] Unless otherwise noted, chlorosilanes (1 mmol) were allowed to react with In (1 mmol) and allyl bromide (1.5 mmol) in DMF at room temperature for 3 h.
[b] Isolated yields based on chlorosilane used.
[c] *Z*/*E* = 5/94.



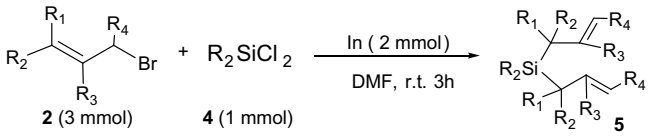
Scheme 1.

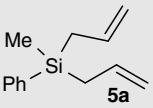
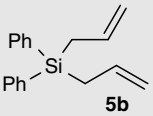
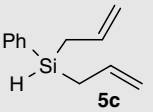
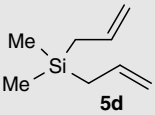
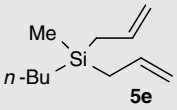
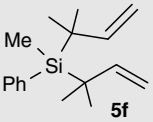
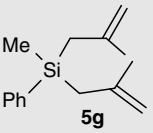
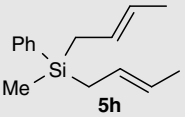
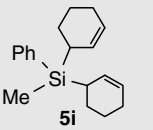
clohex-1-ene and chlorodiphenylsilane were treated with 1 equiv. of indium powder in DMF for 3 h, cyclohex-2-enyldiphenylsilane (**3i**) was obtained in 92% isolated yield (entry 9).

2.2. Indium induced allylation of organodichlorosilanes (R_2SiCl_2) with allyl bromide

Unsaturated chlorosilanes, in which the aryl and aralkyl groups are directly linked with silicon, were widely used in the preparation of functional polysiloxanes with good thermal stability and a rapid cure [10]. The syntheses of unsaturated chlorosilanes was first reported by Hurd [11]. Pure aryl or aralkyl allyldichlorosilanes were prepared from allyl- and vinyltrichlorosilane and the appropriate Grignard reagent [12]. However, in most reactions carried out between Grignard reagent and chlorosilanes to form partially substituted arylchlorosilanes, successive substitution products were always formed [13]. In our studies for the construction of Si–C bond, we found that the substitution reaction between organodichlorosilanes (R_2SiCl_2) and allyl bromide could be controlled at the desired mono- or di- substituted manner. When dichlorosilanes (R_2SiCl_2), indium and allyl bromide were used in a ratio of 1:2:3, the diallyl substituted organosilicons (**5**) were obtained in excellent yields. Noteworthy is the fact that the diallylation of dichlorosilanes (R_2SiCl_2) were generally clean and no mono-allylated products could be detected by GC–MS spectra of the crude products. The results are listed in Table 2.

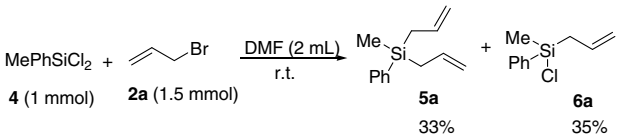
Table 2
Diallylation of organodichlorosilanes (R_2SiCl_2) with allyl bromides[a]



Entry	Ally bromide	R_2SiCl_2	Product	Yields[b] (%)
1	**2a**	$PhMeSiCl_2$	 **5a**	98
2	**2a**	Ph_2SiCl_2	 **5b**	99
3	**2a**	$PhHSiCl_2$	 **5c**	94
4	**2a**	Me_2SiCl_2	 **5d**	91
5	**2a**	*n*-$BuMeSiCl_2$	 **5e**	92
6	**2b**	$MePhSiCl_2$	 **5f**	92
7	**2c**	$MePhSiCl_2$	 **5g**	88
8	**2d**	$MePhSiCl_2$	 **5h**	87[c]
9	**2e**	$MePhSiCl_2$	 **5i**	82

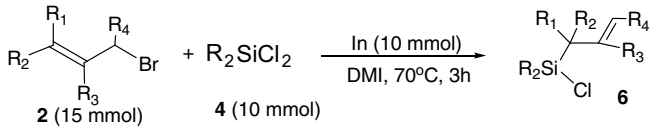
[a] Unless otherwise noted, chlorosilanes (1 mmol) were allowed to react with In (2 mmol) and allyl bromide (3 mmol) in DMF at room temperature for 3 h.
[b] Isolated yields based on **4**.
[c] *Z*/*E* = 4/95.

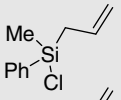
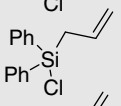
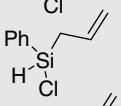
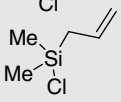
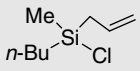
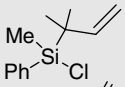
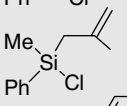
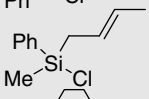
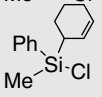
While dichloro(methyl)phenylsilane ($MePhSiCl_2$), indium and allyl bromide were used in a ratio of 1:1:1.5, a mixture of mono- and di-allylated products, diallyl(methyl)(phenyl)silane (**5a**, 33%) and allylchloro(methyl)phenylsilane (**6a**, 35%) were detected.



(1)

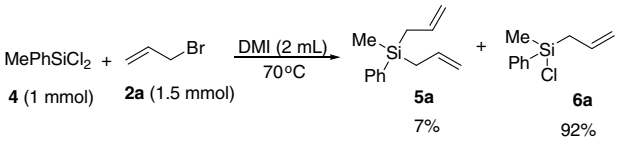
Table 3
Monoallylation of organodichlorosilanes (R_2SiCl_2) with allyl bromide[a]



Entry	Ally bromide	R_2SiCl_2	Product	Yields[b] (%)
1	**2a**	$PhMeSiCl_2$		**6a** (92), **5a** (7)
2	**2a**	Ph_2SiCl_2		**6b** (96), **5b** (3)
3	**2a**	$PhHSiCl_2$		**6c** (94), **5c** (4)
4	**2a**	Me_2SiCl_2		**6d** (90), **5d** (8)
5	**2a**	*n*-$BuMeSiCl_2$		**6e** (90), **5e** (7)
6	**2b**	$MePhSiCl_2$		**6f** (81), **5f** (10)
7	**2c**	$MePhSiCl_2$		**6g** (89), **5g** (8)
8	**2d**	$MePhSiCl_2$		**6h** (91[c]), **5h** (5)
9	**2e**	$MePhSiCl_2$		**6i** (89), **5i** (9)

[a] Unless otherwise noted, chlorosilanes (10 mmol) were allowed to react with In (10 mmol) and allyl bromide (15 mmol) in DMI at 70 °C for 3 h.
[b] Isolated yields based on **4**.
[c] *Z*/*E* = 5/93.

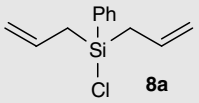
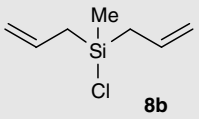
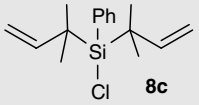
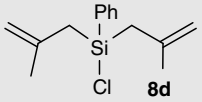
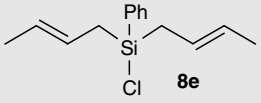
When the similar reaction was performed in DMI at room temperature for 12 h, **6a** was obtained in 11% isolated yield and only trace amount of gem-allylated product **5a** could be detected in the ^1H NMR spectra of the crude product. When the reaction temperature was increased from room temperature to 70 °C, allylchloro(methyl)phenylsilane (**6a**) was obtained in good yield (Eq. (2))



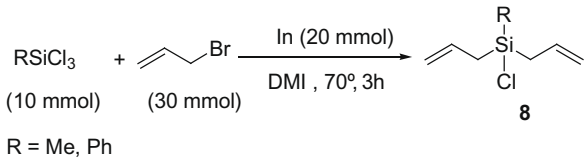
(2)

On the basis of the results obtained with simple dichloromethylphenylsilane, it seemed logical to investigate the possibility of extending this methodology to the controlled monoallylation of various organodichlorosilanes. The results and the scope of this reaction are summarized in Table 3, which clearly indicates that the present strategy affords a general protocol for the synthesis of allyl substituted chlorosilanes.

