A convenient route to distannanes, oligostannanes, and polystannanes

Aman Khan, Robert A. Gossage, and Daniel A. Foucher

Abstract: The quantitative conversion of the tertiary stannane $(n-Bu)_3$ SnH (2) into $(n-Bu)_6$ Sn₂ (4) was achieved by heating the neat hydride material under low pressure or under closed inert atmosphere conditions. A 31% conversion of Ph₃SnH (3) to Ph₆Sn₂ (5) was also observed under low pressure; however, under closed inert atmosphere conditions afforded Ph₄Sn (6) as the major product. A mixed distannane, $(n-Bu)_3$ SnSnPh₃ (7), can also be prepared in good yield utilizing an equal molar ratio of 2 and 3 and the same reaction conditions used to prepare 4. This solvent-free, catalyst-free route to distannanes was extended to a secondary stannane, $(n-Bu)_2$ SnH₂ (8), which yielded evidence (NMR) for hydride terminated distannane H(*n*-Bu)₂SnSn(*n*-Bu)₂H (9), the polystannane [$(n-Bu)_2$ Sn]_n (10), and various cyclic stannanes [$(n-Bu)_2$ Sn]_{n=5,6} (11, 12). Further evidence for 10 was afforded by gel permeation chromatography (GPC) where a broad, moderate molecular weight, but highly dispersed polymer, was obtained ($M_w = 1.8 \times 10^4$ Da, polydispersity index (PDI) = 6.9) and a characteristic UV-vis absorbance (λ_{max}) of ≈ 370 nm observed.

Key words: solvent free, catalyst free, dehydrogenation, stannanes, polystannanes.

Résumé : On a effectué la conversion quantitative du stannane tertiaire $(n-Bu)_3$ SnH (2) en $(n-Bu)_6$ Sn₂ (4) par chauffage de l'hydrure net, à basse pression ou dans des conditions atmosphériques inertes, sans contact avec l'extérieur. On a aussi observé une conversion de 31 % du Ph₃SnH (3) en Ph₆Sn₂ (5) dans des conditions de basse pression; toutefois, dans des conditions atmosphériques inertes sans contact avec l'extérieur, le produit majeur est le Ph₄Sn (6). Un distannane mixte $(n-Bu)_3$ SnSnPh₃ (7) peut aussi être préparé avec un bon rendement en utilisant un rapport molaire égal à l'unité des composés 2 et 3 dans les mêmes conditions que celles utilisées pour préparer le composé 4. On a étendu cette nouvelle voie de préparation des distannanes, sans solvant et sans catalyseur, pour obtenir un distannane secondaire, le $(n-Bu)_2$ SnH₂ (8) qui, sur la base de données de RMN, contient aussi un distannane à hydrure terminal, H $(n-Bu)_2$ SnSn $(n-Bu)_2$ H (9), du polystannane, [$(n-Bu)_2$ Sn]_n (10), et divers stannanes cycliques [$(n-Bu)_2$ Sn]_{n=5,6} (11, 12) dans lesquels n = 5 et 6. La chromatographie par perméation de gel (CPG) a aussi permis d'obtenir des données mettant en évidence la présence d'un polymère de poids moléculaire modéré, mais hautement dispersé ($M_w = 1,8 \times 10^4$ Da, indice de polydispersion (IPD) = 6,9) et d'observer une absorbance caractéristique dans le spectre UV–vis avec un $\lambda_{max} \approx 370$ nm.

Mots-clés : sans solvant, sans catalyseur, déshydrogénation, stannanes, polystannanes.

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Introduction

Hexaorganodistannanes are a convenient source of stannyl radicals and have found applications in organic chemistry in a variety of reduction reactions,¹ in addition to their utility in palladium-catalyzed cross-coupling processes.² Distannanes also serve as useful models for polystannanes.³ Industrially, distannanes show considerable antibacterial and fungicidal activity and were previously used as wood preservatives.⁴ The distannane class of compounds are the tin analogues of ethanes but possess a Sn–Sn bond that is comparatively weaker (154 vs 356 kJ/mol) and longer (2.80 vs 1.54 Å) than typical C–C bonds.^{5,6} Organodistannanes are generally thermally stable but are chemically sensitive to the presence of oxygen (more so than that of water, mild acids, or alkalis) and can readily decompose to form stannoxanes (i.e., R₃Sn–O–SnR₃) such as **1** (Fig. 1).⁷

