

## Supporting Information

### **Catalyst-free Depolymerization of Polycaprolactone to Silylated Monoesters and Iodide Derivatives Using Iodosilanes.**

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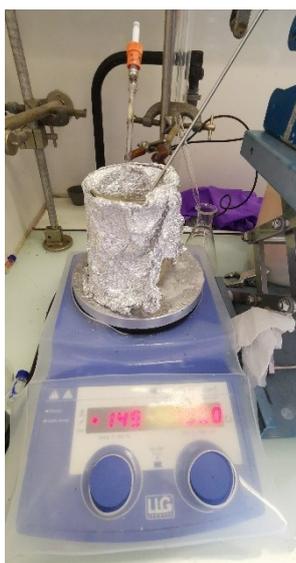
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## I. General considerations

All manipulations were performed using standard Schlenk techniques under Ar atmosphere or using a recirculating *mBraunLabMasterDP* inert atmosphere (Ar) glovebox ( $O_2 < 0.1$  ppm,  $H_2O < 0.1$  ppm). The commercial plastic polycaprolactone (PCL), iodotrimethylsilane ( $Me_3SiI$ ), chlorotrimethylsilane ( $Me_3SiCl$ ), trimethylsilyl trifluoromethanesulfonate ( $Me_3SiOTf$ ), bromotrimethylsilane ( $Me_3SiBr$ ), trimethylsilyl cyanide ( $Me_3SiCN$ ), trimethylsilyl azide ( $Me_3SiN_3$ ), diiodosilane ( $SiH_2I_2$ ) were purchased from Sigma-Aldrich. The deuterated solvents dichloromethane ( $CD_2Cl_2$ ), acetonitrile ( $CD_3CN$ ) were obtained from Eurisotop. They were used as received without any purification. Dodecane and mesitylene (used as internal standards) were purchased from Sigma-Aldrich ; they were distilled under reduced pressure and stored over molecular sieves in the gloves-box. All the liquid reagents as well as deuterated solvents were stored over molecular sieves (4 Å) in the glovebox. Glassware was dried at least overnight at 80°C before using. The 4 Å molecular sieve (Aldrich) was activated by drying under dynamic vacuum at 250 °C for 48 h prior to use. NMR measurement ( $^1H$  and  $^{13}C$ ) were performed at room temperature (19°C) on Bruker Advance Neo 400 MHz instrument. Chemical shifts ( $\delta$ ) were referenced to solvent residual peaks and are given in parts per millions (ppm) relative to tetramethylsilane ( $^1H$  and  $^{13}C$ ). Coupling constants (J) are given in Hz, multiplicities are named as singlet (s), doublet (d), triplet (t), quartet (q), quintuplet (quin), multiplet or overlapping signals (m) and broad signal (br), solvent is given in parenthesis.

### Heating of the reaction mixtures:

Reactions carried out in a J-Young NMR tube are heated in thermostated oil baths or in commercial (CLOUP) aluminium heating systems (see pictures). The tubes are fitted with Teflon airtight plugs and the valve screwed onto the NMR tube allows reaction systems with low-boiling solvents to be heated and pressure maintained ( $P < 5$  bar) without the need for flame-sealing.



For reactions carried out in larger quantities, glassware solvent seal joint (Andrew Glass) are used. As shown in the pictures, the round bottom flask is connected to a right angle tap using a solv-seal joint (Teflon and butyl seal). The two glass parts are firmly connected by a *rotulex* metallic clamp that holds the whole. This assembly enables reactions using low-boiling solvents to be heated beyond their boiling point and the pressure to be maintained (<5 bar).



## II. Study of $\text{Me}_3\text{SiX}$ with esters

Prior to the investigation on polyesters, a scope of the reactivity of silylated  $\text{Me}_3\text{SiX}$  ( $\text{X} = \text{I}, \text{Cl}, \text{Br}, \text{OTf}, \text{CN}, \text{N}_3$ ) reagents on ethyl acetate ( $\text{MeCO}_2\text{Et}$ ) was achieved. The tube was charged with ethyl acetate (9 mL, 0.1 mmol), followed by the deuterated solvent,  $\text{CD}_2\text{Cl}_2$  (0.4 mL) and dodecane as the internal standard (10  $\mu\text{L}$ , 0.04 mmol, 0.14 equiv.). At the end, the corresponding reagent  $\text{Me}_3\text{SiX}$  ( $\text{X} = \text{I}, \text{Cl}, \text{Br}, \text{OTf}, \text{CN}$  and  $\text{N}_3$ ) was added. The NMR tube was then heated in a silicon oil bath at 50 °C or 100 °C during the required time for the reaction. After heating, we obtained a colorless solution without any deposit. Samples were cooled to room temperature and then analyzed by  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy. The conversion of ethyl acetate and the yield of products were determined by integration of the signals versus those of dodecane ( $\delta_{\text{H}} = 1.26$  and 0.88 in  $\text{CD}_2\text{Cl}_2$ ). The reaction conditions and yields of products are presented in Figure S1.

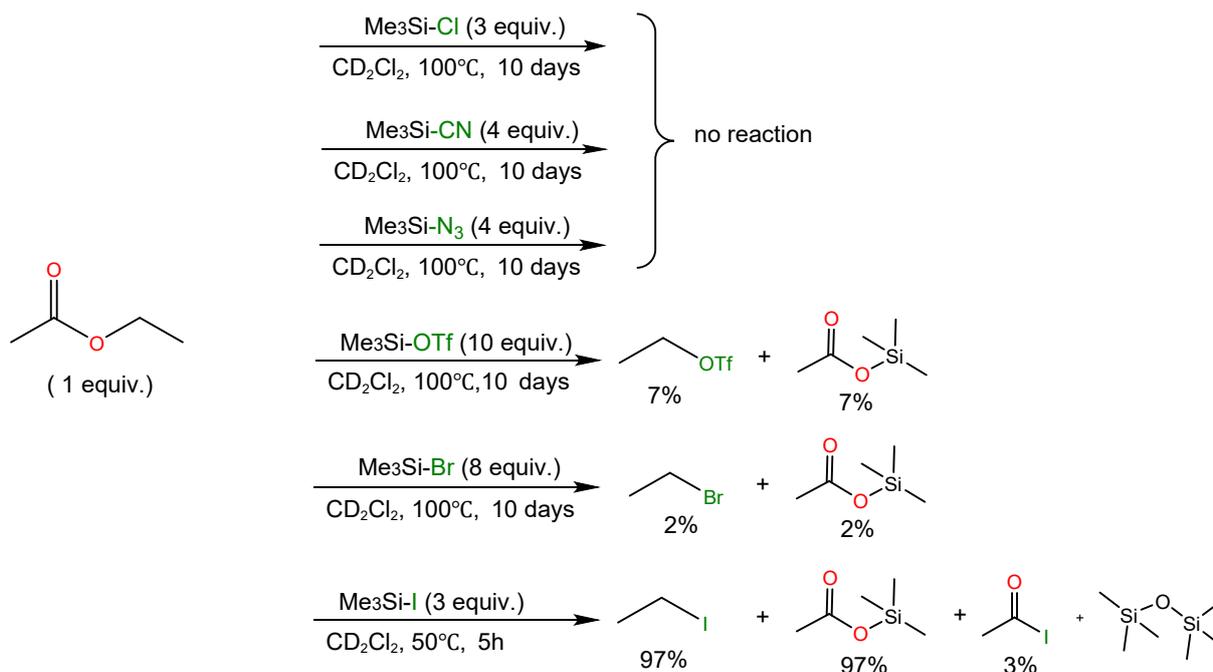
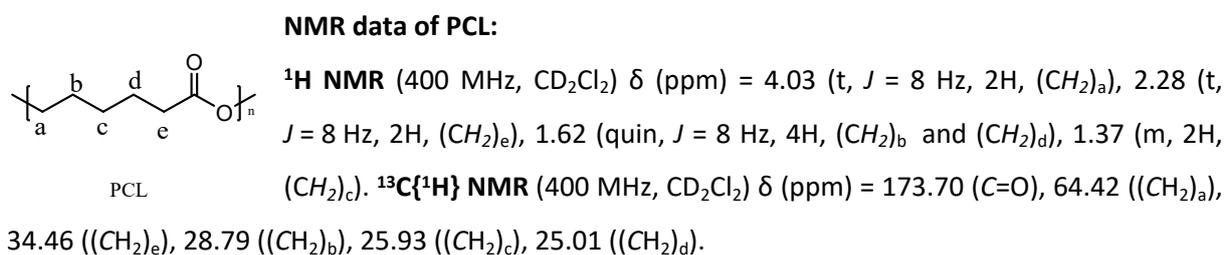


Figure S1 : Scope of  $\text{Me}_3\text{SiX}$  reagents ( $X = \text{I}, \text{Cl}, \text{Br}, \text{OTf}, \text{CN}$  and  $\text{N}_3$ ) with ethyl acetate

### III. Depolymerization of commercial PCL

#### 1. NMR Characterization of the commercial PCL pellets

The polymer **PCL** completely dissolved after sonication for 10 min in acetonitrile and dichloromethane and displays greater solubility in the latter. The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of pure **PCL** are shown in Figure S2, respectively.



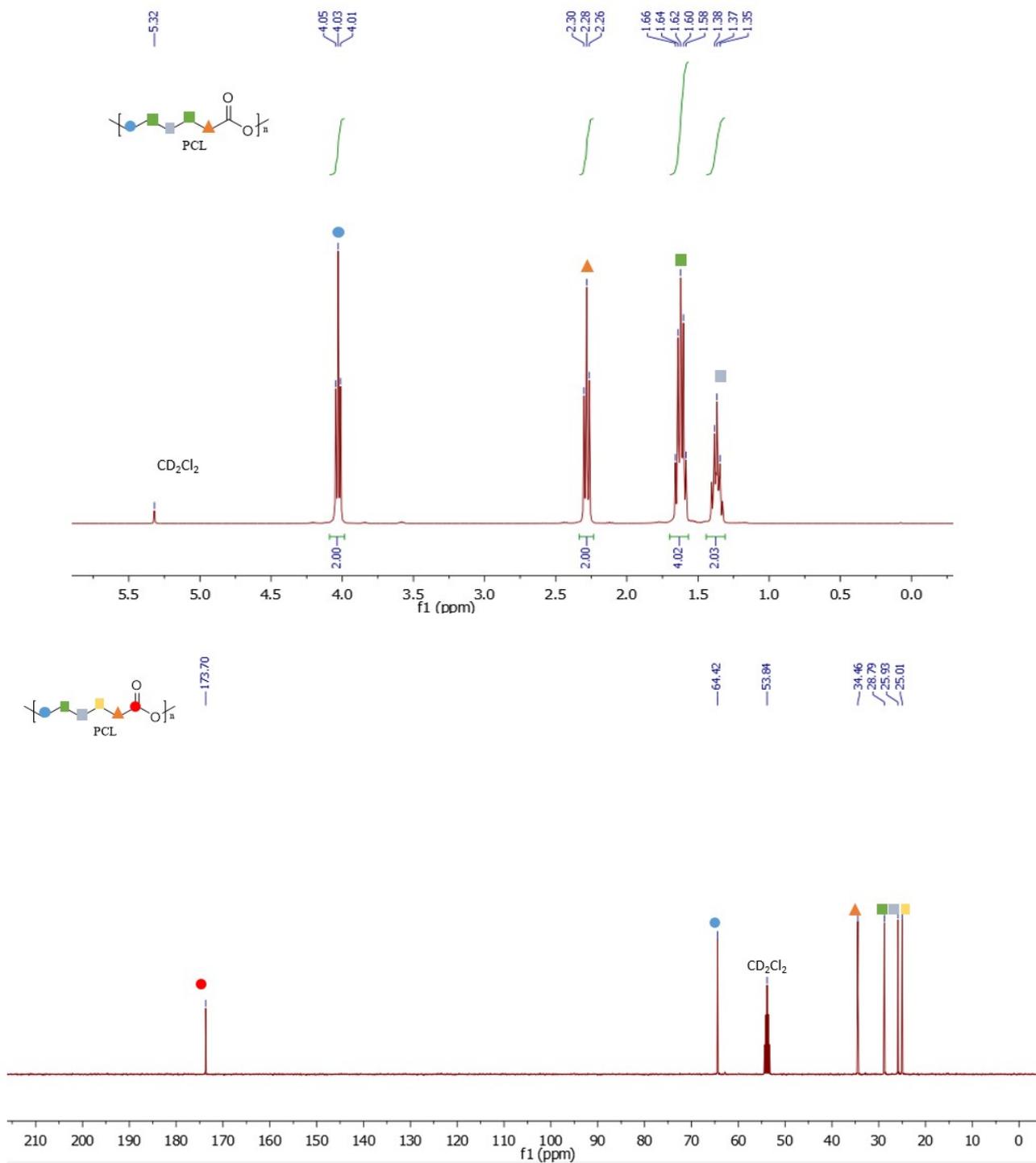


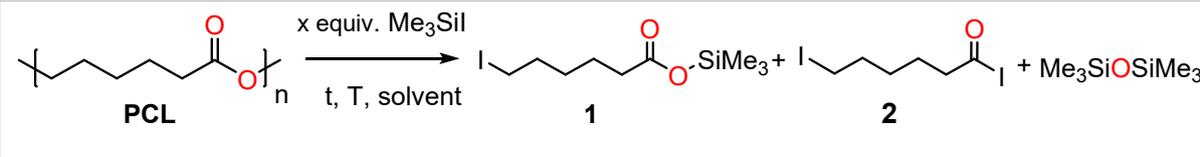
Figure S2 : <sup>1</sup>H and <sup>13</sup>C NMR spectra of **PCL** pellets (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 298 K)

## 2. General procedure for the reaction of PCL with Me<sub>3</sub>SiI

### 2.1 General procedure for the optimization of reaction

A typical depolymerization reaction was performed in a dry J. Young NMR tube. The tube was charged with **PCL** (32 mg, 0.28 mmol, 1 equiv.), followed by the corresponding deuterated solvent CD<sub>2</sub>Cl<sub>2</sub> or CD<sub>3</sub>CN (0.4 mL) and dodecane as the internal standard (10 μL, 0.04 mmol, 0.14 equiv.). At the end, the reagent Me<sub>3</sub>SiI (80 μL, 0.56 mmol, 2 equiv.) was syringed on the suspension. The pellet of **PCL** completely dissolved after sonication for 10 min. The tube was then heated in a silicon oil bath maintained at the required temperature (25 °C, 50 °C, 130 °C, 150 °C) during the required time. After the considered reaction time, the clear solution was pale yellow without any deposit. Samples were cooled down to room temperature and analyzed by <sup>1</sup>H and <sup>13</sup>C NMR. The conversion of **PCL** and the yield of product **1** and **2** were determined by integration of the signals versus those of dodecane (δ<sub>H</sub> = 1.26 and 0.88 ppm in CD<sub>2</sub>Cl<sub>2</sub>, δ<sub>H</sub> = 1.3 and 0.92 in CD<sub>3</sub>CN).