Table 4
Monoallylation of organotrichlorosilanes ($RSiCl_3$) with allyl bromide[a]

Entry	Ally bromide	$RSiCl_3$	Product	Yields[b] (%)
1	**2a**	$PhSiCl_3$	 **8a**	92
2	**2a**	$MeSiCl_3$	 **8b**	91
3	**2b**	$PhSiCl_3$	 **8c**	87
4	**2c**	$PhSiCl_3$	 **8d**	87
5	**2d**	$PhSiCl_3$	 **8e**	89[c]

[a] Chlorosilanes (10 mmol) were allowed to react with In (20 mmol) and allyl bromide (30 mmol) in DMI at 70 °C for3 h.
[b] Isolated yields based on $RSiCl_3$ used.
[c] *Z*/*E* = 4/95.



Scheme 2.

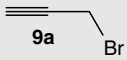
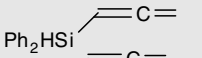
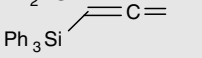
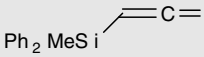
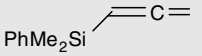
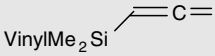
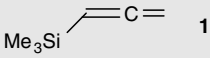
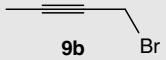
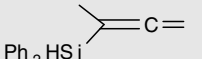
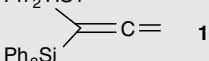
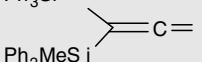
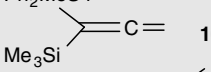
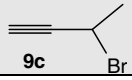
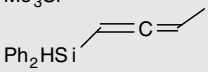
2.3. Indium induced allylation of organotrichlorosilanes ($RSiCl_3$) with allyl bromide

With the success for the synthesis of allyl substituted organosilanes and chlorosilanes, we subsequently investigated the allylation of trichlorosilanes ($RSiCl_3$) with allylindium bromide. When trichlorophenylsilane (10 mmol) and indium powder (20 mmol) were treated with allyl bromide (30 mmol), the diallylchlorophenylsilane was obtained in high yield (92%) (Scheme 2). Under similar reaction conditions, trichloromethylsilane also reacted with allylindium bromide smoothly, giving the corresponding products in good yields. The results are summarized in Table 4.

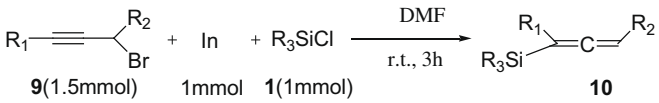
2.4. The reaction of trisubstituted chlorosilanes (R_3SiCl) with propargyl bromide

Functional allenes such as allenylsilanes have proved to be extremely versatile, key intermediates in modern organic synthesis [14]. Regioselective reactions of propargyl and allenyl organometallics with chlorosilanes provide a convenient route for the synthesis of these compounds. However, these organometallics often exist as an equilibrium mixture [14a]. We found that organoindium was a useful reagent for the regioselective allenylation of chlorosilanes. When 3-bromoprop-1-yne (1.5 mmol) and chlorodiphenylsilane (1 mmol) were treated with 1 equiv. of indium

Table 5
Monoallenylation of trisubstituted chlorosilanes (R_3SiCl)[a]

Entry	Propargyl bromide	Substrate	Product	Yields[b](%)
1	 **9a**	Ph_2HSiCl	 **10a**	95
2	**9a**	Ph_3SiCl	 **10b**	98
3	**9a**	$Ph_2MeSiCl$	 **10c**	98
4	**9a**	$PhMe_2SiCl$	 **10d**	96
5	**9a**	$VinylMe_2SiCl$	 **10e**	94
6	**9a**	Me_3SiCl	 **10f**	81
7	 **9b**	Ph_2HSiCl	 **10g**	97
8	**9b**	Ph_3SiCl	 **10h**	98
9	**9b**	$Ph_2MeSiCl$	 **10i**	94
10	**9b**	Me_3SiCl	 **10k**	79
11	 **9c**	Ph_2HSiCl	 **10j**	93

[a] Unless otherwise noted, chlorosilanes (1 mmol) were allowed to react with In (1 mmol) and propargyl bromide (1.5 mmol) in DMF at room temperature for 3 h.
[b] Isolated yields based on **1**.



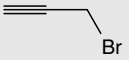
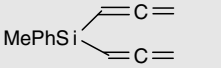
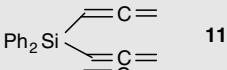
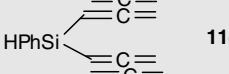
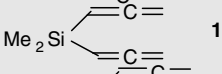
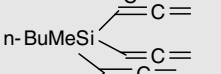
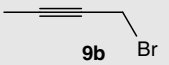
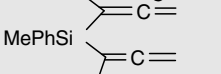
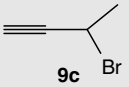
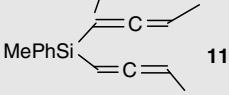
Scheme 3.

powder in DMF for 3 h at room temperature to give allenyldiphenylsilane (**10a**) in 95% isolated yield (entry 1). When under the similar reaction conditions, 1-bromobut-2-yne was treated with chlorodiphenylsilane, chlorotriphenylsilane, chlorodiphenylmethylsilane ane chlorotrimethylsilane, the regioselective products were obtained in good yields, respectively (entries 8–10). When 3-bromobut-1-yne and chlorodiphenylsilane were used as the substrates, the buta-1,2-dienyldiphenylsilane was produced in an excellent yield (entry 11) (see Table 5 and Scheme 3).

2.5. The reaction of disubstituted chlorosilanes (R_2SiCl_2) with propargyl bromide

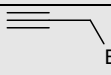
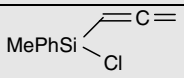
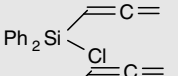
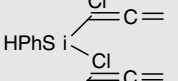
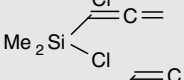
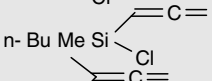
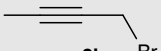
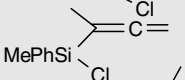
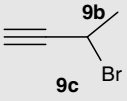
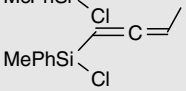
On the basis of the results obtained with the monoallenylation of R_3SiCl, we subsequently investigated the mono- and di-allenyla-

Table 6
Diallenylation of disubstituted dichlorosilanes (R_2SiCl_2)[a]

Entry	Propargyl bromide	Substrate	Product	Yields[b] (%)
1		$PhMeSiCl_2$	 **11a**	97
2	**9a**	Ph_2SiCl_2	 **11b**	98
3	**9a**	$PhHSiCl_2$	 **11c**	97
4	**9a**	Me_2SiCl_2	 **11d**	91
5	**9a**	*n*-$BuMeSiCl_2$	 **11e**	93
6	 **9b**	$PhMeSiCl$	 **11f**	94
7	 **9c**	$PhMeSiCl_2$	 **11g**	97

[a] Unless otherwise noted, chlorosilanes (1 mmol) were allowed to react with In (2 mmol) and propargyl bromide (3 mmol) in DMF at room temperature for 3 h.
[b] Isolated yields based on (R_2SiCl_2) **2**.

