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Preparation of γ-trimethylsilylallyldibutylstannane grafted on solid support: a clean and easily recyclable reagent for the synthesis of 2,6-disubstituted dihydropyrans

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ABSTRACT

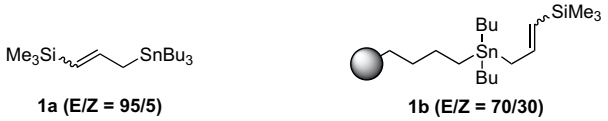
The synthesis of the γ-trimethylsilyldibutylallylstannane grafted on an insoluble macroporous polymer is reported. This bimetallic reagent was treated with aldehydes in the presence of indium trichloride to afford in good yields both symmetrical and unsymmetrical *cis*-2,6-disubstituted dihydropyrans, practically uncontaminated with organotin residues (less than 20 ppm). The potential for regeneration and reuse of this supported bimetallic reagent is pointed out.

1. Introduction

2,6-Disubstituted dihydropyrans are common structural elements of many biological active natural products.[1] In addition, the olefin function of these compounds is particularly attractive since it could serve as useful building blocks for further functionalization in order to obtain polysubstituted tetrahydropyrans.[2,3] As a result, several approaches have been reported for the construction of *cis*-2,6-disubstituted dihydropyrans such as the hetero Diels–Alder cycloadditions,[4–7] the intramolecular silylmodified Sakurai reaction (ISMS),[8] the olefin metathesis,[9–11] and the Prins-cyclization.[12] The Prins-cyclization, which involves the coupling of homoallylic alcohols with simple carbonyl compounds under acid catalysis is one of the most effective reaction for the preparation of either tetrahydropyran or dihydropyran rings.[12] Thus, considerable efforts have been directed toward improving the efficiency of the Prins-cyclization, mainly by increasing the nucleophilicity of the alkene reagent. If, the alkene moiety in the homoallylic alcohol bears a silyl substituent, the reaction can be terminated after cyclization by direct elimination of the silyl group leading to the unsaturated product.[13] Accordingly, an interesting method for the preparation of dihydropyran units using a novel tandem carbonylallylation/Prins-cyclization of aldehydes with the 3-trimethylsilylallyltributylstannane **1a** was reported by Li and co-workers,[14] but in this case the toxicity of the tin reagent and the difficulty of completely removing organotin residues from final products constitute two limitations of this elegant methodology.

To circumvent this problem, a recent silyl-Prins alternative was described by Dobbs and co-workers,[12c,d] which involves the cross-coupling between γ-silylated homoallylic alcohols and aldehydes under Lewis acid catalysis to obtain dihydropyran skeletons. However, this method requires extra-steps in formation of γ-silylated homoallylic alcohols as cyclization precursors. These two methods allow the preparation of dihydropyran rings in good yields with high diastereoselectivities for cis isomers.

Taking into account the above mentioned remarks, our involvement in the development of polymer-supported organometallic reagents[15a–c] led us to an alternative route to obtain 2,6-disubstituted dihydropyrans using the 3-trimethylsilylallyldibutylstannane **1b** anchored onto an insoluble macroporous polymer through a tin–carbon linkage in order to remove easily organotin residues from products by simple filtration (Fig. 1). This strategy should therefore combine the advantages of the method previously described by Li and co-workers[14] with those expected from polymer-supported tin reagents in terms of purification and low pollution by tin residues in final products. Herein, we wish to report our results concerning this study focusing on the efficiency of the first heterogenous tandem carbonylallylation/Prins-cyclization of



1a (E/Z = 95/5) **1b (E/Z = 70/30)**

Figure 1.

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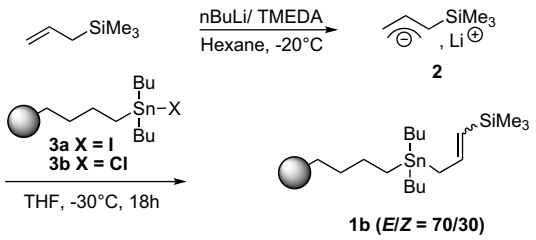


Scheme 1. Synthesis of the polymer-supported bimetallic reagent **1b**.

aldehydes, on the potential of recycling the polymer-supported bimetallic reagent **1b** and on the tin contamination in isolated dihydropyrans.

2. Results and discussion

2.1. Preparation of the polymer-supported bimetallic reagent 1b

The desired polymer-supported bimetallic reagent **1b** was easily prepared in one step by adding under an argon atmosphere a solution of the lithiated allyltrimethylsilane[16] **2**, to a mixture of the pre-cooled solid supported di-*n*-butyltin halide **3a**[15a] in THF. The reaction mixture was stirred at −30 °C for 18 h before work-up and filtration (Scheme 1).

The expected polymer-supported bimetallic reagent **1b** was successively washed with THF, absolute ethanol and was then dried under vacuum. The formation of the polymer-supported bimetallic **1b** was established through it's IR spectrum, which exhibits a well defined band around 1620 cm^{-1} indicative of the C=C double bond of the allylic moiety. Chemical informations on both the tin and silicon environment were also well established through solid state ^{119}Sn MAS-NMR and ^{29}Si MAS-NMR analysis allowing us to ascertain the level of conversion of resin **3a** to resin **1b**.

Indeed, comparison of the relative intensities of the signal due to the polymer-supported triorganotin iodide **3a** with those due to the supported bimetallic reagent **1b** was indicative of the conversion rate of Sn–I (δ ^{119}Sn=+80.5 ppm) into Sn–allyl (δ ^{119}Sn=−18 ppm (*E*-isomer) and −16 ppm (*Z*-isomer)); reference $SnPh_4$, ($\delta^{119}Sn$=−121 ppm). The presence of the silicon atom on the vinylic unit was also characterized by typical signals at −8.1 ppm (*Z*-isomer) and −8.6 ppm (*E*-isomer) in ^{1}H–^{29}Si CP MAS-NMR spectrum (reference $SiMe_4$, $\delta^{29}Si$=0 ppm). The loading of the solid-supported reagent **1b** was evaluated to be 1 mmol g^{-1} from tin and silicon elemental analyses (Fig. 2).

2.2. Synthesis of 2,6-disubstituted dihydropyrans

*2.2.1. Synthesis of 2,6-disubstituted dihydropyrans with soluble reagent **1a***

For the optimization of the tandem carbonylallylation/silyl-Prins-cyclization, initial studies were performed in solution using the soluble γ-trimethylsilylallyltri-*n*-butylstannane **1a**[16,17] and heptanal with a range of Lewis acids such as boron trifluoride, iron trichloride, and indium trihalides ($InCl_3$, $InBr_3$) in solvents such as acetonitrile or dichloromethane. These solvents are those used for their compatibility with polystyrene resin in our previous work involving polymer-supported tin reagents.[15] Among the Lewis acids screened, indium trichloride was the most effective but, yields of Prins products were dependent on the amount of indium trichloride with the best conditions being 1.5 equiv of indium trichloride, 2 equiv of aldehyde, and 1 equiv of **1a** at room temperature in dichloromethane or at 60 °C in acetonitrile (Table 1).