Distannanes can be synthesized directly from the dehvdrogenative dimerization of tin hydrides (e.g., 2 and 3) with either amines or alkoxides acting as the catalyst.⁸ Organotin hydrides can also be dehydrogenatively coupled using transition metal catalysts such as $Pd(PPh_3)_4$, $PdCl_2(NCMe)_2$,⁹ or ruthenium-allenylidene complexes.¹⁰ Electrochemical preparations of R_3SnSnR_3 (e.g., $R = n - C_4H_9$ (4), C_6H_5 (5), p- $CH_3C_6H_4-$, or $C_6H_5CH_2-$) compounds involving the reduction of R_3SnX (X = Cl, NO₃, H, SPh, OCHO, OCOCH₃, etc.) have also been reported.^{11,12} Stoichiometrically, 5 can be prepared via the reductive coupling of triphenyltin derivatives (Ph₃SnX, where X = Cl, I, or OH) in a THF/aq NH₄Cl solution containing Zn metal.^{13,14} The first high yield synthesis of **4** was reported by Sawyer¹⁵ from the treatment of distannoxane 1 with 2 at 100 °C for several days (Scheme 1).

Alternative methods for the synthesis of 4 from 1 include

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Scheme 1.

Fig. 1. Various stannanes.



reactions with formic acid,¹⁶ or reductions utilizing Mg, Na, or K metal in THF¹⁷ solution; NaBH₄¹⁸ or SmI₂¹⁹ in hexamethylphosphoramide (HMPA) has also been used. Recently, an improvement in the synthesis of 4^{20} was reported, which involves a high temperature (200 °C), catalyst-free protocol using **1** and **2** at a molar ratio of 1:2.2. This method gives **4** in a quantitative yield. Interestingly, these same authors also reported a lower yield (52%) of **4** by simply heating **2** at a lower temperature (150 °C) for 6 h under vacuum (Scheme 2).

In this study, we reinvestigate the solvent and catalystfree dehydrocoupling of 2 to produce 4 in an effort to identify the optimum reaction conditions for a variety of distannanes. This direct approach was thus extended to the aryl tin hydride (3) to obtain $Ph_3SnSnPh_3$ (5). We also report on the catalyst-free reactions involving equimolar ratios of alkyl (2) and aryl (3) tin hydrides. Finally, we present evidence that this approach can be extended to alkyl dihydrostannanes for the production of both oligostannanes and polystannanes.

Results and discussion

The reaction conditions for both 2 and 3 to produce distannanes 4 and 5 are listed in Table 1. An attempt to distill 2 (200 $^{\circ}$ C, in vacuo) using a long path distillation condenser was initiated with the intention to further purify 2. Surprisingly, the product of this distillation was not 2, but a nearly quantitative conversion (¹H and ¹¹⁹Sn NMR, yield: 97%) to distannane 4. We investigated the impact of heating 2 to reflux temperature (200 °C) under reduced pressure using a long path reflux condenser. After 6 h, analysis by ¹H and ¹¹⁹Sn NMR indicated a 75% conversion of **2** into **4**. The sample was further heated (6 h) under these conditions, but NMR analysis showed virtually no change in the proportions of the product and starting material. A plausible reason for this observation is that the more volatile hydride is retained by the cool portion of the reflux condenser rather than in close proximity to the heat source. To improve this conversion, 2 was heated (200 °C) under static vacuum conditions in a sealed Schlenk flask. An analysis (119Sn NMR) of a small aliquot of the reaction mixture taken every hour revealed that after 5 h, 2 had completely converted to the distannane 4. A single ¹¹⁹Sn resonance (δ –83.6 ppm) was observed for 4, with characteristic Sn satellites $(J_{119}Sn - 117Sn =$ 1280 Hz), which is in agreement with reported literature values.²⁰ The reaction was also carried out in a sealed flask under a nitrogen atmosphere. Analysis by ¹¹⁹Sn NMR showed a small peak for **2** after 5 h, which was completely consumed after heating for an additional 1 h (Fig. 2). There was no evidence of redistribution products, which were reported when **2** was thermally dehydrocoupled in the presence of group 4 or 6 transition metal complexes.²¹

Similar dehydrocoupling conditions were used for hydride 3. After 6 h at reflux (200 °C) under reduced pressure, analysis by NMR showed that approximately 31% of the starting material had converted to distannane 5, with most of the remainder represented by the starting material 3 in addition to a significant fraction of the redistribution product (24%) Ph₄Sn (6). Product 5 precipitated from the reaction mixture as a crystalline solid as it cooled and could be easily recovered from the starting material by recrystallization. The reaction was also repeated in a heated (200 °C) and sealed Schlenk flask under static vacuum. The 119Sn NMR spectrum showed evidence of a thermal redistribution reaction with the bulk of the material converted (87%) to **6** and a considerably lower fraction of 5 (10%), in addition to a trace of gravish sediment, which was attributed to elemental tin (3%).