Table 7
Monoallenylation of disubstituted dichlorosilanes (R_2SiCl_2)[a]

Entry	Propargyl bromide	Substrate	Product	Yields[b](%)
1		$PhMeSiCl_2$		**12a** (89), **11a** (9)
2	**9a**	Ph_2SiCl_2		**12b** (93), **11b (5)**
3	**9a**	$PhHSiCl_2$		**12c** (90), **11c** (7)
4	**9a**	Me_2SiCl_2		**12d** (87), **11d** (9)
5	**9a**	*n*-$BuMeSiCl_2$		**12e** (87), **11e** (10)
6	 **9b**	$PhMeSiCl_2$		**12f** (92), **11f** (4)
7	 **9c**	$PhMeSiCl_2$		**12g** (93), **11g** (5)

[a] Unless otherwise noted, chlorosilanes (10 mmol) were allowed to react with In (10 mmol) and propargyl bromide (15 mmol) in DMI at r.t. for 3 h.
[b] Isolated yields based on **2** (R_2SiCl_2).

tion of R_2SiCl_2. When dichloromethylphenylsilanes ($MePhSiCl_2$), indium and propargyl bromide were used in a ratio of 1:2:3, diallenylated product was obtained in 97% isolated yield. The results and scopes are listed in Table 6.

When dichloromethylphenylsilanes ($MePhSiCl_2$), indium and propargyl bromide were used in a ratio of 1:1:1.5 in DMI at room temperature, diallenylmethyl(phenyl)silane (**11a**, 9%) and allenylchloro(methyl)(phenyl)silane (**12a**, 89%) was detected. Under similar reaction conditions, a variety of allenylated chlorosilanes were obtained in good yields (Table 7).

In conclusion, we present the novel selective allylation and allenylation of chlorosilanes with organoindium reagents. By applying this method, aryl and aralkyl unsaturated chlorosilanes as well as diallyl chlorosilanes containing different allyl and allenyl groups were prepared conveniently. The new types of allyl- and allenyl substituted chlorosilanes prepared herein possess unsaturated carbon–carbon bonds and will meet our further requirements to permit additional polymerization across the double bonds so as to synthesize functional polymers.

3. Experimental

Tetrahydrofuran was distilled from sodium-benzophenone immediately prior to use. DMF and DMI were distilled from GaH_2 at reduced pressure. All reactions were conducted under a nitrogen atmosphere. ^{1}H NMR spectra were recorded on a BRUKER AV-400 MHz instrument as $CDCl_3$ solutions using TMS as an internal standard. Chemical shifts (δ) are reported in ppm and coupling constants *J* are given in Hz. IR spectra were taken as thin films with a BRUKER TENSOR-27 infrared spectrometer. Elemental analysis was performed on a VARIO EL-3 instrument. Indium powder, the starting chlorosilanes and all reagents were purchased from commercial sources and were used without further purification.

3.1. General procedure for the synthesis of allylaralkyl silanes (*3a–3i*)

Allyl bromide (1.5 mmol) and indium (1 mmol) in dry DMF (2 mL) were added to a three-necked flask with stirring at room temperature under a nitrogen atmosphere. The mixture was stirred for about 1 h. Chlorosilanes (1 mmol) were added dropwise. The reaction mixture was stirred for 3 h and then was quenched with 0.1 M hydrochloric acid (2 mL). The resulting mixture was extracted with diethyl ether (3 × 5 mL), the diethyl ether solution was washed with saturated NaCl (2 × 5 mL) and dried over anhydrous $MgSO_4$. The solvent was removed by evaporation under reduced pressure. The crude product was purified by preparative TLC on silica gel (cyclohexane as eluent).

Allyldiphenylsilane (***3a***) [2c] *IR*: ν_{max} (liquid film) 3069.3, 3003.1, 2972.5, 2920.0, 2125.3, 1629.8, 1427.0, 1155.0, 1114.1 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ *7.32–7.64 (10H,* m, ArH), 5.79–5.89 (1H, m, CH), 4.88–4.97 (2H, m, CH_2=), 4.86 (1H, s, SiH), 2.12–2.15 (2H, d, *J* = 7.3 Hz, CH_2CH=CH_2); ^{13}C NMR (100 MHz, $CDCl_3$): δ 135.40, 133.73, 133.57, 129.39, 127.05, 114.79, 19.77; MS: *m*/*z* (%): 224 (M^+, 2.17), 183 (100), 105 (13.62).

Allyltriphenylsilane (***3b***) [15a] *IR*: ν_{max} (KBr) 3066.0, 3041.0, 2996.0, 2923.3, 2863.4, 1628.1, 1427.3, 1112.6 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ *7.34–7.53 (15H,* m, ArH), 5.84–5.90 (1H, m, CH), 4.87–4.97 (2H, d, d, *J* = 10.1, 15.2 Hz, CH_2=), 2.38–2.40 (2H, d, *J* = 7.4 Hz, CH_2CH=CH_2); ^{13}C NMR (100 MHz, $CDCl_3$): δ 135.76, 134.55, 133.82, 129.56, 127.85,115.10, 21.19; MS: *m*/*z* (%): 301 (M^++1, 2.21), 260 (23.58), 259 (100), 181 (9.92), 105 (3.74).

Allyldiphenylmethylsilane (***3c***) [15a] *IR*: ν_{max} (liquid film) 3069.6, 2924.0, 2853.5, 1630.4, 1427.6, 1251.5, 1151.9, 1112.9 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ *7.32–7.36 (10H,* m, ArH), 5.74–5.85 (1H, m, CH), 4.85–4.93 (2H, d, d, *J* = 10.2, 15.3 Hz, CH_2=), 2.06–2.08 (2H, d, *J* = 7.2 Hz, CH_2CH=CH_2), 0.55 (3H, s, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 136.41, 134.41, 133.92, 129.16, 127.70, 114.13, 22.03, −4.95; MS: *m*/*z* (%): 278 (M^+, 4.00), 198 (27.09), 197 (100).

Allyldimethylphenylsilane (***3d***) [15a] *IR*: ν_{max} (liquid film) 3070.3, 2998.6, 2957.6, 2915.9, 1630.0, 1426.8, 1249.9, 1155.4, 1114.3 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ *7.33–7.50 (5H,* m, ArH), 5.72–5.80 (1H, m, CH), 4.83–4.88 (2H, d, d, *J* = 10.1, 15.2 Hz, CH_2=), 1.74–1.76 (2H, d, *J* = 7.2 Hz, CH_2CH=CH_2), 0.27 (3H, s, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.46, 134.43, 133.43, 128.81, 127.64, 113.19, 23.49, −3.70; MS: *m*/*z* (%): 176 (M^+, 1.00), 161 (0.88), 136 (12.52), 135 (100), 105 (2.97).

Allyltrimethylsilane (***3e***) [15a]: ^{1}HNMR (400 MHz,$CDCl_3$): δ *5.66–5.71 (1H,* m, CH), 4.77–4.83 (2H, m, CH_2=), 1.74 (2H, d, *J* = 7.8 Hz, CH_2CH=CH_2), 0.21–0.33 (9H, s, CH_3); MS: *m*/*z* (%): 114 (M^+, 2.56), 74 (29.04), 73(43.76), 45(100).