Having established the best experimental conditions for the dihydropyran synthesis, further aldehydes were then investigated in the reaction and all gave moderate to good yields of 2,6-disubstituted dihydropyrans, again with a high diastereoselectivity (Table 2). Attempt to carry out the reaction with aromatic aldehydes under the same experimental conditions resulted in the recovery of the starting materials. This observation is in agreement with previously reported findings on the Prins-cyclization using indium trichloride.[14]

Intrigued by the general moderate yields of these reactions (Table 2), we chose to investigate the synthesis of 2,6-disubstituted dihydropyrans **4** in two steps, in order to elucidate the exact structure of the homoallylic alcohols as cyclization precursors in these experimental conditions. Indeed, as the effective species in

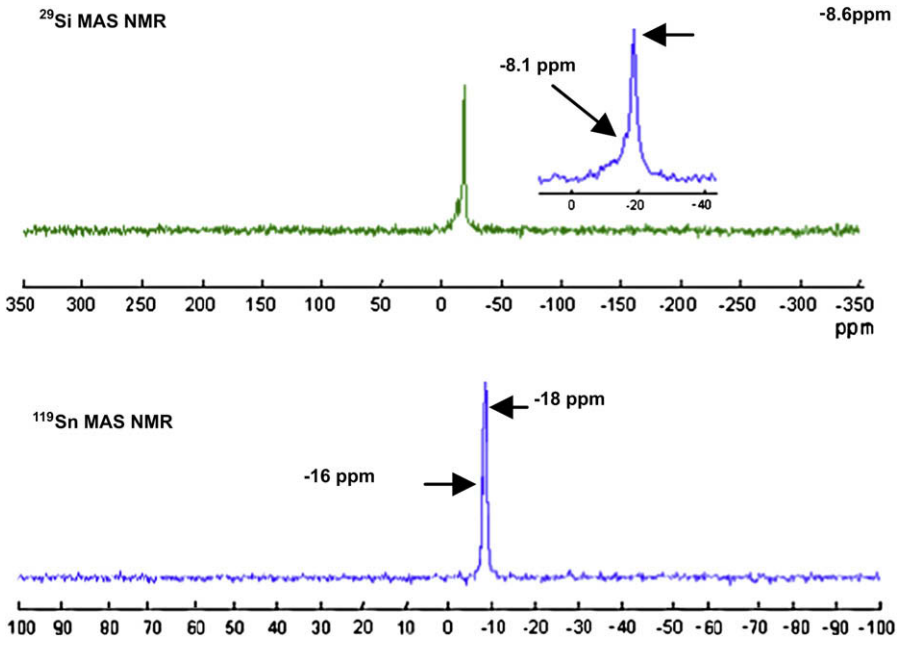
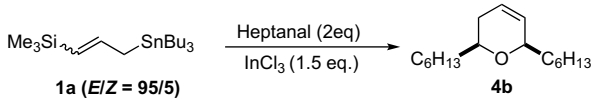


Figure 2.

Table 1
Determination of the best experimental conditions for the DHP synthesis

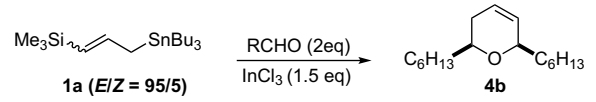


1a (*E*/*Z* = 95/5) **4b**

Entry	Experimental conditions		cis/trans[a] [%]	Yield[b] [%] of **4**
1	$InCl_3$, (1 equiv), rt	CH_2Cl_2	>(*99*/01)	28
2	*$InCl_3$, (1.5 equiv), rt*	*CH_2Cl_2*	*>(99/01)*	*55*
3	$InCl_3$, (2 equiv), rt	CH_2Cl_2	>(*99*/01)	39
4	$InCl_3$, (1 equiv), rt	CH_3CN	(*95*/05)	35
5	$InCl_3$, (1.5 equiv), rt	CH_3CN	(*95*/05)	51
6	*$InCl_3$, (1.5 equiv), 60 °C*	*CH_3CN*	*(95/05)*	*63*

[a] The diastereoisomeric ratio was determined by GC analysis of crude reaction mixtures.
[b] Isolated yields of pure *cis*-DHP only, after column chromatography on silica gel.

Table 2
Synthesis of 2,6-disubstituted dihydropyrans **4** in one-step procedure



1a (*E*/*Z* = 95/5) **4b**

Entry	RCHO	DHP **4**	Yield[a] [%] (cis/trans),[b] CH_2Cl_2	Yield[a] [%] (cis/trans),[b] CH_3CN
1	C_3H_7CHO	**4a**	30[c] (*99*/*01*)	30[c] (*95*/*05*)
2	$C_6H_{13}CHO$	**4b**	55 (*99*/*01*)	63 (*95*/*05*)
3	*c*-$C_6H_{11}CHO$	**4c**	50 (*99*/*01*)	70 (*93*/*07*)
4	*n*-$C_7H_{15}CHO$	**4d**	43 (*99*/*01*)	82 (*92*/*08*)
5	$Ph(CH_2)_2CHO$	**4e**	41 (*99*/*01*)	47 (*95*/*05*)

[a] Isolated yields of pure *cis*-DHP **4** only, after column chromatography on silica gel.
[b] Diastereoisomeric ratio was determined by GC analysis of crude reaction mixtures.
[c] Volatile compound.

the γ-substituted allyltin series can be either the γ-trimethylsilylallyltin **1a** initially added (path A) or its regioisomer **1a**′ formed after a 1,3 metallotropy process (path B), two homoallylic alcohols can be formed as it is depicted in Scheme 2 and previously thoroughly discussed in crotyltin series.[15c]

To study the sequence outlined in Scheme 2, the first step of the reaction was carried out with 1 equiv of each component at room temperature in dichloromethane or at 60 °C in acetonitrile and, followed by GC chromatography. Interestingly, the aldehyde was consumed within 2 or 3 h and surprisingly the exclusive isolated product of these reactions was the γ-silylated homoallylic alcohol **5**, which was fully characterized by ^1H NMR analysis and, not the α-silylated homoallylic alcohol **6** or a mixture of these two regioisomers as we have observed in the crotylation reaction in the presence of $InCl_3$.[15c] On the other hand, all of these γ-silylated homoallylic alcohols **5** were obtained with a poor stereoselectivity (*E*/*Z*) whatever the nature of the solvents and the temperature of the reaction (Table 3).

