



# Synthesis and desilylation of some bis(trimethylsilyl)alkenes and polymers bearing bis(silyl)alkenyl groups

Kazem D. Safa<sup>a,b,\*</sup>, Mina Namvari<sup>a</sup>, Akbar Hassanpour<sup>a</sup>, Shahin Tofangdarzadeh<sup>a</sup>

<sup>a</sup> Organosilicon Research Laboratory, Faculty of Chemistry, University of Tabriz, 51664 Tabriz, Iran

<sup>b</sup> Research Institute for Fundamental Sciences, Tabriz, Iran

## ARTICLE INFO

### Article history:

Received 21 January 2009

Received in revised form 1 March 2009

Accepted 11 March 2009

Available online 17 March 2009

### Keywords:

Tris(trimethylsilyl)methane

Peterson olefination

1,1-Bis(silyl)-1-alkenes

Functionalized poly(styrene)

Friedel–Crafts reactions

## ABSTRACT

The synthesis of various vinylbis(silanes) from some aryl and heteroaryl aldehydes and  $(\text{Me}_3\text{Si})_3\text{CLi}$  in  $\text{Et}_2\text{O}$  is described. Friedel–Crafts reaction of 1,1-bis(trimethylsilyl)-2-(2-naphthyl)ethene with various acyl chlorides ( $\text{RCOCl}$ ,  $\text{R} = \text{Me}$ ,  $\text{Et}$ ,  $i\text{-Pr}$ ,  $i\text{-Bu}$ ,  $n\text{-pent}$ ) gave the corresponding  $\alpha$ -silyl- $\alpha,\beta$ -unsaturated enones with high  $E$  stereoselectivity. Moreover, poly(styrene)-*co*-[2,2-bis(trimethylsilyl)ethenyl(styrene)] obtained via the reaction of polymers bearing pendant enone functions and  $(\text{Me}_3\text{Si})_3\text{CLi}$ , reacts with the same acyl chlorides in the presence of catalytic amount of  $\text{AlCl}_3$  to give the new macromolecules bearing  $\alpha$ -silyl- $\alpha,\beta$ -unsaturated enones and  $\alpha,\beta$ -unsaturated enones.

© 2009 Elsevier B.V. All rights reserved.

## 1. Introduction

1,1-Disilylated-1-alkenes have gained attention as intermediates in the organic and organosilicon synthesis [1–4]. They have been recognized as useful synthetic reagents since the carbon–silicon bonds are readily cleaved by various electrophiles in a regio- and stereoselective manner [5,6].

Sterically overloaded tris(trimethylsilyl)methane and its derivatives ('trisyl' compounds), show exceptional steric hindrance and structural versatility and have been studied extensively in organometallic chemistry [7]. More recently, these moieties have found their place in the field of polymer chemistry and have been applied in the preparation of novel polymeric materials [8,9].

We have recently been engaged in the development of 1,1-bis(silyl)-1-alkene derivatives [4,10], which are used as precursors for the preparation of ketones as well as variety of important organosilicon intermediates such as acylsilanes, epoxysilanes, 1-halovinylsilanes, silylenoethers, ( $E$ )-alkenylsilanes, and silylenolacetates [1]. We also reported a convenient and stereoselective route for the synthesis of  $\alpha$ -silyl- $\alpha,\beta$ -unsaturated enones from 1,1-bis(trimethylsilyl)-2-phenylethene [6]. In an effort to extend the range of 1,1-bis(silyl)-1-alkenes and  $\alpha$ -silyl- $\alpha,\beta$ -unsaturated enones, new 1,1-bis(trimethylsilyl)-1-alkenes were prepared and the reactions of 1,1-bis(trimethylsilyl)-2-(2-naphthyl)ethene were studied. We

demonstrate that these synthetic methodologies may be applied to formylated polystyrenes.

## 2. Results and discussion

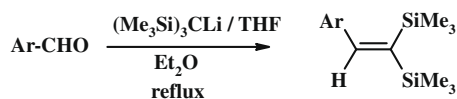
Tris(trimethylsilyl)methyl lithium, made in almost quantitative yield from the reaction between tris(trimethylsilyl)methane and methyl lithium [11–13], reacts with some non-enolisable aldehydes such as 2-naphthaldehyde, 2-thiophenealdehyde, 5-methylfurfural, 3-pyridinaldehyde, *p*-chlorobenzaldehyde and 2,6-dichlorobenzaldehyde with the formation of a series of 1,1-bis(trimethylsilyl)-2-arylalkenes containing heteroaryl and chloro substituents in the aromatic ring. The Peterson reaction readily gives the appropriate vinylbis(silanes) (Table 1).

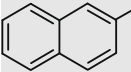
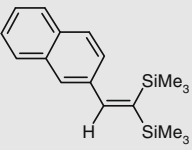

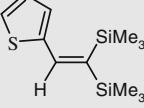
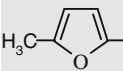
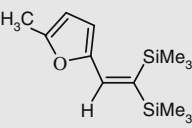

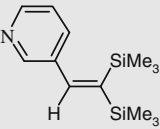
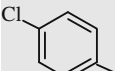
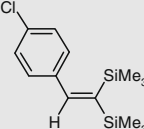
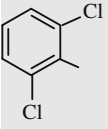
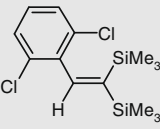
$\alpha$ -Silyl- $\alpha,\beta$ -unsaturated enones are usually prepared by Zr-promoted ene-yne cyclization–carbonylation [14–17], Pd-catalyzed acylation of  $\alpha$ -silylalkenylmetals [18], and the Grignard reaction of vinylsilanes with carbonyl compounds [19] with poor selectivity and expensive reagents. More recently, we have reported a convenient and selective route for the synthesis of  $\alpha$ -silyl- $\alpha,\beta$ -unsaturated enones from 1,1-bis(trimethylsilyl)-2-phenylethene [6]. To investigate the generality of this reaction, 1,1-bis(trimethylsilyl)-2-(2-naphthyl)ethene was treated under optimum conditions (0 °C, 120 min  $\text{AlCl}_3/\text{RCOCl} = 1.5$ ) with various acyl chlorides ( $\text{RCOCl}$ ,  $\text{R} = \text{Me}$ ,  $\text{Et}$ ,  $i\text{-Pr}$ ,  $i\text{-Bu}$ ,  $n\text{-pent}$ ) in the presence of  $\text{AlCl}_3$  as a catalyst. The optimum reaction conditions, were discovered through the reaction of vinylbis(silane) **1** with acetyl chloride, using the same amount of  $\text{AlCl}_3$ , in three different reaction times

\* Corresponding author. Address: Organosilicon Research Laboratory, Faculty of Chemistry, University of Tabriz, 51664 Tabriz, Iran. Tel.: +98 411 3393124; fax: +98 411 3340191.