(2-Methylbut-3-en-2-yl)diphenylsilane (***3f***): ^{1}H NMR (400 MHz, $CDCl_3$): δ *7.25–7.62(10H,* m, ArH), 5.72–5.76(1H, m, CH=), 4.80 (1H, s, SiH), 4.58–4.65 (2H, m, CH_2=), 1.03 (6H, s, CH_3); ^{13}C NMR

(100 MHz, $CDCl_3$): δ 137.23, 134.89, 133.77, 130.21, 127.05, 114.63, 24.28, 3.1; MS: *m*/*z* (%): 252 (M^+, 1.32), 183 (100), 175(27.8); Anal. Calc. for $C_{17}H_{20}Si$: C, 80.89; H, 7.99; Si, 11.13. Found: C, 80.76; H, 7.78; Si, 11.25%.

*(2-Methylallyl)diphenylsilane (**3g**)*: IR ν_{max} (liquid film) 3071.2, 3013,3, 2972.2, 2925.3, 2856.3, 2127.2, 1648.2, 1435.8, 1111.2 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ *7.31–7.68 (10H,* m, ArH), 4.80 (1H, s, SiH), 4.62 (2H, s, CH_2=), 2.15 (2H, s, Si-CH_2), 1.73 (3H, s, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.21, 135.29, 134.67, 134.32, 131.12, 129.87, 115.23, 25.42, 19.28; MS: *m*/*z* (%): 238(M^+, 0.25), 223 (12.28), 183 (100); Anal. Calc. for $C_{16}H_{18}Si$: C, 80.61; H, 7.61; Si, 11.78. Found: C, 80.52; H, 7.76; Si, 11.69%.

*(E)-But-2-enyldiphenylsilane (**3h**)* IR: ν_{max} (liquid film) 3072.5, 3015.8, 2956.3, 2925.2, 2857.2, 2128.3, 1651.2, 1478.3, 1429.4, 1118.2 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ *7.27–7.65 (10H,* m, ArH), 5.65–5.50 (2 H, m, CH=CH), 4.81 (1H, s, SiH), 2.13 (2H, d, *J* = 6.2 Hz, Si-CH_2), 1.56 (3H, d, *J* = 7.3 Hz, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 135.23, 134.02, 130.22, 129.12, 124.73, 123.58, 17.23, 13.12; MS: *m*/*z* (%): 238(M^+, 1.52), 223 (23.52), 183 (100); Anal. Calc. for $C_{16}H_{18}Si$: C, 80.61; H, 7.61; Si, 11.78. Found: C, 80.55; H, 7.71; Si, 11.70%.

*Cyclohex-2-enyldiphenylsilane (**3i**)* [15b] *IR*: ν_{max} (liquid film) 3059.1, 3014.3, 2927.9, 2857.8, 2132.0, 1653.1, 1428.4, 1118.6, 1067.9, 852.9, 728.1, 702.8 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ *7.20–7.62 (10H,* m, ArH), 5.70–5.54 (2H, m, CH=CH), 4.77 (1H, s, SiH), 1.98–1.26 (7H, m); ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.38, 135.38, 134.77, 134.37, 130.26, 129.65, 128.79, 127.90, 31.32, 25.00, 23.32, 19.28; MS: *m*/*z* (%): 264(M^+, 2.34), 183 (100), 105 (23.18).

*But-3-en-2-yldiphenylsilane (**3j**)* [15a]: ^1H NMR (400 MHz, $CDCl_3$): δ *7.26–7.63 (10H,* m, ArH), 5.72–5.76 (1H, m, CH=), 4.77 (1H, s, SiH), 4.58–4.65 (2H, m, CH_2=), 2.21 (1H, m, CH), 1.02 (3H, d, *J* = 6.2 Hz, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.24, 134.88, 133.77, 130.21, 127.06, 114.63, 26,32, 24.28; MS: *m*/*z* (%): 238 (M^+, 2.42), 223 (22.52), 183 (100).

3.2. General procedure for the synthesis of diallyl substituted silanes (**5a**–**5i**)

Allylindium bromide (2 mmol) was prepared using the above procedure. Dichlorosilanes (1 mmol) were added dropwise. The reaction mixture was stirred for 3 h and then was quenched with 0.1 M hydrochloric acid (2 mL). The resulting mixture was extracted with diethyl ether (3 × 5 mL), the diethyl ether solution was washed with saturated NaCl (2 × 5 mL) and dried over anhydrous $MgSO_4$. The solvent was removed by evaporation under reduced pressure. The crude product was purified by preparative TLC on silica gel (cyclohexane as eluent).

*Diallylmethylphenylsilane (**5a**)* [9] *IR*: ν_{max} (liquid film) 3072.5, 2971.3, 2916.2, 1630.0, 1426.9, 1252.1, 1154.2, 1113.2 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ *7.32–7.50 (5H,* m, ArH), 5.73–5.79 (2H, m, 2 × CH), 4.83–4.90 (4H, m, 2 × CH_2=), 1.79–1.81 (4H, d, *J* = 7.1 Hz, 2 × CH_2CH=CH_2), 0.28 (3H, s, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 136.71, 134.05, 133.79, 129.06, 127.62, 113.73, 21.44, −5.98; MS: *m*/*z* (%): 202 (M^+, 2.1), 161 (100), 121 (30.5), 105 (11.9).

*Diallyldiphenylsilane (**5b**)* [9] *IR*: ν_{max} (liquid film) 3069.6, 2998.2, 1629.9, 1427.9, 1110.8, 907.9, 732.7 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ *7.32–7.52 (10H,* m, ArH), 5.78 (2H, m, 2 × CH), 4.86–4.94 (4H, t, 2 × CH_2=), 2.11–2.13 (4H, d, *J* = 7.2 Hz, 2 × CH_2CH=CH_2); ^{13}C NMR (100 MHz, $CDCl_3$): δ 134.84, 134.12, 133.55, 129.32, 127.65, 114.59, 19.85; MS: *m*/*z* (%): 264 (M^+, 6.96), 223 (100), 183 (27.66), 145 (32.05).

*Diallylphenylsilane (**5c**)* [9]: ^1H NMR (400 MHz, $CDCl_3$): δ *7.31–7.51 (5H,* m, ArH), 5.75–5.79 (2H, m, 2 × CH), 4.86–4.94 (4H, m, 2× CH_2=), 4.77 (1H, s, Si–H), 2.12 (4H, d, *J* = 7.2 Hz, 2 × CH_2CH=CH_2); ^{13}C NMR (100 MHz, $CDCl_3$): δ 134.84, 134.12, 133.55, 129.32, 127.65, 114.59, 19.85; MS: *m*/*z* (%): 188 (M^+, 2.31), 147 (100).

*Diallyldimethylsilane (**5d**)* [9]: ^1H NMR (400 MHz, $CDCl_3$): δ*5.77–5.86 (2H,* m, 2 × CH), 4.92–5.01 (4H, m, 2 × CH_2=), 1.85 (4H, d, *J* = 7.3 Hz, 2 × CH_2CH=CH_2), 0.23 (6H, s, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 133.54, 115.92, 19.85, −2.32; MS: *m*/*z* (%): 140 (M^+, 0.89), 125 (54.28), 99 (100).

*Diallylmethylbutylsilane (**5e**)* [9]: ^1H NMR (400 MHz, $CDCl_3$): δ *5.63–5.69 (2H,* m, 2 × CH), 4.97–5.03 (4H, m, 2 × CH_2=), 1.31–1.42 (8H, m), 0.92–1.07 (2H, m, CH_2CH_3), 0.52–0.68 (3H, t, CH_3CH_2), 0.21 (3H, s, CH_3Si); ^{13}C NMR (100 MHz, $CDCl_3$): δ 133.89, 115.13, 32.13, 30.24, 25.62, 19.76, 15.32, −2.67; MS: *m*/*z* (%): 182 (M^+, 1.34), 167 (47.36), 141 (100).