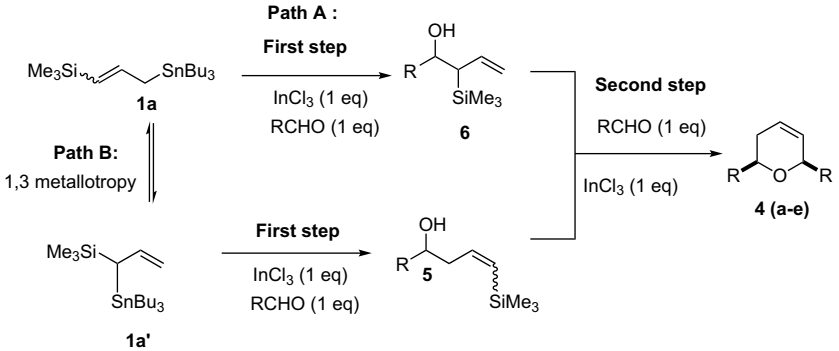
Table 3
Synthesis of 2,6-disubstituted dihydropyrans **4** in two-step sequence

Entry	Aldehyde	Homoallylic alcohol **5** yield[a] [%] (*E*/*Z*)[b]		DHP **4** yield[a] [%] (cis/trans)[b]		Overall yield [%]
1	C_3H_7CHO	**5a**	CH_2Cl_2: 59 (*79*/*21*)	**4a**	CH_2Cl_2: 39 (*99*/*01*)	23[c]
			CH_3CN: 69 (*34*/*66*)		CH_3CN: 40 (*95*/*05*)	28[c]
2	$C_6H_{13}CHO$	**5b**	CH_2Cl_2: 67 (*62*/*38*)	**4b**	CH_2Cl_2: 77 (*99*/*01*)	52
			CH_3CN: 73 (*57*/*43*)		CH_3CN: 82 (*90*/*10*)	60
3	*c*-$C_6H_{11}CHO$	**5c**	CH_2Cl_2: 67 (*62*/*38*)	**4c**	CH_2Cl_2: 68 (*99*/*01*)	46
			CH_3CN: 84 (*44*/*56*)		CH_3CN: 70 (*95*/*05*)	58
4	*n*-$C_7H_{15}CHO$	**5d**	CH_2Cl_2: 59 (*61*/*39*)	**4d**	CH_2Cl_2: 58 (*99*/*01*)	35
			CH_3CN: 86 (*45*/*55*)		CH_3CN: 85 (*95*/*05*)	73
5	$Ph(CH_2)_2CHO$	**5e**	CH_2Cl_2: 40 (*61*/*39*)	**4e**	CH_2Cl_2: 58 (*99*/*01*)	24
			CH_3CN: 62 (*45*/*55*)		CH_3CN: 65 (*95*/*05*)	40

[a] Isolated yields of homoallylic alcohols **5** and *cis*-DHP **4** only, after column chromatography on silica gel.
[b] Diastereoisomeric ratio was determined by GC analysis of crude reaction mixtures.
[c] Volatile compound.

Although not examined in details in terms of mechanisms, the exclusive formation of **5** is consistent with a reaction occurring mainly through path B (Scheme 2).[16] In the case of path A, the effective species should be **1a***E* and **1a***Z* according to TS1, but steric hindrance brought by the trimethylsilyl group disfavored this reaction, which is in competition with 1,3 metallotropy (Fig. 3). In path B, the effective species is **1a**′, which allows an easier approach of the complex aldehyde–$InCl_3$ through transition states TS2 and TS3. These two competitive transition states close in energy could explain the poor stereoselectivity observed for γ-silylated homoallylic alcohols **5** (with a slight *E* preference in dichloromethane: from 79/21 to 61/39, but without clear preference in acetonitrile) (Table 3).

Then, monitoring the cyclization of isolated compounds **5** into dihydropyrans **4** by reacting with 1 equiv of aldehyde and 1 equiv of $InCl_3$ at room temperature in dichloromethane or at 60 °C in acetonitrile indicates that the reaction proceeds smoothly (2–5 h) whatever the reaction temperature and the aldehyde used (Table 3). Whatever the geometry of the vinylsilane double bond of **5**, the major Prins products of these reactions were the *cis*-dihydropyrans **4**(**a**–**e**). Moreover, the overall yields of dihydropyrans **4**(**a**–**e**) in this two-step synthetic sequence were similar to those obtained in the one step procedure (Table 2). The stereochemical outcome of the Prins-cyclization is in agreement with previous observations and can be rationalized through a reaction occurring via a chair like transition state on the primarily formed (*E*)-oxocarbenium cation. Whatever the *E* or *Z* configuration of the vinylsilane, the R groups



Scheme 2. Synthesis of 2,6-disubstituted dihydropyrans **4**(**a**–**e**) in two-step sequence.

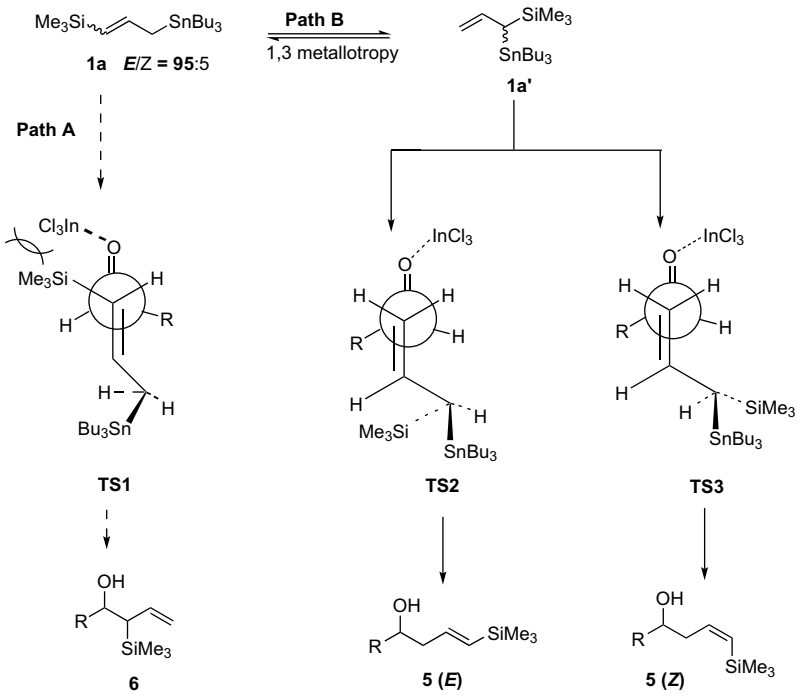


Figure 3.

adopt equatorial positions in order to minimize the 1,3 diaxial interactions (Fig. 4).[12h,k]

It is worthy to highlight that an attempt to carry out the cross-coupling between the α-silylated homoallylic alcohol **6b** (prepared according to literature procedures[17,18]), and heptanal in the above experimental conditions did not take place probably due to a competitive Peterson elimination in these conditions. Indeed, only significant amount of the 1,3 diene product and heptanal was observed at the end of the reaction. This result must be compared with related methods in which a Peterson elimination was also observed with Lewis acids.[19] Based on these results, we assumed that the tandem carbonylallylation/Prins-cyclization would proceed via the γ-silylated homoallylic alcohols **5**(**a**–**e**) in these experimental conditions and that the geometry of the vinylsilane double bond is of no importance in determining the cis/trans ratio of the dihydropyrans (**4a**–**e**). Moreover, the experimental records clearly establish that the carbonyl allylation giving the γ-silylated homoallylic alcohols **5** described in this paper as well as the Prins-cyclization leading to 2,6-disubstituted dihydropyrans (**4a**–**e**) proceed rapidly and with a high regioselectivity (**1**→**5**) and a high stereoselectivity (**5**→**4**).