E-mail address: [dsafa@tabrizu.ac.ir](mailto:dsafa@tabrizu.ac.ir) (K.D. Safa).

**Table 1**  
Synthesis of 1,1-bis(trimethylsilyl)-2-arylethenes via Peterson olefination.



Ar	Time (h)	Product structure	Yield (%)
	3	 (1)	91
	18	 (2)	69
	18	 (3)	75
	7	 (4)	85
	3	 (5)	86
	3	 (6)	81

(Table 2). It was found that after 1 h, the reaction was incomplete, and that longer reaction times gave higher yields of the  $\alpha$ -silyl- $\alpha,\beta$ -unsaturated enone.

In all cases, the monodesilylation of 1,1-bis(trimethylsilyl)-2-(2-naphthyl)ethene was complete within two hours giving  $\alpha$ -silyl- $\alpha,\beta$ -unsaturated enones as the major product (by GC-MS). Substitution of the second silyl group by hydrogen usually required a longer time (3 h) and an increase in the amount of  $\text{AlCl}_3$ . In these reactions, high stereoselectivity was observed and only *E* stereoisomers were obtained. Moreover, in the case of *i*-Bu and *n*-pent substituted products (entries e and d, Table 3), desilylation was accompanied with the formation of trace of the corresponding *Z* stereoisomers (7% and 3% yields respectively (by GC-MS)). As an extension to the present study, we have found out that our method

**Table 2**

The effect of reaction time and amount of  $\text{AlCl}_3$  in the reaction of **1** with acetyl chloride.

Entry	Time (min)	$\text{AlCl}_3$ (mequiv.)	Product <b>7</b> (%) <sup>a</sup>	Product <b>8</b> (%) <sup>a</sup>
1	60	15.3	35	29
2	120	15.3	78	17
3	180	15.3	39	55

<sup>a</sup> The yields have been obtained by GC-MS.

can also be applied in the desilylation of containing bis(trimethylsilyl)alkenyl groups.

The method reported earlier [4] for the modification of formylated polymer precursors via Peterson protocol has been applied for the preparation of poly(styrene)-co-[2,2-bis(trimethylsilyl)ethenyl(styrene)] ( $\text{P}_{\text{Si}}$ ) (Scheme 1). Linear poly(styrene) (*P*) random homopolymer (*P*) was obtained by solution free radical polymerization at  $70(\pm 1)^\circ\text{C}$  using  $\alpha,\alpha'$ -azobis(isobutyronitrile) (AIBN) as an initiator. The formyl groups were introduced by direct electrophilic substitution of polymer *P* using methyl dichloromethyl ether ( $\text{Cl}_2\text{CHOMe}$ ) in the presence of tin (IV) chloride in nitrobenzene. The percentage of formyl groups in the side chain of the formylated polymer  $\text{P}_{\text{CHO}}$  can be determined by  $^1\text{H}$  NMR (49 mol%). Polymer  $\text{P}_{\text{Si}}$  was prepared by the reaction of its formyl precursor with organolithium reagent  $(\text{Me}_3\text{Si})_3\text{CLi}$ . After modification of polymer  $\text{P}_{\text{CHO}}$  with  $(\text{Me}_3\text{Si})_3\text{CLi}$ , all signals from formyl groups at 9.91 ppm disappeared and the signals from  $\text{SiMe}_3$  groups were detected at 0.20 ppm (Fig. 1). Moreover, the FT-IR spectra of the obtained copolymer  $\text{P}_{\text{Si}}$  did not show a sharp peak at  $1696\text{ cm}^{-1}$  which indicates the absence of  $-\text{CHO}$  groups. It is worth noting that the reaction of polymer  $\text{P}_{\text{Si}}$  under the same reaction conditions with acyl chlorides led to the desilylated products  $\text{P}_{\text{COR}}$ . As an example, Fig. 1 shows the  $^1\text{H}$  NMR spectrum of the polymer  $\text{P}_{\text{COCH}_3}$ . In addition to the peaks at 1.50–2.27 ppm corresponding to the CH and  $\text{CH}_2$  groups in the backbone of the polymer, a singlet at 2.35 ppm assigned to  $\text{CH}_3\text{CO}$ , is observed. It is interesting to compare the integrated intensities of the peaks assigned to  $\text{CH}_3\text{CO}$  and  $-\text{SiMe}_3$  as they contain important information about the incorporation of  $\text{CH}_3\text{CO}$  groups to the side chain of the polymer.

The percentage of formyl in  $\text{P}_{\text{CHO}}$  side chain was calculated by measuring the integrate peak areas of the formyl proton and total aliphatic protons. The expression in Eq. (1) was used to determine the composition of polymers, where  $m_1$  is the mole fraction of formyl styrene and  $1 - m_1$  is that of styrene. Both formyl styrene and styrene contain five aliphatic protons.

$$\frac{I_A}{I_a} = \frac{\text{Integrated peak area of formyl protons}}{\text{Integrated peak area of aliphatic}} \quad (1)$$