**Table S1** : Depolymerization of **PCL** with Me<sub>3</sub>SiI- Optimization of the reaction conditions <sup>[a]</sup>

						
Entry	x	Solvent	T [°C]	t [h]	Yield in <b>1</b> [%] <sup>[b]</sup>	Yield in <b>2</b> [%] <sup>[b]</sup>
<b>1</b>	1.2	CD <sub>2</sub> Cl <sub>2</sub>	25	20	Traces	0
<b>2</b>	1.2	CD <sub>2</sub> Cl <sub>2</sub>	50	5	24	0
<b>3</b>	1.2	CD <sub>2</sub> Cl <sub>2</sub>	100	5	46	0
<b>4</b>	1.2	CD <sub>2</sub> Cl <sub>2</sub>	130	2	78	0
<b>5</b>	1.2	CD <sub>2</sub> Cl <sub>2</sub>	150	2	88	0
<b>6</b>	2	CD <sub>2</sub> Cl <sub>2</sub>	100	5	74	0
				40	>99	Traces
<b>7</b>	2	CH <sub>2</sub> Cl <sub>2</sub>	100	15	95 <sup>[c]</sup>	2
<b>8</b>	2	CD <sub>3</sub> CN	100	5	90	10
<b>9</b>	2	CD <sub>3</sub> CN	130	2	83	17
<b>10</b> <sup>[d]</sup>	2	CD <sub>3</sub> CN	150	2	68	32
<b>11</b> <sup>[d]</sup>	6	CD <sub>3</sub> CN	150	16	23	74
<b>12</b> <sup>[e]</sup>	3	CD <sub>2</sub> Cl <sub>2</sub>	150	10	23	77

<sup>[a]</sup>Conditions: PCL (1a, 0.28 mmol with respect to the monomer unit), solvent (0.4 mL); <sup>[b]</sup>Yield in **1** and **2** determined by integration of their <sup>1</sup>H NMR signals vs those of dodecane (standard); <sup>[c]</sup>Isolated yield; <sup>[d]</sup>Approximate ratio by <sup>1</sup>H NMR due to H/D exchange; <sup>[e]</sup>Addition of 1 equiv. I<sub>2</sub>.

## 2.2 Procedure for the scale up depolymerization of PCL

A 25 mL round bottom flask was charged with **PCL** (146.4 mg, 1.28 mmol, 1 equiv.),  $\text{CH}_2\text{Cl}_2$  (3 mL), followed by  $\text{Me}_3\text{SiI}$  (365  $\mu\text{L}$ , 2.57 mmol, 2 equiv.). After 30 min of sonication, the yellowish solution was stirred vigorously at  $100^\circ\text{C}$  during 15 h. At the end, the mixture was a clear yellow solution without any deposit. The solvent and excess  $\text{Me}_3\text{SiI}$  were evaporated off under the vacuum and the remaining product **1** was collected in the flask as a yellowish oil. The residue was extracted by pentane (2 x 10 mL). Final yield in product **1** is 95% (96% purity). The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of **1** are presented in the Figure S3.

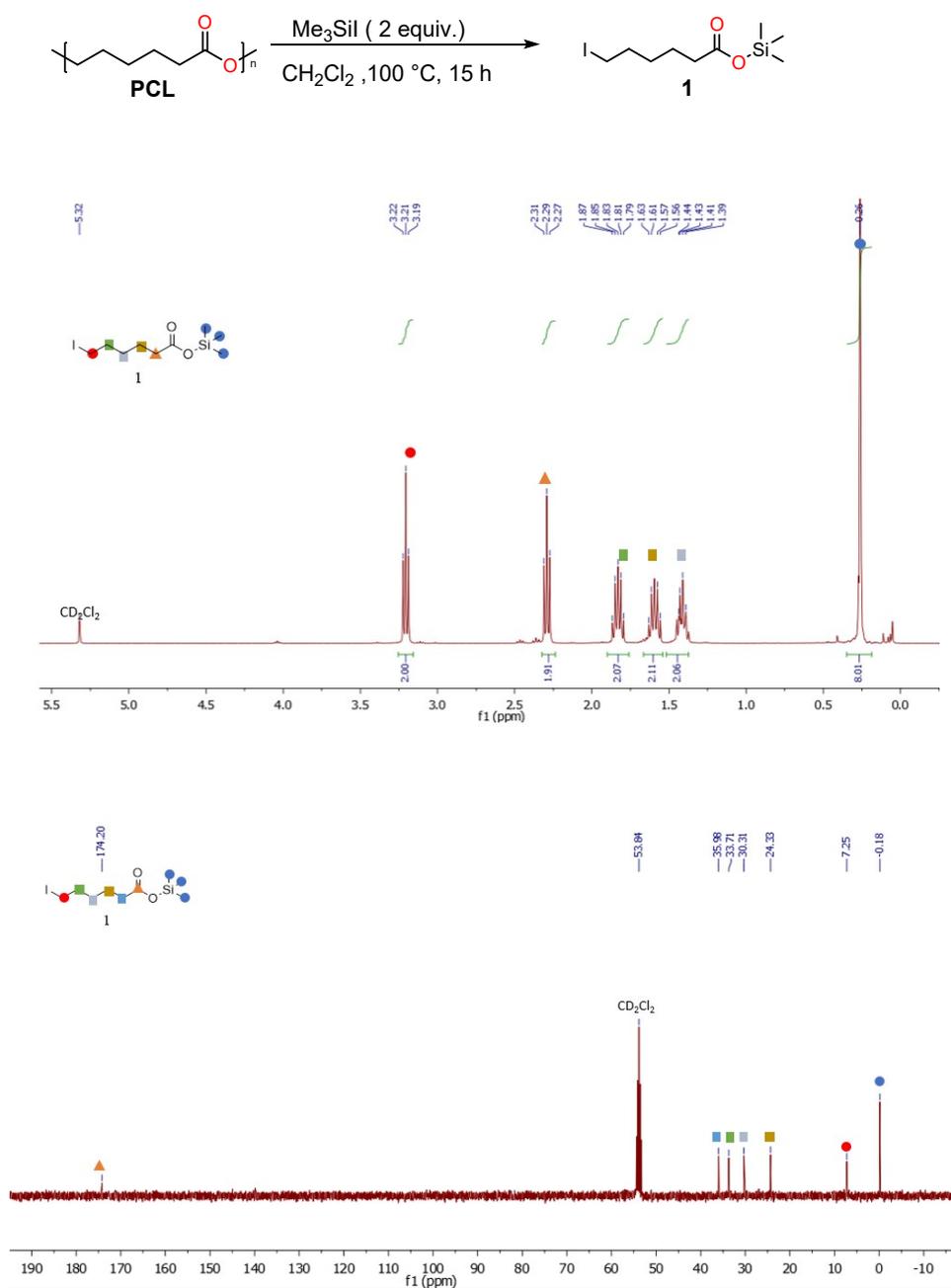
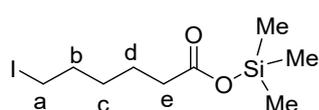


Figure S3:  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of **1** (400 MHz,  $\text{CD}_2\text{Cl}_2$ , 298 K)

### NMR data of **1** :

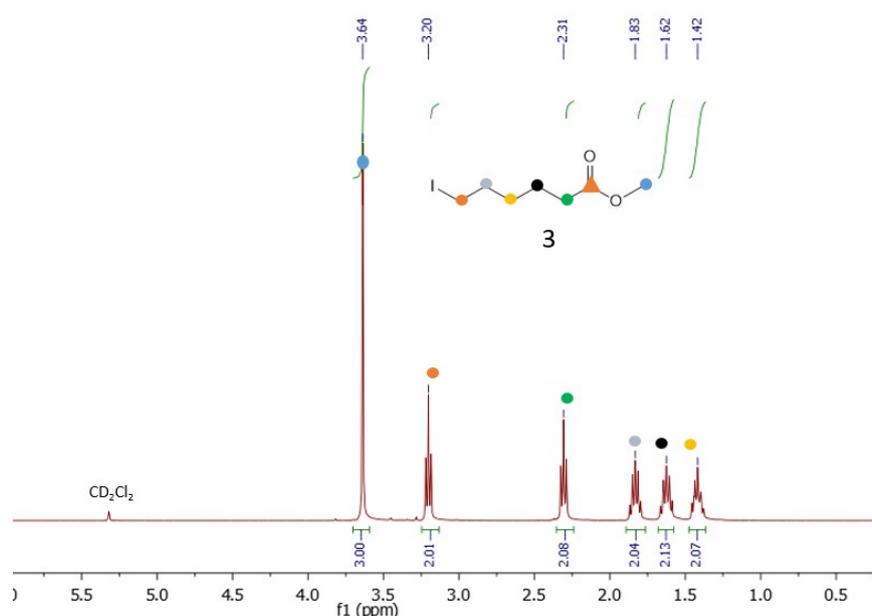


$^1\text{H NMR}$  (400 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  (ppm) = 3.21 (t,  $J = 8$  Hz, 2H,  $(\text{CH}_2)_a$ ), 2.29 (t,  $J = 8$  Hz, 2H,  $(\text{CH}_2)_e$ ), 1.83 (quin,  $J = 8$  Hz, 2H,  $(\text{CH}_2)_b$ ), 1.59 (quin,  $J = 8$  Hz, 2H,  $(\text{CH}_2)_d$ ), 1.43 (m, 2H,  $(\text{CH}_2)_c$ ), 0.26 (s, 9H,  $\text{CH}_3$ ).

$^{13}\text{C}\{^1\text{H}\}$  NMR (400 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  (ppm) = 174.20 (C=O), 35.98 ( $(\text{CH}_2)_e$ ), 33.71 ( $(\text{CH}_2)_b$ ), 30.31 ( $(\text{CH}_2)_c$ ), 24.33 ( $(\text{CH}_2)_d$ ), 7.25 ( $(\text{CH}_2)_a$ ), -0.18 ( $\text{CH}_3$ ).

### 2.3 Procedure for the methanolysis of the mixture **1** and **2**

A 25 mL round bottom flask was charged with pellets of **PCL** (138 mg, 1.21 mmol, 1 equiv.),  $\text{Me}_3\text{SiI}$  (344  $\mu\text{L}$ , 2.42 mmol, 2 equiv.) and then  $\text{CH}_2\text{Cl}_2$  (3 mL). After 30 min sonication, the yellowish solution was stirred vigorously at 100 °C for 24 h. At the end, we obtained a clear yellow solution. The solvent and the excess  $\text{Me}_3\text{SiI}$  were evaporated off under vacuum and the products **1** and **2** were collected in the flask as yellowish oils. The oily residue was then extracted with pentane (2 x 10 mL). NMR of the extracted oil gave a 1:2 ratio of 87%:13%. Then methanol was added (3 mL, 75 mmol, 62 equiv.). The flask was heated in an oil bath at 100 °C for 2 h and the solution stirred. The excess methanol was evaporated under primary vacuum and the residue extracted with pentane (2 x 10 mL). Compound methyl 6-iodohexanoate (**3**) was isolated pure as a yellow oil in 83% ( $m = 257$  mg). The  $^1\text{H}$ ,  $^{13}\text{C}$  NMR spectra are in the Figure S4.



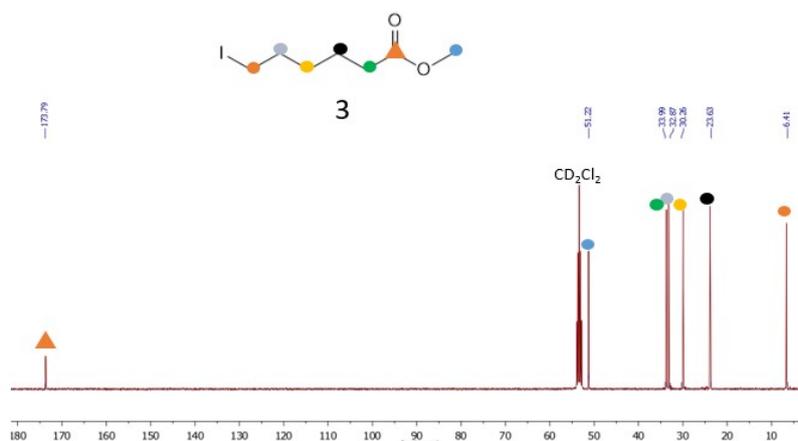
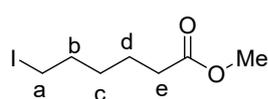


Figure S4 :  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of **3** (400 MHz,  $\text{CD}_2\text{Cl}_2$ , 298 K)

#### NMR data of **3**:



$^1\text{H}$  NMR (400 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  (ppm) = 3.64 (s, 3H, Me), 3.20 (t,  $J$  = 8 Hz, 2H,  $(\text{CH}_2)_a$ ), 2.31 (t,  $J$  = 8 Hz, 2H,  $(\text{CH}_2)_e$ ), 1.83 (quin,  $J$  = 8 Hz, 2H,  $(\text{CH}_2)_b$ ), 1.62 (quin,  $J$  = 8 Hz, 2H,  $(\text{CH}_2)_d$ ), 1.42 (m, 2H,  $(\text{CH}_2)_c$ ).