*2.2.2. Synthesis of 2,6-disubstituted dihydropyrans with polymer-supported reagent **1b***

By using the above optimized reaction conditions, we therefore studied the efficiency of the polymer-supported trimethylsilylallyldibutylstannane **1b** in the tandem carbonylallylation/silyl-Prins-cyclization with various aldehydes for comparison with the liquid phase synthesis using the soluble reagent **1a**. The reactions were conducted by stirring a mixture of resin **1b** in solvent containing the indium trichloride and the aldehyde (in suitable tubes for parallel synthesis equipment with use of ellipsoidal stirring). The reactions conducted at room temperature in dichloromethane were slow, but simple elevation of the reaction temperature to 60 °C in acetonitrile for 18 h gave 2,6-disubstituted dihydropyrans **4**(**a**–**e**) with moderate to good yields and excellent stereoselectivities. These results are summarized in Table 4.

The use of the polymer-supported bimetallic reagent **1b** constitutes a major improvement in this tandem carbonyl allylation/-Prins-cyclization because the organotin residues are linked on the support and are removed by simple filtration, so that the Prins products (in the filtrate) are recovered with a very low level of tin pollution. Indeed, when compared to the ^{1}H NMR spectra of the dihydropyrans **4**(**a**–**e**) obtained by using the soluble reagent **1a**, the ^{1}H NMR spectra of crude dihydropyrans **4**(**a**–**e**) prepared by using

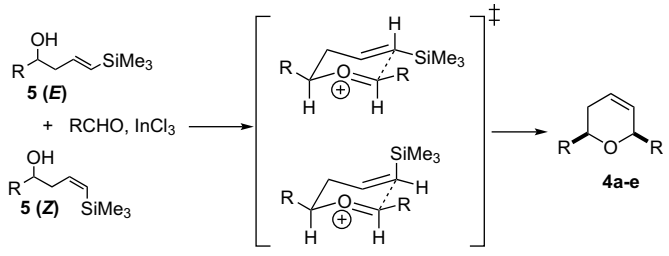
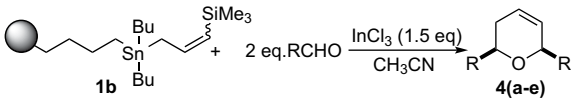


Figure 4.

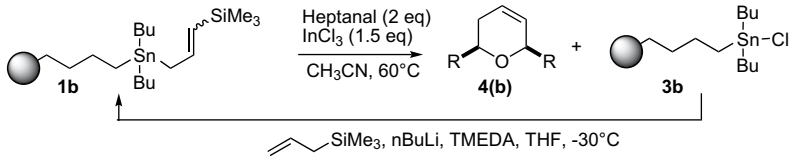
Table 4
Synthesis of 2,6-disubstituted dihydropyrans **4** with the polymer-supported reagent **1b**



Entry	RCHO	DHP **4**	Yield[a] [%] (cis/trans),[b] CH_3CN	Sn[c] (ppm)
1	C_3H_7CHO	**4a**	28 (*95*/*05*)	19
2	$C_6H_{13}CHO$	**4b**	74 (*95*/*05*)	20
3	*c*-$C_6H_{11}CHO$	**4c**	65 (*95*/*05*)	19
4	*n*-$C_7H_{15}CHO$	**4d**	62 (*95*/*05*)	19
5	$Ph(CH_2)_2CHO$	**4e**	53 (*95*/*05*)	nd

[a] Isolated yields of pure *cis*-DHP **4** only, after column chromatography on silica gel.
[b] Diastereoisomeric ratio were determined by GC analysis on the crude reaction mixtures.
[c] Quantification of tin residues in DHP **4** by ICP-MS.

Table 5
Functional group capacity values and yields of dihydropyrans **4b**



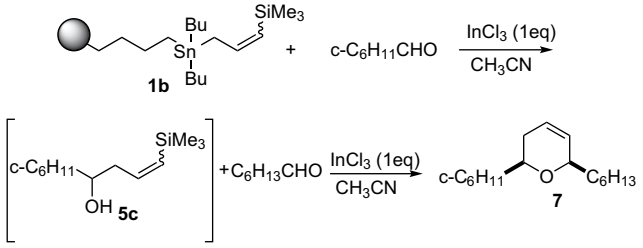
Run	Yields[a] (%)	Tin loading[b] (mmol g^{-1})	Silicon loading[b] (mmol g^{-1})	Tin content[c] in DHP **4b** (ppm)
1	65	1.00	1.00	19
2	62	nd	nd	nd
3	60	0.97	0.97	20
4	63	nd	nd	nd
5	63	0.98	0.98	19

[a] Isolated yields of DHP **4** after column chromatography on silica gel.
[b] Tin and silicon loading on the regenerated polymer **1b** determined by elemental analysis.
[c] Quantification of tin residues in DHP **4b** by ICP-MS.

the polymer-supported reagent **1b** were indicative of no meaningful contamination by organotin residues. This observation was subsequently confirmed by ICP-MS analyses of dihydropyrans **4**(**a**–**e**), which exhibited insignificant contamination by tin residues (<20 ppm) after chromatography on silica gel. In comparison, the reaction using soluble reagent **1a** gave dihydropyrans **4** with a tin pollution of about 60.000 ppm after chromatography on silica gel. This low contamination by organotin by-products demonstrates the efficiency of this polymer-supported reagent as non-polluting reagent. In this way, its use in the synthesis of biologically active molecules may be considered even if used in a last step of the synthetic strategy.

At this stage, complete validation of the method required the potential to recycle the recovered polymer-supported tin reagent at the end of the reaction. For this purpose, the resin particles recovered at the end of the reaction were washed with THF, absolute ethanol, dried under vacuum, and analyzed by ^{119}Sn MAS-NMR spectroscopy before regenerated and reused for a similar reaction. In the ^{119}Sn MAS-NMR spectra of recovered resins, the signal at +147 ppm is indicative of a polymer-supported triorganotin chloride (SnCl). This observation led us to explore the possibility of recycling it and reusing it in the tandem carbonyl allylation/silyl-Prins cyclization reaction. Gratifyingly, the resin **1b** was successfully regenerated from **3b** following the procedure described previously for its synthesis and recycled up to five turns without much lost in its effectiveness (Table 5). We have additionally checked the presence of tin in the final products by ICP-MS and found low level (<20 ppm). These results are in agreement with the constant loading in polymer **1b** showing that the loss of tin from reagent **1b** is negligible after five runs.

Having successfully demonstrated the efficiency of the polymer-supported trimethylsilylallyldibutylstannane **1b** for the synthesis of symmetrical 2,6-disubstituted dihydropyrans **4**, we then turned our attention toward the synthesis of the unsymmetrical 2,6-disubstituted dihydropyran **7** with the polymer-supported reagent **1b** according to the two-step sequence described above. The initial silylated homoallylic alcohol **5c** was prepared by allylation of cyclohexanecarbaldehyde (1 equiv) with **1b** in the presence of indium trichloride (1 equiv) at 60 °C in acetonitrile. Once the cyclohexanecarbaldehyde was consumed (5–7 h) 1 equiv of heptanal and indium trichloride were added to the same flask and the reaction mixture was stirred until the initial silylated homoallylic alcohol **5c** was consumed (overnight). Good yield (58%) of the corresponding unsymmetrical *cis*-2,6-disubstituted dihydropyran **7** with excellent diastereoselectivity was obtained (Scheme 3). Once again, NMR analysis of the crude product **7** did not show the presence of any tin residues.