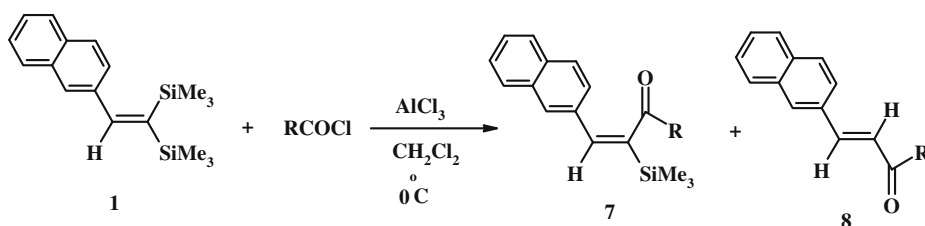
Since all  $-\text{CHO}$  groups are converted into bis(silyl) groups in  $\text{P}_{\text{Si}}$ ,  $m_1$  and  $m_2$  are still the same. In  $\text{P}_{\text{COCH}_3}$ , *X* and *Y* are calculated by the following equation:

$$A = \frac{I_A}{I_a} = \frac{\text{Integrated peak area of SiMe}_3 \text{ group}}{\text{Integrated peak area of CH}_3\text{CO}}$$

$$A = \frac{9X}{3X + 3Y} \quad (2)$$

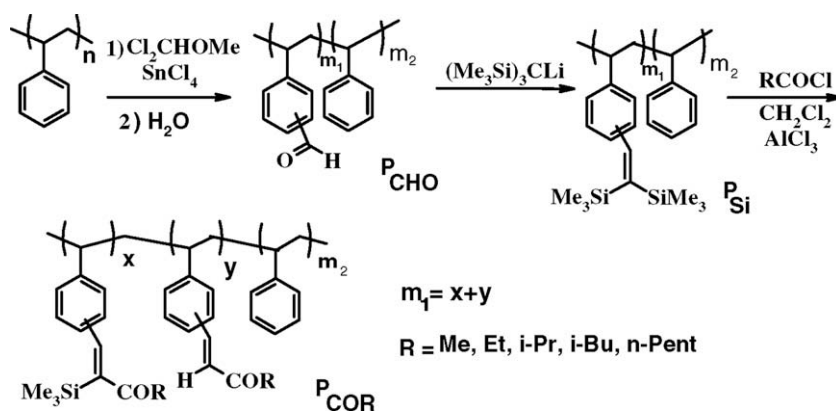
The polymer  $\text{P}_{\text{COCH}_3}$  shows approximately a 3:6 ratio between the peaks at 2.35 and 0.15 ppm, suggesting that nearly 34% of the side chain of the polymer are changed into  $\alpha$ -silyl- $\alpha,\beta$ -unsaturated enone groups. The percentage of  $\alpha$ -silyl- $\alpha,\beta$ -unsaturated enone and  $\alpha,\beta$ -unsaturated enone groups in polymers are listed in Table 4. The FT-IR spectra of all polymers  $\text{P}_{\text{COR}}$  showed two peaks around  $1667, 1972\text{ cm}^{-1}$  due to  $\text{C}=\text{O}$  stretching.

**Table 3**  
The Friedel–Crafts reaction of **1** with acyl chlorides **2a–e**.



Entry	RCOCl <b>2</b>	<b>7</b> (%)		<b>8</b> (%)
		E	Z	
a		72 ( <b>7a</b> )	–	15 ( <b>8a</b> )
b		65 ( <b>7b</b> )	–	26 ( <b>8b</b> )
c		74 ( <b>7c</b> )	–	21 ( <b>8c</b> )
d		64 ( <b>7d</b> )	7	23 ( <b>8d</b> )
e		68 ( <b>7e</b> )	3	30 ( <b>8e</b> )

(a) Reactions carried out on 3.4 mmol scale of **1** in the presence of 15.3 mequiv. in  $\text{CH}_2\text{Cl}_2$  (20 ml) at  $0^\circ\text{C}$  for 2 h. (b)  $\text{AlCl}_3/\text{RCOCl} = 1.5$ .



**Scheme 1.** Synthesis route for preparation of  $\text{P}_{\text{CHO}}$ ,  $\text{P}_{\text{Si}}$  and  $\text{P}_{\text{COR}}$  polymers.

### 3. Conclusion

We have developed a method for the facile generation and reaction of some 1,1-bis(silyl) alkenes and studied their reactions with a

variety of acyl chlorides to give the corresponding  $\alpha$ -silyl- $\alpha,\beta$ -unsaturated enones and  $\alpha,\beta$ -unsaturated enones in high yields with high stereoselectivities. These compounds have potential for conversion into new materials with a variety of chemically reactive groups.

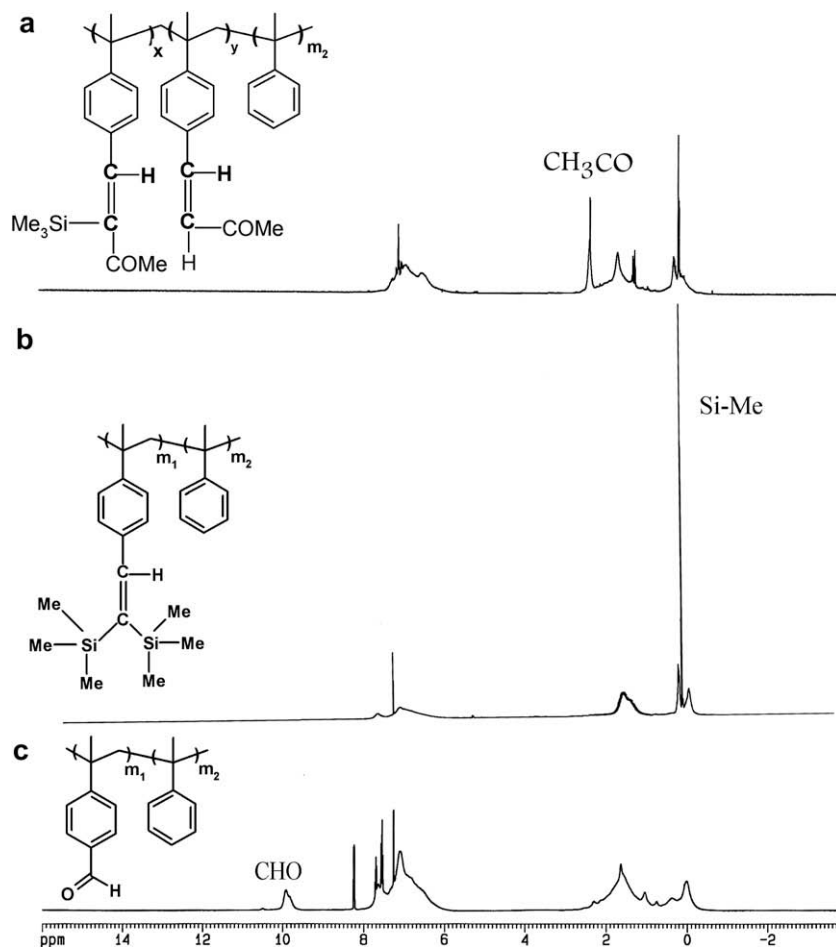


Fig. 1. The  $^1\text{H}$  NMR spectra of (a)  $\text{P}_{\text{CHO}}$ , (b)  $\text{P}_{\text{Si}}$  and (c)  $\text{P}_{\text{COCH}_3}$ .