*Di-(2-methylbut-3-en-2-yl)methylphenylsilane (**5f**)*: ^1H NMR (400 MHz, $CDCl_3$): δ *7.28–7.47 (5H,* m, ArH), 5.74–5.77 (2H, m, 2 × CH), 4.91–5.03 (4H, m, 2 × CH_2=), 1.21 (12H, s, 4 × CH_3), 0.31 (3H, s, CH_3Si); ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.35, 135.02, 134.13, 130.35, 128.98 114.13, 23.67, 2.92; MS: *m*/*z* (%): 258 (M^+, 1.32), 243 (10.35), 181 (100); Anal. Calc. for $C_{17}H_{26}Si$: C, 79.00; H, 10.14; Si, 10.87. Found: C, 78.88; H, 10.82 Si, 10.79%.

*Di-(2-methylallyl)methylphenylsilane (**5g**)*: ^1H NMR (400 MHz, $CDCl_3$): δ *7.21–7.40 (5H,* m, ArH), 4.75 (4H, s, 2 × CH_2=), 2.15 (4H, s, 2 × Si-CH_2), 1.72 (6H, s, 2 × CH_3), 0.35 (3H, s, CH_3Si); ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.01, 134.32, 133.87, 133.15, 130.78, 129.15, 115.11, 20.23, 17.23, −2.56; MS: *m*/*z* (%): 230 (M^+, 0.56), 215 (3.24), 175 (100), 120 (65.32); Anal. Calc. for $C_{15}H_{22}Si$: C, 78.19; H, 9.62; Si, 12.19. Found: C, 78.28; H, 9.54; Si, 12.26%.

*Di-[(E)-but-2-enyl]methylphenylsilane (**5h**)*: ^1H NMR (400 MHz, $CDCl_3$): δ *7.28–7.55 (5H,* m, ArH), 5.52–5.57 (4H, m, 2 × CH=CH), 2.16 (4H, d, *J* = 7.2 Hz, 2 × Si-CH_2), 1.74 (6H, d, *J* = 7.3 Hz, CH_3), 0.33 (3H, s, CH_3Si); MS: *m*/*z* (%): 230 (M^+, 0.77), 215 (5.76), 175 (100), 120 (58.35); Anal. Calc. for $C_{15}H_{22}Si$: C, 78.19; H, 9.62; Si, 12.19. Found: C, 78.10; H, 9.70; Si, 12.11%.

*Di-(cyclohex-2-enyl)methylphenylsilane (**5i**)*: ^1H NMR (400 MHz, $CDCl_3$): δ *7.27–7.45 (5H,* m, ArH), 5.55–5.62 (4H, m, 2 × CH=CH), 1.26–1.97 (14H, m), 0.30 (3H, s, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.13, 135.33, 134.22, 133.87, 130.65, 129.78, 128.67, 127.96, 31.56, 26.11, 23.35, 19.78; MS: *m*/*z* (%): 282 (M^+, 5.70), 267 (19.00), 201 (100), 120 (67.23); Anal. Calc. for $C_{19}H_{26}Si$: C, 80.78; H, 9.28; Si, 9.94. Found: C, 80.70; H, 9.33; Si, 9.88%.

3.3. General procedure for the synthesis of allyl substituted chlorosilanes (**6a**–**6i**)

Allylindium bromide (10 mmol) was prepared using the above procedure in DMF. Dichlorosilanes (10 mmol) were added dropwise, and then the reaction mixture was stirred for 3 h at 70 °C. The inorganic precipitate was filtered off and washed with dry diethyl ether. The solvent was removed by evaporation and the residual liquid was fractionally distilled.

*Allylchloromethylphenylsilane (**6a**)* [9] *IR*: ν_{max} (liquid film) 3071.2, 2969.5, 1630.5, 1427.8, 1256.2, 1157.0, 1118.3 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ *7.25–7.45 (5H,* m, ArH), 5.66–5.71 (1H, m, CH), 4.77–4.83 (2H, m, CH_2=), 1.73–1.75 (2H, d, *J* = 7.2 Hz, CH_2CH=CH_2), 0.21–0.33 (3H, s, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 133.7, 133.2, 133.16, 129.36, 127.54, 113.73, 21.43, −1.62; MS: *m*/*z* (%): 161 (100), 155 (21.83), 121 (37.22), 105 (14.01).

*Allylchlorodiphenylsilane (**6b**)* [9] *IR*: ν_{max} (liquid film) 3069.9, 3023.2, 2919.9,1630.0,1590.6,1428.0,1117.5 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ *7.26–7.57 (10H,* m, ArH), 5.80–5.89 (1H, m, CH), 4.88–5.01 (2H, m, CH_2=), 2.18–2.22 (2H, d, *J* = 7.1 Hz, CH_2CH=CH_2); ^{13}C NMR (100 MHz, $CDCl_3$): δ 133.79, 130.27, 130.05, 129.32, 127.56, 114.60, 19.83; MS: *m*/*z* (%): 258 (M^+, 2.54), 217 (100), 181 (13.60).

*Allylchlorophenylsilane (**6c**)* [15c]: ^{1}H NMR (400 MHz, $CDCl_3$): δ *7.35–7.68 (5H,* m, ArH), 5.77–5.89 (1H, m, CH), 4.85–4.95 (2H, m, CH_2=), 4.81 (1H, s, SiH), 2.13 (2H, d, J = 7.3 Hz, CH_2CH=CH_2); ^{13}C NMR (100 MHz, $CDCl_3$): δ 135.10, 134.65, 134.13, 130.25, 129.13, 115.32, 19.76; MS: m/z (%): 182 (M^+, 2.07), 141 (100).

*Allylchlorodimethylsilane (**6d**)* [15c]: ^{1}HNMR (400 MHz, $CDCl_3$): δ *5.63–5.73 (1H,* m, CH), 4.74–4.82 (2H, m, CH_2=), 1.74 (2H, d, J = 7.1 Hz, CH_2CH=CH_2), 0.28 (6H, s, CH_3Si); ^{13}C NMR (100 MHz, $CDCl_3$): δ 134.12, 115.78, 20.01, −2.36; MS: m/z (%): 134 (M^+, 1.24), 119 (23.78), 93 (100).

*Allylchloromethylbutylsilane (**6e**)* [15c]: ^{1}HNMR (400 MHz, $CDCl_3$): δ *5.62–5.74 (1H,* m, CH), 4.74–4.84 (2H, m, CH_2=), 1.94–1.35 (4H, m), 0.87–0.96 (2H, t, CH_2CH_3), 0.60–0.65 (3H, t, CH_3CH_2), 0.29 (3H, s, CH_3Si); MS: m/z (%): 176 (M^+, 2.32), 162 (30.28), 135 (100).

*Chloro(2-methylbut-3-en-2-yl)methylphenylsilane (**6f**)*: δ 7.25–7.47 (5H, m, ArH), 5.71–5.75 (1H, m, CH), 4.91–5.03 (2H, m, CH_2=), 1.21 (6H, s, 2 CH_3), 0.31 (3H, s, CH_3Si); ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.10, 135.39, 134.77, 130.12, 127.76 114.55, 24.13, 3.02; MS: m/z (%): 224 (M^+, 2.03), 209 (8.23), 147 (100); Anal. Calc. for $C_{12}H_{17}ClSi$: C, 64.11; H, 7.62; Si, 12.49. Found: C, 64.19; H, 7.70; Si, 12.55%.