$^{13}\text{C}\{^1\text{H}\}$  NMR (400 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  (ppm) = 173.79 (C=O), 51.22( $\text{CH}_3$ ), 33.99 ( $(\text{CH}_2)_e$ ), 32.87 ( $(\text{CH}_2)_b$ ), 30.26 ( $(\text{CH}_2)_c$ ), 23.63 ( $(\text{CH}_2)_d$ ), 6.41( $\text{CH}_2)_a$ ).

#### 2.4 Procedure for the hydrolysis of the mixture of **1** and **2**

A 25 mL round bottom flask was charged with pellets of **PCL** (125 mg, 1 mmol, 1 equiv.) suspended in  $\text{CH}_2\text{Cl}_2$  (3 mL) and  $\text{Me}_3\text{SiI}$  (350  $\mu\text{L}$ , 2.4 mmol, 2.5 equiv.) was then syringed into the mixture. The pellet of **PCL** completely dissolved after 30 min sonication. The solution was stirred vigorously at 100  $^\circ\text{C}$  during 20 h affording a yellowish clear solution. The solvent and excess  $\text{Me}_3\text{SiI}$  were evaporated off at room temperature under primary vacuum overnight. The residual oil contained a mixture of **1:2** ratio of 80:20, as observed by  $^1\text{H}$  NMR. A small amount of the mixture (41 mg, 0.13 mmol, 1 equiv.) was weighed in a 25 ml round bottom flask and dissolved in  $\text{CH}_2\text{Cl}_2$  (3 mL). Distilled water (0.1 ml, 5.6 mmol, 43 equiv. ) was then introduced. The solution was sonicated 30 min at room temperature and the pink suspension was dried under vacuum overnight. Compound **4** was isolated pure as a yellow powder in 97% yield ( $m$  = 234 mg). The  $^1\text{H}$ ,  $^{13}\text{C}$  NMR spectra are in Figure S5.

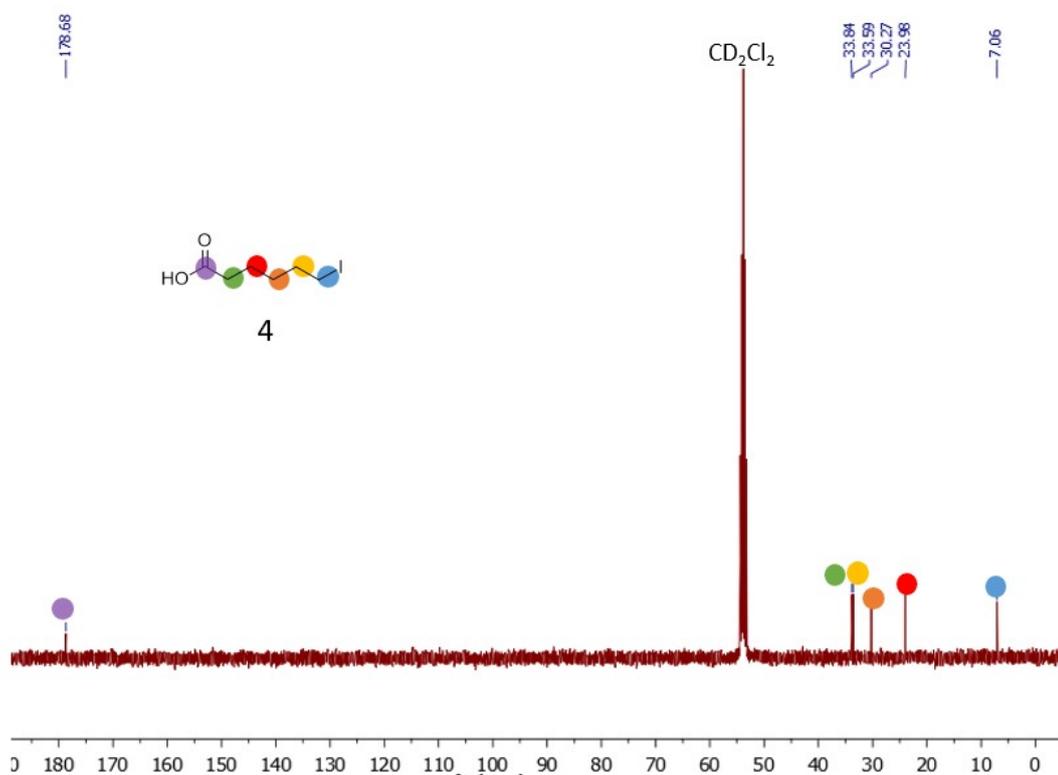
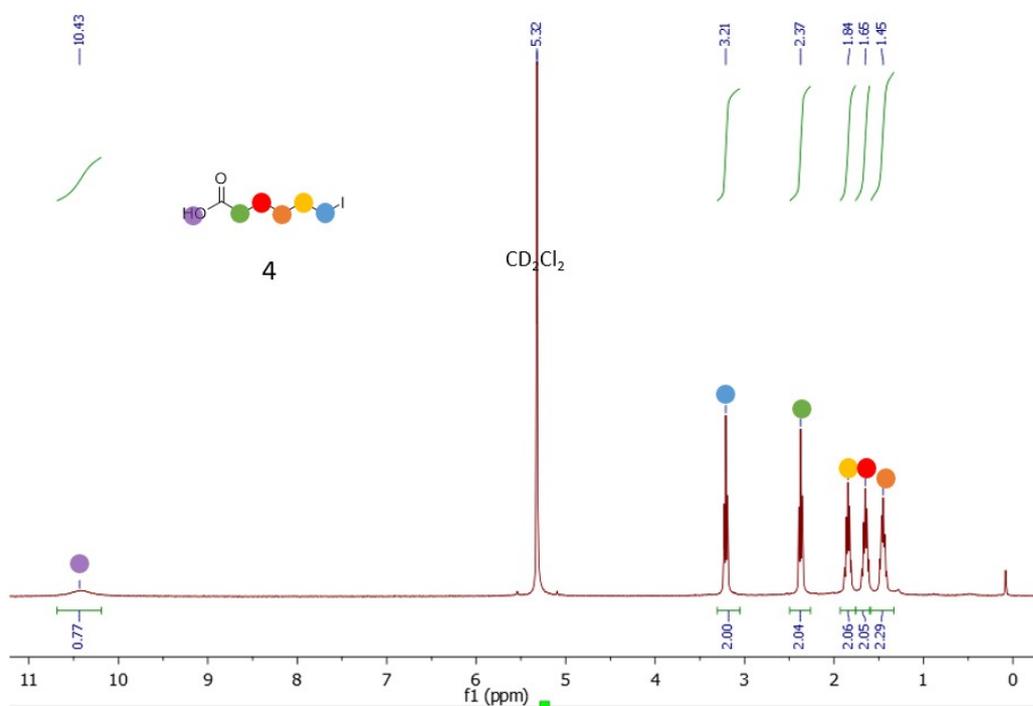
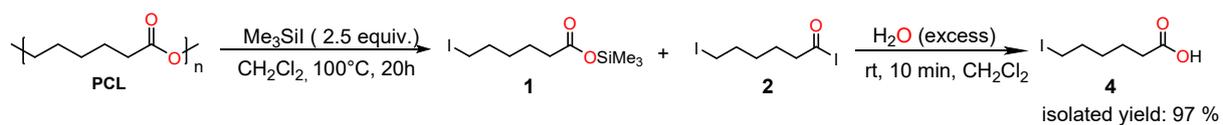
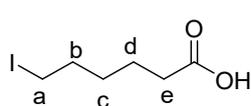


Figure S5 : <sup>1</sup>H and <sup>13</sup>C NMR spectra of 4 (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 298 K)

#### NMR data of 4:



$^1\text{H NMR}$  (400 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  (ppm) = 10.43 (s, 1H,  $\text{CO}_2\text{H}$ ), 3.21 (t,  $J = 8$  Hz, 2H,  $(\text{CH}_2)_a$ ), 2.37 (t,  $J = 8$  Hz, 2H,  $(\text{CH}_2)_e$ ), 1.84 (quin,  $J = 8$  Hz, 2H,  $(\text{CH}_2)_b$ ), 1.65 (quin,  $J = 8$  Hz, 2H,  $(\text{CH}_2)_d$ ), 1.45 (m, 2H,  $(\text{CH}_2)_c$ ).

$^{13}\text{C}\{^1\text{H}\}$  NMR (400 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  (ppm) = 178.68 (C=O), 33.84 ( $(\text{CH}_2)_e$ ), 33.59 ( $(\text{CH}_2)_b$ ), 30.27 ( $(\text{CH}_2)_c$ ), 23.98( $(\text{CH}_2)_d$ ), 7.06( $\text{CH}_2)_a$ ).

#### 2.5 Reaction of PCL with the mixture $\text{Me}_3\text{SiI}$ and $\text{I}_2$ in the solvent $\text{CD}_2\text{Cl}_2$ or $\text{CD}_3\text{CN}$ .

a) A J. Young NMR tube was charged with a pellet of **PCL** (27 mg, 0.24 mmol, 1 equiv.), iodine (64 mg, 0.25 mmol, 1 equiv.),  $\text{CD}_2\text{Cl}_2$  (0.4 mL) and dodecane as the internal standard (10  $\mu\text{L}$ , 0.04 mmol, 0.14 equiv.).  $\text{Me}_3\text{SiI}$  (136  $\mu\text{L}$ , 0.95 mmol, 4 equiv.) was then syringed in the mixture. The pellet of **PCL** dissolved completely after 10 min sonication. The brown solution was then heated in a silicon oil bath maintained at 150  $^\circ\text{C}$  during the required time. At the end, the dark brown solution was clear without deposit. NMR spectra were carried out after 2 h, 4 h, 7 h, 9 h and 10 h at 150 $^\circ\text{C}$  as followed : the hot reaction mixture was cooled down to room temperature and the  $^1\text{H}$  and  $^{13}\text{C}$  NMR analyses were performed at 19 $^\circ\text{C}$  (Figure S6). The conversions of **PCL** and the yields in products **1** and **2** were determined by integration of the  $^1\text{H}$  NMR signals versus those of dodecane ( $\delta_{\text{H}} = 1.26$  and 0.88 in  $\text{CD}_2\text{Cl}_2$ ).

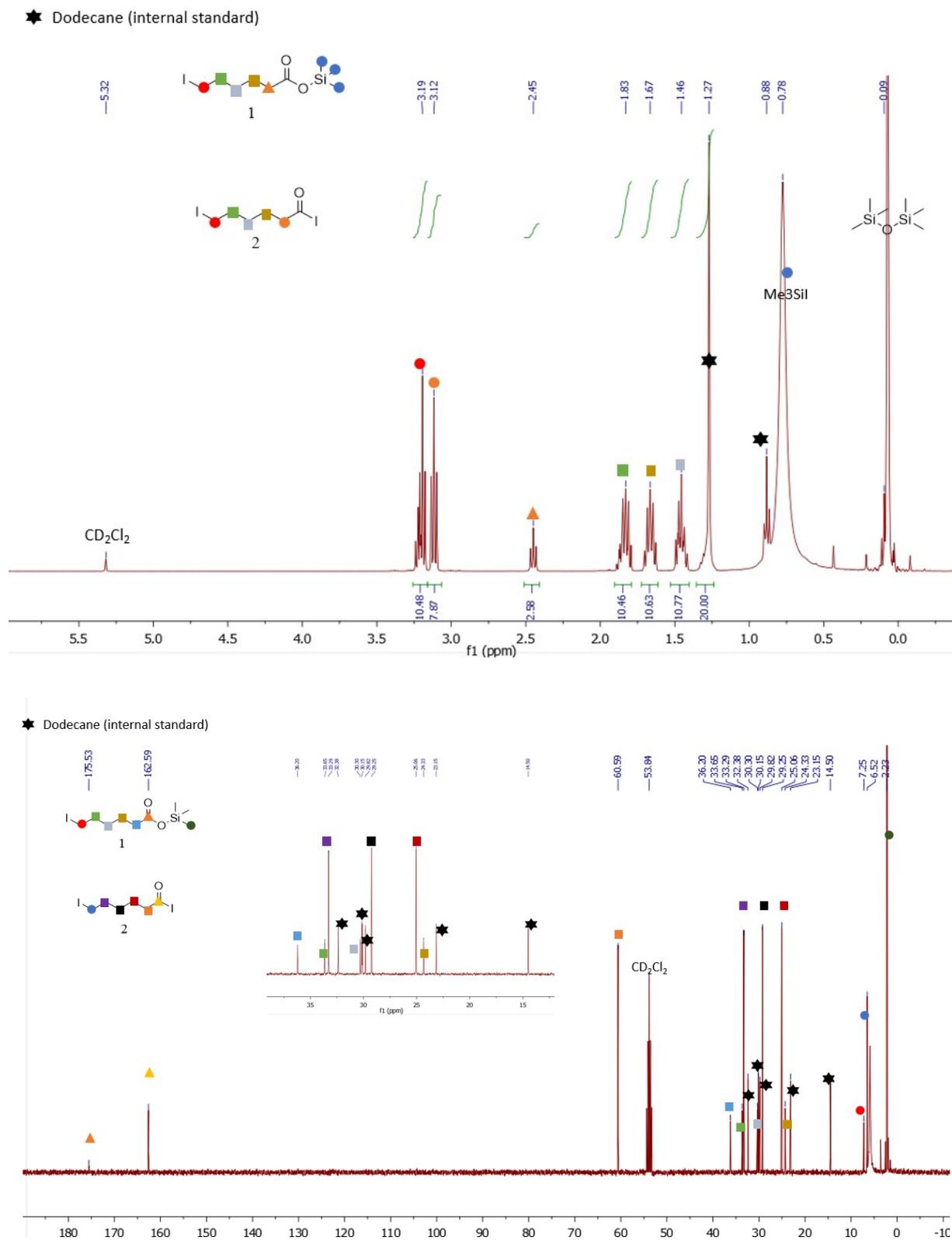


Figure S6 :  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of reaction of PCL and  $\text{Me}_3\text{SiI}$  and  $\text{I}_2$  (ratio 4:1) after 10 h at 150 °C in  $\text{CD}_2\text{Cl}_2$  (400 MHz,  $\text{CD}_2\text{Cl}_2$ , 298 K)

b) A J. Young NMR tube was charged with a pellet of **PCL** (27 mg, 0.24mmol, 1 equiv.), iodine (64 mg, 0.25 mmol, 1 equiv.), CH<sub>3</sub>CN (0.4 mL) and dodecane as the internal standard (10 μL, 0.04 mmol, 0.14 equiv.). Me<sub>3</sub>SiI (136 μL, 0.95 mmol, 4 equiv.) was then syringed in the mixture. The pellet of **PCL** dissolved completely after 10 min sonication. The brown solution was then heated in a silicon oil bath maintained at 100 °C during 4 h (see Table 2). At these different times and temperatures, the tube was cooled down to room temperature and a few drops of the solution were pipetted and inserted into another NMR tube containing CD<sub>2</sub>Cl<sub>2</sub> (0.4 mL) to carry out the <sup>1</sup>H NMR spectra. At the end, the solution was dark brown with brown deposit. The conversions of **PCL** and the yields in products **1** and **2** were determined by integration of the <sup>1</sup>H NMR signals versus those of dodecane (δ<sub>H</sub> = 1.26 and 0.88 ppm in CD<sub>2</sub>Cl<sub>2</sub>). The targeted products **1** and **2** were degraded, while another product was formed due to the reaction with solvent CH<sub>3</sub>CN. The <sup>1</sup>H NMR spectra are in Figure S7 and the results in Table 2.