## 4. Experimental

### 4.1. Solvents and reagents

The reactions were carried out under dry argon. Solvents were dried by standard methods. Substrates for the preparation of tris(trimethylsilyl)methyl lithium, viz.  $\text{Me}_3\text{SiCl}$  (Merck),  $\text{Li}$  (Merck),  $\text{CHCl}_3$  (Merck), all the aldehyde derivatives (Merck), dichloromethyl ether (Merck) and tin (IV) chloride (Merck) were used as received. All acyl chlorides were purchased from Merck and distilled before use.  $\text{AlCl}_3$  was used after sublimation.

### 4.2. Spectra

The  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were recorded with a Bruker FT-400 MHz spectrometer at room temperature and  $\text{CDCl}_3$  as a solvent. The mass spectra were obtained with a GC-Mass Agilent,

quadrupole mode 5973N instrument, operating at 70 eV. The FT-IR spectra were recorded on a Bruker-Tensor 270 spectrometer. Elemental analyses were carried out with an Elementar vario EL III instrument.

### 4.3. General procedure for the synthesis of vinylbis(silanes)

Tris(trimethylsilyl)methyl lithium (15 mmol) and aldehyde (15 mmol) in dry THF (50 ml) were refluxed for a specific time mentioned in Table 1 and then poured into water (50 ml) and extracted twice with 50 ml of ether. The combined organic layers were dried ( $\text{Na}_2\text{SO}_4$ ) and filtered. The solvent was evaporated and the residue was then purified by preparative TLC (silica gel) to give the corresponding vinylbis(silane).

#### 4.3.1. Preparation of 1,1-bis(trimethylsilyl)-2-(2-naphthyl)ethene (1)

A white solid:  $R_f = 0.44$  (*n*-hexane); Yield: 91%; m.p. 40–42 °C; FT-IR ( $\text{KBr cm}^{-1}$ ): 3051 (Ar-H), 1553, 1497 (C=C), 1248, 835 ( $\text{Si-CH}_3$ );  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  -0.00 (s, 9H,  $\text{SiMe}_3$ ), 0.27 (s, 9H,  $\text{SiMe}_3$ ), 7.35–7.83 (m, 7H, Ar), 7.92 (s, 1H, vinyl);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  -0.4 ( $\text{SiMe}_3$ ), 1.0 ( $\text{SiMe}_3$ ), 122.3–153.8 (Ar and C=C);  $m/z$  (EI): 298 (50%,  $[\text{M}]^+$ ), 283 (64%,  $[\text{M}-\text{Me}]^+$ ), 209 (64%), 185 (100%), 73 (51%,  $[\text{SiMe}_3]^+$ ). Anal. Calc. for  $\text{C}_{18}\text{H}_{26}\text{Si}_2$ : C, 72.5; H, 8.7. Found: C, 72.1; H, 8.3%.

#### 4.3.2. Preparation of 1,1-bis(trimethylsilyl)-2-(2-thiophenyl)ethene (2)

A yellowish liquid:  $R_f = 0.32$  (*n*-hexane); Yield: 69%; FT-IR ( $\text{KBr cm}^{-1}$ ): 3073 (Ar-H), 1551, 1424 (C=C), 1252, 837 ( $\text{Si-CH}_3$ );  $^1\text{H}$

Table 4

The molar compositions of  $\text{P}_{\text{COR}}$  polymers.

	$X^a$ (%)	$Y^a$ (%)	$m_2$ (%)
$\text{P}_{\text{COCH}_3}$	34	15	51
$\text{P}_{\text{COC}_2\text{H}_5}$	31	18	51
$\text{P}_{\text{COi-Pr}}$	33	14	51
$\text{P}_{\text{COi-Bu}}$	32	17	51
$\text{P}_{\text{COi-Pent}}$	31	18	51

<sup>a</sup>  $X$  is the mole fraction of  $\alpha$ -silyl- $\alpha,\beta$ -unsaturated enone in polymer and  $Y$  is that of the  $\alpha,\beta$ -unsaturated enone in polymer.

NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  -0.28 (s, 9H, SiMe<sub>3</sub>), -0.29 (s, 9H, SiMe<sub>3</sub>), 6.45, 6.80 (m, 3H, Ar), 7.1 (s, 1H, vinyl); <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  -0.5 (SiMe<sub>3</sub>), 0.61 (SiMe<sub>3</sub>), 124.4–147.8 (Ar and C=C); *m/z* (EI): 254 (23%, [M]<sup>+</sup>), 239 (30%, [M–Me]<sup>+</sup>), 181 (36%, [M–SiMe<sub>3</sub>]<sup>+</sup>), 141 (100%), 73 (40%, [SiMe<sub>3</sub>]<sup>+</sup>). Anal. Calc. for C<sub>12</sub>H<sub>22</sub>Si<sub>2</sub>S: C, 71.7; H, 8.7. Found: C, 71.9; H, 8.3%.