Scheme 3. Synthesis of unsymmetrical 2,6-disubstituted dihydropyran **7**.

This one-pot two-step procedure constitutes an alternative method for the preparation of unsymmetrical 2,6-disubstituted dihydropyrans.

3. Conclusion

In summary, we have demonstrated that the polymer-supported γ-trimethylsilyldibutylallylstannane **1b** can be used efficiently in the tandem carbonyl allylation/silyl-Prins-cyclization in order to limit organotin pollution at very low levels. Moreover, the recovered resin can be regenerated and reused several times without appreciable loss of activity. This new supported reagent is particularly adaptable to automated parallel synthesis without significant tin contamination, allowing access to libraries of both silylated homoallylic alcohols and symmetrical 2,6-disubstituted dihydropyrans. Furthermore, the one-pot two-step procedure may be employed to incorporate many different substituents in 2,6-disubstituted dihydropyrans.

4. Experimental section

4.1. General information

Commercially available organic and inorganic compounds, as well as solvents were purchased and used without further purification. The γ-trimethylsilylallyltri-*n*-butylstannane **1a** was prepared from tri-*n*-butyltin chloride using an already described procedure.[16,17]

^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance 300 spectrometer operating at 300 MHz for ^{1}H and 75.5 MHz for ^{13}C in $CDCl_3$ solution. Chemical shifts (δ) are expressed in parts per million downfield to the tetramethylsilane (TMS) as the internal standard and coupling constants (J) are expressed in hertz.

Solid state MAS-NMR experiments were performed at room temperature on a Bruker Avance 500 spectrometer operating at 186.5 MHz for ^{119}Sn using a 4 mm double-bearing Bruker

probehead. ^{119}Sn MAS spectra were acquired with ^{1}H TPPM decoupling during acquisition and a MAS frequency of 10 kHz.[20] Repetition time was set to 20 s for quantitative purposes since ^{119}SnT_1 were measured to be of the order of 3 s. Spectra were referenced to Me_4Sn using Ph_4Sn as a secondary reference (−121.15 ppm). ^{1}H–^{29}Si CPMAS (cross-polarization magic-angle-spinning) NMR spectra were acquired using a ramp-amplitude sequence, a 7 ms contact time, and a repetition time of 4 s. MAS frequency was set to 5 kHz and ^{1}H decoupling during acquisition was achieved using the SPINAL64 method with a RF field of approximately 60 kHz. Spectra were referenced to TMS.

Mass spectra were recorded on a HP 5989 A spectrometer (EI, 70 eV or/and CI, NH_3) in direct introduction mode.

IR spectra were recorded on a Bruker Vector 22 FT-IR spectrometer from dry KBr pellets (400 mg) with substance (4 mg) or polymer (10 mg). Polystyrene bands (cm^{-1}): aromatic C–H stretchings, 3082, 3059, 3025; aliphatic C–H stetchings, 2921, 2850; weak overtone bands, 1942, 1870, 1802, 1719 (monosubstituted aromatic rings); aromatic C–C stretchings: 1601, 1586, 1493, 1452; weak in-plane aromatic C–H bending band: 1028; out-of-plane aromatic C–H bending bands, 759, 698 (monosubstituted aromatic rings).

Elemental analysis were carried out by the CNRS Analysis Central Laboratory, Vernaison, France, on a Perkin–Elmer 2400 analyzer.

ICP-MS analyses were carried out by the Ecole des Mines of Nantes, CNRS, Subatech UMR 6457 on a VG Elemental PQ Excell apparatus (Thermo-Electron GB). The ICP was operated at 1350 W and all parameters were optimized to obtain the maximum sensitivity (ions optics, flow rates, glassware position…). Nebulization was performed with a Meinhart nebulizer working at 1 mL min^{-1}. A fully quantified analytical method was set up, using eight points of calibration between 0 and 1 ppb of tin. The material was dissolved in a mixture (5 mL) of nitric acid (2%) and acetone and interferences of the matrix were studied to correct the analytical results. No internal reference was used but the stability over time was checked on every samples, and memory effect was also checked between each sample.

GC analyses were performed with an HP 6890 apparatus (FID, carrier gas N_2, split: 98:2) by using a methyl/phenyl silicone capillary column (Macherey Nagel, Optima δ^3: 30 m, 0.25 mm, 25 μm). The flow rate was 1.3 mL min^{-1} and the same programme was used for every required analyses of homoallylic alcohols and DHP: initial temperature, 80 °C (1 min) then 12 °C min^{-1} until 250 °C.

4.2. Synthesis of polymer-supported γ-trimethylsilyl-di-*n*-butylallylstannane 1b

A solution of the lithiated allyltrimethylsilane[16,17] (19.6 mmol, 5 equiv) was added to a suspension of polymer **3a** (3.90 g, 3.90 mmol) at −30 °C in dry THF (30 mL), and the resulting mixture was stirred at −30 °C for 18 h. The polymer was successively washed with a mixture of THF/aqueous NH_4Cl (1:1 v/v, 40 mL), THF (6×40 mL), and absolute ethanol (4×40 mL) and dried under vacuum (0.5 mbar) at 60 °C for 5 h.

Polymer **1b** was obtained as a white resin and was found to contain 1.00 mmol of Sn and Si per gram of resin: ^{119}Sn MAS-NMR: δ=−18 ppm (*E*-isomer) and −16 ppm (*Z*-isomer); ^{1}H–^{29}Si CP MAS-NMR: δ=−8.6 ppm (*E*-isomer) and −8.1 ppm (*Z*-isomer); IR (KBr): ν=1620 cm^{-1}; elemental analysis (%) found: C 71.19, H 8.54, Sn 12.02, Si 2.75, I <0.19.

4.3. General procedure for the allylstannation of aldehydes with soluble reagent 1a

To a solution of aldehyde (1 mmol) in 10 mL of acetonitrile (or CH_2Cl_2) were added reagent **1a** (1 mmol) and $InCl_3$ (1 mmol). The reaction mixture was stirred at 60 °C (or at 25 °C in CH_2Cl_2) and monitored by TLC. After consumption of the aldehyde, the reaction was quenched with HCl (0.1 M, 10 mL) and extracted with ether (3×20 mL). Organic layers were then washed with brine, dried over $MgSO_4$, and concentrated under vacuum. The crude homoallylic alcohol **5** was used for GC analyses and purified by chromatography on silica gel for NMR spectroscopic determinations.

4.4. General procedure for the Prins-cyclization with homoallylic alcohol 5

To a solution of homoallylic alcohol **5** (1 mmol) in 10 mL of acetonitrile (or CH_2Cl_2) were added aldehyde (1 mmol) and $InCl_3$ (1 mmol). The reaction mixture was stirred at 60 °C (or at 25 °C in CH_2Cl_2) and monitored by TLC. After consumption of the initial homoallylic alcohol **5**, the reaction was quenched with 10 mL of a saturated aqueous solution of $NaHCO_3$ and extracted with ether (3×20 mL). Organic layers were then washed with brine, dried over $MgSO_4$, and concentrated under vacuum. The crude DHP **4** was used for GC analyses and purified by chromatography on silica gel for NMR spectroscopic determinations.