Utilizing closed, reduced-pressure reaction conditions, an equimolar mixture reaction of **2** and **3** was heated (200 °C) for 5 h. Analysis by ¹¹⁹Sn NMR spectroscopy (Fig. 3) revealed resonances at δ –145.8 and –67 ppm consistent with the formation of **7**.²² The NMR evaluation of the reaction mixture also indicated that compound **7** was present in a 36.6% yield. Traces of the starting materials, along with **4** (11.9%) and **5** (37.6%), the redistribution product **6** (12.9%), recovered tin metal (1.2%), and two unassigned peaks were also noted. These unidentified materials may be other higher molecular weight redistribution products.

The solvent-free, catalyst-free reaction $N_2(g)$ conditions were also employed with the secondary stannane, (*n*-Bu)₂SnH₂ (**8**; Scheme 3). After 6 h of heating (160 °C), ¹¹⁹Sn NMR spectroscopic analysis of the bright yellow oily solid material revealed a multitude of resonances.

Clearly identifiable in this spectrum, however, was a resonance at $\delta \approx -208$ ppm, which is attributed to the hydride terminated distannane $(n-Bu_2SnH)_2$ (9).²³ Additionally, a resonance at $\delta \approx -189$ ppm can be assigned to linear dibutyl-

Scheme 2.

2 <u>150°C, 6 h</u> **4** (52%)

Starting material	Reaction conditions	Reaction time (h)	Product	Yield (%)
2	200 °C, N ₂	6	4	97
	200 °C, reflux/reduced pressure	12	4	75
	200 °C, static/reduced pressure	5	4	95
3	200 °C, reflux/reduced pressure	6	5, 6	31, 24
	200 °C, static/reduced pressure	4	5, 6	10, 87
2 and 3	200 °C, static/reduced pressure	5	4	12
			5	37
			6	13
			7	37

Table 1. Catalyst- and solvent-free thermal couplings of tin hydrides.

Scheme 3.

$$(n-Bu)_{2}SnH_{2} \xrightarrow{160^{\circ}C} H(n-Bu)_{2}Sn-Sn(n-Bu)_{2}H + H - (n-Bu)_{2}Sn - H + [(n-Bu)_{2}Sn]_{5} + [(n-Bu)_{2}Sn]_{6}$$

$$8 \qquad 9 \qquad 10 \qquad 11 \qquad 12$$

Fig. 2. ¹¹⁹Sn NMR spectra of the products from the dehydrocoupling of **2** at (A) 4 h at 200 $^{\circ}$ C and (B) 5 h at 200 $^{\circ}$ C under static reduced pressure.



Fig. 3. ¹¹⁹Sn NMR spectrum of the products from the dehydrocoupling of **2** and **3** at 200 °C for 5 h. Peaks with an asterisk are unassigned.



polystannane (10).²⁴ Two cyclic species (11 and 12) were identified by comparison with the literature ¹¹⁹Sn chemical shift values.^{25,26} The assignments of the rest of the minor signals has not yet been made but these are likely due to the presence of higher molecular weight hydride terminated oligomers (e.g., n-Bu₂SnH(n-Bu₂Sn) $_n$ SnHn-Bu₂). Analysis of this material by gel permeation chromatography (GPC) showed a broad polymer distribution and a modest molecular

Oligomers and polymer

lar weight polystannane ($M_w = 1.8 \times 10^4$ Da, polydispersity index (PDI) = 6.9), along with a considerable fraction of lower molecular weight linear and cyclic products. A UV– vis spectrum (Fig. 4) of the mixture containing the polymer **10** displayed a broad absorbance with a λ_{max} centered at ≈ 370 nm. This absorbance can be attributed to the σ – σ * of the polystannane, which is in good agreement with reported values.²⁴

When the dehydrocoupling of **8** was attempted at a higher temperature (200 °C, 6 h), evidence of multitude of alkyl redistribution products was found (Scheme 4). Analysis by ¹¹⁹Sn NMR spectroscopy showed resonances attributed to **2**, as well as to dimeric **4** and higher tributylstannane terminated oligomers (i.e., **13** and **14**), which were identified by comparison to literature values.¹⁶ A large unassigned resonance was observed at +156 ppm. This downfield shift is characteristic of a four-coordinate dialkyl tin alkoxide species, e.g., $R_2Sn(OR)_2$, which typically have resonances in the range of +90 to +200 ppm.²⁷ There is no evidence of cyclic products nor hydride terminated oligomers.