#### 4.3.3. Preparation of 1,1-bis(trimethylsilyl)-2-[2-(5-methylfuryl)ethene] (3)

A yellowish liquid: *R<sub>f</sub>* = 0.40 (*n*-hexane); Yield: 52%; FT-IR (KBr cm<sup>-1</sup>): 2955 (Ar–H), 1559, 1483 (C=C), 1250, 841 (Si–CH<sub>3</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  0.17 (s, 9H, SiMe<sub>3</sub>), 0.18 (s, 9H, SiMe<sub>3</sub>), 2.34 (s, 3H, CH<sub>3</sub>), 6.00–6.22 (d, 2H, *J*<sub>HH</sub> = 3 Hz, Ar), 7.16 (s, 1H, vinyl); <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  -0.40 (SiMe<sub>3</sub>), 0.64 (SiMe<sub>3</sub>), 12.6 (CH<sub>3</sub>), 106.8–152.4 (Ar and C=C); *m/z* (EI): 252 (23%, [M]<sup>+</sup>), 237 (30%, [M–Me]<sup>+</sup>), 179 (36%, [M–SiMe<sub>3</sub>]<sup>+</sup>), 139 (100%), 73 (40%, [SiMe<sub>3</sub>]<sup>+</sup>). Anal. Calc. for C<sub>13</sub>H<sub>24</sub>OSi<sub>2</sub>: C, 61.7; H, 10.5. Found: C, 61.3; H, 10.2%.

#### 4.3.4. Preparation of 1,1-bis(trimethylsilyl)-2-(3-pyridyl)ethene (4)

A yellowish liquid: *R<sub>f</sub>* = 0.64 (2:1 *n*-hexane:ethyl acetate as eluent); Yield: 70%; FT-IR (KBr cm<sup>-1</sup>): 3030, 3078 (Ar–H), 1253, 832 (Si–CH<sub>3</sub>), 1551, 1470 (C=C); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  0.08 (s, 9H, SiMe<sub>3</sub>), 0.16 (s, 9H, SiMe<sub>3</sub>), 7.17–8.45 (m, 5H, Ar and vinyl); <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  -0.7 (SiMe<sub>3</sub>), 0.9 (SiMe<sub>3</sub>), 121.5–149.3 (Ar and C=C); *m/z* (EI): 249 (38%, [M]<sup>+</sup>), 248 (75%, [M–H]<sup>+</sup>), 234 (100%, [M–Me]<sup>+</sup>), 176 (27%, [M–SiMe<sub>3</sub>]<sup>+</sup>), 73 (64%, [SiMe<sub>3</sub>]<sup>+</sup>). Anal. Calc. for C<sub>13</sub>H<sub>23</sub>NSi<sub>2</sub>: C, 62.7; H, 9.6; N, 5.6. Found: C, 62.2; H, 10; N, 5.4%.

#### 4.3.5. Preparation of 1,1-bis(trimethylsilyl)-2-(4-chloro)phenylethene (5)

A colorless liquid: *R<sub>f</sub>* = 0.48 (*n*-hexane); Yield: 74%; FT-IR (KBr cm<sup>-1</sup>): 3027 (Ar–H), 1551, 1484 (C=C), 1251, 837 (Si–CH<sub>3</sub>), 927 (C–Cl); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  0.01 (s, 9H, SiMe<sub>3</sub>), 0.23 (s, 9H, SiMe<sub>3</sub>), 7.1–7.3 (d, 4H, *J*<sub>HH</sub> = 8 Hz, Ar), 7.7 (s, 1H, vinyl); <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  -0.5 (SiMe<sub>3</sub>), 1.0 (SiMe<sub>3</sub>), 126.9–152.3 (Ar and C=C); *m/z* (EI): 267 (64%, [M–Me]<sup>+</sup>), 193 (60%, [M–Ph–Cl]<sup>+</sup>), 169 (71%), 73 (100%, [SiMe<sub>3</sub>]<sup>+</sup>). Anal. Calc. for C<sub>14</sub>H<sub>23</sub>ClSi<sub>2</sub>: C, 59.8; H, 8.4. Found: C, 59.2; H, 8.2%.

#### 4.3.6. Preparation of 1,1-bis(trimethylsilyl)-2-(2,6-dichloro)phenylethene (6)

A colorless liquid: *R<sub>f</sub>* = 0.28 (*n*-hexane); Yield: 70%; FT-IR (KBr cm<sup>-1</sup>): 3057 (Ar–H), 1600, 1427 (C=C), 1253, 840 (Si–CH<sub>3</sub>), 930 (C–Cl); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  -0.10 (s, 9H, SiMe<sub>3</sub>), 0.25 (s, 9H, SiMe<sub>3</sub>), 7.1–7.3 (m, 4H, vinyl and Ar), <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  -0.6 (SiMe<sub>3</sub>), -0.5 (SiMe<sub>3</sub>), 126.4–149.2 (Ar and C=C); *m/z* (EI): 301 (100%, [M–Me]<sup>+</sup>), 227 (56%, [M–Ph–Cl]<sup>+</sup>), 73 (72%, [SiMe<sub>3</sub>]<sup>+</sup>). Anal. Calc. for C<sub>14</sub>H<sub>22</sub>Cl<sub>2</sub>Si<sub>2</sub>: C, 52.6; H, 6.5. Found: C, 52.4; H, 6.9%.

### 4.4. General procedure for Friedel–Crafts reactions using 1,1-bis(trimethylsilyl)-2-(2-naphthyl)ethene as a precursor

A solution of 1,1-bis(trimethylsilyl)-2-(2-naphthyl)ethene (1.0 g, 3.7 mmol) in dry CH<sub>2</sub>Cl<sub>2</sub> (20 ml) was added during 15 min at 0 °C under argon to a stirred solution of anhydrous aluminum trichloride (7.1 g, 15.3 mequiv.) in dry CH<sub>2</sub>Cl<sub>2</sub> (30 ml) containing acyl chloride (3.36 mmol), and the mixture was stirred at 0 °C for a further 105 min. The reaction mixture was poured into water (50 ml) and extracted twice with 50 ml of ether. The combined organic layers were dried (Na<sub>2</sub>SO<sub>4</sub>) and filtered. The solvent was evaporated and the residue was then purified by preparative TLC (silica gel) to give the products.

#### 4.4.1. Reaction of 1 with CH<sub>3</sub>COCl

The reaction of 1 with 2a (0.27 g). TLC on silica gel (7:2 *n*-hexane:diethyl ether as eluant) gave 7a (*R<sub>f</sub>* = 0.25) and 8a (*R<sub>f</sub>* = 0.27,

*m.p.* 92 °C). 7a: FT-IR (KBr cm<sup>-1</sup>), 3065 (Ar–H), 1674 (C=O), 1594, 1500 (Ar and C=C), 1249, 841 (Si–CH<sub>3</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  0.26 (s, 9H, SiMe<sub>3</sub>), 2.08 (s, 3H, CH<sub>3</sub>), 6.90–7.83 (m, 8H, vinyl and Ar); <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  -2.6 (SiMe<sub>3</sub>), 30.2 (CH<sub>3</sub>), 124.8–149.7 (Ar and C=C), 215.6 (C=O); *m/z* (EI): 268 (42%, [M]<sup>+</sup>), 253 (100%, [M–Me]<sup>+</sup>), 179 (58%).