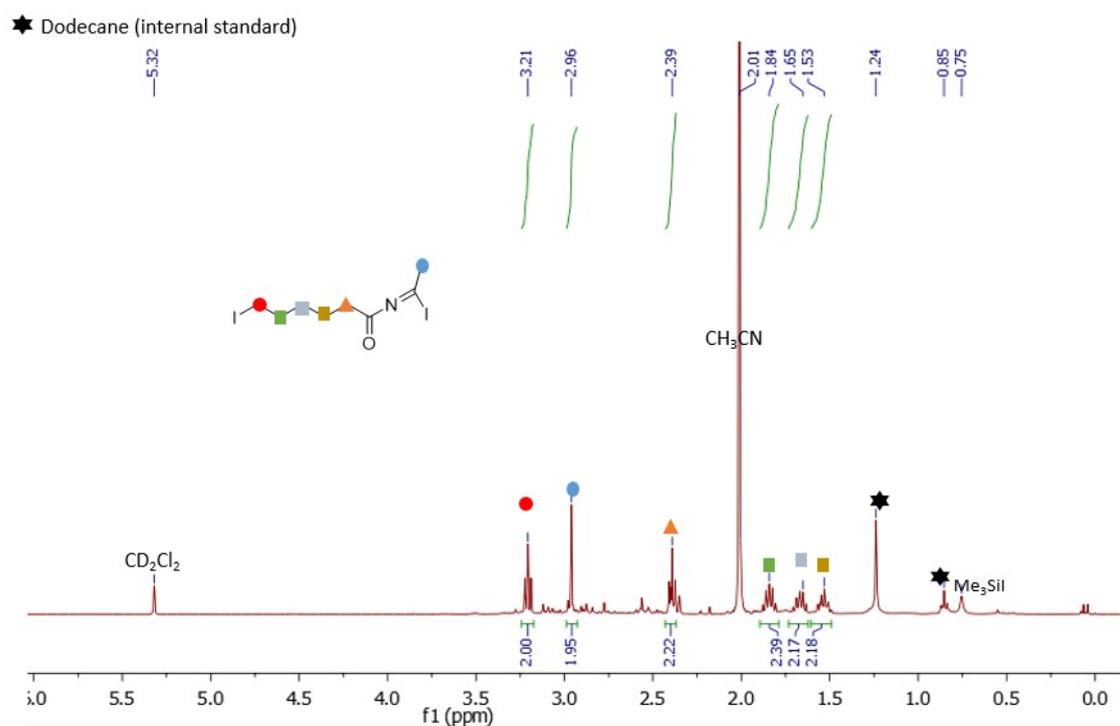
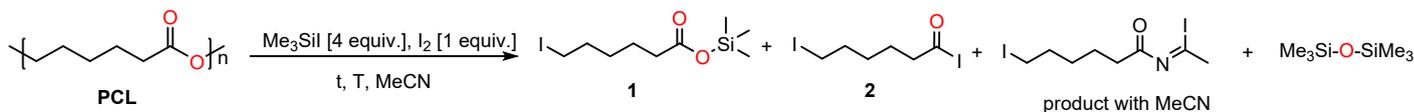


Figure S7 : <sup>1</sup>H NMR spectrum of the reaction of **PCL** with Me<sub>3</sub>SiI and I<sub>2</sub> (ratio 4:1) after 5 h at 150 °C in CH<sub>3</sub>CN (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 298 K)

**Table S2** : Depolymerization of **PCL** with the mixture Me<sub>3</sub>Sil- I<sub>2</sub> in MeCN-Optimization of the reaction conditions <sup>[a]</sup>

Entry	T [°C]	t [h]	Yield in <b>1</b> [%] <sup>[b]</sup>	Yield in <b>2</b> [%] <sup>[b]</sup>	yield in product with MeCN [%] <sup>[b]</sup>
<b>1</b>	rt	17	41	6	0
		6 days	78	9	0
<b>2</b>	100	4	0	0	100

<sup>[a]</sup>conditions: **PCL** (1a, 0.28 mmol with respect to the monomer unit), solvent (0.4 mL); <sup>[b]</sup> Yield in **1** and **2** determined by integration of their <sup>1</sup>H NMR signals vs those of dodecane (standard).

## 2.6 Exchange H/D of **1** and **2** and Me<sub>3</sub>Sil in CD<sub>3</sub>CN

A J. Young NMR tube was charged with a pellet of **PCL** (35 mg, 0.31 mmol, 1 equiv), the deuterated solvent, CD<sub>3</sub>CN (0.4 mL) and dodecane as the internal standard (10 μL, 0.04 mmol, 0.14 equiv.). Me<sub>3</sub>Sil (65 μL, 0.65 mmol, 2.1 equiv.) was then syringed in the mixture. The pellet of **PCL** dissolved completely after 10 min sonication. The yellow solution was then heated in a silicon oil bath at 150°C. The <sup>1</sup>H NMR spectra (performed after cooling the tube to room temperature) were recorded after 30 min, 1 h, 2 h and 5 h heating (Figure S8). At the end, the solution was orange without deposit. By monitoring the evolution of the <sup>1</sup>H NMR signals over time, the peak at 3.2 ppm relative to the CH<sub>2</sub> group in α-position of the carbonyl group of **2** initially appeared and then disappeared. At the meantime, the CD<sub>3</sub>CN peak continued to increase while this signal should remain constant. Other peaks for the two compounds **1** and **2** remained unaffected indicating the absence of degradation. Additionally, the peak at 1.59 ppm (brown square) related to **1**, consistently decreased, whereas the peak at 1.65 ppm (brown circle) of **2**, continued to increase throughout the reaction without any exchange or degradation, which can be used to calculate the yield of **1** and **2**. Consequently, the yield in **1** and **2** were determined by integration of these two peaks versus those of dodecane (δ<sub>H</sub> = 1.3 and 0.92 ppm in CD<sub>3</sub>CN). The peaks of Me<sub>3</sub>Sil and -OMe<sub>3</sub>Si were superposed at 0.5 ppm in MeCN.

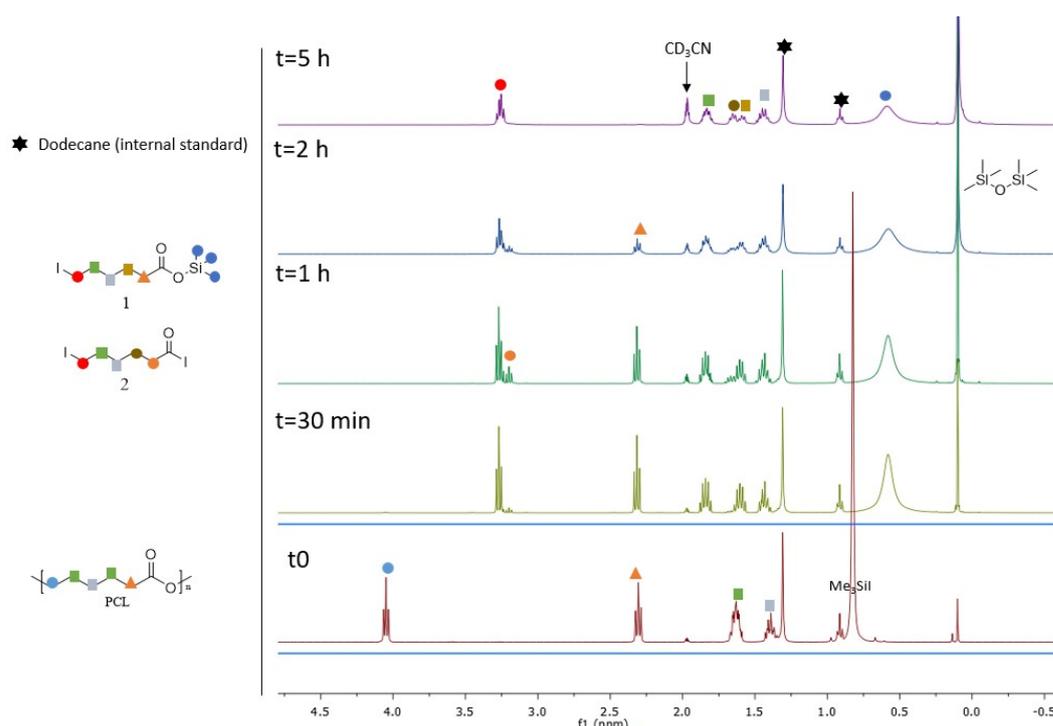
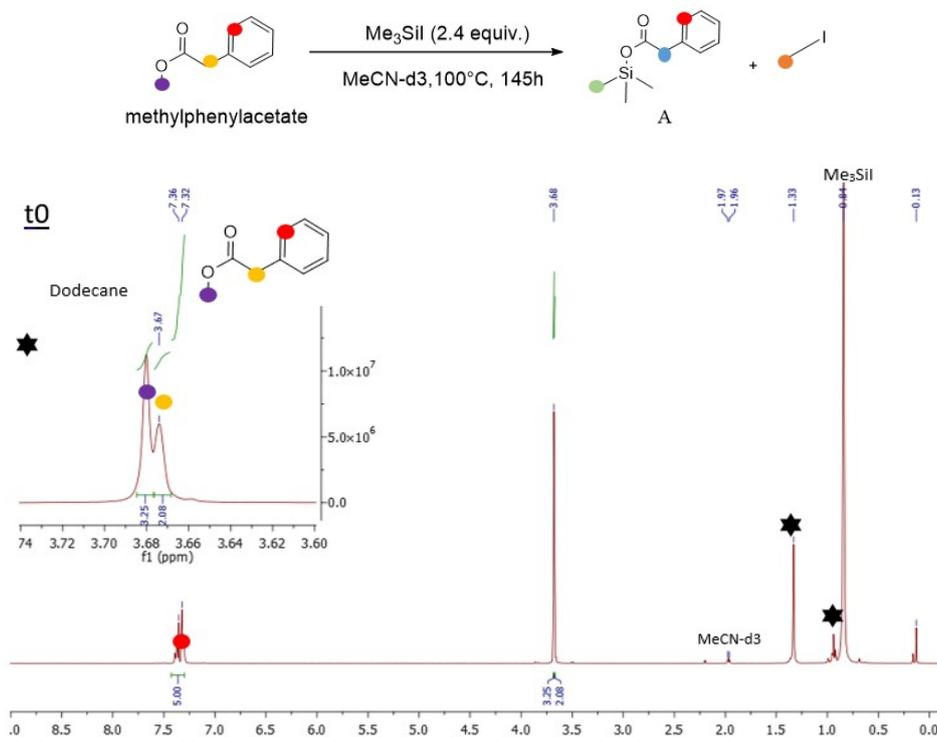


Figure S8 :  $^1\text{H}$  NMR spectrum of reaction of **PCL** with  $\text{Me}_3\text{SiI}$  in  $\text{CD}_3\text{CN}$  at initial time ( $t_0$ ) and after heating at  $150\text{ }^\circ\text{C}$  for 30 min, 1 h, 5 h (400 MHz,  $\text{CD}_3\text{CN}$ , 298 K)

## 2.7 Exchange H/D on methyl phenylacetate ( $\text{PhCH}_2\text{CO}_2\text{Me}$ ) in $\text{CD}_3\text{CN}$ and $\text{CH}_3\text{CN}$