4.5. General procedure for tandem carbonylallylation/silyl-Prins-cyclization with bimetallic reagent 1a

To a solution of reagent **1a**[16,17](1.0 g, 1.0 mmol) in 10 mL of acetonitrile (or CH_2Cl_2) were added aldehyde (2.0 mmol) and $InCl_3$ (1.5 mmol). The reaction mixture was stirred at 60 °C (or at 25 °C in CH_2Cl_2) and monitored by TLC. After consumption of the aldehyde, the reaction was quenched with 10 mL of a saturated aqueous solution of $NaHCO_3$ and extracted with ether (3×20 mL). Organic layers were then washed with brine, dried over $MgSO_4$, and concentrated under vacuum. The crude DHP **4** was used for GC analyses and purified by chromatography on silica gel for NMR spectroscopic determinations.

4.6. General procedure for tandem carbonylallylation/silyl-Prins-cyclization with polymer-supported bimetallic reagent 1b

To a suspension of polymer **1b** (1.0 g, 1.0 mmol) in acetonitrile were added aldehyde (2.0 mmol) and $InCl_3$ (1.5 mmol). The reaction mixture was stirred for 18 h at 60 °C and then quenched with HCl (0.1 M, 10 mL). The reaction mixture was filtered and the polymer was washed with THF (6×30 mL). The filtrate was extracted with diethyl ether, washed with brine (50 mL), dried over $MgSO_4$, and concentrated under vacuum. The resulting crude product **4** was purified by chromatography on silica gel. The identity of the product was confirmed by ^{1}H NMR, ^{13}C NMR, and MS. On the other hand, the resulting polymer was washed with absolute ethanol (6×30 mL) and dried under vacuum (0.5 mbar) at 60 °C for 6 h before solid state MAS-NMR experiments and regeneration. The polymer was obtained as a white resin, and was found to be an Sn–Cl type polymer containing 0.98 mmol of Sn–Cl g^{-1}. ^{119}Sn MAS-NMR: δ=+147 ppm.

4.7. General procedure for the synthesis of DHP 7 with polymer-supported bimetallic reagent 1b

To a suspension of polymer **1b** (1.0 g, 1.0 mmol) in acetonitrile were added cyclohexanecarbaldehyde (1.0 mmol) and $InCl_3$ (1.0 mmol). The reaction mixture was stirred at 60 °C and once the cyclohexanecarbaldehyde was consumed (GC), 1 equiv of heptanal and of $InCl_3$ were then added and the reaction mixture was stirred until the initial homoallylic alcohol **5c** was consumed (GC). The reaction mixture was then quenched with HCl (0.1 M, 10 mL) and the polymer was washed with THF (6×30 mL). The filtrate was extracted with diethyl ether, washed with brine (50 mL), dried over $MgSO_4$, and concentrated under vacuum. The resulting crude product **7** was purified by chromatography on silica gel. On the other hand, the

resulting polymer was washed with absolute ethanol (6×30 mL) and dried under vacuum (0.5 mbar) at 60 °C for 6 h before solid state MAS-NMR measurements and regeneration. The polymer was obtained as a white resin, and was found to be an Sn–Cl type polymer containing 0.98 mmol of Sn–Cl g^{-1}. ^{119}Sn MAS-NMR: δ=+147 ppm.

Products distribution in 2,6-disubstituted dihydropyrans **4** and **7** were firmly characterized on the basis of their ^{1}H NMR spectra. Their isomeric distribution was determined by GC analysis of crude reaction mixtures.

4.7.1. 2,6-cis-Dipropyl-5,6-dihydro-2H-pyran **4a**

^{1}H NMR ($CDCl_3$) δ (ppm): 5.71 (1H, br ddt, ^3J=10.4 and 4.2 Hz, ^4J=2.3 Hz), 5.45 (1H, br ddt, ^3J=10.4 and 4.2 Hz, ^4J=1.8 Hz), 4.05 (1H, m, H), 3.45 (1H, ddt, ^3J=7.2 and 7 Hz), 1.98 (2H, m), 1.75–1.15 (8H, m), 0.95 (6H, t, ^3J=5.2 Hz). ^{13}C NMR ($CDCl_3$) δ (ppm): 130.7, 124.6, 74.6, 72.7, 38.2, 37.8, 31.5, 18.8, 18.5, 14.1. GC $t_{R\ (cis)}$=4.84 min (>99%).

MS (CI/NH_3, 70 eV) *m*/*z* (*I*%): 186 ($M+NH_4^+$), 169 ($M+H^+$).

IR (film, cm^{-1}): 3027, 2956–2805, 1652, 1182, 1087.

Anal. Calcd for $C_{11}H_{20}O$: C, 78.51; H, 11.98. Found: C, 78.49; H, 11.95.

4.7.2. 2,6-Dihexyl-5,6-dihydro-2H-pyran **4b**

cis-Isomer: ^{1}H NMR ($CDCl_3$) δ (ppm): 5.77 (1H, br ddt, ^3J=10.6 and 4.1 Hz, ^4J=2.3 Hz), 5.62 (1H, br ddt, ^3J=10.6 and 4.1 Hz, ^4J=1.76 Hz), 4.05 (1H, m, H), 3.47 (1H, ddt, ^3J=7.2 and 7 Hz), 1.98 (2H, 2×ddd, ^2J=5 Hz, ^3J=4.1 Hz, ^4J=2.3 Hz), 1.62–1.20 (10H, m), 0.95–0.75 (6H, m). ^{13}C NMR ($CDCl_3$) δ (ppm): 129.5, 123, 74, 73, 35.5, 34.5, 30.5, 28, 24.5, 21, 13. GC t_R=11.06 min (95%).

trans-Isomer: ^{1}H NMR ($CDCl_3$) δ (ppm): 5.74 (1H, br ddt, ^3J=10.1 and 4.6 Hz, ^4J=2.1 Hz), 5.60 (1H, br ddt, ^3J=10.1 and 4.6 Hz, ^4J=1.8 Hz), 4.04 (1H, m), 3.55 (1H, ddt, ^3J=8.1 and 8.4 Hz), 1.90–1.75 (2H, m), 1.61–1.13 (10H, m), 0.90–0.74 (6H, m). ^{13}C NMR ($CDCl_3$) δ (ppm): 129, 122.3, 73.5, 70.1, 34.9, 32.9, 30, 27, 24.5, 21, 12.5. GC t_R=11.50 min (5%).

MS (EI, 70 eV) *m*/*z* (*I*%): 252 (8), 195 (19), 182 (35), 167 (100), 149 (12), 113 (22), 81 (45), 55 (55), 29 (38).

IR (film, cm^{-1}): 3029, 2955–2804, 1652, 1182, 1087.

Anal. Calcd for $C_{17}H_{32}O$: C, 80.88; H, 12.78. Found: C, 80.59; H, 12.85.