*Chloro(2-methylallyl)methylphenylsilane (**6g**)*: ^{1}H NMR (400 MHz, $CDCl_3$): δ *7.31–7.50 (5H,* m, ArH), 4.71 (2H, s, CH_2=), 2.11 (2H, s, Si-CH_2), 1.70 (3H, s, CH_3), 0.35 (3H, s, CH_3Si); ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.33, 135.67, 134.23, 134.01, 131.55, 129.63, 115.31, 24.23, 18.12, −2.56; MS: m/z (%): 210(M^+, 1.01), 195 (13.23), 155 (100); Anal. Calc. for $C_{11}H_{15}ClSi$: C, 62.68; H, 7.17; Si, 13.32. Found: C, 62.59; H, 7.11; Si, 13.41%.

*Chloro((E)-but-2-enyl)methylphenylsilane (**6h**)* [15d]: ^{1}H NMR (400 MHz, $CDCl_3$): δ *7.28–7.55 (5H,* m, ArH), 5.52–5.55 (2H, m, CH=CH), 2.14 (2H, d, J = 7.1 Hz, Si-CH_2), 1.77 (3H, d, J = 7.3 Hz, CH_3), 0.33 (3H, s, CH_3Si); MS: m/z (%): 210(M^+, 1.24), 195 (10.25), 155 (100).

*Chloro(cyclohex-2-enyl)methylphenylsilane (**6i**)*: ^{1}H NMR (400 MHz, $CDCl_3$): δ *7.26–7.46 (5H,* m, ArH), 5.61–5.53 (2H, m, CH=CH), 1.98–1.31 (7H, m, $CHCH_2CH_2CH_2$), 0.29 (3H, s, CH_3Si); ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.23, 135.11, 134.77, 133.56, 130.42, 129.35, 128.36, 127.88, 31.02, 26.78, 23.23, 19.13; MS: m/z (%): 236 (M^+, 7.76), 267 (19.00), 155 (100); Anal. Calc. for $C_{13}H_{17}ClSi$: C, 65.93; H, 7.24; Si, 11.86. Found: C, 65.89; H, 7.31; Si, 11.79%.

3.4. The reaction of trichlorosilanes ($RSiCl_3$) with allylindium bromide (**8a–8e**)

Allylindium bromide (20 mmol) was prepared using the above procedure in DM. Trichlorosilanes (10 mmol) were added dropwise, and then the reaction mixture was stirred for 3 h at 70 °C. The inorganic precipitate was filtered off and washed with dry diethyl ether. The solvent was removed by evaporation and the residual liquid fractionally distilled.

*Diallylchlorophenylsilane (**8a**)* [9] *IR*: ν_{max} (liquid film) 3073.0, 3002.4, 2974.2, 2919.8, 1632.0, 1428.9, 1121.7 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ *7.33–7.47 (5H,* m, ArH), 5.74–5.82 (2H, m, 2 × CH), 4.98–5.02 (4H, t, 2 × CH_2=), 2.09–2.11 (4H, d, J = 7.3 Hz, 2 × CH_2CH=CH_2); ^{13}C NMR (100 MHz, $CDCl_3$): δ 133.85, 131.38, 130.62, 128.09, 127.77, 116.34, 15.32; MS: m/z (%): 222 (M^+, 7.63), 183 (35.03), 181 (100), 145 (84,91), 142 (4.27).

*Diallylchloromethylsilane (**8b**)* [9]: ^{1}H NMR (400 MHz, $CDCl_3$): δ *5.70–5.82 (2H,* m, 2 × CH), 4.95–5.04 (4H, m, 2 × CH_2=), 2.10 (4H, d, J = 7.1 Hz, 2 × CH_2CH=CH_2), 0.30 (3H, s, CH_3Si); ^{13}C NMR (100 MHz, $CDCl_3$): δ 133.87, 114.23, −3.36; MS: m/z (%): 160 (M^+, 0.35), 109 (100).

*Di-(2-methylbut-3-en-2-yl)chlorophenylsilane (**8c**)*: ^{1}H NMR (400 MHz, $CDCl_3$): δ *7.28–7.47 (5H,* m, ArH), 5.74–5.80 (2H, m, 2 × CH), 4.91–5.03 (4H, m, 2 × CH_2=), 1.21 (12H, s, 4 × CH_3); MS: m/z (%): 278 (M^+, 1.32), 263 (13.38), 201 (100); Anal. Calc. for $C_{16}H_{23}ClSi$: C, 68.91; H, 8.31; Si, 10.07. Found: C, 68.84; H, 8.26; Si, 10.00%.

*Di-(2-methylallyl)chlorophenylsilane (**8d**)*: ^{1}H NMR (400 MHz, $CDCl_3$): δ *7.21–7.40 (5H,* m, ArH), 4.75 (2H, s, 2 × CH_2=), 4.64 (2H, s, 2 × CH_2=), 2.15 (4H, s, 2 × Si-CH_2), 1.72 (6H, s, 2 × CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.86, 135.17, 134.63, 134.10, 132.23, 130.02, 115.11, 22.38, 17.89; MS: m/z (%): 250(M^+, 1.66), 235 (32.35), 195 (100); Anal. Calc. for $C_{14}H_{19}ClSi$: C, 67.03; H, 7.63; Si, 11.20. Found: C, 67.11; H, 7.56; Si, 11.15%.

*Di-((E)-but-2-enyl)chlorophenylsilane (**8e**)* [15d]: ^{1}H NMR (400 MHz, $CDCl_3$): δ *7.28–7.55 (5H,* m, ArH), 5.57–5.62 (4H, m, 2 × CH=CH), 2.16 (4H, d, J = 7.2 Hz, 2 × Si-CH_2), 1.72 (6H, d, J = 7.3 Hz, CH_3); MS: m/z (%): 250(M^+, 1.02), 235 (25.35), 195 (100); Anal. Calc. for $C_{14}H_{19}ClSi$: C, 67.03; H, 7.63; Si, 11.20. Found: C, 67.09; H, 7.57; Si, 11.14%.

3.5. General procedure for the synthesis of allenylaralkyl silanes (**10a–10k**)

Propargyl bromide (1.5 mmol) and indium (1 mmol) in dry DMF (2 mL) were added to a three-necked flask with stirring at room temperature under a nitrogen atmosphere. The mixture was stirred for about 1 h. Chlorosilanes (1 mmol) were added dropwise. The reaction mixture was stirred for 3 h and quenched with 0.1 M hydrochloric acid (2 mL). The resulting mixture was extracted with diethyl ether (3 × 5 mL), the diethyl ether solution was washed with saturated NaCl (2 × 5 mL) and dried over anhydrous $MgSO_4$. The solvent was removed by evaporation under reduced pressure. The crude product was purified by preparative TLC on silica gel (cyclohexane as eluent).

*Allenyldiphenylsilane (**10a**)* [14a] *IR*: (liquid film) 3068.7, 3050.1, 2924.9, 2852.2, 2135.0, 1931.3, 1589.0, 1428.8, 1117.1 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ *7.25–7.58* (10H, m, ArH), 5.25 (1H, t, J = 6.3 Hz, CH=C=CH_2), 5.14 (1H, s, H-Si), 4.44 (2H, d, J = 6.3 Hz, CH_2=C=CH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 210.88, 135.30, 133.26, 129.93, 128.04, 75.34, 68.20; MS: m/z (%): 222 (M^+, 14.72), 183 (100), 144 (54.56).

*Allenyltriphenylsilane (**10b**)* [14a] *IR*: (liquid film) 3293.4, 3060.1, 3009.1, 1925.1, 1588.9, 1425.5, 1114.8 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ *7.23–7.64 (15H,* m, ArH), 5.48 (1H, t, J = 6.2 Hz, CH=C=CH_2), 4.40 (2H, d, J = 6.2 Hz, CH_2=C=CH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 215.55, 135.60, 134.18, 129.98, 127.86, 76.74, 68.53; MS: m/z (%): 298 (M^+, 7.22), 259 (100), 181 (17.07).