To confirm the H/D exchange that occurs in deuterated acetonitrile between the solvent and the products **1** and **2** at the  $\text{CH}_2$  fragment in  $\alpha$ -position of the carbonyl group, we used the modeled molecule  $\text{PhCH}_2\text{CO}_2\text{SiMe}_3$  prepared in-situ from  $\text{PhCH}_2\text{CO}_2\text{Me}$  and  $\text{Me}_3\text{SiI}$  to follow the H/D exchange with deuterated acetonitrile. Methyl phenylacetate (44 mg, 0.3 mmol, 1 equiv.) was weighed in a dry J. Young NMR tube and dissolved in  $\text{CD}_3\text{CN}$  (0.4 mL) with dodecane as the internal standard (10  $\mu\text{L}$ , 0.04 mmol, 0.14 equiv.).  $\text{Me}_3\text{SiI}$  (100  $\mu\text{L}$ , 0.70 mmol, 2.4 equiv.) was then syringed and the yellowish solution was sonicated for 10 min. The tube was then heated at  $100\text{ }^\circ\text{C}$  (oil bath) and was removed at 3 h and 145 h from the bath and rapidly cooled down to room temperature to carried out the  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR characterizations. After 145 h, the solution was pale yellow without any deposit. In Figure S9, we show the  $^1\text{H}$  NMR spectra at  $t = 0$ , then 3 h and 145 h. After 3 h at  $100\text{ }^\circ\text{C}$ , compound  $\text{PhCH}_2\text{CO}_2\text{Me}$  has been totally transformed into the silylated derivative  $\text{PhCH}_2\text{CO}_2\text{SiMe}_3$  (**A**) and  $\text{Me-I}$ , as observed by  $^1\text{H}$  NMR (Figure S9–Middle and top). Then the evolution of reaction was tracked after 7 h, 24 h, 50 h until 145 h. The  $\alpha\text{-CH}_2$  signal ( $\delta = 3.63$ , indicated by a blue circle) decreased progressively and has totally disappeared after 145 h at  $100\text{ }^\circ\text{C}$  while the intensity of the  $\text{MeCN-}d_3$  signal ( $\delta = 1.94$

ppm) raised concomitantly (Figure S9). This suggests the formation of the D-labeled species  $\text{PhCD}_2\text{CO}_2\text{SiMe}_3$  and transfer of the H atoms of the  $\text{CH}_2$  group in **A** to the solvent. At this time (145 h), the solvent and excess  $\text{Me}_3\text{SiI}$  were evaporated off and the residue dissolved in 0.4 mL non-deuterated  $\text{CH}_3\text{CN}$ . The solution was further stirred at  $100^\circ\text{C}$  for 2 days. After evaporation of the solvent, the residue was monitored by  $^1\text{H}$  NMR in  $\text{CD}_2\text{Cl}_2$ . The conversion of  $\text{PhCD}_2\text{CO}_2\text{SiMe}_3$  into  $\text{PhCH}_2\text{CO}_2\text{SiMe}_3$  was complete as observed by the appearance of the  $\alpha\text{-CH}_2$  signal at  $\delta = 3.63$  (Figure S10) which integrates for 2H in comparison to the other signals. A mechanism for this H/D exchange has been previously proposed by Olah.<sup>1</sup>



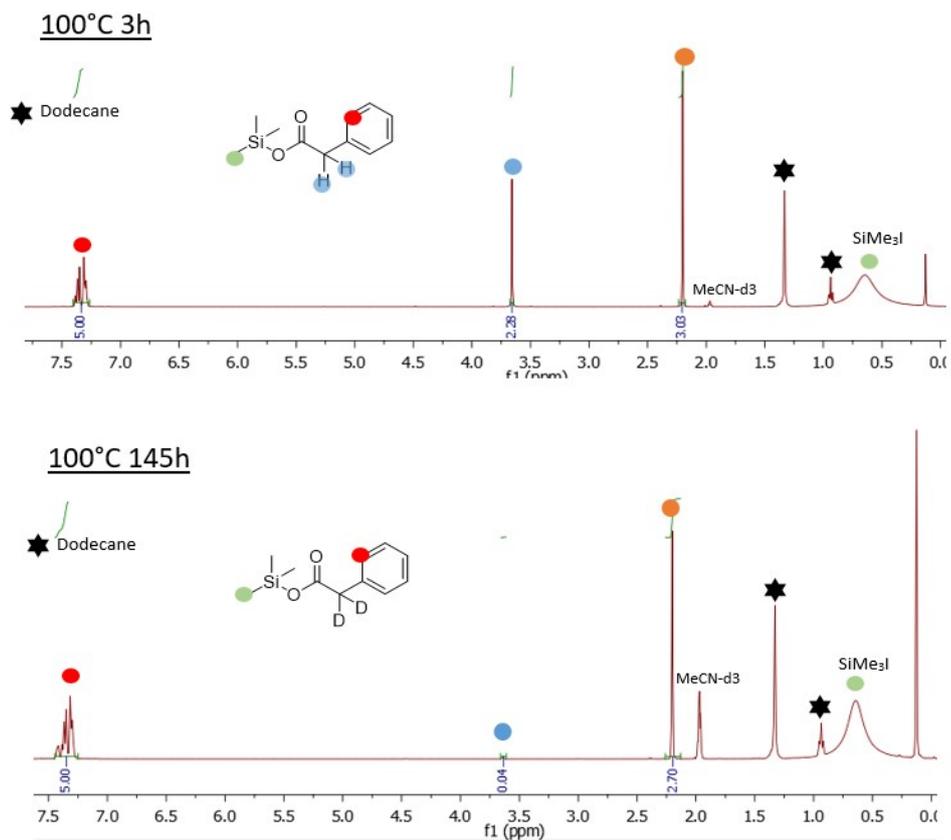


Figure S9 :  $^1\text{H}$  NMR spectra of  $\text{PhCH}_2\text{CO}_2\text{SiMe}_3$  and  $\text{PhCD}_2\text{CO}_2\text{SiMe}_3$  : reaction of  $\text{PhCH}_2\text{CO}_2\text{Me}$  with  $\text{Me}_3\text{SiI}$  in  $\text{MeCN-d}_3$  at initial time ( $t = 0$ ) and after 3 h and 145 h at 100 °C (400 MHz,  $\text{CD}_3\text{CN}$ , 298K)

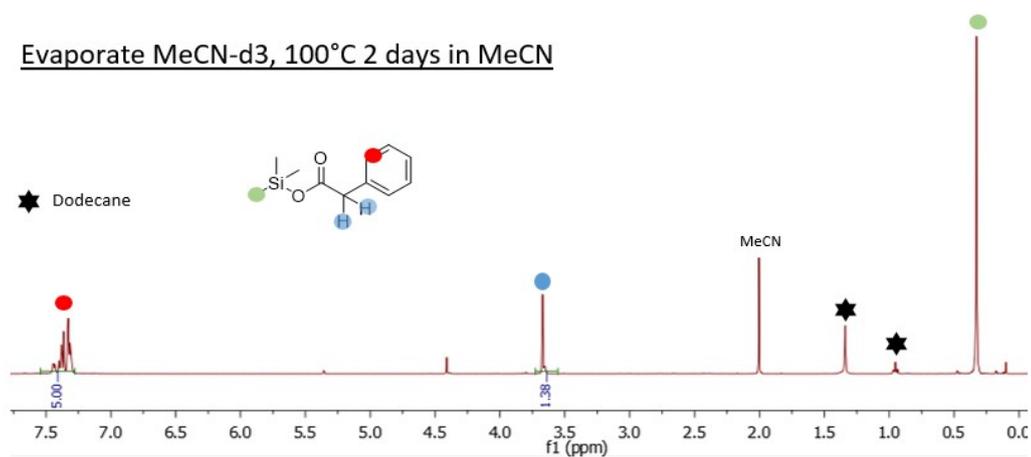


Figure S10 :  $^1\text{H}$  NMR spectrum of the evolution of  $\text{PhCD}_2\text{CO}_2\text{SiMe}_3$  into  $\text{PhCH}_2\text{CO}_2\text{SiMe}_3$  in  $\text{MeCN}$  (100 °C, 2 d) (400 MHz,  $\text{CD}_2\text{Cl}_2$ , 298 K)

### 3. Procedures for the reaction of iodobutane and PCL with $\text{SiH}_2\text{I}_2$

#### 3.1 Reactions of 2-iodobutane and $\text{SiH}_2\text{I}_2$ in $\text{CD}_2\text{Cl}_2$

A J. Young NMR tube was charged with a 2-iodobutane (48 mg, 0.26 mmol), followed by the  $\text{CD}_2\text{Cl}_2$  (0.4 mL), and  $\text{SiH}_2\text{I}_2$  (110 mg, 0.4 mmol, 1.5 equiv.). The reaction was heated at 150 °C during 30 h and the NMR tube was removed from the oil bath and cooled down to room temperature to carry out the  $^1\text{H}$  NMR spectra (Figure S11). The solution is colorless with colourless crystals of  $\text{SiI}_4$  at the bottom. All the 2-iodobutane was transformed to *n*-butane.

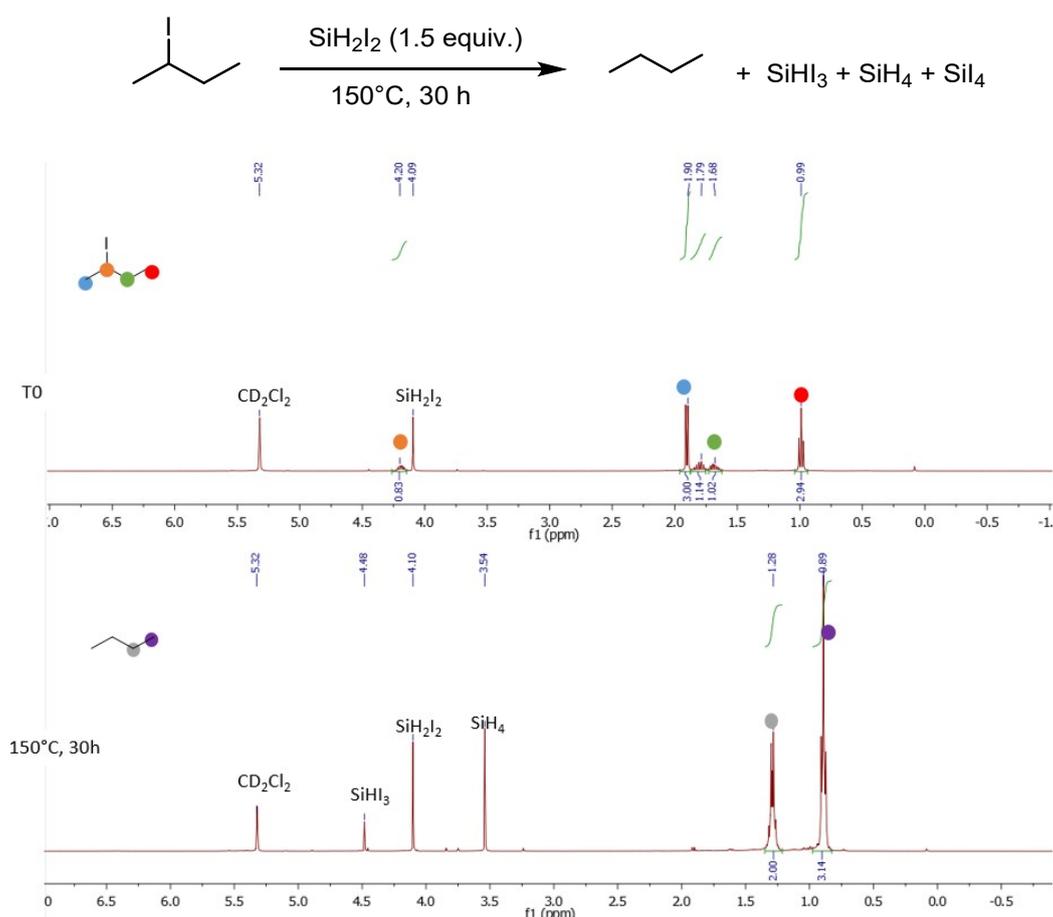


Figure S11 :  $^1\text{H}$  NMR spectra of the reaction of 2-iodobutane with  $\text{SiH}_2\text{I}_2$  in  $\text{CD}_2\text{Cl}_2$  : after 30 h at 150 °C (400 MHz,  $\text{CD}_2\text{Cl}_2$ , 298 K)

#### 3.2 Reactions of PCL and $\text{SiH}_2\text{I}_2$ in $\text{CD}_2\text{Cl}_2$ , $\text{CD}_3\text{CN}$ or in the absence of solvent

a) A J. Young NMR tube was charged with a pellet of PCL (29 mg, 0.26 mmol), followed by  $\text{CD}_2\text{Cl}_2$  (0.4 mL), and dodecane as the internal standard (10  $\mu\text{L}$ , 0.04 mmol, 0.15 equiv.). The reagent  $\text{SiH}_2\text{I}_2$  (37 mg, 1.3 mmol, 5 equiv.) was then syringed. The reaction was heated at 150 °C and the tube was removed from the bath and cooled down to room temperature at 15 h and 120 h to carry out  $^1\text{H}$  NMR spectra (Figure S12). The solution is colorless with colourless crystals of  $\text{SiI}_4$  at the bottom. The conversion of PCL and the yield in product **1'**, **2**, **5** and **6** were determined by integration of the signals *versus those*

of dodecane ( $\delta_H = 1.26$  and  $0.88$  ppm in  $CD_2Cl_2$ ). The signals of *n*-hexane are superposed with dodecane. Mesitylene was used as internal standard for the next experiments.