Mechanistic considerations

The catalyst- and solvent-free, presumably radically driven, dehydrocoupling reactions described herein (Scheme 5) are apparently activated through the thermolysis of the relatively weak Sn–H bonds of R₃SnH (R = *n*-Bu₃, Ph). The small differences between the ground state bond dissociation energies for known stannanes (e.g., Me₃SnH = 305 ± 17 kJ/mol, Me₃SnEt = 284 ± 17 kJ/mol, Me₃SnPh = 339 ± 21 kJ/mol, and Me₃SnSnMe₃ = 317 ± 25 kJ/mol) provides little insight to identifying clear redistribution trends with these systems.²⁸

In the case of **3**, additional redistribution reactions to yield products such as **6** also occur. The Sn–aryl bonds also appear to be thermally labile at 200 $^{\circ}$ C and redistribution chemistry is competitive with dehydrogenation. In contrast, trialkyl stannanes seem less active towards such redistribution at this temperature. To maximize yields of distannanes and reduce the potential of unwanted redistribution products, it is essential to identify the optimum reaction conditions



(e.g., temperature and duration of the reaction). Closed reaction vessels under slight reduced pressure produce the highest yields for all products (4, 5, and 7). A likely driving force in these reactions is the liberation of $H_2(g)$ along with the formation of the persistent tin alkyl and aryl radicals that later combine to form distannanes. Attempts to carry out dehydrocoupling reactions at higher temperatures (>200 $^{\circ}$ C) resulted in the decomposition of the starting materials and (or) lower product yields. Reaction of the secondary stannane 8 at lower temperatures (160 °C) resulted in the formation of linear and cyclic polystannane species including a modest molecular weight polymer (10). The broad polydispersity found for this sample is typical of other radical polymers prepared from an uncontrolled polymerization process. The mechanism of propagation for this species is unclear, but may occur through the coupling of two growing oligomeric species that contain active radical end groups. When **8** is heated at 200 °C, redistribution to tributylstannyl terminated species are dominant but no evidence for cyclics or polymers was noted.

Conclusion

Compound 4 was successfully synthesized in a high yield from the thermally driven dehydrocoupling of the tertiary stannane 2 under a variety of catalyst- and solvent-free conditions. Compound 5 was also obtained in a similar way with lower conversion from the tertiary stannane 3. A mixed distannane 7 was also prepared from the equimolar reaction of 2 and 3 under similar conditions. Evidence for the redistribution product 6 was found when any stannane (3) was used. Solvent- and catalyst-free dehydrogenative coupling of the secondary distannane 8 at 160 °C resulted in the formation of a modest molecular weight polystannane (10) and other linear and cyclic stannanes, but favours only redistribution products at 200 °C. This work has demonstrated that dehydrocoupling of stannanes in the absence of a catalyst under a variety of conditions may provide a viable route to valuable organic radical sources. Future efforts will be directed to the coupling of tertiary and secondary stannanes using other metal-free routes, including the use of light and microwave mediated coupling processes.

Experimental methods

Equipment and procedures

¹H, ¹³C{¹H}, and ¹¹⁹Sn{¹H} NMR spectra were recorded on a Bruker Avance 400 MHz NMR spectrometer. ¹H spectra were referenced to the residual solvent peaks in the deuterated solvents, whereas the ¹³C spectra are referenced internally to the deuterated solvent resonances, which are in turn referenced to SiMe₄ (δ 0 ppm), whereas ¹¹⁹Sn was referenced to SnMe₄ (δ 0 ppm). UV–vis measurements were carried out in THF solutions using a PerkinElmer Lamda 40 spectrometer. Molecular weights of polymers were deterScheme 5.