*Allenyldiphenylmethylsilane (**10c**)* [14d] *IR*: (liquid film) 3068.5, 3049.3, 2960.5, 2921.2, 2179.5, 1930.4, 1716.0, 1589.7, 1428.2, 1113.8 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ *7.26–7.57 (10H,* m, ArH), 5.29 (1H, t, J = 6.3 Hz, CH=C=CH_2), 4.44 (2H, d, J = 6.3 Hz, CH_2=C=CH), 0.67(3H, s, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 214.47, 136.25, 134.67, 129.51, 127.89, 78.07, 68.02, −3.71; MS: m/z (%): 236 (M^+, 6.77), 221 (5.23), 197 (100), 105 (18.50).

*Allenyldimethylphenylsilane (**10d**)* [14a]: ^{1}H NMR (400 MHz, $CDCl_3$): *δ7.46–7.68 (5H,* m, ArH), 5.19 (1H, t, J = 6.2 Hz, CH=C=CH_2), 4.53 (2H, d, J = 6.1 Hz, CH_2=C=CH), 0.53(6H, s, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 212.38, 139.87, 133.67, 133.06, 129.31, 127.87, 79.48, 67.44, −2.38; MS: m/z (%): 174 (M^+, 18.62), 159 (14.45), 135 (100), 105 (13.01).

*Allenyldimethylvinylsilane (**10e**)* [14e]: ^{1}H NMR (400 MHz, $CDCl_3$): δ *5.72–5.85 (3H,* m, CH_2=CH), 5.16 (1H, t, J = 6.2 Hz, CH=C=CH_2), 4.48 (2H, d, J = 6.2 Hz, CH_2=C=CH), 0.60 (6H, s, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 212.33, 142.13, 139.56, 75.28, 66.15, −2.76; MS: m/z (%): 126 (M^+, 12.80), 83 (25.94), 73 (100).

*Allenyltrimethylsilane (**10f**)* [14a]: ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.29 (1H, t, J = 6.2 Hz, CH=C=CH_2), 4.42 (2H, d, J = 6.2 Hz,

CH_2=C=CH), 0.63 (9H, s, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 211.18, 77.32, 67.72, −3.13; MS: *m*/*z* (%): 112 (M^+, 9.23), 73 (100).

*(3-Methylallenyl)diphenylsilane (**10g**)* [14d]: ^{1}H NMR (400 MHz, $CDCl_3$): δ *7.26–7.65 (10H,* m, ArH), 5.16 (1H, s, H-Si), 4.43 (2H, s, CH_2=C=C), 1.84 (3H, s, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 211.88, 135.56, 132.95, 129.91, 128.02, 84.73, 68.72, 16.57; MS: *m*/*z* (%): 236 (M^+, 10.65), 221 (16.32), 183 (100), 158 (16.89).

*(3-Methylallenyl)triphenylsilane (**10h**)* [14e]: ^{1}H NMR (400 MHz, $CDCl_3$): δ*7.21–7.65 (15H,* m, ArH), 4.41 (2H, s, CH_2=C=C), 1.84 (3H, s, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ212.57, 135.13, 133.56, 129.87, 128.13, 85.12, 69.54, 17.11; MS: *m*/*z* (%): 312 (M^+, 9.35), 297 (13.68), 259 (100), 235 (21.35).

*(3-Methylallenyl)diphenylmethylsilane (**10i**)* [14d] *IR*: (liquid film) 3068.5, 3049.3, 2917.4, 2856.0, 1931.0, 1589.3, 1428.2, 1113.0 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ *7.26–7.68 (10H,* m, ArH), 4.40 (2H, s, CH_2=C=C), 1.78 (3H, s, CH_3-C=), 0.62 (3H, s, CH_3-Si); ^{13}C NMR (100 MHz, $CDCl_3$): δ 211.18, 135.59, 135.03, 129.55, 127.83, 86.78, 68.53, 16.37, −3.86; MS: *m*/*z* (%): 250 (M^+, 8.22), 197 (100), 105 (14.21).

*(3-Methylallenyl)trimethylsilane (**10j**)* [14d]: ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.41 (2H, s, CH_2=C=C), 1.76 (3H, s, CH_3-C=), 0.55 (9H, s, CH_3-Si); ^{13}C NMR (100 MHz, $CDCl_3$): δ 210.72, 90.03, 69.12, 17.10, −3.81; MS: *m*/*z* (%): 126 (M^+, 12.80), 83 (25.94), 73 (100).

*Buta-1, 2-dienyldiphenylsilane (**10k**)* [14e]: ^{1}H NMR (400 MHz, CDCl3): δ *7.21–7.61 (10H,* m, ArH), 5.13 (1H, s, H-Si), 4.82–4.85 (1H, m, CH(CH_3)=C), 4.42 (1H, s, CHSi=C), 1.78 (3H, d, *J* = 6.8 Hz, CH_3-CH=); ^{13}C NMR (100 MHz, $CDCl_3$): δ 211.93, 135.71, 133.34, 129.95, 128.63, 85.65, 69.12, 15.36, −3.77; MS: *m*/*z* (%): 236 (M^+, 12.32), 221 (17.11), 183 (100), 158 (21.33).

3.6. General procedure for the synthesis of diallenyl substituted silanes (**11a–11g**)

Propargylindium bromide (2 mmol) was prepared using the above procedure. Dichlorosilanes (1 mmol) were added dropwise. The reaction mixture was stirred for3 h and then quenched with 0.1 M hydrochloric acid (2 mL). The resulting mixture was extracted with diethyl ether (3 × 5 mL), the diethyl ether solution was washed with saturated NaCl (2 × 5 mL) and dried over anhydrous $MgSO_4$. The solvent was removed by evaporation under reduced pressure. The crude product was purified by preparative TLC on silica gel (cyclohexane as eluent).

*Diallenylmethylphenylsilane (**11a**)* [14a] *IR*: (liquid film) 3069.2, 2961.0, 2924.8, 2856.2, 2180.1, 1931.0, 1721.4, 1620.6, 1428.0, 1258.3 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.23–7.64 (5H, m, ArH), 5.11 (2H, t, *J* = 6.2 Hz, 2 × CH=C=CH_2), 4.42 (4H, d, *J* = 6.2 Hz, 2 × CH_2=C=CH), 0.46 (3H, s, CH_3-Si); ^{13}C NMR (100 MHz, $CDCl_3$): δ 214.16, 136.42, 134.08, 129.76, 128.06, 77.96, 68.09, −3.91; MS: *m*/*z* (%): 198 (M^+, 6.86), 159 (100), 131 (72.57).

*Diallenydiphenylsilane (**11b**)* [14a] *IR*: (liquid film) 3069.4, 3049.6, 2917.7, 2856.2, 2181.4, 1928.9, 1720.4, 1667.4, 1589.4, 1429.2, 1116.2 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.23–7.58 (10H, m, ArH), 5.31 (2H, t, *J* = 6.3 Hz, 2 × CH=C=CH_2), 4.42 (4H, d, *J* = 6.3 Hz, 2 × CH_2=C=CH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 210.28, 135.12, 134.21, 129.83, 128.10, 87.47, 69.89; MS: *m*/*z* (%): 260 (M^+, 13.36), 221 (84.91), 182 (30.31), 105 (100).