Compound 8a: FT-IR (KBr cm<sup>-1</sup>), 3053 (Ar–H), 1667 (C=O), 1615, 1503 (Ar and C=C), 1244, 823 (Si–CH<sub>3</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  2.43 (s, 3H, CH<sub>3</sub>), 6.8 (d, 1H, *J* = 16 Hz, ArHC=CH), 7.50–7.69 (m, 8H, ArCH=CH and Ar); <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  -2.6 (SiMe<sub>3</sub>), 30.2 (CH<sub>3</sub>), 124.8–149.7 (Ar and C=C), 209.6 (C=O); *m/z* (EI): 268 (42%, [M]<sup>+</sup>), 253 (100%, [M–Me]<sup>+</sup>), 179 (58%).

#### 4.4.2. Reaction of 1 with C<sub>2</sub>H<sub>5</sub>COCl

The reaction of 1 with 2b (0.31 g). TLC on silica gel (5:1 *n*-hexane:diethyl ether as eluant) gave 7b (*R<sub>f</sub>* = 0.55) and 8b (*R<sub>f</sub>* = 0.19, *m.p.* 78 °C). 7b: FT-IR (KBr cm<sup>-1</sup>), 3056 (Ar–H), 1673 (C=O), 1592, 1504 (Ar and C=C), 1250, 839 (Si–CH<sub>3</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  0.31 (s, 9H, SiMe<sub>3</sub>), 1.02 (t, 3H, <sup>3</sup>*J*<sub>HH</sub> = 7, CH<sub>3</sub>), 2.34–2.36 (q, 2H, CH<sub>2</sub>), 7.03–7.86 (m, 8H, vinyl and Ar); <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  -2.5 (SiMe<sub>3</sub>), 6.98 (CH<sub>3</sub>), 35.5 (CH<sub>2</sub>), 124.8–149.6 (Ar and C=C), 212.3 (C=O); *m/z* (EI): 282 (17%, [M]<sup>+</sup>), 267 (20%, [M–Me]<sup>+</sup>), 253 (100%, [M–Et]<sup>+</sup>), 73 (35%, [SiMe<sub>3</sub>]<sup>+</sup>).

Compound 8b: FT-IR (KBr cm<sup>-1</sup>), 3051 (Ar–H), 1667 (C=O), 1618, 1503 (Ar and C=C); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  1.20 (t, 3H, *J*<sub>HH</sub> = 7, CH<sub>3</sub>), 2.71–2.76 (q, 2H, CH<sub>2</sub>), 6.91 (d, 1H, *J* = 16 Hz, ArHC=CH), 7.50–7.96 (m, 8H, ArC=CH and Ar); <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  7.5 (CH<sub>3</sub>), 33.1 (CH<sub>2</sub>), 122.5–141.2 (Ar and C=C), 199.8 (C=O).

#### 4.4.3. Reaction of 1 with *i*-C<sub>3</sub>H<sub>7</sub>COCl

The reaction of 1 with 2c (0.36 g). TLC on silica gel (4:1 *n*-hexane:diethyl ether as eluant) gave 7c (*R<sub>f</sub>* = 0.64) and 8c (*R<sub>f</sub>* = 0.36, *m.p.* 86–88 °C). 7c: FT-IR (KBr cm<sup>-1</sup>), 3056 (Ar–H), 1671 (C=O), 1588, 1504 (Ar and C=C), 1250, 841 (Si–CH<sub>3</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  0.31 (s, 9H, SiMe<sub>3</sub>), 1.00 (d, 6H, <sup>3</sup>*J*<sub>HH</sub> = 7, CH(CH<sub>3</sub>)<sub>2</sub>), 2.49–2.52 (m, 1H, CH(CH<sub>3</sub>)<sub>2</sub>), 7.17–7.86 (m, 8H, vinyl and Ar); <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  -1.9 (SiMe<sub>3</sub>), 17.7 (CH(CH<sub>3</sub>)<sub>2</sub>), 39.8 (CH(CH<sub>3</sub>)<sub>2</sub>), 125.1–149.1 (Ar and C=C), 215.1 (C=O); *m/z* (EI): 224 (22%, [M–HCOCH(CH<sub>3</sub>)<sub>2</sub>]<sup>+</sup>), 181 (100%, [ArCH=CCOH]<sup>+</sup>), 152 (29%, [ArCH]<sup>+</sup>).

8c: FT-IR (KBr cm<sup>-1</sup>), 3058 (Ar–H), 1677 (C=O), 1603, 1462 (Ar and C=C); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  1.22 (d, 6H, <sup>3</sup>*J*<sub>HH</sub> = 7, CH(CH<sub>3</sub>)<sub>2</sub>), 2.96–3.00 (m, 1H, CH(CH<sub>3</sub>)<sub>2</sub>), 6.94 (s, 1H, ArHC=CH), 7.50–7.96 (m, 8H, Ar and ArHC=CH); <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  17.5 (CH(CH<sub>3</sub>)<sub>2</sub>), 38.3 (CH(CH<sub>3</sub>)<sub>2</sub>), 122.5–141.4 (Ar and C=C), 202.8 (C=O).