4.7.3. 2,6-Dicyclohexyl-5,6-dihydro-2H-pyran **4c**[21]

cis-Isomer: ^{1}H NMR ($CDCl_3$) δ (ppm): 5.73 (1H, br ddt, ^3J=10.2 and 7.5 Hz, ^4J=2.5 Hz), 5.59 (1H, br ddt, ^3J=10.2 and 7 Hz, ^4J=2.2 Hz), 3.72 (1H, m), 3.10 (1H, ddt, ^3J=7.3 Hz and 7 Hz), 1.85 (2H, m), 1.75–0.81 (20H, m), 1.45–0.30 (2H, m). ^{13}C NMR ($CDCl_3$) δ (ppm): 129, 125.3, 79.2, 78, 42.9, 31.2, 29.7, 28.7, 28.3, 26.7, 26. GC t_R=12.86 min (95%).

trans-Isomer: NMR ^{1}H ($CDCl_3$) δ (ppm): 5.78 (2H, m), 3.68 (1H, dd, ^3J=8.6 and 8.5 Hz), 3.25 (1H, br dt, ^3J=8.3 and 5.1 Hz), 1.99 (2H, m), 2.05–1.19 (20H, m), 0.90–0.82 (2H, m). ^{13}C NMR ($CDCl_3$) δ (ppm): 128.4, 124.3, 76.5, 72.3, 42.6, 41.8, 29.9, 29.6, 28.3, 27.2, 26.5, 19.6. GC t_R=13.46 min (5%).

MS (EI, 70eV) *m*/*z* (*I*%): 248 (35), 165 (100), 147 (26), 95 (18), 83 (34), 67 (26), 55 (25), 29 (8).

IR (film, cm^{-1}): 3030, 2923–2792, 1652, 1188, 1087.

Anal. Calcd for $C_{17}H_{28}O$: C, 82.20; H, 11.36. Found: C, 82.09; H, 11.35.

4.7.4. 2,6-cis-Diheptyl-5,6-dihydro-2H-pyran **4d**

^{1}H NMR ($CDCl_3$) δ (ppm): 5.72 (1H, br ddt, ^3J=10.4 and 4 Hz, ^4J=2.3 Hz), 5.57 (1H, br ddt, ^3J=10.4 and 4 Hz, ^4J=1.8 Hz), 4.03 (1H, m), 3.43 (1H, ddt, ^3J=7.2 and 6.9 Hz), 1.89 (2H, 2×ddd, ^2J=5 Hz, ^3J=4.3 Hz, ^4J=2.2 Hz), 1.55–1.13 (14H, m), 0.87–0.79 (6H, m). ^{13}C NMR ($CDCl_3$) δ (ppm): 130.5, 124.4, 74.9, 73.8, 35.5, 31.9, 31.4, 29, 28.5, 25.3, 22.7, 13. GC $t_{R\ (cis)}$=12.83 min (≥95%); GC $t_{R\ (trans)}$=13.46 min (<5%).

MS (EI, 70 eV) *m*/*z* (*I*%): 280 (17), 209 (20), 196 (32), 181 (100), 81 (31), 67 (29), 57 (21), 55 (19), 43 (11).

IR (film, cm^{-1}): 3030, 2965–2802, 1652, 1180, 1081.

Anal. Calcd for $C_{19}H_{36}O$: C, 81.36; H, 12.94. Found: C, 81.29; H, 12.75.

4.7.5. 2,6-cis-Di-(1-phenylethyl)-5,6-dihydro-2H-pyran **4e**[16,21]

^{1}H NMR ($CDCl_3$) δ (ppm): 7.30–7.15 (10H, m), 5.78 (1H, m), 5.60 (1H, m), 4.05 (1H, m), 3.49 (1H, m), 2.82 (4H, m), 1.91 (6H, m). ^{13}C NMR ($CDCl_3$) δ (ppm): 142.5, 130.7, 128.8, 128.5, 125.9, 125.1, 74, 73, 37.4, 32, 31.7, 31.6. GC $t_{R\ (cis)}$=17.33 min (≥99%); GC $t_{R\ (trans)}$=17.77 min (≤1%).

MS (CI /NH_3, 70 eV) *m*/*z* (*I*%): 310 ($M+NH_4^+$), 293 ($M+H^+$).

IR (film, cm^{-1}): 3029, 2955–2804, 1655, 1182, 1087.

Anal. Calcd for $C_{21}H_{24}O$: C, 86.26; H, 8.27. Found: C, 86.23; H, 8.15.

4.7.6. 1-(Trimethyl)silylhept-1-en-4-ol **5a**

E-isomer: ^{1}H NMR ($CDCl_3$) δ (ppm): 6.03 (1H, br dt, ^3J=6.8 and 18.6 Hz), 5.66 (1H, br dt, ^3J=18 Hz, ^4J=1.15 Hz), 3.55 (1H, m), 2.15 (2H, m), 1.35 (2H, m), 0.82 (3H, m), 0.13 (9H, s). ^{13}C NMR ($CDCl_3$) δ (ppm): 144, 132, 71, 44, 41, 39, 18, 14, 0. GC $t_{R\ (trans)}$=5.59 min (79%).

Z-isomer: ^{1}H NMR ($CDCl_3$) δ (ppm): 6.34 (1H, br dt, ^3J=7, 8, and 21 Hz), 5.58 (1H, br dt, ^3J=14 Hz, ^4J=1.15 Hz), 3.55 (1H, m), 2.15 (2H, m), 1.35 (2H, m), 0.82 (3H, m), 0.02 (9H, s). ^{13}C NMR ($CDCl_3$) δ (ppm): 142, 132, 71, 45, 43, 39, 18, 14, −1. GC $t_{R\ (cis)}$=5.82 min (21%).

MS (EI, 70 eV) *m*/*z* (*I*%): 171 (15), 145 (70), 114 (26), 99 (100).

IR (film, cm^{-1}): 3353, 2955–2855, 1606, 1247, 1125, 837.

Anal. Calcd for $C_{10}H_{22}OSi$: C, 64.44; H, 11.90; Si, 15.07. Found: C, 64.23; H, 8.15; Si, 15.00.

4.7.7. 1-(Trimethylsilyl)dec-1-en-4-ol **5b**[16]

E-isomer: ^{1}H NMR ($CDCl_3$) δ (ppm): 5.96 (1H, br dt, ^3J=6.8 and 18.6 Hz), 5.71 (1H, br dt, ^3J=18.6 Hz, ^4J=1.15 Hz), 3.62 (1H, m), 2.14 (2H, m), 1.48 (1H, d, ^3J=4.3 Hz), 1.50–1.21 (10H, m), 0.92–0.74 (3H, m), −0.3 (9H, s). ^{13}C NMR ($CDCl_3$) δ (ppm): 142, 134, 70.5, 45, 36.5, 31, 29, 25, 22, 14, −1. GC $t_{R\ (trans)}$=9.70 min (62%).

Z-isomer: ^{1}H NMR ($CDCl_3$) δ (ppm): 6.28 (1H, br dt, ^3J=6.8 and 14.7 Hz), 5.62 (1H, br dt, ^3J=14.7 Hz, ^4J=1.15 Hz), 3.62 (1H, m), 2.30 (2H, m), 1.48 (1H, d, ^3J=4.3 Hz), 1.50–1.21 (10H, m), 0.92–0.74 (3H, m), 0.5 (9H, s). ^{13}C NMR ($CDCl_3$) δ (ppm): 144, 132, 71, 41, 36.5, 31, 29, 25, 22, 14, 0. GC $t_{R\ (cis)}$=9.90 min (38%).