*Diallenylphenylsilane (**11c**)* [14d]: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.21–7.53 (5H, m, ArH), 5.29 (2H, t, *J* = 6.2 Hz, 2 × CH=C=CH_2), 5.14 (1H, s, H-Si), 4.43 (4H, d, *J* = 6.3 Hz, 2 × CH_2=C=CH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 211.13, 135.82, 134.13, 130.13, 129.13, 75.67, 68.78; MS: *m*/*z* (%): 184 (M^+, 9.12), 145 (76.12), 106 (100).

*Diallenyldimethylsilane (**11d**)* [14d]: ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.33 (2H, t, *J* = 6.2 Hz, 2 × CH=C=CH_2), 4.44 (4H, d, *J* = 6.2 Hz, 2 × CH_2=C=CH), 0.62 (6H, s, CH_3Si); ^{13}C NMR (100 MHz, $CDCl_3$): δ 211.37, 76.76, 67.13, −3.78; MS: *m*/*z* (%): 135 (M^+, 15.96), 121 (62.41), 97 (100).

*Diallenylmethylbutylsilane (**11e**)* [14d] *IR*: (liquid film) 2924.6, 2854.8, 1461.0, 1377.1, 1257.7, 1021.6, 908.3, 735.5 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.31 (2H, t, *J* = 6.2 Hz, 2 × CH=C=CH_2), 4.42 (4H, d, *J* = 6.2 Hz, 2 × CH_2=C=CH), 1.17–1.71 (9H, m, C_4H_9), 0.75 (3H, s, CH_3Si); ^{13}C NMR (100 MHz, $CDCl_3$): δ 212.56, 77.31, 76.68, 33.50, 29.69, 24.83, 14.58; MS: *m*/*z* (%): 184 (M^+, 13.23), 169 (45.61), 145 (100).

*Di-(3-methylallenyl)methylphenylsilane (**11f**)* [14e]: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.26–7.60 (5H, m, ArH), 4.36 (4H, d, *J* = 6.4 Hz, 2 × CH_2=C), 1.78 (6H, s, 2 × CH_3-C(Si)=), 0.46 (3H, s, CH_3-Si); ^{13}C NMR (100 MHz, $CDCl_3$): δ 211.34, 135.61, 135.13, 129.73, 128.12, 85.13, 68.78, 16.54, −3.68; MS: *m*/*z* (%): 226 (M^+, 1.21), 211 (62.41), 97 (100).

*Di-(buta-1,2-dienyl)methylphenylsilane (**11g**)* [14e]: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.26–7.63 (5H, m, ArH), 4.82–4.86 (2H, m, 2 × CH(CH_3)=C), 4.43 (2H, s, 2 × CHSi=C), 1.75 (6H, d, *J* = 6.8 Hz, 2 × CH_3-CH=), 0.46 (3H, s, CH_3-Si); ^{13}C NMR (100 MHz, $CDCl_3$): δ 210.56, 135.63, 135.23, 129.77, 128.34, 86.34, 69.13, 15.88, −3.91; MS: *m*/*z* (%): 226 (M^+, 2.13), 211 (22.23), 145 (100).

3.7. General procedure for the synthesis of allenyl substituted chlorosilanes (**12a–12g**)

Allylindium bromide (10 mmol) was prepared using the above procedure in DMI. Dichlorosilanes (10 mmol) were added dropwise. The reaction mixture was stirred for about 3 h at room temperature. The inorganic precipitate was filtered off and washed with dry diethyl ether. The solvent was removed by evaporation and the residual liquid fractionally distilled.

*Allenylchloromethylphenylsilane (**12a**)*: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.18–7.56 (5H, m, ArH), 5.09 (1H, t, *J* = 6.2 Hz, CH=C=CH_2), 4.40 (2H, d, *J* = 6.2 Hz, CH_2=C=CH), 0.42(3H, s, CH_3-Si); ^{13}C NMR (100 MHz, $CDCl_3$): δ 214.32, 135.82, 134.38, 128.77, 127.82, 76.96, 70.10, −3.34; MS: *m*/*z* (%): 194 (M^+, 5.12), 155 (100), 140 (72.57); Anal. Calc. for $C_{10}H_{11}ClSi$: C, 61.68; H, 5.69; Si, 14.42. Found: C, 61.59; H, 5.62; Si, 14.49%.

*Allenylchlorodiphenylsilane (**12b**)* [14c]: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.24–7.55 (10H, m, ArH), 5.27 (1H, t, *J* = 6.2 Hz, CH=C=CH_2), 4.44 (2H, d, *J* = 6.2 Hz, CH_2=C=CH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 213.53, 135.34, 134.25, 129.91, 128.10, 87.52, 69.78; MS: *m*/*z* (%): 256 (M^+, 8.22), 219 (72.35), 105 (100).

*Allenylchlorophenylsilane (**12c**)*: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.20–7.59 (5H, m, ArH), 5.30 (1H, t, *J* = 6.3 Hz, CH=C=CH_2), 5.17 (1H, s, H-Si), 4.40 (2H, d, *J* = 6.3 Hz, CH_2=C=CH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 212.01, 136.23 134.76, 131.36, 129.89, 75.88, 68.32; MS: *m*/*z* (%): 180 (M^+, 6.12), 165 (35.68), 141 (100); Anal. Calc. for C_9H_9ClSi: C, 59.82; H, 5.02; Si, 15.54. Found: C, 59.77; H, 5.08; Si, 15.61%.

*Allenylchlorodimethylsilane (**12d**)* [14d]: ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.29 (1H, t, *J* = 6.3 Hz, CH=C=CH_2), 4.44 (2H, d, *J* = 6.3 Hz, CH_2=C=CH), 0.67(6H, s, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 211.13, 76.35, 67.01, −4.56; MS: *m*/*z* (%): 132 (M^+, 6.23), 83 (100), 48 (53.12).

*Allenylchloromethylbutylsilane (**12e**)*: ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.33 (1H, t, *J* = 6.2 Hz, CH=C=CH_2), 4.38 (2H, d, *J* = 6.2 Hz, CH_2=C=CH), 1.13–1.80 (9H, m, C_4H_9), 0.58 (3H, s, CH_3Si); ^{13}C NMR (100 MHz, $CDCl_3$): δ 211.89, 77.42, 76.14, 33.35, 30.12, 25.13, 14.67; MS: *m*/*z* (%): 174 (M^+, 9.35), 159 (39.46), 135 (100); Anal. Calc. for $C_8H_{15}ClSi$: C, 54.99; H, 8.65; Si, 16.07. Found: C, 54.91; H, 8.61; Si, 16.01%.

*(3-Methylallenyl)chloromethylphenylsilane (**12f**)* [14e]: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.26–7.68 (5H, m, ArH), 4.40 (2H, s, CH_2=C=C), 1.77 (3H, s, CH_3-C=), 0.62 (3H, s, CH_3-Si); ^{13}C NMR (100 MHz, $CDCl_3$): δ 211.36, 135.76, 135.35, 129.88, 127.13,

86.25, 68.48, 16.02, −4.23; MS: *m*/*z* (%):208 (M^+, 8.33), 193 (41.23), 155 (100).

Buta-1,2-dienylchloromethylphenylsilane (***12g***) [14e]: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.26–7.65 (5H, m, ArH), 4.88–4.93 (1H, m, $CH(CH_3)$═C), 4.46 (1H, d, J = 6.2 Hz, SiCH═C), 1.56 (3H, d, J = 6.8 Hz, CH_3-C═), 0.42(3H, s, CH_3-Si); ^{13}C NMR (100 MHz, $CDCl_3$): δ 211.71, 135.13, 133.76, 130.03, 128.78, 85.52, 68.87, 15.77, −4.13; MS: *m*/*z* (%): 208 (M^+, 7.12), 193 (33.15), 155 (100).

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