#### 4.4.4. Reaction of 1 with *i*-C<sub>4</sub>H<sub>9</sub>COCl

The reaction of 1 with 2d (0.41 g). TLC on silica gel (8:1 *n*-hexane:diethyl ether as eluant) gave 7d (*R<sub>f</sub>* = 0.56) and 8d (*R<sub>f</sub>* = 0.21). Compound 7d: FT-IR (KBr cm<sup>-1</sup>), 3056 (Ar–H), 1675 (C=O), 1589, 1505 (Ar and C=C), 1249, 841 (Si–CH<sub>3</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  0.28 (s, 9H, SiMe<sub>3</sub>), 0.81 (d, 6H, <sup>3</sup>*J*<sub>HH</sub> = 6 Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 2.11–2.19 (m, 1H, CH<sub>2</sub>CH(CH<sub>3</sub>)<sub>2</sub>), 2.22 (d, 2H, <sup>3</sup>*J*<sub>HH</sub> = 6 Hz, COCH<sub>2</sub>CH(CH<sub>3</sub>)<sub>2</sub>), 6.98–7.90 (m, 8H, vinyl and Ar); <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  -2.4 (SiMe<sub>3</sub>), 21.6 (CH(CH<sub>3</sub>)<sub>2</sub>), 22.4 (CH(CH<sub>3</sub>)<sub>2</sub>), 50.7 (CH<sub>2</sub>CH(CH<sub>3</sub>)<sub>2</sub>), 125.1–149.7 (Ar and C=C), 210.7 (C=O); *m/z* (EI): 310 (64%, [M]<sup>+</sup>), 295 (73%, [M–Me]<sup>+</sup>), 267 (87%, [M–CH(CH<sub>3</sub>)<sub>2</sub>]<sup>+</sup>), 253 (100%, [M–CH<sub>2</sub>CH(CH<sub>3</sub>)<sub>2</sub>]<sup>+</sup>), 73 (59%, [SiMe<sub>3</sub>]<sup>+</sup>).

Compound 8d: FT-IR (KBr cm<sup>-1</sup>), 3056 (Ar–H), 1687 (C=O), 1605, 1464 (Ar and C=C); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  1.02 (d, 6H, <sup>3</sup>*J*<sub>HH</sub> = 6 Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 2.24–2.34 (m, 1H, CH<sub>2</sub>CH(CH<sub>3</sub>)<sub>2</sub>), 2.58 (d, 2H, <sup>3</sup>*J*<sub>HH</sub> = 6 Hz, COCH<sub>2</sub>CH(CH<sub>3</sub>)<sub>2</sub>), 6.86 (s, 1H, ArHC=CH), 7.46–7.94 (m, 8H, Ar and ArHC=CH); <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  21.7 (CH(CH<sub>3</sub>)<sub>2</sub>), 24.2 (CH(CH<sub>3</sub>)<sub>2</sub>), 48.9 (CH<sub>2</sub>CH(CH<sub>3</sub>)<sub>2</sub>), 122.4–153.7 (Ar and C=C), 199.1 (C=O).

#### 4.4.5. Reaction of **1** with *n*-C<sub>5</sub>H<sub>11</sub>COCl

The reaction of **1** with **2e** (0.47 g). TLC on silica gel (4:1 *n*-hexane:diethyl ether as eluant) gave **7e** (*R<sub>f</sub>* = 0.64) and **8e** (*R<sub>f</sub>* = 0.45). Compound **7e**: FT-IR (KBr cm<sup>-1</sup>), 3056 (Ar-H), 1675 (C=O), 1591, 1460 (Ar and C=C), 1249, 843 (Si-CH<sub>3</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 0.31 (s, 9H, SiMe<sub>3</sub>), 0.80 (t, 3H, <sup>3</sup>J<sub>HH</sub> = 7 Hz, CH<sub>2</sub>CH<sub>3</sub>), 1.11–1.21 (m, 4H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.53–1.60 (m, 2H, COCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 2.33 (t, 2H, <sup>3</sup>J<sub>HH</sub> = 8 Hz, COCH<sub>2</sub>CH<sub>2</sub>), 7.03–7.86 (m, 8H, vinyl and Ar); <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ -2.4 (SiMe<sub>3</sub>), 12.8 (CH<sub>2</sub>CH<sub>3</sub>), 21.5 (CH<sub>2</sub>CH<sub>3</sub>), 22.3 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 30.2 (COCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 42.2 (COCH<sub>2</sub>), 124.9–149.7 (Ar and C=C), 211.6 (C=O); *m/z* (EI): 281 (37%, [M-(CH<sub>2</sub>)<sub>2</sub>CH<sub>3</sub>]<sup>+</sup>), 267 (100%, [M-(CH<sub>2</sub>)<sub>3</sub>CH<sub>3</sub>]<sup>+</sup>), 253 (66%, [M-(CH<sub>2</sub>)<sub>4</sub>CH<sub>3</sub>]<sup>+</sup>), 73 (34%, [SiMe<sub>3</sub>]<sup>+</sup>).

**8e**: FT-IR (KBr cm<sup>-1</sup>), 3055 (Ar-H), 1685 (C=O), 1613, 1460 (Ar and C=C); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 0.98 (t, 3H, <sup>3</sup>J<sub>HH</sub> = 7 Hz, CH<sub>2</sub>CH<sub>3</sub>), 1.39–1.42 (m, 4H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.74, 178 (m, 2H, COCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 2.72 (t, 2H, <sup>3</sup>J<sub>HH</sub> = 8 Hz, COCH<sub>2</sub>CH<sub>2</sub>), 6.89 (s, 1H, ArHC=CH), 7.54–7.97 (m, 8H, Ar and ArCH=CH); <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 12.9 (CH<sub>2</sub>CH<sub>3</sub>), 21.5 (CH<sub>2</sub>CH<sub>3</sub>), 22.0 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 30.5 (COCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 39.9 (COCH<sub>2</sub>), 122.4–153.7 (Ar and C=C), 199.6 (C=O).

#### 4.5. Preparation of polymer bearing 1,1-bis(silyl)-1-alkene side chains (P<sub>Si</sub>)

(Me<sub>3</sub>Si)<sub>3</sub>ClLi (15.8 mmol) was added dropwise with stirring to solutions of copolymers P<sub>CHO</sub> (15.8 mmol) in THF at room temperature. The reaction was quenched by adding a small amount of acidic methanol after 2 h and the reaction mixture was poured into cooled acidic methanol to precipitate the polymer P<sub>Si</sub>. FT-IR (KBr cm<sup>-1</sup>), 3025 (Ar-H), 1251, 837 (Si-CH<sub>3</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 0.08 (s, SiMe<sub>3</sub>), 1.25–2.20 (m, Aliphatic), 6.50–7.72 (m, Aromatic).