MS (EI, 70 eV) *m*/*z* (*I*%): 227 (15), 114 (40), 99 (70), 73 (100), 43 (23).

IR (film, cm^{-1}): 3353, 2955–2855, 1606, 1247, 1125, 837.

Anal. calcd for $C_{13}H_{28}OSi$: C, 68.35; H, 12.35; Si, 12.30. Found: C, 68.28; H, 12.15; Si, 12.00.

4.7.8. 1-Cyclohexyl-4-(trimethylsilyl)but-3-en-1-ol **5c**

E-isomer: ^{1}H NMR ($CDCl_3$) δ (ppm): 5.90 (1H, br dt, ^3J=6.8 and 18.6 Hz), 5.64 (1H, br dt, ^3J=18 Hz, ^4J=1.2 Hz), 3.60 (1H, m), 2.07 (2H, m), 1.48 (1H, s), 1.52–0.65 (11H, m), −0.07 (9H, s). ^{13}C NMR ($CDCl_3$) δ (ppm): 143.2, 134.1, 74.3, 43, 41.6, 28.8, 27.8, 26.2, 26, 25.9, −1.49. GC $t_{R\ (trans)}$=9.53 min (62%).

Z-isomer: ^{1}H NMR ($CDCl_3$) δ (ppm): 6.20 (1H, br dt, ^3J=7.2 and 14 Hz), 5.55 (1H, br dt, ^3J=14 Hz, ^4J=1.2 Hz), 3.60 (1H, m), 2.14 (2H, m), 1.49 (1H, s), 1.52–0.65 (11H, m), 0.00 (9H, s). ^{13}C NMR ($CDCl_3$) δ (ppm): 144.8, 132.6, 74.9, 43, 37.6, 28.8, 27.8, 26.2, 26, 25.9, 0. GC $t_{R\ (cis)}$=9.72 min (38%).

MS (EI, 70 eV) *m*/*z* (*I*%): 185 (40), 114 (23), 99 (100), 83 (15), 73 (55).

IR (film, cm^{-1}): 3385, 2925–2852, 1605, 1247, 1085, 837.

Anal. Calcd for $C_{13}H_{26}OSi$: C, 68.95; H, 11.57; Si, 12.40. Found: C, 68.78; H, 11.35; Si, 12.15.

4.7.9. 1-(Trimethylsilyl)undec-1-en-4-ol ***5d***

E-isomer: ^{1}H NMR ($CDCl_3$) δ (ppm): 5.90 (1H, ddd, ^3J=7, 7.5, and 18.6 Hz), 5.64 (1H, br dt, ^3J=18 Hz, ^4J=1.15 Hz), 3.57 (1H, m), 2.08 (2H, m), 1.49 (1H, m), 1.45–1.05 (10H, m), 0.85–0.7 (3H, m), −0.75 (9H, s). ^{13}C NMR ($CDCl_3$) δ (ppm): 142.6, 134.1, 70.3, 44.7, 36.8, 36.6, 31.5, 29, 25.4, 22.3, 14, −1.5. GC $t_{R\ (trans)}$=9.20 min (61%).

Z-isomer: ^{1}H NMR ($CDCl_3$) δ (ppm): 6.20 (1H, ddd, ^3J=7, 7.5, and 14 Hz), 5.55 (1H, br dt, ^3J=14 Hz, ^4J=1.15 Hz), 3.57 (1H, m), 2.2 (2H, m), 1.49 (1H, m), 1.45–1.05 (10H, m), 0.85–0.7 (3H, m), 0.00 (9H, s). ^{13}C NMR ($CDCl_3$) δ (ppm): 144.2, 132.4, 71, 41, 36.8, 36.6, 31.5, 29, 25.4, 22.3, 14, −0.0. GC $t_{R\ (cis)}$=9.30 min (39%).

MS (EI, 70 eV) *m*/*z* (*I*%): 187 (24), 114 (25), 99 (53), 73 (100), 43 (17).

IR (film, cm^{-1}): 3358, 2955–2855, 1608, 1247, 1129, 837.

Anal. Calcd for $C_{14}H_{30}OSi$: C, 69.34; H, 12.47; Si, 11.58, Found: C, 69.30; H, 12.35; Si, 11.25.

4.7.10. 1-Phenyl-6-(trimethylsilyl)hex-5-en-3-ol ***5e***[16]

E-isomer: ^{1}H NMR ($CDCl_3$) δ (ppm): 7.22–7.02 (5H, m), 6.08 (1H, br dt, ^3J=7, 8, and 18 Hz), 5.84 (1H, br dt, ^3J=18 Hz, ^4J=1 Hz), 3.77 (1H, m), 2.82 (2H, m), 2.36 (2H, m), 1.86 (2H, m), 0.11 (9H, s). ^{13}C NMR ($CDCl_3$) δ (ppm): 144, 133.1, 128.3, 125.8, 70.5, 45.0, 38.5, 32.0, 0.2. GC $t_{R\ (trans)}$=11.80 min (61%).

Z- isomer: ^{1}H NMR ($CDCl_3$) δ (ppm): 7.22–7.02 (5H, m), 6.38 (1H, br dt, ^3J=7, 8, and 14 Hz), 5.85 (1H, br dt, ^3J=14 Hz, ^4J=1 Hz), 3.77 (1H, m), 2.82 (2H, m), 2.36 (2H, m), 1.86 (2H, m), 0.19 (9H, s). ^{13}C NMR ($CDCl_3$) δ (ppm): 142.3, 134.9, 128.3, 126.1, 69.7, 41.3, 38.5, 32.0, −1.30. GC $t_{R\ (cis)}$=12.08 min (39%).

MS (EI, 70eV) *m*/*z* (*I*%): 135 (10), 113 (5), 99 (15), 97 (25), 84 (100), 49 (85).

IR (film, cm^{-1}): 3385, 2927–2852, 1605, 1247, 1083, 836.

Anal. Calcd for $C_{15}H_{24}OSi$: C, 72.51; H, 9.74; Si, 11.31. Found: C, 72.30; H, 9.65; Si, 11.25.

4.7.11. 2,6-cis-6-Cyclohexyl-2-hexyl-3,4-dihydropyran ***7***

^{1}H NMR ($CDCl_3$) δ (ppm): 5.71 (1H, m), 5.52 (1H, m), 4.00 (1H, m), 3.16 (1H, m), 2.07–1.82 (2H, m), 1.75–0.73 (24H, m). ^{13}C NMR ($CDCl_3$) δ (ppm): 129.7, 124.2, 78.1, 74, 42, 35, 30, 28, 28.6, 28.5, 28, 27.5, 25.7, 25.2, 24, 24.4, 22, 13. GC $t_{R\ (cis)}$=12.36 min ($\geq$99%).

MS (CI/NH_3, 70 eV) *m*/*z* (*I*%): 268 ($M+NH_4^+$), 251 ($M+H^+$).

IR (film, cm^{-1}): 3029, 2955–2804, 1652, 1182, 1087.

Anal. Calcd for $C_{17}H_{30}O$: C, 81.53; H, 12.08. Found: C, 81.30; H, 12.25.

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