2
$$(n-Bu)_3$$
SnH $\frac{200^{\circ}C}{-H_2}$ 2 $(n-Bu)_3$ Sn \circ $\frac{200^{\circ}C}{}$ $(n-Bu)_3$ Sn $-$ Sn $(n-Bu)_3$
2 4

mined by gel permeation chromatography (GPC) using a Viscotek Triple Model 302 detector system equipped with a refractive index detector (RI), a four capillary differential viscometer (VISC), a right angle (90°) laser light scattering detector ($\lambda_0 = 670$ nm), and a low angle (7°) laser light scattering detector. GPC columns were calibrated versus polystyrene standards (American Polymer Standards). A flow rate of 1.0 mL/min was used with ACS grade THF as the eluent. GPC samples were prepared using 3-10 mg of polymers per mL THF, and filtered using a 0.45 μ m filter. All samples were run with and without ultraviolet absorbers (UVA; concn ≈ 0.001 mol/L) for comparison. All reactions were carried out under a nitrogen atmosphere using Schlenk techniques unless otherwise described. Thermally driven dehydrocoupling reactions were performed under a variety of conditions in Schlenk flasks, including in an inert N2 atmosphere, or in a sealed Schlenk flask placed under a static reduced pressure (closed), or finally in a Schlenk flask exposed to dynamic reduced pressure (open). Pressures were measured using a mercury manometer attached to the Schlenk line.

Materials

(*n*-Bu)₃SnH (**2**, 99%), Ph₃SnH (**3**, 97%), (*n*-Bu)₂SnCl₂ (97%), LiAlH₄ (1.0 mol/L in ether), and anhydrous CaCl₂ were purchased commercially and used without further purification. (*n*-Bu)₆Sn₂ (**4**) and Ph₆Sn₂ (**5**) were purchased from Strem and used as reference samples. (*n*-Bu)₂SnH₂ (**8**) was prepared from (*n*-Bu)₂SnCl₂ and LiAlH₄ according to literature preparation.^{24,25} Solvents were dried by standard procedures prior to use.

Large-scale thermal dehydrocoupling of 2 under reduced pressure (open system)

The tin hydride **2** (50 g, 0.17 mol) was added to a 100 mL round-bottom flask connected to a long path distillation condenser (13 cm) and the volatile components distilled at 200 °C under reduced pressure ($\approx 1 \times 10^{-2}$ mm Hg; 1 mm Hg = 133.32 Pa). The product of this distillation was then analyzed by NMR spectroscopy. The ¹H and ¹¹⁹Sn NMR spectra revealed that **2** had been consumed and converted (recovered yield: 97%) into **4**. The NMR data provided here are in good agreement with literature values.^{18,20,22}

Small-scale thermal dehydrocoupling of 2 under reduced pressure (open system)

To a 25 mL round-bottom flask equipped with long path reflux condenser (20 cm), was added tin hydride 2 (1.0 g,



Fig. 4. UV-vis (THF) spectrum of the mixture containing 10.

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3.44 mmol). The sample was heated to reflux temperature (200 °C) under reduced pressure ($\approx 2 \times 10^{-2}$ mm Hg) for 6 h. Analysis (¹H and ¹¹⁹Sn NMR spectroscopy) of a small aliquot of the reaction mixture revealed 75% conversion of **2** into **4**, while the remainder was unreacted **2**. Additional heating for 6 h under these conditions showed no further reactant conversion (NMR).

Small-scale thermal dehydrocoupling of 2 under reduced pressure (closed system)

To a 25 mL Schlenk flask equipped with a glass stopper was added **2** (530 mg, 1.82 mmol). The neat hydride was placed under static reduced pressure ($\approx 5 \times 10^{-1}$ mm Hg), the vessel was then sealed and subsequently heated (200 °C) for 5 h. Analysis (¹H and ¹¹⁹Sn NMR spectroscopy) showed that the majority of **2** had been consumed and was converted to **4** (recovered yield: 95%).

Small-scale thermal dehydrocoupling of 2 under inert atmosphere (open system)

Compound **2** (530 mg, 1.82 mmol) was added to a 25 mL Schlenk flask equipped with a long path (20 cm) reflux condenser that was open to a N₂(g) atmosphere. The flask was then heated (200 °C) for 6 h. Analysis (¹H and ¹¹⁹Sn NMR spectroscopy) of the reaction mixture indicated that **2** had been consumed and was converted to **4** (recovered yield: 97%). ¹H NMR (C₆D₆, ppm) δ : 0.97 (3H, t, CH₃CH₂CH₂CH₂-Sn), 1.16 (2H, m, CH₃CH₂CH₂CH₂-Sn), 1.42 (2H, m,

Small-scale thermal dehydrocoupling of 3 under reduced pressure (open system)