#### 4.6. General procedure for Fridelle–Crafts reactions using P<sub>Si</sub> as a precursor

A solution of polymer (1.0 g, 3.4 mmol) in dry CH<sub>2</sub>Cl<sub>2</sub> (20 ml) was added during 15 min at 0 °C under argon to a stirred solution of anhydrous aluminum trichloride (7.1 g, 15.3 mequiv.) in dry CH<sub>2</sub>Cl<sub>2</sub> (30 ml) containing acyl chloride (3.36 mmol), and the mixture was stirred at 0 °C for a further 105 min. The reaction mixture was then poured into methanol to precipitate the product.

##### 4.6.1. Reaction of P<sub>Si</sub> with MeCOCl

FT-IR (KBr cm<sup>-1</sup>), 3054 (Ar-H), 1672, 1667 (C=O), 1255, 840 (Si-CH<sub>3</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 0.09 (s, SiMe<sub>3</sub>), 1.23–2.22 (m, Aliphatic), 2.35 (s, COCH<sub>3</sub>), 6.65–7.86 (m, Aromatic).

##### 4.6.2. Reaction of P<sub>Si</sub> with EtCOCl

FT-IR (KBr cm<sup>-1</sup>), 3023 (Ar-H), 1670, 1663 (C=O), 1251, 834 (Si-CH<sub>3</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 0.11 (s, SiMe<sub>3</sub>), 1.30–

2.26 (m, Aliphatic), 1.26 (t, CH<sub>3</sub>), 2.69 (CH<sub>2</sub>), 6.69–7.96 (m, Aromatic).

##### 4.6.3. Reaction of P<sub>Si</sub> with *i*-C<sub>3</sub>H<sub>7</sub>COCl

FT-IR (KBr cm<sup>-1</sup>), 3054 (Ar-H), 1688, 1605 (C=O), 1251, 835 (Si-CH<sub>3</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 0.10 (s, SiMe<sub>3</sub>), 1.25–2.36 (m, Aliphatic, CH(CH<sub>3</sub>)<sub>2</sub>), 2.92 (m, CH(CH<sub>3</sub>)<sub>2</sub>), 6.76–7.82 (m, Aromatic).

##### 4.6.4. Reaction of P<sub>Si</sub> with *i*-C<sub>4</sub>H<sub>9</sub>COCl

FT-IR (KBr cm<sup>-1</sup>), 3026 (Ar-H), 1686, 1657 (C=O), 1251, 843 (Si-CH<sub>3</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 0.10 (s, SiMe<sub>3</sub>), 1.31–2.82 (m, Aliphatic, CH(CH<sub>3</sub>)<sub>2</sub>), CH<sub>2</sub>CH(CH<sub>3</sub>)<sub>2</sub>, COCH<sub>2</sub>CH(CH<sub>3</sub>)<sub>2</sub>), 6.99–7.26 (m, Aromatic).

##### 4.6.5. Reaction of P<sub>Si</sub> with *n*-C<sub>5</sub>H<sub>11</sub>COCl

FT-IR (KBr cm<sup>-1</sup>), 3024 (Ar-H), 1687, 1663 (C=O), 1250, 840 (Si-CH<sub>3</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 0.12 (s, SiMe<sub>3</sub>), 1.28–2.97 (m, Aliphatic, *n*-C<sub>5</sub>H<sub>11</sub>), 6.99–7.95 (m, Aromatic).

#### Acknowledgment

This work has been supported by the Research Institute for Fundamental Sciences, Tabriz, Iran.

#### References

- [1] P. Pawluc, G. Hreczycho, B. Marciniak, J. Org. Chem. 71 (2006) 8676.
- [2] G. Hreczycho, P. Pawluc, B. Marciniak, Synthesis (2006) 1370.
- [3] D.M. Hodgson, P.J. Comina, M.G.B. Drew, J. Chem. Soc., Perkin Trans. 1 (1997) 2279.
- [4] K.D. Safa, A. Hassanpour, S. Tofangdarzadeh, J. Organomet. Chem. 693 (2008) 3622.
- [5] A. Alimardanov, E.I. Negishi, Tetrahedron Lett. 40 (1999) 3839.
- [6] K.D. Safa, S.P. Samani, Sh. Tofangdarzadeh, A. Hassanpour, J. Organomet. Chem. 693 (2008) 2004.
- [7] C. Eaborn, J.D. Smith, J. Chem. Soc., Dalton Trans. (23) (2001) 1541.
- [8] A. Kowalewska, J. Organomet. Chem. 693 (2008) 2193.
- [9] A. Kowalewska, W.A. Stańczyk, S. Boileau, L. Lestel, J.D. Smith, Polymer 40 (1999) 813.
- [10] K.D. Safa, A. Hassanpour, S. Tofangdarzadeh, Synth. Commun. (in press).
- [11] K.D. Safa, M. Babazadeh, Eur. Polym. J. 40 (2004) 1659.
- [12] B.T. Gröbel, D. Seebach, Chem. Ber. 110 (1977) 825.
- [13] M.A. Cook, C. Eaborn, A.E. Jukes, D.R.M. Walton, J. Organomet. Chem. 24 (1970) 529.
- [14] E.I. Negishi, S.J. Holmes, J.M. Tour, J.A. Miller, J. Am. Chem. Soc. 107 (1985) 2568.
- [15] E.I. Negishi, F.E. Cederbaum, T. Tkahashi, Tetrahedron Lett. 27 (1986) 2829.
- [16] E.I. Negishi, S.J. Holmes, J.M. Tour, J.A. Miller, F.E. Cederbaum, D.R. Swanson, T. Tkahashi, J. Am. Chem. Soc. 111 (1989) 3336.
- [17] T. Takahashi, Z. Xi, Y. Nishihara, S. Huo, K. Kasai, K. Aoyagi, V. Denisov, E.I. Negishi, Tetrahedron 53 (1997) 9123.
- [18] E.I. Negishi, V. Bagheri, S. Chatterjee, F.T. Luo, J.A. Miller, A.T. Stoll, Tetrahedron Lett. 24 (1983) 5181.
- [19] G. Stork, B. Ganem, J. Am. Chem. Soc. 95 (1973) 6152.