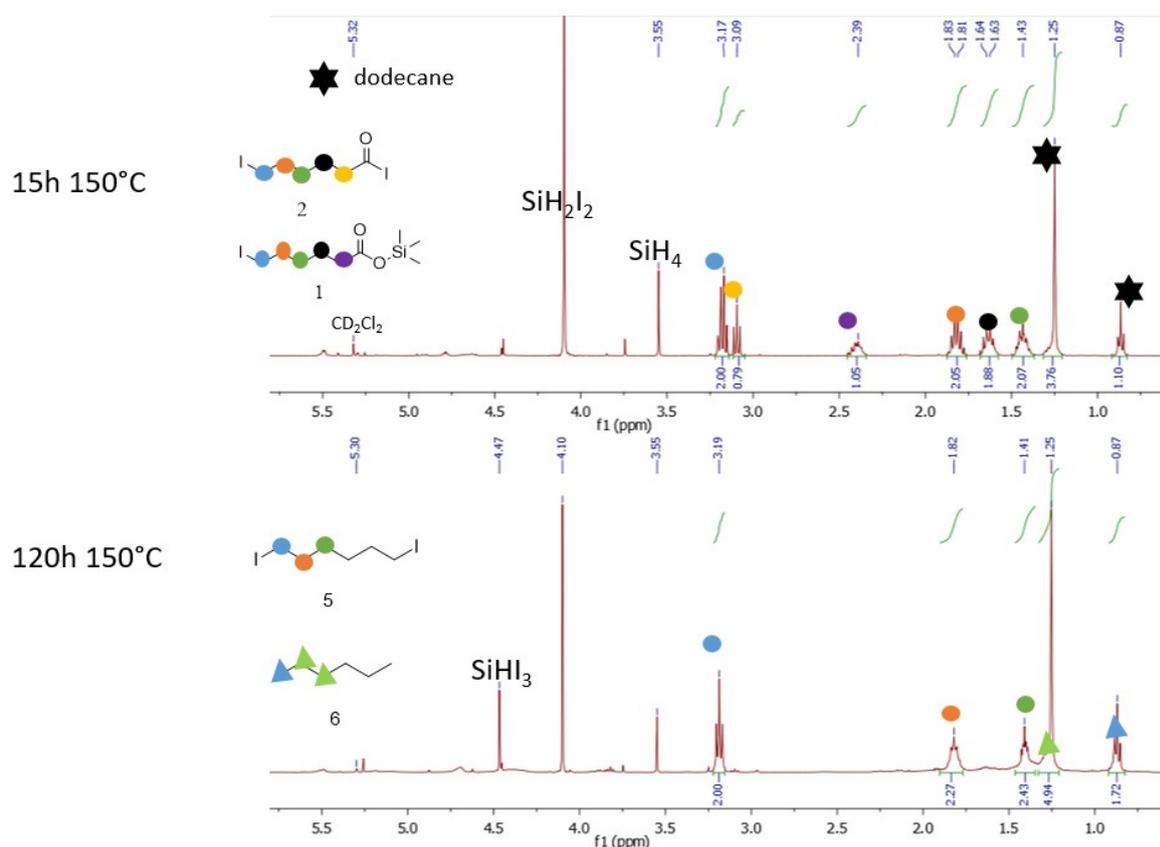
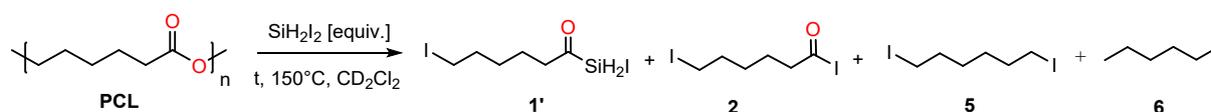


Figure S12:  $^1H$  NMR spectra of the reaction of PCL in diiodosilane in  $CD_2Cl_2$ : after 15 h at  $150^\circ C$  and after 120 h at  $150^\circ C$  (400 MHz,  $CD_2Cl_2$ , 298 K)

b) The tube was charged with a pellet of PCL (29 mg, 0.26 mmol), followed by the  $CD_3CN$  (0.4 mL) and  $SiH_2I_2$  (37 mg, 1.3 mmol, 5 equiv.) was then syringed. The reaction was heated at  $150^\circ C$ . After 1 h, the solution is dark brown and showed a brown deposit. The  $^1H$  NMR spectrum in Figure S13 can't be interpreted.

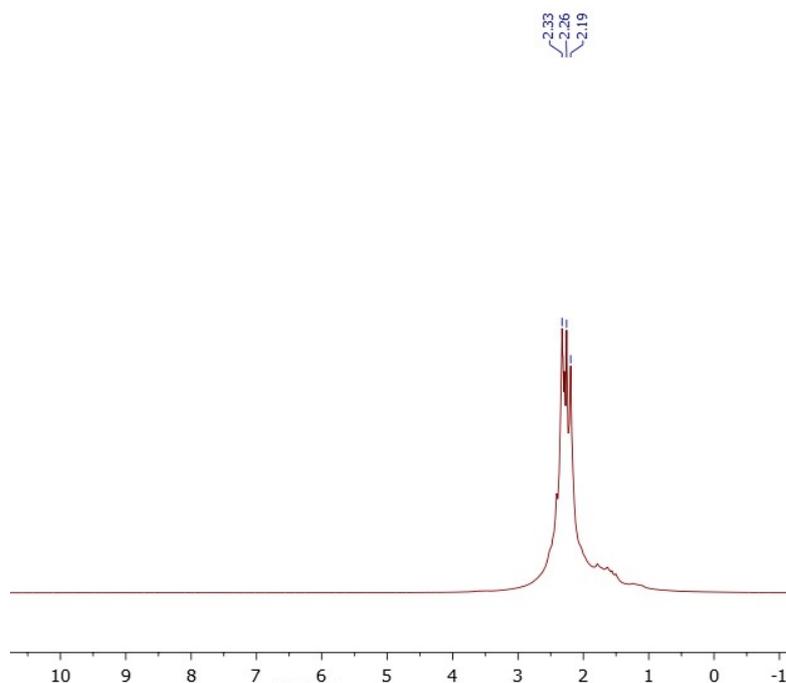


Figure S13 :  $^1\text{H}$  NMR spectrum of the reaction of **PCL** with  $\text{SiH}_2\text{I}_2$  in  $\text{CD}_3\text{CN}$ : after 1 h at  $150\text{ }^\circ\text{C}$  (400 MHz,  $\text{CD}_3\text{CN}$ , 298 K)

c) A J. Young NMR tube was charged with a pellet of **PCL** (29 mg, 0.26 mmol, 1 equiv.), followed by the liquid reagent  $\text{SiH}_2\text{I}_2$  (37 mg, 1.27 mmol, 5 equiv.) without any solvent, and mesitylene as the internal standard (18  $\mu\text{L}$ , 0.13 mmol, 0.5 equiv.). The reaction was heated at  $150\text{ }^\circ\text{C}$  for 4 h and 17 h. At these different times, the tube was cooled down to room temperature and a few drops of the solution were pipetted and insert in another NMR tube containing  $\text{CD}_2\text{Cl}_2$  (0.4 mL) to carried out the  $^1\text{H}$  NMR spectra (Figures S14 and S15). The conversion of **PCL** and the yields in product **1'**, **2**, **5** and **6** were determined by integration of the signals *versus those* of mesitylene ( $\delta_{\text{H}} = 6.78$  and 2.25 ppm in  $\text{CD}_2\text{Cl}_2$ ). The  $^1\text{H}$  NMR spectrum at 4 h evidenced a mixture of **1'** (44%), **2** (40%), **5** (8%) and **6** (8%) while at 17 h only a mixture of **5** (56%) and **6** (44%) were observed. The tube was left to stand at r.t. and colourless crystals deposited at the bottom. An X-ray diffraction collect showed that these were in fact  $\text{SiI}_4$ , the structure of which has already been published.<sup>2,3</sup>

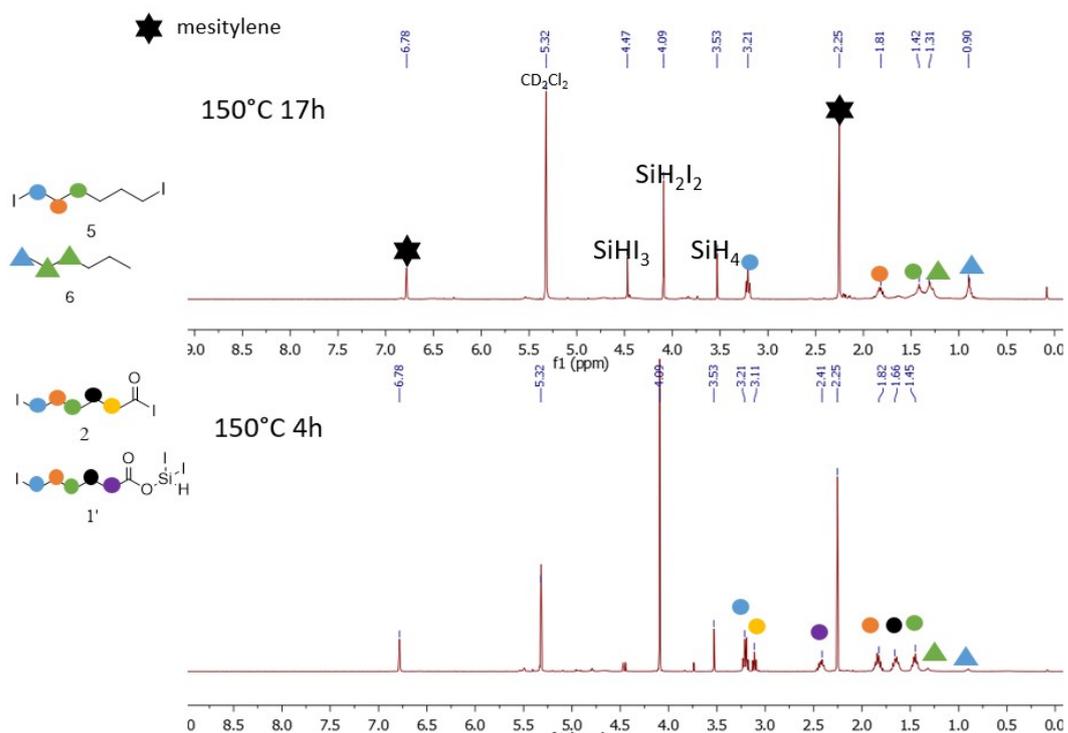


Figure S14 :  $^1\text{H}$  NMR spectrum of the reaction of **PCL** in diiodosilane : after 4h at 150°C and after 17 h at 150 °C, residue then dissolved in  $\text{CD}_2\text{Cl}_2$  (400 MHz,  $\text{CD}_2\text{Cl}_2$ , 298 K)

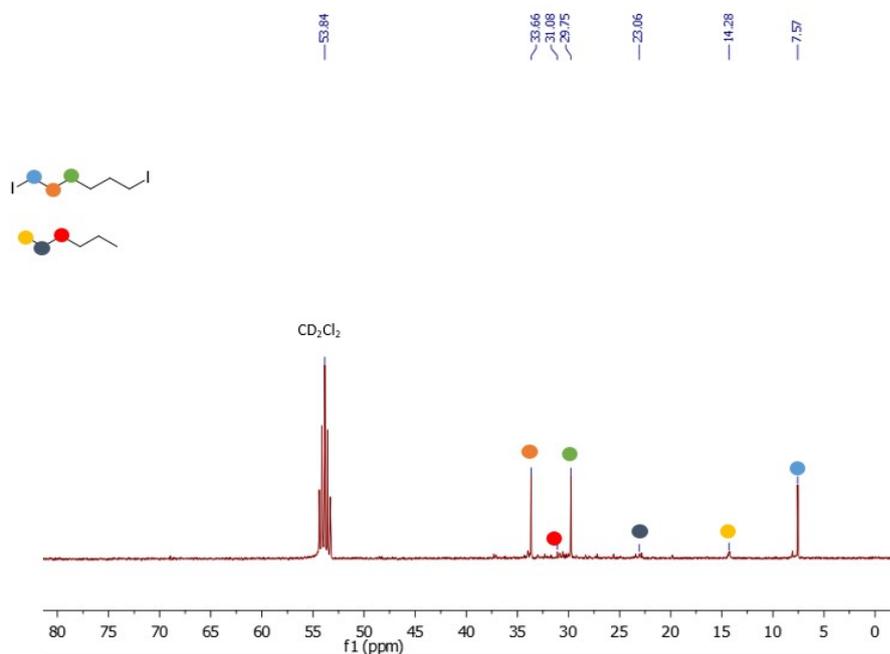
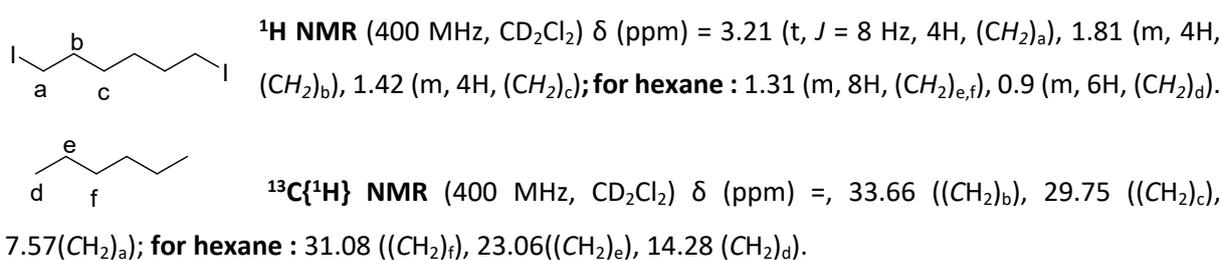


Figure S15 :  $^{13}\text{C}$  NMR spectrum of **5** and **6** after 15 h at 150 °C (400 MHz,  $\text{CD}_2\text{Cl}_2$ , 298 K)

### NMR data of 5:



**Table S3** : Depolymerization of PCL with  $\text{SiH}_2\text{I}_2$  : optimization of the reaction conditions<sup>[a]</sup>

Entry	Solvent	t(h)	Yield [%] <sup>[b]</sup>			
			1'	2	5	6
1	$\text{CD}_2\text{Cl}_2$	15	53	42	0	0
		120	1	2	35	~50
2	$\text{CD}_3\text{CN}$	1	Degradation			
3	None <sup>[c]</sup>	4	44	40	8	8
		17	0	0	56	44

Equiv. of  $\text{SiH}_2\text{I}_2$  given per monomeric fragment  $\text{C}_6\text{H}_{10}\text{CO}_2$ .

<sup>[a]</sup> Conditions: PCL (0.28 mmol with respect to the monomer unit), solvent (0.4 mL); <sup>[b]</sup> Yield in **1'**, **2**, **5** and **6** determined by  $^1\text{H}$  NMR vs those of the standard (dodecane for entry 1 and mesitylene for entry 2). <sup>[c]</sup> NMR in  $\text{CD}_2\text{Cl}_2$  after evaporation of the  $\text{SiH}_2\text{I}_2$ .