Compound **3** (471 mg, 1.34 mmol) was added to a 25 mL round-bottom flask equipped with a long path reflux condenser (20 cm). The sample was heated (200 °C) under reduced dynamic pressure ($\approx 1 \times 10^{-3}$ mm Hg) for 6 h. During this time period, clear and colourless crystals formed on the sides of the reaction flask that were then collected and analyzed (¹H and ¹¹⁹Sn NMR spectroscopy). These data indicated that a considerable fraction of **3** (41%) was unreacted. Approximately 59% of **3** was consumed and was converted to both **5** (31%),²⁹ **6** (24%),³⁰ and Sn metal (4%). Major product **5**: ¹H NMR (CDCl₃, ppm) δ : 7.28–7.36 (12H, m), 7.39–7.52 (12H, m), 7.60–7.63 (6H, m). ¹³C{¹H} NMR (CDCl₃, ppm) δ : 139.24 (C1), 137.61 (C2, C6), 128.82 (C3, C5), 128.94 (C4). ¹¹⁹Sn{¹H} (CDCl₃, ppm) δ : -143.7.

Small-scale thermal dehydrocoupling of 3 under reduced pressure (closed system)

To a 50 mL Schlenk flask equipped with a glass stopper

was added **3** (394 mg, 1.12 mmol). The neat hydride was kept under static reduced pressure ($\approx 5 \times 10^{-1}$ mm Hg), the flask sealed, and heated (200 °C) for 4 h. Analysis (¹H and ¹¹⁹Sn NMR) of the reaction mixture indicated that **3** had been consumed and was converted to both **6** (yield: 87%),³⁰ **5** (yield: 10%),²⁹ and Sn metal (3%). Major product **6**: ¹³C{¹H} NMR (CDCl₃, ppm) δ : 138.04 (C1), 137.39 (C2, C6), 128.79 (C3, C5), 128.28 (C4). ¹¹⁹Sn{¹H} NMR (CDCl₃, ppm) δ : -129.6.

Small-scale thermal dehydrocoupling of 2 and 3 under reduced pressure (closed system)

To a 50 mL Schlenk flask equipped with a glass stopper was added **2** (291 mg, 1.00 mmol) and **3** (351 mg, 1.00 mmol). Neat tin hydrides were then placed under static reduced pressure ($\approx 5 \times 10^{-1}$ mm Hg), sealed, and heated (200 °C) for 5 h. Analysis (¹H and ¹¹⁹Sn NMR) of the reaction products indicated the conversion of **2** and **3** into a mixture containing **4** (12%), **5** (37%), **6** (13%), **7** (37%), and trace of elemental tin (1%).

Small-scale thermal dehydrocoupling of 8 under nitrogen (open system)

To a 50 mL Schlenk flask equipped with a glass stopper was added **8** (428 mg, 1.82 mmol). The flask containing **8** was then placed under an atmosphere of N₂ and heated (160 °C) for 6 h. Analysis (¹H and ¹¹⁹Sn NMR spectroscopy) of a small aliquot of the reaction mixture indicated the conversion of **8** to a mixture containing **9**, **10**, **11**, and **12** along with unassigned oligomers. UV–vis λ_{max} (nm): 370. ¹¹⁹Sn{¹H} NMR (C₆D₆, ppm) δ : **10**: –189.3; **12**: –202.1; **8**: –203.2; **9**: –207.9; others: –195.6, –209.5, –220.1. Analysis by GPC revealed a molecular weight of $M_w = 1.8 \times$ 10⁴ Da, PDI = 6.9.

Small-scale thermal dehydrocoupling of 8 under reduced pressure (open system)

To a 50 mL Schlenk flask equipped with a glass stopper was added **8** (500 mg, 2.12 mmol). The flask containing **8** was then placed under an atmosphere of N₂ and heated (200 °C) for 6 h. Analysis (¹H and ¹¹⁹Sn NMR spectroscopy) of a small aliquot of the reaction mixture indicated the conversion of **8** to a mixture containing **2**, **4**, **13**, and **14** along with other unassigned peaks. ¹¹⁹Sn{¹H} NMR (C₆D₆, ppm) δ : **14**: -75.3, -213.4; **13**: -76.2, -227.0; **4**: -83.2; **2**: -87.3; others: +155.9, -57.7, -66.6, -210.2.

Supplementary data

Supplementary data of ¹H and ¹¹⁹Sn{¹H} NMR spectra for compounds **4**, **5**, **6**, and the products of the dehydrocoupling of **8** at two different temperatures are provided.

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