### 3.3 Reactions of **1** with $\text{Me}_3\text{SiI}$ and $\text{SiH}_2\text{I}_2$

#### a) Reaction of **1** with $\text{Me}_3\text{SiI}$ in $\text{CD}_2\text{Cl}_2$ (Table S4, Entry 1):

A J. Young NMR tube was charged with  $\text{I}(\text{CH}_2)_5\text{CO}_2\text{SiMe}_3$  (**1**), (13 mg, 0.04 mmol), dodecane (10  $\mu\text{L}$ , 0.04 mmol, 1 equiv.),  $\text{CD}_2\text{Cl}_2$  (0.4 mL) and  $\text{Me}_3\text{SiI}$  (28  $\mu\text{L}$ , 0.2 mmol, 5 equiv.) was syringed into it. The tube was heated at 150 °C during the required time. The tube was removed from the oil bath and cooled down to room temperature to perform the  $^1\text{H}$  and  $^{13}\text{C}$  NMR analyses at 19 °C (Figures S16). After 10 h at 150 °C in  $\text{CD}_2\text{Cl}_2$ , transformation of **1** gave only 7% of **2**. Prolonged reaction time (124 h) induced the formation of **2** in 74% yield (Table S4, Entry 1). Conversion and the yield in products **2**, **5** and **6** were determined by integration of the signals versus those of dodecane ( $\delta_{\text{H}} = 1.26$  and 0.88 ppm in  $\text{CD}_2\text{Cl}_2$ ).

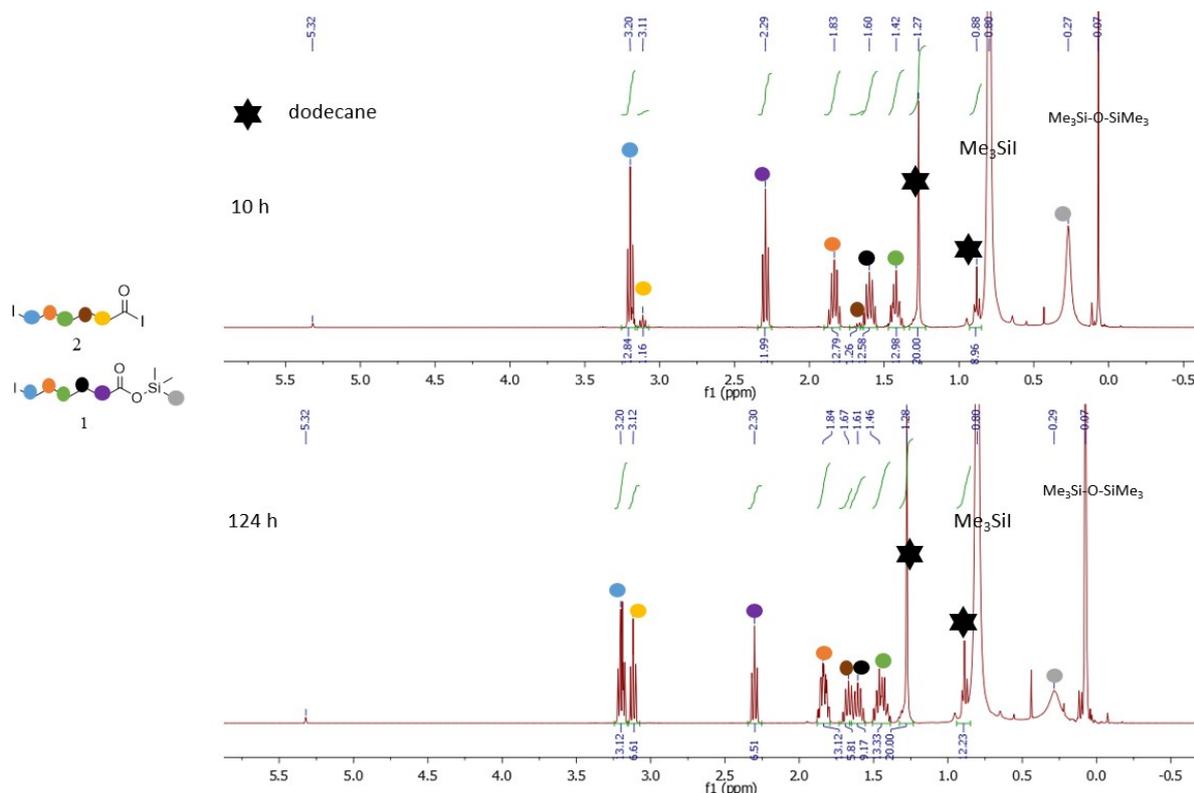


Figure S16 :  $^1\text{H}$  NMR spectrum in  $\text{CD}_2\text{Cl}_2$  of reaction mixture with 5 equiv.  $\text{Me}_3\text{SiI}$  after 10 h and 124 h at  $150^\circ\text{C}$  (400 MHz, 298 K) (Entry 1, table S4)

b) Reaction of **1** with 2 or 5 equiv.  $\text{SiH}_2\text{I}_2$  in  $\text{CD}_2\text{Cl}_2$  (Table S4, Entries 2-3):

A J. Young NMR tube was charged with  $\text{I}(\text{CH}_2)_5\text{CO}_2\text{SiMe}_3$  (**1**), (13 mg, 0.04 mmol), dodecane (10  $\mu\text{L}$ , 0.04 mmol, 1 equiv.),  $\text{CD}_2\text{Cl}_2$  (0.4 mL) and  $\text{SiH}_2\text{I}_2$  (22.8 mg, 0.08 mmol, 2 equiv or 57 mg, 0.2 mmol, 5 equiv.) was syringed into it. The tube was heated at  $150^\circ\text{C}$  during the required time and, was removed from the oil bath and cooled down to room temperature to perform the  $^1\text{H}$  and  $^{13}\text{C}$  NMR analyses (Figures S17 and S18). At the end, the solution was colorless and showed colourless crystals of  $\text{SiI}_4$  as well as a white powder at the bottom. The absence of Si-O-Si species visible by NMR would suggest that the white powder is a mixture of insoluble siloxane aggregates. Conversion and yield in products **2**, **5** and **6** were determined by integration of the signals versus those of dodecane ( $\delta_{\text{H}} = 1.26$  and  $0.88$  ppm in  $\text{CD}_2\text{Cl}_2$ ). The signals of *n*-hexane are superposed with dodecane. Mesitylene was used as internal standard for the next experiments.

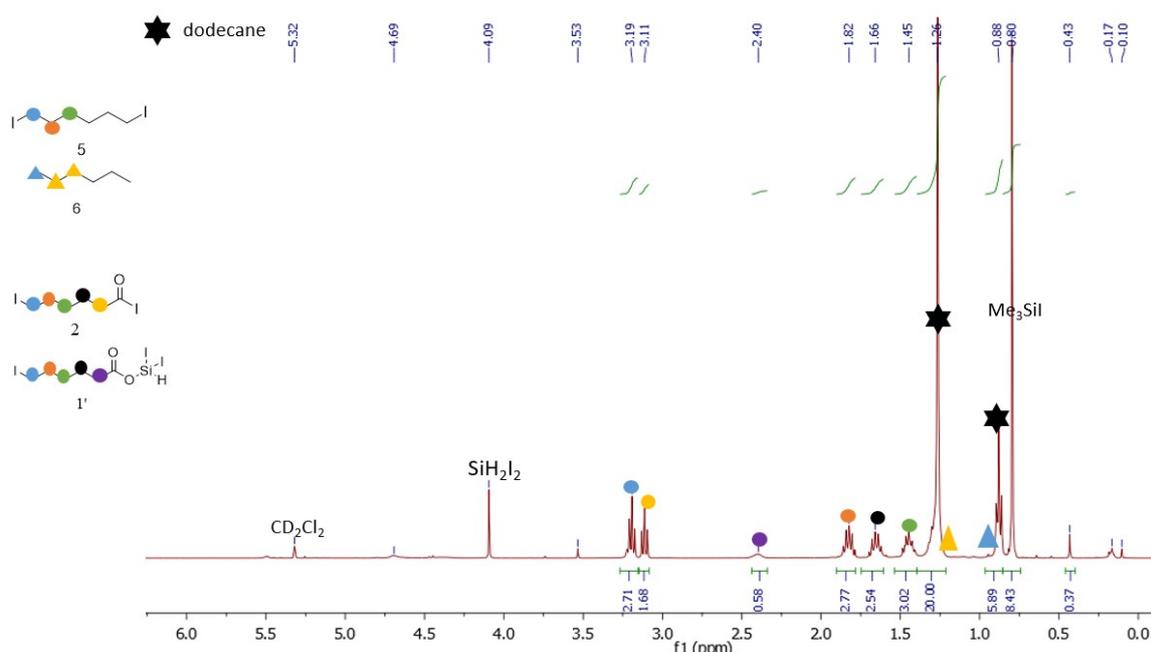


Figure S17 :  $^1\text{H}$  NMR spectrum in  $\text{CD}_2\text{Cl}_2$  of reaction mixture with 2 equiv.  $\text{SiH}_2\text{I}_2$  after 12 h at  $150^\circ\text{C}$  (400 MHz, 298 K) (Entry 2, table S4)

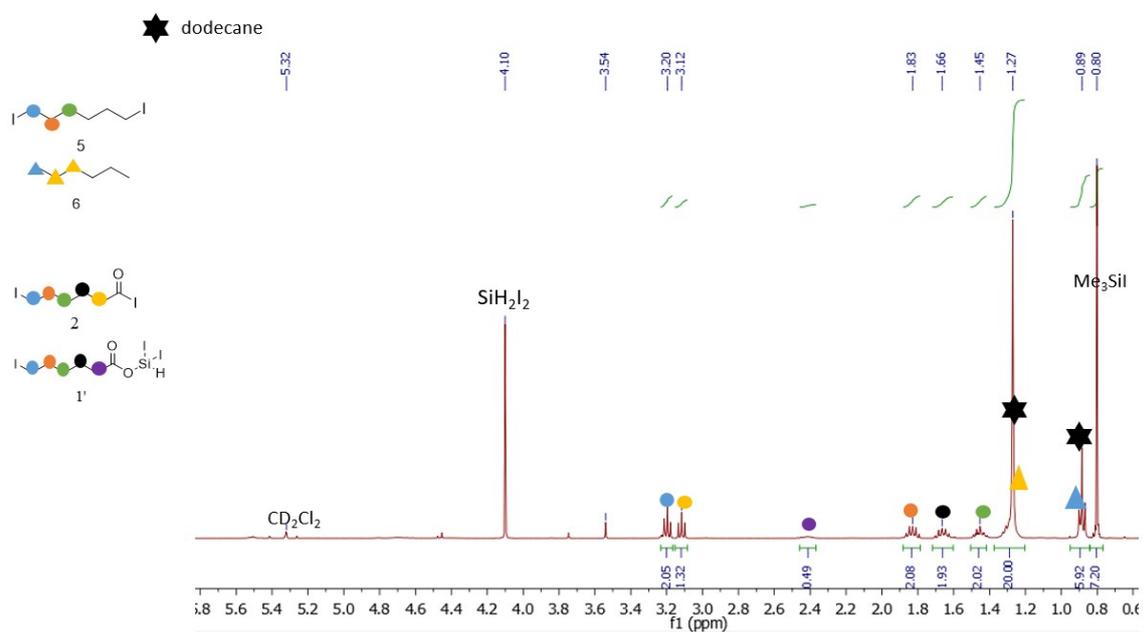


Figure S18 :  $^1\text{H}$  NMR spectrum in  $\text{CD}_2\text{Cl}_2$  of reaction mixture with 5 equiv.  $\text{SiH}_2\text{I}_2$  after 12 h at  $150^\circ\text{C}$  (400 MHz, 298 K) (Entry 3, table S4)

c) Reaction of **1** with  $\text{SiH}_2\text{I}_2$  without solvent (Table S4, Entries 4 and 5):

Two J. Young NMR tubes were charged with  $\text{I}(\text{CH}_2)_5\text{CO}_2\text{SiMe}_3$  (**1**), (13 mg, 0.04 mmol), mesitylene (10 mg, 0.08 mmol, 2 equiv.), and  $\text{SiH}_2\text{I}_2$  (57 mg, 0.2 mmol, 5 equiv.) was syringed into it. The tubes were heated at 150 °C during 2 h for one and 19 h for the other. The tubes were removed from the oil bath and cooled down to room temperature. Then 0.4 ml of  $\text{CD}_2\text{Cl}_2$  was added into each of the tube to perform the  $^1\text{H}$  NMR analyses (Figures S19 and S20). At the end, the solution were colorless and showed colourless crystals of  $\text{SiI}_4$  as well as a white powder at the bottom. The absence of Si-O-Si species visible by NMR would suggest that the white powder is a mixture of insoluble siloxane aggregates. The conversion and the yield in products **2**, **5** and **6** were determined by integration of the signals versus those of mesitylene ( $\delta_{\text{H}} = 6.79, 2.27$  ppm).

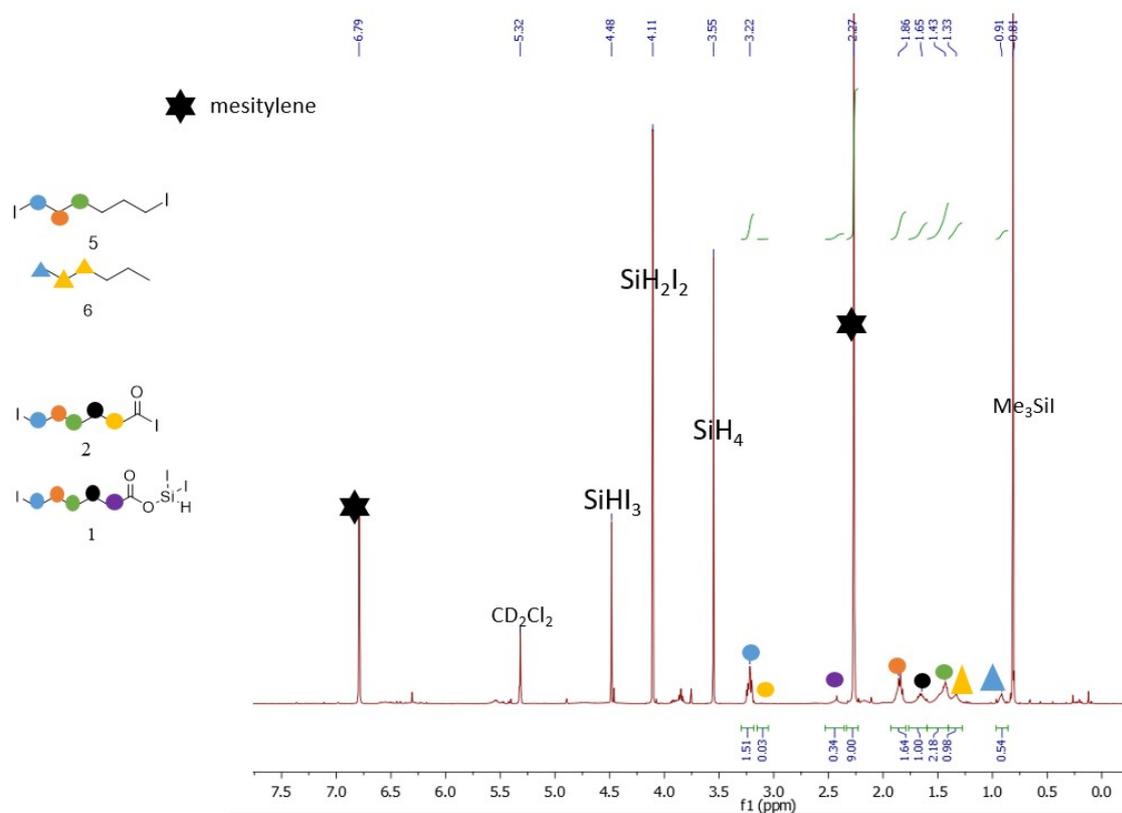


Figure S19:  $^1\text{H}$  NMR spectrum in  $\text{CD}_2\text{Cl}_2$  of drops of the reaction mixture of **1** in neat (5 equiv.)  $\text{SiH}_2\text{I}_2$  after 2 h at 150 °C (400 MHz, 298 K) (Entry 4, table S4)

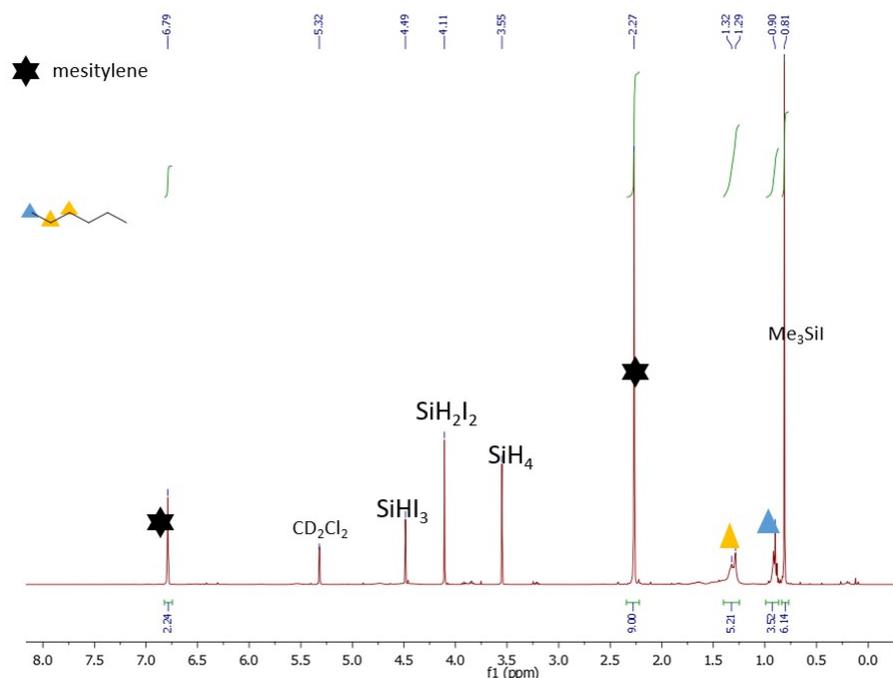
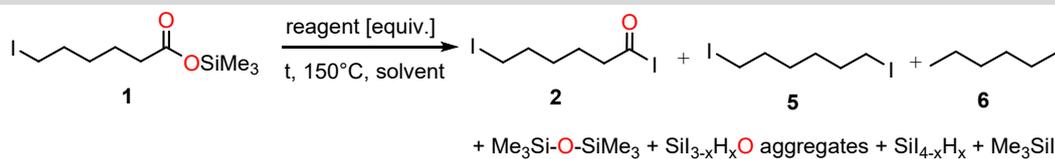


Figure S20 :  $^1\text{H}$  NMR spectrum in  $\text{CD}_2\text{Cl}_2$  of drops of the reaction mixture of **1** in neat (5 equiv.)  $\text{SiH}_2\text{I}_2$  after 19 h at  $150^\circ\text{C}$  (400 MHz, 298 K) (Entry 5, table S4)

**Table S4** : Reaction of **1** with  $\text{Me}_3\text{SiI}$  and  $\text{SiH}_2\text{I}_2$  – optimization of the reaction conditions



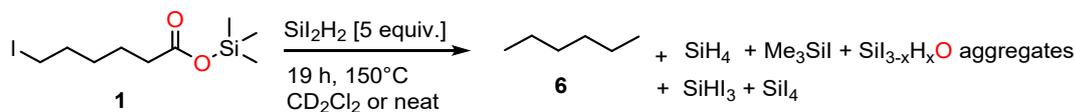
Entry	reagent [equiv.] <sup>[1]</sup>	solvent	T [°C]	t [h]	Conversion [%] <sup>[2]</sup>	Yield of <b>2</b> [%] <sup>[2]</sup>	Yield of <b>5</b> [%] <sup>[2]</sup>	Yield of <b>6</b> [%] <sup>[2]</sup>
1	$\text{Me}_3\text{SiI}$ [5]	$\text{CD}_2\text{Cl}_2$	150	10	7	7	0	0
	$\text{Me}_3\text{SiI}$ [5]	$\text{CD}_2\text{Cl}_2$	150	124	74	74	0	0
2	$\text{SiH}_2\text{I}_2$ [2]	$\text{CD}_2\text{Cl}_2$	150	12	77	68	7	2
3	$\text{SiH}_2\text{I}_2$ [5]	$\text{CD}_2\text{Cl}_2$	150	12	100	80	13	7
4	$\text{SiH}_2\text{I}_2$ [5]	None	150	2	98	2	17	12
5	$\text{SiH}_2\text{I}_2$ [5]	None	150	19	100	0	0	88*

<sup>[1]</sup> Equiv. of  $\text{SiH}_2\text{I}_2$  given per monomeric fragment  $\text{C}_6\text{H}_{10}\text{CO}_2$ ; <sup>[2]</sup>  $^1\text{H}$  NMR yields (mesitylene as

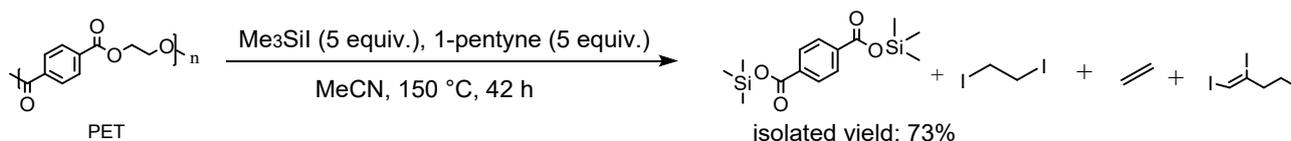
standard for entries 1, 2, 3 and 4). \* Traces of unknown compounds also detected

Note : We observed by  $^1\text{H}$  NMR that **1** is also converted into **1'** ( $\text{I}(\text{CH}_2)_5\text{CO}_2[\text{Si}]$ ) by reaction with  $\text{SiH}_2\text{I}_2$

For the reaction corresponding to entries 2-5, a number of by- and side-products are formed which are listed below:

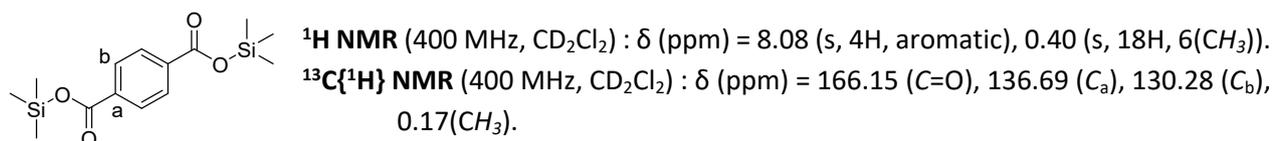


#### 4. Reaction of PET with Me<sub>3</sub>SiI



An Evian bottle made of PET was cut in small rectangular pieces. A 25 mL round bottom flask was charged with **PET** pieces (163 mg, 0.85 mmol) in suspension in CH<sub>3</sub>CN (3 mL) and Me<sub>3</sub>SiI (0.6 mL, 4 mmol, 5 equiv.) then 1-pentyne (184 mg, 2.7 mmol, 3.2 equiv.) were syringed in it. After 30 min in an ultrasonic bath, the yellowish solution was stirred vigorously at 150 °C during 48 h giving a clear dark brown solution. The solvent and excess Me<sub>3</sub>SiI were evaporated under vacuum and the remaining white solid residue dried under vacuum for 20 h at room temperature. Extraction by pentane (3 × 10 mL) afforded 1,4-(Me<sub>3</sub>SiO<sub>2</sub>C)<sub>2</sub>C<sub>6</sub>H<sub>4</sub> ( M = 310.50 g/M) in 73% yield (m = 192 mg). It was characterized by <sup>1</sup>H and <sup>13</sup>C NMR (Figure S21). The presence of pentyne is required to trap iodine (released from diiodoethane) that otherwise induand avoid degradation of the products.

#### NMR data:



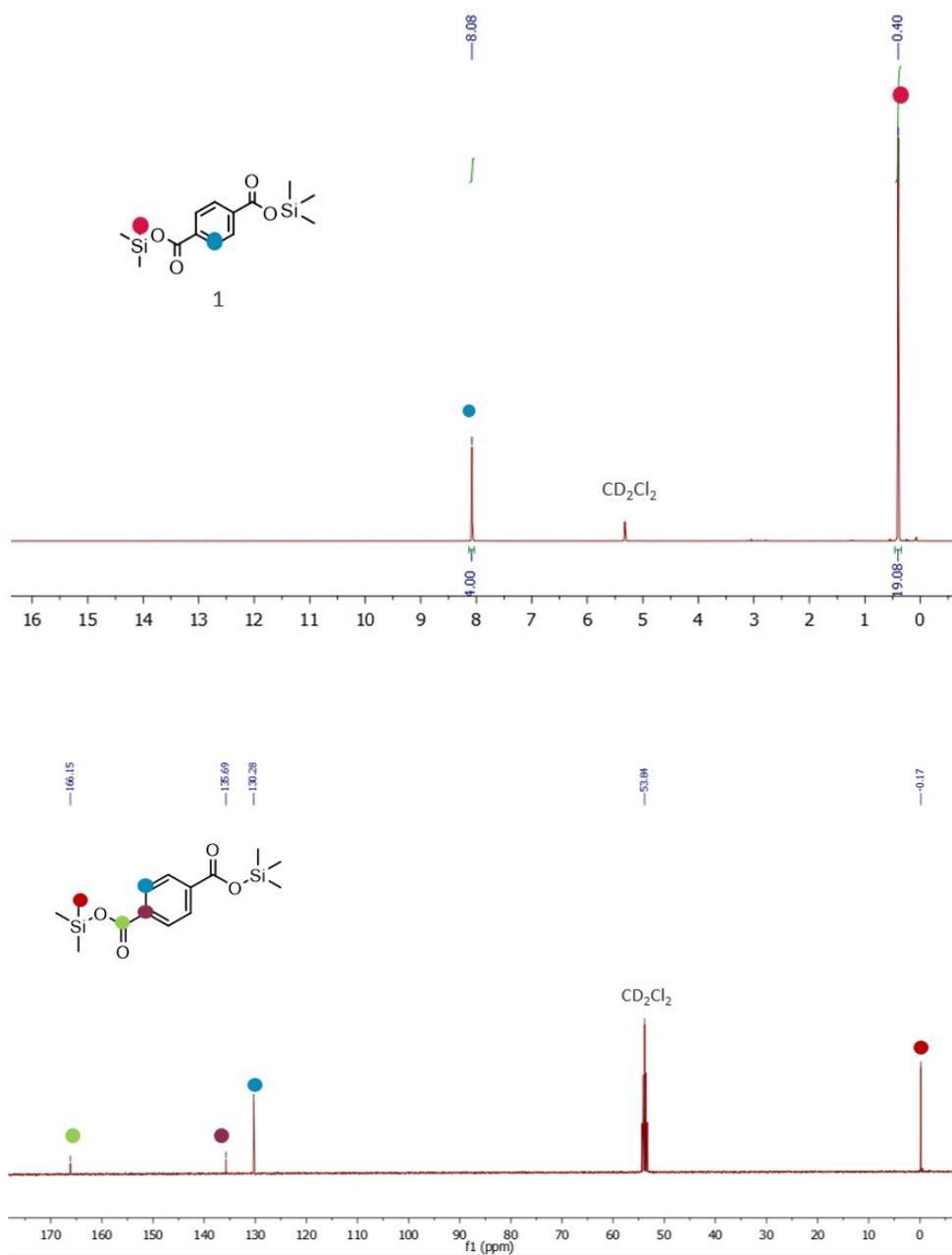


Figure S21  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectrum of bis(trimethylsilyl) terephthalate (400MHz,  $\text{CD}_2\text{Cl}_2$ , 298K)

## References

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